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# Supporting information
# for
# An Unexpected Reaction to Methodology: An Unprecedented Approach to transamidation

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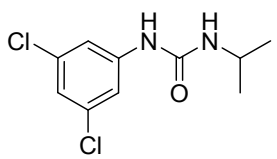
**General Consideration:**

All chemicals and reagents obtained from Sigma Aldrich (India), Merck (India) and Avra Synthesis (India) were used without further purification. Melting points were determined on a Superfit melting point apparatus (India) and are uncorrected. $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a Agilent Technologies (USA) using DMSO (d6) and $CDCl_3$ as solvent. High resolution mass spectroscopic analysis was performed on a Bruker MicroTOF QII mass spectrometer in positive mode. Progress of the reaction was monitored by TLC using silica gel 60 F254, with the solvent system comprising hexane and ethylacetate in the ratio 03:01 and the compounds on the TLC plates were detected by under UV light.

**General Synthesis procedure of N'-substituted ureas (3a-r):**

The ureas (1a-r, 1 mmol) was separately dissolved in 5 mL of THF and added anhydrous sodium hydride (1mmol) to the solution, after 5 minutes, isocyanates (1 mmol) were added to the solutions, after completion of the reaction (monitored by TLC), reaction mass was poured in to ice cold water and then extracted with EtOAc, the organic layer was washed with water and dried over anhydrous sodium sulphate. The organic solvent was removed under vacuum to get crude products (3a-r). The solid product was further purified by column chromatography by using hexane and ethyl acetate (95:5) as eluent to give pure products.

**$^1$H, $^{13}$C-NMR and Mass details**

| Name & Structure | Yield % | Melting point in °C | | Spectroscopic data |
|---|---|---|---|---|
| | | Observed | Literature | |
| **1-(3,5-dichlorophenyl)-3-isopropylurea 3a**  | 88 | 135-137 | -- | $^1$H NMR (400 MHz, DMSO-$d_6$) δH: 1.08 (d, 6H, *J*=6.4 Hz, Me2, 3.69-3.78 (m, 1H, CH), 6.21 (d, 1H, *J*=7.6 Hz, NH), 7.03 (t, 1H, *J*=3.6 Hz, NH), 7.44 (d, 2H, *J*=2.0 Hz, ArH), 8.67 (s, 1H, ArH); $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ: 22.7, 41.8, 115.6, 119.9, 134.0, 143.1, 154.0; HRMS m/z: 247.0570 [M$^+$], 249.0564 [M+2] |
| **1-(*tert*-butyl)-3-(3,5-** | 86 | 140-141 | -- | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.30 (s, 9H, Me3), 3.90 |

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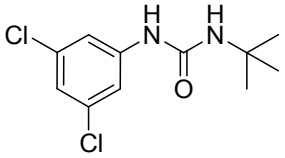
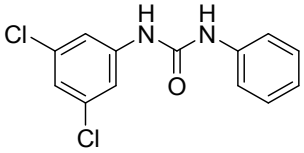
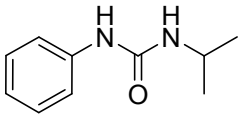
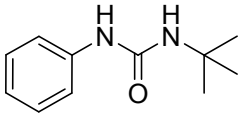
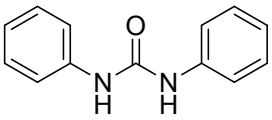
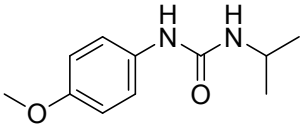
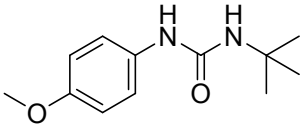
| **dichlorophenyl)urea 3b**  | | | | (s, 2H, NH), 6.53 (d, 2H, *J* = 1.6 Hz, ArH), 7.04 (t, 1H, *J* = 2.8 Hz, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 29.2, 50.2, 113.1, 118.2, 135.3, 148.2, 157.1; HRMS m/z: 261.0737 [$M^+$], 263.0721 [M+2] |
| **1-(3,5-dichlorophenyl)-3-phenylurea 3c**  | 78 | 137-139 | -- | $^1$H NMR (400 MHz, DMSO-$d_6$ and $CDCl_3$) δH: 6.84-6.90 (m, 2H, ArH), 7.14-7.19 (m, 3H, ArH), 7.33 (t, 3H, *J*=6.8 Hz, ArH), 8.20 (d, 1H, *J*=8.4 Hz, ArH), 8.53 (s, 1H, ArH); $^{13}$C NMR (100 MHz, DMSO-$d_6$ and $CDCl_3$) δ: 121.2, 123.3, 126.8, 127.3, 133.6, 139.5, 143.8, 146.7, 157.3; HRMS m/z: 281.0413 [$M^+$], 283.0336 [M+2] |
| **1-isopropyl-3-phenylurea 3d**  | 91 | 153-154 | 155-156 [1] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.10 (d, 6H, *J* = 6.4 Hz, Me2), 3.91-3.96 (m, 1H, CH), 5.20 (s, 1H, NH), 6.98 (t, 1H, *J*=14.4 Hz, ArH), 7.19-7.28 (m, 4H, ArH), 7.41 (s, 1H, NH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 23.1, 41.9, 120.2, 123.0, 129.0, 139.0, 155.7; HRMS m/z: 179.1410 [M+1] |
| **1-(*tert*-butyl)-3-phenylurea 3e:**  | 88 | 165-166 | 171-173[2] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.33 (s, 9H, Me3), 5.30 (s, 1H, NH), 6.97 (t, 1H, *J* = 14.8 Hz, ArH), 7.15 (s, 1H, NH), 7.20-7.29 (m, 4H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 29.3, 50.5, 120.1, 122.9, 129.0, 139.2, 155.3; HRMS m/z: 193.1501 [M+1] |
| **1,3-Diphenylurea 3f:**  | 75 | 238-239 | 241-242 [3] | $^1$H NMR (400 MHz, DMSO-*d*6 and $CDCl_3$) δH: 6.77-6.81 (m, 1H, ArH), 7.05-7.09 (m, 2H, ArH), 7.25 (t, 2H, 8 Hz, ArH), 8.02 (s, 1H, NH); $^{13}$C NMR (100 MHz, DMSO-*d*6 and $CDCl_3$) δ: 118.5, 122.0, 128.6, 139.4, 153.0; HRMS m/z: 213.1219 [M+1] |
| **1-isopropyl-3-(4-methoxy phenyl)urea 3g**  | 90 | 150-152 | 156-157 [4] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.11 (d, 6H, *J* = 7.2 Hz, Me2), 3.81 (s, 3H, $OCH_3$), 3.83 (d, *J* = 6.8 Hz, 1H, NH), 3.95 (t, 1H, *J* = 12.8 Hz, CH), 6.60 (s, 1H, NH). 6.80-6.84 (m, 2H, ArH), 7.14-7.17 (m, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 23.2, 42.0, 55.4, 114.5, 124.1, 131.3, 156.0, 156.6; HRMS m/z: 209.0832 [M+1] |
| **1-(*tert*-butyl)-3-(4-methoxy phenyl)urea (3h):**  | 88 | 132-134 | 129-130 [5] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.31 (s, 9H, Me3), 3.75 (s, 3H, $OCH_3$), 4.90 (s, 1H, NH), 6.60 (s, 1H, NH), 6.78-6.82 (m, 2H, ArH), 7.13-7.17 (m, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 29.3, 50.5, 55.4, 114.4, 123.8, 131.6, 155.9, 156.4; HRMS m/z: 223.1034 [M+1] |

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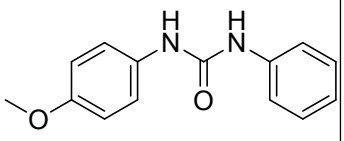
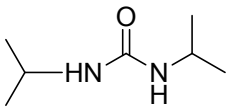
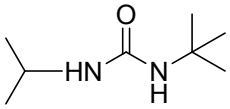
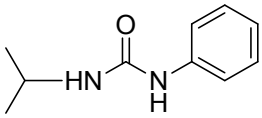
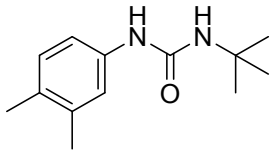
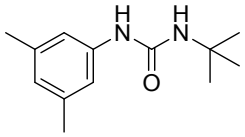
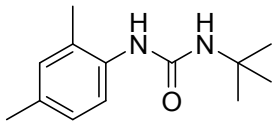
| **1-(4-Methoxyphenyl)-3-phenylurea (3i):**  | 80 | 193-194 | 194-196 [2] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 3.82 (s, 3H, $OCH_3$), 6.10 (s, 1H, NH), 6.95-6.96 (m, 2H, ArH), 7.10 (s, 1H, NH), 7.20-7.66 (m, 7H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 56.1, 113.4, 118.5, 121.9, 127.2, 128.6, 131.8, 138.7, 155.9, 158.4; HRMS m/z: 243.2451 [M+1] |
| **1,3-Diisopropyl urea 3j:**  | 80 | 183-184 | 185-188 [1] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.11 (d, 12H, *J*= 6.4 Hz, Me4), 3.80-3.86 (m, 1H, CH), 4.20 (s, 1H, NH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 23.4, 41.9, 157.1; HRMS m/z: 145.1514 [M+1] |
| **1-(*tert*-butyl)-3-isppropylurea 3k:**  | 77 | 185-186 | 190-191 [6] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.09 (d, 6H, *J*= 6.4 Hz, Me2), 1.29 (s, 9H, Me3), 3.78 (t, 1H, *J*= 13.2 Hz, CH), 4.19 (s, 2H, NH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 23.4, 29.5, 41.8, 50.2, 157.0; HRMS m/z: 159.1657 [M+1] |
| **1-isopropyl--3-phenylurea 3l:**  | 79 | 155-157 | 155-156 [1] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.11 (d, 6H, *J*= 6.8 Hz, Me2), 3.91-3.97 (m, 1H, CH), 4.22 (s, 1H, NH), 6.97-7.00 (m, 1H, ArH), 7.19-7.25 (m, 4H, ArH), 7.27 (d, 1H, *J*= 1.2 Hz, NH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 23.1, 42.0, 120.3, 123.1, 129.0, 138.9, 155.7; HRMS m/z: 179.1351 [M+1] |
| **1-(*tert*-butyl)-3-(3,4-dimethylphenyl)urea 3m:**  | 70 | 136-137 | -- | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.31 (s, 1H, NH), 1.33 (s, 9H, Me3), 2.18 (s, 6H, ArMe2), 6.49 (s, 1H, NH), 6.94-6.96 (m, 1H, ArH), 7.01 (d, 1H, *J*= 7.6 Hz, ArH), 7.05 (d, 1H, *J*= 1.6 Hz, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 19.0, 19.7, 29.3, 50.6, 118.8, 122.8, 130.2, 132.0, 136.4, 137.5, 155.4; HRMS m/z: 221.1787 [M+1] |
| **1-(*tert*-butyl)-3-(3,5-dimethylphenyl)urea 3n:**  | 68 | 140-141 | -- | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.31 (s, 2H, NH), 1.34 (s, 9H, Me3), 2.23 (s, 6H, ArMe2), 6.65 (s, 1H, ArH), 6.88 (s, 2H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 21.2, 29.3, 50.5, 118.2, 124.9, 138.7, 138.9, 155.2; HRMS m/z: 221.1787 [M+1] |
| **1-(*tert*-butyl)-3-(2,4-dimethylphenyl)urea 3o**  | 66 | 166-167 | 168 -170 [7] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.30 (s, 9H, Me3), 2.20 (s, 3H, ArMe), 2.27 (s, 3H, ArMe), 4.70 (s, 1H, NH), 6.04 (s, 1H, NH), 6.97 (t, 2H, *J* =15.6 Hz, ArH), 7.23(t, 1H, *J* =15.2 Hz, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.7, 20.7, 29.3, 50.1, 125.5, 127.5, 131.5, 132.5, 133.7, 135.3, 155.9; HRMS m/z: 221.1201 [M+1] |

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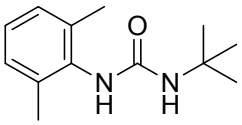
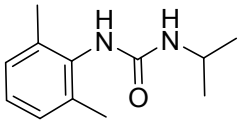
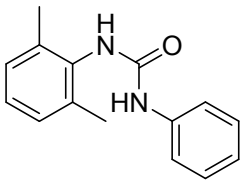
| **1-(*tert*-butyl)-3-(2,6-dimethylphenyl)urea 3p**  | 60 | 162-163 | 169-171 [8] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.34 (s, 9H, Me3), 2.12 (s, 6H, ArMe2), 6.62 (s, 2H, NH), 7.16-7.19 (m, 3H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 18.3, 23.4, 42.1, 127.3, 128.4, 134.4, 137.4, 156.4; HRMS m/z: 221.1215 [M+1] |
| **1-(2,6-dimethylphenyl)-3-isopropylurea 3q**  | 61 | 199-203 | 204 -205 [9] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 1.05 (d, 6H, *J*= 6.8 Hz. Me2), 2.26 (s, 6H, ArMe2), 3.82 (m, 2H, CH and NH), 5.87 (s, 1H, NH), 7.08-7.13 (m, 3H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 18.1, 23.2, 41.9, 127.7, 128.6, 134.0, 137.2, 156.0; HRMS m/z: 207.1066 [M+1] |
| **1-(2,6-dimethylphenyl)-3-phenylurea 3r**  | 58 | 241-244 | 247-248 [10] | $^1$H NMR (400 MHz, $CDCl_3$) δH: 2.11 (s, 6H, ArMe2), 6.58 (s, 1H, NH), 7.17-7.22 (m, 4H, ArH), 7.24 (s, 1H, NH), 7.41-7.66 (m, 4H, ArH); $^{13}$C NMR (100 MHz, $CDCl_3$) δ: 17.4, 121.1, 126.7, 127.3, 128.1, 128.8, 133.5, 136.2, 138.9, 153.4; HRMS m/z: 241.1248 [M+1]. |

**References:**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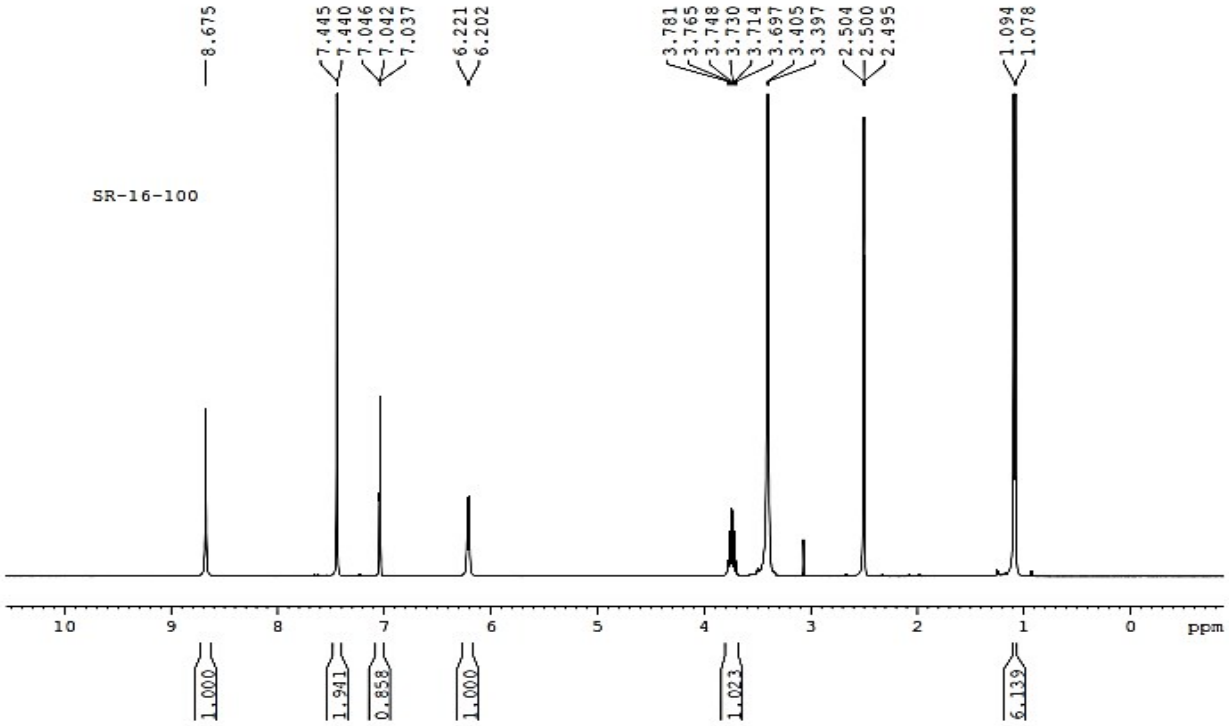
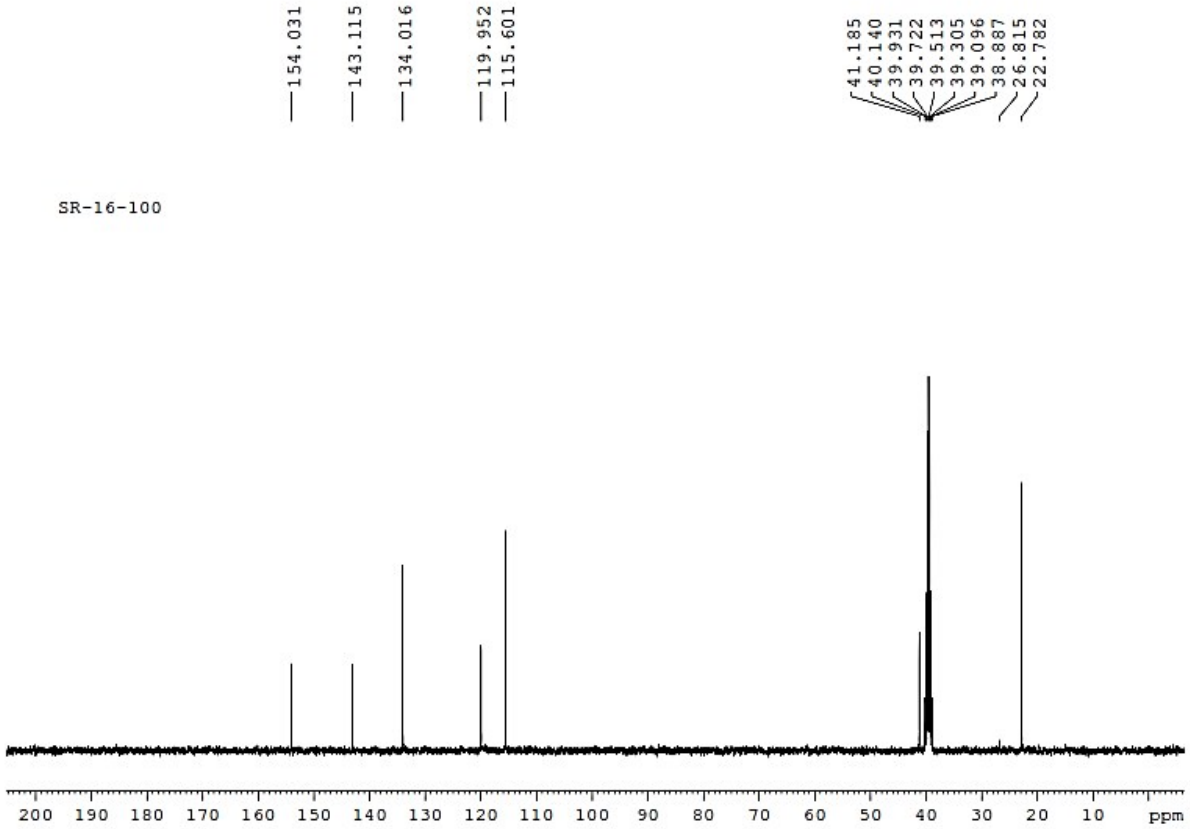
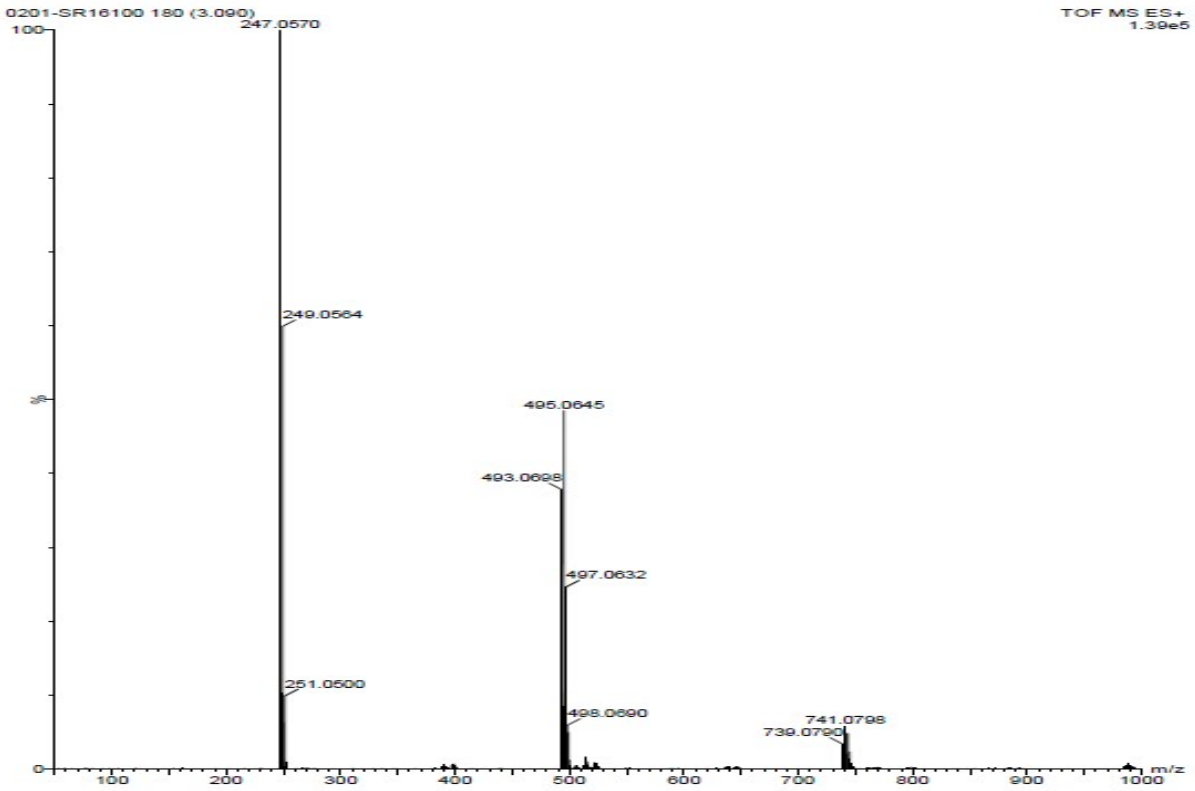
**$^{1}$H, $^{13}$C & Mass spectra of selected compounds**



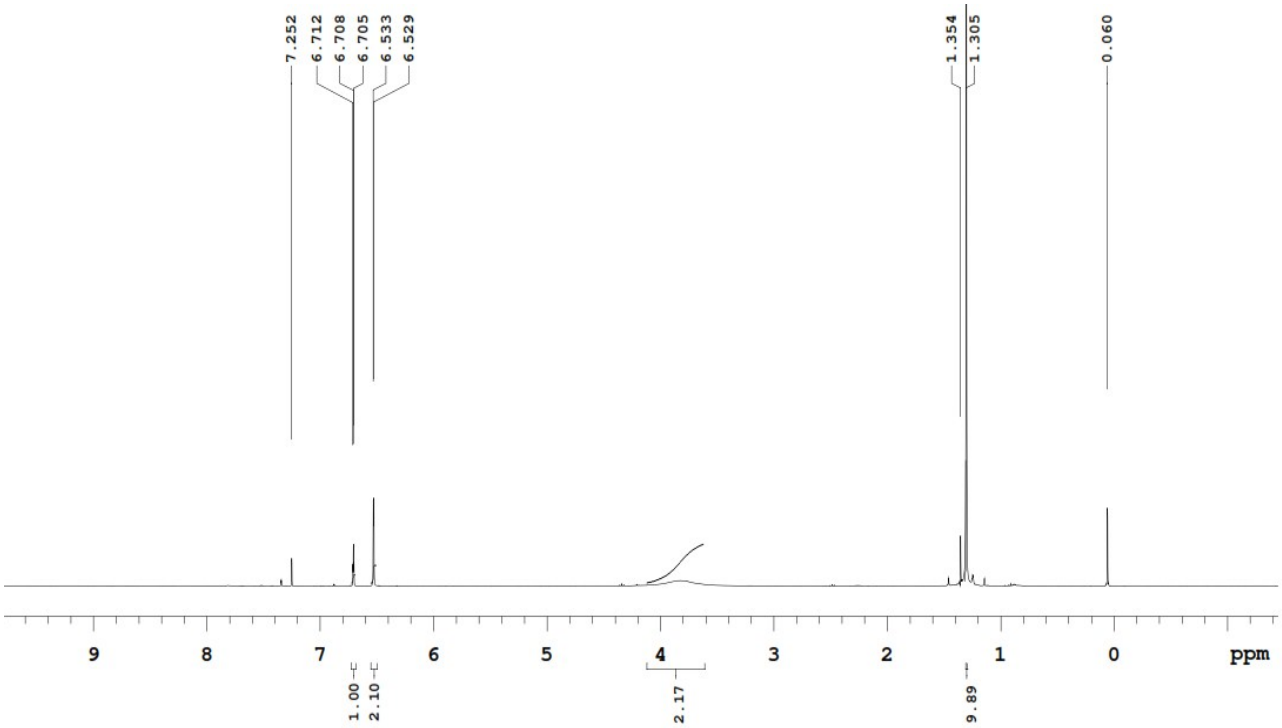

***$^{1}$H NMR spectra of*** **1-(3,5-dichlorophenyl)-3-isopropylurea 3a:**



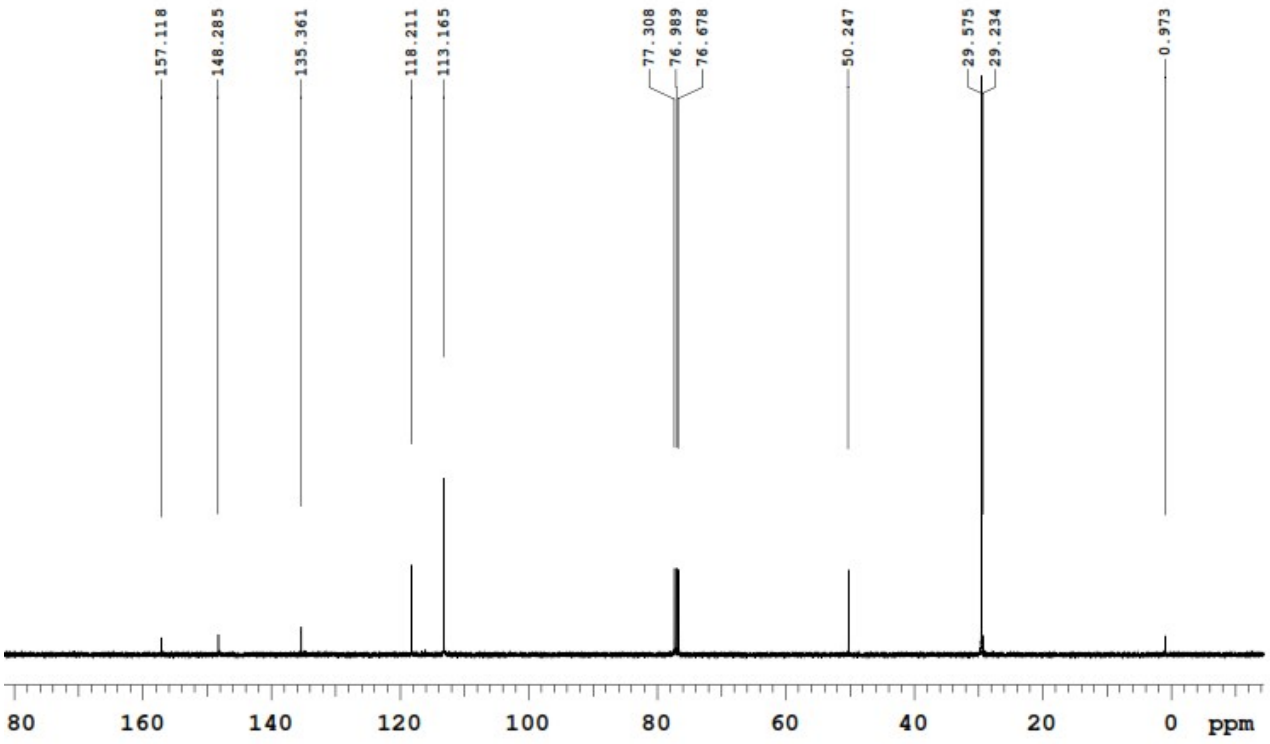

***$^{13}$C NMR spectra of*** **1-(3,5-dichlorophenyl)-3-isopropylurea 3a**



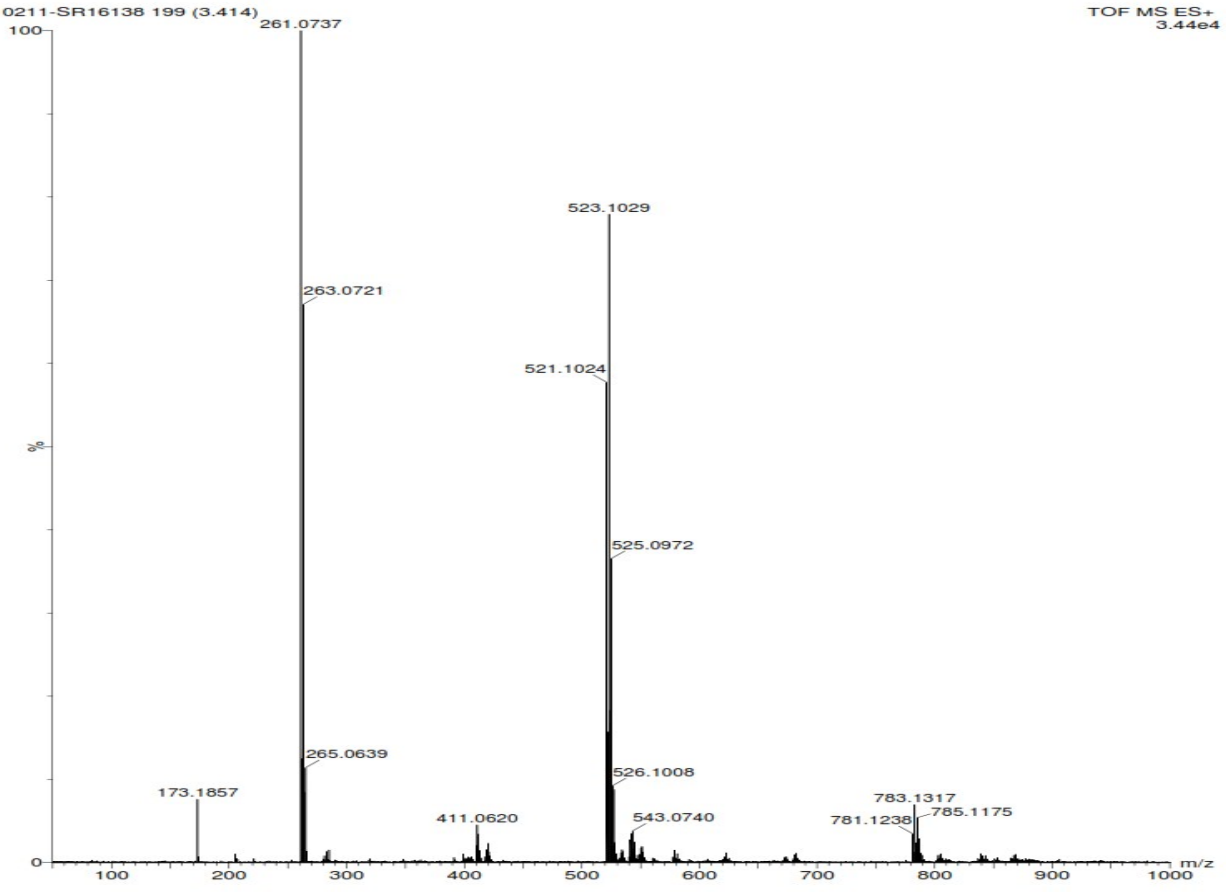

***Mass spectra of 1-(3,5-dichlorophenyl)-3-isopropylurea 3a:***



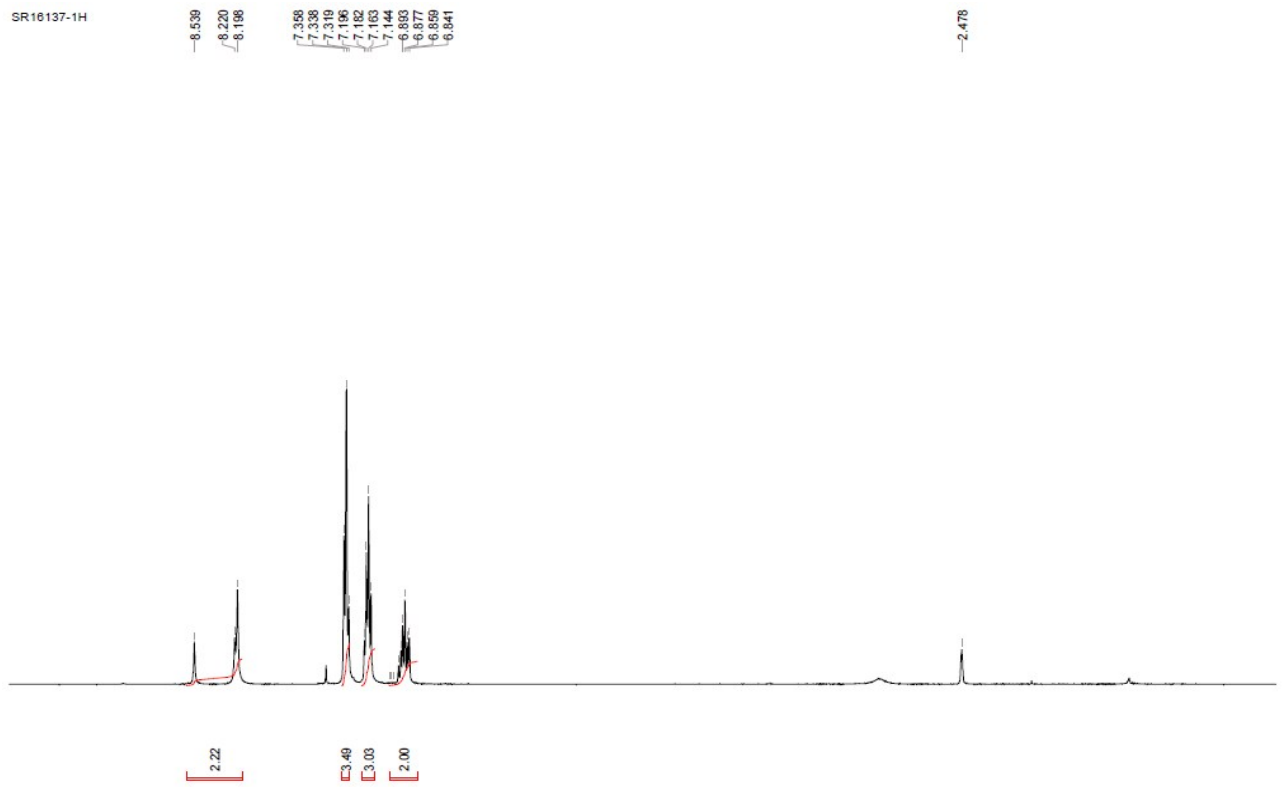

***$^{1}$H NMR spectra of 1-(tert-butyl)-3-(3,5-dichlorophenyl)urea 3b:***



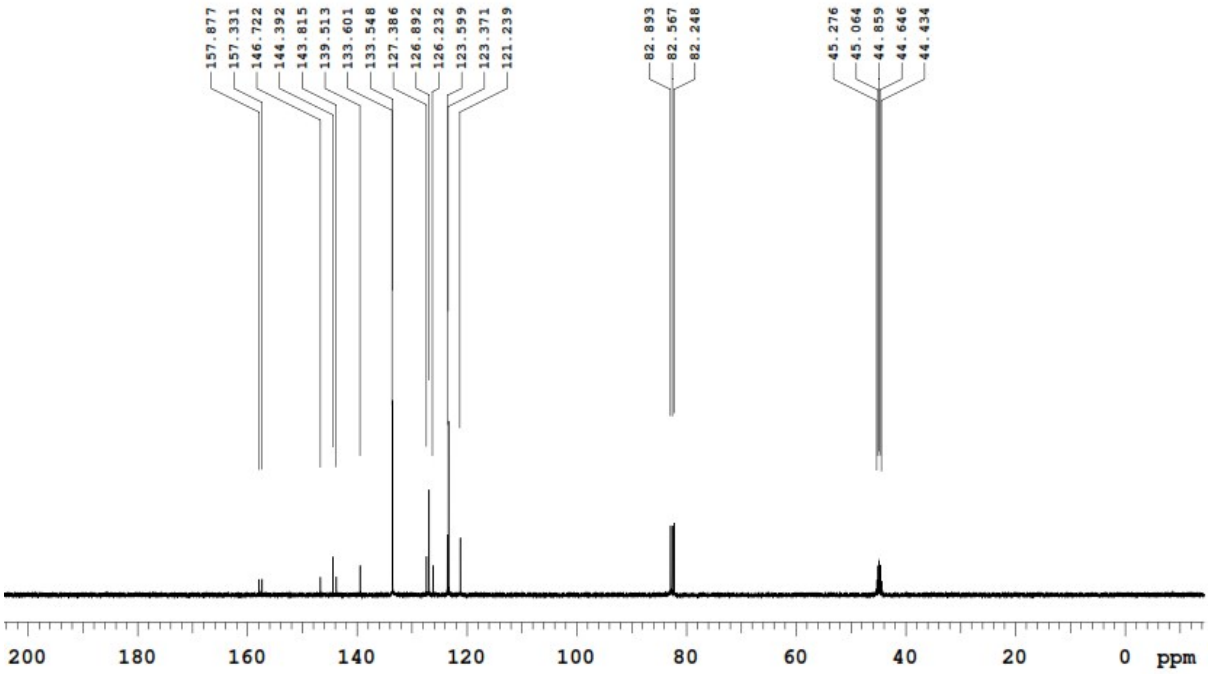

*$^{13}$C NMR spectra of 1-(tert-butyl)-3-(3,5-dichlorophenyl)urea 3b:*



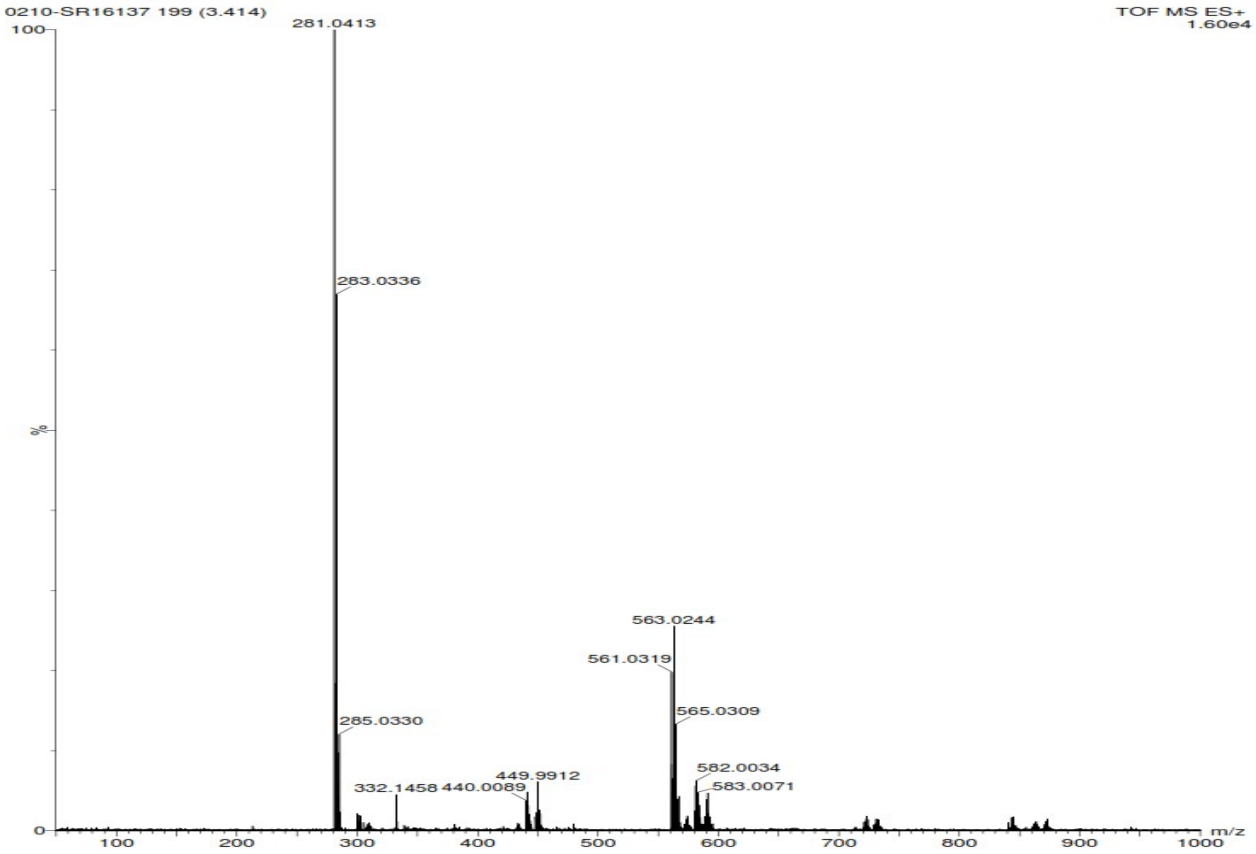

*Mass spectra of 1-(tert-butyl)-3-(3,5-dichlorophenyl)urea 3b:*



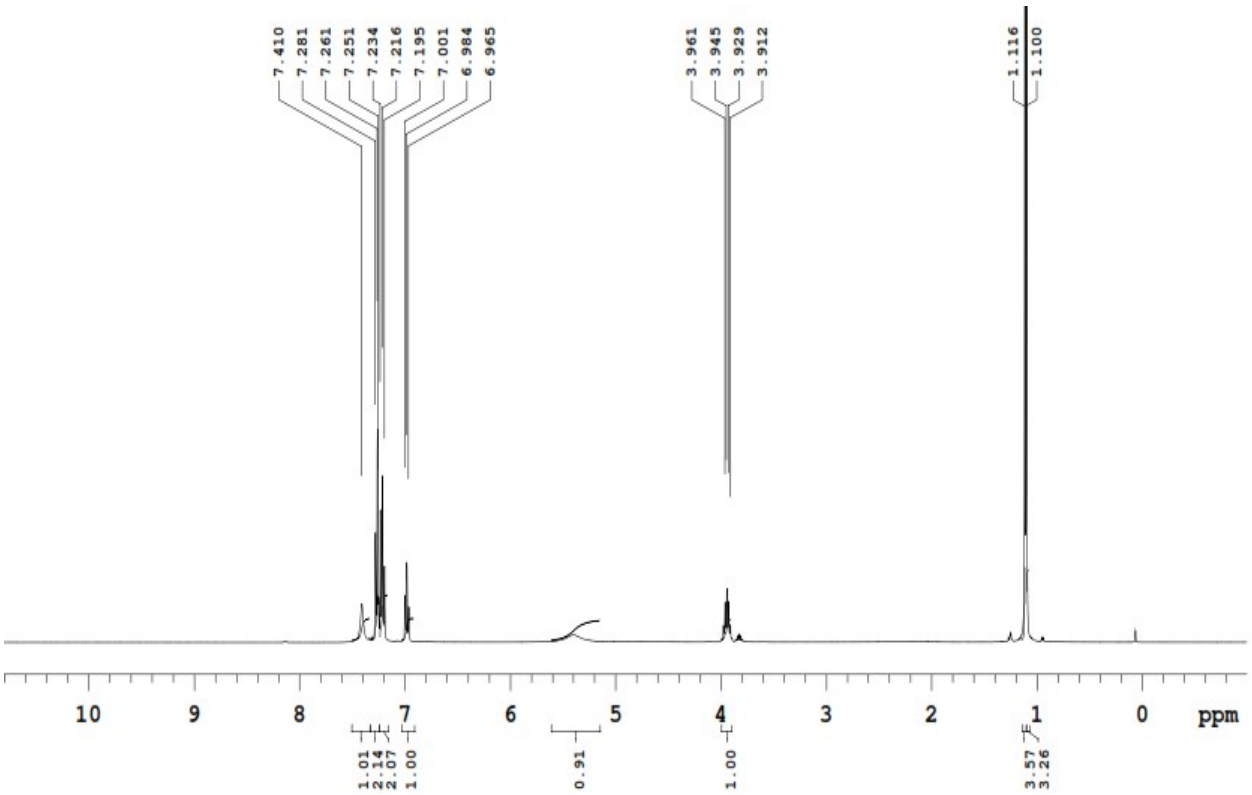

**$^{1}$H NMR spectra of 1-(3,5-dichlorophenyl)-3-phenylurea (3c)**



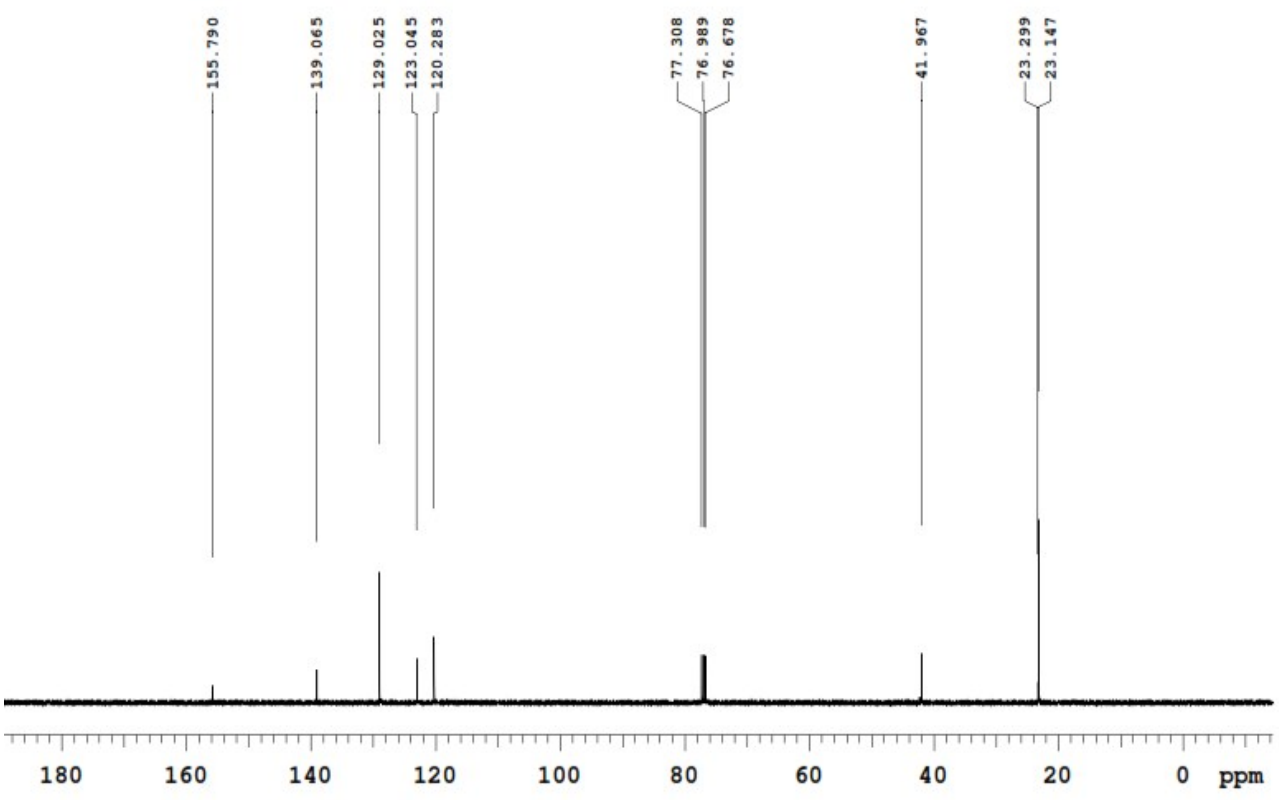

**$^{13}$C NMR spectra of 1-(3,5-dichlorophenyl)-3-phenylurea (3c)**



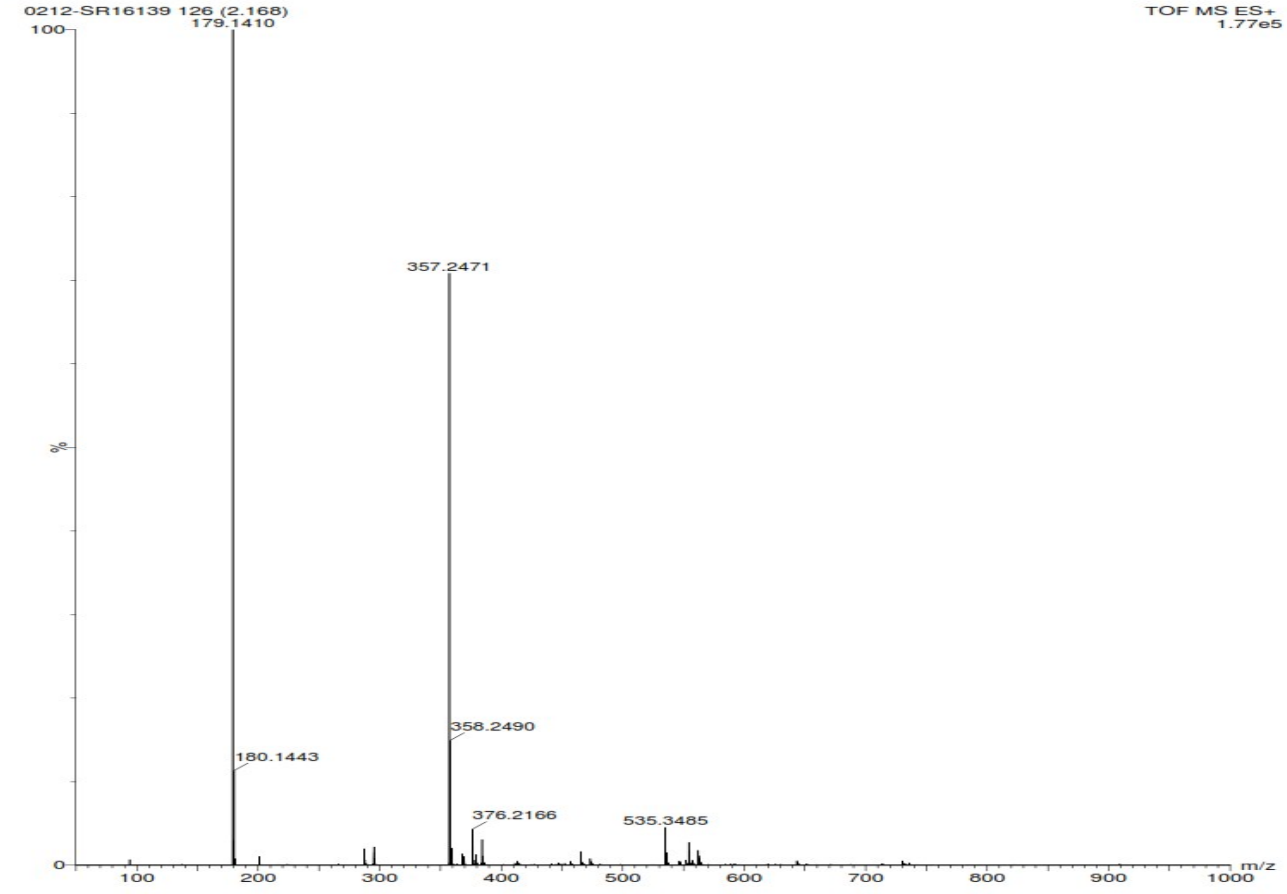

**Mass spectra of 1-(3,5-dichlorophenyl)-3-phenylurea (3c)**



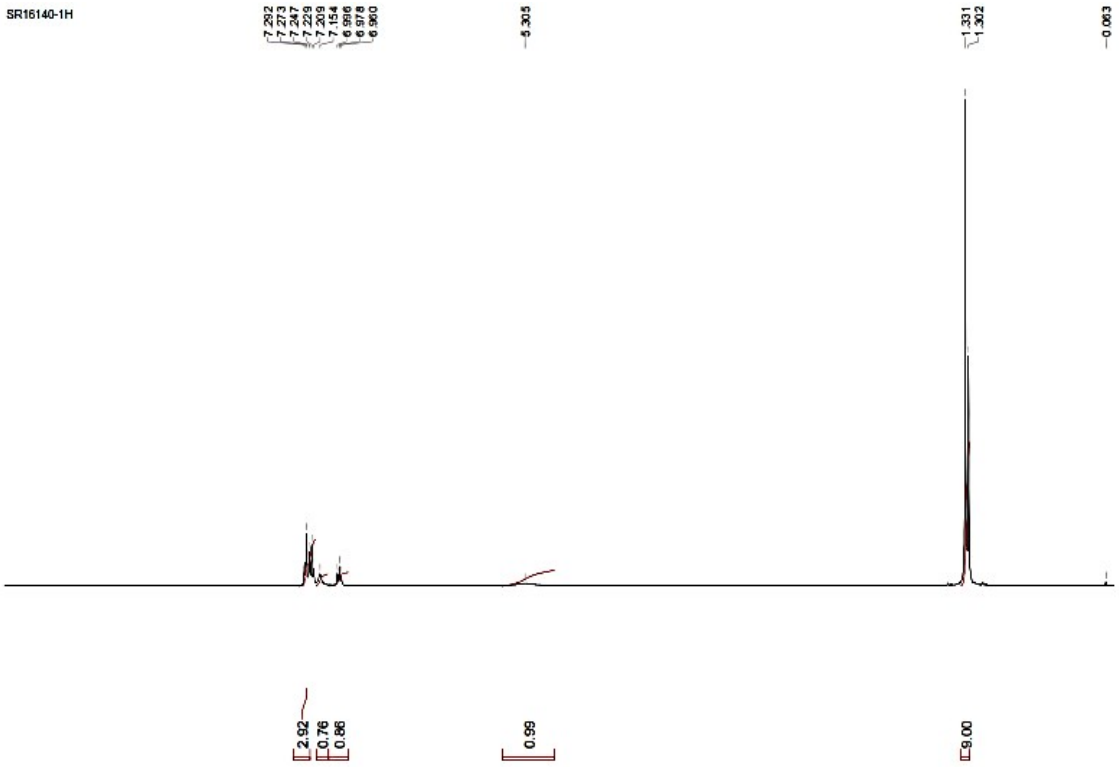

**$^{1}$H NMR spectra of 1-isopropyl-3-phenylurea 3d**



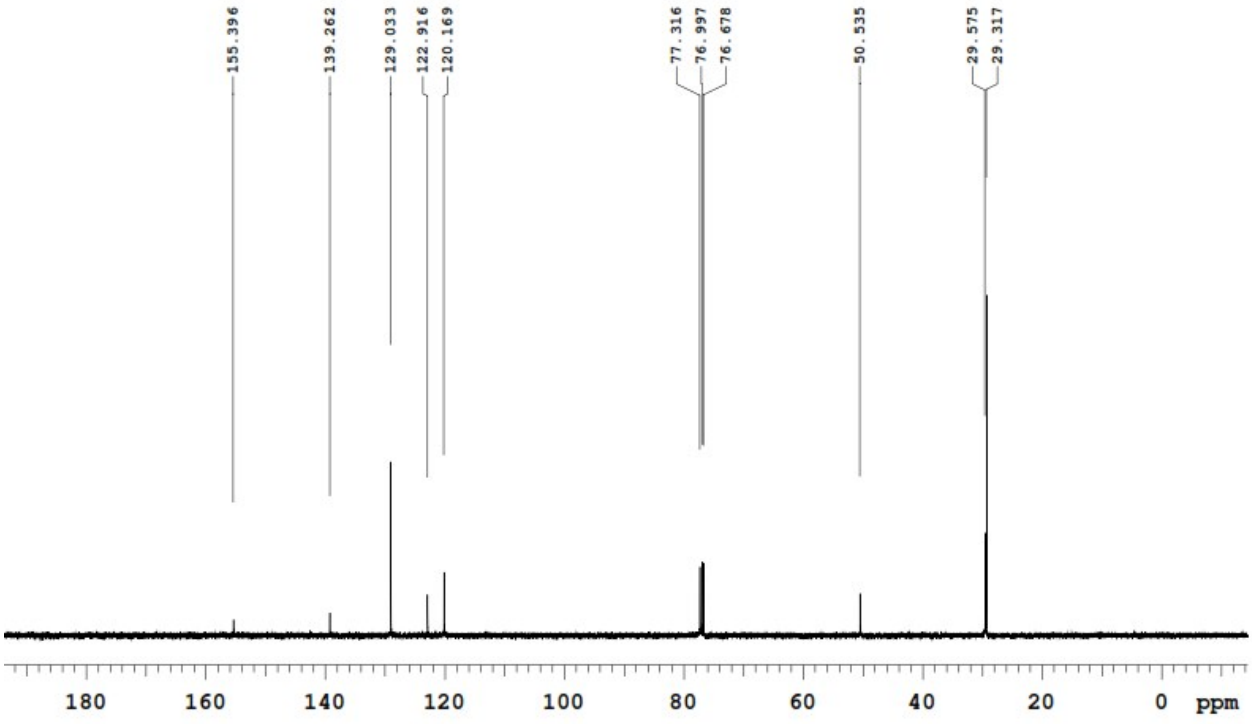

**$^{13}$C NMR spectra of 1-isopropyl-3-phenylurea 3d**



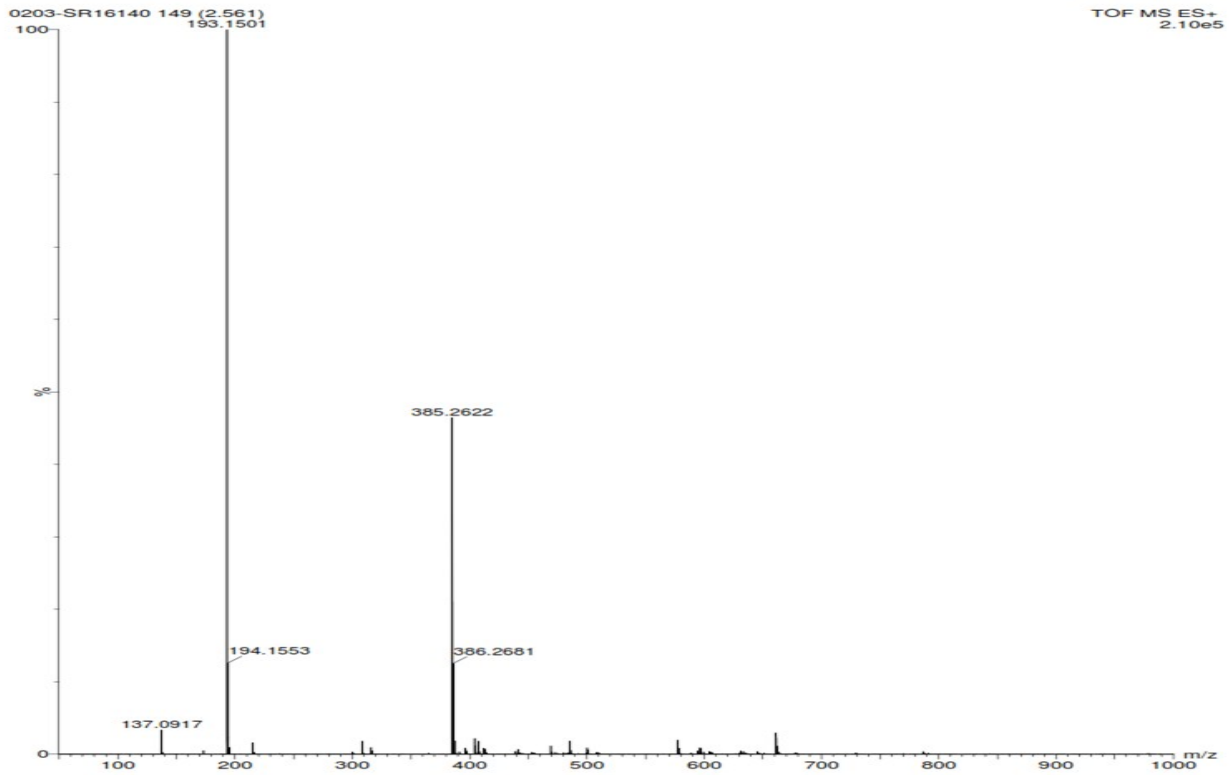

**Mass spectra of 1-isopropyl-3-phenylurea 3d**



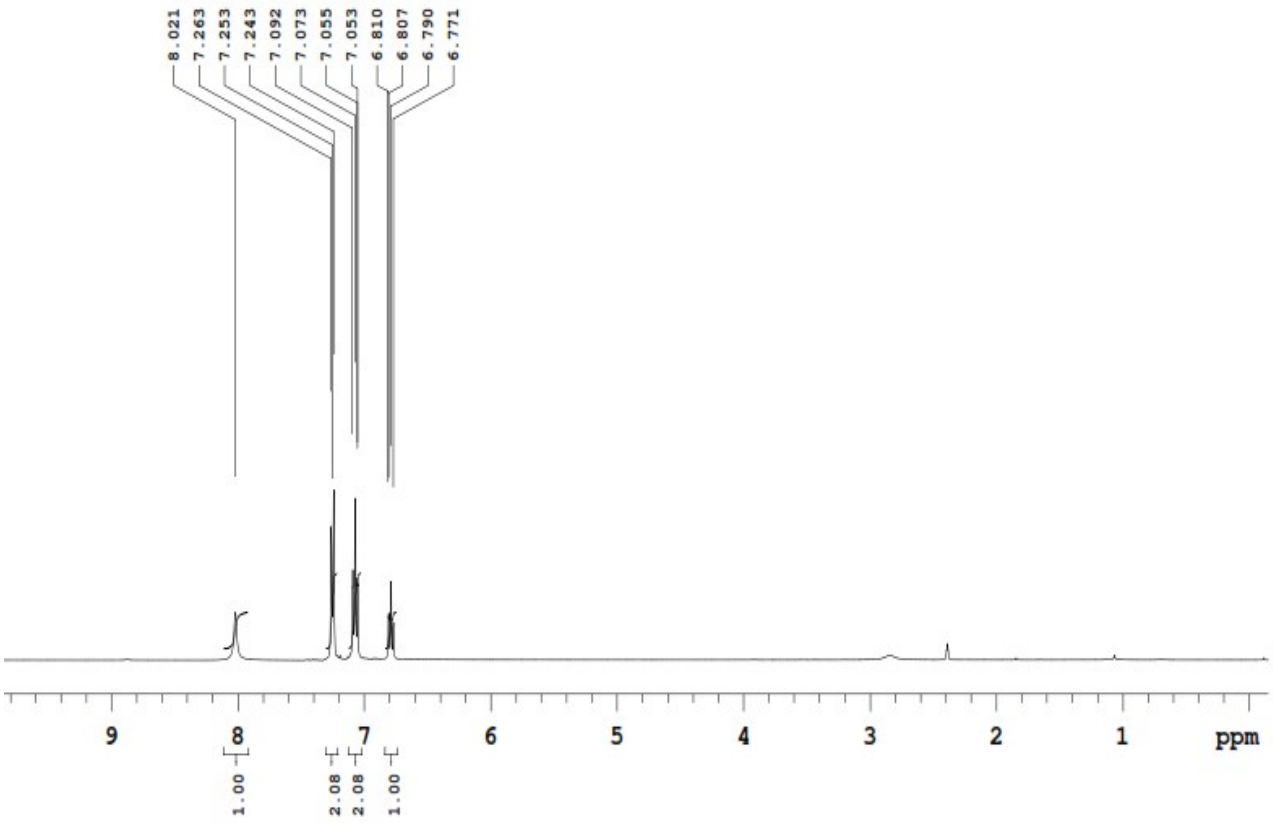

**$^{1}$H NMR spectra of 1-(*tert*-butyl)-3-phenylurea 3e**



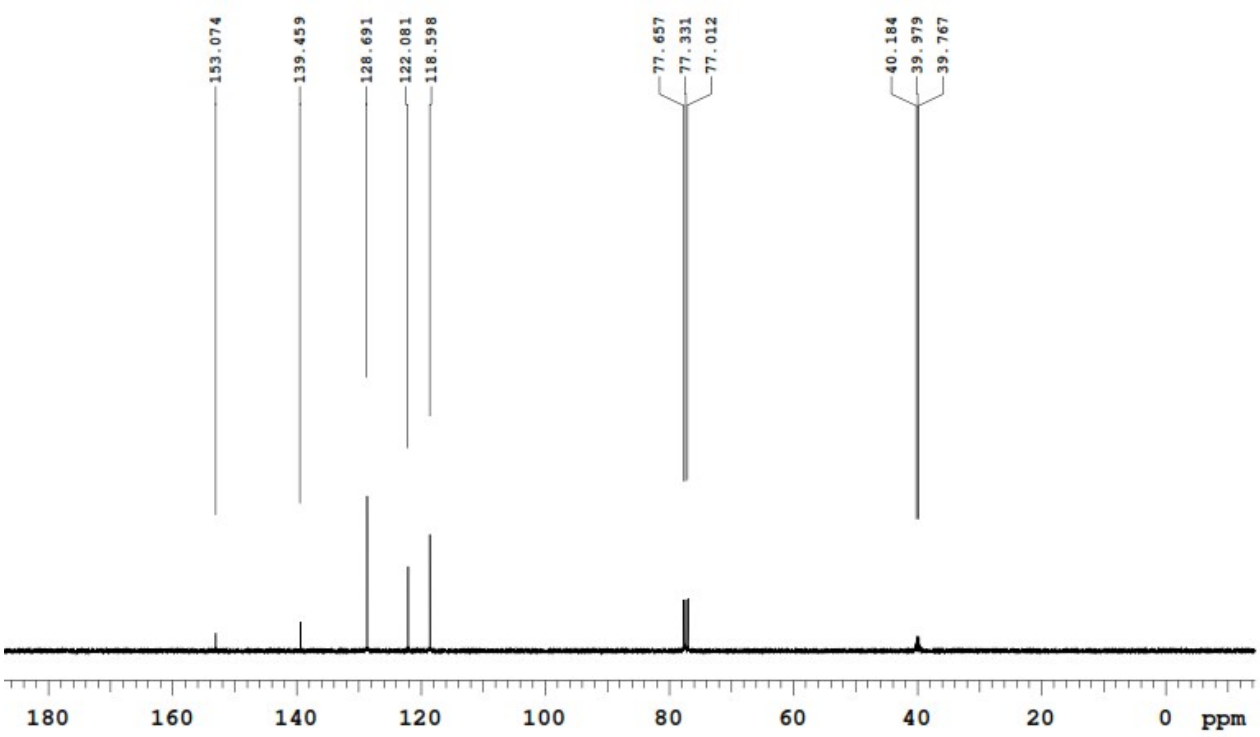

**$^{13}$C NMR spectra of 1-(*tert*-butyl)-3-phenylurea 3e**



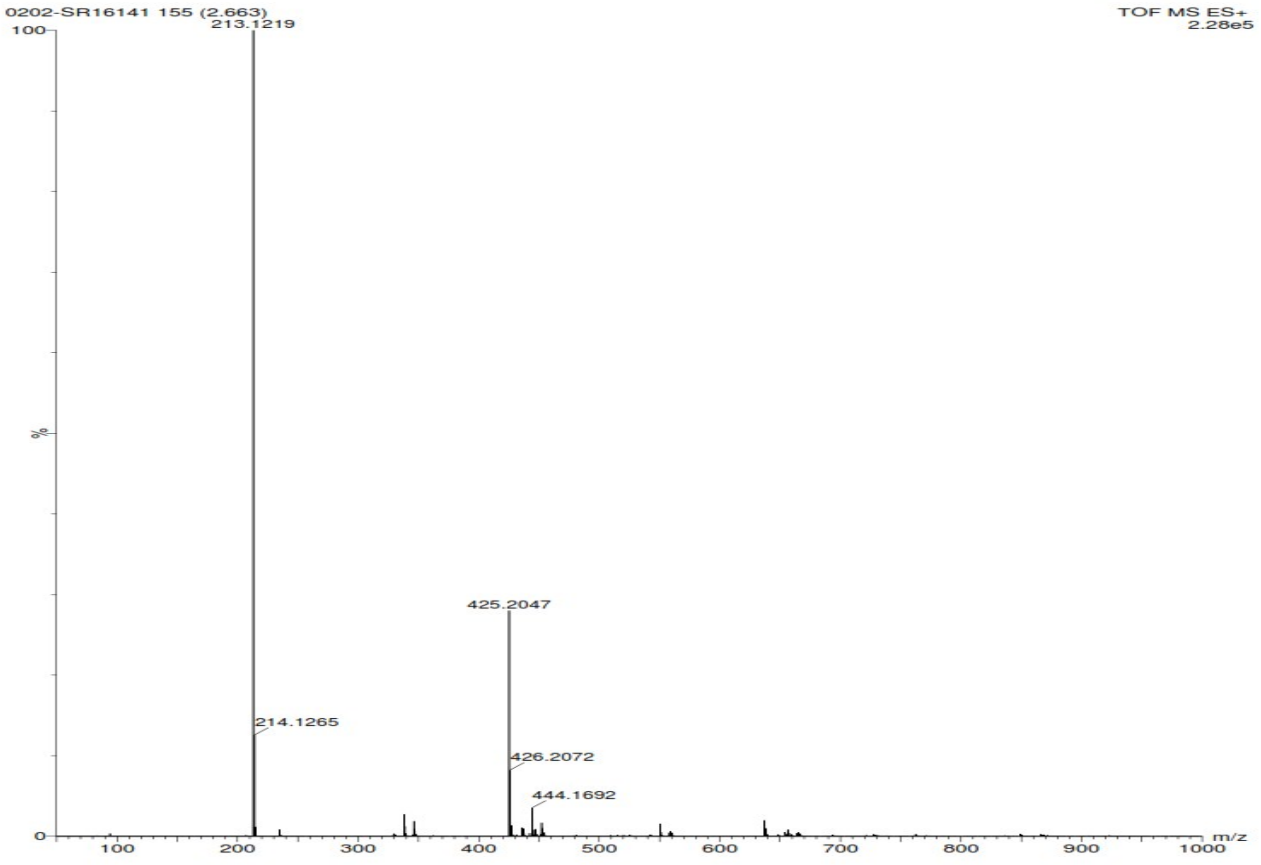

**Mass spectra of 1-(*tert*-butyl)-3-phenylurea 3e**



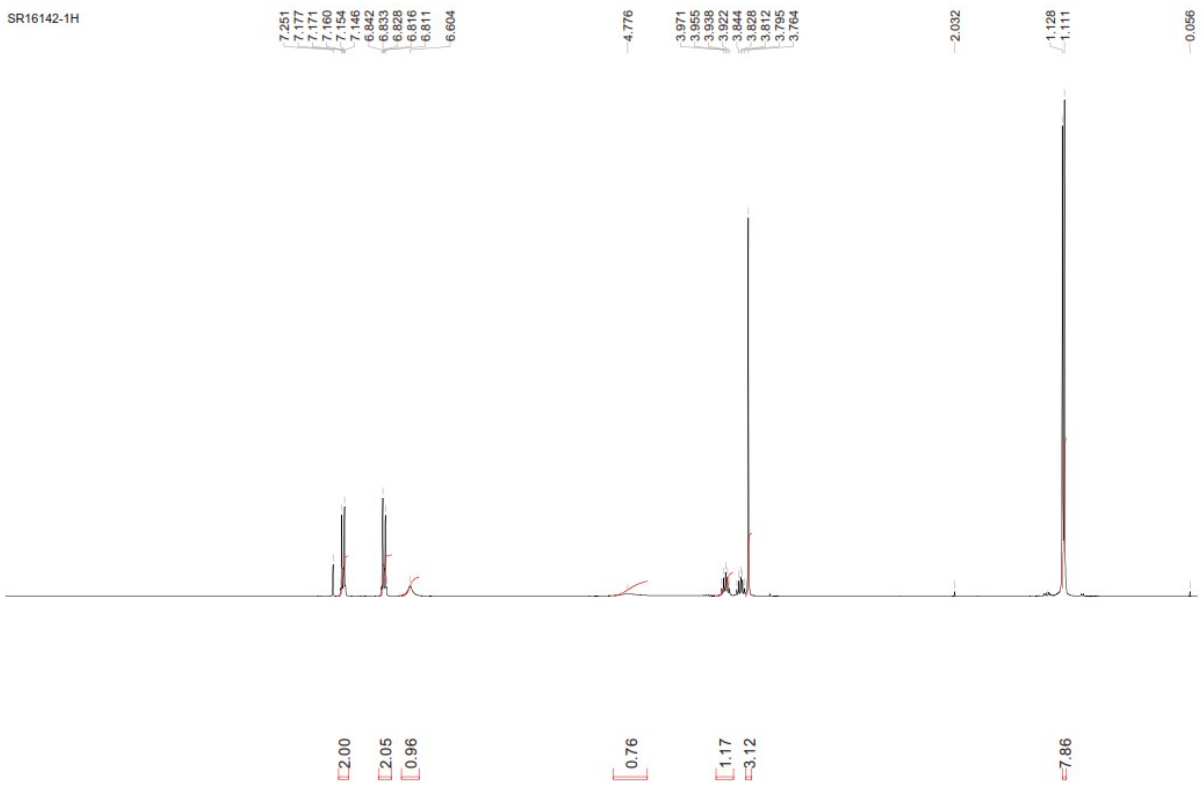

**$^{1}$H NMR spectra of 1,3-Diphenylurea 3f:**



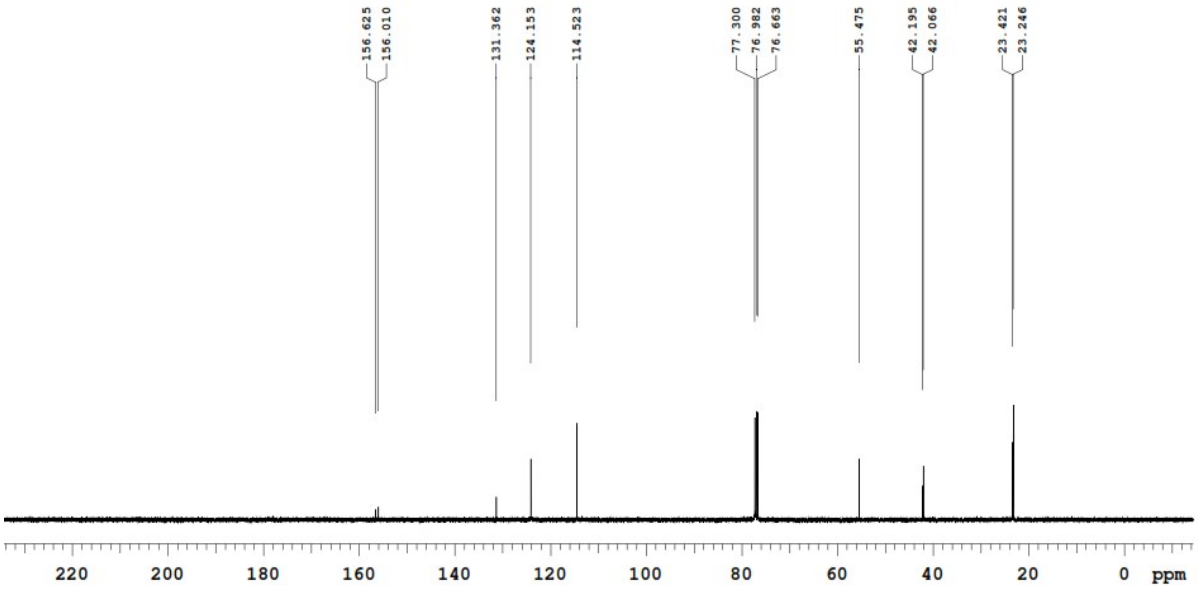

**$^{13}$H NMR spectra of 1,3-Diphenylurea 3f:**



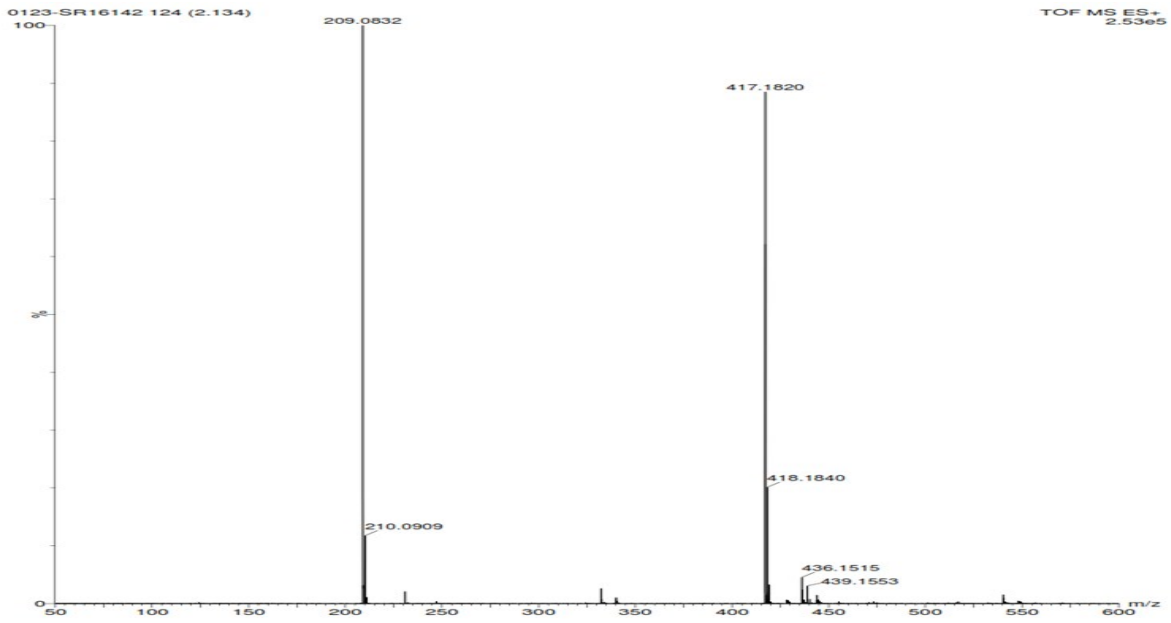

**Mass spectra of 1,3-Diphenylurea 3f:**



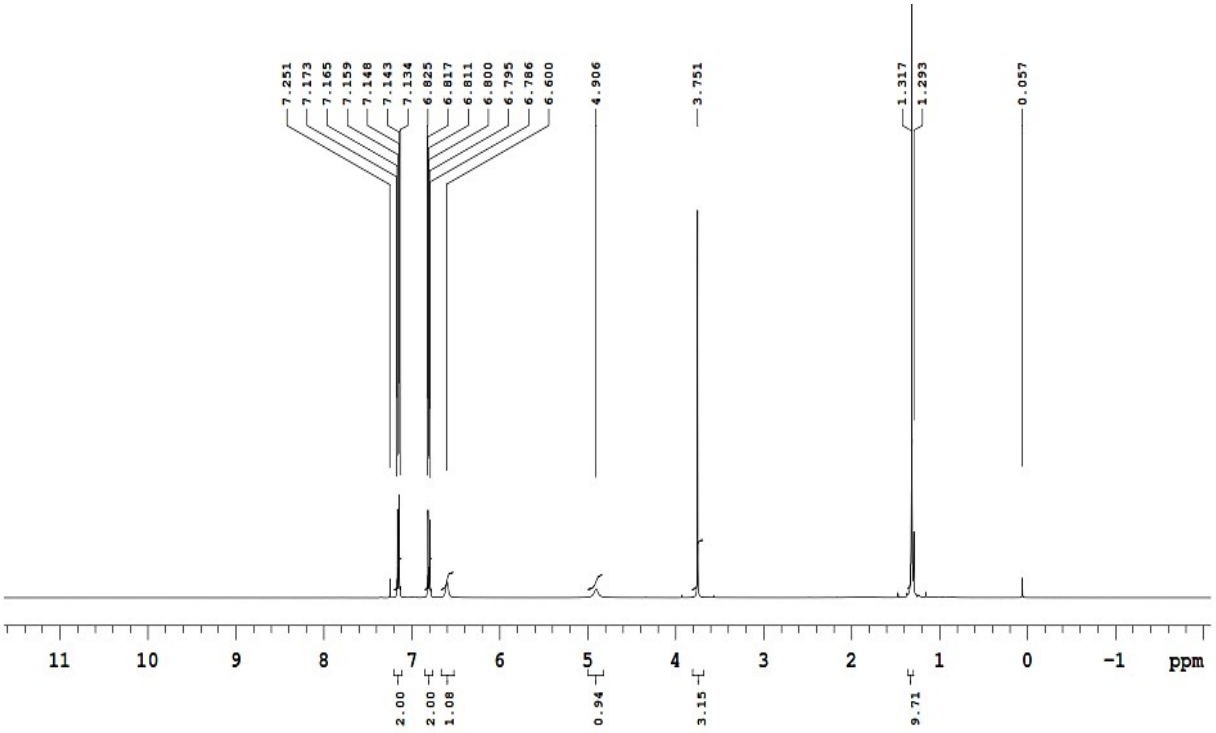

**$^{1}$H NMR spectra of 1-isopropyl-3-(4-methoxy phenyl)urea 3g**



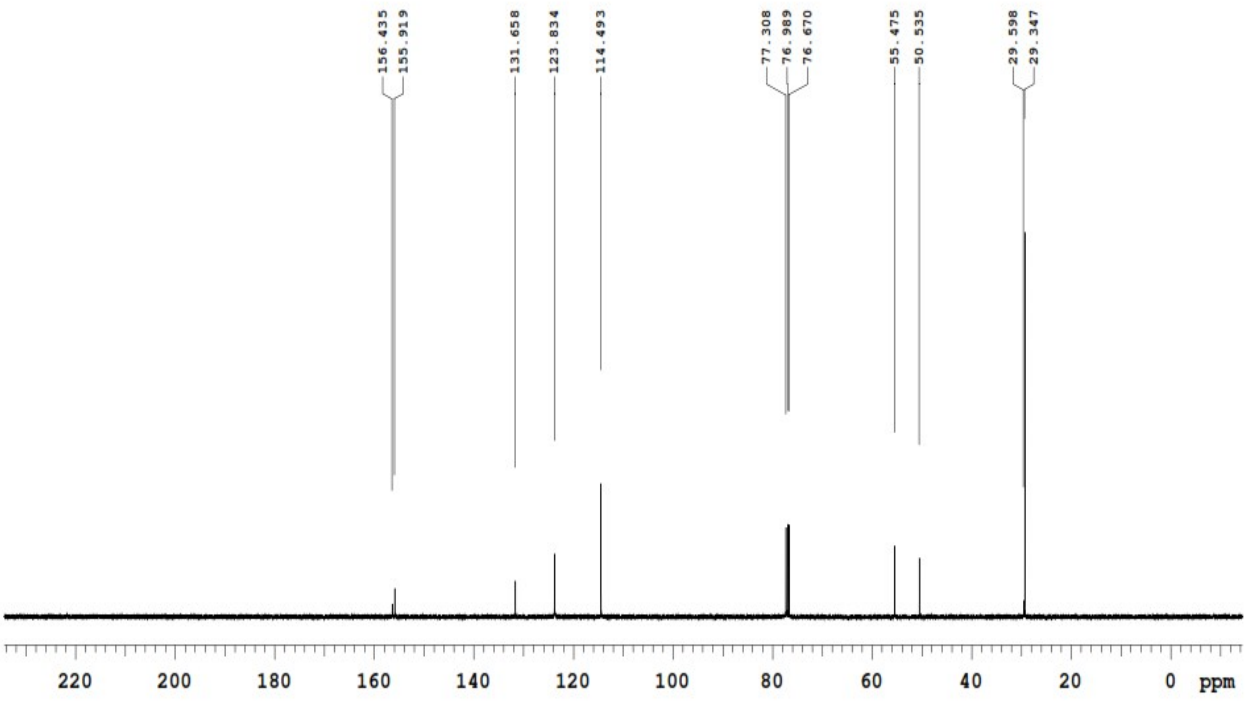

**$^{13}$H NMR spectra of 1-isopropyl-3-(4-methoxy phenyl)urea 3g**



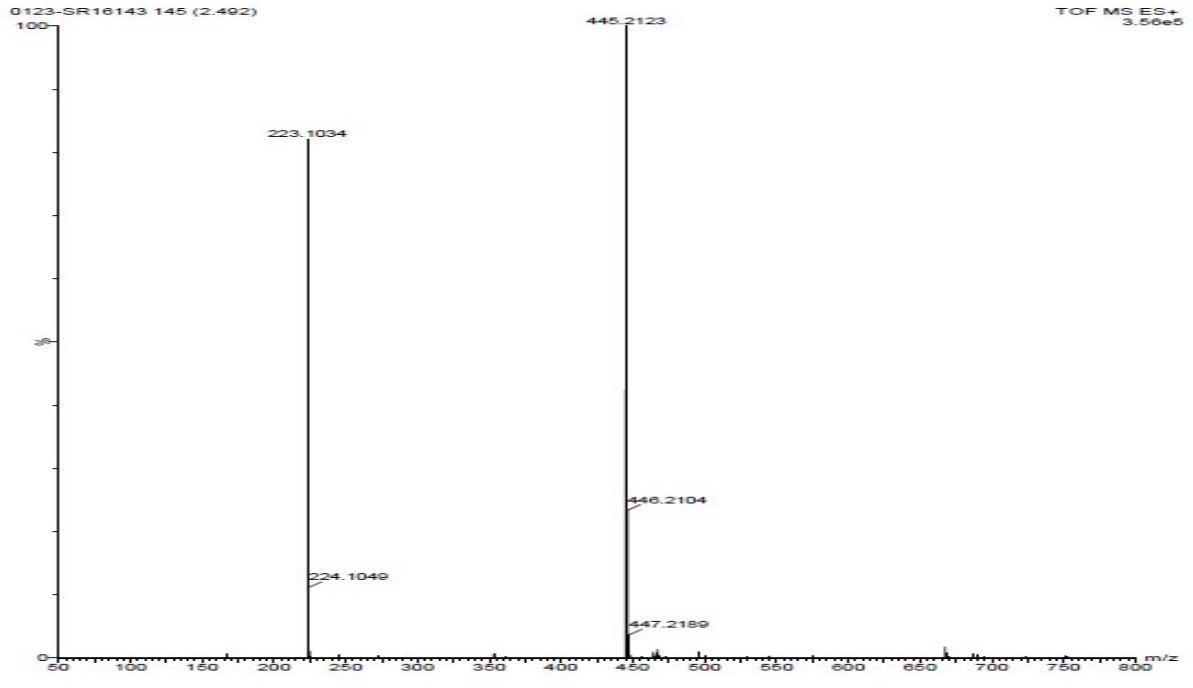

**Mass spectra of 1-isopropyl-3-(4-methoxy phenyl)urea 3g**



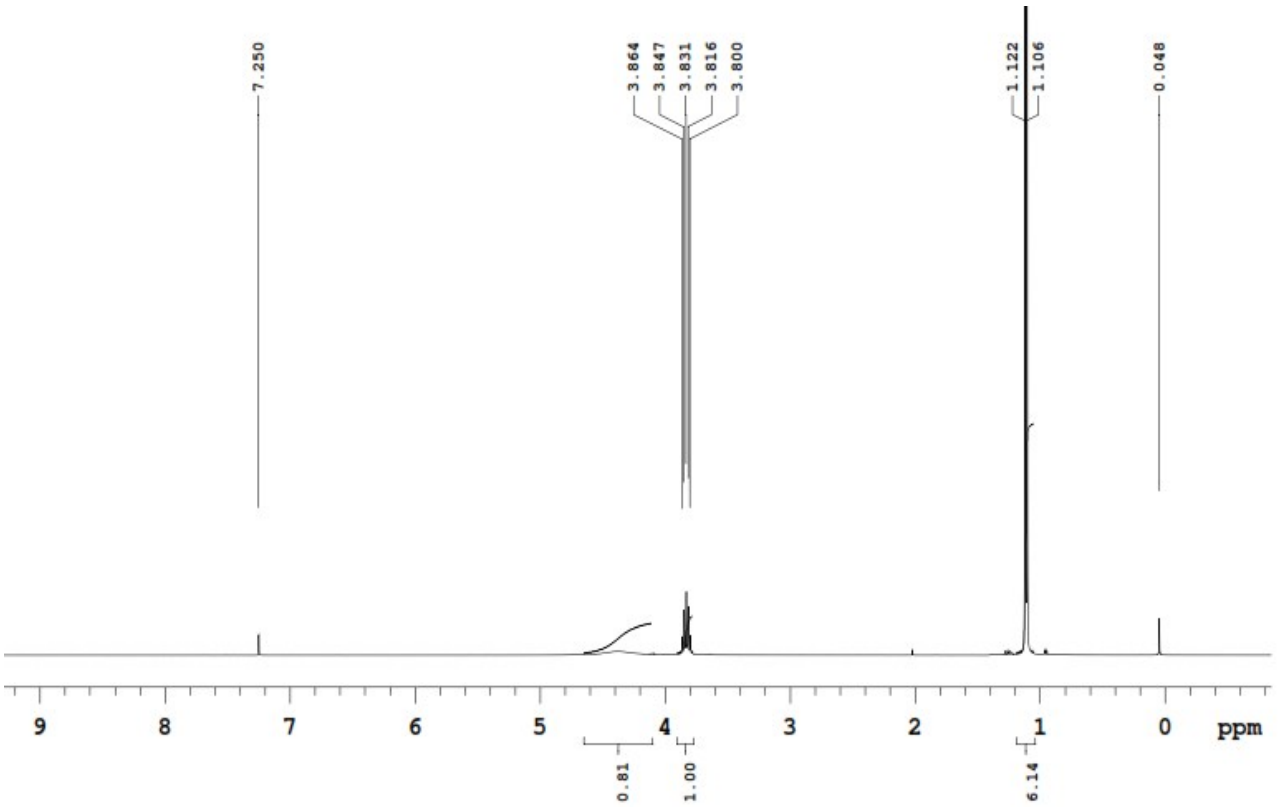

**$^{1}$H NMR spectra of 1-(*tert*-butyl)-3-(4-methoxy phenyl)urea 3h:**



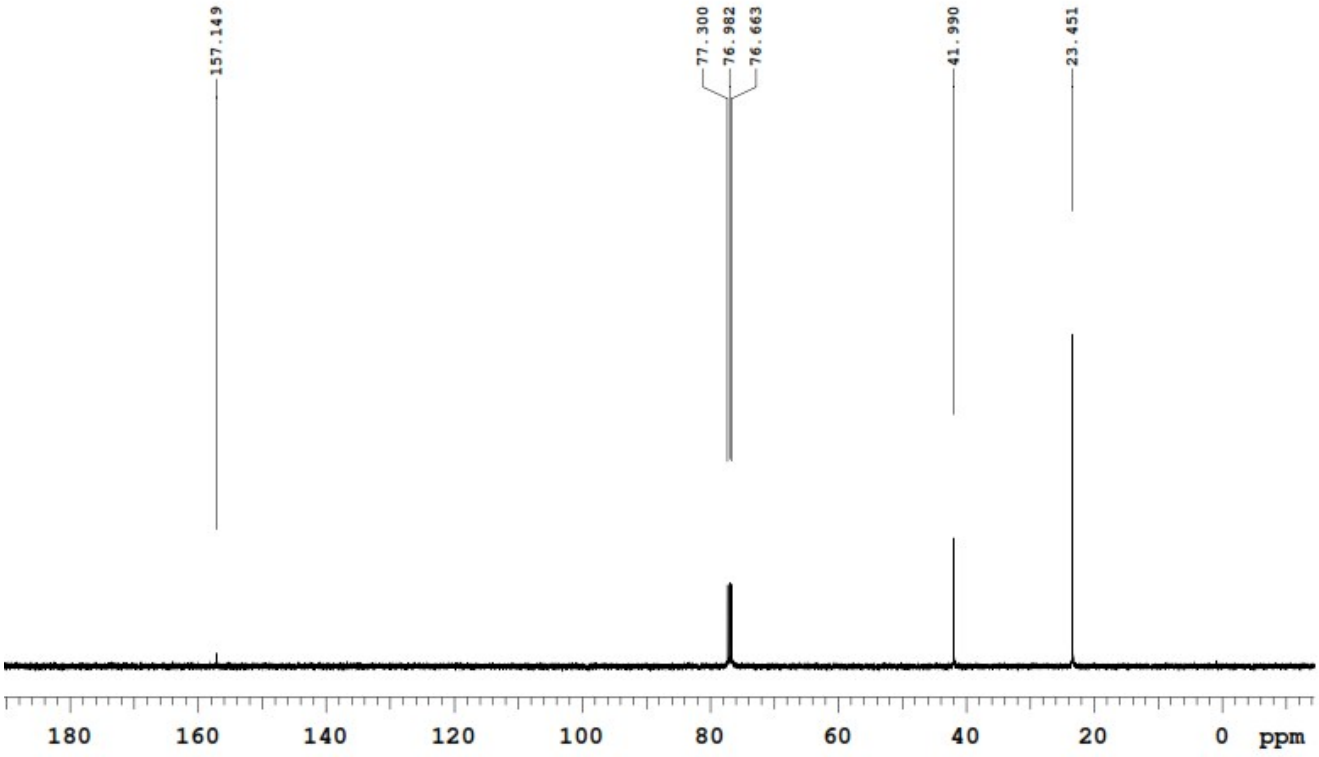

**$^{13}$C NMR spectra of 1-(*tert*-butyl)-3-(4-methoxy phenyl)urea 3h:**



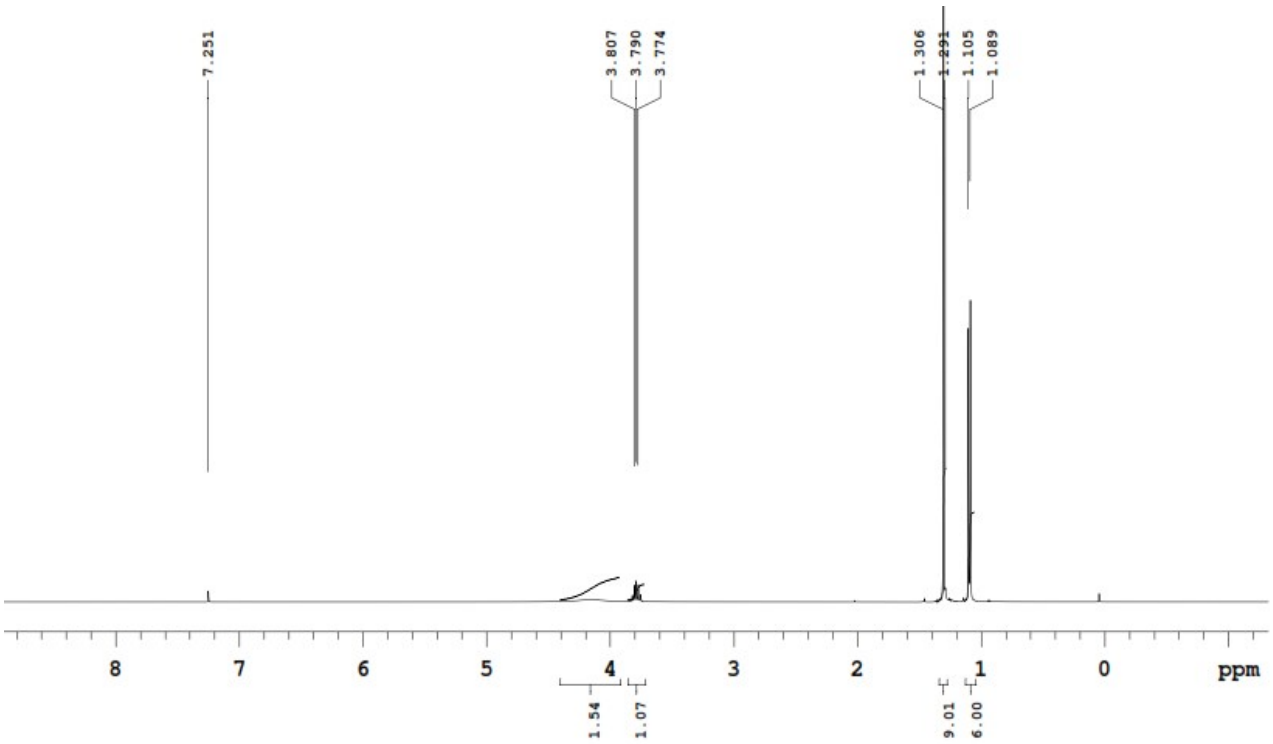

**Mass spectra of 1-(*tert*-butyl)-3-(4-methoxy phenyl)urea 3h:**



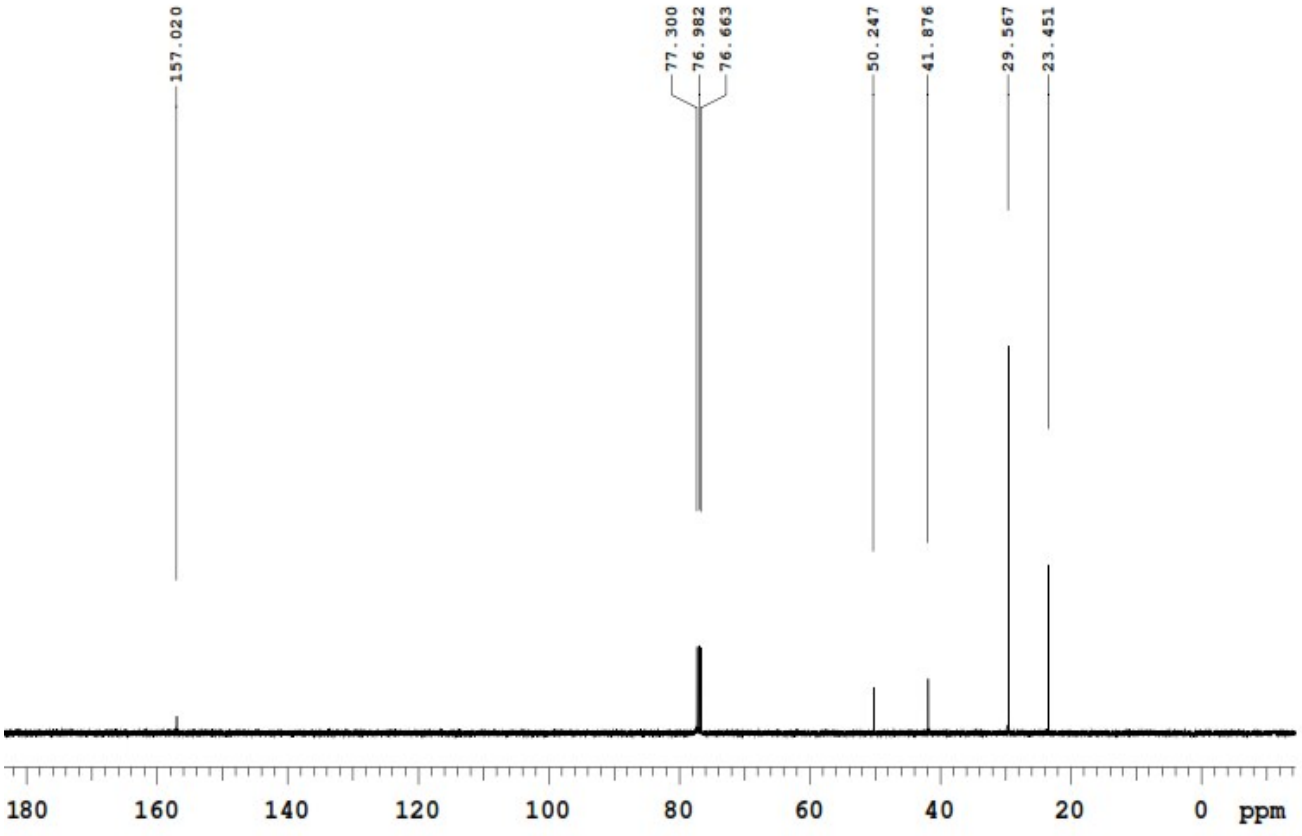

**$^{1}$H NMR spectra of 1,3-Diisopropyl urea 3j:**



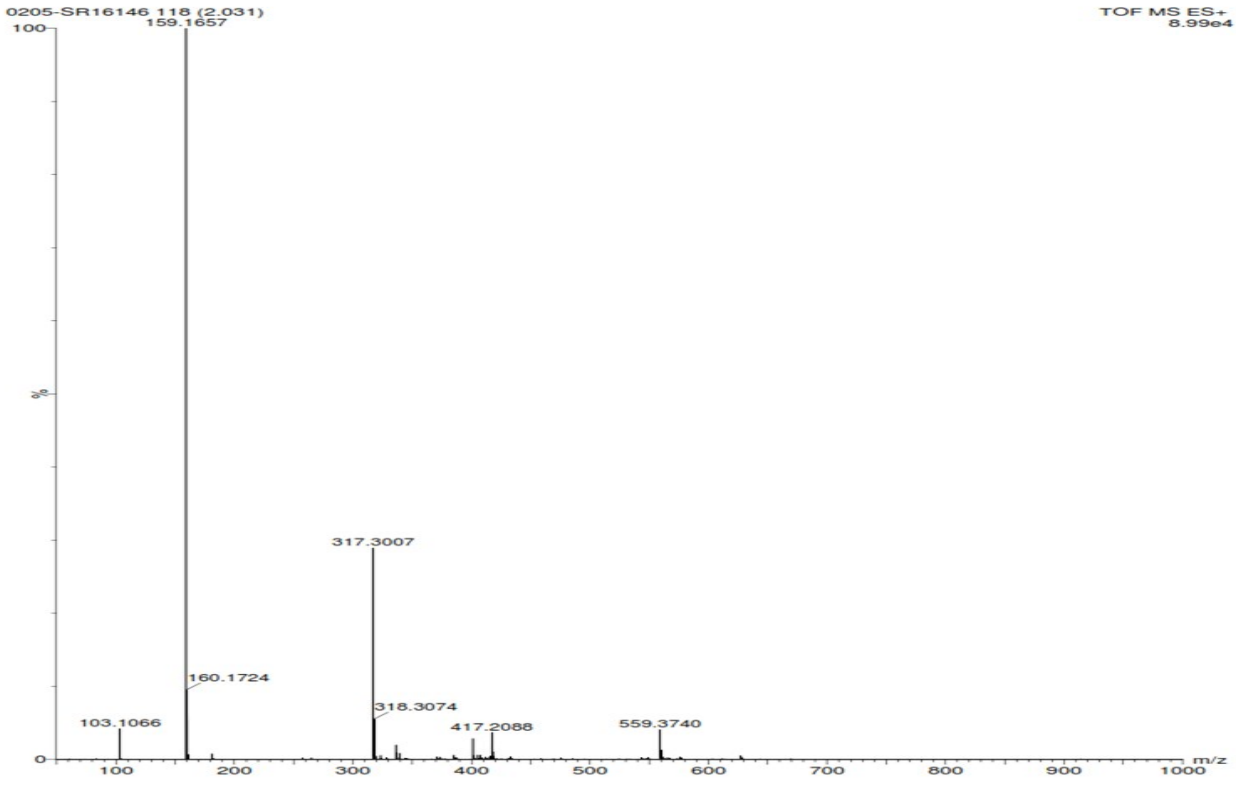

**$^{13}$C NMR spectra of 1,3-Diisopropyl urea 3j:**



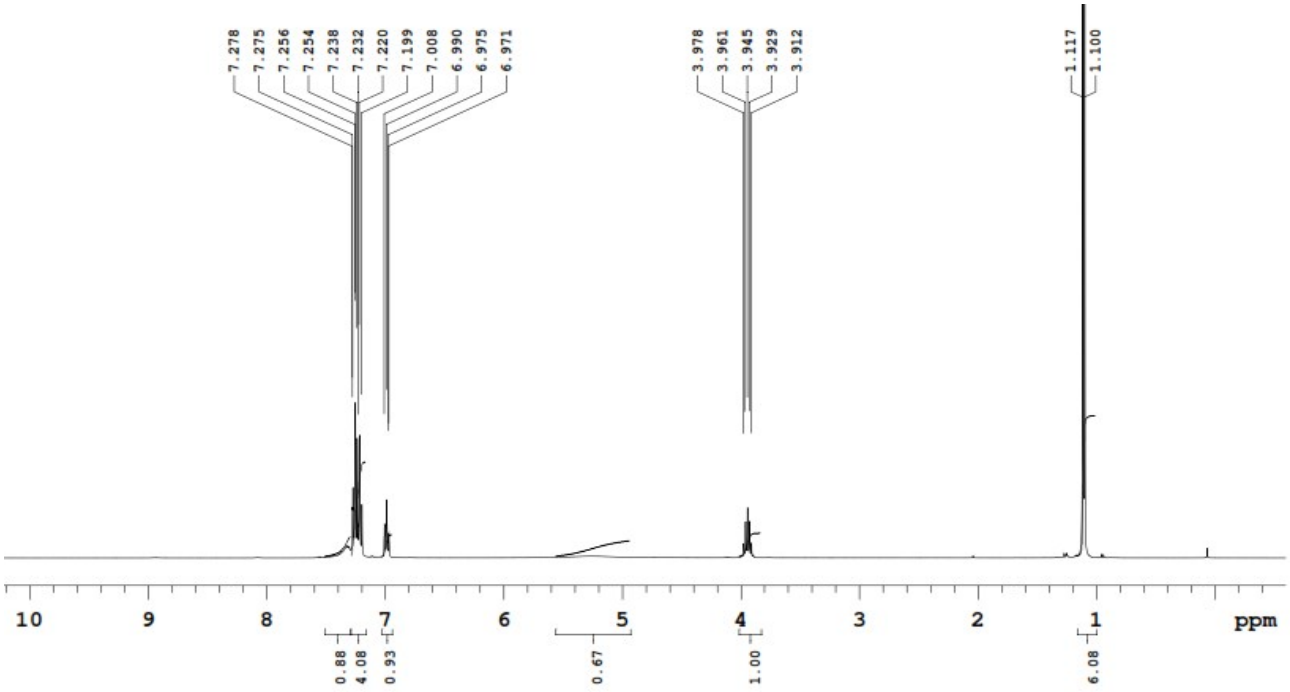

**$^{1}$H NMR spectra of 1-(*tert*-butyl)-3-ispropylurea 3k:**



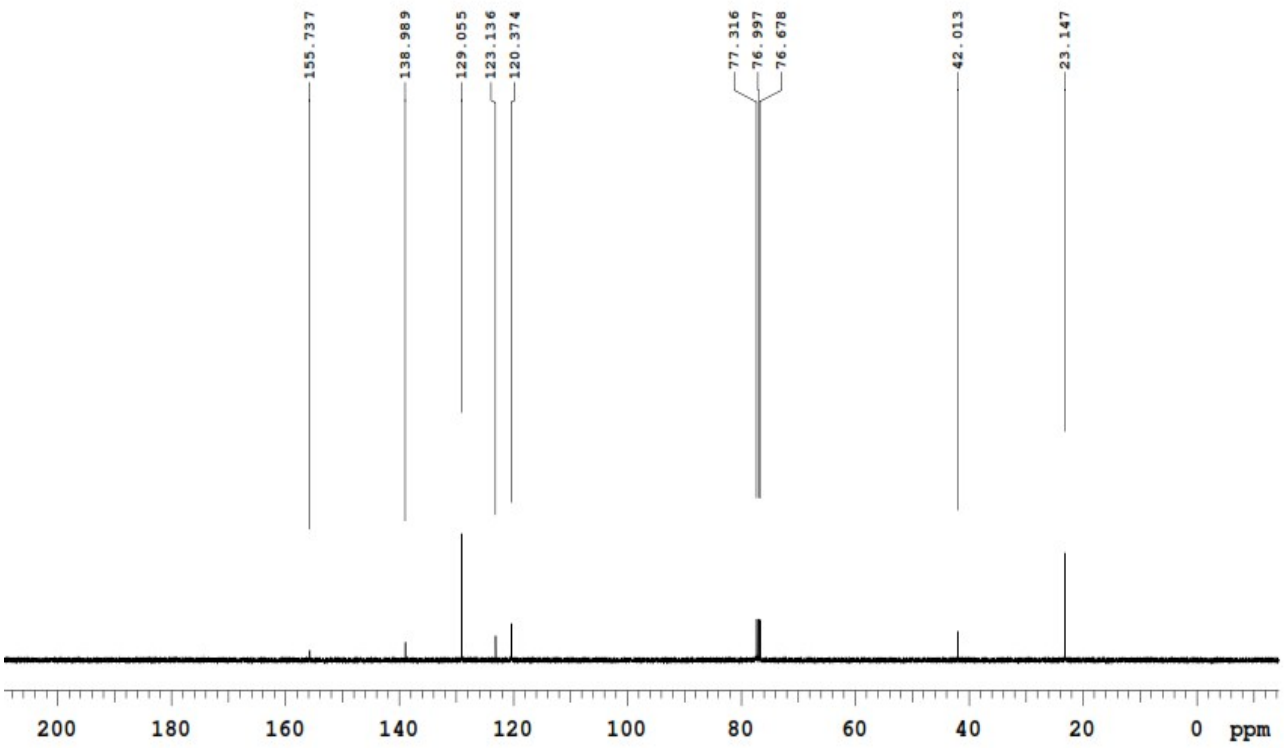

**$^{13}$C NMR spectra of 1-(*tert*-butyl)-3-ispropylurea 3k:**



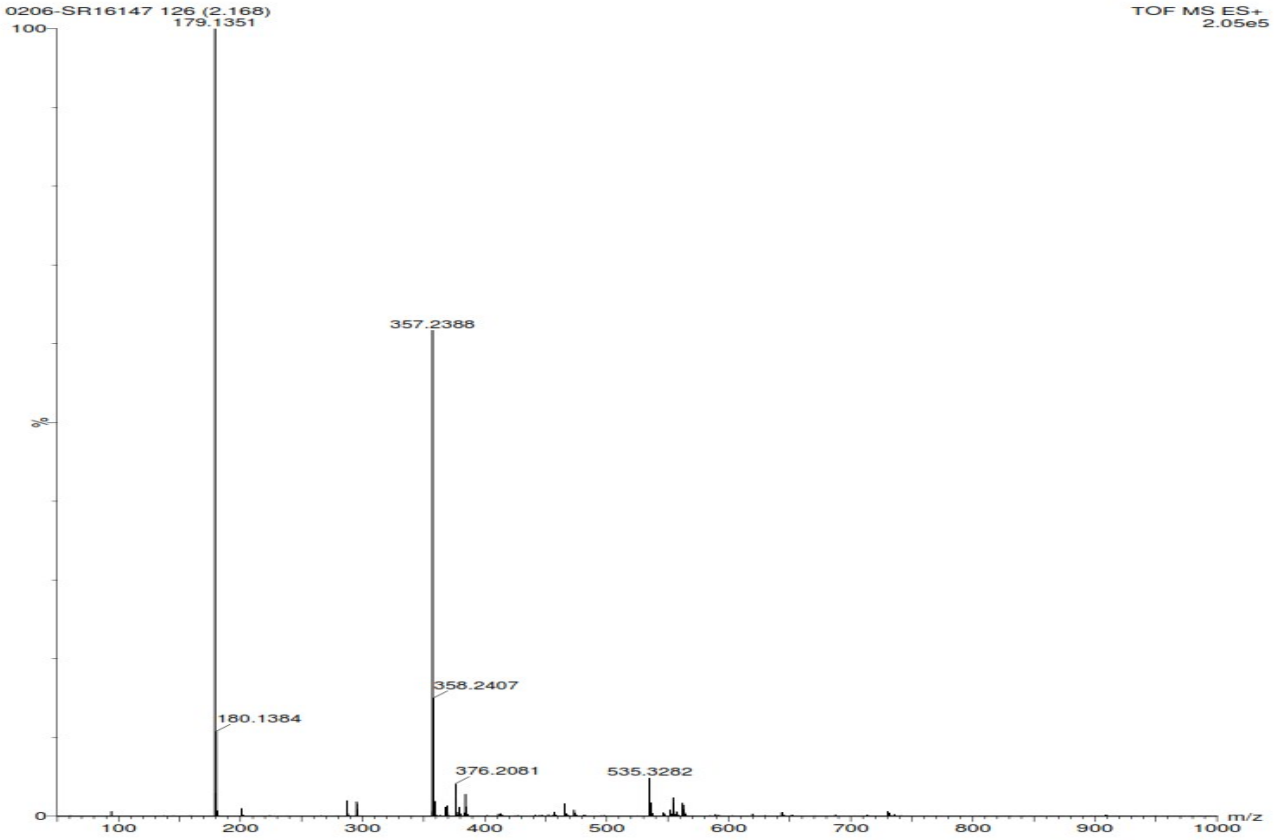

**Mass spectra of 1-(*tert*-butyl)-3-isppropylurea 3k:**



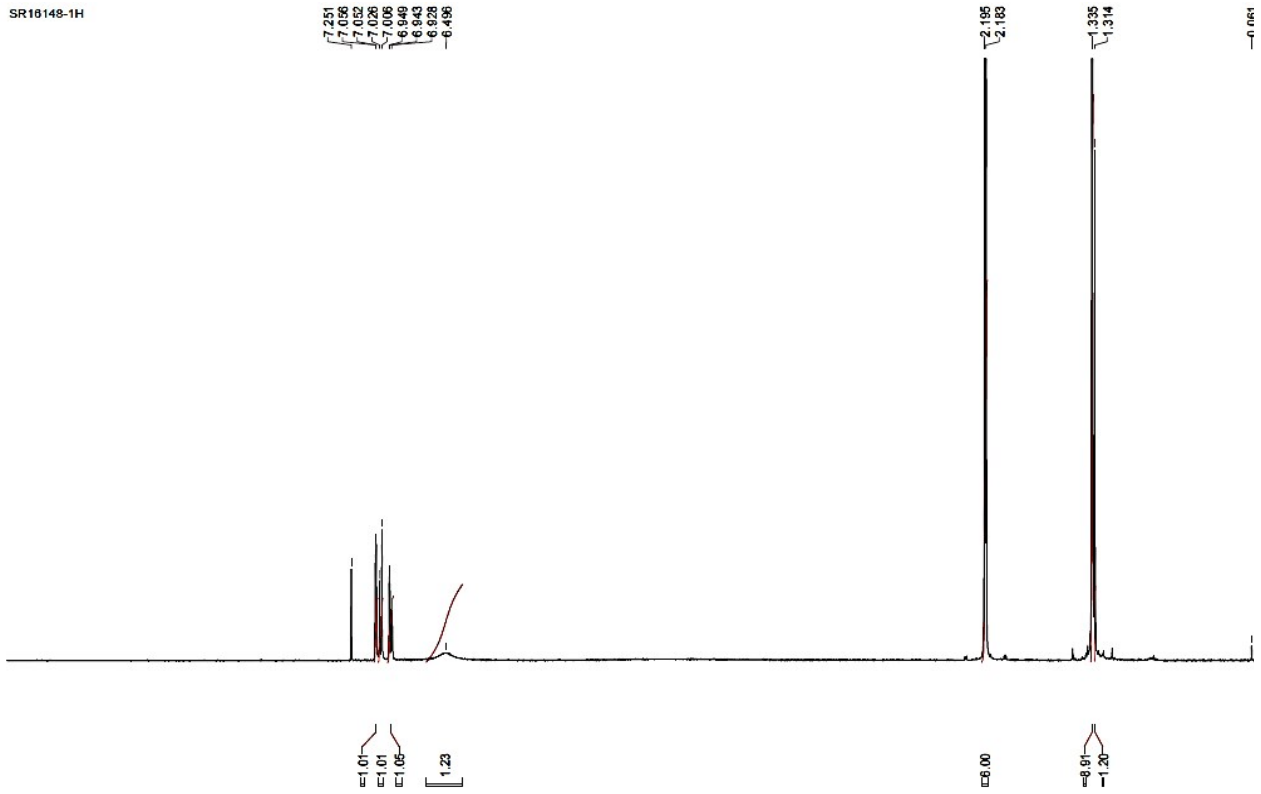

**$^{1}$H NMR spectra of 1-isopropyl--3-phenylurea 3l:**



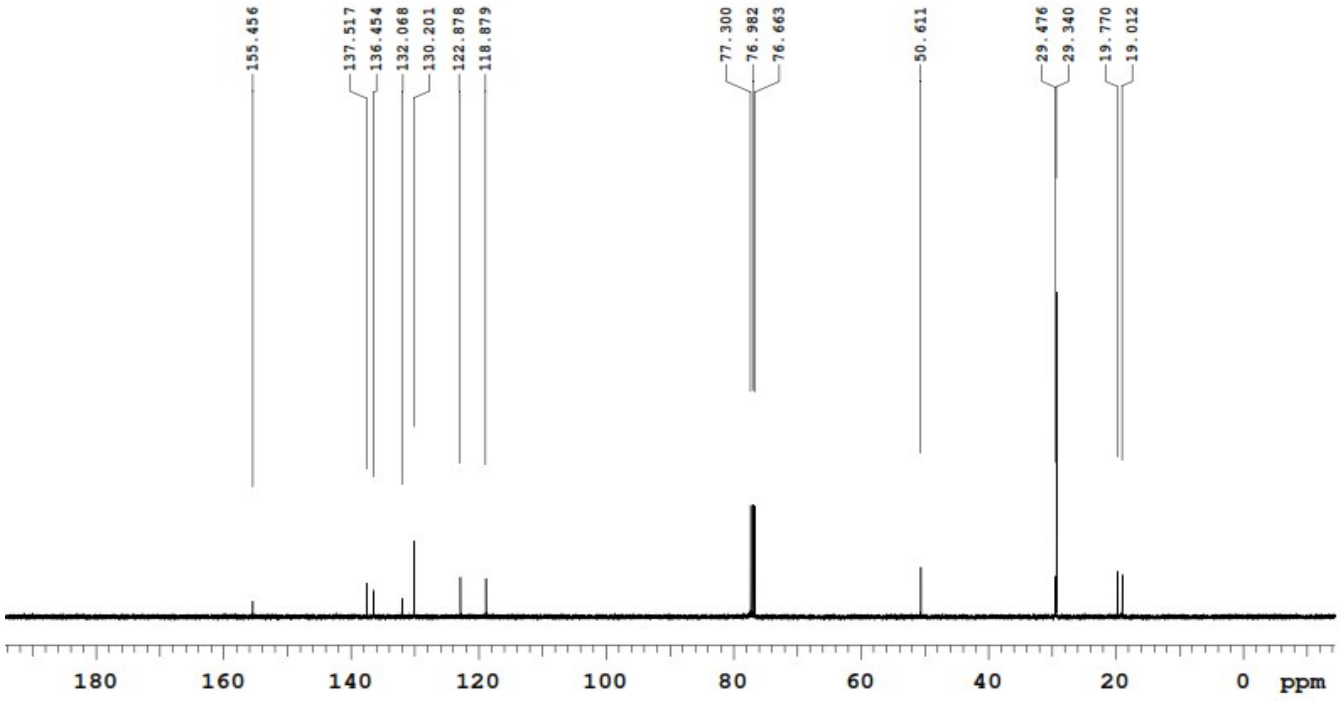

**$^{13}$C NMR spectra of 1-isopropyl--3-phenylurea 3l:**



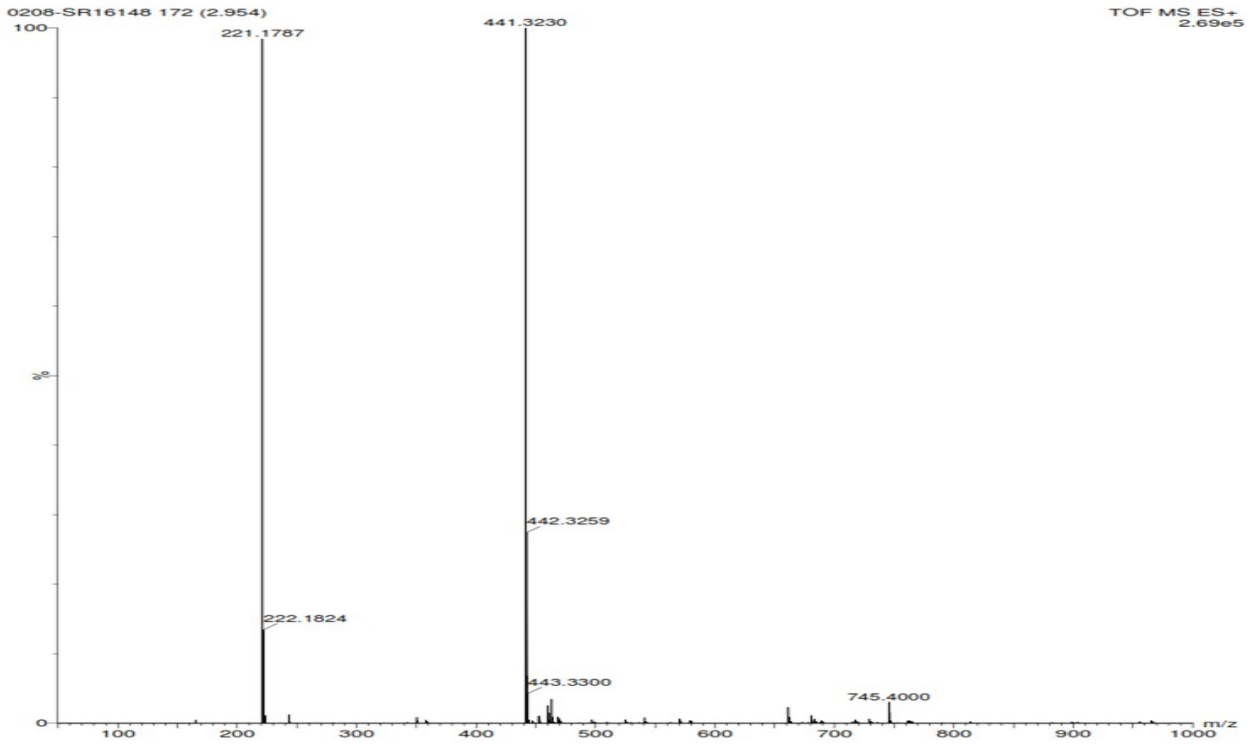

**Mass spectra of 1-isopropyl--3-phenylurea 3l:**



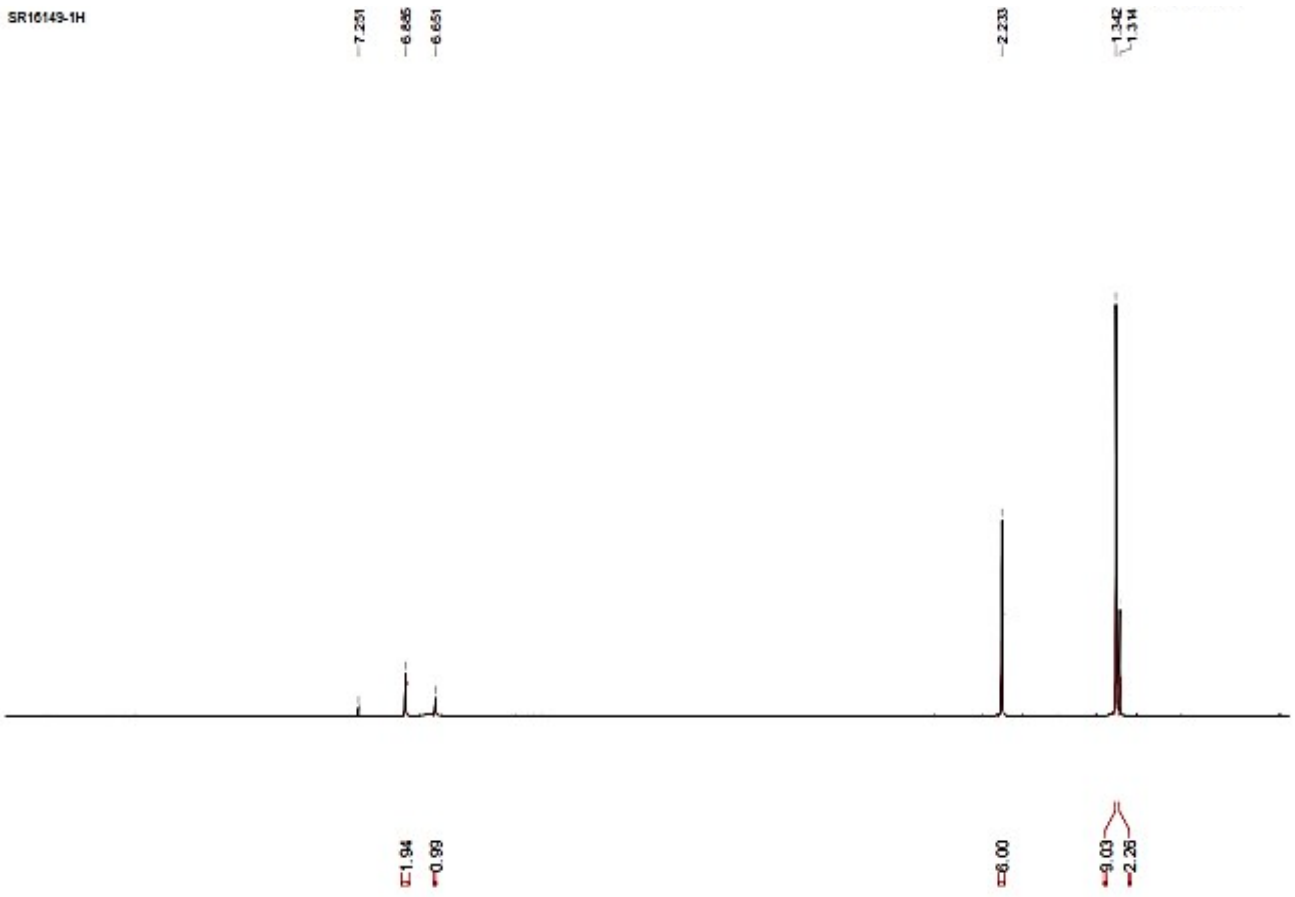

**[1]H NMR spectra of 1-(*tert*-butyl)-3-(3,4-dimethylphenyl)urea 3m:**



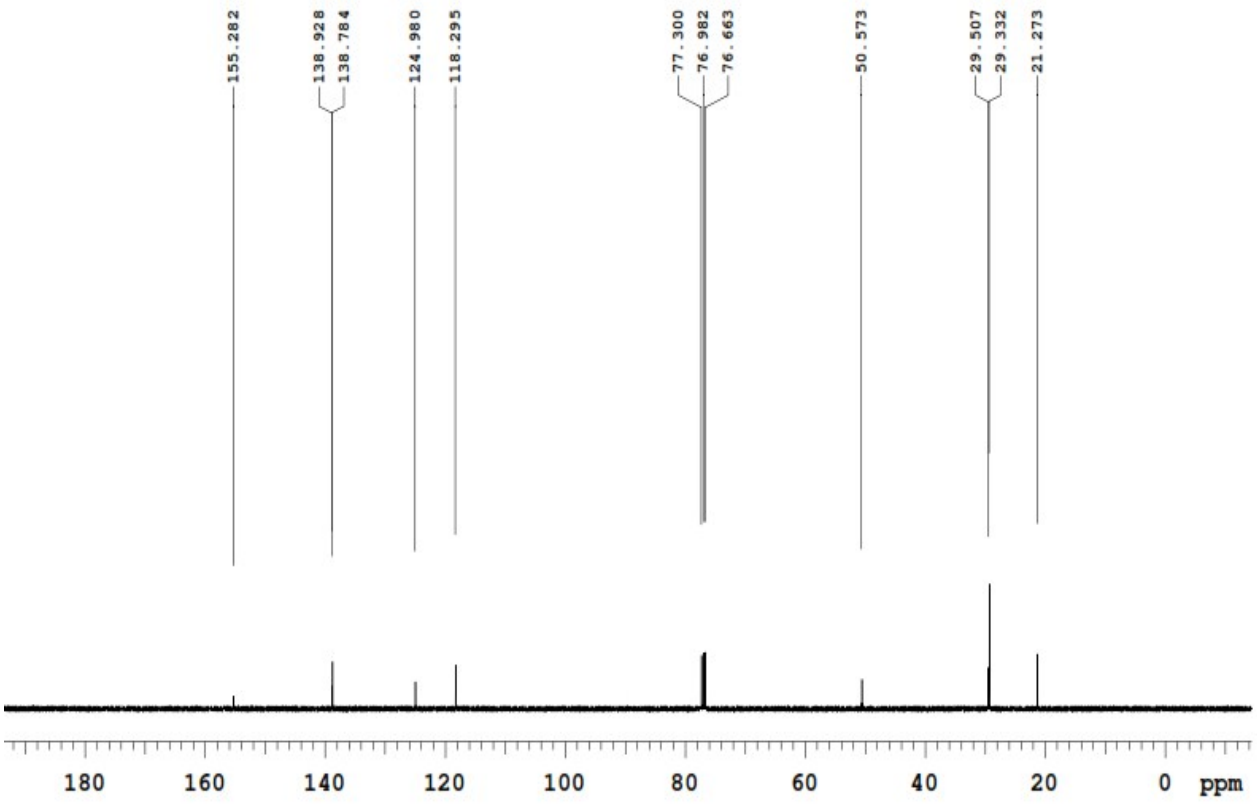

**[13]C NMR spectra of 1-(*tert*-butyl)-3-(3,4-dimethylphenyl)urea 3m:**



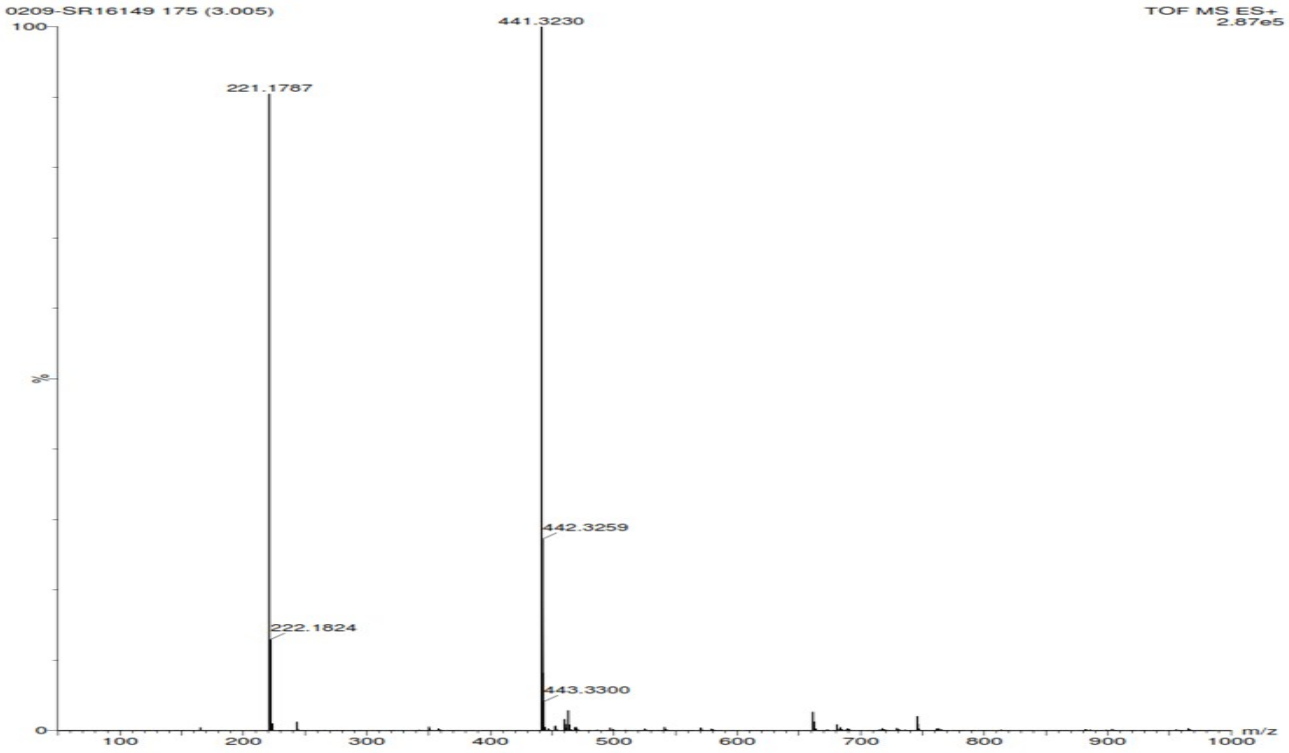

**Mass spectra of 1-(*tert*-butyl)-3-(3,4-dimethylphenyl)urea 3m:**



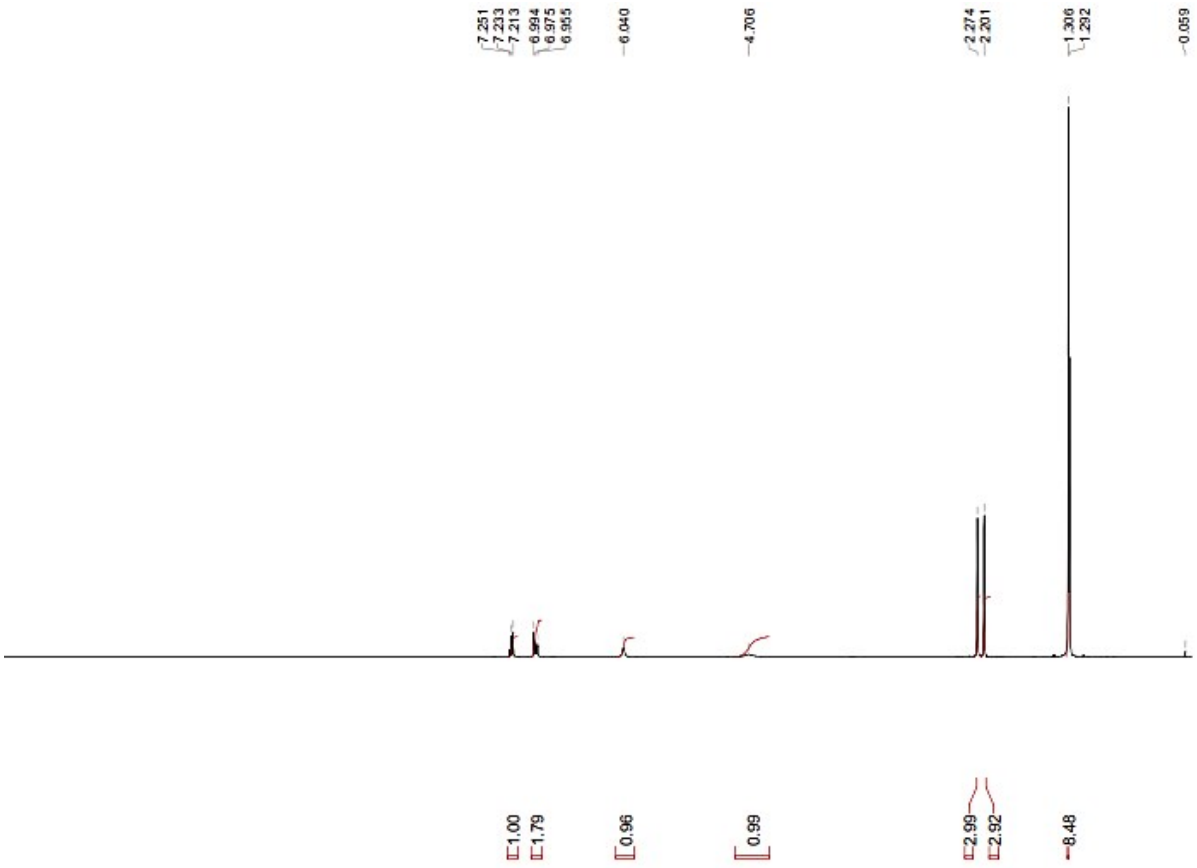

**$^{1}$H NMR spectra of 1-(tert-butyl)-3-(3,5-dimethylphenyl)urea 3n:**



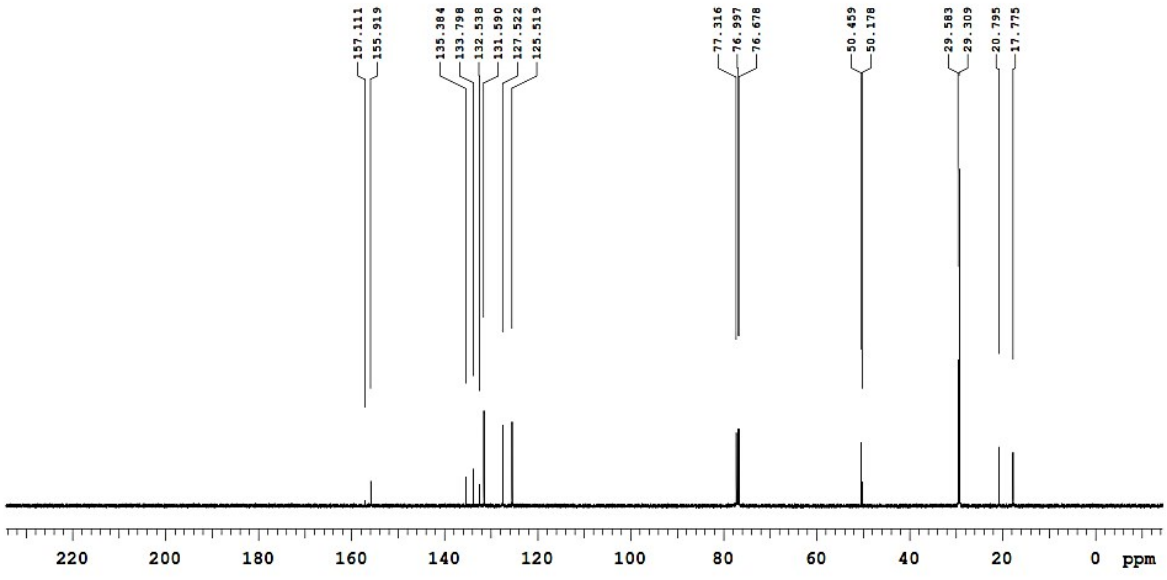

**$^{13}$C NMR spectra of 1-(tert-butyl)-3-(3,5-dimethylphenyl)urea 3n:**



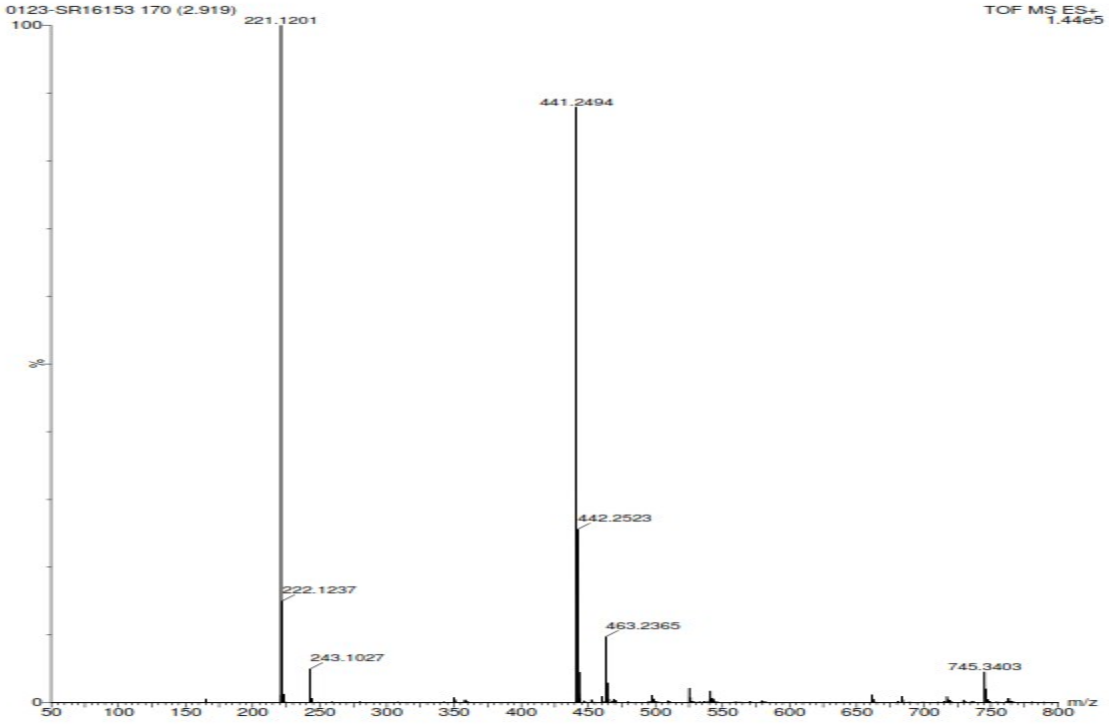

**Mass spectra of 1-(tert-butyl)-3-(3,5-dimethylphenyl)urea 3n:**



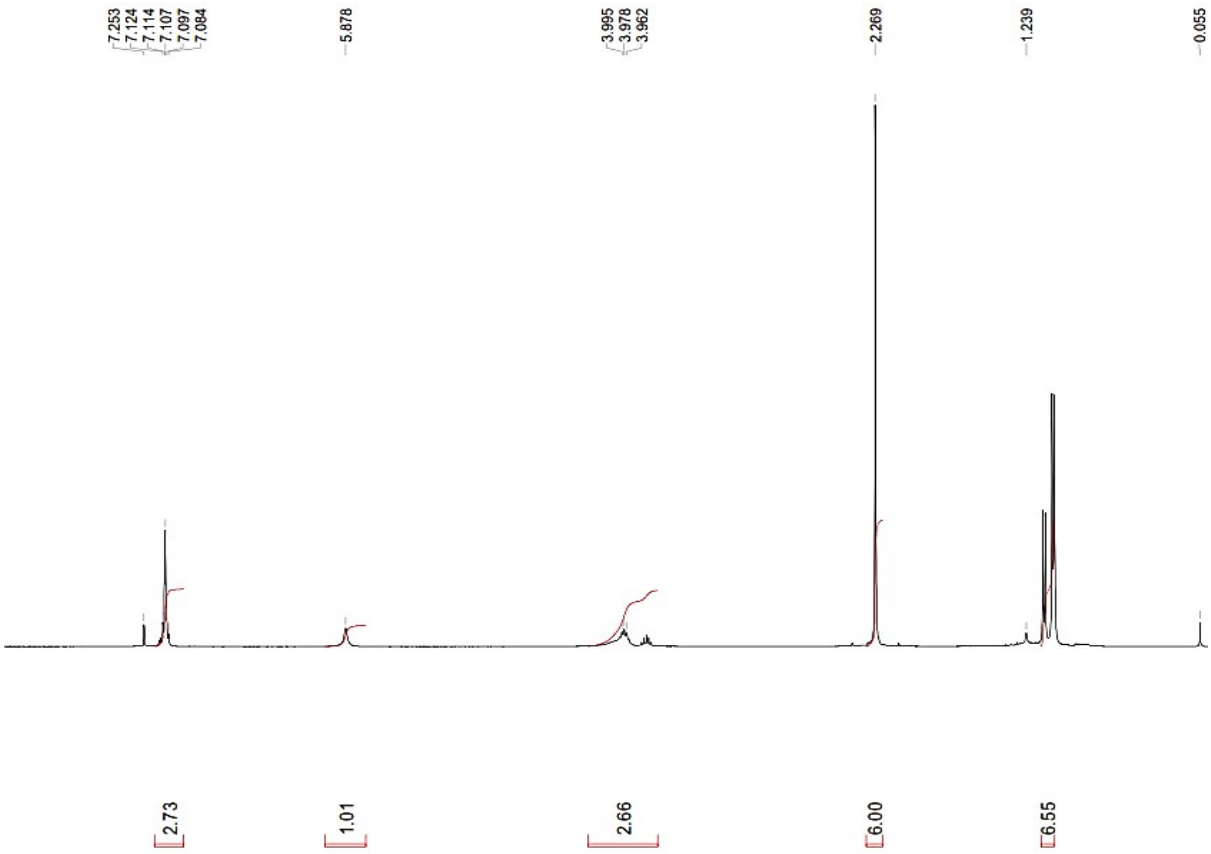

**$^{1}$H NMR spectra of 1-(*tert*-butyl)-3-(2,4-dimethylphenyl)urea 3o:**



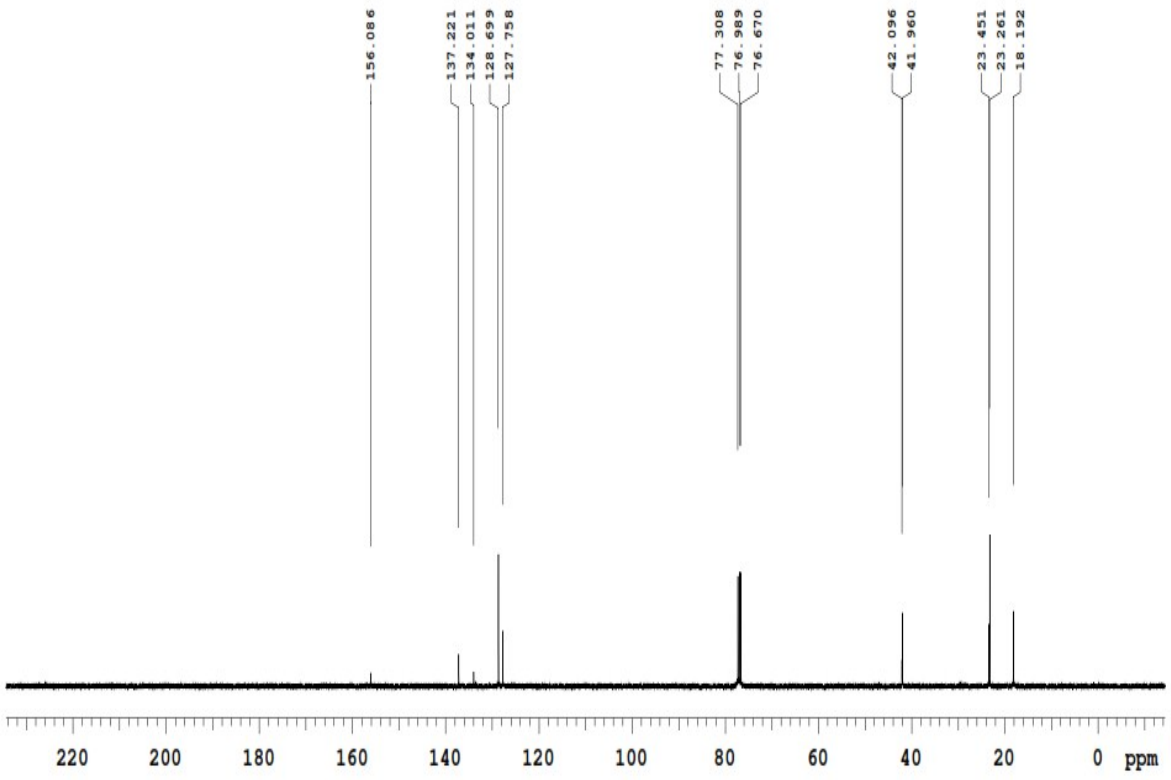

**$^{13}$C NMR spectra of 1-(*tert*-butyl)-3-(2,4-dimethylphenyl)urea 3o**



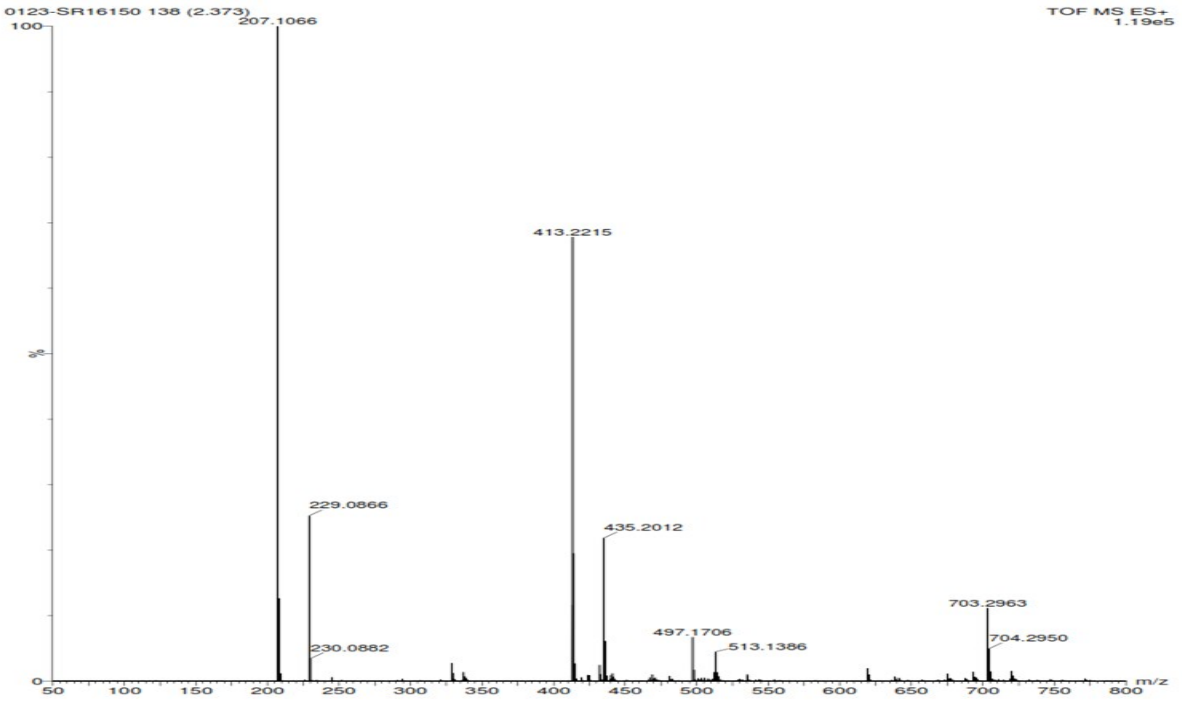

**Mass spectra of 1-(*tert*-butyl)-3-(2,4-dimethylphenyl)urea 3o**




**$^{1}$H NMR spectra of 1-(2,6-dimethylphenyl)-3-isopropylurea 3q**




**$^{13}$C NMR spectra of 1-(2,6-dimethylphenyl)-3-isopropylurea 3q**




**Mass spectra of 1-(2,6-dimethylphenyl)-3-isopropylurea 3q**