

## Electronic Supplemental Information (ESI)

### Synthesis of unsymmetrical phenylurea derivatives *via* oxidative cross coupling of aryl formamides with amines under metal free conditions†

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## 1. General Information :

All chemicals were purchased from Sigma-Aldrich and S.D Fine Chemicals, Pvt. Ltd. India and used as received. ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-pre-coated silica gel 60-F<sub>254</sub> plates and visualized by UV-light and developed by Iodine. All the other chemicals and solvents were obtained from commercial sources and purified using standard methods. All <sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on a Avance-300, Inova-400, Inova-500 MHz Spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm, using TMS ( $\delta = 0$ ) as an internal standard in CDCl<sub>3</sub>. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quintet; dd, doublet of doublet; dt, doublet of triplet. The coupling constants (*J*), are reported in Hertz (Hz). The IR values are reported in reciprocal centimeters (cm<sup>-1</sup>) using Bruker Alpha FT-IR spectrometer. Mass was recorded on Thermo Trace DSQ GC-MS spectrometer using BP-01 (30M x 0.25 mm x 1 $\mu$ m) column. Mass spectral data were compiled using MS (ESI), HRMS mass spectrometers.

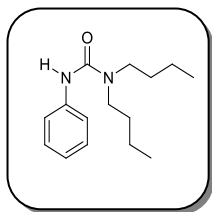
## 2. Expérimental Section :

General procedure:

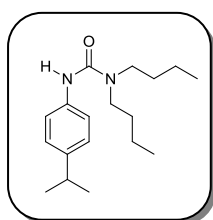
In a reaction vessel 1 mmol of formamide (N-formyl aniline derivative) was dissolved in 3 mL of dichloroethane solvent and slowly added the [bis(trifluoroacetoxy)iodo]benzene (Oxidant, 1mmol) to the solution with stirring over a period of 2 minutes. Then 2 mmol of amine was added to the above reaction mixture and stirred at room temperature for two hours under inert atmosphere in presence of molecular sieves.

After completion of reaction time, solvent was removed under reduced pressure or directly proceeded for the conventional work up with ethyl acetate, water mixture. The organic layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent under reduced pressure afforded the crude product, which was purified by column chromatography on silica gel using hexane and ethyl acetate (8:2) mixture to afford the required product (3). TLC's have to be monitored by both UV and iodine.

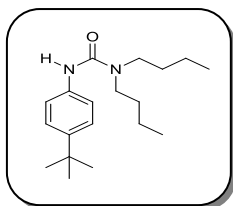
### 3. Spectroscopic data for the products:



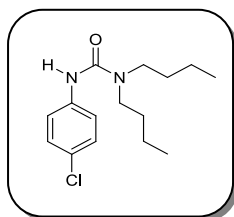
**1,1-dibutyl-3-phenylurea:**(compound **3a**): (**Isolated yield** = 85%): **IR**  $\text{cm}^{-1}$ : 3320, 2858, 2920, 1528, 1380, 1253, 731, 670.  **$^1\text{H}$  NMR**  $\delta$  ( 500 MHz,  $\text{CDCl}_3$ ): 7.38 (d,  $J=9.4$  Hz, 2H), 7.26 (t,  $J=8.2$  Hz, 2H), 7.00 (t,  $J=7.4$  Hz, 1H), 6.32 (br, 1H), 3.28 (t,  $J=7.6$  Hz, 4H), 1.59 (m, 4H), 1.37 (m, 4H), 0.95 (t,  $J=7.3$  Hz, 6H).  **$^{13}\text{C}$  NMR**  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 154.8, 139.2, 128.7, 122.7, 119.6, 47.4, 30.7, 20.1, 13.8. **MS (ESI):**  $m/z$  =249 (M+H)<sup>+</sup>. **HRMS** (ESI) (M+H)<sup>+</sup>  $m/z$  calcd for  $\text{C}_{15}\text{H}_{25}\text{N}_2\text{O}$  (M+H)<sup>+</sup> = 249.19614, found = 249.19710



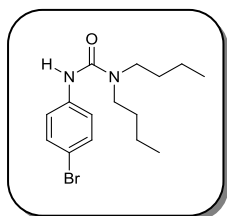
**1,1-dibutyl-3-(4-isopropylphenyl)urea:**(compound **3b**): (**Isolated yield** = 83%):**IR**  $\text{cm}^{-1}$  : 3327, 2958, 2929, 1638, 1518, 1420, 1221, 828, 732, 641.  **$^1\text{H}$  NMR**  $\delta$  (300 MHz,  $\text{CDCl}_3$ ): 7.27 (d,  $J=8.3$  Hz, 2H), 7.13 (d,  $J=8.3$  Hz, 2H), 6.24 (br, 1H), 3.27 (t,  $J=7.4$  Hz, 4H), 2.85 (m, 1H), 1.59 (m, 4H), 1.35 (m, 4H), 1.22 (d,  $J=7.0$  Hz, 6H), 0.95 (t,  $J=7.3$  Hz, 6H).  **$^{13}\text{C}$  NMR**  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 155.1, 143.5, 136.7, 126.6, 120.1, 47.5, 33.4, 30.8, 24.0, 20.2, 13.8. **MS** (ESI):  $m/z$  = 291(M+H)<sup>+</sup>, **HRMS:** ESI (M+H)<sup>+</sup>  $m/z$  calcd for  $\text{C}_{18}\text{H}_{31}\text{N}_2\text{O}$  (M+H)<sup>+</sup> = 291.24309, found = 291.24308.



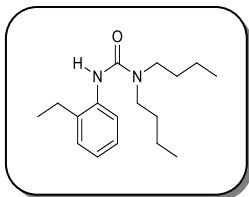
**1,1-dibutyl-3-(4-(tert-butyl)phenyl)urea:** (compound **3c**): (**Isolated yield** = 88%): **IR**  $\text{cm}^{-1}$ : 3304, 2959, 2431, 1639, 1520, 1417, 1295, 829, 732, 636.  **$^1\text{H}$  NMR**  $\delta$  (300 MHz,  $\text{CDCl}_3$ ): 7.63 (br, 4H), 6.62 (br, 1H), 3.65 (t,  $J=7.6$  Hz, 4H), 1.95 (m, 4H), 1.71 (m, 4H), 1.64 (s, 9H), 1.32 (t,  $J=7.3$  Hz, 6H).  **$^{13}\text{C}$  NMR**  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 155.1, 145.7, 136.4, 125.5, 119.7, 47.4, 34.1, 31.3, 30.7, 20.1, 13.8. **MS** (ESI):  $m/z$  = 305 (M+H)<sup>+</sup>, **HRMS:** ESI (M+H)<sup>+</sup>  $m/z$  calcd for  $\text{C}_{19}\text{H}_{33}\text{N}_2\text{O}$  (M+H)<sup>+</sup> = 305.25874, found = 305.25849.



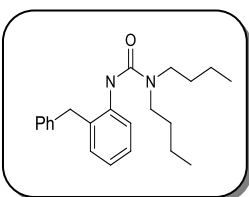
**1,1-dibutyl-3-(4-chlorophenyl)urea:** (compound **3d**): (**Isolated yield** = 73%): **IR**  $\text{cm}^{-1}$ : 3357, 2931, 2868, 1640, 1490, 1288, 1091, 823, 688.  **$^1\text{H}$  NMR**  $\delta$  (300 MHz,  $\text{CDCl}_3$ ) : 7.68 (d,  $J=8.8$  Hz, 2H), 7.55 (d,  $J=7.7$  Hz, 2H), 6.67 (br, 1H), 3.62 (t,  $J=7.4$  Hz, 4H), 1.93(m, 4H), 1.71 (m, 4H), 1.30 (t,  $J=7.3$  Hz, 6H).  **$^{13}\text{C}$  NMR**  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 154.6, 137.8, 128.5, 127.4, 120.9, 47.3, 30.6, 20.0, 13.7. **MS** (ESI):  $m/z$  = 283(M+H)<sup>+</sup>, **HRMS:** ESI (M+H)<sup>+</sup>  $m/z$  calcd for  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{OCl}$  (M+H)<sup>+</sup> = 283.15717, found = 283.15592



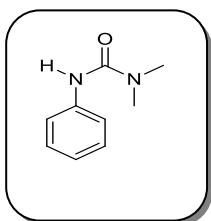
**3-(4-bromophenyl)-1,1-dibutylurea:** (compound **3e**): **Isolated yield** = 77%): **IR**  $\text{cm}^{-1}$ : 3314, 2958, 2929, 1641, 1523, 1488, 1222, 1009, 820, 632.  **$^1\text{H}$  NMR**  $\delta$  (300 MHz,  $\text{CDCl}_3$ ): 7.38 (d,  $J=9.0$  Hz, 2H), 7.29 (d,  $J=8.3$  Hz, 2H), 6.33 (br, 1H), 3.30 (t,  $J=7.5$  Hz, 4H), 1.62 (m, 4H), 1.37 (m, 4H), 0.98 (t,  $J=6.7$  Hz, 6H).  **$^{13}\text{C}$  NMR**  $\delta$  (75 MHz,  $\text{CDCl}_3$ ): 154.5, 138.3, 131.5, 121.2, 114.9, 47.3, 30.6, 20.1, 13.7. **MS** (ESI):  $m/z$  = 349 (M+Na)<sup>+</sup>, **HRMS:** ESI (M+H)<sup>+</sup>  $m/z$  calcd for  $\text{C}_{15}\text{H}_{24}\text{N}_2\text{OBr}$  (M+H)<sup>+</sup> = 327.10665, found = 327.10668.



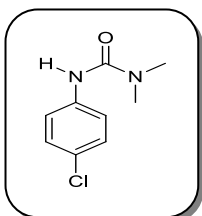
**1,1-dibutyl-3-(2-ethylphenyl)urea:** (Compound **3f**): (Isolated yield = 80%): IR $\text{cm}^{-1}$ : 3315, 2958, 2930, 1632, 1516, 1374, 1252, 1032, 748, 626.  $^1\text{H NMR } \delta$  (300 MHz,  $\text{CDCl}_3$ ): 8.12 (d,  $J=7.9$  Hz, 1H), 7.15 (t,  $J=6.5$  Hz, 2H), 7.36 (t,  $J=7.3$  Hz, 1H), 6.58 (br, 1H), 3.65 (t,  $J=7.6$  Hz, 4H), 2.91 (q,  $J=7.6$  Hz, 2H), 1.96 (m, 4H), 1.72 (m, 4H), 1.56 (t,  $J=7.6$  Hz, 3H), 1.31 (t,  $J=7.3$  Hz, 4H).  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 155.0, 136.5, 133.5, 128.0, 126.3, 123.5, 122.7, 47.4, 30.6, 24.3, 20.0, 13.7. MS (ESI):  $m/z = 277$  (M+H) $^+$ , HRMS: ESI (M+H) $^+$   $m/z$  calcd for  $\text{C}_{17}\text{H}_{29}\text{N}_2\text{O}$  (M+H) $^+$  = 277.22744, found = 277.22705.



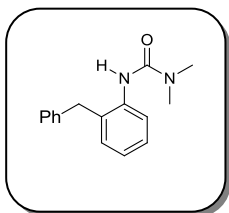
**3-(2-benzylphenyl)-1,1-dibutylurea:**(compound **3g**): (Isolated yield = 78%): IR  $\text{cm}^{-1}$ : 3338, 2957, 2930, 1638, 1516, 1450, 1297, 1030, 752, 698.  $^1\text{H NMR } \delta$  (500 MHz,  $\text{CDCl}_3$ ): 7.82 (d,  $J=7.5$  Hz, 1H), 7.27 (m, 5H), 7.10 (m, 3H), 5.96 (br, 1H), 4.01 (s, 2H), 3.01 (t,  $J=7.5$  Hz, 4H), 1.33 (m, 4H), 1.15 (m, 4H), 0.83 (t,  $J=7.5$  Hz, 6H).  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 155.0, 136.5, 133.5, 132.4, 128.0, 126.3, 123.5, 122.7, 47.4, 30.6, 24.3, 20.0, 13.7. MS (ESI):  $m/z = 339$  (M+H) $^+$ , HRMS (ESI) (M+H) $^+$   $m/z$  calcd for  $\text{C}_{22}\text{H}_{31}\text{N}_2\text{O}$  (M+H) $^+$  = 339.24309, found = 339.24144



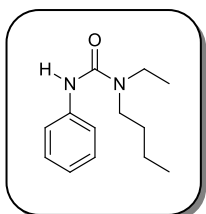
**1,1-dimethyl-3-phenylurea:** (compound **3h**): (Isolated yield=82%): IR $\text{cm}^{-1}$ : 3251, 2926, 2856, 1727, 1642, 1598, 1513, 1245, 752, 631.  $^1\text{H NMR } \delta$  (300 MHz,  $\text{CDCl}_3$ ): 7.39 (d,  $J=9.0$  Hz, 2H), 7.29 (t,  $J=7.5$  Hz, 2H), 7.04 (t,  $J=6.7$  Hz, 1H), 6.47 (br, 1H), 3.03 (s, 6H).  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 155.7, 139.1, 128.6, 122.7, 119.8, 36.3. MS (ESI):  $m/z = 165$  (M+H) $^+$ , HRMS: ESI (M+H) $^+$   $m/z$  calcd for  $\text{C}_9\text{H}_{13}\text{N}_2\text{O}$  (M+H) $^+$  = 165.10224, found = 165.10179.



**3-(4-chlorophenyl)-1,1-dimethylurea:** (compound **3i**): (Isolated yield =72%): IR  $\text{cm}^{-1}$ : 3260, 2930, 2867, 1650, 1590, 1278, 730, 650.  $^1\text{H NMR } \delta$  (500 MHz,  $\text{CDCl}_3$ ): 7.30 (d,  $J=9.0$  Hz, 2H), 7.24 (d,  $J=9.0$  Hz, 2H), 6.34 (br, 1H), 3.02 (s, 6H).  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 155.4, 137.7, 128.7, 127.8, 121.0, 36.4. MS (ESI):  $m/z = 199$  (M+H) $^+$ .

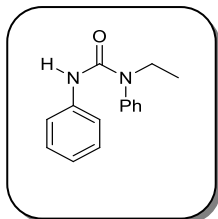


**3-(2-benzylphenyl)-1,1-dimethylurea:** (compound **3j**): (Isolated yield =76%): IR  $\text{cm}^{-1}$ : 3254, 2927, 2858, 1650, 1493, 1394, 1166, 1068, 731, 622.  $^1\text{H NMR } \delta$  (500 MHz,  $\text{CDCl}_3$ ): 7.84 (d,  $J=7.5$  Hz, 1H), 7.30 (m, 5H), 7.13 (m, 3H), 5.98 (br, 1H), 4.01 (s, 2H), 3.02 (s, 6H).  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 158.0, 137.1, 133.3, 132.1, 130.5, 128.9, 128.3, 126.4, 36.6, 36.4. MS (ESI):  $m/z = 255$  (M+H) $^+$ , HRMS: ESI (M+H) $^+$   $m/z$  calcd for  $\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}$  (M+H) $^+$  = 255.14919, found = 255.14852.

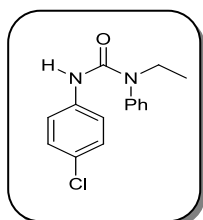


**1-butyl-1-ethyl-3-phenylurea:** (compound **3k**): (Isolated yield =82%): IR  $\text{cm}^{-1}$ : 3337, 2960, 2930, 1639, 1531, 1444, 1308, 1241, 751, 693.  $^1\text{H NMR } \delta$  (300 MHz,  $\text{CDCl}_3$ ): 7.39 (d,  $J=7.5$  Hz, 2H), 7.26 (t,  $J=7.5$  Hz, 2H), 7.00 (t,  $J=7.5$  Hz, 1H), 6.36 (br, 1H), 3.30 (m, 4H), 1.59 (m, 2H), 1.37 (m, 2H), 1.20 (t,  $J=6.7$  Hz, 3H), 0.95 (t,  $J=7.5$  Hz, 3H).  $^{13}\text{C NMR } \delta$  (75 MHz,  $\text{CDCl}_3$ ): 154.7, 139.2, 128.5, 122.5, 119.7, 46.7, 41.8, 30.7, 20.0, 13.7,

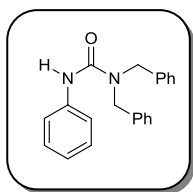
13.5. **MS** (ESI):  $m/z = 221(M+H)^+$ , **HRMS**: ESI  $(M+H)^+$   $m/z$  calcd for  $C_{13}H_{21}N_2O$   $(M+H)^+ = 221.16484$ , found = 221.16380.



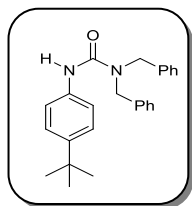
**1-ethyl-1,3-diphenylurea**: (compound **3l**): (Isolated yield = 70% ): **IR**  $cm^{-1}$ : 3424, 2932, 2873, 1669, 1594, 1440, 1238, 1142, 750, 696.  **$^1H$  NMR**  $\delta$  (300 MHz,  $CDCl_3$ ): 7.85 (t,  $J=7.7$  Hz, 2H), 7.76 (t,  $J=7.1$  Hz, 1H), 7.63 (m, 6H), 7.32 (t,  $J=7.3$  Hz, 1H), 6.47 (br, 1H), 4.16 (q,  $J=7.1$  Hz, 2H), 1.53 (t,  $J=7.1$  Hz, 3H).  **$^{13}C$  NMR**  $\delta$  (75 MHz,  $CDCl_3$ ): 153.8, 141.0, 138.8, 130.1, 128.6, 128.0, 122.6, 119.1, 44.1, 13.6. **MS** (ESI):  $m/z = 241$   $(M+H)^+$ , **HRMS**: ESI  $(M+H)^+$   $m/z$  calcd for  $C_{15}H_{17}N_2O$   $(M+H)^+ = 241.13354$ , found = 241.13249.



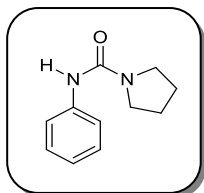
**3-(4-chlorophenyl)-1-ethyl-1-phenylurea**: (compound **3m**): (Isolated yield = 68%): **IR**  $cm^{-1}$ : 3421, 2974, 2930, 1667, 1592, 1494, 1371, 1283, 753, 628.  **$^1H$  NMR**  $\delta$  (300 MHz,  $CDCl_3$ ): 7.50 (t,  $J=7.6$  Hz, 2H), 7.31 (t,  $J=8.2$  Hz, 5H), 7.17 (d,  $J=8.8$  Hz, 2H), 6.07 (br, 1H), 3.78 (q,  $J=7.0$  Hz, 2H), 1.16 (t,  $J=7.0$  Hz, 3H).  **$^{13}C$  NMR**  $\delta$  (75 MHz,  $CDCl_3$ ): 154.2, 141.4, 139.2, 130.5, 129.0, 128.4, 123.0, 119.5, 44.5, 14.0. **MS** (ESI):  $m/z = 275$   $(M+H)^+$ , **HRMS**: ESI  $(M+H)^+$   $m/z$  calcd for  $C_{15}H_{16}N_2OCl$   $(M+H)^+ = 275.09457$ , found = 275.09446.



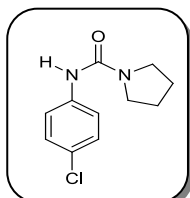
**1,1-dibenzyl-3-phenylurea**: (compound **3n**): (Isolated yield = 65%): **IR**  $cm^{-1}$ : 3356, 2925, 2839, 1641, 1535, 1446, 1237, 1019, 750, 694.  **$^1H$  NMR**  $\delta$  (500 MHz,  $CDCl_3$ ): 7.74 (t,  $J=6.7$  Hz, 4H), 7.68 (t,  $J=7.4$  Hz, 6H), 7.59 (d,  $J=7.2$  Hz, 4H), 7.36 (m, 1H), 6.76 (br, 1H), 4.97 (s, 4H).  **$^{13}C$  NMR**  $\delta$  (75 MHz,  $CDCl_3$ ): 156.2, 146.2, 137.4, 129.1, 127.9, 127.5, 125.8, 120.0, 50.9. **MS** (ESI):  $m/z = 317$   $(M+H)^+$ , **HRMS**: ESI  $(M+H)^+$   $m/z$  calcd for  $C_{21}H_{21}N_2O$   $(M+H)^+ = 317.16382$ , found = 317.16304.



**1,1-dibenzyl-3-(4-(tert-butyl)phenyl)urea**: (compound **3o**): (Isolated yield = 70%): **IR**:  $cm^{-1}$ : 3342, 2920, 2842, 1638, 1545, 1452, 1235, 1018, 753, 687.  **$^1H$  NMR**  $\delta$  (300 MHz,  $CDCl_3$ ): 7.71 (m, 4H), 7.67 (m, 6H), 7.60 (m, 2H), 7.51 (d,  $J=8.3$  Hz, 2H), 6.67 (br, 1H), 4.97 (s, 4H), 1.63 (s, 9H).  **$^{13}C$  NMR**  $\delta$  (75 MHz,  $CDCl_3$ ): 156.0, 146.0, 137.2, 136.1, 128.9, 127.7, 127.3, 125.5, 119.7, 50.7, 34.1, 31.3. **MS** (ESI):  $m/z = 373$   $(M+H)^+$ , **HRMS**: ESI  $(M+H)^+$   $m/z$  calcd for  $C_{25}H_{29}N_2O$   $(M+H)^+ = 373.22682$ , found = 373.22773.

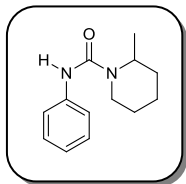


**N-phenylpyrrolidine-1-carboxamide**: (compound **3p**): (Isolated yield = 83%): **IR**  $cm^{-1}$ : 3307, 2970, 1644, 1530, 1442, 1380, 1242, 753, 693.  **$^1H$  NMR**  $\delta$  (300 MHz,  $CDCl_3$ ): 7.41 (d,  $J=8.2$  Hz, 2H), 7.26 (m, 2H), 7.00 (t,  $J=6.4$  Hz, 1H), 6.29 (br, 1H), 3.43 (br, 4H), 1.93 (br, 4H).  **$^{13}C$  NMR**  $\delta$  (75 MHz,  $CDCl_3$ ): 153.8, 138.0, 129.0, 120.8, 46.0, 25.8. **MS** (ESI):  $m/z = 191$   $(M+H)^+$ , **HRMS**: ESI  $(M+H)^+$   $m/z$  calcd for  $C_{11}H_{15}N_2O$   $(M+H)^+ = 191.11789$ , found = 191.11707.

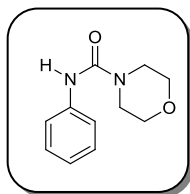


**N-(4-chlorophenyl)pyrrolidine-1-carboxamide**: (compound **3q**): (Isolated yield = 80%): **IR**  $cm^{-1}$ : 3315, 2973, 1653, 1525, 1458, 1382, 1247, 751, 692.  **$^1H$  NMR**  $\delta$  (300

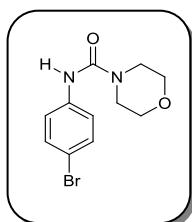
MHz, CDCl<sub>3</sub>): 7.41 (d, *J*=8.8 Hz, 2H), 7.26 (d, *J*=8.8 Hz, 2H), 6.25 (br, 1H), 3.42 (t, *J*=6.7 Hz, 4H), 1.99 (t, *J*=6.6 Hz, 4H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 153.6, 137.7, 128.7, 127.5, 120.6, 45.7, 25.5. MS (ESI): *m/z* = 225 (M+H)<sup>+</sup>, HRMS: ESI (M+H)<sup>+</sup> *m/z* calcd for C<sub>11</sub>H<sub>14</sub>N<sub>2</sub>OCl (M+H)<sup>+</sup> = 225.07892, found = 225.07889.



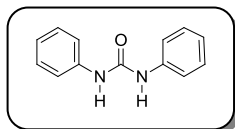
**2-methyl-N-phenylpiperidine-1-carboxamide:** (compound **3r**): (Isolated yield =76%): IR cm<sup>-1</sup>: 3315, 2929, 2856, 1633, 1532, 1442, 1238, 1060, 750, 693. <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 7.36 (d, *J*=8.6 Hz, 2H), 7.26 (t, *J*=7.3 Hz, 2H), 7.02 (t, *J*=7.3 Hz, 1H), 6.35 (br, 1H), 4.38 (m, 1H), 3.88 (br, 1H), 3.00 (br, 1H), 1.75-1.62 (m, 6H), 1.24 (d, *J*=7.0 Hz, 3H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 154.9, 139.3, 128.7, 122.7, 119.9, 46.6, 39.0, 30.2, 25.5, 18.5, 15.7. MS (ESI): *m/z* = 219 (M+H)<sup>+</sup>, HRMS: ESI (M+H)<sup>+</sup> *m/z* calcd for C<sub>13</sub>H<sub>19</sub>N<sub>2</sub>O (M+H)<sup>+</sup> = 219.14919, found = 219.14831.



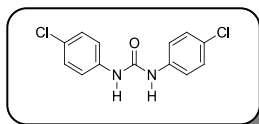
**N-phenylmorpholine-4-carboxamide:** (compound **3s**): (Isolated yield=84%): IR cm<sup>-1</sup>: 3320, 2771, 1648, 1532, 1460, 1378, 1245, 755, 687. <sup>1</sup>H NMR δ (500 MHz, CDCl<sub>3</sub>): 7.35 (d, *J*=7.4 Hz, 2H), 7.28 (t, *J*=7.4 Hz, 2H), 7.04 (t, *J*=7.3 Hz, 1H), 6.48 (br, 1H), 3.71 (t, *J*=5.0 Hz, 4H), 3.46 (t, *J*=5.0 Hz, 4H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 155.1, 138.6, 128.8, 123.3, 120.0, 66.4, 44.2. MS (ESI): *m/z* = 207 (M+H)<sup>+</sup>, HRMS: ESI (M+H)<sup>+</sup> *m/z* calcd for C<sub>11</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> (M+H)<sup>+</sup> = 207.11280, found = 207.11223.



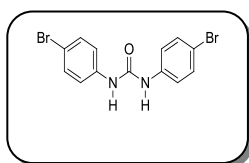
**N-(4-bromophenyl)morpholine-4-carboxamide:** (compound **3t**): (Isolated yield =80%): IR cm<sup>-1</sup>: 3327, 2768, 1644, 1530, 1467, 1375, 1245, 751, 682. <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 7.41 (d, *J*=9.06 Hz, 2H), 7.27 (d, *J*=9.02 Hz, 2H), 6.36 (br, 1H), 3.74 (t, *J*=4.5 Hz, 4H), 3.47 (t, *J*=4.5 Hz, 4H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 154.8, 137.8, 131.7, 121.6, 115.8, 66.4, 44.2. MS (ESI): *m/z* = 285 (M+H)<sup>+</sup>.



**1,3-diphenylurea:** (compound **5a**): (Isolated yield =67%). IR cm<sup>-1</sup>: 3330, 1655, 1589, 1558, 1240. <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 8.37 (br, 2H), 7.46 (d, *J*=7.7 Hz, 4H), 7.26 (t, *J*=7.55 Hz, 4H), 6.99 (t, *J*=7.3 Hz, 2H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub> + DMSO): 152.4, 138.9, 128.1, 121.4, 117.9. MS (ESI): *m/z* = 213 (M+H)<sup>+</sup>, HRMS: ESI (M+H)<sup>+</sup> *m/z* calcd for C<sub>13</sub>H<sub>13</sub>N<sub>2</sub>O (M+H)<sup>+</sup> = 213.10224, found = 213.10253.

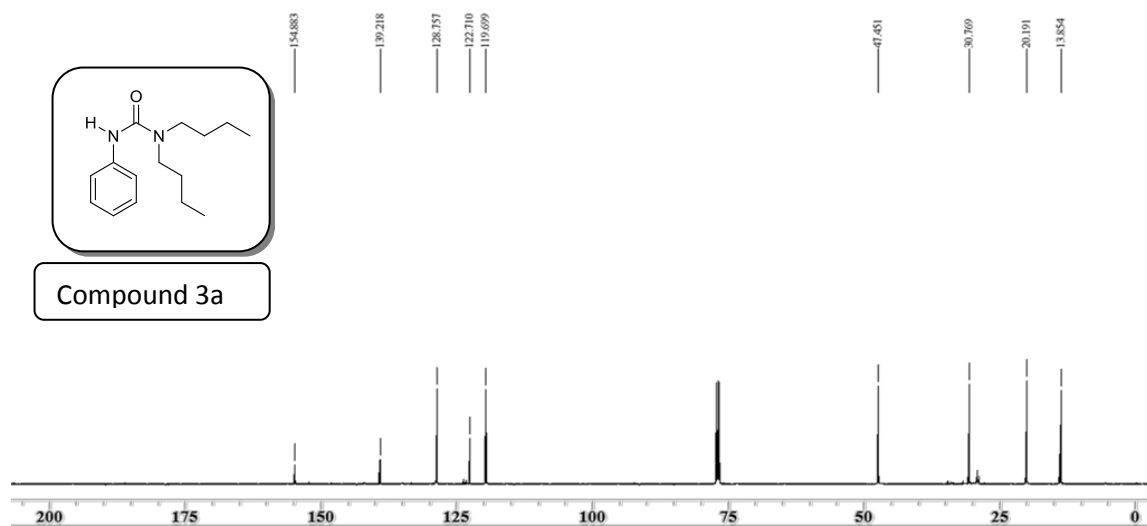
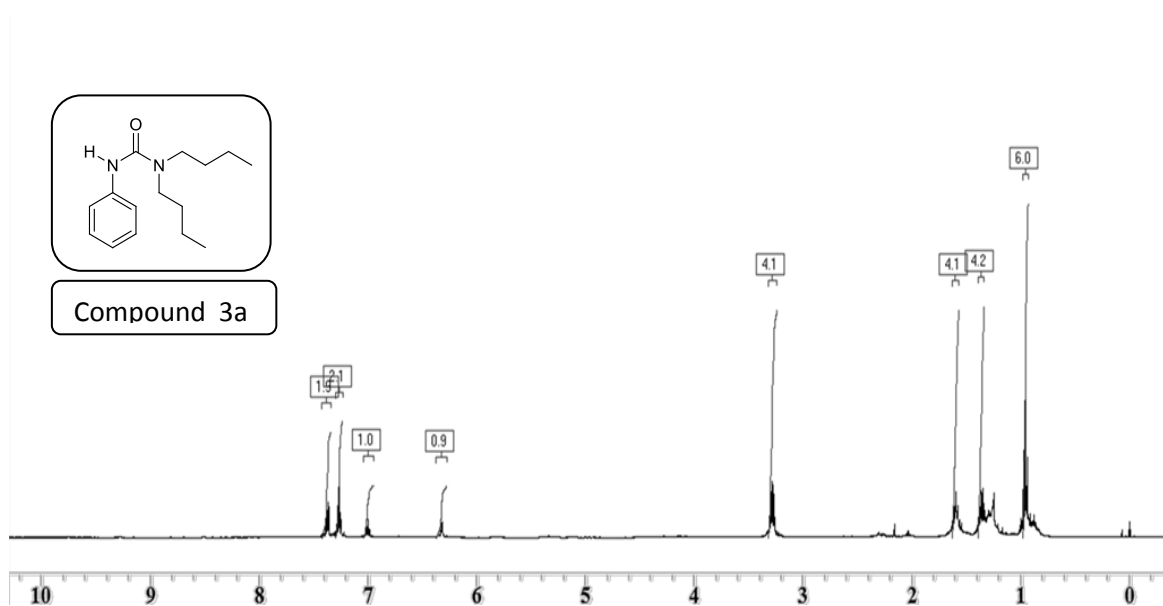


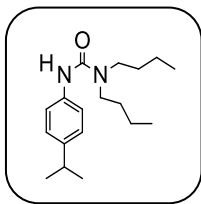
**1,3-bis(4-chlorophenyl)urea:** (compound **5b**): (Isolated yield =60%): IR cm<sup>-1</sup>: 3329, 1657, 1589, 1560, 1232. <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 8.05 (br, 2H), 7.56 (m, 8H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 154.8, 134.1, 132.4, 121.9, 119.3. MS (ESI): *m/z* = 298 (M+NH<sub>4</sub>)<sup>+</sup>.



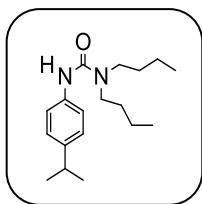
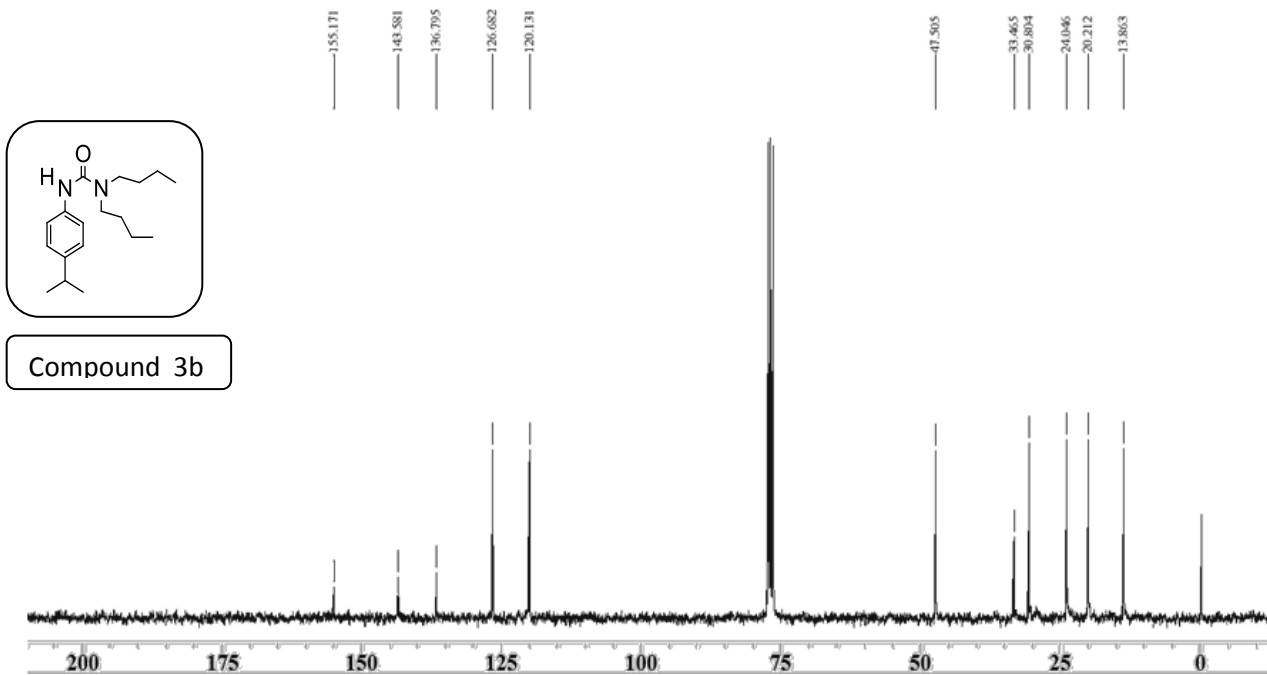
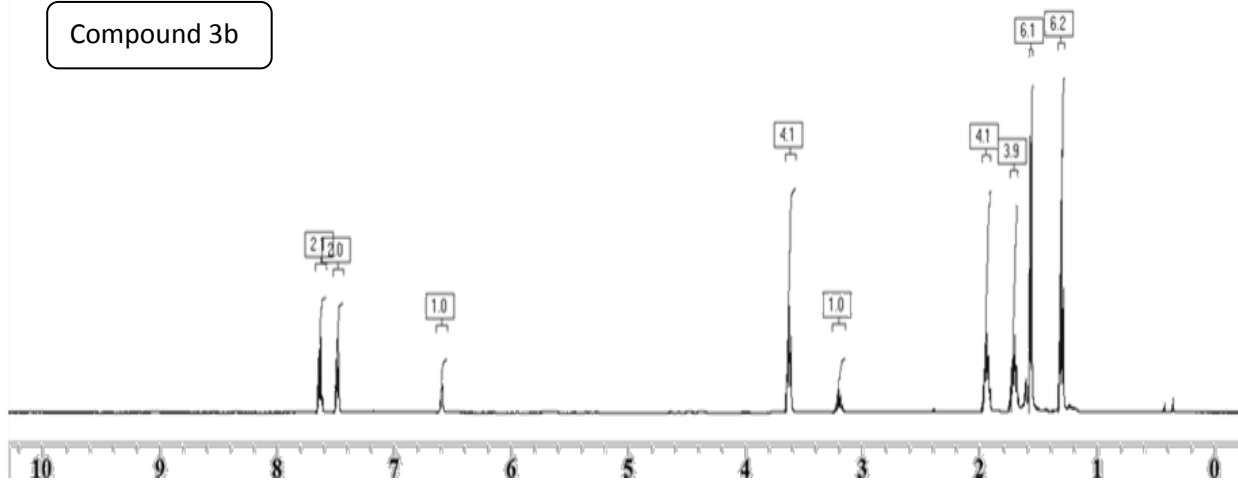
**1,3-bis(4-bromophenyl)urea:** (compound **5c**): (Isolated yield =62%): IR cm<sup>-1</sup>: 3328, 1653, 1598, 1552, 1233. <sup>1</sup>H NMR δ (300 MHz, CDCl<sub>3</sub>): 8.04 (br, 2H), 7.54 (m, 8H). <sup>13</sup>C NMR δ (75 MHz, CDCl<sub>3</sub>): 154.6, 134.1, 132.3, 122.1, 119.4. MS (ESI): *m/z* = 368 (M+H)<sup>+</sup>, HRMS: ESI (M+H)<sup>+</sup> *m/z* calcd for C<sub>13</sub>H<sub>11</sub>ON<sub>2</sub>Br<sub>2</sub> (M+H)<sup>+</sup> = 368.89946, found = 368.90629.

#### 4 Copies of $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra for products



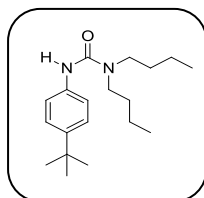


Compound 3b

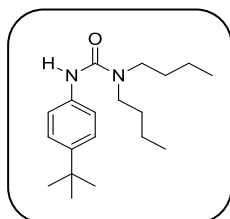
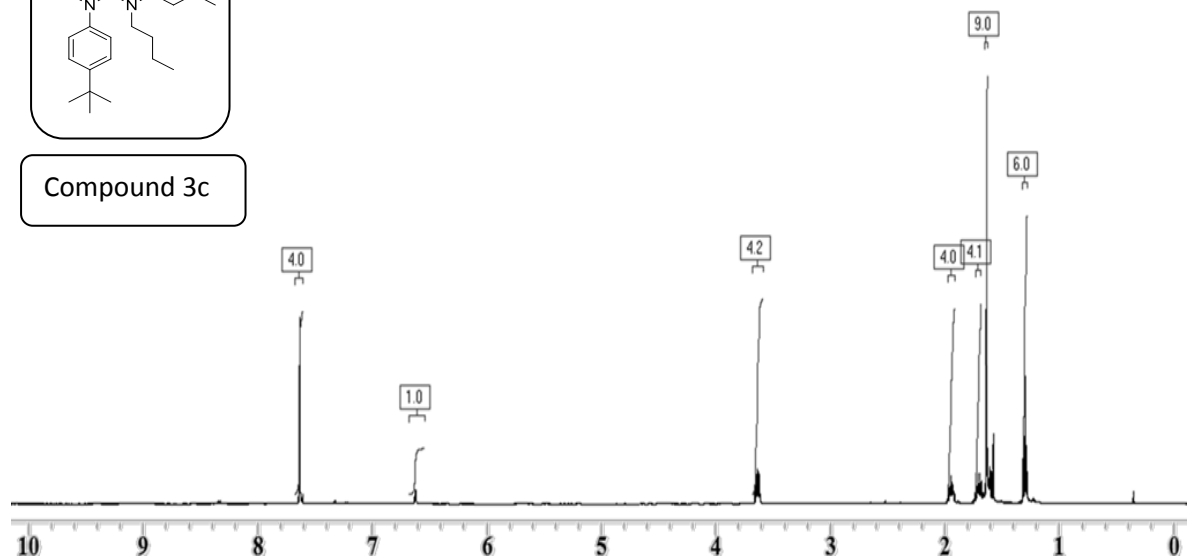


Compound 3b

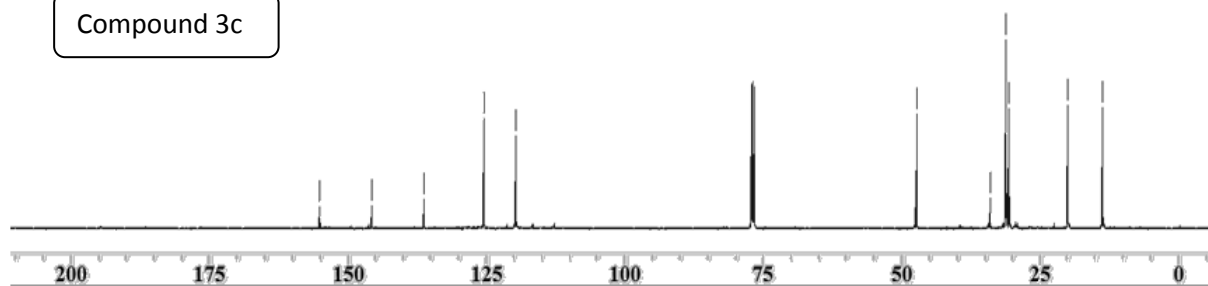


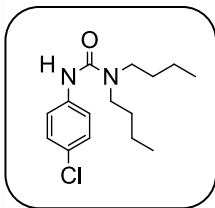


Compound 3c

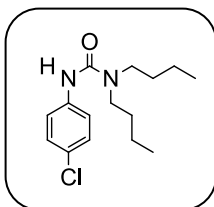
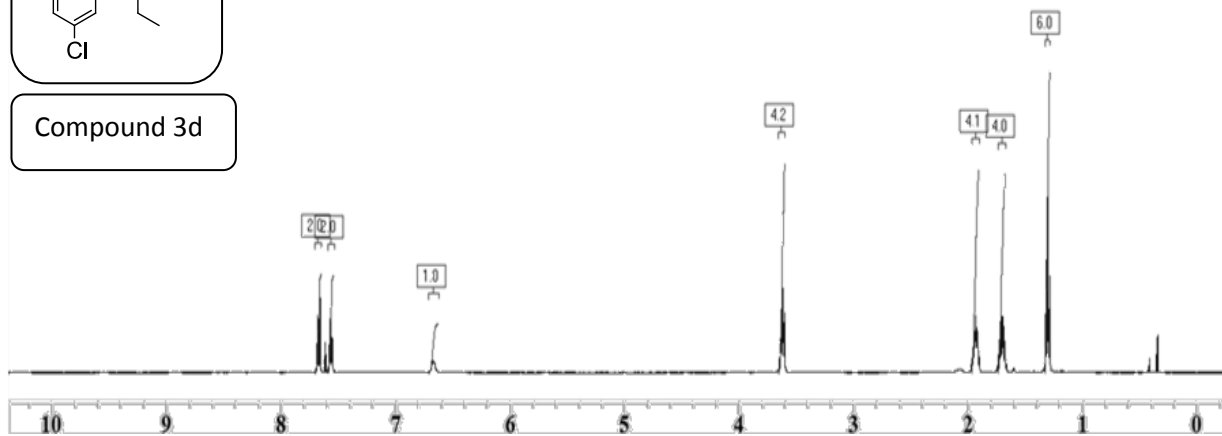


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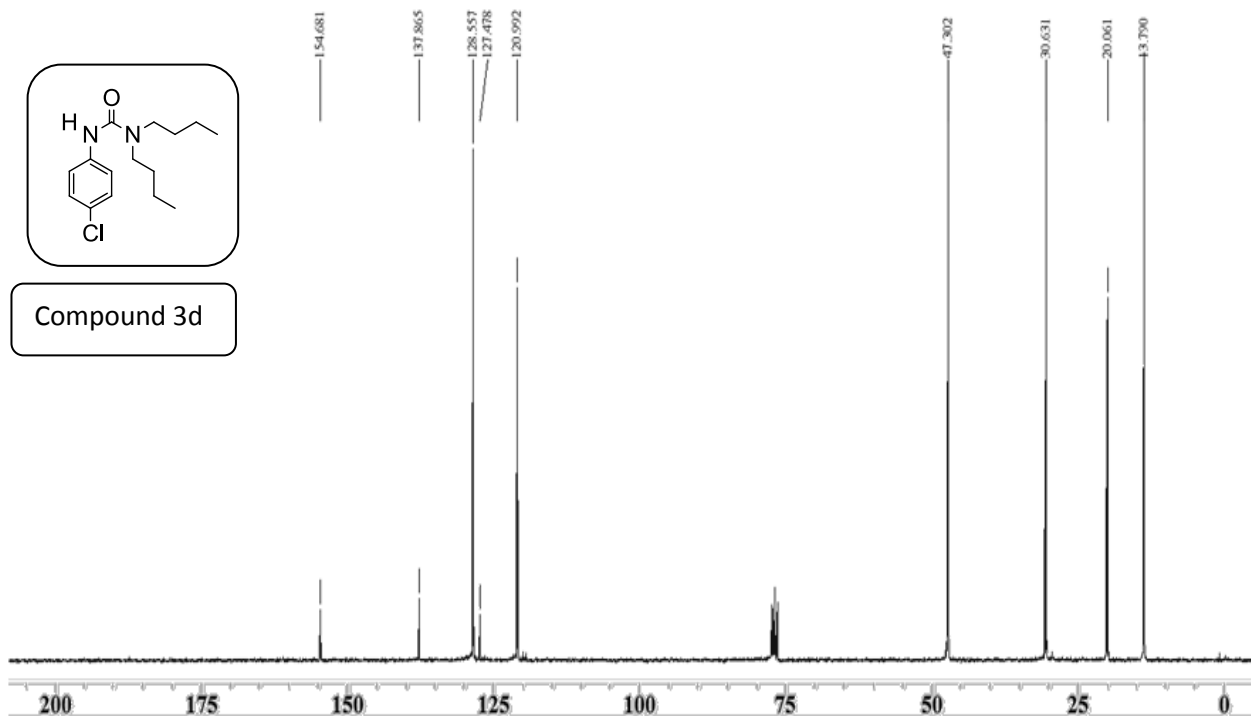


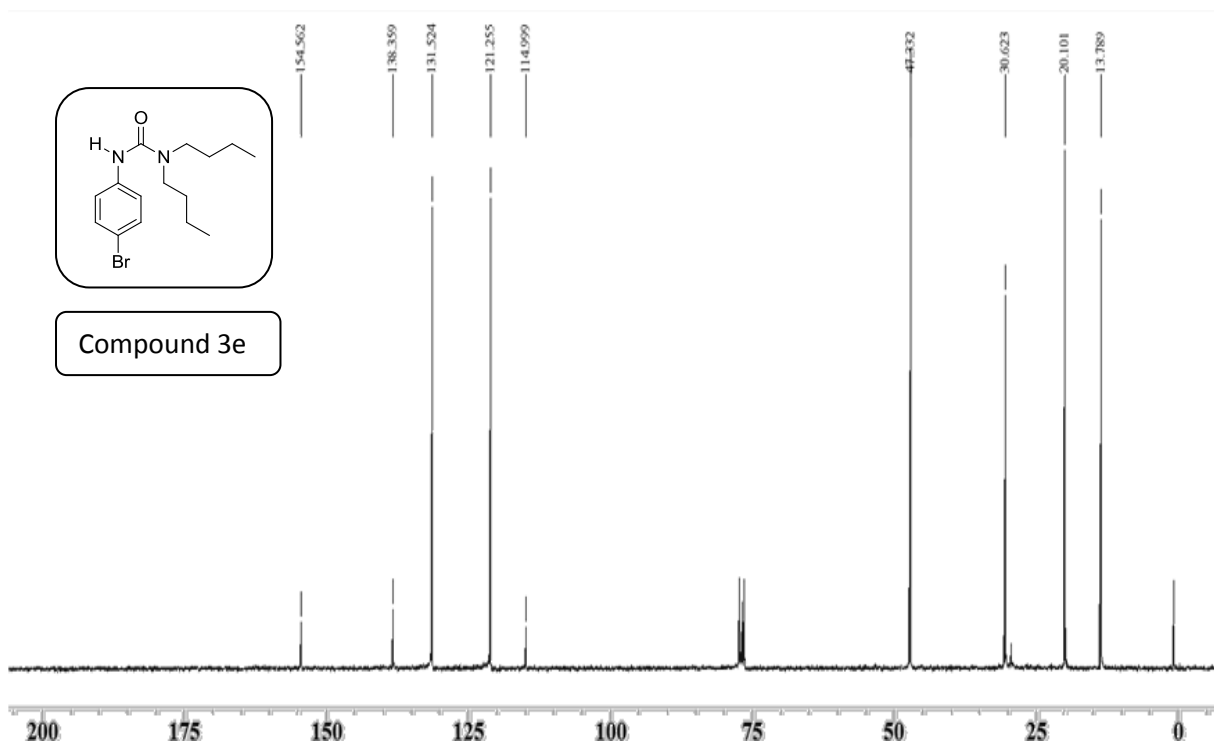
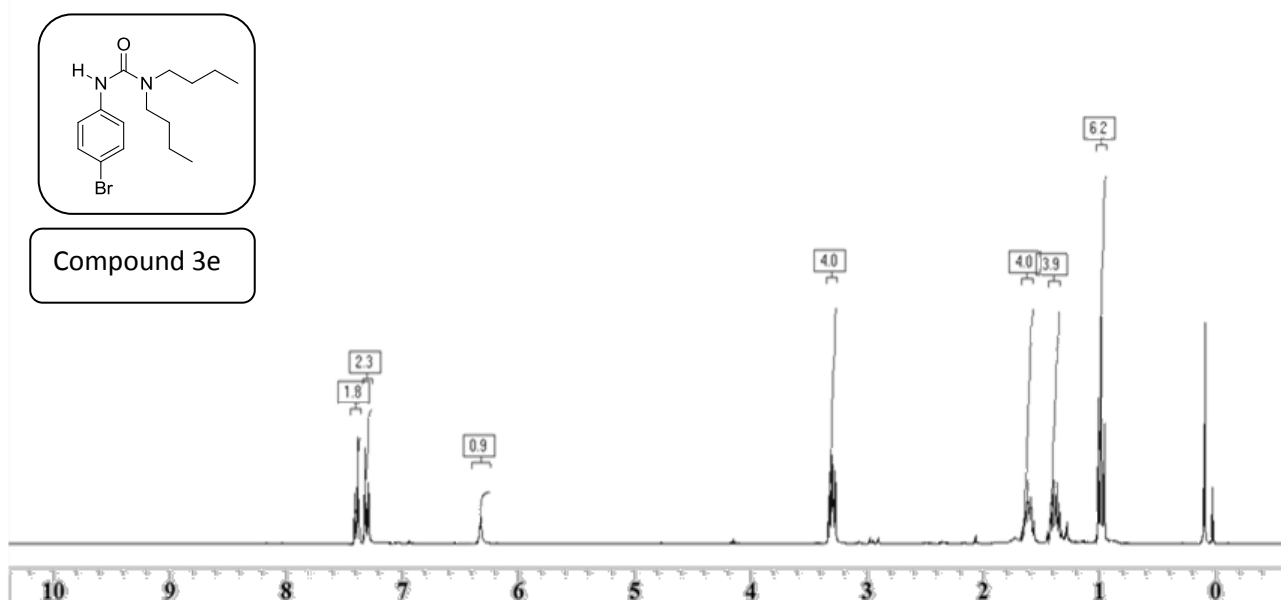


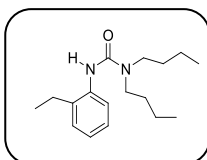
Compound 3d



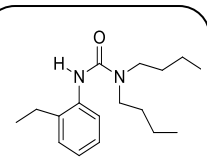
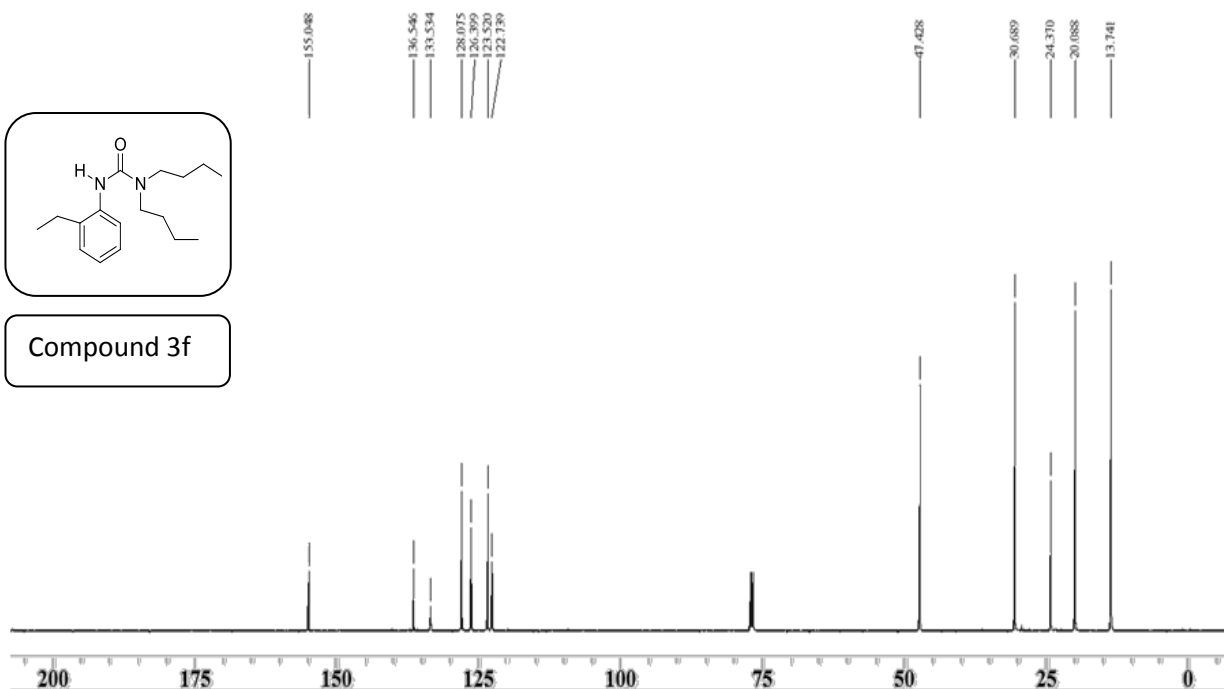
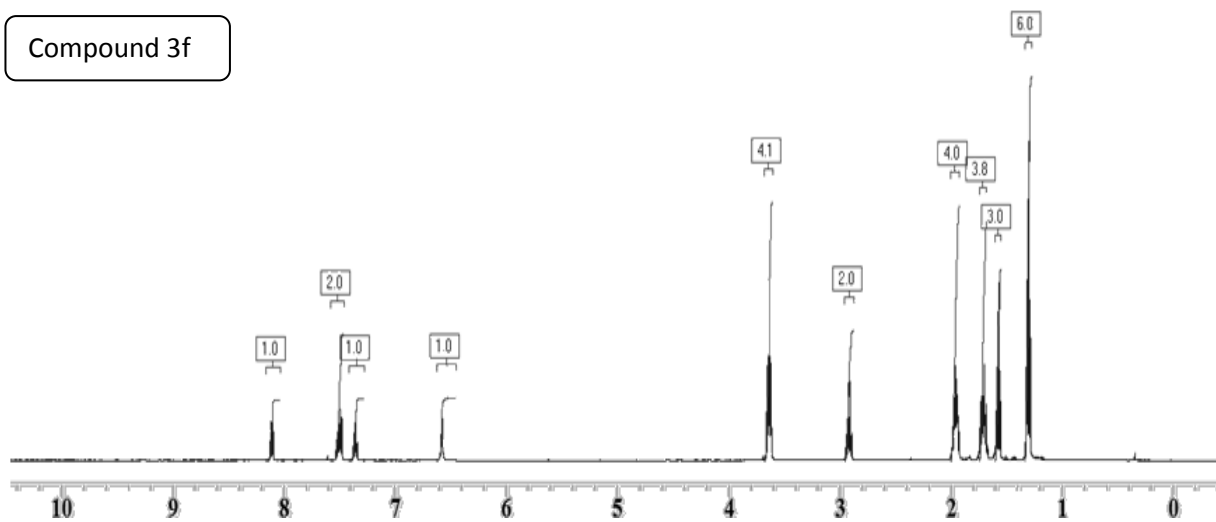
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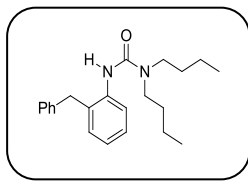




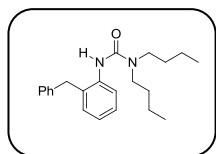
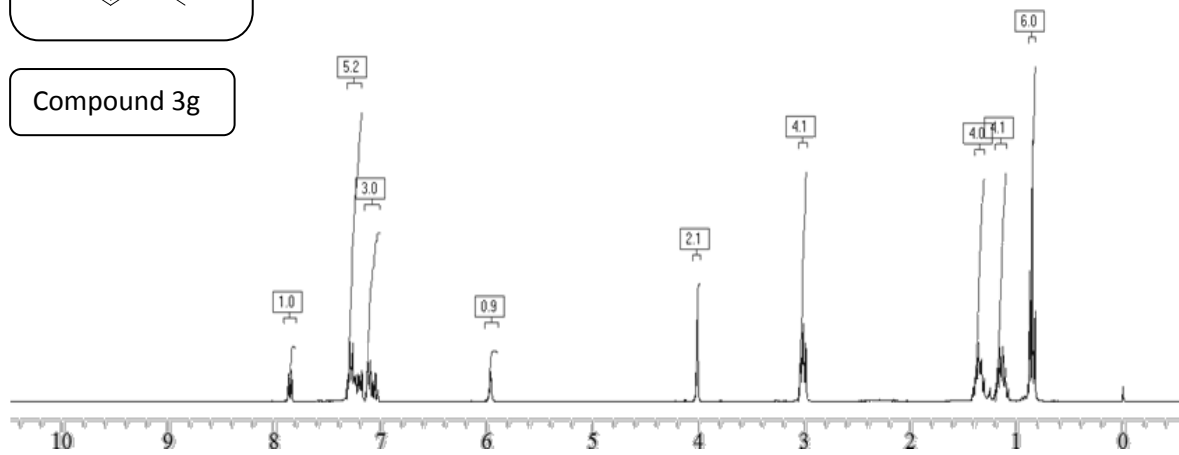
Compound 3f



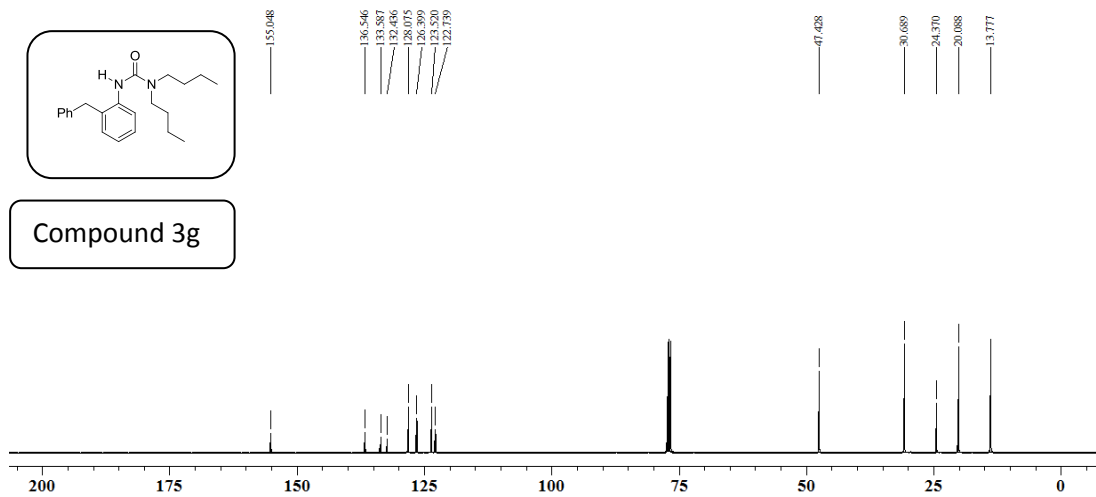
Compound 3f

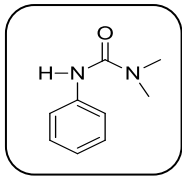


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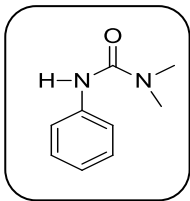
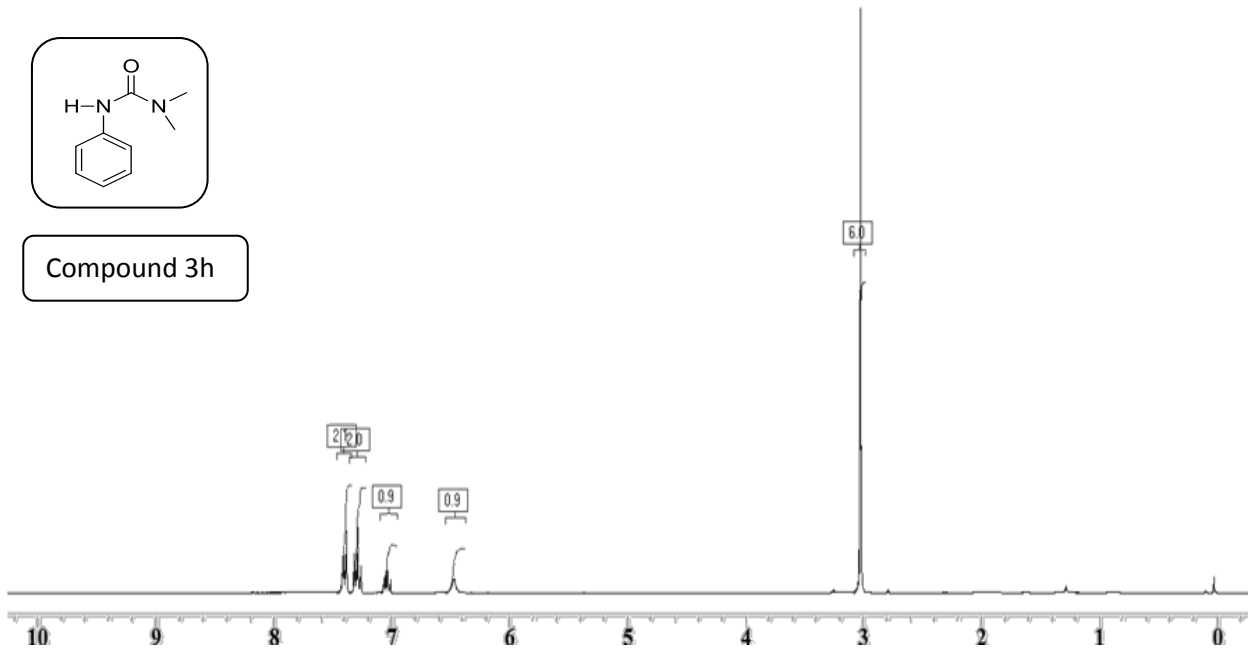


Compound 3g

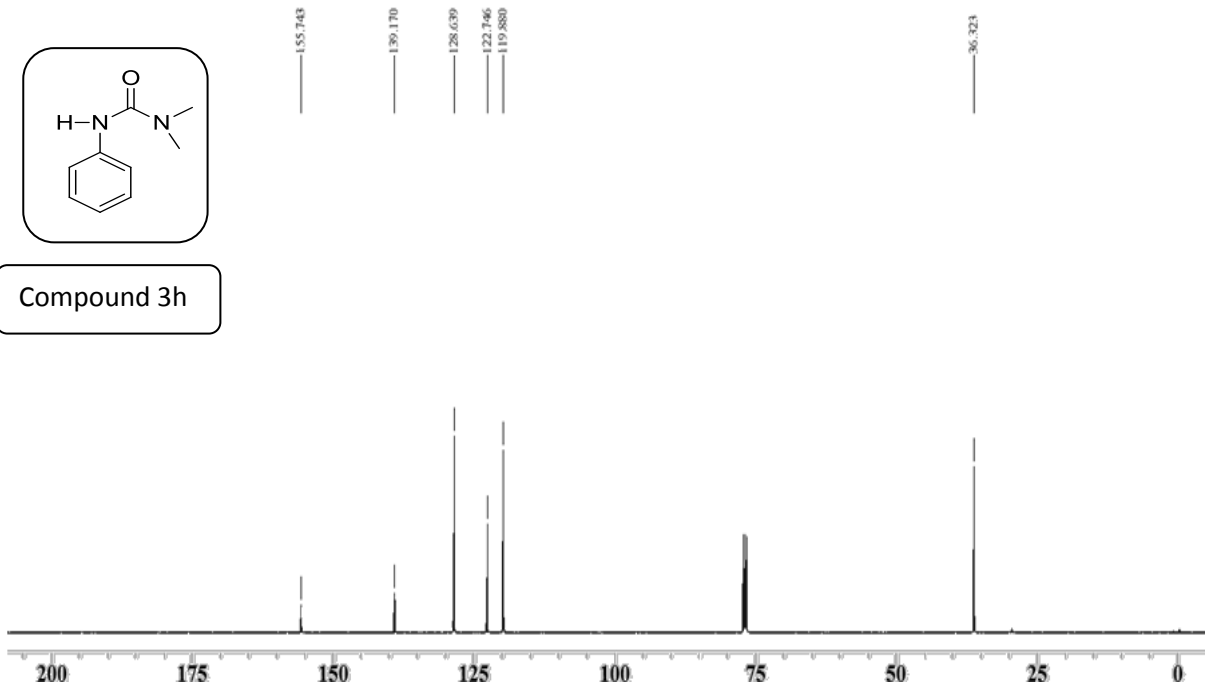


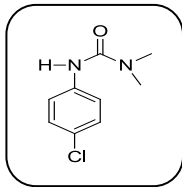


Compound 3h

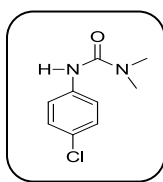
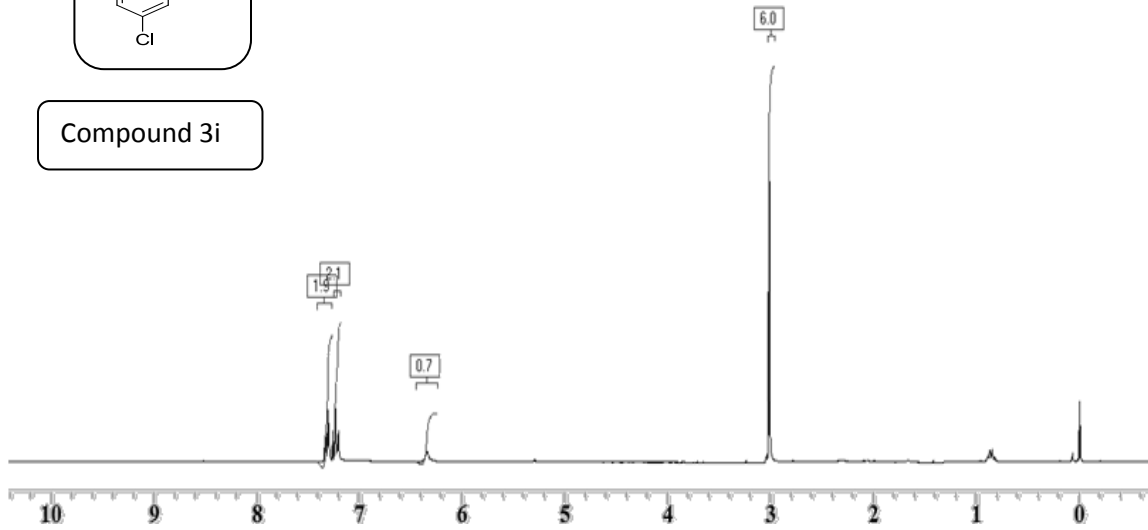


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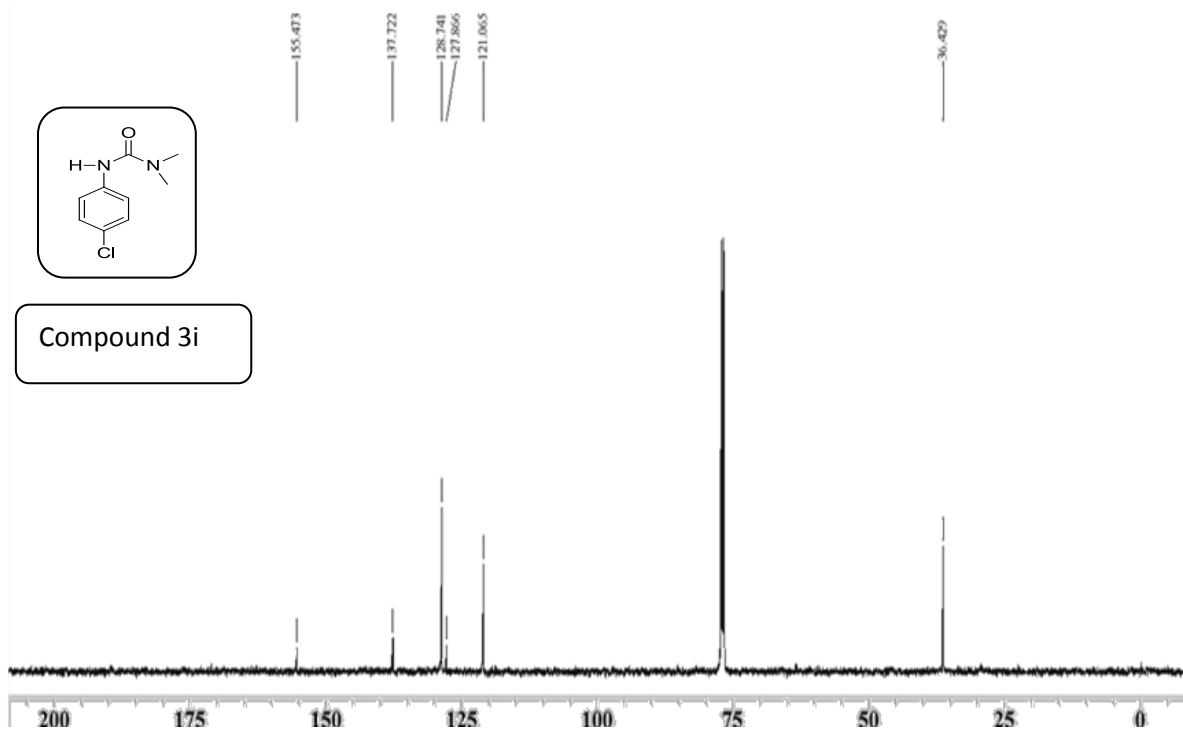


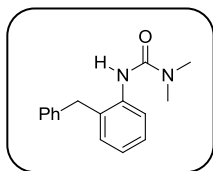


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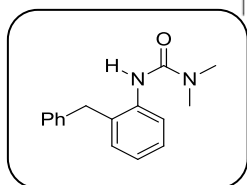
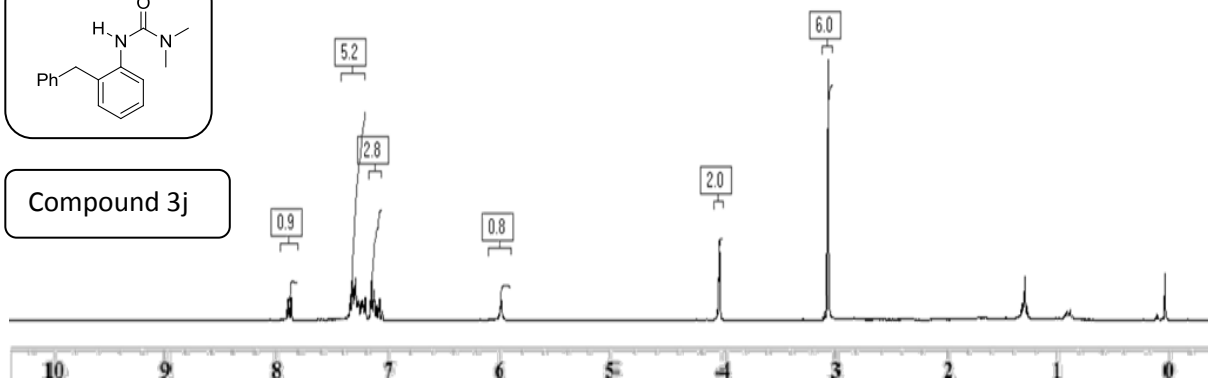


Compound 3i

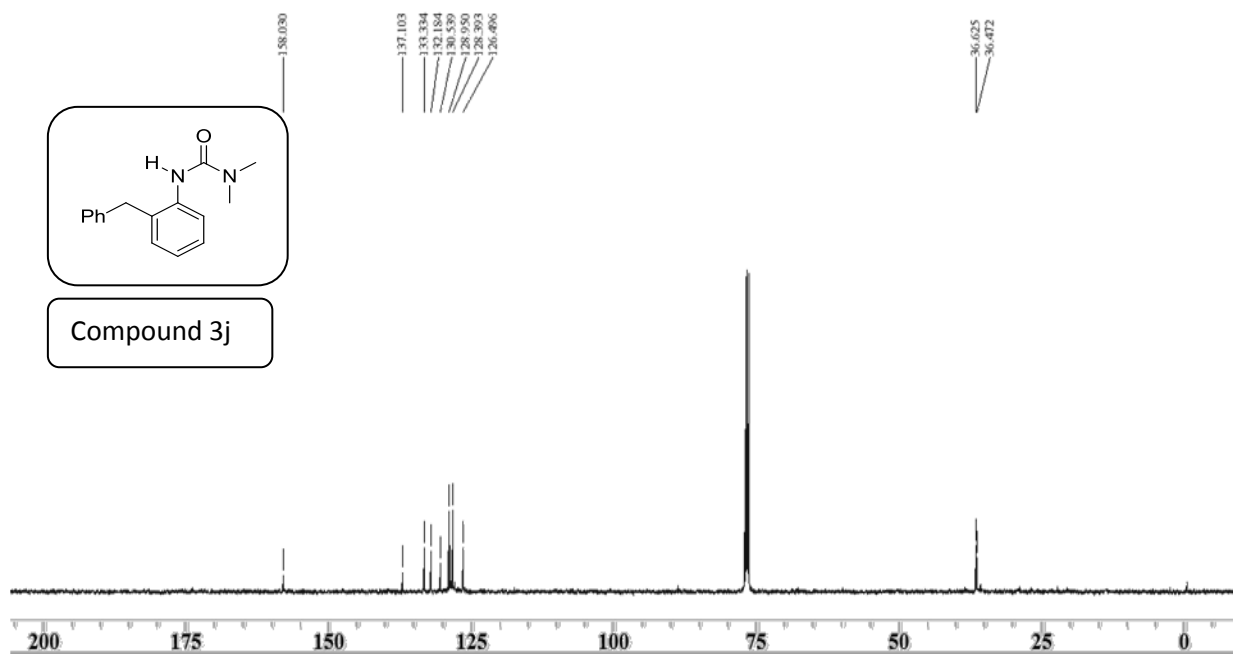




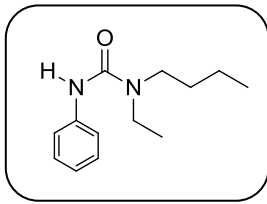
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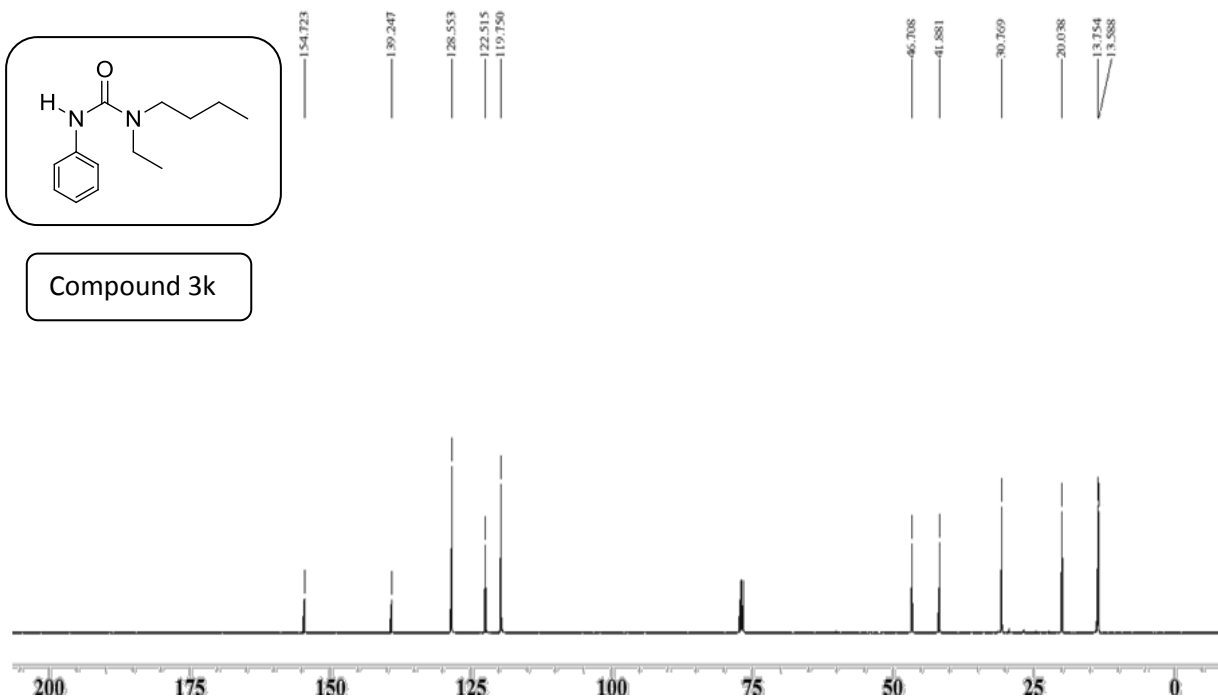
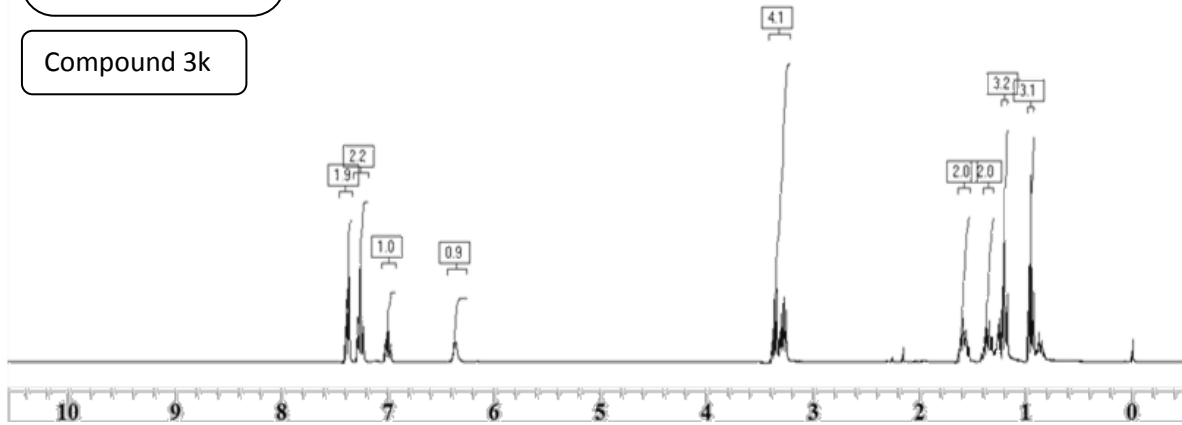
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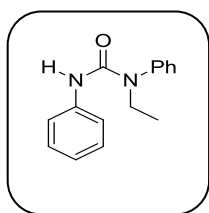




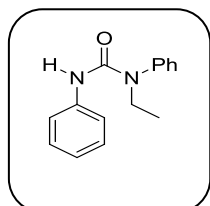
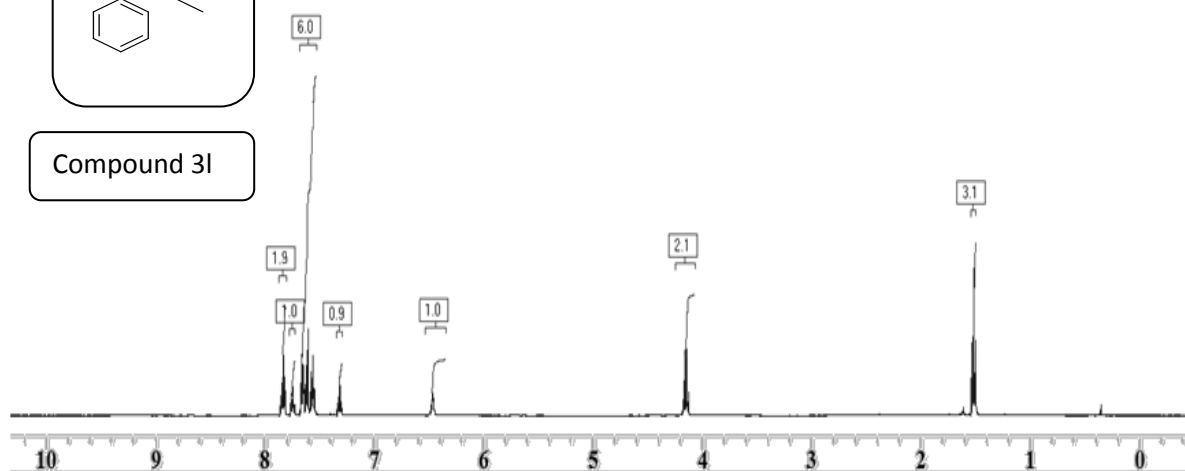


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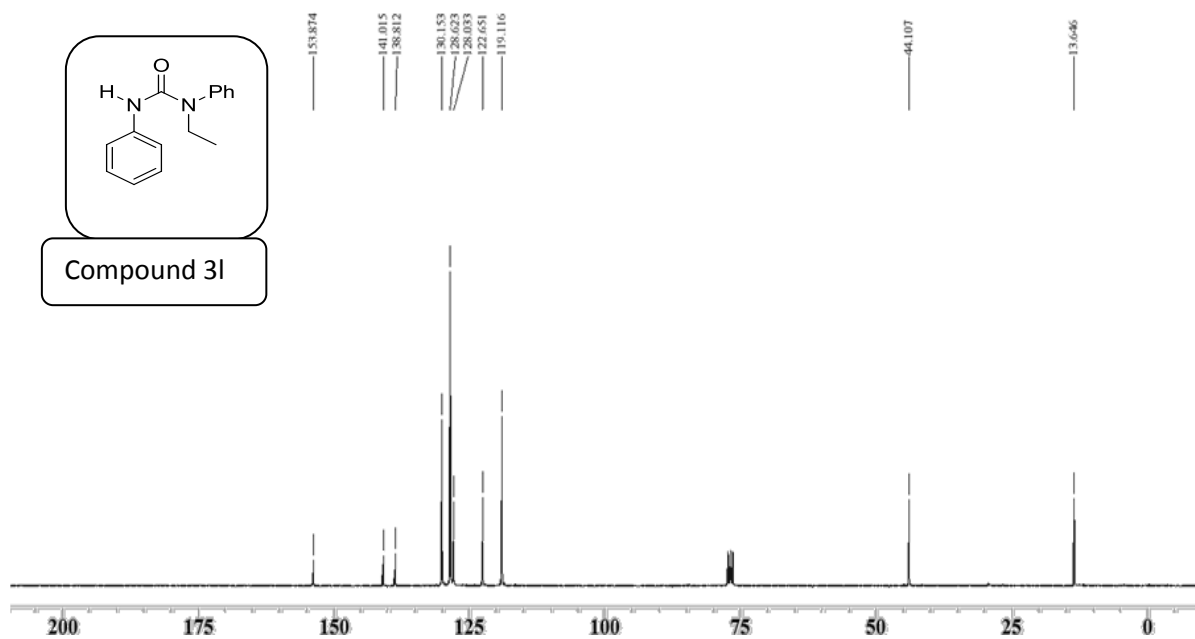


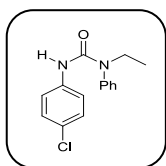


Compound 3I

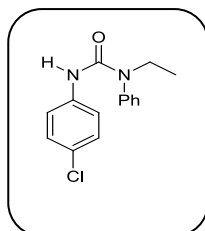
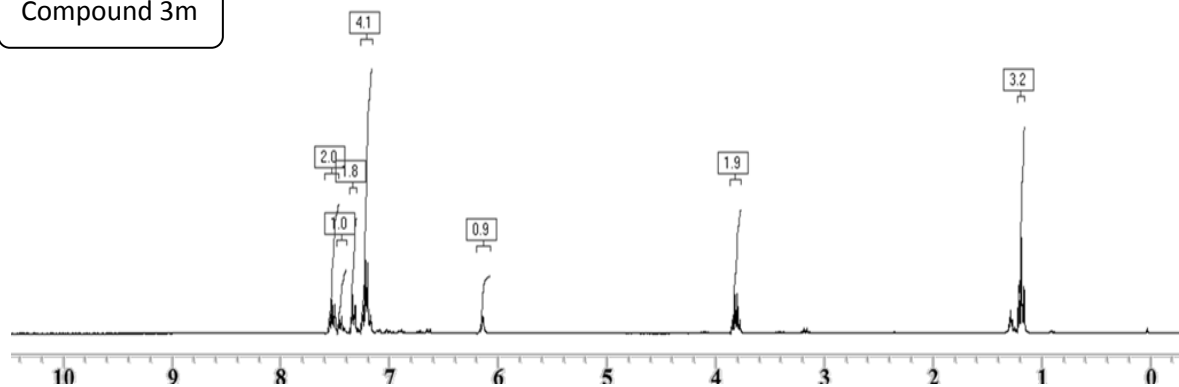


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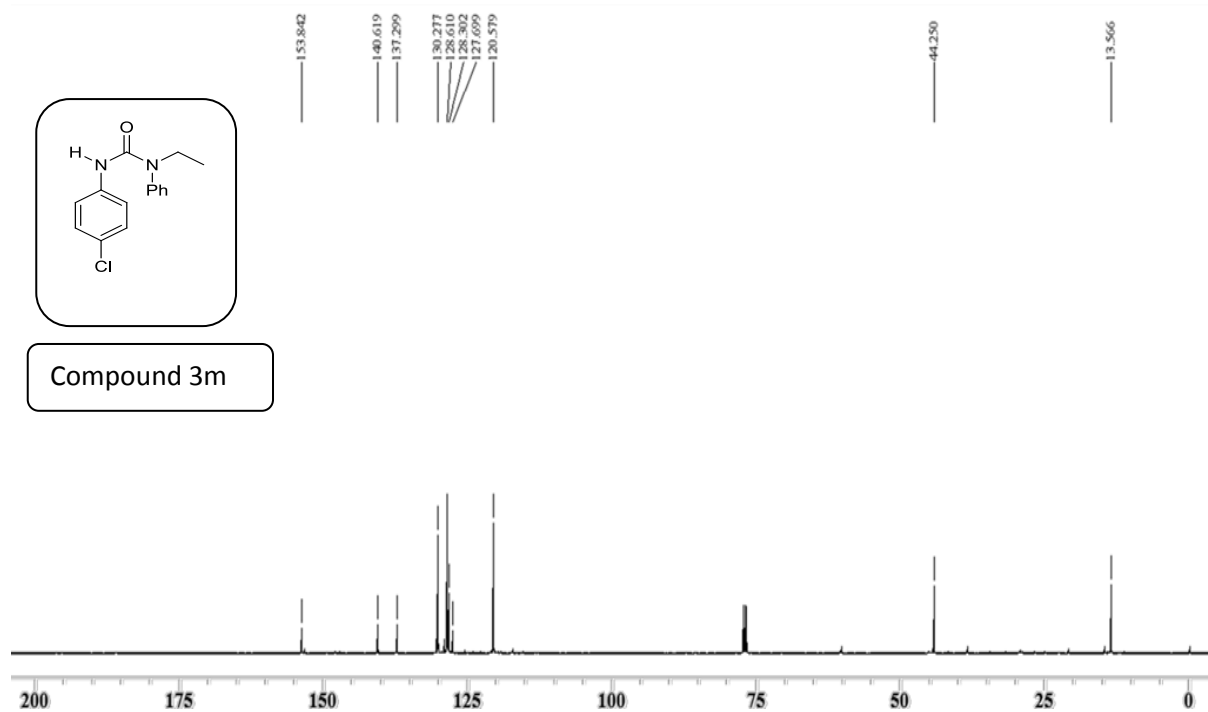


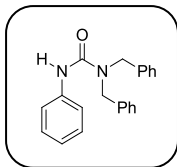


Compound 3m

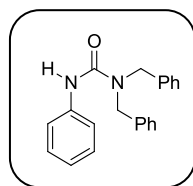
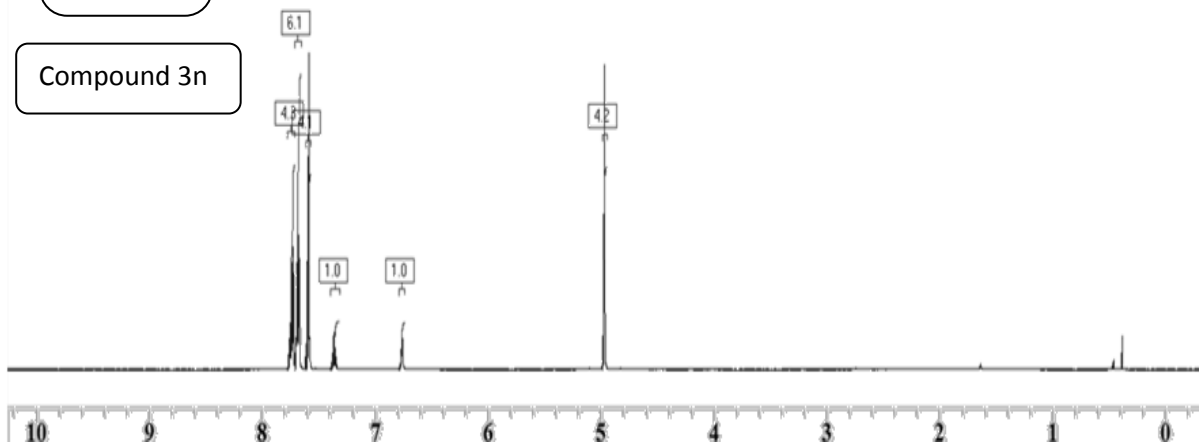


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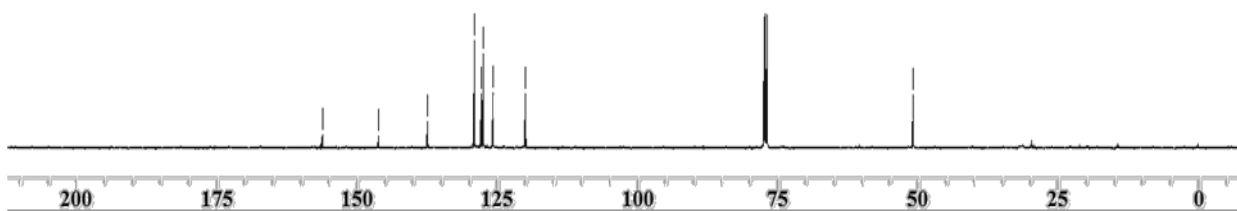


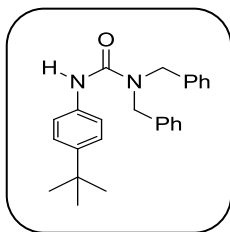


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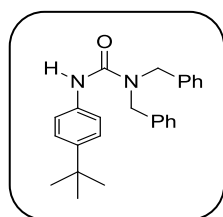
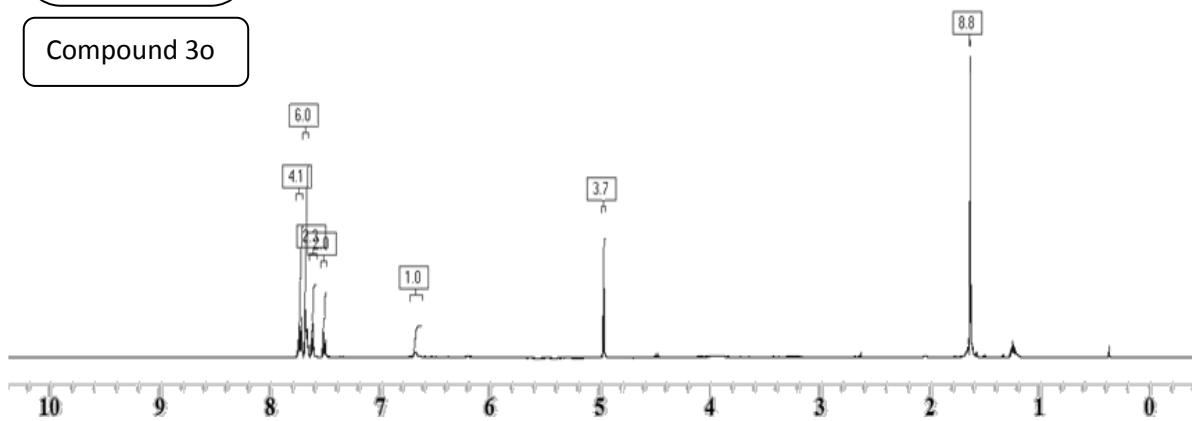


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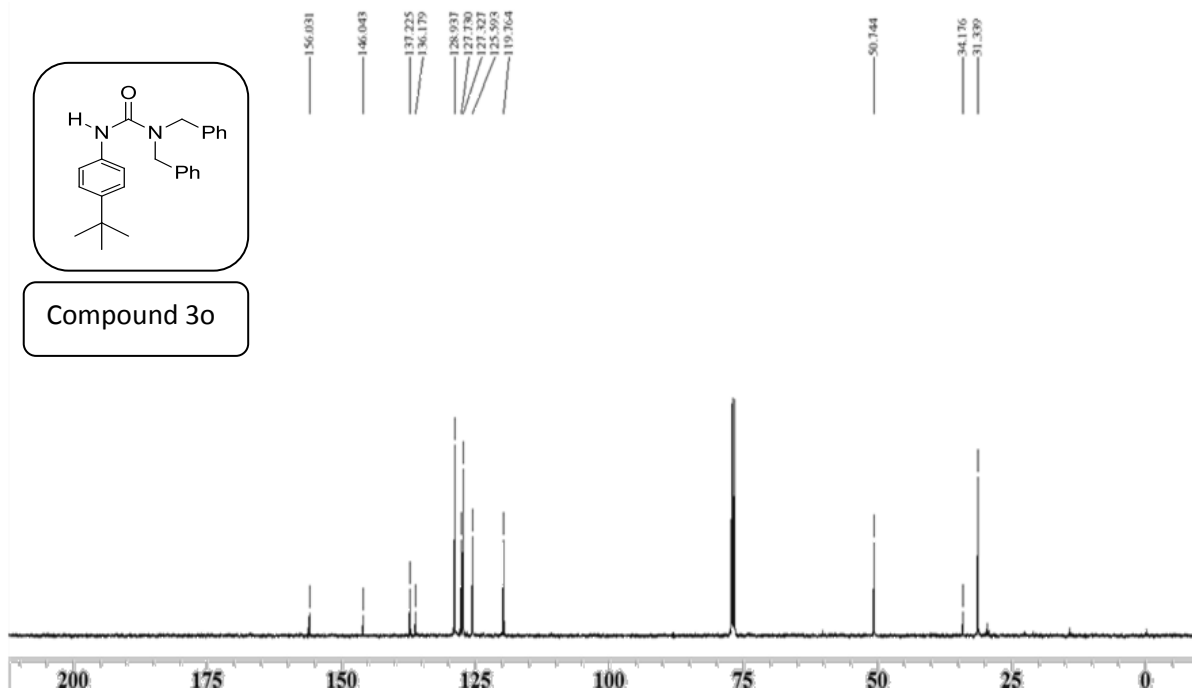


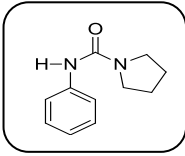


Compound 30

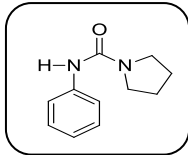
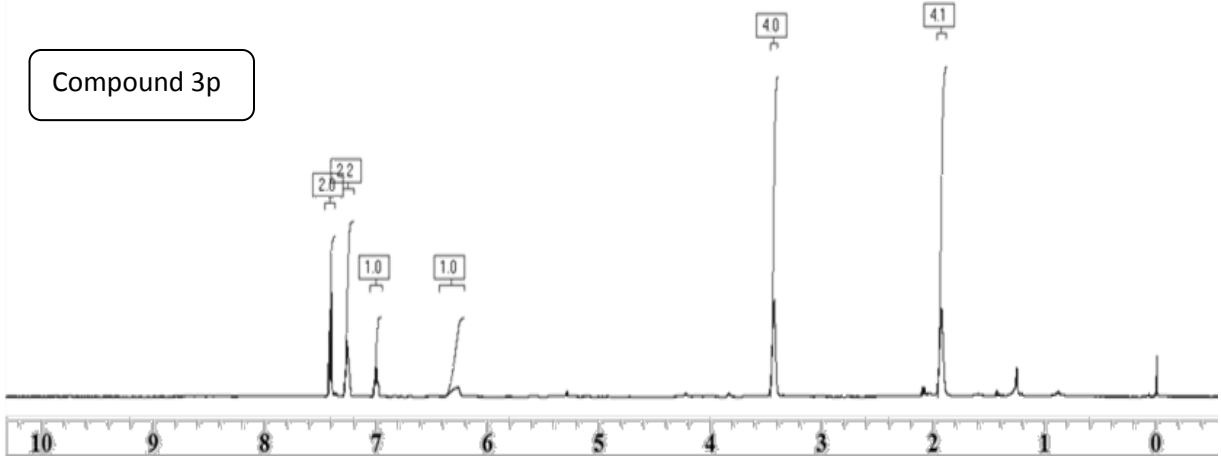


Compound 30

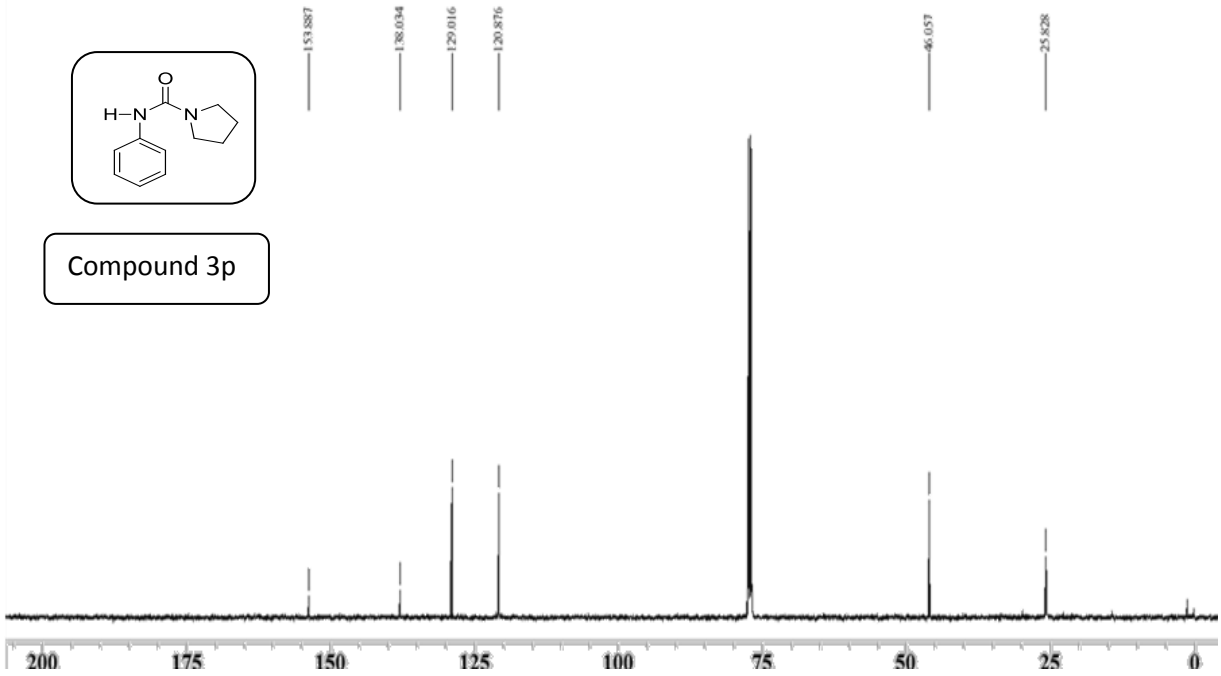


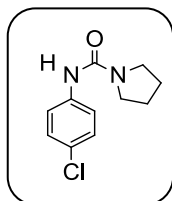


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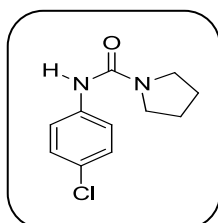
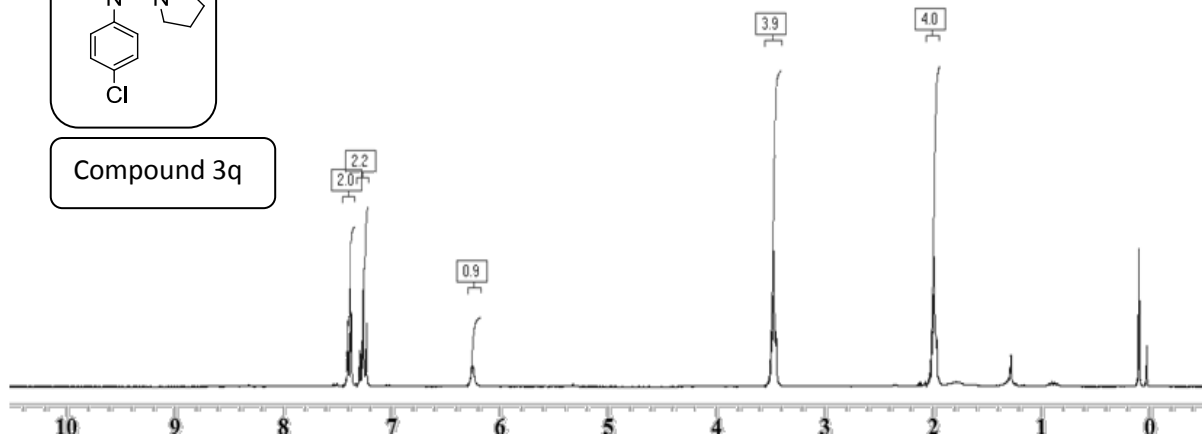


Compound 3p

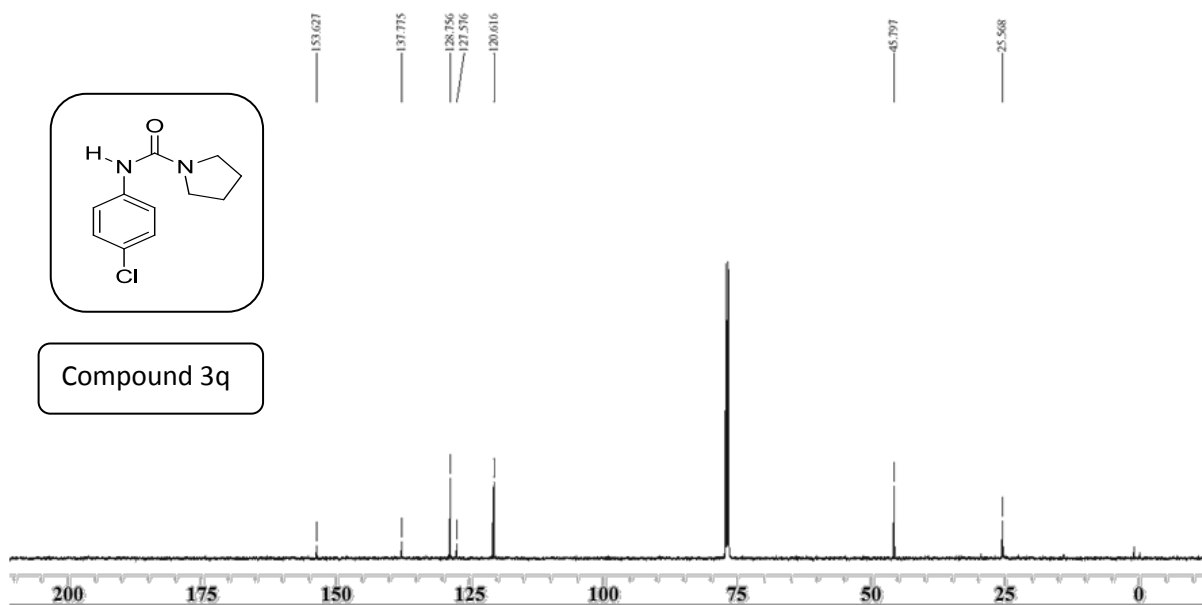


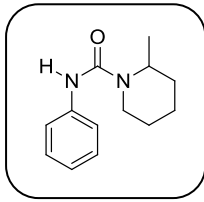


Compound 3q

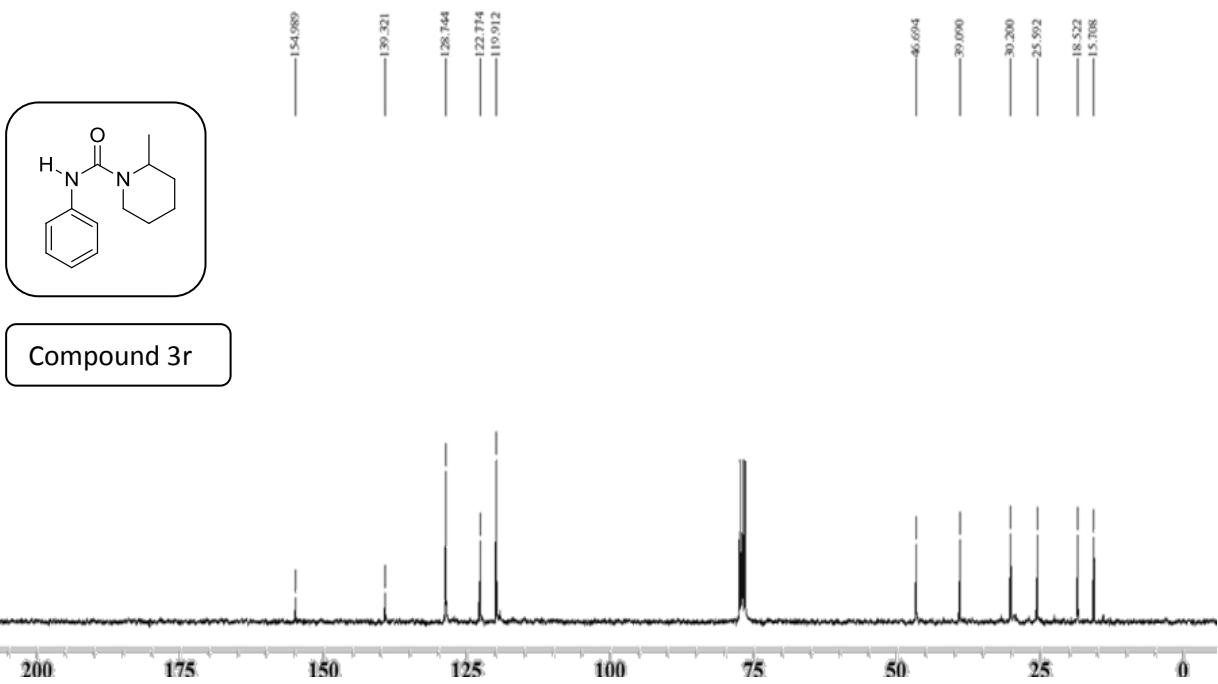
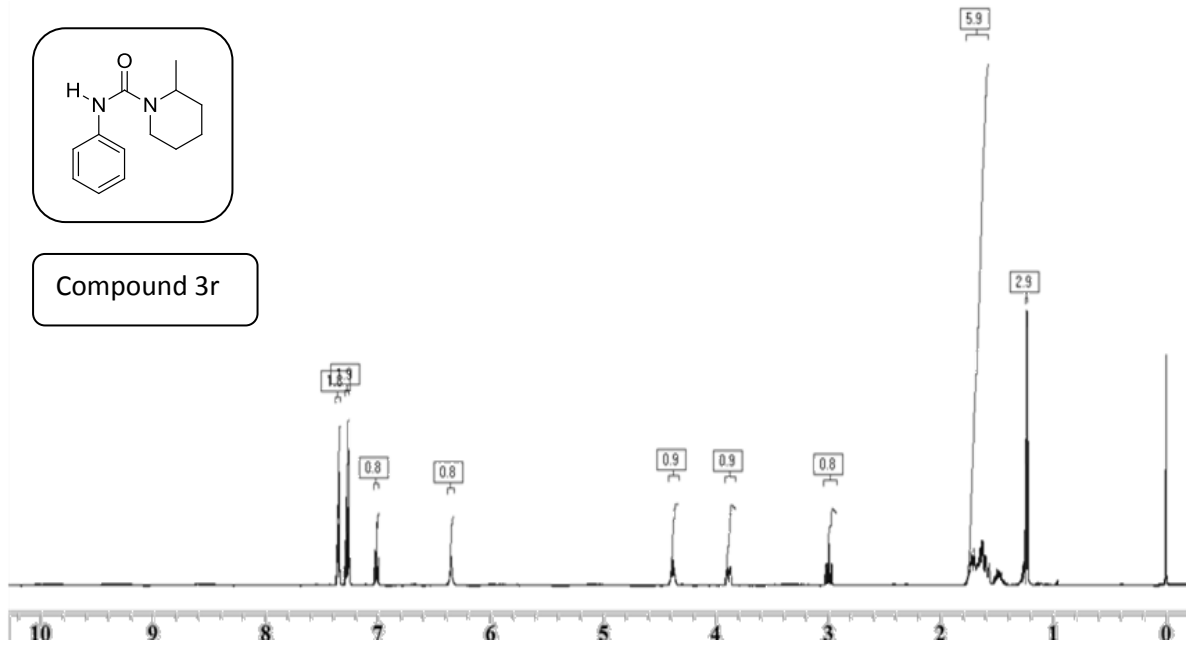


Compound 3q

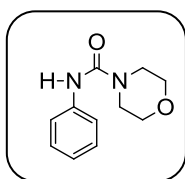




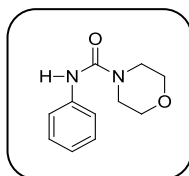
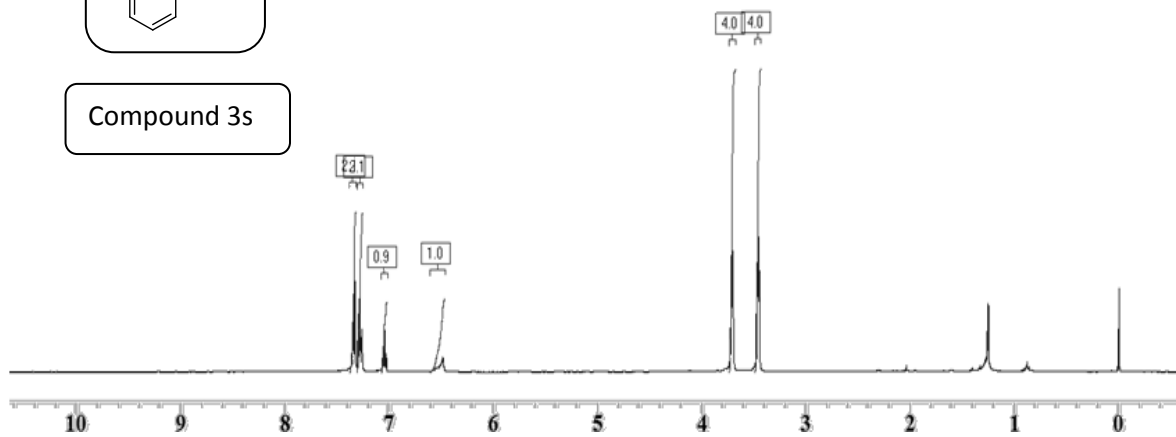
Compound 3r



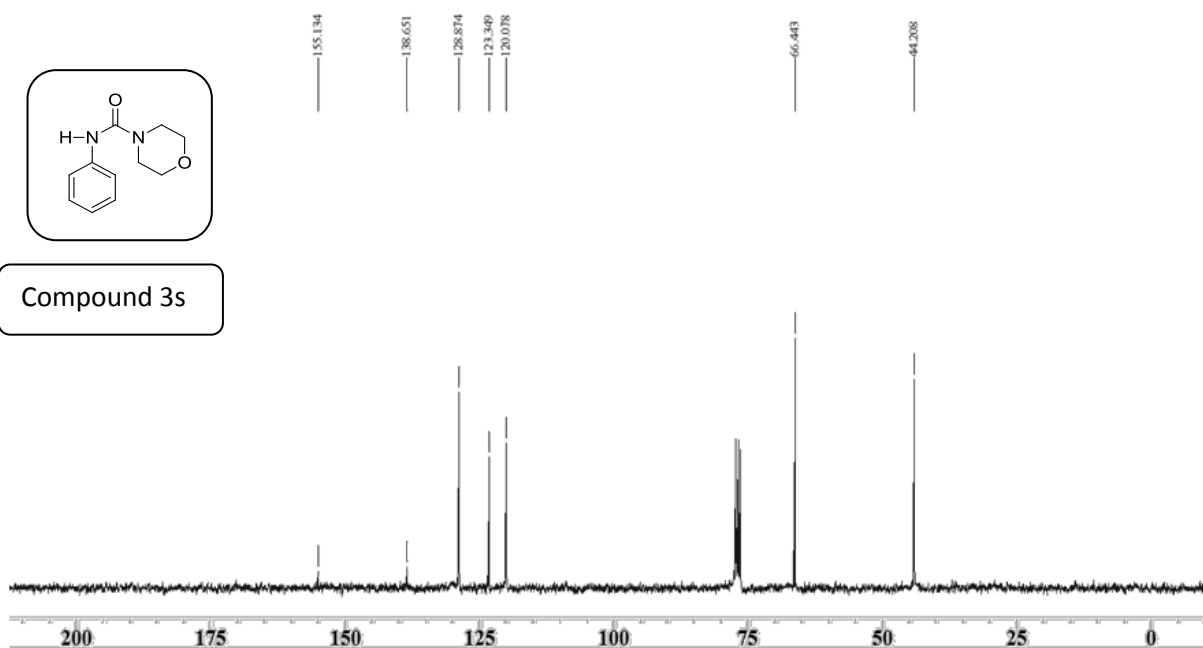


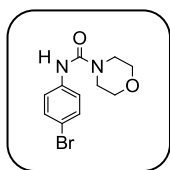


Compound 3s

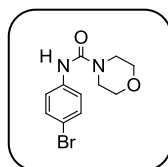
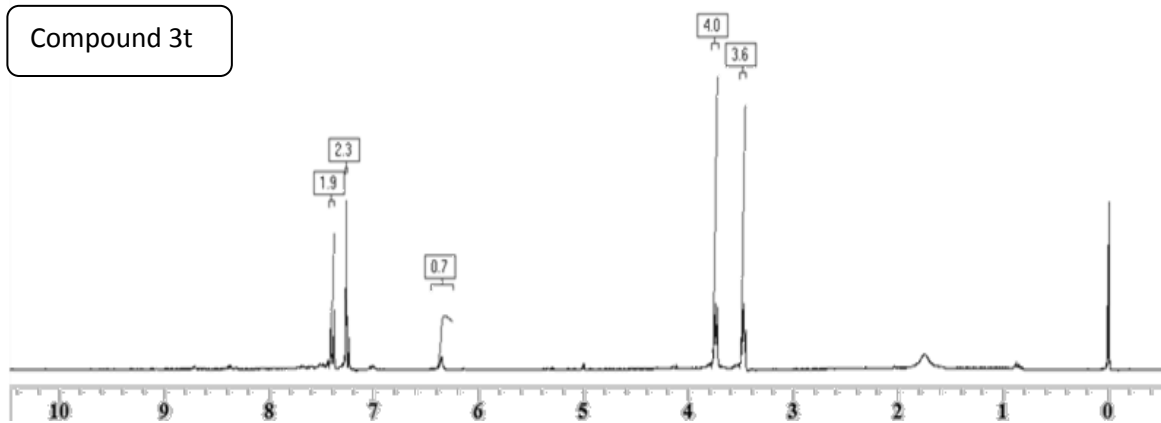


Compound 3s

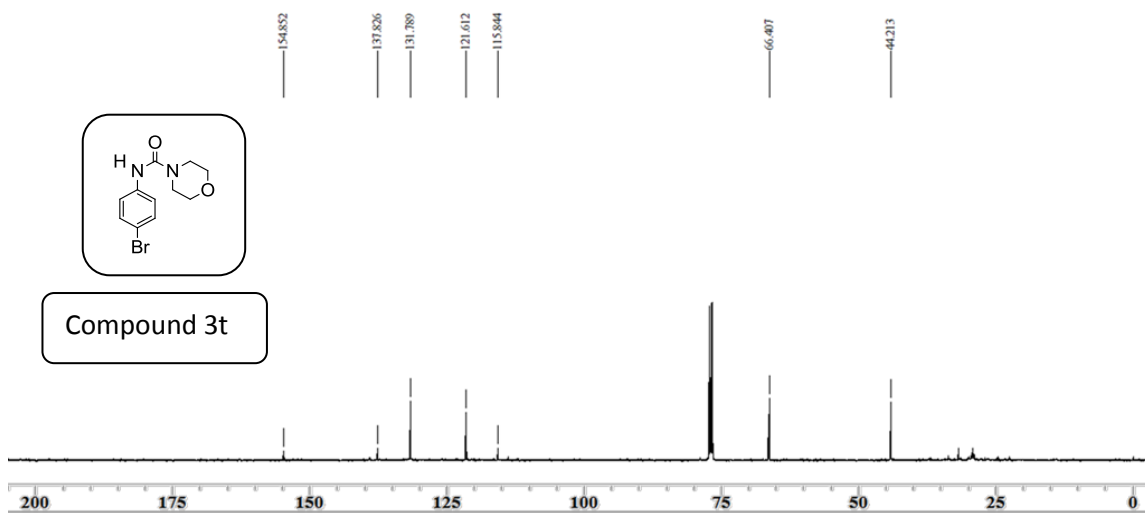


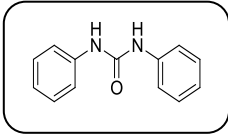


Compound 3t

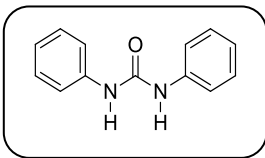
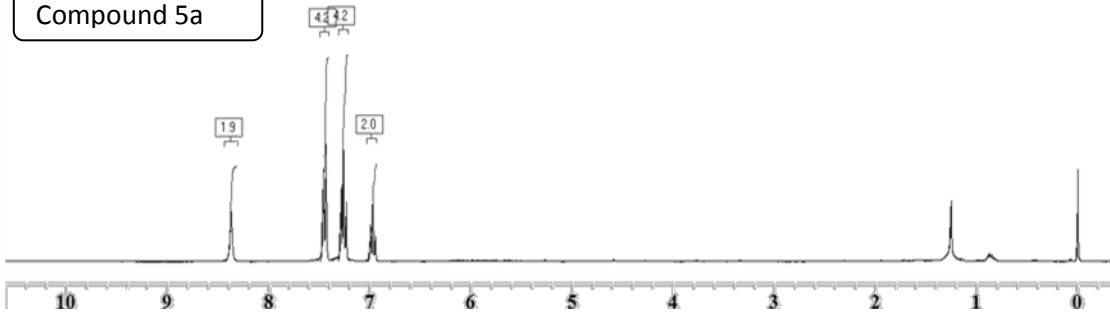


Compound 3t





Compound 5a



Compound 5a

