# Electronic Supplemental Information (ESI)

# Metal free oxidative coupling of aryl formamides with alcohols for the synthesis of carbamates

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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-$F_{254}$ 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 $^{1}H$, $^{13}C$ 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 $CDCl_3$. 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 ($cm^{-1}$) using Bruker Alpha FT-IR spectrometer. Mass was recored on Thermo Trace DSQ GC-MS spectrometer using BP-01 (30M x 0.25 mm x 1µm) column. Mass spectral data were compiled using MS (ESI), HRMS mass spectrometers.

## 2. Experimental Section :

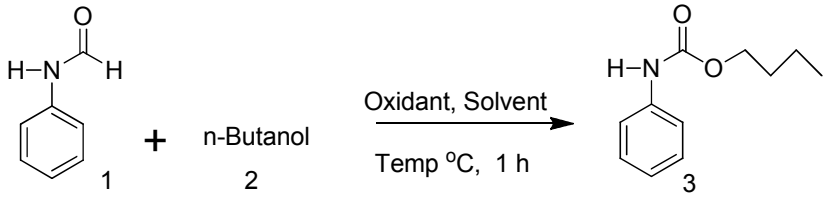
General procedure:

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 5 mmol of alcohol was added to the above reaction mixture and temperature was increased to 60 $^{o}C$ and stirred for one hour.

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 $Na_2SO_4$. 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 (9:1) mixture to afford the required product (3). TLC's have to be monitored by both UV and iodine.

## Optimization of reaction conditions:

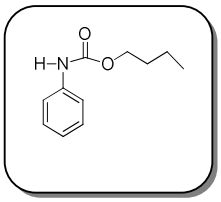
Reaction conditions [a]:



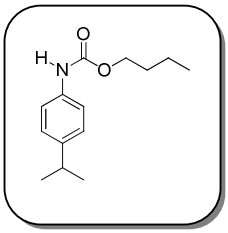

| Entry | Oxidant | Solvent | Temp °C | Isolated Yield[%][b] |
|---|---|---|---|---|
| 1 | $PhI(OAc)_2$ | DCM | RT | NR |
| 2 | $PhI(OAc)_2$ | DCM | 40 | 15 |
| 3 | $PhI(OAc)_2$ | THF | 60 | NR |
| 4 | $PhI(OAc)_2$ | DCE | 60 | 25 |
| 5 | TBHP, $Cu(OAc)_2$ | DCE | 60 | 5 |
| 6 | $H_2O_2$, $Cu(OAc)_2$ | DCE | 60 | NR |
| 7 | $PhI(OCOCF_3)_2$ | DCE | RT | 40 |
| 8 | $PhI(OCOCF_3)_2$ | DCE | 60 | 82 |

[a]Reaction conditions: N-Formyl aniline (**1)** (1 mmol), n-Butanol (**2) (**5 mmol), dichloro ethane (3 mL, solvent), Oxidant (1 mmol), 60 °C, MS 4A°, $N_2$, 1 h. [b]Isolated yields.

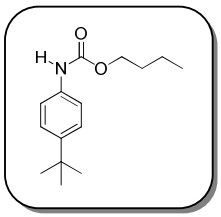
## 3. Spectroscopic data for the products:



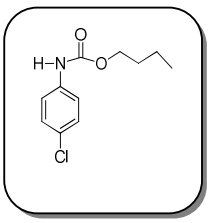
**Butyl phenylcarbamate: (**compound **3a)**: (**Isolated yield** = 82%): **IR** $cm^{-1}$: 3372, 2940, 1725, 1532, 1297, 1078, 745, 632. **$^{1}$H NMR** δ ( 500 MHz, $CDCl_3$): 7.38 (d, *J*=7.6 Hz, 2H), 7.30 (t, *J*=7.4 Hz, 2H), 7.03 (t, *J*=7.4 Hz, 1H), 6.74 (br, 1H), 4.16 (t, *J*=6.7 Hz, 2H), 1.67-1.61 (m, *J*=7.1 Hz, 2H), 1.43-1.37 (m, *J*=7.6 Hz, 2H), 0.94 (t, *J*=7.4 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.7, 137.9, 128.9, 123.2, 118.5, 65.0, 30.8, 19.0, 13.6. **MS (ESI):** *m/z* =216 $(M+Na)^+$, **HRMS** : ESI $(M+H)^+$ m/z calcd for $C_{11}H_{16}O_2N$ $(M+H)^+$ = 194.11810, found = 194.11717.



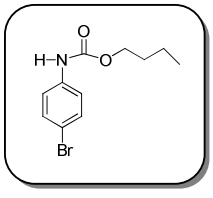
**Butyl (4-isopropylphenyl)carbamate: (**compound **3b)**: (**Isolated yield**=75%): (Liquid). **IR** $cm^{-1}$: 3350, 2958, 1707, 1530, 1415, 1224, 1071, 831, 633. **$^{1}$H NMR** δ ( 500 MHz, $CDCl_3$): 7.29 (d, *J*=7.3 Hz, 2H), 7.15 (d, *J* =8.5 Hz, 2H), 6.54 (br, 1H), 4.15 (t, *J*=6.7 Hz, 2H), 2.89-2.83 (m, 1H), 1.65 (p, *J*=7.1 Hz, 2H) ,1.45-1.37 (m, 2H), 1.21 (d, *J*=6.8 Hz, 6H), 0.95 (t, *J*=7.3 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.8, 143.9, 135.8, 126.8, 123.5, 118.8, 64.9, 33.4, 30.9, 24.0, 19.0, 13.6. **MS** (ESI): *m/z* =258 $(M+Na)^+$, **HRMS (**ESI) $(M+H)^+$ m/z calcd for $C_{14}H_{22}NO_2$ $(M+H)^+$ = 236.16451, found = 236.16316.



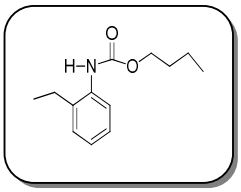
**Butyl(4-(tert-butyl)phenyl)carbamate:** (Compound **3c**): (**Isolated yield** =68%): (liquid). **IR** $cm^{-1}$: 3392, 2957, 1721, 1519, 1220, 1018, 826, 630. **$^{1}$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.31 (m, 4H), 6.52 (br, 1H), 4.15 (t, *J*=6.7 Hz, 2H), 1.67-1.62 (p, *J*=7.9 Hz, 2H), 1.43-1.39 (m, 2H), 1.29 (s, 9H), 0.95 (t, *J*=7.3 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.8, 146.2, 135.2, 125.8, 118.4, 117.3, 65.0, 34.2, 31.3, 29.6, 19.0, 13.7. **MS** (ESI):249($M^+$), **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{15}H_{24}O_2N$ $(M+H)^+$ = 250.18016, found = 250.17872.



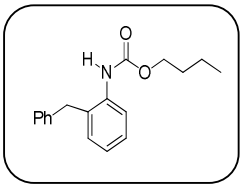
**Butyl (4-chlorophenyl)carbamate**: **(**compound **3d)** : (**Isolated yield**=65%) : (Liquid). IR $cm^{-1}$: 3342, 2920, 1732, 1609, 1502, 1198, 1058, 810, 658. **$^{1}$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.32 (d, *J*=8.3 Hz, 2H), 7.26 (d, *J*=9.0 Hz, 2H), 6.69 (br, 1H), 4.16 (t, *J*=6.7 Hz, 2H), 1.65 (p, *J*=7.1 Hz, 2H), 1.43-1.37 (m, 2H), 0.95 (t, *J*=7.3 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.5, 136.5, 128.9, 128.2, 119.8, 65.2, 29.6, 19.0, 13.6. **MS** (GC): *m/z* = 227($M^+$).



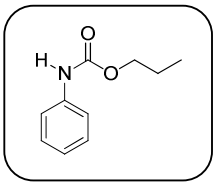
**Butyl (4-bromophenyl)carbamate: (**compound **3e)** : (**Isolated yield** = 72%):(Liquid). **IR** $cm^{-1}$: 3350, 2928, 1714, 1601, 1528, 1224, 1074, 821, 621. **$^{1}$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.41 (d, *J*=8.8 Hz, 2H), 7.29 (d, *J*=9.1 Hz, 2H), 6.59 (br, 1H), 4.16 (t, *J*=6.8 Hz, 2H ), 1.65 (m, 2H), 1.42-1.38 (m, 2H), 0.95 (t, J=7.4 Hz, 3H). **$C^{13}$ NMR** $\delta$ (75 MHz, $CDCl_3$): 153.5, 142.0, 137.1, 131.7, 129.5, 120.1, 65.2, 30.8, 18.9, 13.6. **MS** (GC): *m/z* = 271 ($M^+$).



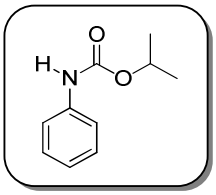
**Butyl (2-ethylphenyl)carbamate: (compound 3f): Isolated yield = 61%): IR** $cm^{-1}$: 3361, 2961, 1710, 1523, 1216, 1068, 752, 631. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.77 (br, 1H), 7.22-7.06 (m, 3H), 6.40 (br, 1H), 4.17 (t, *J*=6.7 Hz, 2H), 2.57 (q, *J*=7.6 Hz, 2H), 1.69 (p, *J*=7.1 Hz, 2H), 1.45-1.38 (m, 2H), 1.23 (t, *J*=7.4 Hz, 3H), 0.95 (t, *J*=7.3 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 154.2, 135.1, 128.4, 126.6, 124.4, 121.7, 65.1, 30.9, 29.6, 24.1, 19.0, 13.8. **MS** (ESI): *m/z* = 222 $(M+H)^+$, **HRMS**: ESI $(M+H)^+$ m/z calcd for $C_{13}H_{20}NO_2$ $(M+H)^+$ = 222.14886, found = 222.14752.



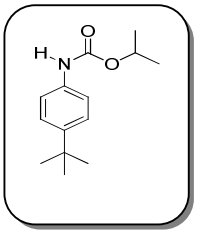
**Butyl (2-benzylphenyl)carbamate: (**compound **3g)** : (**Isolated yield** = 56%): **IR** $cm^{-1}$: 3317, 2959, 1699, 1524, 1224, 1068, 737, 620. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$) : 7.75 (br, 1H), 7.31-7.20 (m, 5H), 7.18-7.07 (m, 3H), 6.29 (br, 1H), 4.09 (t, *J*=6.7 Hz, 2H), 3.96 (s, 2H), 1.60 (p, *J*=7.1 Hz, 2H), 1.38-1.31 (m, 2H), 0.92 (t, *J*=7.3 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 154.1, 138.1, 135.9, 130.5, 128.7, 128.4, 127.4, 126.5, 124.4, 122.6, 65.0, 38.0, 30.8, 18.9, 13.6. **MS** (ESI): *m/z* = 284$(M+H)^+$, **HRMS**: ESI $(M+H)^+$ m/z calcd for $C_{18}H_{22}NO_2$ $(M+H)^+$ = 284.16451, found = 284.16275.



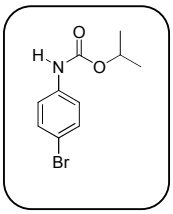
**Propyl phenylcarbamate: (**compound **3h)**: (**Isolated yield=72**%): (Liquid). **IR**$cm^{-1}$: 3350, 2933, 1709, 1536, 1315, 1225, 1070, 732, 633. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.37 (d, *J*=7.7 Hz, 2H), 7.30 (t, *J*=7.4 Hz, 2H), 7.05 (t, *J*=7.3 Hz, 1H), 6.63 (br, 1H), 4.12 (t, *J*=6.7 Hz, 2H), 1.70-1.66 (m, 2H), 0.98 (t, *J*=7.3 Hz, 3H).**$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.7, 137.9, 128.9, 123.2, 118.5, 66.8, 22.2, 10.3. **MS** (GC): *m/z* = 179$(M^+)$.



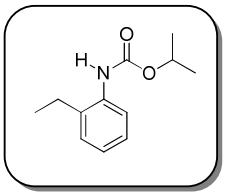
**Isopropyl phenylcarbamate: (**compound **3i)**: (**Isolated yield** =70%): (Solid). **IR** $cm^{-1}$: 3329, 2968, 1725, 1502, 1403, 1259, 1078, 732, 653. **$^1$H NMR** $\delta$ (500 MHz, $CDCl_3$): 7.38 (d, *J*=7.3 Hz, 2H), 7.29 (t, *J*=7.4 Hz, 2H), 7.04 (t, *J*=7.3 Hz, 1H), 6.64 (br, 1H), 5.02 (m, 1H), 1.29 (d, *J*=6.2 Hz, 6H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.2, 138.0, 128.8, 123.0, 118.5, 68.51, 21.97. **MS (ESI):** m/z =202 $(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{10}H_{14}O_2N$ $(M+H)^+$ = 180.10245, found = 180.10148**.**



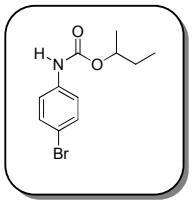
**Isopropyl (4-(tert-butyl)phenyl)carbamate: (**compound **3j)**: (**Isolated yield** =72%): **IR** $cm^{-1}$: 3319, 2962, 1704, 1527, 1376, 1231, 1110, 1019, 795, 632. **$^1$H NMR** $\delta$ (500 MHz, $CDCl_3$): 7.30 (m, 4H), 6.54 (br, 1H), 5.03 (m, 1H), 1.29 (m, 15H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.3, 146.1, 135.3, 125.7, 118.4, 120.2, 68.5, 34.2, 31.3, 22.0. **MS** (GC): *m/z* =258 $(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{14}H_{22}O_2N$ $(M+H)^+$ = 236.16451, found =236.19349.



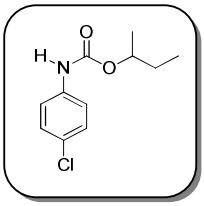
**Isopropyl (4-bromophenyl)carbamate**: **(**compound **3k)**: (**Isolated yield** =67%): **IR** $cm^{-1}$: 3316, 2927, 1704, 1528, 1394, 1230, 1111, 824, 636. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.41 (d, *J*=8.8 Hz, 2H), 7.28 (d, *J*=8.6 Hz, 2H), 6.53 (br, 1H), 5.02 (m, 1H), 1.30 (d, *J*=6.2 Hz, 6H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.2, 142.1, 137.1, 120.1, 115.5, 69.2, 21.9. **MS** (GC): *m/z* = 257$(M^+)$.



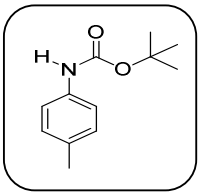
**Isopropyl (2-ethylphenyl)carbamate:** (compound **3l**):(**Isolated yield** = 65% ): (Liquid). **IR** $cm^{-1}$: 3308, 2951, 1732, 1509, 1358, 1242, 1075, 802, 647. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.78 (br, 1H), 7.22-7.06 (m, 3H), 6.37 (br, 1H), 5.0 (m, 1H), 2.60 (q, *J*=7.6 Hz, 2H), 1.30 (d, *J*=6.2 Hz, 6H), 1.22 (t, *J*=7.6 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.7, 135.2, 136.1, 128.3, 126.6, 124.2, 121.7, 68.6, 24.0, 22.0, 13.7. **MS** (GC): *m/z* = 230 $(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{12}H_{18}O_2N$ $(M+H)^+$ = 208.13375, found = 208.13271.



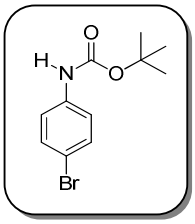
**Sec-butyl (4-bromophenyl)carbamate:** (compound **3m**): (**Isolated yield** =62%): (Liquid). **IR** $cm^{-1}$: 3318, 2971, 1705, 1527, 1394, 1227, 1050, 823, 768, 647. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.41 (d, *J*=8.8 Hz, 2H), 7.29 (d, *J*=8.5 Hz, 2H), 6.59 (br, 1H), 4.84 (m, 1H), 1.68-1.57 (m, 2H), 1.27 (d, *J*=6.2 Hz, 3H), 0.94 (t, *J*=7.4 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.2, 137.2, 131.8, 120.0, 115.5, 73.5, 28.9, 19.6, 9.6. **MS** (ESI): *m/z* = 272$(M+H)^+$.



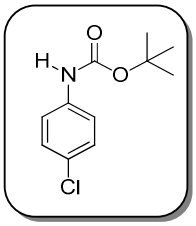
**Sec-butyl (4-chlorophenyl)carbamate: (**compound **3n**):(**Isolated yield** =55%): **IR** $cm^{-1}$: 3325, 2952, 1713, 1532, 1403, 1248, 1077, 820, 682. **$^1$H NMR** $\delta$ (500 MHz, $CDCl_3$): 7.32 (d, *J*=8.3 Hz, 2H), 7.26 (d, *J*=8.8 Hz, 2H), 6.66 (br, 1H), 4.83 (m, 1H), 1.67-1.55 (m, 2H), 1.27 (d, *J*=8.8 Hz, 3H), 0.93 (t, *J*=7.4 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.4, 136.8, 128.7, 119.9, 73.3, 28.8, 19.5, 9.5. **MS** (ESI): *m/z* = 227$(M^+)$, **HRMS:** ESI $(M^+)$ m/z calcd for $(M)^+$ = 227.07076, found = 227.06925



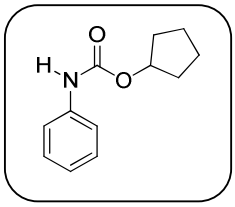
**Tert-butyl p-tolylcarbamate: (**compound **3o**): (**Isolated yield** =62%): (Solid). **IR:**$cm^{-1}$: 3352, 2938, 1683, 1529, 1405, 1262, 1195, 1073, 792, 621. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.22 (d, *J*=7.7 Hz, 2H), 7.09 (d, *J*=8.0 Hz, 2H), 6.40 (br, 1H), 2.29 (s, 3H), 1.51 (s, 9H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 152.8, 135.6, 132.4, 129.3, 118.6, 80.2, 28.3, 20.6. **MS** (ESI): *m/z* = 230$(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{12}H_{18}O_2N$ $(M+H)^+$ = 208.13321, found = 208.13213.



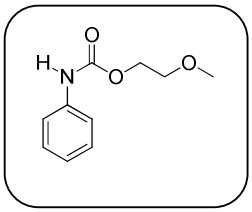
**Tert-butyl (4-bromophenyl)carbamate: (**compound **3p**): (**Isolated yield** =70%): (Solid). **IR** $cm^{-1}$: 3368, 2947, 1694, 1516, 1393, 1239, 1161, 1020, 763, 616. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.36 (d, *J*=8.3 Hz, 2H), 7.24 (d, *J*=8.3 Hz, 2H), 6.68 (br, 1H), 1.50 (s, 9H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 152.4, 137.4, 131.8, 120.0, 115.3, 80.8, 28.2. **MS** (ESI): *m/z* =289$(M+NH_4)^+$, **HRMS:** ESI $(M+NH_4)^+$ m/z calcd for $C_{11}H_{18}O_2N_2Br$ $(M+NH_4)^+$ = 289.05462, found = 289.05324.



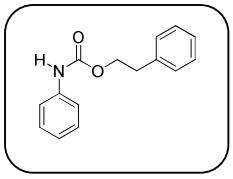
**Tert-butyl (4-chlorophenyl)carbamate: (**compound **3q**): (**Isolated yield** =60%): (Solid.). **IR** $cm^{-1}$: 3308, 2921, 1702, 1553, 1698, 1257, 1188, 1029, 774, 612. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.30 (d, *J*=8.5 Hz, 2H), 7.23 (d, *J*=8.6 Hz, 2H), 6.62 (br, 1H), 1.50 (s, 9H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 152.5, 136.9, 128.9, 127.9, 119.6, 80.4, 28.2. **MS** (ESI): *m/z* = 250$(M+Na)^+$.



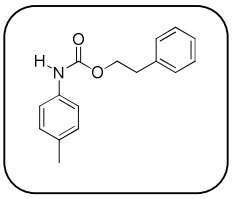
**Cyclopentyl phenylcarbamate: (**compound **3r**): (**Isolated yield** =66 %): **IR** $cm^{-1}$: 3325, 2966, 1709, 1508, 1396, 1252, 1070, 738, 648. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.38 (d, *J*=7.7 Hz, 2H), 7.04 (t, *J*= 7.3 Hz, 2H), 7.04 (t, *J*=7.3 Hz, 1H), 5.21 (br, 1H), 1.92-1.85 (m, 2H), 1.79-1.72 (m, 4H), 1.64-1.59 (m, 2H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.4, 138.0, 128.9, 123.1, 118.4, 78.0, 32.7, 23.6. **MS**(ESI): *m/z* =228 $(M+Na)^+$, **HRMS**: ESI $(M+H)^+$ m/z calcd for $C_{12}H_{16}O_2N$ $(M+H)^+$ = 206.11810, found = 206.11725.



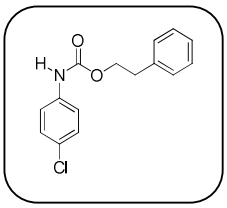
**2-methoxyethyl phenylcarbamate: (**compound **3s)**: (**Isolated yield**=60%): (Liquid). **IR** $cm^{-1}$: 3360, 2936, 1699, 1546, 1317, 1229, 1071, 750, 630. **$^1$H NMR** $\delta$ (500 MHz, $CDCl_3$): 7.36 (d, *J*=7.9 Hz, 2H), 7.30 (t, *J*=8.3 Hz, 2H), 7.06 (t, *J*=7.3 Hz, 1H), 6.77 (br, 1H), 4.34 (t, *J*=4.5 Hz, 2H), 3.64 (t, *J*=4.4 Hz, 2H), 3.42 (s, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.3, 137.7, 129.0, 123.4, 118.5, 70.7, 64.0, 58.9. MS (ESI): m/z = 218 $(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{10}H_{14}O_3N$ $(M+H)^+$ = 196.09682, found = 196.09600.



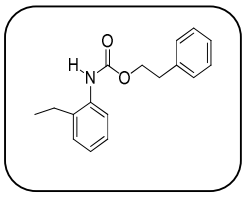
**Phenethyl phenylcarbamate: (**compound **3t)**: (**Isolated yield** =58%): (Liquid). **IR** $cm^{-1}$: 3319, 2927, 1711, 1535, 1314, 1223, 1067, 750, 696. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.74-7.59 (m, 9H), 7.44 (t, *J*=8.5 Hz, 1H), 7.18 (br, 1H), 4.76 (t, *J*=7.0 Hz, 2H), 3.36 (t, *J*=7.0 Hz, 2H). **$^{13}$C NMR** $\delta$ (75 MHz , $CDCl_3$): 160.4, 137.0, 128.4, 128.1, 126.2, 63.76, 34.4. **MS** (ESI): *m/z* = 264$(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{15}H_{16}O_2N$ $(M+H)^+$ = 242.11756, found = 242.11623.



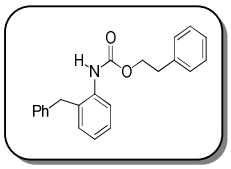
**Phenethyl p-tolylcarbamate: (**compound **3u)**: (Liquid). (**Isolated yield** =63%). **IR** $cm^{-1}$: 3330, 2928, 1696, 1528, 1313, 1235, 1078, 817, 696. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.33-7.23 (m, 7H), 7.10 (d, *J*=8.2 Hz, 2H), 6.5 (br, 1H), 4.37 (t, *J*=7.0 Hz, 2H), 2.98 (t, *J*=7.0 Hz, 2H), 2.29 (s, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.5, 137.7, 135.1, 132.8, 129.3, 128.7, 128.4, 126.4, 118.8, 65.4, 35.3, 20.6. **MS** (GC): m/z = 278 $(M+Na)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{16}H_{18}O_2N$ $(M+H)^+$ = 256.13375, found = 256.13240.



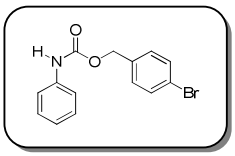
**Phenethyl (4-chlorophenyl)carbamate: (**compound **3v)**: (**Isolated yield** =56%): (Solid). **IR** $cm^{-1}$: 3361, 2935, 1716, 1523, 1225, 1066, 748, 629. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.33-7.23 (m, 9H), 6.64 (br, 1H), 4.39 (t, *J*=7.0 Hz, 2H), 2.98 (t, *J*=7.0 Hz, 2H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.2, 137.6, 136.3, 128.9, 128.5, 126.6, 119.8, 65.7, 35.3. **MS** (GC): *m/z* = 275($M^+$).



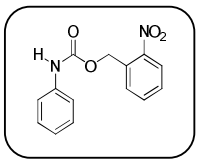
**Phenethyl (2-ethylphenyl)carbamate: (**compound **3w)**: (**Isolated yield** =58%): (Solid ). **IR** $cm^{-1}$: 3296, 2928, 1693, 1531, 1453, 1248, 1079, 749, 657. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.69 (br, 1H), 7.32-7.16 (m, 7H), 7.08 (t, *J*=7.3 Hz, 1H), 4.40 (t, *J*=7.0 Hz, 2H), 2.99 (t, *J*=8.2 Hz, 2H), 2.55 (q, *J*=7.4 Hz, 2H), 1.22 (t, *J*=7.4 Hz, 3H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 154.0, 137.7, 134.9, 128.9, 126.6, 126.5, 124.6, 65.6, 35.4, 24.1, 13.8. **MS** (ESI): *m/z* =270$(M+H)^+$ , **HRMS :** ESI $(M+H)^+$ m/z calcd for $C_{17}H_{20}NO_2$ $(M+H)^+$ = 270.14886, found = 270.14736.



**Phenethyl (2-benzylphenyl)carbamate: (**compound **3x)**: (**Isolated yield** = 52%): (Solid). **IR** $cm^{-1}$: 3399, 2931, 1721, 1521, 1220, 1065, 740, 698. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.72 (br, 1H), 7.31-7.11 (m, 13H), 6.28 (br, 1H), 4.31 (t, *J*=7.0 Hz, 2H), 3.93 (s, 2H), 2.92 (t, *J*=6.8 Hz, 2H). **$^{13}$C NMR** δ (75 MHz, $CDCl_3$): 153.9, 138.8, 137.7, 135.7, 130.6, 128.9, 128.4, 127.5, 126.4, 124.5, 65.6, 38.1, 35.3. **MS** (ESI): *m/z* = 332 $(M+H)^+$, **HRMS:** ESI $(M+H)^+$ m/z calcd for $C_{22}H_{22}NO_2$ $(M+H)^+$ = 332.16451, found = 332.16277.

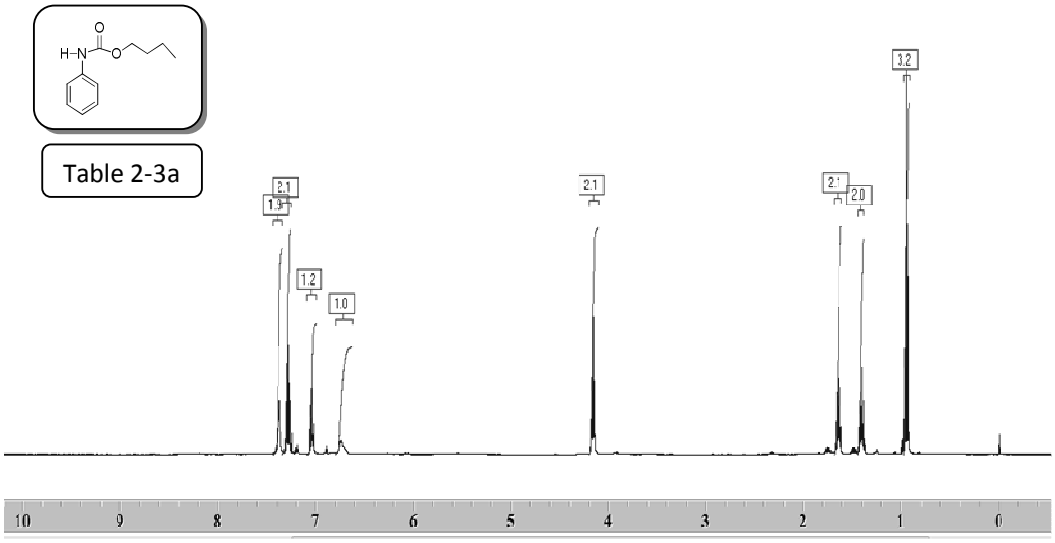


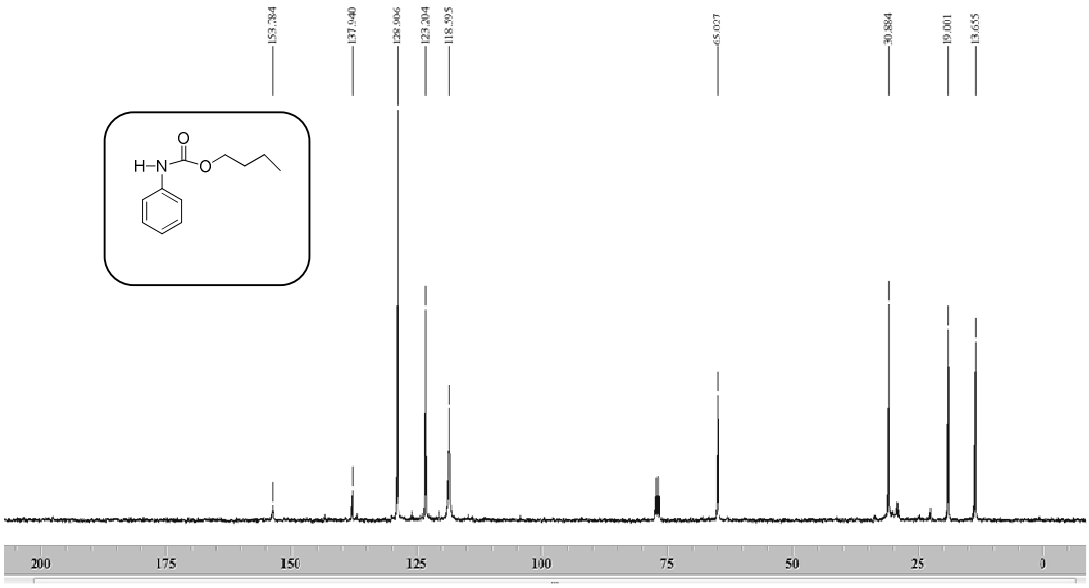
**4-bromobenzyl phenylcarbamate: (compound 3y)**: (**Isolated yield** = 55%): (Solid). **IR** $cm^{-1}$: 3329, 2927, 1703, 1537, 1447, 1238, 1160, 1066, 802, 755, 627. **$^1$H NMR** $\delta$ (300 MHz, $CDCl_3$): 7.91-7.86 (m, 2H), 7.75-7.61 (m, 6H), 7.43 (t, *J*=7.0 Hz, 1H), 7.07 (br, 1H), 5.49 (s, 2H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 153.1, 137.5, 135.0, 131.6, 129.8, 128.9, 126.2, 123.2, 120.5, 118.6, 66.0. **MS** (M+Na): *m/z* = 328$(M+Na)^+$, **HRMS**: ESI $(M+H)^+$ m/z calcd for $C_{14}H_{13}O_2NBr$ $(M+H)^+$ = 306.01297, found = 306.01195.



**2-nitrobenzyl phenylcarbamate: (**compound **3z)**: (**Isolated yield** = 60%): (Solid). **IR** $cm^{-1}$: 3357, 2928, 1716, 1604, 1526, 1343, 1219, 1061, 731, 691. **$^1$H NMR** δ (300 MHz, $CDCl_3$): 8.12 (d, *J*=8.0 Hz, 1H), 7.64 (m, 2H), 7.50-7.38 (m, 3H), 7.31 (t, *J*=7.4 Hz, 2H), 7.08 (t, *J*=7.3 Hz, 1H), 6.85 (br, 1H), 5.61 (s, 2H). **$^{13}$C NMR** $\delta$ (75 MHz, $CDCl_3$): 160.1, 147.4, 137.4, 133.7, 131.2, 129.0, 125.1, 123.7, 118.5, 62.3. **MS** (ESI): m/z =295$(M+Na)^+$, **HRMS:**ESI $(M+Na)^+$ m/z calcd for $C_{14}H_{12}N_2O_4Na$ $(M+Na)^+$ = 295.06893, found = 295.06874.

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



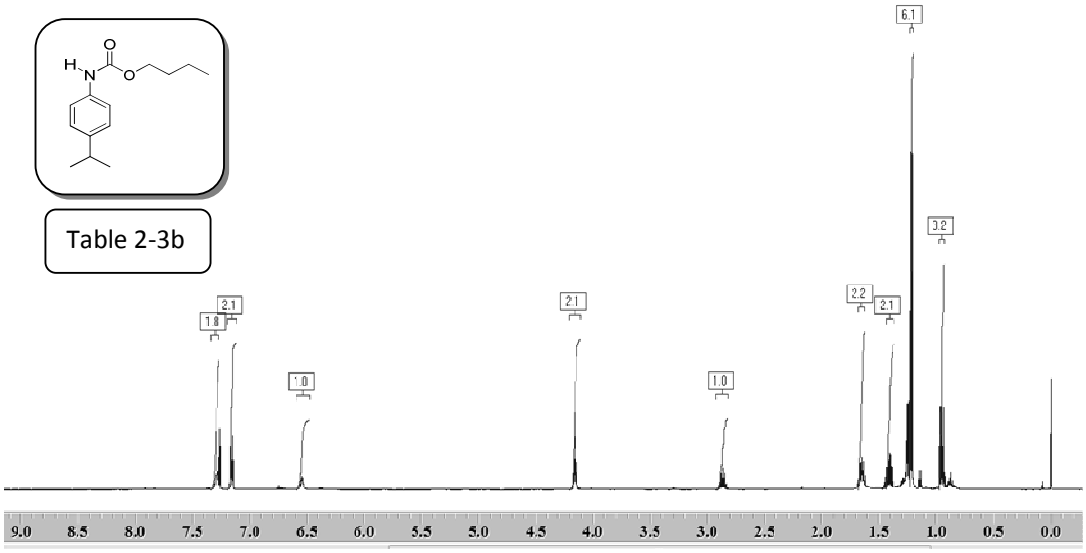
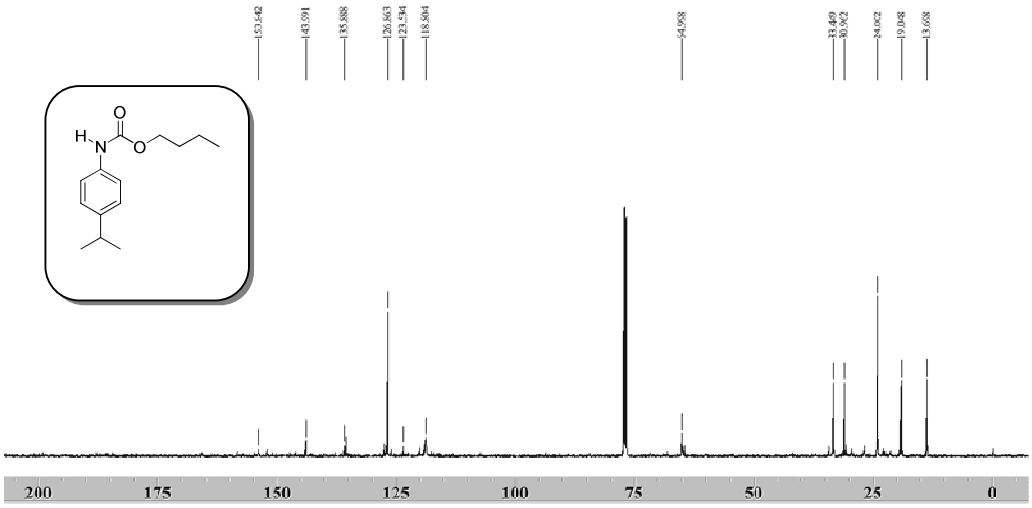


Table 2-3b
6.1
3.2
2.2
2.1
2.1
1.0
1.0
1.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


153.642
143.591
135.888
126.663
123.534
118.804
64.958
33.469
30.902
24.062
19.048
13.608
200
175
150
125
100
75
50
25
0

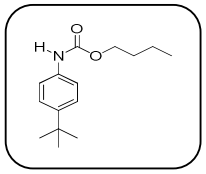
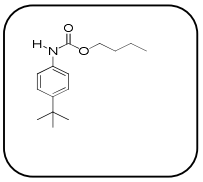


Table 2-3c


9.1
4.1
3.0
2.3
2.0
1.9
0.9
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0




153.879
146.274
135.969
126.027
118.486
117.352
65.035
34.243
31.152
29.691
19.071
13.726
200 175 150 125 100 75 50 25 0

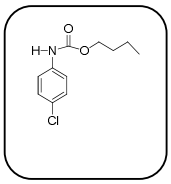
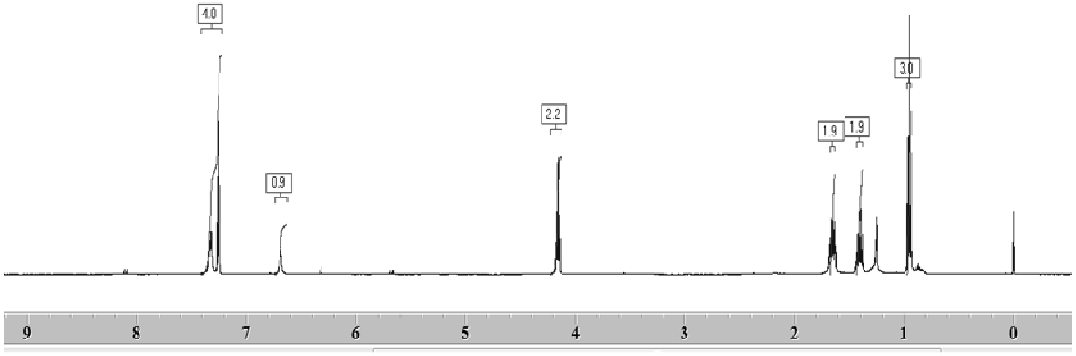
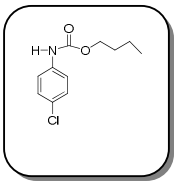


Table 2- 3d


4.0
0.9
2.2
1.9
1.9
3.0
9
8
7
6
5
4
3
2
1
0




153.583
136.506
128.941
126.229
119.803
65.269
29.661
19.025
13.667
200
175
150
125
100
75
50
25
0

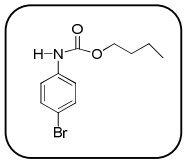
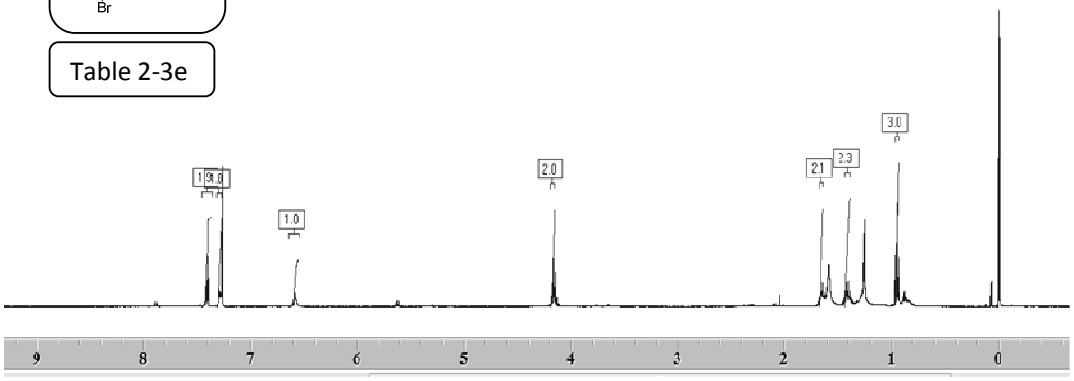
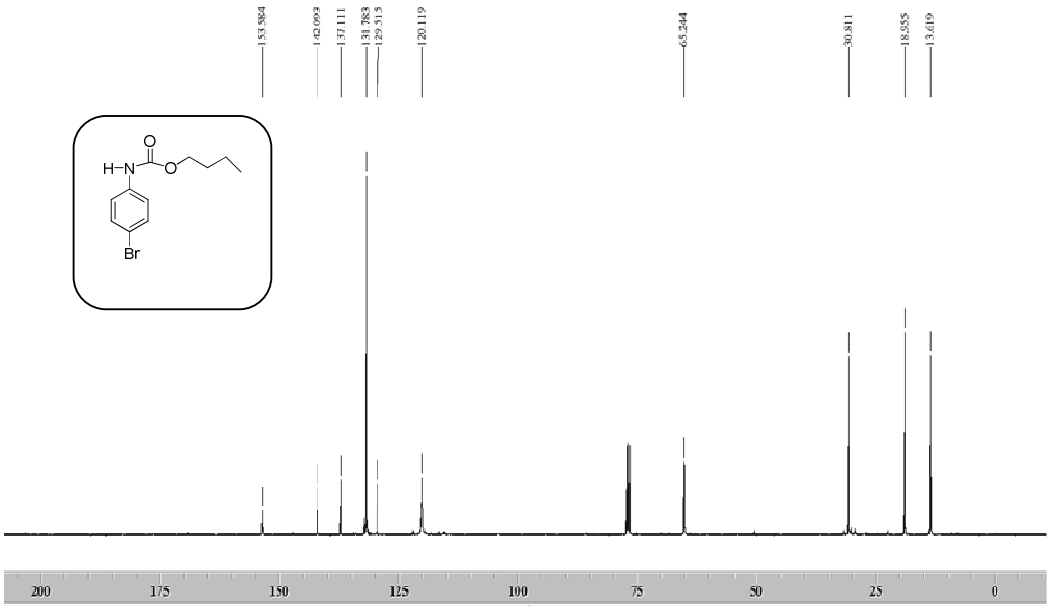

H–N
O
O
Br

Table 2-3e


1.9
1.0
2.0
2.1
2.3
3.0
9
8
7
6
5
4
3
2
1
0


153.384
142.093
137.111
131.788
125.513
120.119
65.244
30.811
18.555
13.619
H–N
O
O
Br
200
175
150
125
100
75
50
25
0

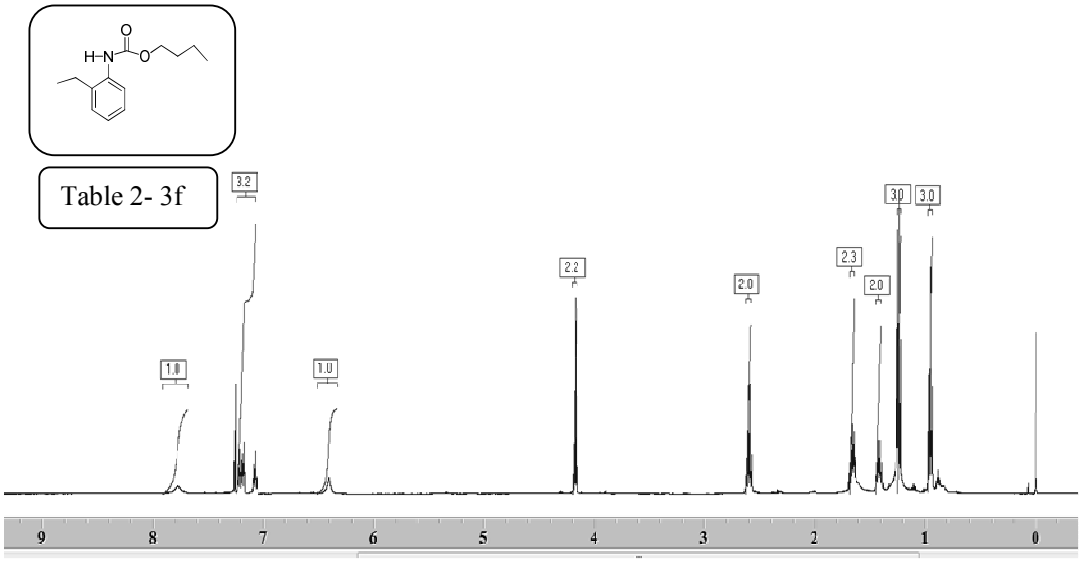
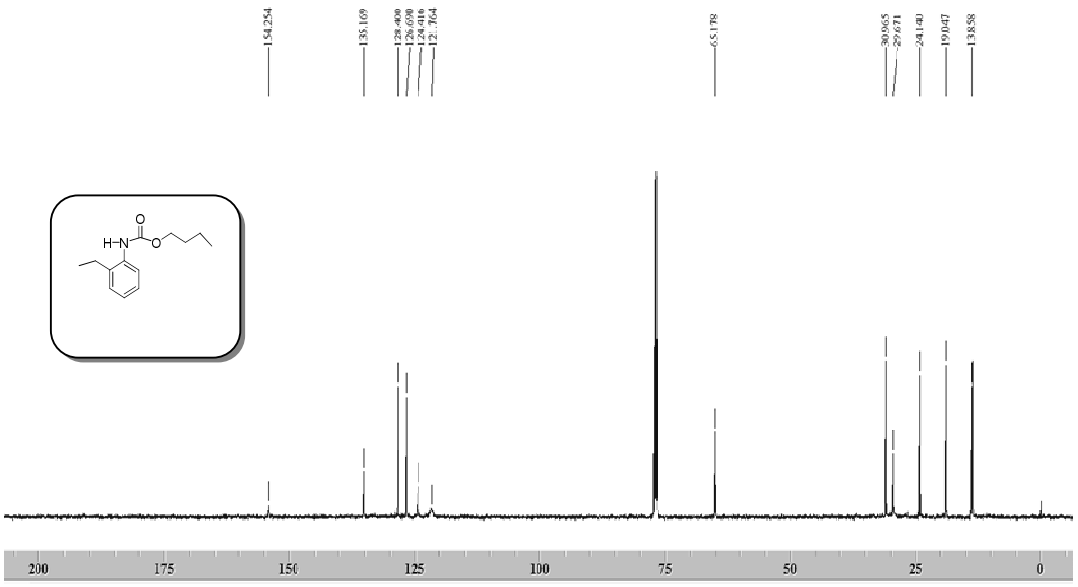


Table 2- 3f
3.2
1.0
1.0
2.2
2.0
2.3
2.0
3.0
3.0
9
8
7
6
5
4
3
2
1
0


154.254
135.169
128.400
126.698
124.446
122.764
65.178
30.965
29.871
24.140
19.047
13.858
200
175
150
125
100
75
50
25
0

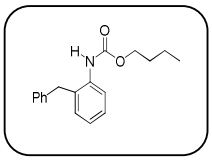
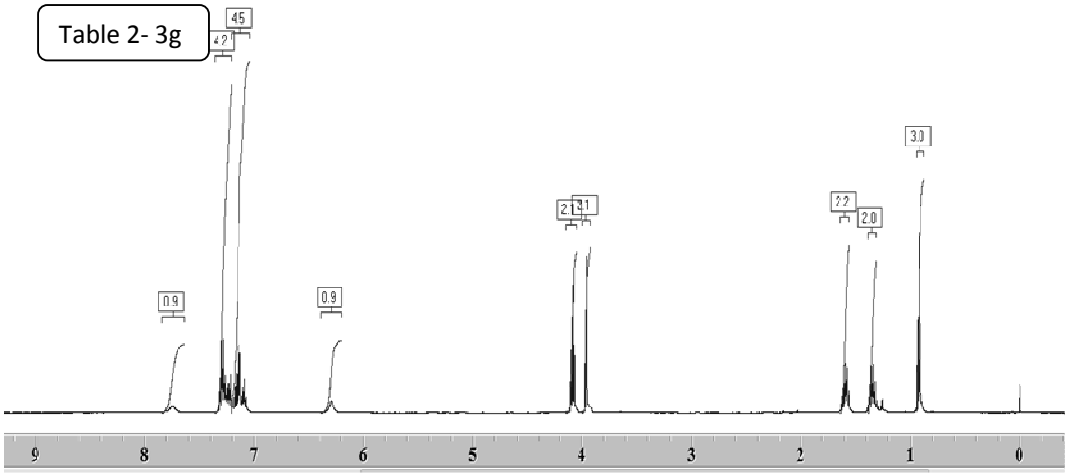
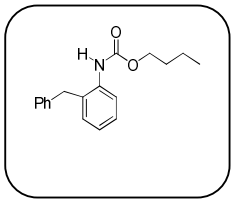
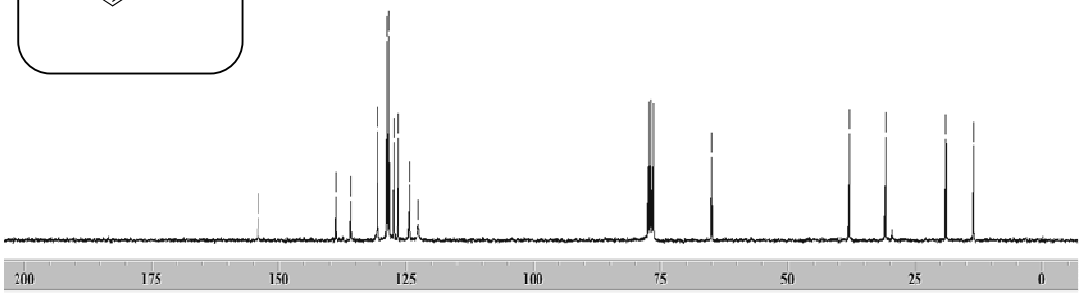

H
N
O
O
Ph

Table 2- 3g


4.5
4.2
0.9
0.9
2.1
2.1
2.2
2.0
3.0
9
8
7
6
5
4
3
2
1
0


54.105
38.892
35.956
30.390
28.788
28.419
27.492
26.359
24.424
22.639
65.091
88.050
30.882
18.995
13.689


H
N
O
O
Ph


200
175
150
125
100
75
50
25
0

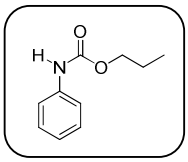
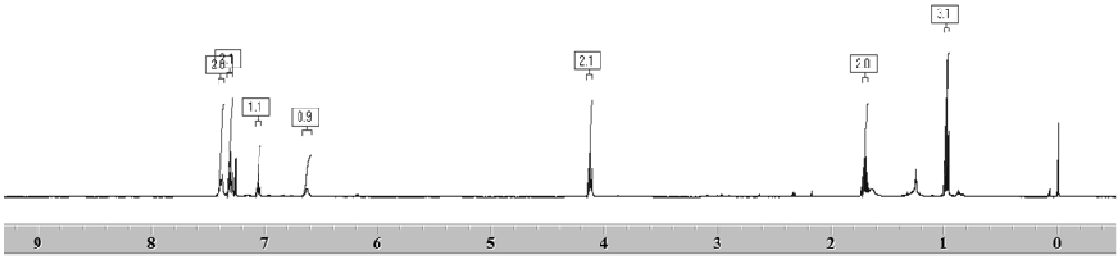


Table 2- 3h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2.1
2.0
3.1
9
8
7
6
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4
3
2
1
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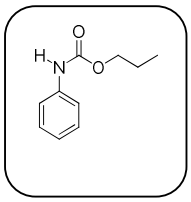


153.713
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118.587
66.825
21.238
10.316
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175
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100
75
50
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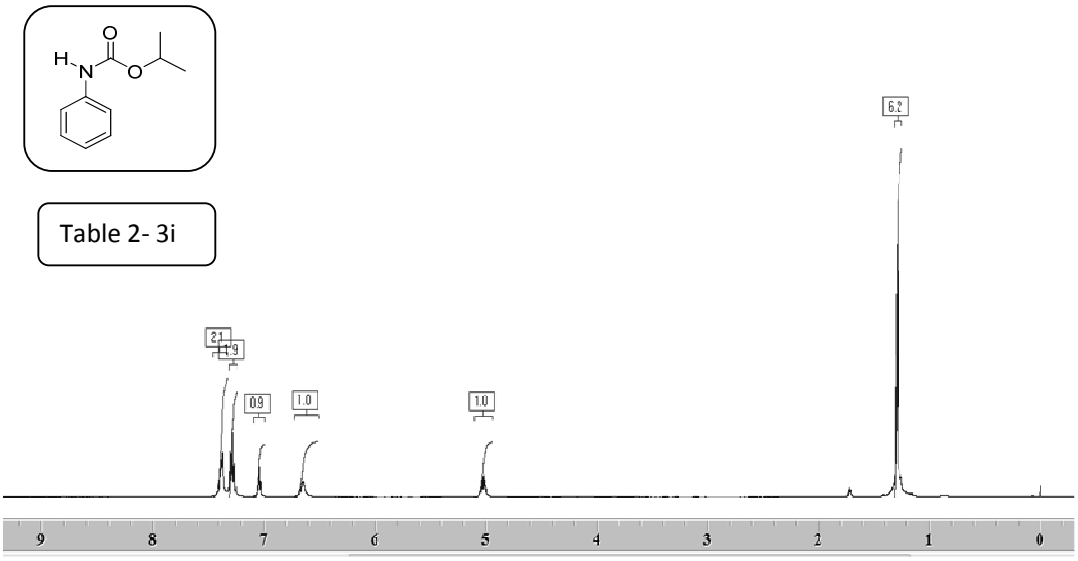
Table 2- 3i
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1.0
6.2
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8
7
6
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4
3
2
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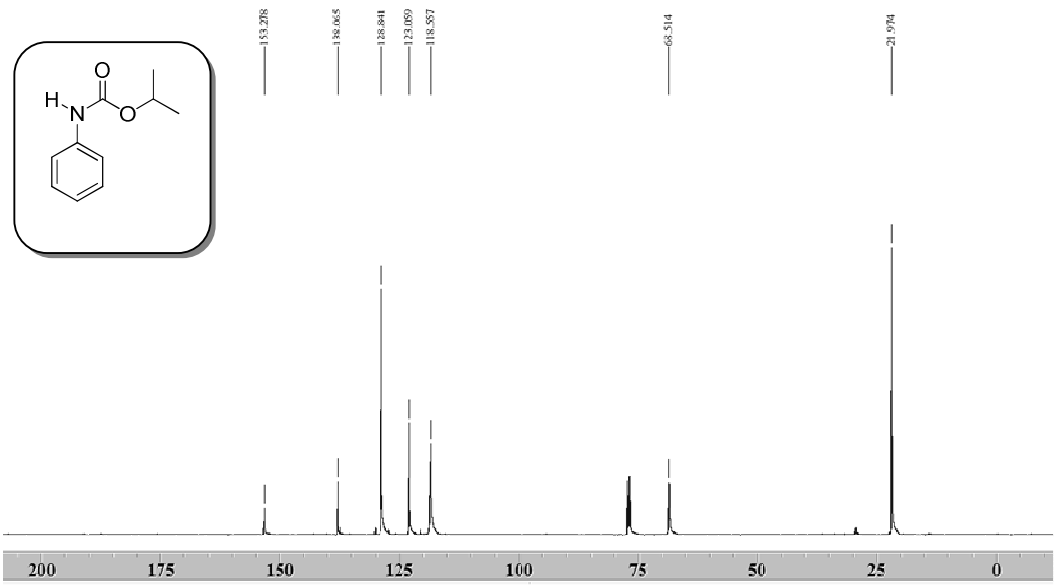
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123.069
118.557
63.514
21.974
200
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100
75
50
25
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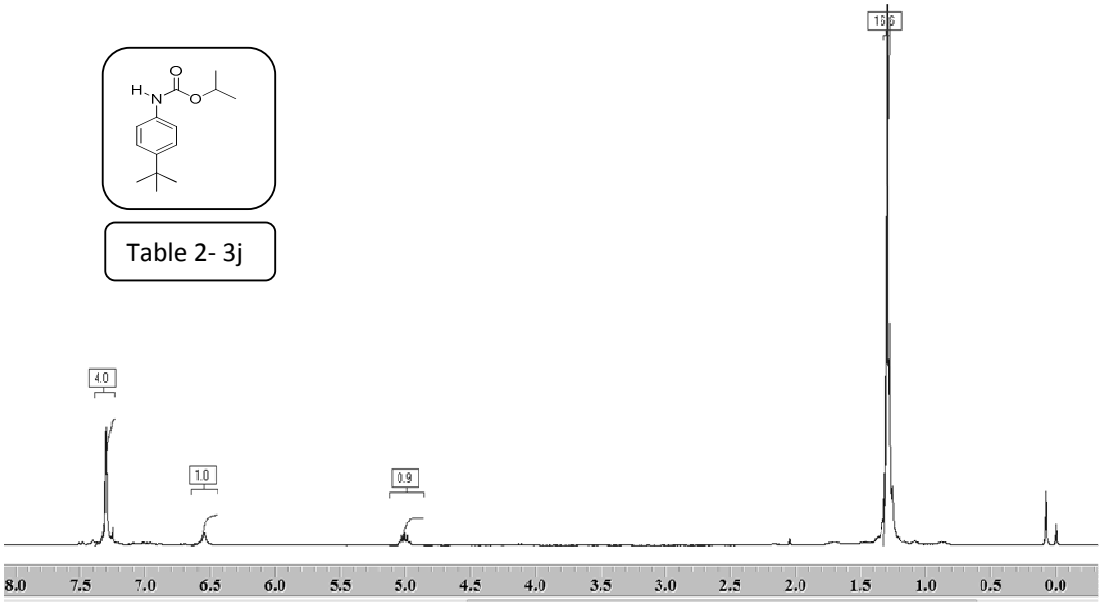
Table 2- 3j
4.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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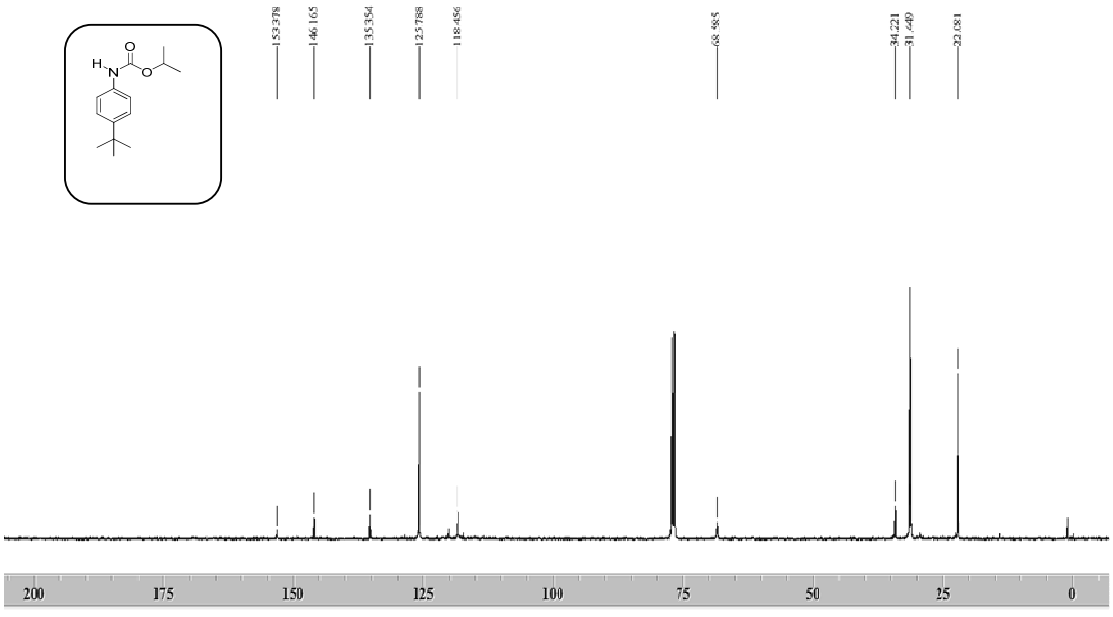
1.0
0.5
0.0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150
125
100
75
50
25
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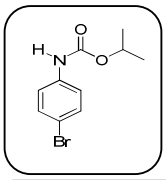

Table 2- 3k


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2.0
1.0
1.0
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8
7
6
5
4
3
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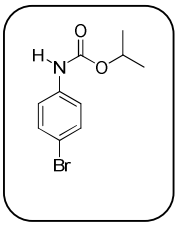
0




153.112
142.888
137.859
131.738
120.440
115.519
69.202
21.936
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175
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75
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25
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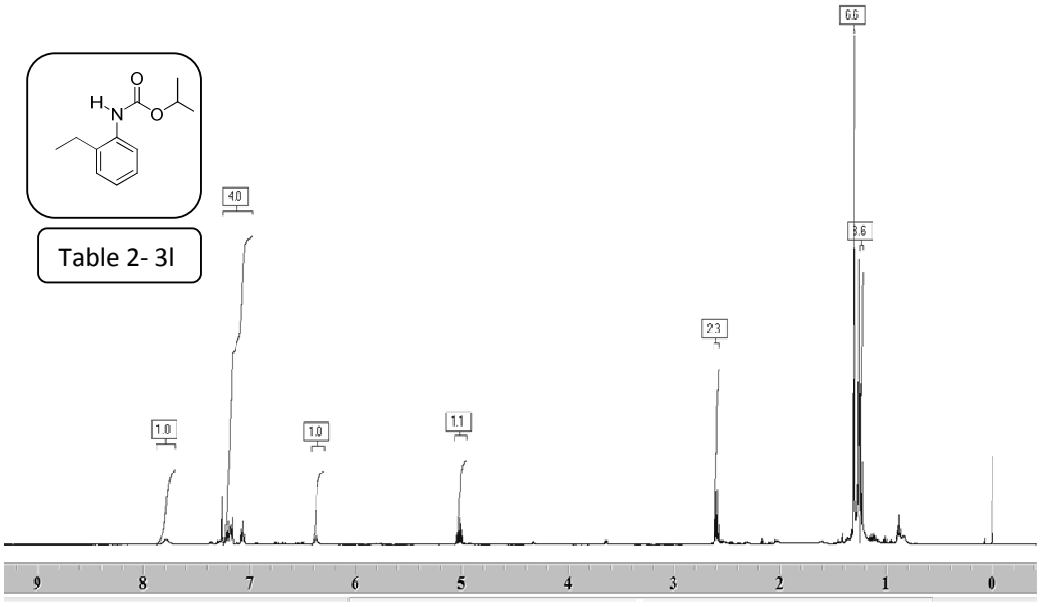
Table 2- 3l
6.6
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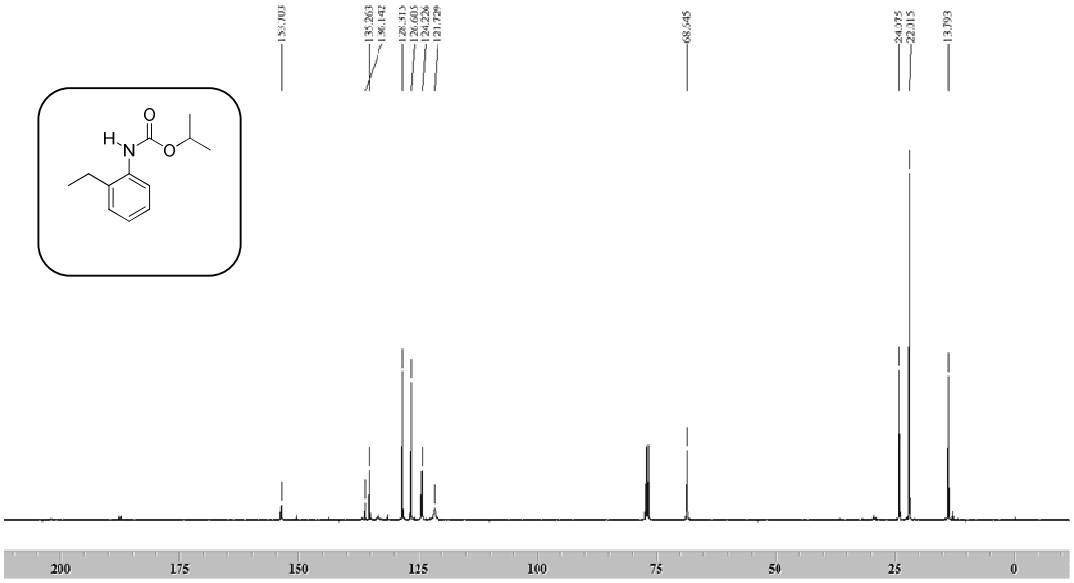
3.6
2.3
1.0
1.0
1.1
9
8
7
6
5
4
3
2
1
0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24.975
22.015
13.793
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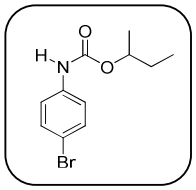
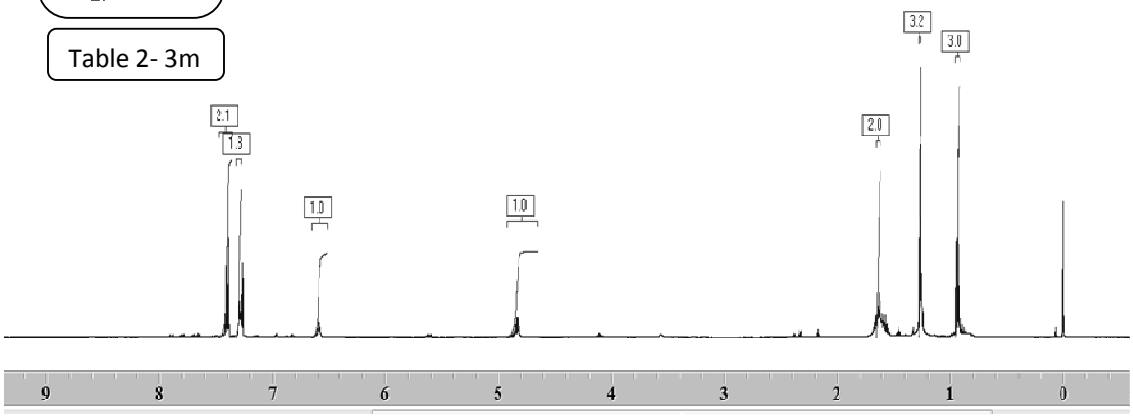
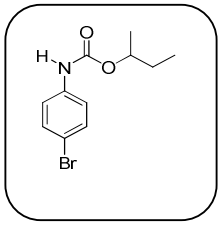


Table 2- 3m


2.1
1.3
1.0
1.0
2.0
3.2
3.0
9
8
7
6
5
4
3
2
1
0




153.223
137.212
131.832
120.862
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78.526
28.896
19.610
9.616
200
175
150
125
100
75
50
25
0

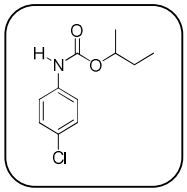
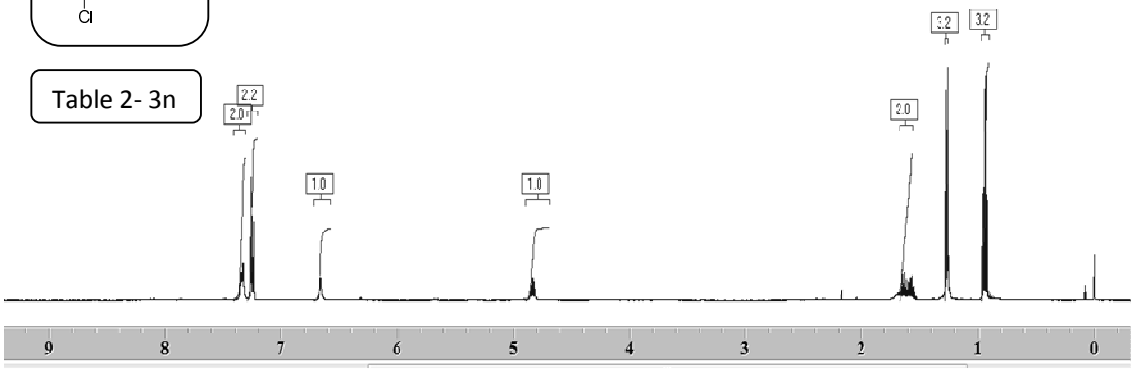


Table 2- 3n


2.2
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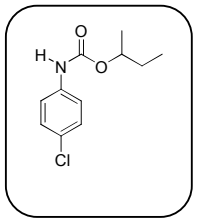
2.0
3.2
3.2
9
8
7
6
5
4
3
2
1
0




153.416
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119.918
73.332
28.863
19.555
9.544
200
175
150
125
100
75
50
25
0

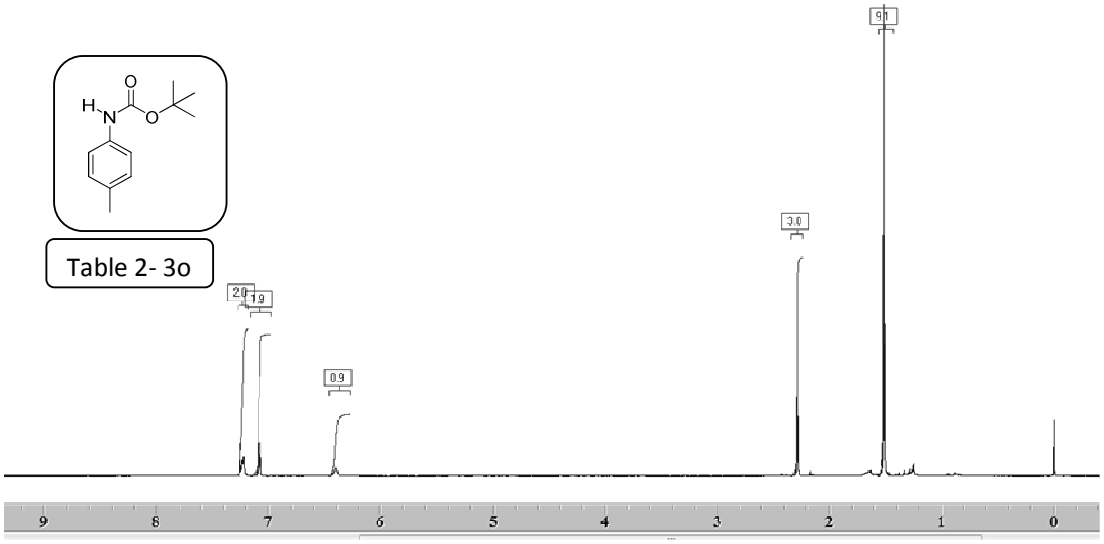
Table 2- 3o
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0.9
3.0
9.1
9
8
7
6
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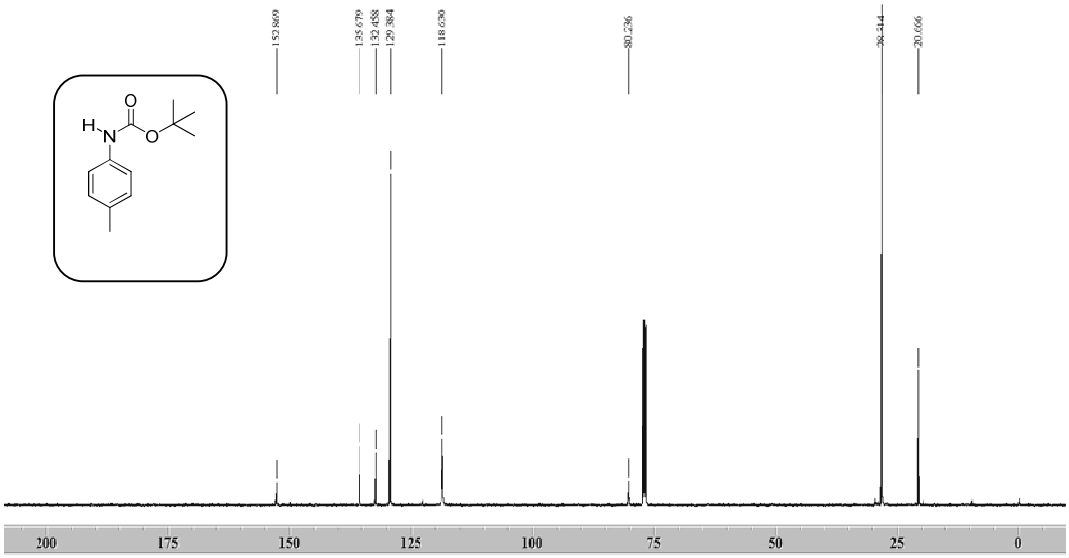
4
3
2
1
0


153.869
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129.384
118.650
80.236
28.414
20.066
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175
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100
75
50
25
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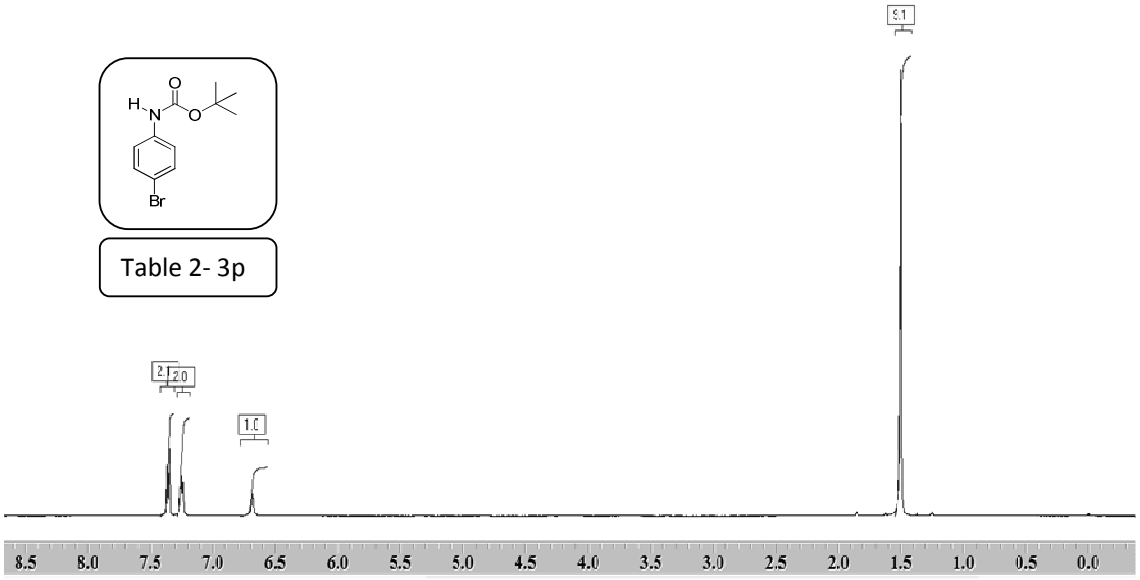
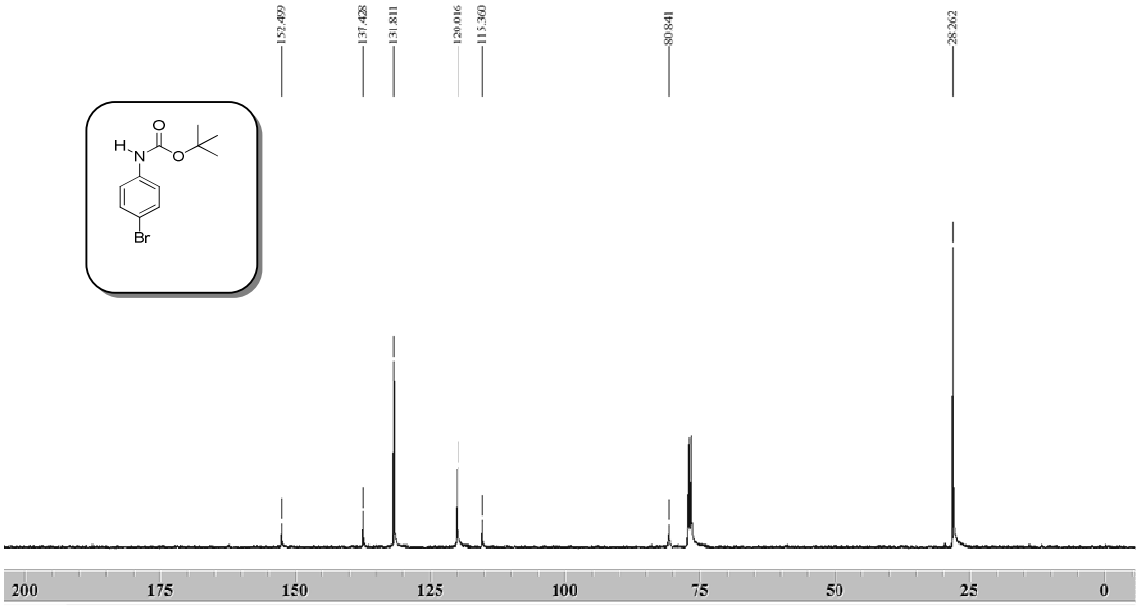


Table 2- 3p
9.1
2.20
1.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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120.016
115.300
80.841
28.262
200
175
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125
100
75
50
25
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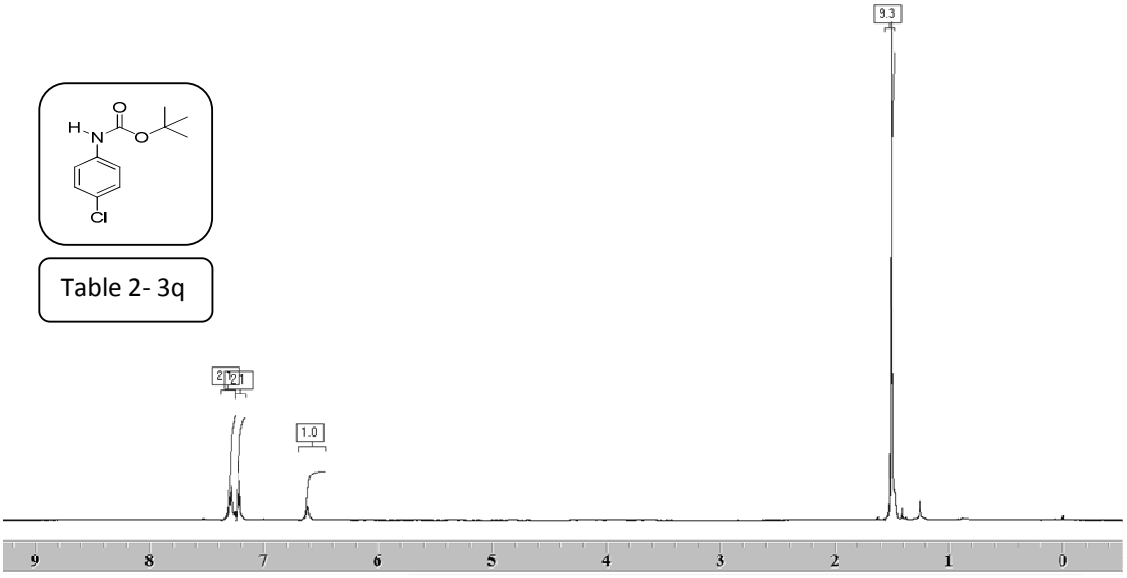
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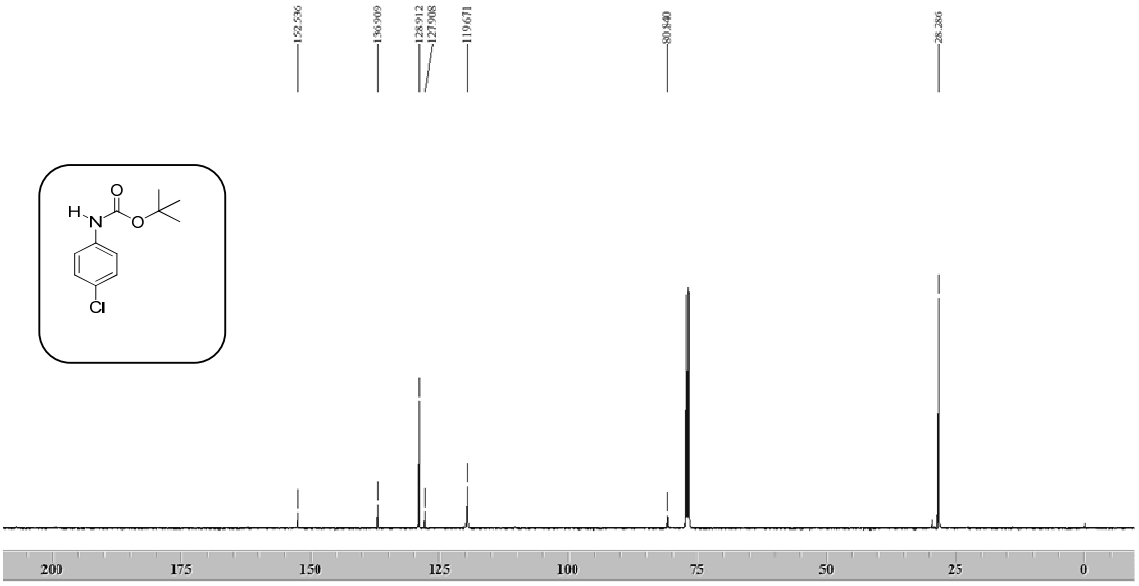
9.3
9
8
7
6
5
4
3
2
1
0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128.912
127.908
119.671
80.840
28.306
200
175
150
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75
50
25
0

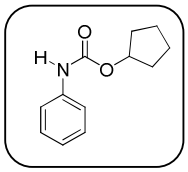
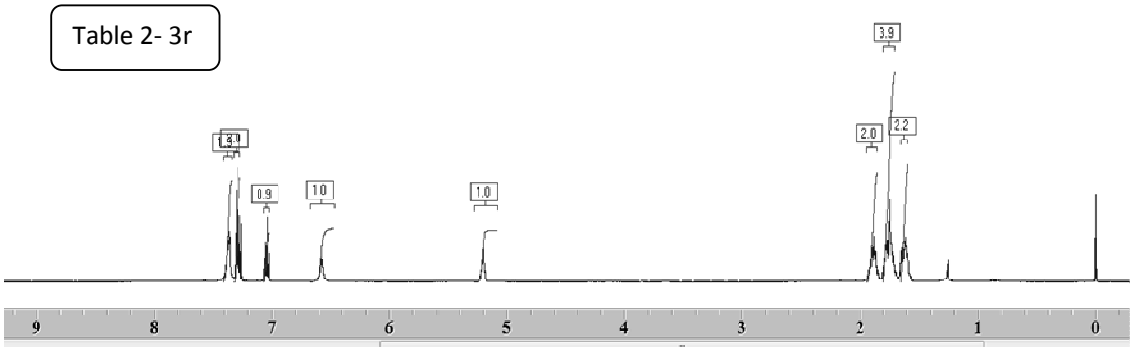
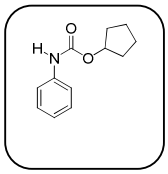


Table 2- 3r


3.9
3.9
2.0
2.2
0.9
1.0
1.0
9
8
7
6
5
4
3
2
1
0




153.4204
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78.1031
32.7946
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25
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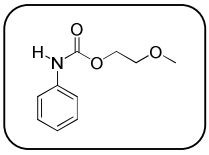
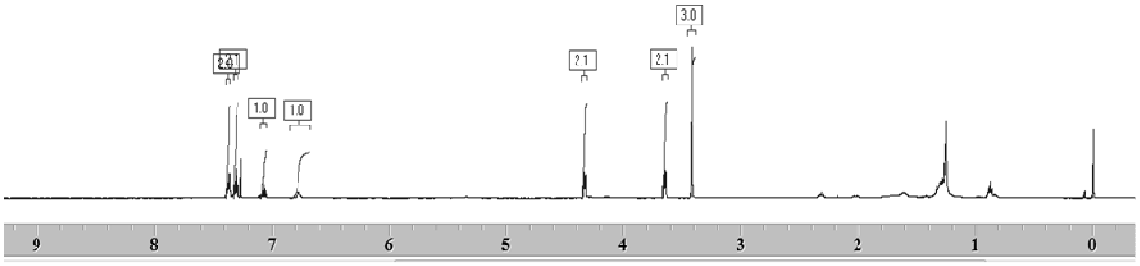


Table 2- 3s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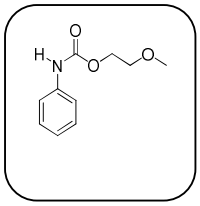
2.1
1.0
1.0
9
8
7
6
5
4
3
2
1
0




158.330
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64.045
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25
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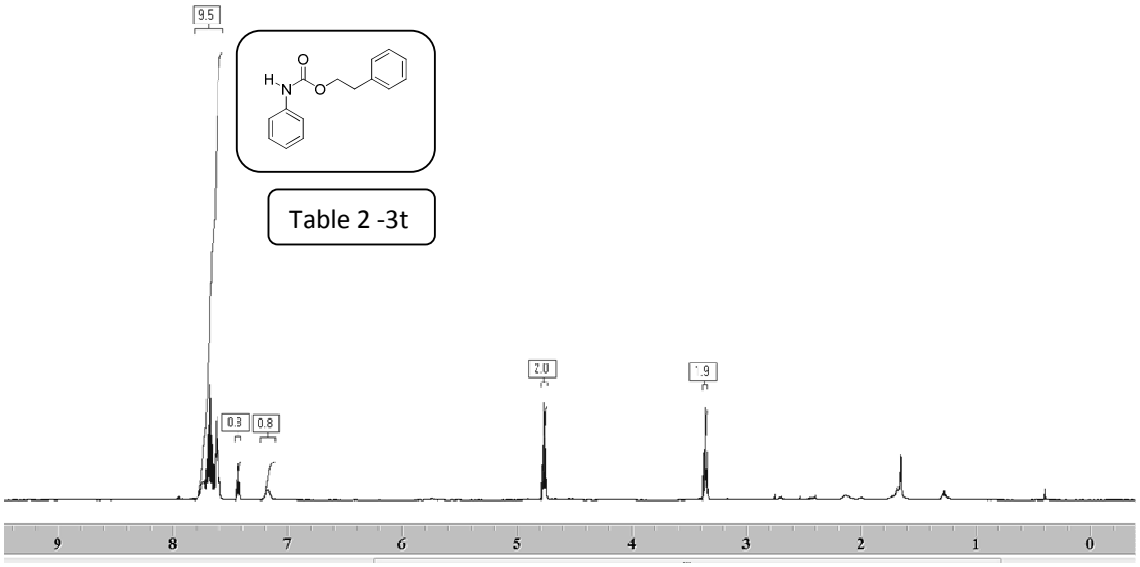
9.5
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2.0
1.9
Table 2 -3t
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8
7
6
5
4
3
2
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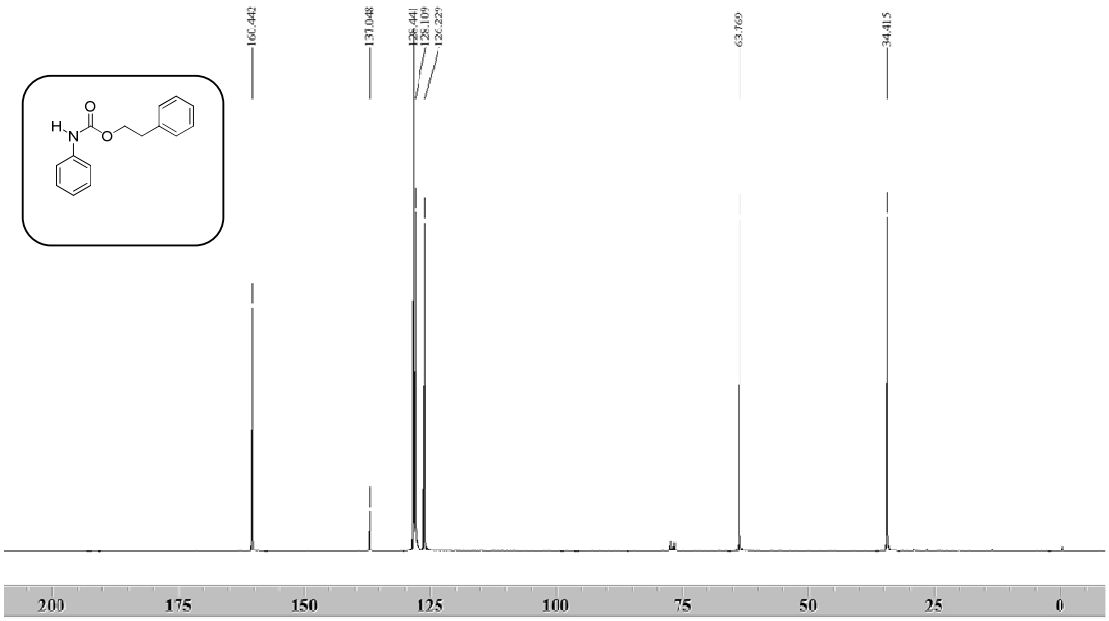
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128.109
126.229
63.769
34.415
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50
25
0

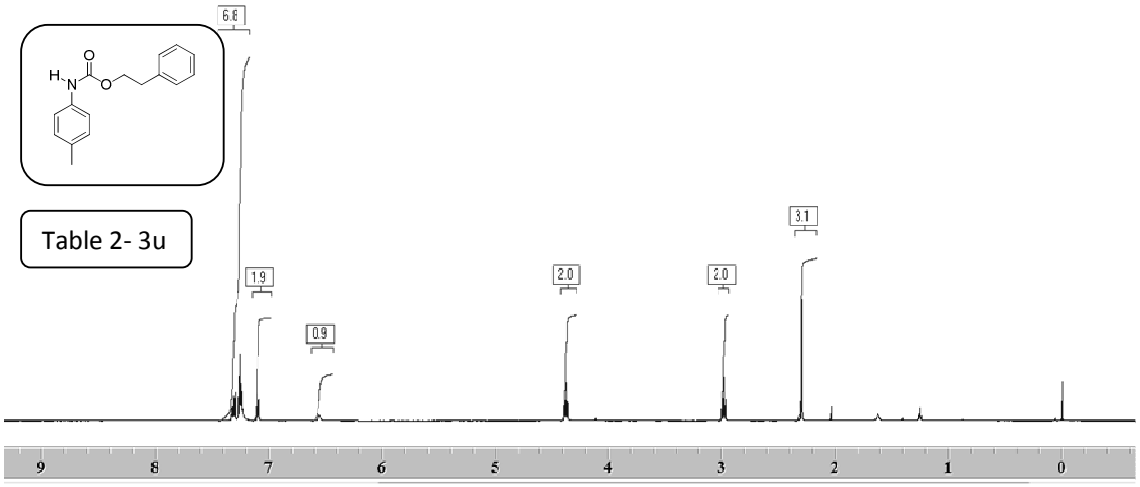
Table 2- 3u
6.8
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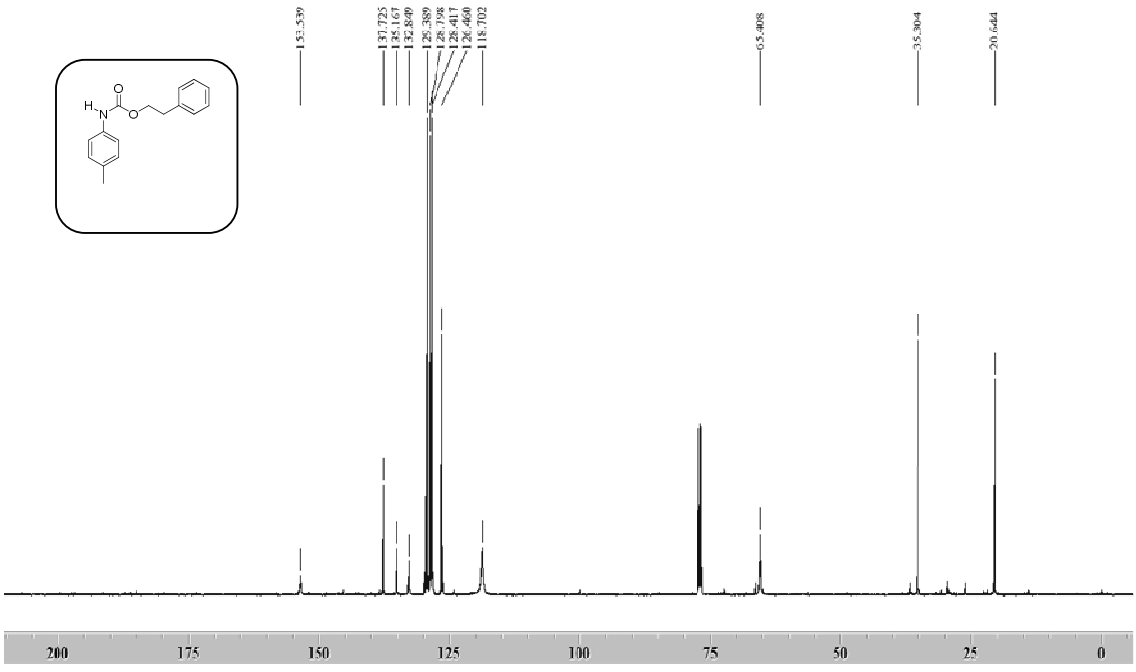
2.0
2.0
3.1
9
8
7
6
5
4
3
2
1
0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132.849
129.389
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50
25
0

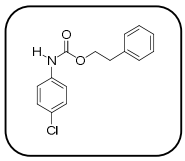
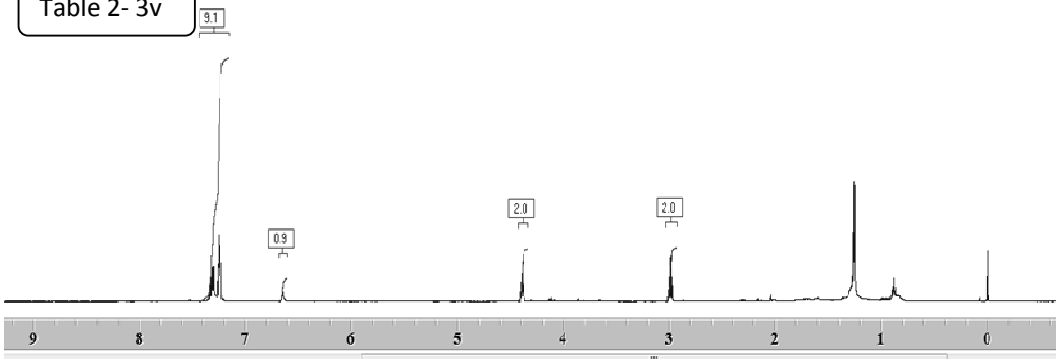


Table 2- 3v


9.1
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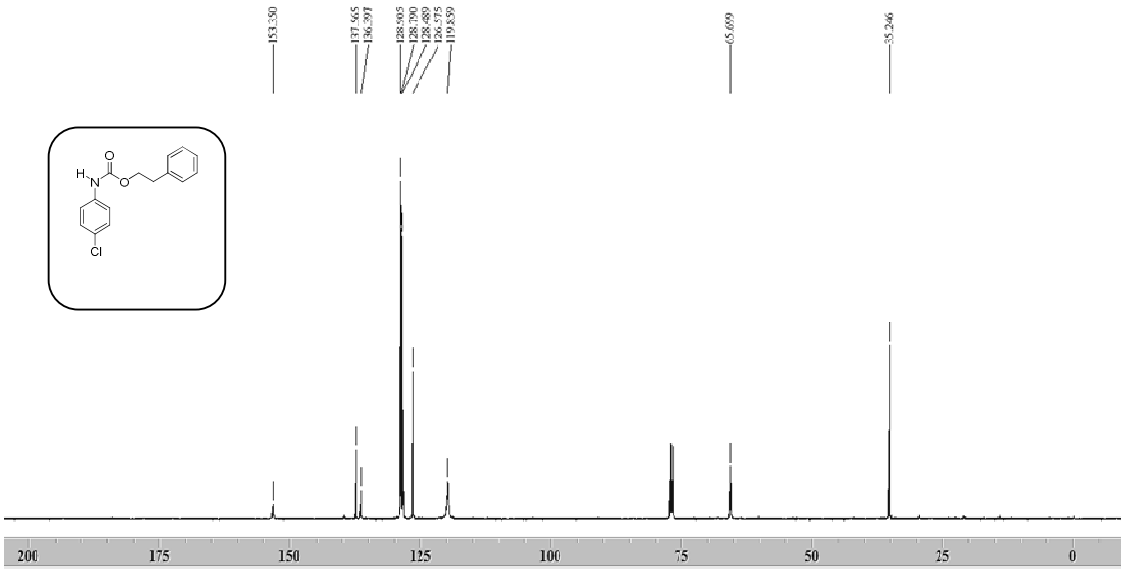
2.0
2.0
9
8
7
6
5
4
3
2
1
0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136.397
128.905
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128.489
126.595
119.839
65.659
35.246
200
175
150
125
100
75
50
25
0

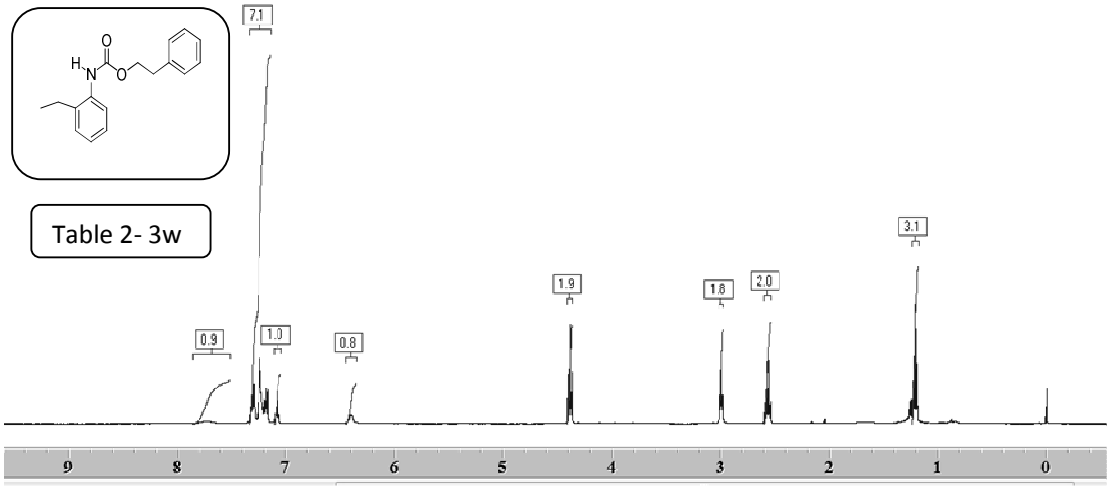
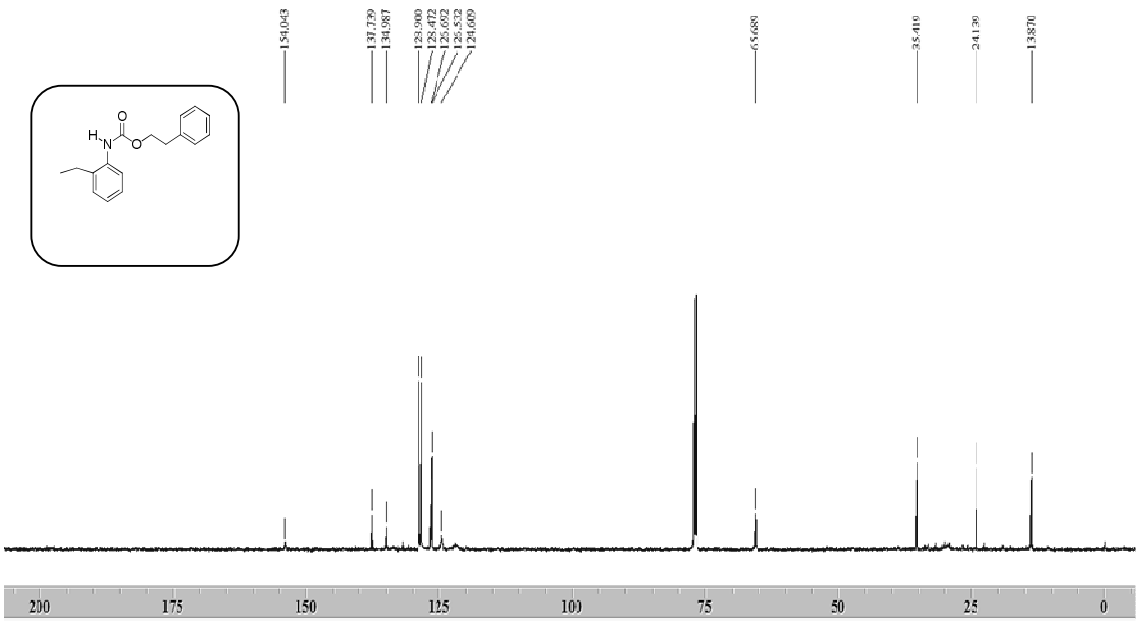

7.1
0.9
1.0
0.8
1.9
1.8
2.0
3.1
9
8
7
6
5
4
3
2
1
0

Table 2- 3w


154.043
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129.472
125.692
125.532
124.609
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35.410
24.139
13.870
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125
100
75
50
25
0

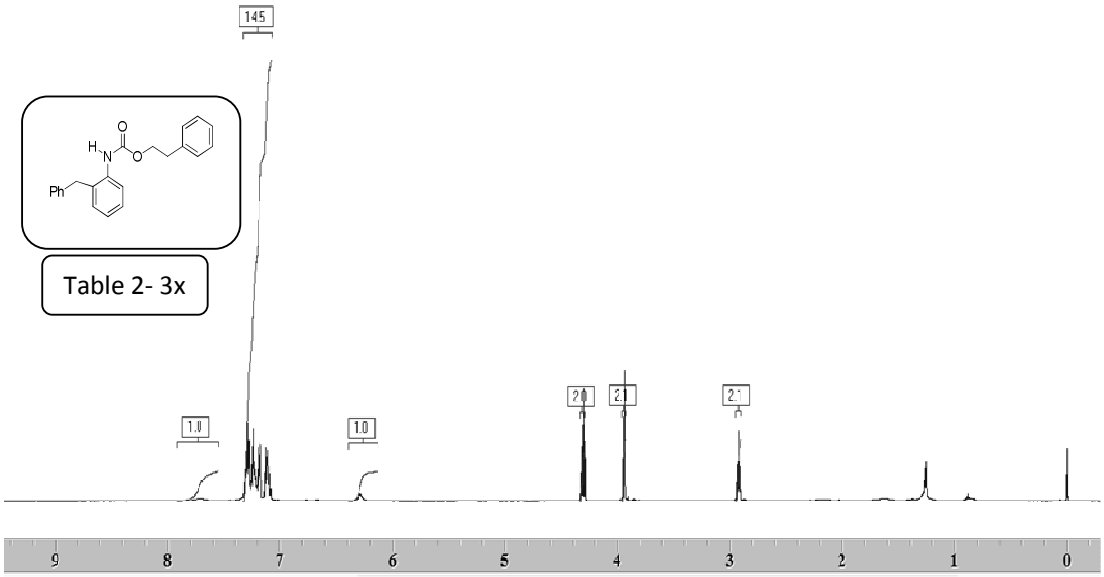
Table 2- 3x
Ph
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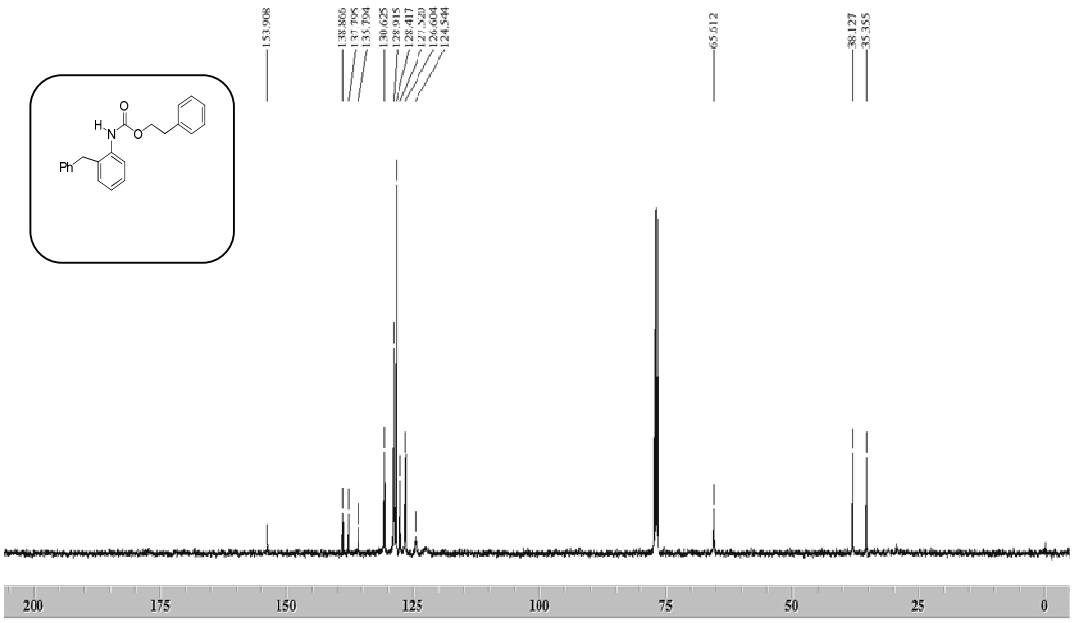
1.0
9
8
7
6
5
4
3
2
1
0


153.908
138.806
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133.794
130.625
128.915
128.417
127.230
126.604
124.594
65.612
38.127
35.355
Ph
200
175
150
125
100
75
50
25
0

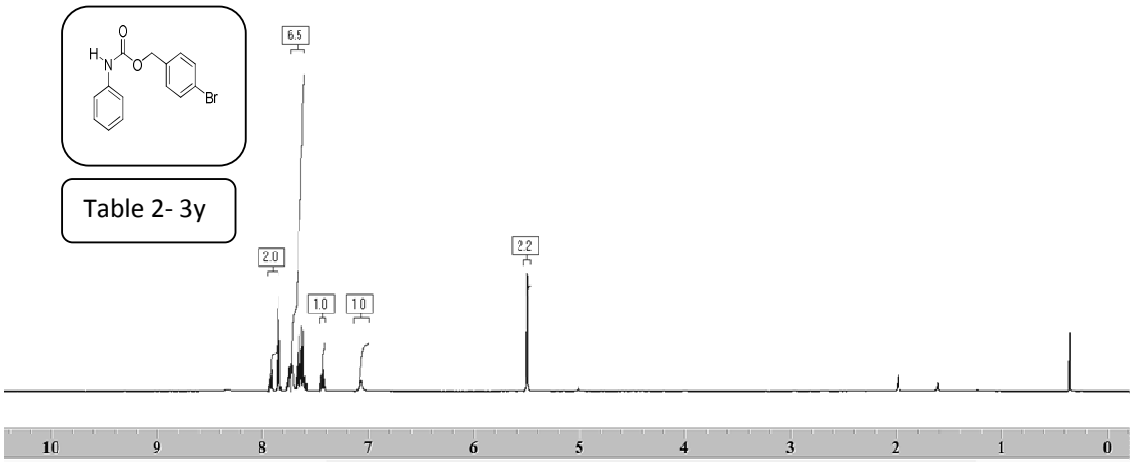
Table 2- 3y
6.5
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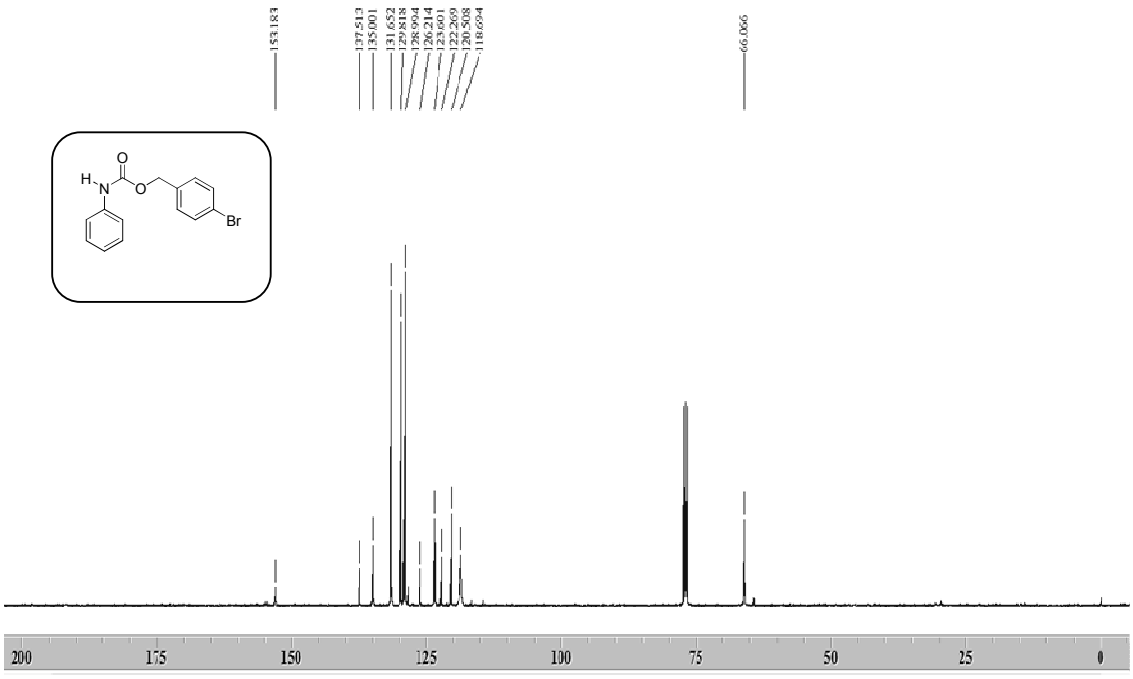
1.0
1.0
2.2
10
9
8
7
6
5
4
3
2
1
0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135.001
131.652
129.818
128.904
126.214
123.691
122.269
120.508
118.654
66.066
200
175
150
125
100
75
50
25
0

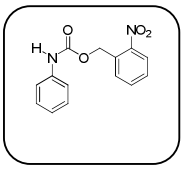
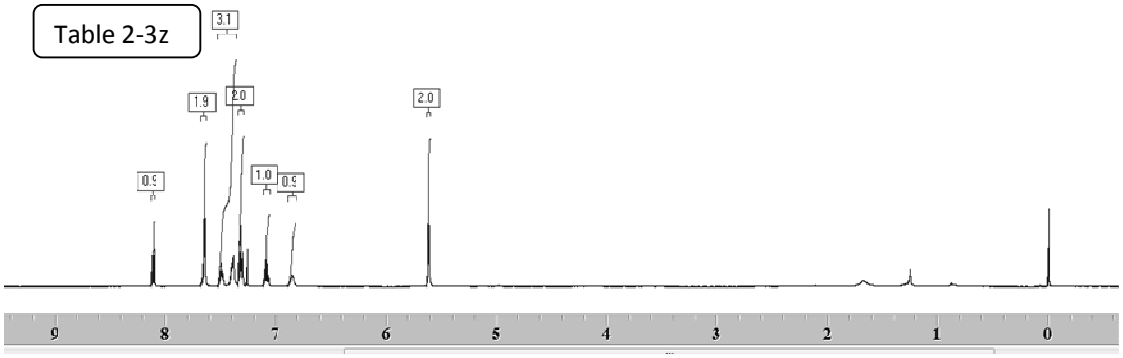
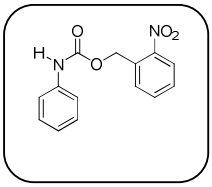


Table 2-3z

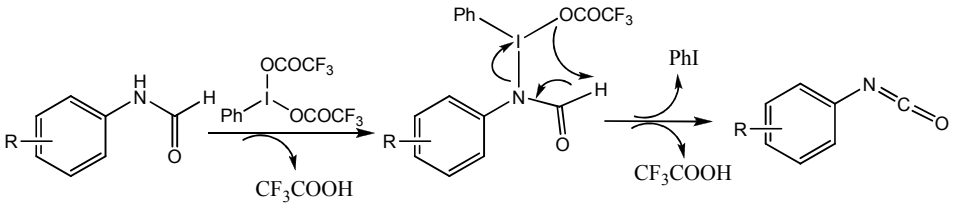

3.1
1.9
2.0
2.0
0.9
1.0
0.9
9
8
7
6
5
4
3
2
1
0




160.159
147.407
137.413
133.796
131.247
129.360
125.196
123.716
118.882
62.380
200
175
150
125
100
75
50
25
0

**Proposed Mechanism:**

A mechanism involving amidoiodanes are generally proposed for the Hoffman rearrangement of amides to isocyanates with hypervalent iodine reagents (ref: *J. Org. Chem.* 2012, **77**, 2087) and a similar mechanism as shown below may be possible with the formamides also.




**Observation of isocyanate formation by GC-MS:** GC-MS analysis of blank reaction mixture showing the formation of isocyanate. The starting N-phenyl formamide and iodobenzene are observed at 13.49 and 9.19 min respectively.