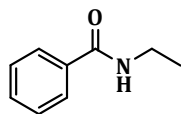


### 1. General procedure

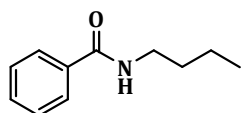
In a sealed tube, to hydrochloric salts of butylamine (1mmol),  $\text{CaCO}_3$  (2.2 equiv) and  $\text{Fe}_3\text{O}_4@\text{SiO}_2\text{-APTMS-Cu}$  (40 mg, 2mol%) in  $\text{CH}_3\text{CN/Toluene}$  (2 ml, in a ratio of 4/1 respectively), and 8equiv TBHP (70 wt % in  $\text{H}_2\text{O}$ ) and the mixture was stirred at  $80^\circ\text{C}$  under Ar balloon for 10 h. After end of the reaction and cooling to room temperature, 1N HCl (2.5 mL) and EtOAc (5 mL) was added. The mixture was extracted with EtOAc and the organic phase was washed with a saturated aqueous solution of  $\text{NaHCO}_3$  (5 mL), brine (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , After removal the solvent under vacuum, survived the crude product, then purified by column chromatography to afford the desired product.



Compound **1b** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 52 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.78-7.74 (m, 2H), 7.53-7.39 (m, 3H), 6.12-6.11 (br s, 1H), 3.56-3.45 (q, 2H,  $J$  = 6.7 Hz), 1.29-1.23 (t, 3H,  $J$  = 7.1 Hz).

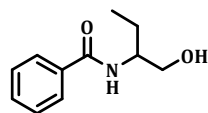
Analytical data was similar to those previously reported. <sup>[2]</sup>



Compound **1c** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 80 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.99-8.00 (m, 2H), 7.43-7.20 (m, 3H), 6.32 (br s, 1H), 3.40-3.42 (q, 2H,  $J$  = 6.8 Hz), 1.57-1.46 (m, 2H), 1.37-1.28 (m, 2H), 0.90-0.84 (t, 3H,  $J$  = 7.0 Hz).

Analytical data was similar to those previously reported. <sup>[3]</sup>

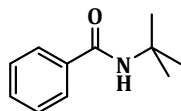


Compound **1d** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 67 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.71-7.69 (m, 2H), 7.42-7.32 (m, 3H), 6.35 (s, 1H), 3.99 (br s, 1H), 3.73-3.60 (dd, 2H,  $J$  = 10.8, 2.6 Hz), 2.95-2.97 (br s, 1H), 1.51-1.67 (m, 2H), 0.95-0.93 (t, 3H,  $J$  = 7.0 Hz).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 168.3, 134.4, 131.6, 128.6, 127.0, 65.2, 53.7, 24.3, 10.7.

Analytical data was similar to those previously reported. <sup>[4]</sup>

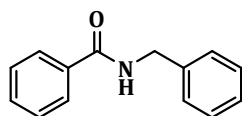


Compound **1e** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 56 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.80-7.90 (m, 2H), 7.50-7.35 (m, 3H), 6.12 (br s, 1H), 1.40 (s, 9H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 167.7, 136.0, 131.2, 128.6, 126.8, 51.8, 29.00.

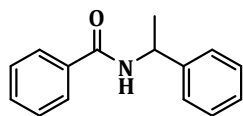
Analytical data was similar to those previously reported. <sup>[3]</sup>



Compound **1f** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 84 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.81-7.66 (m, 2H), 7.51-7.26 (m, 8H), 6.39 (br s, 1H), 4.67-4.65 (d, 2H,  $J$  = 5.5 Hz).

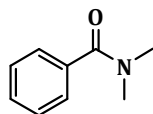
Analytical data was similar to those previously reported. <sup>[5]</sup>



Compound **1g** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 80 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) 7.80-7.78 (m, 2H), 7.54-7.30 (m, 8H), 6.34 (d,  $J$  = 7.0 Hz, 1H), 5.37 (q,  $J$  = 7.2 Hz, 1H), 1.64 (d,  $J$  = 7.1 Hz, 3H).

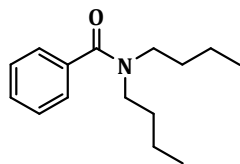
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 166.6, 143.2, 134.6, 131.5, 128.7, 128.6, 127.4, 126.9, 126.3, 49.3, 21.8.  
Analytical data was similar to those previously reported.<sup>[6]</sup>



Compound **1i** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 67 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.39-7.26 (m, 5H), 2.97 (s, 3H), 3.09 (s, 3H).

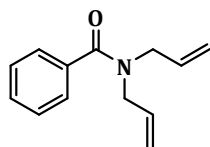
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 171.7, 136.5, 129.7, 128.5, 127.2, 39.7, 35.47.  
Analytical data was similar to those previously reported.<sup>[7]</sup>



Compound **1j** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give a 43 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.73-7.28 (m, 5H), 3.47 (m, 2H), 3.18 (m, 2H), 1.62-1.61 (m, 2H), 1.47-1.39 (m, 2H), 1.14-0.97 (m, 4H), 0.99-0.97 (m, 3H), 0.80-0.77 (m, 3H).

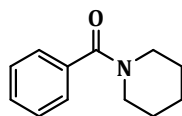
Analytical data was similar to those previously reported.<sup>[8]</sup>



Compound **1m** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 69 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.44-7.38 (s, 5H), 5.90 (br s, 1H), 5.74 (br s, 1H), 5.26-5.18 (s, 4H), 4.15 (s, 2H), 3.84 (s, 2H).

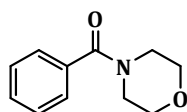
**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 171.8, 136.3, 133.2, 132.8, 129.6, 128.4, 126.6, 117.6, 50.7, 46.92.  
Analytical data was similar to those previously reported.<sup>[4]</sup>



Compound **1k** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 72 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.39 (s, 5H), 3.71 (s, 2H), 3.49 (s, 2H), 1.41-1.68 (m, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 170.3, 136.5, 129.5, 128.5, 126.9, 48.8, 43.2, 26.7, 25.8, 24.8.  
Analytical data was similar to those previously reported.<sup>[5]</sup>

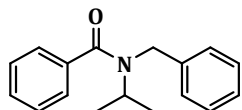


Compound **1l** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 81 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):** δ (ppm) = 7.40 (s, 5H), 3.70 (br s, 2H), 3.46 (br s, 2H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ (ppm) = 170.5, 135.4, 130.0, 128.7, 127.2, 67.0.

Analytical data was similar to those previously reported.<sup>[3]</sup>

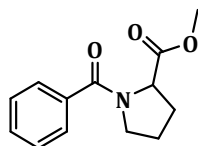


Compound **1n** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give a 45 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):** δ (ppm) = 7.44 (m, 5H), 7.36-7.24 (m, 5H), 4.7 (br s, 2H), 4.15 (br s, 1H), 1.11 (s, 6H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ (ppm) = 166.6, 143.1, 134.6, 131.5, 128.8, 128.6, 127.5, 127.0, 126.3, 49.2, 21.7.

Analytical data was similar to those previously reported.<sup>[4]</sup>

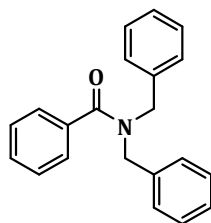


Compound **1o** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 78 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):** δ (ppm) = 7.57-7.54 (m, 2H), 7.44-7.35 (m, 3H), 4.68-4.54 (dd, 1H (79%), *J* = 7.5, 4.4 Hz), 4.32 (d, 1H (21%), *J* = 8.5 Hz), 3.79-3.68 (s, 3H (78%)), 3.54-3.52 (s, 3H (20%)), 3.68-3.42 (m, 2H), 2.32-2.27 (m, 1H), 2.05-1.85 (m, 3H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ (ppm) = 172.9, 169.8, 136.3, 130.3, 128.3, 127.4, 59.2, 52.4, 50.0, 29.5, 25.5.

Analytical data was similar to those previously reported.<sup>[6]</sup>

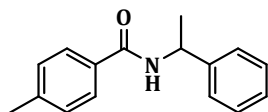


Compound **1p** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 60 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):** δ (ppm) = 7.52-7.27(m, 7H), 7.16 (s, 1H), 4.71 (s, 2H), 4.41 (s, 2H).

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz):** δ (ppm) = 172.3, 136.9, 136.4, 136.2, 129.7, 128.8, 128.6, 128.4, 127.6, 127.0, 51.5, 46.9.

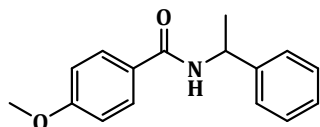
Analytical data was similar to those previously reported.<sup>[6]</sup>



Compound **1v** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 73 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.78-7.75 (d, 2H,  $J$  = 8.3 Hz), 7.46-7.26 (m, 9H), 6.30 (d, 1H,  $J$  = 6.8 Hz), 5.37-5.31 (m, 1H), 2.40 (s, 3H), 1.63-1.60 (d, 3H,  $J$  = 7.1 Hz).

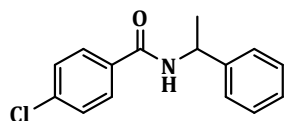
Analytical data was similar to those previously reported. <sup>[6]</sup>



Compound **1w** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 87 % yield.

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.76-7.72 (d, 2H,  $J$  = 9 Hz), 7.38-7.26 (m, 6H), 6.93-6.89 (m, 2H), 6.23 (d, 1H,  $J$  = 7.3 Hz), 5.36-5.30 (p, 1H,  $J$  = 6.9 Hz), 3.84 (s, 3H), 1.61-1.59 (d, 3H,  $J$  = 6.8 Hz).

Analytical data was similar to those previously reported. <sup>[6]</sup>



Compound **1x** was prepared according to the general procedure and purified by column chromatography (n-Hexane: EtOAc= 4:1) to give 75 % yield.

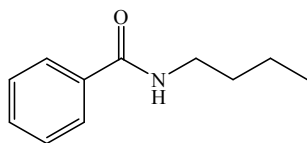
**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):**  $\delta$  (ppm) = 7.72-7.68 (dd, 2H,  $J$  = 8.0, 1.1 Hz), 7.39-7.26 (m, 7H), 6.38-6.40 (br s, 1H), 5.33-5.28 (p, 1H,  $J$  = 6.8 Hz), 1.62-1.58 (d, 3H,  $J$  = 7).

Analytical data was similar to those previously reported. <sup>[6]</sup>

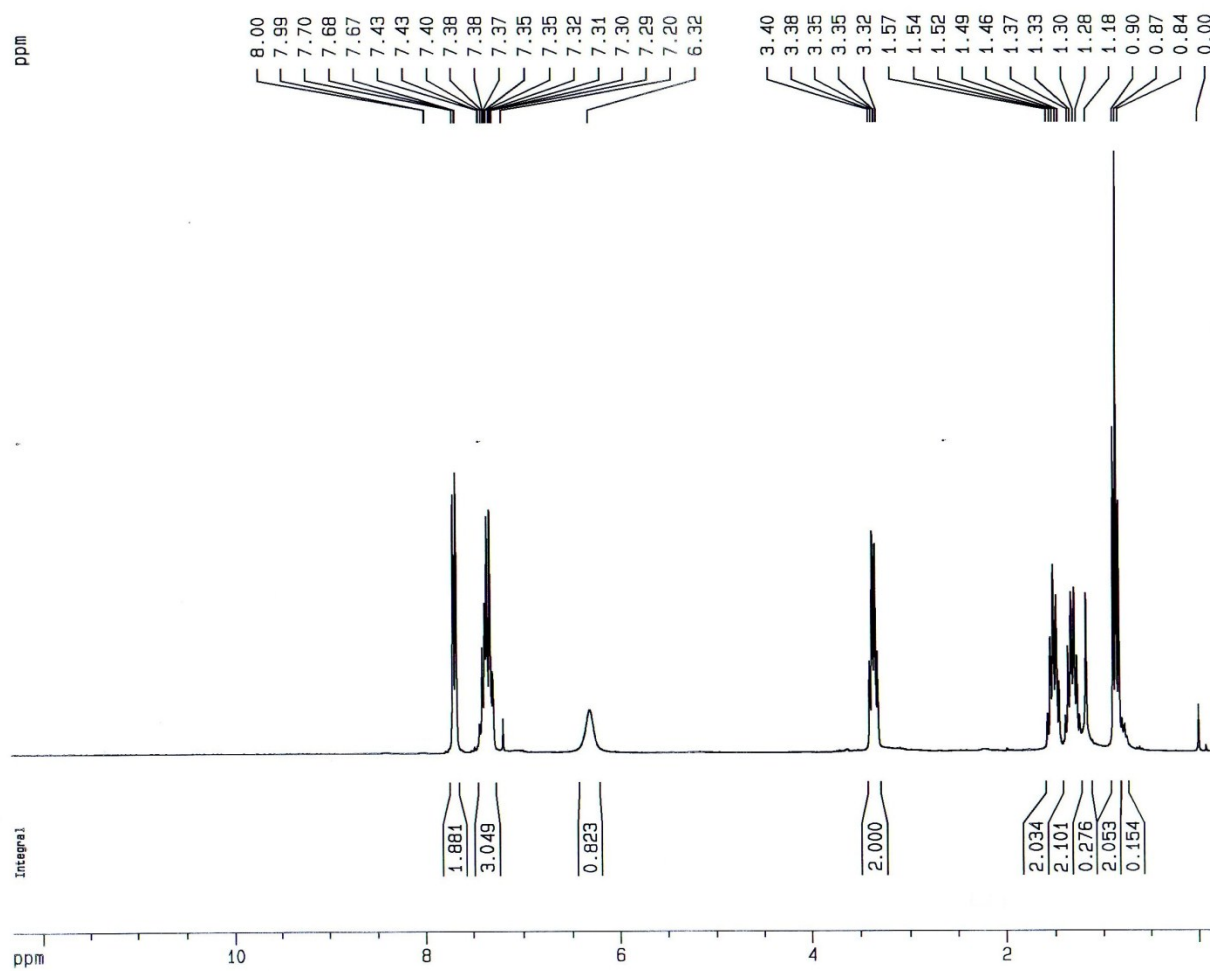
## References

- [1] Y. Wang, K. Yamaguchi, Mizuno, N. *Angew. Chem. Int. Ed.*, **2012**, 51, 1 – 5.
- [2] W. Yoo, C. Li, *J. Am. Chem. Soc.* **2006**, 128, 13064-13065.
- [3] X. Wu, M. Sharif, A. Pews-Davtyan, P. Langer, K. Ayub, M. Beller, *Eur. J. Org. Chem.* **2013**, 2783–2787.
- [4] D. Saberi, A. Heydari, *Appl. Organometal. Chem.* **2014**, 28, 101-108.
- [5] S. Ch. Ghosh, S. Muthaiah, Y. Zhang, X. Xu, S. H. Hong, *Adv. Synth. Catal.* **2009**, 351, 2643 – 2649.
- [6] X. Bantreil, C. Fleith, J. Martinez, F. Lamaty, *ChemCatChem*. **2012**, 41, 922-925.
- [7] K. Xu, Y. Hu, S. Zhang, Zh. Zha, .Zh. Wang, *Chem. Eur. J.* **2012**, 18, 9793-9797.
- [8] S. Wang, J. Wang, R. Guo, G. Wang, Sh. Chen, X. Yu, *Tet. Lett.* **2013**, 54, 6233–6236.

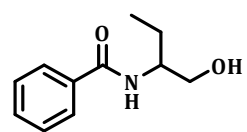
1b)



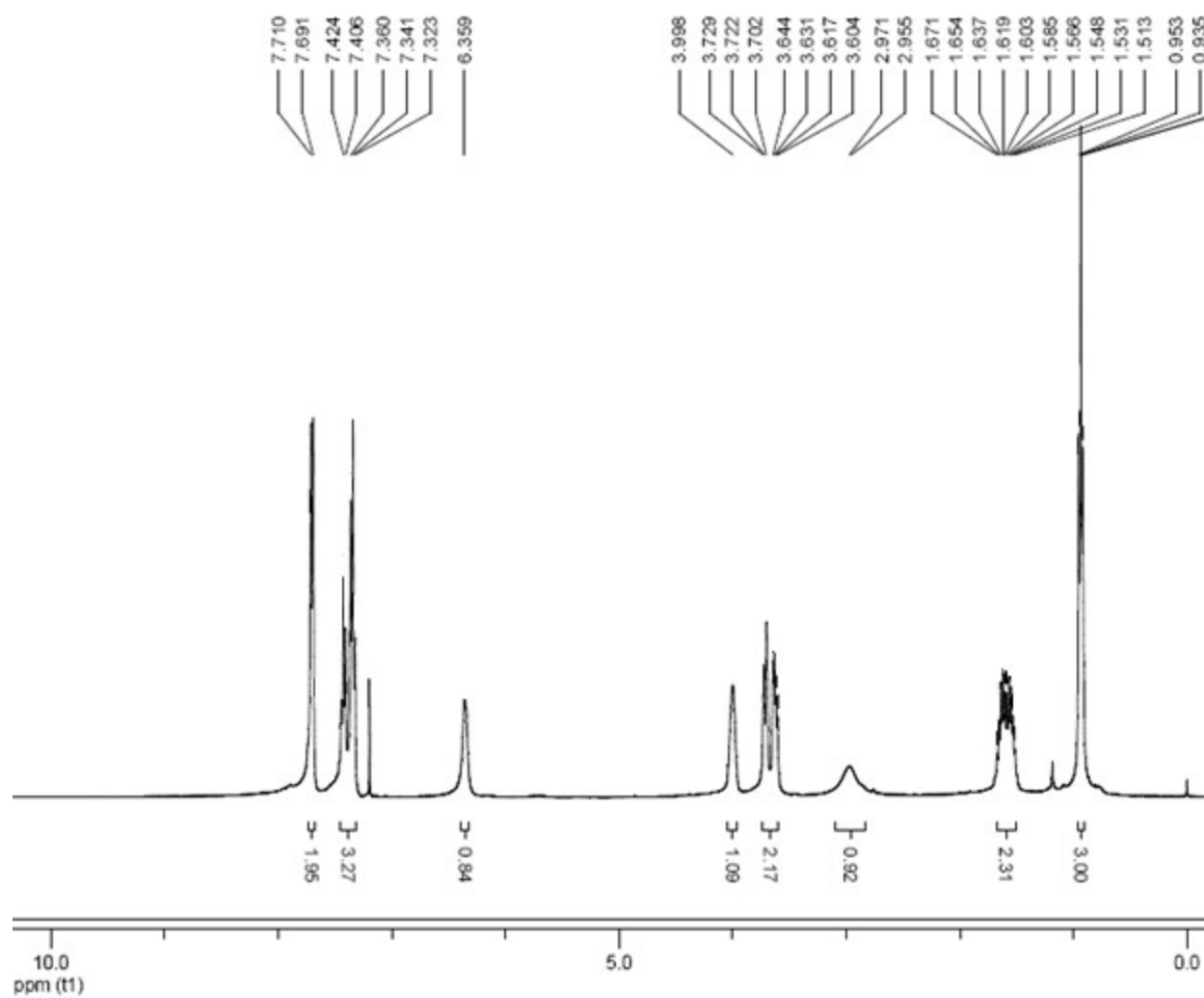
(<sup>1</sup>H-NMR)



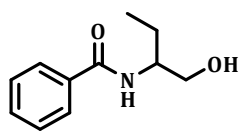
1c)



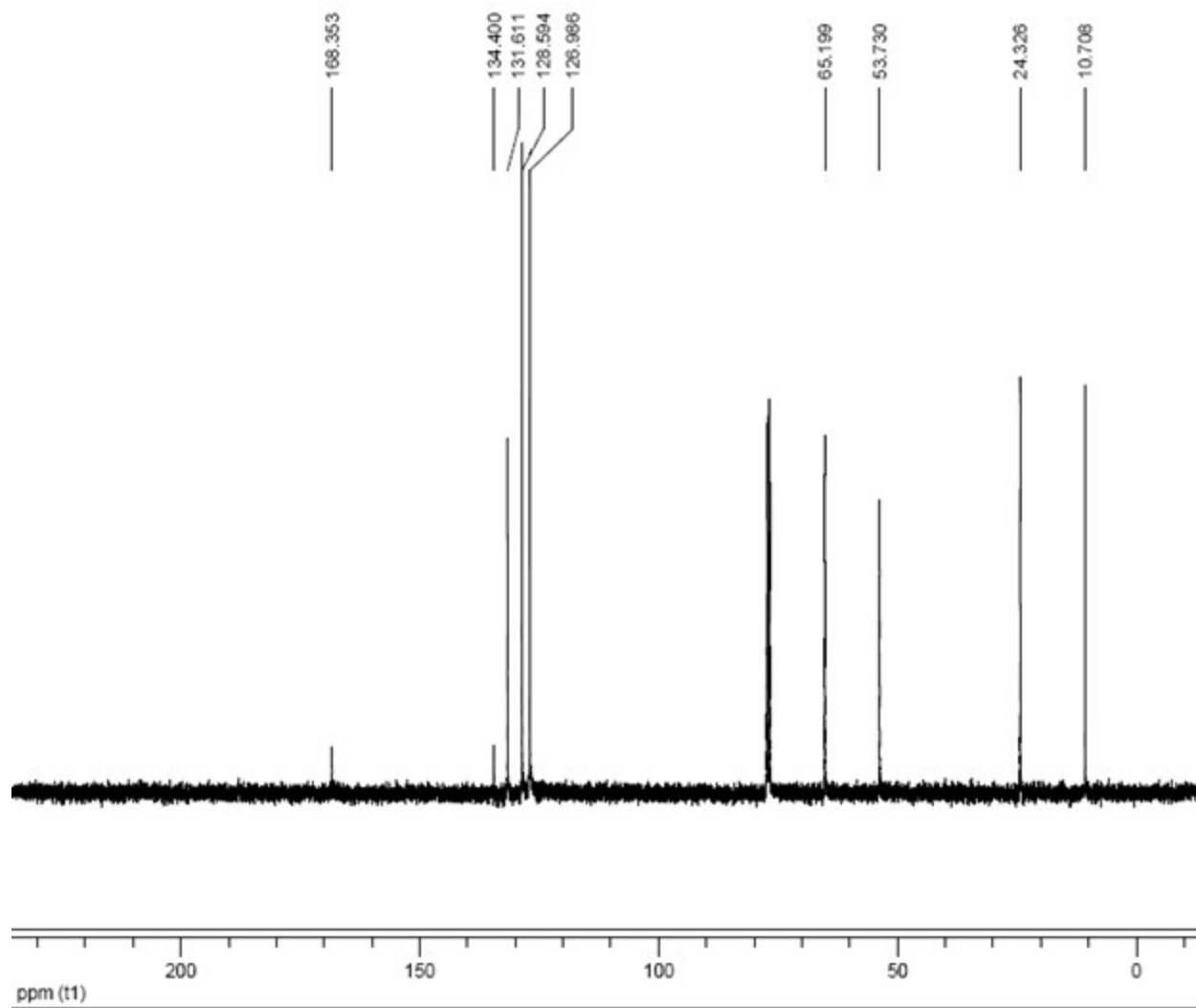
(<sup>1</sup>H-NMR)



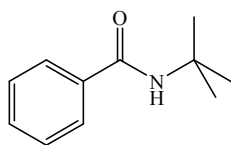
1c)



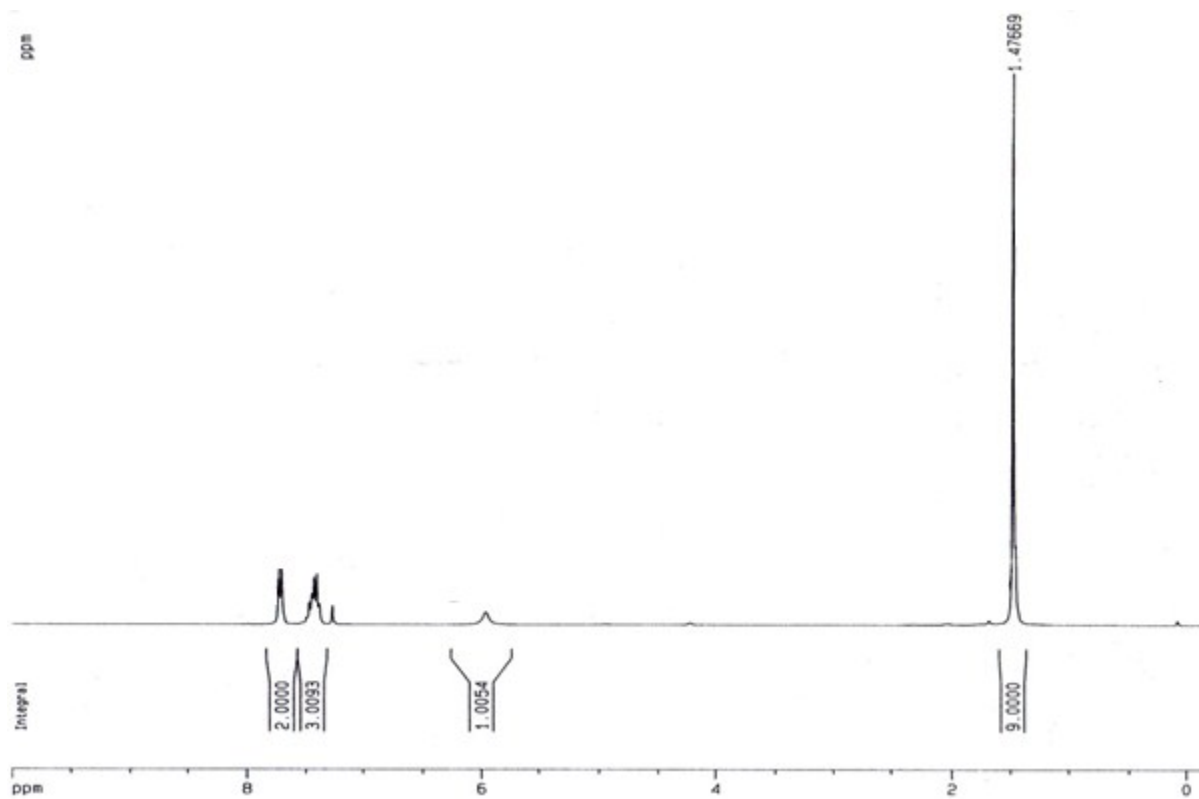
(<sup>13</sup>C-NMR)



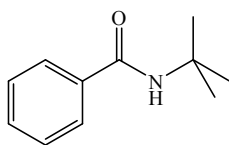
1d)



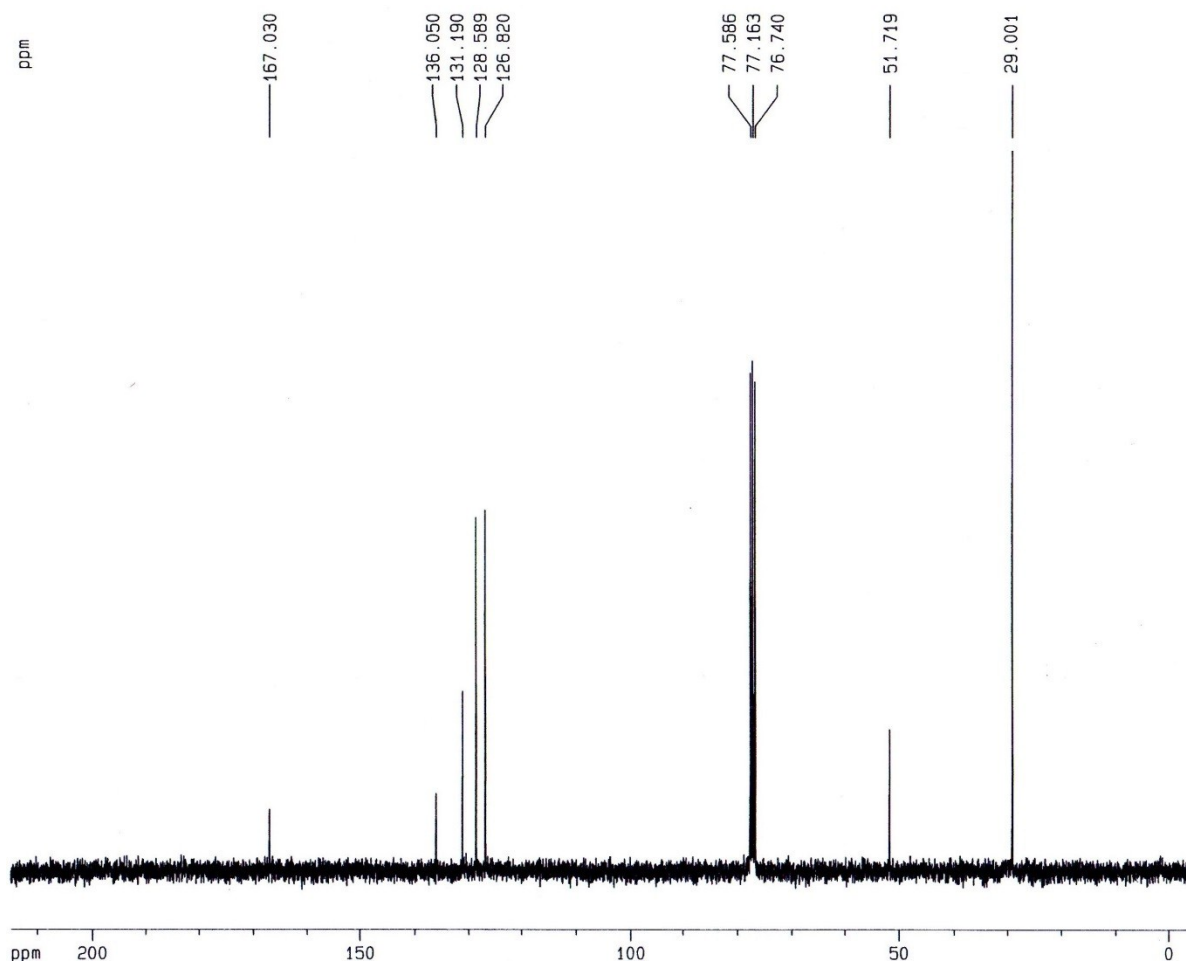
(<sup>1</sup>H-NMR)



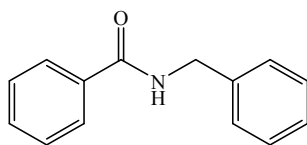
1d)



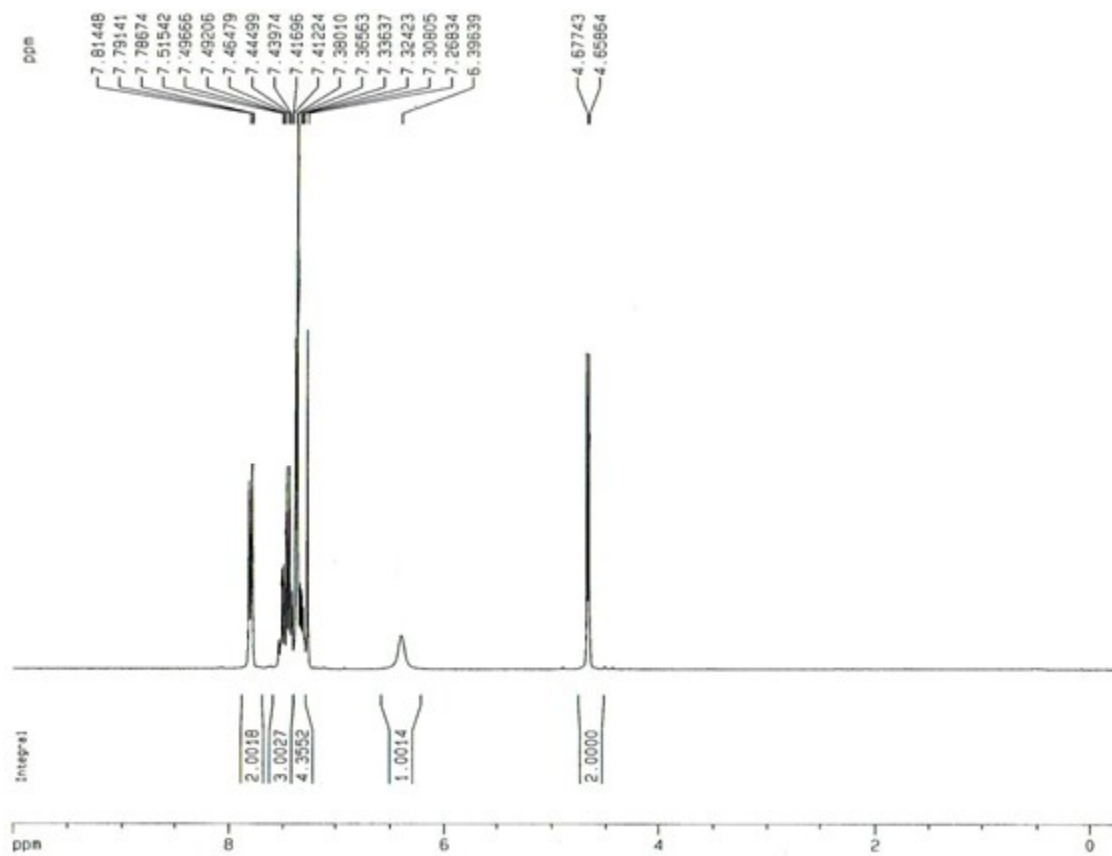
( $^{13}\text{C}$ -NMR)




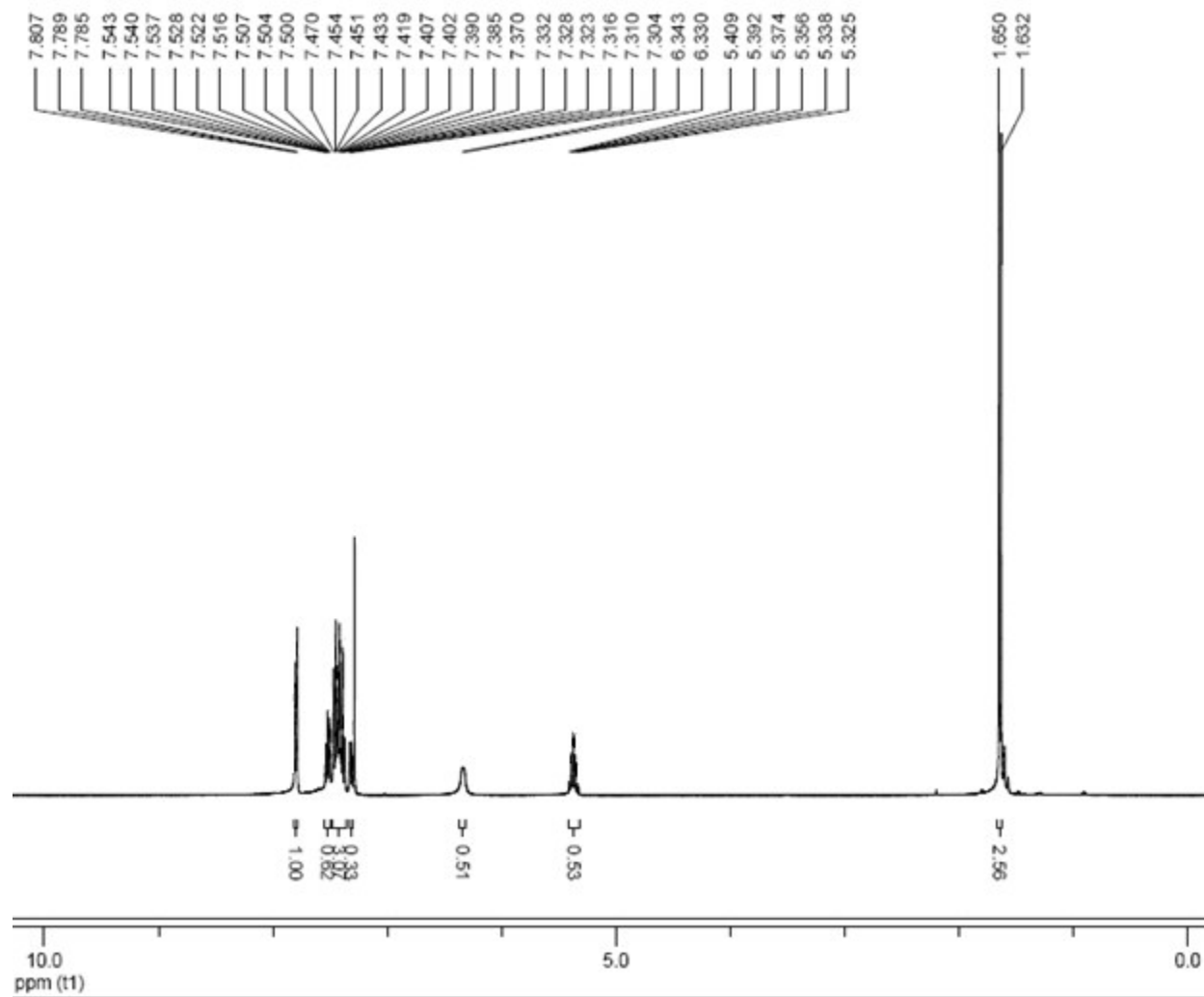
1e)



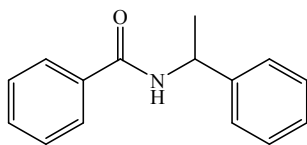
(<sup>1</sup>H-NMR)



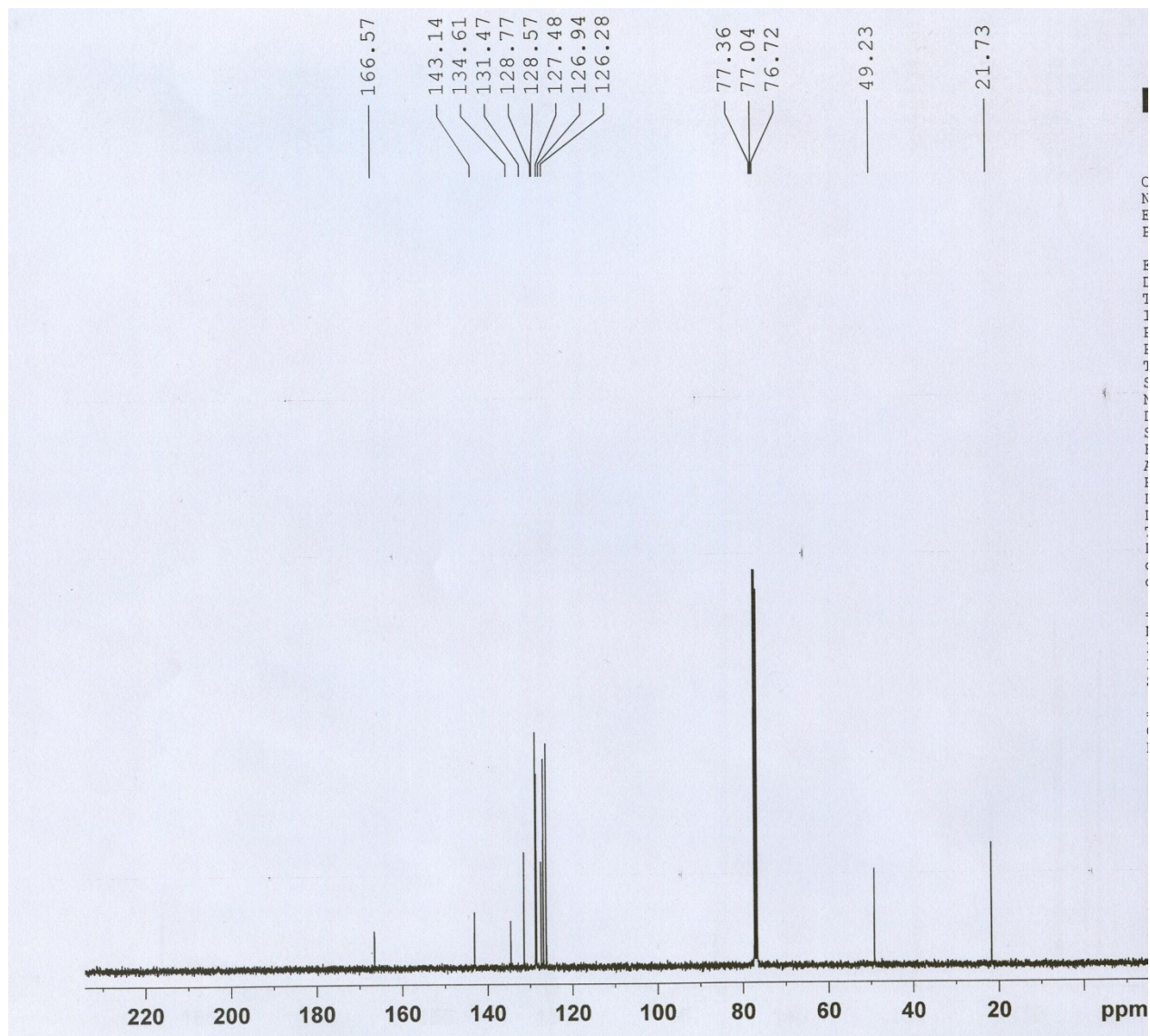
  
(<sup>1</sup>H-NMR)



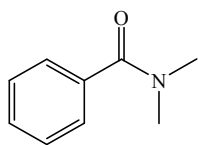
1f)



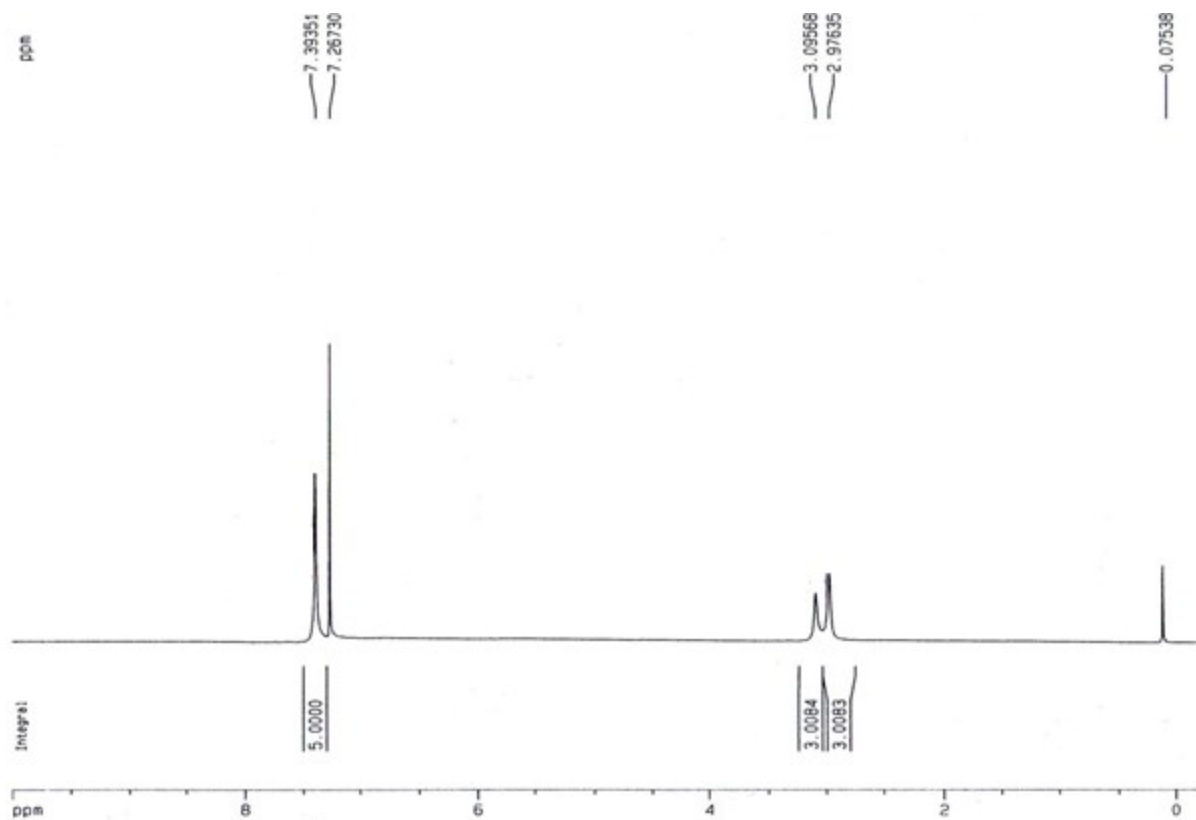
(C-NMR)



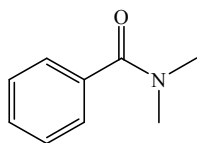
1h)



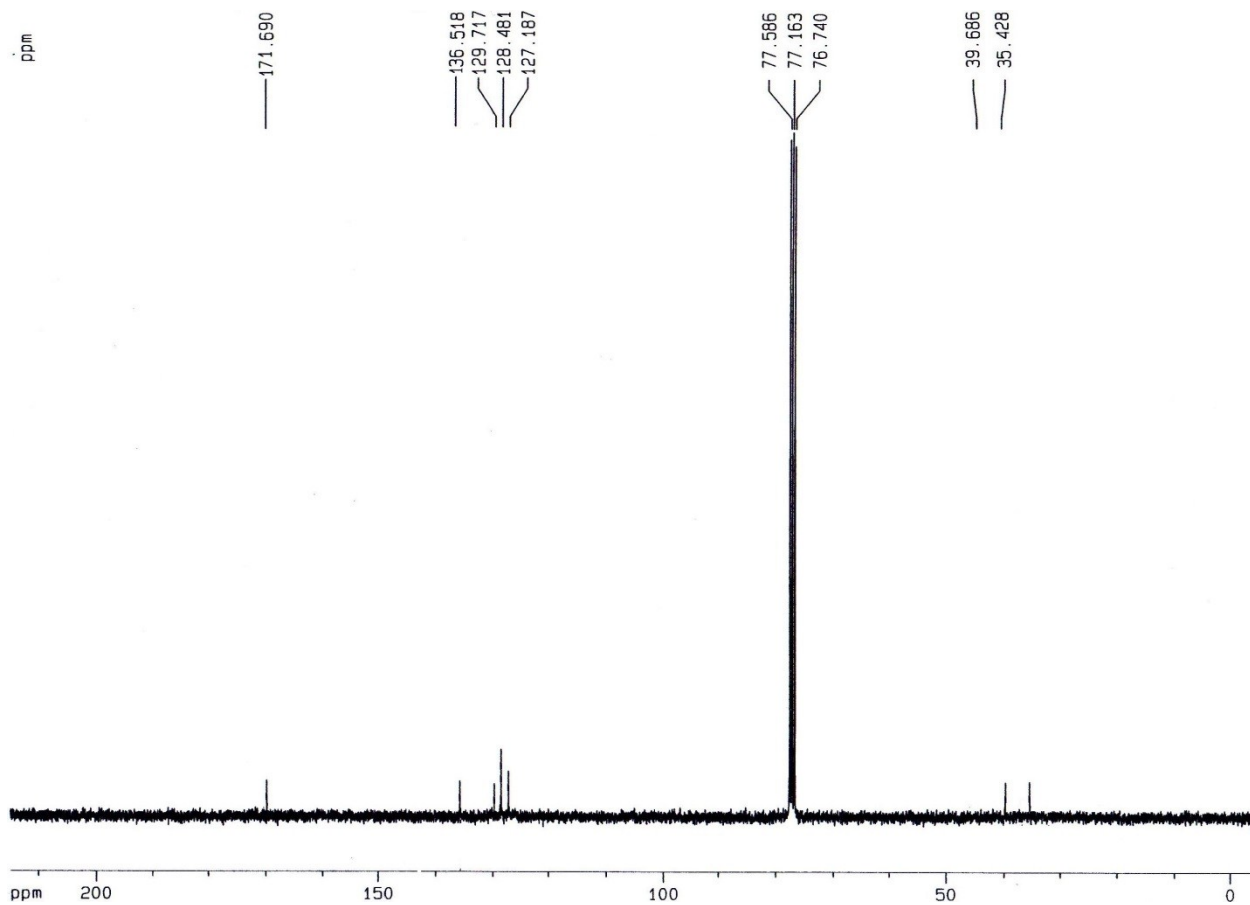
(<sup>1</sup>H-NMR)



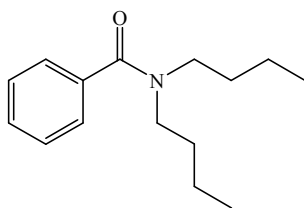
1h)



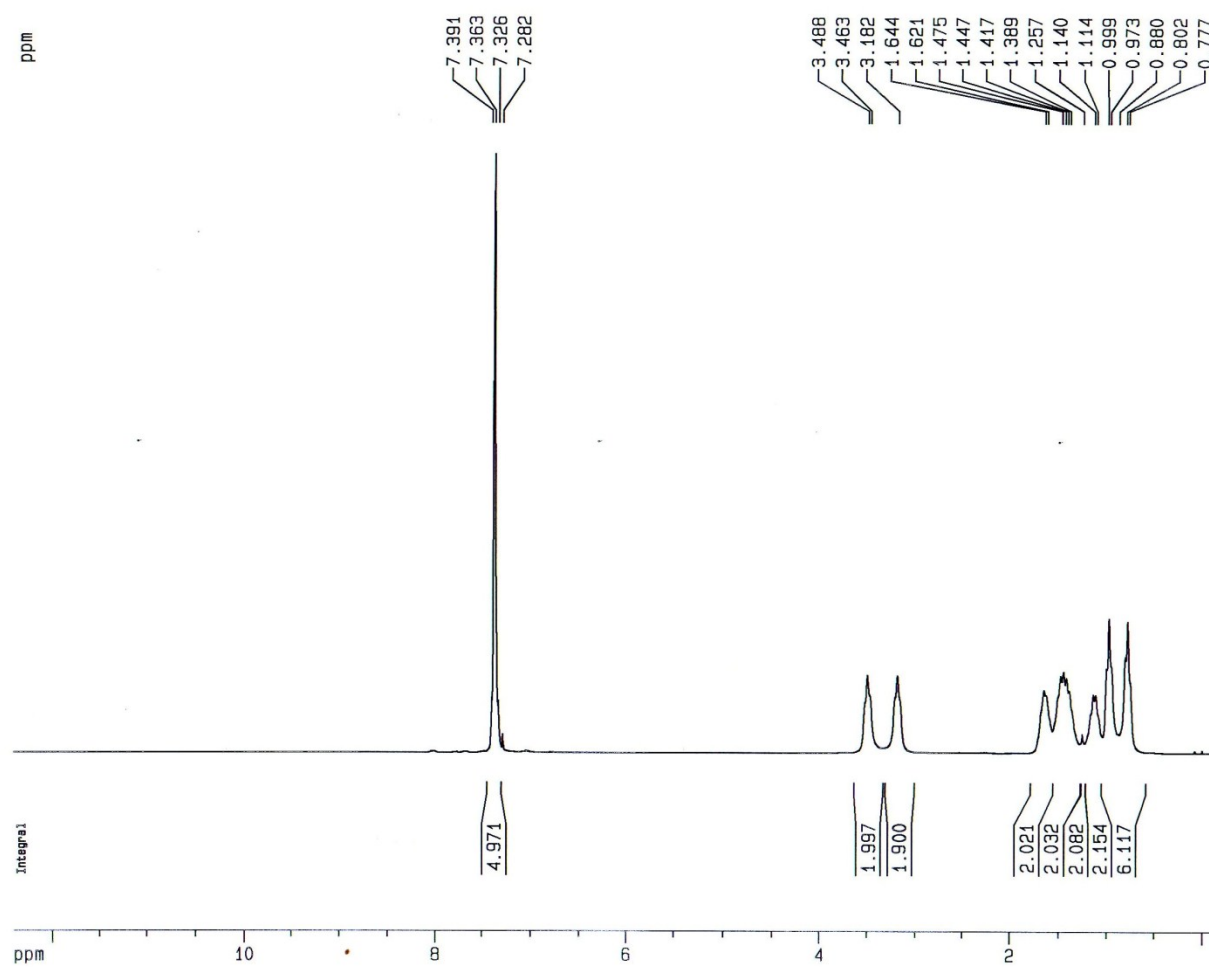
( $^{13}\text{C}$ -NMR)



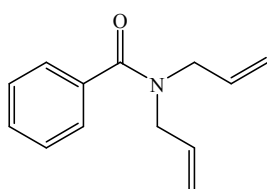
1i)



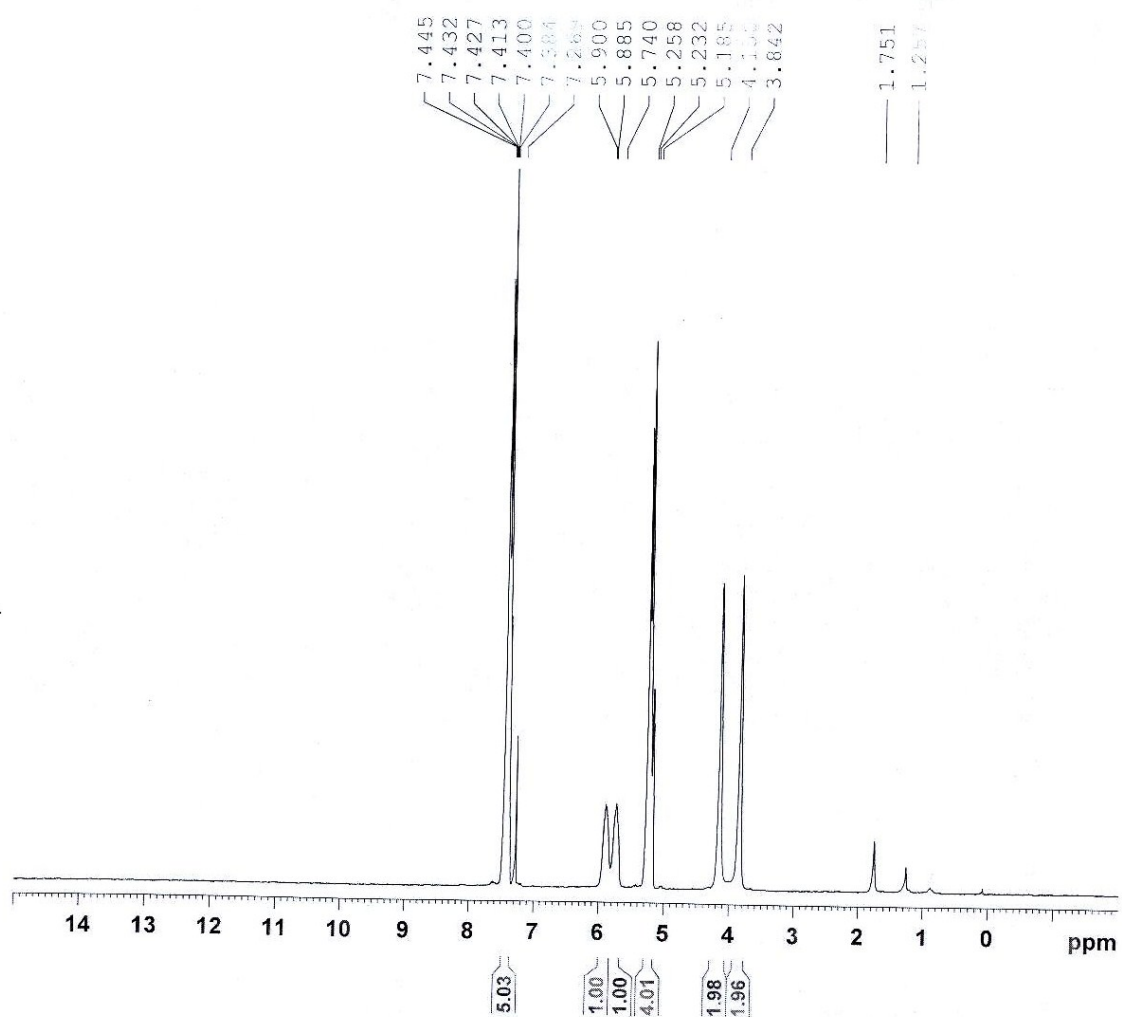
(<sup>1</sup>H-NMR)



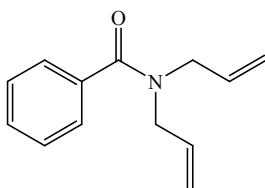
1j)



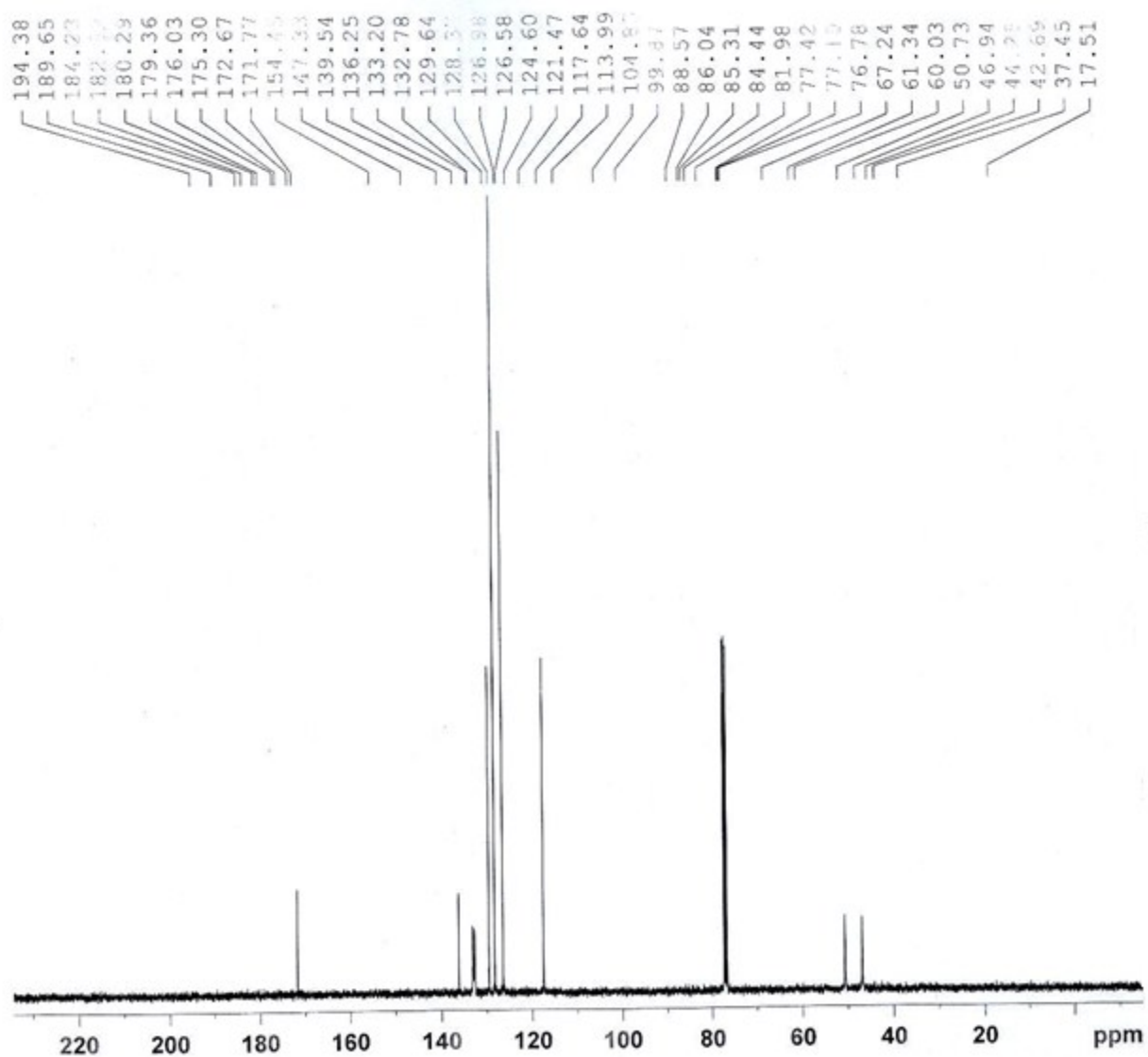
(<sup>1</sup>H-NMR)



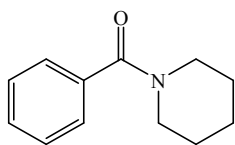
1j)



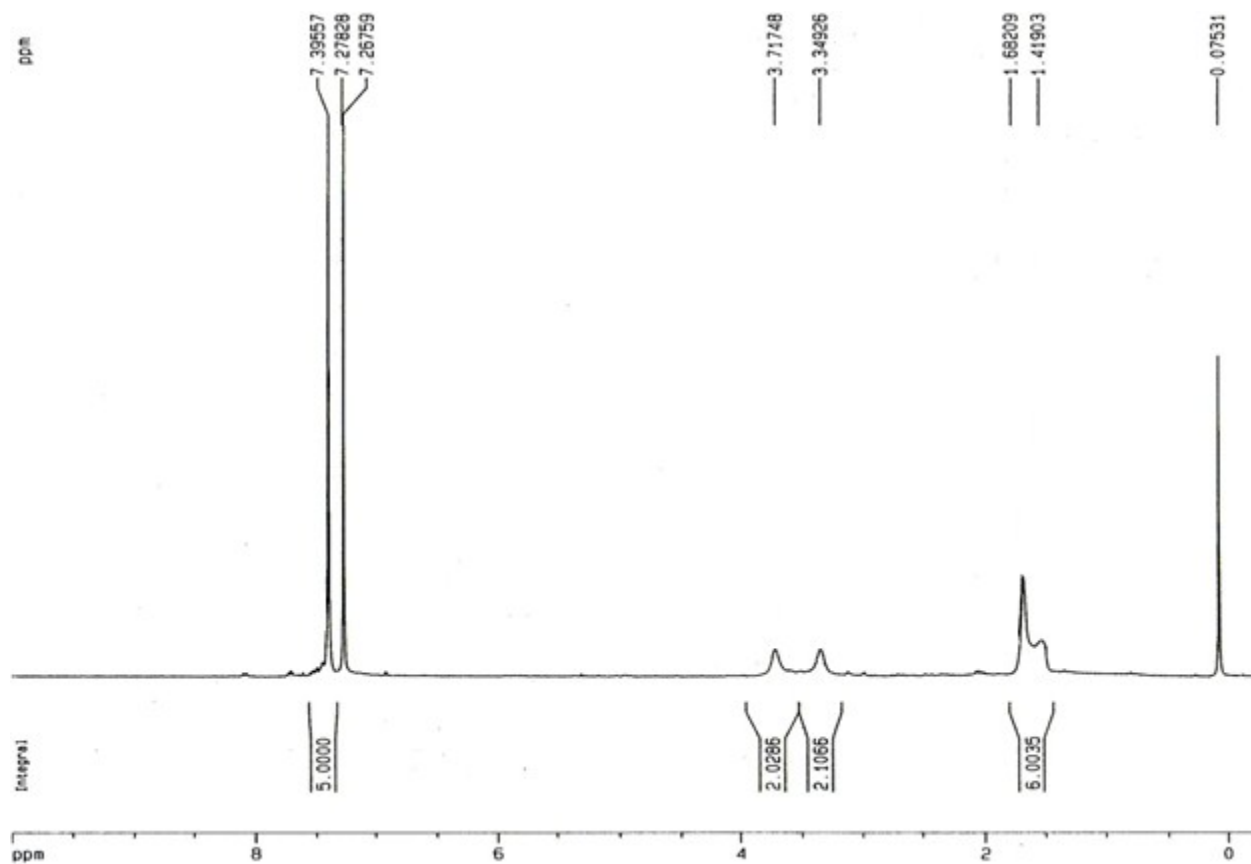
(<sup>13</sup>C-NMR)



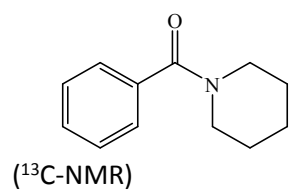
1k)

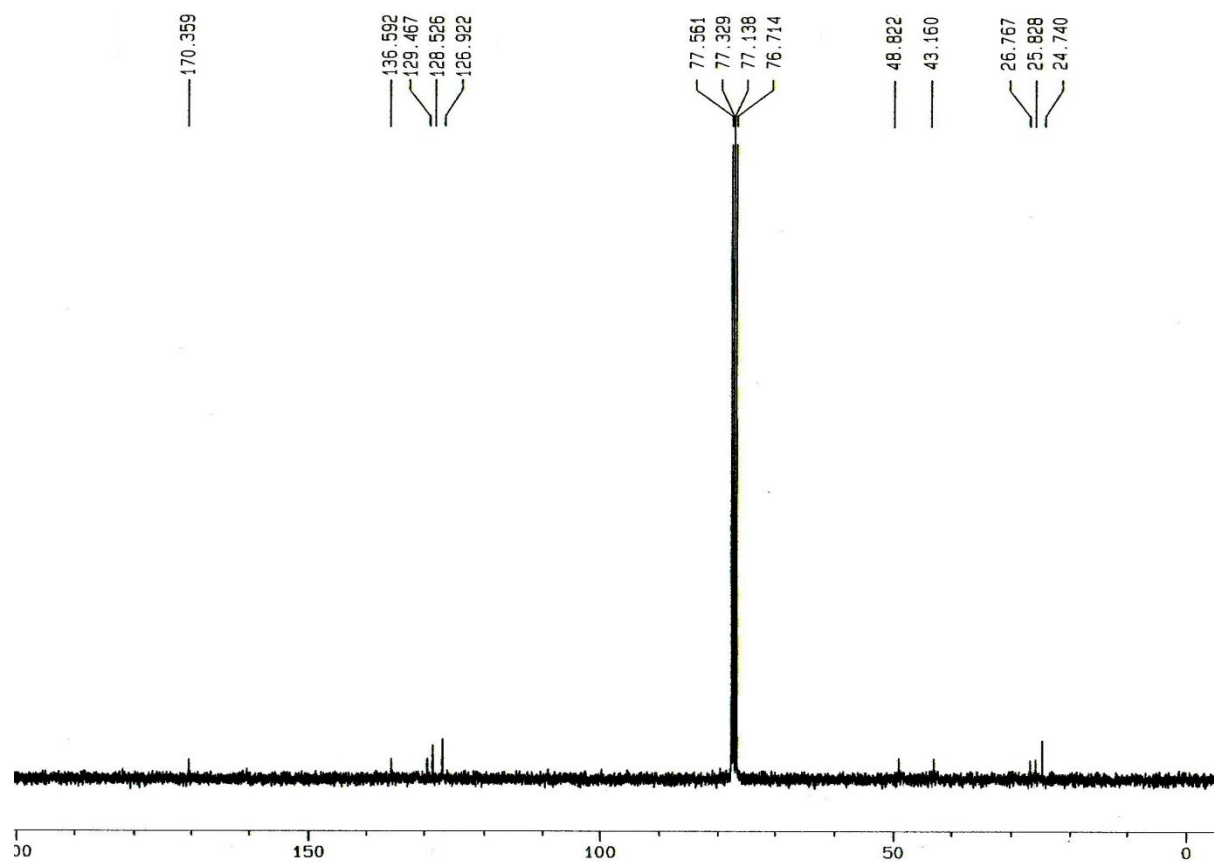


(<sup>1</sup>H-NMR)

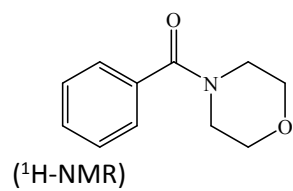


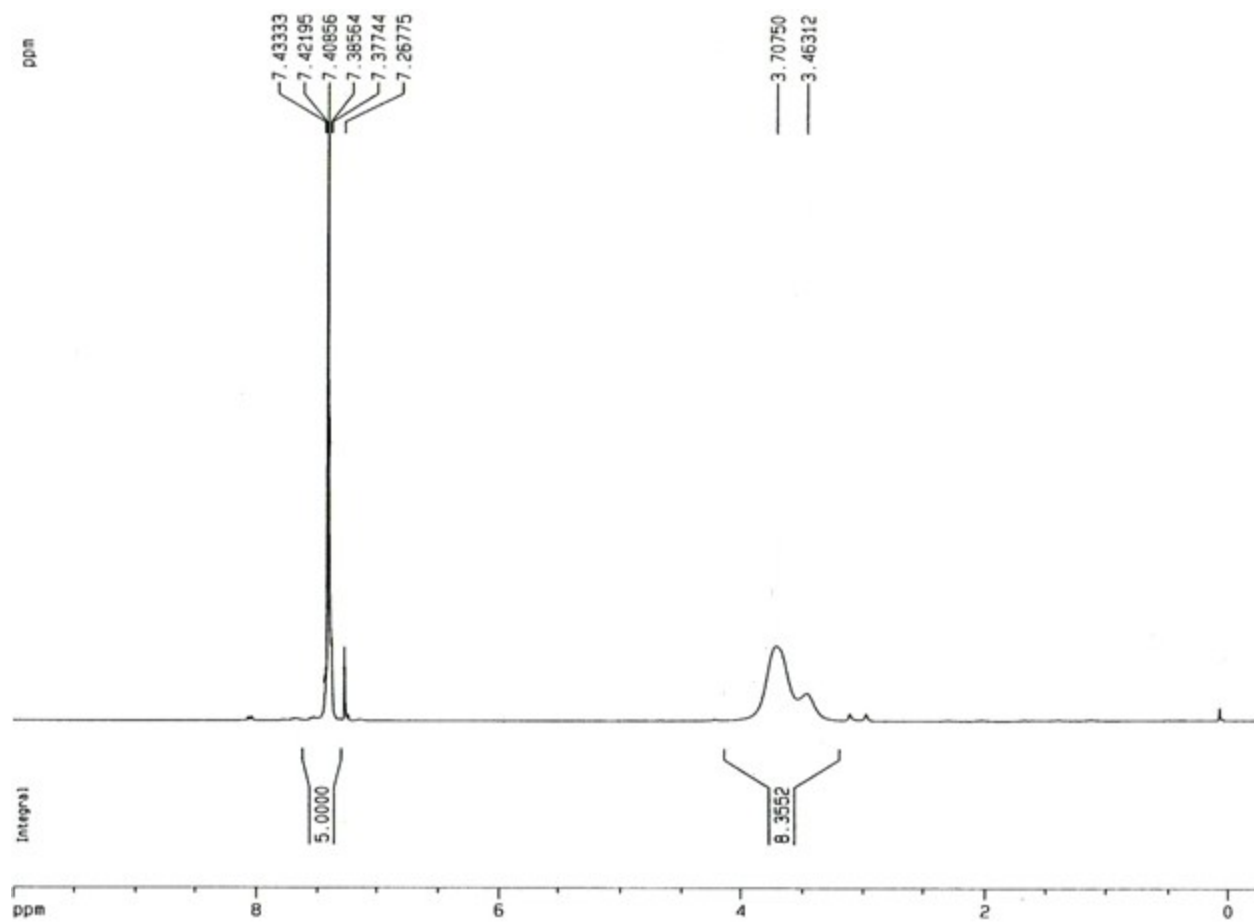
1j)



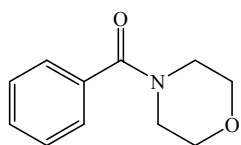


1l)

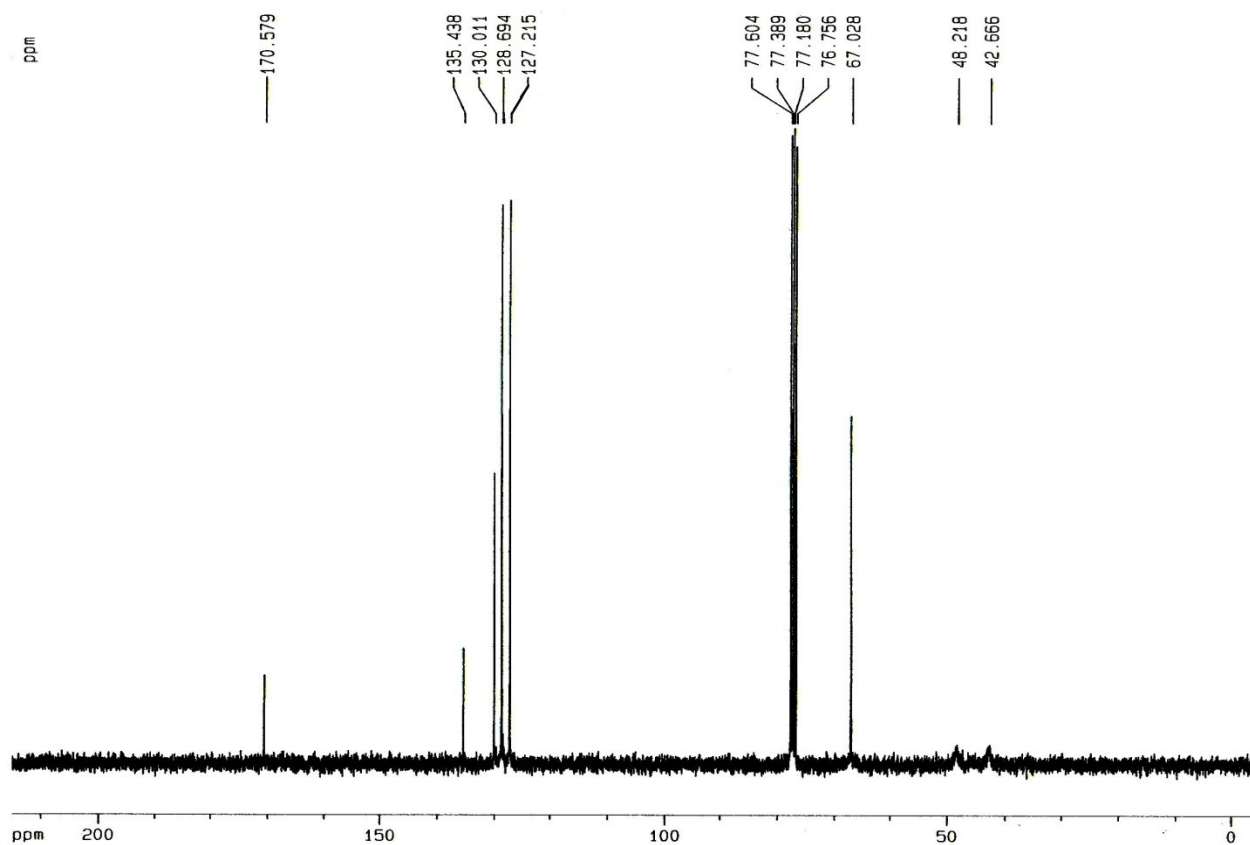




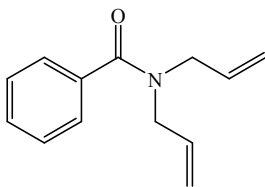
1l)



(<sup>13</sup>C-NMR)

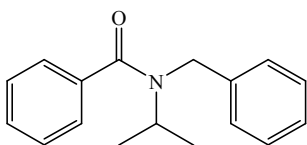


1m)

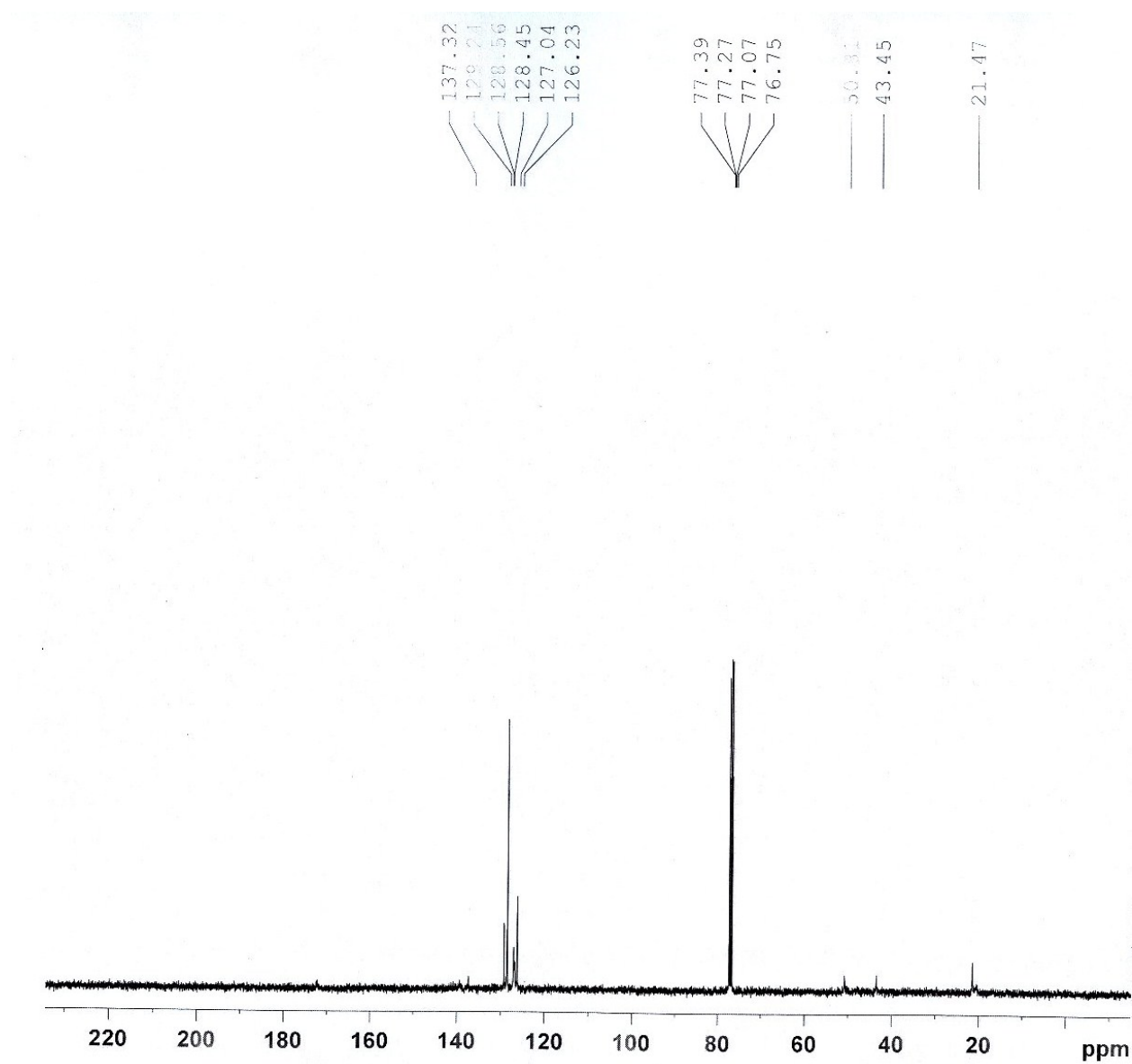


(<sup>1</sup>H-NMR)

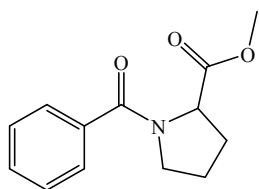
1m)



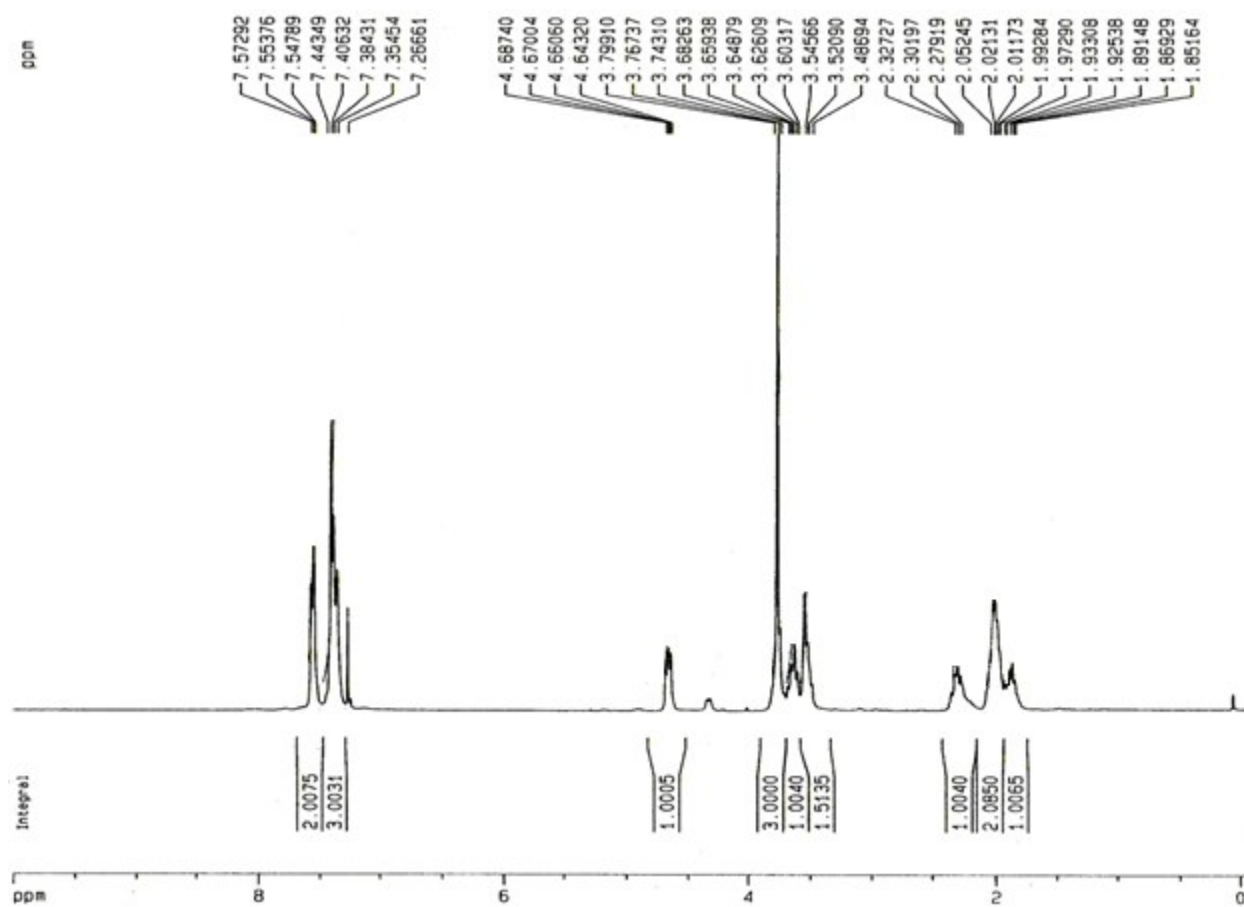
( $^{13}\text{C}$ -NMR)



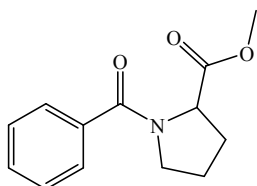
1n)



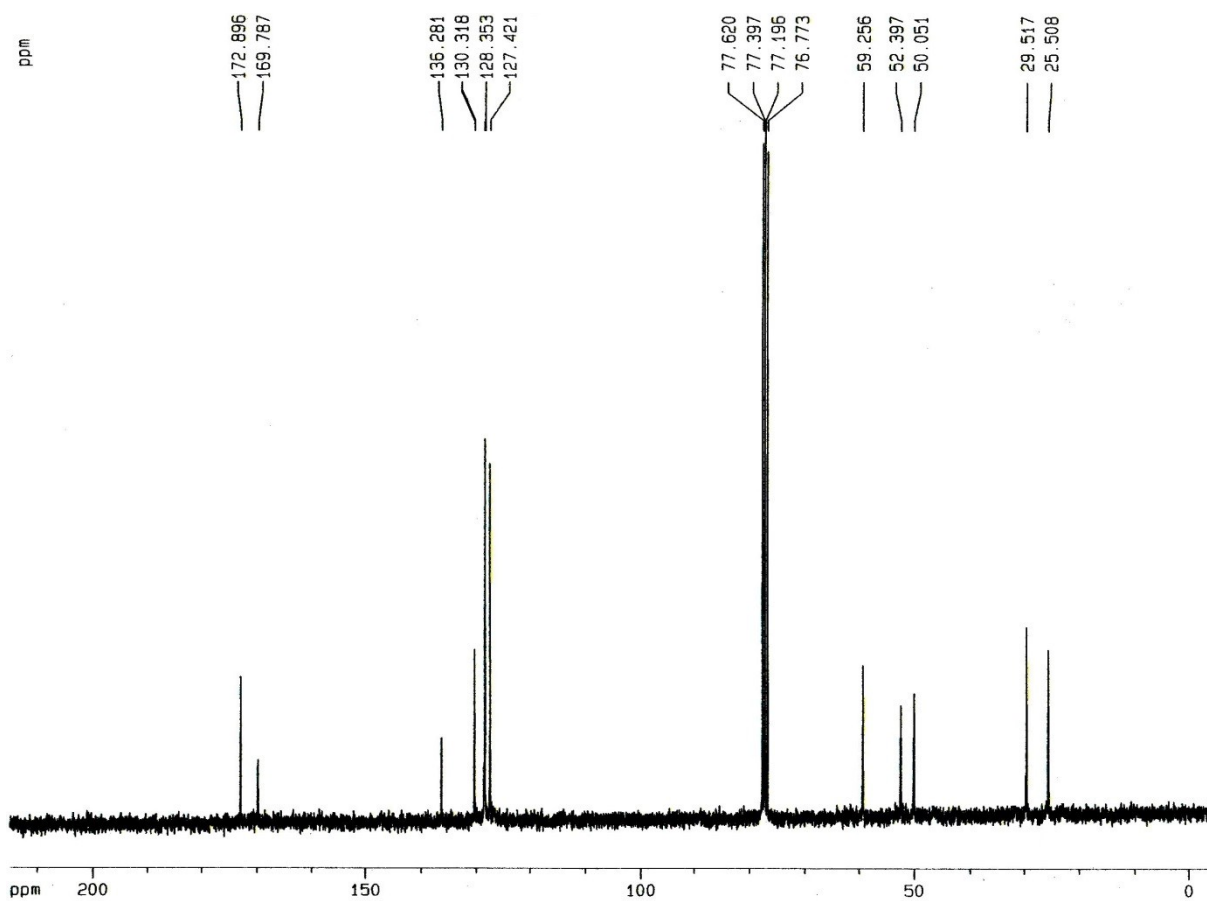
(<sup>1</sup>H-NMR)



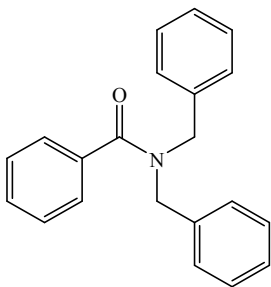
1n)



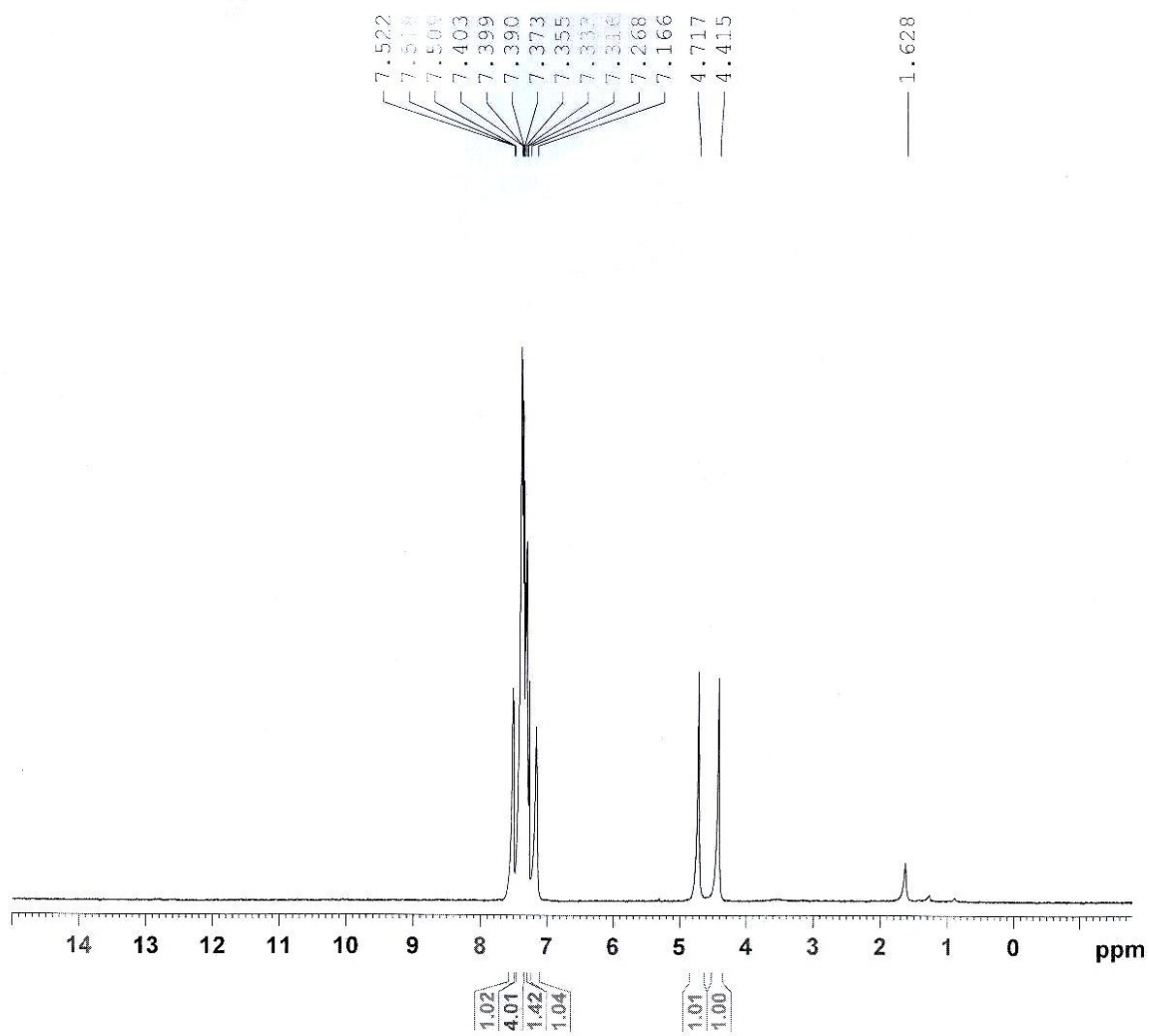
( $^{13}\text{C}$ -NMR)



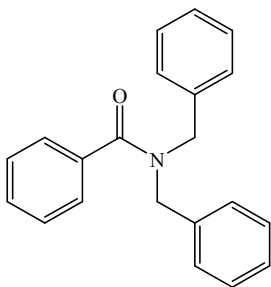
10)



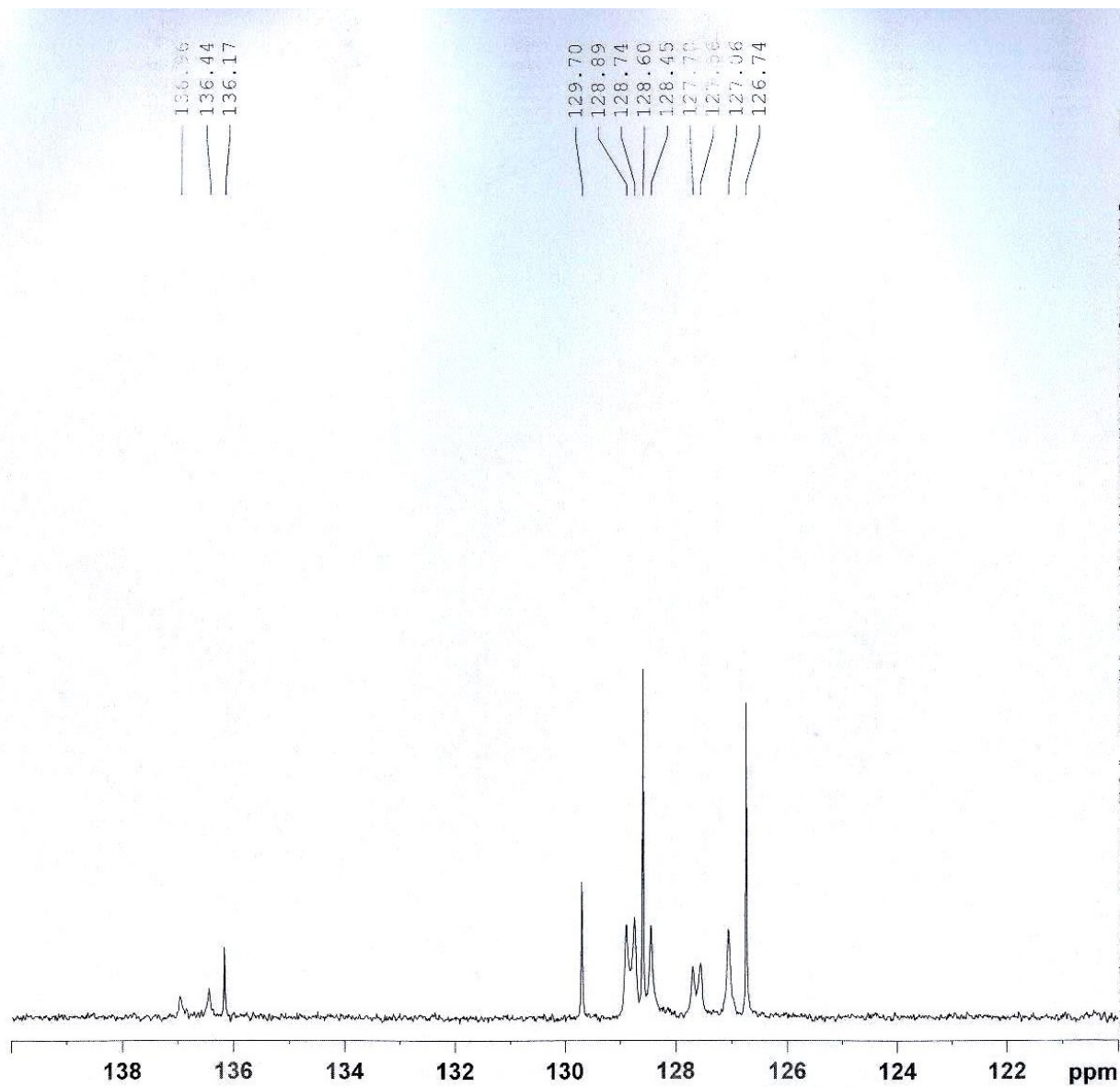
( $^1\text{H}$ -NMR)



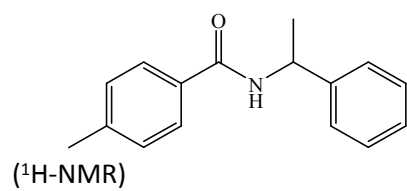
1o)

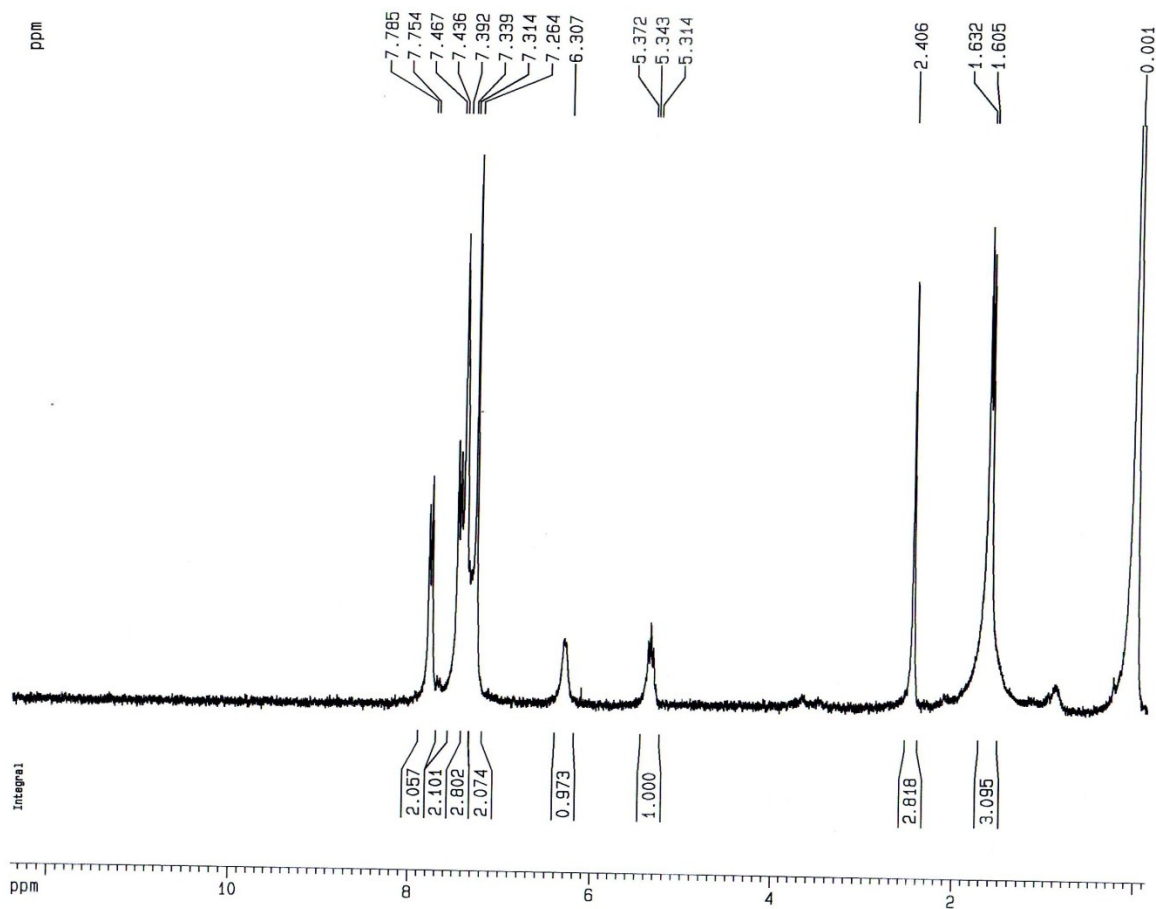


(<sup>13</sup>C-NMR)

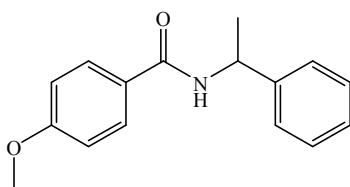


1p)

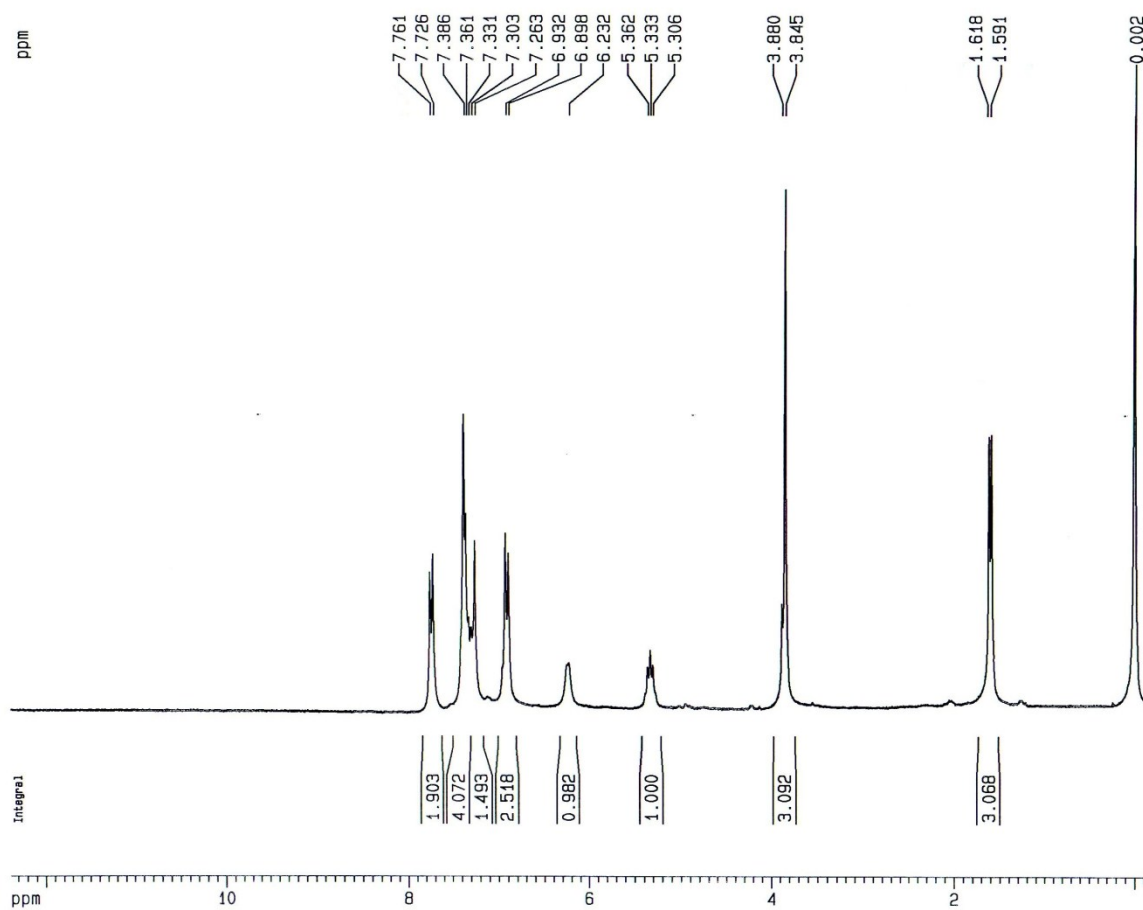




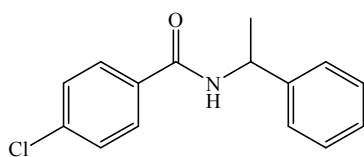
1q)



(<sup>1</sup>H-NMR)



1r)



(<sup>1</sup>H-NMR)

