**Electronic Supplementary Information**

# Low loading of metal in metal-organic framework-derived $NiN_x$@NC promotes amide formation through C–N coupling

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## Chemicals

Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), methanol, 1,4-dioxane and silica gel were purchased from Merck Pvt. Ltd India. 2-methylimidazole was purchased from Avra. Chloroform-D was purchased from Sigma Aldrich. Benzaldehyde and primary and secondary amines were obtained commercially from various chemical companies (Sigma Aldrich, Avra, Alfa Aesar and SRL Pvt. Ltd. India). All catalytic experiments were carried out in a round bottom flask (volume 25 mL, from Borosil).

## Instruments

High-resolution X-ray diffractions (HR-XRD) of the catalysts were carried out in the Rigaku SmartLab 9kW Powder X-ray diffractometer (RIGAKU Corporation). Raman spectra were recorded in an STR-300 spectrometer (AIRIX Corp.) with a 532 nm excitation source.

Scanning Electron Microscopy (FE-SEM) studies were carried out in Nova Nano SEM 450, FEI Company of USA (S.E.A.) PTE, LTD. Energy dispersive X-ray spectroscopy (EDX) images were collected by Team Pegasus Integrated EDS-EBSD with Octane plus and Hikari Pro EDX System. Elemental mapping was performed with the analyzer attached to SEM. High resolution transmission electron spectroscopy (HR-TEM) studies were carried out on Tecnai G2 20 TWIN transmission electron microscope connected with an energy-dispersive X-ray spectrometer (EDAX, r-TEM SUTW). Fast Fourier Transform (FFT) and Selected Area Electron Diffraction (SEAD) was performed by the HR-TEM.

The X-ray photoelectron spectroscopy (XPS) measurements were performed in a K-Alpha X-ray photoelectron spectrometer from Thermo Fisher Scientific. The binding energies were calibrated using the C 1s peak located at 284.6 eV as the reference.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) measurements were conducted on the Agilent 7800 ICP-MS mainframe from Agilent Technologies for the metal elemental analysis.

$^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on AVH D 500 AVANCE III HD 500 MHZ, One Bay NMR Spectrometer from Bruker Bio Spin International and Bruker India Scientific AVANCE NEO 600 MHz NMR Spectrometer. The Chemical shifts were reported in ppm. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet,

bs = broad singlet d = doublet, t = triplet, and m = multiple. The residual solvent signals were used as references for $^{1}H$ and $^{13}C$ NMR spectra ($CDCl_3$: $\delta_H$ = 7.28–7.29 ppm, $\delta_C$ = 77.01–77.16 ppm.

**Experimental**

**Synthesis of Ni-ZIF-8**[S1]

$Ni(NO_3)_2.6H_2O$ (0.3 mmol) and $Zn(NO_3)_2.6H_2O$ (0.7 mmol) was each dissolved in 20 mL methanol and stirred for 10 minutes to get the solution A. 2-methylimidazole (4 mmol) was separately dissolved in 20 mL methanol and stirred for 10 minutes to get the solution B. Then, solution B was added to A at a time and stirred for 24 h at room temperature. The precipitate of Ni-ZIF-8 was obtained. The precipitate was collected by centrifugation (13000 rpm for 15 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.

**Synthesis of ZIF-8**

$Zn(NO_3).6H_2O$ (1 mmol) was dissolved in 20 mL methanol and stirred for 10 minutes to get the solution A. 2-methylimidazole (4 mmol) was separately dissolved in 20 mL methanol and stirred for 10 minutes to get the solution B. Then solution B was added to A at a time and stirred for 24 h at room temperature. The precipitate of ZIF- was obtained and collected by centrifugation (13000 rpm for 15 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 $^{o}$C in hot air oven over night.

**Synthesis of $NiN_x$@NC**[S2]

300 mg of Ni-ZIF-8 was ground in a mortar pestle to get a fine powder. The powder was placed in a crucible boat and heated at 900 °C in the presence of $N_2$ for 3 h (in a tubular furnace with heating rate: 5 °C/min from 35 °C). The furnace was allowed to cool down to room temperature. The black powder was collected and denoted as $NiN_x$@NC.

Similarly, $NiN_x$@NC-1 and $NiN_x$@NC-2 were prepared at 800 and 700 °C, respectively.

**Synthesis of NC**[S1]

300 mg of ZIF-8 was ground into mortar pastel to get a fine powder. The powder was placed into crucible boat and heated at 900 °C in the presence of $N_2$ for 3h with the heating rate 5 °C/min from 35 °C. The furnace was allowed to cool down to room temperature. The black powder was collected and denoted as NC (N-doped carbon).

**Synthesis of Ni@C**[S2]

100 mg vulcan carbon was dispersed in 20 mL methanol solution and stirred 30 minute. $Ni(NO_3)_2.6H_2O$ (1 mmol) was added in the vulcan carbon solution and stirred 10 minute to get solution A. $NaBH_4$ (2 mmol) was dissolved in 20 mL methanol and stirred for 10 minute to form the solution B. The solution B was added to A at a time and stirred for 24 h. The mixture yielded a black suspension of Ni@C. The precipitate was collected by centrifugation (11000 rpm for 10

minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.
Similarly, Ni@$SiO_2$ and Co@C were prepared respectively.

**Synthesis of Ni@C (0.45% of Ni)**[S2]

100 mg vulcan carbon was dispersed in 20 mL methanol solution and stirred 30 minute. $Ni(NO_3)_2.6H_2O$ (0.007 mmol) was added in the vulcan carbon solution and stirred 10 minute to get solution A. $NaBH_4$ (0.014 mmol) was dissolved in 20 mL methanol and stirred for 10 minute to form the solution B. The solution B was added to A at a time and stirred for 24 h. The mixture yielded a black suspension of Ni@C. The precipitate was collected by centrifugation (11000 rpm for 10 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.

**Synthesis of Ni@NC-1**[S2]

100 mg NC was dispersed into 20 mL methanol solution and stirred 30 minute. $Ni(NO_3)_2.6H_2O$ (0.007 mmol) was added in the vulcan carbon solution and stirred 10 minute to get solution A. $NaBH_4$ (0.014 mmol) was dissolved in 20 mL methanol and stirred for 10 minute to form the solution B. The solution B was added to A at a time and stirred for 24 h. The mixture yielded a black suspension of Ni@NC-1. The precipitate was collected by centrifugation (11000 rpm for 10 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.

**Synthesis of Ni@NC-2**[S2]

$Ni(NO_3)_2.6H_2O$ (0.007 mmol) was dispersed in 10 mL methanol and stirred 10 minute to get solution A. $NaBH_4$ (0.014 mmol) was dissolved in 20 mL methanol and stirred for 10 minute to form the solution B. The solution B was added to A at a time and stirred for 10 minute to get reaction mixture C. 100 mg NC was added in the reaction mixture C and stirred 24 h. The mixture yielded a black suspension of Ni@NC. The precipitate was collected by centrifugation (11000 rpm for 10 minutes) and washed five times with methanol. The obtained precipitate was dried at 60 °C in a hot air oven over night.

**Figure**

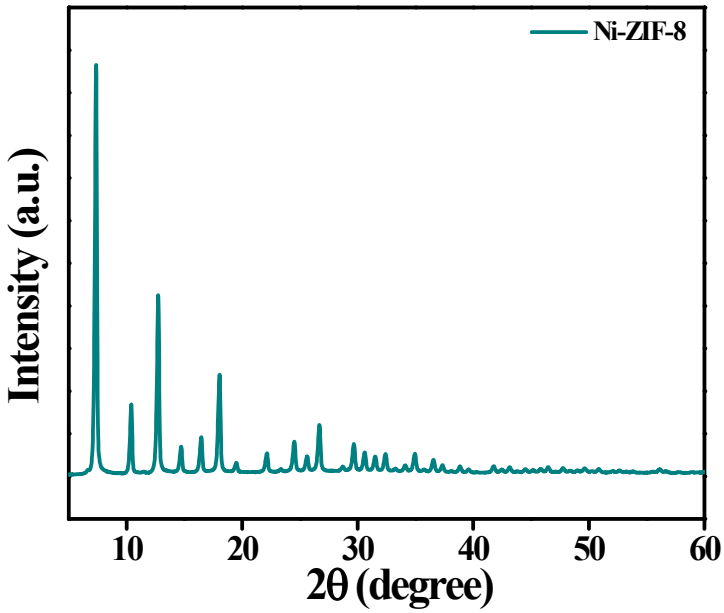



**Figure S1.** The PXRD pattern of Ni-ZIF-8 showed the characteristic peaks of ZIF-8 (JCPDS 00-062-1030).[S1, S3,S4]

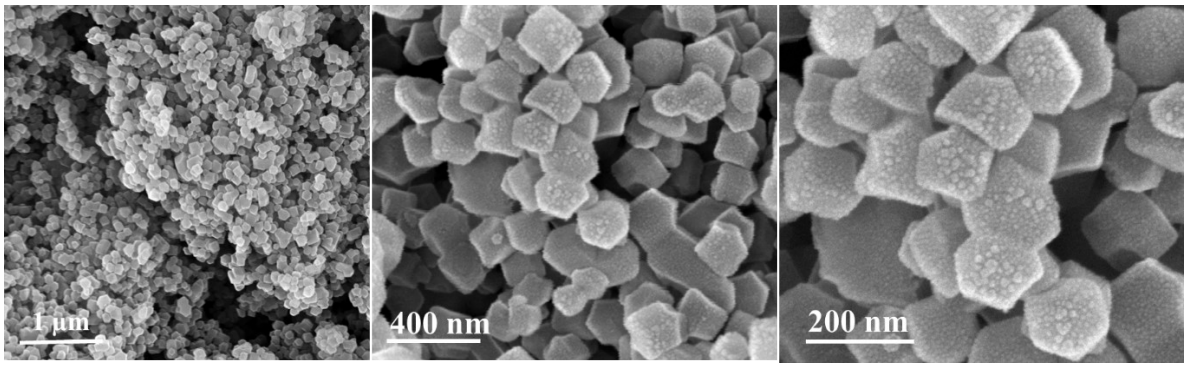



**Figure S2.** FE-SEM images of the Ni-ZIF-8 showed rhombic dodecahedron morphology at different resolutions.

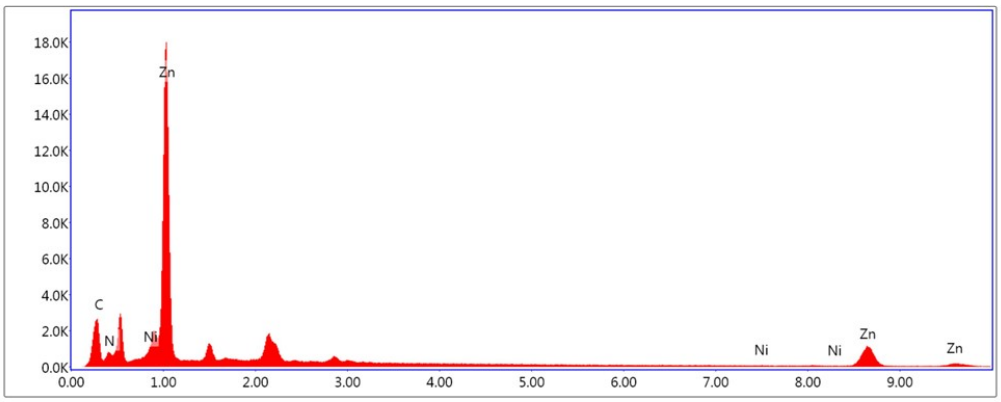



**Figure S3.** EDX spectrum of Ni-ZIF-8 showing Ni, Zn, N and C.

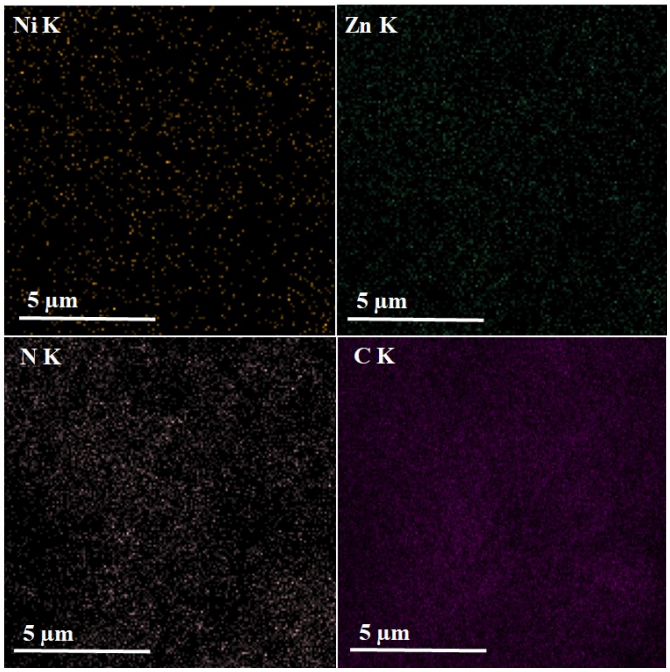



**Figure S4.** Elemental mapping of Ni-ZIF-8 showing the homogeneously distributed of Ni, Zn, C and N.

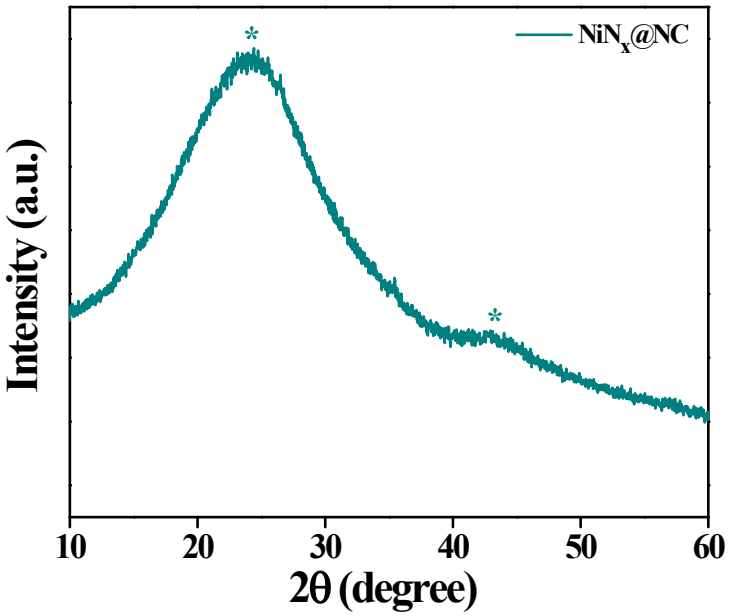



**Figure S5**. The PXRD pattern of $NiN_x$@NC. The XRD of $NiN_x$@NC exhibited two diffraction peaks at 24.1 ° and 42.9 ° for the planes (002) and (100) of graphene.[S5,S6]

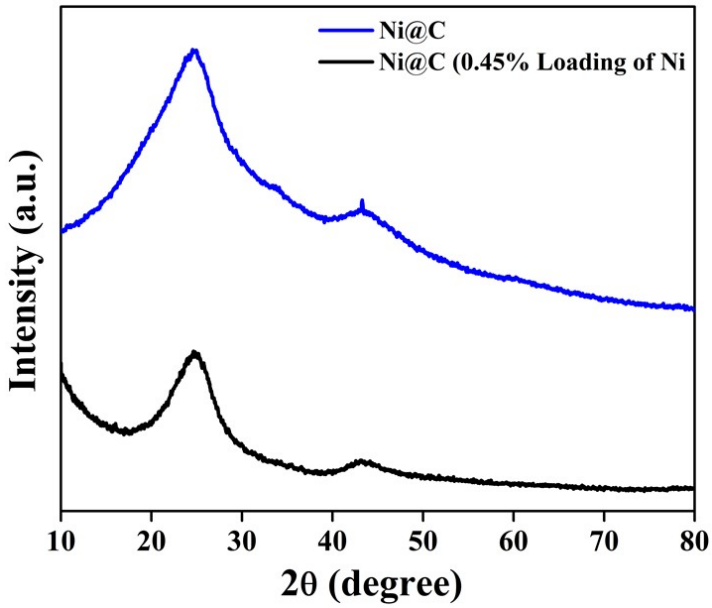



**Figure S6**. The PXRD pattern of Ni@C with different loading of Ni. The diffraction peaks at 24.75° and 43.31° originated for the planes (002) and (100) of graphene. In the XRD data of Ni@C (high loading) showed the peak at 43.21° corresponding to (111) plane of Ni nanoparticle.[S7] We have calculated the particle size 24.86 nm of Ni@C (high loading). In the Ni@C catalyst the particle size is not equivalent to $NiN_x$@NC.

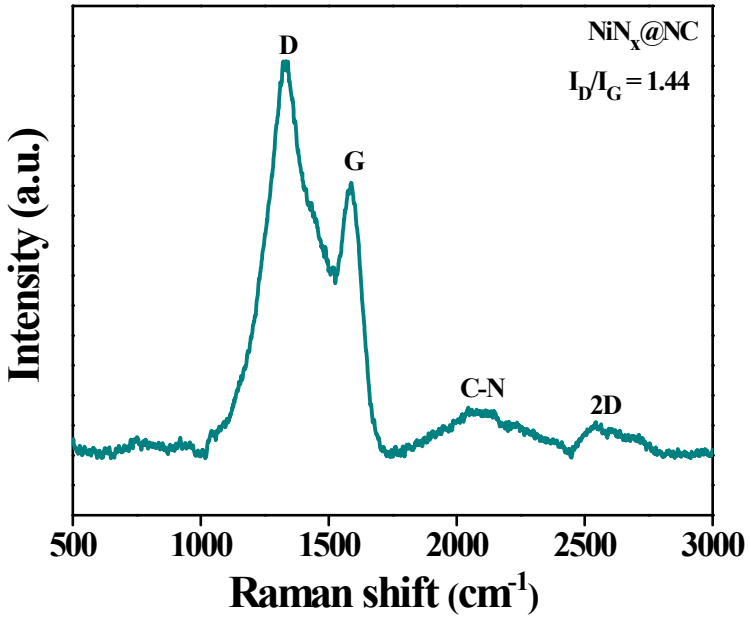



**Figure S7**. Raman spectrum of $NiN_x$@NC showed peaks at 1326 and 1584 $cm^{-1}$ corresponding to D and G bands of carbon matrix. The peaks at 2074 and 2555 $cm^{-1}$ observed for C–N and 2D bands of graphene.[S8]

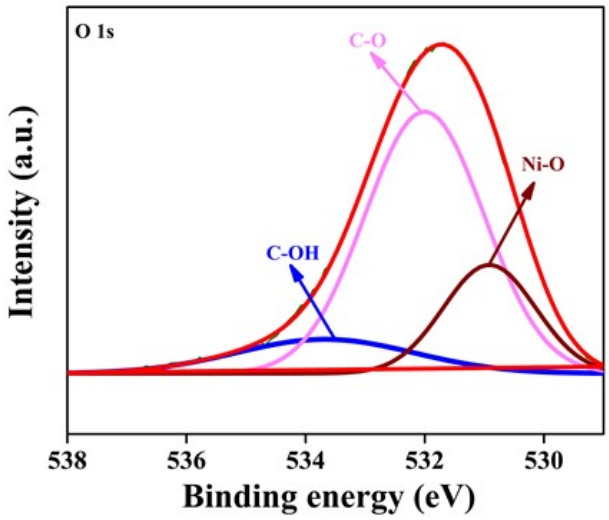



**Figure S8**. The O 1s XPS spectrum was deconvulated into three peaks of Ni–O, C–O, and C–OH.[S9, S10]

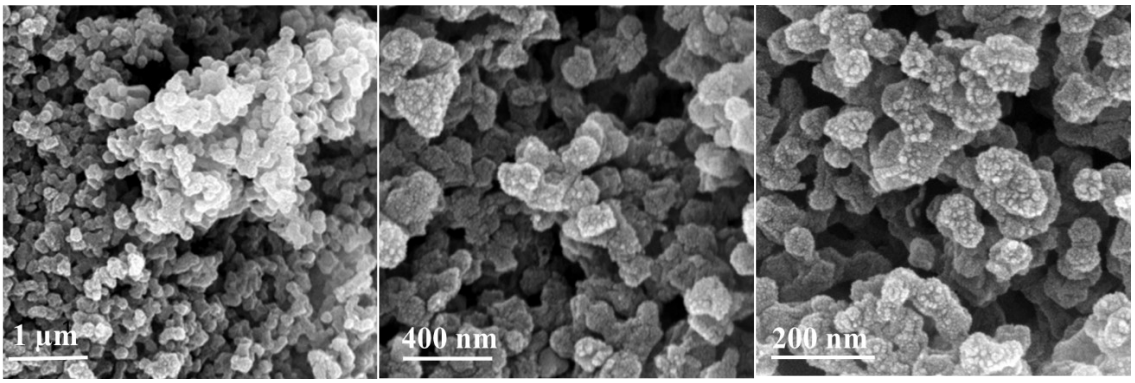
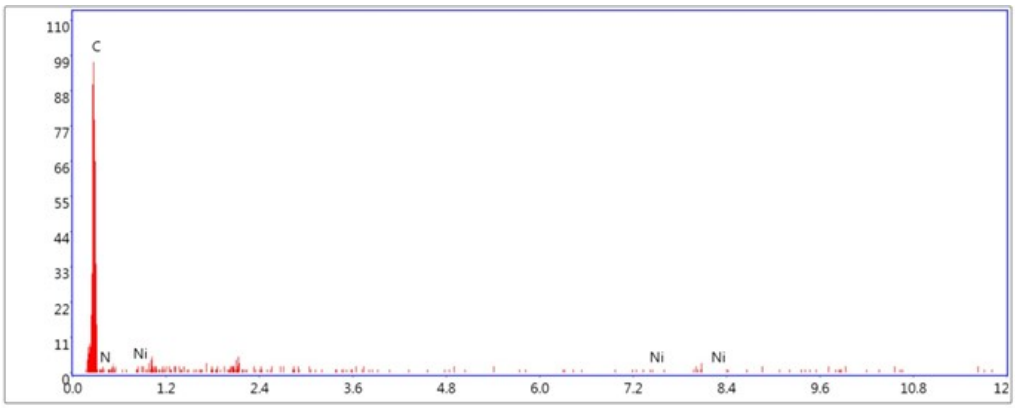



**Figure S9**. FE-SEM images of the $NiN_x$@NC showed rhombic dodecahedron shapes deformed after evaporation of Zn from the materials.



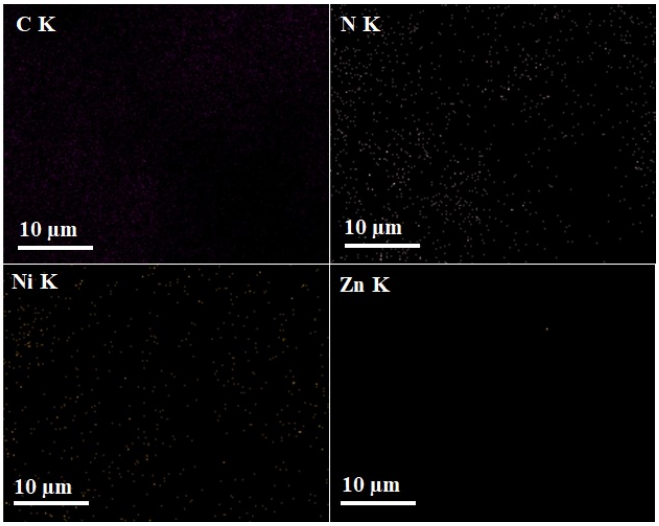
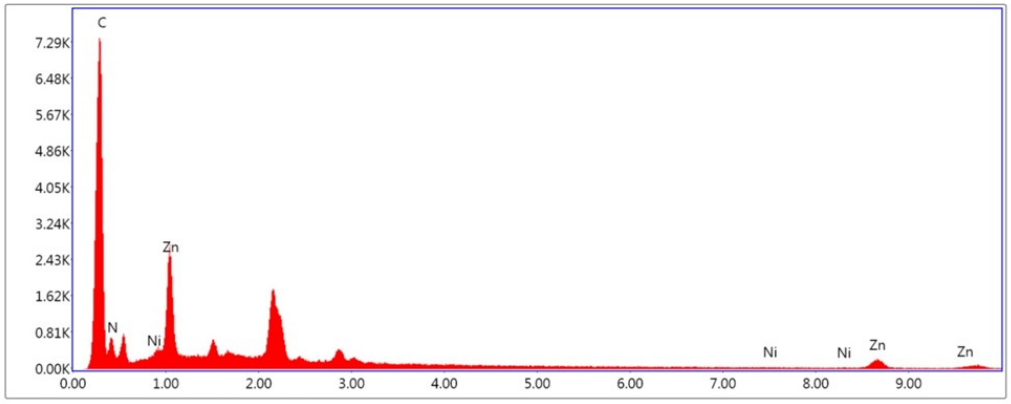




**Figure S10.** EDX and Elemental mapping of $NiN_x$@NC showing the homogeneously distributed of Ni, C, and N.



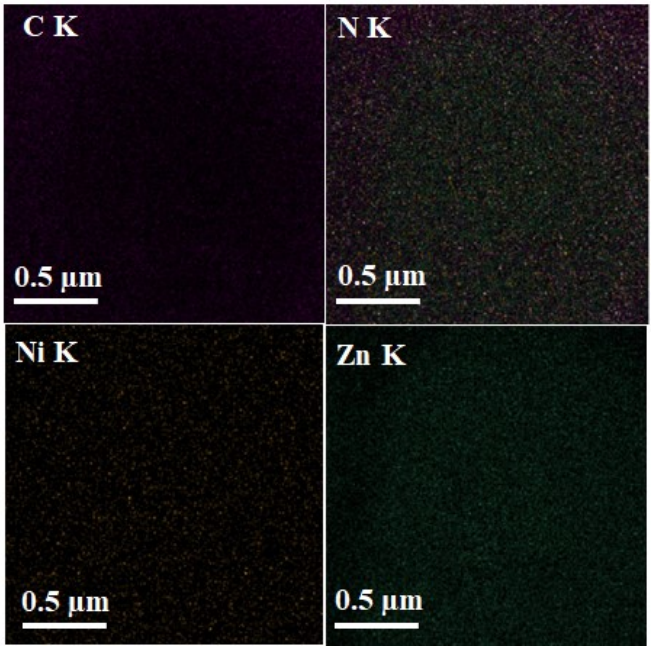
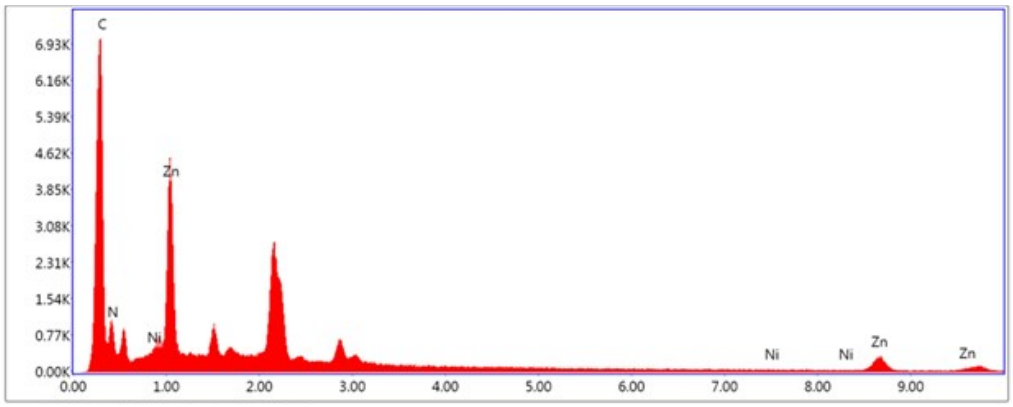




**Figure S11.** EDX and elemental mapping of $NiN_x$@NC−1 ($NiN_x$@NC-800) catalyst showing homogeneously distributed C, N, Ni and Zn elements.



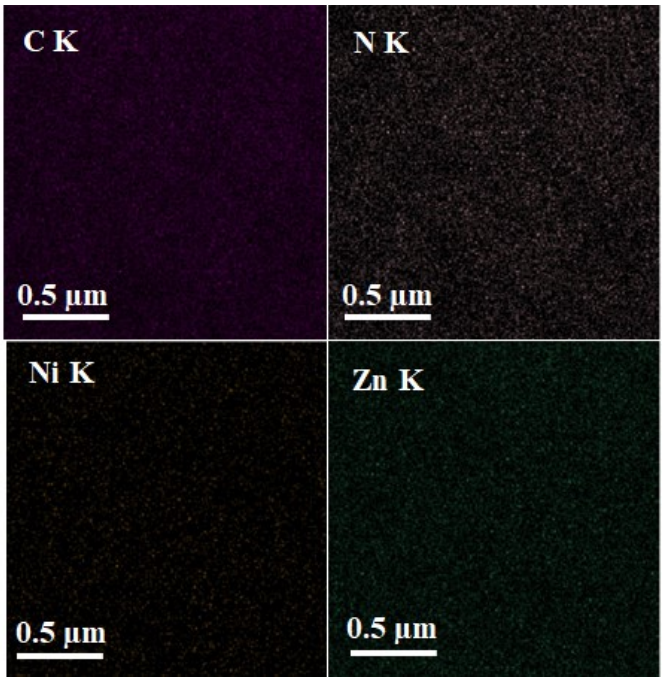
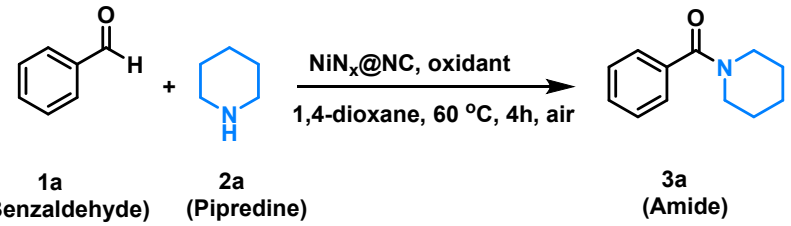




**Figure S12.** EDX and elemental mapping of $NiN_x$@NC−2 ($NiN_x$@NC-700) catalyst showing homogeneously distributed C, N, Ni and Zn elements.

**Table S1**. Optimization table for the amide formation by the reaction of aldehyde and amine.




**1a (Benzaldehyde)** **2a (Pipredine)** **3a (Amide)**

| Entry | Catalyst | Solvent | Oxidant | Temp. (°C) | Time (h) | Yield (%) |
|---|---|---|---|---|---|---|
| Variation of oxidant | | | | | | |
| 1. | $NiN_x$@NC | Dioxane | TBHP (0.35 eq) | 60 | 4 | 98 |
| 2. | $NiN_x$@NC | Dioxane | Air | 60 | 4 | 62 |
| 3. | No catalyst | Dioxane | TBHP (0.35 eq) | 60 | 4 | 45 |
| 4. | $NiN_x$@NC | Dioxane | $H_2O_2$ (1 eq) | 60 | 4 | 82 |
| 5. | $NiN_x$@NC | Dioxane | $O_2$ | 60 | 24 | 73 |
| 6. | $NiN_x$@NC | Dioxane | $N_2$, TBHP (0.35 eq) | 60 | 4 | 91 |
| Variation of temperature[S11] | | | | | | |
| 7. | $NiN_x$@NC | Dioxane | TBHP (0.35 eq) | 50 | 4 | 81 |
| 8. | $NiN_x$@NC | Dioxane | TBHP (0.35 eq) | 60 | 4 | 98 |
| 9. | $NiN_x$@NC | Dioxane | TBHP (0.35 eq) | 70 | 4 | 97 |
| Variation of the catalysts | | | | | | |
| 10. | $NiN_x$@NC | Dioxane | TBHP (0.35 eq) | 60 | 4 | 98 |
| 11. | $NiN_x$@NC-1 | Dioxane | TBHP (0.35 eq) | 60 | 4 | 86 |
| 12. | $NiN_x$@NC-2 | Dioxane | TBHP (0.35 eq) | 60 | 4 | 82 |
| 13. | NC | Dioxane | TBHP (0.35 eq) | 60 | 4 | 54 |
| 14. | Ni@C | Dioxane | TBHP (0.35 eq) | 60 | 4 | 75 |
| 15. | Ni@C (0.45% Ni) | Dioxane | TBHP (0.35 eq) | 60 | 4 | 72 |
| 16. | Ni@NC-1 | Dioxane | TBHP (0.35 eq) | 60 | 4 | 79 |
| 17. | Ni@NC-2 | Dioxane | TBHP (0.35 eq) | 60 | 4 | 80 |
| 18. | $Ni@SiO_2$ | Dioxane | TBHP (0.35 eq) | 60 | 4 | 75 |
| 19. | Co@C | Dioxane | TBHP (0.35 eq) | 60 | 4 | 70 |
| Variation of the amount of catalyst | | | | | | |
| 20. | $NiN_x$@NC (1mg) | Dioxane | TBHP (0.35 eq) | 60 | 4 | 76 |
| 21. | $NiN_x$@NC (2 mg) | Dioxane | TBHP (0.35 eq) | 60 | 4 | 78 |
| 22. | $NiN_x$@NC (3 mg) | Dioxane | TBHP (0.35 eq) | 60 | 4 | 85 |
| 23. | $NiN_x$@NC (5 mg) | Dioxane | TBHP (0.35 eq) | 60 | 4 | 98 |
| 24. | $NiN_x$@NC (10 mg) | Dioxane | TBHP (0.35 eq) | 60 | 4 | 98 |
| Variation of solvent | | | | | | |
| 25. | $NiN_x$@NC | DMF | TBHP (0.35 eq) | 60 | 4 | 55 |
| 26. | $NiN_x$@NC | THF | TBHP (0.35 eq) | 60 | 4 | 83 |
| 27. | $NiN_x$@NC | $H_2O$ | TBHP (0.35 eq) | 60 | 4 | 31 |
| 28. | $NiN_x$@NC | $CH_3CN$ | TBHP (0.35 eq) | 60 | 4 | 80 |
| 29. | $NiN_x$@NC | Methanol | TBHP (0.35 eq) | 60 | 4 | 35 |
| 30. | $NiN_x$@NC | Dioxane | TBHP (0.35 eq) | 60 | 4 | 98 |

Reaction conditions: Benzaldehyde (1 mmol), piperidine (1 mmol), catalyst (5 mg), TBHP (0.35 eq), dioxane (2 mL), 60 °C, and 4 h.

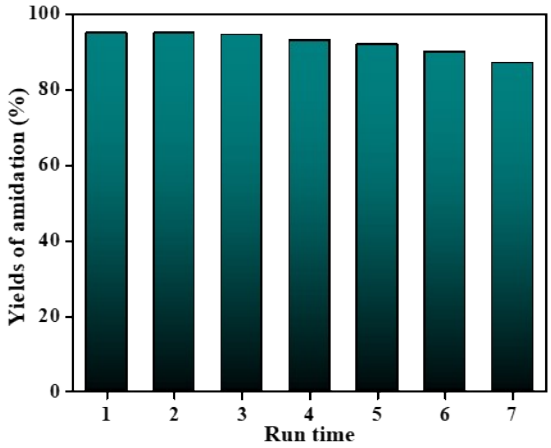



**Figure S13**. Recyclability of $NiN_x$@NC catalyst for amidation reaction.
Reaction conditions: Benzaldehyde (1 mmol), piperidine (1 mmol), catalyst (5 mg), TBHP (0.35 eq), dioxane (2 mL), 60 $^oC$, and 4 h.

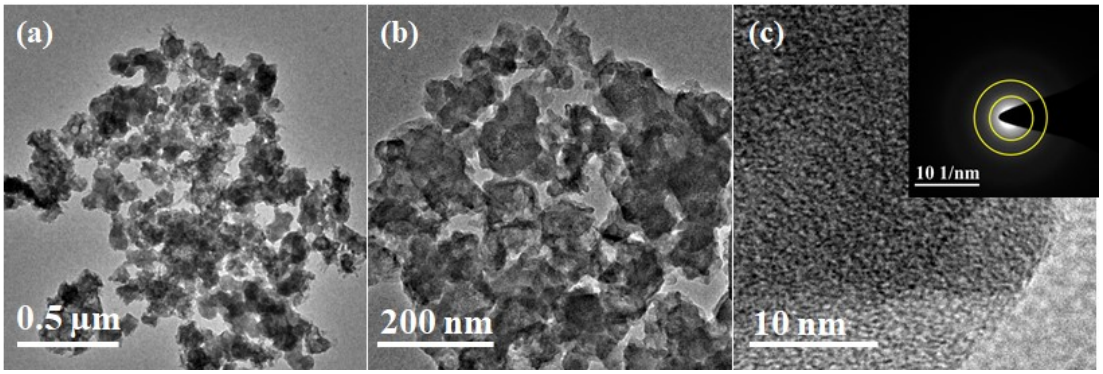



**Figure S14.** (a) & (b) shows the TEM images after the seven cycle of the $NiN_x$@NC catalyst for amidation reactions. (c) Image shows the HR-TEM image of the $NiN_x$@NC catalyst and inset iamge shows the SEAD pattern.

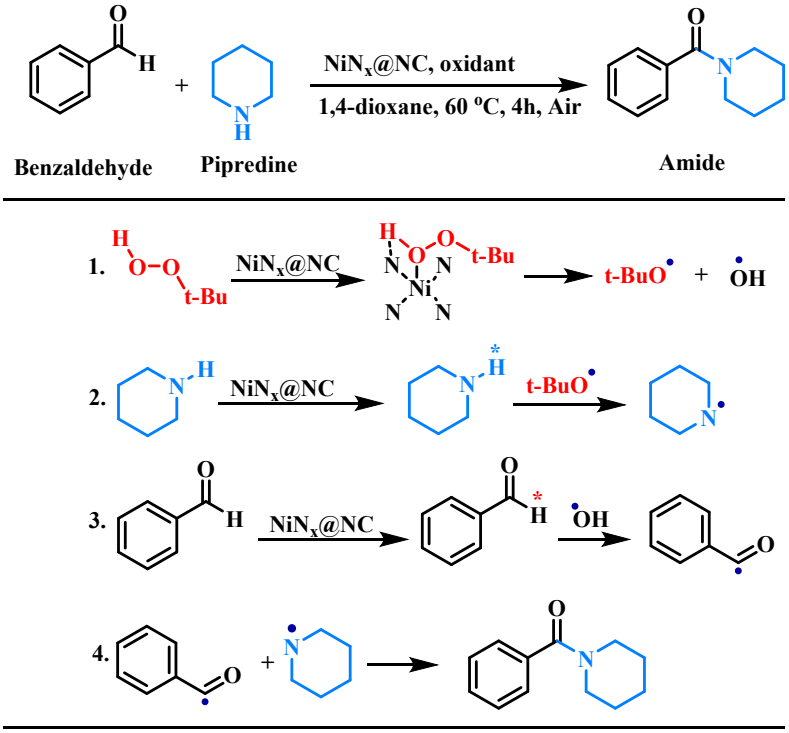



**Figure S15**. Reaction mechanism of for the amide bond formation reaction with $NiN_x$@NC catalyst.[S12]

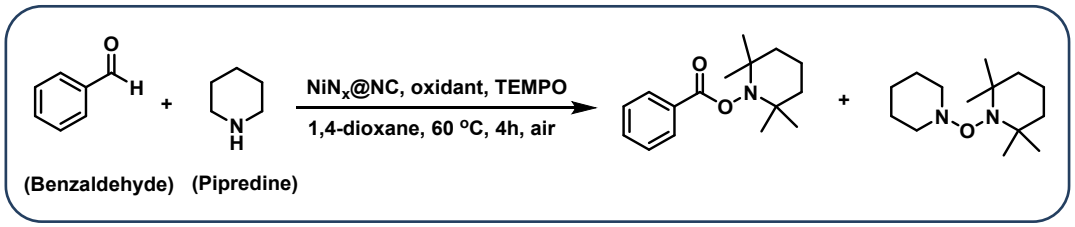



**Figure S16.** Trapping of acyl and piperidine radical by TEMPO.[S13, S14]

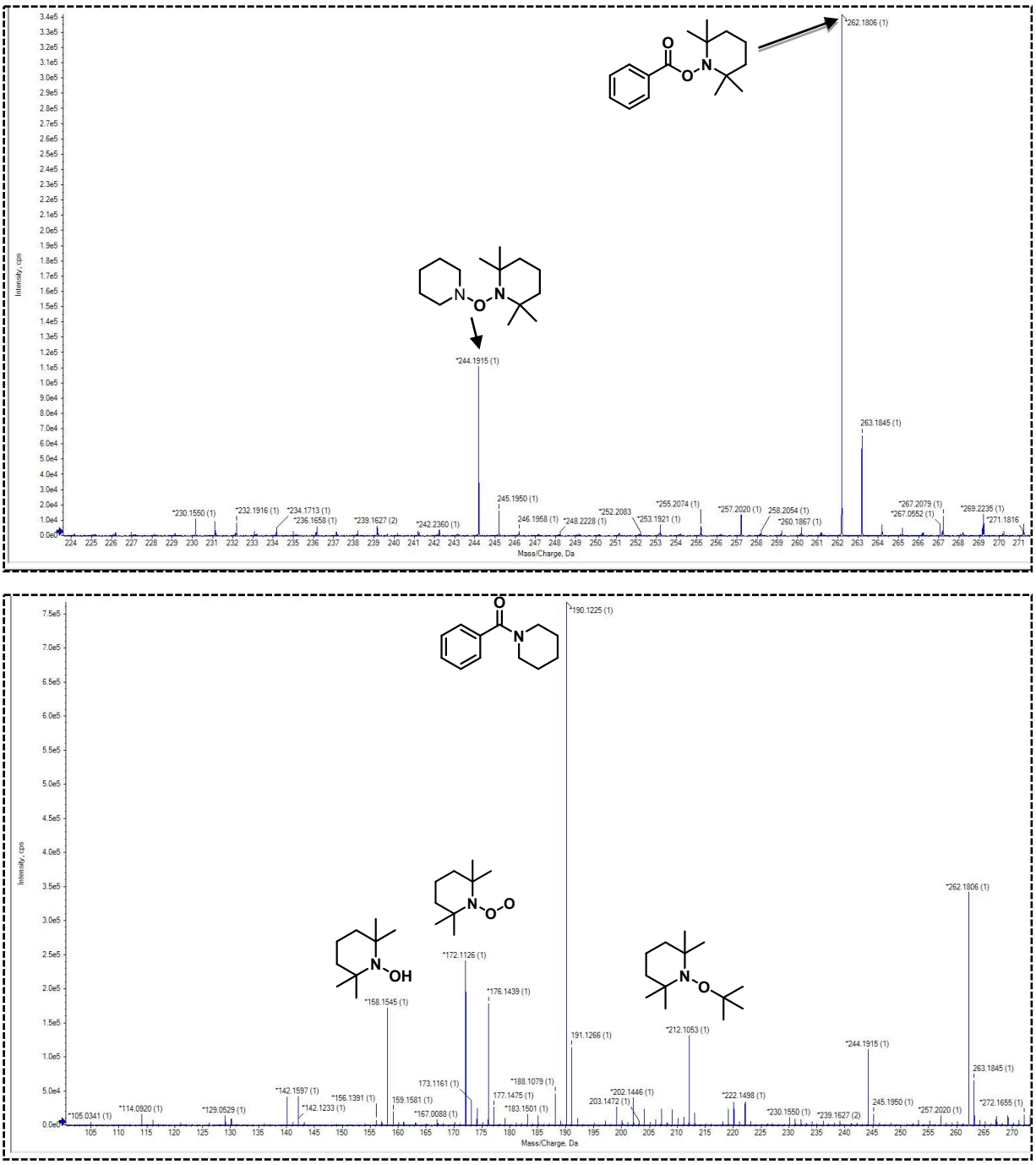



**Figure S17:** Mass spectrometry pattern of acyl and piperidine radical intermediate trapped by 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO).[S14, S13]

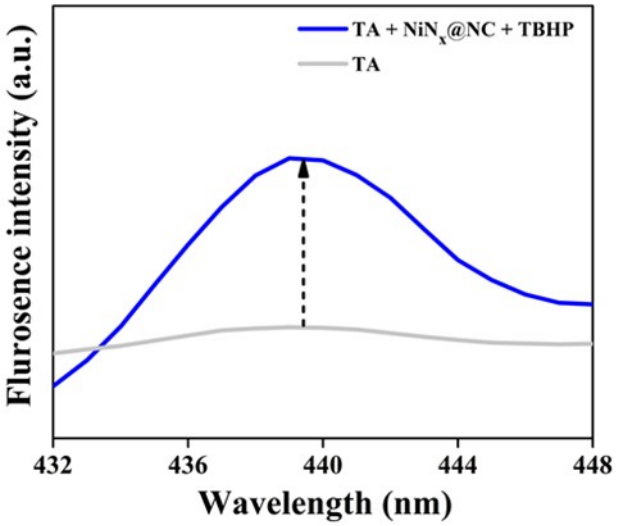
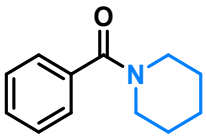
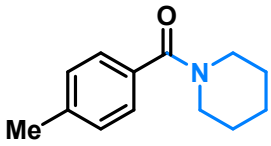
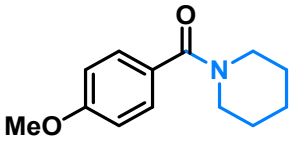
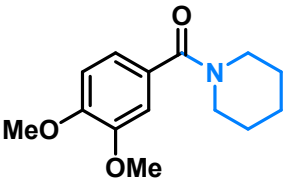
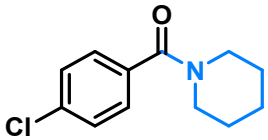
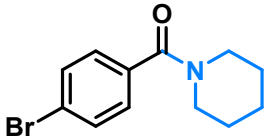



**Figure S18.** The detection of •OH radical in the reaction mixture of amidation reactions by the fluorescence spectroscopy (produced by TBHP with $NiN_x$@NC catalyzed activation) using terephthalic acid (TA). The presence of •OH in the reaction mixture was confirmed by a peak at 439.4 nm of TAOH.[S15]

**Table S2: $^{1}$H NMR and $^{13}$C NMR data of the amide products.**[S16,S17,S18,S19]

| | |
|---|---|
| **3a: phenyl(piperidin-1-yl) methanone**  | The reaction was carried out with 106.12 mg aldehyde and the titled product was obtained 185.5 mg, 98%. The residue was separated by silica gel column chromatography. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, $J$ = 3.9 Hz, 5H), 3.73 (m, 2H), 3.36 (m, 2H), 1.61 (d, $J$ = 79.3 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.41, 136.45, 129.37, 128.40, 126.81, 48.75, 43.19, 26.07, 25.60, 24.59. |
| **3b: piperidin-1-yl(p-tolyl) methanone**  | The reaction was carried out with 60 mg aldehyde and the titled product was obtained 90 mg, 89%. The residue was separated by silica gel column chromatography. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, $J$ = 8.0 Hz, 2H), 7.19 (d, $J$ = 7.8 Hz, 2H), 3.70 (m, 2H), 3.36 (m, 2H), 2.37 (s, 3H), 1.70 – 1.47 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.59, 139.45, 133.48, 128.98, 126.92, 24.61, 21.34. |
| **3c: (4-methoxyphenyl) (piperidin-1-yl)methanone**  | The reaction was carried out with 136.2 mg aldehyde and the titled product was obtained 188 mg, 86%. The residue was separated by silica gel column chromatography. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, $J$ = 5.5 Hz, 2H), 6.90 (d, $J$ = 5.4 Hz, 2H), 3.83 (s, 3H), 3.56 (dd, $J$ = 97.8, 19.7 Hz, 4H), 1.64 (d, $J$ = 43.8 Hz, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.38, 160.56, 128.88, 128.63, 113.67, 55.35, 24.68. |
| **3d: (3,4-dimethoxyphenyl) (piperidine-1-yl)methanone**  | The reaction was carried out with 83.09 mg aldehyde according to the procedure. The titled compound was obtained 100.97 mg, 81%. The residue was separated by silica gel column chromatography. $^{1}$H NMR (600 MHz, $CDCl_3$) δ 6.98 – 6.94 (m, 2H), 6.85 (d, 1H), 3.89 (d, 6H), 3.55 (t, 4H), 1.63 (m, 6H). $^{13}$C NMR (150 MHz, $CDCl_3$) δ 170.24, 150.00, 148.84, 128.69, 119.78, 110.68, 110.47, 55.92, 24.60. |
| **3e: (4-chlorophenyl) (piperidin-1-yl) methanone**  | The reaction was carried out with 70.3 mg aldehyde according to the procedure. The titled compound was obtained 104 mg, 93%. The residue was separated by silica gel column chromatography. $^{1}$H NMR (CDCl3, 500 MHz): $\delta$ 7.36-7.42 (m, 4H), 3.71 (br s, 2H), 3.34 (br s, 2H), 1.53-1.70 (m, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 169.24, 135.41, 134.86, 128.69, 128.38, 48.77, 43.24, 26.55, 25.58, 24.54. |
| **3f: (4-bromophenyl) (piperidin-1-yl) methanone**  | The reaction was carried out with 93 mg aldehyde according to the procedure. The titled compound was obtained 120.7 mg, 90%. The residue was separated by silica gel column chromatography. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, $J$ = 8.3 Hz, 2H), 7.37 – 7.22 (m, 2H), 3.70 (br, s, 2H), 3.34 (br, s, 2H), 1.78 – 1.49 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.31, 135.26, 131.64, 128.59, 123.65, 48.80, 43.30, 26.01, 24.52. |
| **3g: (3-nitrophenyl) (piperidine-1-yl) methanone** | The reaction was carried out with 135.6 mg aldehyde according to the procedure. The titled compound was obtained 162 mg, 92%. |

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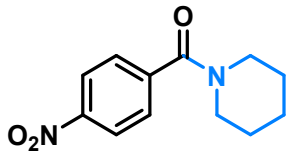
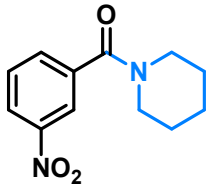
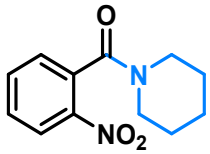
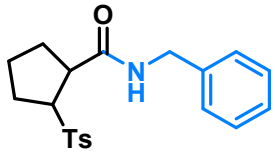
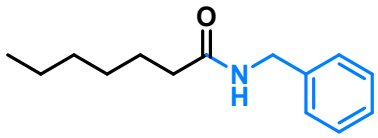
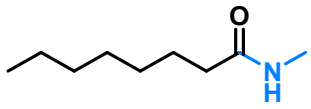
|  | The residue was separated by silica gel column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 1H), 7.56 (d, *J* = 8.7 Hz, 1H), 3.74 (s, 1H), 3.29 (s, 1H), 1.71 (s, 2H), 1.54 (s, 1H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.93, 148.21, 142.68, 127.81, 123.85, 48.66, 43.23, 26.51, 25.50, 24.39. |
| **3h: (3-nitrophenyl) (piperidine-1-yl) methanone**<br>  | The reaction was carried out with 117 mg aldehyde according to the procedure. The titled compound was obtained 178 mg, 93%. The residue was separated by silica gel column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.1 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.4 Hz, 1H), 3.74 (br s, 2H), 3.35 (br, s, 2H), 1.64 (m, *J* = 76.7 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.60, 148.07, 138.08, 132.90, 129.73, 124.22, 122.05, 48.84, 43.37, 26.52, 25.51, 24.41. |
| **3i: (2-nitrophenyl) (piperidin-1-yl) methanone**<br>  | The reaction was carried out with 135.6 mg aldehyde according to procedure. The titled compound was obtained 190 mg, 90%. The residue was separated by silica gel column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 1.3 Hz, 1H), 3.76 (s, 2H), 3.16 (t, *J* = 5.6 Hz, 2H), 1.77 – 1.44 (m, 6H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 166.24, 145.19, 134.40, 133.36, 129.56, 127.96, 124.69, 47.92, 42.70, 25.76, 25.08, 24.41. |
| **3j: N-benzyl-2-tosylcyclopentane-1-carboxamide**<br>  | The reaction was carried out with 65 mg aldehyde according to procedure. The titled compound was obtained 63.47 mg, 69%. The residue was separated by silica gel column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 4H), 7.38 – 7.29 (m, 14H), 4.52 (d, *J* = 5.6 Hz, 4H), 4.39 (s, 1H), 4.16 (d, *J* = 7.6 Hz, 2H), 3.60 – 3.49 (m, 2H), 3.19 (d, *J* = 6.0 Hz, 2H), 2.47 (s, 6H), 2.23 (s, 2H), 1.75 (t, *J* = 12.6 Hz, 2H), 1.63 (d, *J* = 7.5 Hz, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.22, 144.48, 137.96, 132.73, 130.02, 128.72, 127.90, 127.46, 62.69, 49.95, 43.58, 30.18, 24.42, 21.59. |
| **3k: N-benzylheptanamide**<br>  | The reaction was carried out with 57 mg aldehyde according to procedure. The titled compound was obtained 72.2 mg, 66%. The residue was separated by silica gel column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.20 – 8.19 (m, 1H), 7.34 – 7.31 (m, 2H), 7.28 (d, *J* = 6.8 Hz, 3H), 4.44 (s, 2H), 2.23 – 2.20 (m, 2H), 1.68 – 1.64 (m, 2H), 1.41 – 1.24 (m, 6H), 0.90 (d, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 173.07, 138.56, 128.65, 127.80, 127.40, 43.52, 39.14, 36.73, 31.48, 25.46, 22.39, 13.92. |
| **3l: N-methyloctanamide**<br>  | The reaction was carried out with 128.5 mg aldehyde according to procedure. The titled compound was obtained 100.8 mg, 64%. The residue was separated by silica gel column chromatography. $^1$H NMR (500 MHz, $CDCl_3$) δ 5.96 (s, 1H), 2.78 (d, *J* = 4.8 Hz, 3H), 2.19 – 2.12 (m, 2H), 1.64 – 1.56 (m, 2H), 1.31 – 1.22 (m, 8H), 0.86 (t, *J* = 6.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 174.04, 36.65, 31.67, 29.28, 29.00, 26.19, 25.80, 22.57, 14.02. |
| **4a: N-benzylbenzamide** | The reaction was carried out with 54.19 mg aldehyde according to procedure. The titled compound was obtained 96 mg, 89%. The residue was separated by silica gel column chromatography. |

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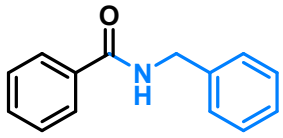
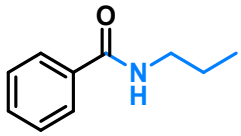
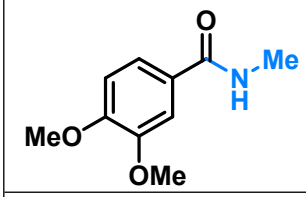
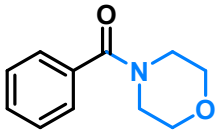
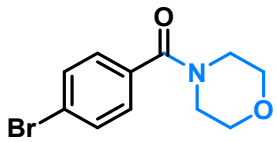
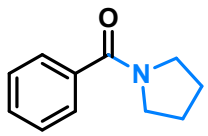
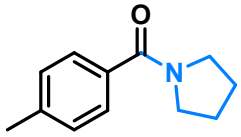
|  | $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.5 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.43 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.29 (m, 5H), 6.78 (s, 1H), 4.65 (s, 2H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.51, 138.31, 134.43, 131.54, 128.77, 128.58, 127.89, 127.57, 127.06, 44.11. |
| **4c: N-propylbenzamide**<br>  | The reaction was carried out with 106 mg aldehyde according to procedure. The titled compound was obtained 127.1 mg, 78%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.44 (d, 3H), 6.56 (s, 1H), 3.48 – 3.35 (m, 2H), 1.72 – 1.57 (m, 2H), 1.04 – 0.92 (m, 3H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.67, 134.89, 131.24, 128.47, 126.90, 41.77, 22.91, 11.44. |
| **4d: 3,4-dimethoxy-N-methyl benzamide**<br>  | The reaction was carried out with 84 mg aldehyde according to the procedure. The titled compound was obtained 76.9 mg, 78%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.27 (s, 1H), 7.67 (s, 1H), 7.41 (d, *J* = 24.1 Hz, 1H), 7.07 (s, 1H), 3.84 (d, *J* = 25.3 Hz, 6H), 2.96 (s, 3H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 168.35, 151.60, 148.81, 127.20, 121.83, 119.86, 110.53, 55.94, 26.83. |
| **4e: phenyl(morpholine) Methanone**<br>  | The reaction was carried out with 53.06 mg aldehyde according to procedure. The titled compound was obtained 86.05 mg, 90%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 5H), 3.81 – 3.42 (t, 8H).<br>$^{13}$C NMR (150 MHz, $CDCl_3$) δ 163.46, 128.26, 122.89, 121.55, 120.07, 59.87, 41.24. |
| **4f: (4-bromophenyl)(morpholine) methanone**<br>  | The reaction was carried out with 93 mg aldehyde according to procedure. The titled compound was obtained 122.2 mg, 90%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 6.5 Hz, 2H), 3.84 (dd, *J* = 2.8, 1.1 Hz, 2H), 3.71 (s, 2H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 170.46, 160.93, 129.21, 127.32, 113.81, 66.92, 55.36. |
| **4g: phenyl(pyrrolidin-1-yl) methanone**<br>  | The reaction was carried out with 56.06 mg aldehyde according to the procedure. The titled compound was obtained 77.10 mg, 88%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.36 (m, 3H), 3.64 (t, *J* = 7.0 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 1.97 – 1.93 (m, 2H), 1.86 (m, 2H).<br>$^{13}$C NMR (150 MHz, $CDCl_3$) δ 169.81, 137.10, 129.81, 128.24, 127.06, 49.63, 46.20, 26.35, 24.43.<br>Yield of product: 123.5 mg, 88%. |
| **4h: pyrrolidin-1-yl(p-tolyl)methanone**<br>  | The reaction was carried out with 120.15 mg aldehyde according to the procedure. The titled compound was obtained 166 mg, 88%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 3.64 (t, *J* = 6.8 Hz, 2H), 3.44 (t, *J* = 6.5 Hz, 2H), 2.37 (s, 3H), 1.97 – 1.91 (m, 2H), 1.89 – 1.82 (m, 2H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.84, 139.87, 134.31, 128.80, 127.21, 49.63, 46.18, 26.40, 24.44, 21.36. |

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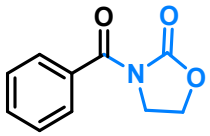
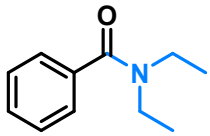
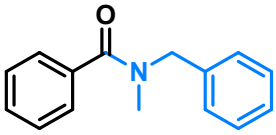
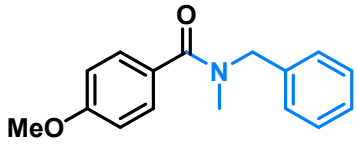
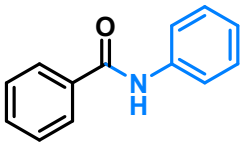
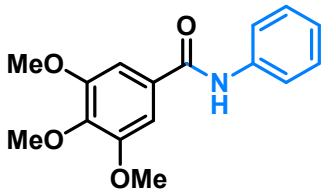
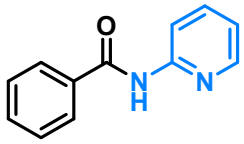
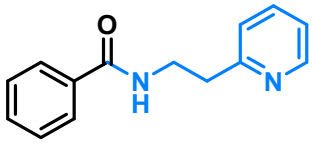
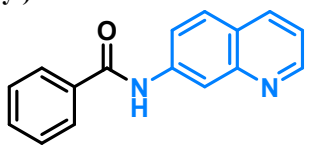
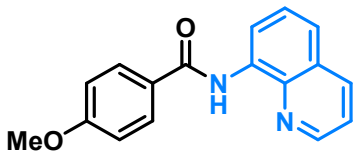
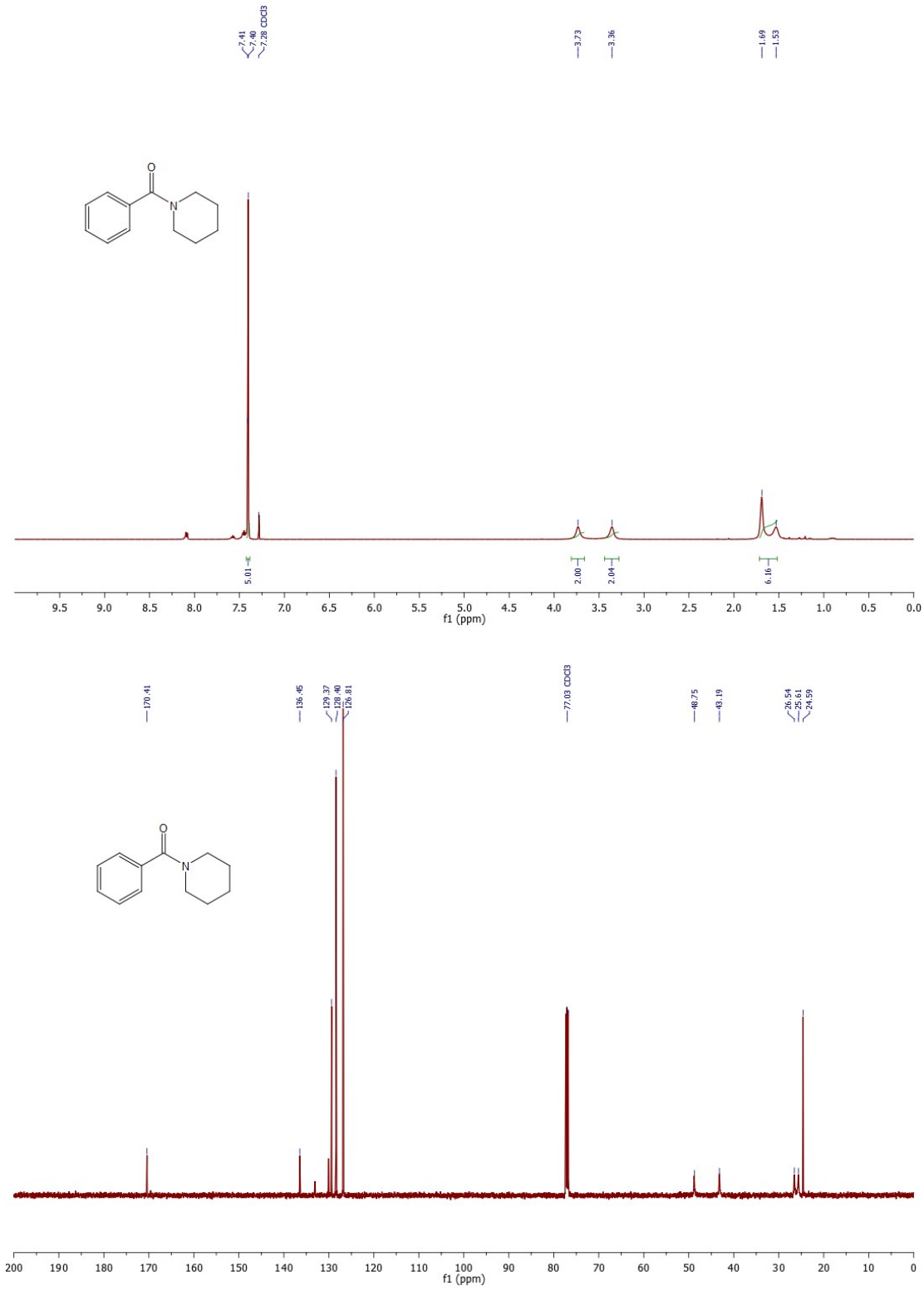
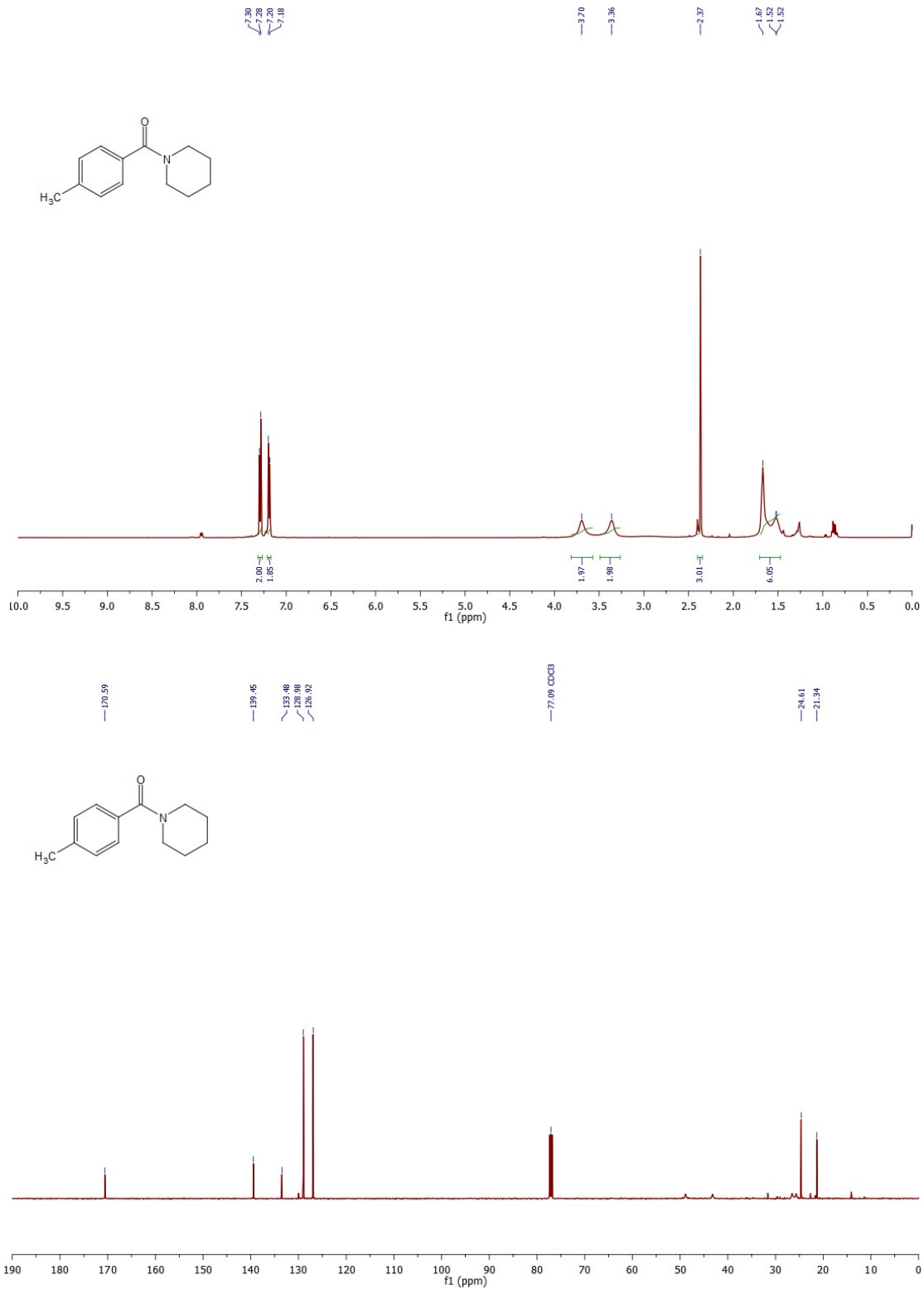
| **4i: 3-benzoyloxazolidin-2-one**  | The reaction was carried out with 106.5 mg aldehyde according to procedure. The titled compound was obtained 163 mg, 83%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.49 (t, *J* = 7.8 Hz, 2H), 4.18 (t, *J* = 7.8 Hz, 2H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 169.81, 153.24, 132.66, 132.41, 129.09, 127.89, 62.27, 43.72. |
| **4j: N,N-diethylbenzamide**  | The reaction was carried out with 106.5 mg aldehyde according to procedure. The titled compound was obtained 161.40 mg, 91%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 5H), 3.42 (d, 4H), 1.19 (d, 6H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 171.30, 137.32, 129.07, 128.38, 126.28, 43.26, 39.23, 14.23, 12.90. |
| **4k: N-benzyl -N-methylbenzamide**  | The reaction was carried out with 53 mg aldehyde according to procedure. The titled compound was obtained 100.25 mg, 89%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (600 MHz, $CDCl_3$) δ 7.47 (d, 2H), 7.38 (m, 6H), 7.32 (d, 1H), 7.19 (d, 1H), 4.79 (s, 2H), 3.06 (s, 3H).<br>$^{13}$C NMR ($CDCl_3$, 150 MHz): *δ* 160.51, 136.47, 130.24, 129.01, 128.57, 128.37, 128.15, 127.23, 126.41, 55.16, 35.14. |
| **4l: N-benzyl-4-methoxy-N-methylbenzamide**  | The reaction was carried out with 68 mg aldehyde according to procedure. The titled compound was obtained 112.2 mg, 88%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 3H), 7.31 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 6.9 Hz, 2H), 4.66 (s, 2H), 3.83 (s, 3H), 2.98 (s, 3H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 160.73, 137.08, 129.63, 128.99, 128.00, 126.93, 113.69, 55.33, 50.81, 37.07. |
| **4m: N-phenylbenzamide**  | The reaction was carried out with 53 mg aldehyde according to procedure. The titled compound was obtained 80.9 mg, 82%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (d, 2H), 7.40-7.45 (m, 5H), 7.17 (t, 1H), 7.09 (d, 2H).<br>$^{13}$C NMR (125 MHz, CDCl3) δ 166.51, 137.32, 136.80, 132.13, 130.18, 129.90, 128.12, 124.30, 122.53, 60.95, 56.36. |
| **4n: 3,4,5-trimethoxy-N-phenylbenzamide**  | The reaction was carried out with 50 mg aldehyde according to procedure. The titled compound was obtained 54.9 mg, 75%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.65 (d, *J* = 7.8 Hz, 4H), 7.37 (dd, *J* = 17.0, 9.0 Hz, 4H), 7.17 (dd, *J* = 14.0, 6.6 Hz, 2H), 7.09 (s, 4H), 3.90 (t, *J* = 7.2 Hz, 19H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.65, 153.32, 141.20, 137.93, 130.48, 129.09, 124.61, 120.30, 104.53, 60.95, 56.36. |
| **4o: N-(pyridine-2-yl)-benzamide** | The reaction was carried out with 53 mg aldehyde according to procedure. The titled compound was obtained 80.28 mg, 81%. The residue was separated by silica gel column chromatography.<br>$^1$H NMR (600 MHz, $CDCl_3$) δ 9.33 (s, 1H), 8.45 (d, *J* = 8.4 Hz, |

| | |
|---|---|
|  | 1H), 8.23 (d, *J* = 4.8 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.78 (t, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.08 (dd, *J* = 7.2, 5.0 Hz, 1H).<br>$^{13}$C NMR (150 MHz, $CDCl_3$) δ 166.08, 151.76, 147.47, 138.75, 134.28, 132.23, 128.77, 127.44, 119.88, 114.57. |
| **4p: N-(2-(pyridine-2-yl)benzamide**<br>  | The reaction was carried out with 53 mg aldehyde according to procedure. The titled compound was obtained 81.30 mg, 72%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 4.2 Hz, 1H), 7.79 (d, J = 8.5 Hz, 2H), 7.64 (m, 1H), 7.59 (s, 1H), 7.48 (dd, J = 8.2, 6.4 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.24 – 7.16 (m, 2H), 3.88 (t, J = 12.3, 5.6 Hz, 2H), 3.12 (t, J = 6.3 Hz, 2H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 167.31, 159.84, 149.10, 136.83, 134.79, 131.23, 128.47, 126.93, 123.59, 121.69, 77.06, 39.22, 36.61. |
| **4q: 3p. 1-phenyl-2-(quinolin-7-yl)ethan-1-one**<br>  | The reaction was carried out with 37 mg aldehyde according to procedure. The titled compound was obtained 60.5 mg, 70%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.77 (s, 2H), 8.97 (d, *J* = 7.6 Hz, 2H), 8.86 (s, 2H), 8.19 (t, *J* = 7.7 Hz, 2H), 8.12 (d, *J* = 7.3 Hz, 4H), 7.58 (d, *J* = 9.5 Hz, 11H), 7.48 (dd, *J* = 7.5, 4.7 Hz, 2H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.46, 148.30, 138.82, 136.39, 135.21, 134.63, 131.84, 128.81, 128.02, 127.48, 127.31, 121.69, 116.56. |
| **4r: 4-methoxy-N-(quinolone-8-yl) benzamide**<br>  | The reaction was carried out with 34 mg aldehyde according to the procedure. The titled compound was obtained 47.2 mg, 68%. The residue was separated by silica gel column chromatography.<br>$^{1}$H NMR (500 MHz, $CDCl_3$) δ 10.70 (s, 1H), 8.95 (d, *J* = 7.6 Hz, 1H), 8.87 (d, *J* = 4.2 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H).<br>$^{13}$C NMR (125 MHz, $CDCl_3$) δ 165.03, 162.54, 148.22, 138.81, 136.39, 134.80, 132.83, 129.19, 128.03, 127.52, 121.64, 121.40, 116.39, 114.01, 55.48. |

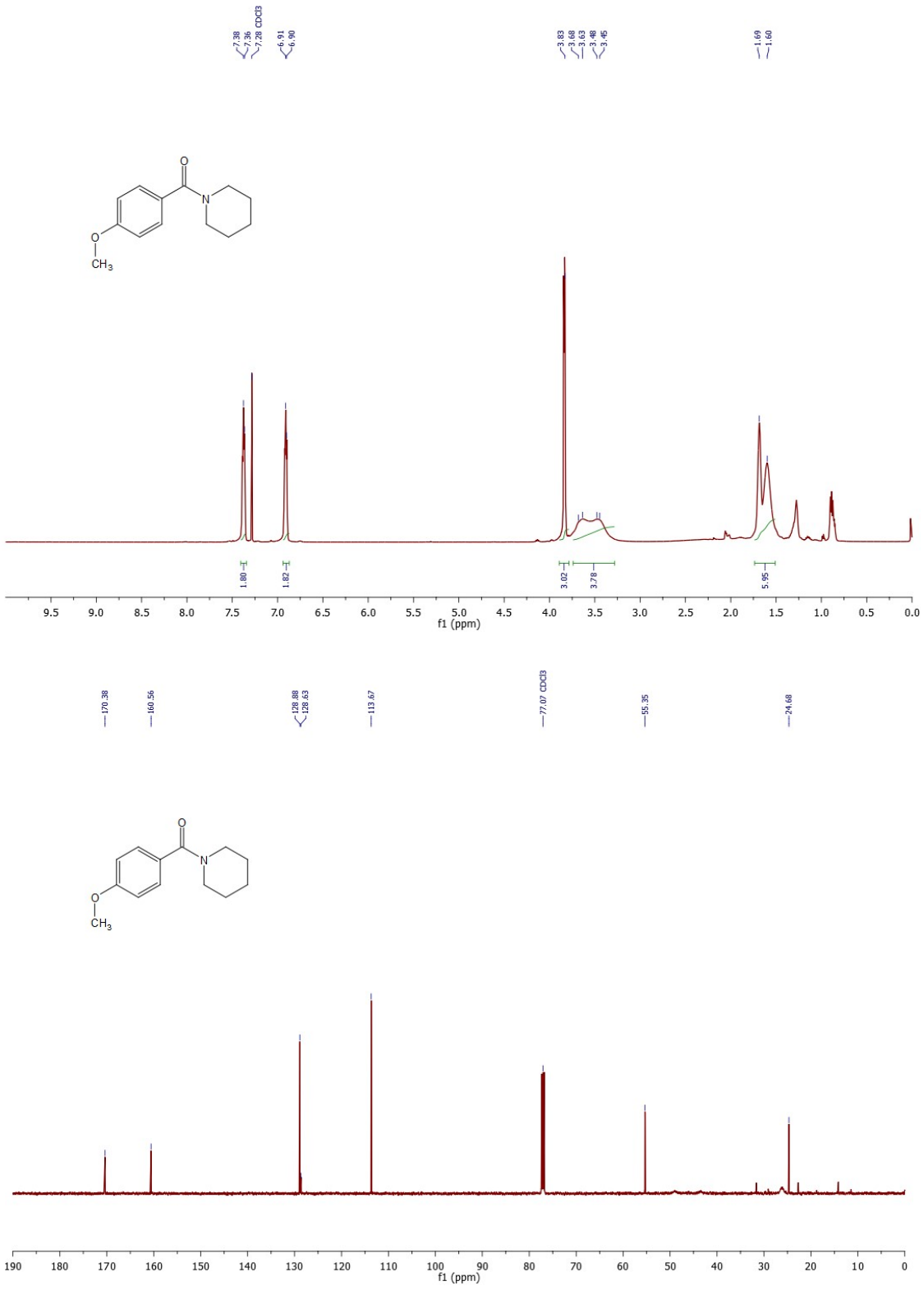
**$^{1}$H NMR and $^{13}$C NMR spectra of product 3a.**



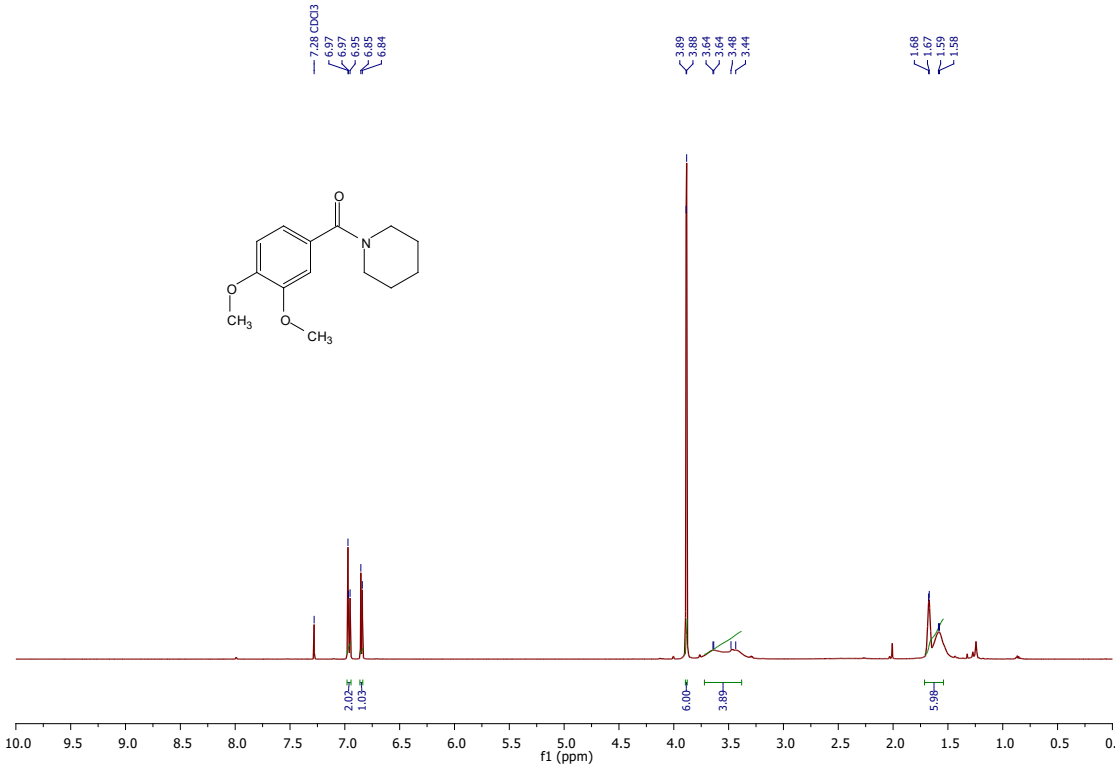

**$^{1}$H NMR and $^{13}$C NMR spectra of product 3b.**

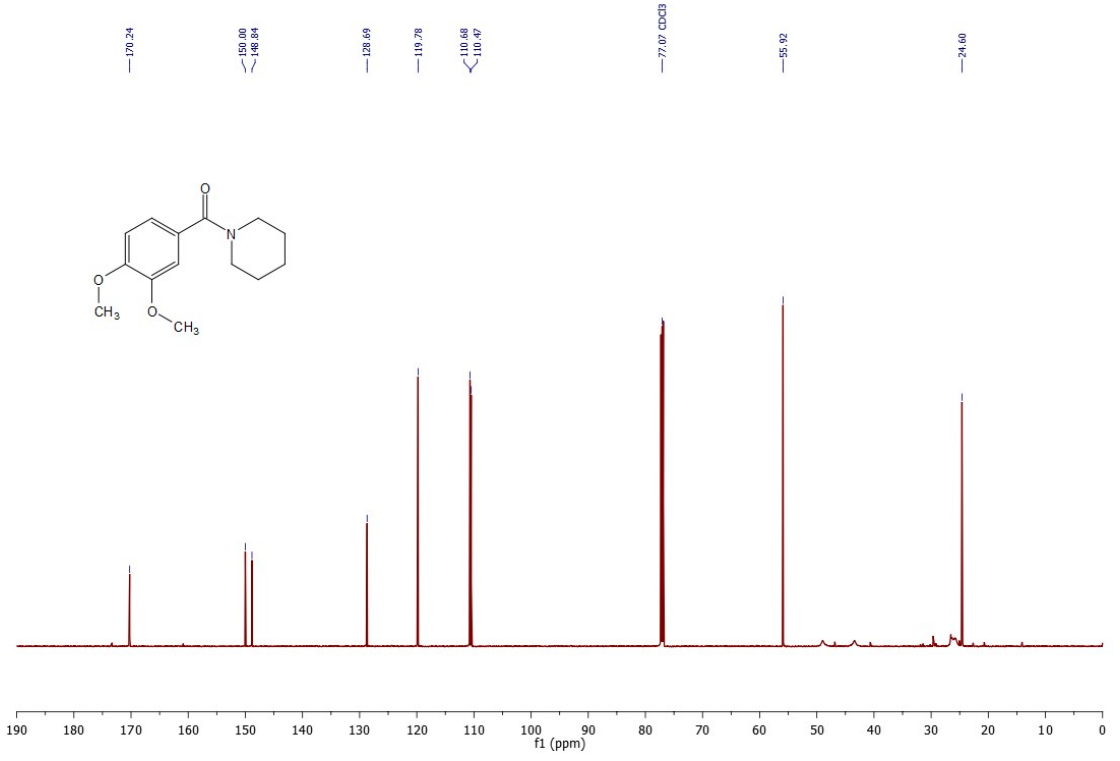



**$^{1}$H NMR and $^{13}$C NMR spectra of product 3c.**

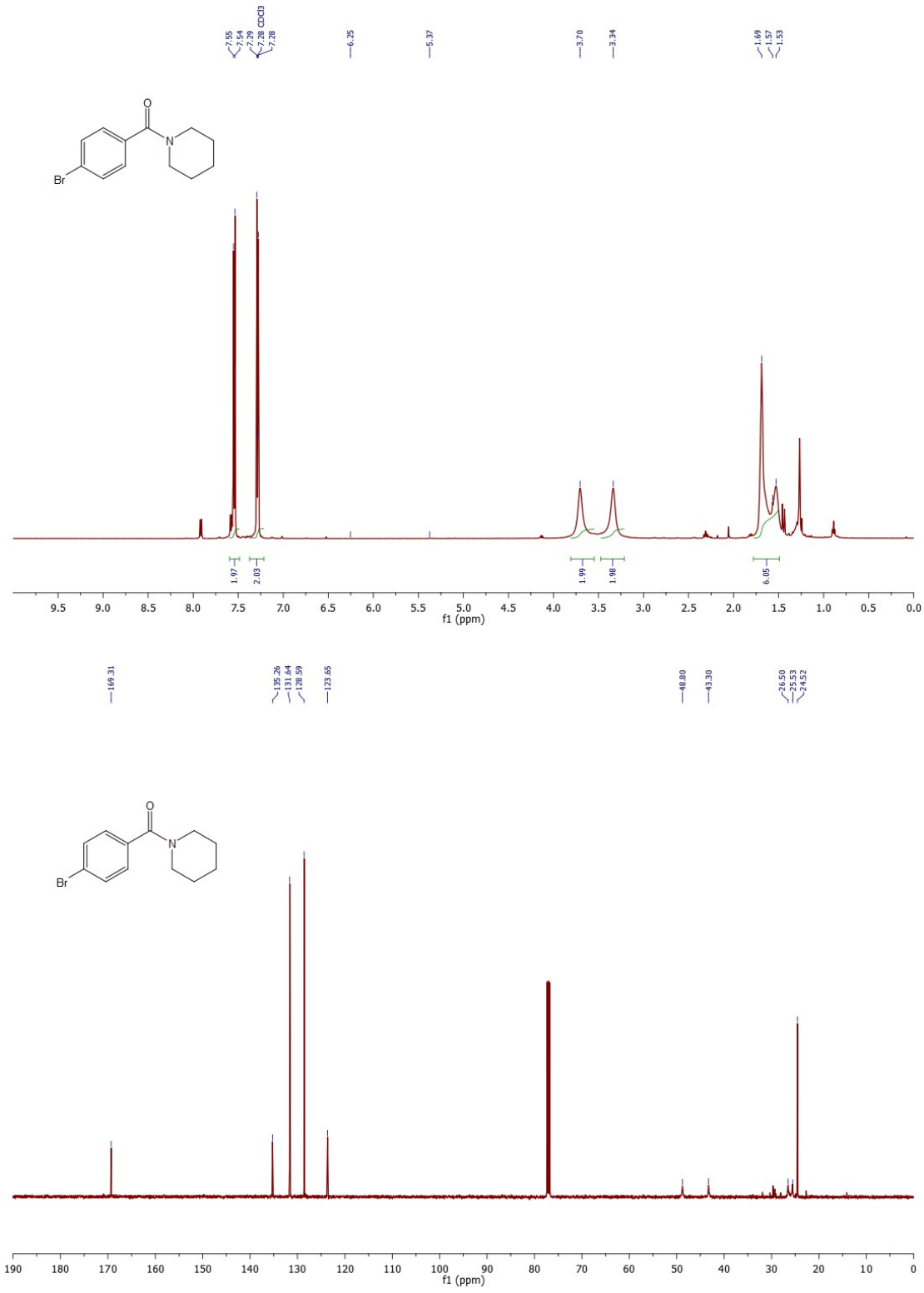



**$^{1}$H NMR and $^{13}$C NMR spectra of product 3d.**



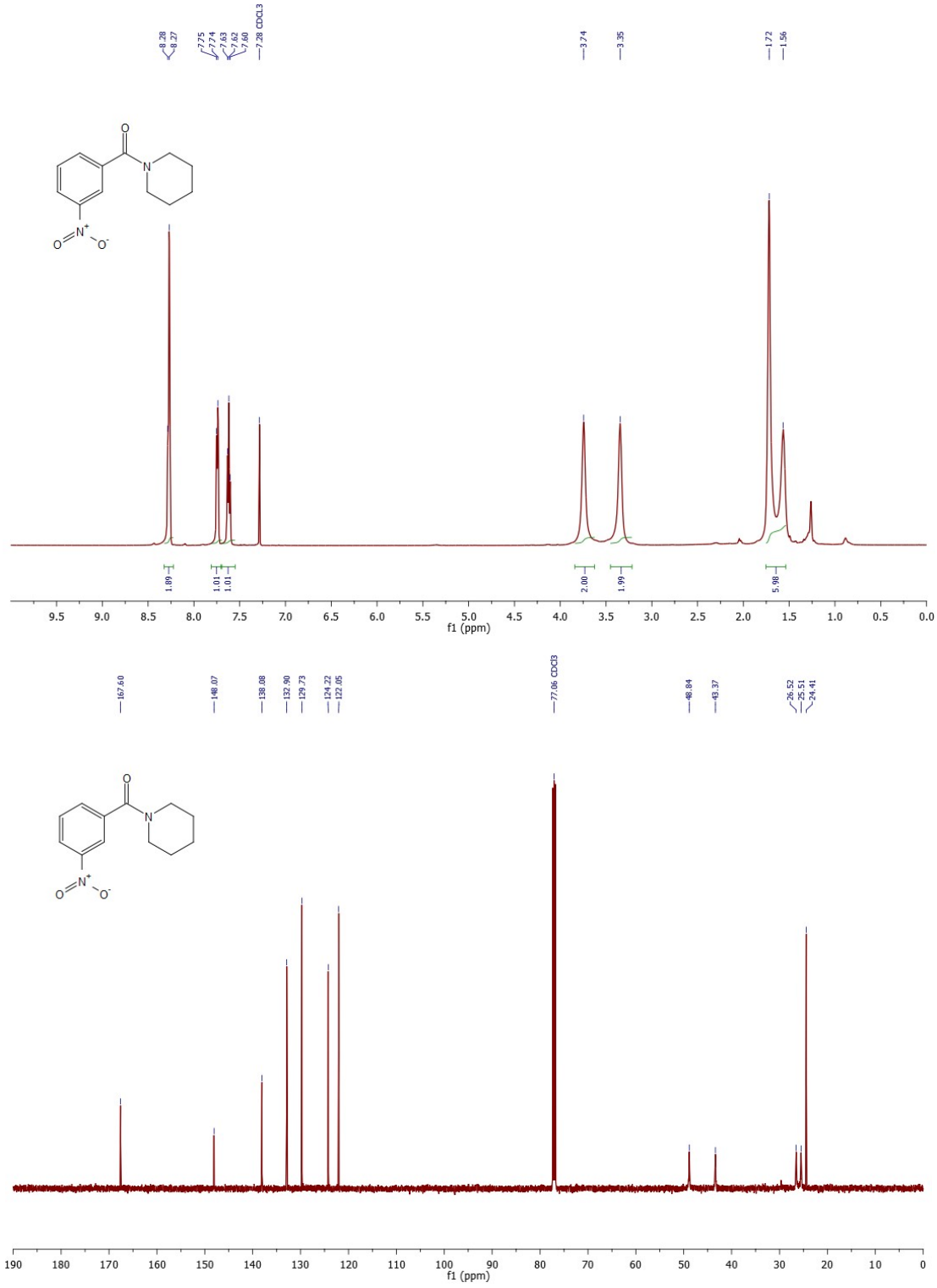




**$^{1}$H NMR and $^{13}$C NMR spectra of product 3f.**

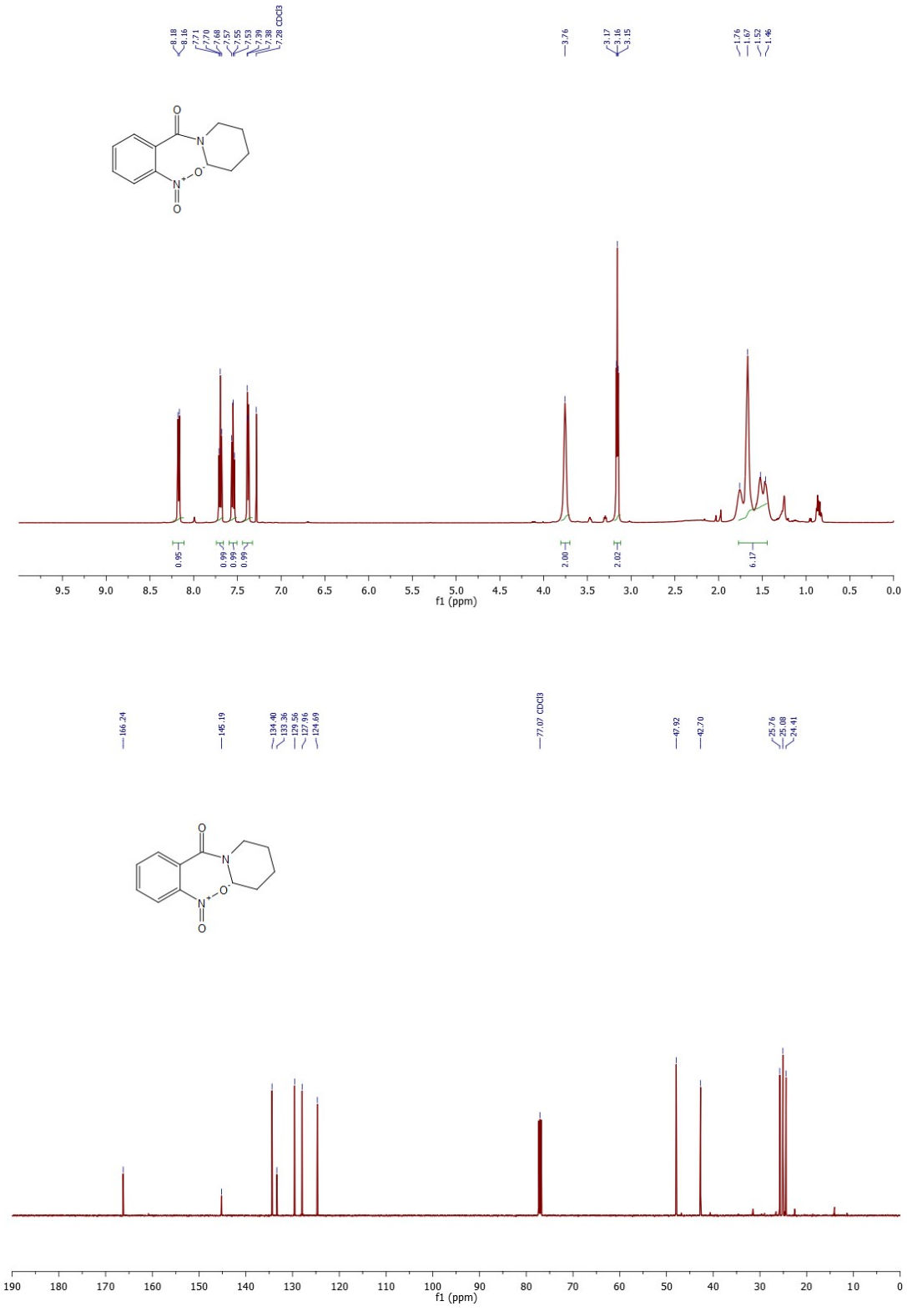



**$^{1}$H NMR and $^{13}$C NMR spectra of product 3g.**

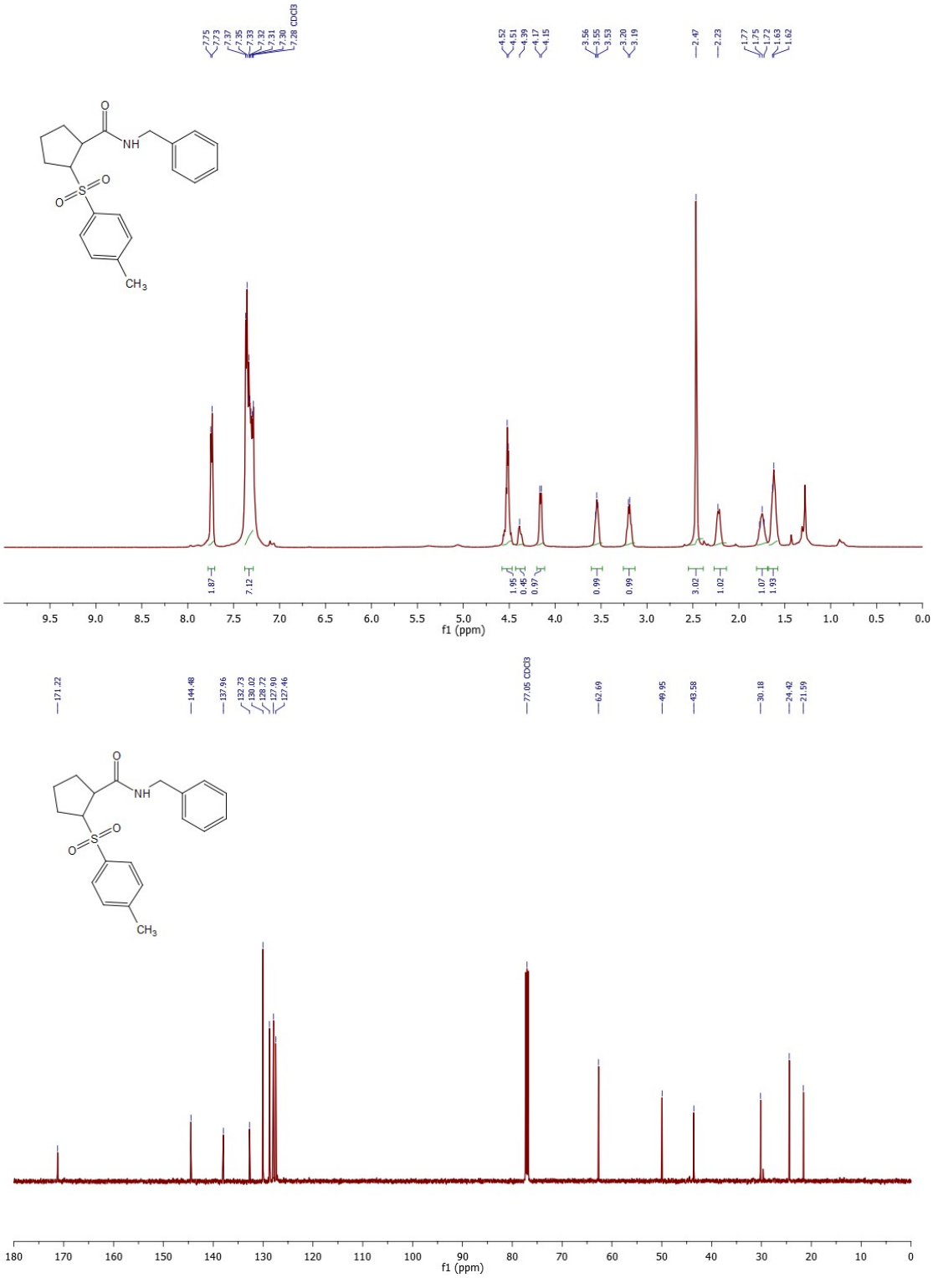

**$^{1}$H NMR and $^{13}$C NMR spectra of product 3h.**




**$^{1}$H NMR and $^{13}$C NMR spectra of product 3i.**

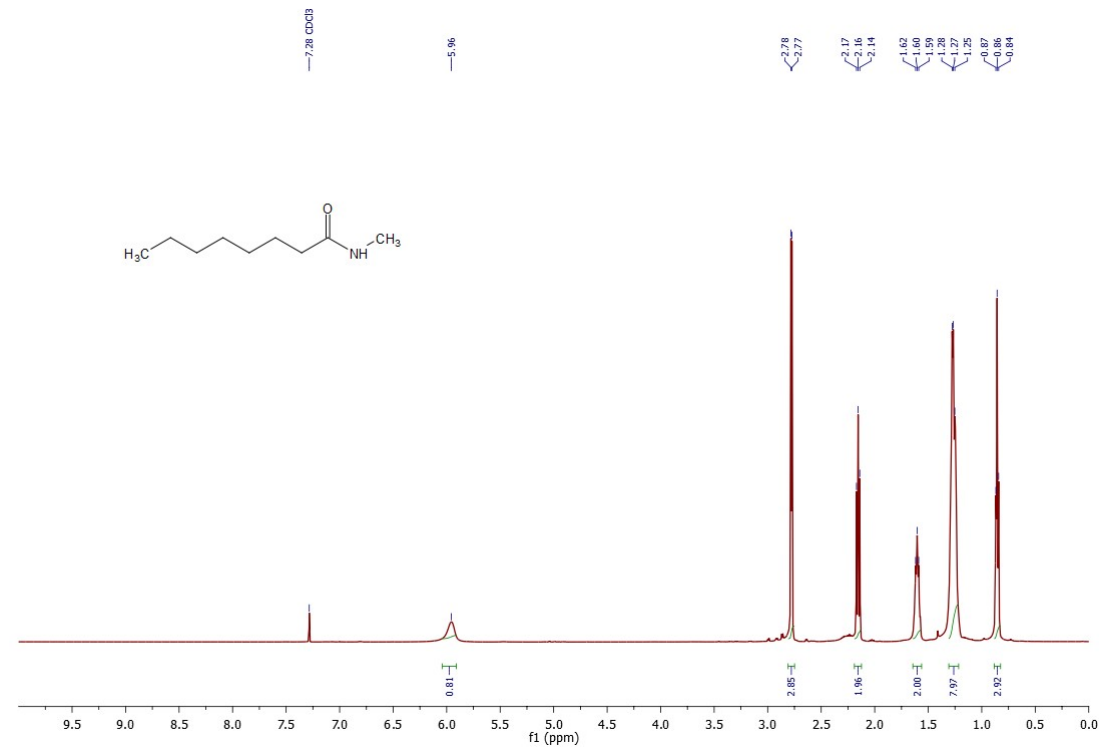


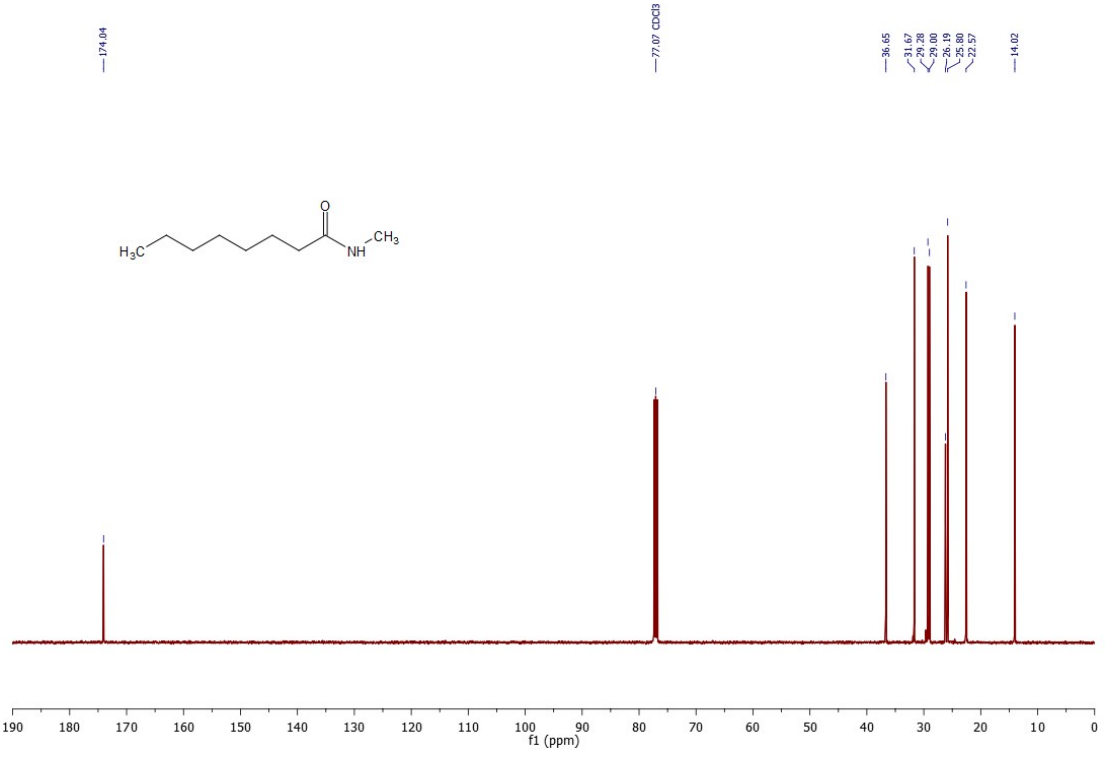

**$^{1}$H NMR and $^{13}$C NMR spectra of product 3j.**



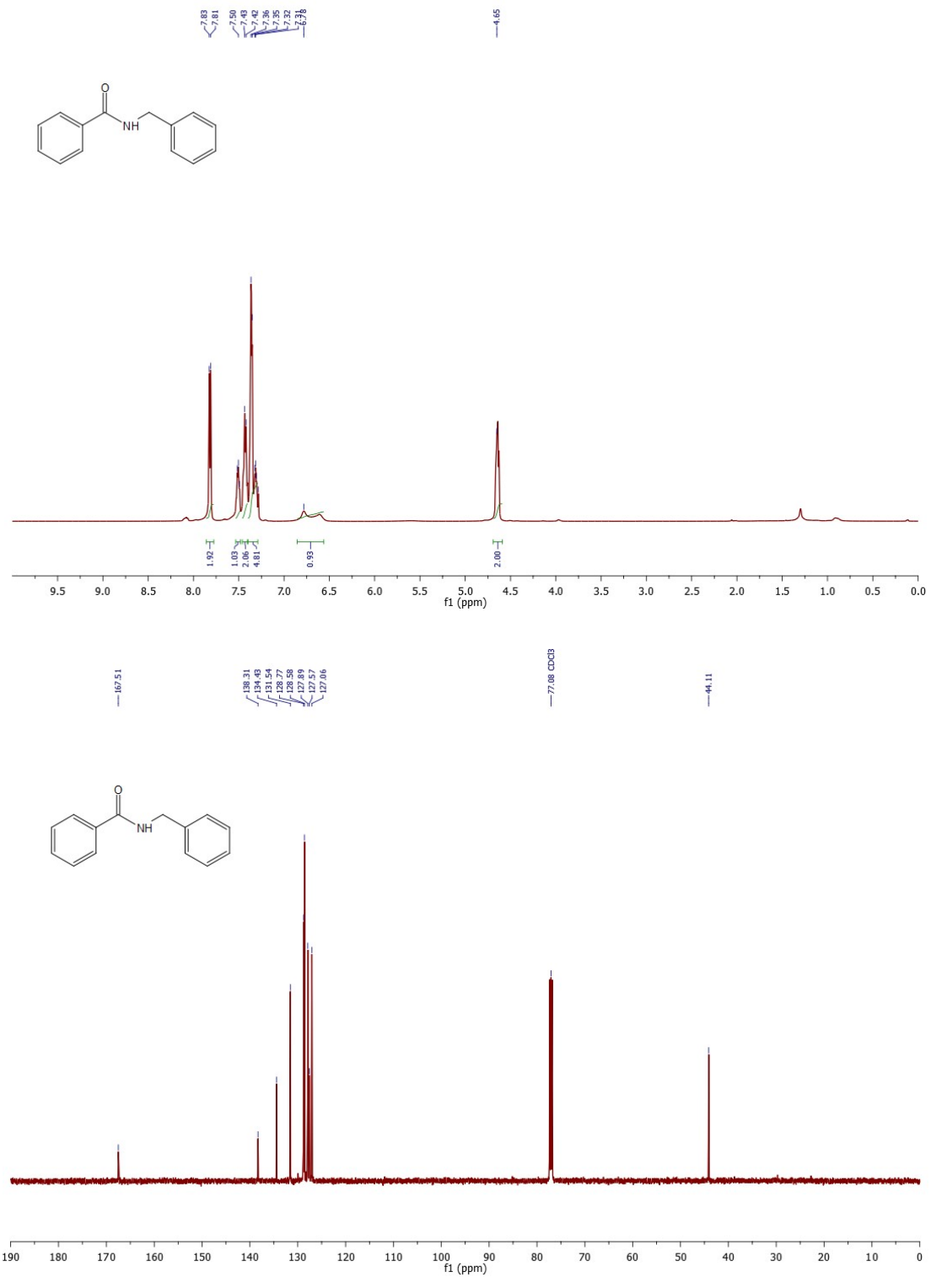

**$^{1}$H NMR and $^{13}$C NMR spectra of product 3k.**


**$^{1}$H NMR and $^{13}$C NMR spectra of product 3l.**

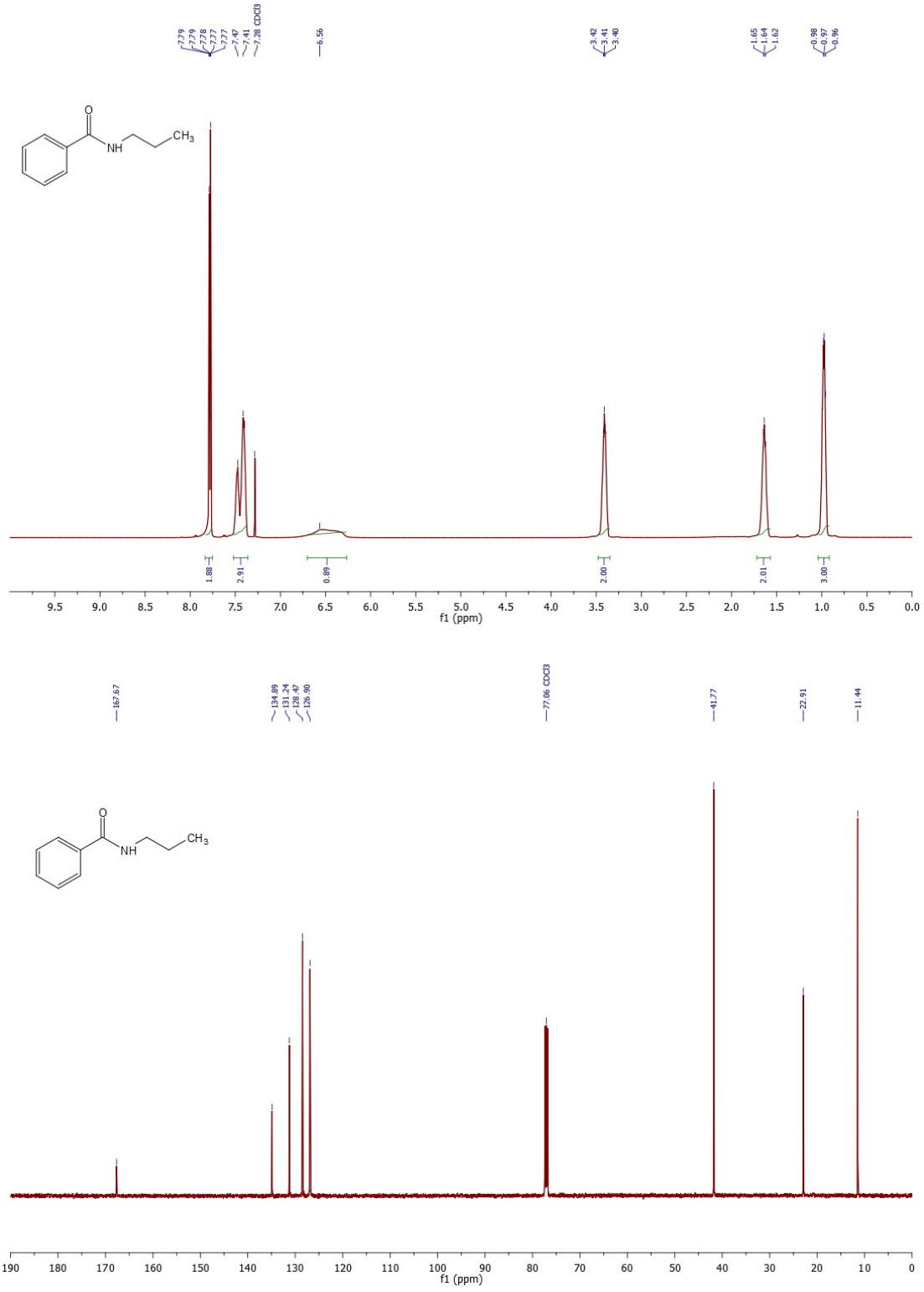


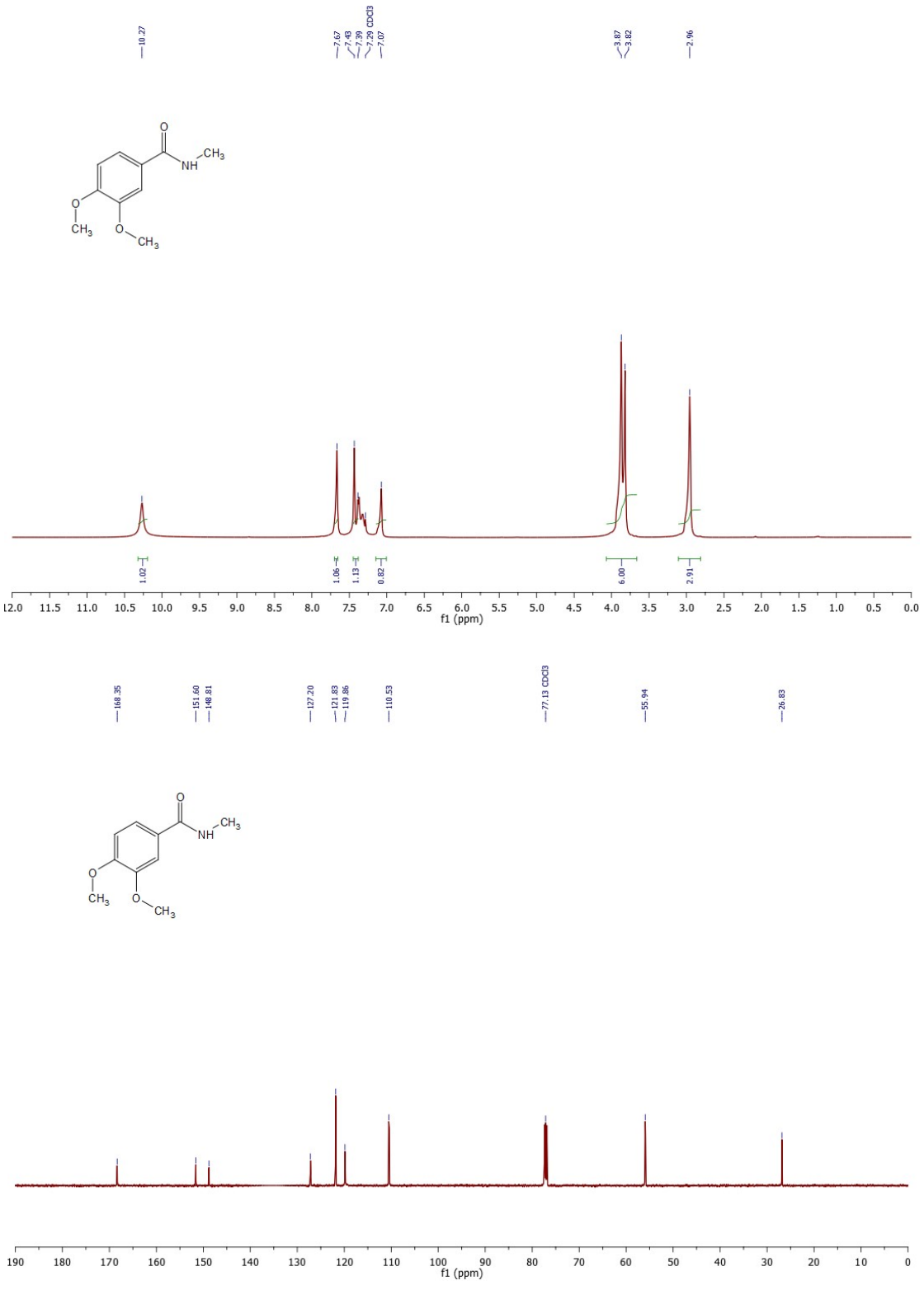

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4a.**



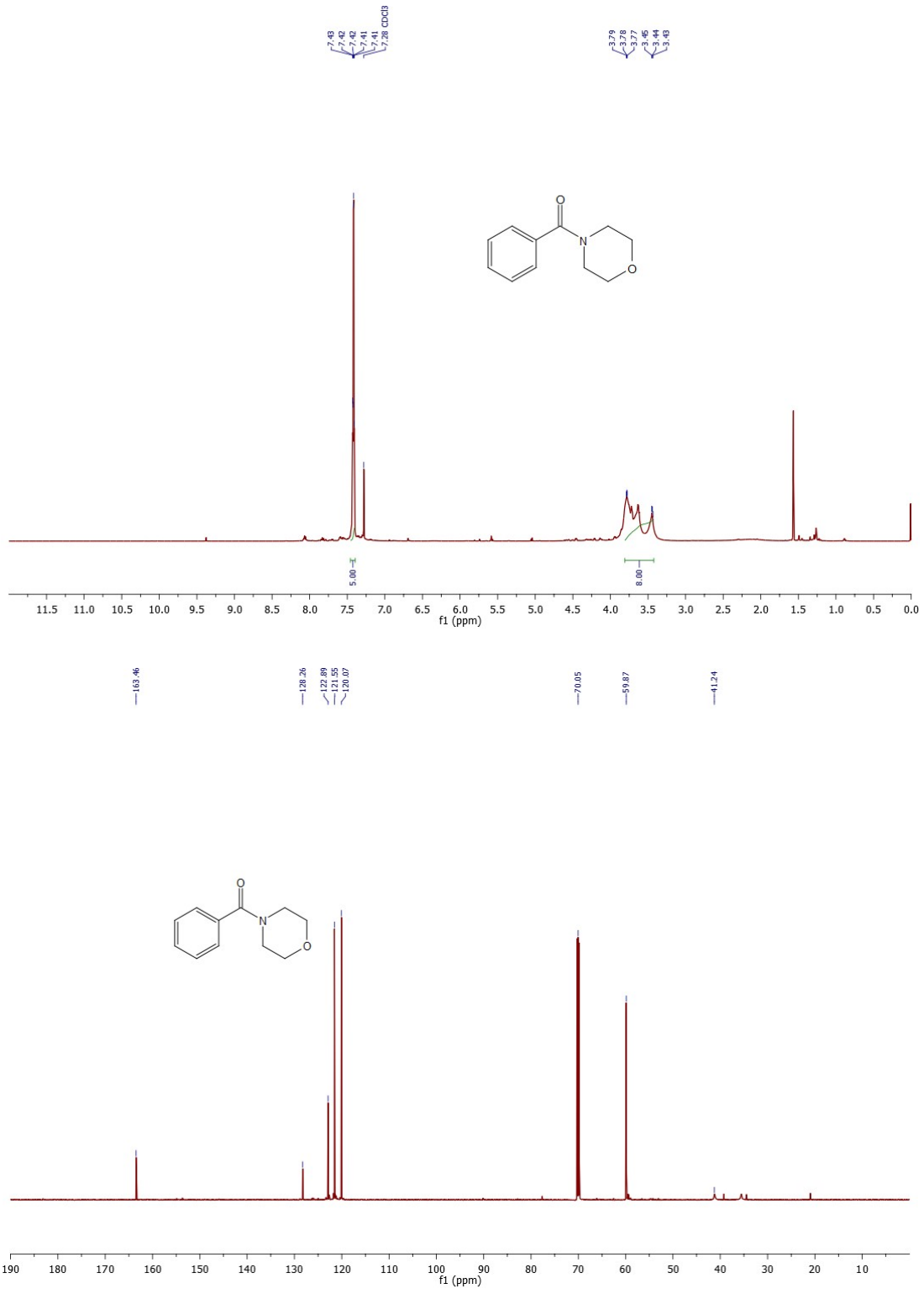

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4c.**



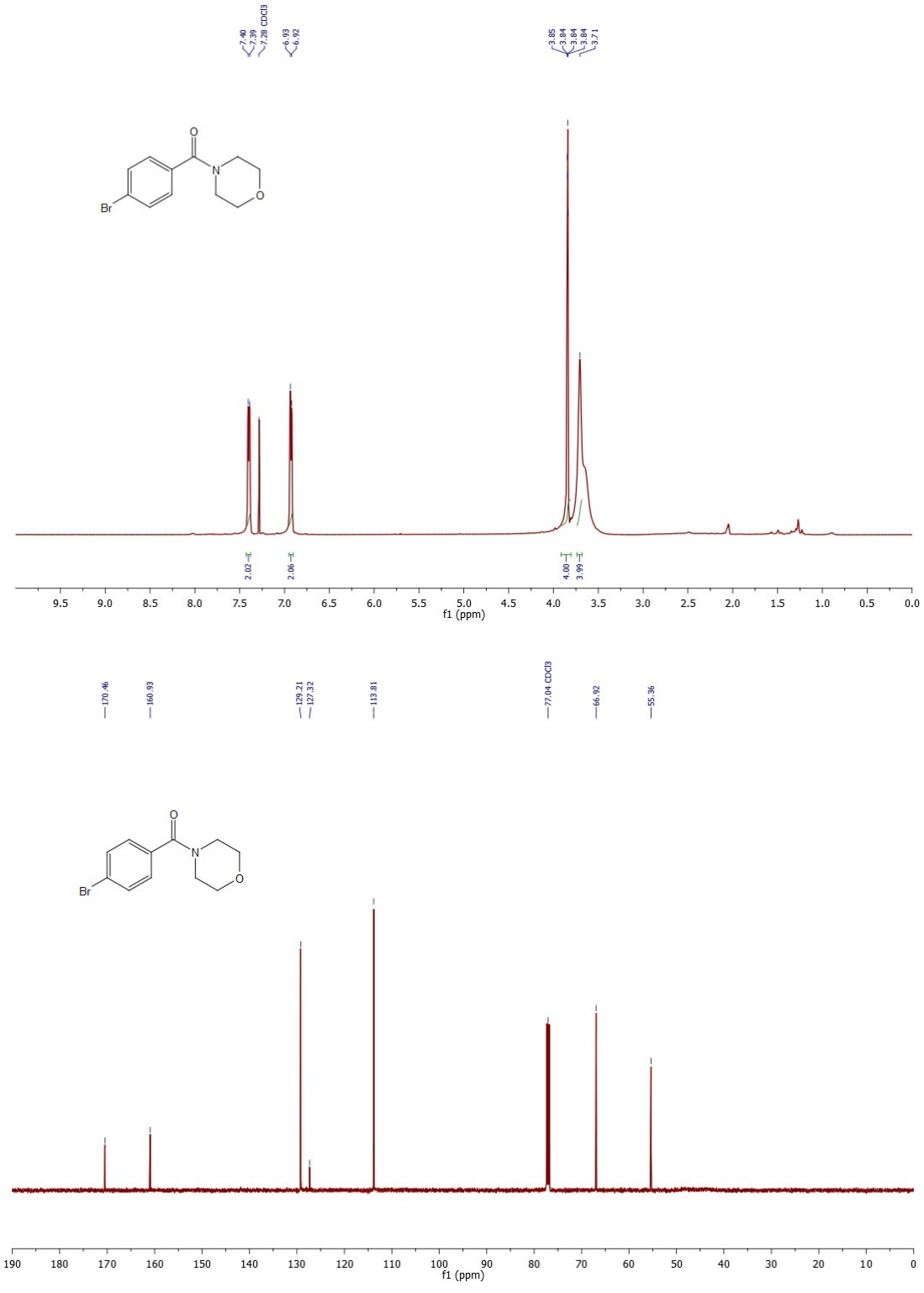

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4d.**



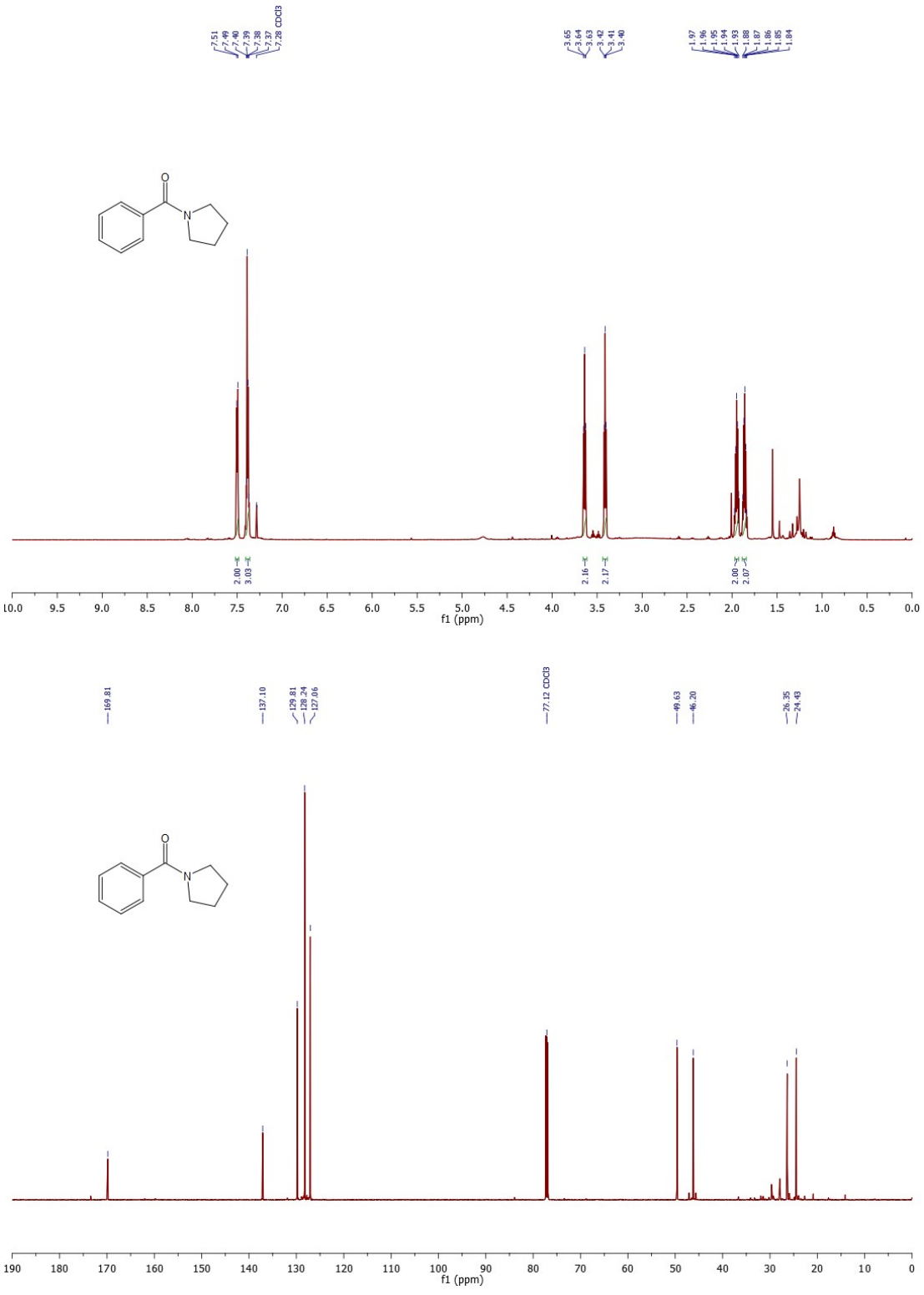

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4e.**



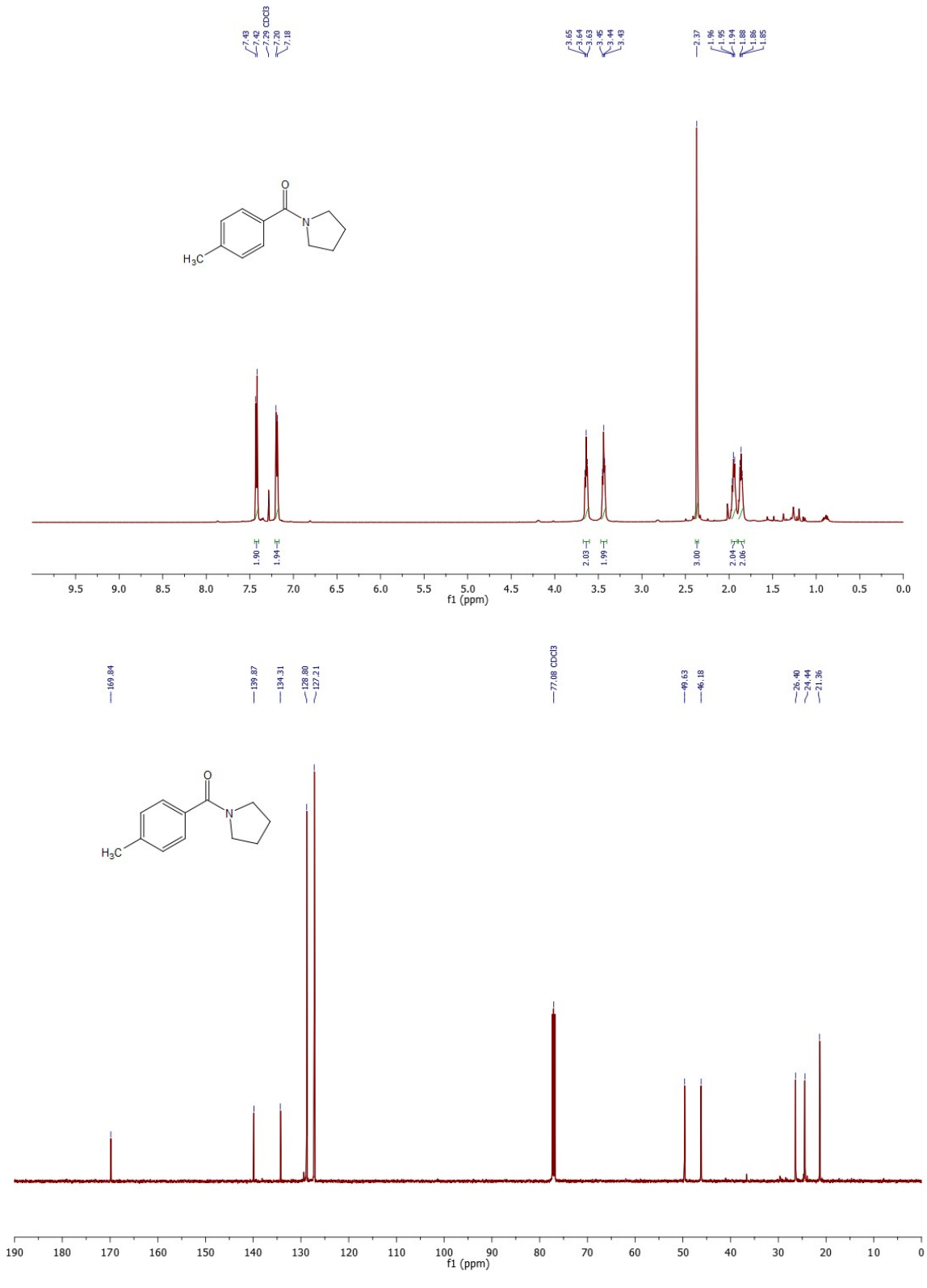

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4f.**



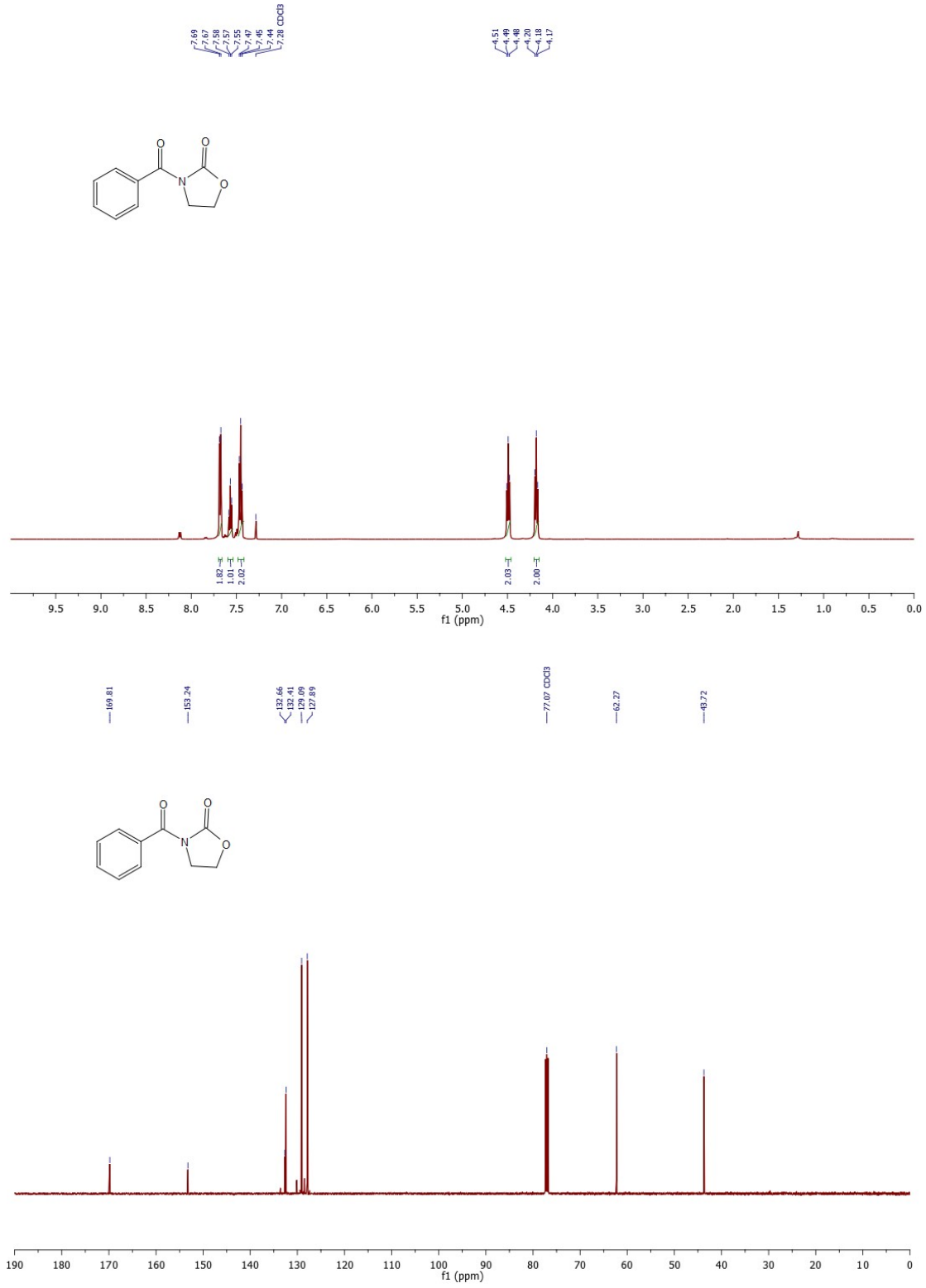

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4g.**



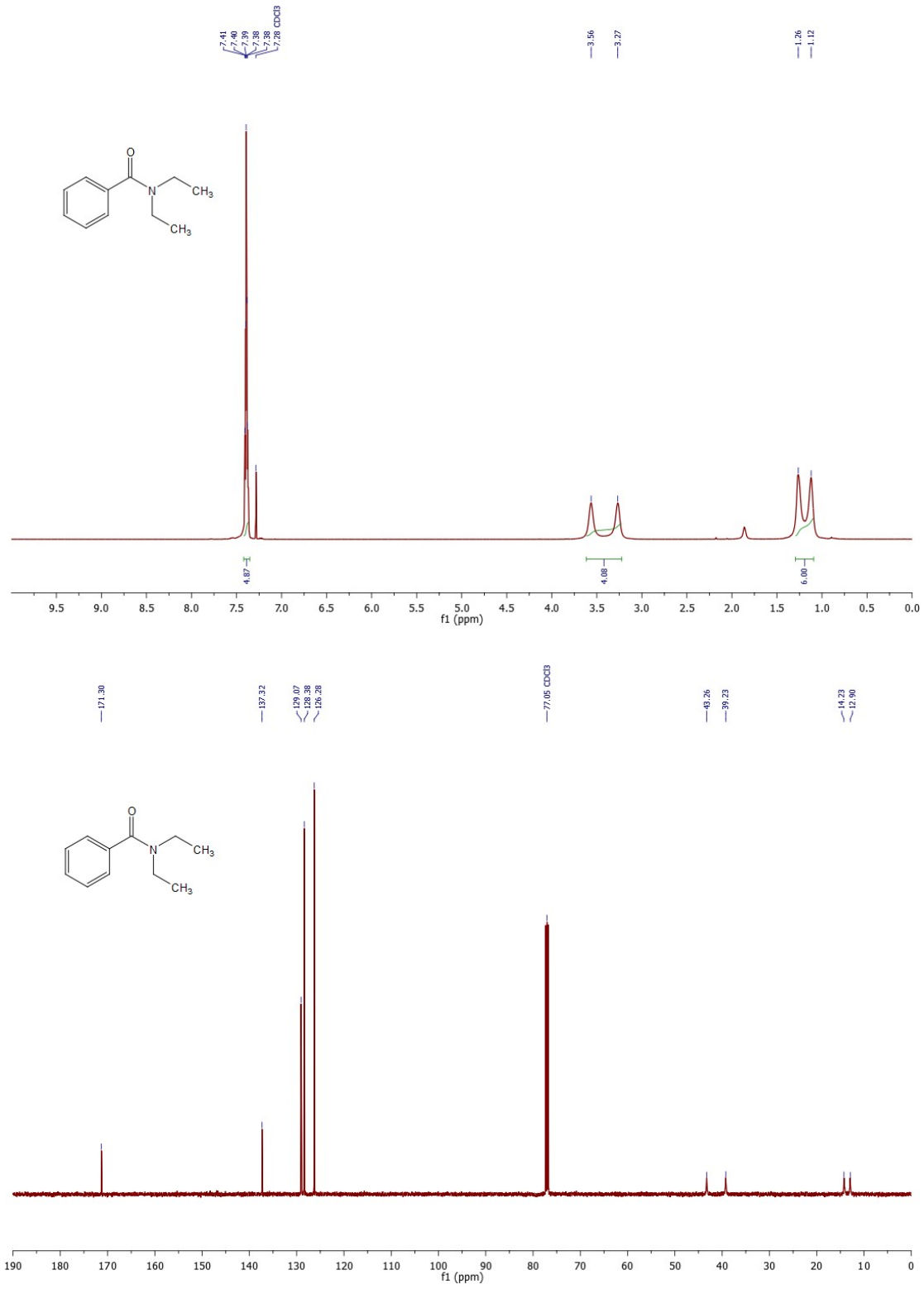

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4h.**



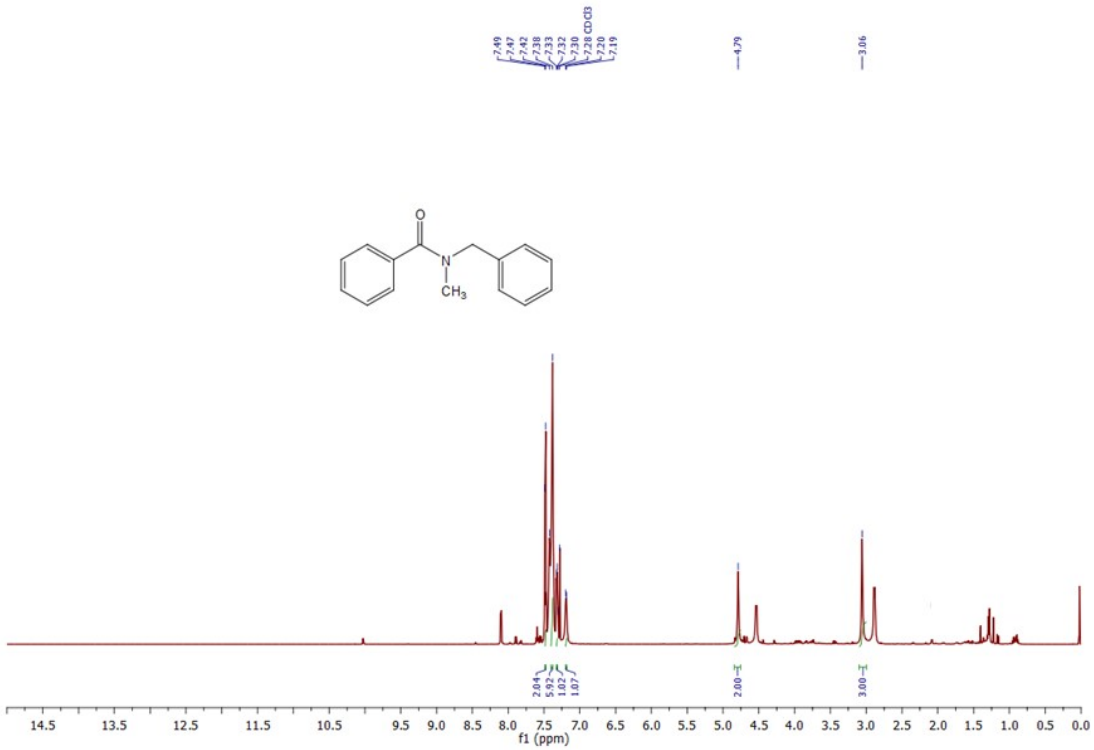

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4i.**



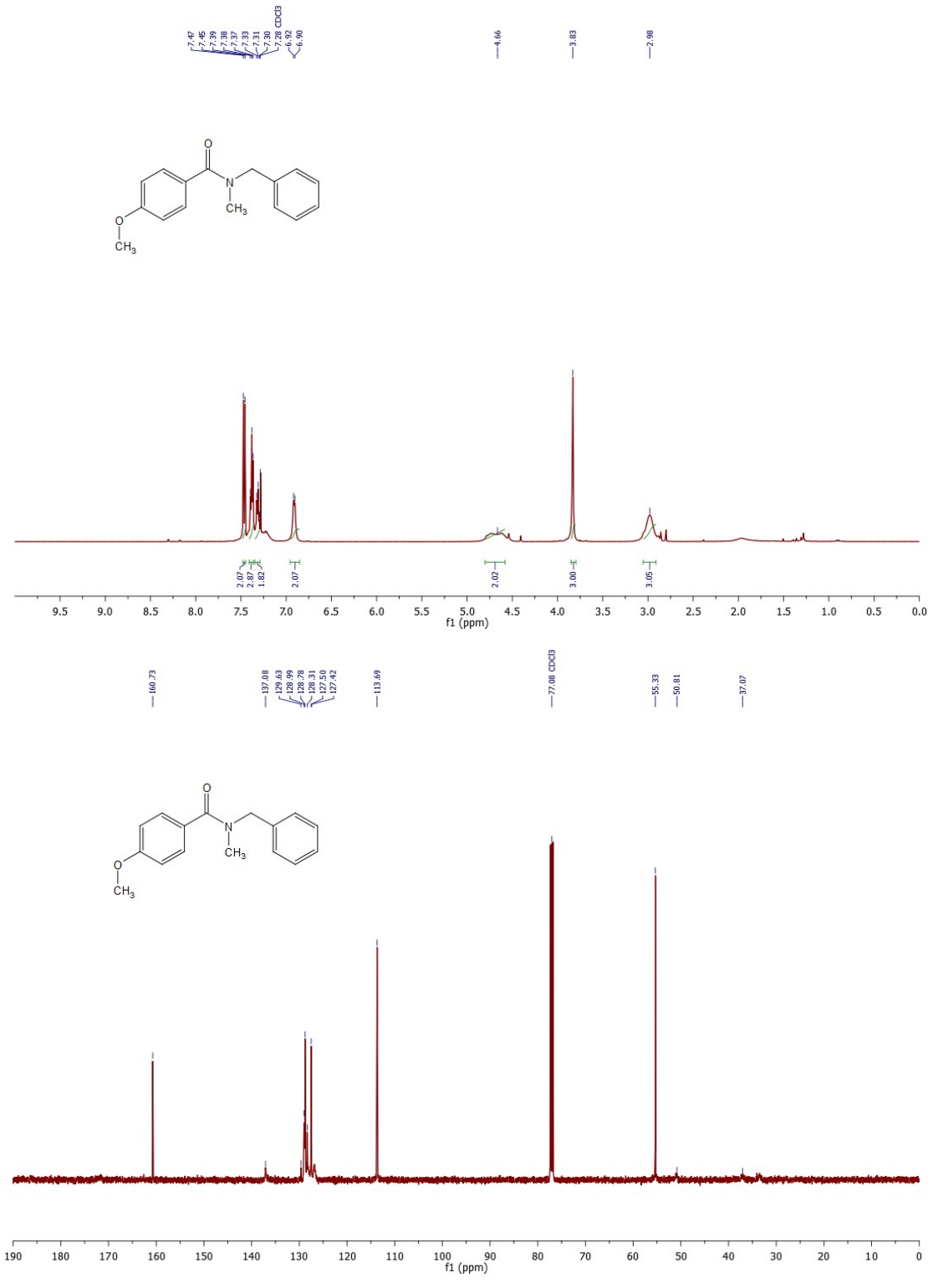

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4j.**



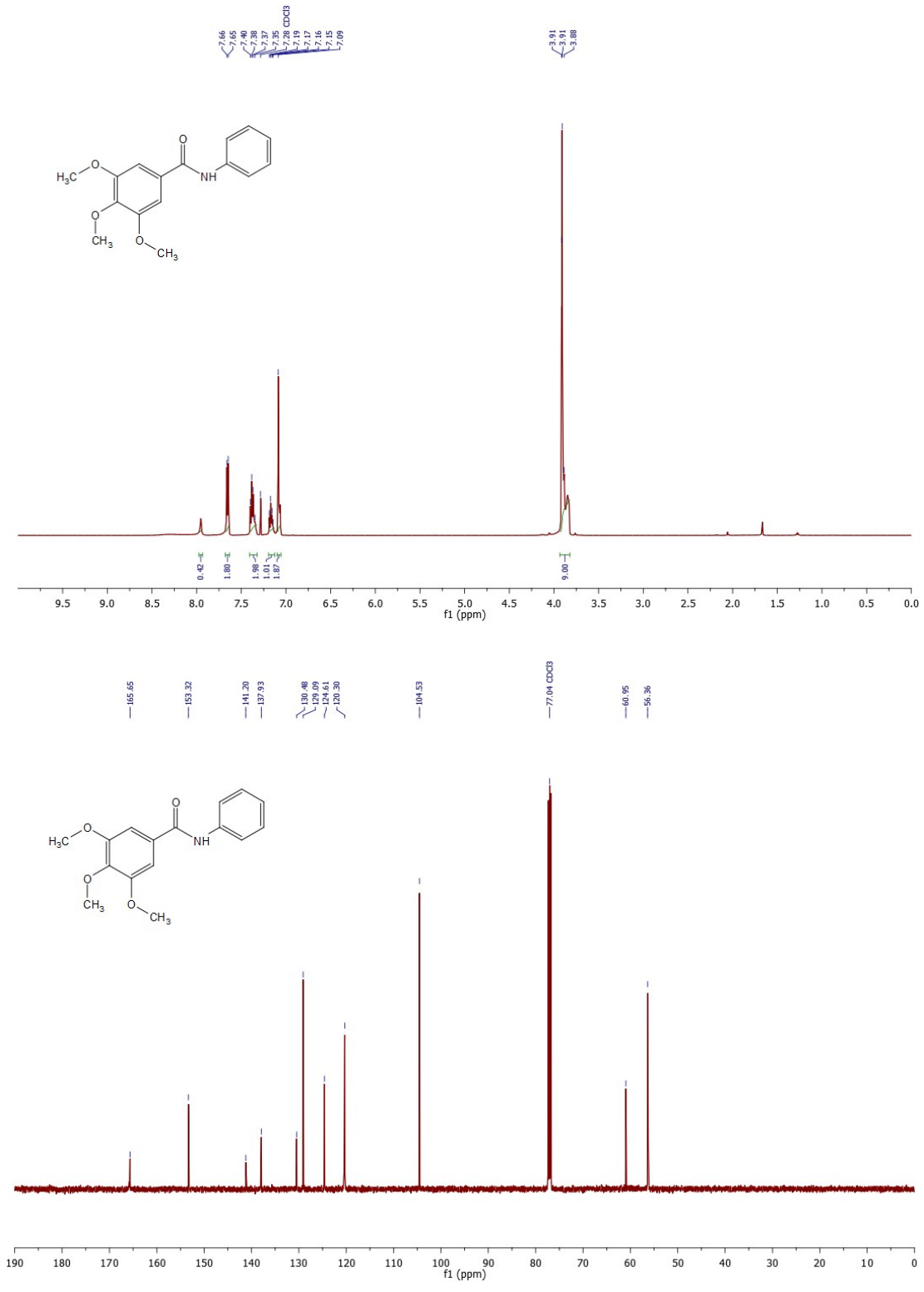

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4k.**



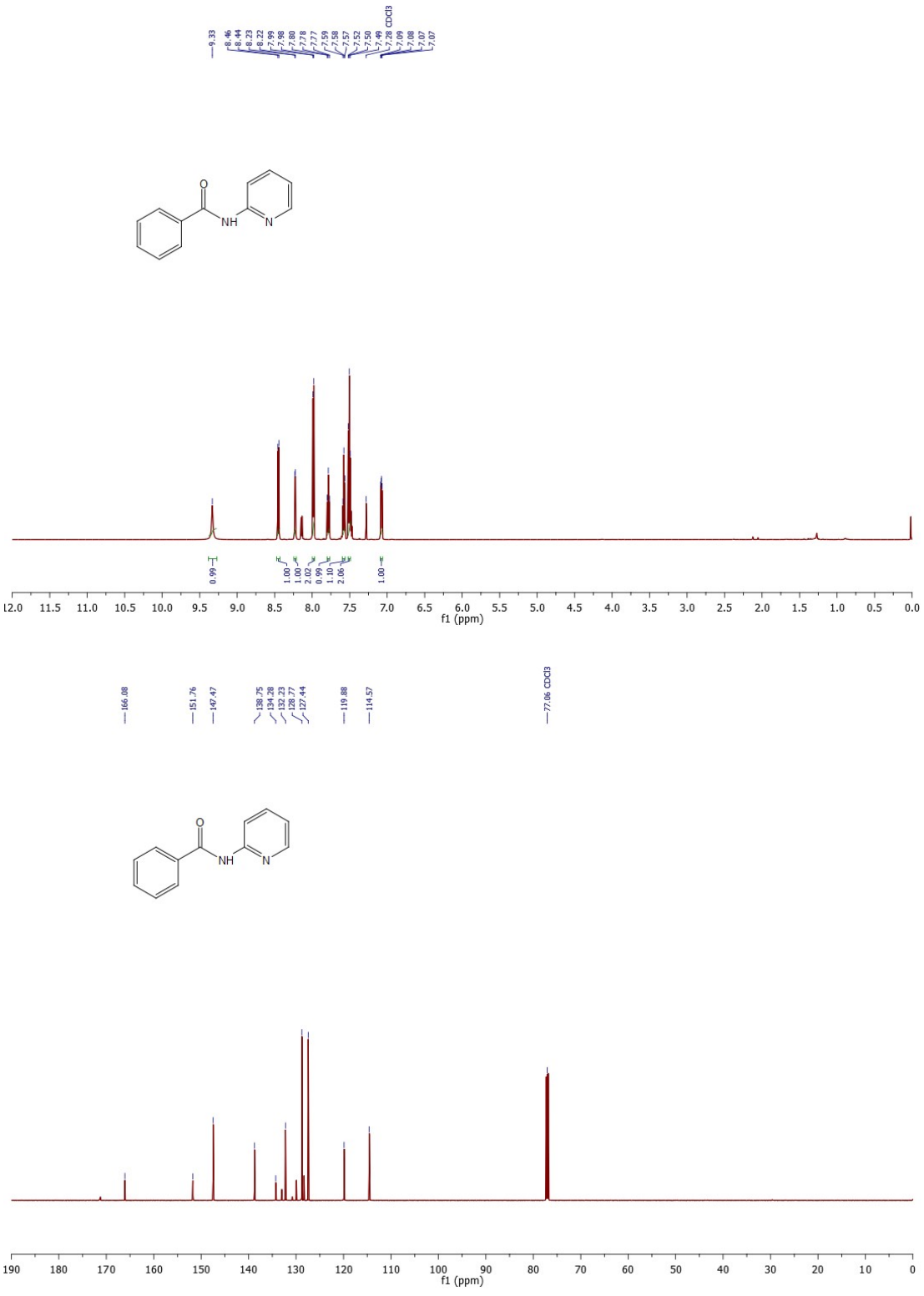

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4l.**



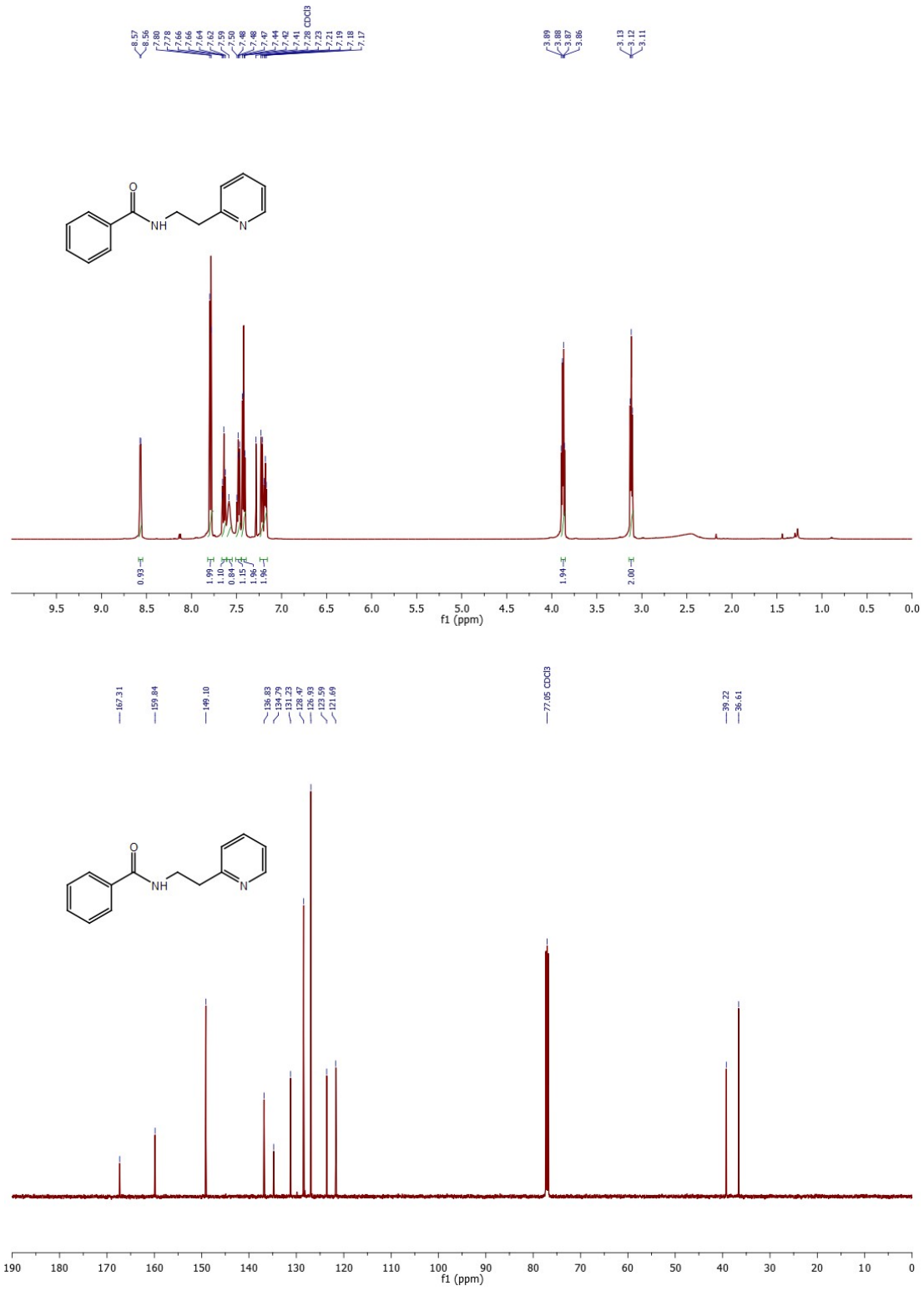

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4n.**



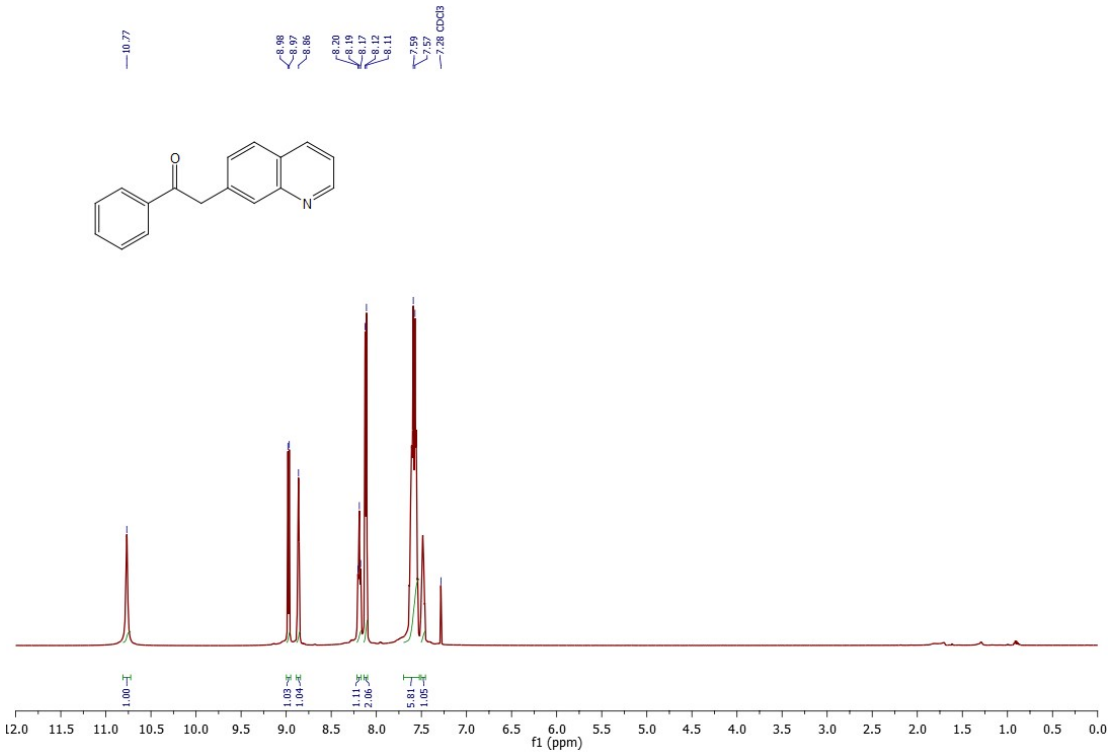

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4o.**

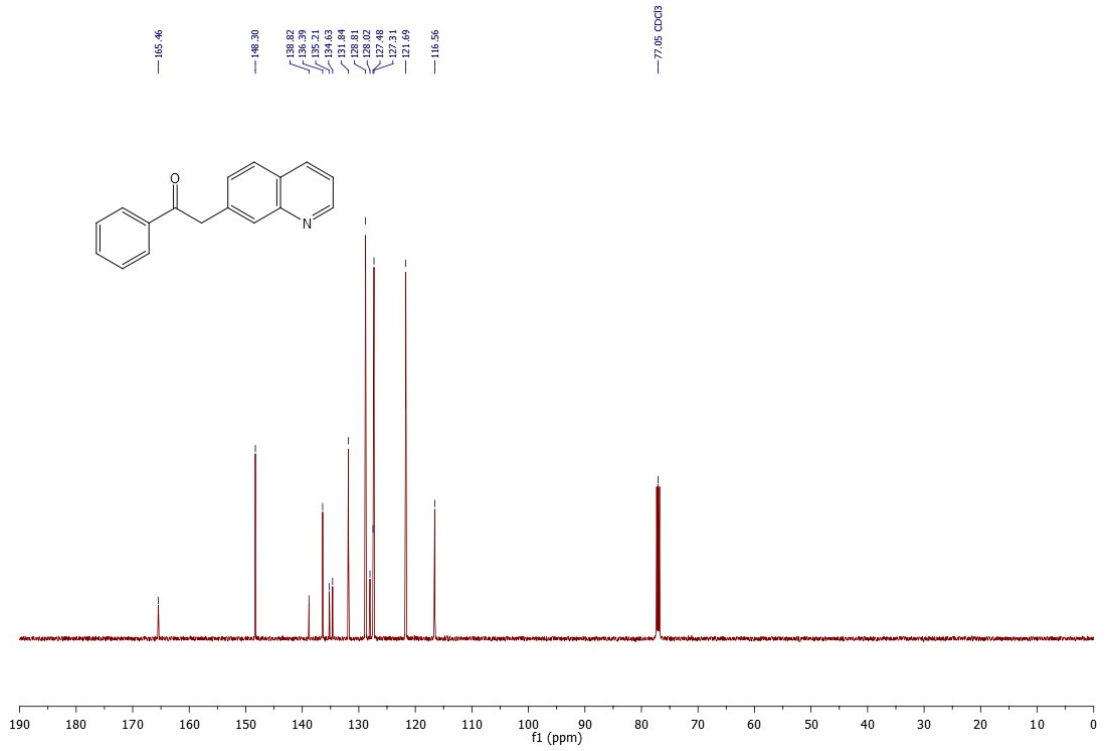



**$^{1}$H NMR and $^{13}$C NMR spectra of product 4p.**

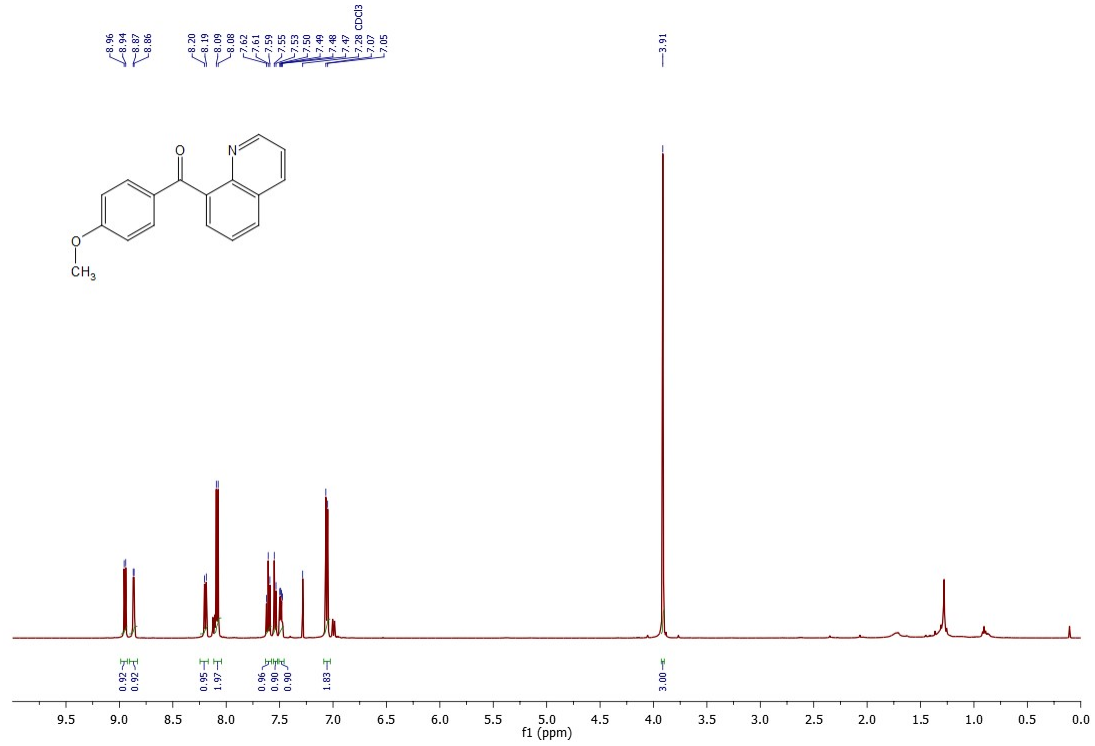


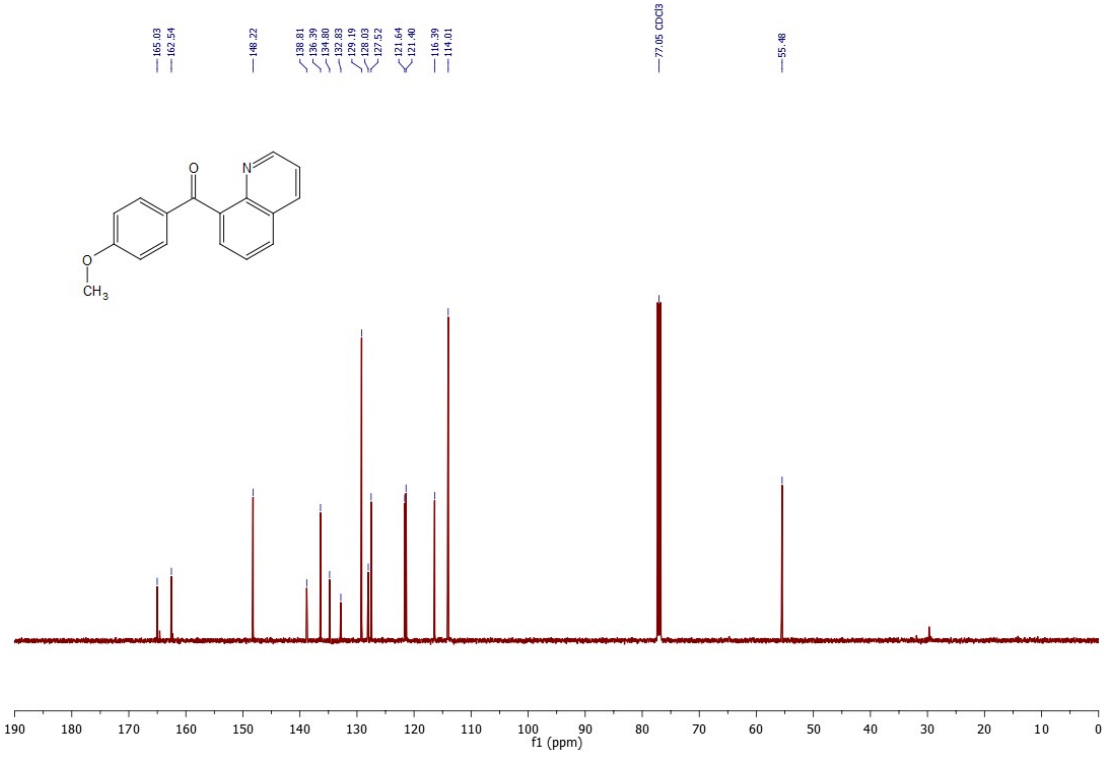

**$^{1}$H NMR and $^{13}$C NMR spectra of product 4q.**




**$^{1}$H NMR and $^{13}$C NMR spectra of product 4r.**


8.96
8.94
8.87
8.86
8.20
8.19
8.09
8.08
7.62
7.61
7.59
7.55
7.53
7.50
7.49
7.48
7.40
7.26 CDCl3
7.07
7.05
3.91
O
N
O
CH3
0.92
0.92
0.95
1.97
0.96
0.90
0.90
1.83
3.00
f1 (ppm)


165.03
162.54
148.22
138.81
136.39
134.80
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129.19
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127.52
121.64
121.40
116.39
114.01
77.05 CDCl3
55.48
O
N
O
CH3
f1 (ppm)

**Reference:**

S1 A. Baghban, H. Ezedin Nejadian, S. Habibzadeh and F. Zokaee Ashtiani, *Sci. Rep.*, 2022, **12**, 19428.

S2 V. Vyas, P. Maurya and A. Indra, *Chem. Sci.*, 2023, **14**,12339–12344.

S3 P. Maurya, V. Vyas, A. N. Singh and A. Indra, *Chem. Commun.*, 2023, **59**, 7200-7203.

S4 J. Yang, F. Zhang, H. Lu, X. Hong, H. Jiang, Y. Wu and Y. Li, *Angew. Chem. Int. Ed.*, 2015, **127**, 11039–11043.

S5 H. Su, P. Gao, M. Y. Wang, G. Y. Zhai, J. J. Zhang, T. J. Zhao, J. Su, M. Antonietti, X. H. Li and J. S. Chen, *Angew. Chem. Int. Ed.*, 2018, **57**, 15194–15198.

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S7 L. Fan, P. F. Liu, X. Yan, L. Gu, Z. Z. Yang, H. G. Yang, S. Qiu and X. Yao, *Nat. Commun.*, 2016, **7**, 10667.

S8 J. Bin Wu, M. L. Lin, X. Cong, H. N. Liu and P. H. Tan, *Chem. Soc. Rev.*, 2018, **47**, 1822–1873.

S9 Y. Zhang, L. Jiao, W. Yang, C. Xie and H. L. Jiang, *Angew. Chem. Int. Ed.*, 2021, **60**, 7607–7611.

S10 P. Yin, T. Yao, Y. Wu, L. Zheng, Y. Lin, W. Liu, H. Ju, J. Zhu, X. Hong, Z. Deng, G. Zhou, S. Wei and Y. Li, *Angew. Chem. Int. Ed.*, 2016, **128**, 10958–10963.

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S13 R. Deshidi, M. A. Rizvi and B. A. Shah, *RSC Adv.*, 2015, **5**, 90521–90524.

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