An Adaptable and Efficient Approach for the Formation of C–N bond Using Copper Schiff-Base Graphitic Carbon Nitride as Reusable and Heterogeneous Catalyst

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Contents

General Information:

All necessary chemicals were purchased from Sigma-Aldrich, Spectrochem, and TCI and utilized without further purification. Infrared (IR) spectra were recorded on a Spectrum BX Fourier transform infrared (FT-IR) instrument (PerkinElmer) (υmax in cm^{-1}) on KBr disks. ^{1}H and ^{13}C NMR (400 and 100 MHz, respectively) spectra were recorded on a Bruker Avance II-400 spectrometer in $CDCl_3$ and DMSO d_6 (chemical shifts in δ with TMS as internal standard). Mass spectra were recorded on a Waters Xevo-G2-XS QT of Mass Spectrometer. Transmission electron microscopy (TEM) images and Energy Dispersive X-ray (EDX) were recorded on a FEI Tecnai G2 20 S-Twin. Scanning electron microscopy (SEM) images was recorded on a JSM-6360 instrument (JEOL). Powder XRD was recorded on a Bruker D8 ADVANCE ECO P-XRD. Thermogravimetric Analysis (TGA) was recorded on a Perkin Elmer Precisely STA 6000 simultaneous thermal analyzer. XPS analysis was carried out on a PHI 5000 VersaProbe III. Silica gel (E-Merck, 60-120 and 100-200 mesh) was used for column chromatography. Hexane refers to the fraction boiling between 60 °C and 80 °C.

Preparation of Cu-SBg-C_3N_4:

Synthesis of graphitic carbon nitride[1]:

10g of urea was taken in a covered ceramic crucible and continuously heated in a muffle furnace at 550 °C for 3 h. After heating, the furnace was cooled down to room temperature, resulting in the formation of yellowish mass and the yellowish mass was crushed into a fine powdered form. The residue was washed with nitric acid (0.1 $molL^{-1}$) and deionized. Finally, it was dried at 80 °C for 24 h and pure form of graphitic carbon nitride was achieved.

Synthesis of Copper Schiff Base graphitic carbon nitride[2]:

500 mg graphitic carbon nitride was dispersed in 30 mL of ethanol and refluxed. 2.4 g of salicylaldehyde was added dropwise under nitrogen atmosphere and reflux was continue for 24 h. The resulting mass was collected by centrifugation followed by filtration. Then residue was washed with ethanol (3 × 10mL) and diethyl ether (3 × 10mL). Lastly, the obtained solid was dried at 60 °C to achieve Schiff Base graphitic carbon nitride. Thereafter, in a 100 mL round bottom flask 400 mg of Schiff Base graphitic carbon nitride was dispersed in 30 mL of ethanol. To that mixture 25 mL of aqueous solution of $Cu(OAc)_2.H_2O$ (250 mg) was added and the resulting mixture was refluxed for 24 h with constant stirring. The formed Cu-SBg-C_3N_4 was

collected by centrifugation and filtration. Then it was washed with ethanol (3 × 10 mL) and diethyl ether (3 × 10 mL) and dried at 60 °C to achieve pure Cu-SBg-C_3N_4.

Synthesis of secondary amine derivatives:

To a stirred solution of aryl boronic acid (1.2 mmol), aniline (1.0 mmol) in 2 mL EtOH and Cu-SBgC_3N_4 (20mg) was added. The reaction mixture was stirred at room temperature for required time mentioned in Table 1. After completion, the reaction mixture was filtered and the filtrate part was evaporated under vacuum to get the crude product. The crude was purified by column chromatography using ethyl acetate / hexane as eluent.

Synthesis of secondary amide derivatives:

In a typical reaction, aldehyde (1 mmol), aniline (2 mmol), Cu-SBg-C_3N_4 (15 mg), and TBHP (70 % aqueous, 2 mmol) were mixed in DMSO (2 mL) in a 10 mL round bottom flask. The reaction mixture was subjected to continuous stirring at 80 °C for 12 h. After completion, the catalyst was separated using filtration, DMSO was removed and the reaction mixture was taken in ethyl acetate. The organic layer was washed with saturated brine solution and dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography using 100-200 silica mesh with ethyl acetate and hexane as the eluent to obtain the desired product.

Characterization of the Reuse catalyst:

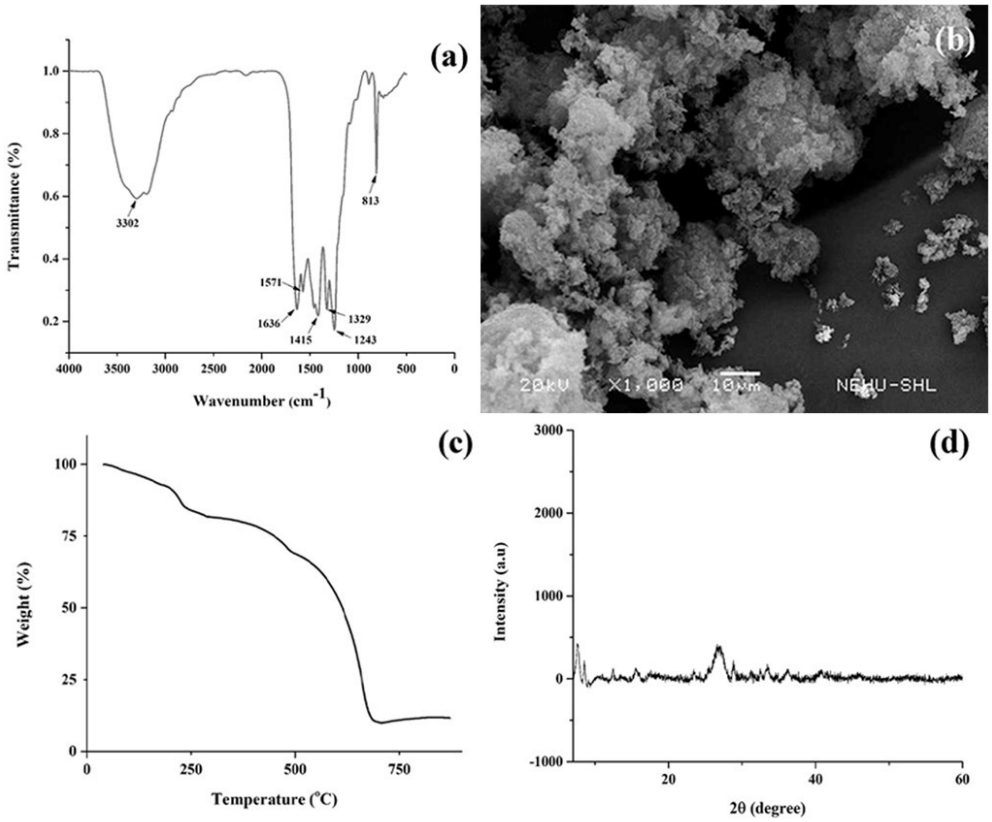
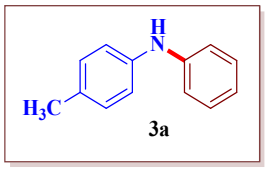


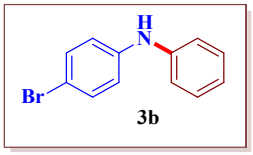
Figure S1. (a) IR spectrum, (b) SEM image, (c) TGA thermogram and (d) PXRD pattern of Cu-SBg-C_3N_4.

Spectral data of the compounds



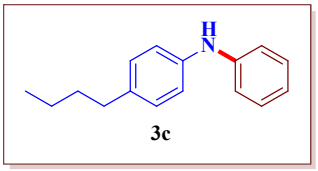
3a

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.16 (d, 2H, J= 4 Hz), 7.02 (d, 2H, J= 8 Hz), 6.95 (s, 4H), 6.82 (s, 1H), 2.22 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 143.6, 139.9, 131.3, 129.9, 129.3, 120.7, 119.1, 117.2, 20.7.[3]



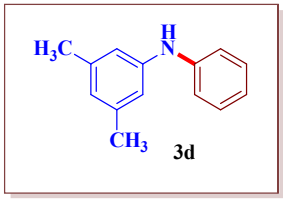
3b

Brown solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.27 (d, 2H, J= 8 Hz), 7.22 (t, 2H, J= 8 Hz), 6.77 (d, 2H, J= 8 Hz), 6.91-6.85 (m, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 142.3, 142.3, 132.2, 129.5, 121.7, 119.1, 118.3, 112.7.[4]



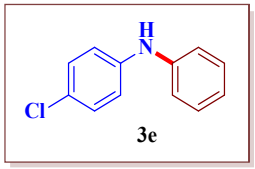
3c

Yellow liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.18 (t, 2H, J= 8 Hz), 7.02 (d, 2H, J= 8 Hz). 6.95 (s, 4H), 6.83 (d, 1H, J= 8 Hz), 2.49 (t, 2H, J= 6 Hz), 1.52 (t, 2H, J= 8 Hz), 1.30-1.25 (m, 2H), 0.85 (t, 3H, J= 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 143.7, 140.3, 136.3, 129.3, 129.2, 120.5, 118.8, 117.1, 34.9, 33.8, 22.4, 14.0.[5]



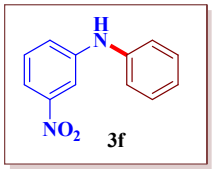
3d

Red solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.44 (s, 1H), 7.18 (d, 2H, J= 8 Hz), 7.03-6.98 (m, 2H), 6.84 (s, 1H), 6.64 (s, 1H), 6.51 (s, 1H), 2.33 (s, 3H), 2.18 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 152.9, 143.2, 143.0, 139.0, 138.7, 132.5, 129.3, 122.9, 120.7, 120.5, 117.8, 115.6, 21.4, 21.3.[6]



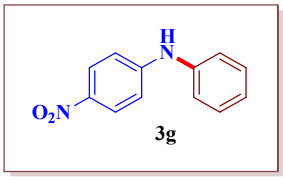
3e

Brown solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.22 (t, 2H, J= 8 Hz), 7.14 (d, 2H, J= 8 Hz), 6.99 (d, 2H, J= 8 Hz), 6.93 (t, 3H, J= 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 142.5, 141.7, 129.4, 129.3, 125.6, 121.6, 118.9. 118.1.[7]



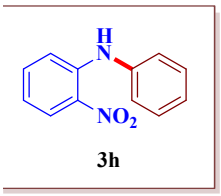
3f

Red solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.77 (s, 1H), 7.62 (d, 1H, J= 4 Hz), 7.27 (s, 3H), 7.22 (t, 1H, J= 8 Hz), 7.08 (d, 2H, J= 8 Hz), 7.02 (d, 1H, J= 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 149.3, 145.0, 140.9, 130.0, 129.7, 123.2, 121.8, 119.8, 114.6, 110.2.[8]



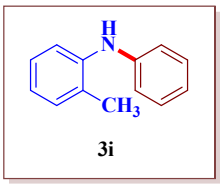
3g

Yellow solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 8.06 (d, 2H, J= 8 Hz), 7.32 (d, 2H, J= 4 Hz), 7.19-7.10 (m, 4H), 6.88 (d, 2H, J= 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 129.7, 126.2, 124.6, 121.9, 113.6.[9]



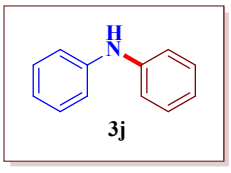
3h

Yellow liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.36-7.27 (m, 1H), 7.22-7.14 (m, 4H), 7.03 (d, 2H, J= 8 Hz), 6.97-6.82 (m, 2H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 142.9, 135.7, 129.7, 129.3, 126.7, 125.6, 124.4, 121.7, 121.1, 117.9, 117.5, 116.0.[10]



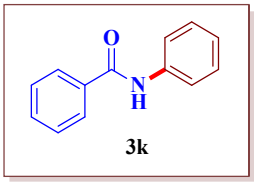
3i

Yellow solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.17-7.11 (m, 4H), 7.06 (s, 1H), 6.89-6.82 (m, 4H), 2.18 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 143.8, 141.1, 131.0, 129.3, 128.3, 126.8, 122.0, 120.5, 118.8, 117.5, 17.9.[11]



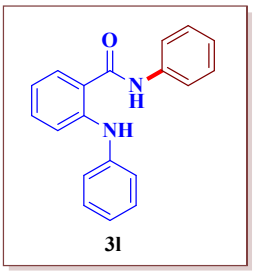
3j

Yellow liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.21 (t, 4H, J= 8 Hz), 7.02 (d, 4H J= 8 Hz), 6.88 (t, 2H, J= 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 142.9, 129.4, 121.2, 117.9.[12]



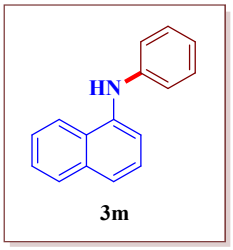
3k

Brown solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.81 (d, 2H, J= 8 Hz), 7.58 (d, 2H, J= 8 Hz), 7.48-7.41 (m, 3H), 7.32 (t, 2H, J= 8 Hz), 7.10 (t, 1H, J= 6 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 165.8, 137.9, 134.9, 131.8, 129.1, 128.8, 127.0, 124.6, 120.2.[13]



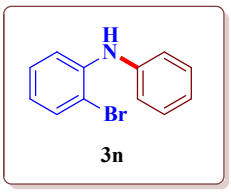
3l

White solid. **^{1}H NMR ($CDCl_3$ + DMSO d_6, 400 MHz): δ=** 7.70 (s, 1H), 7.50-7.49 (m, 3H), 7.41 (d, 1H, J= 8 Hz), 7.30-7.25 (m, 3H), 7.19 (s. 2H), 7.12-7.06 (m, 3H), 6.66-6.65 (m, 2H). **^{13}C NMR ($CDCl_3$ + DMSO d_6, 100 MHz): δ=** 168.2, 132.2, 128.6, 127.4, 123.8, 120.9, 117.0, 116.6, 116.0.[14]



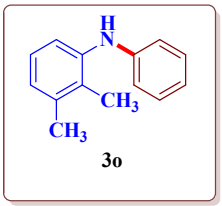
3m

Yellow solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 8.06 (d, 1H, J= 8 Hz), 7.90 (d, 1H, J= 8 Hz), 7.60-7.59 (m, 1H), 7.51 (s, 2H), 7.41 (s, 2H), 7.29 (s, 2H), 7.03-6.94 (m, 3H), 5.98 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 149.8, 144.6, 138.6, 134.7, 129.3, 128.5, 127.7, 126.1, 126.0, 125.7, 123.0, 121.8, 120.6, 117.4, 117.4, 115.9, 90.6.[15]



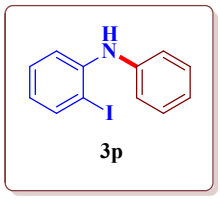
3n

Yellow liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.51 (d, 1H, J= 8 Hz), 7.29-7.22 (m, 3H), 7.13-7.12 (m, 3H), 7.03 (d, 1H, J= 8 Hz), 6.72 (t, 1H, J= 6 Hz), 6.06 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 141.6, 141.4, 133.0, 129.8, 129.7, 128.1, 122.7, 120.9, 120.3, 118.9, 115.8, 112.2.[16]



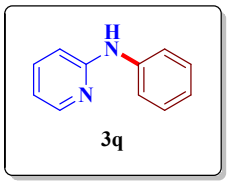
3o

Yellow liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.24 (t, 2H, J= 8 Hz), 7.10-7.02 (m, 2H), 6.90-6.84 (m, 4H), 5.38 (s, 1H), 2.31 (s, 3H), 2.15 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 144.9, 140.8, 137.8, 129.2, 128.5, 125.9, 124.6, 119.8, 118.6, 116.6, 20.7, 13.6.[17]



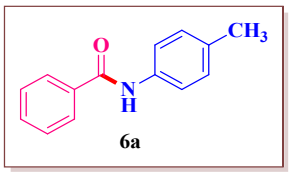
3p

White liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.77-7.76 (m, 1H), 7.33 (t, 2H, J= 8 Hz), 7.20-7.19 (m, 2H), 7.13-7.12 (m, 2H), 7.05 (t, 1H, J= 8 Hz), 6.63-6.59 (m, 1H), 5.91 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 143.9, 141.9, 139.5, 129.4, 129.0, 122.5, 121.9, 119.9, 115.8, 88.7.[18]



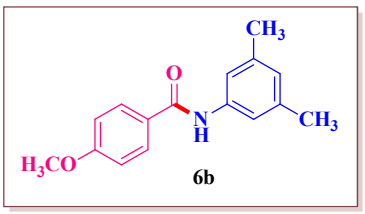
3q

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 8.20-8.19 (m, 1H), 7.51 (t, 1H), 7.33-7.32 (m, 4H), 7.07-7.05 (m, 1H), 6.89 (d, 1H, J= 8 Hz), 6.75-6.72 (m, 1H), 6.67 (s, 1H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 155.9, 148.3, 140.3, 137.7, 129.3, 122.8, 120.3, 115.0, 108.2.[19]



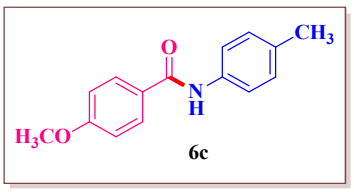
6a

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 8.05 (s, 1H), 7.83 (d, 2H, J= 8 Hz), 7.51 (t, 3H, J= 8 Hz), 7.43 (t, 2H, J= 8 Hz), 7.13 (d, 2H, J= 8 Hz), 2.31 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 165.9, 135.4, 134.2, 131.6, 129.5, 128.6, 127.1, 120.5, 20.9.[20]



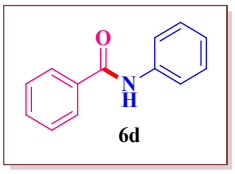
6b

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.83 (d, 2H, J= 8 Hz), 7.71 (s, 1H), 7.26 (s, 2H), 6.97 (d, 2H, J= 8Hz), 6.78 (s, 1H), 3.86 (s, 3H), 2.31 (s, 6H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 165.2, 162.4, 138.7, 137.9, 128.8, 127.2, 126.1, 117.9, 113.9, 55.4, 21.4.[21]



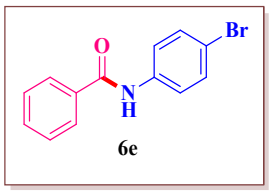
6c

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.83 (d, 2H, J= 8 Hz), 7.51 (d, 2H, J= 8 Hz), 7.15 (d, 2H, J= 8 Hz), 6.95 (d, 2H, J= 12 Hz), 3.85 (s, 3H), 2.32 (s, 3H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 165.3, 162.3, 135.5, 133.9, 129.5, 128.9, 127.2, 120.3, 113.9, 55.4, 20.9.[22]



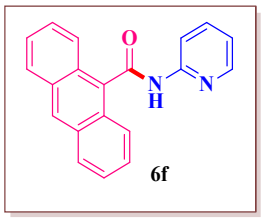
6d

Brown solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.81 (d, 2H, J= 8 Hz), 7.58 (d, 2H J= 8 Hz), 7.48-7.41 (m, 3H), 7.32 (t, 2H, J= 8 Hz), 7.10 (t, 1H J= 6 Hz)**. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 165.8, 137.9, 134.9, 131.8, 129.1, 128.8, 127.0, 124.6, 120.2.[23]



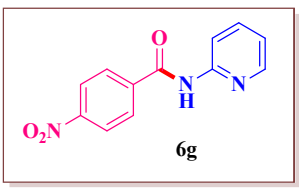
6e

White solid. **^{1}H NMR ($CDCl_3$ + DMSO d_6, 400 MHz): δ=** 10.13 (s, 1H), 7.96 (d, 2H, J= 8 Hz), 7.76 (d, 2H, J= 8 Hz), 7.55-7.41 (m, 5H). **^{13}C NMR ($CDCl_3$ + DMSO d_6, 100 MHz): δ=** 166.3, 138.6, 135.1, 131.7, 131.4, 128.4, 127.9, 122.4, 115.9.[24]



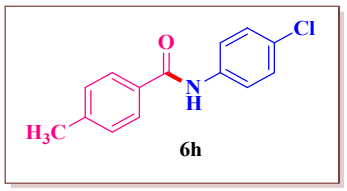
6f

Yellow solid. **^{1}H NMR ($CDCl_3$ + DMSO d_6, 400 MHz): δ=** 8.43 (s, 1H), 8.16 (d, 3H, J= 8 Hz), 7.95 (d, 3H, J= 8 Hz), 7.46 (d, 6H, J= 8 Hz). **^{13}C NMR ($CDCl_3$ + DMSO d_6, 100 MHz): δ=** 171.0, 134.3, 129.5, 128.5, 127.7, 126.7, 126.2, 125.5, 125.3.[25]



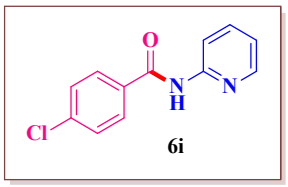
6g

White solid. **^{1}H NMR ($CDCl_3$ + DMSO d_6, 400 MHz): δ=** 10.71 (s, 1H), 8.30 (s, 1H), 8.23 (d, 5H, J= 8 Hz), 7.73 (t, 1H, J= 8 Hz), 7.06 (s, 1H). **^{13}C NMR ($CDCl_3$ + DMSO d_6, 100 MHz): δ=** 164.5, 152.0, 149.6, 147.9, 140.1, 138.2, 129.5, 123.4, 120.2, 115.1.[26]



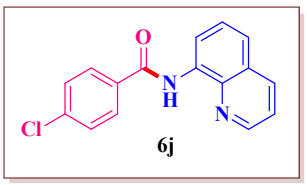
6h

White solid. **^{1}H NMR ($CDCl_3$ + DMSO d_6, 400 MHz): δ=** 9.93 (s, 1H), 7.97 (d, 2H, J= 8 Hz), 7.63 (d, 2H, J= 8 Hz), 7.45 (d, 2H, J= 8 Hz), 7.14 (d, 2H, J= 8 Hz), 2.32 (s, 3H). **^{13}C NMR ($CDCl_3$ + DMSO d_6, 100 MHz): δ=** 164.9, 137.1, 136.3, 133.8, 133.4, 129.4, 129.1, 128.4, 120.9, 20.9.[27]



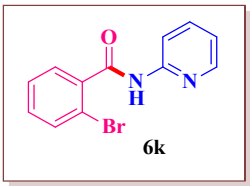
6i

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 9.03 (s, 1H), 8.39 (d, 2H, J= 8 Hz), 8.22 (s, 1H), 7.89 (d, 2H, J= 8 Hz), 7.79 (t, 1H, J= 8 Hz), 7.47 (d, 2H, J= 8 Hz), 7.09 (t, 1H, J= 6 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 164.7, 151.4, 147.7, 138.6, 138.6, 132.6, 129.1, 128.7, 120.1, 114.3.[28]



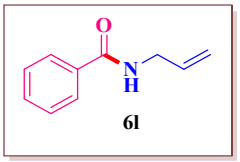
6j

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 10.73 (s, 1H), 8.92-8.85 (m, 2H), 8.19 (s, 1H), 8.04 (d, 2H, J= 8 Hz), 7.62-7.48 (m, 5H). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 164.3, 148.3, 138.7, 138.1, 136.4, 134.3, 133.5, 129.0, 128.7,128.0, 127.4, 121.9, 121.7, 116.6.[29]



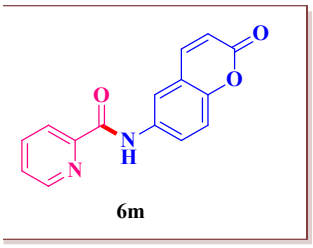
6k

White solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 9.63 (s, 1H), 8.40 (d, 1H, J= 12 Hz), 7.79-7.72 (m, 2H), 7.62 (t, 2H, J= 8 Hz), 7.40-7.30 (m, 2H), 6.97 (t, 1H, J= 6 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 166.2, 151.3, 147.5, 138.5, 137.7, 133.5, 131.6, 129.3, 127.6,120.0, 119.5, 114.5.[30]



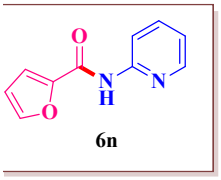
6l

Yellow liquid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.73 (d, 2H, J= 8 Hz), 7.46-7.34 (m, 3H), 5.91-5.84 (m, 1H), 5.22-5.11 (m, 2H), 4.04 (t, 2H, J= 6 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 166.0, 133.3, 133.0, 127.5, 125.8, 115.7, 41.4, 13.1.[31]



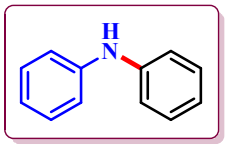
6m

Brown solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 10.09 (s, 1H), 8.57 (d, 1H, J= 4 Hz), 8.24-8.20 (m, 2H), 7.88 (s, 1H), 7.69 (d, 1H, J= 8 Hz), 7.63-7.60 (m, 1H), 7.47 (d, 1H, J= 4 Hz), 7.27 (d, 1H, J= 8 Hz), 6.41 (d, 1H, J= 8 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 161.1, 159.7, 149.4, 148.1, 147.0, 142.4, 136.8, 133.2, 125.7, 122.4, 121.4, 118.1, 116.9, 116.3, 116.2. HRMS (ESI, $M^+ + H$) calcd for $C_{15}H_{11}N_2O_3$ 267.0770, found 267.0771.



6n

Yellow solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 8.87 (s, 1H), 8.28-8.23 (m, 2H), 7.70 (d, 1H, J= 8 Hz), 7.47 (s, 1H), 7.23 (d, 1H, J= 4 Hz), 7.01 (s, 1H), 6.51 (t, 1H, J= 4 Hz). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 155.2, 149.9, 146.7, 146.2, 143.8, 137.5, 118.9, 114.9, 113.2, 111.6.[32]



Yellow solid. **^{1}H NMR ($CDCl_3$, 400 MHz): δ=** 7.60 (d, 4H, J= 7.6 Hz), 7.461 (t, 4H, J= 7.4 Hz), 7.36 (t, 2H, J= 7.4). **^{13}C NMR ($CDCl_3$, 100 MHz): δ=** 141.2, 128.7, 127.2, 127.1.[33]

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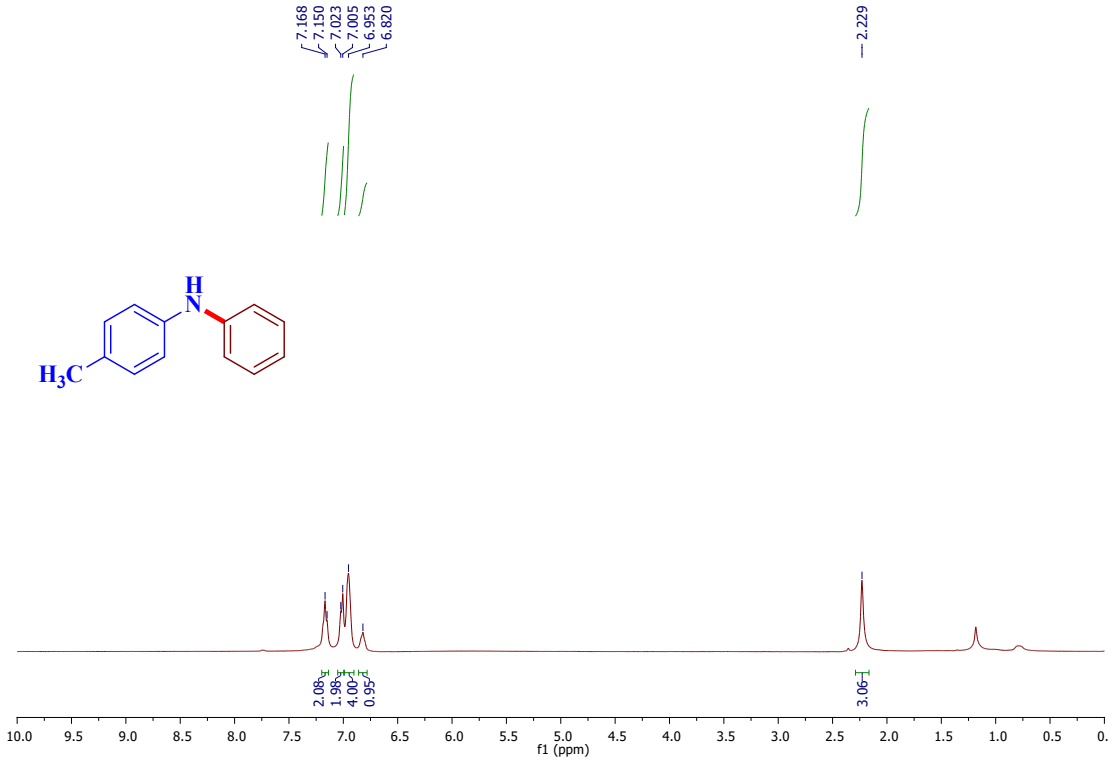
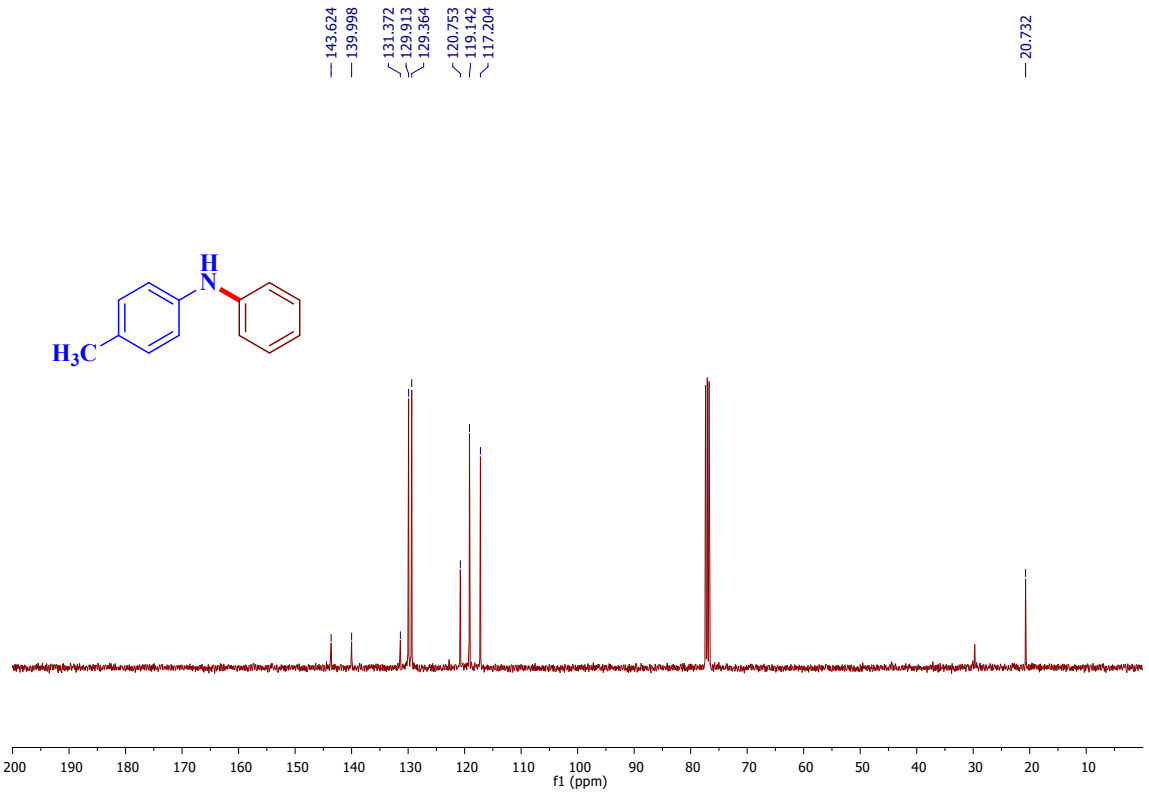
^{1}H and ^{13}C NMR spectra of the compounds:

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N
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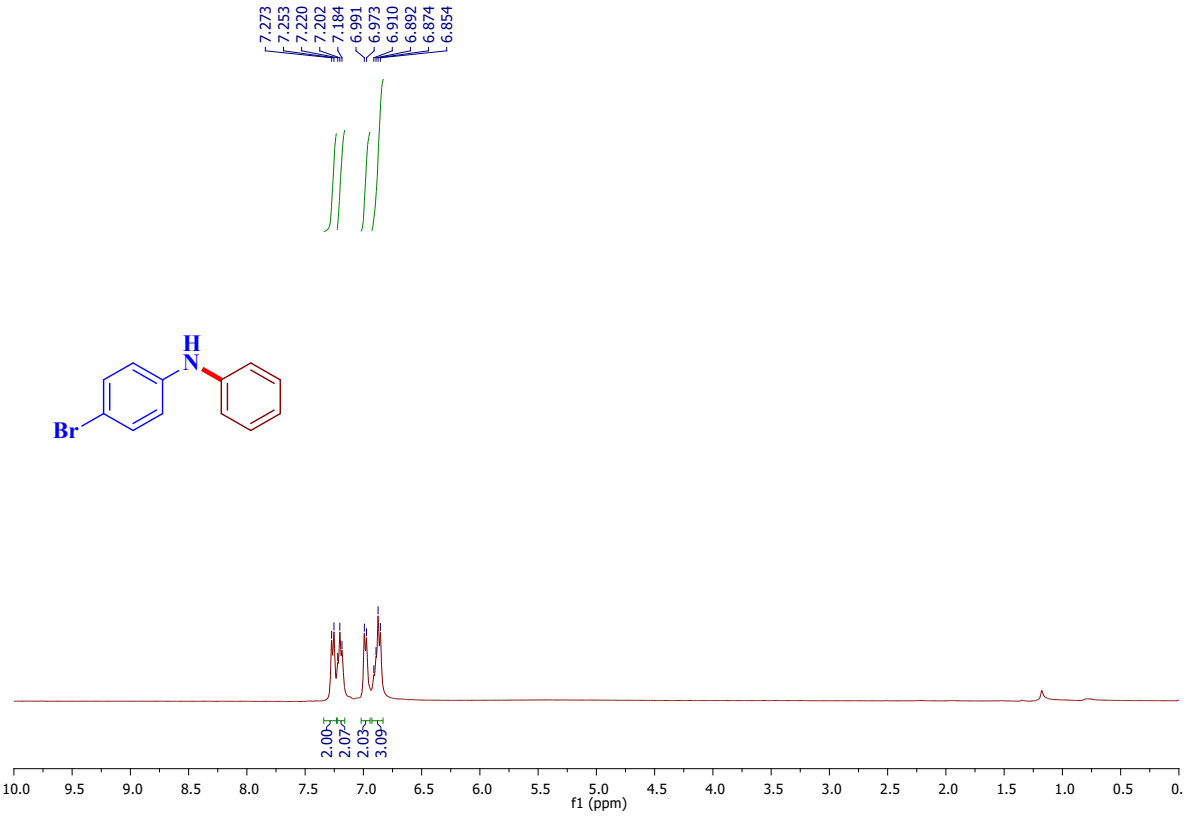
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N
Br
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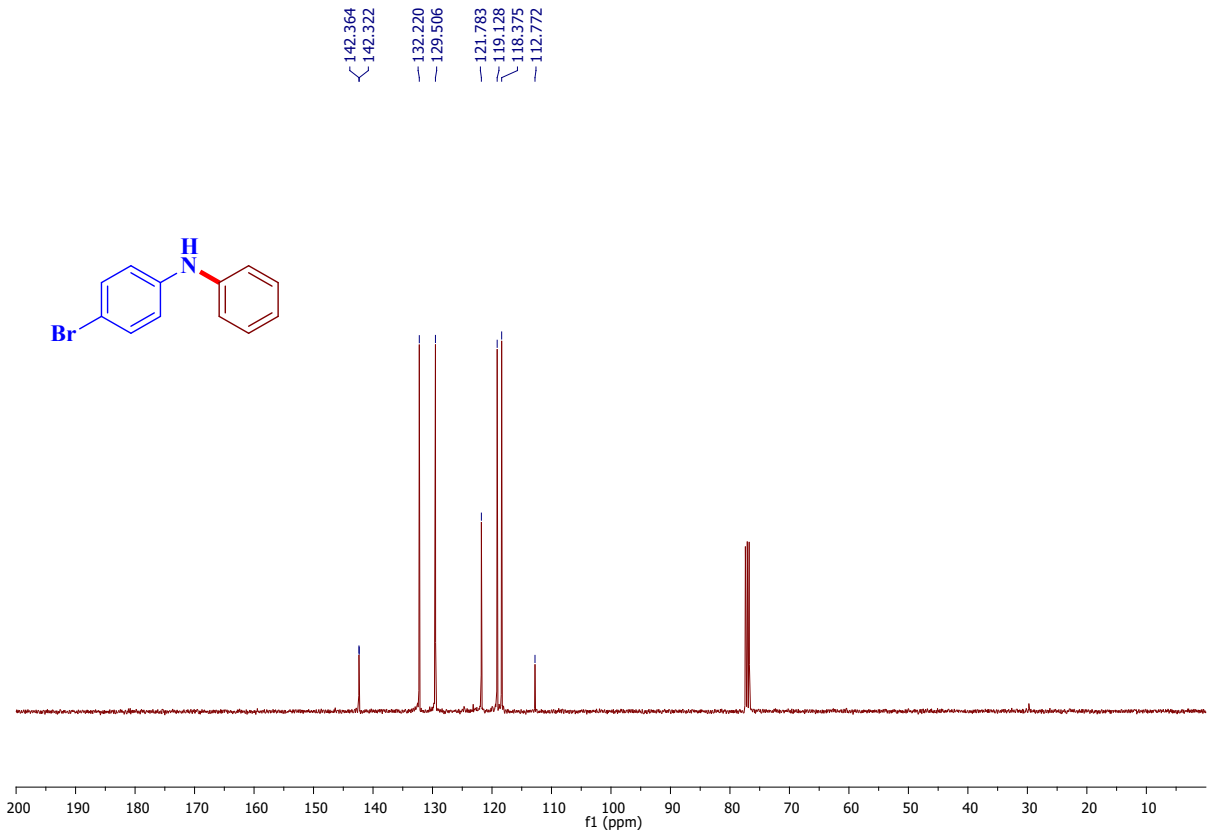
2.07
2.03
3.09
f1 (ppm)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Br
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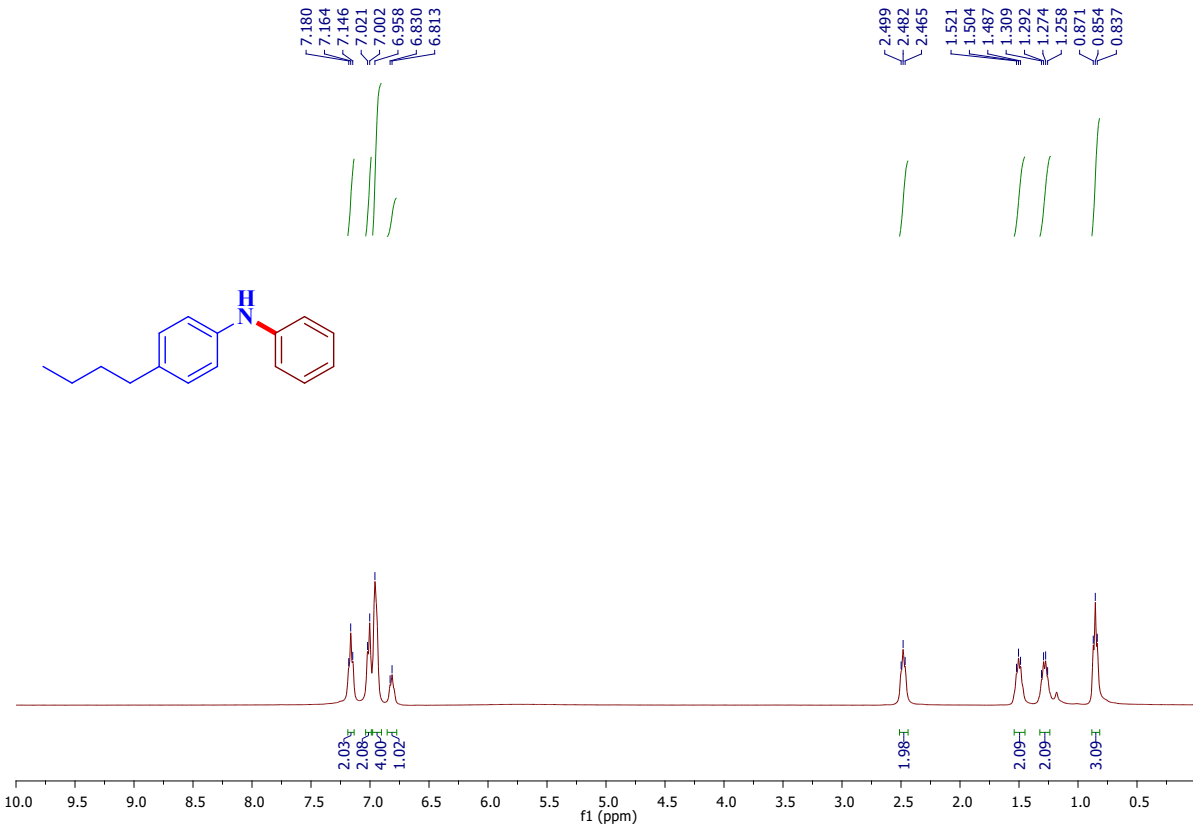
f1 (ppm)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1.504
1.487
1.309
1.292
1.274
1.258
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N
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2.08
4.00
1.02
1.98
2.09
2.09
3.09
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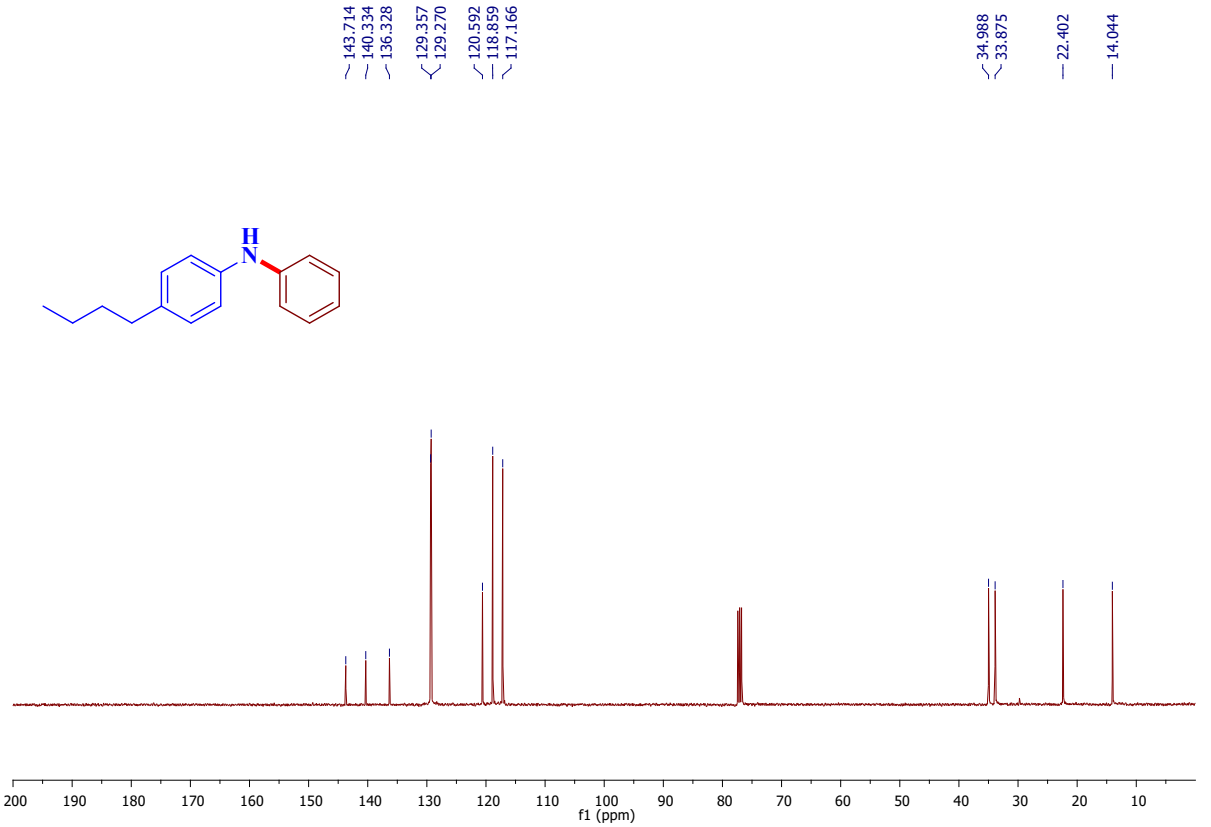
f1 (ppm)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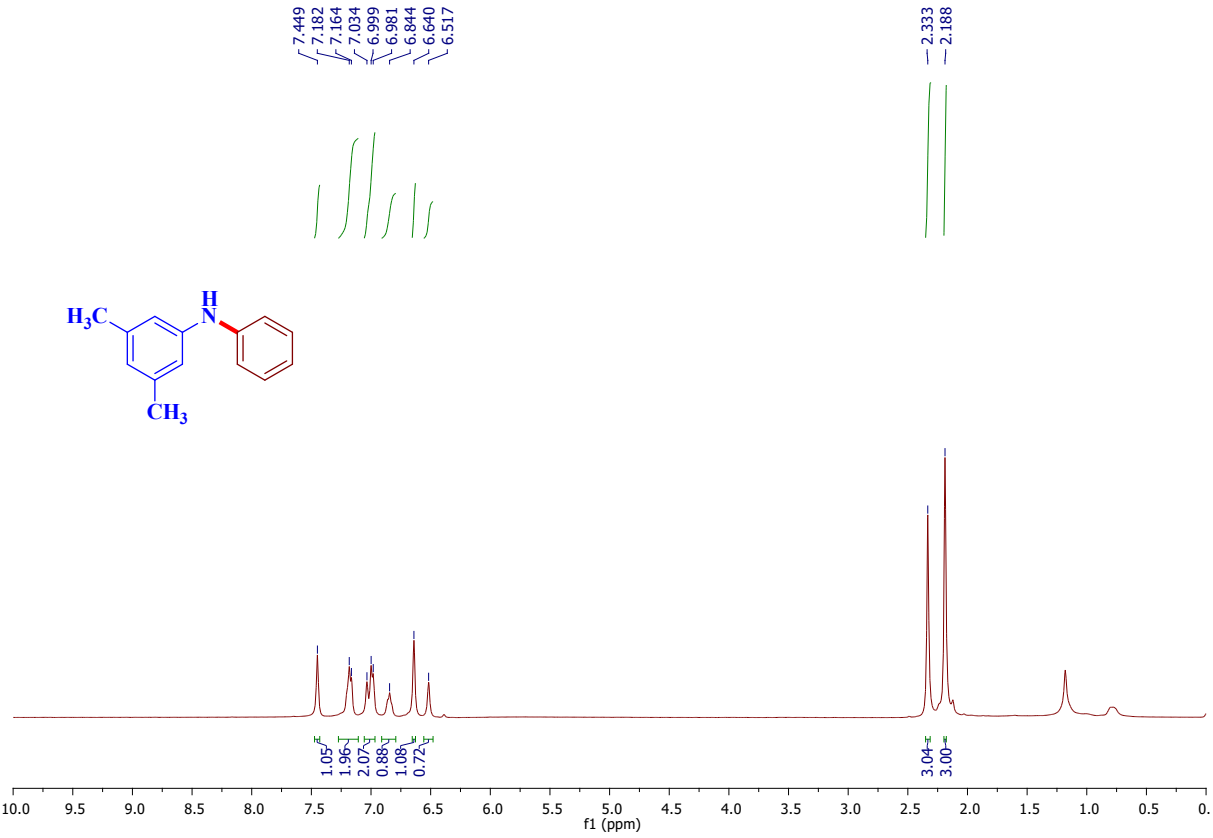
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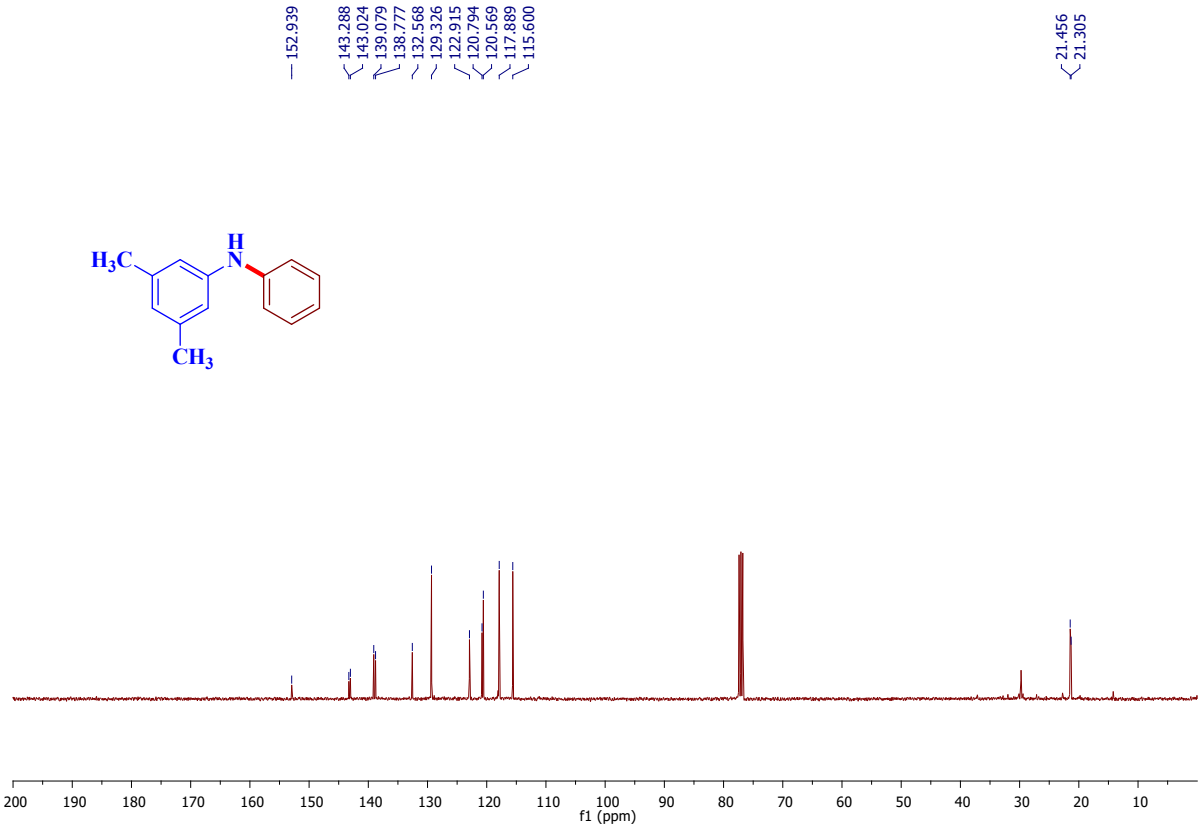
3.00
f1 (ppm)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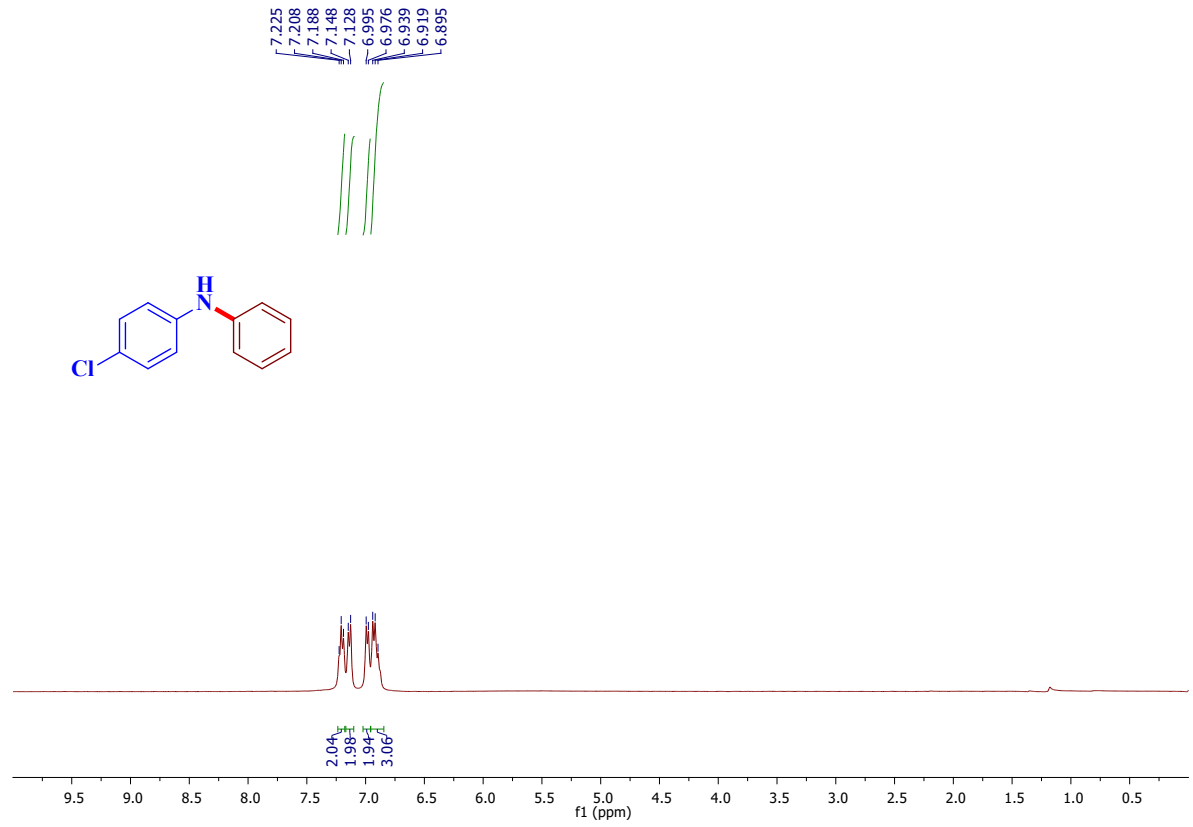
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1.94
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
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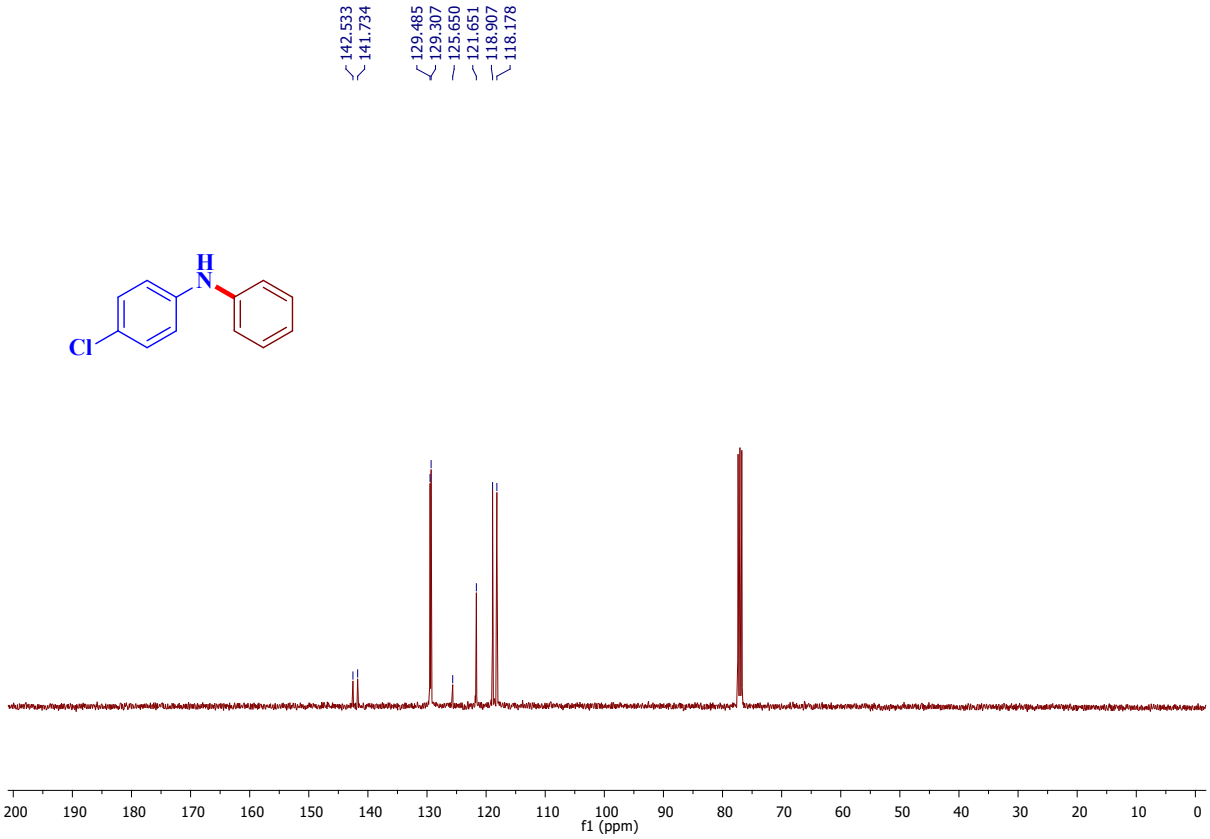
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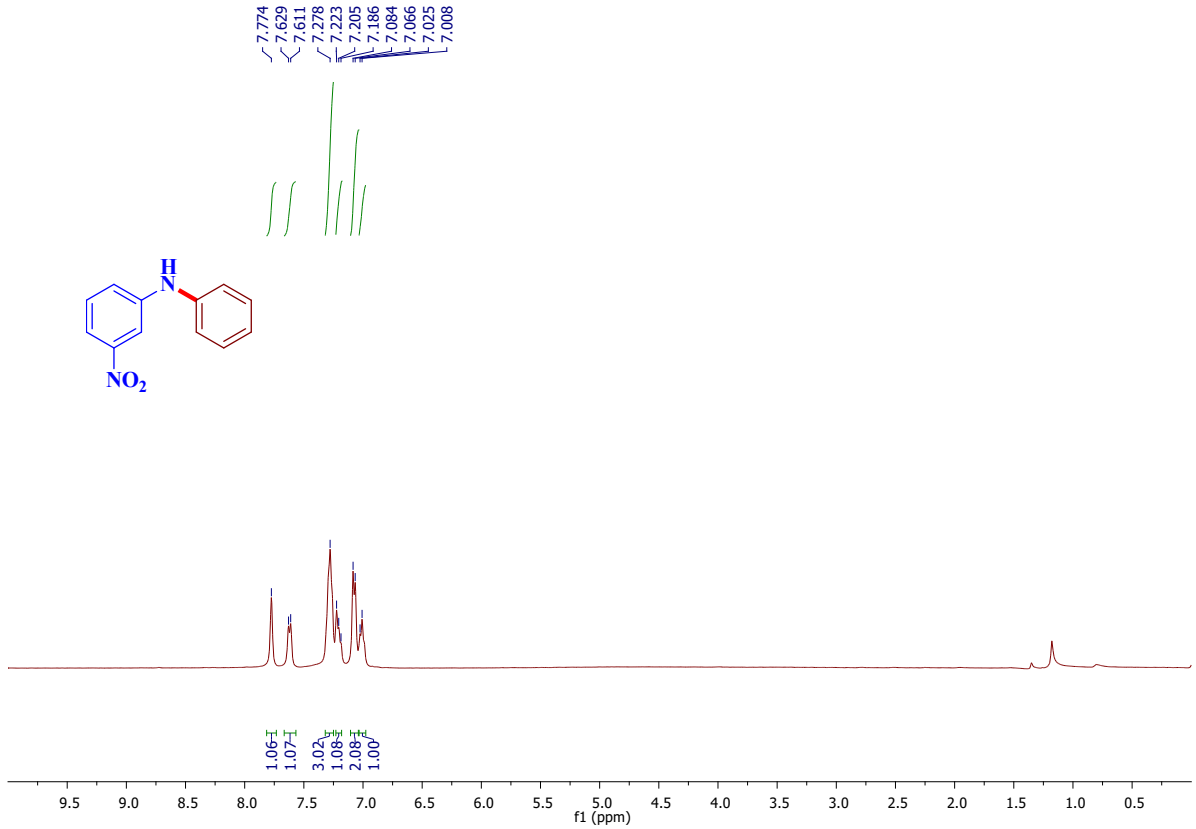
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2.08
1.00
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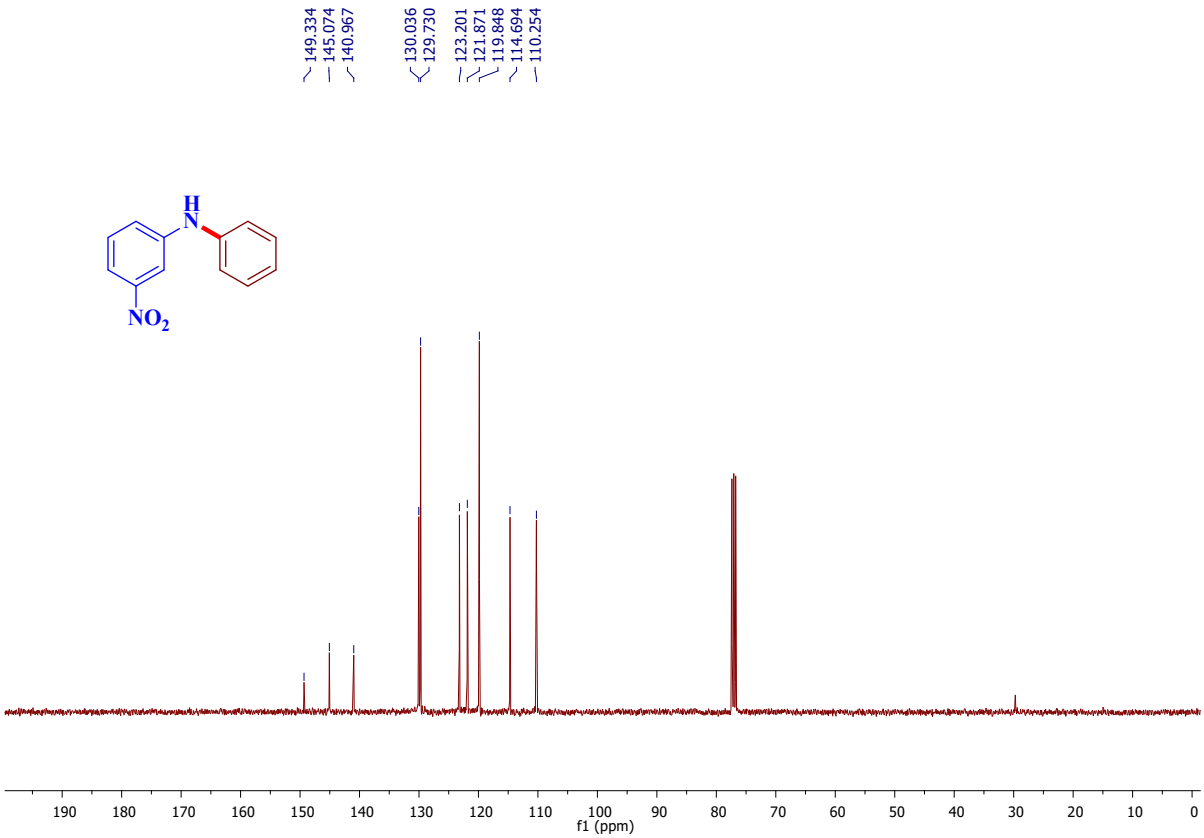
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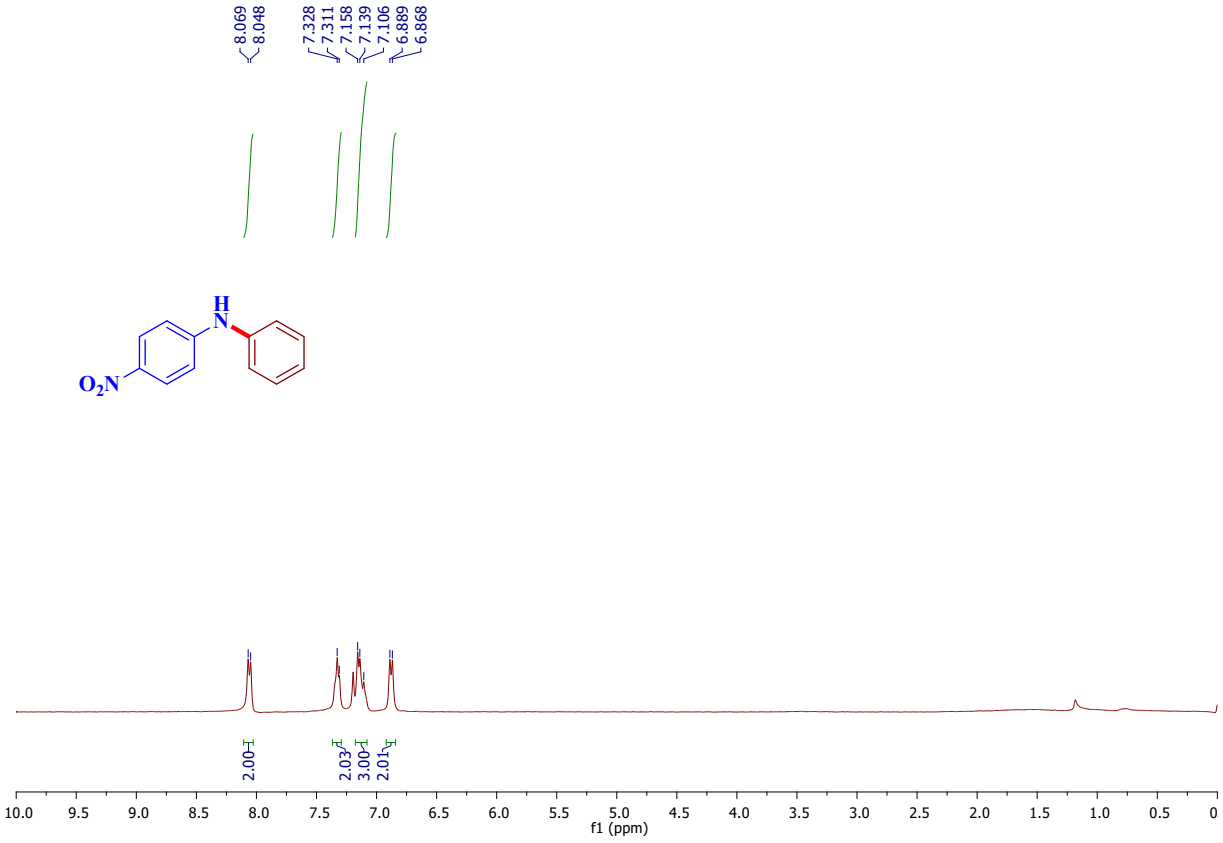
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2.01
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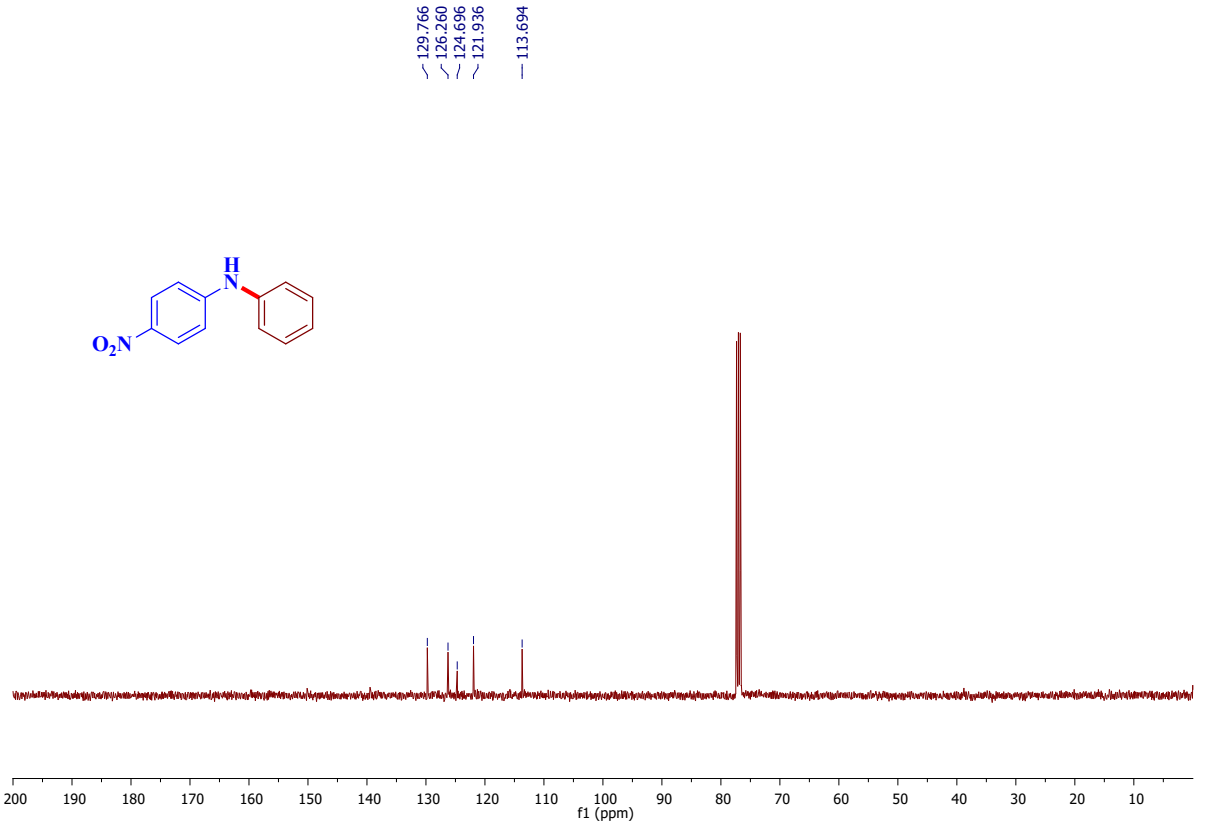
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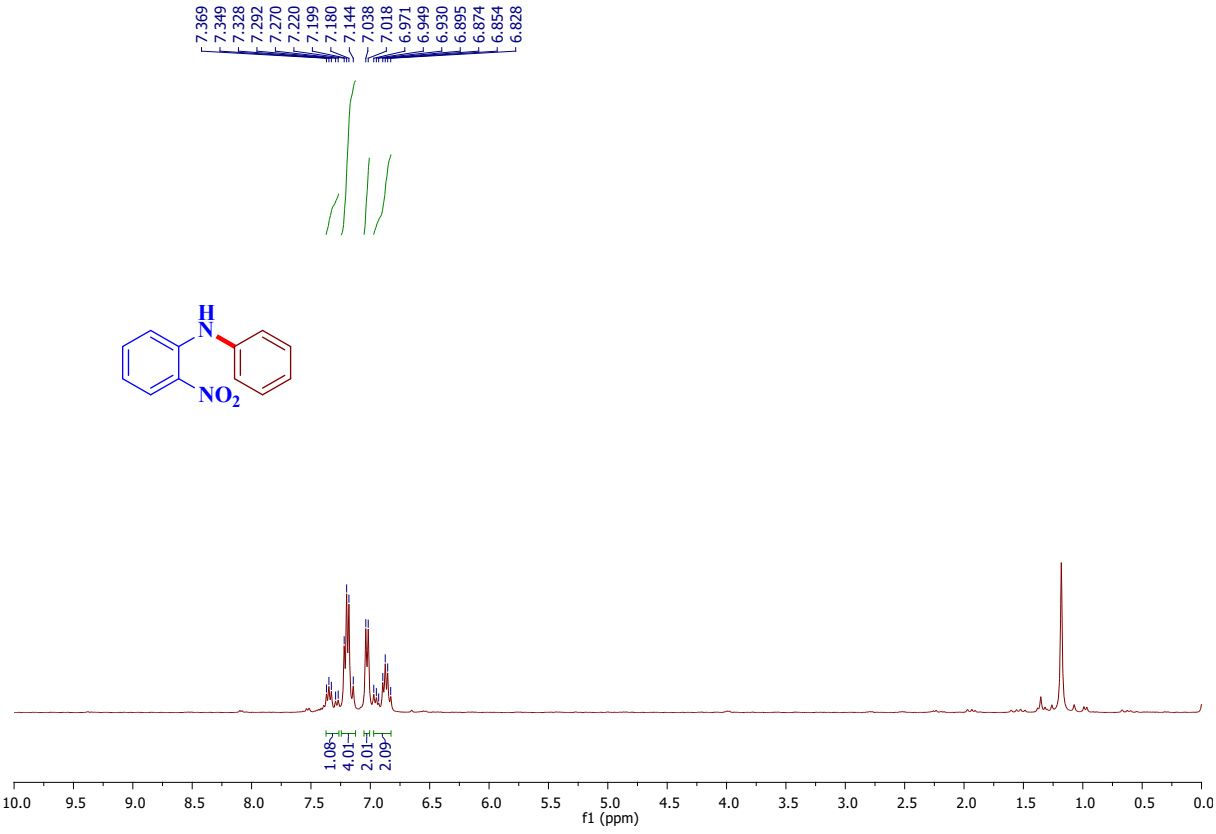
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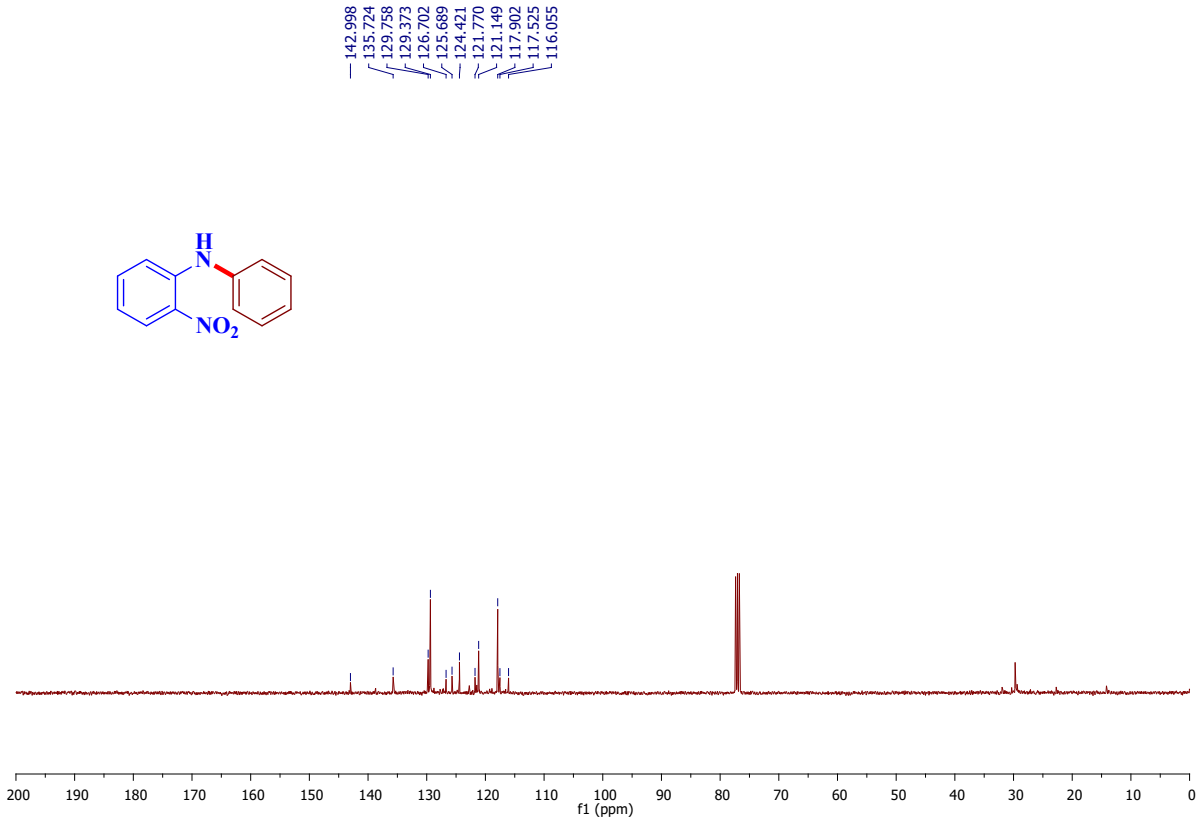
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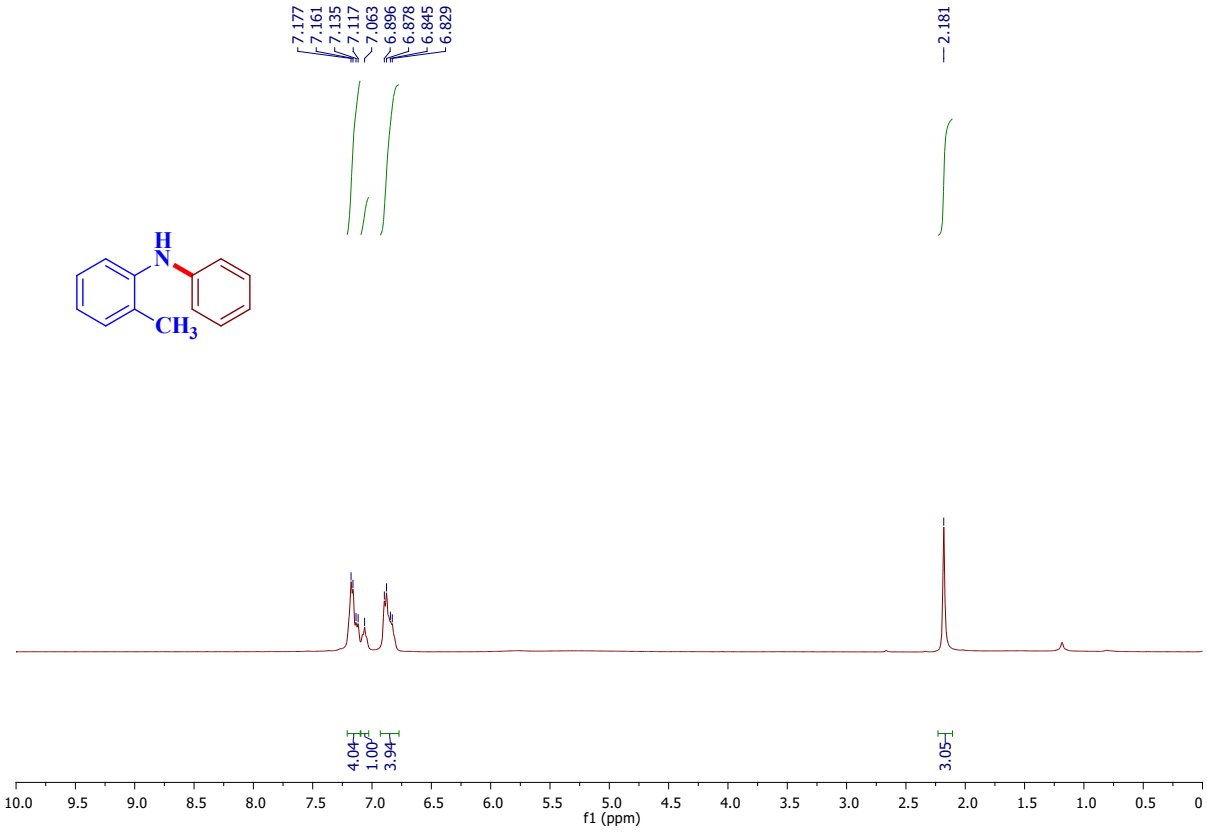
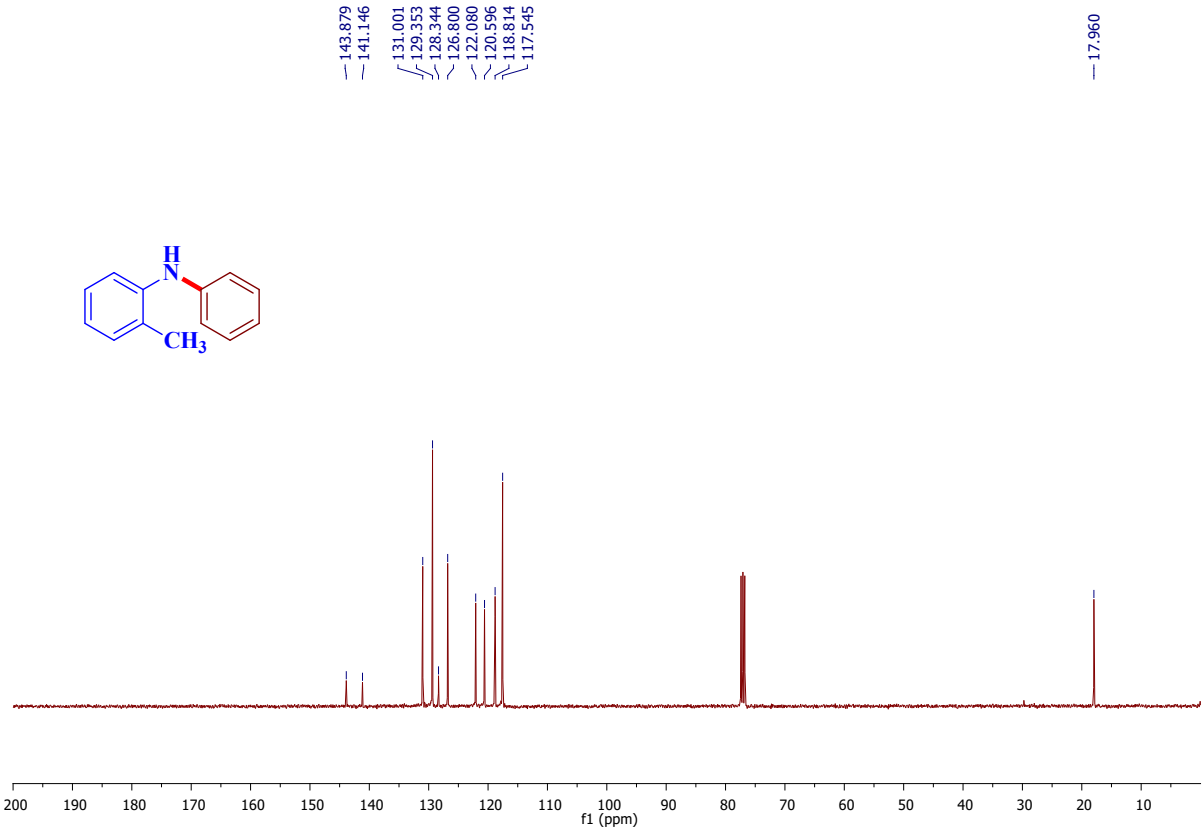
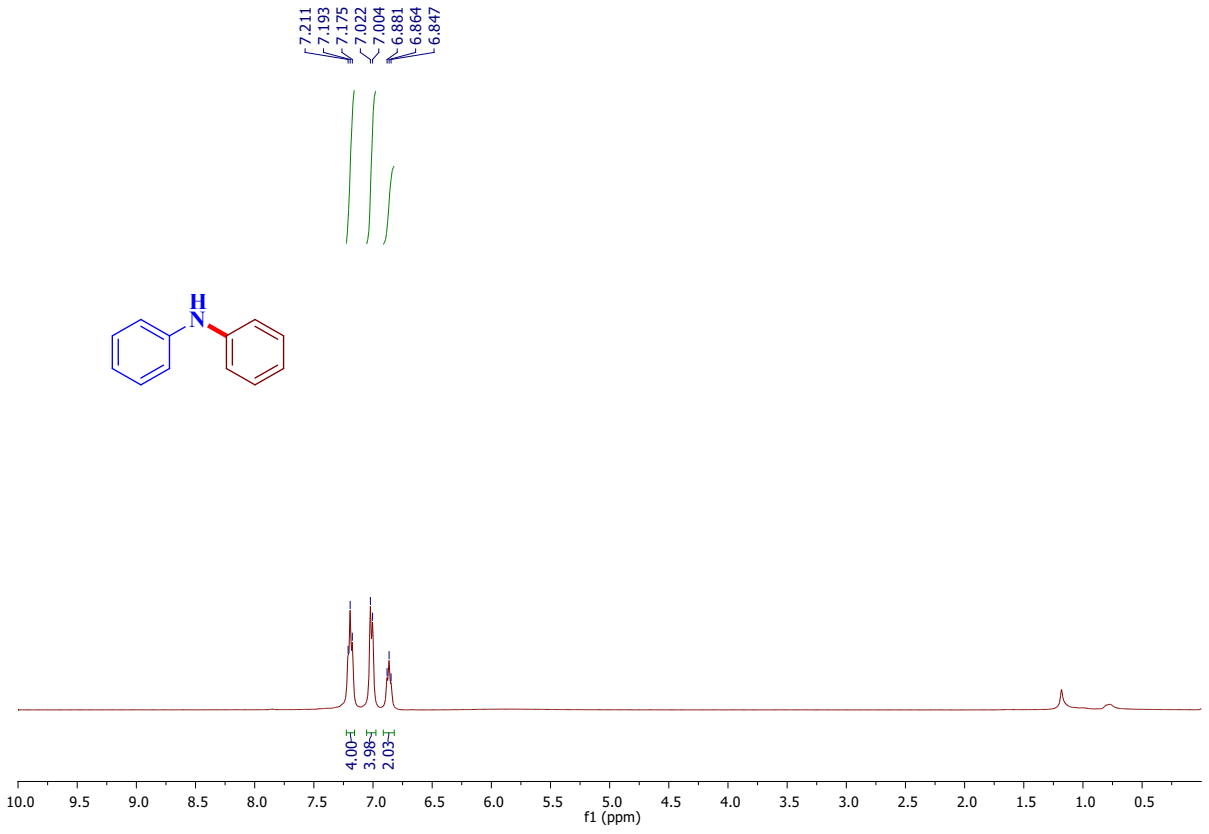
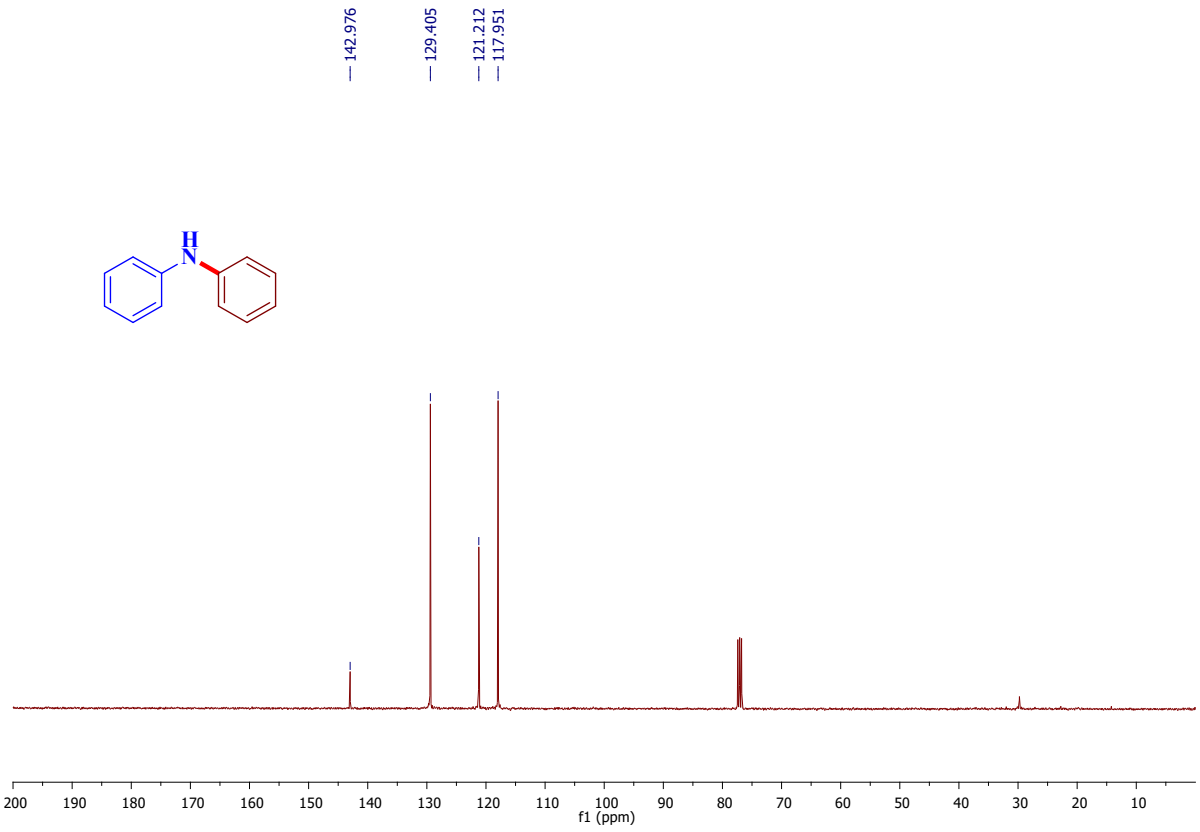
f1 (ppm)


7.177
7.161
7.135
7.117
7.063
6.896
6.878
6.845
6.829
2.181
H
N
CH3
4.04
1.00
3.94
3.05
10.0 9.5 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
f1 (ppm)


143.879
141.146
131.001
129.353
128.344
126.800
122.080
120.596
118.814
117.545
17.960
H
N
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.211
7.193
7.175
7.022
7.004
6.881
6.864
6.847
H
N
4.00
3.98
2.03
10.0 9.5 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
f1 (ppm)


142.976
129.405
121.212
117.951
H
N
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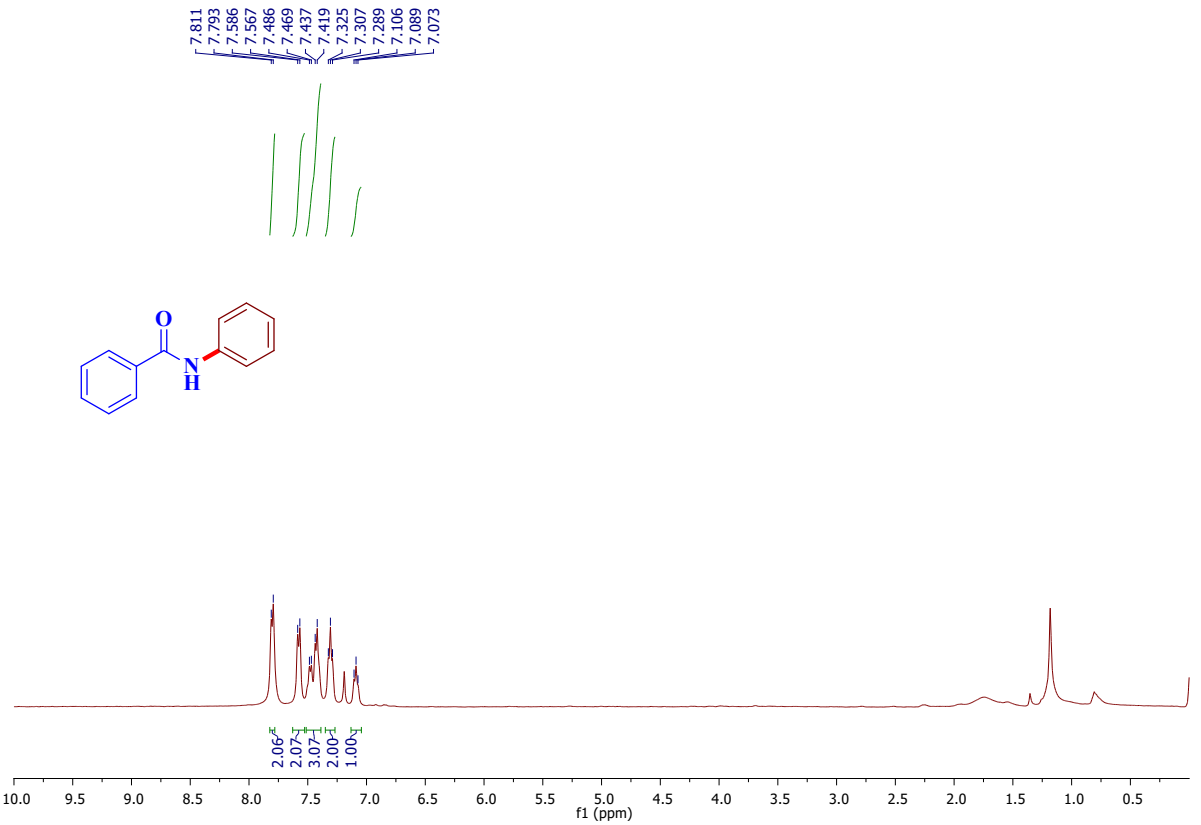
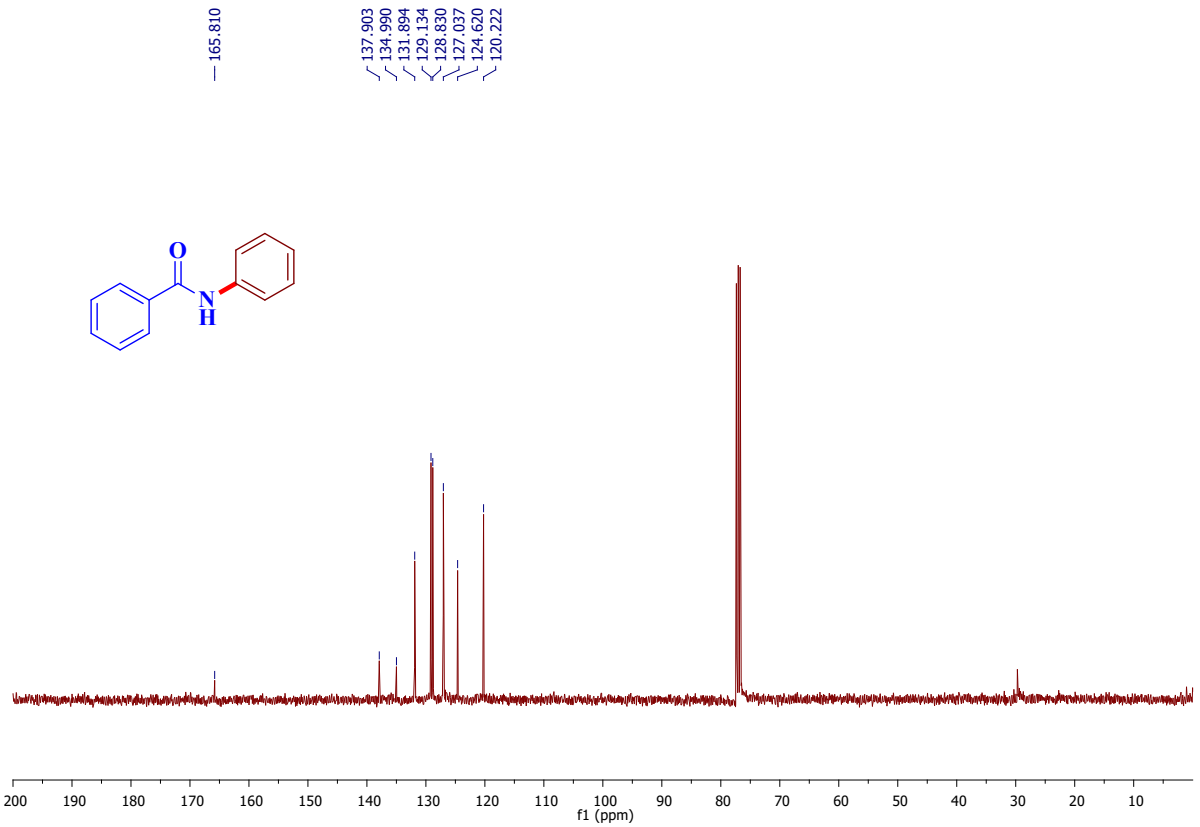
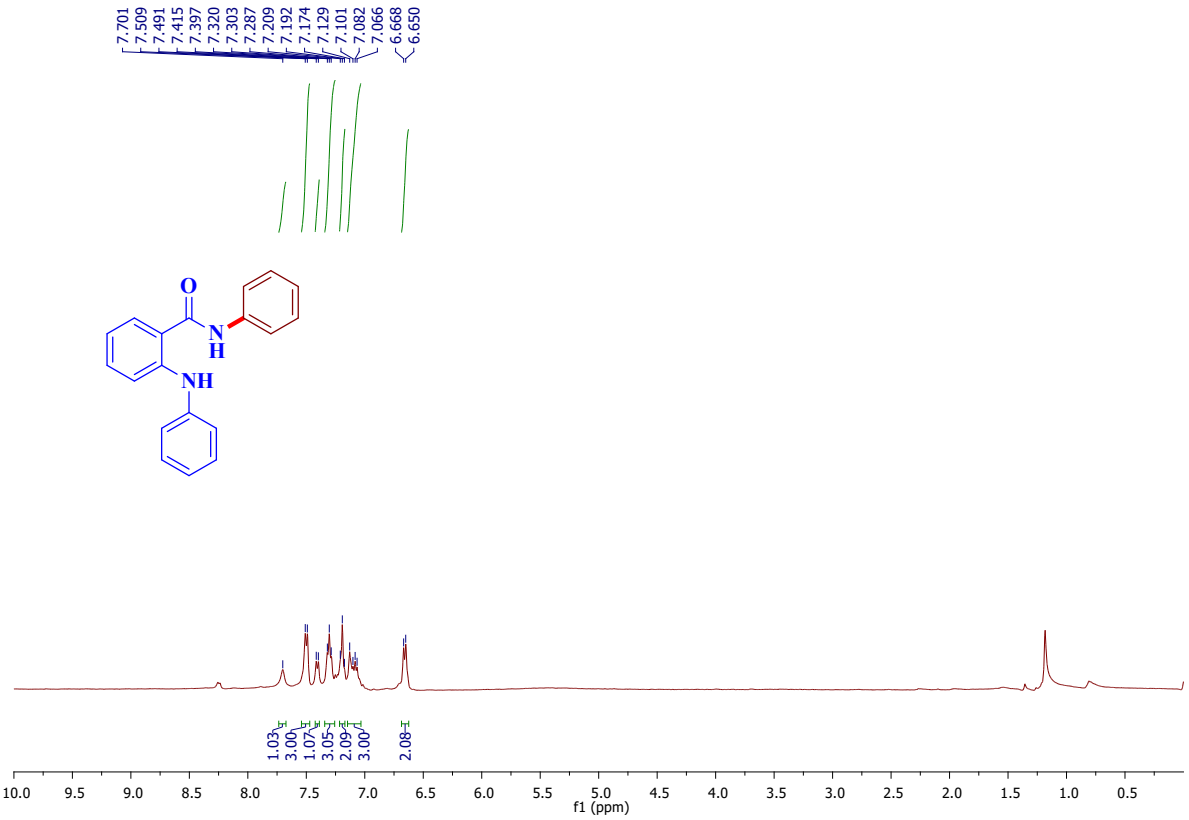
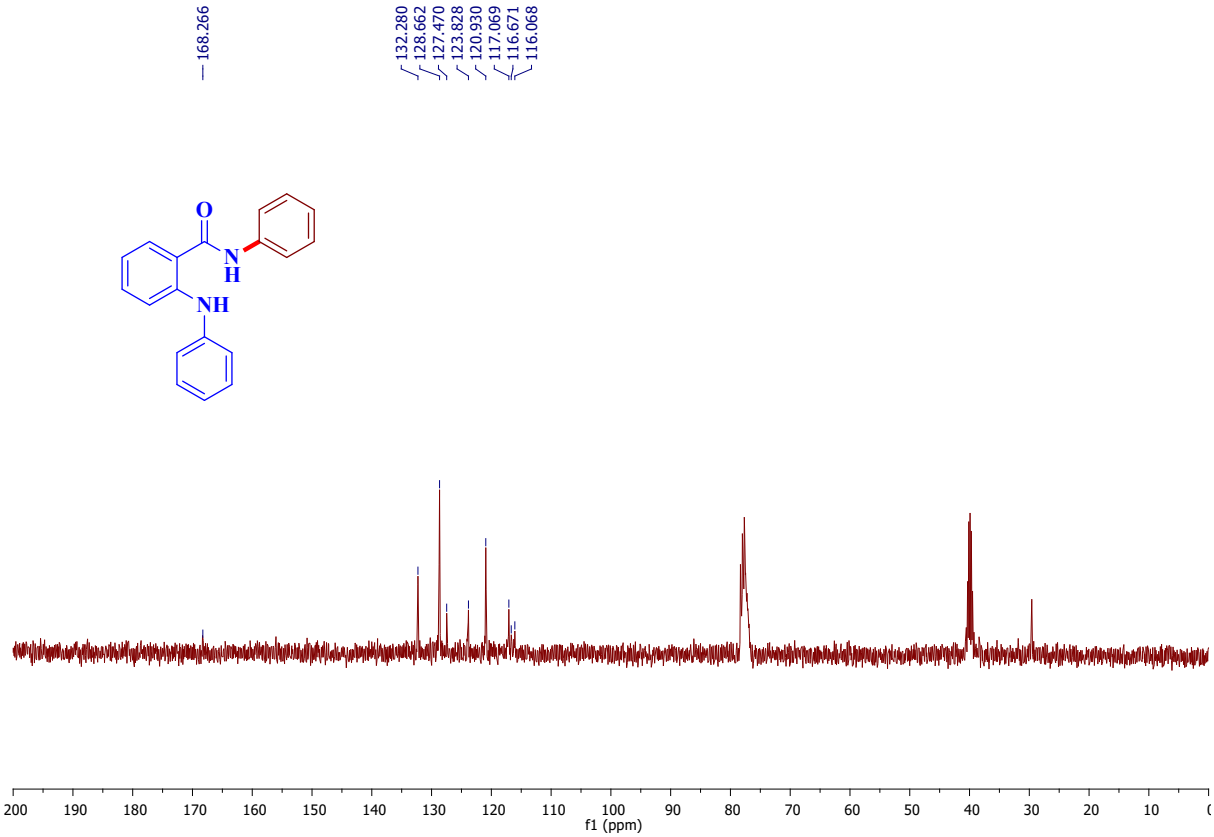
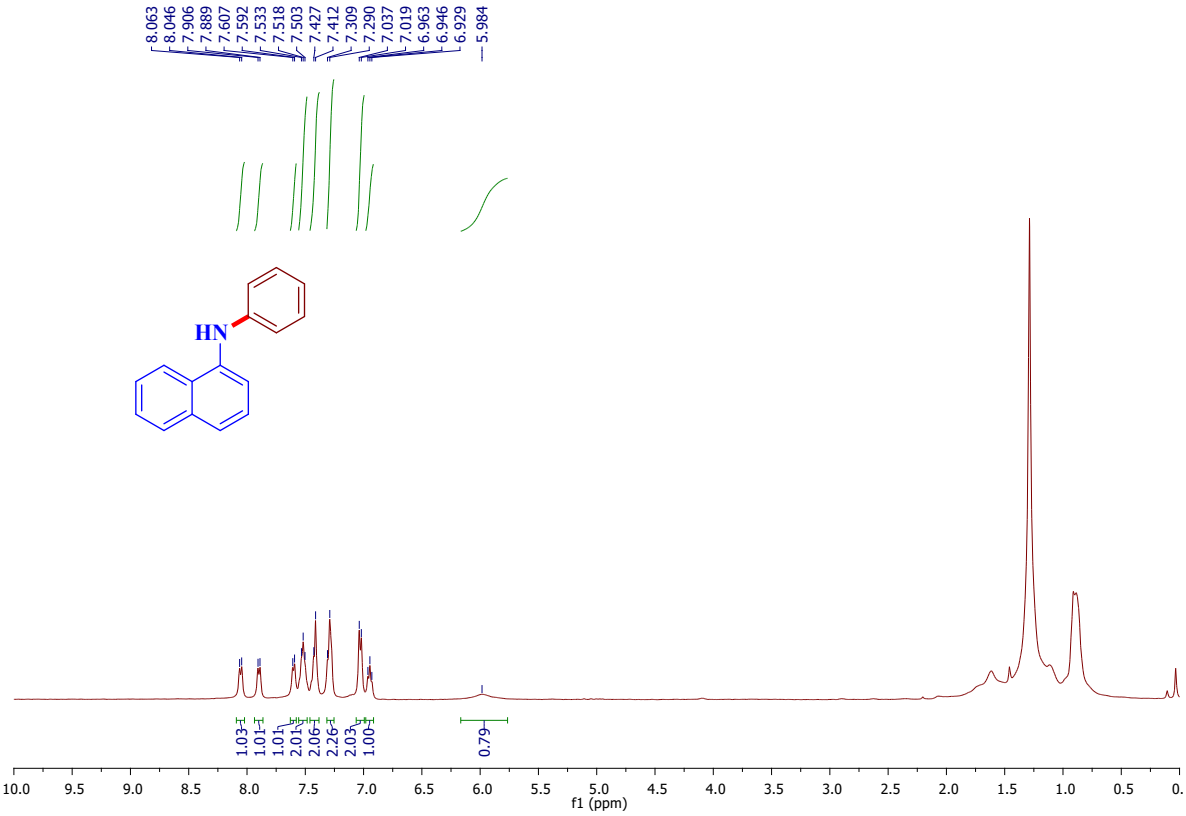
f1 (ppm)

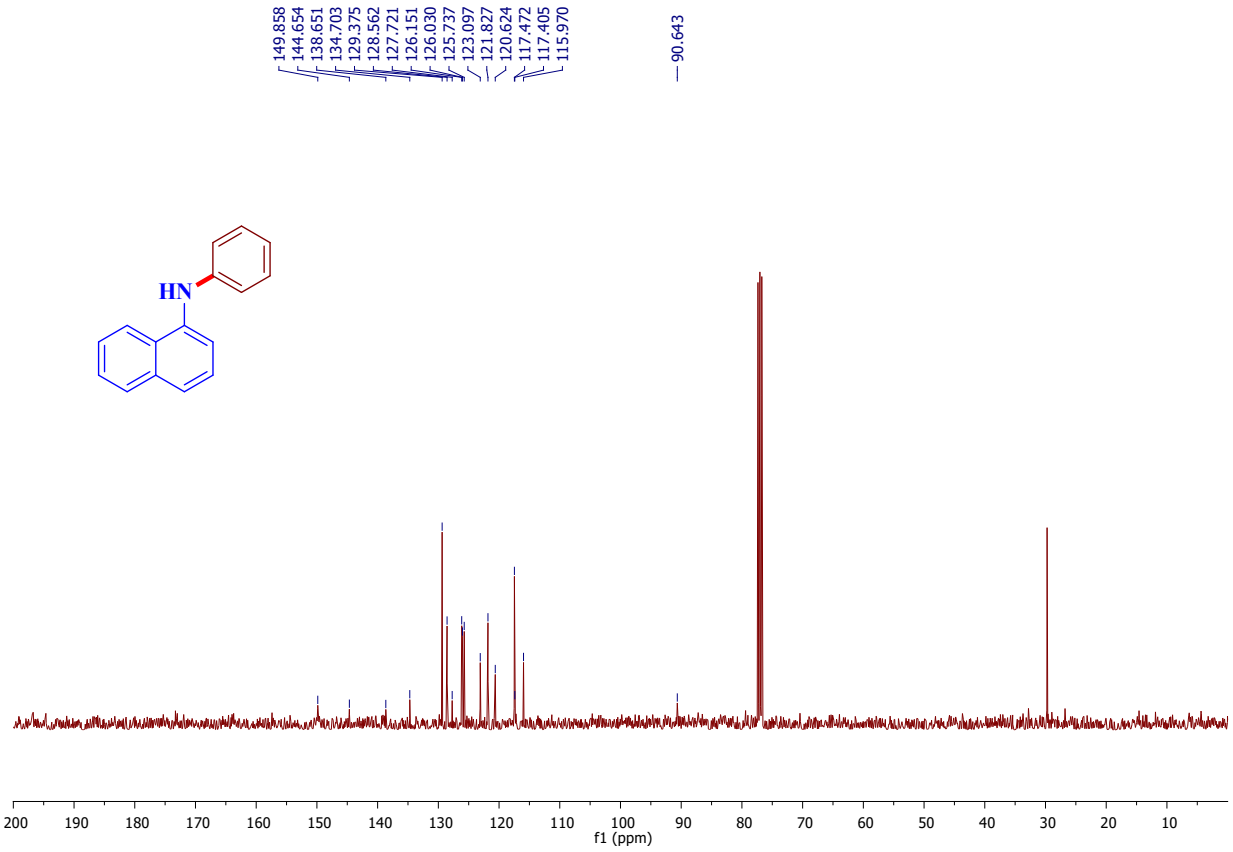

7.811
7.793
7.586
7.567
7.486
7.469
7.437
7.419
7.325
7.307
7.289
7.106
7.089
7.073
O
N
H
2.06
2.07
3.07
2.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

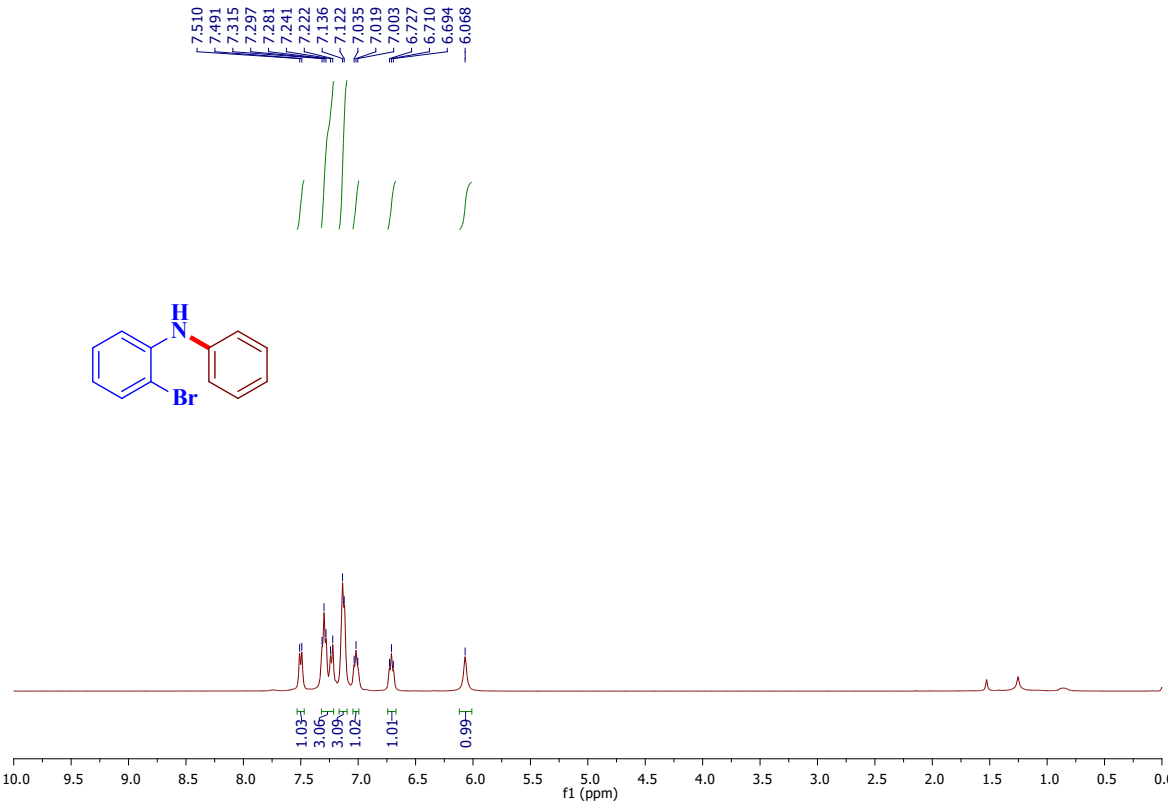

165.810
137.903
134.990
131.894
129.134
128.830
127.037
124.620
120.222
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

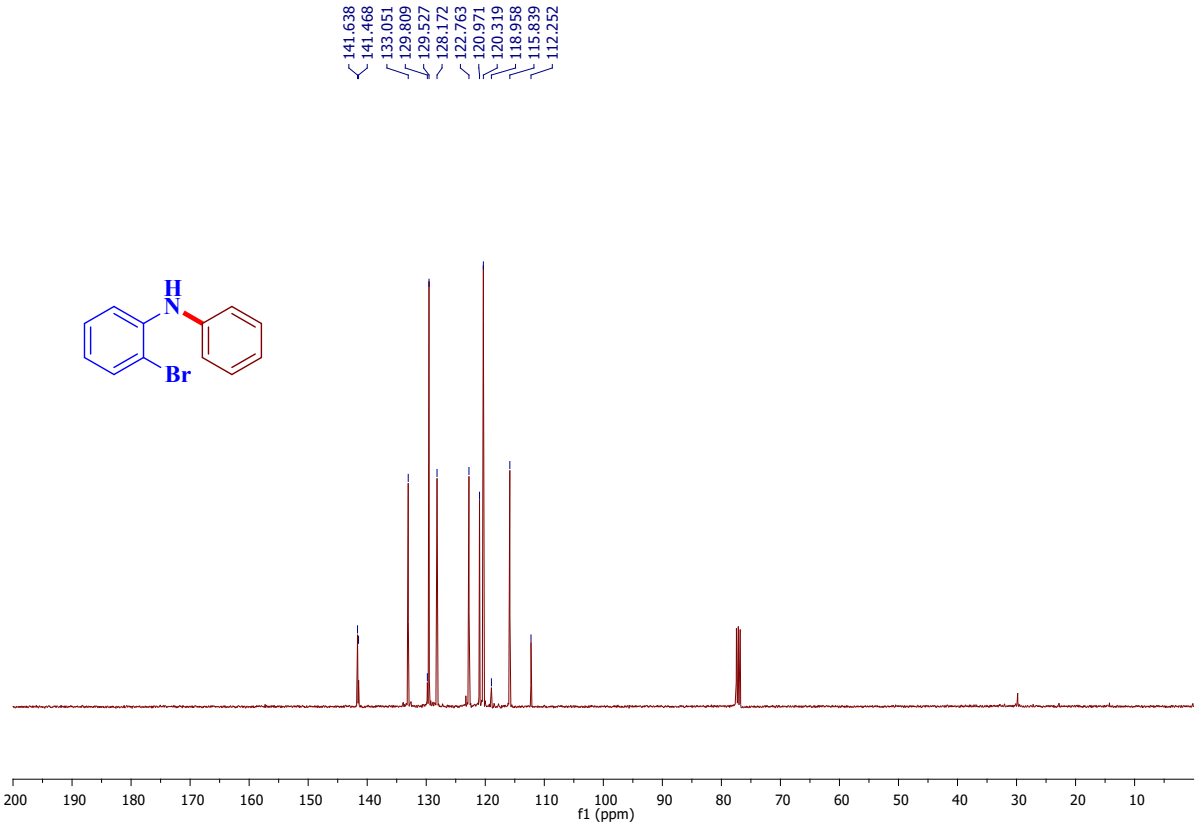

7.701
7.509
7.491
7.415
7.397
7.320
7.303
7.287
7.209
7.192
7.174
7.129
7.101
7.082
7.066
6.668
6.650
O
N
H
NH
1.03
3.00
1.07
3.05
2.09
3.00
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

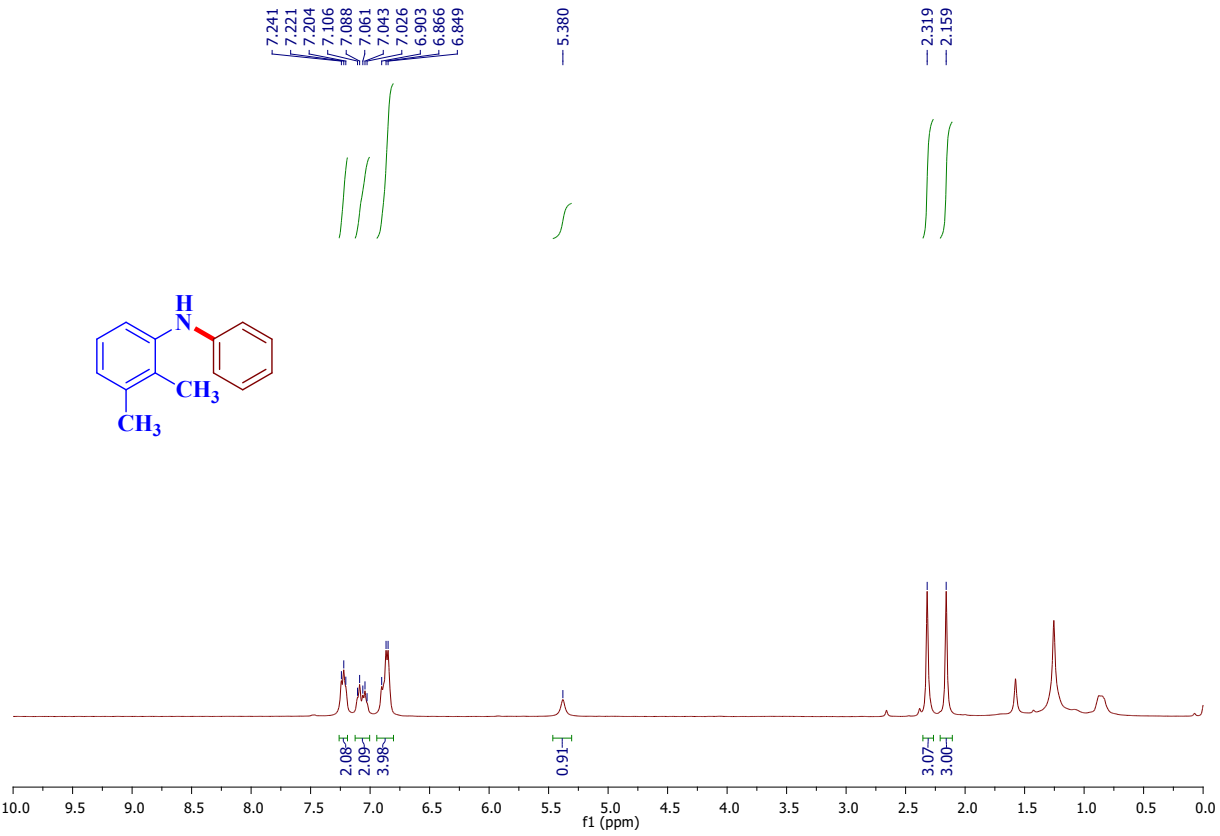

168.266
132.280
128.662
127.470
123.828
120.930
117.069
116.671
116.068
O
N
H
NH
f1 (ppm)

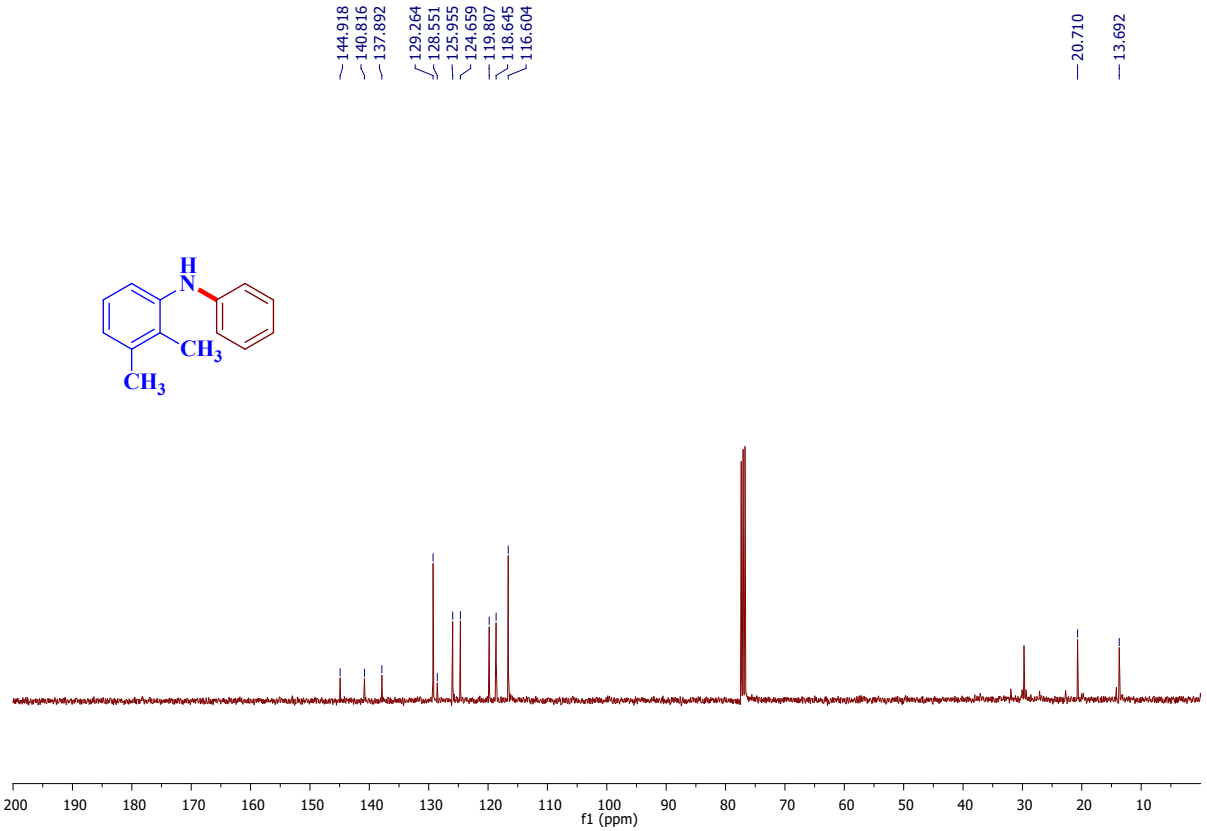

8.063
8.046
7.906
7.889
7.607
7.592
7.533
7.518
7.503
7.427
7.412
7.309
7.290
7.037
7.019
6.963
6.946
6.929
5.984
HN
1.03
1.01
1.01
2.01
2.06
2.26
2.03
1.00
0.79
f1 (ppm)


149.858
144.654
138.651
134.703
129.375
128.562
127.721
126.151
126.030
125.737
123.097
121.827
120.624
117.472
117.405
115.970
90.643
HN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.510
7.491
7.315
7.297
7.281
7.241
7.222
7.136
7.122
7.035
7.019
7.003
6.727
6.710
6.694
6.068
H
N
Br
1.03
3.06
3.09
1.02
1.01
0.99
10.0 9.5 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
f1 (ppm)


141.638
141.468
133.051
129.809
129.527
128.172
122.763
120.971
120.319
118.958
115.839
112.252
H
N
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.241
7.221
7.204
7.106
7.088
7.061
7.043
7.026
6.903
6.866
6.849
5.380
2.319
2.159
H
N
CH3
CH3
2.08
2.09
3.98
0.91
3.07
3.00
10.0 9.5 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
f1 (ppm)


144.918
140.816
137.892
129.264
128.551
125.955
124.659
119.807
118.645
116.604
20.710
13.692
H
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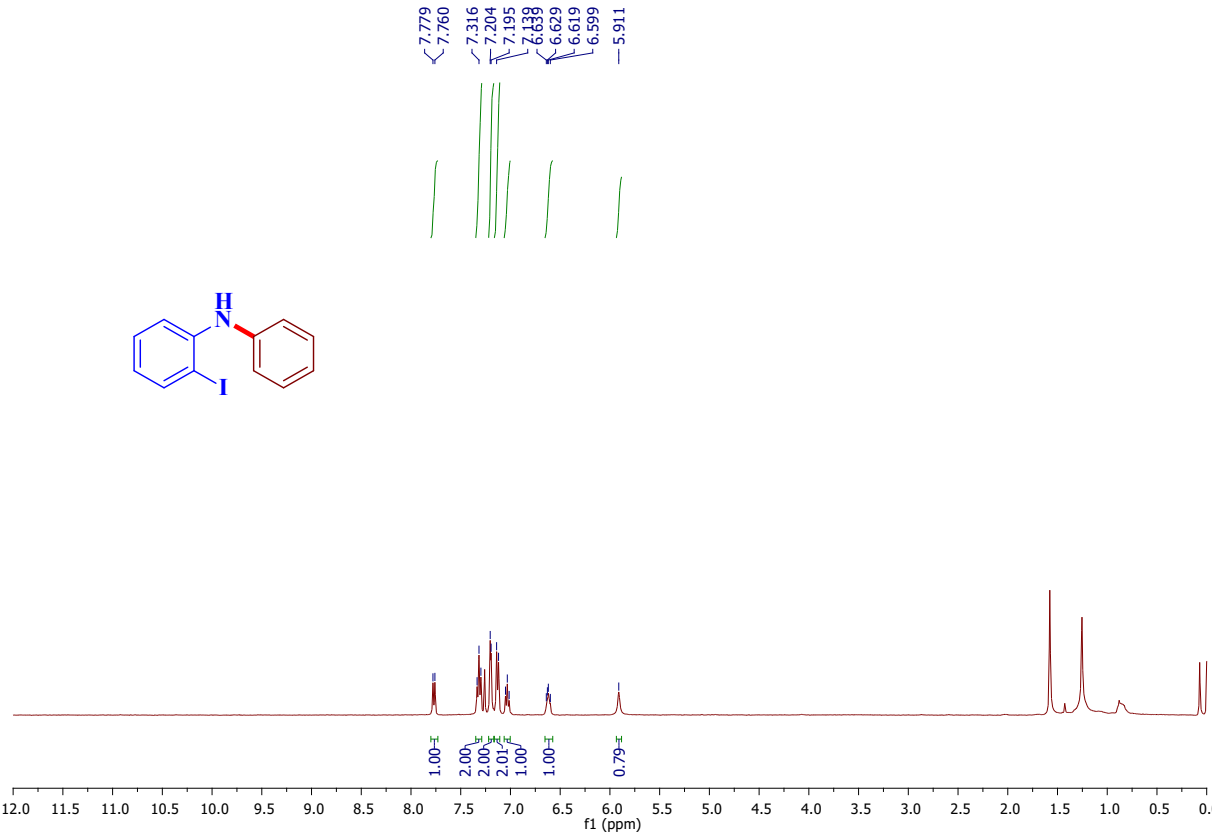
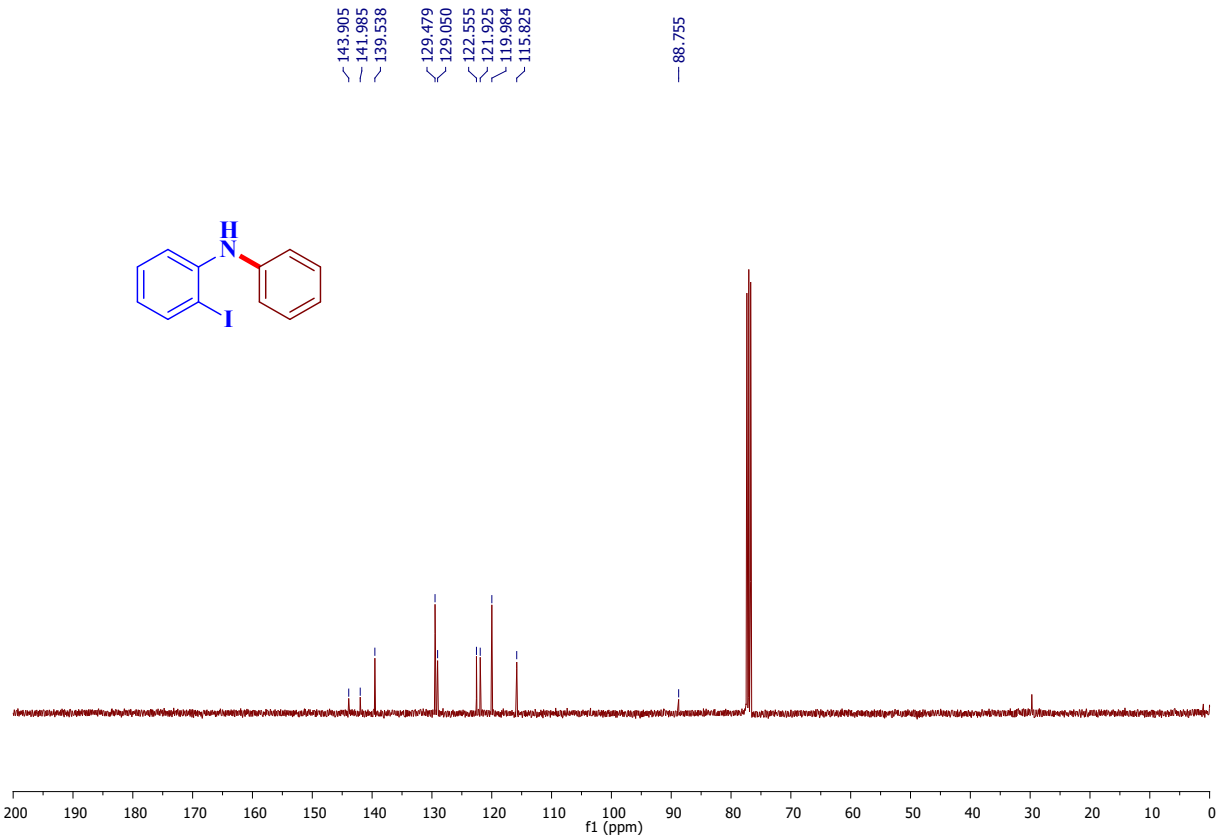
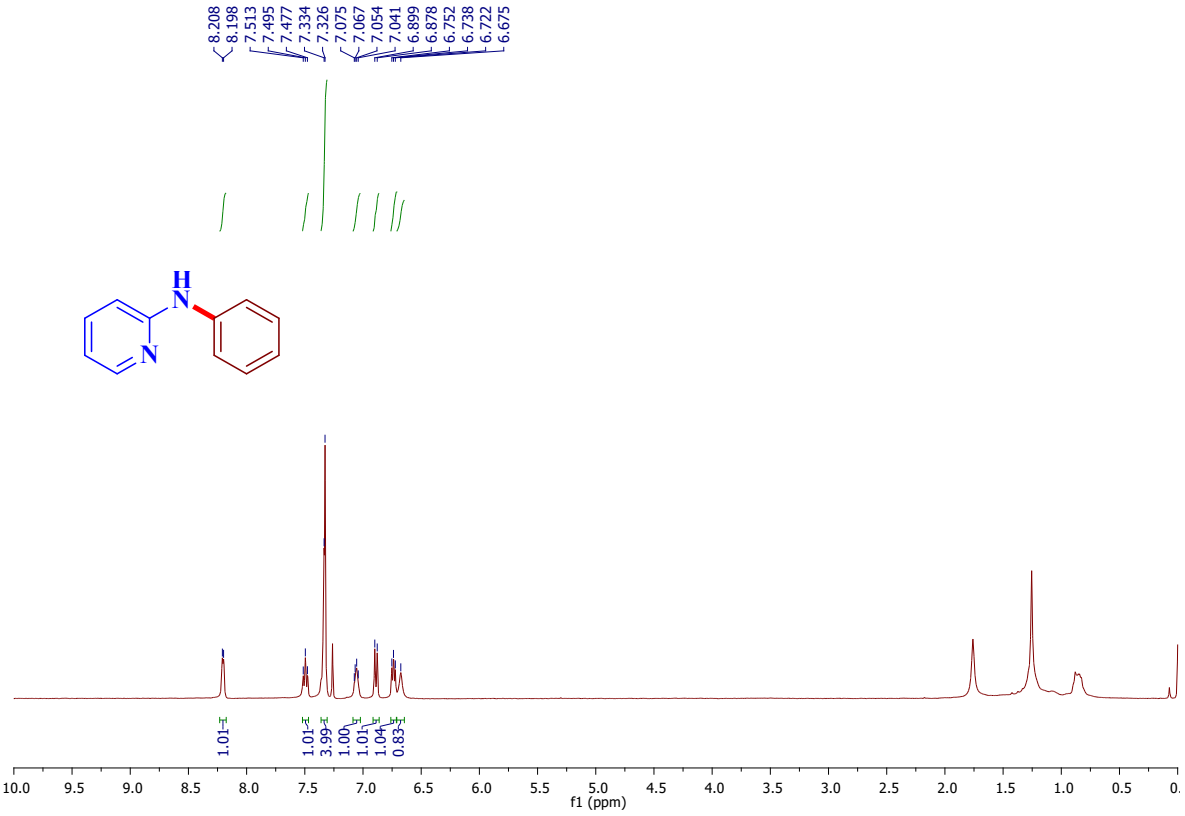
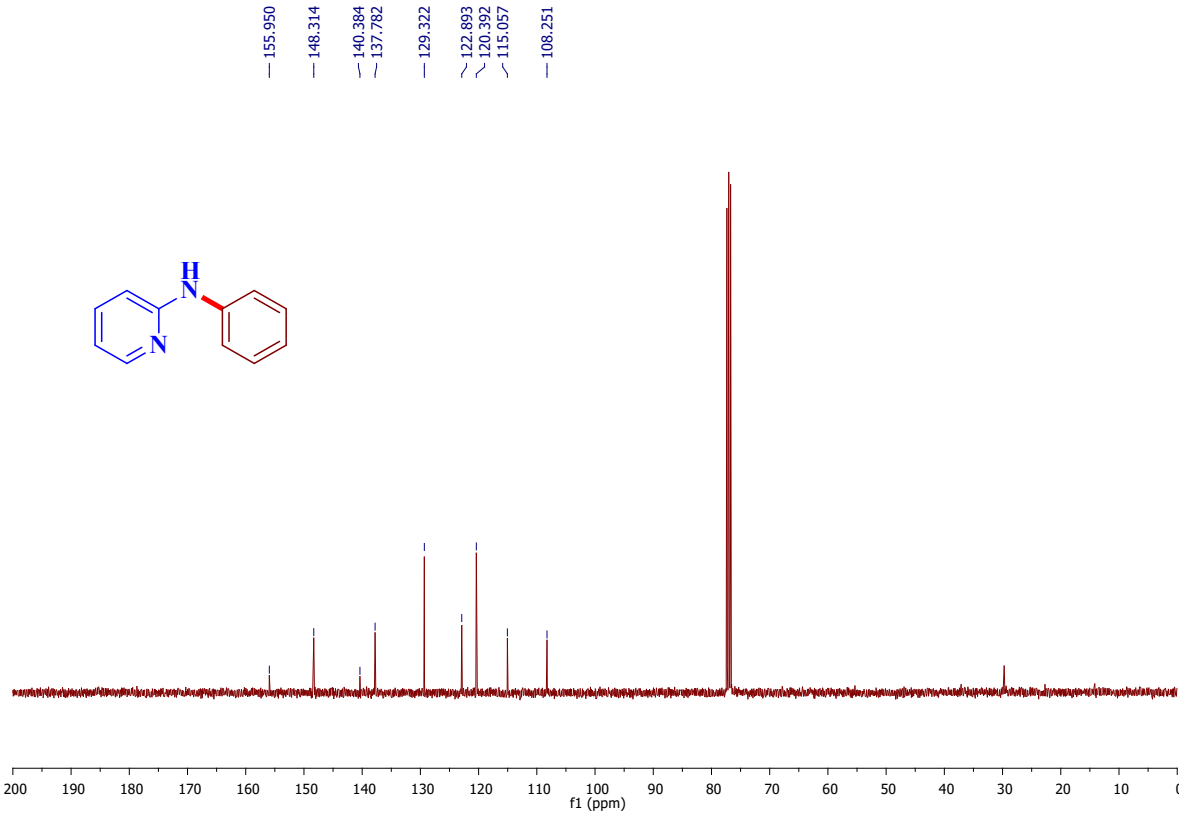
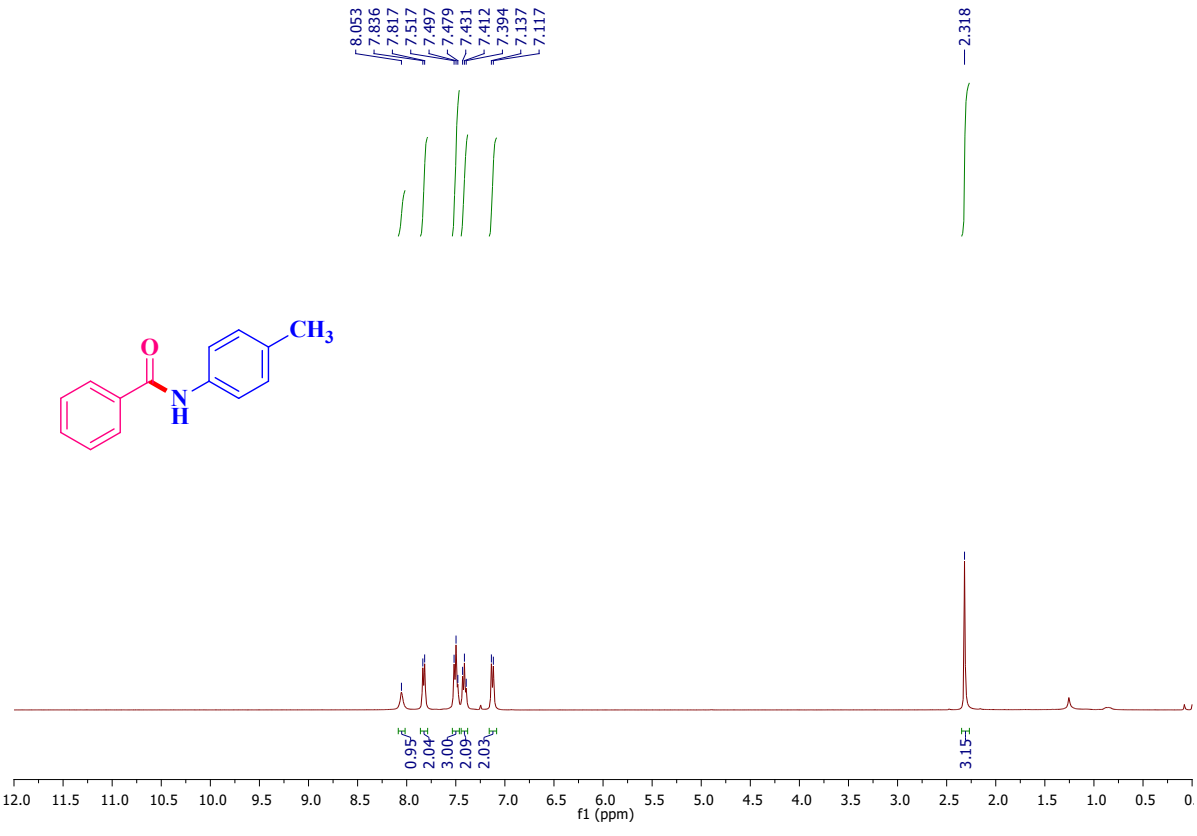
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

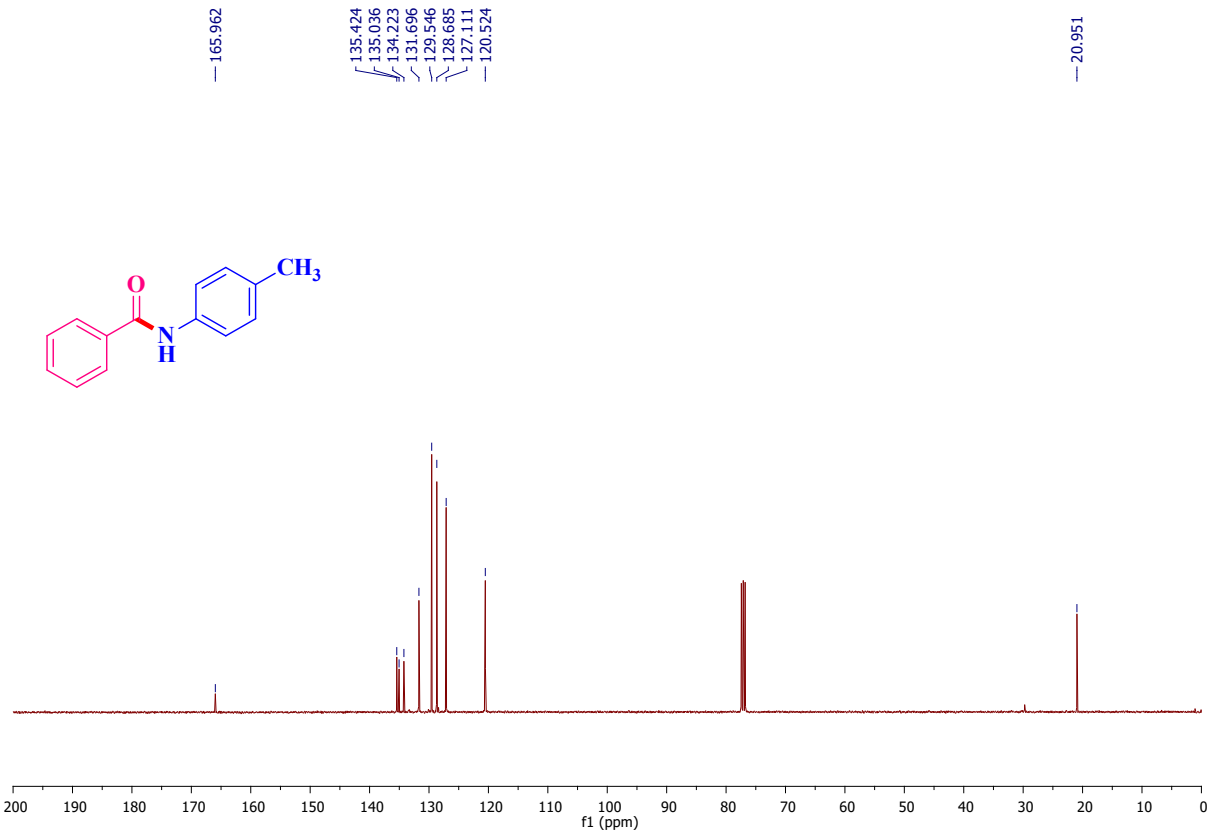

7.779
7.760
7.316
7.204
7.195
6.629
6.619
6.599
5.911
H
N
I
1.00
2.00
2.00
2.01
1.00
1.00
0.79
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

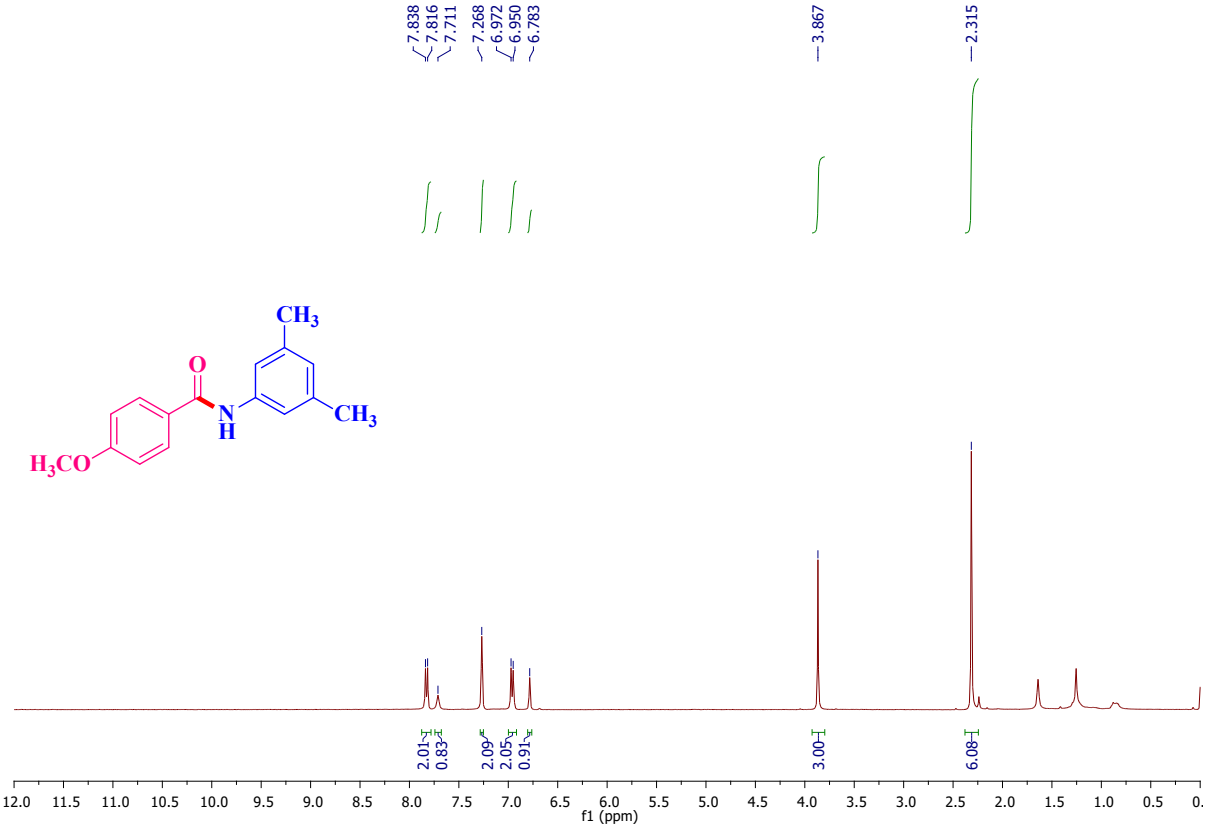

143.905
141.985
139.538
129.479
129.050
122.555
121.925
119.984
115.825
88.755
H
N
I
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

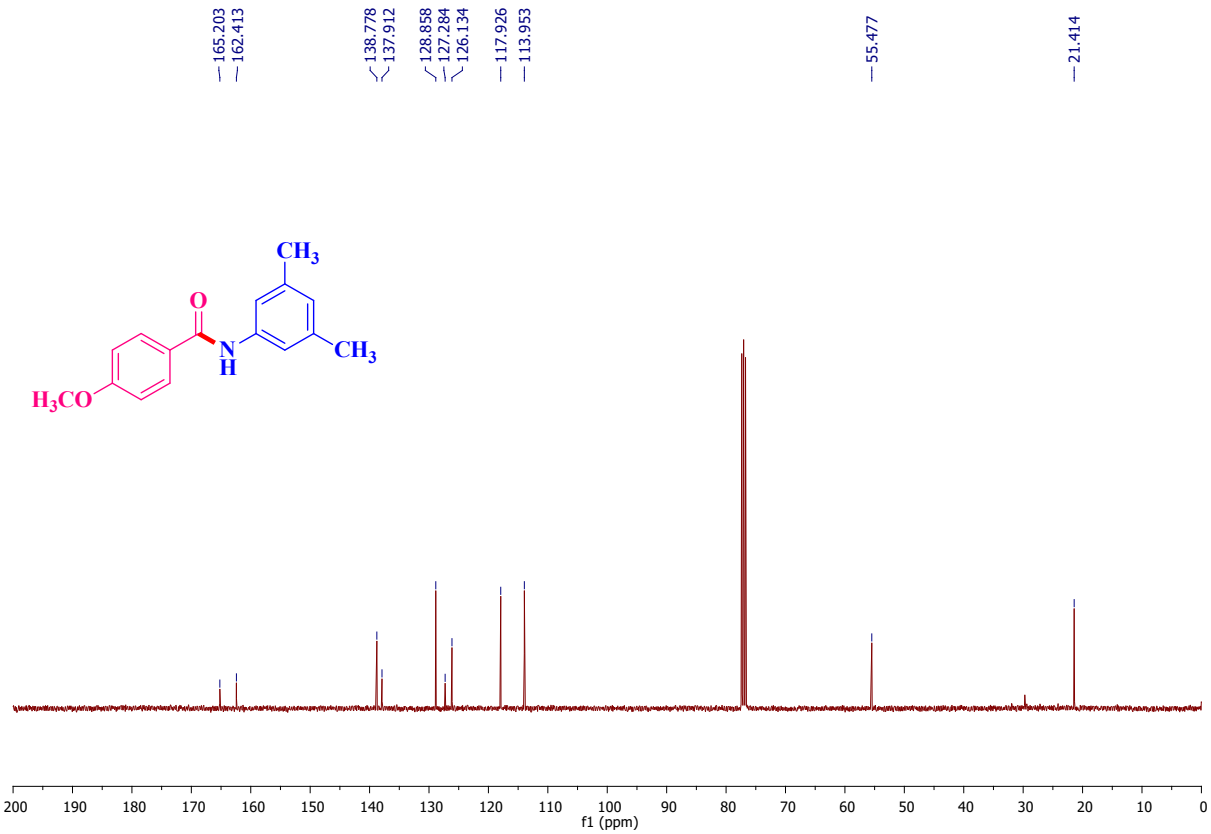

8.208
8.198
7.513
7.495
7.477
7.334
7.326
7.075
7.067
7.054
7.041
6.899
6.878
6.752
6.738
6.722
6.675
H
N
N
1.01
1.01
3.99
1.00
1.01
1.04
0.83
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

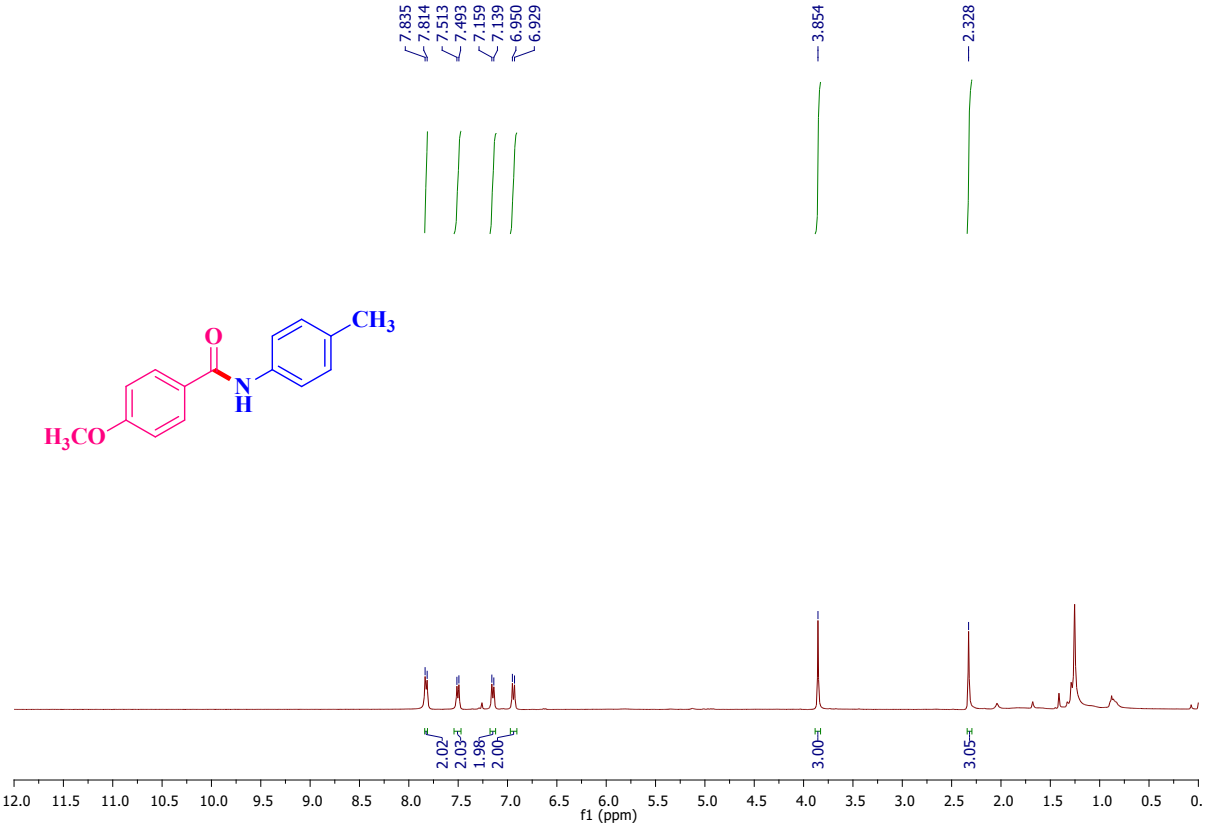

155.950
148.314
140.384
137.782
129.322
122.893
120.392
115.057
108.251
H
N
N
f1 (ppm)

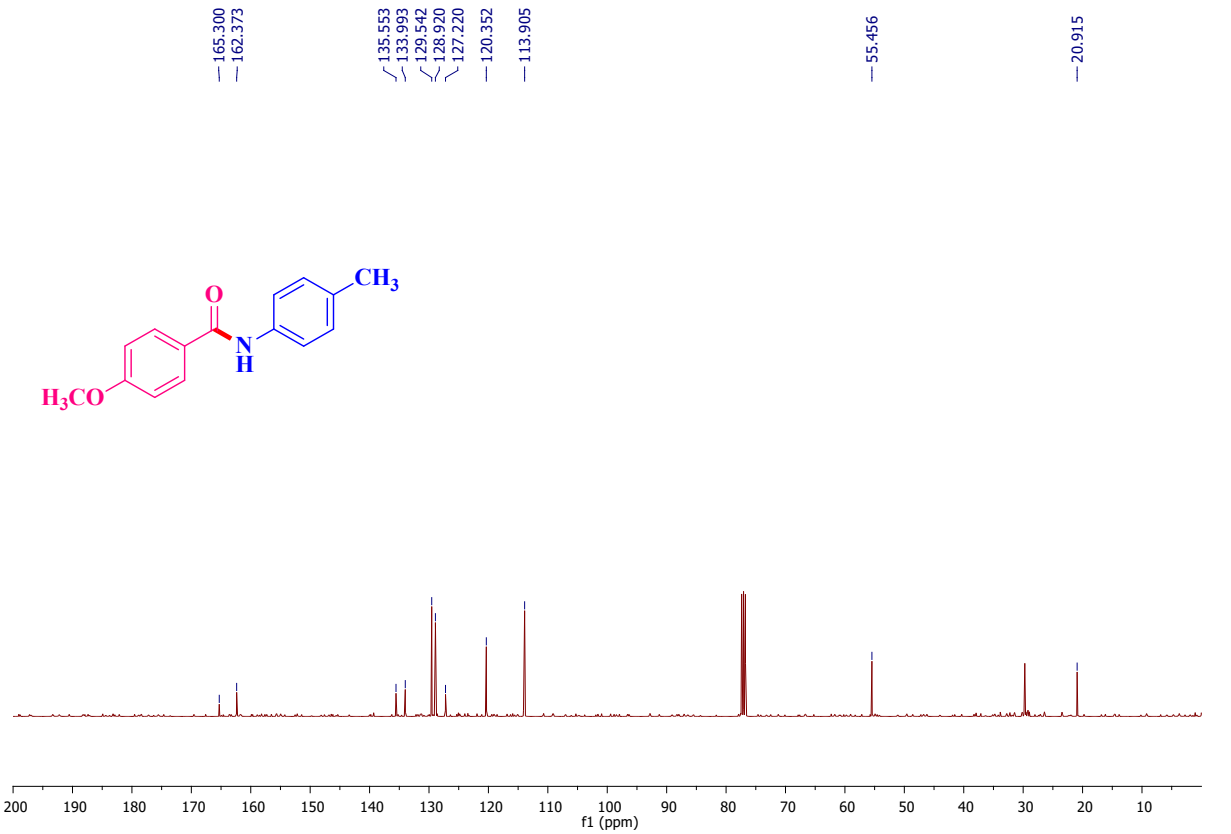

8.053
7.836
7.817
7.517
7.497
7.479
7.431
7.412
7.394
7.137
7.117
2.318
O
N
H
CH3
0.95
2.04
3.00
2.09
2.03
3.15
f1 (ppm)

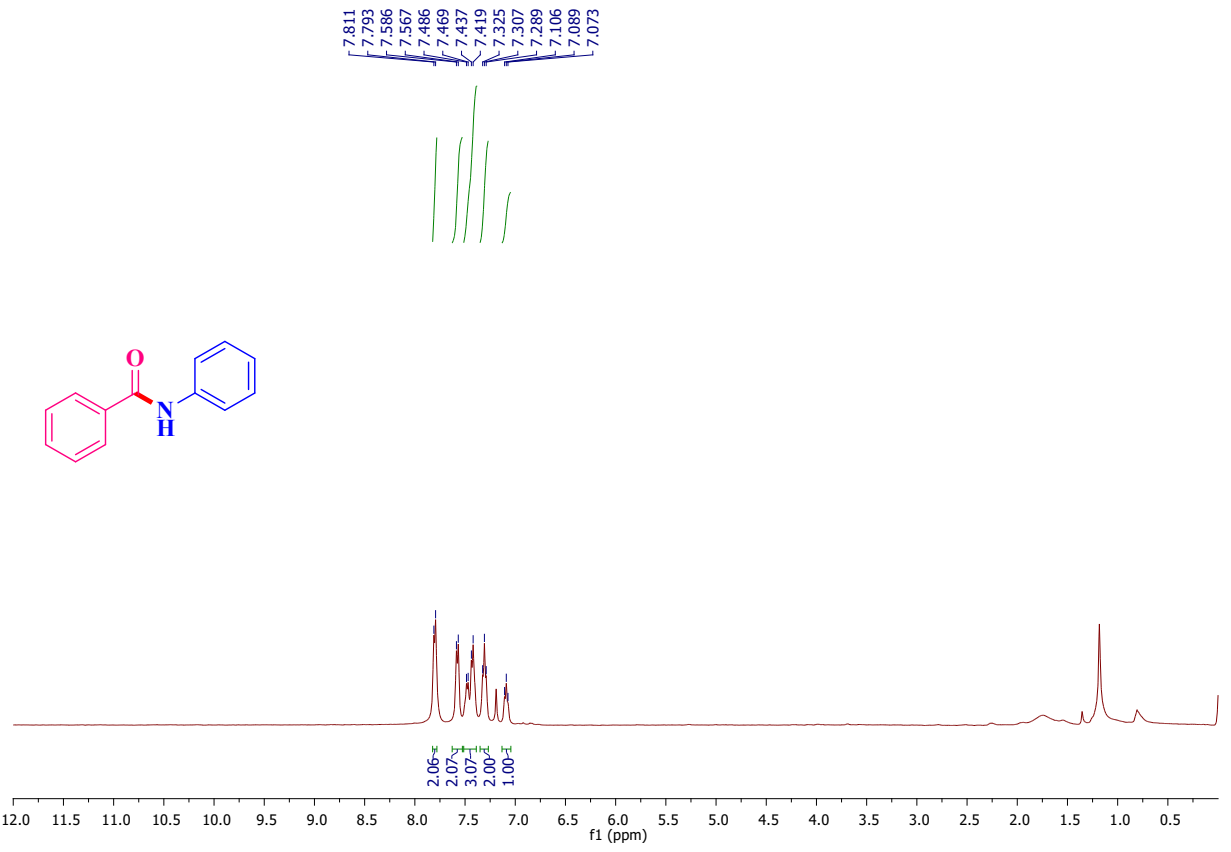

165.962
135.424
135.036
134.223
131.696
129.546
128.685
127.111
120.524
20.951
O
N
H
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

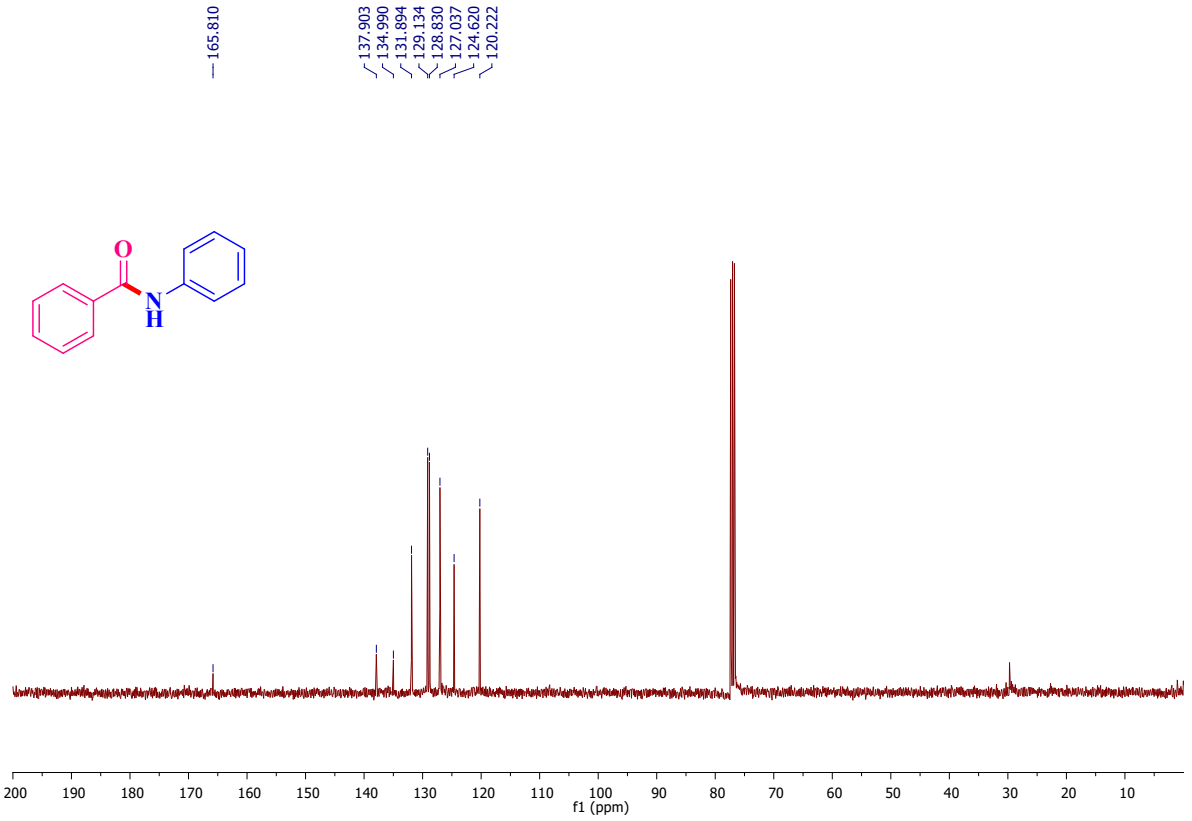

7.838
7.816
7.711
7.268
6.972
6.950
6.783
3.867
2.315
CH3
O
N
H
CH3
H3CO
2.01
0.83
2.09
2.05
0.91
3.00
6.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

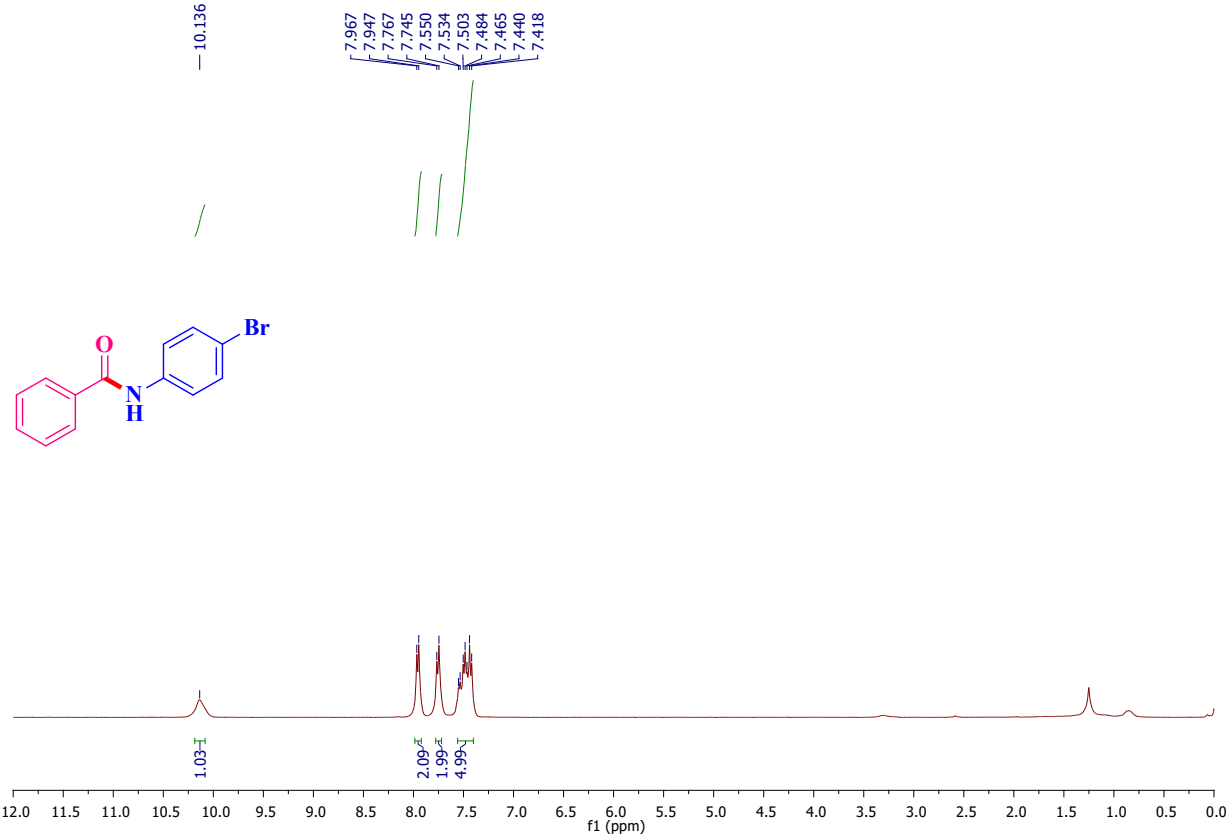

165.203
162.413
138.778
137.912
128.858
127.284
126.134
117.926
113.953
55.477
21.414
CH3
O
N
H
CH3
H3CO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.835
7.814
7.513
7.493
7.159
7.139
6.950
6.929
3.854
2.328
CH3
O
N
H
H3CO
2.02
2.03
1.98
2.00
3.00
3.05
12.0 11.5 11.0 10.5 10.0 9.5 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.
f1 (ppm)


165.300
162.373
135.553
133.993
129.542
128.920
127.220
120.352
113.905
55.456
20.915
O
N
H
CH3
H3CO
f1 (ppm)


7.811
7.793
7.586
7.567
7.486
7.469
7.437
7.419
7.325
7.307
7.289
7.106
7.089
7.073
O
N
H
2.06
2.07
3.07
2.00
1.00
f1 (ppm)


165.810
137.903
134.990
131.894
129.134
128.830
127.037
124.620
120.222
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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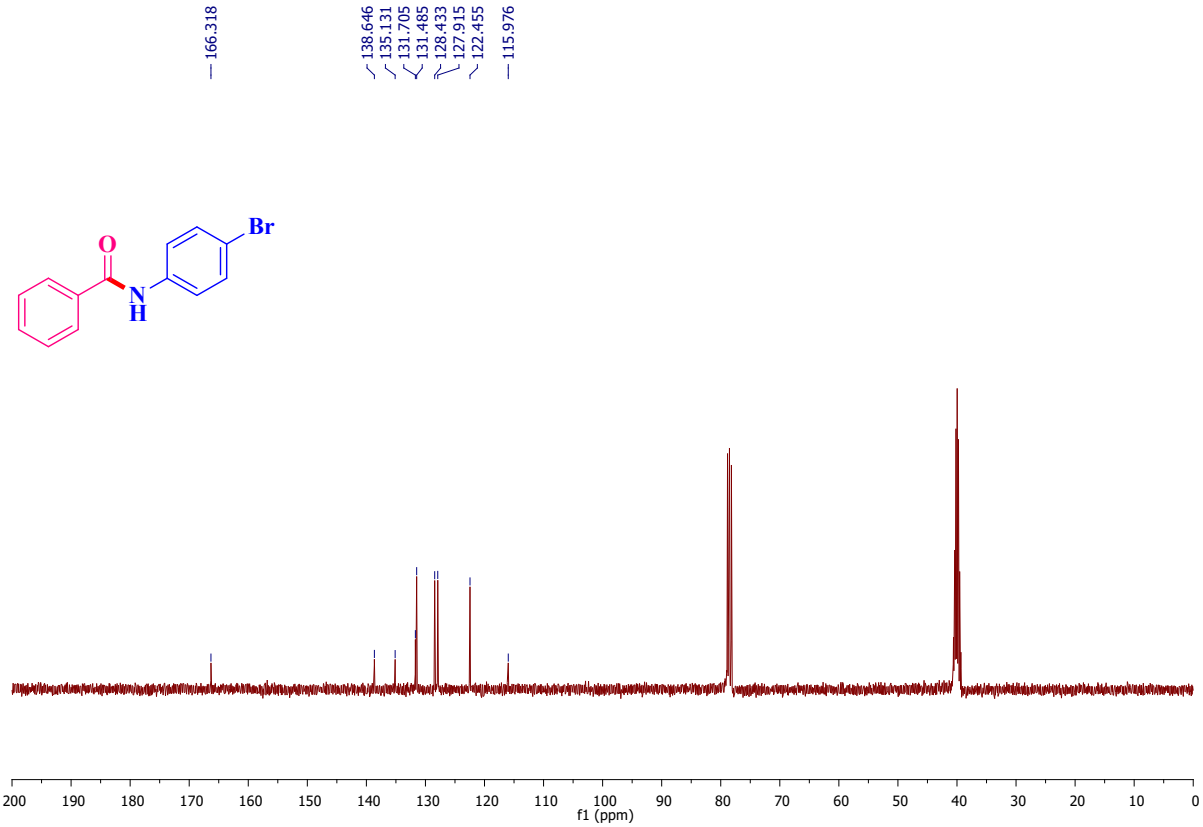
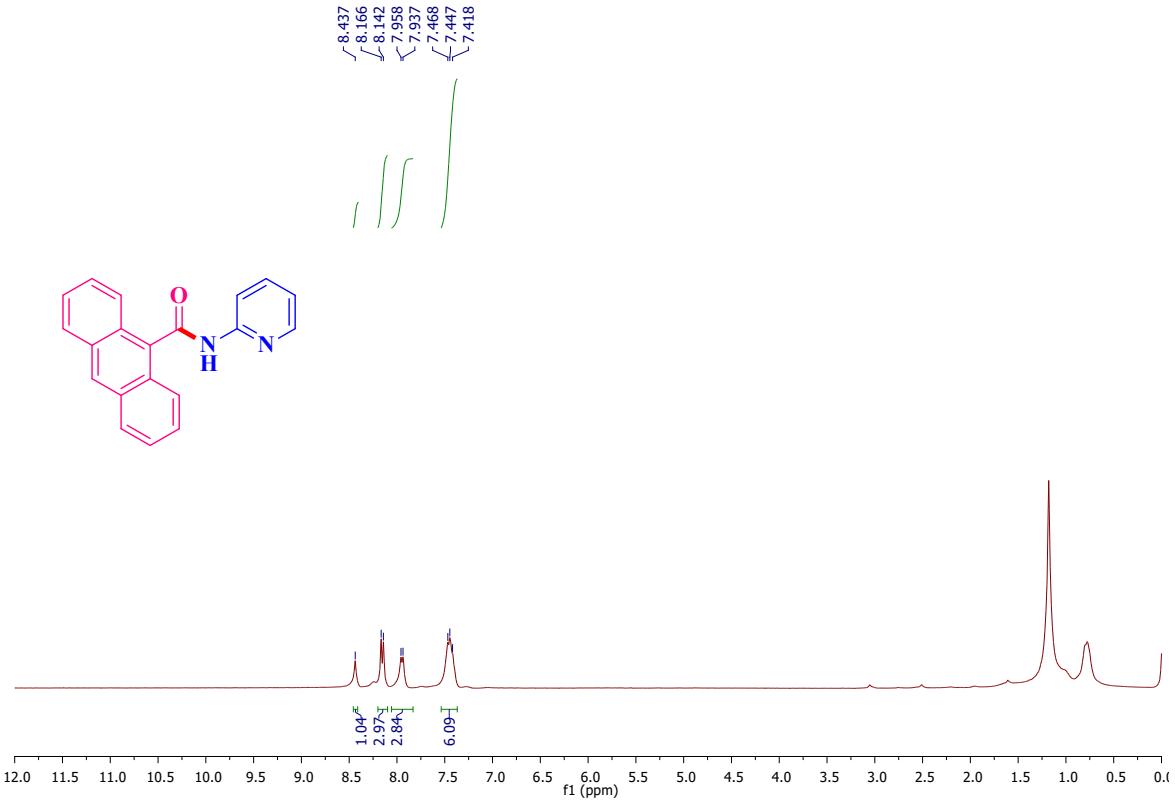
7.767
7.745
7.550
7.534
7.503
7.484
7.465
7.440
7.418
O
N
H
Br
1.03
2.09
1.99
4.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.318
138.646
135.131
131.705
131.485
128.433
127.915
122.455
115.976
O
N
H
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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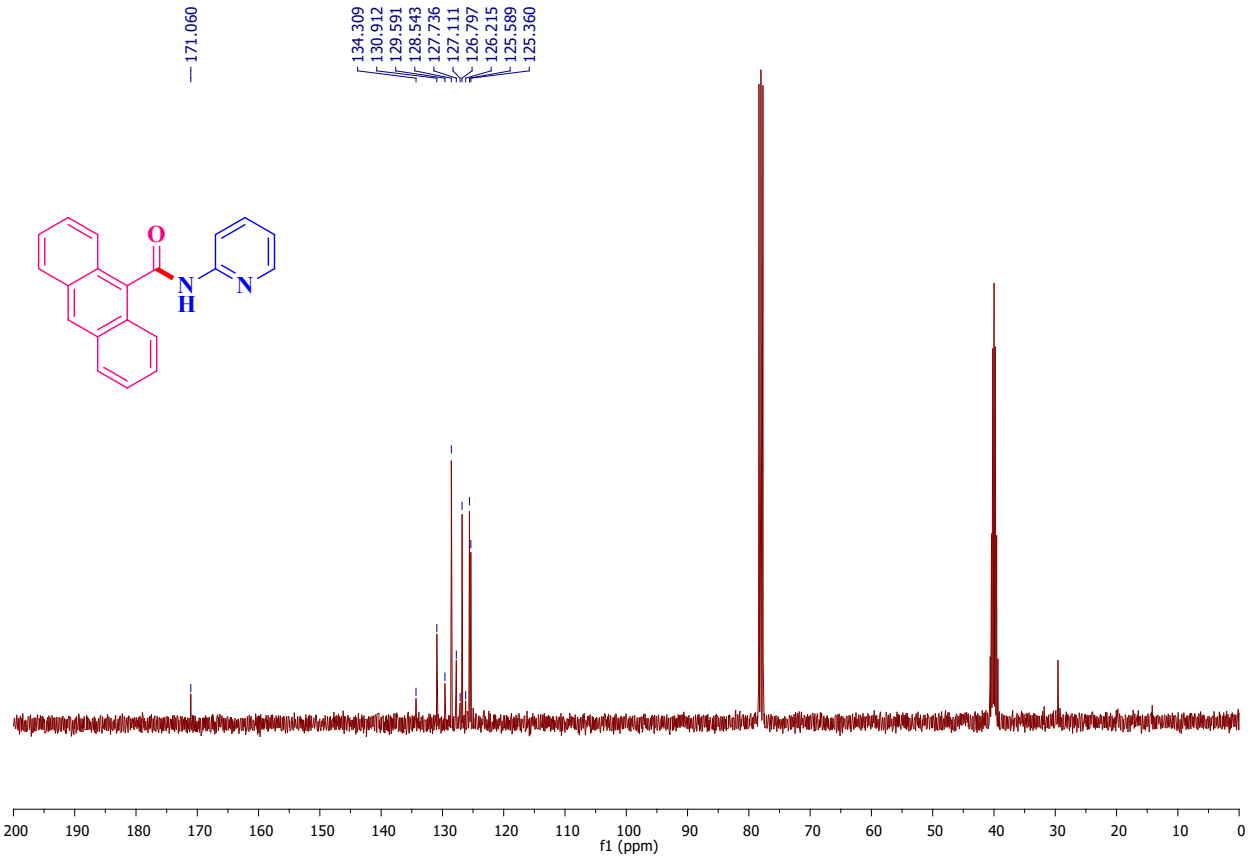
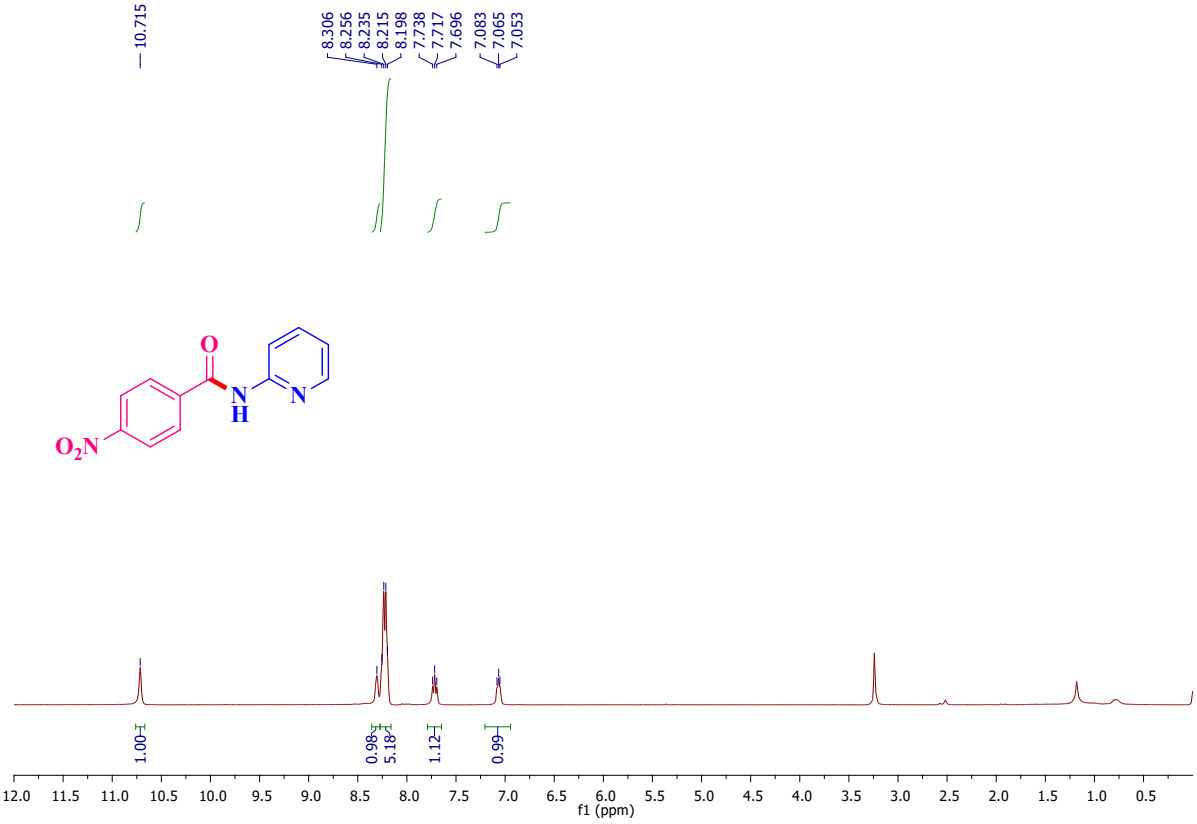
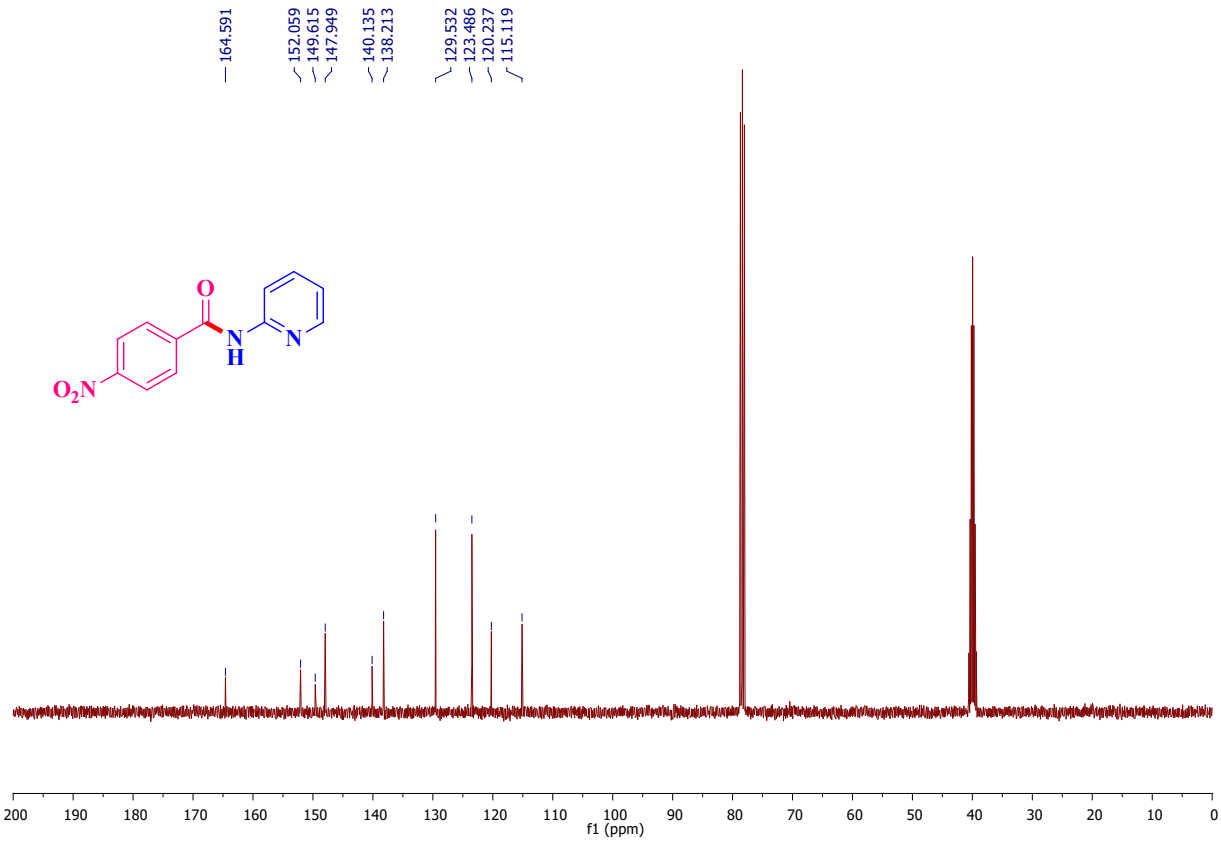
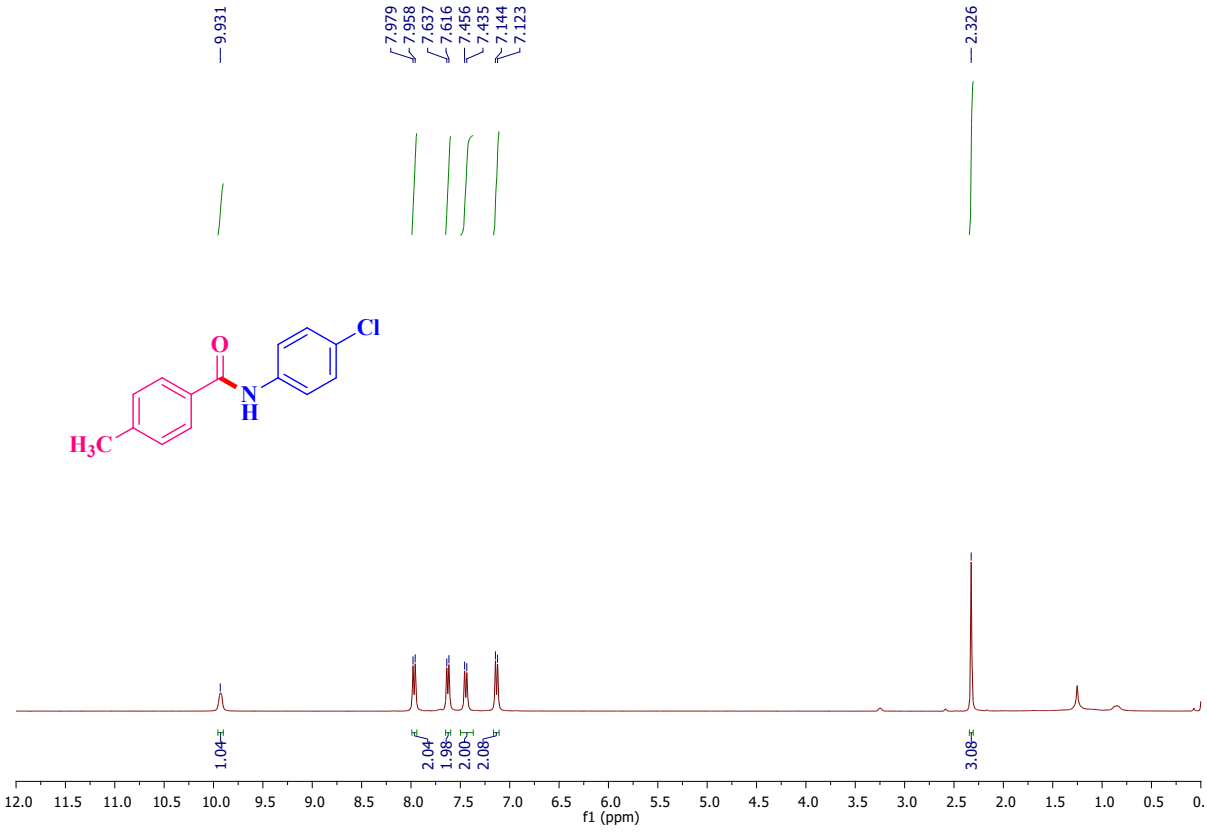
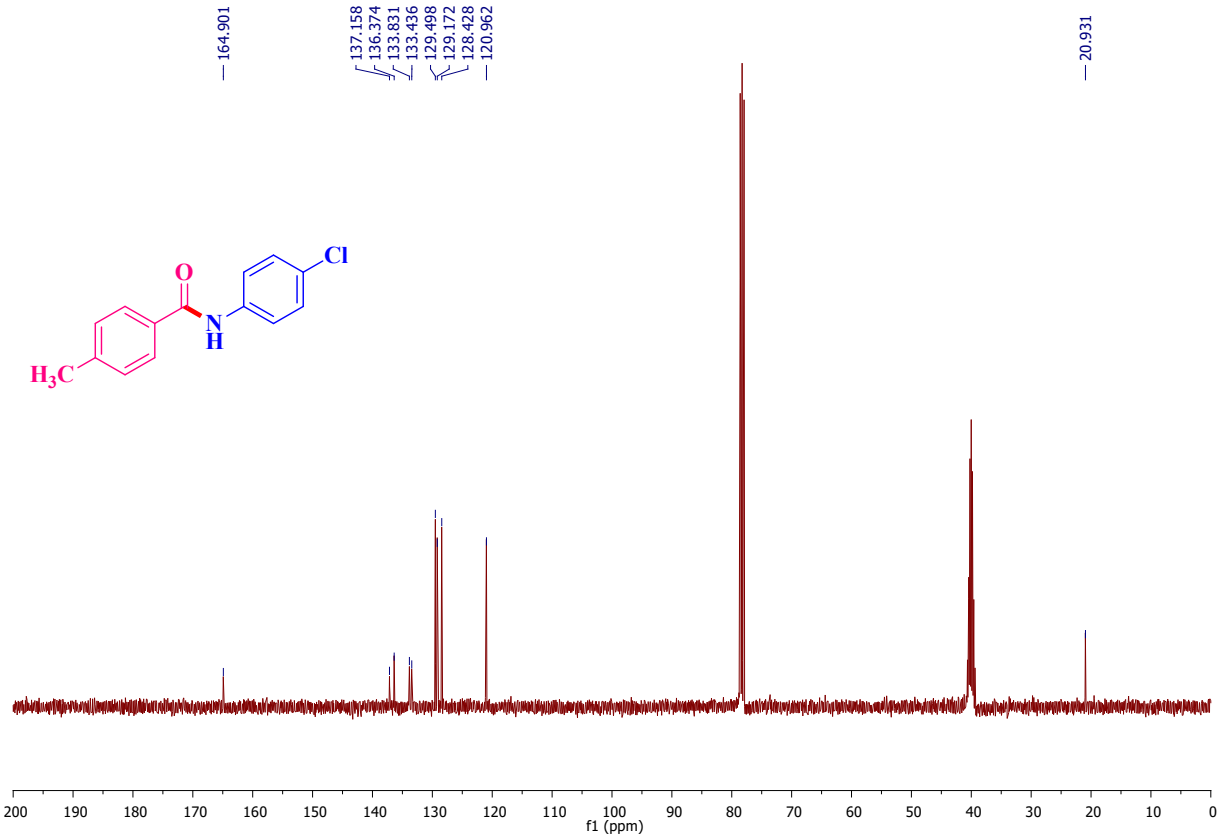
8.166
8.142
7.958
7.937
7.468
7.447
7.418
O
N
H
N
1.04
2.97
2.84
6.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

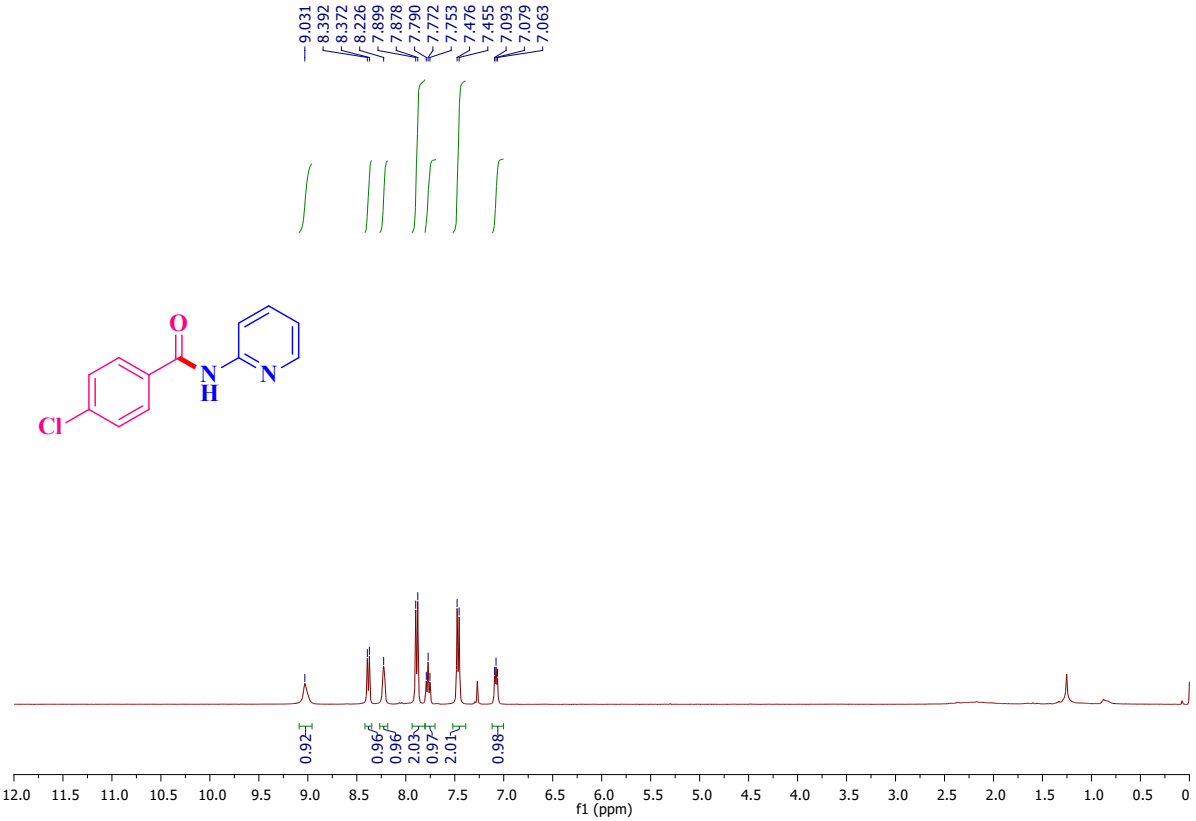

171.060
134.309
130.912
129.591
128.543
127.736
127.111
126.797
126.215
125.589
125.360
O
N
H
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

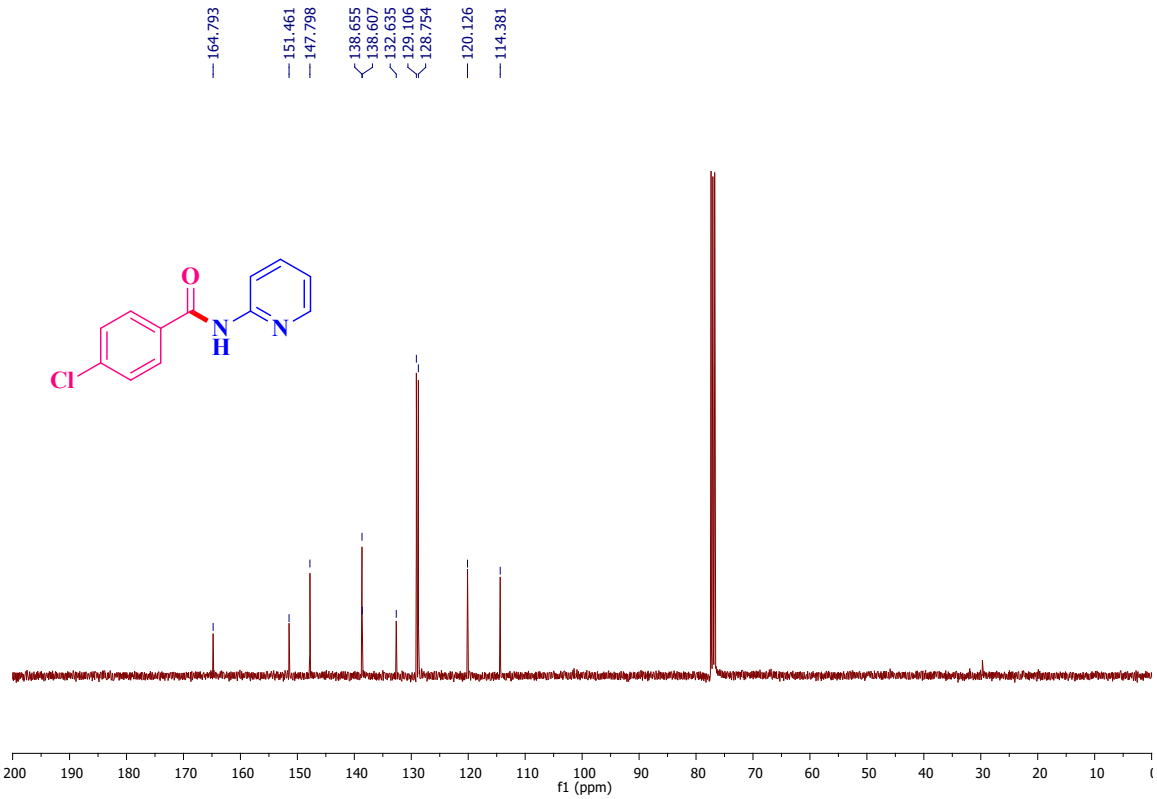

10.715
8.306
8.256
8.235
8.215
8.198
7.738
7.717
7.696
7.083
7.065
7.053
O
N
H
N
O2N
1.00
0.98
5.18
1.12
0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

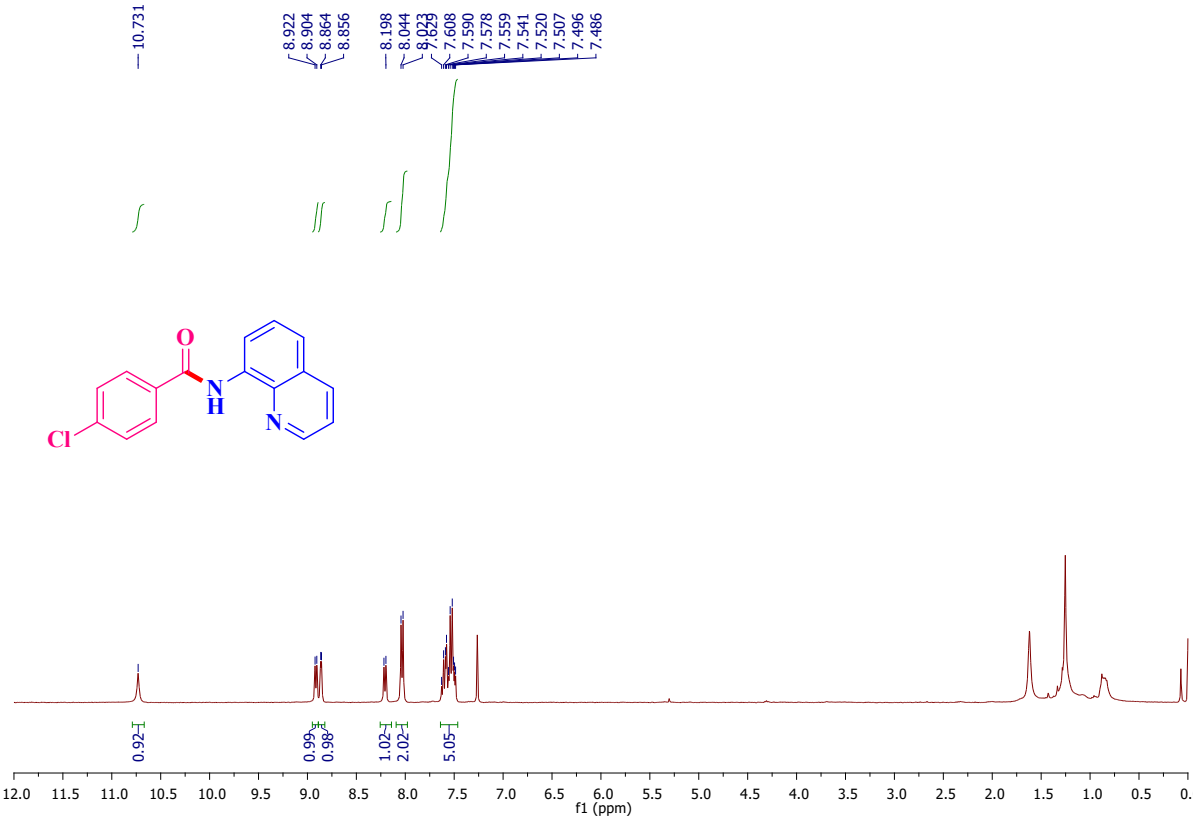

164.591
152.059
149.615
147.949
140.135
138.213
129.532
123.486
120.237
115.119
O
N
H
N
O2N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

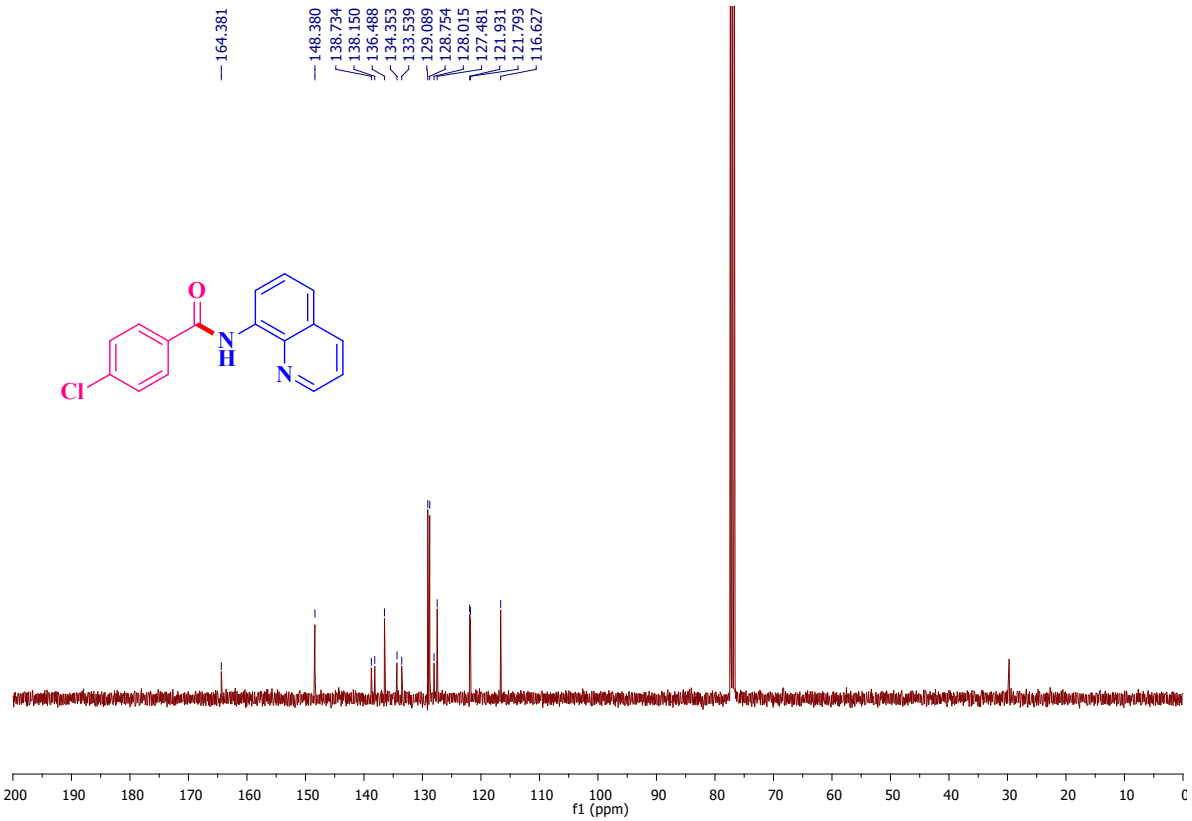

9.931
7.979
7.958
7.637
7.616
7.456
7.435
7.144
7.123
2.326
Cl
O
N
H
H3C
1.04
2.04
1.98
2.00
2.08
3.08
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

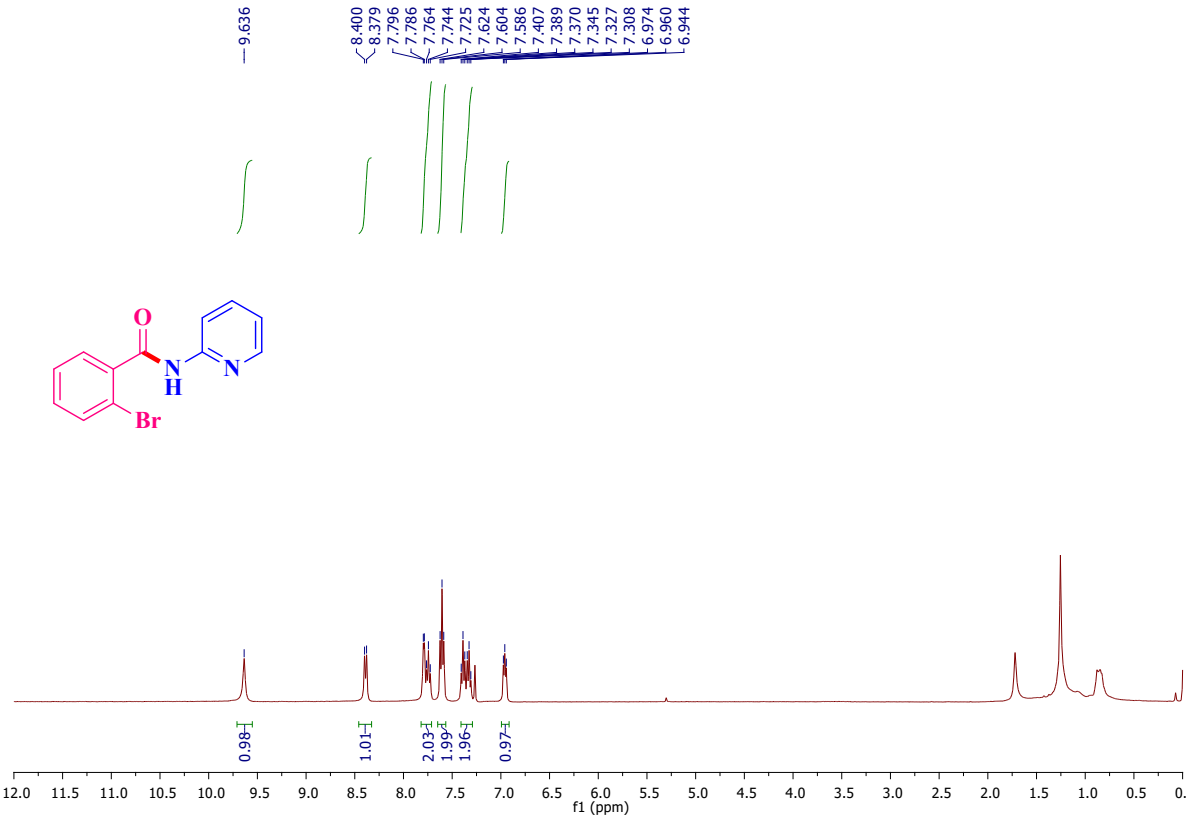

164.901
137.158
136.374
133.831
133.436
129.498
129.172
128.428
120.962
20.931
O
N
H
Cl
H3C
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

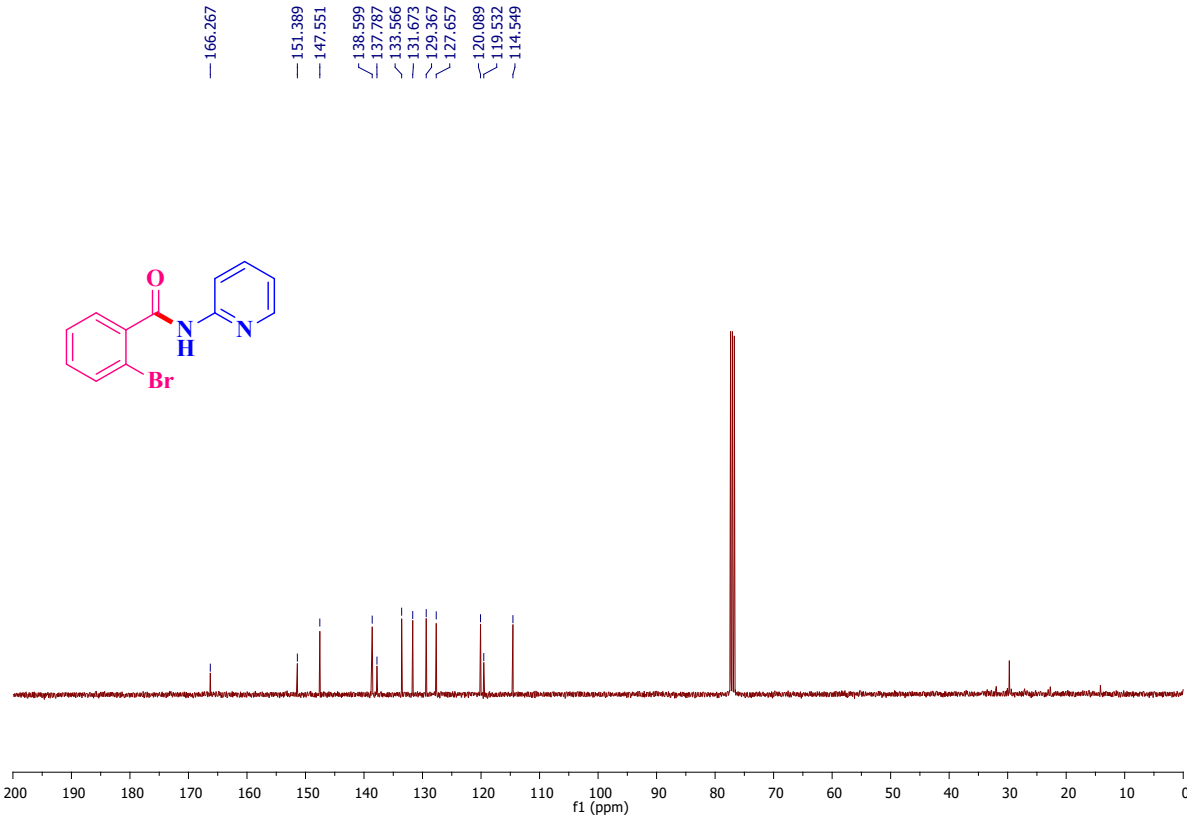

9.031
8.392
8.372
8.226
7.899
7.878
7.790
7.772
7.753
7.476
7.455
7.093
7.079
7.063
O
N
H
N
Cl
0.92
0.96
0.96
2.03
0.97
2.01
0.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

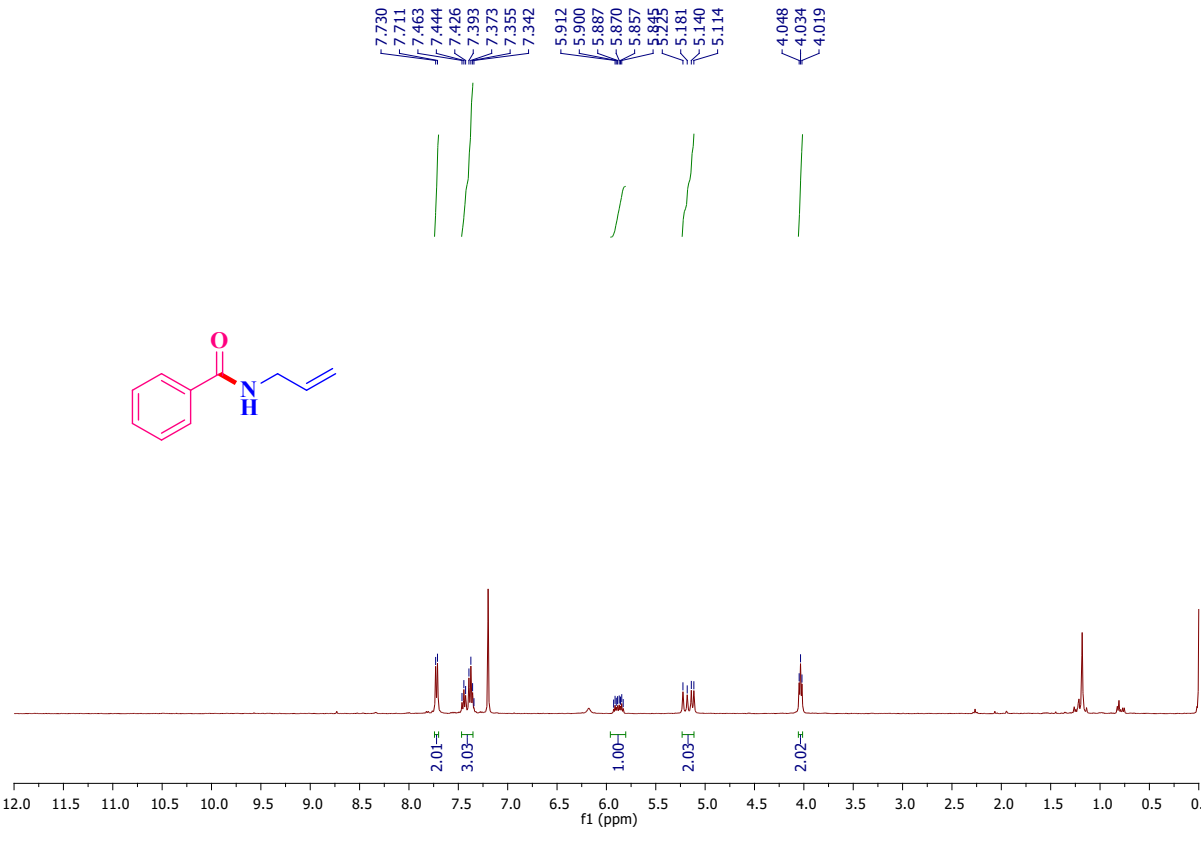

164.793
151.461
147.798
138.655
138.607
132.635
129.106
128.754
120.126
114.381
O
N
H
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

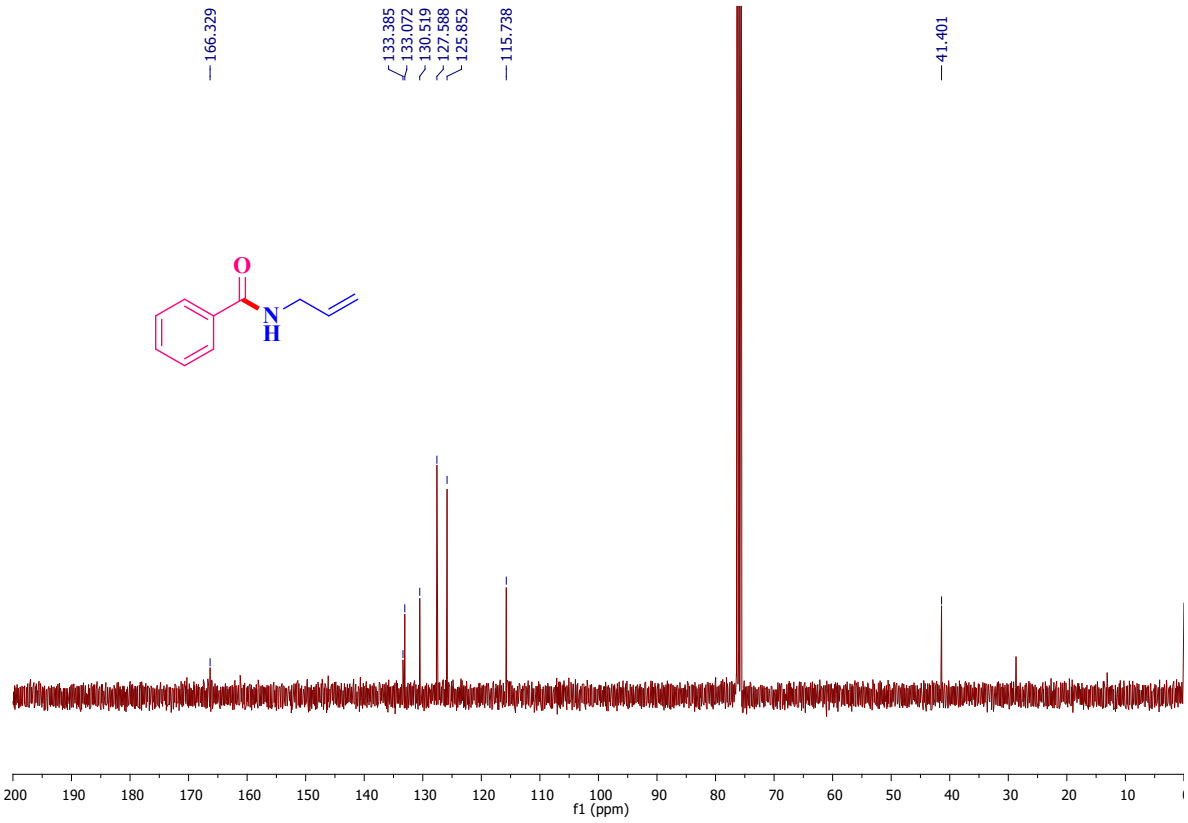

10.731
8.922
8.904
8.864
8.856
8.198
8.044
8.023
7.623
7.608
7.590
7.578
7.559
7.541
7.520
7.507
7.496
7.486
O
N
H
N
Cl
0.92
0.99
0.98
1.02
2.02
5.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

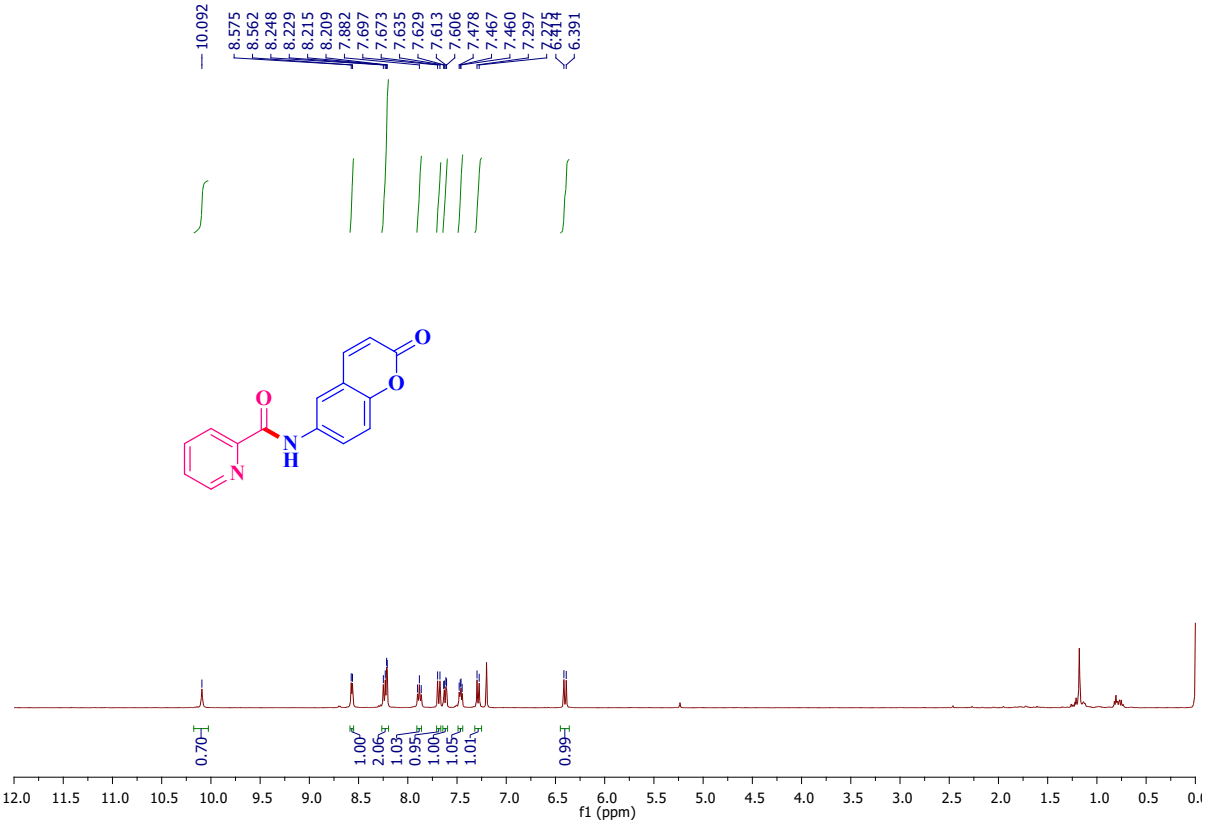

164.381
148.380
138.734
138.150
136.488
134.353
133.539
129.089
128.754
128.015
127.481
121.931
121.793
116.627
O
N
H
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

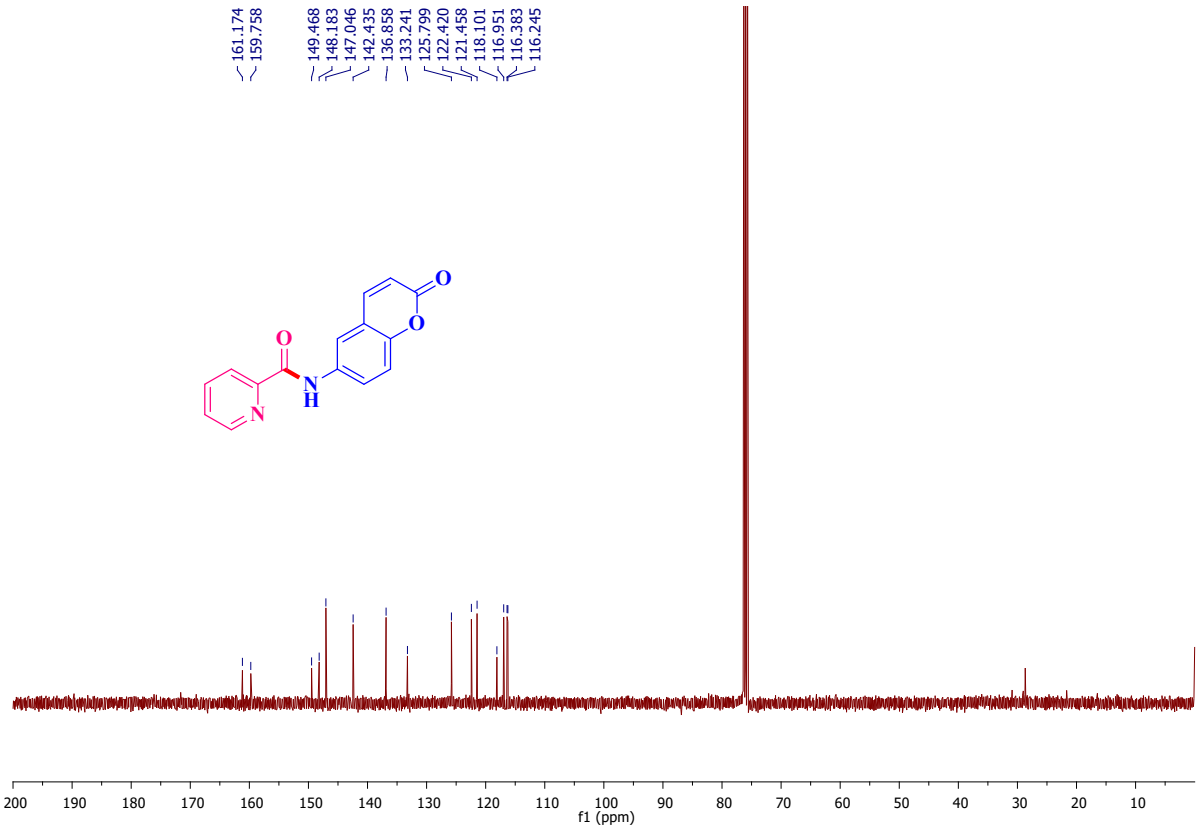

9.636
8.400
8.379
7.796
7.786
7.764
7.744
7.725
7.624
7.604
7.586
7.407
7.389
7.370
7.345
7.327
7.308
6.974
6.960
6.944
O
N
H
N
Br
0.98
1.01
2.03
1.99
1.96
0.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

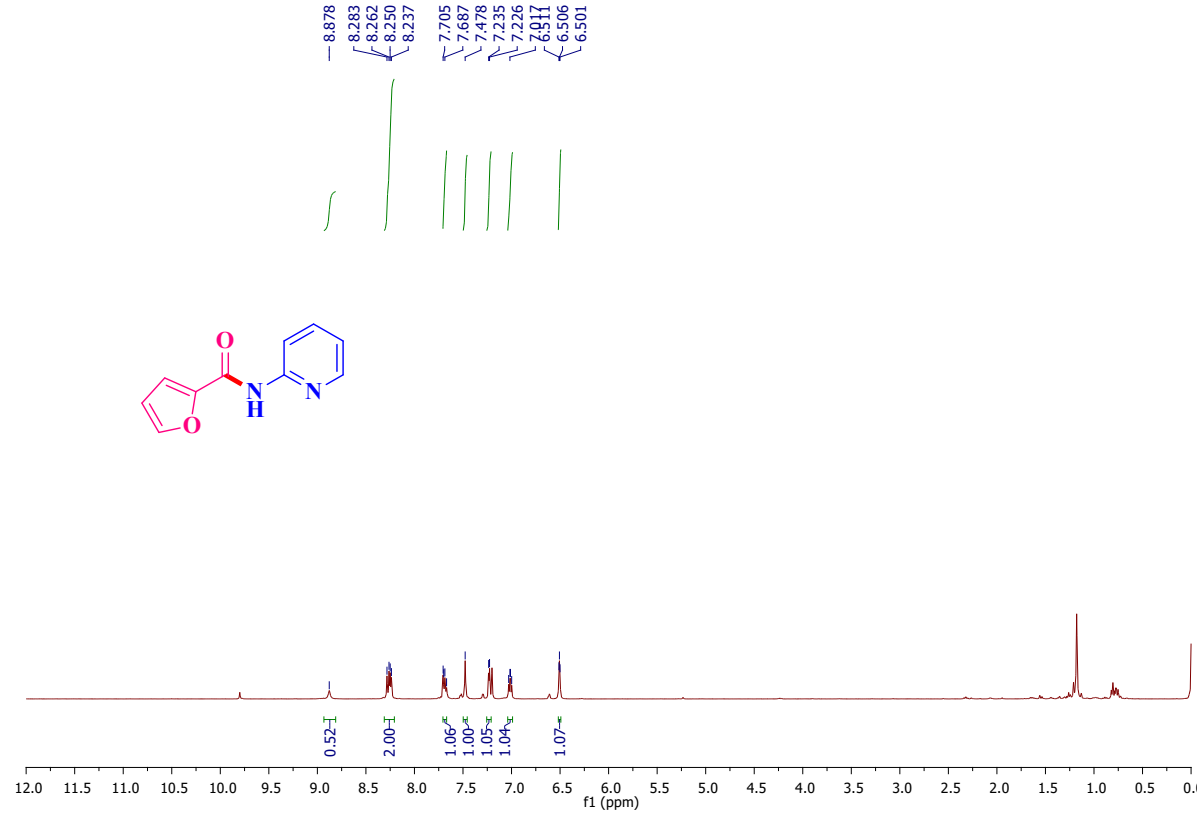

166.267
151.389
147.551
138.599
137.787
133.566
131.673
129.367
127.657
120.089
119.532
114.549
O
N
H
N
Br
f1 (ppm)

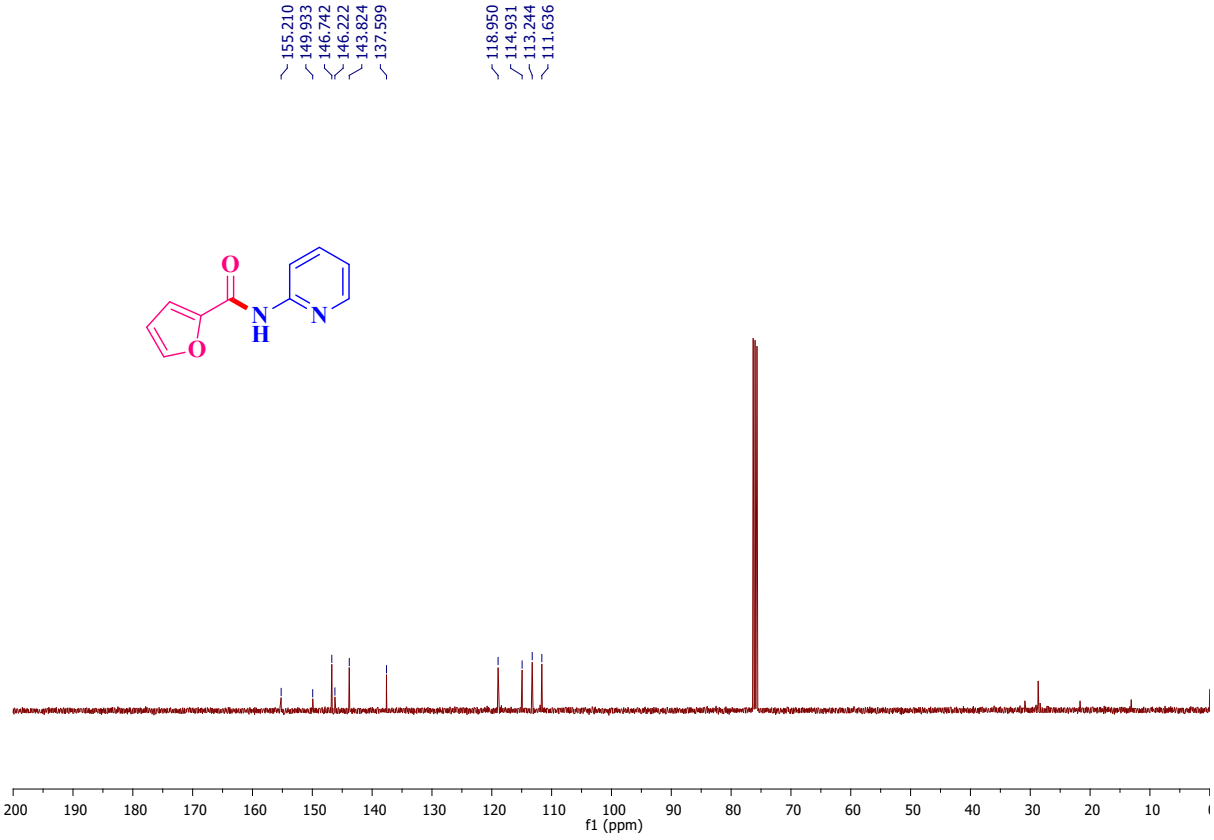

7.730
7.711
7.463
7.444
7.426
7.393
7.373
7.355
7.342
5.912
5.900
5.887
5.870
5.857
5.181
5.140
5.114
4.048
4.034
4.019
O
N
H
2.01
3.03
1.00
2.03
2.02
f1 (ppm)

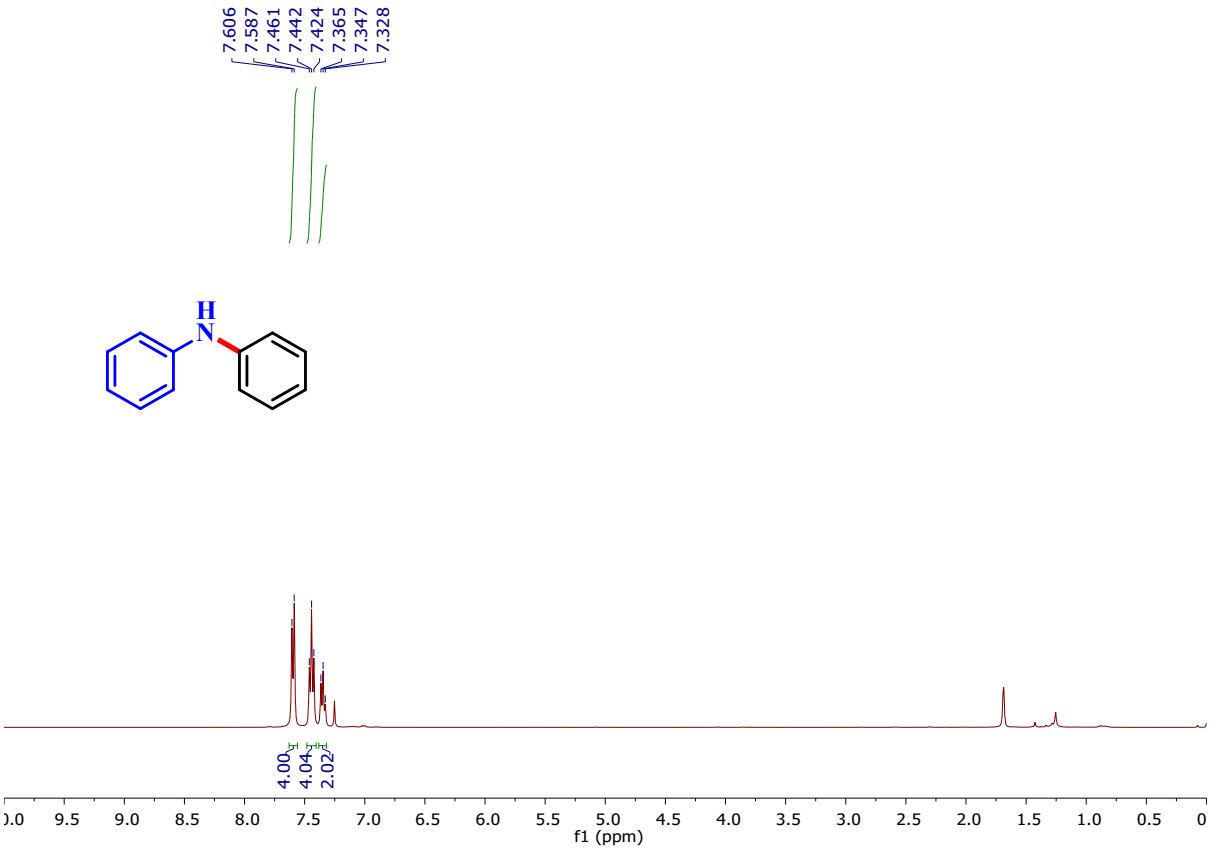

166.329
133.385
133.072
130.519
127.588
125.852
115.738
41.401
O
N
H
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

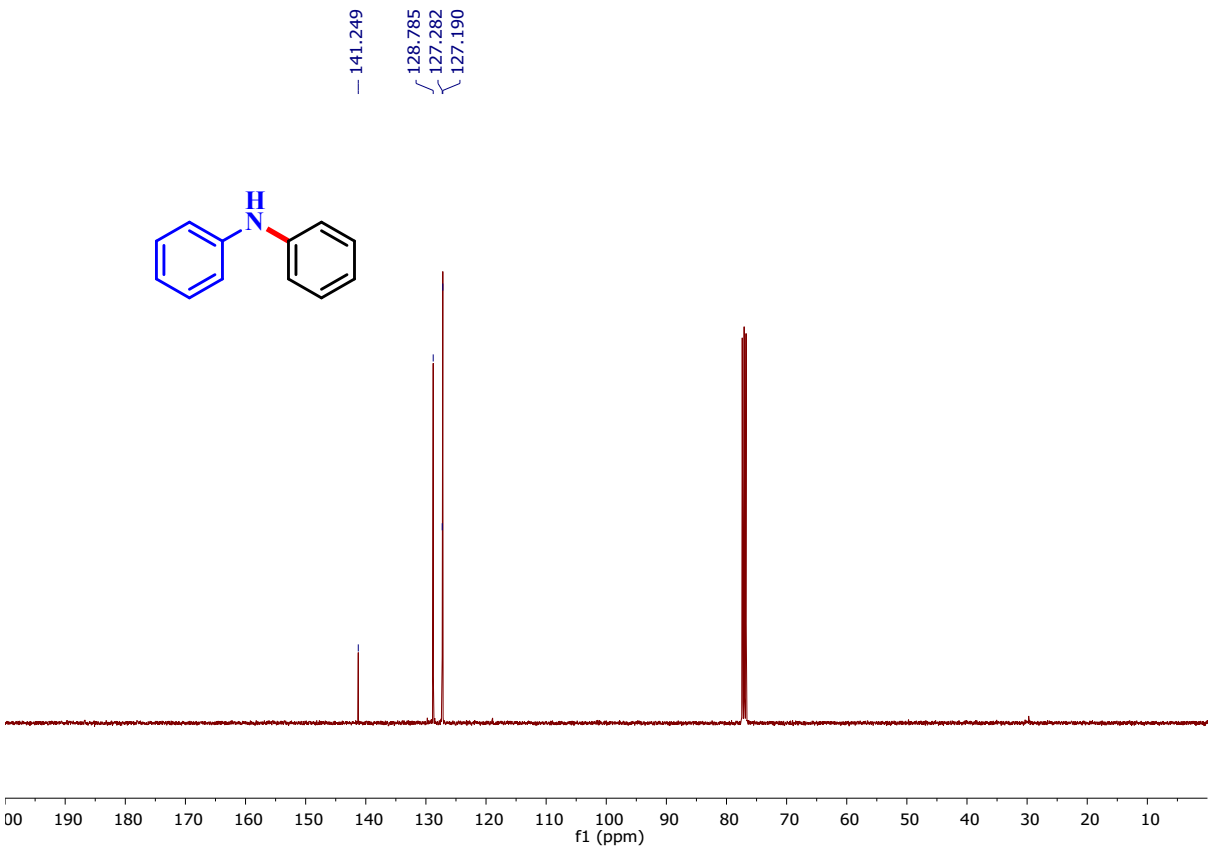

10.092
8.575
8.562
8.248
8.229
8.215
8.209
7.882
7.697
7.673
7.635
7.629
7.613
7.606
7.478
7.467
7.460
7.297
7.275
7.414
6.391
O
O
O
N
H
N
0.70
1.00
2.06
1.03
0.95
1.00
1.05
1.01
0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


161.174
159.758
149.468
148.183
147.046
142.435
136.858
133.241
125.799
122.420
121.458
118.101
116.951
116.383
116.245
O
O
O
N
H
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


8.878
8.283
8.262
8.250
8.237
7.705
7.687
7.478
7.235
7.226
7.017
6.511
6.506
6.501
O
O
N
H
N
0.52
2.00
1.06
1.00
1.05
1.04
1.07
12.0 11.5 11.0 10.5 10.0 9.5 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
f1 (ppm)


155.210
149.933
146.742
146.222
143.824
137.599
118.950
114.931
113.244
111.636
O
N
H
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.606
7.587
7.461
7.442
7.424
7.365
7.347
7.328
H
N
4.00
4.04
2.02
0.0 9.5 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
f1 (ppm)


141.249
128.785
127.282
127.190
H
N
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)