Thiolated Molybdenum diselenide Quantum Dots as a Bifunctional Catalyst towards the Synthesis of Benzimidazoles

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Supporting Information

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1. General considerations:

Chemicals: Spectrochem, SRL, Hi-Media, Alfa Aesar, ThermoFisher, TCI, BLD Pharm, ChemPure, ChemScene, Avra, and Sigma Aldrich (used without further purification).

Solvents: SD Fine Chemicals Limited, India (distilled for column chromatography).

Silica gel: Isochem (100-200 mesh for Column Chromatography) and silica gel 60 F_{254} precoated plates (0.25 mm) from Sigma Aldrich (for Thin Layer Chromatography or TLC).

LEDs: commercial suppliers.

For the biological assays, HPLC grade DMSO (Finar) was used. Unless mentioned otherwise, the solutions were prepared in distilled water. The LB media and PBS solutions were autoclaved at 120ºC before use. The kinetic assays were done in transparent, flat-bottomed, polystyrene, sterile 96-well plates (Biofil).

Data plotting/smoothening/fitting/deconvolution was done in OriginPro 9.1, GraphPad, and Image J software. All the figures were processed in Adobe Illustrator CS6, while the chemical structures were made in ChemDraw 20.1.1.

2. Instrumentation:

NMR spectroscopy: Bruker Ultrashield spectrometer (400 MHz for ^{1}H, 376 MHz for ^{19}F and 100 MHz for ^{13}C); data has been reported as chemical shift in ppm (multiplicity, coupling

constant in Hertz and integration) for ^{1}H spectra. The NMR spectra was processed in Topspin 3.6.4.

HRMS: Waters XEVO G2-XS QTof instrument.

UV-visible spectroscopy: UV-3600 Shimadzu UV-Vis-NIR Spectrophotometer from Japan Analytical Instruments (1 mL quartz cuvette with a 10 mm optical path).

Fluorescence spectroscopy: Varian Cary Eclipse Fluorescence Spectrophotometer.

FT-IR spectroscopy: CaF_2 cell in Bruker alfa FT-IR instrument.

Zeta Potential: Malvern Zetasizer Nano ZS System.

TGA: TA Q-50 thermogravimetric analyzer (temperature range 25-700°C).

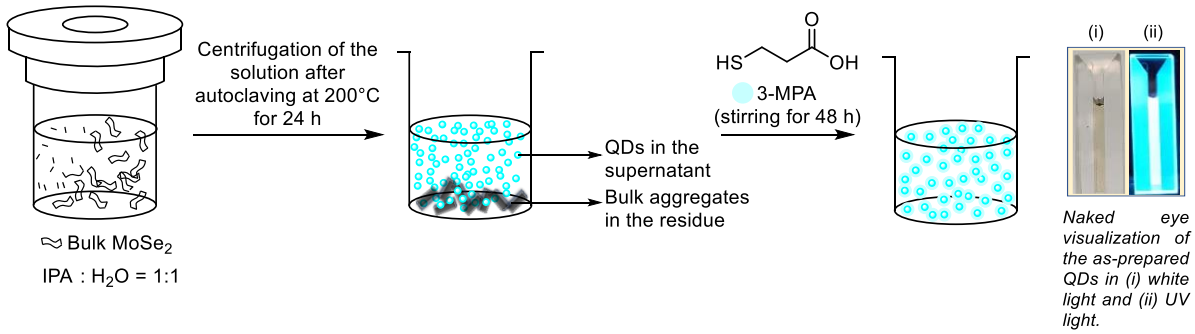
TEM: JOEL JEM-2100F with an accelerating voltage of 200 kV.

XPS: ESCALAB 250 (Thermo Electron) instrument with monochromatic Al Kα (1486.6 eV) as the X-ray source.

CV: Electrochemical Analyser (HCH Instruments CHI604E); platinum working electrode, platinum wire counter electrode and Ag/AgCl reference electrode were procured from CH Instruments, Inc.

Optical density: ThermoFisher Scientific Microplate Reader

3. Preparation of MPA@$MoSe_2$ QDs:



Scheme S1: Schematic representation of the preparation of $MoSe_2$ QDs and its functionalization with 3-MPA.

The $MoSe_2$ QDs were synthesized based on literature report with slight modifications.[1] A hydrothermal strategy was used. 100 mg of bulk $MoSe_2$ powder was taken in 60 mL of 1:1 isopropyl alcohol : water mixture. The solution was probe-sonicated for 60 mins and transferred to Teflon-lined autoclave chambers. The setup was kept for 24 h at 200°C. Afterwards, the solution was cooled to room temperature and centrifuged for 30 mins at 12,000 rpm. The supernatant was carefully retrieved and stored at 4°C.

For functionalization, the QDs and the ligand, 3-MPA (3-Mercaptopropionic acid) were mixed (for 1 mL of the QDs having a strength of 0.1 mg/mL, about 50 mg of ligand was taken) in a vial and stirred for 24 h to get MPA@$MoSe_2$ QDs.

All solutions were kept wrapped in aluminium foils to avoid quenching of the luminescent materials. The as-synthesized materials were characterized using optical and microscopic techniques.

4. Optical/microscopic characterization:

4.1 Procedure for optical/microscopic characterization and sample preparation:

UV-Visible Absorption spectroscopy: A 1 mL quartz cuvette with 10 mm path length was used. The stock solution was diluted such that the absorbance is less than 1. The scan was done from 200 to 800 nm (step size = 1 nm).

Fluorescence spectroscopy: A diluted solution of the material was taken and excited at the wavelength at which the absorption maxima was observed. The excitation dependent emission spectra were also recorded for each sample. The slit width was kept as 10 throughout.

Fourier transform-InfraRed (FT-IR) spectroscopy: About 50 μL of the sample was lyophilized, dissolved in methanol and spread on a CaF_2 cell. The residual solvent was removed by drying. The spectra was recorded from 4000 to 430 cm^{-1}.

Zeta Potential: The aqueous solution of the QDs was loaded in the relevant cuvette.

Thermogravimetric analysis (TGA): TGA data was recorded on a TA Q-50 unit in the temperature range 25-700ºC. The rate of heating was maintained at 10ºC/min under a static air atmosphere.

Transmission Electron Microscopy (TEM): A Formvar/carbon 200 mesh copper grid was cleaned by dipping gently in water. An extremely dilute sample of the MPA@$MoSe_2$ QDs was drop-casted on the grid and dried overnight. Finally, any residual solvent was removed by drying in vacuum.

X-ray Photoelectron Spectroscopy (XPS): Samples were prepared on Silicon wafers. The wafers were cut as 0.5 cm X 0.5 cm squares and cleaned in isopropyl alcohol (heating at 60ºC for 20 mins followed by decantation of the solvent, the process being repeated thrice). Finally, the surfaces were rinsed with acetone, dried and a

concentrated solution of the sample was drop-casted. The samples were allowed to dry in air and then in vacuum for 24 h.

4.2 Optical characterization:

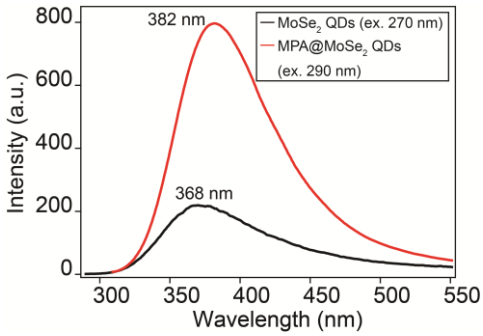


Figure S1: Comparative plots of the emission spectra of $MoSe_2$ QDs and MPA@$MoSe_2$ QDs, showing the shift in the emission maxima.

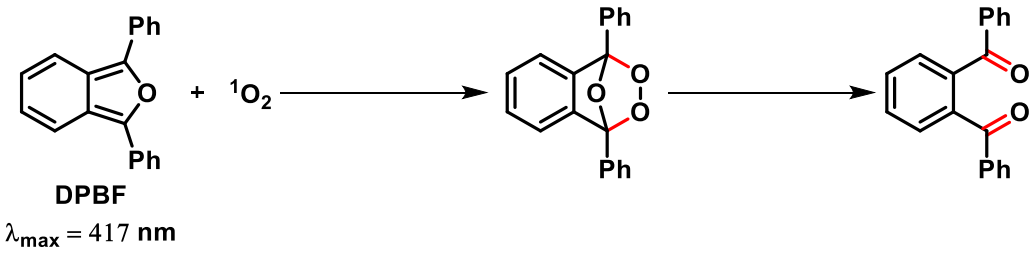
5. General procedure for the mechanistic analysis:

5.1 Quenching experiments for electron/energy transfer processes:

For mechanistic investigations, the quenching experiments were performed using Na_2CrO_4 (sodium chromate) as the electron scavenger, DIPEA (*N*,*N*-diisopropylethylamine) as the hole scavenger, and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as the radical scavenger, keeping the optimal conditions intact. Further, the possibility of energy transfer was also investigated using various quenchers such as benzil, pyrene and benzophenone.

5.2 Experiment to detect the generation of singlet oxygen ($^1O_2$):

1,3-Diphenylisobenzofuran (DPBF) was also used to detect the possibility of singlet oxygen ($^1O_2$) generation. The MPA@$MoSe_2$ QDs were taken with DPBF (100 µL of 20 ppm stock in MeCN) and irradiated with a 10 W blue LED. The absorption spectra was recorded after 2 h and 4 h.



DPBF

λ_{max} = 417 nm

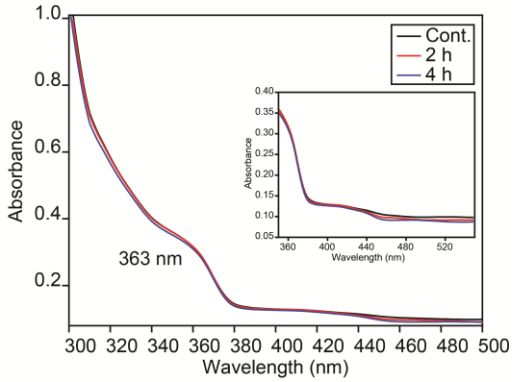


Figure S2: Photophysical characterization to confirm the absence of $^1O_2$ using DPBF probe.

5.3 Experiment to check the operation of a radical chain propagation pathway:

In order to explore the possibility of radical chain propagation pathway, the reaction vessel was exposed to light and kept in dark for a definite time period as indicated below, following which, the yield was determined.

Table S1: Light On-Off Study to explore the possibility of radical chain propagation

Entry	Irradiation Conditions	Yield (%)[a]
1	No light	<5
2	6 h hν	17
3	6 h hν, 18 h dark	23
4	12 h hν	45
5	12 h hν, 12 h dark	50
6	18 h hν	79
7	18 h hν, 6 h dark	85
8	24 h hν	90

0.2 mmol (1 equiv.) of 4-fluorobenzylamine **1a** and 0.4 mmol (2 equiv.) of *o*-phenylenediamine **2a** were taken in a clean reaction tube equipped with a magnetic stir-bar. 1.8 mL of MeCN was added to solubilize the components, followed by addition of the catalyst MPA@$MoSe_2$ QDs. The reaction tube was purged with O_2 and irradiated using a 10 W blue LED or kept in dark (as indicated) at 25ºC.
[a]the product **3a** was quantified using ^{19}F-NMR in DMSO-d_6 solvent post work-up (using EtOAc/H_2O mixture).

5.4 Detection of H_2O_2 in the reaction mixture:

Photophysical characterizations were also done to check the formation of any H_2O_2. For detection of H_2O_2, permanganometric estimation method was employed. A 1:1 mixture (by volume) of aqueous $KMnO_4$ (N/20) and H_2SO_4 (4 N) were taken and added slowly to a beaker containing the aqueous layer collected from the reaction mixture post work-up. The end point was marked as the appearance of a persistent light pink color. The UV spectra for the solutions were recorded before as well as after the titration to analyze the ligand to metal charge transfer (LMCT) bands of $KMnO_4$.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

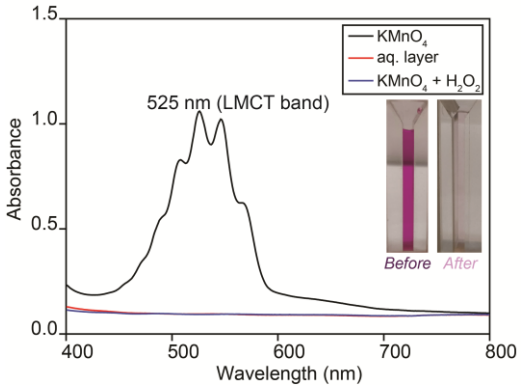
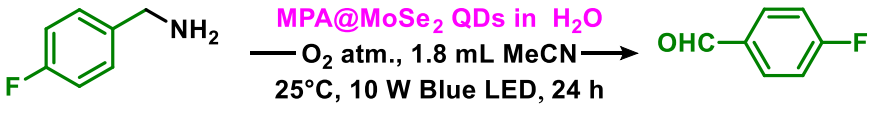


Figure S3: Permanganometric assay to detect H_2O_2 in the reaction mixture.

5.5 Detection of intermediate species in the cyclization process:

In order to check for the generation of 4-fluorobenzaldehyde as the intermediate, the reaction was done as per the optimized conditions but without including any *o*-phenylenediamine **2a**. 4-fluorobenzaldehyde was purified on a silica gel column (100-200 mesh) with EtOAc/Hexane as the eluent.



54%

5.6 Role of QDs as a Lewis acid (thermal) catalyst:

The role of the QDs as thermal catalyst was confirmed using 4-fluorobenzaldehyde and *o*-phenylenediamine **2a**. In a clean reaction tube equipped with a magnetic stir-bar, 4-fluorobenzaldehyde (0.2 mmol; separated from the acid derivative, if any, using a work-up procedure with saturated aqueous $NaHCO_3$ solution) and *o*-phenylenediamine (0.4 mmol) were dissolved in 1.8 mL MeCN. The MPA@$MoSe_2$ QDs were added and the resulting solution was irradiated with a 10 W blue LED or

kept in dark for 24 h. Then, the reaction mixture was extracted with EtOAc (at least thrice) (if necessary, MeCN was removed before initiating the work-up). The combined organic phases were washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation. The product was quantified using ^{19}F-NMR in DMSO-d_6 solvent.

Table S2: Evaluating the role of MPA@$MoSe_2$ QDs as a Lewis acid in the cyclization process

Entry	Conditions	Yield (%)[a,b]
1	MPA@$MoSe_2$ QDs, no hν	67
2	MPA@$MoSe_2$ QDs, hν	69

Reaction conditions: 0.2 mmol of 4-fluorobenzaldehyde and 0.4 mmol of *o*-phenylenediamine **2a** were taken in a clean reaction tube equipped with a magnetic stir-bar. 1.8 mL of MeCN was added to solubilize the components, followed by addition of the catalyst MPA@$MoSe_2$ QDs (200 µL). The reaction tube was irradiated using 10 W blue LED or kept in dark (as indicated) for 24 h at 25°C.

[a]the product **3a** was quantified using ^{19}F-NMR in DMSO-d_6 solvent post work-up (using EtOAc/H_2O mixture); [b]**around 20-22% of 4-fluorobenzoic acid was also obtained in each case.**

6 General procedure for recyclability studies:

The heterogeneous nature of the nanomaterial was established by testing its ability to catalyze the coupling process in subsequent cycles. The reaction mixture was concentrated to remove MeCN and subjected to work-up with EtOAc. The aqueous layer containing the catalyst was collected carefully. Any excess water added during the work-up could be removed by lyophilization such that the residual catalyst remains suspended in 0.2 mL water. **1a**, **2a** and 1.8 mL MeCN was further added and the reaction vessel was irradiated as per the optimal conditions after purging with O_2. The studies were done for 5 cycles in total and the yields were reported in each case. The absorption profile was captured to characterize the nanomaterial post recyclability.

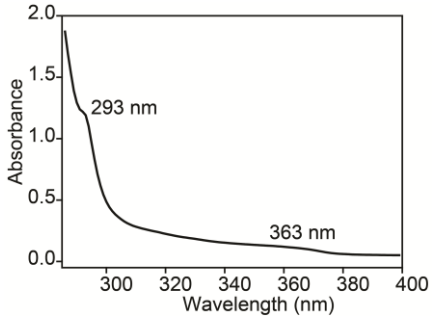


Figure S4: Absorption profile of the recycled MPA@$MoSe_2$ QDs.

7 General procedure for Cyclic Voltammetry (CV) studies:

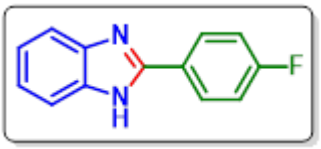
The electrodes used for CV studies included a Pt wire electrode (counter electrode; cleaned by dipping the wire in conc. HNO_3 and heating over a burner flame), platinum electrode (working electrode; cleaned by rubbing over alumina sheet followed by rinsing with distilled H_2O) and Ag/AgCl electrode (reference electrode; cleaned using H_2O). 40 mL of a solution of 5 mM $K_4[Fe(CN)_6]$ and 0.1 M KCl (electrolyte) was taken. The readings were taken in static mode (to prevent analyte deposition on the working electrode) (scan rate = 0.1 V/s) in the absence as well as presence of the material.

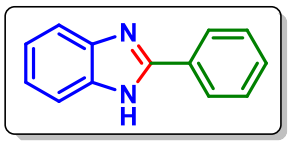
8 Procedure for studying the efficacy of the molecules against bacteria:

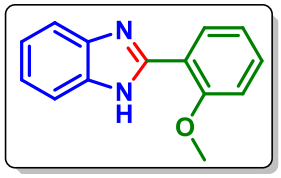
Considering the vast range of infections (such as skin diseases, respiratory ailments, etc.) that it can cause, SA (*Staphylococcus aureus*) was taken as the strain of interest. The frozen stock of the bacteria was cultured on a freshly prepared nutrient agar plate. The primary stock was obtained by culturing a few colonies from this plate in Luria Broth (LB, 20 g/L) for 10-12 h. Prior to each study, the secondary culture was generated by mixing 0.2 mL of the primary stock with 1.7 mL of LB incubated at 37ºC. The bacteria were harvested when the mid-log phase was attained, i.e., the O.D.@620 nm reached 0.2-0.3. The O.D.@620 nm was finally adjusted to 0.01 (which implies a count of 10^6-10^7 cells/mL).

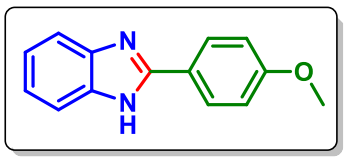
The benzimidazoles were prepared as a stock solution in 5% DMSO/H_2O mixture. A microbroth dilution method was employed to estimate the minimum inhibitory concentration (MIC) in a 96-well plate. The two-fold serial dilution was done using phosphate buffer saline (PBS, pH = 7.4), such that the volume of the compound in buffer is 100 μL for each well. Finally, 100 μL of the bacterial solution having O.D.@620 nm as 0.01 was added in each well. The bacterial growth kinetics was monitored for 16 h, wherein, the O.D.@620 nm was recorded every 10 mins (with shaking in between consecutive readings). The thermostat was set to 37ºC throughout the course of the experiment. MIC was noted as the value at which atleast 95% of the population ceased to grow. The data was normalized, smoothed and plotted in GraphPad.

9 Characterization data:[2-18]

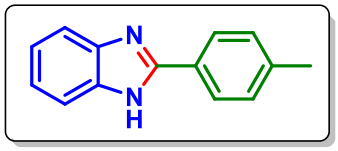
2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 9-10% EtOAc/Hexane eluent;  **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.93 (s, 1H), 8.25-8.21 (m, 2H), 7.68-7.66 (d, *J* = 7.2 Hz, 1H), 7.55-7.53 (d, *J* = 6.8 Hz, 1H), 7.44-7.39 (t, *J* = 8.9 Hz, 2H), 7.25-7.18 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 164.28, 161.82, 150.36, 143.73, 135.00, 128.75, 128.67, 126.80, 126.77, 122.55, 121.71, 118.83, 116.13, 115.91, 111.32; **^{19}F NMR** (376 MHz, DMSO-d_6): δ (ppm) = -111.17; HRESI-MS (m/z): Calculated for $C_{13}H_9FN_2H$ $(M + H)^+$: 213.0828, Found $(M + H)^+$: 213.0832.

2-phenyl-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 7-8% EtOAc/Hexane eluent;  **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.92 (s, 1H), 8.19-8.17 (d, *J* = 7.7 Hz, 2H), 7.68-7.66 (d, *J* = 7.5 Hz, 1H), 7.58-7.48 (m, 4H), 7.25-7.17 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 151.21, 143.81, 134.95, 130.16, 129.87, 128.97, 126.42, 122.55, 121.68, 118.86, 111.33; HRESI-MS (m/z): Calculated for $C_{13}H_{10}N_2H$ $(M + H)^+$: 195.0922, Found $(M + H)^+$: 195.0923.

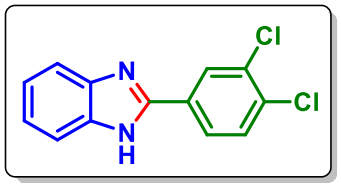
2-(2-methoxyphenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 11-12% EtOAc/Hexane eluent;  **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.14 (s, 1H), 8.34-8.32 (d, *J* = 7.9 Hz, 1H), 7.64-7.62 (m, 2H), 7.51-7.47 (m, 1H), 7.26-7.24 (d, *J* = 8.3 Hz, 1H), 7.20-7.18 (m, 2H), 7.14-7.10 (t, *J* = 7.5 Hz, 1H), 4.03 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 156.78, 148.95, 131.28, 129.75, 121.79, 120.89, 118.10, 112.12, 55.78; HRESI-MS (m/z): Calculated for $C_{14}H_{12}N_2OH$ $(M + H)^+$: 225.1028, Found $(M + H)^+$: 225.1024.

2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 13-14% EtOAc/Hexane eluent;  **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.74 (s, 1H), 8.13-8.11 (d, *J* = 8.6 Hz, 2H), 7.63-7.61 (d, *J* = 7.5 Hz, 1H), 7.50-7.48 (d, *J* = 7.1 Hz, 1H), 7.19-7.10 (m, 4H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 160.56, 151.30, 143.85, 134.93, 127.96, 122.66, 122.04, 121.41, 118.46, 114.34, 111.00, 55.31; HRESI-MS (m/z): Calculated for $C_{14}H_{12}N_2OH$ $(M + H)^+$: 225.1028, Found $(M + H)^+$: 225.1029.

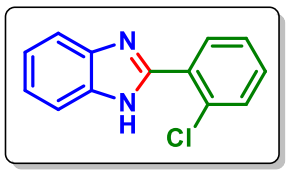
2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 13-14% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.82 (s, 1H), 8.08-8.06 (d, *J* = 7.8 Hz, 2H), 7.65-7.63 (d, *J* = 7.3 Hz, 1H), 7.52-7.50 (d, *J* = 7.3 Hz, 1H), 7.38-7.36 (d, *J* = 7.9 Hz, 2H), 7.23-7.16 (m, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 151.33, 143.76, 139.53, 134.91, 129.48, 127.40, 126.34, 122.30, 121.51, 118.66, 111.14, 20.95; HRESI-MS (m/z): Calculated for $C_{14}H_{12}N_2H$ $(M + H)^+$: 209.1079, Found $(M + H)^+$: 209.1082.



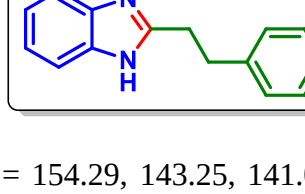
2-(3,4-dichlorophenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 14-15% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 13.12 (s, 1H), 8.41-8.40 (d, *J* = 1.6 Hz, 1H), 8.17-8.15 (dd, *J* = 8.4 Hz, *J* = 1.6 Hz, 1H), 7.86-7.84 (d, *J* = 8.4 Hz, 1H), 7.70-7.56 (m, 2H), 7.27-7.23 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 148.89, 143.60, 135.01, 132.31, 131.86, 131.37, 130.72, 127.98, 126.46, 123.19, 122.12, 119.14, 111.61; HRESI-MS (m/z): Calculated for $C_{13}H_8Cl_2N_2H$ $(M + H)^+$: 263.0143, Found $(M + H)^+$: 263.0142.



2-(2-chlorophenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 5-6% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.72 (s, 1H), 7.92-7.90 (m, 1H), 7.72-7.66 (m, 2H), 7.58-7.53 (m, 3H), 7.29-7.21 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 149.07, 143.18, 134.65, 132.07, 131.61, 131.19, 130.33, 129.95, 127.42, 122.72, 121.67, 119.07, 111.68; HRESI-MS (m/z): Calculated for $C_{13}H_9ClN_2H$ $(M + H)^+$: 229.0533, Found $(M + H)^+$: 229.0528.



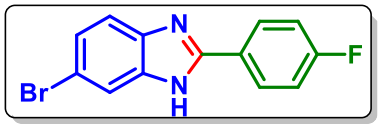
2-phenethyl-1*H*-benzo[*d*]imidazole: Off-white solid; isolated using silica gel (100-200 mesh) column chromatography in 24-25% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.24 (s, 1H), 7.54-7.41 (m, 2H), 7.34-7.26 (m, 4H), 7.22-7.17 (m, 1H), 7.15-7.09 (m, 2H), 3.12 (s, 4H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 154.29, 143.25, 141.00, 134.20, 128.33, 128.21, 126.00, 121.39, 120.77, 118.08, 110.70, 33.27, 30.35; HRESI-MS (m/z): Calculated for $C_{15}H_{14}N_2H$ $(M + H)^+$: 223.1235, Found $(M + H)^+$: 223.1239.



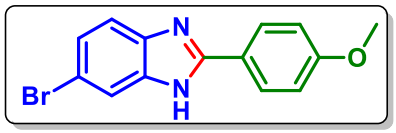
2-(3-bromophenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 24-25% EtOAc/Hexane eluent; **^{1}H**

NMR (400 MHz, DMSO-d_6): δ (ppm) = 13.05 (s, 1H), 8.38-8.37 (t, *J* = 2.0 Hz, 1H), 8.20-8.18 (d, *J* = 7.9 Hz, 1H), 7.71-7.68 (t, *J* = 7.3 Hz, 2H), 7.56-7.51 (m, 2H), 7.27-7.20 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 149.56, 132.53, 132.23, 131.23, 128.90, 125.40, 122.55, 122.27; HRESI-MS (m/z): Calculated for $C_{13}H_9BrN_2H$ $(M + H)^+$: 273.0027, Found $(M + H)^+$: 273.0030.

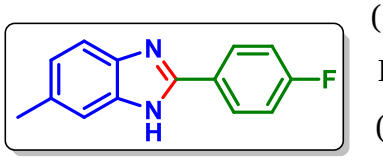
6-bromo-2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 25-30% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 13.15 (s, 1H), 8.24-8.17 (m, 2H), 7.86-7.50 (m, 2H), 7.47-7.29 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 164.54, 162.07, 151.61, 129.04, 128.95, 126.23, 125.08, 116.27, 116.05, 114.34; **^{19}F NMR** (376 MHz, DMSO-d_6): δ (ppm) = -110.44; HRESI-MS (m/z): Calculated for $C_{13}H_8BrFN_2H$ $(M + H)^+$: 290.9933, Found $(M + H)^+$: 290.9935.



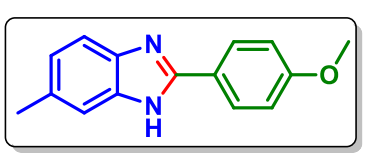
6-bromo-2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole: Off-white solid; isolated using silica gel (100-200 mesh) column chromatography in 13-14% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.97 (s, 1H), 8.13-8.10 (d, *J* = 8.9 Hz, 2H), 7.81-7.46 (m, 2H), 7.34-7.29 (m, 1H), 7.14-7.12 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 160.89, 152.59, 128.21, 124.59, 122.07, 114.44, 113.88, 55.36; **^{19}F NMR** (376 MHz, DMSO-d_6): δ (ppm) = -110.44; HRESI-MS (m/z): Calculated for $C_{14}H_{11}BrN_2OH$ $(M + H)^+$: 303.0133, Found $(M + H)^+$: 303.0137.



2-(4-fluorophenyl)-6-methyl-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 17-18% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.78 (s, 1H), 8.22-8.18 (m, 2H), 7.47 (br s, 1H), 7.42-7.38 (t, *J* = 8.8 Hz, 3H), 7.04-7.02 (d, *J* = 8.1 Hz, 1H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 164.20, 161.74, 150.05, 131.46, 128.63, 128.55, 126.90, 126.88, 123.66, 116.10, 115.88, 21.34; **^{19}F NMR** (376 MHz, DMSO-d_6): δ (ppm) = -111.38; HRESI-MS (m/z): Calculated for $C_{14}H_{11}FN_2H$ $(M + H)^+$: 227.0985, Found $(M + H)^+$: 227.0982.

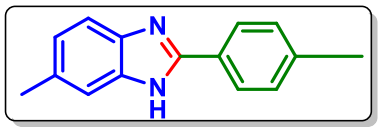


2-(4-methoxyphenyl)-6-methyl-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 20-21% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.60 (s, 1H), 8.10-8.08 (d, *J* = 8.8 Hz, 2H), 7.44-7.33

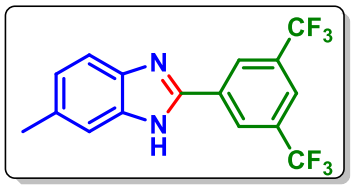


(m, 2H), 7.11-7.09 (d, *J* = 8.7 Hz, 2H), 7.00-6.98 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 160.40, 150.96, 130.73, 128.97, 128.49, 127.80, 123.11, 122.79, 114.26, 113.59, 113.42, 55.26, 21.27; HRESI-MS (m/z): Calculated for $C_{15}H_{14}N_2OH$ $(M + H)^+$: 239.1181, Found $(M + H)^+$: 239.1184.

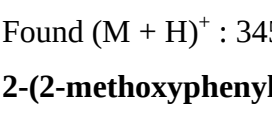
6-methyl-2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 19-20% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.67 (s, 1H), 8.05-8.03 (d, *J* = 8.2 Hz, 2H), 7.49-7.42 (m, 1H), 7.36-7.34 (d, *J* = 7.9 Hz, 3H), 7.02-7.01 (d, *J* = 7.9 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 150.93, 141.94, 139.36, 135.20, 131.64, 129.48, 127.56, 126.25, 123.74, 123.14, 118.28, 110.93, 21.34, 20.97; HRESI-MS (m/z): Calculated for $C_{15}H_{14}N_2H$ $(M + H)^+$: 223.1235, Found $(M + H)^+$: 223.1233.



2-(3,5-bis(trifluoromethyl)phenyl)-6-methyl-1*H*-benzo[*d*]imidazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 14-15% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 13.22 (s, 1H), 8.80 (s, 2H), 8.24 (s, 1H), 7.63-7.41 (m, 2H), 7.15-7.08 (m, 1H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 148.10, 147.73, 143.89, 141.68, 135.37, 133.28, 133.16, 132.70, 131.60, 131.54, 131.27, 130.94, 130.61, 127.33, 126.60, 126.56, 126.51, 126.48, 125.25, 124.61, 124.16, 122.84, 121.89, 119.18, 119.02, 111.46, 21.42; **^{19}F NMR** (376 MHz, DMSO-d_6): δ (ppm) = -61.48; HRESI-MS (m/z): Calculated for $C_{16}H_{10}F_6N_2H$ $(M + H)^+$: 345.0826, Found $(M + H)^+$: 345.0826.



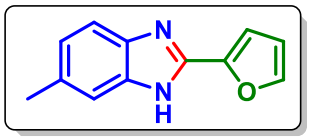
2-(2-methoxyphenyl)benzo[*d*]oxazole: White solid; isolated using silica gel (100-200 mesh) column chromatography in 8-9% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.16-8.14 (d, *J* = 7.8 Hz, 1H), 7.87-7.85 (m, 1H), 7.62-7.59 (m, 1H), 7.54-7.50 (t, *J* = 7.9 Hz, 1H), 7.38-7.34 (m, 2H), 7.13-7.09 (t, *J* = 8.0 Hz, 2H), 4.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 161.42, 158.89, 150.09, 133.69, 131.38, 125.56, 124.93, 120.95, 120.21, 116.25, 112.28, 110.70, 56.46; HRESI-MS (m/z): Calculated for $C_{14}H_{11}NO_2H$ $(M + H)^+$: 226.0868, Found $(M + H)^+$: 226.0876.



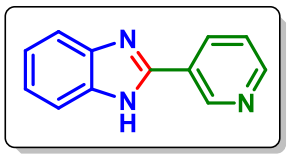
2-(furan-2-yl)-1*H*-benzo[*d*]imidazole: Orangish solid; isolated using silica gel (100-200 mesh) column chromatography in 26-28% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.93 (s, 1H), 7.95 (s, 1H),

7.63-7.61 (d, *J* = 7.4 Hz, 1H), 7.50-7.48 (d, *J* = 7.4 Hz, 1H), 7.24-7.19 (m, 3H), 6.74-6.73 (m, 1H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 145.55, 144.68, 143.65, 134.24, 122.68, 121.84, 118.78, 112.37, 111.38, 110.51; HRESI-MS (m/z): Calculated for $C_{11}H_8N_2OH$ $(M + H)^+$: 185.0715, Found $(M + H)^+$: 185.0712.

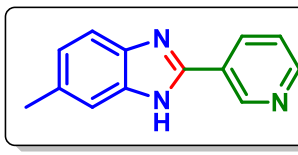
2-(furan-2-yl)-6-methyl-1*H*-benzo[*d*]imidazole: Brown solid; isolated using silica gel (100-200 mesh) column chromatography in 28-30% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.77 (s, 1H), 7.93 (s, 1H), 7.45 (br s, 1H), 7.34 (br s, 1H), 7.17-7.16 (d, *J* = 3.4 Hz, 1H), 7.04-7.02 (d, *J* = 8.2 Hz, 1H), 6.73-6.72 (m, 1H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 146.13, 144.91, 143.77, 132.30, 124.08, 118.88, 112.75, 111.55, 110.59, 21.77; HRESI-MS (m/z): Calculated for $C_{12}H_{10}N_2OH$ $(M + H)^+$: 199.0871, Found $(M + H)^+$: 199.0869.



2-(pyridin-3-yl)-1*H*-benzo[*d*]imidazole: Yellow solid; isolated using silica gel (100-200 mesh) column chromatography in 40-45% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 9.36 (s, 1H), 8.70-8.69 (d, *J* = 4.8 Hz, 1H), 8.52-8.50 (d, *J* = 7.9 Hz, 1H), 7.67-7.60 (m, 3H), 7.27-7.25 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 151.01, 149.27, 147.94, 134.29, 126.52, 124.55, 123.04; HRESI-MS (m/z): Calculated for $C_{12}H_9N_3H$ $(M + H)^+$: 196.0875, Found $(M + H)^+$: 196.0872.



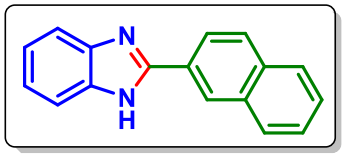
6-methyl-2-(pyridin-3-yl)-1*H*-benzo[*d*]imidazole: Yellow solid; isolated using silica gel (100-200 mesh) column chromatography in 45-50% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-d_6): δ (ppm) = 12.96 (s, 1H), 9.33 (s, 1H), 8.68-8.66 (d, *J* = 4.6 Hz, 1H), 8.49-8.47 (d, *J* = 8.1 Hz, 1H), 7.60-7.36 (m, 3H), 7.11-7.04 (m, 1H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ (ppm) = 150.36, 148.39, 147.38, 133.62, 126.26, 124.03, 123.63, 118.65, 111.20, 21.35; HRESI-MS (m/z): Calculated for $C_{13}H_{11}N_3H$ $(M + H)^+$: 210.1031, Found $(M + H)^+$: 210.1027.



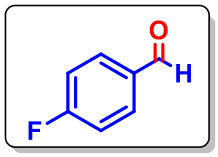
6-bromo-2-(pyridin-3-yl)-1*H*-benzo[*d*]imidazole: Yellow solid; isolated using silica gel (100-200 mesh) column chromatography in 35-40% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 10.36 (s, 1H), 9.26 (s, 1H), 8.75-8.74 (d, *J* = 4.7 Hz, 1H), 8.47-8.45 (d, *J* = 8.0 Hz, 1H), 7.70 (br s, 1H), 7.52-7.48 (dd, *J* = 8.0

Hz, *J* = 4.8 Hz, 1H), 7.45-7.43 (d, *J* = 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, DMSO-*d*$_6$): δ (ppm) = 150.82, 147.60, 133.92, 125.68, 124.02; HRESI-MS (m/z): Calculated for $C_{12}H_8BrN_3H$ (M + H)$^+$: 273.9980, Found (M + H)$^+$: 273.9984.

2-(naphthalen-2-yl)-1*H*-benzo[*d*]imidazole: Yellow solid; isolated using silica gel (100-200 mesh) column chromatography in 10-12% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, DMSO-*d*$_6$): δ (ppm) = 13.10 (s, 1H), 8.75 (s, 1H), 8.34-8.31 (d, *J* = 8.6 Hz, 1H), 8.10-8.08 (d, *J* = 8.7 Hz, 1H), 8.07-8.04 (m, 1H), 8.01-7.99 (m, 1H), 7.71-7.70 (m, 1H), 7.64-7.59 (m, 3H), 7.24-7.23 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-*d*$_6$): δ (ppm) = 151.21, 143.90, 135.08, 133.43, 132.78, 128.54, 128.43, 127.78, 127.55, 127.11, 126.92, 125.78, 123.90, 122.67, 121.77, 118.88, 111.37; HRESI-MS (m/z): Calculated for $C_{17}H_{12}N_2H$ (M + H)$^+$: 245.1079, Found (M + H)$^+$: 245.1080.



4-fluorobenzaldehyde: Colourless liquid; isolated using silica gel (100-200 mesh) column chromatography in 2-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 9.99 (s, 1H), 7.96-7.92 (dd, *J* = 8.6 Hz, *J* = 5.5 Hz, 2H), 7.26-7.22 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 190.66, 167.93, 165.38, 133.08, 133.06, 132.41, 132.32, 116.60, 116.38; **^{19}F NMR** (376 MHz, $CDCl_3$): δ (ppm) = -102.35; HRESI-MS (m/z): Calculated for C_7H_5FOH (M + H)$^+$: 125.0403, Found (M + H)$^+$: 125.0406.



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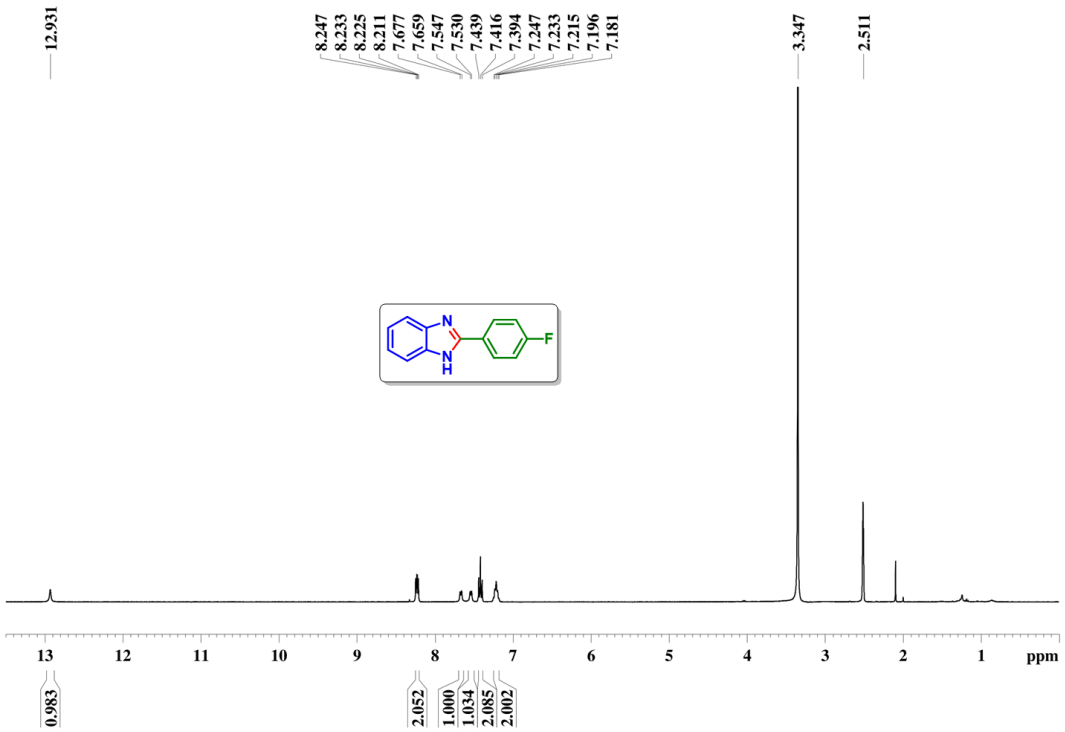
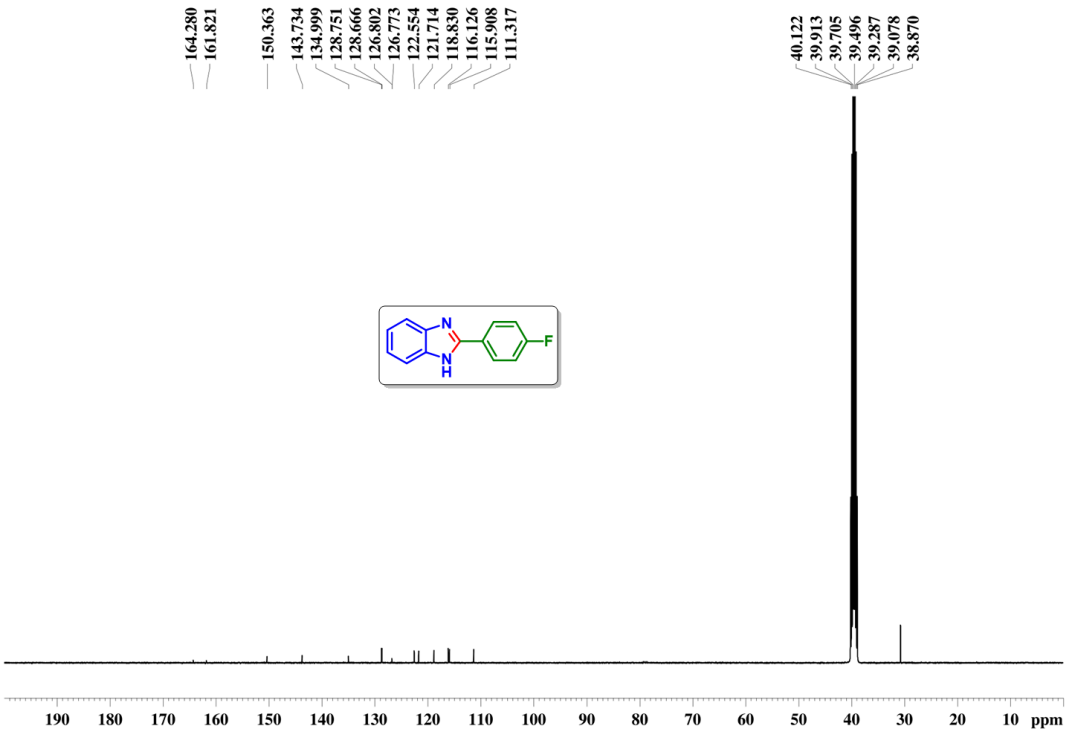
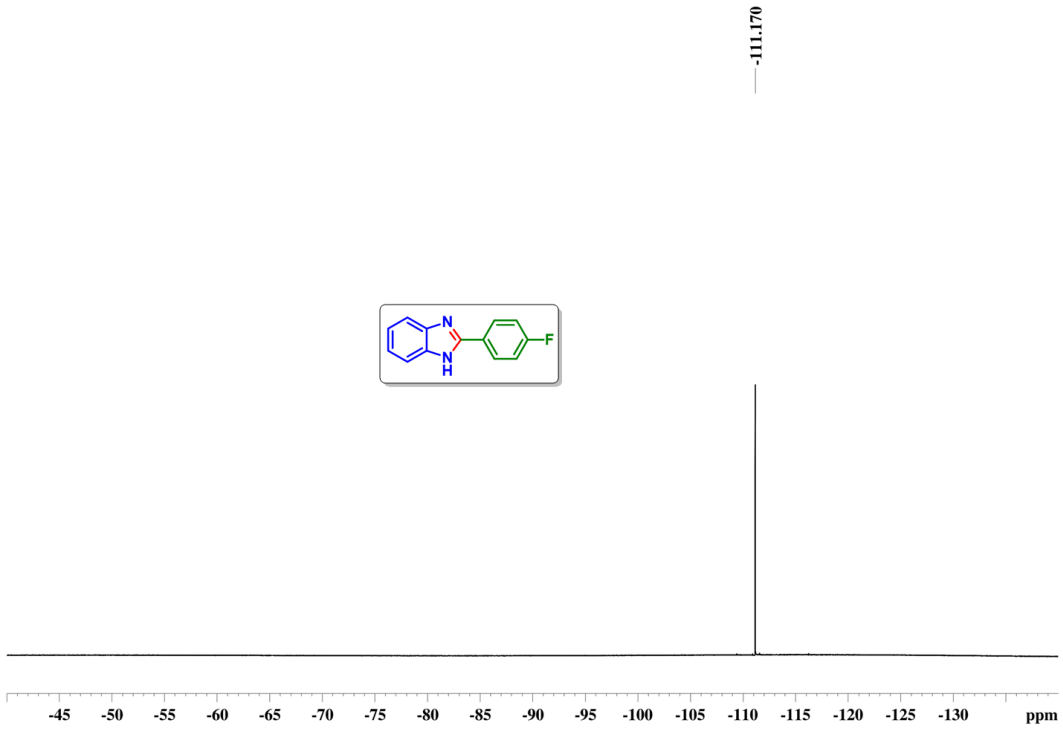
11 NMR Spectra:



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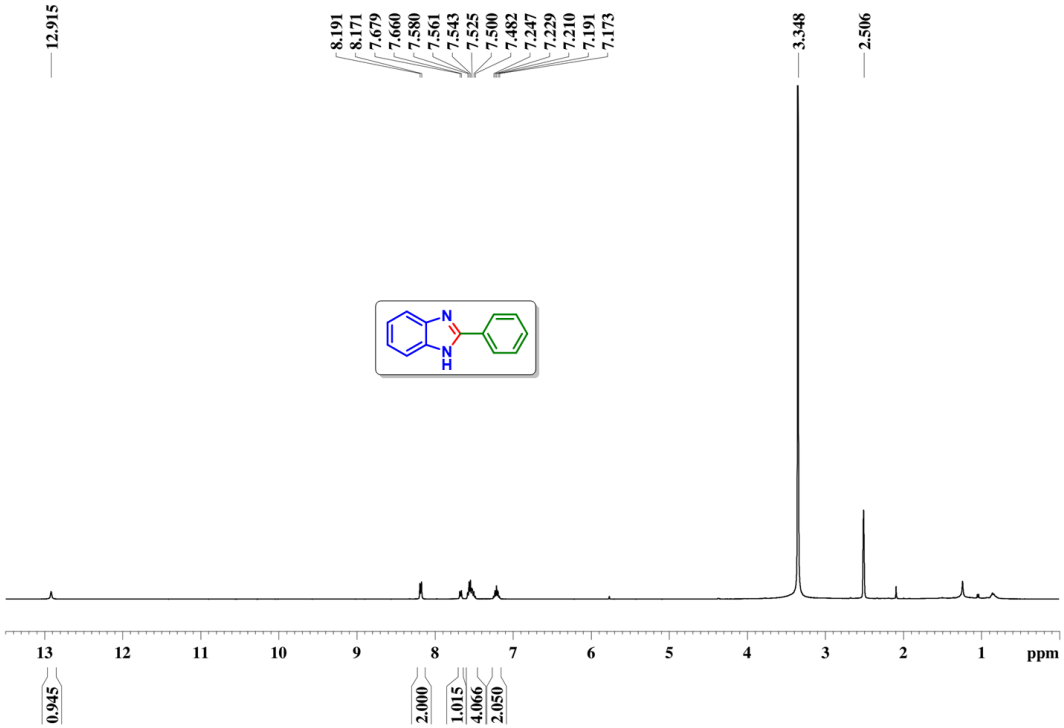
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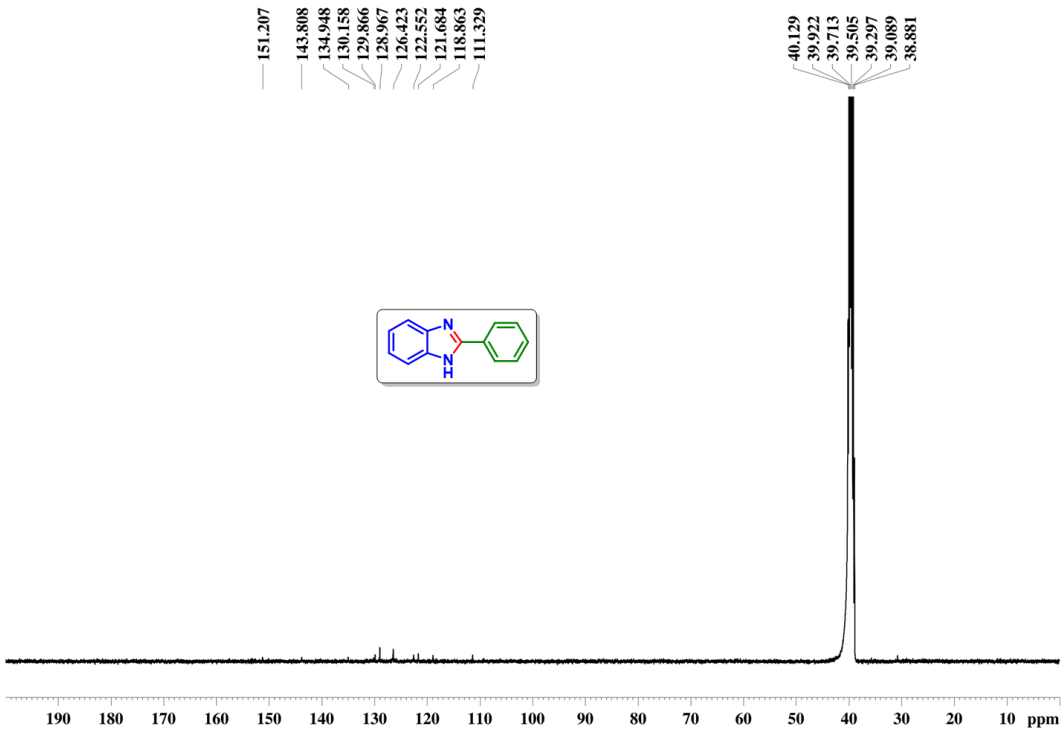
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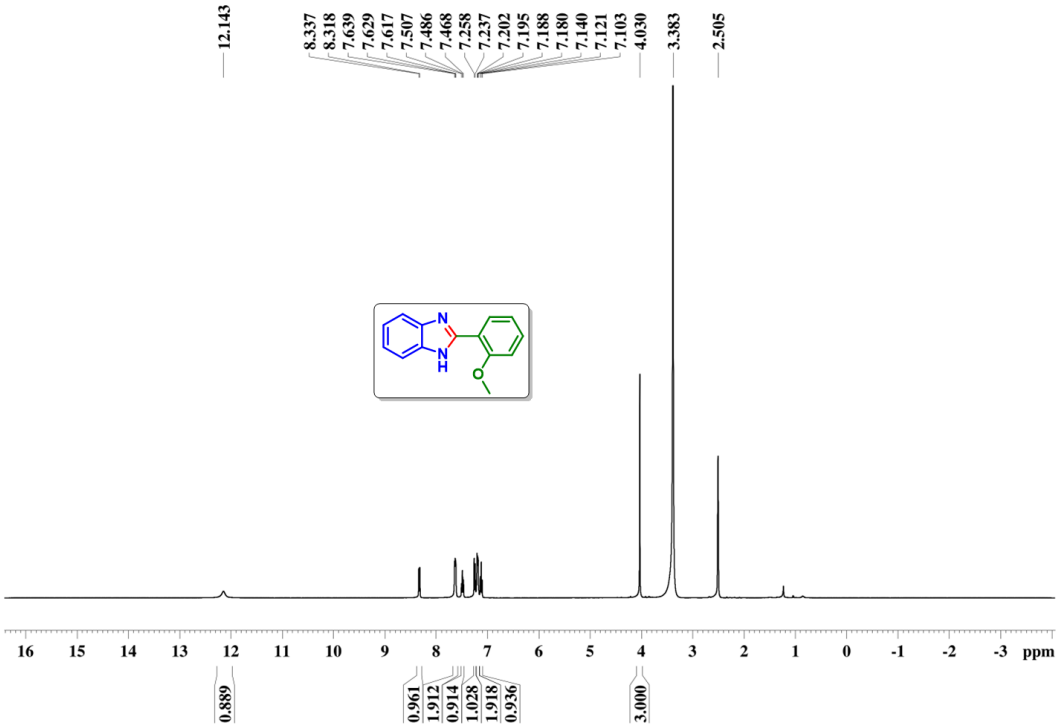
70
60
50
40
30
20
10
ppm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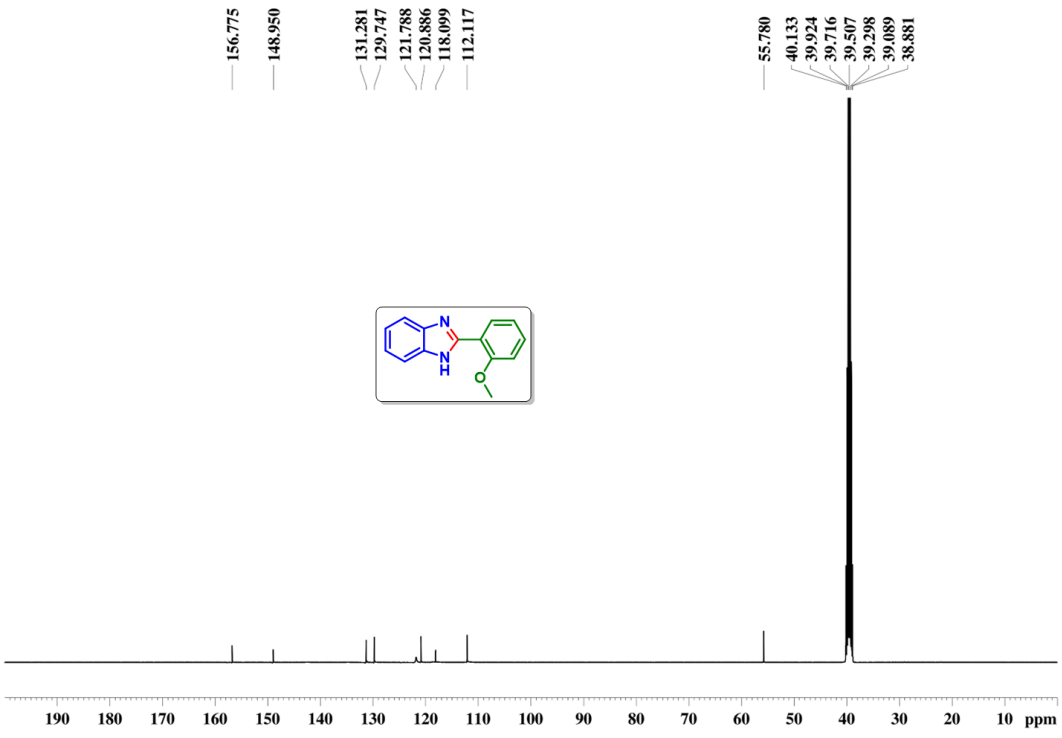
8.337
8.318
7.639
7.629
7.617
7.507
7.486
7.468
7.258
7.237
7.202
7.195
7.188
7.180
7.140
7.121
7.103
4.030
3.383
2.505
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
0.889
0.961
1.912
0.914
1.028
1.918
0.936
3.000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131.281
129.747
121.788
120.886
118.099
112.117
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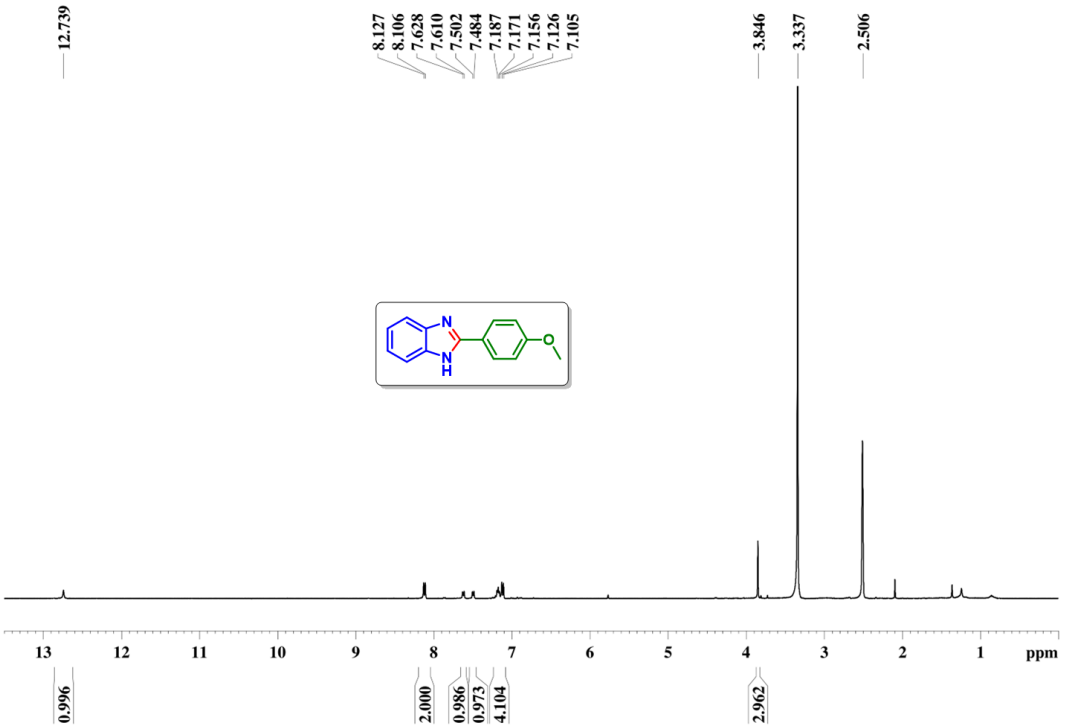
40.133
39.924
39.716
39.507
39.298
39.089
38.881
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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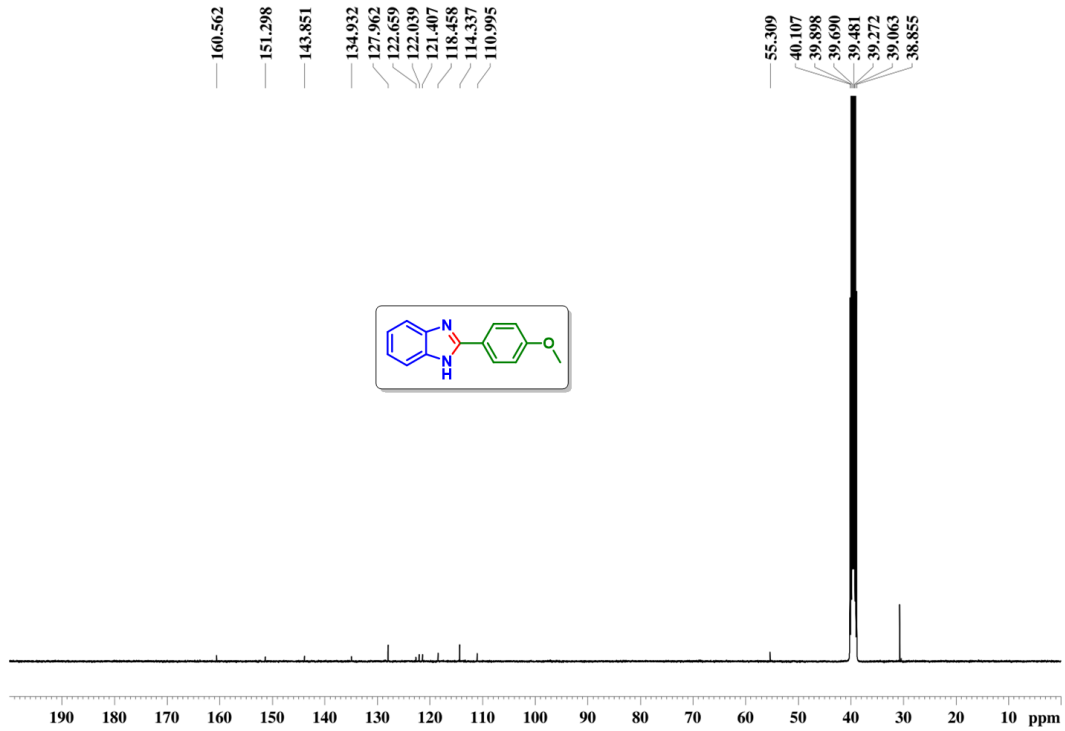
8.127
8.106
7.628
7.610
7.502
7.484
7.187
7.171
7.156
7.126
7.105
3.846
3.337
2.506
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.996
2.000
0.986
0.973
4.104
2.962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151.298
143.851
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127.962
122.659
122.039
121.407
118.458
114.337
110.995
55.309
40.107
39.898
39.690
39.481
39.272
39.063
38.855
190
180
170
160
150
140
130
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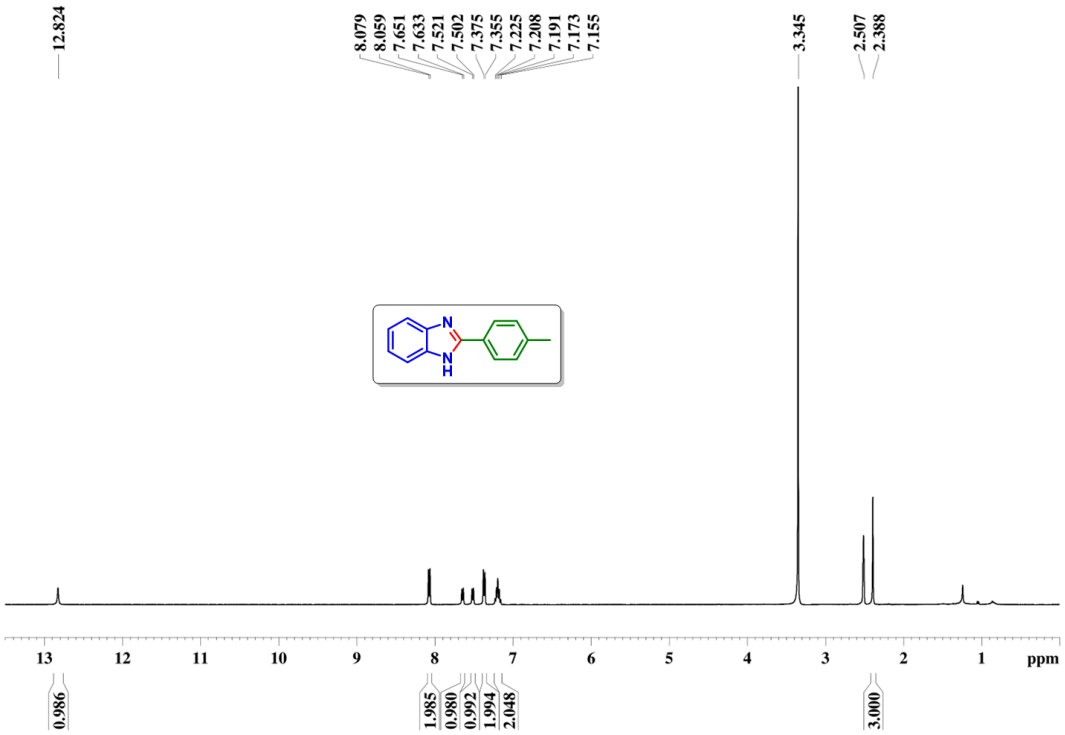
110
100
90
80
70
60
50
40
30
20
10
ppm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8.059
7.651
7.633
7.521
7.502
7.375
7.355
7.225
7.208
7.191
7.173
7.155
3.345
2.507
2.388
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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1.985
0.980
0.992
1.994
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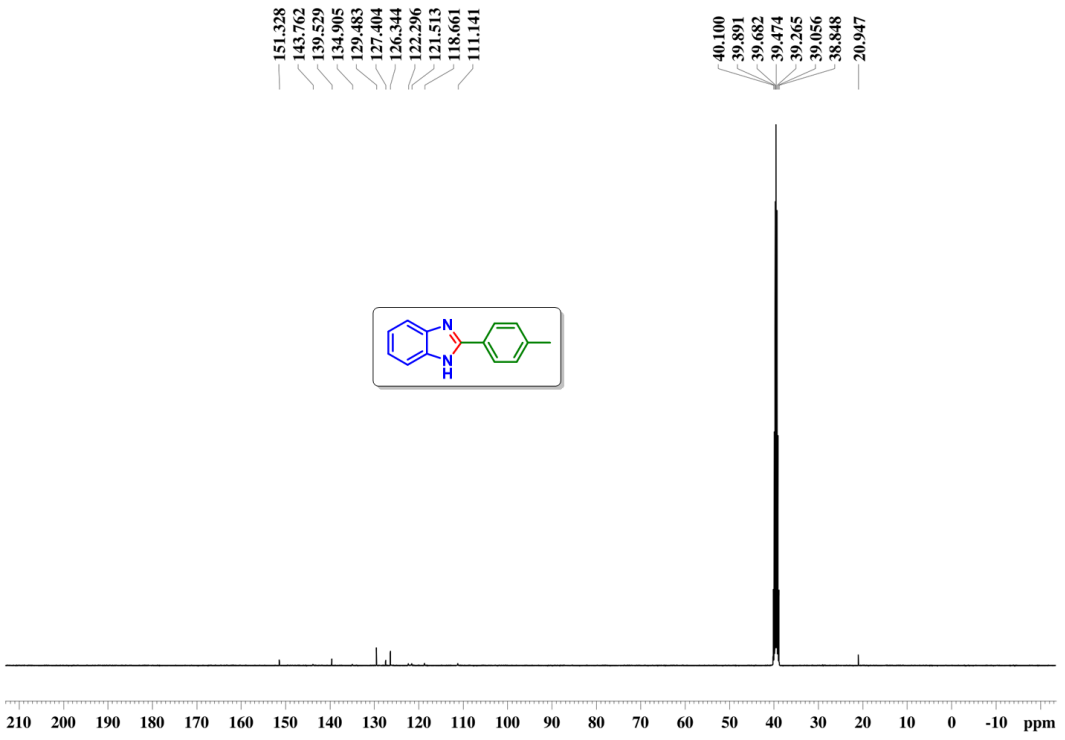
3.000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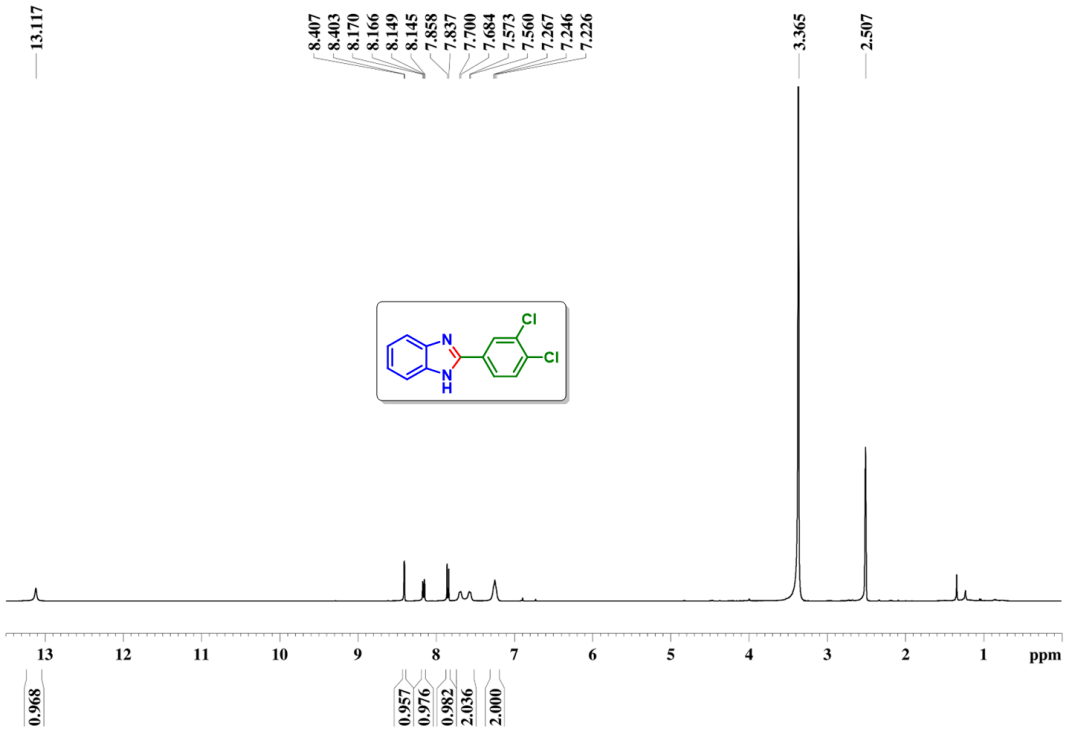
143.762
139.529
134.905
129.483
127.404
126.344
122.296
121.513
118.661
111.141
40.100
39.891
39.682
39.474
39.265
39.056
38.848
20.947
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


13.117
8.407
8.403
8.170
8.166
8.149
8.145
7.858
7.837
7.700
7.684
7.573
7.560
7.267
7.246
7.226
3.365
2.507
Cl
Cl
N
H
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
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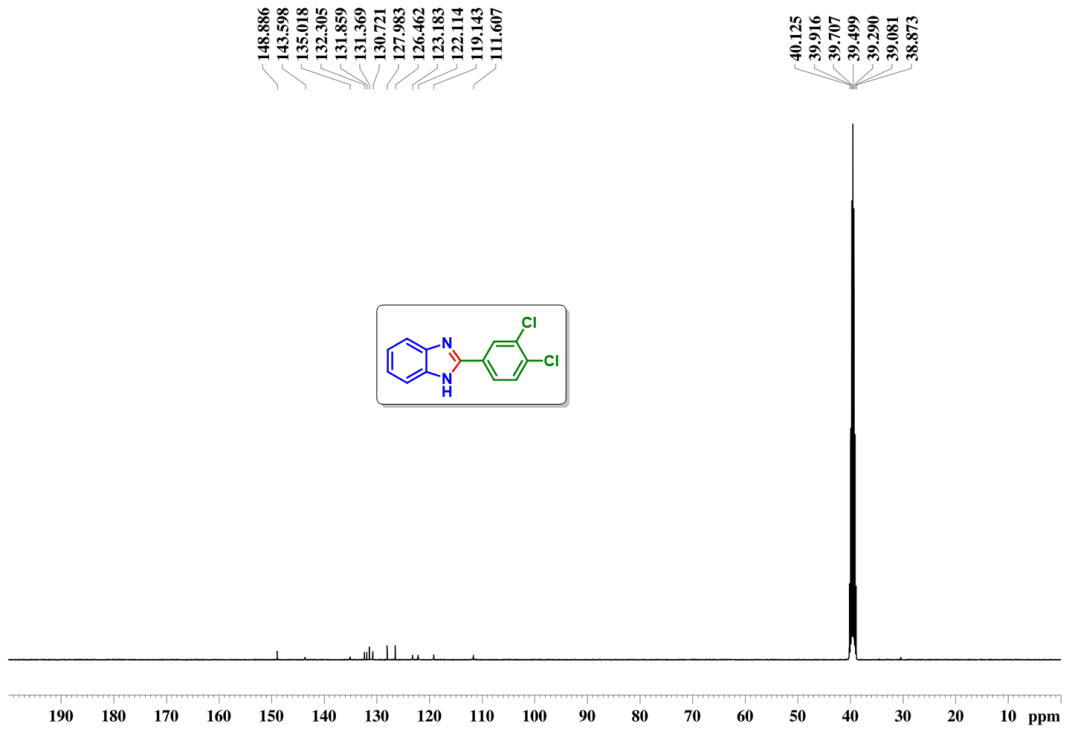
0.957
0.976
0.982
2.036
2.000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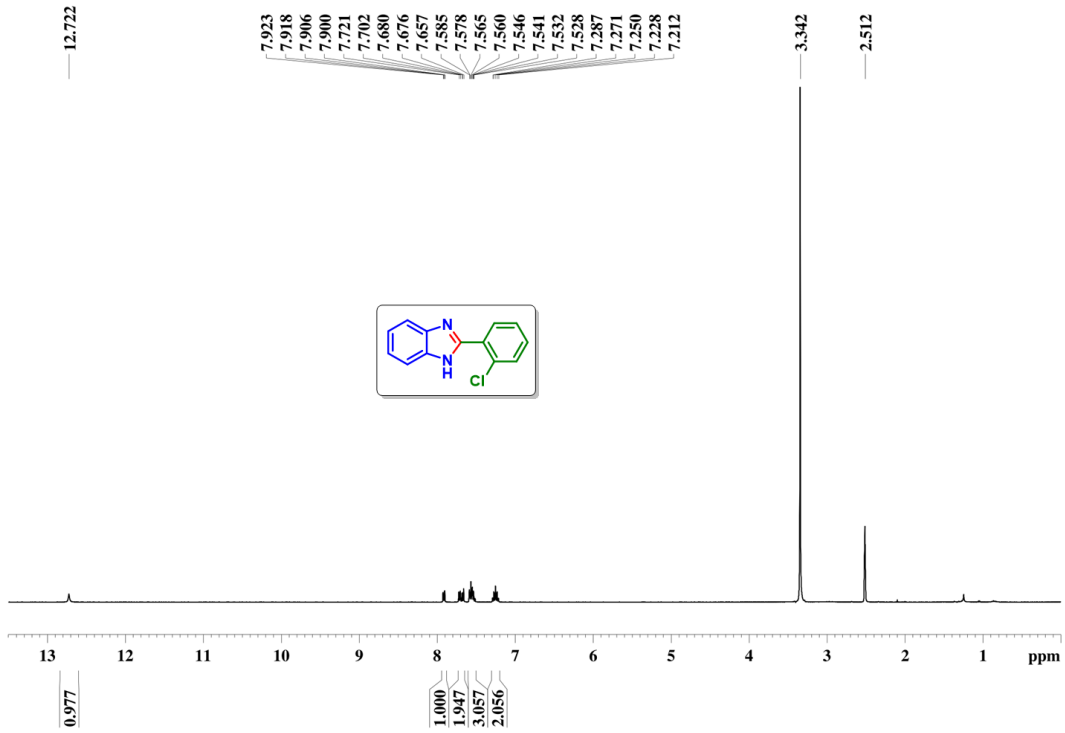
135.018
132.305
131.859
131.369
130.721
127.983
126.462
123.183
122.114
119.143
111.607
40.125
39.916
39.707
39.499
39.290
39.081
38.873
Cl
Cl
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


12.722
7.923
7.918
7.906
7.900
7.721
7.702
7.680
7.676
7.657
7.585
7.578
7.565
7.560
7.546
7.541
7.532
7.528
7.287
7.271
7.250
7.228
7.212
3.342
2.512
N
H
N
Cl
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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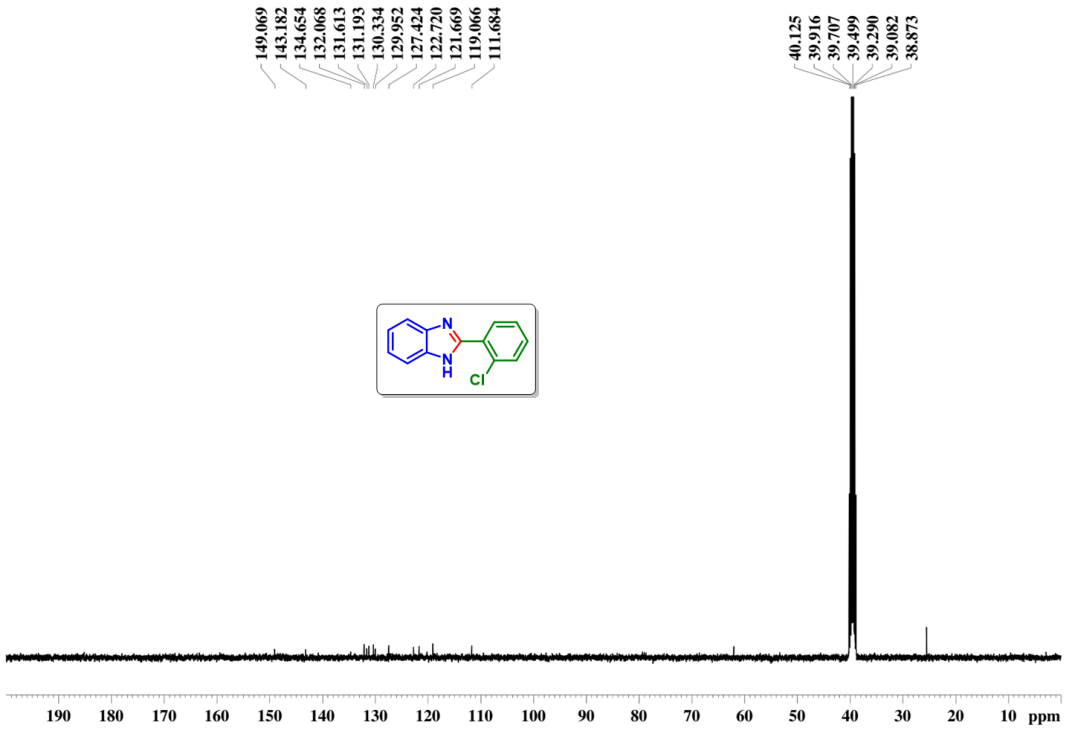
1.000
1.947
3.057
2.056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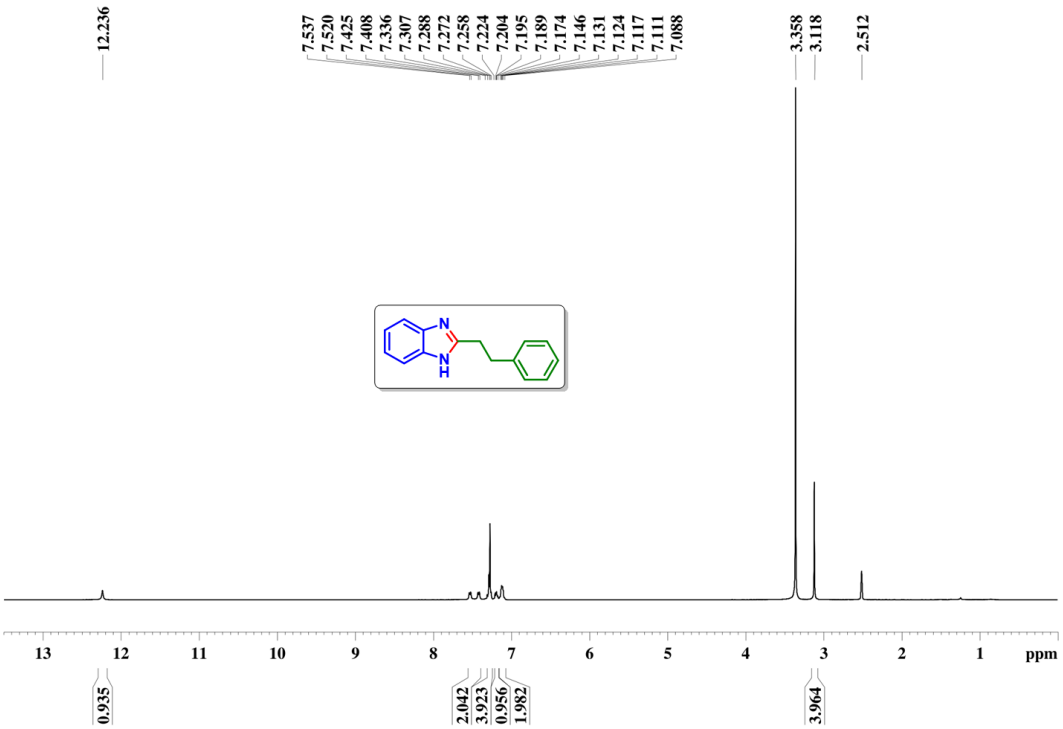
143.182
134.654
132.068
131.613
131.193
130.334
129.952
127.424
122.720
121.669
119.066
111.684
40.125
39.916
39.707
39.499
39.290
39.082
38.873
N
H
N
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.537
7.520
7.425
7.408
7.336
7.307
7.288
7.272
7.258
7.224
7.204
7.195
7.189
7.174
7.146
7.131
7.124
7.117
7.111
7.088
3.358
3.118
2.512
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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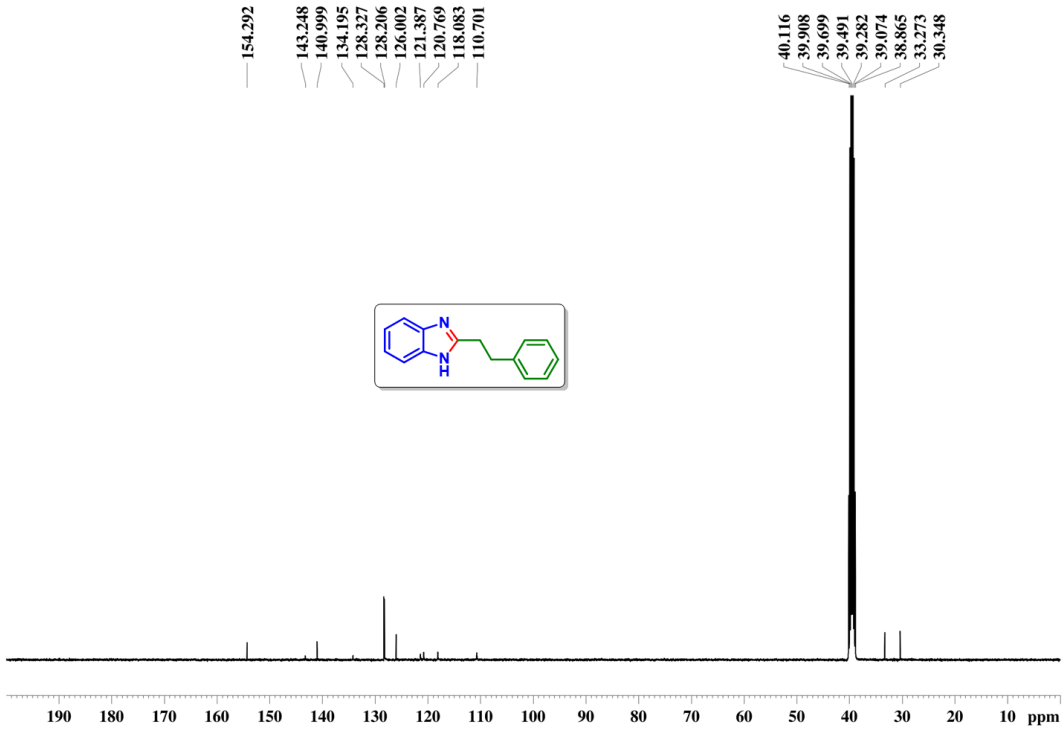
2.042
3.923
0.956
1.982
3.964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140.999
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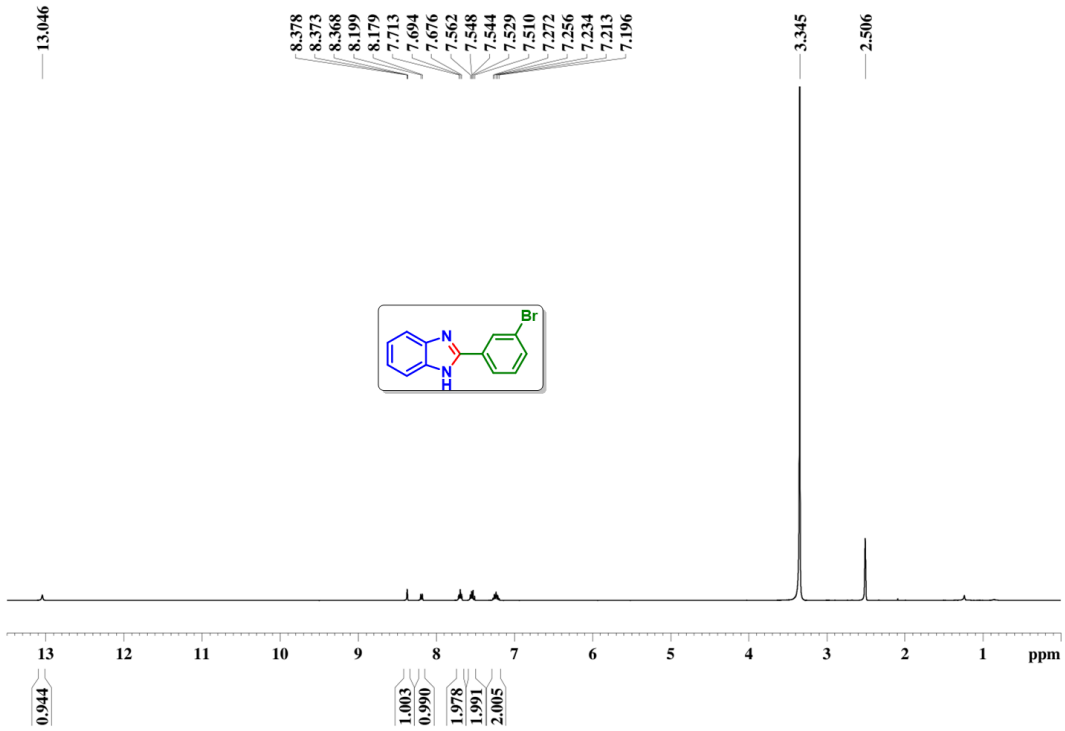
128.206
126.002
121.387
120.769
118.083
110.701
40.116
39.908
39.699
39.491
39.282
39.074
38.865
33.273
30.348
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.046
8.378
8.373
8.368
8.199
8.179
7.713
7.694
7.676
7.562
7.548
7.544
7.529
7.510
7.272
7.256
7.234
7.213
7.196
3.345
2.506
Br
N
N
H
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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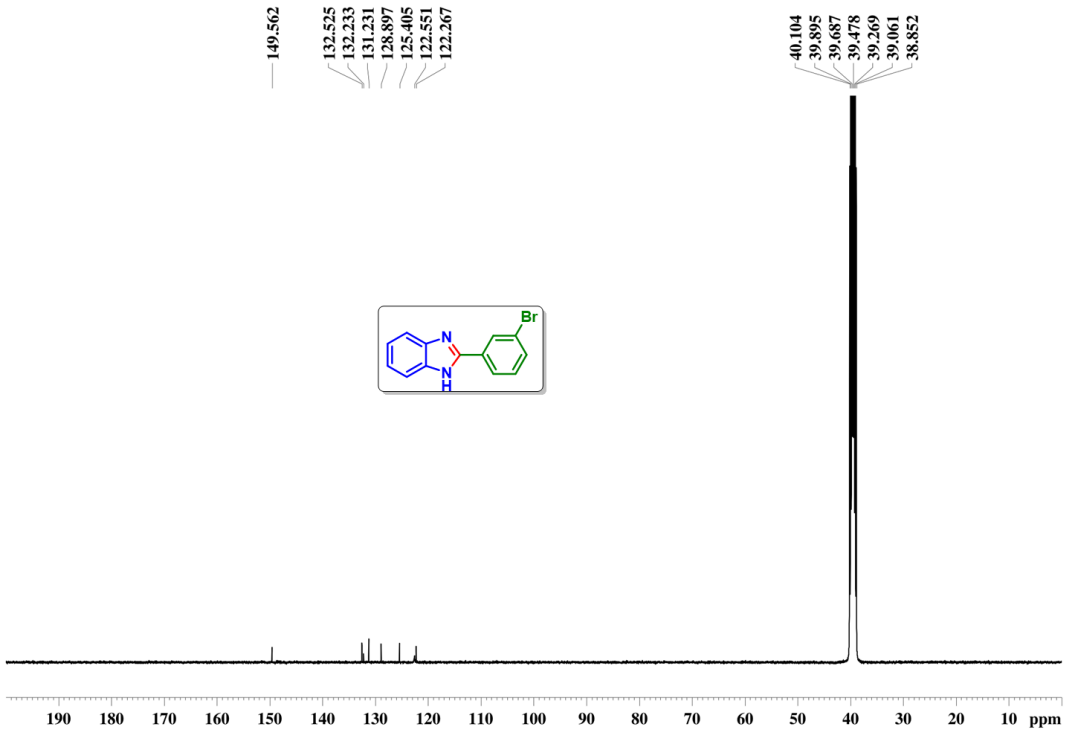
0.990
1.978
1.991
2.005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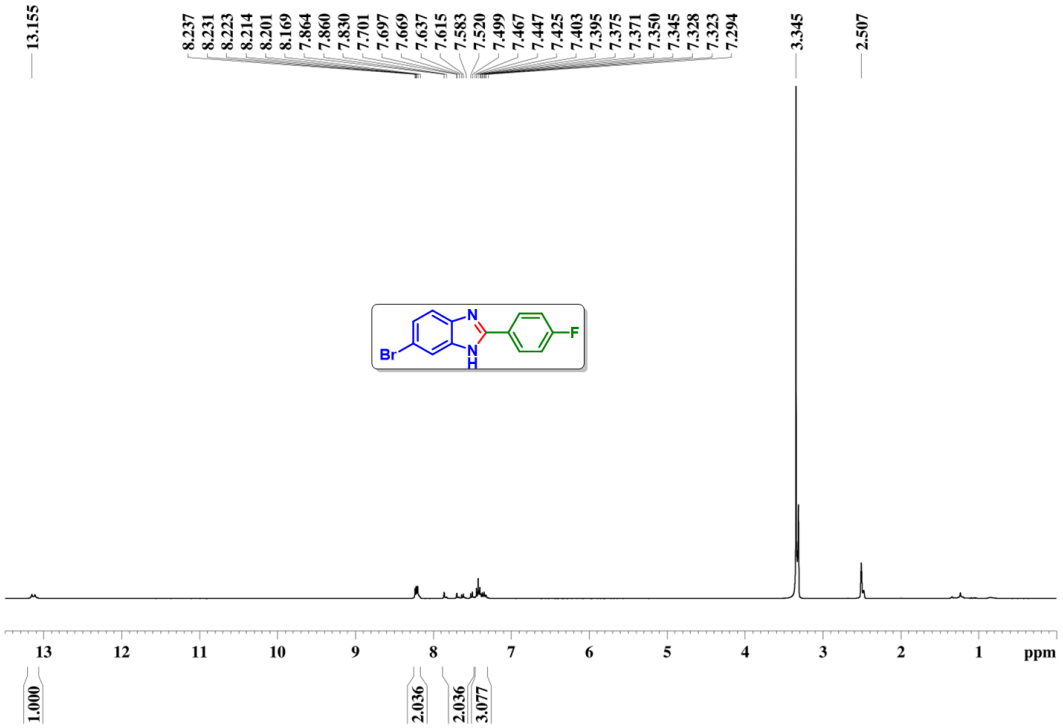
132.233
131.231
128.897
125.405
122.551
122.267
40.104
39.895
39.687
39.478
39.269
39.061
38.852
Br
N
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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8.231
8.223
8.214
8.201
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7.864
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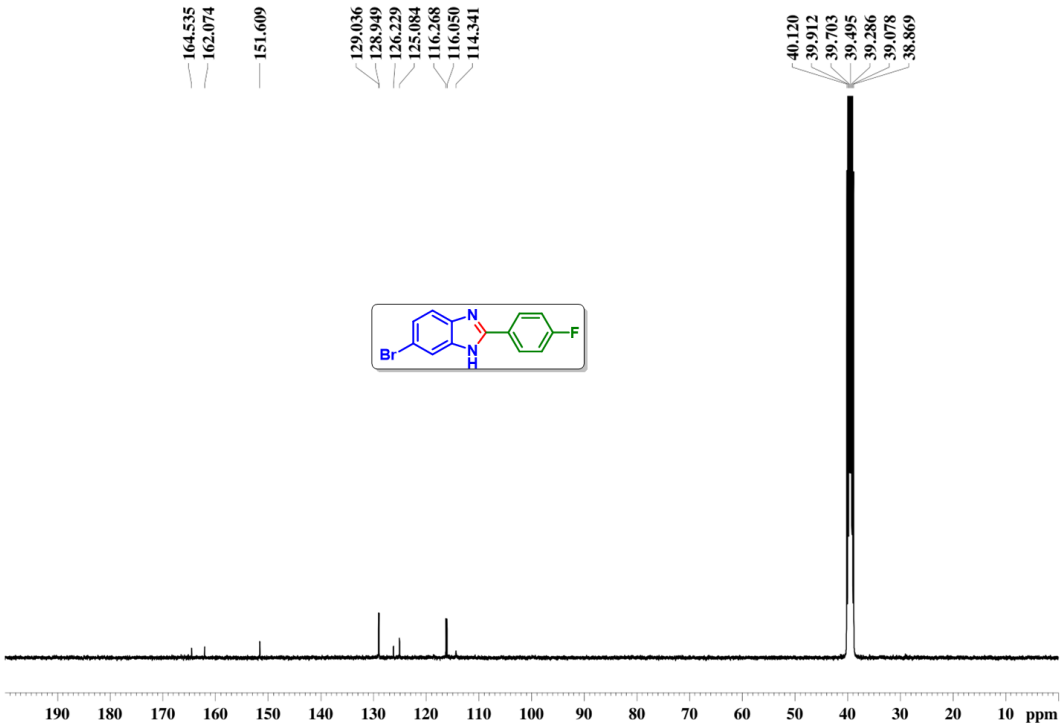
7.830
7.701
7.697
7.669
7.637
7.615
7.583
7.520
7.499
7.467
7.447
7.425
7.403
7.395
7.375
7.371
7.350
7.345
7.328
7.323
7.294
3.345
2.507
Br
N
H
N
F
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.000
2.036
2.036
3.077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126.229
125.084
116.268
116.050
114.341
40.120
39.912
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39.286
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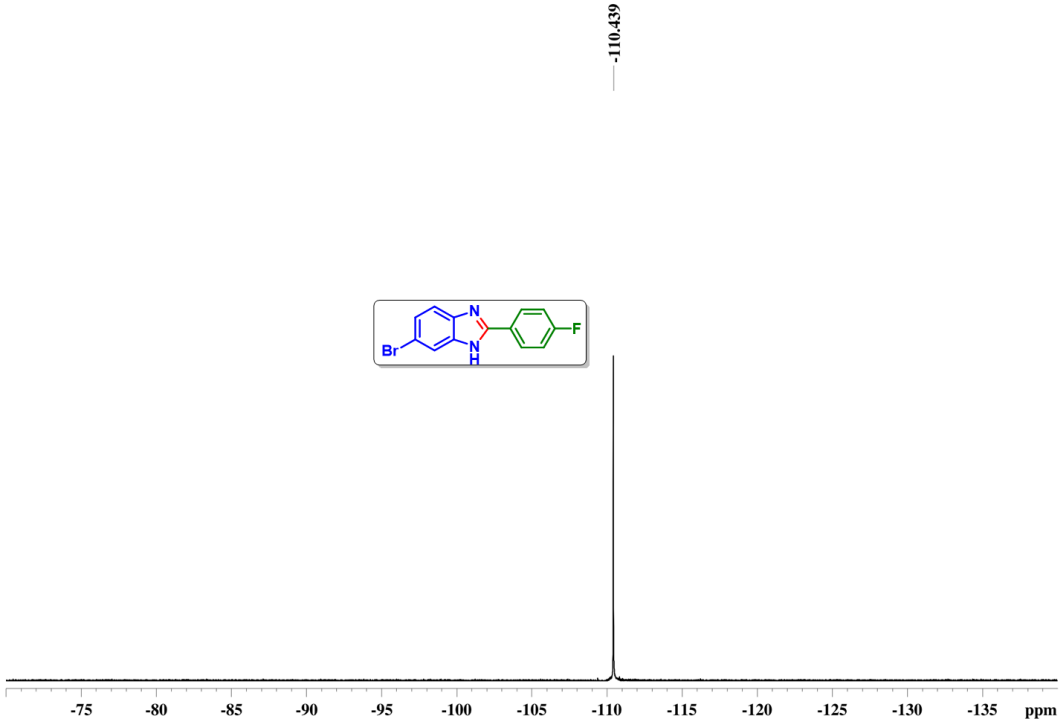
38.869
Br
N
H
N
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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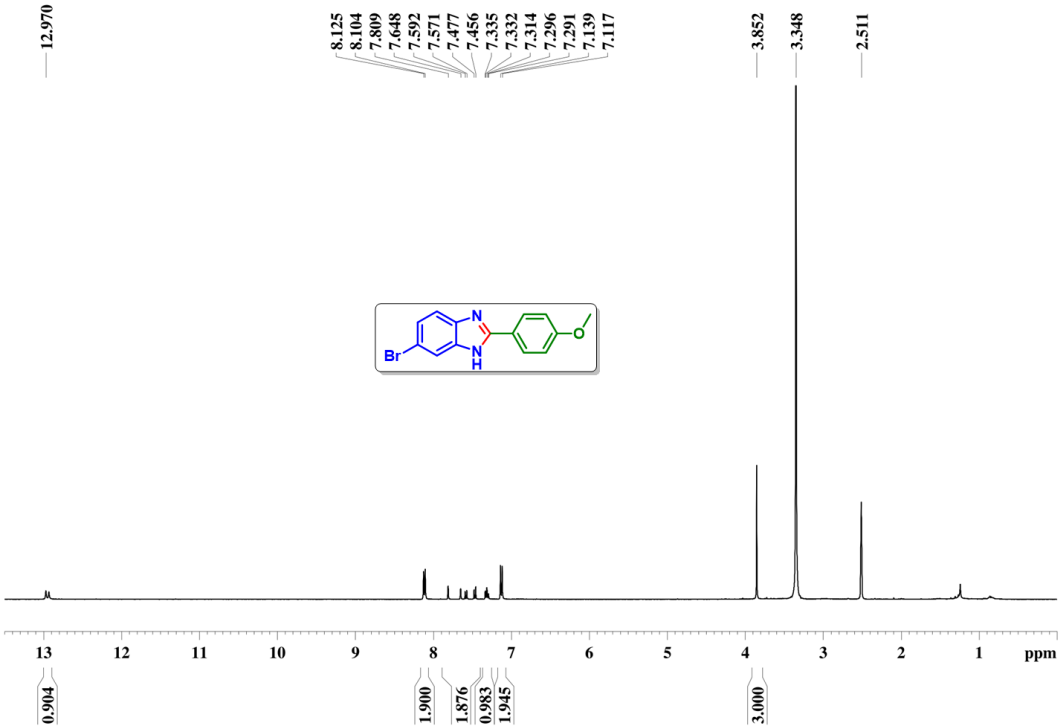
N
N
H
Br
F
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
ppm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7.809
7.648
7.592
7.571
7.477
7.456
7.335
7.332
7.314
7.296
7.291
7.139
7.117
3.852
3.348
2.511
Br
N
H
O
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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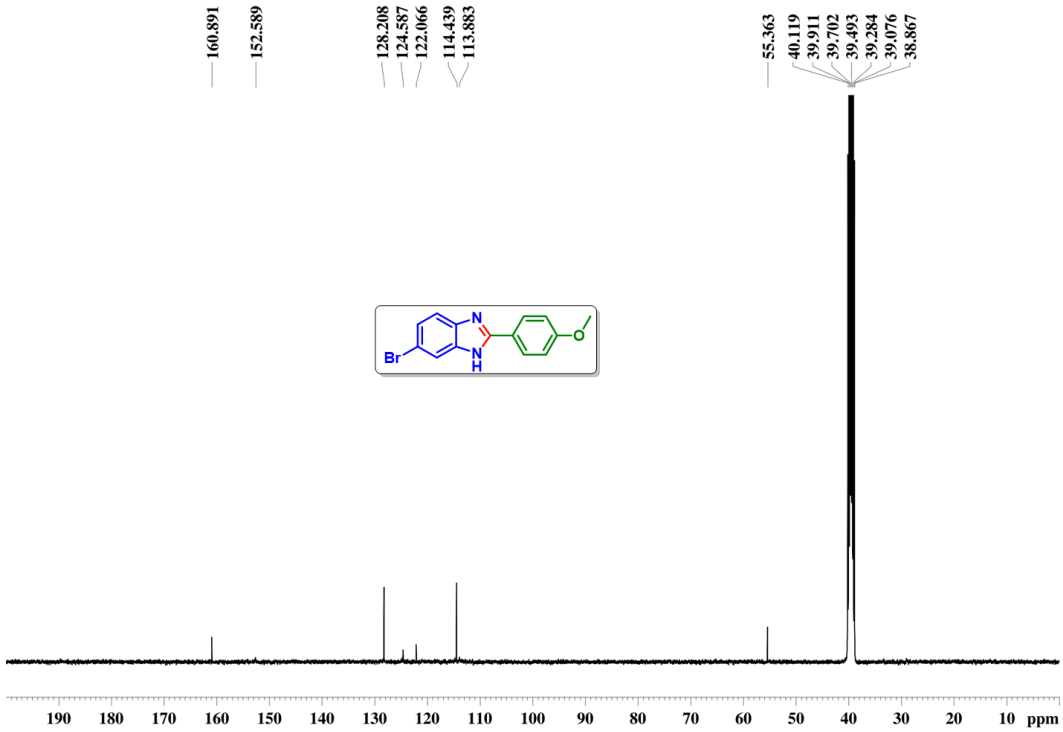
3.000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55.363
40.119
39.911
39.702
39.493
39.284
39.076
38.867
Br
N
H
O
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180
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150
140
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120
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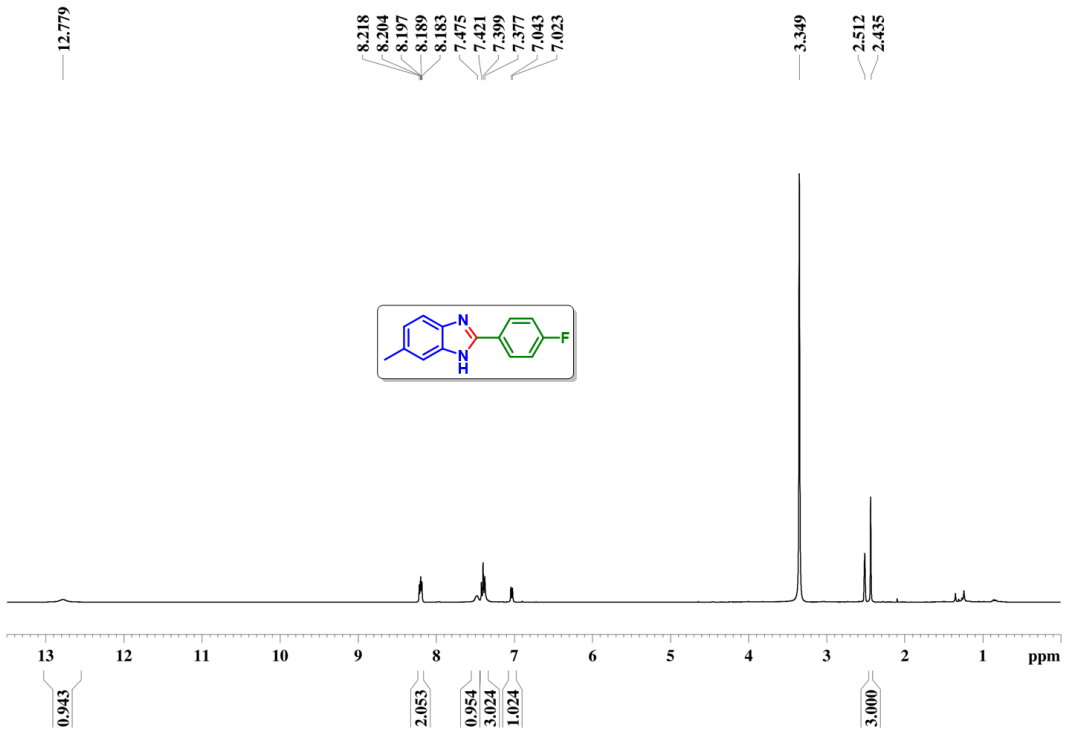
80
70
60
50
40
30
20
10
ppm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8.183
7.475
7.421
7.399
7.377
7.043
7.023
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2.512
2.435
N
N
H
F
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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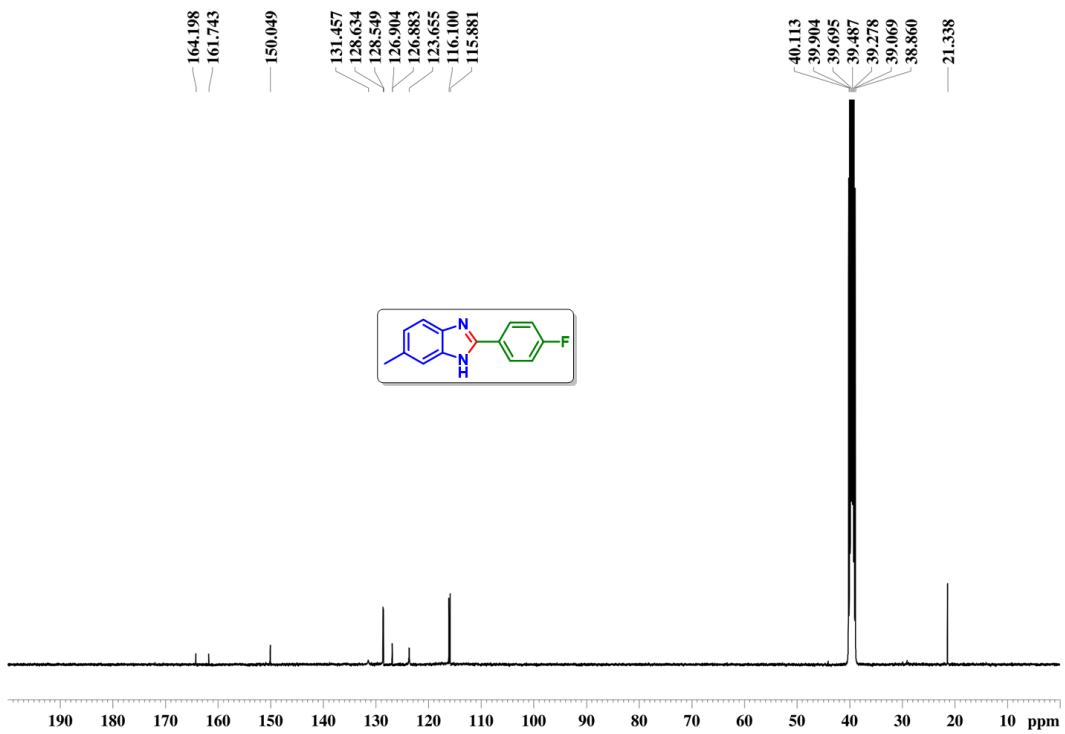
1.024
3.000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131.457
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128.549
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126.883
123.655
116.100
115.881
40.113
39.904
39.695
39.487
39.278
39.069
38.860
21.338
N
N
H
F
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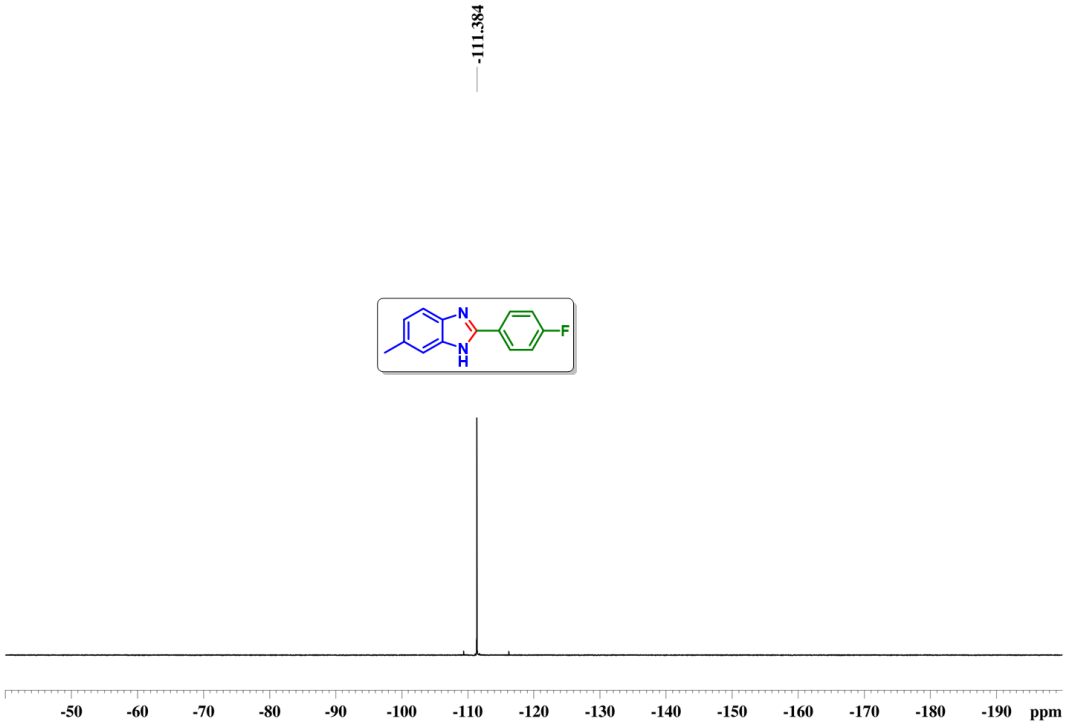
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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N
N
H
F
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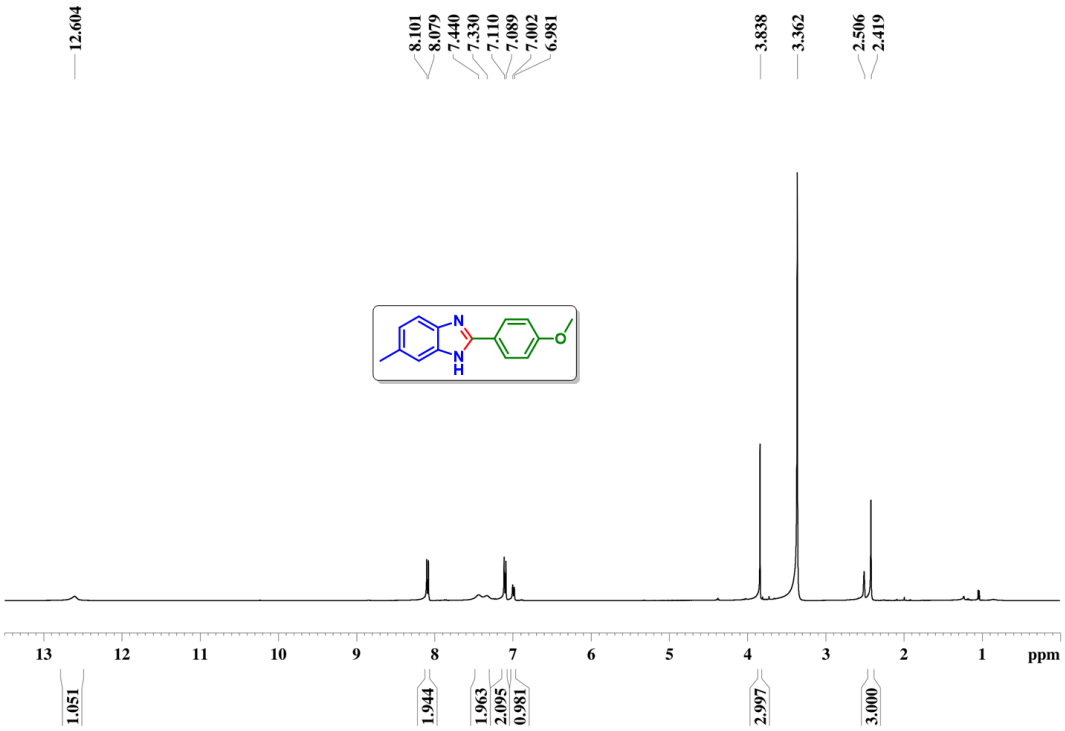
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
ppm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7.110
7.089
7.002
6.981
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3.362
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2.419
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12
11
10
9
8
7
6
5
4
3
2
1
ppm
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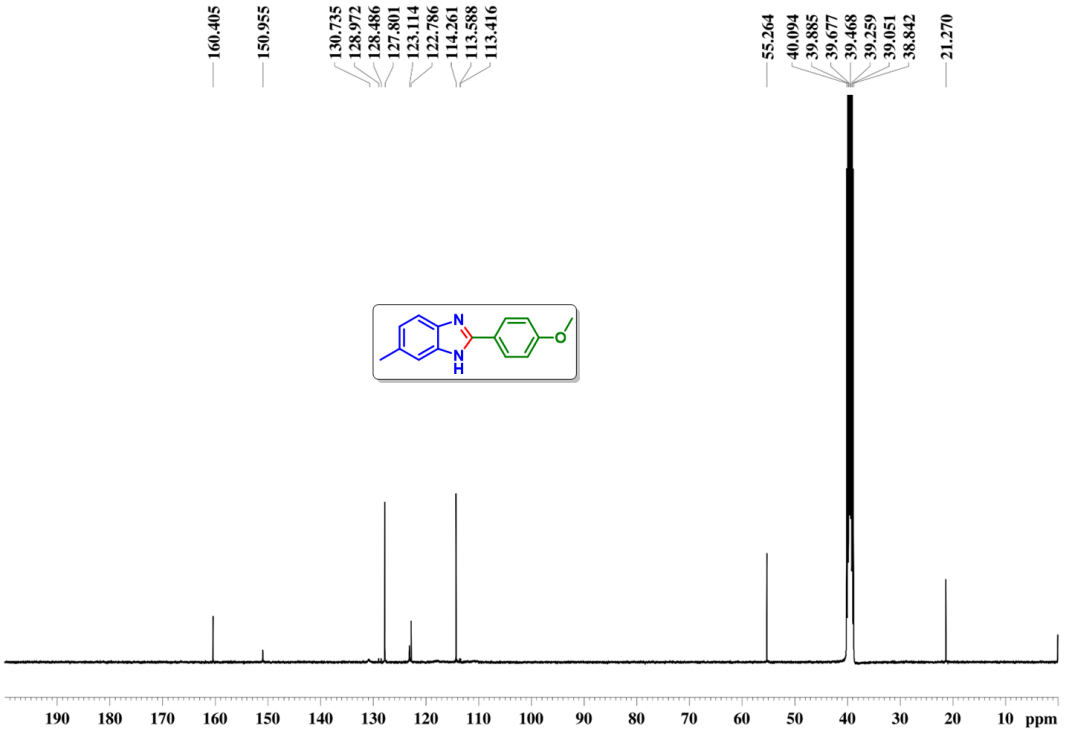
1.963
2.095
0.981
2.997
3.000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122.786
114.261
113.588
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55.264
40.094
39.885
39.677
39.468
39.259
39.051
38.842
21.270
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180
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150
140
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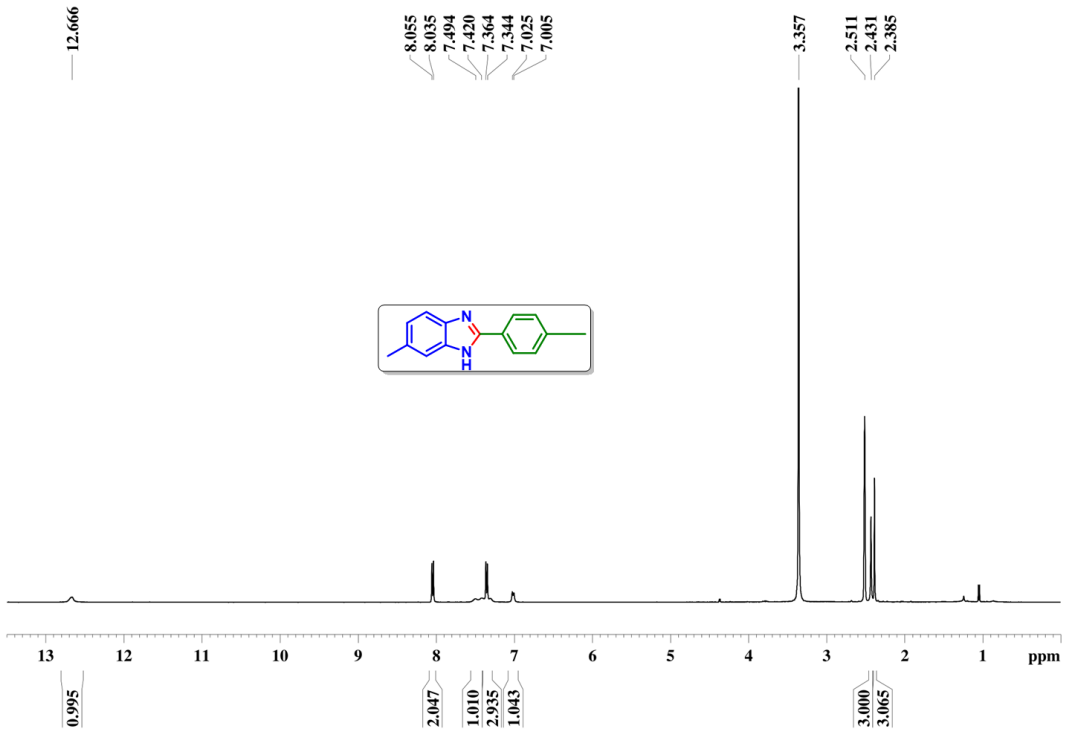
90
80
70
60
50
40
30
20
10
ppm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7.344
7.025
7.005
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2.511
2.431
2.385
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
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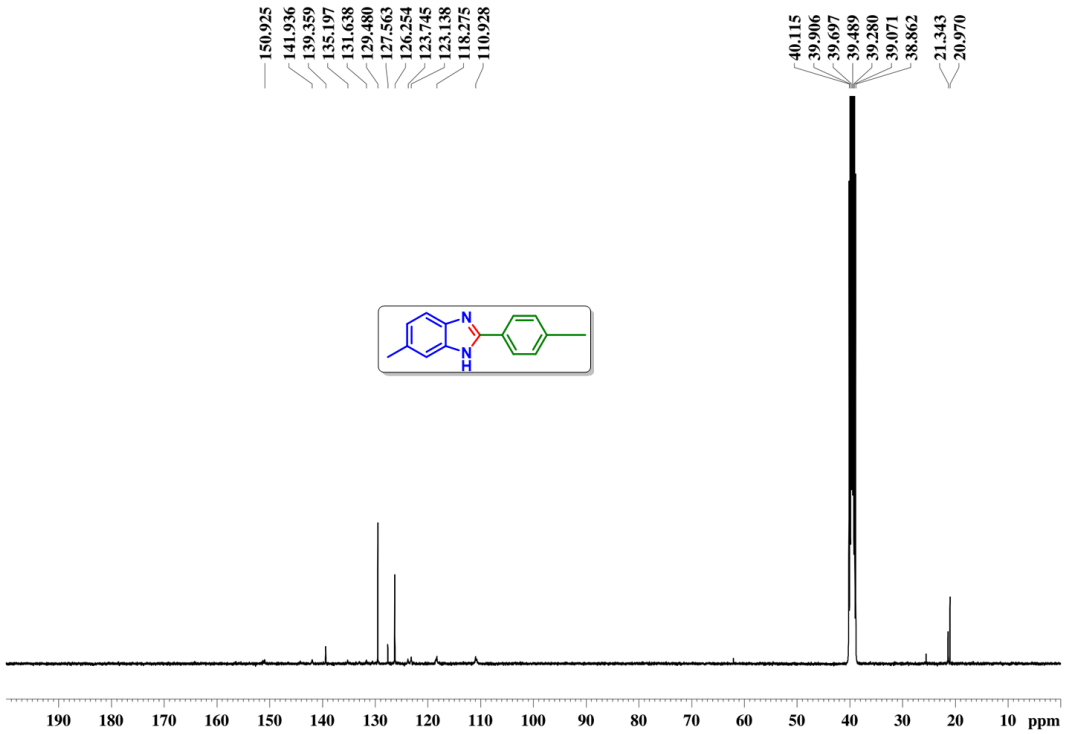
1.010
2.935
1.043
3.000
3.065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126.254
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123.138
118.275
110.928
40.115
39.906
39.697
39.489
39.280
39.071
38.862
21.343
20.970
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150
140
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70
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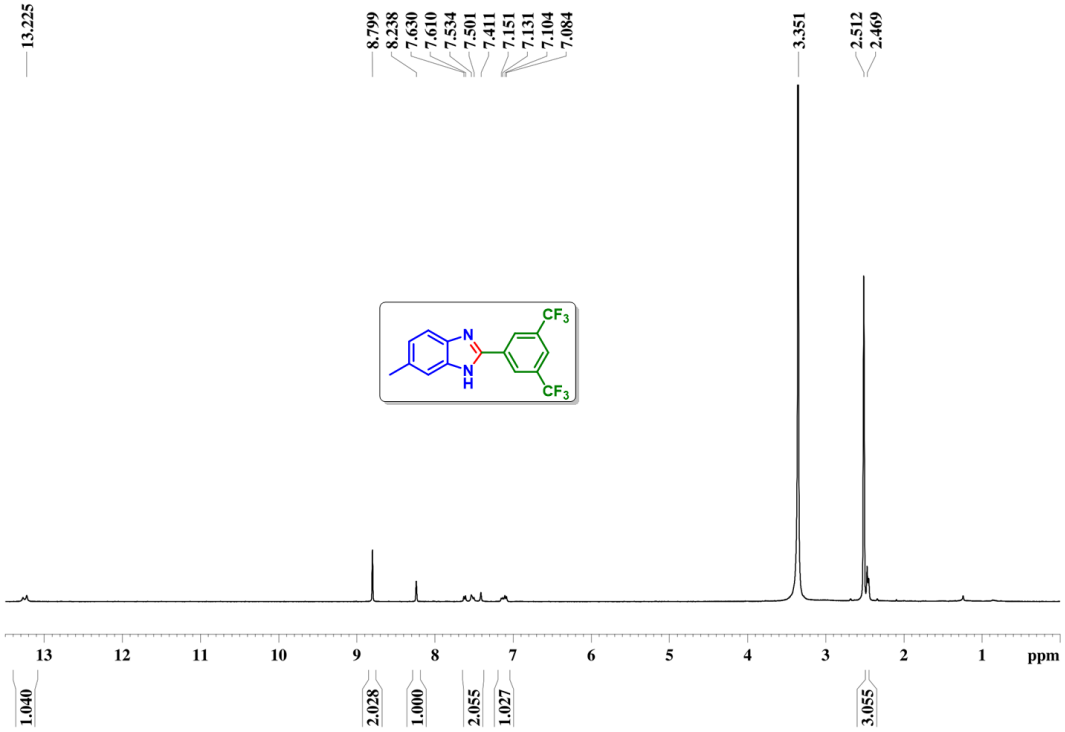
50
40
30
20
10
ppm


13.225
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7.610
7.534
7.501
7.411
7.151
7.131
7.104
7.084
3.351
2.512
2.469
CF3
CF3
N
H
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
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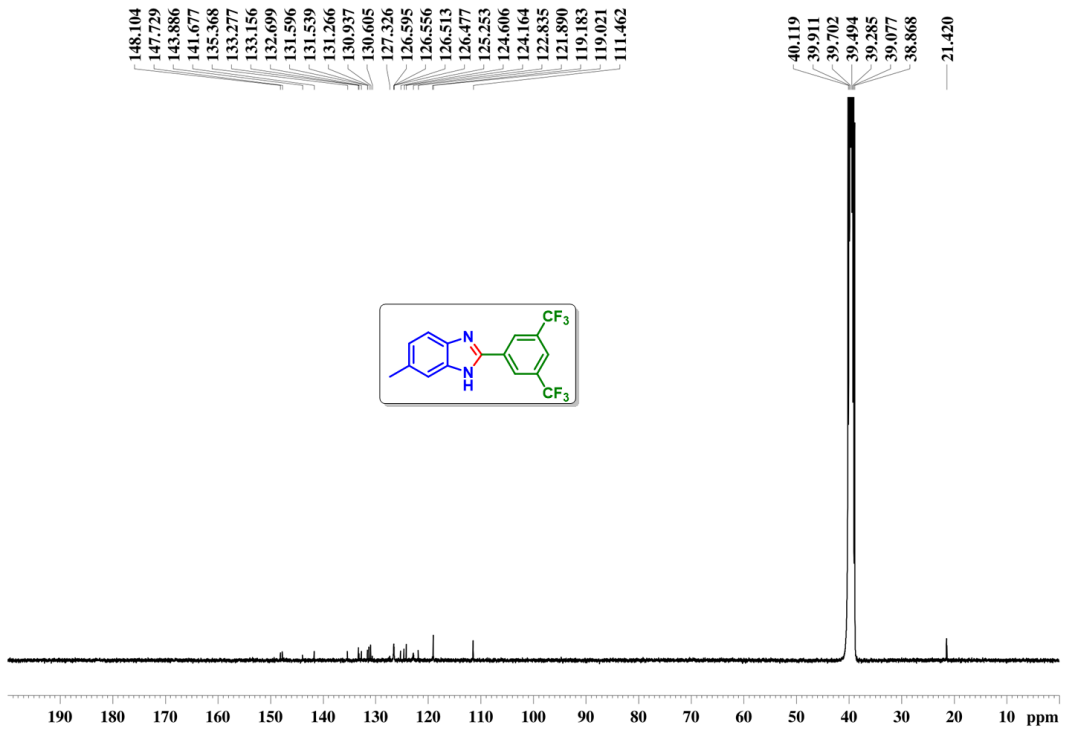
2.028
1.000
2.055
1.027
3.055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143.886
141.677
135.368
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132.699
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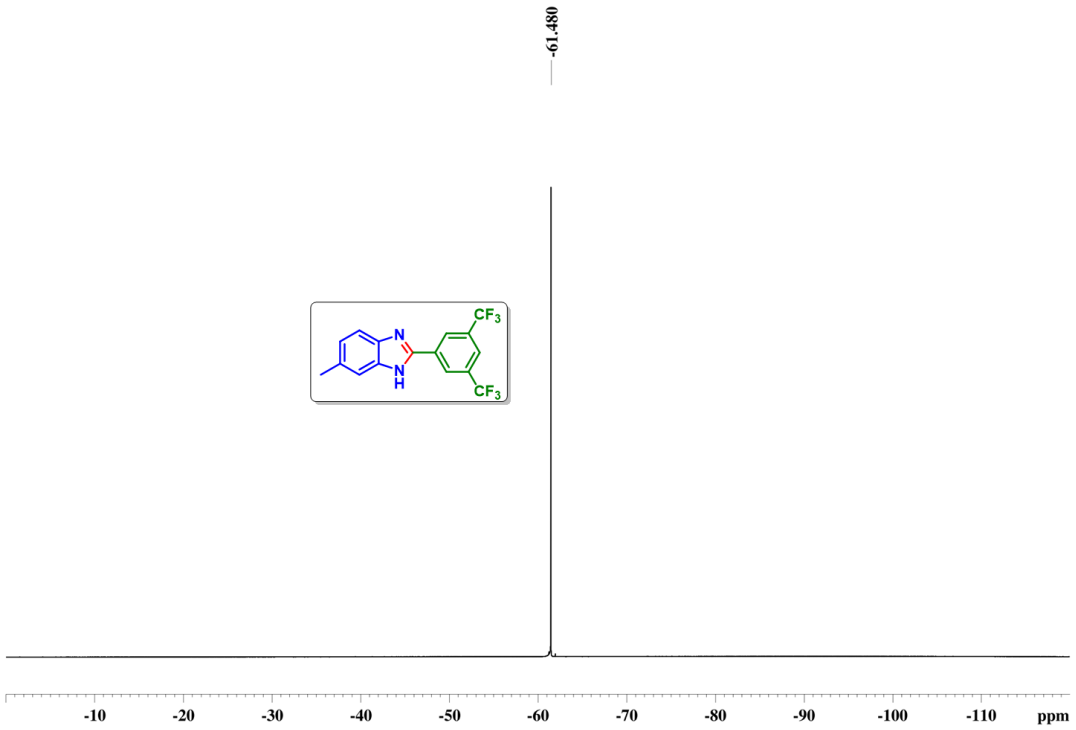
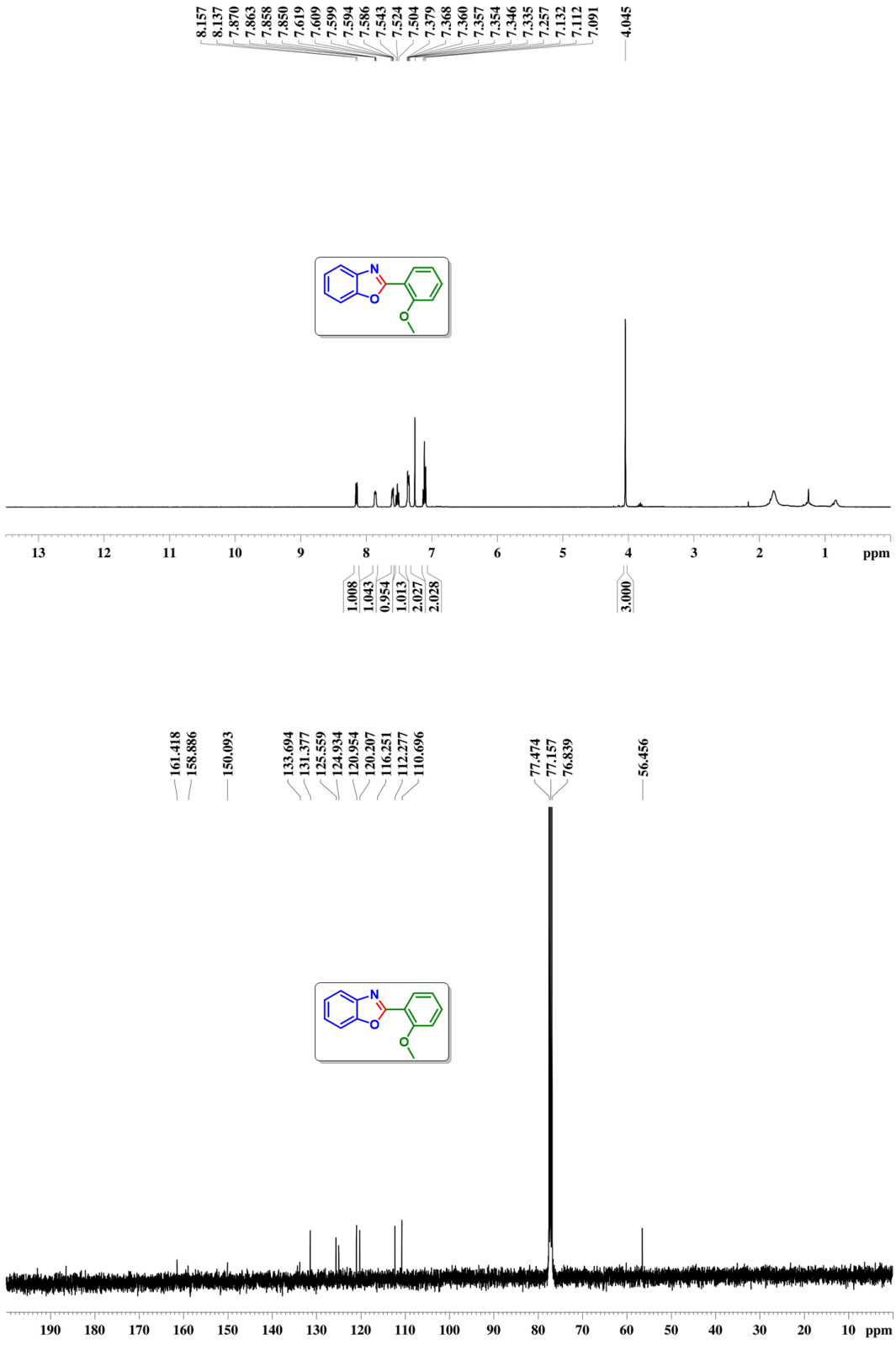
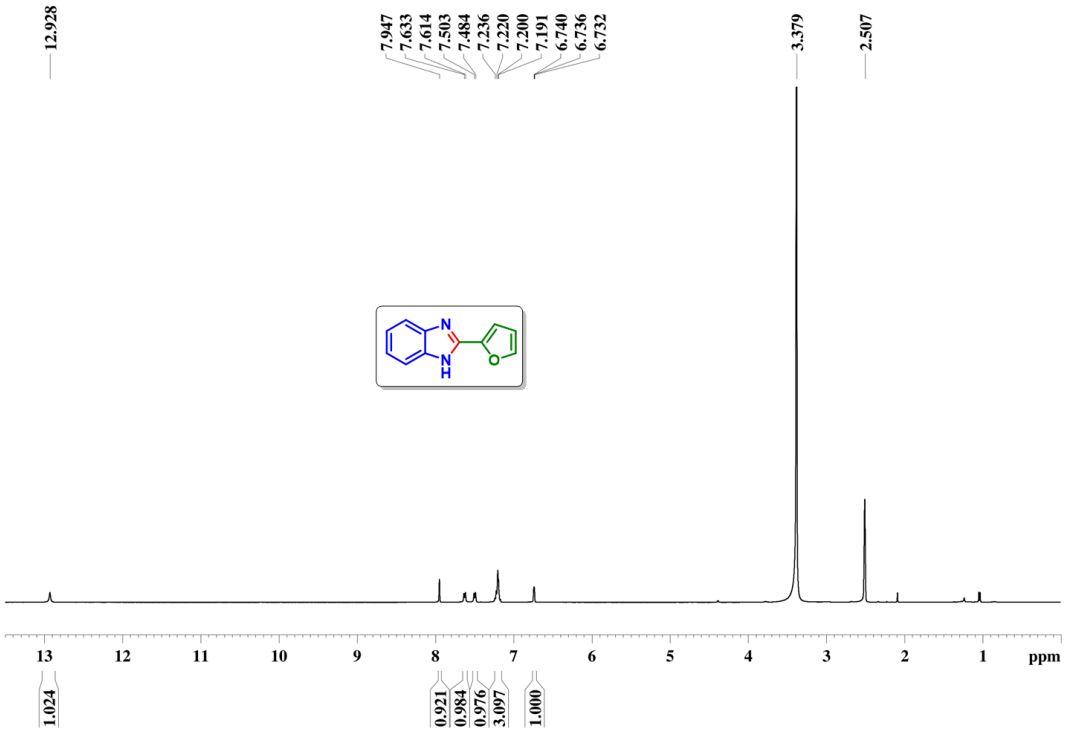
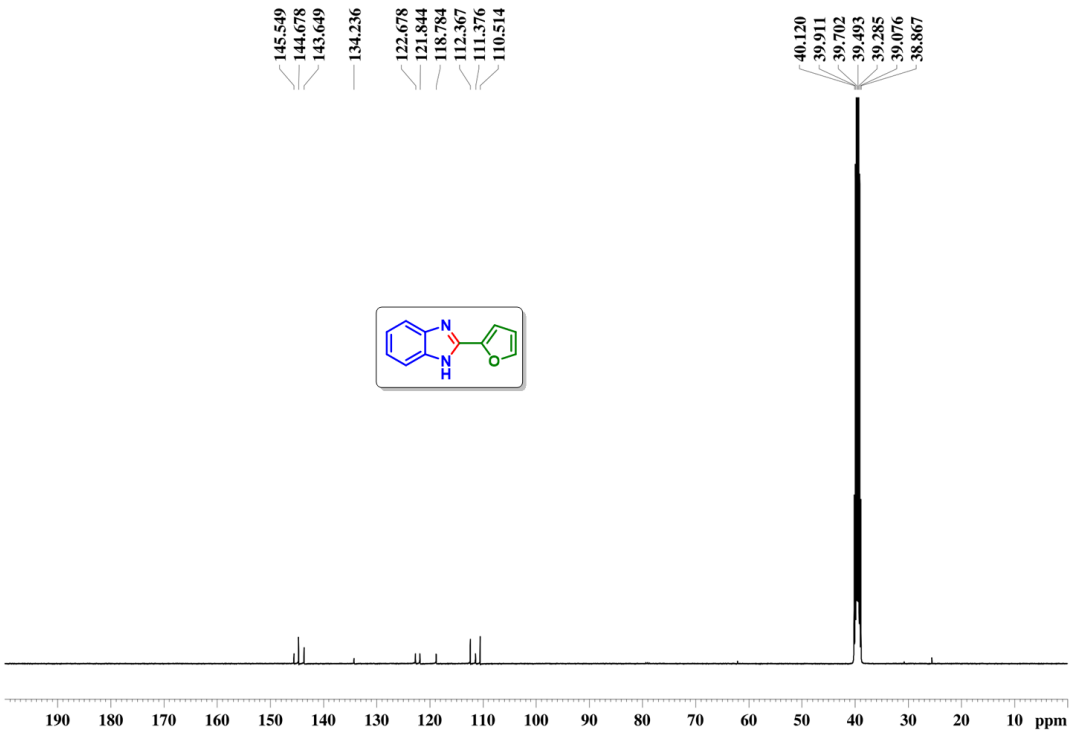
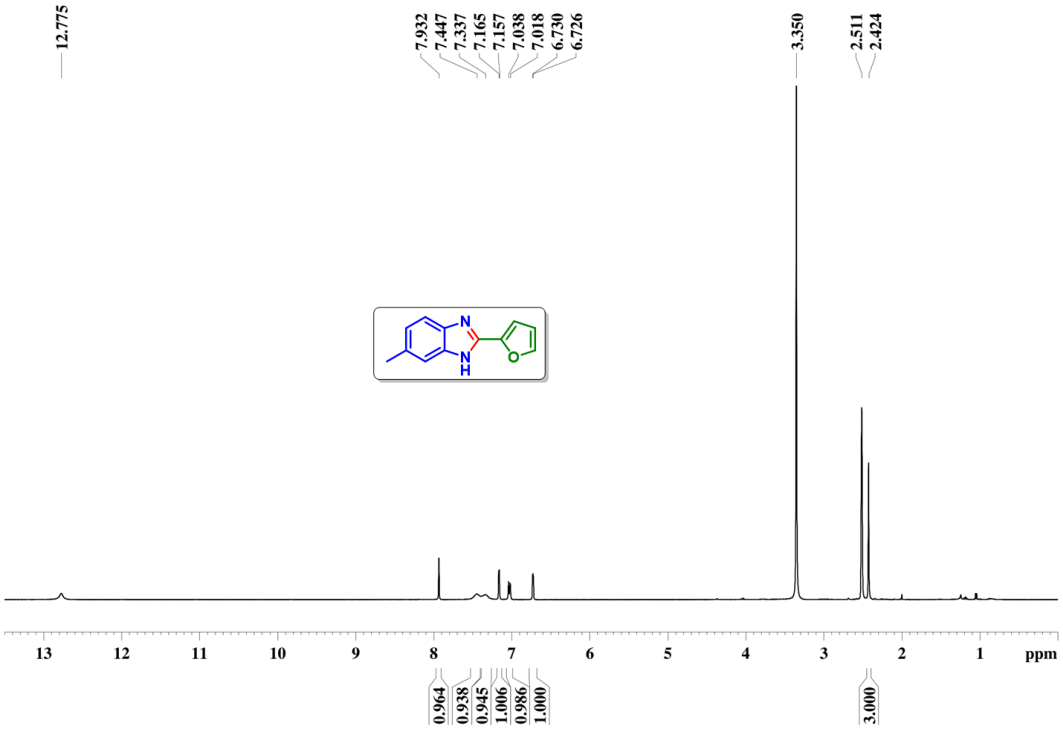
131.539
131.266
130.937
130.605
127.326
126.595
126.556
126.513
126.477
125.253
124.606
124.164
122.835
121.890
119.183
119.021
111.462
40.119
39.911
39.702
39.494
39.285
39.077
38.868
21.420
CF3
CF3
N
H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

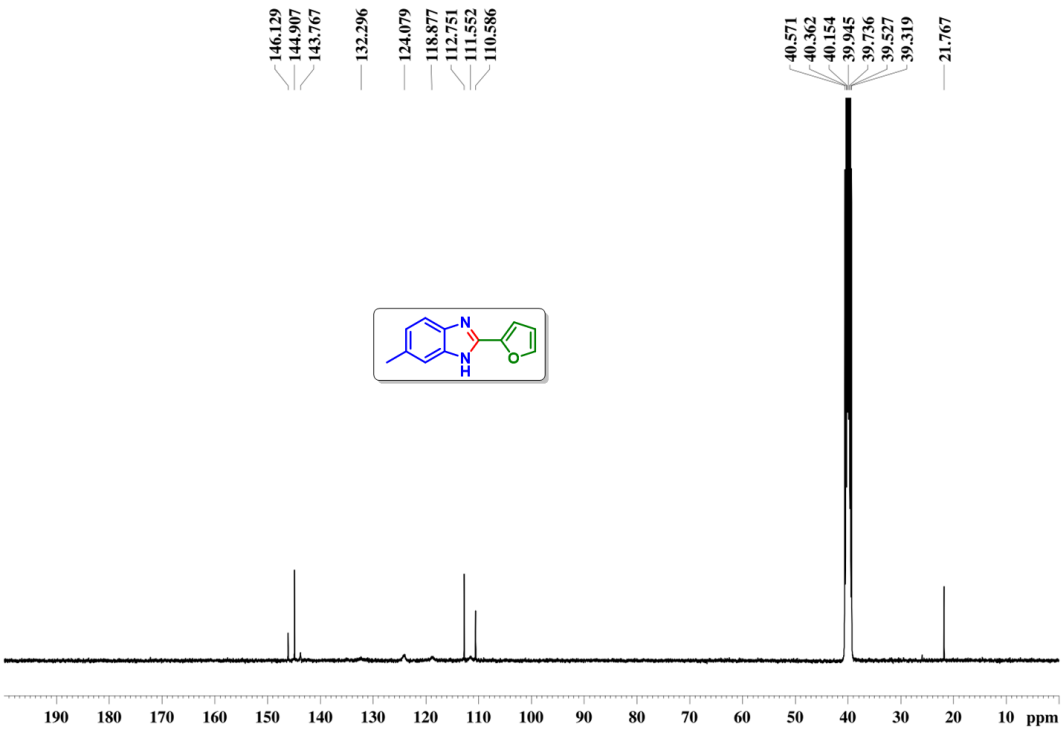

-61.480
CF3
CF3
N
H
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
ppm

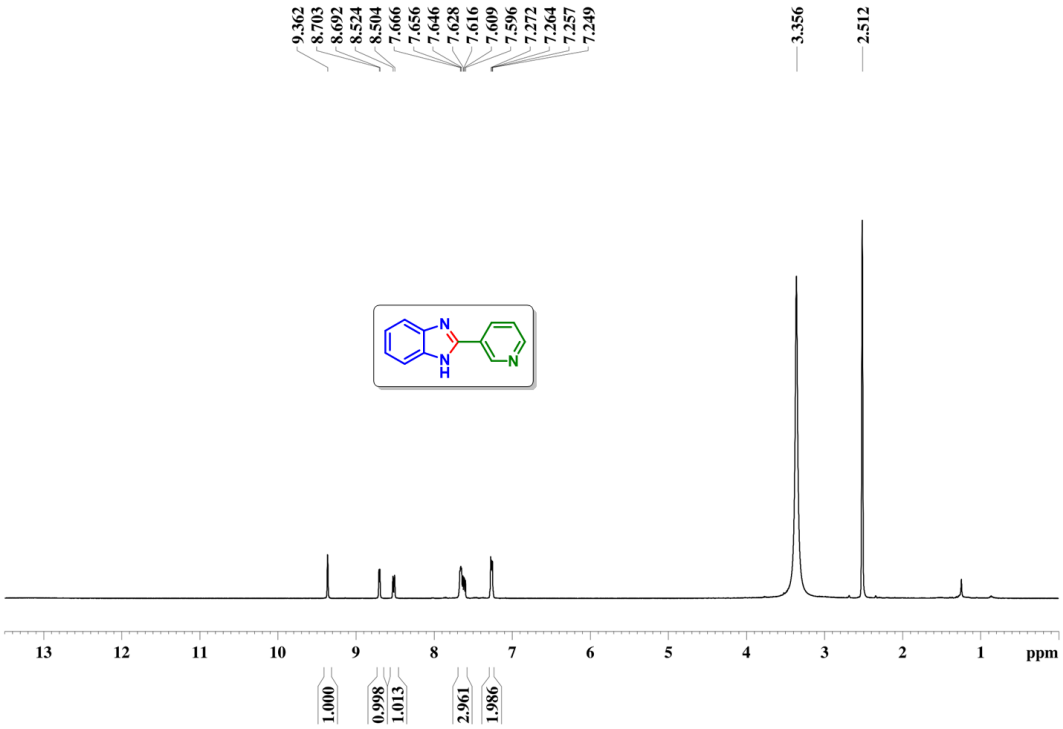

8.157
8.137
7.870
7.863
7.858
7.850
7.619
7.609
7.599
7.594
7.586
7.543
7.524
7.504
7.379
7.368
7.360
7.357
7.354
7.346
7.335
7.257
7.132
7.112
7.091
4.045
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
1.008
1.043
0.954
1.013
2.027
2.028
3.000
161.418
158.886
150.093
133.694
131.377
125.559
124.934
120.954
120.207
116.251
112.277
110.696
77.474
77.157
76.839
56.456
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

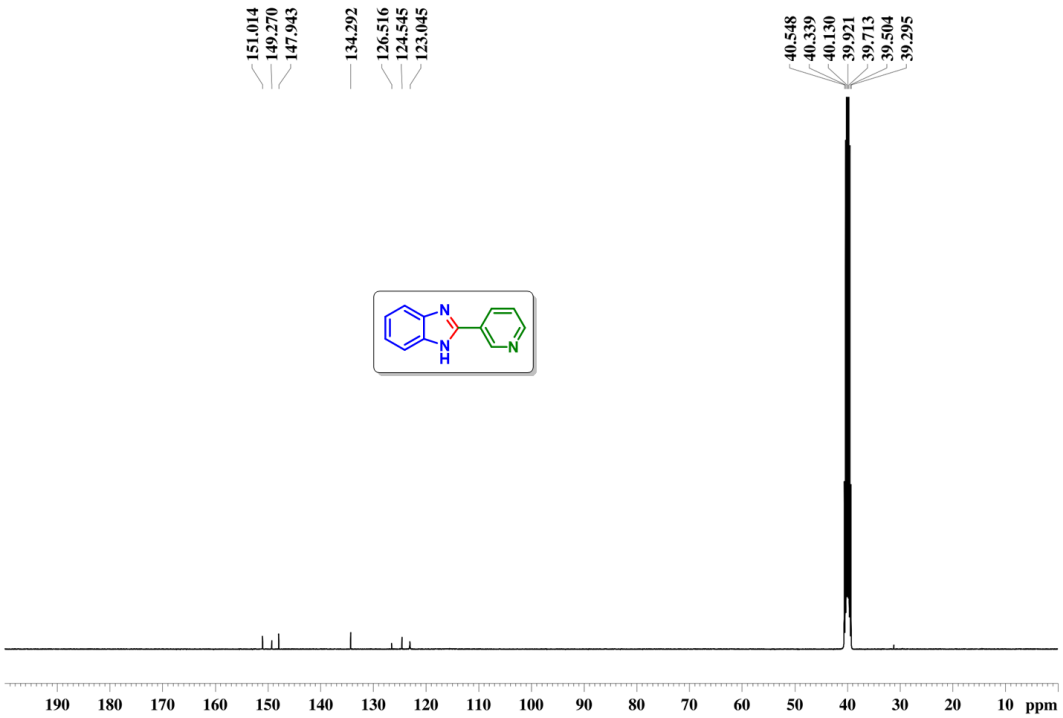

12.928
7.947
7.633
7.614
7.503
7.484
7.236
7.220
7.200
7.191
6.740
6.736
6.732
3.379
2.507
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.024
0.921
0.984
0.976
3.097
1.000

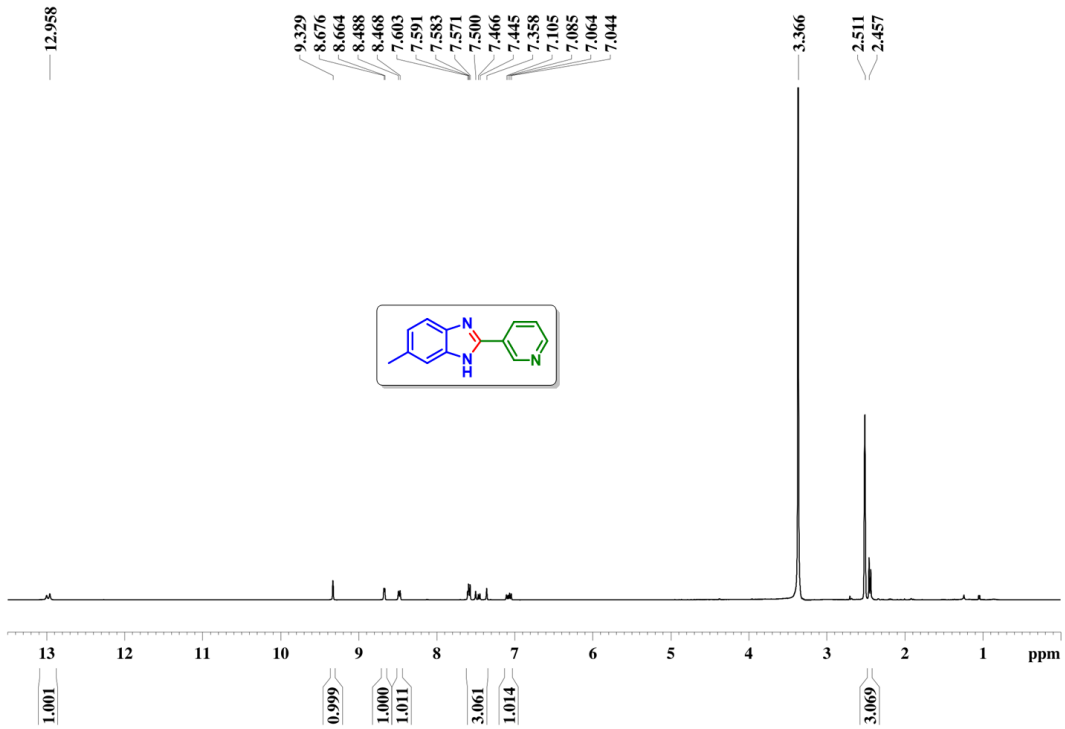

145.549
144.678
143.649
134.236
122.678
121.844
118.784
112.367
111.376
110.514
40.120
39.911
39.702
39.493
39.285
39.076
38.867
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

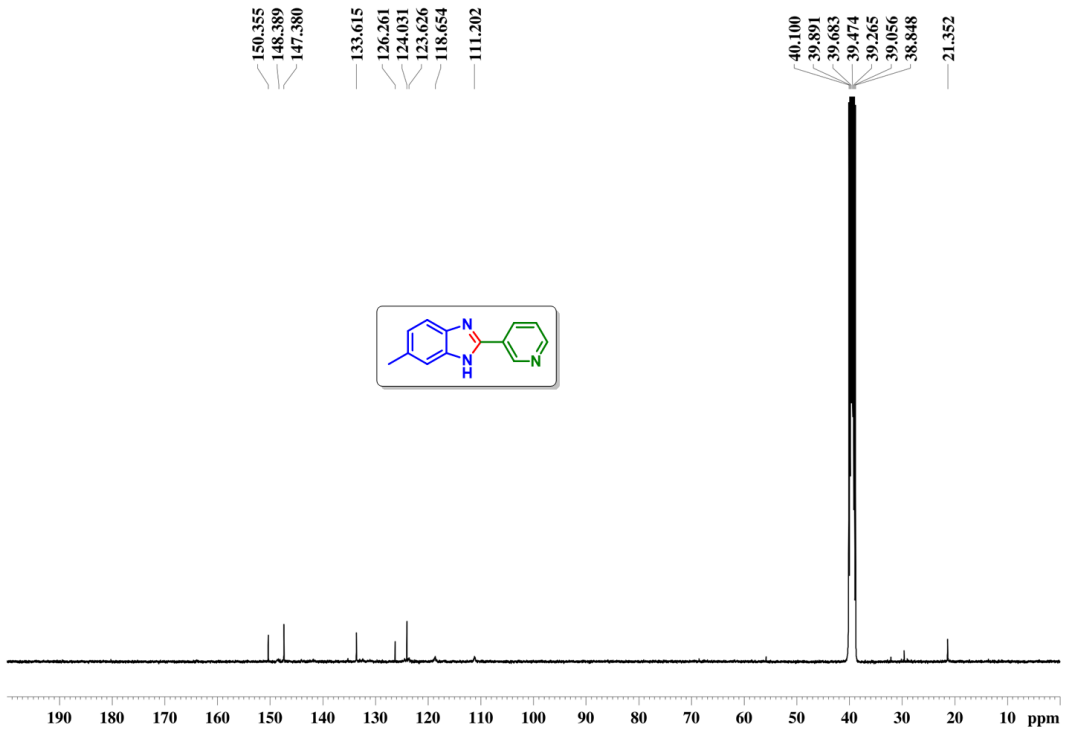

12.775
7.932
7.447
7.337
7.165
7.157
7.038
7.018
6.730
6.726
3.350
2.511
2.424
13 12 11 10 9 8 7 6 5 4 3 2 1 ppm
0.964
0.938
0.945
1.006
0.986
1.000
3.000

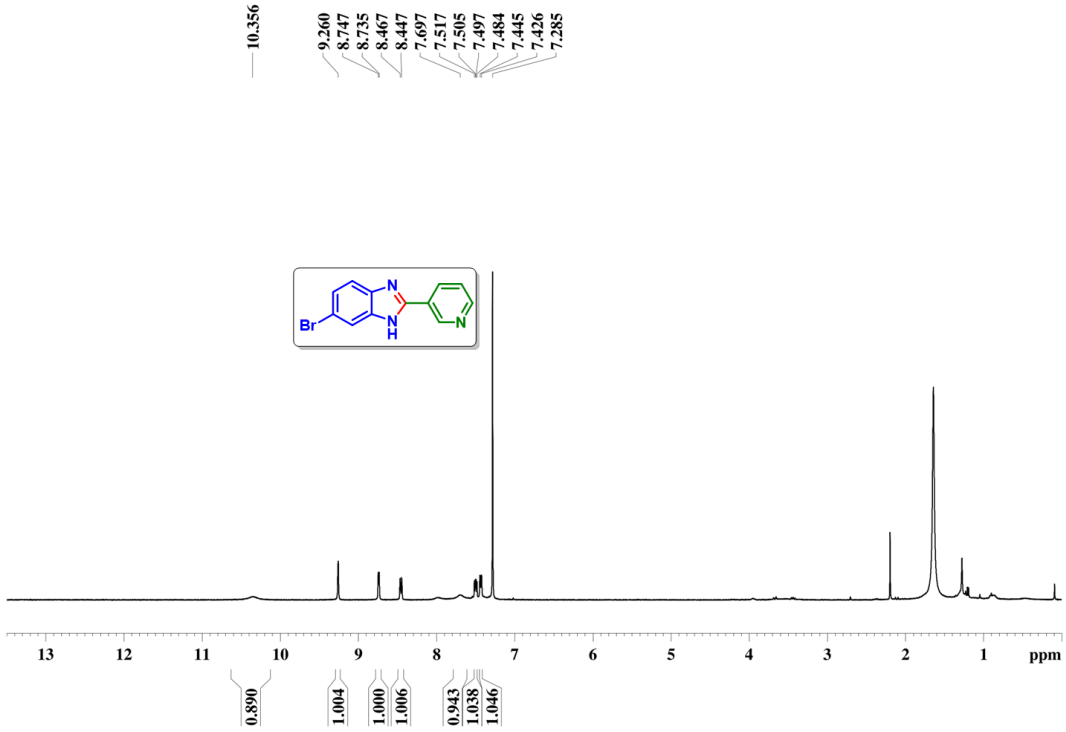

146.129
144.907
143.767
132.296
124.079
118.877
112.751
111.552
110.586
40.571
40.362
40.154
39.945
39.736
39.527
39.319
21.767
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

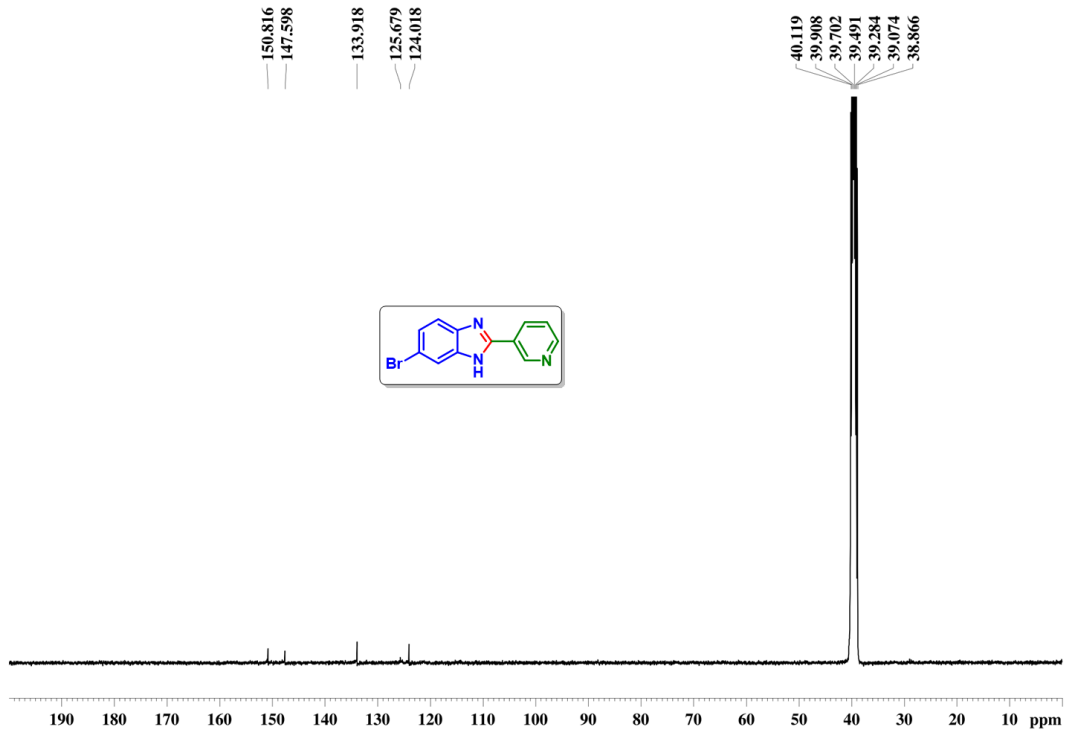

9.362
8.703
8.692
8.524
8.504
7.666
7.656
7.646
7.628
7.616
7.609
7.596
7.272
7.264
7.257
7.249
3.356
2.512
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.000
0.998
1.013
2.961
1.986

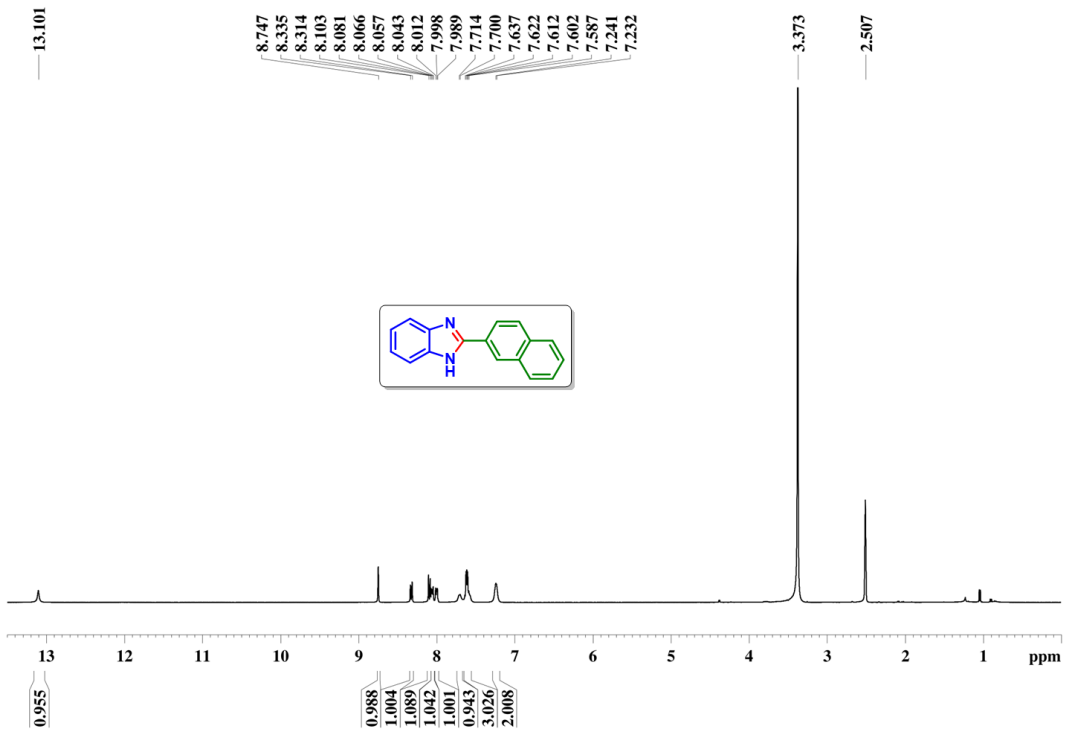

151.014
149.270
147.943
134.292
126.516
124.545
123.045
40.548
40.339
40.130
39.921
39.713
39.504
39.295
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

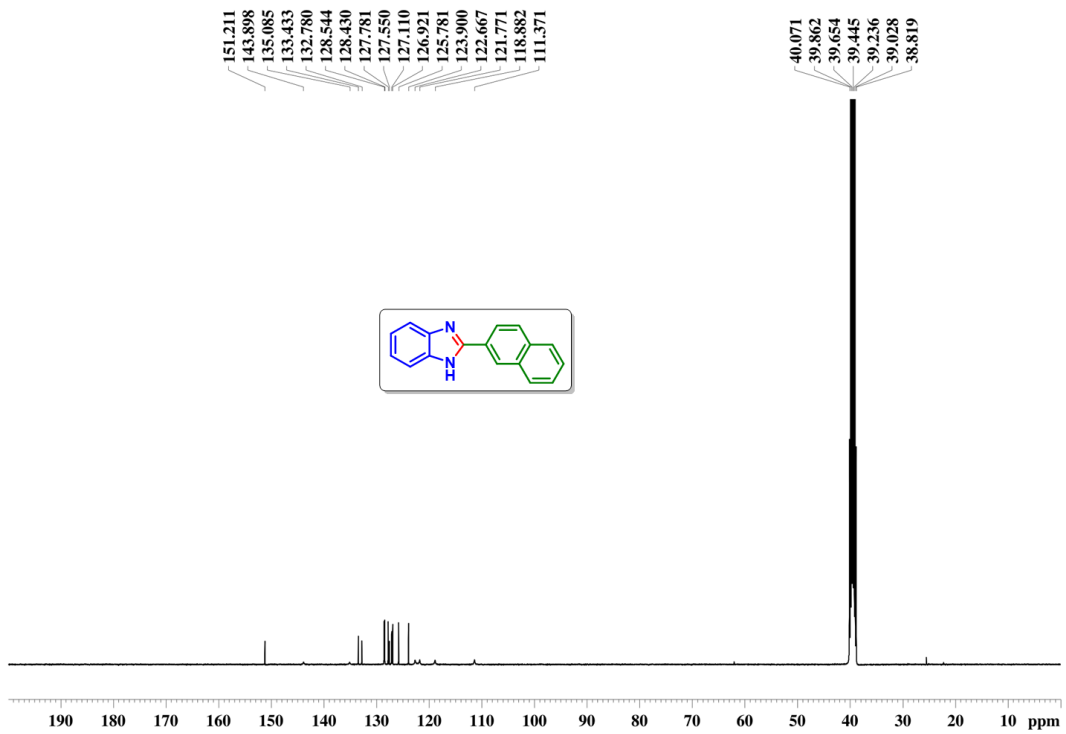

12.958
9.329
8.676
8.664
8.488
8.468
7.603
7.591
7.583
7.571
7.500
7.466
7.445
7.358
7.105
7.085
7.064
7.044
3.366
2.511
2.457
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.001
0.999
1.000
1.011
3.061
1.014
3.069

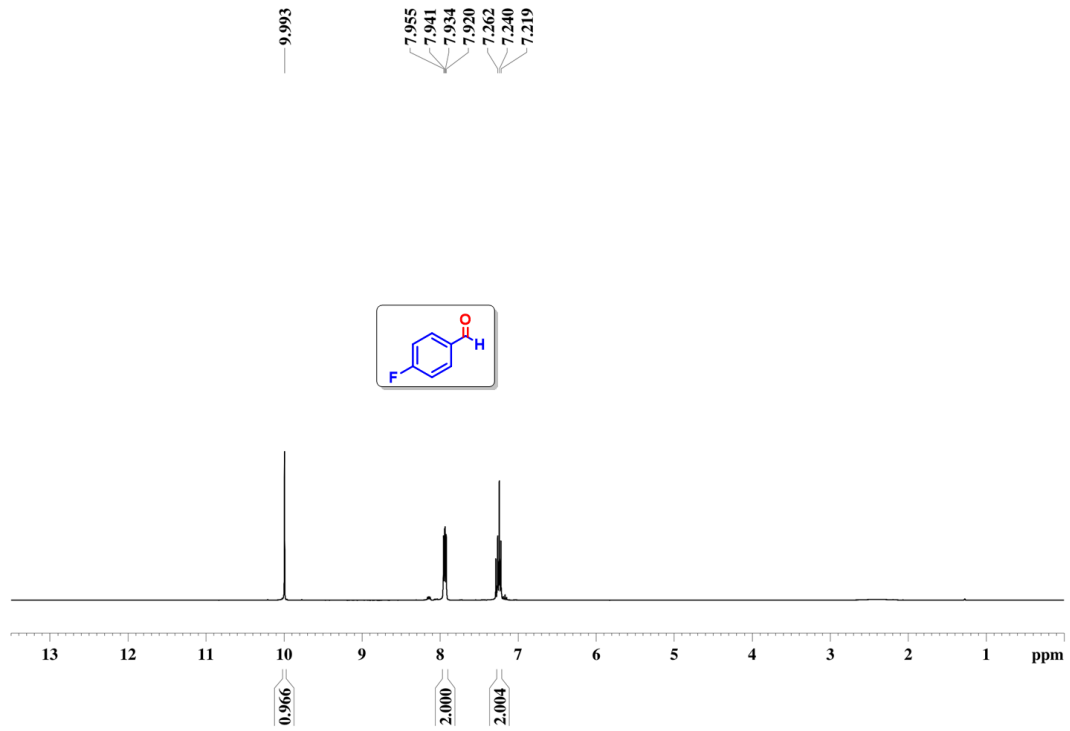

150.355
148.389
147.380
133.615
126.261
124.031
123.626
118.654
111.202
40.100
39.891
39.683
39.474
39.265
39.056
38.848
21.352
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

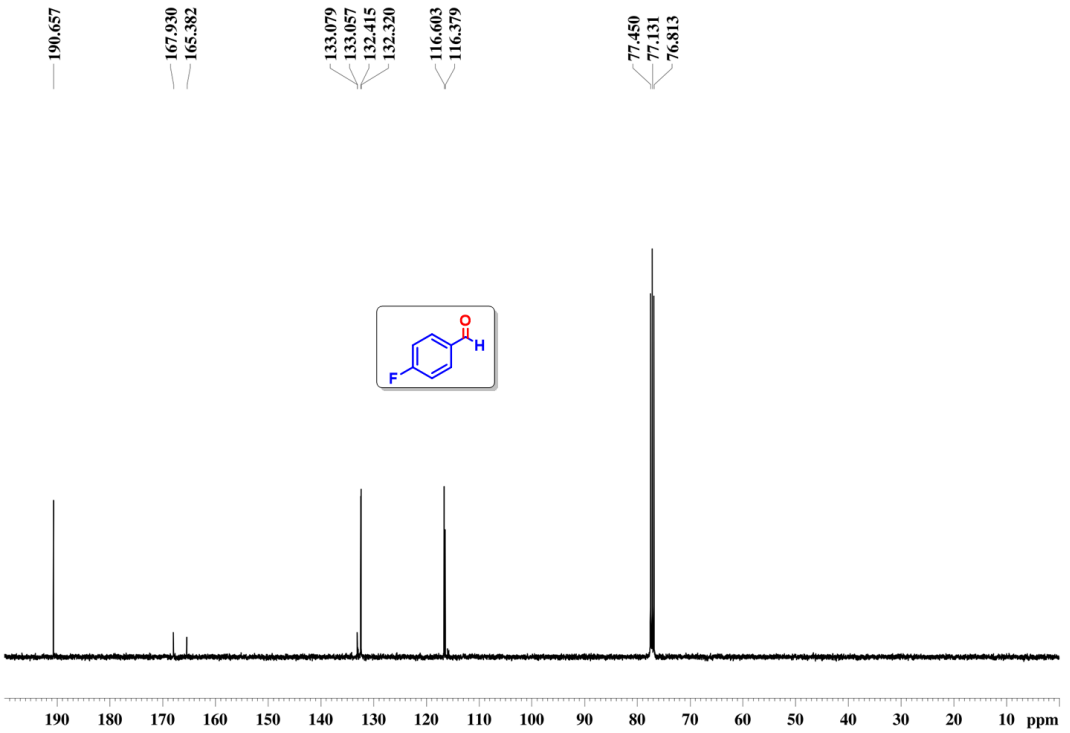

10.356
9.260
8.747
8.735
8.467
8.447
7.697
7.517
7.505
7.497
7.484
7.445
7.426
7.285
Br
N
N
H
N
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.890
1.004
1.000
1.006
0.943
1.038
1.046

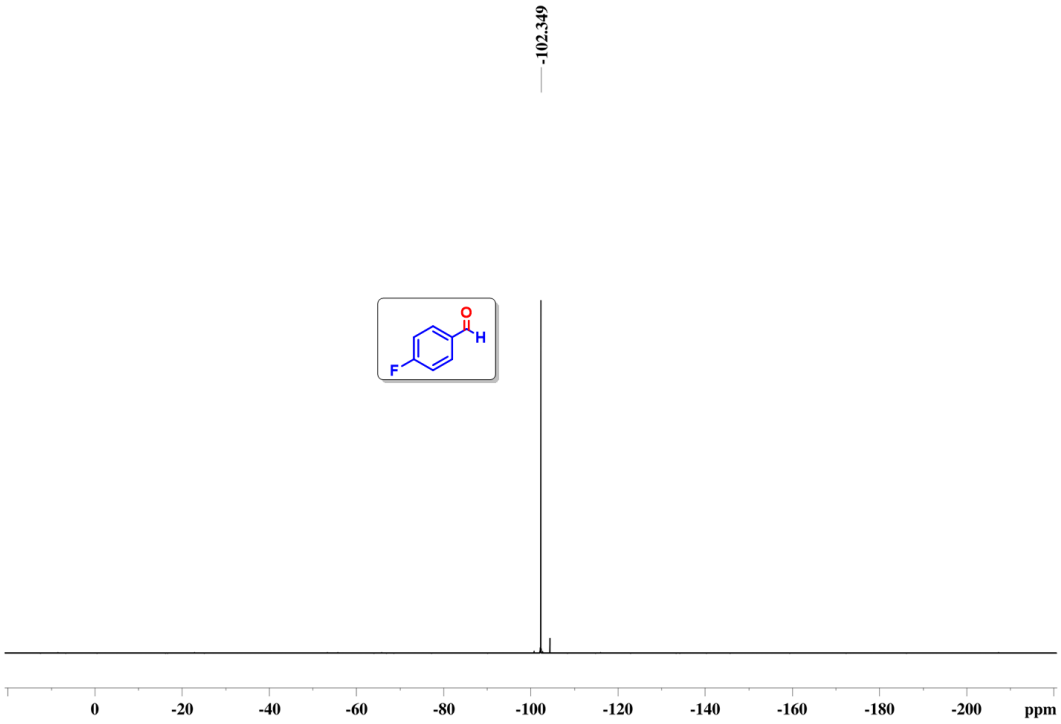

150.816
147.598
133.918
125.679
124.018
40.119
39.908
39.702
39.491
39.284
39.074
38.866
Br
N
N
H
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


13.101
8.747
8.335
8.314
8.103
8.081
8.066
8.057
8.043
8.012
7.998
7.989
7.714
7.700
7.637
7.622
7.612
7.602
7.587
7.241
7.232
3.373
2.507
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.955
0.988
1.004
1.089
1.042
1.001
0.943
3.026
2.008


151.211
143.898
135.085
133.433
132.780
128.544
128.430
127.781
127.550
127.110
126.921
125.781
123.900
122.667
121.771
118.882
111.371
40.071
39.862
39.654
39.445
39.236
39.028
38.819
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


9.993
7.955
7.941
7.934
7.920
7.262
7.240
7.219
O
H
F
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.966
2.000
2.004


190.657
167.930
165.382
133.079
133.057
132.415
132.320
116.603
116.379
77.450
77.131
76.813
O
H
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-102.349
O
H
F
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm