Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Dual palladium-photoredox catalyzed chemoselective C-H arylation of phenylureas

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General Information:

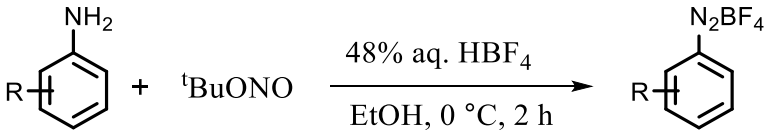
Unless and otherwise noted, all the vials (Borosil) used for carrying out the reactions were dried overnight on hot air oven at 120°C. The diazonium salts were prepared as reported in literature,[1] and the phenylurea derivatives were prepared according to the literature procedure.[2] All the chemicals were purchased from Sigma Aldrich, TCI and Spectrochem and used without any further purification. Reactions were monitored using precoated Aluminum supported silica gel 60 F_{254} TLC (thin layer chromatography) plates (Merck) and are visualised by UV light at 254 nm. The final product was purified using column chromatography (230-400 mesh silica gel purchased from Merck). ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{13}C NMR (101 MHz) spectra were recorded on the Bruker AVANCE NEO 400 MHz spectrometer. Deuterated chloroform, DMSO-d_6 were used as solvents, and Chemical shifts (δ) for 1H- and ^{13}C-NMR spectra are given in ppm relative to tetramethylsilane (TMS) [δ 7.27 for ^{1}H (chloroform-d), δ 77.0 for ^{13}C (chloroform-d); δ 2.50 for 1H (DMSO-d_6), δ 39.52 for 13C (DMSO-d_6)], ^{19}F-NMR spectra are not externally calibrated and chemical shifts is given relative to CCl_3F as received from the automatic data processing. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; dd, doublet of doublet; m, multiplet. GC-MS analysis was carried out by using Agilent (7890B GC and 5977B MSD). All fluorescent spectra were recorded by using an FP-8500 spectro-fluorometer (JASCO). High resolution mass spectra (HRMS) was obtained from Orbitrap Elite HybridIon Trap-Orbitrap (Thermofischer scientific, Newington, NH, USA) Mass Spectrometer in electrospray ionization mode (ESI^{+}). All the anhydrous solvents required were purchased from Sigma Aldrich.

2. Experimental section

2.1 Synthesis of starting materials

a) General procedure for the synthesis of aryldiazonium tetrafluoroborates

To a 50 ml round bottom flask containing a mixture of aniline (10 mmol) and 5 mL of ethanol was added HBF_4 (48% in water, 3 equiv.) at rt and the reaction mixture was stirred for 5 min. The mixture was cooled to 0 °C and then tert-butyl nitrite (1.5 eqiv.) was added dropwise via syringe under argon atmosphere. After completion of addition the reaction mixture was stirred at 0 °C for 2 hours. Diethyl ether (20 mL) was added to precipitate the arenediazonium tetrafluoroborate. The resulting solid was filtered off and washed with diethyl ether (3 × 15 mL) then dried under high vacuum to get desired product and used without further purification. Spectral datas are in agreement with the data available in literature.[1]



Hazard Statement: "Most diazonium salts are thermally unstable and sensitive to friction and shock."

b) General procedure for the synthesis of phenylurea (1a – 1i)

To a solution of aniline (0.005 mol) in 10% acetic acid (50 mL), potassium cyanate (0.05 mol dissolved in 25 mL warm water) solution was added via syringe with continuous stirring. The reaction mixture was stirred at rt for 30 min and cooled to 0 °C for 30 min. the resulting solid was filtered off and washed with distilled water. Pure product was obtained by recrystallization from boiling water and dried in oven. Spectral data are in agreement with the data available in the literature.[2a]

c) General procedure for the synthesis of Diphenylurea (4a & 4b)

To a solution of appropriate aniline (0.2 mmol) in CH_2Cl_2 (4.5 mL) was added the corresponding phenyl isocyanate slowly at room temperature with continuous stirring. The resulting mixture was stirred at room temperature and the reaction was monitored by TLC (2-3 h). After completion of the reaction, solvent was removed in vacuo. The remaining residue was purified by recrystallization in EtOH. Spectral data are in agreement with the data available in literature.[2b, 2c]

d) General procedure for the synthesis of phenylurea derivatives (1n, 1p & 1q)

Phenyl isocyanate (2 mmol) solution was added slowly to a solution of amine (4 mmol) in chloroform (8.5 mL) at 0 °C. Then the reaction mixture was stirred at room temperature for 3-4 h. After completion of the reaction, solvent was evaporated under vacuum. The remaining residue was recrystallized from n-pentane. Spectral data are in agreement with the available literature data. [2d]

2.2 General procedure for dual palladium-photoredox catalyzed chemoselective C-H arylation of free phenylureas

To an oven dried reaction vial equipped with a magnetic stir bar, phenylurea derivative (0.1mmol, 1 equiv), freshly prepared aryldiazonium salt (0.4 mmol, 4 equiv), $Pd(OAc)_2$ (0.05 equiv), $Ru(bpy)_3Cl_2.6H_2O$ (0.01 equiv), and MeOH (0.15 M with respect to phenylurea), were sequentially added. The vial was sealed and irradiated with blue LED light until the completion of starting material. The solvent was then evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: EtOAc/Hexane) to afford the desired product.

Practical applications of the dual catalytic C-H arylation protocol

2.3 General procedure for gram scale synthesis

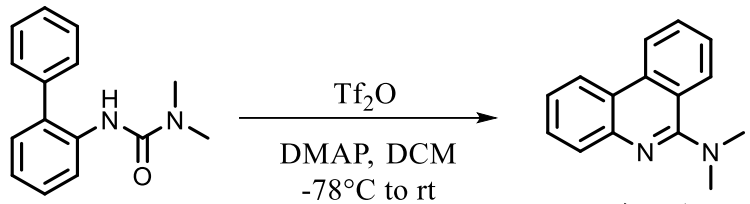
An oven dried 250 mL round bottom flask containing magnetic stir bar was charged with phenylurea **1a** (0.0073 mol, 1 g), aryldiazonium salt **2b** (0.0293 mol, 5.623 g), $Pd(OAc)_2$ (82.4 mg), $Ru(bpy)_3Cl_2.6H_2O$ (46.7 mg), and 49 mL of anhydrous methanol was added. The round-bottom flask was sealed and placed on magnetic stirrer with three 34 W Kessil LED bulbs placed about 3 cm away irradiated at room temperature with constant stirring. After 3h solvent was evaporated by using reduced pressure, water was added to the residue remaining and extracted with EtOAc (3 x 60 mL). Finally the combined organic layer was washed with brine and dried over Na_2SO_4 (anhydrous) and concentrated in vacuo. Then the residue was purified by silica gel column chromatography with EtOAc and hexane to get the desired C-H arylated phenylurea **(3ab)** in gram scale.

2.4 Reducing catalytic loading via portion wise addition

After first catalytic run between 1a and 2b in the presence of 1 mol% of $Ru(bpy)_3Cl_2.6H_2O$ and 5 mol% of $Pd(OAc)_2$ in MeOH under standard conditions, the yield of the product 3ab observed was 88% (isolated). In the same reaction vial fresh **1a** and **2b** were placed, and the reaction was continued further without the addition of catalysts. After 5 h, reaction was completed as visualized by TLC in other words completion of second cycle. The third cycle was continued by addition of fresh **1a** and **2b** (2 equiv.) followed by addition of 0.2 mL MeOH solvent to the same reaction vial without addition of catalysts. After constant stirring of reaction mixture for 9 h reaction was completed. Then purification was performed as mentioned in experimental procedure and the overall yield of the reaction was found to be 76% (isolated, after 3 cycles), after third cycle it was found out that the reaction was sluggish for the fourth cycle.

2.5 Synthesis of phenanthridine (8):

To an oven dried 4 mL reaction tube with magnetic stir bar was charged with 0.1 mmol (24 mg) of **3ma**, 0.3 mmol (36.6 mg) of DMAP followed by addition of dry dichloromethane solvent (1mL) and the tube was sealed with Teflon septum screw cap. Then reaction mixture was cooled to -78 °C and added 0.5 mmol (84 µL) trifluoromethanesulfonic anhydride via hamilton (100 µL) GC-syringe under argon atmosphere, reaction continued for overnight with constant stirring at room temperature. After completion, reaction mixture was quenched with aq. $NaHCO_3$ solution and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were washed with brine solution, dried over anhydrous Na_2SO_4 and concentrated under the reduced pressure. The crude product was purified by column chromatography on silica gel (quenched with trimethylamine) using a mixture of hexanes and EtOAc as eluent to afford the corresponding phenanthridine derivative **(8)**.

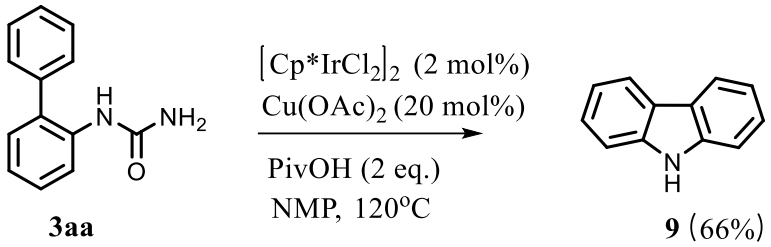


3ma **8** (80%)

2.6 Synthesis of carbazole

To a 5 mL schlenk tube with a reflux condenser were added **3aa** (0.1 mmol, 21.2 mg), $[Cp^*IrCl_2]_2$ (0.002 mmol, 1.6 mg), $Cu(OAc)_2$ (0.02 mmol, 3.6 mg), PivOH (0.2 mmol, 20.4 mg) in NMP (0.6 mL). The resulting mixture was stirred under air at 120 °C for 18h. After cooling, the reaction mixture was quenched with $NaHCO_3$ and extracted with EtOAc (30 mL) and dried over anhydrous Na_2SO_4. The resulting residue was purified by silica gel column chromatography by using a mixture of EtOAc and hexane as eluent to afford the

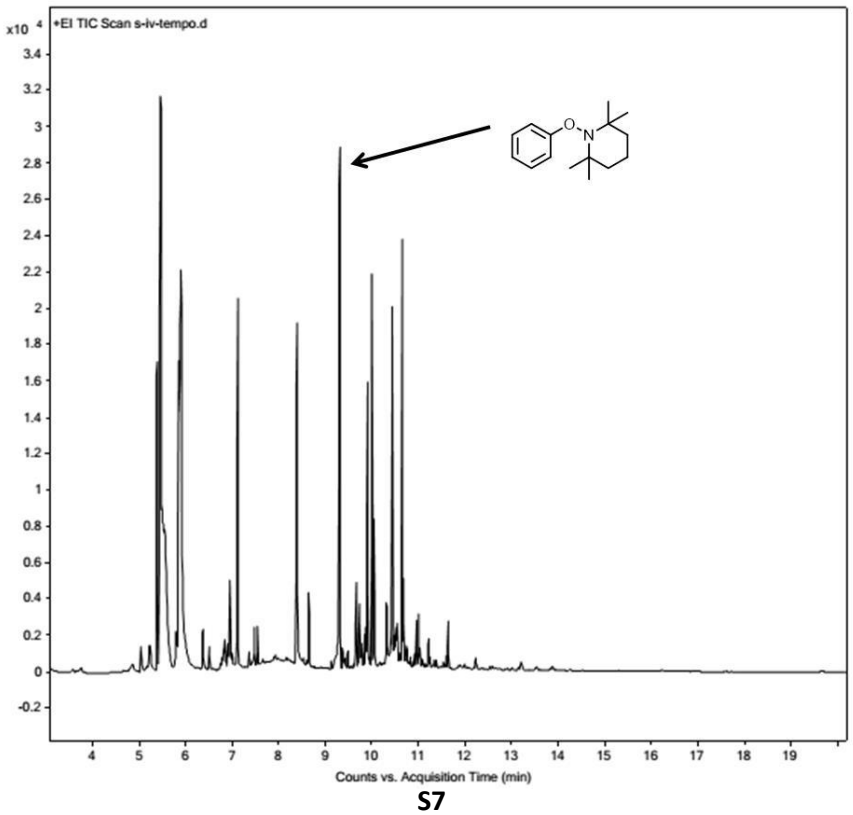
desired carbazole product **(9)**. Spectral data are in agreement with the literature data available.[3]

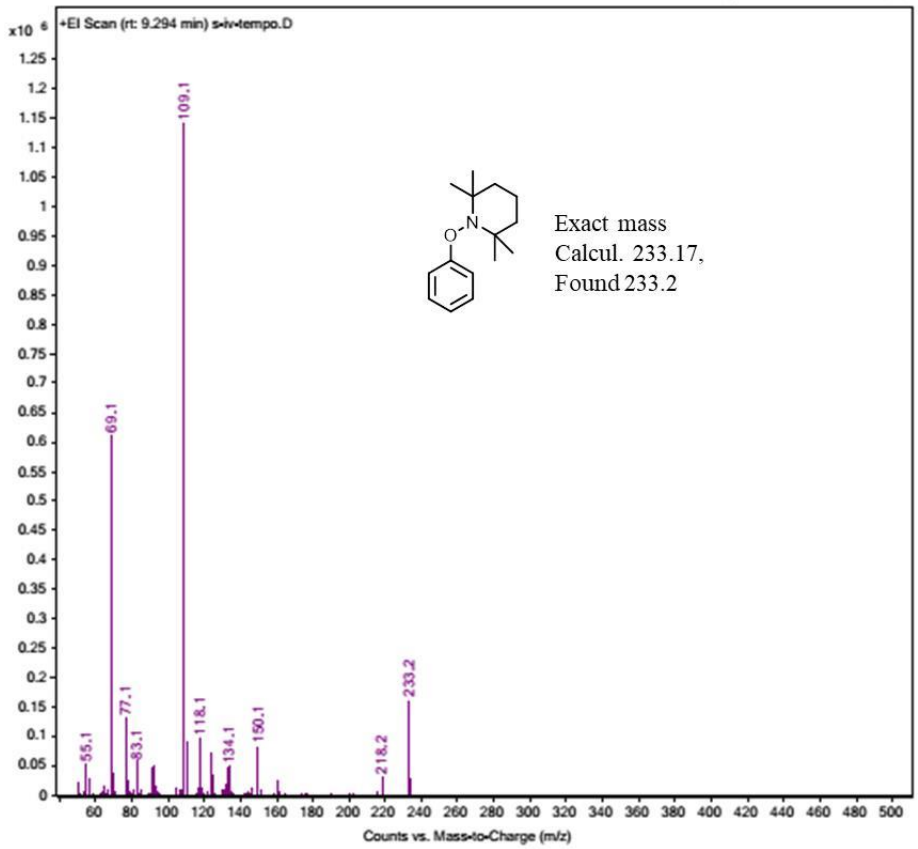


2.5 Mechanistic investigation

2.5.1 Radical trapping experiment:

In an oven dried 4 mL reaction vial with a magnetic stir bar was charged with phenylurea **1a** (0.1 mmol, 13.6 mg), aryldiazonium salt **2a** (0.4 mmol, 76.7 mg), $Ru(bpy)_3Cl_2.6H_2O$ (0.6 mg), $Pd(OAc)_2$ (1 mg), TEMPO (0.4 mmol, 62.5 mg), and MeOH (0.6 mL). Then the reaction vial was sealed and irradiated with blue LED strip with constant stirring at room temperature for 19 h, After completion, reaction mixture was analysed by GC-MS and the formation of O-arylated-TEMPO product was observed.





2.5.2 Stern-Volmer study

Fluorescence quenching experiment

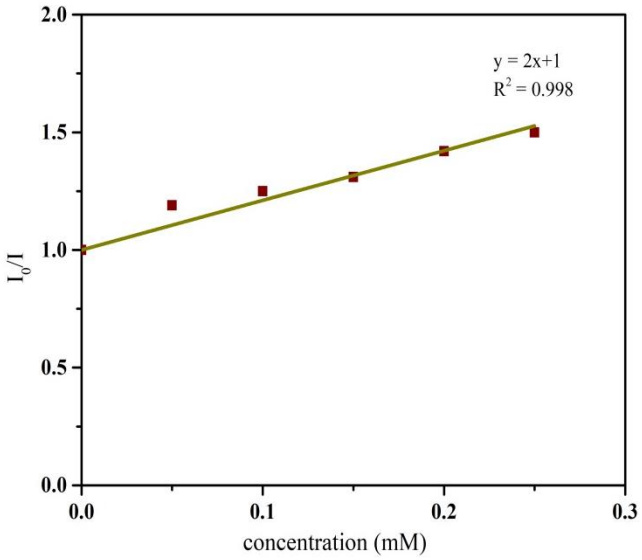
Fluorescence quenching experiments were performed using a FP-8500 fluorescence spectrometer (JASCO). In each experiment, measurement was carried out mixing a 2.5 x 10^{-4} M solution of $Ru(bpy)_3(Cl)_2$ in MeOH (2 mL) with appropriate amount of quencher in quartz cuvette. The sample solutions were previously degassed with argon. The solution was irradiated at 450 nm, and the emission intensity was overserved at 611 nm. Plots were derived according to the Stern-Volmer equation and K_{sv} calculated.

$$\text{Stern-Volmer equation } I_0/I = 1 + K_{sv}[Q]$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, [Q] is the concentration of added quencher and K_{sv} is the Stern-Volmer quenching constant.

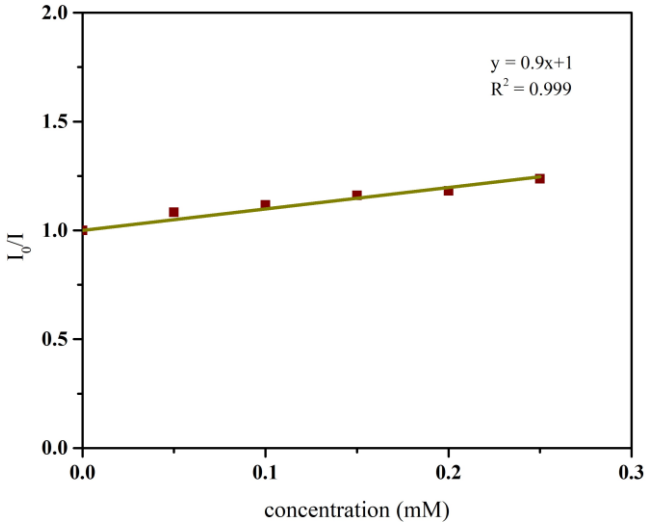
a) Stern-Volmer Quenching Studies with Diazonium salt

Increasing amounts of simple aryldiazonium tetrafluoroborate were added to the solution of $Ru(bpy)_3(Cl)_2$ in MeOH. Emission spectra were recorded after each addition. Here Stern-Volmer plot was drawn by taking average of three individual experimental (I_0/I) values with a calculated K_{sv} of 2 mM^{-1}.



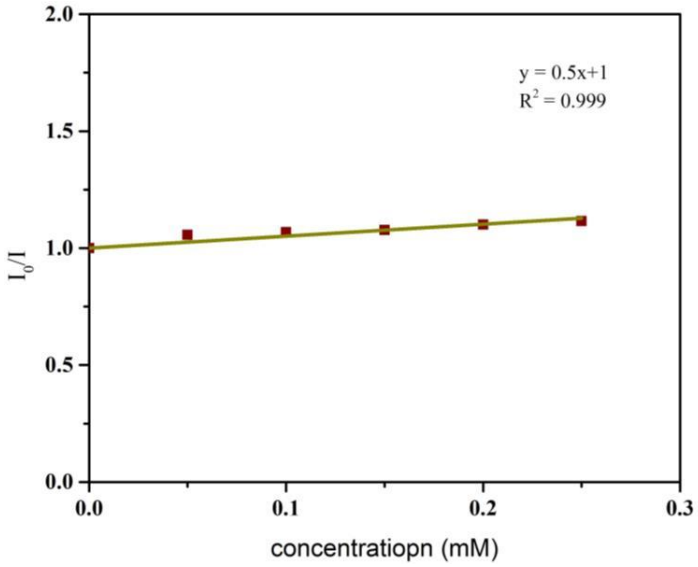
b) Stern-Volmer Quenching Studies with $Pd(OAc)_2$+phenylurea

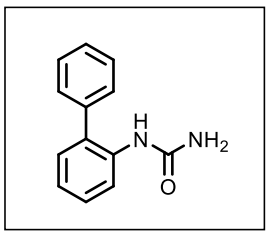
Increasing amounts of simple $Pd(OAc)_2$+phenylurea were added to the solution of $Ru(bpy)_3(Cl)_2$ in MeOH. Emission spectra were recorded after each addition. Here Stern-Volmer plot was drawn by taking average of three individual experimental (I_0/I) values with a calculated K_{sv} of 0.9 mM^{-1}.



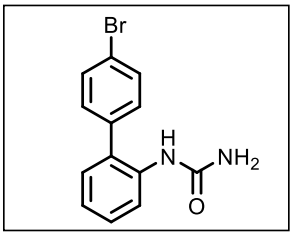
c) Stern-Volmer Quenching Studies with phenylurea

Increasing amounts of simple phenylurea were added to the solution of $Ru(bpy)_3(Cl)_2$ in MeOH. Emission spectra were recorded after each addition. Here Stern-Volmer plot was drawn by taking average of three individual experimental (I_0/I) values with a calculated K_{sv} of 0.5 mM^{-1} .

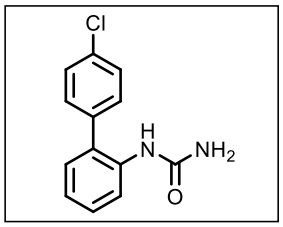




1-([1,1'-biphenyl]-2-yl)urea: The title compound **(3aa)** was prepared by adding 13.6 mg of **1a,** 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 19 h of reaction time to give the desired product as a pale yellow solid (95%, 20.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 4H), 7.22 – 7.18 (m, 2H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.17 (s, 1H), 4.54 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.22, 138.36, 135.17, 134.18, 130.57, 129.27, 128.97, 128.60, 127.83, 124.73, 123.18; **HRMS** m/z (ESI)**:** Exact mass calculated for $C_{13}H_{13}N_2O^+$ $(M+H)^+$ 213.1022, found 213.1020.

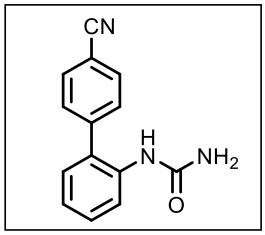


1-(4'-bromo-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ab)** was prepared by adding 13.6 mg of **1a,** 108.3 mg of **2b**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 2 h of reaction time to give the desired product as a brownish white solid (88%, 25.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.39 (td, *J* = 8.0, 7.6, 1.9 Hz, 1H), 7.26 – 7.19 (m, 4H), 6.11 (s, 1H), 4.58 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.02, 137.22, 134.98, 133.38, 132.14, 130.91, 130.39, 129.01, 125.14, 123.76, 122.18; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}N_2OBr^+$ $(M+H)^+$ 291.0128; 293.0107, found: 291.0121; 293.0100.

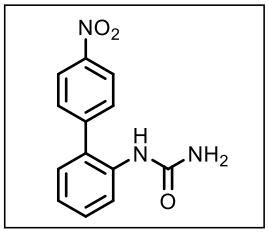


1-(4'-chloro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ac)** was prepared by adding 13.6 mg of **1a,** 90.5 mg of **2c**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 2 h of reaction time to give the desired product as a white solid (85%, 20.9 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.38 (td, *J* = 8.1, 7.6, 1.9 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.19 (m, 2H), 6.17 (s, 1H), 4.62

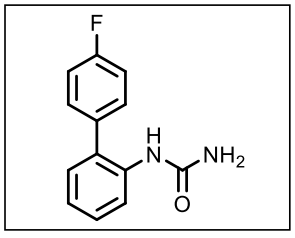
(s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.14, 136.77, 135.04, 133.98, 133.41, 130.60, 130.46, 129.15, 128.96, 125.12, 123.80; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}ClN_2O^+$ $(M+H)^+$ 247.0633, found 247.0627.



1-(4'-cyano-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ad)** was prepared by adding 13.6 mg of **1a**, 86.8 mg of **2d**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 2 h of reaction time to give the desired product as a white solid (61%, 14.5 mg). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 1H), 7.59 – 7.55 (m, 3H), 7.37 – 7.31 (m, 1H), 7.21 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.13 (td, *J* = 7.5, 1.1 Hz, 1H), 5.94 (s, 2H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 156.57, 144.51, 137.02, 133.02, 131.81, 130.60, 130.41, 129.09, 123.87, 123.64, 119.37, 110.40; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{12}N_3O^+$ $(M+H)^+$ 238.0975, found 238.0981.

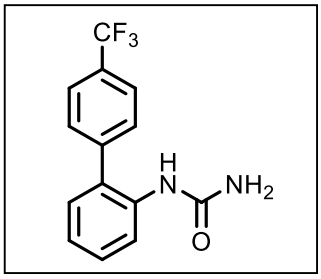


1-(4'-nitro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ae)** was prepared by adding 13.6 mg of **1a**, 94.7 mg of **2e**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 7 h of reaction time to give the desired product as a yellow solid (78%, 20.0 mg). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.32 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.61 (s, 1H), 7.39 – 7.33 (m, 1H), 7.25 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.93 (s, 2H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 156.50, 147.01, 146.70, 137.14, 131.36, 130.96, 130.41, 129.34, 124.23, 123.80, 123.63; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}N_3O_3^+$ $(M+H)^+$ 258.0873, found 258.0886.

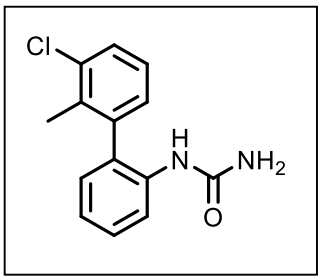


1-(4'-fluoro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3af)** was prepared by adding 13.6 mg of **1a**, 84 mg of **2f**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography

after 6.5 h of reaction time to give the desired product as a white solid (70%, 16.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.6 Hz, 1H), 7.38- 7.32 (m, 3H), 7.26 – 7.18 (m, 2H), 7.16 – 7.10 (m, 2H), 6.27 (s, 1H), 4.71 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.4 (d, *J* = 252.5 Hz), 156.43, 135.14, 134.31 (d, *J* = 3.0 Hz), 133.67, 131.00, 130.77 (d, *J* = 30.3 Hz), 128.75, 125.06, 123.81, 115.88 (d, *J* = 22.2 Hz); **^{19}F NMR (376 MHz, $CDCl_3$)** δ -114.14; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}FN_2O^+$ $(M+H)^+$ 231.0928, found 231.0924.

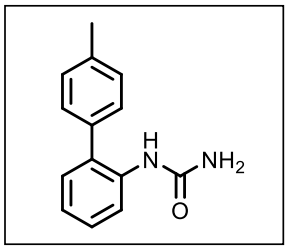


1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ag)** was prepared by adding 13.6 mg of **1a**, 104 mg of **2g**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 1 h of reaction time to give the desired product as a white solid (72%, 20.1 mg). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.79 (d, *J* = 7.7 Hz, 3H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.50 (s, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 5.91 (s, 2H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 156.65, 143.70, 137.04, 131.81, 130.56, 130.41, 128.86, 128.02, 126.22, 125.98 (q, *J* = 4.0 Hz), 123.77, 123.54; **^{19}F NMR: (376 MHz, DMSO-d_6)** δ -60.88. **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{12}N_2F_3O^+$ $(M+H)^+$ 281.0896, found 281.0903.

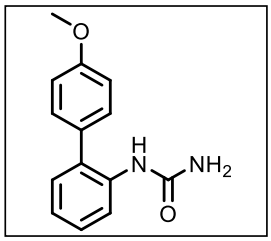


1-(3'-chloro-2'-methyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ah)** was prepared by adding 13.6 mg of **1a**, 92.4 mg of **2h**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 2 h of reaction time to give the desired product as a white solid (65%, 16.9 mg). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.49 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.36 – 7.25 (m, 2H), 7.10 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.06 (s, 1H), 7.04 – 7.00 (m, 2H), 6.03 (s, 2H), 2.04 (s, 3H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 156.44, 140.71, 137.68, 134.76, 134.64, 130.94, 130.30, 129.63,

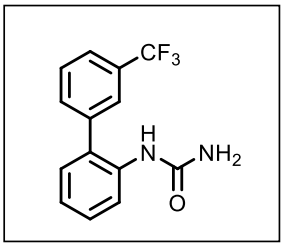
129.00, 128.41, 127.88, 122.42, 121.75, 17.49; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{14}N_2ClO^+$ $(M+H)^+$ 261.0789, found 261.0797.



1-(4'-methyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ai)** was prepared by adding 13.6 mg of **1a**, 82.4 mg of **2i**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 12 h of reaction time to give the desired product as a white solid (84%, 19.0 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.85 (d, *J* = 8.2 Hz, 1H), 7.35 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.21 (m, 3H), 7.13 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 5.99 (s, 2H), 2.36 (s, 3H); **^{13}C NMR: (101 MHz, DMSO-*d*$_6$)** δ 156.70, 137.03, 136.95, 136.25, 132.64, 130.52, 129.81, 129.44, 127.85, 123.09, 123.04, 21.24; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.1179, found 227.1185**.**

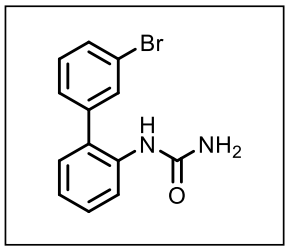


1-(4'-methoxy-[1,1'-biphenyl]-2-yl)urea: The title compound **(3aj)** was prepared by adding 13.6 mg of **1a**, 88.8 mg of **2j**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a white solid (50%, 12.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.36 – 7.32 (m, 1H), 7.31 (d, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 2.2 Hz, 1H), 7.26 (d, *J* = 5.1 Hz, 1H), 7.19 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.25 (s, 1H), 4.63 (s, 2H), 3.84 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.28, 156.24, 135.28, 133.90, 130.61, 130.47, 130.41, 128.28, 124.73, 123.11, 114.41, 55.36; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{15}N_2O_2^+$ $(M+H)^+$ 243.1128, found 243.1135.

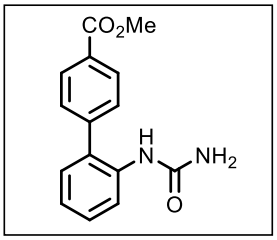


1-(3'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ak)** was prepared by adding 13.6 mg of **1a**, 104 mg of **2k**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure

described above and purified by using silica gel column chromatography after 1 h of reaction time to give the desired product as a white solid (63%, 17.6 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.53 (m, 4H), 7.41 (td, *J* = 8.1, 7.6, 2.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 6.21 (s, 1H), 4.65 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.29, 139.31, 135.01, 133.51, 132.62, 131.20, 130.55, 129.32, 129.30, 126.08 (q, J = 4.0 Hz), 125.41, 124.56 (q, *J* = 4.0 Hz) 124.40, 122.59; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -62.61; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{12}N_2F_3O^+$ $(M+H)^+$ 281.0896, found 281.0877.

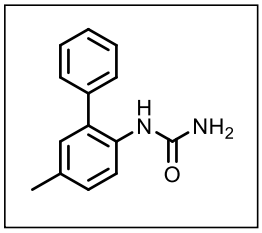


1-(3'-bromo-[1,1'-biphenyl]-2-yl)urea: The title compound **(3al)** was prepared by adding 13.6 mg of **1a**, 108.3 mg of **2l**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 4 h of reaction time to give the desired product as a brownish white solid (50%, 14.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.50 (m, 2H), 7.39 (td, *J* = 7.6, 1.9 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.26 – 7.17 (m, 2H), 6.17 (s, 1H), 4.61 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.04, 140.49, 135.07, 132.98, 132.26, 130.93, 130.45, 130.41, 129.15, 127.88, 124.99, 123.65, 122.99; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}N_2BrO^+$ $(M+H)^+$ 291.0128; 293.0107, found 291.0134; 293.0114.

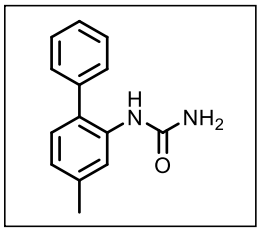


methyl 2'-ureido-[1,1'-biphenyl]-4-carboxylate: The title compound **(3am)** was prepared by adding 13.6 mg of **1a**, 100 mg of **2m**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 30 min. of reaction time to give the desired product as a brownish white solid (61%, 16.5 mg). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 8.05 – 7.99 (m, 2H), 7.82 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.47 (s, 1H), 7.32 – 7.27 (m, 1H), 7.19 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.08 (td, *J* = 7.4, 1.3 Hz, 1H), 5.93 (s, 2H), 3.86 (s, 3H).**^{13}C NMR (101 MHz, DMSO-d_6)** δ 166.63, 156.60, 144.36, 137.04, 132.02, 130.41, 130.00,

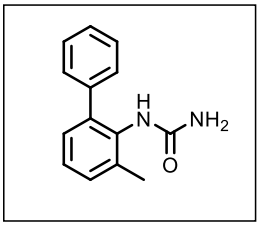
129.05, 128.83, 128.79, 123.57, 123.42, 118.18, 52.68; **HRMS** m/z (ESI): Exact mass calculated for $C_{15}H_{15}N_2O_3^+$ $(M+H)^+$ 271.1077, found 271.1090.



1-(5-methyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ba)** was prepared by adding 15 mg of **1b**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (83%, 18.8 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 7.38 (d, *J* = 1.5 Hz, 1H), 7.36 (t, *J* = 1.3 Hz, 1H), 7.34 (s, 1H), 7.10 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.01 (d, *J* = 2.1 Hz, 1H), 5.91 (s, 2H), 2.30 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 156.93, 139.43, 134.30, 133.30, 132.33, 131.02, 129.51, 129.08, 128.58, 127.66, 123.98, 20.78; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.1179, found 227.1189.

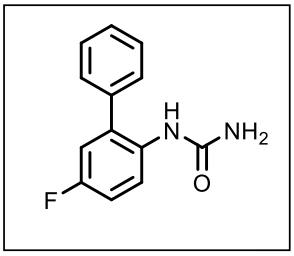


1-(4-methyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ca)** was prepared by adding 15 mg of **1c**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (70%, 15.8 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.66 (s, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.44 (s, 1H), 7.39 – 7.36 (m, 1H), 7.35 – 7.32 (m, 3H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.91 – 6.87 (m, 1H), 5.96 (s, 2H), 2.30 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 156.74, 139.27, 137.26, 136.71, 130.44, 130.18, 129.56, 129.14, 127.56, 124.00, 123.89, 21.46; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.1179, found 227.1178.

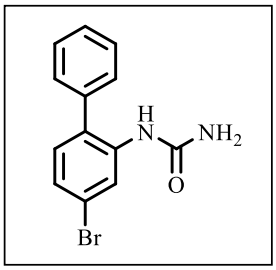


1-(3-methyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3da)** was prepared by adding 15 mg of **1d**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described

above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (76%, 17.2 mg). **^{1}H NMR: (400 MHz, DMSO-*d*$_6$)** δ 7.44- 7.41 (m, 1H), 7.40 (s, 1H), 7.38 – 7.31 (m, 4H), 7.25 – 7.18 (m, 2H), 7.14 – 7.10 (m, 1H), 5.61 (s, 2H), 2.23 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 157.66, 140.54, 140.26, 137.86, 135.06, 129.91, 129.30, 128.54, 128.14, 127.31, 126.60, 18.79; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{15}N_2O^+$ $(M+H)^+$ 227.1179, found 227.1181.

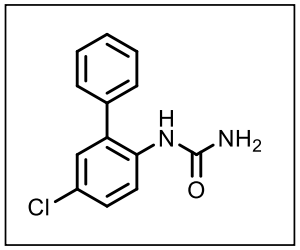


1-(5-fluoro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ea)** was prepared by adding 15.4 mg of **1e**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (72%, 16.6 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.76 (dd, *J* = 9.0, 5.6 Hz, 1H), 7.52 – 7.46 (m, 2H), 7.44 – 7.36 (m, 4H), 7.15 – 7.09 (m, 1H), 7.02 (dd, *J* = 9.5, 3.1 Hz, 1H), 5.94 (s, 2H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 158.26 (d, *J* = 240.3 Hz), 138.20, 135.36 (d, *J* = 7.0 Hz), 133.2 (d, J = 3.0 Hz), 129.45, 129.22, 128.20, 126.09 (d, *J* = 8.0 Hz), 116.69 (d, *J* = 22.2 Hz), 114.58 (d, *J* = 22.2 Hz); **^{19}F NMR: (376 MHz, DMSO-*d*$_6$)** δ -120.35; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}N_2FO^+$ $(M+H)^+$ 231.0928, found 231.0927.

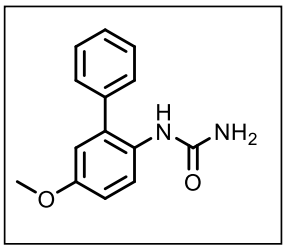


1-(4-bromo-[1,1'-biphenyl]-2-yl)urea: The title compound **(3fa)** was prepared by adding 21.5 mg of **1f**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (73%, 21.2 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.48 (s, 1H), 7.45 – 7.39 (m, 1H), 7.37 – 7.33 (m, 2H), 7.22 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 1H), 6.19 (s, 2H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 156.35, 138.76, 137.97, 132.46, 131.01, 129.52, 129.43, 128.24, 125.26, 124.20,

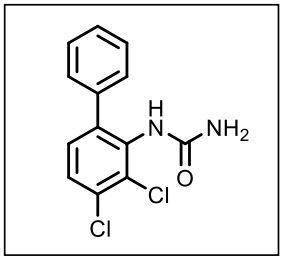
120.96; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}N_2BrO^+$ $(M+H)^+$ 291.0128; 293.0107, found 291.0137; 293.0046.



1-(5-chloro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ga)** was prepared by adding 17 mg of **1g**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (71%, 17.5 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.40 – 7.36 (m, 2H), 7.32 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.18 (d, *J* = 2.5 Hz, 1H), 6.08 (s, 2H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 156.50, 137.79, 136.17, 134.30, 129.91, 129.52, 129.37, 128.35, 127.83, 126.65, 124.51; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{12}N_2ClO^+$ $(M+H)^+$ 247.0633, found 247.0629.

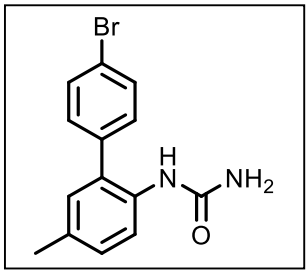


1-(5-methoxy-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ha)** was prepared by adding 16.6 mg of **1h**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (70%, 17.0 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.53 (d, *J* = 8.9 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.41 – 7.35 (m, 3H), 7.29 (s, 1H), 6.88 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.75 (d, *J* = 3.0 Hz, 1H), 5.77 (s, 2H), 3.75 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 156.85, 155.45, 138.94, 135.39, 129.25, 128.98, 128.51, 127.28, 126.45, 114.79, 113.27, 55.24; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{15}N_2O_2^+$ $(M+H)^+$ 243.1128, found 243.1121.

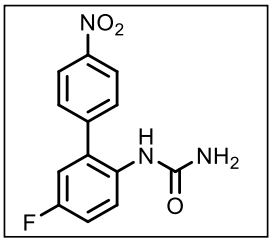


1-(3,4-dichloro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ia)** was prepared by adding 18.8 mg of **1i**, 76.7 mg of **2a**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described

above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a white solid (69%, 19.3 mg). **^{1}H NMR: (400 MHz, DMSO-d_6)** δ 7.84 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.40 – 7.34 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 1H), 5.81 (s, 2H**); ^{13}C NMR: (101 MHz, DMSO-d_6)** δ 156.87, 141.31, 138.84, 136.12, 132.99, 131.21, 129.74, 129.07, 128.71, 128.42, 128.06; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{11}Cl_2N_2O^+$ $(M+H)^+$ 281.0243; 283.0213, found 281.0242; 283.0212.

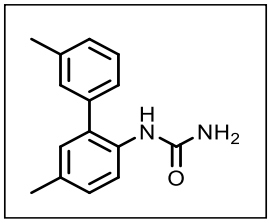


1-(4'-bromo-5-methyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ja)** was prepared by adding 15 mg of **1b**, 108.3 mg of **2b**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 6 h of reaction time to give the desired product as a brownish white solid (72%, 22.0 mg). **^{1}H NMR: (400 MHz, DMSO-d_6)** δ 7.68 – 7.62 (t, 3H), 7.37 (s, 1H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.09 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.98 (d, *J* = 1.9 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR: (101 MHz, DMSO-d_6)** δ 156.81, 138.70, 134.37, 132.46, 132.13, 131.96, 131.72, 130.76, 128.98, 123.94, 121.10, 20.75; **HRMS** m/z (ESI): Exact mass calculated for $C_{14}H_{14}N_2BrO^+$ $(M+H)^+$ 305.0284; 307.0264, found 305.0296; 307.0276.

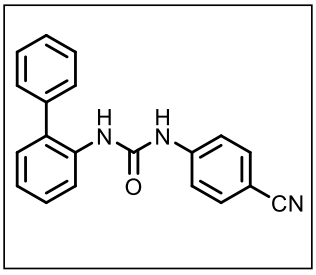


1-(5-fluoro-4'-nitro-[1,1'-biphenyl]-2-yl)urea: The title compound **(3ka)** was prepared by adding 15.4 mg of **1e**, 94.7 mg of **2e**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 8 h of reaction time to give the desired product as a brownish white solid (78%, 21.4 mg). **^{1}H NMR (400 MHz, DMSO-d_6)** δ 7.76 (dd, *J* = 9.0, 5.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.47 (s, 1H), 7.36 – 7.31 (m, 2H), 7.14 (td, *J* = 8.6, 3.1 Hz, 1H), 7.05 (dd, *J* = 9.4, 3.0 Hz, 1H), 5.92 (s, 2H); **^{13}C NMR (101 MHz, DMSO-d_6)** δ 158.42 (d, J = 240.3 Hz), 156.79, 137.43, 134.18 (d J = 8.0 Hz), 133.32, 132.09, 131.69, 126.04 (d, J = 8.0 Hz), 121.71, 116.55 (d, J = 23.2 Hz),

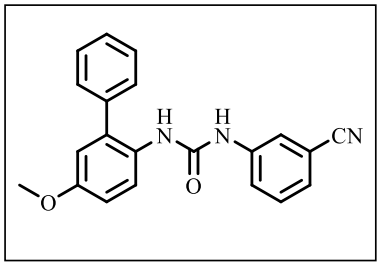
114.98 (d, J = 21.2 Hz); **^{19}F NMR (376 MHz, DMSO-*d*$_6$)** δ -120.21; **HRMS** m/z (ESI): Exact mass calculated for $C_{13}H_{11}N_3FO_3^+$ $(M+H)^+$ 276. 0779, found 276.0777.



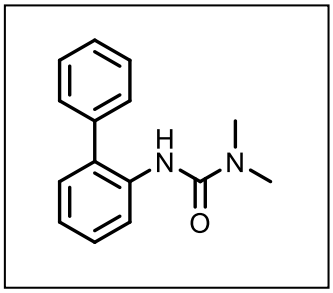
1-(3',5-dimethyl-[1,1'-biphenyl]-2-yl)urea: The title compound **(3la)** was prepared by adding 15 mg of **1b**, 82.4 mg of **2n**, 1 mg of $Pd(OAc)_2$, 0.6 mg of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (78%, 21.4 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27 (s, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.16 (s, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.08 – 7.04 (m, 1H), 6.96 (d, *J* = 1.9 Hz, 1H), 5.90 (s, 2H), 2.36 (s, 3H), 2.27 (s, 3H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 156.88, 139.31, 138.21, 134.36, 133.12, 132.07, 130.94, 130.18, 128.95, 128.47, 128.31, 126.59, 123.61, 21.60, 20.77; **HRMS** m/z (ESI): Exact mass calculated for $C_{15}H_{17}N_2O^+$ $(M+H)^+$ 241.1335, found 241.1345.



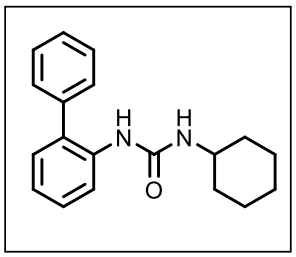
1-([1,1'-biphenyl]-2-yl)-3-(4-cyanophenyl)urea: The title compound **(5aa)** was prepared by adding 23.7 mg of **4a**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 1.6 mg (2.5 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above but used higher catalyst loading that is 10 mol% of $Pd(OAc)_2$ and 2.5 mol% photocatalyst (instead 5 & 1 mol%) and purified by using silica gel column chromatography after 36 h of reaction time to give the desired product as a brownish white solid (55%, 17.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.48 – 7.36 (m, 8H), 7.30 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.26 – 7.21 (m, 1H), 6.87 (s, 1H), 6.52 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 151.94, 142.64, 138.20, 134.32, 133.89, 133.25, 130.66, 129.35, 129.11, 128.78, 128.02, 125.04, 122.77, 118.99, 105.92; **HRMS** m/z (ESI): Exact mass calculated for $C_{20}H_{16}N_3O^+$ $(M+H)^+$ 314.1288, found 314.1284.



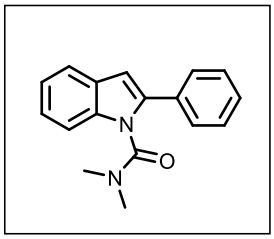
1-(3-cyanophenyl)-3-(5-methoxy-[1,1'-biphenyl]-2-yl)urea: The title compound **(5ba)** was prepared by adding 26.7 mg of **4b**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 1.6 mg (2.5 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above but used higher catalyst loading that is 10 mol% of $Pd(OAc)_2$ and 2.5 mol% photocatalyst (intead 5 & 1 mol%) and purified by using silica gel column chromatography after 36 h of reaction time to give the desired product as a brownish white solid (64%, 22.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.57 (s, 1H), 7.50 – 7.31 (m, 7H), 7.29 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.95 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.89 (d, *J* = 3.0 Hz, 1H), 6.68 (s, 1H), 6.22 (s, 1H), 3.84 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.63, 153.14, 139.30, 138.25, 129.77, 129.04, 128.93, 128.72, 128.06, 126.83, 126.67, 126.61, 123.71, 122.57, 118.53, 116.06, 114.06, 112.88, 55.63; **HRMS** m/z (ESI): Exact mass calculated for $C_{21}H_{18}N_3O_2^+$ $(M+H)^+$ 344.1394, found 344.1406.



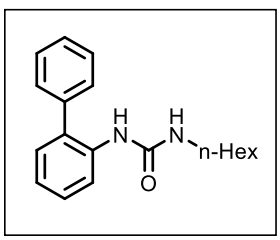
3-([1,1'-biphenyl]-2-yl)-1,1-dimethylurea: The title compound **(3ma)** was prepared by adding 16.4 mg of **1m**, 76.7 mg of **2a**, 1 mg (5 mol%) of $Pd(OAc)_2$, 0.6 mg (1 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 6 h of reaction time to give the desired product as a brownish white solid (80%, 19.2 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.50- 7.46 (m, 2H), 7.42- 7.32 (m, 4H), 7.20 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.08 (tt, *J* = 7.5, 1.0 Hz, 1H), 6.50 (s, 1H), 2.80 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.48, 138.69, 136.32, 131.33, 129.59, 129.30, 129.09, 128.49, 127.86, 122.54, 120.33, 36.17; **HRMS** m/z (ESI): Exact mass calculated for $C_{15}H_{17}N_2O^+$ $(M+H)^+$ 241.1335, Found 241.1329.



1-([1,1'-biphenyl]-2-yl)-3-cyclohexylurea: The title compound **(3na)** was prepared by adding 21.8 mg of **1n**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 0.6 mg (1 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (66%, 19.4 mg).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.40 – 7.33 (m, 4H), 7.26 – 7.24 (m, 1H), 7.15 (td, *J* = 8.0, 1.5 Hz, 1H), 6.06 (s, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 3.44 (d, *J* = 10.9 Hz, 1H), 1.85 (dd, *J* = 12.9, 4.1 Hz, 2H), 1.68 - 1.63 (m, 2H), 1.59 – 1.53 (m, 1H), 1.34 – 1.22 (m, 2H), 1.14 – 0.97 (m, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.72, 138.54, 135.64, 133.36, 130.43, 129.25, 128.99, 128.56, 127.76, 123.89, 122.38, 49.37, 33.64, 25.50, 24.90; **HRMS** m/z (ESI): Exact mass calculated for $C_{19}H_{23}N_2O^+$ $(M+H)^+$ 295.1805, found 295.1796.

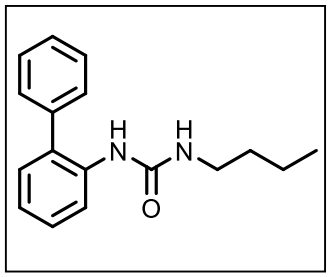


N,N-dimethyl-2-phenyl-1H-indole-1-carboxamide: The title compound **(3oa)** was prepared by adding 18.8 mg of **1o**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 0.6 mg (1 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 12 h of reaction time to give the desired product as a brownish white solid (70%, 18.5 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.52 – 7.48 (m, 1H), 7.45 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 7.30 – 7.24 (m, 1H), 7.21 -7.17 (m, 1H), 6.72 (d, *J* = 0.8 Hz, 1H), 3.04 (s, 3H), 2.47 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.22, 139.34, 136.85, 132.30, 128.71, 128.56, 128.12, 127.26, 123.41, 121.62, 120.72, 111.57, 104.42, 37.83, 36.57; **HRMS** m/z (ESI): Exact mass calculated for $C_{17}H_{17}N_2O^+$ $(M+H)^+$ 265.1335, found 265.1336.

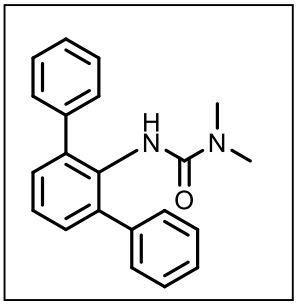


1-([1,1'-biphenyl]-2-yl)-3-hexylurea: The title compound **(3pa)** was prepared by adding 22 mg of **1p**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 0.6 mg (1 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as

general procedure described above and purified by silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (50%, 14.8 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.87 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.47 (tt, *J* = 7.5, 1.4 Hz, 2H), 7.42 – 7.32 (m, 3H), 7.28 (s, 1H), 7.27 – 7.23 (m, 1H), 7.14 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.04 (td, *J* = 7.4, 1.3 Hz, 1H), 6.54 (t, *J* = 5.6 Hz, 1H), 3.00 (q, *J* = 8.0, 4.0 Hz, 2H), 1.39 – 1.21 (m, 8H), 0.91 – 0.82 (m, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.54, 138.50, 135.55, 133.53, 130.47, 129.25, 128.98, 128.57, 127.79, 124.05, 122.60, 40.58, 31.47, 30.01, 26.50, 22.56, 14.02; **HRMS** m/z (ESI): Exact mass calculated for $C_{19}H_{25}N_2O^+$ $(M+H)^+$ 297.1961, found 297.1954.

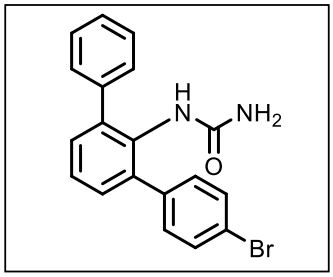


1-([1,1'-biphenyl]-2-yl)-3-butylurea: The title compound **(3qa)** was prepared by adding 19.2 mg of **1q**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 0.6 mg (1 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light as general procedure described above and purified by using silica gel column chromatography after 24 h of reaction time to give the desired product as a brownish white solid (69%, 18.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.23 (m, 4H), 7.20 – 7.16 (m, 1H), 7.08 (td, *J* = 7.5, 1.3 Hz, 1H), 6.02 (s, 1H), 4.50 (t, *J* = 5.9 Hz, 1H), 3.05 (q, *J* = 8.0, 4.0 Hz, 2H), 1.37- 1.30 (m, , 2H), 1.21 (dq, *J* = 14.1, 7.1 Hz, 2H), 0.82 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 155.55, 138.52, 135.56, 133.52, 130.47, 129.25, 128.96, 128.56, 127.76, 124.03, 122.63, 40.25 , 32.12, 20.00, 13.76; **HRMS** m/z (ESI): Exact mass calculated for $C_{17}H_{21}N_2O^+$ $(M+H)^+$ 269.1648, found 269.1644.

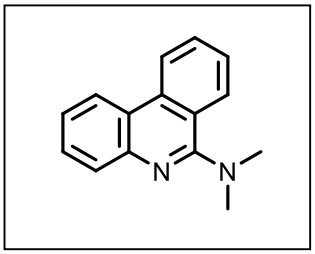


3-([1,1':3',1''-terphenyl]-2'-yl)-1,1-dimethylurea: The title compound **(6)** was prepared by adding 16.4 mg of **1m**, 76.7 mg of **2a**, 2.2 mg (10 mol%) of $Pd(OAc)_2$, 1.6 mg (2.5 mol%) of PC and 0.6 mL of MeOH to a reaction vial and stirred under blue light for 24 h. The solvent was then evaporated under reduced pressure and the residue was purified by silica gel column chromatography (eluent: EtOAc/Hexane) to give the desired product as colourless solid (78%, 24.6 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 7.61 (s, 1H), 7.45

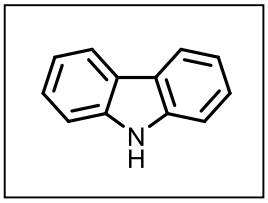
(dt, *J* = 8.6, 2.0 Hz, 4H), 7.40 (dd, *J* = 6.3, 1.9 Hz, 2H), 7.39 – 7.36 (m, 3H), 7.34 – 7.29 (m, 4H), 2.52 (s, 6H); **^{13}C NMR (101 MHz, DMSO-*d*$_6$)** δ 157.78, 142.41, 140.52, 134.54, 129.83, 129.42, 128.18, 127.34, 127.26, 36.50; **HRMS** m/z (ESI): Exact mass calculated for $C_{21}H_{21}N_2O^+$ $(M+H)^+$ 317.1648, found 317.1654.



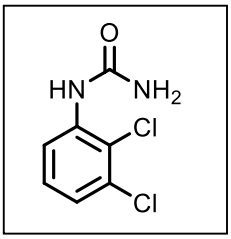
3-(4-bromo-[1,1':3',1''-terphenyl]-2'-yl)-1,1-dimethylurea (**7**): To an oven dried reaction vial equipped with a magnetic stir bar was sequentially added **3aa** (0.1mmol, 21.2 mg), freshly prepared aryldiazonium salt (**2b)** (0.4 mmol, 108.3 mg), $Pd(OAc)_2$ (10 mol%, 2.2 mg), $Ru(bpy)_3Cl_2.6H_2O$ (1 mol%, 0.6 mg), and MeOH (0.6 mL), then the vial was sealed and irradiated with blue LED strip for 24 h. After completion the solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: EtOAc/Hexane) to get the product **6** (80%, 31.6 mg) as white solid. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.45 – 7.38 (m, 6H), 7.36 (dd, *J* = 6.9, 2.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 4.25 (s, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 156.64, 140.71, 139.49, 138.83, 138.14, 131.71, 131.58, 130.76, 130.52, 130.27, 128.89, 128.63, 127.96, 127.74, 121.90; **HRMS** m/z (ESI): Exact mass calculated for $C_{19}H_{16}N_2BrO^+$ $(M+H)^+$ 367.0441; 369.0420, found 367.0447; 369.0425.



N,N-dimethylphenanthridin-6-amine: The title compound **(8)** was prepared by using general procedure described above and purified by using silica gel column chromatography after 12 h of reaction time to get the desired product (80%, 17.8 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.54 (d, *J* = 8.2 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 8.1 Hz, 2H), 7.44 (t, *J* = 8.2 Hz, 1H), 3.16 (s, 6H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 160.74, 143.89, 135.07, 129.90, 128.68, 128.08, 127.10, 126.34, 124.11, 122.59, 122.26, 121.77, 121.49, 42.89; **HRMS** m/z (ESI): Exact mass calculated for $C_{15}H_{15}N_2^+$ $(M+H)^+$ 223.1230, found 223.1226.



9H-carbazole: The title compound **(9)** was prepared by using general procedure as described above and the desired product obtained as a yellowish white solid (66%, 11.0 mg). **^{1}H NMR (400 MHz, DMSO-*d*$_6$)** δ 11.25 (s, 1H), 8.11 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.50 (dt, *J* = 8.1, 0.9 Hz, 2H), 7.39 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.16 (ddd, *J* = 7.9, 7.1, 1.1 Hz, 2H); **^{13}C NMR (101 MHz, CDCl$_3$)** δ 139.48, 125.83, 123.35, 120.33, 119.44, 110.56; **HRMS** m/z (ESI): Exact mass calculated for $C_{12}H_{10}N^+$ $(M+H)^+$ 168.0808, found 168.0810.



1-(2,3-dichlorophenyl)urea: The title compound (**1i**) was prepared by slow addition of 2,3-dichlorophenylisocyanate in acetone to ammonia solution (10 eq) at 0°C. Then the reaction mixture was stirred at 0°C for 0.5 h and then 2h at room temperature. After completion of the reaction, the solid formed was filtered off and washed with DCM and then dried in oven to get a white solid with 85% yield. **^{1}H NMR: (400 MHz, DMSO-*d*$_6$)** δ 8.21 (s, 1H), 8.15 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.29 – 7.18 (m, 2H), 6.49 (s, 2H); **^{13}C NMR: (101 MHz, DMSO-*d*$_6$)** δ 155.83, 139.28, 131.84, 128.39, 123.21, 120.03, 119.76; **HRMS** m/z (ESI): Exact mass calculated for $C_7H_7Cl_2N_2O^+$ $(M+H)^+$ 204.9930; 206.9900, found 204.9928; 206.9898.

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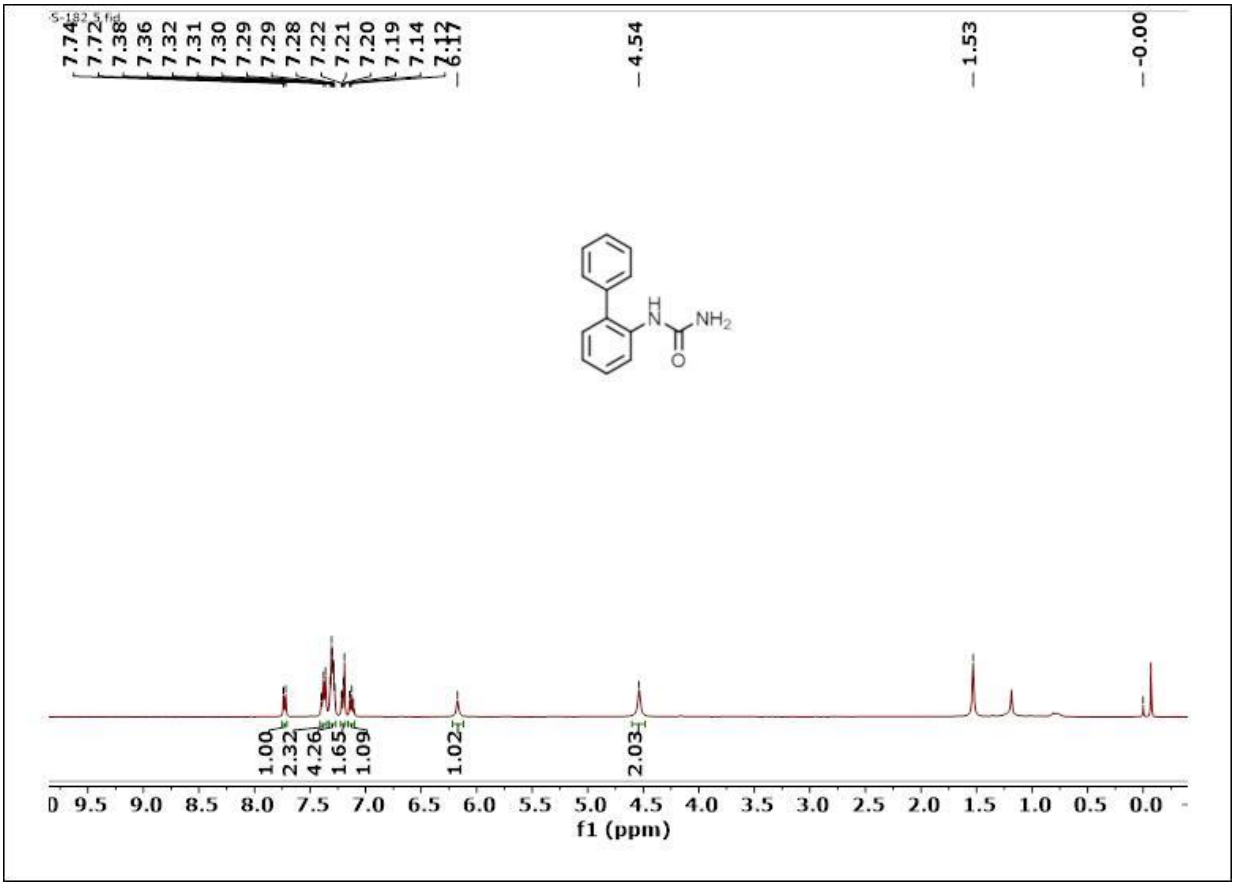
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7.19
7.14
7.12
6.17
4.54
1.53
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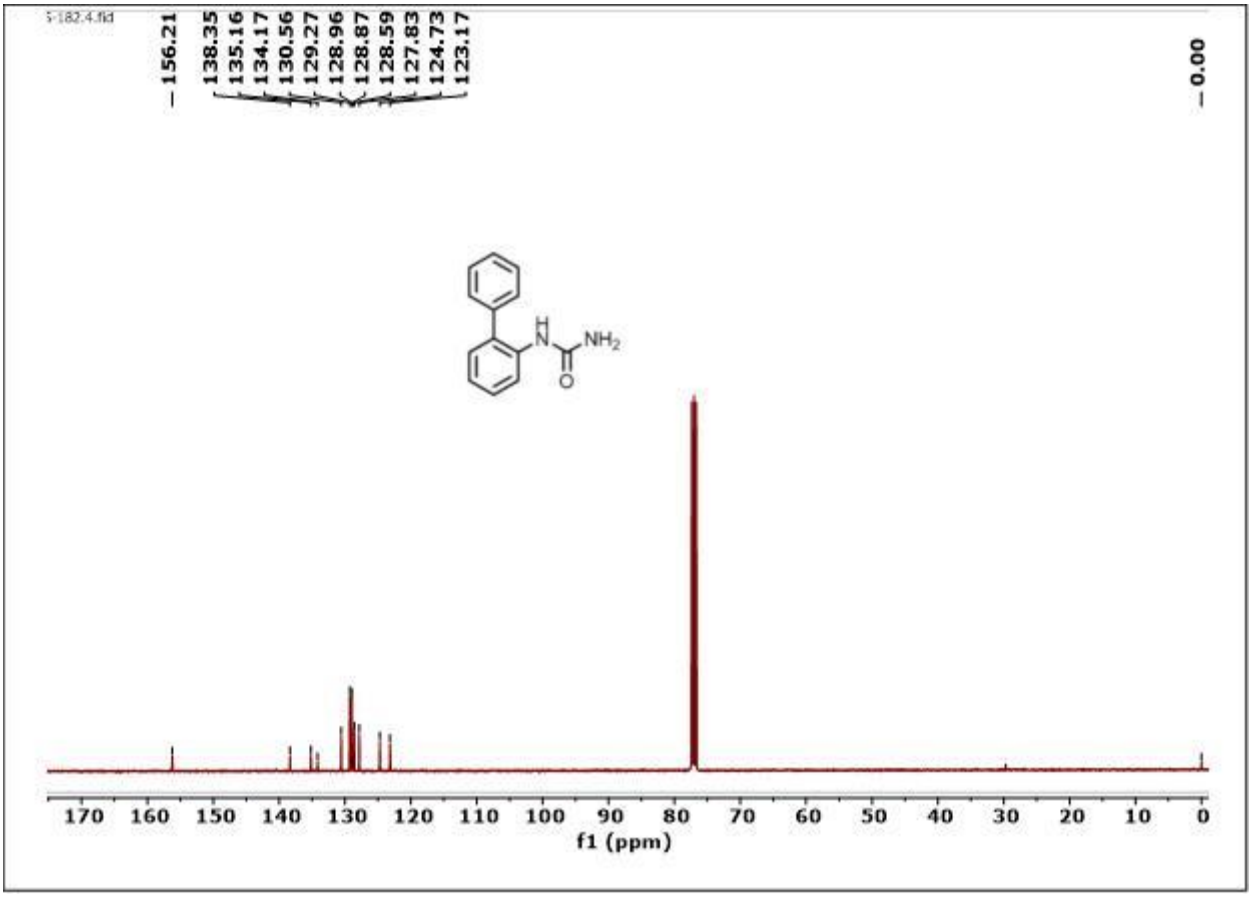
NH2
1.00
2.32
4.26
1.65
1.09
1.02
2.03
f1 (ppm)


S-182.4.fid
156.21
138.35
135.16
134.17
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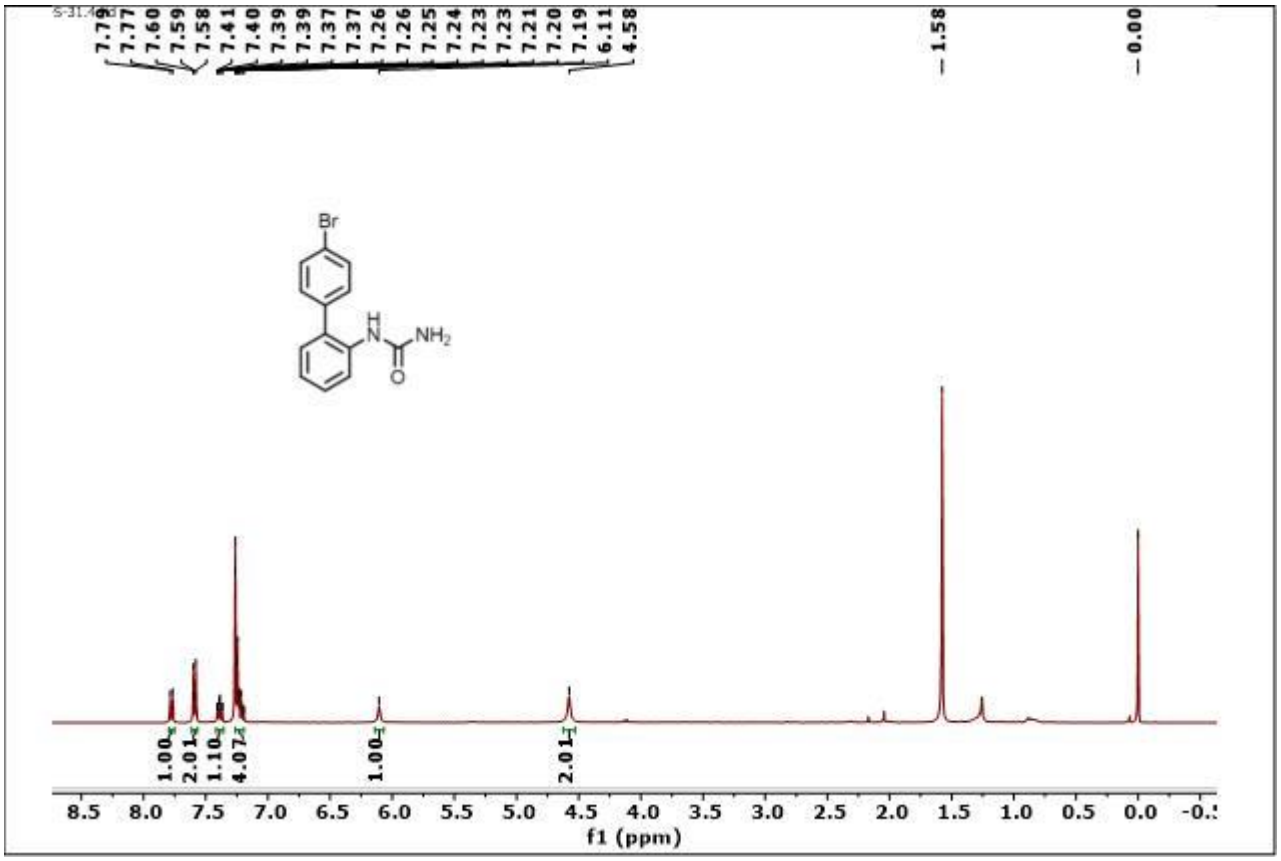
128.87
128.59
127.83
124.73
123.17
0.00
NH2
f1 (ppm)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7.77
7.60
7.59
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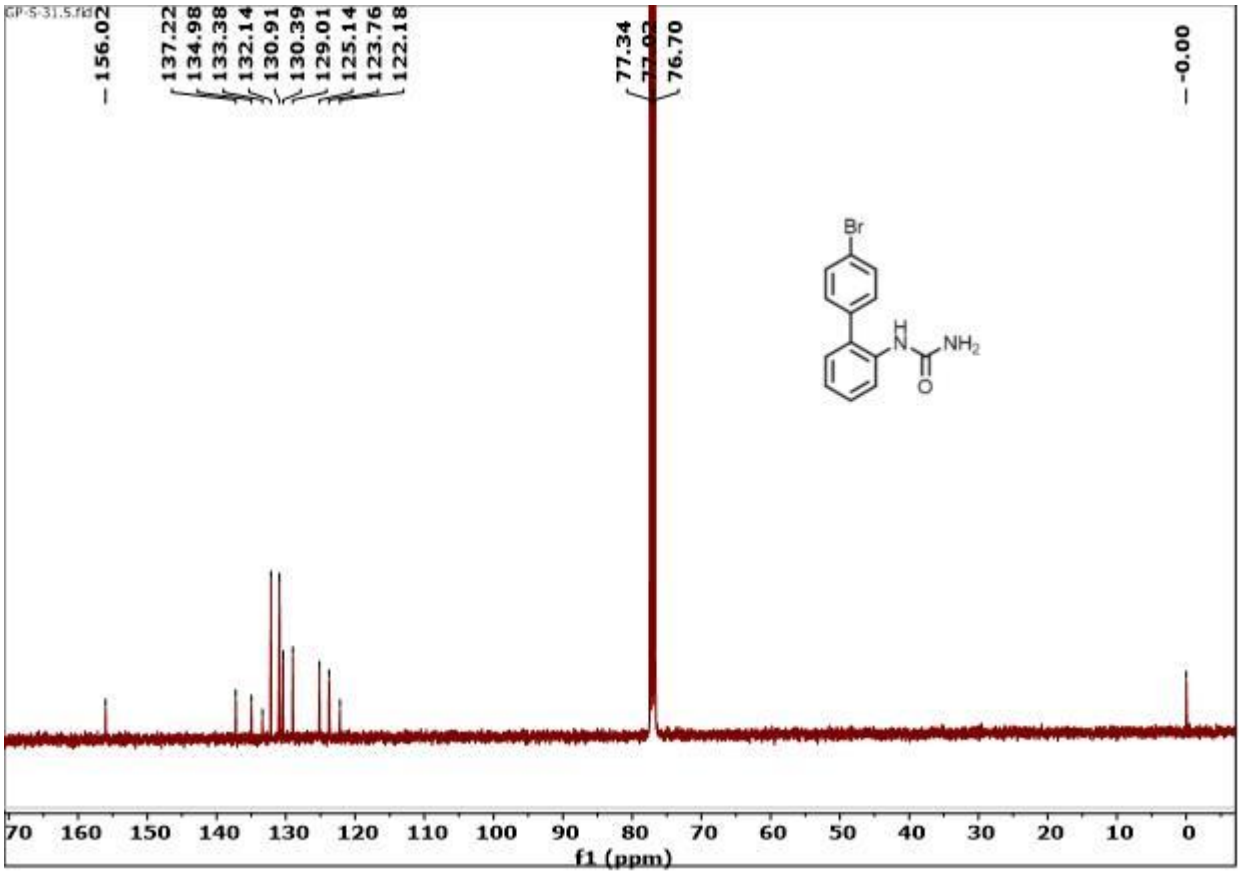
7.41
7.40
7.39
7.39
7.37
7.37
7.26
7.26
7.25
7.24
7.23
7.23
7.21
7.20
7.19
6.11
4.58
1.58
0.00
Br
H
N
NH2
O
1.00
2.01
1.10
4.07
1.00
2.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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137.22
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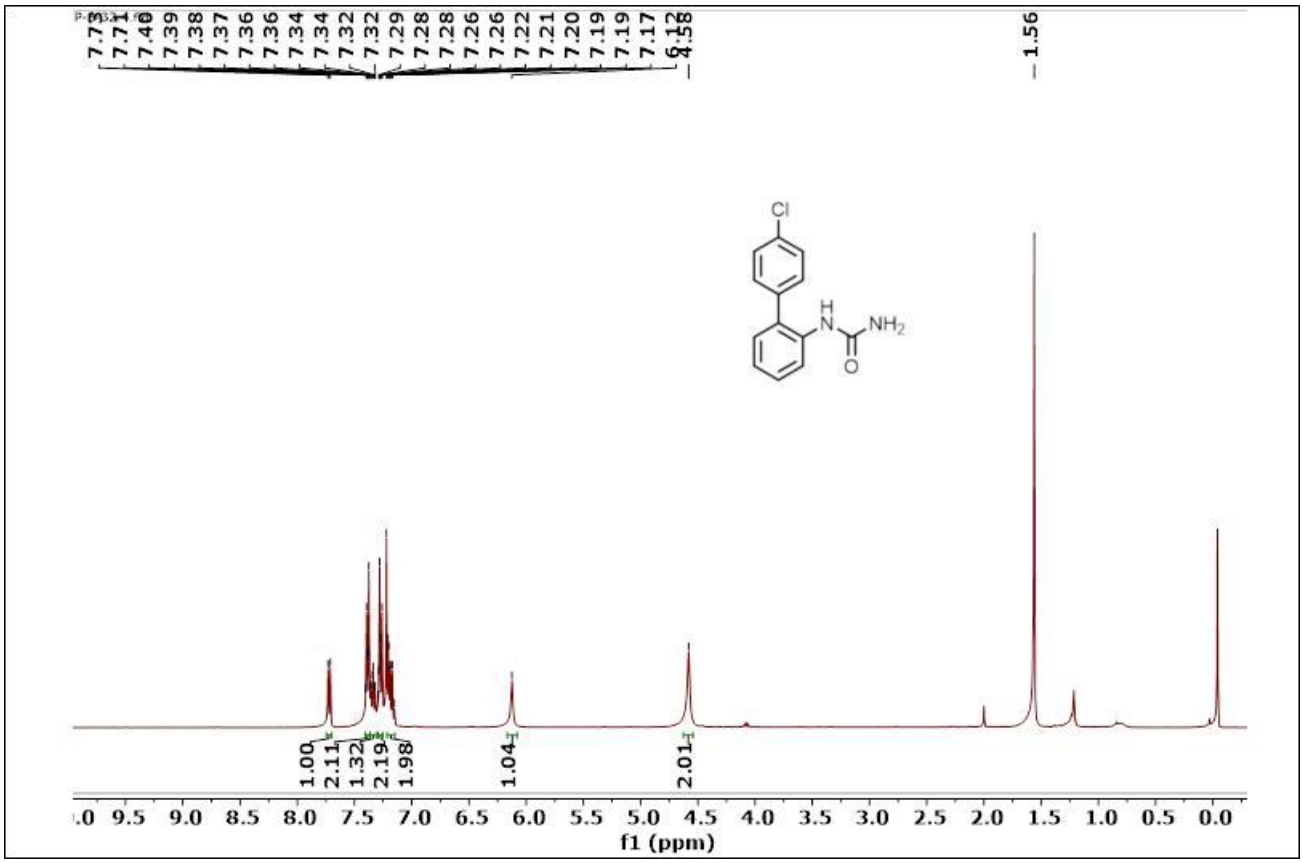
132.14
130.91
130.39
129.01
125.14
123.76
122.18
77.34
77.03
76.70
0.00
Br
H
N
NH2
O
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.71
7.40
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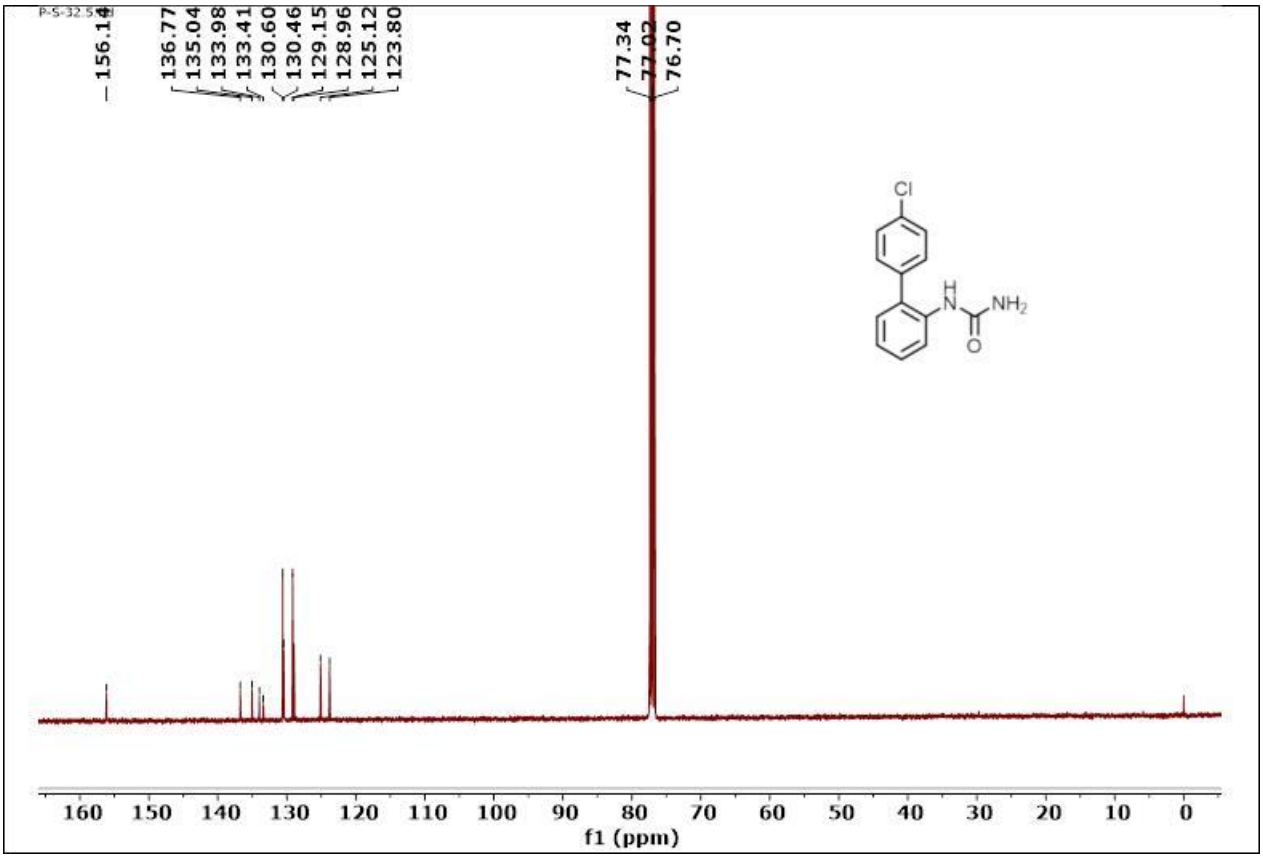
7.37
7.36
7.36
7.34
7.34
7.32
7.32
7.29
7.28
7.28
7.26
7.26
7.22
7.21
7.20
7.19
7.19
7.17
6.12
4.58
1.56
Cl
NH2
1.00
2.11
1.32
2.19
1.98
1.04
2.01
f1 (ppm)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125.12
123.80
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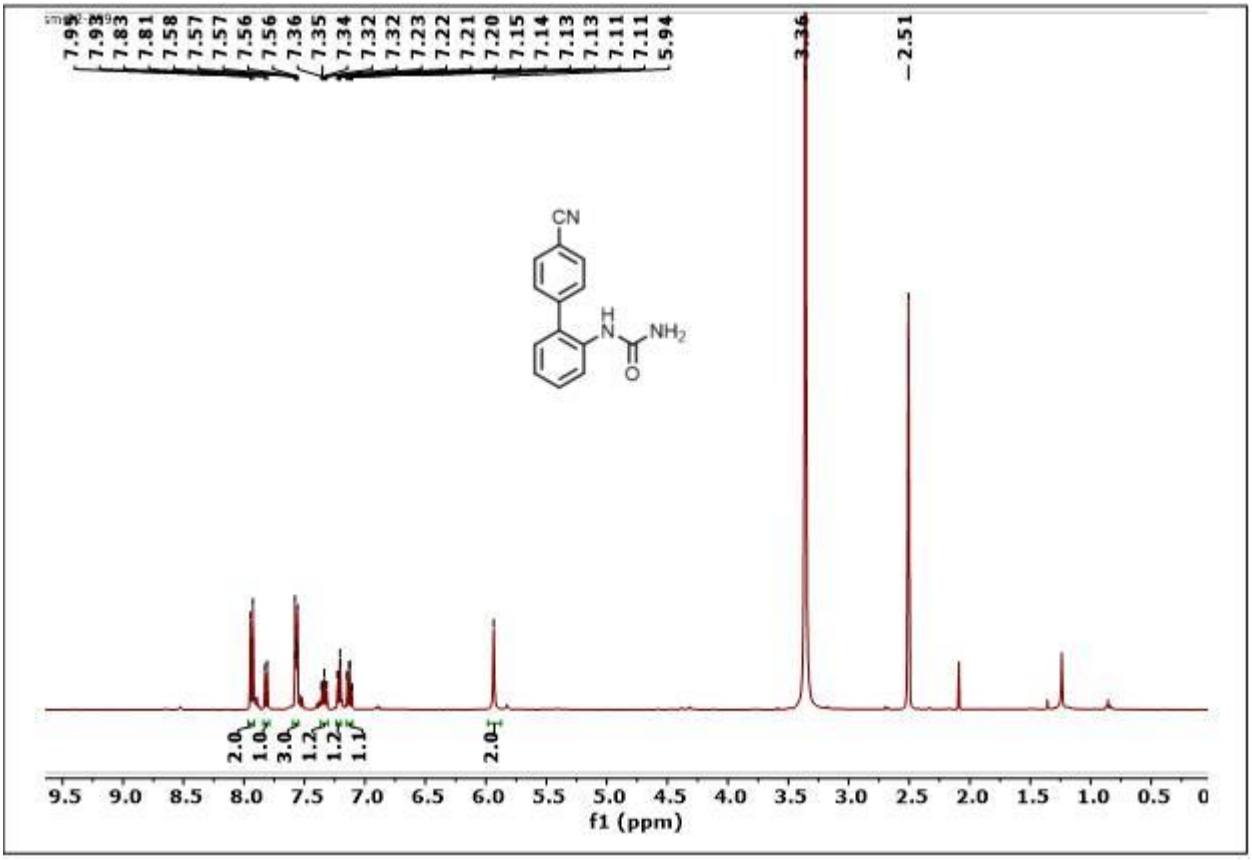
77.02
76.70
Cl
NH2
f1 (ppm)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7.93
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7.81
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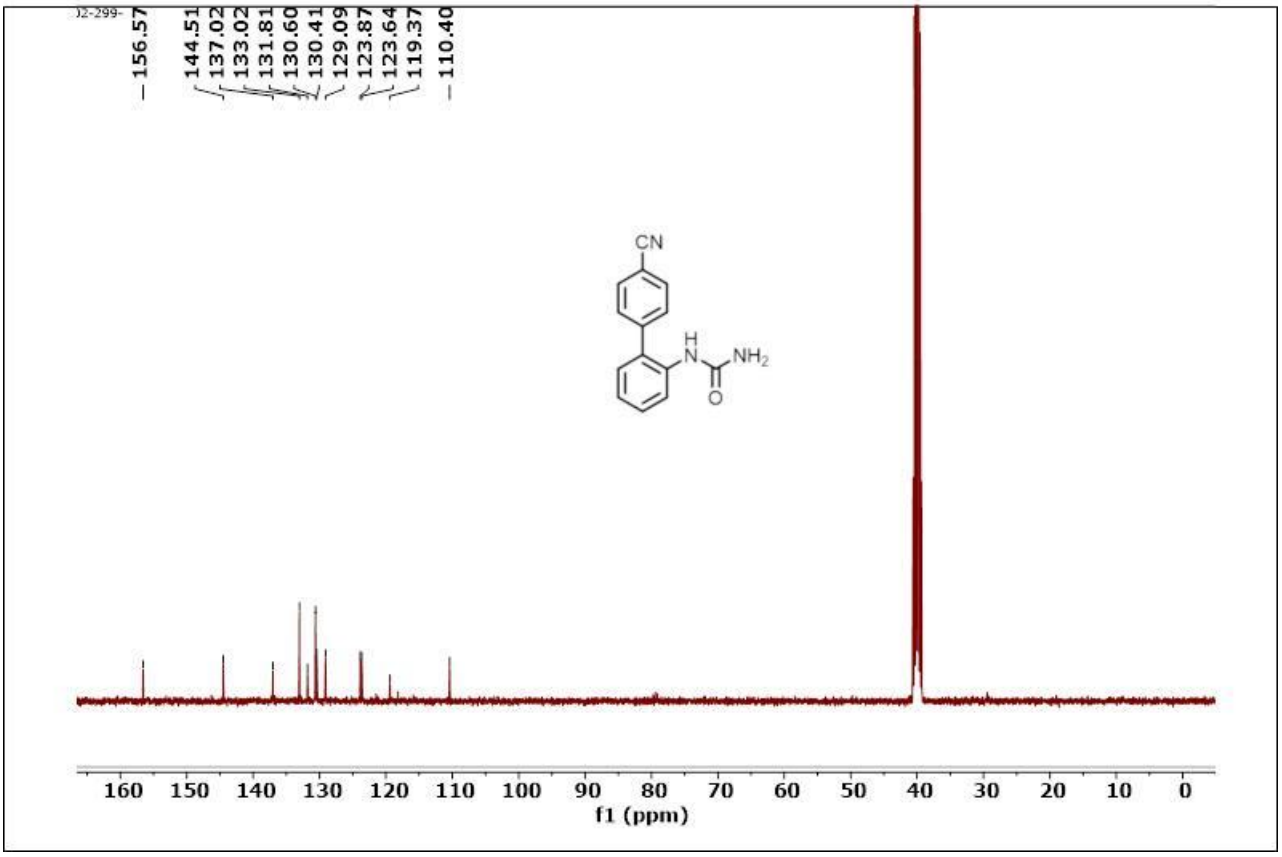
7.57
7.56
7.56
7.36
7.35
7.34
7.32
7.32
7.23
7.22
7.21
7.20
7.15
7.14
7.13
7.13
7.11
7.11
5.94
3.36
2.51
CN
H
N
NH2
O
2.0
1.0
3.0
1.2
1.2
1.1
2.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)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144.51
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133.02
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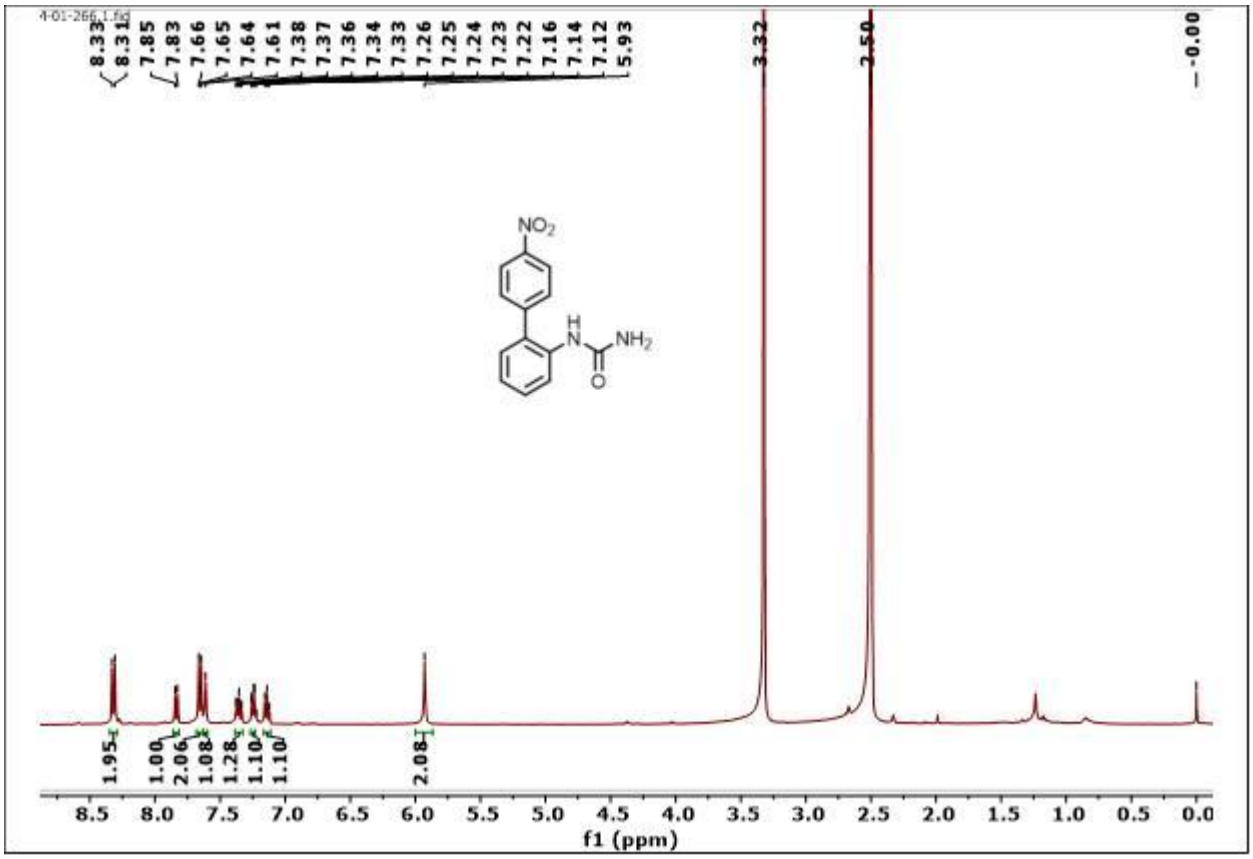
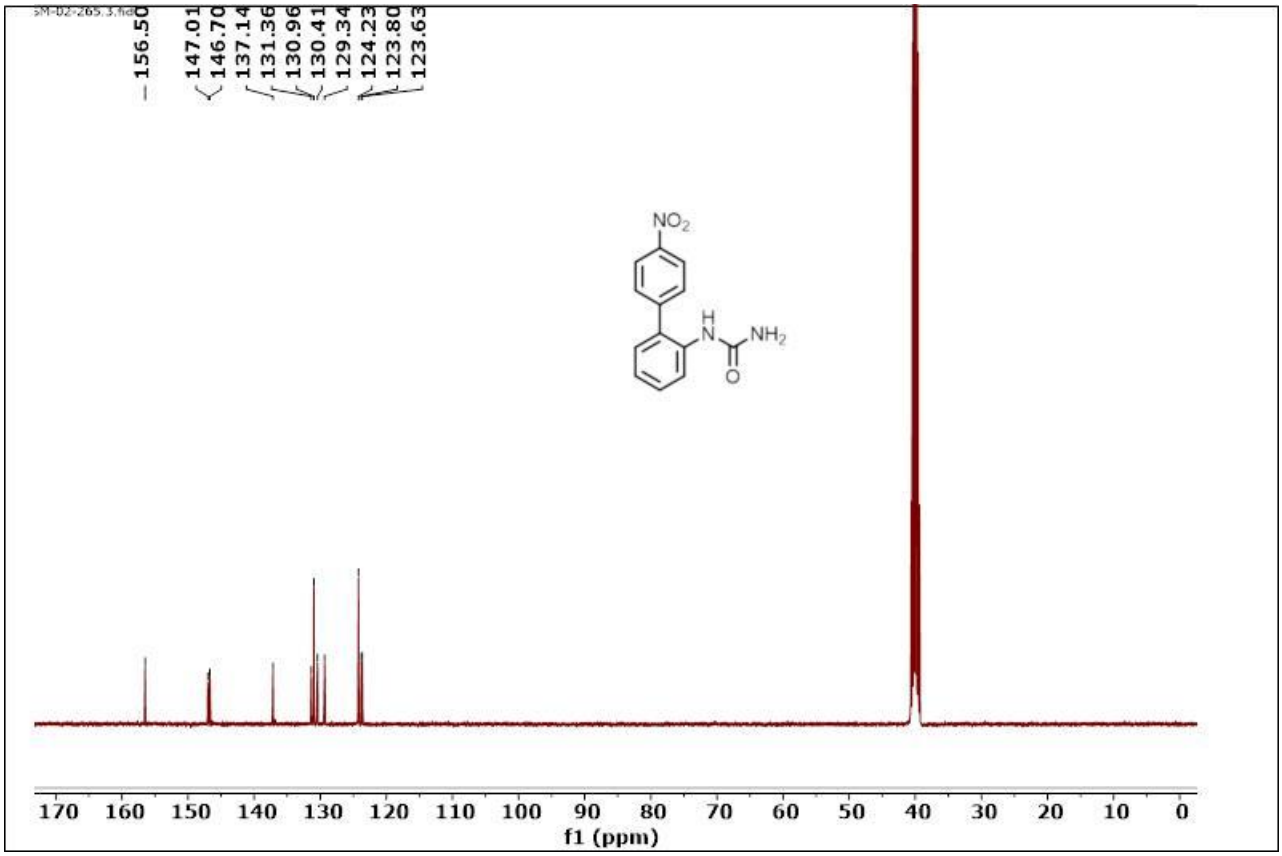
130.60
130.41
129.09
123.87
123.64
119.37
110.40
CN
H
N
NH2
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.33
8.31
7.85
7.83
7.66
7.65
7.64
7.61
7.38
7.37
7.36
7.34
7.33
7.26
7.25
7.24
7.23
7.22
7.16
7.14
7.12
5.93
3.32
2.50
0.00
NO2
NH
NH2
O
1.95
1.00
2.06
1.08
1.28
1.10
1.10
2.08
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)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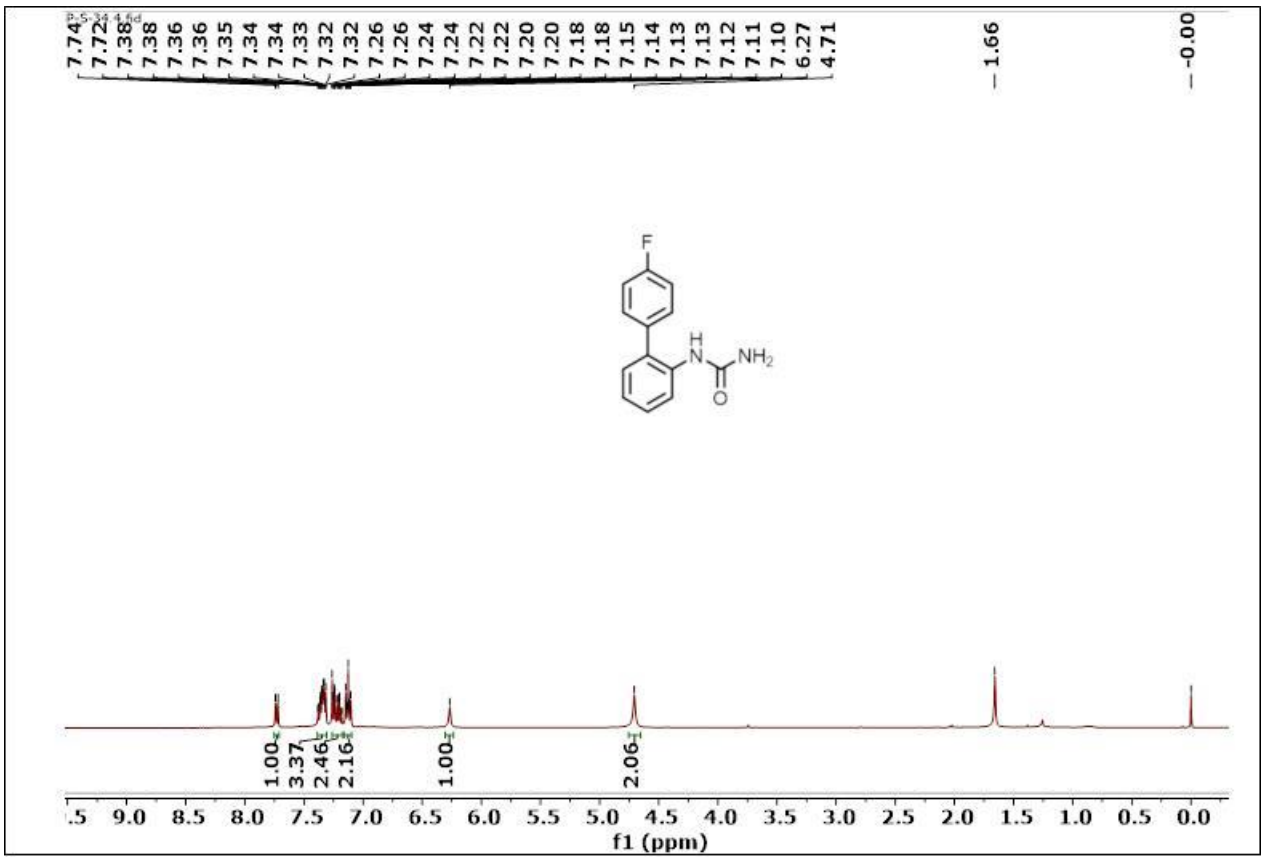
147.01
146.70
137.14
131.36
130.96
130.41
129.34
124.23
123.80
123.63
NO2
NH
NH2
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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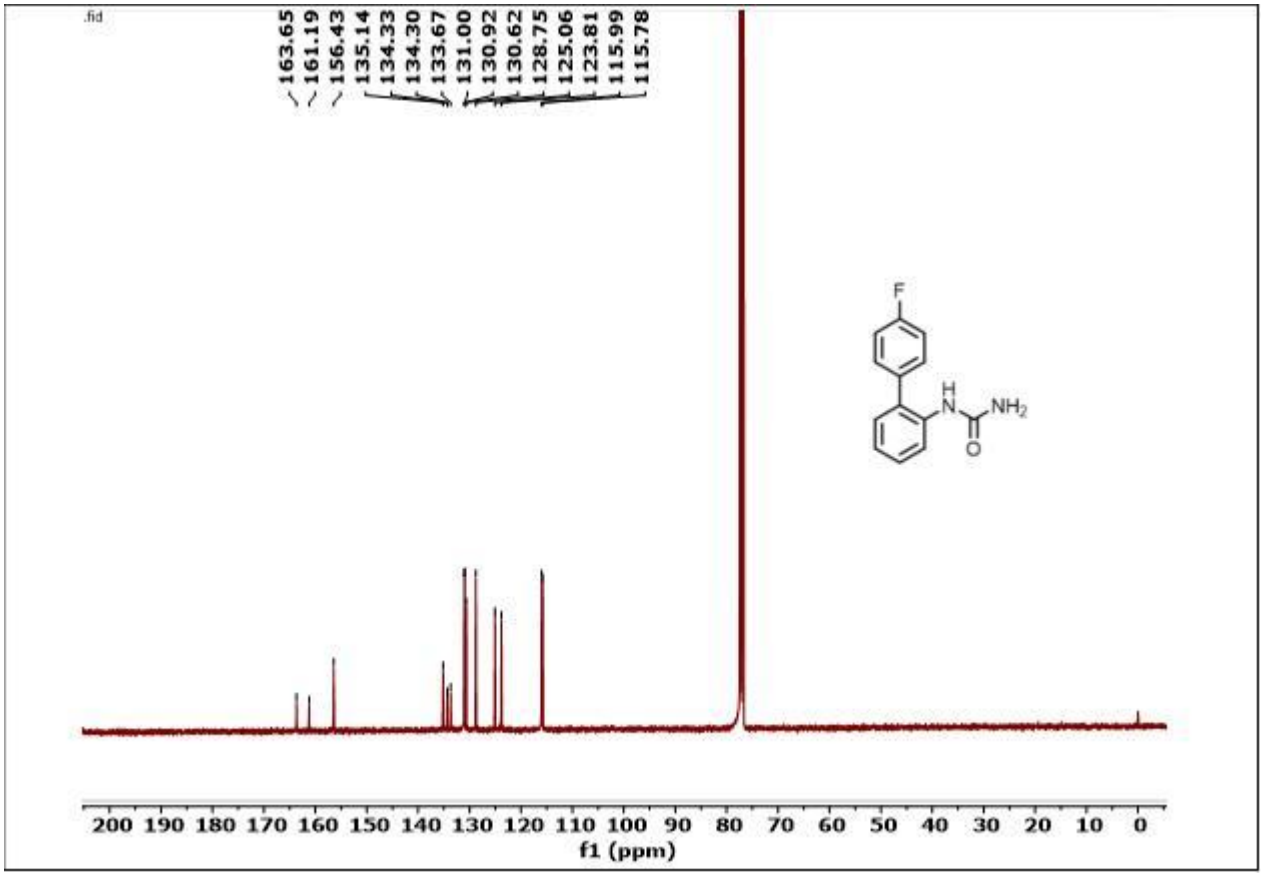
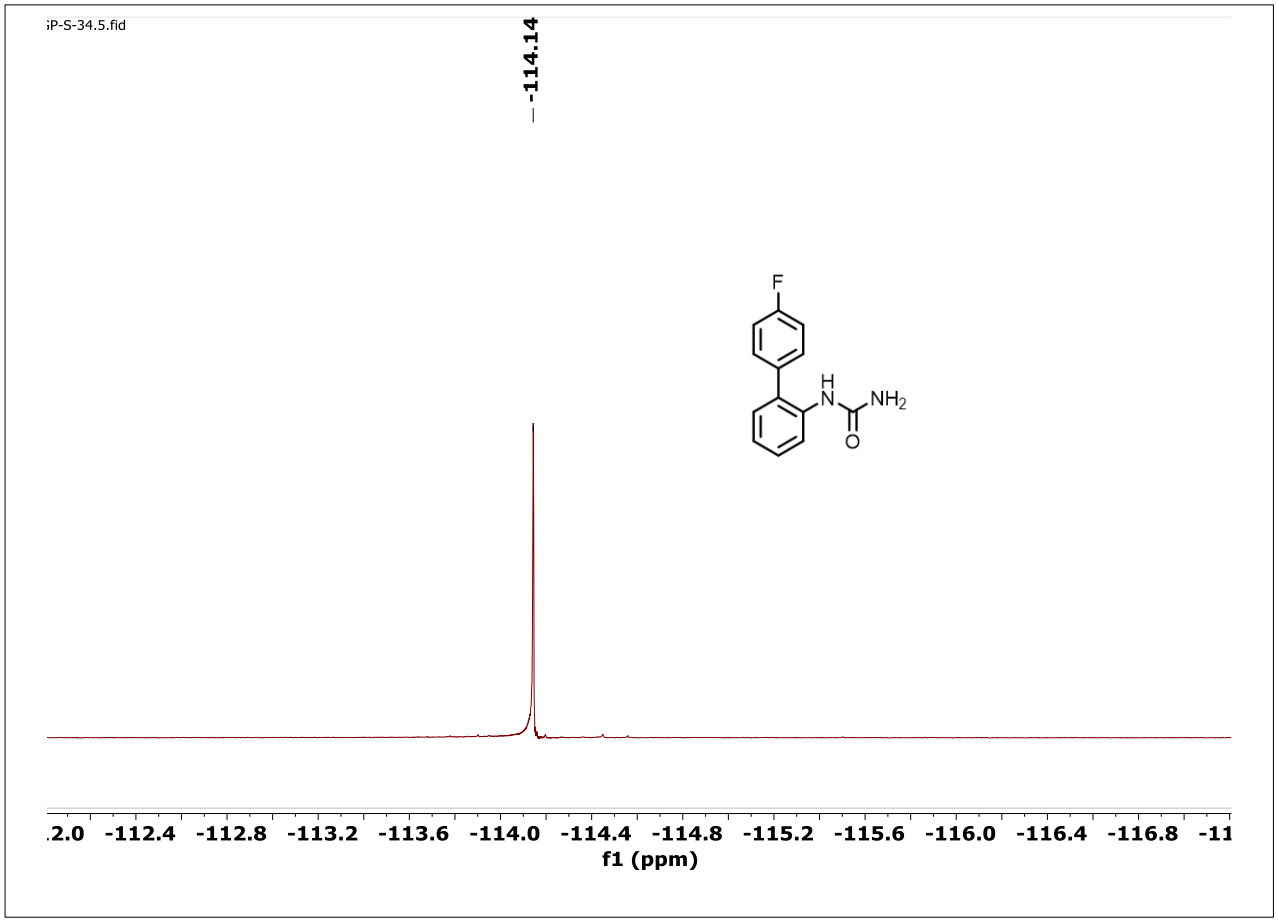
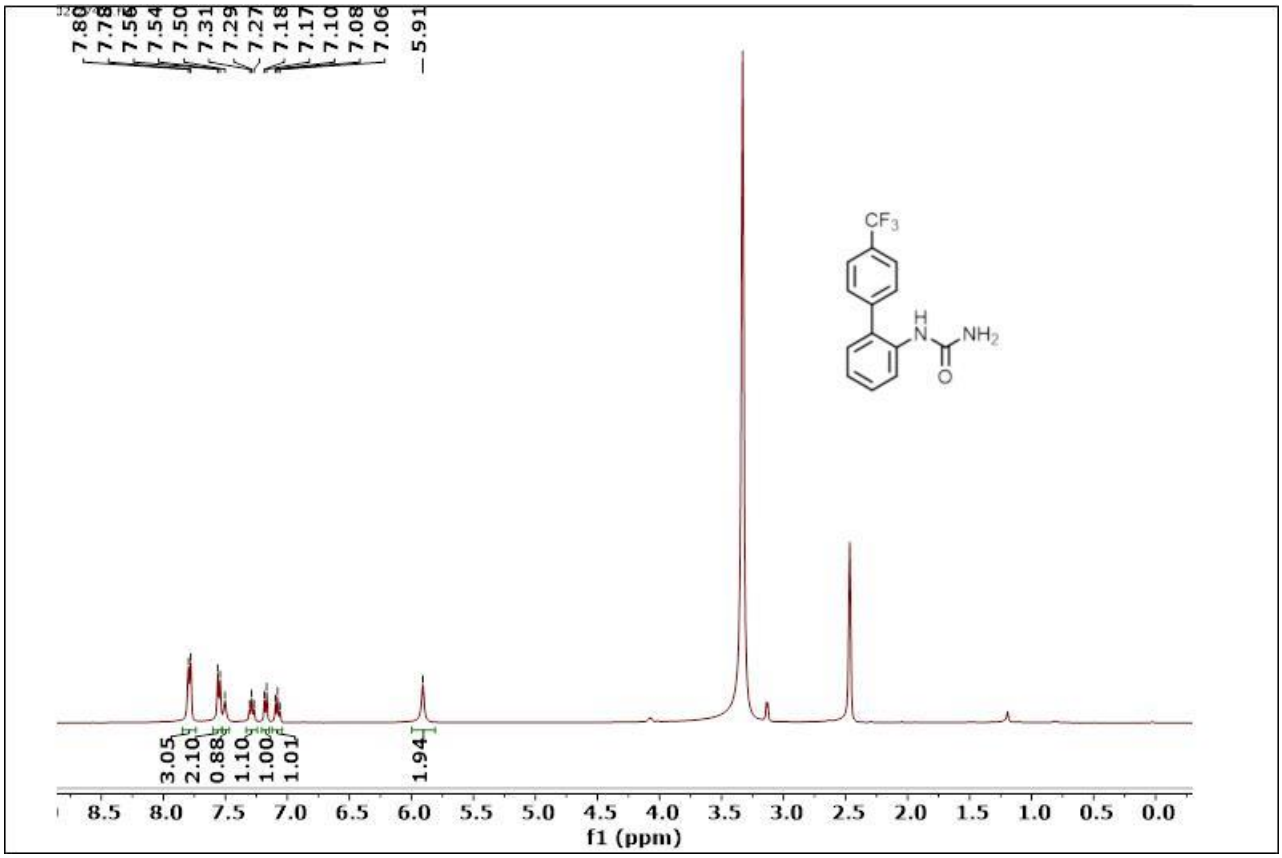
7.72
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.26
7.26
7.24
7.24
7.22
7.22
7.20
7.20
7.18
7.18
7.15
7.14
7.13
7.13
7.12
7.11
7.10
6.27
4.71
1.66
0.00
F
NH2
1.00
3.37
2.46
2.16
1.00
2.06
f1 (ppm)


.fid
163.65
161.19
156.43
135.14
134.33
134.30
133.67
131.00
130.92
130.62
128.75
125.06
123.81
115.99
115.78
F
NH2
f1 (ppm)


iP-S-34.5.fid
-114.14
F
H
N
NH2
O
.2.0 -112.4 -112.8 -113.2 -113.6 -114.0 -114.4 -114.8 -115.2 -115.6 -116.0 -116.4 -116.8 -11
f1 (ppm)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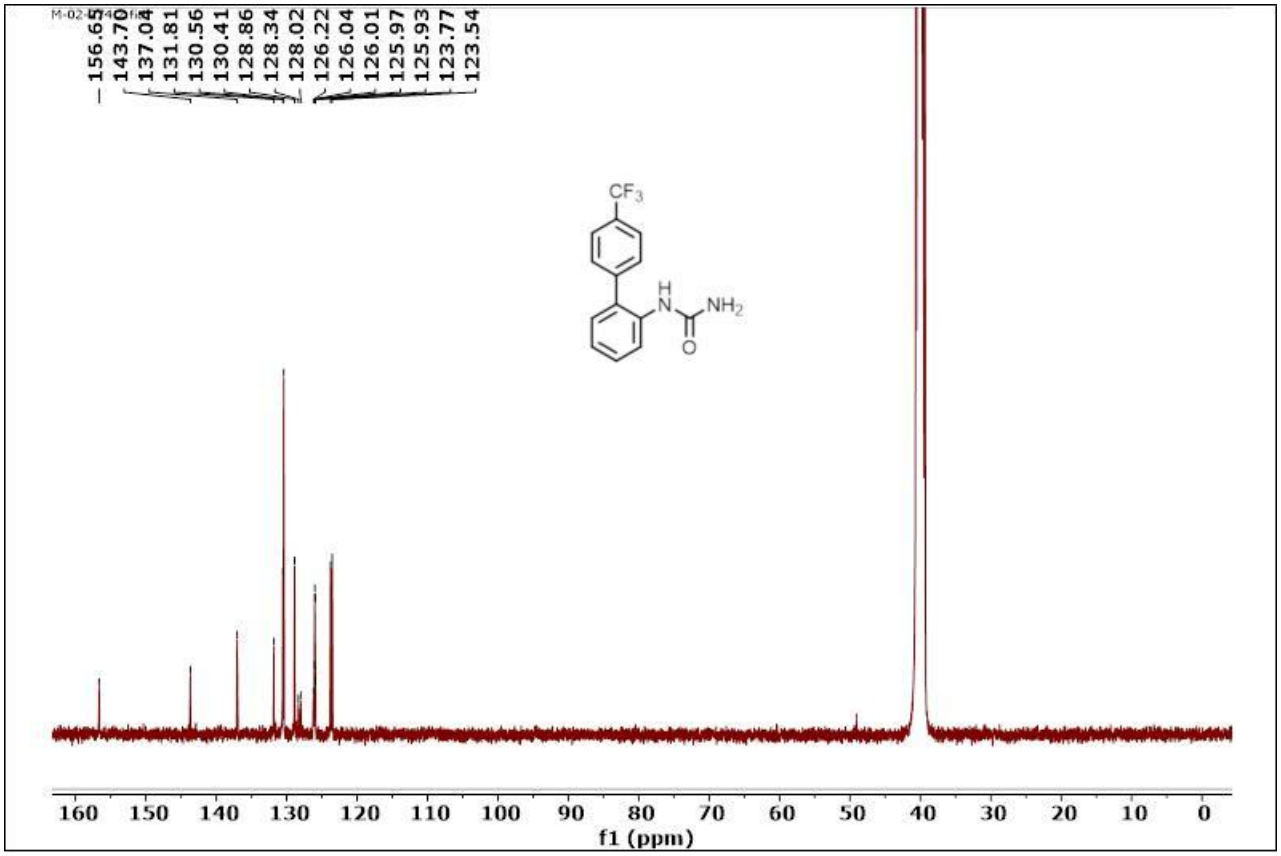
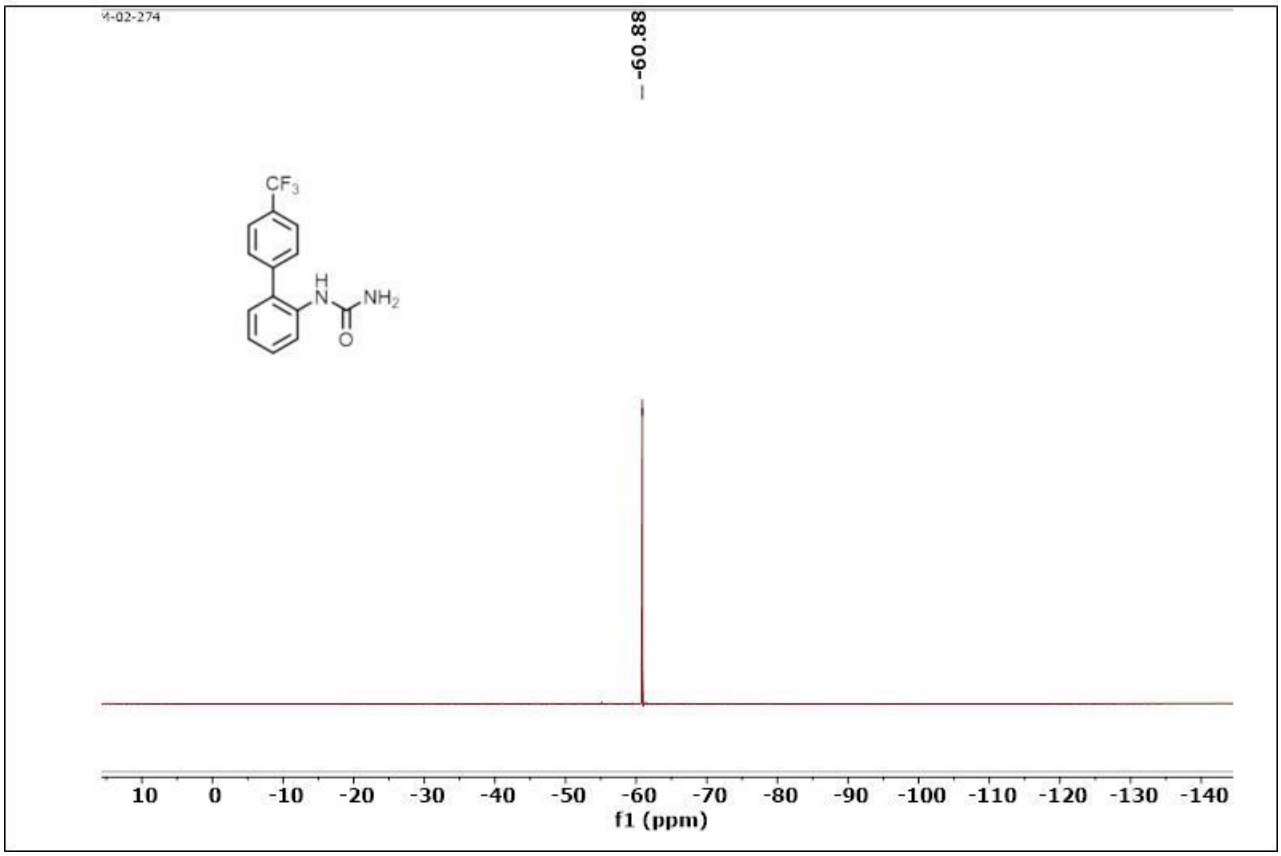
7.78
7.56
7.54
7.50
7.31
7.29
7.27
7.18
7.17
7.10
7.08
7.06
5.91
3.05
2.10
0.88
1.10
1.00
1.01
1.94
CF3
NH2
f1 (ppm)


156.65
143.70
137.04
131.81
130.56
130.41
128.86
128.34
128.02
126.22
126.04
126.01
125.97
125.93
123.77
123.54
CF3
NH2
f1 (ppm)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CF3
H
N
NH2
O
10
0
-10
-20
-30
-40
-50
-60
-70
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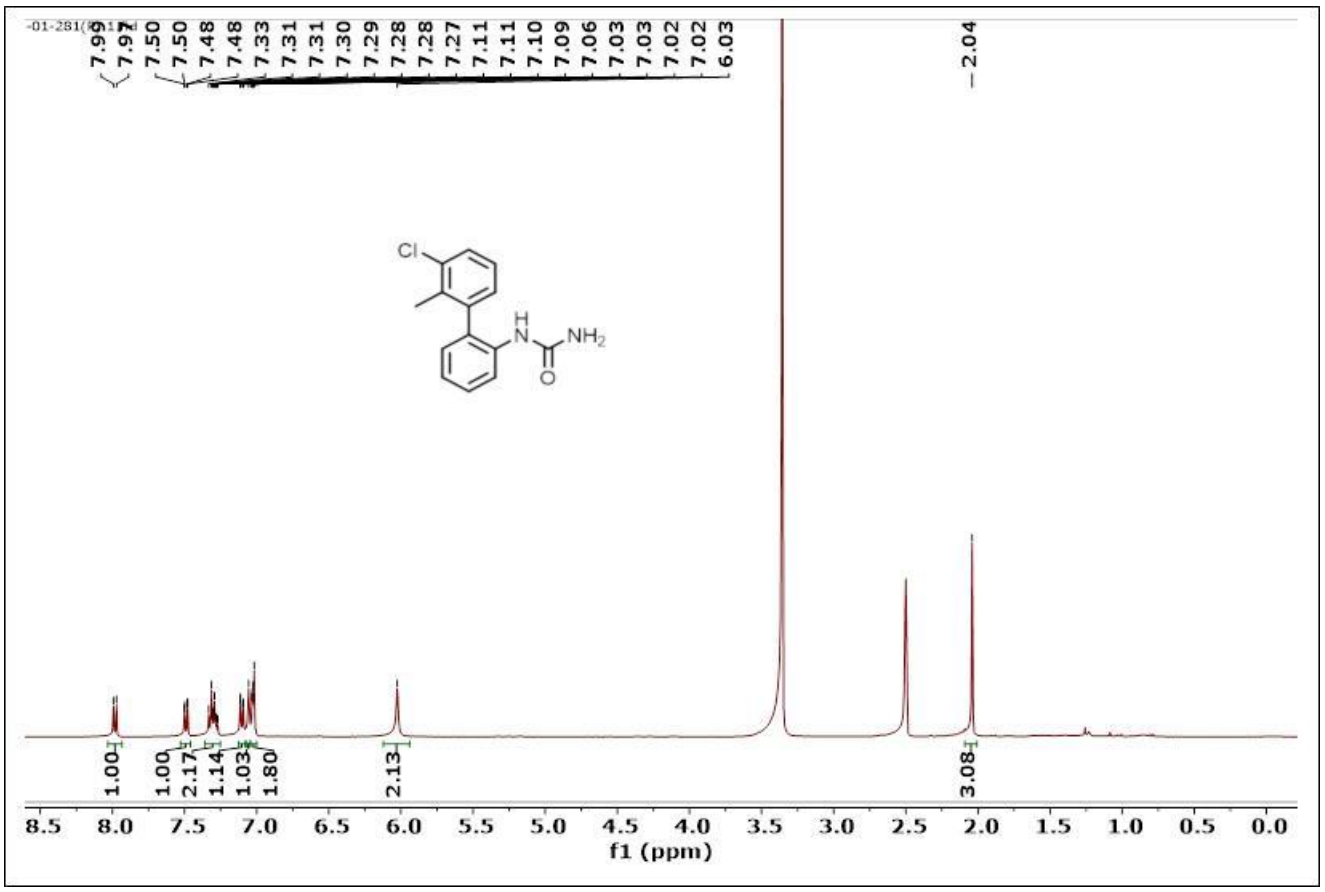
-90
-100
-110
-120
-130
-140
f1 (ppm)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7.97
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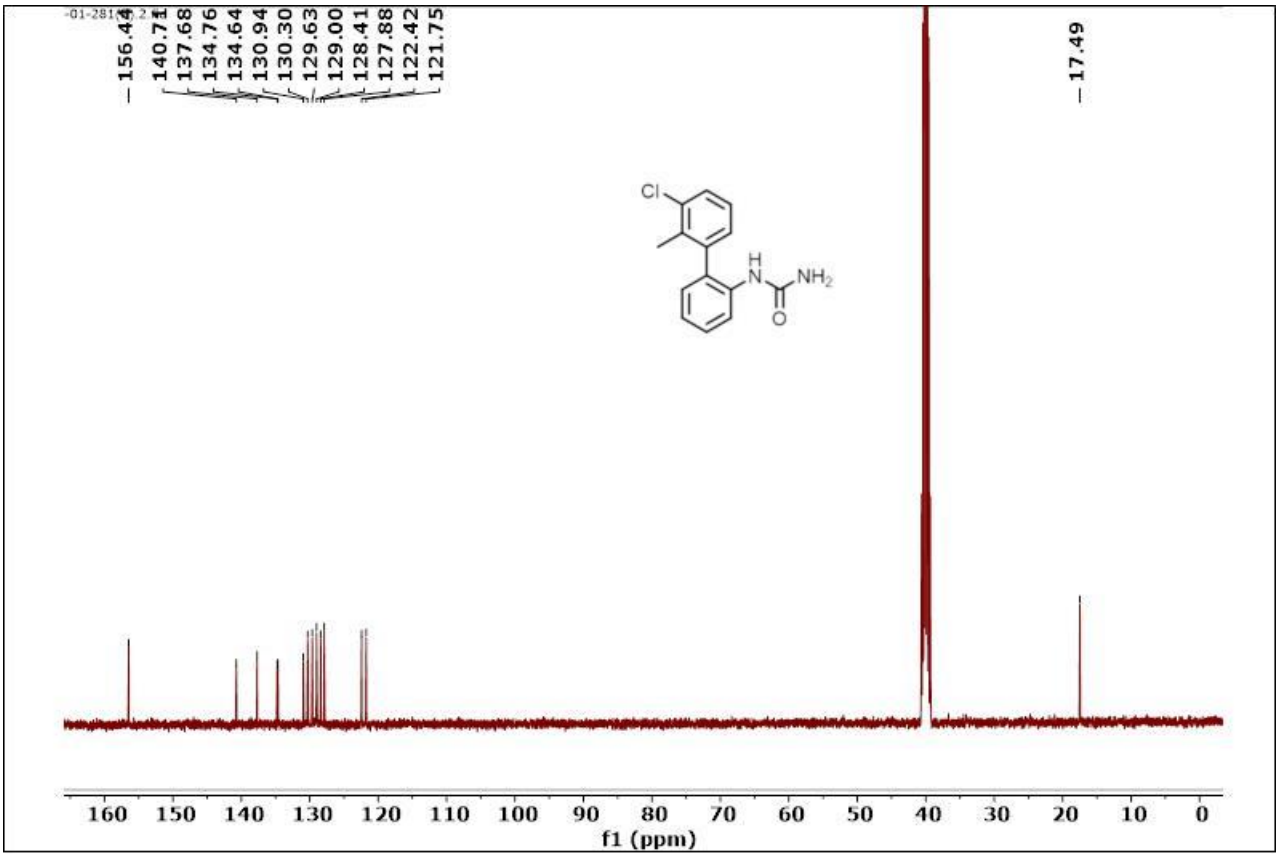
7.48
7.48
7.33
7.31
7.31
7.30
7.29
7.28
7.28
7.27
7.11
7.11
7.10
7.09
7.06
7.03
7.03
7.02
7.02
6.03
2.04
Cl
H
N
NH2
O
1.00
1.00
2.17
1.14
1.03
1.80
2.13
3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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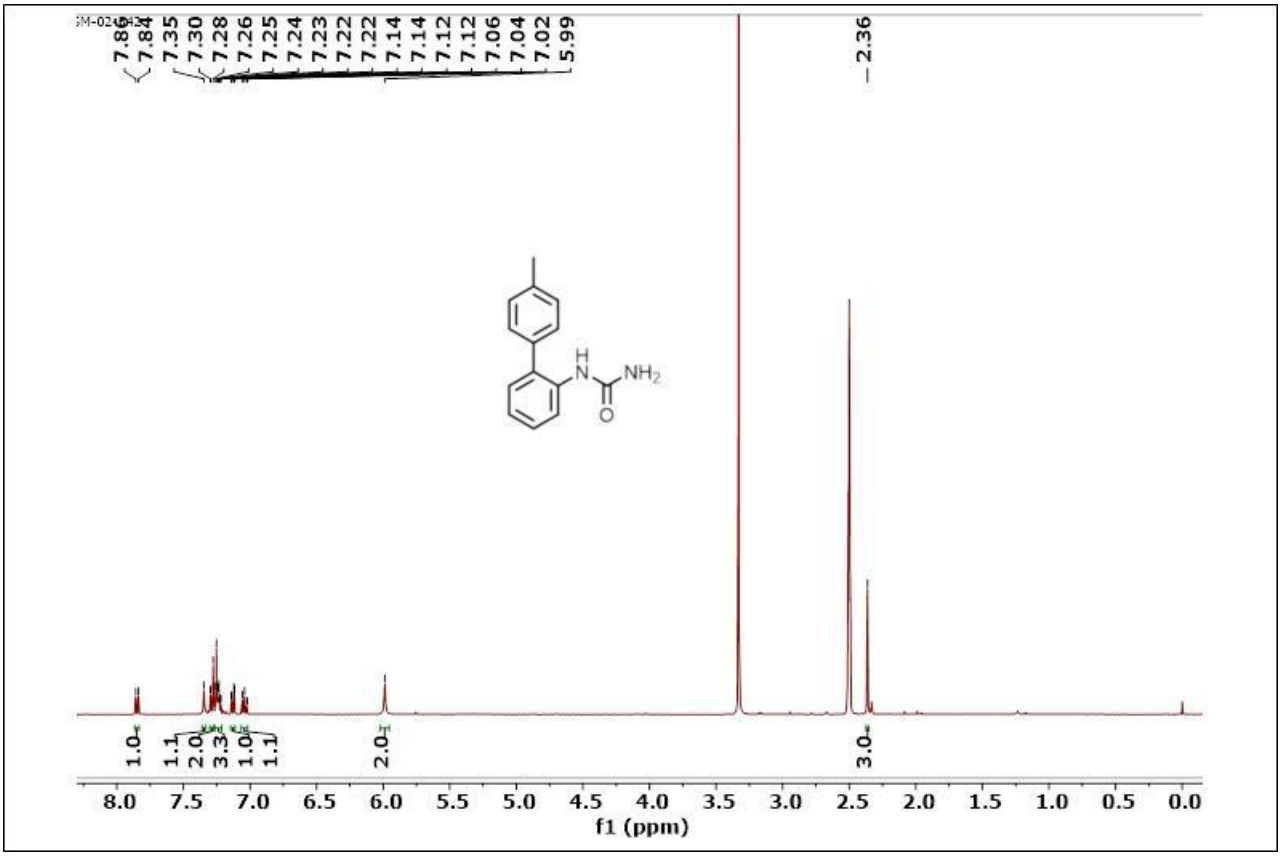
134.64
130.94
130.30
129.63
129.00
128.41
127.88
122.42
121.75
17.49
Cl
H
N
NH2
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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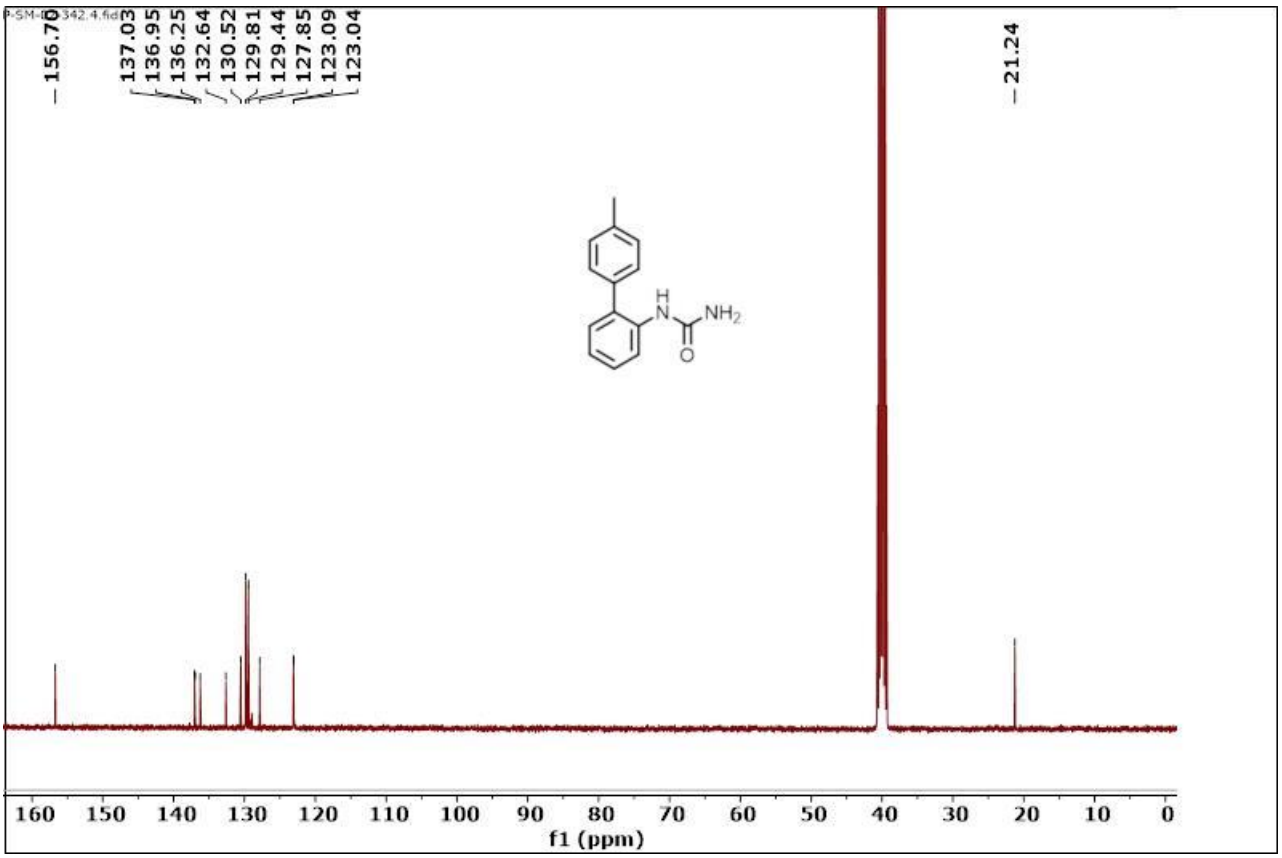
7.84
7.35
7.30
7.28
7.26
7.25
7.24
7.23
7.22
7.22
7.14
7.14
7.12
7.12
7.06
7.04
7.02
5.99
2.36
NH2
1.0
1.1
2.0
3.3
1.0
1.1
2.0
3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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137.03
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136.25
132.64
130.52
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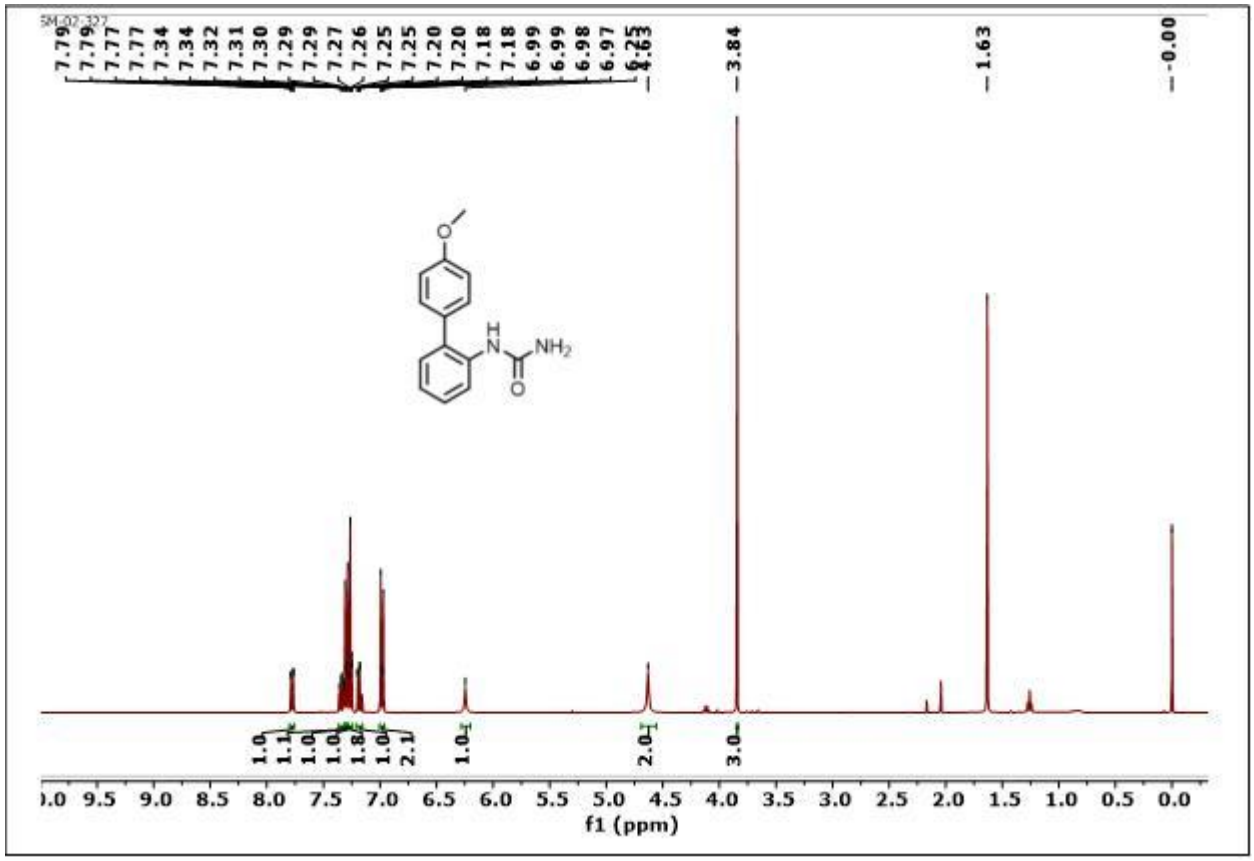
129.44
127.85
123.09
123.04
21.24
NH2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.79
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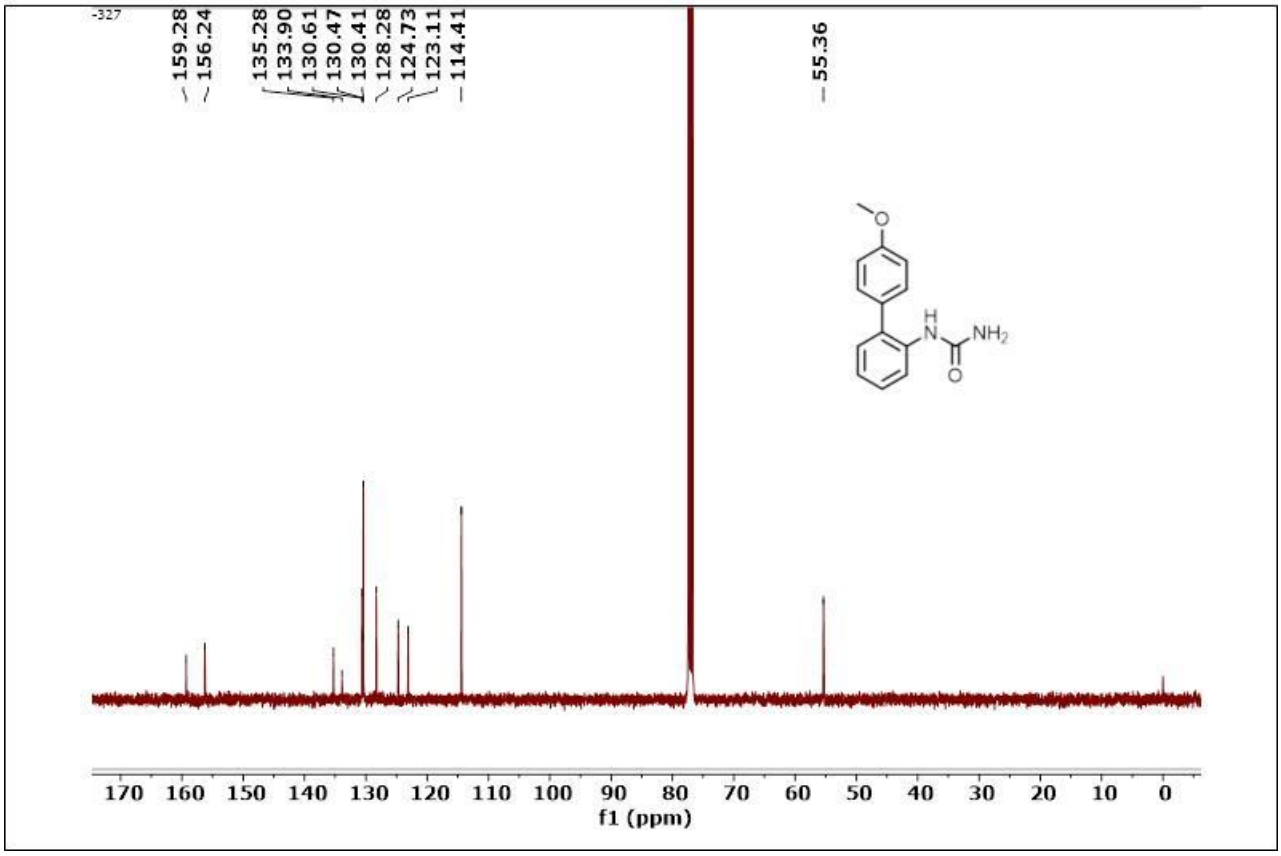
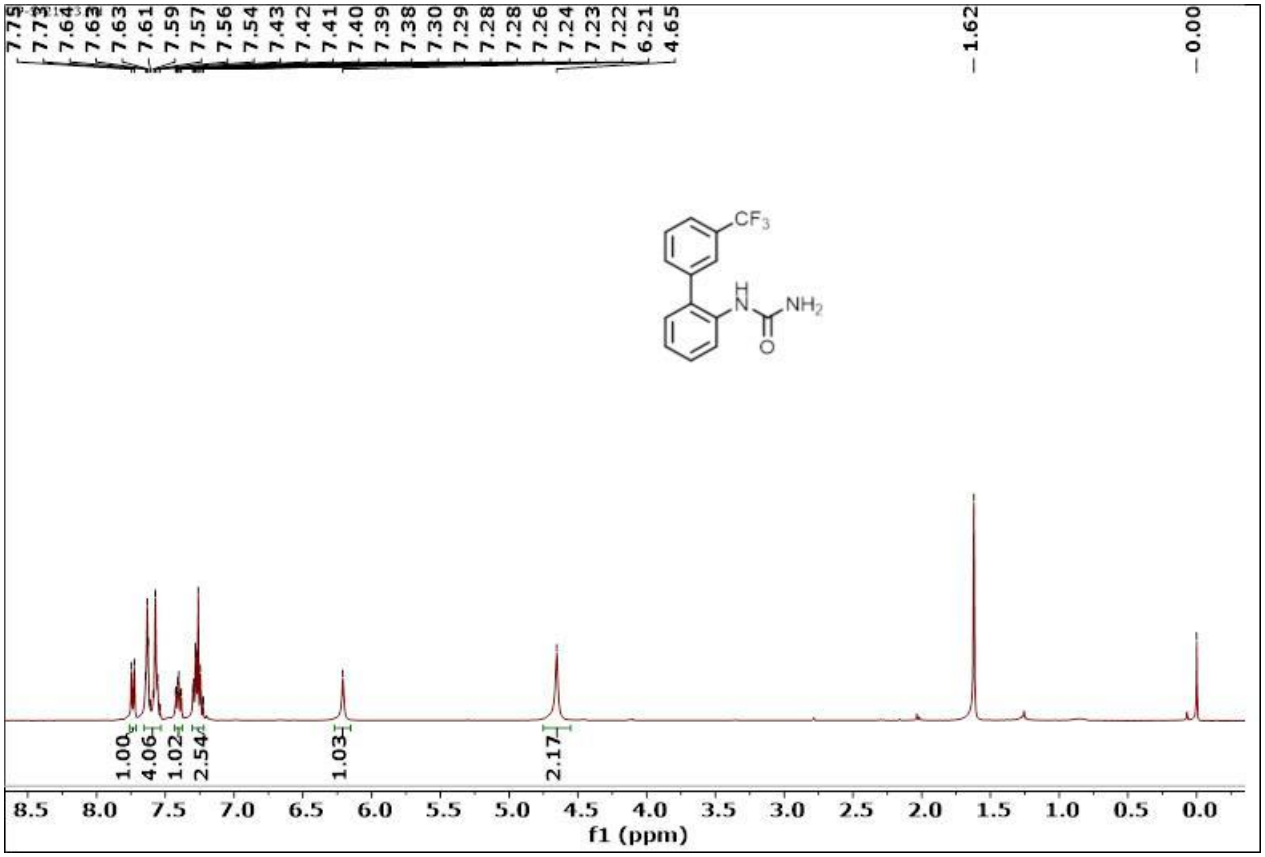
7.77
7.34
7.34
7.32
7.31
7.30
7.29
7.29
7.27
7.26
7.25
7.25
7.20
7.20
7.18
7.18
6.99
6.99
6.98
6.97
6.25
4.63
3.84
1.63
0.00
1.0
1.1
1.0
1.0
1.8
1.0
2.1
1.0
2.0
3.0
f1 (ppm)


159.28
156.24
135.28
133.90
130.61
130.47
130.41
128.28
124.73
123.11
114.41
55.36
f1 (ppm)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7.59
7.57
7.56
7.54
7.43
7.42
7.41
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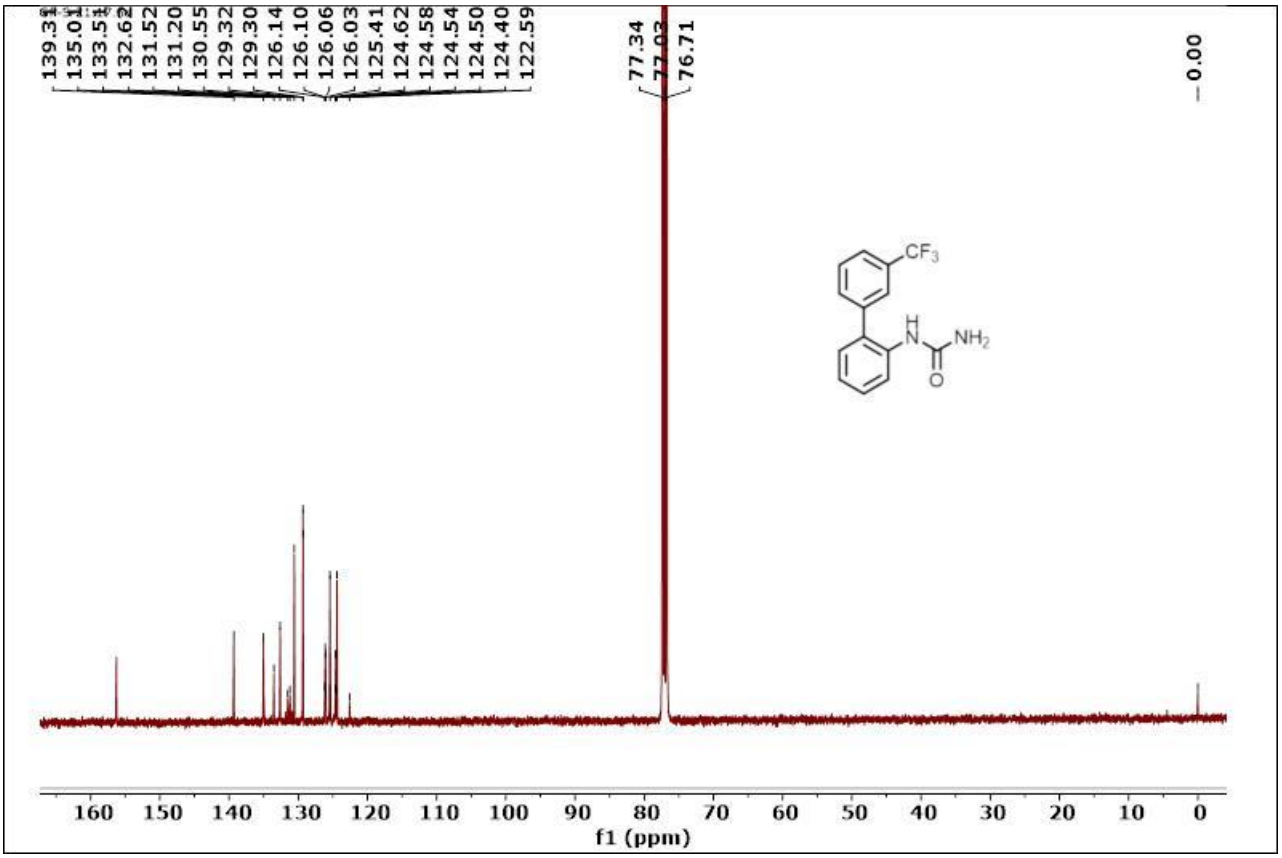
7.39
7.38
7.30
7.29
7.28
7.28
7.26
7.24
7.23
7.22
6.21
4.65
1.62
0.00
CF3
NH2
1.00
4.06
1.02
2.54
1.03
2.17
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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132.62
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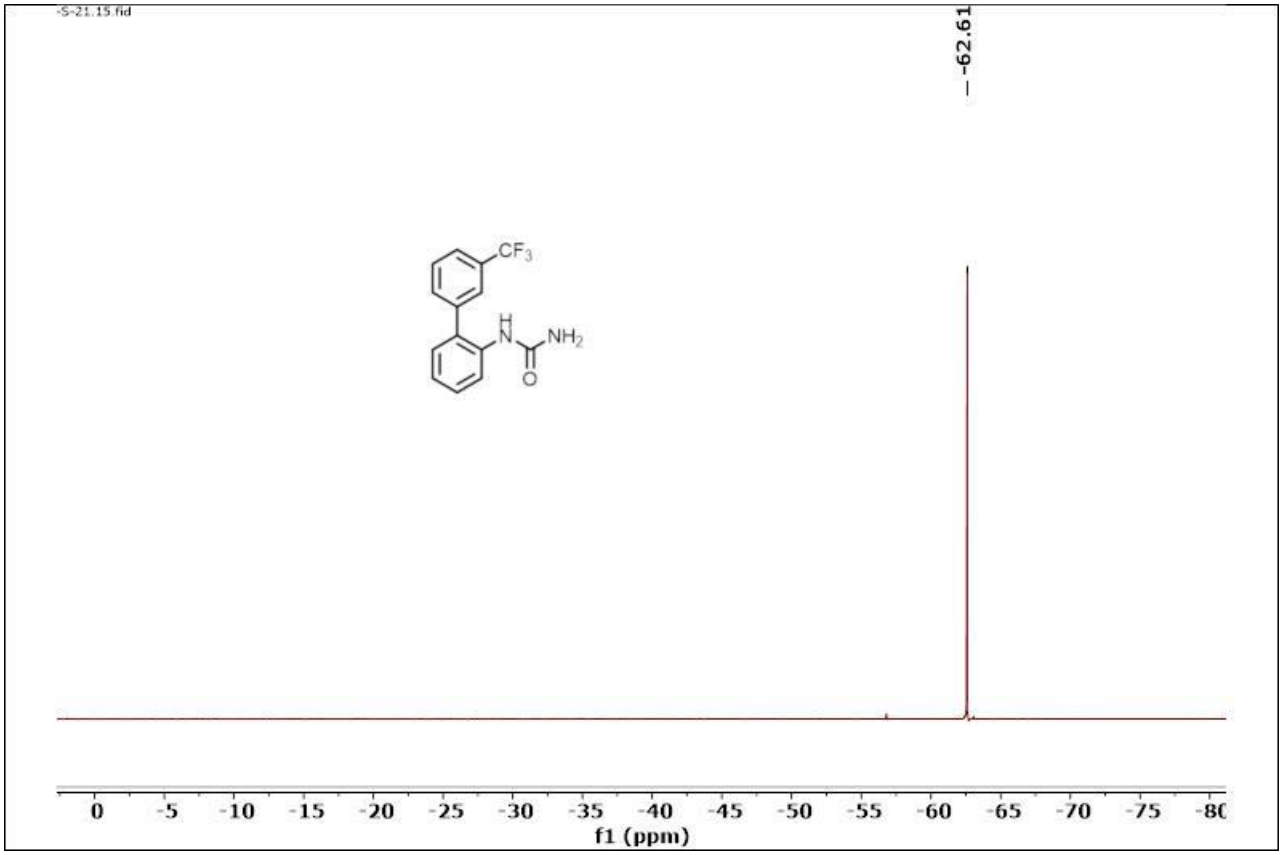
129.32
129.30
126.14
126.10
126.06
126.03
125.41
124.62
124.58
124.54
124.50
124.40
122.59
77.34
77.03
76.71
0.00
CF3
NH2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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N
NH2
O
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-5
-10
-15
-20
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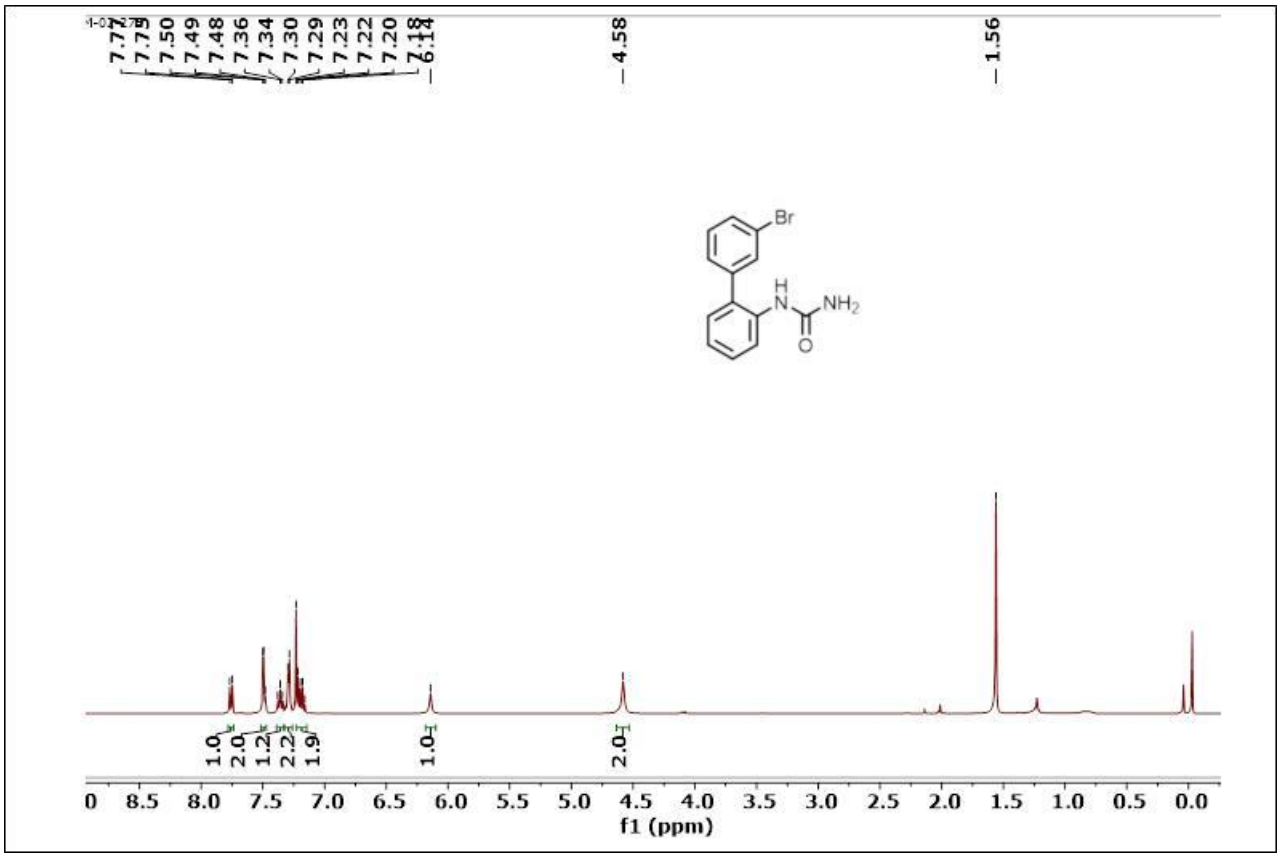
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
f1 (ppm)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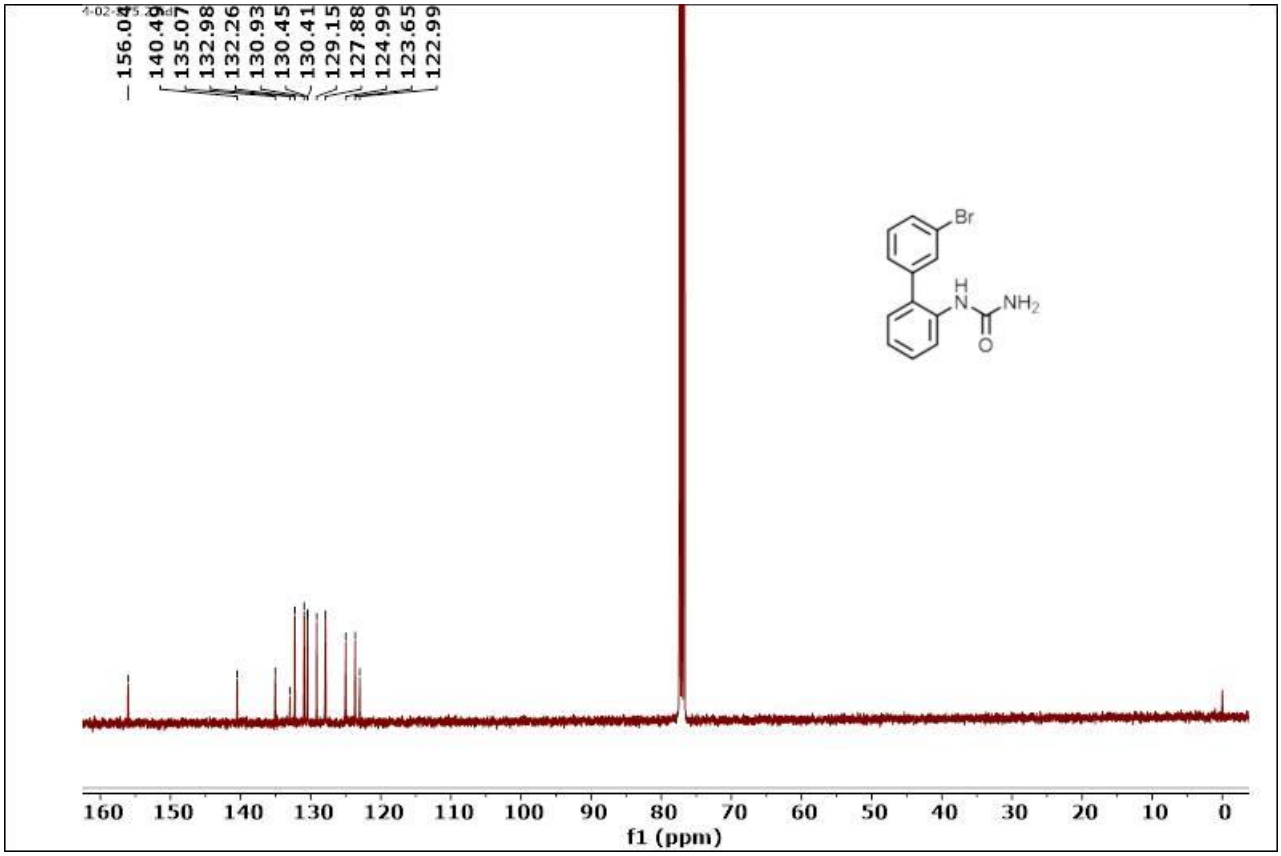
7.34
7.30
7.29
7.23
7.22
7.20
7.18
6.14
4.58
1.56
Br
H
N
NH2
O
1.0
2.0
1.2
2.2
1.9
1.0
2.0
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.49
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132.26
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130.45
130.41
129.15
127.88
124.99
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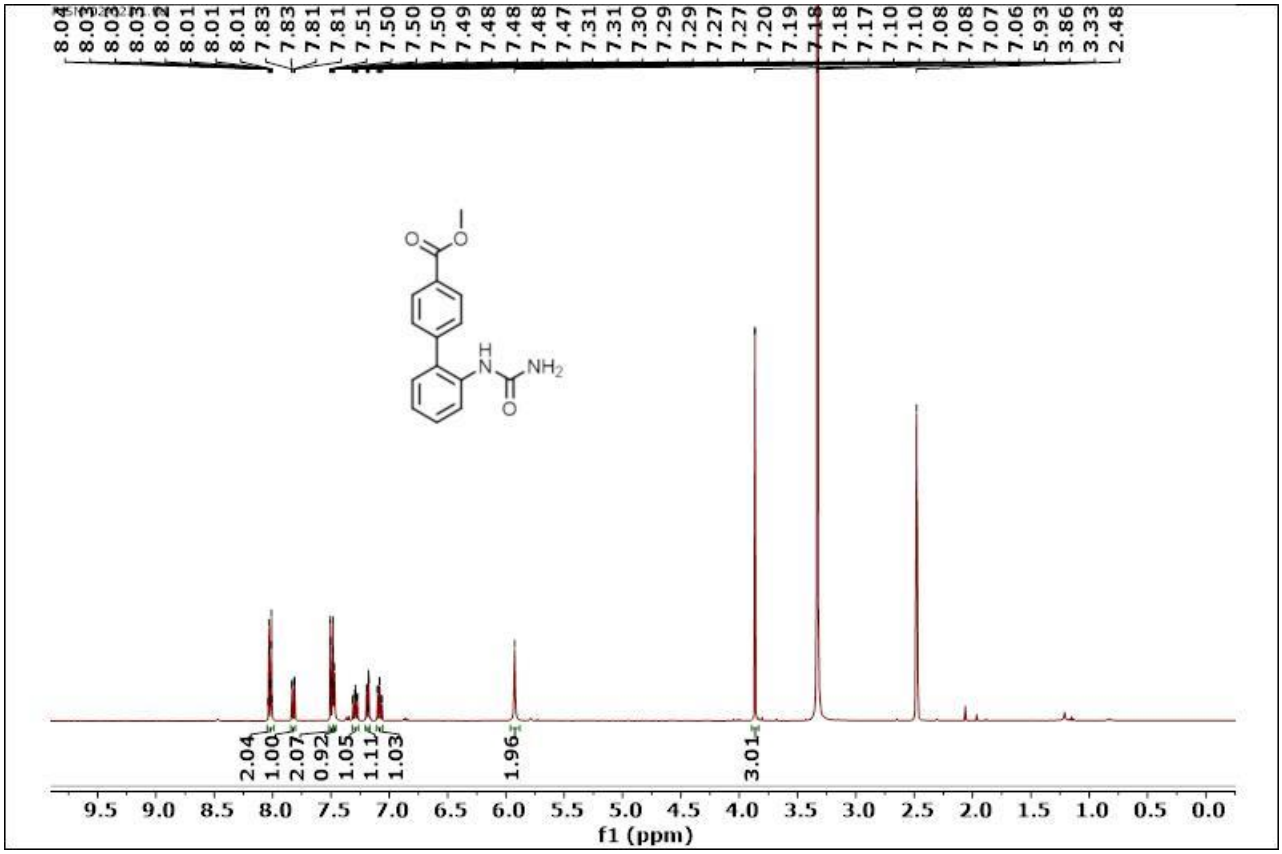
122.99
Br
H
N
NH2
O
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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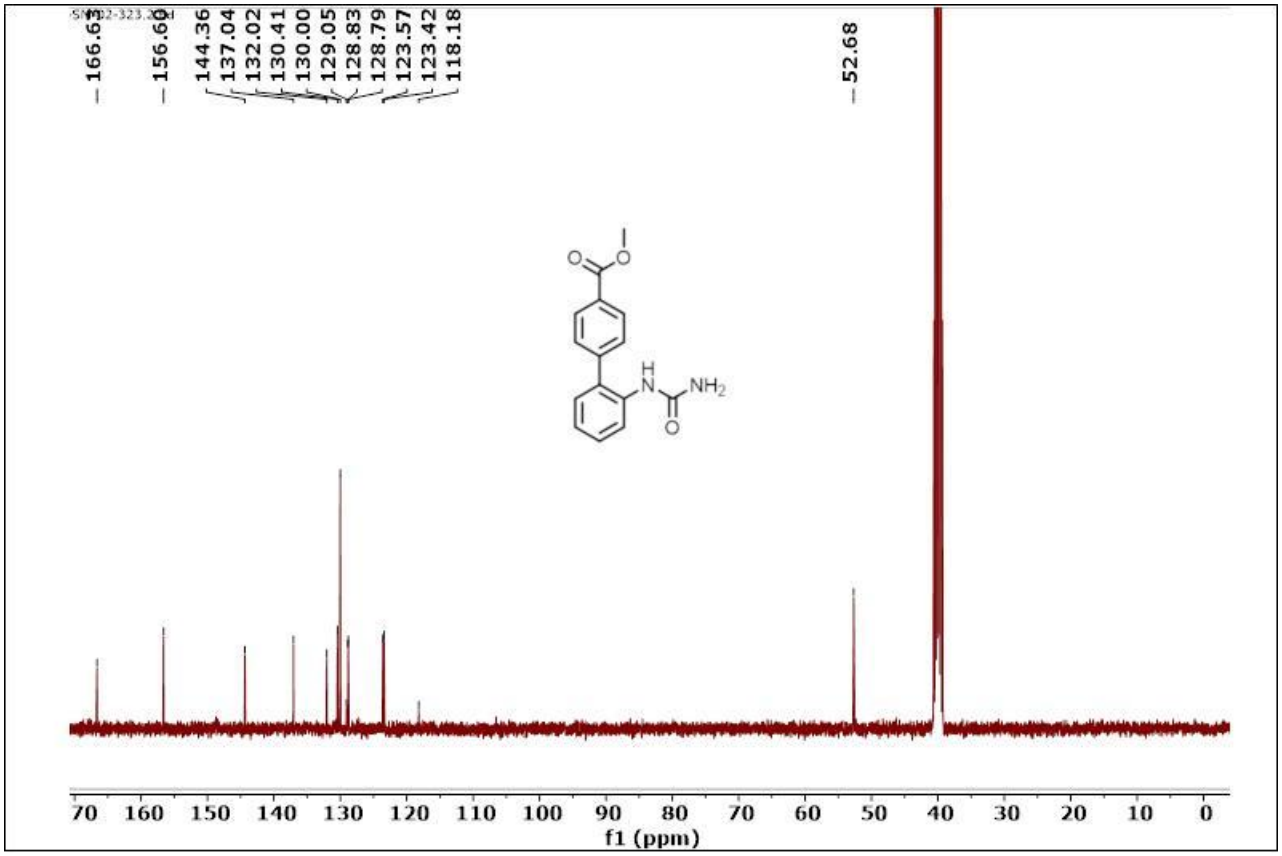
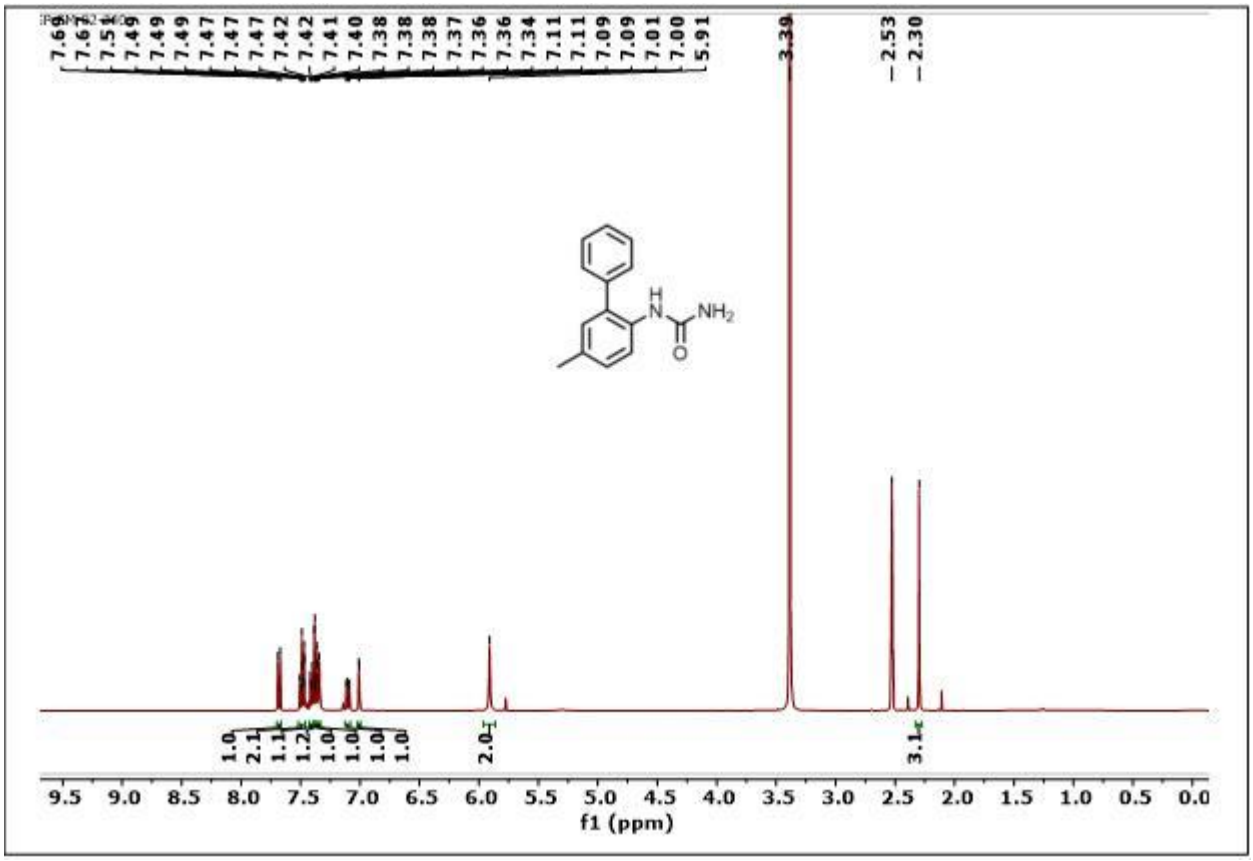
2.04 1.00 2.07 0.92 1.05 1.11 1.03 1.96 3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
NH2


166.63
156.60
144.36
137.04
132.02
130.41
130.00
129.05
128.83
128.79
123.57
123.42
118.18
52.68
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
NH2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7.49
7.49
7.47
7.47
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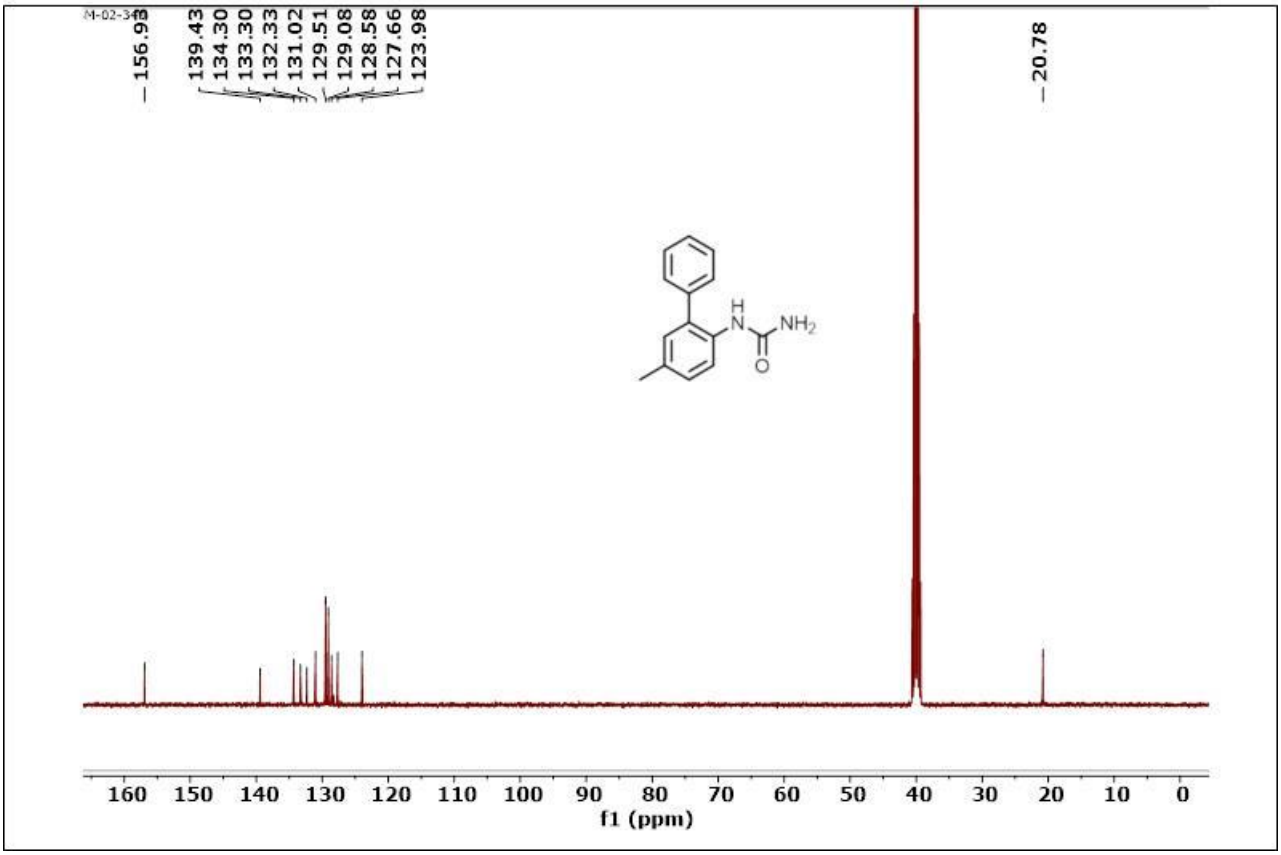
7.42
7.41
7.40
7.38
7.38
7.38
7.37
7.36
7.36
7.34
7.11
7.11
7.09
7.09
7.01
7.00
5.91
3.39
2.53
2.30
NH2
1.0
2.1
1.1
1.2
1.0
1.0
1.0
1.0
2.0
3.1
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

go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139.43
134.30
133.30
132.33
131.02
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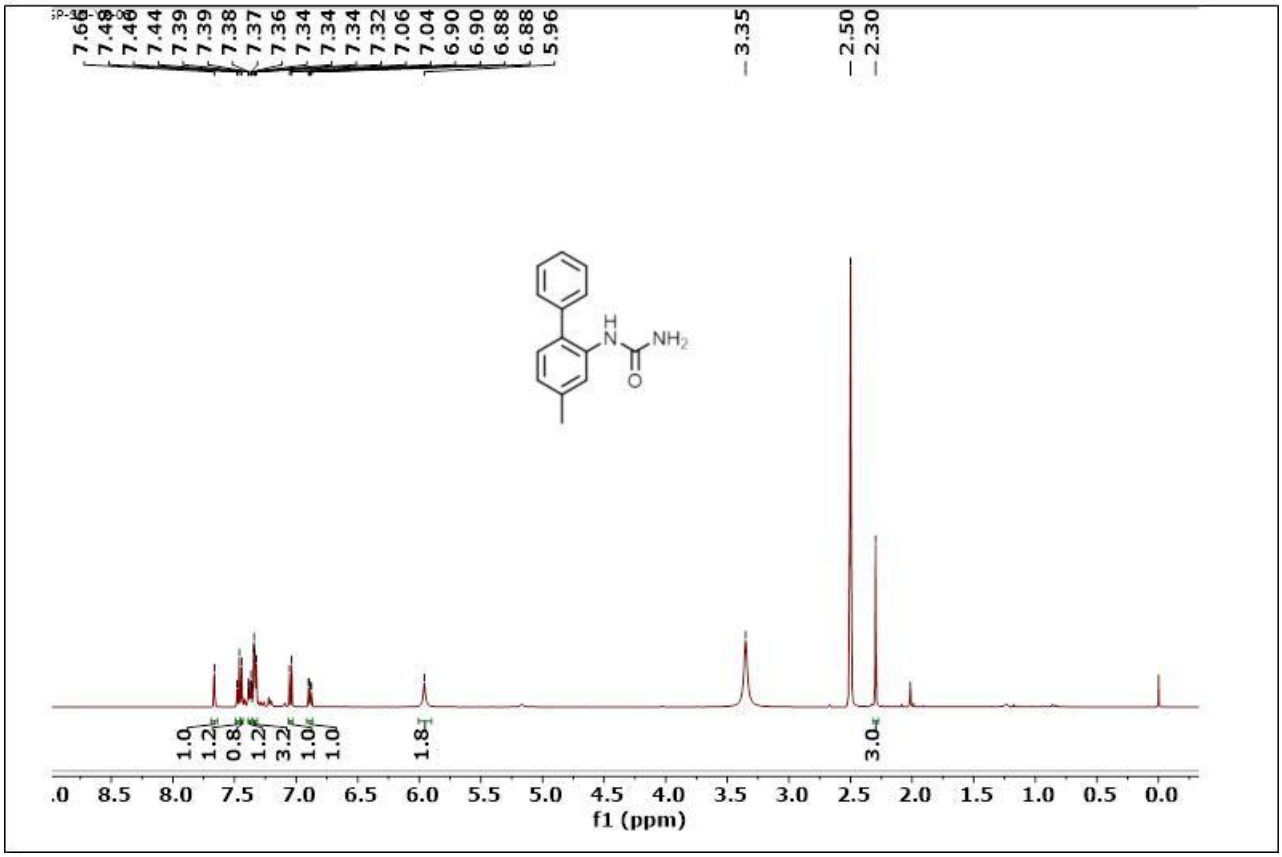
129.08
128.58
127.66
123.98
20.78
NH2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.48
7.48
7.44
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7.39
7.38
7.37
7.36
7.34
7.34
7.34
7.32
7.06
7.04
6.90
6.90
6.88
6.88
5.96
3.35
2.50
2.30
NH2
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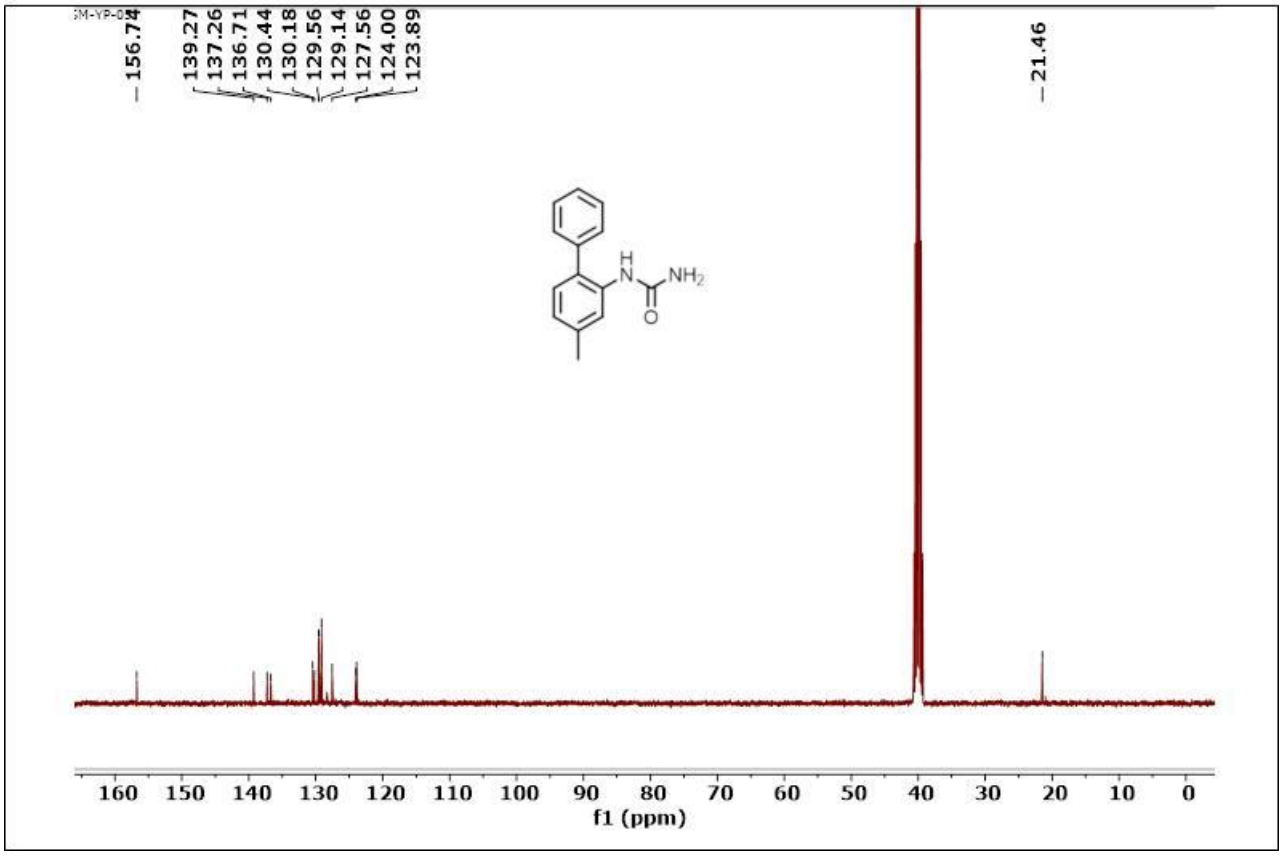
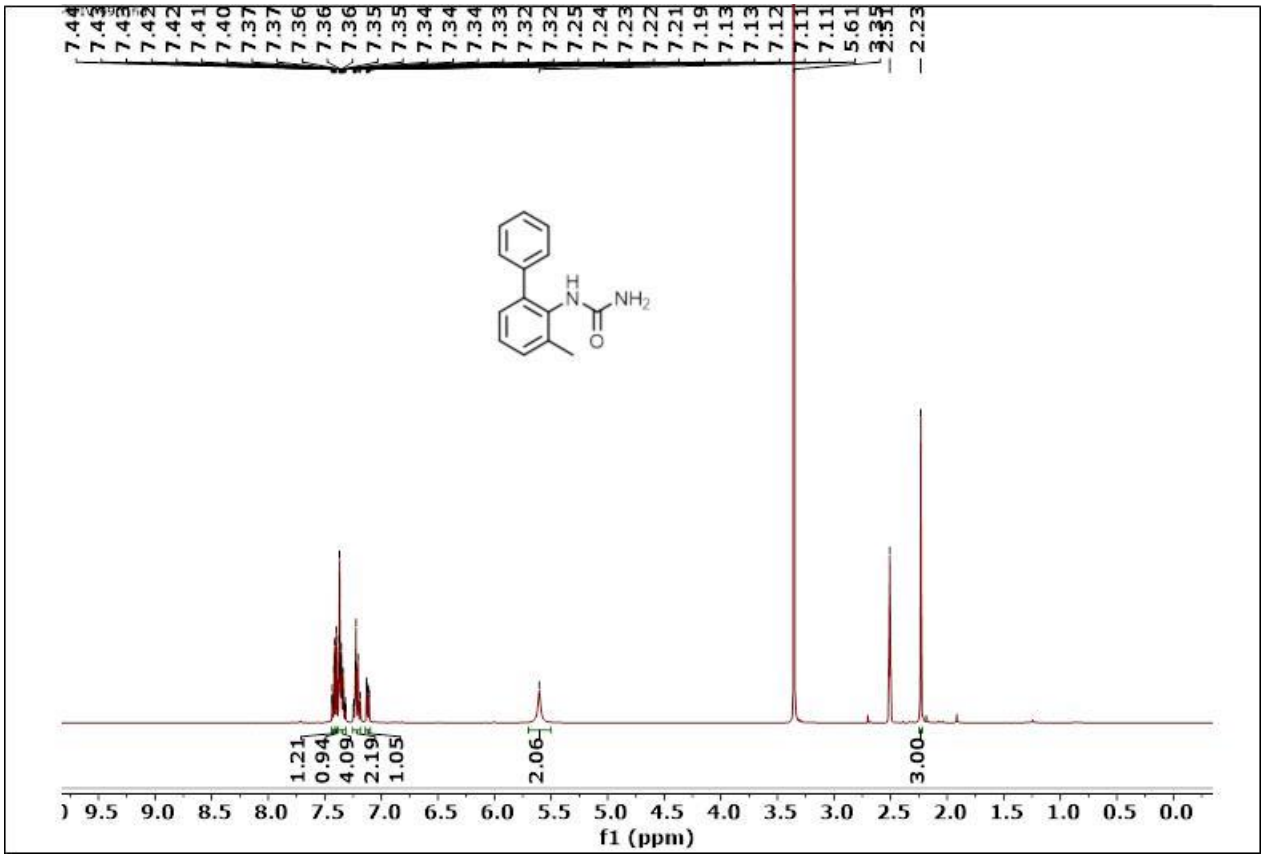
1.2
0.8
1.2
3.2
1.0
1.0
1.8
3.0
f1 (ppm)


156.74
139.27
137.26
136.71
130.44
130.18
129.56
129.14
127.56
124.00
123.89
21.46
NH2
f1 (ppm)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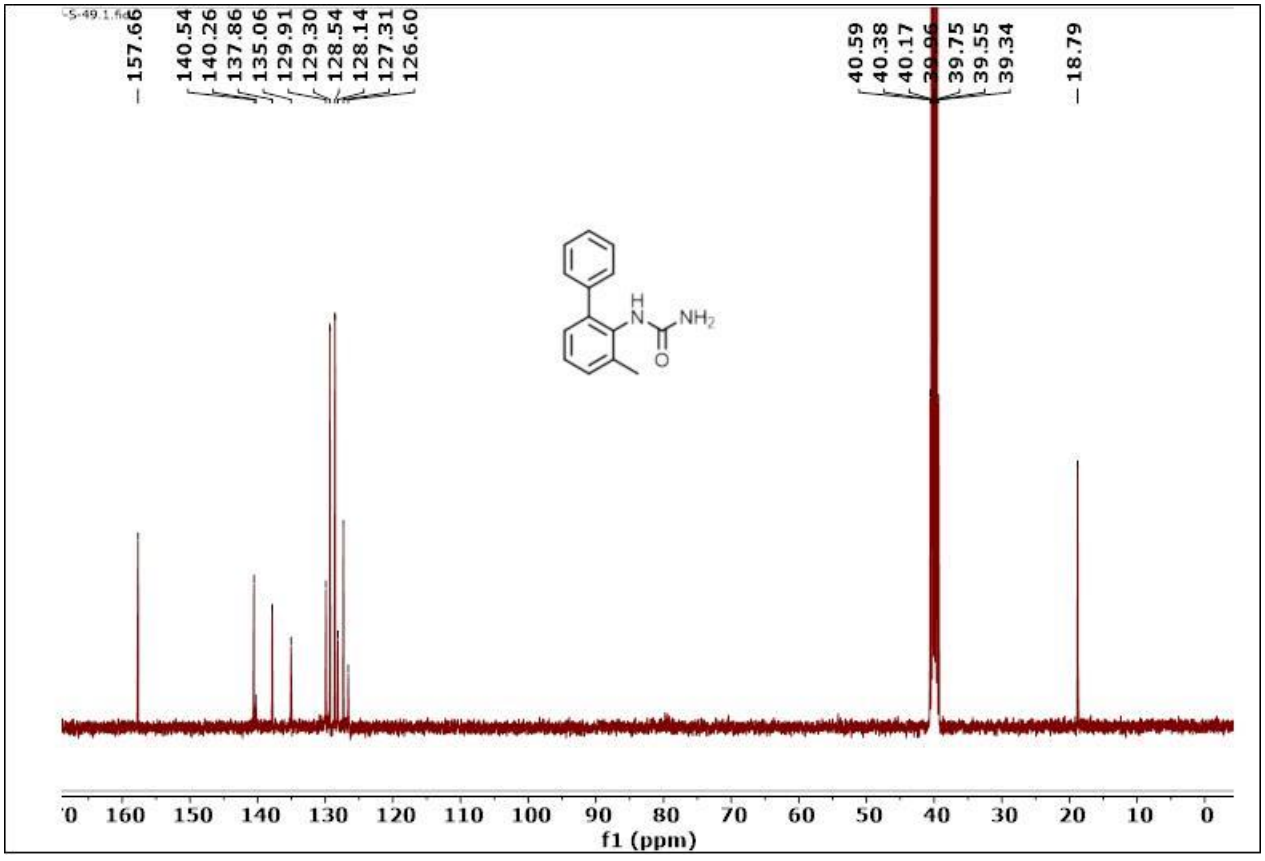
7.43
7.43
7.42
7.42
7.41
7.40
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.25
7.24
7.23
7.22
7.21
7.19
7.13
7.13
7.12
7.11
7.11
5.61
2.31
2.23
NH2
1.21
0.94
4.09
2.19
1.05
2.06
3.00
f1 (ppm)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140.54
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128.54
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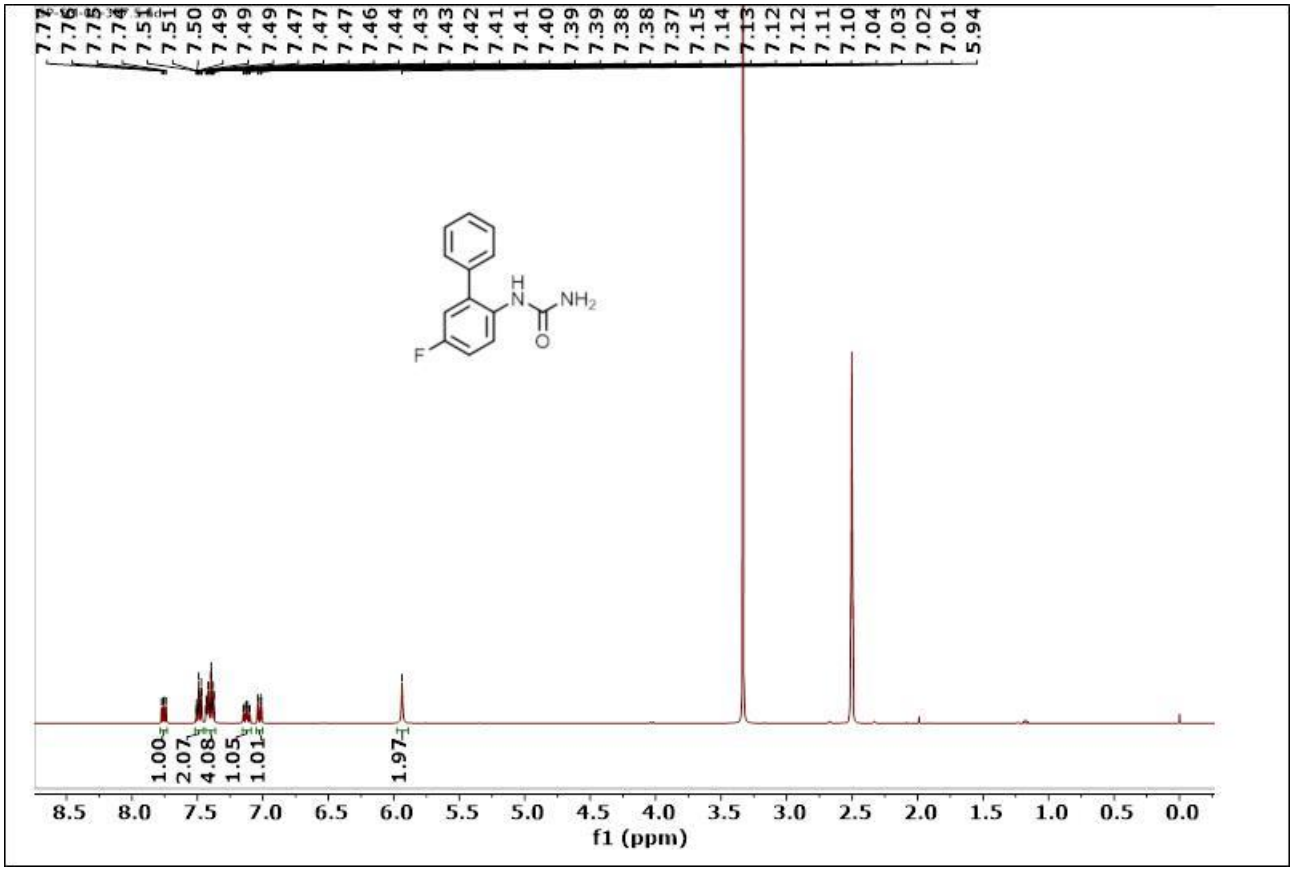
40.59
40.38
40.17
39.75
39.55
39.34
18.79
NH2
f1 (ppm)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7.76
7.75
7.74
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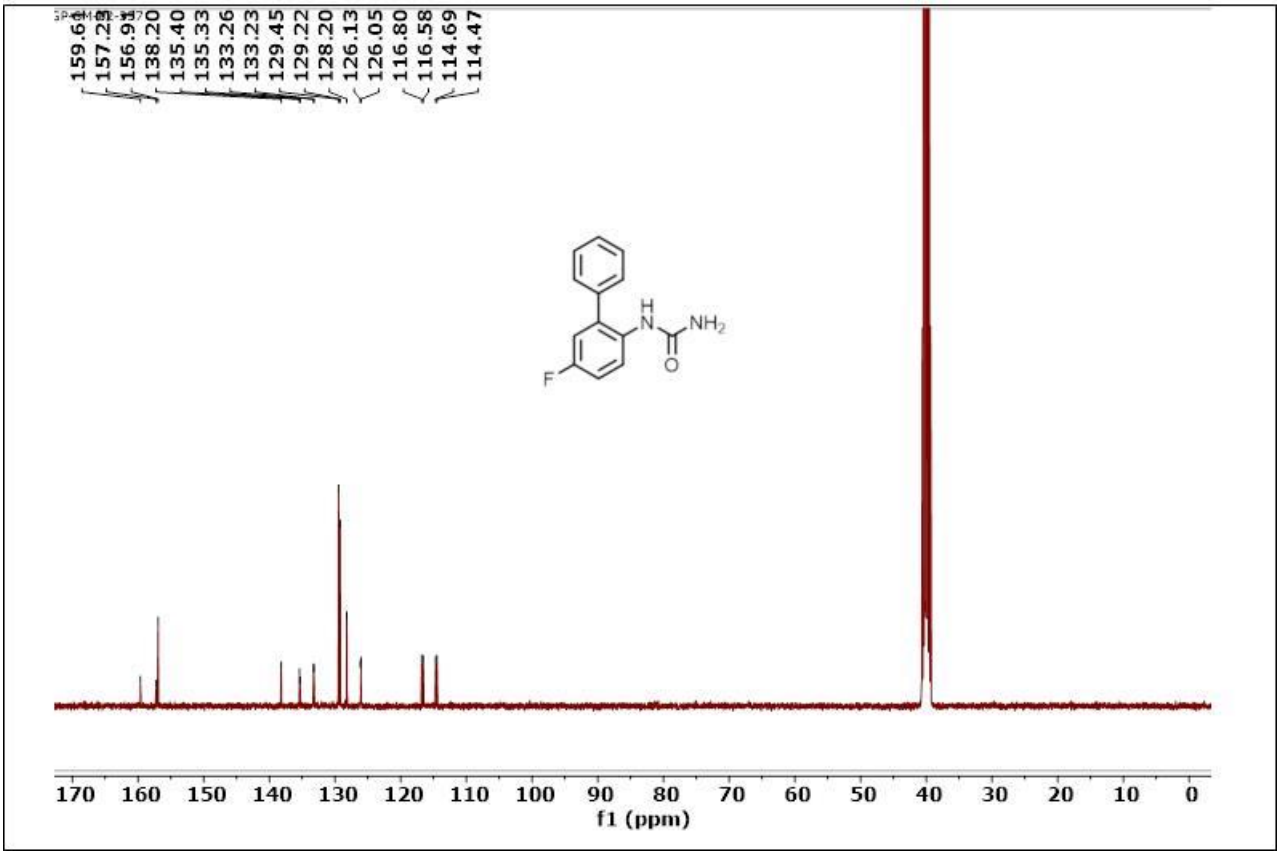
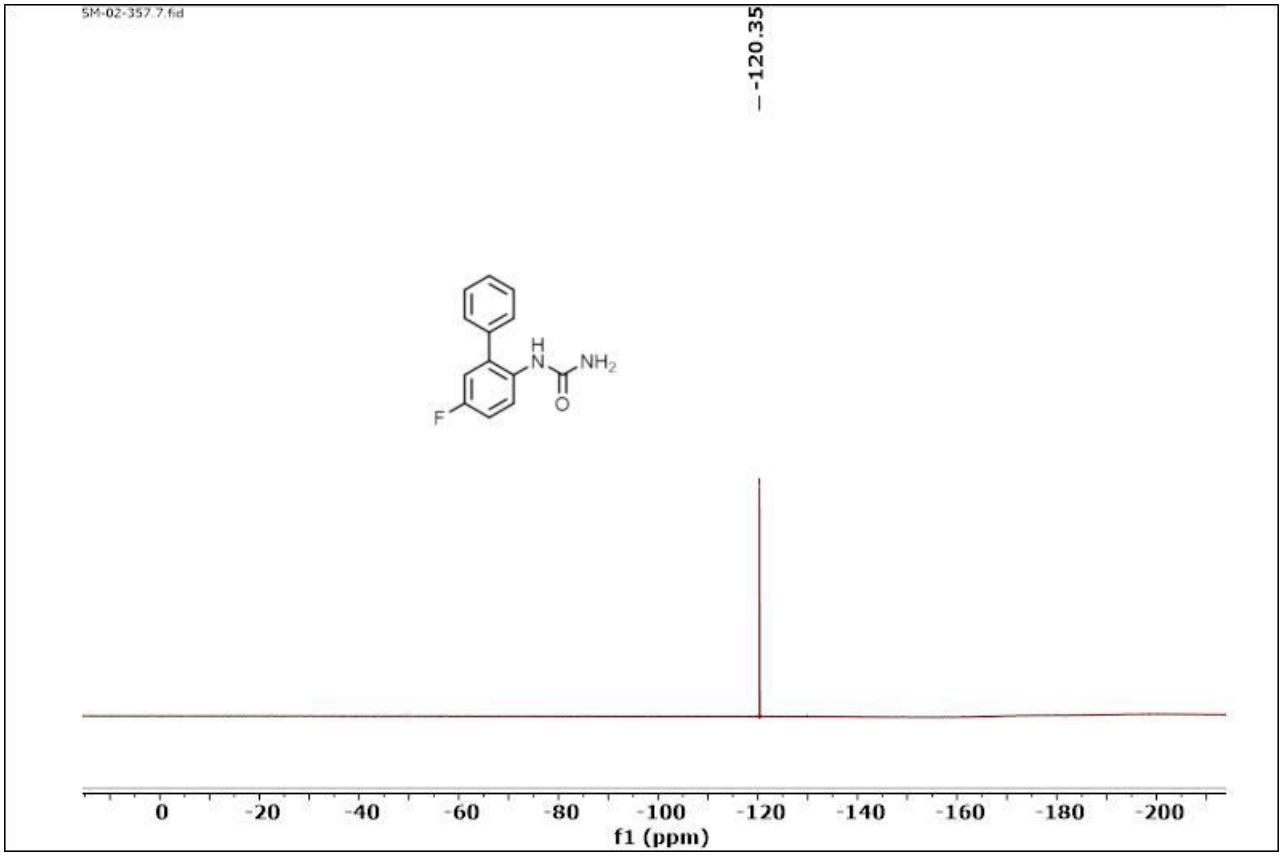
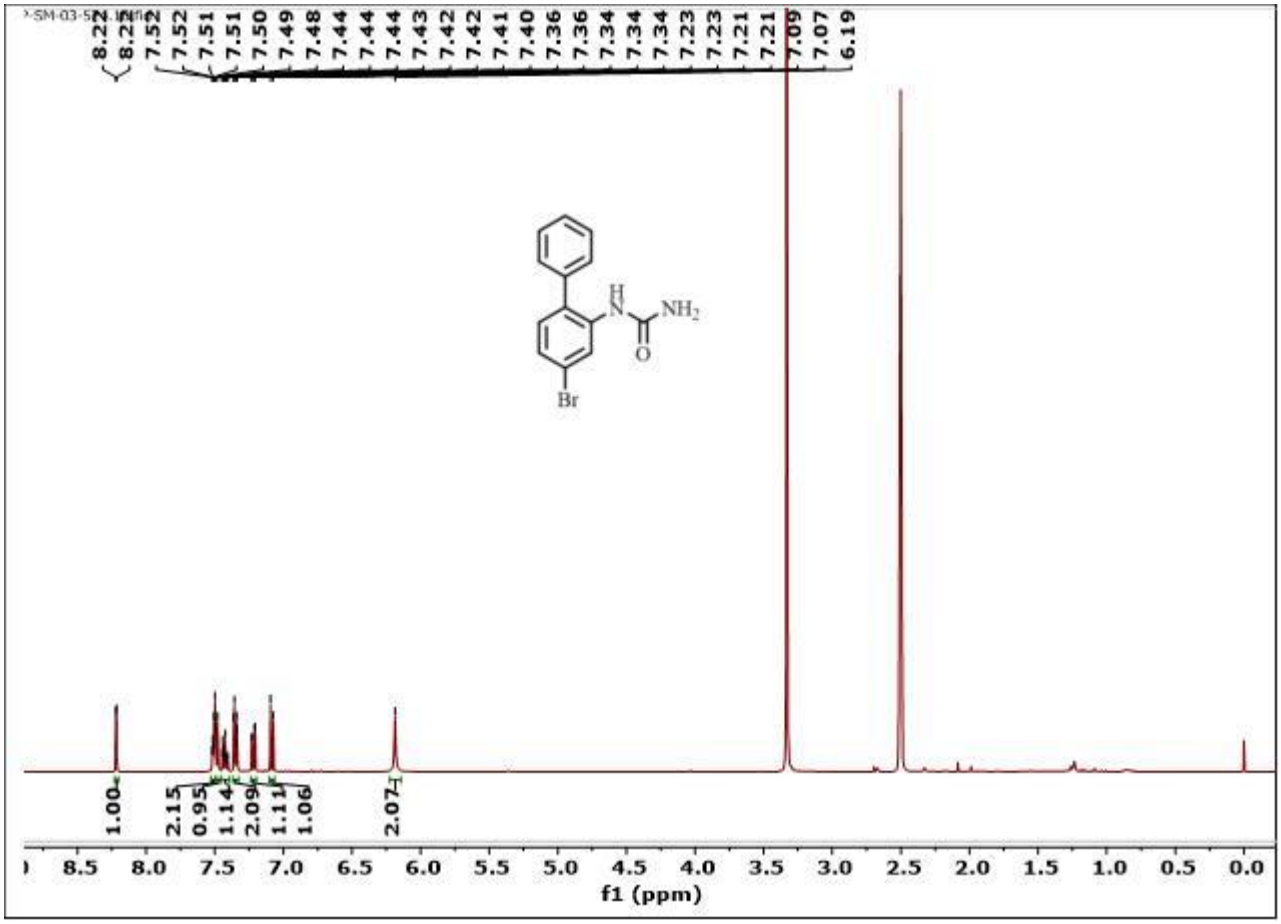
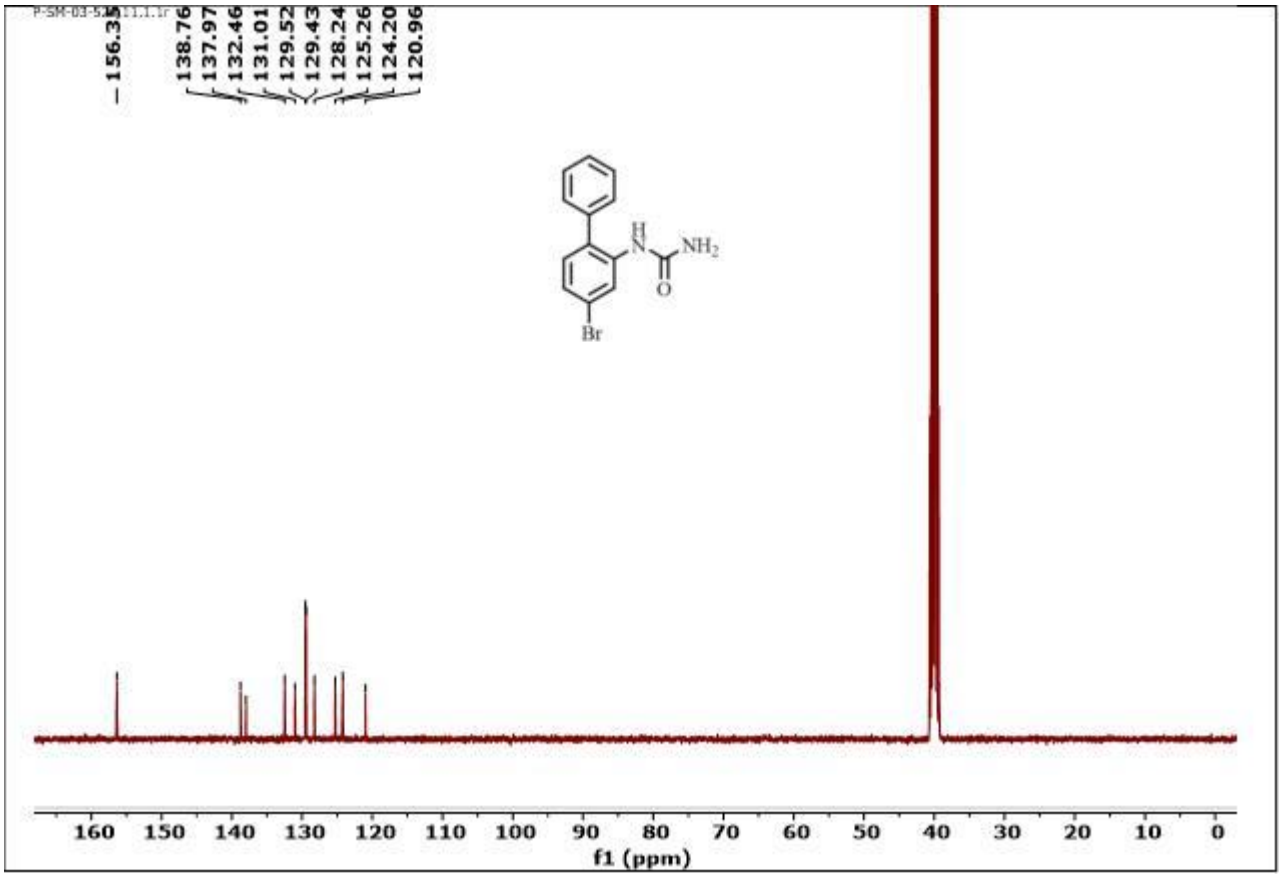
7.51
7.50
7.49
7.49
7.49
7.47
7.47
7.47
7.46
7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.15
7.14
7.13
7.12
7.12
7.11
7.10
7.04
7.03
7.02
7.01
5.94
1.00
2.07
4.08
1.05
1.01
1.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
NH2
F


159.61
157.23
156.93
138.20
135.40
135.33
133.26
133.23
129.45
129.22
128.20
126.13
126.05
116.80
116.58
114.69
114.47
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
NH2
F


SM-02-357.7.fid
-120.35
H
N
NH2
O
F
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)


8.22
8.22
7.52
7.52
7.51
7.51
7.50
7.49
7.48
7.44
7.44
7.44
7.43
7.42
7.42
7.41
7.40
7.36
7.36
7.34
7.34
7.34
7.23
7.21
7.21
7.09
7.07
6.19
1.00
2.15
0.95
1.14
2.09
1.11
1.06
2.07
f1 (ppm)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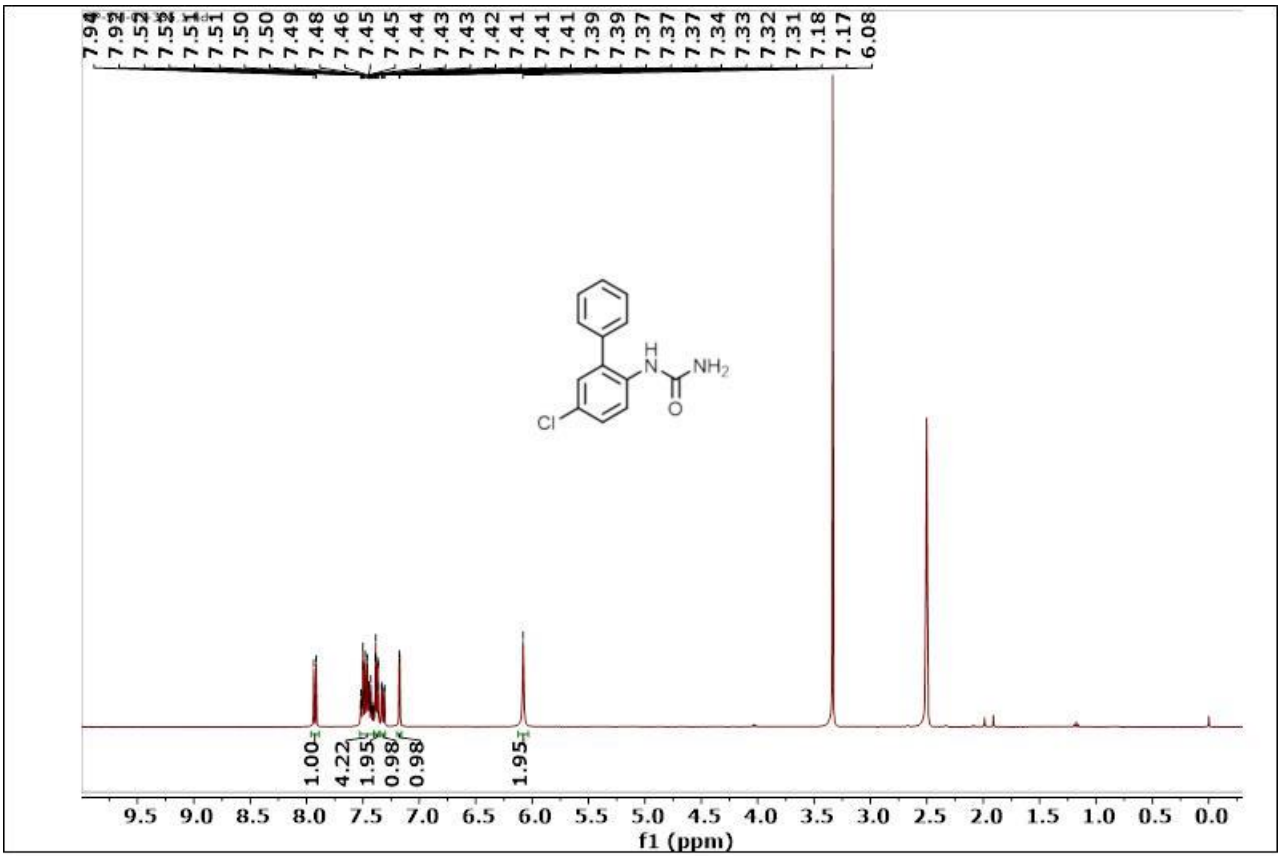
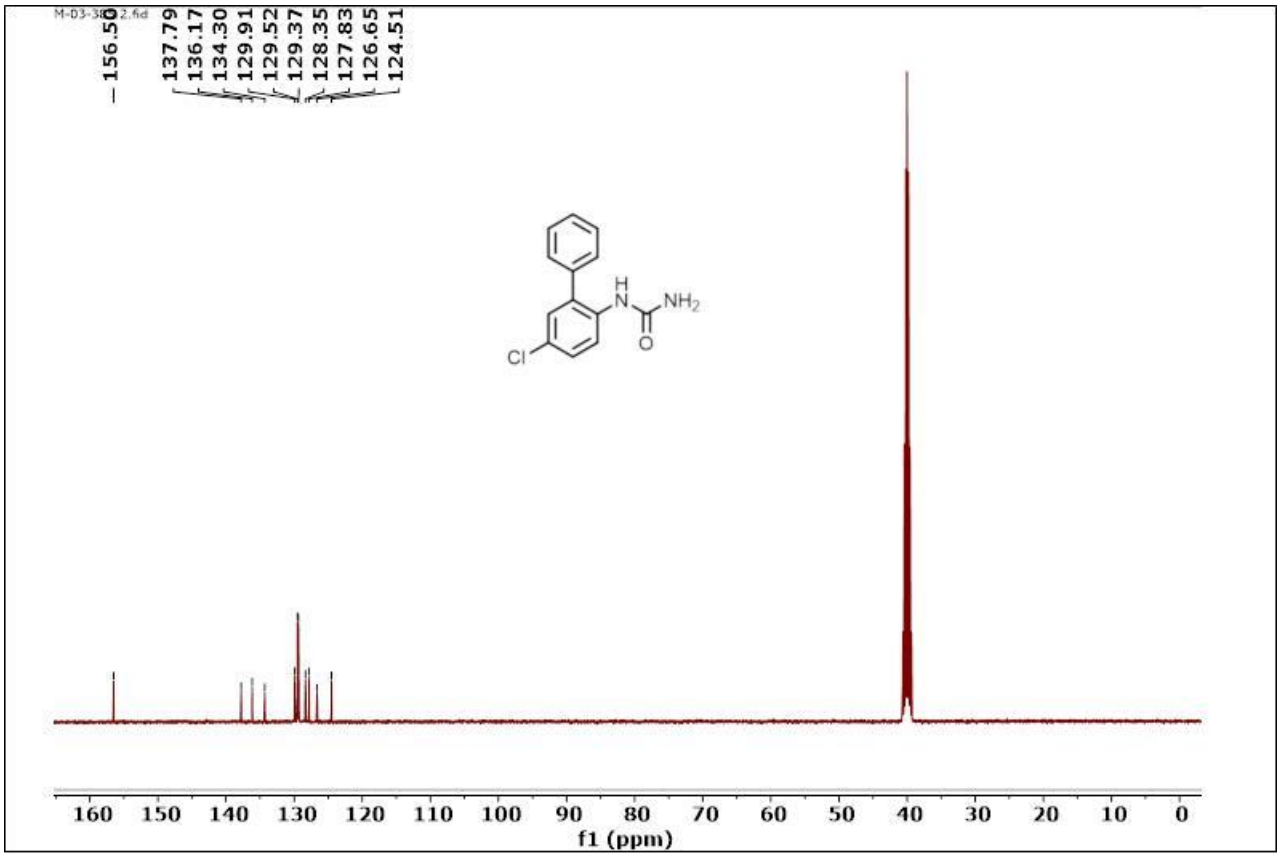
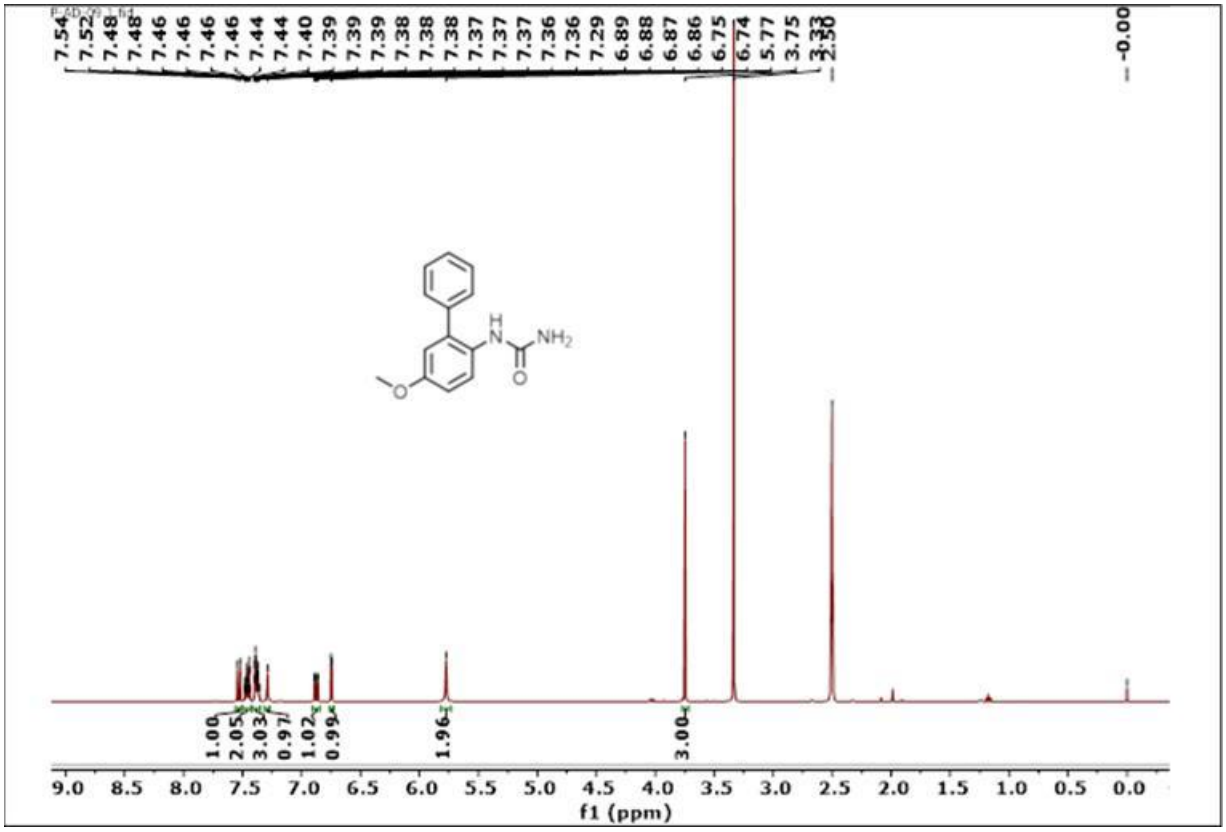
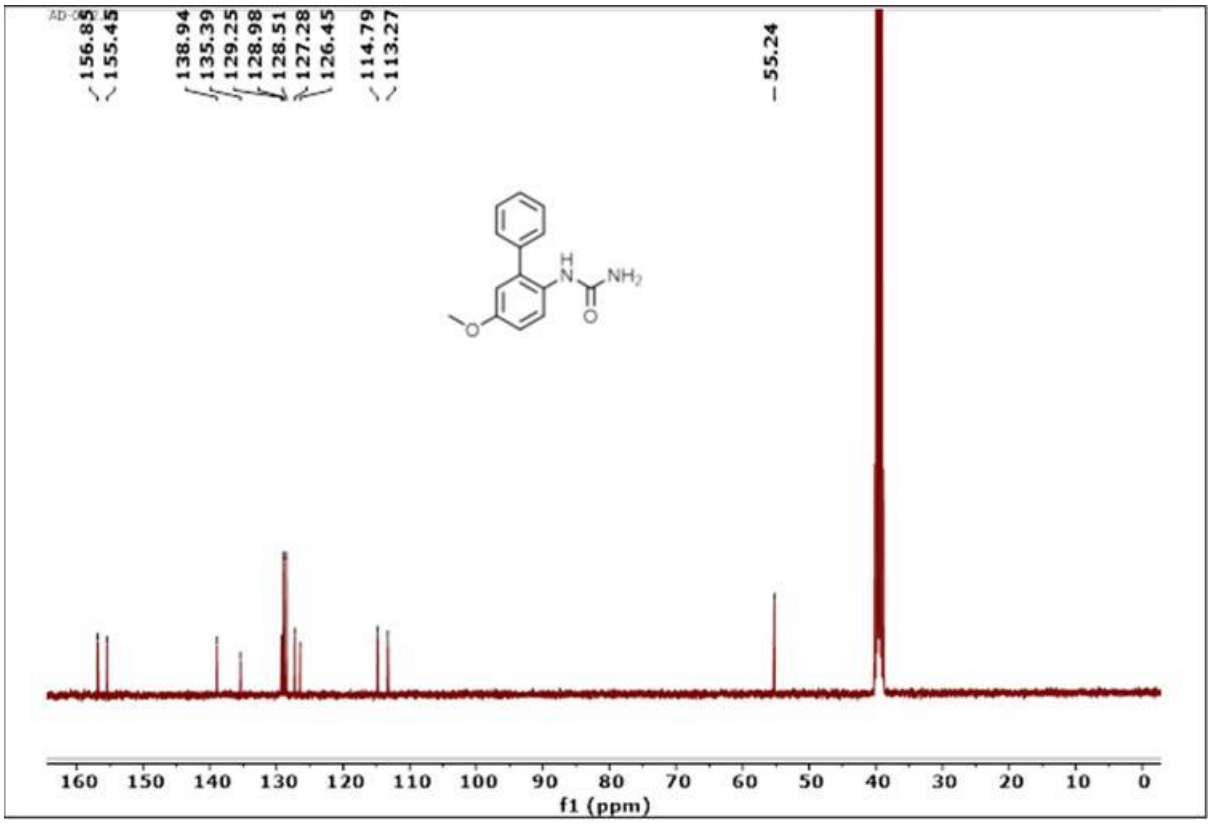
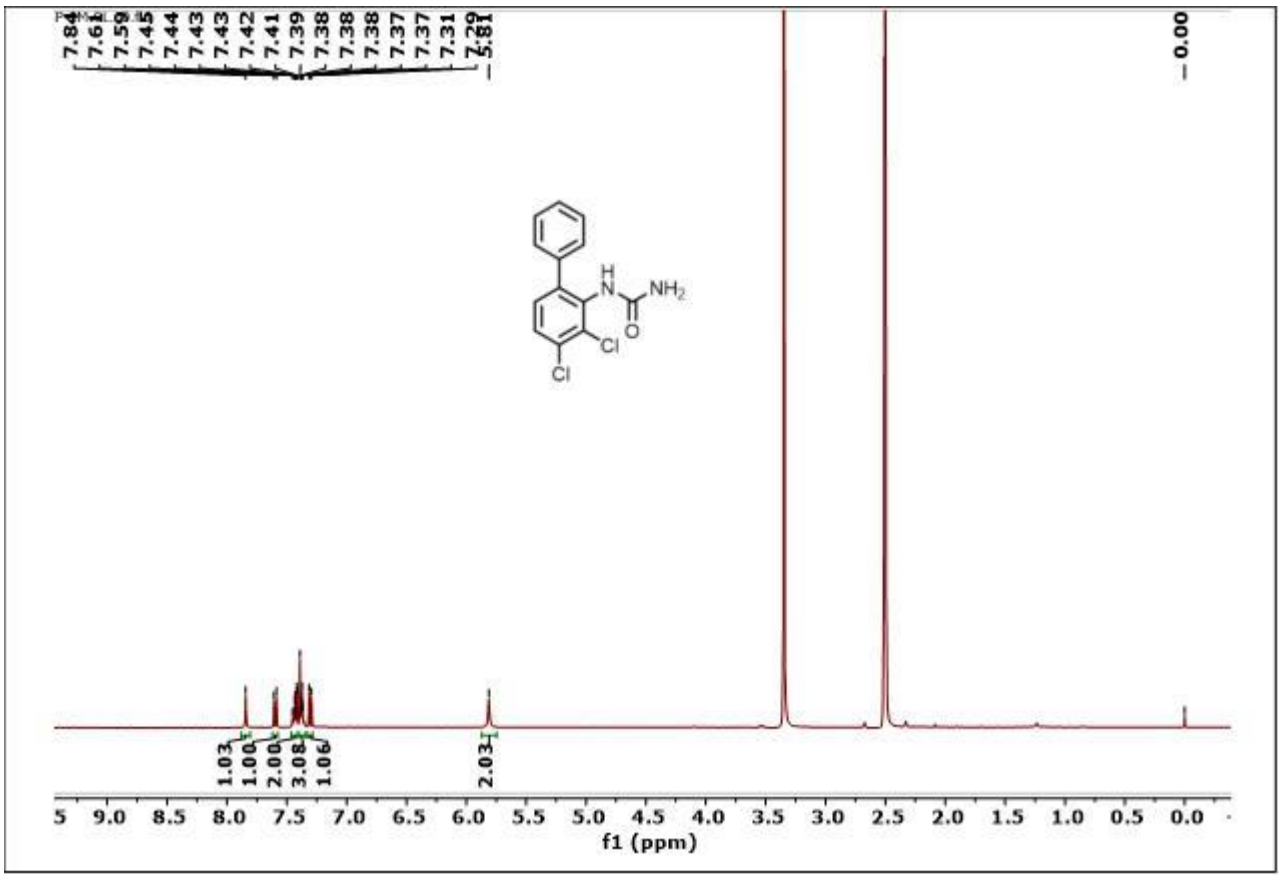
138.76
137.97
132.46
131.01
129.52
129.43
128.24
125.26
124.20
120.96
f1 (ppm)


7.94
7.92
7.52
7.51
7.50
7.49
7.48
7.46
7.45
7.44
7.43
7.42
7.41
7.39
7.37
7.34
7.33
7.32
7.31
7.18
7.17
6.08
1.00
4.22
1.95
0.98
0.98
1.95
Cl
NH2
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)


156.56
137.79
136.17
134.30
129.91
129.52
129.37
128.35
127.83
126.65
124.51
Cl
NH2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.54 7.52 7.48 7.48 7.46 7.46 7.46 7.46 7.44 7.44 7.40 7.39 7.39 7.39 7.38 7.38 7.38 7.37 7.37 7.37 7.36 7.29 6.89 6.88 6.87 6.86 6.75 6.74 5.77 3.75 3.33 2.50 -0.00
1.00 2.05 3.03 0.97 1.02 0.99 1.96 3.00
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)
H
N
NH2
O
O


156.85 155.45 138.94 135.39 129.25 128.98 128.51 127.28 126.45 114.79 113.27 55.24
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
H
N
NH2
O
O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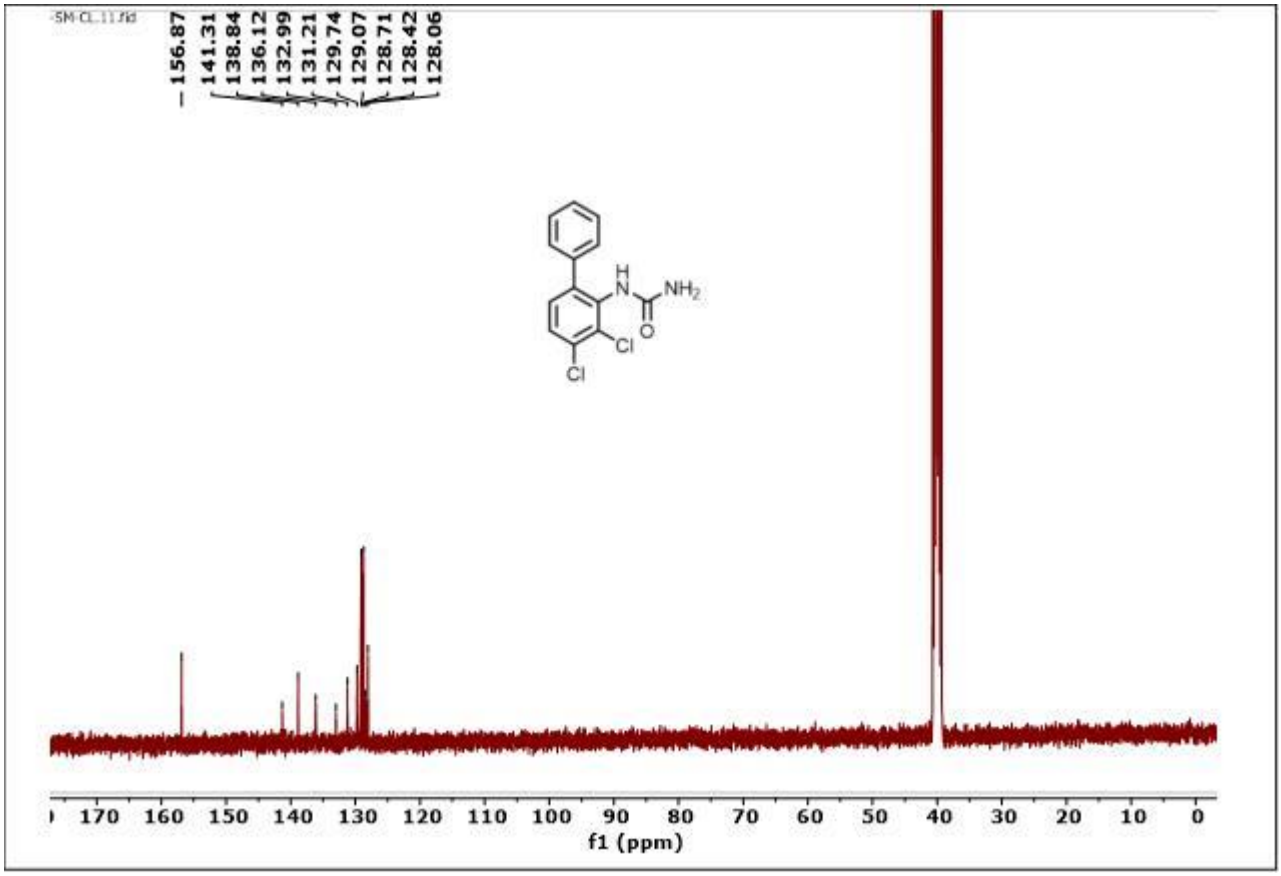
7.61
7.59
7.45
7.44
7.43
7.43
7.42
7.41
7.39
7.38
7.38
7.38
7.37
7.37
7.31
5.81
0.00
NH2
Cl
Cl
1.03
1.00
2.00
3.08
1.06
2.03
f1 (ppm)


156.87
141.31
138.84
136.12
132.99
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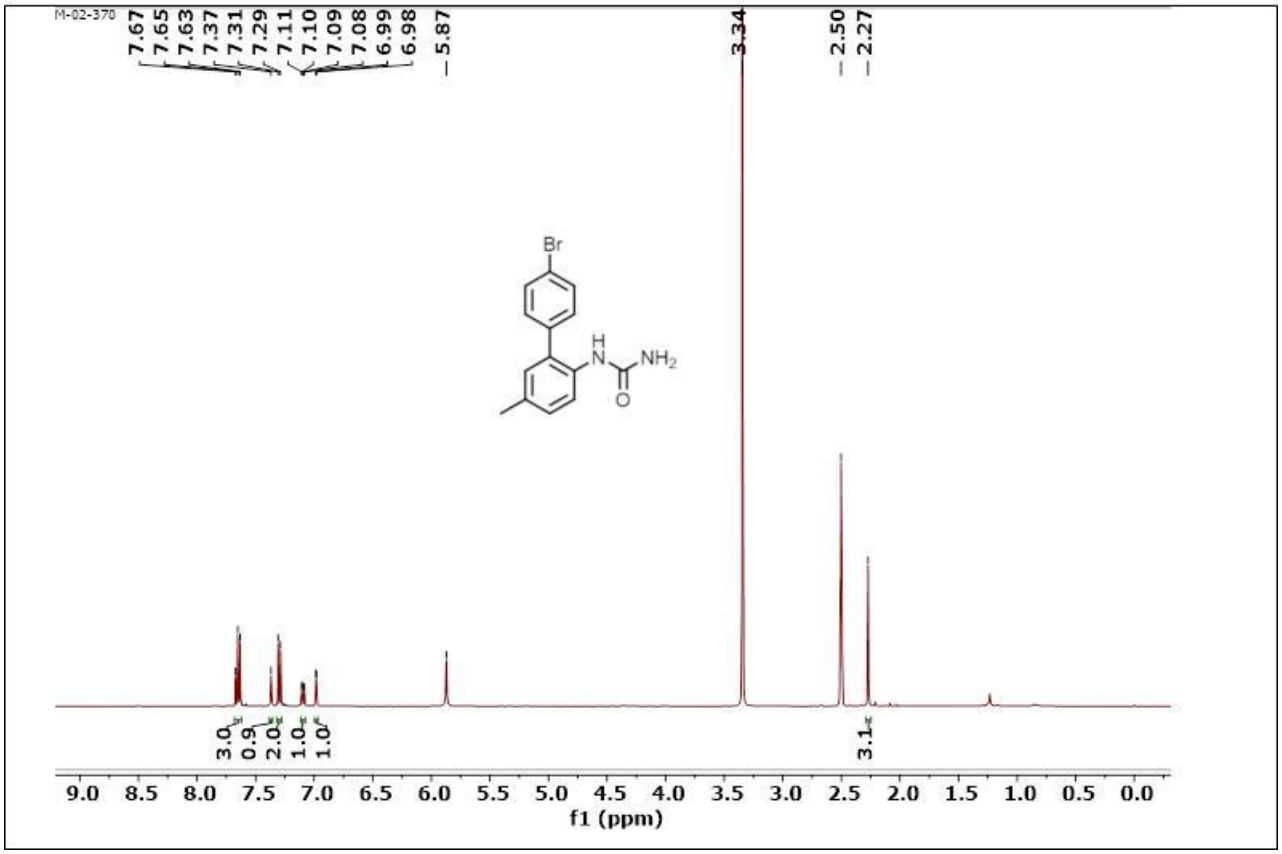
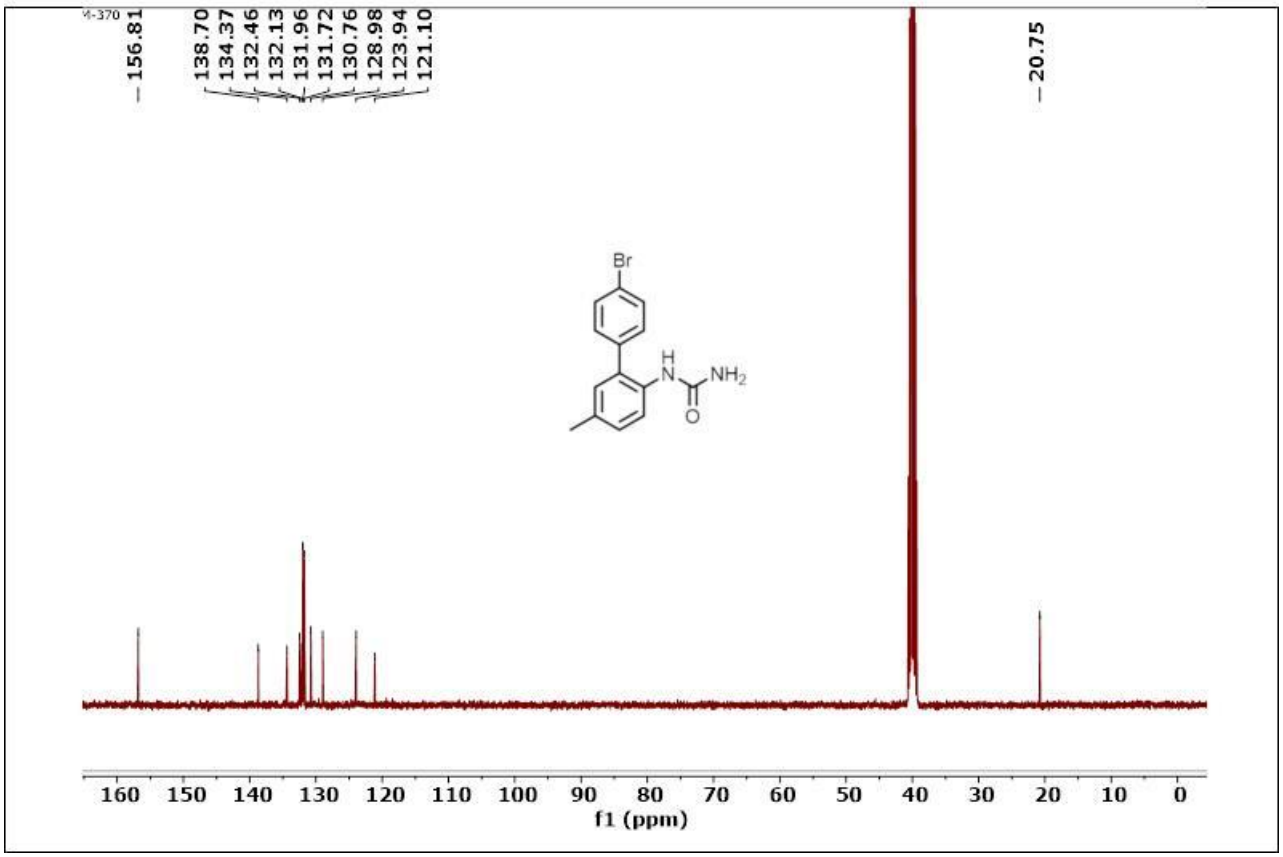
129.74
129.07
128.71
128.42
128.06
NH2
Cl
Cl
f1 (ppm)


M-02-370
7.67
7.65
7.63
7.37
7.31
7.29
7.11
7.10
7.09
7.08
6.99
6.98
5.87
3.34
2.50
2.27
Br
NH2
3.0
0.9
2.0
1.0
1.0
3.1
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)


M-370
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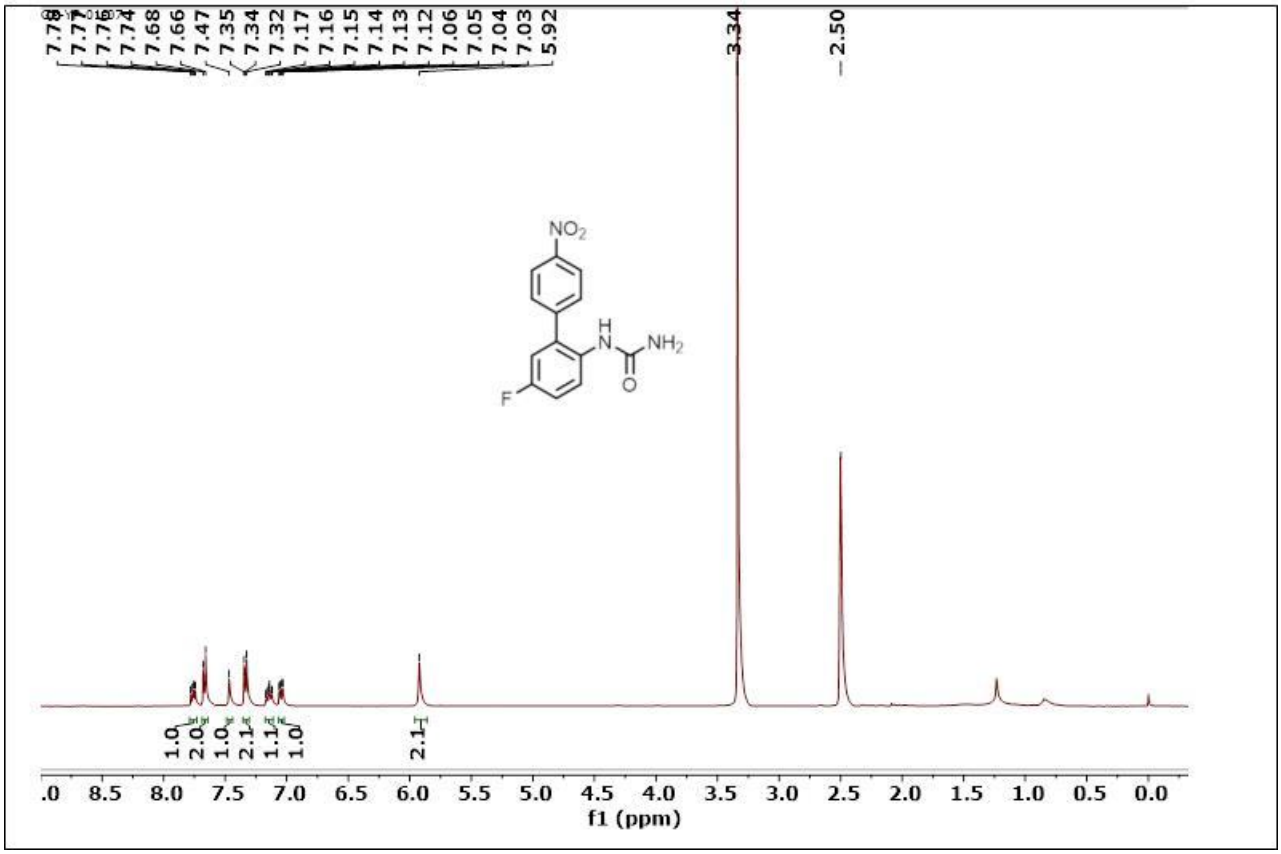
134.37
132.46
132.13
131.96
131.72
130.76
128.98
123.94
121.10
20.75
Br
NH2
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.77
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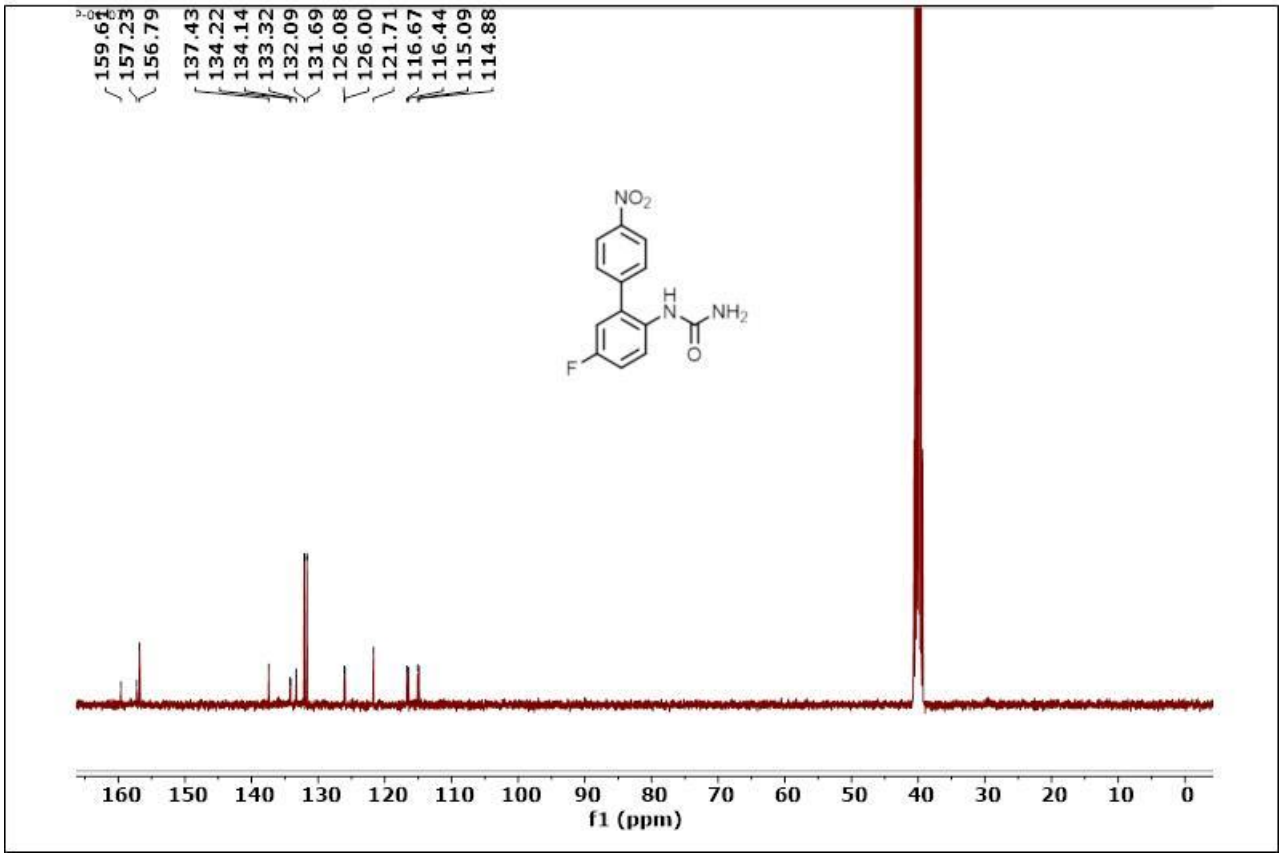
7.34
7.32
7.17
7.16
7.15
7.14
7.13
7.12
7.06
7.05
7.04
7.03
5.92
3.34
2.50
NO2
NH2
F
1.0
2.0
1.0
2.1
1.1
1.0
2.1
f1 (ppm)


159.61
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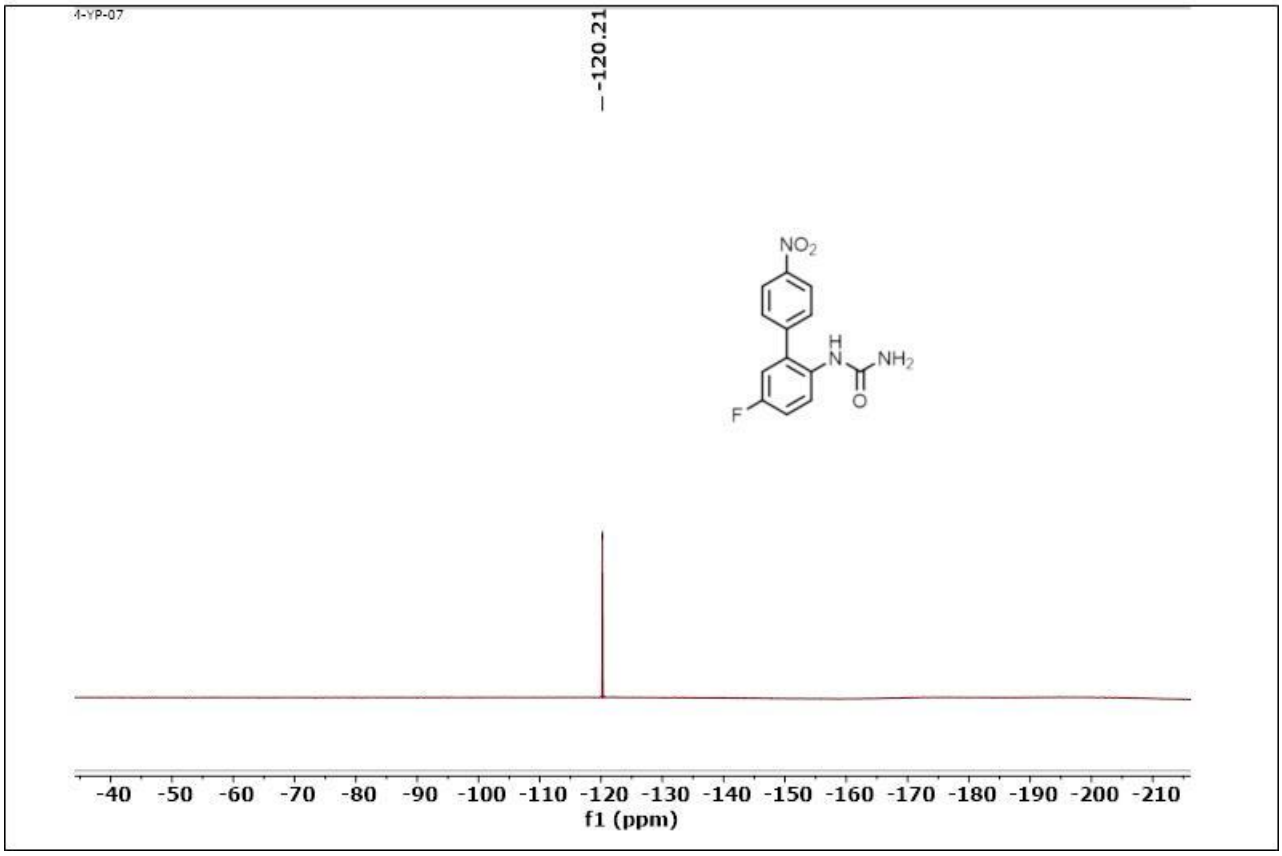
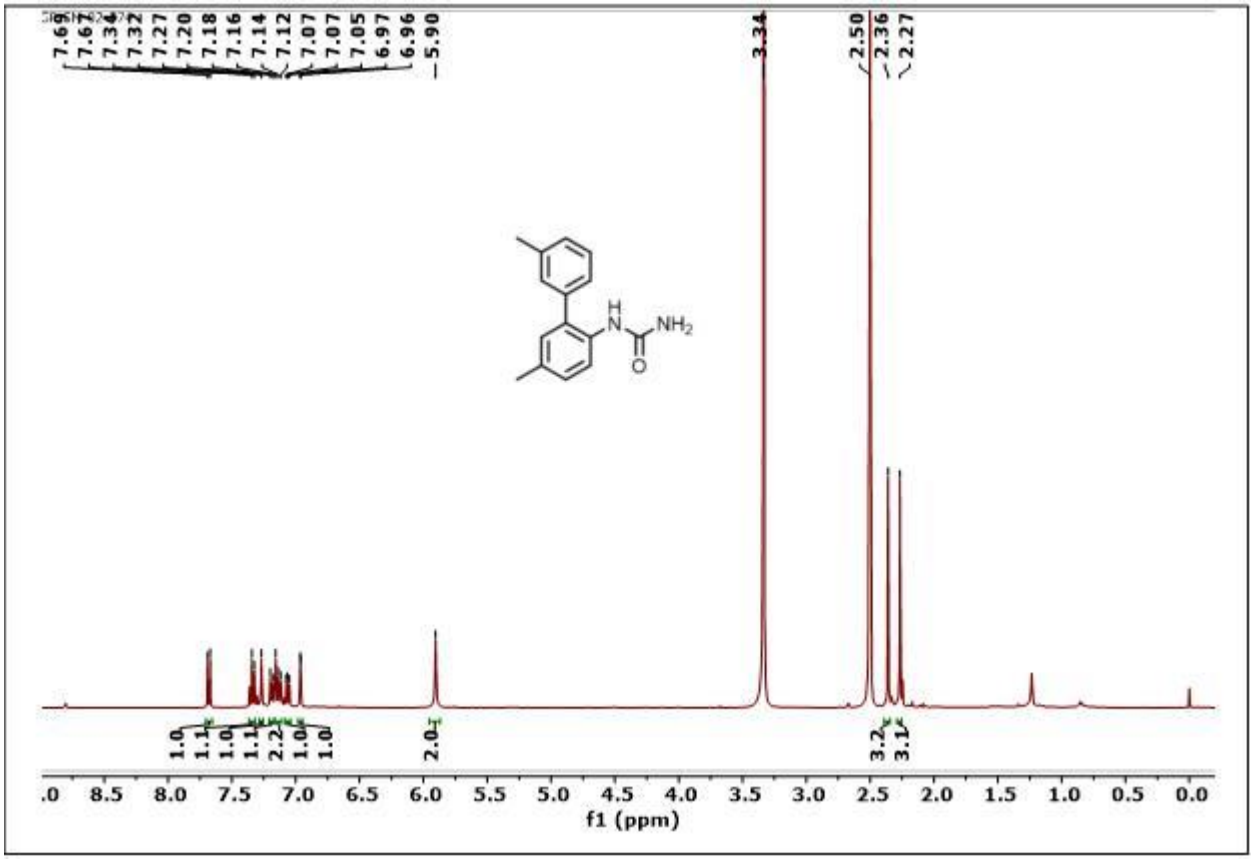
134.22
134.14
133.32
132.09
131.69
126.08
126.00
121.71
116.67
116.44
115.09
114.88
NO2
NH2
F
f1 (ppm)


4-YP-07
-120.21
NO2
H
N
NH2
O
F
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.67
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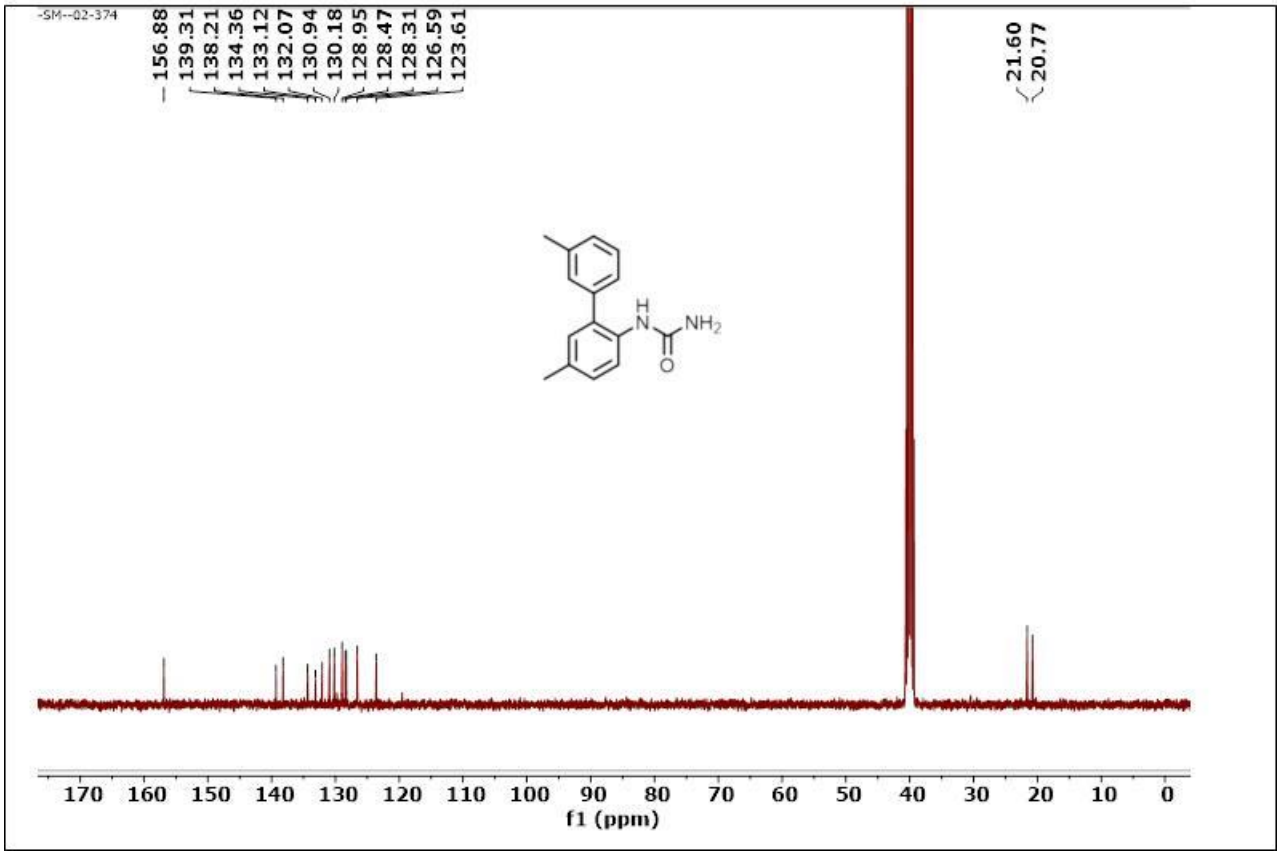
7.27
7.20
7.18
7.16
7.14
7.12
7.07
7.07
7.05
6.97
6.96
5.90
3.34
2.50
2.36
2.27
NH2
1.0
1.1
1.0
1.1
2.2
1.0
1.0
2.0
3.2
3.1
f1 (ppm)


-SM--02-374
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138.21
134.36
133.12
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130.94
130.18
128.95
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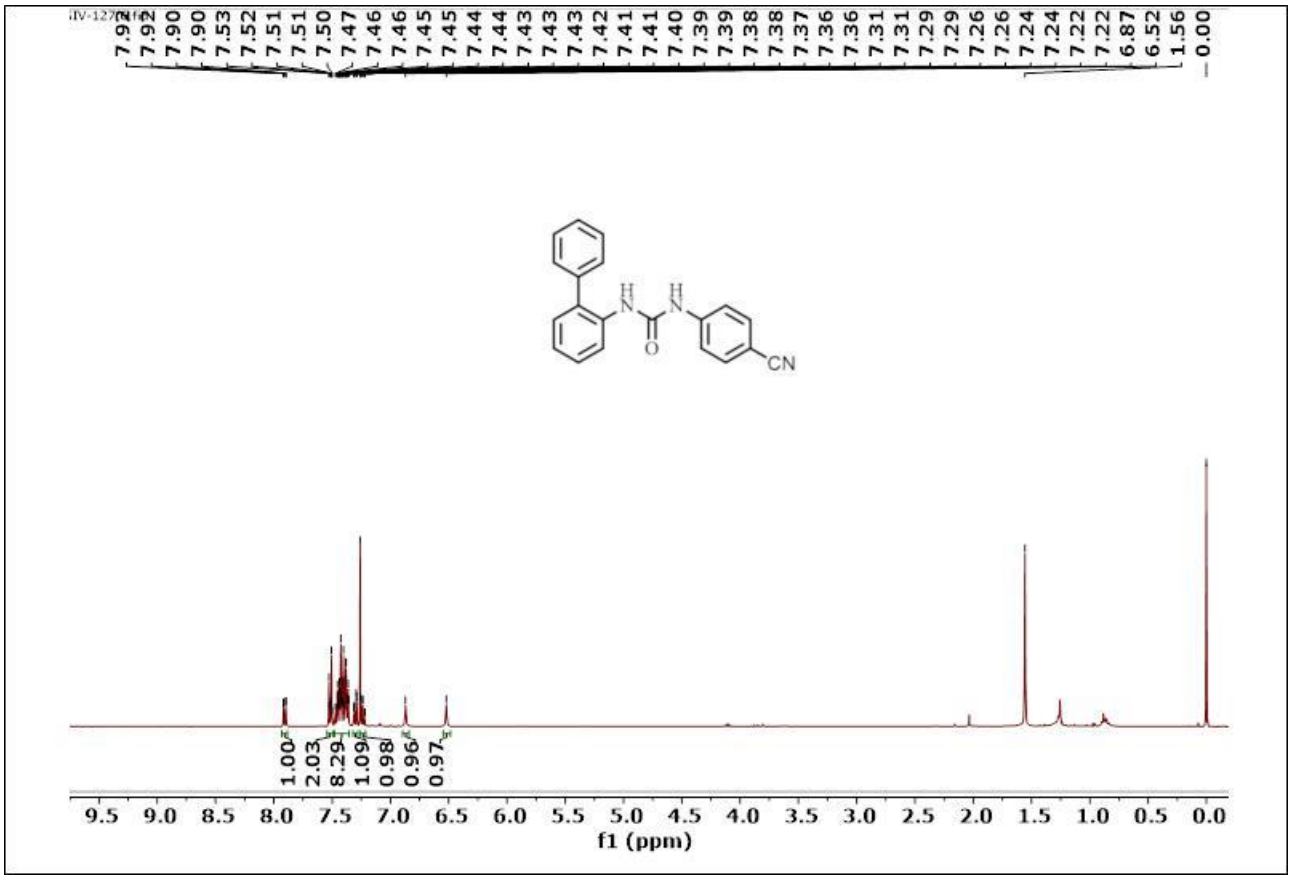
128.31
126.59
123.61
21.60
20.77
NH2
f1 (ppm)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7.92
7.90
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7.53
7.52
7.51
7.51
7.50
7.47
7.46
7.46
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7.45
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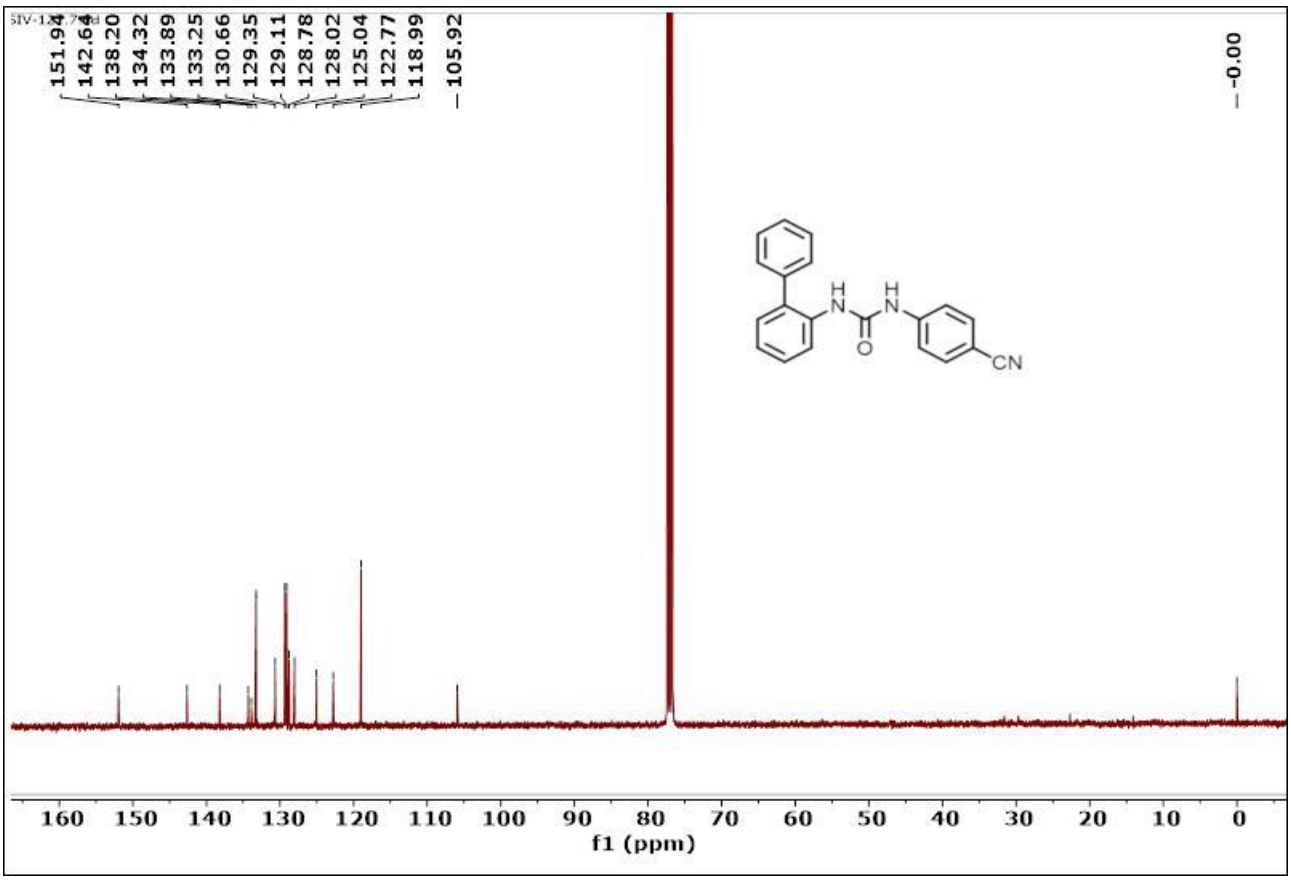
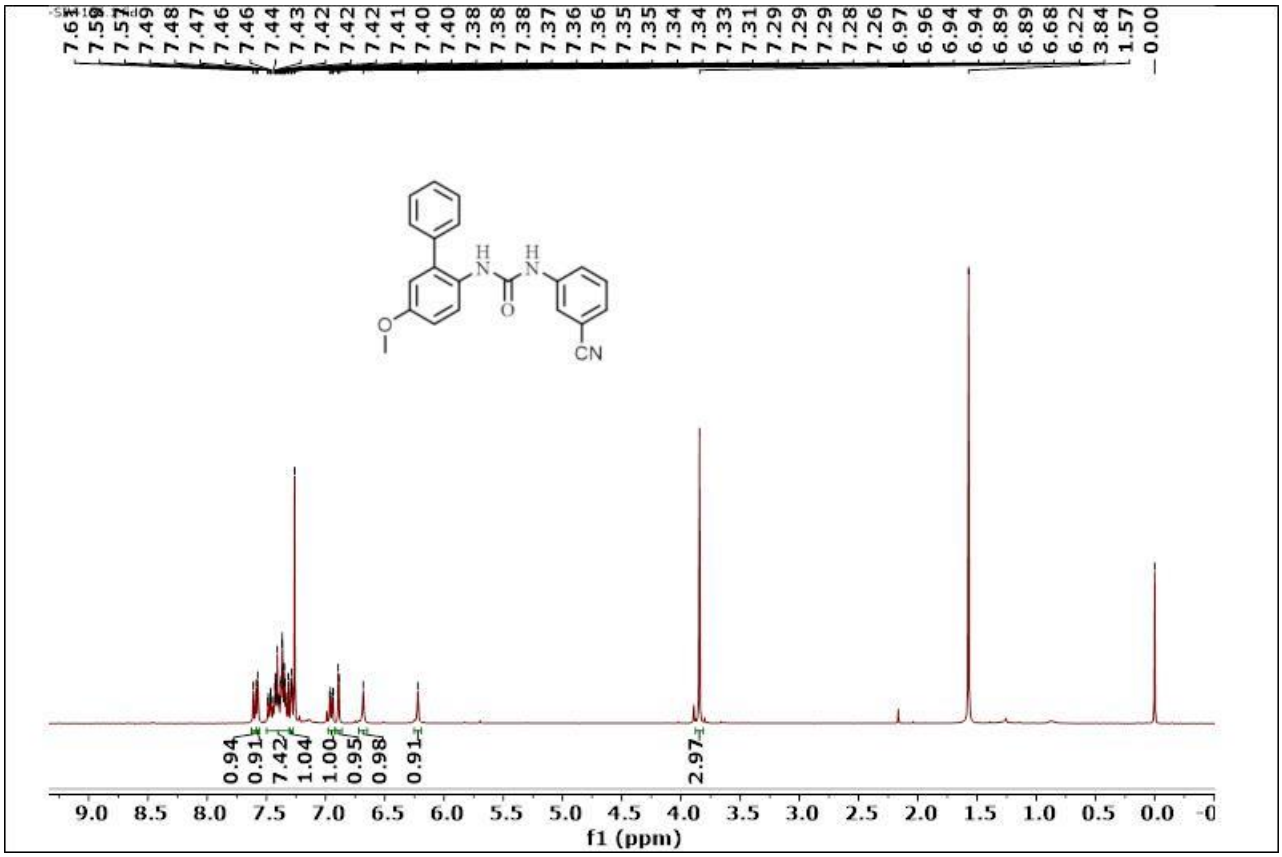
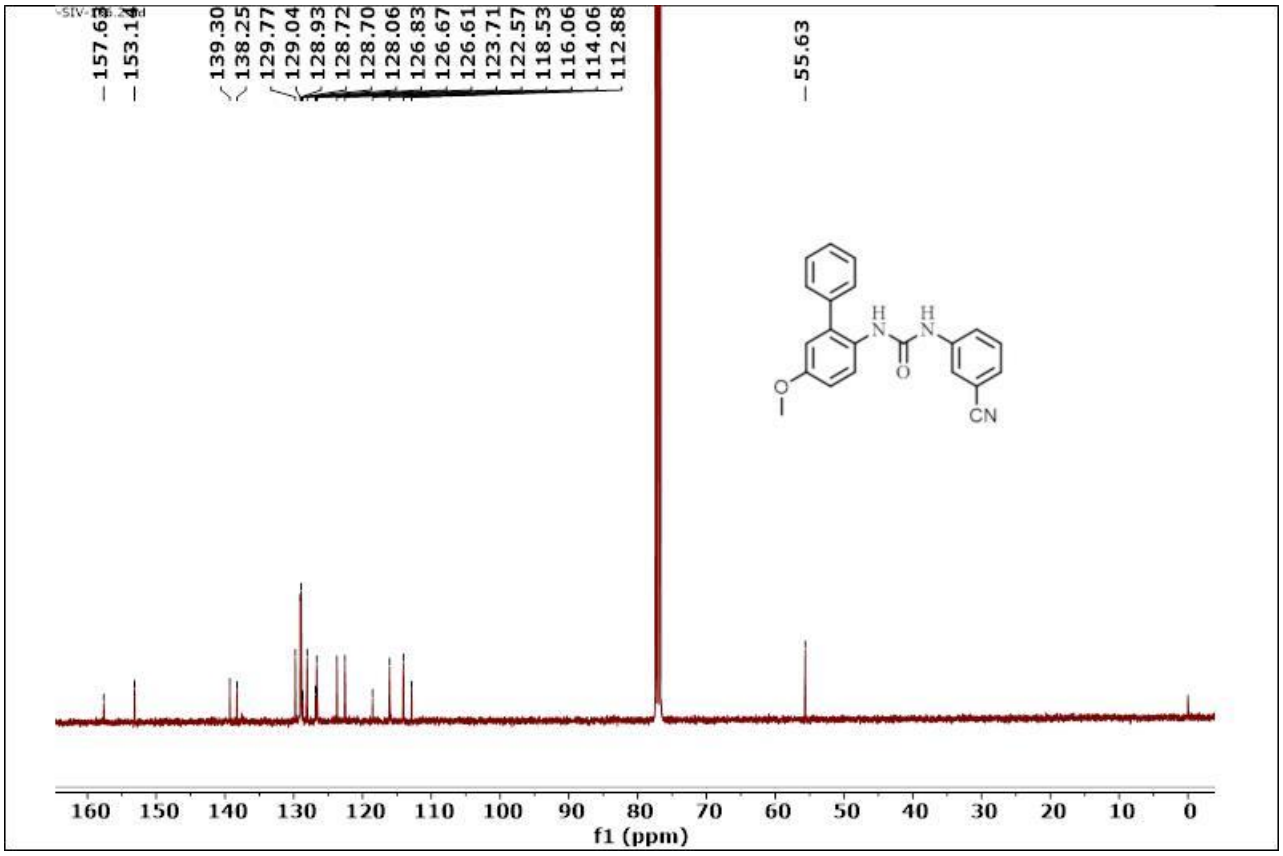
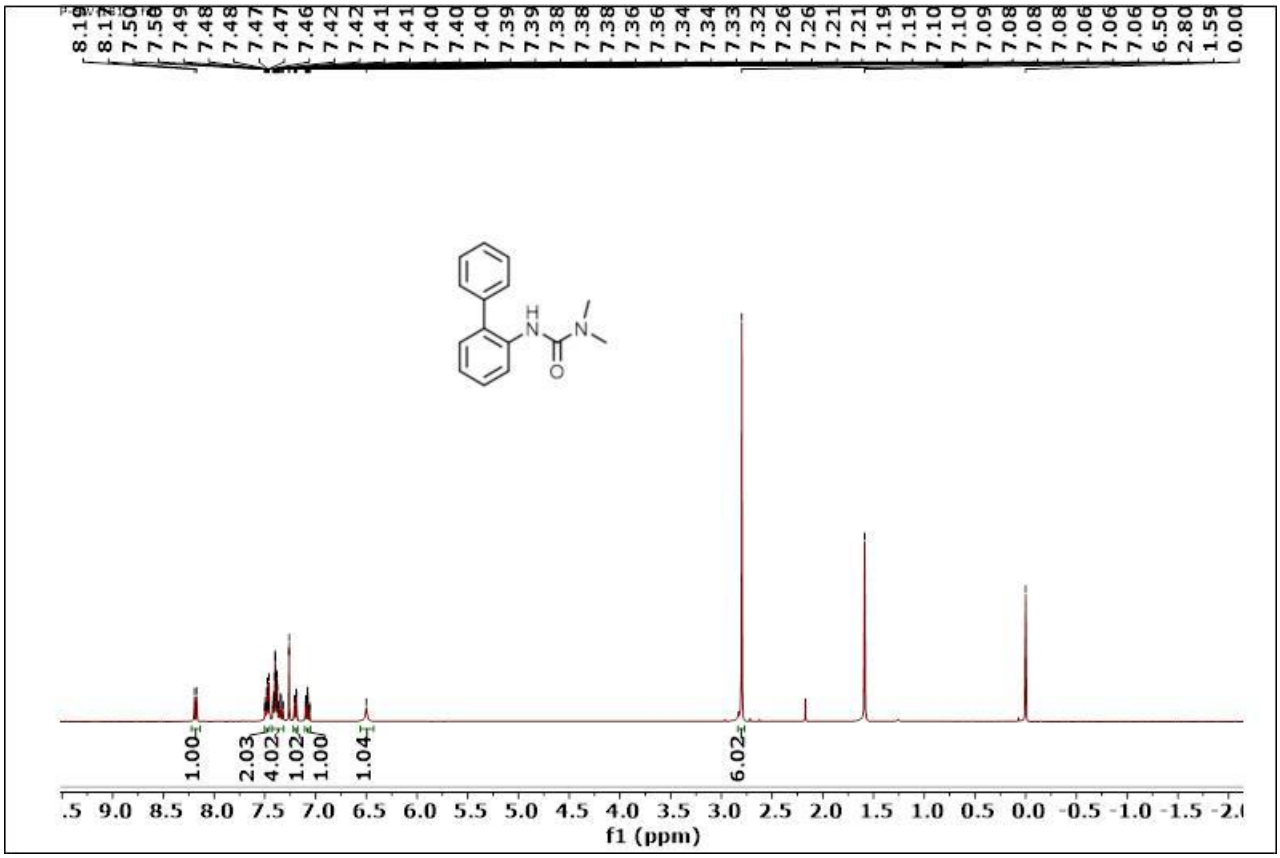
7.41
7.40
7.39
7.39
7.38
7.38
7.37
7.36
7.36
7.31
7.31
7.29
7.29
7.26
7.26
7.24
7.24
7.22
7.22
6.87
6.52
1.56
0.00
H
N
H
N
O
CN
1.00
2.03
8.29
1.09
0.98
0.96
0.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


151.94
142.64
138.20
134.32
133.89
133.25
130.66
129.35
129.11
128.78
128.02
125.04
122.77
118.99
105.92
0.00
H
N
H
N
O
CN
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.63 7.59 7.57 7.49 7.48 7.47 7.46 7.46 7.44 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.38 7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.31 7.29 7.29 7.29 7.28 7.26 6.97 6.96 6.94 6.94 6.89 6.89 6.68 6.22 3.84 1.57 0.00
H N H N O
O
CN
0.94 0.91 7.42 1.04 1.00 0.95 0.98 0.91 2.97
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)


157.63
153.14
139.30 138.25 129.77 129.04 128.93 128.72 128.70 128.06 126.83 126.67 126.61 123.71 122.57 118.53 116.06 114.06 112.88
55.63
H N H N O
O
CN
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.48
7.48
7.47
7.47
7.46
7.42
7.42
7.41
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7.40
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7.38
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7.38
7.36
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7.34
7.33
7.32
7.26
7.26
7.21
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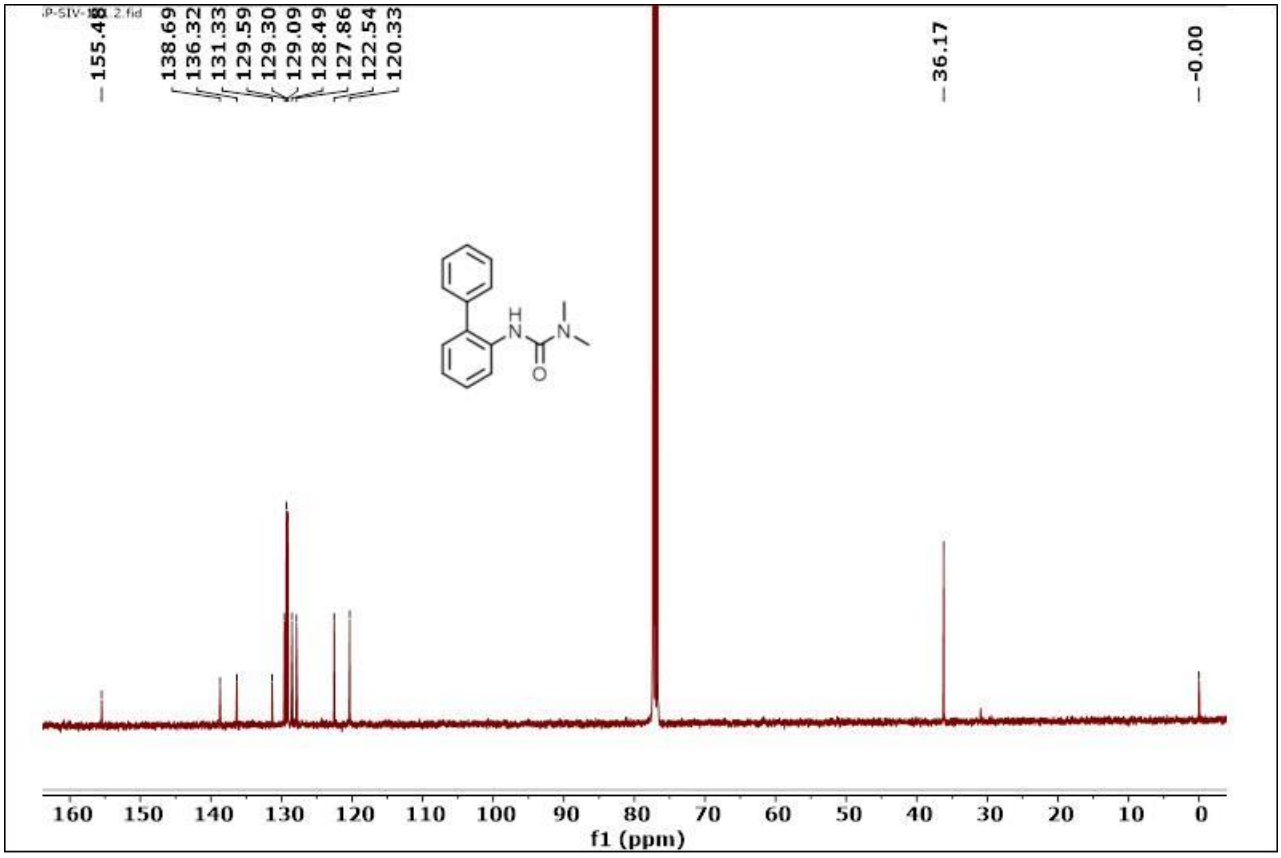
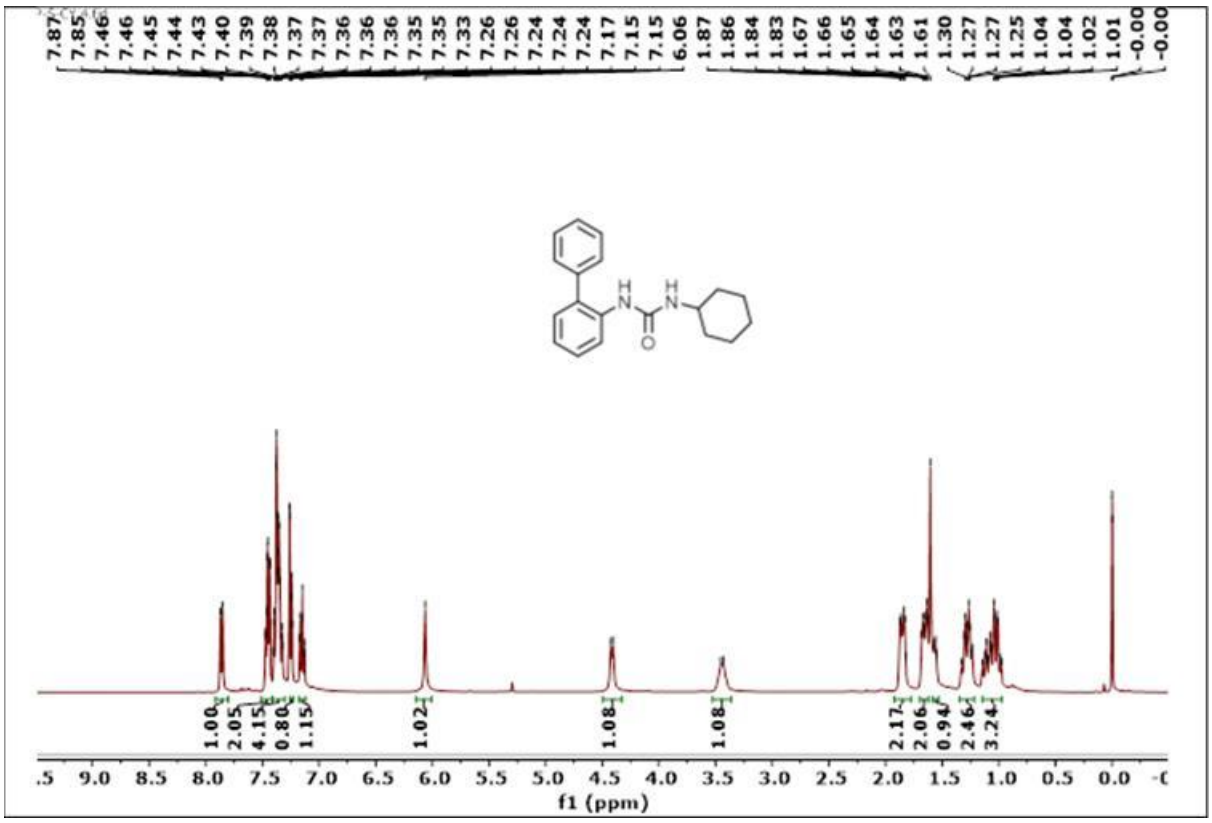
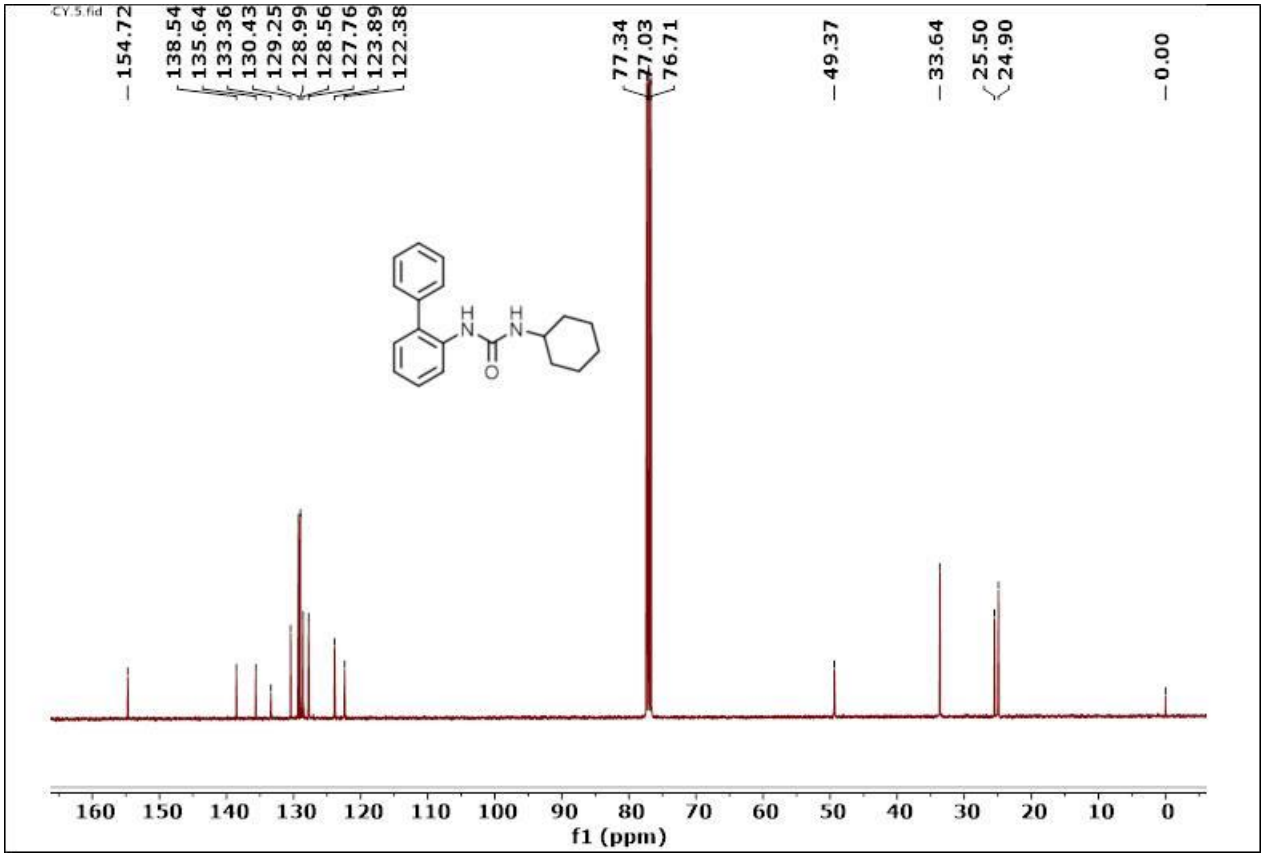
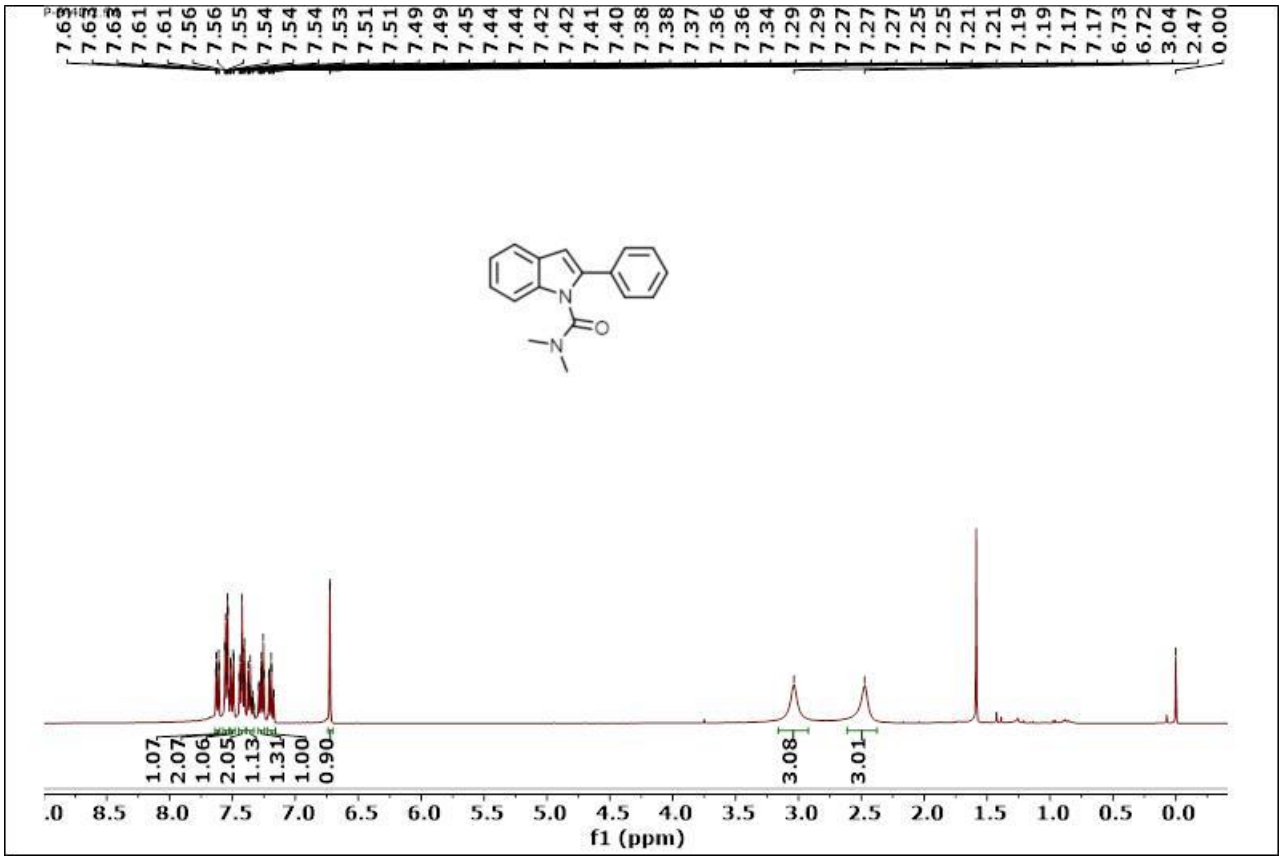
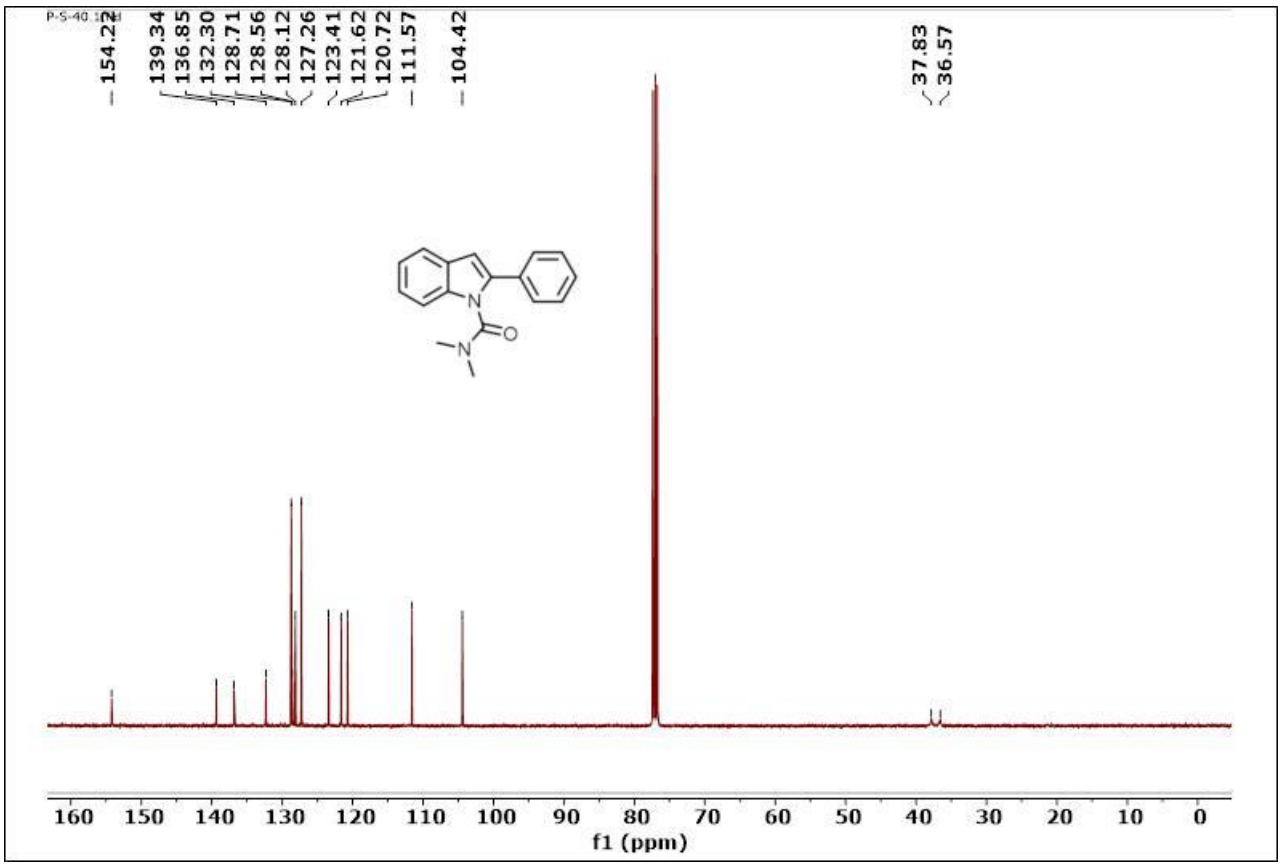
7.19
7.19
7.10
7.10
7.09
7.08
7.08
7.08
7.06
7.06
7.06
6.50
2.80
1.59
0.00
1.00
2.03
4.02
1.02
1.00
1.04
6.02
f1 (ppm)

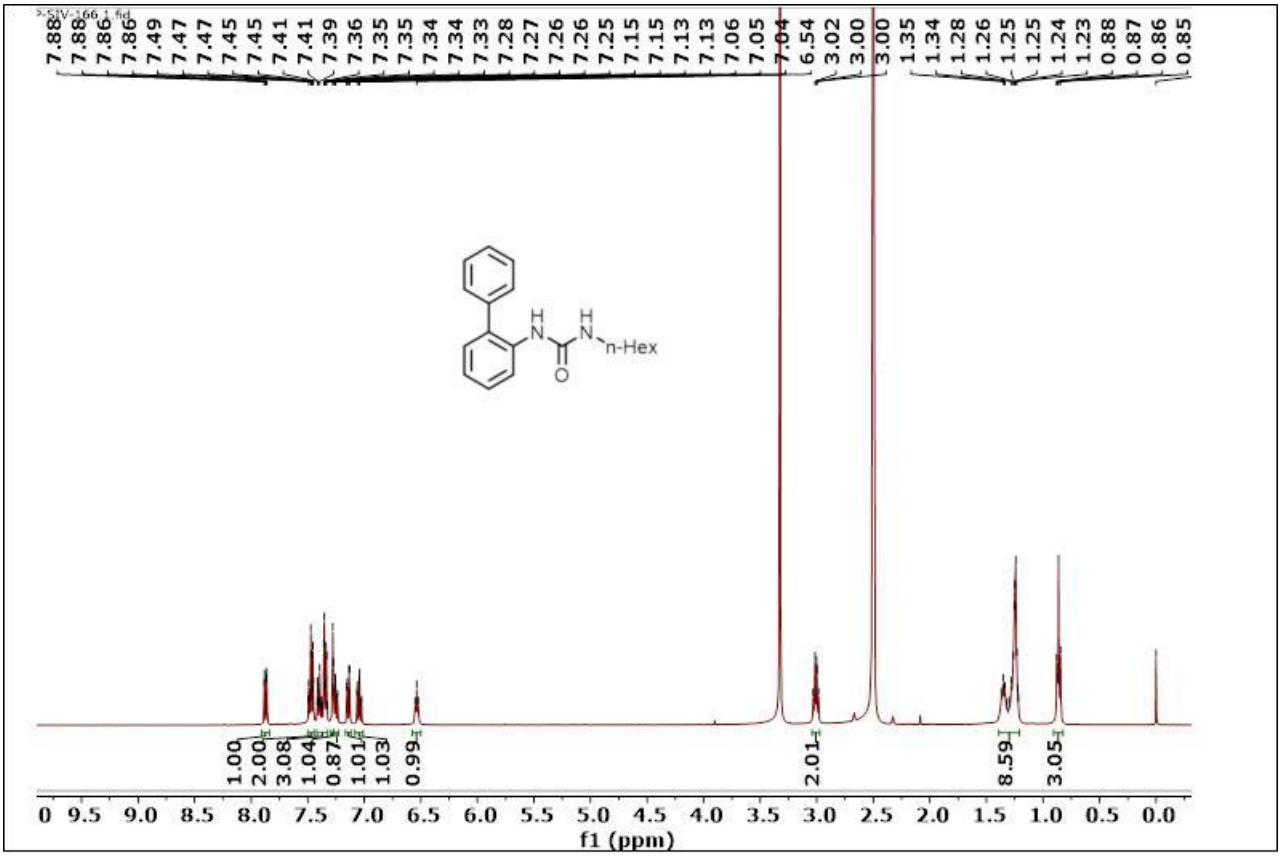

155.48
138.69
136.32
131.33
129.59
129.30
129.09
128.49
127.86
122.54
120.33
36.17
-0.00
f1 (ppm)

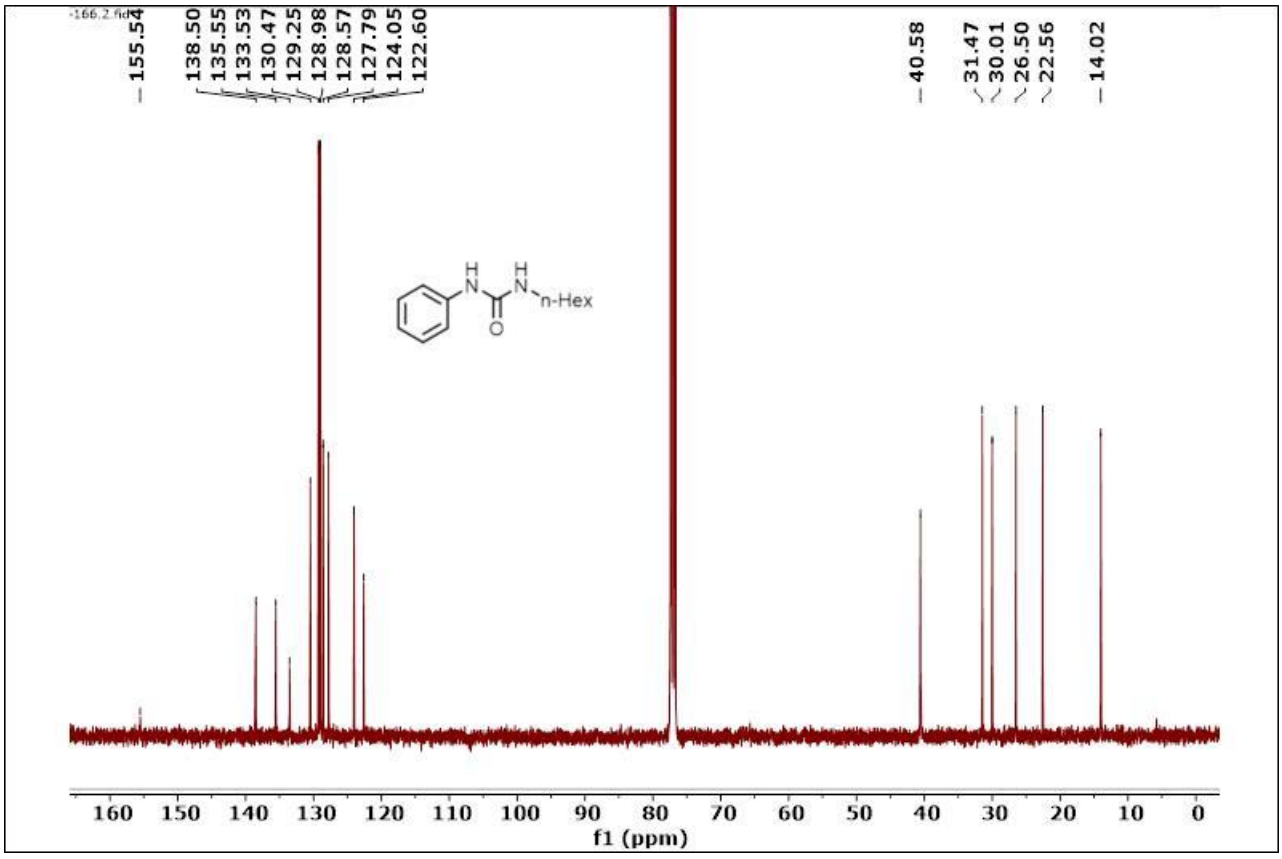

7.87 7.85 7.46 7.46 7.45 7.44 7.43 7.40 7.39 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.33 7.26 7.26 7.24 7.24 7.24 7.17 7.15 7.15 6.06 1.87 1.86 1.84 1.83 1.67 1.66 1.65 1.64 1.63 1.61 1.30 1.27 1.27 1.25 1.04 1.04 1.02 1.01 -0.00 -0.00
1.00 2.05 4.15 0.80 1.15 1.02 1.08 1.08 2.17 2.06 0.94 2.46 3.24
f1 (ppm)

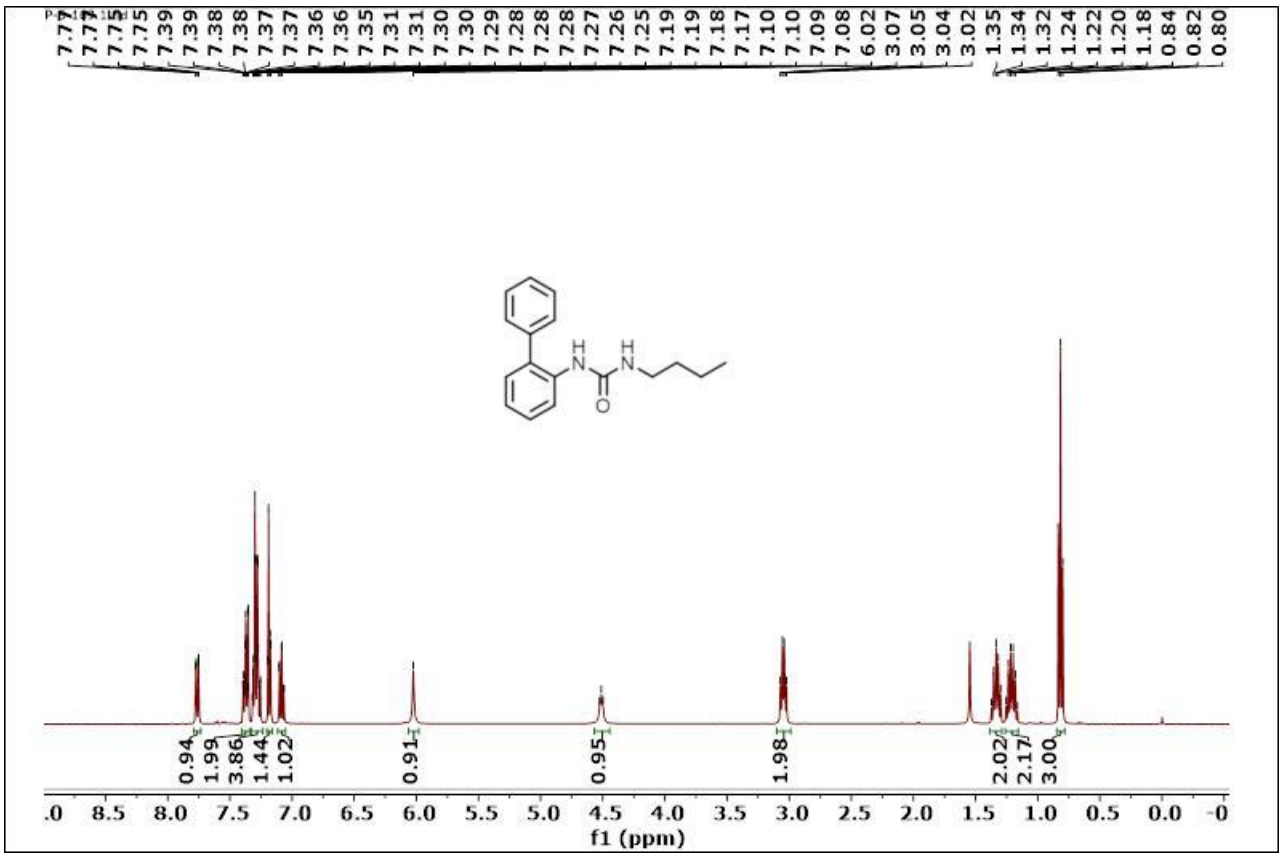

CY-5.fid
154.72 138.54 135.64 133.36 130.43 129.25 128.99 128.56 127.76 123.89 122.38 77.34 77.03 76.71 49.37 33.64 25.50 24.90 0.00
f1 (ppm)

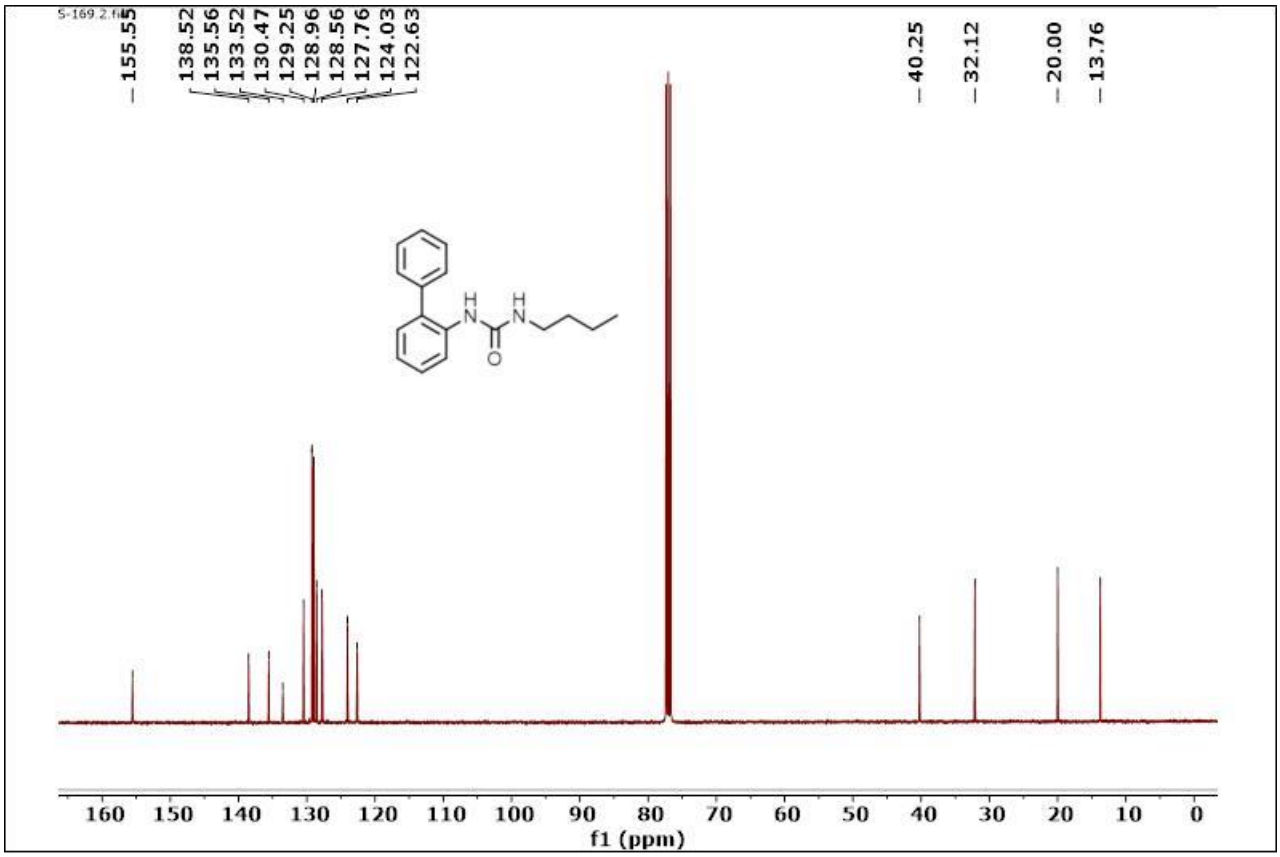

7.63
7.63
7.63
7.61
7.61
7.56
7.56
7.55
7.54
7.54
7.54
7.53
7.51
7.51
7.49
7.49
7.45
7.44
7.44
7.42
7.42
7.41
7.40
7.38
7.38
7.37
7.36
7.36
7.34
7.29
7.29
7.27
7.27
7.27
7.25
7.25
7.21
7.21
7.19
7.19
7.17
7.17
6.73
6.72
3.04
2.47
0.00
1.07
2.07
1.06
2.05
1.13
1.31
1.00
0.90
3.08
3.01
f1 (ppm)

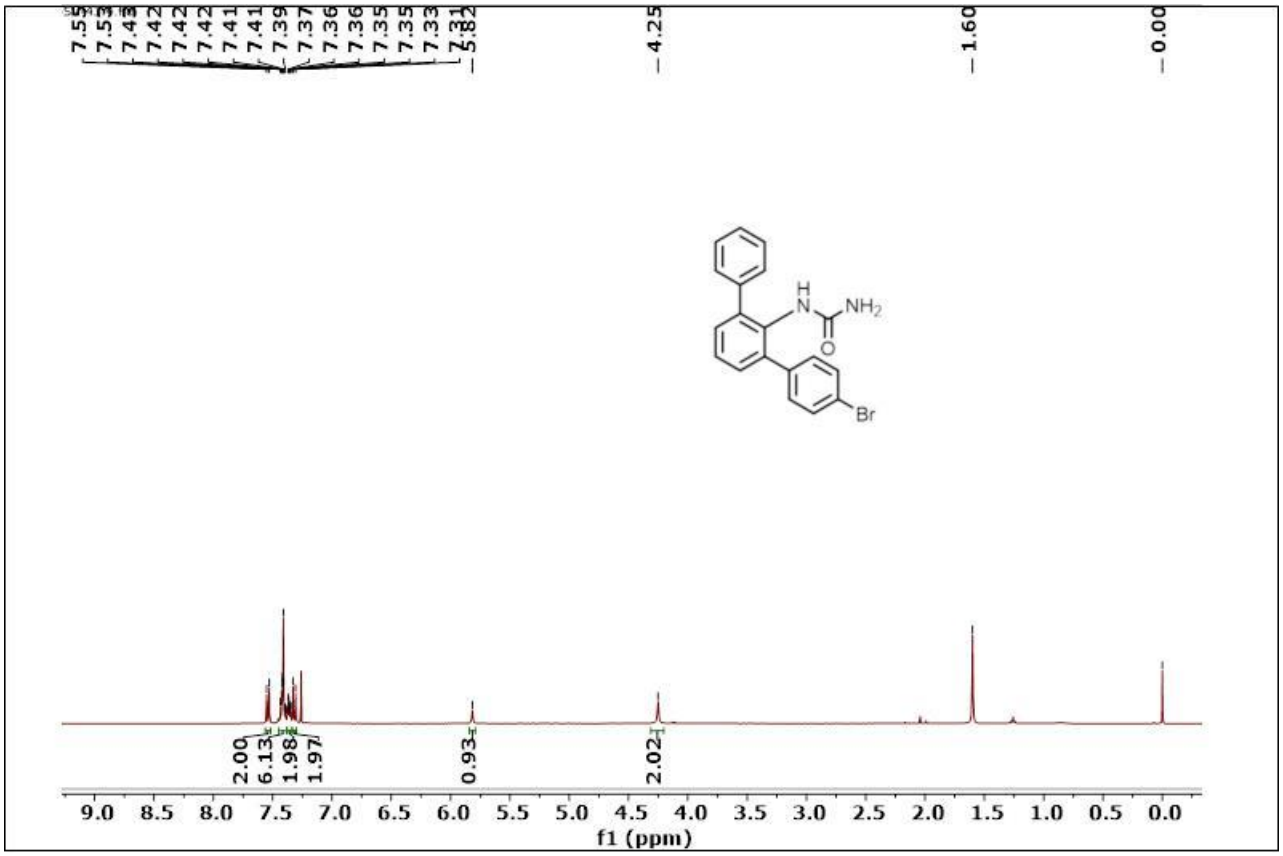

154.22
139.34
136.85
132.30
128.71
128.56
128.12
127.26
123.41
121.62
120.72
111.57
104.42
37.83
36.57
f1 (ppm)

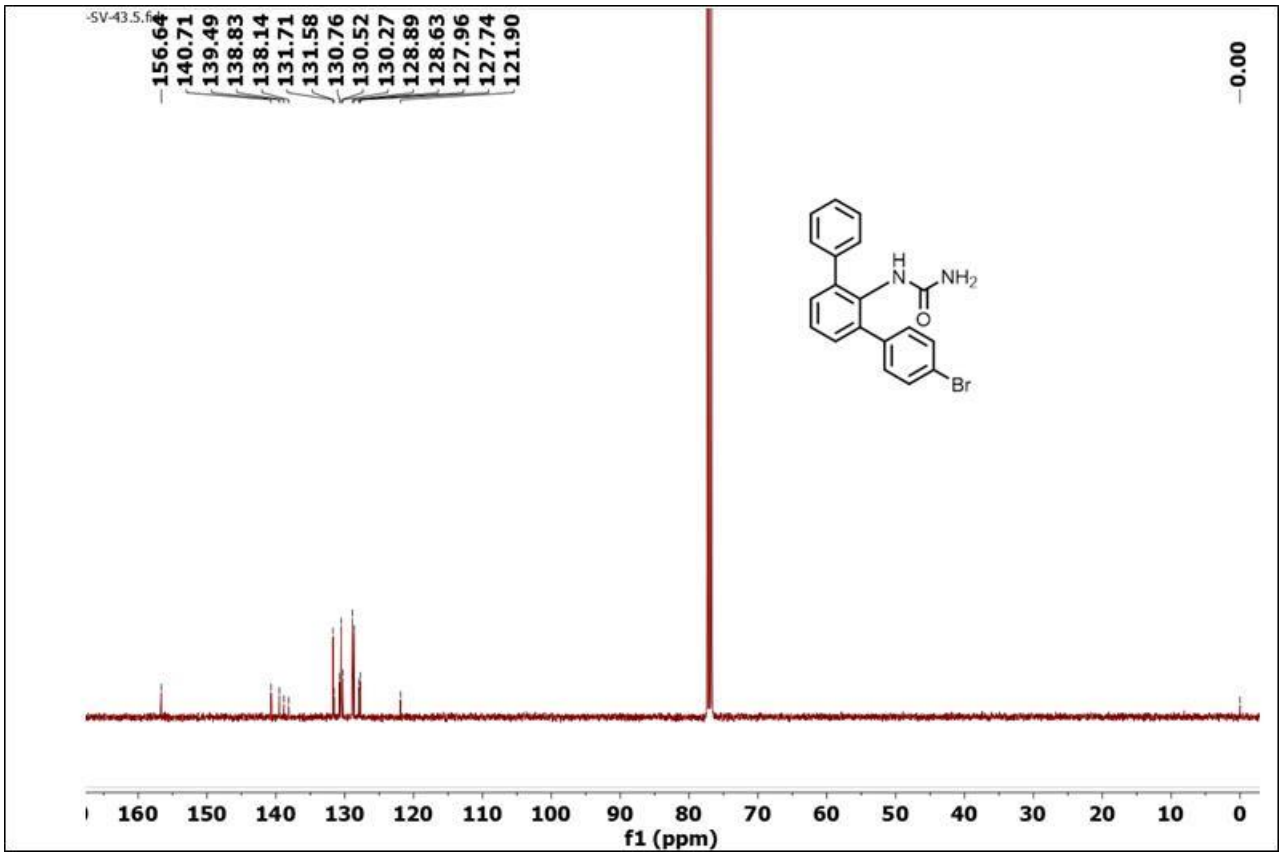

7.88 7.88 7.86 7.86 7.49 7.47 7.47 7.45 7.45 7.41 7.41 7.39 7.36 7.35 7.35 7.34 7.34 7.33 7.28 7.27 7.26 7.26 7.25 7.15 7.15 7.13 7.13 7.06 7.05 7.04 6.54 3.02 3.00 3.00 1.35 1.34 1.28 1.26 1.25 1.25 1.24 1.23 0.88 0.87 0.86 0.85
n-Hex
1.00 2.00 3.08 1.04 0.87 1.01 1.03 0.99 2.01 8.59 3.05
0 9.5 9.0 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)

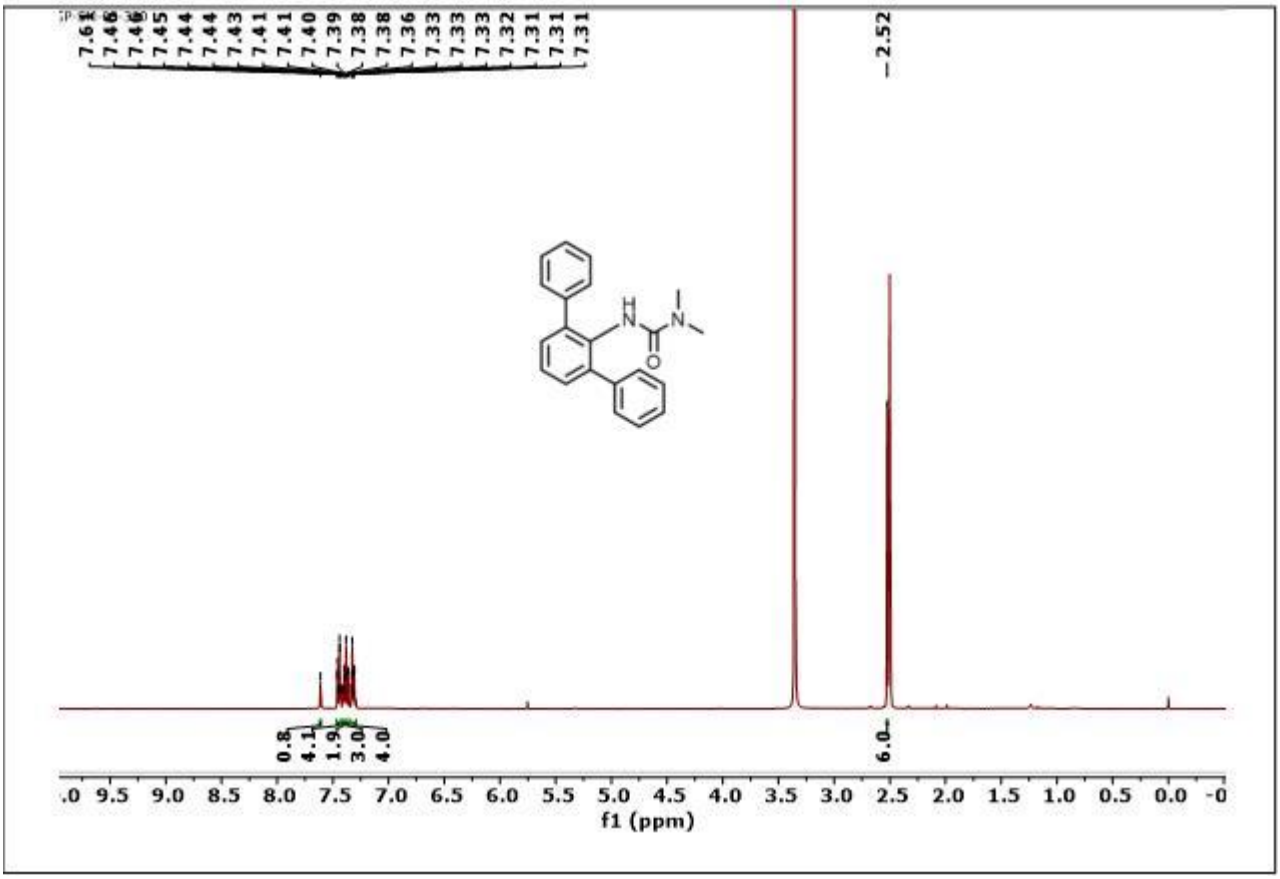

155.54
138.50 135.55 133.53 130.47 129.25 128.98 128.57 127.79 124.05 122.60
40.58 31.47 30.01 26.50 22.56 14.02
n-Hex
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

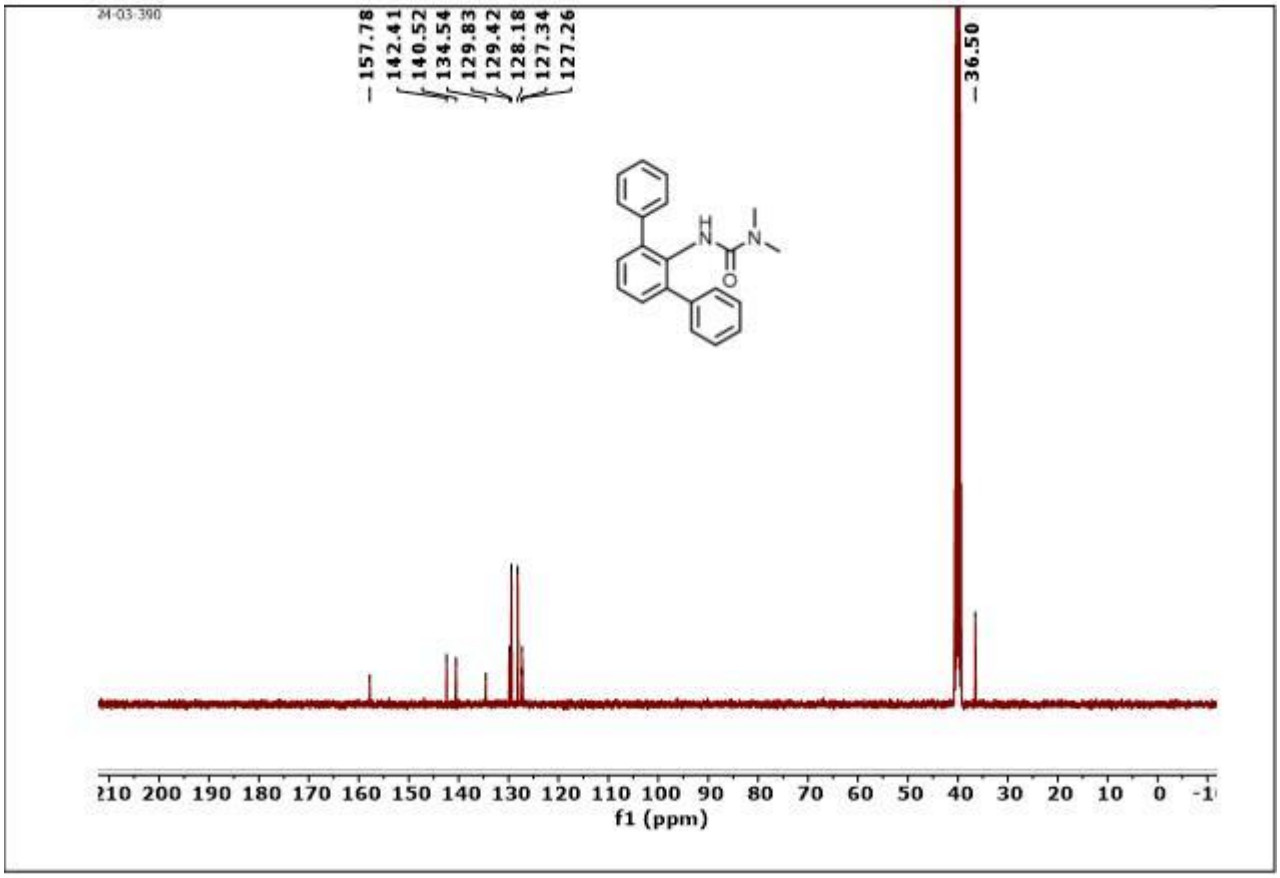

7.77 7.75 7.39 7.38 7.37 7.36 7.35 7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.19 7.18 7.17 7.10 7.09 7.08 6.02 3.07 3.05 3.04 3.02 1.35 1.34 1.32 1.24 1.22 1.20 1.18 0.84 0.82 0.80
0.94 1.99 3.86 1.44 1.02 0.91 0.95 1.98 2.02 2.17 3.00
f1 (ppm)

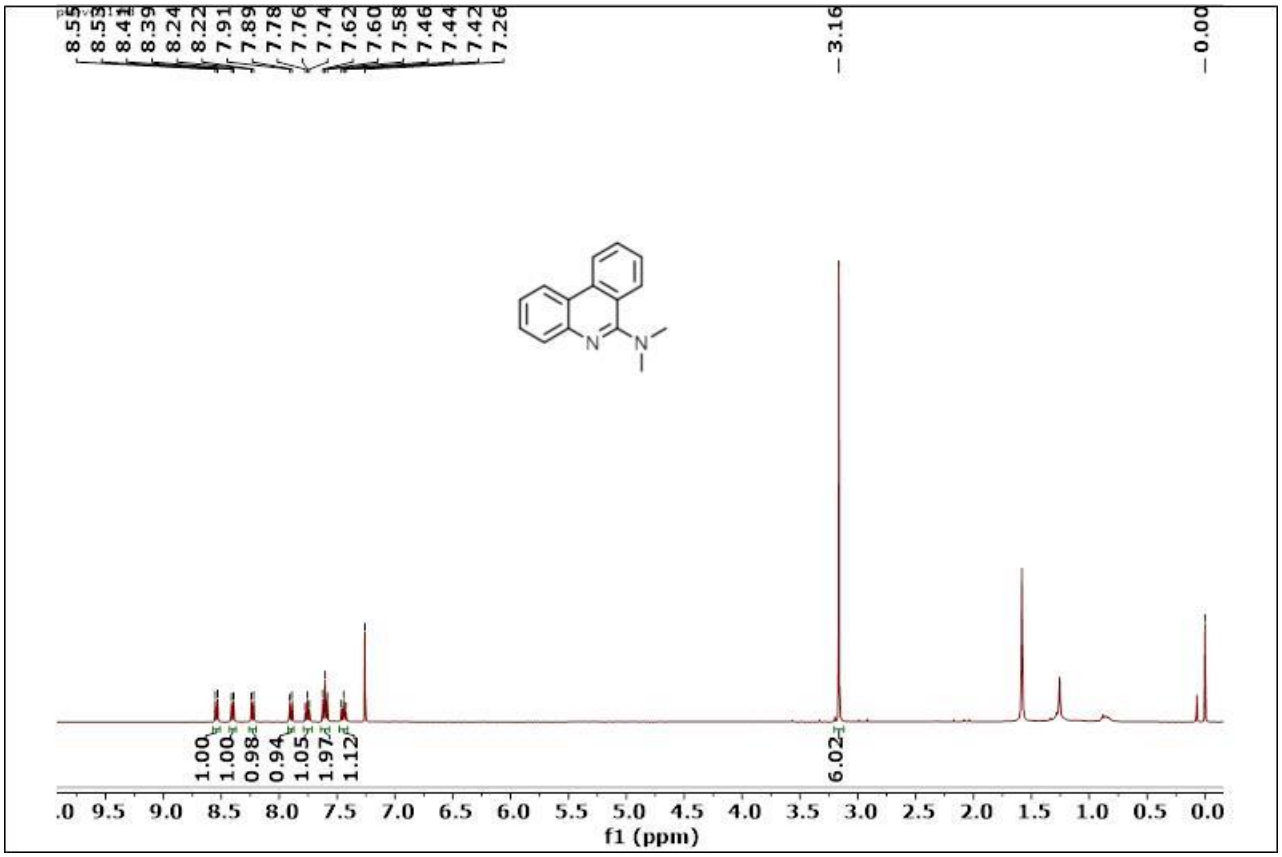

155.55 138.52 135.56 133.52 130.47 129.25 128.96 128.56 127.76 124.03 122.63 40.25 32.12 20.00 13.76
f1 (ppm)

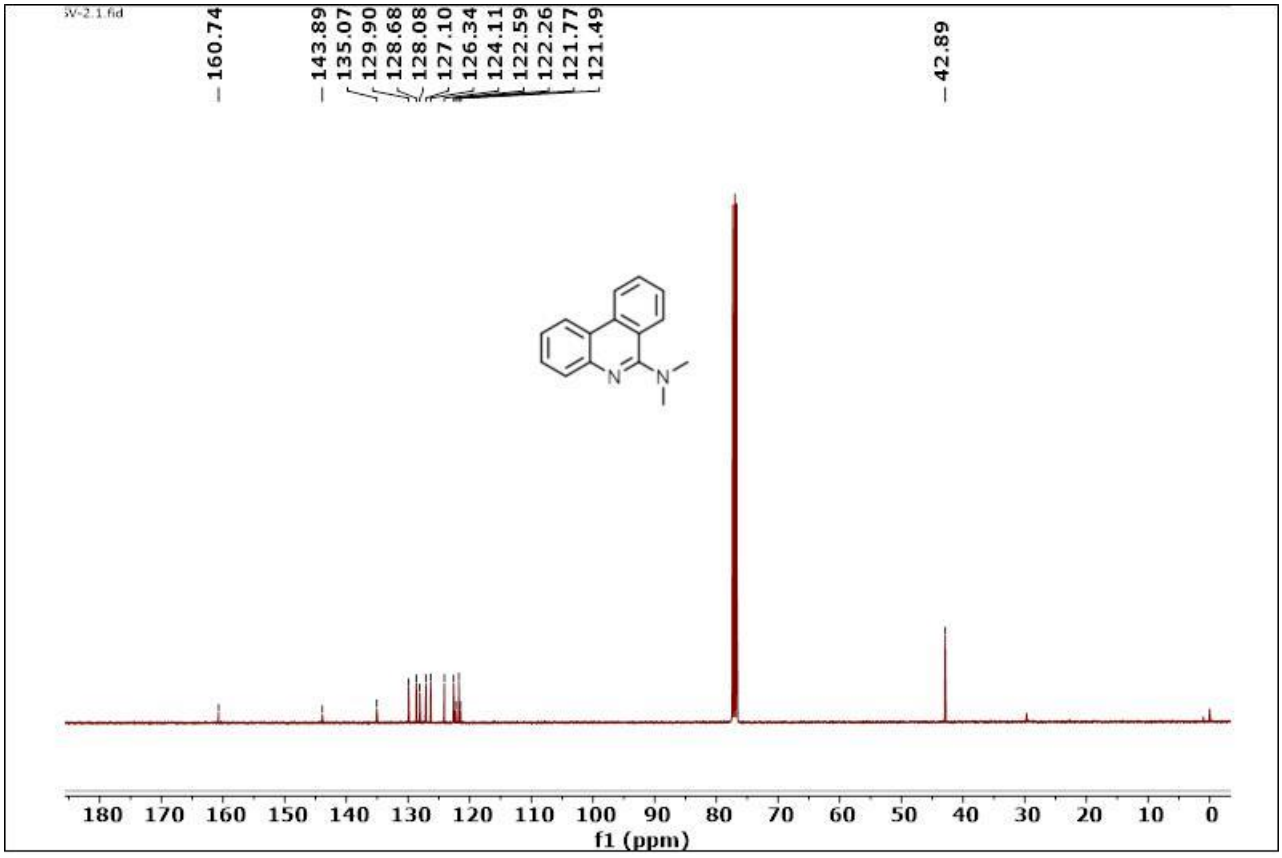

7.55
7.53
7.43
7.42
7.42
7.42
7.41
7.41
7.39
7.37
7.36
7.36
7.35
7.35
7.33
7.31
5.82
4.25
1.60
0.00
NH2
Br
2.00
6.13
1.98
1.97
0.93
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

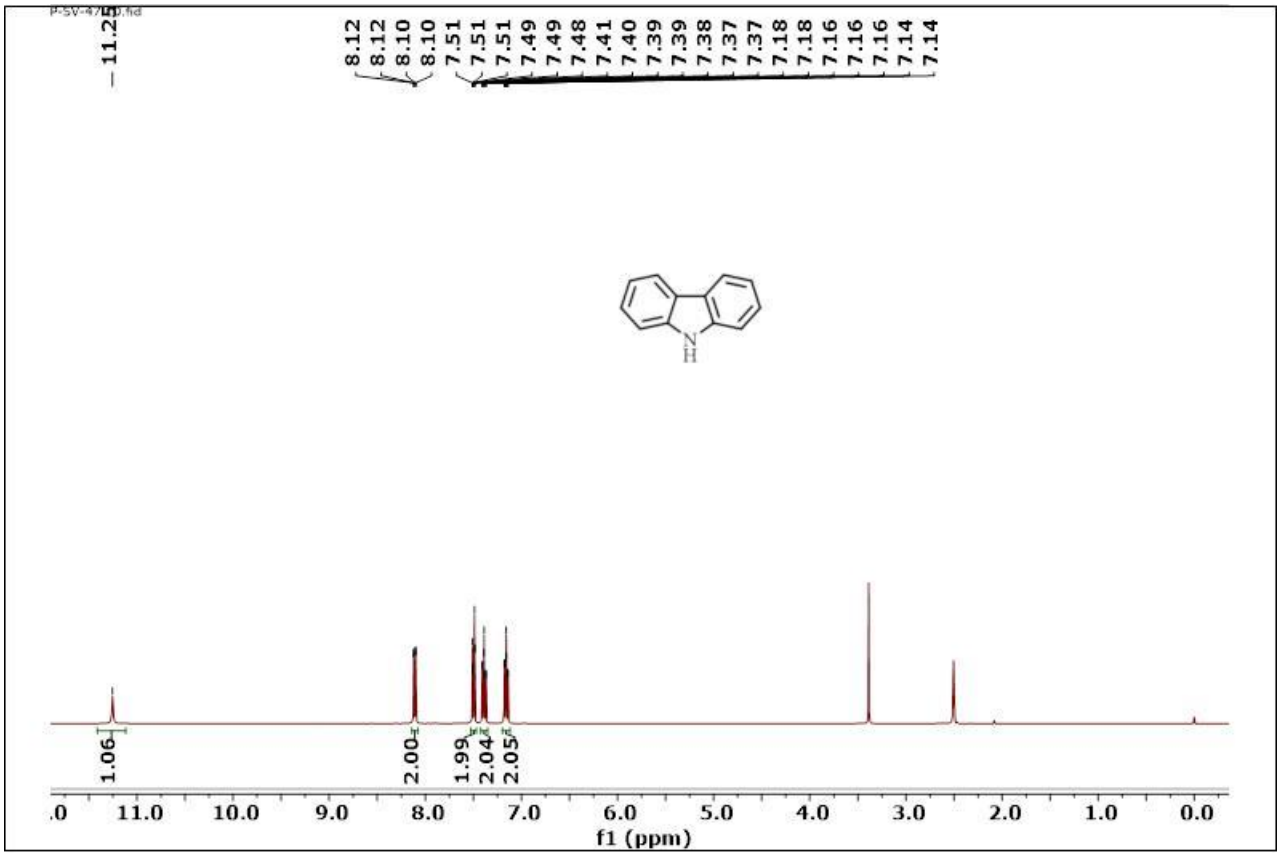

156.64
140.71
139.49
138.83
138.14
131.71
131.58
130.76
130.52
130.27
128.89
128.63
127.96
127.74
121.90
0.00
NH2
Br
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

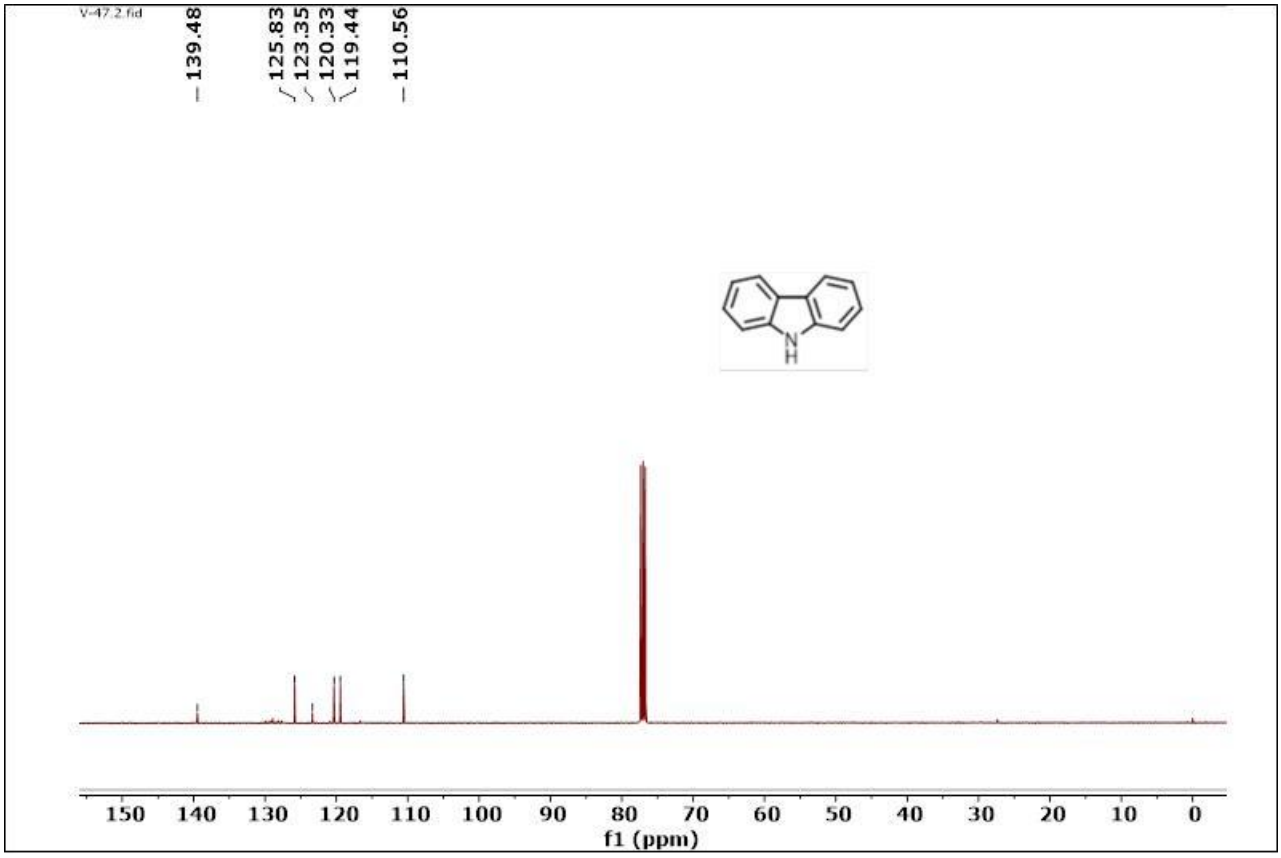

7.61
7.46
7.45
7.44
7.44
7.43
7.41
7.41
7.40
7.39
7.38
7.38
7.36
7.33
7.33
7.33
7.32
7.31
7.31
7.31
2.52
0.8
4.1
1.9
3.0
4.0
6.0
f1 (ppm)

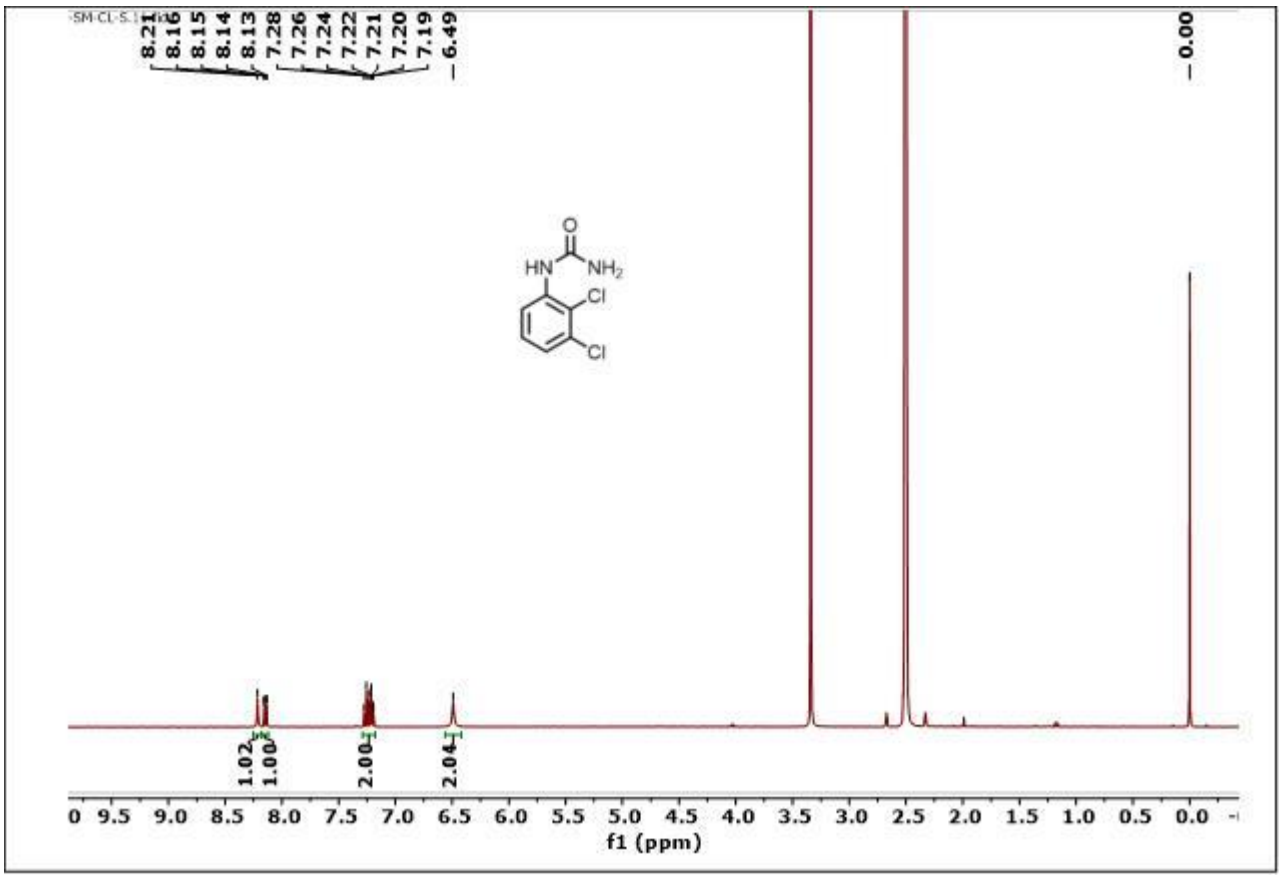

157.78
142.41
140.52
134.54
129.83
129.42
128.18
127.34
127.26
36.50
f1 (ppm)

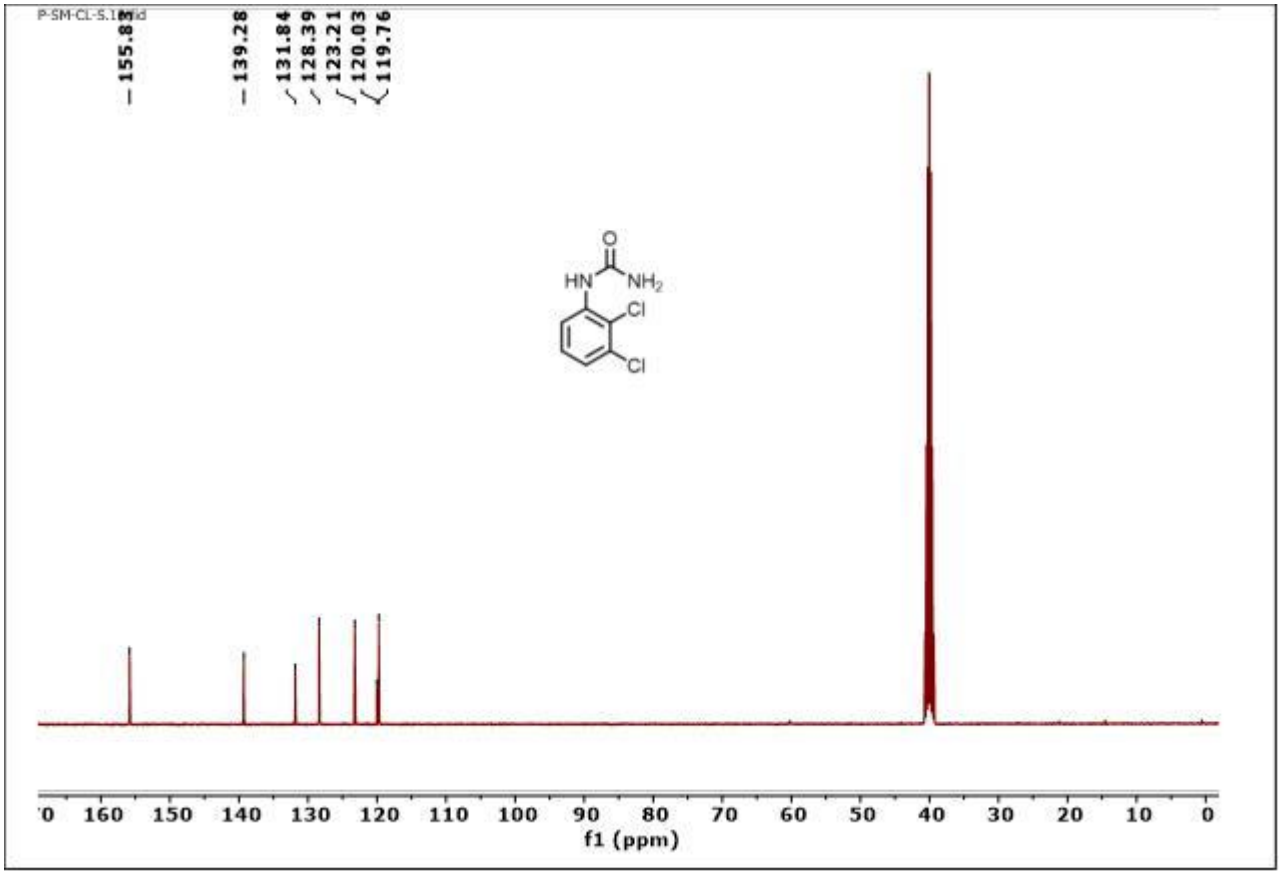

8.55
8.53
8.41
8.39
8.24
8.22
7.91
7.89
7.78
7.76
7.74
7.62
7.60
7.58
7.46
7.44
7.42
7.26
3.16
0.00
1.00
1.00
0.98
0.94
1.05
1.97
1.12
6.02
f1 (ppm)


160.74
143.89
135.07
129.90
128.68
128.08
127.10
126.34
124.11
122.59
122.26
121.77
121.49
42.89
f1 (ppm)


11.25
8.12
8.12
8.10
8.10
7.51
7.51
7.51
7.49
7.49
7.48
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.18
7.18
7.16
7.16
7.16
7.14
7.14
1.06
2.00
1.99
2.04
2.05
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


V-47.2.fid
139.48
125.83
123.35
120.33
119.44
110.56
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.21
8.16
8.15
8.14
8.13
7.28
7.26
7.24
7.22
7.21
7.20
7.19
6.49
0.00
HN
NH2
O
Cl
Cl
1.02
1.00
2.00
2.04
f1 (ppm)


155.83
139.28
131.84
128.39
123.21
120.03
119.76
HN
NH2
O
Cl
Cl
f1 (ppm)