

Graphitic Carbon Nitride Decorated with Cu₂O Nanoparticles for the Visible light Activated Synthesis of Yrones, Aminoindolizine and Pyrrolo [1, 2a] quinoline

Anuj S Sharma^a, Vinay S Sharma^b, Harjinder Kaur^{a}*

^a: Department of Chemistry, School of Sciences, Gujarat University, Ahmedabad, India

^b: Department of Chemistry, Faculty of Basic and Applied Science, Madhav University, Rajasthan

Corresponding author *: *hk_ss_in@yahoo.com*

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Experimental Section

General: Terminal alkynes derivatives, copper nitrate, benzoyl chloride derivatives, quinoline 2-carboxaldehyde and pyridine 2-carboxaldehyde, hydrazine hydrate, GVL, propylene carbonate and EG were purchased from Sigma Aldrich and directly used without further purification. Ethyl acetate, hexane, ethanol and methanol were purchased from Finar Chemicals. Water used in all experiments was purified by Millipore-Q system. Freshly prepared 3:1 HCl/HNO₃ (aqua regia) was used to clean all glassware thoroughly cleaned before use. JEOL JEM 2100 instrument and were used for particle size measurement through High resolution transmission electron microscopy (HR-TEM) as well as Energy dispersive atomic X ray analysis (EDAX). A drop of methanol with dispersed catalyst was placed onto a 200 mesh carbon coated copper grid. The water was evaporated and particle size measurement was done. The powder XRD of the catalyst was recorded on Bruker D₂ Phaser using Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$) and a filter of nickel at 30 kV and 10 mA with step size 0.03 and count time 0.1s. TEM and HR-TEM was performed by using a Hitachi (H-7500) attached with EDX. The swollen beads of resin were milled and a drop of alcoholic suspension was placed into a 200 mesh carbon coated copper grid. It was then dried to evaporate the solvent and used for the analysis. Scanning Electron microscopy analysis (SEM) was carried out through JSM 6100 (JEOL) with acceleration voltage range 0.3 to 30 kV and working distance of 6 to 48 mm. The IR spectra were performed on Bruker FT-IR spectrophotometer by using KBr pellets. The disc containing 1 mg of sample was scanned within a range of 600 to 3600 cm⁻¹. ¹H NMR spectra were measured in Bruker AV 400 MHz and JEOL 400 NMR using C₆D₆ and CDCl₃ as solvent and TMS as internal standard. The ¹³C NMR spectra were recorded on 100 MHz spectrometers in CDCl₃ and C₆D₆. XPS (X-ray photoelectron spectroscopy) data was acquired using PHI 5000 versa probe II to study the

surface composition and chemical state of the prepared samples. XPS data was obtained using monochromatic aluminum with an Al K α X-ray source ($h\nu = 1486.6$ eV) operating at a vacuum of 10^{-7} Pa. All the binding energy values were calibrated using C1s line of 284.7 eV. Deconvolution of the XPS peaks was carried out by using multipack software provided by Phi. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was carried out on a HJY ultima-2 instrument: 1000 W, nebulizer pressure 2.96, nebulizer flow 1.29, wave length 242.795 nm. UV-Vis diffuse reflectance spectra measurements were carried out by taking BaSO₄ as a reference sample on SHIMAZU UV-2600 spectrophotometer (Japan).

Synthesis of Cu₂O NPs/g-C₃N₄ catalyst. The graphitic carbon nitride support (g-C₃N₄) was synthesized by calcinations of urea at 550 °C for 3h in Muffle furnace in inert atmosphere. After that the resulting g-C₃N₄ material was dispersed in methanol by sonication. A methanolic solution of copper nitrate [Cu(NO₃)₂] (8 mg) was added to the dispersed solution of g-C₃N₄ (500 mg). The resulting mixture was reduced by adding hydrazine hydrate (0.5 ml). After sonicating for 3 h at room temperature, the catalyst (Cu₂O NPs/g-C₃N₄) was separated by centrifugation, washed with methanol and stored after drying.

Typical Procedure for the Sonogashira coupling reaction between phenyl acetylene and benzoyl chloride. In 10 mL single neck round bottomed flask (R.B.F), benzoyl chloride (1 mmol), phenyl acetylene (1 mmol), catalyst Cu₂O NPs/g-C₃N₄ (20 mg) were added. The resulting solution was exposed to visible light irradiation using 40 W domestic bulb. The progress of reaction was monitored by using TLC. After the completion of the reaction, the catalyst was separated by centrifugation and the product was extracted using ethyl acetate. The extracted layer was evaporated by rota-evaporator and dried over anhydrous sodium sulfate and further purified by column chromatography and characterized by ¹H-NMR and ¹³C NMR.

Typical Procedure for the synthesis of aminoindolizine and pyrrolo [1, 2a] quinoline. Into a 25 mL round bottomed flask (R.B.F), pyridine 2-carboxaldehyde or quinoline 2-carboxaldehyde (1 mmol), secondary amine (1 mmol), phenyl acetylene (1 mmol), catalyst Cu₂O NPs/g-C₃N₄ (25 mg) and 5 mL of EG were added and the resulting solution was exposed to visible light irradiation using 60 W domestic bulbs. The progress of reaction was

monitored by TLC. After the completion of the reaction, the catalyst was separated by centrifugation and the product was extracted by using ethyl acetate. The extracted layer was evaporated by using rota-evaporated and further purified by column chromatography and characterized using $^1\text{H-NMR}$ and $^{13}\text{C NMR}$.

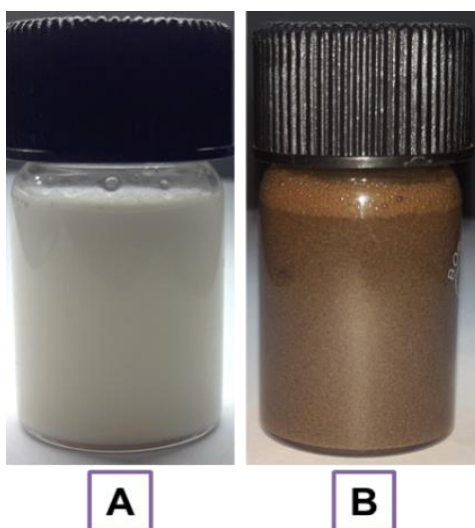


Figure S1. Picture of Graphitic nitride ($\text{g-C}_3\text{N}_4$) (A) and the synthesized $\text{Cu}_2\text{O NPs/g-C}_3\text{N}_4$.

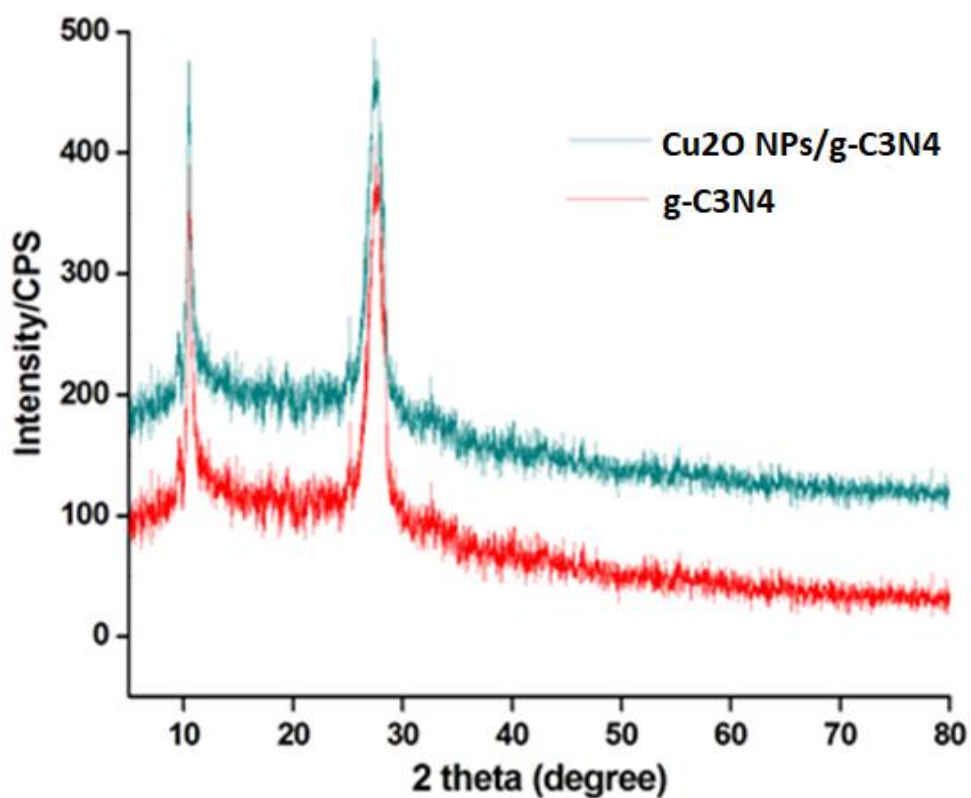


Figure S2. PXRD of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and $\text{Cu}_2\text{O NPs/g-C}_3\text{N}_4$.

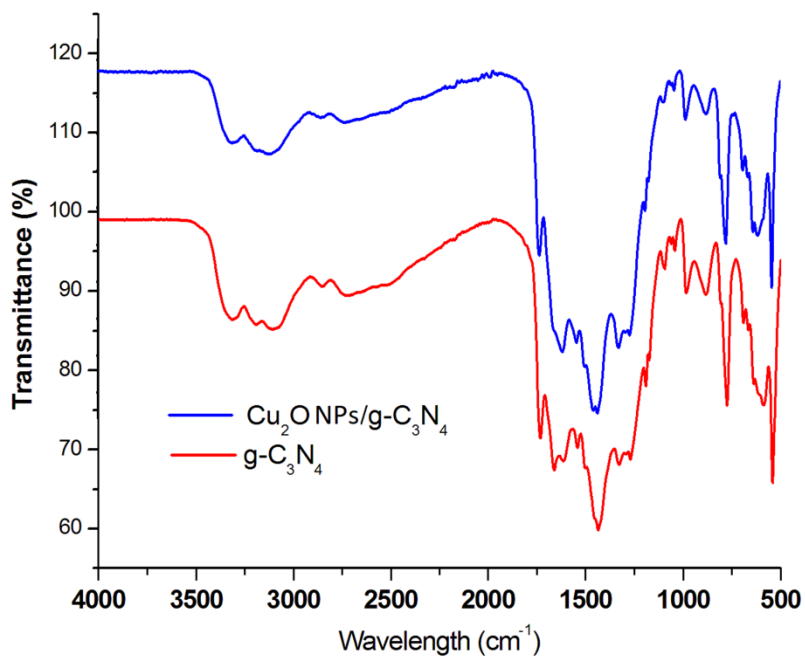


Figure S3. FT-IR spectrum of (1) g-C₃N₄ and (2) Cu₂O NPs/g-C₃N₄.

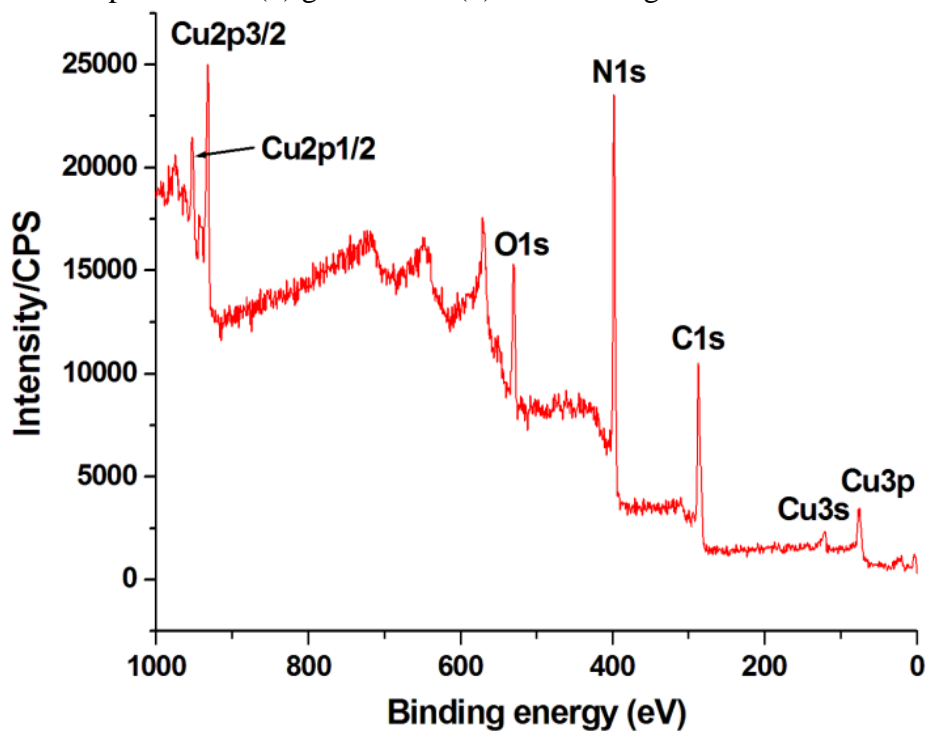


Figure S4. X-ray photoelectron spectrum (XPS) of Cu₂O NPs/g-C₃N₄.

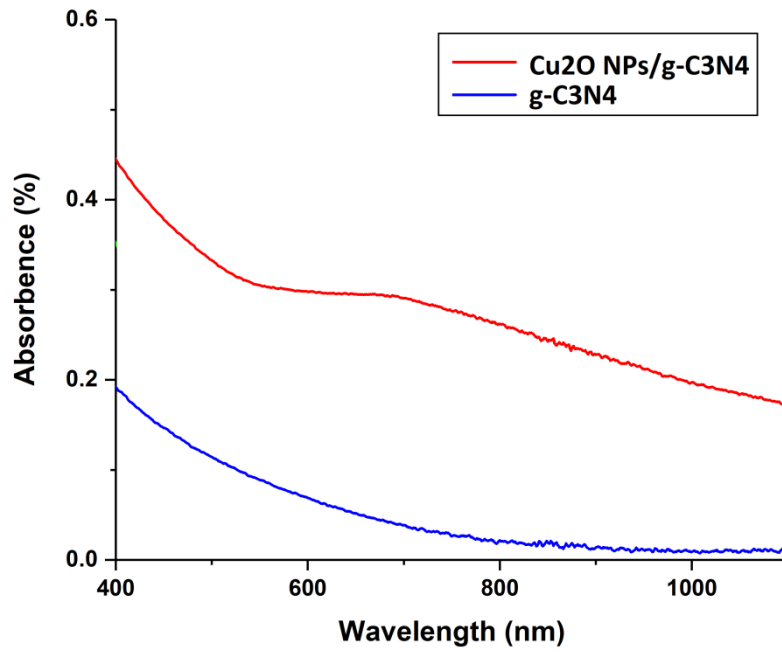


Figure S5. UV-visible diffusion reflectance spectra of g-C₃N₄ and Cu₂O NPs/g-C₃N₄.

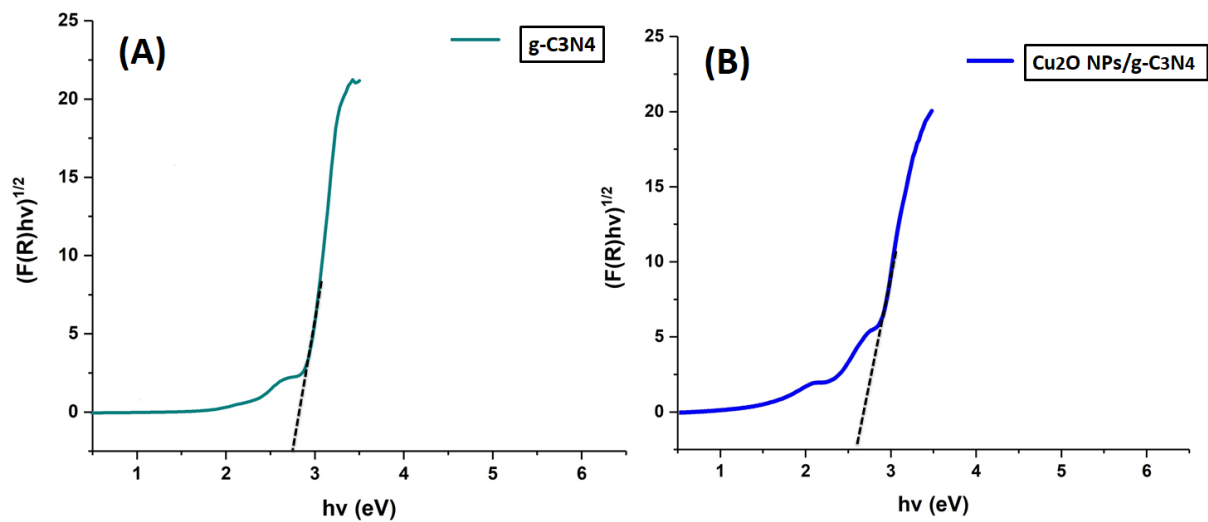


Figure S6. Tauc's plot of g-C₃N₄ and Cu₂O NPs/g-C₃N₄.

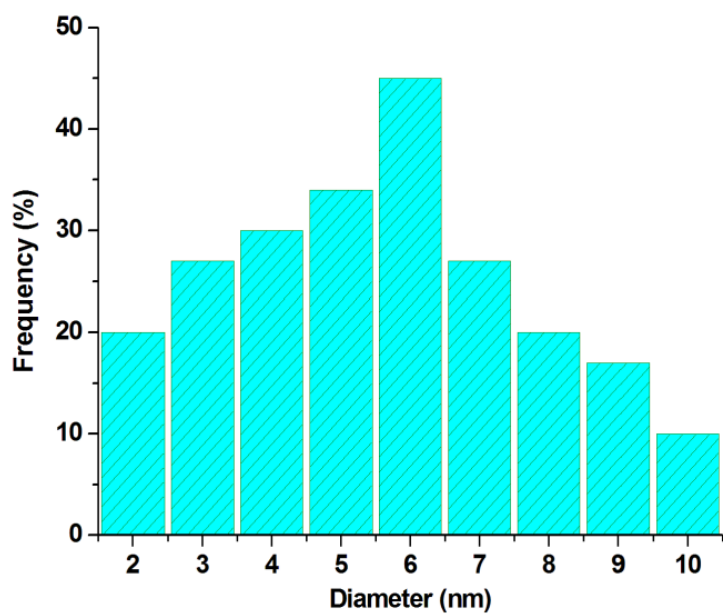


Figure S7. Histogram of Fresh catalyst (Cu_2O NPs/ $\text{g-C}_3\text{N}_4$).

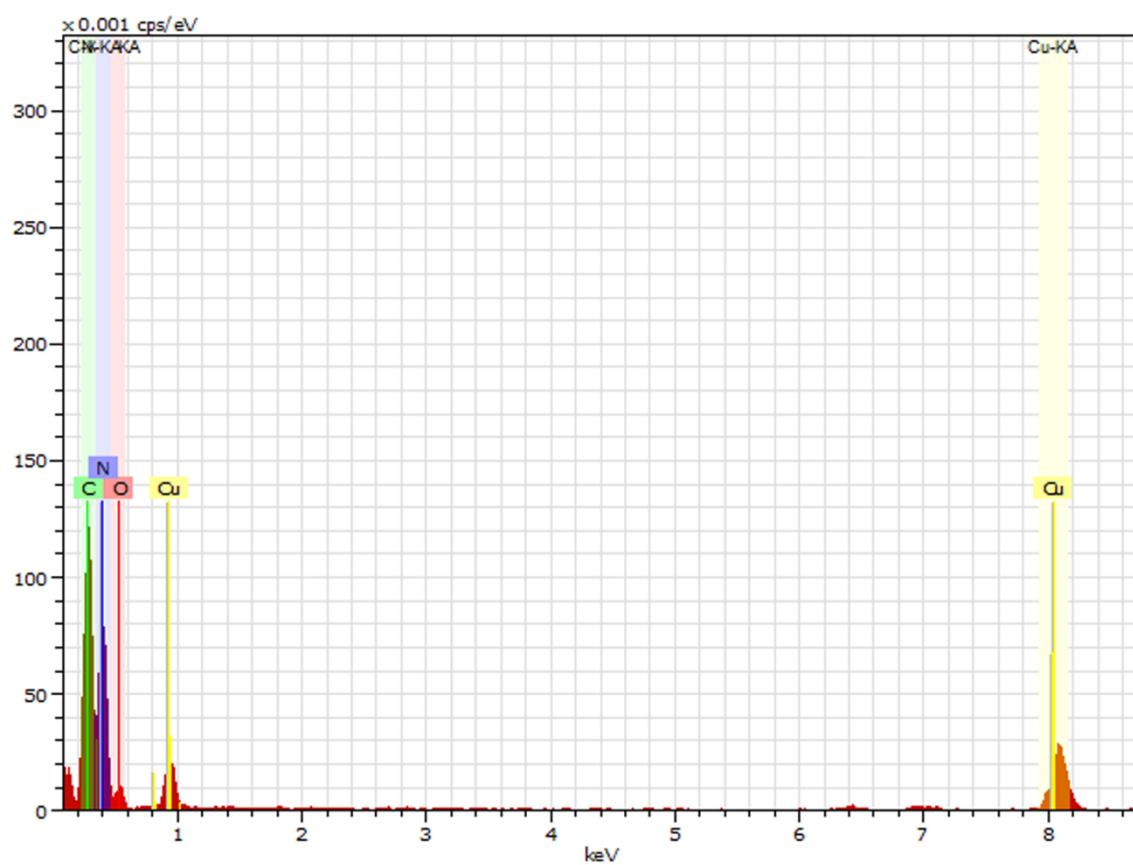


Figure S8. EDX spectra of fresh catalyst (Cu_2O NPs/ $\text{g-C}_3\text{N}_4$).

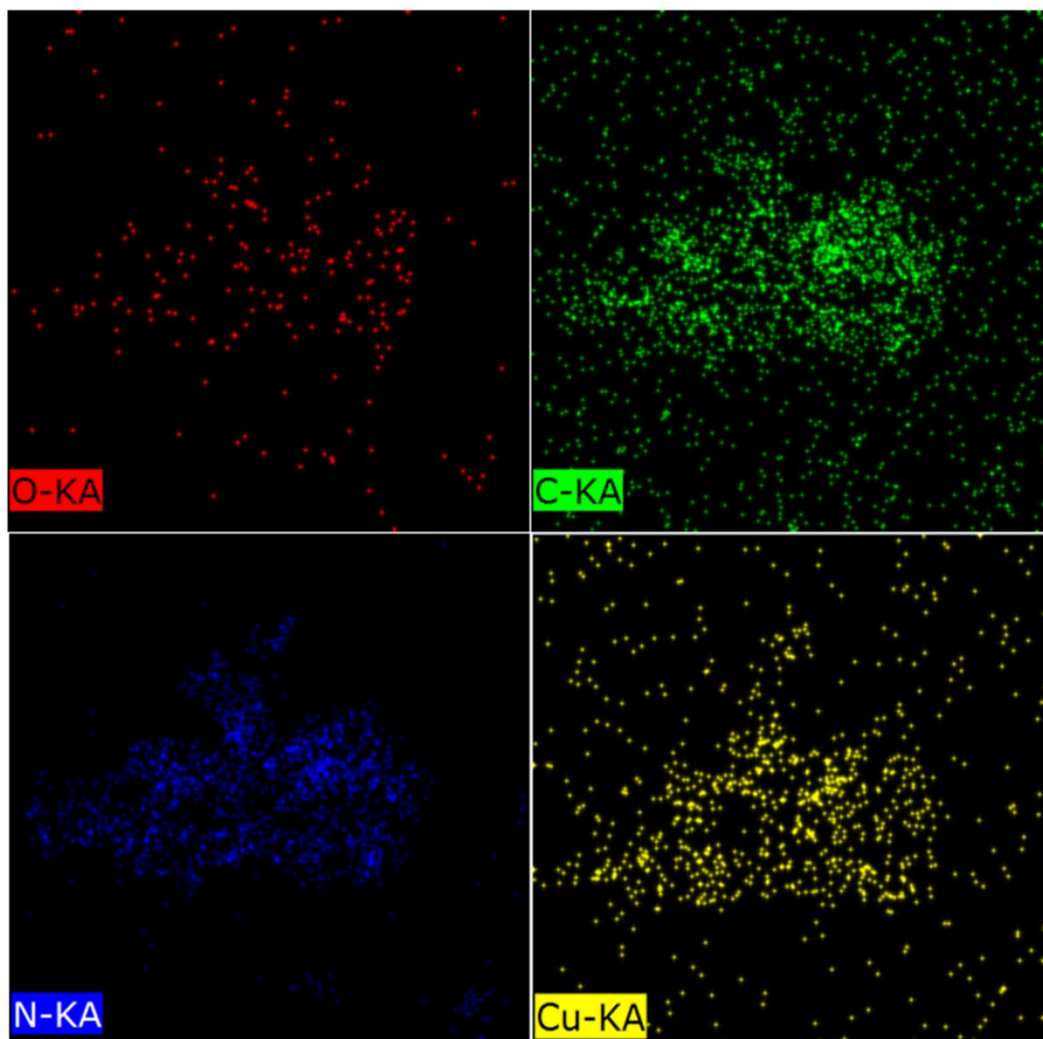


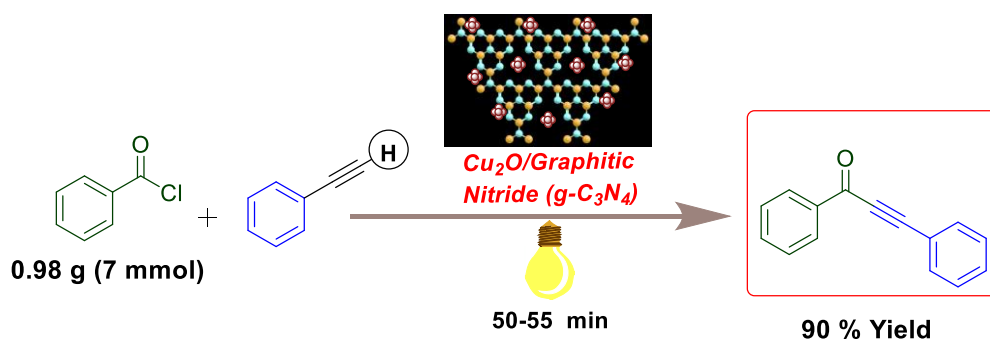
Figure S9. EDS mapping of element O, C, N and Cu present in Cu_2O NPs/g- C_3N_4 catalyst.

Table S1. Comparison of synthesized catalyst Cu₂O NPs/g-C₃N₄ with others reported in Literature.

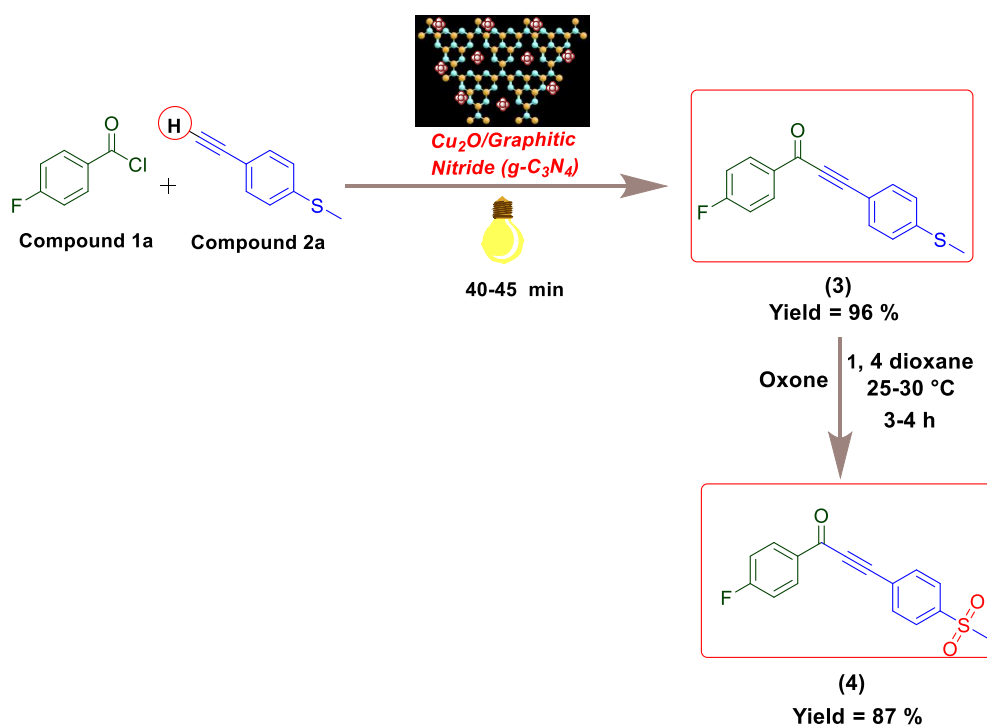
Entry	Catalyst	Experimental Conditions	Yield (%)	TON	TOF	Ref.
1	Cu NPs/ γ -Al ₂ O ₃	40 °C, 24 h, Solvent free	98	98	4.0	1
2	Cu NPs/Silica gel	40 °C, 24 h, Solvent free	98	98	4.0	1
3	Cu/Cu ₂ O NPs	80 °C, 24 h, Toluene	94	6.26	0.26	2
4	Cu NPs@MP-3	40 °C, 6.0 h, Solvent free	96	48	8.0	3
5	CoCuFe ₂ O ₄	R.T, 50 min, DMF	90	18	22	4
6	Pd NPs/MMT k-10	R.T, 3.0 h, 1,4-dioxane	96	6.0	2.0	5
7	Pd-Sc@ASMNPs	R.T, 2.0 h, Acetonitrile:Water	96	559	279.5	6
8	CuFe ₂ O ₄	R.T, 4.0 h, Solvent free	94	47	12	7
9	Cu₂O NPs/g-C₃N₄	Visible light (R.T), 30 min, Solvent Free	99	247	495	This work

Table S2. Comparison of the performance of the Cu₂O NPs/g-C₃N₄ catalyst for the synthesis of product (4aa) to the reported ones.

Entry	Catalyst	Experimental Conditions	Yield (%)	TON	TOF	Ref.
1	Cu NPs/C	70° C, 3 h, CH ₂ Cl ₂	86	172	57.33	8
2	CuI/CSP	100° C, 0.5 h, EG	75	3.80	7.6	9
4	Cu/Cu-BTC-MOF	70° C, 3h, CH ₂ Cl ₂	99.3	9.93	3.31	10
5	Cu/Meso-ZSM-5	70° C, 3h, CH ₂ Cl ₂	93.6	9.36	3.12	11
7	Cu₂O NPs/g-C₃N₄	Visible light, 40 min, EG	98	245	371	This Work



Scheme S1. Gram-Scale Synthesis of Ynone by using the $\text{Cu}_2\text{O}@g\text{-C}_3\text{N}_4$ Catalyst.



Scheme S2. Synthesis of 1-(4-fluorophenyl)-3-(4-(methyl sulfonyl) phenyl) prop-2-yn-1-one (4).

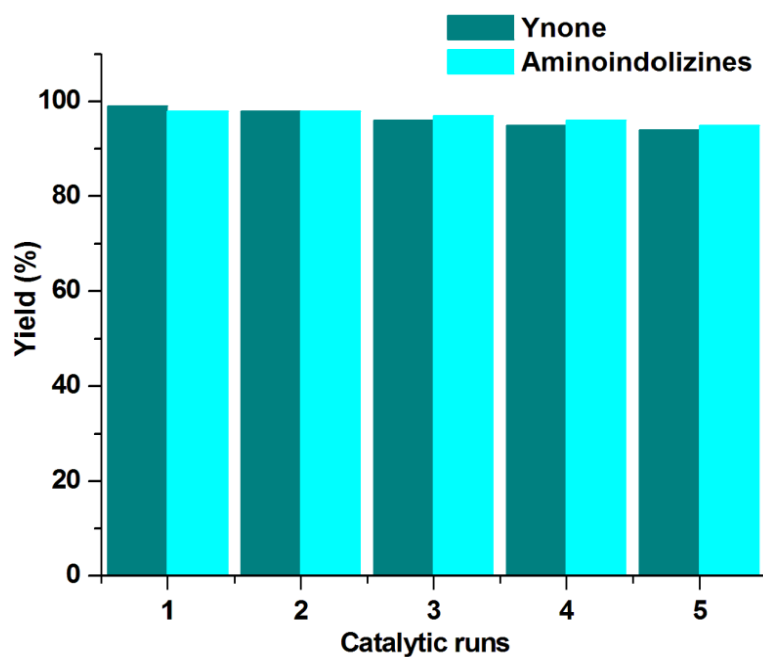


Figure S10. Recyclability of Cu_2O NPs/g- C_3N_4 nanocatalyst for the synthesis of Ynone and Aminoindolizines.

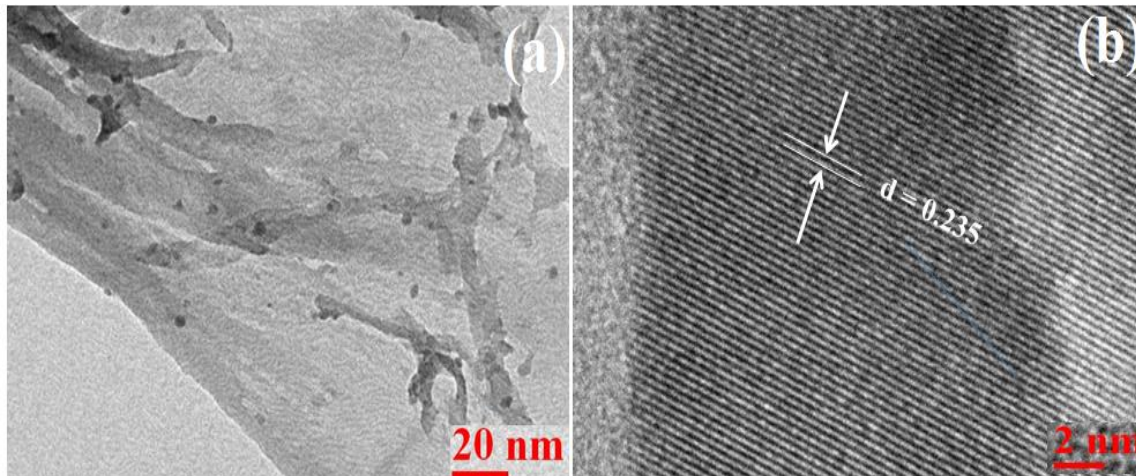


Figure S11. TEM and HR-TEM images of recycled Cu_2O NPs/g- C_3N_4 for the synthesis of Ynone (a-b).

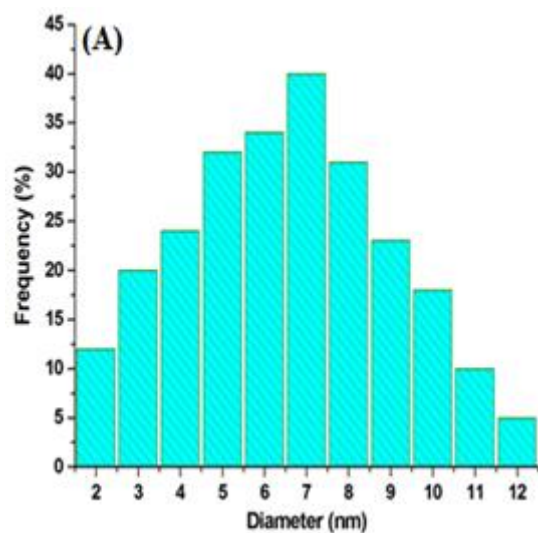


Figure S12. Histogram of recycled catalyst (after fifth run) for the synthesis of Ynone.

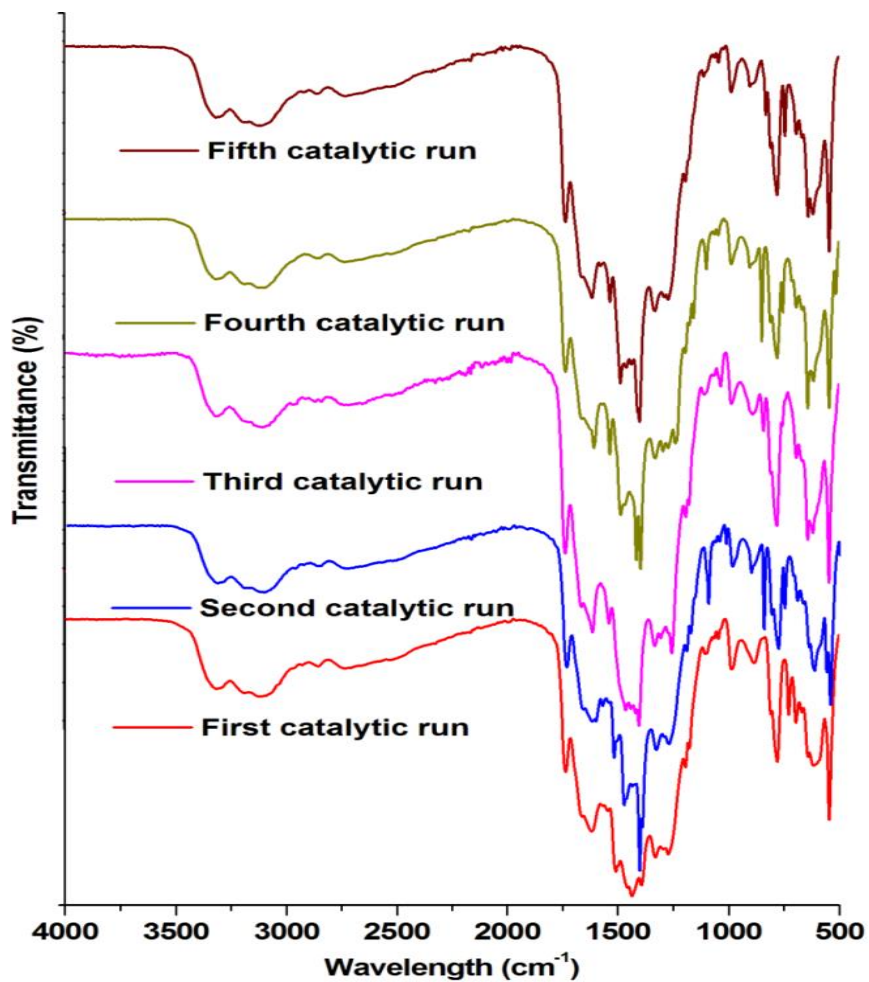
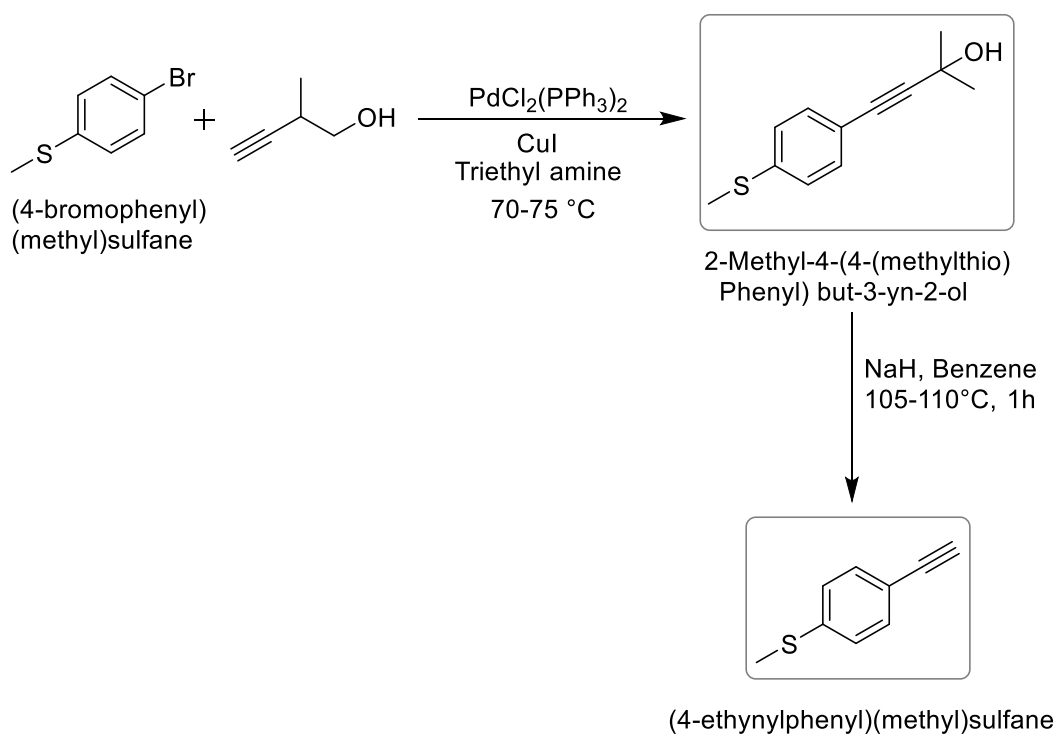


Figure S13. FT-IR spectra of recycled catalyst for the synthesis of Ynone.

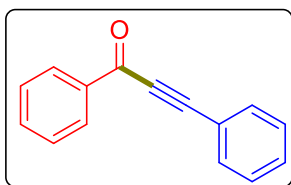
Synthesis of 1-ethynyl-4-methylsulfanylbenzene

Synthesis of 1-ethynyl-4-methylsulfanylbenzene was carried out in two steps reported in literature¹². The Sonogashira coupling of 4-bromothioanisole with 2-methyl-3-butyn-1-ol in the presence of triethylamine, CuI, and PdCl₂(PPh₃)₂ to give para-methylsulfanylphenylacetylene in good yield (60–65%). After the elimination of the isopropanol moiety by using NaH to give desired compound in (40–55%) (Scheme S2).

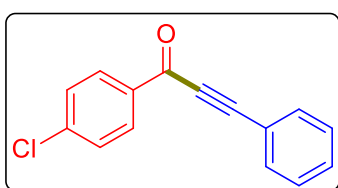


Scheme S3. Synthesis of (4-ethynylphenyl) (methyl) sulfane.

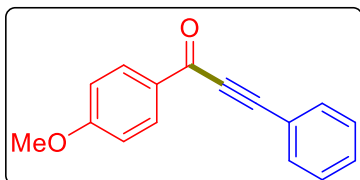
¹H and ¹³C NMR



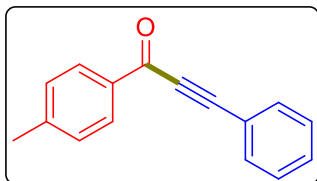
1, 3-diphenylprop-2-yn-1-one(3a):¹H-NMR (400 MHz, CDCl₃): δ 8.25-8.22 (m, 2H), 7.70-7.68 (m, 2H), 7.48 (tt, J = 6.4, 1.2 Hz, 1H), 7.54-7.26 (m, 5H).¹³C NMR (100 MHz, CDCl₃): 178.13, 136.97, 134.15, 133.18, 130.90, 129.67, 128.79, 128.73, 120.22, 93.26, 87.09



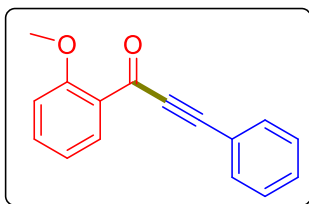
1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one (3b):¹H NMR (400 MHz, CDCl₃): δ 8.12-8.14 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 7.1 Hz, 3H), 7.41 (t, J = 6.8 Hz, 2H).¹³C NMR (100 MHz, CDCl₃): 176.70, 140.01, 135.41, 133.14, 131.05, 130.93, 129.15, 128.83, 119.95, 93.73, 86.66.



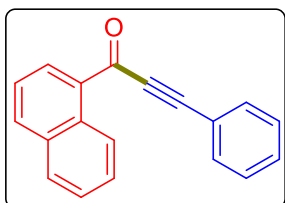
1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-one (3c): ¹H NMR (400 MHz, CDCl₃): δ 8.16-8.19 (d, J = 8.6 Hz, 2H), 7.65-7.66 (d, J = 6.8 Hz, 2H), 7.46-7.38 (m, 3H), 6.97 (d, J = 8.8 Hz, 2H), 3.66 (s, 3H).¹³C NMR (100 MHz, CDCl₃): 176.76, 164.52, 133.01, 132.00, 130.70, 130.45, 128.70, 120.47, 113.93, 92.41, 87.05, 55.65.



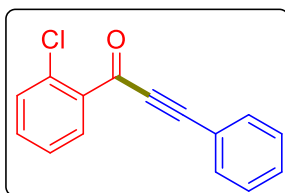
3-phenyl-1-(p-tolyl)prop-2-yn-1-one (3d): ¹H NMR (400 MHz, CDCl₃): δ 8.09-8.11 (d, J = 8.1 Hz, 2H), 7.65-7.67 (d, J = 7.3 Hz, 2H), 7.47-7.38 (m, 3H), 7.28 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H).¹³C NMR (100 MHz, CDCl₃): 177.80, 145.31, 134.73, 133.13, 130.75, 129.80, 129.46, 128.74, 120.33, 92.71, 87.04, 21.33.



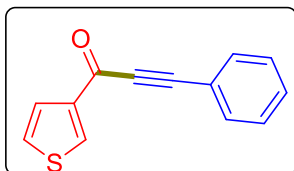
1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one (3e): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.07 (dd, $J = 7.8, 1.9$ Hz, 1H), 7.62 (dt, $J = 7.0, 1.5$ Hz, 2H), 7.53 (t, $J = 7.9$ Hz, 1H), 7.46-7.33 (m, 3H), 7.10-6.97 (m, 2H), 3.95 (s, 3H), $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 176.75, 159.72, 134.97, 132.96, 132.71, 130.41, 128.58, 126.67, 120.62, 120.24, 112.18, 91.52, 89.15, 55.87.



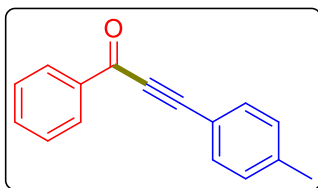
1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-one (3f): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.25 (d, $J = 8.6$ Hz, 1H), 8.63 (d, $J = 8.1$ Hz, 1H), 8.06 (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 8.2$ Hz, 1H), 7.67 (t, $J = 7.4$ Hz, 4H), 7.56 (q, $J = 7.4$ Hz, 3H), 7.41 (ddd, $J = 14.8, 8.0, 6.3$ Hz, 2H), $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 179.77, 135.21, 134.60, 133.86, 132.94, 132.89, 130.72, 130.63, 128.96, 128.71, 128.58, 126.78, 125.99, 124.48, 120.31, 91.75, 88.50.



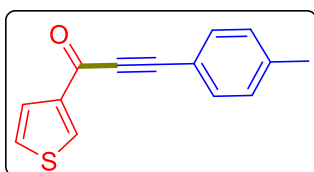
1-(2-chlorophenyl)-3-phenylprop-2-yn-1-one (3g): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.08 (d, $J = 8.3$ Hz, 1H), 7.64 (d, $J = 7.5$ Hz, 2H), 7.50-7.44 (m, 3H), 7.40 (t, $J = 7.3$ Hz, 3H), $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 176.80, 135.81, 133.52, 133.36, 133.03, 132.60, 132.56, 131.54, 130.98, 128.66, 126.79, 119.97, 93.94, 88.29.



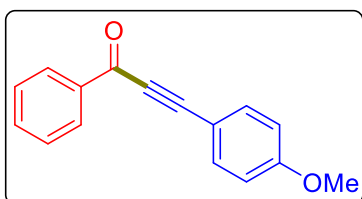
3-phenyl-1-(thiophen-3-yl)prop-2-yn-1-one (3h): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.03-7.95 (m, 1H), 7.71 (d, $J = 4.8$ Hz, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 7.1$ Hz, 1H), 7.40 (t, $J = 7.3$ Hz, 2H), 7.20-7.15 (m, 1H), $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 169.67, 144.86, 135.29, 135.14, 133.00, 130.86, 128.64, 128.35, 119.89, 91.78, 86.43.



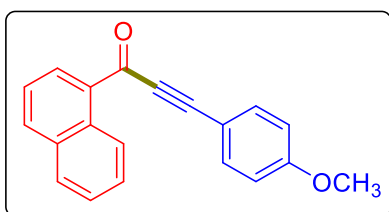
1-phenyl-3-(p-tolyl)prop-2-yn-1-one (3i): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.22 (d, $J = 6.8$ Hz, 2H), 7.63-7.54 (m, 3H), 7.52-7.49 (m, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 2.40 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): 178.16, 141.62, 137.12, 134.02, 133.20, 129.66, 129.54, 128.69, 117.12, 93.94, 86.86, 20.85.



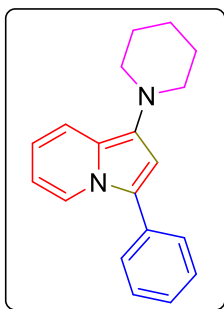
1-(thiophen-3-yl)-3-(p-tolyl)prop-2-yn-1-one (3j): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.98 (d, $J = 3.0$ Hz, 1H), 7.70 (d, $J = 4.8$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 2H), 7.18 (dd, $J = 12.5, 5.8$ Hz, 3H), 2.38 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): 169.88, 145.04, 141.68, 135.09, 134.96, 133.00, 129.44, 128.32, 116.74, 92.47, 86.43, 21.74.



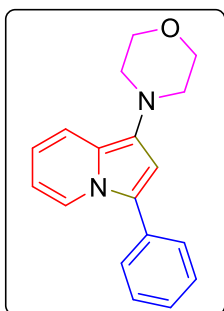
3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-one (3k): $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.20-8.21 (d, $J = 7.2$ Hz, 2H), 7.65-7.59 (m, 3H), 7.50 (t, $J = 8.0$ Hz, 2H), 6.91-6.93 (d, $J = 8.8$ Hz, 2H), 3.64 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): 178.11, 161.86, 137.13, 135.26, 134.01, 129.56, 128.61, 114.51, 111.98, 94.45, 86.95, 55.51.



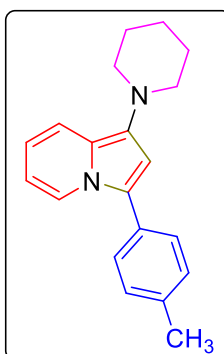
3-(4-methoxyphenyl)-1-(naphthalen-1-yl)prop-2-yn-1-one (3l): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 9.20-9.22 (d, $J = 8.7$ Hz, 1H), 8.60-8.62 (d, $J = 7.0$ Hz, 1H), 8.07-8.09 (d, $J = 8.2$ Hz, 1H), 7.89-7.90 (d, $J = 8.1$ Hz, 1H), 7.68-7.49 (m, 5H), 7.00-6.92 (m, 2H), 3.9289 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): 179.86, 161.59, 135.03, 134.78, 134.14, 133.88, 133.23, 130.72, 128.76, 128.51, 126.67, 126.06, 124.45, 114.36, 112.10, 92.87, 88.44, 55.42.



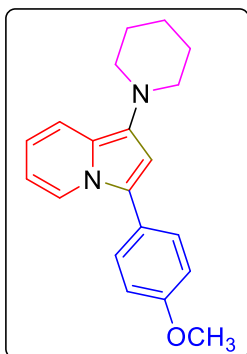
3-phenyl-1-(piperidin-1-yl)indolizine (4aaa): $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 1.38-1.46 (m, 2H), 1.65-1.70 (m, 4H), 2.96-2.98 (t, 4H), 6.01-6.06 (m, 1H), 6.33-6.36 (m, 1H), 6.70 (s, 1H), 7.14-7.38 (m, 3H), 7.36-7.38 (m, 2H), 7.55 (d, $J = 9.2$, 1H), 7.92-7.94 (d, $J = 7.2$, 1H); $^{13}\text{C NMR}$ (101 MHz, C_6D_6): δ 24.87, 27.08, 55.71, 106.66, 111.08, 114.61, 118.61, 121.70, 122.78, 126.11, 126.80, 128.18, 129.11, 132.13, 133.35.



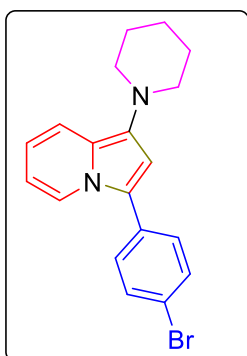
4-(3-phenylindolizin-1-yl)morpholine (4aba): Yellow oil; $^1\text{H NMR}$ (400 MHz, C_6D_6) δ 2.95-2.97 (t, 4H), 3.83-3.86 (t, 4H), 6.11-6.15 (m, 1H), 6.44-6.45 (ddd, $J = 9.0$, $J = 6.3$ Hz, $J = 0.9$, 1H), 6.72 (s, 1H), 7.20-7.29 (m, 3H), 7.44-7.46 (d, $J = 7.2$, 2H), 7.53-7.55 (dt, $J = 9.0$, $J = 1.2$, 1H), 8.00-8.02 (dd, $J = 7.2$, $J = 0.9$, 1H); $^{13}\text{C NMR}$ (101 MHz, C_6D_6): δ 54.84, 67.62, 106.31, 111.11, 114.95, 118.21, 121.85, 123.06, 126.13, 127.05, 128.14, 129.08, 130.70, 133.06.



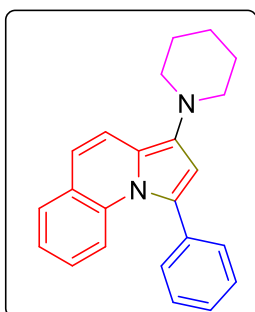
1-(piperidin-1-yl)-3-(p-tolyl)indolizine (4aab): $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 1.50-1.57 (m, 2H), 1.758-1.81 (m, 4H), 2.37 (s, 3H), 3.01 (m, 4H), 6.34 (t, $J = 6.5$, 1H), 6.54 (s, 1H), 6.66 (s, 1H), 7.25, 7.44 (AA'XX' system, 4H), 7.50 (d, $J = 8.4$, 1H), 8.14 (d, $J = 7.2$, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 21.46, 24.28, 26.44, 55.65, 105.55, 110.84, 114.56, 118.25, 121.83, 122.56, 124.83, 127.69, 129.74, 136.74.



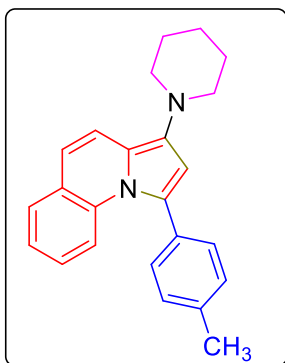
3-(4-methoxyphenyl)-1-(piperidin-1-yl)indolizine (4aac): $^1\text{H NMR}$ (400 MHz, C_6D_6): δ 1.51-1.56 (quintet, 2H), 1.77-1.81 (quintet, 4H), 3.10-3.12 (t, 4H), 3.45 (s, 3H), 6.12-6.18 (m, 1H), 6.43-6.45 (ddd, $J = 9.0, 6.3, 0.9$ Hz, 1H), 6.85 (s, 1H), 6.90, 7.40 (AA'BB' system, 4H), 7.67-7.69 (dt, $J = 9.0, 1.2$, 1H), 8.01-8.03 (dt, $J = 7.2, 0.8$, 1H); $^{13}\text{C NMR}$ (101 MHz, C_6D_6): δ 24.91, 27.32, 54.88, 55.62, 106.18, 110.76, 114.27, 114.59, 118.42, 121.86, 122.60, 125.40, 125.78, 129.89, 131.71, 159.27.



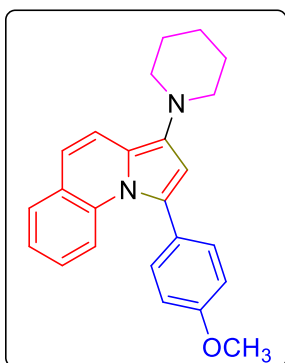
3-(4-bromophenyl)-1-(piperidin-1-yl)indolizine (4aad): $^1\text{H NMR}$ (300 MHz, C_6D_6): δ 1.55-1.56 (m, 2H), 1.75-1.80 (quintet, $J = 5.5$, 4H), 3.06-3.07 (t, $J = 5.5$, 4H), 6.11-6.15 (m, 1H), 6.43-6.44 (ddd, $J = 9.0, 6.5, 1.1$, 1H), 6.75 (s, 1H), 7.00-7.07, 7.36-7.39 (AA'BB' system, 4H), 7.61 (dt, $J = 9.0, 1.2$, 1H), 7.82 (dt, $J = 7.2, 0.9$, 1H); $^{13}\text{C NMR}$ (101 MHz, C_6D_6): δ 24.8, 27.0, 55.7, 106.7, 111.3, 114.9, 118.6, 121.6, 129.4, 132.3, 120.4, 121.4, 126.5, 132.0.



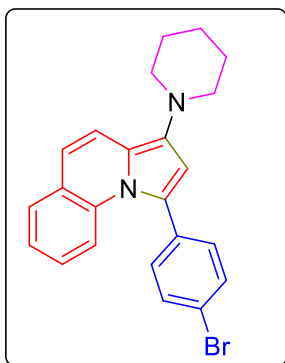
1-phenyl-3-(piperidin-1-yl)pyrrolo[1,2-a]quinoline (4baa): $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.53-1.60 (quintet, 2H), 1.76-1.82 (quintet, 4H), 3.03 (t, 4H), 6.53 (s, 1H), 6.83-6.86 (d, $J = 9.3$, 1H), 7.02-7.05 (m, 1H), 7.15 (td, $J = 7.4, 1.2$, 1H), 7.35-7.46 (m, 8H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 24.43, 26.48, 55.66, 108.71, 116.74, 117.64, 117.91, 126.14, 127.54, 128.32, 128.63, 129.21, 134.20, 135.72.



3-(piperidin-1-yl)-1-(p-tolyl)pyrrolo[1,2-a]quinoline (4bab): $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 1.50-1.55 (quintet, 2H), 1.75-1.79 (quintet, 4H), 2.20 (s, 3H), 3.08-3.10 (t, 4H), 6.71 (s, 1H), 6.81 (d, $J = 9.2$, 1H), 6.90 (dd, $J = 7.8, 1.4$, 1H), 6.92 (ddd, $J = 8.6, 7.2, 1.6$ Hz, 1H), 7.00-7.05 (m, 1H), 7.08, 7.40 (AA'XX' system, 4H), 7.65 (d, $J = 9.2$, 1H), 7.76 (d, $J = 8.6$, 1H), $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 21.41, 24.39, 26.39, 55.68, 108.25, 116.37, 117.67, 117.80, 123.24, 126.09, 126.67, 127.75, 128.21, 129.11, 129.36, 132.18, 132.82, 134.29, 137.34.

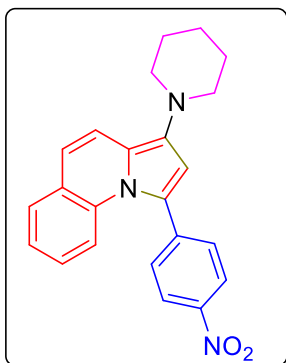


1-(4-methoxyphenyl)-3-(piperidin-1-yl)pyrrolo[1,2-a]quinoline (4bac): $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.54-1.59 (quintet, 2H), 1.75-1.81 (quintet, 4H), 3.00-3.01 (m, 4H), 3.81 (s, 3H), 6.46 (s, 1H), 6.79-6.84 (t, $J = 7.0$, 1H), 6.95-6.97 (d, $J = 6.3$, 2H), 7.01-7.13 (t, $J = 8.4$, 1H), 7.14 (t, $J = 7.4$, 1H), 7.37-7.42 (m, 4H), 7.50-7.52 (d, $J = 7.6$, 1H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3): δ 24.44, 26.49, 55.69, 108.03, 114.09, 116.50, 117.68, 123.23, 123.41, 126.03, 127.58, 128.27, 130.71, 133.73, 134.29, 134.36, 159.22.

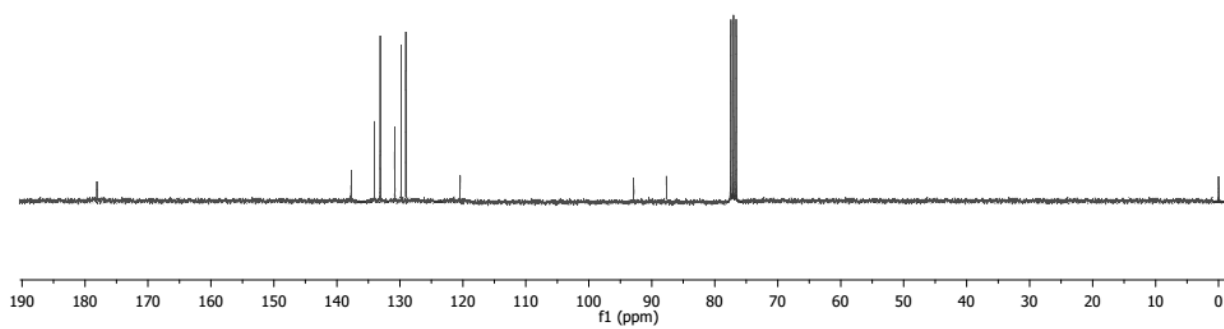
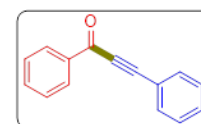
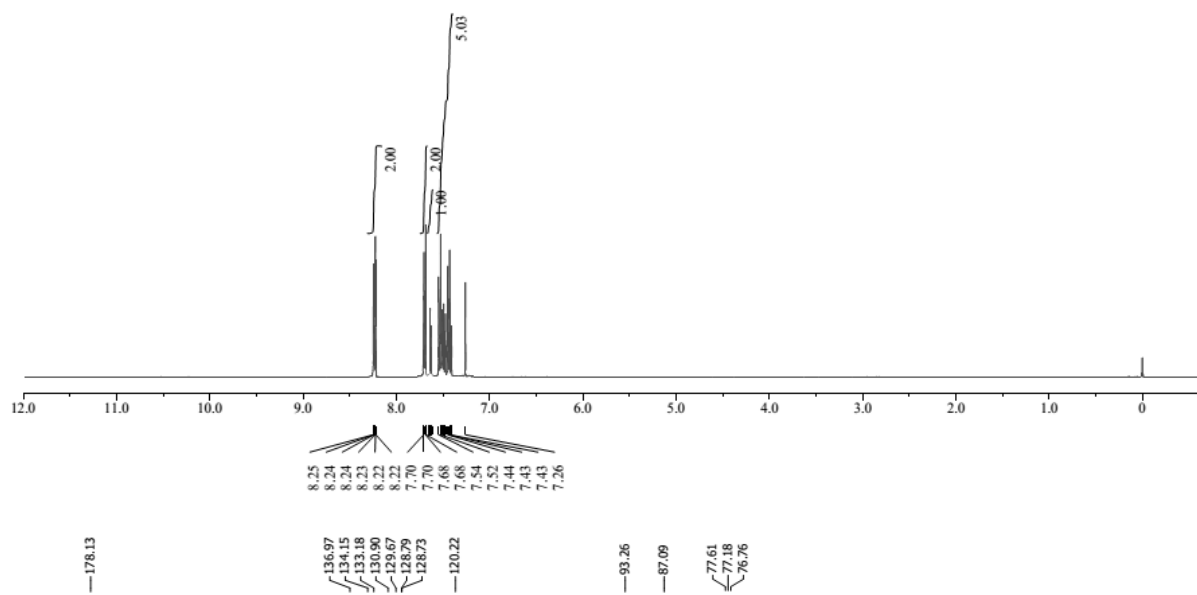
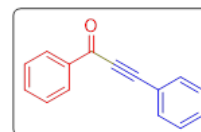


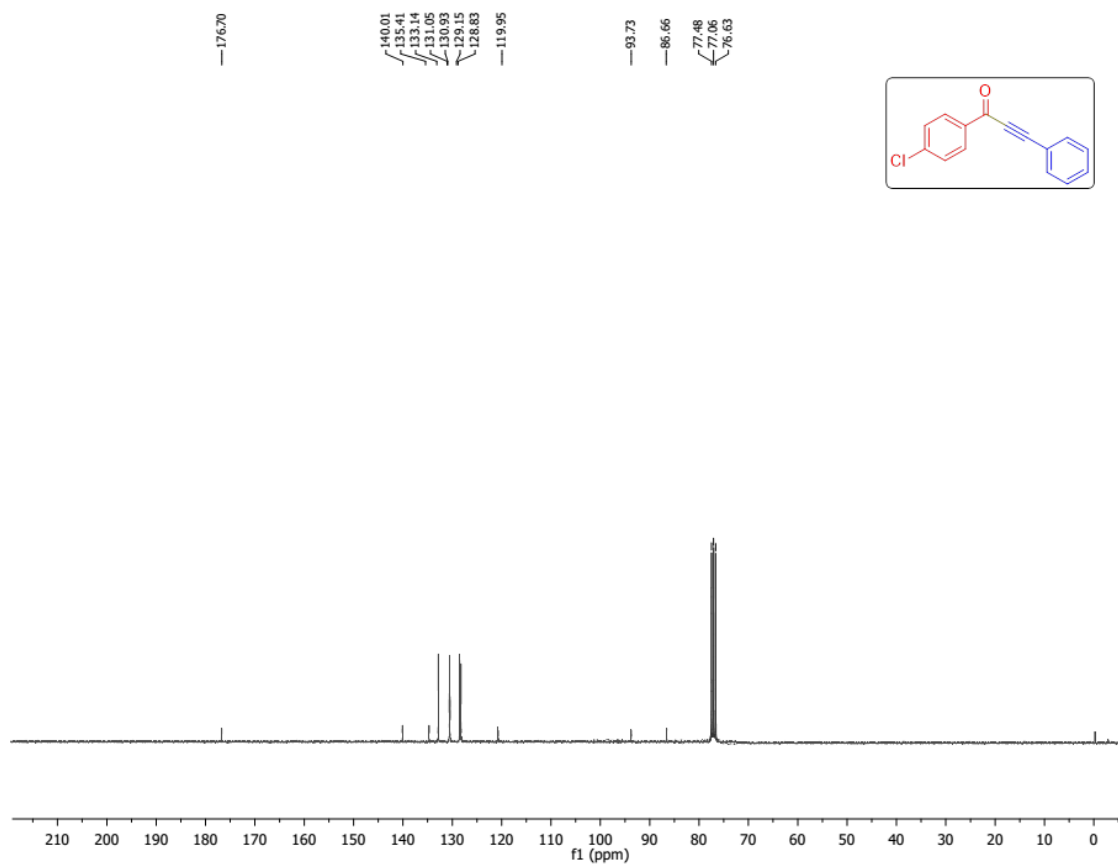
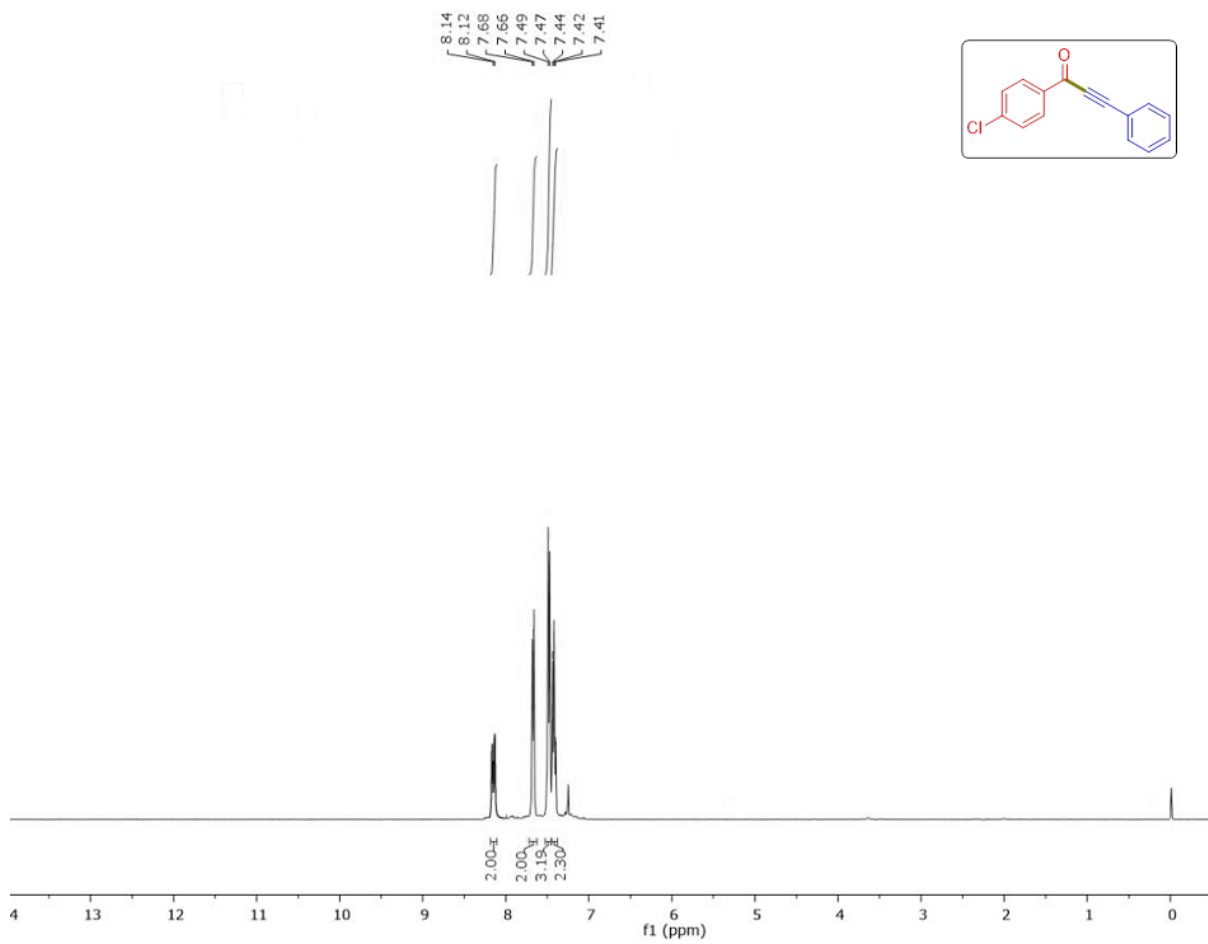
1-(4-bromophenyl)-3-(piperidin-1-yl)pyrrolo[1,2-a]quinoline (4aad): Yellow solid; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 1.51-1.56 (quintet, 2H), 1.75-1.81 (quintet, 4H), 3.07-3.08 (t, 4H), 6.58 (s, 1H), 6.81 (d, $J = 9.6$, 1H), 6.85-6.89 (m, 1H), 7.00-7.05 (m, 3H), 7.33-7.43 (m, 2H), 7.52 (dd, $J = 7.8, 1.4$, 1H),

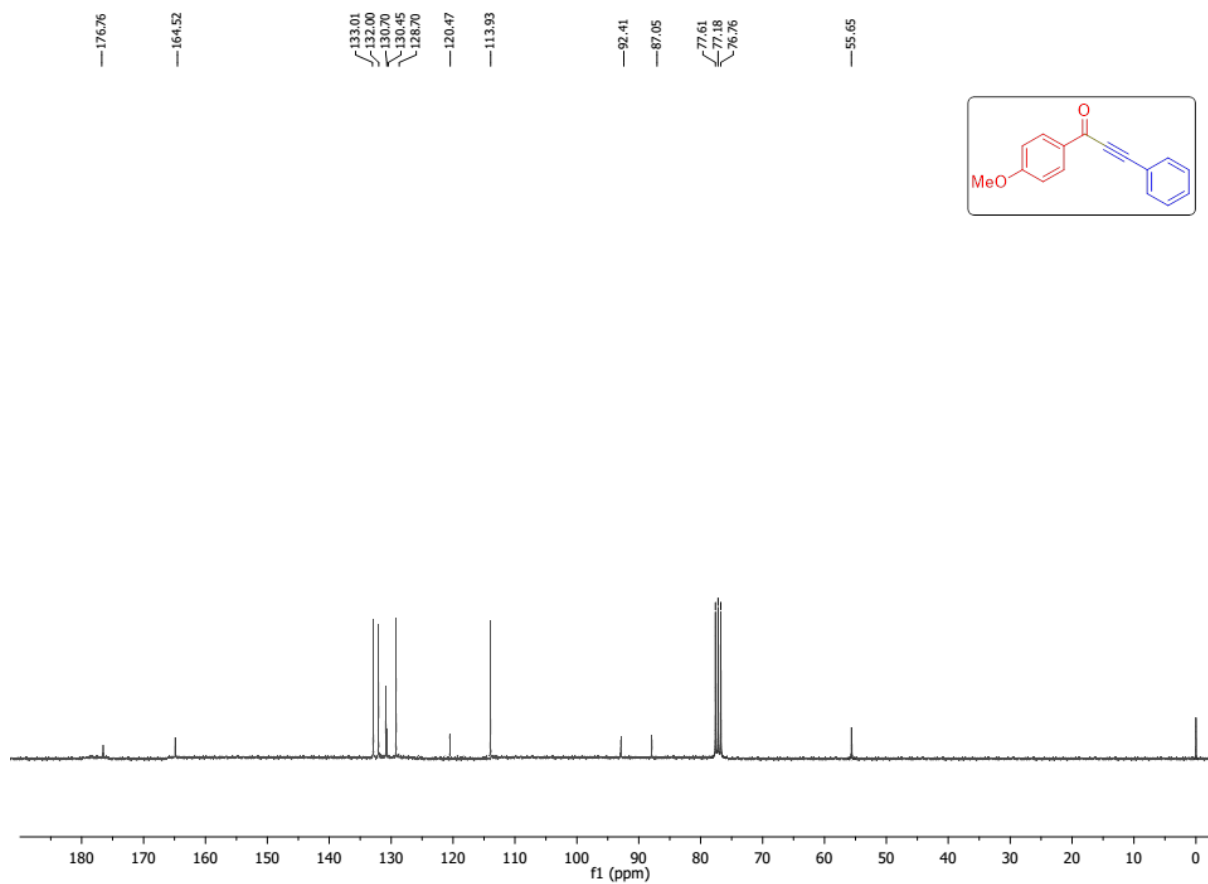
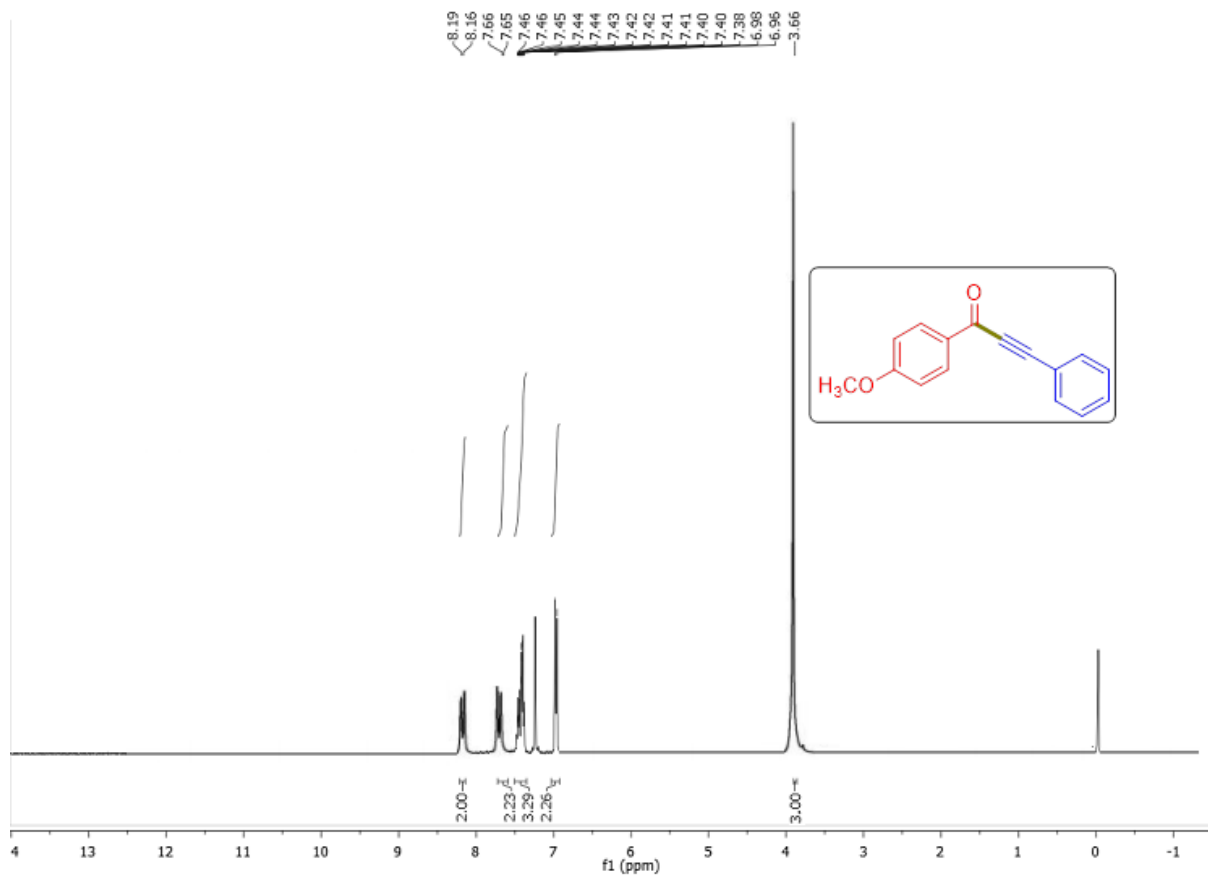
7.54 (d, $J = 8.4$, 1H), 7.61-7.63 (d, $J = 9.2$, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 24.58, 26.91, 55.80, 109.58, 117.12, 118.09, 121.55, 123.60, 125.22, 126.39, 126.56, 128.70, 130.81, 131.88, 134.47, 134.53, 135.04.

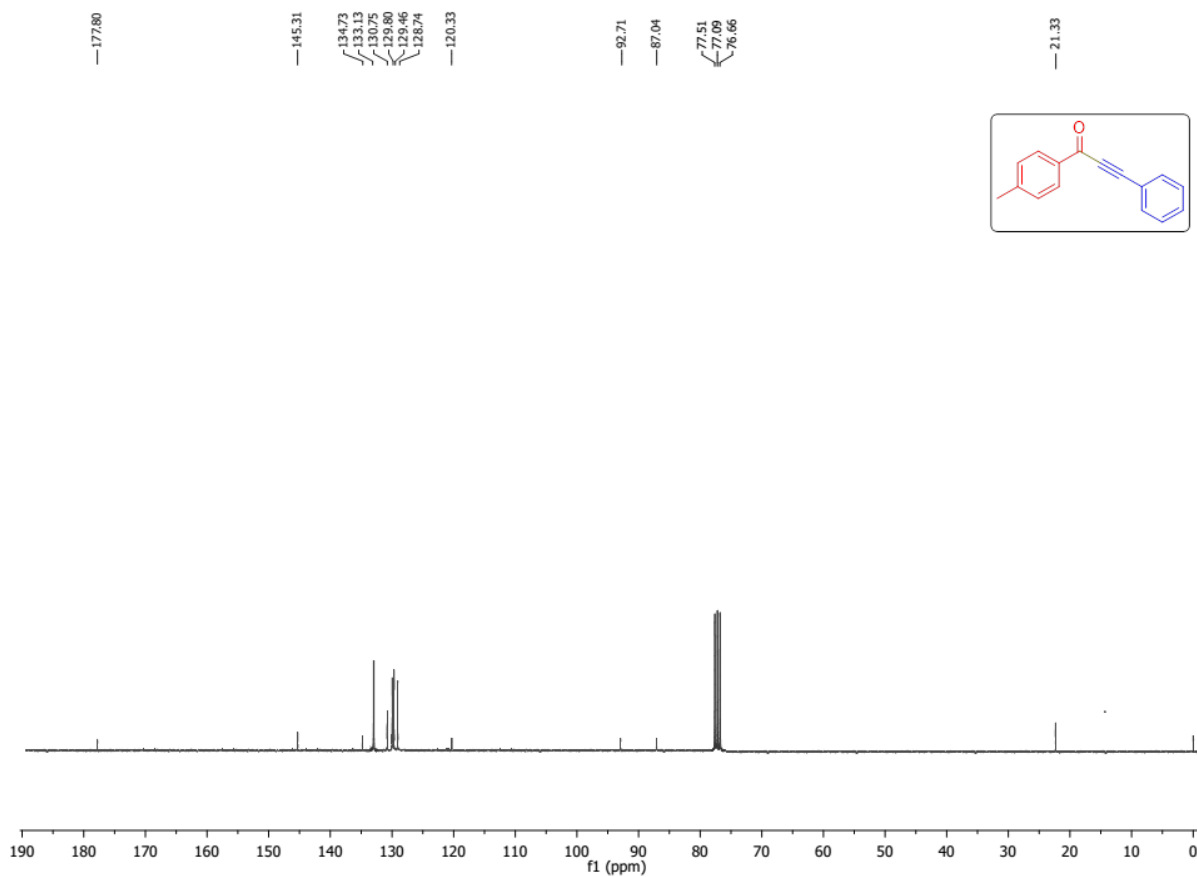
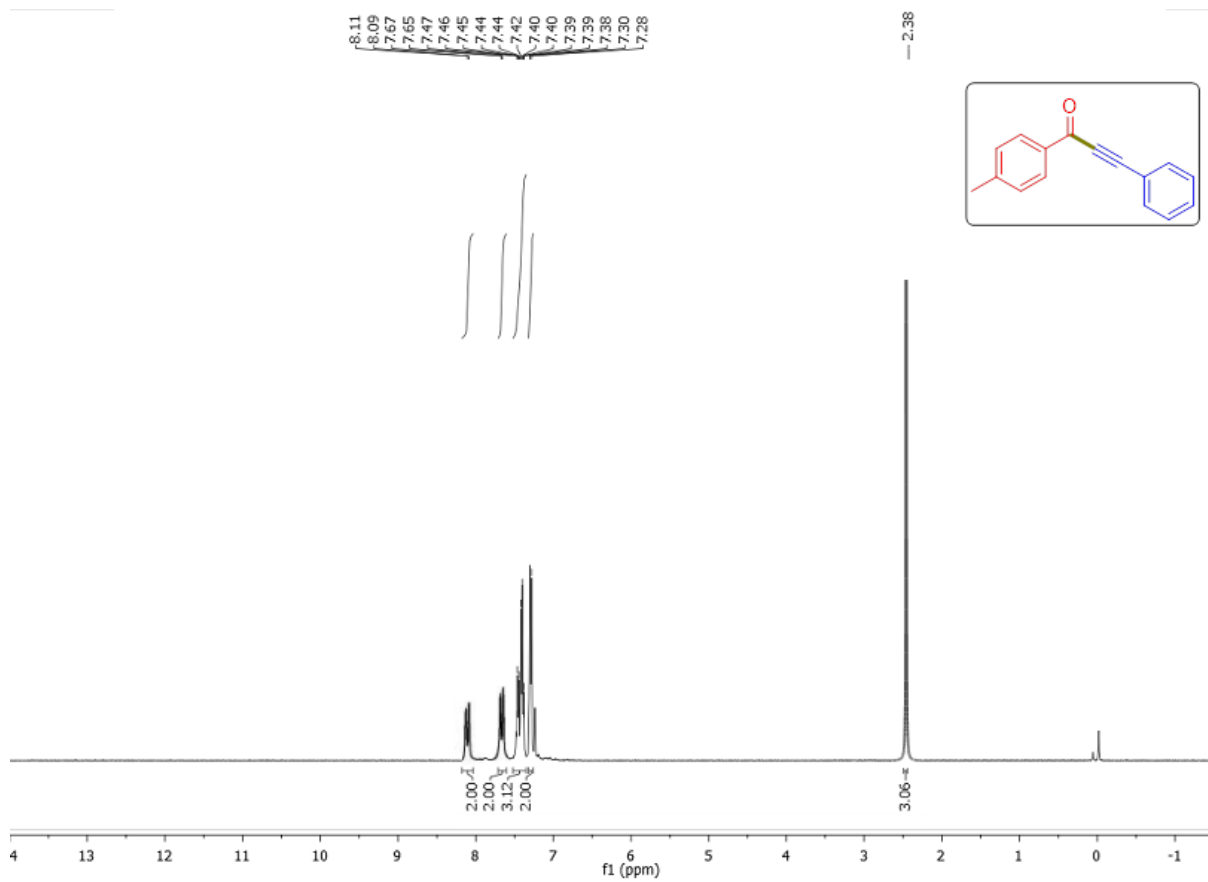


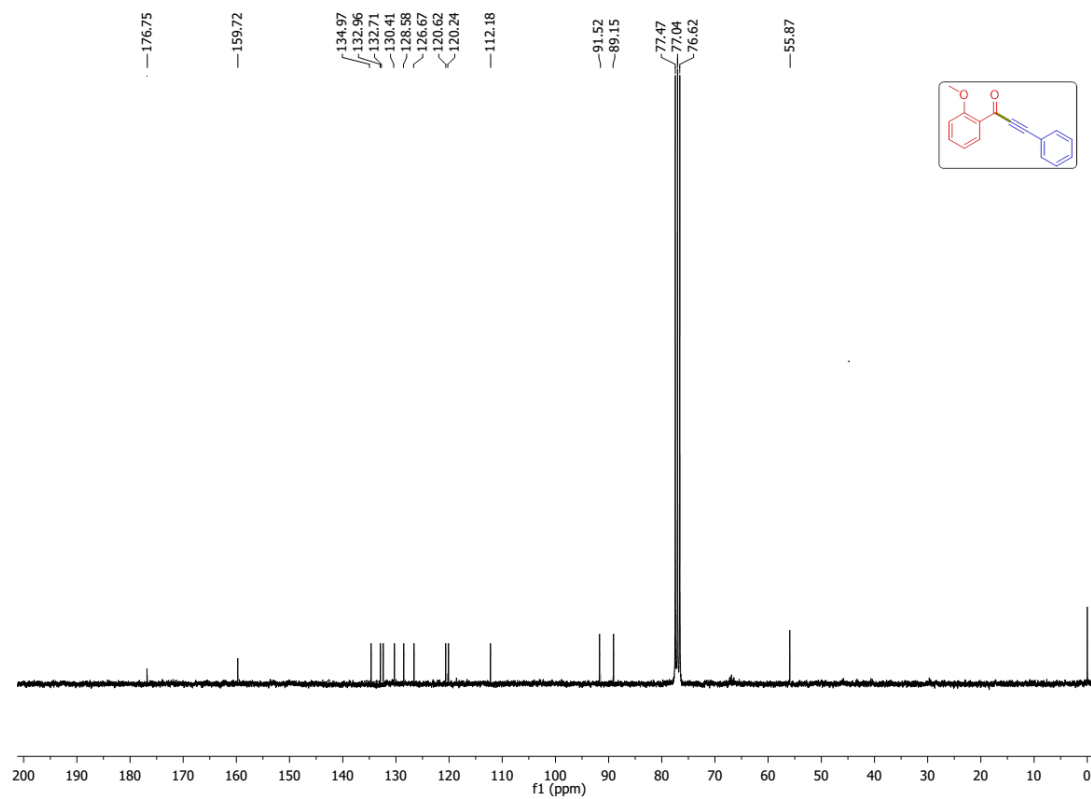
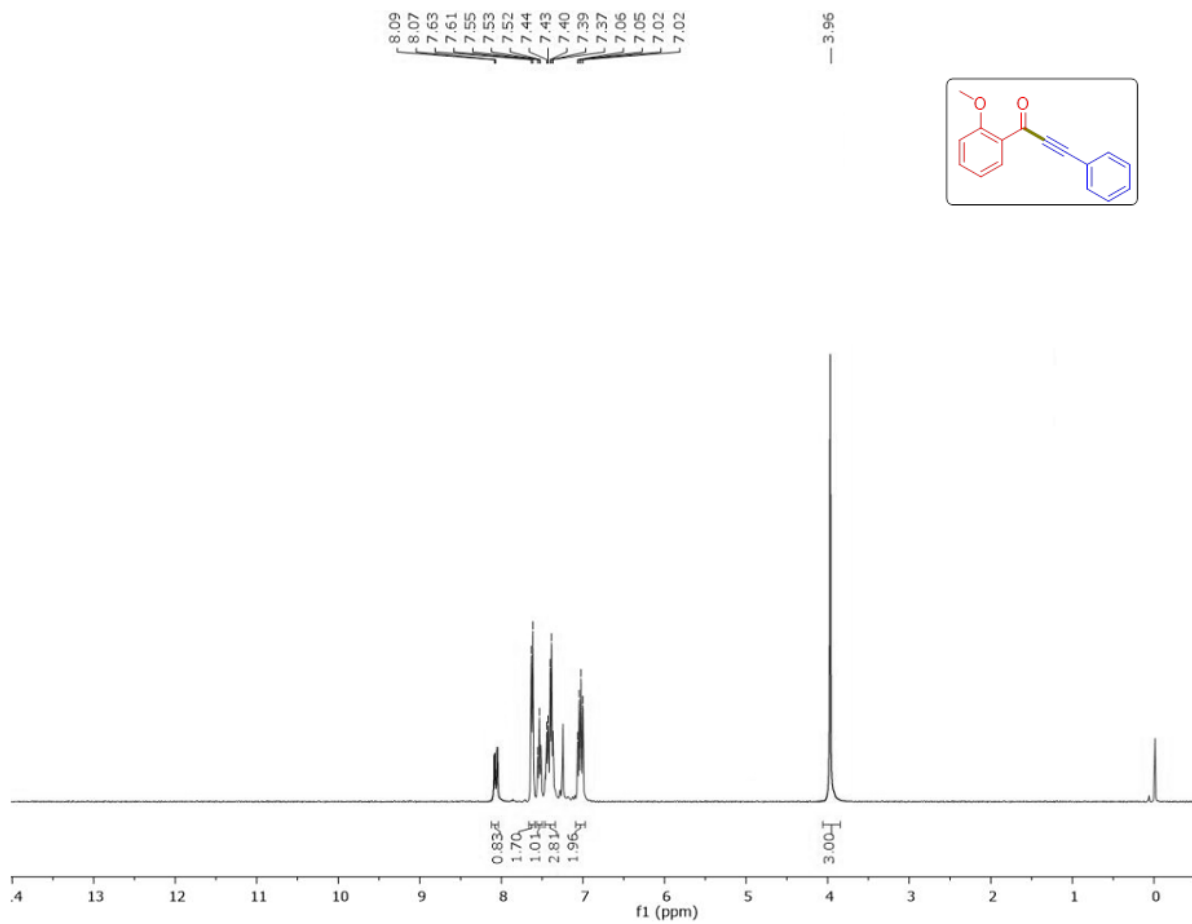
1-(4-nitrophenyl)-3-(piperidin-1-yl)pyrrolo[1,2-a]quinoline (4bad): ^1H NMR (400 MHz, CDCl_3): δ 1.66 (br s, 2H), 1.80 (br s, 4H), 3.06 (br s, 4H), 6.59 (s, 1H), 6.94-6.96 (d, $J = 8.5$, 1H), 7.10-7.14 (m, 1H), 7.21-7.24 (t, $J = 7.4$, 1H), 7.34-7.36 (d, $J = 8.5$, 1H), 7.56 (m, 3H), 7.59, 7.67 (AA'XX' system, 4H); ^{13}C NMR (101 MHz, CDCl_3): δ 24.43, 26.49, 55.58, 116.76, 117.60, 117.62, 126.16, 127.52, 128.32, 128.58, 129.22, 140.69, 142.17, 147.88.

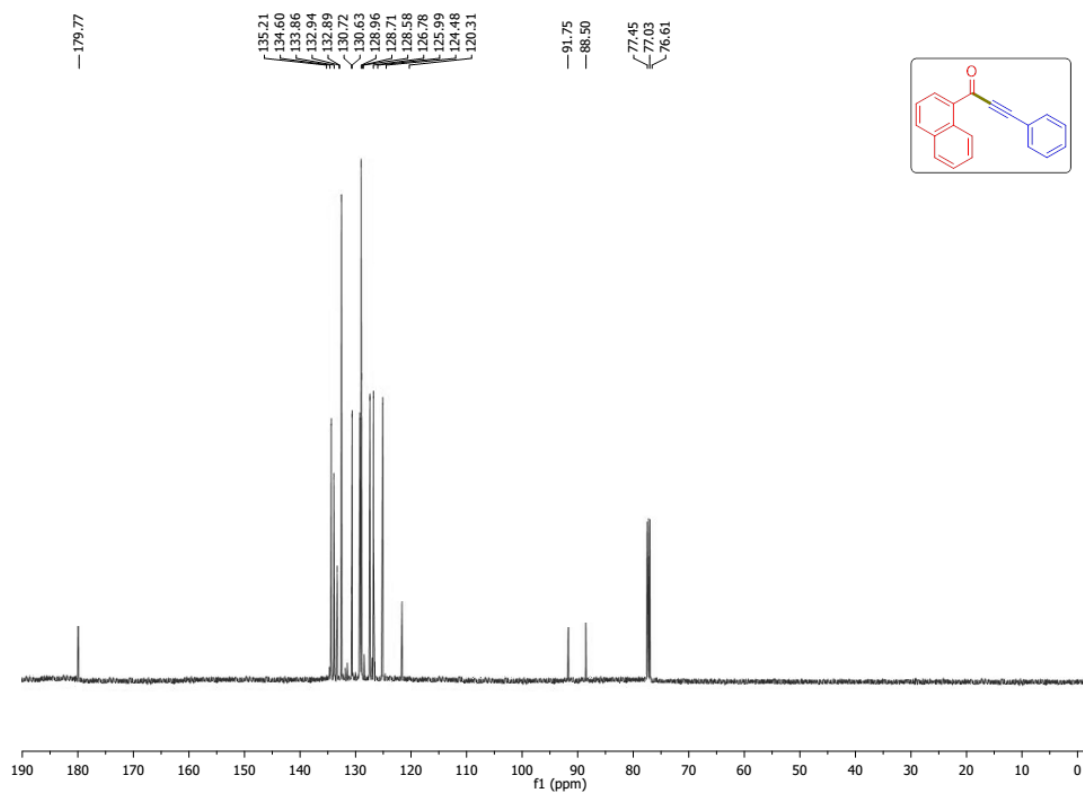
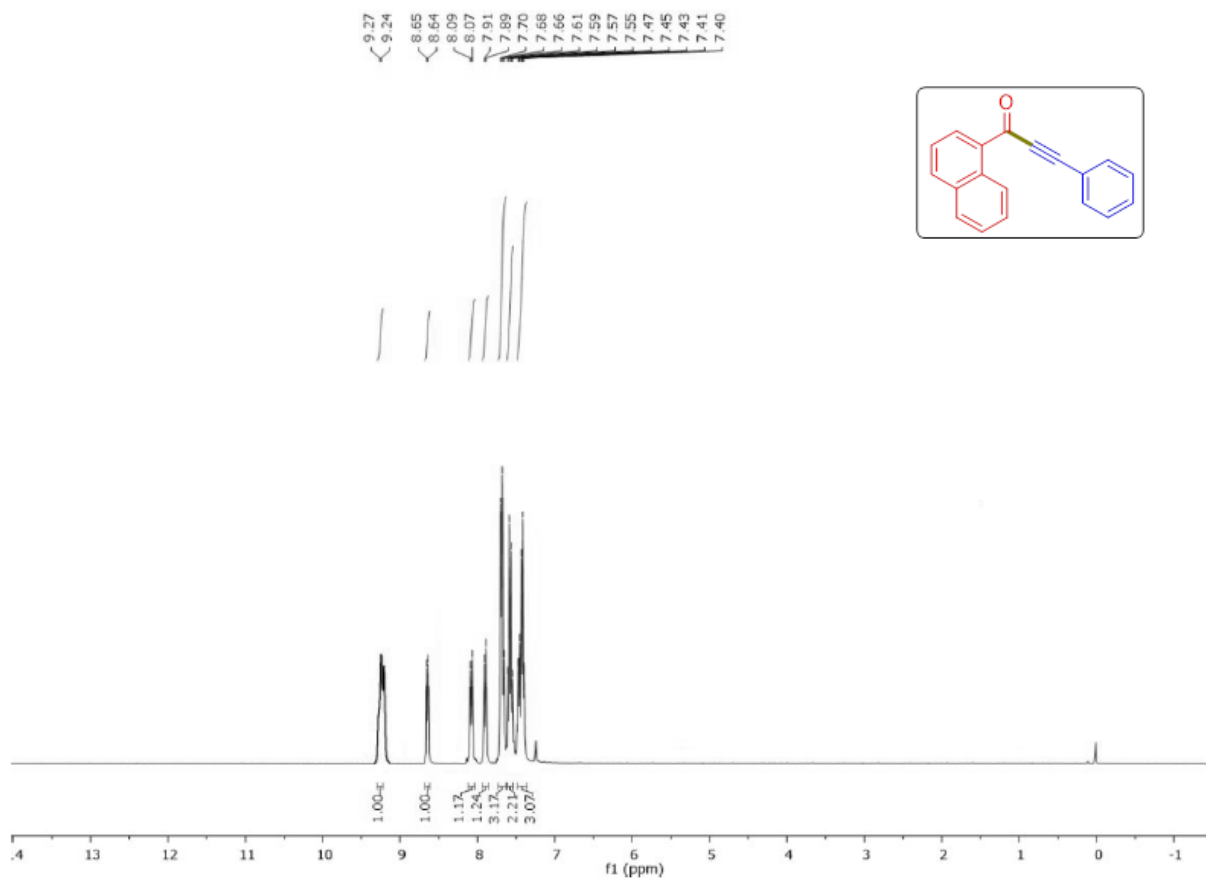


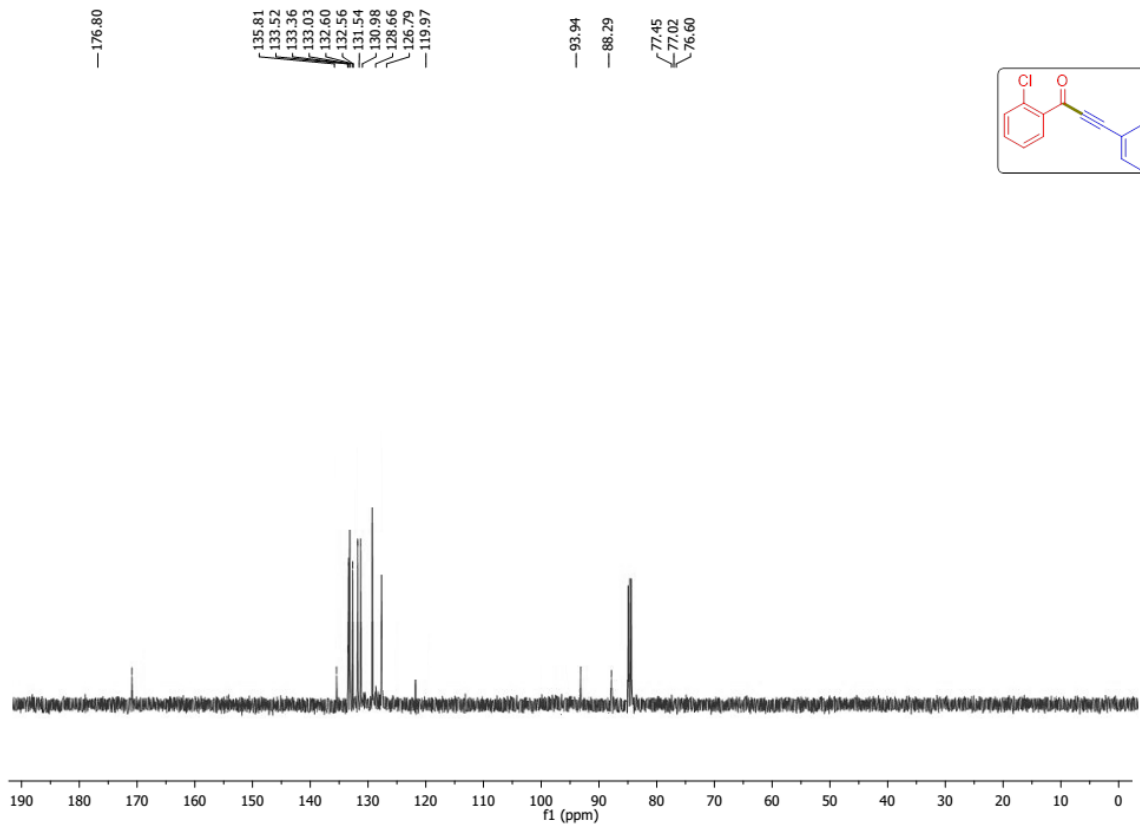
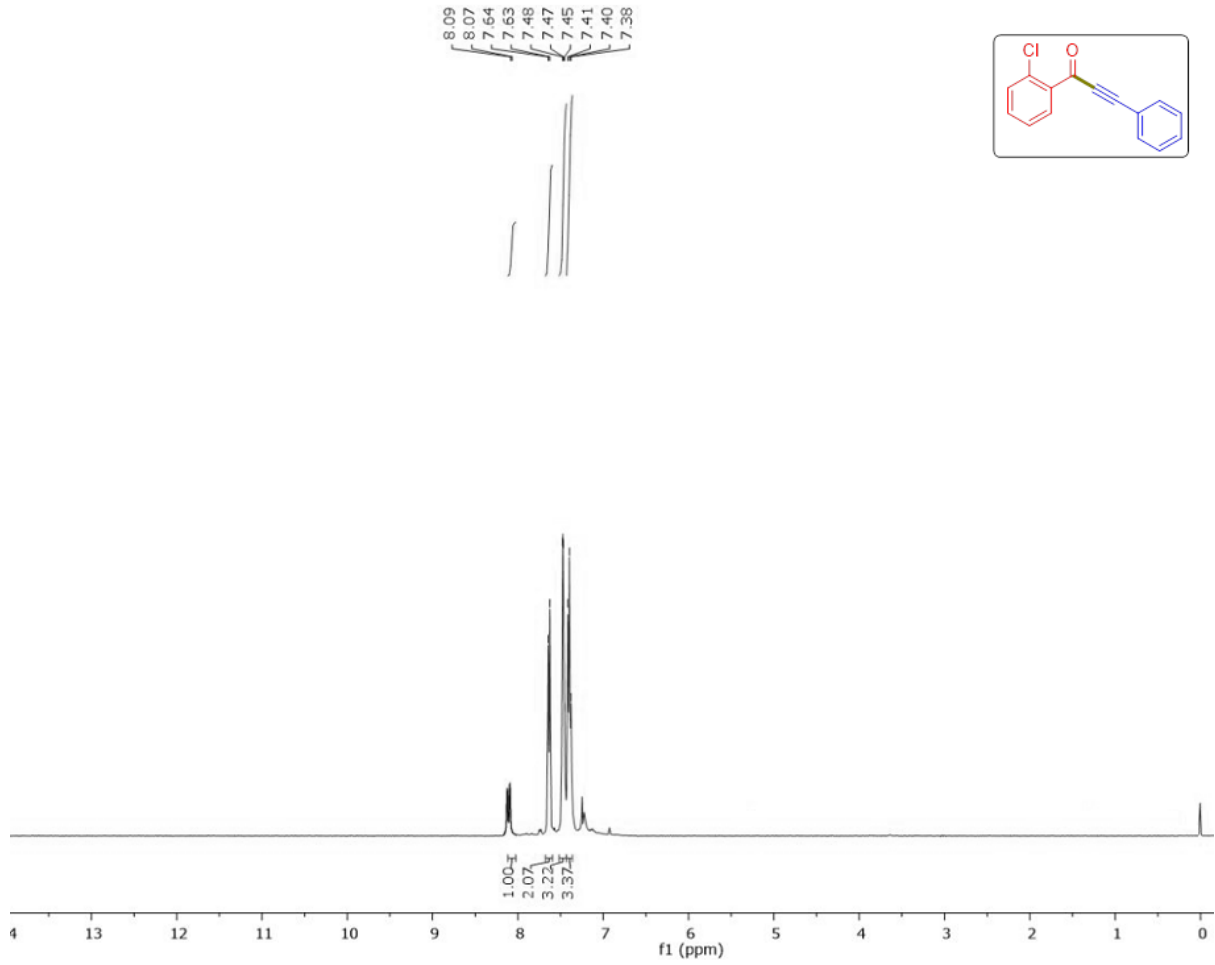


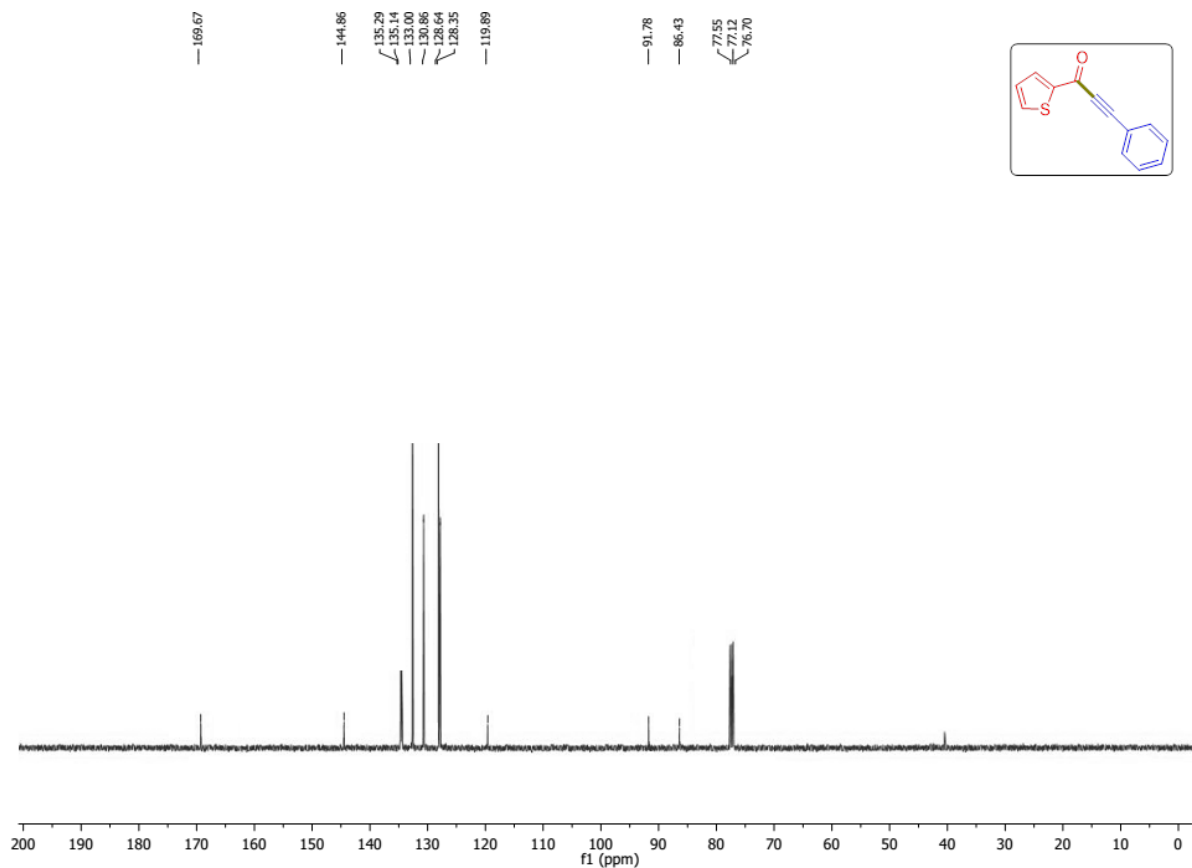
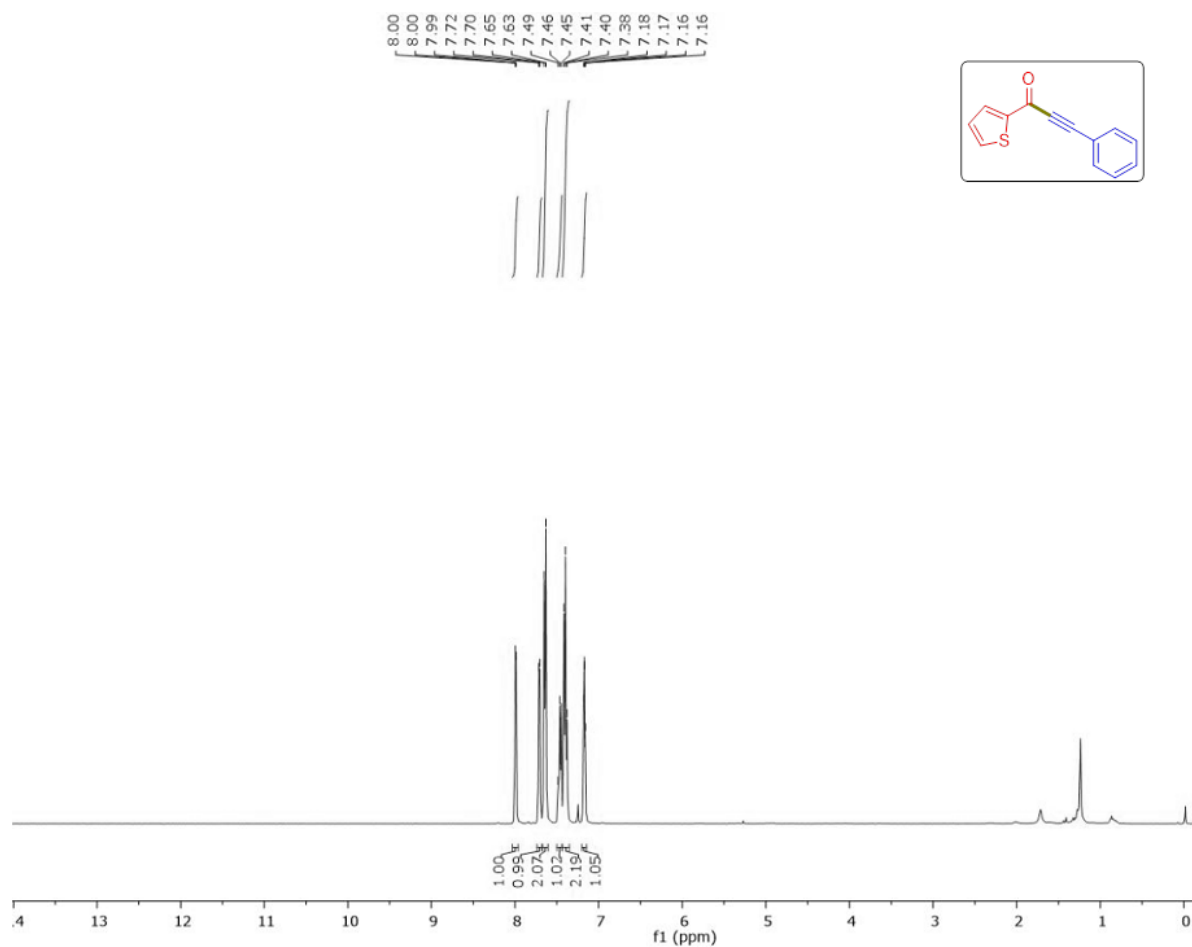


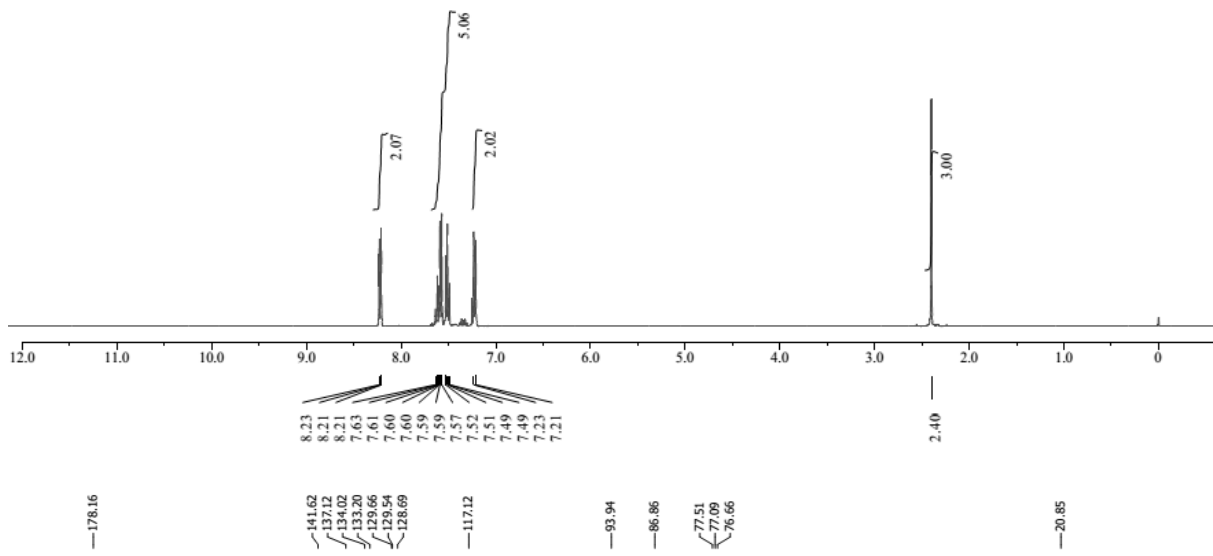
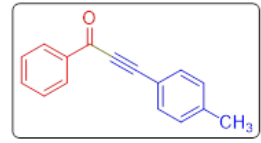




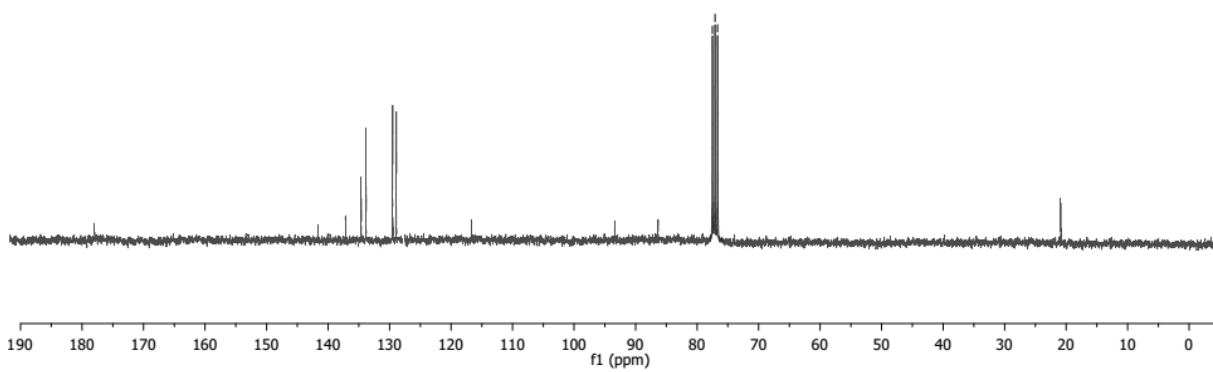
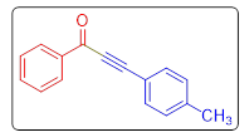


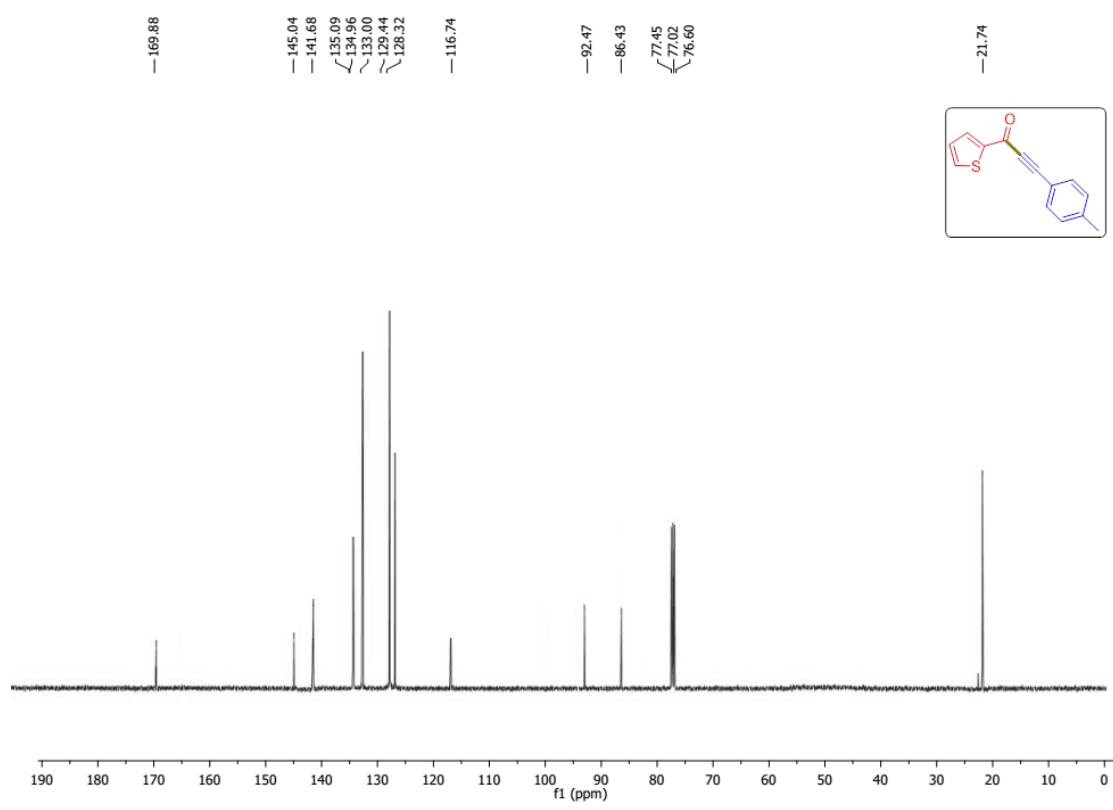
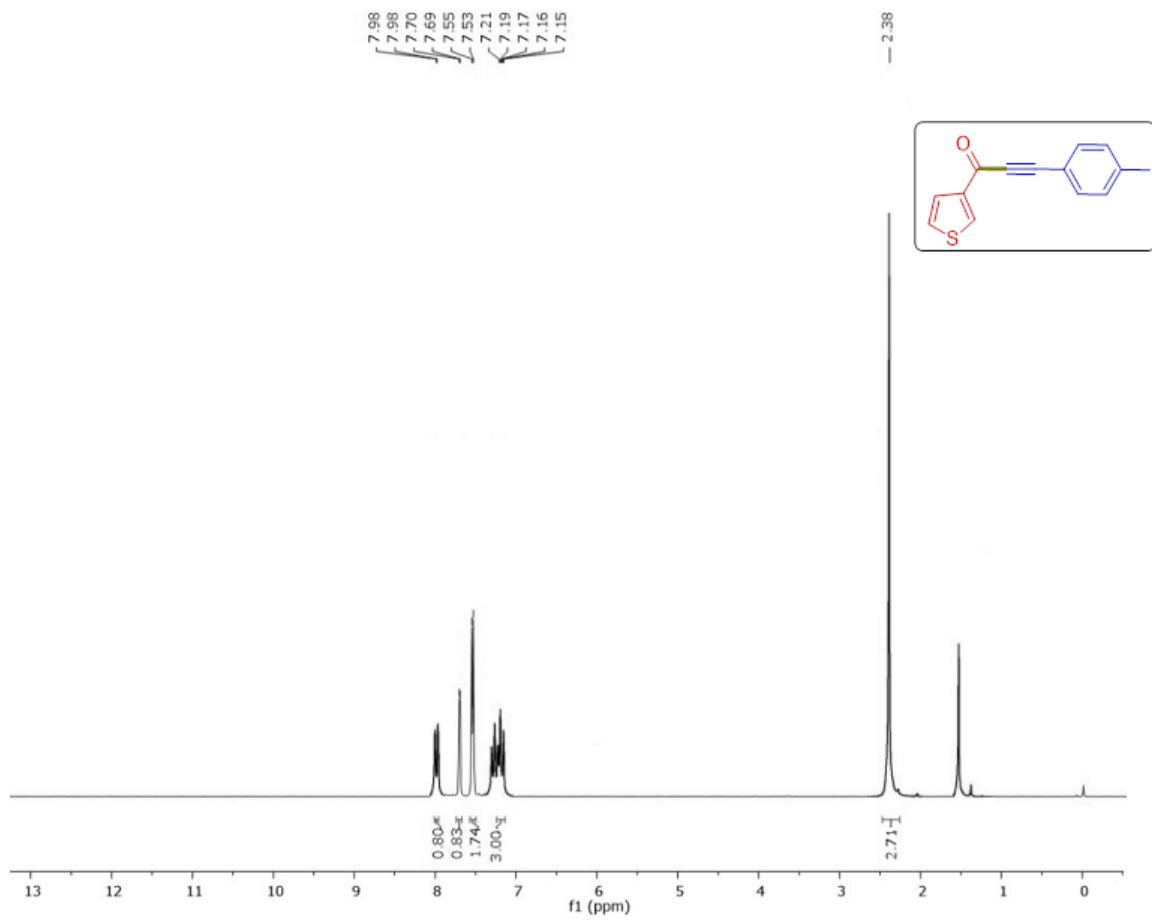


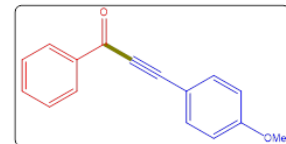
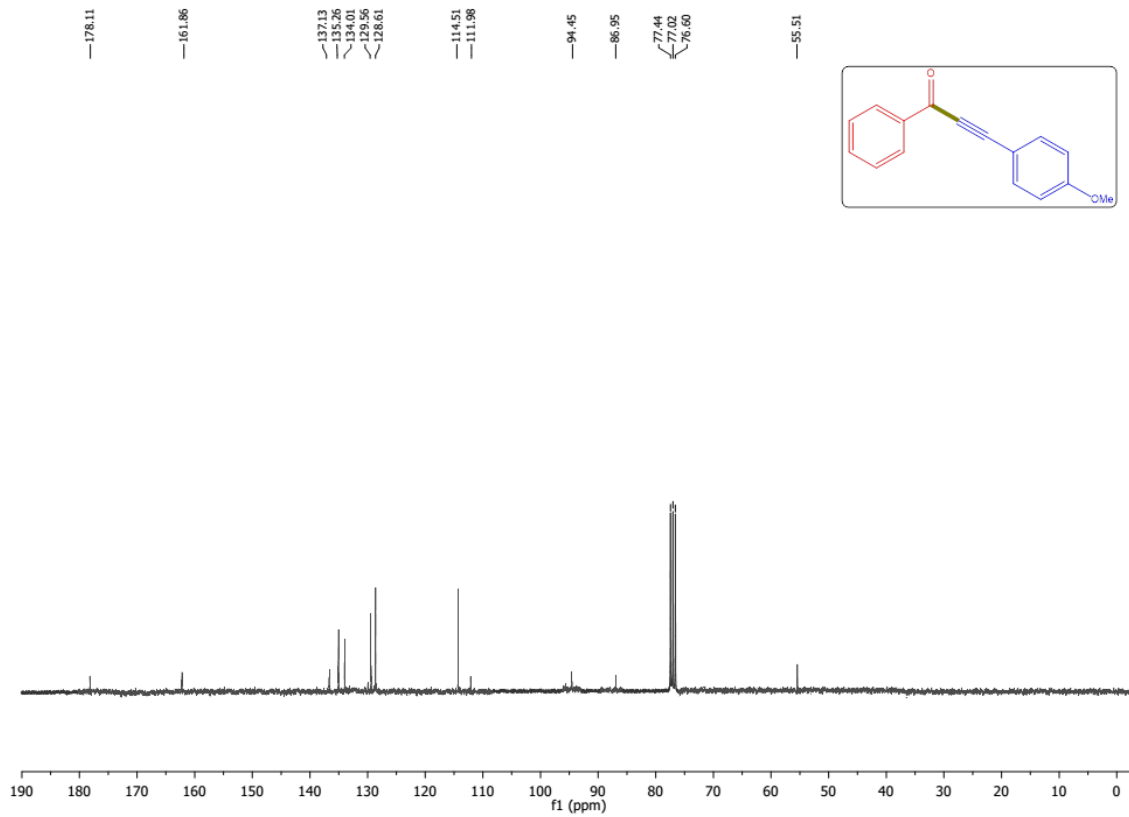
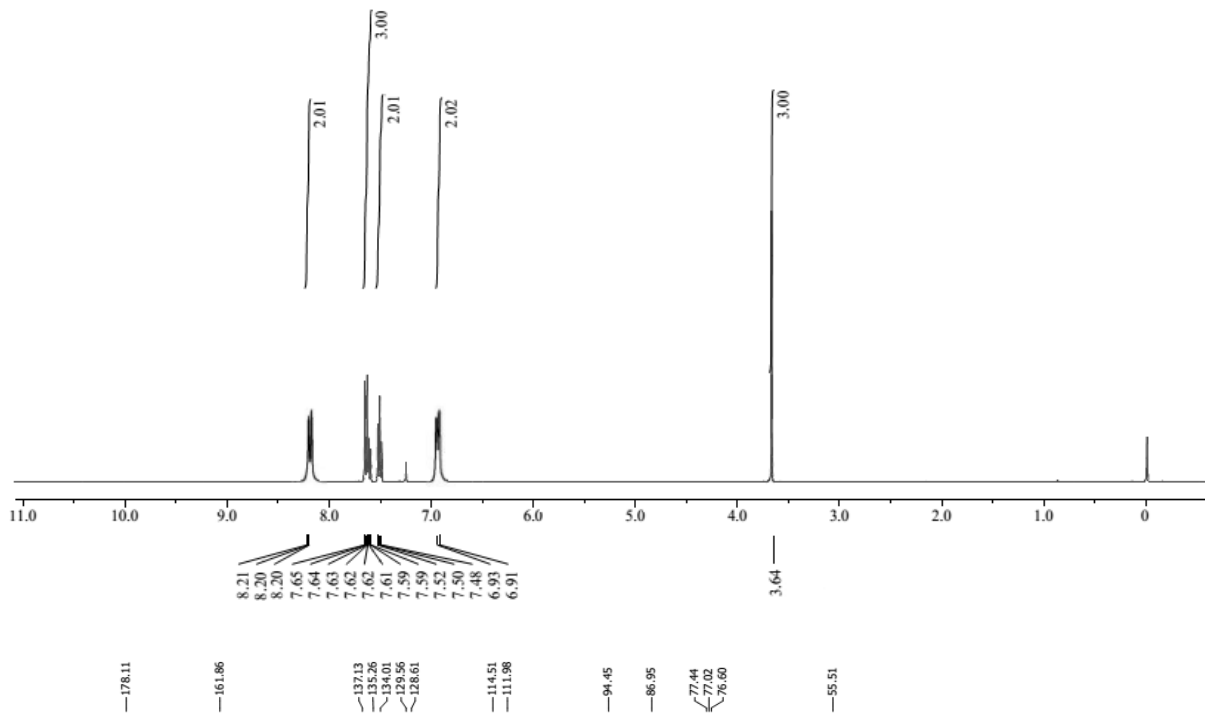
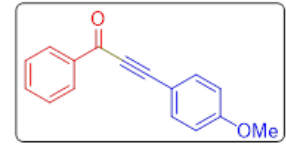


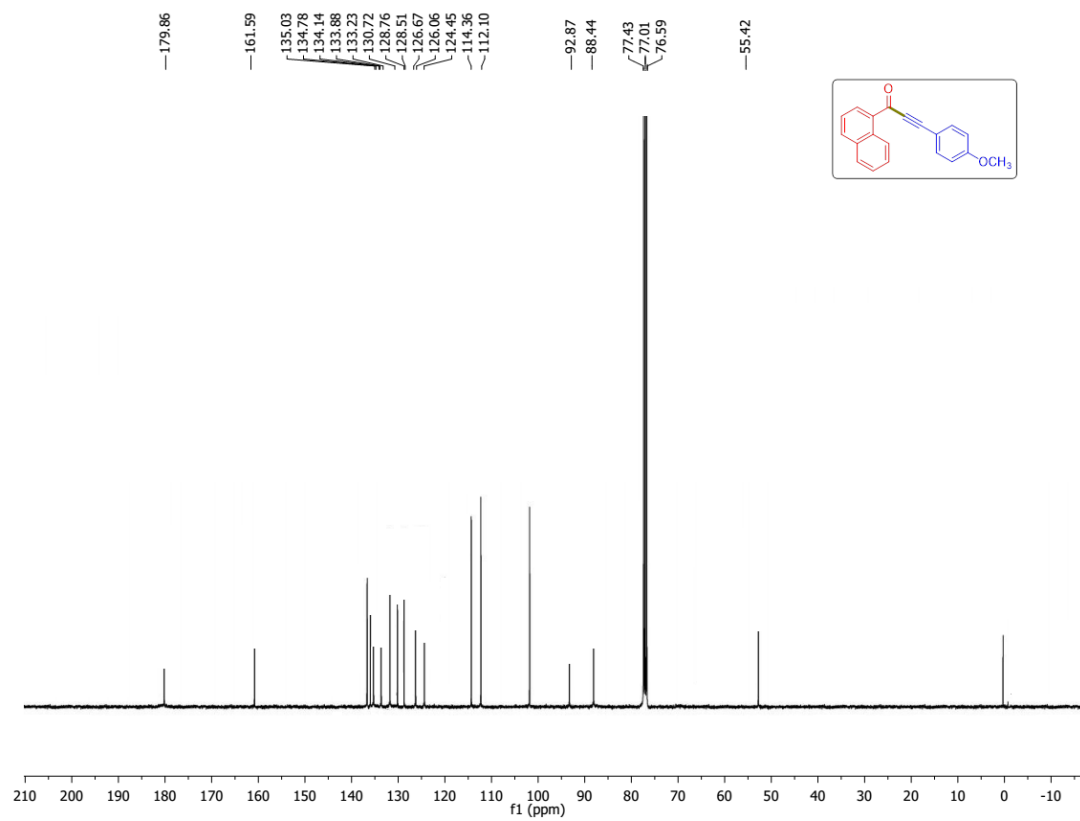
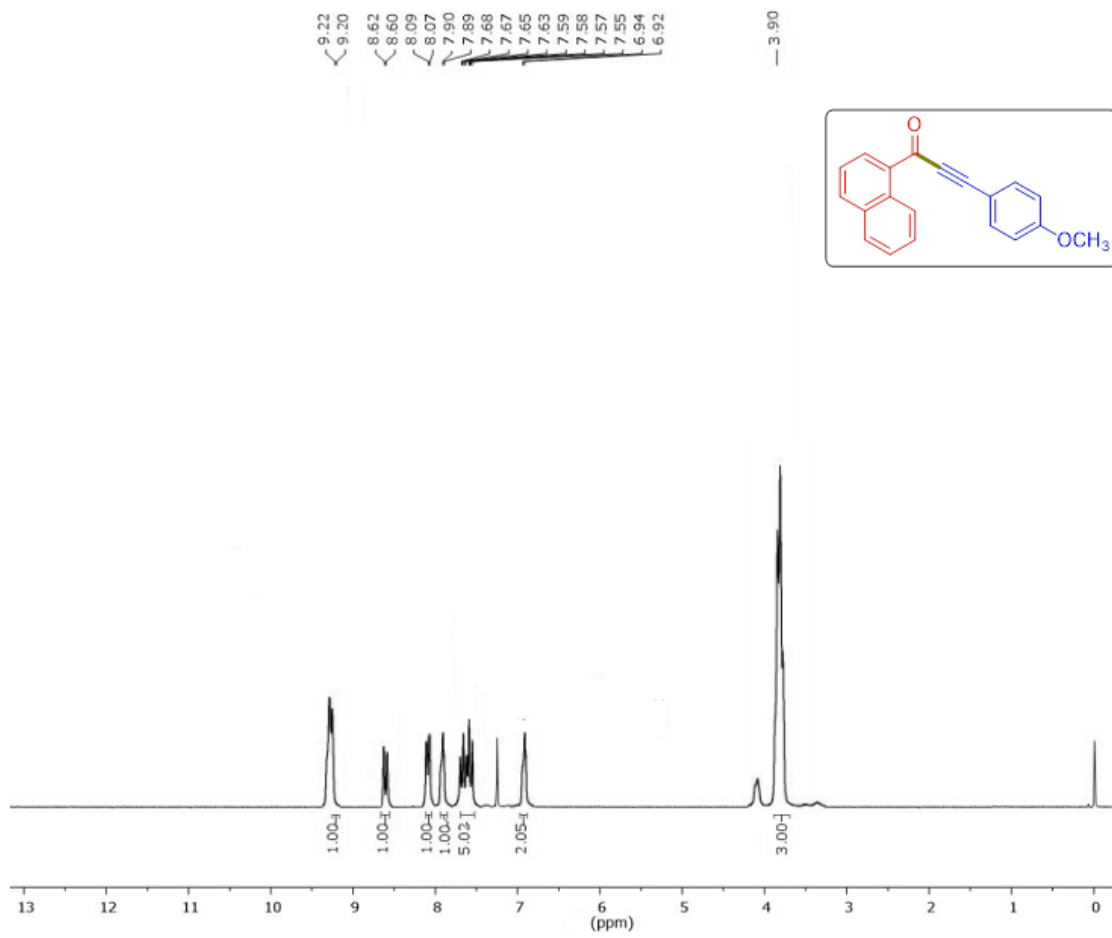


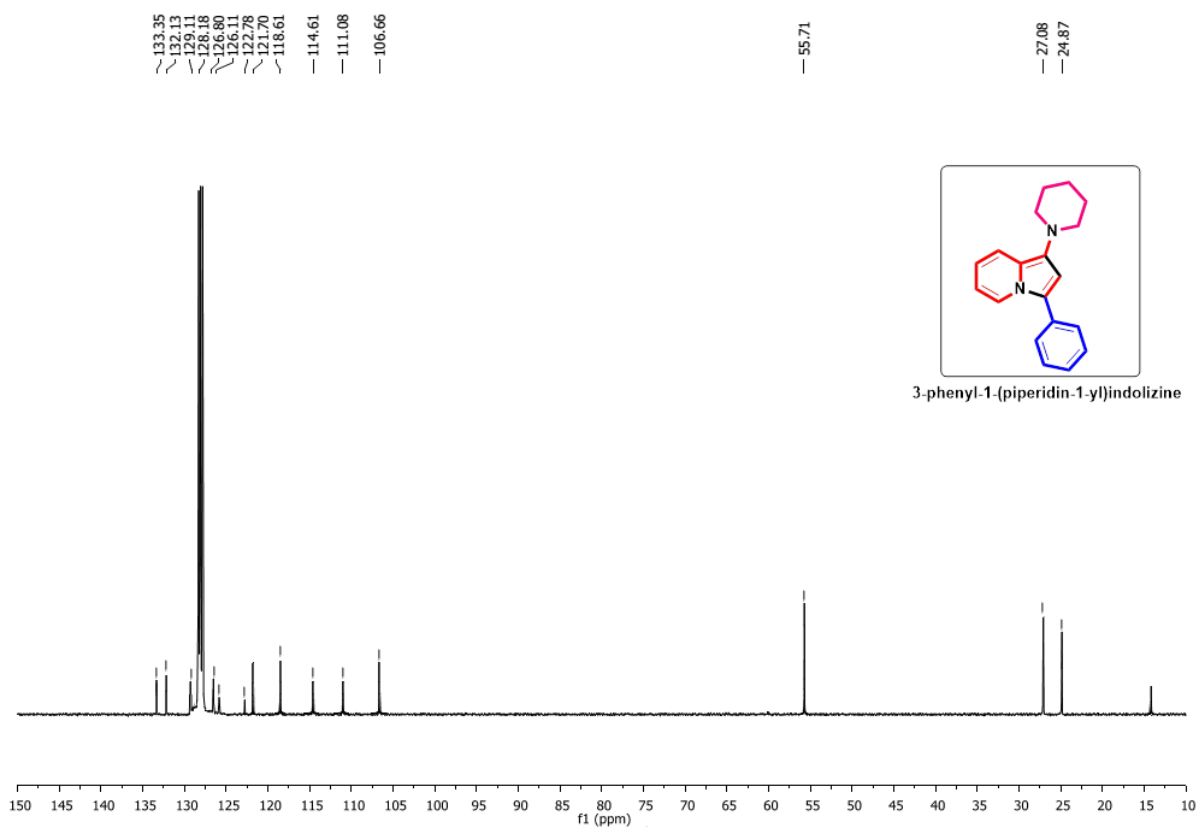
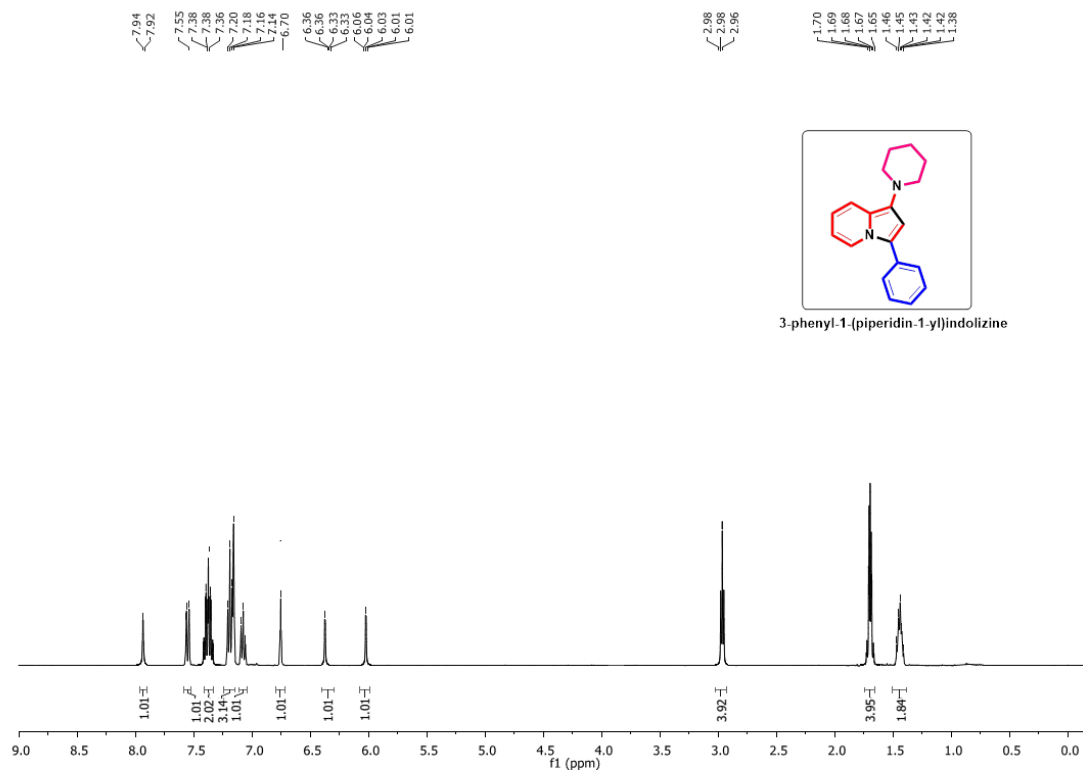
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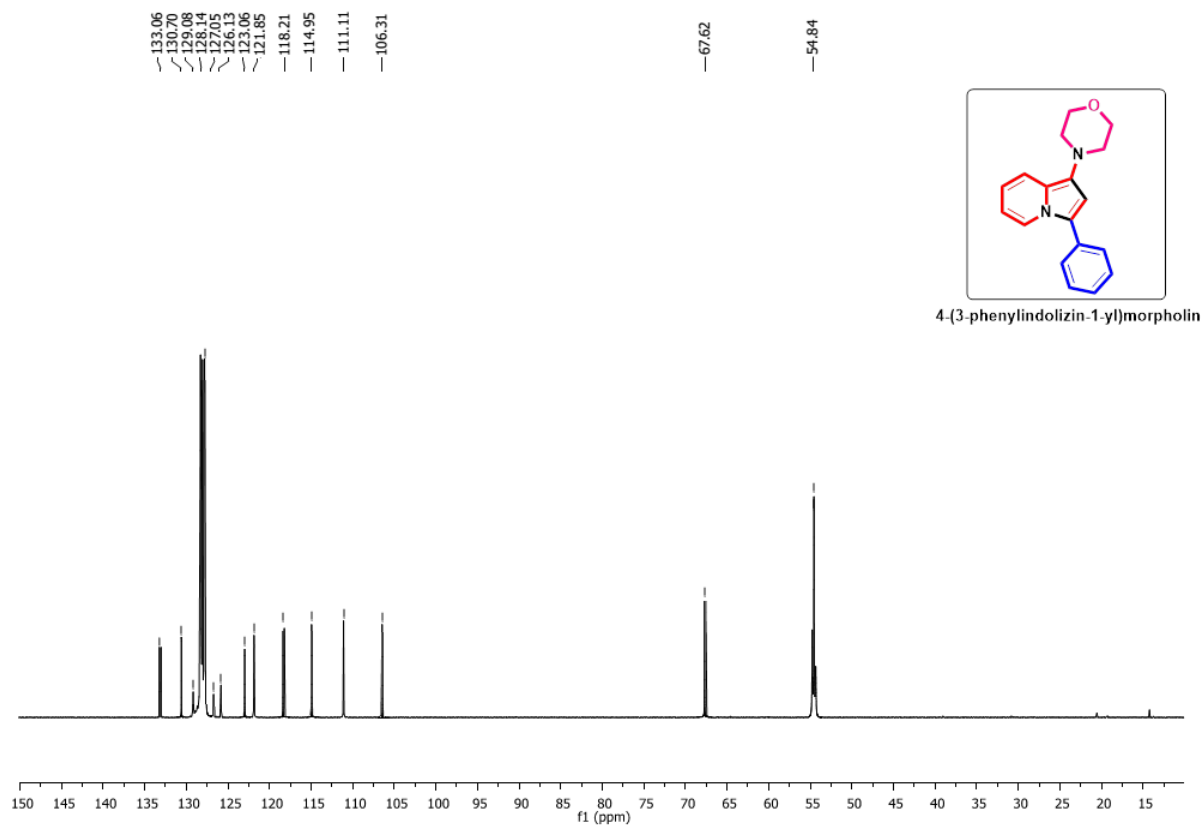
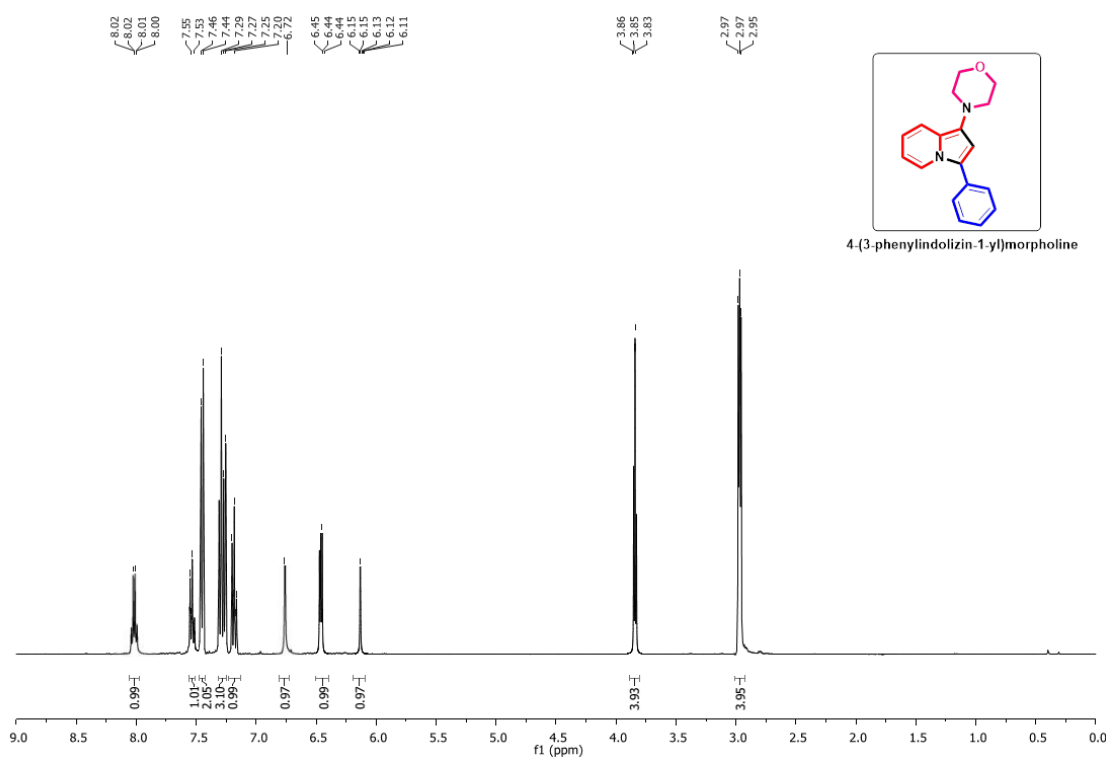


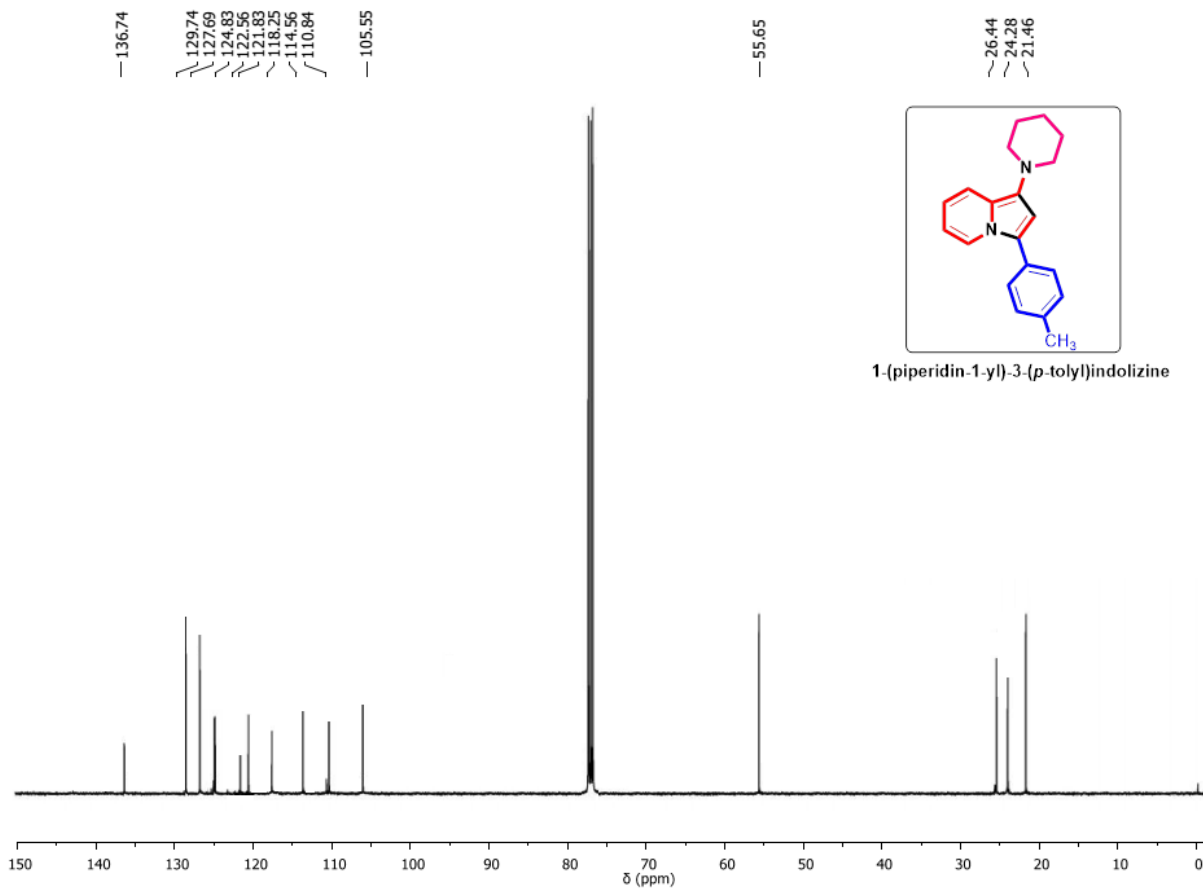
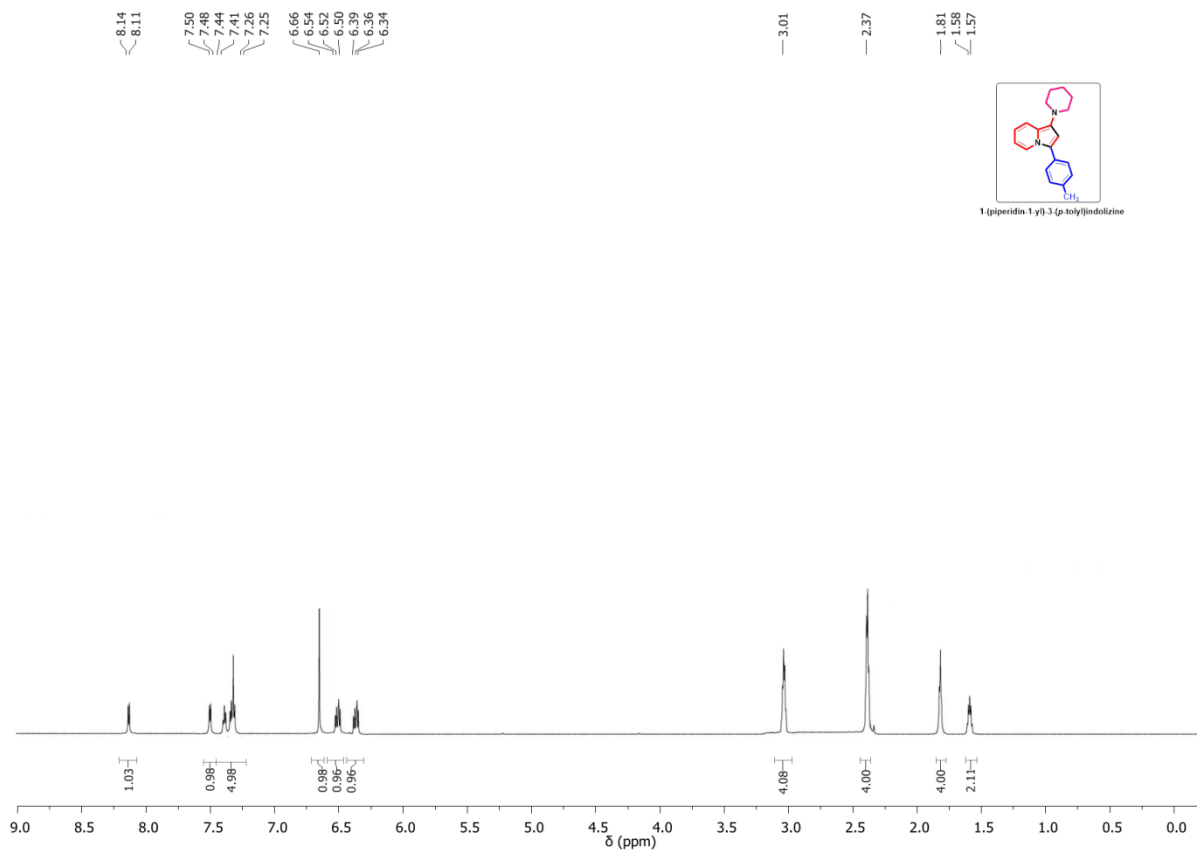


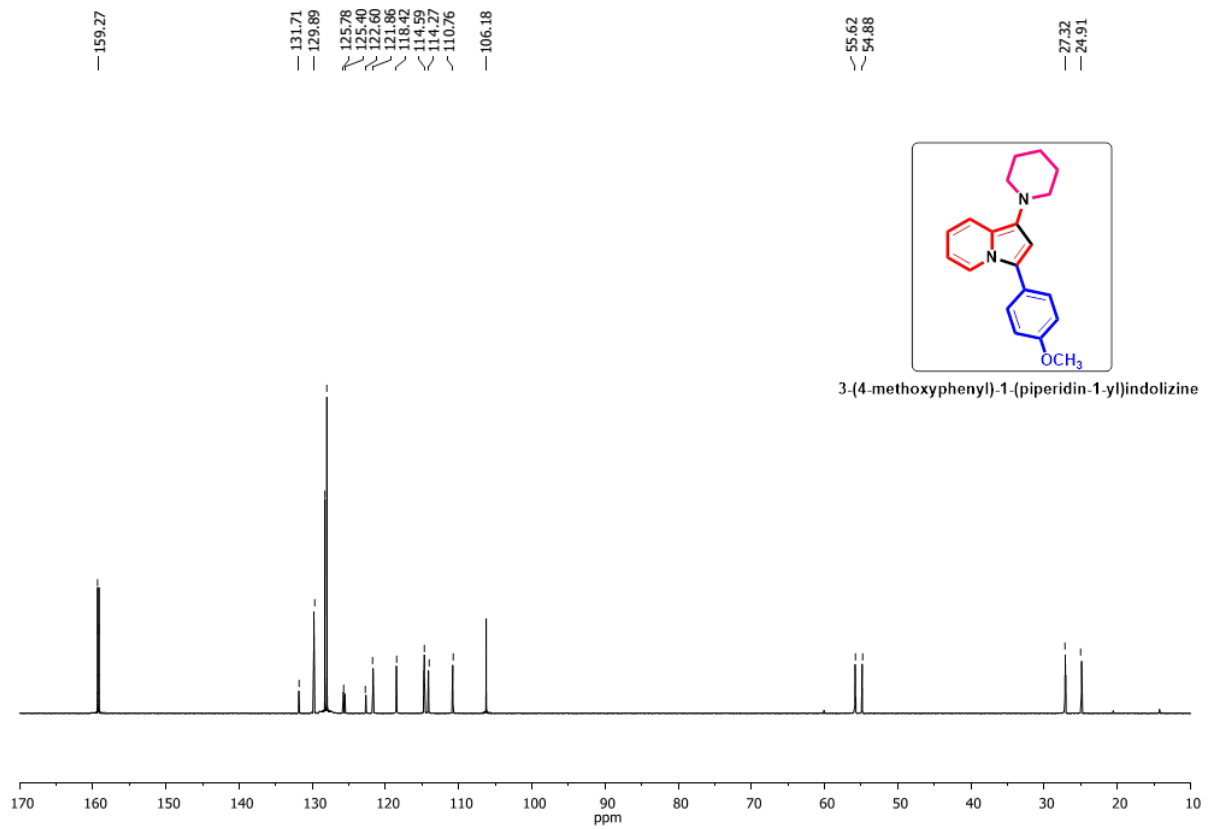
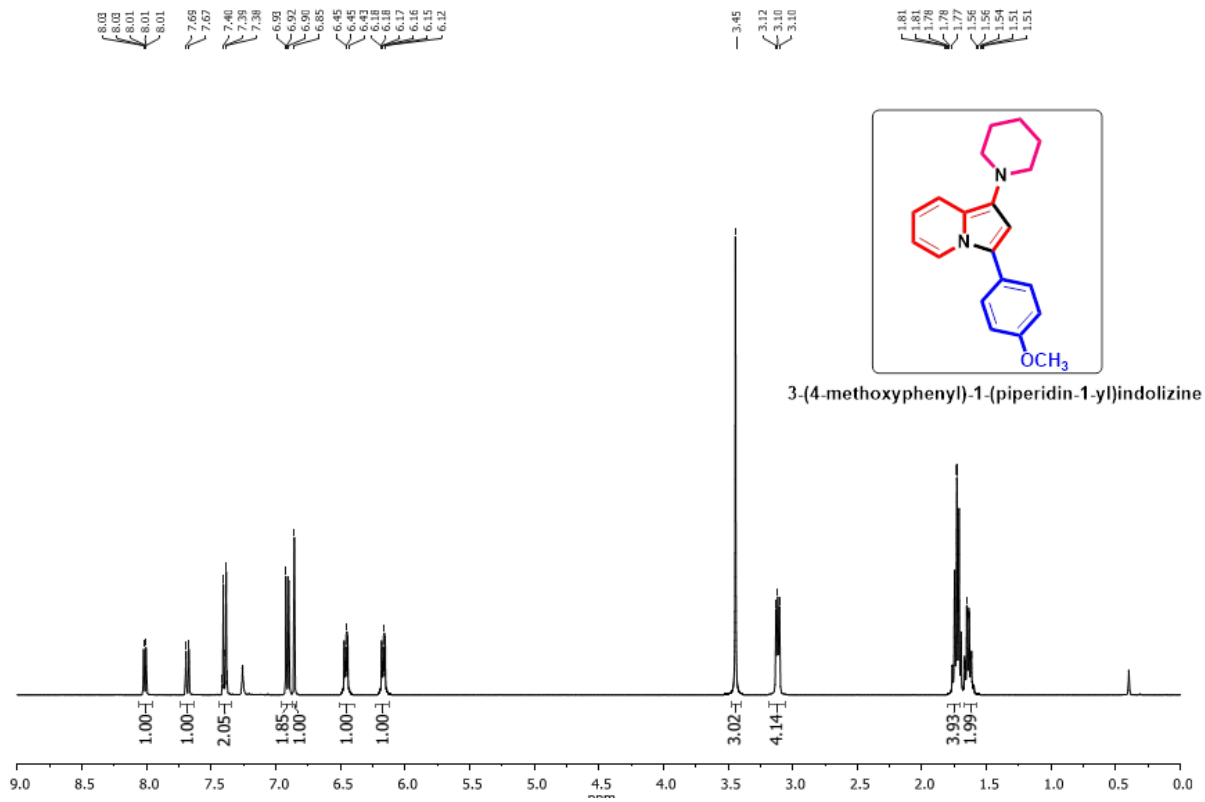


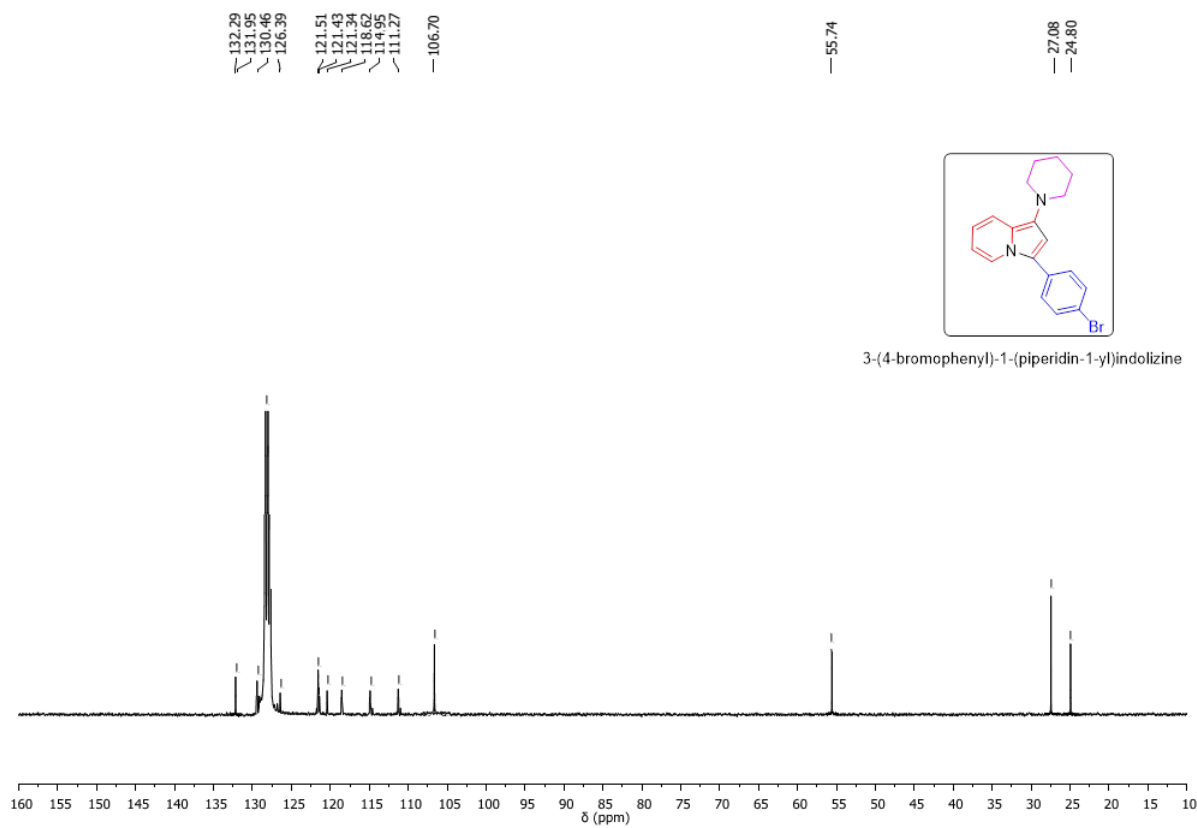
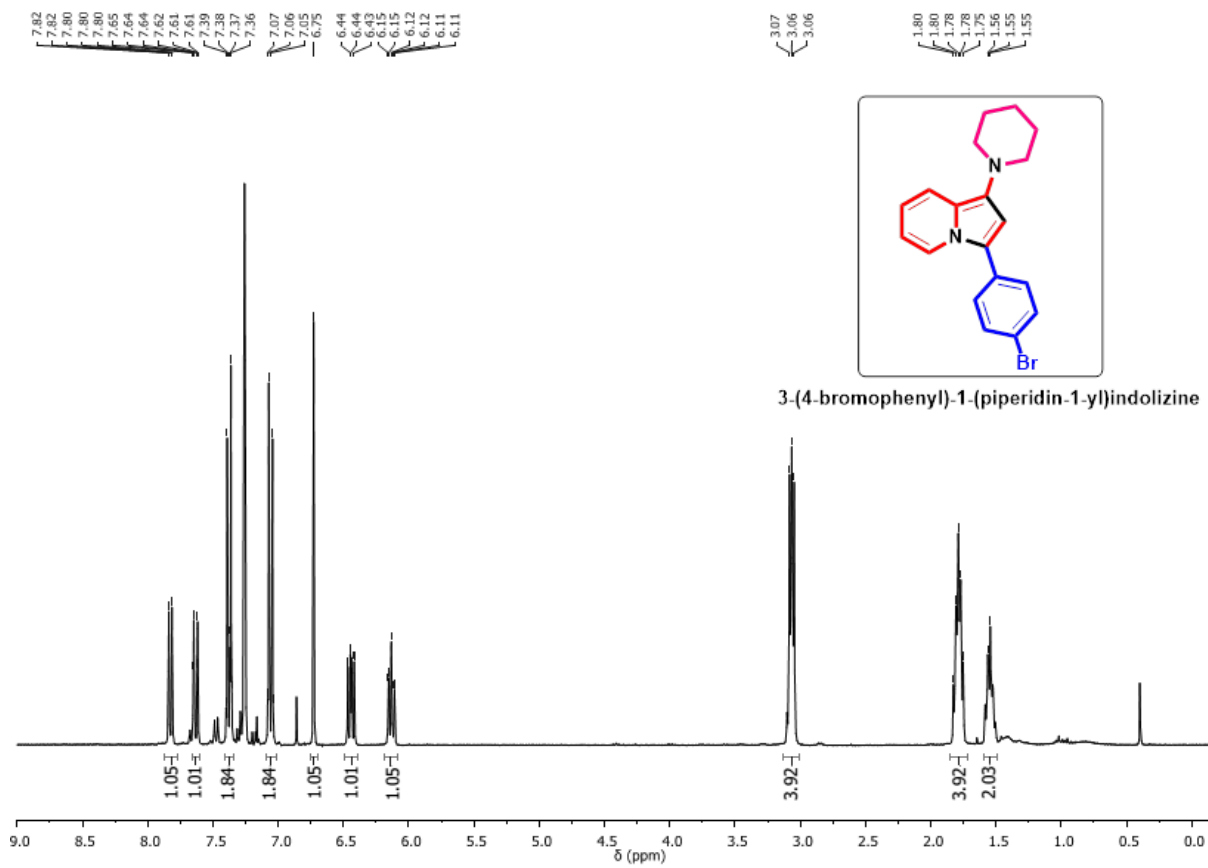


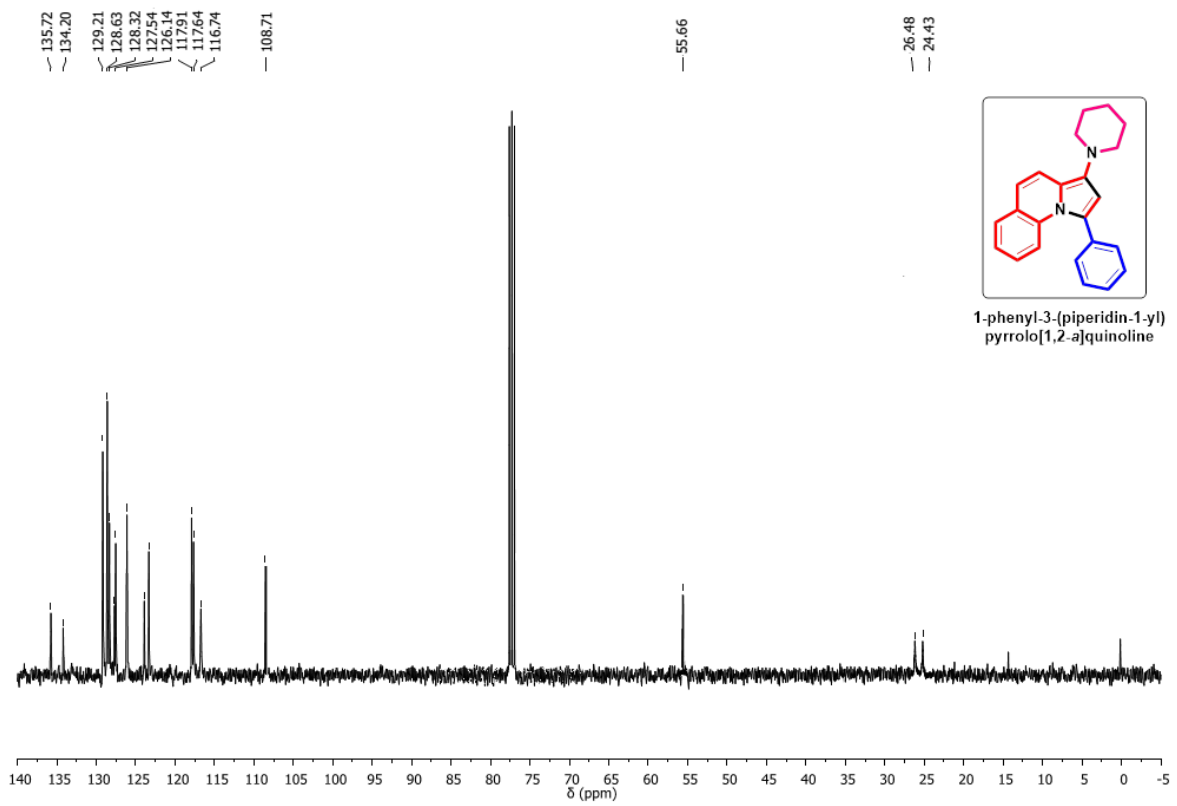
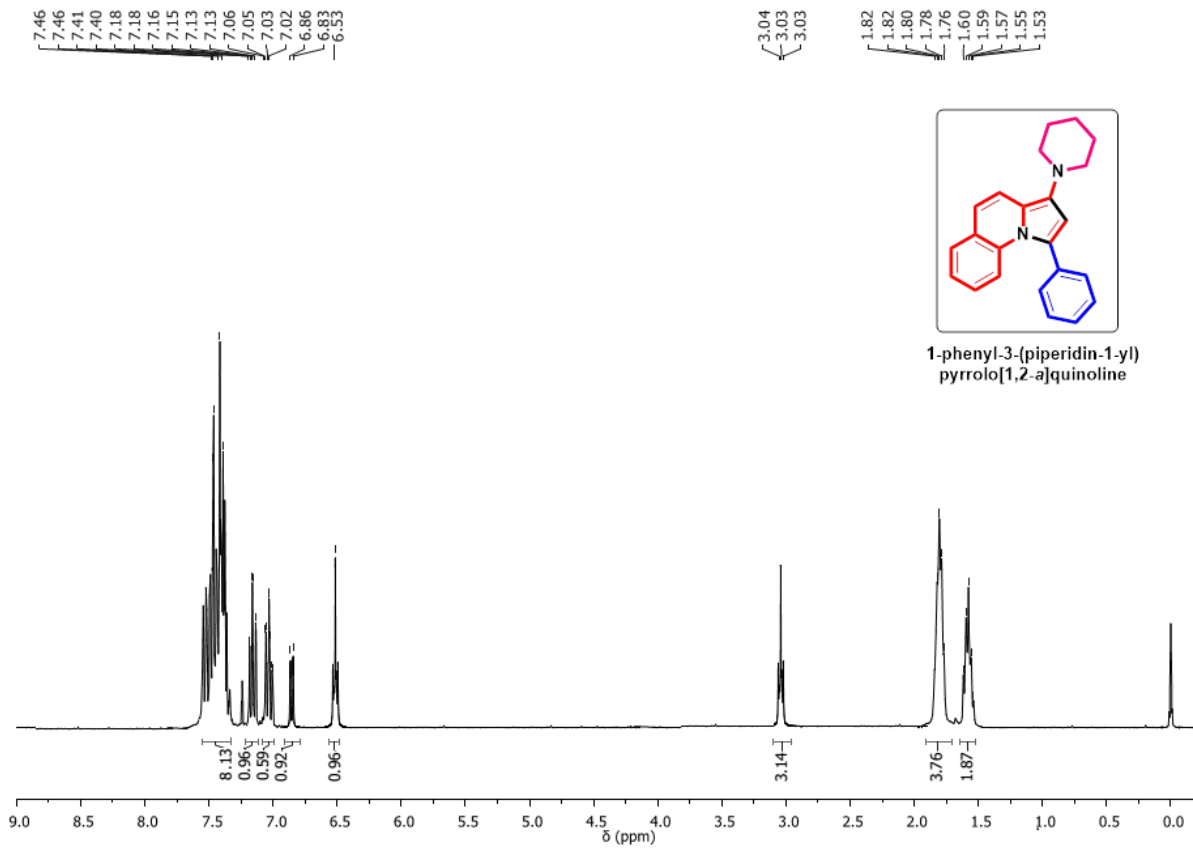


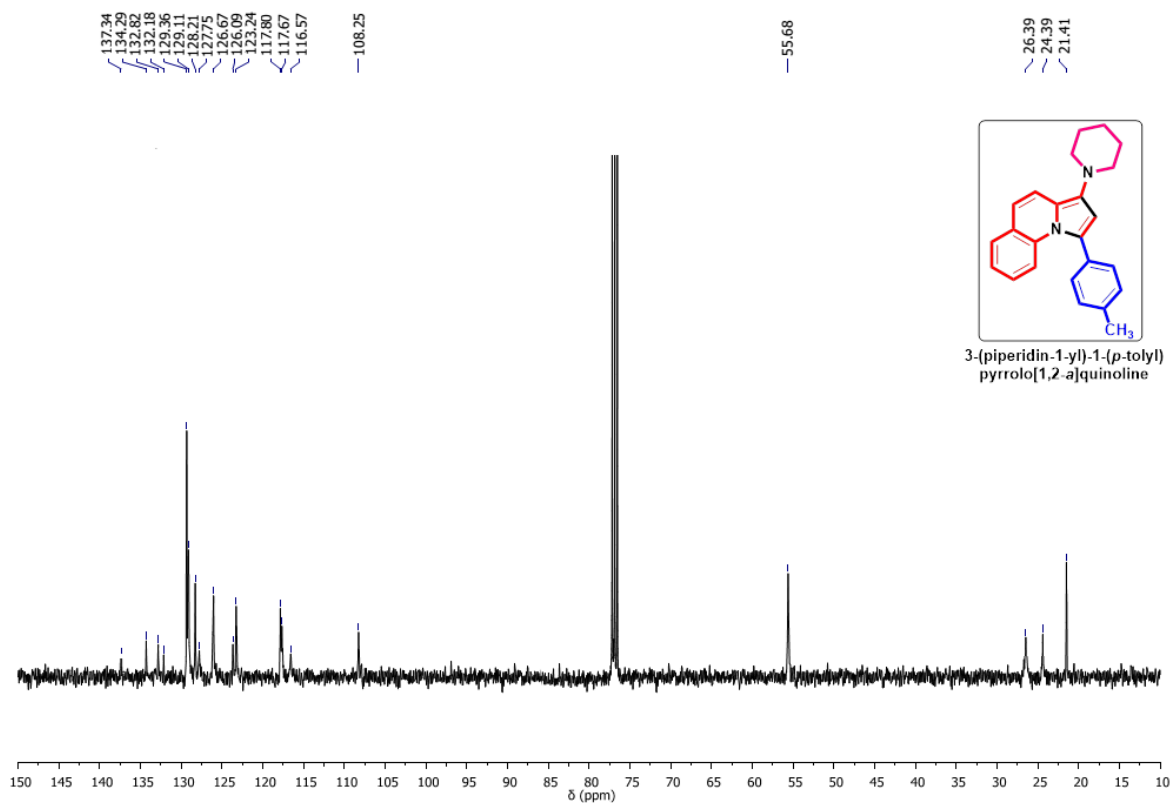
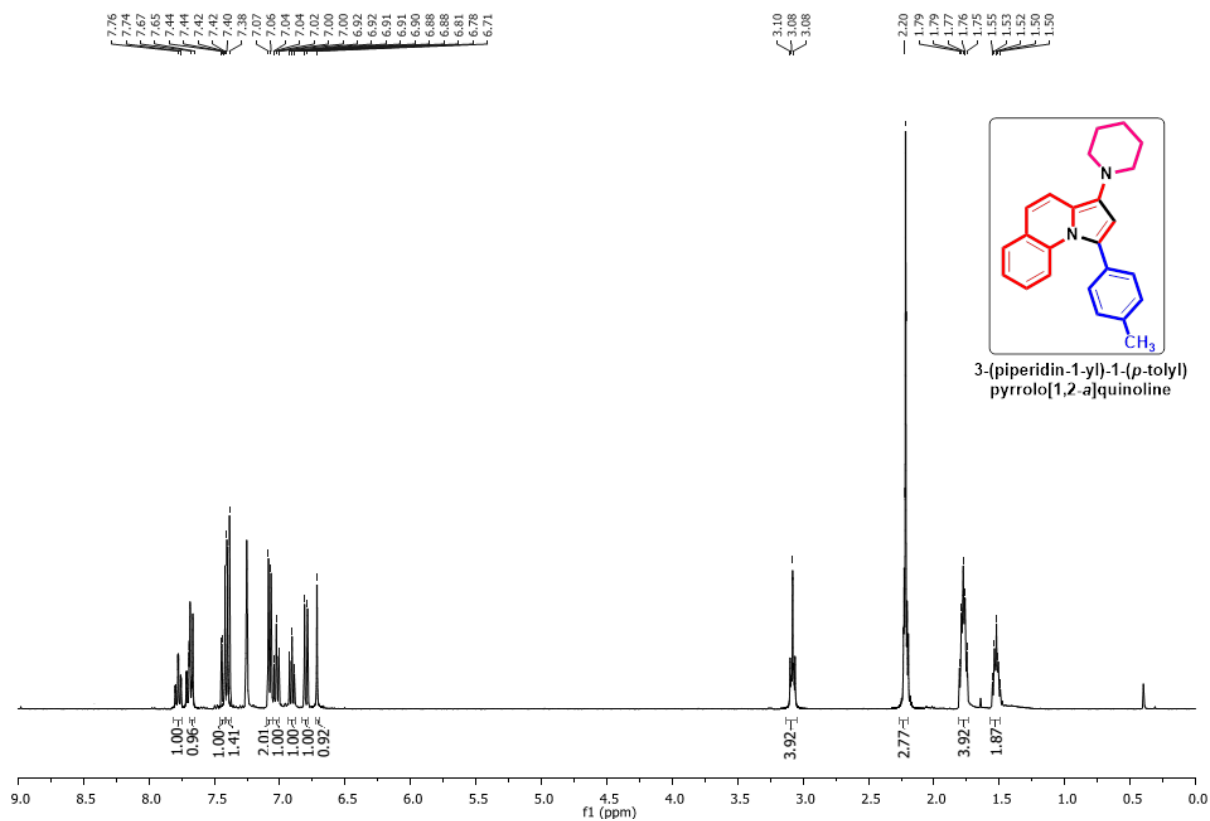


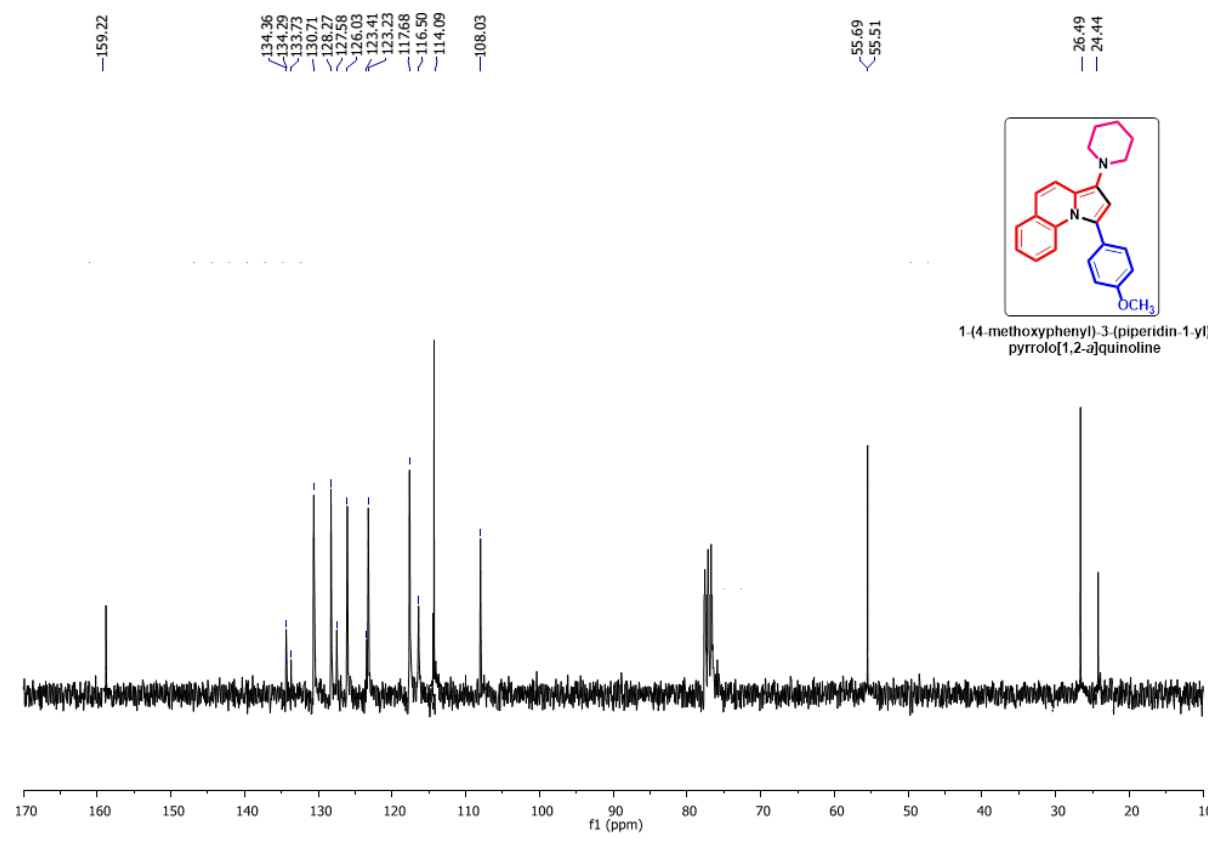
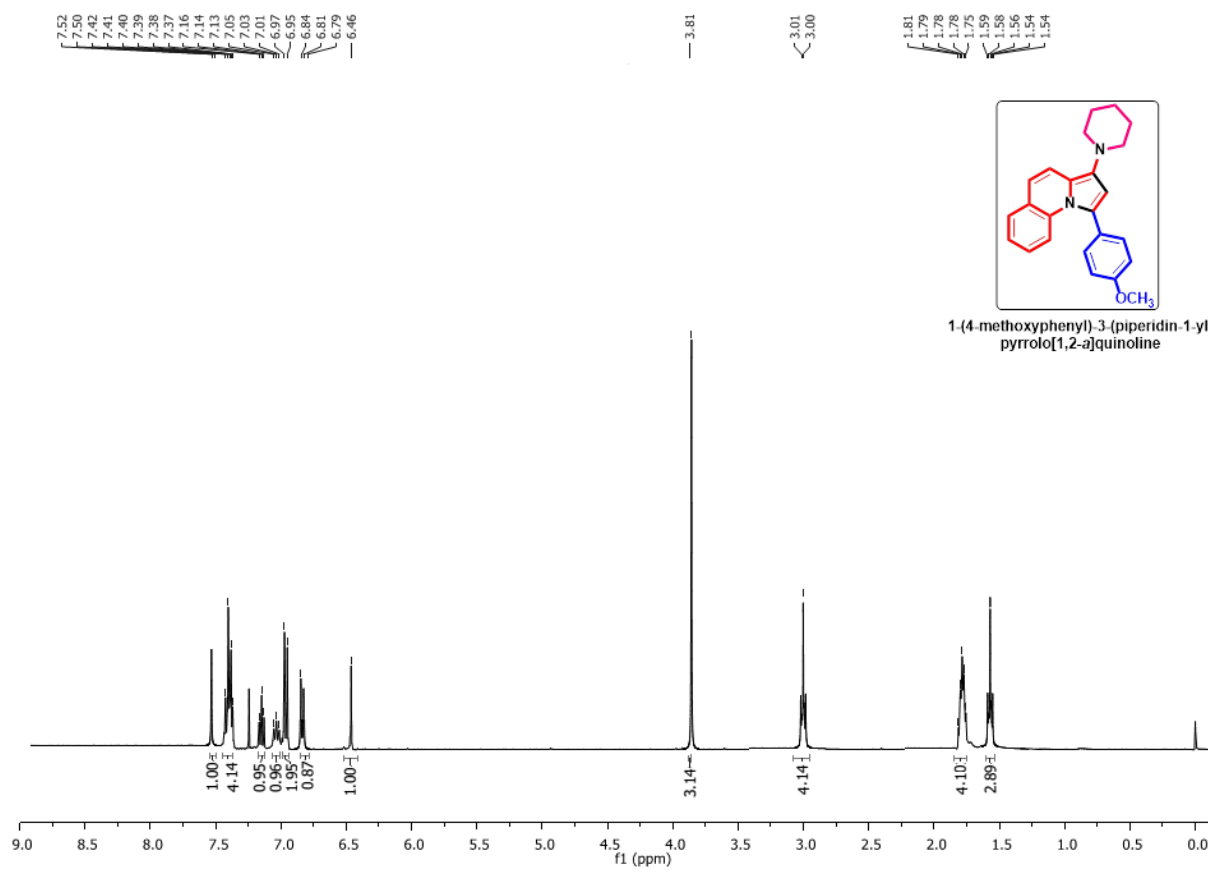


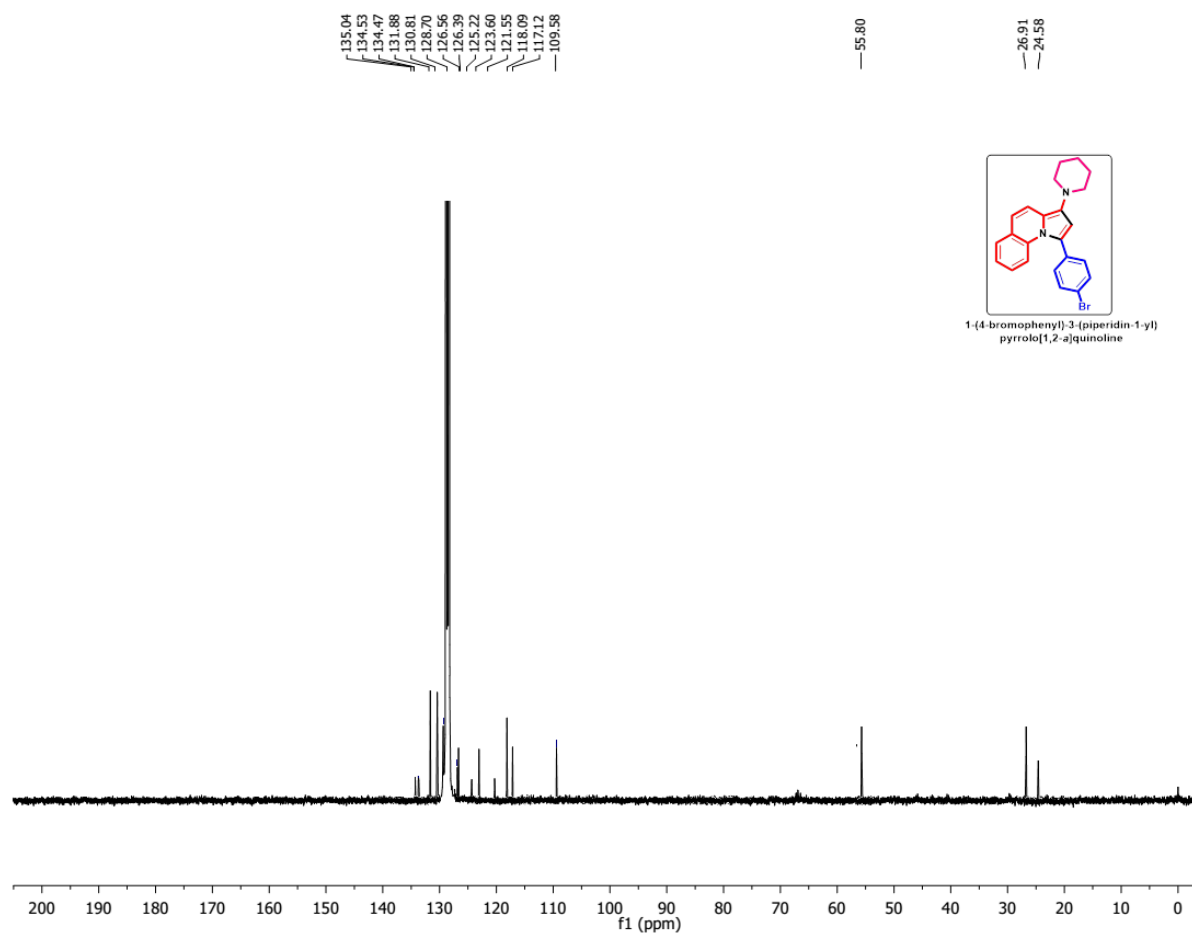
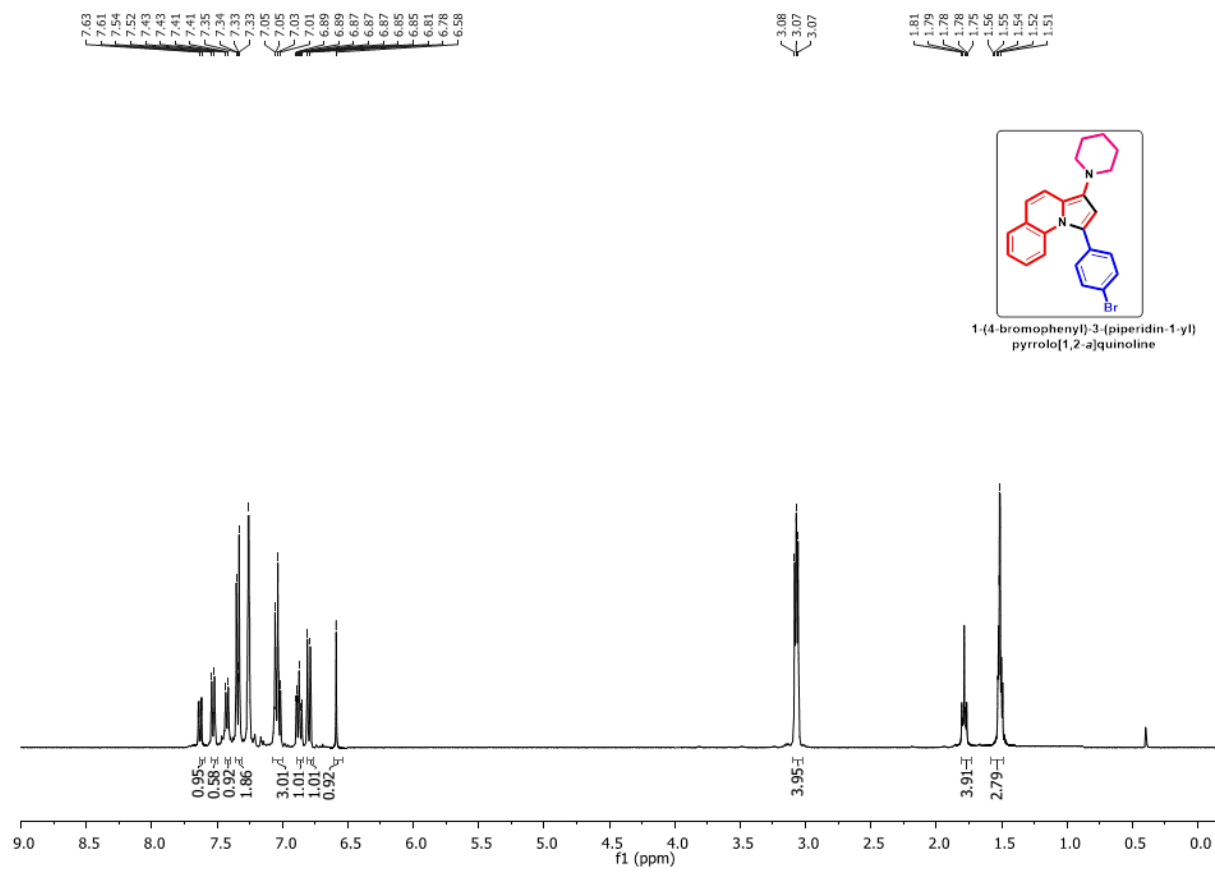


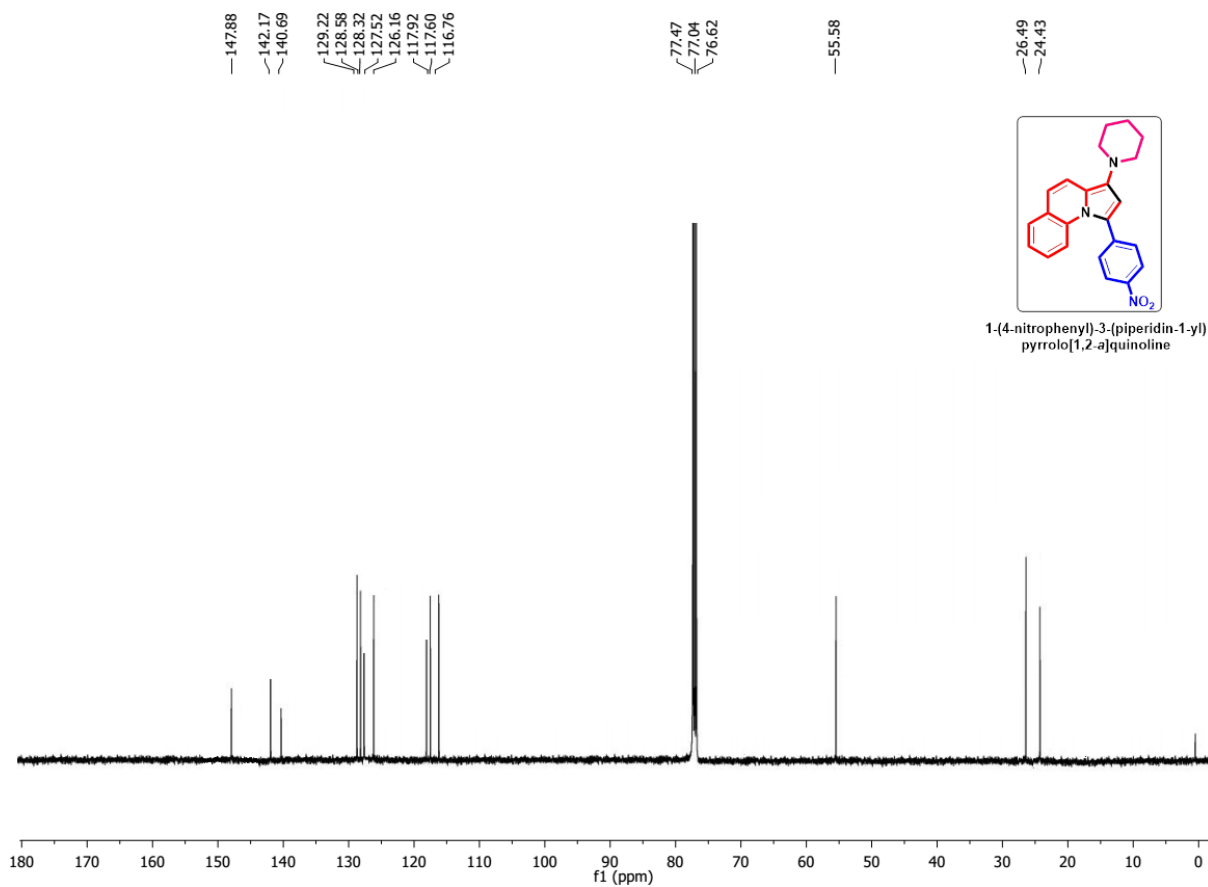
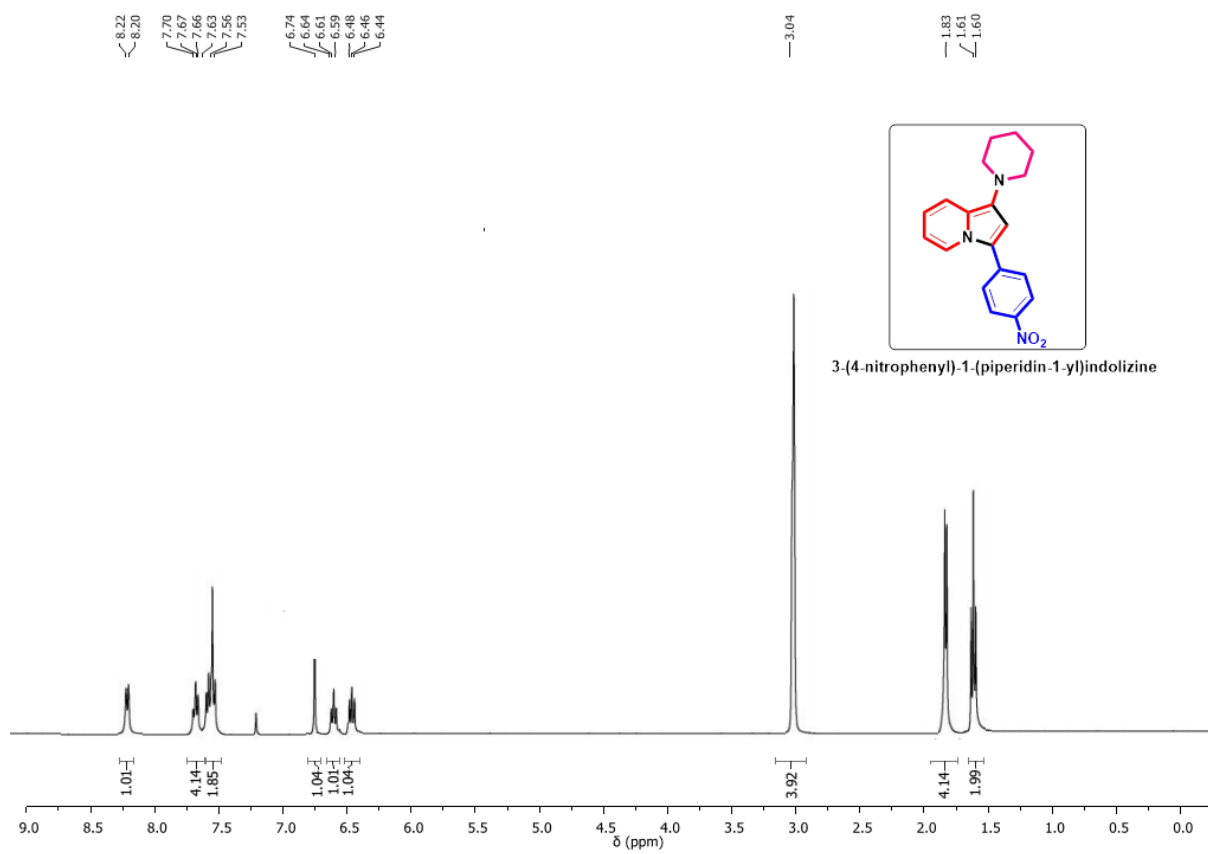












References

1. W. Sun, Y. Wang, X. Wu, X. Yao, *Green Chem.*, **2013**, *15* (9), 2356-2360
2. M. A. Bhosale, T. Sasaki, B. M. Bhanage, *Catal. Sci. Technol.*, **2014**, *4* (12), 4274-4280
3. K. Wang, L. Yang, W. Zhao, L. Cao, Z. Sun, F. Zhang, *Green Chem.*, **2017**, *19* (8), 1949-1957
4. F. M. Moghaddam, R. Pourkaveh, M. Ahangarpour, *Catal. Comm.*, **2017**, *102*, 71-75
5. R. K. Loganathan, S. N. Ramachandra, Shekharappa, V. V. Sureshbabu, *Chemistry Select.*, **2017**, *2*, 8059-8062
6. Rakesh K. Sharma, Manavi Yadav, Rashmi Gaur, Radhika Gupta, Alok Adholeya and Manoj B. Gawande, *ChemPlusChem.*, **2016**, *81*, 1312-1319.
7. R. Chutia, B. Chetia, *Tetrahedron Letters.*, **2017**, *58*, 3864-3867.
8. M. J. Albaladejo, F. Alonso, M. J. G. Soria, *ACS Catal.*, **2015**, *5*, 3446-3456
9. U. C. Rajesh, G. Purohit D. S. Rawat, *ACS Sustainable Chem. Eng.*, **2015**, *3*, 2397-2404
10. P. Rania, P. F. Siril, R. Srivastava, *Molecular Catalysis*, **2017**, **433**, 100-110
11. B. Sarmah, B. Satpati, R. Srivastava, *RSC Adv.*, **2016**, **6**, 87066-87081.
12. P. N. P. Rao, Q. H. Chen, E. E. Knaus, *J. Med. Chem.*, **2006**, *49* (5), 1668-1683.

