Electronic Supplementary Material (ESI) for RSC Advances.

Nickel-palladium bimetallic nanoparticles supported on multi-walled Carbon nanotubes; versatile catalyst for Sonogashira cross-coupling reactions

Katherine A. Wilson, Lacey A. Picinich, and Ali R. Siamaki*

Department of Chemistry, Physics, and Materials Science, Fayetteville State University, Fayetteville, NC, USA 28301

Correspondence: asiamaki@uncfsu.edu; Tel.: 1-910-672-1619

Supplemental Information

General Experimental Procedure

Nickel (II) acetate tetrahydrate and palladium acetate were obtained from Sigma-Aldrich. Aryl iodides and bromides, and functionalized terminal alkynes were purchased from MilliporeSigma, Alfa Aesar, and ACROS Organics and used as received. Multi-walled carbon nanotubes (MWCNTs) 50-85 nm was purchased from Graphene Supermarket. A mixture of ethanol-deionized water was used as the solvent system for all the reactions. Transmission Electron Microscopy was performed on ThermoFisher Talos F200X G2, a 200 kV FEG (Field Emission Gun) Analytical Scanning Transmission Electron Microscope (S/TEM). X-ray Diffraction (XRD) was accomplished on Rigaku MiniFlex 600 X-ray Diffractometer. X-ray Photoelectron spectroscopy (XPS) was performed on Kratos Axis Supra x-ray photoelectron spectrometer. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis was completed using NexION 300D (PerkinElmer, Inc.). Gas Chromatography-Mass Spectroscopy (GC-MS) of organic products was analyzed using a Shimadzu GC-MS QP2010 SE. ^{1}H and ^{13}C NMR spectra were acquired on a JEOL 400 MHz spectrometer equipped with autosampler. All Sonogashira cross-coupling reactions were performed using Anton-Paar Monowave 50 heating reactor.

Preparation of Ni-Pd/MWCNTs nanoparticles

To examine the effect of Ni and Pd nanoparticles ratios and the loading of nanoparticles on MWCNTs support on the catalysis in Sonogashira coupling reactions, four different catalytic systems were prepared as follows:

Catalyst 1: Nickel acetate tetrahydrate (42.39 mg, 10% Ni content) and multi-walled carbon nanotubes (MWCNTs) (90 mg) were mixed in a 20 mL volume zirconium ceramic vial (SPEX CertiPrep). After adding two zirconium balls, the vial was subjected to mechanical shaking using SPEX 8000M ball-mill mixer for 45 min mixer with 1060 cycles per minutes with 5.9 cm back and forth and 2.5 cm side to side mechanical movements. The final product of (Ni/MWCNTs) nanoparticles were obtained as black powder. Similar ball -mill procedures were used for the preparation of other Ni-Pd/MWCNTs using different concentration of nickel and palladium as follows:

Catalyst 2: Ni-Pd/MWCNTs (10% Ni, 10% Pd): Nickel acetate tetrahydrate (42.39 mg, 10% Ni content), palladium acetate (21.13 mg, 10% Pd content), and multi-walled carbon nanotubes (MWCNTs) (80 mg).
Catalyst 3: Ni-Pd/MWCNTs (10% Ni, 1% Pd): Nickel acetate tetrahydrate (42.39 mg, 10% Ni content), palladium acetate (2.11 mg, 1% Pd content), and multi-walled carbon nanotubes (MWCNTs) (89 mg).
Catalyst 4: Pd/MWCNTs (1% Pd): Palladium acetate (2.11 mg, 1% Pd content), and multi-walled carbon nanotubes (MWCNTs) (99 mg).

The actual metal contents in all catalysts were determined by means of inductively coupled plasma equipped with mass spectroscopy (ICP-MS). For this purpose, a solution of 70% HNO_3 (0.5 mL) was added to 20 mg of each catalyst sample and kept at 70 ^oC overnight. Concentrated HCl (1.5 mL) was added to this mixture and incubated further at 70 ^oC overnight. The entire catalyst sample was diluted with 2% nitric acid and subjected to ICP-MS analysis. The metal contents were determined to be for catalyst 1, 8.2% of nickel, catalyst 2, Ni: 8.5%, Pd: 7.8%, catalyst 3, Ni: 7.9%, Pd: 0.81%, and catalyst 4, Pd: 0.86%.

Procedure for recycling the Ni-Pd/MWCNTs

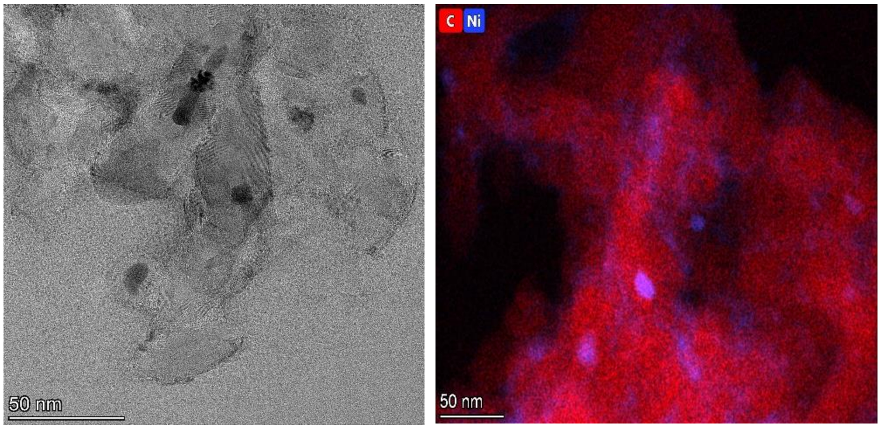
4-Iodobenzaldehyde (50 mg, 0.22 mmol, 1 eq.) and 4-*tert*-butylphenylacetylene (41.7 mg, 0.26 mmol, 1.2 eq.) were added to a mixture of water:ethanol (4 mL) in 10 mL Monowave 50 vial. To this was added potassium carbonate (91.1 mg, 0.66 mmol, 3 eq.) and Ni-Pd/MWCNTs nanoparticles catalyst 2 or catalyst 3 (6.60 µmol, 3 mol%). The reaction was sealed and heated at 120 ^oC for 20 minutes in Monowave 50 heating reactor. After the reaction was completed, the reaction solution was diluted with ethanol (4 mL), dichloromethane (4 mL), and the entire mixture was centrifuged for 5 minutes at 5000 RPM. The aqueous solution was decanted and the organic layer including dichloromethane was combined to give the Ni-Pd/MWCNTs nanoparticles as a precipitate. This procedure was repeated twice to ensure the removal of all organic materials from the surface of the catalyst. The clean catalyst was reused for the subsequent reaction by adding fresh reagents. The recycling procedure was repeated for every run and the formation of product was analyzed by GC-MS spectroscopy.

Procedure for Sonogashira Cross-Coupling Reactions:

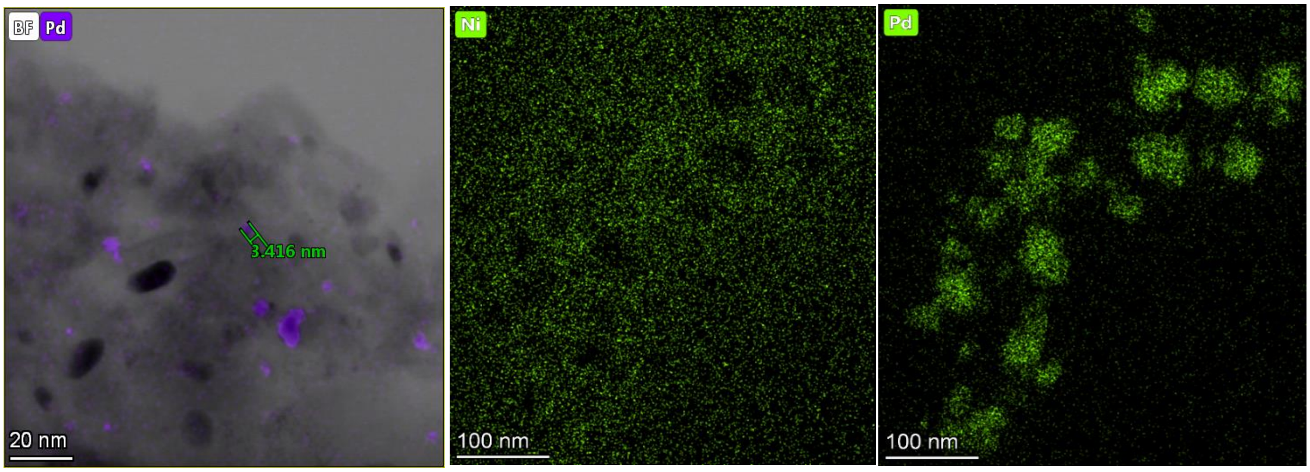
Substituted Aryl halides (0.25 mmol, 1 eq.) and terminal alkynes (0.3 mmol, 1.2 eq.) were added to a mixture of water:ethanol (4 mL) and placed in 10 mL Monowave 50 vial. After adding potassium carbonate (0.75 mmol, 3 eq.) and catalyst 3 (7.50 mg, 5.0 µmol, 2 mol%), the reaction mixture was heated at 120 ^oC for 20 minutes (or the time indicated in Table 4) in Monowave 50 heating reactor in a sealed vial. Upon the completion of the reaction, the mixture was extracted with dichloromethane (2 × 5mL). The organic layers were combined, dried over sodium sulfate, and filtered. The solvent was removed in *vacuo* and the final products was purified by flash chromatography on silica gel using hexane: ethyl acetate as the eluent.

Additional TEM images of Catalysts 1-4:

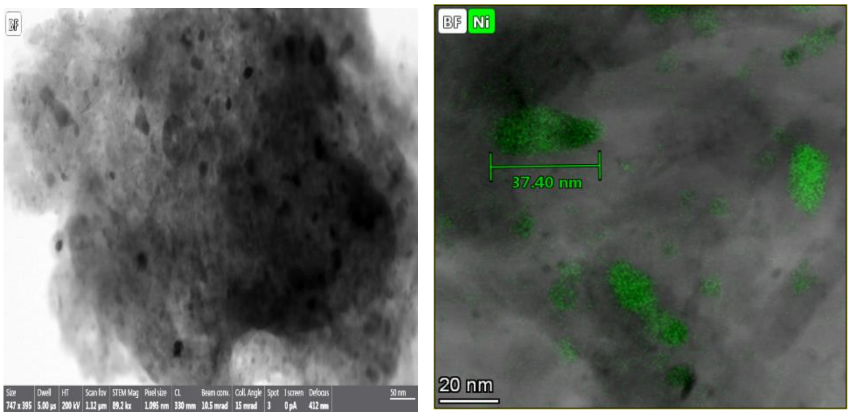
a) **Catalyst 1:** Ni/MWCNTs (Ni: 10%)



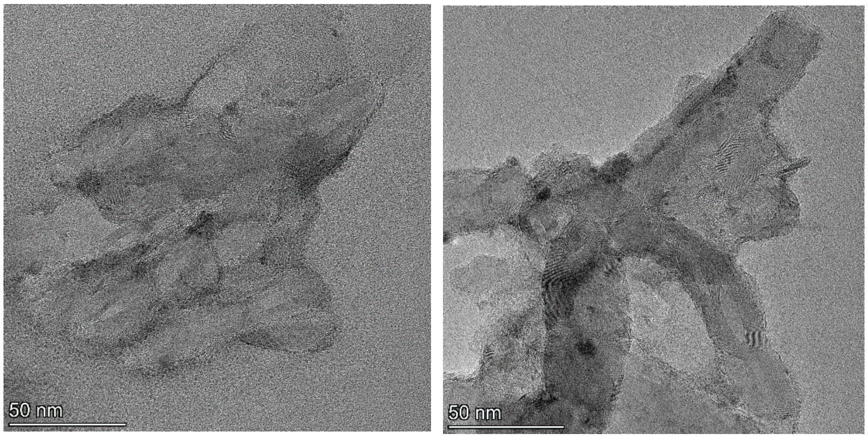
b) **Catalyst 2:** Ni-Pd/MWCNTs (Ni: 10%, Pd: 10%)



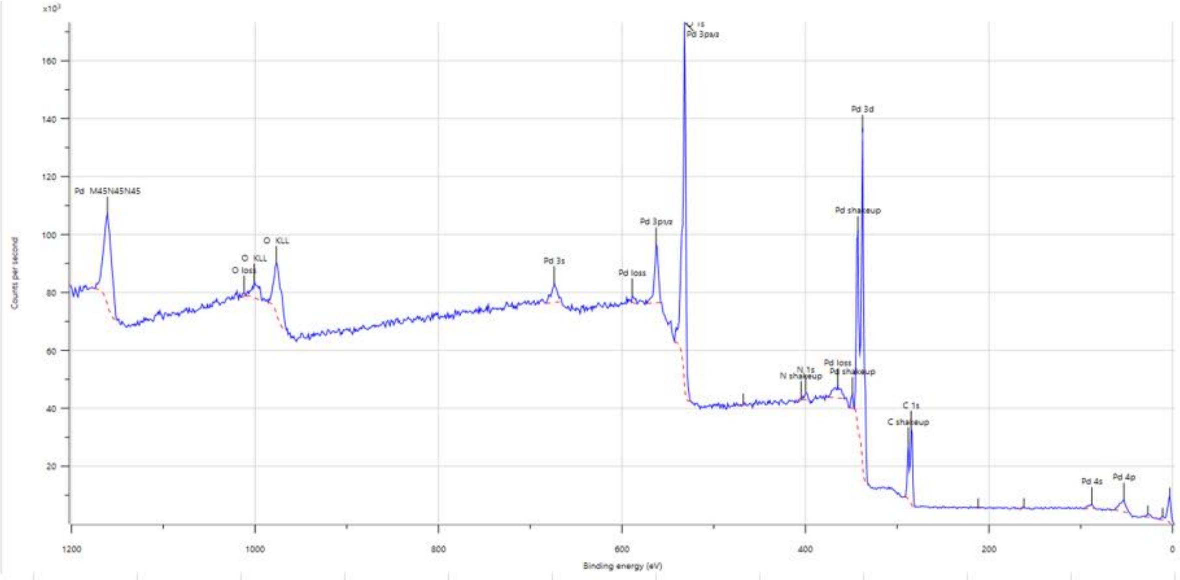
c) **Catalyst 3:** Ni-Pd/MWCNTs (Ni: 10%, Pd: 1%)



d) Catalyst 4: Pd/MWCNTs (Pd: 1%)



XPS Survey Scan of Catalyst 2: Ni-Pd/MWCNTs (Ni: 10%, Pd: 10%)

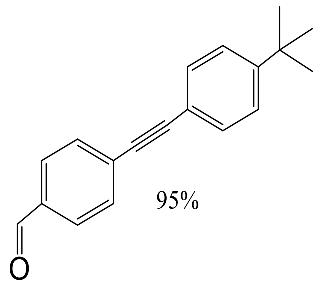


^{1}H NMR and ^{13}C NMR of compounds in Table 4:

1a: 4-[(4-*tert*-butylphenyl)ethynyl]benzaldehyde (M$^{\cdot+}$: 262.14 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 10.06-9.95 (s, 1H), 7.91-7.80 (d, 2H), 7.71-7.61 (d, 2H), 7.53-7.43 (d, 2H), 7.44-7.34 (d, 2H), 1.38-1.28 (s, 9H)

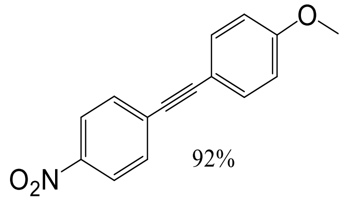
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 191.52, 152.48, 135.34, 132.14, 131.64, 129.98, 129.66, 125.60, 119.54, 93.88, 88.09, 77.43, 77.12, 76.80, 34.98, 31.23



1b: 1-methoxy-4-[(4-nitrophenyl)ethynyl]benzene (M$^{\cdot+}$: 253.07 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.28-8.13 (d, 2H), 7.67-7.57 (d, 2H), 7.53-7.44 (d, 2H), 6.96-6.86 (d, 2H), 3.87-3.81 (s, 3H)

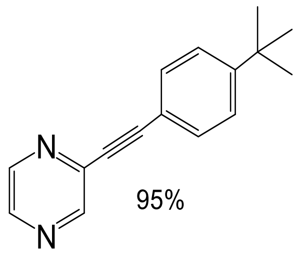
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 160.51, 146.77, 133.54, 132.07, 130.79, 123.72, 114.30, 114.20, 95.23, 86.73, 77.43, 77.11, 76.79, 55.45



1c: 2-[(4-*tert*-butylphenyl)ethynyl]pyrazine (M$^{\cdot+}$: 236.13 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.76-8.71 (s, 1H), 8.59-8.52 (d, 1H), 8.49-8.42 (d, 1H), 7.59-7.49 (d, 2H), 7.45-7.35 (d, 2H), 1.36-1.27 (s, 9H)

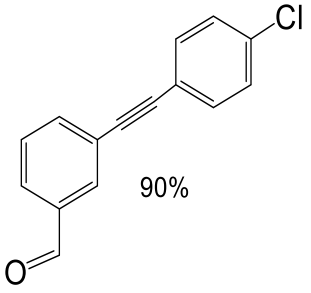
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 153.17, 147.82, 144.48, 142.66, 140.70, 132.04, 125.65, 118.51, 93.81, 85.42, 77.44, 77.13, 76.81, 35.04, 31.20



1d: 3-[(4-chlorophenyl)ethynyl]benzaldehyde (M$^{\cdot+}$: 240.03 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 10.06-9.96 (s, 1H), 8.05-7.97 (d, 1H), 7.90-7.81 (d, 1H), 7.80-7.70 (t, 1H), 7.56-7.49 (1H), 7.49-7.43 (d, 2H), 7.37-7.30 (d, 2H)

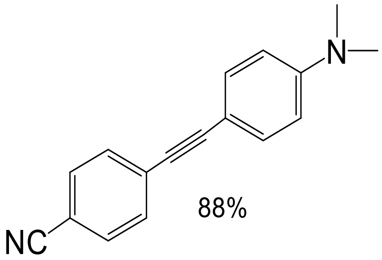
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 191.66, 137.18, 136.56, 134.89, 132.99, 129.28, 128.92, 124.27, 121.21, 89.84, 88.83, 77.43, 77.11, 76.79.



1e: 4-{[4-(dimethylamino)phenyl]ethynyl}benzonitrile (M$^{\cdot+}$: 246.12 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.62-7.56 (d, 2H), 7.56-7.50 (d, 2H), 7.44-7.37 (d, 2H), 6.71-6.61 (d, 2H), 3.05-2.98 (s, 6H)

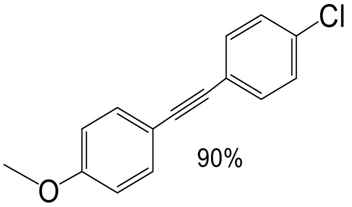
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 150.64, 133.17, 132.05, 131.63, 129.36, 118.98, 111.79, 110.35, 108.65, 95.93, 86.47, 77.45, 77.13, 76.81, 40.24



1f: 1-chloro-4-[(4-methoxyphenyl)ethynyl]benzene (M$^{\cdot+}$: 242.05 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 7.48-7.40 (d, 4H), 7.33-7.26 (d, 2H), 6.94-6.84 (d, 2H), 3.84-3.79 (s, 3H)

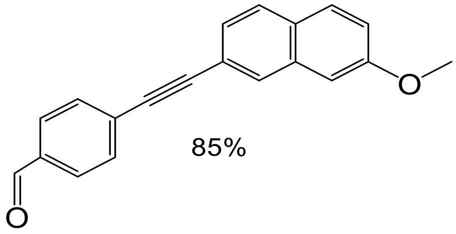
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 159.84, 133.16, 132.73, 128.74, 127.88, 122.18, 115.06, 114.26, 114.12, 90.43, 87.07, 77.43, 77.12, 76.79, 55.42.



1g: 4-[(7-methoxynaphthalen-2-yl)ethynyl]benzaldehyde ($M^{\cdot+}$: 286.10 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 10.04-9.97 (s, 1H), 8.05-7.96 (d, 1H), 7.91-7.82 (d, 2H), 7.75-7.66 (m, 4H), 7.60-7.48 (d, 1H), 7.22-7.13 (d, 1H), 7.13-7.09 (m, 1H), 3.95-3.89 (s, 3H)

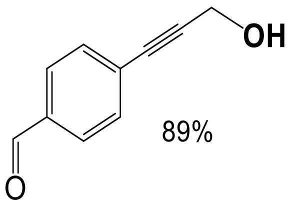
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 191.59, 158.72, 135.32, 134.59, 132.13, 131.92, 129.95, 129.73, 129.58, 128.95, 128.50, 127.10, 119.75, 117.38, 105.91, 94.37, 88.41, 77.45, 77.14, 76.82, 55.49.



1h: 4-(3-hydroxyprop-1-yn-1-yl)benzaldehyde ($M^{\cdot+}$: 160.05 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 10.04-9.96 (s, 1H), 7.86-7.79 (d, 2H), 7.61-7.52 (d, 2H), 4.55-4.50 (s, 2H)

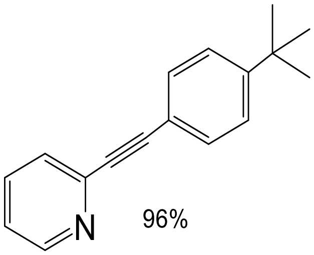
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 191.60, 135.71, 132.29, 129.65, 128.90, 91.32, 84.87, 77.44, 77.33, 77.12, 76.80, 51.68.



1i: 2-[(4-*tert*-butylphenyl)ethynyl]pyridine ($M^{\cdot+}$: 235.14 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.66-8.55 (d, 1H), 7.70-7.61 (t, 1H), 7.55-7.50 (d, 2H), 7.50-7.48 (d, 1H), 7.41-7.33 (d, 2H), 7.24-7.18 (t, 1H), 1.35-1.29 (s, 9H).

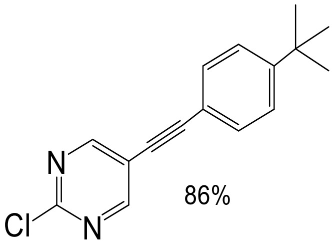
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 152.43, 150.09, 143.75, 136.22, 131.90, 127.20, 125.51, 122.65, 119.28, 89.66, 88.14, 77.43, 77.12, 76.80, 34.95, 31.23.



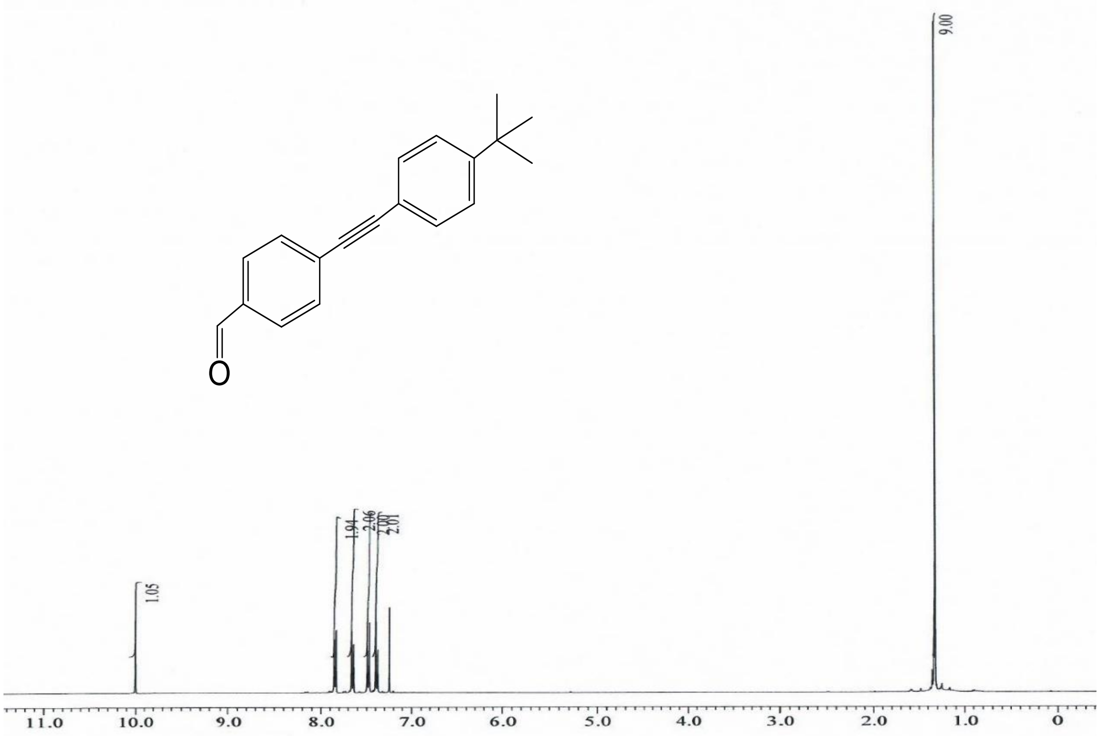
1j: 5-[(4-*tert*-butylphenyl)ethynyl]-2-chloropyrimidine (M$^{\cdot+}$: 270.09 *m/z*)

^{1}H-NMR (400 MHz, CHLOROFORM-D) δ 8.71 (s, 2H), 7.48-7.46 (d, 2H), 7.41-7.39 (d, 2H), 1.32 (s, 9H).

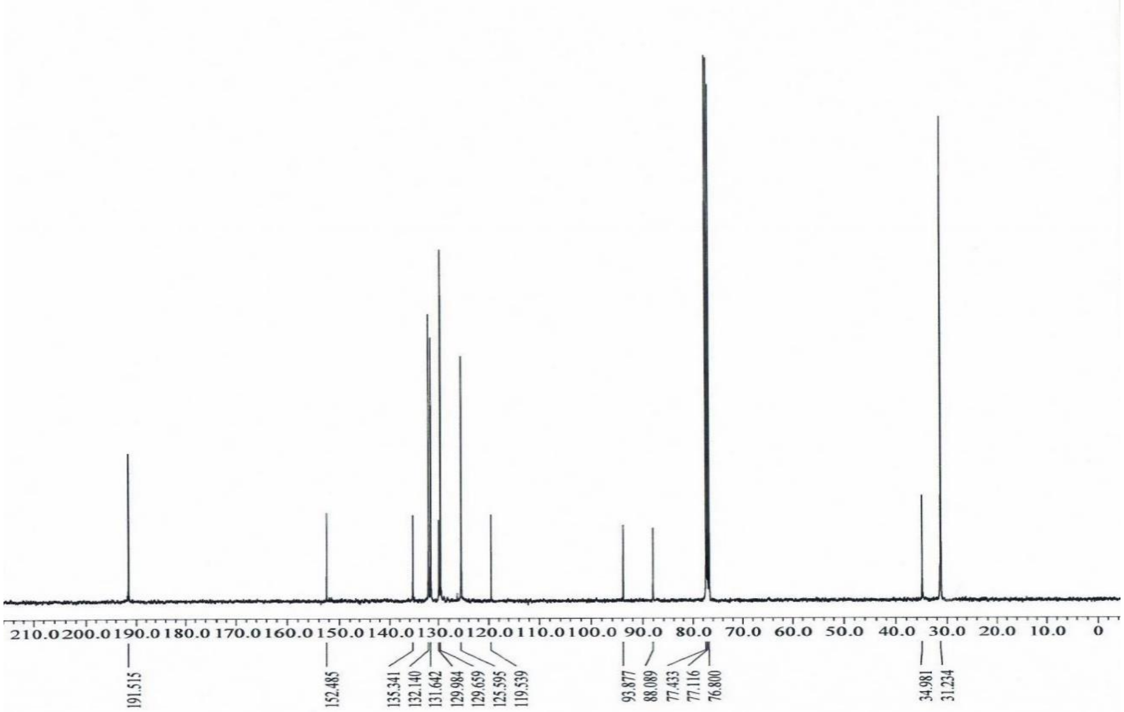
^{13}C-NMR (101 MHz, CHLOROFORM-D) δ 160.99, 159.15, 153.21, 131.65, 125.75, 118.79, 118.48, 97.94, 80.61, 77.44, 77.12, 76.80, 35.06, 31.21.



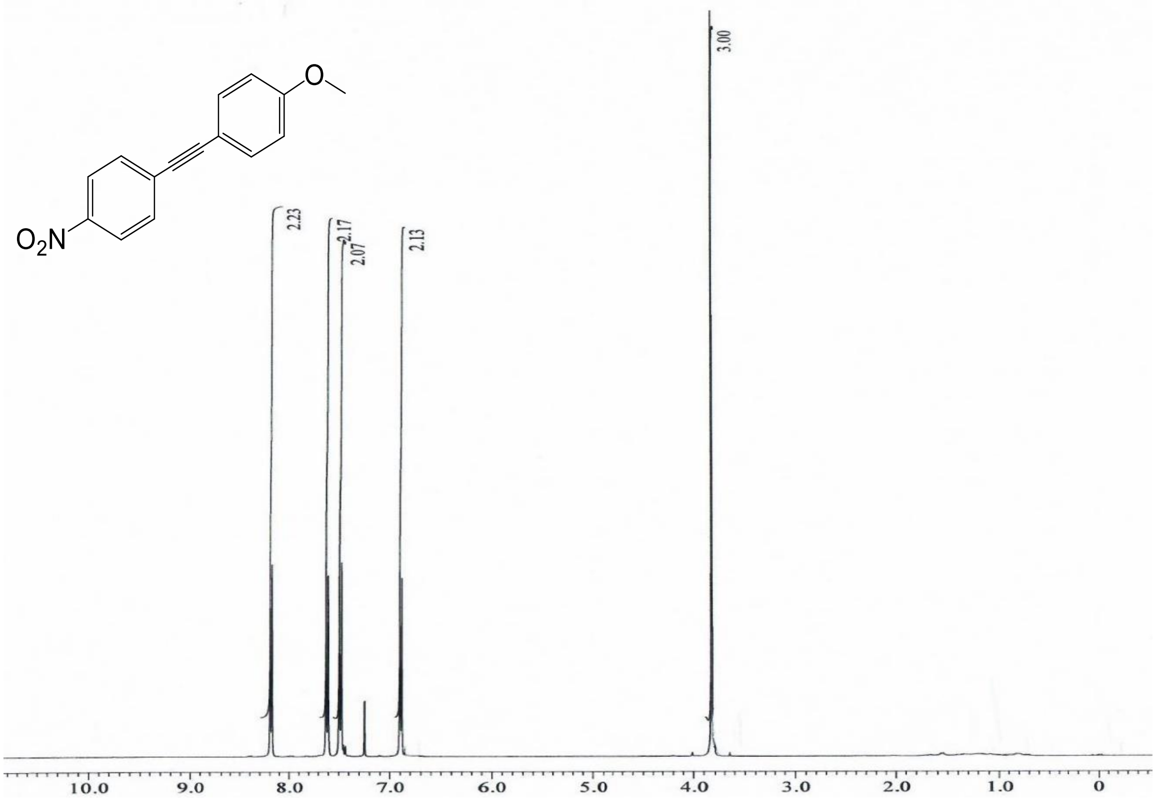
^{1}H NMR: 4-[(4-*tert*-butylphenyl)ethynyl]benzaldehyde **(1a)**:



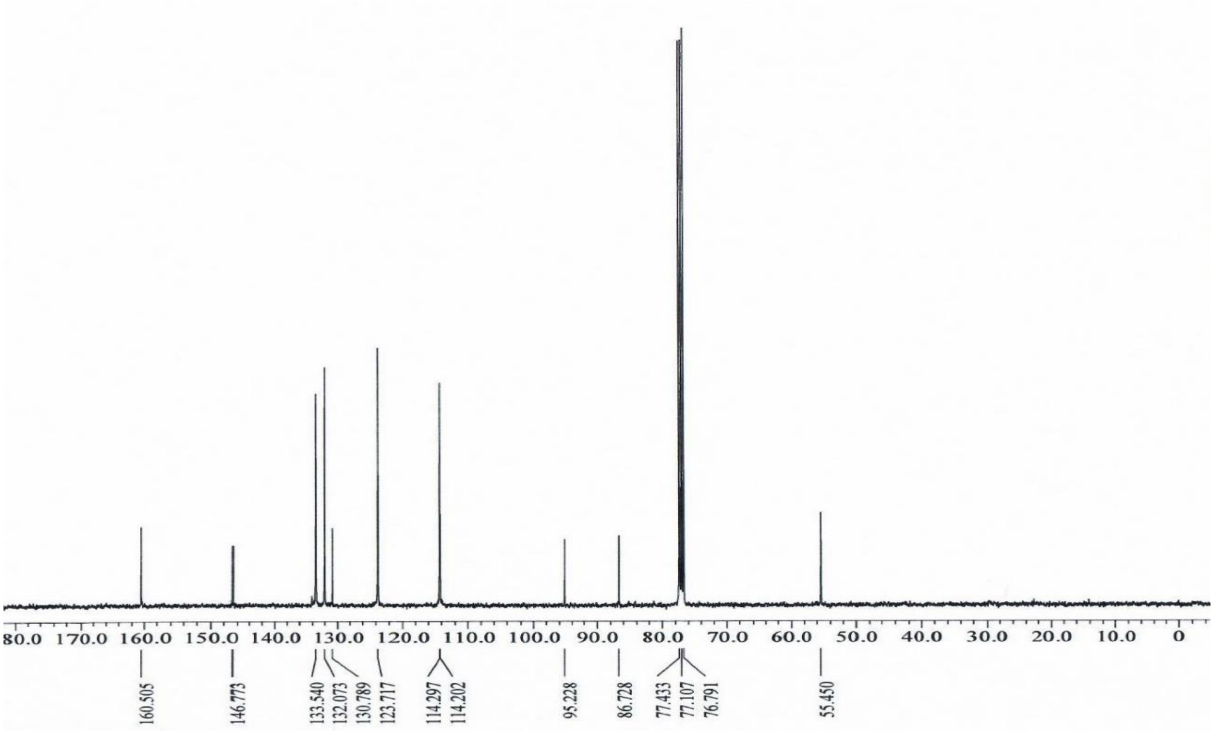
^{13}C NMR: 4-[(4-*tert*-butylphenyl)ethynyl]benzaldehyde **(1a)**:



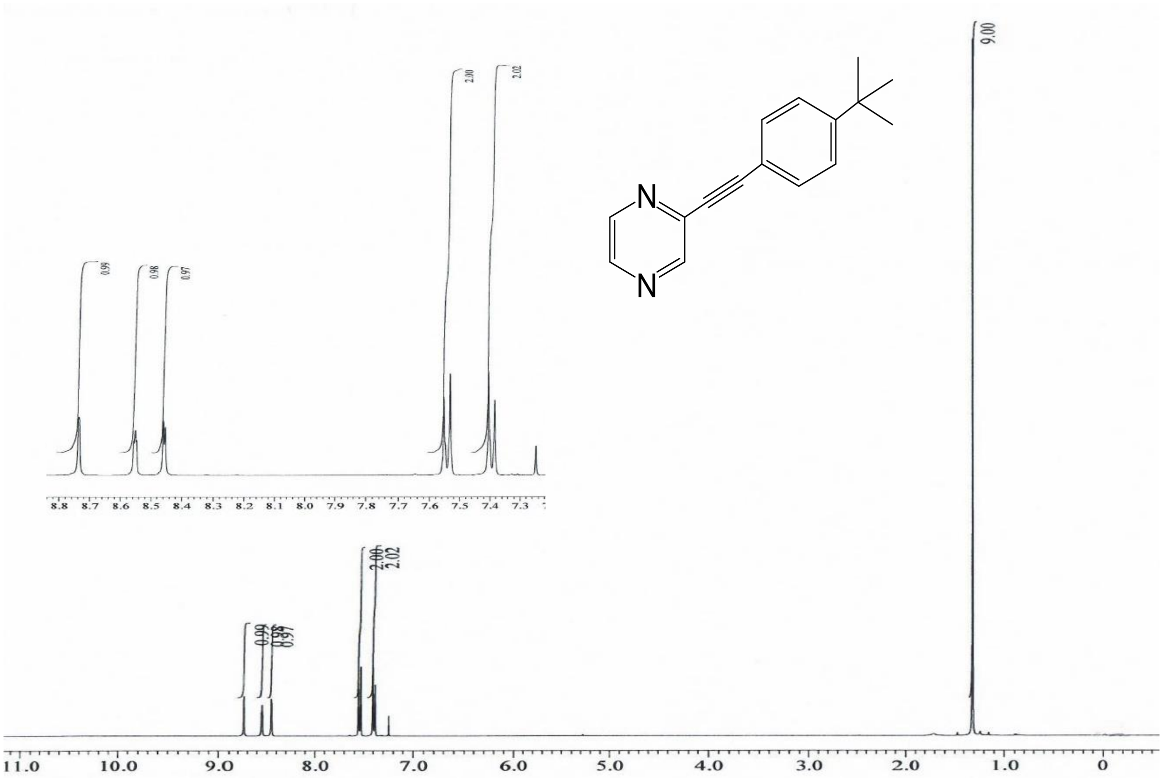
^{1}H NMR: 1-methoxy-4-[(4-nitrophenyl)ethynyl]benzene **(1b):**



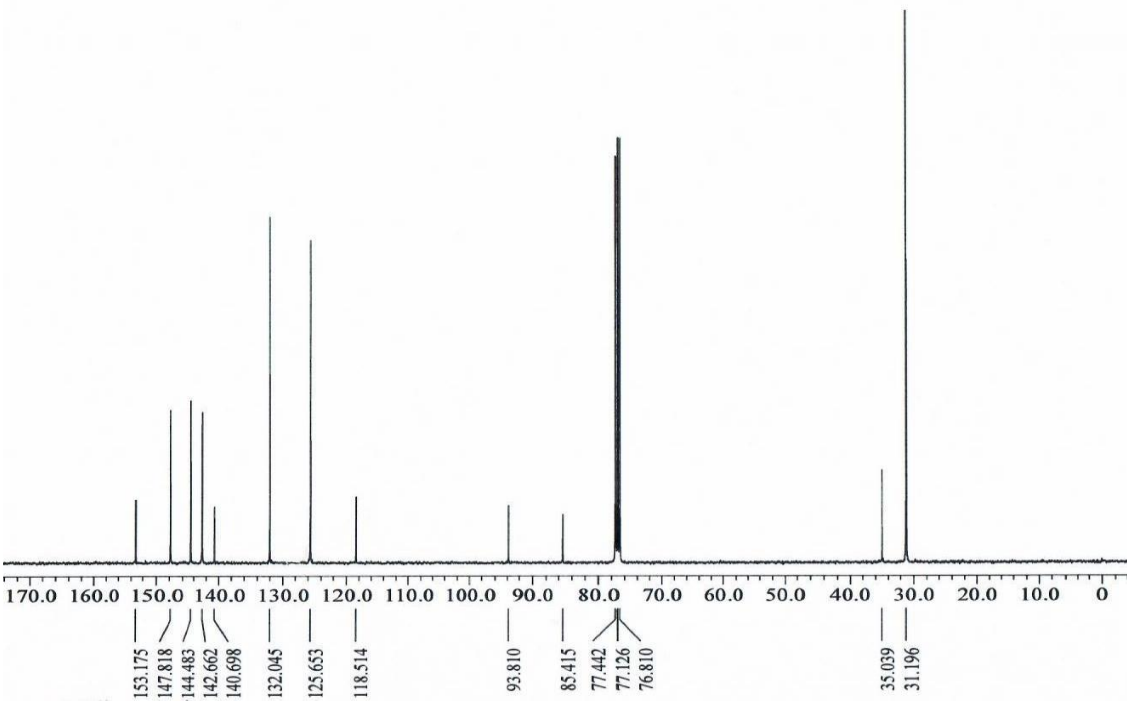
^{13}C NMR: 1-methoxy-4-[(4-nitrophenyl)ethynyl]benzene **(1b):**



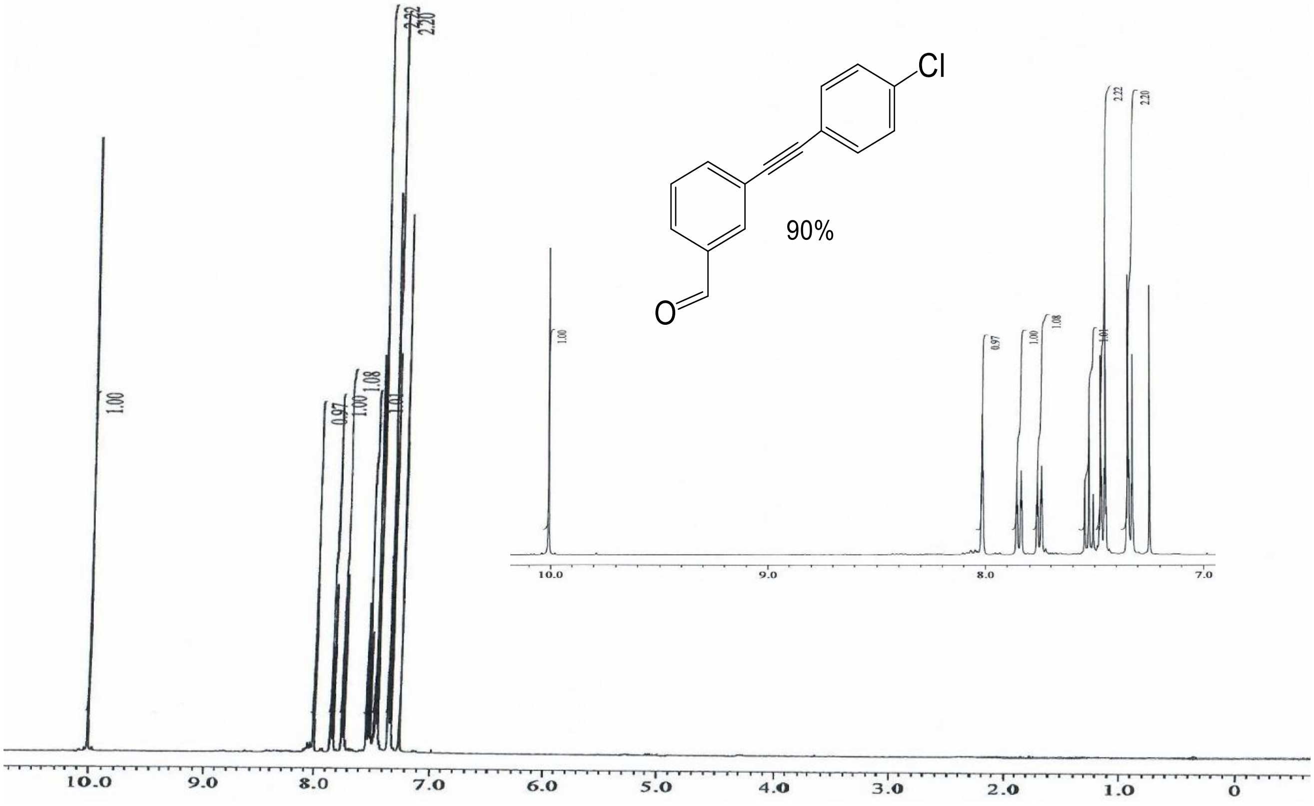
^{1}H NMR: 2-[(4-*tert*-butylphenyl)ethynyl]pyrazine (**1c**):



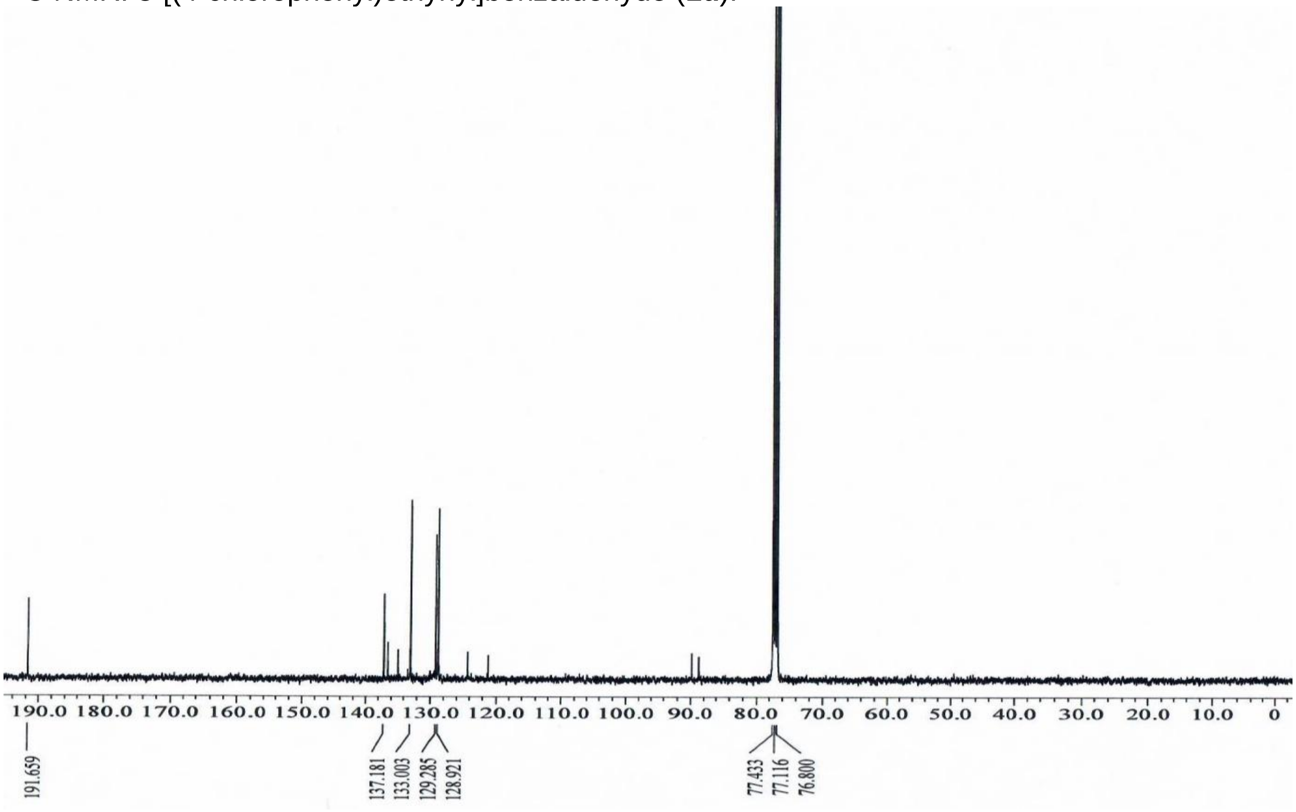
^{13}C NMR: 2-[(4-*tert*-butylphenyl)ethynyl]pyrazine (**1c**):



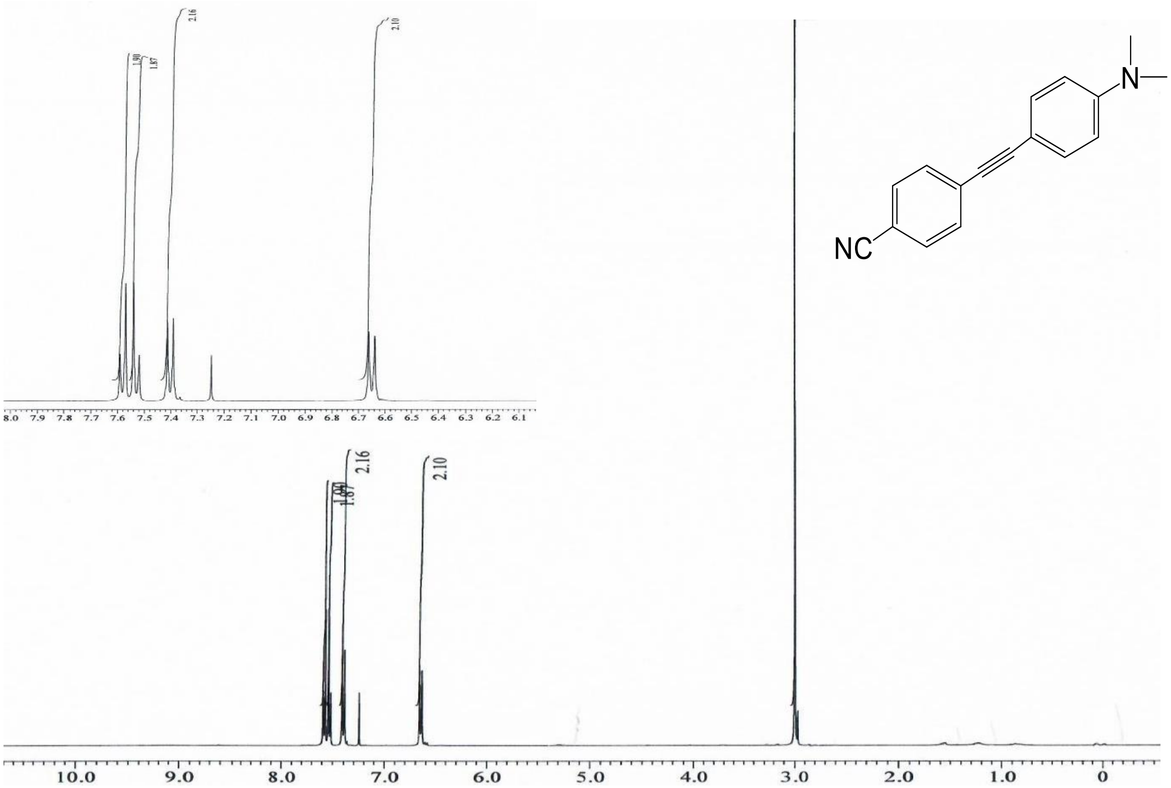
^{1}H NMR: 3-[(4-chlorophenyl)ethynyl]benzaldehyde (**1d**):



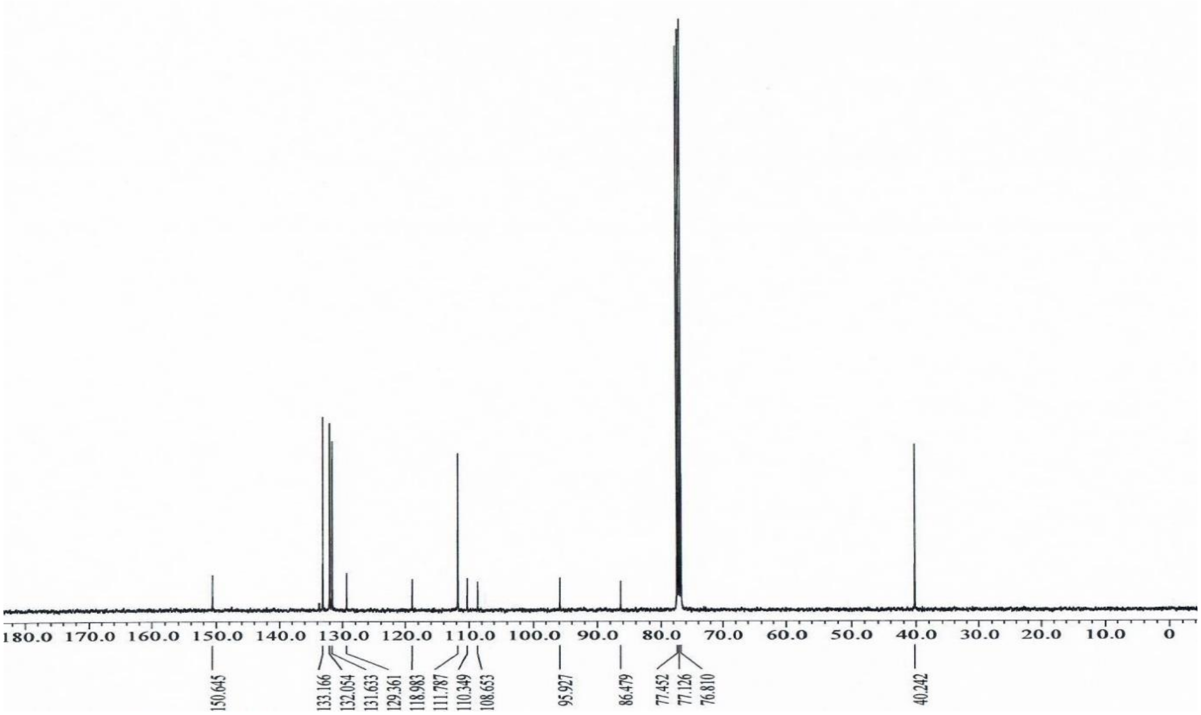
^{13}C NMR: 3-[(4-chlorophenyl)ethynyl]benzaldehyde (**1d**):



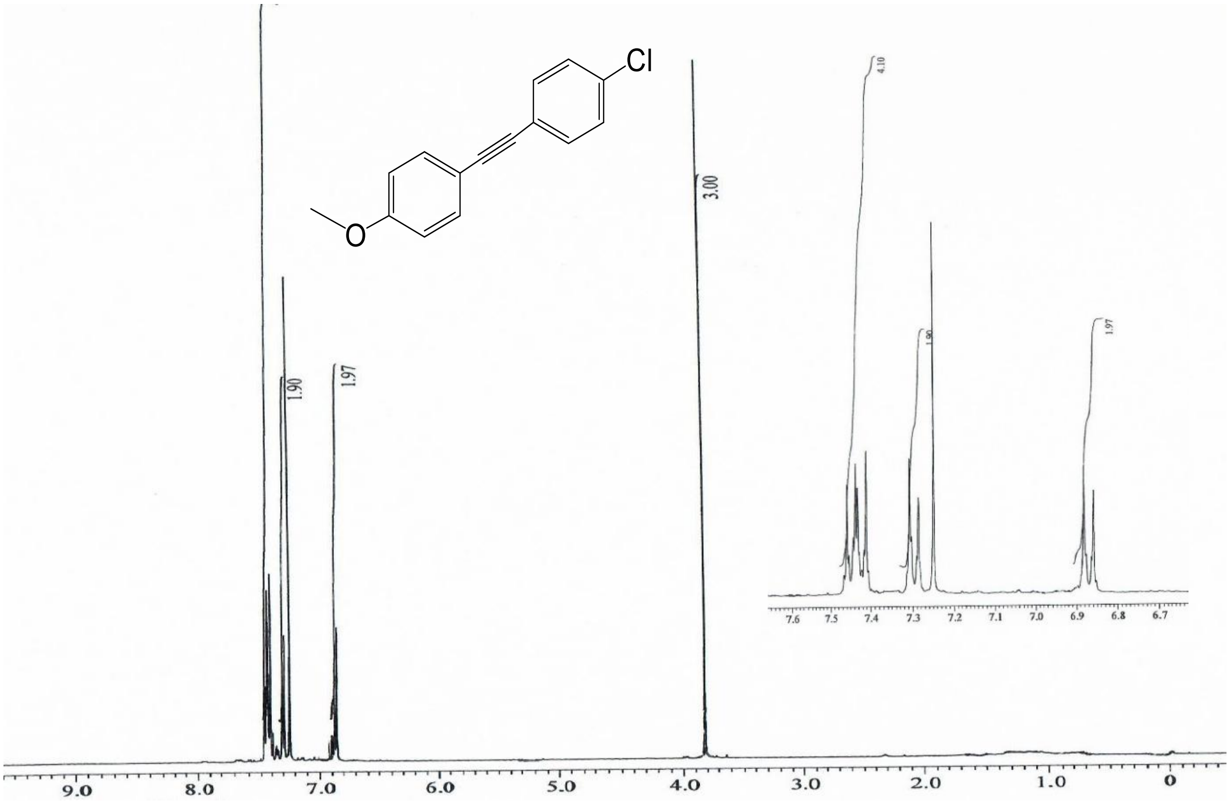
^{1}H NMR: 4-{[4-(dimethylamino)phenyl]ethynyl}benzonitrile **(1e)**:



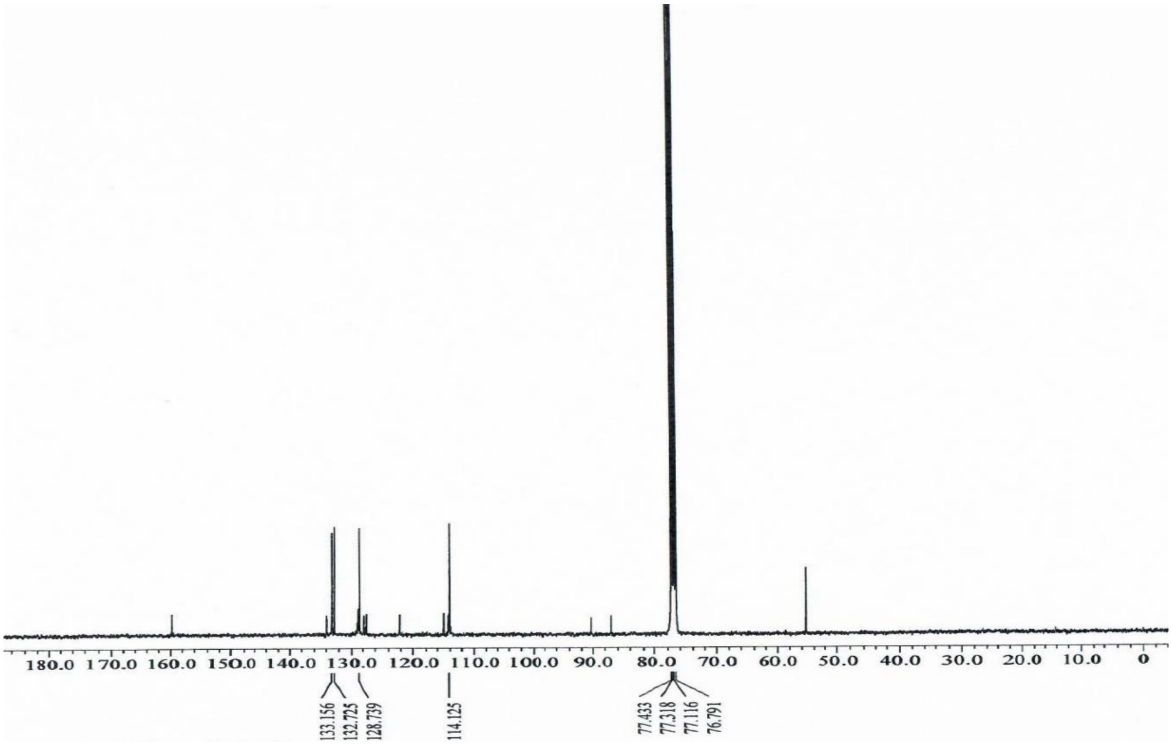
^{13}C NMR: 4-{[4-(dimethylamino)phenyl]ethynyl}benzonitrile **(1e)**:



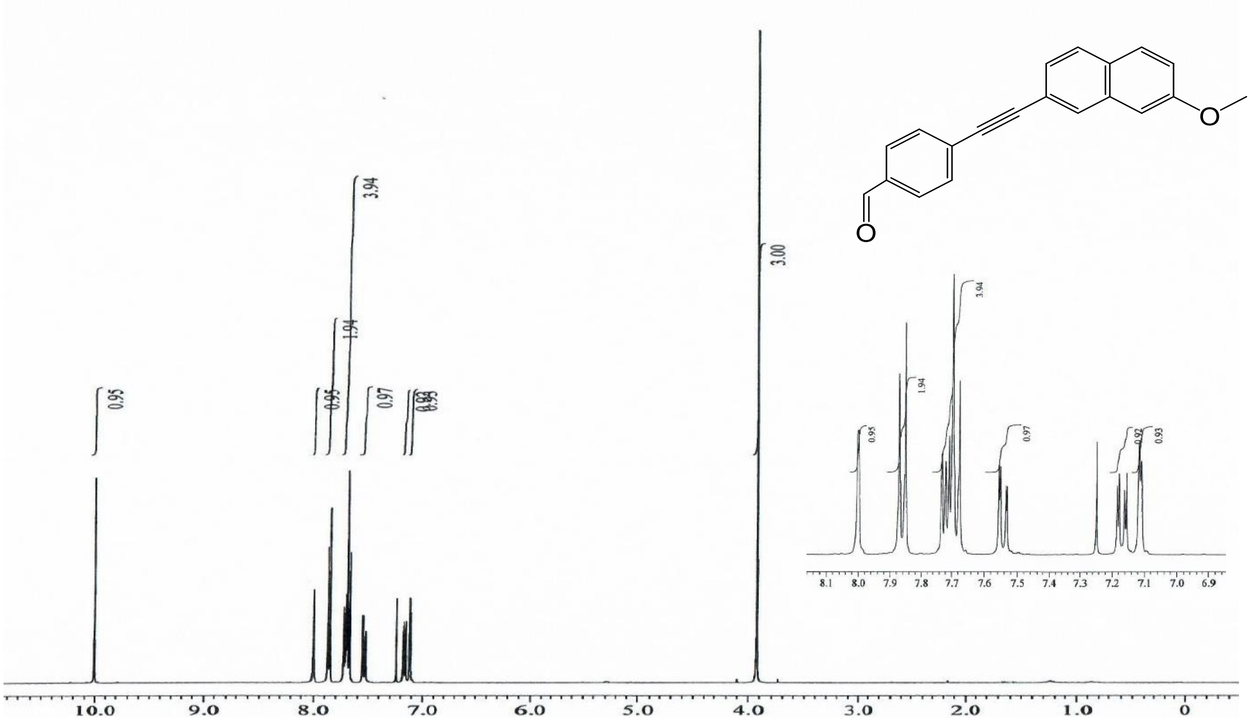
^{1}H NMR**:** 1-chloro-4-[(4-methoxyphenyl)ethynyl]benzene (**1f):**



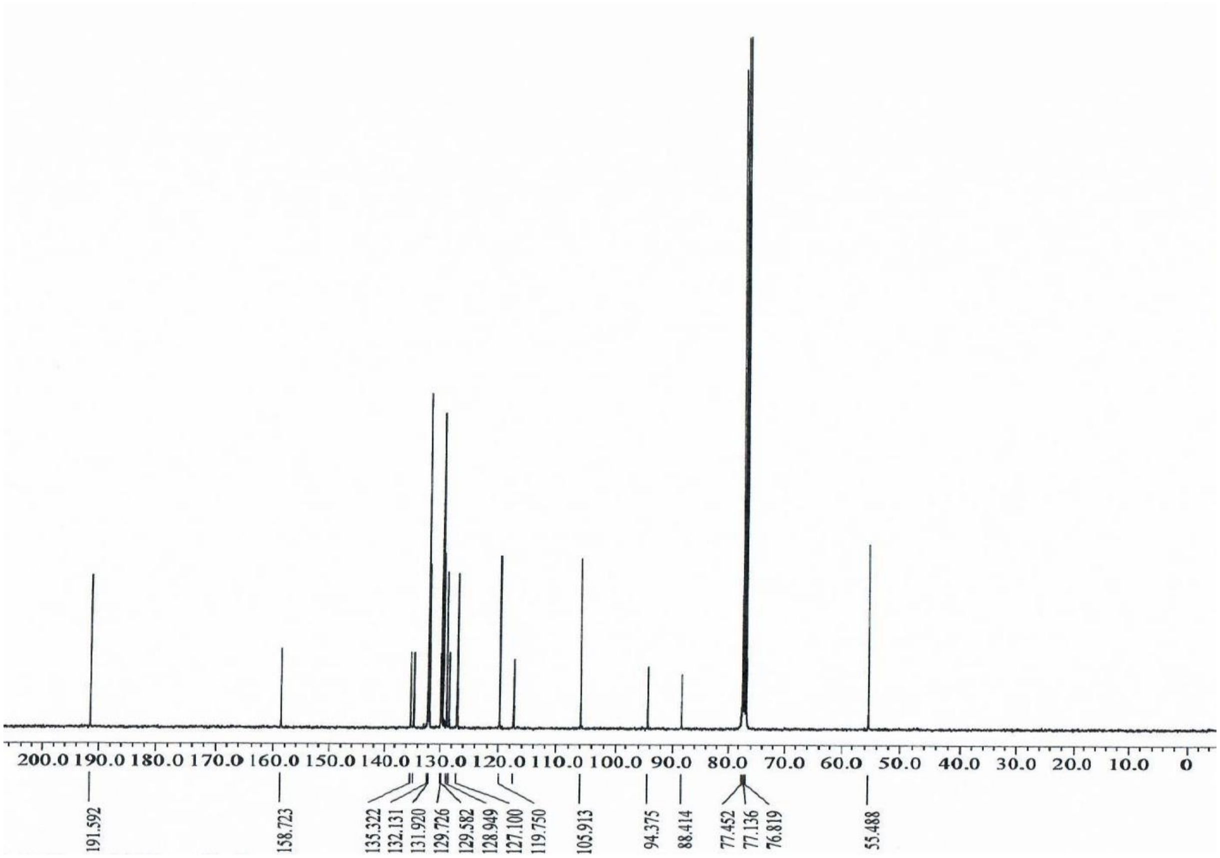
^{13}C NMR: 1-chloro-4-[(4-methoxyphenyl)ethynyl]benzene **(1f)**:



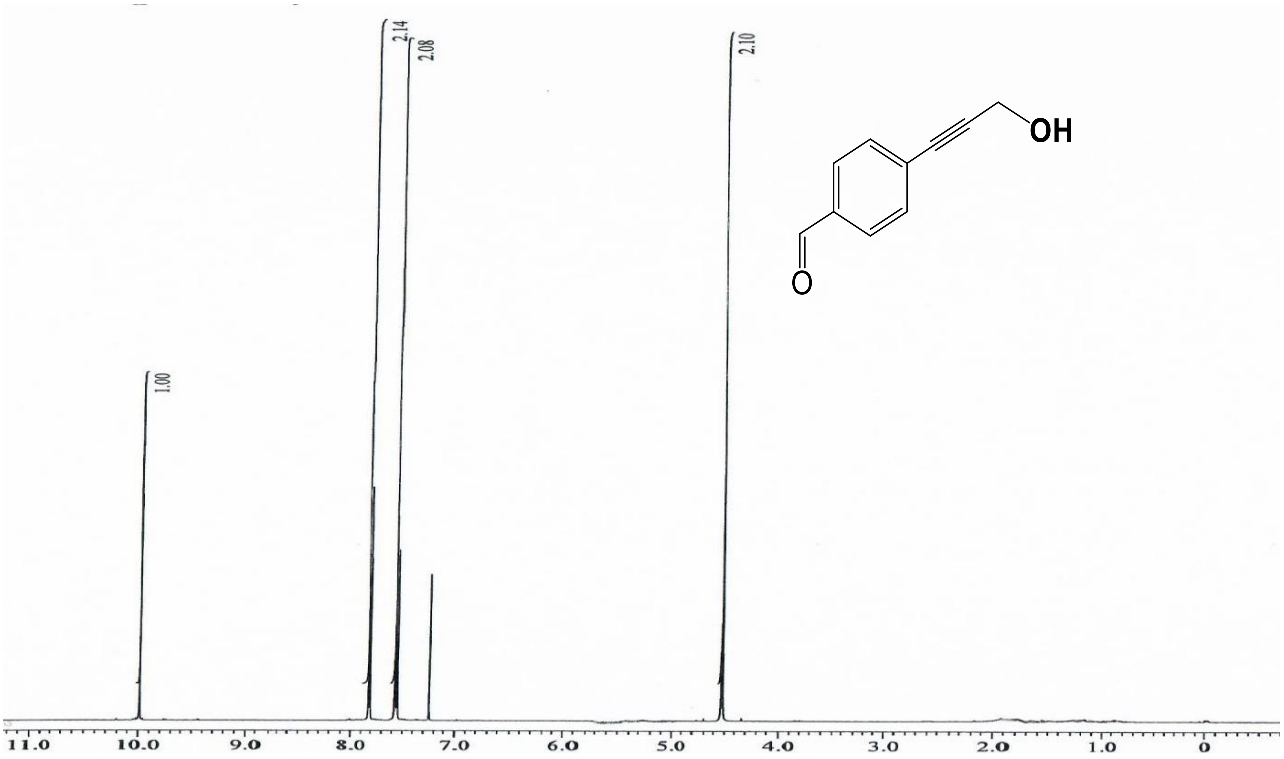
^{1}HNMR: 4-[(7-methoxynaphthalen-2-yl)ethynyl]benzaldehyde (**1g):**



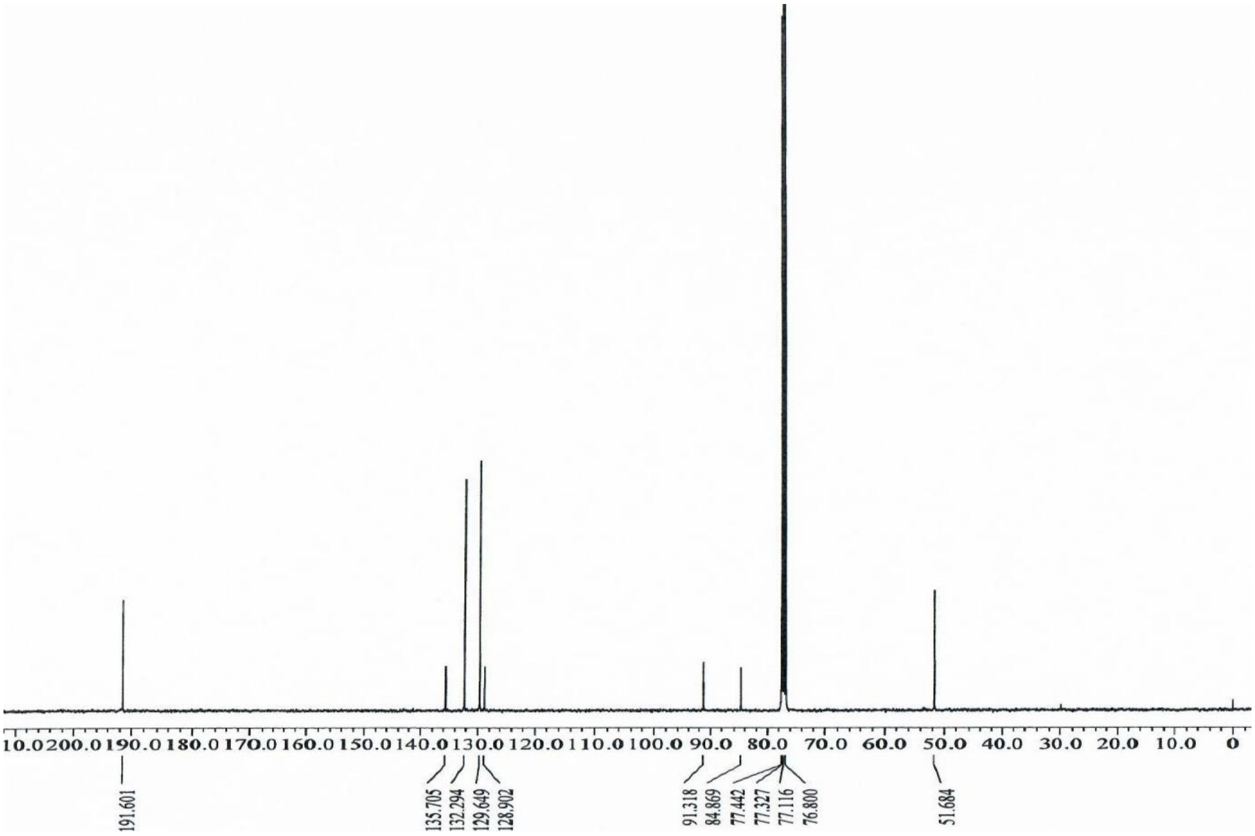
^{13}CNMR: 4-[(7-methoxynaphthalen-2-yl)ethynyl]benzaldehyde (**1g):**



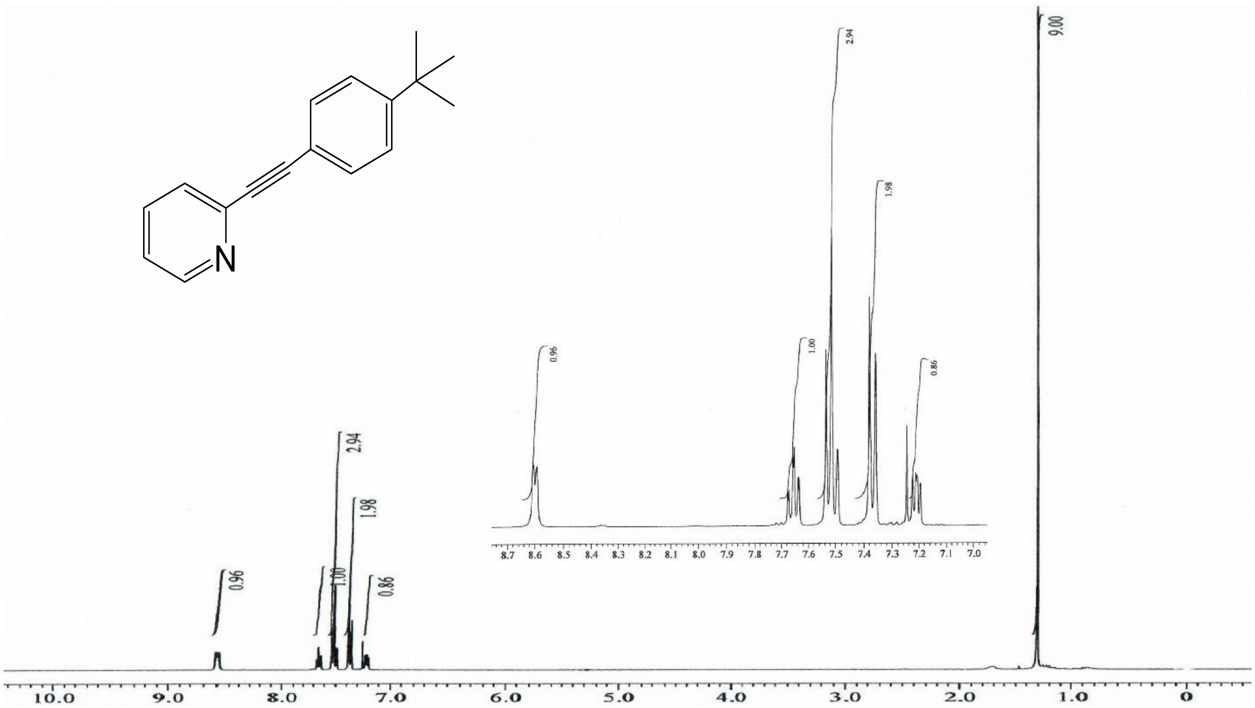
^{1}HNMR: 4-(3-hydroxyprop-1-yn-1-yl)benzaldehyde **(1h)**:



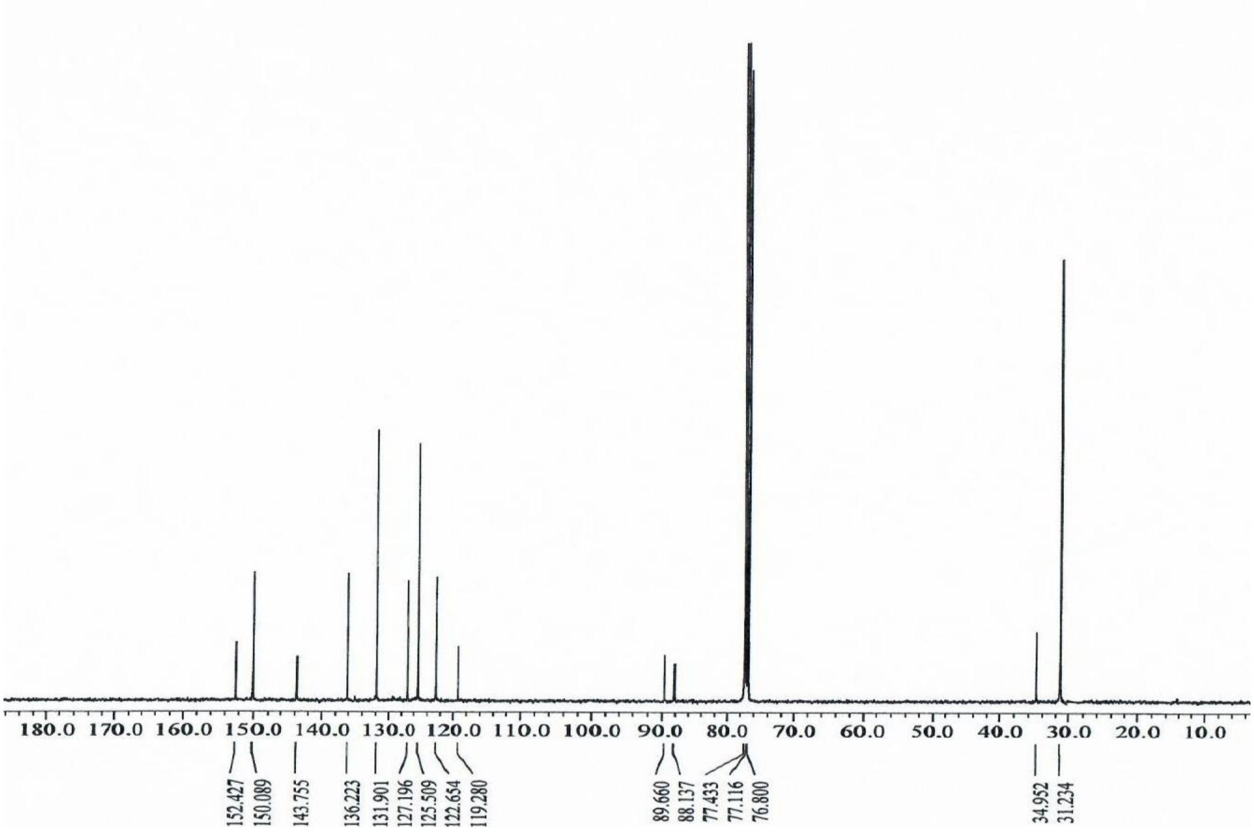
^{13}CNMR: 4-(3-hydroxyprop-1-yn-1-yl)benzaldehyde **(1h)**:



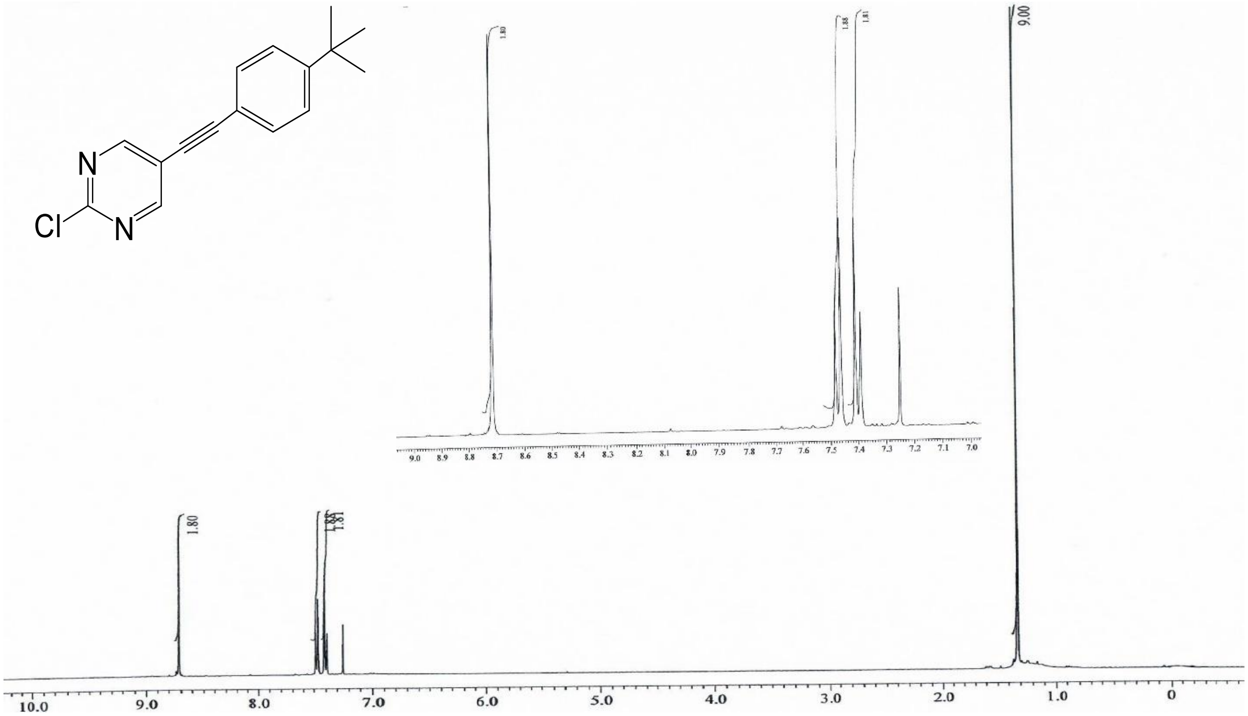
^{1}HNMR: 2-[(4-*tert*-butylphenyl)ethynyl]pyridine **(1i)**:



^{13}CNMR: 2-[(4-*tert*-butylphenyl)ethynyl]pyridine **(1i)**:



^{1}HNMR: 5-[(4-*tert*-butylphenyl)ethynyl]-2-chloropyrimidine **(1j)**:



^{13}CNMR: 5-[(4-*tert*-butylphenyl)ethynyl]-2-chloropyrimidine **(1j)**: