Copper-free Sonogashira cross-coupling of aryl chlorides with (hetero)arylacetylenes in the presence of ppm molar loading of [{Pd(μ-OH)Cl(NHC)}$_2$] complexes. Formation of hydrogen chloride as a coupling product. Co-catalytic effect of water.

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Supplementary Information

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1. Procedure for catalytic test of Sonogashira cross-coupling of 4-chlorotoluene with phenylacetylene in the presence of various palladium complexes

Ethanol (96%) (2 mL), phenylacetylene (17 µL, 0.15 mmol), 4-chlorotoluene (92 µL, 0.76 mmol) and dodecane (10 µL) were successively introduced into a glass reactor equipped with a magnetic stirrer, reflux condenser and gas introduction cap under an argon atmosphere. The mixture was then heated to 80°C and the corresponding palladium complex (0.001 mol %) and KOH (2 equiv. relative to Pd) were added simultaneously. Reactions were carried out with continuous stirring at 80°C for 24 hours, monitoring the reaction by gas chromatography (GC) and gas chromatography with mass detection (GC-MS).

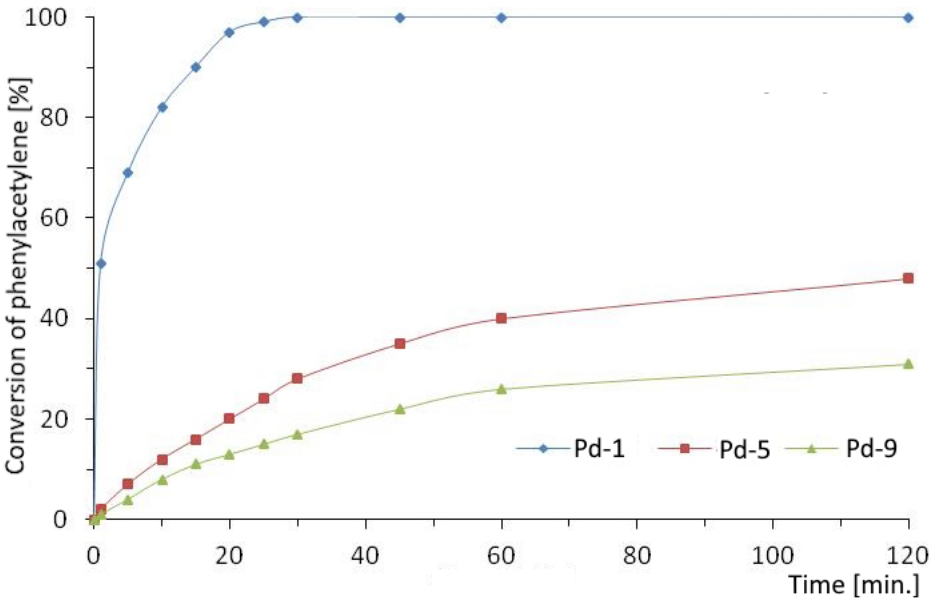


Figure S1 Conversion vs time plot for Sonogashira cross-coupling of 4-chlorotoluene with phenylacetylene catalysed by: [{Pd(µ-OH)Cl(IPr)}$_2$] (Pd-1) (blue diamonds), [{Pd(µ-Cl)Cl(IPr)}$_2$] (Pd-5) (red squares) and [PdCl2(IPr)(3-chloropyridine)] (Pd-9) (green triangles). Reaction conditions: [ArCl]:[acetylene] = 5:1, 80 °C, [Pd] (0.01 mol%), [Pd]:[KOH] =1:2; 24 h, argon, dodecane (internal standard); Conversions were calculated from GC analyses.

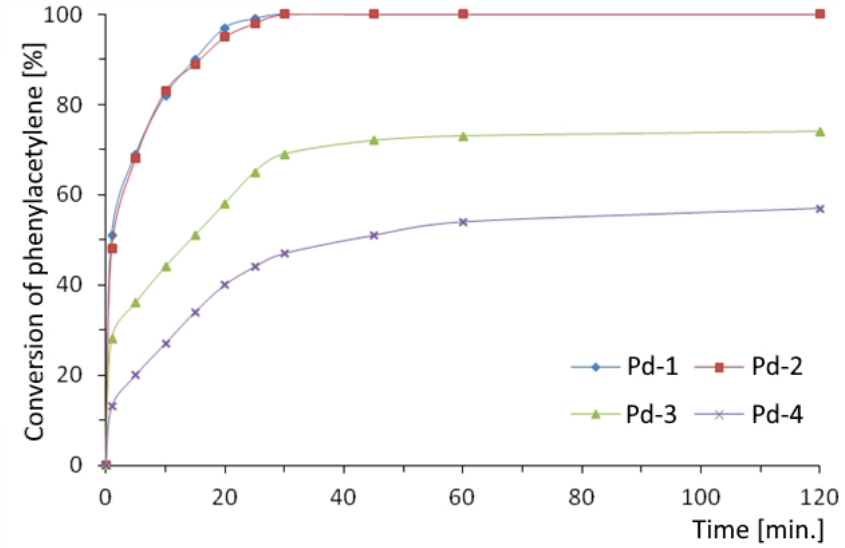


Figure S2 Reaction profiles for Sonogashira cross-coupling of 4-chlorotoluene with phenylacetylene catalysed by: [{Pd(μ-OH)Cl(IPr)}$_2$] **(Pd-1),** [{Pd(μ-OH)Cl(SIPr)}$_2$] **(Pd-2),** [{Pd(μ-OH)Cl(IMes)}$_2$] **(Pd-3),** [{Pd(μ-OH)Cl(SIMes)}$_2$] **(Pd-4).** Reaction conditions asnabove.

2. Determination of kinetic isotopic effect

In a dry and degassed ventilation vial equipped with a magnetic bar, phenylacetylene 17 µL (0.155 mmol), 4-chlorotoluene 92 µL (1.55 mmol), dodecane 10 µL as an internal standard, and ethanol (dry ethanol and ethanol 96%, respectively) were placed. Then the mixture was heated to 80 °C and 10 µL of toluene solution of [{Pd(µ-OH)Cl(IPr)}$_2$] (11 mg of Pd-1 in 1 mL of toluene) and 100 µL of ethanol solution of KOH were simultaneously added dropwise (9 mg of KOH in 1 mL of EtOH). The mixture was stirred at 80°C for one hour and the sample was taken for analysis by gas chromatography after 0, 2, 5, 7, 10, 15, 20, 25, 30, 40, 50 and 60 minutes, respectively. A sample for GC analysis was prepared by taking 10 µL of the reaction mixture, which was diluted in 1 mL of pure dichloromethane.

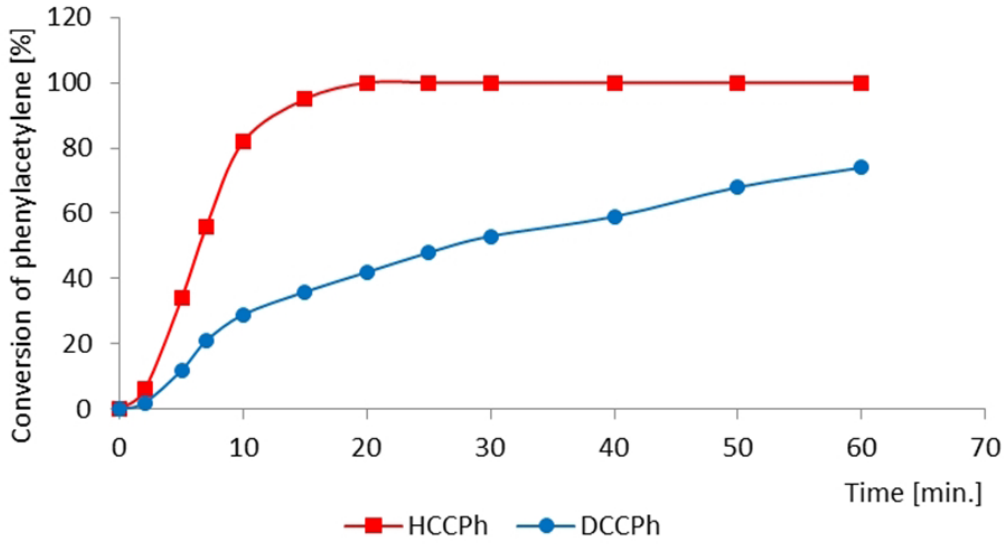


Figure S3. Conversion vs time plot for Sonogashira cross-coupling of phenylacetylene with 4-chlorotoluene in the presence of **Pd-1**. Reaction conditions: [ArCl]:[acetylene] = 5:1, 80 °C, [Pd] (0.01 mol%), [Pd]:[KOH] = 1:2; 24 h, argon, dodecane (internal standard); Conversions were calculated from GC analyses.

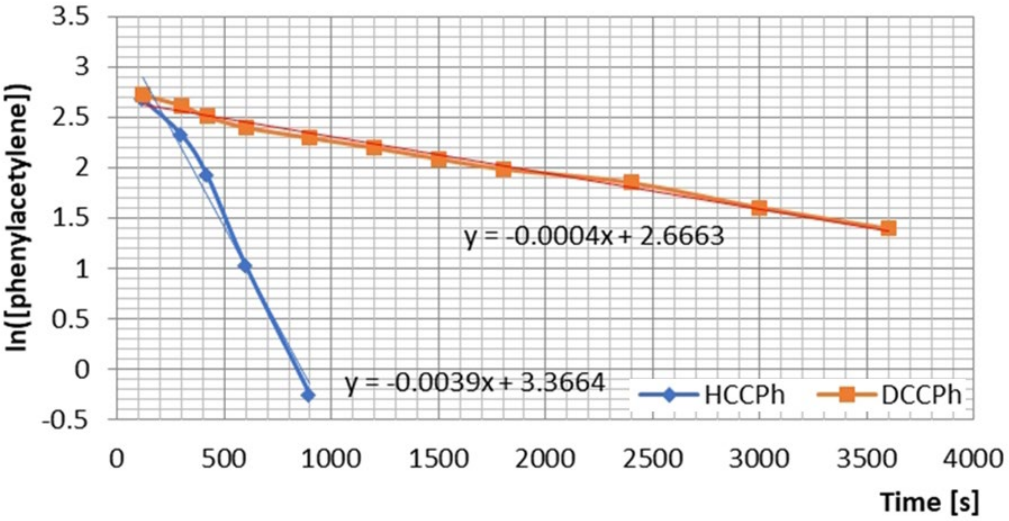


Figure S4. Determination of the primary kinetic isotopic effect.

3. Reduction of Pd(II) via ethanol oxidation

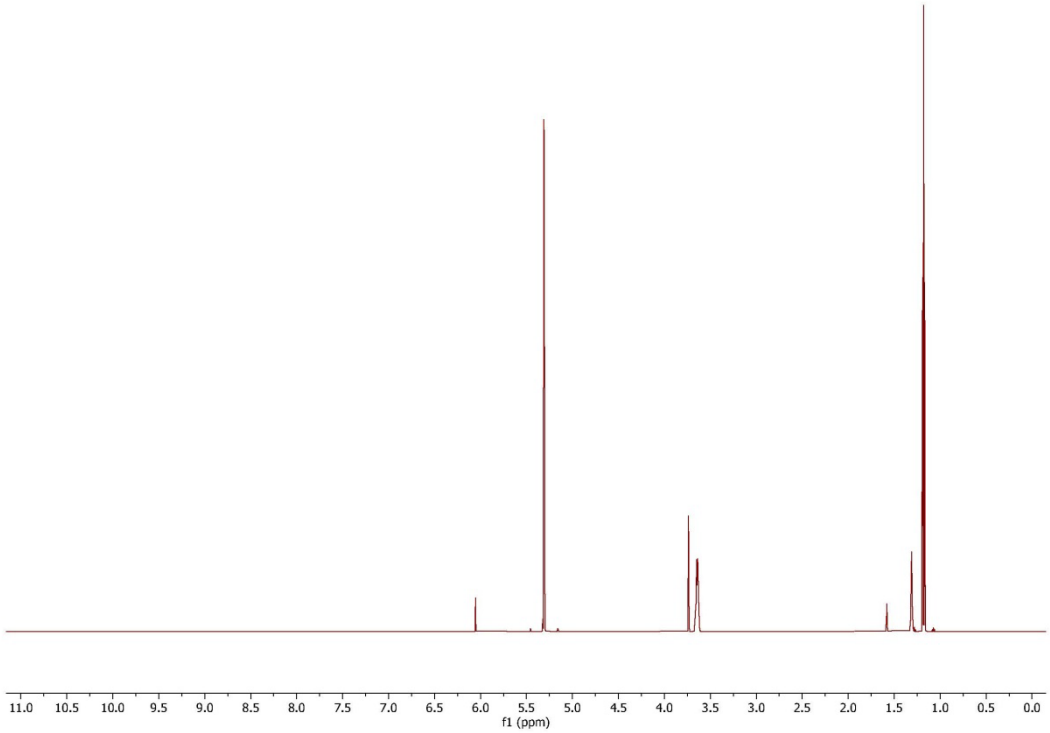


Figure S5. Initial ^{1}H NMR spectrum of the reaction of Pd-1 with an excess of EtOH in CD_2Cl_2.

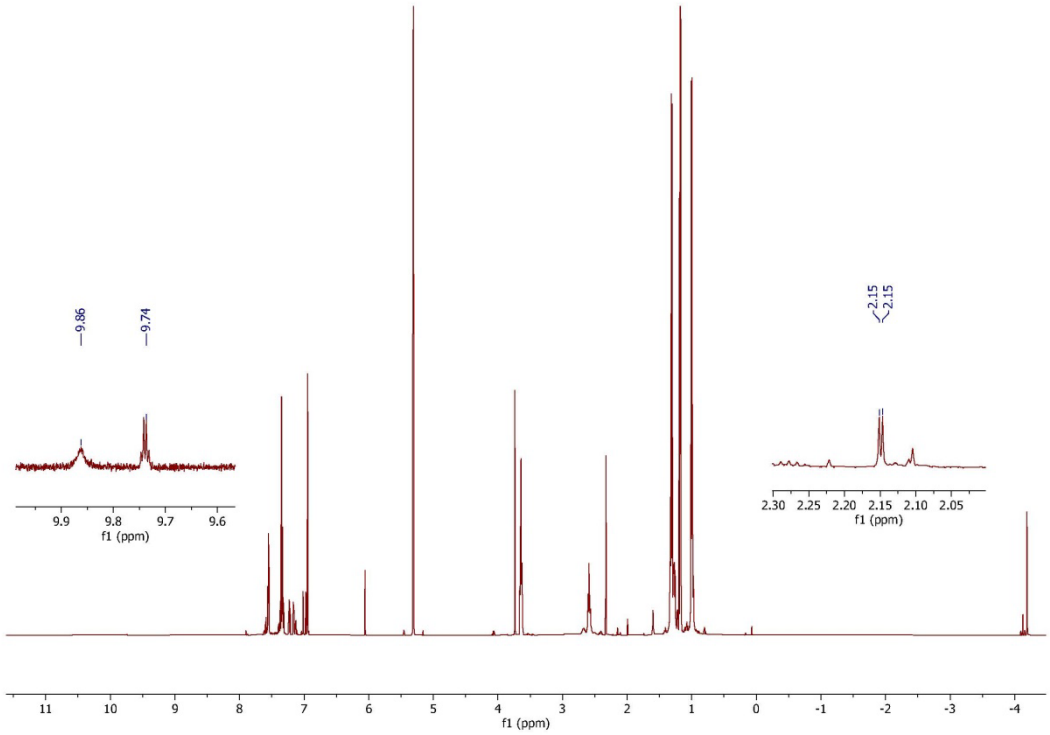
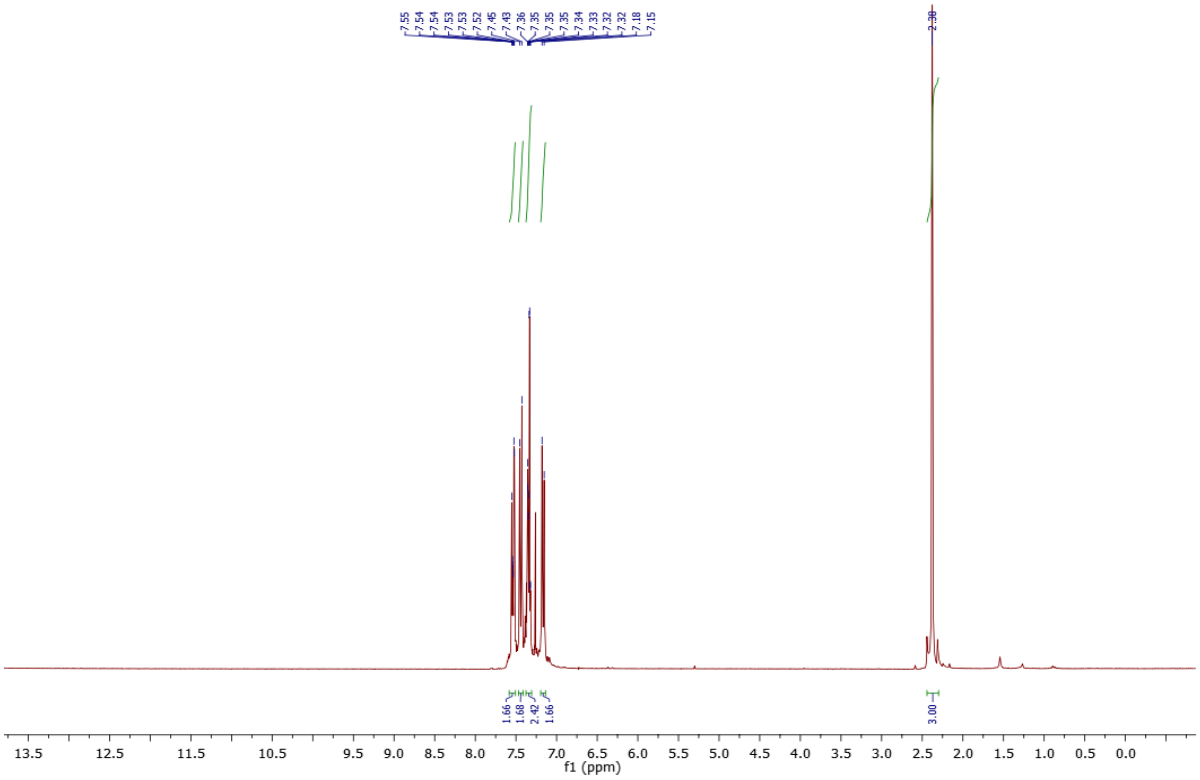
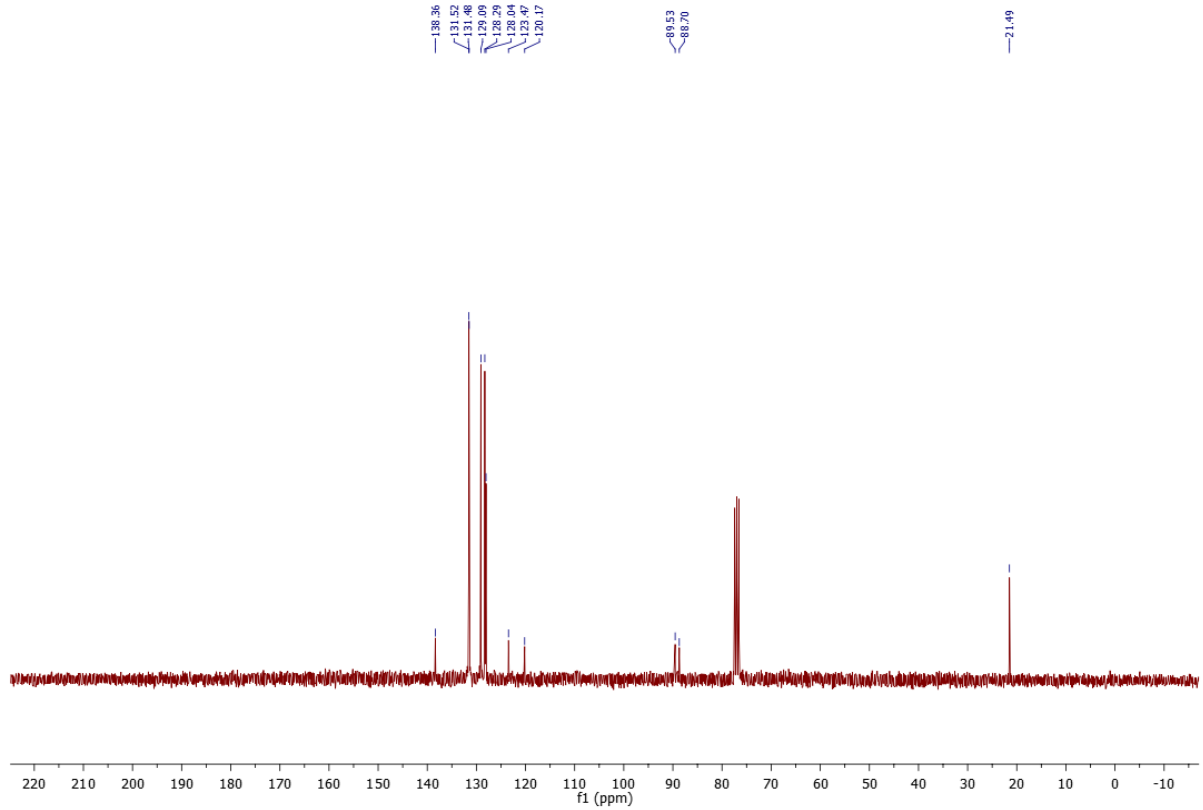


Figure S6. ^{1}H NMR spectrum of the reaction of Pd-1 with an excess of EtOH in CD_2Cl_2 after 22 h.

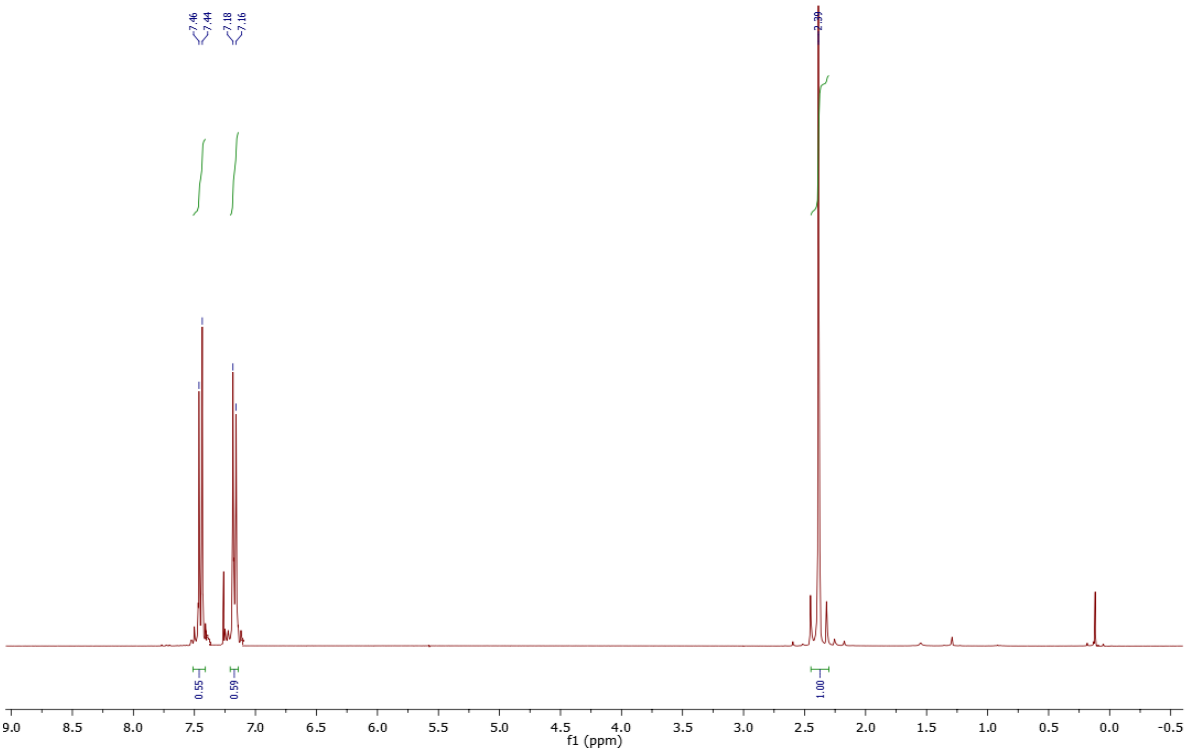
4. ^{1}H and ^{13}C NMR spectra of isolated products of Sonogashira cross-coupling



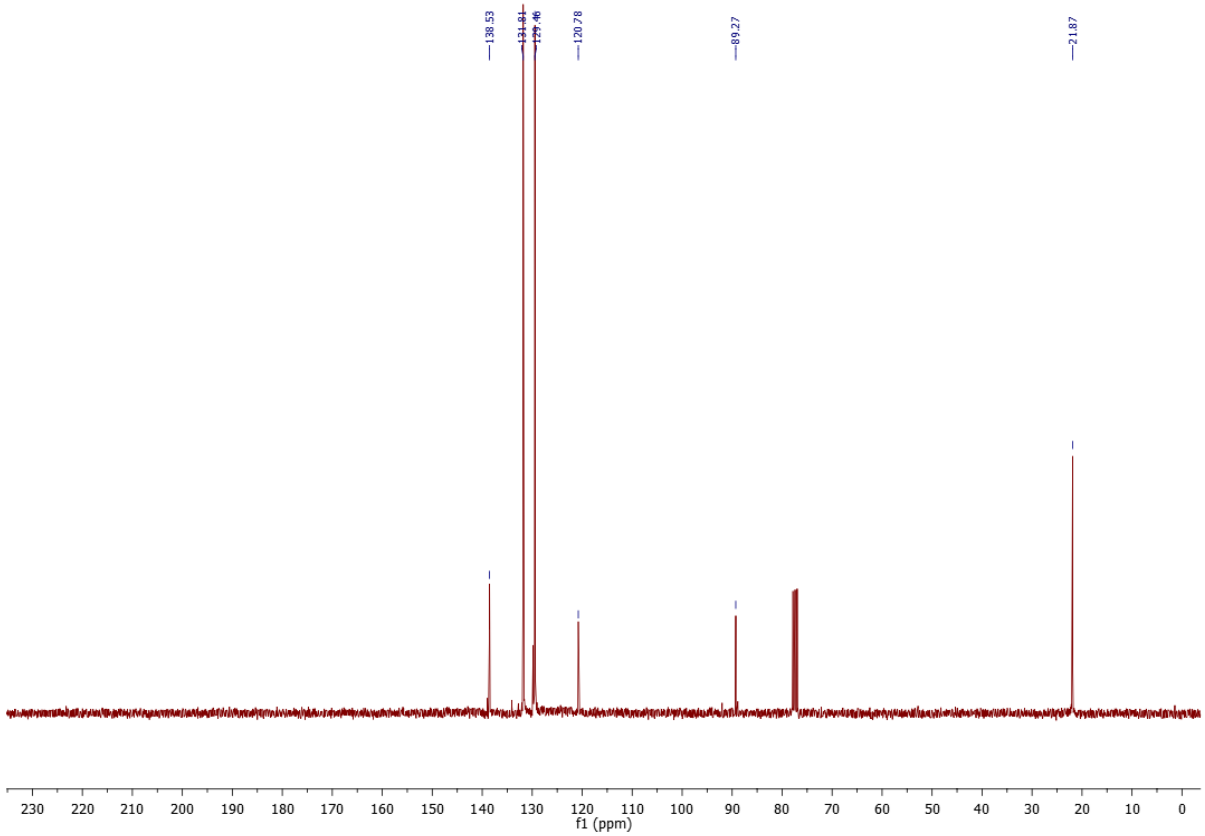
^{1}H NMR spectrum of 1-methyl-4-(phenylethynyl)benzene (3a)



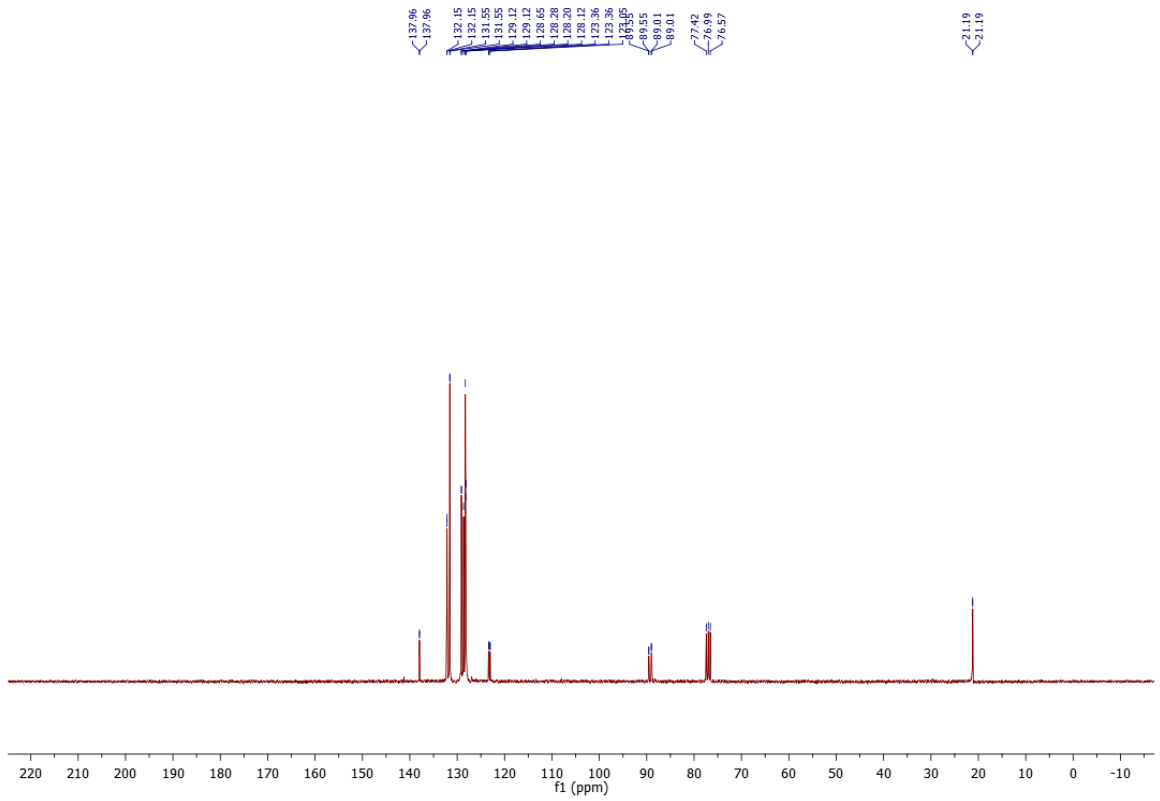
^{13}C NMR spectrum of 1-methyl-4-(phenylethynyl)benzene (3a)



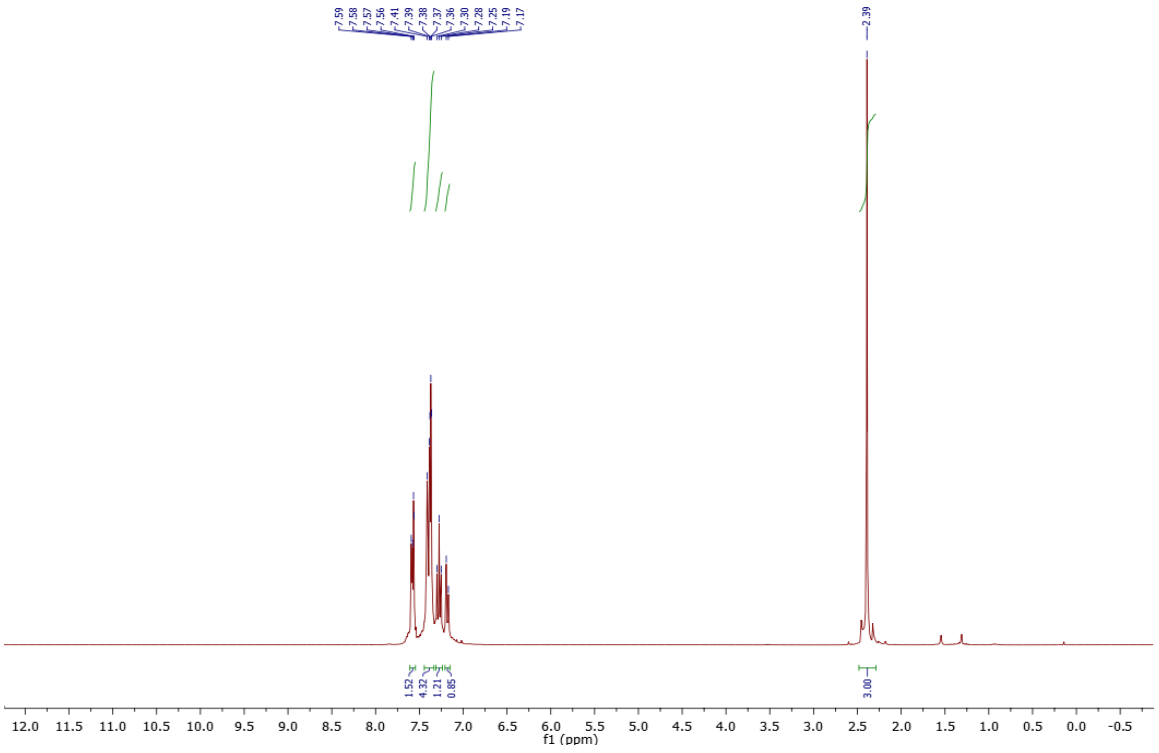
^{1}H NMR spectrum of 1,2-di-p-tolylethyne (3b)



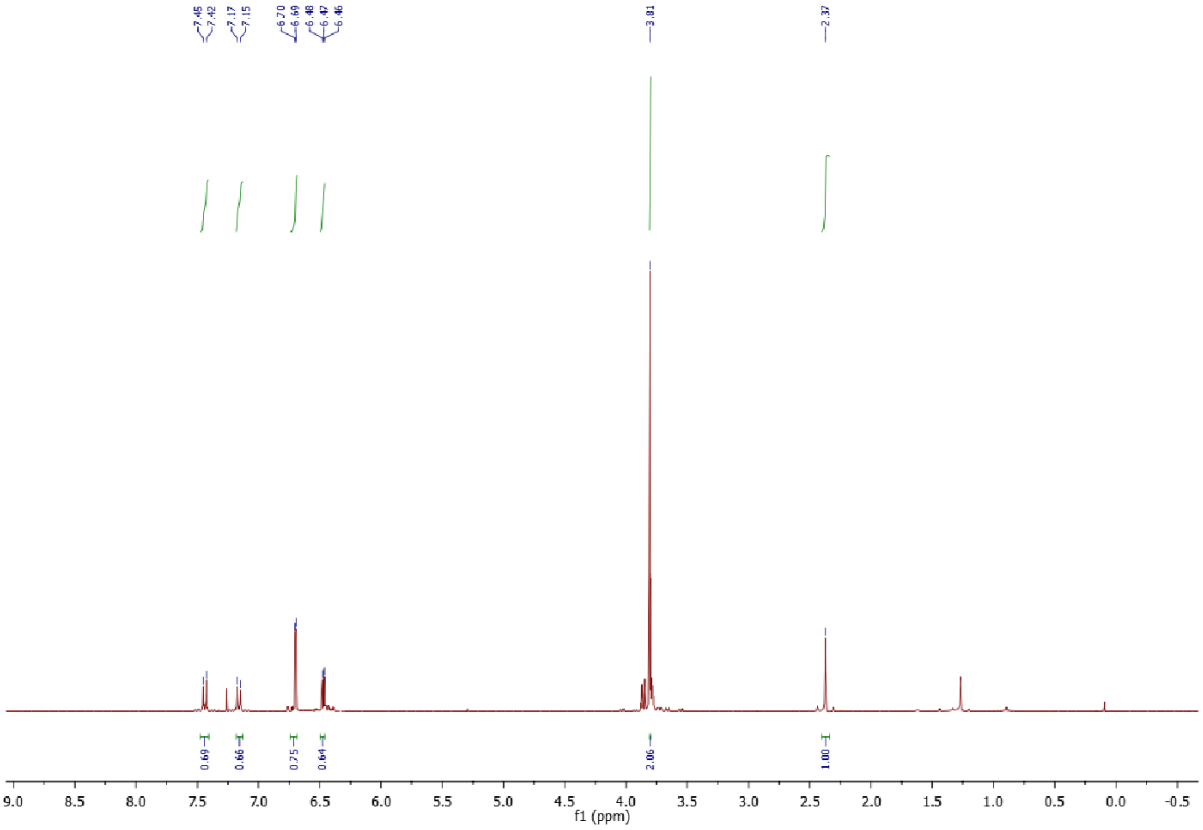
^{13}C NMR spectrum of 1,2-di-p-tolylethyne (3b)



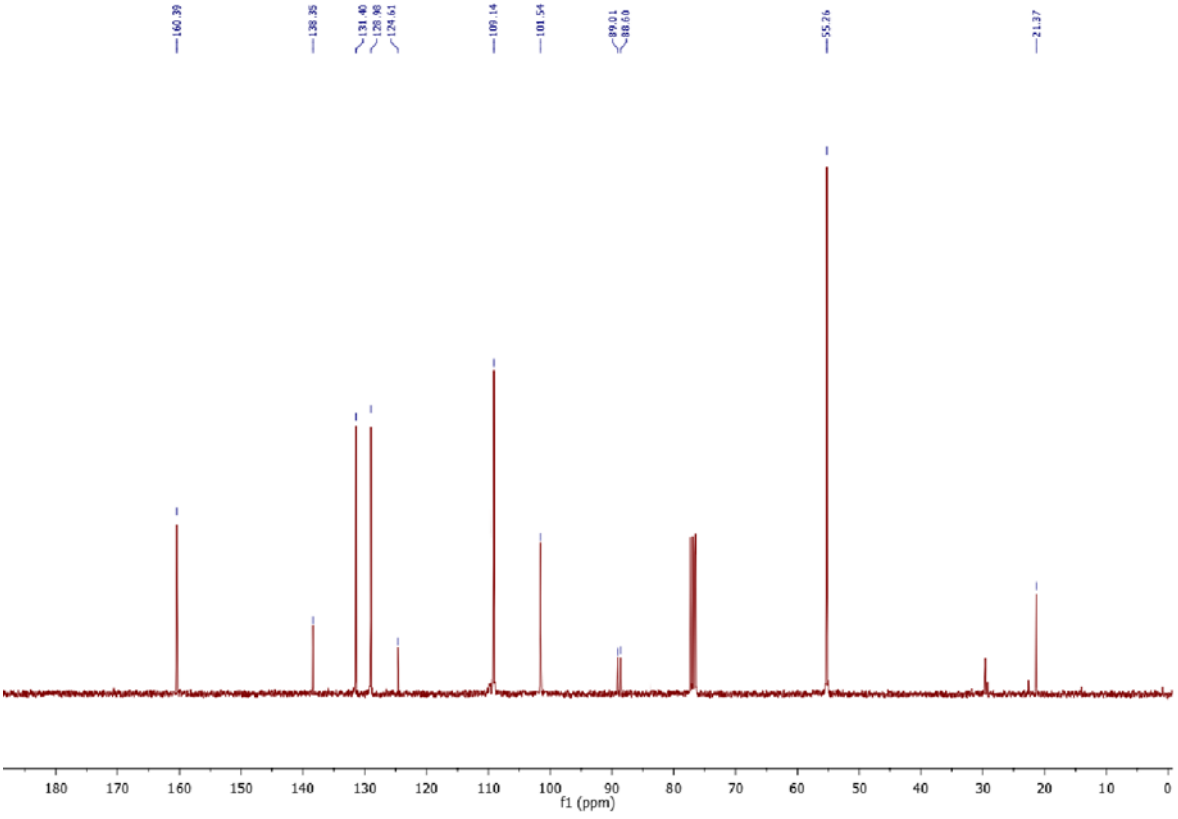
^{1}H NMR spectrum of 1-methyl-3-(phenylethynyl)benzene (3c)



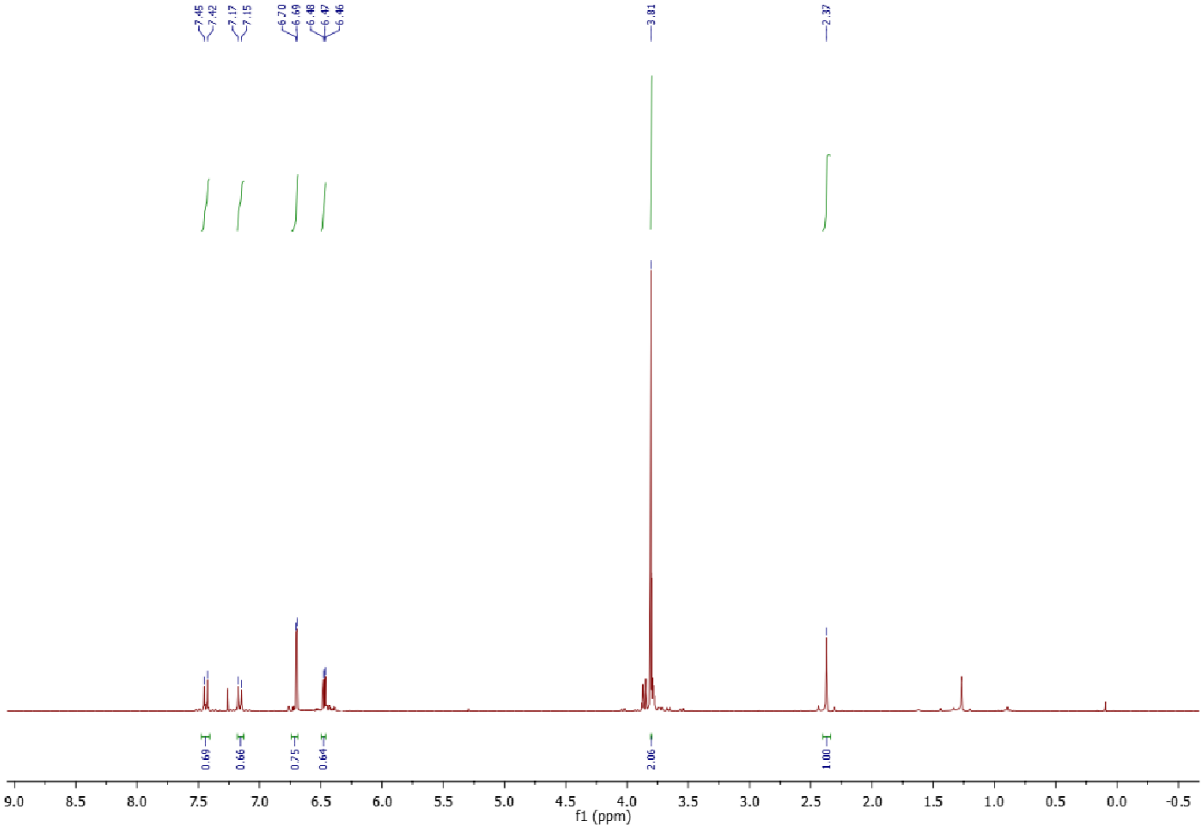
^{13}C NMR spectrum of 1-methyl-3-(phenylethynyl)benzene (3c)



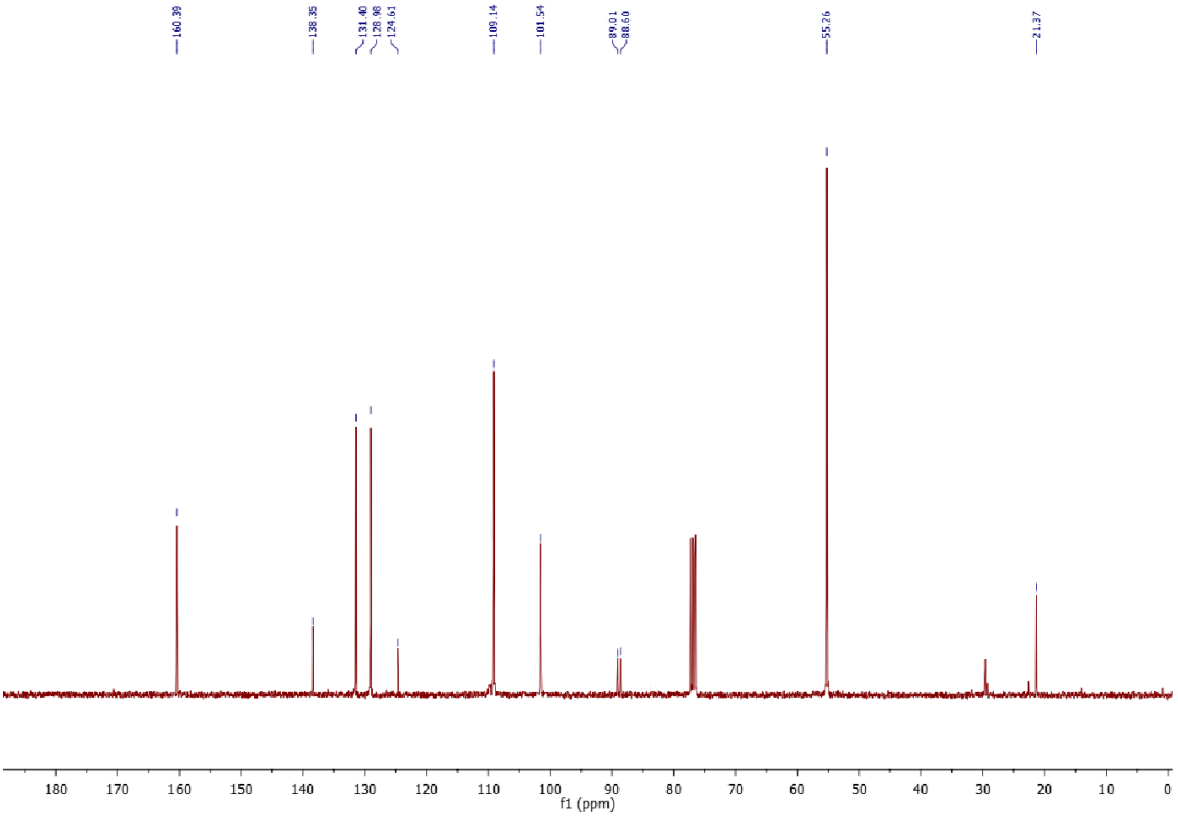
^{1}H NMR of 1,3-dimethoxy-5-(p-tolylethynyl)benzene (3d)



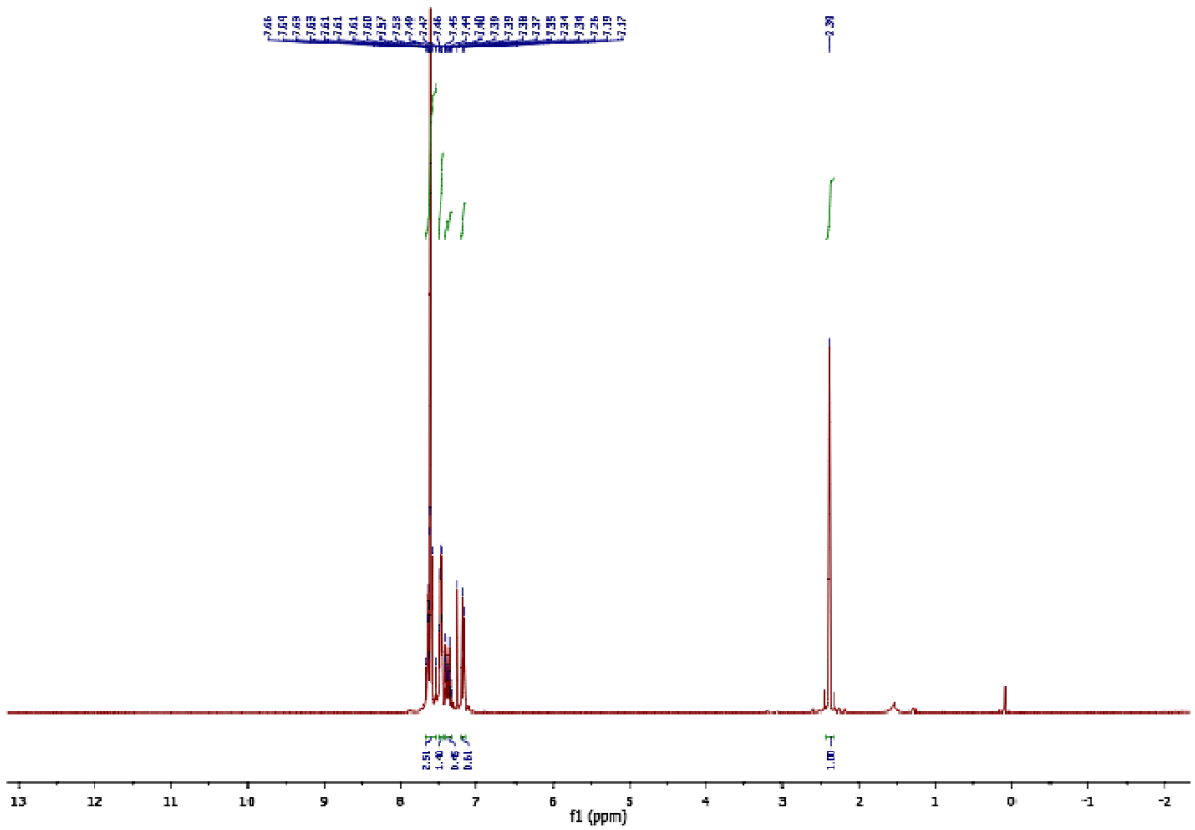
^{13}C NMR of 1,3-dimethoxy-5-(p-tolylethynyl)benzene (3d)



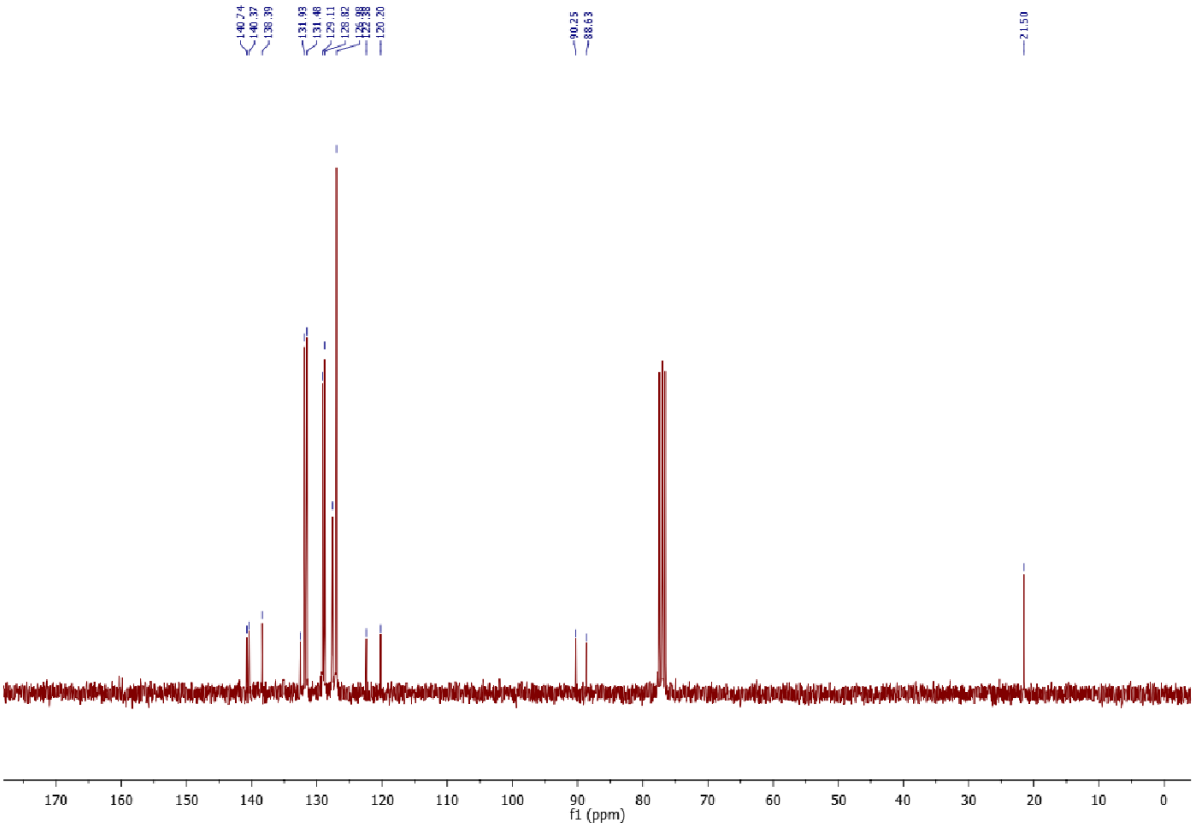
^{1}H NMR of 1,3-dimethoxy-5-(p-tolylethynyl)benzene (3e)



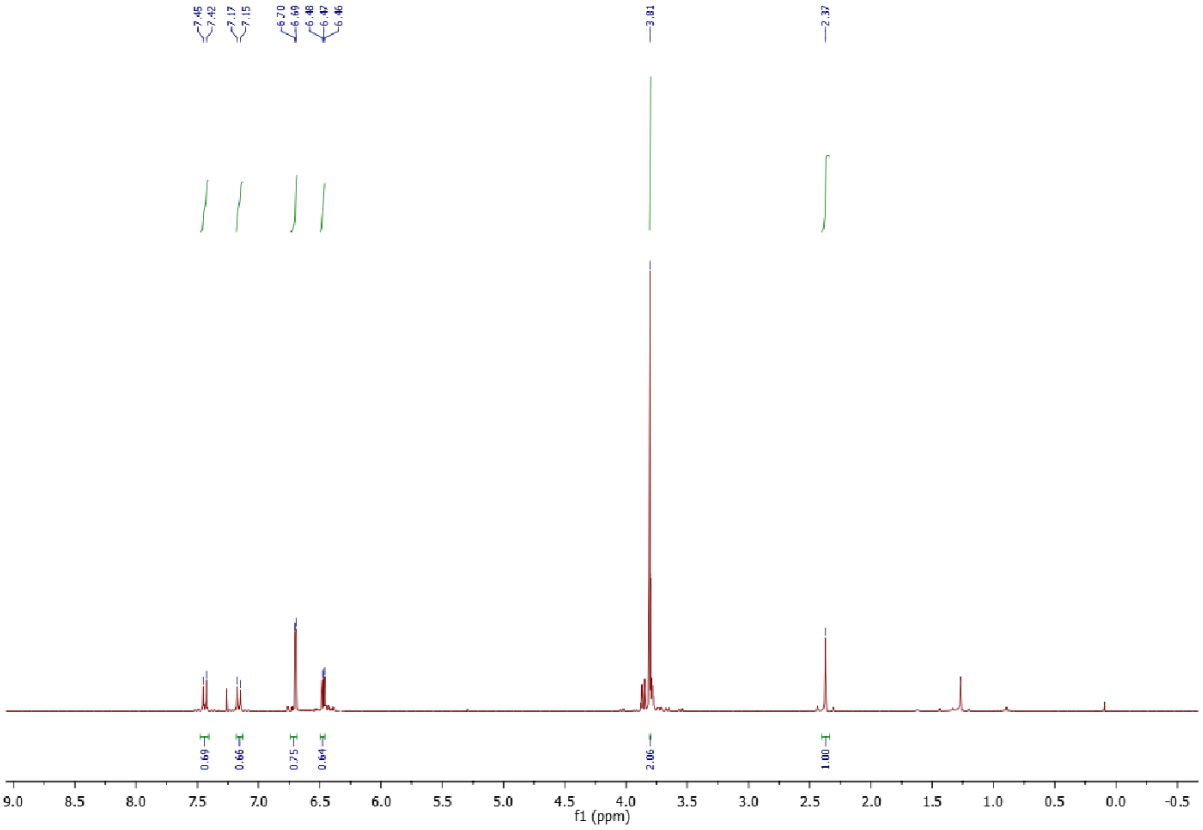
^{13}C NMR of 1,3-dimethoxy-5-(p-tolylethynyl)benzene (3e)



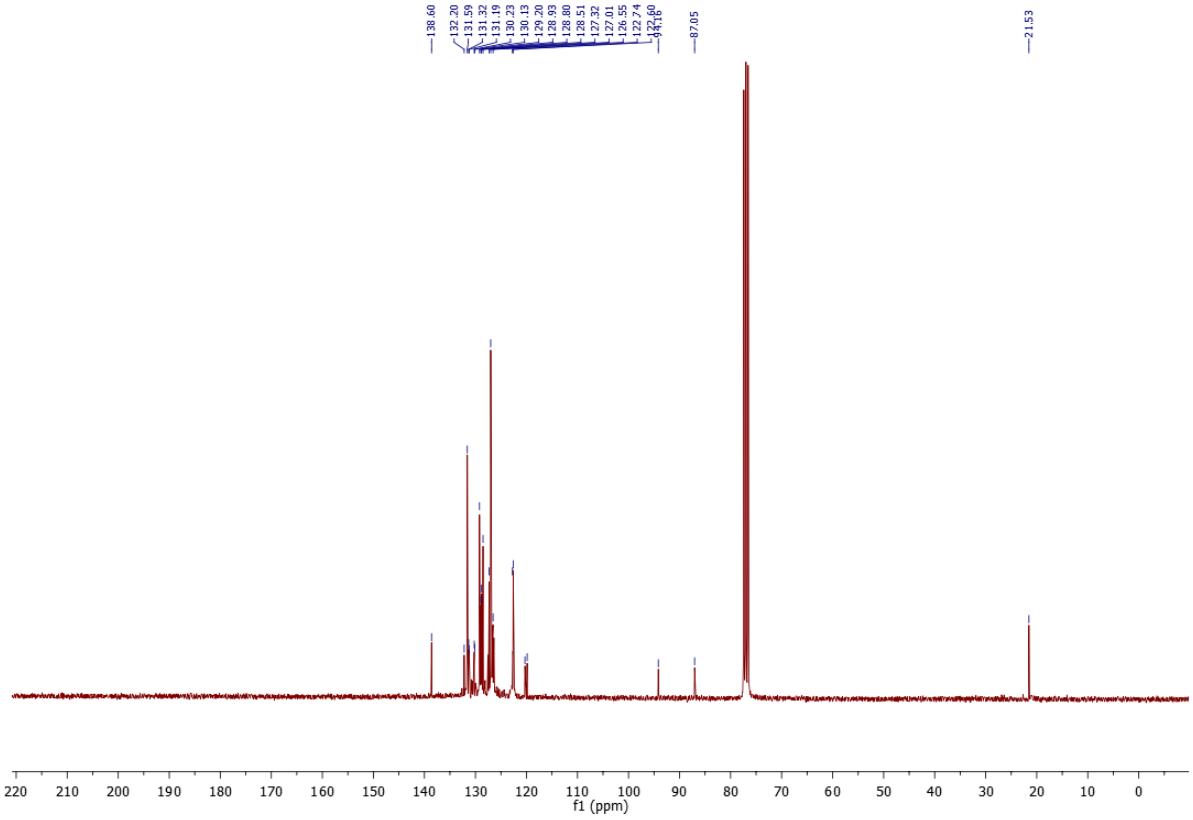
^{1}H NMR spectrum of 4-(p-tolylethynyl)-1,1'-biphenyl (3f)



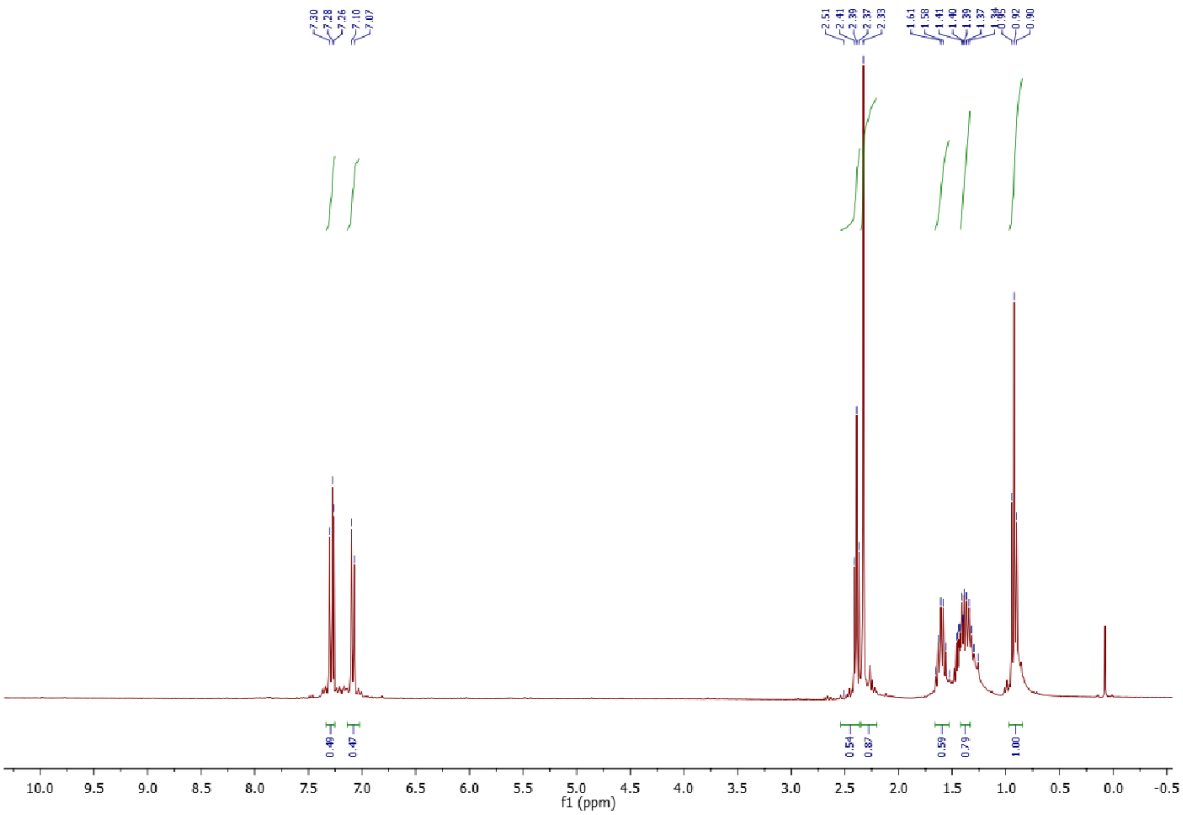
^{13}C NMR spectrum of 4-(p-tolylethynyl)-1,1'-biphenyl (3f)



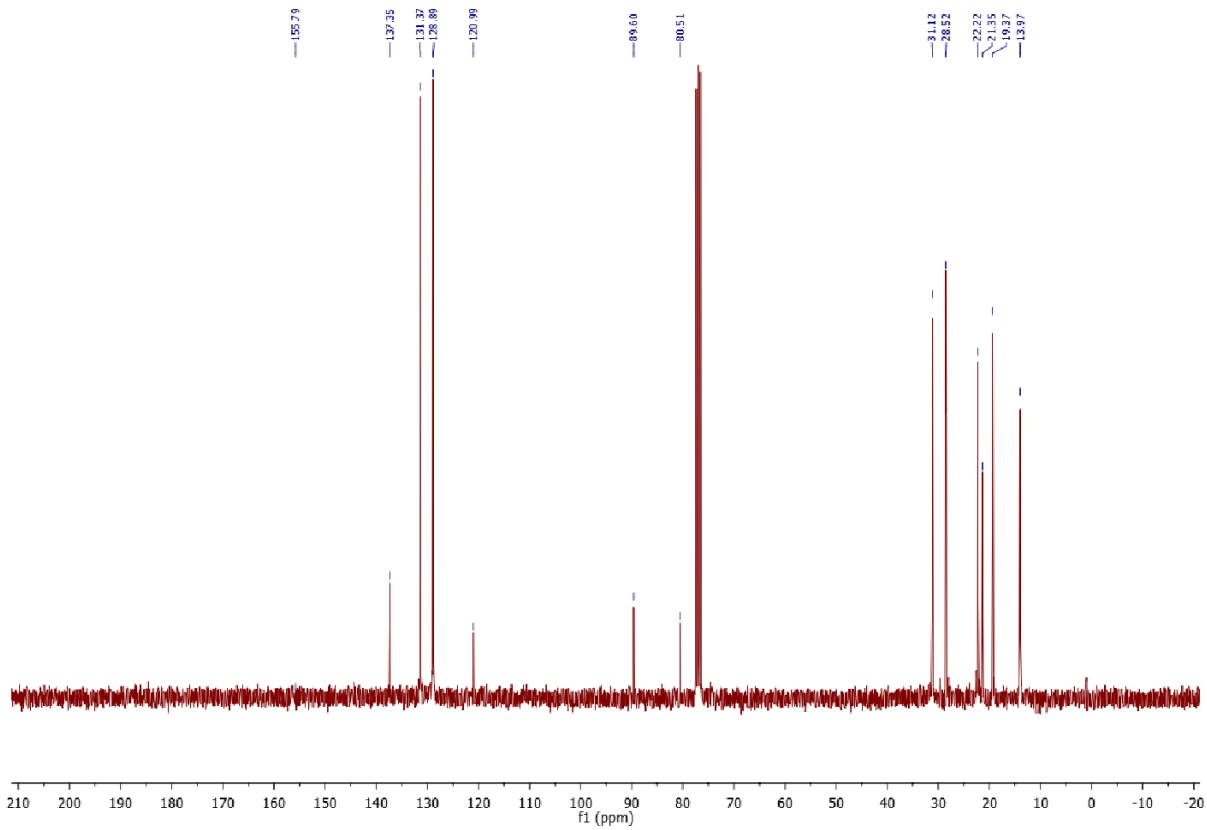
^{1}H NMR of 9-(p-tolylethynyl)phenanthrene (3g)



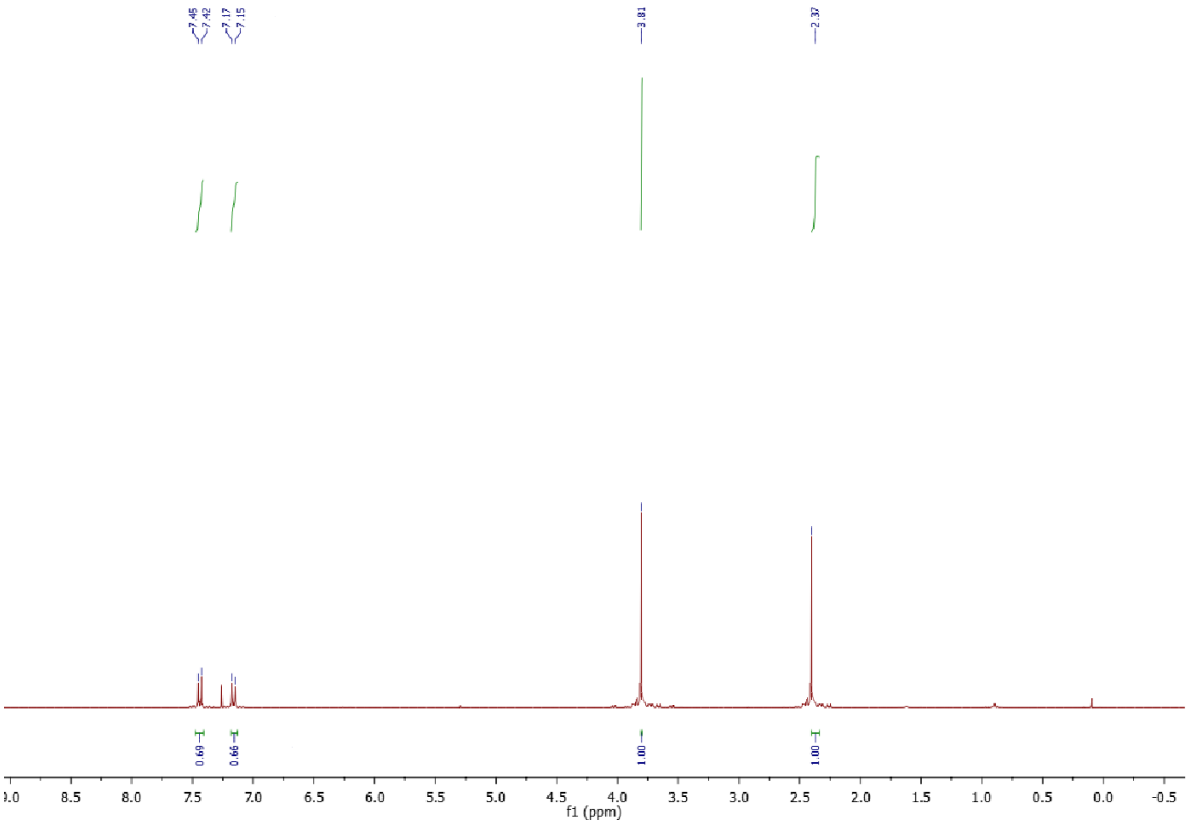
^{13}C NMR of 9-(p-tolylethynyl)phenanthrene (3g)



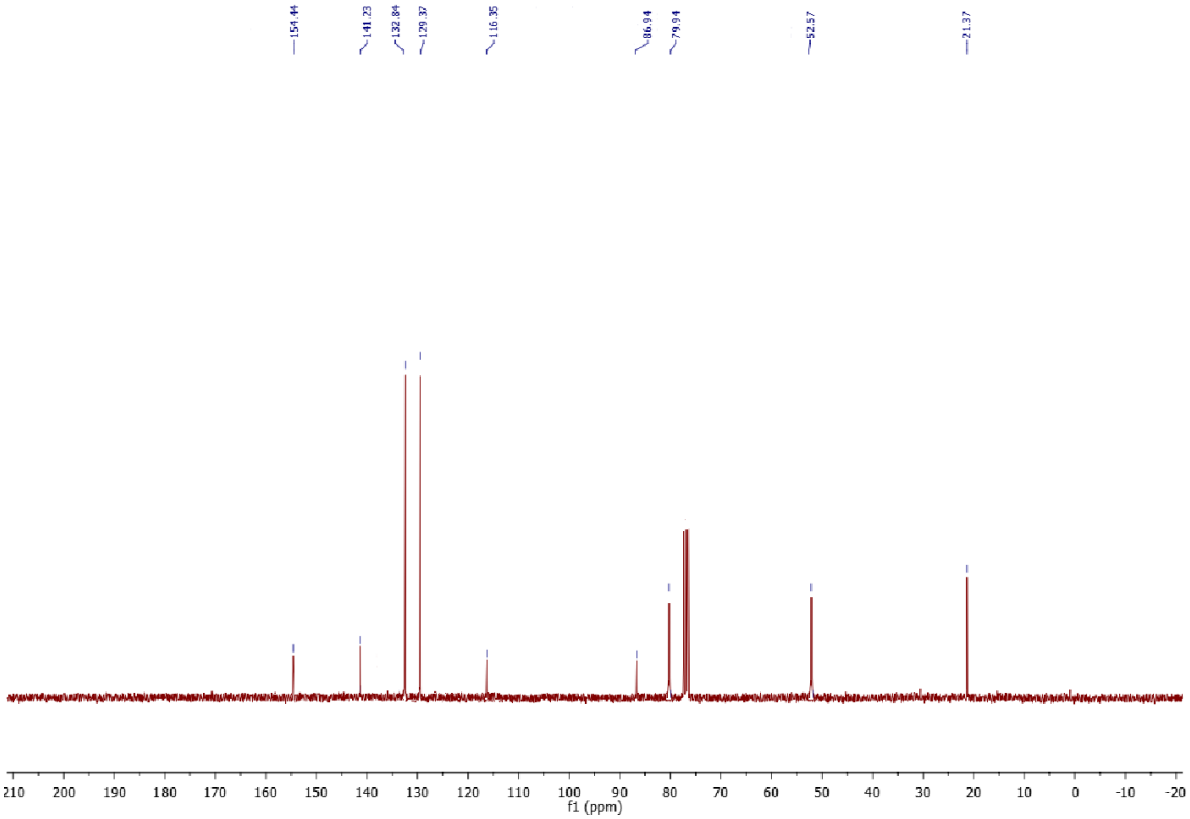
^{1}H NMR of 1-methyl-4-(oct-1-yn-1-yl)benzene (3h)



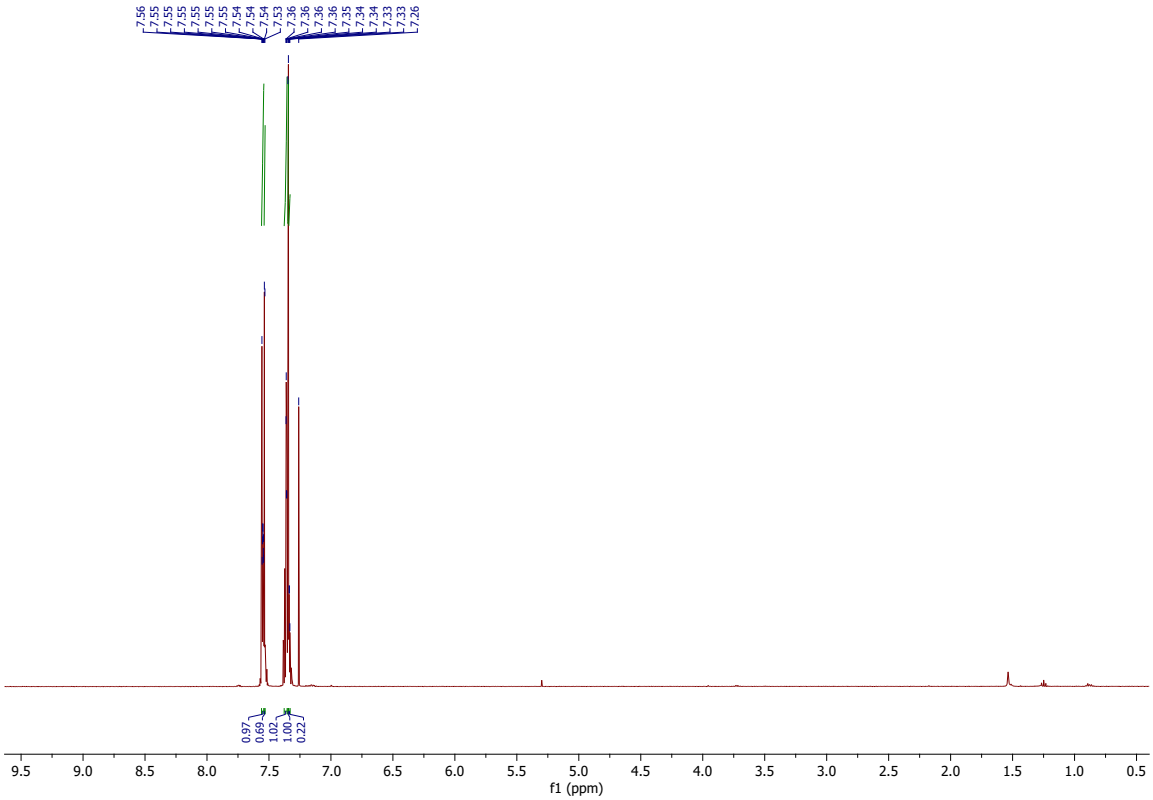
^{13}C NMR of 1-methyl-4-(oct-1-yn-1-yl)benzene (3h)



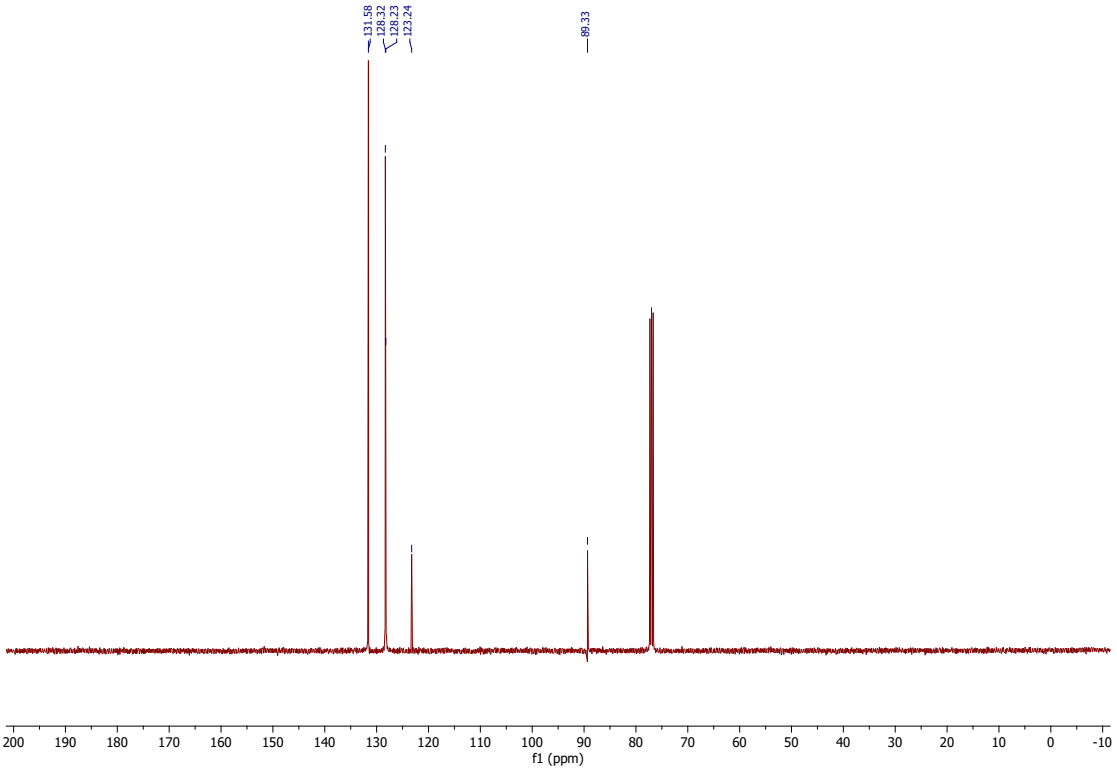
^{1}H NMR of methyl 3-(p-tolyl)propiolate (3i)



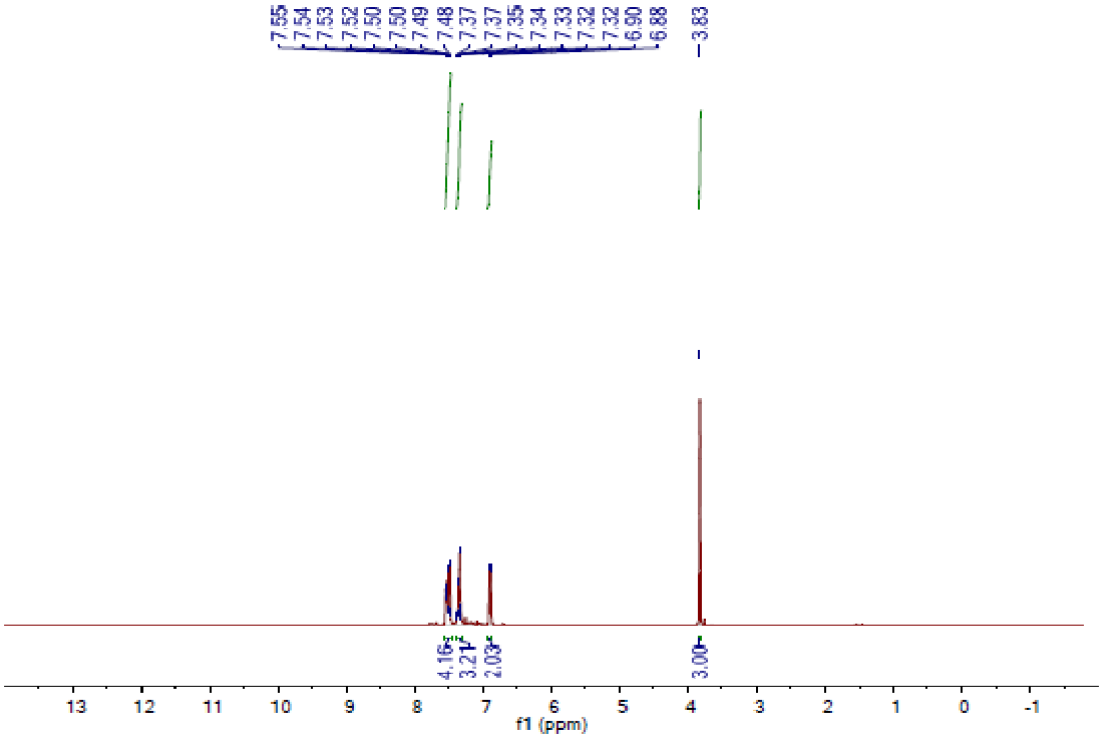
^{13}C NMR of methyl 3-(p-tolyl)propiolate (3i)



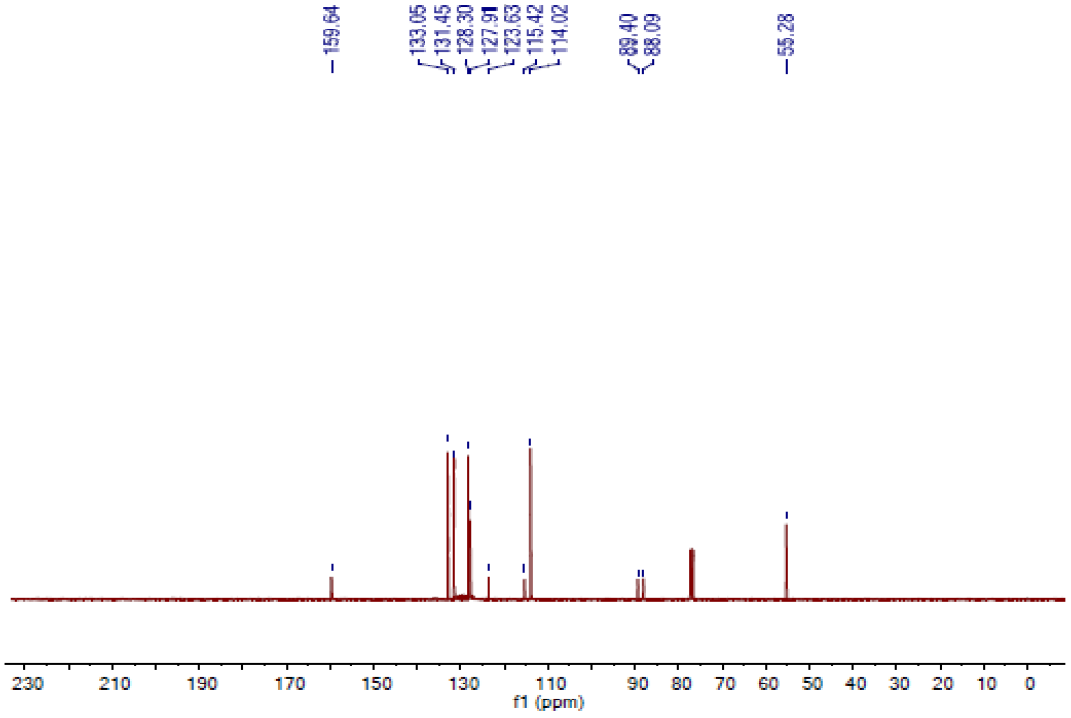
^{1}H NMR spectrum of 1,2-diphenylethyne (3j)



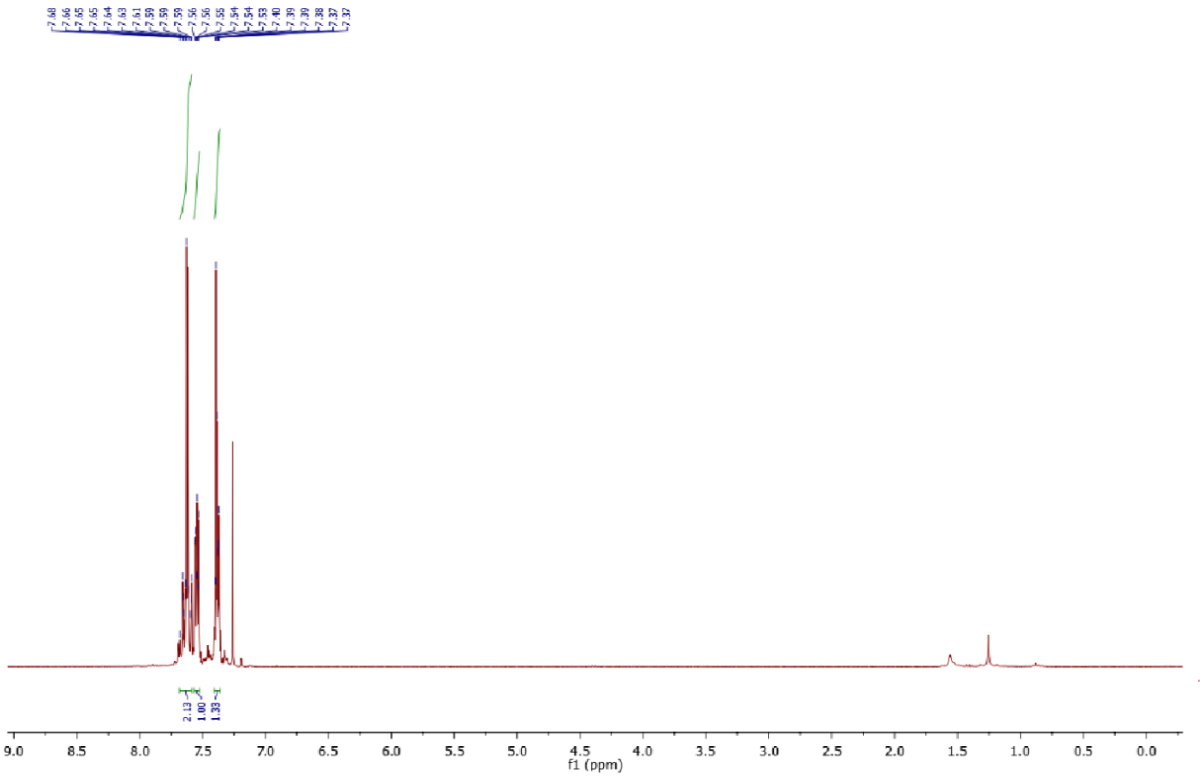
^{13}C NMR spectrum of 1,2-diphenylethyne (3j)



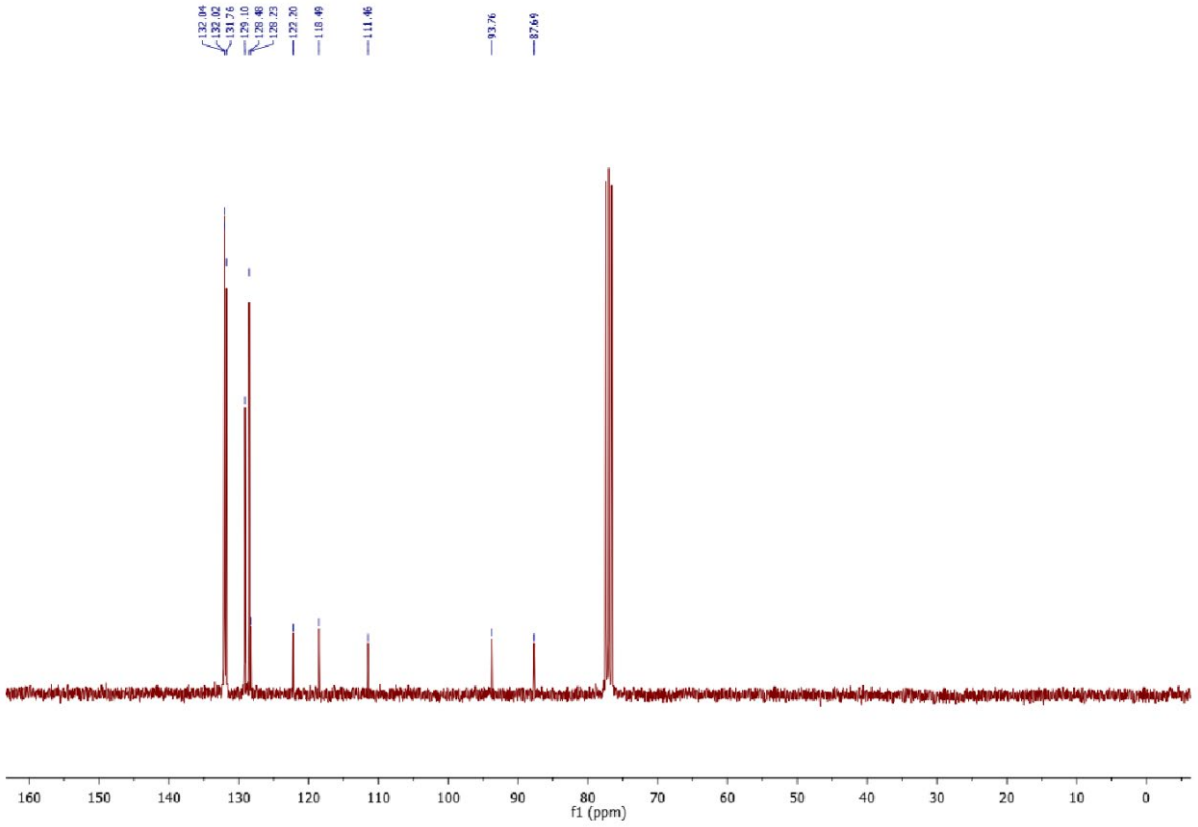
^{1}H NMR spectrum of 1-methoxy-4-(phenylethynyl)benzene (3k)



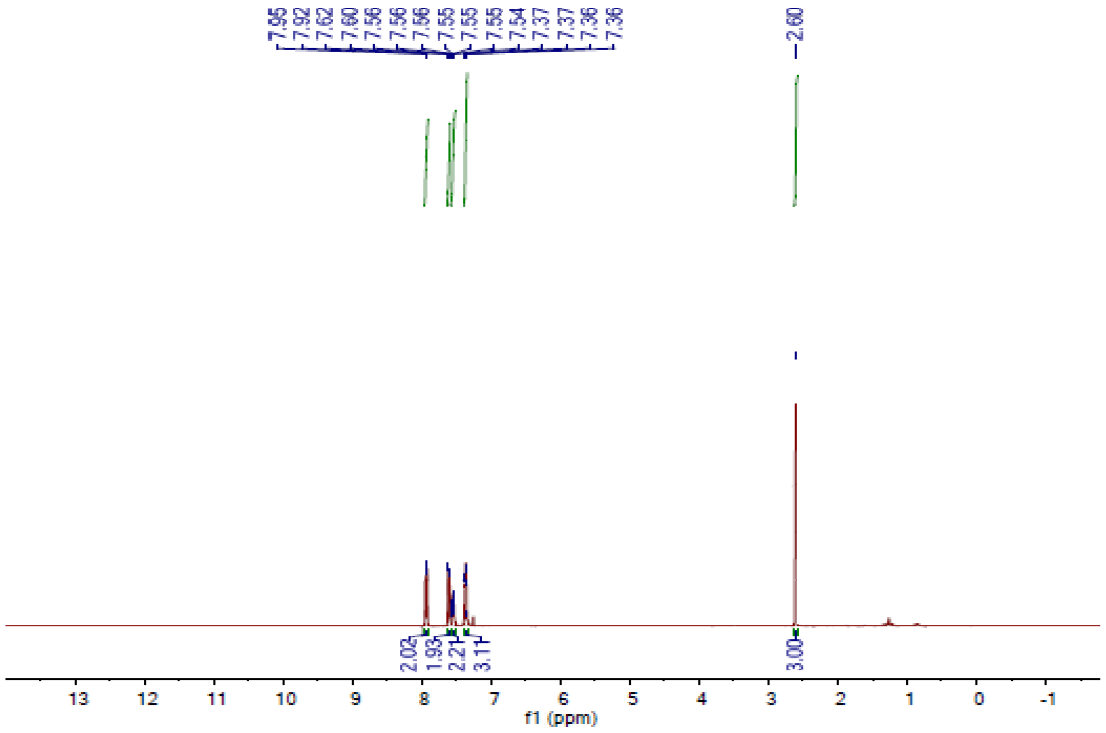
^{13}C NMR spectrum of 1-methoxy-4-(phenylethynyl)benzene (3k)



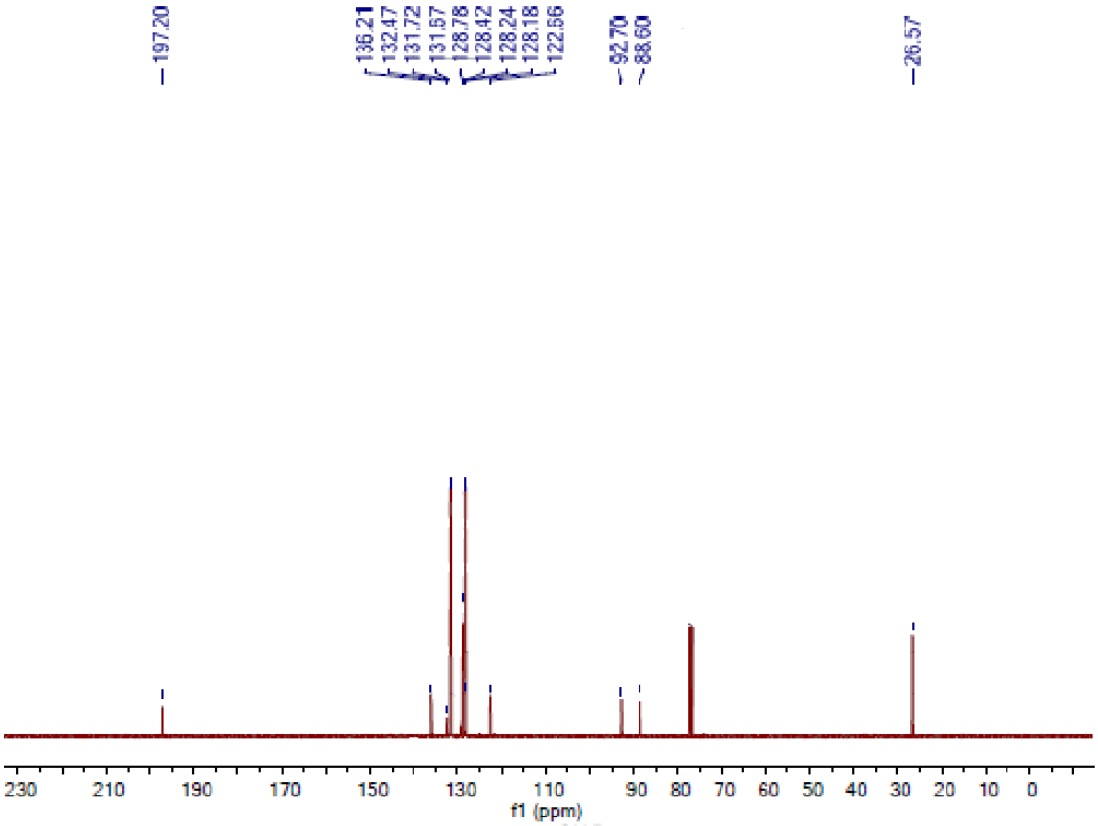
^{1}H NMR of 4-(phenylethynyl)benzonitrile (3l)



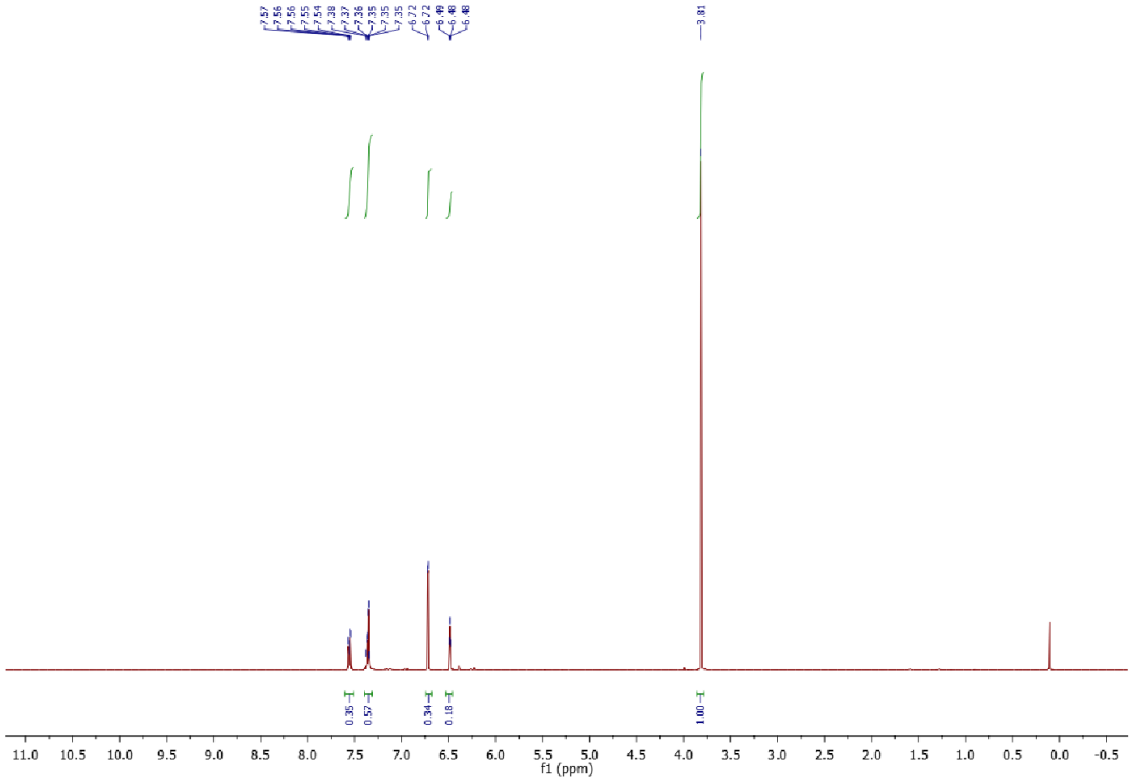
^{13}C NMR of 4-(phenylethynyl)benzonitrile (3l)



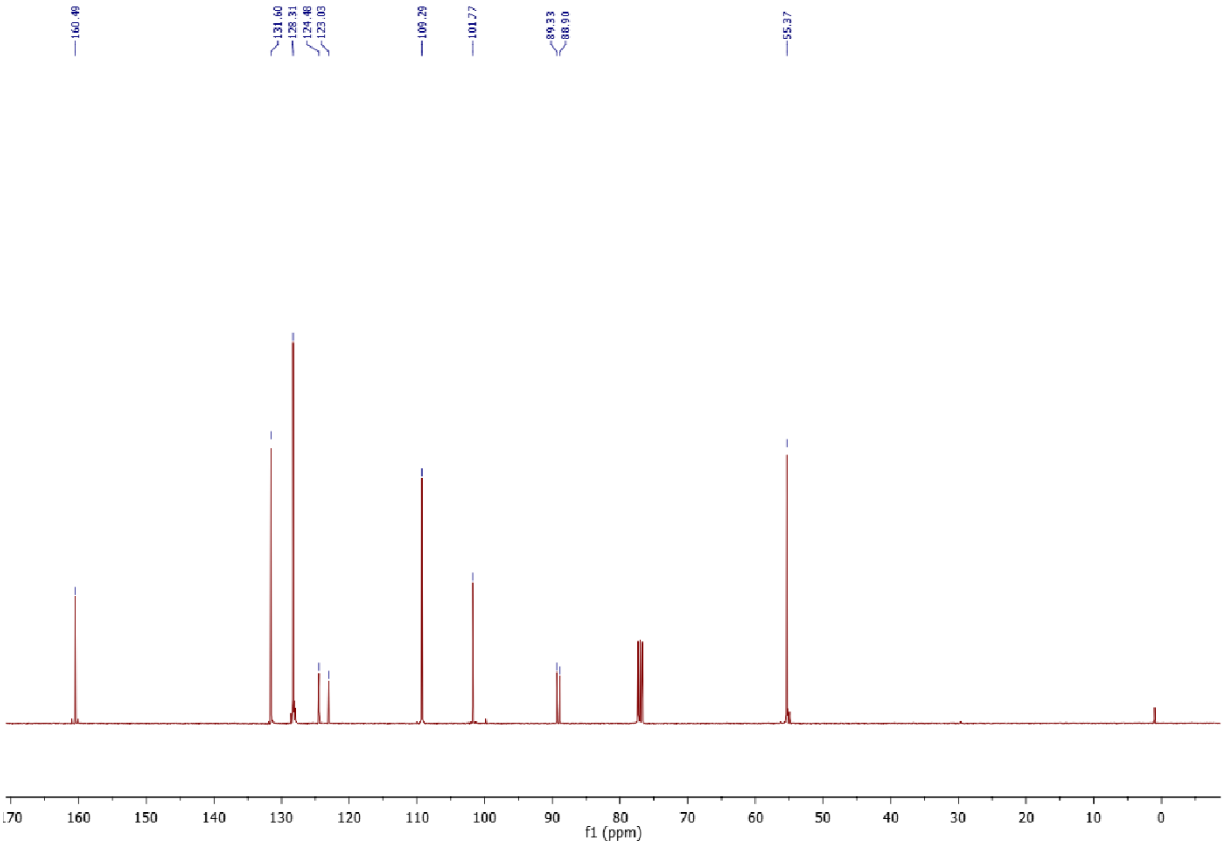
^{1}H NMR spectrum of 1-(4-(phenylethynyl)phenyl)ethan-1-one (3m)



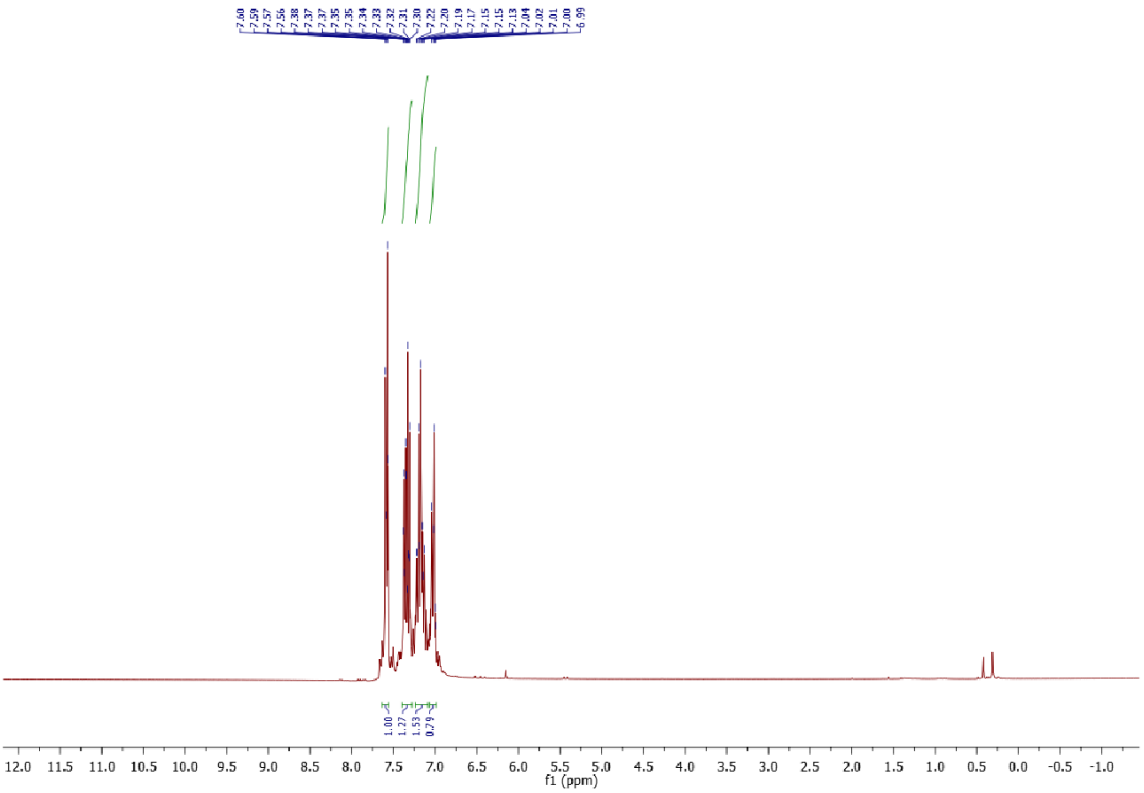
^{13}C NMR spectrum of 1-(4-(phenylethynyl)phenyl)ethan-1-one (3m)



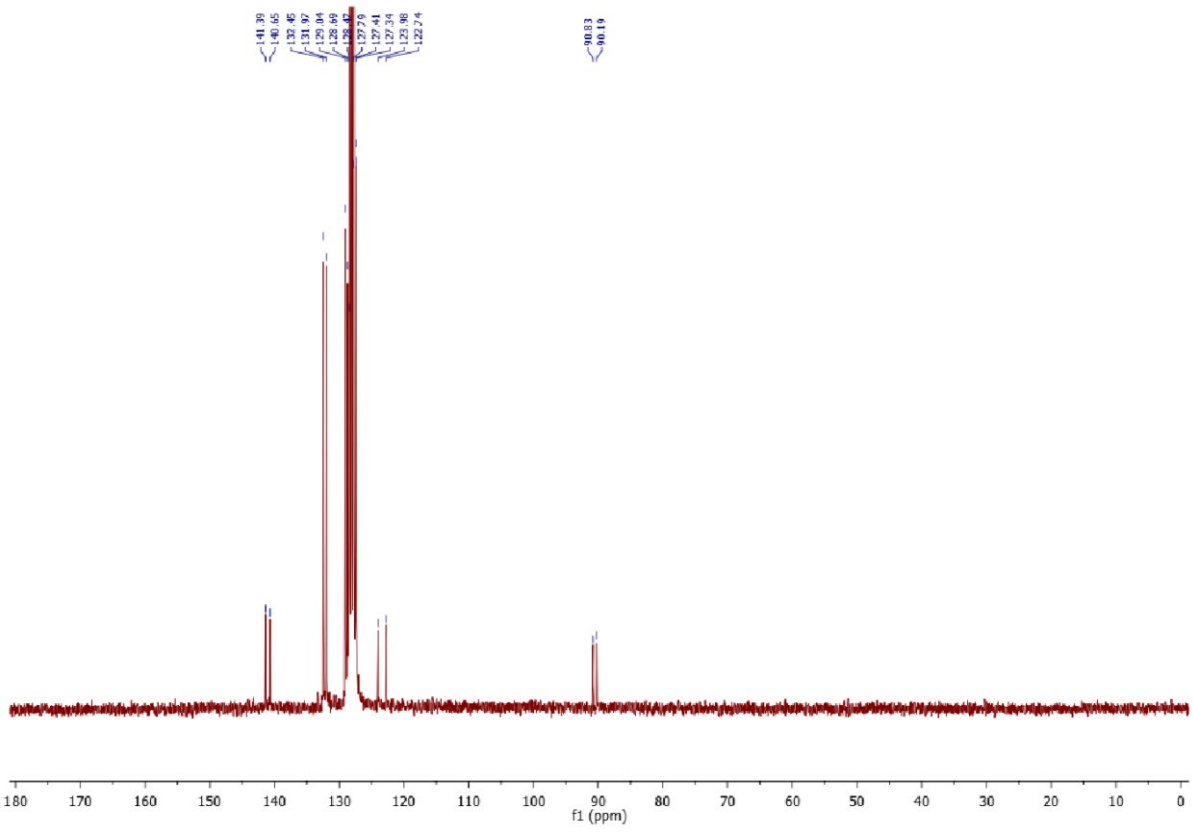
^{1}H NMR of 1,3-dimethoxy-5-(phenylethynyl)benzene (3n)



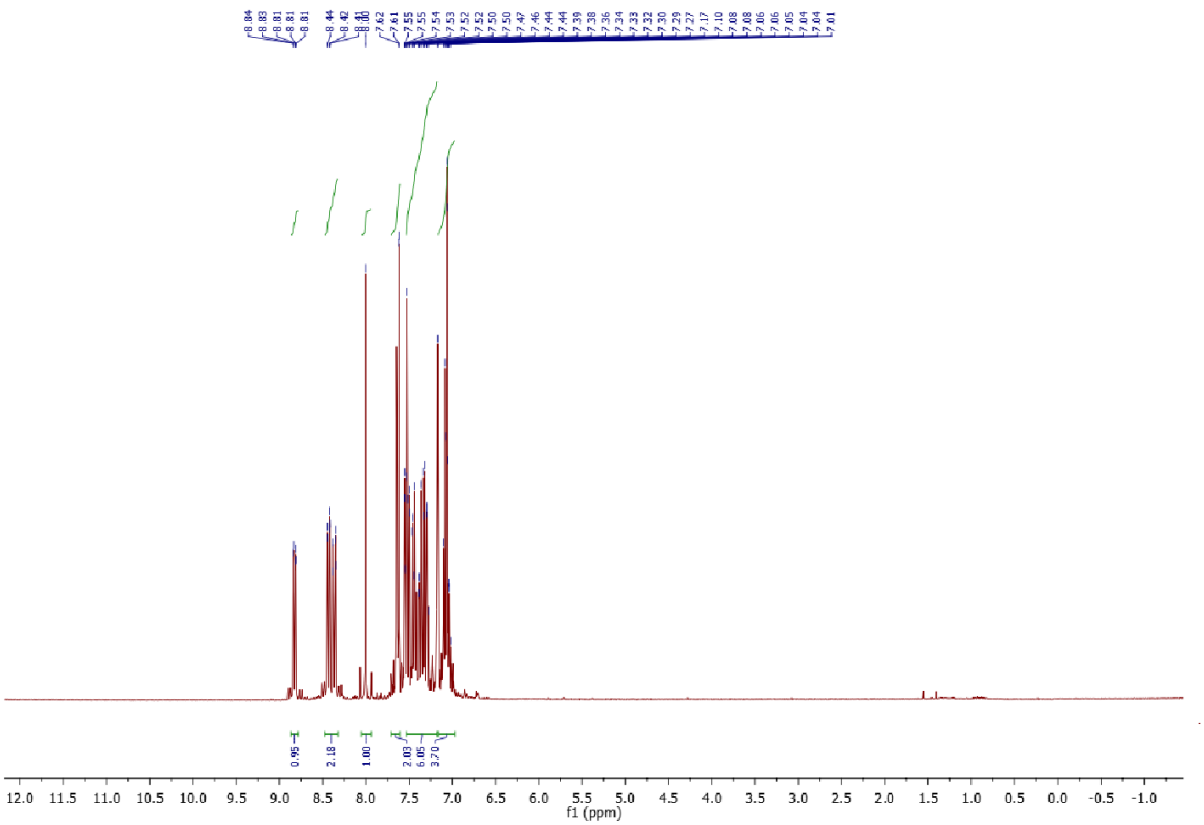
^{13}C NMR of 1,3-dimethoxy-5-(phenylethynyl)benzene (3n)



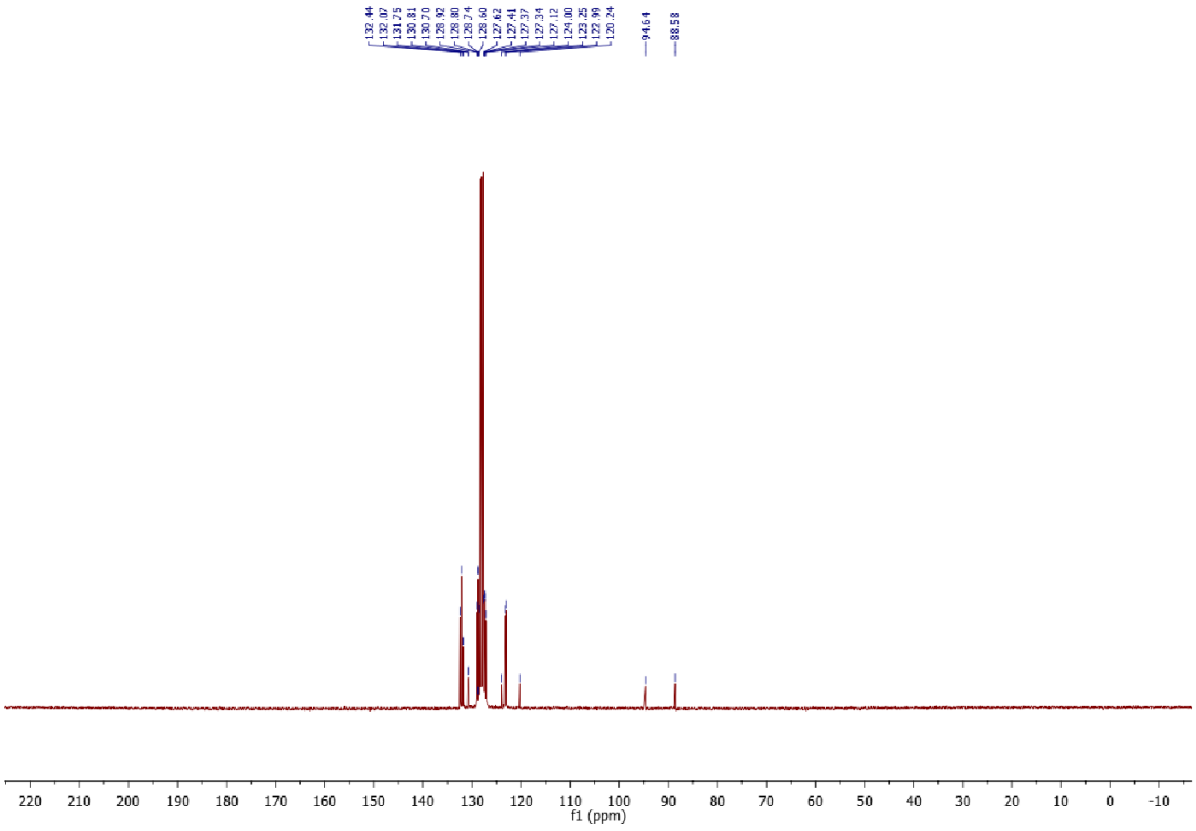
^{1}H NMR spectrum of 4-(phenylethynyl)-1,1'-biphenyl (3o)



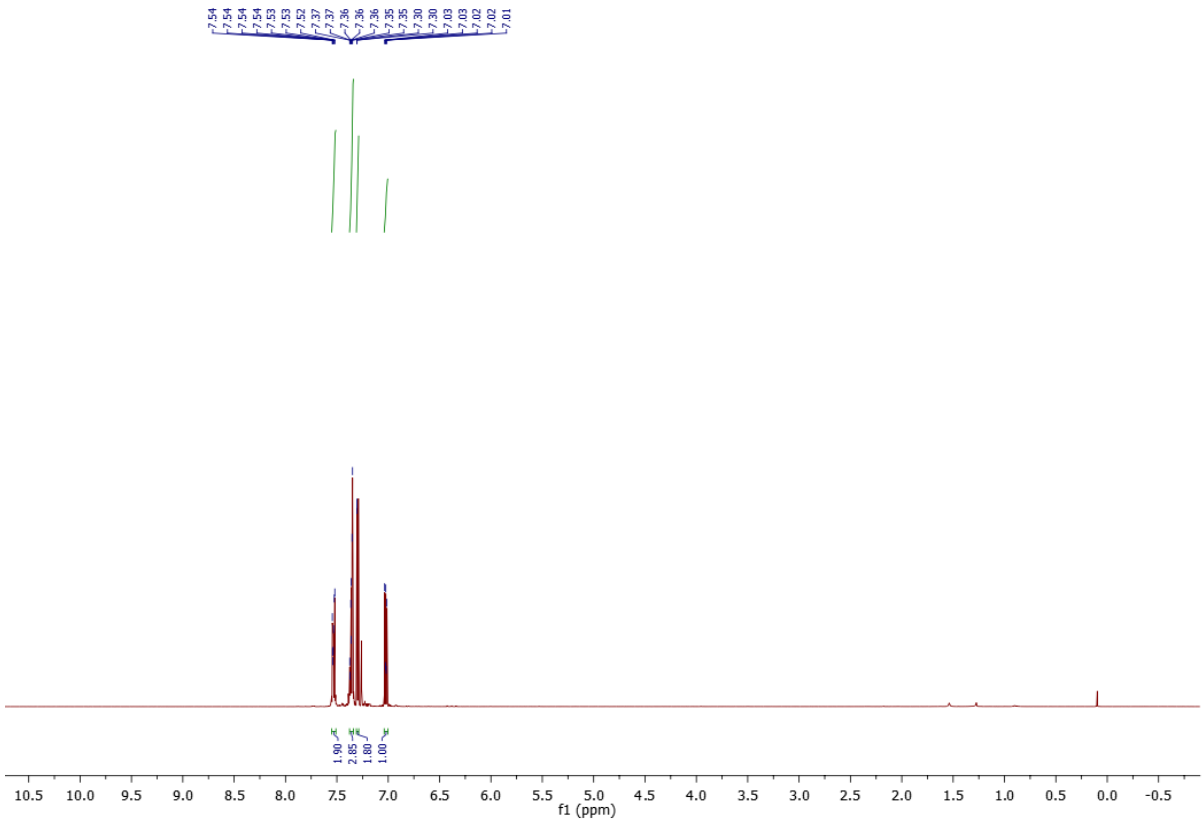
^{13}C NMR spectrum of 4-(phenylethynyl)-1,1'-biphenyl (3o)



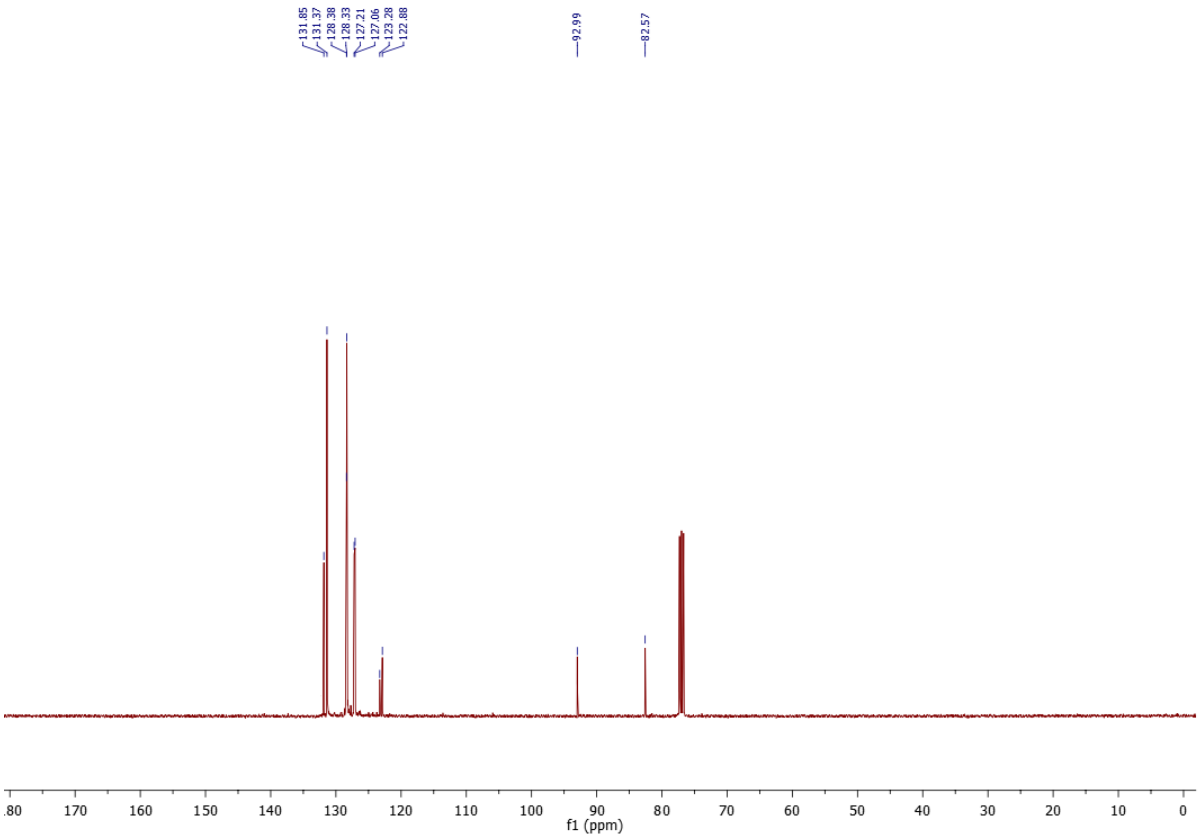
^{1}H NMR of 9-(phenylethynyl)phenanthrene (3p)



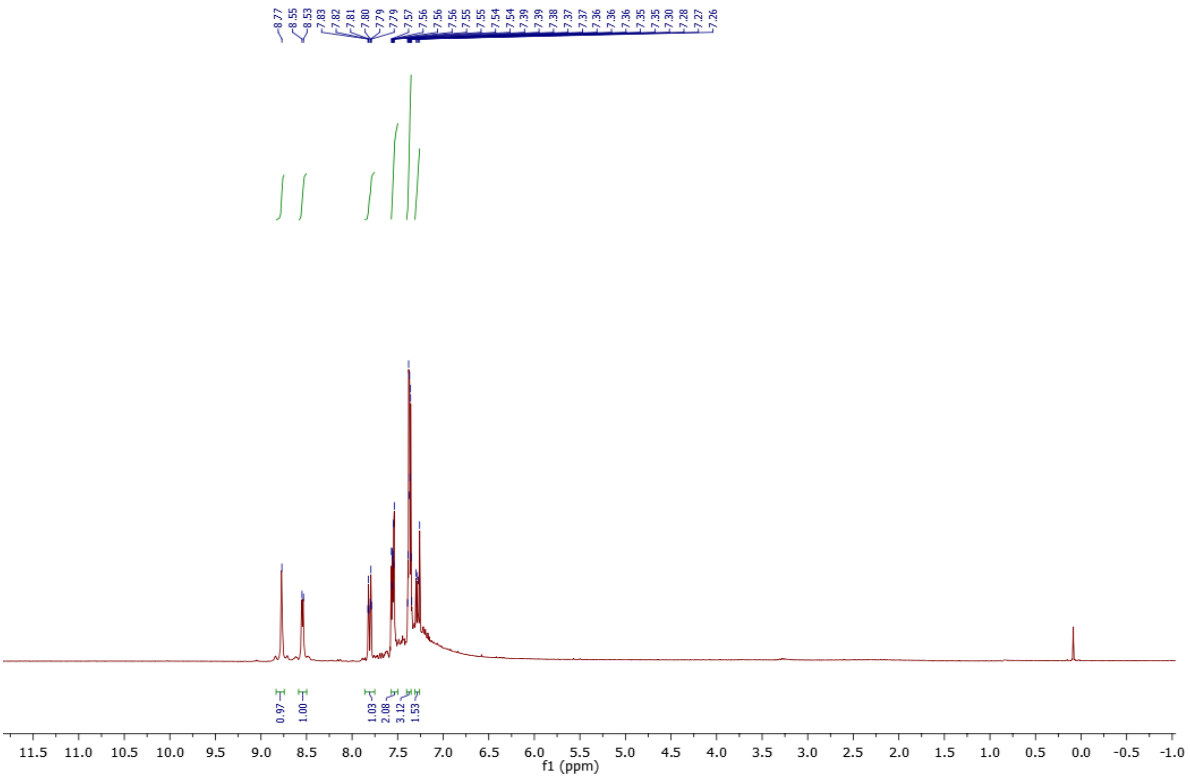
^{13}C NMR of 9-(phenylethynyl)phenanthrene (3p)



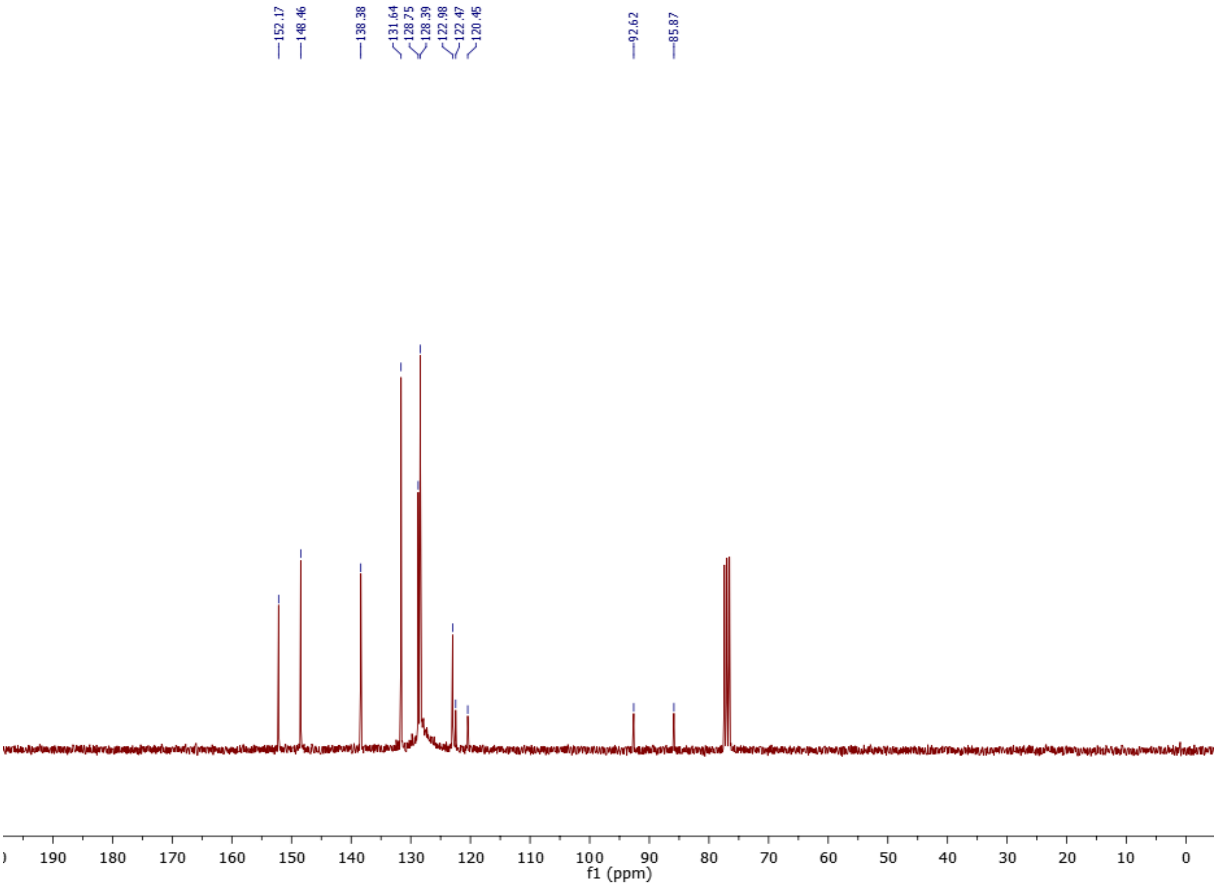
^{1}H NMR spectrum of 2-(phenylethynyl)thiophene (3q)



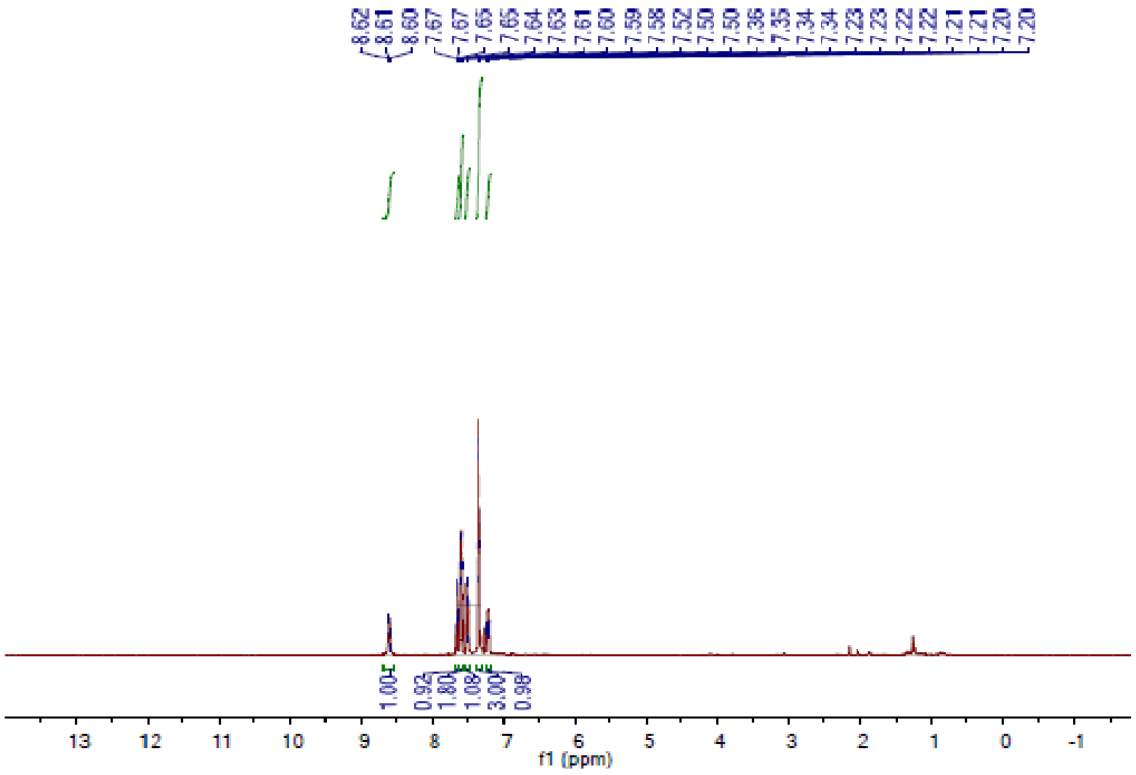
^{13}C NMR spectrum of 2-(phenylethynyl)thiophene (3q)



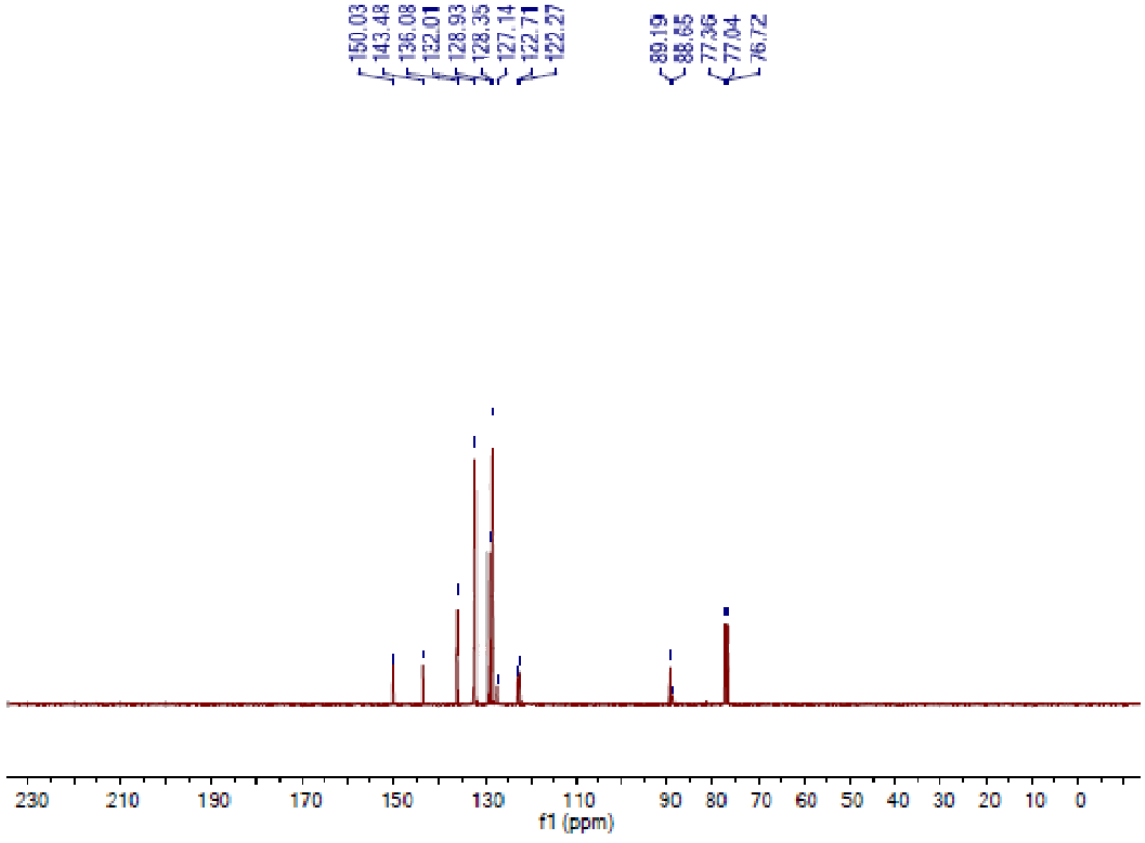
^{1}H NMR spectrum of 3-(phenylethynyl)pyridine (3r)



^{13}C NMR spectrum of 3-(phenylethynyl)pyridine (3r)



^{1}H NMR spectrum of 2-(phenylethynyl)pyridine (3s)



^{13}C NMR spectrum of 2-(phenylethynyl)pyridine (3s)