Supporting Information for

Ligand and Additive free Aerobic Synthesis of Diynes using Pd-$CuFe_2O_4$ Magnetic Nanoparticles as an efficient reusable catalyst

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1. General information

All the reagents used in this work were purchased from Sigma-Aldrich chemical co. and used without further purification. The solvents are purchased from Merck co. and used after distillation under desired procedure. All reactions were monitored by thin layer chromatography (TLC) on silica gel plates ((Merck Kieselgel 60 F254) which were visualizing with ultraviolet light. Melting points were determined on a Thomas Hoover capillary apparatus. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 500 MHz and 125 MHz respectively on FT–NMR Brukar Avance-500, 500 MHz instrument in $CDCl_3$, and tetramethylsilane (TMS, δ=0.00) as internal standard. Multiplicities were designated as broad (br), singlet (s), doublet (d), and multiplet (m).

2. Characterization methods for Pd-$CuFe_2O_4$ MNPs:

Powder X-ray diffraction pattern of the NPs were measured at Rigaku/Ultima-IV with Cu Kα X-ray source of λ= 1.54056 A°. The morphology of the synthesized NPs were obtained by scanning electron microscope (SEM) images using scanning electron microscope (model: JSM-6360 JEOL) with accelerating voltage 20 kV and magnification range 10,000X to 27,000X. Transmission electron microscope (TEM) and high resolution-TEM images were recorded with transmission electron microscope (Model: JEM-100 CX II) with accelerating voltage 20-100kV. The presence of elemental copper, iron and oxygen were further determined through energy dispersive spectroscopy (EDS). The magnetic measurements were done by Vibrating Sample Magnetometer (VSM) (Model: 7410 series). ARCOS, Simultaneous ICP Spectrometer was used for the determination of ICP-AES analysis. XPS analysis was done in PHI 5000 Versa Prob II,FEI Inc, with carbon 1s binding energy at 282.69 eV for the fresh catalyst and for the recycled catalyst C 1s at 282.41 eV. Quantachrome instrument (Quantachrome Autosorb-iQ analyser, Boynton Beach, FL, USA) was used for the surface area measurement at liquid nitrogen temperature as obtained from the linear plot following Brunauer–Emmett–Teller (BET) method.

3. Experimental Details

3.1 Materials and Method

Ferric Chloride ($FeCl_3$), Cupric Acetate Monohydrate [$(CH_3.COO)_2Cu.H_2O$], Sodium Hydroxide (NaOH), ethanol, diethylether, anhydrous Na_2SO_4, Palladium acetate [$Pd(OAc)_2$], hydrazine hydrate ($NH_2NH_2.H_2O$) and different terminal alkynes were purchased from commercial suppliers and used as received without further purification. The reagents used were of spectroscopic grade and ultrapure water was used in all the systems. Thin Layer Chromatography (TLC) on silica gel plates (60 F_{254}) was used to monitor the progress of the reaction. The products were confirmed by GC-MS, ^{1}H NMR and ^{13}C NMR spectroscopy.

Supplementary Table

Table S1: BET analysis of the catalyst:

Catalyst	Surface Area (m^2/g)	Pore Diameter Dv(d) (nm)	Total Pore Volume (cc/g)
$CuFe_2O_4$	20.309 m^2/g	4.035 nm	0.026 cc/g
$Pd/CuFe_2O_4$	39.748 m^2/g	3.425 nm	0.076 cc/g

Supplementary Figure

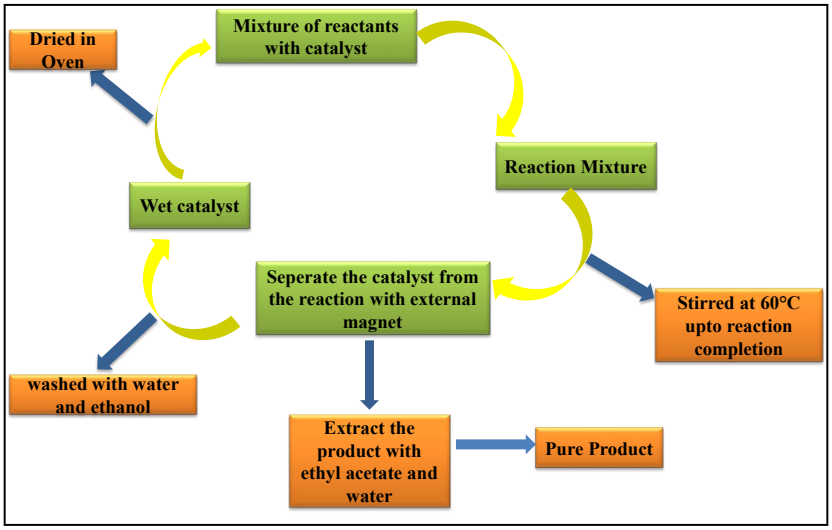


Figure S1: Schematic diagram for the recyclability of the catalyst

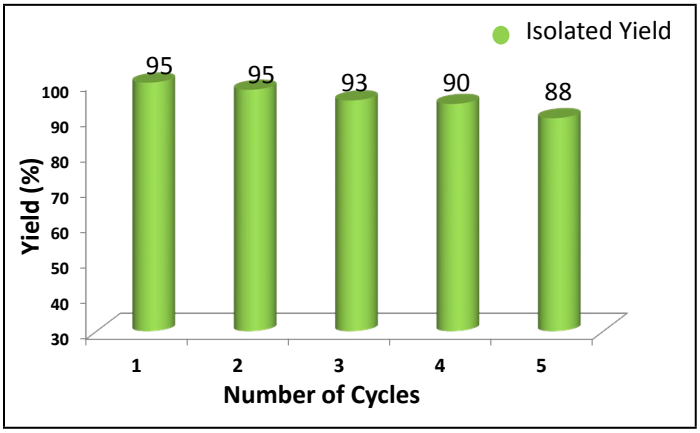
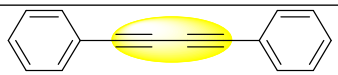
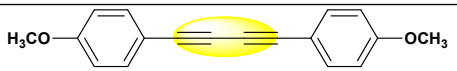
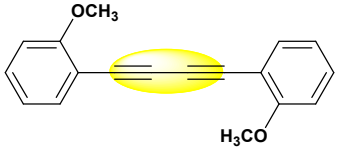
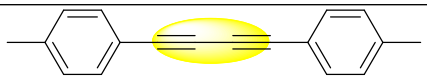
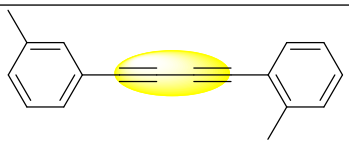
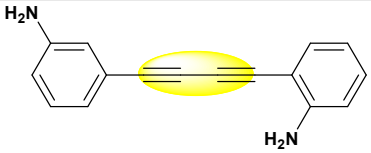
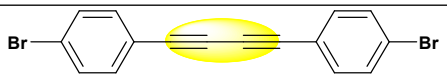
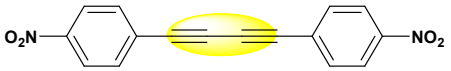
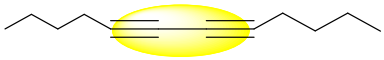
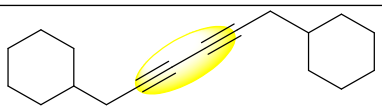


Figure S2: Recyclability of the catalyst

Spectral data of the synthesized diynes:

1,4-diphenylbuta-1,3-diyne (3a) The product was isolated as a white solid; m/z= 202.08; m.pt 86-87°C; Yield= 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53-7.51 (d, J= 8Hz, 4H), 7.41–7.31 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 132.55, 129.17, 128.23, 121.72, 81.54, 73.50.	
1,4-bis(4-methoxyphenyl)buta-1,3-diyne The product was isolated as a white solid; m.pt 138-140°C; m/z= 262; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J= 8Hz, 4H), 7.15 (d, J= 8Hz, 4H), 4.15 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.56, 133.02, 129.75, 114.22, 113.61, 81.19, 74.00, 57.13 ppm	
1,4-bis(2-methoxyphenyl)buta-1,3-diyne The product was isolated as a white solid; m.pt 137-138°C; m/z= 262; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (dd, 2H), 7.34 (ddd, 2H, J = 5 Hz), 6.93 (dd, 2H), 6.90 (dd, 2H), 3.91 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.34, 134.61, 130.80, 121.28, 111.39, 104.07, 81.50, 80.21, 56.35.	
1,4-di-p-tolylbuta-1,3-diyne (3b) The product was isolated as a white solid; mpt 138-140°C; m/z = 230; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (d, 4H, J = 10 Hz), 7.15 (d, 4H, J = 10 Hz), 2.39(s, 6H) ppm; ^{13}C NMR (125 MHz, CDCl3) δ: 139.47, 132.45, 129.30, 118.76, 81.20, 72.96, 21.72.	
1,3-di-*p*-tolylbuta-1,3-diyne The product was isolated as a white solid; m.pt 70-80°C, ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37 (m, 4H), 7.26-7.18 (m, 4H), 2.32 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.19, 133.09, 130.58, 129.59, 128.01, 121.33, 81.56, 72.03, 22.99.	
1,4-bis(m-aminophenyl)buta-1,3-diyne The product was isolated as a yellow solid; m/z= 232; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74-7.53 (t, 2H), 7.34-7.22 (t, 2H), 7.11-7.02 (t, 2H), 6.90-6.66 (d, 2H), 3.05-3.01 (m, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 146.21, 129.23, 122.65, 122.31, 118.22, 115.76, 83.88, 76.52 ppm.	
1,4-bis(4-bromophenyl)buta-1,3-diyne The product was isolated as a pale yellow solid; m/z= 238; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45-7.02 (m, 4H), 7.46-7.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 132.42, 129.14, 124.88, 82.36, 81.25, 77.50.	
1,4-bis(4-nitrophenyl)buta-1,3-diyne The product was isolated as a white solid; m/z= 292.05; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (d, 4H), 8.18 (d, 4H) ppm; ^{13}C NMR (125	

MHz, $CDCl_3$) δ: 148.13, 133.17, 129.22, 124.13, 82.55, 81.97. ppm.	
5,7-dodecadiyne The product was isolated as a pale yellow oil; m/z= 162; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.22 (t, J= 7.3 Hz, 4H), 1.26 (m, 4H), 1.19 (m, 4H), 0.90 (t, J= 7.3 Hz, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 76.67, 64.52, 29.81, 22.46, 18.42, 14.15 ppm	
1,6-dicyclohexylhexa-2,4-diyne The product was isolated as white oily**;** m/z=242; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.15(d, 4H), 1.69-0.83 (m, 22 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ: 66.18, 37.26, 32.84, 27.13, 26.56, 26.16 ppm.	

^{1}H and ^{13}C NMR of some synthesized 1,3-diynes:

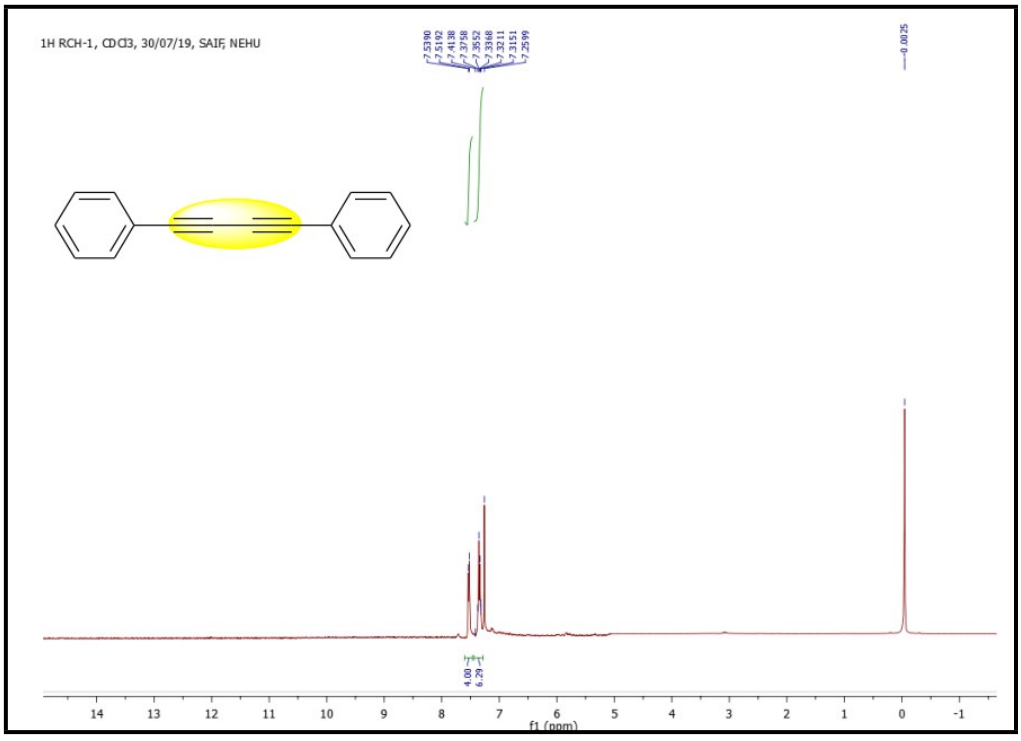


Figure S3: ^{1}H NMR spectrum of 1,4-diphenylbuta-1,3-diyne

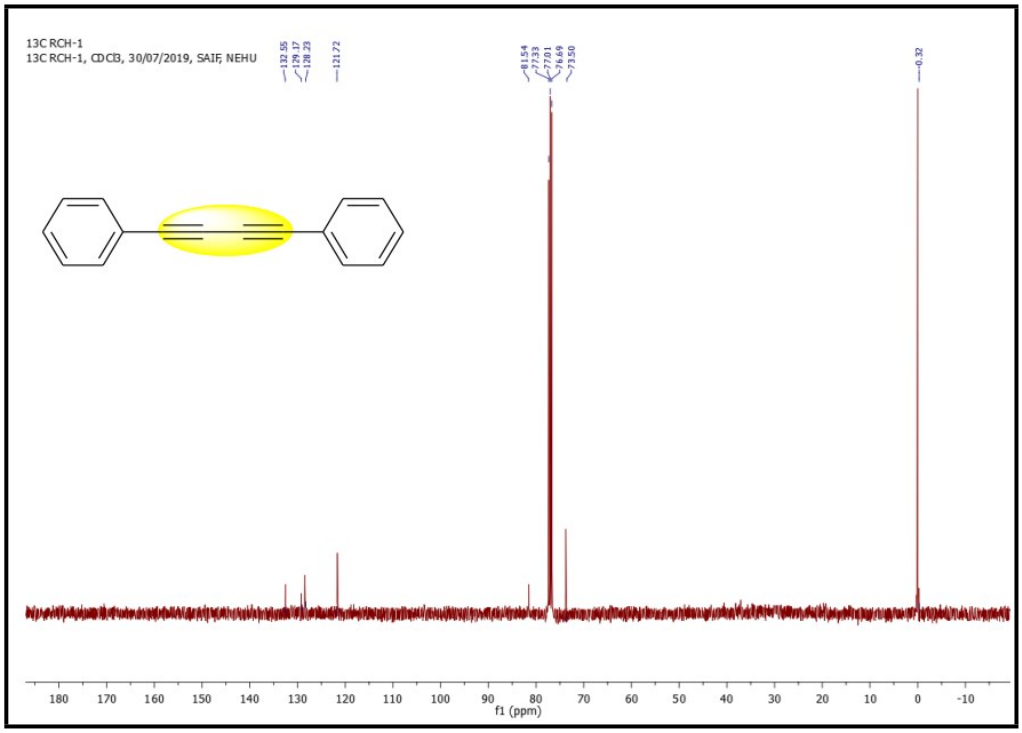


Figure S4: ^{13}C NMR spectrum of 1,4-diphenylbuta-1,3-diyne

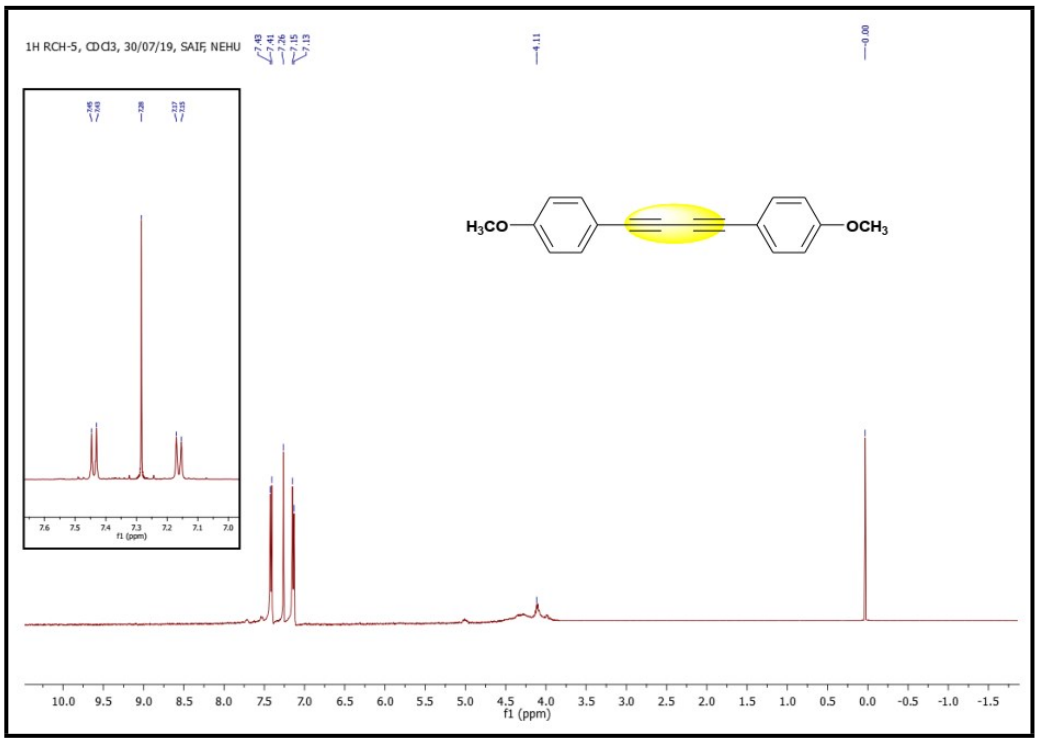


Figure S5: ^{1}H NMR spectrum of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne

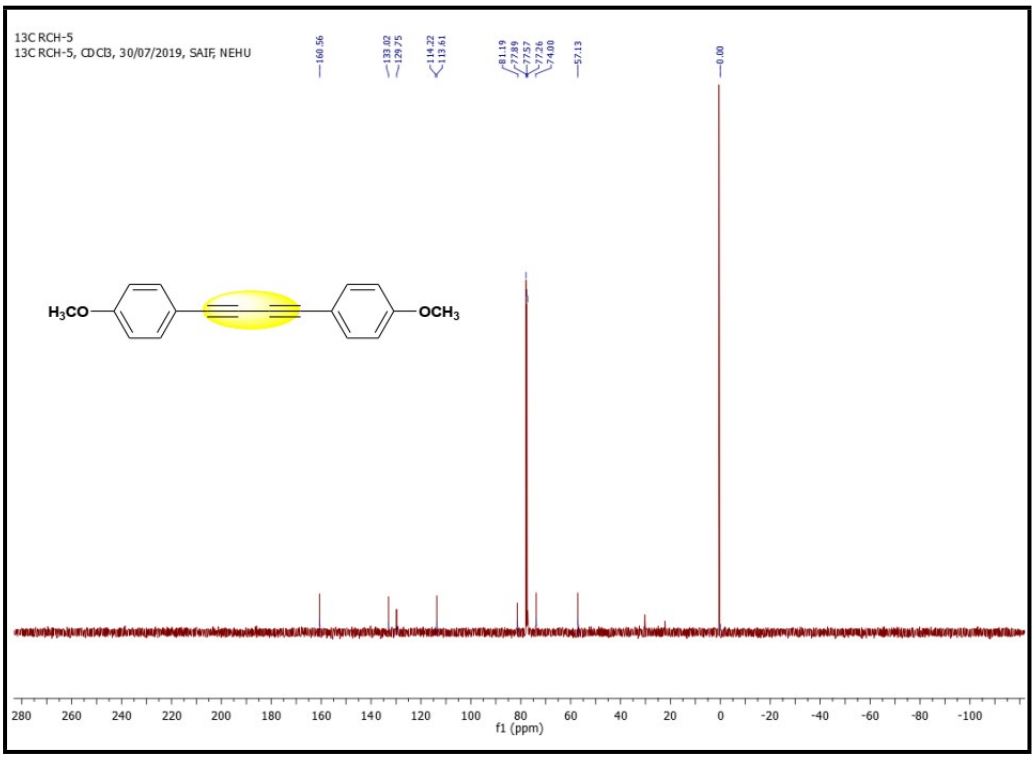


Figure S6: ^{13}C NMR spectrum of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne (500 MHz, $CDCl_3$)

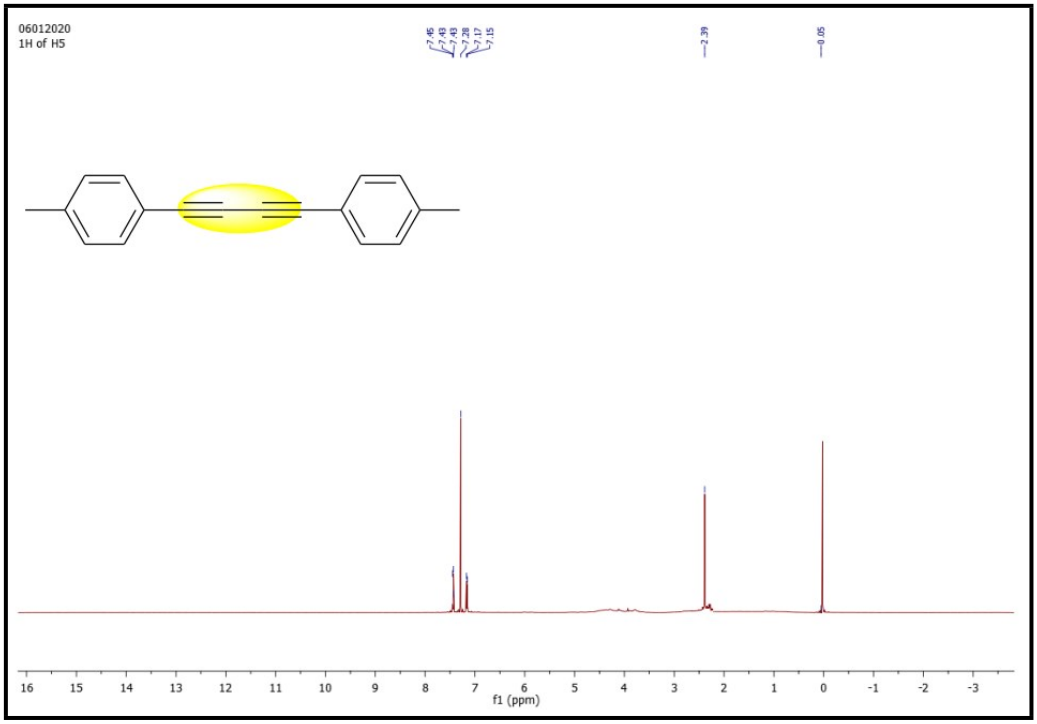


Figure S7: ^{1}H NMR spectra of 1,4-di-p-tolylbuta-1,3-diyne

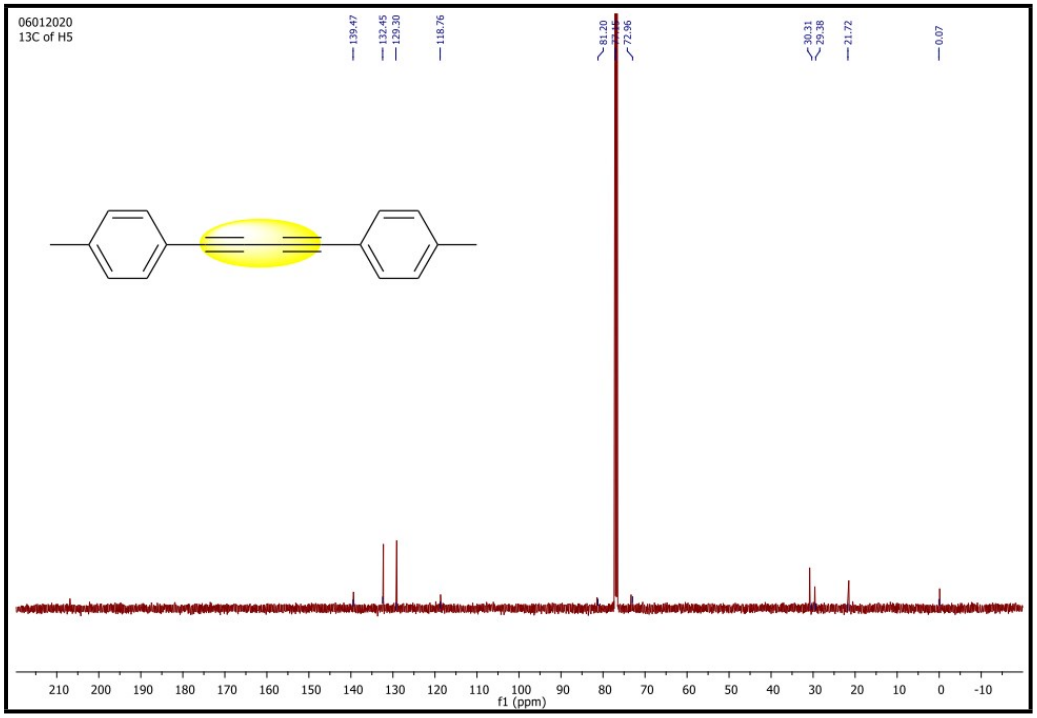


Figure S8: ^{13}C NMR spectrum of 1,4-di-p-tolylbuta-1,3-diyne

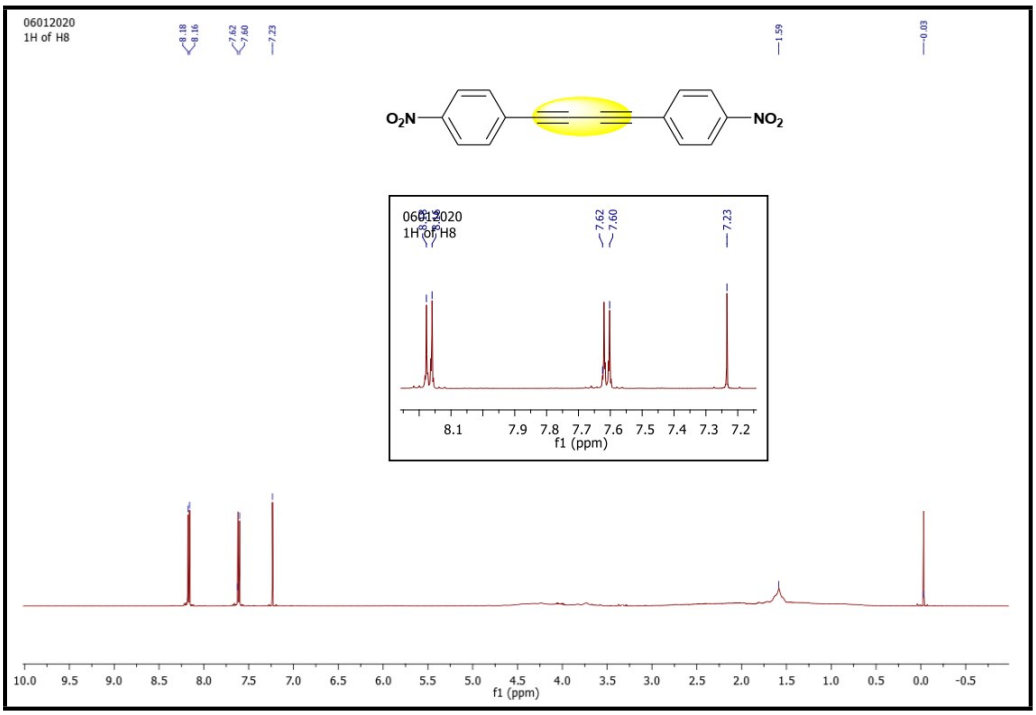


Figure S9: ^{1}H NMR spectrum of 1,4-bis(4-nitrophenyl)buta-1,3-diyne

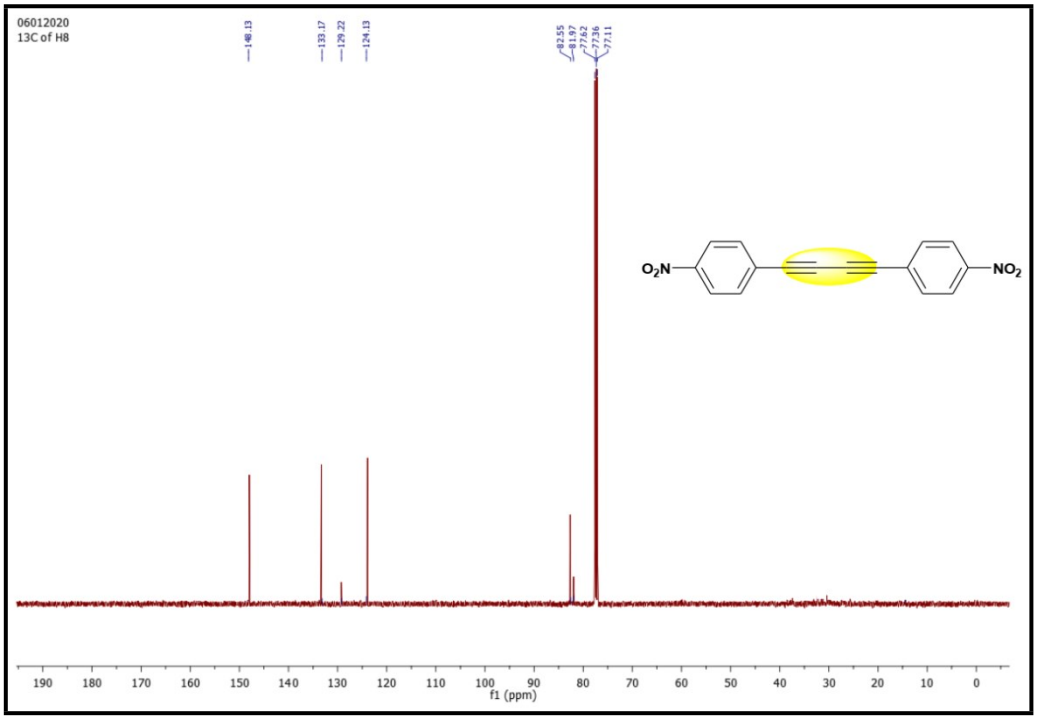


Figure S10: ^{13}C NMR spectrum of 1,4-bis(4-nitrophenyl)buta-1,3-diyne