Supporting Information

AgNPs Encapsulated by Amine-Functionalized Polymer Nanocatalyst for the CO_2 Fixation as Carboxylic Acid and Oxidation of Cyclohexane under Ambient Conditions

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Materials

Macroporous polystyrene beads cross-linked with divinylbenzene were purchased from Aldrich Chemical Company, USA. Silver nitrate ($AgNO_3$), Tris(hydroxymethyl) aminomethane (TRIS) and Sodium borohydride ($NaBH_4$) were obtained from Spectrochem, India. Other reagents were purchased from E-Merck, India.

Characterization techniques

Powder X-ray diffraction (XRD) patterns of different samples were analyzed with a Bruker D8 Advance X-ray diffractometer using Ni–filtered Cu Kα (λ=0.15406 nm) radiation. Transmission electron microscopy (TEM) image of the nanocomosite was obtained using a JEOL JEM 2010 transmission electron microscope operating at 200 kV. Scanning electron microscopy (SEM) measurements were performed with a JEOL JEM 6700F field-emission scanning electron microscope. UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. FT-IR spectra of the samples were recorded on KBr pellets by using a Perkin-Elmer FT-IR 783 spectrophotometer. Thermogravimetry (TG) analysis of the samples was done by using

Mettler Toledo TGA/DTA 851e. The reaction products were analyzed through a Varian 3400 gas chromatograph equipped with a 30 m CP-SIL 8CB capillary column and a flame ionization detector. During GC analysis, the injection volume of the sample was 0.20 μL and temperature condition was: Oven temperature 250 degree, ramp 10 degree / min, start temperature 50 degree, end temperature 250 degree. The isolated products were characterized by ^{1}H NMR spectroscopy. The pure products were isolated by performing column chromatography (EtOAc/Petrolium ether = 1:9).

Synthesis of microporous polymer-supported 2-pyridinecarbaldehyde (m-PS-PC)

Preparation of polymer supported silver nanomaterial was illustrated in Scheme 1. At first, *p*-amino polystyrene was synthesized according to the previous report.[1] Then the suspension of 2 g of porous amino polystyrene in toluene was taken in a 25 ml round bottom flask and the resulting mixture was stirred for 30 mins, after that 5 ml of 2-pyridinecarbaldehyde was added dropwise under stirring condition. The mixture was refluxed at 120 °C temperature for 48 h to get the polymer-supported 2-pyridinecarbaldehyde ligand (m-PS-PC). The reaction mixture obtained was cooled to reach it at the room temperature. It was filtered and the subsequent mixture was washed with methanol. Then it was dried under vacuum.

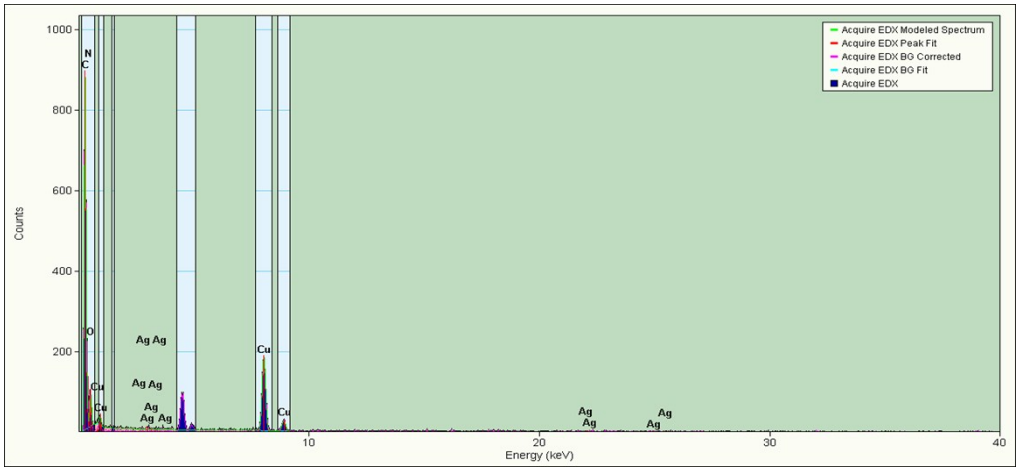


Figure S1. EDX spectrum of AgNPs@m-PS-PC nanocomposite

FTIR spectra

FT-IR spectra of porous m-PS-PC ligand and AgNPs@m-PS-PC nanocomposite are provided in the Figure S2. The absorption band centered at 1605 cm^{-1} can be ascribed by presence of the C=N bond of the pyridine ring in the ligand, which also confirms the attachment of the carbonyl compound on the polymer matrix. After grafting with silver nanopartcles it is observed that the frequency of the C=N (azomethine groups) bond is reduced and appears at 1600 cm^{-1} which provided the formation of a metal-ligand bond.[2] FT-IR spectra of AgNPs@m-PS-PC nanocomposite is given in the Figure S3.

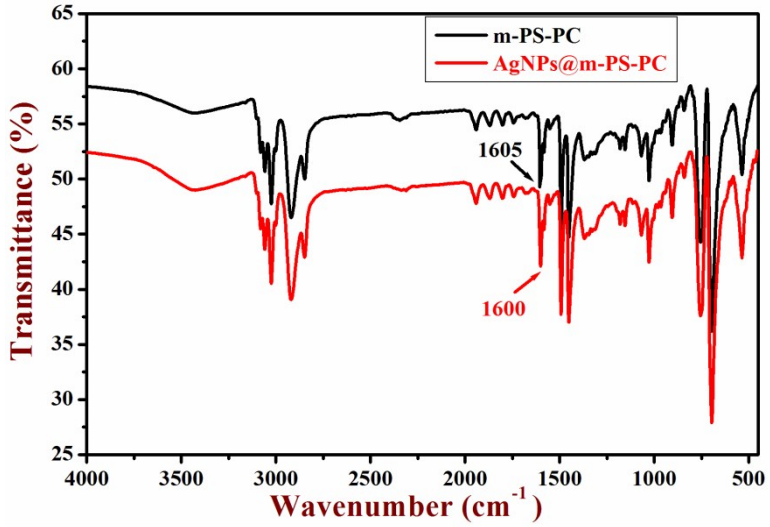


Figure S2. FTIR spectra of m-PS-PC and AgNPs@m-PS-PC nanocomposite.

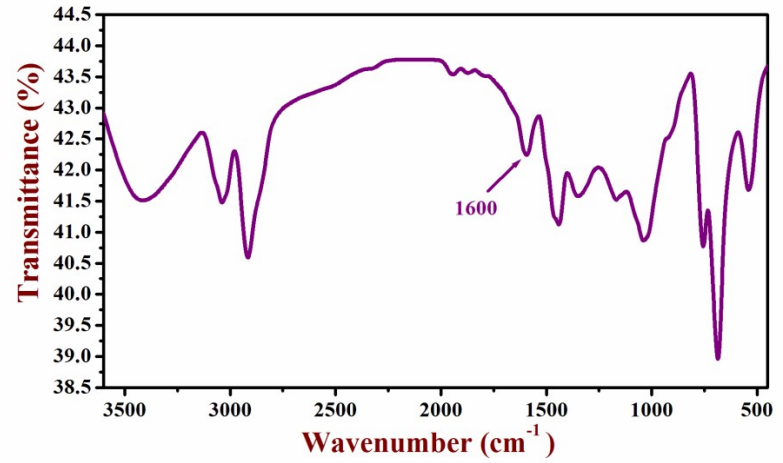


Figure S3. FTIR spectra of reused AgNPs@m-PS-PC nanocomposite.

Optimization of reaction conditions:

Table S1. Optimization of reaction parameter for synthesis of propiolic acid from phenyl acetylene[a]

SL. No.	Catalyst	Catalyst amount (mg)	Yield (%)[b]
1	$AgNO_3$	5	11
2	Ag(OAc)	5	54
3	AgNPs@m-PS-PC	50	91

[a]**Reaction conditions:** alkyne (1.0 mmol), DMF (3 mL), temperature (70 °C), Cs_2CO_3 (1.2 mmol), 10 h, CO_2 (1 atm), catalyst. [b]Yield was determined by GC.

Plausible Reaction mechanism for oxidation of cyclohexane

We have proposed a probable mechanistic pathway, based on some reported articles[3,4] for the oxidation of cyclohexane with H_2O_2 using AgNPs@m-PS-PC nanocatalyst (Figure S4).

$$Ag^0 + H_2O_2 \longrightarrow HO^{\cdot} + Ag^I + OH^- \quad (1)$$
$$Ag^I + H_2O_2 \longrightarrow HOO^{\cdot} + H^+ + Ag^0 \quad (2)$$
$$HO^{\cdot} + CyH \longrightarrow H_2O + Cy^{\cdot} \quad (3)$$
$$Cy^{\cdot} + O_2 \longrightarrow CyOO^{\cdot} \quad (4)$$
$$CyOO^{\cdot} + H_2O_2 \longrightarrow CyOOH + HOO^{\cdot} \quad (5)$$
$$CyOOH + Ag^0 \longrightarrow CyO^{\cdot} + Ag^I + OH^- \quad (6)$$
$$CyOOH + Ag^I \longrightarrow CyOO^{\cdot} + H^+ + Ag^0 \quad (7)$$
$$CyO^{\cdot} + CyH \longrightarrow CyOH + Cy^{\cdot} \quad (8)$$
$$2CyOO^{\cdot} \longrightarrow CyOH + Cy_{-H}{=}O + O_2 \quad (9)$$

Figure S4. Plausible reaction mechanism for oxidation of cyclohexane.

Kinetic curves (conversion vs. time) for both the reactions:

We have studied the conversion rates for both the reactions with time in presence of AgNPs@m-PS-PC nanocatalyst and from the obtained data the kinetic curves for synthesis of propiolic acids (Figure S5) and for cyclohexane oxidation (Figure S6) have been drawn. The conversion rates of different recycling runs for both the reactions have been studied and compared (Figure S7 and Figure S8). Those figures suggested that there were minimal decrease in the conversion rates after five recycling runs indicating the AgNPs@m-PS-PC catalyst is reusable with similar activity for both the reactions.

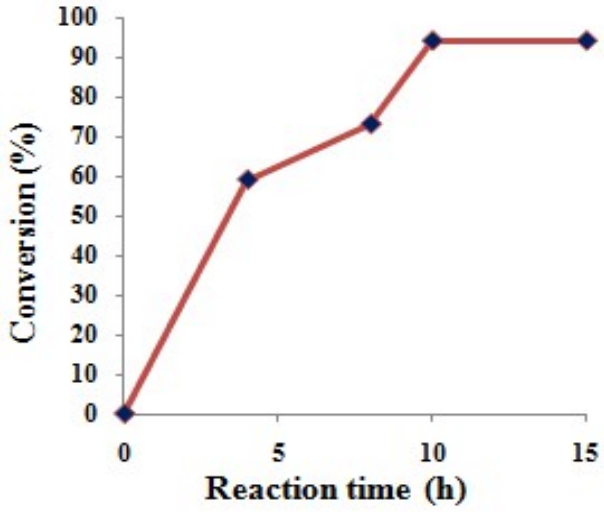


Figure S5. Kinetic curve for terminal carboxylation reaction

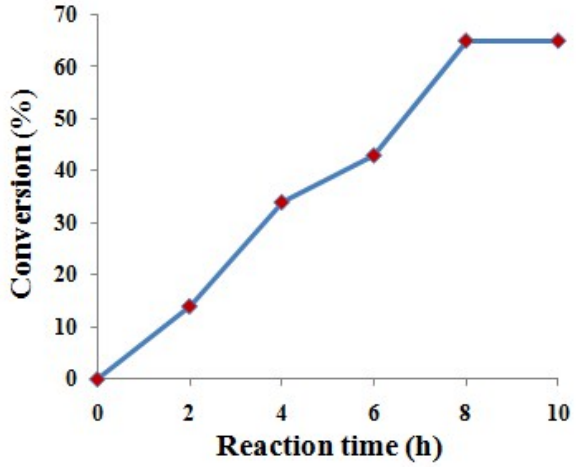


Figure S6. Kinetic curve for cyclohexane oxidation reaction.

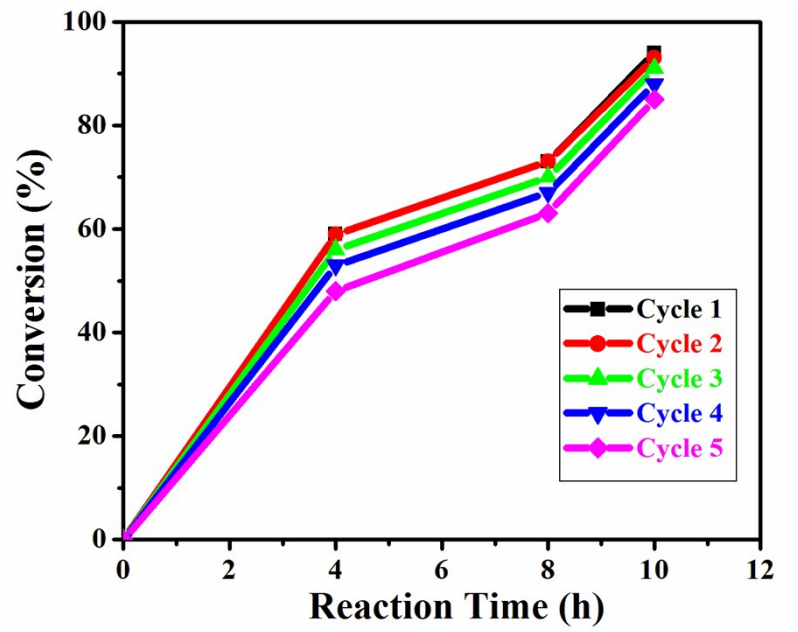


Figure S7. Comparison of conversion rates of different recycling runs for terminal carboxylation reaction.

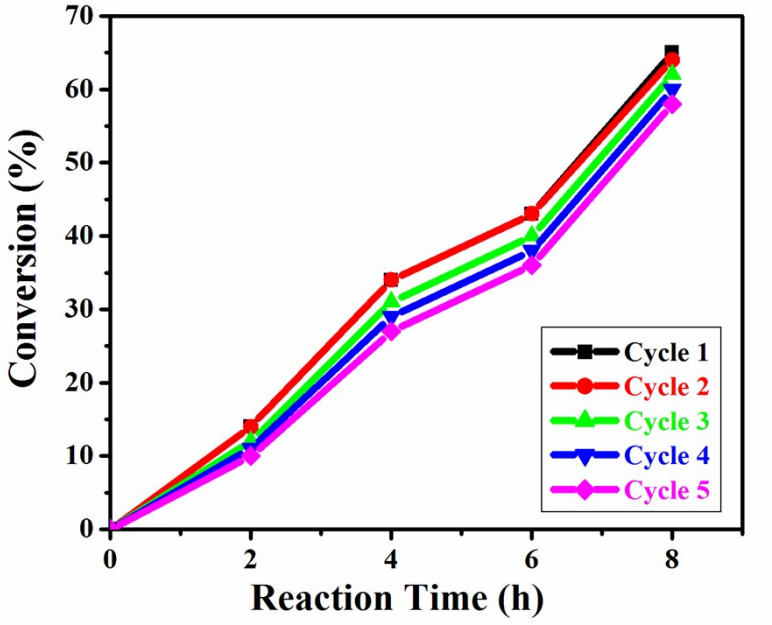
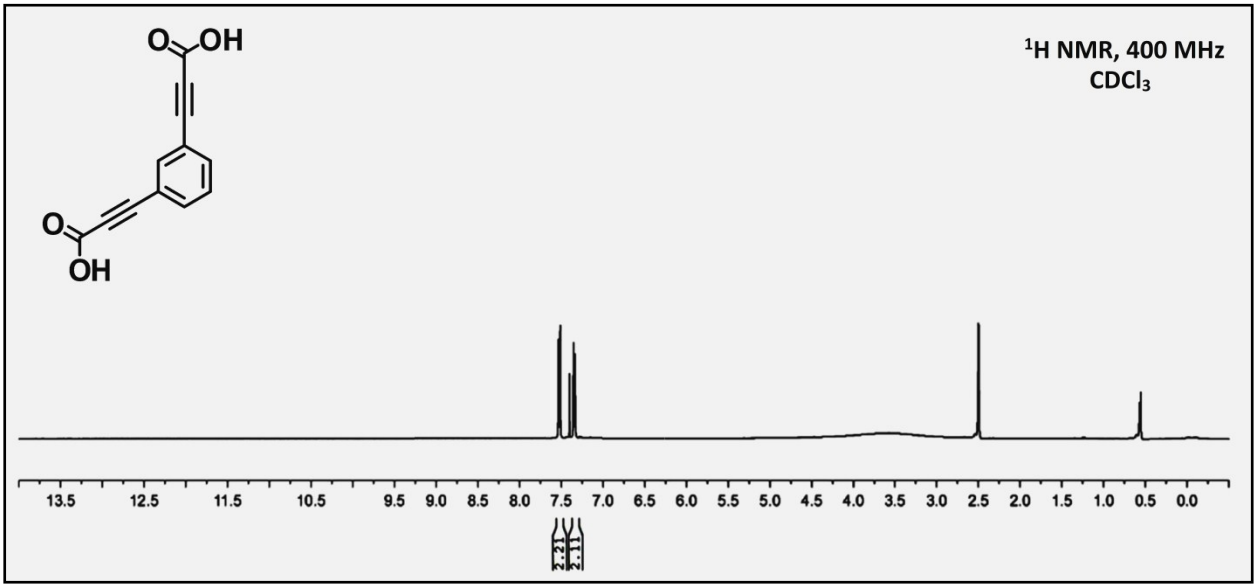


Figure S8. Comparison of conversion rates of different recycling runs for cyclohexane oxidation reaction.

NMR Spectra

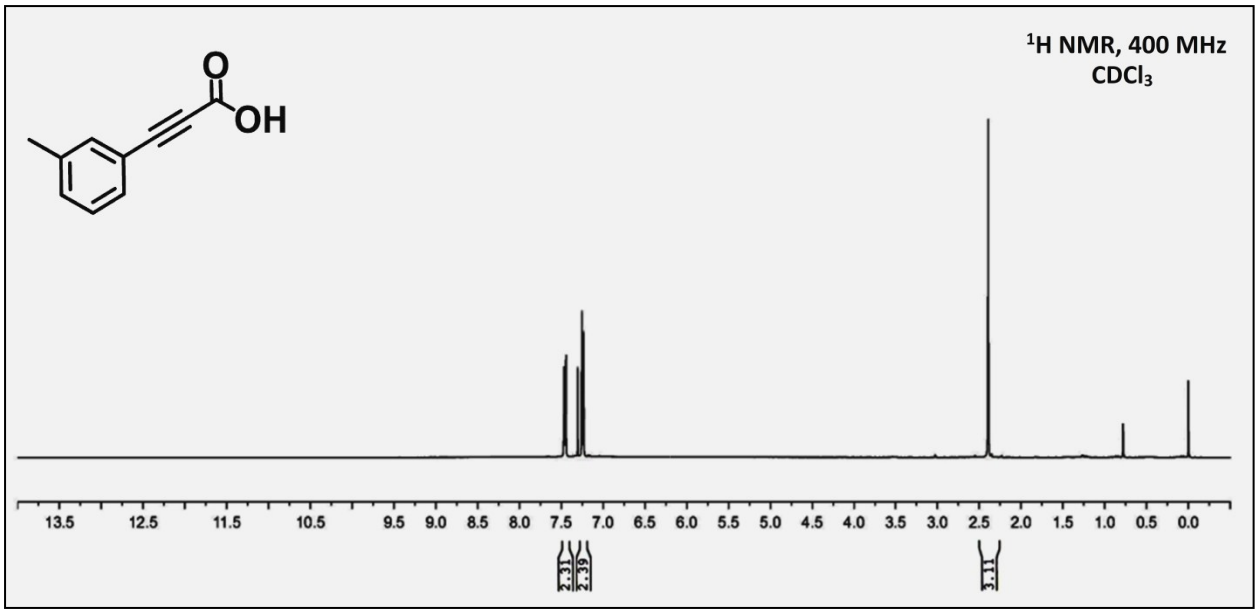
(3-Carboxyethynyl-phenyl)-propynoic acid

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.29-7.36 (m, 2H), 7.50-7.52 (m, 2H)



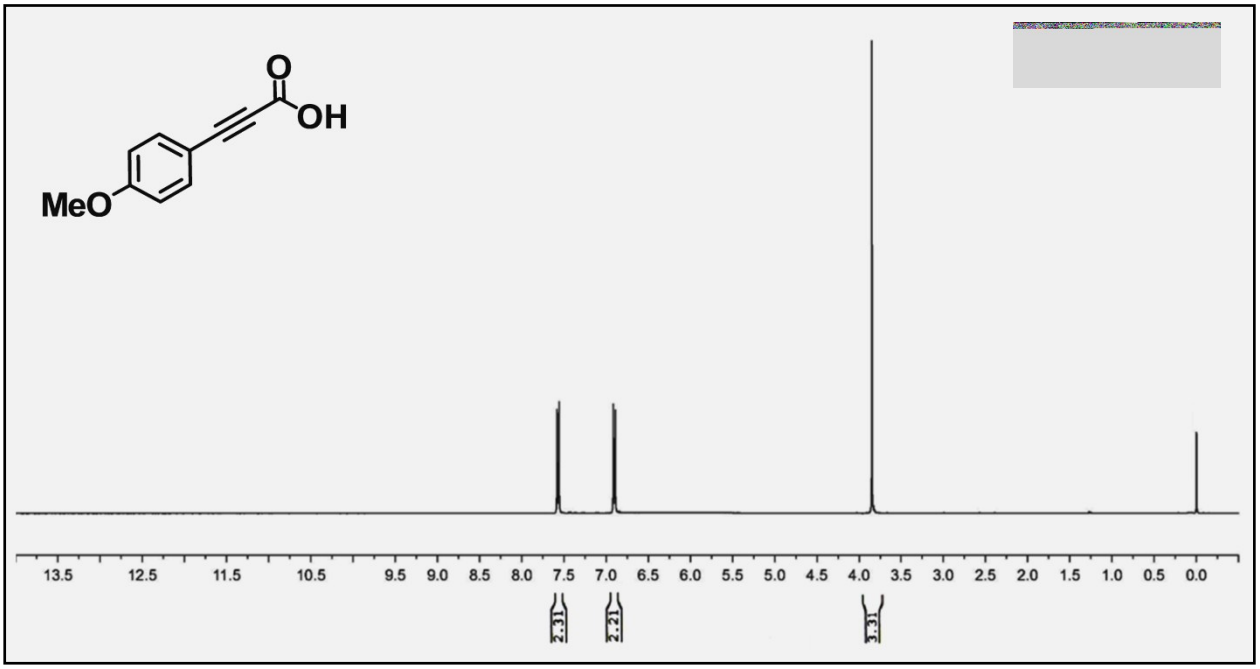
3-methylphenylpropiolic acid

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.27-7.30 (m, 2H), 7.38-7.47 (m, 2H), 2.38 (s, 3H)



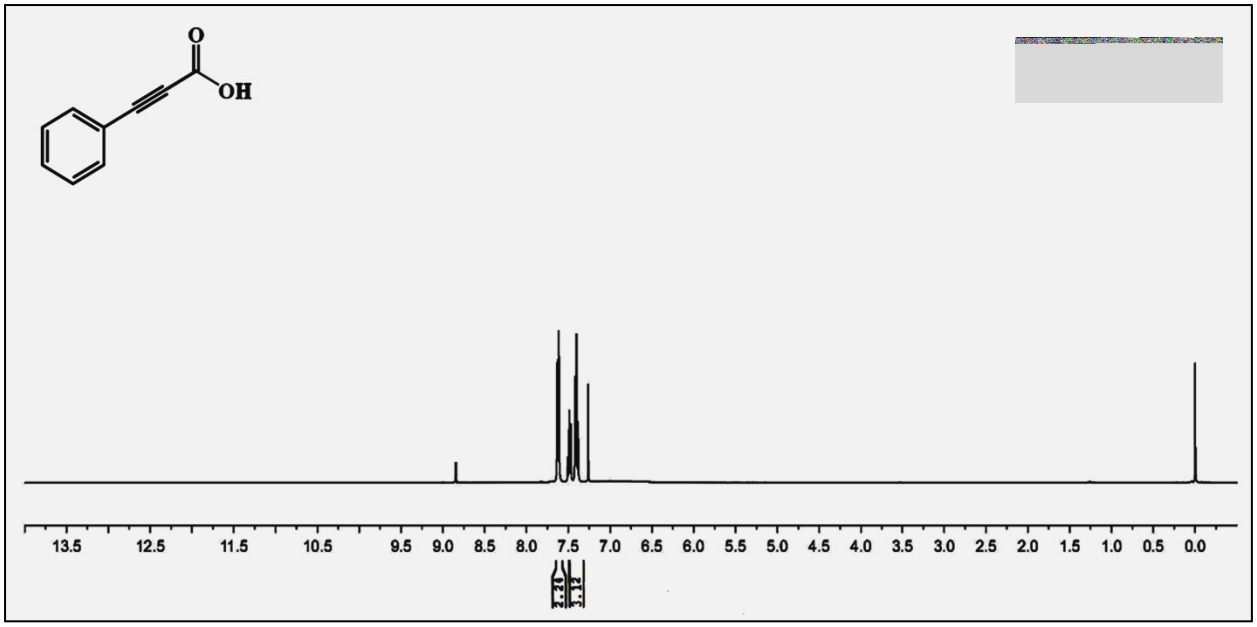
4-methoxyphenylpropiolic acid

^{1}H NMR (400 MHz, $CDCl_3$): δ =6.88-6.93 (d, 2H), 7.54-7.59 (d, 2H), 3.82 (s, 3H)



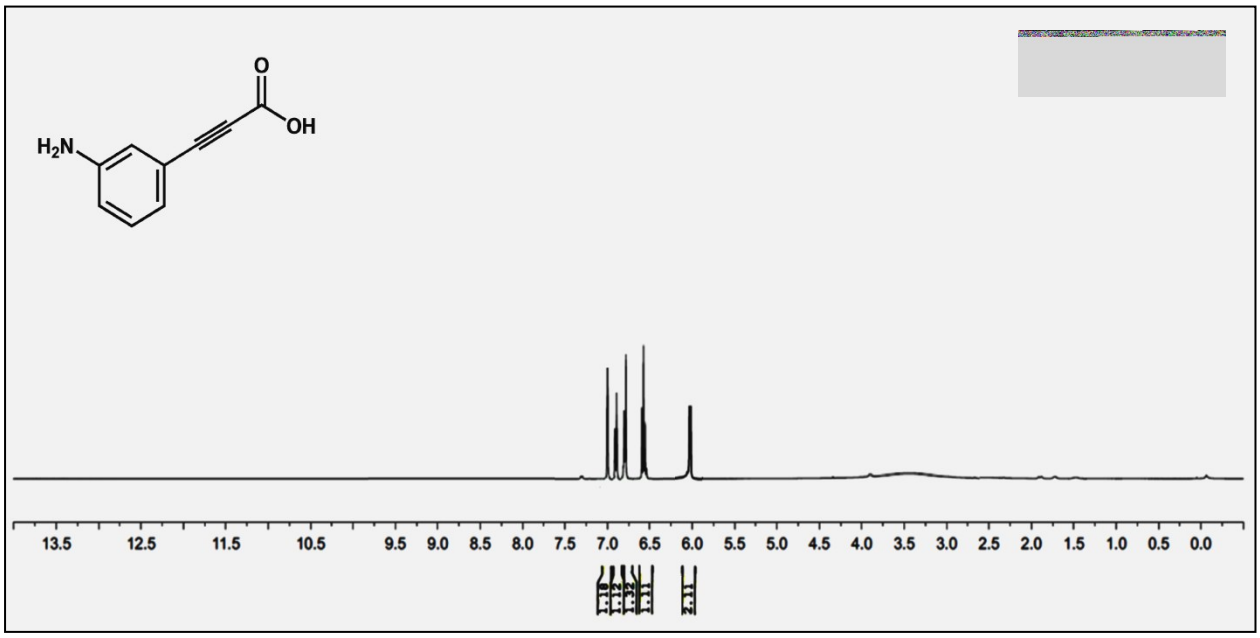
Phenylpropiolic acid

^{1}H NMR (400 MHz, $CDCl_3$): δ =7.37-7.42 (m, 2H), 7.45-7.51 (m, 1H), 7.61-7.63 (m, 2H)



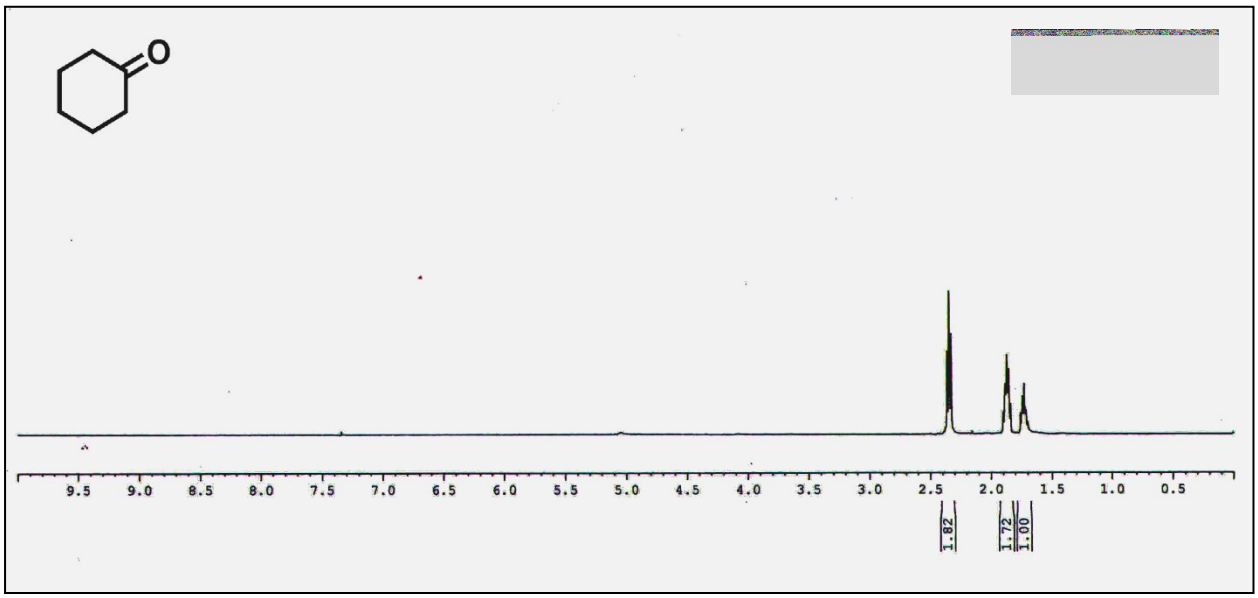
3-aminophenylpropiolic acid

^{1}H NMR (400 MHz, $CDCl_3$): δ =6.62-6.65 (m, 1H), 6.79-6.81 (m, 1H), 6.86-6.90 (m, 1H), 6.97-6.99 (m, 1H), 6.02 (s, 2H).



Cyclohexanone

^{1}H NMR (400 MHz, $CDCl_3$): δ =1.70-1.75 (m, 1H), 1.84-1.90 (m, 2H), 2.32-2.36 (m, 2H).



Reference

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