

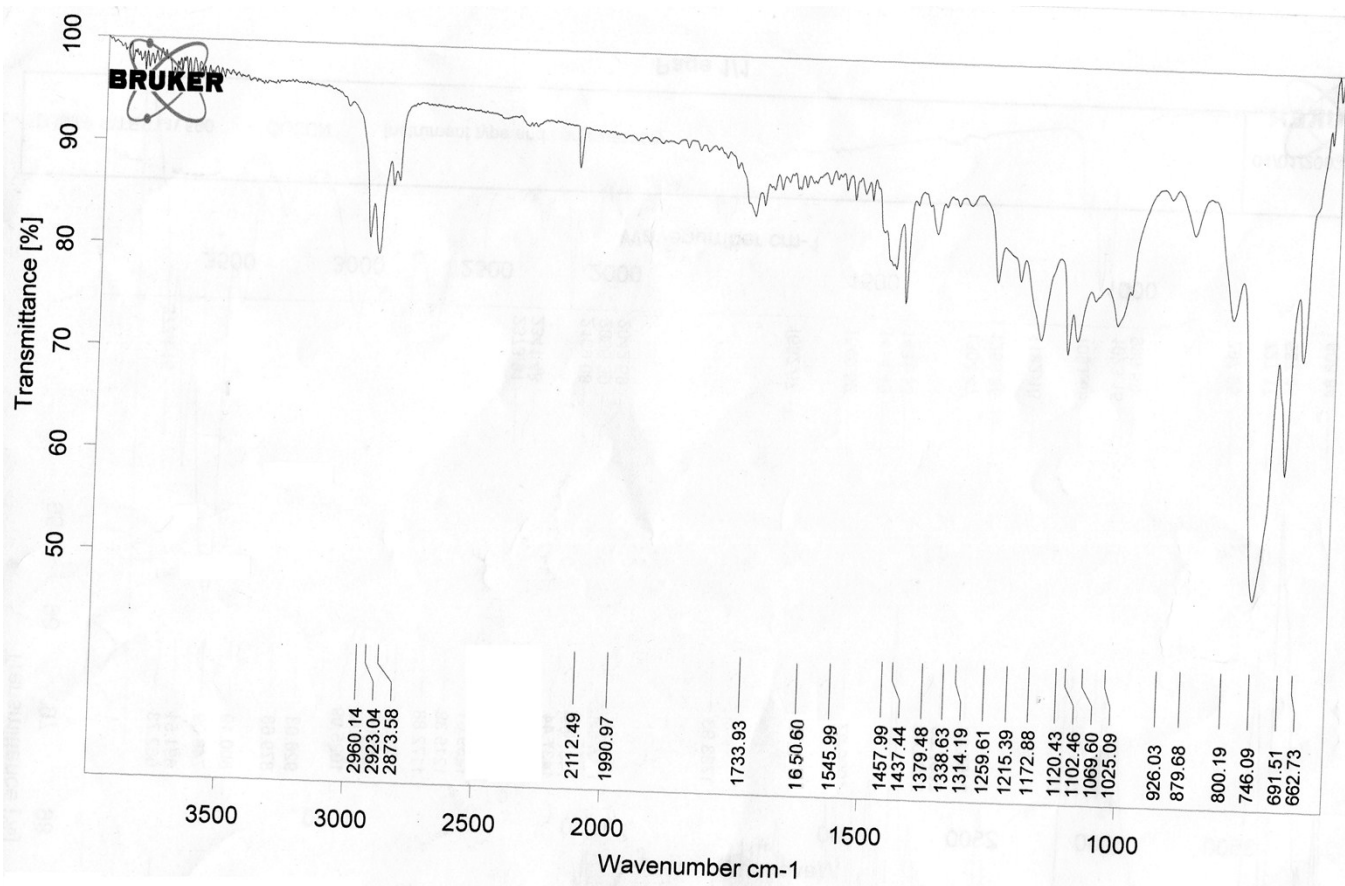
Supplementary Information

***cis*-1,2-bis(diphenylphosphino)ethylene copper(I) catalyzed C-H activation and
carboxylation of terminal alkynes**

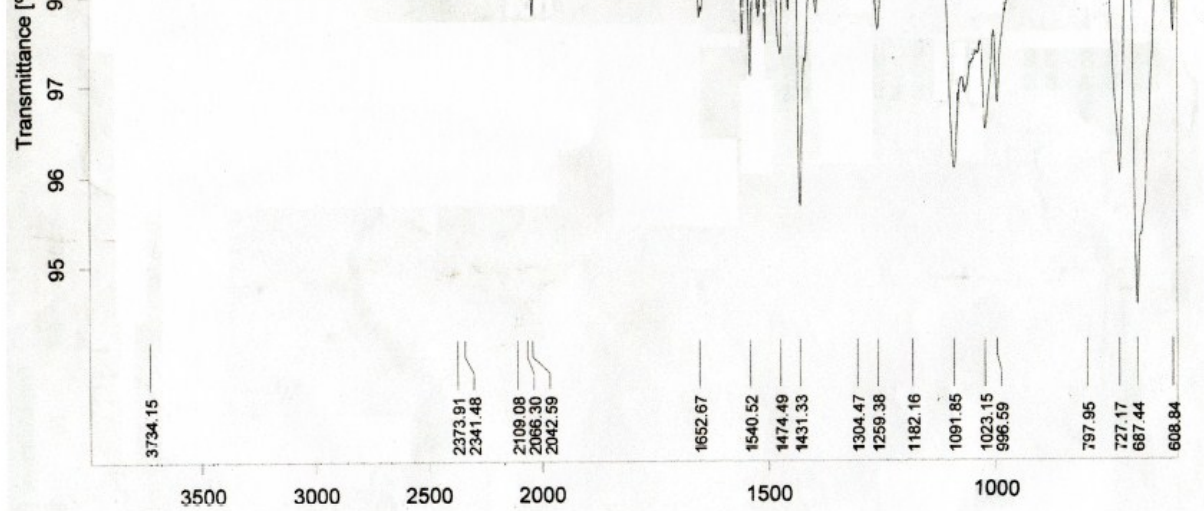
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Rath^{c*}**

E-mail address: manojtri@gmail.com (MT); rathn@umsl.edu(NPR).

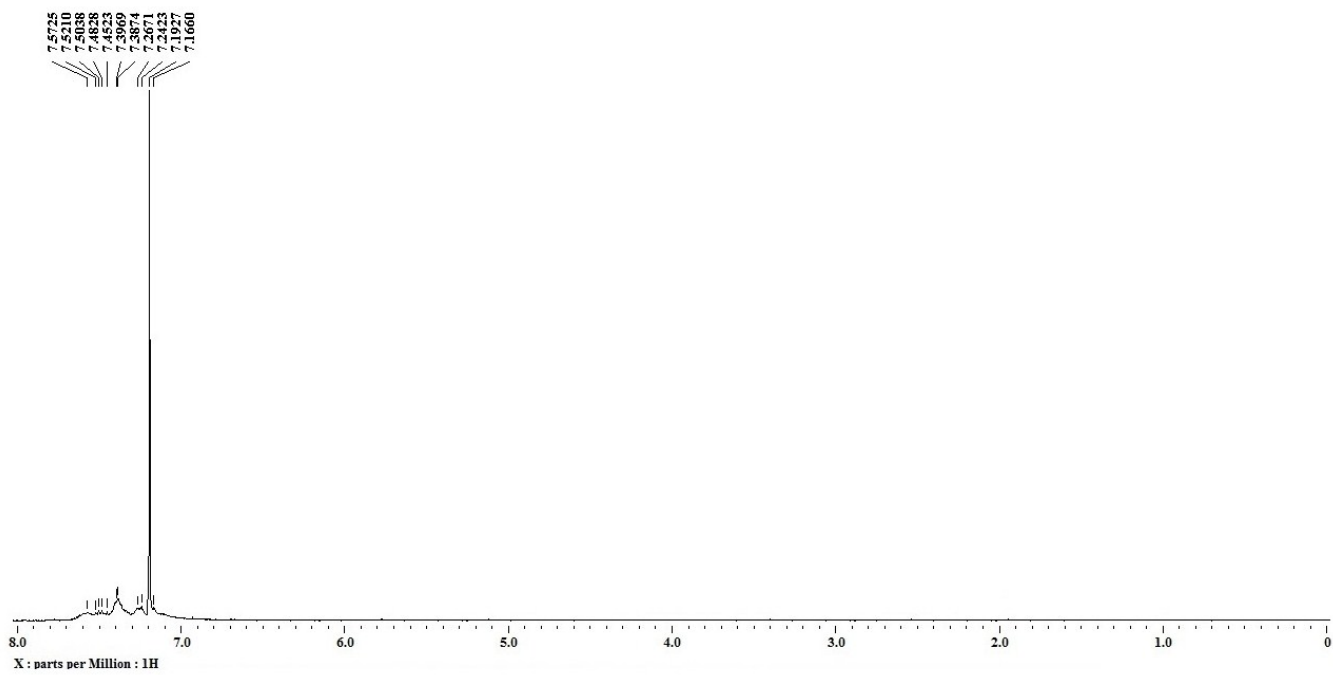
Corresponding author. Tel.: + 91 9811730475 (MT); (314) 516-5333 (NPR).



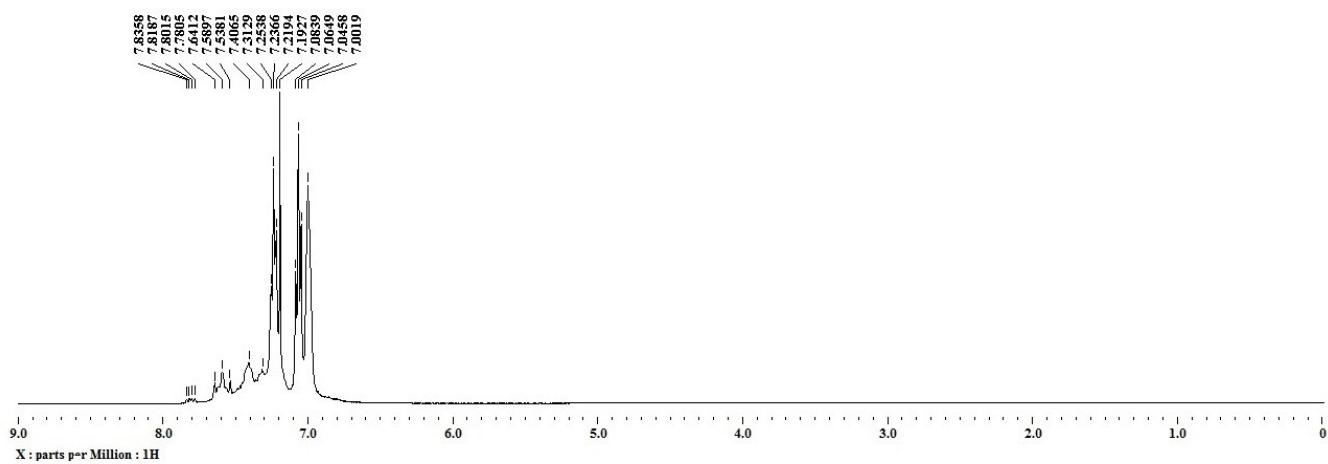
S-1. IR spectrum of complex 1.



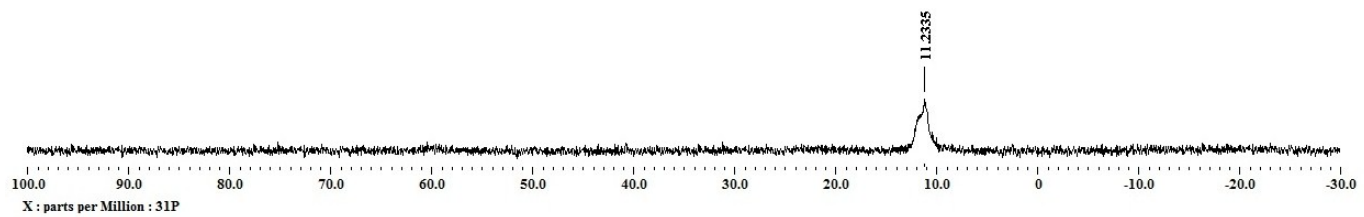
S-2. IR spectrum of complex 2.



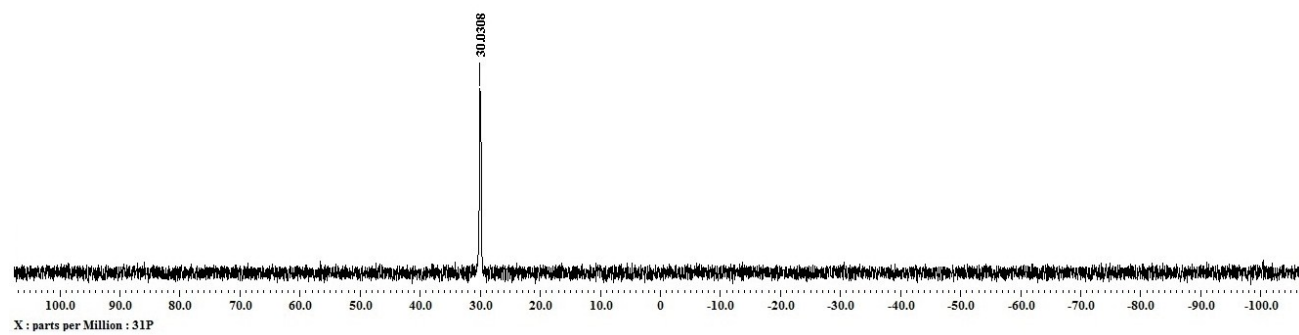
S-3. ^1H NMR spectrum of complex **1** in CDCl_3 .



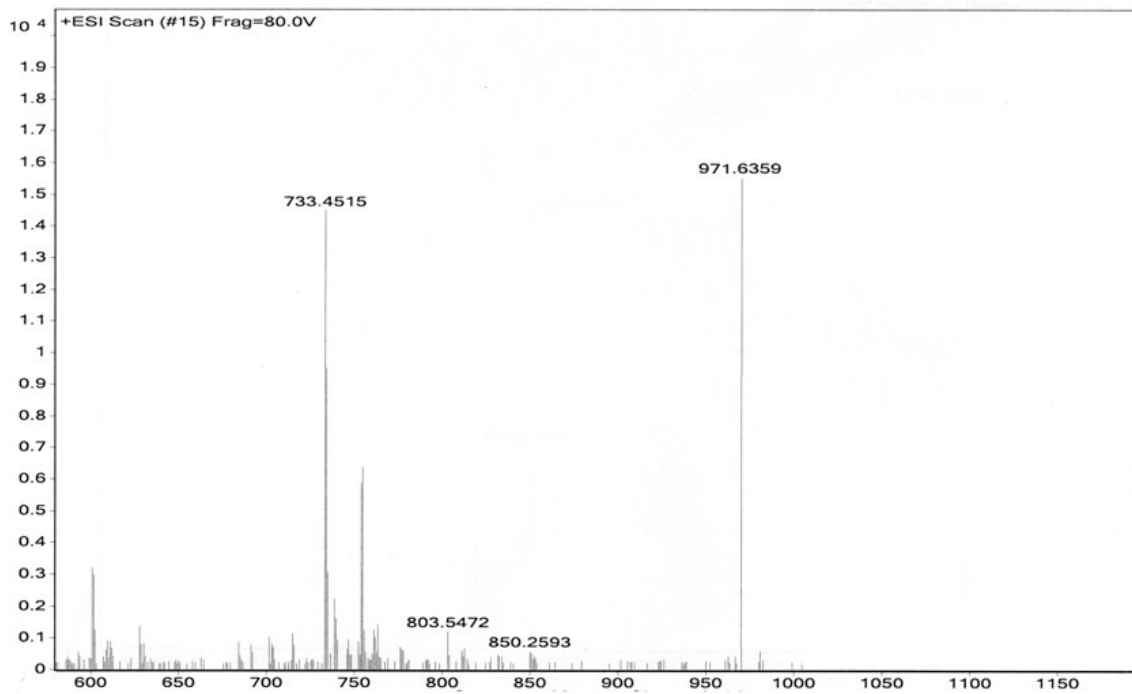
S-4. ^1H NMR spectrum of complex **2** in CDCl_3 .



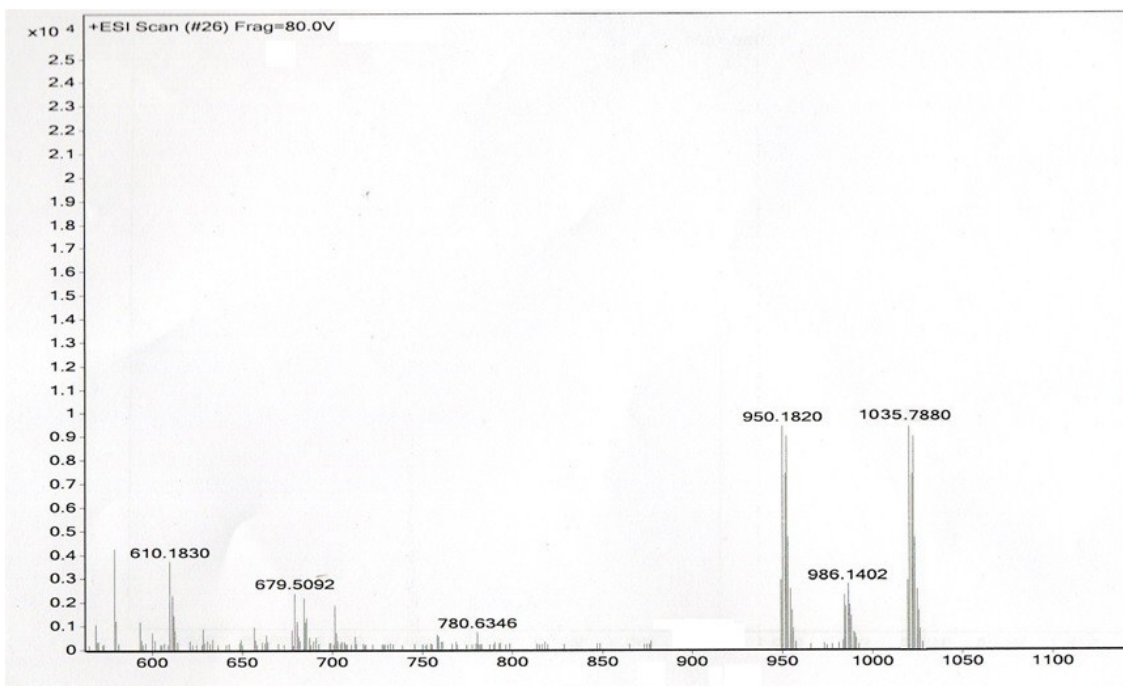
S-5. ^{31}P NMR spectrum of complex **1** in CDCl_3 .



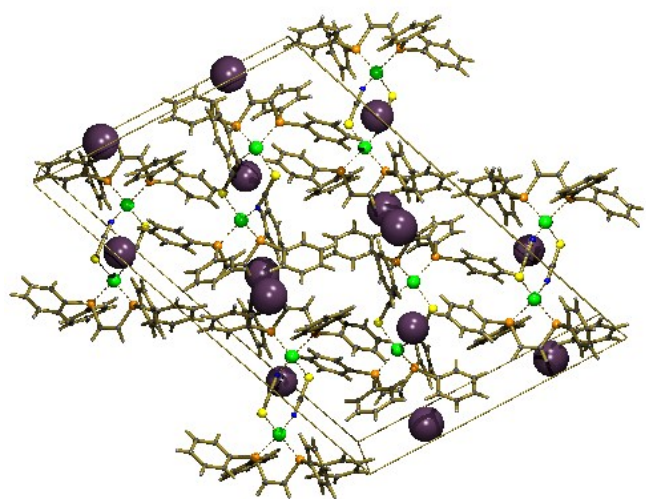
S-6. ^{31}P NMR spectrum of complex 2 in CDCl_3 .



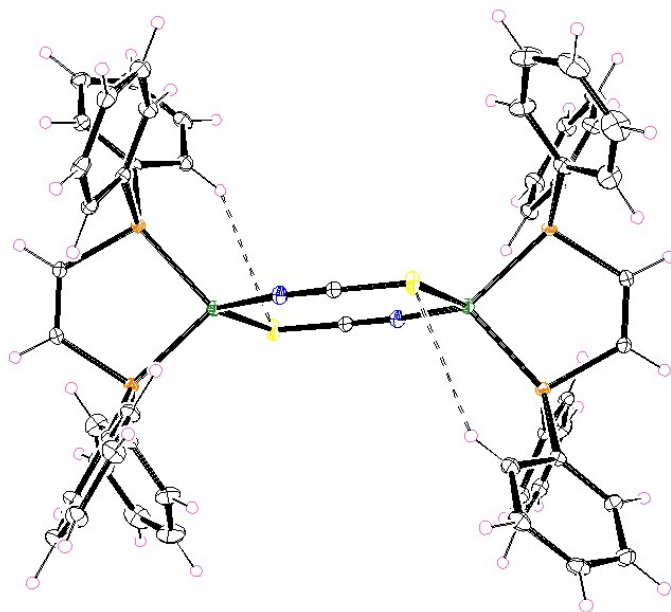
S-7. ESI-MS spectrum of complex 1.



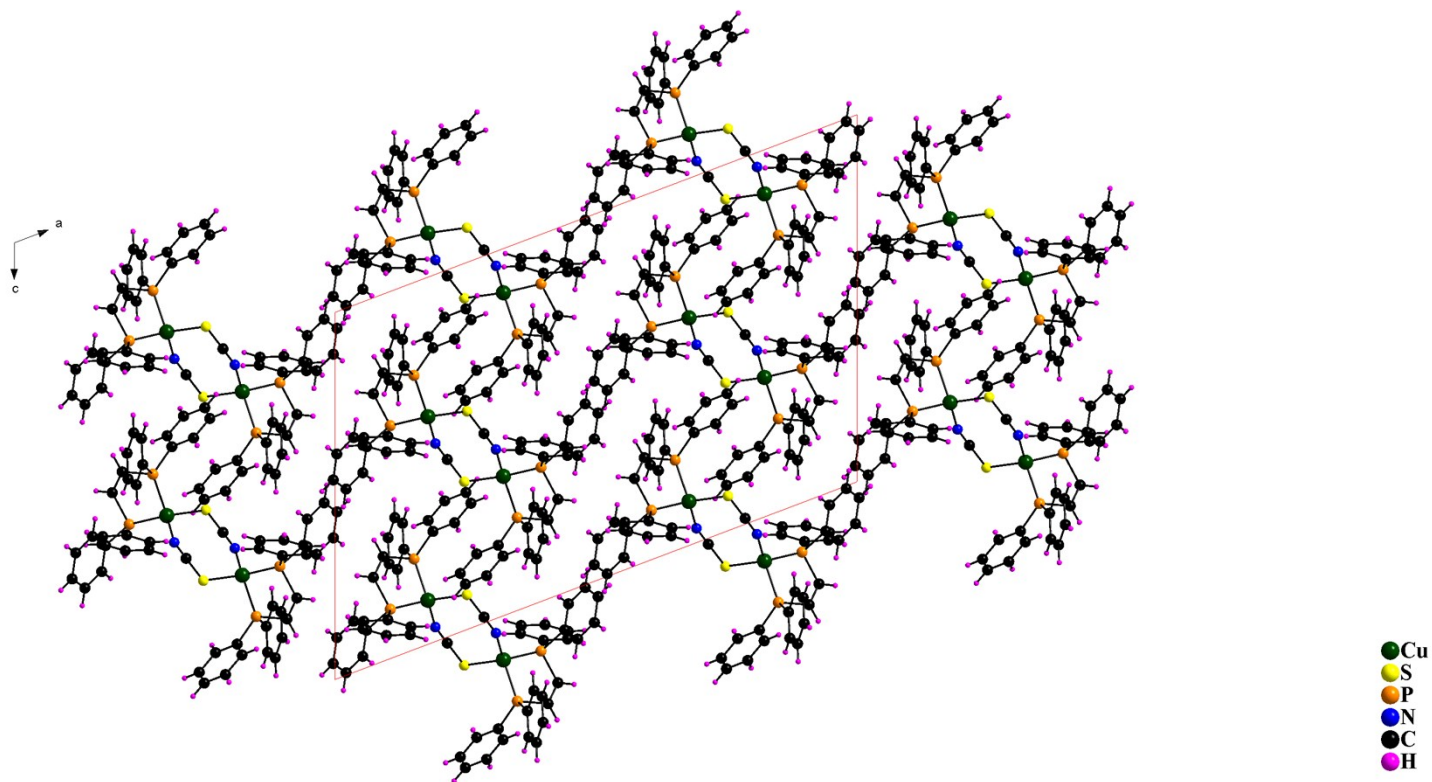
S-8. ESI-MS spectrum of complex 2.



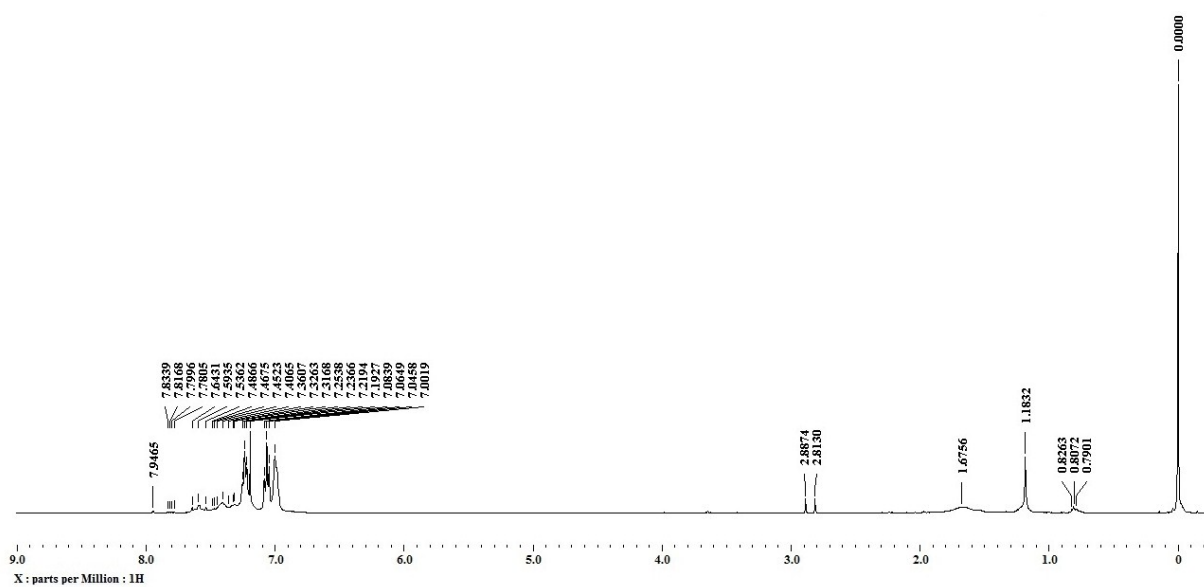
S-9. Self-assembly of complex **2** showing solvent accessible voids in the crystal lattice.



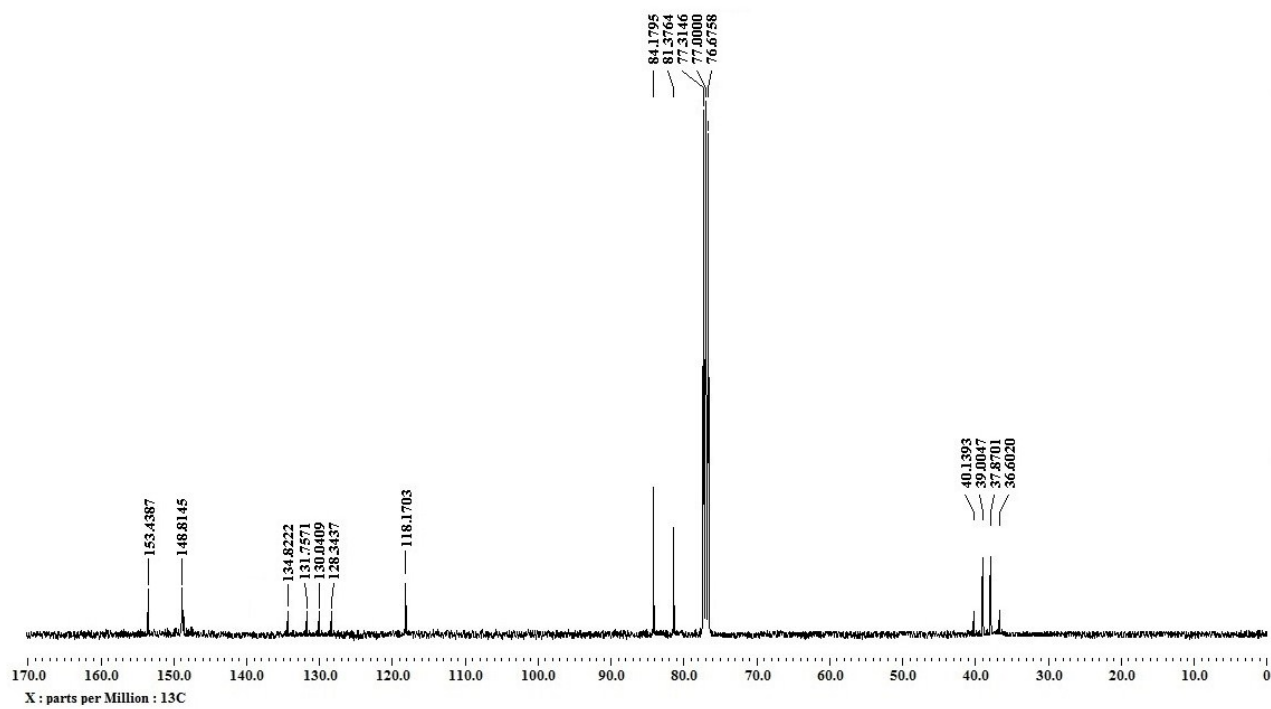
S-10. Ortep diagram of complex **2** showing C-H...S hydrogen bond interactions in the crystal lattice [C(27)-H(27)···S1[#](3.131Å, 148.93°);C(27)[#]-H(27)[#]···S1(3.131Å, 148.93°)].



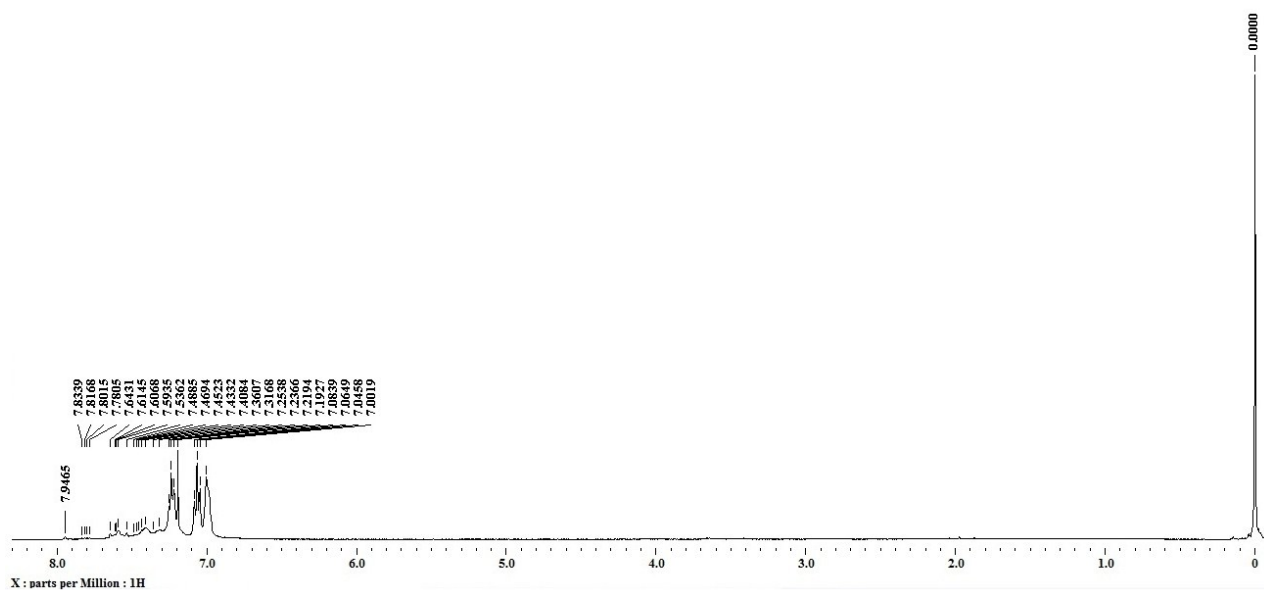
S-11. Crystal packing diagram of complex 2 viewed along the *b* axis.



S-12. ¹H NMR spectrum of the reaction mixture for the synthesis of 3-phenylpropionic acid from CO₂ and Phenylacetylene catalysed by complex **2** in CDCl₃ after 5h at room temperature.



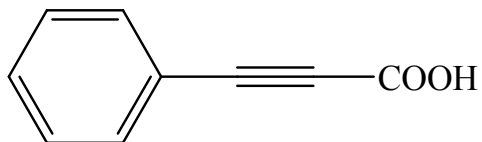
S-13. ^{13}C NMR spectrum of the reaction mixture for the synthesis of 3-phenylpropionic acid from CO_2 and Phenylacetylene catalysed by complex **2** in CDCl_3 after 5h at room temperature.



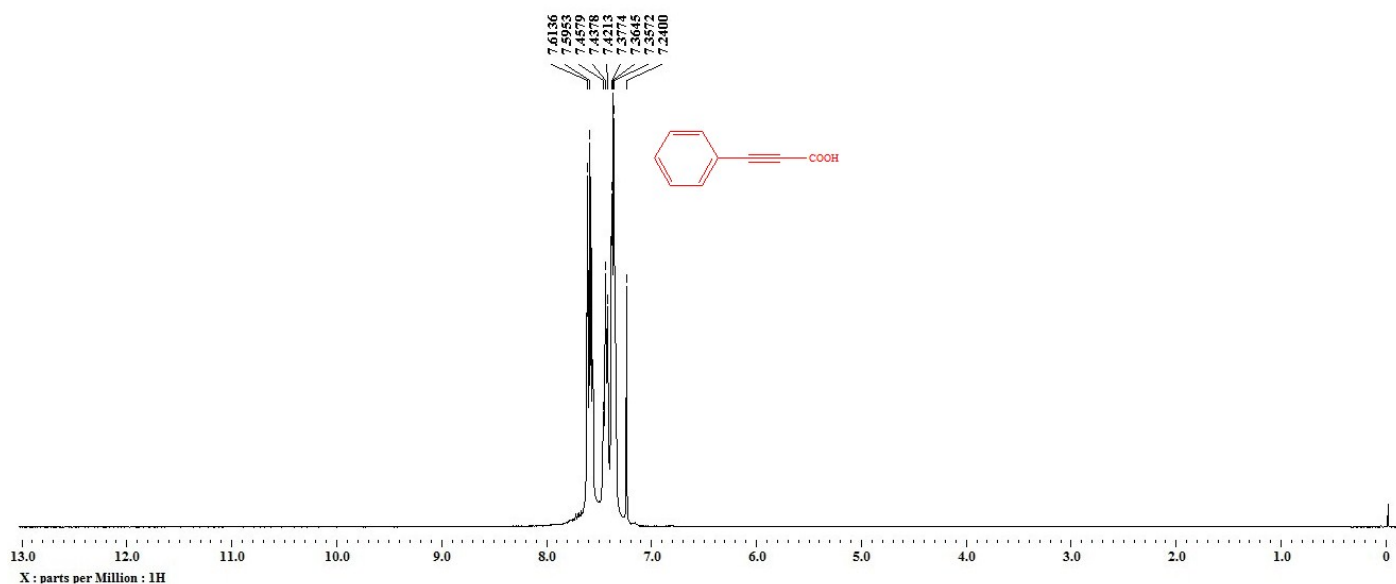
S-14. ^1H NMR spectrum of the reaction mixture for the synthesis of 3-phenylpropionic acid from CO_2 and Phenylacetylene catalysed by complex **2** in CDCl_3 after 12h at room temperature

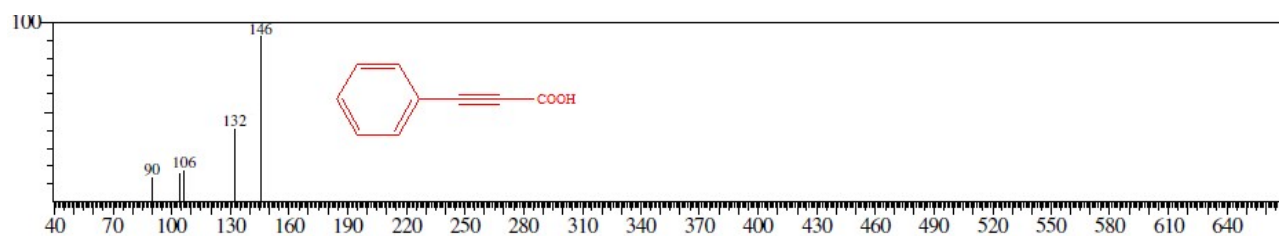
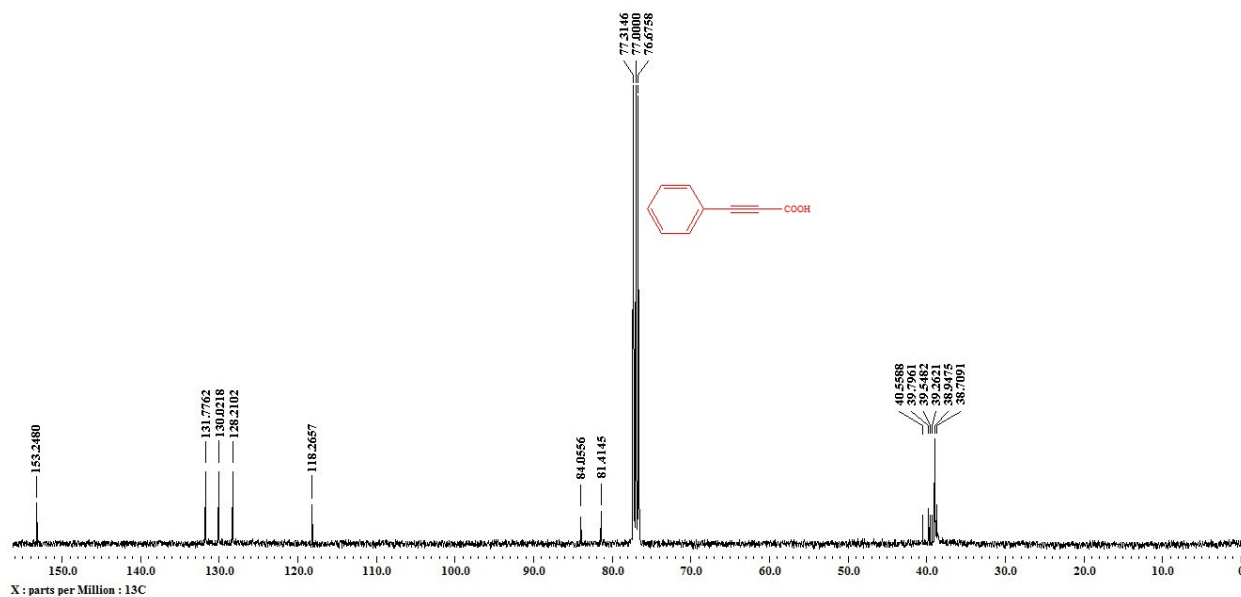
Characterization Data:

3-phenylpropionic acid:

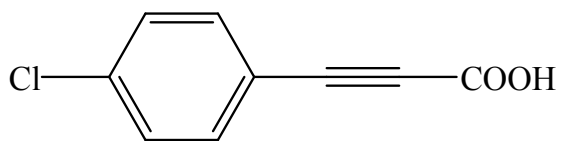


^1H NMR (400 MHz, CDCl_3): $\delta = 7.60$ (d, $J = 7.3$ Hz, 2H, Ar-H), 7.43 (t, $J = 8.0$ Hz, 1H, Ar-H), 7.36 (t, $J = 5.1$ Hz, 2H, Ar-H); ^{13}C NMR (400 MHz, CDCl_3): $\delta = 153.24$ (-COOH), 131.77, 130.02, 128.21, 118.26, 84.05, 81.41, 40.55, 39.77, 39.54, 39.26, 38.94, 38.70; GCMS m/z (% rel. inten.) 146 (M^+ , 100).

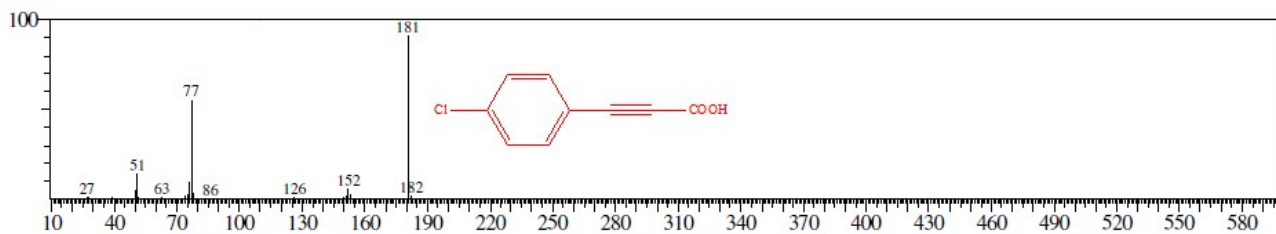
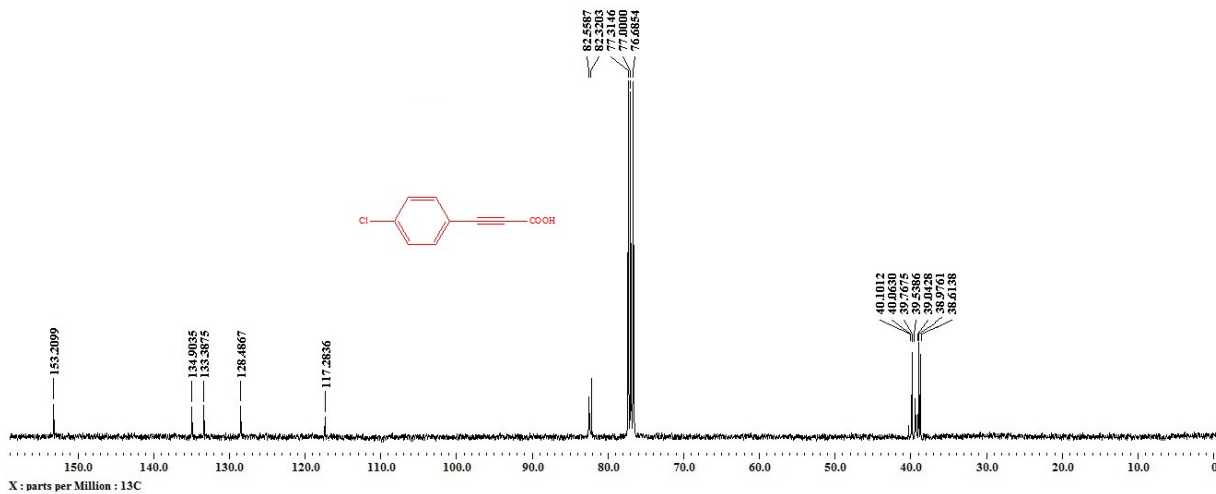
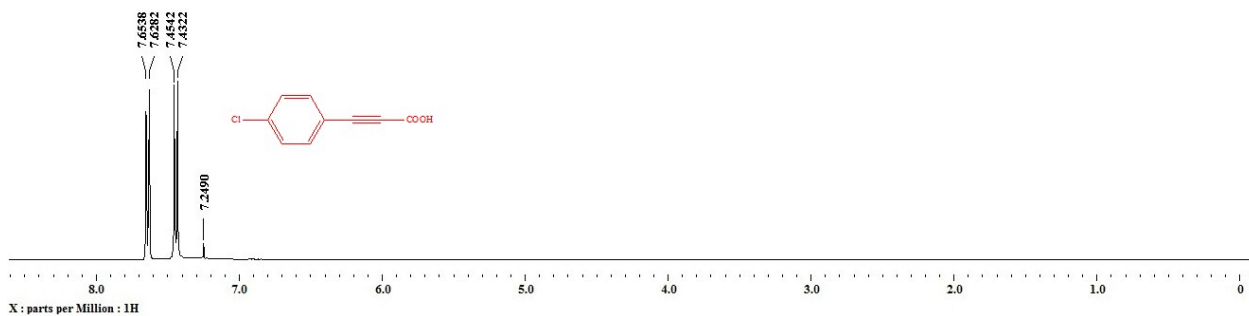




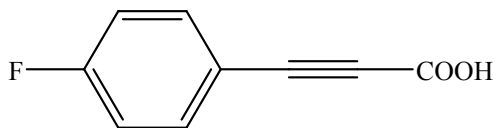
3-(4-chlorophenyl)propionic acid:



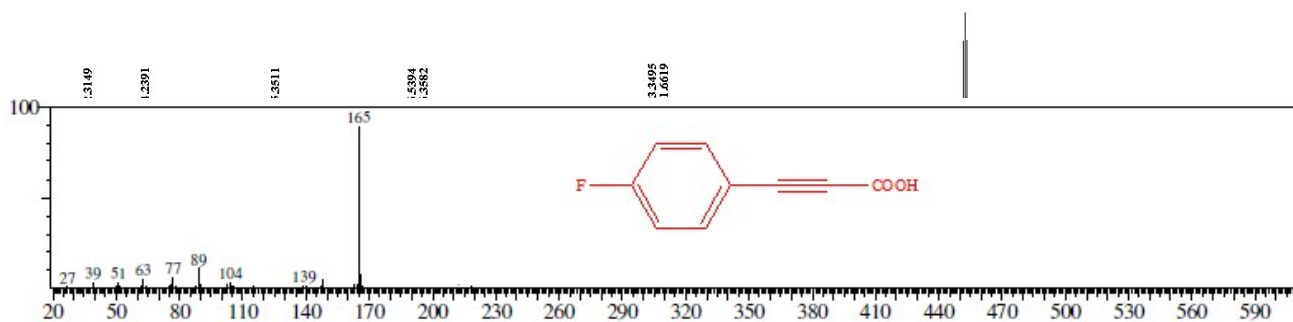
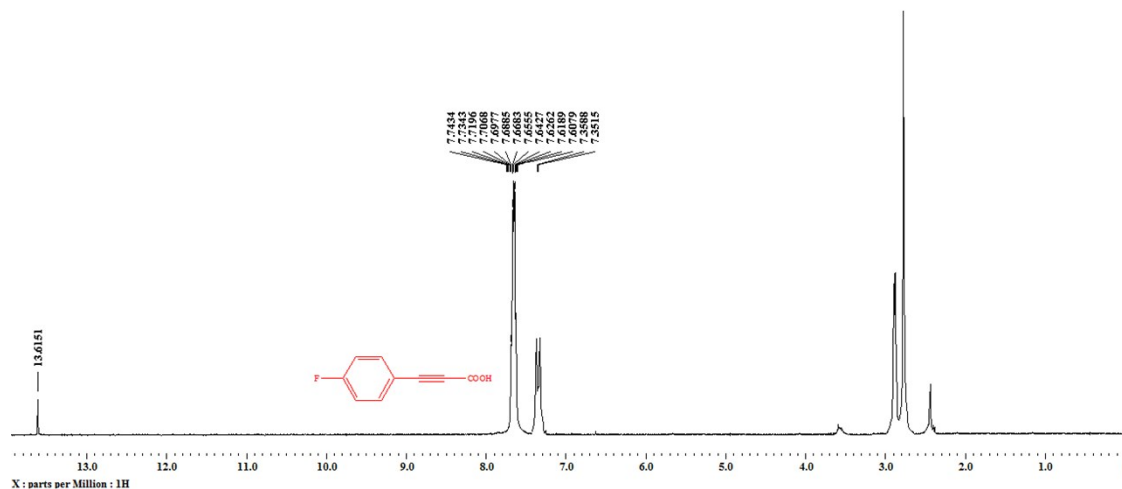
^1H NMR (400 MHz, CDCl_3): δ = 7.64 (d, J = 10.2 Hz, 2H, Ar-H), 7.44 (d, J = 8.8 Hz, 2H, Ar-H); ^{13}C NMR (400MHz, CDCl_3): δ = 153.20 (-COOH), 134.90, 133.38, 128.48, 117.28, 82.55, 82.32, 40.10, 40.06, 39.76, 39.53, 39.04, 38.97, 38.61; GCMS m/z (% rel. inten.) 181 (M^+ , 100).



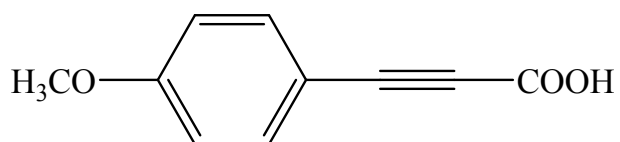
4-Fluorophenylacetylenic acid:



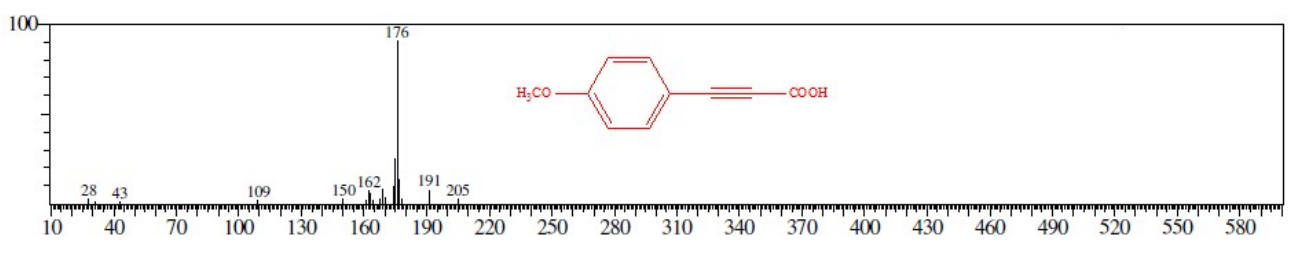
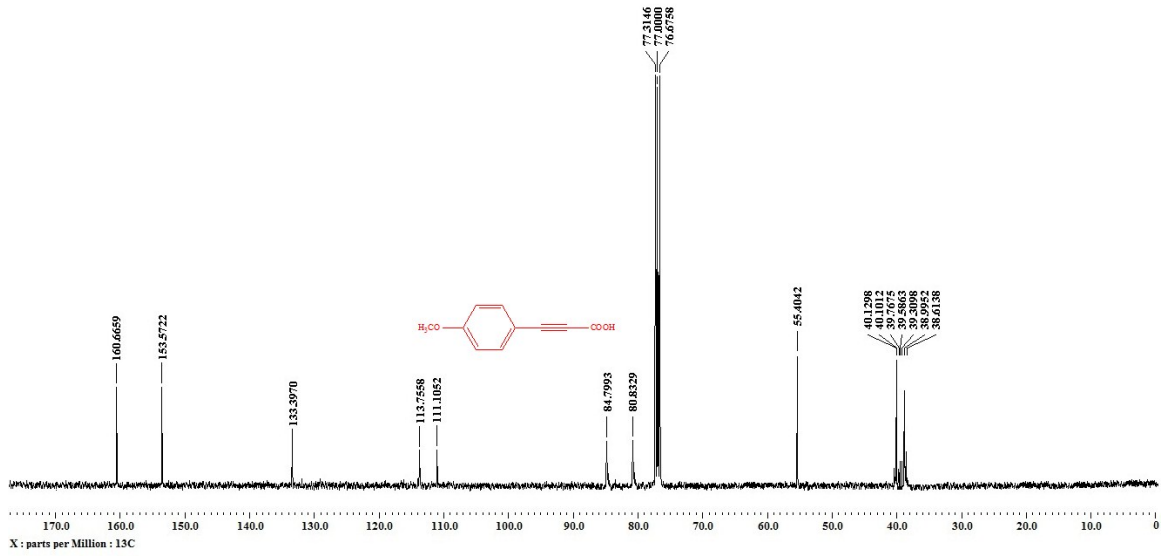
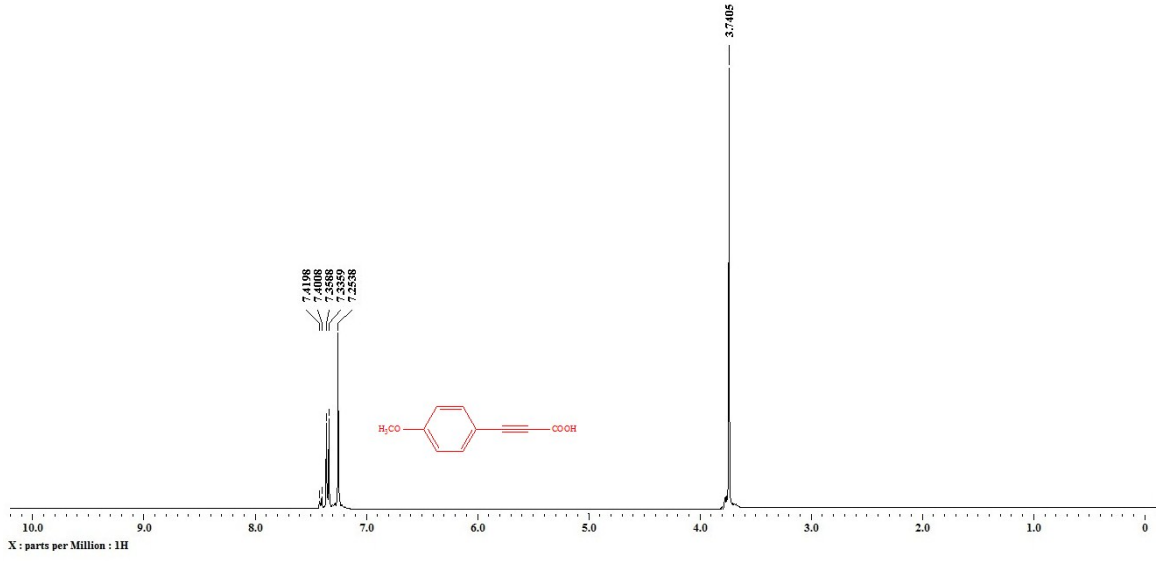
$^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ =13.61 (s, 1H), 7.74-7.60 (m, 2H), 7.35 (d, J = 2.9 Hz, 2H); $^{13}\text{C NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ = 162.31 (-COOH), 154.23, 135.35, 116.53, 116.35, 83.34, 81.66; GCMS m/z (% rel. inten.) 165 (M^+ , 100).



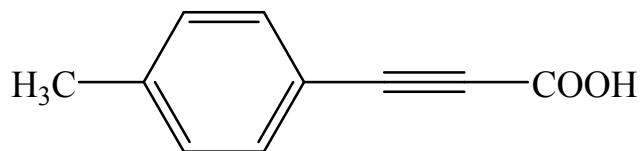
3-(4-methoxyphenyl)propionic acid:



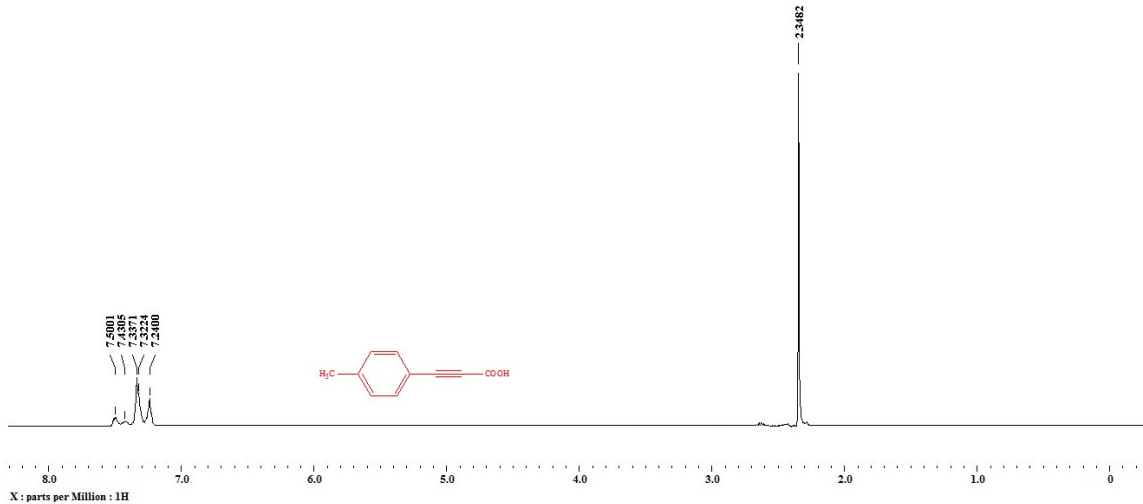
^1H NMR (400 MHz, CDCl_3): δ = 7.41 (d, J = 7.6 Hz, 2H, Ar-H), 7.34 (d, J = 9.1 Hz, 2H, Ar-H), 3.74 (s, 3H, CH_3); ^{13}C NMR (400 MHz, CDCl_3): δ = 160.66(-COOH), 153.57, 133.39, 113.75, 111.10, 84.79, 80.83, 55.40, 40.12, 40.10, 39.76, 39.58, 39.30, 38.99, 38.61; GCMS m/z (% rel. inten.) 176 (M^+ , 100).

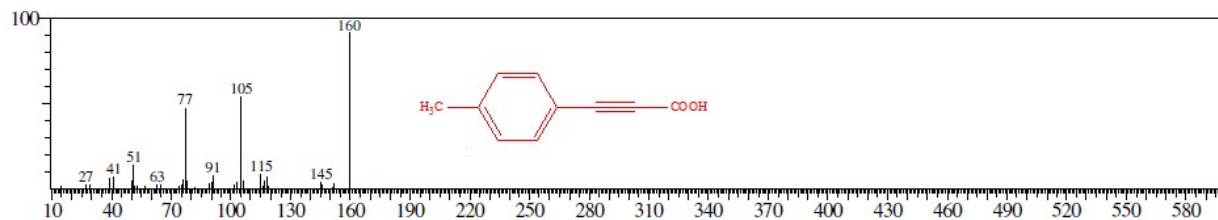
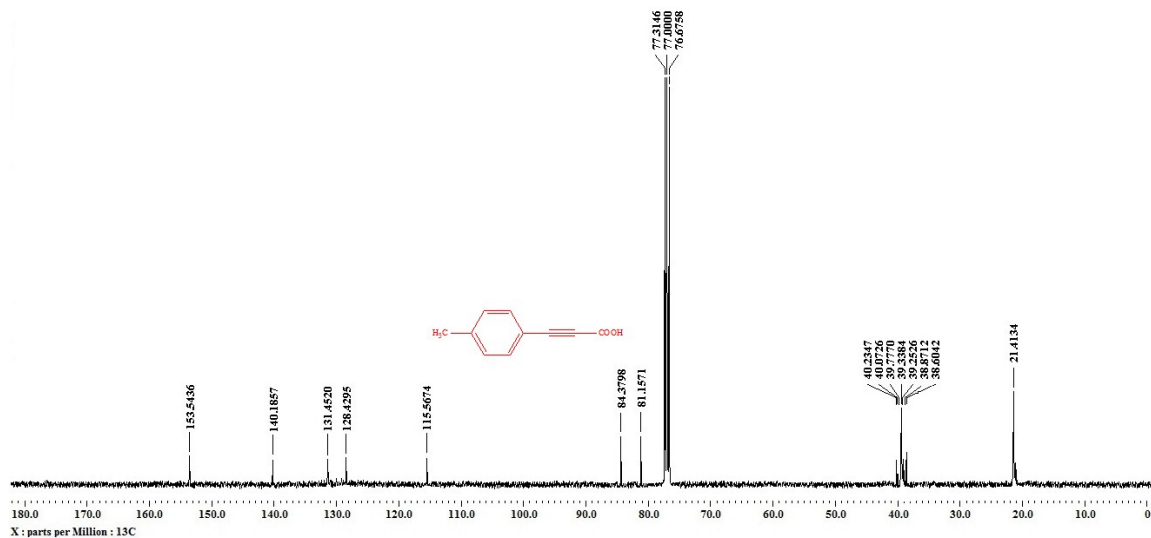


3-p-tolylpropionic acid:

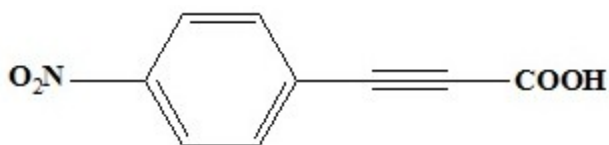


¹H NMR (400 MHz, CDCl₃): δ = 7.46 (d, J = 27.8 Hz, 2H, Ar-H), 7.32 (d, J = 5.8 Hz, 2H, Ar-H), 2.34 (s, 3H, CH₃); ¹³C NMR (400 MHz, CDCl₃): δ = 153.54 (-COOH), 140.18, 131.45, 128.42, 115.56, 84.37, 81.15, 40.23, 40.07, 39.77, 39.33, 39.25, 38.87, 38.60, 21.41; GCMS m/z (% rel. inten.) 160 (M⁺, 100).

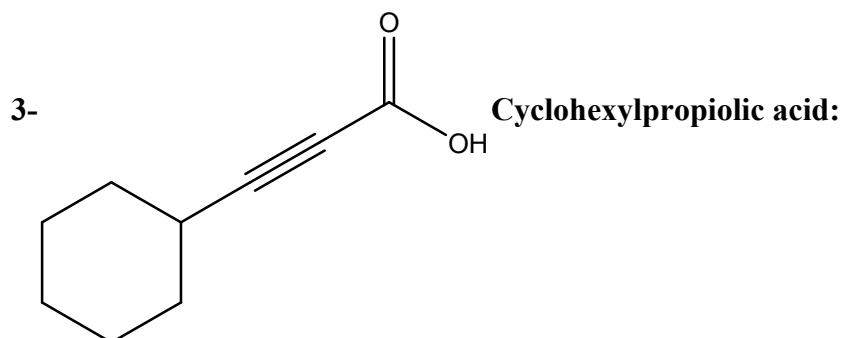
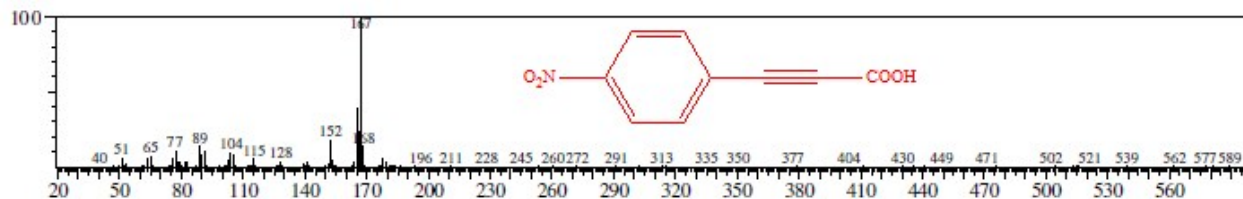
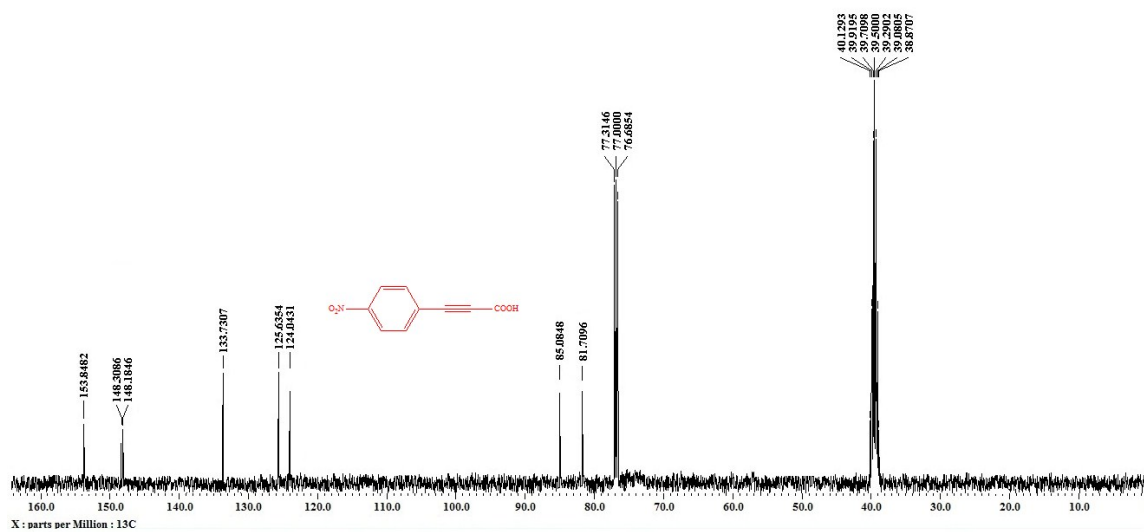
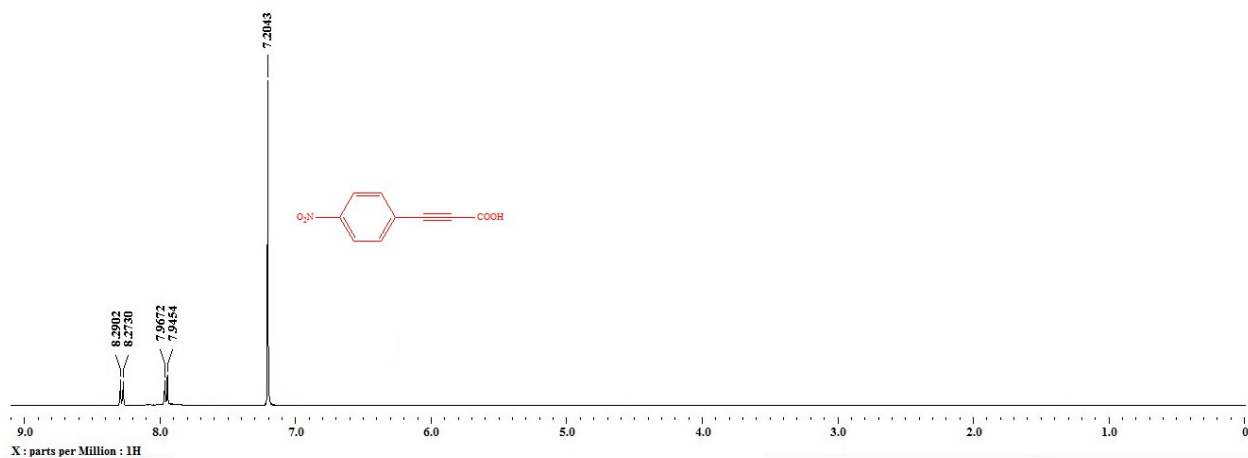




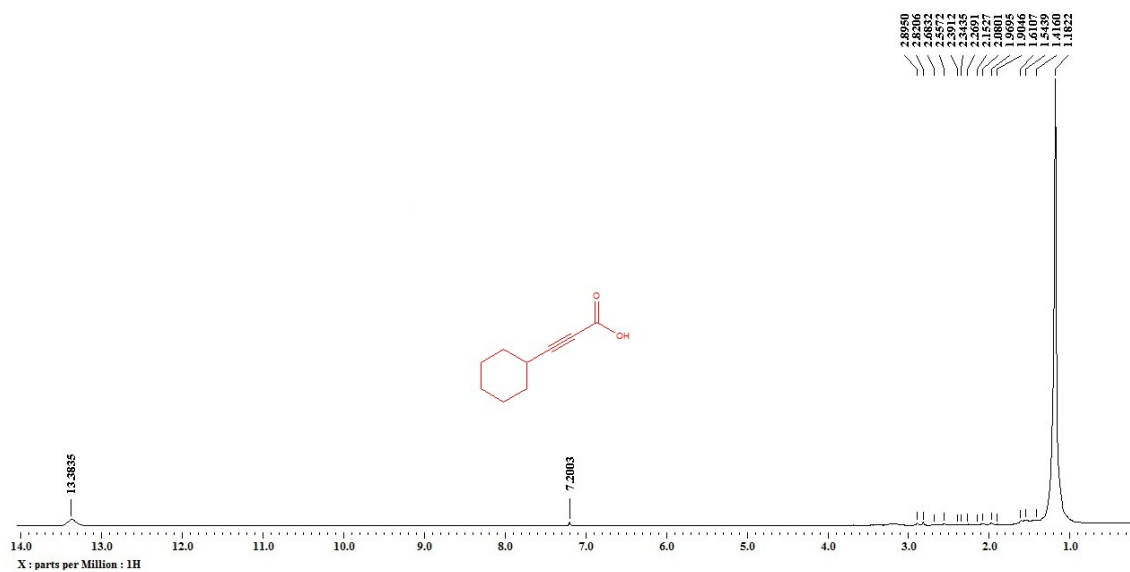
4-nitrophenylpropionic acid:

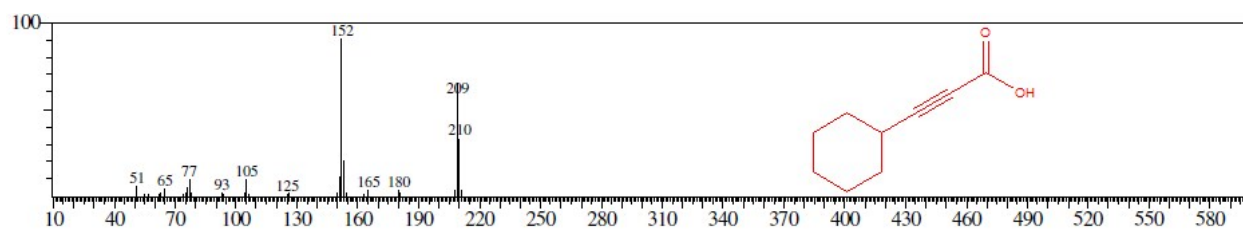
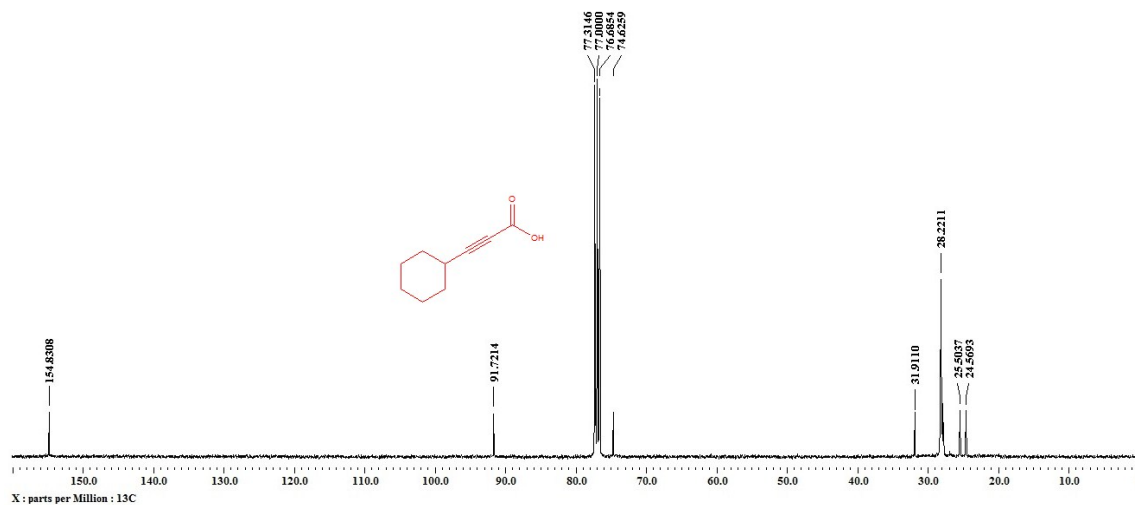


^1H NMR (400 MHz, CDCl_3): δ = 8.28 (d, J = 6.8 Hz, 2H, Ar-H), 7.95 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (400MHz, CDCl_3): δ = 153.84 (-COOH), 148.30, 148.18, 133.73, 125.63, 124.04, 85.08, 81.70, 40.12, 39.91, 39.70, 39.50, 39.29, 39.08, 38.87; GCMS m/z (% rel. inten.) 167 (M^+ , 100).

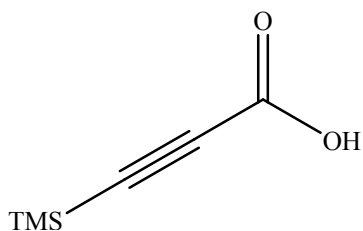


^1H NMR (400 MHz, CDCl_3): δ = 13.38 (br, s, 1H), 2.89- 2.55 (m, 1H), 2.26-2.39 (m, 2H), 1.90-2.15 (m, 2H), 1.61-1.18 (m, 6H); ^{13}C NMR (400 MHz, CDCl_3): δ = 154.83, 91.72, 74.62, 31.91, 28.22, 25.50, 24.56; GCMS m/z (% rel. inten.) 152 (M^+ , 100).

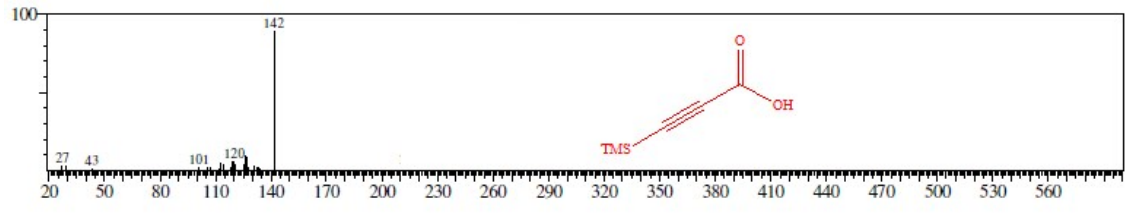
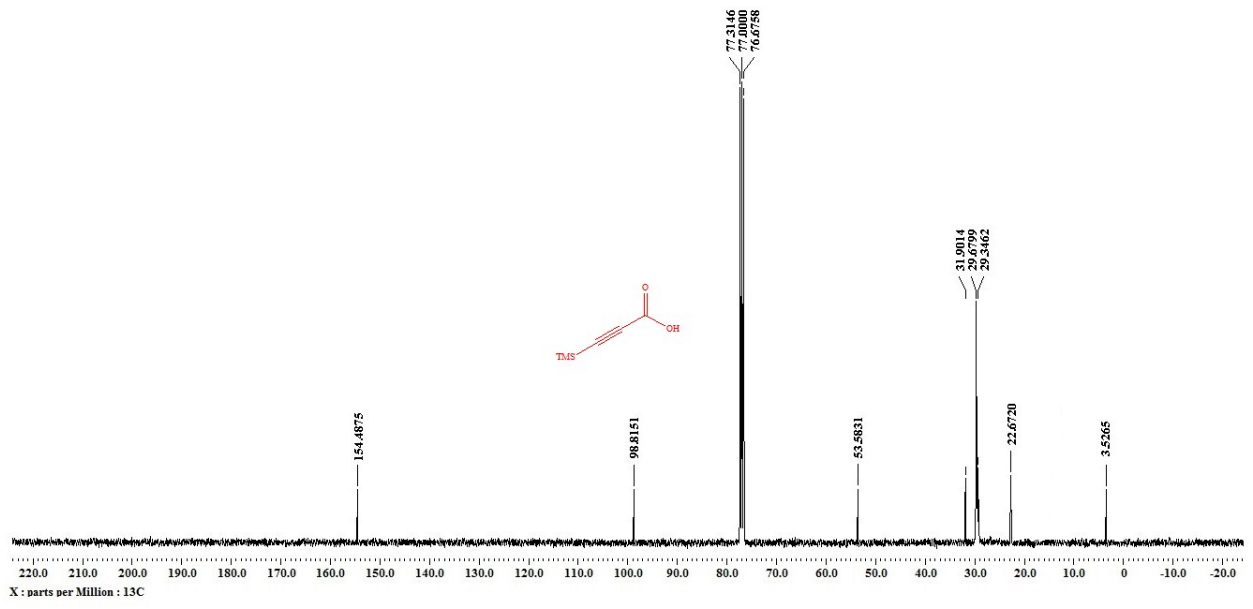
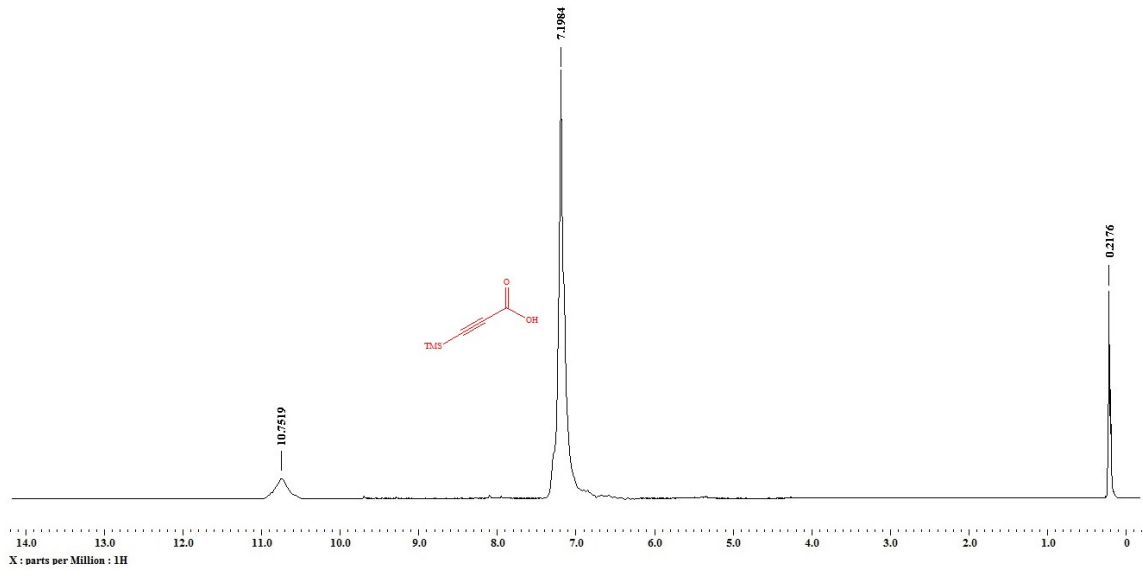




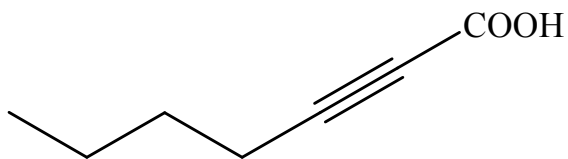
3-(trimethylsilyl)propionic acid:



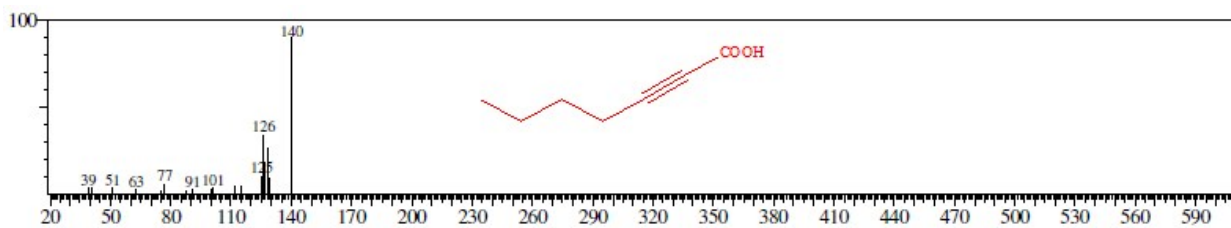
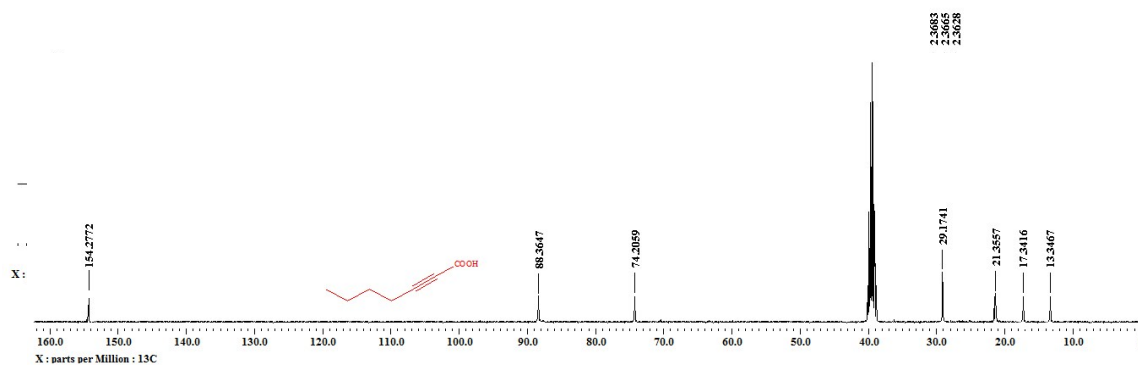
^1H NMR (400 MHz, CDCl_3): $\delta = 10.75(\text{br, s, 1H})$, $0.21(\text{s, 9H, CH}_3\text{Si})$; ^{13}C NMR (400 MHz, CDCl_3): $\delta = 154.48$, 98.81 , 53.58 , 31.90 , 29.67 , 29.34 , 22.67 , 3.52 ; GCMS m/z (% rel. inten.) $142(\text{M}^+, 100)$.



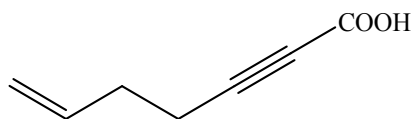
Hept-2-ynoic acid:



^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ = 13.12 (s, 1H), 2.36 (t, J = 1.4 Hz, 2H, CH_2); 1.46 (p, J = 2.9 Hz, 2H, CH_2); 1.36 (h, J = 1.4 Hz, CH_2); 0.89 (t, J = 2.2 Hz, 3H, CH_3); ^{13}C NMR (400 MHz, $\text{DMSO-}d_6$): δ = 154.27, 88.36, 74.20, 29.17, 21.35, 17.34, 13.34; GCMS m/z (% rel. inten.) 140 (M^+ , 100).



Hept-6-en-2-ynoic acid:



^1H NMR (400 MHz, $\text{DMSO-}d_6$): $\delta=13.12$ (s, 1H), 5.87 (dd, $J = 3.0$ Hz, 1H, CH), 5.08 (dd, $J = 1.0$ Hz, 2H, CH_2), 2.46 (t, $J = 1.2$ Hz, 2H, CH_2), 2.28 (q, $J = 1.0$ Hz, 2H, CH_2);

^{13}C NMR (400 MHz, $\text{DMSO-}d_6$): $\delta = 154.24, 136.31, 116.30, 87.68, 74.40, 31.12, 17.34$;

GCMS m/z (% rel. inten.) 138 (M^+ , 100).

