1,1′-bis(di-*tert*-butylphosphino) ferrocene copper(I) complex catalyzed C-H activation and carboxylation of terminal alkynes

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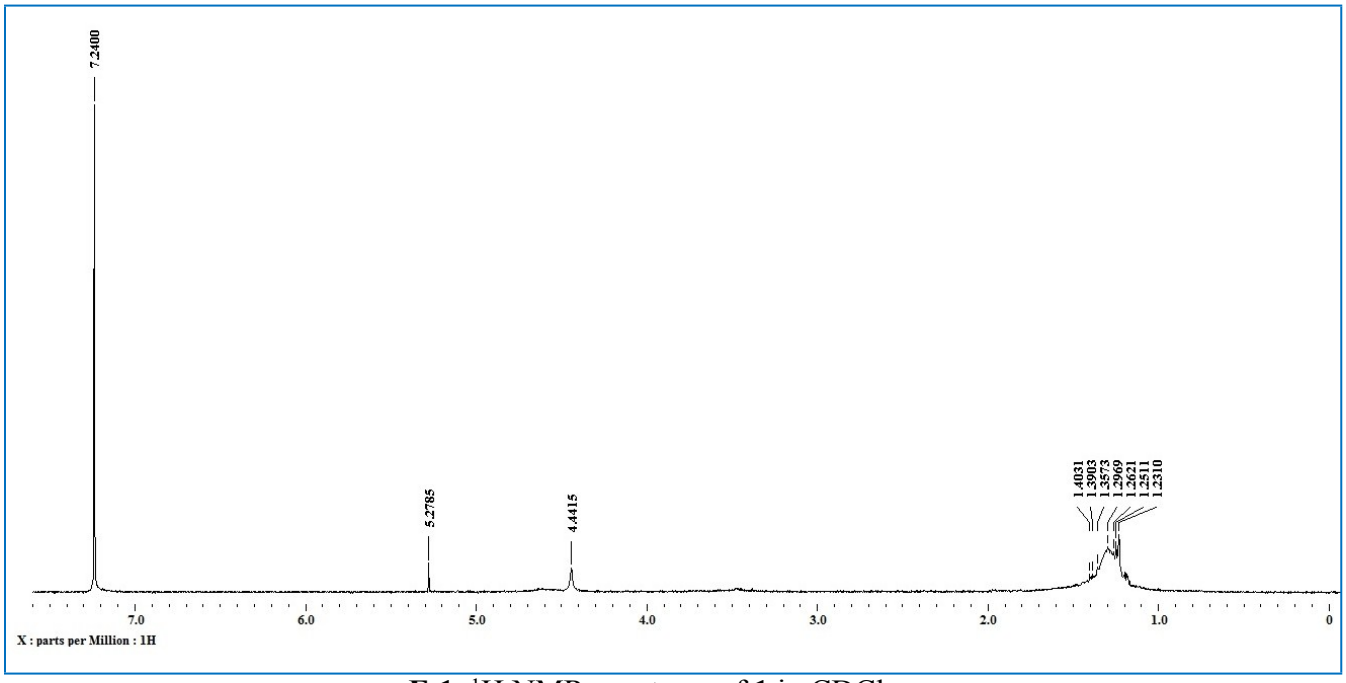
Supporting Information

Table 1: Crystallographic data for **2**, and **4**.

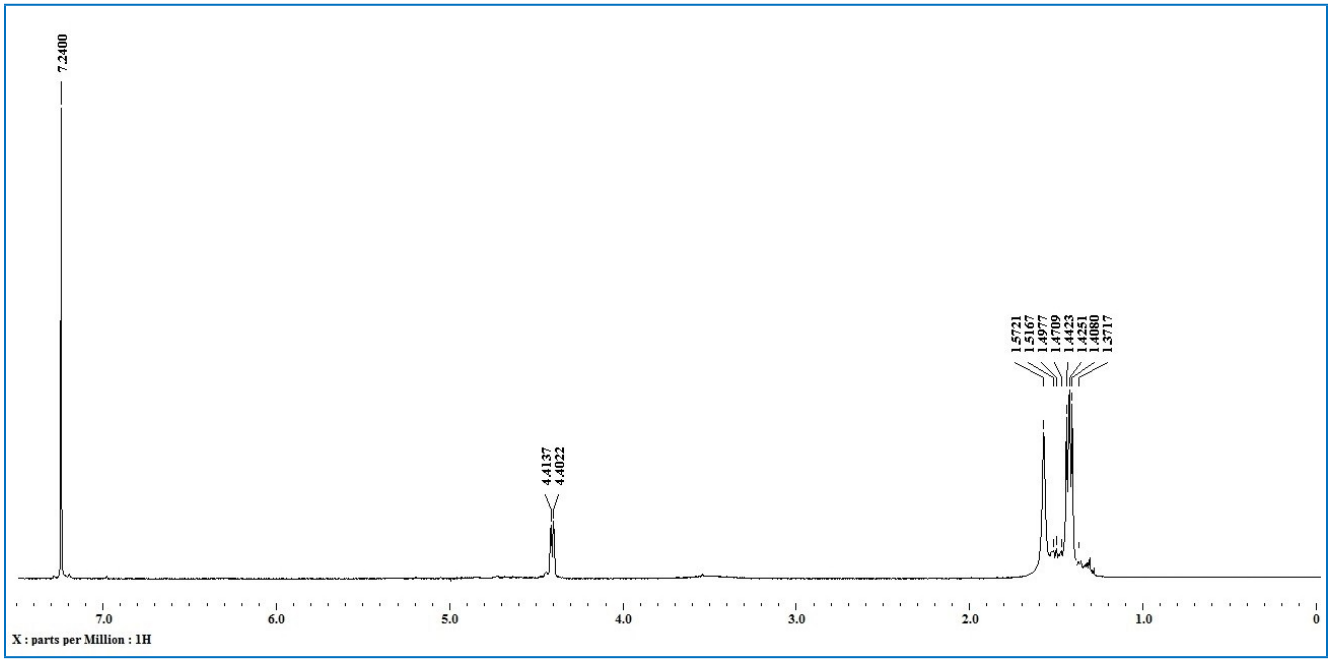
	2	**4**
Empirical Formula	$C_{26}H_{44}CuFeIP_2$	$C_{56}H_{94}Cu_6Fe_2I_6N_2P_4$
FW	664.84	2173.55
crystal system	Orthorhombic	Triclinic
space group	P n a 2_1	P $\bar{1}$
a, Å	16.6781(8)	11.0201(6)
b, Å	8.5263(4)	11.8953(7)
c, Å	19.8071(9)	14.7688(9)
α, deg	90.00	107.370(3)
β, deg	90.00	93.230(3)
γ, deg	90.00	105.503(3)
V, Å^3	2816.6(2)	1760.87(18)
Z	4	1
d_{calc}, g cm^{-3}	1.568	2.050
μ, mm^{-1}	2.492	4.931
T, K	100(2)	100(2)
R_1 all	0.0430	0.0495
R_1 [I > 2σ(I)]	0.0293	0.0366
wR_2	0.0483	0.0939
wR_2 [I > 2σ(I)]	0.0452	0.0870
GoF	0.988	1.004

Table 3: Weak interactions for the complexes **2** and **4** [Å and °].

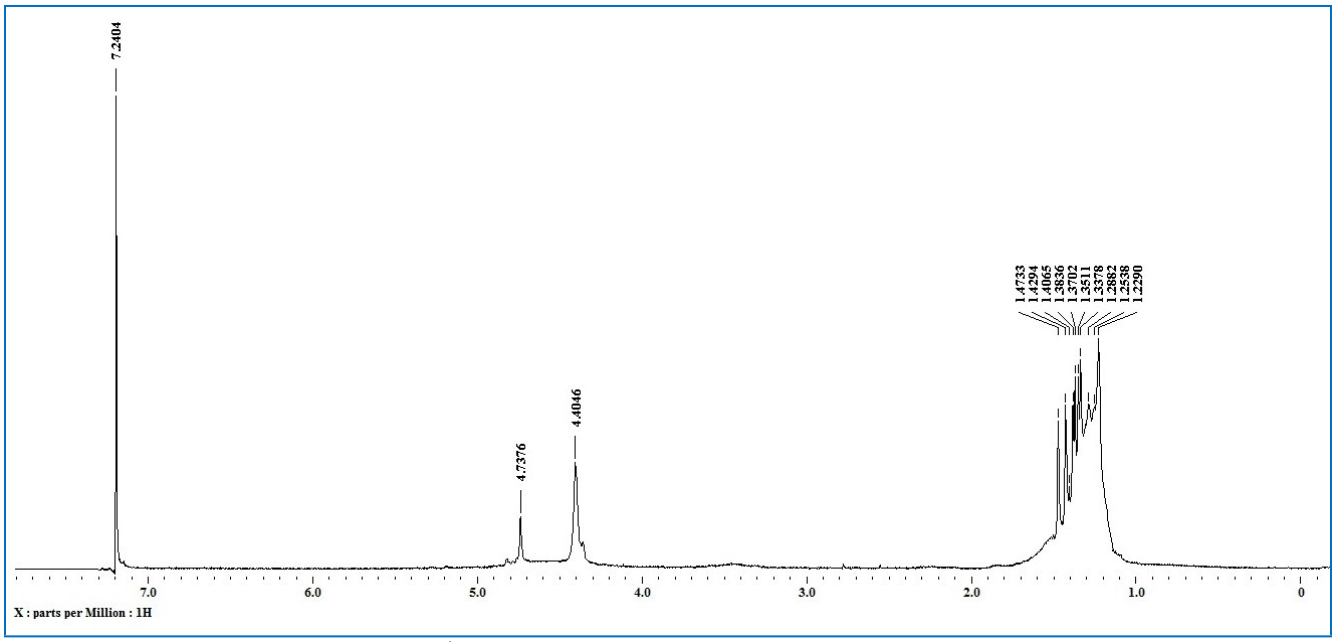
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
Complex-2				
C(7)-H(7)···I(1)$^{\#1}$	0.95	3.23	3.8299(17)	122.8
C(10)-H(10)···I(1)$^{\#2}$	0.95	3.00	3.7770(19)	140.5
C(13)-H(13C)···I(1)	0.98	3.32	4.258(3)	160.3
C(24)-H(24A)···I(1)	0.98	3.18	4.138(2)	165.8
Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x,y-1,z, $^{\#2}$ x+1/2,-y+3/2,z				
Complex-4				
C(7)-H(7)...N(1S)	0.95	2.52	3.373(4)	148.8
Symmetry transformations used to generate equivalent atoms: $^{\#1}$ -x+1,-y+1,-z+2				



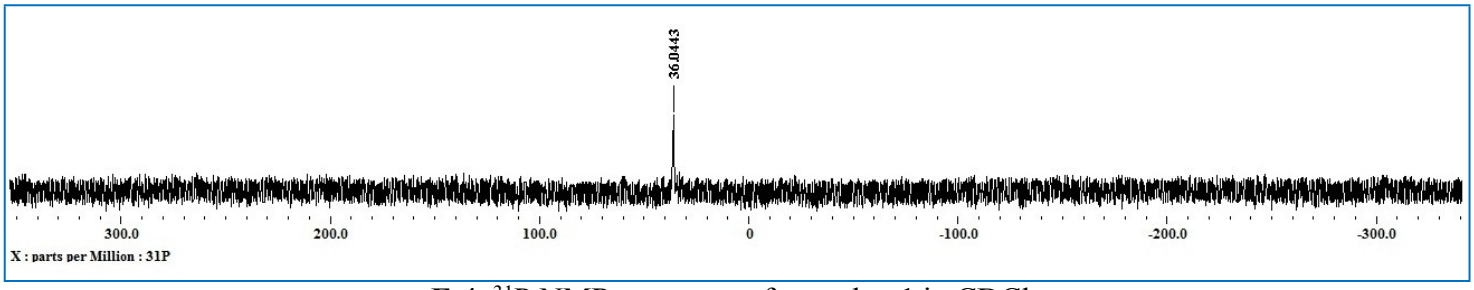
F-1. ^{1}H NMR spectrum of **1** in $CDCl_3$**.**



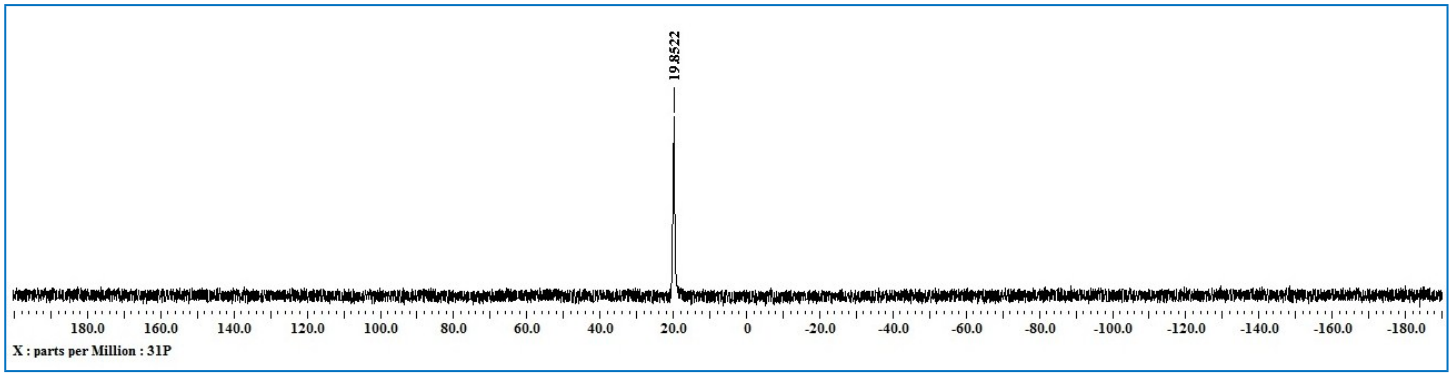
F-2. ^{1}H NMR spectrum of **2** in $CDCl_3$**.**



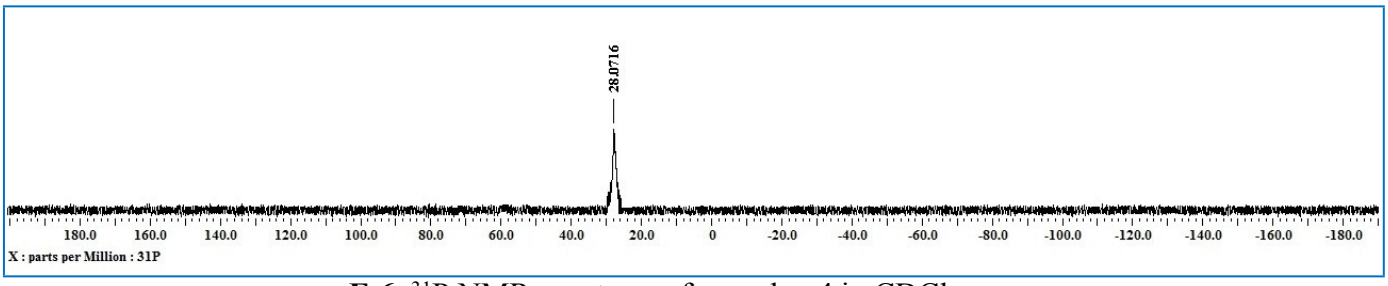
F-3. ^{1}H NMR spectrum of **4** in $CDCl_3$**.**



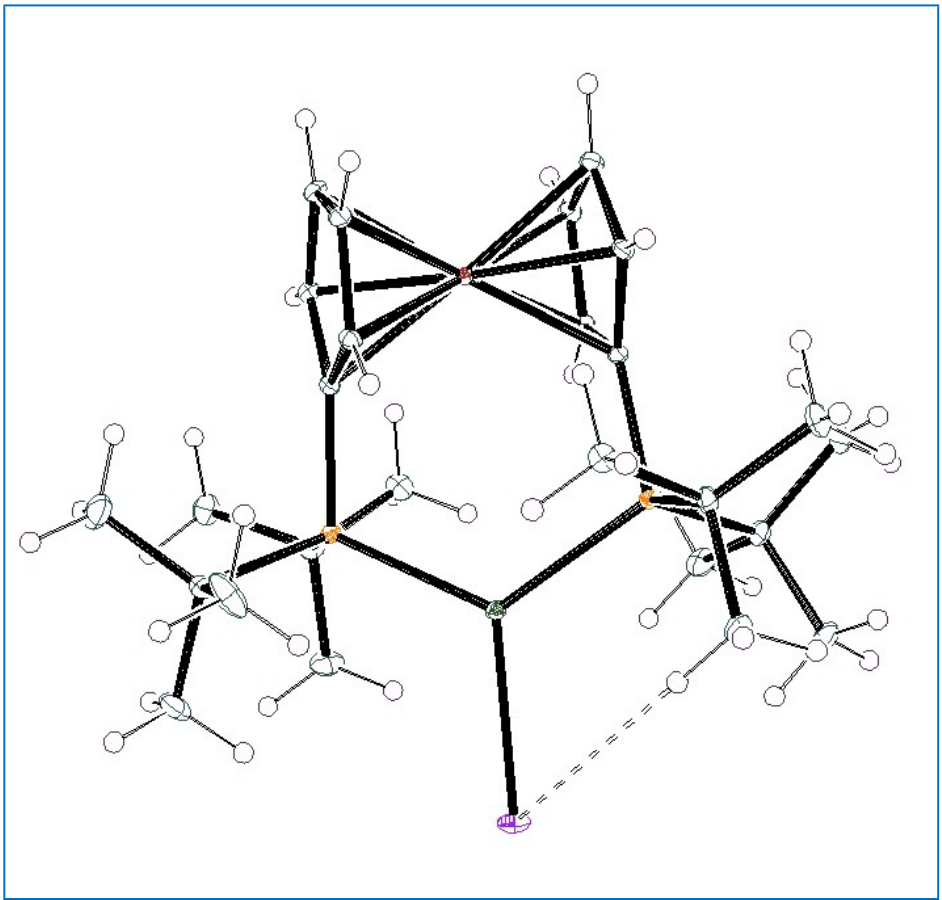
F-4. ^{31}P NMR spectrum of complex **1** in $CDCl_3$.



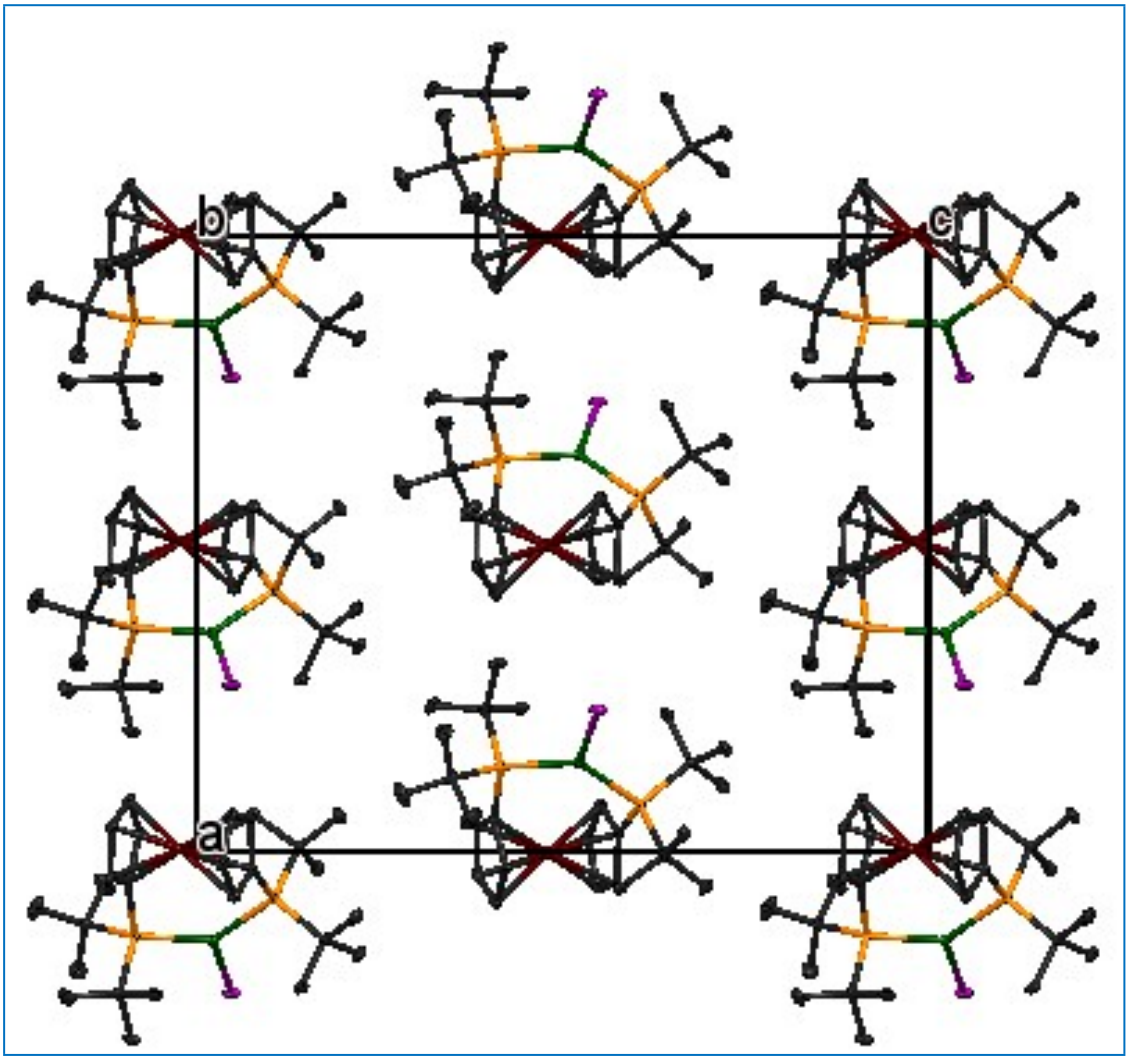
F-5. ^{31}P NMR spectrum of complex **2** in $CDCl_3$.



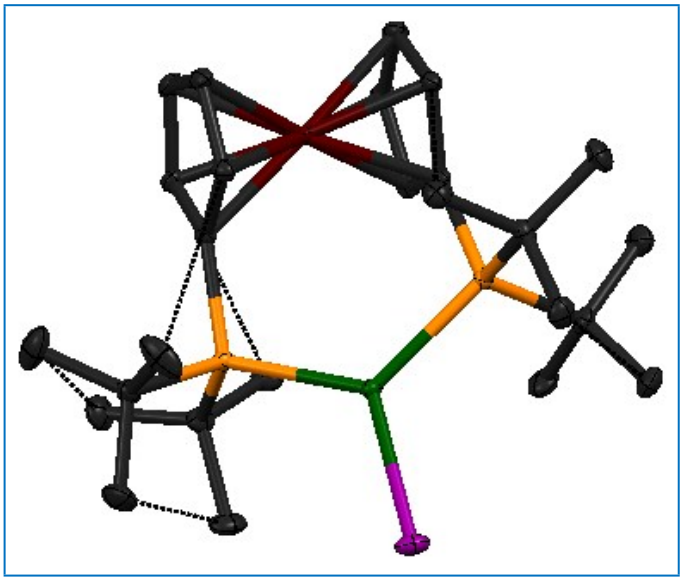
F-6. ^{31}P NMR spectrum of complex **4** in $CDCl_3$.



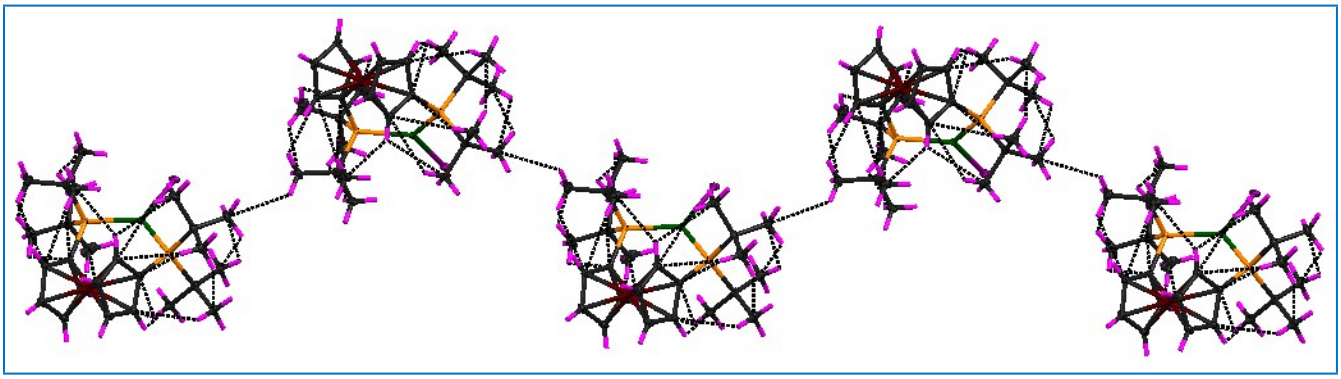
F-7. Ortep diagram of **2** showing C-H···I weak interactions in the crystal lattice.



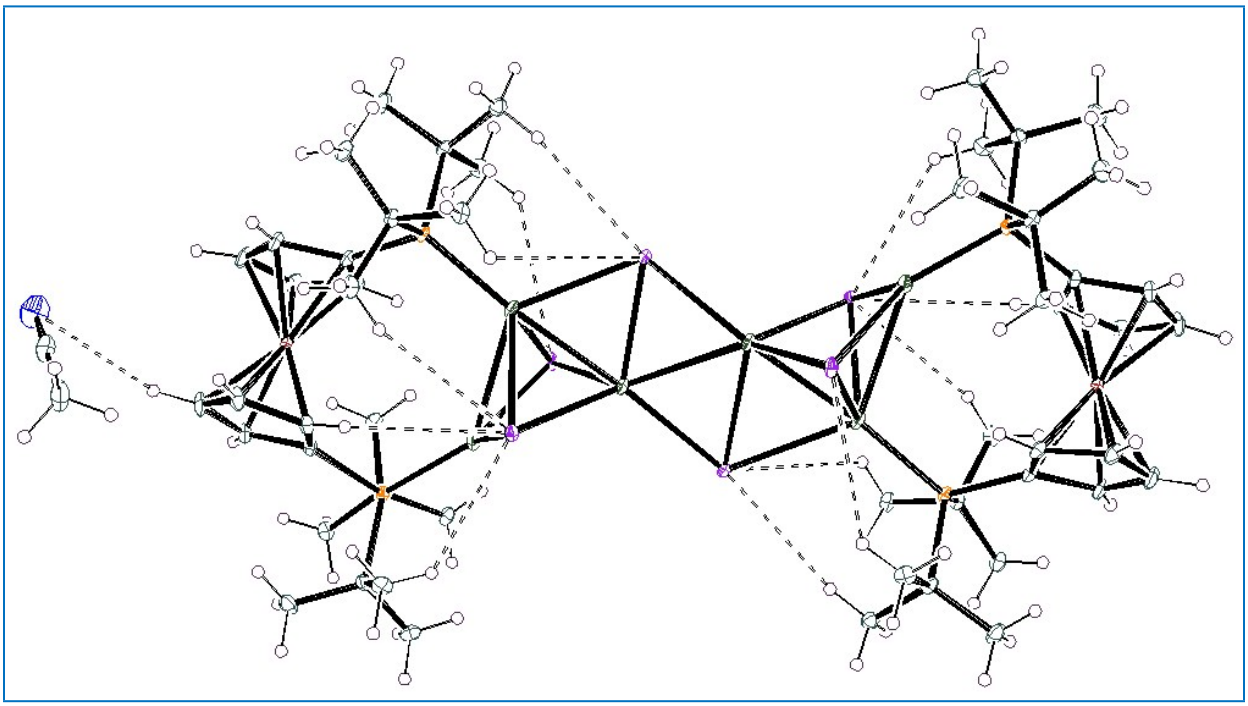
F-8. Crystal packing diagram of **2**, viewed along the *b* axis.



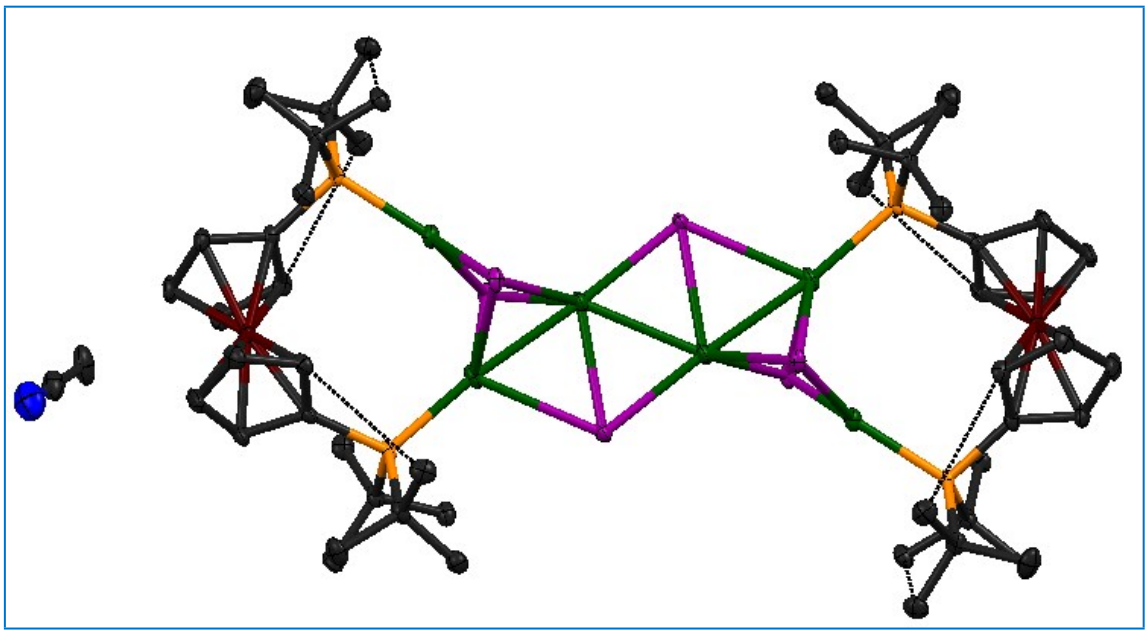
F-9. π ···π interactions in complex **2**.



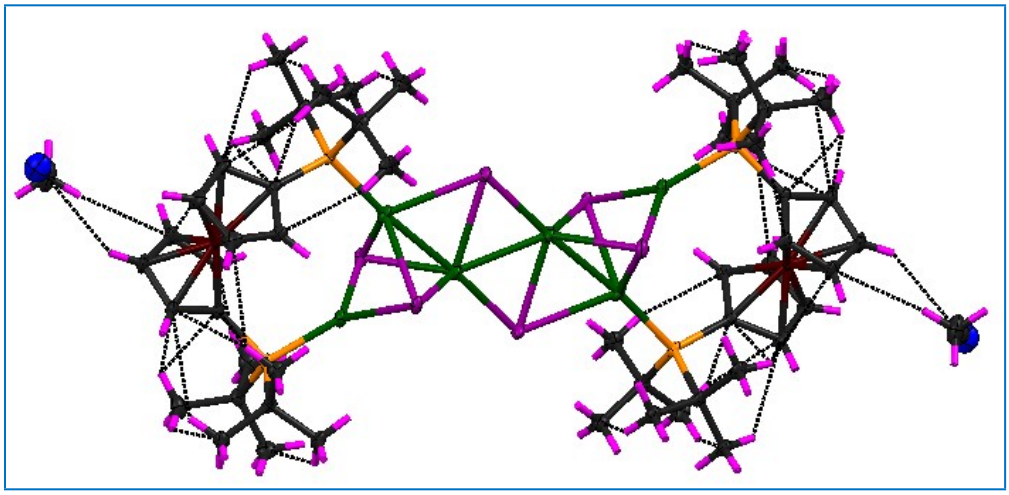
F-10. Single helical motif in complex **2** accompanied by C-H···π interactions along crystallographic '*b*'-axis.



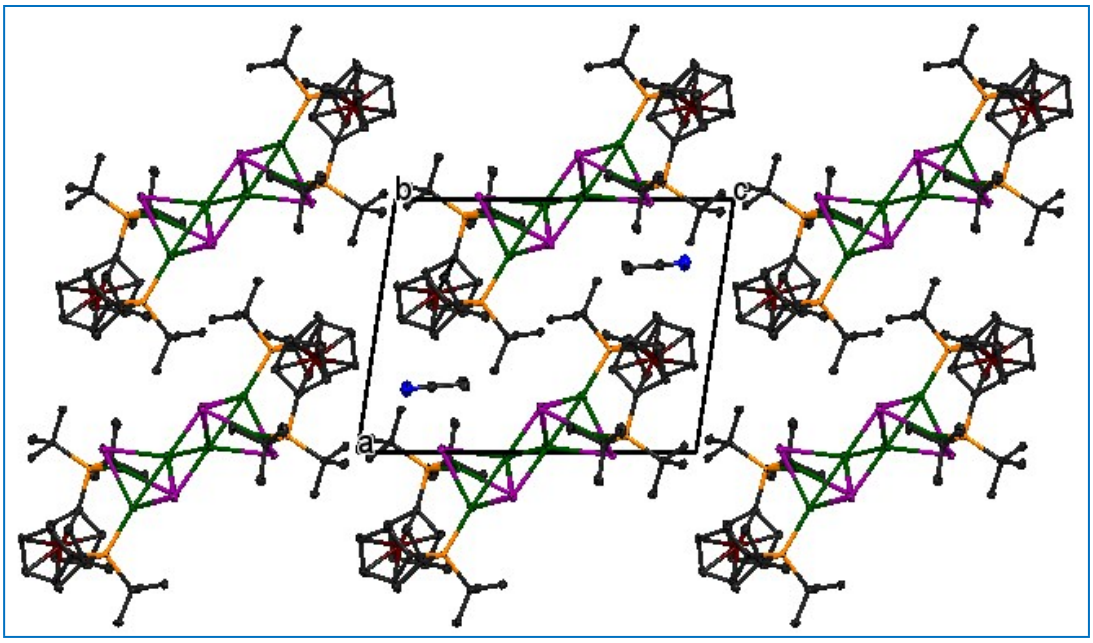
F-11. Ortep diagram of complex **4** showing C-H···I and C-H···N weak interactions in the crystal lattice.



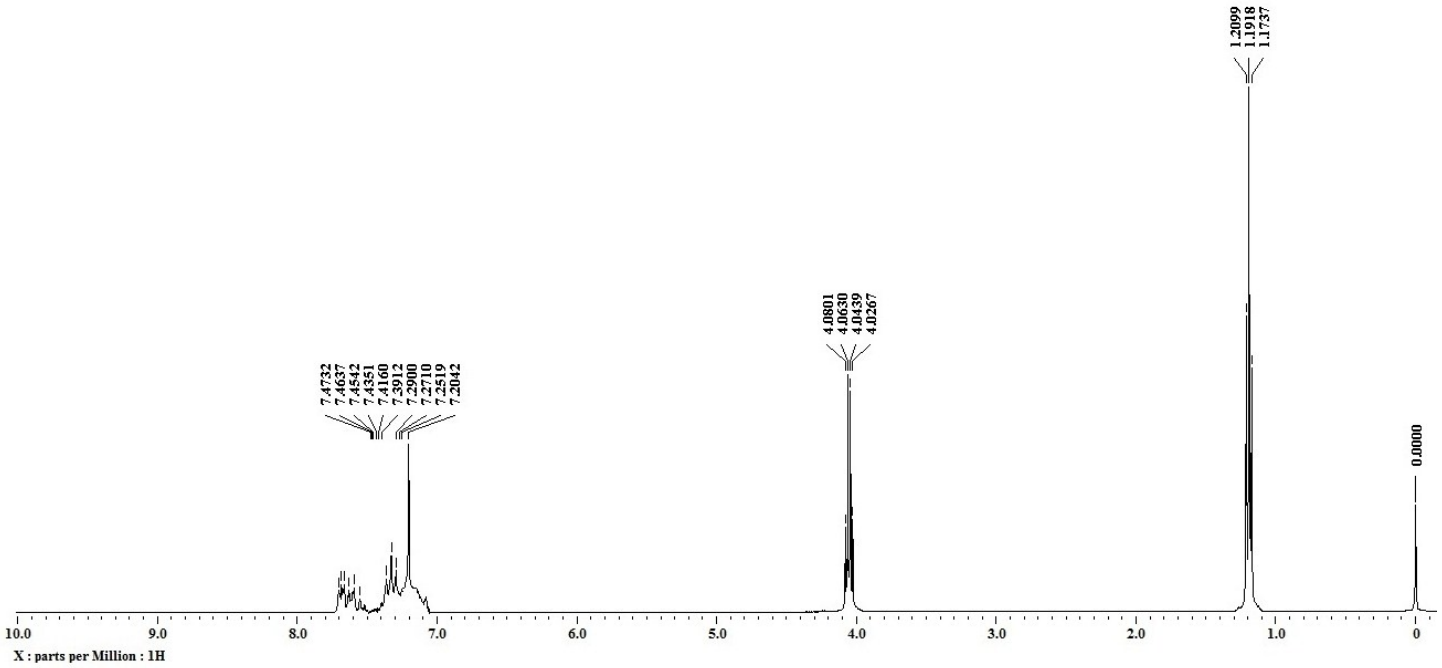
F-12. π ···π interactions in complex **4**.



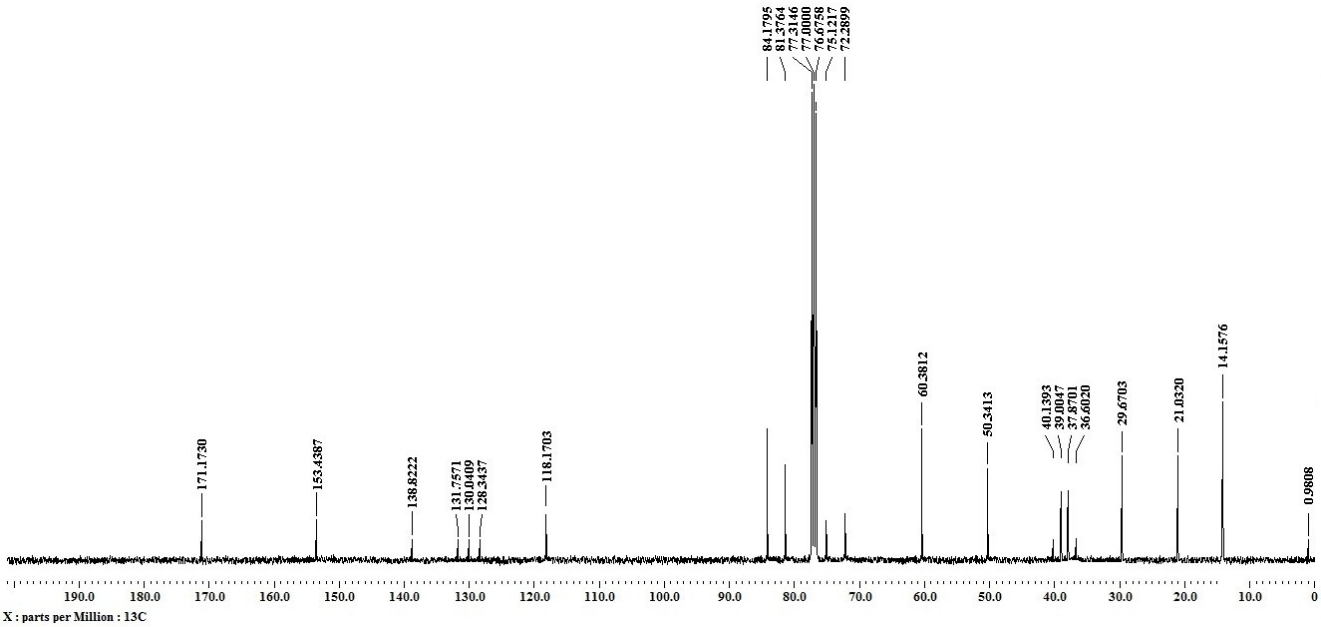
F-13. C-H···π interactions in complex **4**.



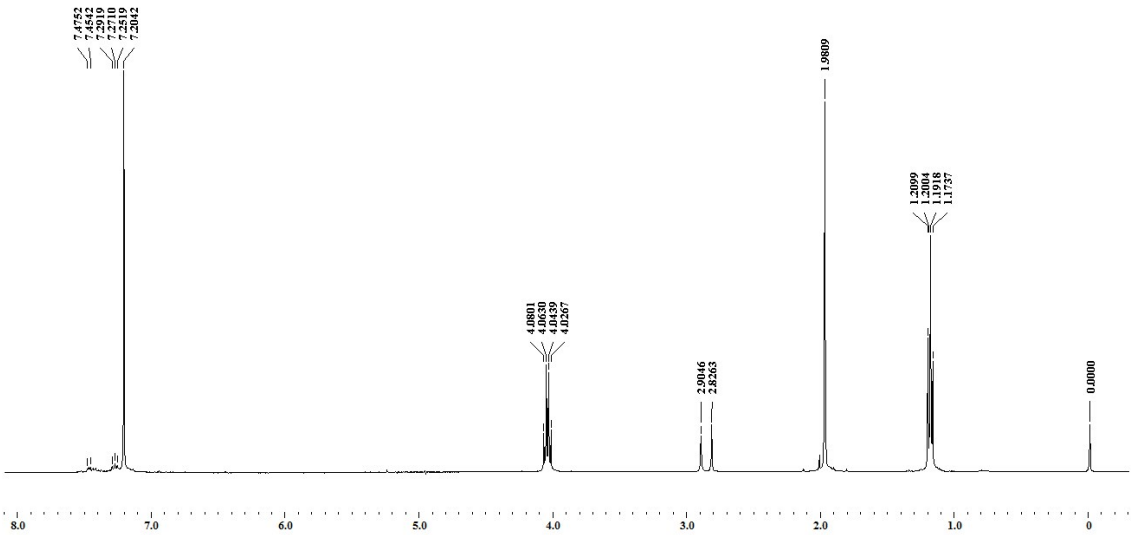
F-14. Crystal packing diagram of **4**, viewed along the *b* axis.



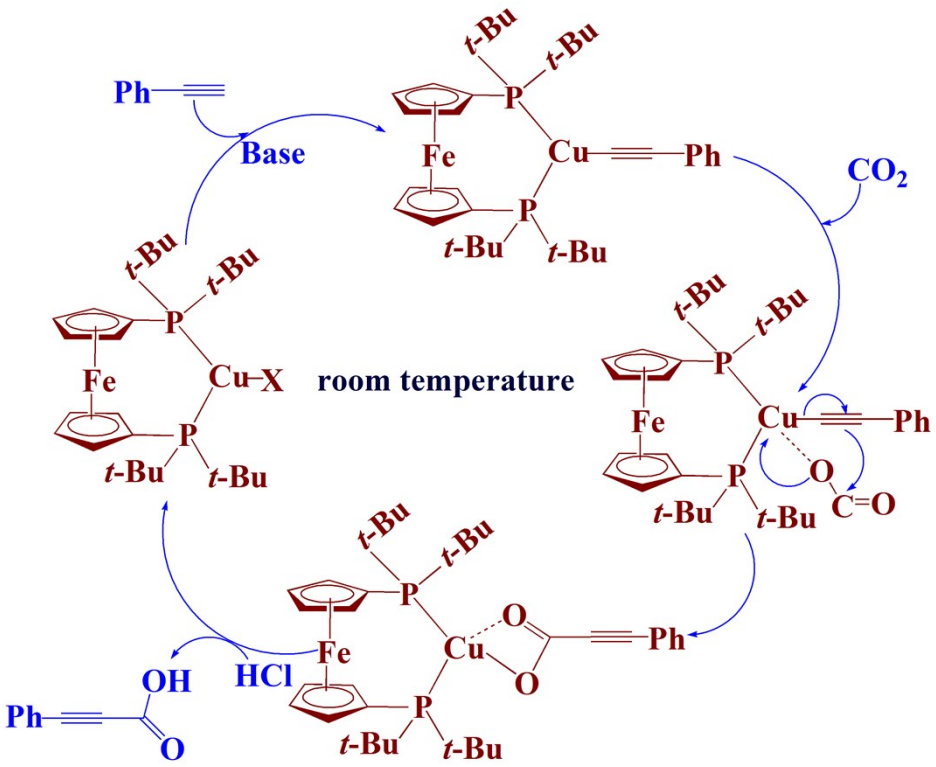
F-15. ^{1}H NMR spectrum of reaction mixture for the synthesis of 3-phenylpropiolic acid from CO_2 and Phenylacetylene catalysed by complex **2** in $CDCl_3$ after 12h at room temperature.



F-16. ^{13}C NMR spectrum of reaction mixture for the synthesis of 3-phenylpropiolic acid from CO_2 and Phenylacetylene catalysed by complex **2** in $CDCl_3$ after 12h at room temperature.



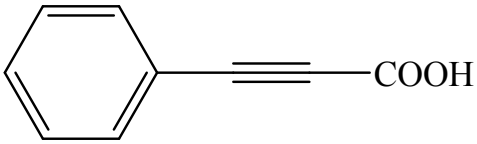
F-17. ^{1}H NMR spectrum of reaction mixture for the synthesis of 3-phenylpropiolic acid from CO_2 and Phenylacetylene catalysed by complex **2** in $CDCl_3$ after 24h at room temperature.



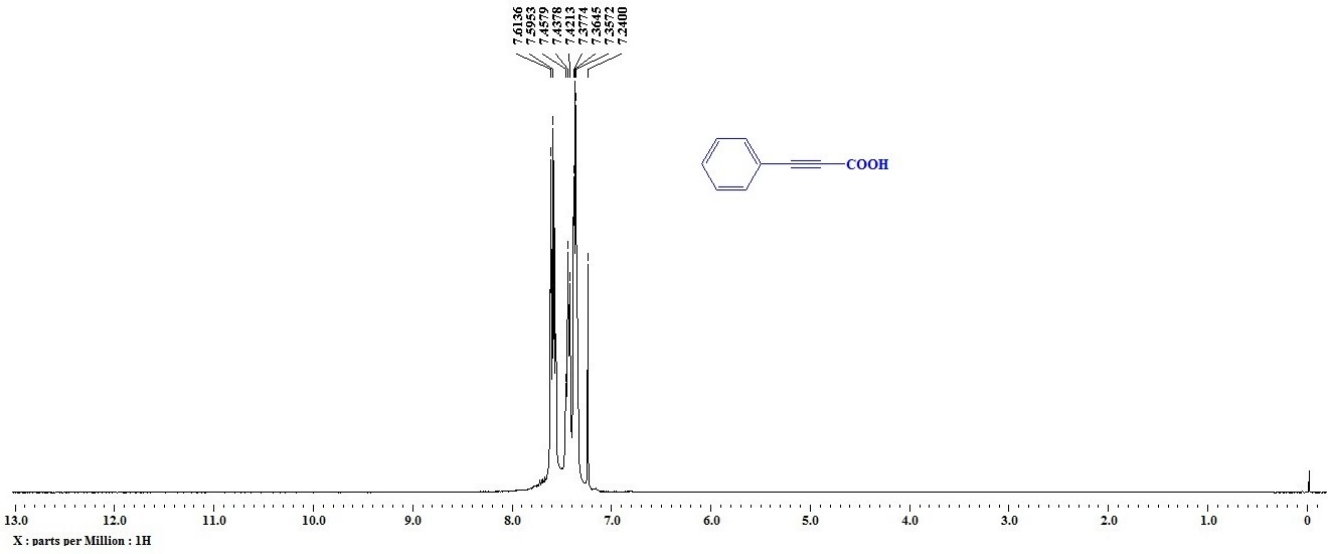
F18. The possible reaction mechanism for Cu(I) complex catalyzed C-H activating carboxylation of terminal alkynes with CO_2.

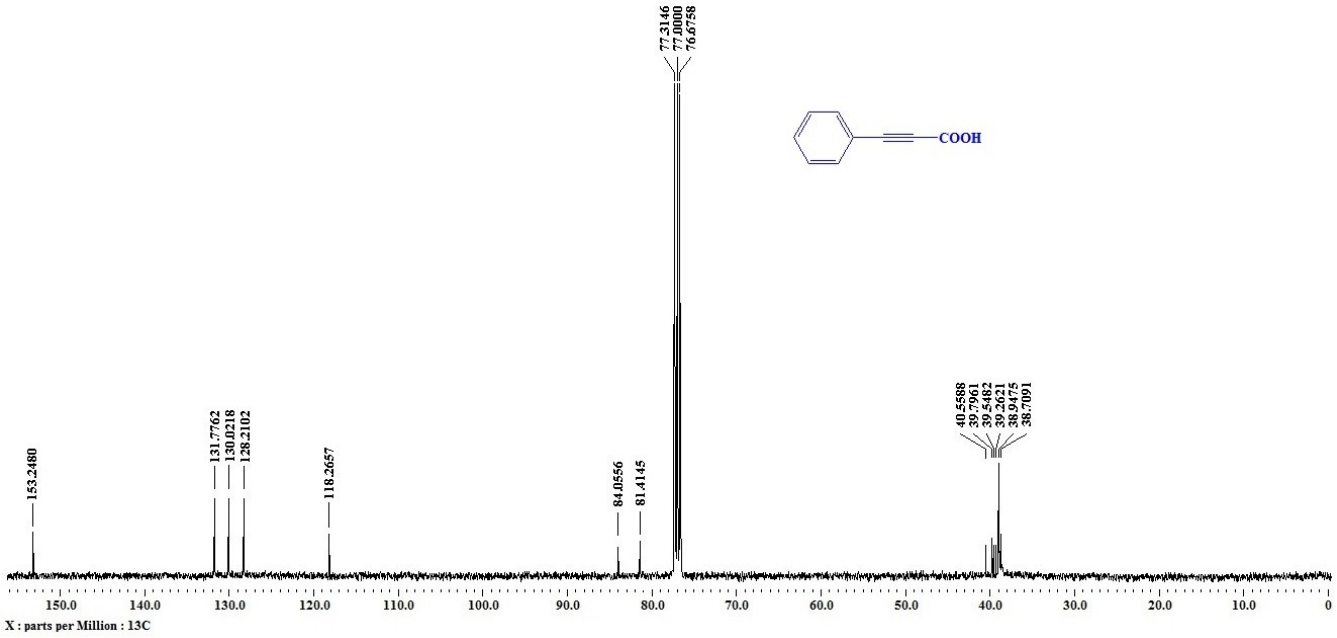
Characterization Data:

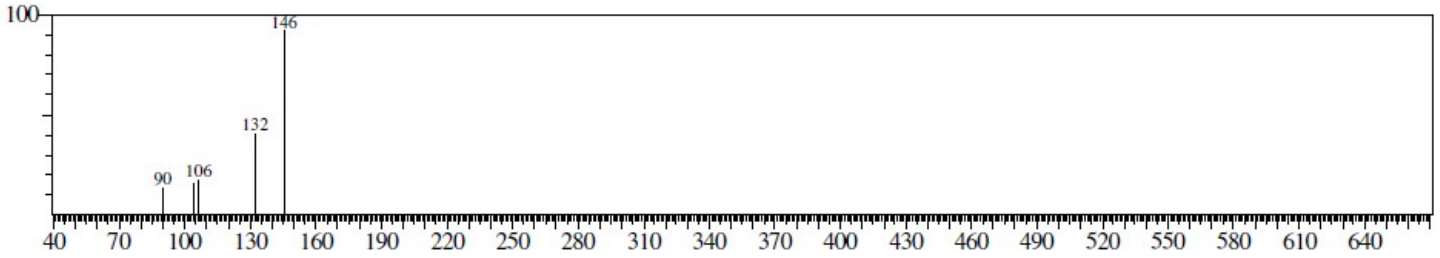
3-phenylpropiolic acid:



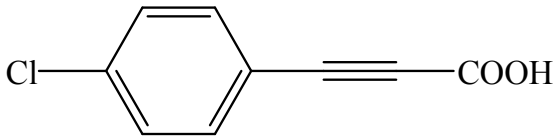
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, J = 7.3 Hz, 2H, Ar-H), 7.43 (t, J = 8.0 Hz, 1H, Ar-H), 7.36 (t, J = 5.1 Hz, 2H, Ar-H); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 153.24 (-COOH), 131.77, 130.02, 128.21, 118.26, 84.05, 81.41, 40.55, 39.77, 39.54, 39.26, 38.94, 38.70; GCMS m/z(% rel. inten.) 146 (M^+,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



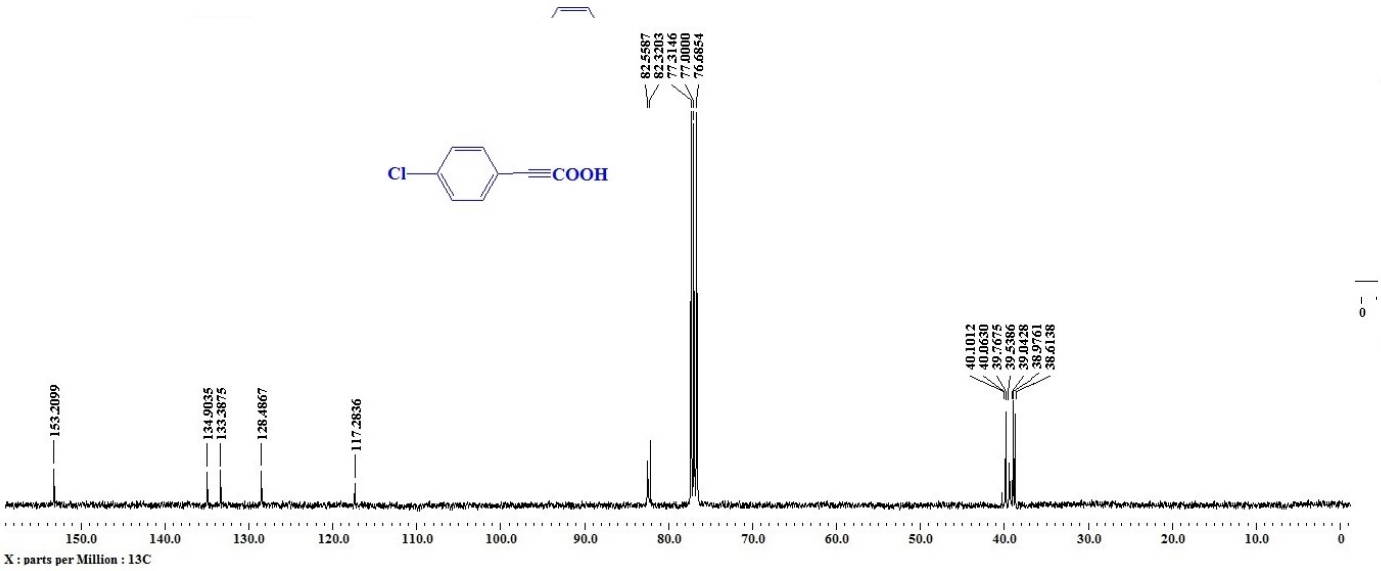


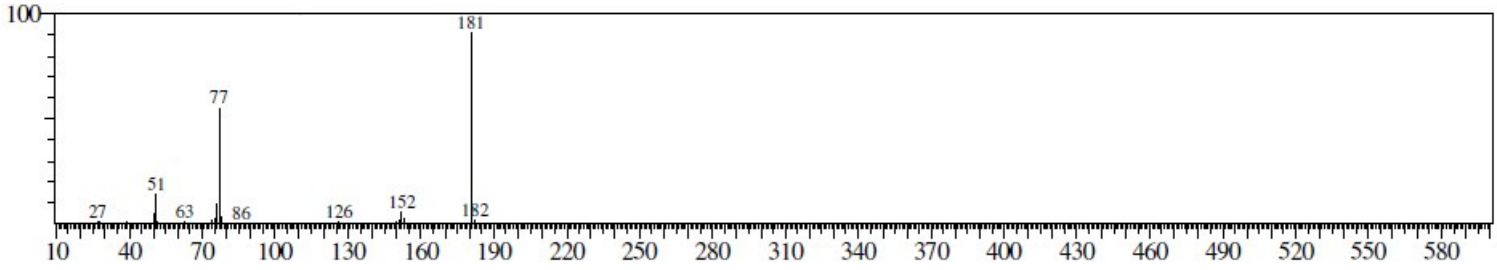


3-(4-chlorophenyl)propiolic acid:

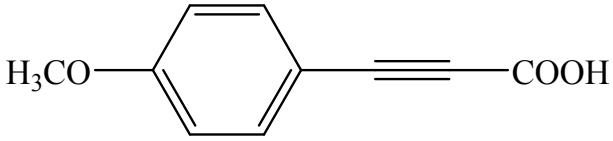


^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 10.2 Hz, 2H, Ar-H), 7.44 (d, J = 8.8 Hz, 2H, Ar-H); ^{13}C NMR (400MHz, $CDCl_3$): δ = 153.20 (-COOH), 134.90, 133.38, 128.48, 117.28, 82.55, 82.32, 40.10, 40.06, 39.76, 39.53, 39.04, 38.97, 38.61; GCMS m/z(% rel. inten.) 181 (M^+, 100).

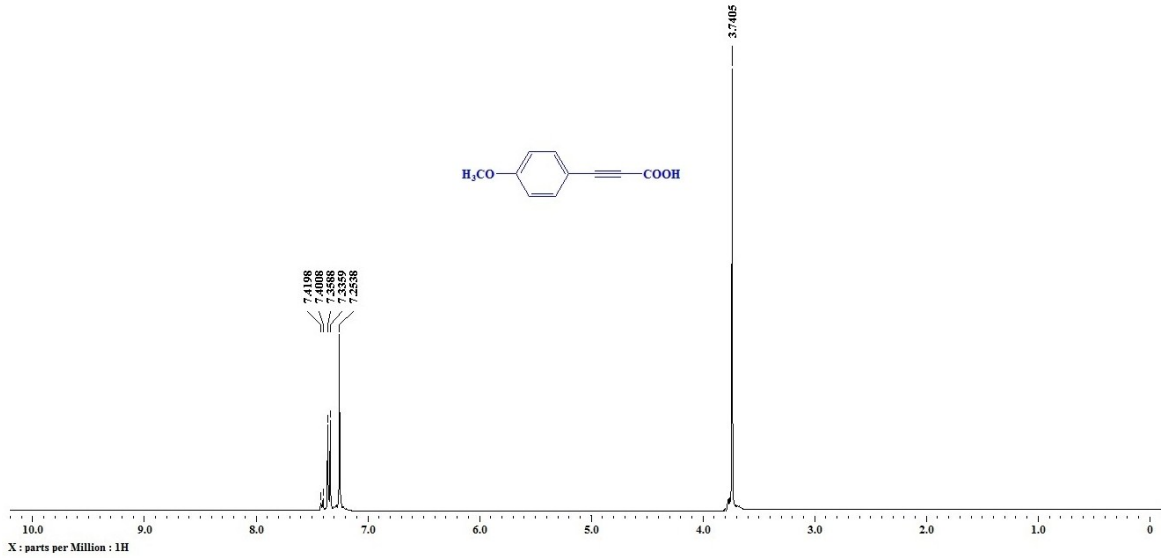


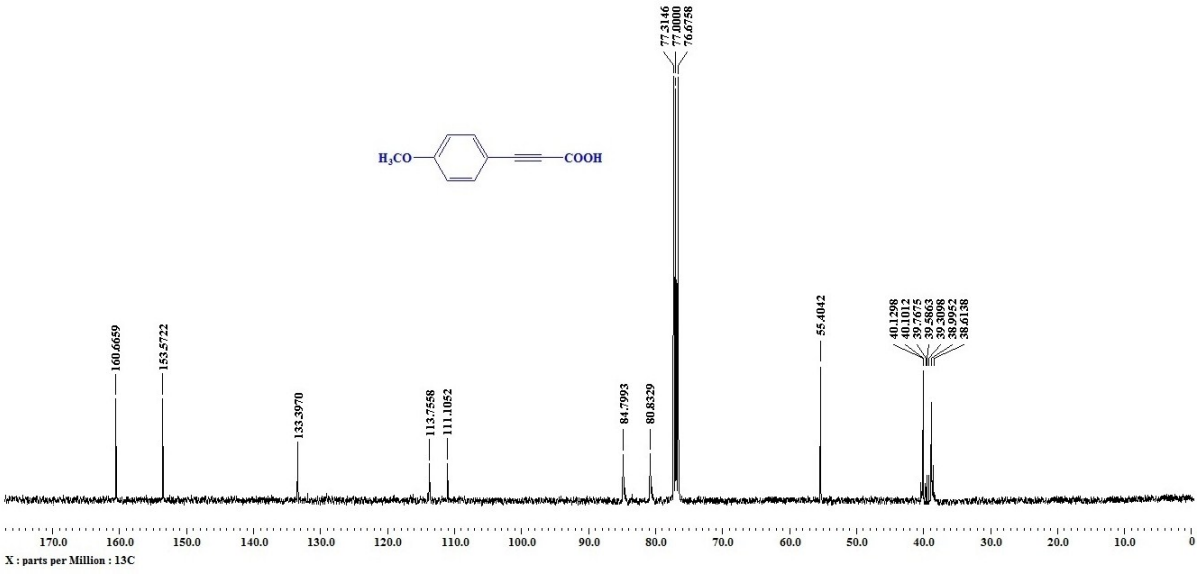


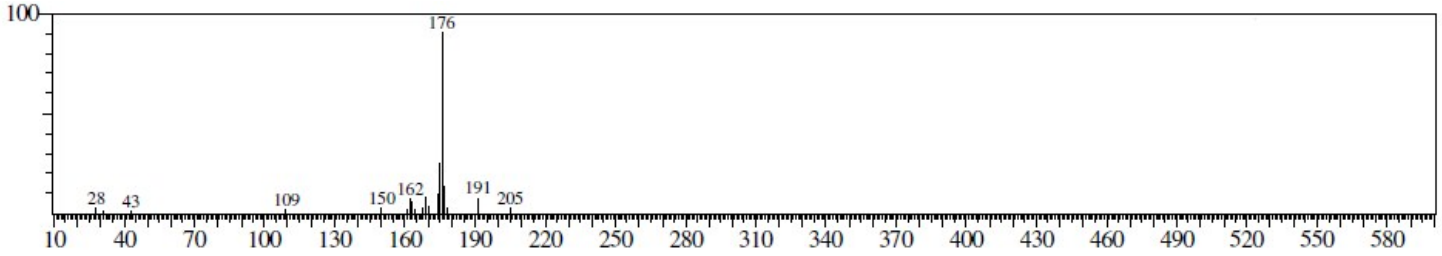
3-(4-methoxyphenyl)propiolic acid:



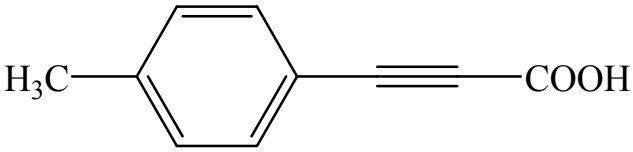
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.6 Hz, 2H, Ar-H), 7.34 (d, J = 9.1 Hz, 2H, Ar-H), 3.74 (s, 3H, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$): δ = 160.66(-COOH), 153.57, 133.39, 113.75, 111.10, 84.79, 80.83, 55.40, 40.12, 40.10, 39.76, 39.58, 39.30, 38.99, 38.61; GCMS m/z(% rel. inten.) 176 (M^+,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



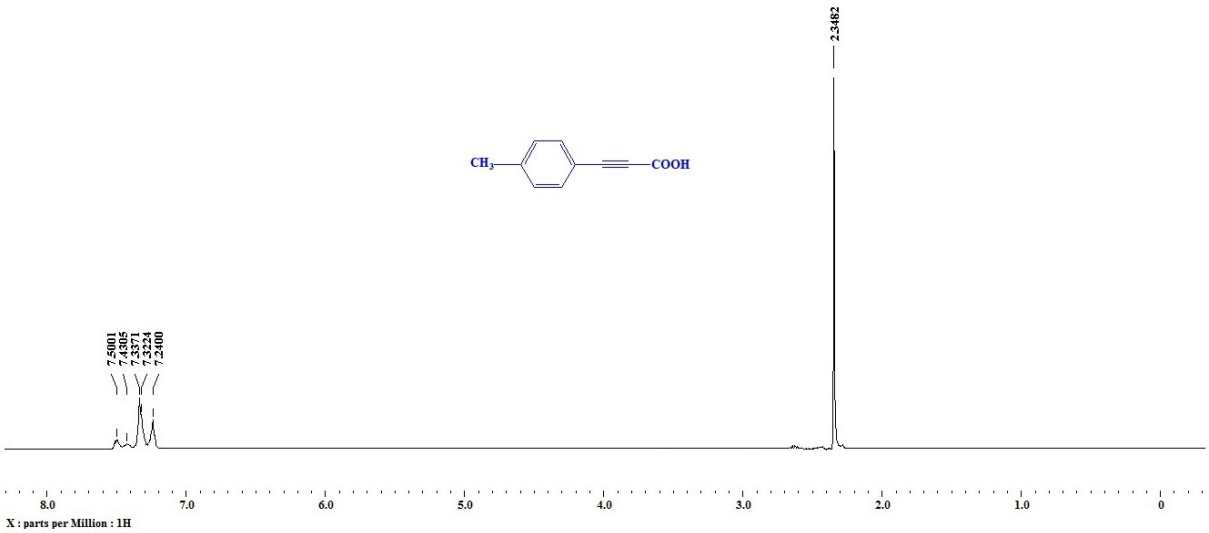


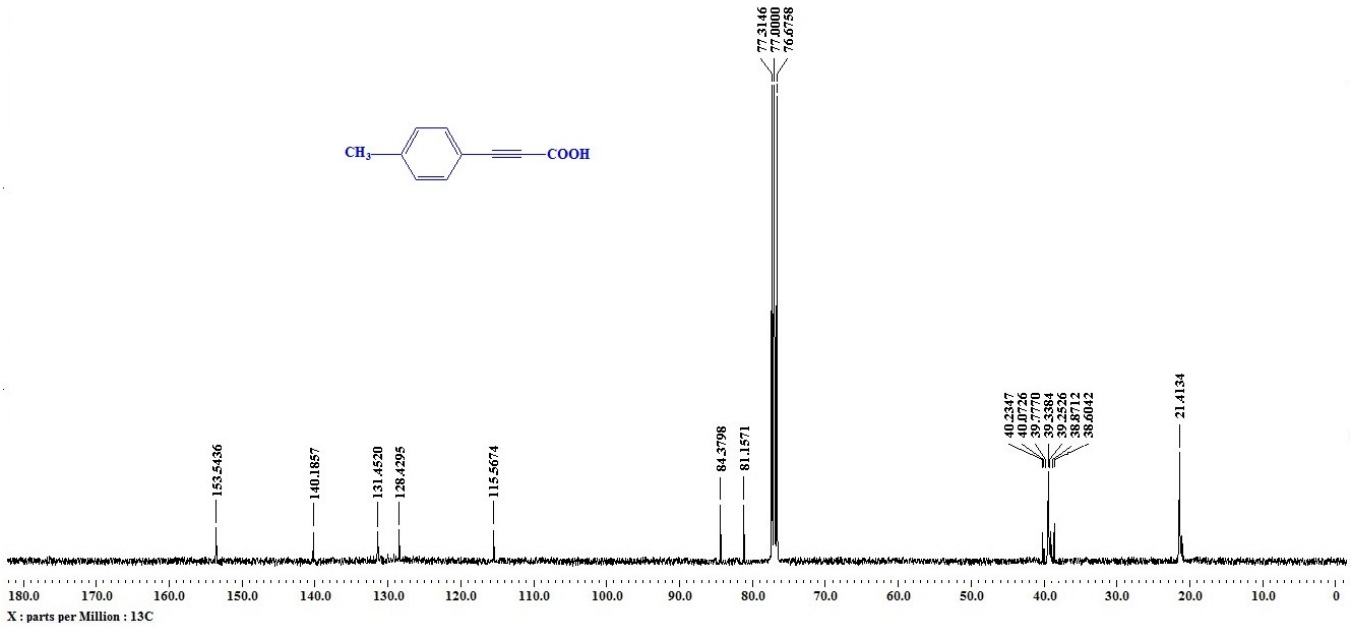


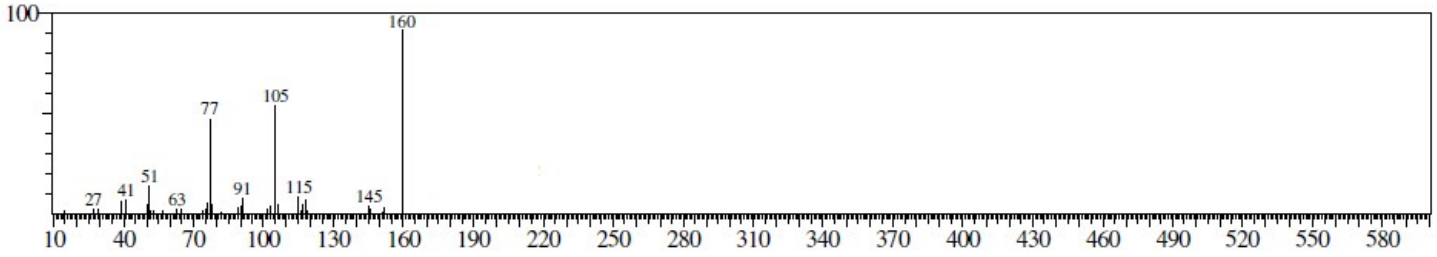
3-p-tolylpropiolic acid:



^{1}H NMR (400 MHz, $CDCl_3$): 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, CH_3); ^{13}C NMR (400 MHz, $CDCl_3$): 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).

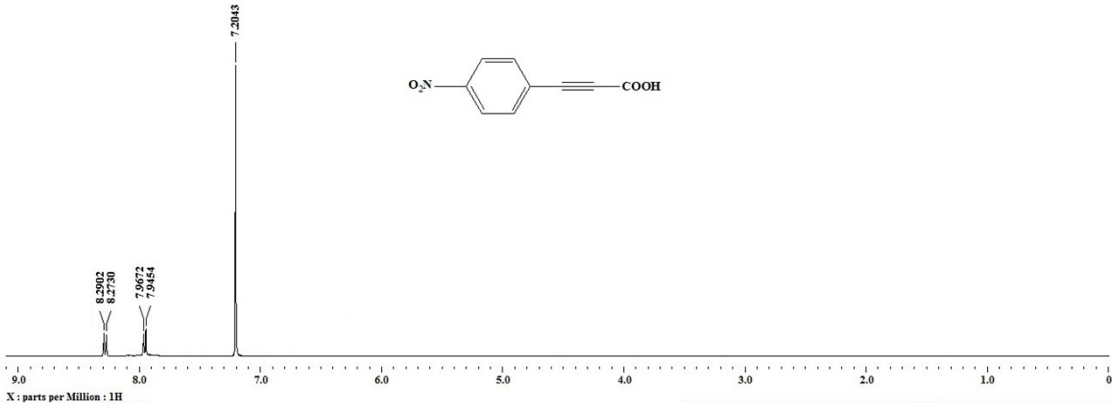


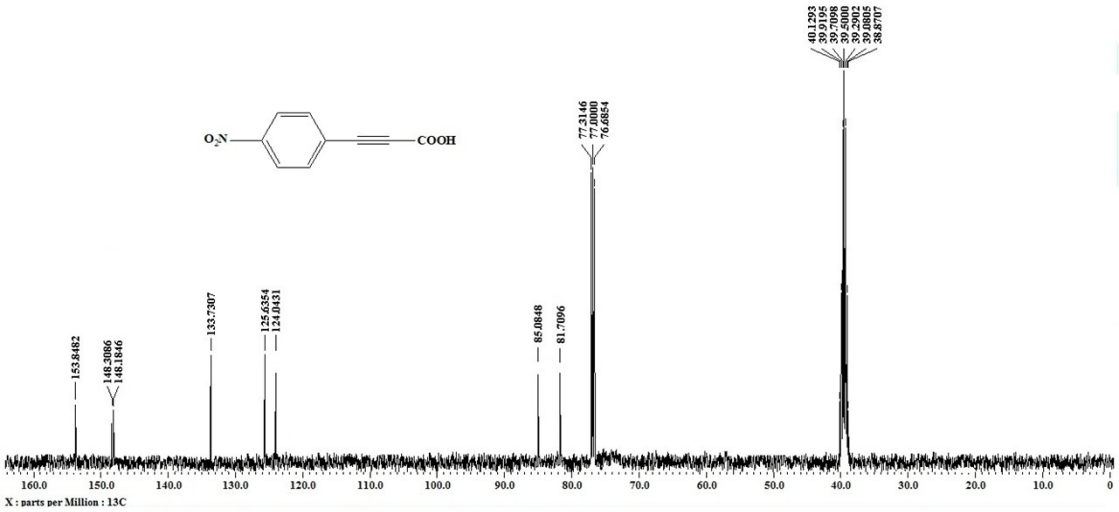


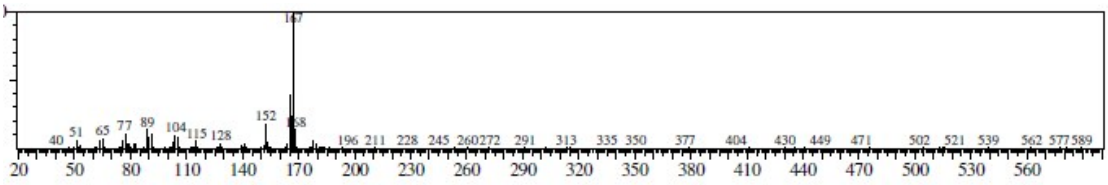


4-nitrophenylpropiolic acid:

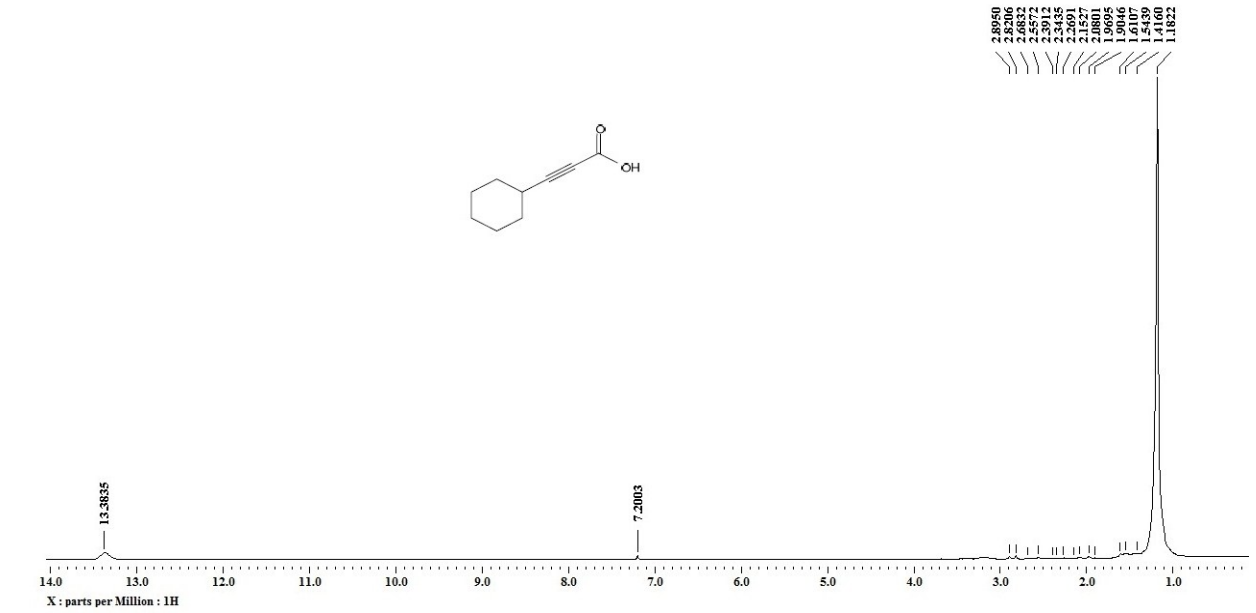
^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 6.8 Hz, 2H, Ar-H), 7.95 (d, J = 8.7 Hz, 2H, Ar-H); ^{13}C NMR (400MHz, $CDCl_3$): δ = 153.84 (-COOH), 148.30, 148.18, 133.73, 125.63, 124.04, 85.08, 81.70, 40.12, 39.91, 39.70, 39.50, 39.29, 39.08, 38.87; GCMS m/z(% rel. inten.) 167 (M^+, 100).

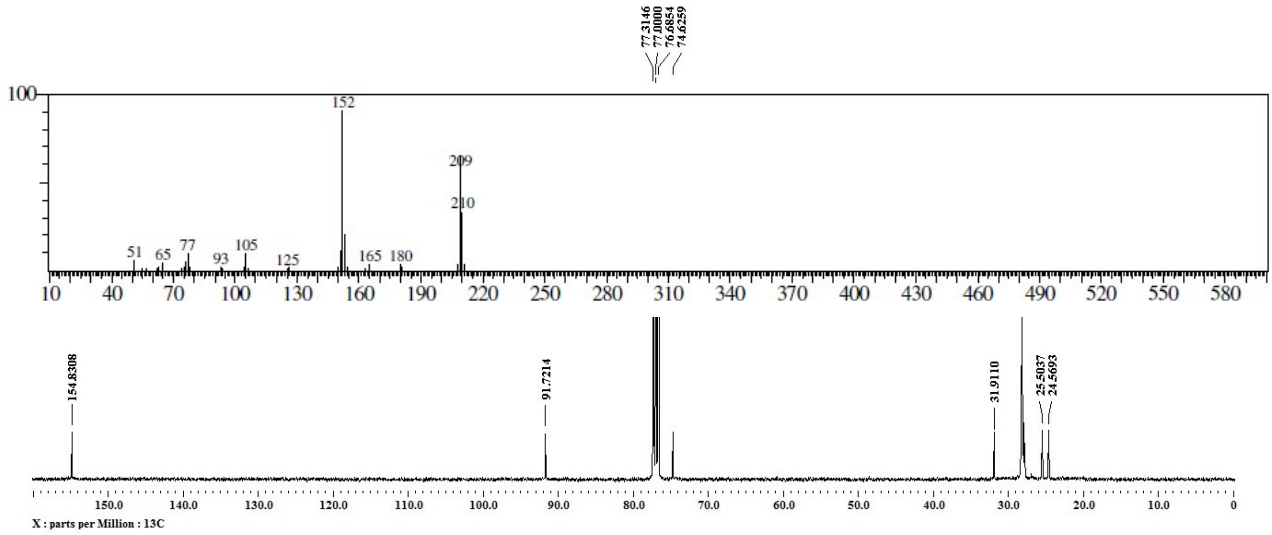




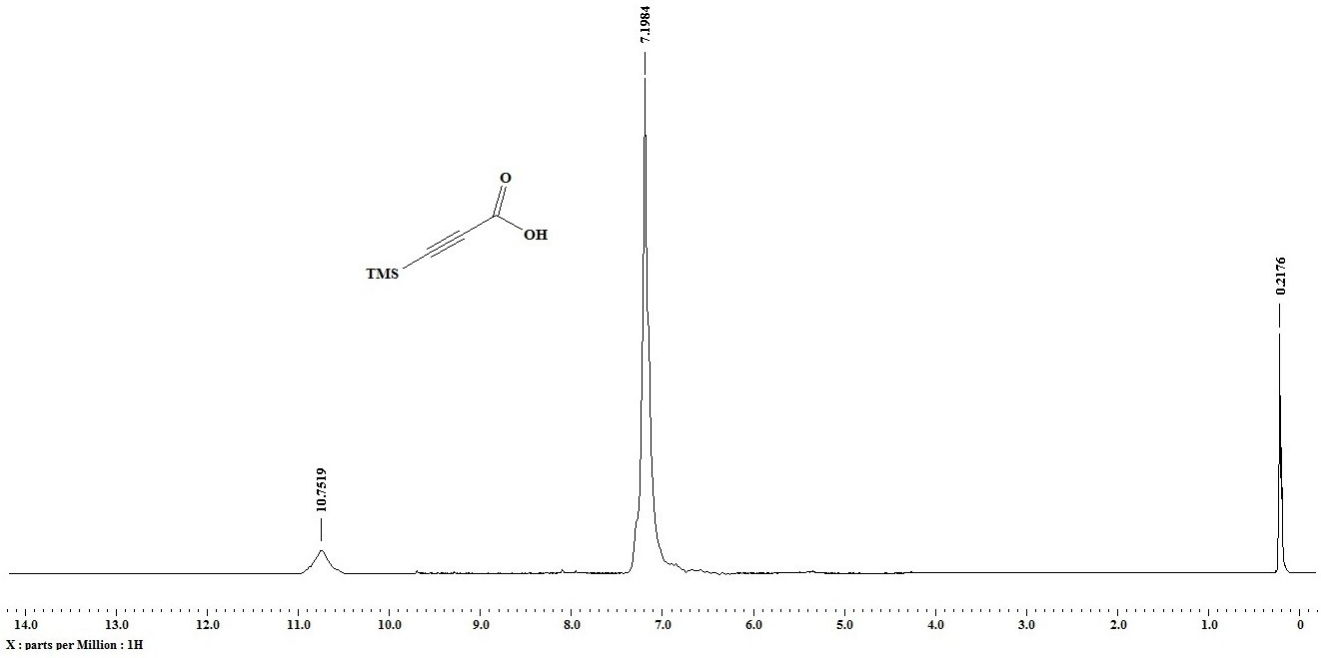


3-Cyclohexylpropiolic acid: ^{1}H NMR (400 MHz, $CDCl_3$): δ =13.38 (br, s, 1H), 2.89-2.55 (m, 1H), 2.26-2.39 (m, 2H), 1.90-2.15 (m, 2H), 1.61-1.18 (m, 6H); ^{13}C NMR (400 MHz, $CDCl_3$): δ= 154.83, 91.72, 74.62, 31.91, 28.22, 25.50, 24.56; GCMS *m*/*z*(% rel. inten.) 152 (M^+, 100).





3-(trimethylsilyl)propiolic acid: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.75(br, s, 1H), 0.21(s, 9H, CH_3Si); ^{13}C NMR (400 MHz, $CDCl_3$): δ= 154.48, 98.81, 53.58, 31.90, 29.67, 29.34, 22.67, 3.52; GCMS *m*/*z*(% rel. inten.) 142 (M^+, 100).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13.0
12.0
11.0
10.0
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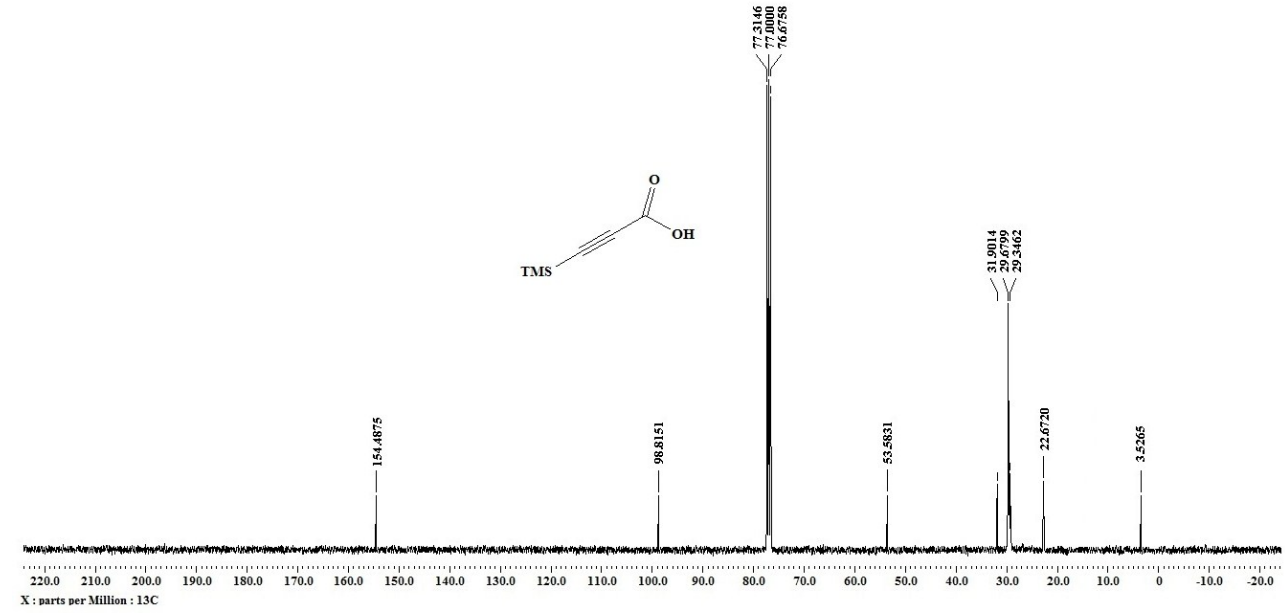
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H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77.0000
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OH
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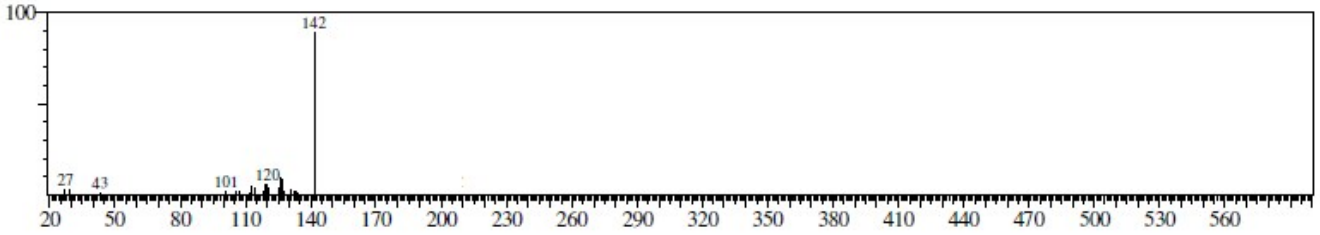
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : 13C


100
142
27
43
101
120
20
50
80
110
140
170
200
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260
290
320
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380
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440
470
500
530
560