Supporting Information

Nano magnetite supported metal ions as a robust, efficient and recyclable catalyst for green synthesis of propargylamines and 1,4-disubstituted 1,2,3-triazoles in water

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1. General Information:

The synthesized magnetite nanoparticles were characterized by various techniques such as elemental analyzed (CHN), NMR, FT-IR, TGA/DTA, SEM, TEM, EDS, XRD, AAS, ICP-OES and VSM which revealed the superparamagnetic nature of the particles. All chemicals were purchased and used without any further purification. NMR spectra were recorded at 400 MHz for proton and at 100 MHz for carbon nuclei in $CDCl_3$ and DMSO-d_6.

1.1 General details

Chemical materials were purchased from Merck and Aldrich Chemical Company in high purity. All the solvents were distilled, dried and purified by standard procedures. Melting points were measured on an Electrothermal 9100 apparatus. The samples were analyzed using FT-IR spectroscopy (Bruker Vector22 Perkin Elmer 65 in KBr matrix). The X-ray powder diffraction (XRD) of the catalyst was carried out on a Philips PW 1830 X-ray diffractometer with CuKα source (λ=1.5418 Å) in a range of Bragg's angle (10-80°) at room temperature. Scanning electron microscope (SEM) pictures-EDS analyses were taken using VEGA//TESCAN KYKY-EM3200 microscope (acceleration voltage 26 kV). Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope. The samples for TEM measurements were suspended in ethanol by sonication and then drop drying on a copper grid (400 mesh) coated with carbon film. ^{1}H, ^{13}C NMR spectra were recorded on a BRUKER DRX-400 AVANCE spectrometer. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 20 eV.Magnetic measurements were performed using vibration sample magnetometry (VSM, (MDK Co. Kashan, Iran) analysis

2. Characterizations of Catalyst:

2.1. FT-IR analysis

Fig. S1 shows the IR spectra of bare MNPs (a), MNPs@SiO_2 (b), MNPs coated CPTES (c), Bim (d), MNPs@Biim (e) and MNPs@BiimCu (f). In Fig. S1(a), the characteristic adsorption band of Fe-O bonds in Fe_3O_4 nanoparticles appeared at 624 cm^{-1}. The broad band at 3300–3500 is due to -OH stretching vibrations. The existence of the characteristic Si –O-Si stretching at 1062 cm^{-1} for SiO_2@MNPs in Fig. S1(b) confirms the formation of the silica shell around the Fe_3O_4 core. FT-IR spectra of MNPs coated CPTES (Fig. 1c), MNPs@Biim ,

Fig. S1 (e), and MNPs@BiimCu(I), Fig. S1 (f), exhibit all the above characteristic peaks, confirming the existence of Fe_3O_4 and SiO_2 components in these samples. The absorption band at about, 2925 cm^{-1} in Fig. 1c is attributed to the CH_2 of chloropropyl group in MNPs coated CPTES. In the specta of MNPs@Biim, Fig. S1(e), and MNPs@biimCu(I) ,Fig. S1 (f), the most important C=N and C-N stretching bands are found for MNPs@Biim at 1689 and 1541 cm^{-1} and MNPs@biimCu(I) at 1639 and 1542 cm^{-1}, could prove successful grafting of the biimidazole on magnetic particles. Lower absorption frequencies of these bands in MNPs@biimCu(I) spectrum relating to biimidazole, Fig. S1 (d) 1681 and 1546 cm^{-1}), could be due to the metal-ligand interactions.

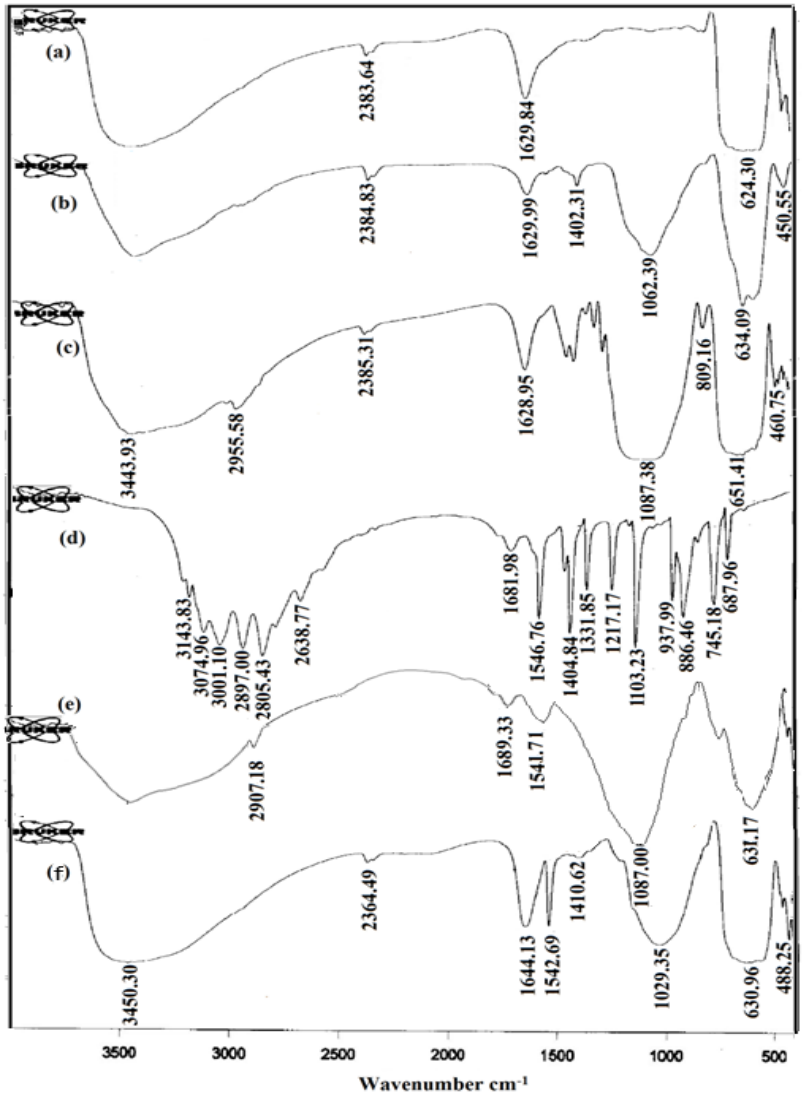


Fig. S1. FTIR spectra of MNPs (a), MNPs@SiO_2 (b), MNPs coated CPTES (c), Bim (d), MNPs@Biim (e), MNPs@BimCu(I) (f)

FT-IR spectra of nanomagnet supported catalyst before and after the catalytic reaction did not show any significant differences (Fig. S2)

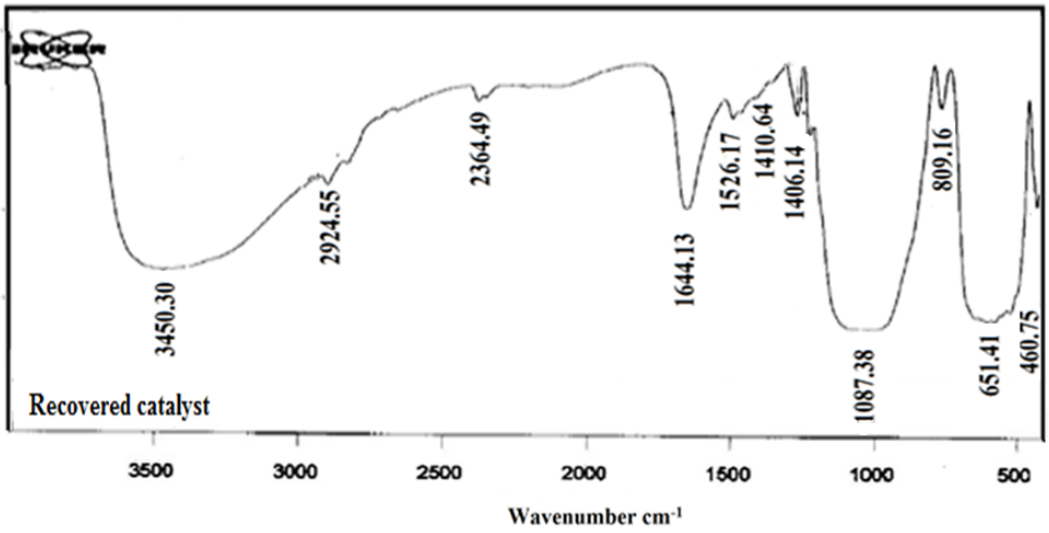
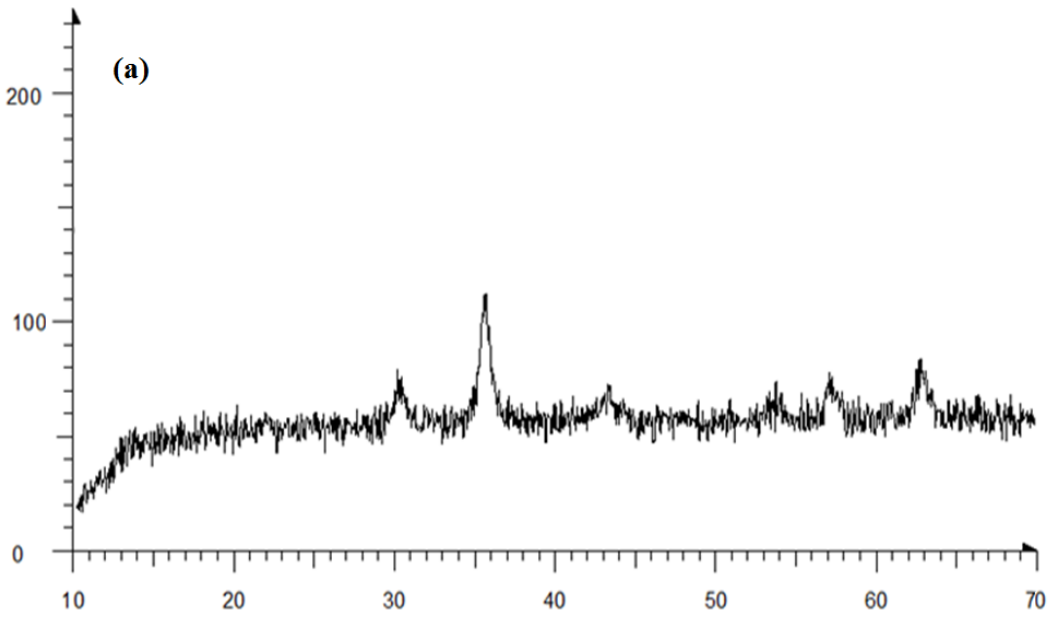


Fig. S2. FTIR spectrum of recoverd MNPs@BimCu(I) catalyst

2.2. XRD patterns

The X-ray diffraction analysis was done in a Philips PW 1830 X-ray diffractometer with CuKα source. The particles before and after coating step were analyzed by XRD. (Fig. S3)



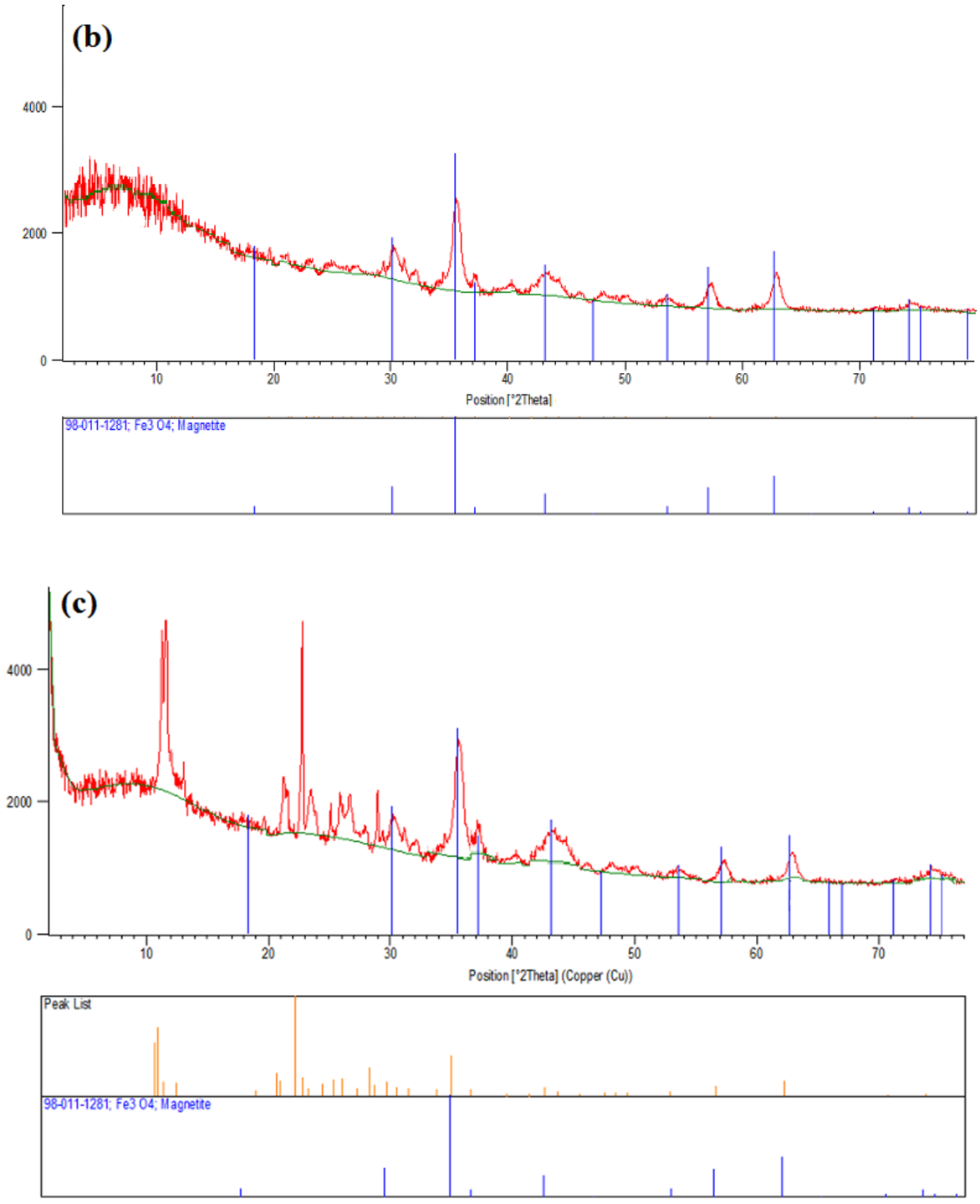


Fig. S3. XRD patterns of a) MNPs, b) MNPs @SiO_2 and c) MNPs@BimCu(I)

2.3. Elemental analysis

The data for AAS, ICP and CHN elemental analysis are tabulated in Table. As it is clear, the content of C in MNPs coated CPTES (7.14%) increased to 13. 94% in MNPs@Biim together with nitrogen composition of 7.43% could indicate the effective displacement of the chlorine

atom by biimidazole. The percentage of organic groups grafted on the magnetite surface was calculated by Eq. (A) according to the elemental analysis of the MNP@Biim nanoparticles.

Eq. (A.)

mmol N = (%N/ 4 × 14 × 100) × 1000 = (9.73/4 × 14 × 100) × 1000 = 1.73 mmol

2.4. ICP-OES and AAS analysis

The amount of copper loading in MNPs@BiimCu(I) was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) and atomic absorption spectrophotometer (AAS) and found to be 10.91 wt% (1.73 mmol/g) and 10.80 wt% (1.71 mmol/g), respectively.

Table. Elemental analysis for for MNPs coated CPTES, MNPs@Biim and MNPs@BiimCu(I) [a, b]

Samples	C%	H%	N%	metal %(Fresh) [a,b]	metal % (reused after 10 times)[a,b]
MNPs coated CPTES	7.14	5.53	-	-	-
MNPs@Biim	17.94	8.05	7.43	-	-
MNPs@BiimCu(I)	17.94	8.05	7.43	10.91[a], 10.80[b]	10.68[a], 10.80[b]
MNPs@BiimCu(II)	17.94	8.05	7.43	8.27[b]	-
MNPs@BiimNi(II)	17.94	8.05	7.43	7.19[b]	-
MNPs@BiimCo(II)	17.94	8.05	7.43	9.14[b]	-

[a,b] The amount of copper was determined using [a]AAS (measurement of separated solution) and [b]ICP

2.5. VSM Curves

Magnetic hysteresis measurements for the MNP@SiO_2, MNP coated CPTES and MNP@BiimCu(I) nanoparticles were carried out in an applied magnetic field, with the field sweeping from −8000 to +8000 Oe and determined by a vibrating sample magnetometer (Fig. S4.a-c). As depicted in Fig. S4.(d) MNPs@BiimCu can be separated easily from reaction mixture.

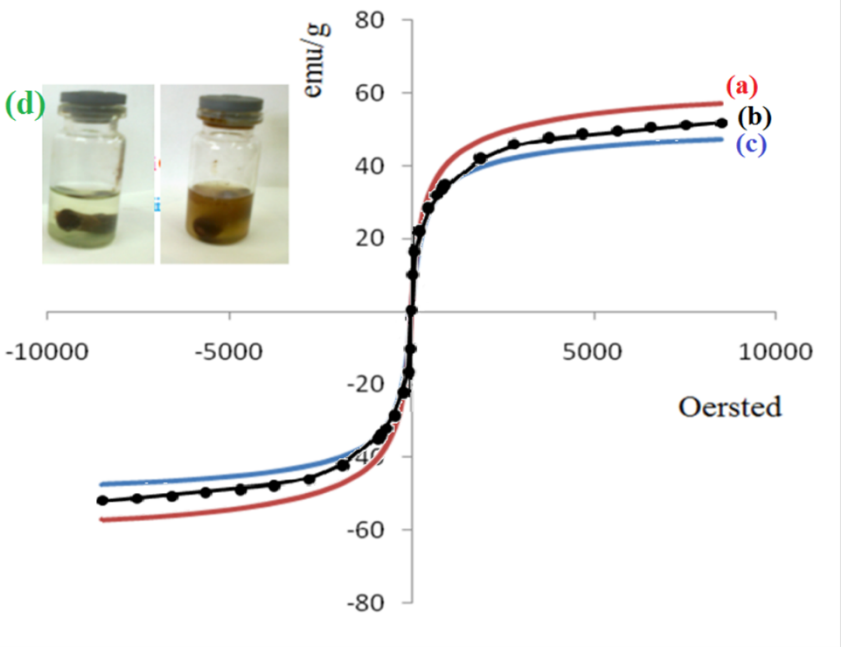


Fig. S4. VSM curve of a) MNPs@SiO_2, b) MNPs coated CPTES, c) MNPs@BiimCu(I)

d) Catalyst ability to effective recovery at the end of reaction

3. Spectral data for selected compounds

Propargylamines (Table 3)

N-[1-(4-Chlorophenyl)-3-phenyl-2-propynyl]piperidine[1]. (Table 3, entry 1)

Dark yellow oil, yield 99%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.66-7.59(m, 2H), 7.59-7.52(m, 2H), 7.41-7.32(m, 5H), 4.79(s, 1H), 2.63-2.52(m, 4H), 1.69-1.54(m, 4H), 1.54-1.43(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 137.35, 133.19, 131.84, 129.83, 128.35, 128.23, 128.22, 123.11, 88.25, 85.3941, 62.22, 61.74, 50.65, 26.20, 24.42.

1-(1,3-Diphenylprop-2-ynyl)piperidine[1] (Table 3, entry 2)

yellow oil, yield 99%;^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.70 − 7.62 (m, 2H), 7.57 − 7.51 (m, 2H) , 7.41− 7.28 (m, 6H), 4.81 (s, 1H), 2.65 − 2.5 (m, 4H), 1.67 − 1.56 (m, 4H), 1.51 − 1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 138.58, 131.81, 128.54, 128.28, 128.06, 127.45, 123.33, 87.81, 86.07, 62.38, 50.69, 26.18, 24.43.

N-[1-(3-Bromophenyl)-3-phenyl-2-propynyl]piperidine[2] (Table 3, entry 6)

Yellow oil, yield 98%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.87-7.80(m, 1H), 7.64-7.60(m, 1H), 7.57-7.53(m, 2H), 7.46-7.43(m, 1H), 7.39-7.34(m, 3H), 7.28-7.24(m, 1H), 4.79(s, 1H), 2.65-2.55(m, 4H),

1.69-1.59(m, 4H), 1.52-1.44(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 141.17, 131.86, 131.14, 130.59, 129.63, 128.34, 128.26, 127.12, 123.03, 122.32, 88.39, 85.04, 61.82, 50.68, 26.13, 24.35**.**

N-[1-(4-Cyanophenyl)-3-phenyl-2-propynyl]piperidine[1] (Table3, entry 7)

a yellow oil, yield 91%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.69-7.62(m, 2H), 7.58-7.51(m, 2H), 7.42-7.36(m, 2H), 7.36-7.30(m, 3H), 4.81(s, 1H), 2.64-2.51(m, 4H), 1.66-1.57(m, 4H), 1.51-1.42(m, 2H); ^{13}C-NMR ($CDCl_3$,100MHz): δ= 144.03, 131.81, 128.52. 128.27, 128.05, 127.43, 118.01, 111.1, 88.80, 86.12, 62.39, 50.95, 26.19, 24.44**.**

N-[1-(2,4-Dimethylphenyl)-3-phenyl-2-propynyl] piperidine.[3] (Table 3, entry 9)

Yellow oil, yield 80%; ^{1}H NMR ($CDCl_3$, 400MHz): δ= 7.62-7.58(m, 1H), 7.58-7.54(m, 1H), 7.53(d, J=2.0Hz, 1H), 7.40-7.31(m, 3H), 7.08-6.98(m, 2H), 4.83(s, 1H), 2.65-2.52(m, 4H), 2.45(s, 3H), 2.35(s, 3H), 1.62-1.50(m, 4H), 1.49-1.40(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 137.42, 137.03, 133.88, 131.79, 131.45, 128.94, 128.27, 127.91, 125.76, 123.57, 87.84, 86.30, 59.94, 50.53, 26.35, 24.66, 21.05, 19.0.

N -[1-(2-furfuryl)-3-phenyl-prop-2-ynyl)-piperidine [4](Table 3, entry 11)

Yellow oil, yield 84%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.55-7.49 (m, 2H), 7.47-7.43(m, 1H), 7.39-7.31(m, 3H), 6.54-6.45(m,1H), 6.41-6.34 (m, 1H), 4.89 (s, 1H), 2.69-2.51 (m, 4H), 1.72-1.59 (m, 4H), 1.49-1.42 (m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 151.62, 142.57, 131.85, 128.28, 122.92, 109.97, 109.26, 86.39, 83.79, 56.55, 50.50, 29.70, 25.94.

N-[1-(1-Naphathyl)- 3-phenyl-2-propynyl]piperidine.[5] (Table 3, entry 13)[4]

Yellow oil, yield 85%; ^{1}H NMR ($CDCl_3$, 400MHz): δ= 8.10(s, 1H), 7.90 − 7.85(m, 3H), 7.81-7.75(m, 1H), 7.64-7.55(m, 2H), 7.53-7.46(m, 2H), 7.44-7.31(m, 3H), 4.97(s, 1H), 2.68-2.61(m, 4H), 1.72-1.54(m, 4H), 1.54-1.40(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 136.22, 133.08, 132.96, 131.87, 128.33, 128.13, 127.76, 127.58, 127.29, 126.71, 125.95, 125.86, 123.35, 88.13, 86.02, 62.53, 50.84, 26.19, 24.46.

N-[1-(4-Cyanophenyl)-3-phenyl-2-propynyl] morpholine.[5] (Table 3, entry 15)

Yellow oil, yield 84%;^{1}H-NMR ($CDCl_3$, 400MHz) δ= 7.85-7.79(m, 2H), 7.72-7.65(m, 2H), 7.57-7.51(m, 2H), 7.41-7.35(m, 3H), 4.86(s, 1H), 3.82-2.70(m, 4H), 2.71-2.57(m, 4H);^{13}C-NMR ($CDCl_3$, 100MHz) δ= 143.47, 131.84, 129.21, 128.67, 128.44, 122.36, 118.80, 111.68, 89.66, 83.22, 67.05, 61.64, 49.82**.**

N-[1-(4-Fluorophenyl)-3-phenyl-2-propynyl] morpholine. [2](Table 3, entry 16)

Yellow oil, yield 85%; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66-7.61 (m, 2H), 7.57-7.50 (m, 2H) , 7.41-7.31 (m, 3H) 7.1-7.03 (m, 2H), 4.79 (s, 1H), 3.82-3.70 (m, 4H), 2.73-2.52 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz,): δ= 162.37(d, J=244 Hz, 1C), 133.59(d, J=3 Hz, 1C), 131.81,130.16(d, J=8 Hz, 1C), 128.39,128.36, 122.78, 115.05(d, J=21 Hz, 1C), 88.76, 84.66, 67.14, 61.30, 49.77**.**

N-[1-(4-Trifluoromethylphenyl)-3-phenyl-2-propynyl]morpholine.[5] (Table 3, entry 17)

Yellow oil, yield 99%; ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.82-7.80(m, 2H), 7.66-7.64(m, 2H), 7.55-7.53(m, 2H), 7.41-7.36 (m, 3H), 4.86(s, 1H), 3.81-3.73(m, 4H), 2.67-2.65(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ142.01, 131.84, 128.70(q, J =32 Hz), 128.40, 125.21(q, J =3.5Hz), 124.15(q, J =270.1Hz), 122.58, 89.25, 83.88, 67.09, 61.61, 49.86**.**

N-[1-(3-hydroxyphenyl)-3-phenyl-2-propynyl]morpholine.[5] (Table 3, entry 18)

Yellow oil, yield 89%; ^{1}H NMR ($CDCl_3$, 400MHz): δ= 7.56-7.50(m, 2H), 7.39-7.32(m, 3H), 7.259(m, 1H), 7.24-7.21(m, 1H), 6.82-6.77(m, 1H), 4.76(s, 4H), 3.81-3.70(m, 1H), 2.73-2.59(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 155.58, 139.72, 131.82, 129.46, 128.33, 122.86, 121.02, 115.43, 114.77, 88.50, 84.78, 67.14, 61.78.

1,4-bis(3-phenyl-1-(morpholin-1-yl)prop-2-ynyl)benzene[3] (Table 3, entry 19)

White solid, yield 81%; m.p:150-153 °C; ^{1}H NMR ($CDCl_3$, 400MHz): δ= 7.69-7.61(s, 2H), 7.56-7.51(m, 2H), 7.39-7.31(m, 3H), 4.81(s, 1H), 3.81-3.65(m, 4H), 2.77-2.69(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz):δ= 137.36, 131.81, 128.50, 128.34, 128.31, 122.90, 88.50, 84.99, 67.17, 61.77, 49.86.

1,4-bis(3-phenyl-1-(piperidin-1-yl)prop-2-ynyl)benzene [3] (Table 3, entry 20)

white solid, yield 86 %; m.p: 157-160 °C; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.67-7.60(s, 2H), 7.56-7.51(m, 2H), 7.37-7.31(m, 3H), 4.83(s, 1H), 2.68-2.5(m, 4H), 1.69-1.59(m, 4H), 1.52-1.44(m, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 137.72, 131.81, 128.27, 128.04, 123.32, 87.78, 86.12, 62.14, 50.69, 26.15, 24.42.

N-4-(1-Phenylhex-1-yn-3-yl)morpholine.[6] (Table 3, entry 21)

Yellow oil, yield 83%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.46-7.41(m, 2H), 7.33-7.28(m, 3H), 3.82-3.73 (m, 4H) , 3.57-3.50 (m, 1H), 2.78-2.71 (m, 2H), 2.61-2.54 (m, 2H), 1.78-1.45 (m, 4H), 1.00-0.95 (m, 3H)); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 131.70, 128.22, 127.93, 123.21, 87.12, 86.12, 67.15, 57.81, 49.75, 35.06, 19.86, 13.86**.**

N-(1-Isopropyl-3-phenyl- 2-propynyl)morpholine.[5] (Table 3, entry 22)

Yellow oil, yield 80%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.49–7.44 (m, 2H), 7.35–7.29 (m, 3H), 3.82–3.72 (m, 4H), 3.04 (d, J = 9.5 Hz, 1H), 2.76–2.70 (m, 2H), 2.59 – 2.51 (m, 2H), 1.94–1.88 (m, 1H),

1.13 (d, J = 6.4 Hz, 3H) , 1.05 (d, J = 6.8 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 131.71, 128.23, 127.87, 123.39, 86.72, 86.61, 67.23, 65.20, 29.92, 20.34, 19.80**.**

N-[1-(1-Naphathyl)- 3-phenyl-2-propynyl]pyrrolidine. [5](Table 3, entry 24)

Yellow oil, yield 81%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 8.07(s, 1H), 7.92 − 7.81(m, 3H), 7.80-7.75(m, 1H), 7.58-7.52(m, 2H), 7.52-7.46(m, 2H), 7.43-7.31(m, 3H), 5.09(s, 1H), 2.85-2.62(m, 4H), 1.85-1.82(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 135.82, 133.10, 131.84, 128.33,128.23, 128.14, 128.06,127.61, 127.01, 126.47, 126.02, 125.86, 123.35, 86.06, 80.9, 59.32, 50.46, 26.72, 23.53**.**

N,N-Diethyl-1-(4-fluorophenyl)-3-phenylprop-2-yn-1-amine[6] (Table 3, entry 25)[7]

Yellow oil, yield 95%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ 7.84 (d, J=8.4Hz, 2H), 7.62 (d, J=8Hz, 2H) , 7.58 − 7.50 (m, 2H),7.41-7.32(m, 3H), 5.08 (s, 1H), 2.66 − 2.55 (m, 4H), 1.10 (t, J = 3.3 Hz, 6H); 13C-NMR (CDCl3, 100MHz, ppm): δ 162.37(d, J=244 Hz, 1C), 133.59(d, J=3 Hz, 1C), 131.80, 129.16(d, J=8 Hz, 1C), 128.36, 128.27, 124.99, 118.01(d, J=21 Hz, 1C), 79.78, 73.41, 56.78, 44.14, 13.59**.**

N,N-Dibenzyl -1,3-diphenyl-2-propynylamine.[1] (Table 3, entry 26)

Yellow oil, yield 91%; ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.80–7.72 (m, 2H), 7.69–7.63 (m, 2H), 7.49–7.44 (m, 4H), 7.44–7.40 (m, 3H), 7.39-7.31 (m, 6H), 7.28–7.22 (m, 3H), 4.96 (s, 1H), 3.79 (d, J = 13.6 Hz, 2H), 3.54 (d, J = 13.6 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 139.56, 139.19, 131.99, 128.92, 128.73, 128.42, 128.30, 128.26, 128.12,127.49, 127.03, 123.29, 86.66, 84.70, 56.05, 54.64**.**

N-4-(1,5-diphenylpent-1-en-4-yn-3-yl)morpholine.[2] (Table 3, entry 27)

Yellow oil, yield 89%; ^{1}H NMR ($CDCl_3$, 400MHz): δ= 7.69-7.64(m, 2H), 7.56-7.53(m, 2H), 7.42-7.39(m, 2H), 7.39-7.33(m, 6H), 4.82(dd, 3J=5.2, 4J=1.2 Hz, 1H), 3.80-3.72(m, 4H), 2.69-2.62(m, 4H); ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 137.77, 131.18, 131.73, 128.61, 128.33, 128.28, 127.25, 126.80, 126.41, 122.96, 88.49, 85.02, 67.17, 62.03, 49.90**.**

1,4-diphenyl-1,3-butadiyne[7] (Table 3, entry 28)

White solid. yield 91%; ^{1}H-NMR: ($CDCl_3$, 400MHz): δ= 7.54-7.56 (m, 2H), 7.28-7.40 (m, 3H). ^{13}C-NMR($CDCl_3$, 100MHz): δ= 132.61, 29.21, 121.82, 82.51, 74.01,

1,2,3-Triazoles (Table 6)

1-benzyl-4-phenyl-1*H*-1,2,3-triazole[8] (Table 6, entry 1)

White yellowish solid, yield 99%; m.p: 129-131ºC, ^{1}H-NMR($CDCl_3$, 400MHz): δ= 7.93 (s, 1H, CH), 7.85-7.88 (m, 2H), 7.35-7.47 (m, 8H), 5.23 (s, 2H, CH_2),. ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 146.02,132.12, 131.31, 130.57, 128.85, 128.73, 128.33, 128.19, 127.21, 125.72, 52.79 (CH_2).

1- phenyl- 2- (4 - phenyl - 1H- 1,2,3- triazol - 1- yl)ethanone (Table 6, entry 8)

White solid, yield 94%; m.p: 146-148 ºC, ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 8.04-8.06 (m, 2H), 7.97 (s, 1H, CH), 7.88-7.90 (m, 2H), 7.68-7.72 (m, 0.97H), 7.56-7.59 (m, 2H), 7.35-7.48 (m, 3H), 5.93 (s, 2H, CH_2). ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 190.28, 148.25, 134.68, 133.95, 130.50, 129.23, 128.85, 128.23, 128.20, 125.84, 121.17, 55.49.

1-allyl-4-phenyl-1H-1,2,3-triazole[8] (Table 6, entry 9)

White solid, yield 96%; m.p: 77-78 ºC ,^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.83-7.87 (m, 2H), 7.78 (s, 1H, CH), 7.46-7.41 (m, 2H), 7.28-7.37 (m, 1H), 6.02-6.12 (m, 1H), 5.33-5.41 (m, 2H), 5.02-5.04 (m, 2H,). ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 148.02, 130.58, 128.86, 128.73, 128.33, 125.72, 120.25, 116.99, 52.79.

1-allyl-4-pentyl-1H-1,2,3-triazole (Table 6, entry 12)

Yellow oil, 99%, ^{1}H NMR ($CDCl_3$, 400MHz): δ= 7.84 (s, 1H, CH), 5.97-6.05 (m, 1H), 5.27-6.35(m, 2H), 4.94-4.96 (m, 2H, CH_2), 2.72 (t, J = 8.0 Hz, 2H, CH_2), 1.65-1.69 (m, 2H, CH_2), 1.34-1.36 (m, 2H, CH_2), 1.26-1.36 (t, 3H, CH_3).^{13}C-NMR ($CDCl_3$, 100MHz): δ= 146.77, 131.58, 120.39, 117.25, 52.68, 31.21, 29.69, 25.66, 22.41, 13.87. ESI HRMS: calcd. For $C_{10}H_{17}N_3$ $[M+H]^+$: 180.1499, found: 180.1495.

2-Naphthalenylmethyl-4-pentyl-1H-1,2,3-triazole (Table 6, entry 13)

White solid. yield 88%; mp: 230-231 °C, ^{1}H-NMR($CDCl_3$, 400MHz): δ= 8.05-8.07 (m, 1H), 7.88-7.94 (m, 2H), 7.42-7.63 (m, 4H), 5.96 (s, 1H, CH), 4.79 ((s, 2H, CH_2), 2.65 (t, J = 8.0 Hz, 2H, CH_2), 1.58-1.63 (m, 2H, CH_2), 1.27-1.31 (m, 4H, $2CH_2$), 0.89 (t, J = 7.2 Hz, 3H, CH_3).

1-(4-bromobenzyl)-4-pentyl-1H-1,2,3-triazole (Table 6, entry 16)

Light yellow solid, yield 97%; m.p: 87-89ºC, ^{1}H-NMR($CDCl_3$, 400MHz): δ= 7.45 (d, J = 8.4 Hz, 2H), 7.21 (s, 1H, CH), 7.09 (d, J = 8.4 Hz, 2H), 5.42 (s, 2H, CH_2), 2.66 (t, J = 8.0 Hz, 2H, CH_2), 1.59-1.64 (m, 2H, CH_2), 1.27-1.30 (m, 4H, $2CH_2$), 0.85 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C-NMR ($CDCl_3$,

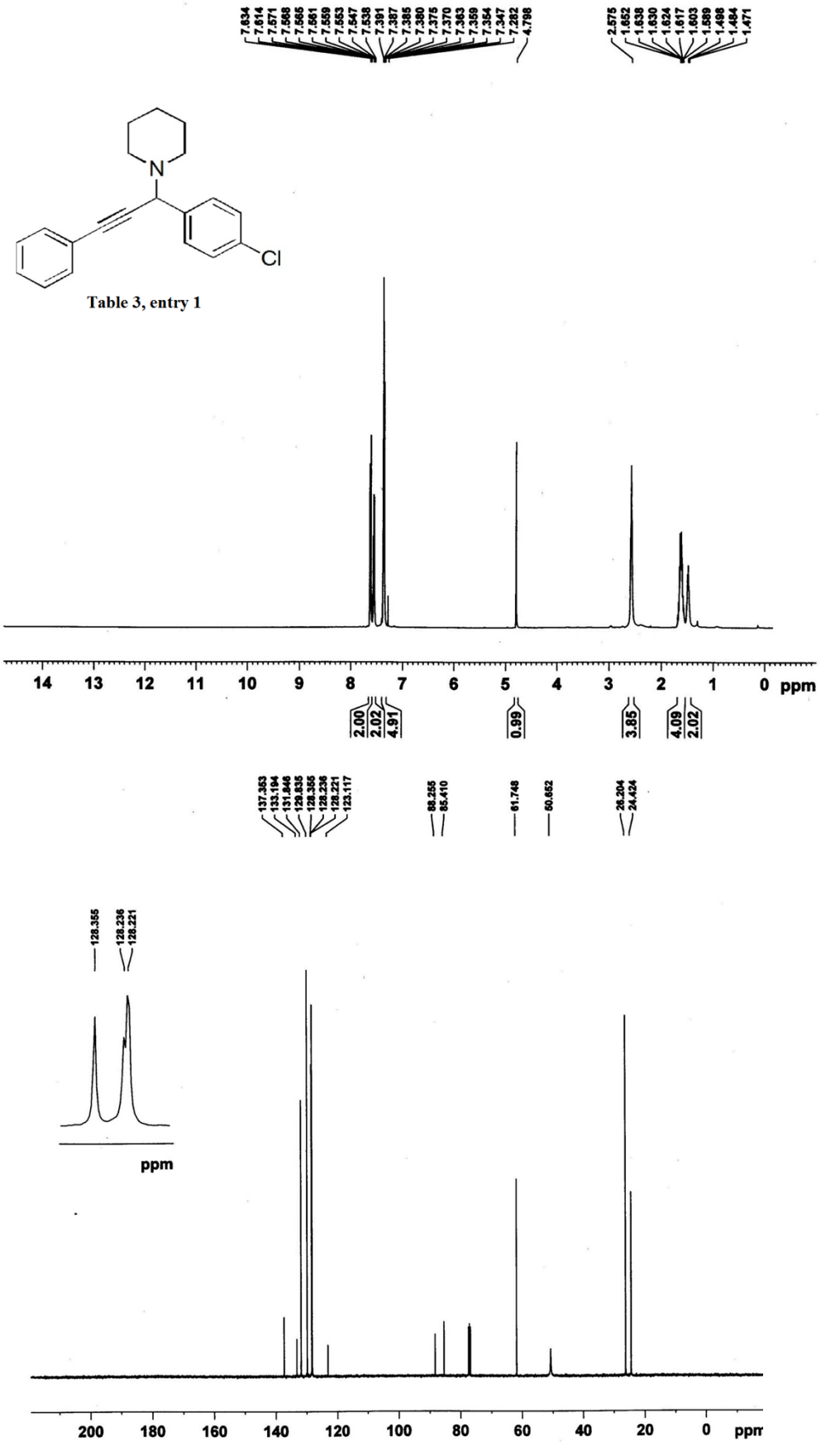
100MHz): δ= 149.13, 134.09, 132.15, 129.54, 122.65, 120.59, 53.20, 31.42, 29.05, 25.64, 22.36, 13.99. ESI HRMS: calcd. For $C_{14}H_{18}BrN_3$ $[M+H]^+$: 309.0636, found: 309.0644.

4-pentyl-1-propyl-1H-1,2,3-triazole (Table 6, entry 19)

Yellow oil, yield 94%; ^{1}H-NMR($CDCl_3$, 400MHz): δ= 7.27(s, 1H,CH), 4.29 (t, *J* = 7.2 Hz, 2H, CH_2), 2.72 (t, *J* = 8.0 Hz, 2H, CH_2), 1.90-1.96 (m, 2H, CH_2), 1.66-1.70 (m, 2H, CH_2), 1.34-1.38(m, 2H, CH_2), 0.92-0.99(m, 8H, $2CH_3$, CH_2). ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 140.12, 120.42, 51.77, 31.45, 28.87, 28.19, 25.63, 22.17, 14.01, 11.08. ESI HRMS: calcd. For $C_{10}H_{19}N_3$ $[M+H]^+$: 182.1531, found: 182.1540.

Ethyl 1-benzyl-1H-1,2,3-triazole-4-carboxylate[8] (Table 6, entry 22)

Colorless solid yield 98%; mp:81-83 °C, ^{1}H-NMR ($CDCl_3$, 400MHz): δ= 7.94 (s, 1H,CH), 7.85-7.88 (m, 2H), 7.43-7.47 (m, 2H), 7.28-7.39 (m, 1H), 5.23 (s, 2H, CH_2), 4.31 (q, *J* = 7.2 Hz, 2H, CH_2), 1.34 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C-NMR ($CDCl_3$, 100MHz): δ= 166.29, 148.30, 130.33, 128.87, 128.32, 125.84, 120.99, 62.52, 50.99, 14.10.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7.363
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7.282
4.786
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1.498
1.484
1.471
N
Cl
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0.99
3.85
4.09
2.02
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133.194
131.846
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128.355
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128.221
123.117
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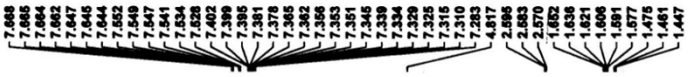

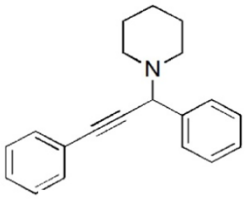

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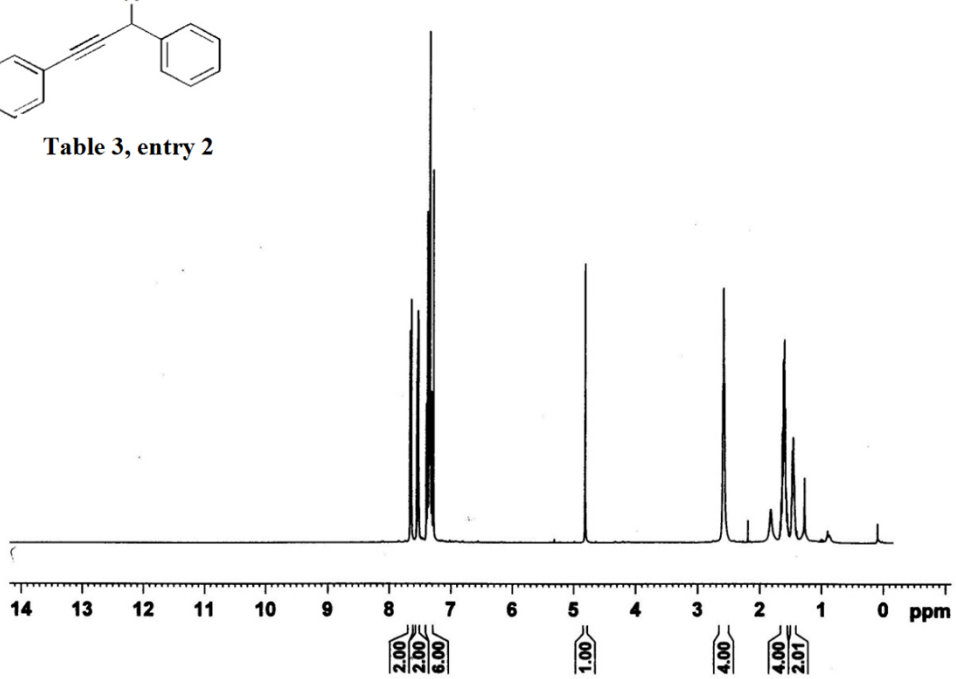

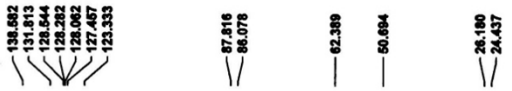

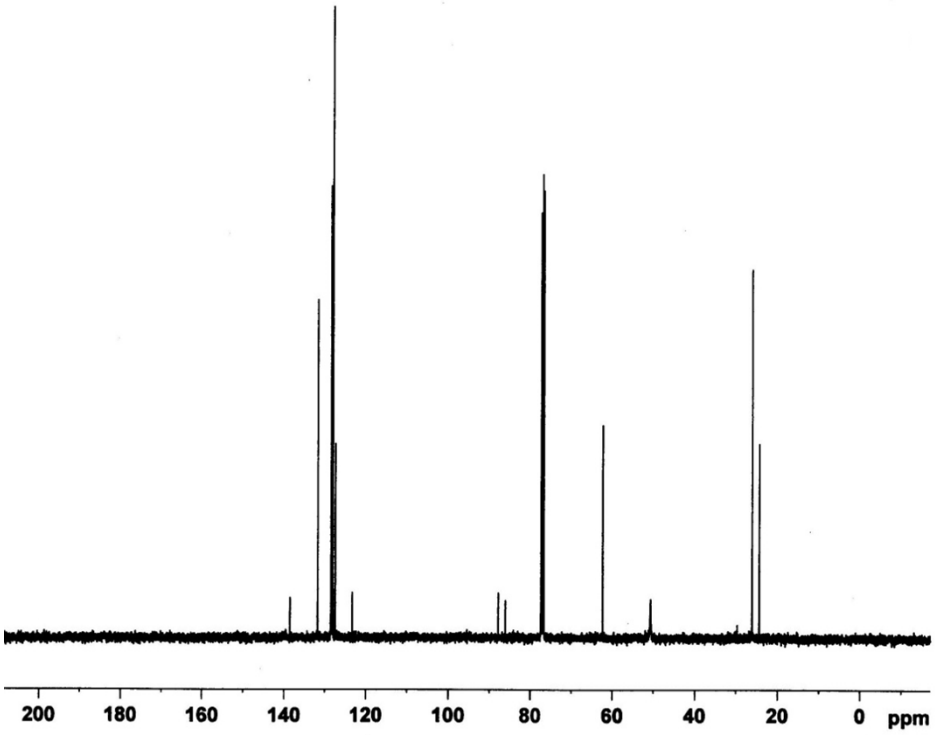

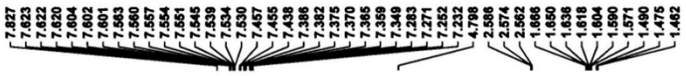

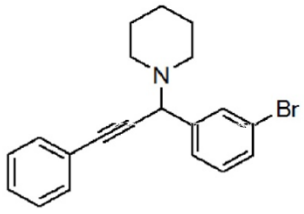

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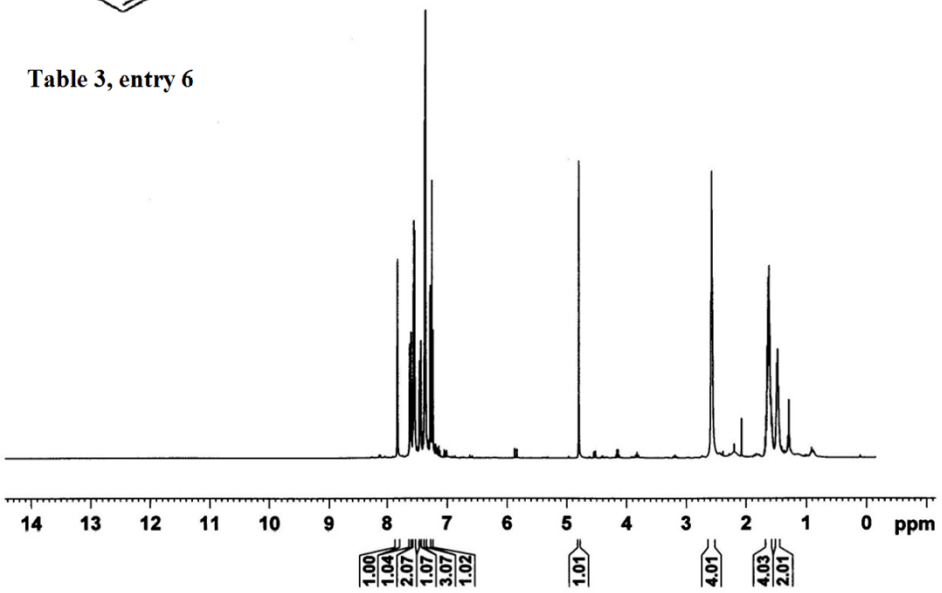

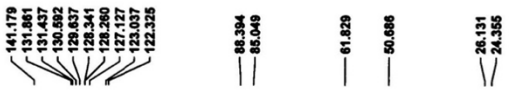

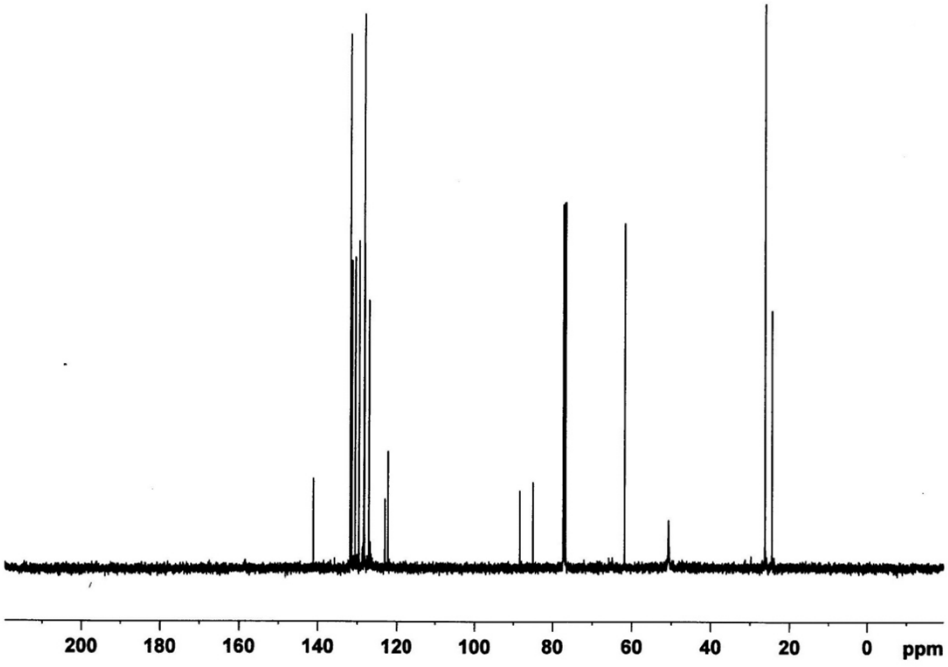

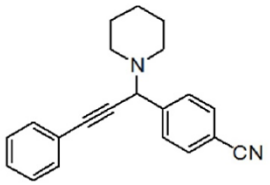

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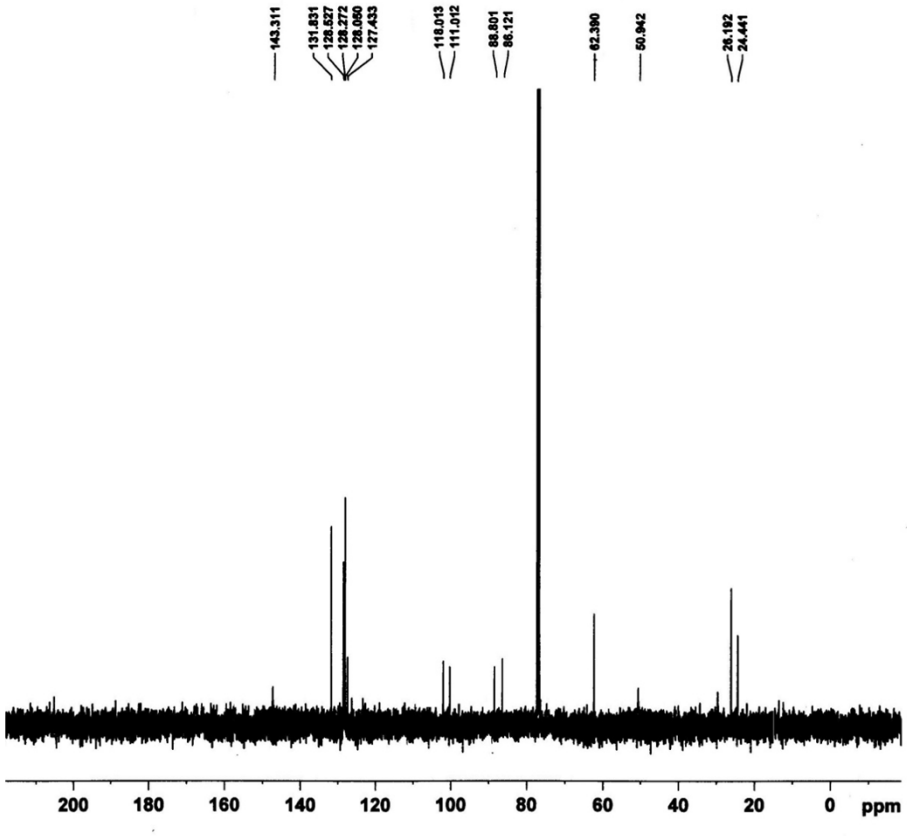

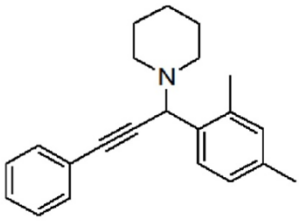

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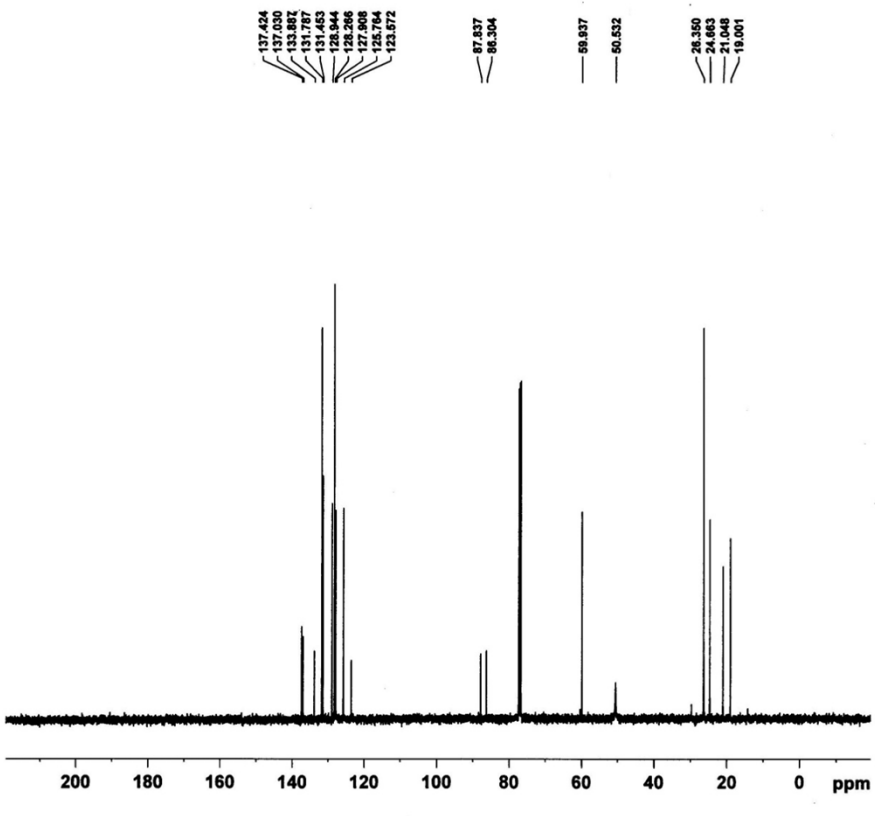

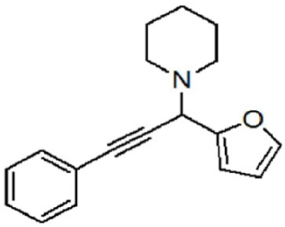

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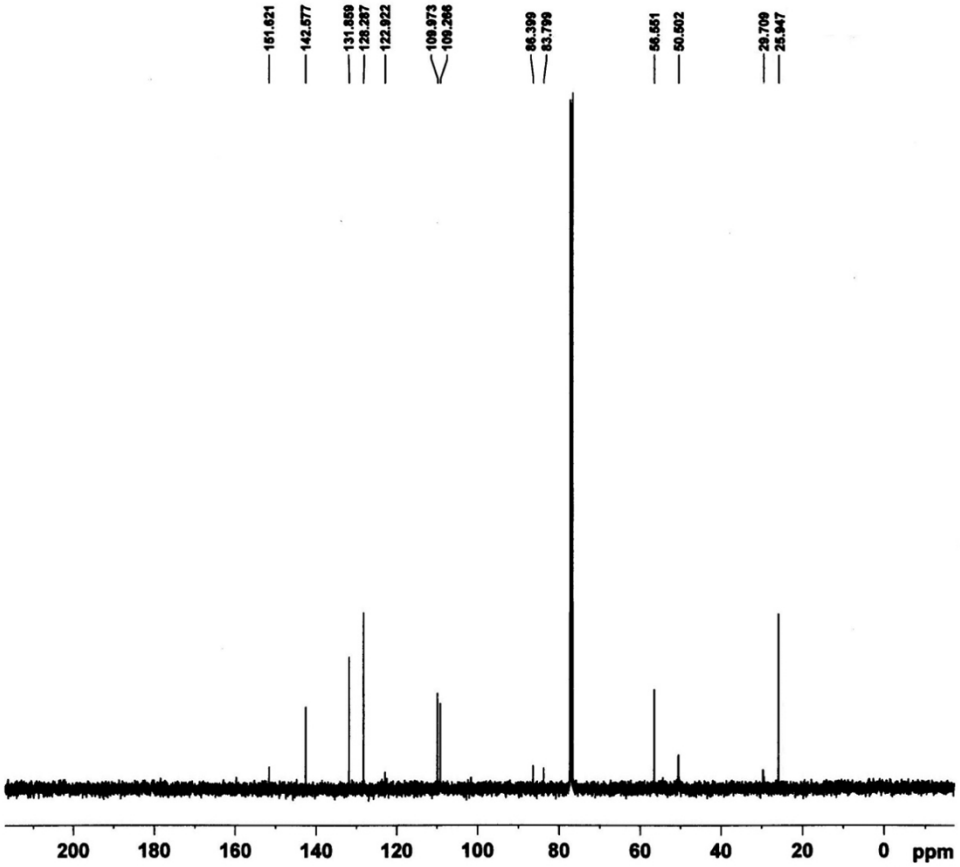

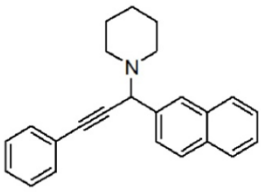

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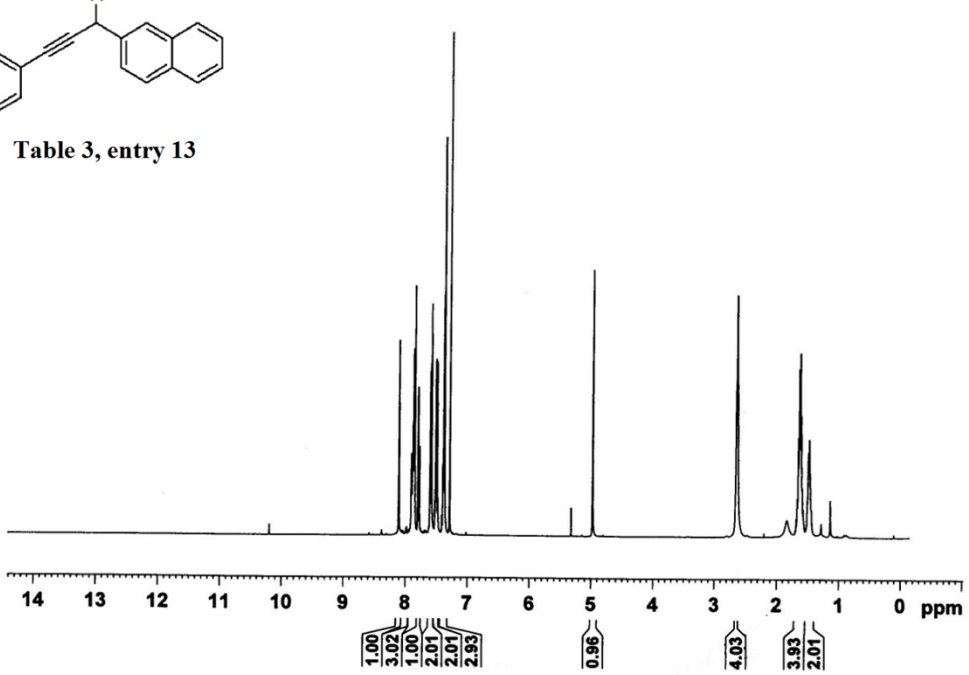

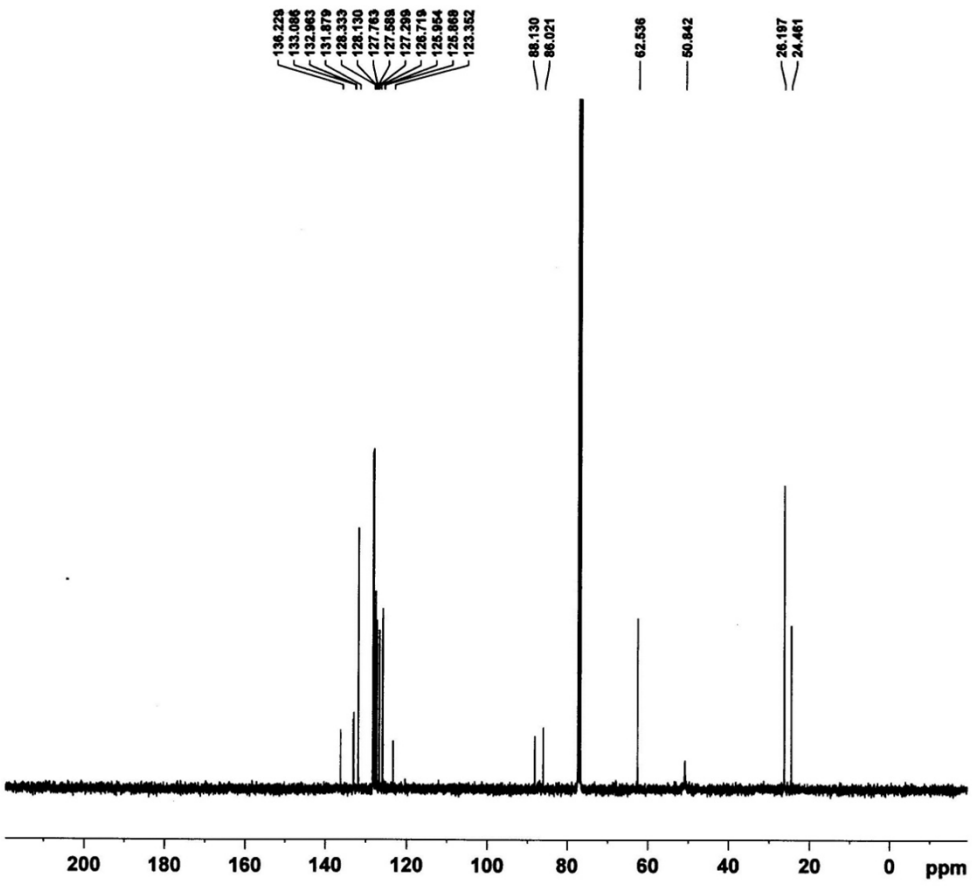

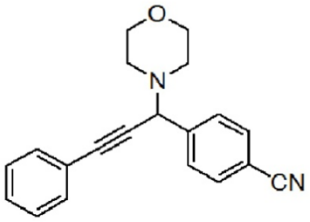

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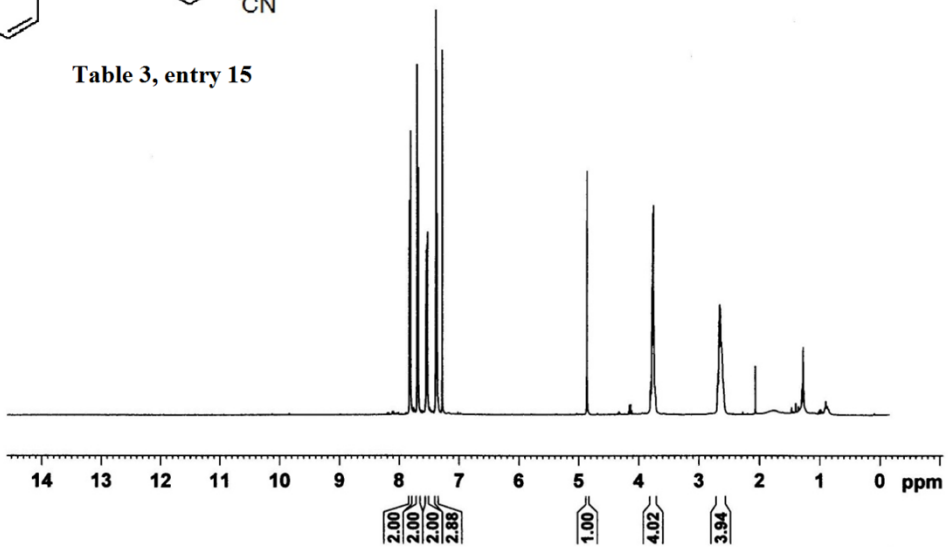

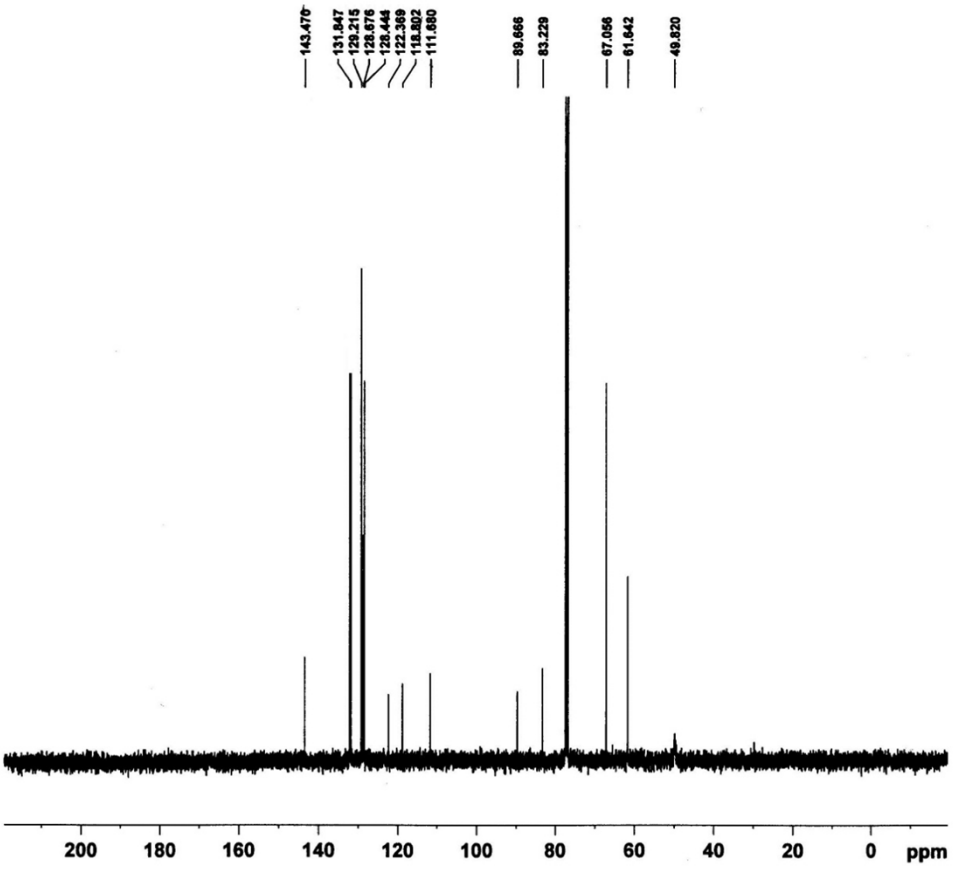

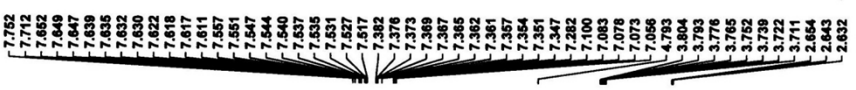

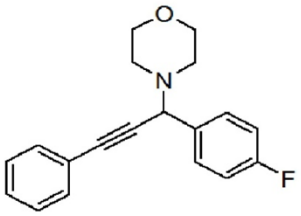

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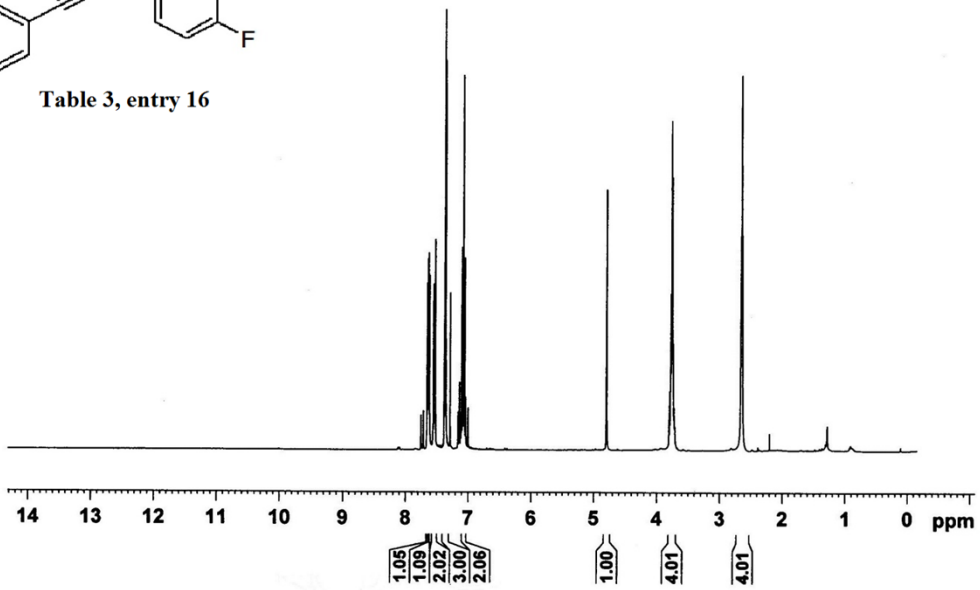

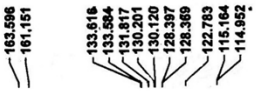

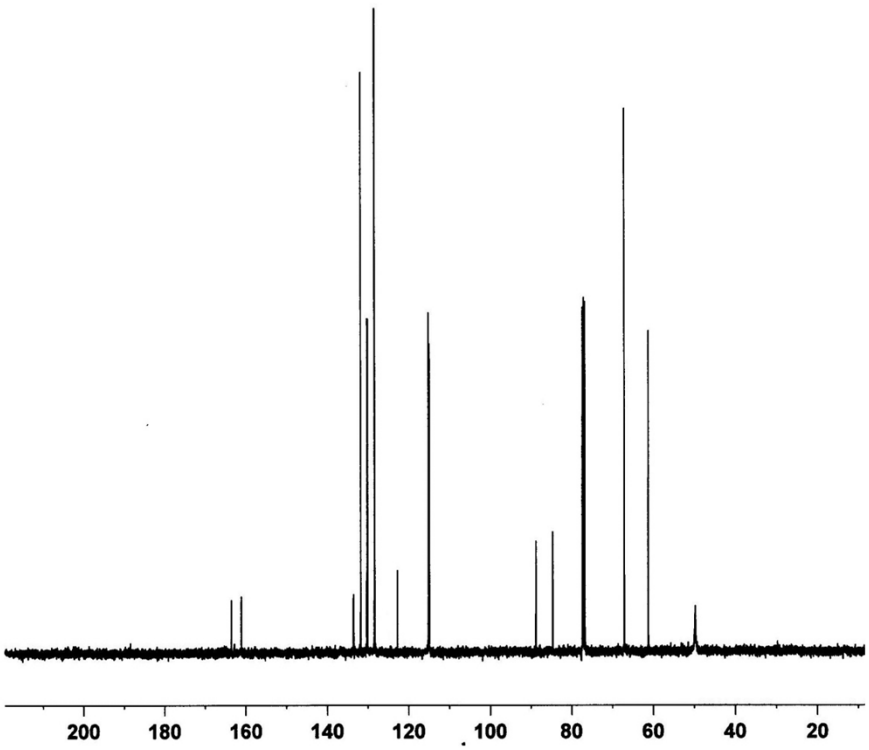

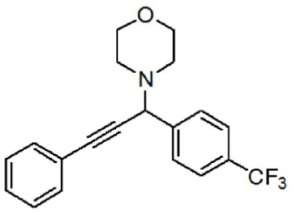

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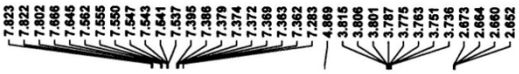

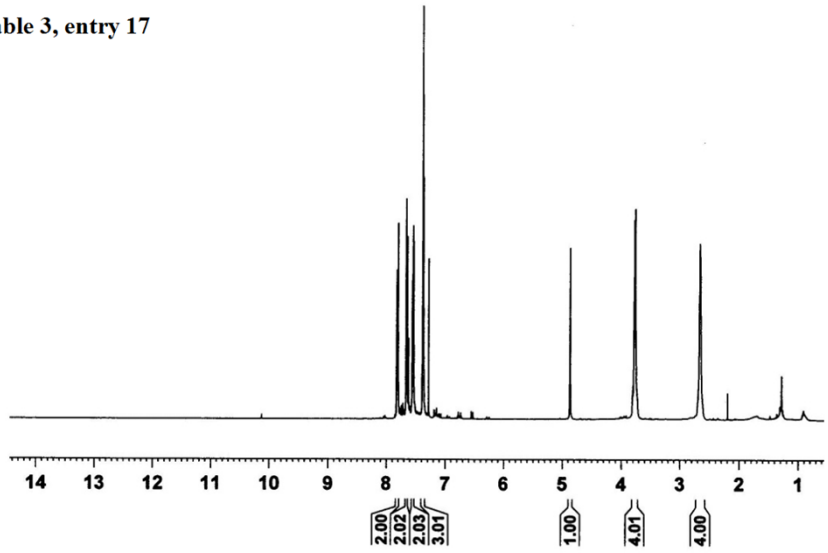

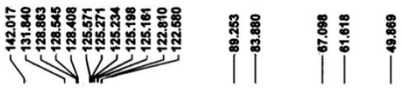

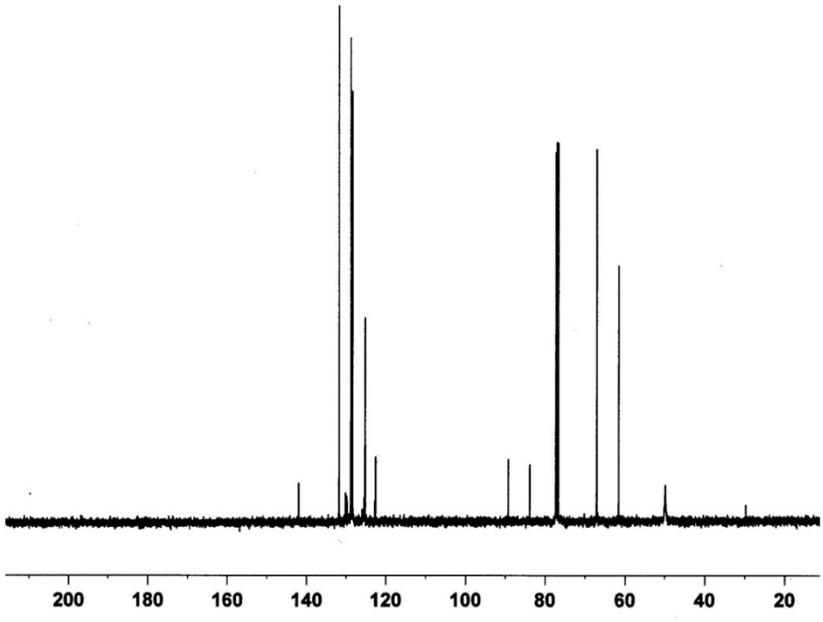

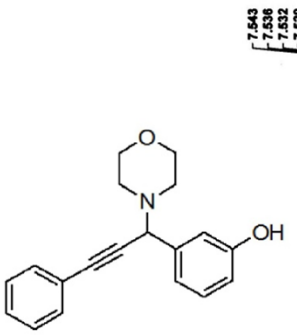

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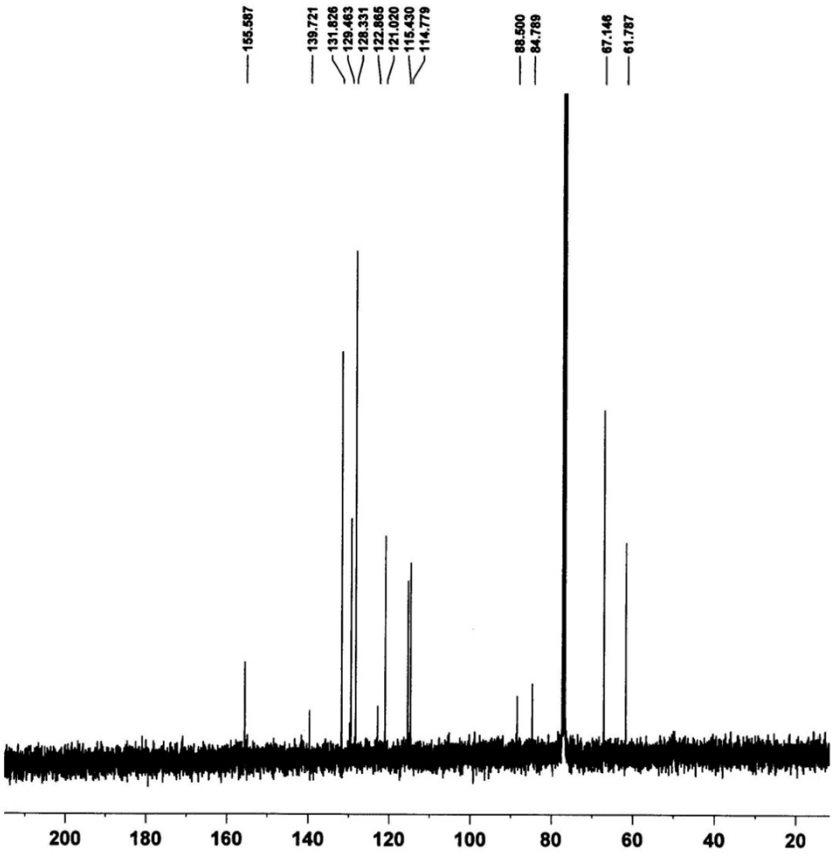

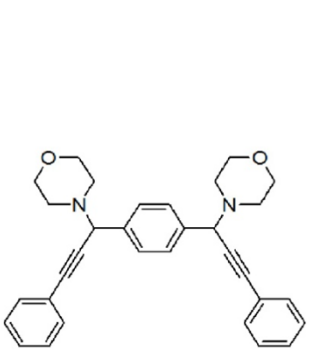

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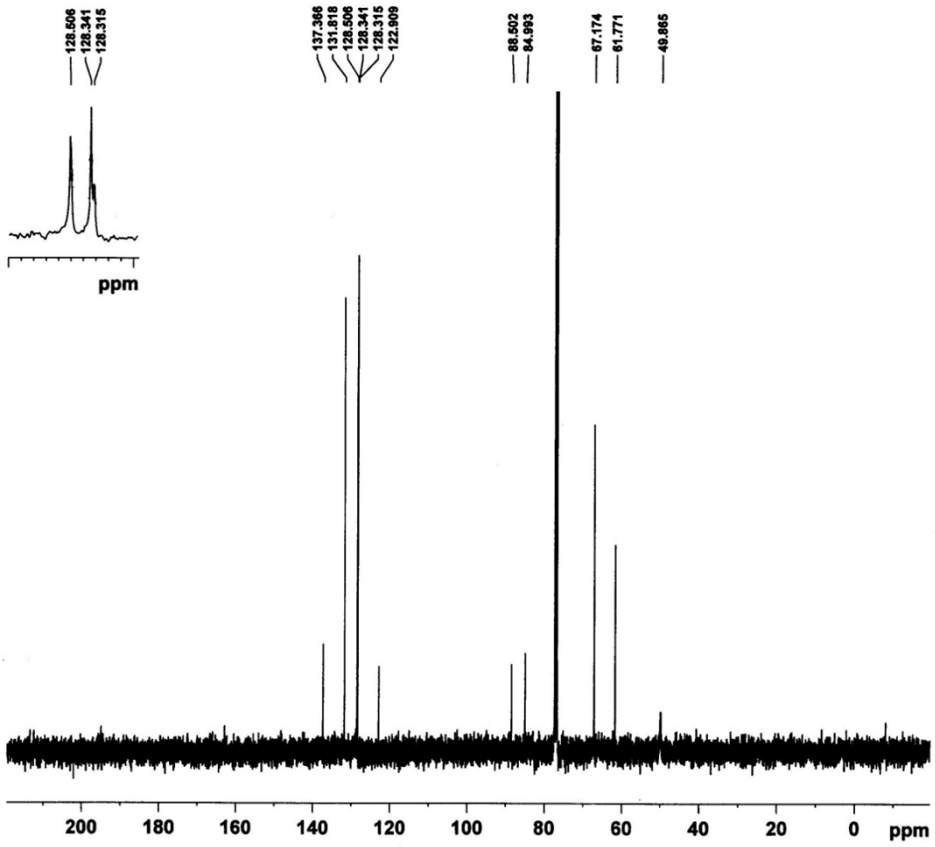

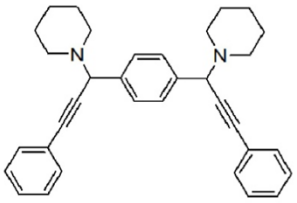

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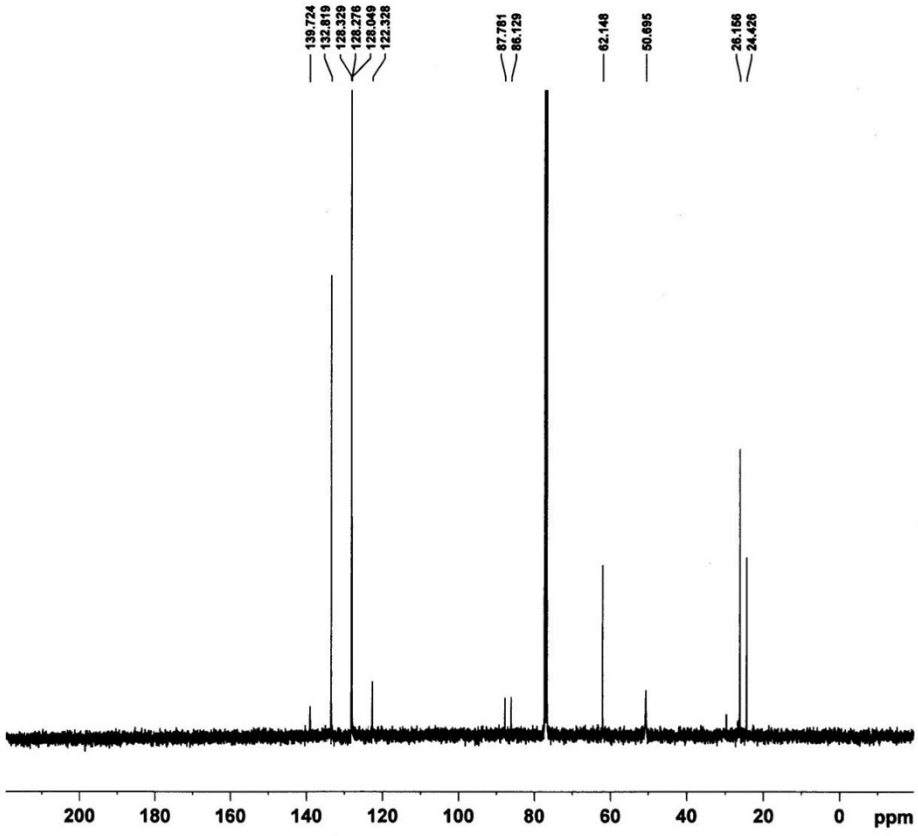

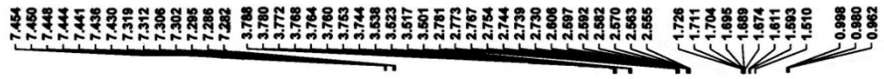

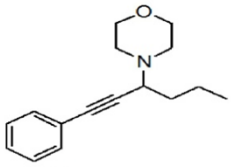

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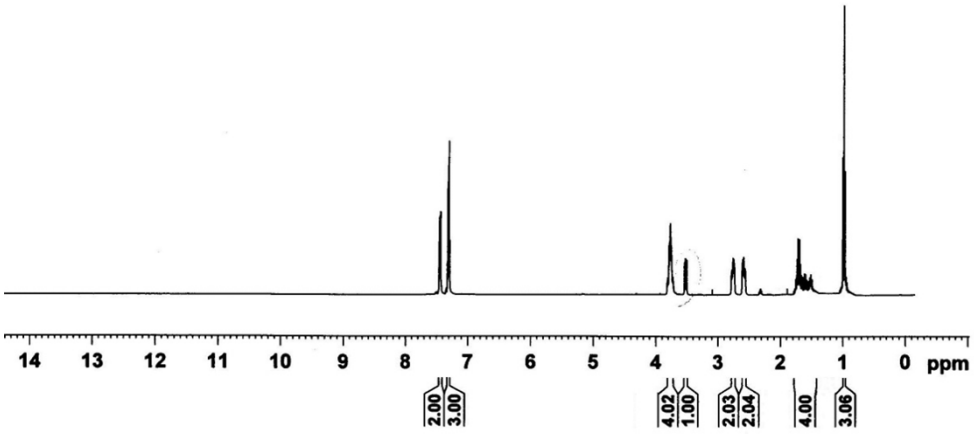
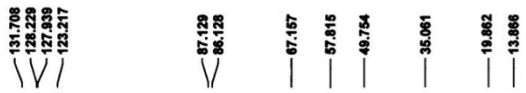
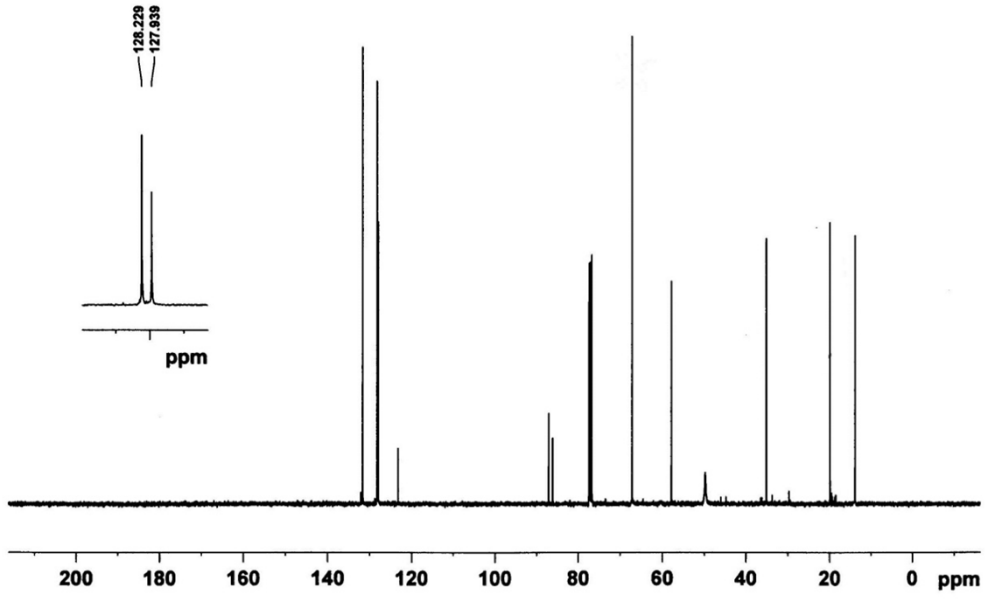
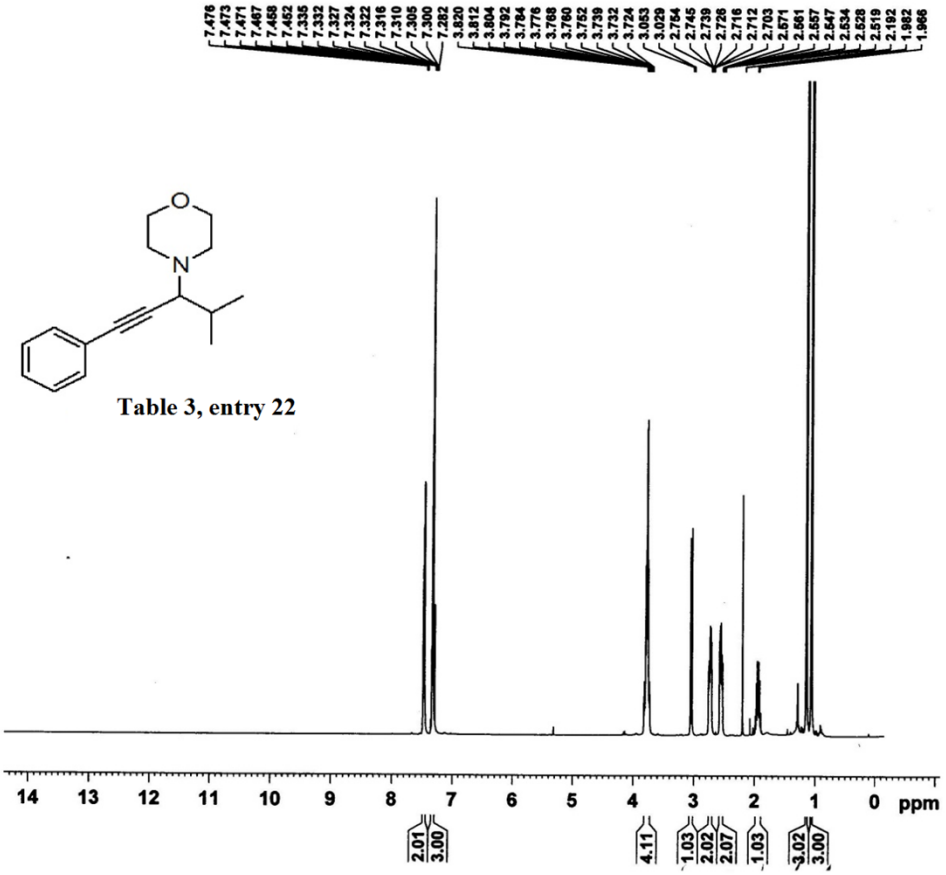
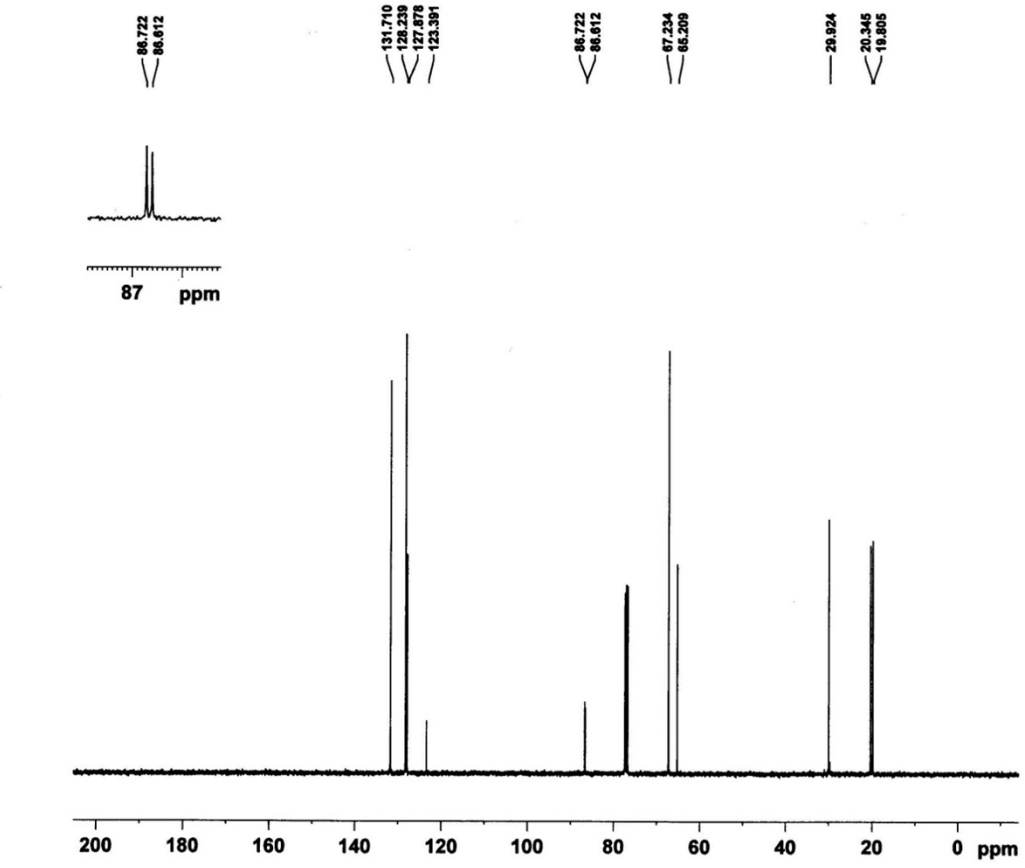







7.476
7.473
7.471
7.467
7.458
7.452
7.335
7.332
7.327
7.324
7.322
7.316
7.310
7.305
7.300
7.282
3.820
3.812
3.804
3.792
3.784
3.776
3.768
3.760
3.752
3.739
3.732
3.724
3.053
3.029
2.764
2.745
2.739
2.726
2.716
2.712
2.703
2.671
2.661
2.557
2.547
2.534
2.528
2.519
2.192
1.982
1.966
O
N
Table 3, entry 22
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.01
3.00
4.11
1.03
2.02
2.07
1.03
3.02
3.00


86.722
86.612
131.710
128.239
127.878
123.391
86.722
86.612
67.234
65.209
29.924
20.345
19.805
87 ppm
200 180 160 140 120 100 80 60 40 20 0 ppm

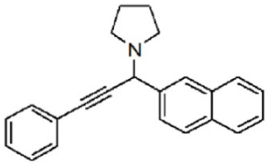
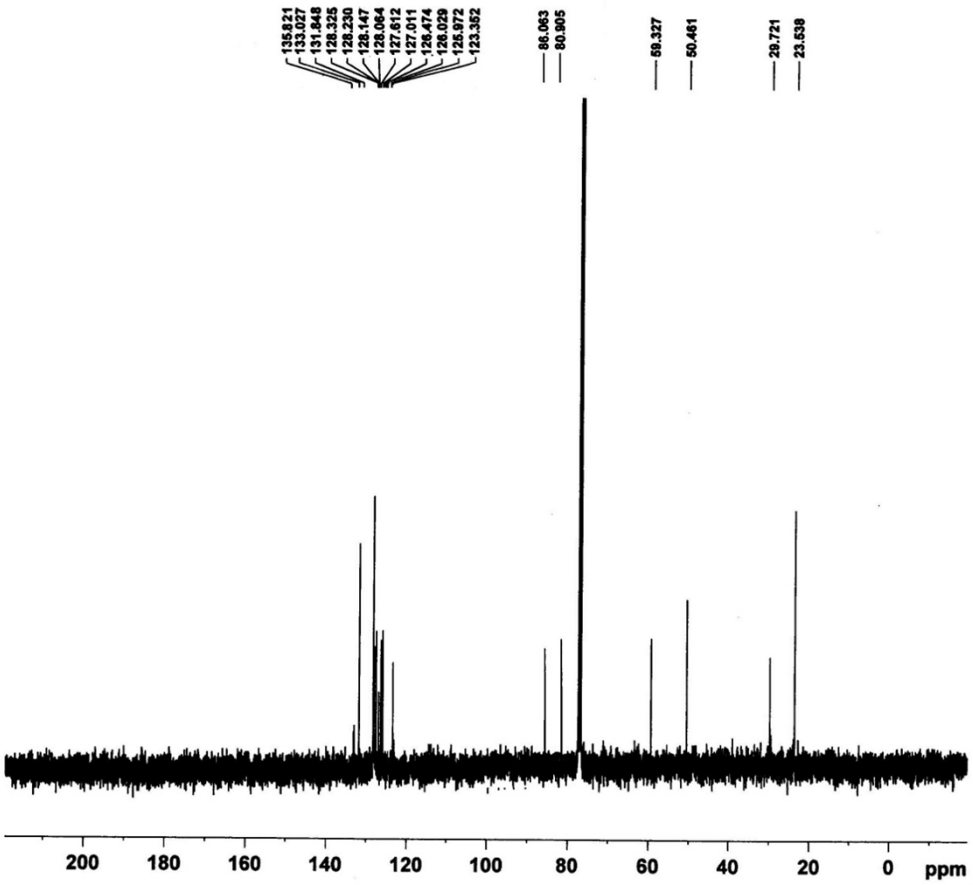


Table 3, entry 24



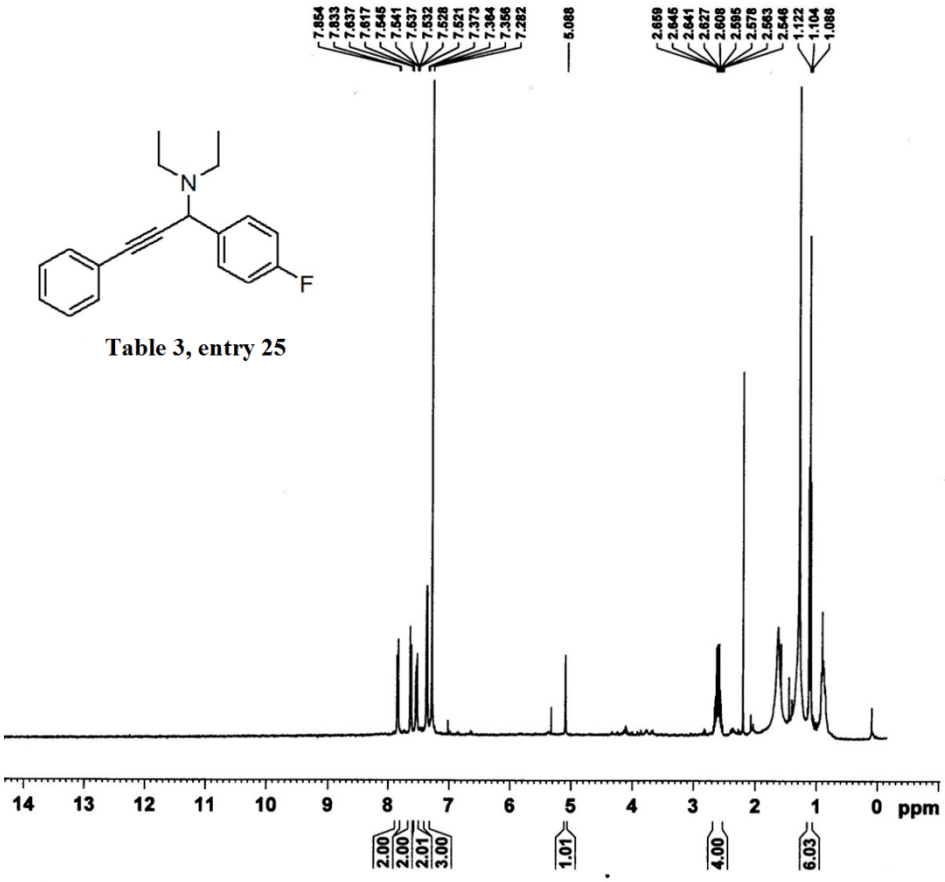
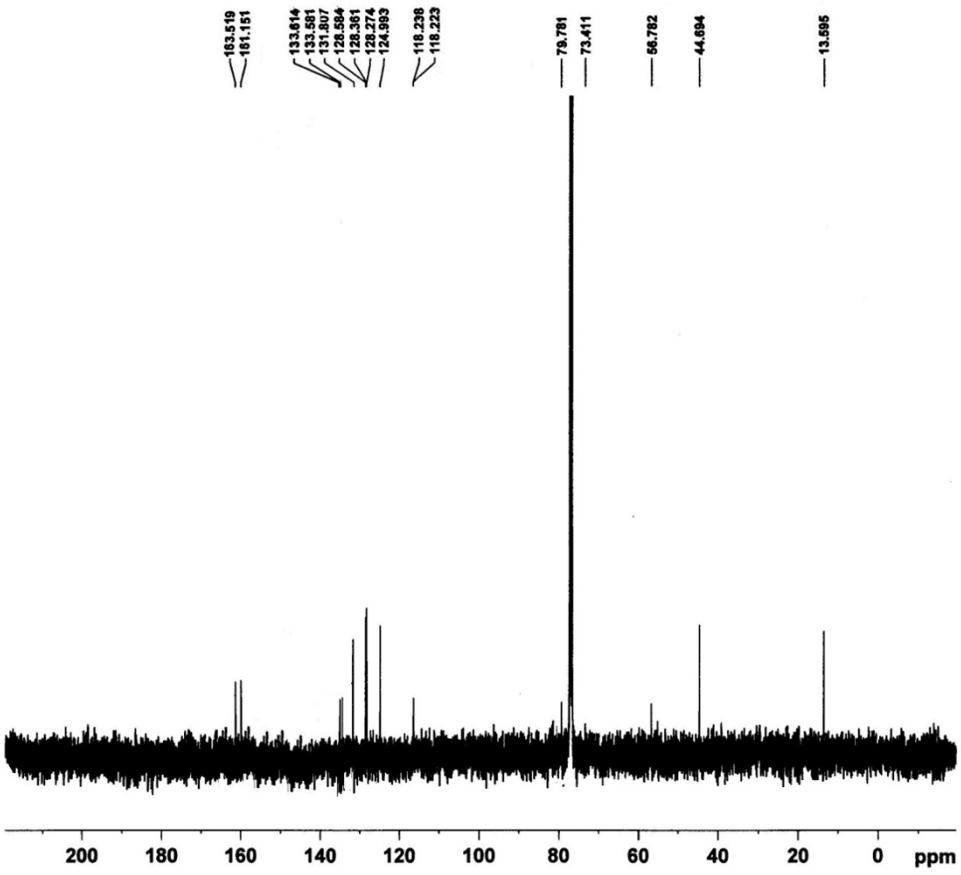


Table 3, entry 25



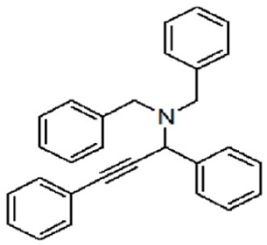
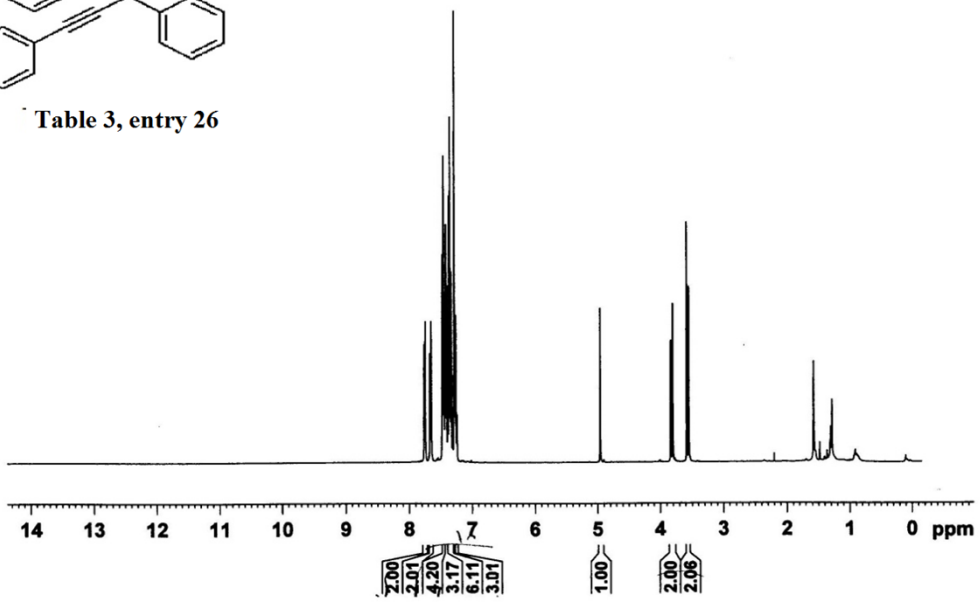
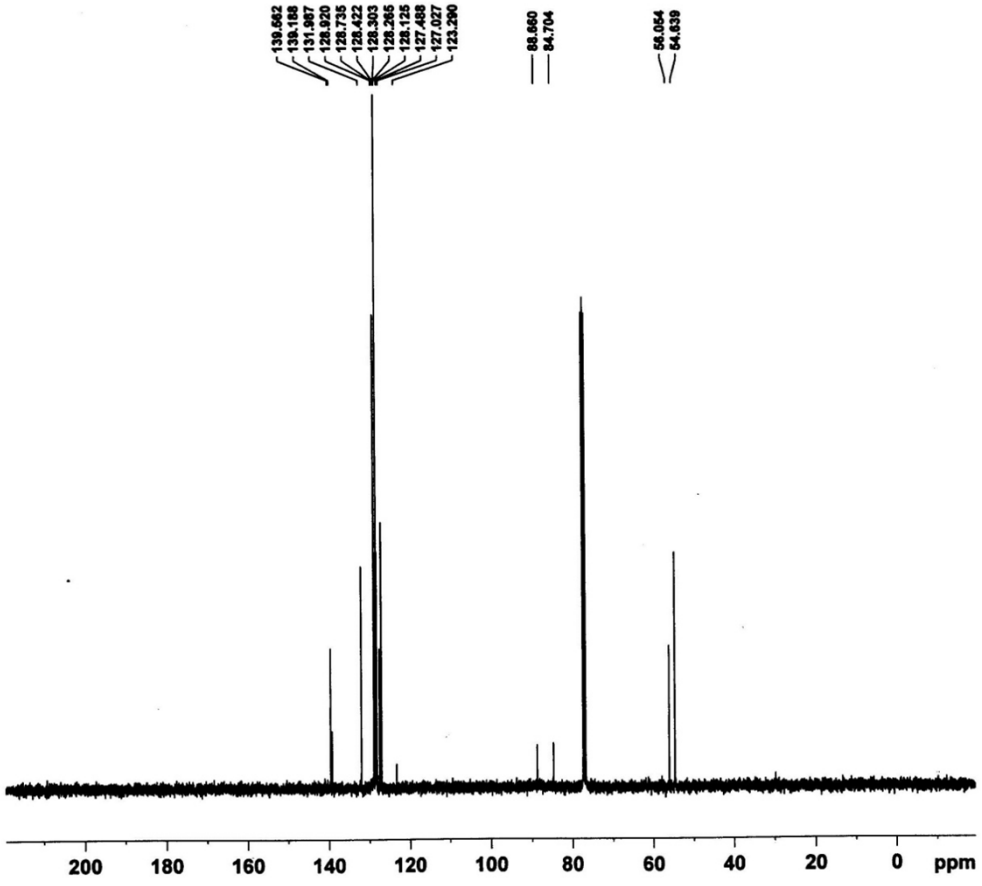


Table 3, entry 26





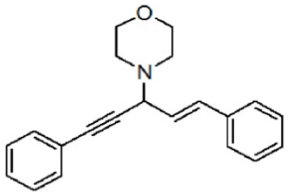
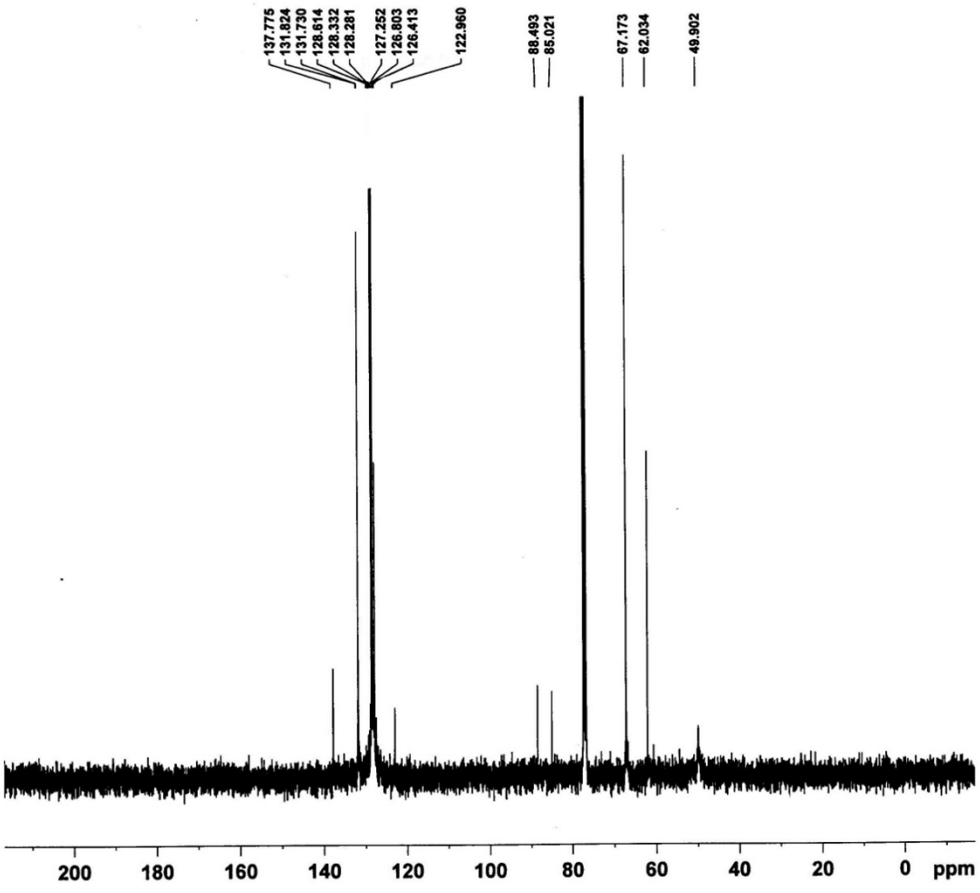
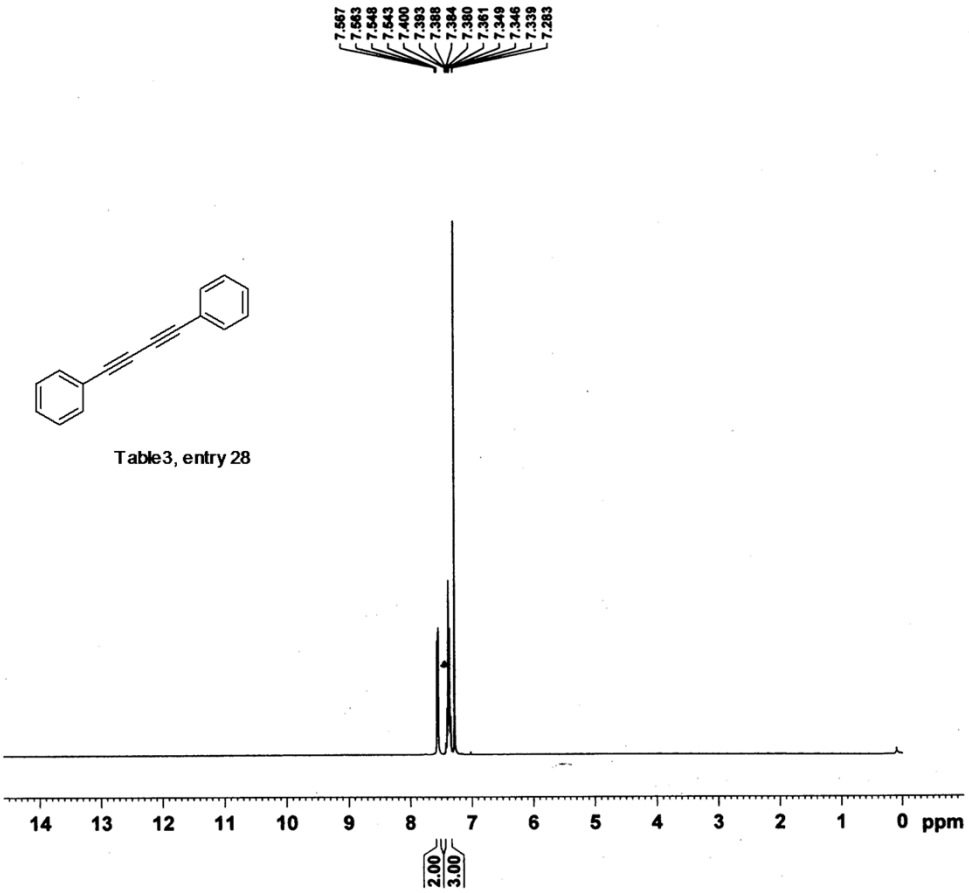
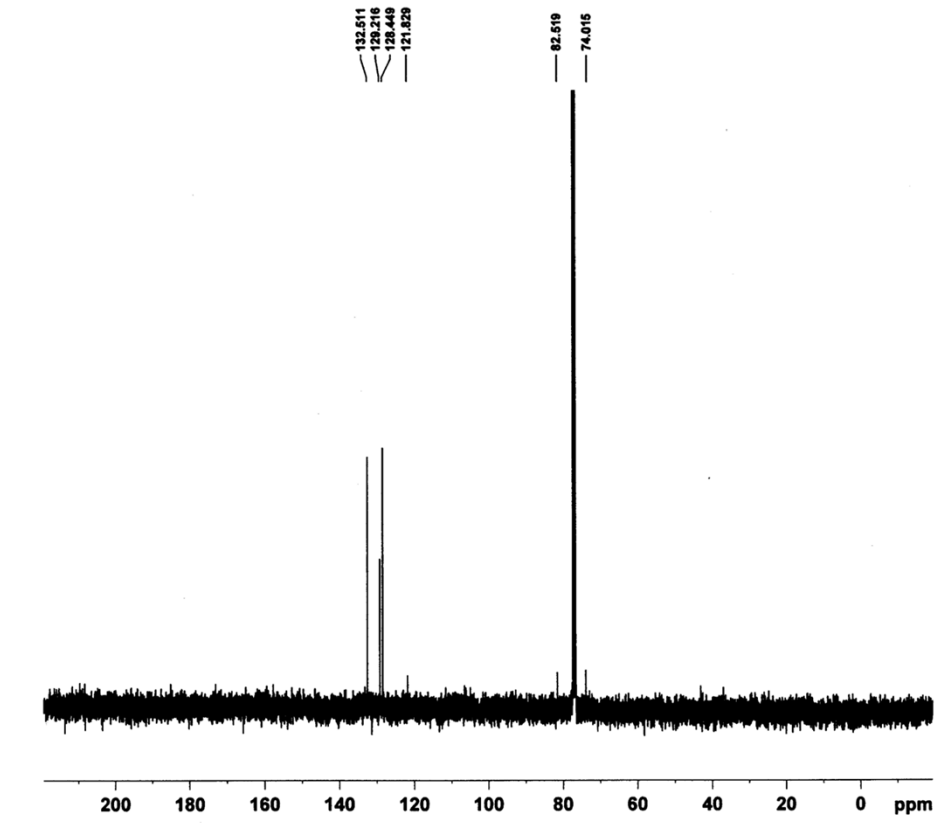
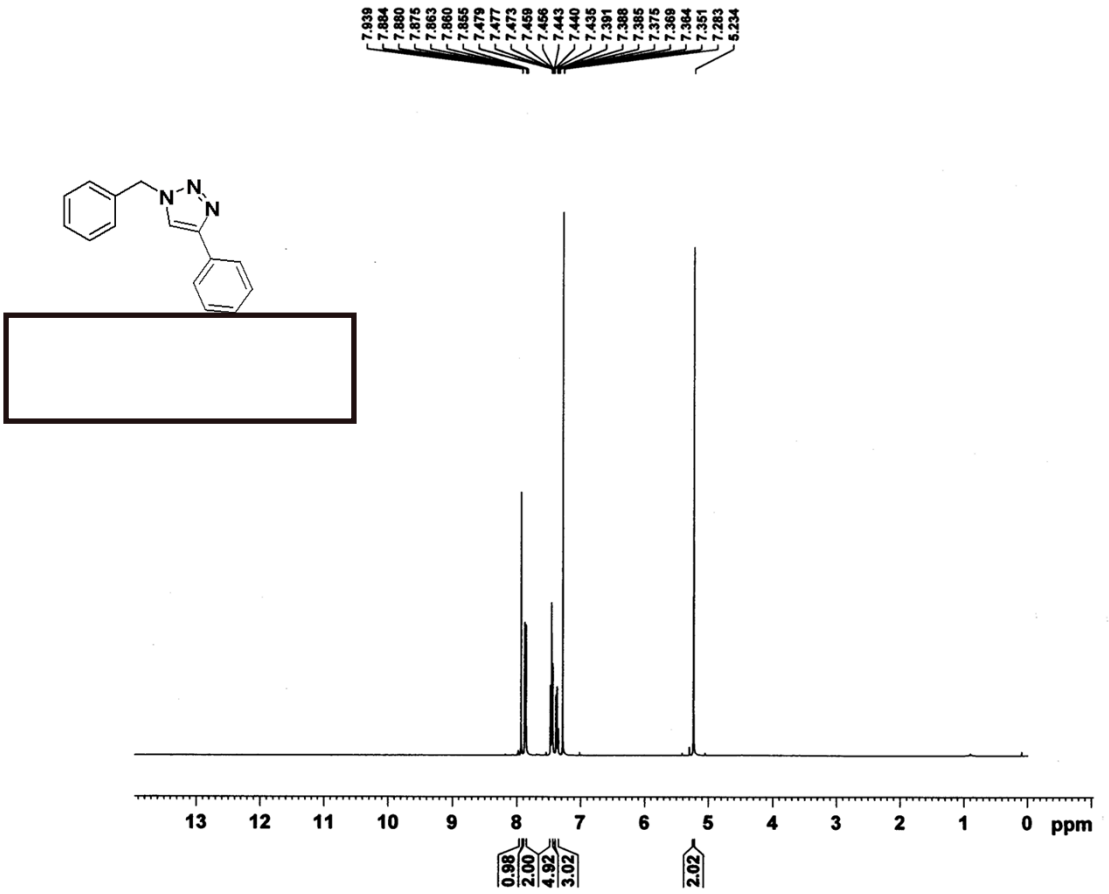


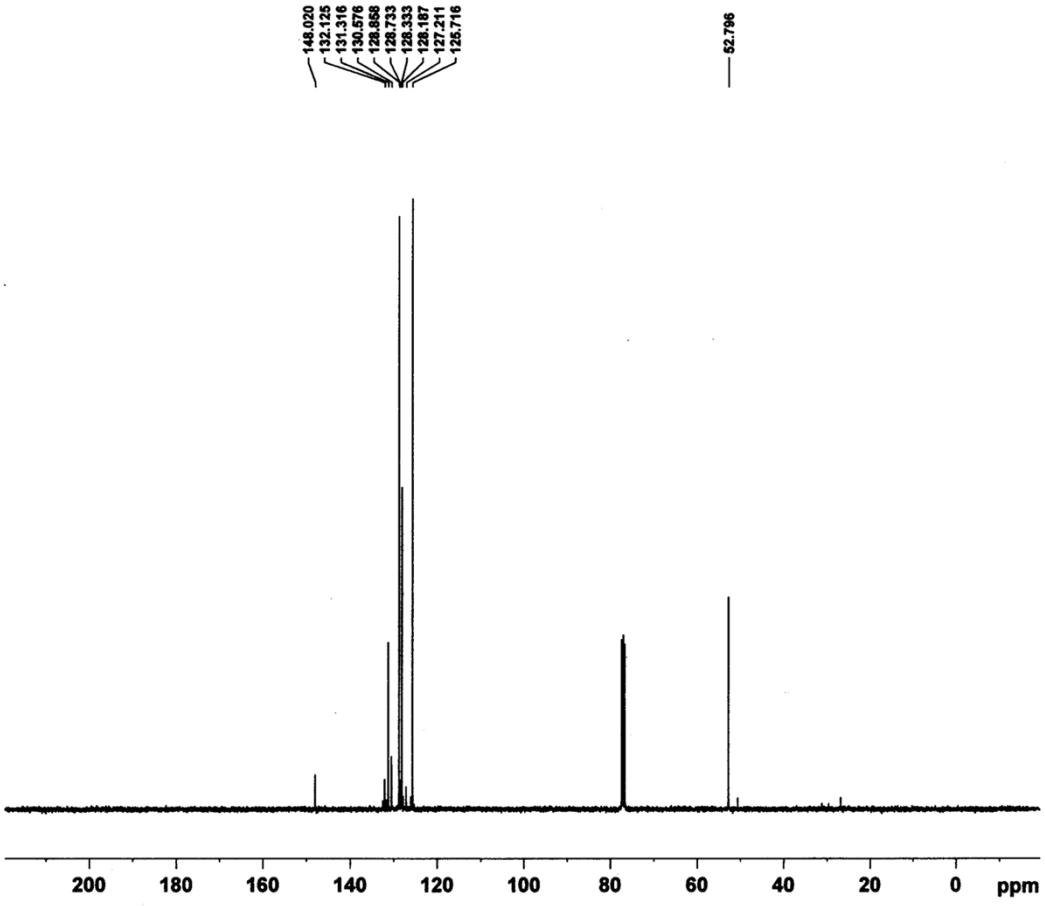
Table 3, entry 27



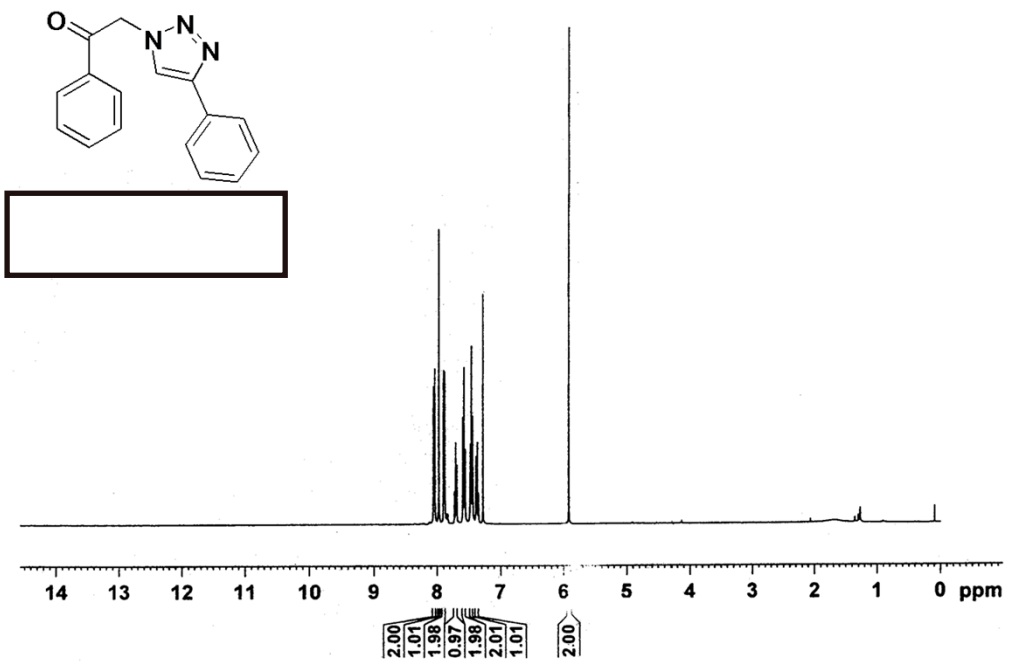

7.567
7.563
7.548
7.543
7.400
7.393
7.388
7.384
7.380
7.361
7.349
7.346
7.339
7.283
Table3, entry 28
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
3.00

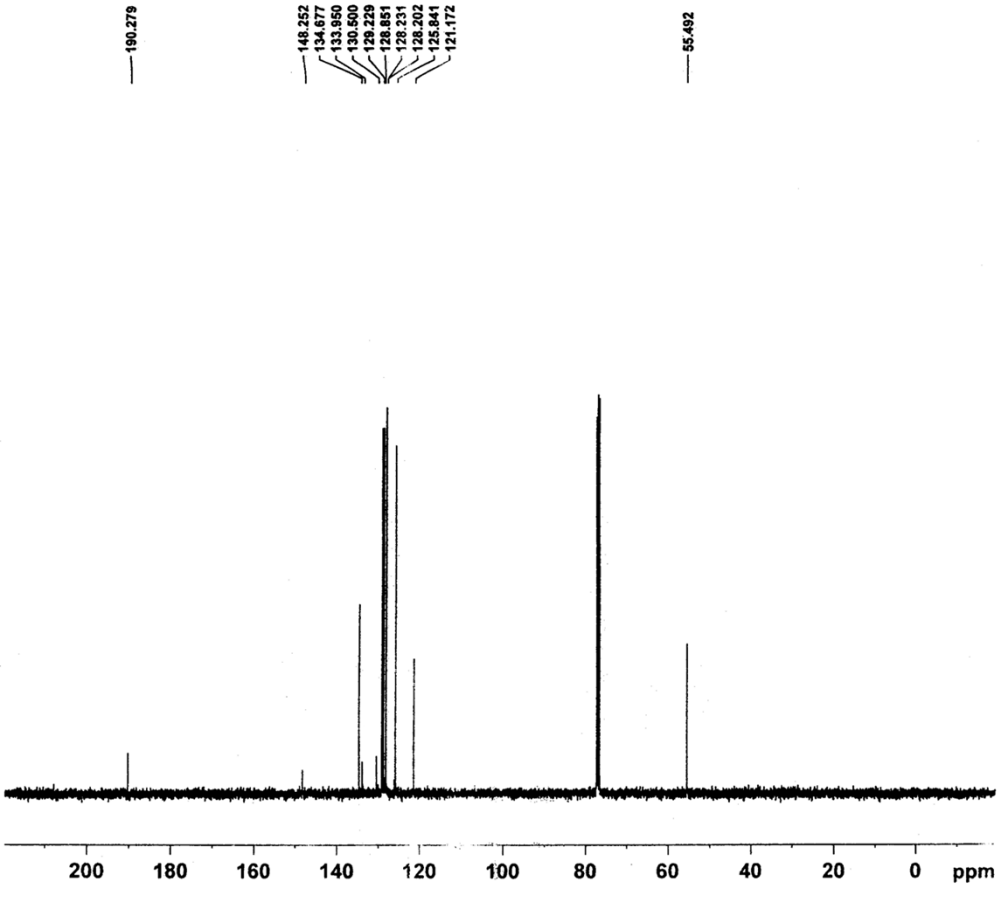

132.511
129.216
128.449
121.829
82.519
74.015
200 180 160 140 120 100 80 60 40 20 0 ppm

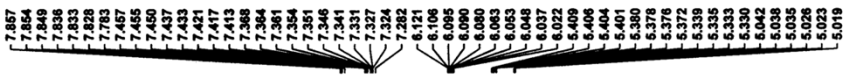

7.939
7.884
7.880
7.875
7.863
7.860
7.855
7.479
7.477
7.473
7.459
7.456
7.443
7.440
7.435
7.391
7.388
7.385
7.375
7.369
7.364
7.351
7.283
5.234
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.98
2.00
4.92
3.02
2.02

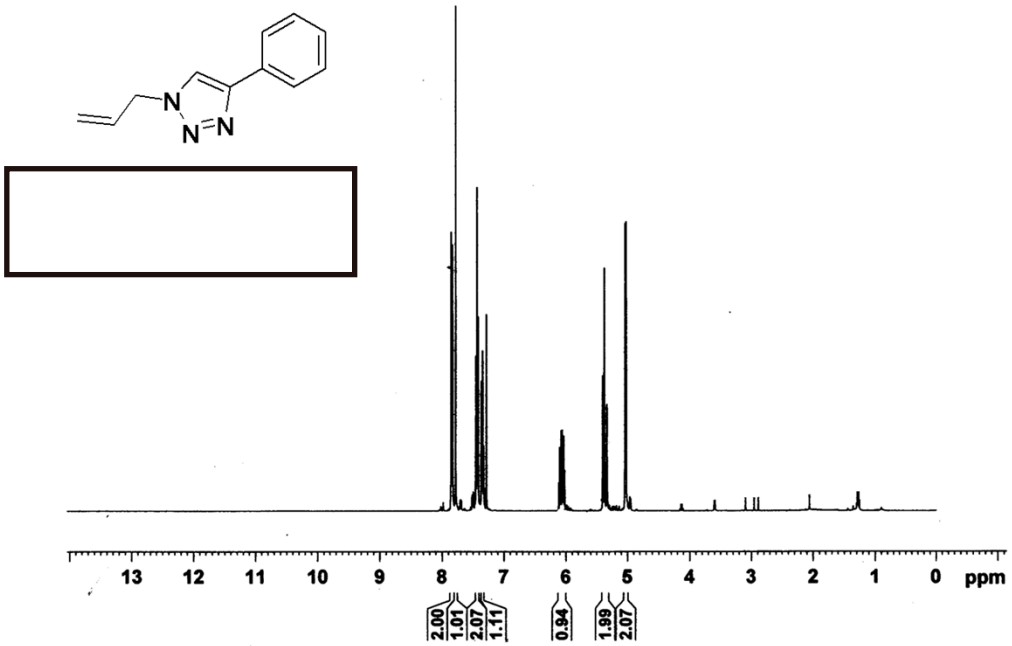

148.020
132.125
131.316
130.576
128.858
128.733
128.333
128.187
127.211
125.716
52.796
200 180 160 140 120 100 80 60 40 20 0 ppm

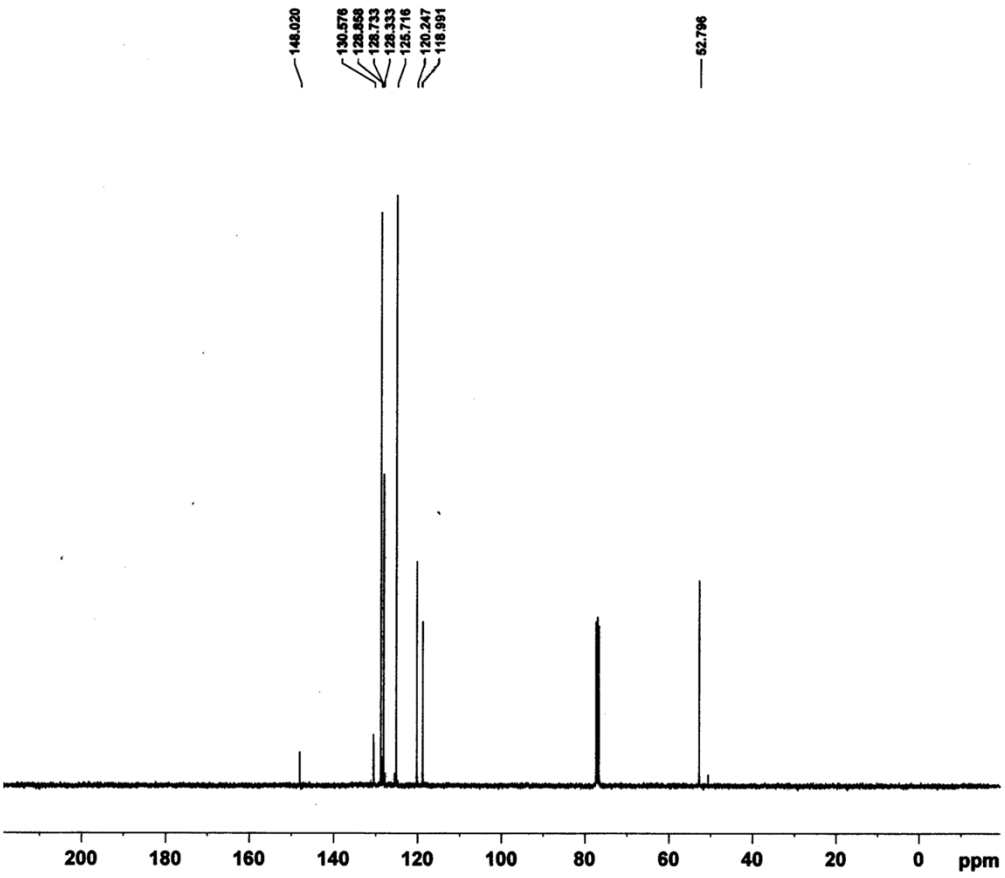

8.064
8.062
8.048
8.044
8.040
7.975
7.905
7.902
7.897
7.884
7.881
7.727
7.713
7.708
7.704
7.693
7.690
7.686
7.599
7.595
7.579
7.564
7.560
7.481
7.479
7.459
7.445
7.442
7.390
7.387
7.384
7.374
7.369
7.363
7.350
5.927

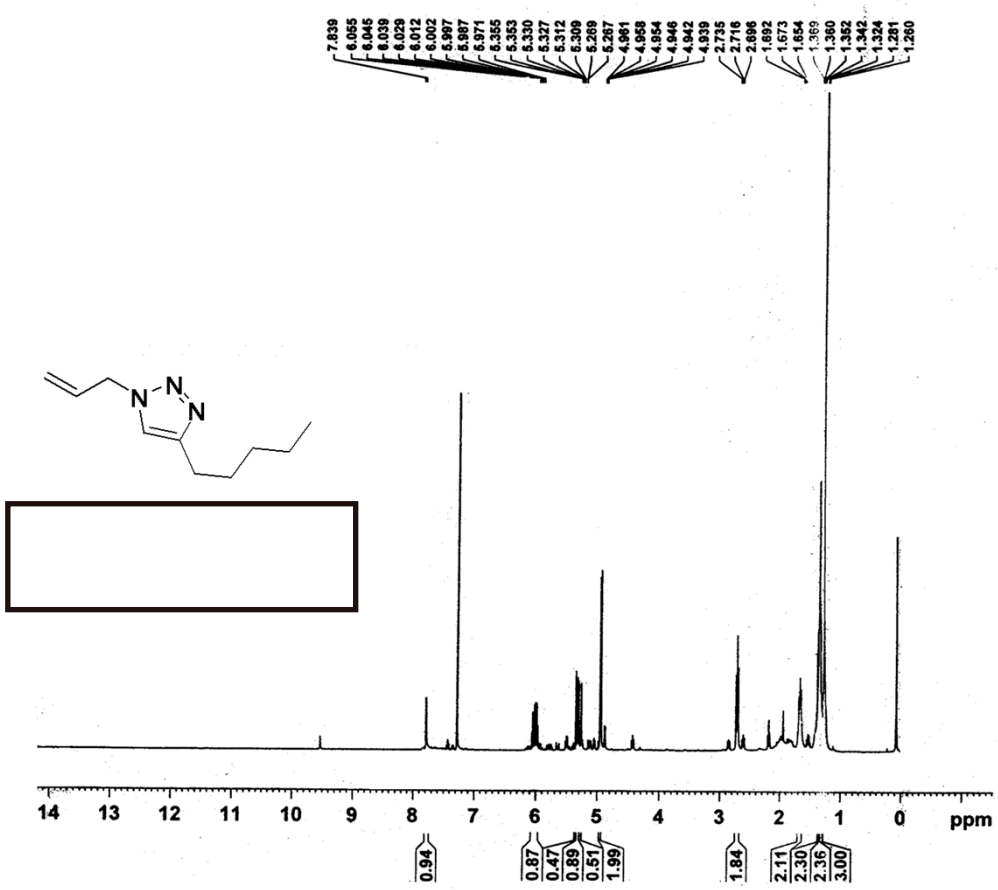

O
N
N
N
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.01
1.98
0.97
1.98
2.01
1.01
2.00

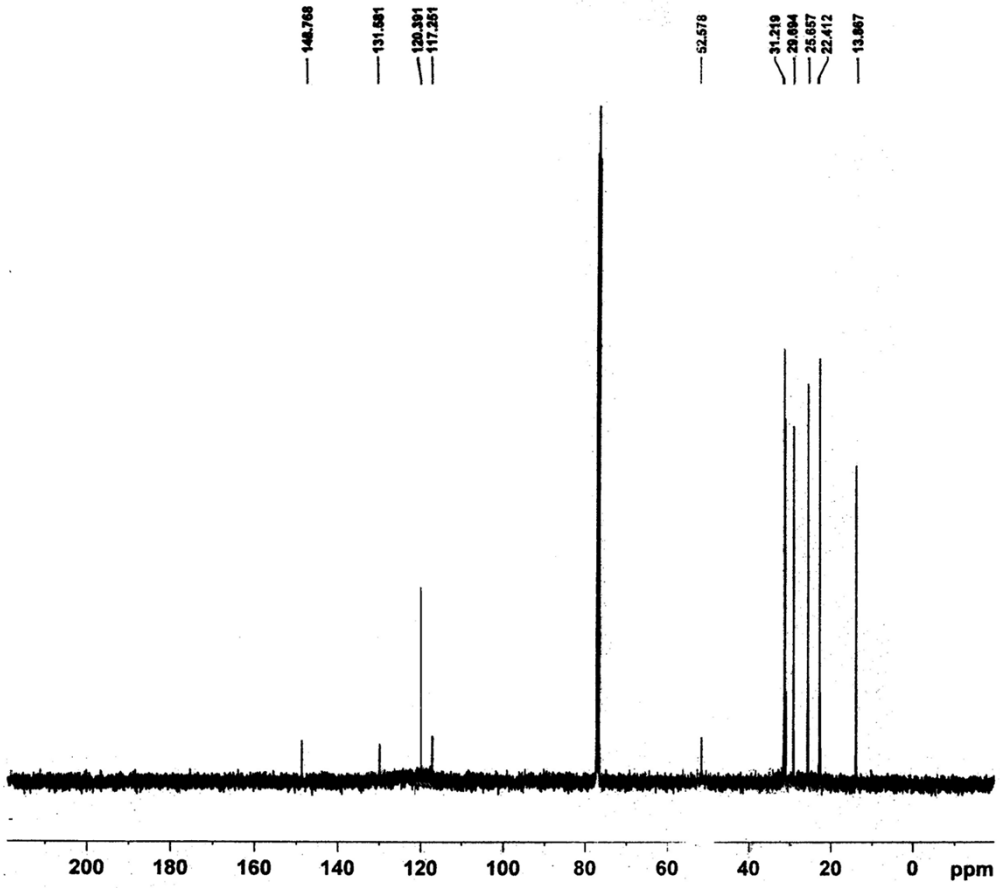

190.279
148.252
134.677
133.950
130.500
129.229
128.851
128.231
128.202
125.841
121.172
55.492
200 180 160 140 120 100 80 60 40 20 0 ppm

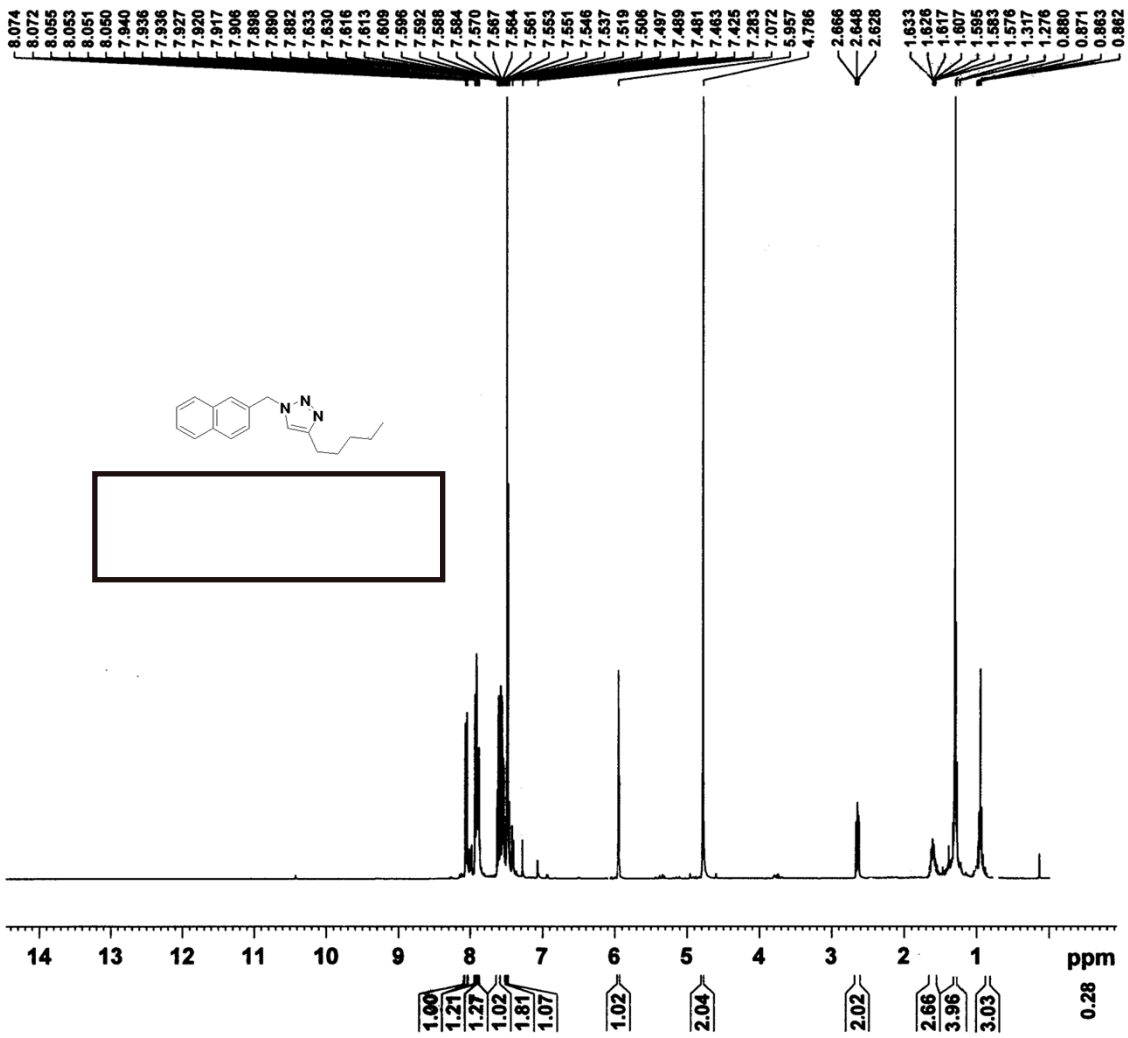

7.857
7.854
7.849
7.836
7.833
7.828
7.783
7.457
7.455
7.450
7.437
7.433
7.421
7.417
7.413
7.368
7.364
7.361
7.354
7.351
7.346
7.341
7.331
7.327
7.324
7.282
6.121
6.106
6.095
6.090
6.080
6.063
6.053
6.048
6.037
6.022
5.409
5.406
5.404
5.401
5.380
5.378
5.376
5.372
5.339
5.335
5.333
5.330
5.042
5.038
5.035
5.026
5.023
5.019

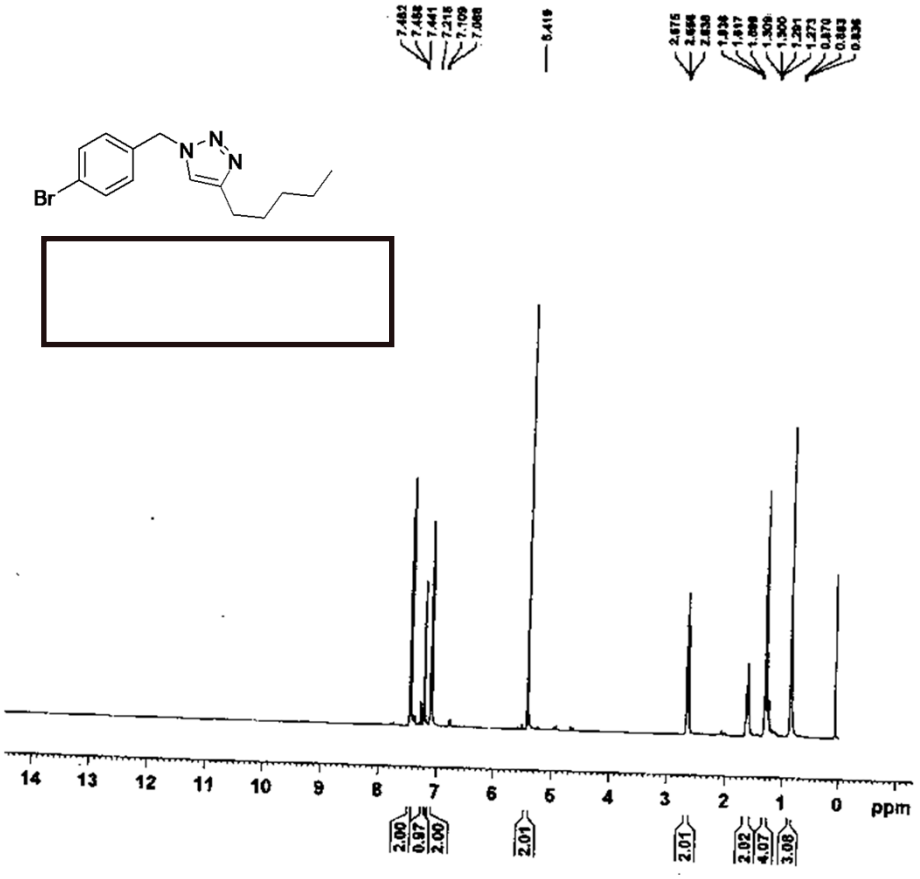

13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.01
2.07
1.11
0.84
1.99
2.07

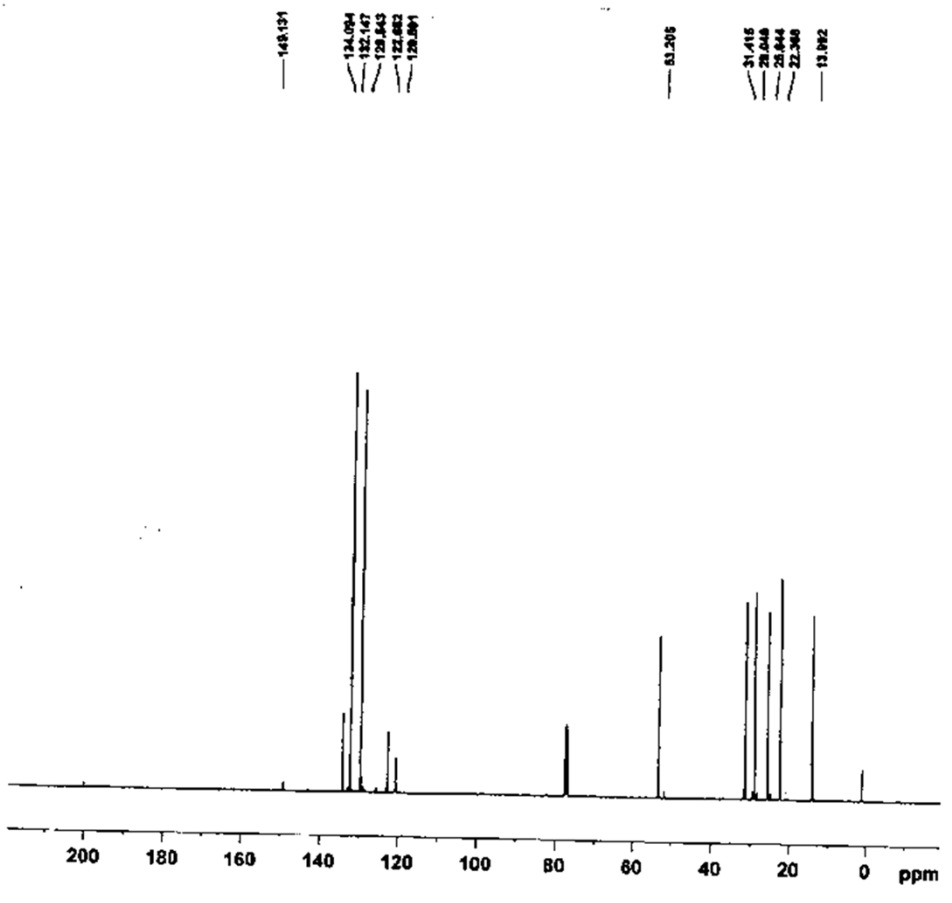

148.020
130.576
128.858
128.733
128.333
125.716
120.247
118.991
52.796
200
180
160
140
120
100
80
60
40
20
0
ppm

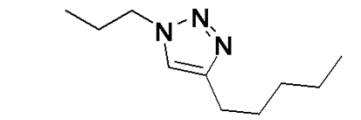

7.839
6.055
6.045
6.039
6.029
6.012
6.002
5.997
5.987
5.971
5.355
5.353
5.330
5.327
5.312
5.309
5.269
5.267
4.961
4.958
4.954
4.946
4.942
4.939
2.735
2.716
2.696
1.692
1.673
1.654
1.369
1.360
1.352
1.342
1.324
1.281
1.260
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.94
0.87
0.47
0.89
0.51
1.99
1.84
2.11
2.30
2.36
3.00

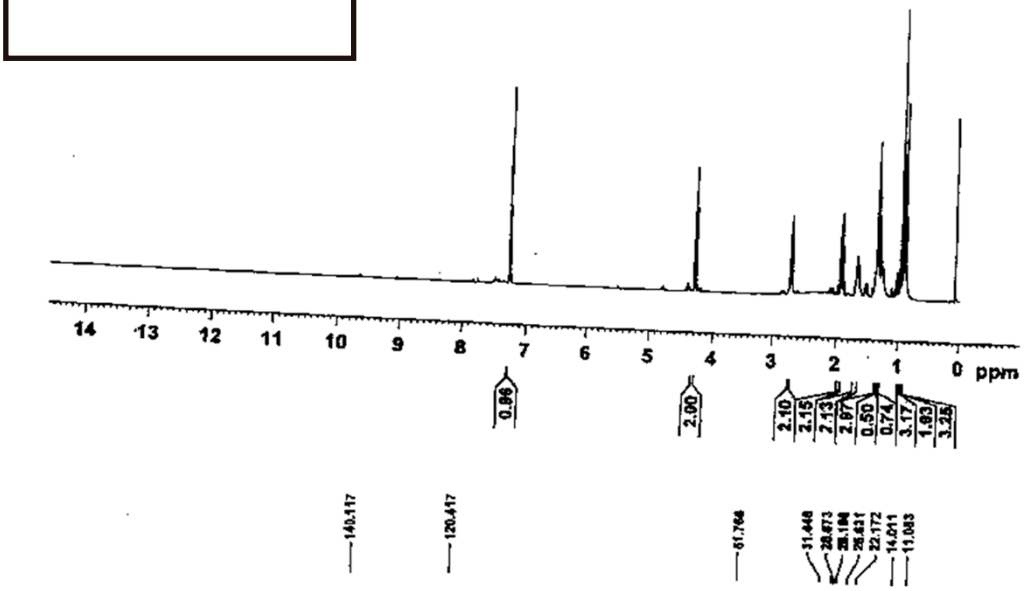

148.768
131.881
120.391
117.251
52.578
31.219
29.884
25.857
22.412
13.867
200 180 160 140 120 100 80 60 40 20 0 ppm

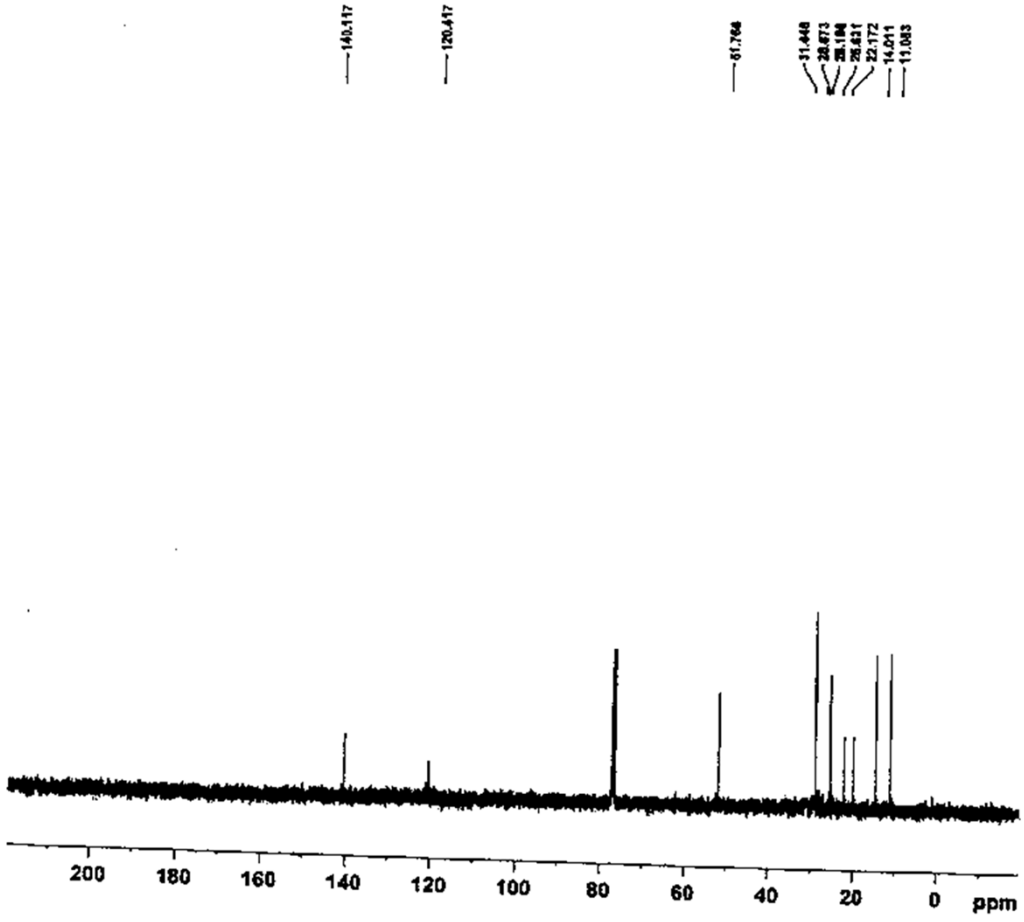

8.074
8.072
8.055
8.053
8.051
8.050
7.940
7.936
7.936
7.927
7.920
7.917
7.906
7.898
7.890
7.882
7.633
7.630
7.616
7.613
7.609
7.596
7.592
7.588
7.584
7.570
7.567
7.564
7.561
7.553
7.551
7.546
7.537
7.519
7.506
7.497
7.489
7.481
7.463
7.425
7.283
7.072
5.957
4.786
2.666
2.648
2.628
1.633
1.626
1.617
1.607
1.595
1.583
1.576
1.317
1.276
0.880
0.871
0.863
0.862
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.21
1.27
1.02
1.81
1.07
1.02
2.04
2.02
2.66
3.96
3.03
0.28

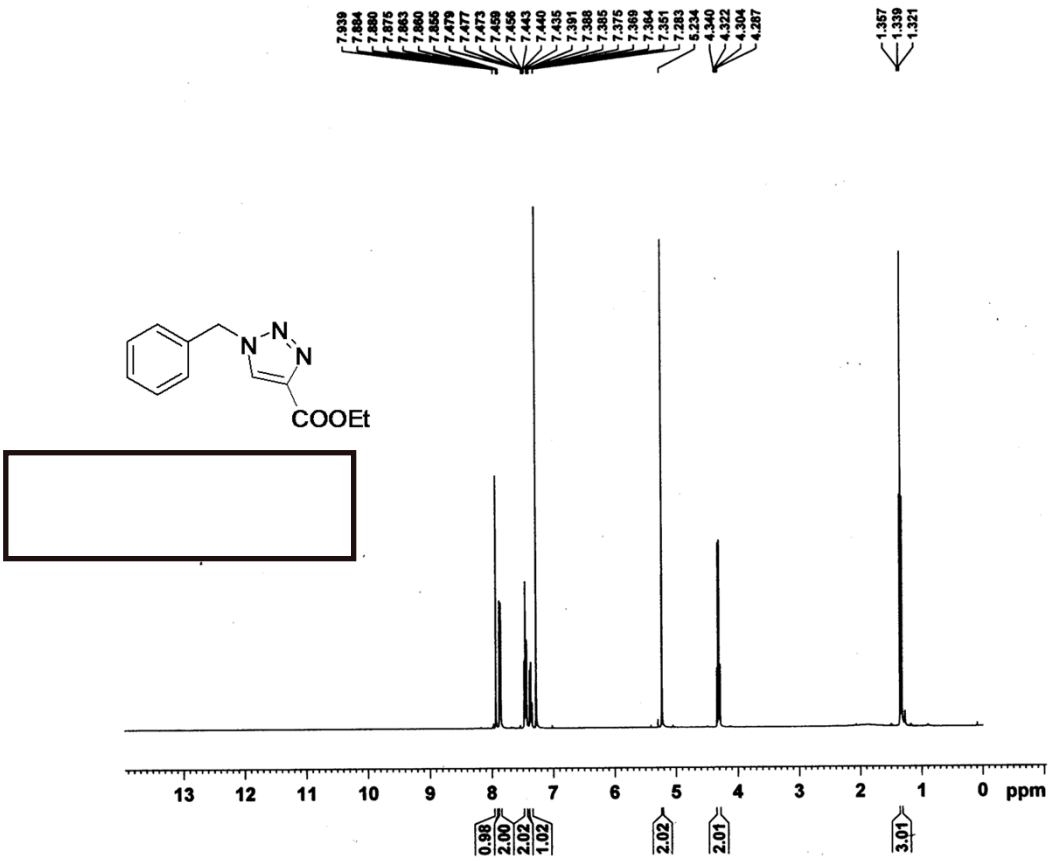

Br
N
N
N
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm

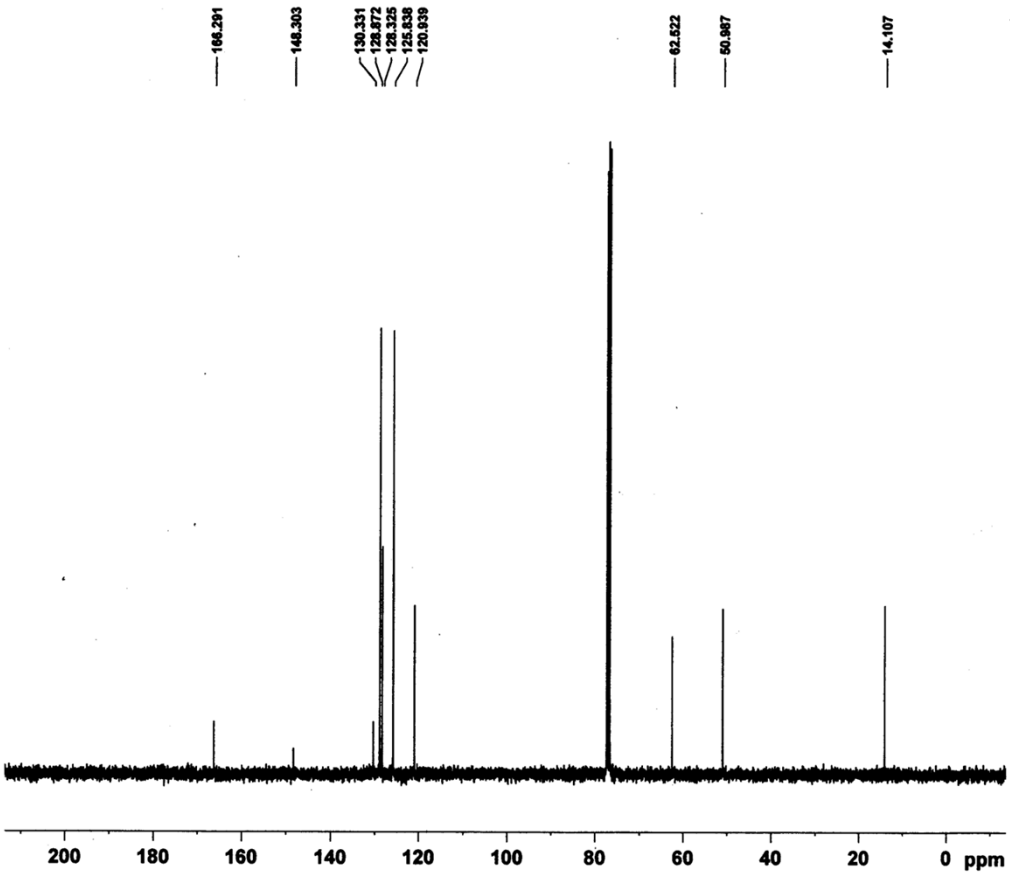

200
180
160
140
120
100
80
60
40
20
0
ppm




7.283
7.270
4.312
4.294
4.278
2.739
2.720
2.700
1.962
1.863
1.846
1.842
1.824
1.806
1.700
1.681
1.661
1.357
1.339
1.349
1.346
1.288
1.880
0.861
0.843
0.923
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.86
2.00
2.10
2.15
2.13
2.07
0.50
0.74
3.17
1.83
3.25


140.117
120.417
61.764
31.448
28.673
28.194
26.431
22.172
14.011
11.083
200 180 160 140 120 100 80 60 40 20 0 ppm


7.939
7.884
7.880
7.875
7.863
7.860
7.856
7.479
7.477
7.473
7.459
7.456
7.443
7.440
7.435
7.391
7.388
7.385
7.375
7.369
7.364
7.351
7.283
5.234
4.340
4.322
4.304
4.287
1.357
1.339
1.321
N
N
N
COOEt
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.98
2.00
2.02
1.02
2.02
2.01
3.01


166.291
148.303
130.331
128.872
128.325
125.838
120.939
62.522
60.987
14.107
200 180 160 140 120 100 80 60 40 20 0 ppm

References

1. L. L. Chng, J. Yang, Y. Wei, J. Y. Ying, *Adv. Synth. Catal*. 2009, **351**, 2887-2896.

2. G. Ren, J. Zhang, Z. Duan, M. Cui, Y. Wu, *Aust. J. Chem*. 2009**, 62**, 75-81.

3. M. Tajbaksh, M. Farhang, H.R. Mardani, R. Hosseinzadeh, Y. Sarrafi, *Chinese J. Catal*. **2013, 34,** 2217–2222.

4. B. Karimi, M. Gholinejad, M. Khorasani*, Chem. Commun*. 2012**, 48**, 8961-8963.

5. E. Ramu, R.Varala, N.R. Sreelatha, S.Adapa, *Tetrahedron Lett*. 2007**, 48**, 7184-7190.

6. W. Sujing, H. Xiaoxiao, S. Lexin, W. Zhiyong, *Synlett*, 2009, 447-450.

7. F. Nador, M.A. Volpe, F.Alonso, A. Feldhoff, A. Kirschning, G. Radivo, *Appl. Catal., A* 2013, **455**, 39-45.

8. S.R. Kale, S.S. Kahandal, M.B. Gawande, R.V. Jayaram, *RSC Adv*. 2013, **3**, 8184-8192.