Electronic Supplementary Material (ESI) for RSC Advances.

A novel superparamagnetic powerful Guanidine-functionalized γ-Fe_2O_3 based Sulfonic acid recyclable and efficient heterogeneous catalyst for microwave-assisted rapid synthesis of Quinazolin- 4(3H)–one derivatives in Green media

Fateme Haji Norouzi[1] Naser Foroughifar[1*] Alireza Khajeh-Amiri[2] Hoda Pasdar[1]

✉ n_foroughifar@yahoo.com

1 Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

2 Toxicology Research Center, Aja University of Medical Sciences, Tehran, Iran.

1. Experimental

1.1 | General

All starting materials and chemicals used in this research were bought from Sigma-Aldrich chemical companies without further purification. All recorded melting points (mp) were taken in an open capillary tube on a stuart scientific melting-point apparatus and are uncorrected. Elemental analysis was performed on a Perkin–Elmer 2400 C, H, N analyzer and values were within the acceptable limits of the calculated values. Infrared (FT-IR) spectra of all samples in our study were recorded in the sub-region 400-4000 cm^{-1} on Perkin Elmer Spectrum one instruments, using potassium bromide discs. Mass spectra were obtained on a HP 5975 Mass Selective Detector at 70 eV. The Proton Magnetic Resonance ^{1}H and ^{13}C spectra were performed on Bruker 400 or 600 spectrometers using $CDCl_3$ and DMSO-d_6 as solvent; all with tetramethylsilane (TMS) as internal standard. The chemical shifts were reported in δ value as parts per million (d ppm) and Coupling constants (J) are expressed in Hertz (Hz). The following abbreviations were used to explain the multiplicities: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet.

Spectral data (IR, mass, and NMR spectra) confirmed the structures of the synthesized compounds. The progress and success of each step, as well as the purity determinations of the obtained compounds were controlled and confirmed by thin layer chromatography (TLC) on readymade silicagel plates (Merck) using chloroform: methanol (9:1) as mobile phase. spots were detected and visualized under the UV light. The X-ray diffraction (XRD) pattern related to the structural phases of the prepared catalyst was accomplished using a Jeol JEM-1010 electron microscope and JEOL JSM-6100 microscope with (Cu kα radiation, λ=1.54 Å) in the region of 2Θ = 20°- 80°. The surface morphology and diameter of the catalyst nanoparticles (γ-Fe_2O_3@ CPTMS - Guanidine @SO_3H) was studied by scanning electron microscopy (SEM) analysis data was also recorded on a FEI Quanta 200 at a 20 kV accelerating voltage. Samples were prepared by dispensing drops of an aqueous suspension of particles on to a glass plate. This was allowed to dry at room temperature and was then coated with a thin Au film. SEM and the energy dispersive X-ray spectroscopy (EDS) analyses were performed. The elemental mapping and compositional analysis were performed by energy-dispersive X-ray spectroscopy (EDX) by a Kevex, Delta Class I, equipped with the SEM instrument. To characterize the magnetic measurement of modified and unmodified nanoparticles, a varying magnetic field from -10000 to 10000 on a BHV-S5 vibrating sample magnetometer (VSM) was utilized at room temperature (MDKFD, University of Kashan, Kashan, Iran). All the catalyst materials were degassed by passing nitrogen overnight at 200°C. The transmission electron microscope (TEM) images of the nanocatalyst was performed using a FEI CM200 field emission at accelerating voltage of 200 kV. The thermal gravimetric analysis (TGA) of nano-magnetic solid acid catalyst was carried out on a Shimadzu Thermogavimetric Analyzer (TG-50) in the temperature range of 25-900 ^oC at a heating rate of 10 ^oC /min in air under N_2 atmosphere. The magnetic property of the catalyst was measured using a vibrating sample magnetometer (VSM, 7400 Lake Shore). The energy dispersive X-ray spectroscopy (EDX) was performed using TESCAN Vega model instrument. The thermogravimetry and differential thermogravimetry (TG-DTG). The fourier-transform infrared spectroscopy (FT-IR). The field emission scanning electron microscopy (FESEM).

1.2 | Spectra data

2-methylquinazolin-4(3H)-one (**4a**, $C_9H_8N_2O$):

White solid; M.p. = 287-289 °C (230-232 °C,); IR (KBr) ν_{max} 3362, 3228 (N-H), 2883 (C-H), 1735, 1596 (C=O), 1597 (C=N), 1507 (C=C), 1161-1211 (C-N) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 11.85 (bs, 1H), 8.28 (d, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 2.60 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 153.4, 149.5, 134.8, 127.0, 126.3, 126.2, 120.2, 22.0 ppm.

2-methyl-3-propylquinazolin-4(3H)-one (**4b**, $C_{12}H_{14}N_2O$):

White solid; M.P.= 81-83 °C (82-83 °C,); IR (KBr) ν_{max} 3062, 2923, 2391, 1673, 1596, 1569, 1474, 1384, 1091, 1022, 682 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 7.75 − 7.66 (m, 1H), 7.60 (d, *J* =8.1 Hz, 1H), 7.43 (d.d., *J* = 7.7, 7.7 Hz, 1H), 4.12 − 4.00 (m, 2H), 2.65 (s, 3H), 1.85−1.70 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}CNMR (125 MHz, $CDCl_3$) δ 162.0, 154.1, 147.2, 134.1, 126.7, 126.5, 126.3, 120.5, 46.1, 23.1, 21.9, 11.3 ppm.

2-methyl-3-butylquinazolin-4(3H)-one (**4c**, $C_{13}H_{16}N_2O$):

White solid; M.P.= 88-90 °C (89 °C); IR (KBr) ν_{max} 2883 (C-H), 1735, 1596 (C=O), 1597 (C=N), 1507 (C=C), 1161-1211 (C-N) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18(d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 4.02 (t, *J* = 7.5 Hz, 1H), 2.59 (s, 3H), 1.69-1.63 (m, 3H), 1.44-1.37 (m, 2H), 0.94(t, *J* = 7.5 Hz, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.8, 154.0, 147.2, 133.9, 126.6, 126.4, 126.1, 120.4, 44.3, 30.6, 22.9, 20.1, 13.6 ppm.

2-methyl-3- cyclohexylquinazolin-4(3H)-one (**4d**, $C_{15}H_{18}N_2O$):

White solid; M.P.= 289-291 °C (>300 °C); IR (KBr) ν_{max} 3100 (s), 2921 (s), 1675 (s), 1582 (s), 755 (s) cm^{-1};^1H NMR (500 MHz, DMSO) δ 8.18 (d.d., *J* = 8.1 Hz, *J* = 1.3 Hz, 1H), 7.72 (d.t., *J* = 7.7 Hz, *J* = 1.3 HZ, 1H), 7.60 (d.d., *J* = 8.2 Hz, *J* = 1.4 Hz, 1H), 7.44(d.t., *J* = 7.4 Hz, *J* = 1.4 HZ, 1H), 4.44 (t., *J* = 5.8 Hz, 1H),

2.74 (s, 3H), 1.86 – 1.79 (m, 2H), 1.71 – 1.65 (m, 2H), 1.60- 1.34 (6H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.0, 153.3, 146.9, 133.7, 127.0, 123.9, 121.1, 54.6, 31.5, 26.2, 24.3, 23.8 ppm.

3-benzyl-2-methylquinazolin-4(3H)-one (**4e**, $C_{16}H_{14}N_2O$):

Yellow; 220-223 °C (230-231 °C); IR (KBr) ν_{max} 3050 (s), 2860 (s), 1640 (s), 1600 (s), 1470 (m), 725 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.45(t, *J* = 8.0 Hz, 1H), 7.31-7.29 (m, 2H), 7.26-7.23 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 5.38 (s, 2H), 2.53 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 154.6, 147.3, 135.8, 134.4, 128.9, 127.6, 127.1, 126.7, 126.5, 120.4, 47.1, 23.3 ppm.

2-methyl-3-phenylquinazolin-4(3H)-one (**4f**, $C_{15}H_{12}N_2O$):

White solid; M.P.=145-146 °C (147-148 °C); IR (KBr) ν_{max} 3100 (s), 2921 (s), 1675 (s), 1582 (s), 755 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d.d., *J* = 8.0 Hz, *J* = 1 Hz, 1H), 7.79-7.76 (m, 1H), 7.69 (d., *J* = 8.0 Hz, 1H), 7.58-7.55 (m, 2H), 7.53-7.51 (m, 1H), 7.49-7.46 (m, 1H), 7.28-7.26 (m, 2H), 2.26 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 154.3, 147.4, 137.7, 134.6, 130.0, 129.3, 128.0, 127.1, 126.7, 126.7, 120.8, 24.3 ppm.

2-methyl-3-(4- chlorophenyl) quinazolin-4(3H)-one (**4g**, $C_{15}H_{11}ClN_2O$):

Yellow solid; M.P.= 154-155°C (156-158 °C); IR (KBr) ν_{max} 3056 (s), 2911 (s), 1710 (s), 1660 (s), 1571 (s), 812 (s), 741 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d.d., *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.79-7.76 (m, 1H), 7.67 (d., *J* = 8.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.23-7.21 (m, 2H), 2.25 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 153.6, 147.3, 136.2, 135.4, 134.7, 130.3, 129.5, 127.0, 126.8, 126.8, 120.6, 24.3 ppm.

2-methyl-3-(4- nitro phenyl) quinazolin-4(3H)-one (**4h,** $C_{15}H_{11}N_3O_3$):

Orang solid; M.P.=193 °C (190-193 °C, [6]); IR (KBr) ν_{max} 3060 (s), 1710 (s), 1662 (s), 1567 (s), 755 (s) cm^{-1}; ^{1}H NMR (500 MHz, DMSO) δ 8.29 - 8.25 (m 3H), 7.75 – 7.71 (m, 3H), 7.63 (d., *J* = 8.2 Hz, *J* = 1.4

Hz, 1H), 7.45 (d.t, J = 8.1 Hz, J = 1.3 Hz, 1H), 2.25 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.5, 155.9, 146.7, 141.4, 141.1, 133.7, 127.9, 126.3, 126.2, 125.4, 123.9, 121.7, 23.7 ppm.

2-methyl-3-(4-methoxy phenylquinazolin-4(3H))-one (**4i**, $C_{16}H_{14}N_2O_2$):

White solid; M.P.= 173 °C (169-171 °C); IR (KBr) ν_{max} 2838 (s), 3051 (s), 1707 (s), 1657 (s), 1568 (s), 755 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d.d., *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.79-7.76 (m, 1H), 7.71 (d., *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 1H), 7.19-7.17 (m, 2H), 7.07-7.05 (m, 2H), 3.88 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 160.0, 155.0, 147.0, 134.6, 130.1, 129.0, 127.1, 126.7, 126.5, 120.7, 115.2, 55.5, 24.2 ppm.

2-methyl-3-(4- methyl phenyl) quinazolin-4(3H)-one (**4j**, $C_{16}H_{14}N_2O$):

White solid; M.P.= 153-155 °C (149-150 °C); IR (KBr) ν_{max} 3048 (s), 2921 (s), 1708 (s), 1658 (s), 1568 (s), 755 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27(d.d., *J* = 8.0 Hz, *J* = 1.0 Hz, 1H), 7.78-7.74 (m, 1H), 7.68-7.67 (m, 1H), 7.47-7.44 (m, 1H), 7.36-7.34 (m, 2H), 7.15-7.13 (m, 2H), 2.45 (s, 3H), 2.25 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 154.5, 147.5, 139.3, 135.1, 134.5, 130.6, 127.7, 127.1, 126.7, 126.5, 120.8, 24.4, 21.2 ppm.

3-(4-bromophenyl)-2-methylquinazolin-4(3H)-one (**4k**, $C_{15}H_{11}BrN_2O$):

White solid; M.p.=170–173°C (171-172 °C); IR (KBr) ν_{max} 3056 (s), 2911 (s), 1710 (s), 1660 (s), 1571 (s), 812 (s), 741 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.70-7.68 (m, 3H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 2.25 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 153.7, 147.3, 136.8, 134.8, 133.3, 129.8, 127.1, 126.9, 126.8, 123.5, 120.6, 24.3 ppm.

3-(2,5-dimethoxyphenyl) quinazolin-4(3H)-one (**4l,** $C_{17}H_{16}N_2O_3$):

White solid; M.P.=159–161°C (159–161°C); IR (KBr) ν_{max} 2838 (s), 3051 (s), 1707 (s), 1657 (s), 1568 (s), 755 (s) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (d.d., *J* = 7.9 Hz, *J* = 1.3 Hz, 1H),

7.73 (d.t., *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.61 (d.d., *J* = 8.2 Hz, *J* = 1.5 Hz, 1H), 7.48 (d.t., *J* = 8.0 Hz, *J* = 1.3 Hz, 1H), 6.96 (d.d., *J* = 8.5 Hz, *J* = 2.5 Hz, 2H), 6.51 (d.d., *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 2.50 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.0, 155.5, 155.4, 148.7, 146.8, 133.7, 129.4, 128.1, 126.2, 123.9, 121.4, 113.5, 111.8, 110.4, 55.55, 55.1, 23.7 ppm.

3-(4-(trifluoromethoxy) phenyl) quinazolin-4(3H)-one (**4m**, $C_{16}H_{11}F_3N_2O_2$):

White solid; Mp=138–139°C (138–139°C); IR (KBr) ν_{max} 2839 (s), 3053 (s), 1709 (s), 1657 (s), 1568 (s), 755 (s) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (d.d., *J* = 8.0 Hz, *J* = 2.2 Hz, 1H), 7.73 (d.t., *J* = 7.8 Hz, *J* = 1.3 Hz, 1H), 7.68 (d.d., *J* = 8.2 Hz, *J* = 1.5 Hz, 1H), 7.47 (d.t. *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.32 (d.d., *J* = 8.6 Hz, *J* = 1.5 Hz, 2H), 7.20 (d.d., *J* = 8.5 Hz, *J* = 1.6 Hz, 2H), 2.51 (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO) δ 161.8, 155.9, 146.8, 143.5, 143.4, 143.3, 143.2, 133.9, 133.6, 129.9, 128.2, 126.2, 123.9, 123.8, 121.8, 121.7, 121.6, 121.6, 119.5, 117.4, 23.7 ppm.

2-methyl-3-(phenylsulfonyl) quinazolin-4(3H)-one (**4n**, $C_{15}H_{12}N_2O_3S$):

Yellow solid; M.P.= 223.0 °C (223 °C, [8]); IR (KBr) ν_{max} 3110 (s), 2950 (s), 1660 (s), 1600 (s), 1320 (s), 1150 (s), 800 (s) cm^{-1}; ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.92-7.96 (m, 3H), 7.51-7.58 (m, 5H), 7.1 (d.d., *J* = 7.5, 2.5 Hz, 1H), 2.10 (s, 3H) ppm; ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 24.9, 116.4, 119.9, 122.5, 127.3, 127.4, 130.97, 131.12, 133.9, 140.7, 148.0, 168.4, 169.9 ppm.

3-(3-hydroxyphenyl)-2-methylquinazolin-4(3H)-one (**4o**, $C_{15}H_{12}N_2O_2$):

White solid; M.P.= 114.5 °C (115 ^{o}C , [8]); IR (KBr) ν_{max} 3610 (m), 3100 (s), 2900 (s), 1645 (s), 1597 (s), 720 (s) cm^{-1}; ^{1}H NMR (250 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.29-8.09 (m, 5H), 6.77 - 6.91 (m, 3H), 2.14 (s, 3H) ppm; ^{13}C NMR (62.9 MHz, DMSO-d_6) δ 23.7, 115.3, 115.9, 118.7, 120.4, 126.2, 126.3, 126.5, 130.2, 134.4, 138.7, 147.2, 154.4, 158.2, 161.1.ppm

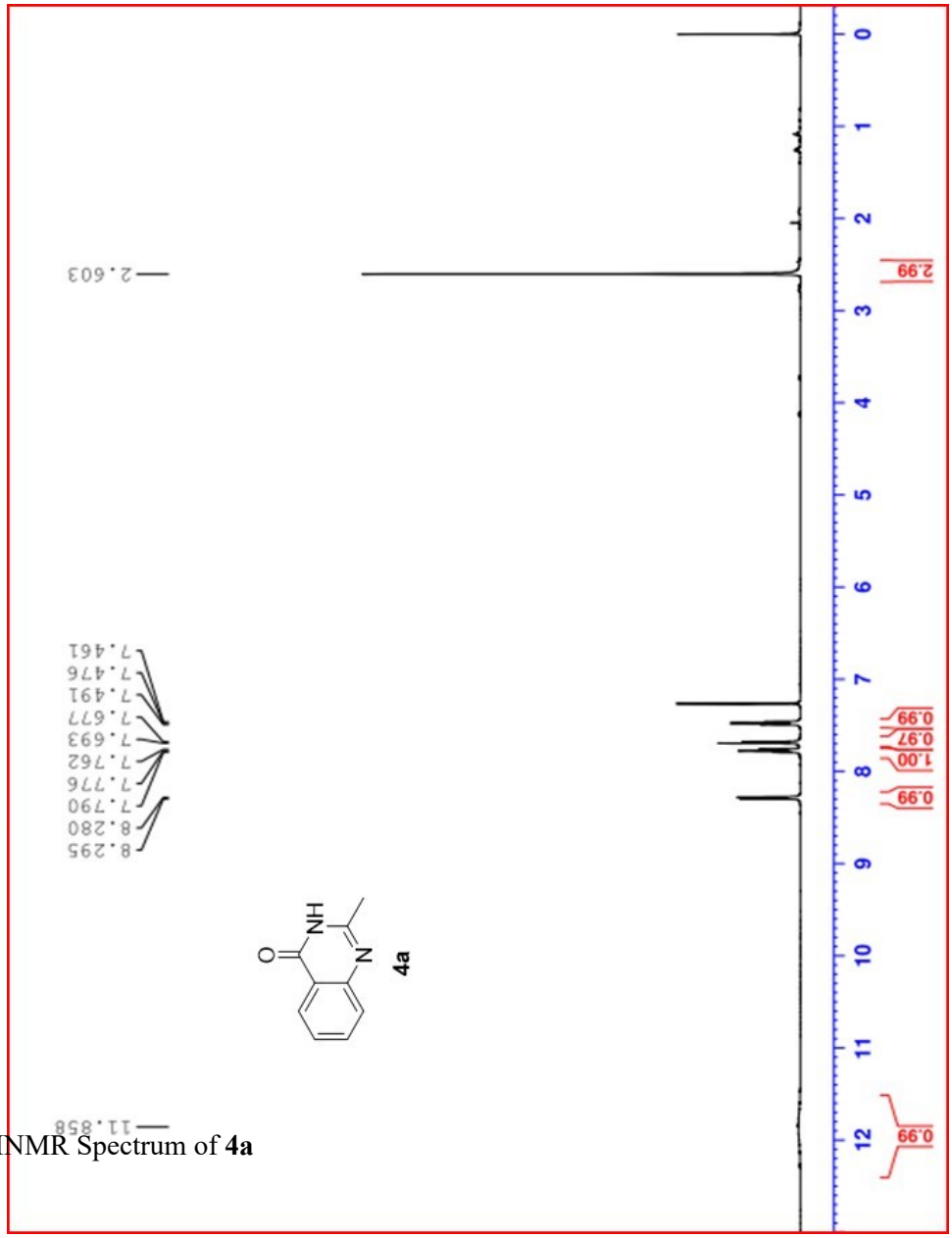

Figure 1 [1]HNMR Spectrum of **4a**

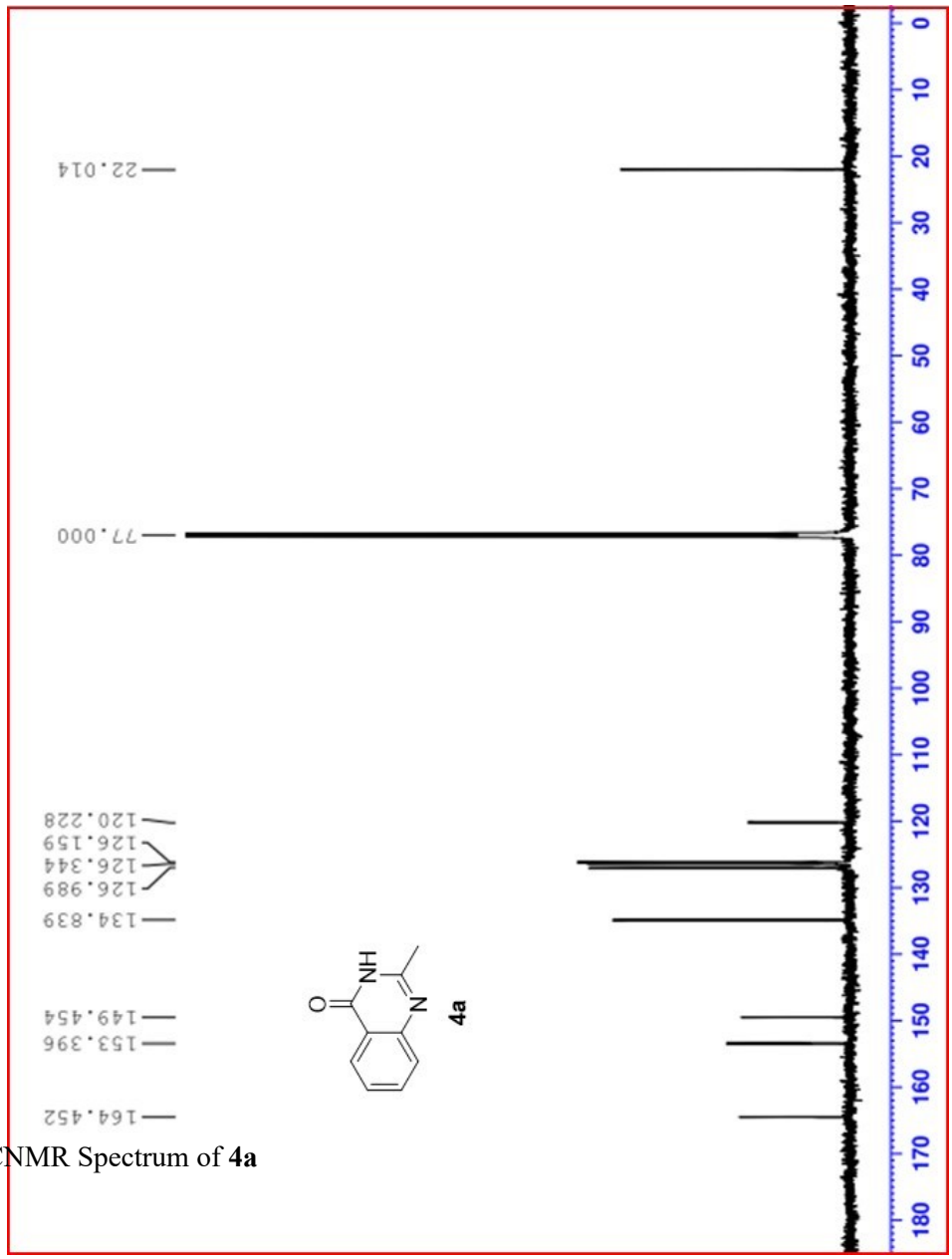

Figure 2 ^{13}CNMR Spectrum of **4a**

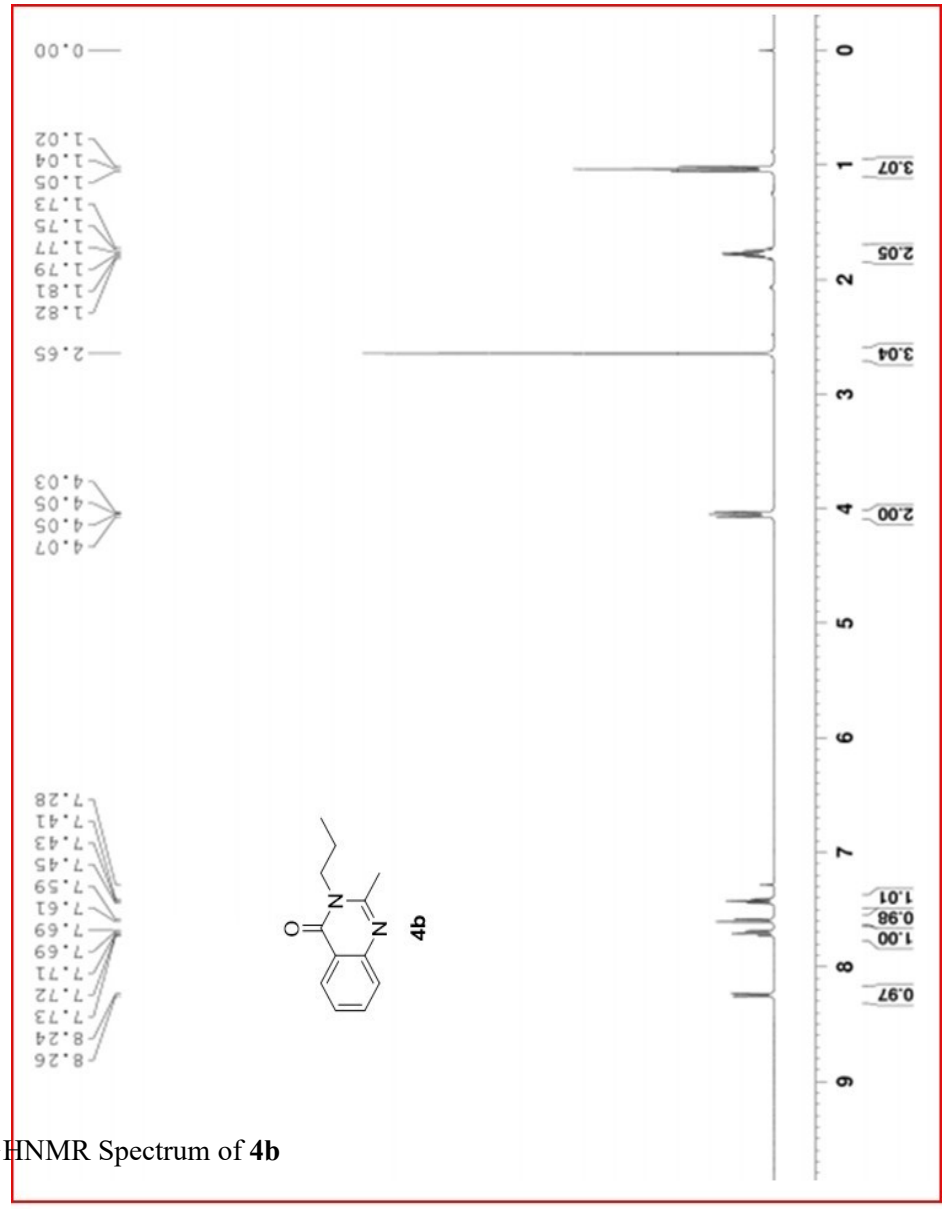

Figure 3 ^{1}HNMR Spectrum of **4b**

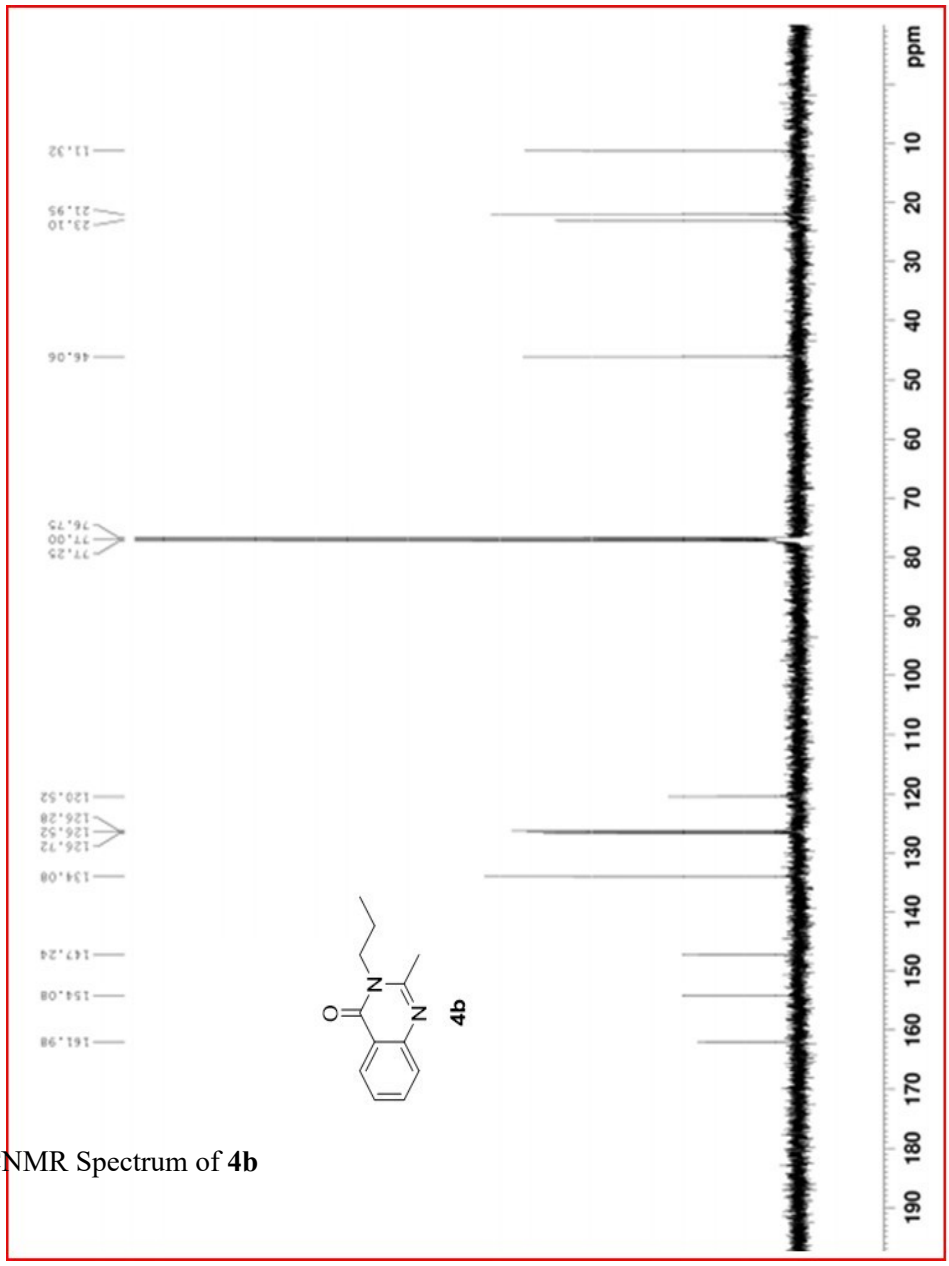

Figure 4 ^{13}CNMR Spectrum of **4b**

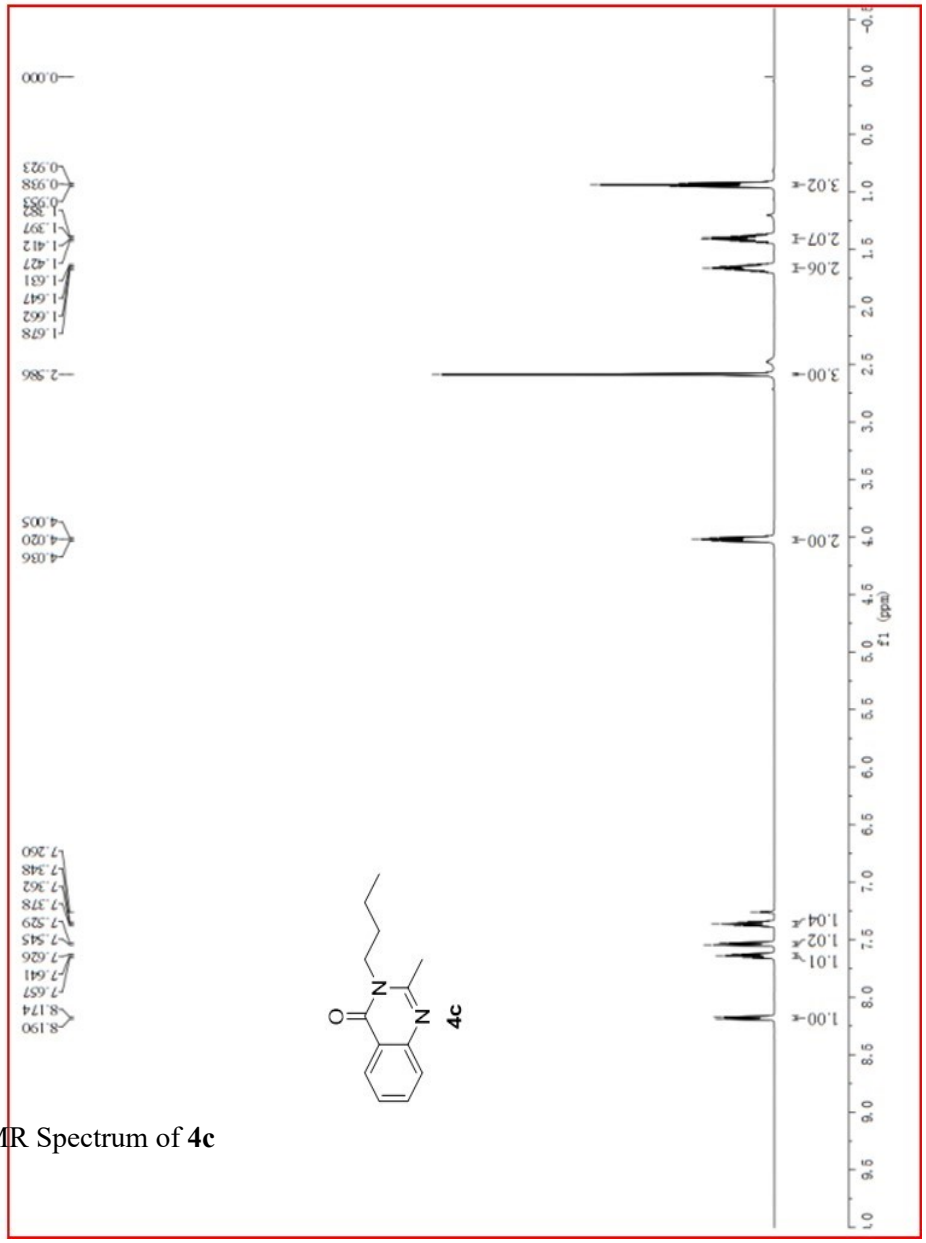

Figure 5 [1]HNMR Spectrum of **4c**

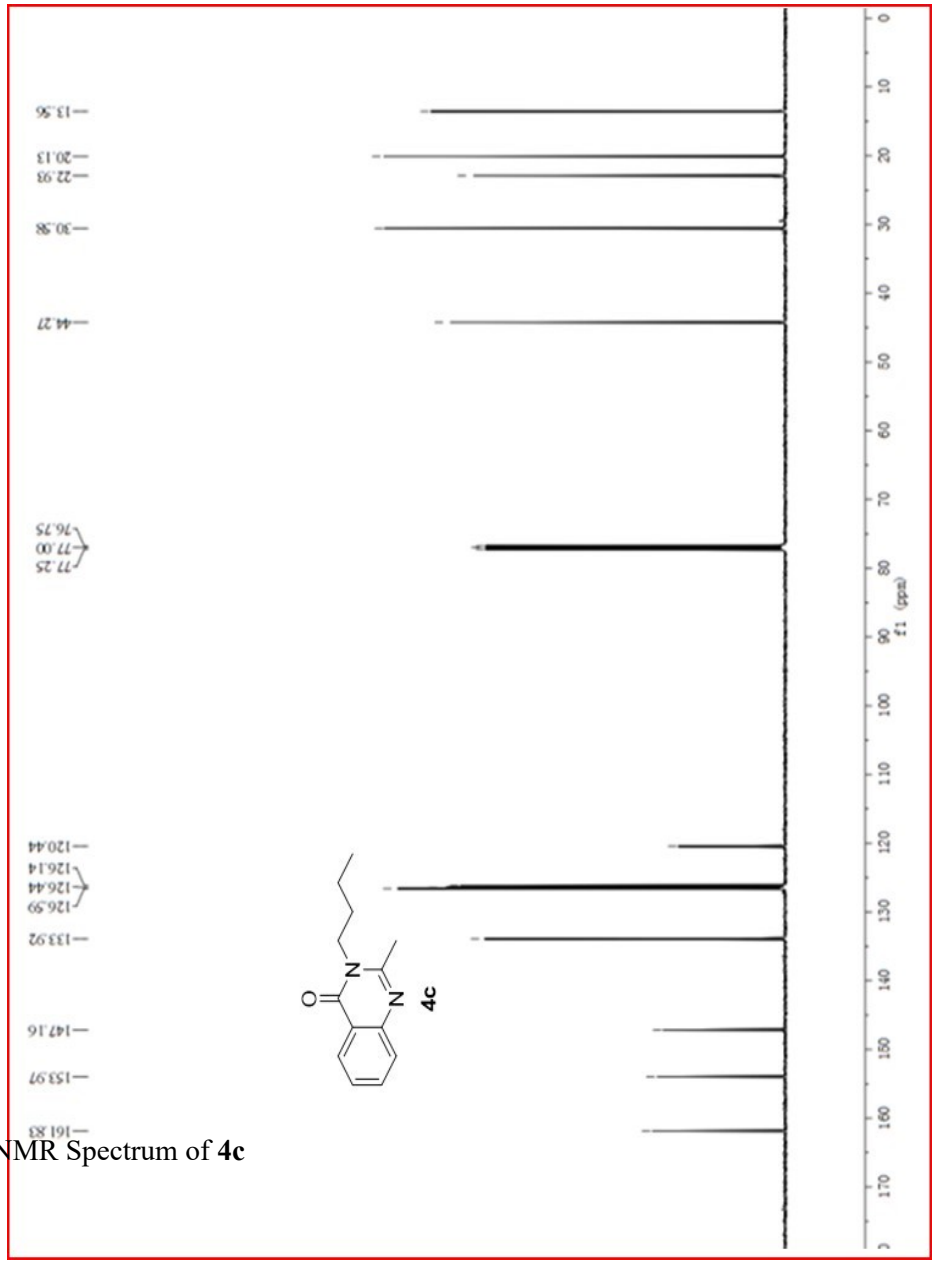

Figure 6 ^{13}CNMR Spectrum of **4c**

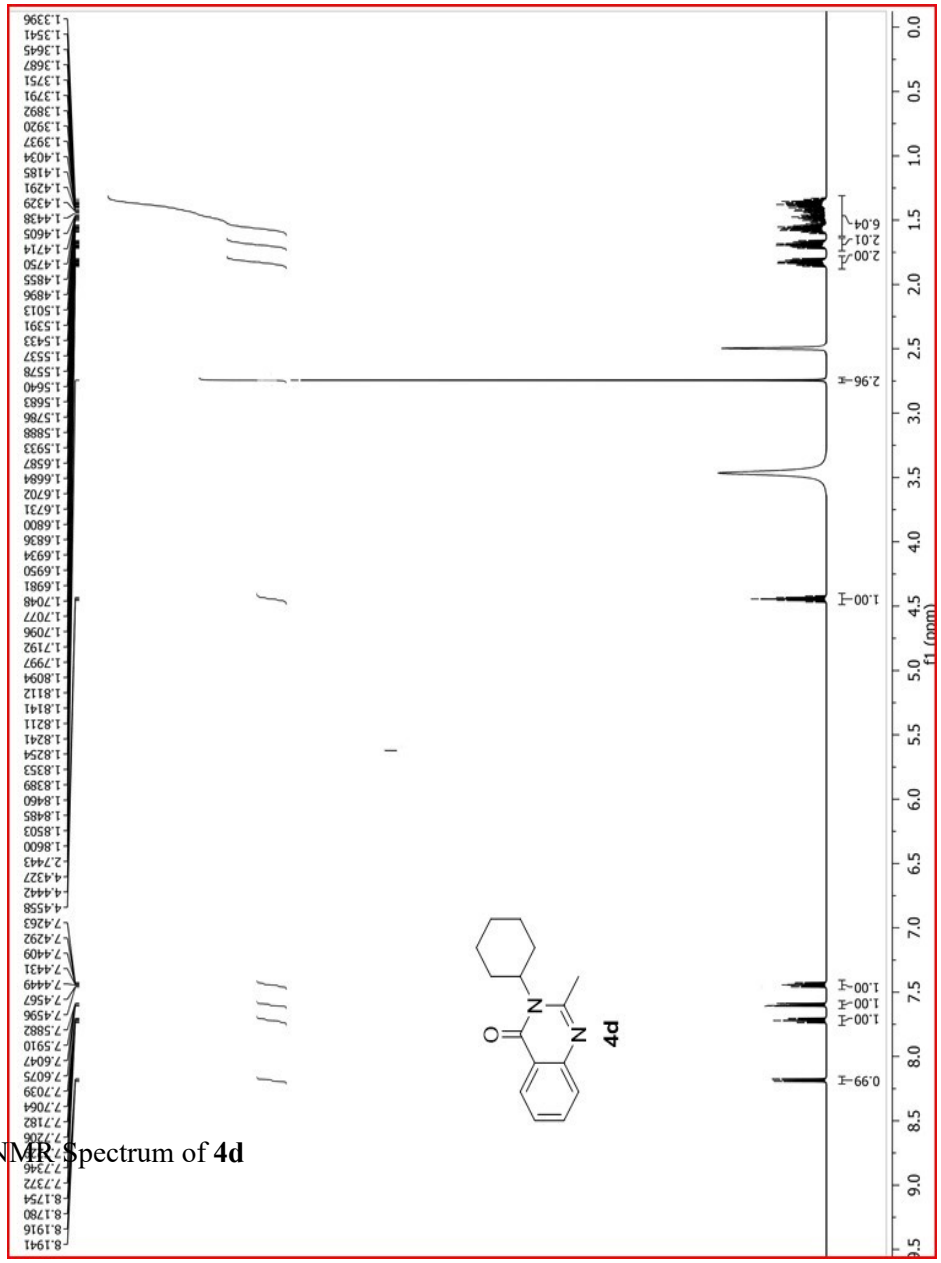

Figure 7 ^{1}HNMR Spectrum of **4d**

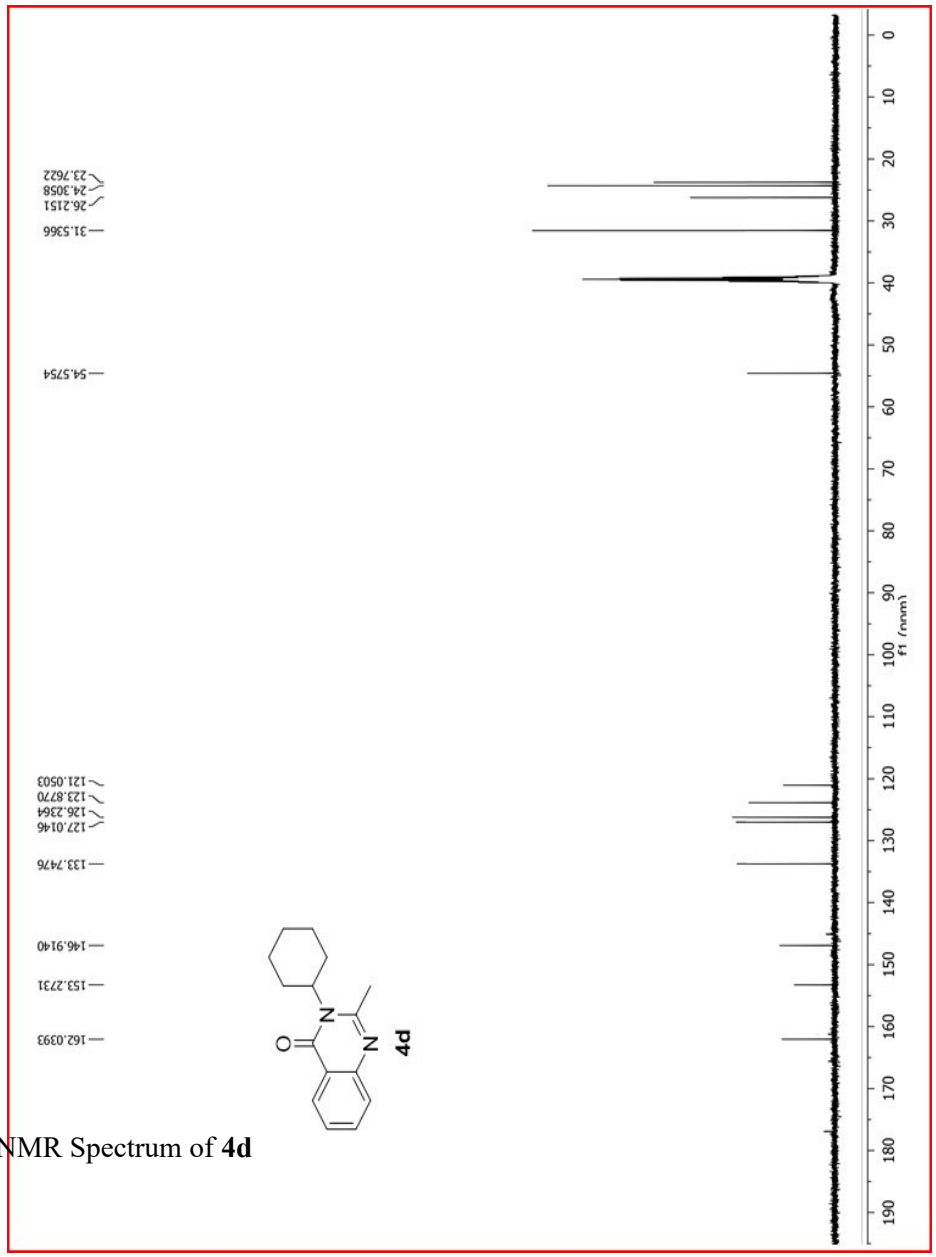

Figure 8 ^{13}CNMR Spectrum of **4d**

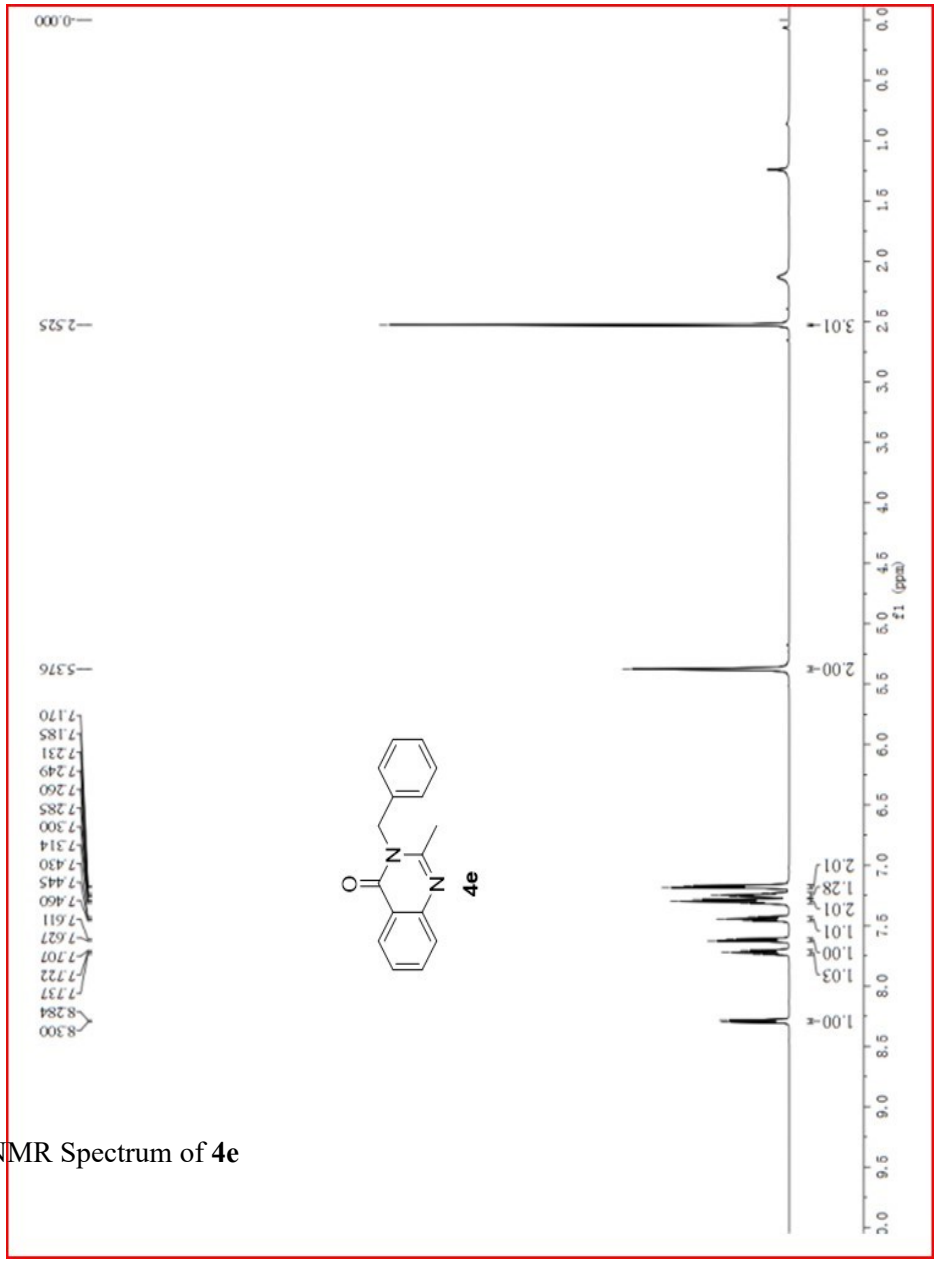

Figure 9 [1]HNMR Spectrum of **4e**

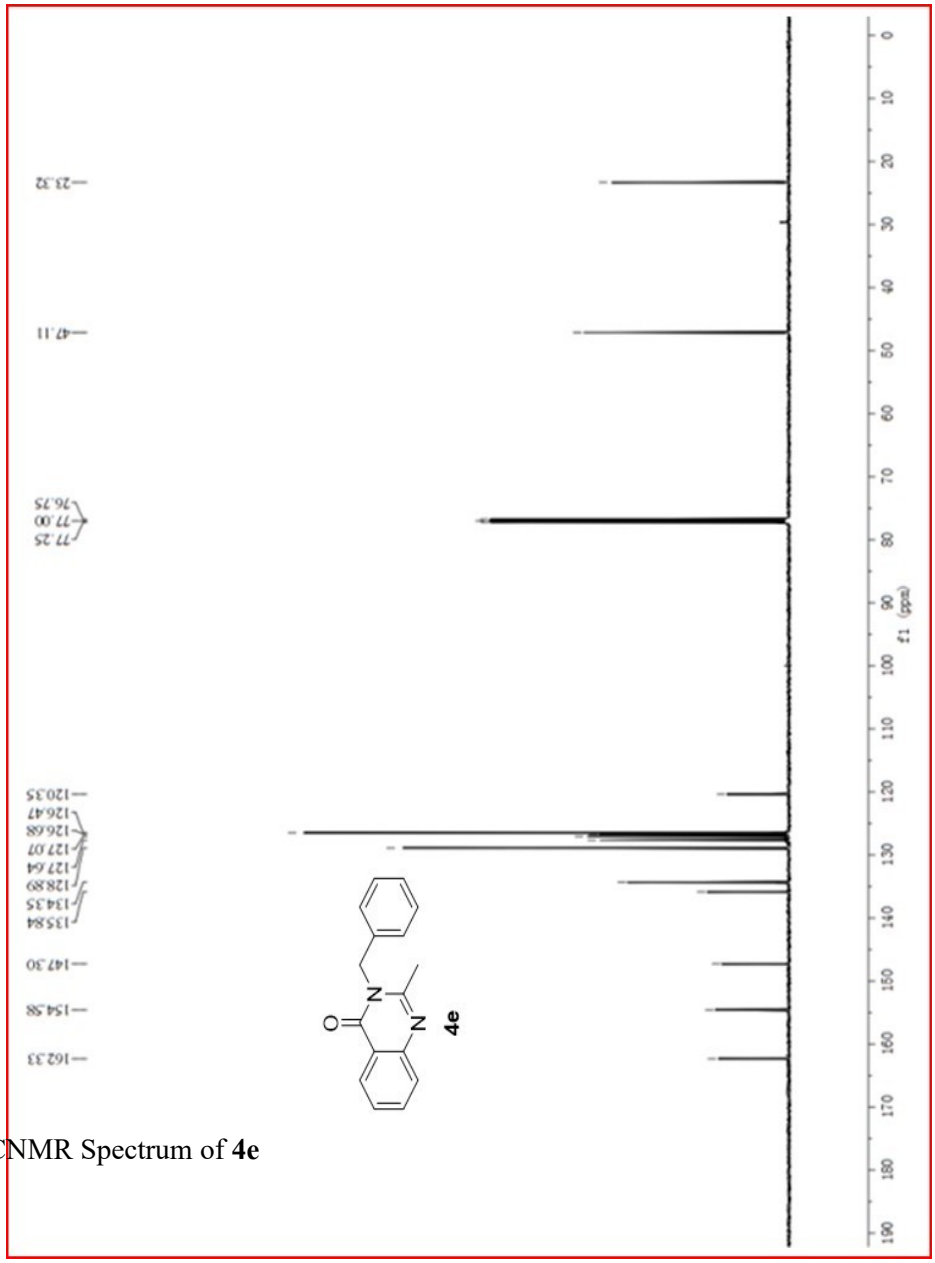

Figure 10 ^{13}CNMR Spectrum of **4e**

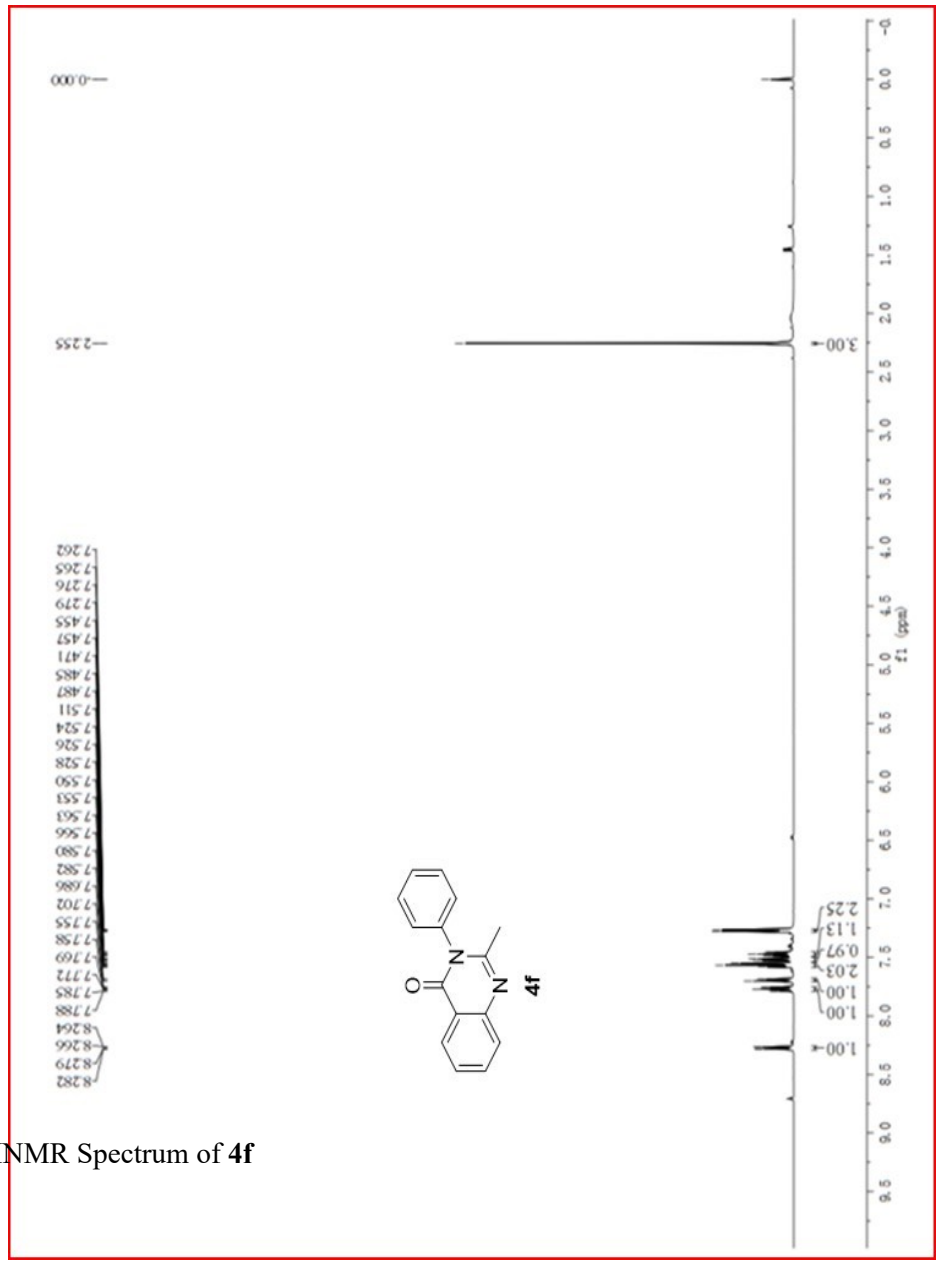

Figure 11 [1]HNMR Spectrum of **4f**

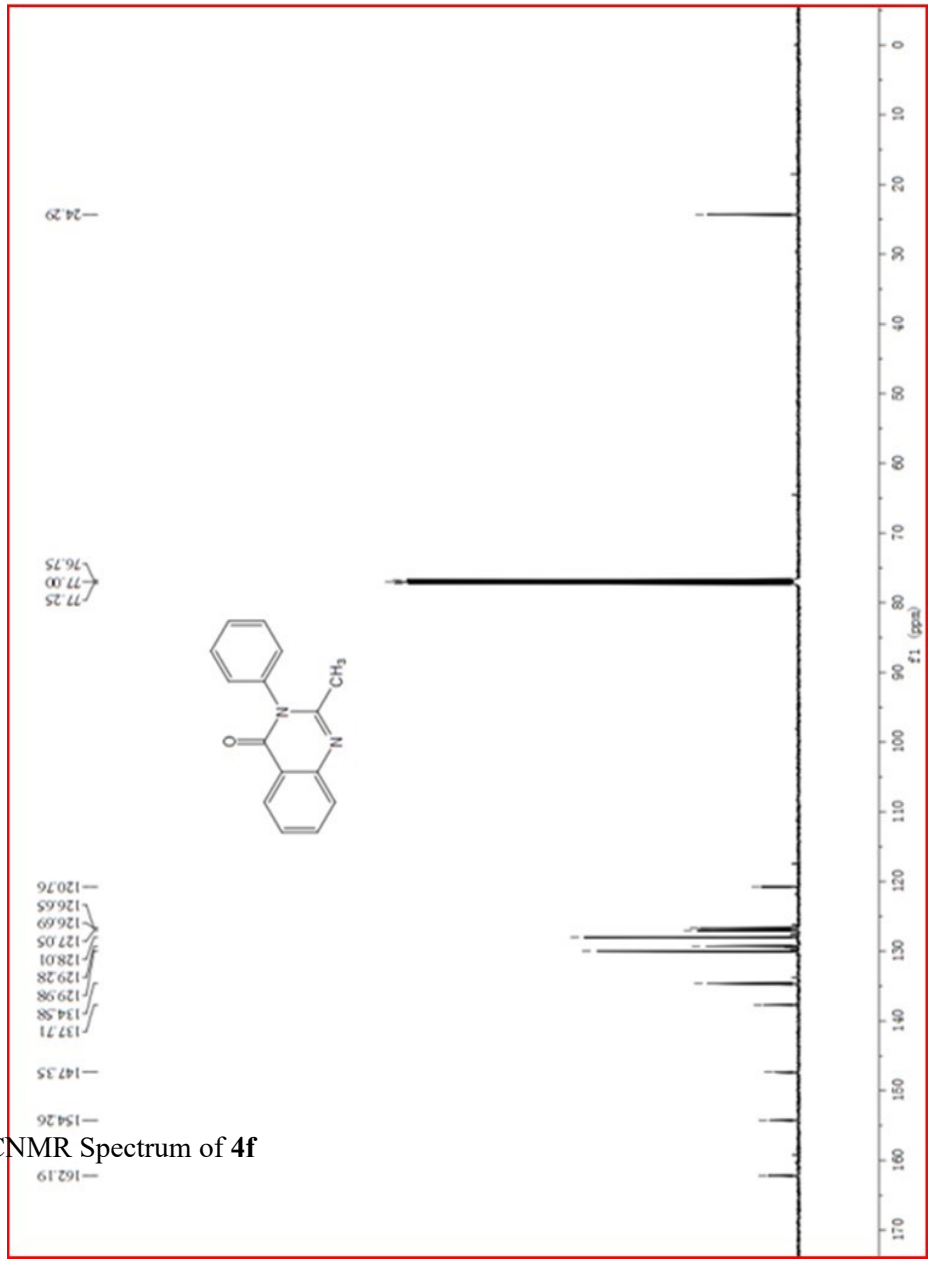

Figure 12 ^{13}CNMR Spectrum of **4f**

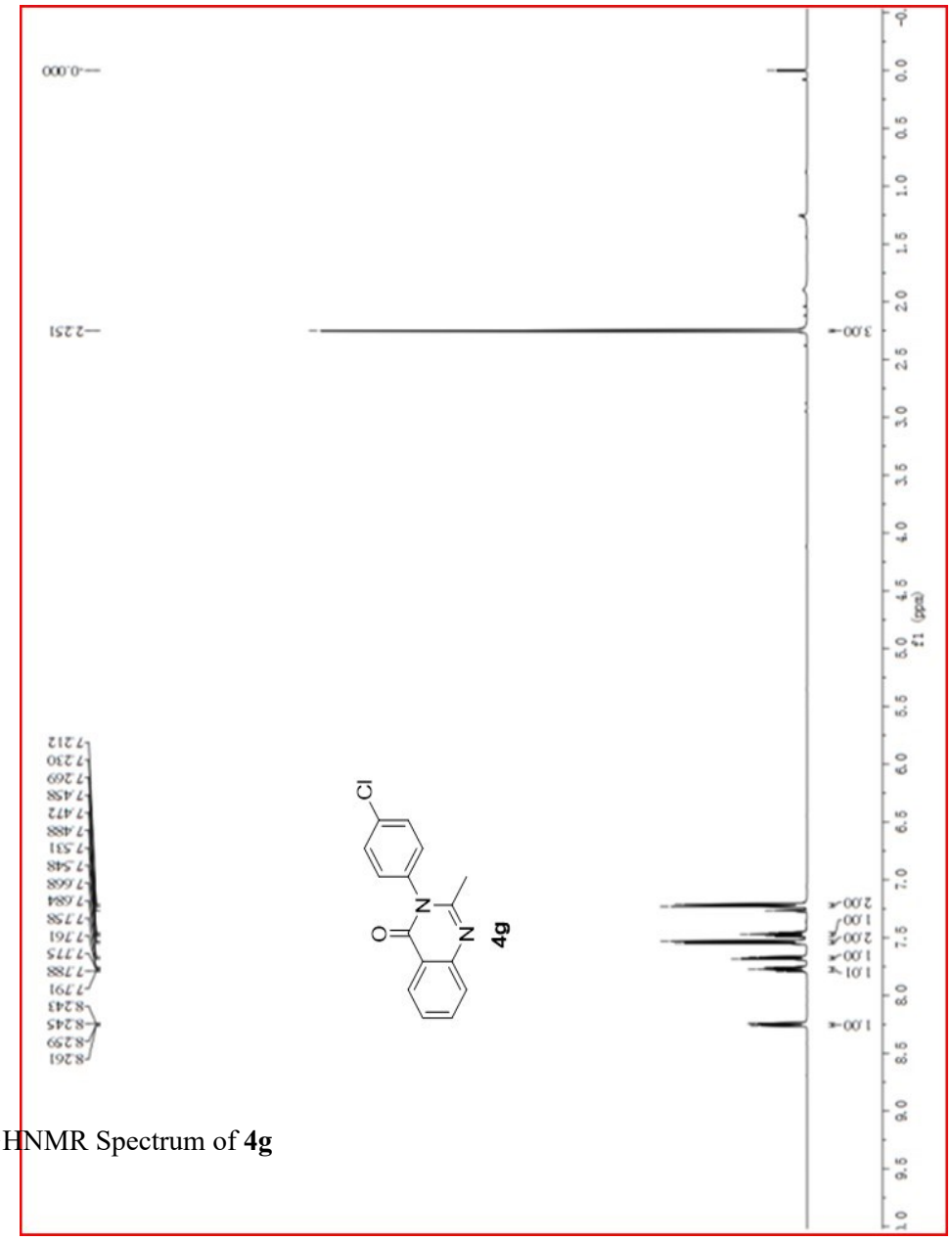

Figure 13 ^{1}HNMR Spectrum of **4g**

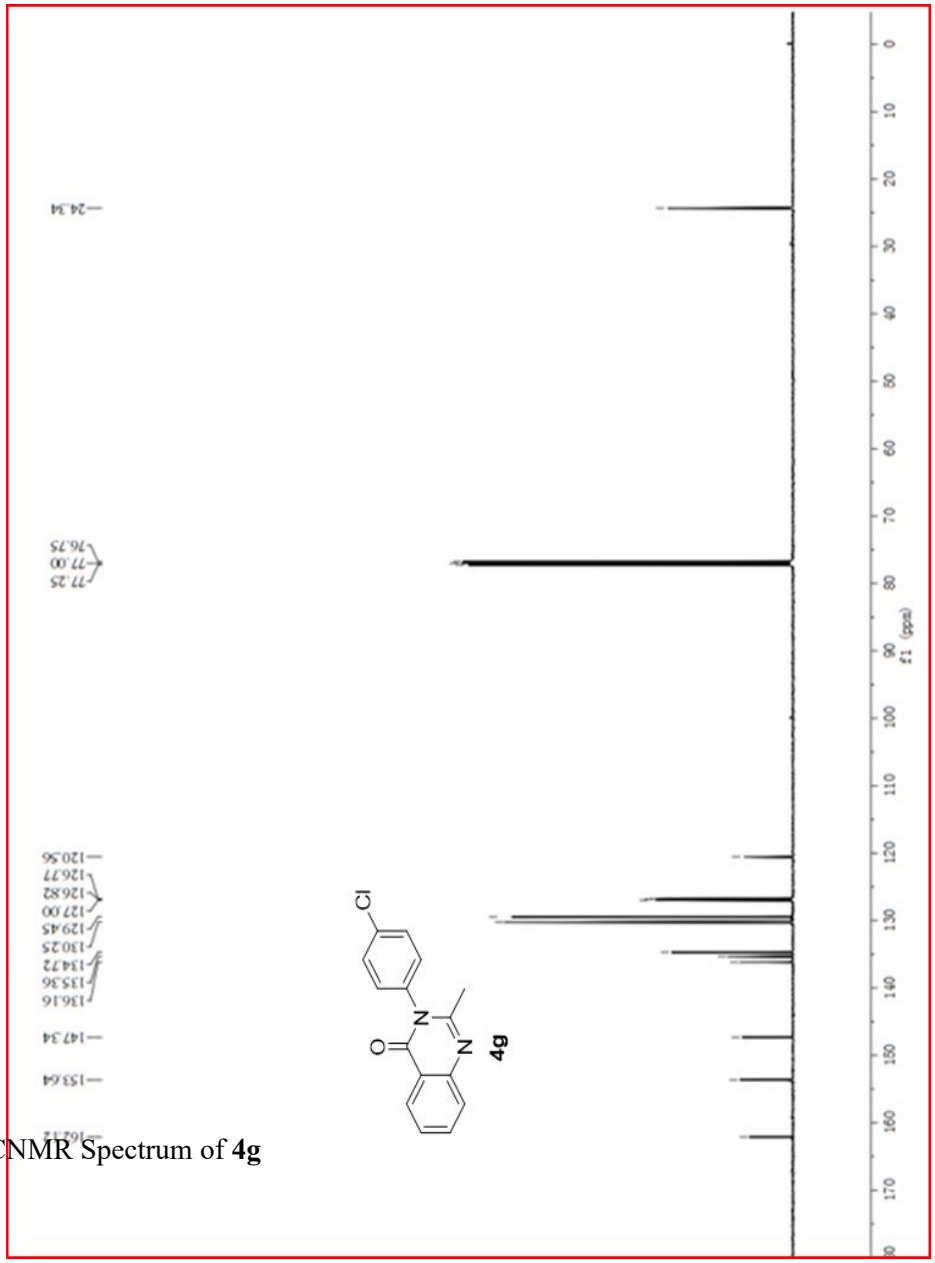

Figure 14 ^{13}CNMR Spectrum of **4g**

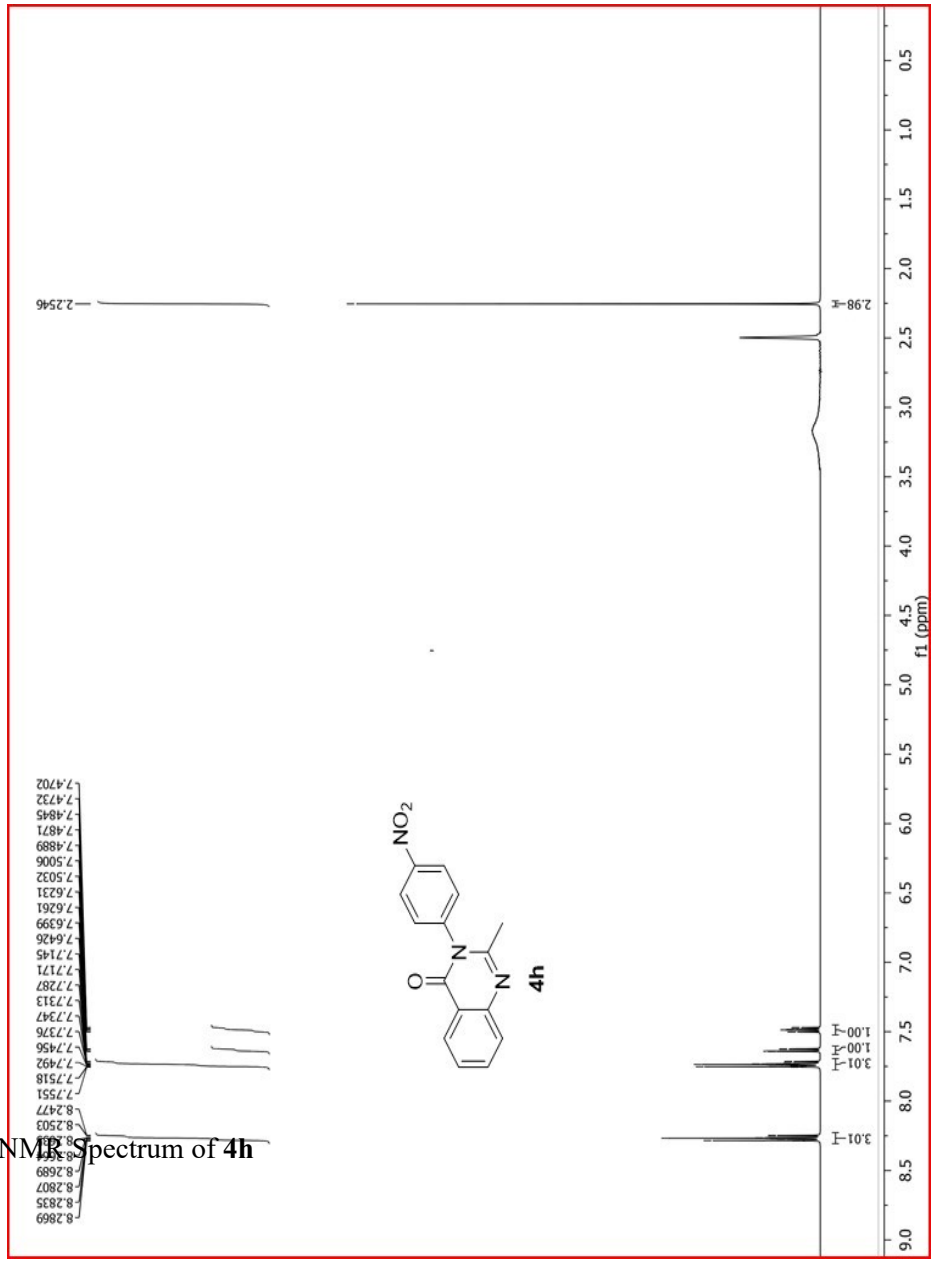

Figure 15 ^{1}HNMR Spectrum of **4h**

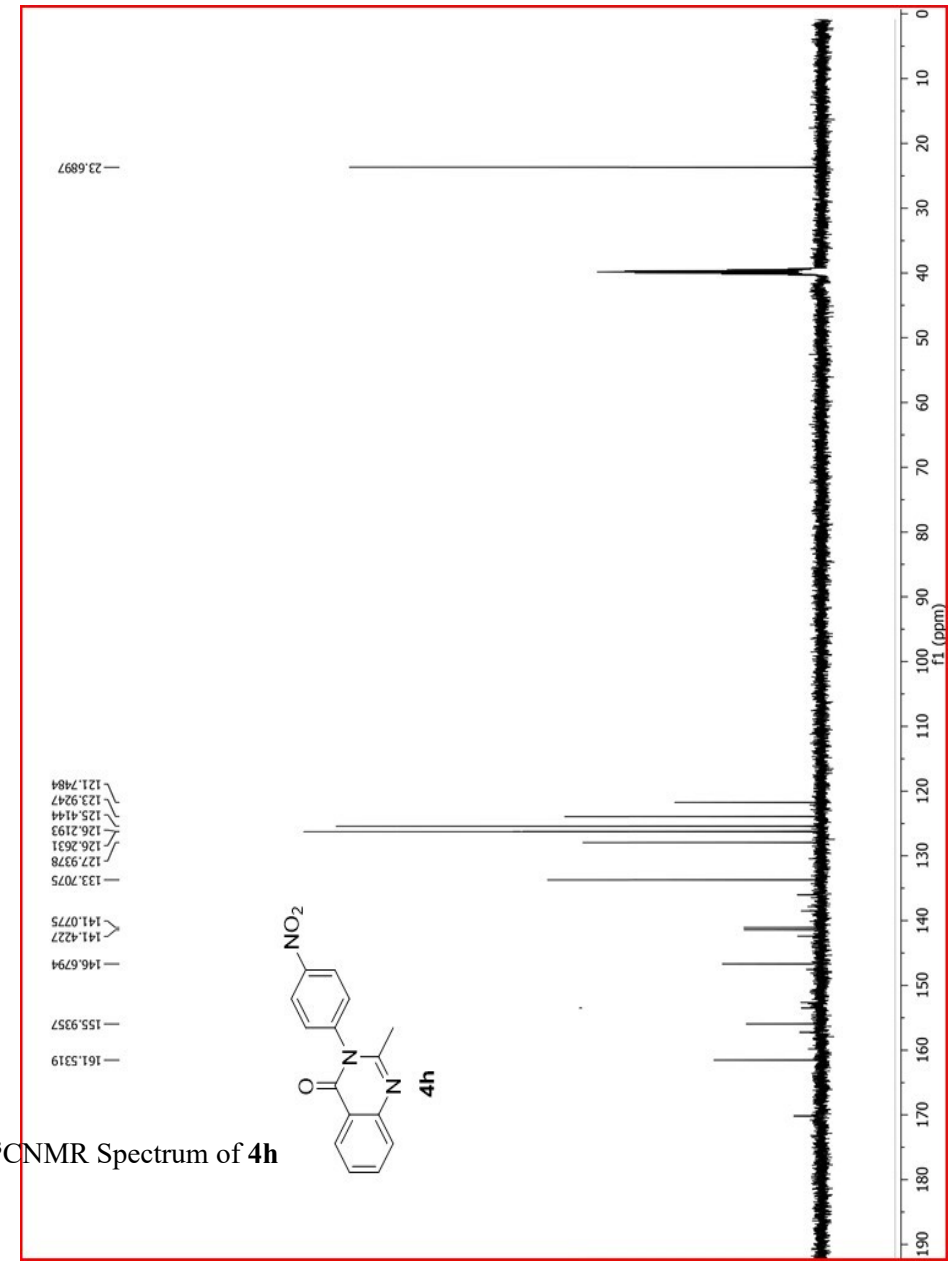

Figure 16 ^{13}CNMR Spectrum of **4h**

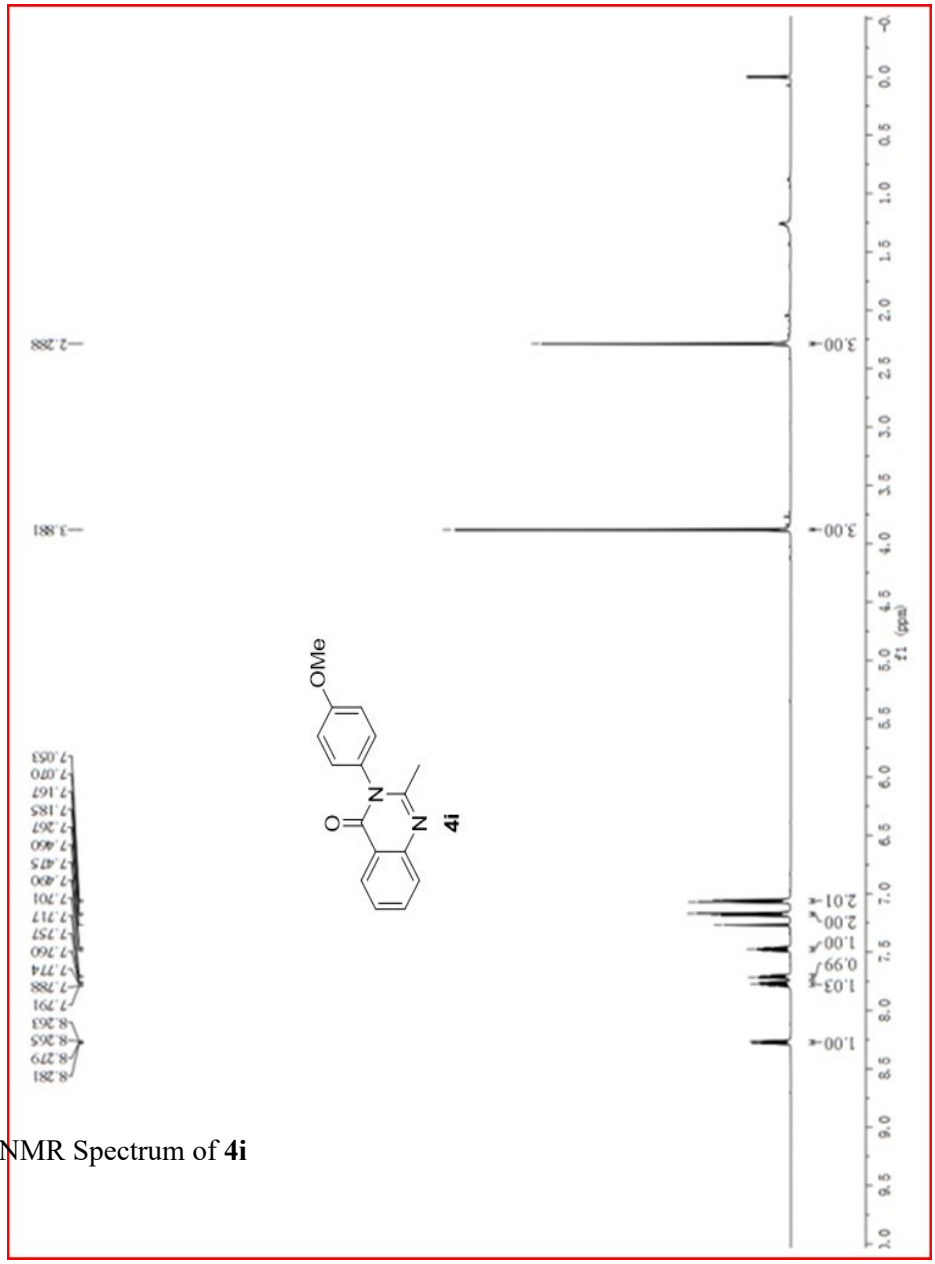

Figure 17 [1]HNMR Spectrum of **4i**

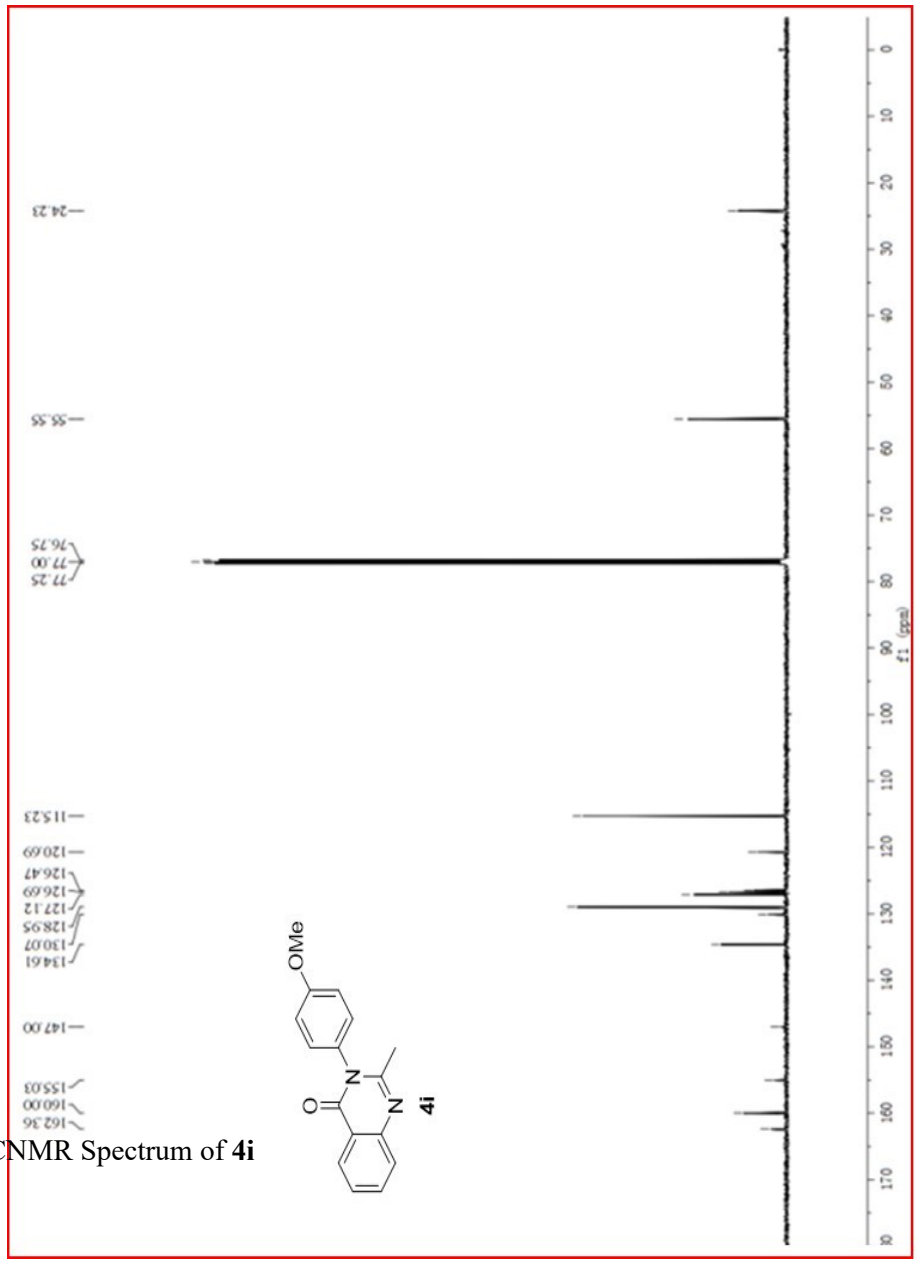

Figure 18 ^{13}CNMR Spectrum of **4i**

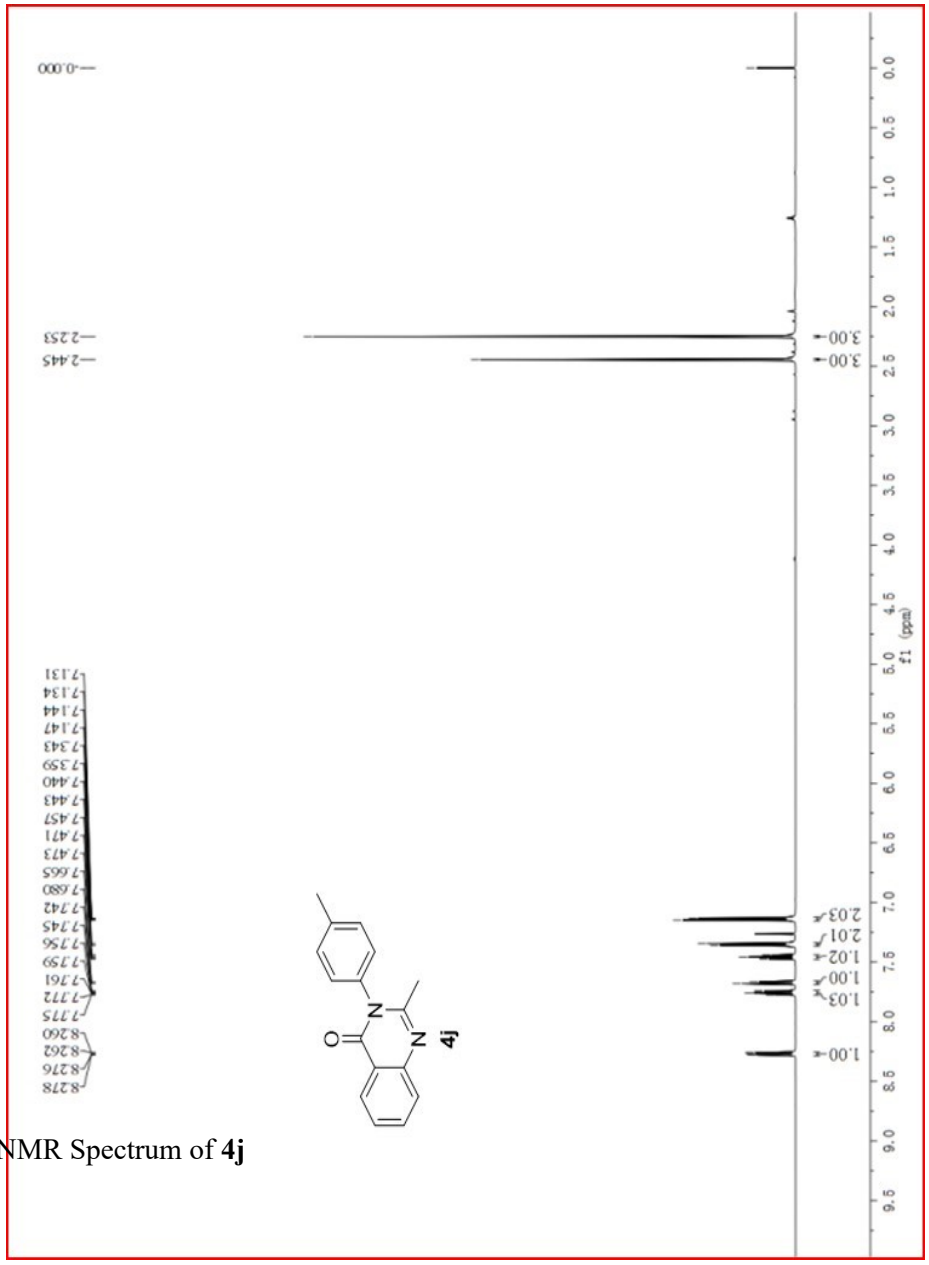

Figure 19 [1]HNMR Spectrum of **4j**

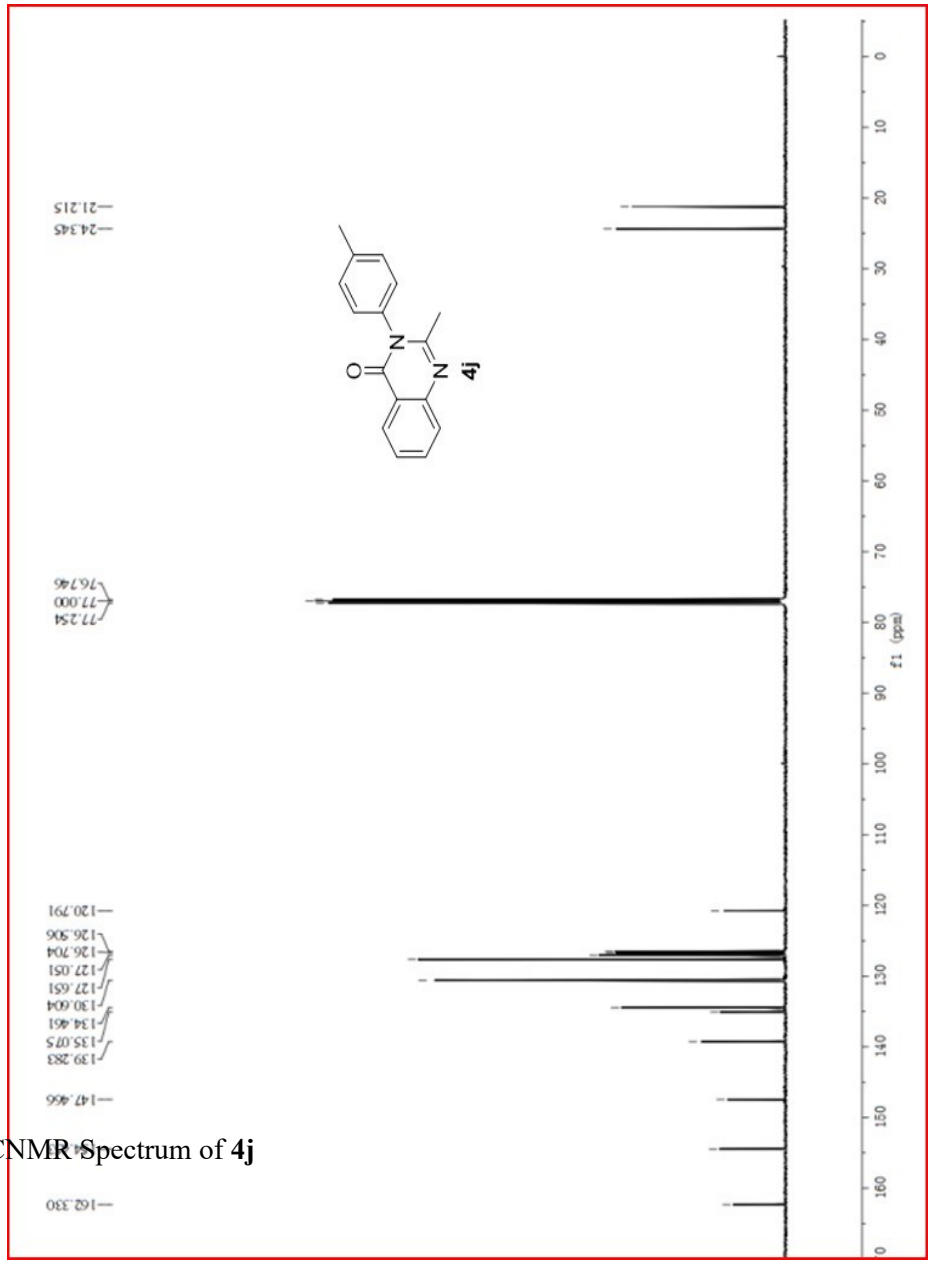

Figure 20 ^{13}CNMR Spectrum of **4j**

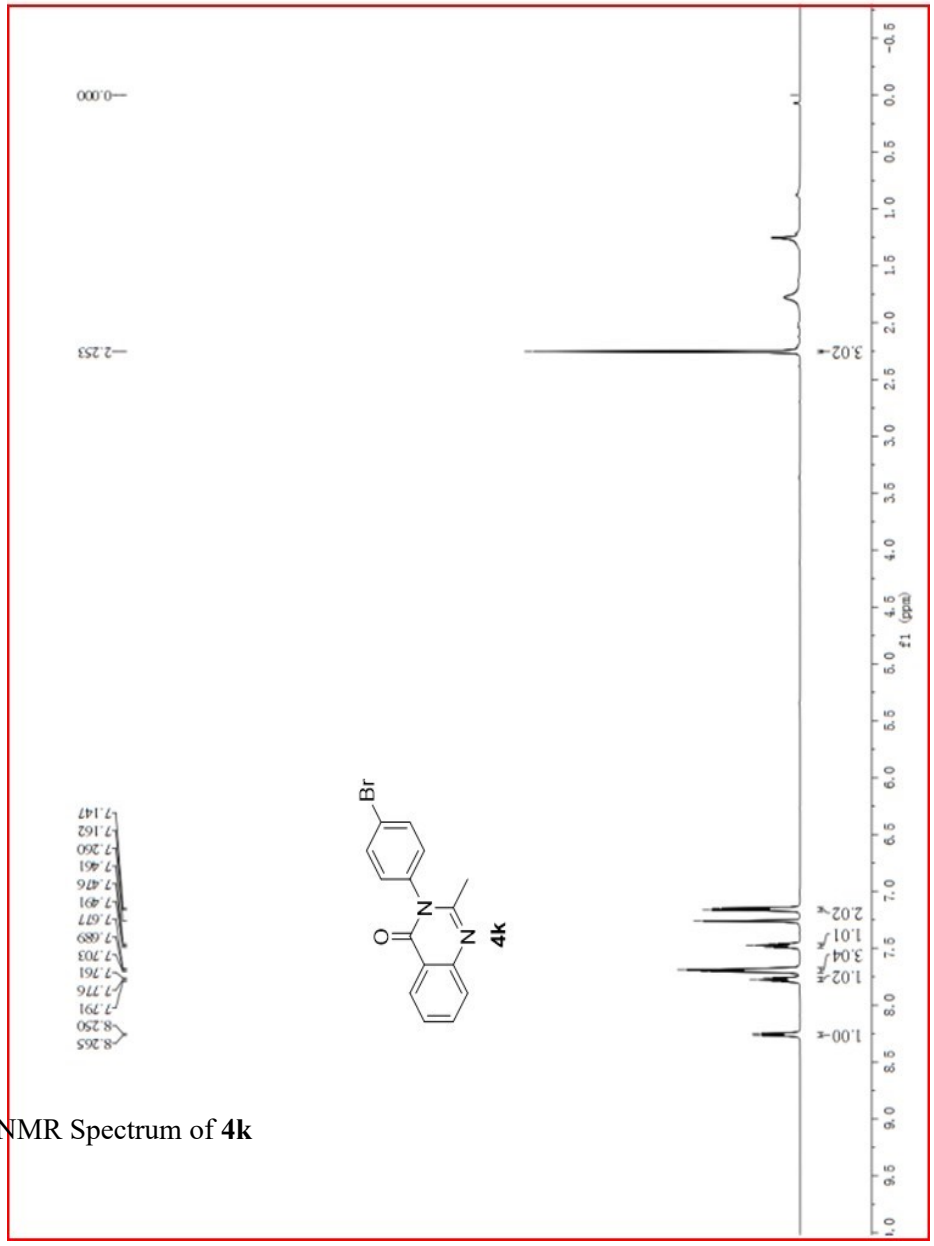

Figure 21 [1]HNMR Spectrum of **4k**

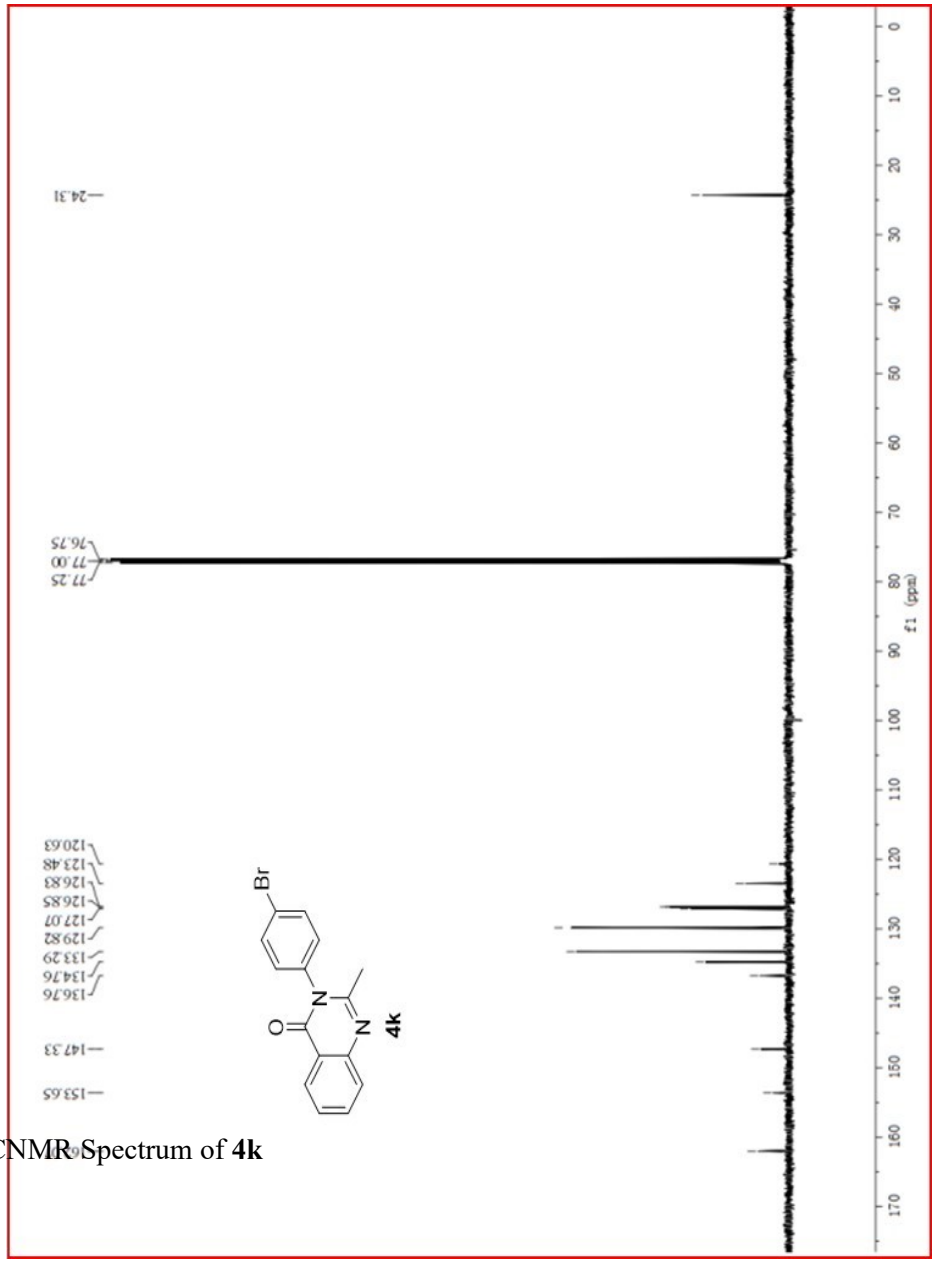

Figure 22 ^{13}CNMR Spectrum of **4k**

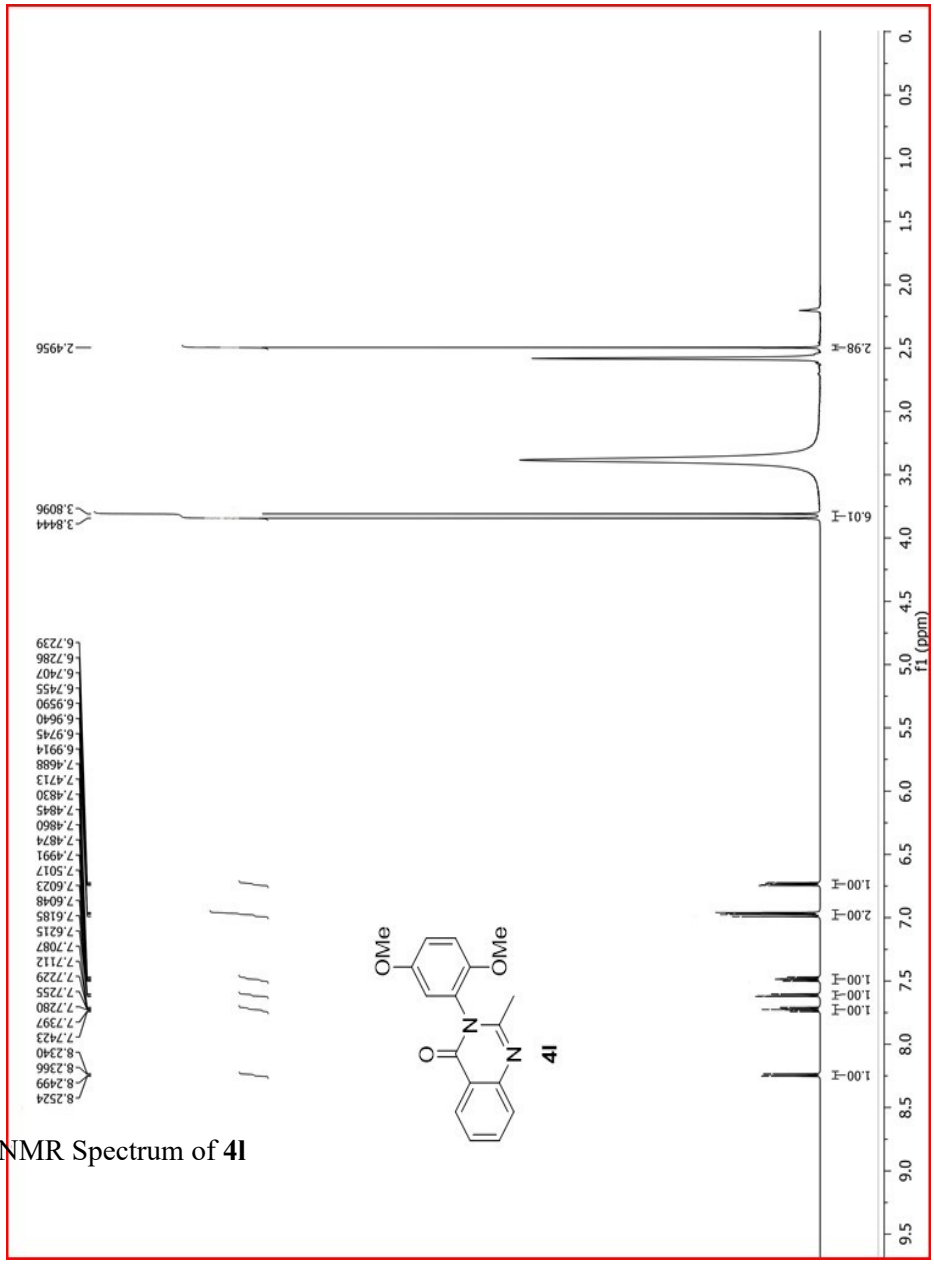

Figure 23 [1]HNMR Spectrum of **4l**

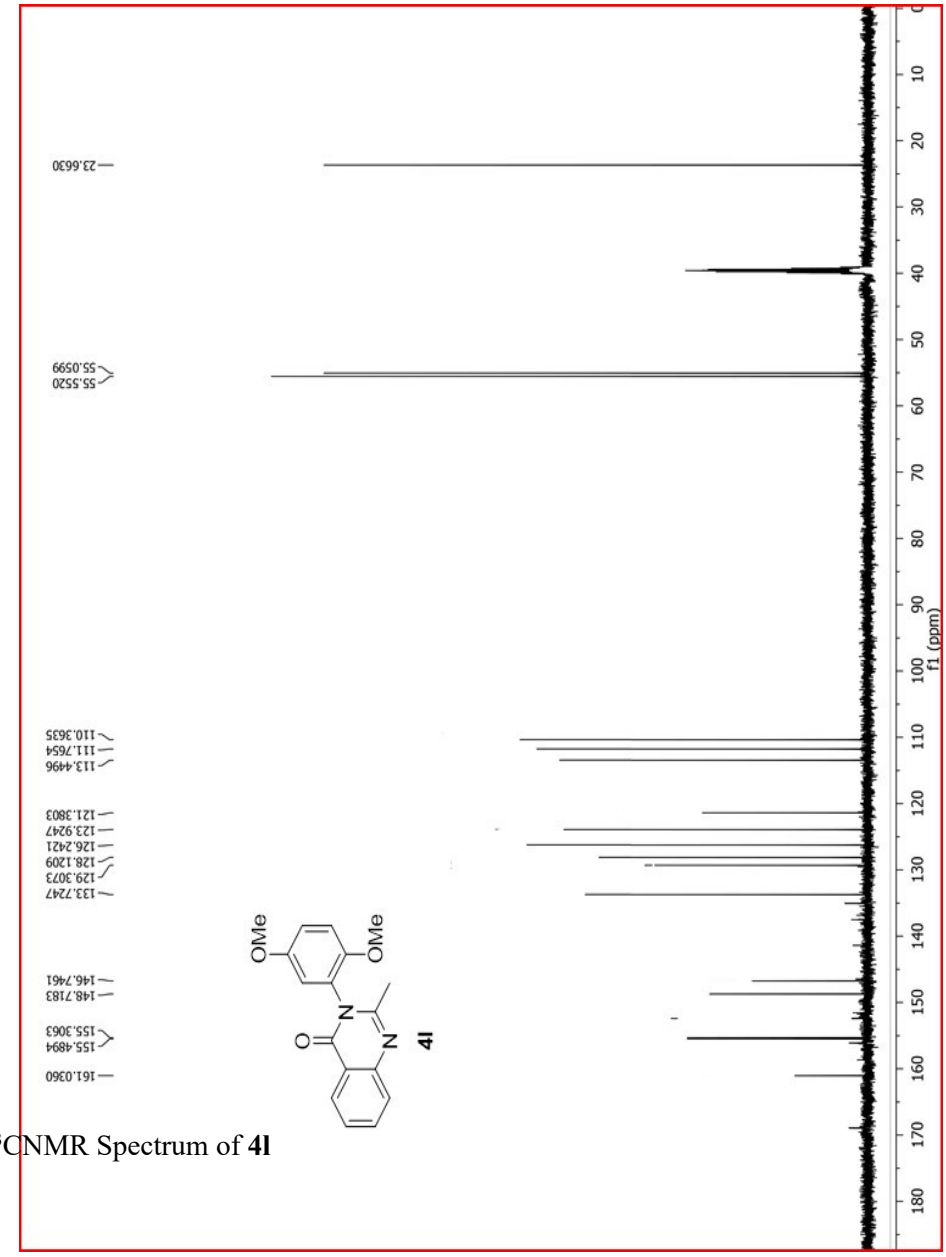

Figure 24 ^{13}CNMR Spectrum of **4l**

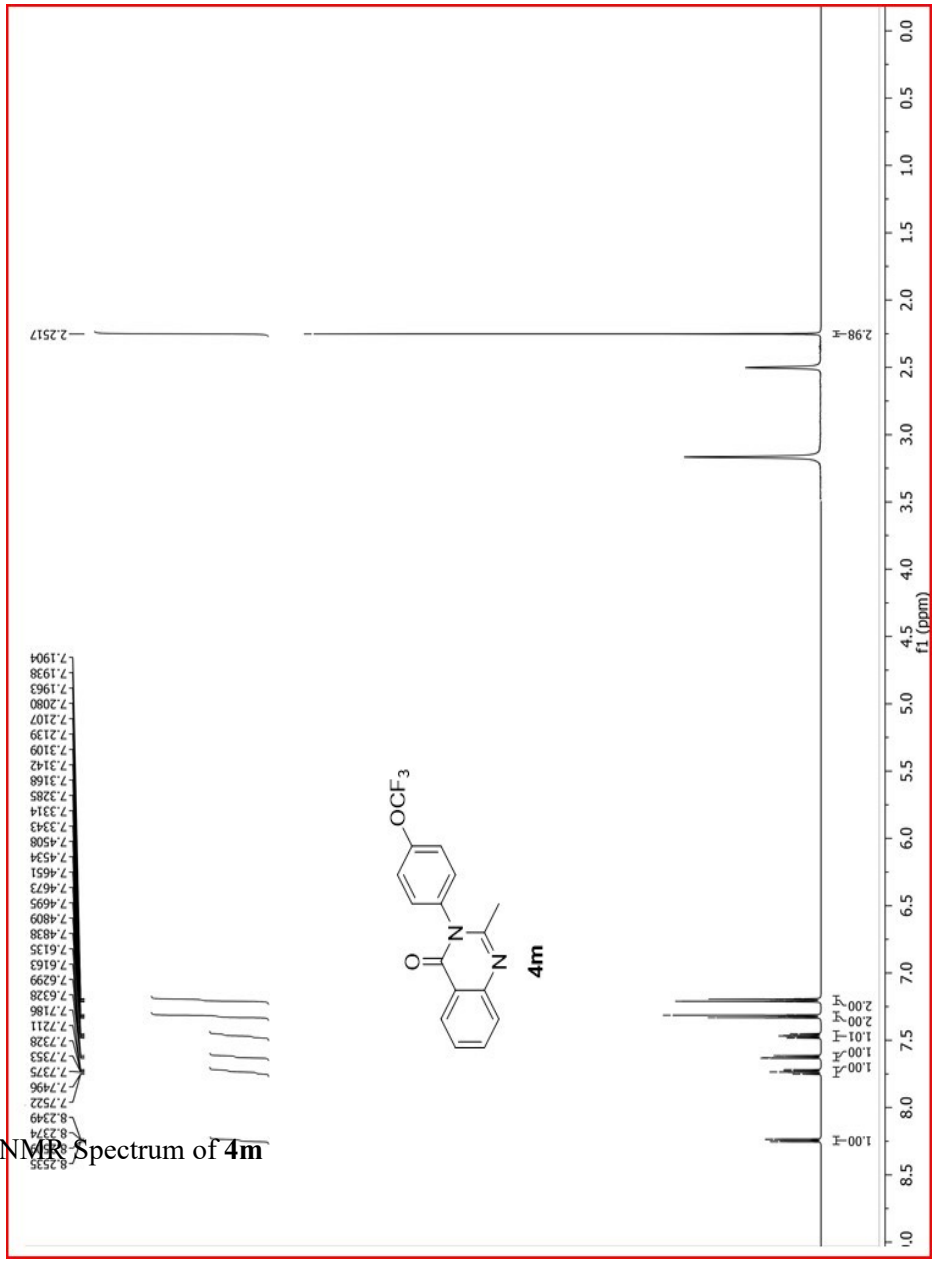

Figure 25 ^{1}HNMR Spectrum of **4m**

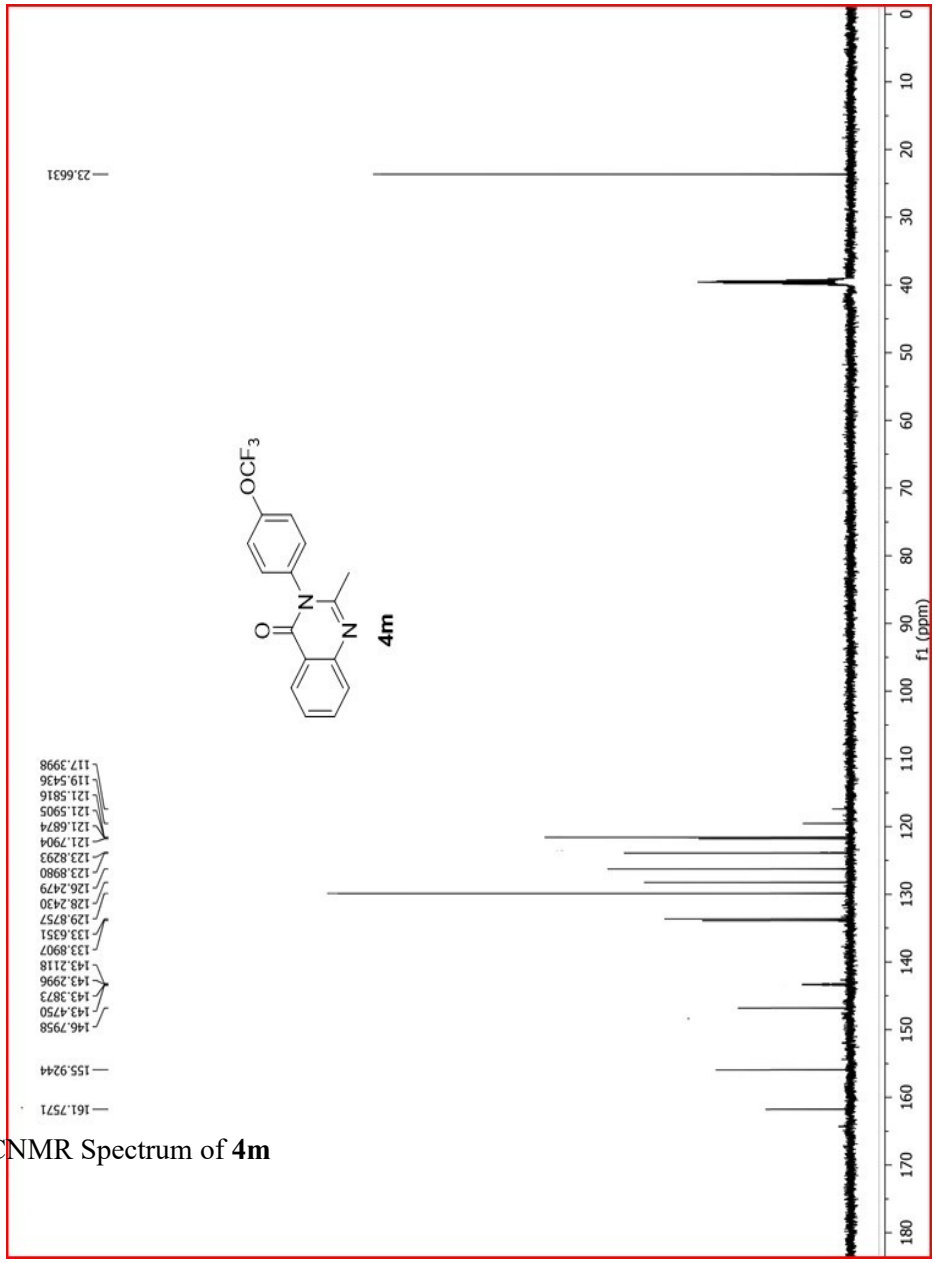

Figure 26 ^{13}CNMR Spectrum of **4m**

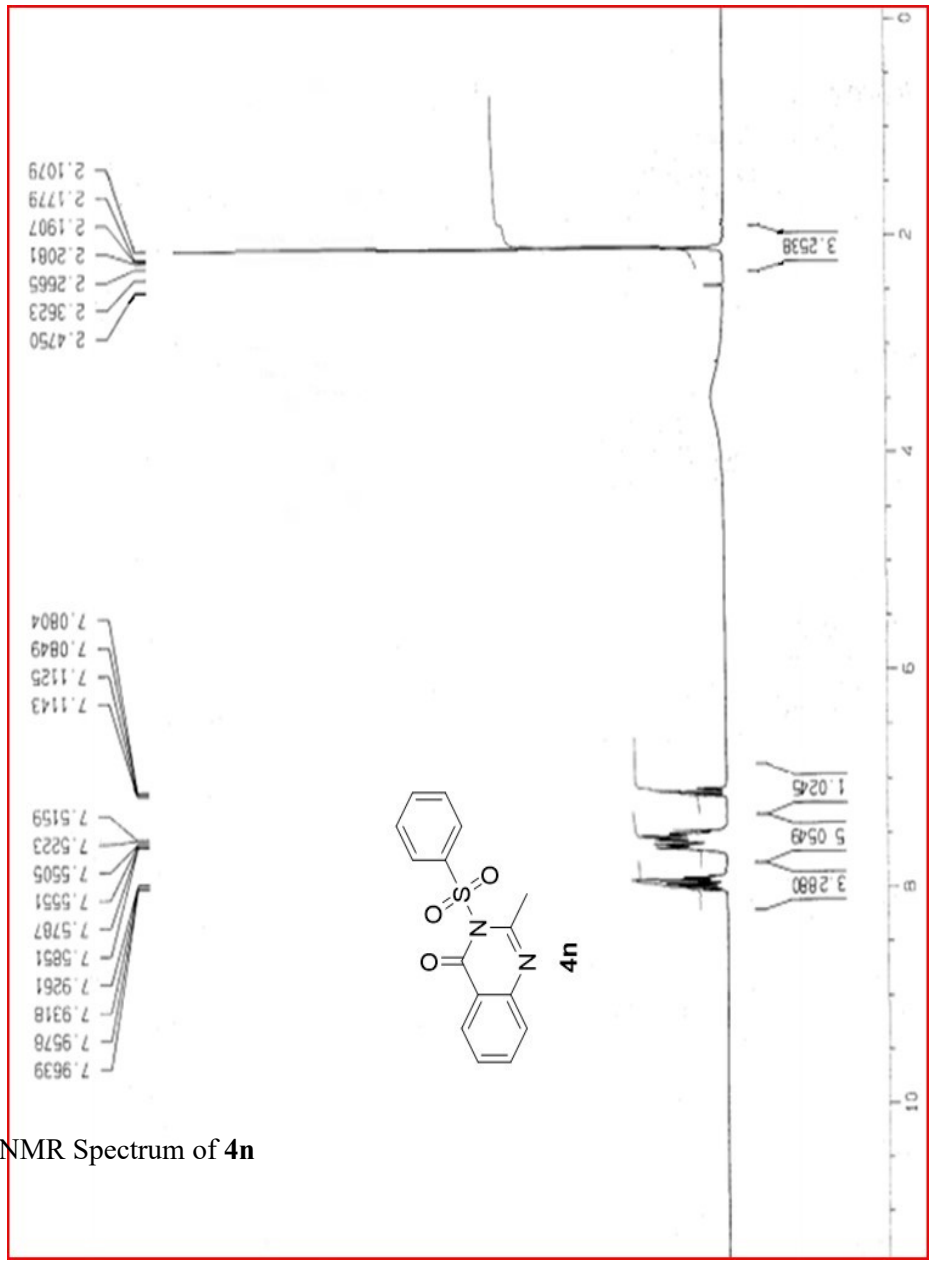

Figure 27 [1]HNMR Spectrum of **4n**

Figure 28 ^{13}CNMR Spectrum of **4n**

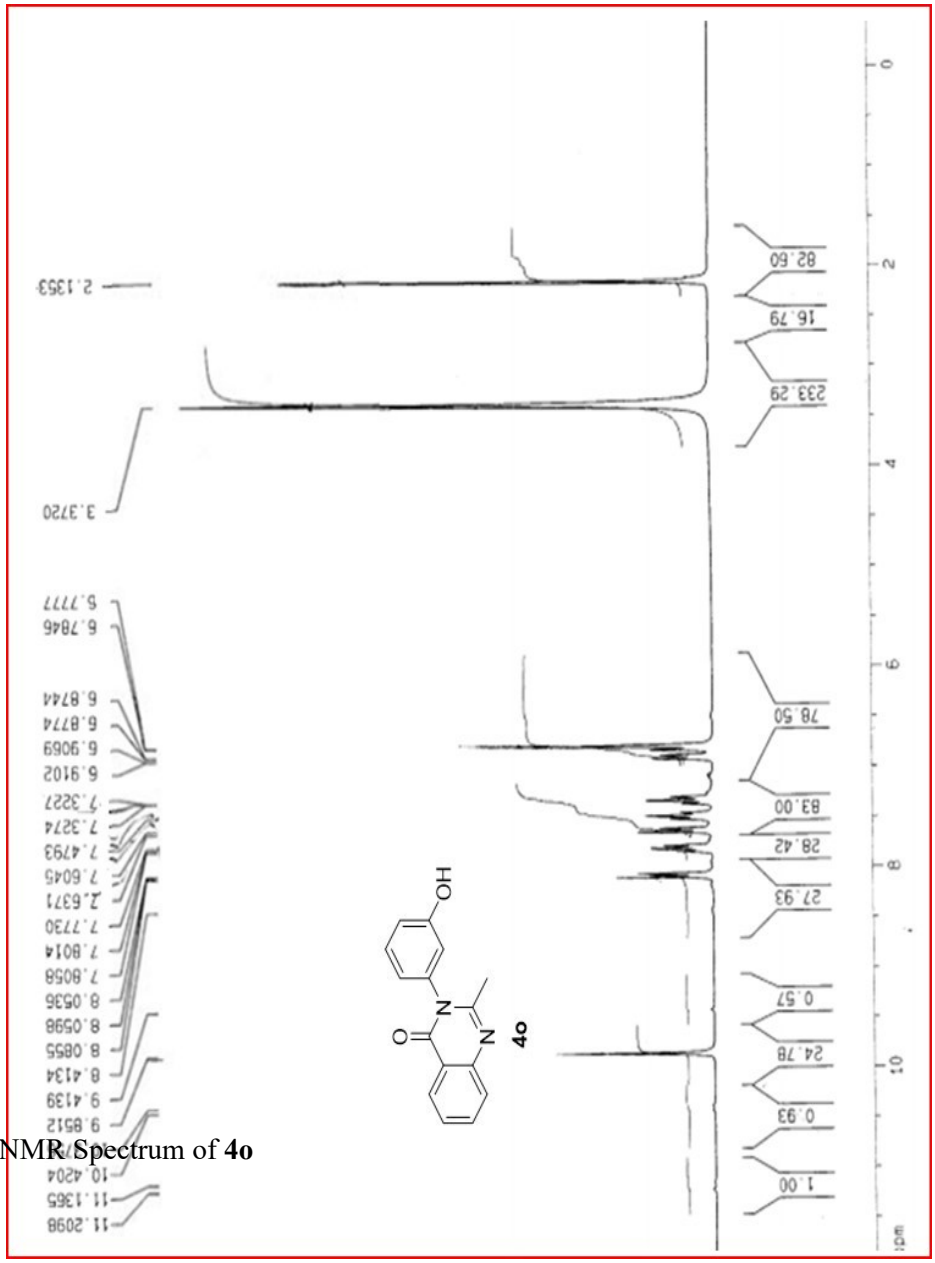

Figure 29 [1]HNMR Spectrum of **4o**

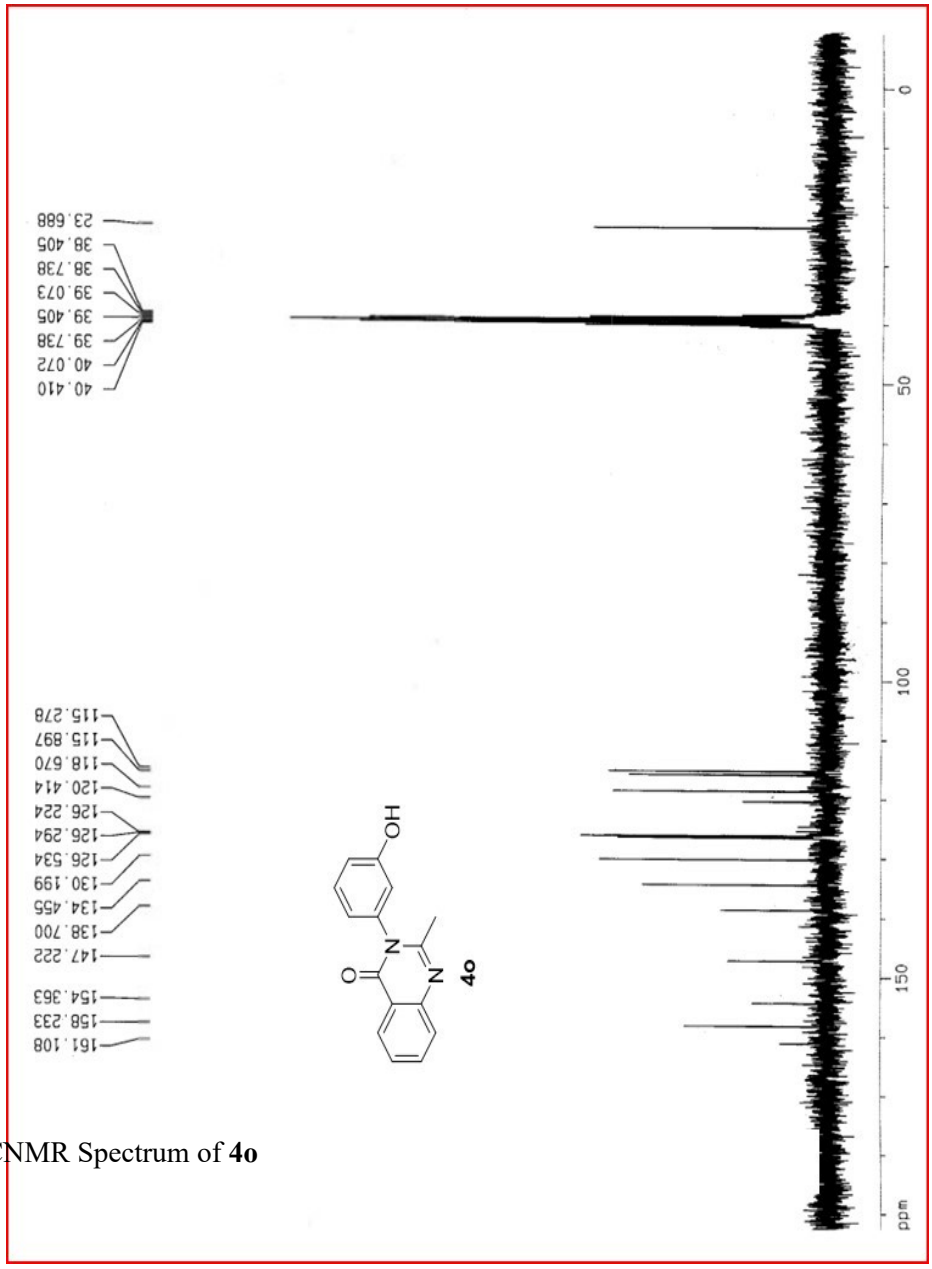

Figure 30 ^{13}CNMR Spectrum of **4o**