Efficient and Green: Biowaste-Derived N-rich Carbon for Palladium-Catalyzed CO Gas-Free Carbonylative Annulation with DFT Insights

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1. General considerations

Fourier transform infrared (FT-IR) spectra were exquisitely captured using a PerkinElmer spectrometer (L160000A, PerkinElmer, USA). The sophisticated gas chromatography-mass spectroscopy (GC–MS) analysis was executed with the Shimadzu GC–MS-TQ8030 system (Tokyo, Japan). Physisorption of N_2 gas molecules facilitated the determination of Brunauer–Emmett–Teller (BET) surface areas, conducted with a BELSORP-max analyzer (MicrotracBEL, Japan). Before analysis, all samples were meticulously degassed at 100 °C for 2 h. Surface morphology and elemental distribution were meticulously examined using field emission scanning electron microscopy (FE-SEM) (JEOL JSM-7100F, JEOL, Singapore) combined with energy dispersive X-ray spectroscopy (EDX). The total Pd content loaded on the PdNPs@NRC-FS-4 nanocatalyst was precisely quantified by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Optima 5300 DV, PerkinElmer, USA). Powder X-ray diffraction (*p*-XRD) measurements were conducted using an Ultima IV X-ray diffractometer (Rigaku, Japan). Thermogravimetric (TG) analysis was performed with a TGA Q500 V20.10 Build 36 analyzer at a heating rate of 10 °C min^{-1} in an N_2 atmosphere. The elemental composition and the element C and N contents of the raw materials were determined by the CHNS Elemental analyzer (CHN-2400, PerkinElmer). Proton and carbon-13 nuclear magnetic resonance (^1H and ^{13}C NMR) spectra were recorded at 500 MHz and 125 MHz in deuterated chloroform and dimethyl sulphoxide ($CDCl_3$ δ = 7.26 ppm, 77.5 ppm; DMSO 2.50 ppm, 39.52 ppm). ^1H coupling constants (J) are reported in Hertz (Hz), with multiplicities specified as follows: s (singlet), d (doublet), t (triplet), and m (multiplet).

2. Experimental section

2.1 Materials

All solvents were utilized without any prior purification. *Labeo catla* FS were gathered from local farmers as N-rich biomass in the Thotapalli Gudur region of Nellore, Andhra Pradesh, India. The aromatic leaves of *Elettaria cardamomum* (cardamom), were obtained as moderate content N biomass from the landscapes of Kerala, India. Meanwhile, the bagasse of *Saccharum officinarum L.,* (sugarcane), was attained as low N content biomass from a local juice shop in Bengaluru city, India. Palladium acetate ($Pd(OAc)_2$), OPD, 2-aminobenzamide, and aryl halides, along with various acids and bases, were obtained from esteemed suppliers such as Sigma-Aldrich and Avra chemical company and employed directly without additional purification. Unless specified otherwise, all reactions were conducted in accurately oven-dried glassware, utilizing magnetic stirring and heating via a silicone oil bath under aerobic conditions. The progress of reactions was monitored using thin-layer chromatography (TLC) on 0.25 mm Merck TLC silica gel plates, with ultraviolet (UV) light serving as the visualizing agent. For the purification of reaction products, column chromatography was executed using silica gel (60–120 mesh, Merck) with hexane and ethyl acetate as eluents. The process of concentrating the solutions involved the removal of volatile solvents using a rotary evaporator attached to a dry diaphragm pump (10–15 mm Hg), followed by further reduction to a constant weight using an oil pump (300 mTorr), a technique referred to as concentration in *vacuo*.

2.2 Methods

General procedure for the synthesis of 2-phenyl quinazoline-4(3*H*)-ones

In a DLV system, PdNPs@NRC-FS-4 nanocatalyst (0.26 mol% Pd), 2-amino benzamide (1.0 equiv.), aryl iodide (1.5 equiv.), potassium carbonate (K_2CO_3) (1.5 equiv.), and dimethyl formamide (DMF) (3.0 mL) was taken in a 5 mL inner vial and this vial was placed inside 50 mL outer vial containing $(COOH)_2.2H_2O$ (6.0 equiv.) and 1.5 mL of DMF. The 50 mL reaction vessel was tightened with a solid PTFE cap and stirred at 130 °C for the required time. The progress of the reaction was monitored through TLC. After completion of the reaction, the mixture was cooled to room temperature, and the PdNPs@NRC-FS-4 nanocatalyst was separated by centrifugation. The reaction mixture was quenched with the help of water, the organic layer was extracted with ethyl acetate in a separatory funnel and dried over anhydrous sodium sulphate (Na_2SO_4). The dried organic layer was concentrated in a vacuum and the products were purified by column chromatography using *n*-hexane and ethyl acetate as eluents to afford the corresponding products in good to excellent yields. ^{1}H and ^{13}C NMR spectra (see supporting information) of all the isolated products were recorded and compared to the standard samples for confirmation.

General procedure for the synthesis of 2-phenyl-1*H*-benzo[*d*]imidazole's

A 5 mL inner vial containing PdNPs@NRC-FS-4 nanocatalyst (0.40 mol% Pd), OPD (1.0 equiv.), aryl iodide (1.5 equiv.), triethyl amine (Et_3N) (0.2 equiv.), and DMF (3.0 mL) was placed inside a 50 mL outer vial that included 1.5 mL of DMF and 6.0 equiv. of $(COOH)_2.2H_2O$ (6.0 equiv.) in a DLV system. A solid PTFE cap was used to secure the 50 mL reaction vessel, and it was swirled for the necessary amount of time at 130 °C. TLC was used to track the reaction's development. The PdNPs@NRC-FS-4 nanocatalyst was separated by centrifugation once the reaction was finished and the mixture had cooled to room temperature. The organic layer was separated using ethyl acetate in a separatory funnel, and the reaction mixture was dried over anhydrous Na_2SO_4 after being quenched with water. The dried organic layer was vacuum-concentrated, and the products were isolated by column chromatography using *n*-hexane and ethyl acetate as eluents to afford the corresponding products in good to excellent yields. All of the separated products had their ^{1}H and ^{13}C NMR spectra recorded and compared to the reference samples for confirmation (see supporting information).

Procedure for recovery of the PdNPs@NRC-FS-4 nanocatalyst

In organic transformations, the endurance and recyclability of the catalyst stand as pivotal factors, particularly in the realm of practical industrial applications. To tackle this difficulty, the PdNPs@NRC-FS-4 nanocatalyst was separated by centrifugation, and washed with water (2 × 20 mL) and methanol (2 × 20 mL), followed by gentle desiccation at 50 °C overnight. For the next round of reactions, the dried PdNPs@NRC-FS-4 nanocatalyst was used as such.

3. Results and discussion

3.1 Barrett–Joyner Halenda (BJH) and Fourier transform-infrared (FT-IR) analyses

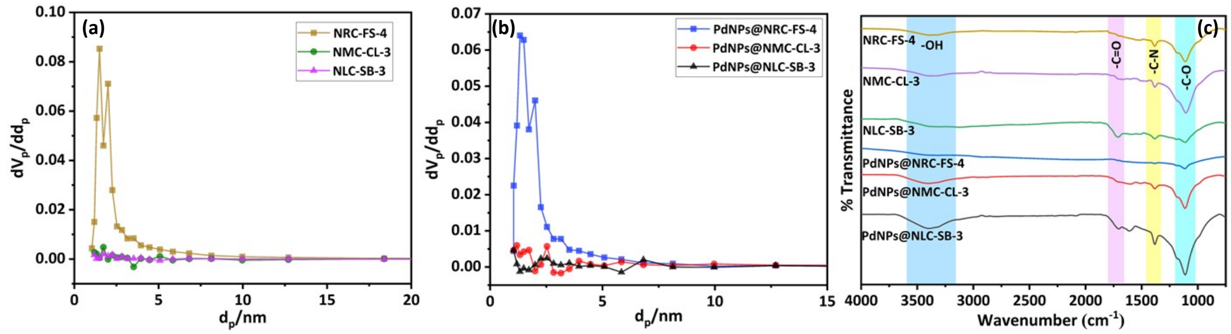


Fig. S1 BJH pore size distribution plot of (a) final supports (b) final Pd-based nanocatalysts and (c) FT-IR analysis of final supports and Pd-based nanocatalysts.

3.2. CHNS analysis

Sample	C (%)	H (%)	N (%)	S (%)
NRC-FS-4	49.22	2.871	24.03	1.471
NMC-CL-3	58.94	4.321	6.00	1.033
NLC-SB-3	54.14	3.351	1.90	1.339
PDNPs@NRC-FS-4	44.78	2.474	21.17	1.059
PdNPs@NMC-CL-3	51.68	3.834	4.75	1.591
PdNPs@NLC-SB-3	47.76	3.013	1.66	1.204

Table S1. CHNS analysis of final supports and Pd-based nanocatalysts.

3.3 FE-SEM analysis and EDX study

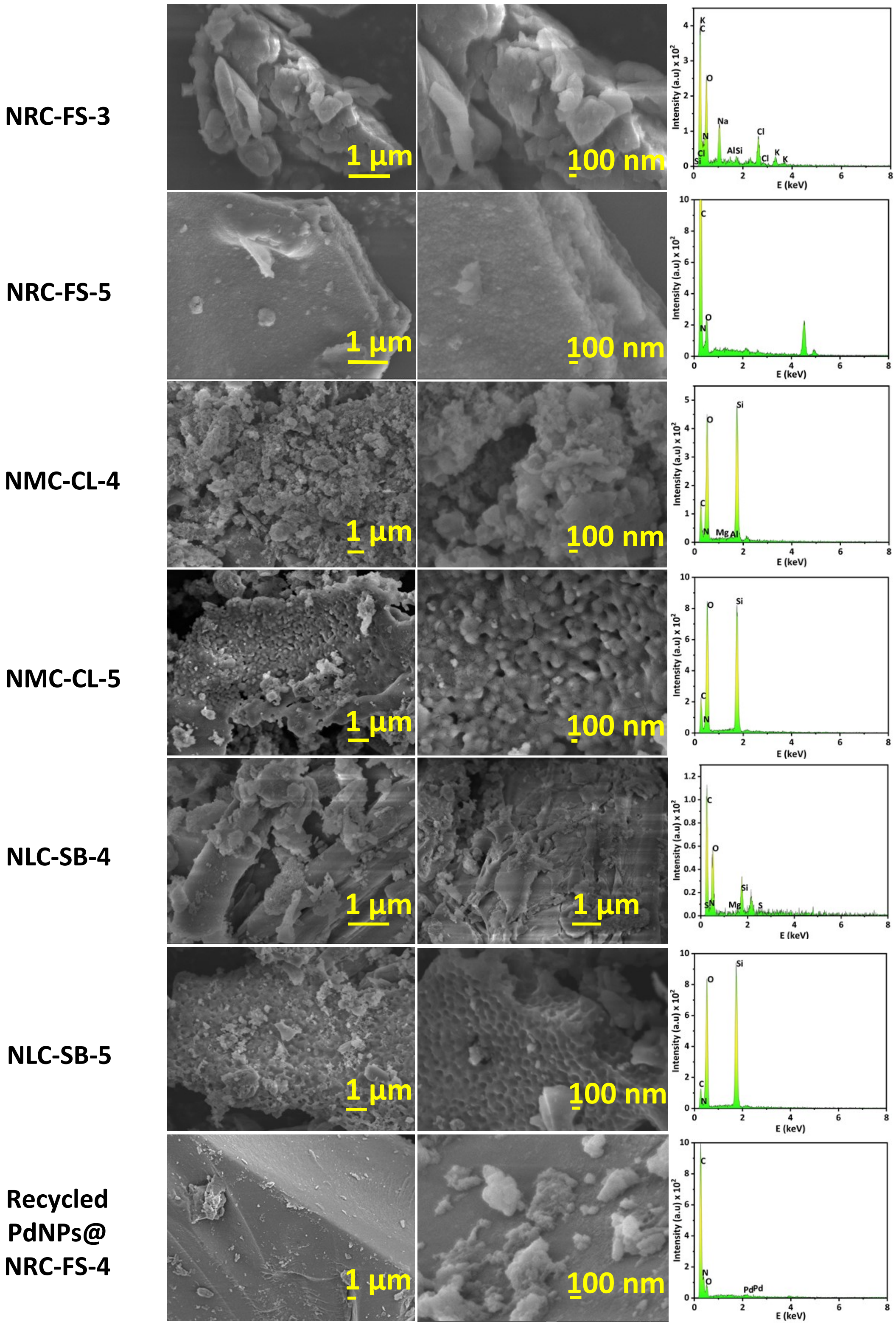


Fig. S2 FE-SEM and EDX of different supports and recycled PdNPs@NRC-FS-4 nanocatalyst.

Sample	C (%)	N (%)	O (%)	Pd (%)
NRC-FS-4	72.00	15.00	10.00	-
NMC-CL-3	28.72	6.63	31.04	-
NLC-SB-3	70.00	3.00	24.00	-
PdNPs@NRC-FS-4	71.80	16.00	11.00	1.20
PdNPs@NMC-CL-3	64.85	5.4	28.50	1.25
PdNPs@NLC-SB-3	62.62	2.1	34.10	1.18

Table S2. Elemental composition of final supports and Pd-based nanocatalysts.

Sample	C (%)	N (%)	O (%)	Pd (%)
NRC-FS-3	42.94	6.95	27.26	-
NRC-FS-5	53.00	16.00	31.00	-
NMC-CL-4	21.41	4.05	42.84	-
NMC-CL-5	20.84	2.99	45.40	-
NLC-SB-4	50.97	0.16	30.16	-
NLC-SB-5	13.63	3.53	45.97	-
Recycled-PdNPs@NRC-FS-4	72.55	15.38	10.23	1.18

Table S3. Elemental composition of residual supports and recycled PdNPs@NRC-FS-4 nanocatalyst.

3.4 XPS analysis

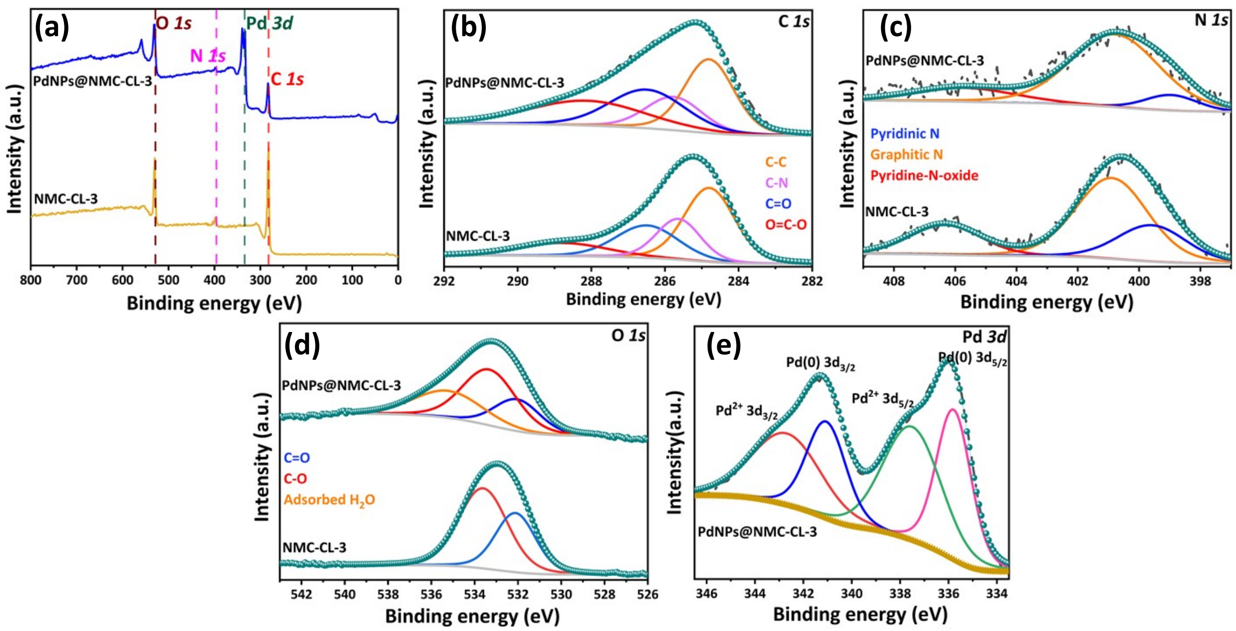


Fig. S3 XPS analysis (a) Survey spectra (b) C *1s* (c) N *1s* (d) O *1s* of NMC-CL-3 and PdNPs@NMC-CL-3 and (e) Pd *3d* spectra of PdNPs@NMC-CL-3.

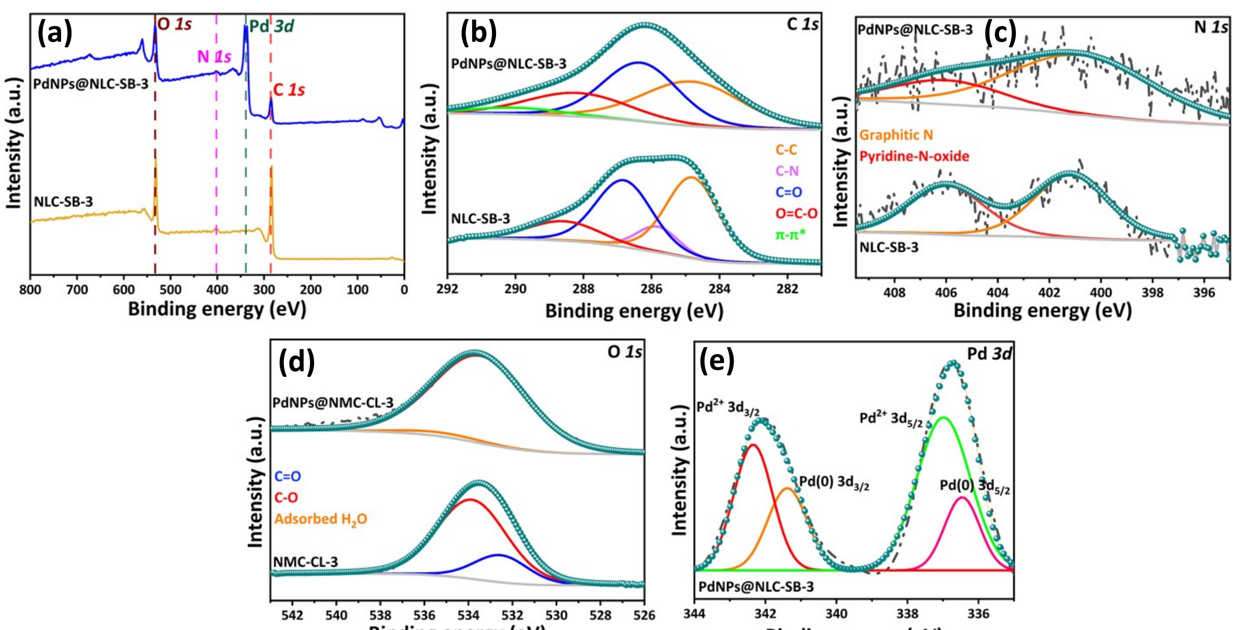
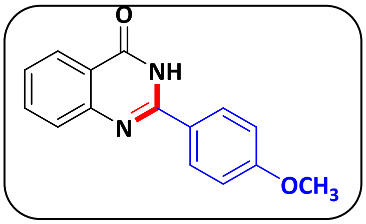


Fig. S4 XPS analysis (a) Survey spectra (b) C *1s* (c) N *1s* (d) O *1s* of NLC-SB-3 and PdNPs@NLC-SB-3 and (e) Pd *3d* spectra of PdNPs@NLC-SB-3.

4. Spectroscopic data of newly obtained Products

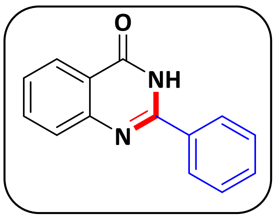
4.1. Quinazolin-4(3*H*)-ones[1]

2-(4-methoxyphenyl) quinazolin-4(3*H*)-one (3a)



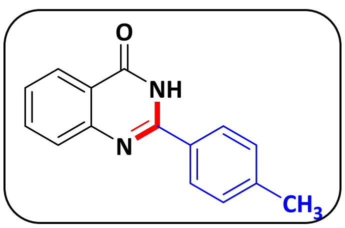
Purified by column chromatography (20% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.42 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 8.0 Hz 1H), 7.48 (t, *J* = 7.25 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.7, 162.3, 152.3, 149.4, 135.0, 129.3, 127.7, 126.6, 126.3, 125.2, 121.1, 114.4, 55.9.

2-phenylquinazolin-4(3*H*)-one (3b)



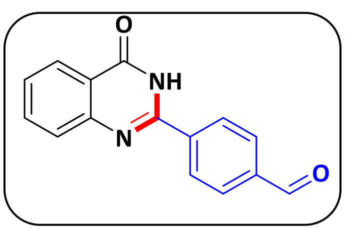
Purified by column chromatography (15% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 3.0 Hz, 2H), 7.86-7.78 (m, 2H), 7.58 (s, 3H), 7.50 (t, *J* = 7.25 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.6, 151.8, 149.1, 135.0, 132.5, 131.8, 129.1, 127.8, 127.4, 126.9, 126.4, 120.7.

2-(p-tolyl) quinazolin-4(3*H*)-one (3c)



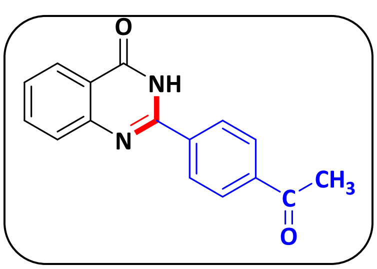
Purified by column chromatography (15% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.46 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.25 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 162.7, 152.6, 149.3, 141.9, 135.0, 130.36, 129.6, 128.1, 127.8, 126.8, 126.3.

4-(4-Oxo-3,4-dihydroquinazolin-2-yl) benzaldehyde (3d)



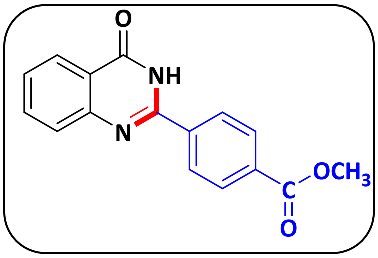
Purified by column chromatography (17% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.73 (s, 1H), 10.12 (s, 1H), 8.38 (d, *J* = 7.5 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 198.1, 197.9, 167.3, 156.6, 153.6, 143.0, 139.9, 134.8, 134.6, 133.8, 132.8, 132.3, 131.2, 131.0, 126.4.

2-(4-Acetylphenyl) quinazolin-4(3*H*)-one (3e)



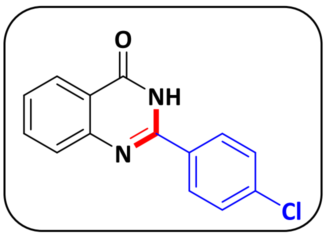
Purified by column chromatography (28% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.71 (s, 1H), 8.32 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 198.1, 148.9, 139.0, 137.0, 135.1, 128.7, 128.5, 128.1, 127.5, 126.3, 27.46.

Methyl 4-(4-oxo-3,4-dihydroquinazolin-2-yl) benzoate (3f)



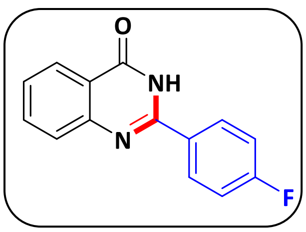
Purified by column chromatography (20% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.72 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 7.75 Hz, 1H), 3.19 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 166.2, 161.9, 155.7, 147.4, 140.0, 134.9, 131.0,129.6, 129.3, 128.6, 127.7, 127.6, 126.6, 120.7, 52.9.

2-(4-Chlorophenyl) quinazolin-4(3*H*)-one (3g)



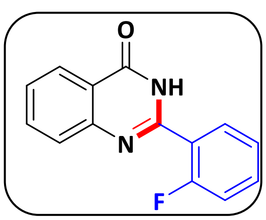
Purified by column chromatography (16% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.62 (s, 1H), 8.20 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 7.75 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.25 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 162.6, 151.8, 149.0, 136.7, 136.1, 132.0, 130.0, 129.1, 128.0, 127.2, 126.3, 121.4.

2-(4-fluorophenyl) quinazolin-4(3*H*)-one (3h)



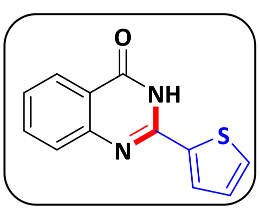
Purified by column chromatography (15% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.58 (s, 1H), 8.25 (t, *J* = 7.0 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 7.75 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 8.25 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 166.5, 163.5, 162.6, 151.8, 149.1, 136.1, 130.8, 129.7, 127.9, 127.0, 126.3, 121.3, 116.1, 116.0.

2-(2-fluorophenyl) quinazolin-4(3*H*)-one (3i)



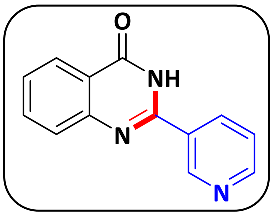
Purified by column chromatography (14% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.58 (s, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 7.86 (t, *J* = 7.75 Hz, 1H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.65-7.61 (m, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.42-7.36 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 162.0, 161.0, 159.0, 150.4, 149.1, 135.0, 133.3, 131.5, 127.9, 127.5, 126.3, 125.1, 125.0, 122.7, 122.6, 121.5, 116.7, 116.5.

2-(thiophen-2-yl) quinazolin-4(3*H*)-one (3j)



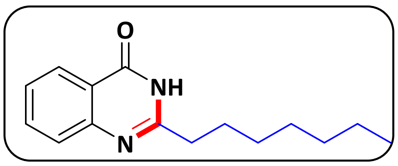
Purified by column chromatography (15% ethyl acetate in hexane), yellow solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.66 (s, 1H), 8.23 (d, *J* = 3.0 Hz, 1H), 8.13 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 5.0 Hz, 1H), 7.81 (t, *J* = 7.75 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 4.0 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 162.2, 149.1, 148.3, 137.8, 135.1, 132.6, 129.8, 128.9, 127.4, 126.8, 126.4, 121.3.

2-(pyridin-3-yl) quinazolin-4(3*H*)-one (3k)



Purified by column chromatography (50% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.75 (s, 1H), 9.30 (s, 1H), 8.77 (s, 1H), 8.50 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.87 (t, *J* = 7.75 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.61-7.55 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 162.6, 152.2, 151.2, 149.1, 135.9, 135.1, 128.0, 127.4, 126.3, 124.0, 121.5.

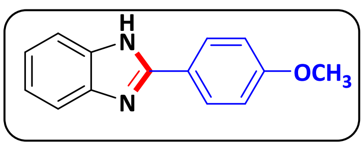
2-(heptyl) quinazolin-4(3*H*)-one (3l)



Purified by column chromatography (13% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 8.14 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 6.49 (t, *J* = 7.25 Hz, 1H), 3.07 (d, *J* = 5.5 Hz, 2H), 2.50 (s, 1H), 1.58-1.54 (m, 2H), 1.35-1.24 (m, 7H), 0.86 (t, *J* = 6.25 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 172.1, 150.4, 133.0, 129.5, 114.0, 111.4, 42.5, 31.7, 29.1, 28.9, 27.0, 22.5, 14.4.

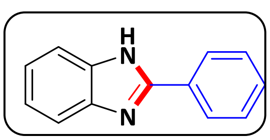
4.2. Benzo[*d*]imidazoles[2]

2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (5a)



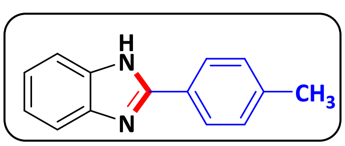
Purified by column chromatography (20% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 2.75 Hz, 2H), 7.19 (t, *J* = 3.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.9, 156.4, 133.4, 133.2, 127.4, 127.2, 119.6, 60.5.

2-phenyl-1*H*-benzo[*d*]imidazole (5b)



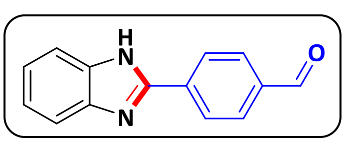
Purified by column chromatography (18% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.93 (s, 1H), 8.19 (d, *J* = 7.5 Hz, 2H), 7.61-7.49 (m, 5H), 7.22-7.21 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 151.6, 130.6, 130.3, 129.4, 126.9, 122.5.

2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (5c)



Purified by column chromatography (16% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.82 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ 151.8, 144.2, 140.0, 135.4, 129.9, 127.9, 126. 8, 122.8, 122.0, 119.1, 111.6, 21.4.

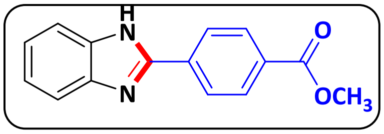
4-(1*H*-benzo[*d*]imidazol-2-yl) benzaldehyde (5d)



Purified by column chromatography (20% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d$_6$) δ 12.94 (s, 1H), 8.19 (d, *J* = 5.6 Hz, 2H), 7.61-7.49 (m, 5H), 7.22-7.21 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d$_6$) δ

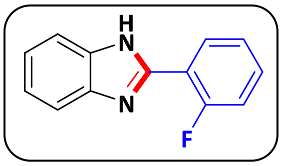
151.6, 130.6, 130.3, 129.4, 126.9, 122.5.

Methyl 4-(1*H*-benzo[*d*]imidazol-2-yl) benzoate (5e)



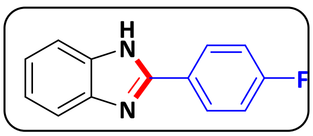
Purified by column chromatography (20% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 13.16 (s, 1H), 8.32 (d, *J* = 6.4 Hz, 2H), 8.13 (d, *J* = 6.4 Hz, 2H), 7.67-7.64 (m, 2H), 7.25 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 166.2, 150.4, 134.7, 130.7, 130.5, 130.3, 130.2, 130.0, 129.8, 127.7, 127.6, 127.0, 52.7.

2-(2-fluorophenyl)-1*H*-benzo[*d*]imidazole (5f)



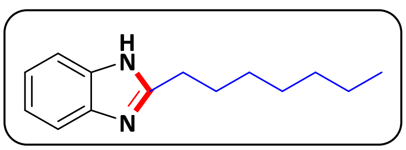
Purified by column chromatography (12% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.6 (s, 1H), 8.24 (t, *J* = 7.25 Hz, 1H), 7.65 (s, 2H), 7.59-7.55 (m, 1H), 7.47-7.39 (m, 2H), 7.25-7.23 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.9, 158.9, 146.8, 132.3, 130.7, 125.5, 122.7, 118.5, 118.4, 117.0, 116.9.

2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (5g)



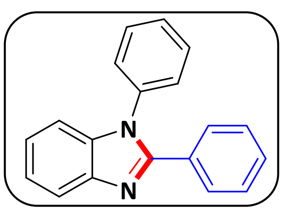
Purified by column chromatography (16% ethyl acetate in hexane), white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.9 (s, 1H), 8.24-8.22 (m, 2H), 7.60 (s, 2H), 7.41 (t, *J* = 8.75 Hz, 2H), 7.22-7.20 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.5, 162.5, 150.8, 132.6, 129.2, 129.1, 127.2, 122.5, 116.5, 116.4.

2-heptyl-1*H*-benzo[*d*]imidazole (5h)



Purified by column chromatography (15% ethyl acetate in hexane), Brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (dd, *J* = 26.4, 6.4 Hz, 1H), 7.27-7.19 (m, 2H), 4.23 (t, *J* = 5.6 Hz, 2H), 1.80-1.74 (m, 2H), 1.29-1.12 (m, 8H), 0.81 (t, *J* = 5.6 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 144.3, 143.3, 134.1, 122.7, 122.0, 119.6, 110.9, 44.6, 31.6, 29.8, 28.6, 26.5, 22.4, 14.3.

1,2-diphenyl-1*H*-benzo[*d*]imidazole (5i)



Purified by column chromatography (18% ethyl acetate in hexane), Brown liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.60 (s, 1H), 7.82 (d, *J* = 5.6 Hz, 1H), 7.72-7.63 (m, 8H), 7.57 (m, 1H), 7.52 (t, *J* = 5.8 Hz, 1H), 7.37-7.32 (m, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 144.3, 143.7, 136.4, 133.5, 133.3, 131.2, 130.5, 129.7, 129.0, 128.2, 124.1, 123.9, 122.9, 120.4, 111.1.

5. Computational details

All calculations were performed employing a DFT method implemented in the Gaussian 16 suite of programs.[3] For geometry optimization and frequency analysis, we adopted the BP86 functional.[4] During geometry optimization, we used the split-valence plus single polarization basis set def2-SVP[5] for non-metals and the Stuttgart/Dresden small core RECP (relativistic effective core potential) plus valence double-ζ-basis set (SDD)[6] for Pd, I. The geometries were optimized without any symmetry constraints. For each transition state, in addition to analyzing the character of the normal mode associated with the imaginary frequency, intrinsic reaction coordinate (IRC) analysis[7] was performed to confirm that it connects the correct reactant and product on the potential energy surface. To refine the computed energy, single-point calculations were performed using the hybrid-meta-GGA M06-2X functional[8-9] with the def2-TZVP[7] basis set for nonmetals and SDD for Pd, I. Solvation energies were evaluated implicitly by a self-consistent reaction field (SCRF) approach for all the intermediates and transition states, in dimethylformamide solvent (ε=37.219), using the SMD continuum solvation model.[10] The free energies (ΔG), calculated at the M06-2X(SMD)/SDD/def2-TZVP//BP86/SDD/def2-SVP level are reported throughout the article unless otherwise mentioned. The ΔG value is obtained by augmenting the in-solvent electronic energy (ΔE), calculated at M06-2X(SMD)/SDD/def2-TZVP, with the corresponding free energy corrections calculated at BP86/SDD/def2-SVP in the gas phase.

Table S4. Cartesian coordinates (Å) of the optimized structures of all intermediates and transition states at BP86/SDD(Pd,I)/def2-SVP level of theory. E_e^S represents the absolute electronic energy in Hartree at the M062x/SDD(Pd,I)/def2-TZVP level of theory in dimethylformamide solvent.

cat 1.
E_e^S = -2537.225329

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3b

***E_e^S* =** -242.9969799

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IM1

***E_e^S* =** -2780.2707100

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TS1

***E_e^S* =** -2780.265029

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O	-6.726564000	14.117093000	3.980250000
C	-8.359338000	15.574967000	-6.870247000
O	-8.359649000	15.049328000	-7.978155000
O	-8.659822000	16.881965000	-6.678201000
C	-8.978249000	17.608984000	-7.871959000
H	-8.127656000	17.598101000	-8.584901000
H	-9.860445000	17.170623000	-8.383334000
H	-9.195673000	18.643283000	-7.548113000
O	-5.560041000	9.625098000	5.530811000
H	-6.682815000	8.673296000	-6.116326000
H	-4.670532000	4.071139000	1.047314000
H	-4.785031000	5.421776000	3.165008000

H	-5.160380000	7.607011000	4.303019000
Pd	-9.574957000	10.893880000	-1.070752000
C	-11.529498000	10.995447000	-1.514104000
C	-11.253943000	11.251282000	-2.890592000
C	-12.224127000	11.954720000	-0.720568000
C	-11.649958000	12.492750000	-3.448386000
C	-12.615876000	13.165260000	-1.309074000
C	-12.333975000	13.435080000	-2.668313000
H	-10.847032000	10.459468000	-3.537614000
H	-12.450618000	11.738578000	0.334347000
H	-11.441358000	12.695803000	-4.511152000
H	-13.145469000	13.913972000	-0.697594000
H	-12.659387000	14.386975000	-3.116527000
I	-11.649642000	8.760009000	-0.827042000

IM2

E_e^S = -2780.309003

C	-7.176496000	13.983709000	-1.316544000
C	-7.381779000	13.392698000	-0.039691000
C	-7.631509000	12.006619000	0.195133000
N	-7.402520000	14.233514000	1.119149000
C	-7.341667000	13.781266000	2.439263000
N	-7.248189000	12.356420000	2.579789000
C	-7.388373000	11.514766000	1.485259000
N	-7.369540000	15.390062000	-1.509795000
C	-7.514279000	15.620477000	0.902262000
C	-7.135633000	11.825069000	3.870803000
N	-7.277978000	10.169537000	1.699918000
C	-7.014130000	9.602058000	2.965173000
N	-7.021631000	10.504951000	4.087366000
C	-7.522254000	16.160437000	-0.344620000
C	-7.405519000	15.975488000	-2.760131000
C	-7.274293000	15.215269000	-3.929053000
C	-7.037564000	13.796061000	-3.762036000
C	-6.930674000	12.989261000	-4.896906000
C	-7.016010000	13.523333000	-6.211184000
C	-6.859984000	13.219916000	-2.482437000
N	-6.455179000	11.926087000	-2.361506000
C	-6.634863000	11.119713000	-3.408160000
N	-6.795949000	11.610159000	-4.705268000
N	-8.004957000	11.100435000	-0.791221000
C	-7.376700000	9.878268000	-0.713436000
C	-6.935223000	9.138827000	-1.876748000
C	-6.762054000	9.704856000	-3.185588000
C	-7.107628000	9.322685000	0.561489000
C	-6.741666000	7.979940000	0.743373000
C	-6.559589000	7.186220000	-0.410175000
C	-6.636411000	7.754506000	-1.691877000
C	-6.929964000	12.580263000	-7.277827000
N	-6.803372000	11.249575000	-7.078750000
C	-6.751922000	10.750568000	-5.845058000
N	-6.614191000	8.854477000	-4.309176000
C	-6.611104000	9.373615000	-5.577548000
C	-6.445945000	7.474335000	-4.116509000
C	-6.401183000	6.909991000	-2.848239000
N	-6.276303000	5.805733000	-0.293676000
C	-6.108310000	5.082885000	-1.454863000
C	-6.180985000	5.273626000	1.009340000
N	-6.601646000	7.424006000	2.039508000
C	-6.714442000	8.277824000	3.130585000

C	-6.331915000	6.058012000	2.119110000
N	-6.162080000	5.559447000	-2.676590000
N	-7.329745000	15.762494000	-5.172490000
C	-7.203807000	14.987659000	-6.249440000
H	-6.971390000	12.930726000	-8.317967000
H	-6.317275000	6.867922000	-5.021334000
H	-7.643386000	17.241042000	-0.491840000
H	-7.544061000	17.064543000	-2.793267000
H	-7.611288000	16.224986000	1.812235000
H	-7.129907000	12.516461000	4.719270000
H	-5.910714000	4.006599000	-1.301111000
O	-7.347519000	14.513936000	3.420967000
C	-7.272315000	15.675206000	-7.586472000
O	-7.133885000	15.108794000	-8.664525000
O	-7.502654000	17.003318000	-7.475823000
C	-7.580265000	17.709186000	-8.722215000
H	-6.633828000	17.613145000	-9.293677000
H	-8.404925000	17.315135000	-9.351599000
H	-7.767354000	18.766452000	-8.460062000
O	-6.892476000	9.992890000	5.246446000
H	-6.498420000	8.676264000	-6.415393000
H	-5.973459000	4.199178000	1.085036000
H	-6.244738000	5.637162000	3.129050000
H	-6.542591000	7.896797000	4.144524000
Pd	-9.715554000	11.313083000	-1.955958000
C	-10.872302000	10.992831000	-0.398989000
C	-11.237880000	9.676729000	-0.057169000
C	-11.275044000	12.077902000	0.403172000
C	-11.994302000	9.449560000	1.110692000
C	-12.031873000	11.835545000	1.567932000
C	-12.389426000	10.524028000	1.926989000
H	-10.947473000	8.829817000	-0.698017000
H	-11.016971000	13.110335000	0.120376000
H	-12.282996000	8.418423000	1.373985000
H	-12.351684000	12.687429000	2.190771000
H	-12.985437000	10.341049000	2.835182000
I	-11.611586000	11.567459000	-3.717129000

$H_2C_2O_4$

***E_e^S* =** -378.3619987

C	-1.966183000	0.338195000	-3.755983000
O	-1.966183000	1.362040000	-3.110211000
O	-1.966183000	-0.909088000	-3.235707000
H	-1.966183000	-0.791147000	-2.258027000
C	-1.966183000	0.338195000	-5.303331000
O	-1.966183000	1.362040000	-5.949103000
O	-1.966183000	-0.909088000	-5.823607000
H	-1.966183000	-0.791147000	-6.801287000

CO_2

***E_e^S* =** -188.5970823

C	-3.541368000	14.478017000	-7.603080000
O	-2.986673000	14.350529000	-6.574878000
O	-4.096062000	14.605505000	-8.631282000

H_2O

***E_e^S* =** -76.4338032

O	-3.554848000	17.747721000	-15.491348000
H	-3.554848000	18.506514000	-14.878006000
H	-3.554848000	16.988929000	-14.878006000

CO

***E_e^S* =** -113.316408

C	-1.103694000	0.000000000	-3.620670000
O	-1.103694000	0.000000000	-4.763098000

IM3

***E_e^S* =** -2893.66108

C	-6.570007000	14.135377000	-1.336107000
C	-6.608446000	13.581158000	-0.026749000
C	-6.963264000	12.235771000	0.290494000
N	-6.335045000	14.438183000	1.078367000
C	-6.154862000	14.013197000	2.399229000
N	-6.191577000	12.593376000	2.576377000
C	-6.583787000	11.753447000	1.546522000
N	-6.631579000	15.548726000	-1.546187000
C	-6.348292000	15.825378000	0.842713000
C	-5.979006000	12.088475000	3.864403000
N	-6.618874000	10.407817000	1.799722000
C	-6.211827000	9.848865000	3.032297000
N	-5.981103000	10.771413000	4.115129000
C	-6.513479000	16.349414000	-0.398861000
C	-6.782578000	16.110387000	-2.798821000
C	-6.893025000	15.318607000	-3.950623000
C	-6.790081000	13.884216000	-3.770173000
C	-6.895116000	13.047735000	-4.879664000
C	-7.086712000	13.560200000	-6.194642000
C	-6.517153000	13.317723000	-2.500393000
N	-6.252195000	11.996968000	-2.375611000
C	-6.594440000	11.190535000	-3.375743000
N	-6.851359000	11.667088000	-4.664122000
N	-7.650724000	11.355121000	-0.561256000
C	-7.081500000	10.081148000	-0.569609000
C	-6.827527000	9.289131000	-1.756523000
C	-6.772540000	9.798322000	-3.098762000
C	-6.681637000	9.528622000	0.673704000
C	-6.373065000	8.168580000	0.847790000
C	-6.391239000	7.341447000	-0.293999000
C	-6.590158000	7.889795000	-1.571134000
C	-7.203603000	12.590778000	-7.231845000
N	-7.156298000	11.255084000	-7.008260000
C	-6.995956000	10.781956000	-5.774674000
N	-6.808056000	8.916366000	-4.204908000
C	-6.920572000	9.405127000	-5.479765000
C	-6.704453000	7.536306000	-3.992018000
C	-6.546699000	7.004077000	-2.720793000
N	-6.180178000	5.948385000	-0.173738000
C	-6.202758000	5.189984000	-1.323803000
C	-5.955584000	5.435752000	1.122550000
N	-6.095090000	7.630238000	2.130389000
C	-5.989358000	8.512069000	3.199167000
C	-5.909672000	6.251063000	2.217331000
N	-6.375163000	5.643516000	-2.541835000
N	-7.055595000	15.842010000	-5.193431000
C	-7.144984000	15.034433000	-6.253084000

H	-7.341641000	12.920376000	-8.270356000
H	-6.721220000	6.899780000	-4.884838000
H	-6.557376000	17.434188000	-0.556569000
H	-6.808237000	17.207227000	-2.848533000
H	-6.245096000	16.445600000	1.741131000
H	-5.796152000	12.797744000	4.677782000
H	-6.056822000	4.106536000	-1.162511000
O	-5.937224000	14.765291000	3.339216000
C	-7.328511000	15.698126000	-7.590094000
O	-7.419638000	15.098374000	-8.655670000
O	-7.383294000	17.047273000	-7.498168000
C	-7.559976000	17.731377000	-8.746086000
H	-6.723960000	17.512549000	-9.442456000
H	-8.506714000	17.425325000	-9.237697000
H	-7.584650000	18.808640000	-8.500027000
O	-5.755805000	10.273816000	5.265400000
H	-6.950948000	8.681777000	-6.302219000
H	-5.812622000	4.351089000	1.201144000
H	-5.721344000	5.847881000	3.220683000
H	-5.704672000	8.140748000	4.191076000
Pd	-9.737431000	11.679656000	-0.775115000
C	-11.582718000	11.930782000	-0.906420000
O	-12.728359000	12.045238000	-0.996949000
C	-9.973177000	10.307519000	-2.282768000
C	-10.079066000	10.716252000	-3.629076000
C	-10.129266000	8.941176000	-1.968216000
C	-10.302311000	9.768208000	-4.649485000
C	-10.356382000	7.995513000	-2.989005000
C	-10.442464000	8.405563000	-4.331168000
H	-10.003499000	11.783624000	-3.894291000
H	-10.083250000	8.602038000	-0.920260000
H	-10.382418000	10.104538000	-5.696207000
H	-10.479929000	6.931550000	-2.727509000
H	-10.633625000	7.666828000	-5.125971000
I	-9.990107000	13.520673000	1.323348000

TS2

$\boldsymbol{E_e^S}$ **=** -2893.643589

C	0.852722000	-2.168641000	-1.329974000
C	-0.563462000	-2.233873000	-1.266250000
C	-1.424925000	-1.178043000	-0.833796000
N	-1.212352000	-3.457696000	-1.634333000
C	-2.581074000	-3.609270000	-1.850320000
N	-3.344753000	-2.404172000	-1.717796000
C	-2.765399000	-1.241495000	-1.224564000
N	1.648933000	-3.360607000	-1.383818000
C	-0.399657000	-4.604628000	-1.751155000
C	-4.721779000	-2.465977000	-1.950354000
N	-3.561417000	-0.130040000	-1.120057000
C	-4.917356000	-0.111931000	-1.521175000
N	-5.504789000	-1.377081000	-1.864439000
C	0.951196000	-4.556277000	-1.611014000
C	3.024555000	-3.346320000	-1.230130000
C	3.725447000	-2.156089000	-1.011497000
C	2.951568000	-0.929487000	-1.017245000
C	3.603666000	0.286458000	-0.802082000
C	5.009613000	0.361438000	-0.588778000
C	1.565597000	-0.931692000	-1.293227000
N	0.895800000	0.235532000	-1.469043000
C	1.459095000	1.349864000	-1.015908000
N	2.820930000	1.442239000	-0.745380000
N	-1.004631000	-0.061944000	-0.097586000
C	-1.552068000	1.124783000	-0.555094000
C	-0.817690000	2.368259000	-0.684616000
C	0.611712000	2.480196000	-0.730174000
C	-2.913499000	1.133596000	-0.955987000
C	-3.649735000	2.315788000	-1.140955000
C	-2.971714000	3.543556000	-0.999490000
C	-1.582254000	3.573384000	-0.796542000
C	5.533677000	1.659141000	-0.338403000
N	4.764046000	2.771097000	-0.281284000
C	3.446334000	2.689733000	-0.460374000
N	1.235138000	3.730749000	-0.587943000
C	2.595955000	3.815917000	-0.438555000
C	0.458889000	4.897444000	-0.560555000
C	-0.920517000	4.858192000	-0.710328000
N	-3.674105000	4.768118000	-1.080425000
C	-2.957020000	5.934803000	-0.938116000
C	-5.065556000	4.701467000	-1.309250000
N	-5.042791000	2.283053000	-1.414395000
C	-5.636065000	1.046470000	-1.632573000
C	-5.707680000	3.506906000	-1.474449000
N	-1.661384000	6.026491000	-0.761040000
N	5.077461000	-2.113987000	-0.841490000
C	5.691274000	-0.949807000	-0.647824000
H	6.612847000	1.788815000	-0.179428000
H	1.001477000	5.843681000	-0.448593000
H	1.559882000	-5.466622000	-1.684052000
H	3.538731000	-4.314659000	-1.297329000
H	-0.943760000	-5.535061000	-1.952481000
H	-5.160287000	-3.428388000	-2.230944000
H	-3.565181000	6.856391000	-0.985625000
O	-3.119845000	-4.668196000	-2.155405000
C	7.185222000	-0.997700000	-0.471100000
O	7.898026000	-0.012167000	-0.319787000
O	7.672245000	-2.260420000	-0.498125000
C	9.093063000	-2.362521000	-0.333573000
H	9.326033000	-3.442235000	-0.375118000
H	9.628043000	-1.820171000	-1.140719000
H	9.413336000	-1.934907000	0.639174000
O	-6.759264000	-1.396446000	-2.099905000
H	3.032859000	4.811554000	-0.304685000
H	-5.600390000	5.658023000	-1.354445000
H	-6.787932000	3.463984000	-1.664615000
H	-6.692356000	0.987972000	-1.921707000
Pd	-0.560600000	-0.400017000	1.993847000
I	0.953316000	1.726330000	2.634505000
C	-0.710935000	-1.207686000	3.654119000
O	-0.678527000	-1.459617000	4.799372000
C	-1.648413000	-2.241977000	2.377000000
C	-1.037629000	-3.467448000	2.026970000
C	-3.059088000	-2.146516000	2.413929000
C	-1.832513000	-4.574477000	1.681173000
C	-3.848174000	-3.254980000	2.060221000
C	-3.235780000	-4.468083000	1.691196000
H	0.060312000	-3.556420000	2.033352000
H	-3.538608000	-1.204693000	2.725273000
H	-1.353592000	-5.527392000	1.404991000
H	-4.947013000	-3.175366000	2.081623000
H	-3.854945000	-5.336717000	1.417417000

IM4

E_e^S = -2893.667432

C	-6.521918000	14.117347000	-1.187651000
C	-6.538073000	13.588406000	0.132182000
C	-6.887478000	12.248203000	0.483922000
N	-6.232632000	14.457006000	1.229680000
C	-5.947452000	14.037492000	2.530453000
N	-5.980587000	12.616160000	2.721226000
C	-6.433768000	11.767880000	1.719342000
N	-6.587827000	15.532081000	-1.409671000
C	-6.234351000	15.842390000	0.970648000
C	-5.662700000	12.109635000	3.986847000
N	-6.426335000	10.422647000	1.973365000
C	-5.960065000	9.863945000	3.184621000
N	-5.643071000	10.790109000	4.239071000
C	-6.426062000	16.345592000	-0.276572000
C	-6.803316000	16.083772000	-2.657873000
C	-6.993166000	15.282918000	-3.789682000
C	-6.888249000	13.850123000	-3.601711000
C	-7.103468000	13.006133000	-4.693394000
C	-7.394407000	13.511884000	-5.989908000
C	-6.525556000	13.290765000	-2.354762000
N	-6.249627000	11.961758000	-2.251416000
C	-6.729982000	11.156747000	-3.199623000
N	-7.088611000	11.627358000	-4.462557000
N	-7.547856000	11.359602000	-0.361125000
C	-7.035559000	10.082451000	-0.357326000
C	-6.922121000	9.265215000	-1.545520000
C	-6.961165000	9.770811000	-2.887553000
C	-6.570456000	9.533386000	0.863076000
C	-6.316006000	8.164065000	1.032901000
C	-6.463790000	7.322334000	-0.090816000
C	-6.743451000	7.860716000	-1.356623000
C	-7.635968000	12.539111000	-7.001702000
N	-7.622582000	11.207774000	-6.764701000
C	-7.376743000	10.740843000	-5.542333000
N	-7.139944000	8.882265000	-3.972437000
C	-7.337334000	9.363199000	-5.239894000
C	-7.091523000	7.497502000	-3.750297000
C	-6.848217000	6.965036000	-2.490145000
N	-6.315007000	5.922908000	0.034662000
C	-6.474047000	5.153984000	-1.096802000
C	-6.004520000	5.418422000	1.315756000
N	-5.968250000	7.630273000	2.300429000
C	-5.766030000	8.519638000	3.348576000
C	-5.833661000	6.245556000	2.390914000
N	-6.728084000	5.600308000	-2.304675000
N	-7.234468000	15.799355000	-5.025211000
C	-7.417867000	14.987277000	-6.064287000
H	-7.848583000	12.864343000	-8.029015000
H	-7.221793000	6.857553000	-4.631341000
H	-6.456681000	17.428617000	-0.450433000
H	-6.822290000	17.180295000	-2.717629000
H	-6.086329000	16.477808000	1.852137000
H	-5.408593000	12.817286000	4.782108000
H	-6.369134000	4.066415000	-0.931645000
O	-5.672745000	14.792880000	3.455446000
C	-7.678285000	15.642004000	-7.394209000
O	-7.822365000	15.035065000	-8.449289000
O	-7.737009000	16.990675000	-7.306337000
C	-7.990746000	17.666125000	-8.545887000
H	-7.191689000	17.453704000	-9.286248000
H	-8.959321000	17.345452000	-8.982288000
H	-8.015273000	18.744246000	-8.303649000
O	-5.331731000	10.298296000	5.373416000
H	-7.475624000	8.635596000	-6.047479000
H	-5.900439000	4.329836000	1.400924000
H	-5.580253000	5.845211000	3.381024000
H	-5.426129000	8.149993000	4.323621000
Pd	-9.378132000	11.801440000	-1.293098000
I	-11.305950000	12.609734000	-2.874570000
C	-10.376658000	10.603548000	-0.117779000
O	-10.249193000	9.407055000	-0.273602000
C	-11.179494000	11.225639000	0.988852000
C	-11.423593000	12.613554000	1.073170000
C	-11.697660000	10.361592000	1.985064000
C	-12.172507000	13.131255000	2.141542000
C	-12.441523000	10.885044000	3.051214000
C	-12.679368000	12.270756000	3.132146000
H	-11.036531000	13.271174000	0.278371000
H	-11.507768000	9.280810000	1.898176000
H	-12.368646000	14.213621000	2.196619000
H	-12.844174000	10.209539000	3.822854000
H	-13.267806000	12.679913000	3.969102000

K_2CO_3

E_e^S= -1463.812686

O	-0.940006000	-1.132150000	0.000351000
O	-0.939022000	1.133006000	-0.000466000
O	1.035445000	-0.000308000	-0.002107000
C	-0.328177000	0.000099000	-0.000600000
K	1.072861000	-2.475246000	0.001682000
K	1.073137000	2.474464000	0.001585000

KHCO3

E_e^S = -864.4395587

O	-0.643503000	-1.194899000	0.024323000
O	-0.992858000	1.023429000	-0.002700000
O	1.130792000	0.207454000	0.016094000
C	-0.141186000	0.091598000	0.011887000
K	0.860069000	2.698428000	-0.012922000
H	0.158769000	-1.756283000	0.033705000

KI

E_e^S = -611.4062925

K	1.905397000	2.988848000	-0.299816000
I	1.905397000	2.988848000	-3.436169000

1

E_e^S= -456.3174961

C	-4.543985000	-3.628021000	2.474950000
C	-5.782230000	-3.625135000	3.155969000
C	-3.337478000	-3.773885000	3.229902000

C	-5.867890000	-3.813191000	4.539425000
C	-3.438420000	-3.962859000	4.632639000
C	-4.680534000	-3.991097000	5.275879000
H	-6.681726000	-3.473335000	2.539250000
H	-6.846651000	-3.819740000	5.042838000
H	-2.511990000	-4.077443000	5.220326000
H	-4.719664000	-4.140619000	6.366984000
C	-4.623028000	-3.458105000	0.977609000
O	-5.616875000	-2.993152000	0.420170000
N	-3.506439000	-3.850683000	0.247358000
H	-3.660508000	-3.889813000	-0.764194000
H	-2.875711000	-4.554771000	0.645506000
N	-2.073627000	-3.773595000	2.628904000
H	-1.295506000	-3.656994000	3.282870000
H	-1.983886000	-3.171872000	1.803012000

IM5
$\boldsymbol{E_e^S}$**=** -3337.948141

C	-6.665979000	14.240621000	-1.513754000
C	-6.861201000	13.788294000	-0.180451000
C	-7.179434000	12.448892000	0.202100000
N	-6.774403000	14.735328000	0.892830000
C	-6.668879000	14.408141000	2.244557000
N	-6.647677000	13.000026000	2.520027000
C	-6.893009000	12.067842000	1.519089000
N	-6.766621000	15.634019000	-1.836885000
C	-6.812431000	16.100613000	0.544832000
C	-6.500707000	12.587483000	3.849278000
N	-6.851188000	10.742874000	1.859297000
C	-6.548911000	10.285557000	3.162679000
N	-6.448436000	11.287958000	4.187981000
C	-6.830643000	16.518552000	-0.748218000
C	-6.797851000	16.100407000	-3.138539000
C	-6.750848000	15.227229000	-4.230811000
C	-6.606175000	13.816613000	-3.934327000
C	-6.580855000	12.901491000	-4.988034000
C	-6.660406000	13.313491000	-6.345344000
C	-6.434017000	13.350948000	-2.608658000
N	-6.106715000	12.050726000	-2.373748000
C	-6.365114000	11.164361000	-3.332403000
N	-6.532509000	11.539595000	-4.666448000
N	-7.661510000	11.471685000	-0.670095000
C	-7.077281000	10.232721000	-0.509827000
C	-6.727841000	9.361488000	-1.610942000
C	-6.567010000	9.786529000	-2.971835000
C	-6.775869000	9.785961000	0.802021000
C	-6.474919000	8.447745000	1.097410000
C	-6.397135000	7.536843000	0.021959000
C	-6.501074000	7.983588000	-1.304027000
C	-6.662442000	12.270968000	-7.317985000
N	-6.620978000	10.959538000	-6.995978000
C	-6.572966000	10.575729000	-5.720376000
N	-6.510107000	8.827943000	-4.012029000
C	-6.513573000	9.224954000	-5.326162000
C	-6.426242000	7.464433000	-3.693788000
C	-6.368287000	7.020924000	-2.379286000
N	-6.189928000	6.157817000	0.261533000
C	-6.127104000	5.317759000	-0.828829000
C	-6.057631000	5.748190000	1.603928000
N	-6.298200000	8.010179000	2.434989000
C	-6.309204000	8.967581000	3.440837000
C	-6.103261000	6.643506000	2.636361000
N	-6.209331000	5.677517000	-2.087192000
N	-6.801006000	15.657516000	-5.522003000
C	-6.752171000	14.778249000	-6.520187000
H	-6.703119000	12.524788000	-8.385905000
H	-6.371330000	6.768266000	-4.539601000
H	-6.888065000	17.586177000	-0.995399000
H	-6.858892000	17.188892000	-3.272073000
H	-6.837527000	16.794006000	1.394164000
H	-6.409369000	13.353603000	4.625343000
H	-5.991693000	4.250014000	-0.577762000
O	-6.585523000	15.229602000	3.150753000
C	-6.806611000	15.340163000	-7.915806000
O	-6.712513000	14.669348000	-8.937145000
O	-6.970353000	16.682996000	-7.928815000
C	-7.033948000	17.270895000	-9.235522000
H	-6.098874000	17.082737000	-9.802967000
H	-7.881127000	16.853826000	-9.818373000
H	-7.174805000	18.355066000	-9.073115000
O	-6.287505000	10.883200000	5.386773000
H	-6.467722000	8.445622000	-6.095057000
H	-5.908515000	4.675095000	1.775752000
H	-5.986664000	6.317465000	3.677857000
H	-6.103913000	8.675527000	4.477851000
Pd	-9.334777000	11.796459000	-1.864414000
C	-10.400126000	10.577794000	-0.748114000
O	-10.168923000	9.383638000	-0.780441000
C	-11.495285000	11.175141000	0.095217000
C	-11.644604000	12.569596000	0.254921000
C	-12.387674000	10.297905000	0.756548000
C	-12.671299000	13.083222000	1.063997000
C	-13.419100000	10.814084000	1.553817000
C	-13.562251000	12.206301000	1.710360000
H	-10.931997000	13.235367000	-0.262330000
H	-12.254311000	9.213142000	0.624006000
H	-12.777695000	14.172184000	1.192923000
H	-14.118458000	10.128349000	2.058288000
H	-14.371679000	12.608969000	2.340202000
N	-10.693902000	12.355239000	-3.219553000
H	-11.151769000	13.259540000	-3.043586000
C	-11.385679000	11.608885000	-4.145773000
C	-12.577930000	12.075943000	-4.815743000
C	-10.882355000	10.326217000	-4.533629000
C	-13.121552000	11.320251000	-5.878756000
C	-11.474119000	9.578835000	-5.550692000
C	-12.595383000	10.078417000	-6.250655000
H	-9.992770000	9.951969000	-4.000587000
H	-13.997209000	11.744799000	-6.394609000
H	-11.051075000	8.595819000	-5.815399000
H	-13.051411000	9.499949000	-7.068724000
C	-13.306555000	13.351426000	-4.492827000
O	-13.961319000	13.977713000	-5.326292000
N	-13.216659000	13.805957000	-3.173341000
H	-13.099148000	13.111320000	-2.427859000
H	-13.870654000	14.566148000	-2.962495000

TS3
$\boldsymbol{E_e^S}$ **=** -3337.937219

C	0.598138000	-1.157755000	2.762867000

C	-0.644319000	-0.503845000	2.985297000
C	-1.574110000	-0.125946000	1.969130000
N	-1.012021000	-0.148149000	4.325231000
C	-2.290300000	0.230929000	4.732264000
N	-3.270772000	0.248276000	3.684661000
C	-2.906158000	0.068867000	2.355923000
N	1.634953000	-1.107075000	3.753250000
C	0.008748000	-0.176890000	5.296397000
C	-4.589809000	0.575572000	4.017821000
N	-3.900180000	0.101904000	1.415043000
C	-5.266742000	0.273362000	1.733084000
N	-5.572062000	0.592902000	3.100092000
C	1.265032000	-0.610672000	5.013477000
C	2.932592000	-1.507073000	3.498087000
C	3.319049000	-1.974194000	2.237678000
C	2.279386000	-2.083098000	1.233003000
C	2.623238000	-2.513626000	-0.050443000
C	3.953817000	-2.882131000	-0.391269000
C	0.922532000	-1.818909000	1.535643000
N	-0.053067000	-2.107210000	0.630264000
C	0.314868000	-2.200387000	-0.649183000
N	1.620167000	-2.514992000	-1.025151000
N	-1.264217000	-0.042112000	0.610942000
C	-2.226038000	-0.566843000	-0.220004000
C	-1.920270000	-1.317930000	-1.417574000
C	-0.652481000	-1.930968000	-1.685163000
C	-3.594798000	-0.392575000	0.110018000
C	-4.631316000	-0.614539000	-0.809042000
C	-4.288319000	-1.107545000	-2.086434000
C	-2.964215000	-1.467457000	-2.381240000
C	4.170956000	-3.261226000	-1.746723000
N	3.197192000	-3.244915000	-2.683721000
C	1.959021000	-2.866963000	-2.366594000
N	-0.354233000	-2.386068000	-2.986161000
C	0.904887000	-2.831765000	-3.299684000
C	-1.358256000	-2.399801000	-3.967498000
C	-2.660196000	-2.007320000	-3.689728000
N	-5.274611000	-1.264688000	-3.087595000
C	-4.874744000	-1.745797000	-4.314799000
C	-6.599956000	-0.922863000	-2.746377000
N	-5.979903000	-0.313381000	-0.485124000
C	-6.262590000	0.099096000	0.810767000
C	-6.926840000	-0.475804000	-1.496043000
N	-3.657077000	-2.104159000	-4.645673000
N	4.595741000	-2.353264000	1.953551000
C	4.907395000	-2.786891000	0.734437000
H	5.171964000	-3.578770000	-2.068712000
H	-1.066137000	-2.772348000	-4.956619000
H	2.053145000	-0.594630000	5.776946000
H	3.644300000	-1.440844000	4.332040000
H	-0.285344000	0.188712000	6.287633000
H	-4.821032000	0.803378000	5.062844000
H	-5.684909000	-1.824167000	-5.062485000
O	-2.592966000	0.521311000	5.884694000
C	6.338699000	-3.191069000	0.509371000
O	6.775621000	-3.646209000	-0.541691000
O	7.111501000	-3.001307000	1.605160000
C	8.486988000	-3.371334000	1.443944000
H	8.584047000	-4.448467000	1.194235000
H	8.964955000	-2.785672000	0.631312000
H	8.974482000	-3.155196000	2.412217000
O	-6.787613000	0.859735000	3.381682000
H	1.088101000	-3.164032000	-4.327326000
H	-7.354486000	-1.042053000	-3.533555000
H	-7.962941000	-0.223849000	-1.235690000
H	-7.301466000	0.272855000	1.116295000
Pd	0.407634000	0.941210000	-0.129466000
C	0.099256000	2.145817000	-1.782628000
O	-0.017785000	1.547878000	-2.843096000
C	-0.493804000	3.505683000	-1.531470000
C	-0.878851000	3.955492000	-0.252651000
C	-0.710754000	4.339942000	-2.653024000
C	-1.460284000	5.224674000	-0.091722000
C	-1.280054000	5.611018000	-2.488613000
C	-1.655896000	6.057489000	-1.207130000
H	-0.736188000	3.279168000	0.606536000
H	-0.426549000	3.967087000	-3.649247000
H	-1.764257000	5.565056000	0.911196000
H	-1.438417000	6.258183000	-3.366496000
H	-2.107539000	7.054535000	-1.079802000
N	1.853014000	2.041235000	-1.087815000
H	2.329752000	1.636623000	-1.917874000
C	2.579356000	3.115129000	-0.591077000
C	3.637017000	3.728209000	-1.354897000
C	2.301100000	3.643003000	0.699819000
C	4.370493000	4.793003000	-0.780213000
C	3.022881000	4.716435000	1.227003000
C	4.074434000	5.299532000	0.491212000
H	1.516242000	3.141107000	1.287697000
H	5.225090000	5.213085000	-1.335086000
H	2.782198000	5.088632000	2.236123000
H	4.669519000	6.123088000	0.914783000
C	3.975621000	3.212148000	-2.720521000
O	3.653434000	2.080099000	-3.119805000
N	4.699095000	4.053602000	-3.537189000
H	4.723328000	5.058862000	-3.369074000
H	4.849032000	3.726375000	-4.493458000

IM6

$\boldsymbol{E_e^S}$ = -800.7037131

H	4.771554000	17.366661000	-1.087199000
C	5.024397000	17.668145000	-0.059063000
C	5.418409000	18.975481000	0.249127000
C	5.748201000	19.302540000	1.576615000
C	5.692803000	18.319953000	2.573944000
C	5.271566000	17.004507000	2.273488000
C	4.920498000	16.668534000	0.934050000
C	4.427791000	15.319266000	0.425853000
N	4.014174000	14.407086000	1.364128000
N	5.263750000	16.015432000	3.306406000
H	5.476969000	19.737155000	-0.543862000
H	6.075362000	20.321733000	1.836609000
H	5.994885000	18.561743000	3.603805000
H	3.923025000	14.660846000	2.350364000
O	4.388694000	15.074404000	-0.780601000
H	5.873162000	15.203267000	3.140172000
C	5.038950000	16.185724000	4.682051000
O	5.604045000	15.447444000	5.486816000
C	4.029521000	17.212523000	5.123055000
C	4.136766000	17.692473000	6.447476000
C	2.941242000	17.628252000	4.322931000
C	3.193013000	18.598670000	6.952480000

C	1.987210000	18.520837000	4.837460000
C	2.116116000	19.015105000	6.147952000
H	4.970520000	17.330064000	7.068141000
H	2.826330000	17.242262000	3.298798000
H	3.291235000	18.976494000	7.982518000
H	1.135949000	18.830900000	4.211064000
H	1.370021000	19.721204000	6.546120000
H	3.588364000	13.546914000	1.013753000

IM7

E_e^S = -800.7024896

H	4.156789000	16.698264000	-1.285716000
C	4.413655000	17.323434000	-0.416301000
C	4.207295000	18.707742000	-0.411187000
C	4.574101000	19.453492000	0.729580000
C	5.132658000	18.828427000	1.851496000
C	5.334360000	17.427096000	1.854913000
C	4.972521000	16.674648000	0.702778000
C	5.238780000	15.213265000	0.659347000
N	5.795498000	14.707338000	1.837136000
C	5.706073000	15.361768000	3.132234000
N	5.922859000	16.777740000	2.934500000
H	3.767901000	19.210867000	-1.285948000
H	4.417503000	20.544172000	0.746703000
H	5.412262000	19.420744000	2.738025000
H	5.967670000	13.697626000	1.831350000
C	6.784182000	14.798214000	4.079539000
C	6.486492000	14.553588000	5.434484000
C	8.094755000	14.571847000	3.607232000
C	7.482697000	14.074287000	6.304456000
C	9.086880000	14.090328000	4.476072000
C	8.782773000	13.839146000	5.827137000
H	5.465703000	14.744480000	5.798532000
H	8.330463000	14.779873000	2.551934000
H	7.238847000	13.884022000	7.361837000
H	10.105917000	13.912500000	4.097171000
H	9.562230000	13.461375000	6.507824000
O	5.052911000	14.492101000	-0.320406000
O	4.394023000	15.224413000	3.706458000
H	4.187533000	14.268860000	3.751642000
H	6.003145000	17.309030000	3.803820000

3b

E_e^S = -724.2672156

H	5.028089000	16.734073000	-1.232297000
C	5.028089000	17.245440000	-0.257114000
C	5.028089000	18.638908000	-0.153145000
C	5.028089000	19.250896000	1.123478000
C	5.028089000	18.476352000	2.285863000
C	5.028089000	17.058936000	2.204509000
C	5.028089000	16.449728000	0.910184000
C	5.028089000	14.977370000	0.801778000
N	5.028089000	14.352808000	2.070743000
C	5.028089000	15.021718000	3.283341000
N	5.028089000	16.322144000	3.384978000
H	5.028089000	19.261557000	-1.061493000
H	5.028089000	20.350029000	1.201494000
H	5.028089000	18.932174000	3.287523000
H	5.028089000	13.326762000	2.059023000
C	5.028089000	14.153648000	4.508240000
C	3.808812000	13.740938000	5.086958000
C	6.247366000	13.740939000	5.086958000
C	3.811097000	12.926943000	6.232218000
C	6.245080000	12.926943000	6.232218000
C	5.028089000	12.518084000	6.805392000
H	2.856207000	14.069767000	4.642096000
H	7.199970000	14.069767000	4.642096000
H	2.855465000	12.613189000	6.681310000
H	7.200712000	12.613189000	6.681310000
H	5.028089000	11.880799000	7.703864000
O	5.028089000	14.311360000	-0.229611000

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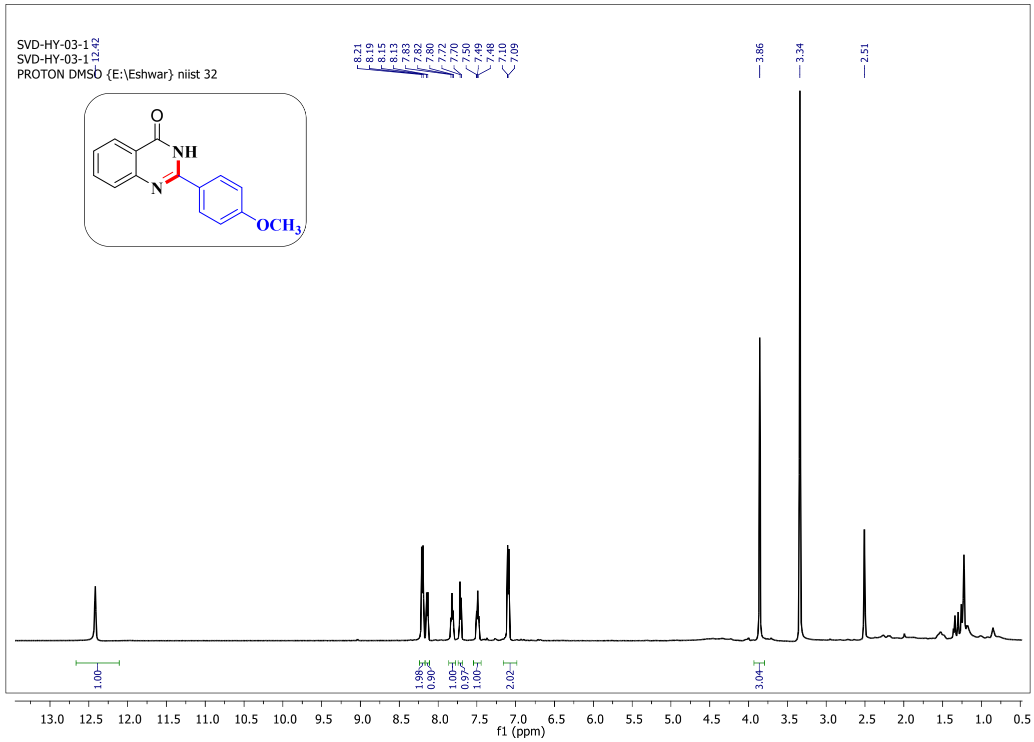
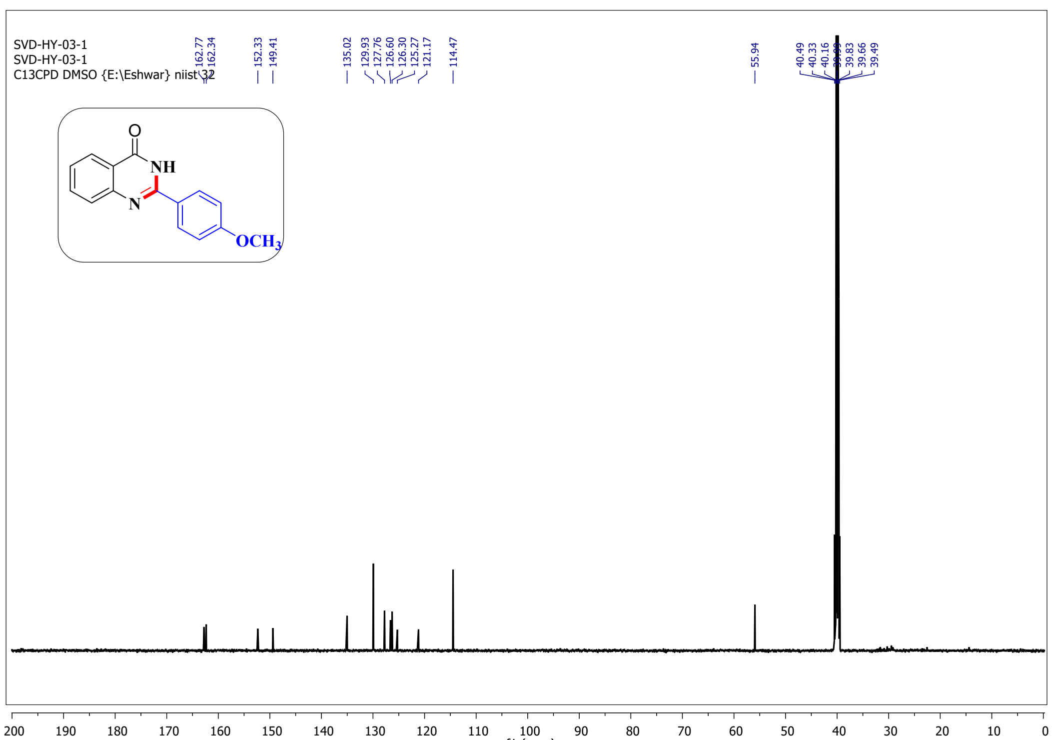
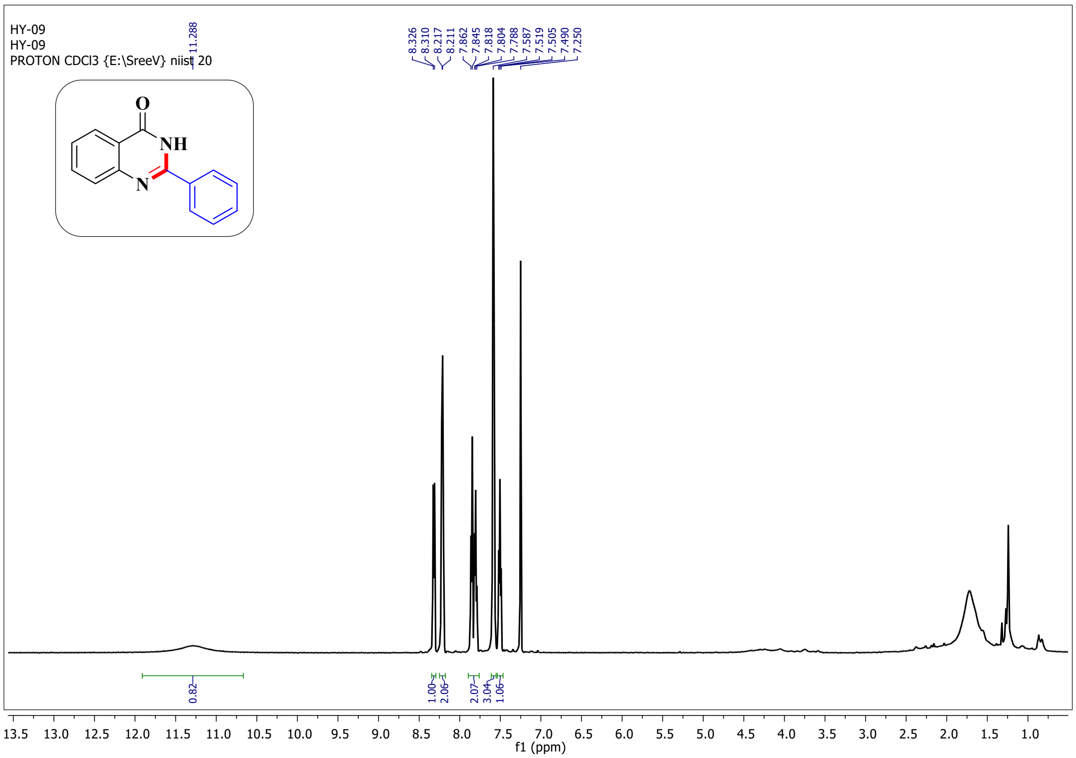
Appendix I: **Spectral copies of ^{1}H and ^{13}C NMR of compounds obtained in this study**

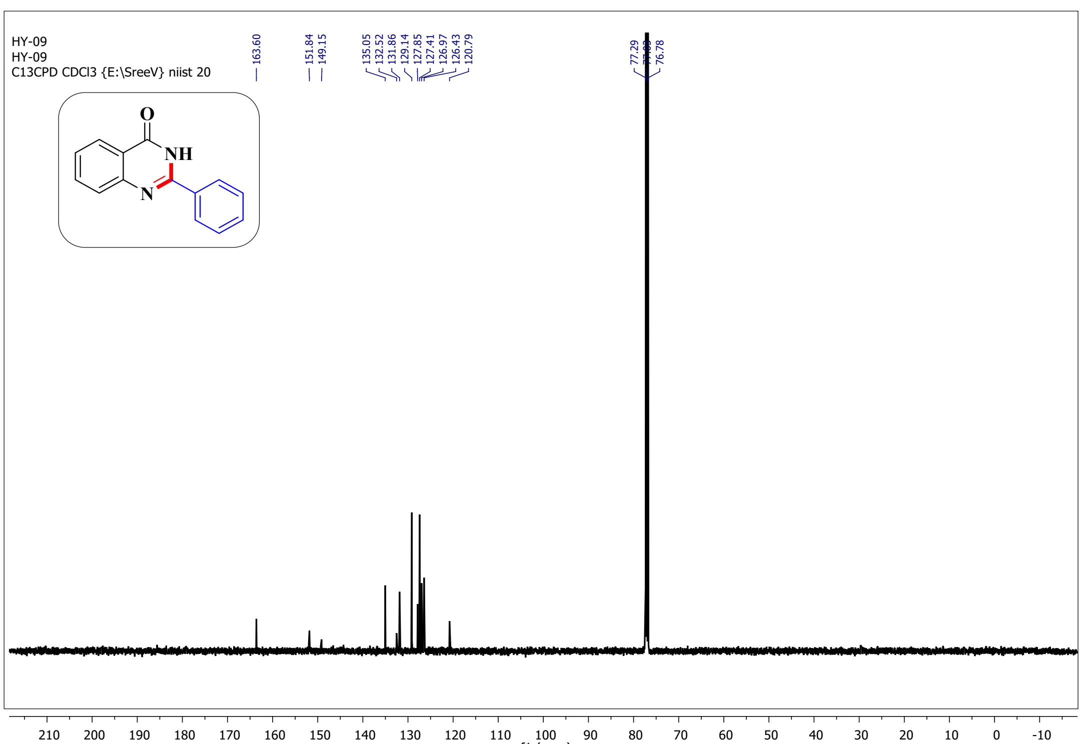
2-(4-methoxyphenyl) quinazolin-4(3*H*)-one (3a)



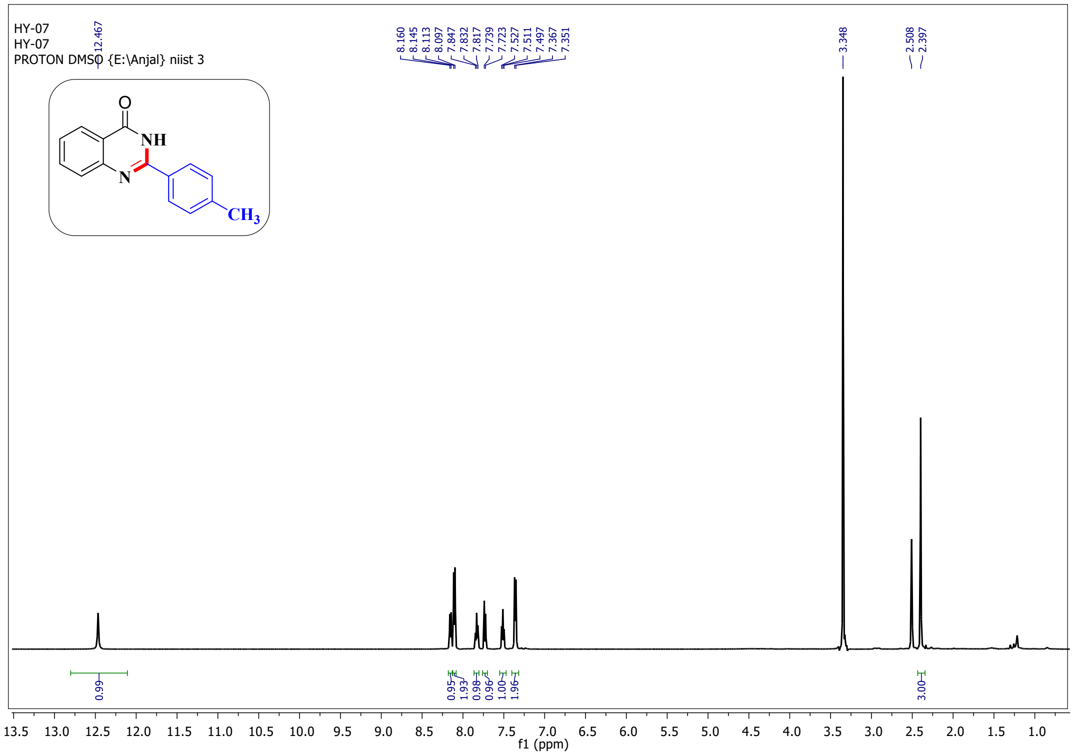


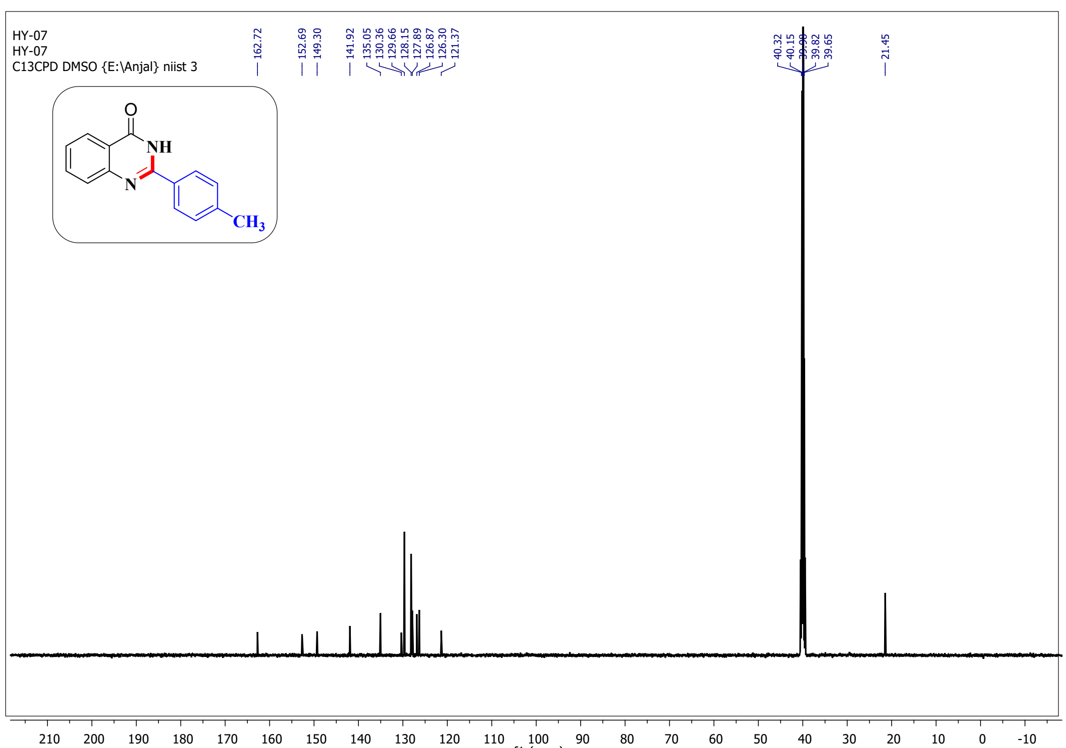
2-phenylquinazolin-4(3*H*)-one (3b)



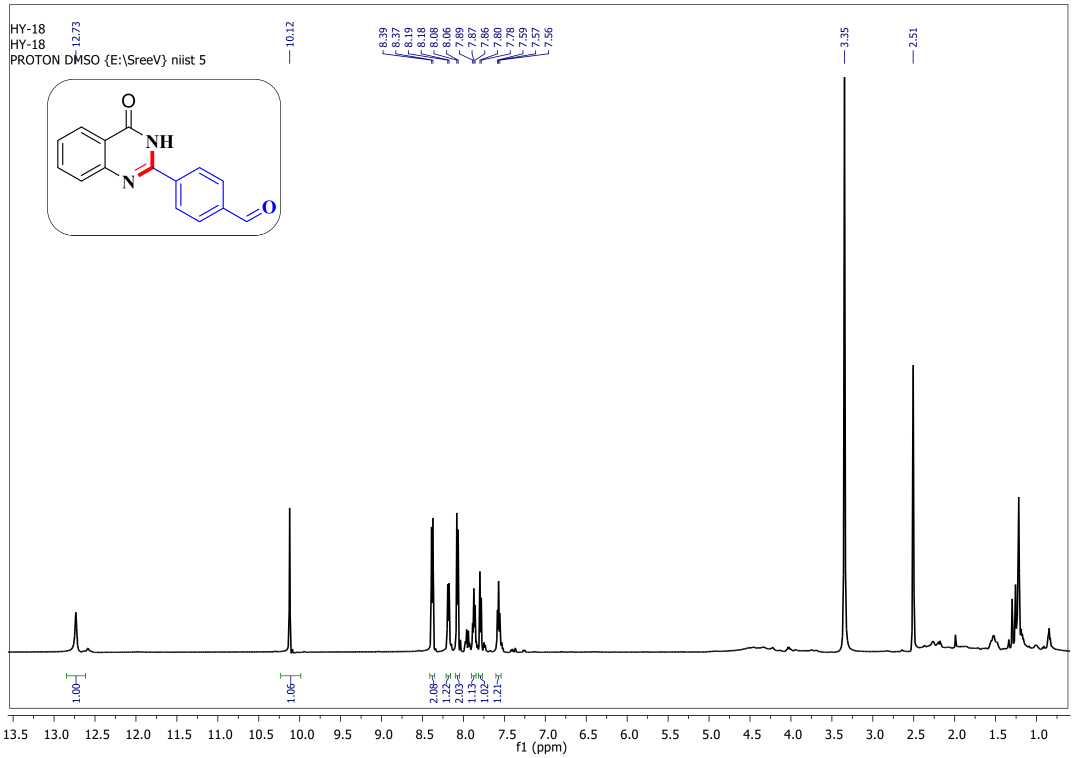


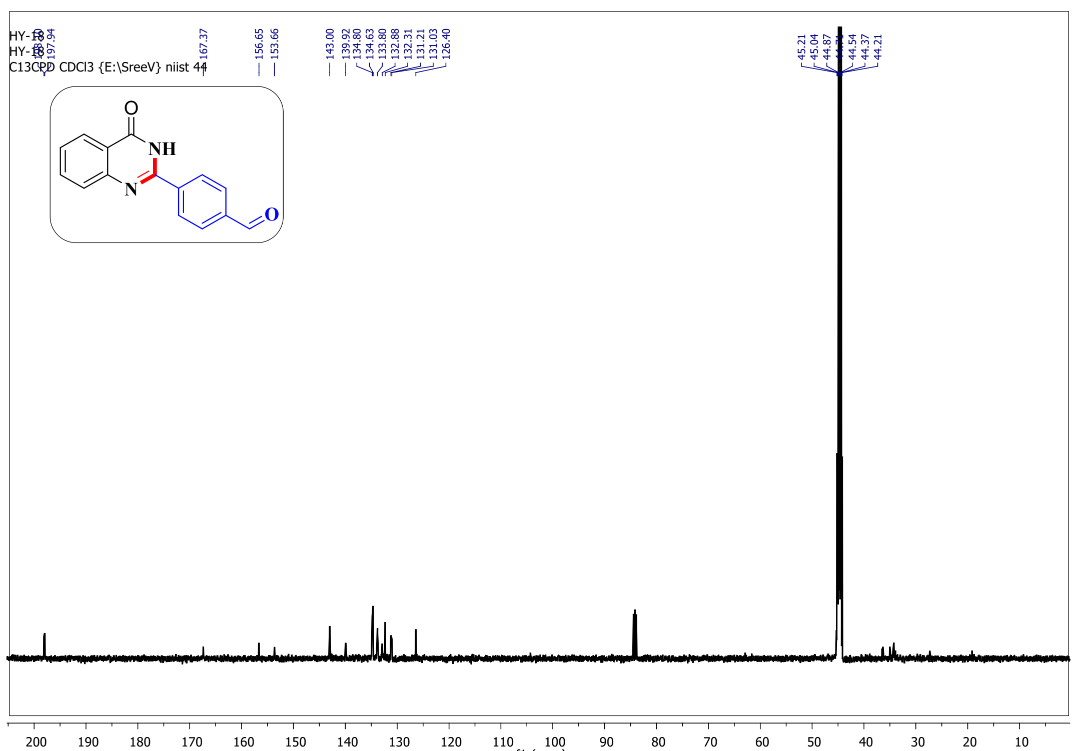
2-(p-tolyl) quinazolin-4(3*H*)-one (3c)



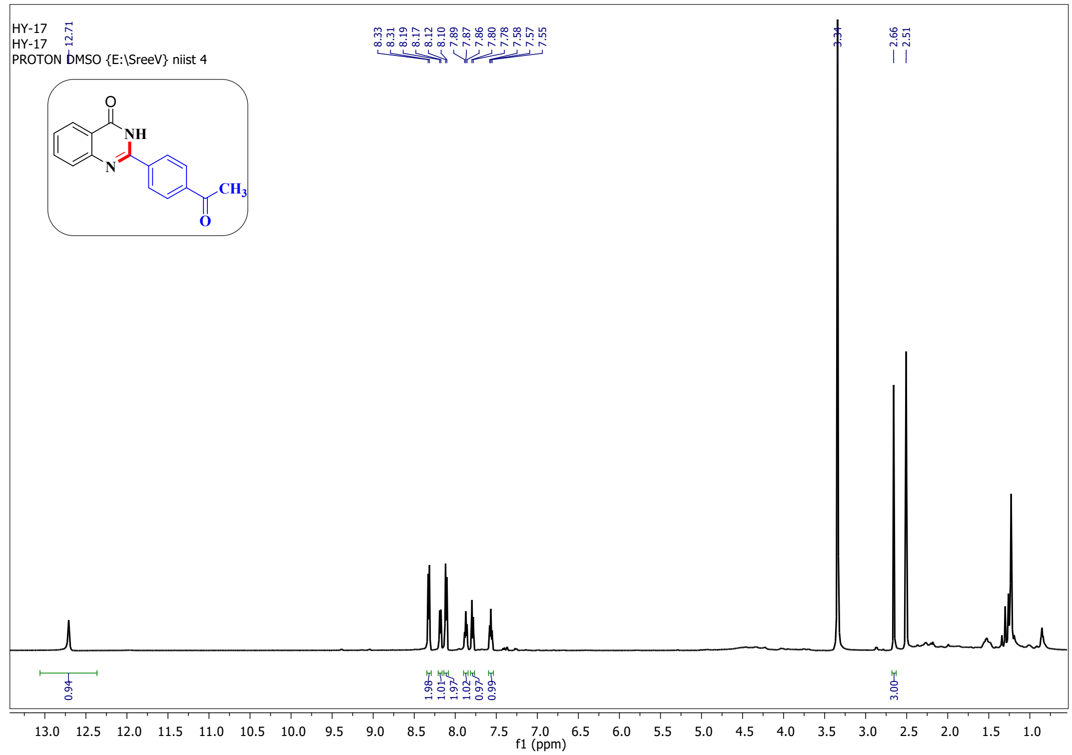


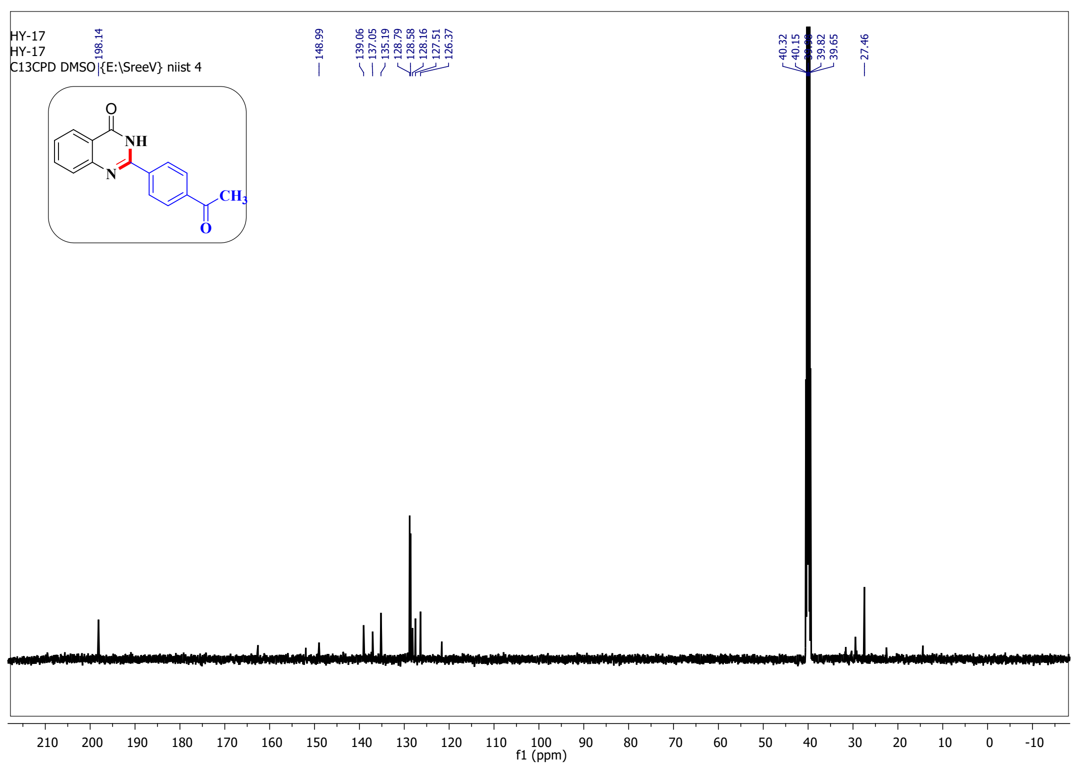
4-(4-Oxo-3,4-dihydroquinazolin-2-yl) benzaldehyde (3d)



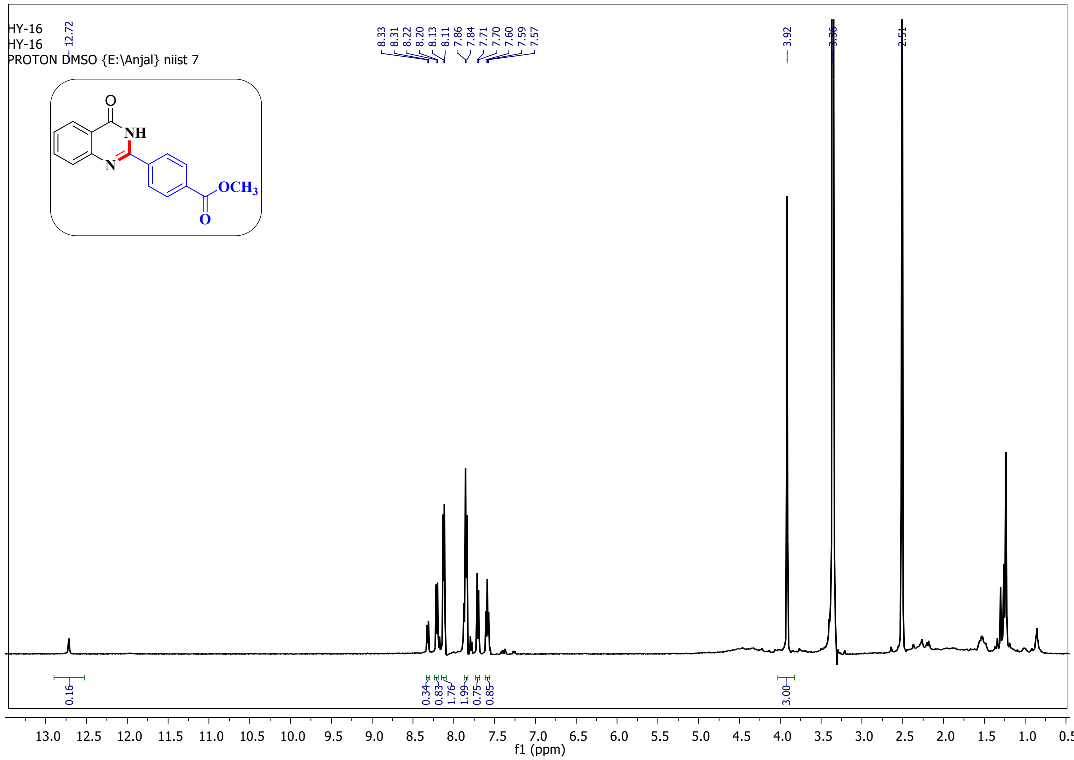


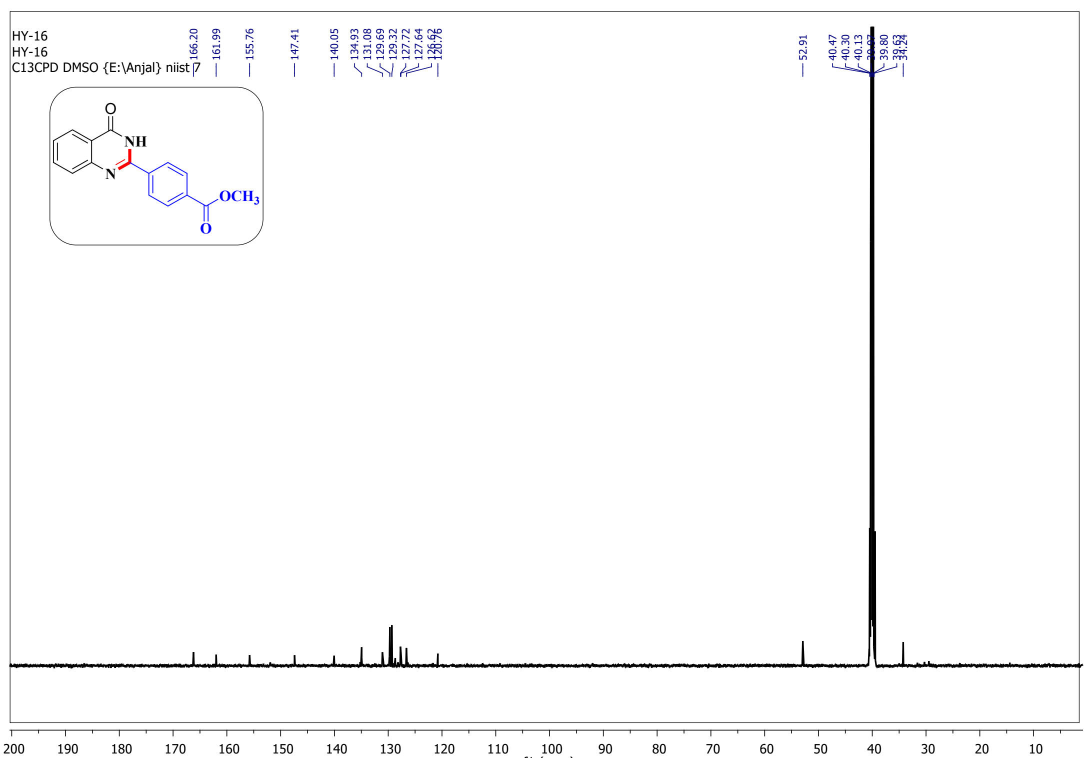
2-(4-Acetylphenyl) quinazolin-4(3*H*)-one (3e)



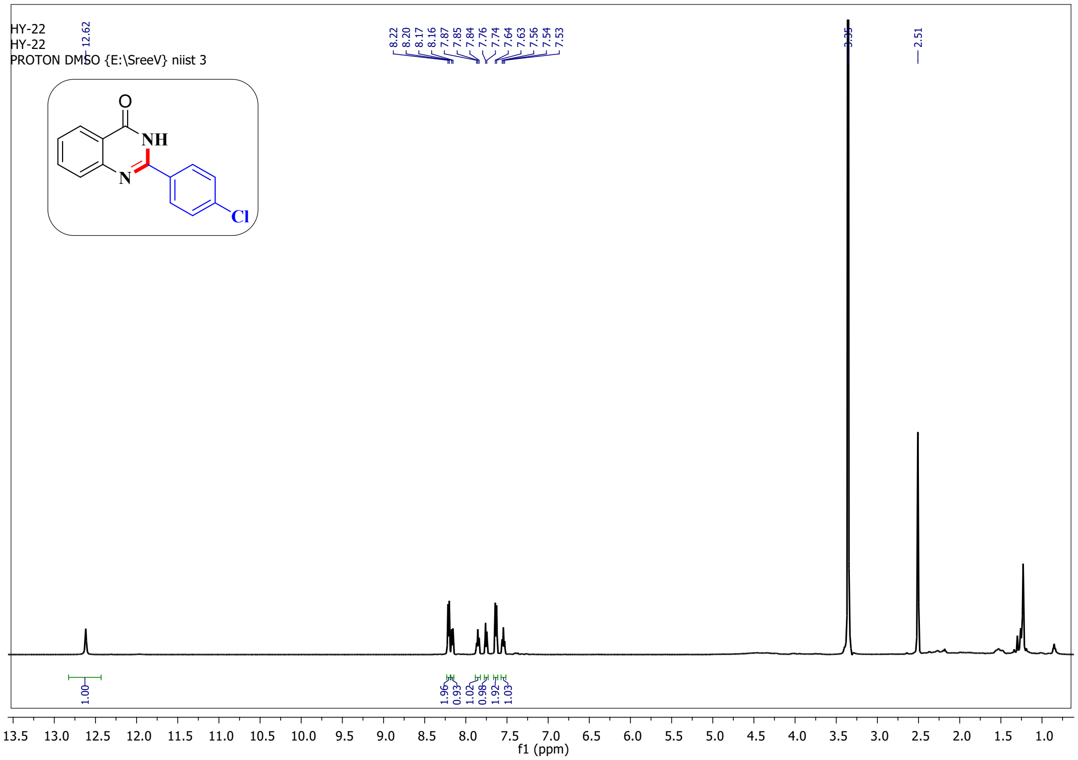


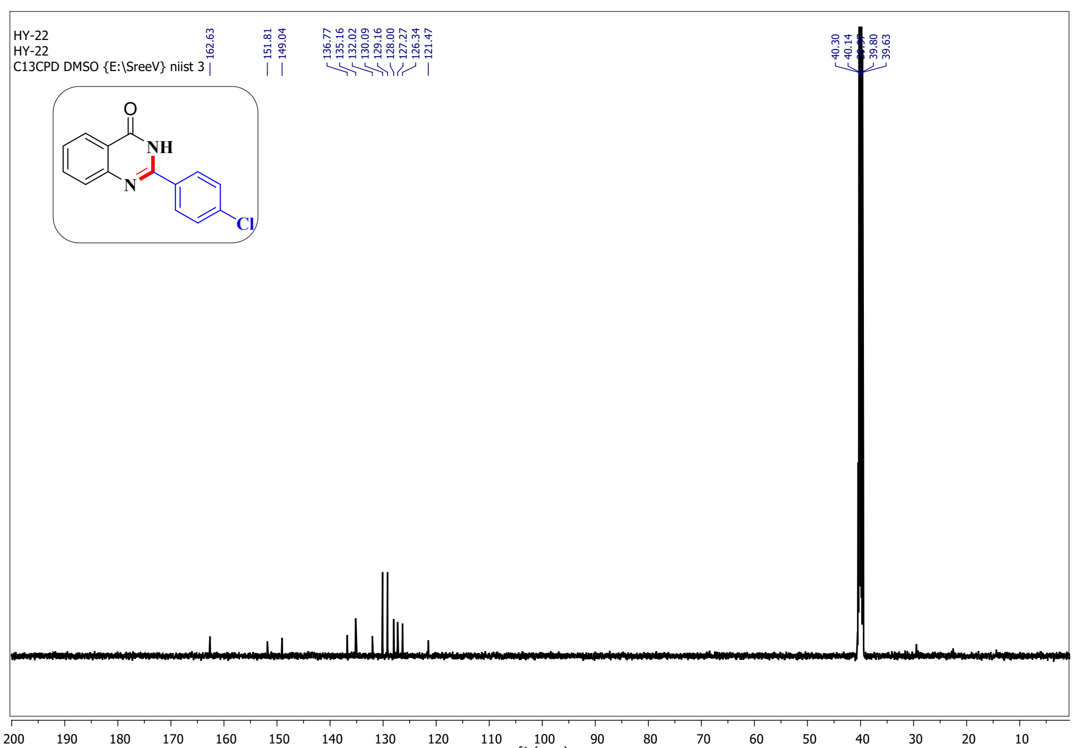
Methyl 4-(4-oxo-3,4-dihydroquinazolin-2-yl) benzoate (3f)



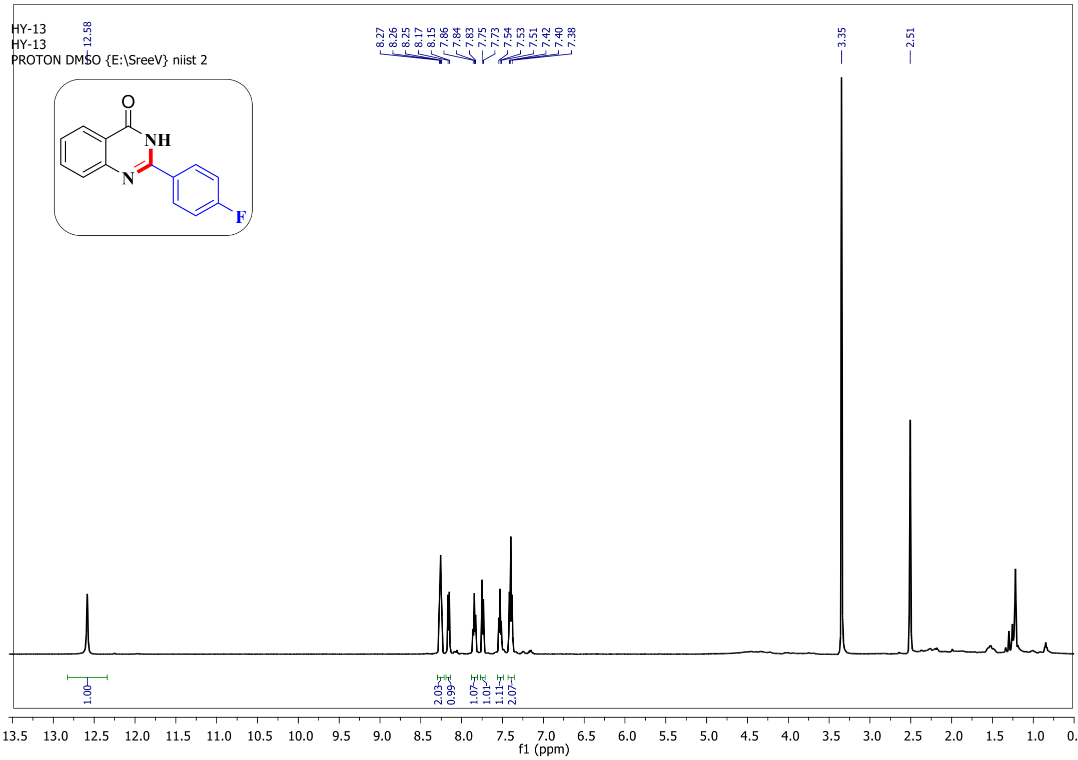


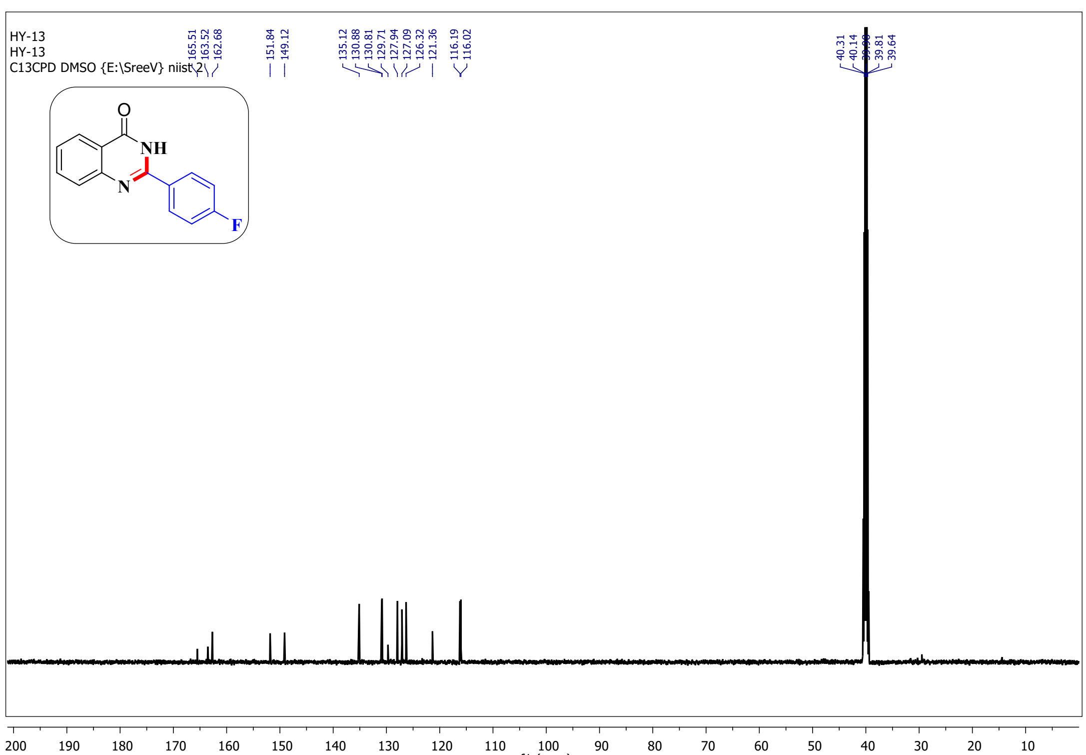
2-(4-Chlorophenyl) quinazolin-4(3*H*)-one (3g)



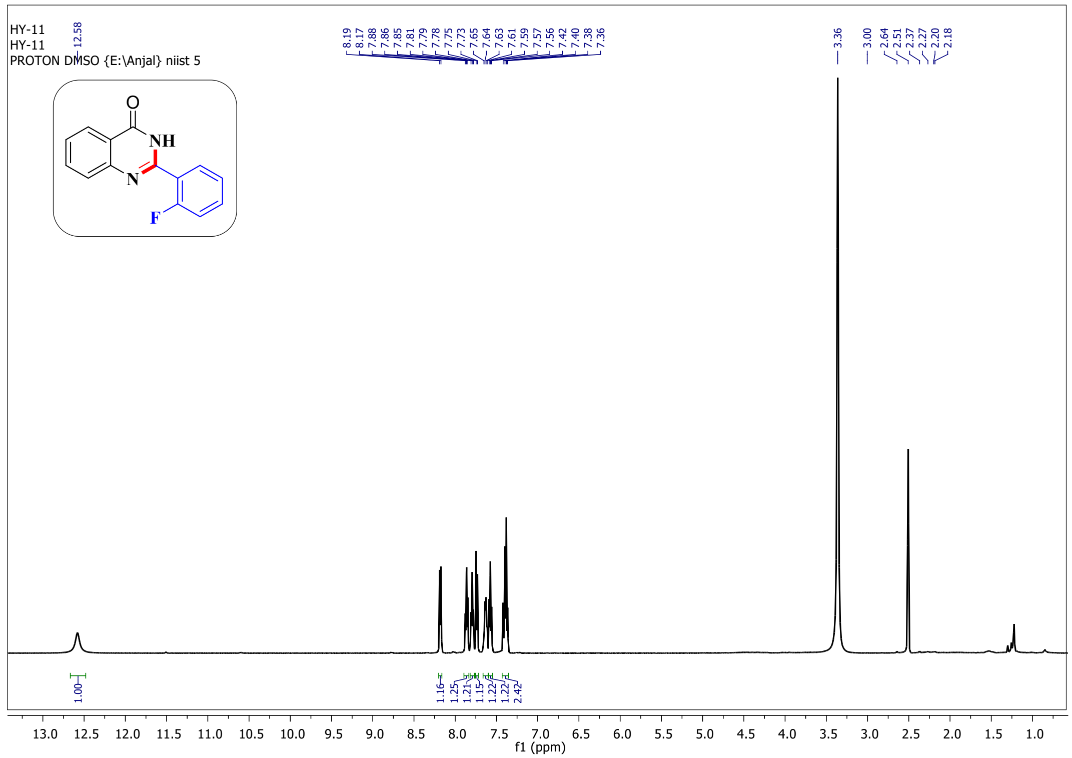


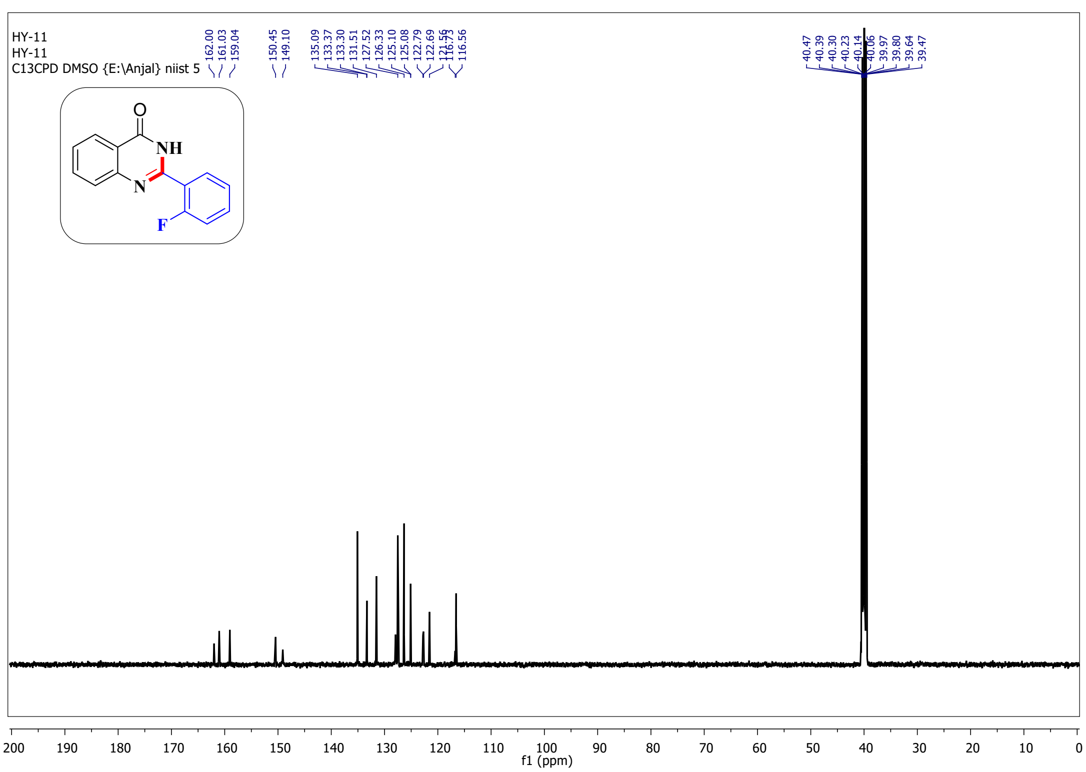
2-(4-fluorophenyl) quinazolin-4(3*H*)-one (3h)



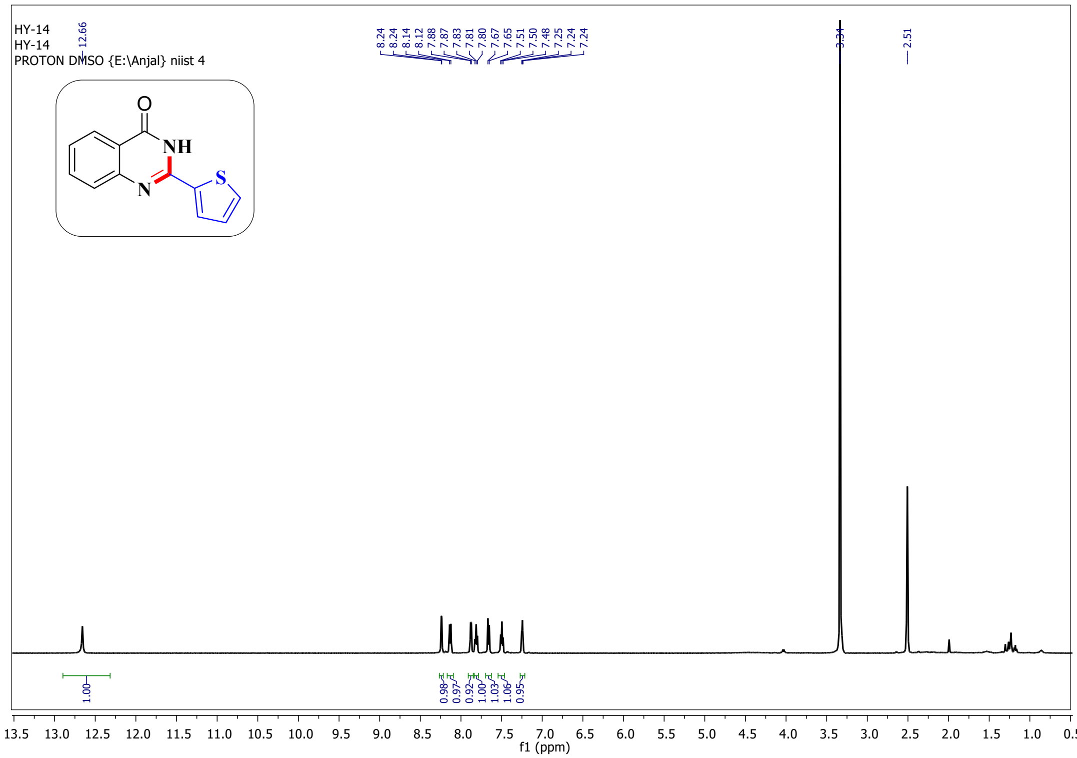


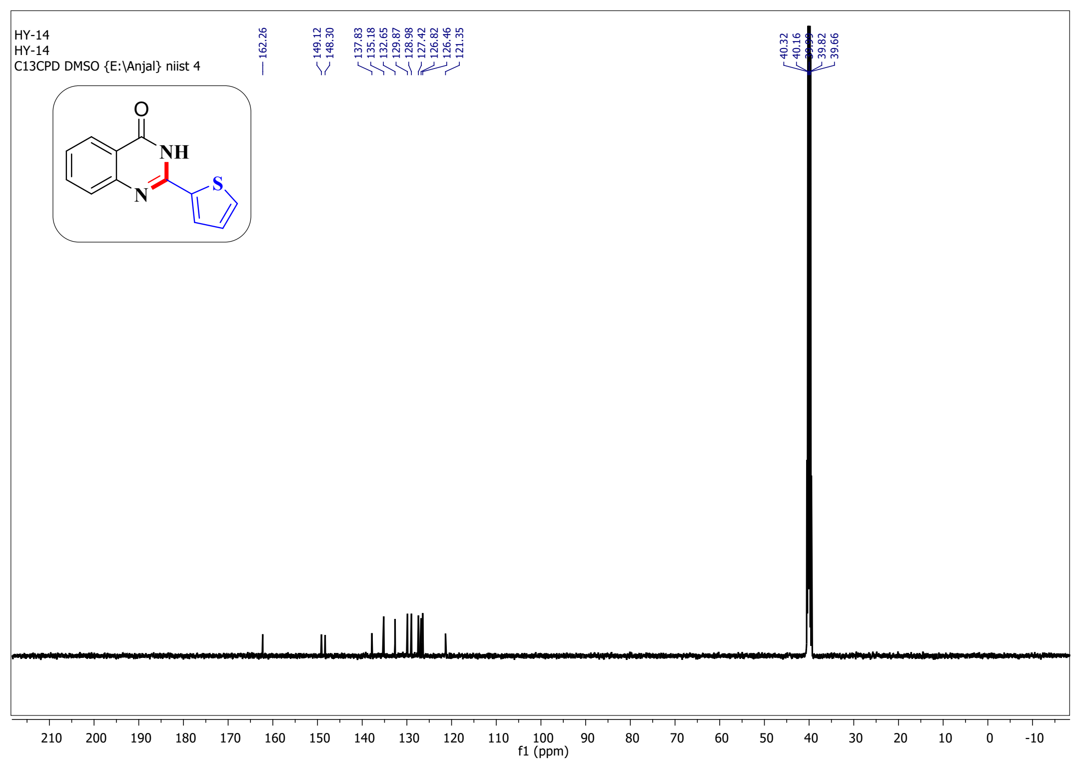
2-(2-fluorophenyl) quinazolin-4(3*H*)-one (3i)



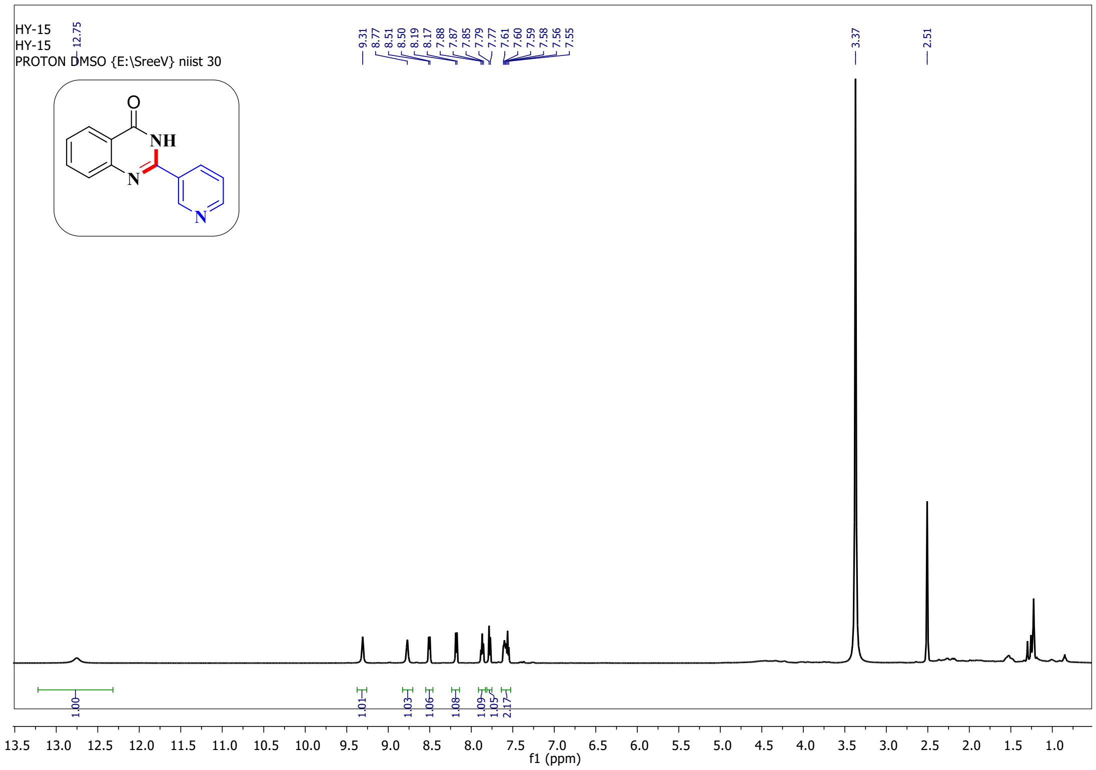


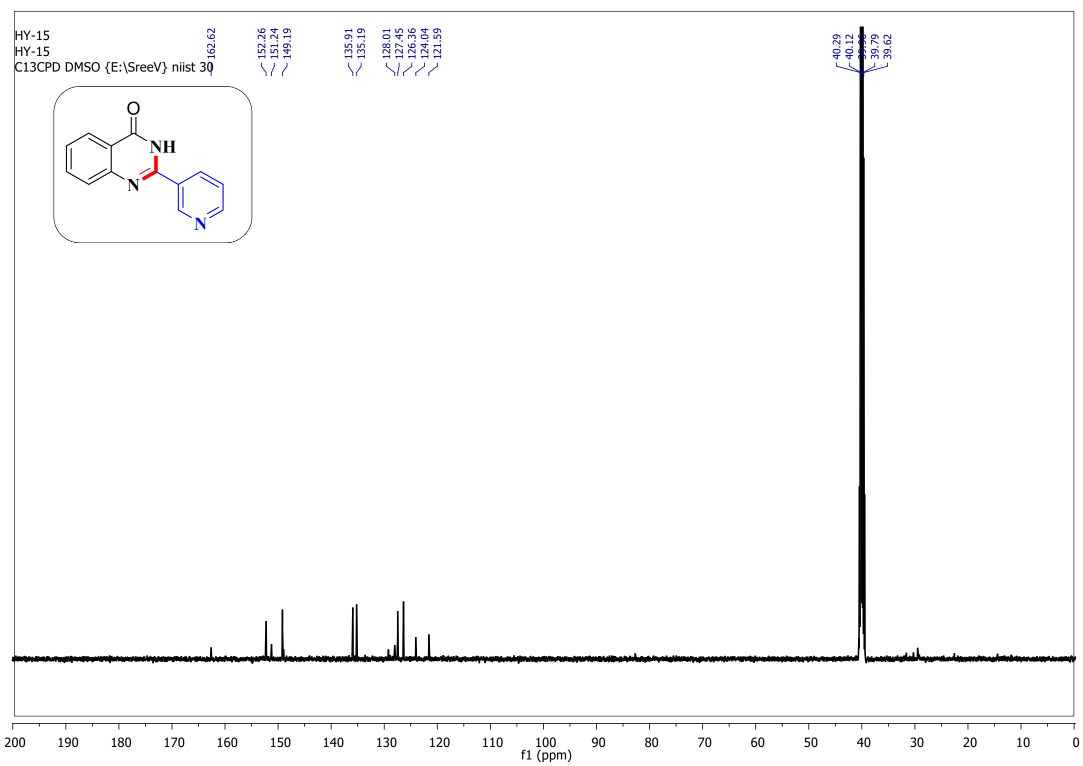
2-(thiophen-2-yl) quinazolin-4(3*H*)-one (3j)





2-(pyridin-3-yl) quinazolin-4(3*H*)-one (3k)





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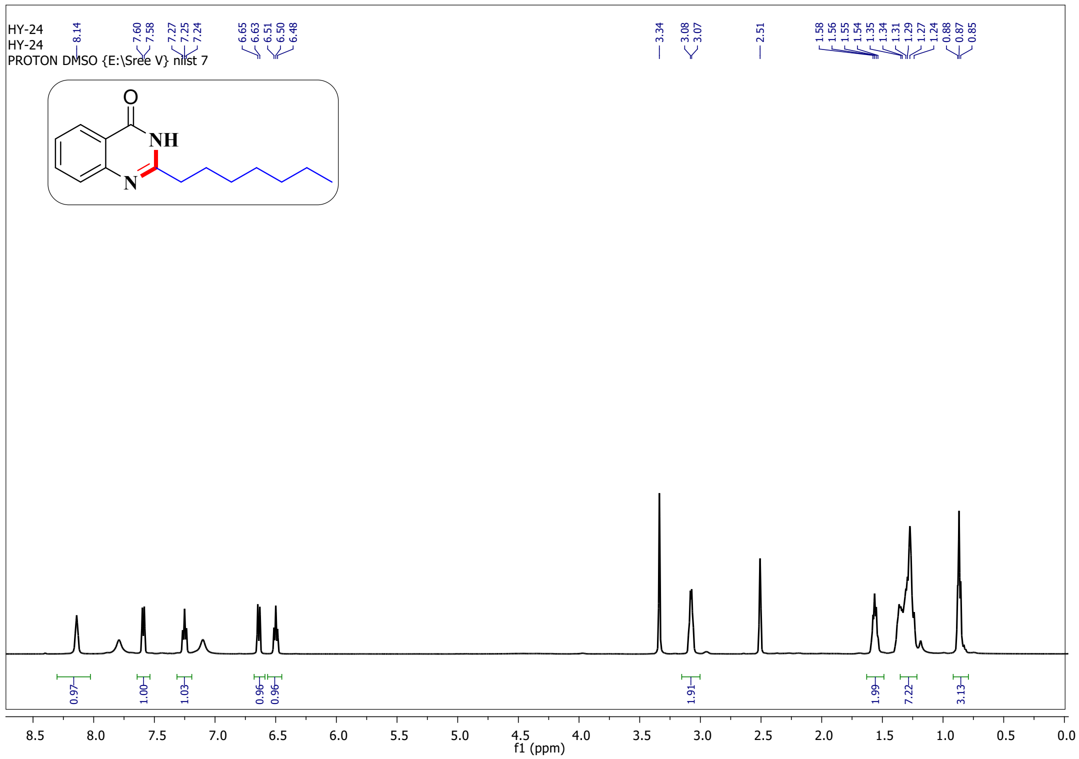
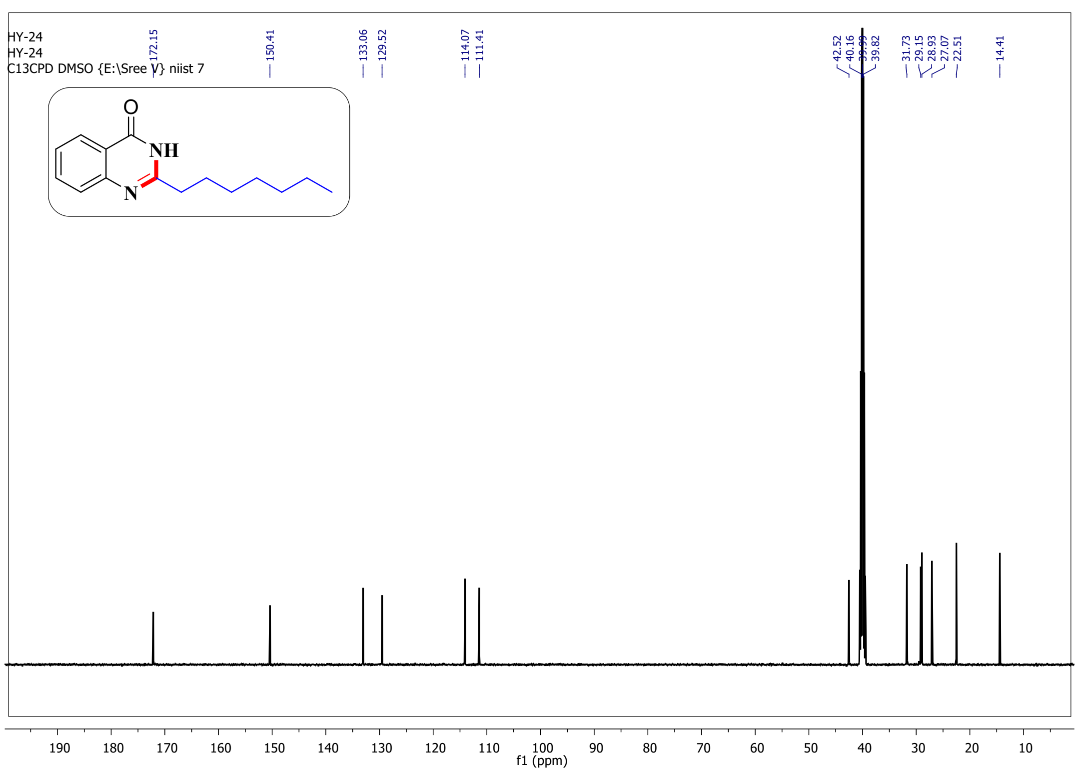
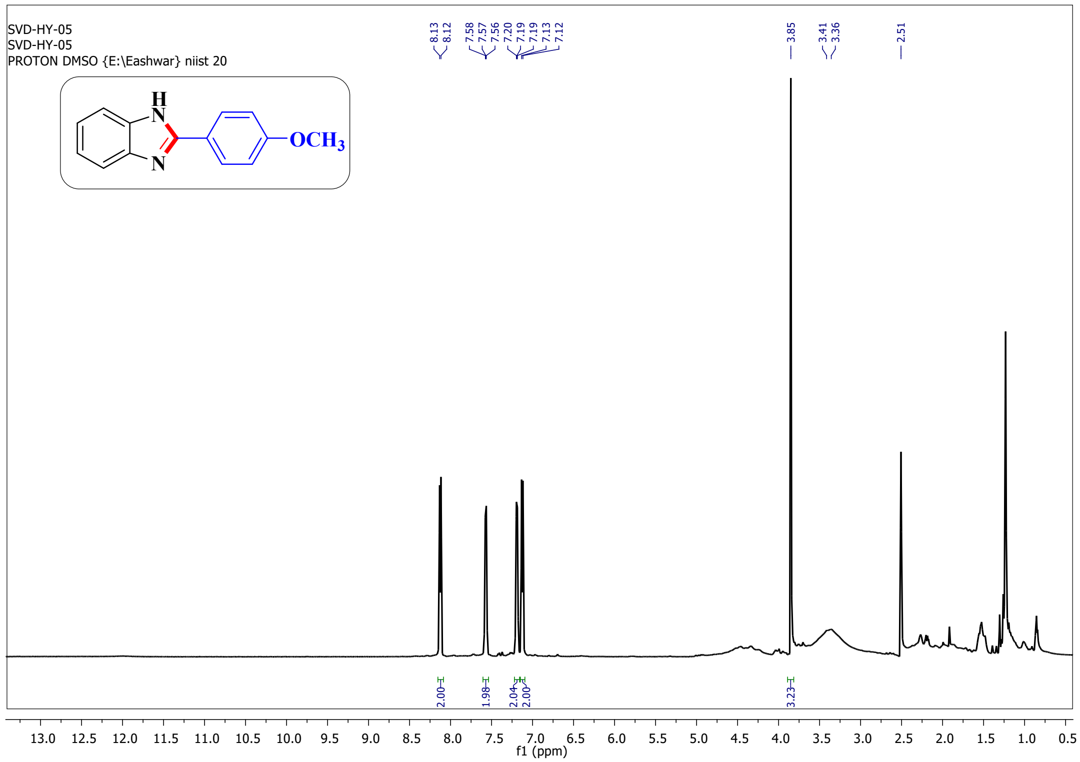
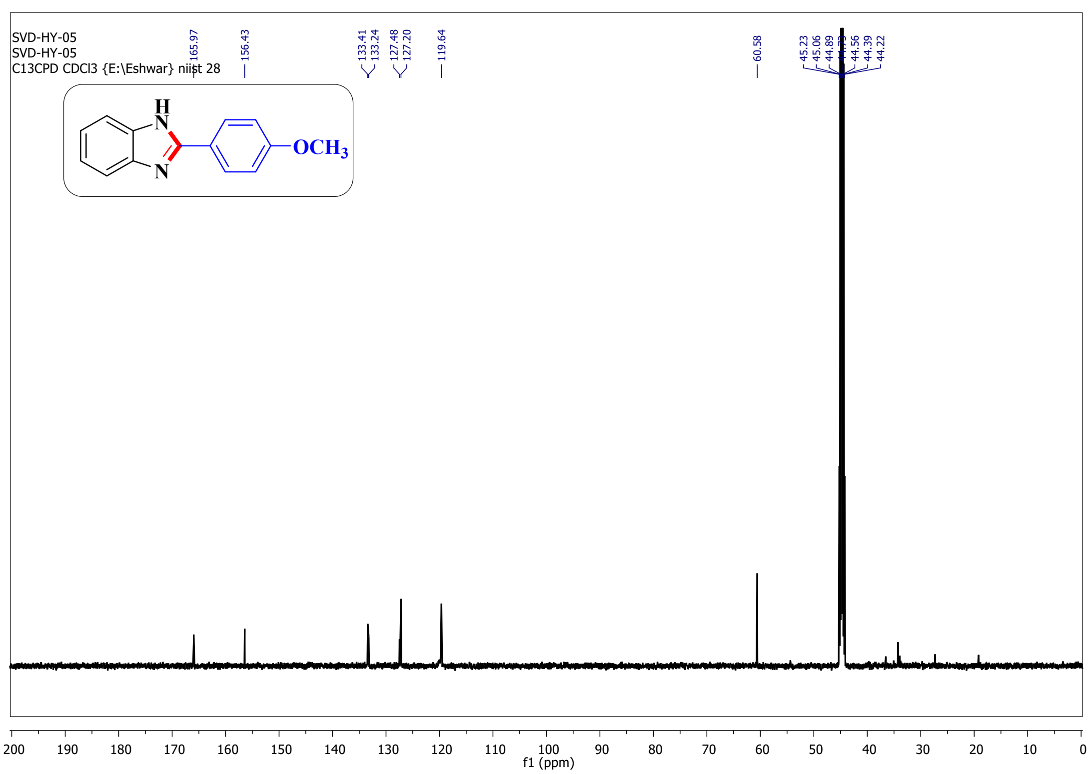


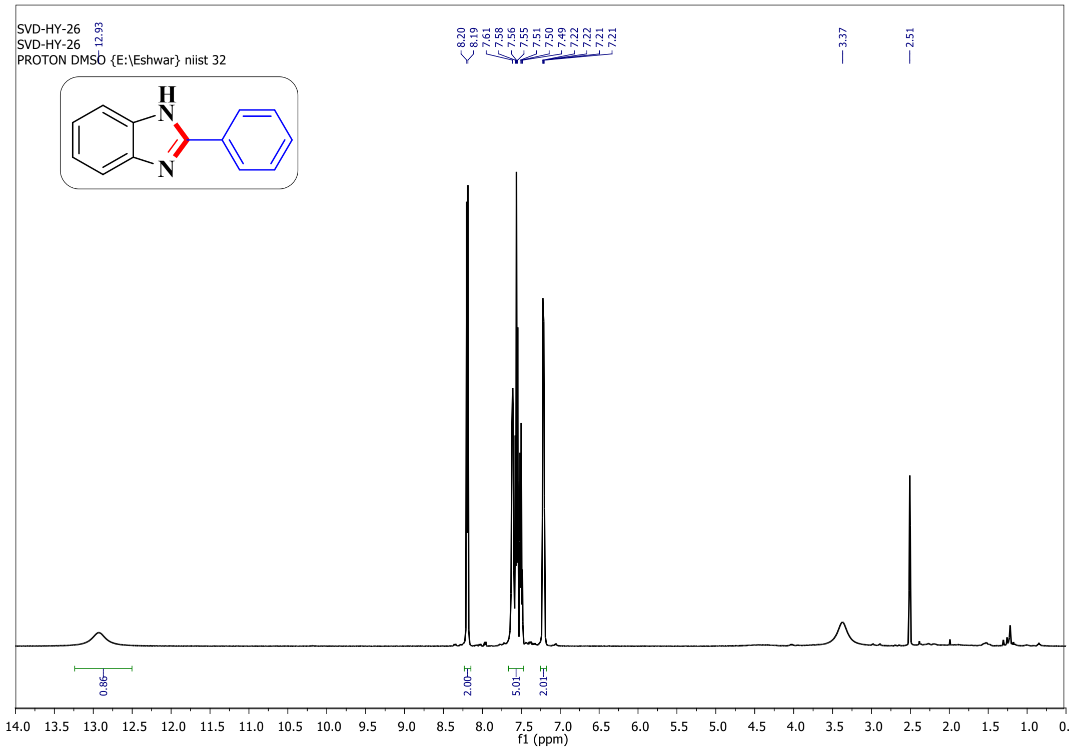


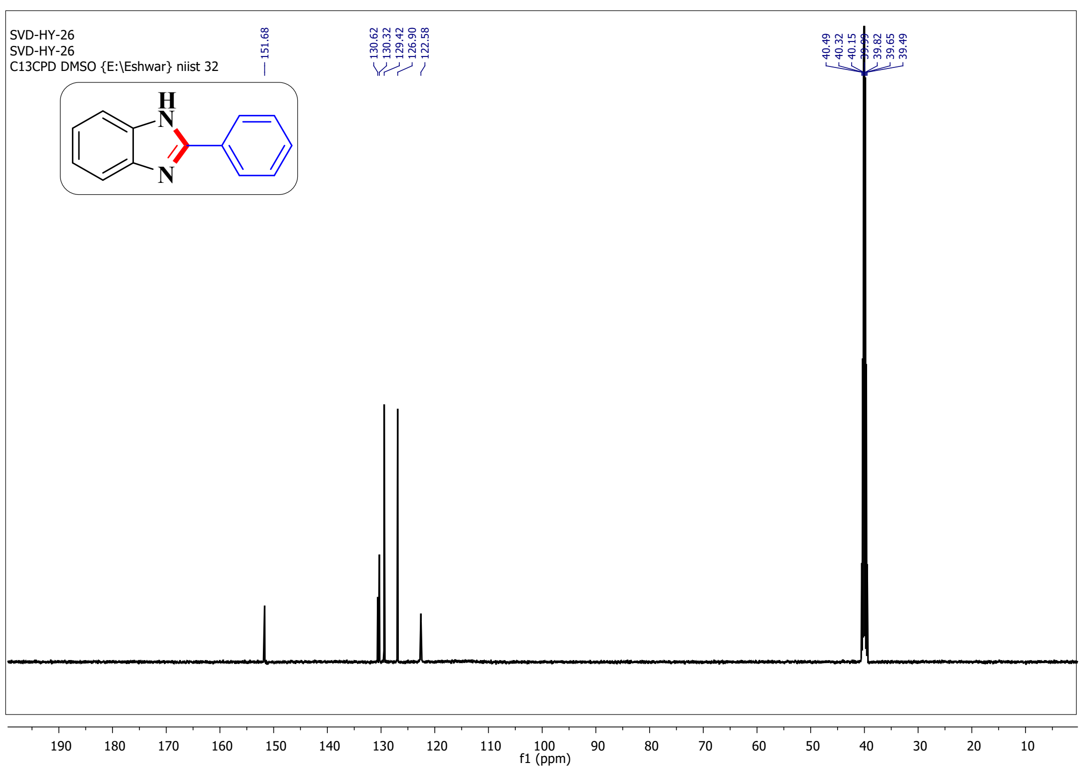
2-(4-methoxyphenyl)-1*H*-benzo[*d*]imidazole (5a)



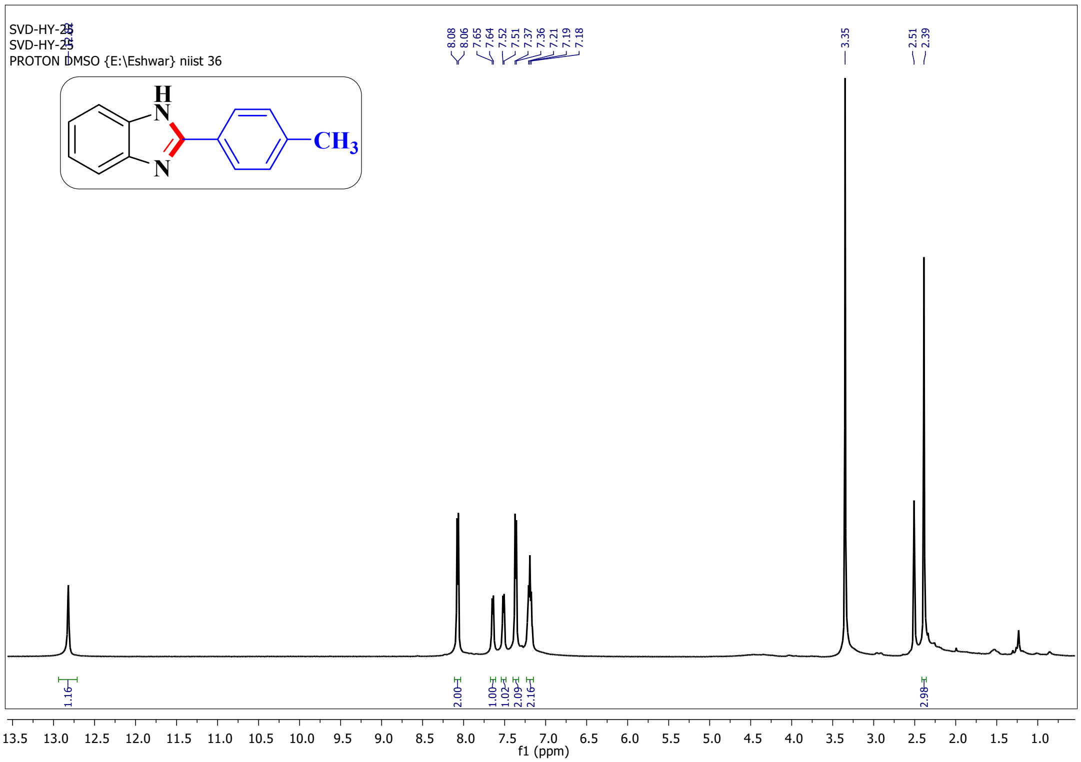


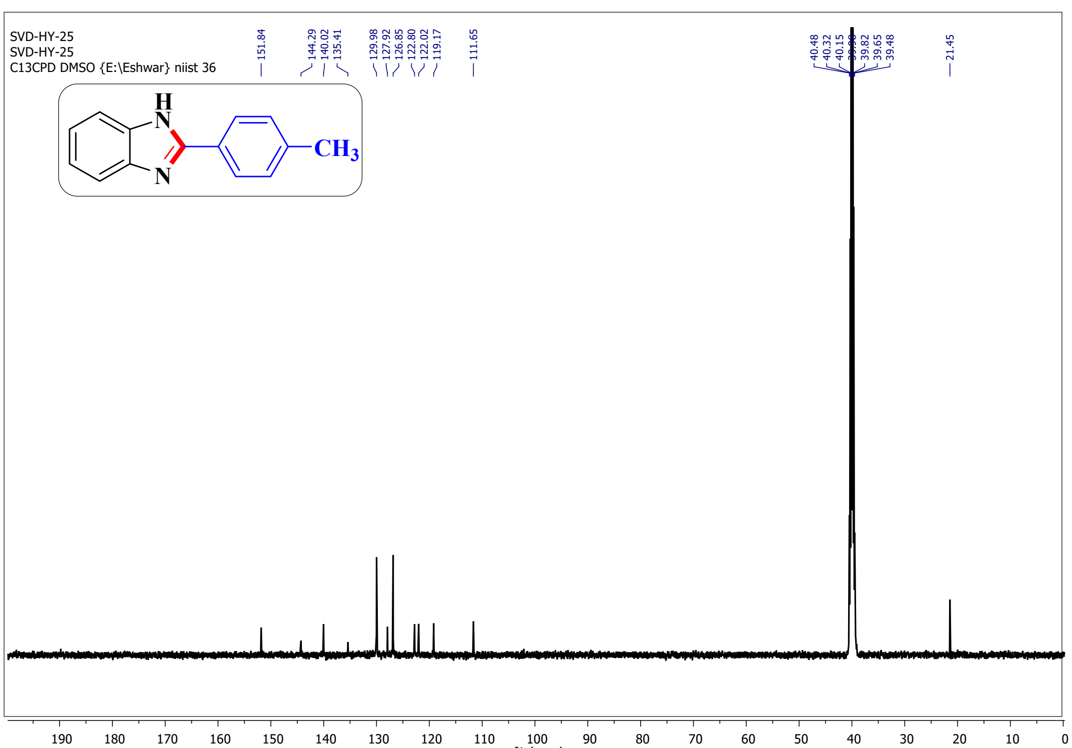
2-phenyl-1*H*-benzo[*d*]imidazole (5b)



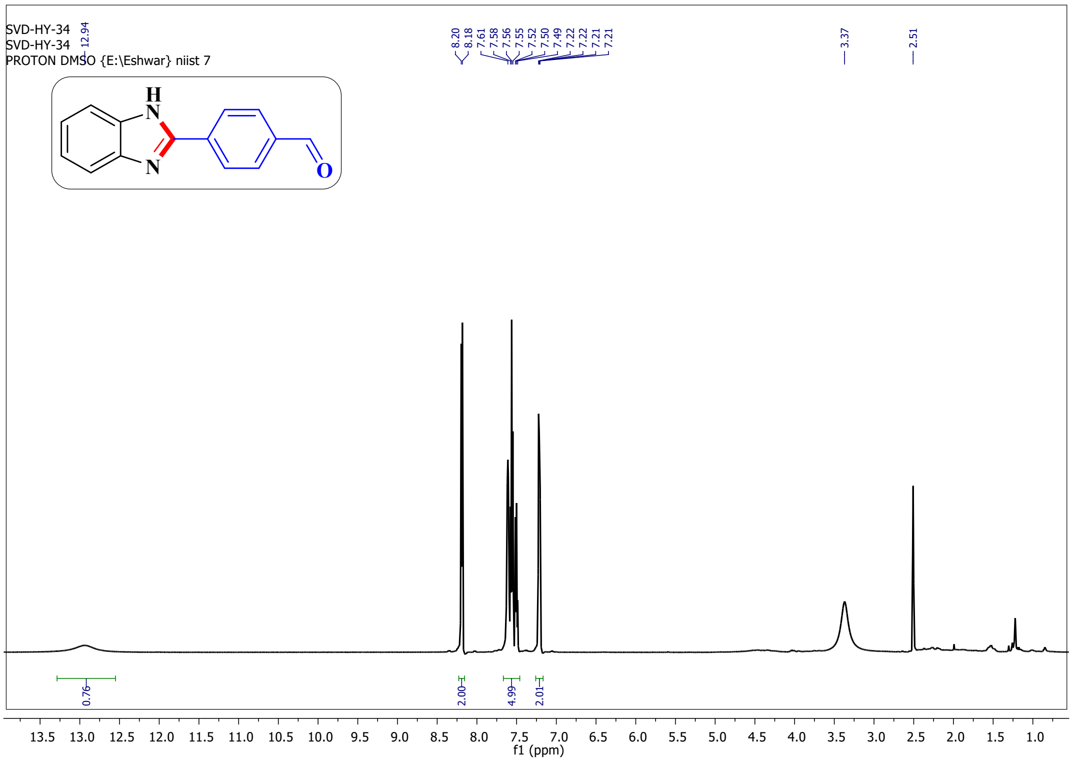


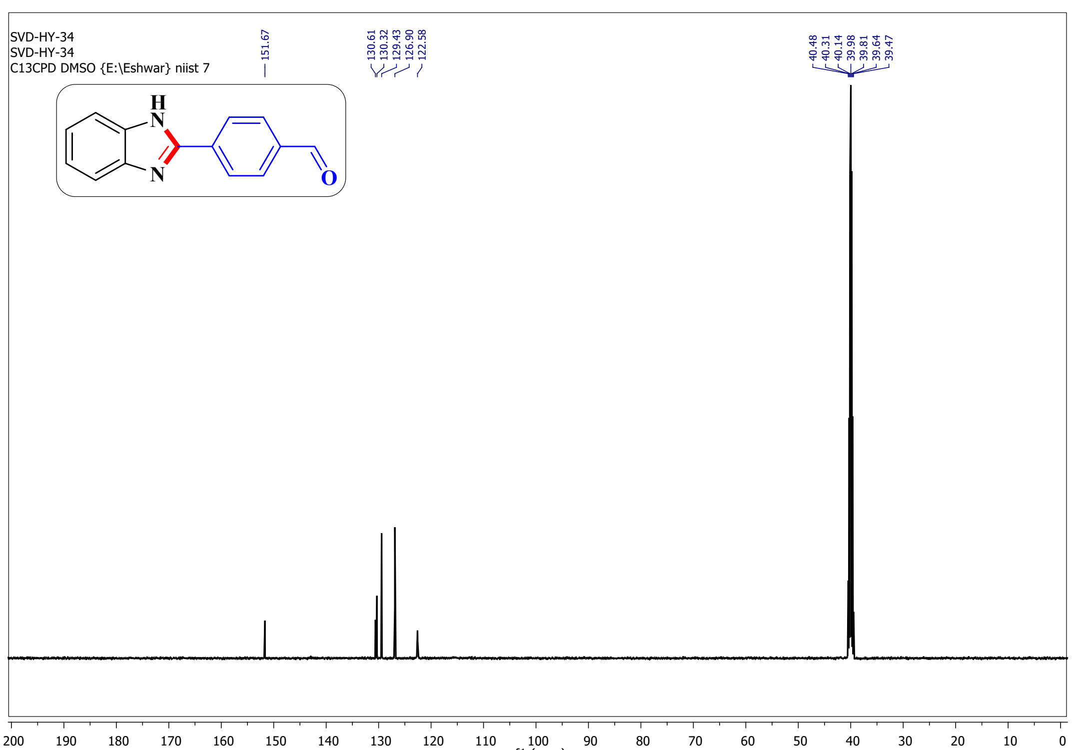
2-(*p*-tolyl)-1*H*-benzo[*d*]imidazole (5c)



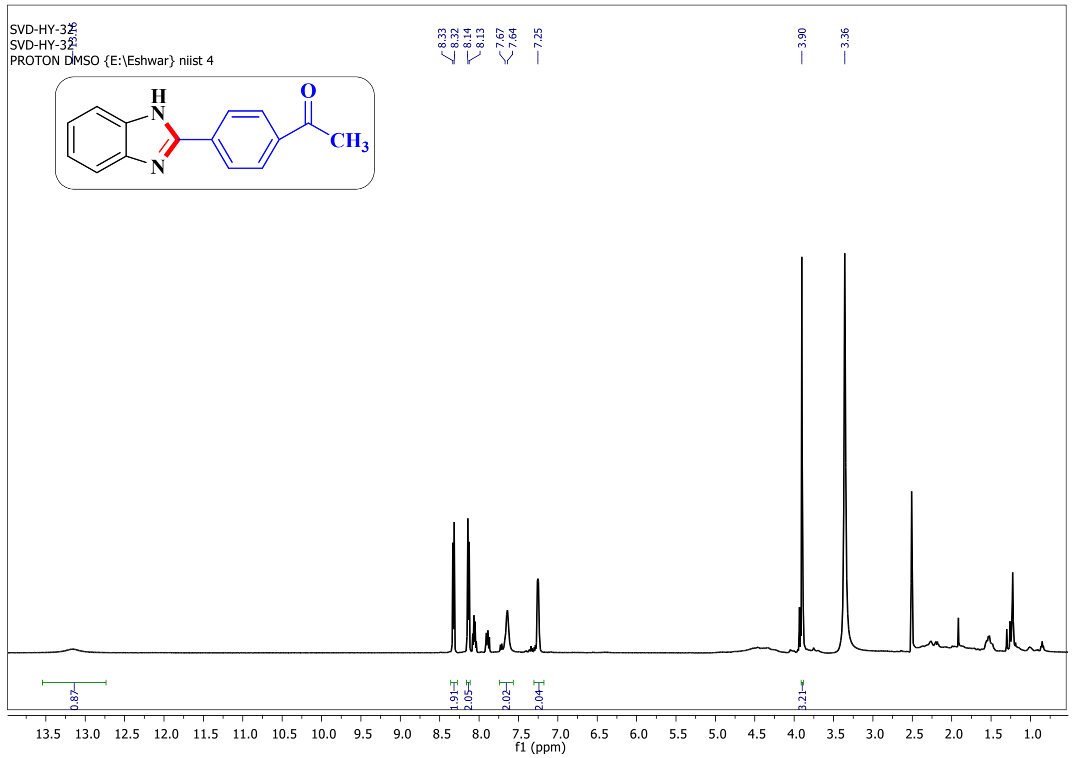


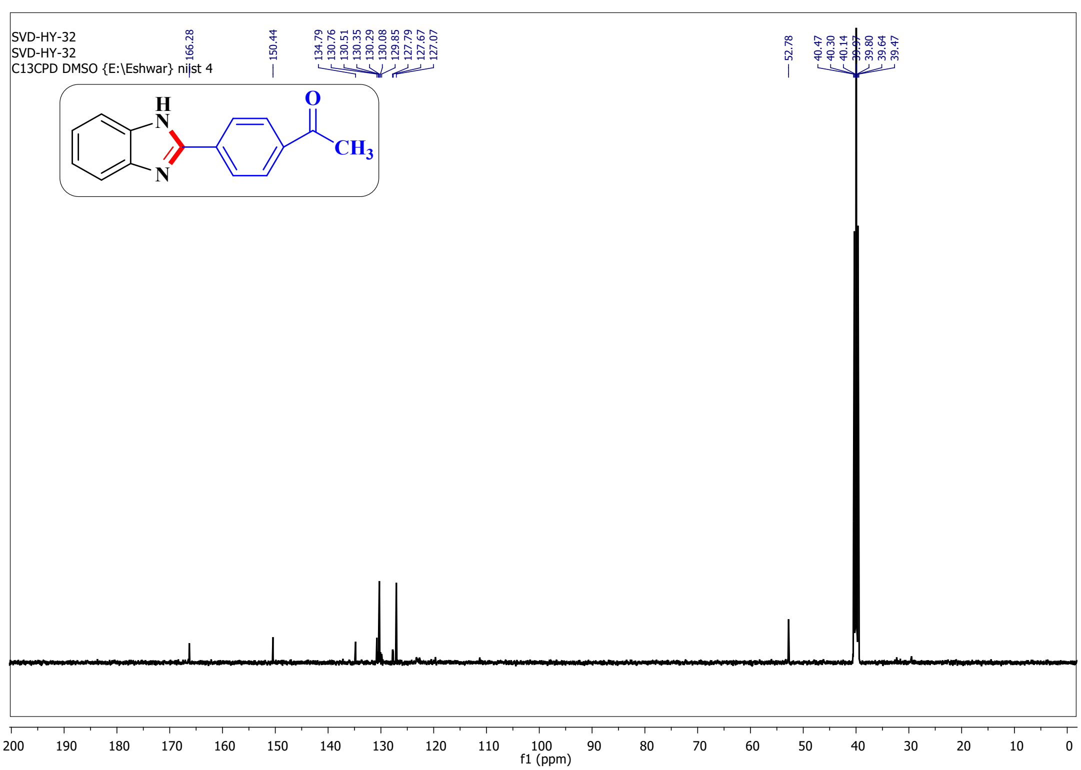
4-(1*H*-benzo[*d*]imidazol-2-yl) benzaldehyde (5d)



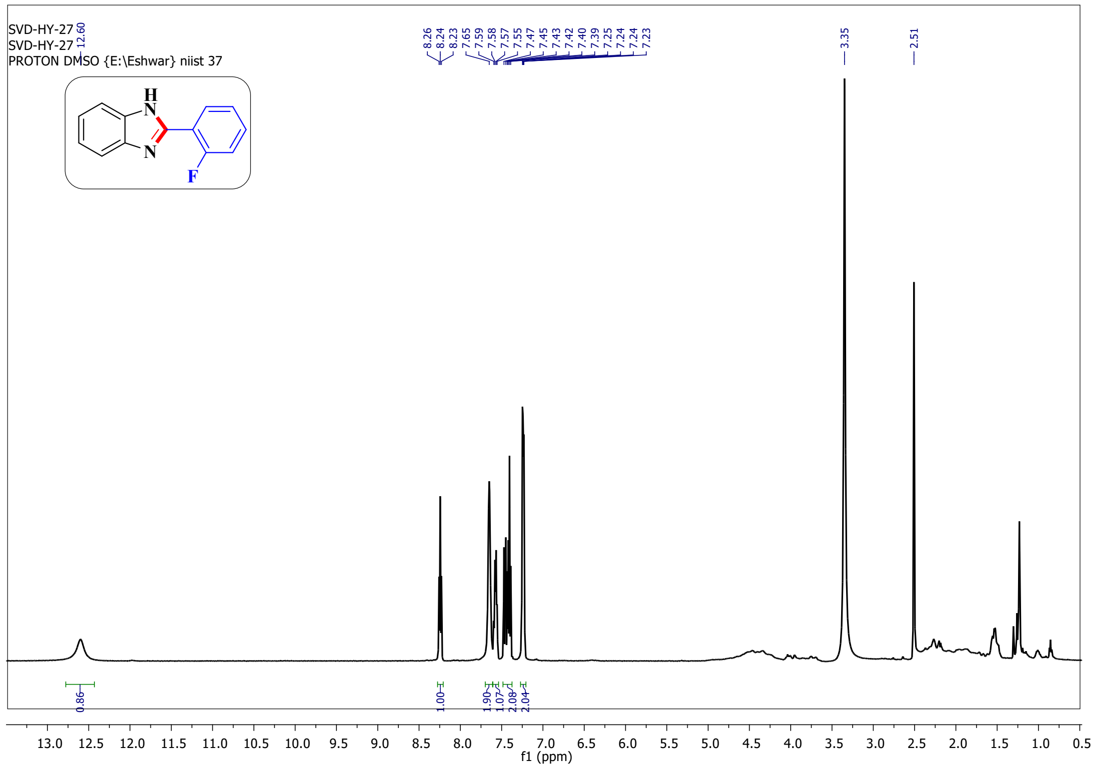


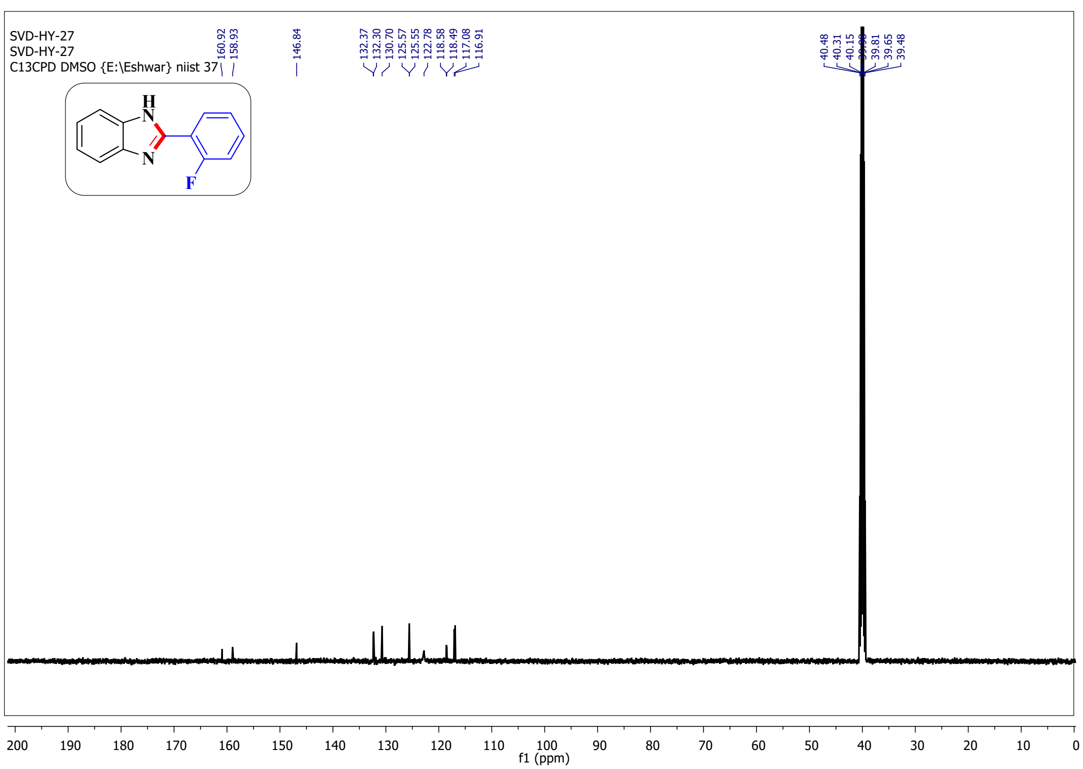
Methyl 4-(1*H*-benzo[*d*]imidazol-2-yl) benzoate (5e)



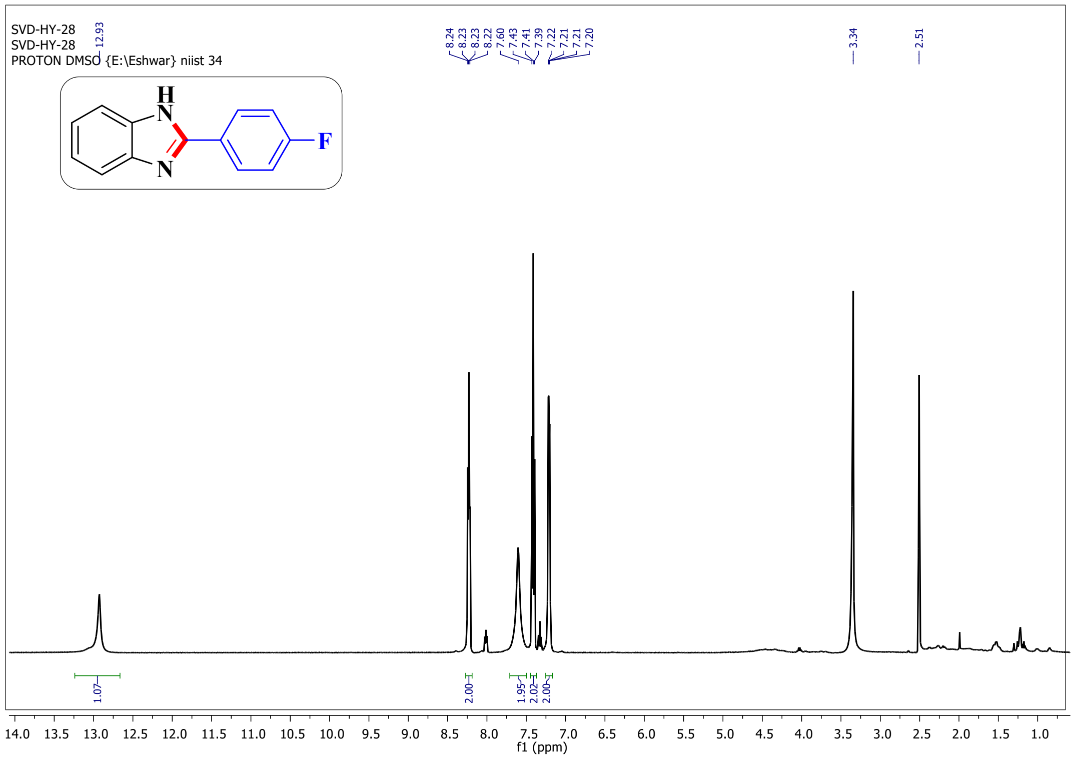


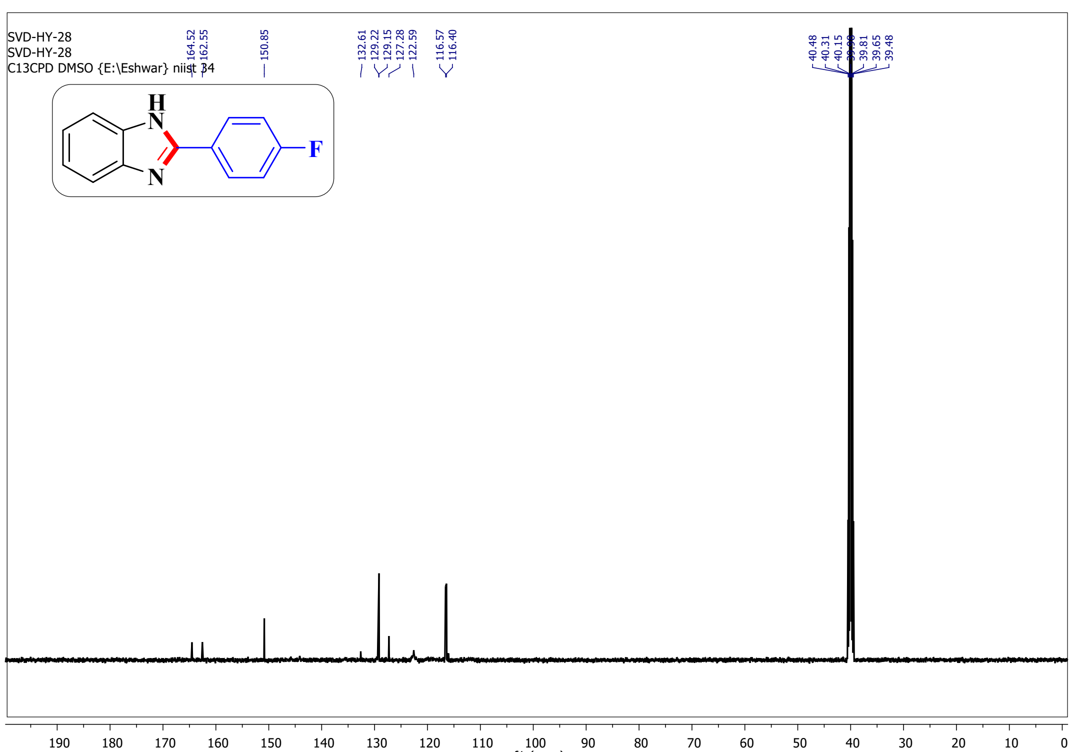
2-(2-fluorophenyl)-1*H*-benzo[*d*]imidazole (5f)



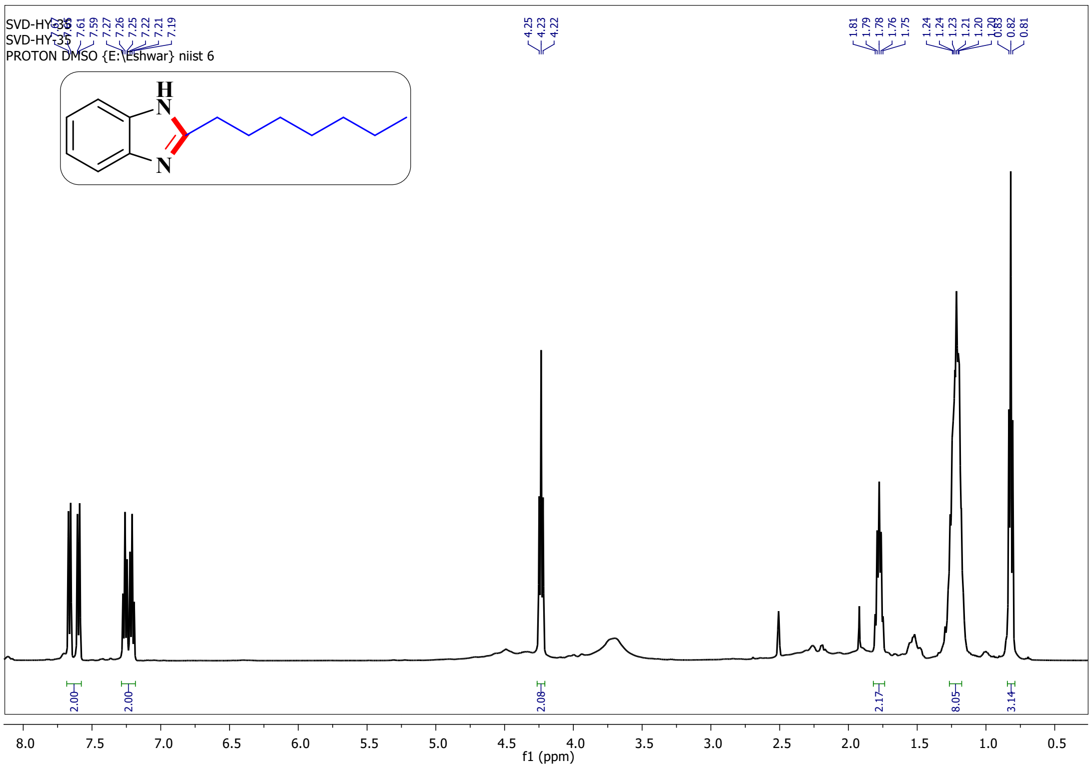


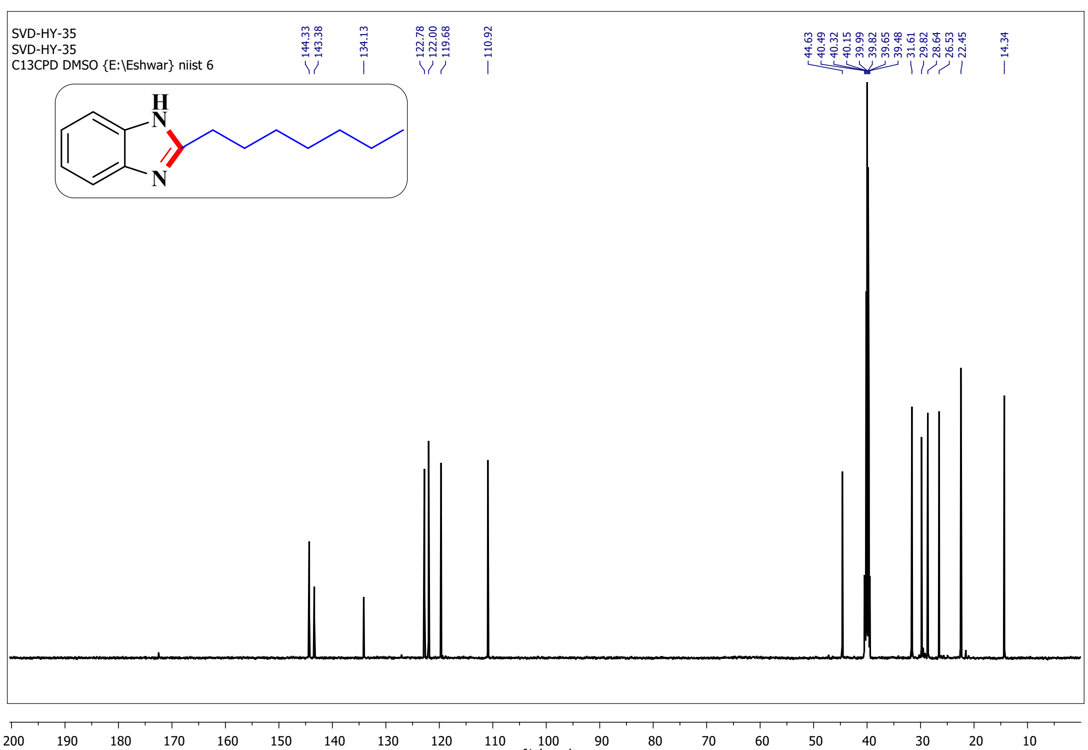
2-(4-fluorophenyl)-1*H*-benzo[*d*]imidazole (5g)





2-heptyl-1*H*-benzo[*d*]imidazole (5h)





1,2-diphenyl-1*H*-benzo[*d*]imidazole (5i)