A novel and eco-friendly method for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones in ionic liquids or ionic liquids/water without the use of any catalyst

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SUPPORTING INFORMATION

Contents:

1. General Experimental Details

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were recorded on Digital Melting Point Apparatus WRS-1B and uncorrected. IR spectra were measured on a Bruker VECTOR55 instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a VARIAN Mercury plus-400 instrument using tetramethylsilane (TMS) as an internal standard and DMSO-d_6 or $CDCl_3$ as the solvent at room temperature. Chemical shifts are given in δ relative to TMS, coupling constants (*J*) values are given in Hz. IR spectra was recorded on a AVATAR 370 FI-Infrared Spectrophotometer. Mass spectra were measured with Thermo Finnigan LCQ-Advantage. Elemental analysis was determined on a Carlo-Erba 1108 instrument.

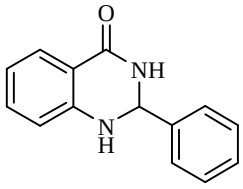
General procedure for synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones: To a solution of anthranilamides (5.5 mmol) and aldehydes (5 mmol), [Bmim]PF_6 (2 mL) was added, The mixture solution was stirred at 75 ^oC for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and the crude product was extracted with ethyl acetate (3×10 mL). The extracted solution was dried over anhydrous magnesium sulfate and concentrated in vacuo. The crude product was purified by recrystallization from ethanol.

General procedure for one-pot synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones: To a solution of isatoic anhydrides (5.5 mmol), ammonium acetate (8.0 mmol) and aldehydes (5.0 mmol), [Bmim]BF_4 (3.0 mL)-H_2O (2.0 mL) was added, The mixture solution was stirred at 80 ^oC for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature and filtered to afford the crude products, which were purified by recrystallization from ethanol. In addition, the filtrate could be also reused for the next batch reaction.

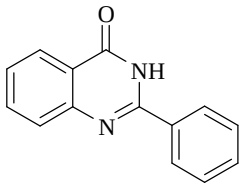
2. Experimental characterisation data for compounds

Compounds **3a-3m**, **3r**, **3t**, **4a** are known, compounds **3n-3q**, **3s**, **3u** are new and described below.

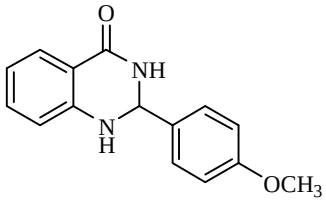
2.1 2,3-Dihydroquinazolin-4(1*H*)-ones



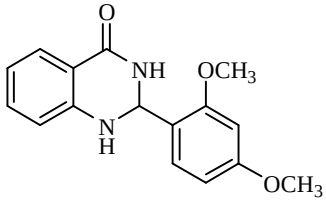
3a: White solid; mp 218–219 °C (Lit.[1] 215–216 °C).
R_f = 0.4 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.30 (s, 1 H), 7.61 (t, *J* = 6.8 Hz, 1 H), 7.50 (d, *J* = 7.2 Hz, 2 H), 7.32 – 7.41 (m, 3 H), 7.22 – 7.26 (m, 1 H), 7.12 (s, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.67 (t, *J* = 7.2 Hz, 1 H), 5.75 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.6, 147.9, 141.6, 133.3, 128.5, 128.3, 127.4, 126.9, 117.1, 115.0, 114.4, 66.6.
MS (EI, 70 eV): *m/z* (%) = 224 (M^+, 26), 223 ($[M - 1]^+$, 33), 147 (100), 120 (66), 92 (44).



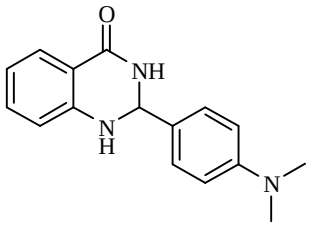
4a: White solid; mp 237-238 °C (Lit.[2] 238 °C).
R_f = 0.5 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.80 (s, 1 H), 8.27 – 8.34 (m, 3 H), 7.79 – 7.87 (m, 2 H), 7.60 (t, *J* = 3.2 Hz, 3 H), 7.49 – 7.54 (m, 1 H).
^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.6, 151.7, 149.4, 134.9, 132.8, 131.7, 129.1, 128.0, 127.3, 126.8, 126.4, 120.9.
MS (EI, 70 eV): *m/z* (%) = 222 (100) [M^+], 119 (92).



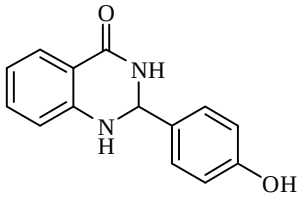
3b: White solid; mp 192-193 °C (Lit.[2] 195°C).
R_f = 0.35 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.19 (s, 1 H), 7.61 (d, *J* = 7.2 Hz, 1 H), 7.42 (d, *J* = 8.4 Hz, 2 H), 7.24 (t, *J* = 7.2 Hz, 1 H), 7.01 (s, 1 H), 6.94 (d, *J* = 7.6 Hz, 2 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 6.67 (t, *J* = 7.2 Hz, 1 H), 5.71 (s, 1 H), 3.74 (s, 3H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.7, 159.4, 148.0, 133.4, 133.2, 128.2, 127.4, 117.1, 115.0, 114.4, 113.6, 66.3, 55.2.
MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 15), 253 ([M - 1]$^+$, 27), 147 (100), 120 (72).



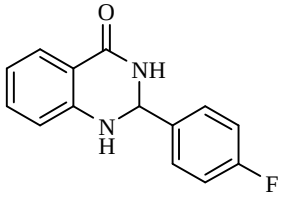
3c: White solid; mp 185.3-186.9 °C (Lit.[3] 187 °C).
R_f = 0.35 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.95 (s, 1 H), 7.62 (d, *J* = 8.0 Hz, 1 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.20 – 7.23 (m, 1 H), 6.76 (d, *J* = 8.0 Hz, 1 H), 6.72 (s, 1 H), 6.66 (t, *J* = 7.6 Hz, 1 H), 6.51 – 6.59 (m, 2 H), 5.95 (s, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.0, 160.7, 157.5, 148.2, 133.2, 127.8, 127.3, 121.3, 117.0, 114.8, 114.5, 104.5, 98.4, 60.8, 55.6, 55.3.
MS (EI, 70 eV): *m/z* (%) = 284 (M^+, 49), 283 ([M - 1]$^+$, 100), 147 (92), 138 (43), 120 (82).



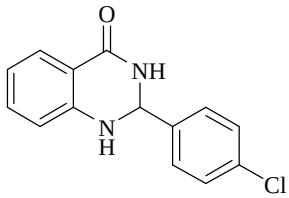
3d: White solid; mp 228-229 °C (Lit.[4] 228 °C); R_f = 0.35 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.08 (s, 1 H), 7.60 (d, *J* = 7.2 Hz, 1 H), 7.30 (d, *J* = 7.2 Hz, 2 H), 7.20 – 7.24 (m, 1H), 6.91 (s, 1 H), 6.64 – 6.74 (m, 4 H), 5.63 (s, 1 H), 2.88 (s, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.8, 150.7, 148.2, 133.1, 128.6, 127.7, 127.3, 116.9, 115.0, 114.4, 111.9, 66.6, 40.2.
MS (EI, 70 eV): *m/z* (%) = 267 (M^+, 70), 266 ($[M - 1]^+$, 100), 147 (51), 120 (61).



3e: White solid; mp 279.1-280.9 °C (Lit.[2]); R_f = 0.3 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.51 (s, 1 H), 8.35 (s, 1 H), 7.59 - 7.61 (m, 3 H), 7.4 (d, *J* = 7.6 Hz, 2 H), 7.23 - 7.27 (m, 1 H), 7.15 (s, 1 H), 6.74 (d, *J* = 7.6 Hz, 1 H), 6.74 (t, *J* = 7.6 Hz, 1 H), 5.75 (s, 1 H).
MS (EI, 70 eV): *m/z* (%) = 240 (M^+, 14), 239 ($[M - 1]^+$, 22), 147 (100), 120 (65), 119 (47), 92 (40), 65 (31).



3f: White solid; mp 199-200 °C (Lit.[5] Not reported); R_f = 0.4 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.30 (s, 1 H), 7.61 (d, *J* = 7.2 Hz, 1 H), 7.54 (dd, *J* = 5.6, 8.4 Hz, 2 H), 7.21 – 7.27 (m, 3 H), 7.11 (s, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.68 (t, *J* = 7.2 Hz, 1 H), 5.78 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.5, 162.0 (d, $^1J_{CF}$ = 242.7 Hz), 147.7, 137.7, 133.3, 128.9 (d, $^3J_{CF}$ = 8.3 Hz), 127.3, 117.2, 115.0 (d, $^2J_{CF}$ = 20.5 Hz), 114.9, 114.4, 65.9.
MS (EI, 70 eV): *m/z* (%) = 242 (M^+, 37), 241 ($[M - 1]^+$, 63), 147 (100), 120 (78), 119 (43), 92 (33) .

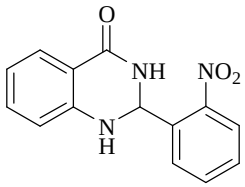


3g: White solid; mp 205-206 °C (Lit.[1] 202–204 °C); R_f = 0.4 (petroleum ether–EtOAc, 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.36 (s, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 8.0 Hz, 2 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.16 (s, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.69 (t, *J* = 7.6 Hz, 1 H), 5.78 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.5, 147.7, 140.7, 133.4, 133.0, 128.8, 128.3, 127.4, 117.3, 115.0, 114.5, 65.8.

MS (EI, 70 eV): *m/z* (%) = 260 ([M + 2]$^+$, 8), 258 (M^+, 25), 147 (100), 120 (52), 119 (37).

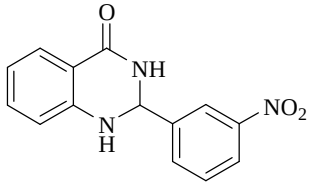


3h: Primrose yellow solid; mp 193-194 °C (Lit.[2] 192 °C); R_f = 0.4 (petroleum ether–EtOAc, 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.24 (s, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.79 (t, *J* = 7.6 Hz, 1 H), 7.61 - 7.67 (m, 2 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 7.02 (s, 1 H), 6.70 – 6.79 (m, 2 H), 6.34 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.3, 147.6, 147.0, 135.9, 133.8, 133.5, 129.8, 128.9, 127.2, 124.6, 117.6, 114.8, 114.5, 62.1.

MS (EI, 70 eV): *m/z* (%) = 269 (M^+, 16), 251 (57), 234 (54), 222 (35), 147 (100), 120 (55), 119 (70), 92 (49).



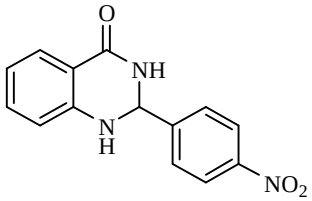
3i: Primrose yellow solid; mp 216.2-217.1 °C (Lit.[6] Not reported); R_f = 0.4 (petroleum ether–EtOAc, 1:1).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.56 (s, 1 H), 8.38 (t, *J* = 2.0 Hz, 1 H), 8.20 – 8.23 (m, 1 H), 7.96 (d, *J* = 7.6 Hz, 1 H), 7.71 (t, *J* = 8.0 Hz, 1 H), 7.63 (dd, *J* = 1.6, 7.6 Hz, 1 H), 7.37 (s, 1 H), 7.26 – 7.30 (m, 1 H), 6.80 (d, *J* = 8.0 Hz, 1 H), 6.69 – 6.73 (m, 1 H), 5.97 (s, 1 H).

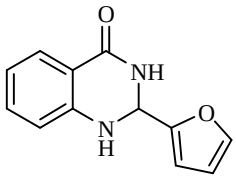
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.5, 147.7, 147.4, 144.3, 133.7, 133.4, 130.1, 127.5, 123.3, 121.6, 117.6, 115.0, 114.7, 65.2.

MS (EI, 70 eV): *m/z* (%) = 269 (M^+, 21), 268 ([M - 1]$^+$, 16), 147 (100), 120 (36), 92

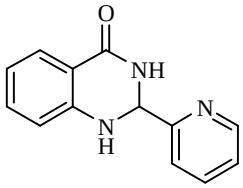
(25).



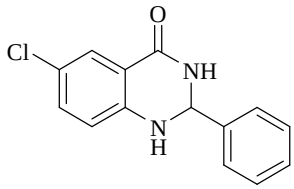
3j: Primrose yellow solid; mp 212.5-214.8 °C (Lit.[6] Not reported); R_f = 0.4 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.53 (s, 1 H), 8.25 – 8.27 (m, 2 H), 7.34 – 7.76 (m, 2 H), 7.60 – 7.63 (m, 1 H), 7.34 (s, 1 H), 7.25 – 7.29 (m, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 6.69 (t, *J* = 7.6Hz, 1 H), 5.92 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.2, 149.3, 147.4, 147.2, 133.5, 128.0, 127.4, 123.5, 117.4, 114.9, 114.5, 65.3.
MS (EI, 70 eV): *m/z* (%) = 269 (M^+, 35), 268 ([M - 1]$^+$, 25), 147 (100), 120 (38), 119 (38), 92 (24).



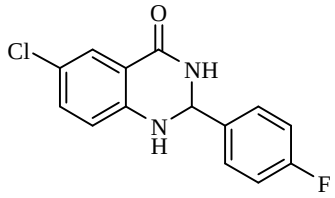
3k: White solid; mp 167.2-168.5 °C (Lit.[7] Not reported); R_f = 0.45 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (s, 1 H), 7.39 (s, 1 H), 7.26 – 7.31 (m, 1 H), 6.83 – 6.87 (m, 2 H), 6.70 (d, *J* = 6.4 Hz, 1 H),6.43 (s, 1 H), 6.33 (s, 1 H), 5.91 (s, 1 H), 4.74 (br s, 1H).
MS (EI, 70 eV): *m/z* (%) = 214 (M^+, 54), 213 ([M - 1]$^+$, 100), 197 (30), 147 (20), 120 (93), 92 (23).



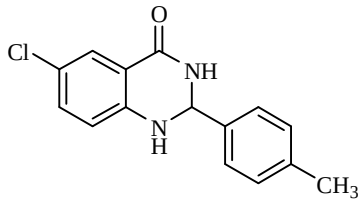
3l: White solid; mp 187–188 °C (Lit.[8] 189-190 °C); R_f = 0.4 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.55 (d, *J* = 4.0 Hz, 1 H), 8.38 (s, 1 H), 7.83 (t, *J* = 7.6 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 7.6 Hz, 1 H), 7.20 – 7.36 (m, 3 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 6.65 (t, *J* = 7.6 Hz, 1 H), 5.71 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.2, 160.2, 148.9, 147.3, 137.0, 133.2, 127.2, 123.4, 20.4, 117.0, 114.8, 114.4, 67.2.
MS (EI, 70 eV): *m/z* (%) = 225 (M^+, 16), 147 (100), 120 (15), 92 (19).



3m: White solid; mp 249-250 °C (Lit.[9] 248-249 °C); R_f = 0.4 (petroleum ether–EtOAc, 1:1).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 5.80 (s, 1 H), 6.79 (d, *J* = 8.8 Hz, 1 H), 7.29 (dd, *J* = 2.4, 8.8 Hz, 1 H), 7.34 – 7.42 (m, 4 H), 7.49 – 7.50 (m, 2 H), 7.56 (d, *J* = 2.0 Hz, 1 H), 8.50 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 66.4, 116.0, 120.7, 126.4, 126.8, 128.3, 128.5, 133.0, 141.2, 146.5, 162.4.
MS (EI, 70 eV): *m/z* (%) = 260 ([M + 2]$^+$, 12), 259 ([M + 1]$^+$, 20), 258 (M$^+$, 35), 257 ([M – 1]$^+$, 45), 183 (35), 181 (100), 183 (31), 154 (39).

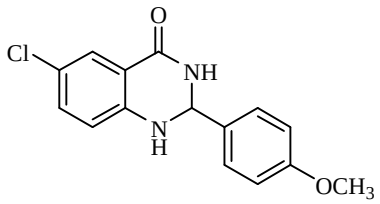


3n: White solid; mp 249-250 °C; R_f = 0.4 (petroleum ether–EtOAc, 1:1).
IR (KBr): 3430 (NH), 1672 (C=O) cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.51 (s, 1 H), 7.54 – 7.57 (m, 3 H), 7.35 (s, 1 H), 7.22 – 7.31 (m, 3 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 5.84 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5, 162.2 (d, $^1J_{CF}$ = 243.4 Hz), 146.6, 137.4, 133.2, 129.1 (d, $^3J_{CF}$ = 8.3 Hz), 126.5, 121.0, 116.5, 116.1, 115.2 (d, $^2J_{CF}$ = 21.2 Hz), 65.9.
MS (EI, 70 eV): *m/z* (%) = 278 ([M + 2]$^+$, 5), 276 (M$^+$, 16), 181 (100), 183 (25), 154 (30), 95 (44).
Anal. Calcd for $C_{14}H_{10}ClFN_2O$: C, 60.77; H, 3.64; Found: C 60.82; H 3.69.

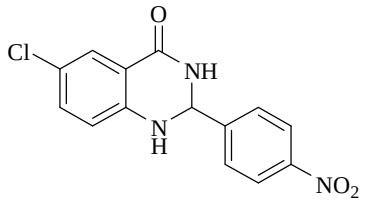


3o: White solid; mp 251 °C; R_f = 0.4 (petroleum ether–EtOAc, 1:1).
IR (KBr): 3390 (NH), 1680 (C=O) cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.44 (s, 1 H), 7.54 (d, *J* = 2.4 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.26 – 7.31 (m, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 5.74 (s, 1 H), 2.29 (s, 3 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5, 146.6, 142.7, 137.9, 133.0, 129.2, 128.9, 126.8, 120.7, 116.4, 116.1, 66.2, 20.7.
MS (EI, 70 eV): *m/z* (%) = 273 ([M + 2]$^+$, 32), 271 (M$^+$, 95), 181 (100), 183 (25), 154

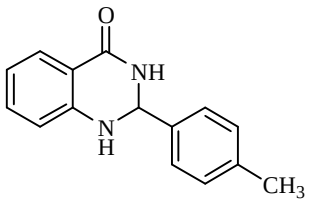
(34).
Anal. Calcd for $C_{15}H_{13}ClN_2O$: C, 66.06; H, 4.80; Found: C 66.01; H 4.88.



3p: White solid; mp 220-221 °C; R_f = 0.35 (petroleum ether–EtOAc, 1:1).
IR (KBr): 3380 (NH), 1660 (C=O) cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.40 (s, 1 H), 7.55 (s, 1 H), 7.42 (d, *J* = 6.4 Hz, 2 H), 7.26 (s, 2 H), 6.96 (d, *J* = 6.0 Hz, 2 H), 6.78 (d, *J* = 7.2 Hz, 1 H), 5.74 (s, 1 H), 3.75 (s, 3 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.4, 159.5 146.7, 133.1, 132.9, 128.1, 126.4, 120.7, 116.4, 116.1, 113.7, 66.1, 55.1.
MS (EI, 70 eV): *m/z* (%) = 290 ($[M + 2]^+$, 21), 289 ($[M + 1]^+$, 42), 288 (M^+, 64), 287 ($[M - 1]^+$, 100), 183 (25), 181 (76), 183 (31), 154 (58).
Anal. Calcd for $C_{15}H_{13}ClN_2O_2$: C, 62.40; H, 4.54; Found: C 62.22; H 4.67.

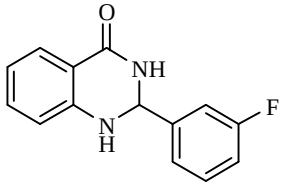


3q: White solid; mp 220 -221 °C; R_f = 0.35 (petroleum ether–EtOAc, 1:1).
IR (KBr): 3440 (NH), 1668 (C=O) cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.01 (s, 1 H), 6.85 (d, *J* = 8.8 Hz, 1 H), 7.32 (dd, *J* = 2.4, 8.8 Hz, 1 H), 7.58 (m, 2 H), 7.77 (d, *J* = 8.8 Hz, 2 H), 8.29 (d, *J* = 8.8 Hz, 2 H), 8.76 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 65.2, 116.0, 116.6, 121.2, 123.7, 126.5, 128.0, 133.4, 146.0, 147.5, 148.9, 162.2.
MS (EI, 70 eV): *m/z* (%) = 305 ($[M + 2]^+$, 10), 303 (M^+, 31), 181 (100), 183 (31), 154 (39).
Anal. Calcd for $C_{14}H_{10}ClN_3O_3$: C, 55.37; H, 3.32; Found: C 55.32; H 3.25.

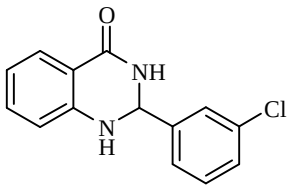


3r: White solid; mp 233–234 °C (Lit.[1] 231-233 °C); R_f = 0.4 (petroleum ether–EtOAc, 1:1).
IR (KBr): 3440 (NH), 1670 (C=O) cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.26 (s, 1 H), 7.62 (d, *J* = 7.6 Hz, 1 H), 7.38 (d, *J*

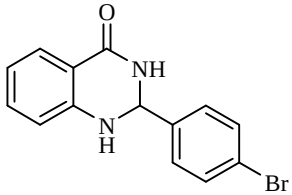
= 8.0 Hz, 2 H), 7.17 – 7.25 (m, 3 H), 7.22 – 7.261 (m, 1 H), 7.07 (s, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 6.66 (t, *J* = 7.6 Hz, 1 H), 5.72 (s, 1 H), 2.28 (s, 3 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.7, 148.0, 138.7, 137.8, 133.3, 128.9, 127.4, 126.9, 117.1, 115.0, 114.5, 66.5, 20.8.
MS (EI, 70 eV): *m/z* (%) = 238 (M^+, 47), 237 ($[M - 1]^+$, 92), 147 (100), 120 (48).



3s: White solid; mp 266-267 °C; R_f = 0.35 (petroleum ether–EtOAc, 1:1).
IR (KBr): 3360 (NH), 1675 (C=O) cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.42 (s, 1 H), 7.62 (d, *J* = 7.2 Hz, 1 H), 7.41 – 7.46 (m, 1 H), 7.15 – 7.35 (m, 5 H), 6.78 (d, *J* = 8.0 Hz, 1 H), 6.69 (t, *J* = 7.2 Hz, 1 H), 5.80 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.5, 162.0 (d, $^1J_{CF}$ = 242.7 Hz), 147.6, 144.8, 133.5, 130.4 (d, $^3J_{CF}$ = 7.6 Hz), 127.4, 122.8, 117.3, 115.2 (d, $^2J_{CF}$ = 21.2 Hz), 115.0, 114.5, 113.6 (d, $^2J_{CF}$ = 22.0 Hz), 65.6.
MS (EI, 70 eV): *m/z* (%) = 242 (M^+, 30), 241 ($[M - 1]^+$, 40), 147 (100), 120 (50), 92 (25).
Anal. Calcd for $C_{14}H_{11}FN_2O$: C, 69.41; H, 4.58; Found: C 69.33; H 4.62.



3t: White solid; mp 189.8-189.9 °C (Lit.[10] Not reported).
^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.42 (s, 1 H), 7.61 – 7.63 (m, 1 H), 7.54 (s, 1 H), 7.40 – 7.47 (m, 3 H), 7.23 – 7.28 (m, 2 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.69 (t, *J* = 7.6 Hz, 1 H), 5.79 (s, 1 H).
^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.4, 147.5, 144.4, 133.5, 133.0, 130.3, 128.3, 127.4, 126.8, 125.4, 117.3, 114.9, 114.5, 65.6.
MS (EI, 70 eV): *m/z* (%) = 260 ($[M + 2]^+$, 7), 258 (M^+, 25), 147 (100), 120 (52), 92 (25).



3u: White solid; mp 206–207 °C; R_f = 0.4 (petroleum ether–EtOAc, 1:1).

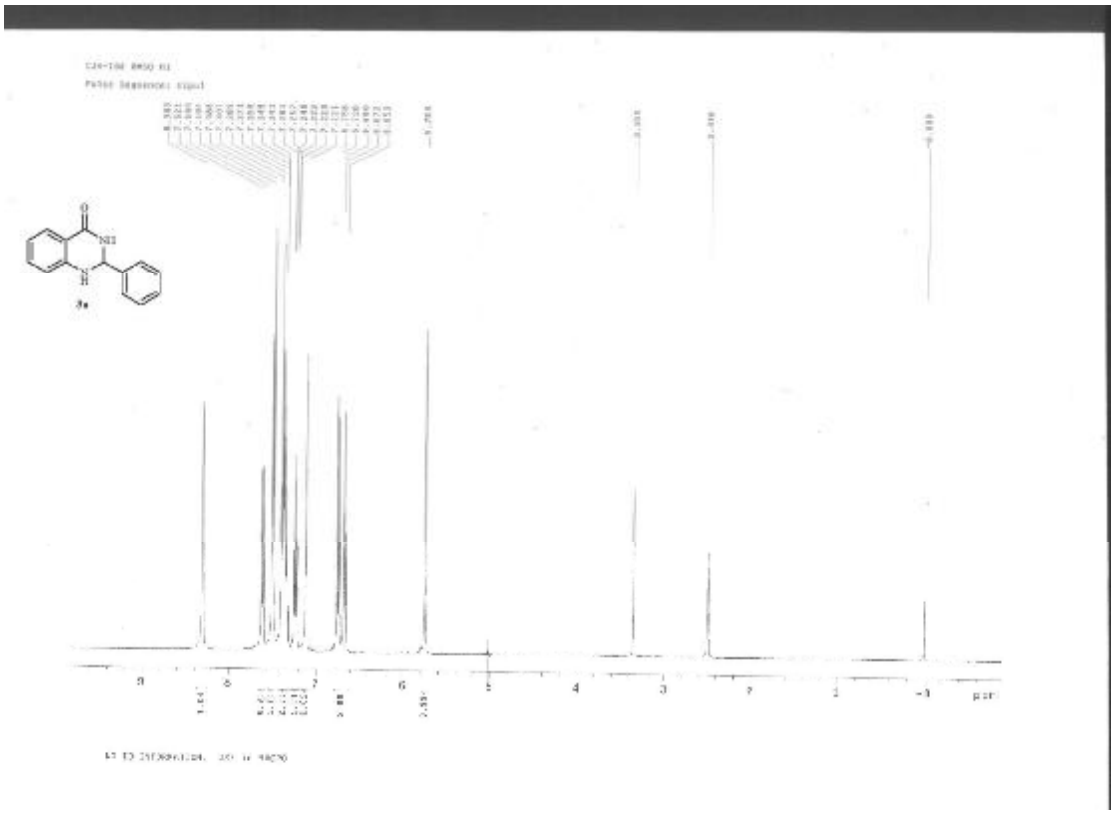
IR (KBr): 3410 (NH), 1670 (C=O) cm^{-1}.

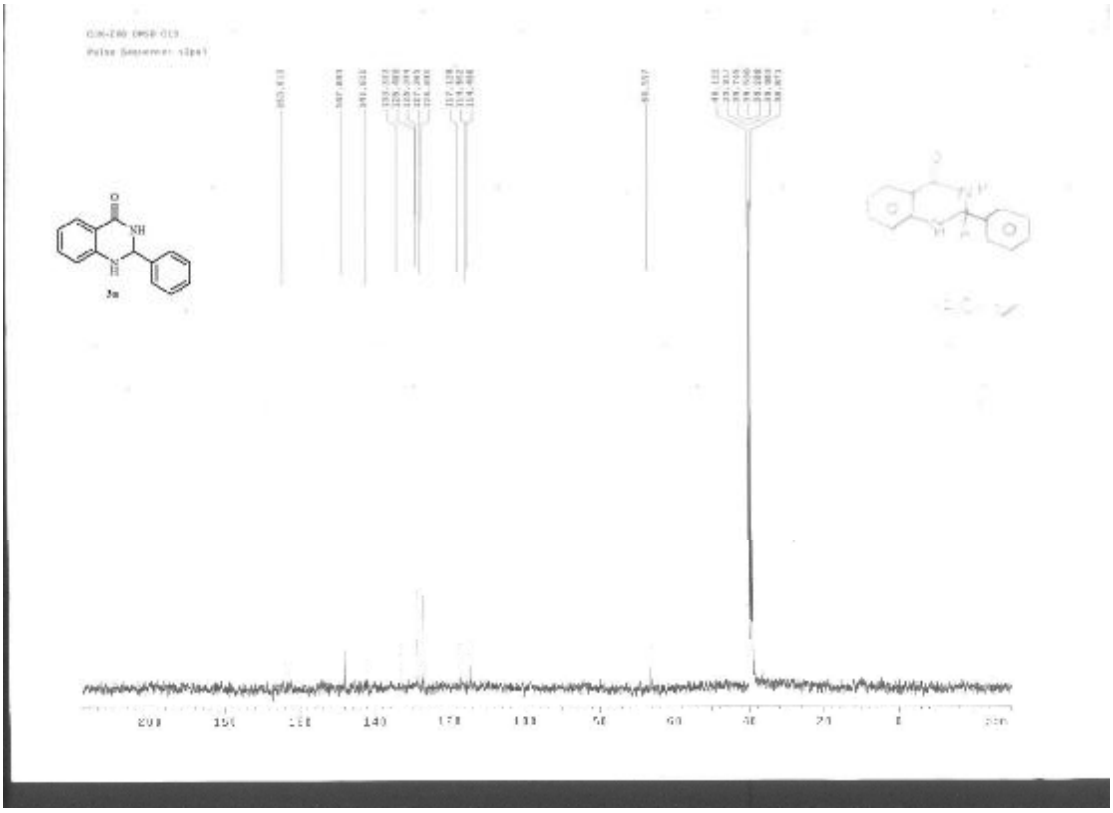
^1H NMR (400 MHz, DMSO-d_6): δ = 8.35 (s, 1 H), 7.59 – 7.61 (m, 3 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.23 – 7.27 (m, 1 H), 7.16 (s, 1 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 6.68 (t, *J* = 7.6 Hz, 1 H), 5.76 (s, 1 H).

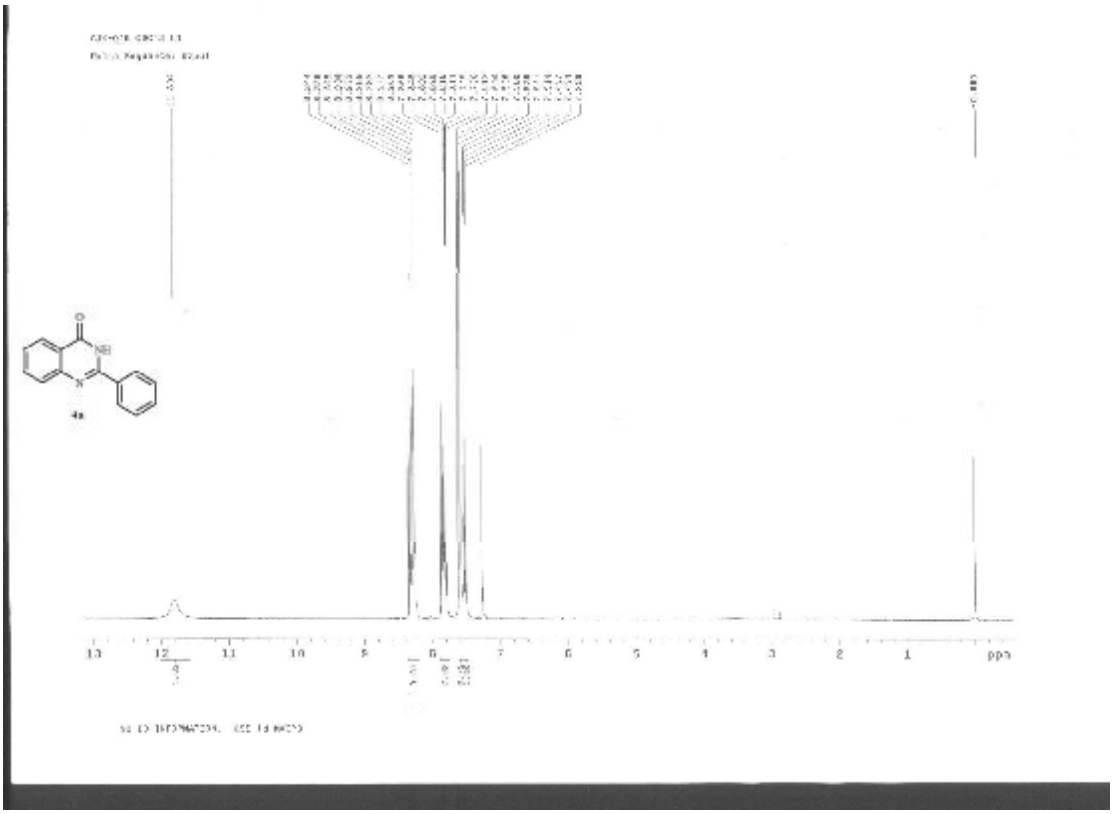
MS (EI, 70 eV) *m/z* (%) = 304 ($[M + 2]^+$, 20), 302 (M^+, 22), 147 (100), 120 (43), 91 (25).

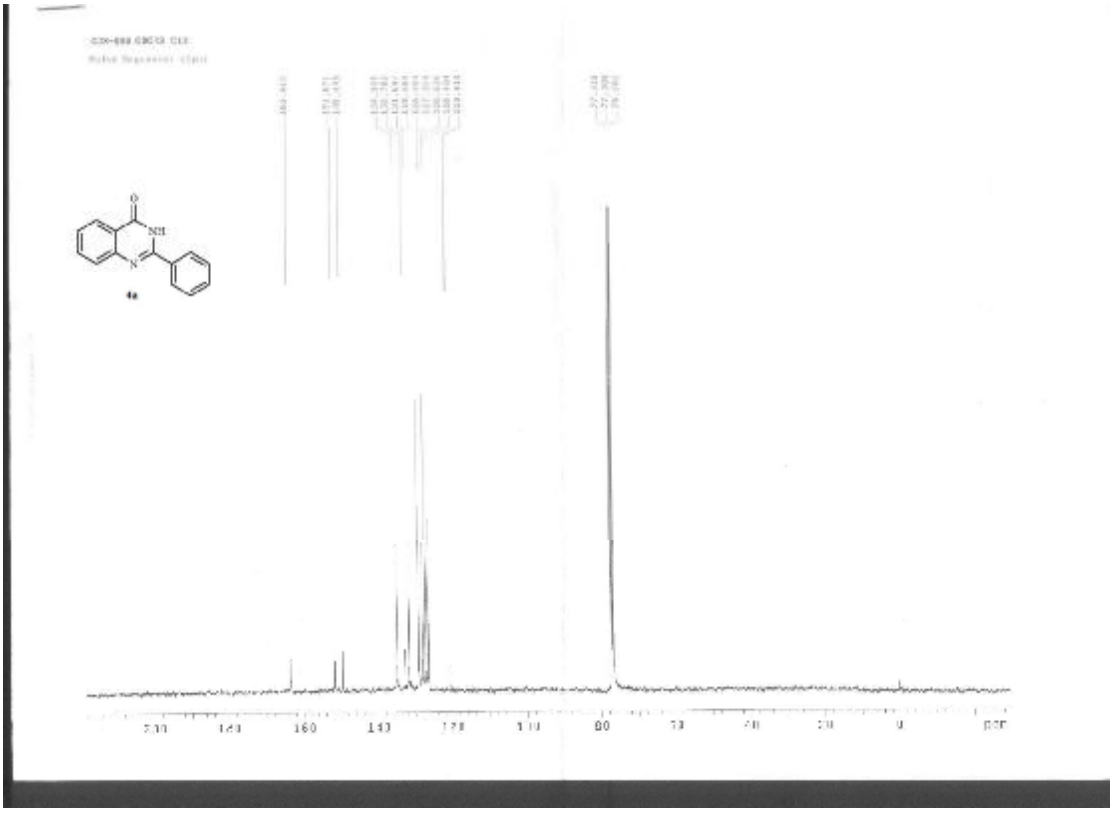
Anal. Calcd for $C_{14}H_{11}BrN_2O$: C, 55.47; H, 3.66; Found: C 55.53; H 3.55.

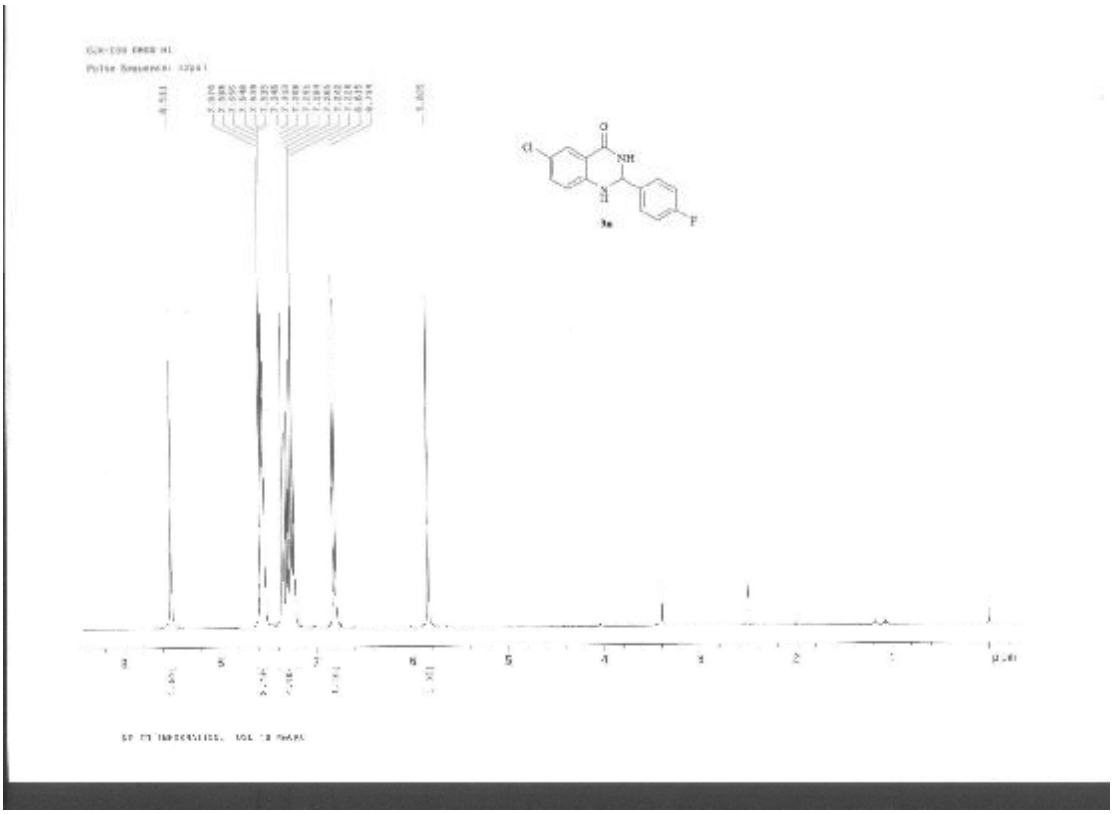
3. Copies of NMR spectra for all new compounds

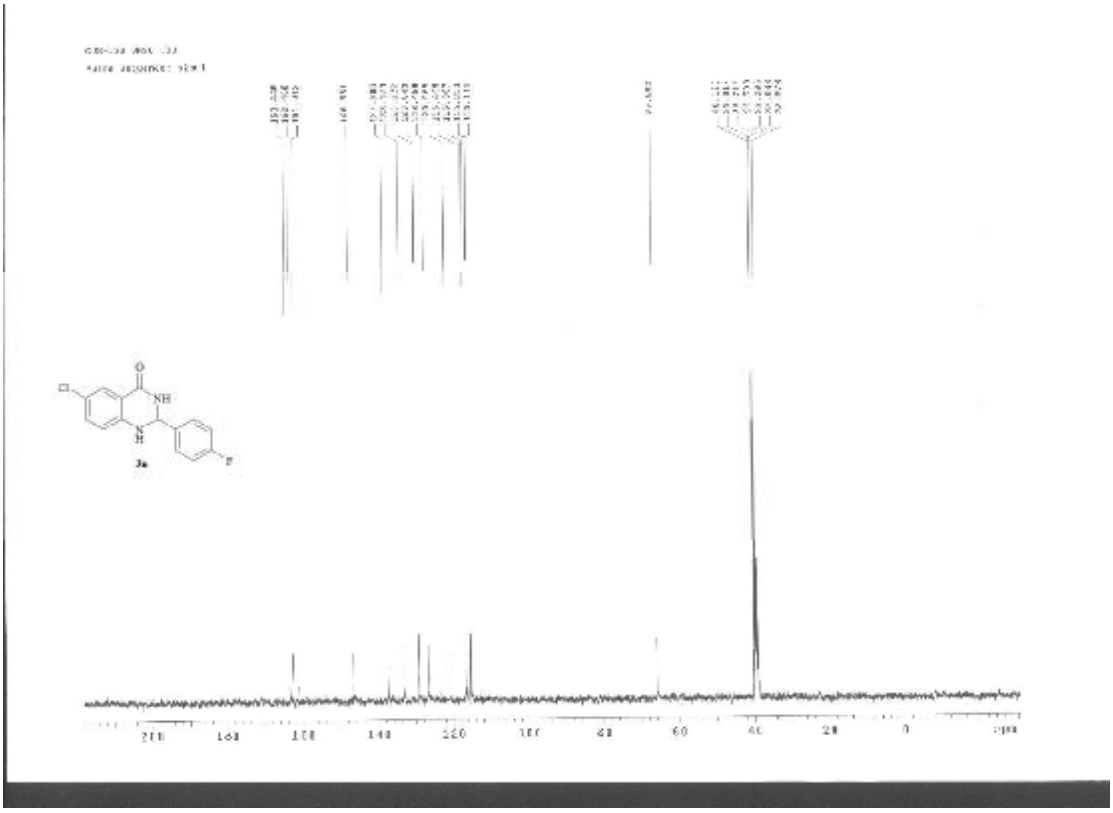


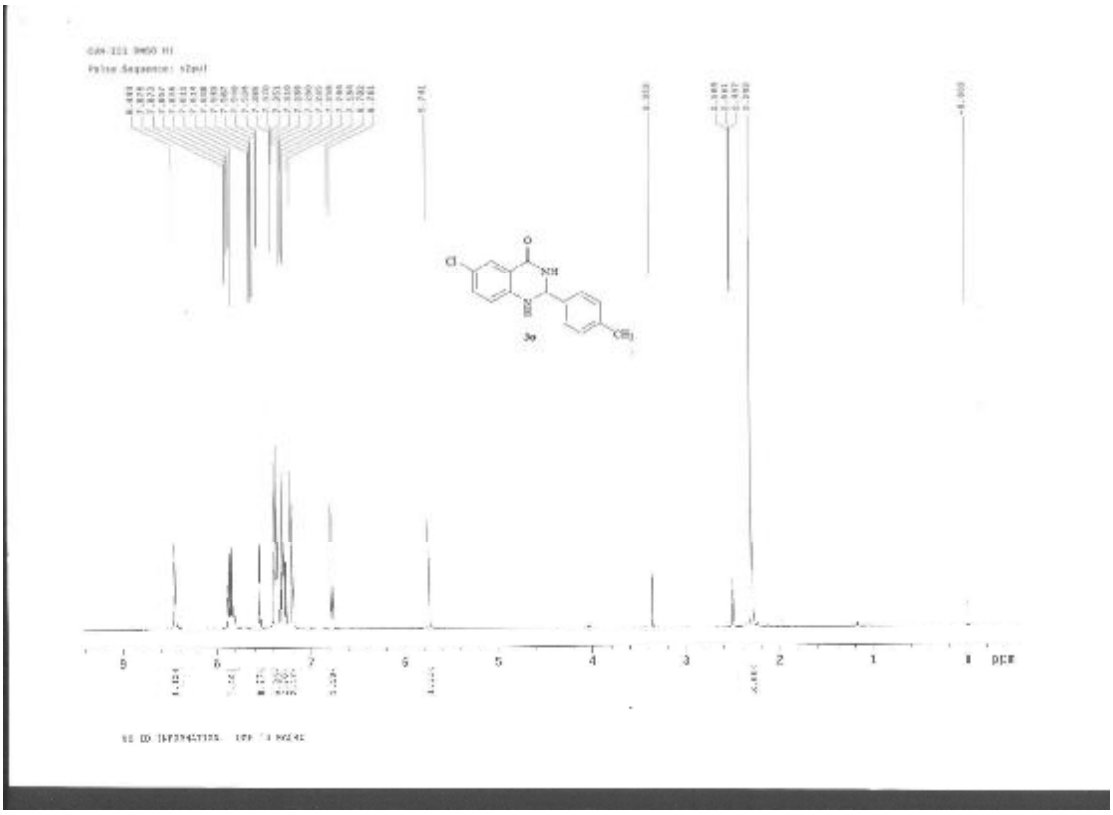


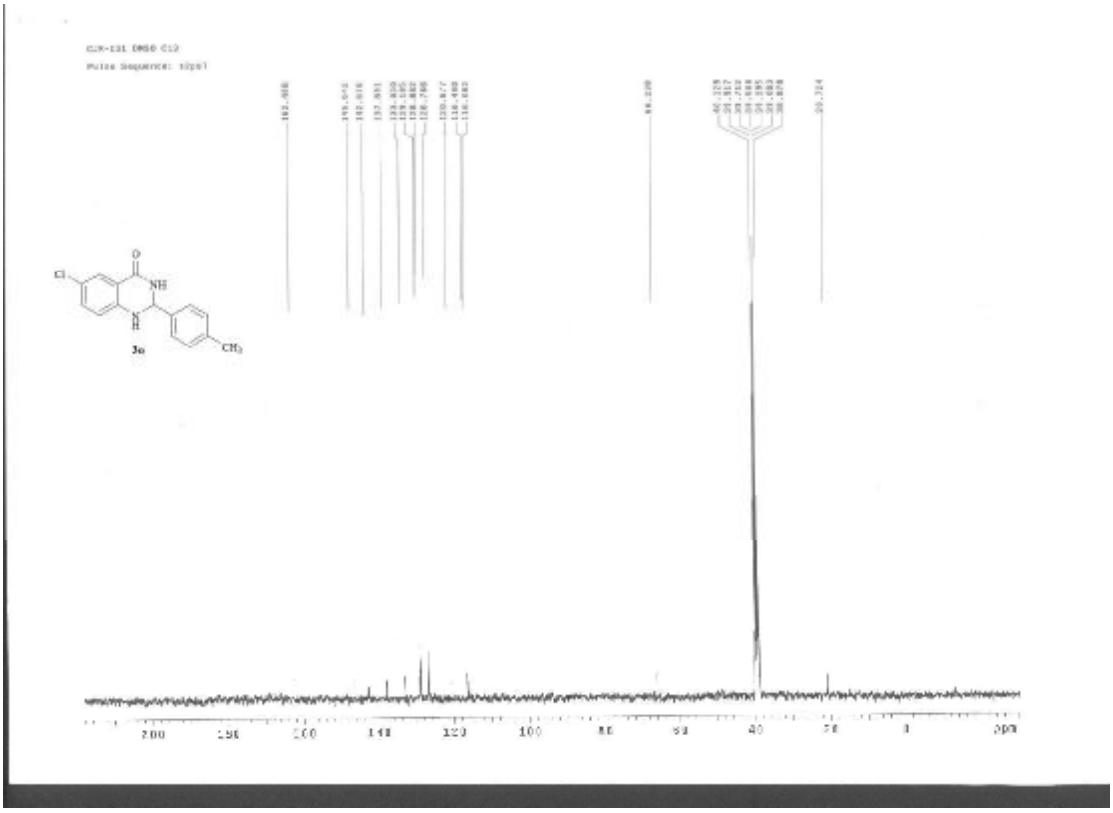








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NH
3o
CH3
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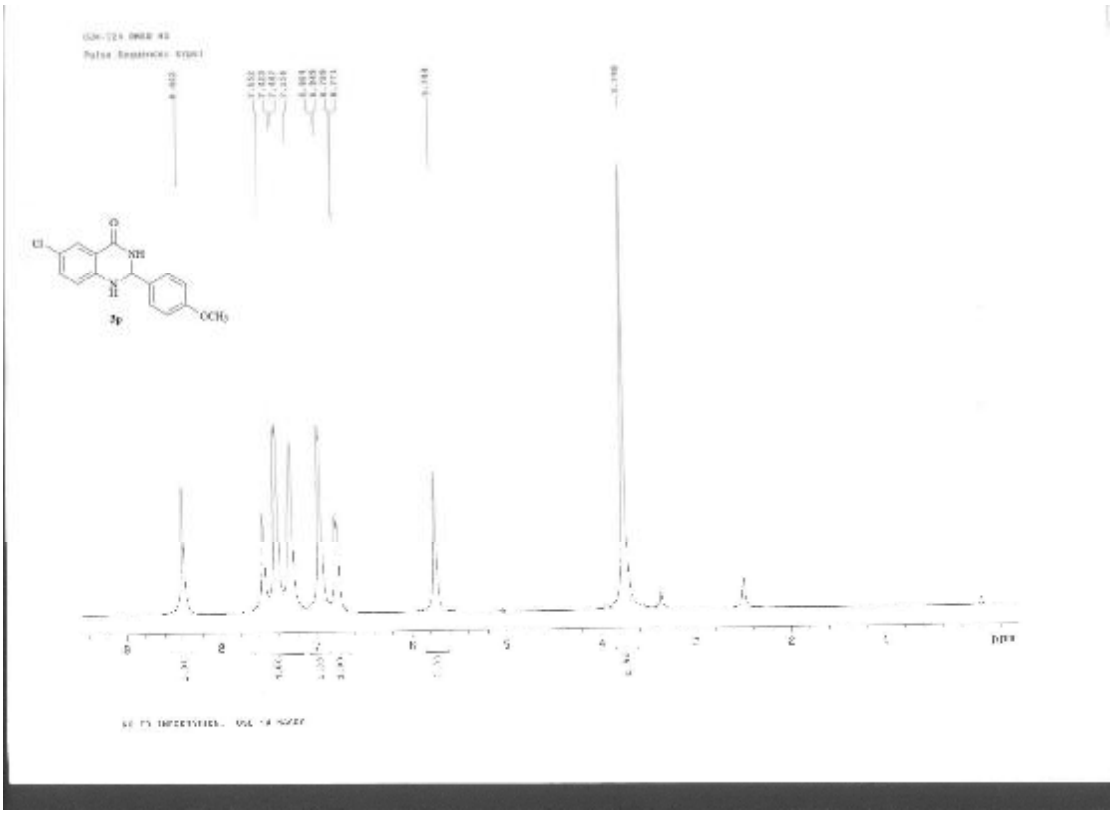
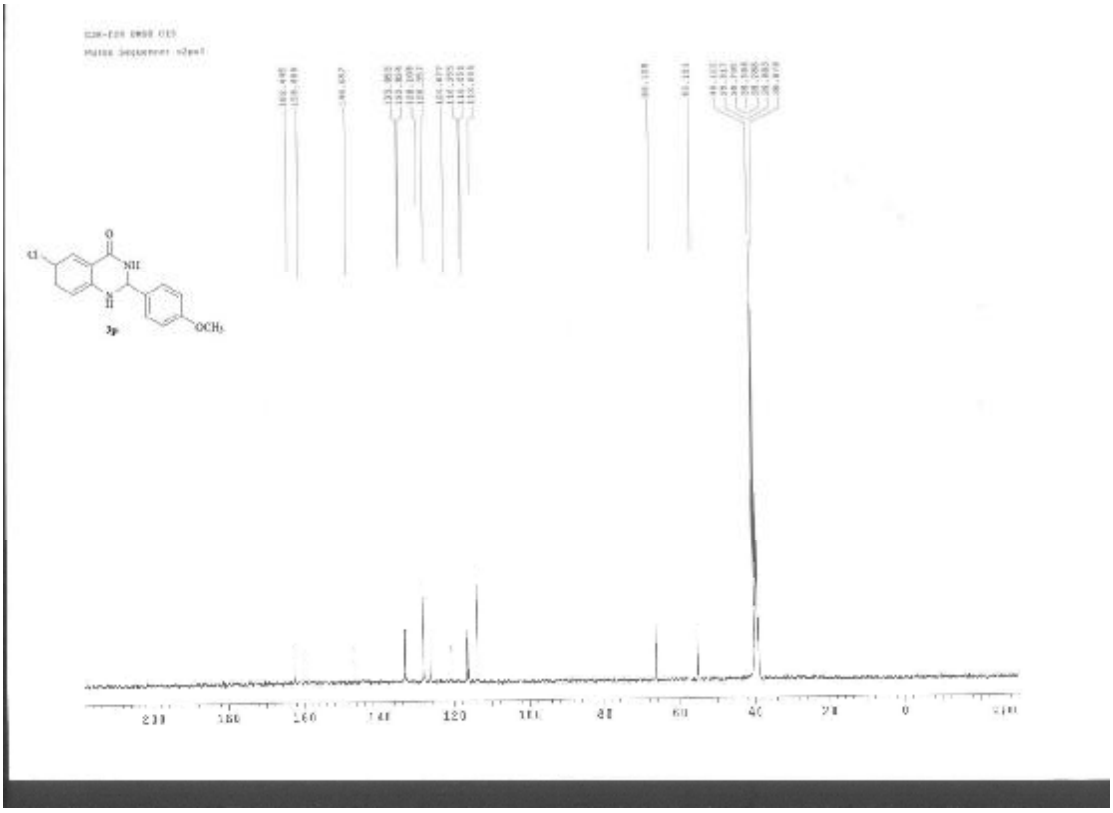
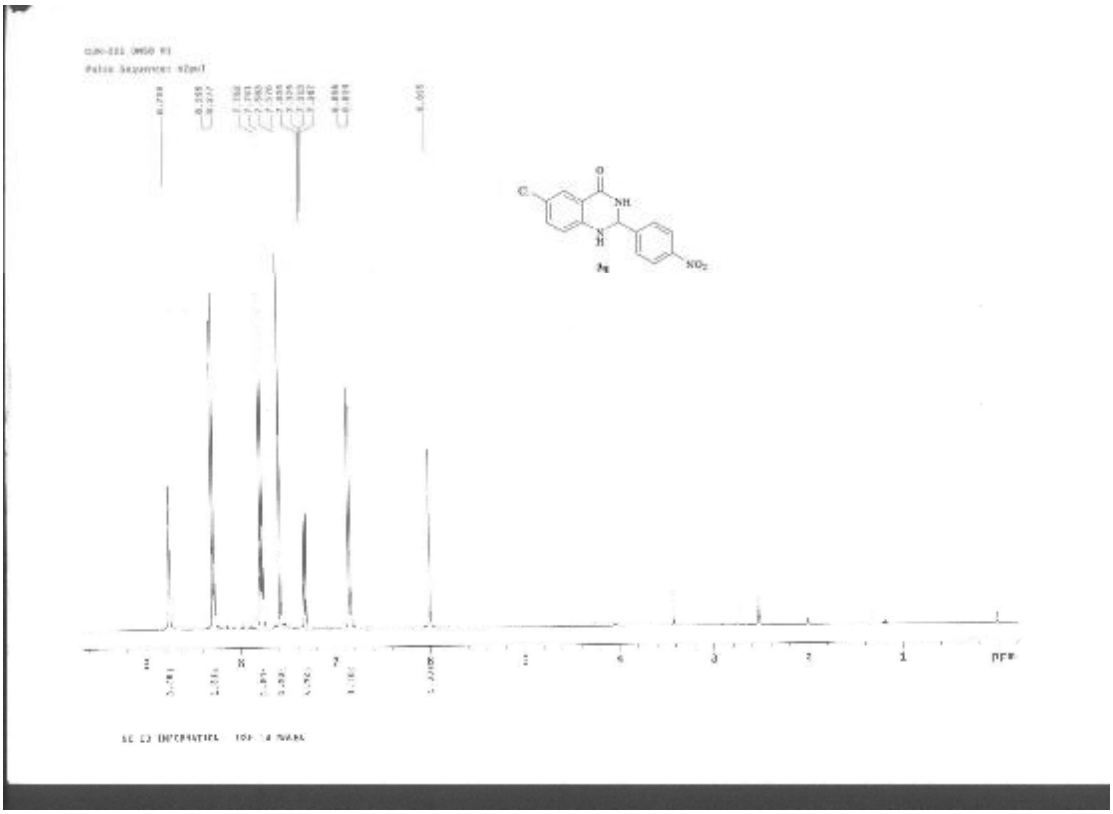
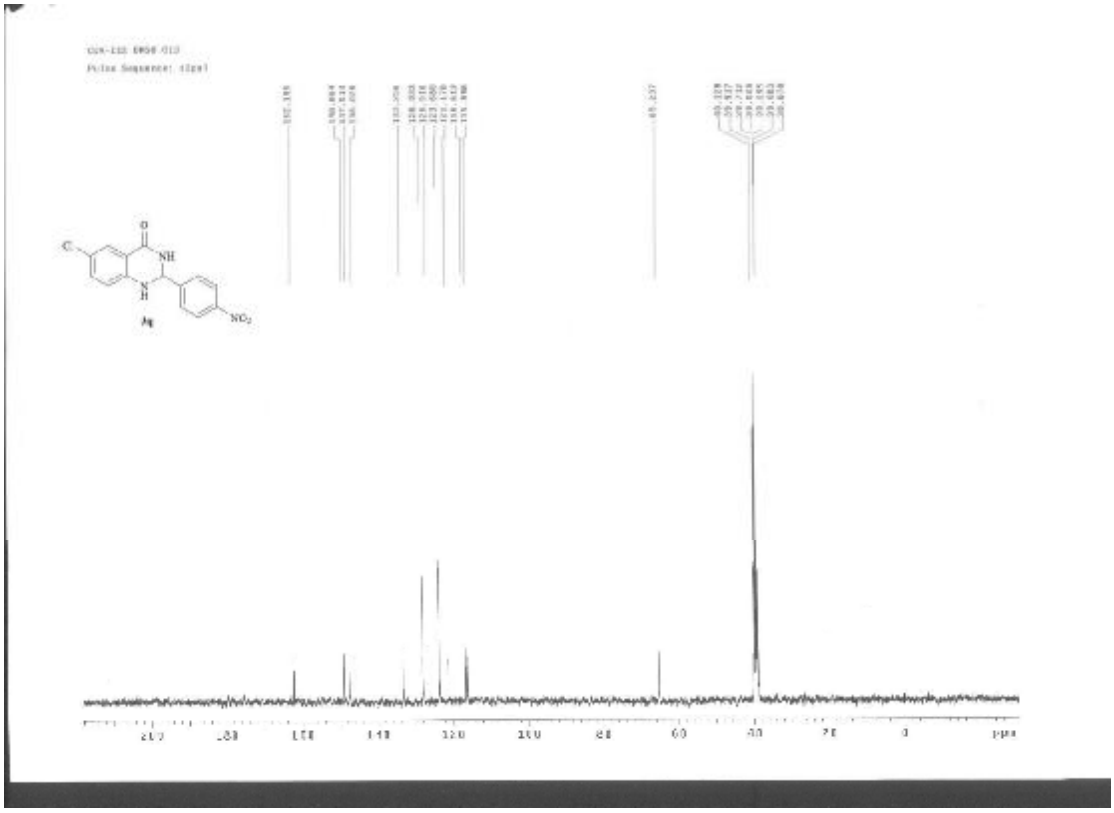
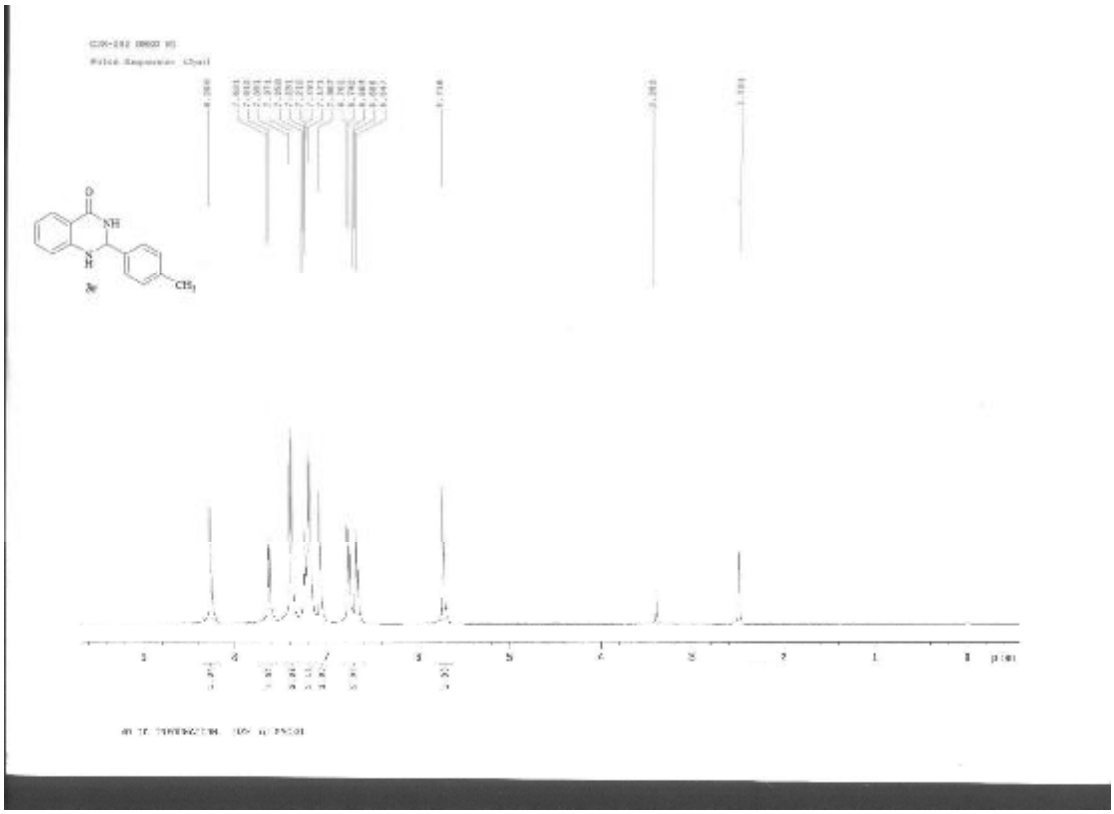
150
100
50
0
ppm

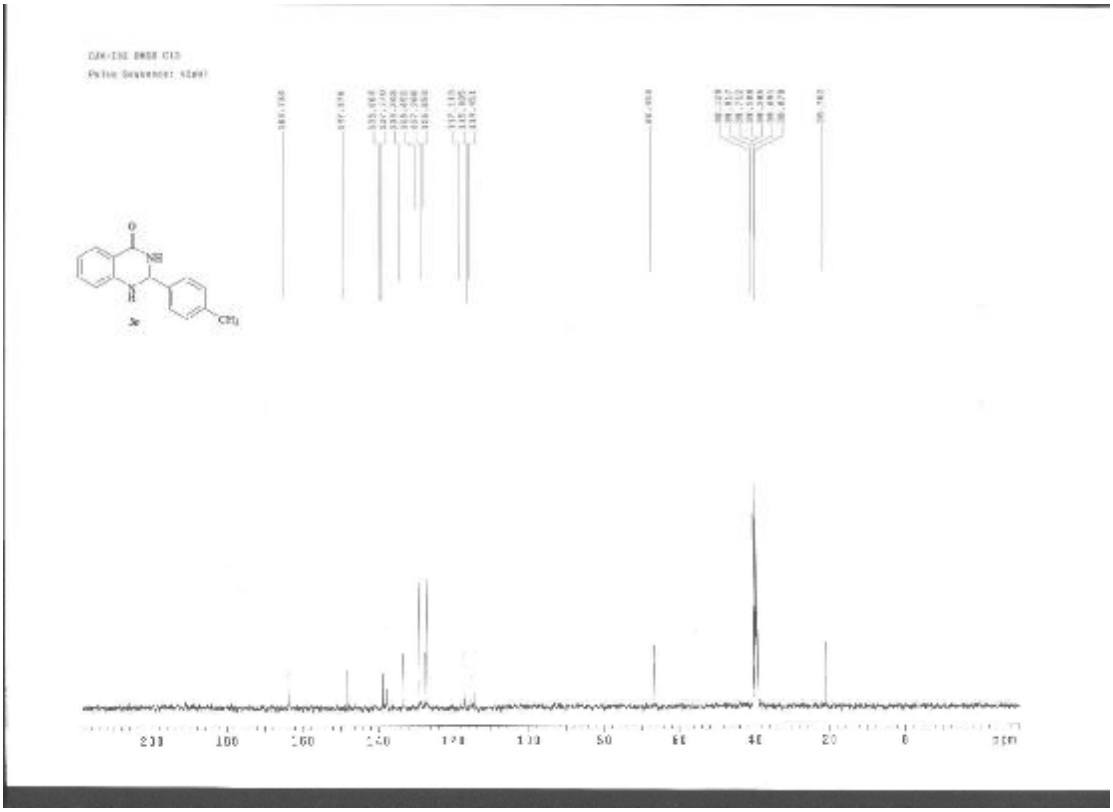

Cl
NH
3p
OCH3
ppm

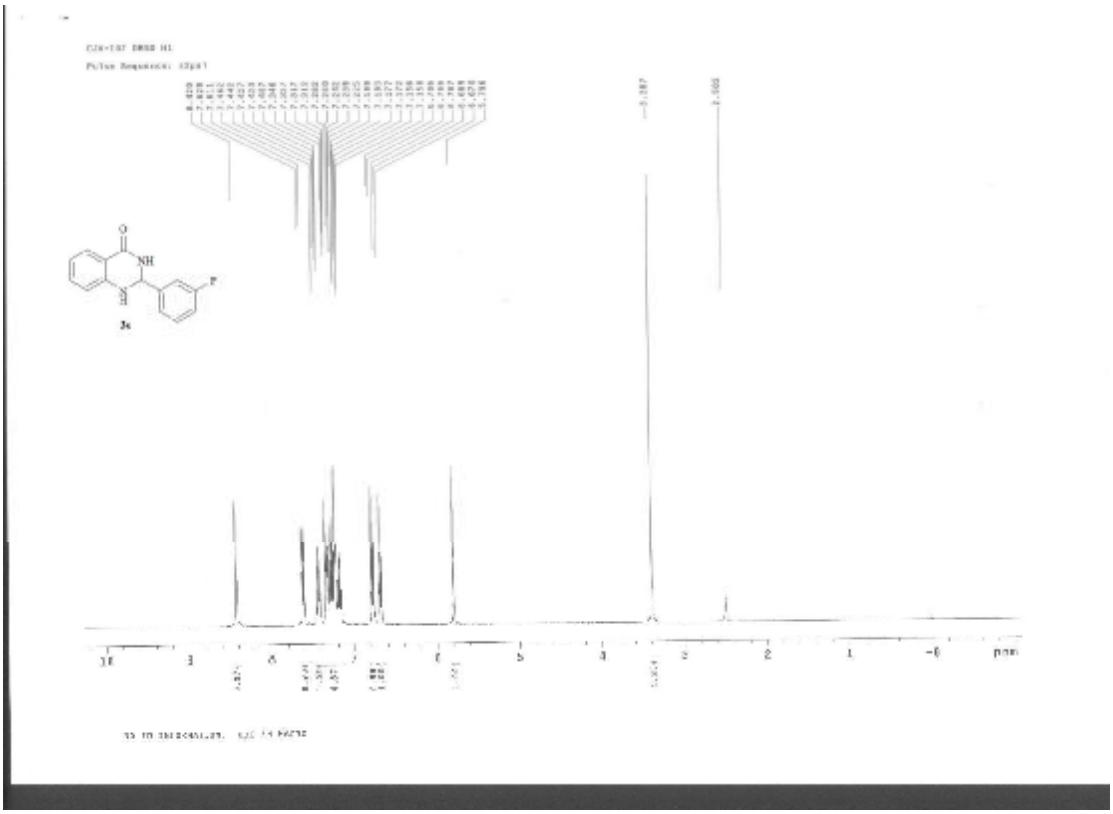


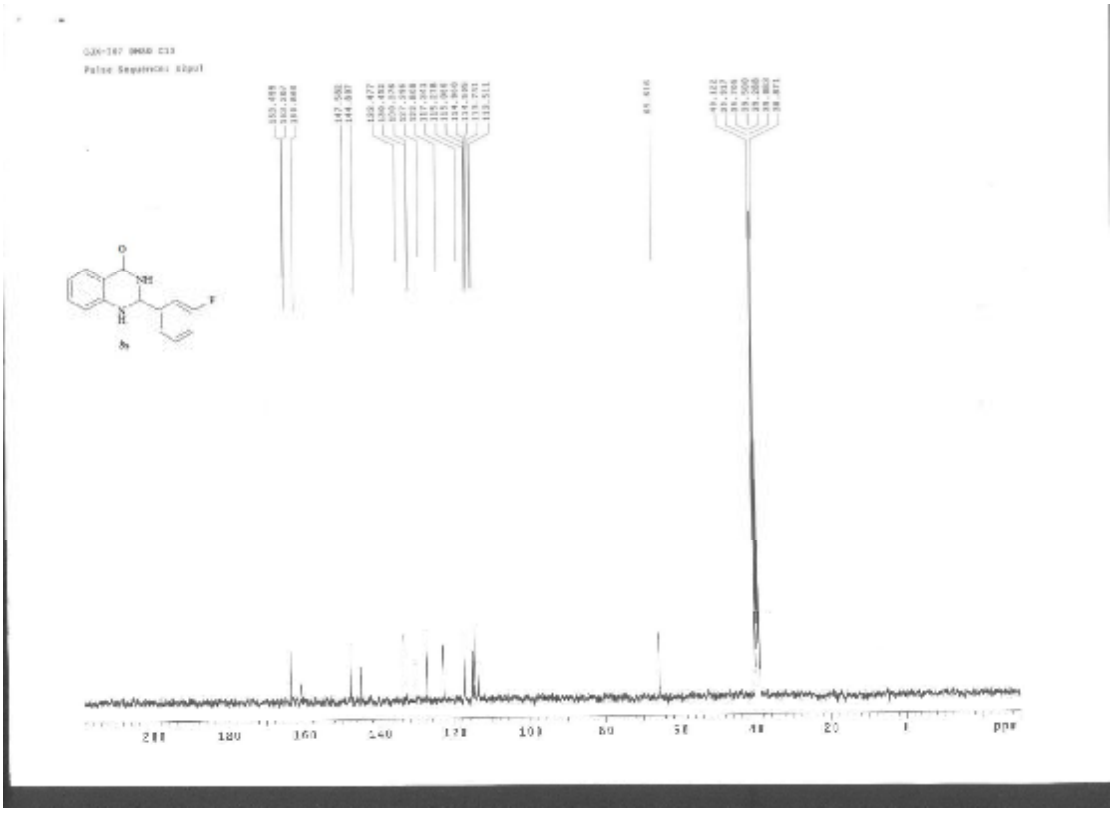


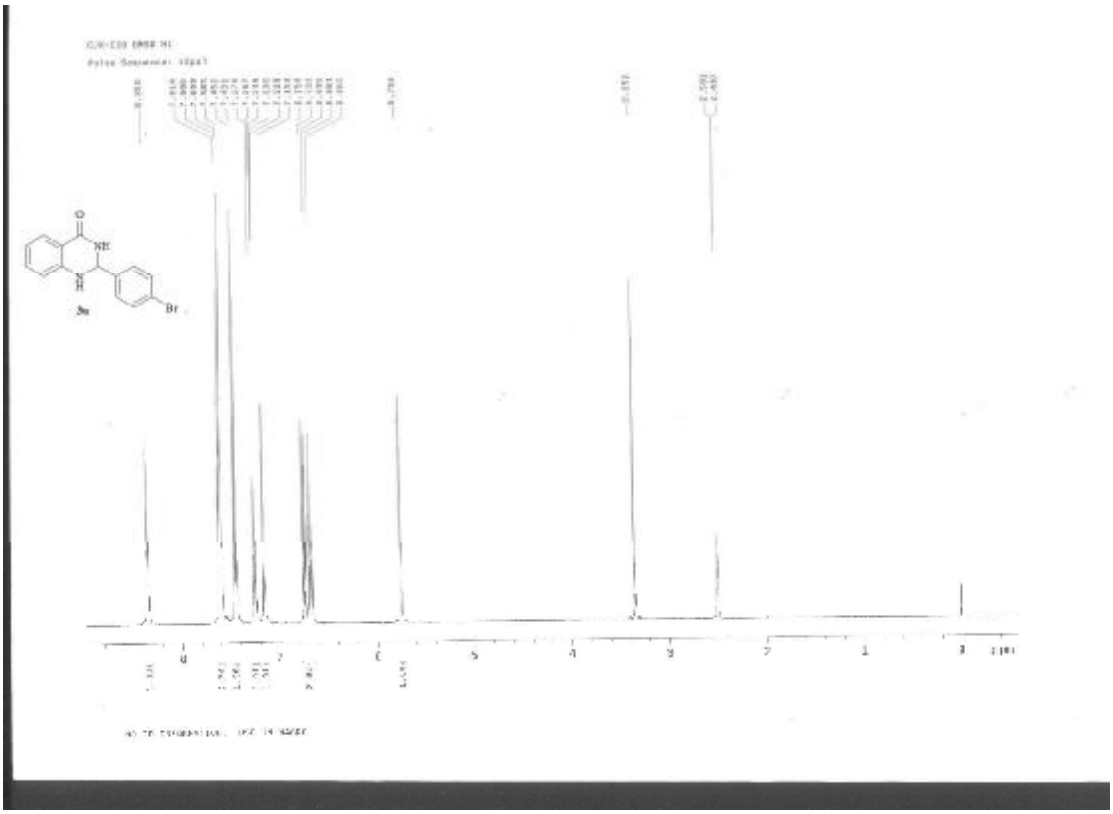












4. References

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