Electro-oxidative C–H Azolation of Quinoxalin-2(1*H*)-ones

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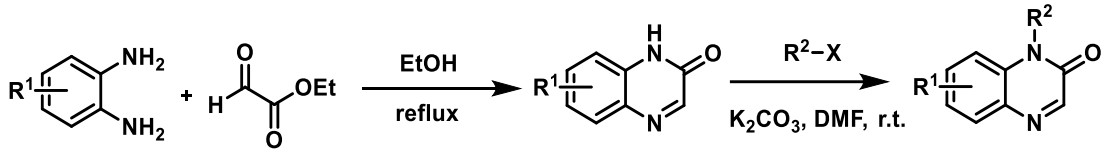
Supporting Information

1. General Information

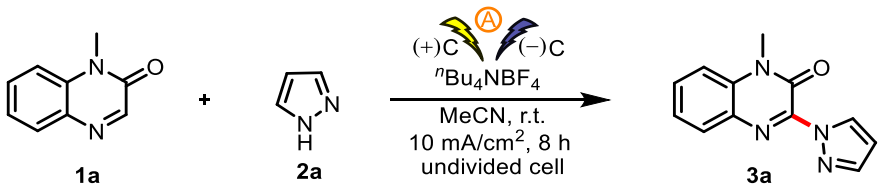
Unless otherwise noted, Reagents were purchased from commercial sources and were used as received. ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 400 Ultrashield NMR spectrometers. Chemical shifts (δ) were given in parts per million (ppm) and were measured downfield from internal tetramethylsilane. High-resolution mass spectrometry (HRMS) data were obtained on an FTICR-MS instrument (Ionspec 7.0 T). The melting points were determined on an X-4 microscope melting point apparatus and are uncorrected. Conversion was monitored by thin layer chromatography (TLC). Flash column chromatography was performed over silica gel (100-200 mesh).

2. Preparation of quinoxalin-2(1*H*)-one



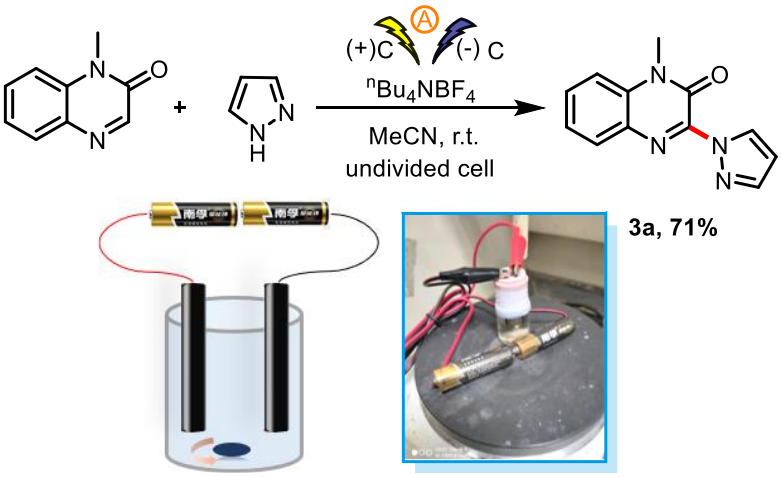
Quinoxalin-2(1*H*)-one was prepared from 1,2-phenylenediamines following the procedure of Cui and co-workers [1] on 5 mmol scale. To a solution of 1,2-phenylenediamines (5 mmol, 1.0 equiv.) in ethanol (40 mL) was added ethyl glyoxalate (6 mmol, 1.2 equiv.). The resultant reaction mixture was stirred at reflux until the raw material disappears. Then, the mixture was filtered and washed by ethanol. The solid was dried *in vacuo*. For alkylation, the corresponding halogenoalkane (1.6 equiv.) was added to a suspension of quinoxalinone (1.0 equiv.) and potassium carbonate (1.2 equiv.) in DMF (16 mL). The mixture was stirred at room temperature overnight. After complete reaction, brine was added, and then extracted three times with EtOAc. The combined organic layers were washed with a saturated solution of NH_4Cl then brine, dried over anhydrous Na_2SO_4, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product.

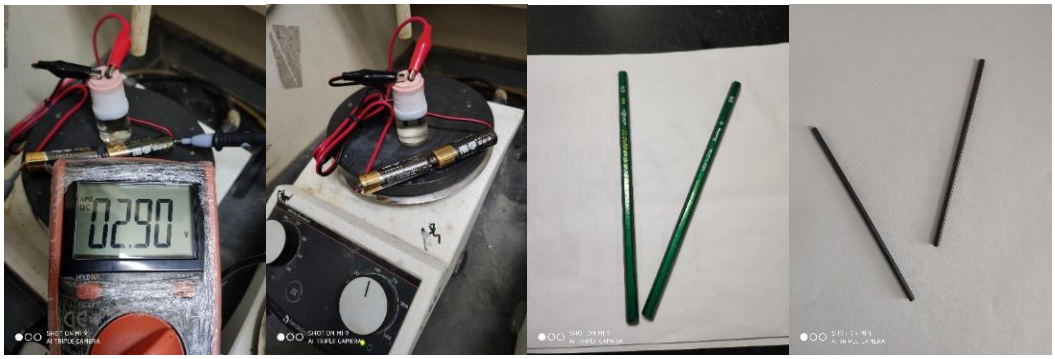
3. General procedure for the electrolysis



An oven-dried 10 mL undivided cell was equipped with two graphite sheet electrodes (10 mm × 10 mm × 3 mm). The corresponding quinoxalin-2(1*H*)-one (80.0 mg, 0.5 mmol, 1.0 equiv.), the pyrazole (68.1 mg, 1.0 mmol, 2.0 equiv.) and $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.) was added into the undivided cell. And then MeCN (5 mL) was added. The reaction mixture was stirred and electrolyzed at a constant current of 10.0 mA at room temperature for 8 h. The solvent was concentrated in vacuo. The pure product was obtained by flash column chromatography on silica gel (petroleum ether/ethyl acetate).

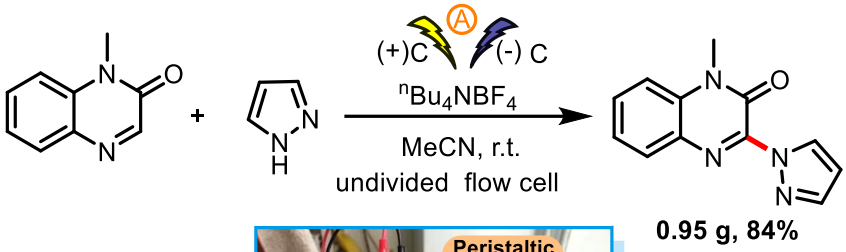
4. Use of 3-V battery as power source

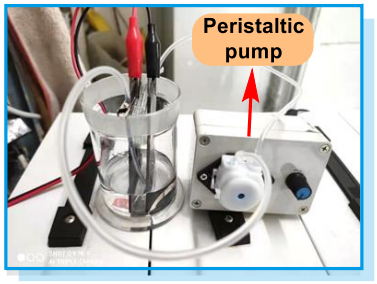




An oven-dried 10 mL undivided cell was charged with quinoxalin-2(1*H*)-one (80.0 mg, 0.5 mmol, 1.0 equiv.), pyrazole (68.1 mg, 1.0 mmol, 2.0 equiv.), $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.) and MeCN (5 mL). Two pencil leadswere first removed from the pencil and inserted into the mixture (30 mm ×Φ A = 2 mm). Two 1.5 v NanFu batteries were connected by copper wires in series and were used as the power source. The reaction mixture was electrolyzed at room temperature for 24 h. After the reaction, the resulting mixture concentrated in vacuo and the crude material was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to furnish the desired product in 71% yield.

5. Gram-scale Reaction





PRODUCT INRTODUCTION

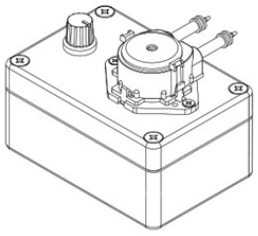
Product model： RZ1020 Peristaltic Pump

Motor type： 12 V DC motor

Speed range： ≤4500 rpm

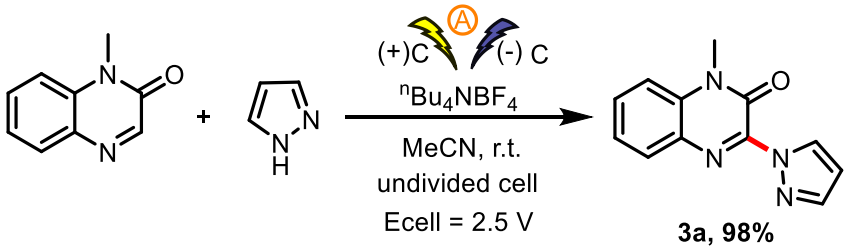
Rated current： 0.15 A

Rated power： 1.6 W



A 200 mL bottle with a stir bar was charged with quinoxalin-2(1*H*)-one (0.80 g, 5.0 mmol, 1.0 equiv.), pyrazole (0.68 g, 10.0 mmol, 2.0 equiv.) and $^{n}Bu_4NBF_4$ (3.30 g, 1.0 mmol, 2.0 equiv.) and MeCN (100 mL). Two graphite sheet electrodes (300 mm × 500 mm × 3 mm) were inserted into the mixture. The reaction mixture was then pumped with a speed of 10 mL/min in the loop by peristaltic pump (Purchased from Taobao.com). Then, the reaction mixture was electrolyzed under a constant current of 60 mA at room temperature for 12 h. After the reaction, the electrodes were removed and rinsed with EtOAc. The solvent was concentrated in vacuo and the crude material was purified by column chromatography (petroleum ether/ethyl acetate = 1:1) to furnish the desired product in 84% yield as a white solid.

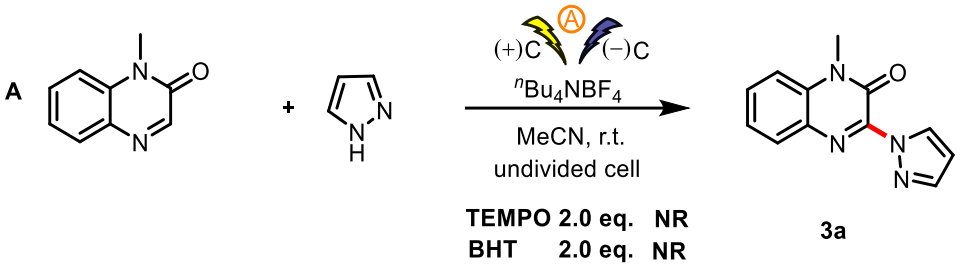
6. Control cell potential electrolysis



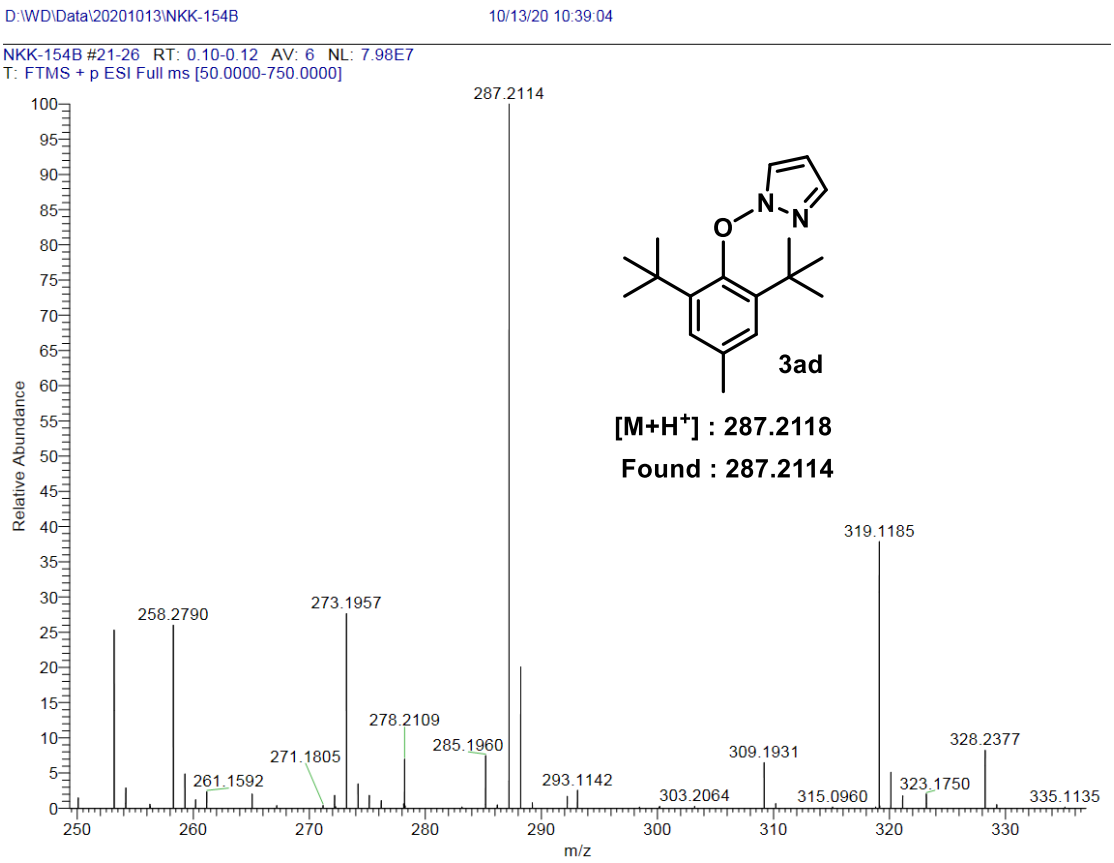
An oven-dried 10 mL undivided bottle was equipped with two graphite sheet electrodes (10 mm × 10 mm × 3 mm). The corresponding quinoxalin-2(1*H*)-one (80.0 mg, 0.5 mmol, 1.0 equiv.), the pyrazole (68.1 mg, 1.0 mmol, 2.0 equiv.) and $^{n}Bu_4NBF_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.) was added

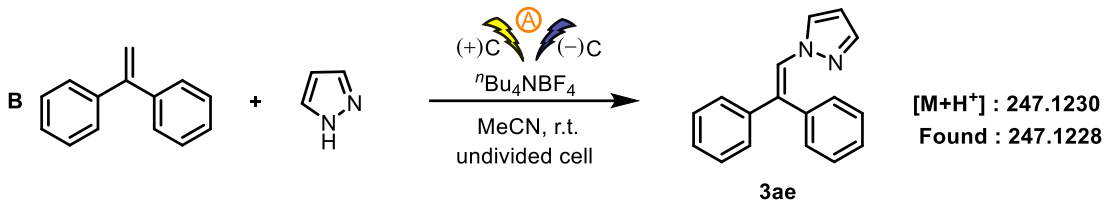
into the undivided cell. And then MeCN (5 mL) was added. The reaction mixture was stirred and electrolyzed at a constant potential of 2.5 V at room temperature for 8 h. The solvent was concentrated in vacuo. The pure product was obtained by column chromatography (petroleum ether/ethyl acetate = 10:1) to furnish the desired product in 98% yield.

7. Mechanistic Studies

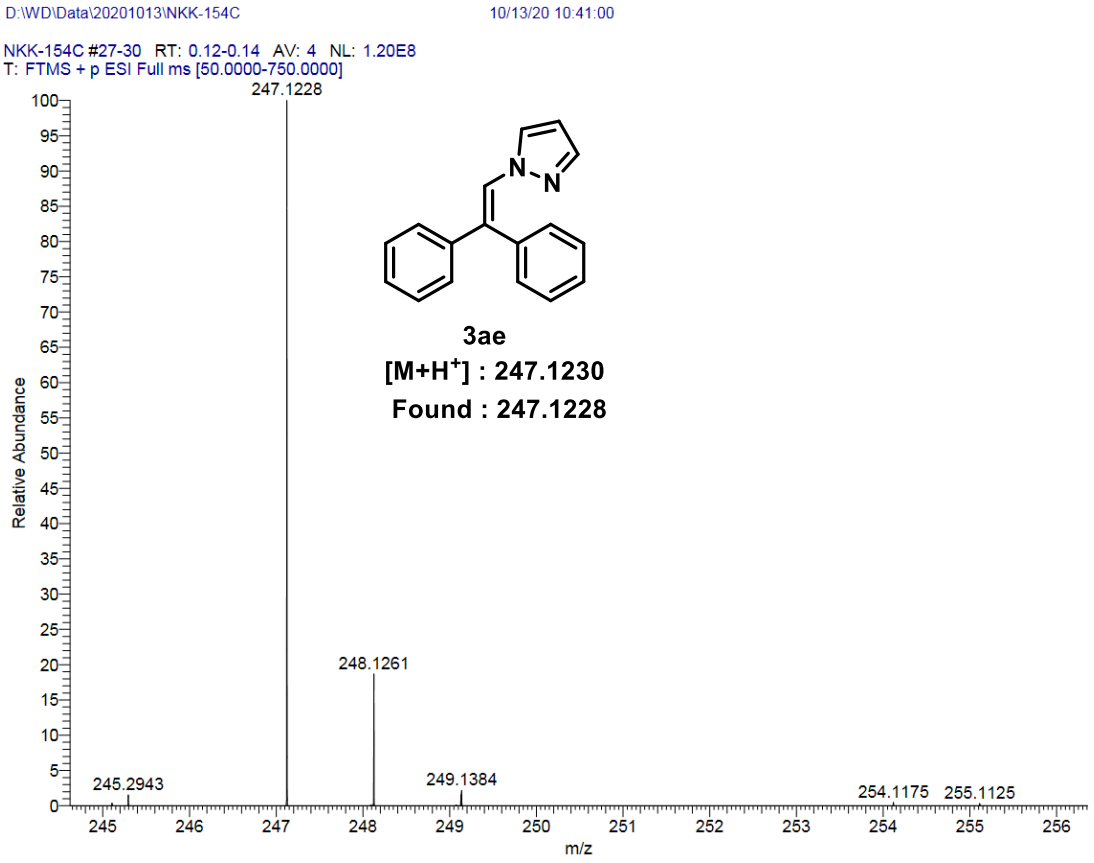


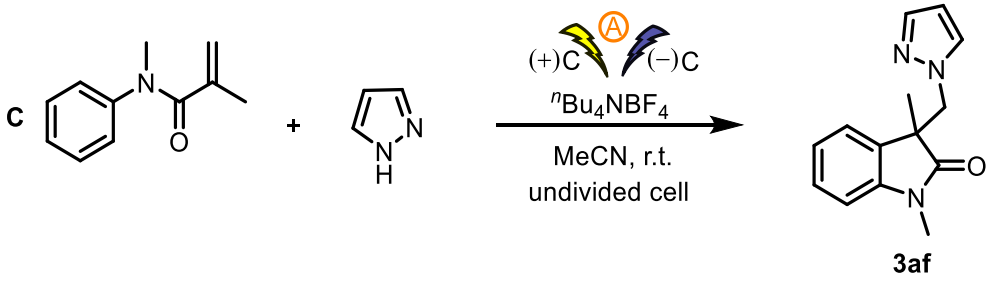
To a 10 mL oven-dried undivided bottle was added quinoxalin-2(1*H*)-one (80.0 mg, 0.5 mmol, 1.0 equiv.), pyrazole (68.1 mg, 1.0 mmol, 2.0 equiv.), ^{n}Bu$_4$NBF$_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), TEMPO (156.3 mg, 1.0 mmol, 2.0 equiv.) and MeCN (5 mL). The reaction mixture was stirred and electrolyzed at a constant current of 10.0 mA at room temperature for 8 h. The reaction was completely suppressed. A similar procedure was conducted with BHT (220.4 mg, 1.0 mmol, 2.0 equiv.). The radical trapping product **3ad** can be observed by HR-MS (positive mode ESI).





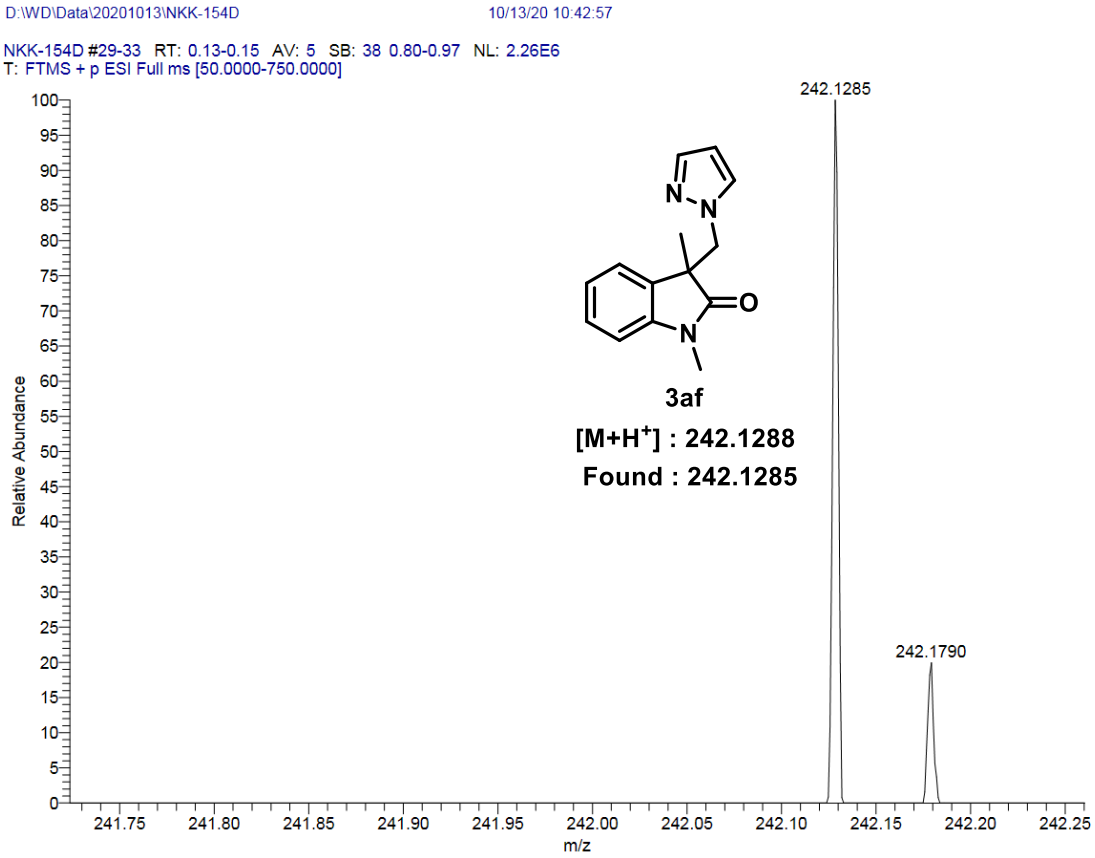
To a 10 mL oven-dried undivided bottle was added 1,1'-(1,2-ethenediyl)dibenzene (88 μL, 0.5 mmol, 1.0 equiv.), pyrazole (68.1 mg, 1.0 mmol, 2.0 equiv.), ^{n}Bu$_4$NBF$_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), TEMPO (156.3 mg, 1.0 mmol, 2.0 equiv.) and MeCN (5 mL). The reaction mixture was stirred and electrolyzed at a constant current of 10.0 mA at room temperature for 8 h. The product **3ae** was observed by HR-MS (positive mode ESI).





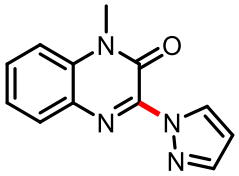
To a 10 mL oven-dried undivided bottle was added N-methyl-N-phenyl methacrylamide (87.6 mg, 0.5 mmol, 1.0 equiv.), pyrazole (68.1 mg, 1.0 mmol, 2.0 equiv.), ^{n}Bu$_4$NBF$_4$ (329.3 mg, 1.0 mmol, 2.0 equiv.), TEMPO (156.3 mg, 1.0 mmol, 2.0 equiv.) and MeCN (5 mL). The reaction mixture was

stirred and electrolyzed at a constant current of 10.0 mA at room temperature for 8 h. The product **3af** was observed by HR-MS (positive mode ESI).



8. Characterization Data for Electrolysis Products

1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3a



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3a** as a white solid (107.8 mg, 95% yield).

M. p. =145 – 146 ℃;

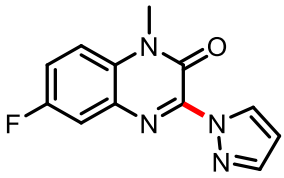
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, *J* = 2.7 Hz, 1H), 8.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.87 (d, *J* = 1.2 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.42 – 7.31 (m, 2H), 6.49 (dd, *J* = 2.6, 1.7 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 143.3, 142.5, 133.2, 132.5, 131.2, 130.1, 130.0, 124.5, 113.6, 108.2, 29.9.

HRMS (ESI): Calcd for $C_{12}H_{11}N_4O$ $[M+H]^+$: 227.0927; found: 227.0924

6-fluoro-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3b



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3b** as a yellow solid (70.1 mg, 57% yield).

M. p. = 188 – 189 ℃;

Rf = 0.2 (Petroleum ether /EtOAc = 1:1);

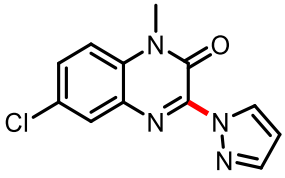
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 7.91 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.41 – 7.26 (m, 2H), 6.53 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 158.0, 150.2, 143.8, 143.4, 133.4, 132.0 (d, *J* = 11.8 Hz), 129.2, 118.0, 117.8, 115.4, 115.2, 114.8 (d, *J* = 8.8 Hz), 108.6, 30.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.2 (s).

HRMS (ESI): Calcd for $C_{12}H_{10}FN_4O$ $[M+H]^+$:245.0833 ; found: 245.0831

6-chloro-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3c



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3c** as a

yellow solid (116.0 mg, 89% yield).

M. p. = 183 – 184 ℃;

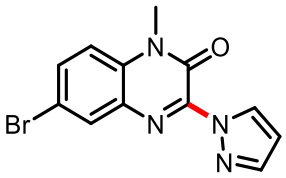
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.94 (d, *J* = 29.9 Hz, 2H), 7.49 (s, 1H), 7.30 – 7.21 (m, 1H), 6.52 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 143.7, 143.2, 133.3, 131.8, 131., 130.0, 129.9, 129.2, 114.8, 108.6, 30.06.

HRMS (ESI): Calcd for $C_{12}H_{10}ClN_4O$ $[M+H]^+$: 261.0538; found: 261.0537

6-bromo-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3d



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3d** as a yellow solid (133.3 mg, 87% yield).

M. p. = 186 – 187 ℃;

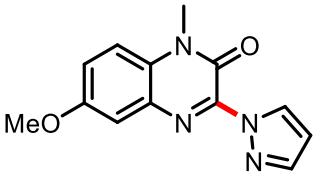
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 1.7 Hz, 1H), 8.12 (s, 1H), 7.89 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.51 (s, 1H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 143.8, 143.1, 133.3, 132.7, 132.3, 132.0, 131.6, 117.2, 115.1, 108.6, 30.1.

HRMS (ESI): Calcd for $C_{12}H_{10}BrN_4O$ $[M+H]^+$: 305.0032; found: 305.0031

6-methoxy-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3e



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3e** as a white solid (90.2 mg, 70% yield).

M. p. = 193 – 194 ℃;

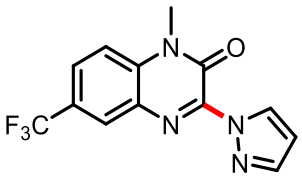
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.91 (s, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.30 (d, *J* = 9.4 Hz, 1H), 7.22 (d, *J* = 2.1 Hz, 1H), 6.53 (s, 1H), 3.89 (s, 3H), 3.83 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7, 150.2, 143.4, 142.9, 133.3, 132.2, 126.8, 119.7, 114.6, 111.3, 108.3, 55.8, 30.0.

HRMS (ESI): Calcd for $C_{13}H_{13}N_4O_2$ $[M+H]^+$:257.1033 ; found: 257.1030

1-methyl-3-(1H-pyrazol-1-yl)-6-(trifluoromethyl)quinoxalin-2(1*H*)-one 3f



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3f** as a white solid (120.4 mg, 82% yield).

M. p. = 218 – 219 ℃;

Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

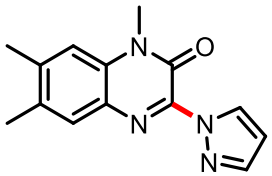
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, J = 2.5 Hz, 1H), 8.31 (s, 1H), 7.91 (s, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.46 (d, J = 8.7 Hz, 1H), 6.53 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 144.0, 143.4, 134.6, 133.3, 130.7, 127.7 – 127.2 (m), 127.1, 126.7, 126.5 – 126.0 (m), 124.9, 122.2, 119.5, 114.4, 110.1 – 109.9 (m), 108.8, 30.2.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2 (s).

HRMS (ESI): Calcd for $C_{13}H_{10}F_3N_4O$ $[M+H]^+$: 295.0801; found: 295.0798

1,6,7-trimethyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3g



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3g** as a white solid (96.1 mg, 76% yield).

M. p. = 205 – 206 ℃;

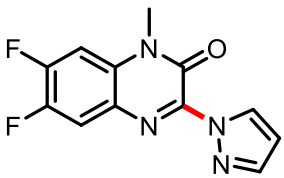
Rf = 0.5 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, J = 2.0 Hz, 1H), 7.87 (s, 1H), 7.73 (s, 1H), 7.06 (s, 1H), 6.49 (s, 1H), 3.75 (s, 3H), 2.37 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 142.9, 141.7, 140.2, 133.6, 132.9, 130.5, 130.0, 129.4, 114.1, 107.9, 29.7, 20.5, 19.3.

HRMS (ESI): Calcd for $C_{14}H_{15}N_4O$ $[M+H]^+$:255.1240; found: 255.1236

6,7-difluoro-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3h



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3h** as a white solid (71.8 mg, 55% yield).

M. p. = 203 – 204 ℃;

Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, J = 2.5 Hz, 1H), 7.92 (s, 1H), 7.87 (dd, J = 10.0, 8.4 Hz, 1H),

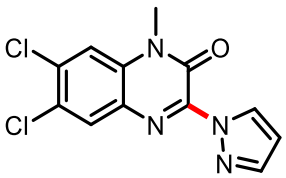
7.20 (dd, *J* = 11.0, 7.0 Hz, 1H), 6.55 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6 (d, *J* = 13.7 Hz), 146.2 (d, *J* = 13.9 Hz), 143.8 (s), 142.8 (s), 133.3 (s), 129.7 (d, *J* = 7.8 Hz), 127.7 (dd, *J* = 10.0, 2.6 Hz), 117.7 (d, *J* = 19.5 Hz), 108.7, 102.6, 102.4, 30.52.

^{19}F NMR (376 MHz, $CDCl_3$) δ -130.2 (d, *J* = 22.5 Hz), -140.0 (d, *J* = 22.4 Hz).

HRMS (ESI): Calcd for $C_{12}H_9F_2N_4O$ $[M+H]^+$: 263.0739; found: 263.0739

6,7-dichloro-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1H)-one 3i



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3i** as a white solid (122.1 mg, 83% yield).

M. p. = 178 – 179 ℃;

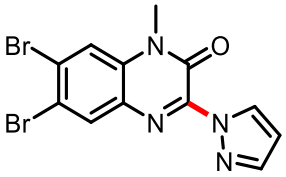
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.10 (s, 1H), 7.91 (s, 1H), 7.46 (s, 1H), 6.54 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 144.0, 143.2, 134.1, 133.4, 131.8, 130.7, 130.4, 128.5, 115.2, 108.9, 30.2.

HRMS (ESI): Calcd for$C_{12}H_9Cl_2N_4O$ $[M+H]^+$:295.0148 ; found: 295.1047

6,7-dibromo-1-methyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3j



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3j** as a white solid (179.7 mg, 94% yield).

M. p. = 182 – 183 ℃;

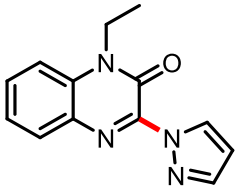
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 2.1 Hz, 1H), 8.26 (s, 1H), 7.91 (s, 1H), 7.63 (s, 1H), 6.53 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 150.2, 144.1, 143.3, 133.9, 133.4, 131.1, 126.3, 120.0, 118.6, 118.3, 108.9, 77.4, 77.1, 76.7, 30.2.

HRMS (ESI): Calcd for $C_{12}H_9Br_2N_4O$ $[M+H]^+$:382.9138 ; found: 382.9135

1-ethyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3k



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was

purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3k** as a white solid (108.8 mg, 91% yield).

M. p. = 114 – 115 ℃;

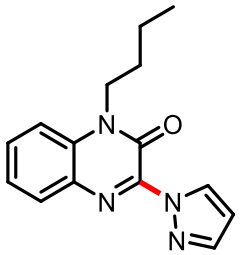
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (d, *J* = 2.3 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.89 (s, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 9.0 Hz, 2H), 6.51 (s, 1H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 143.2, 142.5, 133.2, 131.5, 131.4, 130.3, 130.0, 124.3, 113.5, 108.1, 38.2, 12.3.

HRMS (ESI): Calcd for $C_{13}H_{13}N_4O$ $[M+H]^+$:241.1084 ; found: 241.1080

1-butyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3l



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3l** as a yellow oil (68.0 mg, 51% yield).

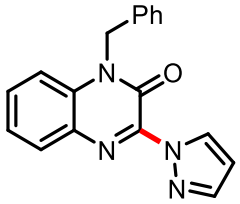
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (d, *J* = 2.3 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.44 – 7.33 (m, 2H), 6.52 (s, 1H), 4.43 – 4.28 (m, 2H), 1.85 – 1.74 (m, 2H), 1.58 – 1.42 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 143.3, 142.5, 133.1, 131.7, 131.5, 130.3, 129.9, 124.3, 113.6, 108.1, 43.0, 29.2, 20.2, 13.7.

HRMS (ESI): Calcd for $C_{15}H_{17}N_4O$ $[M+H]^+$: 269.1397; found: 269.1396

1-benzyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3m



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3m** as a white solid (127.8 mg, 85% yield).

M. p. = 138 – 139 ℃;

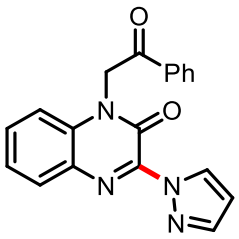
Rf = 0.5 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.92 (s, 1H), 7.49 – 7.40 (m, 1H), 7.35 – 7.20 (m, 7H), 6.51 (s, 1H), 5.58 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 143.4, 142.5, 134.5, 133.2, 131.8, 131.3, 130.1, 130.0, 128.9, 127.8, 126.6, 124.5, 114.3, 108.2, 46.52.

HRMS (ESI): Calcd for $C_{18}H_{15}N_4O$ $[M+H]^+$:303.1240 ; found: 303.1237

1-(2-oxo-2-phenylethyl)-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3n



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3n** as a white solid (143.0 mg, 87% yield).

M. p. = 210 – 211 ℃;

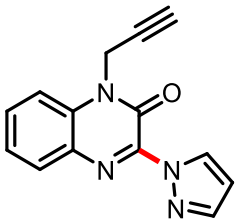
Rf = 0.5 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.5 Hz, 1H), 8.13 – 8.00 (m, 3H), 7.90 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.49 (s, 1H), 5.82 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 150.5, 143.5, 134.6, 134.3, 133.2, 132.0, 131.4, 130.4, 130.2, 129.1, 128.2, 124.7, 113.5, 108.4, 49.2.

HRMS (ESI): Calcd for $C_{19}H_{15}N_4O_2$ $[M+H]^+$:331.1190 ; found: 331.1185

1-(prop-2-yn-1-yl)-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3o



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3o** as a yellow solid (103.6 mg, 83% yield).

M. p. = 200 – 201 ℃;

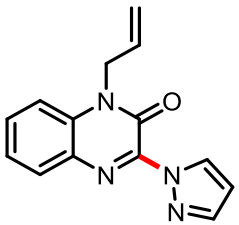
Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.06 (d, *J* = 7.3 Hz, 1H), 7.91 (s, 1H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 6.53 (s, 1H), 5.18 (s, 2H), 2.36 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 143.6, 142.4, 133.2, 131.5, 131.1, 130.3, 130.2, 125.0, 114.1, 108.4, 77.4, 73.7, 32.3.

HRMS (ESI): Calcd for $C_{14}H_{11}N_4O$ $[M+H]^+$: 251.0927; found: 251.0924

1-allyl-3-(1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3p



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3p** as a white solid (102.6 mg, 81% yield).

M. p. = 84 – 85 ℃;

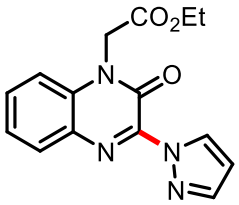
Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 6.03 – 5.89 (m, 1H), 5.30 (d, *J* = 10.4 Hz, 1H), 5.19 (d, *J* = 17.2 Hz, 1H), 5.00 (d, *J* = 3.5 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 143.3, 142.3, 133.1, 131.6, 131.2, 130.1, 129.9, 124.5, 118.3, 114.1, 108.2, 45.1.

HRMS (ESI): Calcd for $C_{14}H_{13}N_4O$ $[M+H]^+$: 253.1084; found: 253.1080

ethyl 2-(2-oxo-3-(1H-pyrazol-1-yl)quinoxalin-1(2*H*)-yl)acetate 3q



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3q** as a yellow solid (100.2 mg, 67% yield).

M. p. = 150 – 151 ℃;

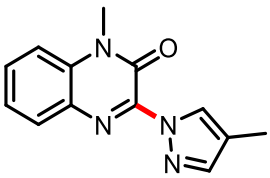
Rf = 0.5(Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (d, *J* = 2.2 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.52 (s, 1H), 5.13 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 150.5, 143.6, 142.4, 133.2, 131.7, 131.3, 130.5, 130.3, 124.9, 113.1, 108.5, 62.3, 44.2, 14.1.

HRMS (ESI): Calcd for $C_{15}H_{15}N_4O_3$ $[M+H]^+$:299.1139 ; found: 299.1136

1-methyl-3-(4-methyl-1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3r



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3r** as a white solid (110.0 mg, 82% yield).

M. p. = 155 – 156 ℃;

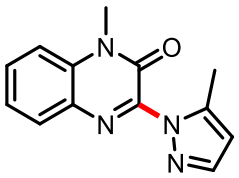
Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.25 (m, 2H), 3.77 (s, 3H), 2.17 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 144.6, 142.4, 132.3, 131.2, 131.1, 129.8, 129.6, 124.3, 118.7, 113.5, 29.7, 8.8.

HRMS (ESI): Calcd for $C_{13}H_{13}N_4O$ $[M+H]^+$: 241.1084 ; found: 241.1082

1-methyl-3-(5-methyl-1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3s



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3s** as a white solid (120.1 mg, 98% yield).

M. p. = 130 – 131 ℃;

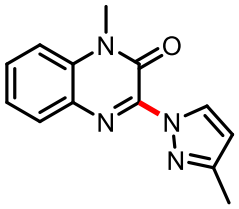
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 1.9 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.43 – 7.30 (m, 2H), 6.32 (d, J = 2.0 Hz, 1H), 3.81 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 150.6, 142.3, 134.1, 132.3, 131.3, 130.1, 129.6, 124.4, 113.6, 109.0, 29.9, 14.1.

HRMS (ESI): Calcd for $C_{13}H_{13}N_4O$ $[M+H]^+$: 241.1084 ; found: 241.1082

1-methyl-3-(3-methyl-1H-pyrazol-1-yl)quinoxalin-2(1*H*)-one 3t



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3t** as a white solid (105.8 mg, 88% yield).

M. p. = 145 – 146 ℃;

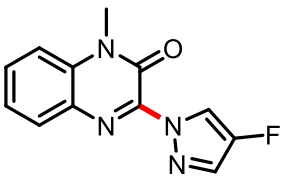
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 2.2 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.42 – 7.28 (m, 2H), 6.31 (d, J = 2.3 Hz, 1H), 3.79 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 150.6, 142.3, 134.1, 132.3, 131.3, 130.1, 129.6, 124.4, 113.6, 109.0, 29.9, 14.1.

HRMS (ESI): Calcd for $C_{13}H_{13}N_4O$ $[M+H]^+$: 241.1084 ; found: 241.1079

3-(4-fluoro-1H-pyrazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3u



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3u** as a yellow solid (85.6 mg, 70% yield).

M. p. = 178 – 179 ℃;

Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.02 (d, J = 6.1 Hz, 1H), 7.80 (s, 1H), 7.59 (d, J = 7.2 Hz,

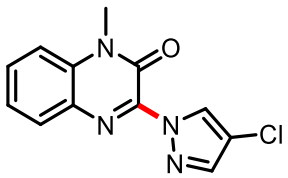
1H), 7.47 – 7.34 (m, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 142.0, 132.7, 132.1 (d, J = 15.8 Hz), 131.1, 130.3 (d, J = 17.4 Hz), 124.7, 118.9 (d, J = 31.5 Hz), 113.8, 29.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -173.5 (s).

HRMS (ESI): Calcd for$C_{12}H_{10}FN_4O$ $[M+H]^+$: 245.0833 ; found: 245.0829

3-(4-chloro-1H-pyrazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3v



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3v** as a yellow solid (92.4 mg, 71% yield).

M. p. = 197 – 198 ℃;

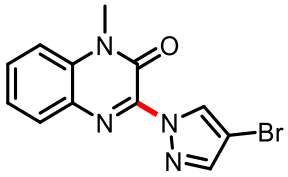
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.09 – 7.99 (m, 1H), 7.83 (d, J = 5.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.48 – 7.35 (m, 2H), 3.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 142.0, 141.8, 132.7, 131.1, 130.8, 130.6, 130.3, 124.8, 113.8, 113.1, 30.0.

HRMS (ESI): Calcd for $C_{12}H_{10}ClN_4O$ $[M+H]^+$: 261.0538; found: 261.0533

3-(4-bromo-1H-pyrazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3w



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3w** as a yellow solid (141.7 mg, 93% yield).

M. p. = 154 – 155 ℃;

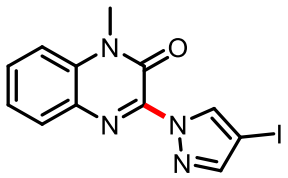
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.87 (s, 1H), 7.62 – 7.55 (m, 1H), 7.44 – 7.32 (m, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 147.8, 141.5, 137.3, 132.6, 130.9, 130.5, 130.2, 124.7, 113.7, 60.4, 30.0.

HRMS (ESI): Calcd for$C_{12}H_{10}BrN_4O$ $[M+H]^+$: 305.0032; found: 305.0041

3-(4-iodo-1H-pyrazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3x



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was

purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3x** as a yellow solid (114.8 mg, 65% yield).

M. p. = 130 – 131 ℃;

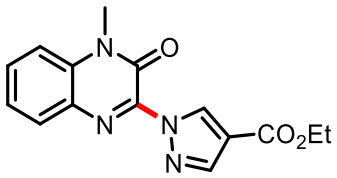
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 2.6 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.45 – 7.34 (m, 2H), 6.66 (d, J = 2.6 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.3, 135.1, 132.6, 131.0, 130.5, 130.4, 124.7, 117.5, 113.7, 102.3, 30.0.

HRMS (ESI): Calcd for $C_{12}H_{10}IN_4O$ $[M+H]^+$: 352.9894; found: 352.9890

ethyl 1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-1H-pyrazole-4-carboxylate 3y



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3y** as a yellow solid (145. 2 mg, 71% yield).

M. p. = 104 – 105 ℃;

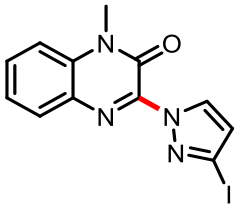
Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.28 (s, 1H), 8.08 – 8.04 (m, 1H), 7.70 – 7.57 (m, 1H), 7.46 (s, 1H), 7.44 – 7.39 (m, 1H), 4.37 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 1.40 (t, J = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 150.4, 143.7, 141.9, 136.5, 132.8, 131.0, 130.5, 124.9, 117.5, 113.8, 60.7, 30.1, 14.4.

HRMS (ESI): Calcd for$C_{15}H_{15}N_4O_3$ $[M+H]^+$: 299.1139; found: 299.1136

3-(3-iodo-1H-pyrazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3z



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3z** as a yellow solid (157.8 mg, 90% yield).

M. p. = 139 – 140 ℃;

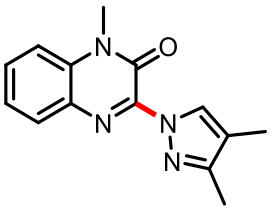
Rf = 0.6 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 2.3 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 – 7.34 (m, 2H), 6.65 (d, J = 2.3 Hz, 1H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 141.2, 135.1, 132.6, 130.9, 130.4, 130.3, 124.6, 123.7, 117.4, 113.7, 102.3, 30.0.

HRMS (ESI): Calcd for $C_{12}H_{10}IN_4O[M+H]^+$: 352.9894; found: 352.9889

3-(3,4-dimethyl-1H-pyrazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3aa



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3aa** as a white solid (90.5 mg, 71% yield).

M. p. = 132 – 133 ℃;

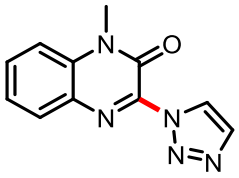
Rf = 0.4 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.32 (m, 2H), 3.81 (s, 3H), 2.37 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.4, 150.8, 142.3, 132.2, 131.8, 131.6, 130.0, 129.3, 124.4, 118.0, 113.5, 29.8, 12.2, 8.6.

HRMS (ESI): Calcd for$C_{14}H_{15}N_4O$ $[M+H]^+$:255.1240; found: 255.1238

1-methyl-3-(1H-1,2,3-triazol-1-yl)quinoxalin-2(1*H*)-one 3ab



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3ab** as a yellow solid (106.6 mg, 94% yield).

M. p. = 148 – 149 ℃;

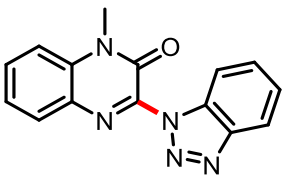
Rf = 0.1 (Petroleum ether /EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 1H), 7.88 (s, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.43 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 141.2, 133.6, 133.4, 131.8, 131.0, 130.9, 125.9, 125.0, 114.0, 30.16.

HRMS (ESI): Calcd for $C_{11}H_{10}N_5O$ $[M+H]^+$: 228.0880; found: 228.0878

3-(1H-benzo[d][1,2,3]triazol-1-yl)-1-methylquinoxalin-2(1*H*)-one 3ac



On 0.5 mmol scale. Electrolysis was conducted following the general procedure. The crude material was purified by flash column chromatography (silica gel, 50% EtOAc in petroleum ether) to give **3ac** as a yellow solid (123.2 mg, 89% yield).

M. p. = 200 – 201 ℃;

Rf = 0.3 (Petroleum ether /EtOAc = 1:1);

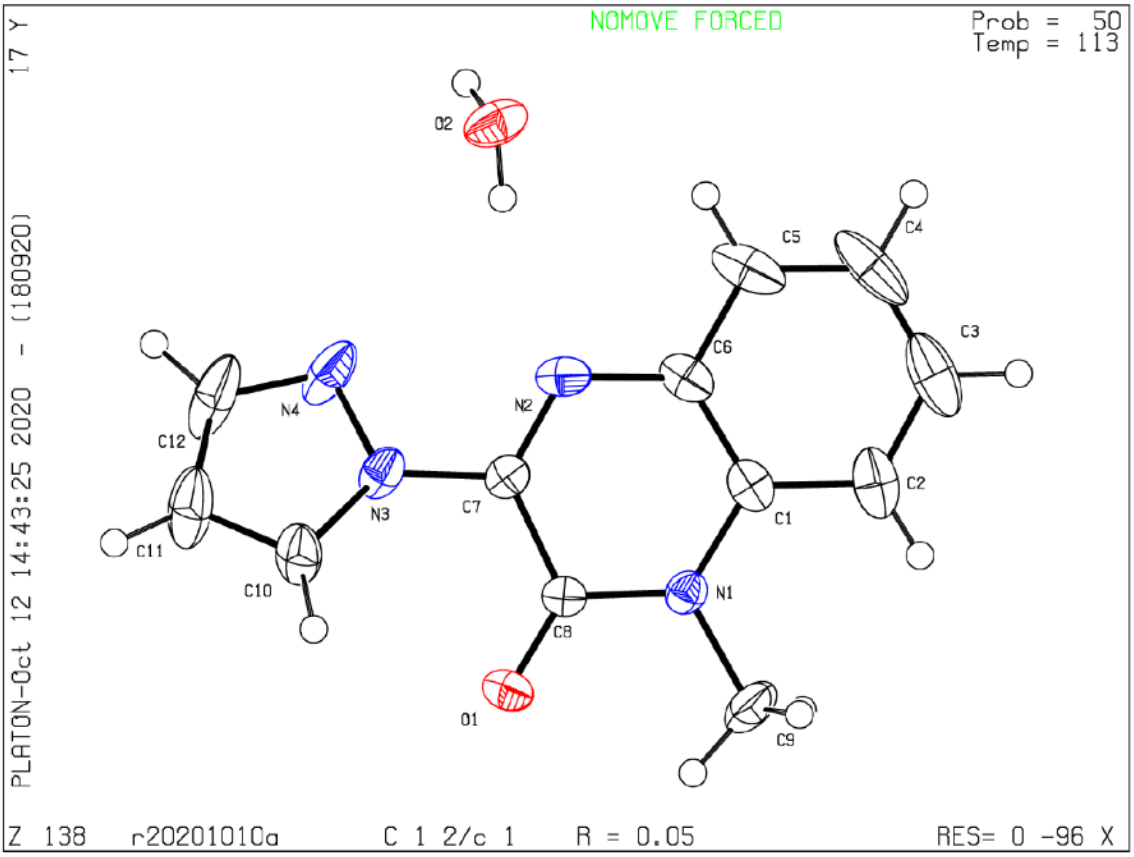
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 7.7 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.61 (t, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 3H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 145.9, 143.5, 133.6, 132.8, 131.7, 130.9, 130.4, 128.8, 125.0, 124.7, 120.2, 114.1, 113.3, 30.2.

HRMS (ESI): Calcd for $C_{15}H_{12}N_5O$ $[M+H]^+$: 278.1036; found: 278.103

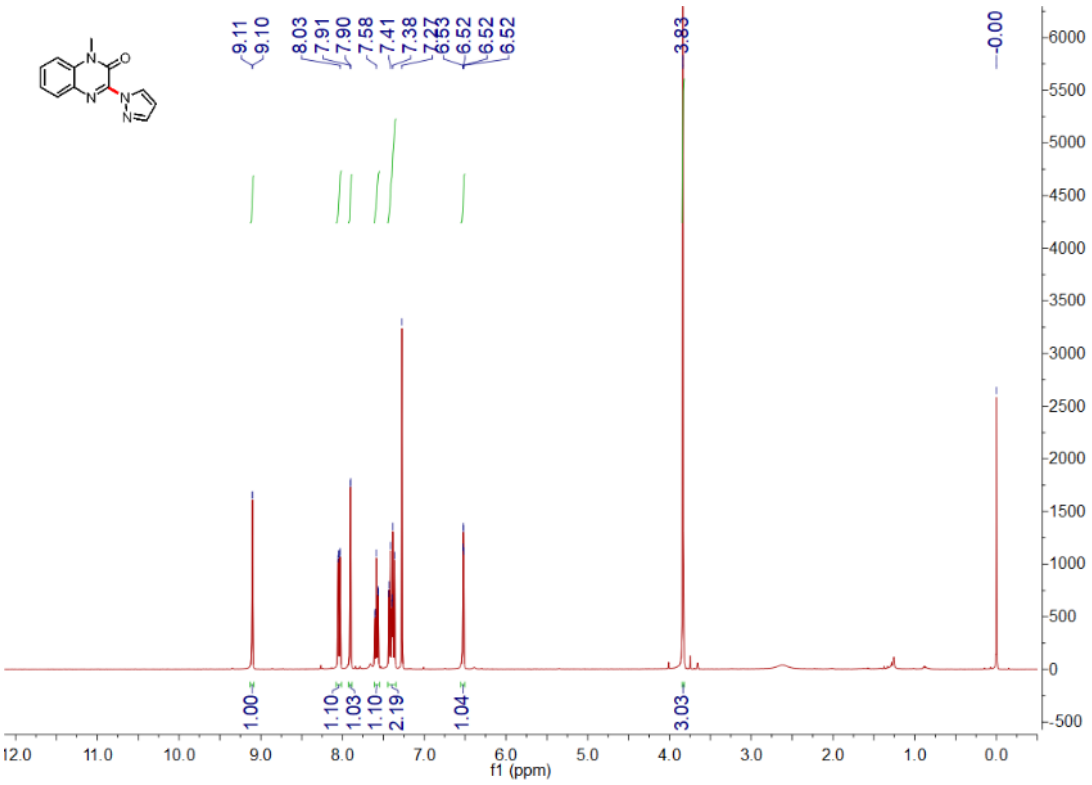
9. X-ray Crystallography

Table 1 Crystal data and structure refinement for r20201010a.	
Identification code	r20201010a
Empirical formula	$C_{12}H_{11}N_4O_{1.5}$
Formula weight	235.25
Temperature/K	113.15
Crystal system	monoclinic
Space group	C2/c
a/Å	18.0472(7)
b/Å	7.0440(3)
c/Å	16.9293(8)
α/°	90
β/°	96.096(4)
γ/°	90
Volume/Å^3	2139.96(16)
Z	8
ρ_{calc}g/cm^3	1.460
μ/mm^{-1}	0.102
F(000)	984.0
Crystal size/mm^3	0.18 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.54 to 52.724
Index ranges	-22 ≤ h ≤ 22, -8 ≤ k ≤ 8, -21 ≤ l ≤ 21
Reflections collected	9092
Independent reflections	2181 [R_{int} = 0.0445, R_{sigma} = 0.0302]
Data/restraints/parameters	2181/1/168
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0471, wR_2 = 0.1138
Final R indexes [all data]	R_1 = 0.0568, wR_2 = 0.1226
Largest diff. peak/hole / e Å^{-3}	0.24/-0.35

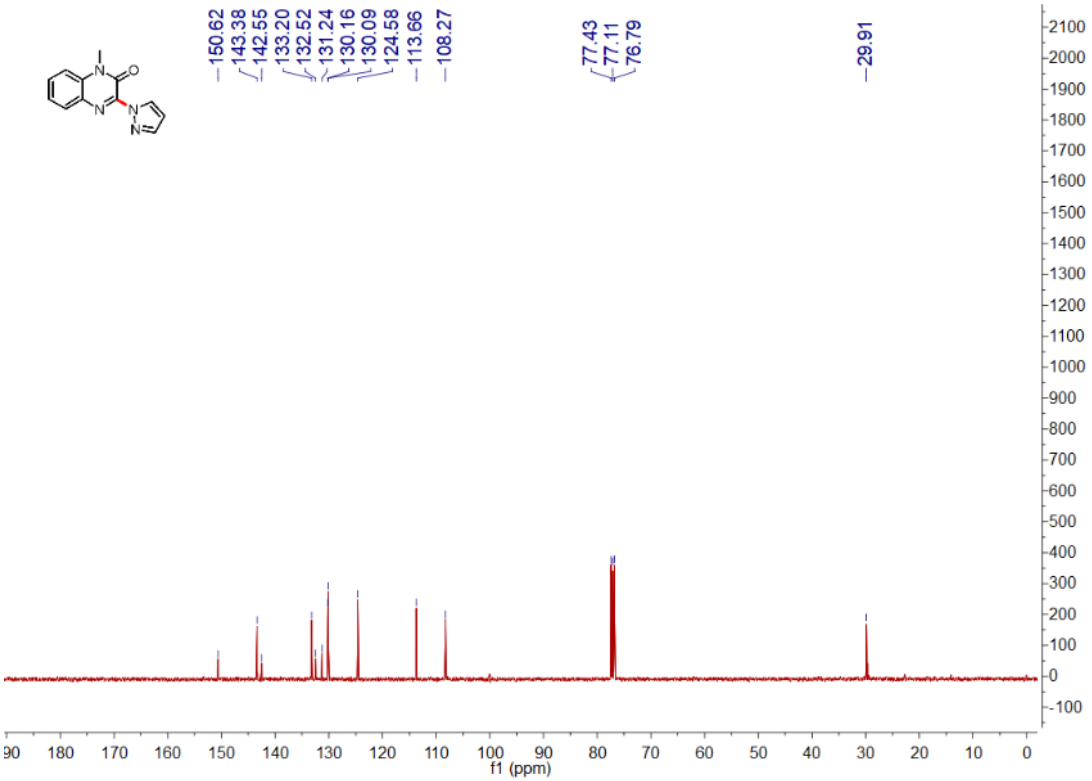

NOMOVE FORCED
Prob = 50
Temp = 113
PLATON-Oct 12 14:43:25 2020 - (180920) 17 Y
O2
C5
C4
C3
C6
N2
N4
C12
C7
N3
C2
C1
C11
C10
N1
C8
O1
C9
Z 138 r20201010a C 1 2/c 1 R = 0.05 RES= 0 -96 X

10. Spectra of prepared compounds

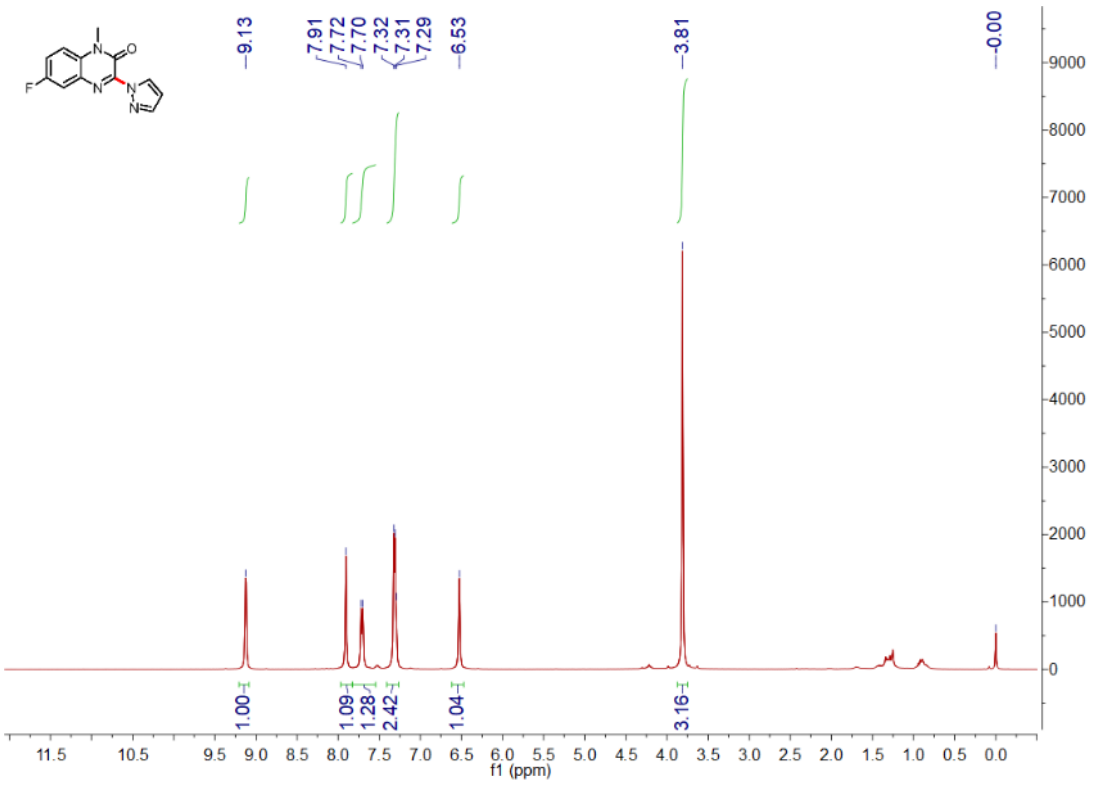
^{1}H NMR spectrum of compound **3a**



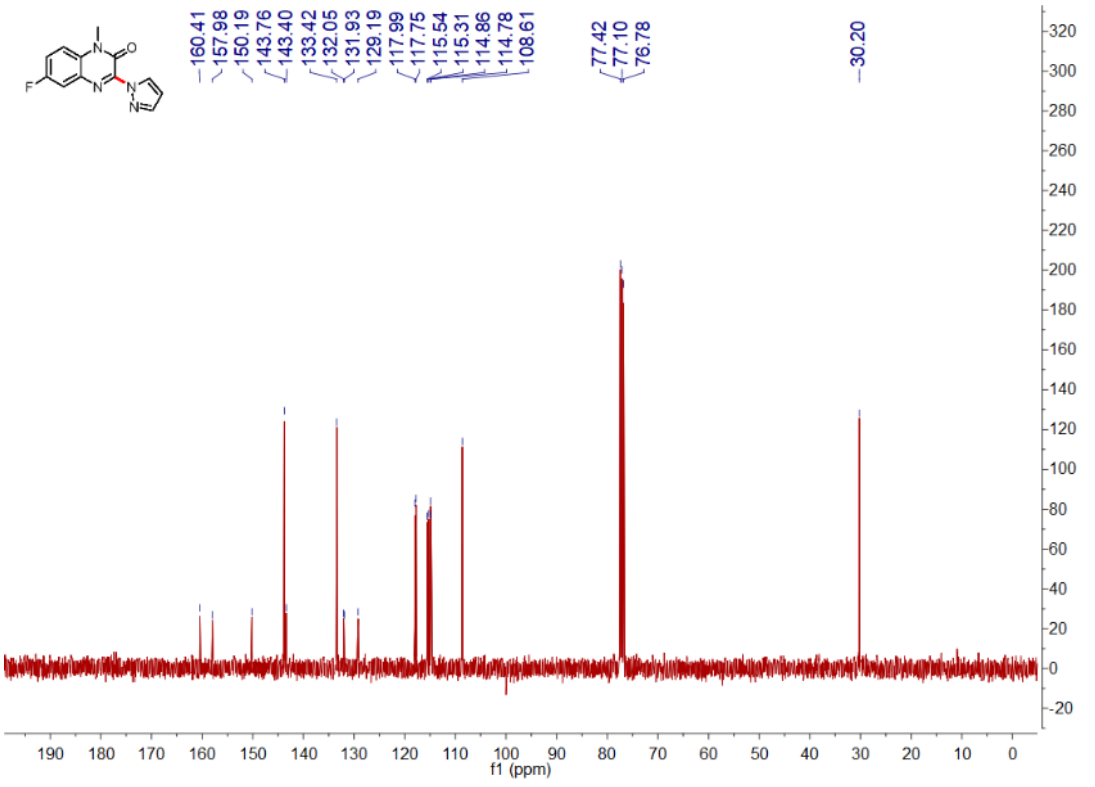
^{13}C NMR spectrum of compound **3a**



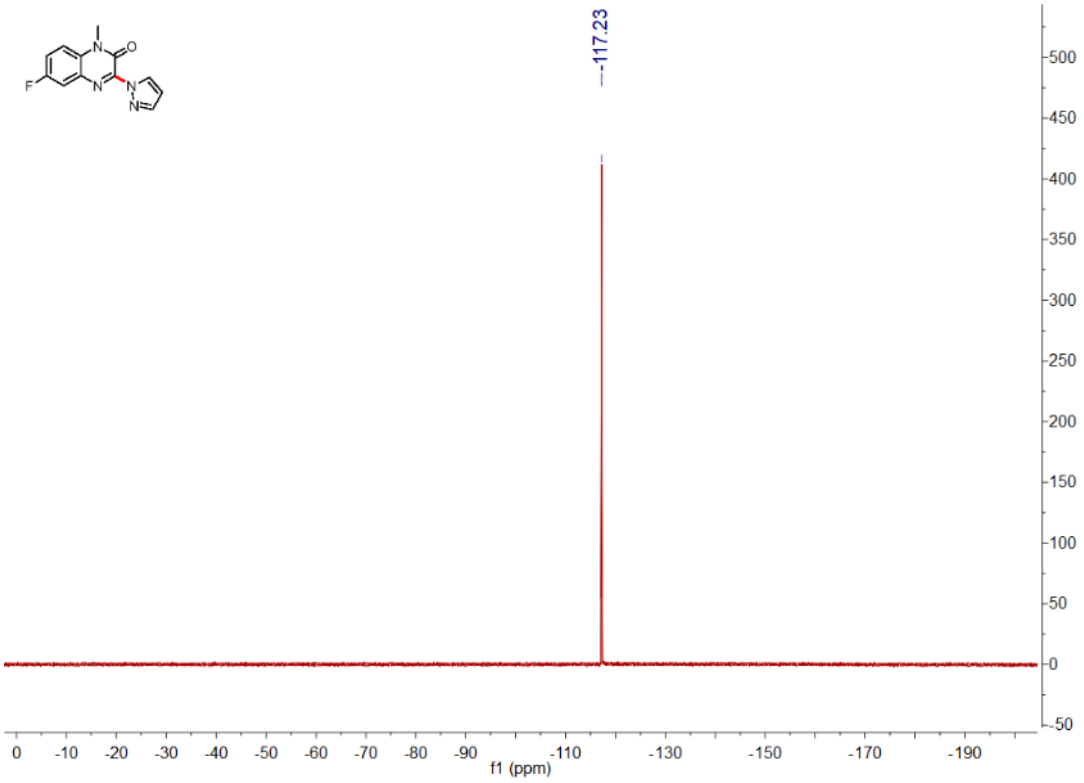
^{1}H NMR spectrum of compound **3b**



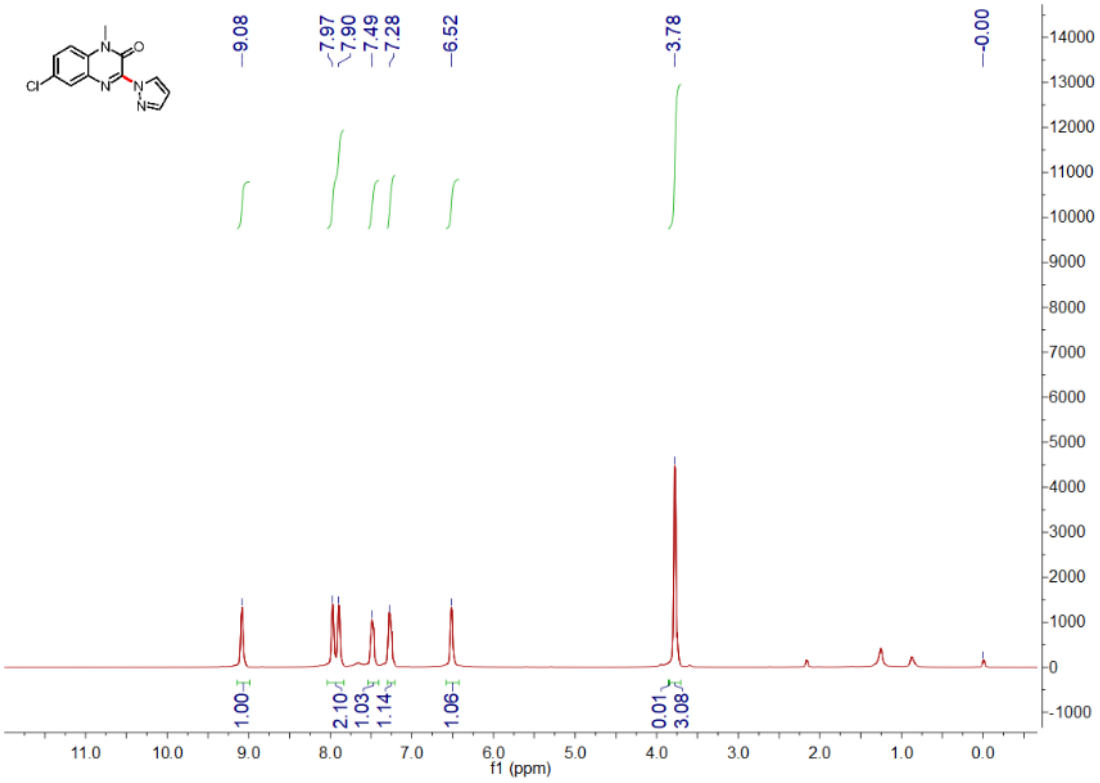
^{13}C NMR spectrum of compound **3b**



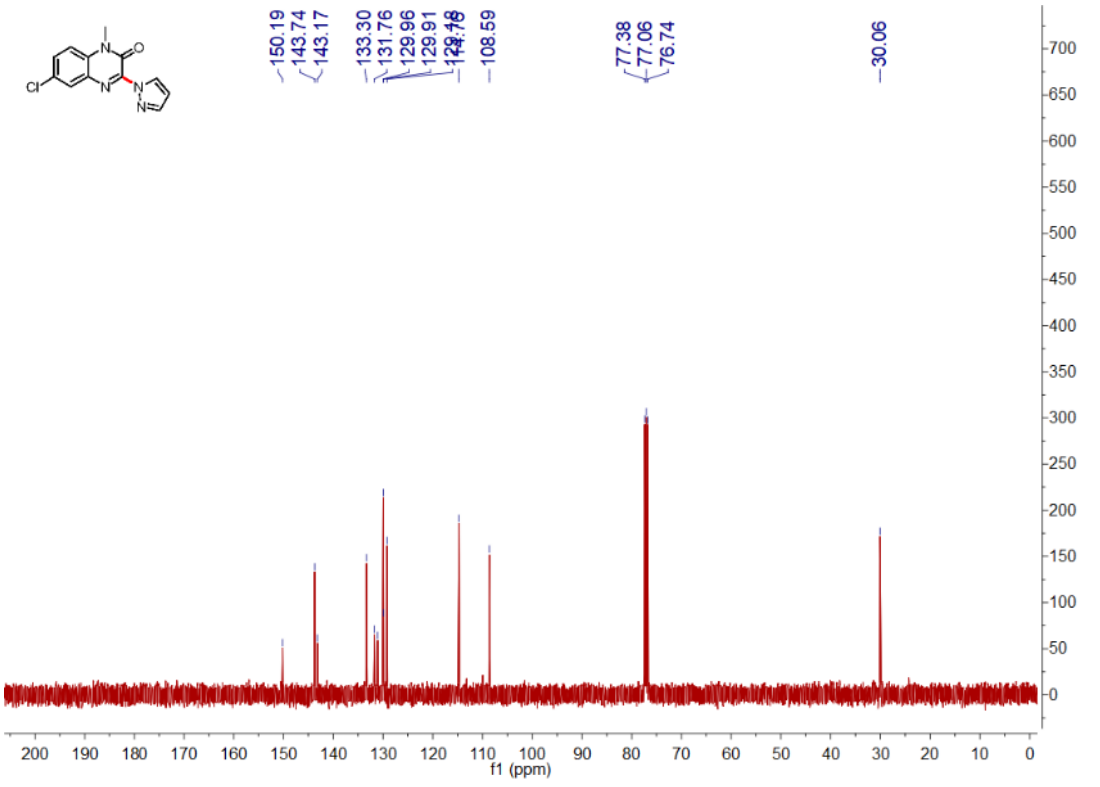
^{19}F NMR spectrum of compound **3b**



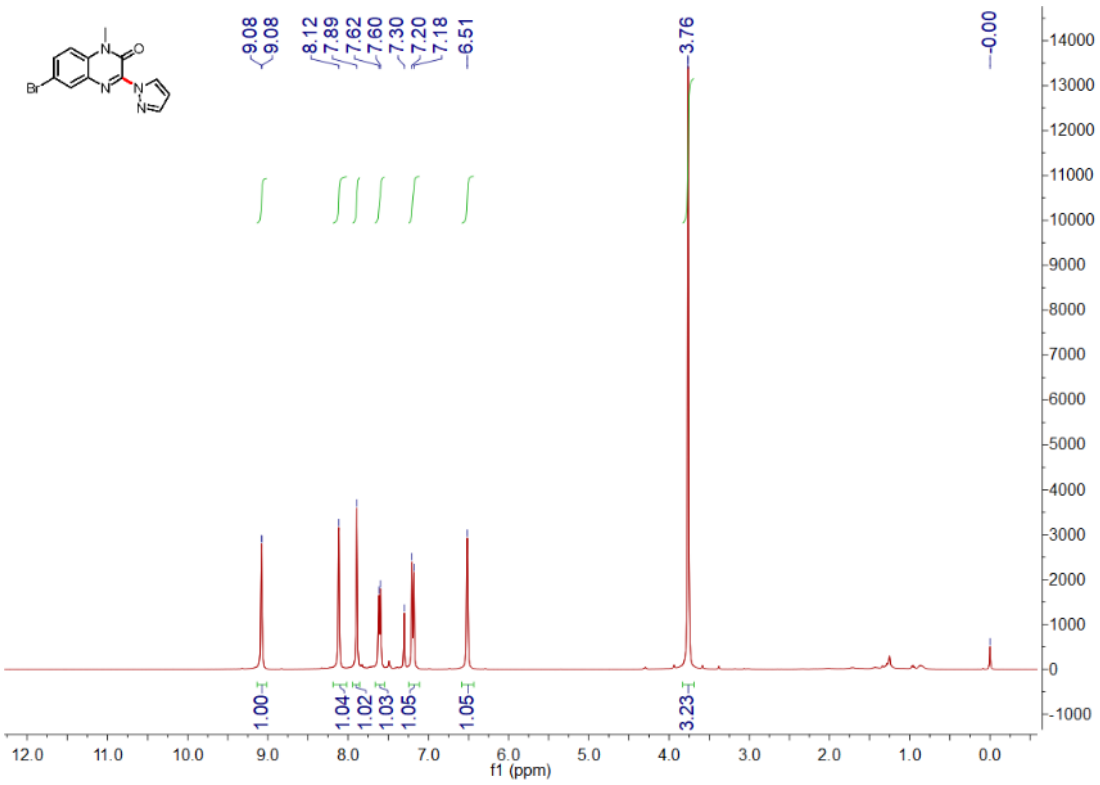
^{1}H NMR spectrum of compound **3c**



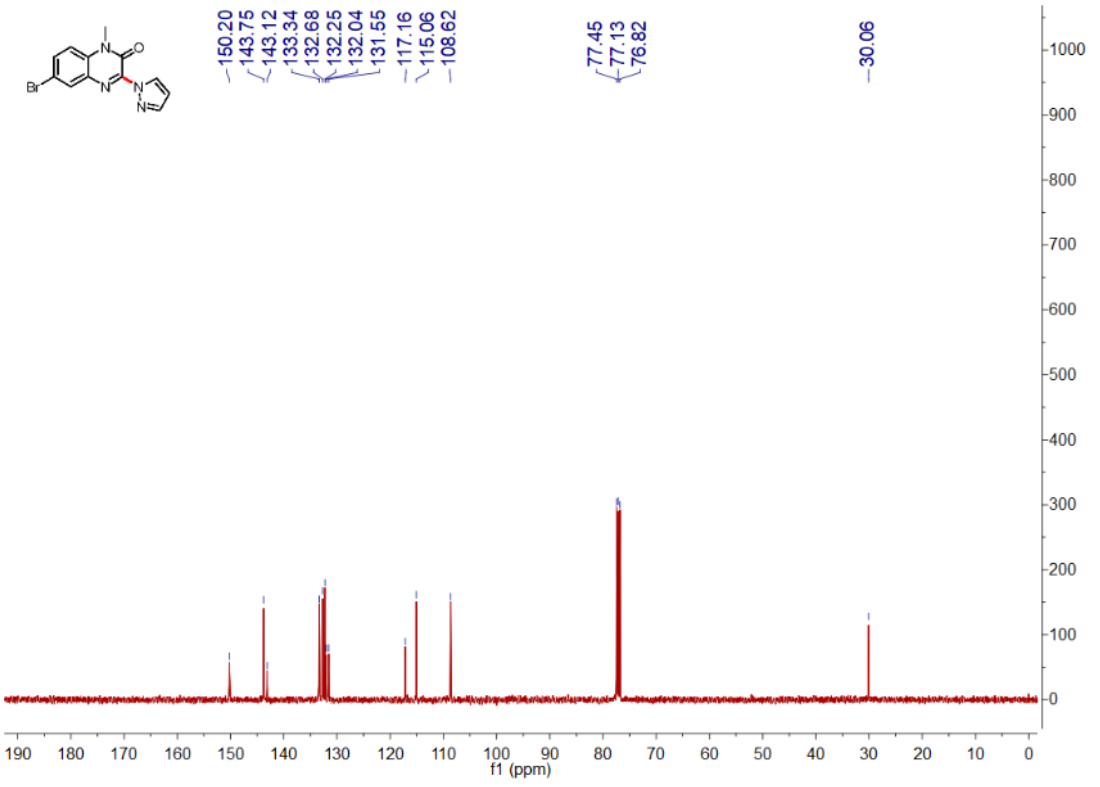
^{13}C NMR spectrum of compound **3c**



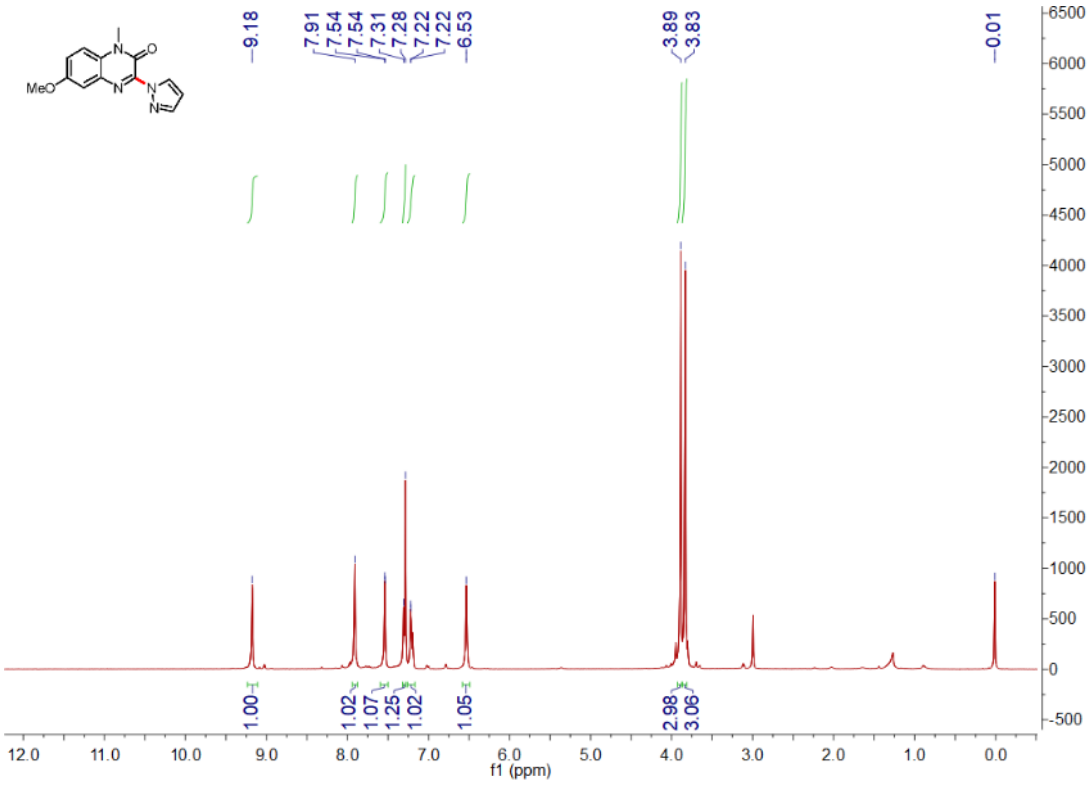
^{1}H NMR spectrum of compound **3d**



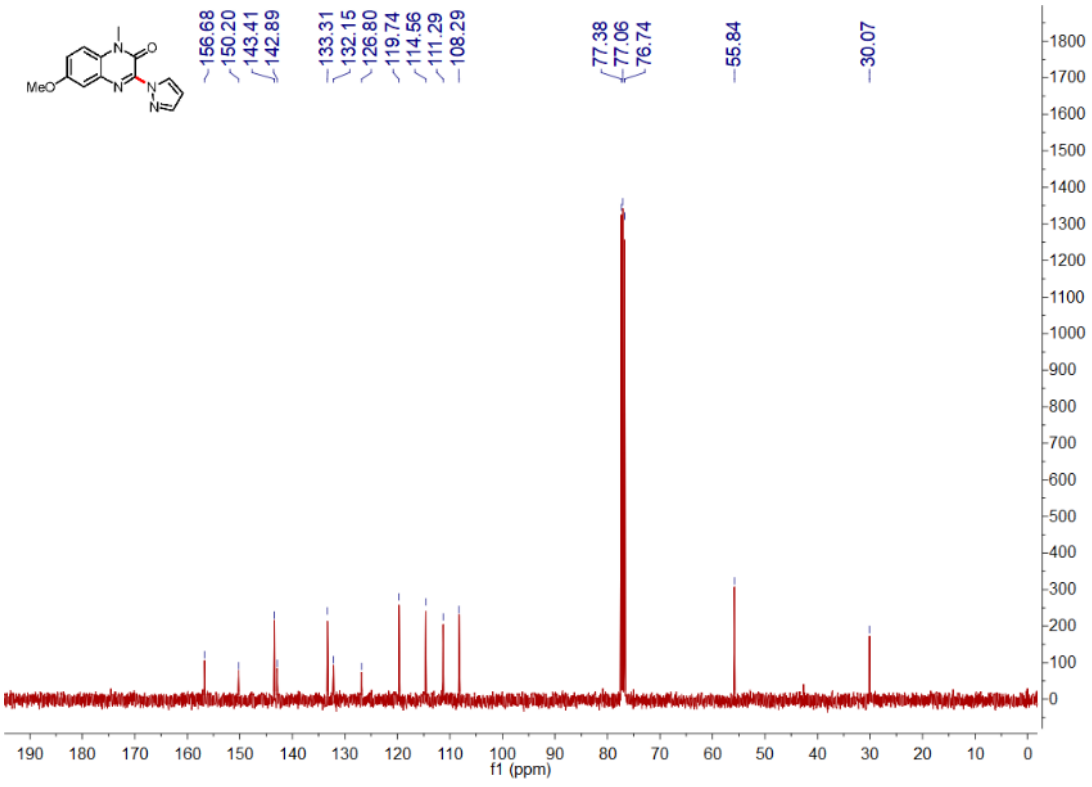
^{13}C NMR spectrum of compound **3d**



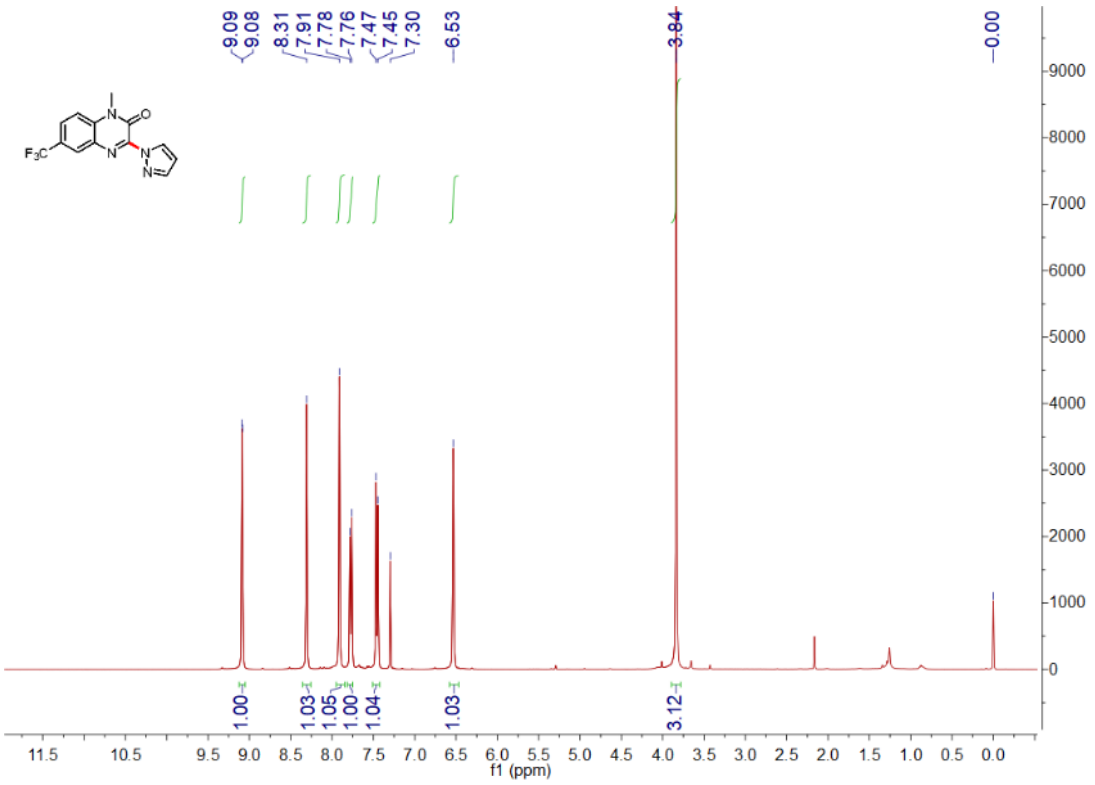
^{1}H NMR spectrum of compound **3e**



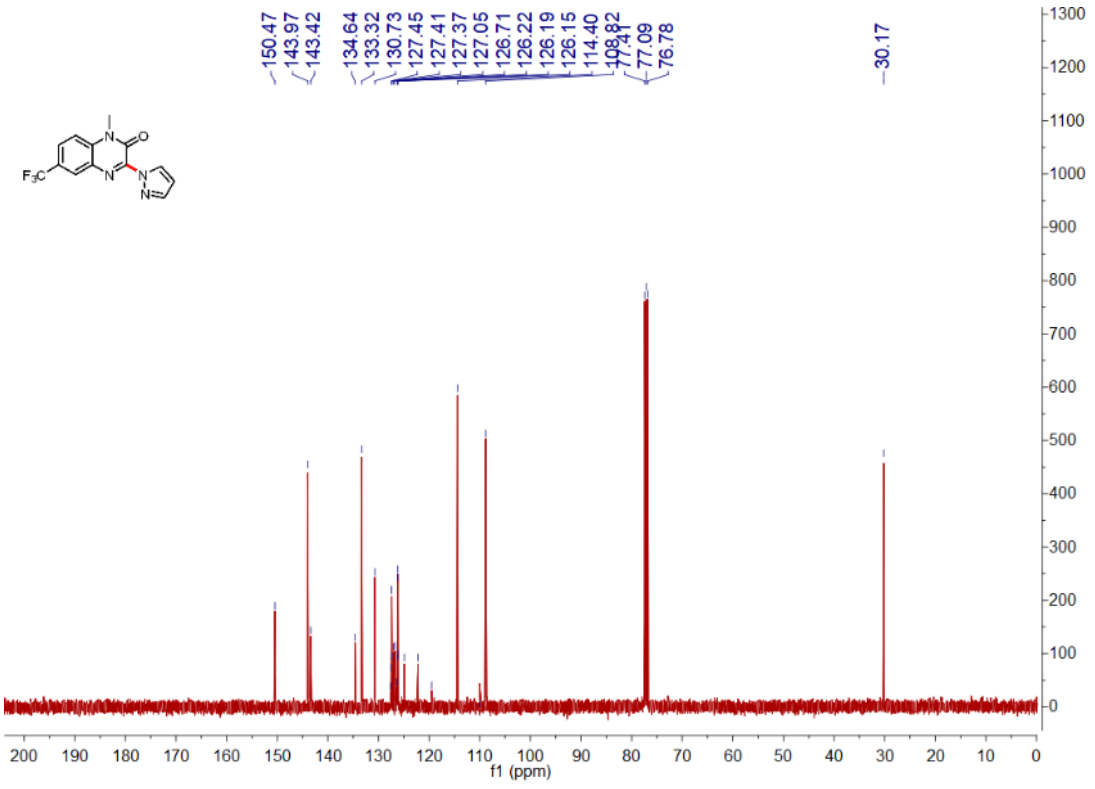
^{13}C NMR spectrum of compound **3e**



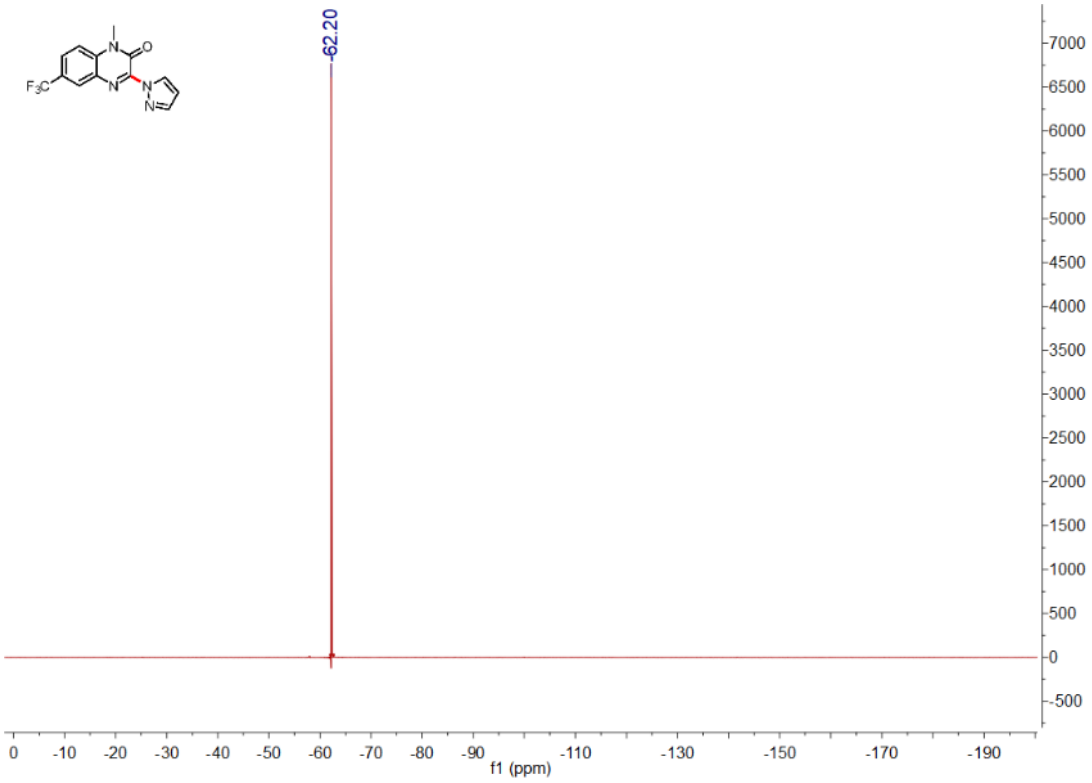
^{1}H NMR spectrum of compound **3f**



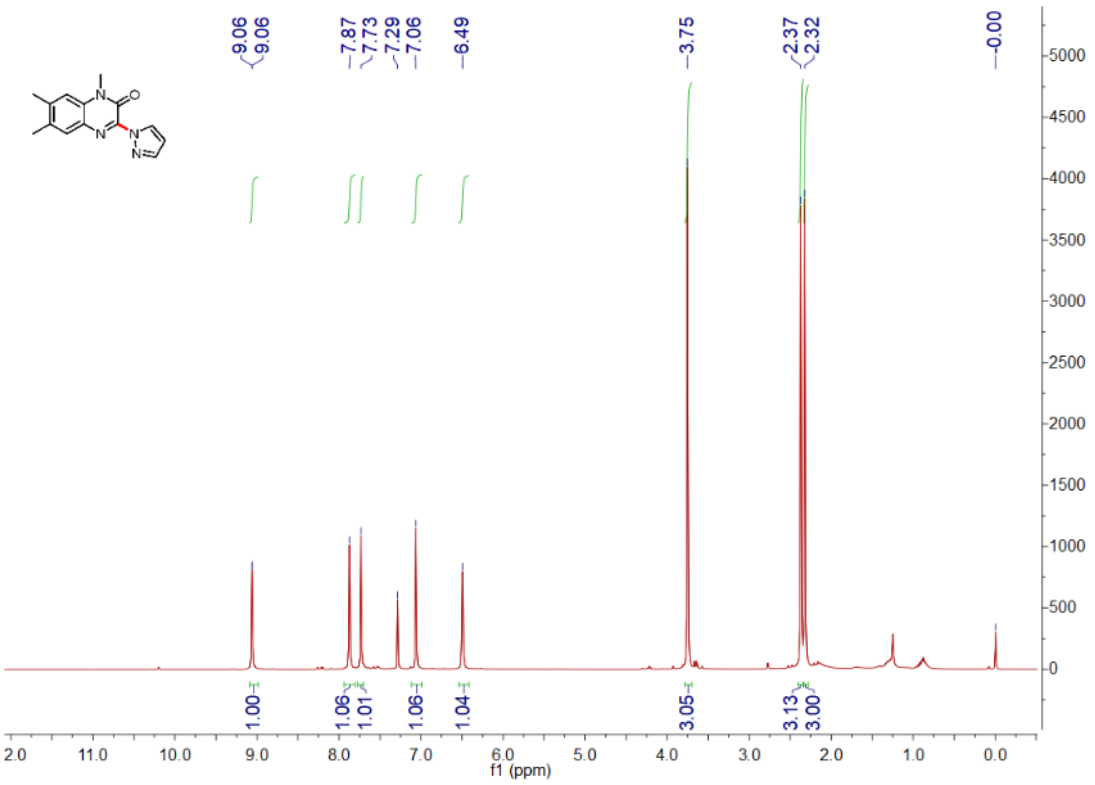
^{13}C NMR spectrum of compound **3f**



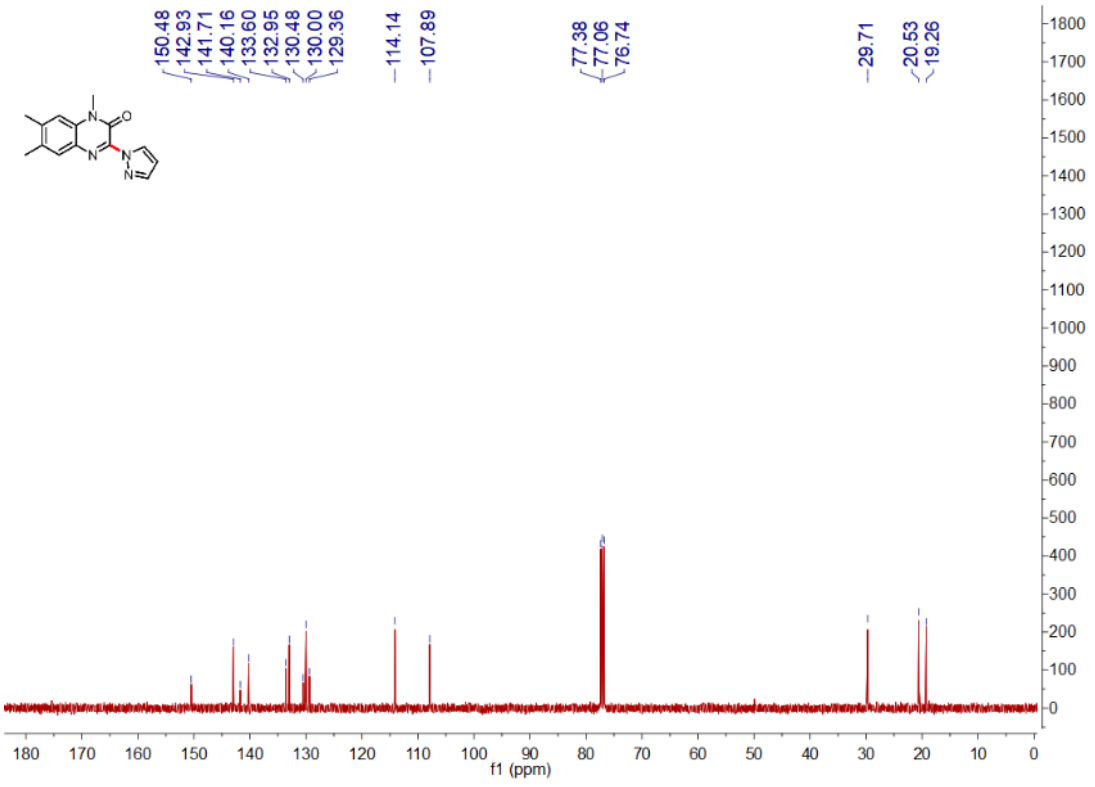
^{19}F NMR spectrum of compound **3f**



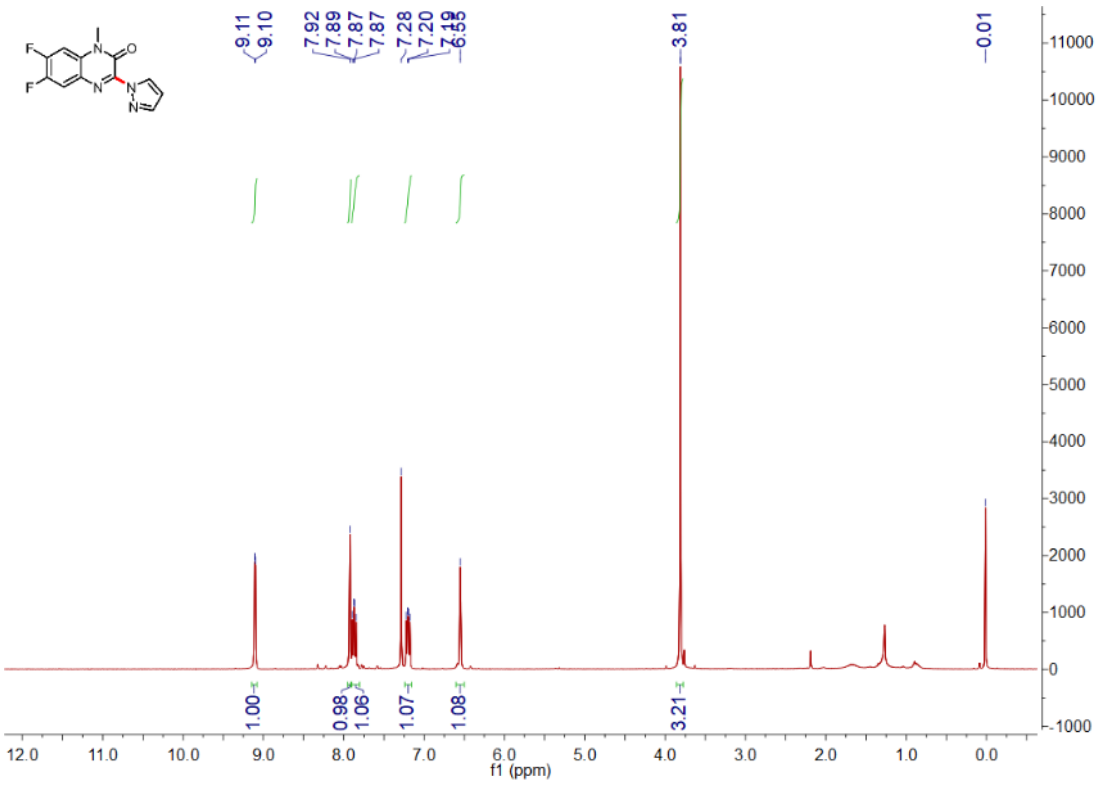
^{1}H NMR spectrum of compound **3g**



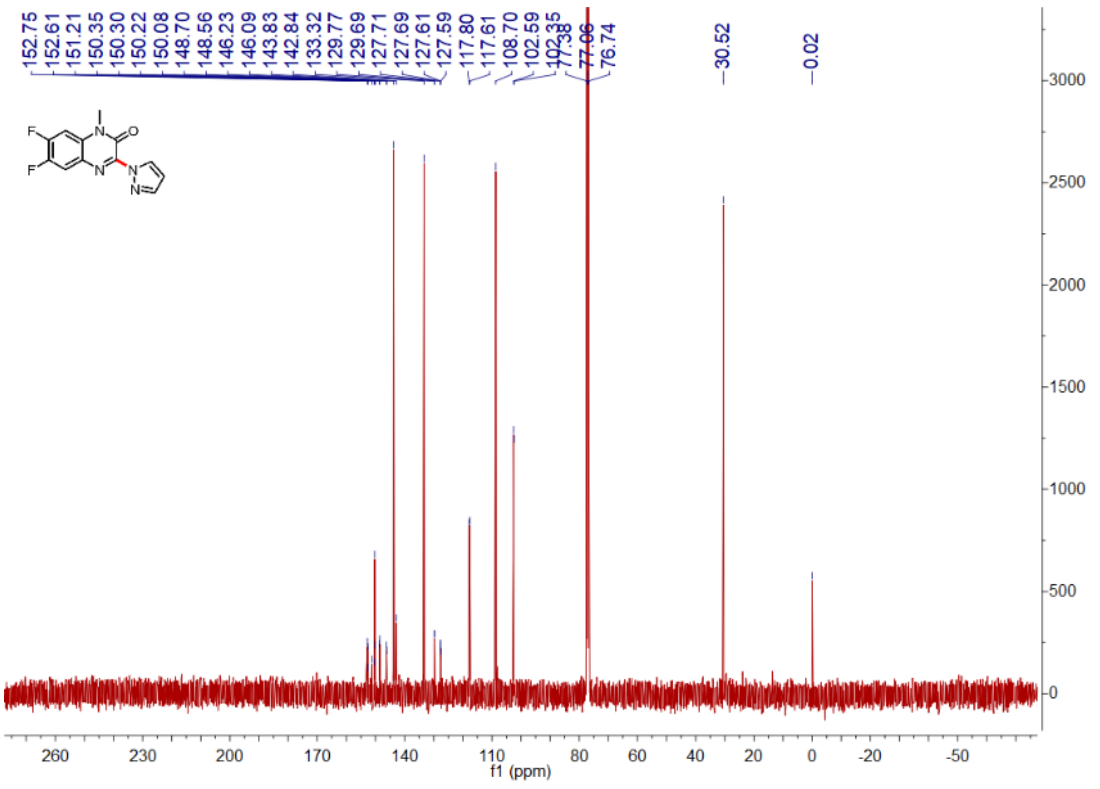
^{13}C NMR spectrum of compound **3g**



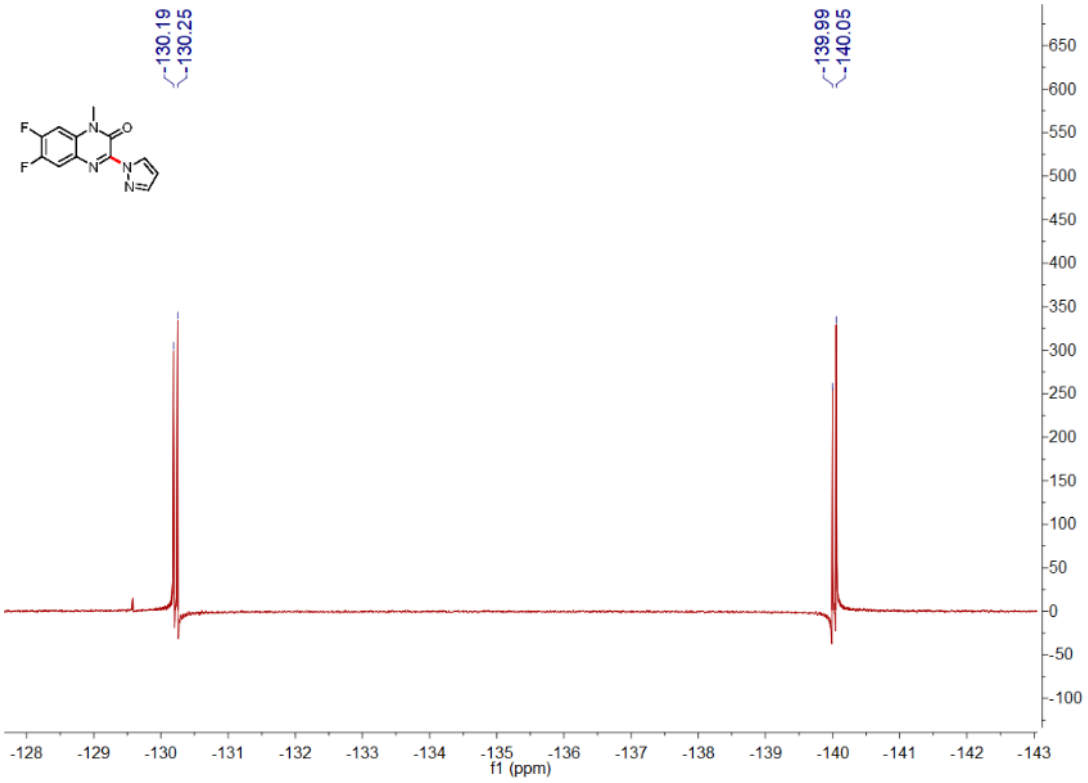
^{1}H NMR spectrum of compound **3h**



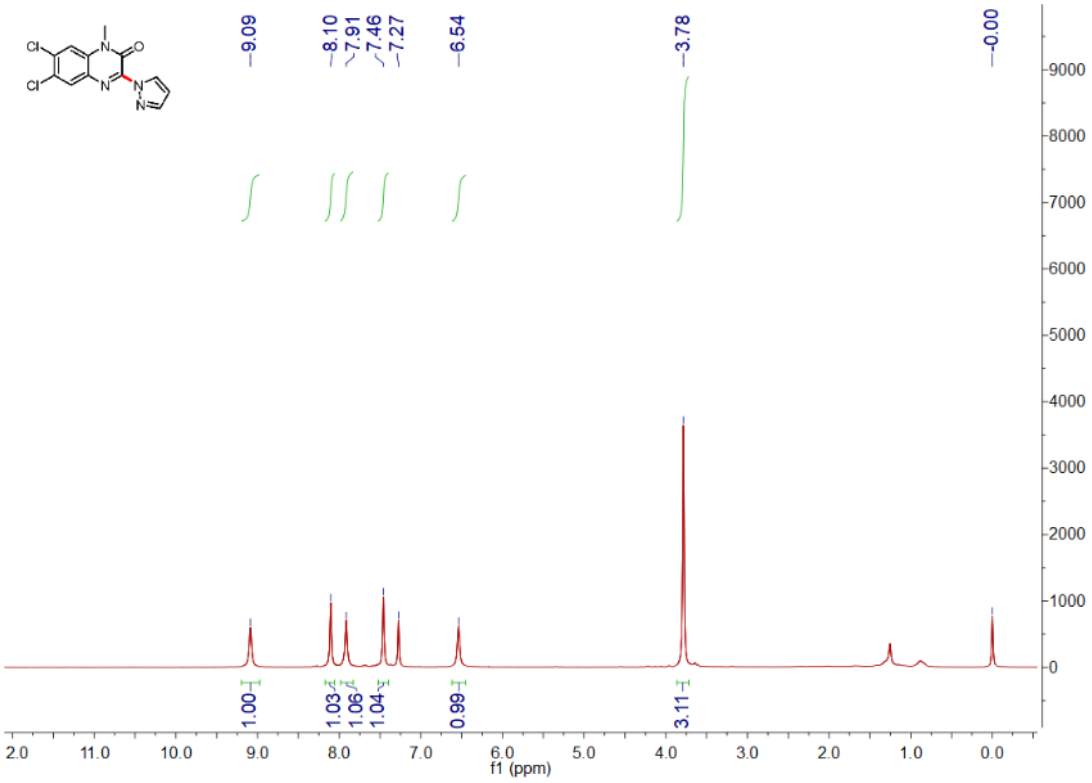
^{13}C NMR spectrum of compound **3h**



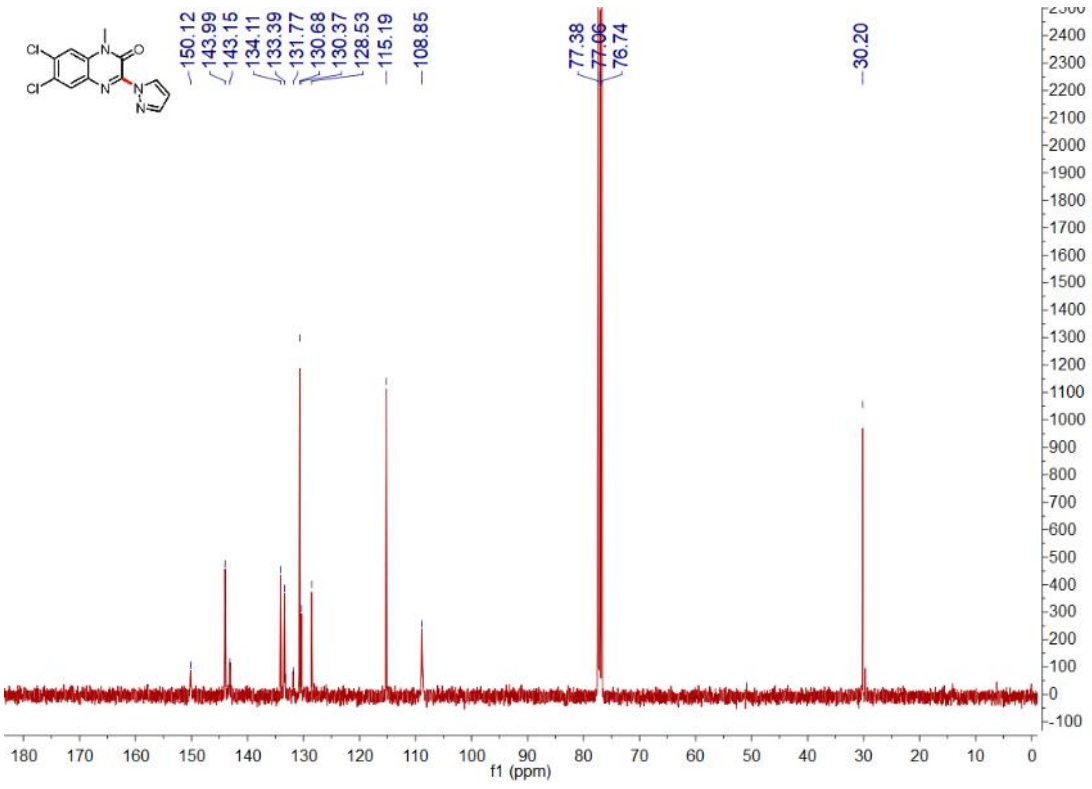
^{19}F NMR spectrum of compound **3h**



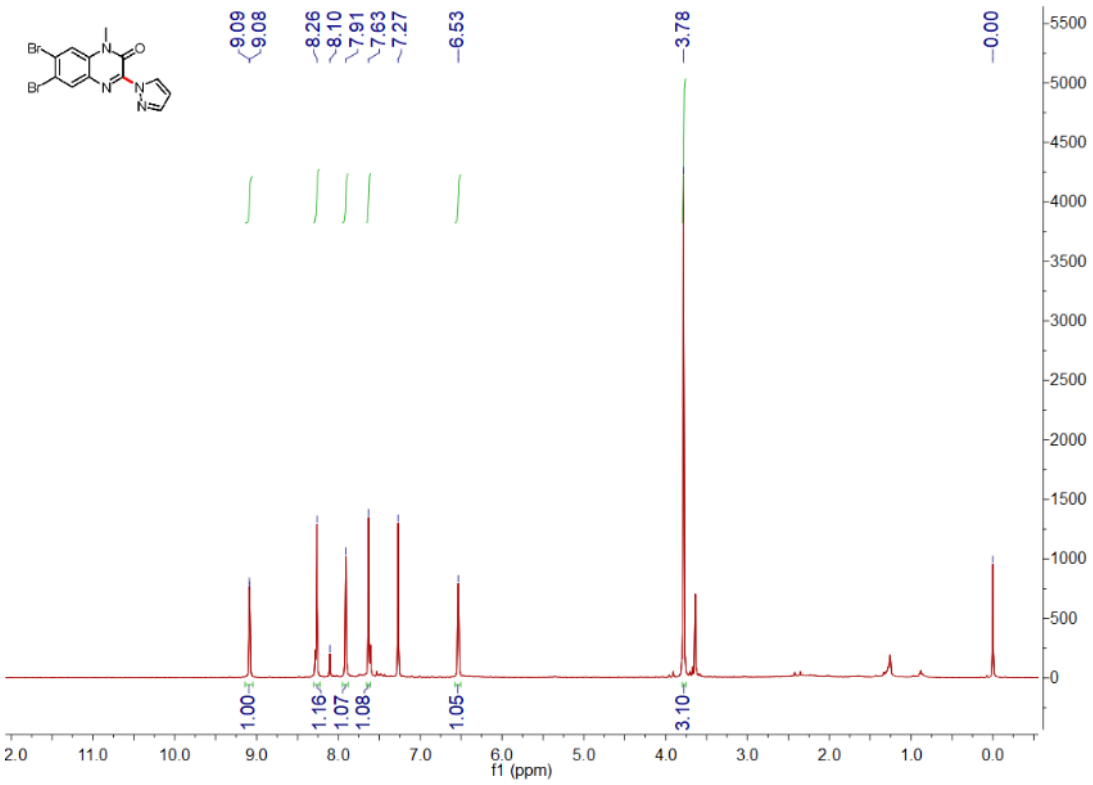
^{1}H NMR spectrum of compound **3i**



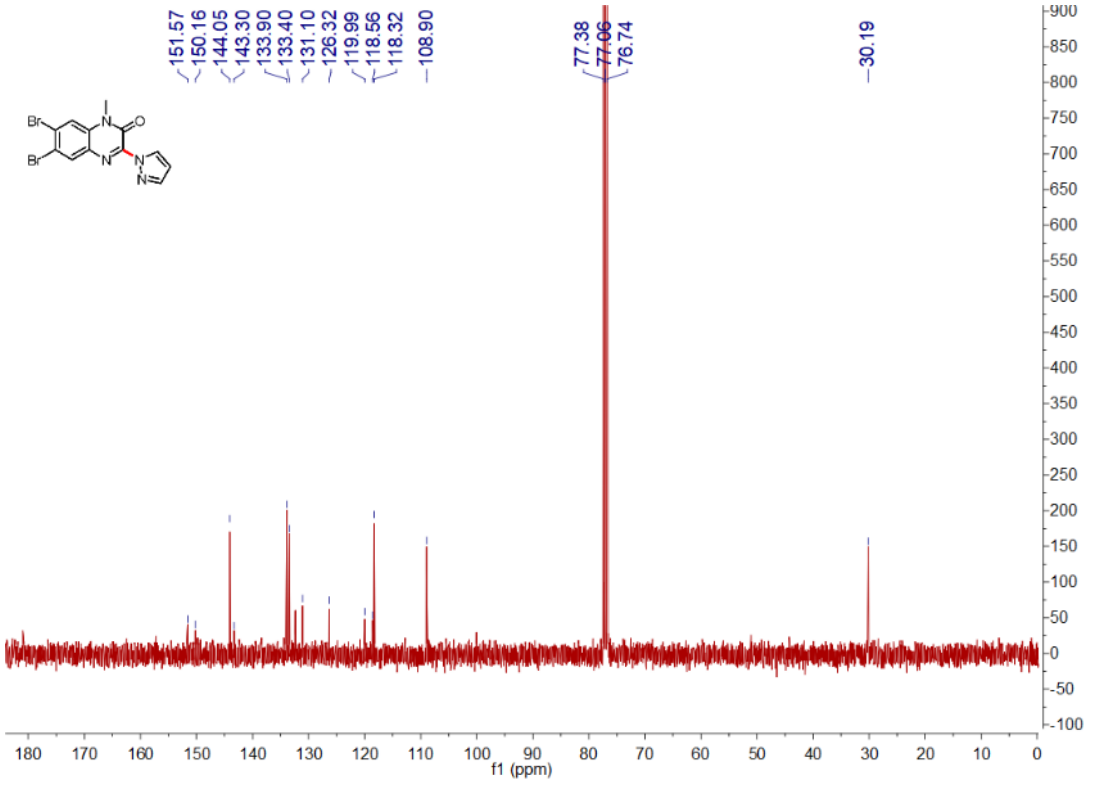
^{13}C NMR spectrum of compound **3i**



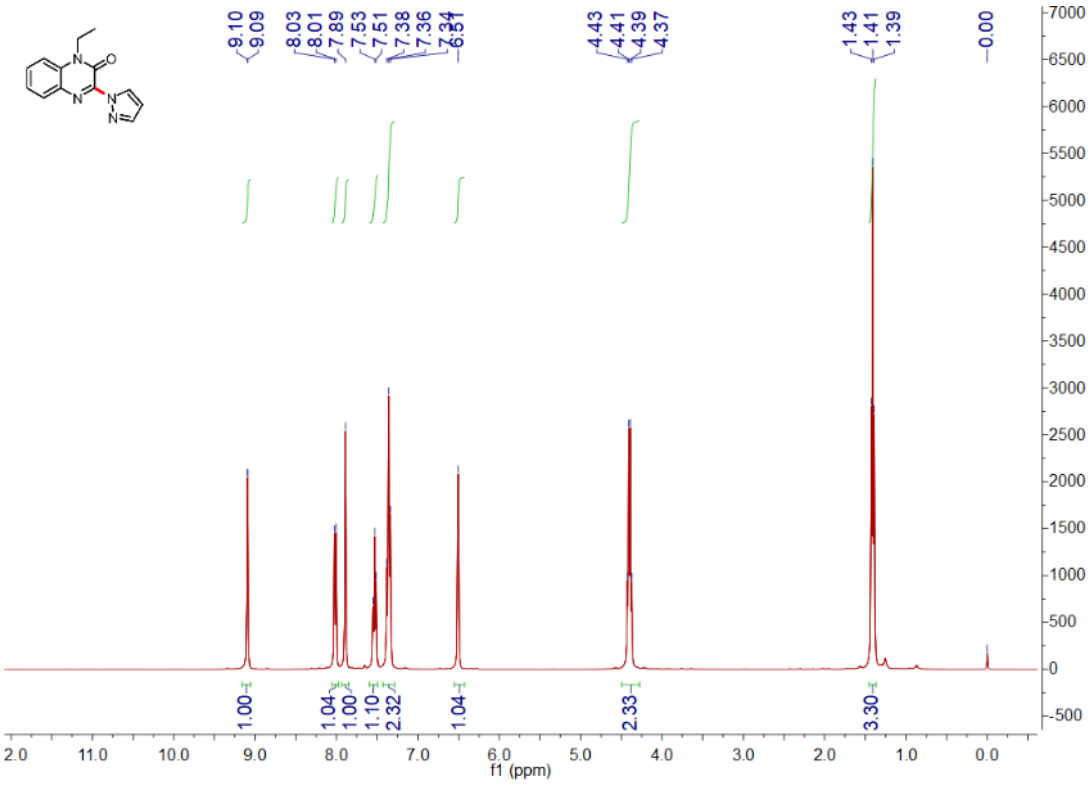
^{1}H NMR spectrum of compound **3j**



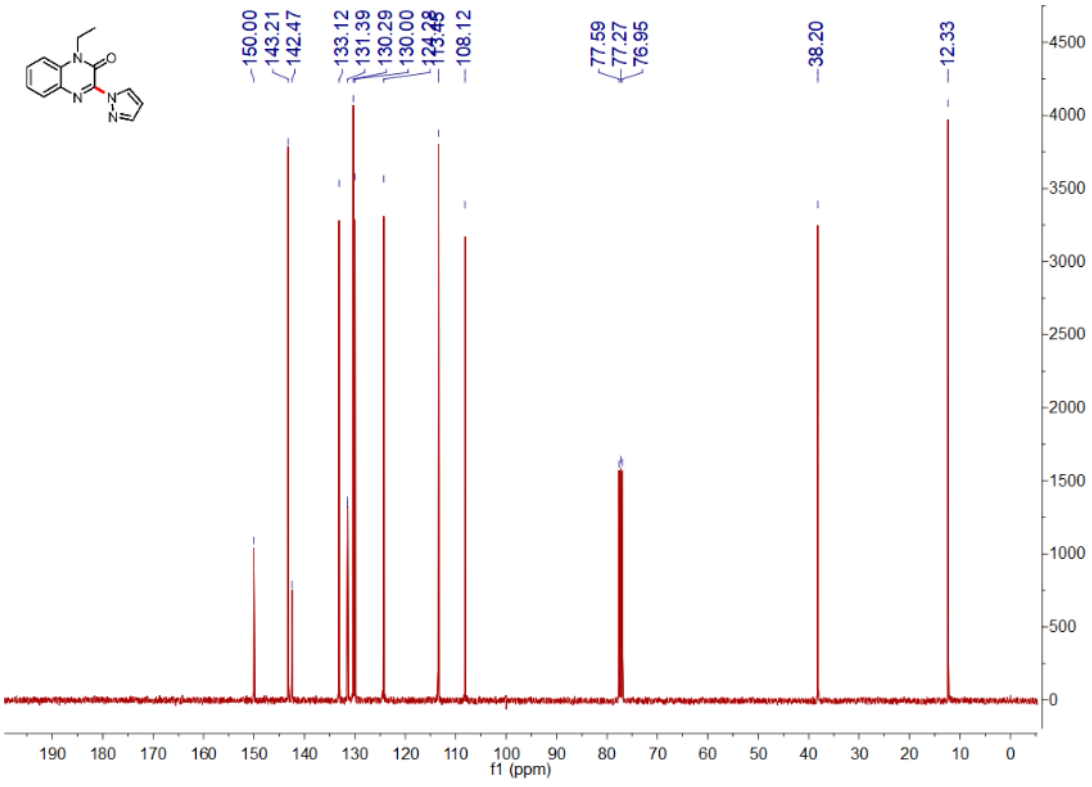
^{13}C NMR spectrum of compound **3j**



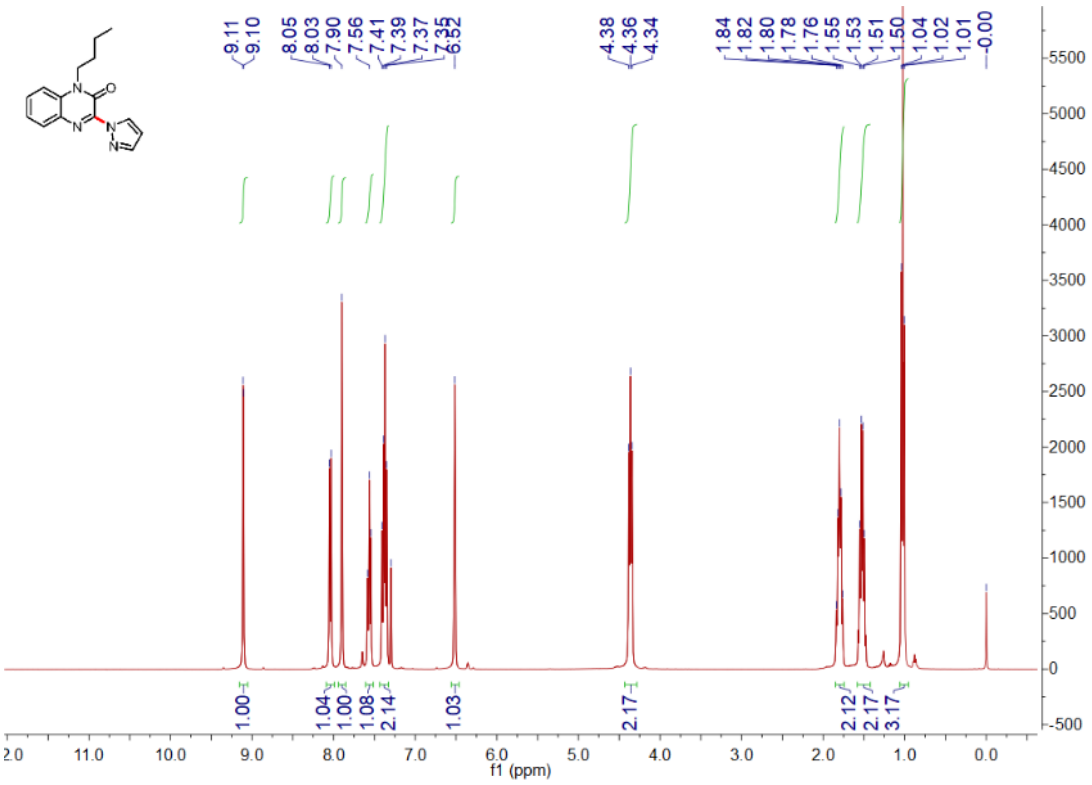
^{1}H NMR spectrum of compound **3k**



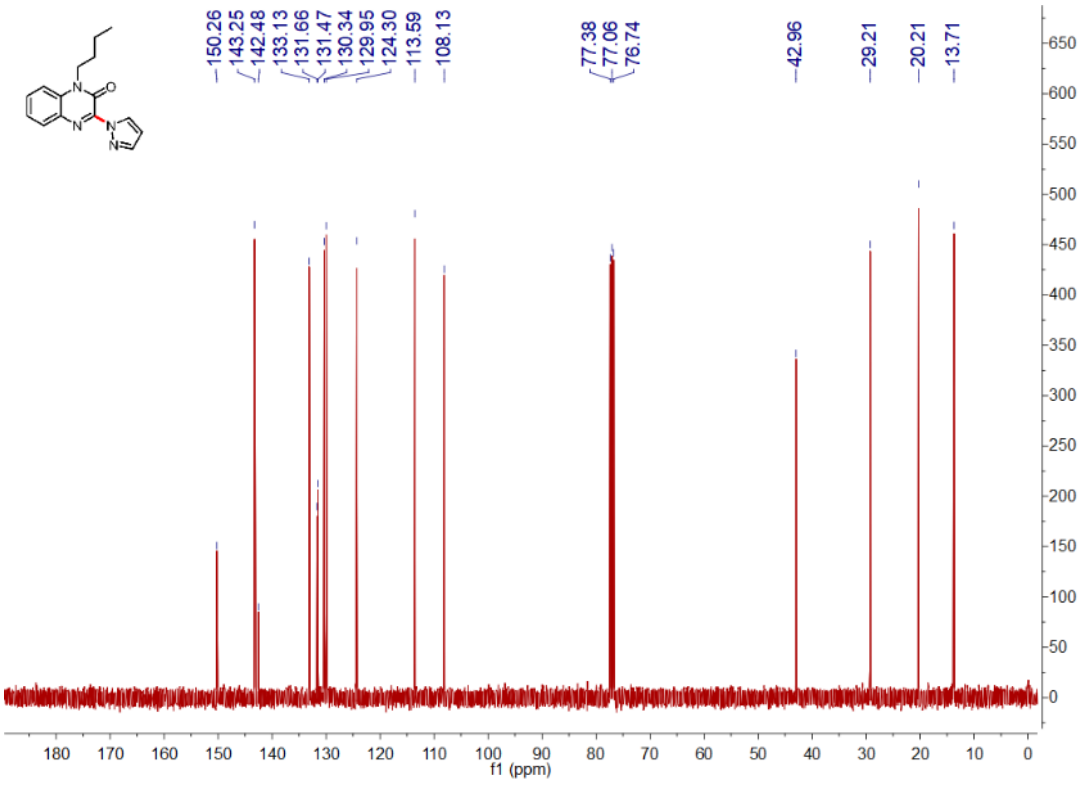
^{13}C NMR spectrum of compound **3k**



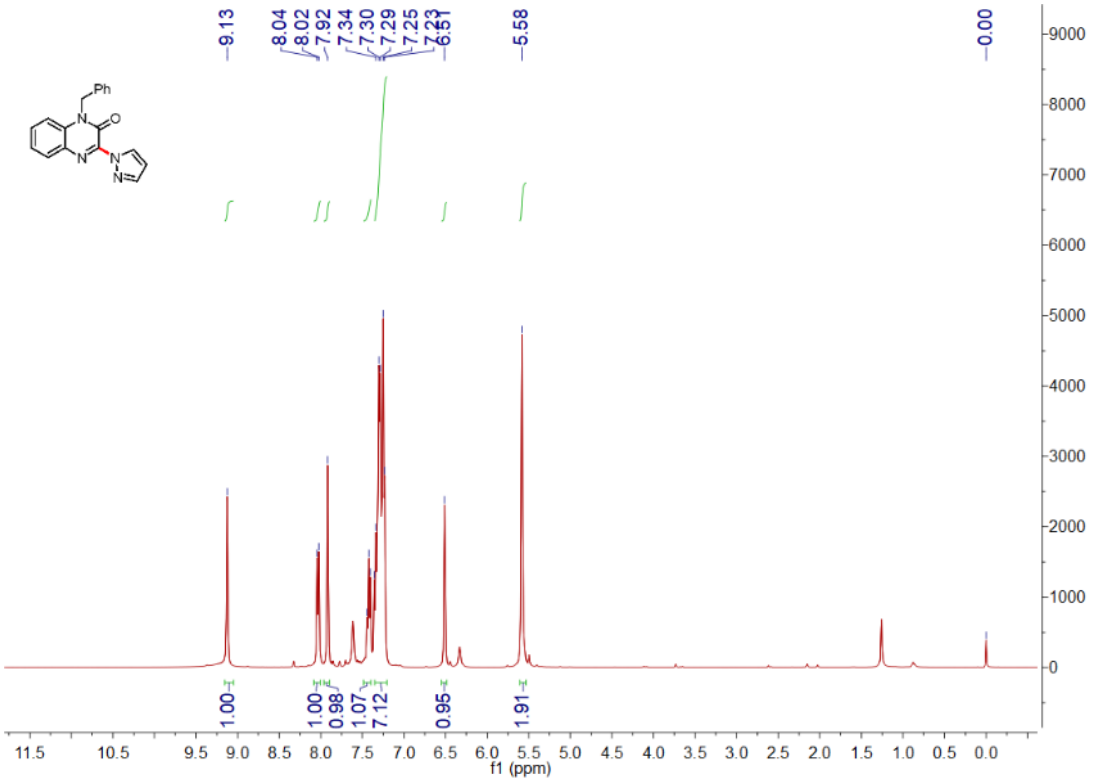
^{1}H NMR spectrum of compound **3l**



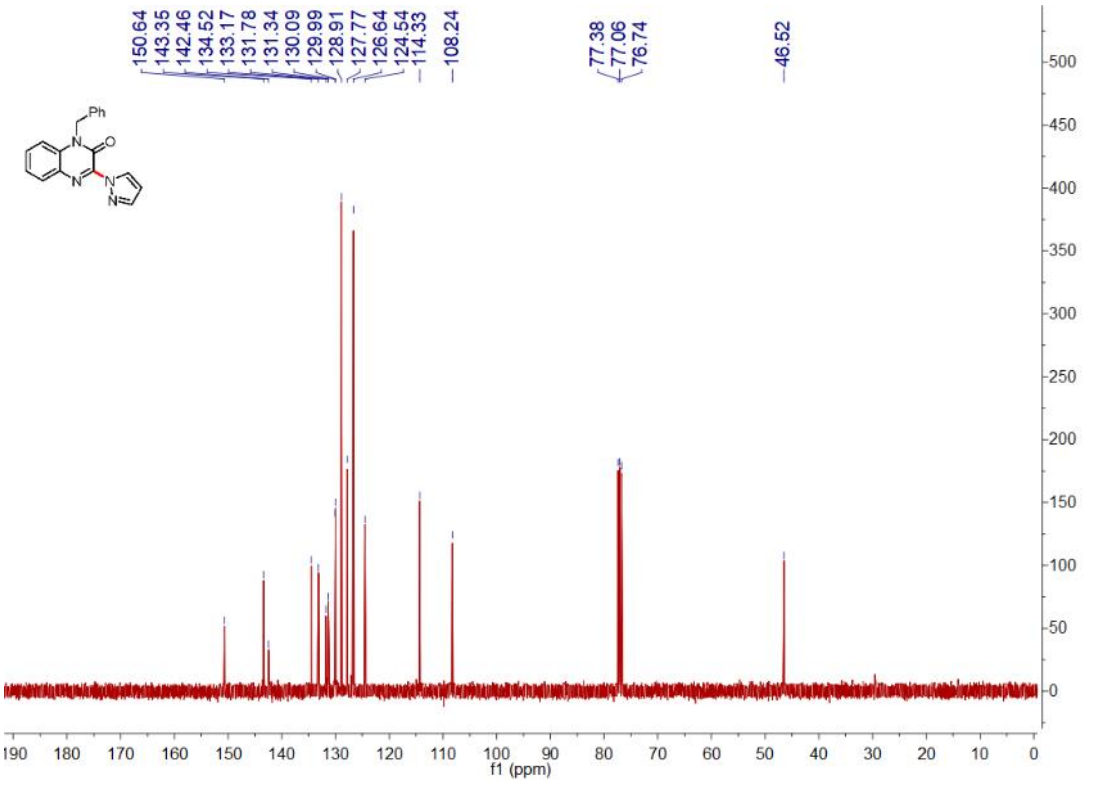
^{13}C NMR spectrum of compound **3l**



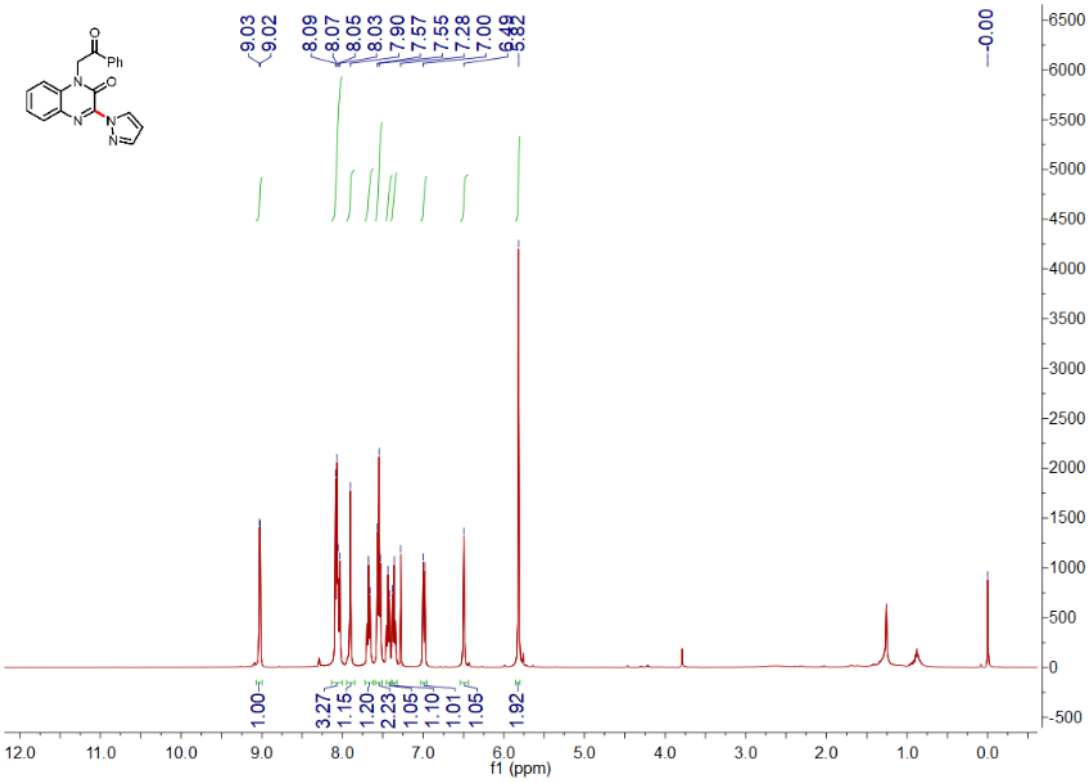
^{1}H NMR spectrum of compound **3m**



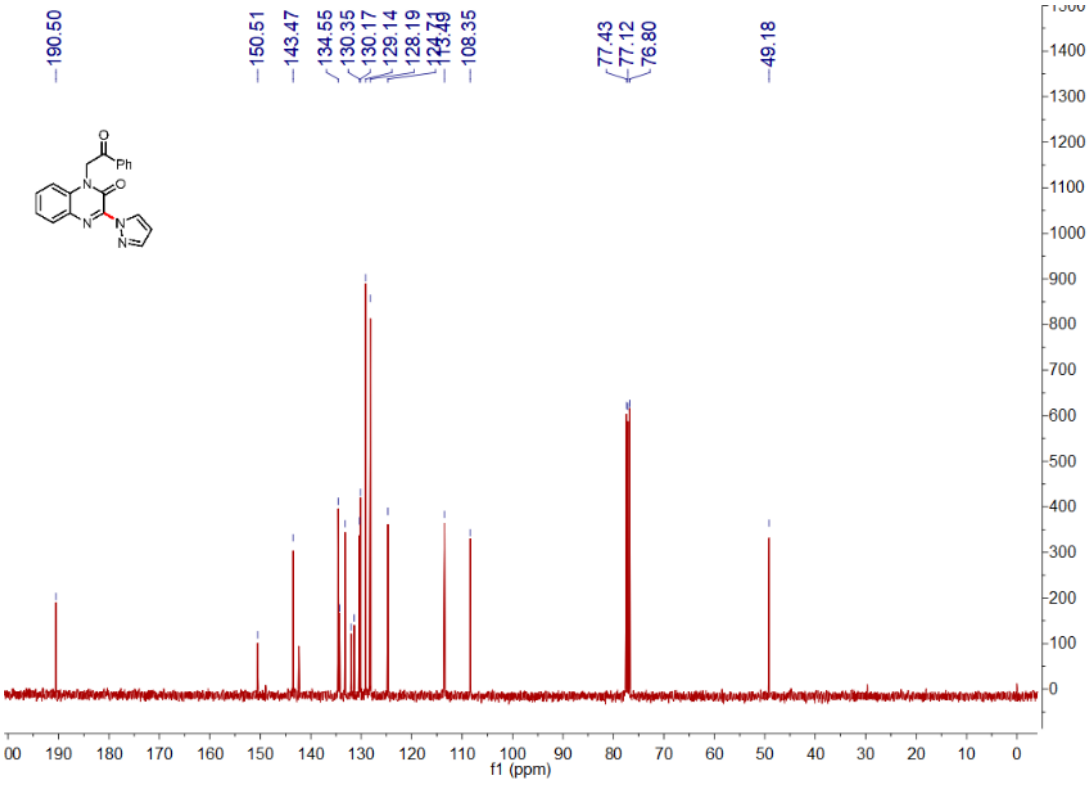
^{13}C NMR spectrum of compound **3m**



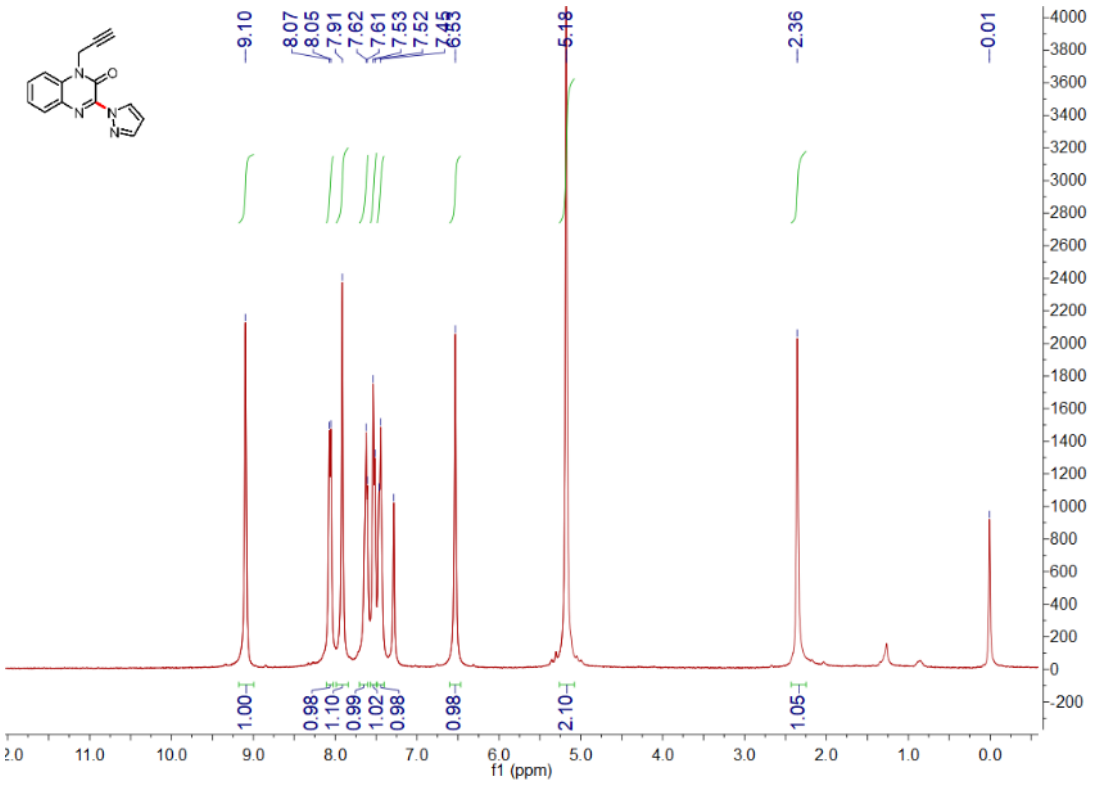
^{1}H NMR spectrum of compound **3n**



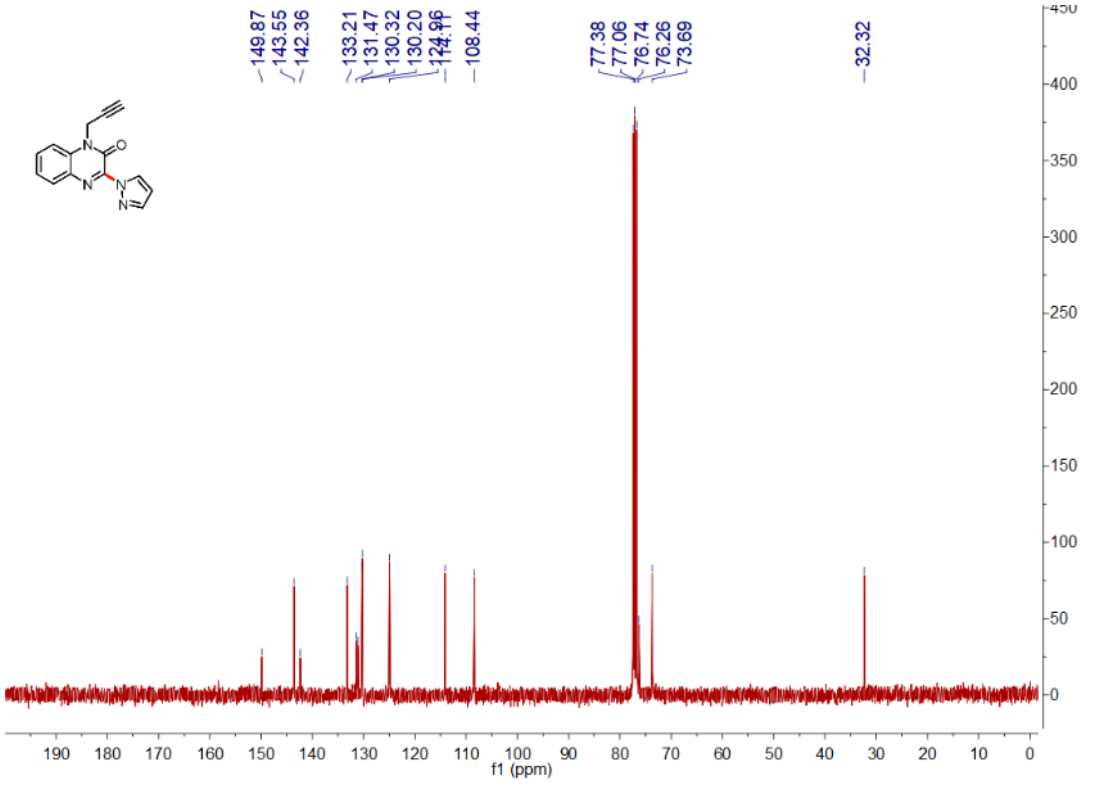
^{13}C NMR spectrum of compound **3n**



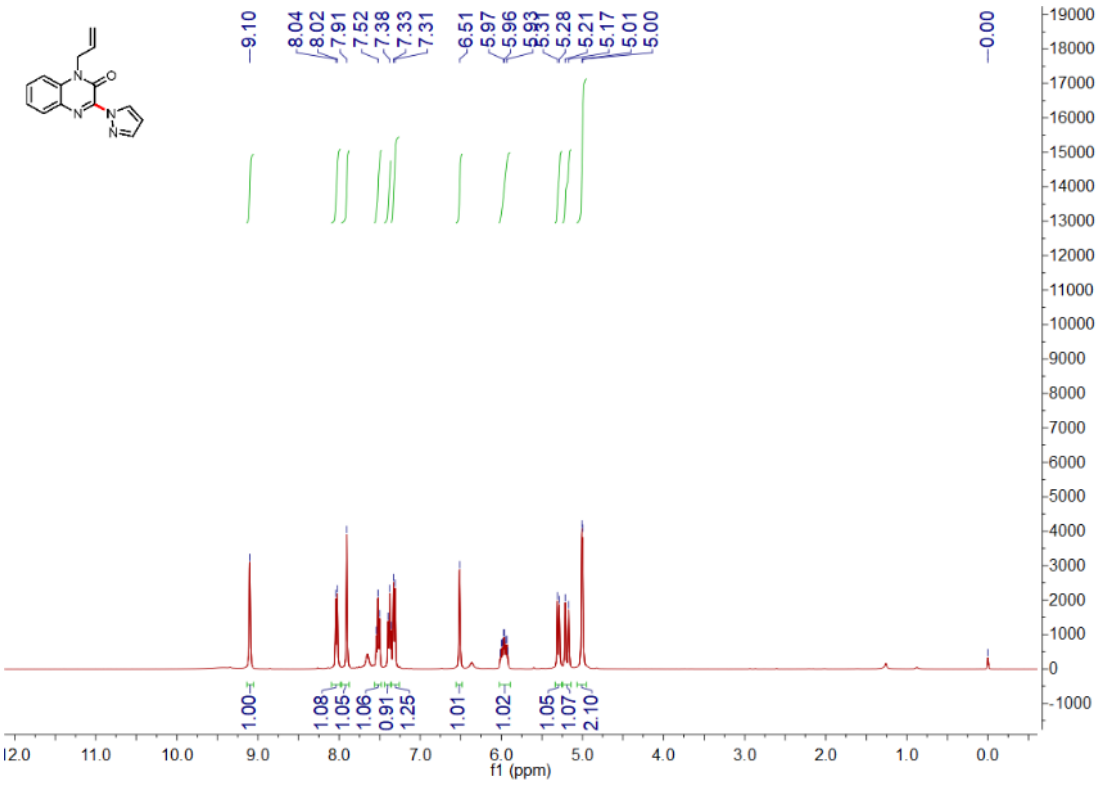
^{1}H NMR spectrum of compound **3o**



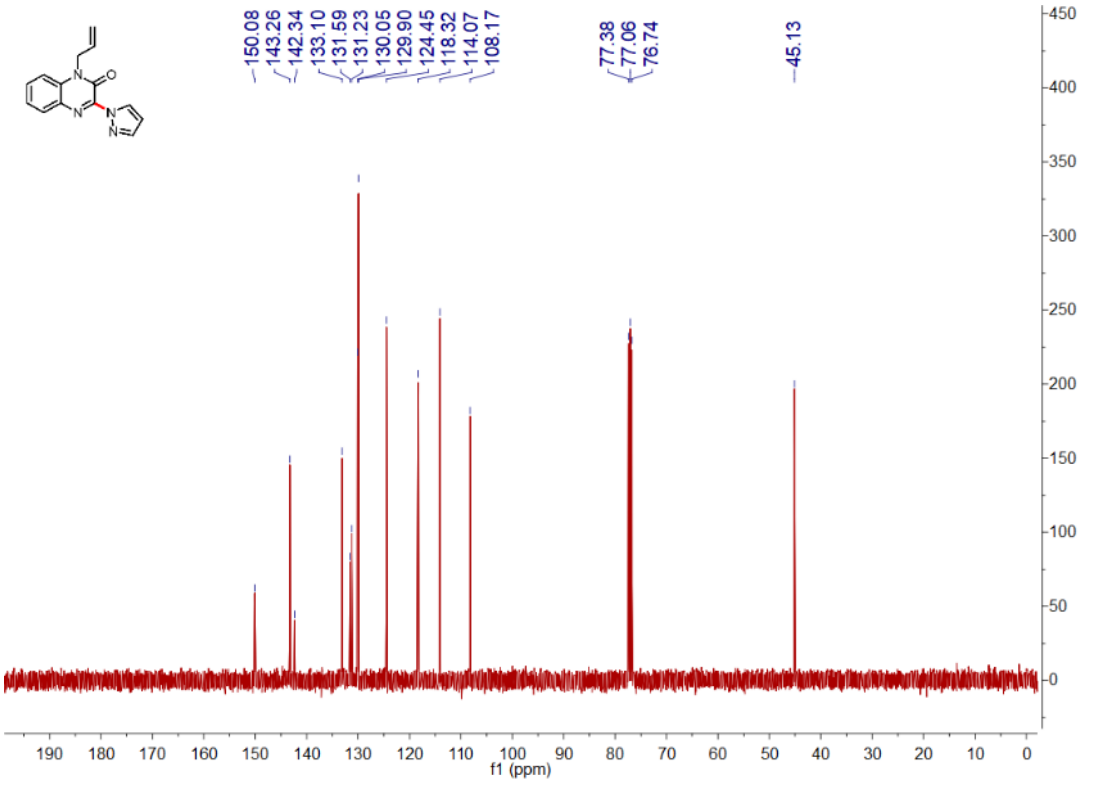
^{13}C NMR spectrum of compound **3o**



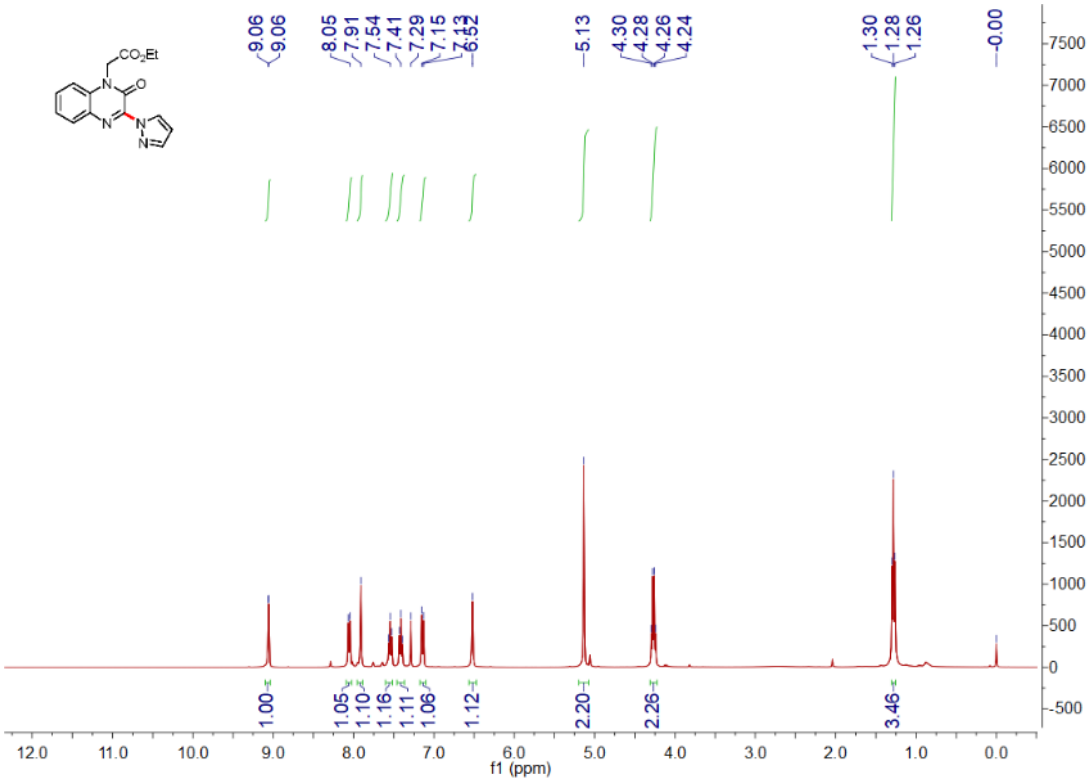
^{1}H NMR spectrum of compound **3p**



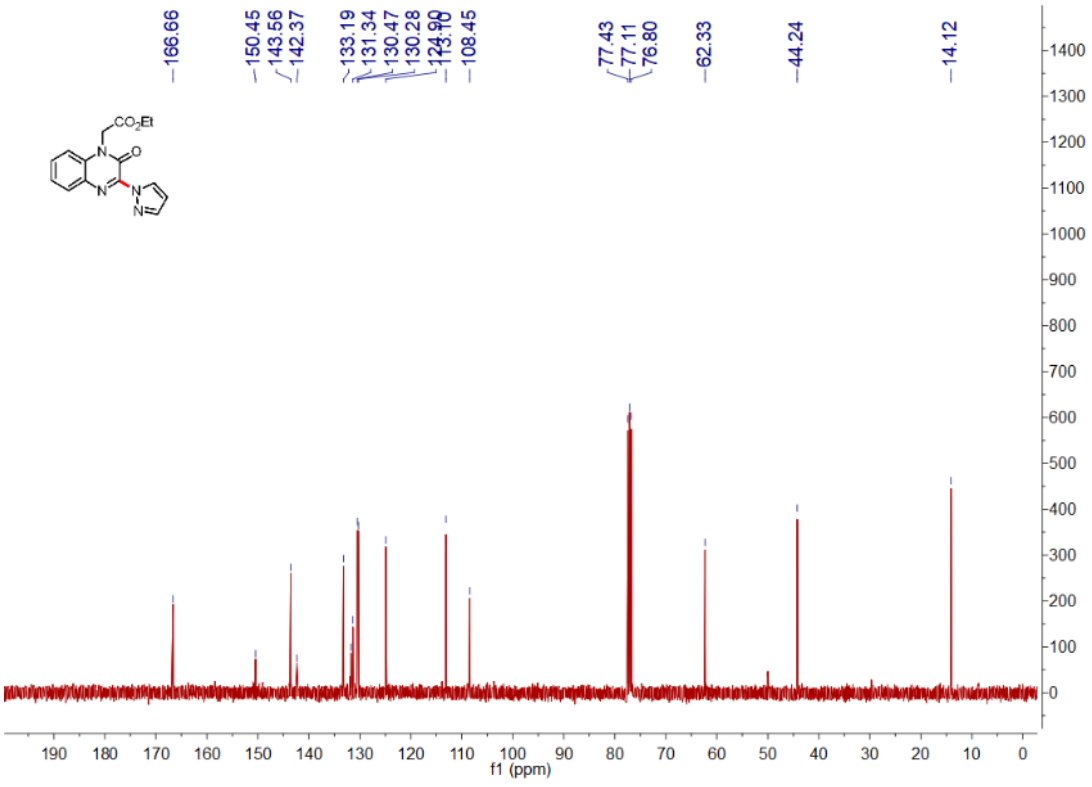
^{13}C NMR spectrum of compound **3p**



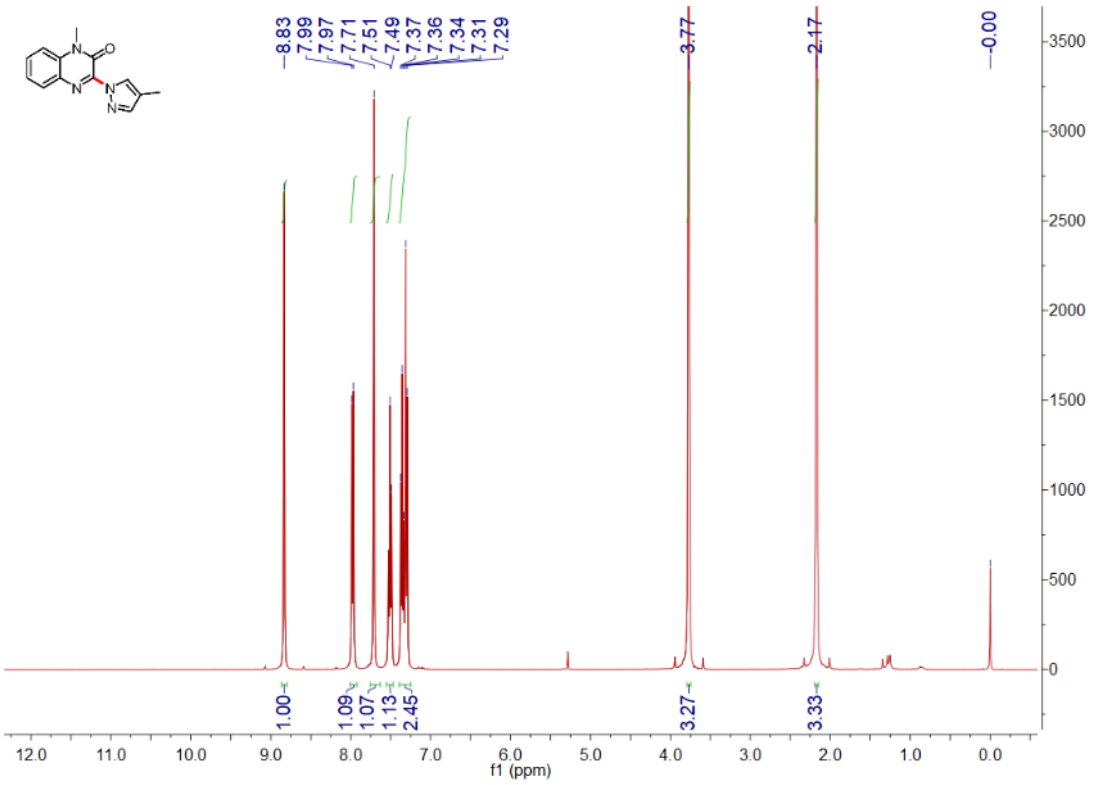
^{1}H NMR spectrum of compound **3q**



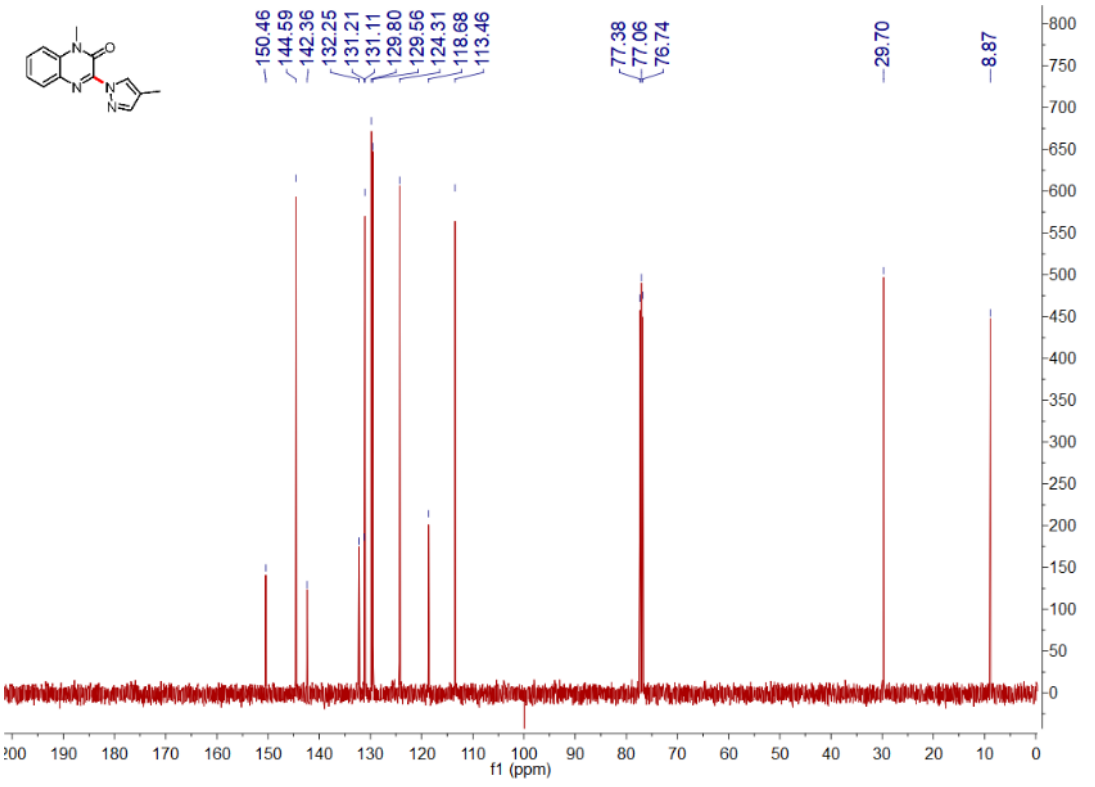
^{13}C NMR spectrum of compound **3q**



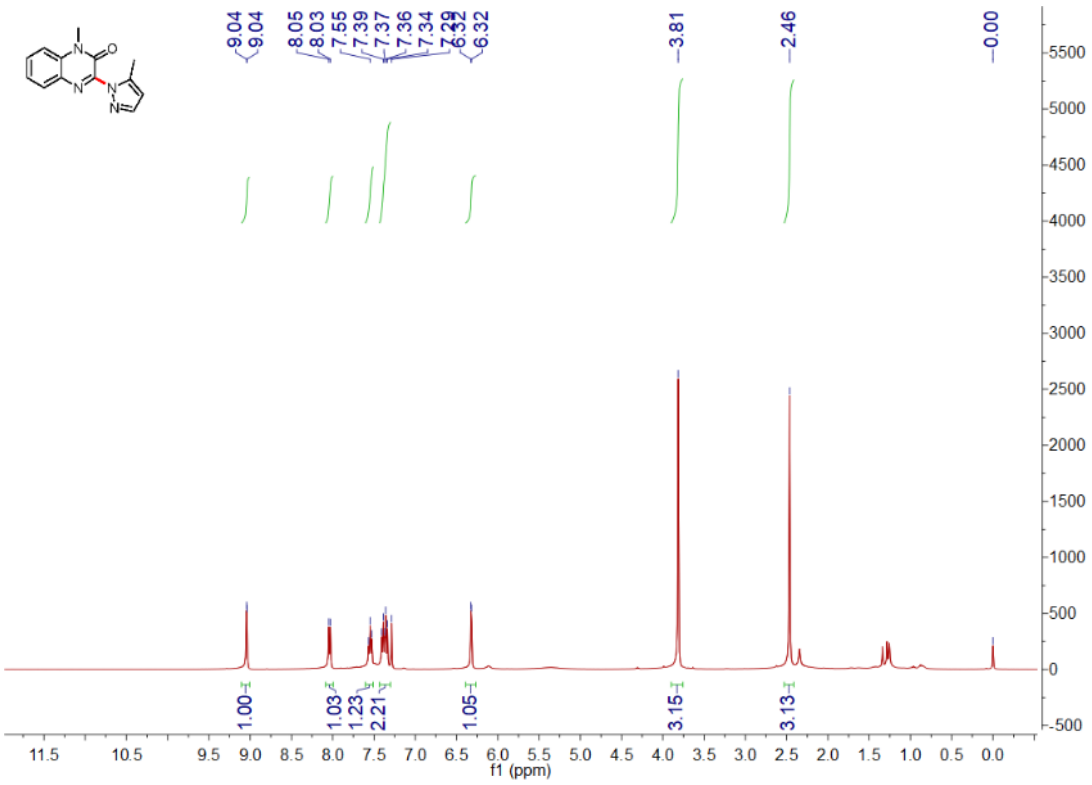
^{1}H NMR spectrum of compound **3r**



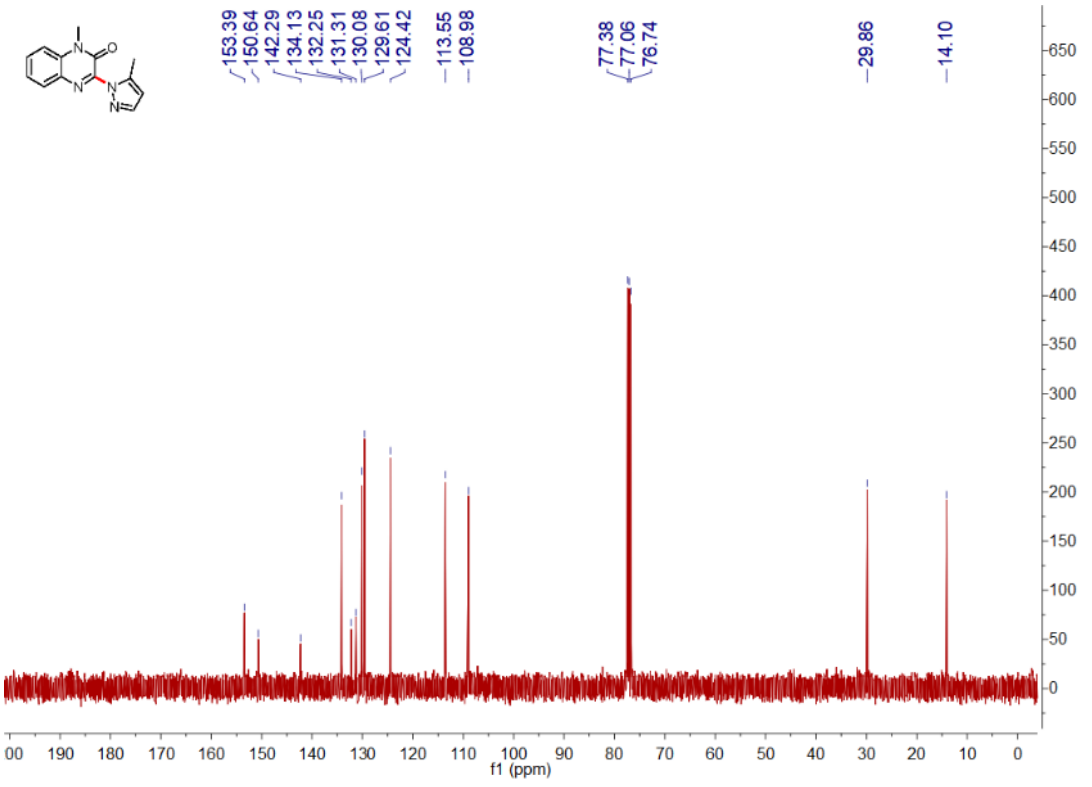
^{13}C NMR spectrum of compound **3r**



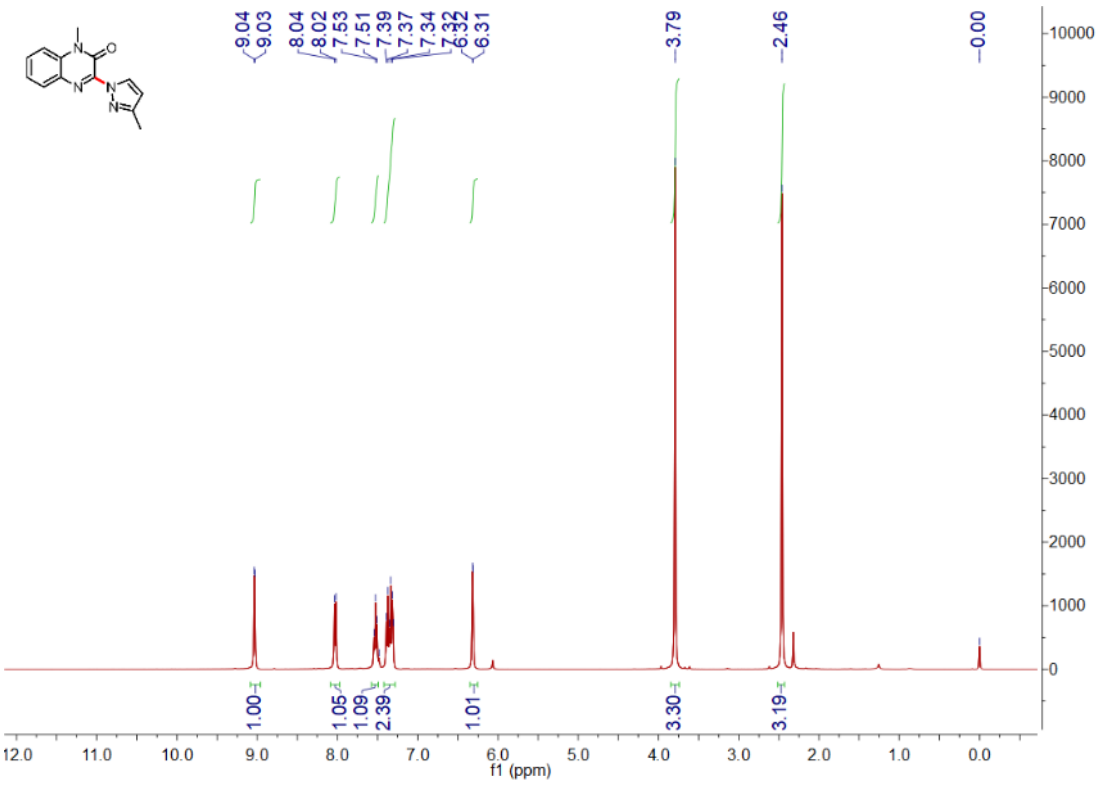
^{1}H NMR spectrum of compound **3s**



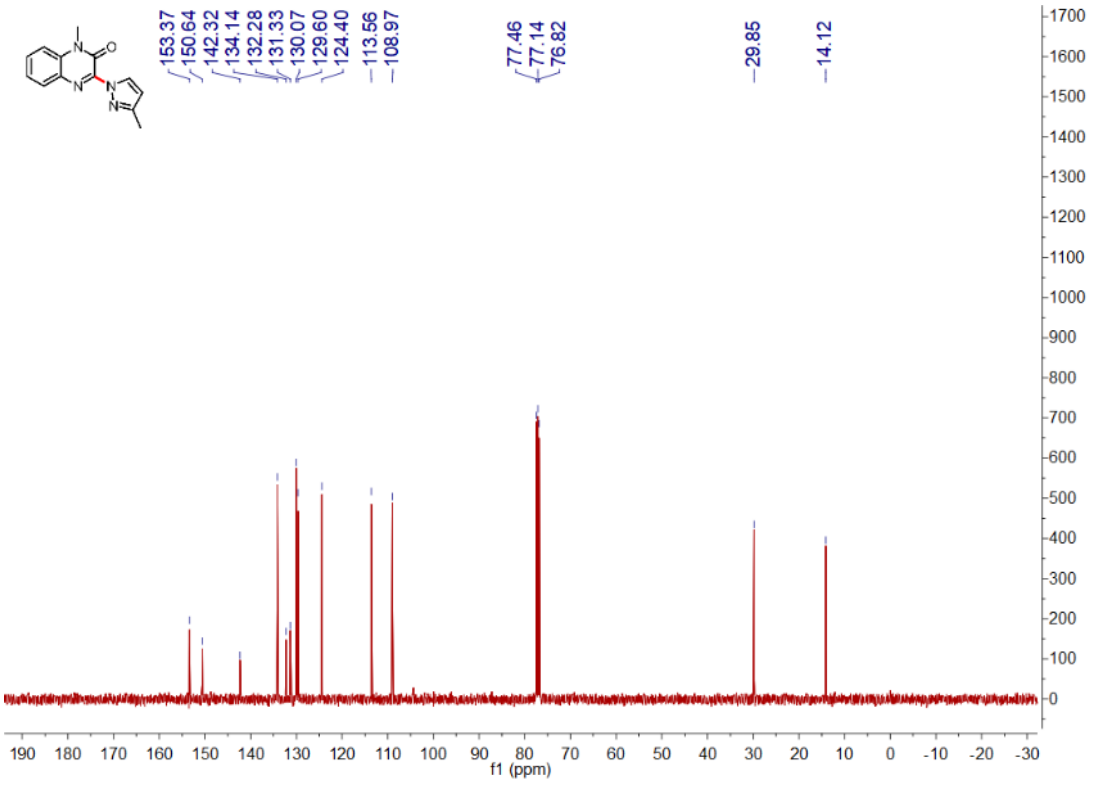
^{13}C NMR spectrum of compound **3s**



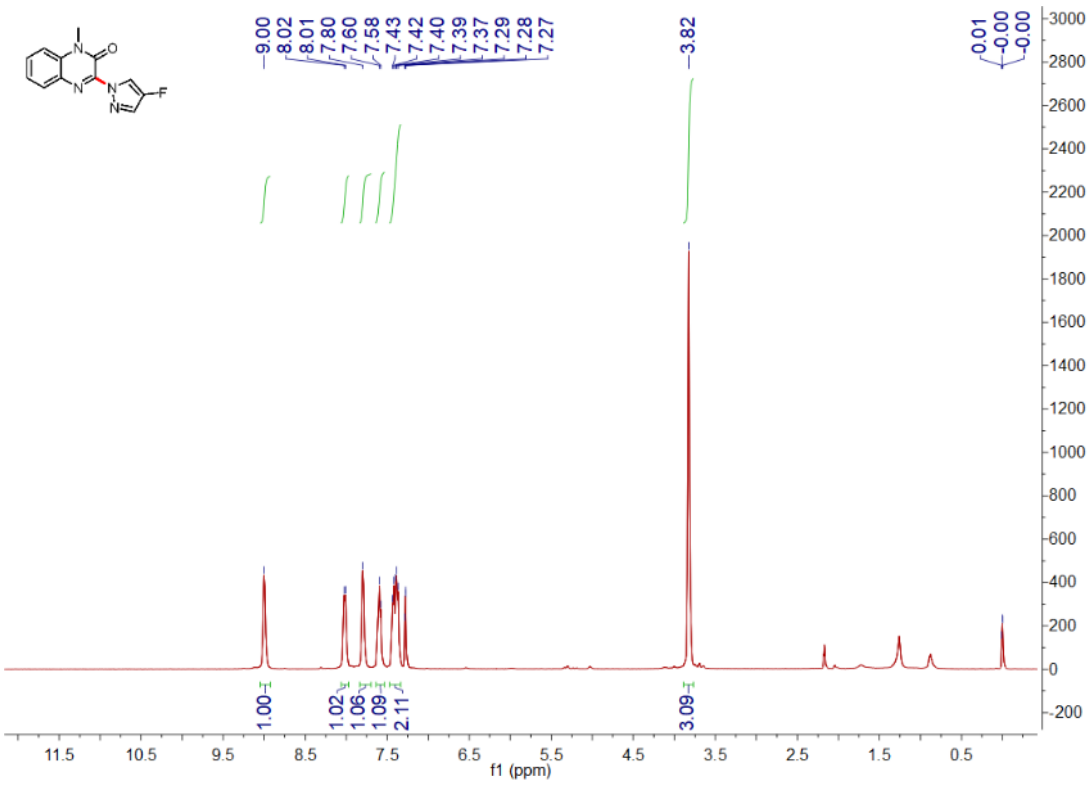
^{1}H NMR spectrum of compound **3t**



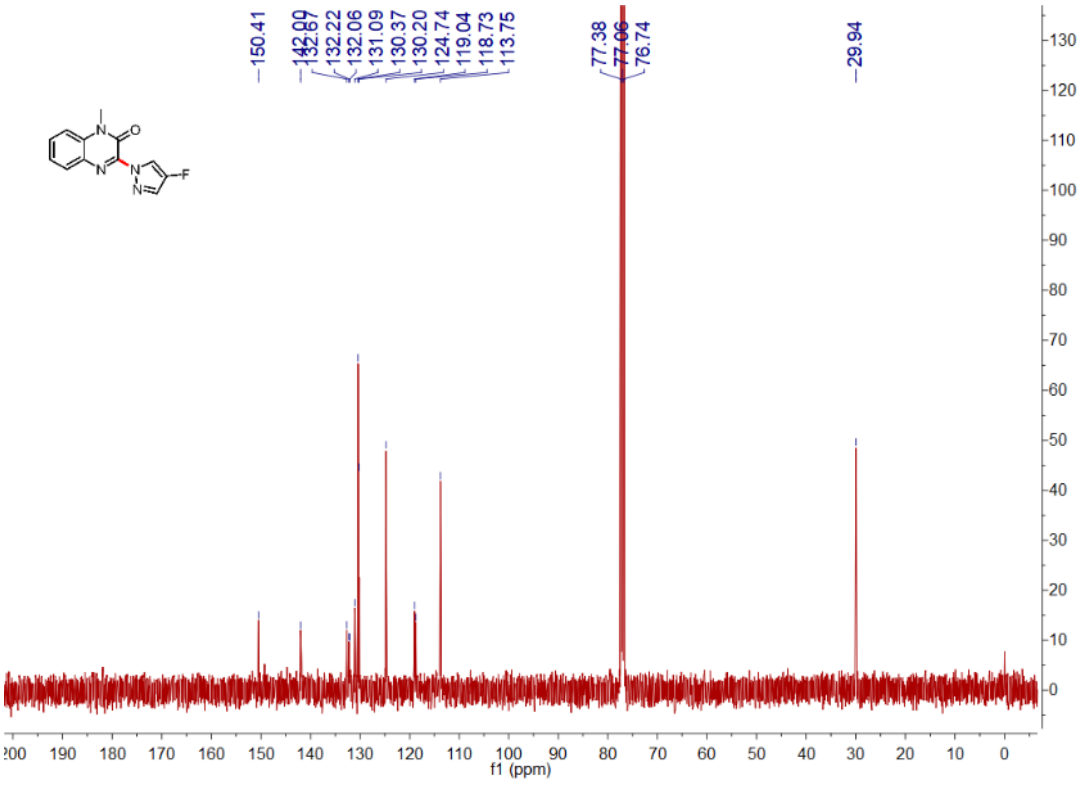
^{13}C NMR spectrum of compound **3t**



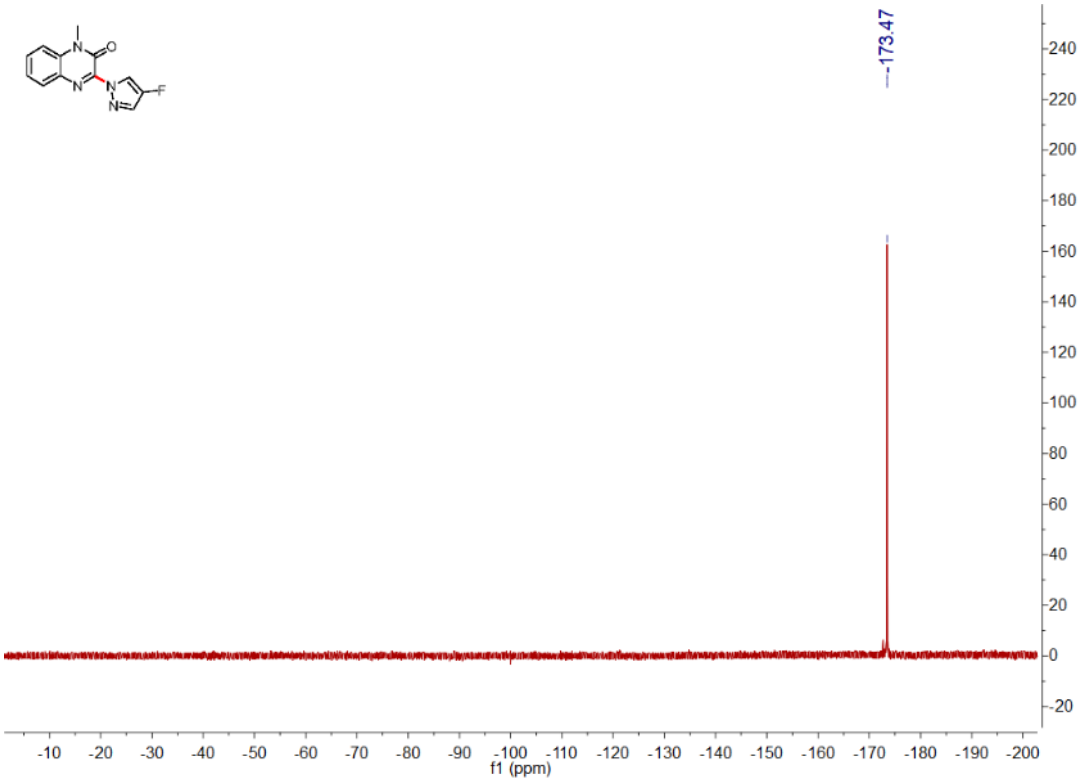
^{1}H NMR spectrum of compound **3u**



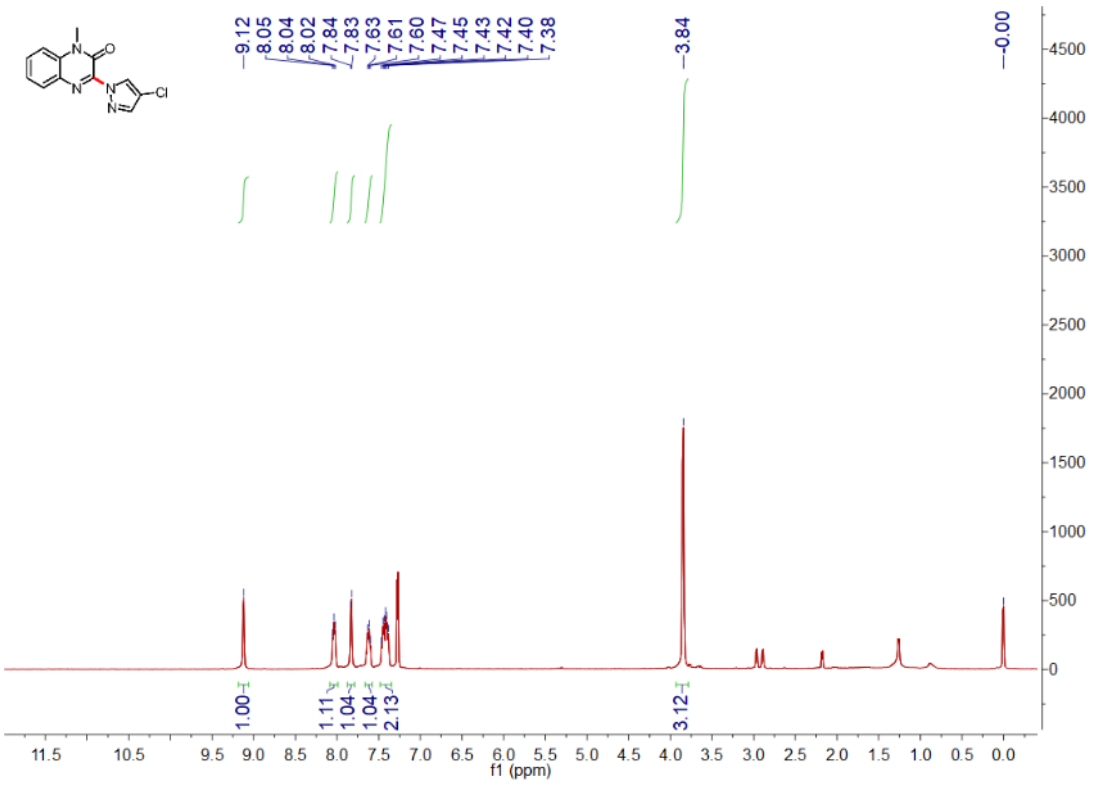
^{13}C NMR spectrum of compound **3u**



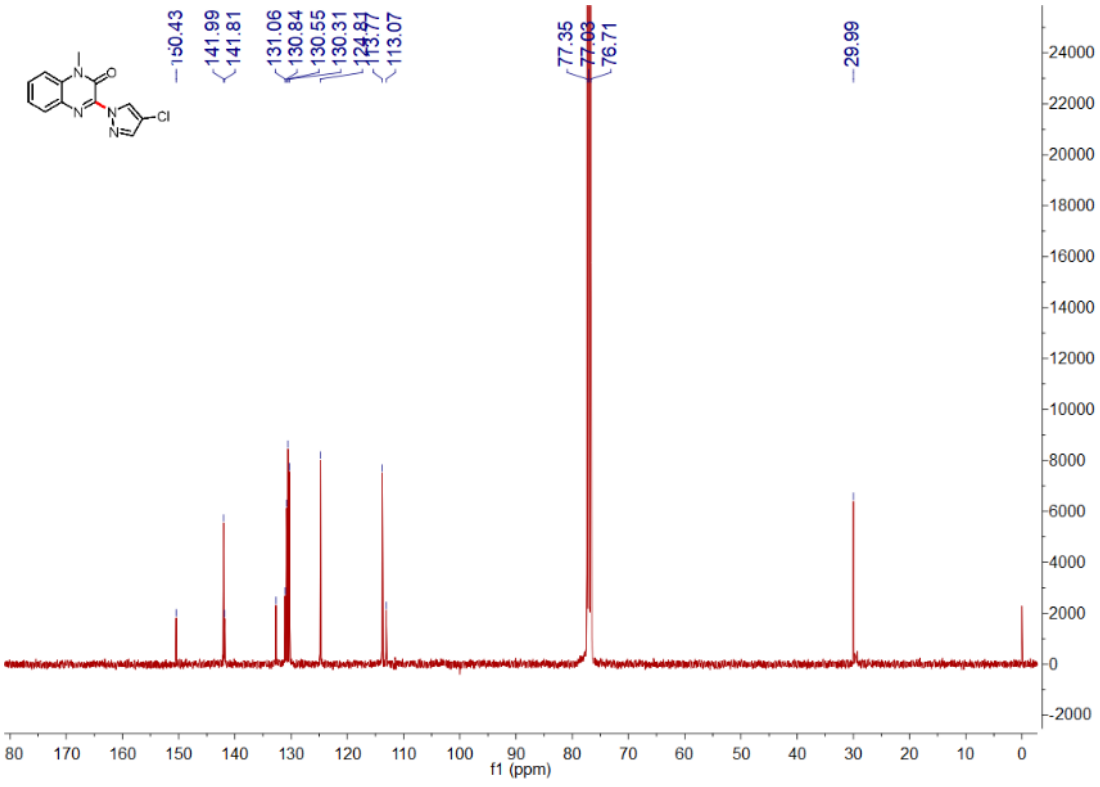
^{19}F NMR spectrum of compound **3u**



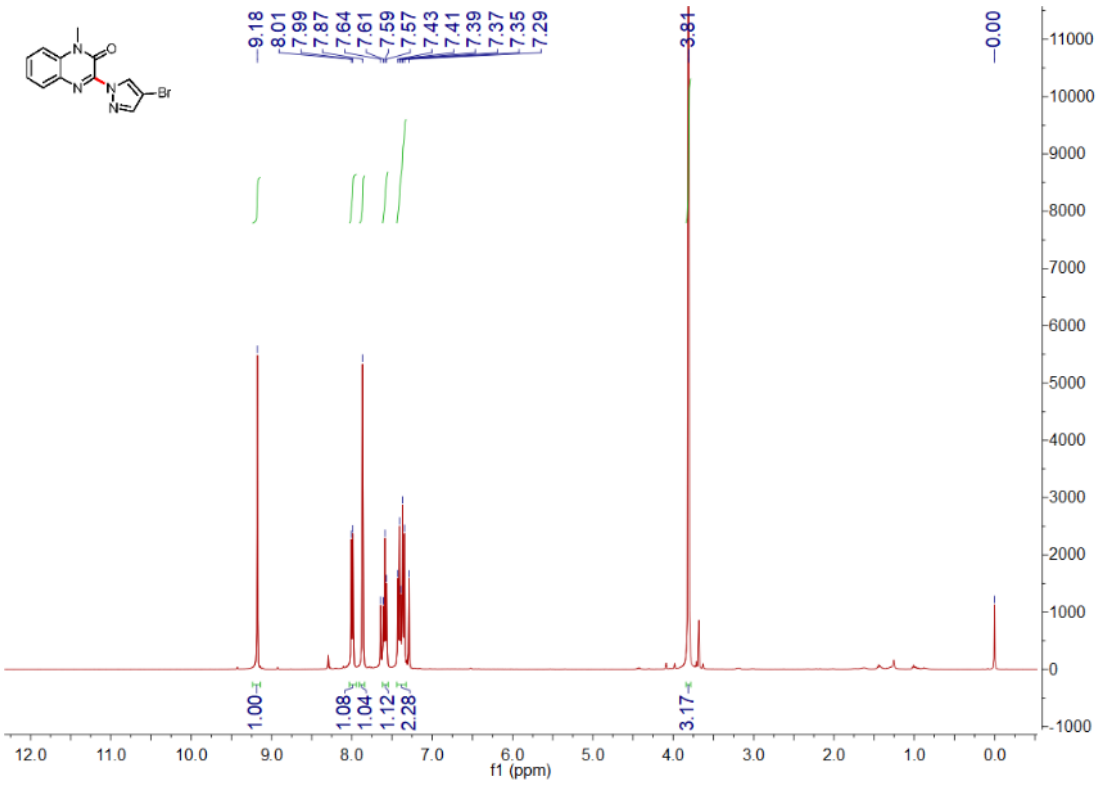
^{1}H NMR spectrum of compound **3v**



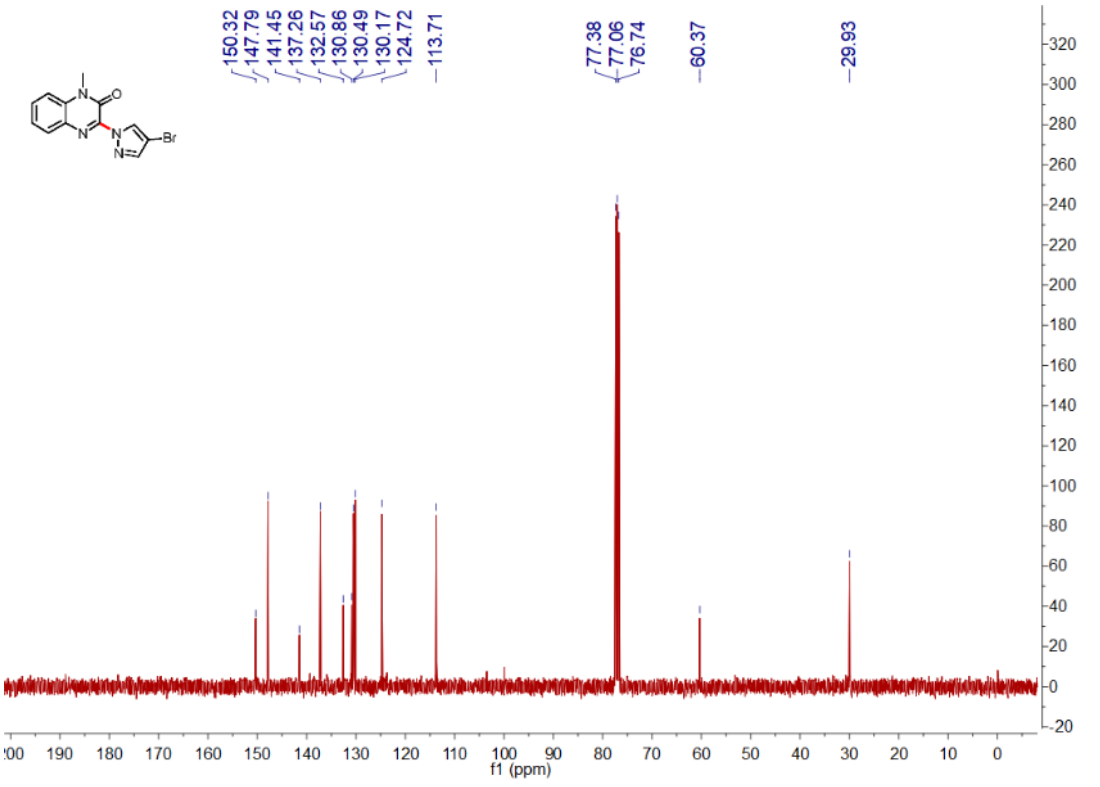
^{13}C NMR spectrum of compound **3v**



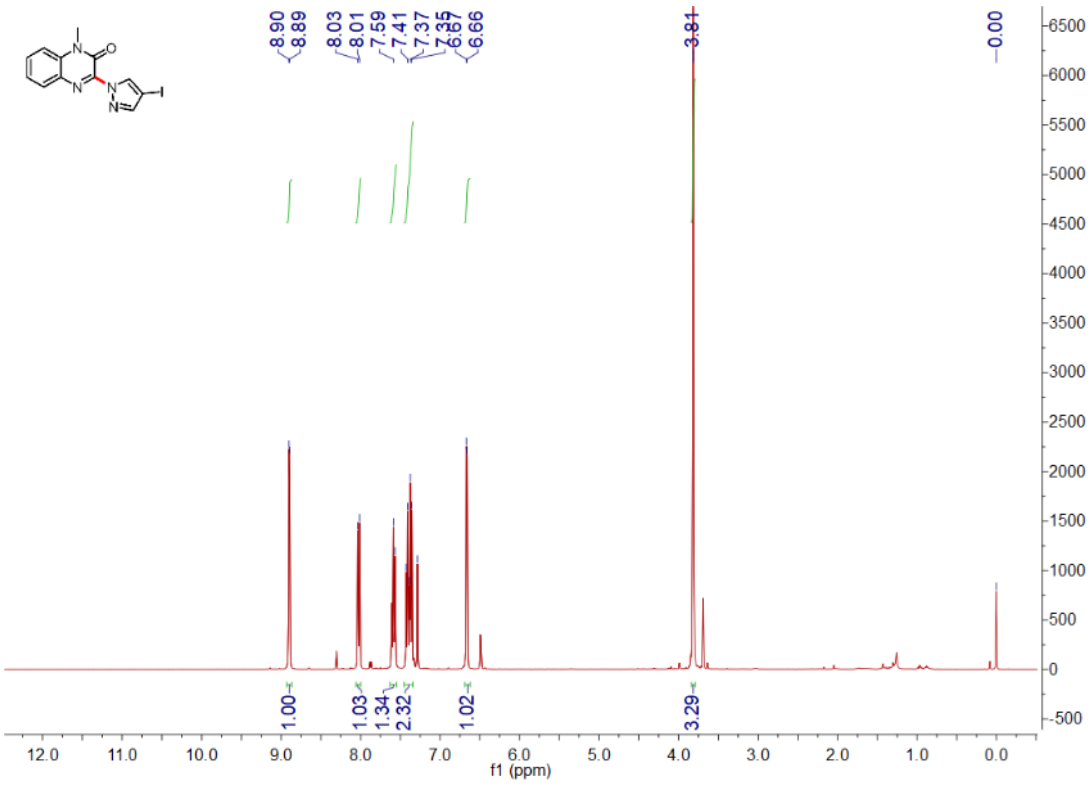
^{1}H NMR spectrum of compound **3w**



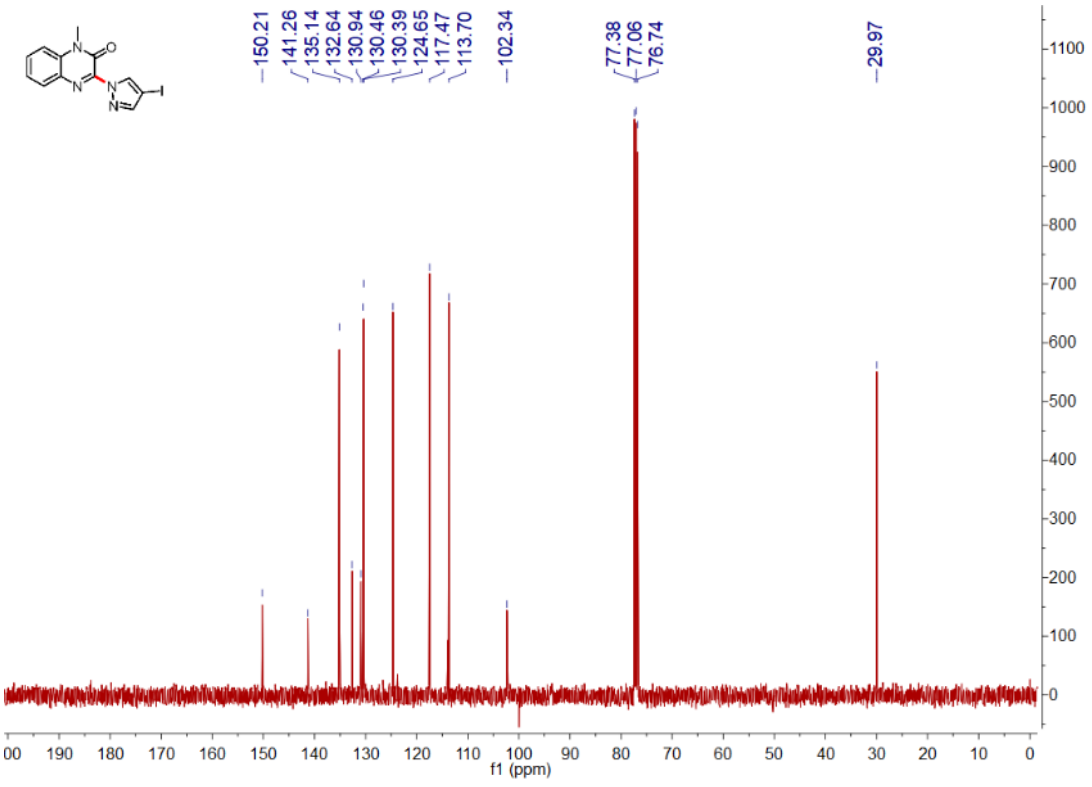
^{13}C NMR spectrum of compound **3w**



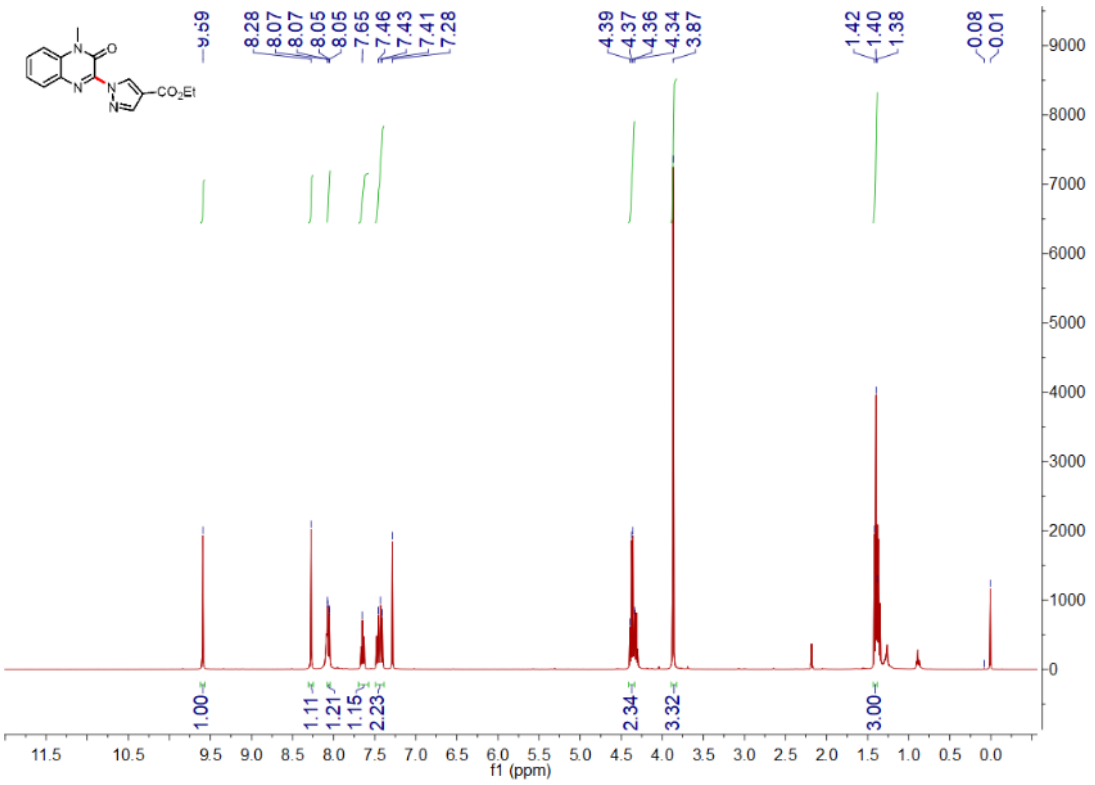
^{1}H NMR spectrum of compound **3x**



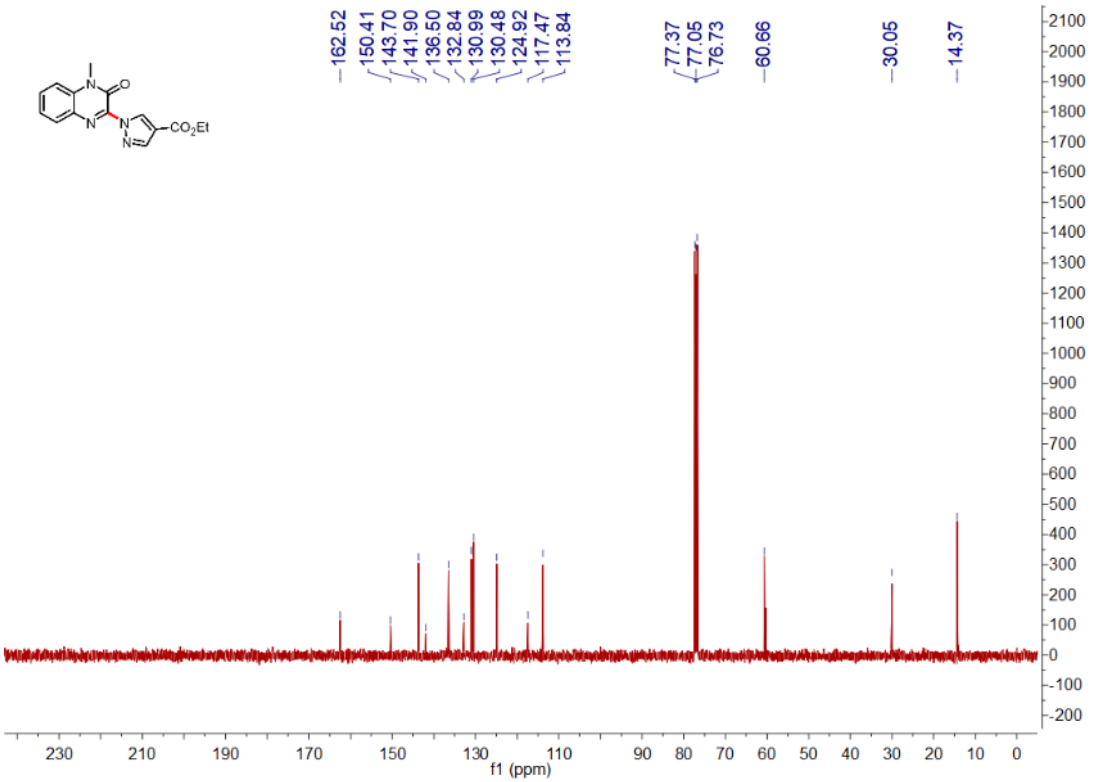
^{13}C NMR spectrum of compound **3x**



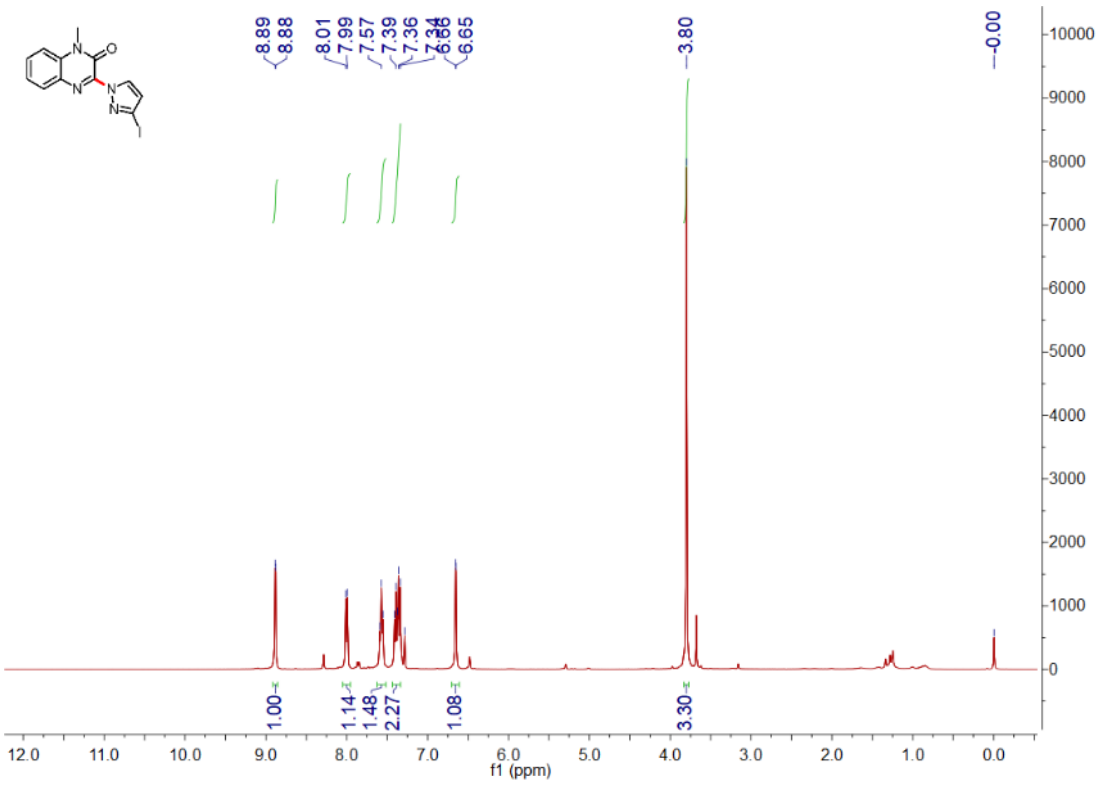
^{1}H NMR spectrum of compound **3y**



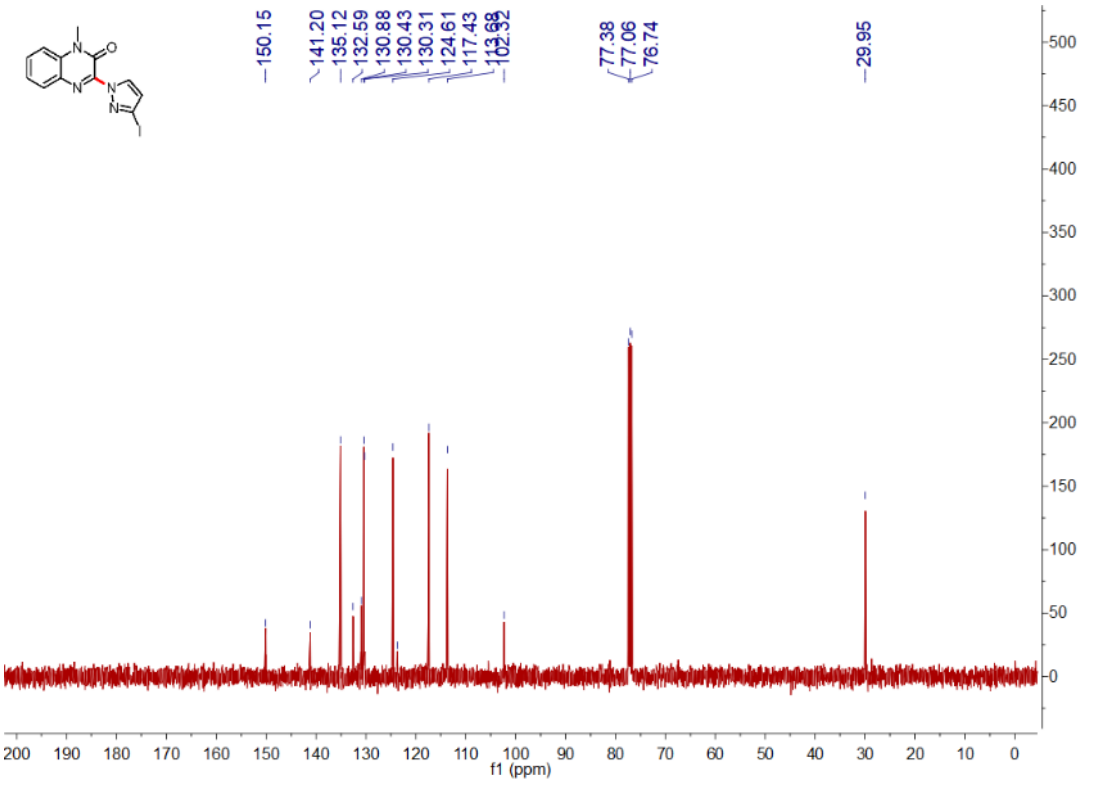
^{13}C NMR spectrum of compound **3y**



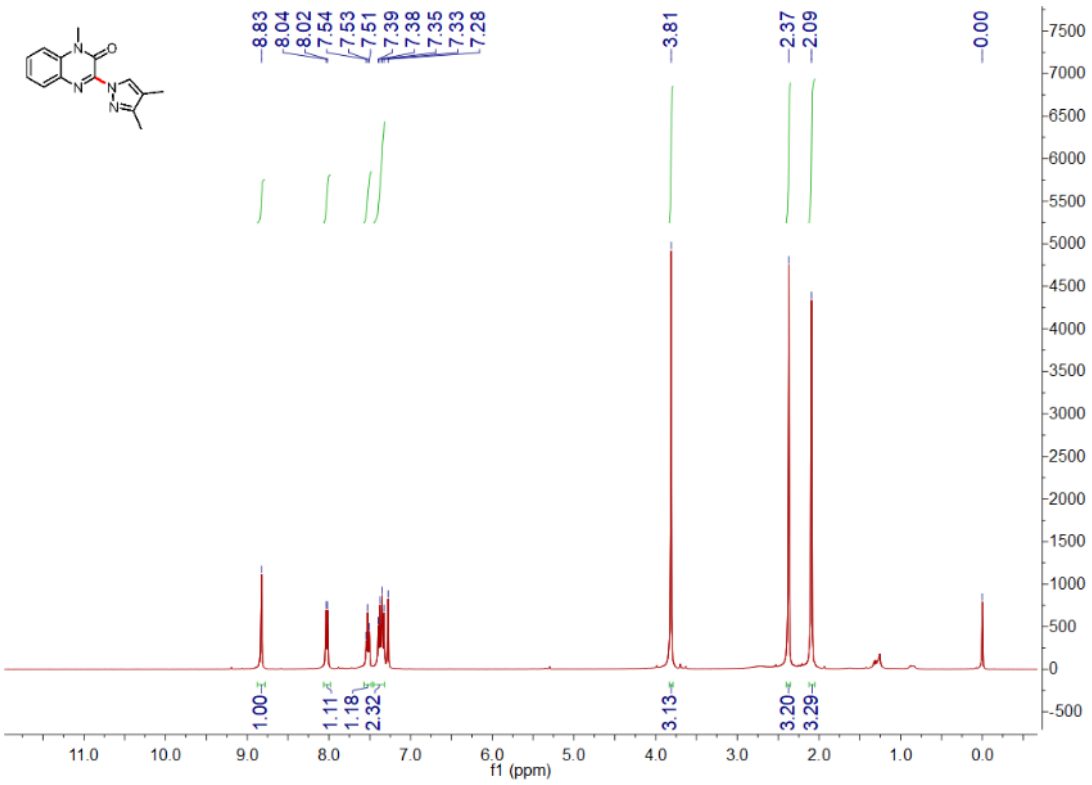
^{1}H NMR spectrum of compound **3z**



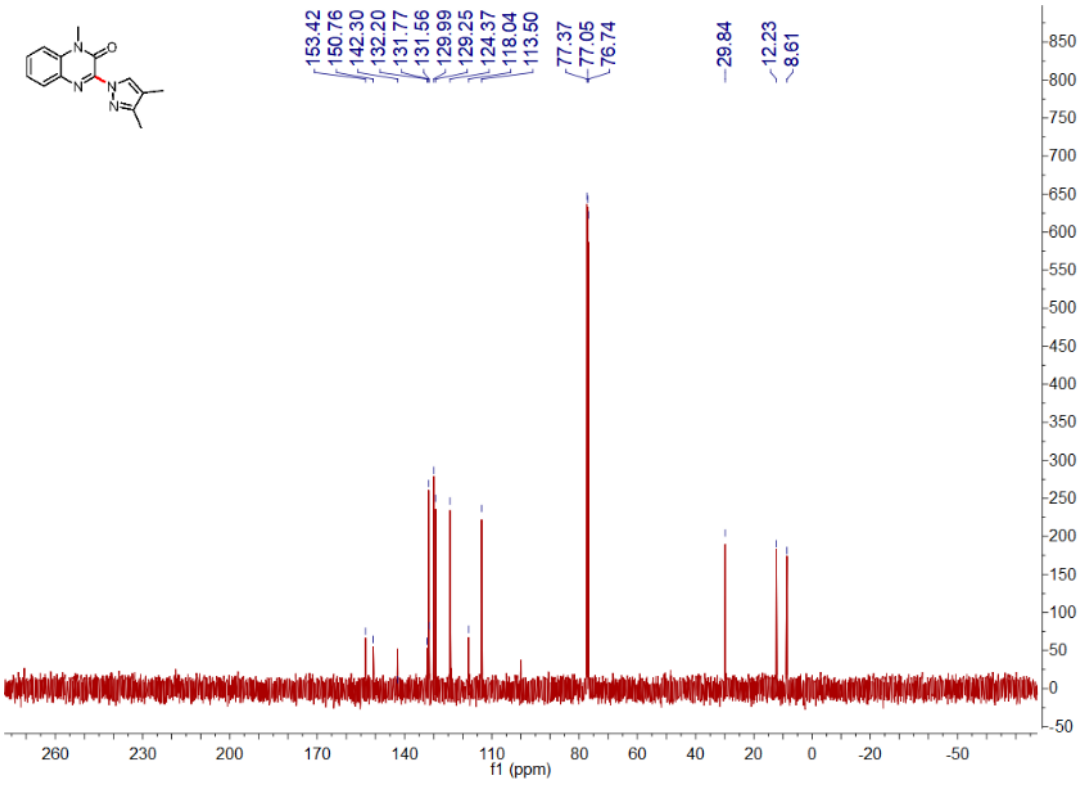
^{13}C NMR spectrum of compound **3z**



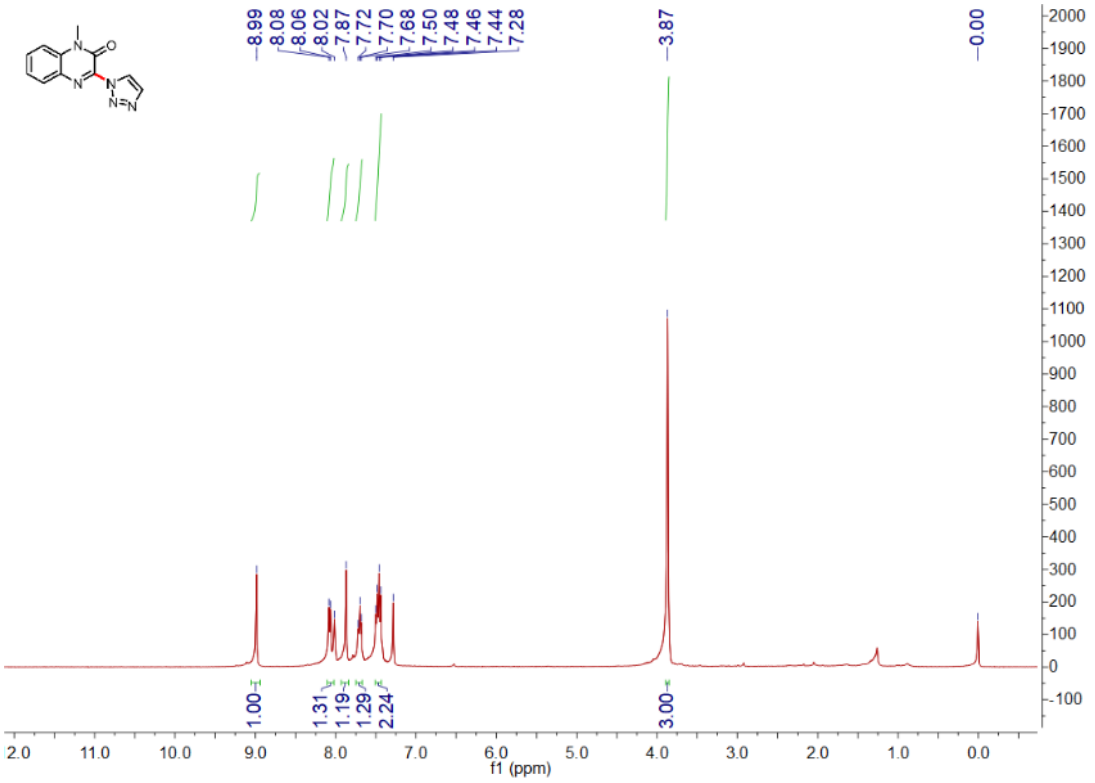
^{1}H NMR spectrum of compound **3aa**



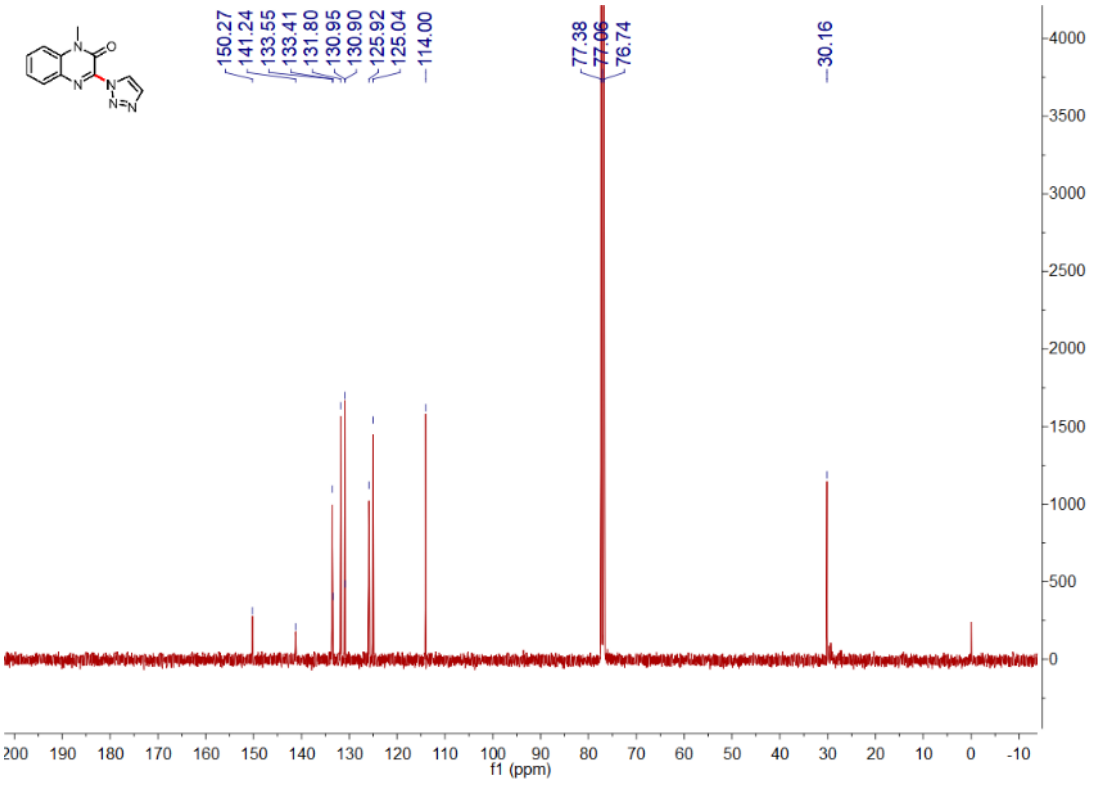
^{13}C NMR spectrum of compound **3aa**



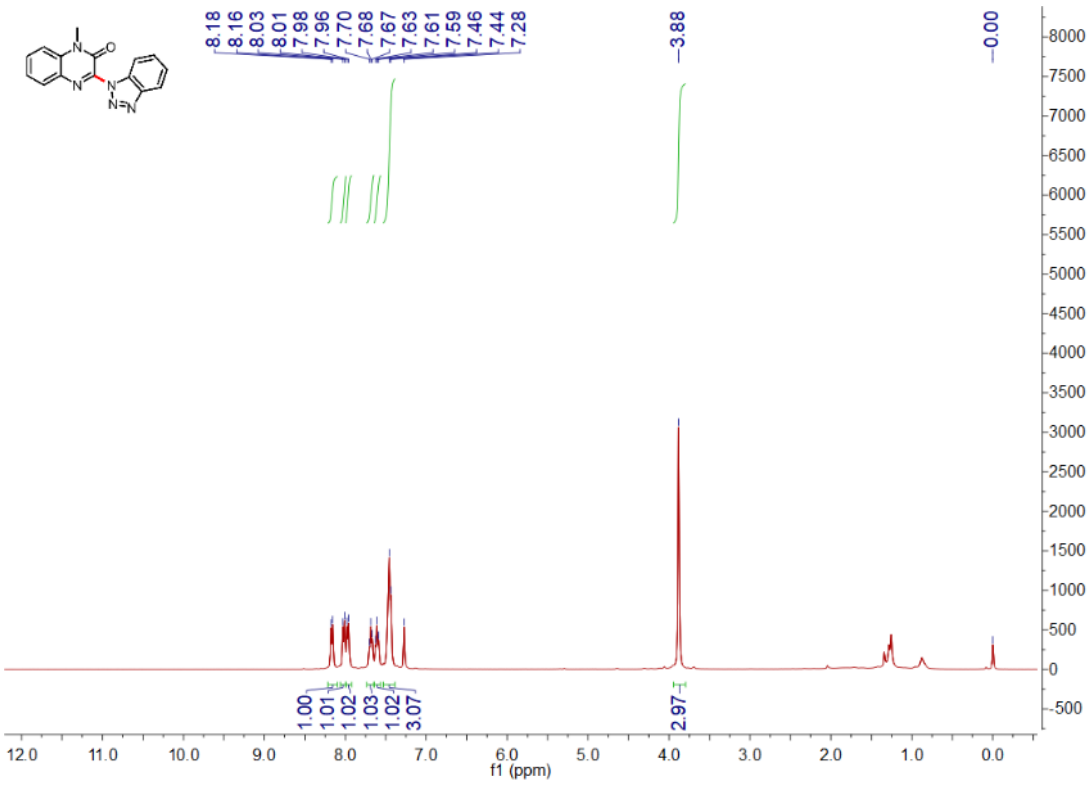
^{1}H NMR spectrum of compound **3ab**



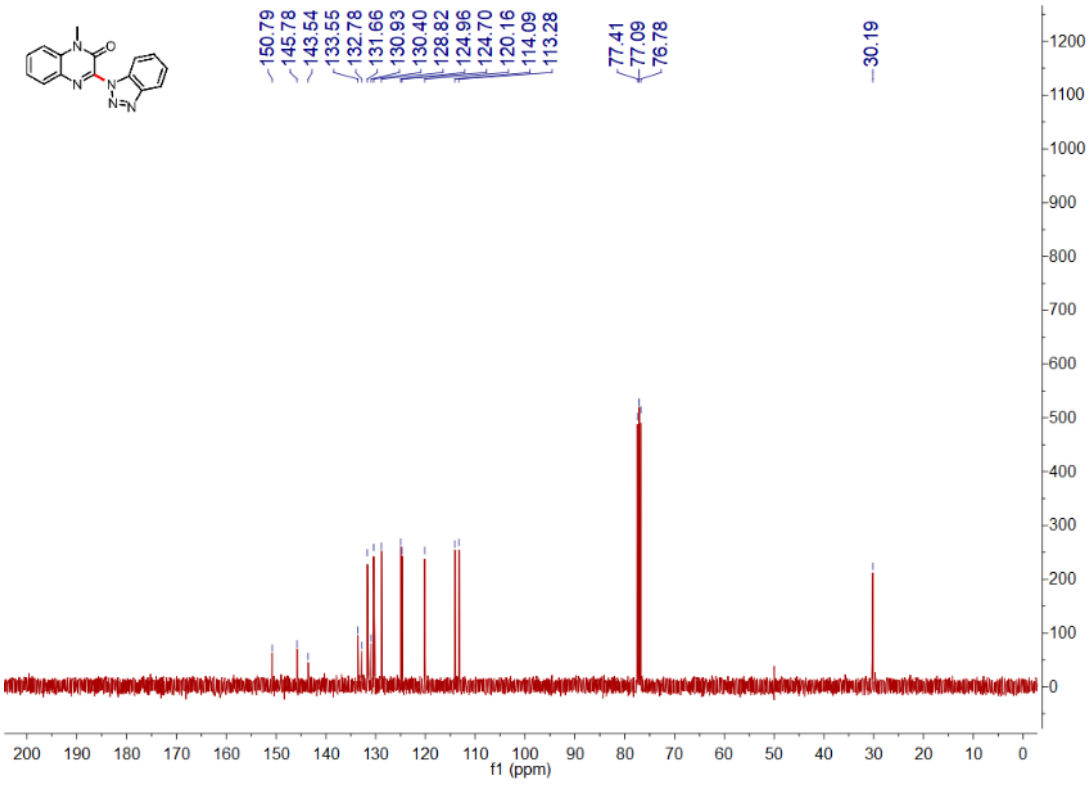
^{13}C NMR spectrum of compound **3ab**



^{1}H NMR spectrum of compound **3ac**



^{13}C NMR spectrum of compound **3ac**



11. References

[1] M. Gao, Y. Li, L. Xie, R. Chauvin, X. Cui, *Chem. Commun.* **2016**, *52*, 2846-2849.