NJC

Supporting Information

Efficient one-step synthesis of 3-(indol-2-yl)quinoxalin-2(*1H*)-ones via electrochemical oxidative cross-dehydrogenative coupling

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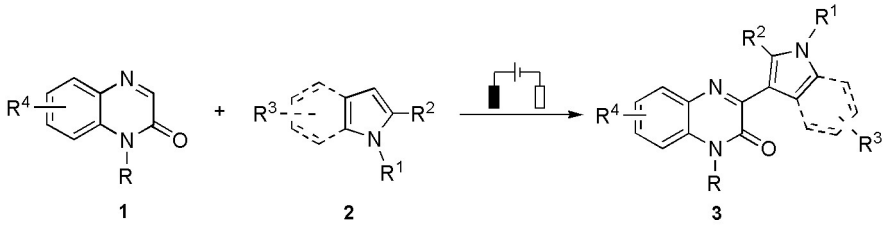
Contents

1. General information

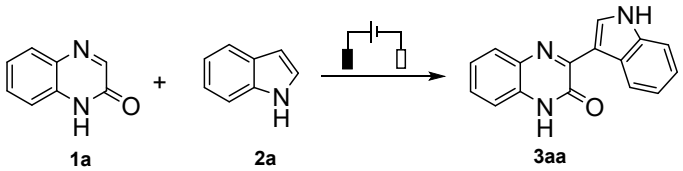
Unless otherwise specially stated, all reagents were purchased from commercial supplies and all solvents were used without any purification. Thin-layer chromatography (TLC) was performed to monitor reaction progress on silica gel GF254 plates (0.2 mm thick, Qingdao Haiyang Chemical Co., Ltd.) and all compounds were visualized with a UV light of 254 nm and 365 nm. NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400 MHz (^{1}H NMR) and 101 MHz (^{13}C NMR). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H: residual internal DMSO (δ 2.51 ppm); ^{13}C: internal DMSO (δ 39.6 ppm). Coupling constants were quoted in Hz (J). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

2. General procedure for the synthesis of compounds 3aa-3ar and 3ba-3ma



An undivided cell was equipped with a graphite rod (Φ = 5 mm) anode and a Pt plate (1.0 cm ×1.0 cm) cathode and connected to a DC regulated power supply. To the cell was added quinoxalinone **1** (0.25 mmol, 1.0 equiv.), indole or pyrrole **2** (0.35 mmol, 1.4 equiv.), $LiClO_4$ (0.5 mmol), and CH_3CN (5.0 mL). The mixture was stirred for 15 minutes at 30 °C, then electrolyzed under a constant current of 4.5 mA for 1.5 hours. After the reaction was completed, the mixture was sonicated for 1 minute to remove the reactants and products adsorbed on electrodes, and then filtered. The residue was washed with cool CH_3CN (3 × 1.0 mL) and deionized water (3 × 1.0 mL) to remove the excess indole and electrolyte. The product was dried under vacuum for 24 hours.

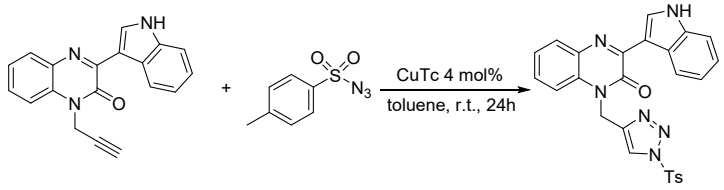
3. Gram-scale experiment



An undivided cell was equipped with a graphite plate (2.0 × 2.0 cm) anode and a Pt plate (2.0 cm × 2.0 cm) cathode and connected to a DC regulated power supply. To the cell was added quinoxalin-2(1*H*)-one **1a** (5.0 mmol, 1.0 equiv.), indole **2a** (7.0 mmol, 1.4 equiv.), $LiClO_4$ (10 mmol), and CH_3CN (100 mL). The mixture was stirred for 15 minutes at 30 °C, then electrolyzed under a constant current of 18.0 mA. After the reaction was completed, the

mixture was sonicated for 1 minute to remove the reactants and products adsorbed on electrodes, and then filtered. The residue was washed with cool CH_3CN (3 × 20 mL) and deionized water (3 × 20 mL) to remove the excess indole and electrolyte. The product was dried under vacuum for 24 hours.

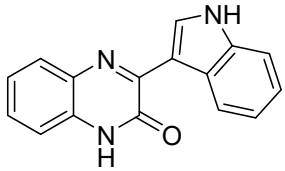
4. Product transformation experiment



3da **4**

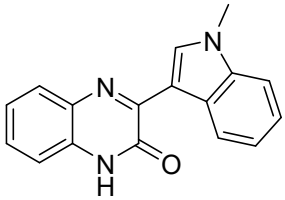
A 10 mL reaction tube was added **3da** (0.1 mmol, 1.0 equiv.), CuTc (0.004 mmol, 0.04 equiv.) and toluene (1.0 mL), and the mixture was stirred for 15 min at room temperature, followed by addition of TsN_3 (0.12 mmol, 1.2 equiv.) via a syringe. The resulting mixture was stirred at room temperature for 24 hours. Then the reaction mixture was filtered and the residue was washed with toluene (3×1.0 mL) to remove the excess TsN_3 and catalyst. The residue was dried under vacuum at room temperature for 24 hours.

5. Characterization data of 3aa-3ar, 3ba-3ma and 4



3-(1H-indol-3-yl)quinoxalin-2(1*H*)-one (3aa)[1]

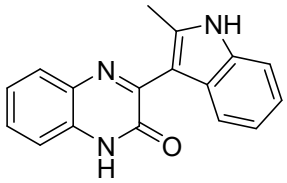
Following the general procedure, the desired compound was obtained as a yellow solid, mp 330-331 °C, 50 mg, 77% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.41 (s, 1H), 11.79 (s, 1H), 8.95 (d, *J* = 2.9 Hz, 1H), 8.93-8.84 (m, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 5.8, 2.6 Hz, 1H), 7.43 (dd, *J* = 11.0, 4.2 Hz, 1H), 7.31 (dd, *J* = 11.7, 4.5 Hz, 2H), 7.24 (m, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.88, 152.46, 136.75, 133.54, 133.12, 130.65, 128.40, 128.05, 126.68, 123.66, 123.45, 123.00, 121.45, 115.39, 112.34, 111.81.



3-(1-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ab)[1]

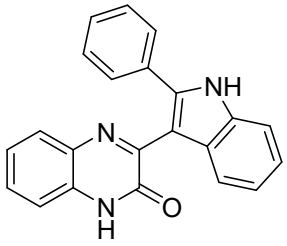
Following the general procedure, the desired compound was obtained as a yellow solid, mp 286-287 °C, 56 mg, 81% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.46 (s, 1H), 8.95 (d, *J* = 2.4 Hz, 1H), 8.90 (t, *J*

= 4.8 Hz, 1H), 7.87 (dd, *J* = 7.4, 2.3 Hz, 1H), 7.62-7.52 (m, 1H), 7.44 (dd, *J* = 8.7, 6.5 Hz, 1H), 7.38-7.22 (m, 4H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.43, 151.73, 136.93, 136.90, 132.74, 130.24, 128.05, 127.65, 126.76, 123.32, 123.21, 122.71, 121.37, 115.01, 110.39, 110.27, 33.10.



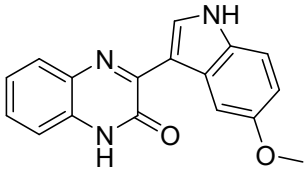
3-(2-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ac)[1]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 290-292 °C, 60 mg, 87% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.33 (s, 1H), 11.49 (s, 1H), 7.78 (dd, *J* = 13.8, 7.8 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.31 (dt, *J* = 15.3, 6.8 Hz, 3H), 7.05 (dt, *J* = 14.3, 6.9 Hz, 2H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.67, 154.63, 139.40, 135.22, 132.61, 131.36, 128.78, 128.04, 127.94, 123.14, 120.91, 119.60, 114.98, 110.64, 109.24, 14.35.



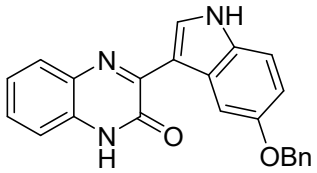
3-(2-phenyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ad)

Following the general procedure, the desired compound was obtained as a yellow solid, mp 347-350 °C, 70 mg, 83% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.27 (s, 1H), 11.83 (s, 1H), 7.73 (dd, *J* = 14.8, 7.9 Hz, 2H), 7.50 (dd, *J* = 13.9, 7.8 Hz, 4H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (q, *J* = 7.2 Hz, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.08 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 155.18, 154.08, 139.40, 136.08, 133.39, 132.50, 131.85, 129.42, 128.60, 128.43, 128.29, 127.78, 123.13, 122.12, 120.24, 120.08, 115.11, 111.50, 108.67. HRMS (ESI) m/z calculated for $C_{22}H_{16}N_3O$ $(M+H)^+$: 338.1288. Found: 338.1289.



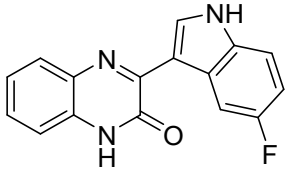
3-(5-methoxy-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ah)[1]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 319-321 °C, 66 mg, 91% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.39 (s, 1H), 11.67 (s, 1H), 8.89 (d, *J* = 3.0 Hz, 1H), 8.46 (d, *J* = 2.5 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.53-7.19 (m, 4H), 6.89 (dd, *J* = 8.7, 2.6 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.98, 154.52, 152.13, 133.52, 132.72, 131.26, 130.19, 127.91, 127.63, 126.99, 123.30, 115.00, 112.56, 112.15, 111.15, 105.18, 55.34.



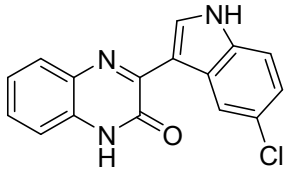
3-(5-(benzyloxy)-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ai)[2]

Following the general procedure, the desired compound was obtained as a solid, mp 274-276 °C, 58 mg, 63% yield. ^{1}H NMR (400 MHz, d_6-DMSO) 12.37 (s, 1H), 11.67 (s, 1H), 8.88 (d, J = 3.0 Hz, 1H), 8.49 (d, J = 2.6 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.56 (d, J = 7.1 Hz, 2H), 7.46-7.37 (m, 4H), 7.37-7.26 (m, 3H), 6.96 (dd, J = 8.7, 2.5 Hz, 1H), 5.24 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.48, 154.00, 152.03, 137.99, 133.56, 132.68, 131.38, 130.16, 128.47, 127.89, 127.69, 127.64, 126.89, 123.24, 114.95, 112.89, 112.57, 111.17, 106.58, 69.82.



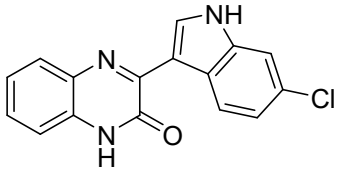
3-(5-fluoro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3aj)

Following the general procedure, the desired compound was obtained as a yellow solid, mp 296-298 °C, 48 mg, 69% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.44 (s, 1H), 11.88 (s, 1H), 8.98 (d, J = 3.0 Hz, 1H), 8.56 (d, J = 10.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 8.8, 4.7 Hz, 1H), 7.44 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.3 Hz, 2H), 7.09 (dd, J = 13.9, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 158.25 (d, J = 232.4 Hz), 154.38, 151.81, 134.66, 132.97, 132.58, 130.27, 128.19, 127.71, 126.70 (d, J = 11.0 Hz), 123.32, 115.03, 113.01 (d, J = 9.9 Hz), 111.42 (d, J = 4.1 Hz), 110.63 (d, J = 26.0 Hz), 107.78 (d, J = 24.4 Hz). HRMS (ESI) m/z calculated for $C_{16}H_{11}FN_3O$ $(M+H)^+$: 280.0881. Found: 280.0881.



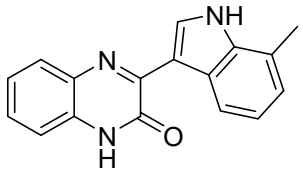
3-(5-chloro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ak)[1]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 312-314 °C, 52 mg, 71% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.48 (s, 1H), 11.97 (s, 1H), 8.98 (d, J = 3.0 Hz, 1H), 8.86 (d, J = 2.2 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.2 Hz, 2H), 7.27 (dd, J = 8.6, 2.2 Hz, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.35, 151.70, 134.85, 134.40, 132.51, 130.32, 128.34, 127.70, 127.32, 125.71, 123.38, 122.56, 122.00, 115.07, 113.54, 110.98.



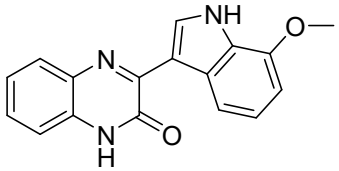
3-(6-chloro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3al)

Following the general procedure, the desired compound was obtained as a yellow solid, mp 308-310 °C, 52 mg, 71% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.46 (s, 1H), 11.88 (s, 1H), 8.95 (d, J = 2.9 Hz, 1H), 8.85 (d, J = 8.6 Hz, 1H), 7.88 (dd, J = 7.2, 1.9 Hz, 1H), 7.57 (d, J = 1.7 Hz, 1H), 7.48-7.41 (m, 1H), 7.33 (d, J = 7.6 Hz, 2H), 7.25 (dd, J = 8.6, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.37, 151.70, 136.88, 133.96, 132.56, 130.38, 128.35, 127.77, 127.20, 125.04, 124.31, 123.35, 121.23, 115.07, 111.70, 111.44. HRMS (ESI) m/z calculated for $C_{16}H_{11}ClN_3O$ $(M+H)^+$: 296.0585. Found: 296.0588.



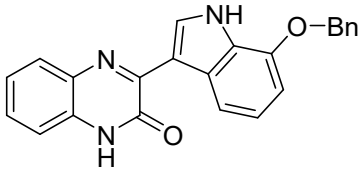
3-(7-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3am)

Following the general procedure, the desired compound was obtained as a yellow solid, mp 284-286 °C, 52 mg, 75% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.40 (s, 1H), 11.78 (s, 1H), 8.93 (d, J = 3.0 Hz, 1H), 8.72 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.54-7.39 (m, 1H), 7.38-7.30 (m, 2H), 7.14 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 7.2 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.51, 152.03, 135.76, 132.81, 132.72, 130.24, 127.99, 127.64, 126.04, 123.25, 121.25, 120.98, 120.69, 114.98, 111.81, 16.83. HRMS (ESI) m/z calculated for $C_{17}H_{14}N_3O$ $(M+H)^+$: 276.1131. Found: 276.1131.



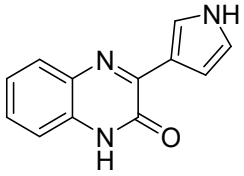
3-(7-methoxy-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3an)[1]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 325-327 °C, 48 mg, 66% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.39 (s, 1H), 11.90 (s, 1H), 8.82 (d, J = 3.0 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.48-7.37 (m, 1H), 7.31 (d, J = 7.6 Hz, 2H), 7.16 (t, J = 7.9 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.47, 152.03, 146.20, 132.70, 132.41, 130.25, 128.05, 127.79, 127.66, 126.30, 123.28, 121.72, 115.75, 115.00, 111.96, 103.40, 55.32.



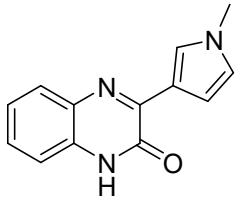
3-(7-(benzyloxy)-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ao)[1]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 281-283 °C, 47 mg, 51% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.41 (s, 1H), 11.90 (s, 1H), 8.84 (d, J = 3.0 Hz, 1H), 8.46 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 7.1 Hz, 2H), 7.47-7.40 (m, 3H), 7.40-7.35 (m, 1H), 7.35-7.28 (m, 2H), 7.14 (t, J = 7.9 Hz, 1H), 6.93 (d, J = 7.8 Hz, 1H), 5.31 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.52, 152.05, 145.26, 137.28, 132.74, 132.62, 130.28, 128.54, 128.12, 128.02, 127.96, 127.86, 127.71, 126.54, 123.35, 121.72, 116.00, 115.05, 112.00, 104.77, 99.63, 69.47.



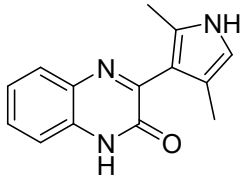
3-(1*H*-pyrrol-3-yl)quinoxalin-2(1*H*)-one (3ap)[1]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 246-248 °C, 42 mg, 80% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.44 (s, 1H), 11.66 (s, 1H), 7.72-7.70 (m, 1H), 7.44-7.40 (m, 2H), 7.31-7.26 (m, 2H), 7.06 (s, 1H), 6.23 (s, 1H). ^{13}C NMR (101 MHz, d_6-DMSO): δ 153.85, 146.54, 132.38, 130.86, 128.31, 128.23, 127.40, 123.77, 123.49, 115.87, 115.19, 109.97.



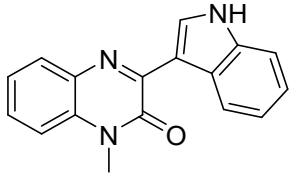
3-(1-methyl-1*H*-pyrrol-3-yl)quinoxalin-2(1*H*)-one (3aq)[1]

Following the general procedure, the desired compound was obtained as a light yellow solid, mp 213-214 °C, 39 mg, 69% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.35 (s, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.55 (dd, J = 4.0, 1.8 Hz, 1H), 7.46-7.38 (m, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.09 (t, J = 2.2 Hz, 1H), 6.14 (dd, J = 4.0, 2.6 Hz, 1H), 4.05 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 153.79, 147.85, 131.77, 130.75, 130.05, 128.64, 127.81, 127.15, 123.24, 118.75, 114.93, 107.51, 38.24.



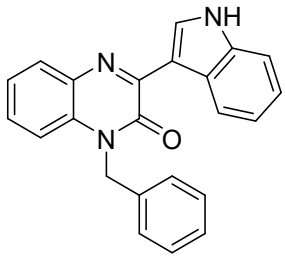
3-(2,4-dimethyl-1*H*-pyrrol-3-yl)quinoxalin-2(1*H*)-one (3ar)[1]

Following the general procedure, the desired compound was obtained as an orange solid, mp 200-201 °C, 50 mg, 84% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.51 (s, 1H), 11.37 (s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.27 (d, J = 7.9 Hz, 2H), 5.89 (s, 1H), 2.50 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 155.34, 146.78, 133.13, 131.21, 129.61, 127.48, 127.25, 126.92, 123.63, 115.06, 111.98, 15.24, 13.09.



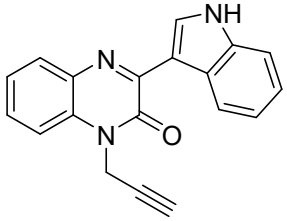
3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ba)[2]

Following the general procedure, the desired compound was obtained as a yellow solid, mp 220-223 °C, 56 mg, 81% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.79 (s, 1H), 8.93 (d, J = 3.0 Hz, 1H), 8.92-8.87 (m, 1H), 7.95-7.90 (m, 1H), 7.60-7.48 (m, 3H), 7.40 (ddd, J = 8.2, 6.0, 2.3 Hz, 1H), 7.28-7.20 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 153.80, 150.75, 136.41, 133.30, 133.09, 131.61, 128.50, 128.42, 126.43, 123.59, 123.14, 122.68, 121.13, 114.57, 112.02, 111.53, 29.24.



1-benzyl-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ca)[2]

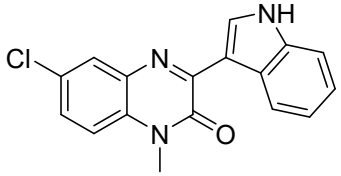
Following the general procedure, the desired compound was obtained as a yellow solid, mp 202-204 °C, 75 mg, 85% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.84 (s, 1H), 8.96 (d, J = 2.8 Hz, 1H), 8.94-8.90 (m, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.53 (dt, J = 6.1, 3.6 Hz, 1H), 7.43 (t, J = 6.6 Hz, 2H), 7.40-7.20 (m, 8H), 5.64 (s, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 152.86, 150.55, 136.40, 133.41, 133.27, 129.92, 128.67, 128.44, 126.31, 123.99, 123.04, 122.75, 121.22, 114.75, 112.03, 111.29, 78.44, 75.12, 31.42.



3-(1*H*-indol-3-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3da)

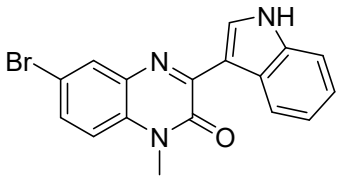
Following the general procedure, the desired compound was obtained as a yellow solid, mp 229-231 °C, 69 mg, 92% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.84 (s, 1H), 8.92 (d, J = 2.5 Hz, 1H), 8.91-8.85 (m, 1H), 7.97 (d, J = 7.9 Hz, 1H), 7.60 (q, J = 8.6 Hz, 2H), 7.56-7.49 (m, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.34-7.16 (m, 2H), 5.22 (s, 2H), 3.35 (s, 1H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 152.83, 150.52,

136.38, 133.38, 133.25, 129.89, 128.64, 128.40, 126.28, 123.95, 123.02, 122.71, 121.18, 114.71, 112.00, 111.27, 78.41, 75.09, 31.39. HRMS (ESI) m/z calculated for $C_{19}H_{14}N_3O$ $(M+H)^+$: 300.1131. Found: 300.1135.



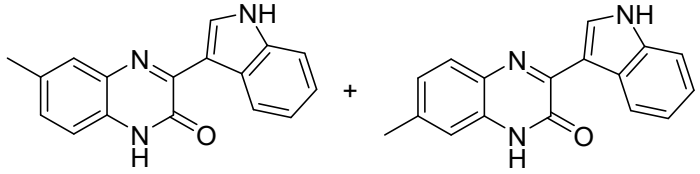
6-chloro-3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ea)

Following the general procedure, the desired compound was obtained as a as yellow solid, mp 265-267 °C, 53 mg, 65% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.82 (s, 1H), 8.92 (d, J = 3.0 Hz, 1H), 8.89-8.81 (m, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 2.2 Hz, 1H), 7.55-7.49 (m, 1H), 7.40 (dd, J = 8.5, 2.2 Hz, 1H), 7.29-7.19 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 153.49, 150.73, 136.38, 133.55, 132.56, 132.40, 131.82, 129.73, 126.31, 123.45, 123.08, 122.69, 121.16, 114.24, 111.99, 111.35, 29.34. HRMS (ESI) m/z calculated for $C_{17}H_{13}ClN_3O$ $(M+H)^+$: 310.0742. Found: 310.0748.



6-bromo-3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3fa)

Following the general procedure, the desired compound was obtained as a yellow solid, mp 286-288 °C, 43 mg, 49% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.83 (s, 1H), 8.93 (d, J = 3.0 Hz, 1H), 8.89-8.82 (m, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.77 (d, J = 2.0 Hz, 1H), 7.53 (ddd, J = 6.4, 5.8, 1.7 Hz, 2H), 7.30-7.20 (m, 2H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 153.56, 150.96, 136.46, 133.68, 132.83, 132.19, 130.03, 126.43, 126.37, 123.16, 122.82, 121.30, 121.00, 117.14, 112.10, 111.47, 29.42. HRMS (ESI) m/z calculated for $C_{17}H_{13}BrN_3O$ $(M+H)^+$: 354.0237. Found: 354.0243.



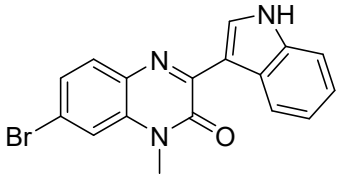
3ga 3ga′

3-(1*H*-indol-3-yl)-6-methylquinoxalin-2(1*H*)-one (3ga)

3-(1*H*-indol-3-yl)-7-methylquinoxalin-2(1*H*)-one (3ga')

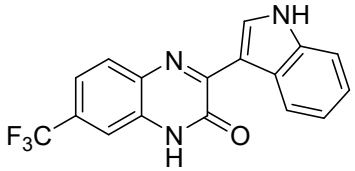
Following the general procedure, the desired compound was obtained as a pale yellow solid, mp 224-226 °C, 60 mg, 87% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.34 (s, 1H), 11.78 (d, J = 10.0 Hz, 1H), 8.99-8.79 (m, 2H), 7.80-7.68 (m, 1H), 7.51 (dt, J = 7.1, 2.4 Hz, 1H), 7.29-7.18 (m, 3H), 7.14 (dd, J =

10.6, 2.5 Hz, 1H), 2.42 (d, *J* = 2.5 Hz, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.65, 154.45, 152.04, 151.14, 138.04, 136.39, 133.06, 132.76, 132.72, 132.49, 130.95, 130.22, 129.22, 128.05, 127.47, 127.41, 126.36, 126.31, 124.69, 123.13, 123.07, 122.59, 122.54, 121.01, 120.95, 114.83, 114.78, 112.01, 111.97, 111.52, 111.43, 21.34, 20.63. HRMS (ESI) m/z calculated for $C_{17}H_{14}N_3O$ $(M+H)^+$: 276.1131. Found: 276.1136.



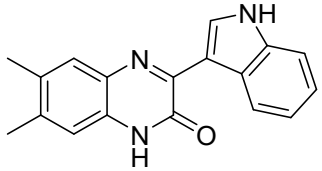
7-bromo-3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ha)

Following the general procedure, the desired compound was obtained as a yellow solid, mp 291-292 °C, 54 mg, 61% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.87 (s, 1H), 8.95 (s, 1H), 8.88 (dd, *J* = 5.9, 3.4 Hz, 1H), 8.10 (t, *J* = 2.2 Hz, 1H), 7.66 (dt, *J* = 8.8, 2.3 Hz, 1H), 7.51 (td, *J* = 8.6, 2.6 Hz, 2H), 7.35-7.14 (m, 2H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 153.49, 151.64, 136.38, 134.20, 133.91, 130.92, 130.36, 130.10, 126.32, 123.26, 122.75, 121.29, 116.52, 115.16, 111.98, 111.37, 29.34. HRMS (ESI) m/z calculated for $C_{17}H_{13}BrN_3O$ $(M+H)^+$: 354.0237. Found: 354.0243.



3-(1*H*-indol-3-yl)-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (3ia)

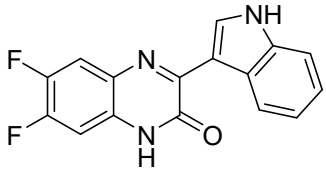
Following the general procedure, the desired compound was obtained as an orange solid, mp 306-308 °C, 80 mg, 97% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.88 (s, 1H), 12.02 (s, 1H), 8.99 (s, 1H), 8.95-8.87 (m, 1H), 8.19 (s, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.53 (ddd, *J* = 14.5, 9.7, 6.1 Hz, 2H), 7.31-7.20 (m, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.66, 153.38, 136.44, 134.01, 133.34, 132.23, 126.26, 124.68 (q, J = 235 Hz), 124.63, 123.87, 123.63 (q, J = 33 Hz), 123.27, 122.82, 121.37, 116.24, 112.07, 111.18. HRMS (ESI) m/z calculated for $C_{17}H_{11}F_3N_3O$ $(M+H)^+$: 330.0849. Found: 330.0854.



3-(1*H*-indol-3-yl)-6,7-dimethylquinoxalin-2(1*H*)-one (3ja)

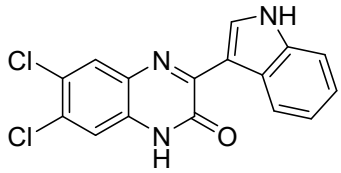
Following the general procedure, the desired compound was obtained as a yellow solid, mp 276-278 °C, 60 mg, 83% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.29 (s, 1H), 11.72 (s, 1H), 8.89 (d, *J* = 7.4 Hz, 2H), 7.66 (s, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.36-7.16 (m, 2H), 7.08 (s, 1H), 2.32 (d, *J* = 4.3 Hz, 6H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.55, 151.08, 137.38, 136.32, 132.58, 131.83, 131.18, 128.26,

127.77, 126.28, 123.08, 122.51, 120.87, 115.13, 111.91, 111.52, 19.82, 19.12. HRMS (ESI) m/z calculated for $C_{18}H_{16}N_3O$ $(M+H)^+$: 290.1288. Found: 290.1289.



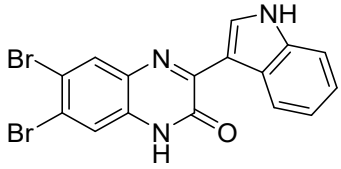
6,7-difluoro-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ka)[3]

Following the general procedure, the desired compound was obtained as a dark yellow solid, mp 264-265 °C, 50 mg, 68% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.50 (s, 1H), 11.85 (s, 1H), 8.93 (d, J = 3.0 Hz, 1H), 8.83 (dd, J = 6.4, 2.4 Hz, 1H), 7.97 (dd, J = 11.4, 8.2 Hz, 1H), 7.51 (dd, J = 6.4, 2.5 Hz, 1H), 7.30-7.13 (m, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.11 , 152.34 , 136.39 , 133.58 , 131.57 , 129.31, 129.21, 128.73, 127.30 (d, J = 10.4 Hz), 126.17 , 123.13 , 122.74 , 121.21 , 115.09 (d, J = 18.7 Hz), 111.99 , 111.19, 102.70 (d, J = 21.1 Hz).



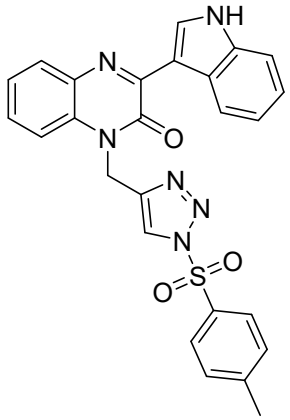
6,7-dichloro-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3la)

Following the general procedure, the desired compound was obtained as a dark yellow solid, mp 279-281 °C, 54 mg, 61% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.52 (s, 1H), 11.91 (s, 1H), 8.96 (d, J = 2.9 Hz, 1H), 8.90-8.81 (m, 1H), 8.14 (s, 1H), 7.52 (dd, J = 6.2, 2.5 Hz, 1H), 7.45 (s, 1H), 7.30-7.19 (m, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.44, 153.54, 136.77, 134.51, 132.83, 130.47, 129.81, 128.80, 126.52, 125.35, 123.62, 123.27, 121.79, 116.27, 112.44, 111.58. HRMS (ESI) m/z calculated for $C_{16}H_{10}Cl_2N_3O$ $(M+H)^+$: 330.0195. Found: 330.0202.



6,7-dibromo-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ma)

Following the general procedure, the desired compound was obtained as a dark yellow solid, mp 310-312 °C, 78 mg, 74% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 12.48 (s, 1H), 11.90 (s, 1H), 8.96 (d, J = 3.0 Hz, 1H), 8.85 (d, J = 6.4 Hz, 1H), 8.23 (s, 1H), 7.60 (s, 1H), 7.51 (s, 1H), 7.25 (dd, J = 7.0, 3.5 Hz, 2H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 154.06, 153.21, 136.40, 134.15, 133.10, 131.42, 130.60, 126.15, 123.29, 122.89, 121.89, 121.42, 118.99, 116.83, 112.06, 111.25. HRMS (ESI) m/z calculated for $C_{16}H_{10}Br_2N_3O$ $(M+H)^+$: 417.9185. Found: 417.9190.

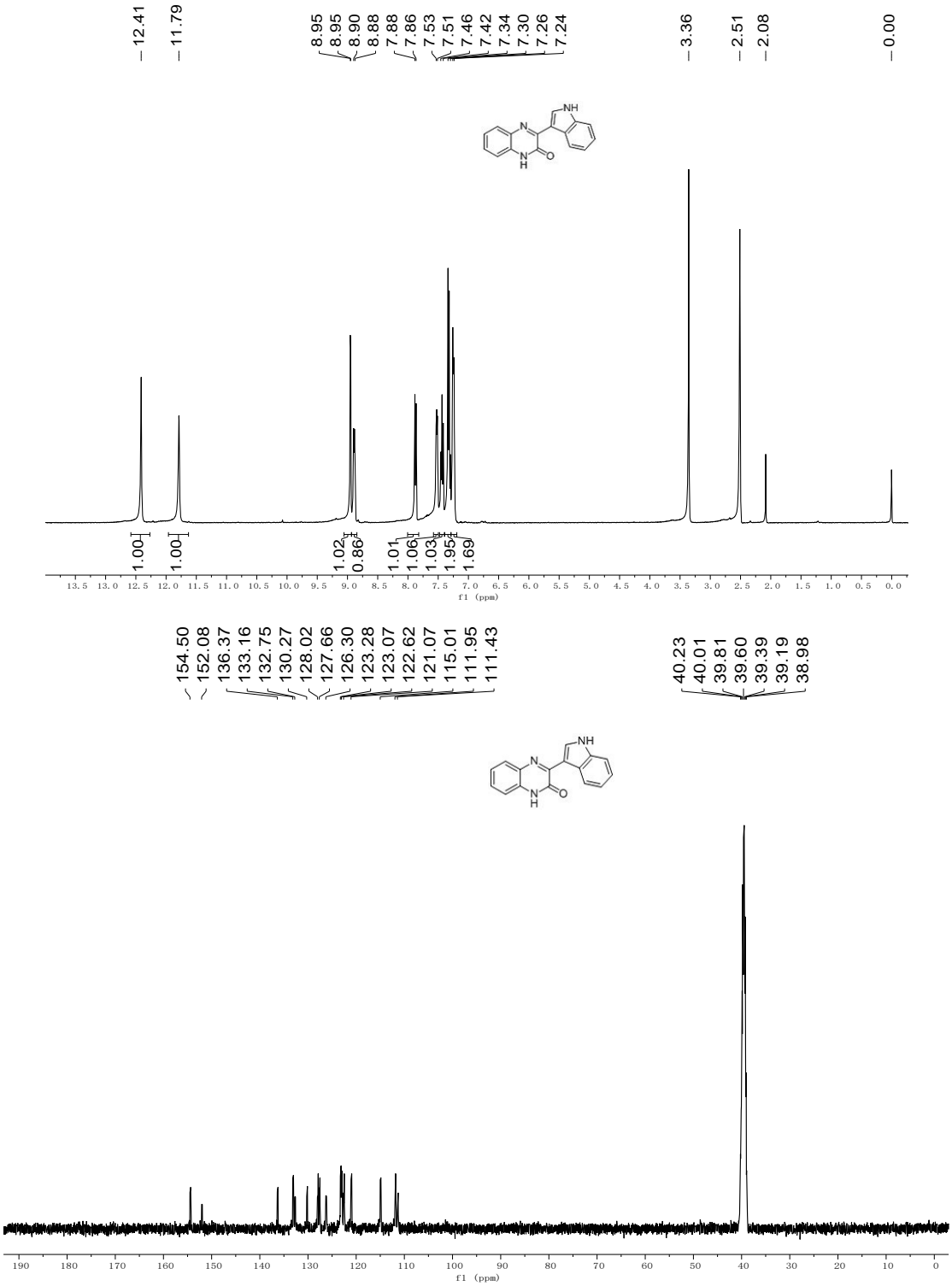


3-(1*H*-indol-3-yl)-1-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)quinoxalin-2(1*H*)-one (4)

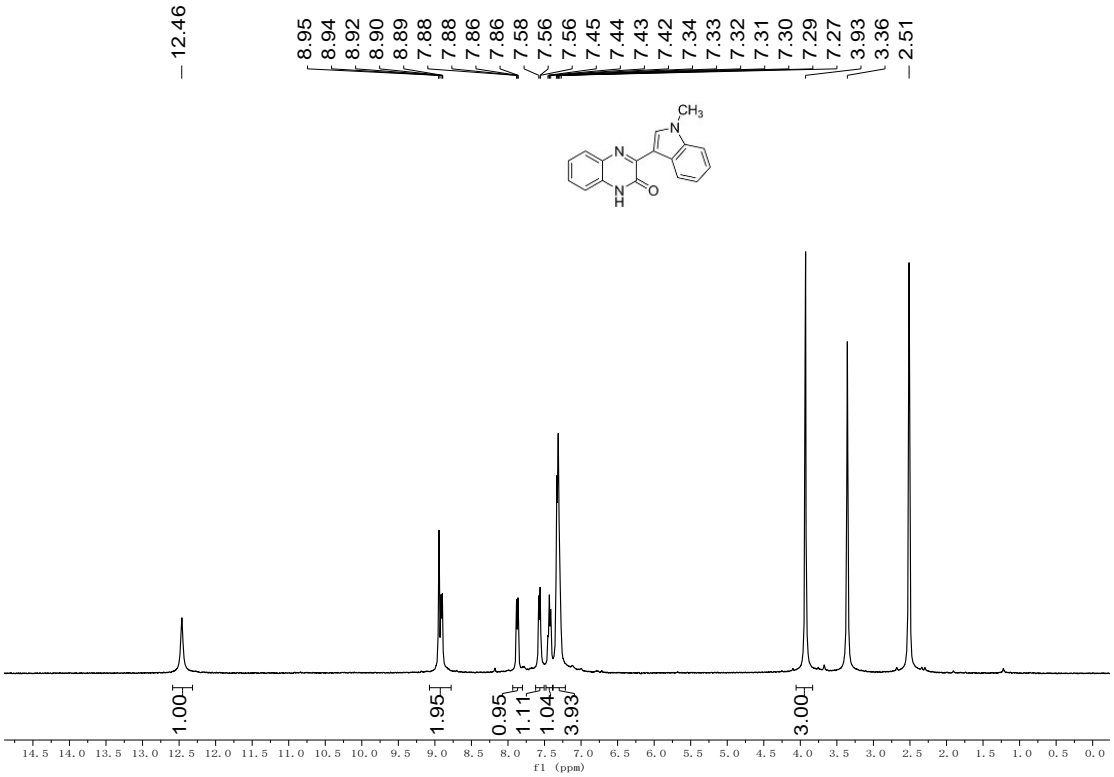
Following the general procedure, the desired compound was obtained as a pale yellow solid, mp 229-231 °C, 46 mg, 92% yield. ^{1}H NMR (400 MHz, d_6-DMSO) δ 11.83 (s, 1H), 8.90 (s, 3H), 7.99 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 7.7 Hz, 1H), 7.56-7.46 (m, 5H), 7.38 (t, J = 7.5 Hz, 1H), 7.29-7.21 (m, 2H), 5.67 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 153.56, 150.74, 147.85, 143.23, 136.35, 133.38, 133.31, 132.18, 130.89, 130.73, 130.59, 128.64, 128.36, 128.28, 127.39, 126.33, 123.88, 123.68, 123.02, 122.62, 121.10, 114.51, 111.95, 111.37, 37.31, 21.31. HRMS (ESI) m/z calculated for $C_{26}H_{21}N_6O_3S$ $(M+H)^+$: 497.1390. Found: 497.1398.

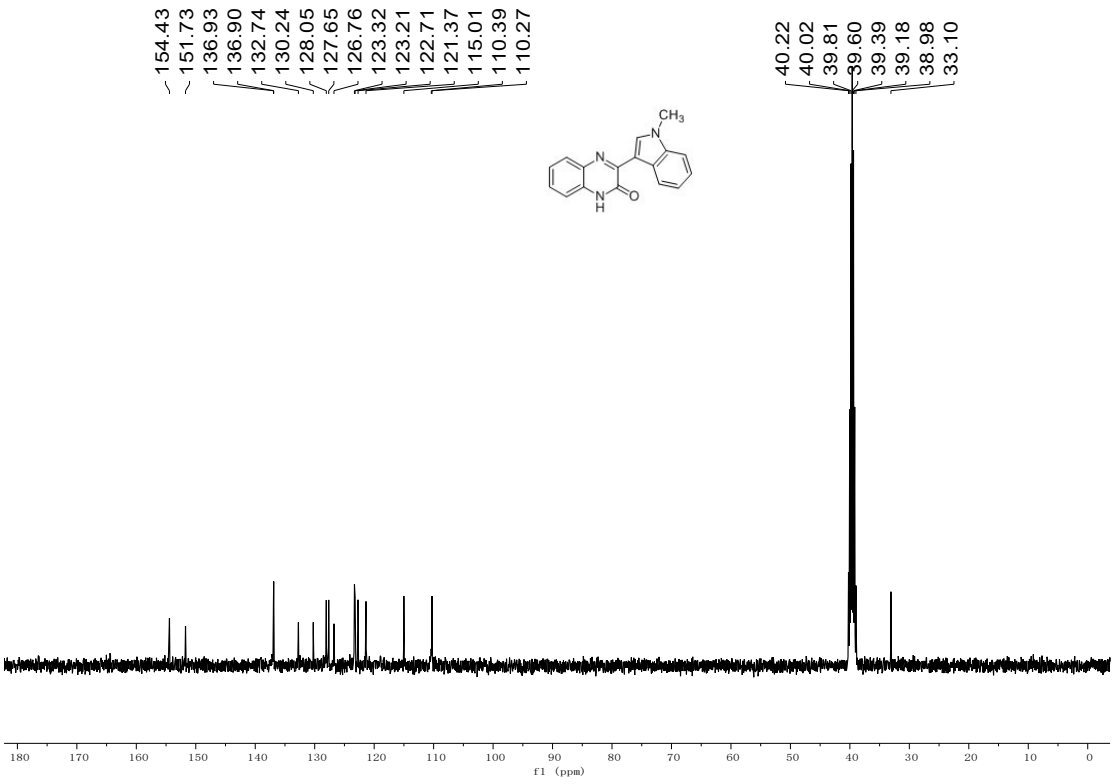
6. Copies of NMR spectra for prepared compounds

3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3aa)

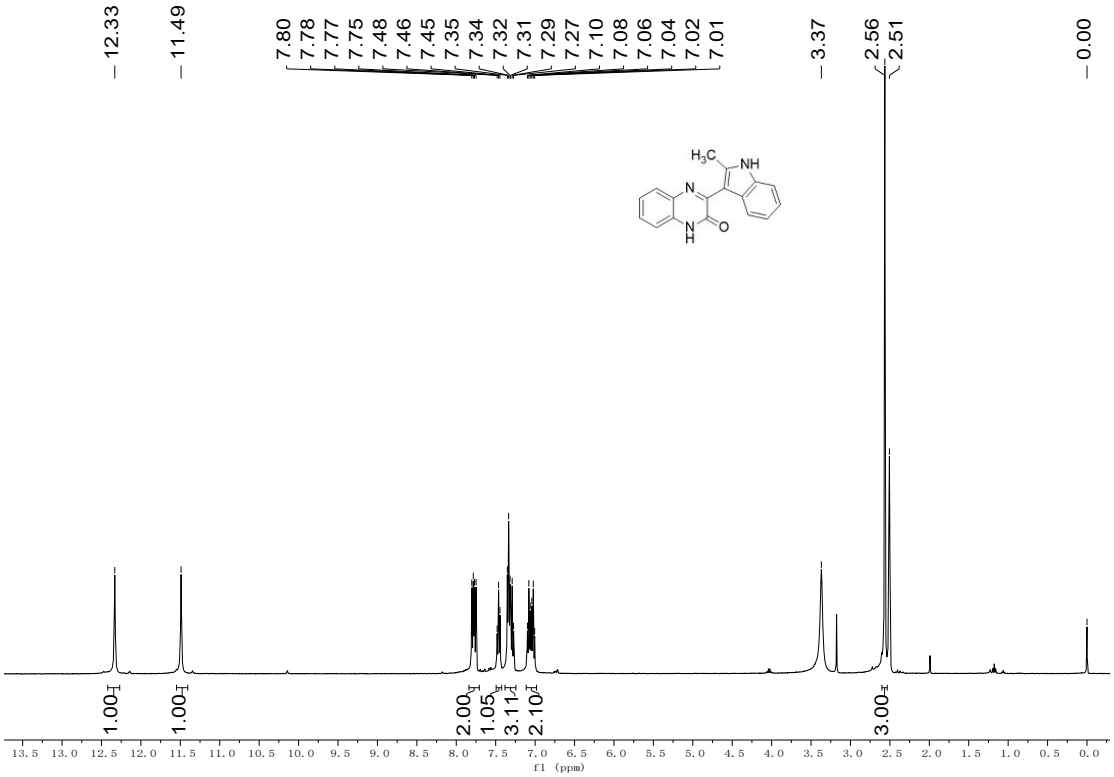


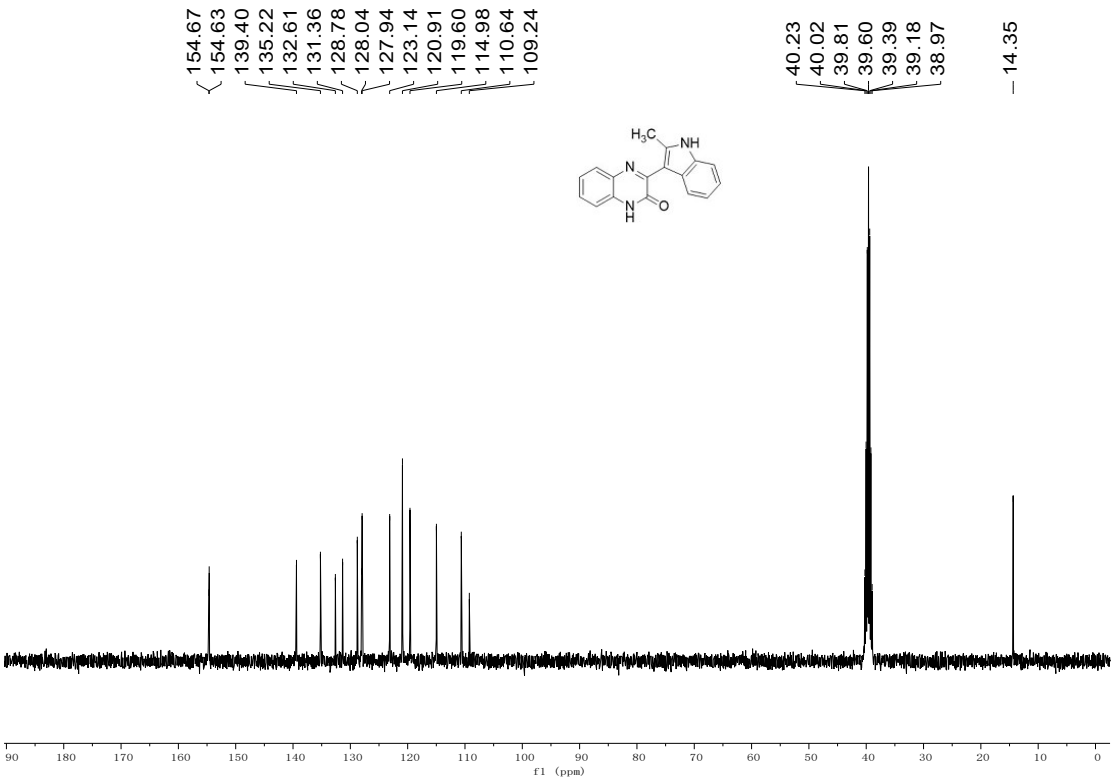
3-(1-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ab)



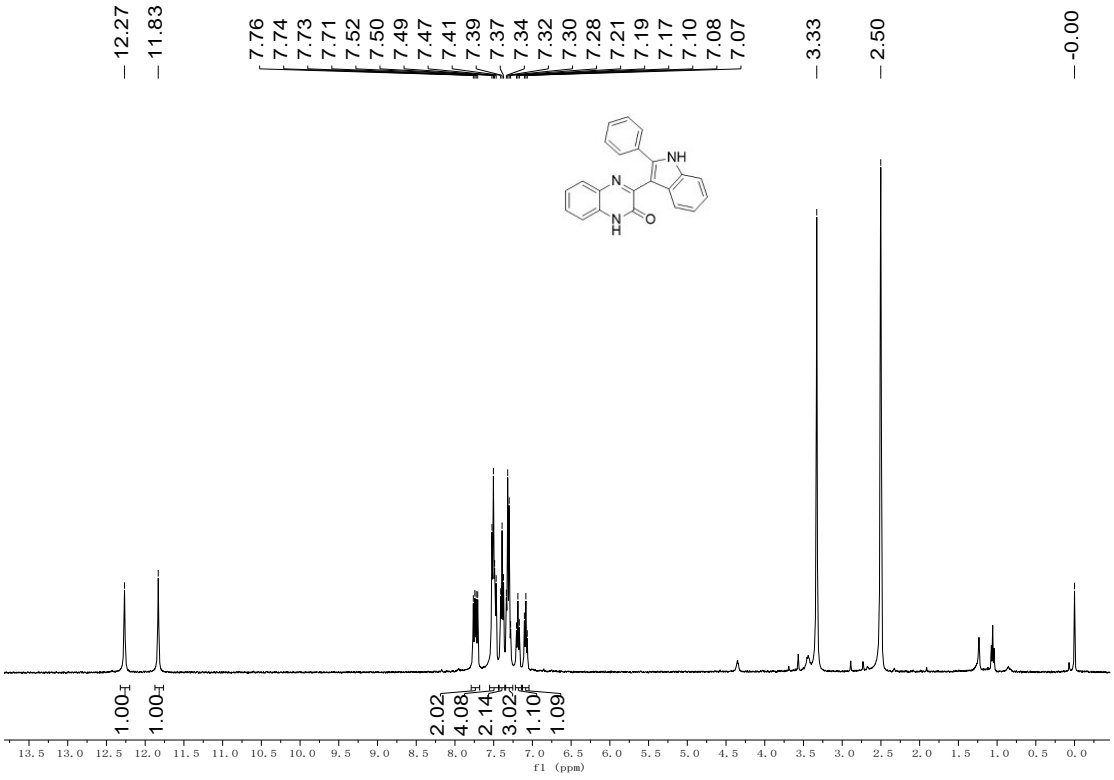


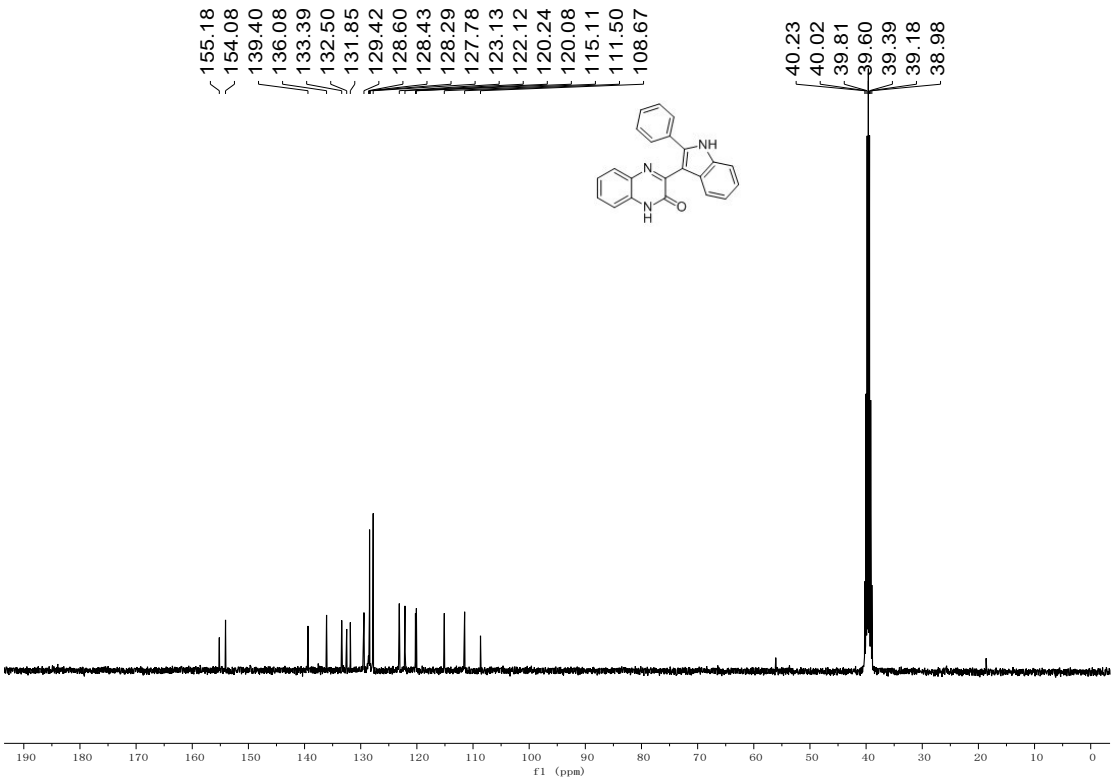
3-(2-methyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ac)



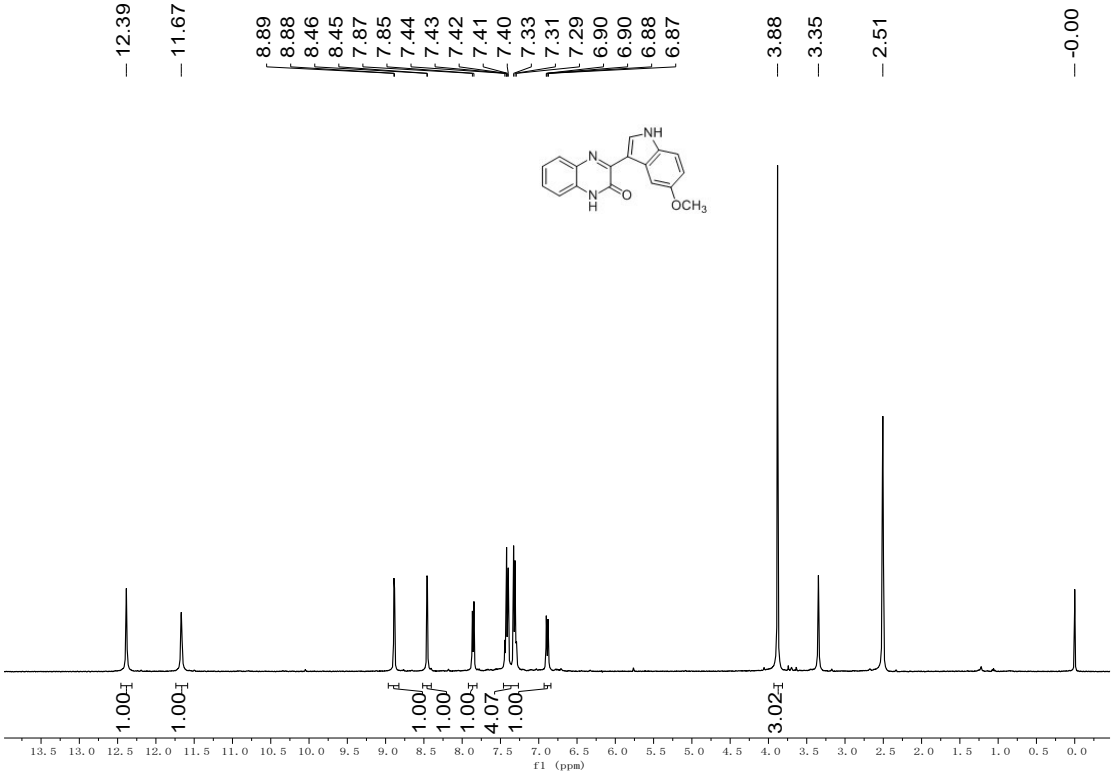


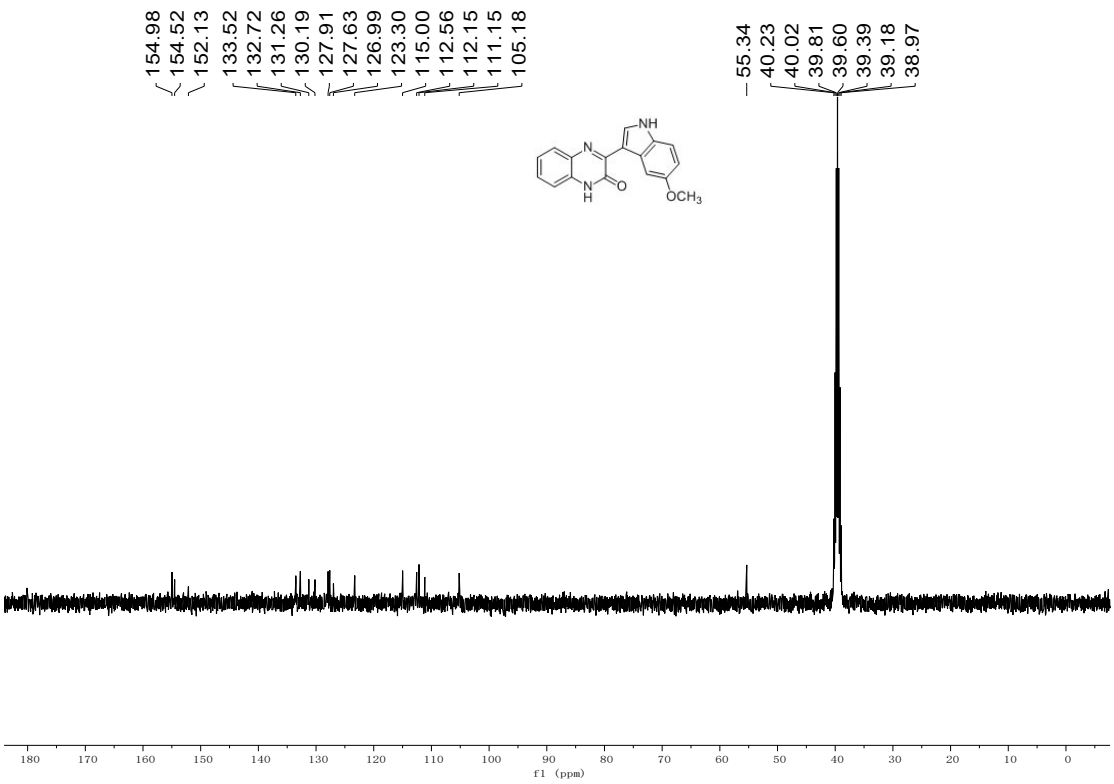
3-(2-phenyl-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ad)



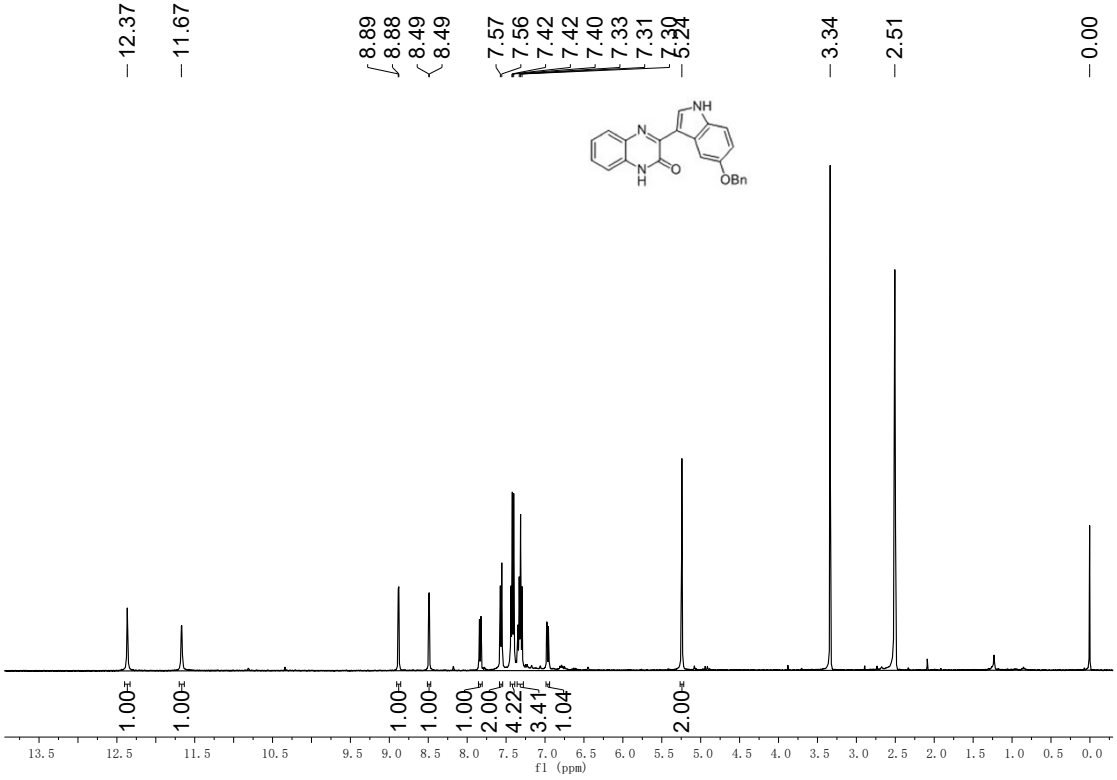


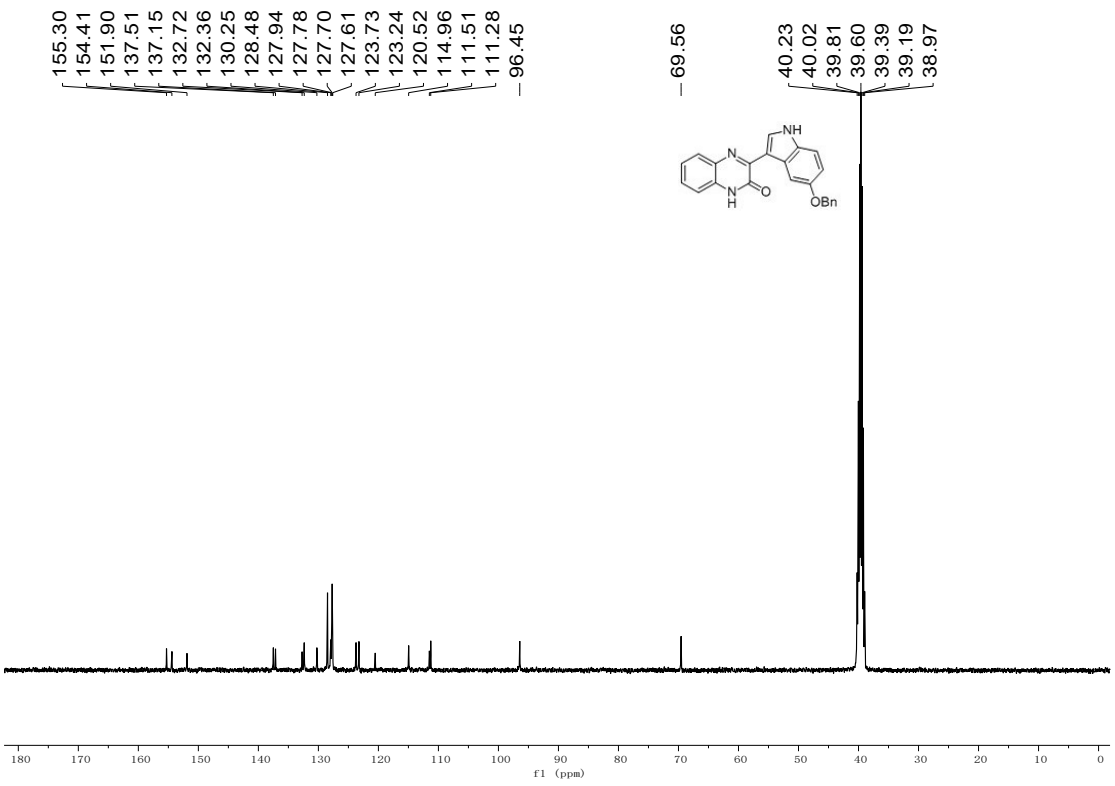
3-(5-methoxy-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ah)



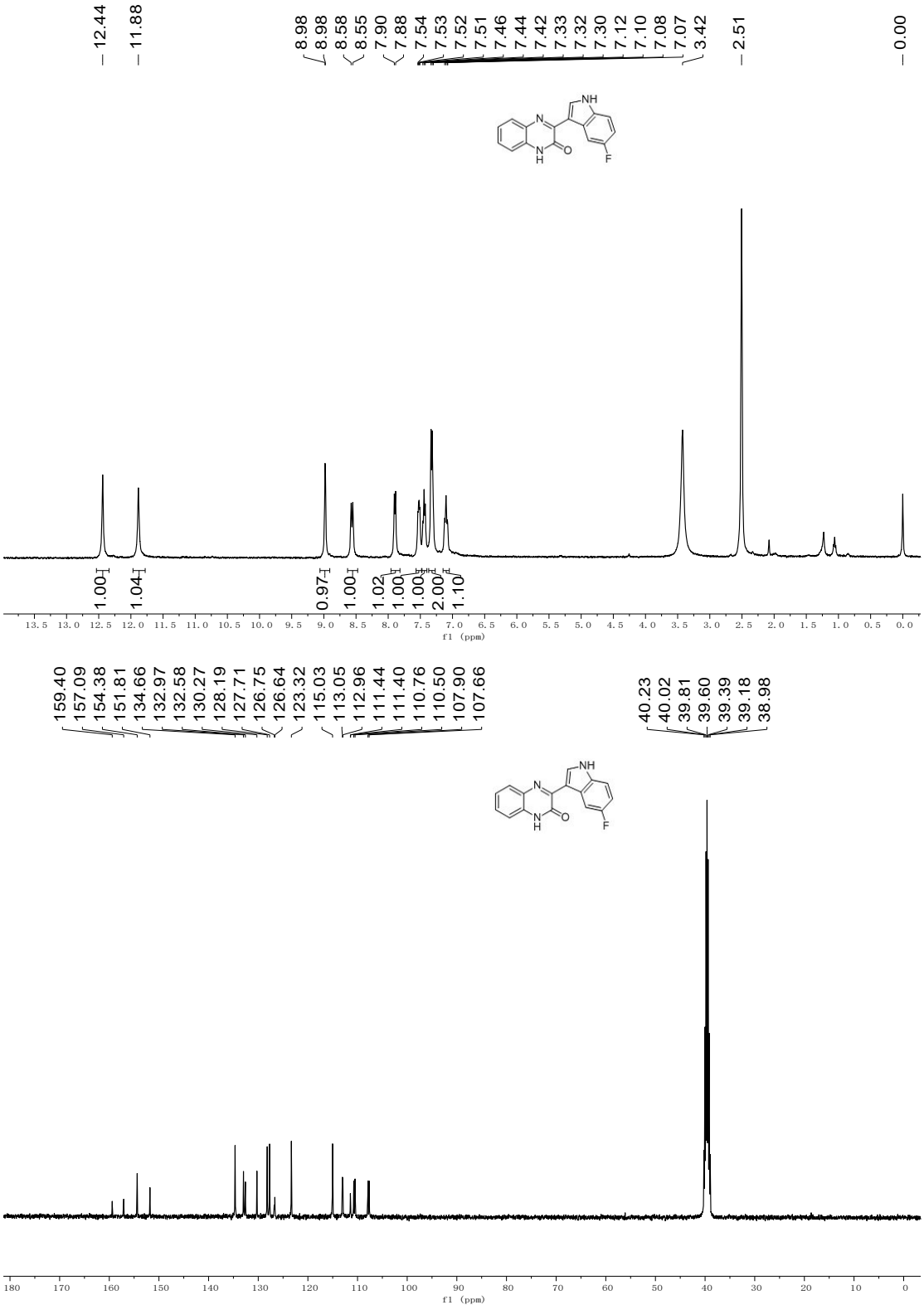


3-(5-(benzyloxy)-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ai)

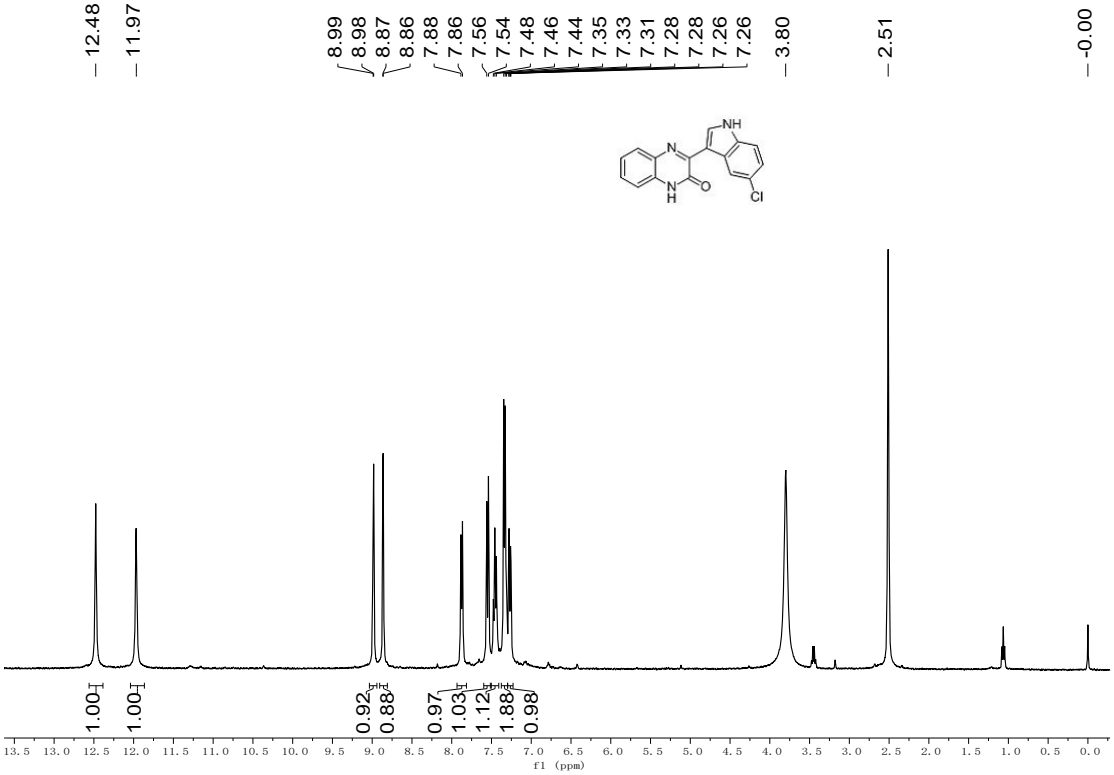


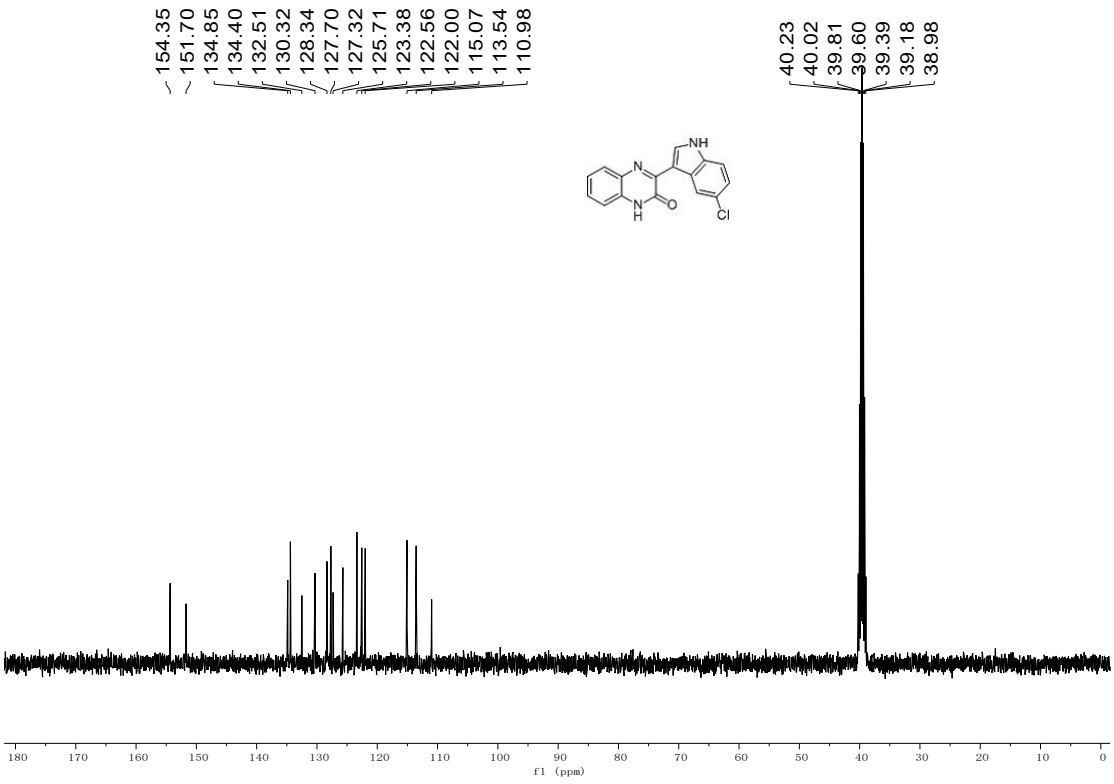


3-(5-fluoro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3aj)

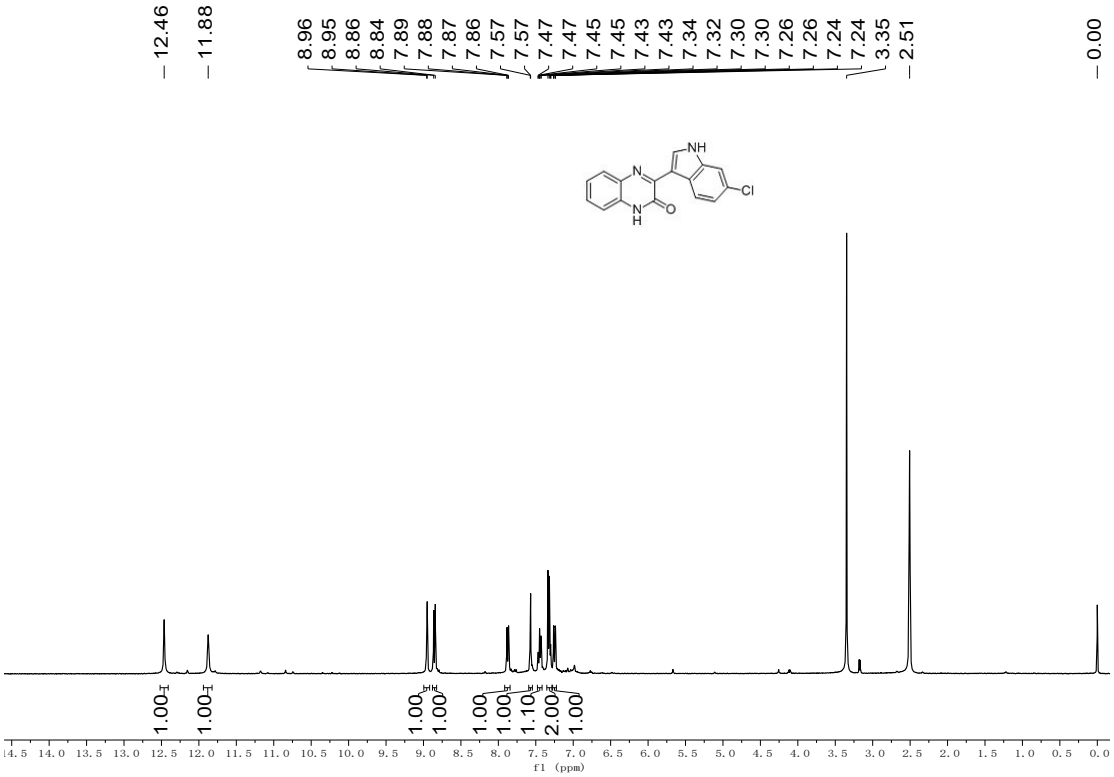


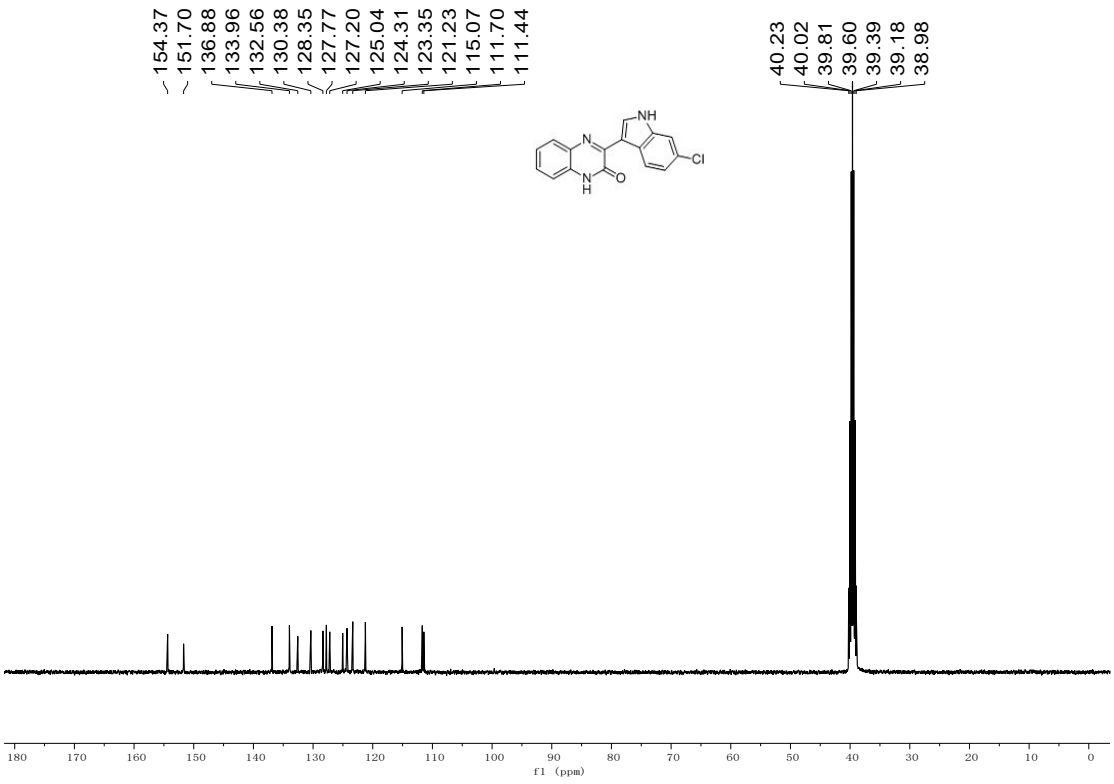
3-(5-chloro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ak)





3-(6-chloro-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3al)





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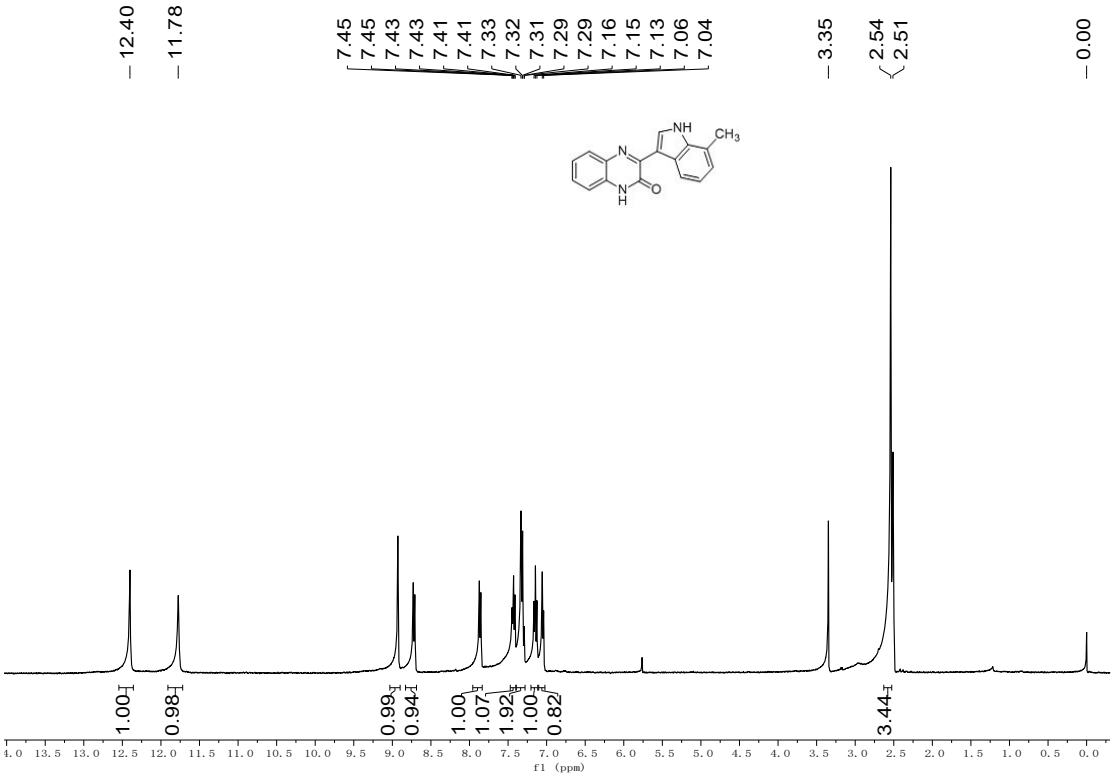
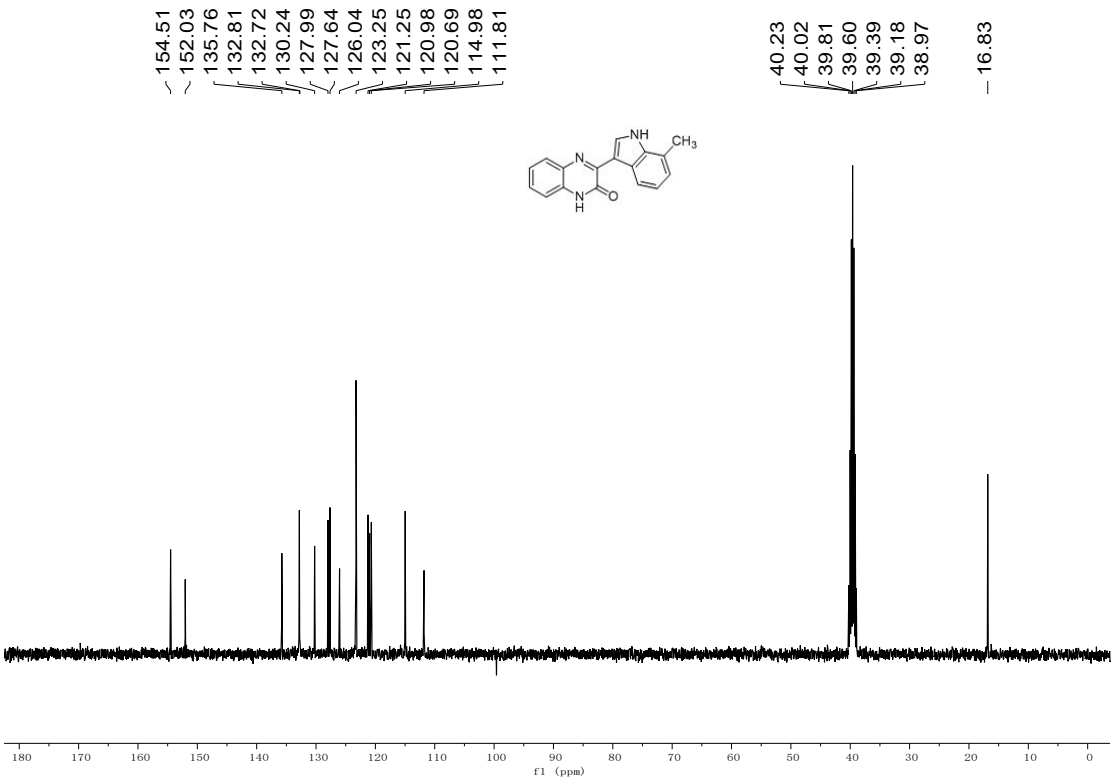
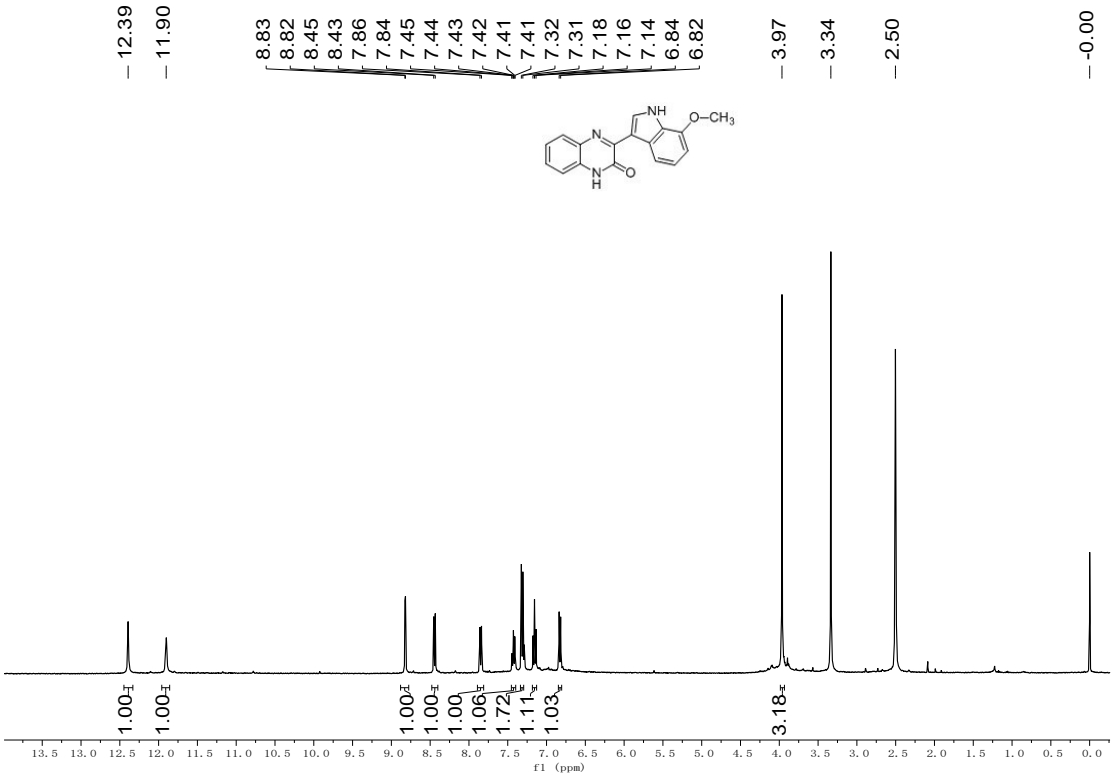
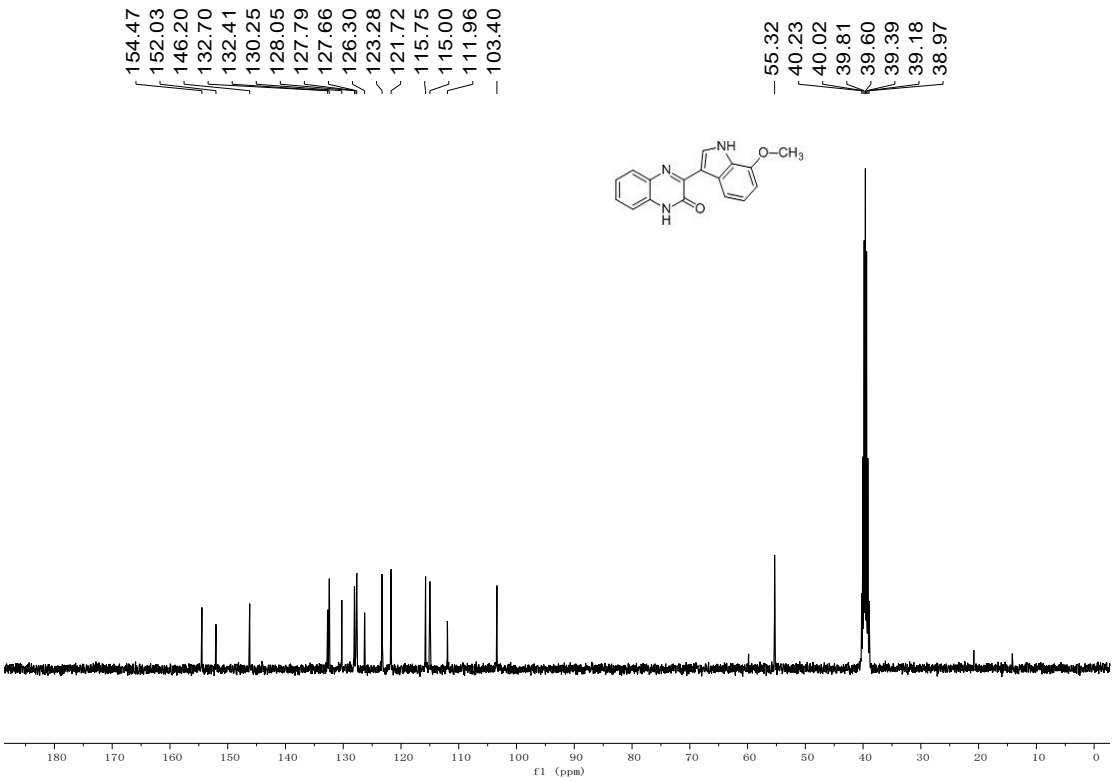


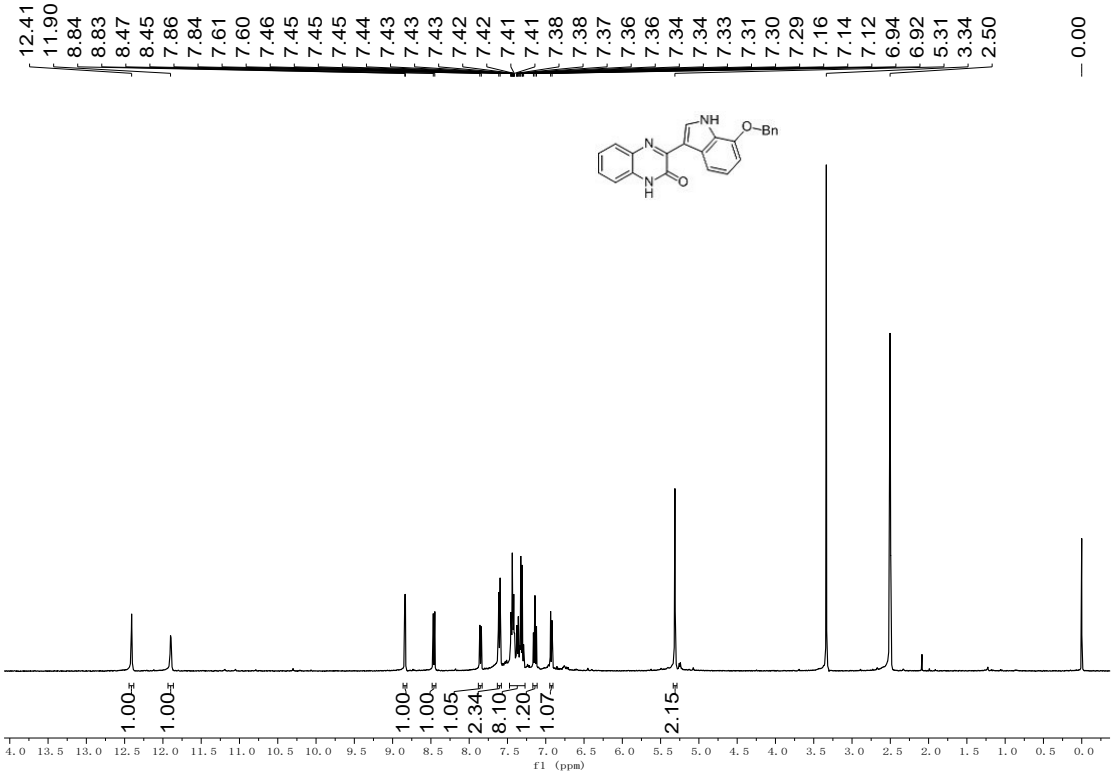


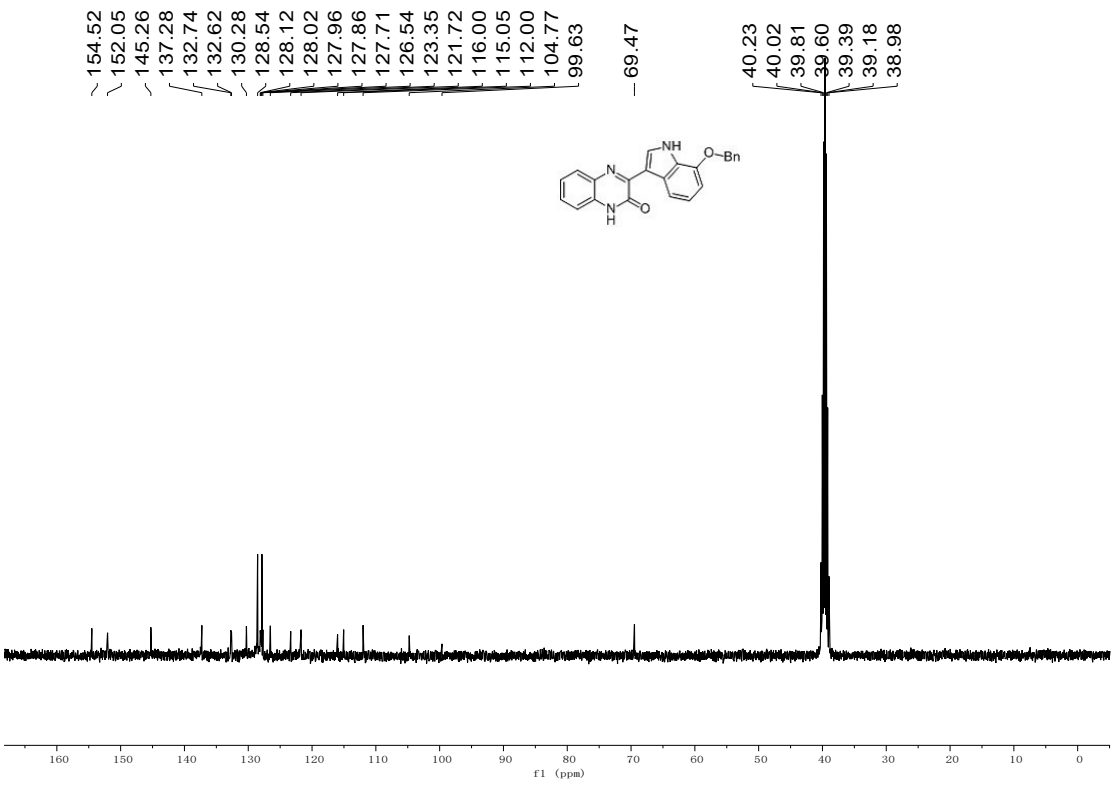
3-(7-methoxy-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3an)



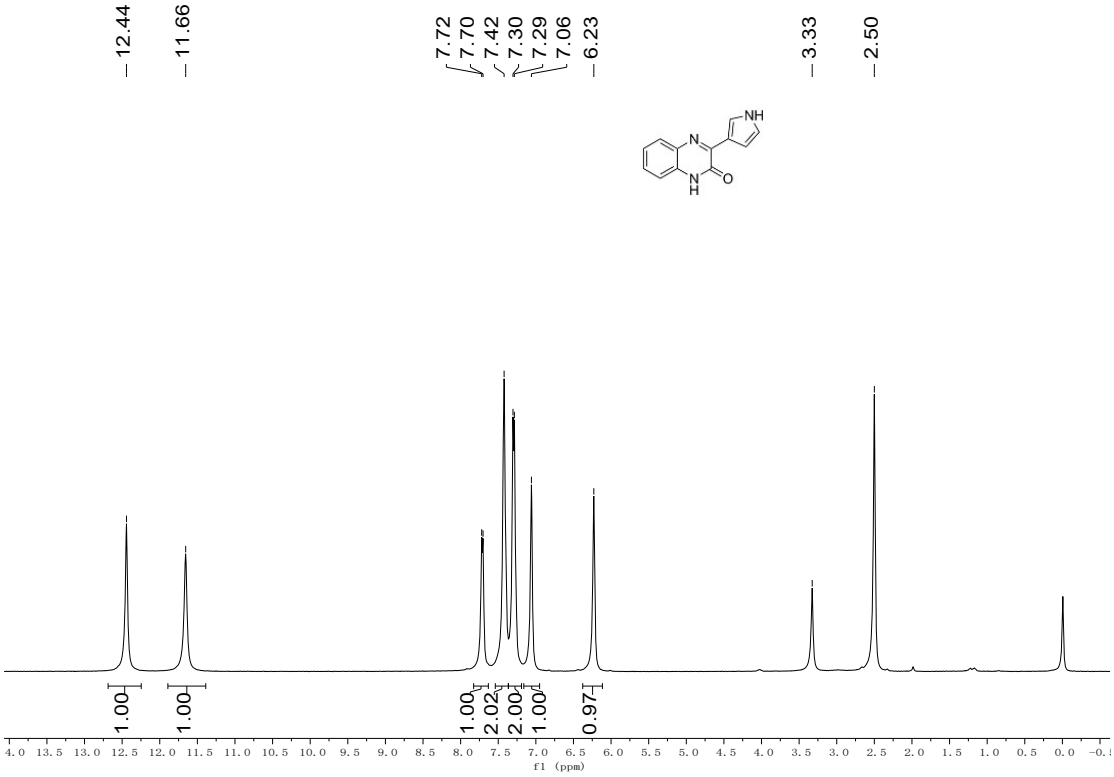


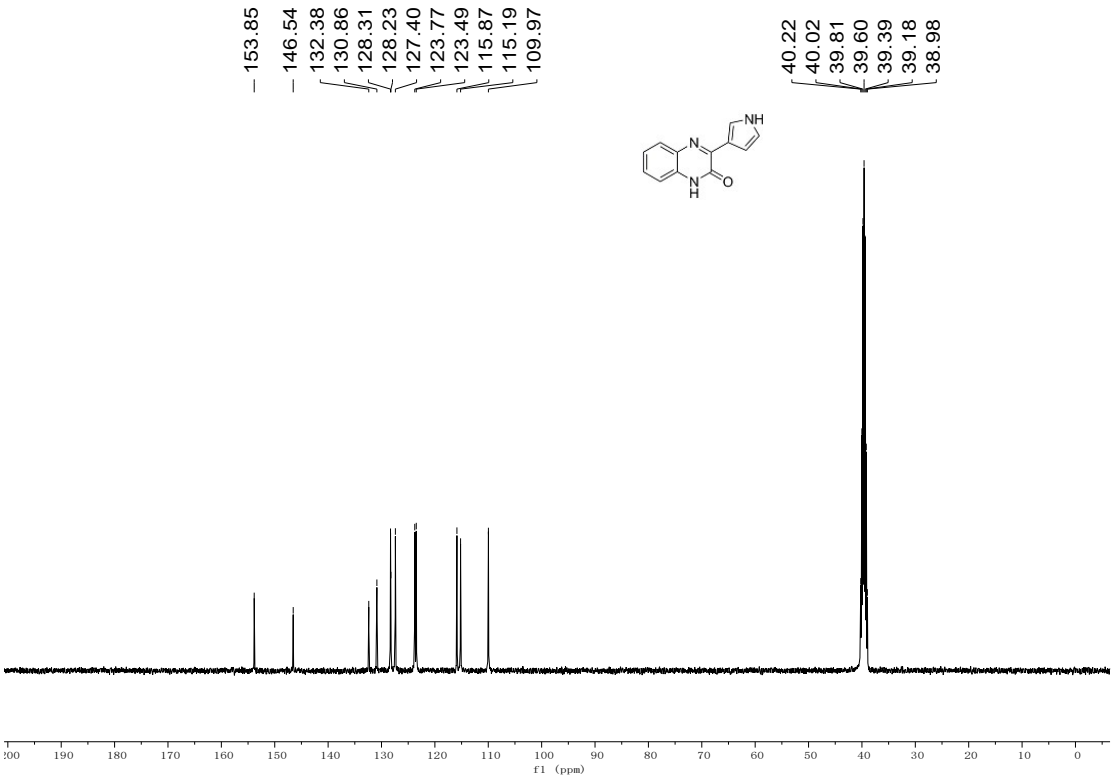
3-(7-(benzyloxy)-1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ao)



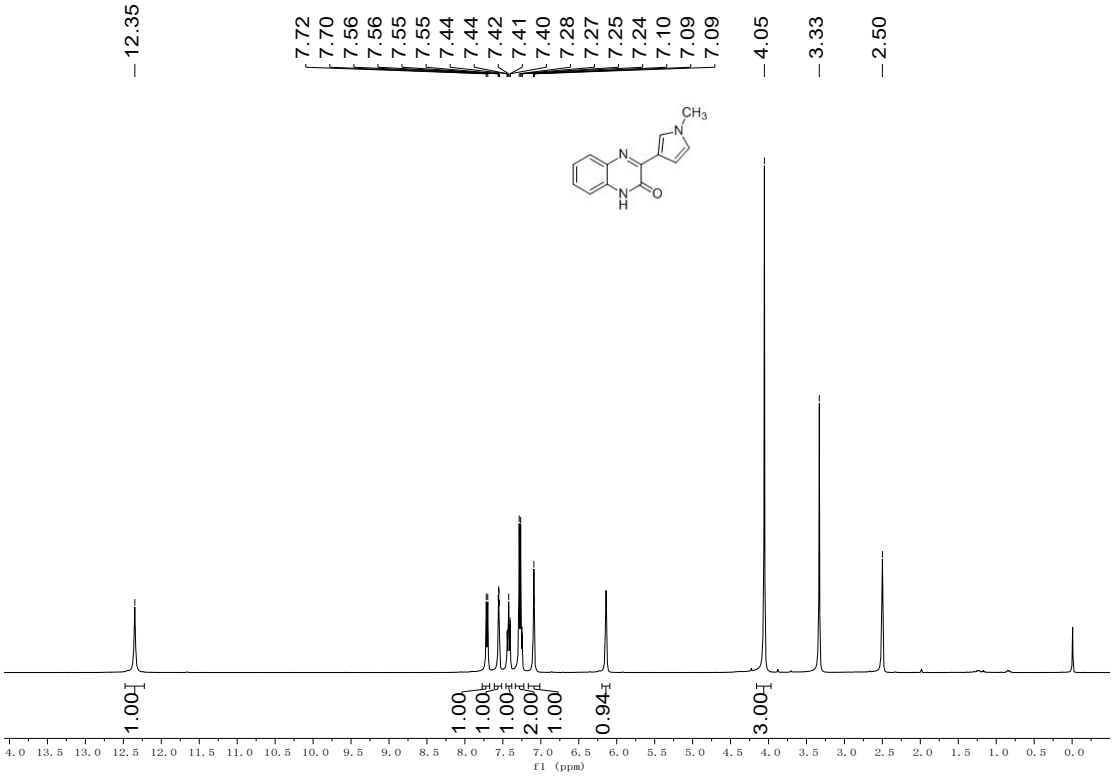


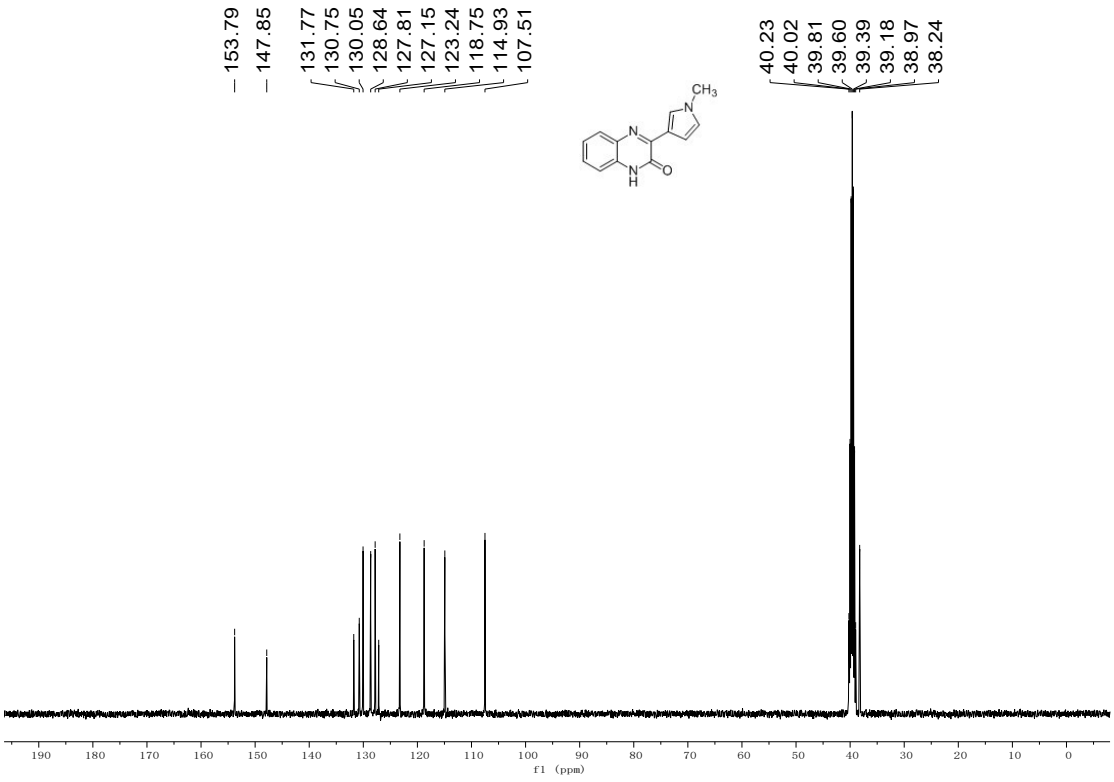
3-(1*H*-pyrrol-3-yl)quinoxalin-2(1*H*)-one (3ap)



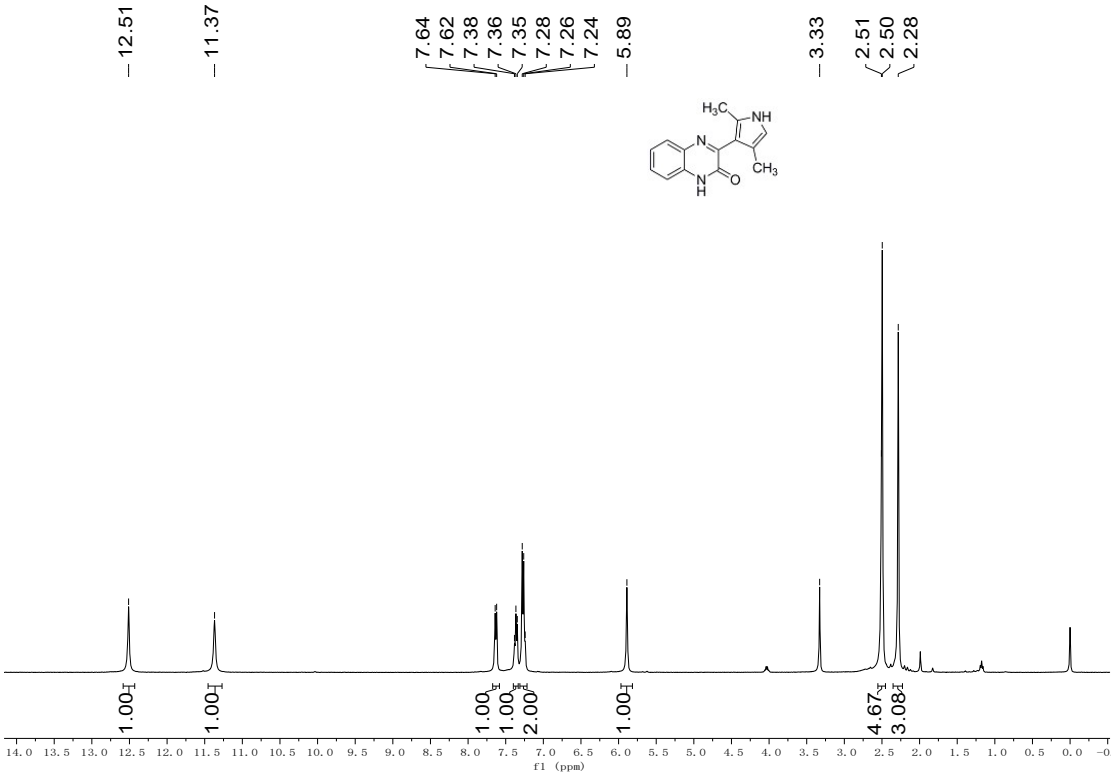


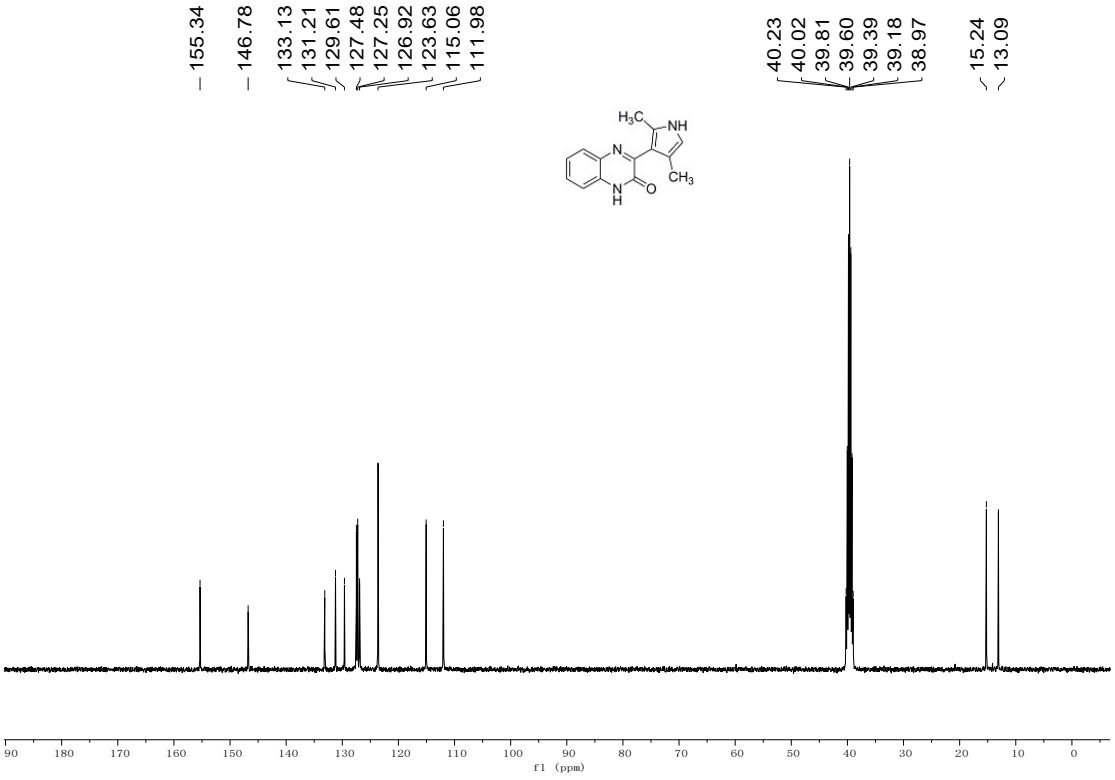
3-(1-methyl-1*H*-pyrrol-3-yl)quinoxalin-2(1*H*)-one (3aq)



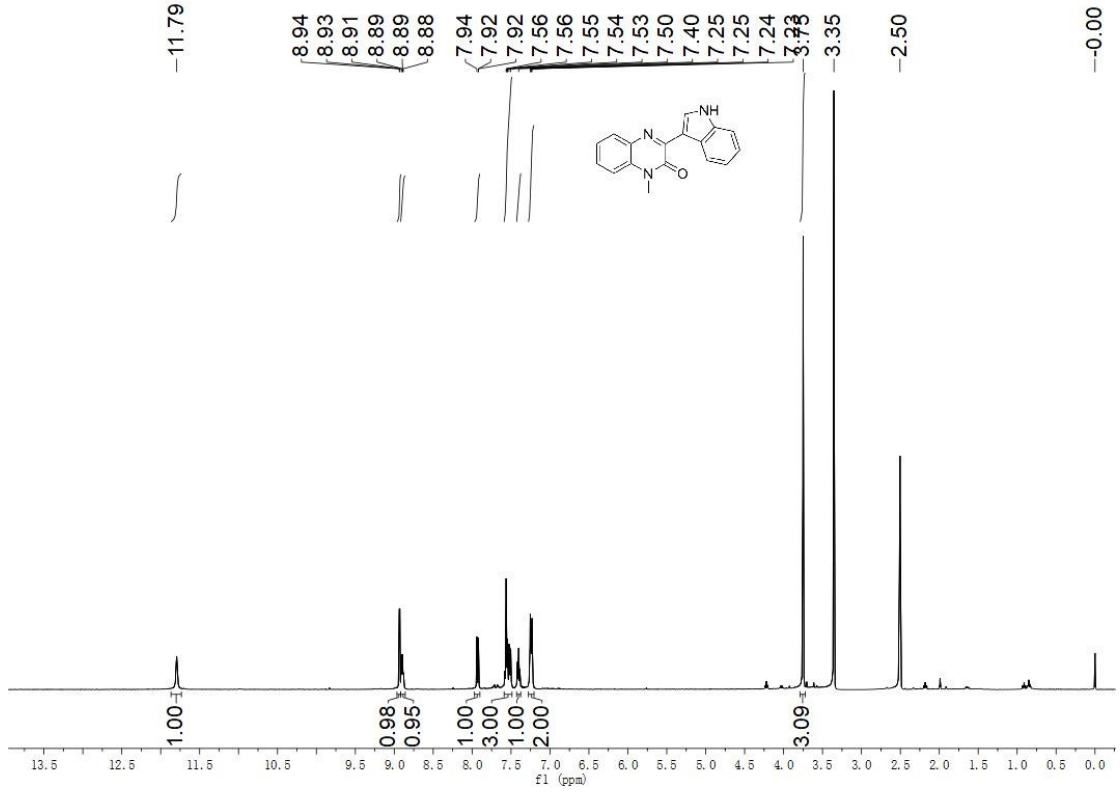


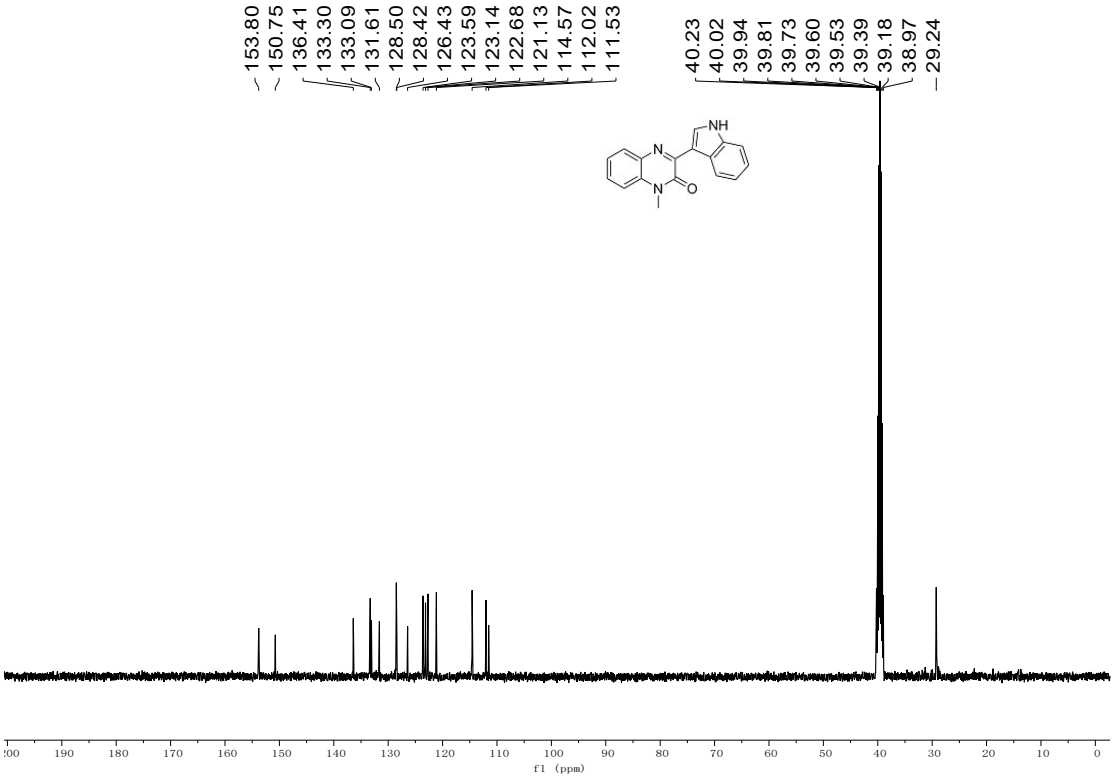
3-(2,4-dimethyl-1*H*-pyrrol-3-yl)quinoxalin-2(1*H*)-one (3ar)



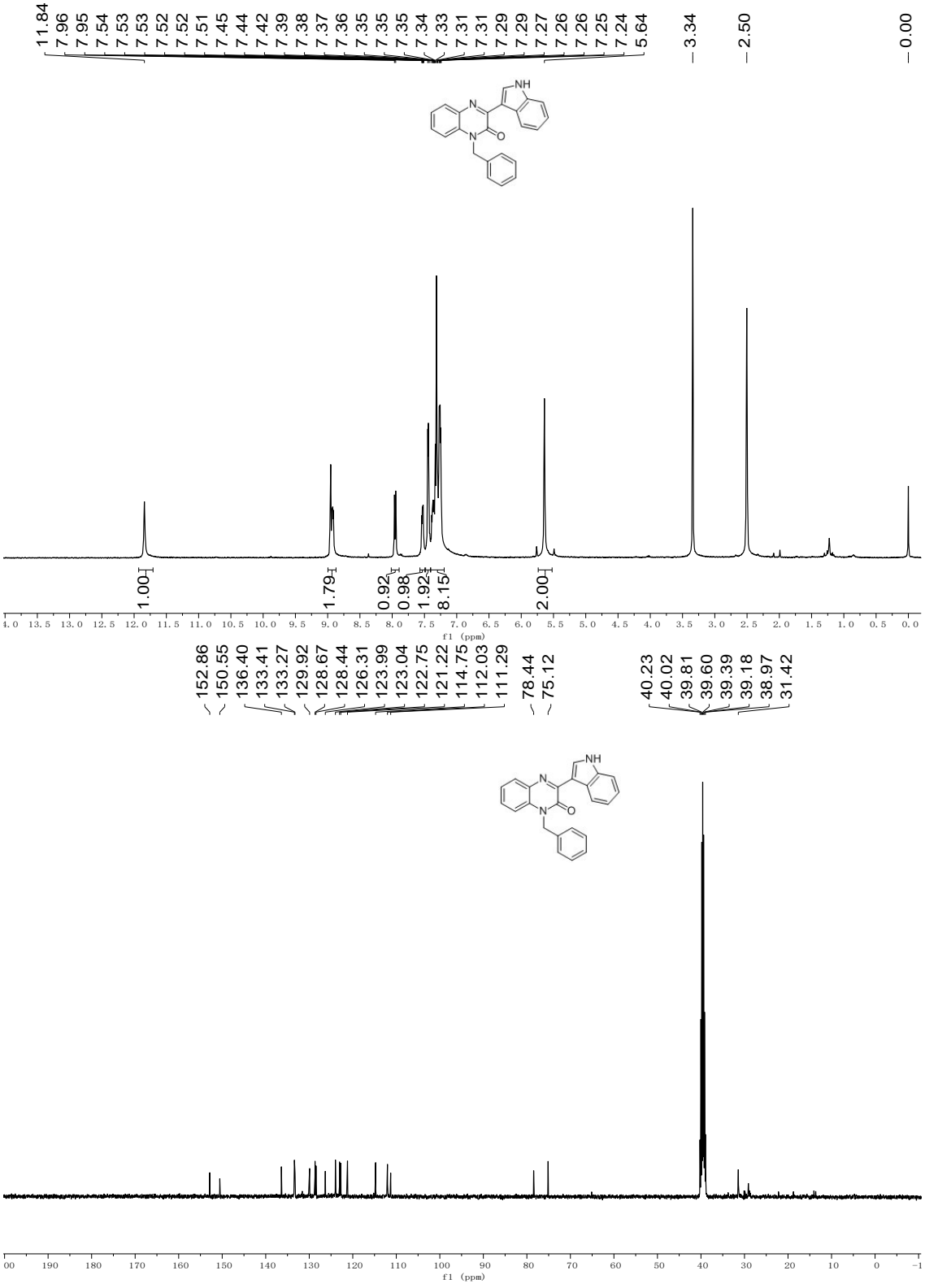


3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ba)

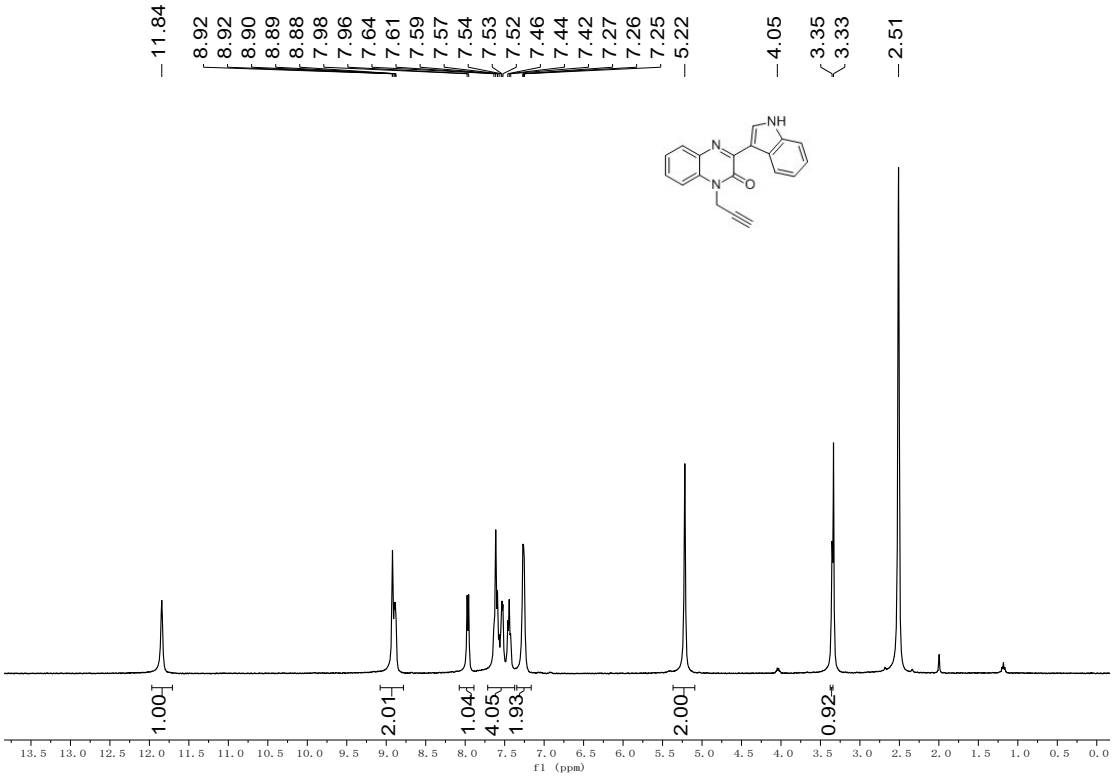


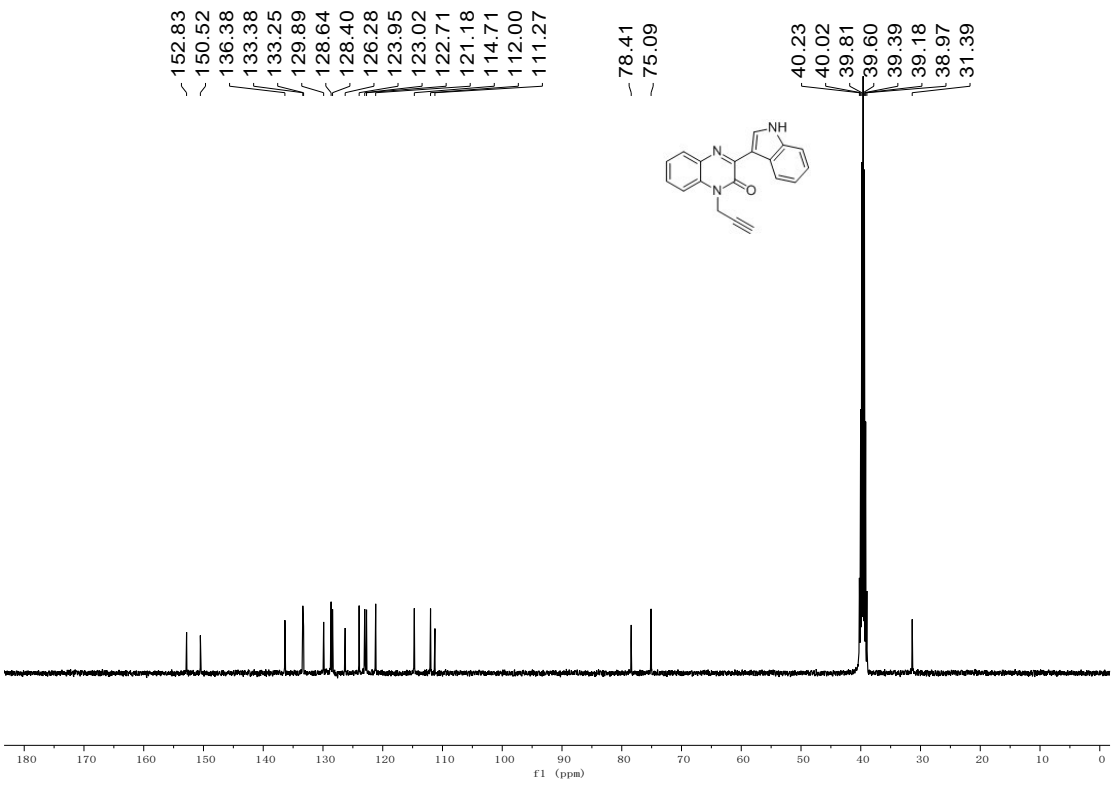


1-benzyl-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ca)

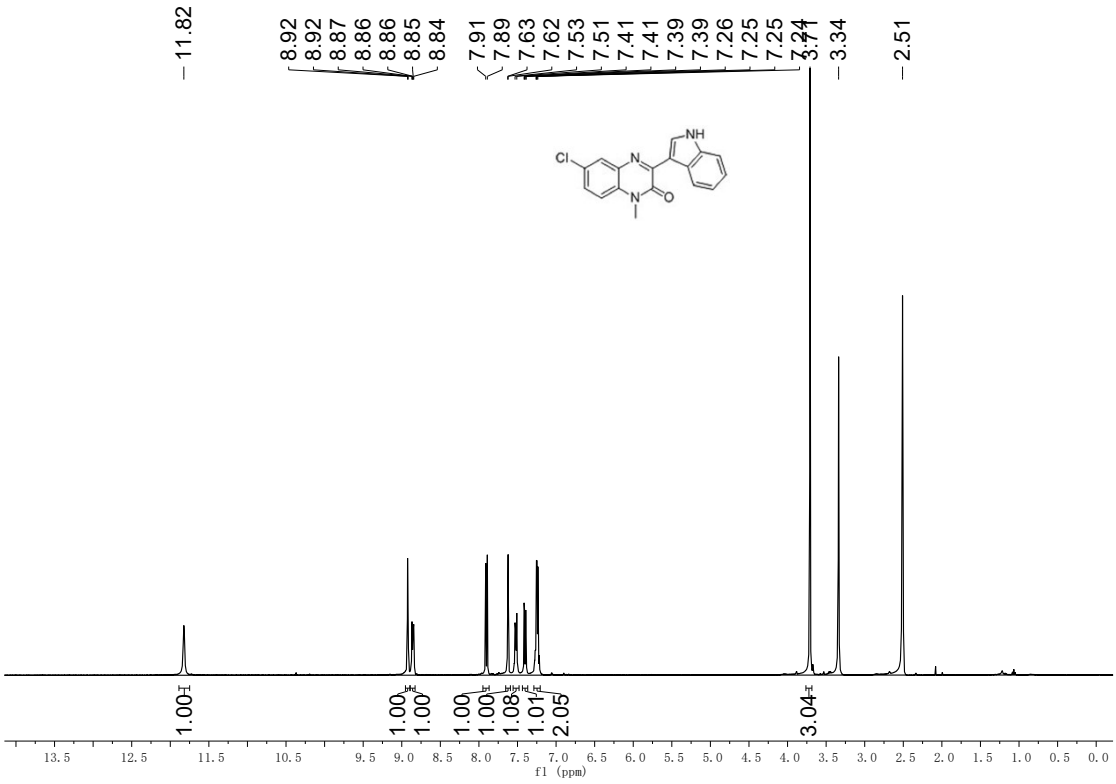


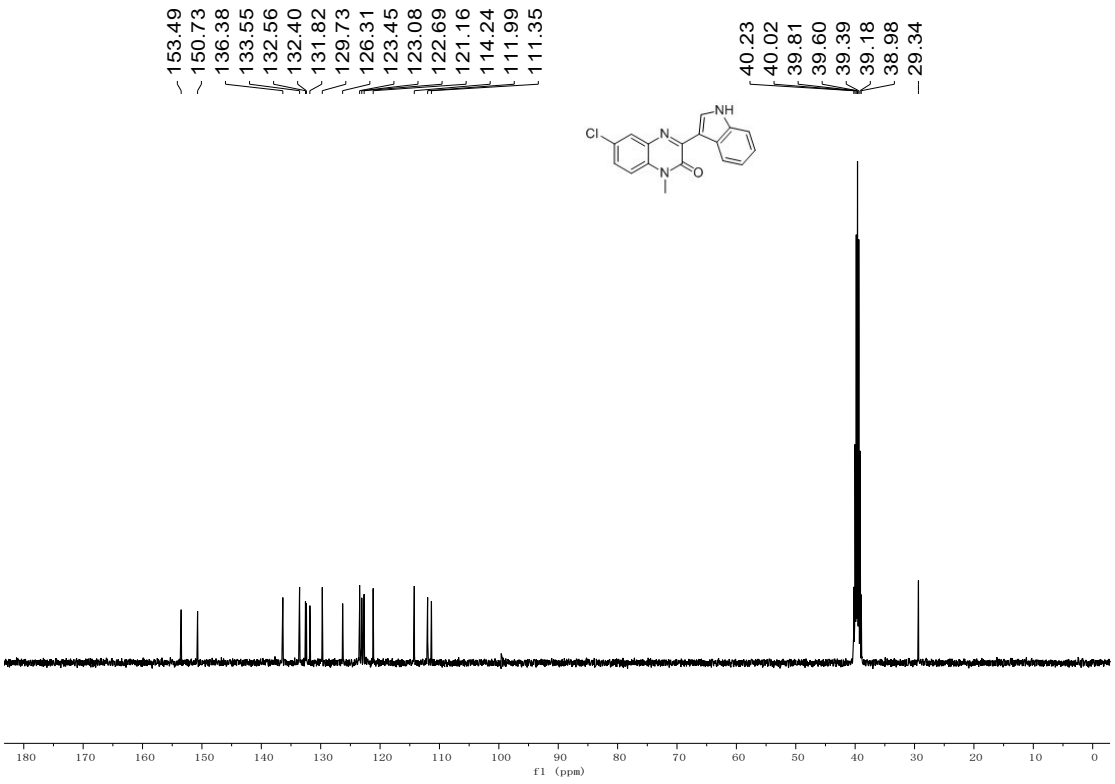
3-(1*H*-indol-3-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1*H*)-one (3da)



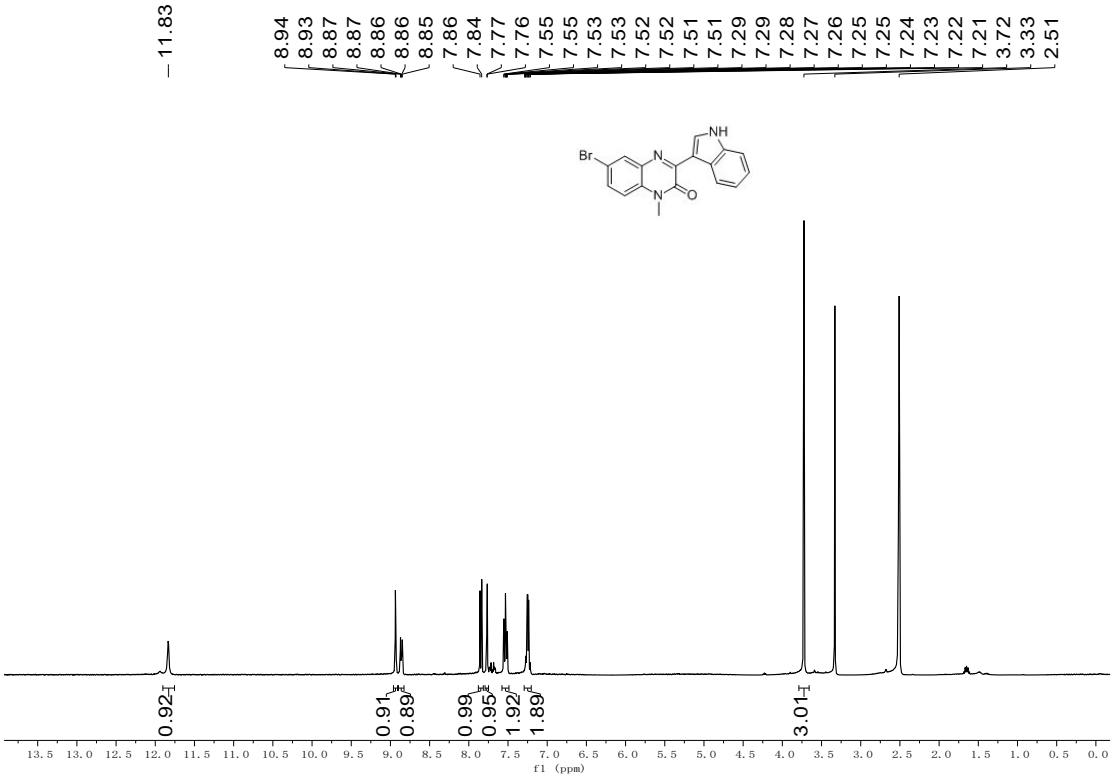


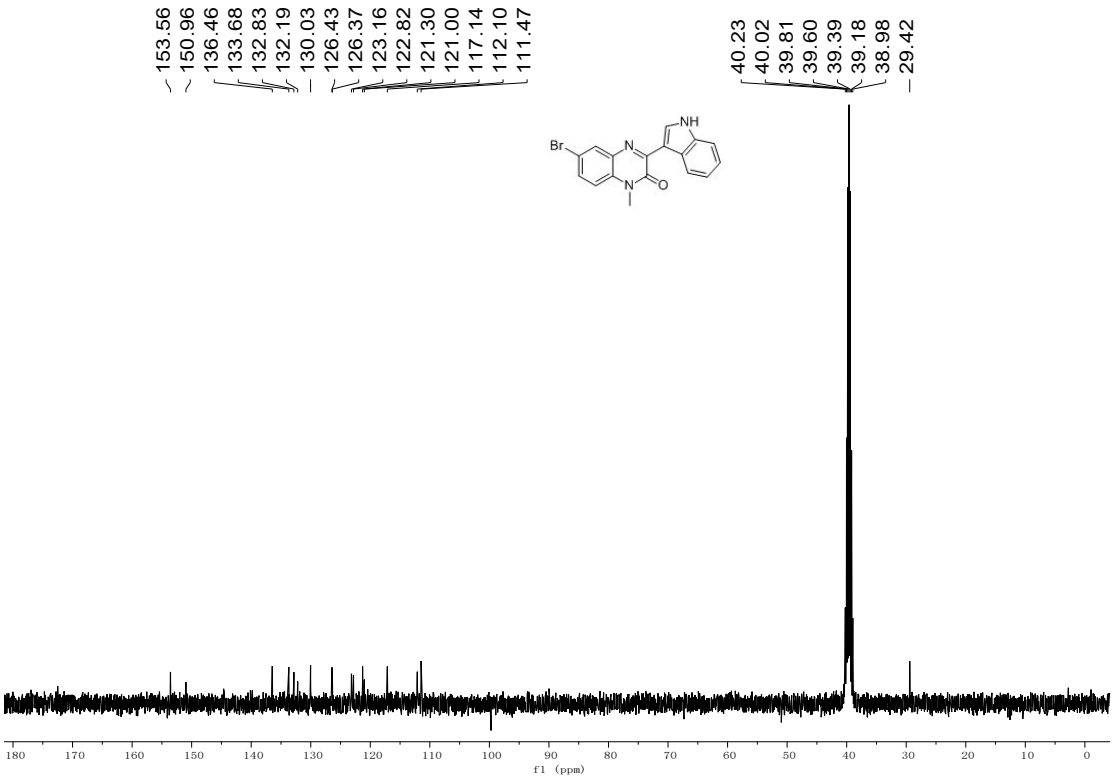
6-chloro-3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ea)





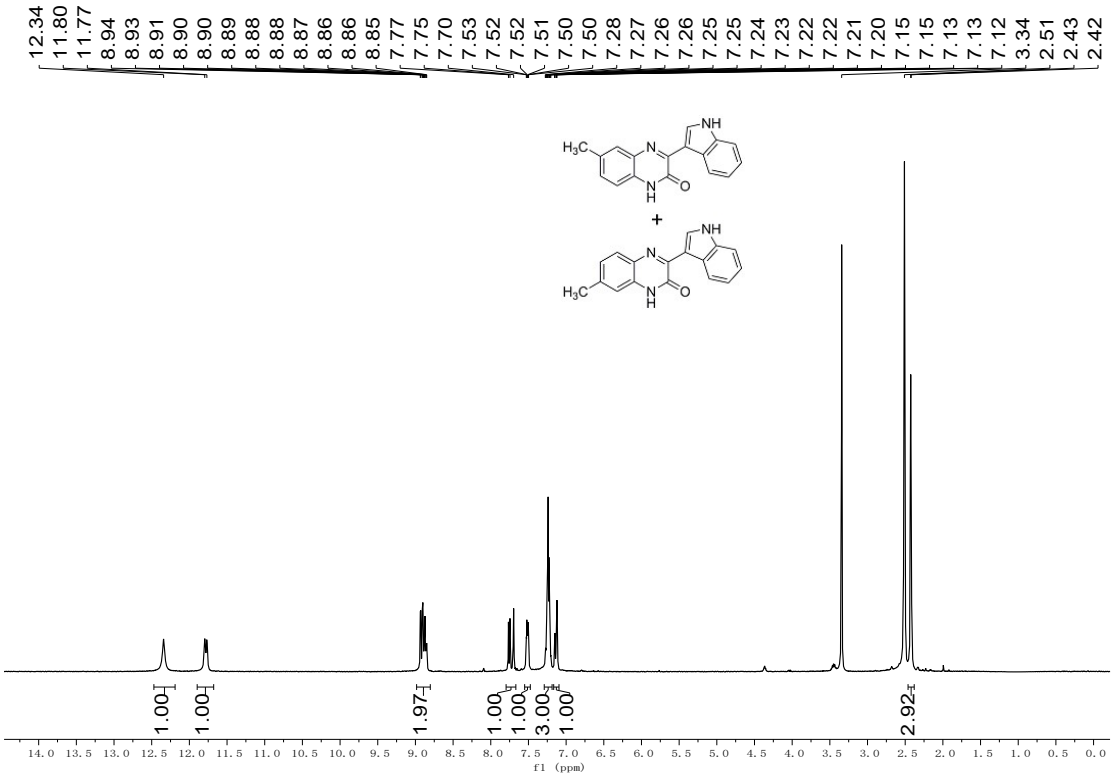
6-bromo-3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3fa)

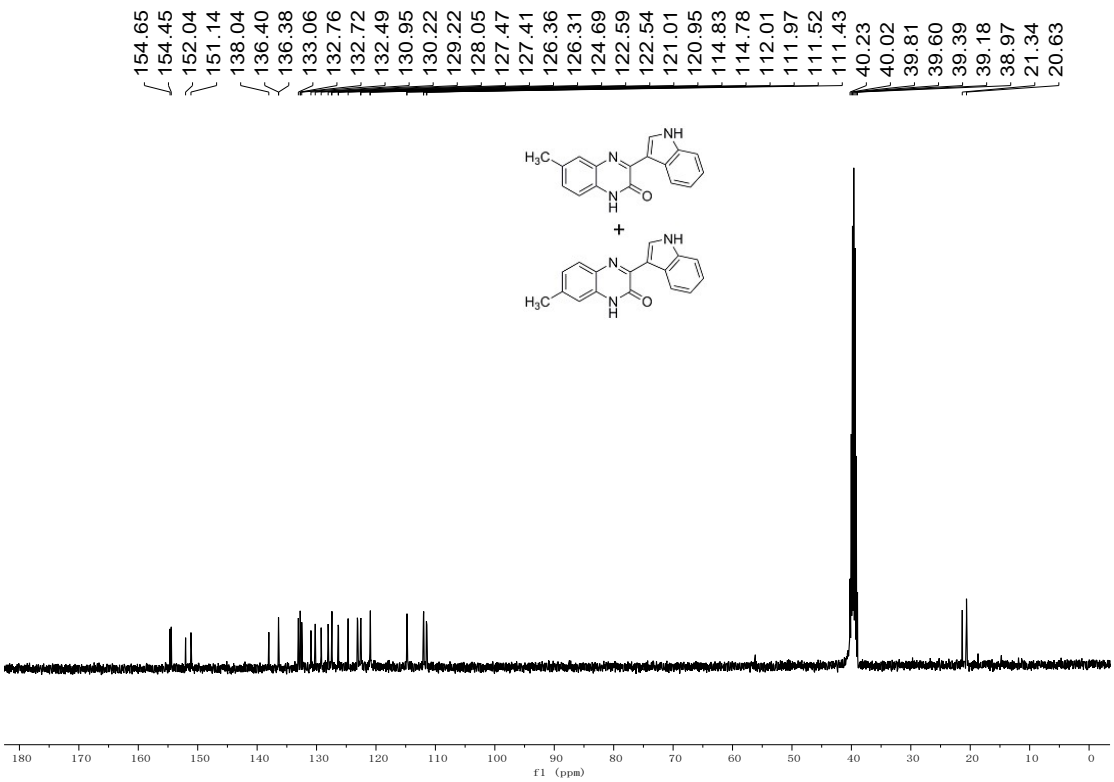




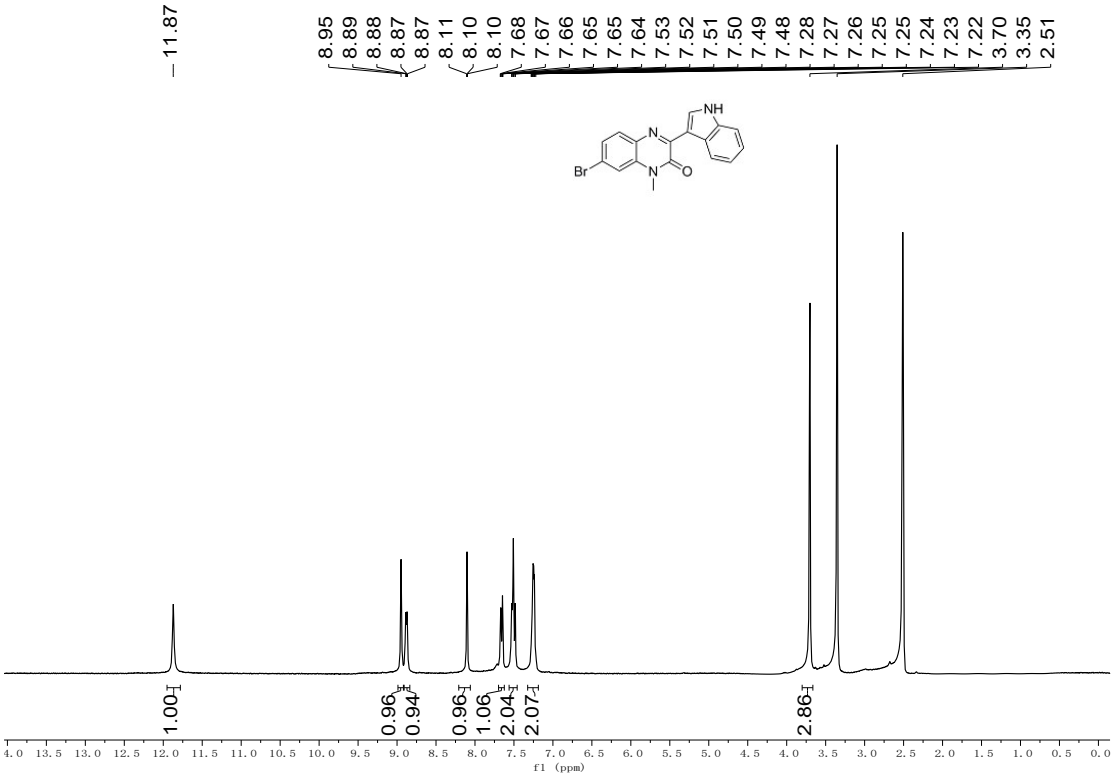
3-(1*H*-indol-3-yl)-6-methylquinoxalin-2(1*H*)-one (3ga)

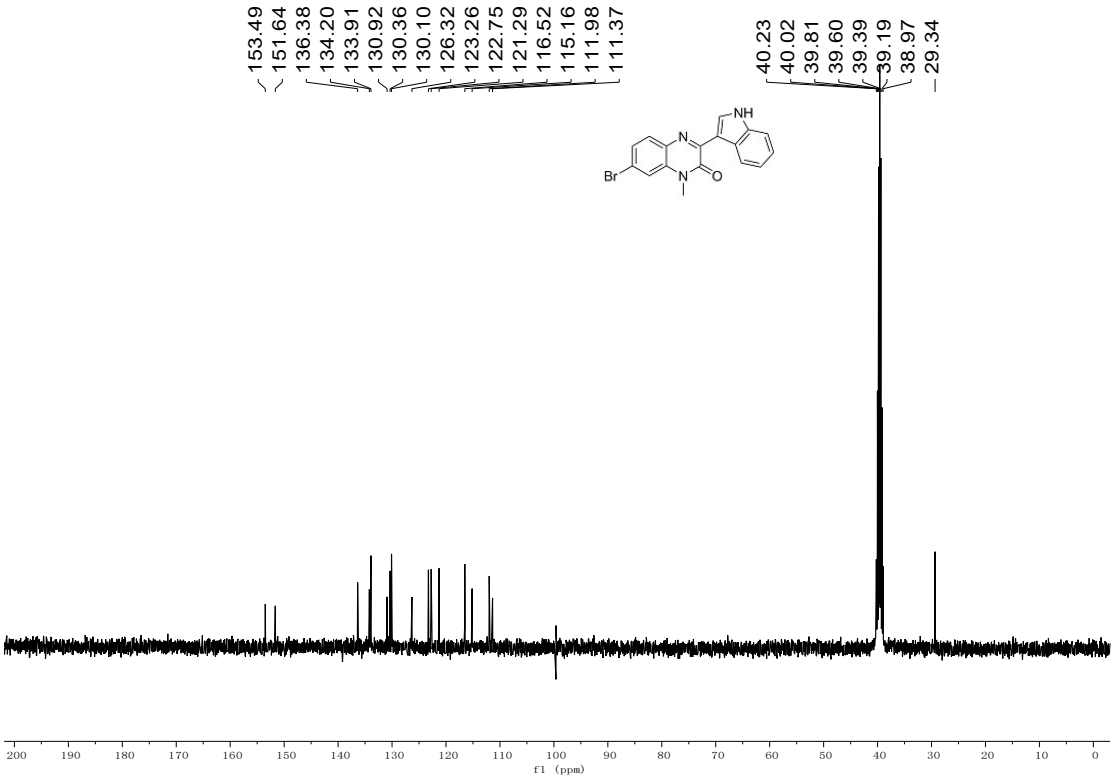
3-(1*H*-indol-3-yl)-7-methylquinoxalin-2(1*H*)-one (3ga')



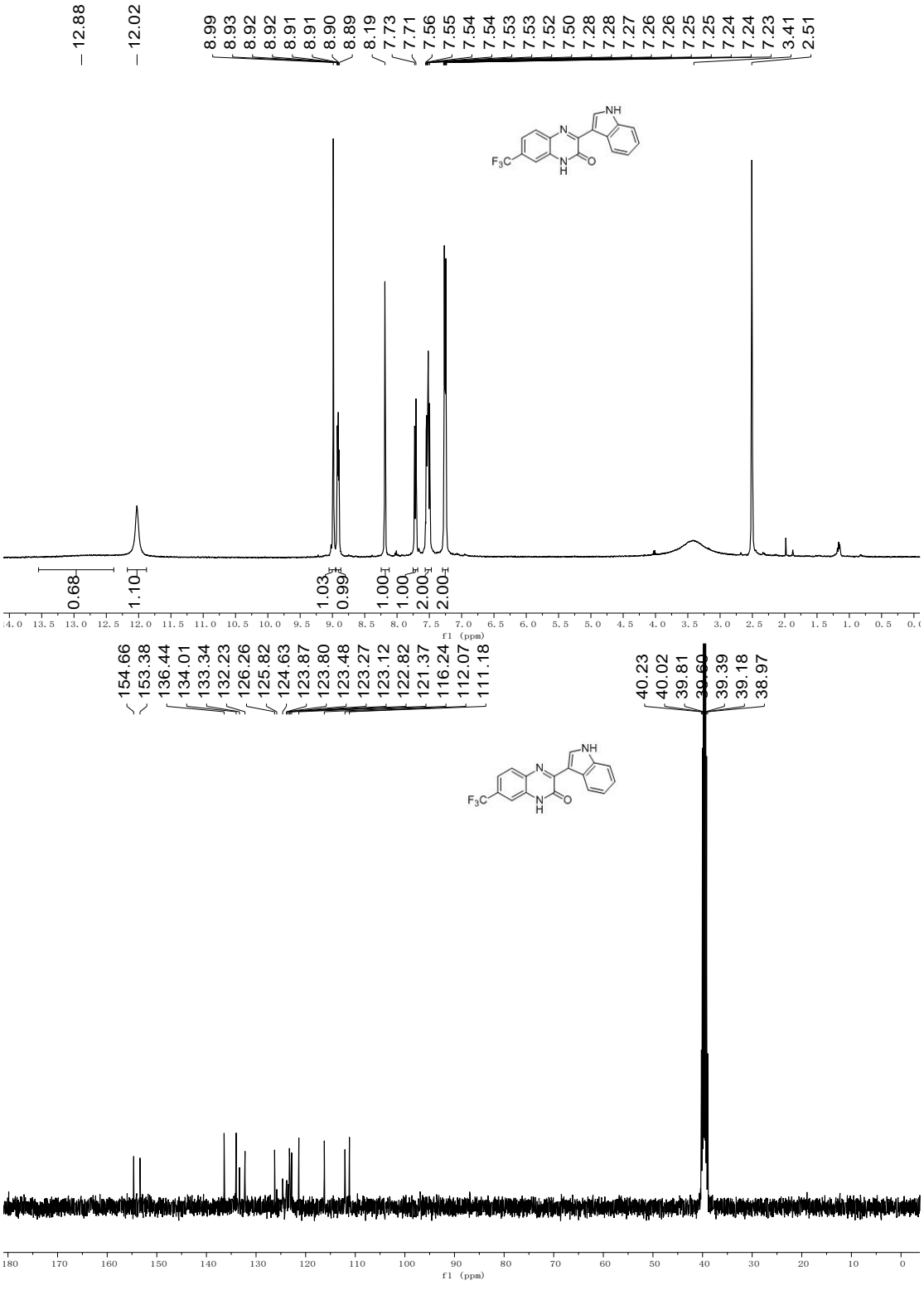


7-bromo-3-(1*H*-indol-3-yl)-1-methylquinoxalin-2(1*H*)-one (3ha)

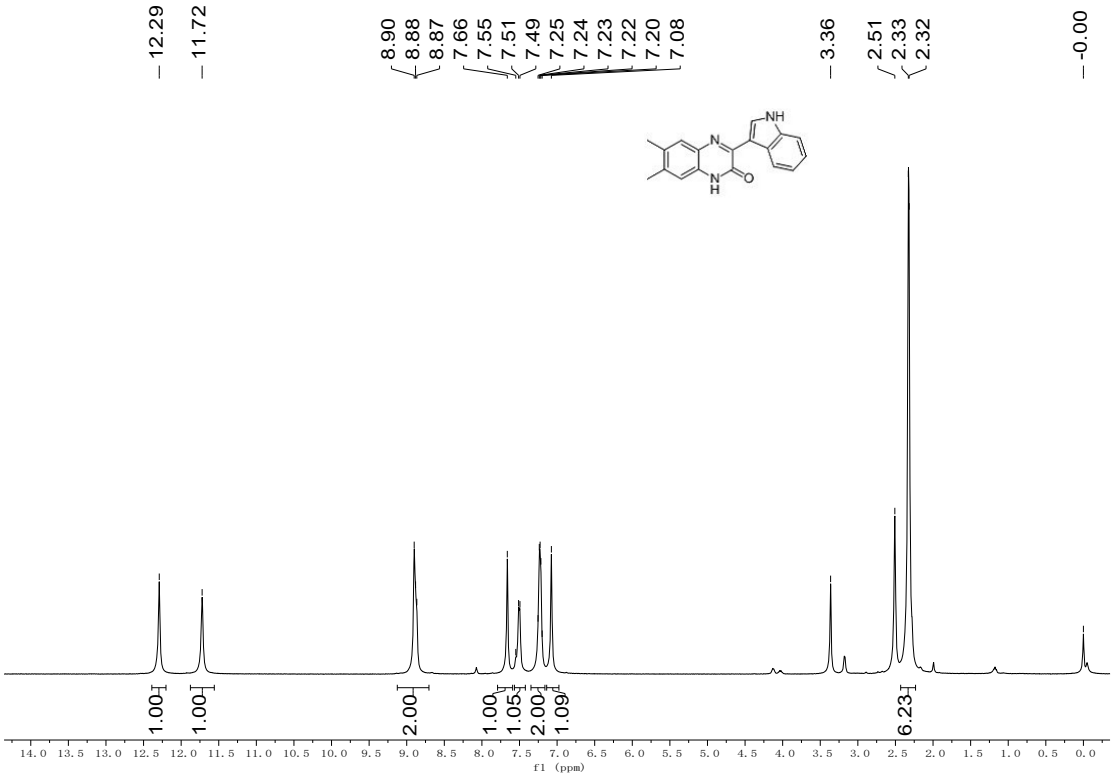


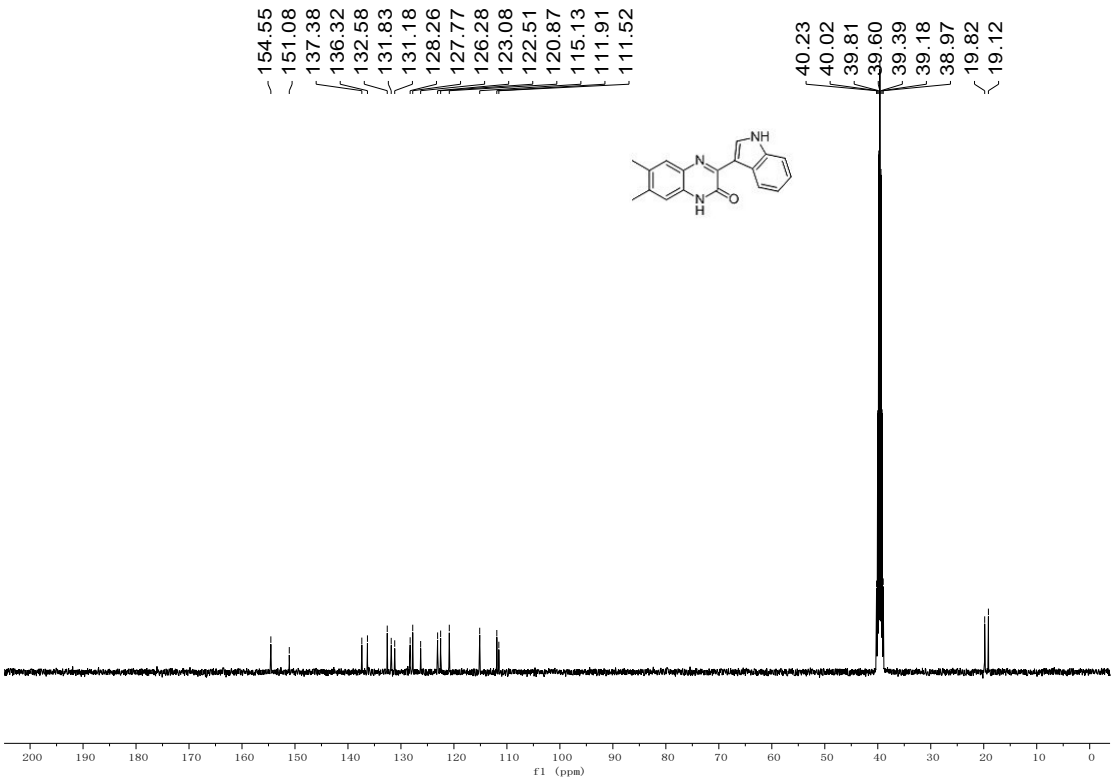


3-(1*H*-indol-3-yl)-7-(trifluoromethyl)quinoxalin-2(1*H*)-one (3ia)

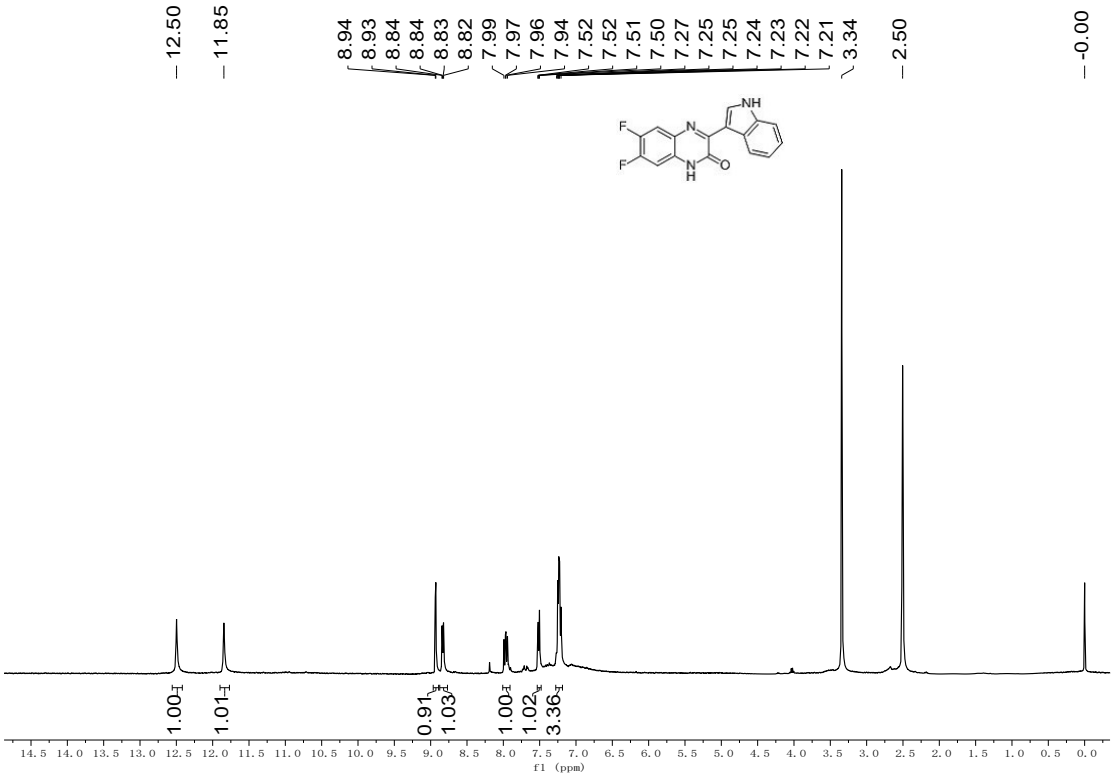


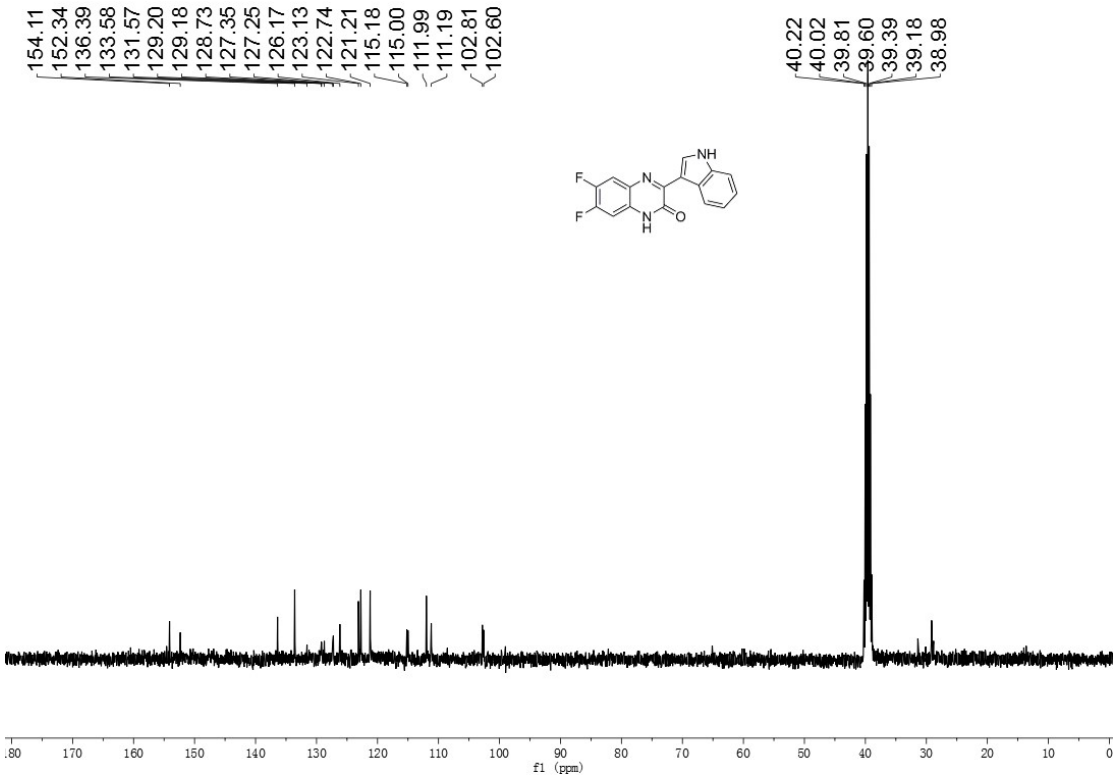
3-(1*H*-indol-3-yl)-6,7-dimethylquinoxalin-2(1*H*)-one (3ja)



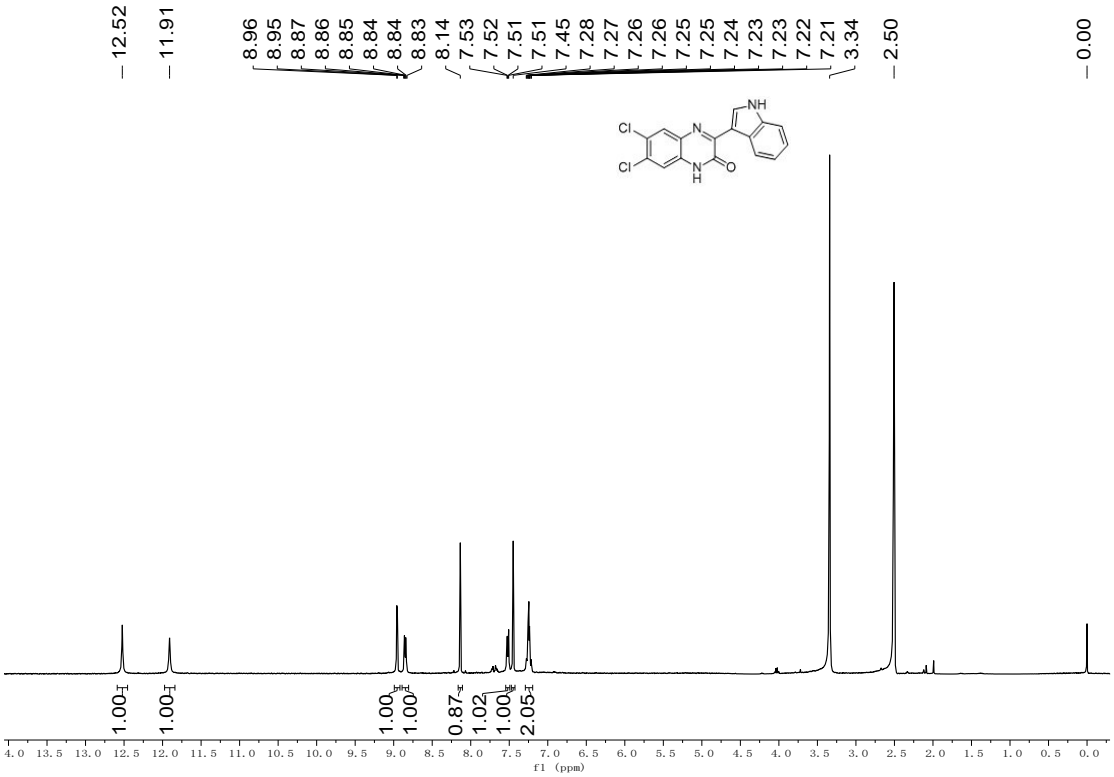


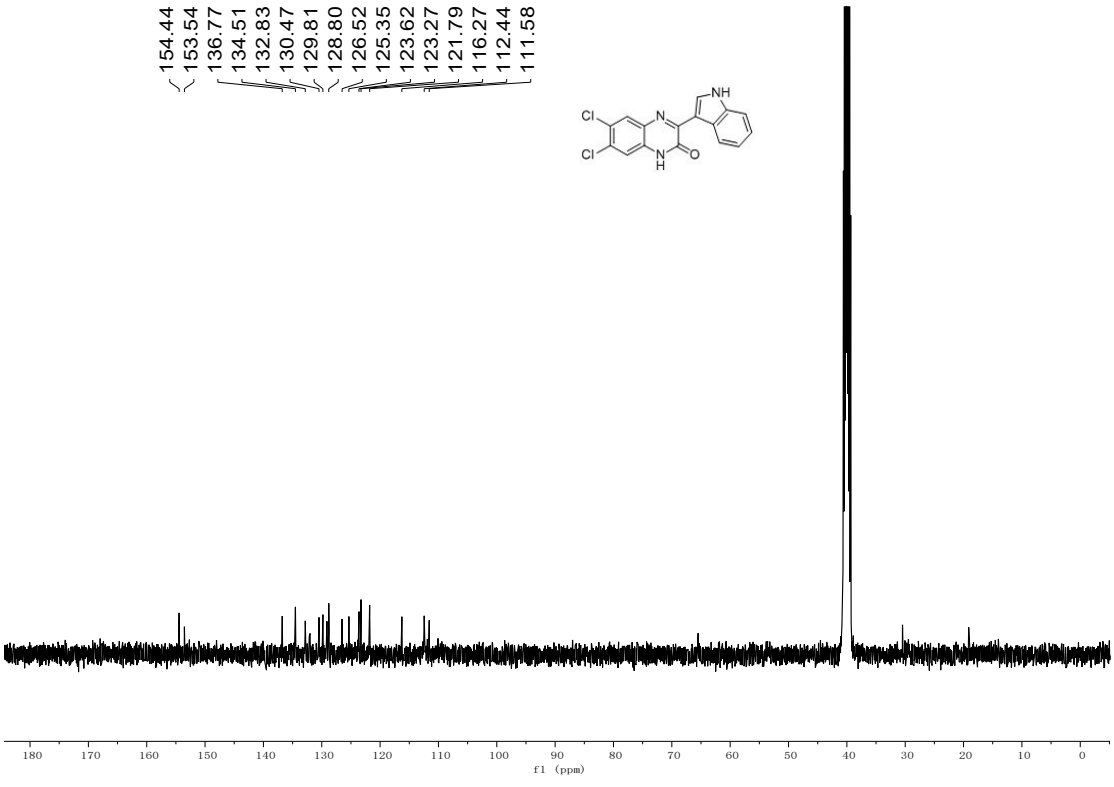
6,7-difluoro-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ka)



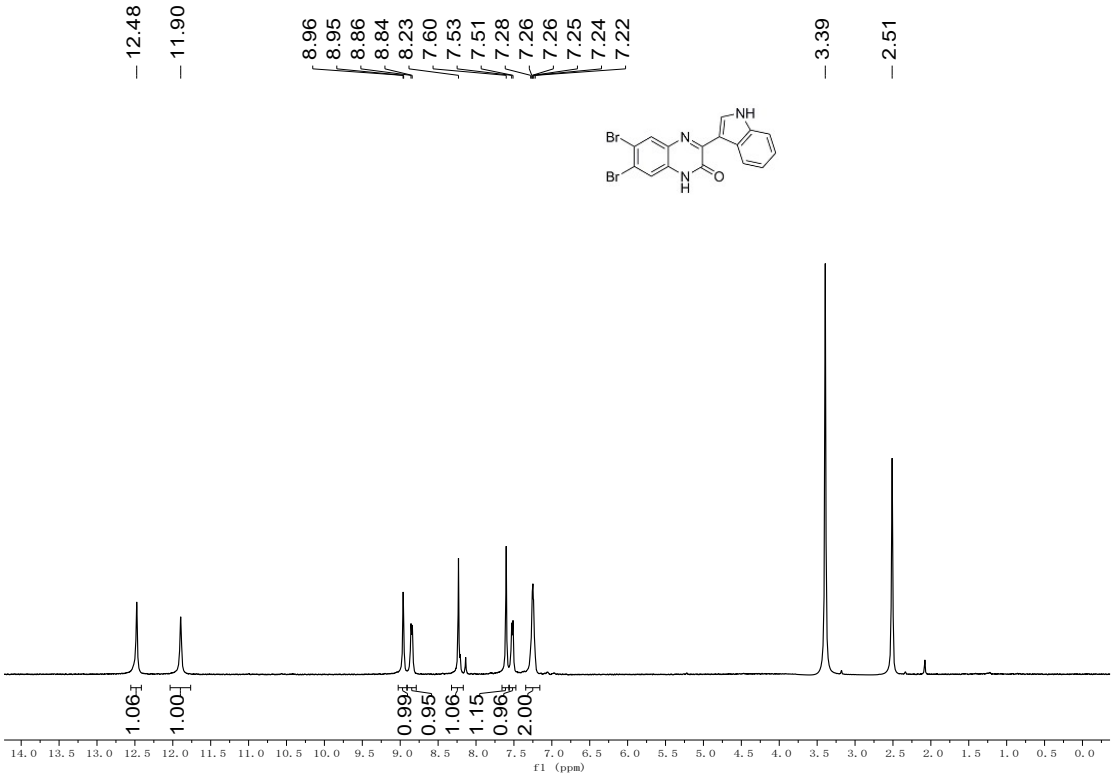


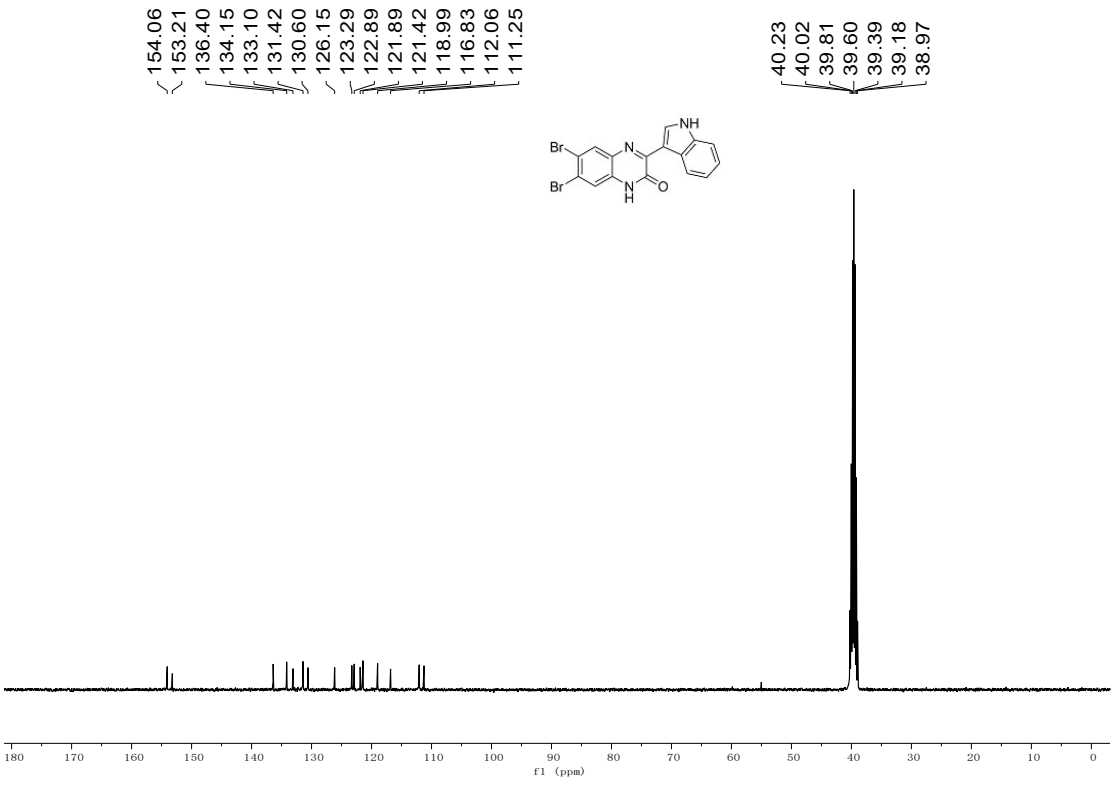
6,7-dichloro-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3la)



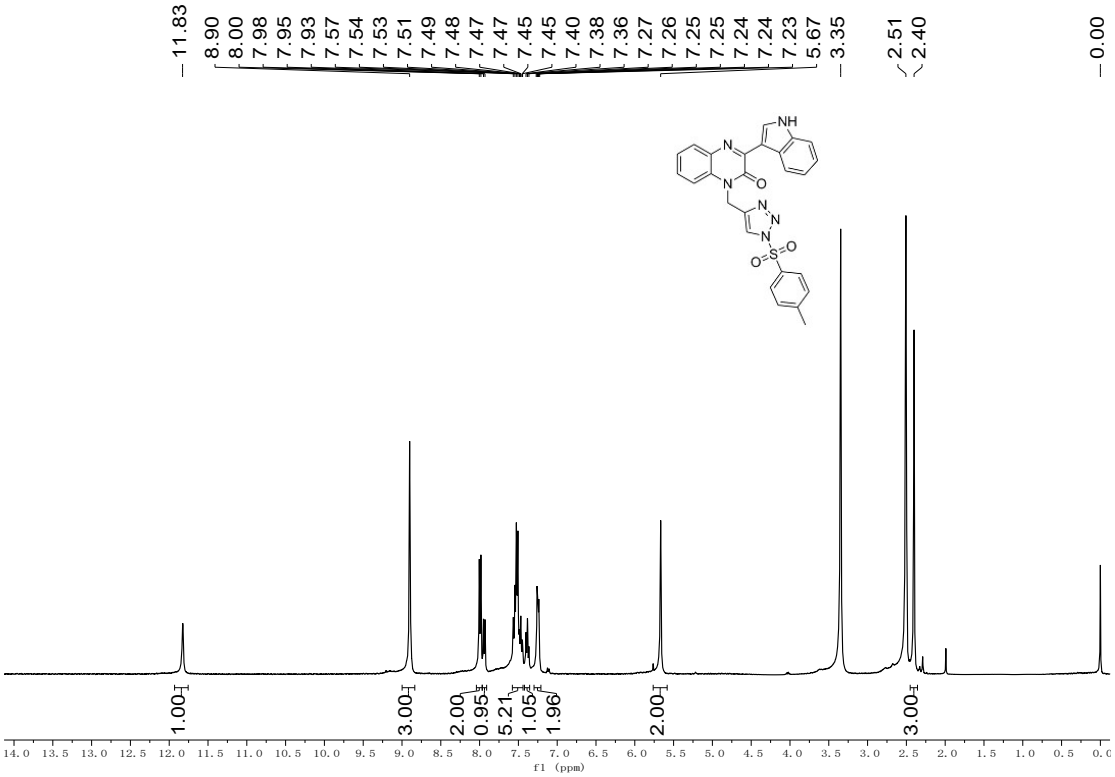


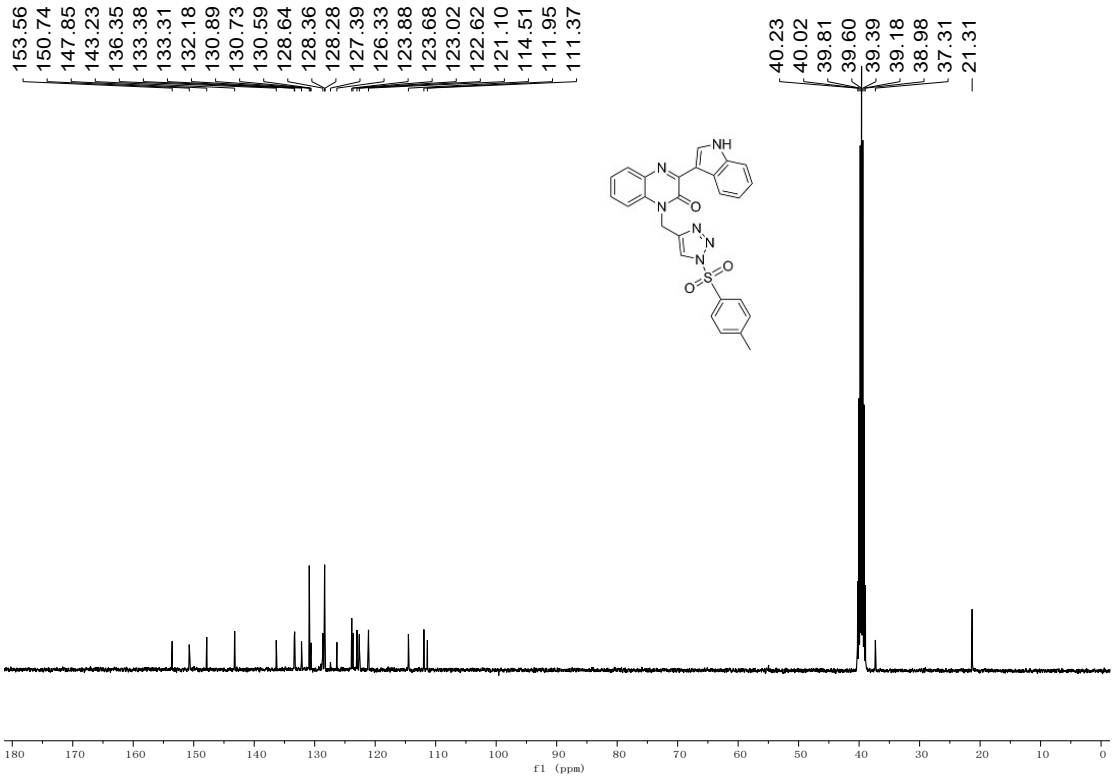
6,7-dibromo-3-(1*H*-indol-3-yl)quinoxalin-2(1*H*)-one (3ma)





3-(1*H*-indol-3-yl)-1-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)quinoxalin-2(1*H*)-one (4)





7. References:

1. M. Noikham, T. Kittikool and S. Yotphan, Iodine-Catalyzed Oxidative Cross-Dehydrogenative Coupling of Quinoxalinones and Indoles: Synthesis of 3-(Indol-2-yl)quinoxalin-2-one under Mild and Ambient Conditions, *Synthesis*, 2018, **50**, 2337.
2. Y.-Y. Han, Z.-J. Wu, X.-M. Zhang and W.-C. Yuan, An Efficient Synthesis of 3-(Indol-3-yl)quinoxalin-2-ones with TfOH-catalyzed Friedel–Crafts Type Coupling Reaction in Air, *Tetrahedron Lett.*, 2010, **51**, 2023.
3. Y. A. Azev, O. S. Ermakova, V. S. Berseneva, V. A. Bakulev, M. A. Ezhikova and M. I. Kodess, Synthesis of Fluoroquinoxalin-2(1H)-one Derivatives Containing Substituents in the Pyrazine and Benzene Fragments, *Russ. J. Org. Chem.*, 2017, **53**, 90.