Mild Iron-Catalyzed Oxidative Cross-Coupling of Quinoxalinones with Indoles

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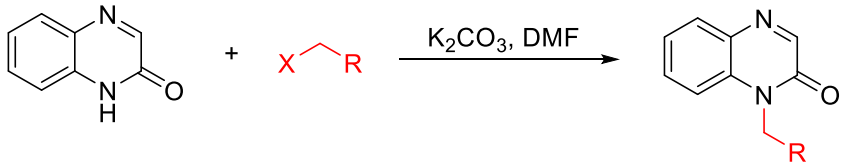
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1. General Information

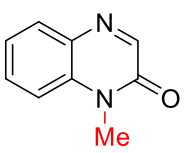
^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE NEO 400MHZ. Spectra were calibrated relative to resonances of the deuterated solvents for proton and carbon chemical shifts: DMSO (δ = 2.50 for ^{1}H NMR and δ= 39.50 for ^{13}C NMR), $CDCl_3$ (δ = 7.26 for ^{1}H NMR and δ = 77.16 for ^{13}C NMR). Data are reported as follows: chemical shift δ/ppm, integration (1H only), multiplicity (s = singlet, d = doublet, t =triplet, dd = doublet of doublets, m = multiplet; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz. HRMS spectra were obtained on a waters G2-XS Qtof. High performance liquid Chromatographic (HPLC) was carried out on a Shimadzu LC-20ADxr. Melting point was recorded on Shanghai INESA Physico-Optical Instrument INESA SGM X-4A. Compounds **1a** and **1c-1f** were prepared using literature methods.[1,2] All other chemicals were purchased from Chemical Co. and used as received unless otherwise specified.

2. General procedure for the synthesis of starting materials (1a and 1c-1f).[1,2]



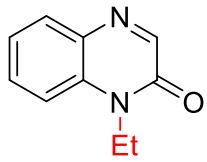
A typical procedure: To a stirred solution of quinoxalin-2(*1H*)-ones (3 mmol) in DMF (10 mL) was added the corresponding halide (1.6 equiv) and potassium carbonate (1.2 equiv.) at room temperature, which was stirred overnight. Then the resulting mixture was added with water (50 mL), and extracted with ethyl acetate (50 mL) for three times. The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to give the desired product **1**.

1-Methylquinoxalin-2(1*H*)-one (1a):



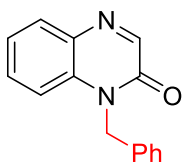
White solid. Yield: 73%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.24 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H) (aromatic *H*), 3.61 (s, 3H) (CH_3). This is a known structure. These data are similar to the reported one.[1]

1-Ethylquinoxalin-2(1H)-one (1c):



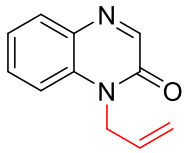
White solid. Yield: 67%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.23 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.69-7.65 (m, 2H), 7.40-7.38 (m, 1H) (aromatic H), 4.26-4.23 (m, 2H) (CH_2), 1.23 (t, J = 7.2 Hz, 3H) (CH_3). ^{13}C NMR (150 MHz, DMSO-d_6): δ 153.86 (CO), 150.10, 132.91, 131.91, 131.16, 129.87, 123.36, 114.54 (aromatic C), 36.40 (CH$_2$), 12.29 (CH$_3$). This is a known structure. These data are similar to the reported one.[1]

1-Benzylquinoxalin-2(1*H*)-one (1d):



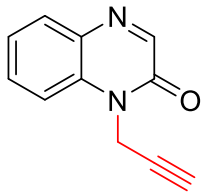
White solid. Yield: 68%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.36 (s, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.5 Hz, 2H), 7.28 – 7.24 (m, 3H) (aromatic H), 5.49 (s, 2H) (CH_2). This is a known structure. These data are similar to the reported one.[2]

1-Allylquinoxalin-2(1*H*)-one (1e):



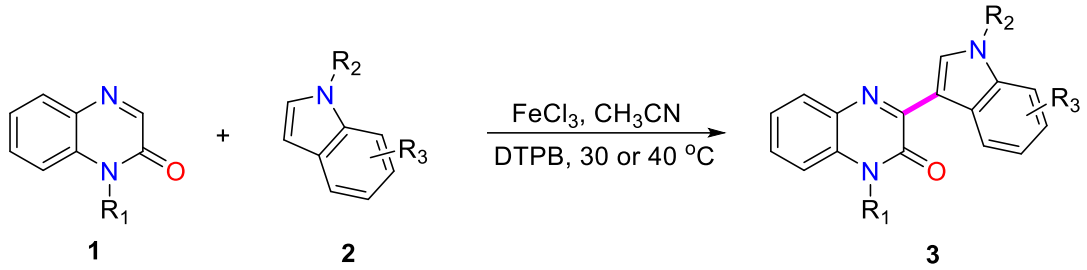
White solid. Yield: 66%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.28 (s, 1H), 7.85 (dd, J = 7.9, 1.2 Hz, 2H), 7.64 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H), 7.51 (dd, J = 8.5, 1.2 Hz, 1H), 7.38 (ddd, J = 8.1, 7.3, 1.2 Hz, 1H) (aromatic H), 5.96 – 5.90 (m, 1H), 5.17 (dd, J = 10.5, 1.5 Hz, 1H), 5.05 (dd, J = 17.3, 1.5 Hz, 1H) (olefinic H), 4.92 – 4.83 (m, 2H) (CH_2). This is a known structure. These data are similar to the reported one.[2]

1-(2-Propynyl)quinoxalin-2(1*H*)-one (1f):



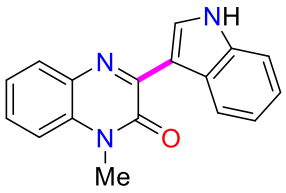
Yellow solid. Yield: 79%. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.29 (s, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H) (aromatic H), 5.07 (d, J = 2.5 Hz, 2H) (CH_2), 3.36 (t, J = 2.4 Hz, 1H) (alkynyl H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 153.32 (CO), 150.04, 132.83, 131.45, 131.18, 129.82, 123.91, 115.08 (aromatic C), 77.83, 75.25 (alkynyl C), 30.83 (CH$_2$). This is a known structure. These data are similar to the reported one.[2]

3. General procedure for the synthesis of product (3a-3t).



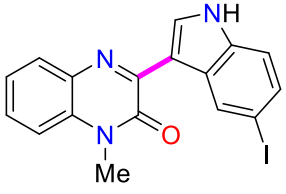
A Schlenk-tube equipped with a magnetic stir bar was charged with **1** (0.5 mmol) and **2** (1.0 mmol, 2.0 equiv). $FeCl_3$ solution (0.01 mmol/mL in CH_3CN, 5 mL) and di-tert-butyl peroxide (DTBP, 1.0 mmol, 2.0 equiv) were added. Then, the reaction mixture was stirred at 30 or 40 °C for 24h. After that, the resulting mixture was analyzed by HPLC, and handled in two ways: (1) For the reaction with precipitant, the mixture was filtered to give the product **3**, which was washed with a small amount of acetonitrile. The solution was further condensed to precipitate the product, and the mixture was filtered; (2) For the reaction without precipitant, the reaction solution was removed under reduced pressure with a rotary evaporator. The crude residue was purified by silica gel column chromatography with ethyl acetate and petrol ether (1:4) as eluent to give the pure product **3**.

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



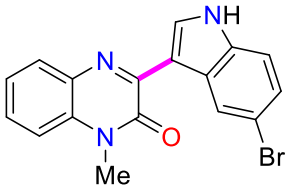
Isolated through filtration to give the yellow solid. Yield: 81%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.79 (s, 1H), 9.03 – 8.85 (m, 2H), 7.92 (d, J = 7.9 Hz, 1H), 7.61 – 7.48 (m, 3H), 7.46 – 7.33 (m, 1H), 7.33 – 7.18 (m, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.66, 150.62, 136.29, 133.18, 132.96, 131.49, 128.36, 128.25, 126.31, 123.42, 123.02, 122.53, 120.98, 114.42, 111.88, 111.41, 29.09. This is a known structure. These data are similar to the reported one.[3]

3-(5-iodo-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3b):



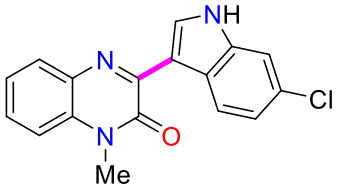
Isolated through filtration to give the yellow solid. M.P.: >300 °C. Yield: 79%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.93 (s, 1H), 9.23 (s, 1H), 8.89 (s, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.60 – 7.47 (m, 3H), 7.47 – 7.32 (m, 2H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.54, 150.22, 135.39, 133.80, 132.72, 131.55, 131.26, 130.51, 128.75, 128.54, 128.34, 123.53, 114.50, 114.36, 110.57, 85.43, 29.10. HRMS (ESI): *m/z* calcd for $C_{17}H_{12}N_3OI$ $[M+Na]^+$: 423.9923. Found: 423.9923.

3-(5-bromo-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3c):



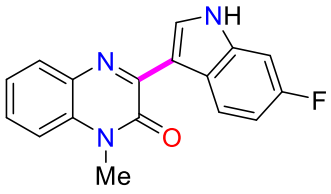
Isolated through filtration to give the yellow solid. Yield: 67%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.96 (s, 1H), 9.01 (s, 1H), 8.93 (s, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.72 – 6.40 (m, 5H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.55, 150.23, 135.04, 134.27, 132.73, 131.56, 128.57, 128.40, 127.99, 125.05, 125.00, 123.53, 114.51, 113.94, 113.78, 110.90, 29.11. This is a known structure. These data are similar to the reported one.[3]

3-(5-chloro-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3d):



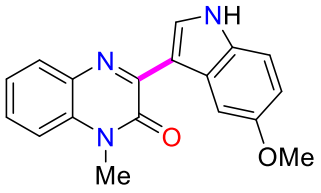
Isolated through filtration to give the yellow solid. Yield: 59%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.86 (s, 1H), 8.92 (s, 1H), 8.85 (s, 1H), 7.89 (s, 1H), 7.53 (m, 3H), 7.37 (s, 1H), 7.23 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.53, 150.23, 136.80, 133.96, 132.78, 131.58, 128.52, 128.45, 127.09, 125.06, 124.26, 123.43, 121.11, 114.44, 111.58, 111.45, 29.08. This is a known structure. These data are similar to the reported one.[3]

3-(6-fluro-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3e):



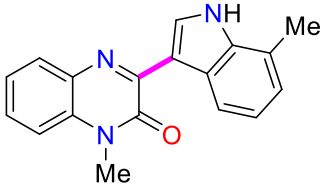
Isolated through filtration to give the yellow solid. M.P.: 261.0-263.0 °C. Yield: 63%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.81 (s, 1H), 8.97 – 8.82 (m, 2H), 7.89 (d, J = 7.9 Hz, 1H), 7.52 (t, J = 2.8 Hz, 2H), 7.37 (s, 1H), 7.30 (d, J = 9.7 Hz, 1H), 7.07 (t, J = 9.3 Hz, 1H), 3.71 (d, J = 2.0 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.25 (d, J = 236.4 Hz), 153.55, 150.30, 136.40 (d, J = 12.5 Hz), 133.73 (d, J = 2.6 Hz), 132.82, 131.58, 128.43, 128.42, 124.14 (d, J = 9.6 Hz), 123.42, 123.01, 114.43, 111.45, 109.07 (d, J = 23.4 Hz), 98.06 (d, J = 25.7 Hz), 29.08. HRMS (ESI): *m/z* calcd for $C_{17}H_{12}N_3OF$ $[M+H]^+$: 294.1043. Found: 294.1046.

3-(5-methoxy-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3f):



Isolated through filtration to give the yellow solid. Yield: 78%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H), 8.88 (s, 1H), 8.47 (s, 1H), 7.90 (d, J = 7.9 Hz, 1H), 7.53 (s, 2H), 7.47 – 7.33 (m, 2H), 6.89 (d, J = 8.7 Hz, 1H), 3.88 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.87, 153.67, 150.68, 133.52, 132.94, 131.42, 131.17, 128.31, 128.14, 126.99, 123.45, 114.44, 112.48, 112.08, 111.13, 105.06, 55.24, 29.09. This is a known structure. These data are similar to the reported one.[3]

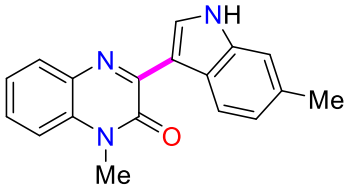
3-(7-methyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3g):



Isolated through filtration to give the yellow solid. M.P.: 289-291 °C. Yield: 83%. ^{1}H NMR (400 MHz, DMSO-d_6)

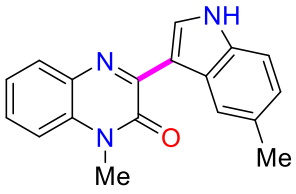
δ 11.78 (s, 1H), 8.92 (s, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 3.9 Hz, 2H), 7.46 – 7.34 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.1 Hz, 1H), 3.73 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 153.70, 150.61, 135.71, 132.96, 132.86, 131.47, 128.36, 128.23, 126.08, 123.41, 123.17, 121.19, 120.93, 120.65, 114.41, 111.81, 29.08, 16.76. HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_3O$ $[M+H]^+$: 290.1293. Found: 290.1298.

3-(6-methyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3h):



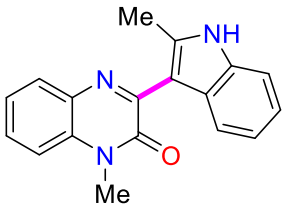
Isolated through filtration to give the yellow solid. Yield: 57%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.65 (s, 1H), 8.85 (d, *J* = 2.9 Hz, 1H), 8.74 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.53 (s, 1H), 7.50 (d, *J* = 9.1 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.30 (s, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 153.64, 150.60, 136.71, 132.99, 132.73, 131.68, 131.46, 128.32, 128.15, 124.18, 123.39, 122.72, 122.63, 114.40, 111.70, 111.40, 29.07, 21.36. This is a known structure. These data are similar to the reported one.[4]

3-(5-methyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3i):



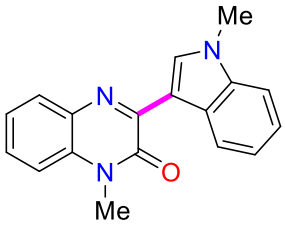
Isolated through filtration to give the yellow solid. M.P.: >300 °C. Yield: 69%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.67 (s, 1H), 8.88 (d, *J* = 2.6 Hz, 1H), 8.71 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 2.2 Hz, 2H), 7.39 (d, *J* = 6.0 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 153.67, 150.67, 134.60, 133.22, 132.99, 131.43, 129.63, 128.35, 128.12, 126.57, 123.97, 123.38, 122.80, 114.40, 111.51, 111.02, 29.06, 21.66. HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_3O$ $[M+H]^+$: 290.1293. Found: 290.1295.

3-(2-methyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3j):



Isolated through silica gel column chromatography with ethyl acetate and petrol ether (1:4) to give the yellow solid. The yellow solid was washed with petrol ether. Yield: 69%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 11.49 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.41 – 7.31 (m, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.03 – 6.97 (m, 1H), 3.71 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 154.01, 153.14, 139.29, 135.08, 132.81, 132.53, 129.02, 128.65, 127.96, 123.30, 120.83, 120.80, 119.49, 114.42, 110.59, 109.48, 29.28, 14.24. This is a known structure. These data are similar to the reported one.[4]

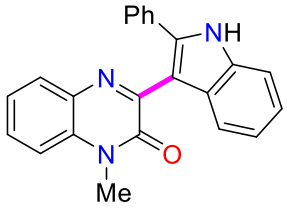
3-(1-methyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3k):



Isolated through filtration to give the yellow solid. Yield: 73%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.95 – 8.88 (m, 2H), 7.92 (d, *J* = 7.4 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 3H), 7.44 – 7.36

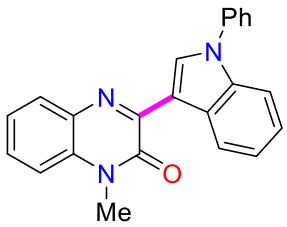
(m, 1H), 7.35 – 7.25 (m, 2H), 3.93 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.60, 150.32, 136.98, 136.87, 132.97, 131.49, 128.37, 128.31, 126.78, 123.48, 123.14, 122.63, 121.31, 114.48, 110.36, 110.25, 33.07, 29.11. This is a known structure. These data are similar to the reported one.[4]

3-(2-phenyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3l):



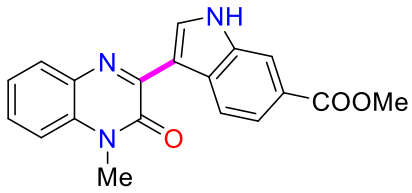
Isolated through silica gel column chromatography with ethyl acetate and petrol ether (1:4) to give the yellow solid. Yield: 57%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.84 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.70 – 7.44 (m, 6H), 7.42 – 7.28 (m, 4H), 7.18 (t, J = 7.2 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.72, 153.56, 139.19, 135.96, 133.14, 133.05, 132.71, 129.74, 129.02, 128.57, 128.40, 127.86, 127.81, 123.35, 122.08, 120.33, 119.99, 114.61, 111.45, 109.13, 29.28. This is a known structure. These data are similar to the reported one.[4]

3-(1-phenyl-*1H*-indol-3-yl)-1-methylquinoxalin-2(*1H*)-one(3m):



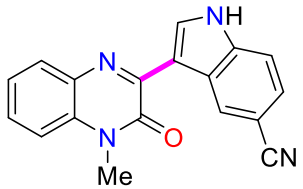
Isolated through filtration to give the yellow solid. Yield: 54%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 9.03 (d, J = 7.4 Hz, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.73 – 7.57 (m, 7H), 7.56 – 7.48 (m, 1H), 7.42 – 7.31 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.68, 144.99, 138.26, 135.79, 134.97, 132.84, 131.72, 130.14, 129.01, 128.76, 127.67, 127.40, 124.52, 123.76, 123.65, 122.25, 114.66, 112.78, 110.74, 29.24. This is a known structure. These data are similar to the reported one.[5]

methyl 3-(4-methyl-3-oxo-3,*4-d*ihydroquinoxalin-2-yl)-*1H*-indole-6-carboxylate (3n):



Isolated through filtration to give the yellow solid. Yield: 66%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.10 (s, 1H), 9.09 (s, 1H), 8.94 (d, J = 8.4 Hz, 1H), 8.15 (s, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.56 (s, 2H), 7.41 (d, J = 5.0 Hz, 1H), 3.89 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.97, 153.55, 150.16, 135.99, 135.65, 132.76, 131.60, 129.88, 128.59, 128.52, 123.43, 122.68, 121.46, 114.43, 113.64, 111.67, 51.93, 29.08. This is a known structure. These data are similar to the reported one.[4]

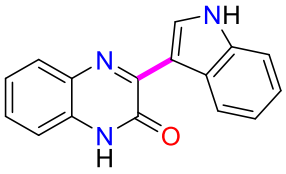
3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-*1H*-indole-5-carbonitrile(3o):



Isolated through filtration to give the yellow solid. M.P.: >300 ºC. Yield: 37%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 9.15 (s, 1H), 8.98 (s, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.61 – 7.44 (m, 3H), 7.37 (t, J = 7.4 Hz, 1H), 3.66 (s, 3H). ^{13}C NMR (101 MHz,

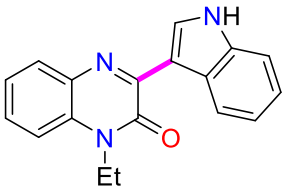
DMSO-d_6) δ 153.44, 149.85, 138.14, 135.00, 132.62, 131.64, 128.91, 128.76, 127.98, 125.95, 125.39, 123.52, 120.73, 114.48, 113.31, 111.77, 103.06, 29.11. HRMS (ESI): *m/z* calcd for $C_{18}H_{12}N_4O$ [M+Na]$^+$: 323.0909. Found: 323.0909.

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



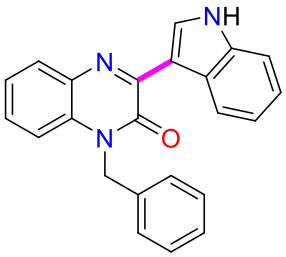
Isolated through filtration to give the yellow solid. Yield: 86%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.41 (s, 1H), 11.78 (s, 1H), 8.94 (s, 1H), 8.91 – 8.85 (m, 1H), 7.86 (d, J = 7.9 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 7.8 Hz, 2H), 7.27 – 7.20 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.41, 151.98, 136.28, 133.09, 132.65, 130.18, 127.99, 127.61, 126.20, 123.24, 122.99, 122.56, 121.00, 114.94, 111.90, 111.32. This is a known structure. These data are similar to the reported one.[4]

1-ethyl-3-(*1H*-indol-3-yl)quinoxalin-2(*1H*)-one(3q):



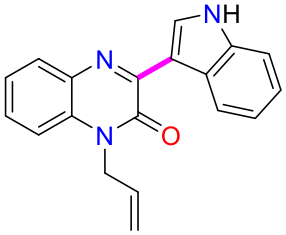
Isolated through silica gel column chromatography with ethyl acetate and petrol ether (1:4) to give the red solid. M.P.: 175-176.5 ºC. Yield: 91%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.80 (s, 1H), 8.96 – 8.87 (m, 2H), 7.93 (d, J = 7.9 Hz, 1H), 7.63 – 7.49 (m, 3H), 7.38 (t, J = 7.5 Hz, 1H), 7.27 – 7.21 (m, 2H), 4.38 (q, J = 6.7, 2H), 1.30 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.17, 150.65, 136.29, 133.26, 133.21, 130.24, 128.73, 128.40, 126.33, 123.36, 123.01, 122.54, 121.00, 114.13, 111.89, 111.34, 36.89, 12.45. HRMS (ESI): *m/z* calcd for $C_{18}H_{15}N_3O$ [M+H]$^+$: 290.1293. Found: 290.1295.

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



Isolated through silica gel column chromatography with ethyl acetate and petrol ether (1:4) to give the orange solid. Yield: 68%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.98 – 8.90 (m, 2H), 7.95 (d, J = 7.8 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.43 (d, J = 3.2 Hz, 2H), 7.38 – 7.29 (m, 5H), 7.29 – 7.23 (m, 3H), 5.63 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.84, 150.77, 136.33, 136.19, 133.39, 133.29, 130.61, 128.73, 128.64, 128.27, 127.26, 126.76, 126.33, 123.62, 123.02, 122.62, 121.10, 114.80, 111.94, 111.40, 44.98. This is a known structure. These data are similar to the reported one.[4]

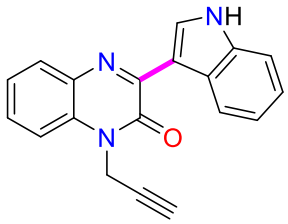
1-allyl-3-(*1H*-indol-3-yl)quinoxalin-2(*1H*)-one(3s):



Isolated through silica gel column chromatography with ethyl acetate and petrol ether (1:4) to give the orange solid. Yield: 72%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.82 (s, 1H), 8.95 – 8.87 (m, 2H), 7.94 (d, J = 7.9 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.38 (m, 1H), 7.28 – 7.21 (m, 2H), 6.08 – 5.94 (m, 1H), 5.20 (d, J = 10.5 Hz, 1H), 5.10 (d, J = 16.9 Hz, 1H), 5.01 (d, J =

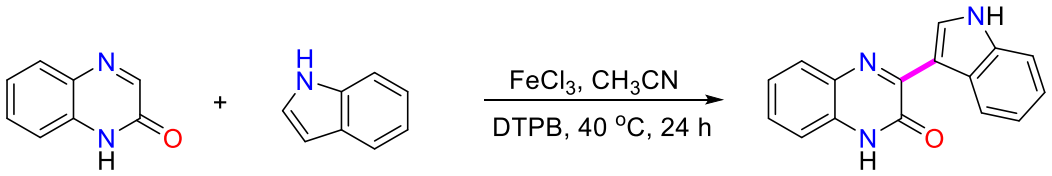
2.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.41, 150.75, 136.40, 133.36, 133.26, 131.94, 130.63, 128.69, 128.42, 126.39, 123.69, 123.10, 122.75, 121.21, 117.06, 114.90, 112.05, 111.45, 44.05. This is a known structure. These data are similar to the reported one.[4]

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



Isolated through silica gel column chromatography with ethyl acetate and petrol ether (1:4) to give the yellow solid. Yield: 73%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.85 (s, 1H), 8.93 – 8.85 (m, 2H), 7.95 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 9.0 Hz, 2H), 7.52 (d, J = 5.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.28 – 7.22 (m, 2H), 5.21 (s, 2H), 3.35 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.78, 150.47, 136.32, 133.34, 133.19, 129.84, 128.60, 128.37, 126.22, 123.92, 122.97, 122.67, 121.14, 114.69, 111.96, 111.20, 78.37, 75.07, 31.34. This is a known structure. These data are similar to the reported one.[4]

4. Gram scale reaction.

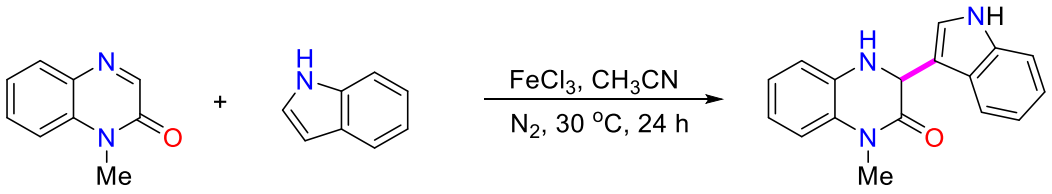


1b (0.73g) **2a** (1.17g) **3p** (1.23g) Yield: 94%

A 100 mL round-bottle equipped with a magnetic stir bar was charged with **1** (5.0 mmol) and **2** (10.0 mmol, 2.0 equiv). $FeCl_3$ solution (0.01 mmol/mL in CH_3CN, 50 mL) and di-tert-butyl peroxide (DTBP, 10.0 mmol, 2.0 equiv) were added. Then, the reaction mixture was stirred at 40 °C for 24h to give the suspension. The resulting mixture was analyzed by HPLC. The mixture was filtered to give the pure yellow product **3p** in 94% yield.

5. Control experiment

(1) Isolation of intermediate 4a



1a **2a** **4a** Yield: 42%

A 10 mL Schlenk-tube equipped with a magnetic stir bar was charged with **1a** (0.5

mmol) and **2a** (1.0 mmol, 2.0 equiv). $FeCl_3$ solution (0.01 mmol/mL in CH_3CN, 5.0 mL) was added. The mixture was bubbled with nitrogen for 20 min. Then, the reaction mixture was stirred at 30 °C for 24h to give the suspension. The resulting mixture was analyzed by HPLC. The mixture was filtered to give the pale-yellow product **4a** in 42% yield (purity: 87% with 13% **3a**). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.93 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 7.03 – 6.92 (m, 3H), 6.90 – 6.80 (m, 2H), 6.74 (t, J = 7.6 Hz, 1H), 6.59 (s, 1H), 5.20 (s, 1H), 3.29 (s, 3H). HRMS (ESI): *m/z* calcd for $C_{17}H_{15}N_3O$ $[M+Na]^+$: 300.1113. Found: 300.1309.

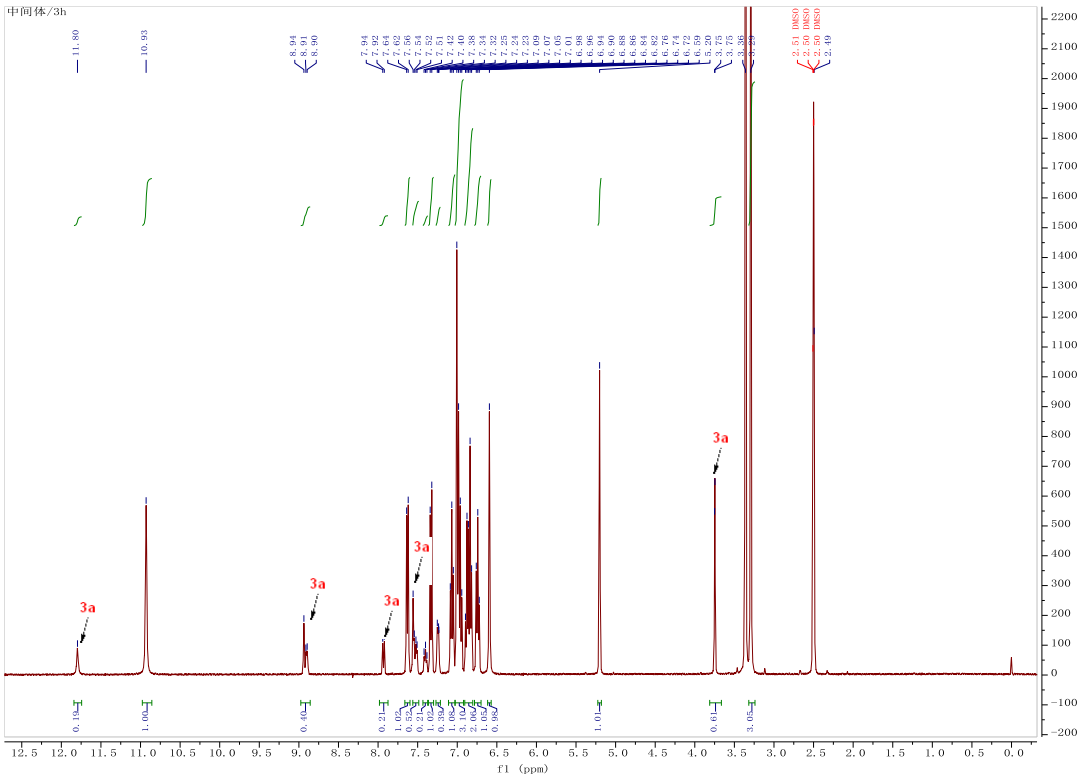
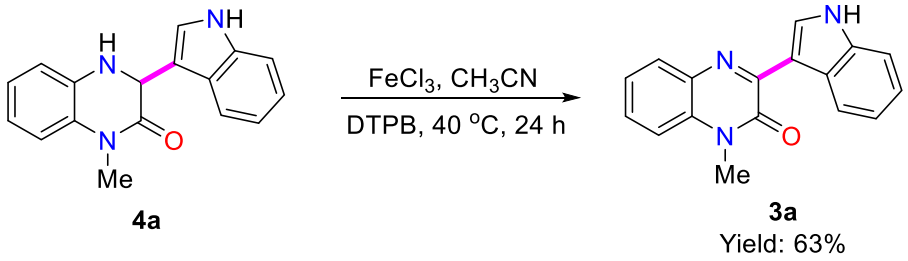


Figure S1. NMR spectra of **4a.**

(2) Conversion of intermediate 4a to 3a



A 10 mL Schlenk-tube equipped with a magnetic stir bar was charged with **4a**

(0.1mmol). $FeCl_3$ solution (0.01 mmol/mL in CH_3CN, 1.0 mL) and di-tert-butyl peroxide (DTBP, 0.2 mmol, 2.0 equiv) were added. Then, the reaction mixture was stirred at 40 ^oC for 24h. The resulting mixture was analyzed by HPLC with biphenyl as the external standard. Yield of product **3a** was determined to be 63%.

6 References:

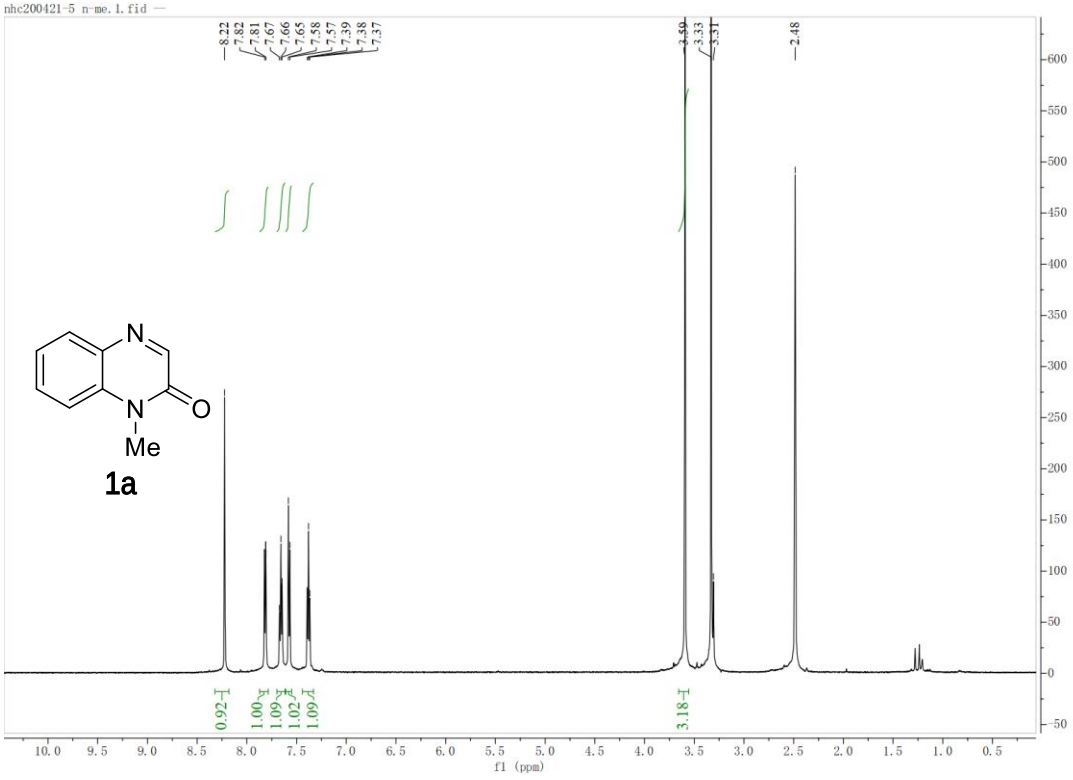
1 H. Ni, Y. Li, X. Shi, Y. Pang, C. Jin, F. Zhao. *Tetrahedron Lett.*, **2021**, 68, 152915.

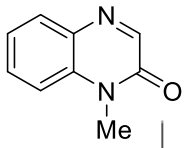
2 H. Ni, X. Shi, Y. Li, X. Zhang, J. Zhao, F. Zhao. *Org. Biomol. Chem*., **2020**, *18*, 6558.

3 Y.-Y. Han, Z.-J. Wu, X.-M. Zhang, W.-C.Yuan, *Tetrahedron Lett.,* **2010**, *51*, 2023.

4 J. Huang, L. Wang, X.-Y. Tang, *Org. Biomol. Chem*., **2023**, *21*, 2709.

5 M. Shen, L. Li, Q. Zhou, J. Wang, L. Wang, *Chin. J. Org. Chem.*, **2023**, *43*, 697.


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8.22
7.82
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7.39
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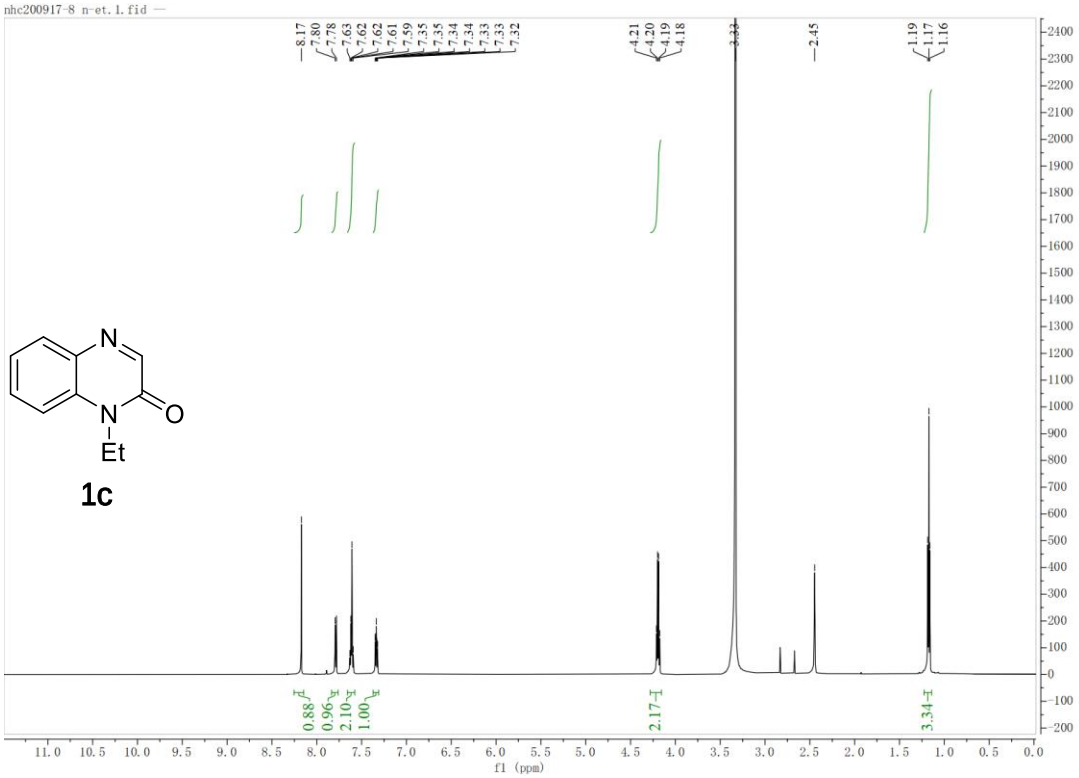

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N
O
Me

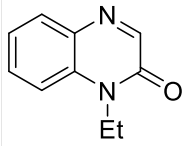
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N
N
O
Me

1a

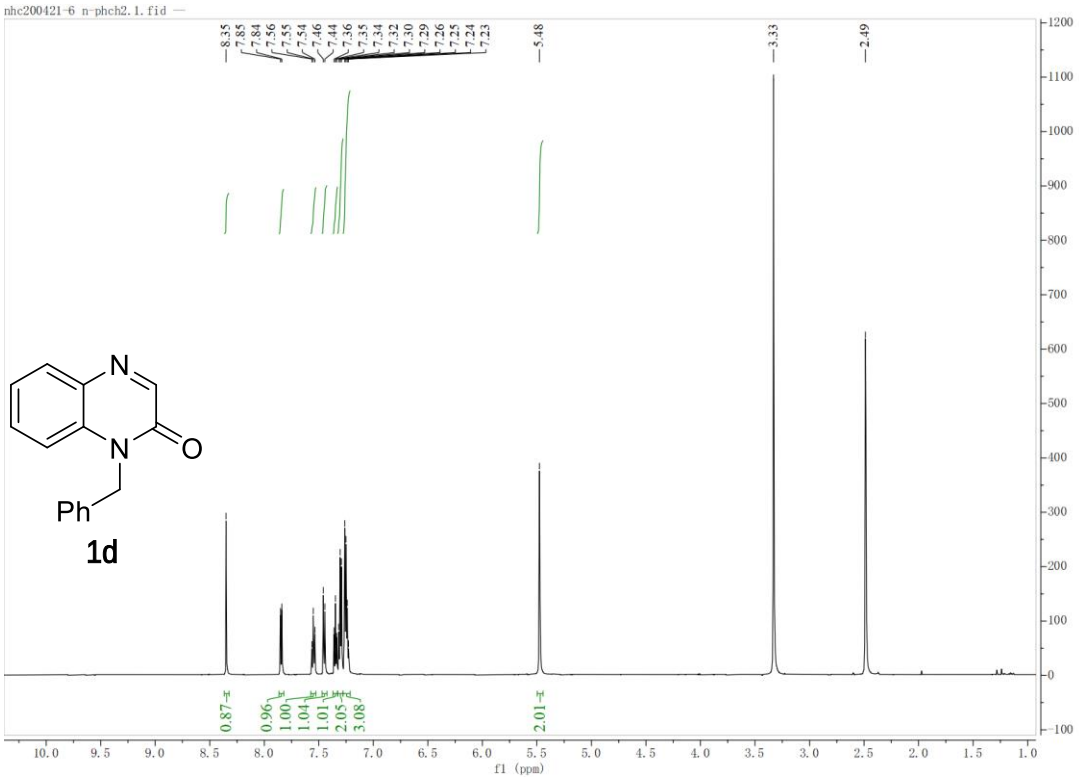

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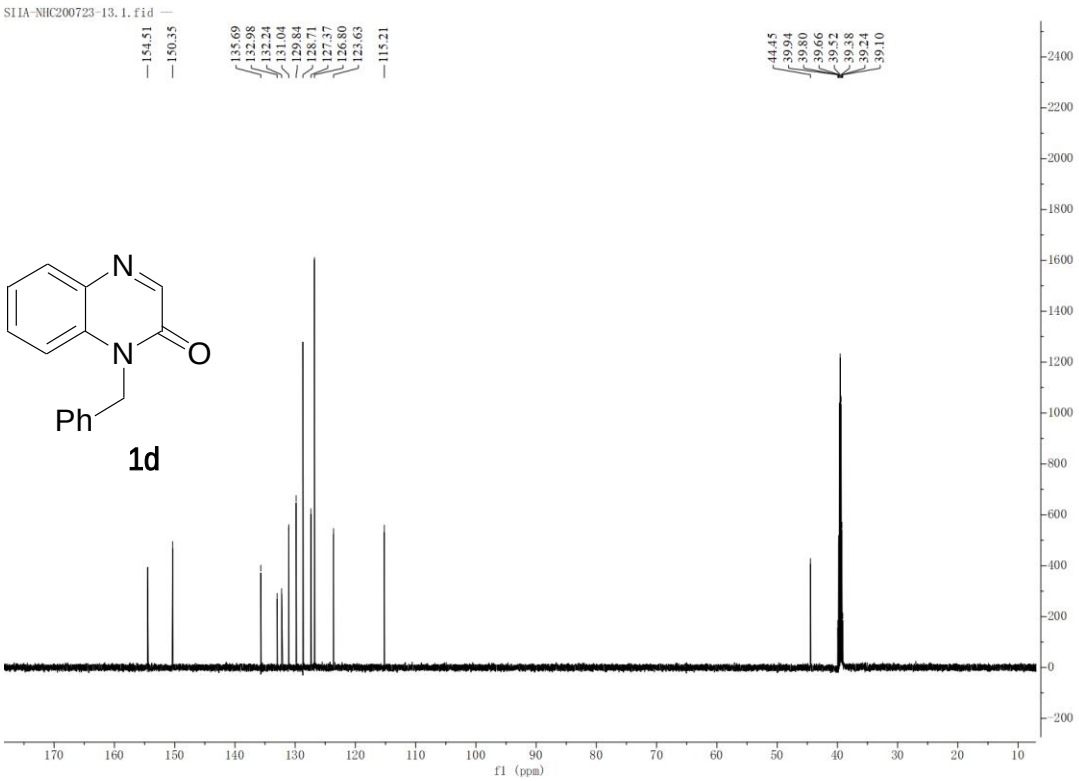


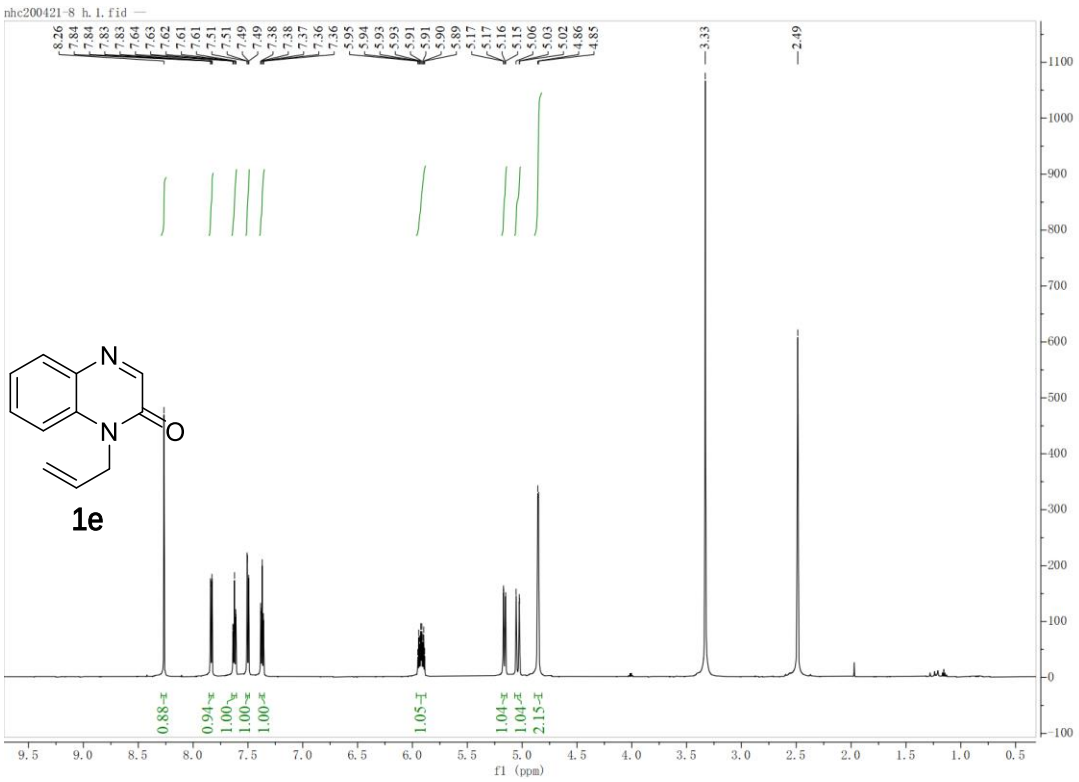
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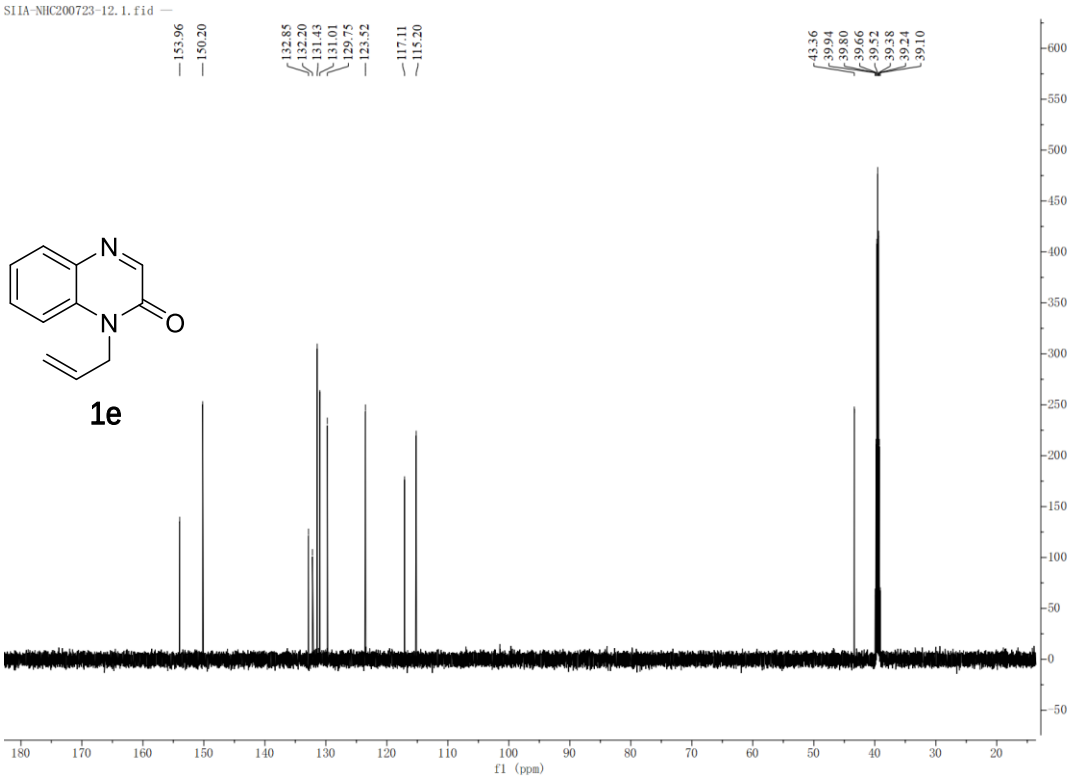
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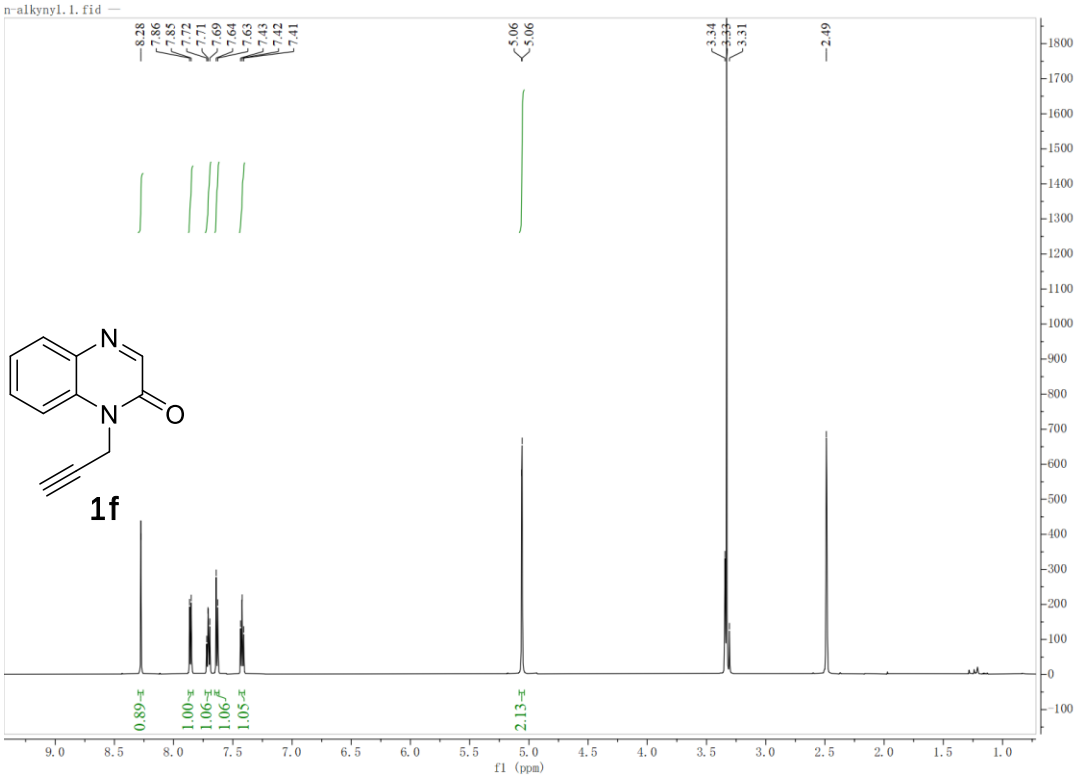
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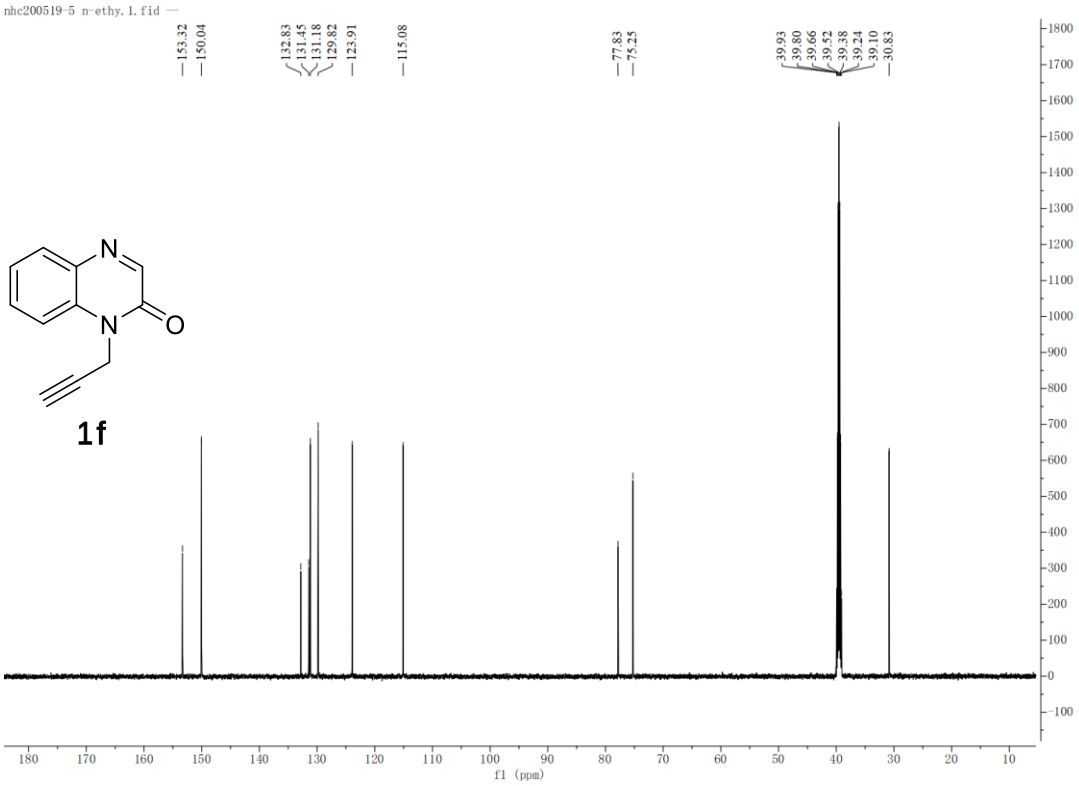

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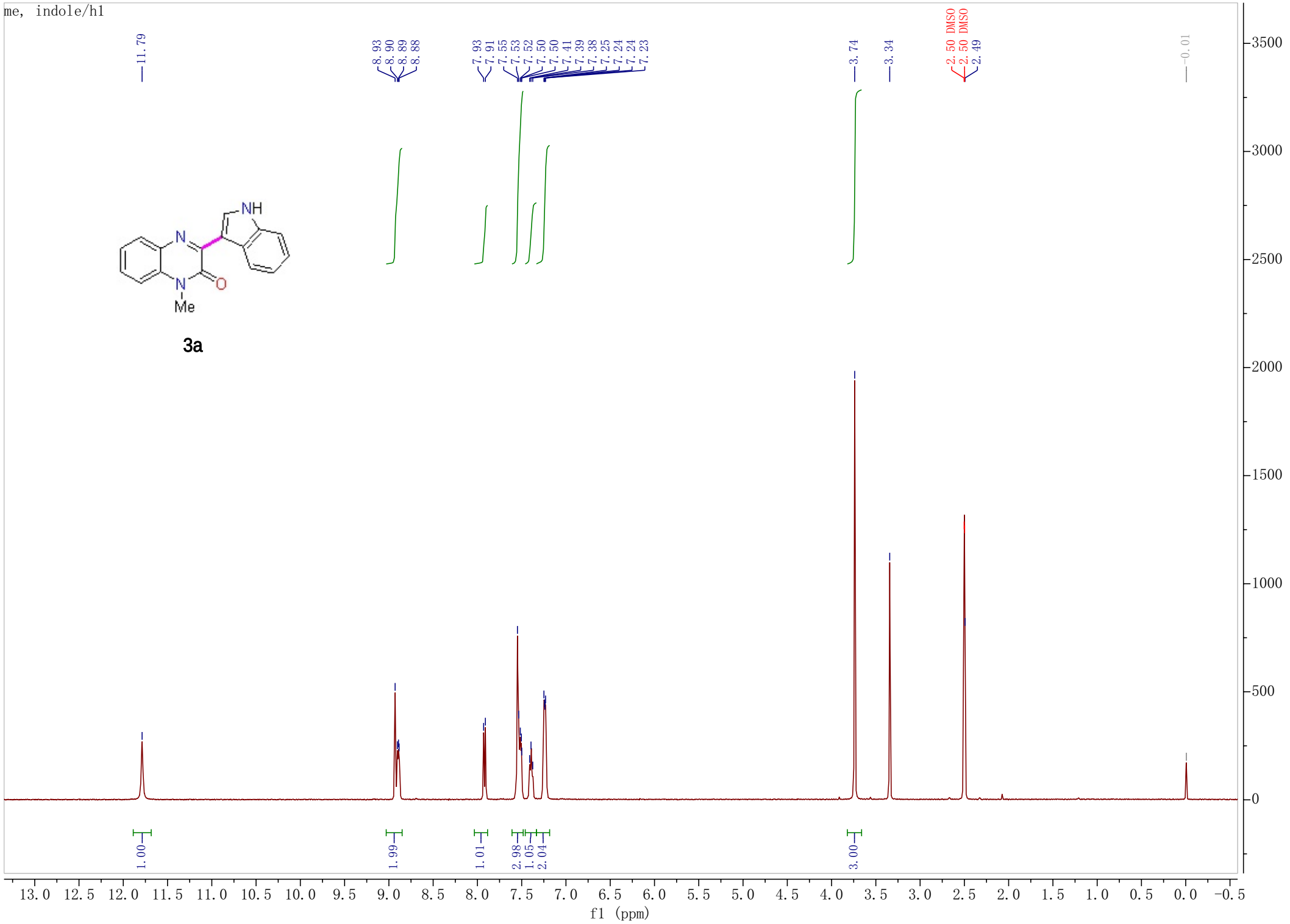

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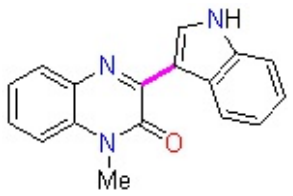

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me, indole/h1
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8.89
8.88
7.93
7.91
7.55
7.53
7.52
7.50
7.50
7.41
7.39
7.38
7.25
7.24
7.24
7.23
3.74
3.34
2.50 DMSO
2.50 DMSO
2.49
-0.01
NH
N
N
O
Me
3a
1.00
1.99
1.01
2.98
1.05
2.04
3.00
f1 (ppm)

me, indole/c

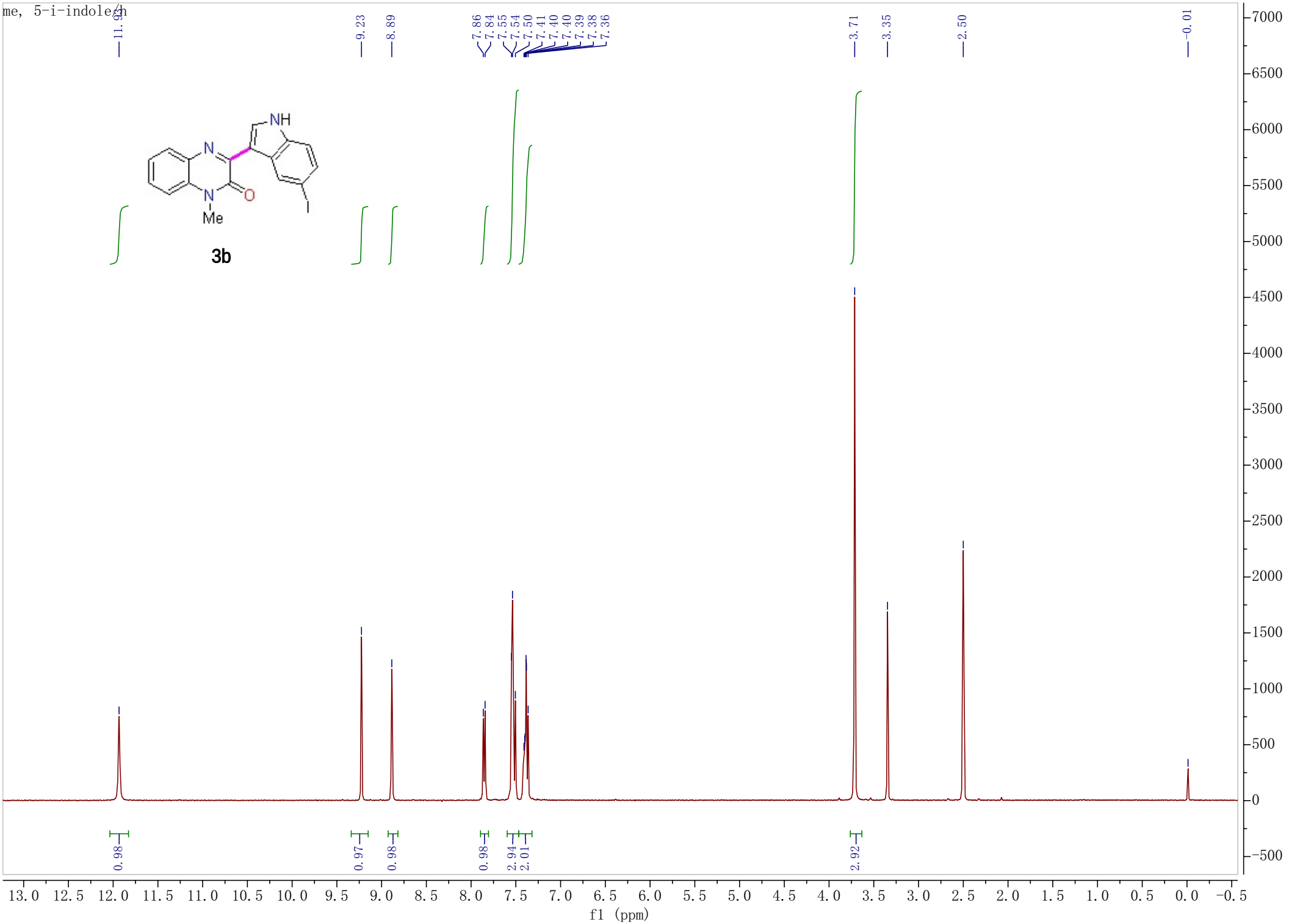


3a

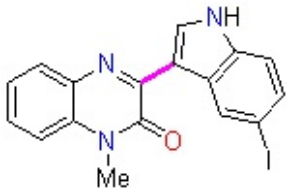
153.66
150.62
136.29
133.18
132.96
131.49
128.36
128.25
126.31
123.42
123.02
122.53
120.98
114.42
111.88
111.41
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.09

f1 (ppm)

me, 5-i-indole/h



me, 5-i-indole/c

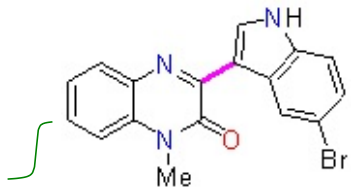


3b

153.54
150.22
135.39
133.80
132.72
131.55
131.26
130.51
128.75
128.54
128.34
123.53
114.50
114.36
110.57
85.43
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.10

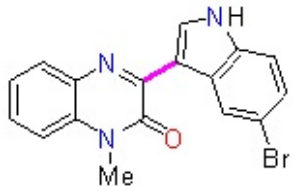
f1 (ppm)

me, 5-br-indole/h 2



3c

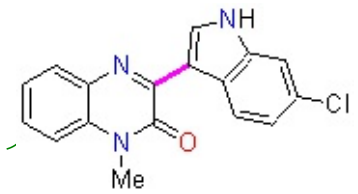
me, 5-br-indole/c 2



3c

f1 (ppm)

me,6-cl/3 h



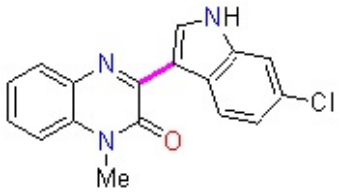
3d

11.86
8.92
8.85
7.89
7.55
7.52
7.37
7.23
3.71
3.36
2.50
-0.01

0.99
0.99
0.95
1.06
2.88
1.11
1.08
2.98

f1 (ppm)

me,6-cl/3 c



3d

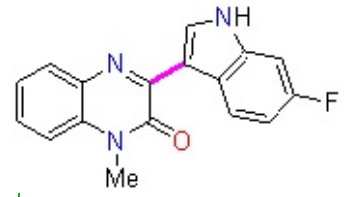
153.53
150.23
136.80
133.96
132.78
131.58
128.52
128.45
127.09
125.06
124.26
123.43
121.11
114.44
111.58
111.45
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.08

11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

me,6-f/2 h



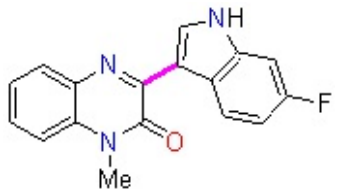
3e

11.81
8.90
8.88
8.86
8.84
7.90
7.88
7.52
7.51
7.51
7.37
7.31
7.28
7.10
7.07
7.05
3.71
3.70
3.36
2.50 DMSO
0.02

1.07
2.11
1.00
1.99
1.09
1.06
1.04
3.30

f1 (ppm)

me,6-f/2 c



3e

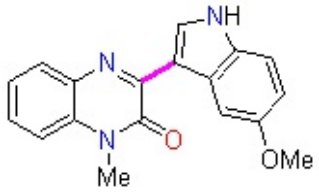
160.43
158.08
153.55
150.30
136.46
136.34
133.74
133.71
132.82
131.58
128.43
128.42
124.18
124.09
123.42
123.01
114.43
111.45
109.19
108.96
98.18
97.93
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.08

17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

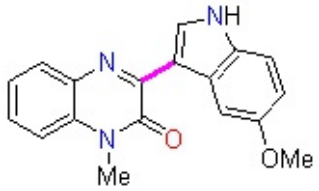
me, 5-ome-indole/h 3



3f

f1 (ppm)

me, 5-ome-indole/c 3



3f

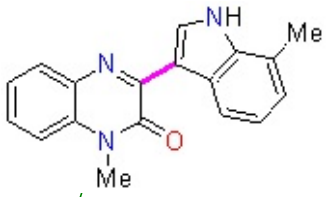
154.87
153.67
150.68
133.52
132.94
131.42
131.17
128.31
128.14
126.99
123.45
114.44
112.48
112.08
111.13
105.06
55.24
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.09

11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

me, 7-me-indole/h



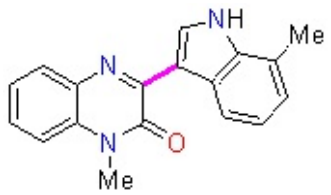
3g

11.78
8.92
8.74
8.72
7.91
7.90
7.53
7.52
7.52
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.16
7.14
7.12
7.05
7.03
3.73
3.35
2.53
2.50
-0.01

1.02
1.04
1.03
1.03
1.99
1.05
1.04
1.03
3.06
3.00

f1 (ppm)

me, 7-me-indole/c

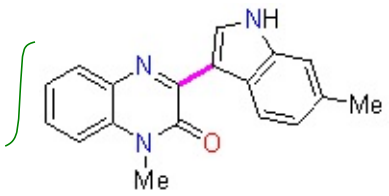


3g

153.70
150.61
135.71
132.96
132.86
131.47
128.36
128.23
126.08
123.41
123.17
121.19
120.93
120.65
114.41
111.81
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.08
16.76

f1 (ppm)

me,6-me/1 h



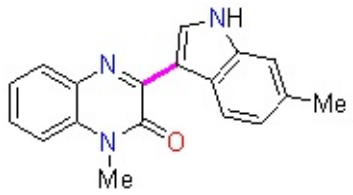
3h

11.65
8.85
8.85
8.75
8.73
7.91
7.89
7.53
7.52
7.49
7.40
7.39
7.38
7.36
7.30
7.07
7.05
3.72
3.35 HDO
2.50 DMSO
2.44
2.07

1.06
1.00
1.01
1.01
1.15
0.87
1.08
1.00
1.01
2.90
2.90

f1 (ppm)

me,6-me/1 c



3h

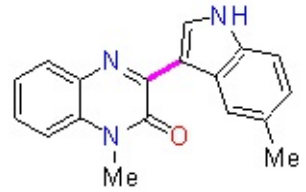
153.64
150.60
136.71
132.99
132.73
131.68
131.46
128.32
128.15
124.18
123.39
122.72
122.63
114.40
111.70
111.40
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.07
21.36

25000
20000
15000
10000
5000
0

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

f1 (ppm)

me, 5-me/5h



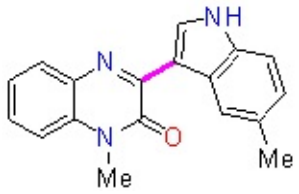
3i

11.67
8.89
8.89
8.88
8.71
7.94
7.92
7.55
7.54
7.51
7.40
7.39
7.08
7.06
3.73
3.34
2.50
0.00
0.00
0.00

1.02
0.99
0.98
1.00
2.03
2.02
1.01
2.94

f1 (ppm)

me,5-me.5.fid

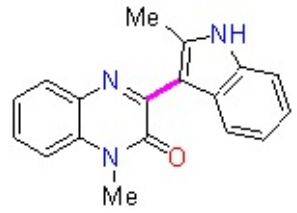


3i

153.67
150.67
134.60
133.22
132.99
131.43
129.63
128.35
128.12
126.57
123.97
123.38
122.80
114.40
111.51
111.02
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
29.06
21.66

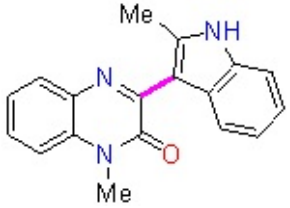
f1 (ppm)

me, 2-me/2h



3j

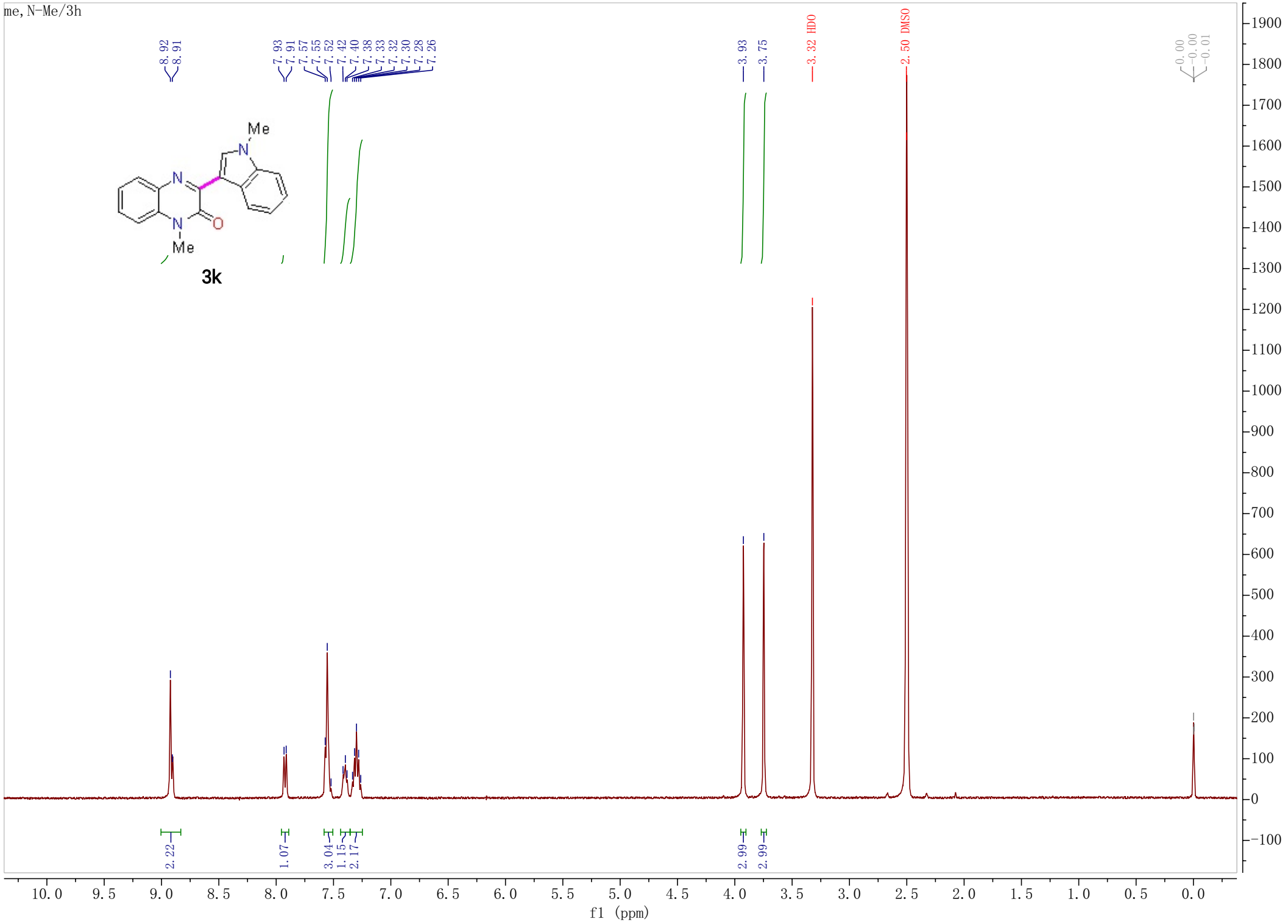
me,2-me.2.fid



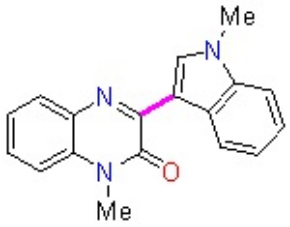
3j

154.01
153.14
139.29
135.08
132.81
132.53
129.02
128.65
127.96
123.30
120.83
120.80
119.49
114.42
110.59
109.48
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO
29.28
14.24
14.09

f1 (ppm)


me, N-Me/3h
8.92
8.91
7.93
7.91
7.57
7.55
7.52
7.42
7.40
7.38
7.33
7.32
7.30
7.28
7.26
3.93
3.75
3.32 HDO
2.50 DMSO
0.00
-0.00
-0.01
Me
N
N
O
Me
3k
2.22
1.07
3.04
1.15
2.17
2.99
2.99
f1 (ppm)

me,N-Me.3.fid

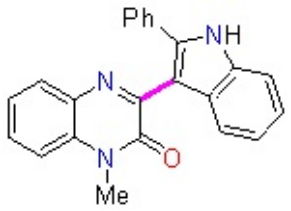


3k

153.60
150.32
136.98
136.87
132.97
131.49
128.37
128.31
126.78
123.48
123.14
122.63
121.31
114.48
110.36
110.25
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
33.07
29.11

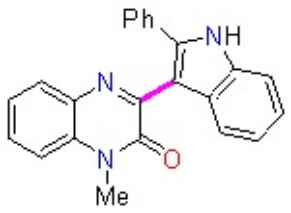
f1 (ppm)

me, 2-ph.2.fid



3l

me, 2-ph/c

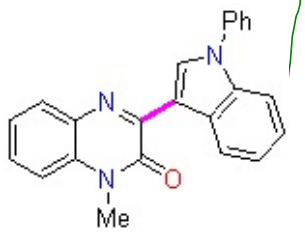


3l

153.72
153.56
139.19
135.96
133.14
133.05
132.71
129.74
129.02
128.57
128.40
127.86
127.81
123.35
122.08
120.33
119.99
114.61
111.45
109.13
59.78
40.15
39.94
39.73
39.52
39.31
39.10
38.89
29.28
20.79
14.10

f1 (ppm)

me, 1-ph.1.fid



3m

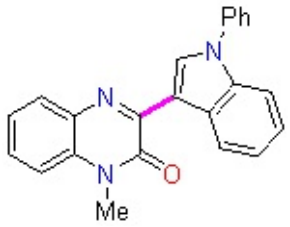
9.09 9.04 9.02 8.00 7.99 7.71 7.69 7.68 7.66 7.64 7.60 7.59 7.54 7.52 7.50 7.45 7.44 7.44 7.43 7.40 7.38 7.36 7.35 7.33 3.76 3.34 HDO 2.50 DMSO

0.96 0.98 0.99 7.02 1.14 2.17 3.14

f1 (ppm)

me, 1-ph/1c

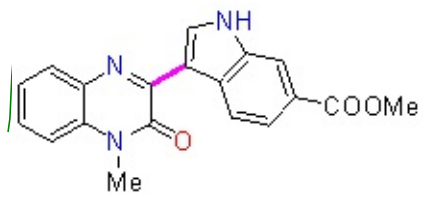
153.68
149.99
138.26
135.79
134.97
132.84
131.72
130.14
129.01
128.76
127.67
127.40
124.52
123.76
123.65
122.25
114.66
112.78
110.74
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.24



3m

f1 (ppm)

me, 6-coome/4h



3n

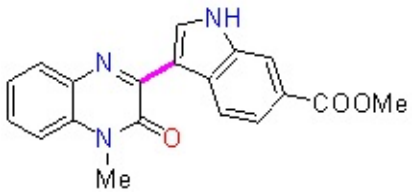
12.10
9.09
8.95
8.93
8.15
7.95
7.93
7.84
7.82
7.56
7.41
7.40
3.89
3.74 HDO

0.89
1.00
1.03
1.00
1.03
1.03
1.97
0.99
2.95
3.10

f1 (ppm)

me,6-coome.4.fid

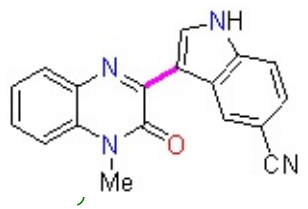
166.97
153.55
150.16
135.99
135.65
132.76
131.60
129.88
128.59
128.52
123.43
122.68
121.46
114.43
113.64
111.67
51.93
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.08



3n

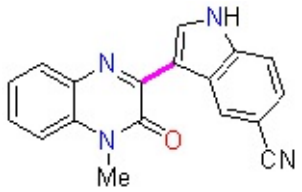
f1 (ppm)

me, 5-cn-indole/h 4



3o

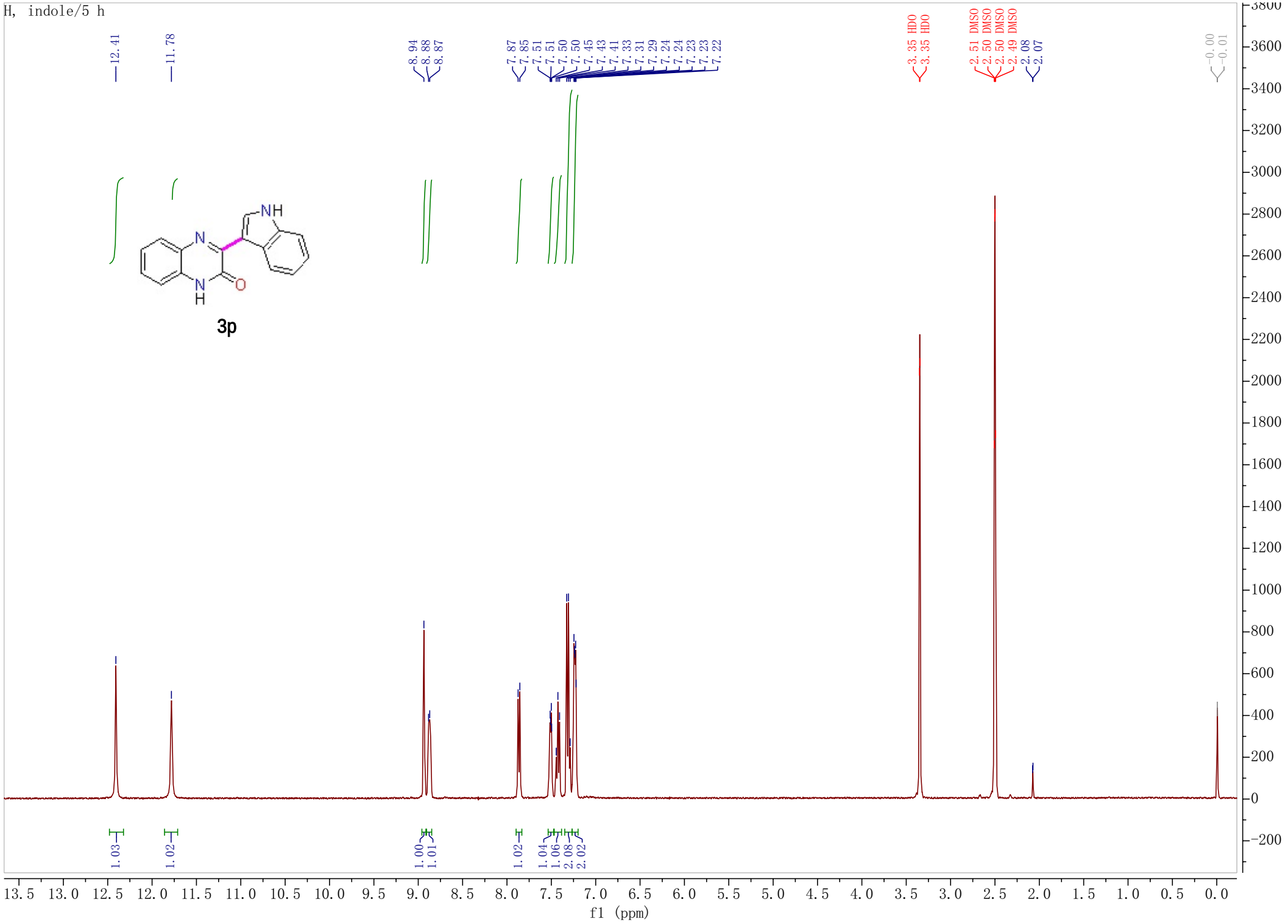
me, 5-cn-indole/c 4



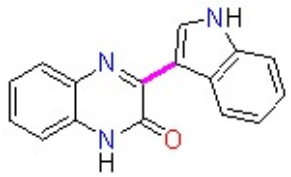
3o

153.44
149.85
138.14
135.00
132.62
131.64
128.91
128.76
127.98
125.95
125.39
123.52
120.73
114.48
113.31
111.77
103.06
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
29.11

f1 (ppm)


H, indole/5 h
12.41
11.78
8.94
8.88
8.87
7.87
7.85
7.51
7.51
7.50
7.50
7.45
7.43
7.41
7.33
7.31
7.29
7.24
7.24
7.23
7.23
7.22
3.35 HDO
3.35 HDO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.49 DMSO
2.08
2.07
0.00
-0.01
NH
N
N
H
O
3p
1.03
1.02
1.00
1.01
1.02
1.04
1.06
2.08
2.02
f1 (ppm)

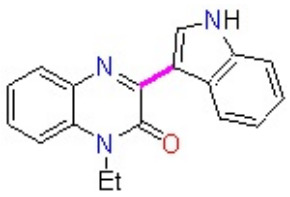
H, indole/5 c



3p

f1 (ppm)

Et, indole/1 h

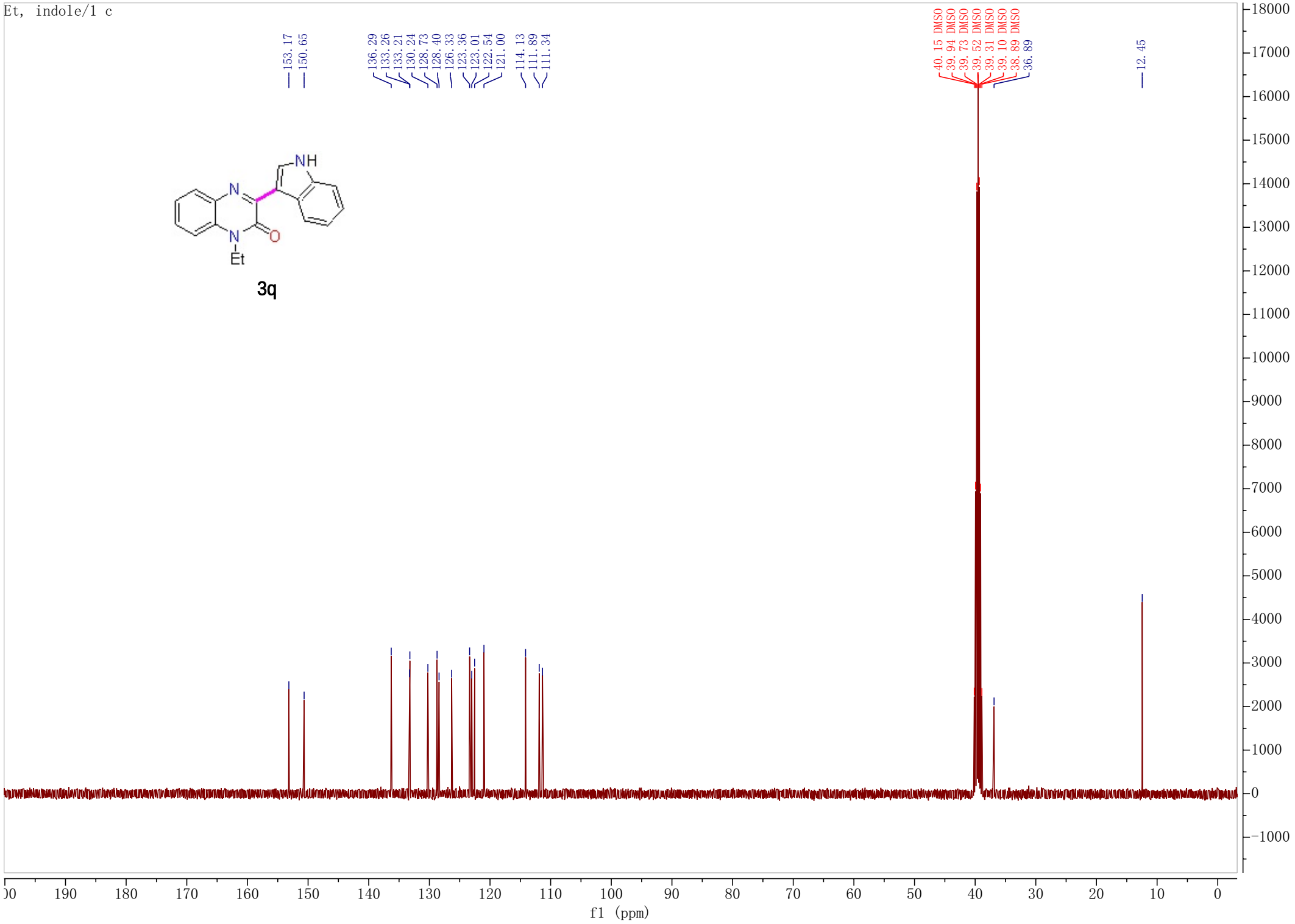


3q

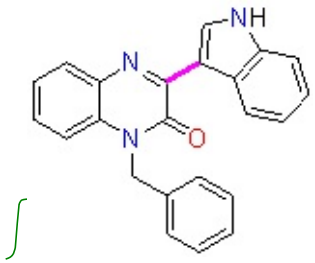
11.80
8.94
8.90
8.89
7.94
7.92
7.61
7.59
7.55
7.53
7.51
7.40
7.38
7.37
7.25
7.24
7.23
4.41
4.39
4.37
4.36
4.35
3.36 HDO
2.50 DMSO
1.32
1.30
1.29
0.01
-0.02

0.97
1.98
1.00
3.00
1.06
1.99
1.98
3.14

f1 (ppm)


Et, indole/1 c
153.17
150.65
136.29
133.26
133.21
130.24
128.73
128.40
126.33
123.36
123.01
122.54
121.00
114.13
111.89
111.34
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
36.89
12.45
NH
N
N
O
Et
3q
f1 (ppm)

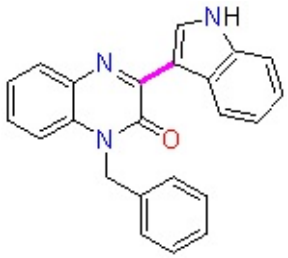
benzyl, indole 3.fid



3r

f1 (ppm)

benzyl, indole.3.fid



3r

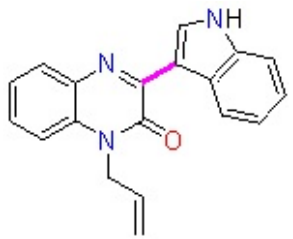
153.84
150.77
136.33
136.19
133.39
133.29
130.61
128.73
128.64
128.27
127.26
126.76
126.33
123.62
123.02
122.62
121.10
114.80
111.94
111.40

44.98
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.90 DMSO

0.11

f1 (ppm)

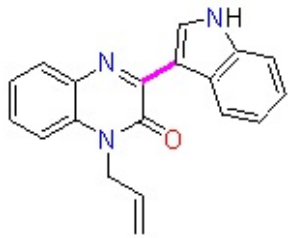
allyl, indole/2 h



3s

f1 (ppm)

allyl, indole/2 c

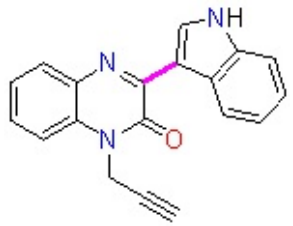


3s

153.41
150.75
136.40
133.36
133.26
131.94
130.63
128.69
128.42
126.39
123.69
123.10
122.75
121.21
117.06
114.90
112.05
111.45
44.05
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO

f1 (ppm)

propargyl, indole/4 h



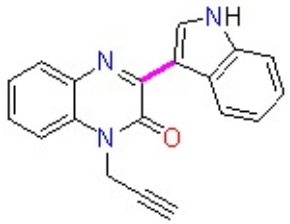
3t

11.85
8.91
8.89
8.87
7.96
7.94
7.62
7.60
7.58
7.53
7.51
7.45
7.43
7.41
7.26
7.25
7.24
5.21
3.35 HDO
2.50 DMSO
-0.01

1.02
2.06
1.04
2.05
0.91
1.08
2.04
1.93
1.27

f1 (ppm)

propargyl, indole/4 c



3t

152.78
150.47
136.32
133.34
133.19
129.84
128.60
128.37
126.22
123.92
122.97
122.67
121.14
114.69
111.96
111.20
78.37
75.07
40.15 DMSO
39.94 DMSO
39.73 DMSO
39.52 DMSO
39.31 DMSO
39.10 DMSO
38.89 DMSO
31.34

f1 (ppm)