Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Direct Alkylation of Quinoxalinones with Electron-deficient Alkenes Enabled by a Paired Electrolysis

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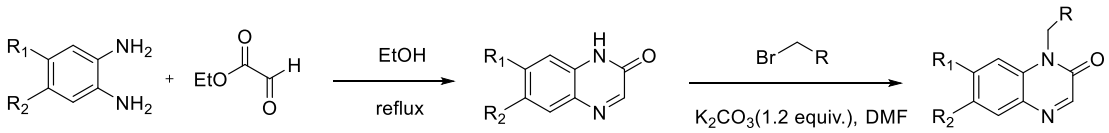
1. General information

Unless indicated otherwise, all the reagents were purchased from commercial supplies unless otherwise stated. All the solvents were used as received. Thin-layer chromatography (TLC) was performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness and all compounds were visualized with a UV light at 254 nm. Flash column chromatography was performed using silica gel (200-300 mesh). NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400 or 600 MHz (^{1}H NMR) and 100 or 150 MHz (^{13}C NMR). HRMS were recorded on a Thermo Fisher Q Exactive mass spectrometer with an Orbitrap detector (Ion source: APCI). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H: residual internal $CHCl_3$ (δ 7.26 ppm); ^{13}C: internal $CDCl_3$ (δ 77.2 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 the starting materials

The alkenes were commercially available, and quinoxalines were synthesized according to the literatures [1-4].



To ethanol (20 ml) suspension solution of *o*-arylenediamine (5 mmol) was added ethyl 2-oxoacetate (1.1 equiv). The reaction mixture was heated to reflux, and then stirred at this temperature for 16 h. After the reaction was completed (as monitored by TLC), the precipitate was filtered and washed with ethanol (3*5 ml), and finally dried to give quinoxalinone.

To a stirred solution of 2-quinoxalinone (5 mmol) in DMF (20 mL) was added the corresponding halide (1.6 equiv) and K_2CO_3 (1.2 equiv). The resulting mixture was stirred at room temperature overnight. Then resulting mixture was transferred to a separatory funnel. Water (60 mL) were added to the reaction mixture, and the aqueous layer was extracted twice with ethyl acetate (30 mL). The combined organic layers were

washed with brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain N-protected quinoxalinone.

3. General procedure for the electrolysis

An undivided cell was equipped with a graphite anode (1.0 × 1.0 cm^2) and a zinc cathode (1.0 × 1.0 cm^2). To the cell was added **1a** (0.3 mmol, 48 mg), **2a** (3 mmol, 10 equiv, 160 mg), Et_4NCl (0.3 mmol, 1 equiv, 50 mg), CH_3COOH (20 μL), and MeCN (4 mL) sequentially. The resulting mixture was electrolyzed under constant current conditions (5 mA/cm^2) at room temperature for 8h. After the reaction, the solvent was removed by distillation. The product was then extracted with DCM (3×15 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired pure product **3** as a white solid (47.9 mg, 75% yield).

4. CV experiments

The CV experiments of the related compounds were carried out in an undivided cell using glassy carbon as the working electrode, Pt wire and Ag/AgCl as the counter and reference electrodes, respectively. Before the experiments, the mixture of the related compounds in anhydrous CH_3CN was degassed using a N_2 balloon for 10 min. Then, the N_2 balloon was removed, and the CV experiment was conducted at a 100 mV/s scan rate.

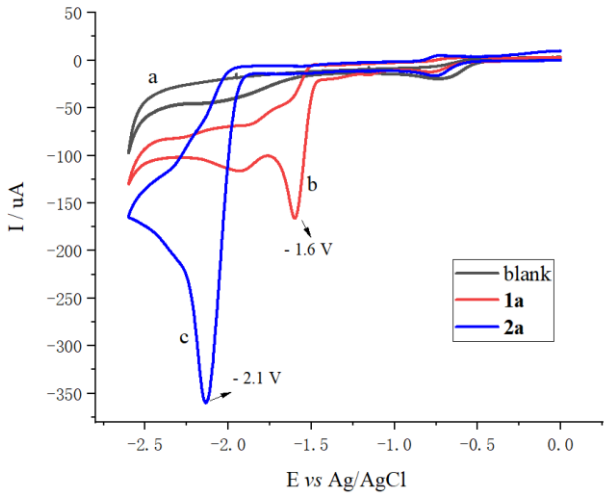
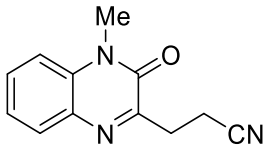


Figure S1. CV of related compounds in CH_3CN with glassy carbon and Pt wire as the working and counter electrodes, and Ag/AgCl as the reference electrode, 100 mV/s. a) blank solution, 0.1 M Et_4NCl in CH_3CN; b) **1a** (5 mM) in blank solution; c) **2a** (5 mM) in blank solution.

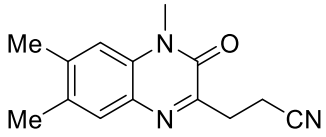
5. Characterization data of the products

3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (3)



Following the general procedure, the title compound was obtained as a white solid, m. p. 157-158 °C, 47.9 mg, 75% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.88 – 7.86 (m, 1H), 7.65 – 7.50 (m, 1H), 7.39 – 7.36 (m, 1H), 7.34 – 7.32 (m, 1H), 3.71 (d, J = 2.2 Hz, 3H), 3.30 (td, J = 7.2, 2.2 Hz, 2H), 2.93 (td, J = 7.2, 1.7 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.9, 154.5, 133.1, 132.4, 130.5, 130.1, 123.9, 119.6, 113.8, 29.4, 29.1, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{12}H_{12}N_3O^+$ 214.0975, Found 214.0973.

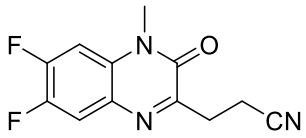
3-(4,6,7-trimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (4)



Following the general procedure, the title compound was obtained as a white solid, m.

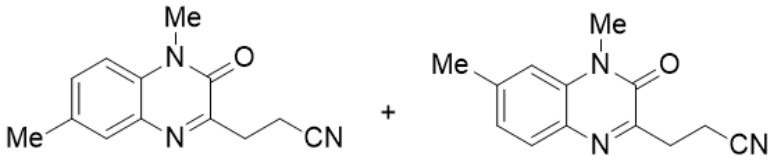
p. 193-194 ºC, 51.4 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.10 (s, 1H), 3.69 (s, 3H), 3.28 (t, *J* = 7.2 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.61, 154.59, 140.4, 132.9, 131.2, 131.0, 130.2, 119.7, 114.4, 29.4, 29.1, 20.7, 19.2, 13.8. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{14}H_{16}N_3O^+$ 242.1288, Found 242.1287.

3-(6,7-difluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (5)



Following the general procedure, the title compound was obtained as a white solid, m. p. 173-174 ºC, 47.8 mg, 64% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 10.1, 8.1 Hz, 2H), 7.16 (dd, *J* = 11.2, 7.0 Hz, 2H), 3.69 (s, 6H), 3.38 – 3.22 (m, 4H), 2.92 (t, *J* = 7.0 Hz, 4H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 156.7 (d, *J* = 3.6 Hz), 154.2, 151.7 (dd, *J* = 254.1, 14.3 Hz), 146.9 (dd, *J* = 247.8, 14.0 Hz), 130.4 (dd, *J* = 9.3, 2.9 Hz), 128.7 (dd, *J* = 9.3, 2.9 Hz), 119.4, 117.9 (dd, *J* = 18.2, 2.5 Hz), 102.6 (d, *J* = 23.1 Hz), 29.7, 29.4, 13.6. ^{19}F NMR (565 MHz, Chloroform-*d*) δ -130.10 (ddd, *J* = 22.3, 11.1, 8.1 Hz), -141.49 (ddd, *J* = 22.3, 10.1, 7.1 Hz). HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{12}H_{10}F_2N_3O^+$ 250.0786, Found 250.0784.

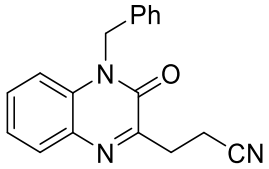
3-(4,6-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile and 3-(4,7-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (6 and 6')



Following the general procedure, the title compound was obtained as a white solid, m. p. 124-127 ºC, 50.4 mg, 74% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.69 (m, 2H), 7.41 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.24 (d, *J* = 8.5 Hz,

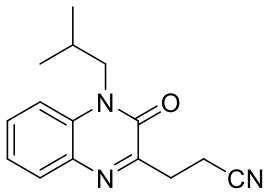
2H), 7.22 – 7.19 (m, 1H), 7.14 (s, 1H), 3.72 (s, 9H), 3.31 (q, *J* = 7.1 Hz, 6H), 2.94 (td, *J* = 7.2, 0.7 Hz, 6H), 2.55 (s, 3H), 2.48 (s, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.9, 154.7, 154.7, 154.5, 141.4, 133.9, 133.2, 132.5, 131.7, 131.1, 130.8, 130.1, 129.9, 125.3, 119.7, 114.0, 113.6, 29.5, 29.5, 29.2, 29.1, 22.2, 20.8, 13.8, 13.8. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{13}H_{14}N_3O^+$ 228.1131, Found 228.1130.

3-(4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (7)



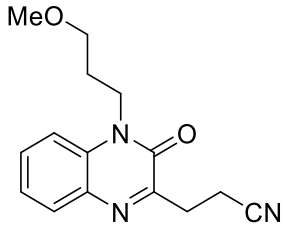
Following the general procedure, the title compound was obtained as a white solid, m. p. 149-150 ºC, 63.4 mg, 73% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.96 – 7.81 (m, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.30 (dd, *J* = 9.3, 4.9 Hz, 3H), 7.26 (d, *J* = 7.5 Hz, 2H), 5.54 (d, *J* = 3.7 Hz, 2H), 3.39 (dd, *J* = 7.1, 4.2 Hz, 2H), 3.00 (dq, *J* = 7.6, 4.7 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 156.1, 154.7, 135.1, 132.8, 132.6, 130.5, 130.4, 129.1, 128.0, 127.0, 124.1, 119.7, 114.7, 46.1, 29.5, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{18}H_{16}N_3O^+$ 290.1288, Found 290.1285.

3-(4-isobutyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (8)



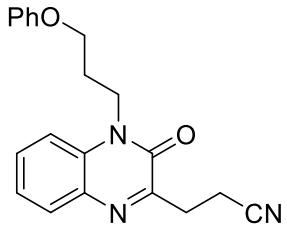
Following the general procedure, the title compound was obtained as a white solid, m. p. 146-147 ºC, 52.1 mg, 68% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.44 – 7.30 (m, 2H), 4.15 (d, *J* = 7.5 Hz, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.28 (dt, *J* = 13.8, 6.9 Hz, 1H), 1.02 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 156.0, 154.7, 132.7, 132.7, 130.4, 130.2, 123.7, 119.6, 114.2, 49.1, 29.5, 27.3, 20.3, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{18}N_3O^+$ 256.1444, Found 256.1442.

3-(4-(3-methoxypropyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (9)



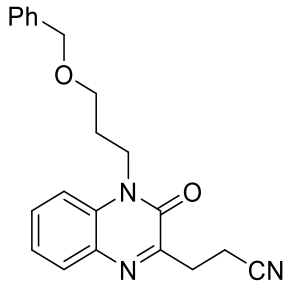
Following the general procedure, the title compound was obtained as a white solid, m. p. 80-81 °C, 51.3 mg, 63% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.88 (m, 1H), 7.60 – 7.56 (m, 1H), 7.50 – 7.47 (m, 1H), 7.42 – 7.31 (m, 1H), 4.46 – 4.30 (m, 2H), 3.50 (t, *J* = 5.7 Hz, 2H), 3.39 (s, 3H), 3.32 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.04 (dq, *J* = 7.5, 5.8 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.9, 154.4, 132.7, 132.6, 130.5, 130.3, 123.8, 119.7, 114.0, 69.8, 58.9, 40.1, 29.3, 27.7, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{18}N_3O_2^+$ 272.1394, Found 272.1390.

3-(3-oxo-4-(3-phenoxypropyl)-3,4-dihydroquinoxalin-2-yl)propanenitrile (10)



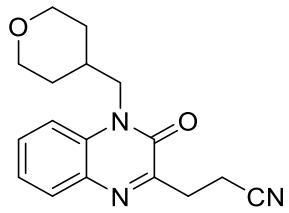
Following the general procedure, the title compound was obtained as a white solid, m. p. 96-97 °C, 60.9 mg, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.90 (m, 1H), 7.61 – 7.43 (m, 2H), 7.42 – 7.21 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.95 – 6.85 (m, 2H), 4.60 – 4.39 (m, 2H), 4.12 (t, *J* = 5.6 Hz, 2H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.38 – 2.19 (m, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 158.5, 155.9, 154.4, 132.7, 132.4, 130.5, 130.4, 129.6, 123.9, 121.2, 119.6, 114.5, 113.8, 65.1, 39.9, 29.3, 27.2, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{20}H_{20}N_3O_2^+$ 334.1550, Found 334.1548.

3-(4-(3-(benzyloxy)propyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (11)



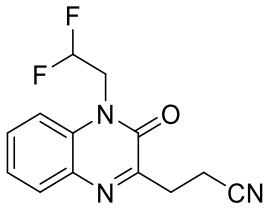
Following the general procedure, the title compound was obtained as a white solid, m. p. 118-119 ºC, 66.7 mg, 64% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.63 – 7.46 (m, 2H), 7.43 – 7.30 (m, 6H), 4.56 (s, 2H), 4.47 – 4.35 (m, 2H), 3.63 (t, *J* = 5.7 Hz, 2H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.10 (dq, *J* = 7.4, 5.7 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.9, 154.4, 138.3, 132.7, 132.6, 130.5, 130.3, 128.6, 127.8, 127.7, 123.8, 119.7, 114.0, 73.2, 67.6, 40.2, 29.3, 27.8, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{21}H_{22}N_3O_2^+$ 348.1707, Found 348.1704.

3-(3-oxo-4-((tetrahydro-2H-pyran-4-yl)methyl)-3,4-dihydroquinoxalin-2-yl)propanenitrile (12)



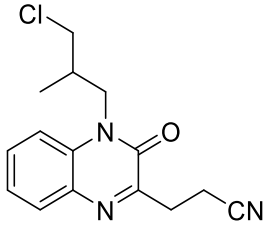
Following the general procedure, the title compound was obtained as a white solid, m. p. 157-158 ºC, 59.8 mg, 67% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.44 – 7.27 (m, 2H), 4.22 (d, *J* = 7.2 Hz, 2H), 3.99 (dt, *J* = 11.4, 3.3 Hz, 2H), 3.39 – 3.26 (m, 4H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.11 (m, 1H), 1.62 – 1.57 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 154.7, 132.74, 132.72, 130.6, 130.4, 123.9, 119.6, 114.0, 67.6, 47.6, 34.2, 30.9, 29.4, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{17}H_{20}N_3O_2^+$ 298.1550, Found 298.1549.

3-(4-(2,2-difluoroethyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (13)



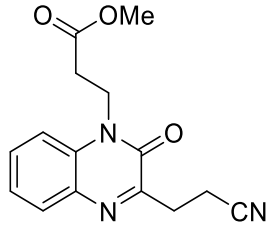
Following the general procedure, the title compound was obtained as a white solid, m. p. 115-116 ºC, 46.6 mg, 59% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.92 (m, 1H), 7.64 – 7.59 (m, 1H), 7.49 – 7.36 (m, 2H), 6.17 (tt, *J* = 55.6, 4.5 Hz, 1H), 4.66 (td, *J* = 13.1, 4.5 Hz, 2H), 3.33 (t, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -120.42. ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.6, 154.7, 132.8, 132.6, 130.8, 130.7, 124.6, 119.5, 113.9, 112.9 (t, *J* = 243 Hz), 44.6 (t, *J* = 29.1 Hz), 29.2, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{13}H_{12}F_2N_3O^+$ 264.0943, Found 264.0940.

3-(4-(3-chloro-2-methylpropyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (14)



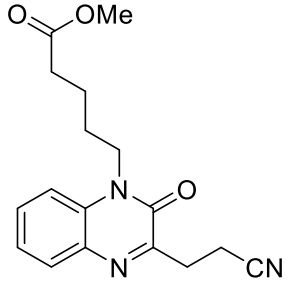
Following the general procedure, the title compound was obtained as a white solid, m. p. 109-110 ºC, 59.8 mg, 69% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.48 – 7.43 (m, 1H), 7.42 – 7.35 (m, 1H), 4.39 (dd, *J* = 13.9, 6.7 Hz, 1H), 4.31 (dd, *J* = 13.9, 7.6 Hz, 1H), 3.67 – 3.51 (m, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.62 – 2.47 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 154.9, 132.8, 132.6, 130.6, 124.1, 119.6, 114.0, 48.6, 45.6, 34.8, 29.4, 16.3, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{17}ClN_3O^+$ 290.1055, Found 290.1052.

methyl 3-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)propanoate (15)



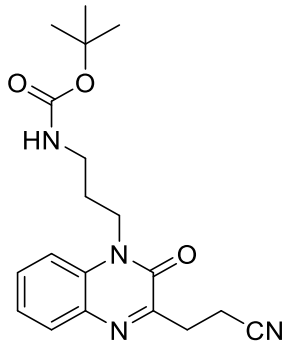
Following the general procedure, the title compound was obtained as a white solid, m. p. 115-116 ºC, 57.3 mg, 67% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.65 – 7.53 (m, 1H), 7.49 – 7.33 (m, 2H), 4.65 – 4.51 (m, 2H), 3.74 (s, 3H), 3.32 (t, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.81 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 171.2, 155.9, 154.2, 132.8, 132.1, 130.7, 130.6, 124.1, 119.6, 113.5, 52.2, 38.3, 31.7, 29.3, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{16}N_3O_3^+$ 286.1186, Found 286.1184.

methyl 5-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)pentanoate (16)



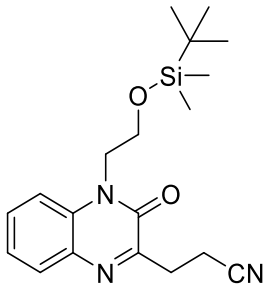
Following the general procedure, the title compound was obtained as a white solid, m. p. 90-91ºC, 65.8 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.44 – 7.30 (m, 2H), 4.35 – 4.15 (m, 2H), 3.67 (s, 3H), 3.30 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.46 – 2.31 (m, 2H), 1.87 – 1.74 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.6, 155.9, 154.2, 132.7, 132.2, 130.5, 130.4, 123.8, 119.6, 113.7, 51.7, 41.9, 33.5, 29.3, 26.7, 22.3, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{18}N_3O_2^+$ 272.1394, Found 272.1390.

tert-butyl (3-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)propyl)carbamate (17)



Following the general procedure, the title compound was obtained as a white solid, m. p. 125-126 ºC, 73.7 mg, 69% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.67 – 7.50 (m, 1H), 7.44 – 7.31 (m, 2H), 5.34 (br, 1H), 4.36 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 3.17 (q, *J* = 6.3 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.00 – 1.97 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.2, 155.7, 154.7, 132.9, 132.1, 130.7, 130.6, 124.1, 119.6, 113.8, 79.4, 39.8, 37.4, 29.4, 28.5, 27.8, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{19}H_{25}N_4O_3^+$ 357.1921, Found 357.1917.

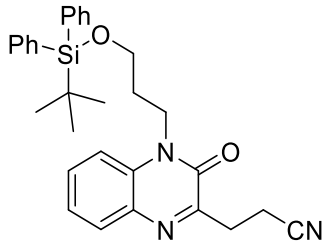
3-(4-(2-((tert-butyldimethylsilyl)oxy)ethyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (18)



Following the general procedure, the title compound was obtained as a white solid, m. p. 87-88 ºC, 75.1 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.85 (m, 1H), 7.63 – 7.48 (m, 2H), 7.37 – 7.29 (m, 1H), 4.43 (t, *J* = 5.8 Hz, 2H), 4.00 (t, *J* = 5.8 Hz, 2H), 3.31 (t, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 0.79 (s, 9H), -0.08 (s, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.7, 154.5, 133.3, 132.6, 130.2, 130.0, 123.8, 119.6, 115.1, 60.4, 44.8, 29.3, 25.8, 18.2, 13. 7, -5.6. HRMS (APCI) m/z: $[M + H]^+$

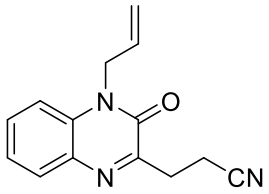
calculated for $C_{19}H_{28}N_3O_2Si^+$ 358.1945, Found 358.1944.

3-(4-(3-((tert-butyldiphenylsilyl)oxy)propyl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (19)



Following the general procedure, the title compound was obtained as a white solid, m. p. 114-115 ºC, 95.1 mg, 64% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.76 – 7.66 (m, 4H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.50 – 7.36 (m, 7H), 4.56 – 4.38 (m, 2H), 3.85 (t, *J* = 5.6 Hz, 2H), 3.32 (t, *J* = 7.2 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.04 – 2.00 (m, 2H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.9, 154.4, 135.7, 133.4, 132.8, 132.6, 130.5, 130.4, 130.0, 127.9, 123.8, 119.7, 114.1, 61.4, 39.9, 30.2, 29.4, 27.0, 19.4, 13.7. HRMS (APCI) m/z: [M + H]$^+$ calculated for $C_{30}H_{34}N_3O_2Si^+$ 496.2415, Found 496.2413.

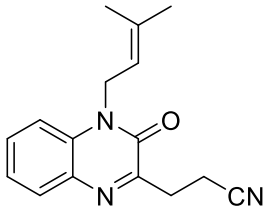
3-(4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (20)



Following the general procedure, the title compound was obtained as a white solid, m. p. 135-136 ºC, 48.8 mg, 68% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57 – 7.54 (m, 1H), 7.39 – 7.37 (m, 1H), 7.33 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.03 – 5.87 (m, 1H), 5.34 – 5.26 (m, 1H), 5.22 – 5.18 (m, 1H), 4.95 – 4.93 (m, 2H), 3.34 (t, *J* = 7.1 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 156.1, 154.2, 132.7, 132.5, 130.53, 130.45, 130.3, 124.0, 119.6, 118.4, 114.4, 44.7, 29.4, 13.7. HRMS (APCI) m/z: [M + H]$^+$ calculated for $C_{14}H_{14}N_3O^+$ 240.1131, Found

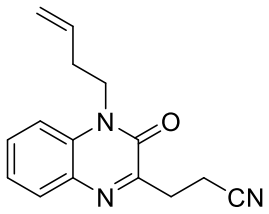
240.1129.

3-(4-(3-methylbut-2-en-1-yl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (21)



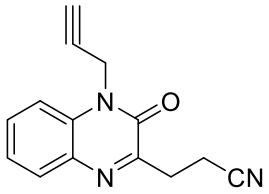
Following the general procedure, the title compound was obtained as a white solid, m. p. 115-116 ºC, 56.1 mg, 70% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.43 – 7.28 (m, 2H), 5.19 – 5.15 (m, 1H), 4.91 (d, *J* = 6.4 Hz, 2H), 3.32 (t, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.93 (d, *J* = 1.4 Hz, 3H), 1.76 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 154.2, 137.8, 132.8, 132.5, 130.4, 130.3, 123.8, 119.7, 117.8, 114.3, 40.9, 29.5, 25.8, 18.5, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{16}H_{18}N_3O^+$ 268.1444, Found 268.1442.

3-(4-(but-3-en-1-yl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (22)



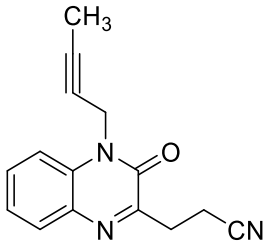
Following the general procedure, the title compound was obtained as a white solid, m. p. 97-98 ºC, 55.1 mg, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.42 – 7.28 (m, 2H), 5.95 – 5.85 (m, 1H), 5.21 – 5.05 (m, 2H), 4.40 – 4.28 (m, 2H), 3.31 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.63 – 2.43 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.0, 154.2, 133.8, 132.7, 132.3, 130.49, 130.46, 123.8, 119.7, 117.9, 113.8, 41.7, 31.6, 29.4, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{16}N_3O^+$ 254.1288, Found 254.1286.

3-(3-oxo-4-(prop-2-yn-1-yl)-3,4-dihydroquinoxalin-2-yl)propanenitrile (23)



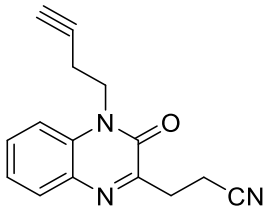
Following the general procedure, the title compound was obtained as a white solid, m. p. 139-140 °C, 50.6 mg, 71% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.90 (m, 1H), 7.65 – 7.61 (m, 1H), 7.52 – 7.49 (m, 1H), 7.44 – 7.40 (m, 1H), 5.08 (d, *J* = 2.6 Hz, 2H), 3.33 (t, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.33 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.9, 153.6, 132.7, 131.7, 130.6, 130.3, 124.4, 119.6, 114.3, 76.6, 73.6, 31.6, 29.4, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{14}H_{12}N_3O^+$ 238.0975, Found 238.0973.

3-(4-(but-2-yn-1-yl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (24)



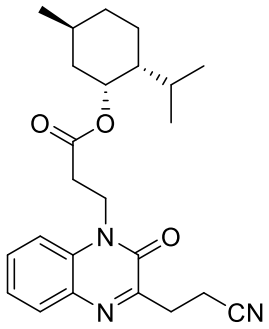
Following the general procedure, the title compound was obtained as a white solid, m. p. 109-110 °C, 54.3 mg, 72% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.53 – 7.51 (m, 1H), 7.43 – 7.39 (m, 1H), 5.01 (q, *J* = 2.4 Hz, 2H), 3.33 (t, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 1.80 (t, *J* = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.0, 153.7, 132.7, 131.9, 130.5, 130.2, 124.2, 119.6, 114.6, 81.5, 72.0, 32.2, 29.5, 13.7, 3.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}N_3O^+$ 252.1131, Found 252.1129.

3-(4-(but-3-yn-1-yl)-3-oxo-3,4-dihydroquinoxalin-2-yl)propanenitrile (25)



Following the general procedure, the title compound was obtained as a white solid, m. p. 105-106 °C, 55.1 mg, 73% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.50 – 7.32 (m, 2H), 4.47 (t, *J* = 7.6 Hz, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.70 (td, *J* = 7.5, 2.7 Hz, 2H), 2.05 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.9, 154.1, 132.7, 132.2, 130.55, 130.53, 124.1, 119.6, 113.7, 79.9, 71.2, 41.0, 29.3, 17.2, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{15}H_{14}N_3O^+$ 252.1131, Found 252.1129.

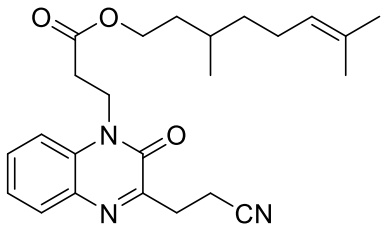
(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 3-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)propanoate (26)



Following the general procedure, the title compound was obtained as a white foam, 78.5 mg, 64% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.45 – 7.37 (m, 2H), 4.77 – 4.70 (m, 1H), 4.63 – 4.45 (m, 2H), 3.32 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.78 (td, *J* = 7.3, 2.4 Hz, 2H), 1.99 – 1.94 (m, 1H), 1.81 – 1.75 (m, 1H), 1.72 – 1.65 (m, 2H), 1.52 – 1.45 (m, 1H), 1.40 – 1.33 (m, 1H), 1.13 – 1.00 (m, 1H), 0.92 – 0.87 (m, 7H), 0.75 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.3, 155.7, 154.1, 132.7, 132.0, 130.6, 130.5, 124.0, 119.5, 113.5, 75.2, 46.9, 40.8, 38.3, 34.1, 32.0, 31.4, 29.2, 26.3, 23.4, 22.0, 20.7, 16.4, 13.5. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{24}H_{32}N_3O_3^+$ 410.2438, Found

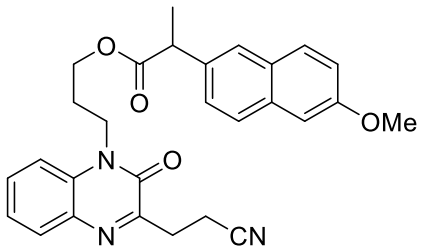
410.2435.

3,7-dimethyloct-6-en-1-yl 3-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)propanoate (27)



Following the general procedure, the title compound was obtained as a white foam, 79.8 mg, 65% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.49 – 7.33 (m, 2H), 5.16 – 5.04 (m, 1H), 4.63 – 4.50 (m, 2H), 4.18 – 4.13 (m, 1H), 3.31 (t, *J* = 7.1 Hz, 2H), 2.94 (t, *J* = 7.1 Hz, 2H), 2.86 – 2.70 (m, 2H), 2.02 – 1.94 (m, 2H), 1.69 (s, 3H), 1.68 – 1.63 (m, 1H), 1.61 (s, 3H), 1.57 – 1.48 (m, 1H), 1.48 – 1.38 (m, 1H), 1.37 – 1.30 (m, 1H), 1.22 – 1.16 (m, 1H), 0.92 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 155.9, 154.2, 132.8, 132.1, 131.5, 130.7, 130.6, 124.6, 124.1, 119.6, 113.5, 63.9, 38.3, 37.0, 35.4, 31.9, 29.6, 29.3, 25.8, 25.5, 19.5, 17.8, 13.6. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{24}H_{32}N_3O_3^+$ 410.2438, Found 410.2435.

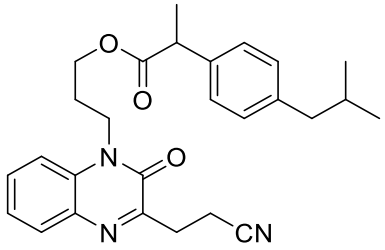
3-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)propyl 2-(6-methoxynaphthalen-2-yl)propanoate (28)



Following the general procedure, the title compound was obtained as a pale yellow foam, 85.9 mg, 61% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.77 – 7.65 (m, 3H), 7.46 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.31 – 7.22 (m, 1H), 7.22 – 7.08 (m, 3H), 6.88 (dd, *J* = 8.5, 1.2 Hz, 1H), 4.37 – 4.26 (m, 1H), 4.26 – 4.12 (m, 3H), 4.00 – 3.84 (m, 4H), 3.27 (t, *J* = 7.1 Hz, 2H), 2.91 (t, *J* = 7.1 Hz, 2H), 2.11 – 1.90 (m,

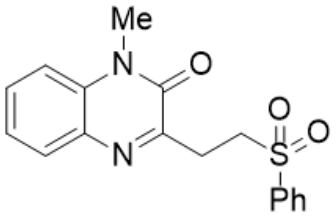
2H), 1.65 – 1.62 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.6, 157.9, 155.8, 154.2, 135.7, 133.9, 132.7, 132.2, 130.5, 130.4, 129.4, 129.1, 127.5, 126.3, 126.1, 123.8, 119.6, 119.3, 113.3, 105.8, 62.2, 55.5, 45.7, 39.6, 29.3, 26.6, 18.5, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{28}H_{28}N_3O_4^+$ 470.2074, Found 470.2072.

3-(3-(2-cyanoethyl)-2-oxoquinoxalin-1(2H)-yl)propyl 2-(4-isobutylphenyl)propanoate (29)



Following the general procedure, the title compound was obtained as a pale yellow foam, 82.8 mg, 62% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47 – 7.43 (m, 1H), 7.39 – 7.20 (m, 3H), 7.14 (d, *J* = 7.9 Hz, 2H), 7.08 – 7.00 (m, 1H), 4.26 – 4.17 (m, 4H), 3.77 (q, *J* = 7.2 Hz, 1H), 3.30 (t, *J* = 7.1 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.44 (d, *J* = 7.2 Hz, 2H), 2.09 – 2.02 (m, 2H), 1.86 – 1.76 (m, 1H), 1.55 (d, *J* = 7.2 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.6 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.6, 155.9, 154.2, 140.9, 137.8, 132.7, 132.3, 130.6, 130.5, 129.6, 127.3, 123.9, 119.6, 113.5, 62.1, 45.3, 45.1, 39.5, 30.3, 29.3, 26.6, 22.5, 22.4, 18.5, 13.7. HRMS (APCI) m/z: $[M + H]^+$ calculated for $C_{27}H_{32}N_3O_3^+$ 446.2438, Found 446.2437.

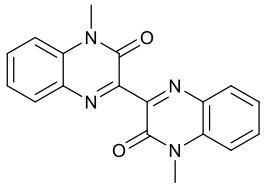
1-methyl-3-(2-(phenylsulfonyl)ethyl)quinoxalin-2(1H)-one (31)



Following the general procedure, the title compound was obtained as a white solid, m. p. 135-136 ºC, 61.1 mg, 62% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.01 – 7.96 (m, 2H), 7.78 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.59 – 7.52 (m, 3H), 7.37 – 7.35 (m, 1H), 7.33 – 7.27 (m, 1H), 3.78 (t, *J* = 6 Hz, 2H), 3.68 (s, 3H), 3.36 (t, *J* = 6 Hz, 2H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 156.2, 154.5, 139.1, 133.7, 133.2, 132.4,

130.4, 130.0, 129.4, 128.5, 123.9, 113.8, 52.7, 29.2, 27.7. HRMS (APCI) m/z: [M + H]$^+$ calculated for $C_{17}H_{17}N_2O_3S^+$ 329.0954, Found 329.0952.

4,4'-dimethyl-[2,2'-biquinoxaline]-3,3'(4H,4'H)-dione (32)



The title compound was obtained as a white solid, m. p. 241-242 °C, 4 mg, 8% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.67 (ddd, *J* = 8.6, 7.4, 1.5 Hz, 1H), 7.49 – 7.37 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 154.6, 154.2, 134.2, 133.1, 131.7, 131.2, 124.0, 113.9, 29.2. HRMS (APCI) m/z: [M + H]$^+$ calculated for $C_{18}H_{15}N_4O_2^+$ 319.1190, Found 319.1188.

6. Reference

[1] G.-Y. Dou, Y.-Y. Jiang, K. Xu and C.-C. Zeng, *Org. Chem. Front.* **2019**, *6*, 2392-2397.

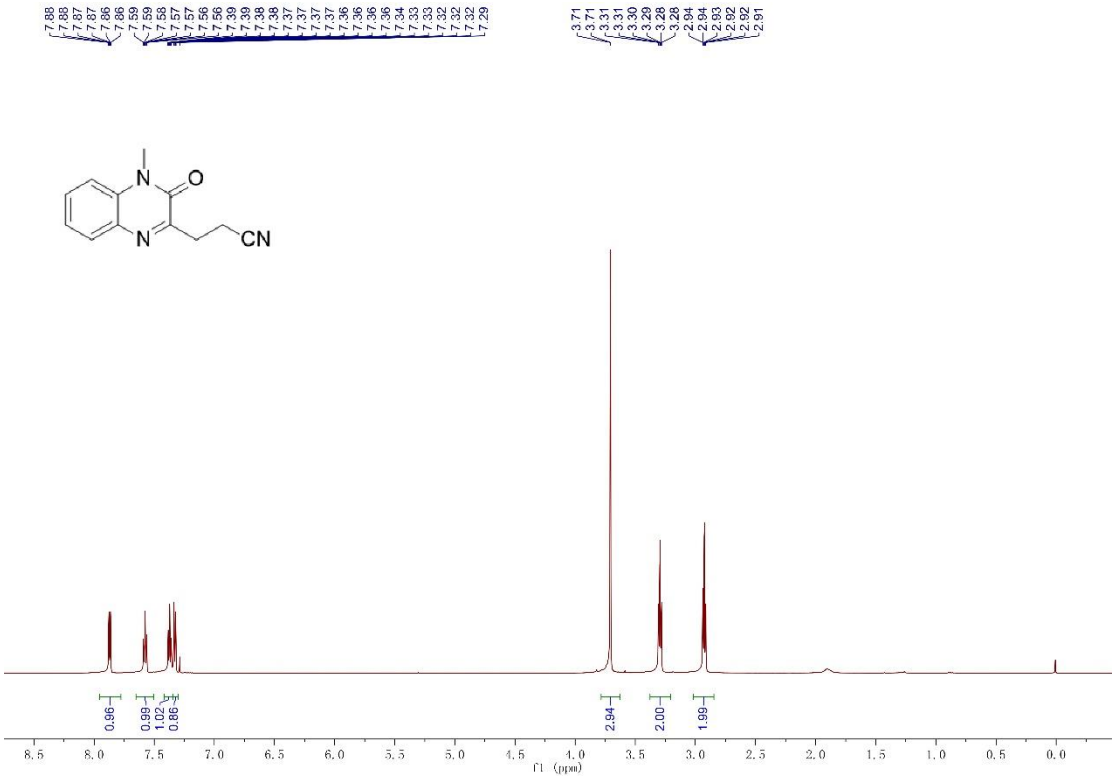
[2] A. Carrër, J.-D. Brion, S. Messaoudi and M. Alami, *Org. Lett.* **2013**, *15*, 5606-5609.

[3] V. V. Khade, A. Bhowmick, A. S. Thube and R. G. Bhat, *J. Org. Chem.* **2023**, *88*, 8010–8023.

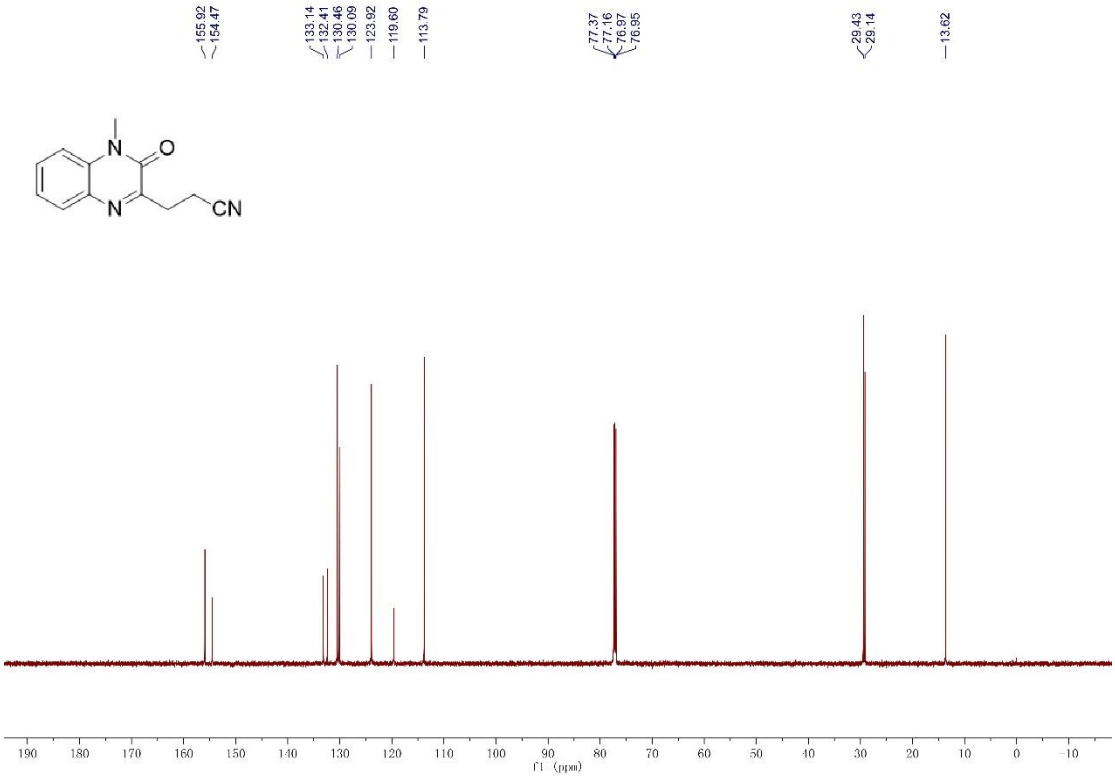
[4] P. Ghosh, N. Y. Kwon, S. Kim, S. Han, S. H. Lee, W. An, N. K. Mishra, S. B. Han, I. S. Kim, *Angew Chem. Int. Ed.* **2021**, *60*, 191-196.

7. NMR spectra

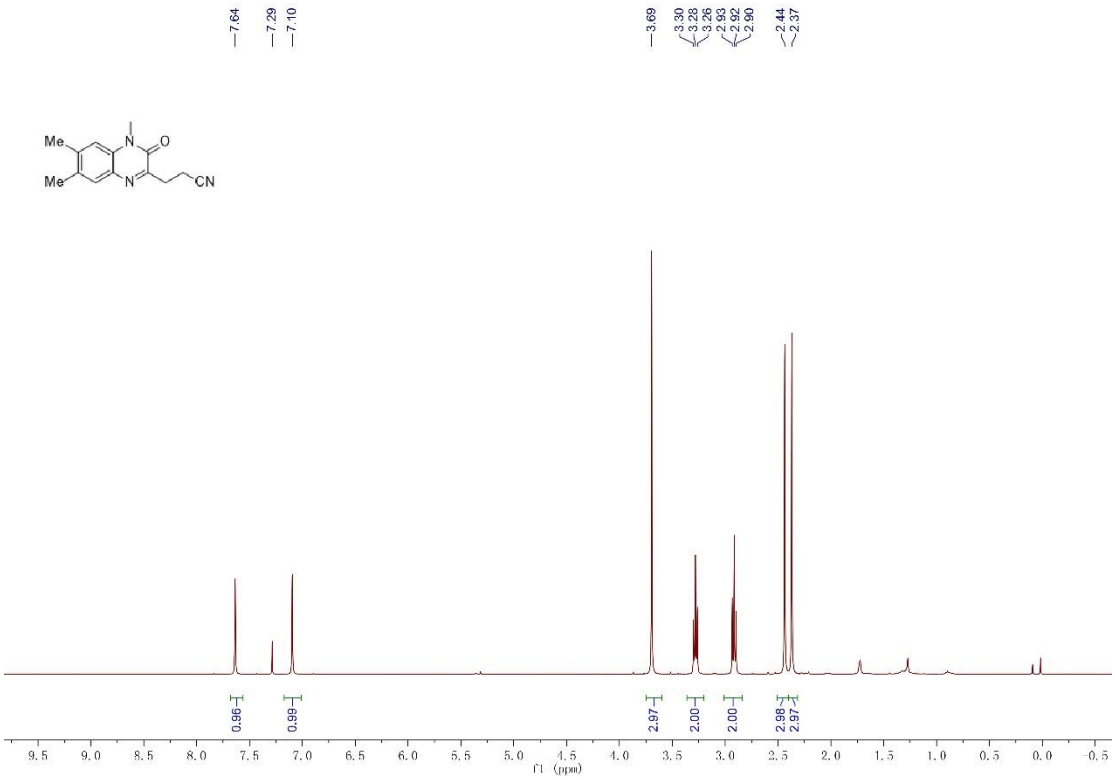
^{1}H NMR of **3**



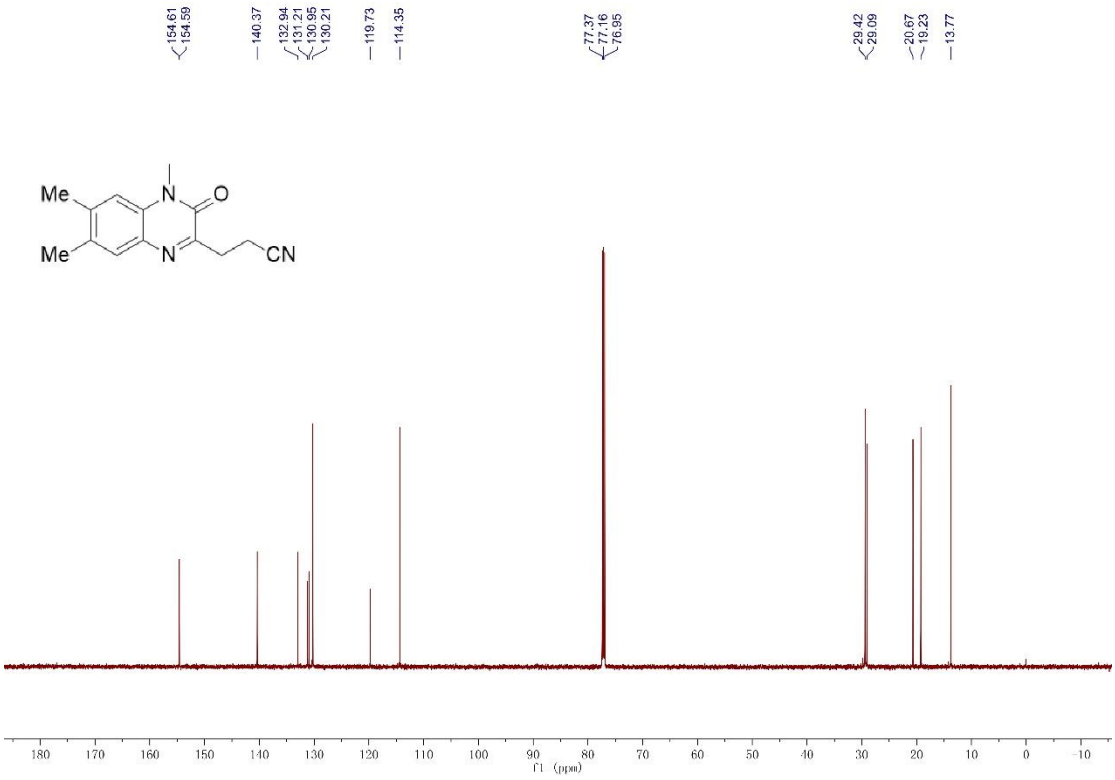
^{13}C NMR of **3**



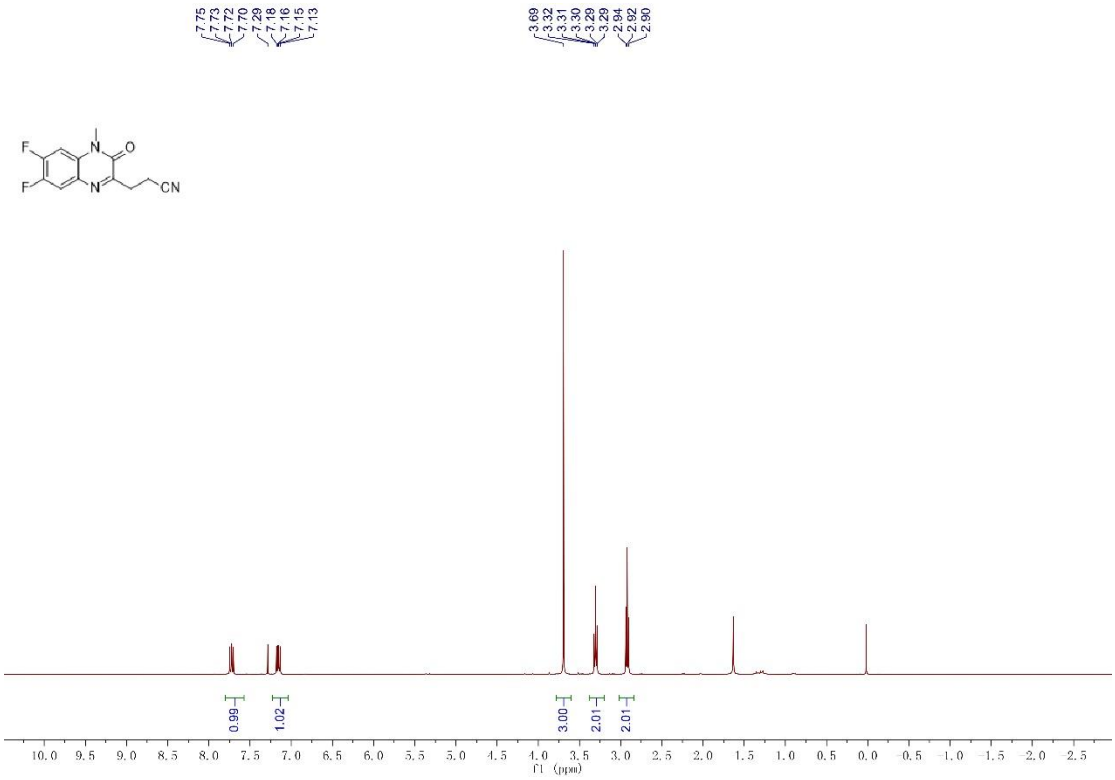
^{1}H NMR of **4**



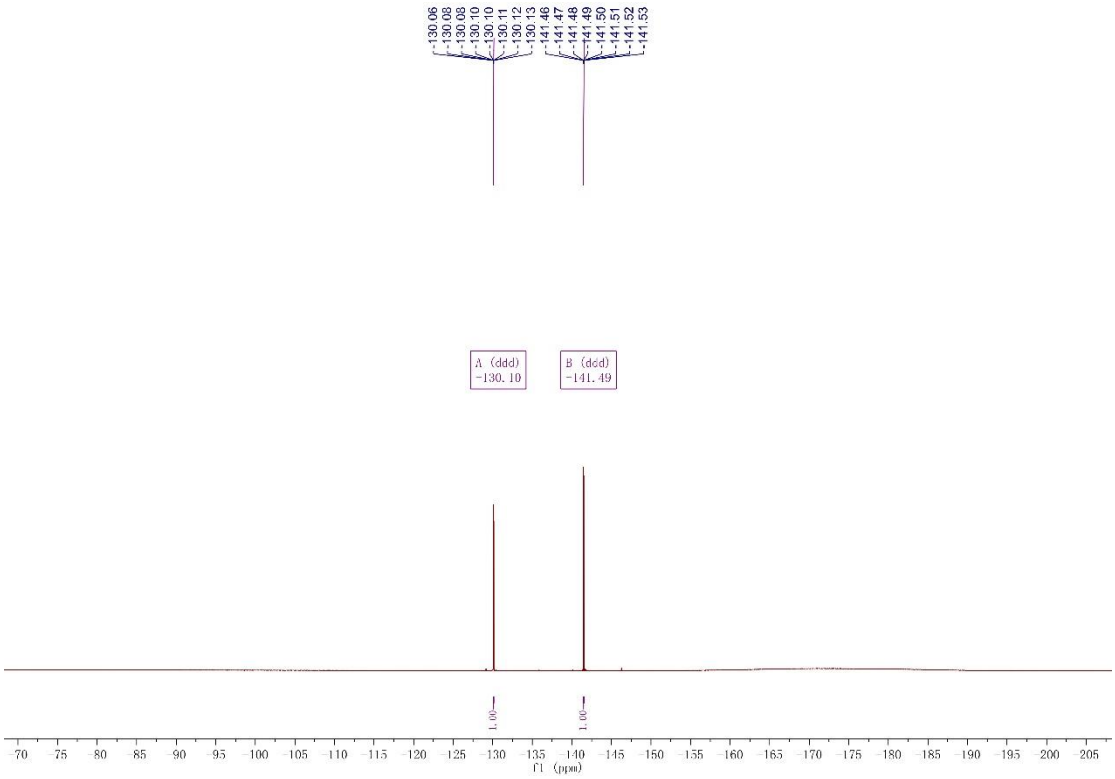
^{13}C NMR of **4**



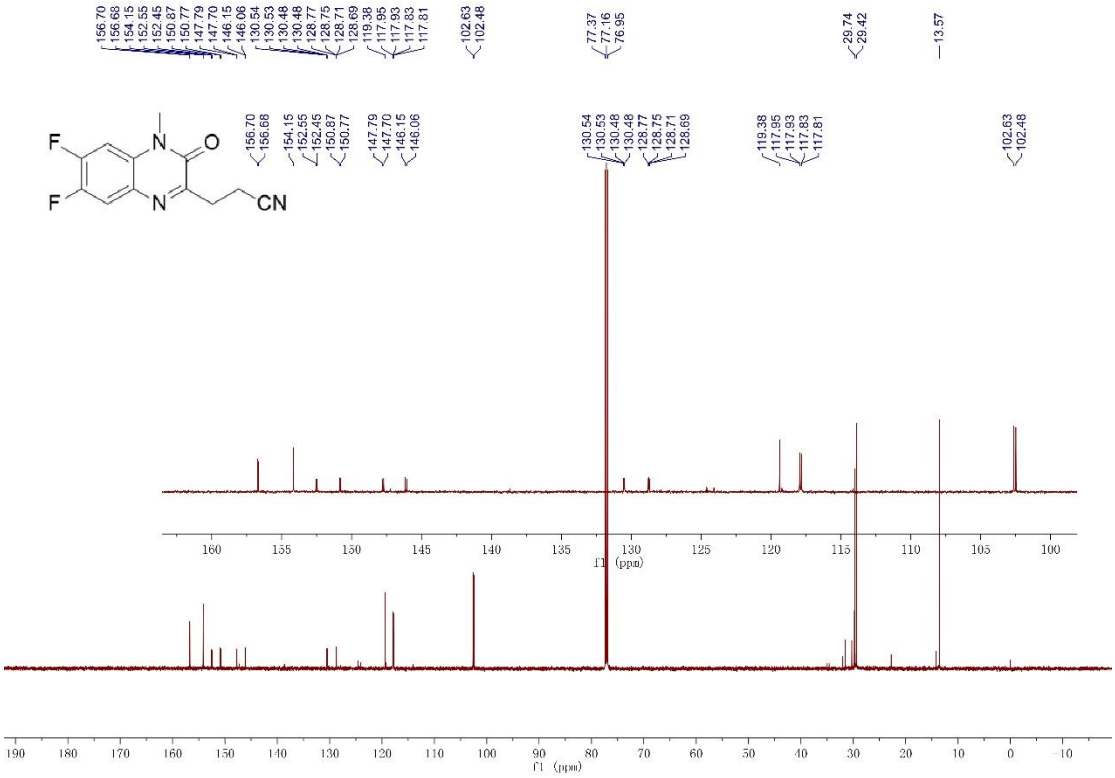
^{1}H NMR of **5**



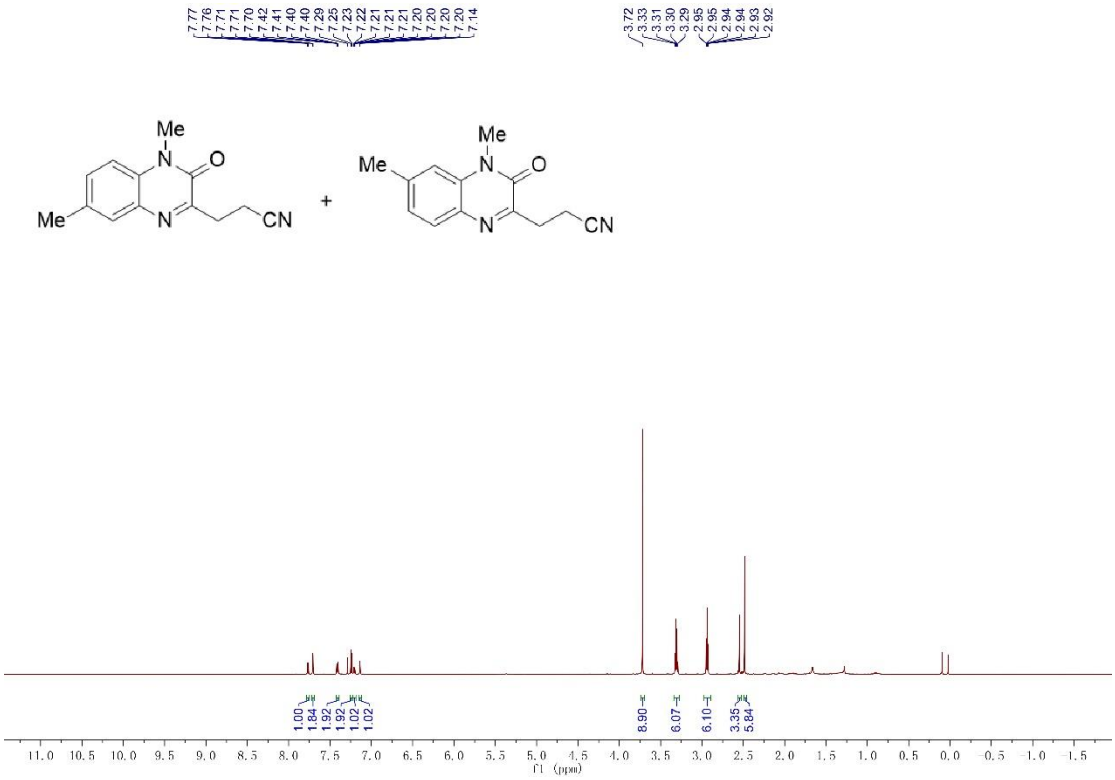
^{19}F NMR of **5**



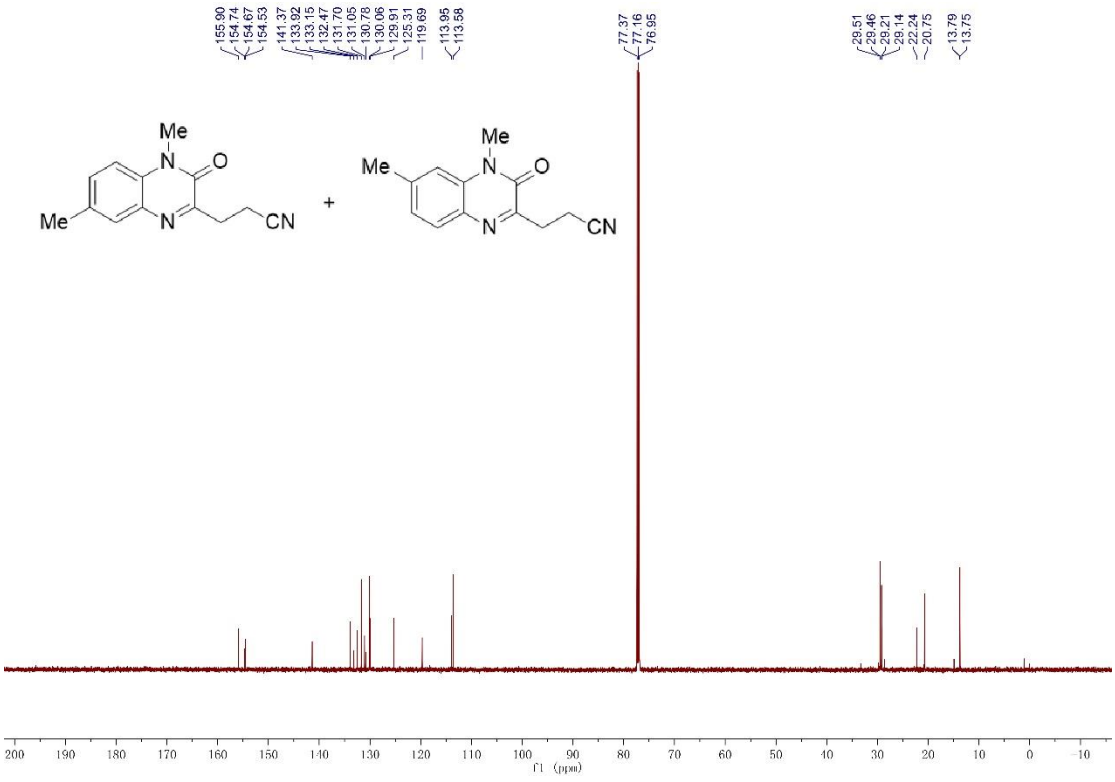
^{13}C NMR of **5**


156.70
156.68
154.15
152.55
152.45
150.87
150.77
147.79
147.70
146.15
146.06
130.54
130.53
130.48
130.48
128.77
128.75
128.71
128.69
119.38
117.95
117.93
117.83
117.81
102.63
102.48
77.37
77.16
76.95
29.74
29.42
13.57
F
F
N
O
N
CN
f1 (ppm)
f1 (ppm)

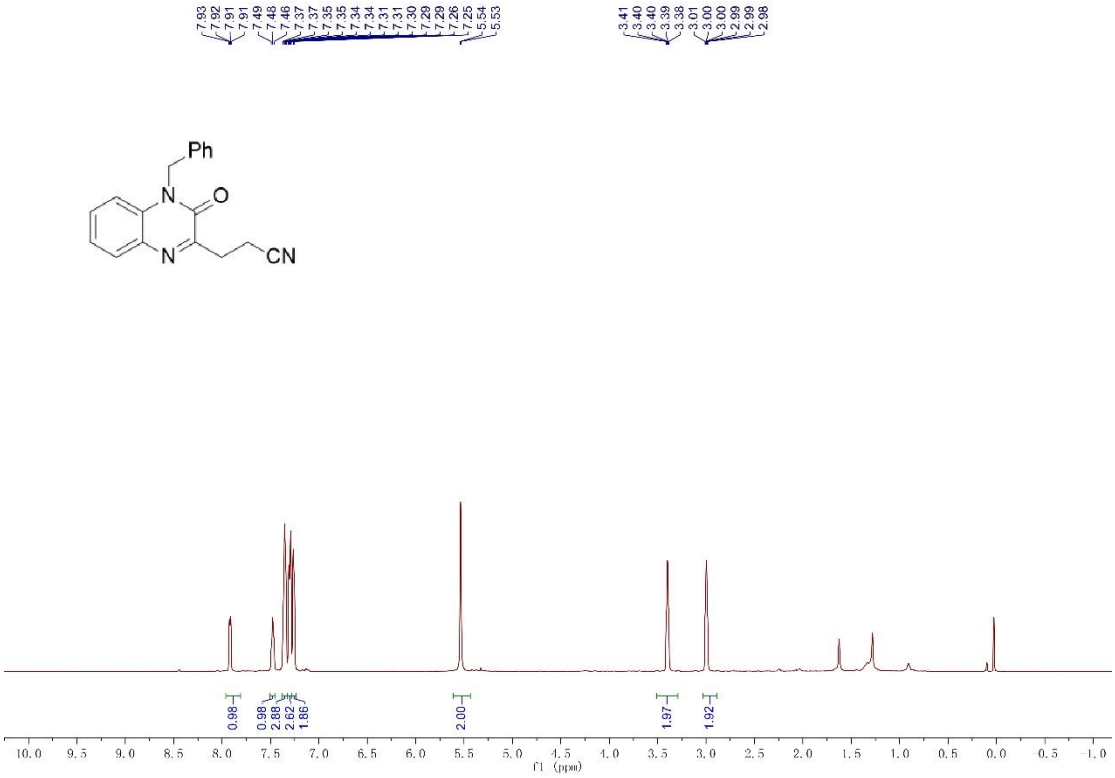
^{1}H NMR of **6**



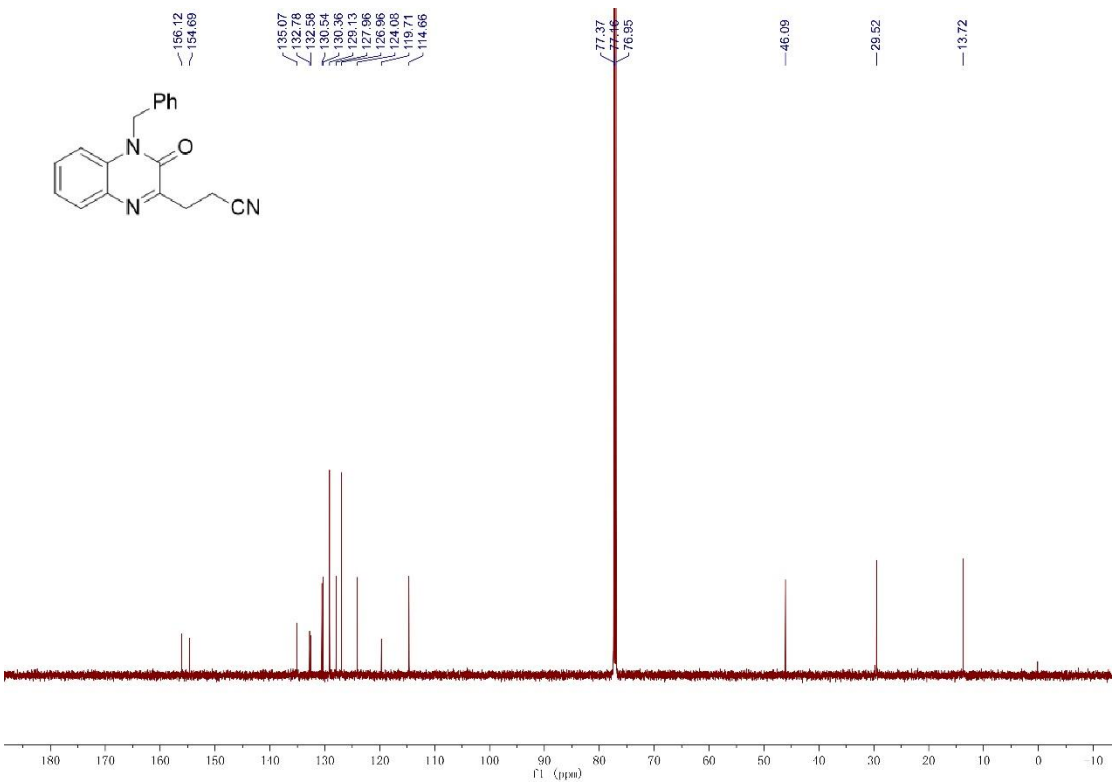
^{13}C NMR of **6**



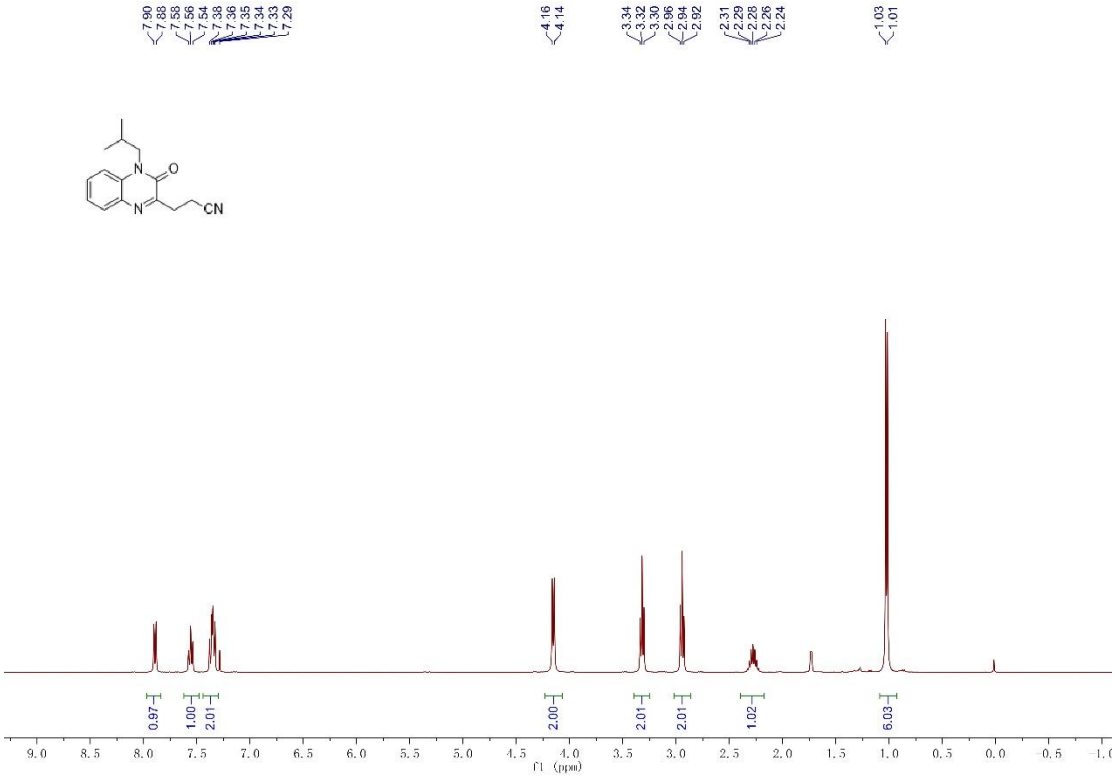
^{1}H NMR of **7**



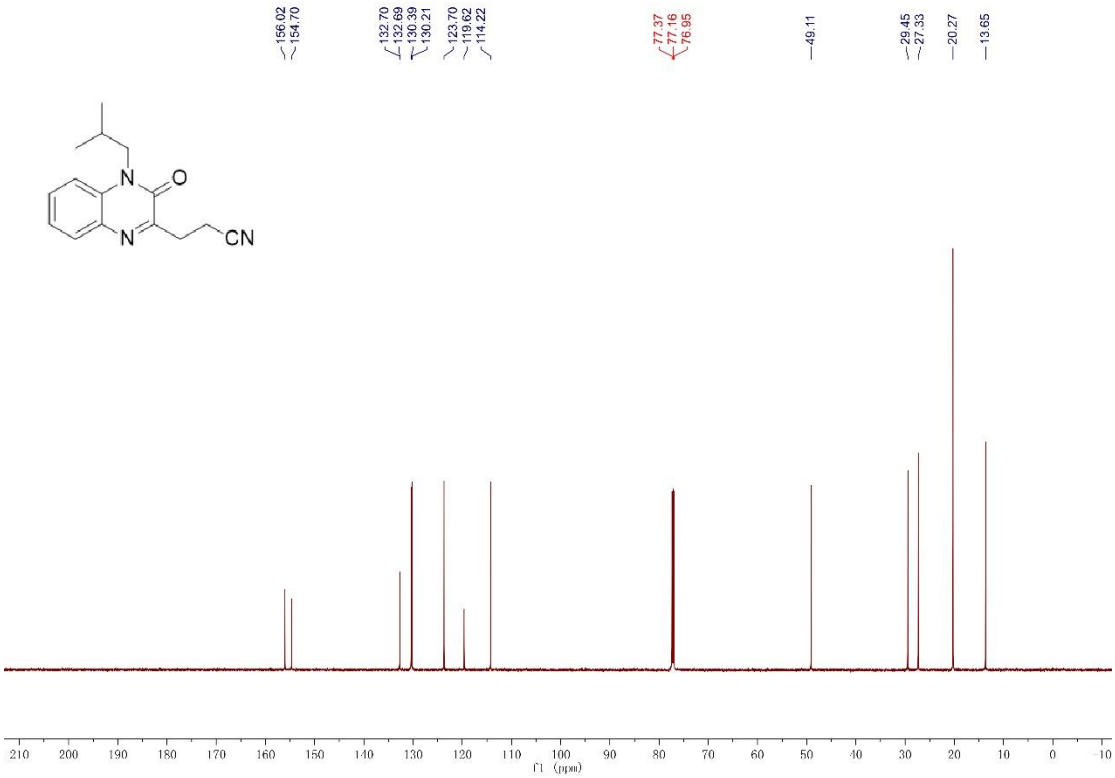
^{13}C NMR of **7**



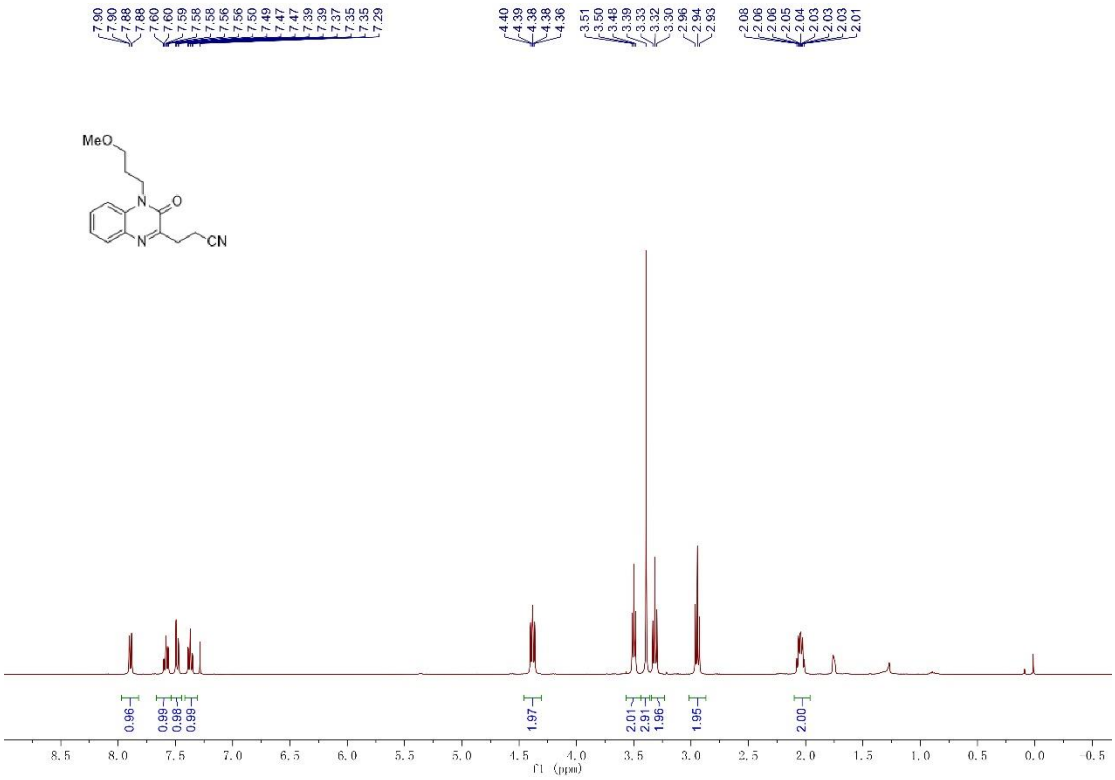
^{1}H NMR of **8**



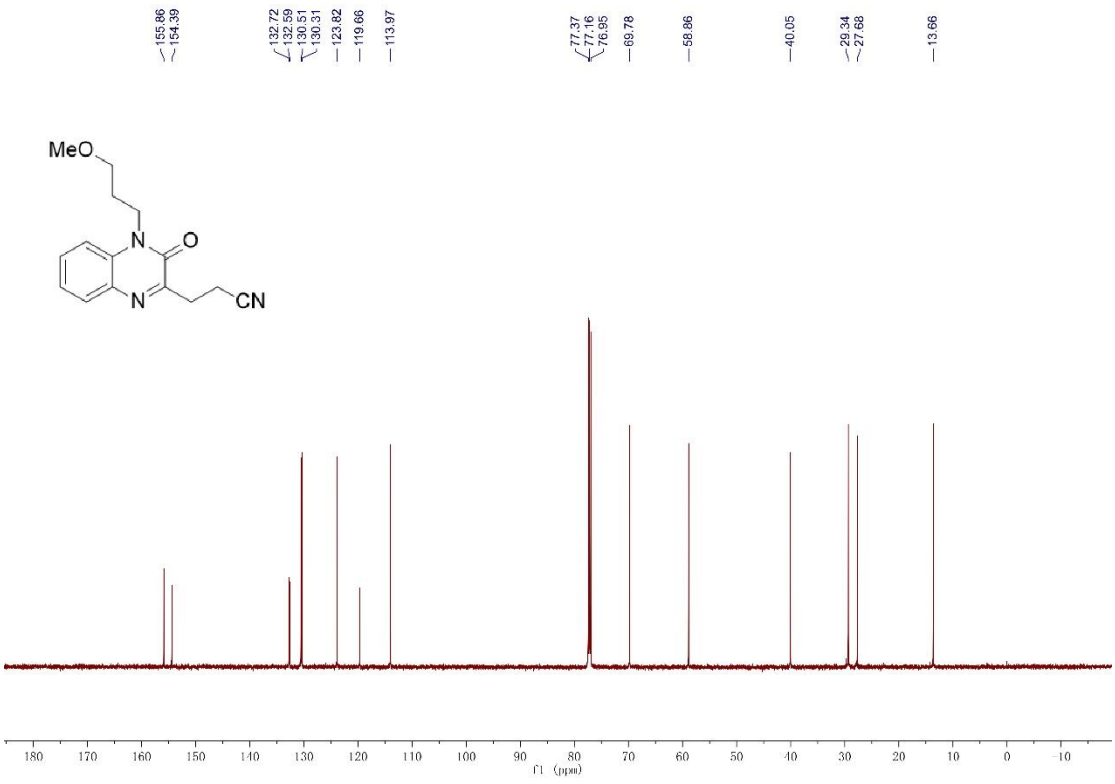
^{13}C NMR of **8**



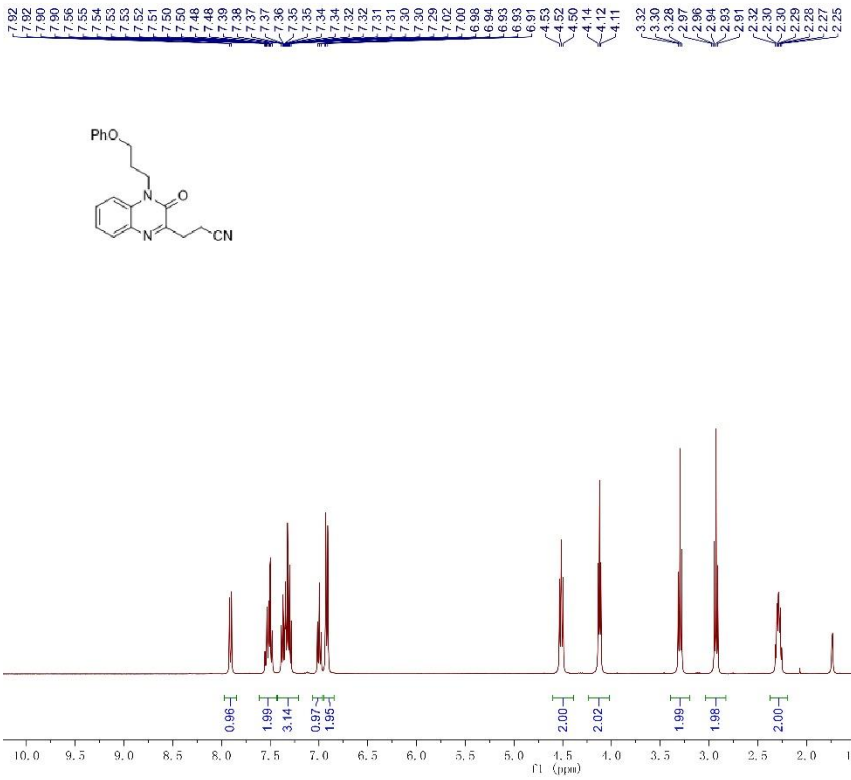
^{1}H NMR of **9**



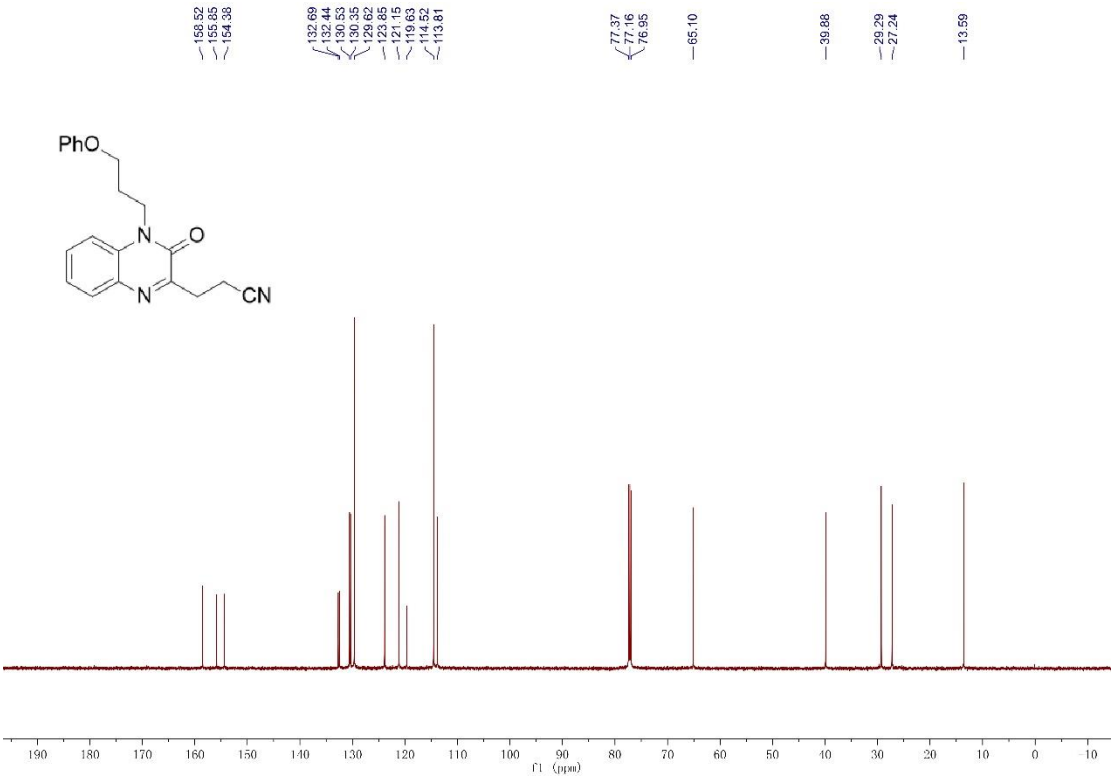
^{13}C NMR of **9**



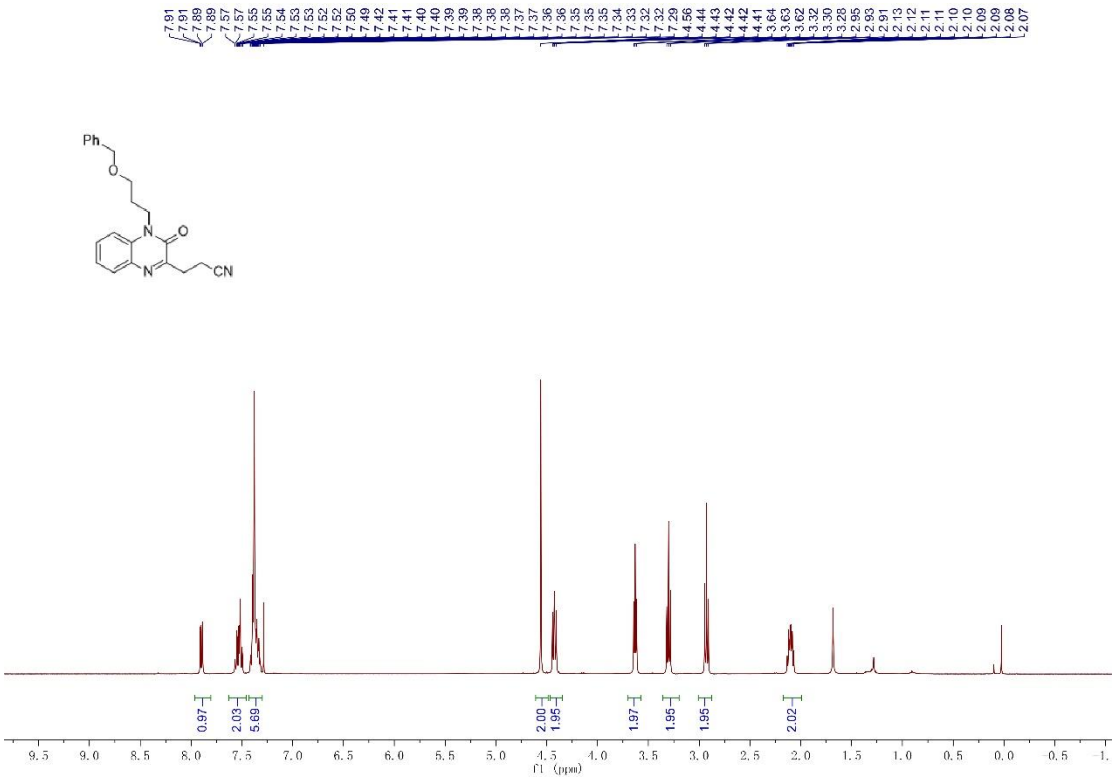
^{1}H NMR of **10**



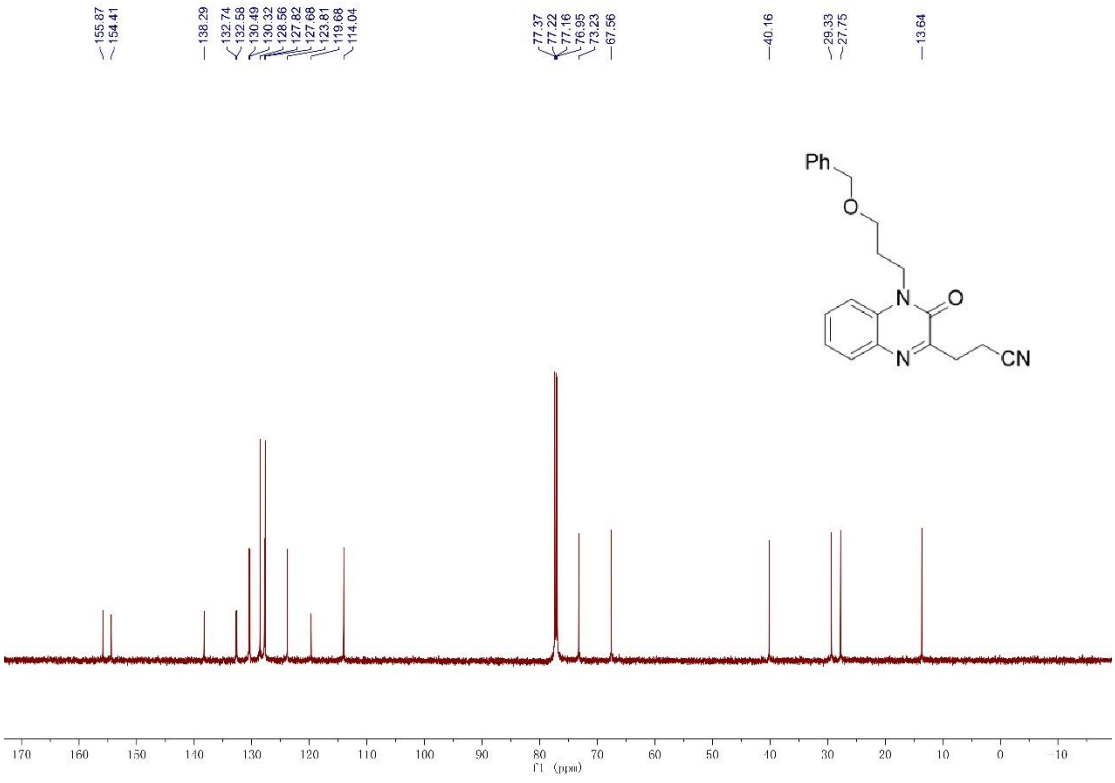
^{13}C NMR of **10**



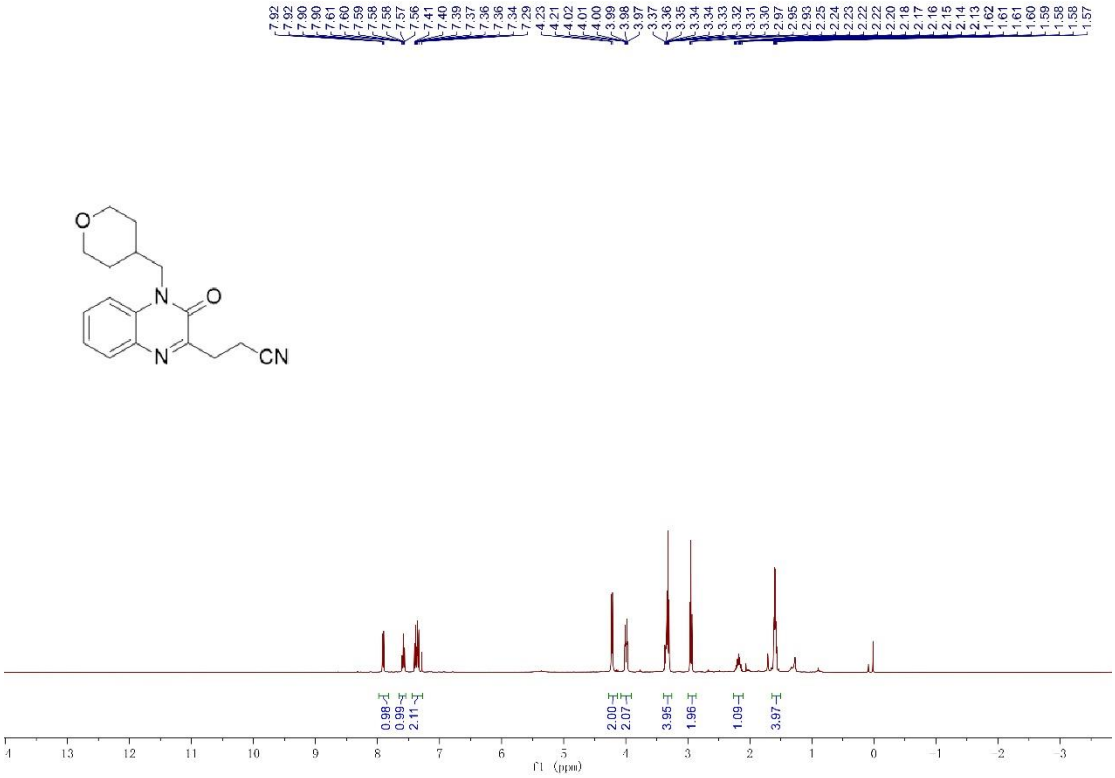
^{1}H NMR of **11**



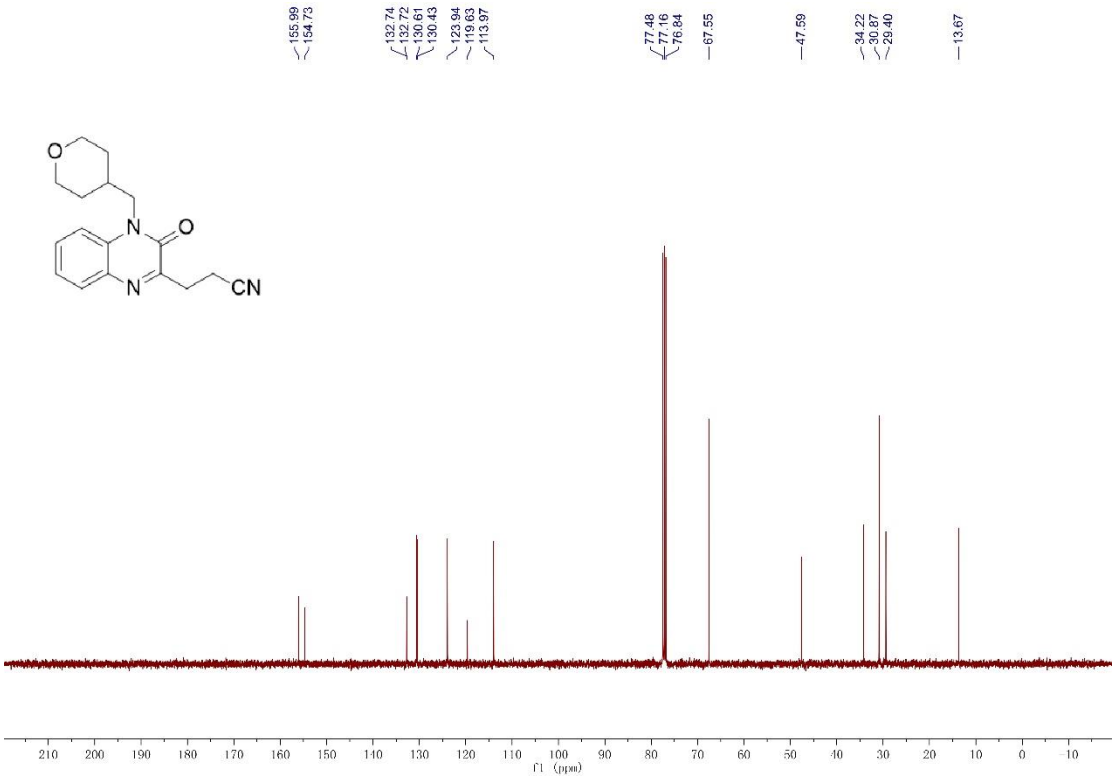
^{13}C NMR of **11**



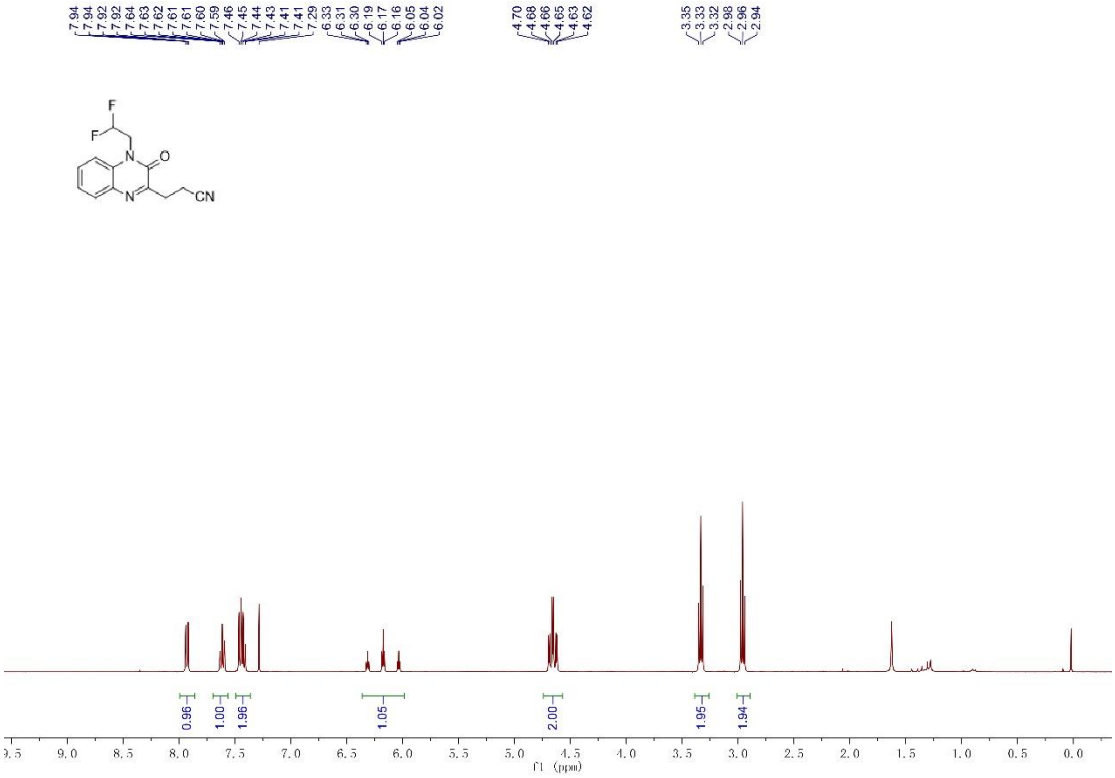
^{1}H NMR of **12**



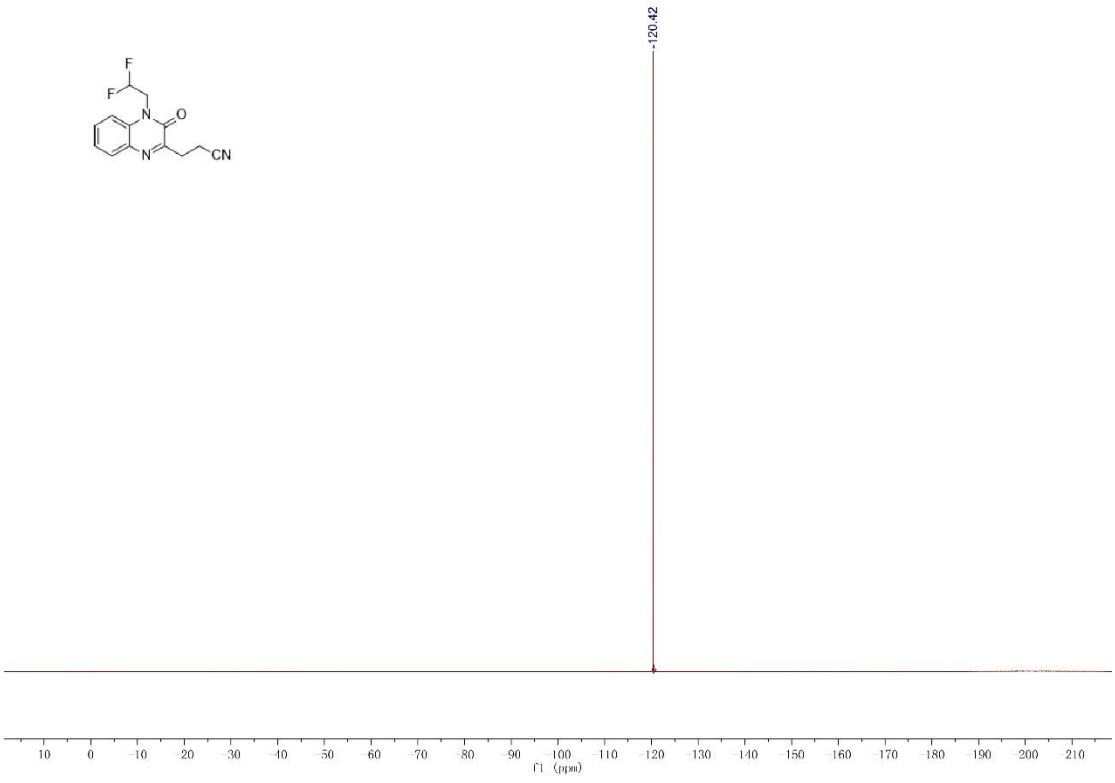
^{13}C NMR of **12**



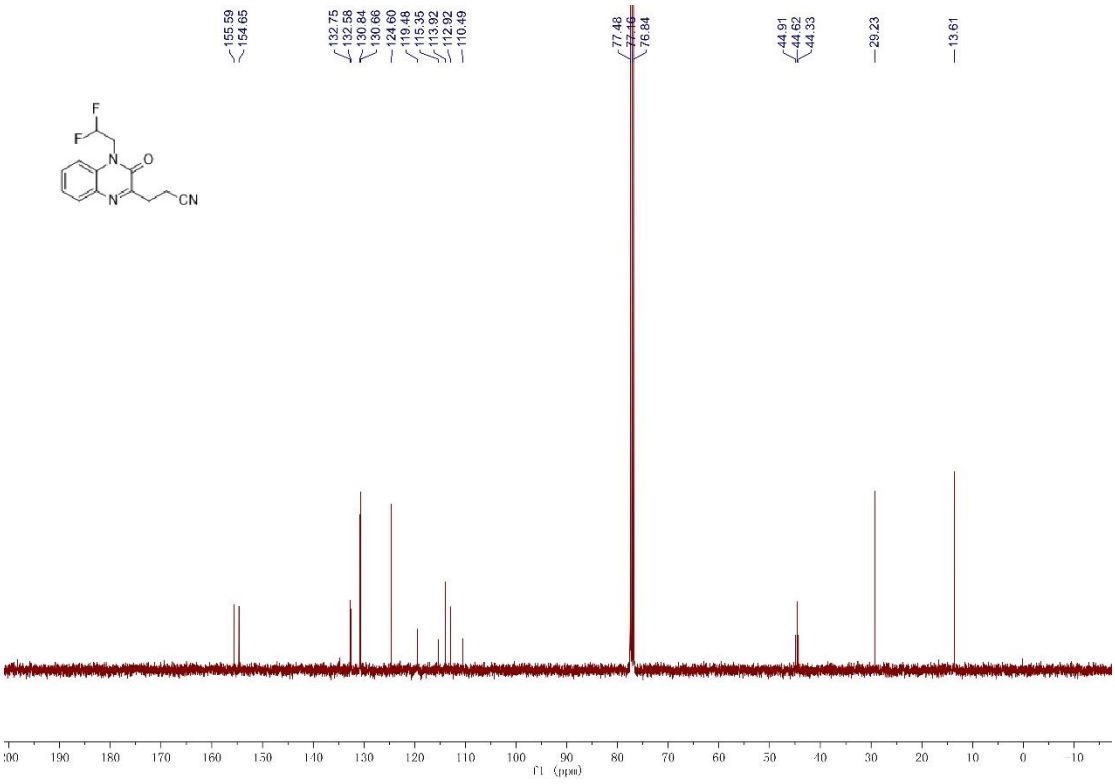
^{1}H NMR of **13**



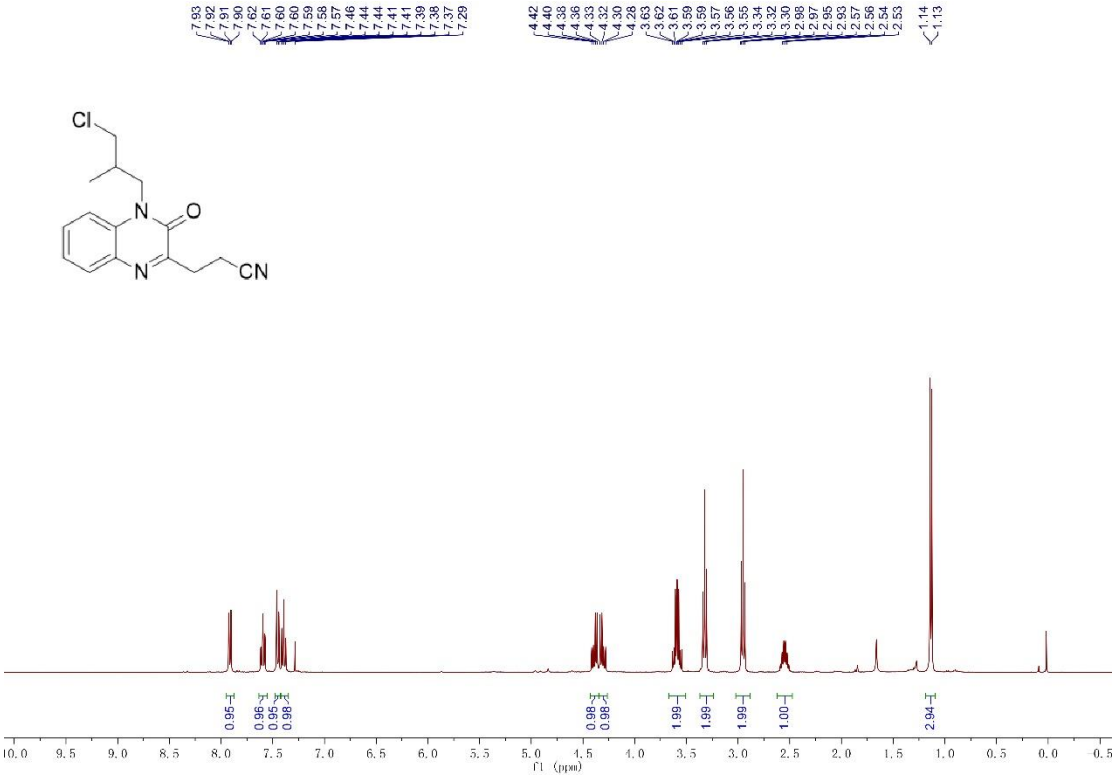
^{19}F NMR of **13**



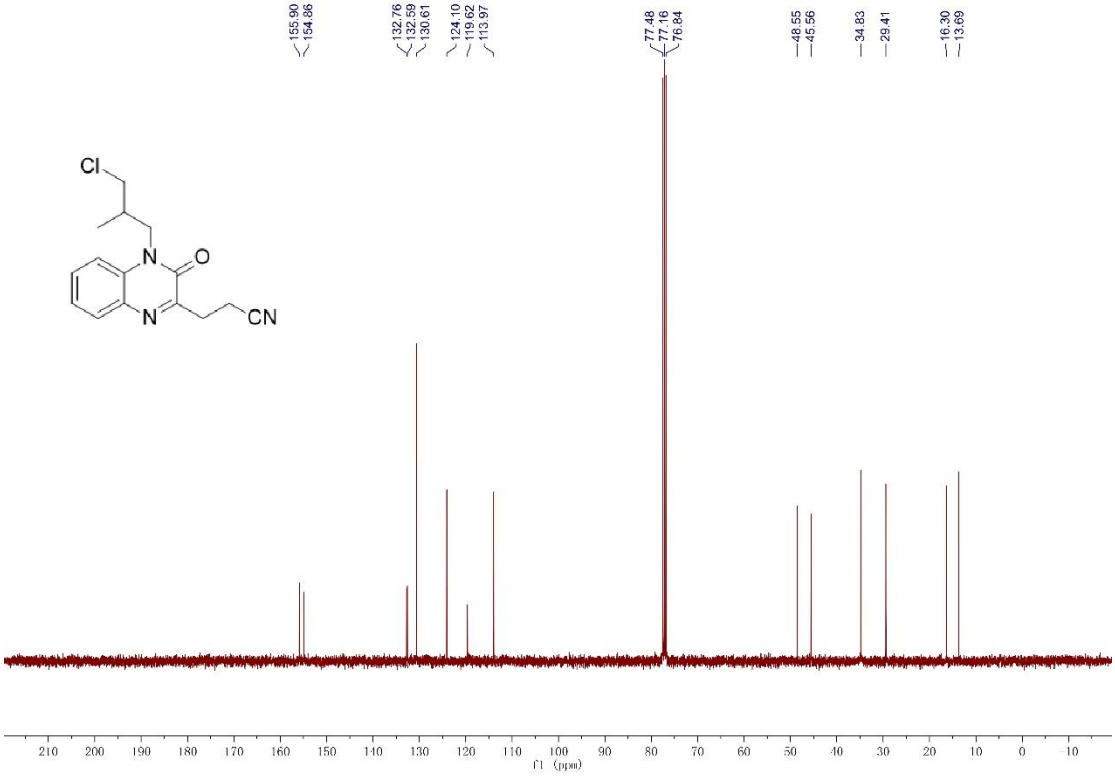
^{13}C NMR of **13**


155.59
154.65
132.75
132.58
130.84
130.66
124.60
119.48
115.35
113.92
112.92
110.49
77.48
77.16
76.84
44.91
44.62
44.33
28.23
13.61
F
F
N
O
N
CN
f1 (ppm)

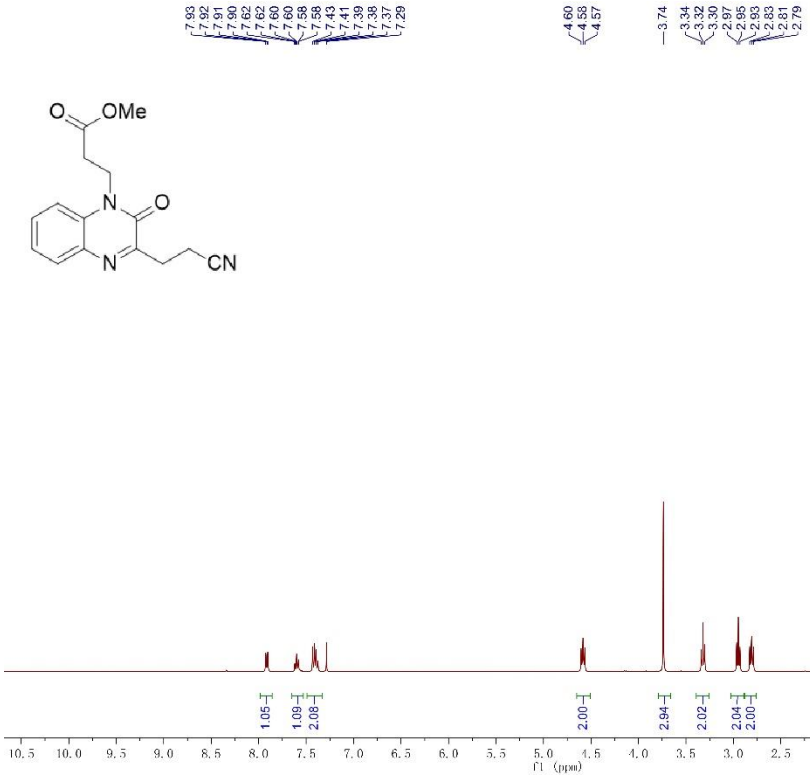
^{1}H NMR of **14**



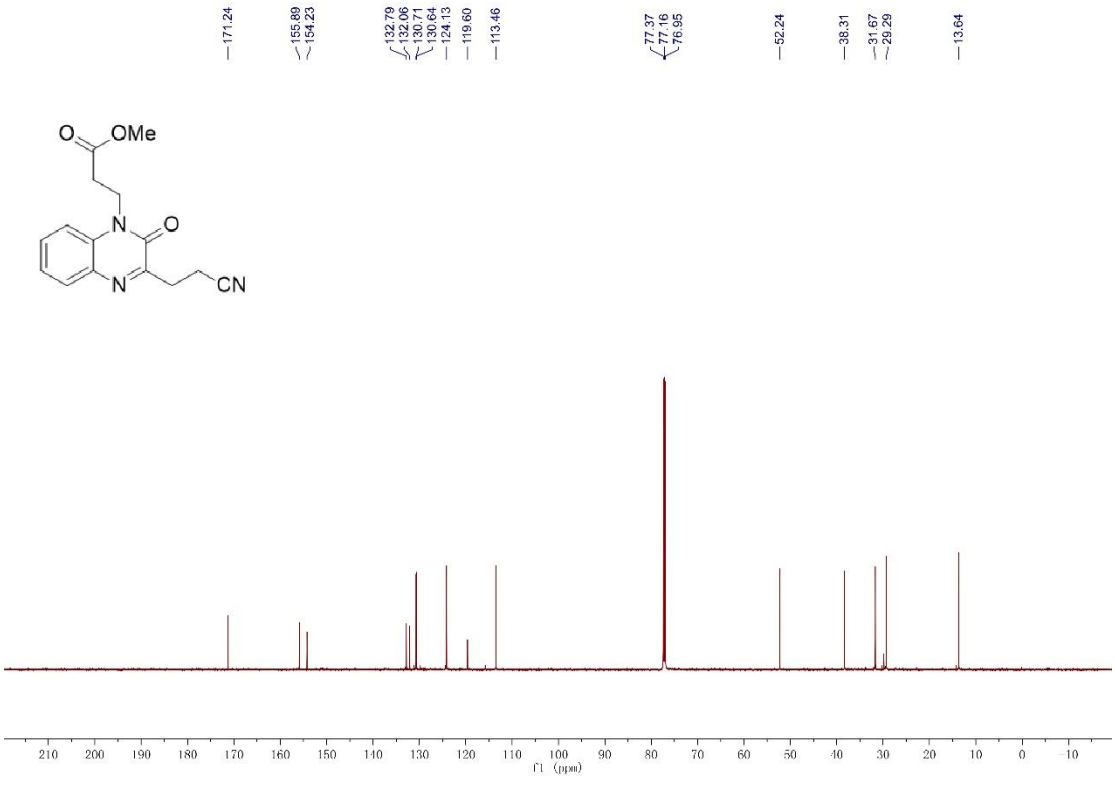
^{13}C NMR of **14**



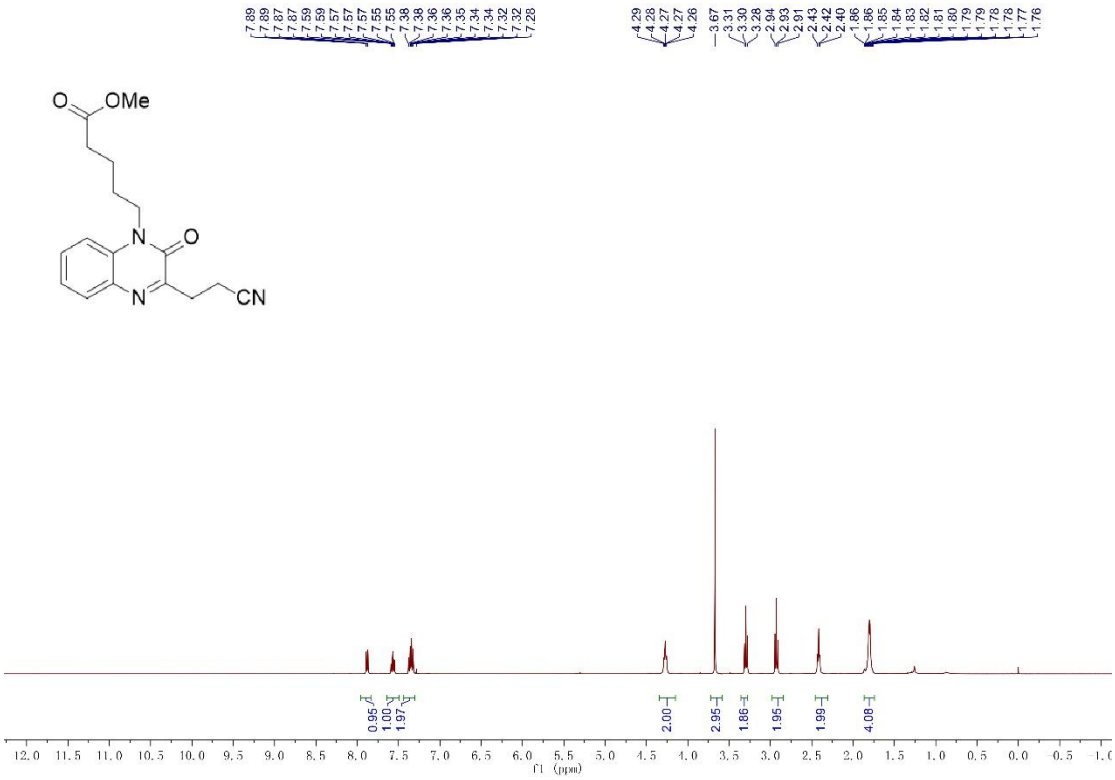
^{1}H NMR of **15**



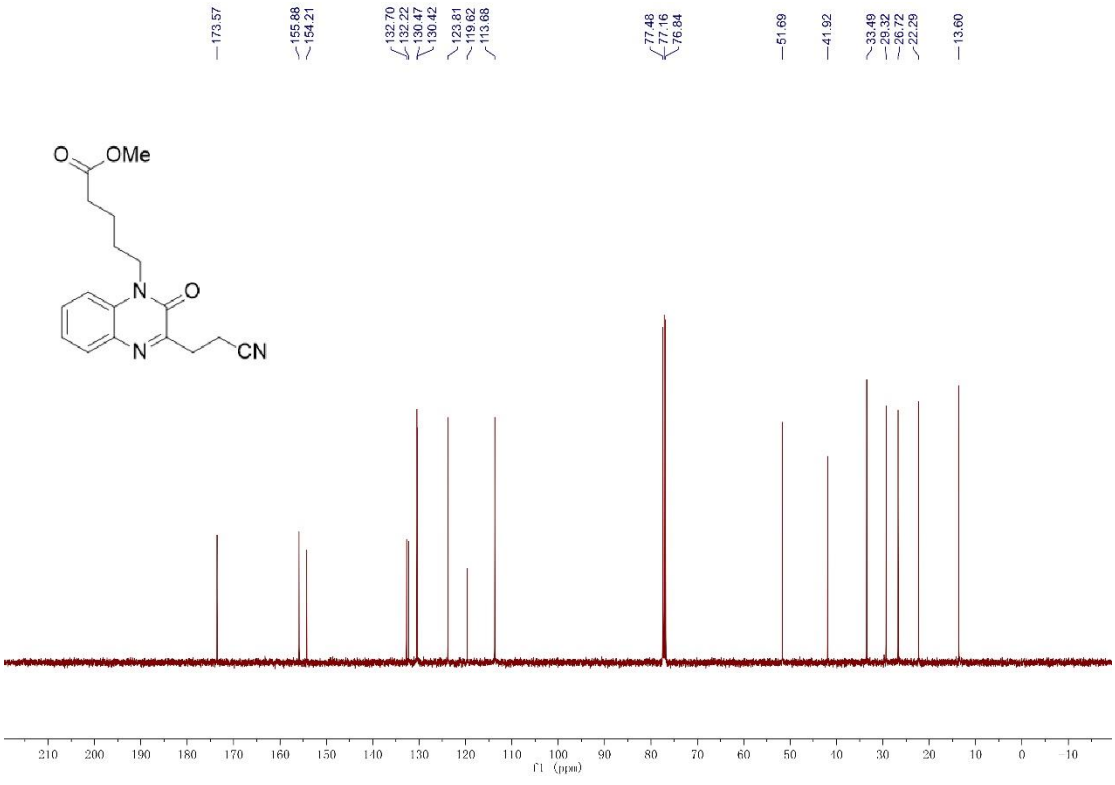
^{13}C NMR of **15**



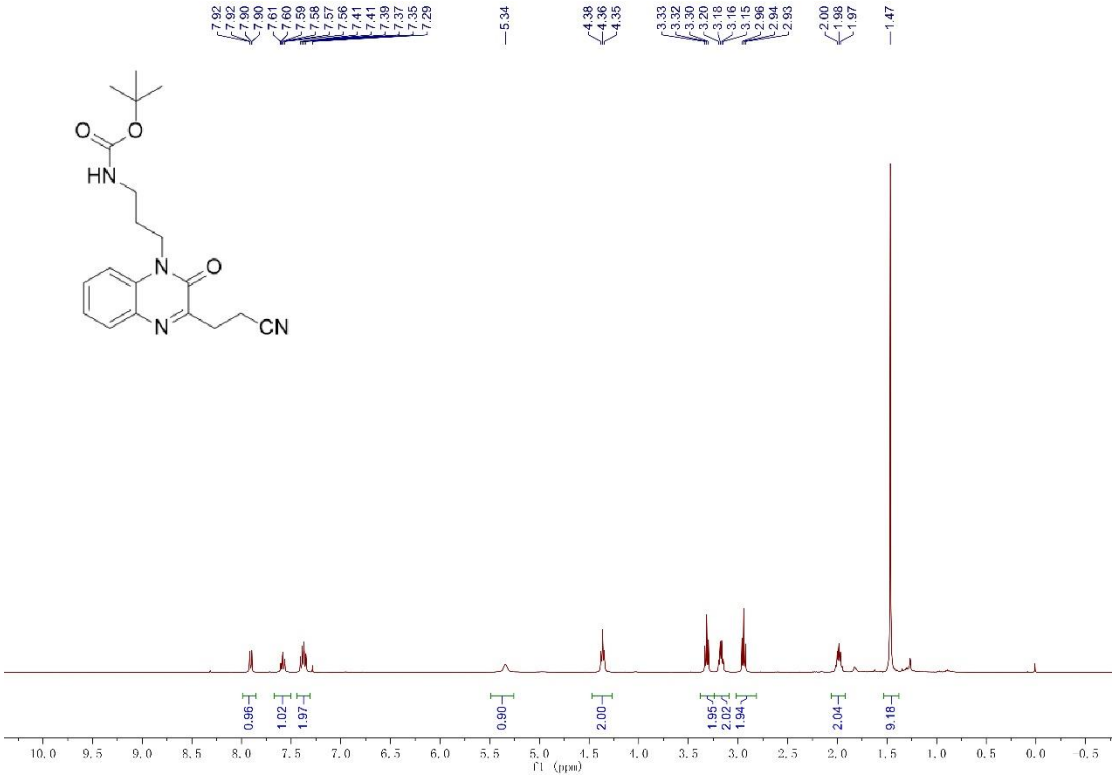
^{1}H NMR of **16**



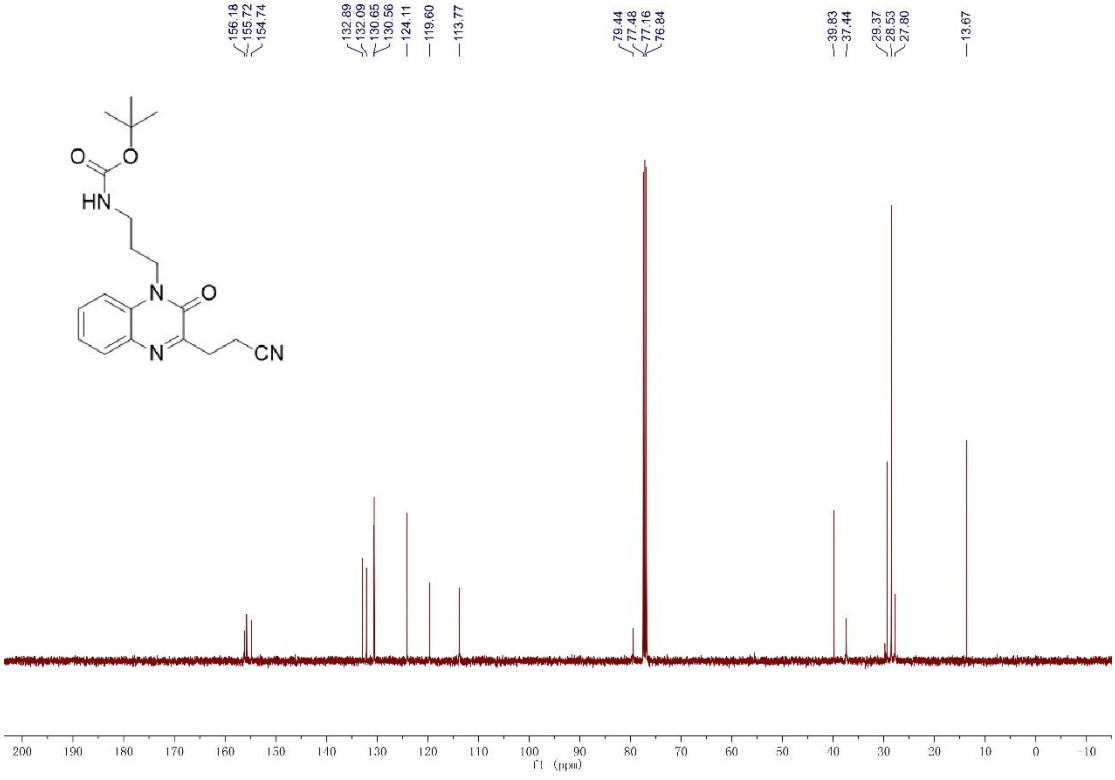
^{13}C NMR of **16**



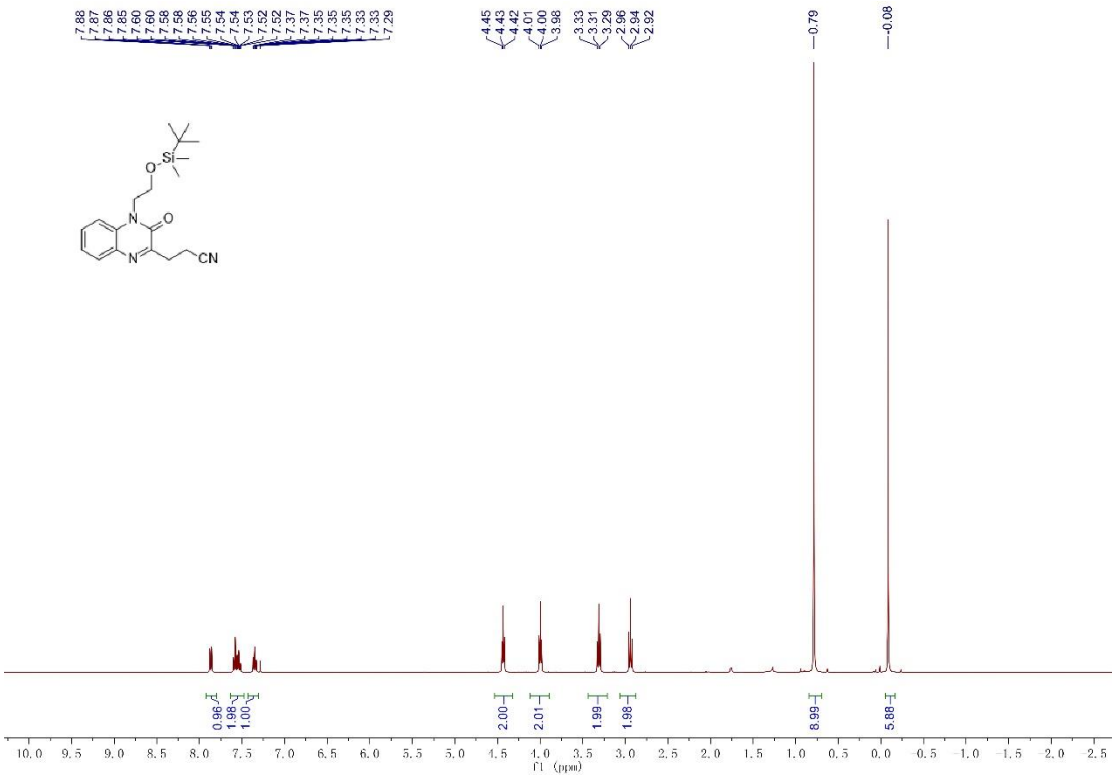
^{1}H NMR of **17**



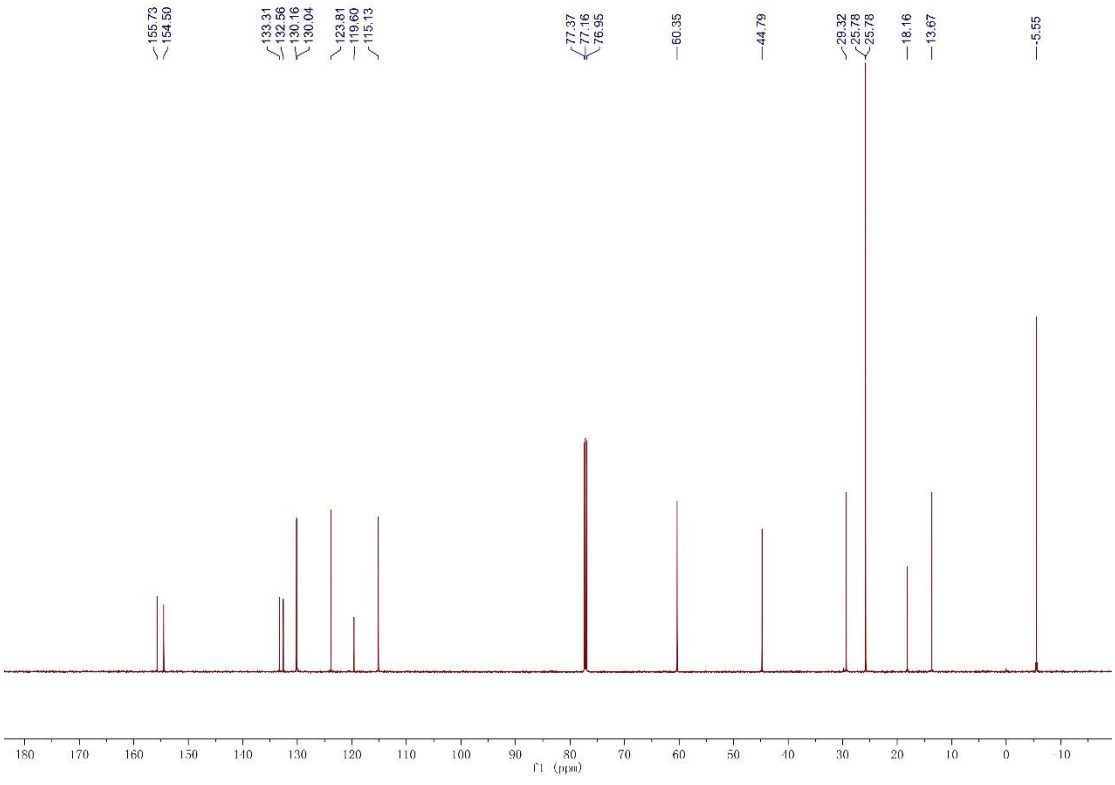
^{13}C NMR of **17**



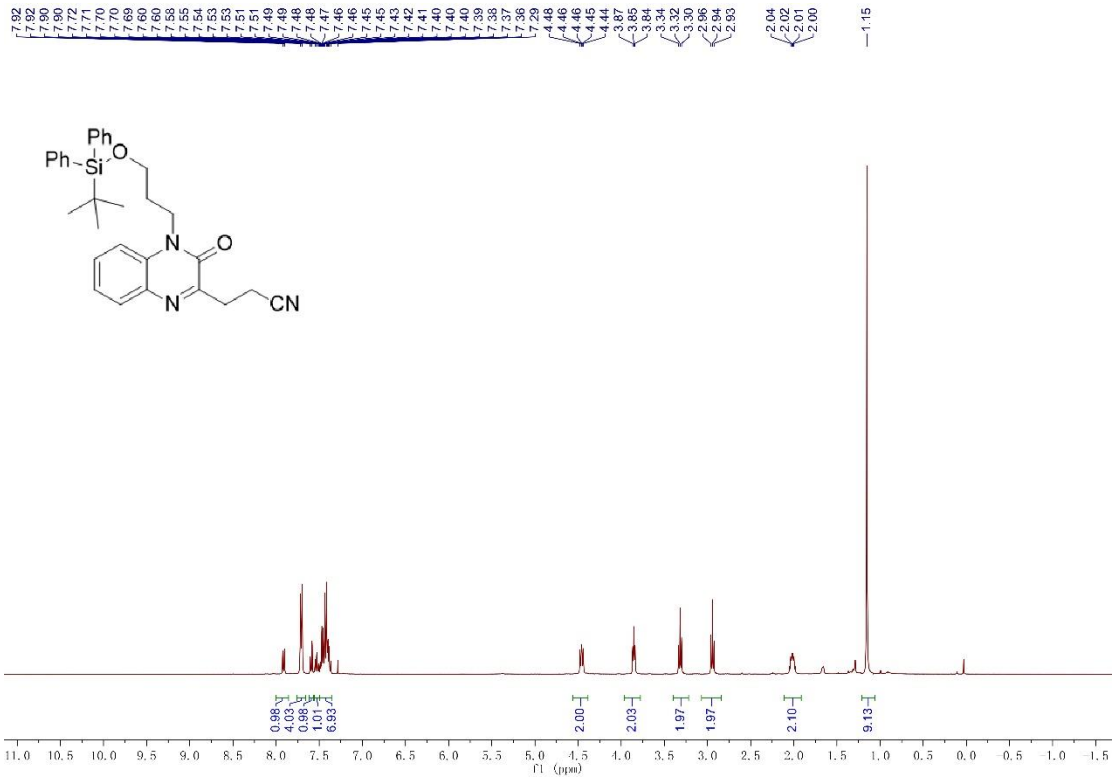
^{1}H NMR of **18**



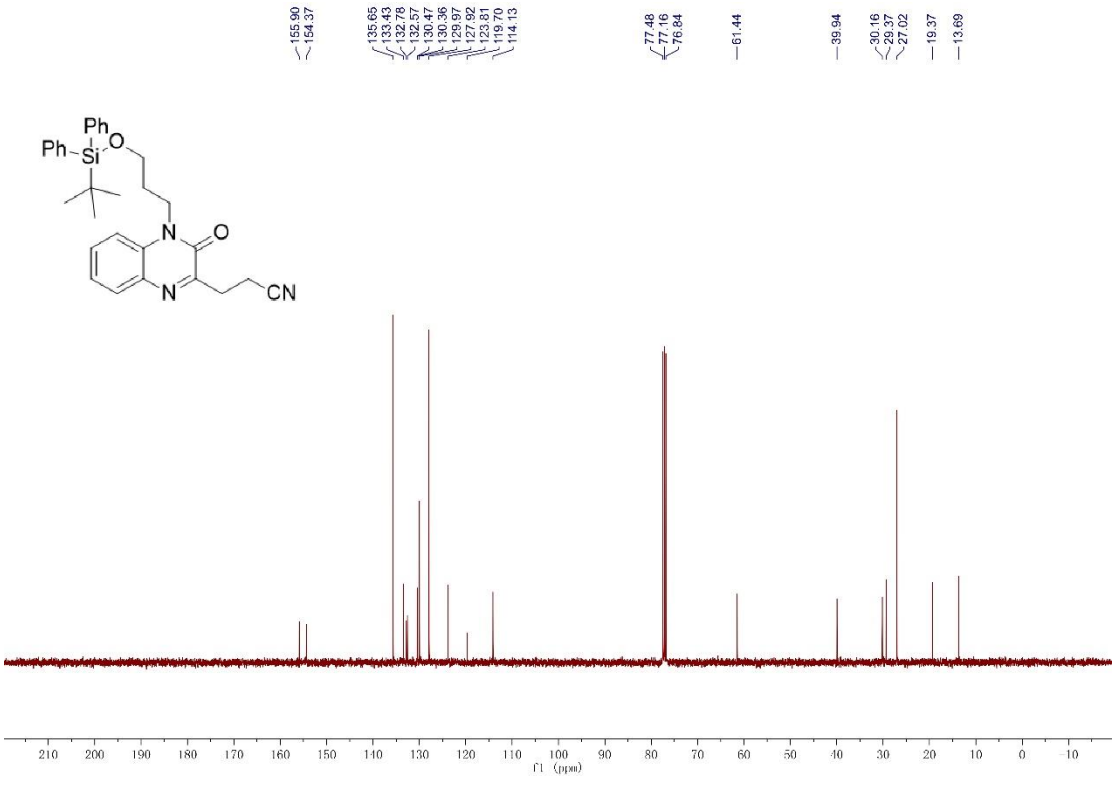
^{13}C NMR of **18**



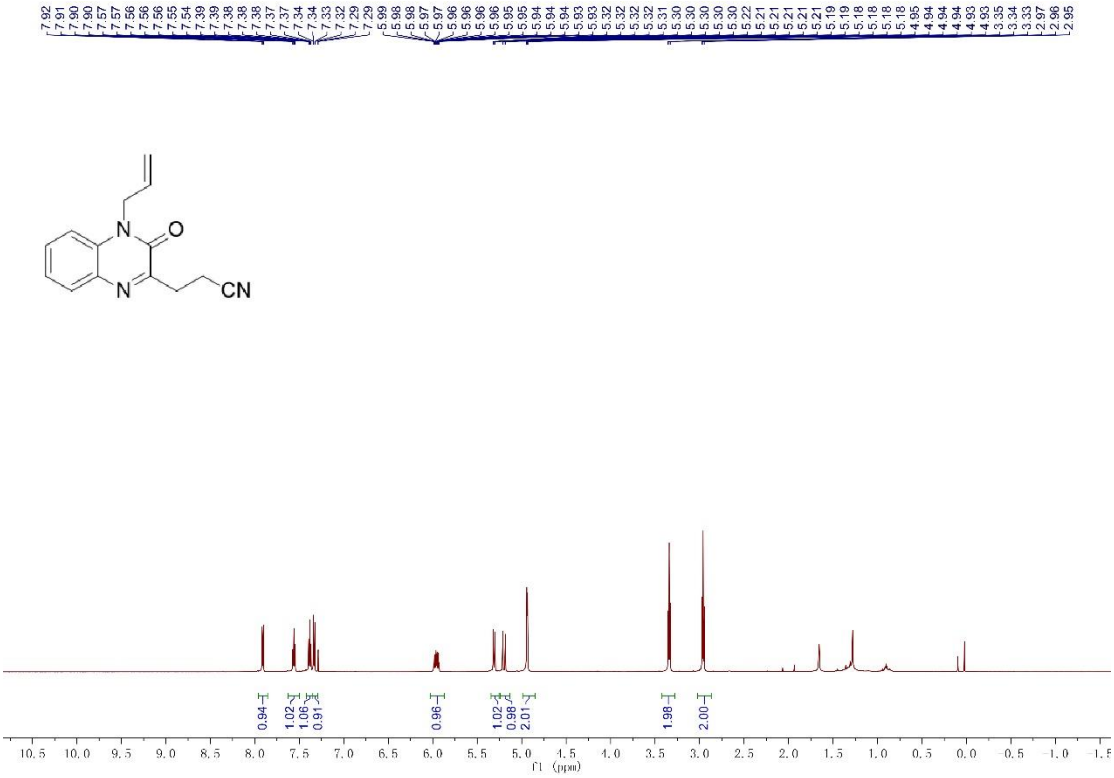
^{1}H NMR of **19**



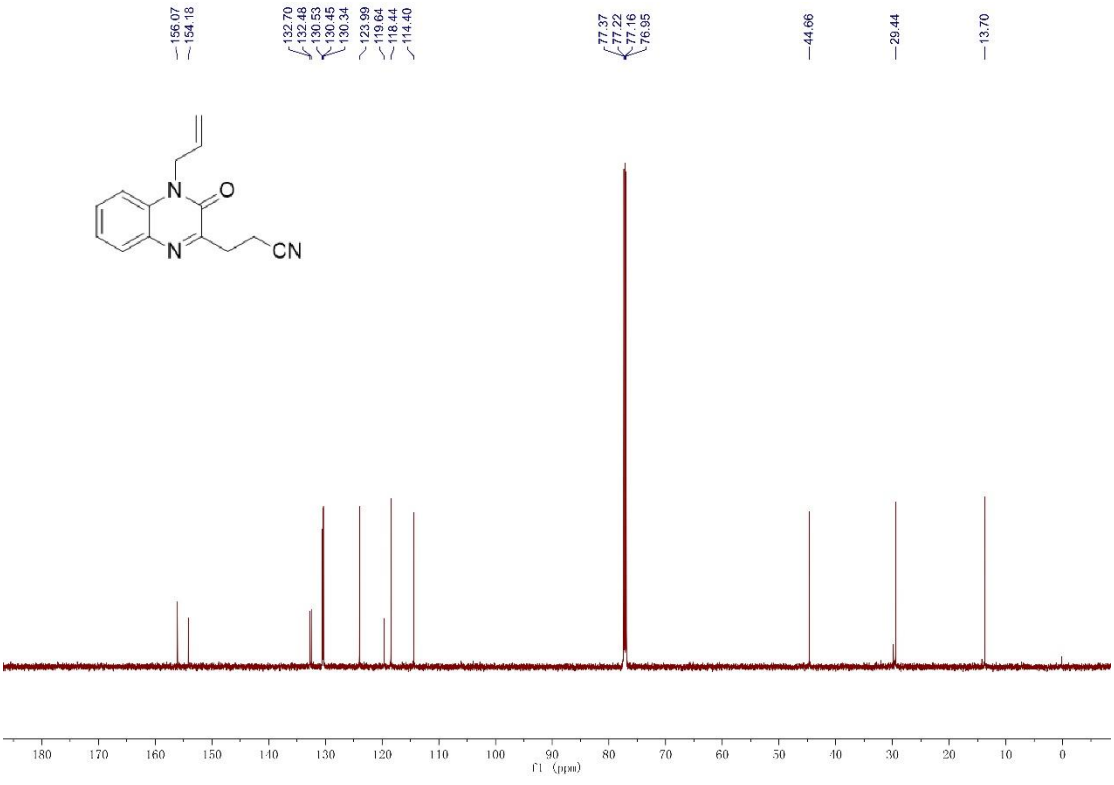
^{13}C NMR of **19**



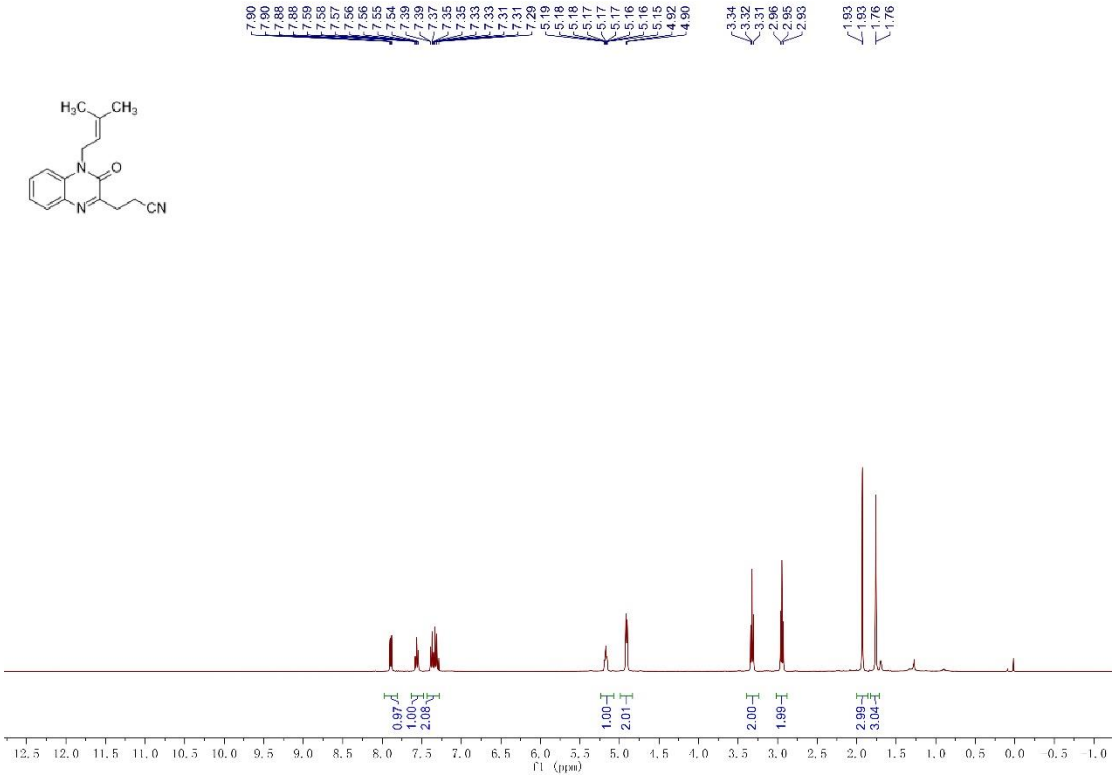
^{1}H NMR of **20**



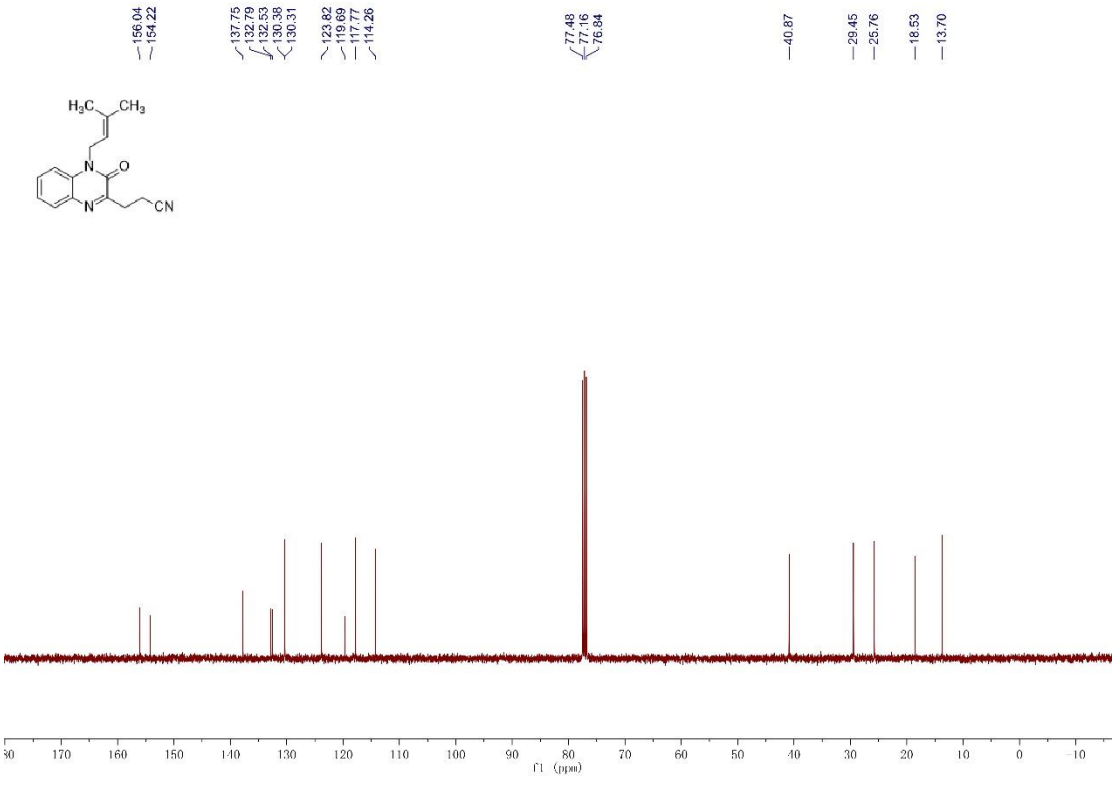
^{13}C NMR of **20**



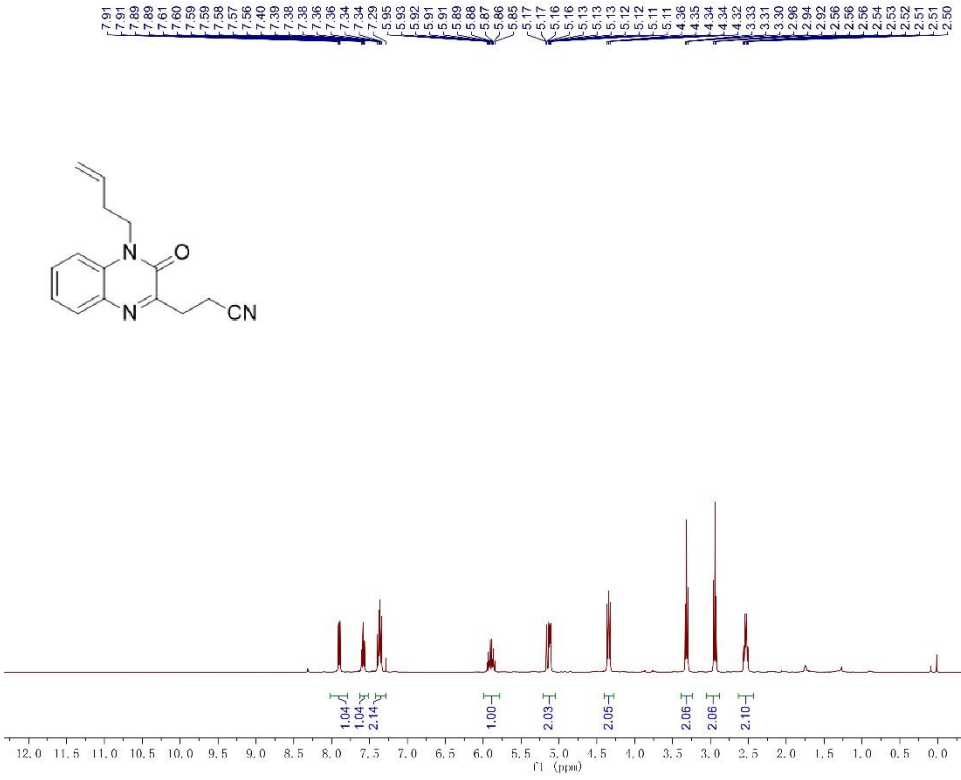
^{1}H NMR of **21**



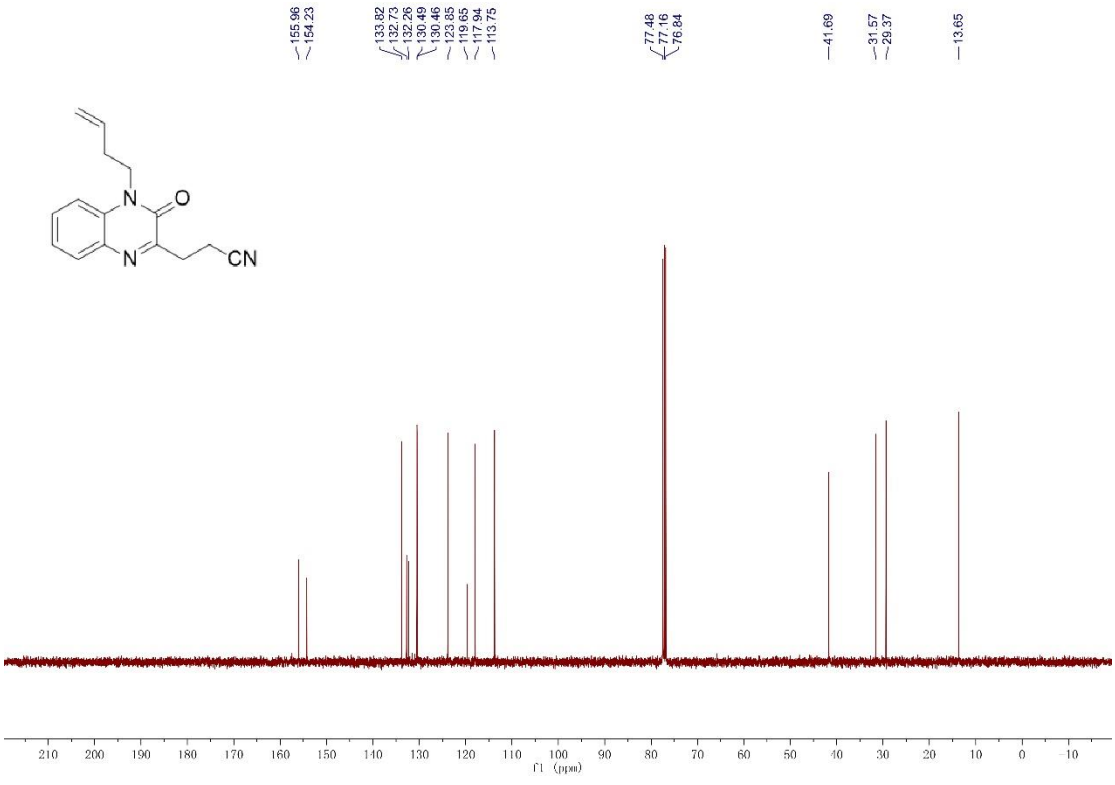
^{13}C NMR of **21**



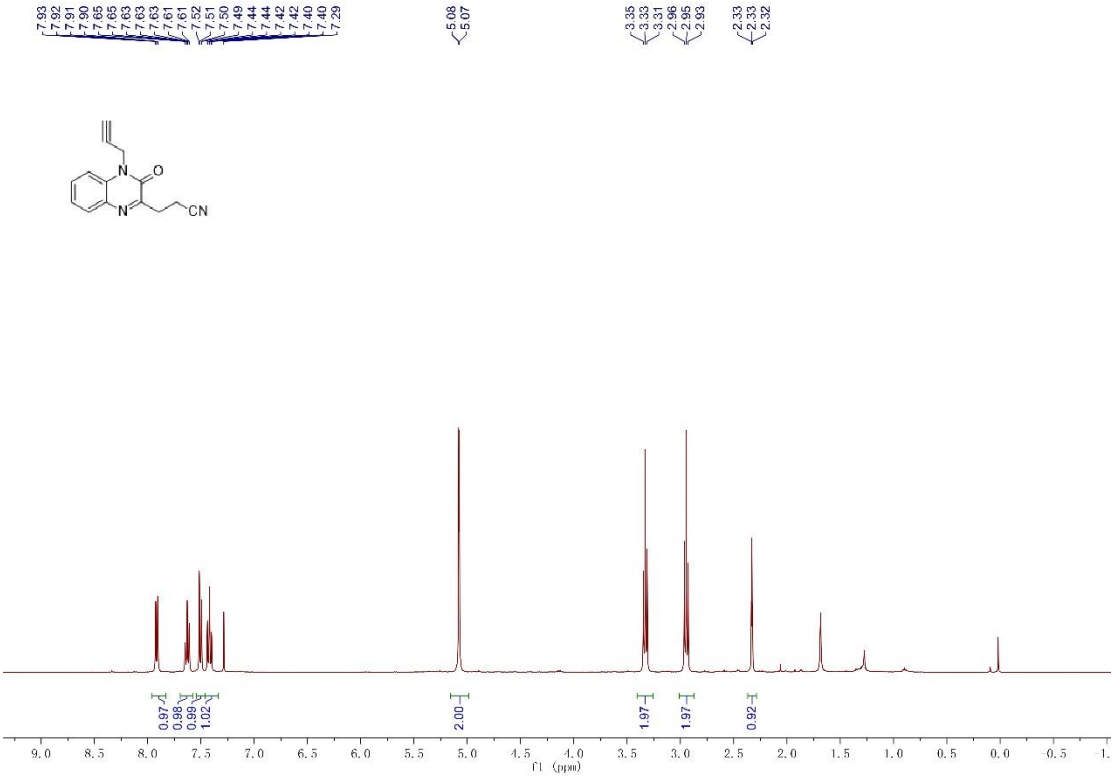
^{1}H NMR of **22**



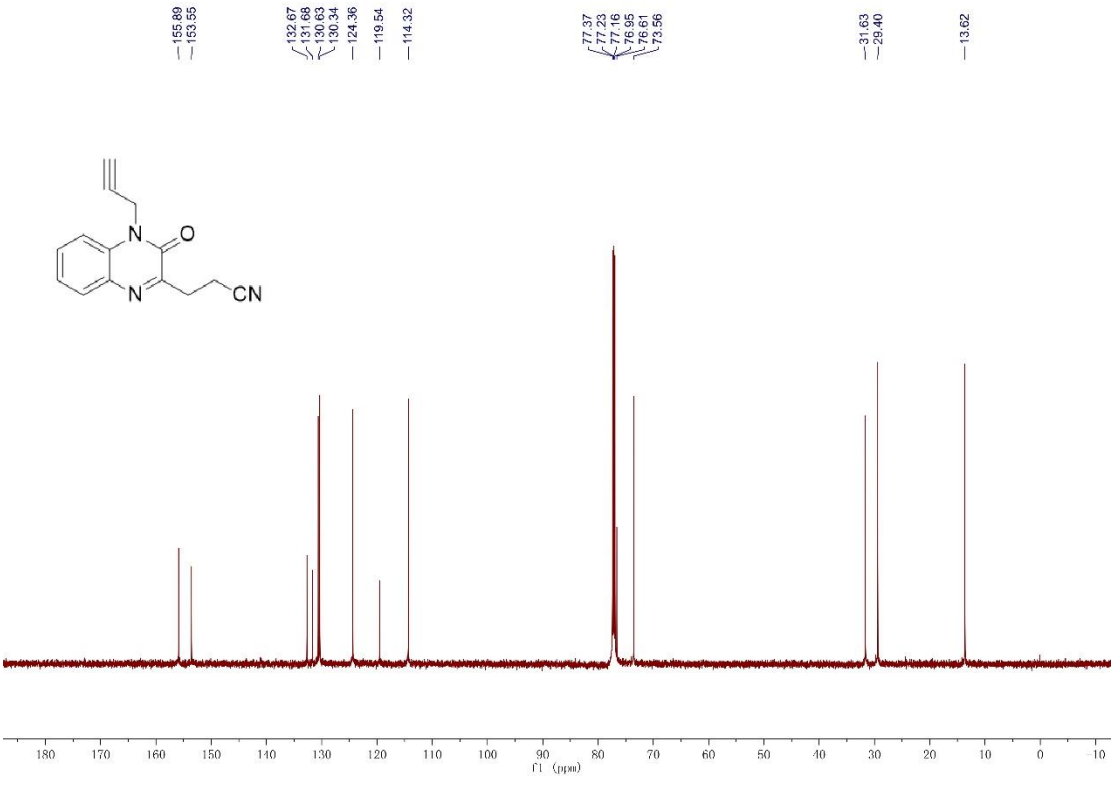
^{13}C NMR of **22**



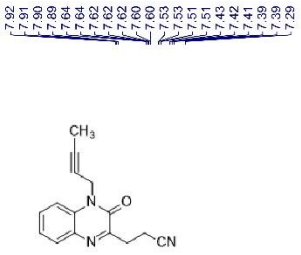
^{1}H NMR of **23**

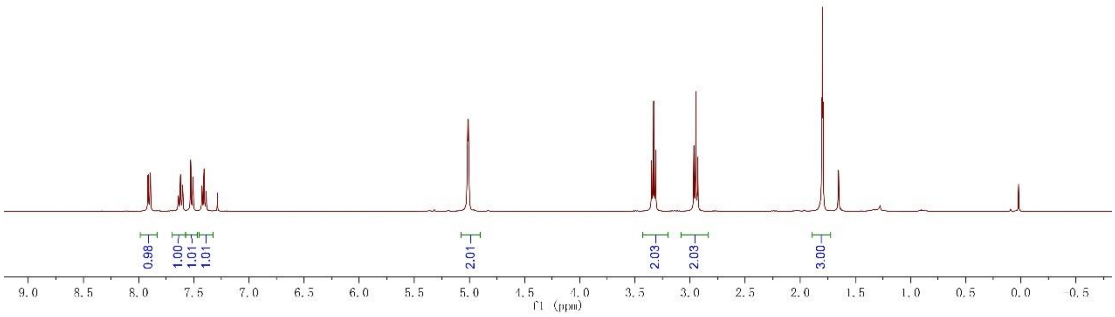


^{13}C NMR of **23**

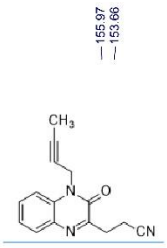


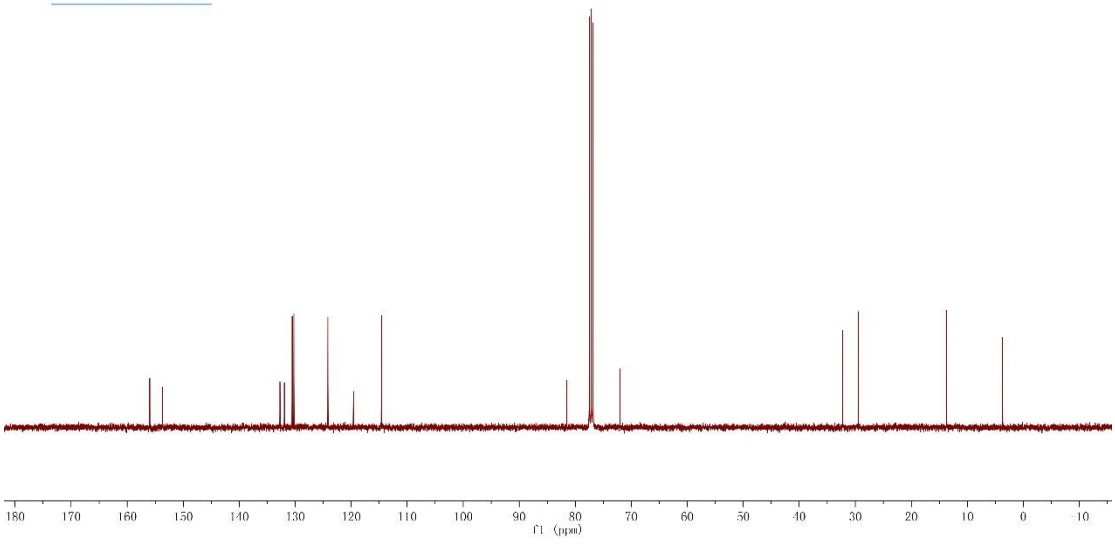
^{1}H NMR of **24**



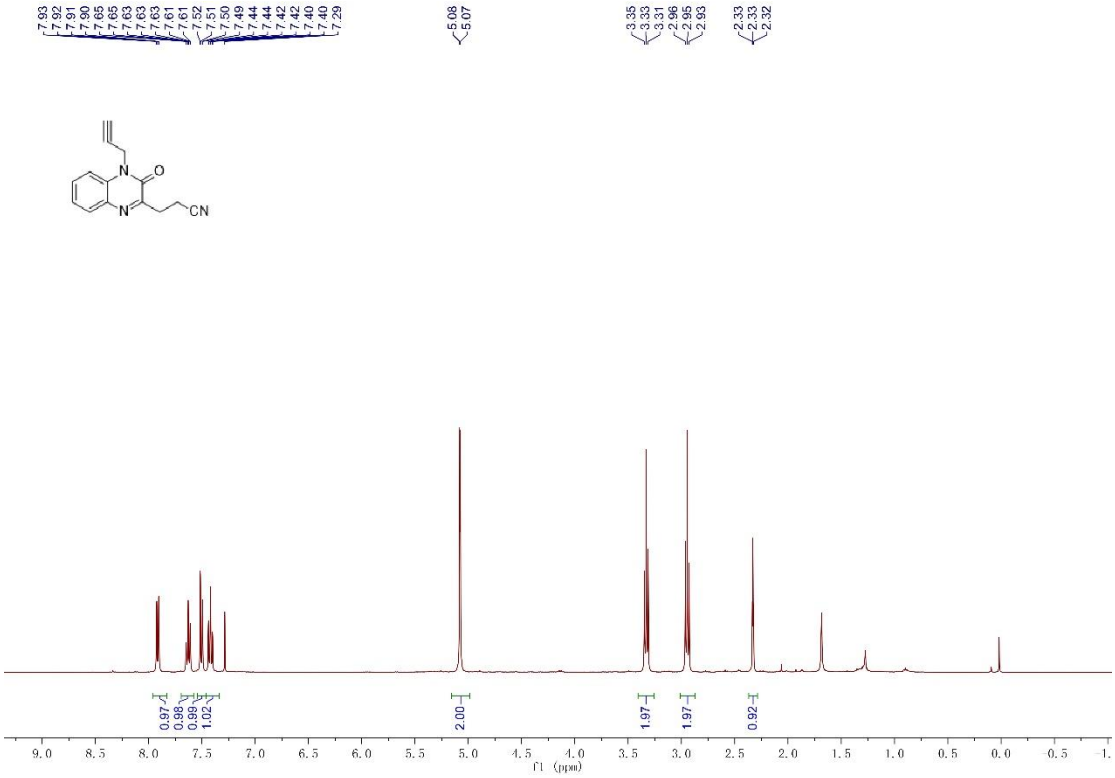


^{13}C NMR of **24**

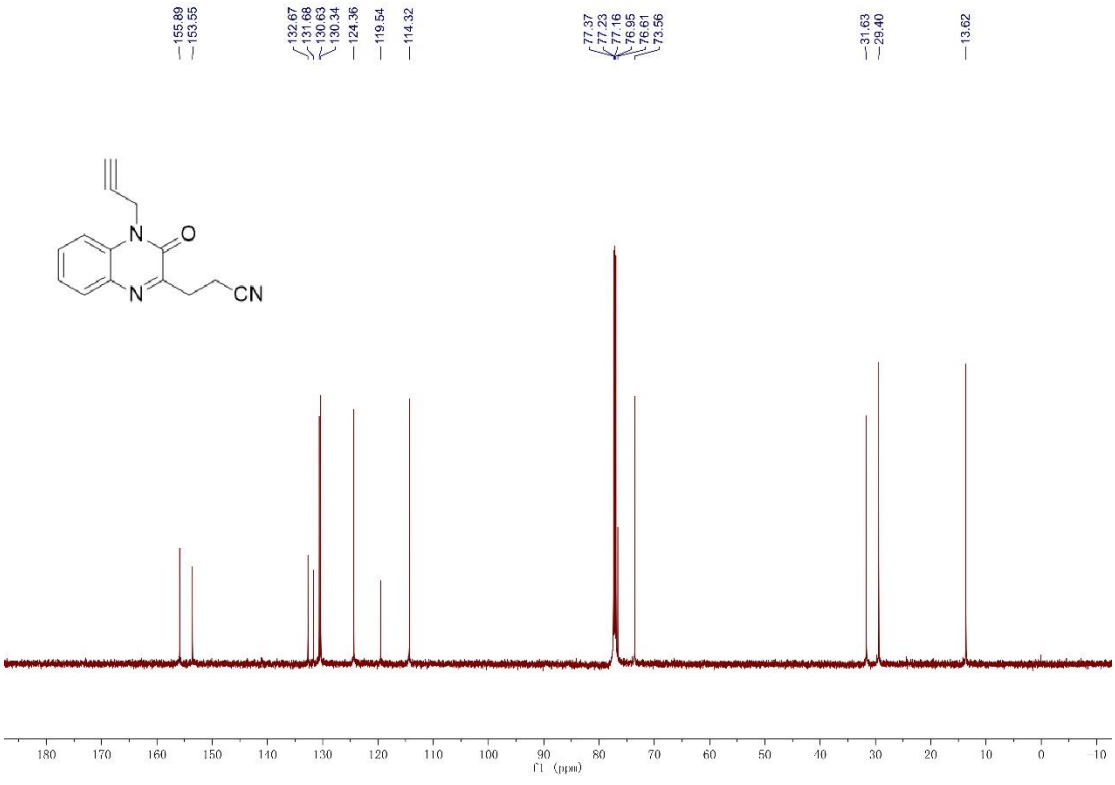




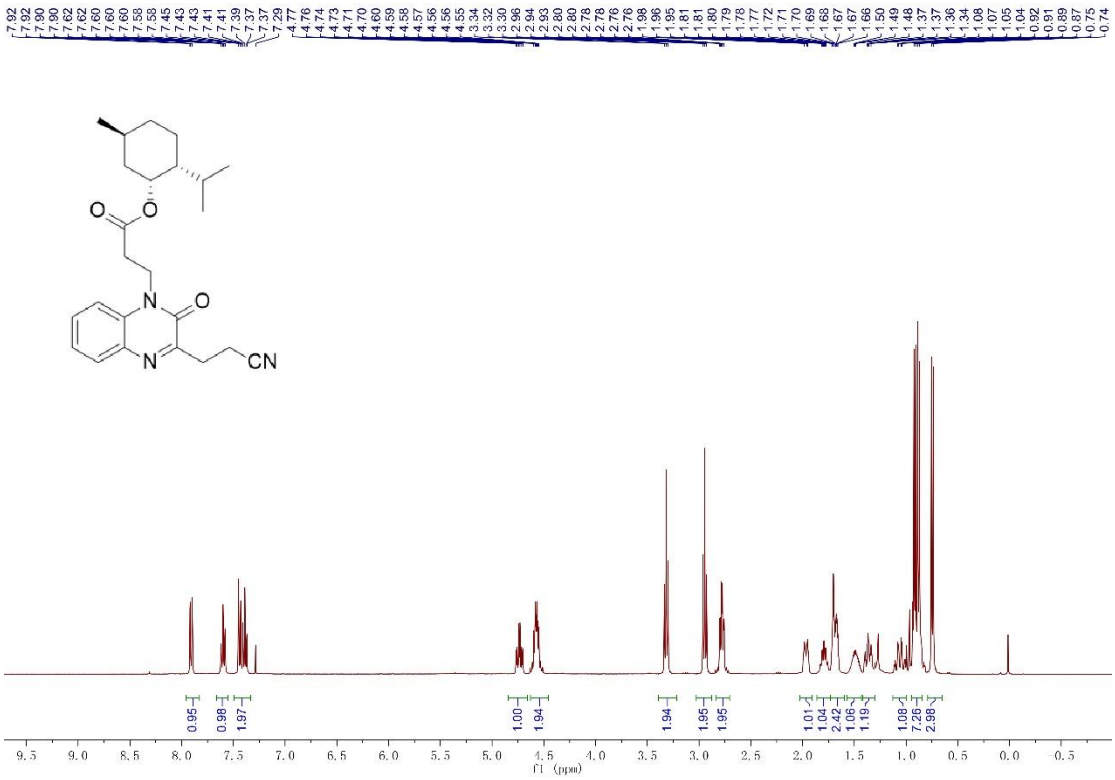
^{1}H NMR of **25**



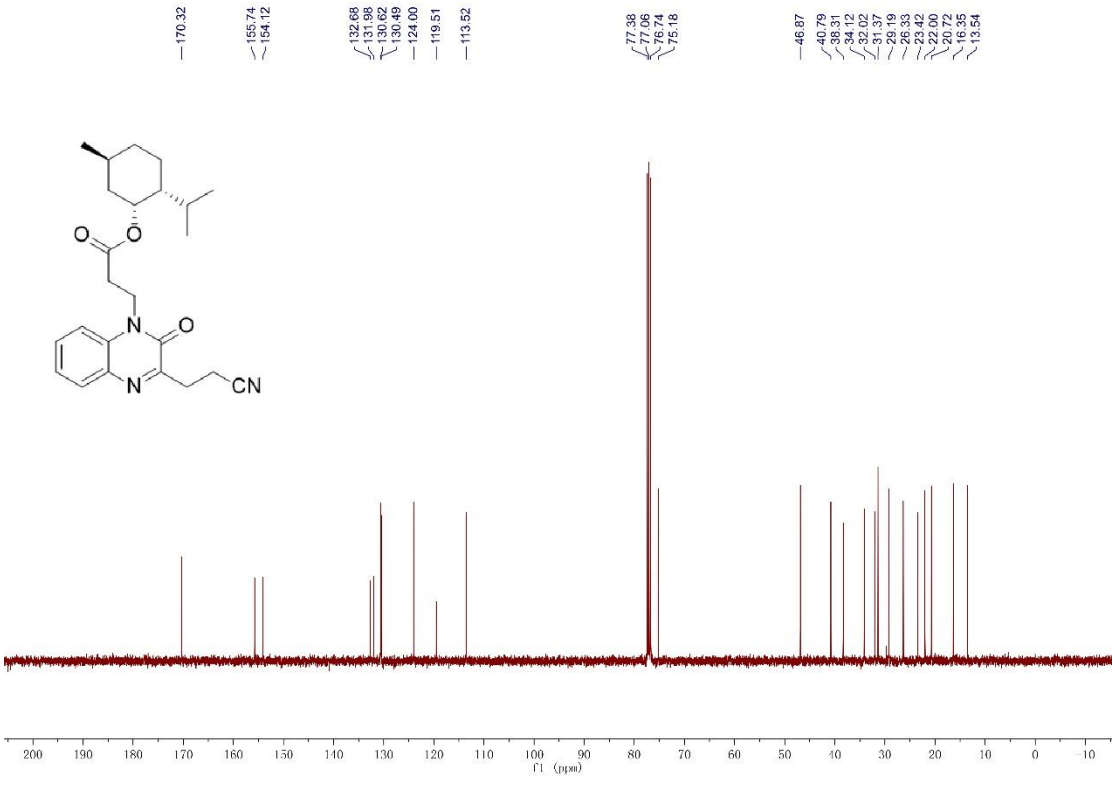
^{13}C NMR of **25**



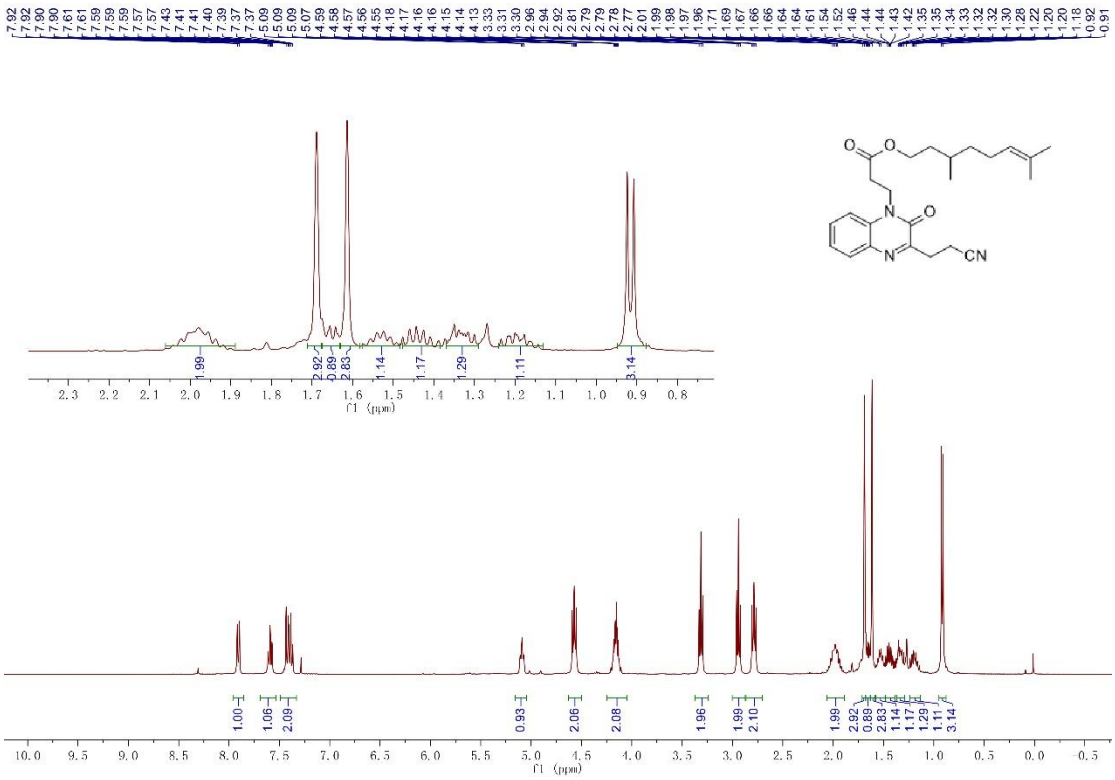
^{1}H NMR of **26**



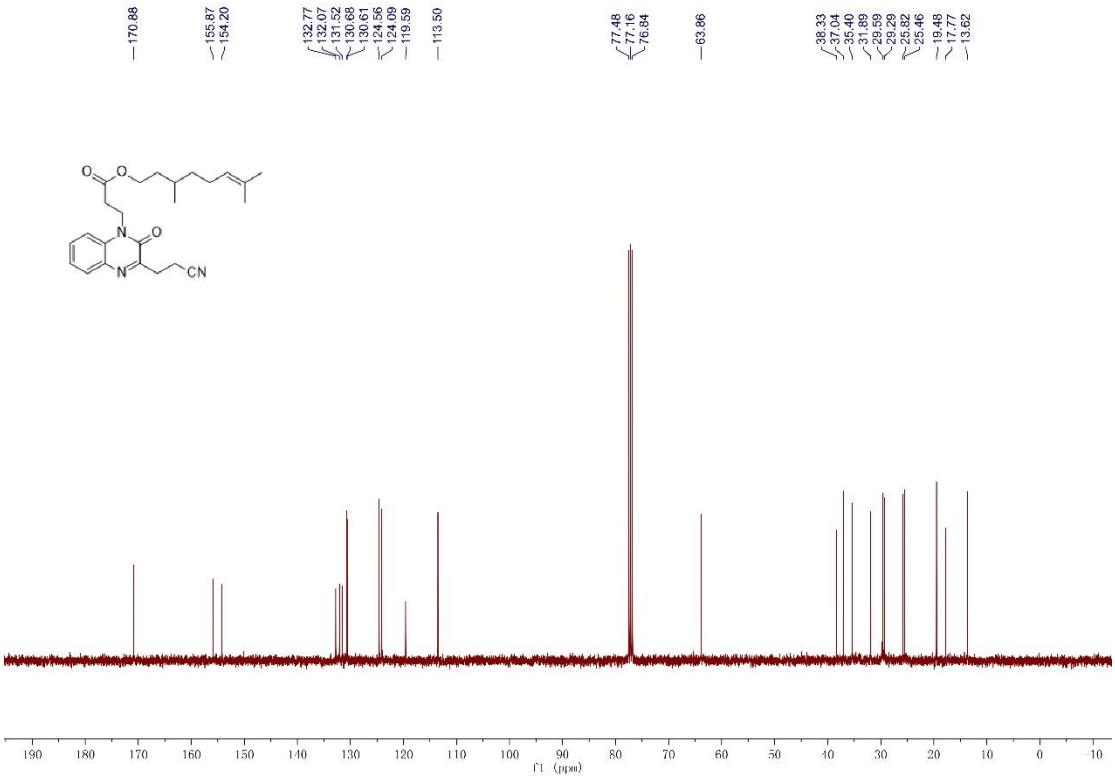
^{13}C NMR of **26**



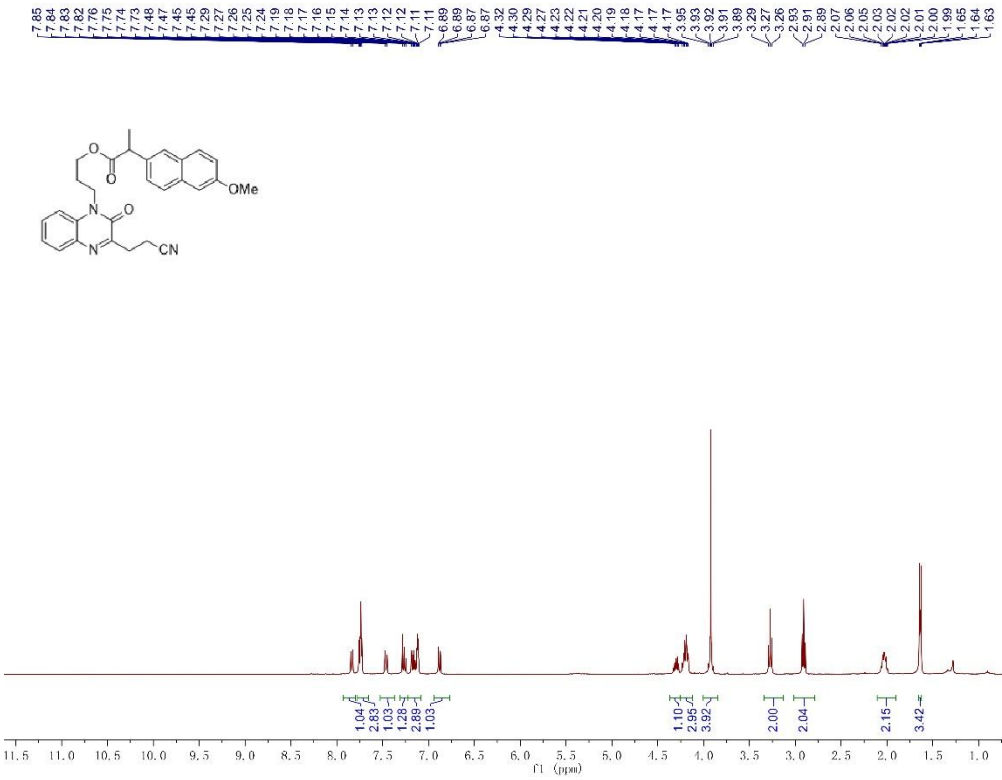
^{1}H NMR of **27**



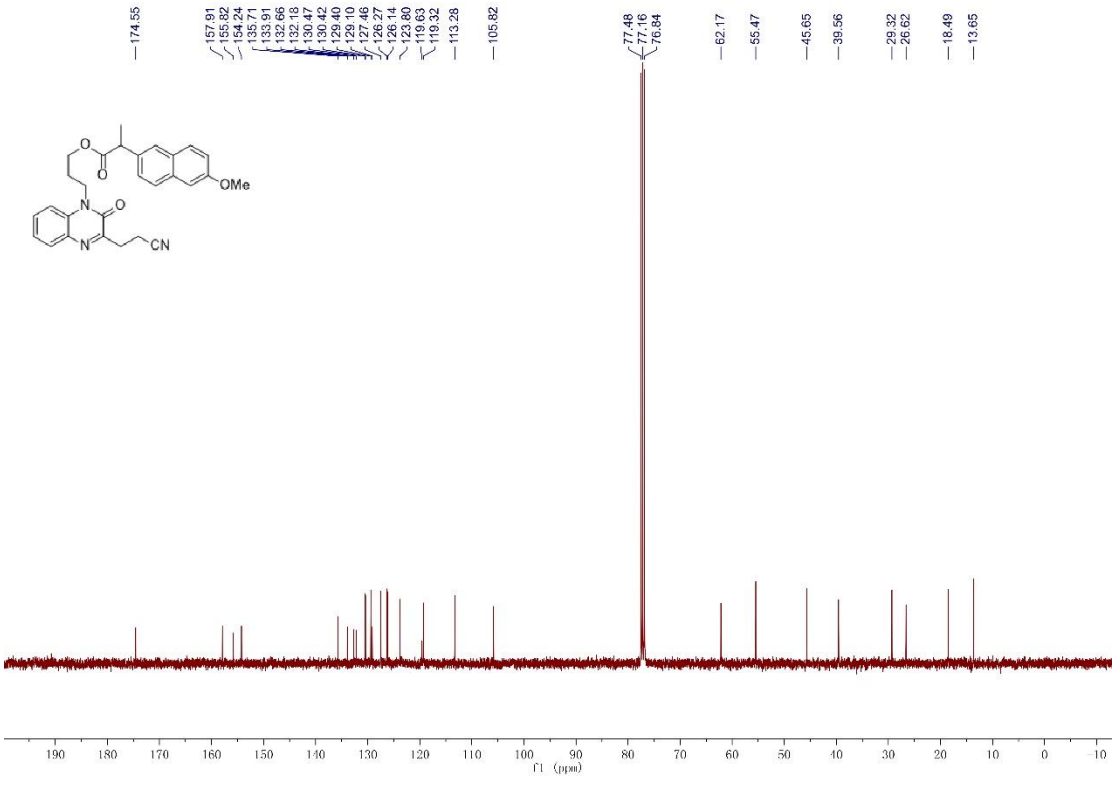
^{13}C NMR of **27**



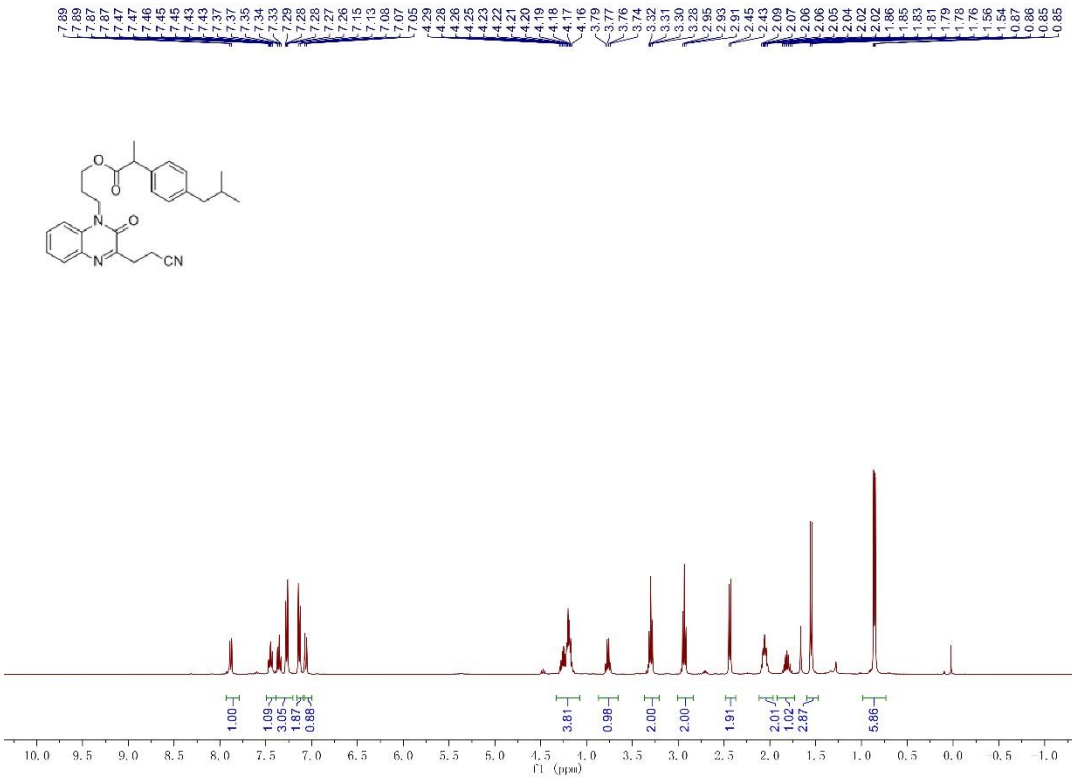
^{1}H NMR of **28**



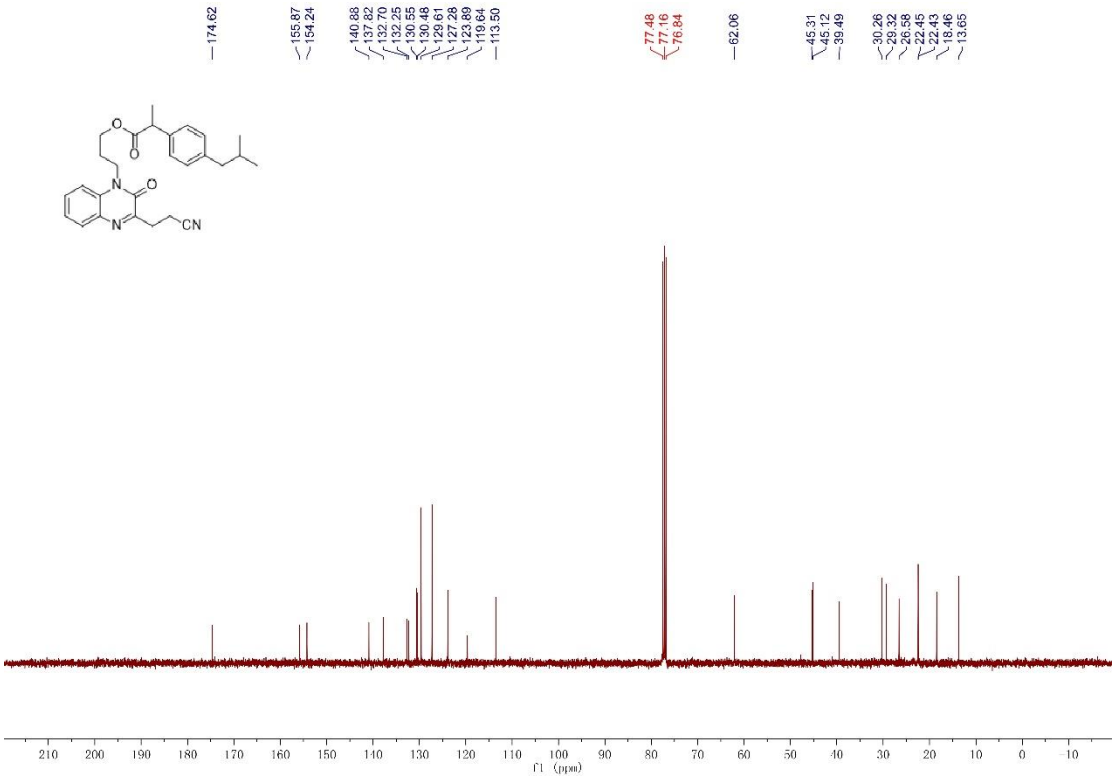
^{13}C NMR of **28**



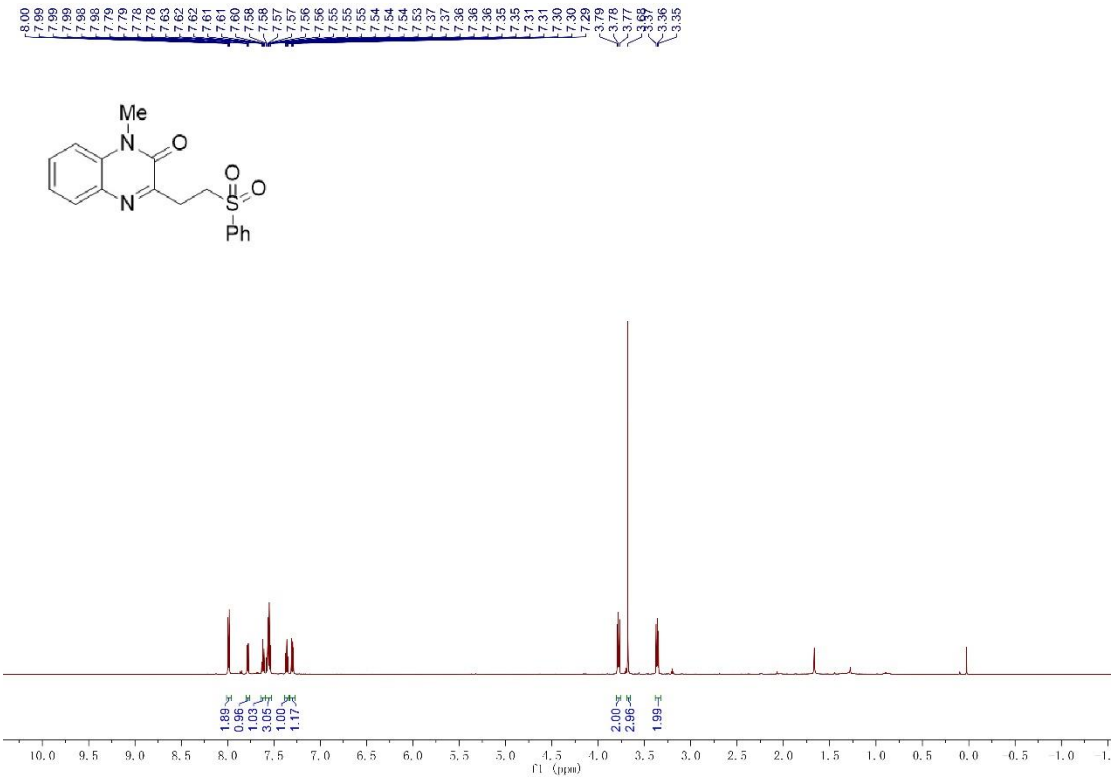
^{1}H NMR of **29**



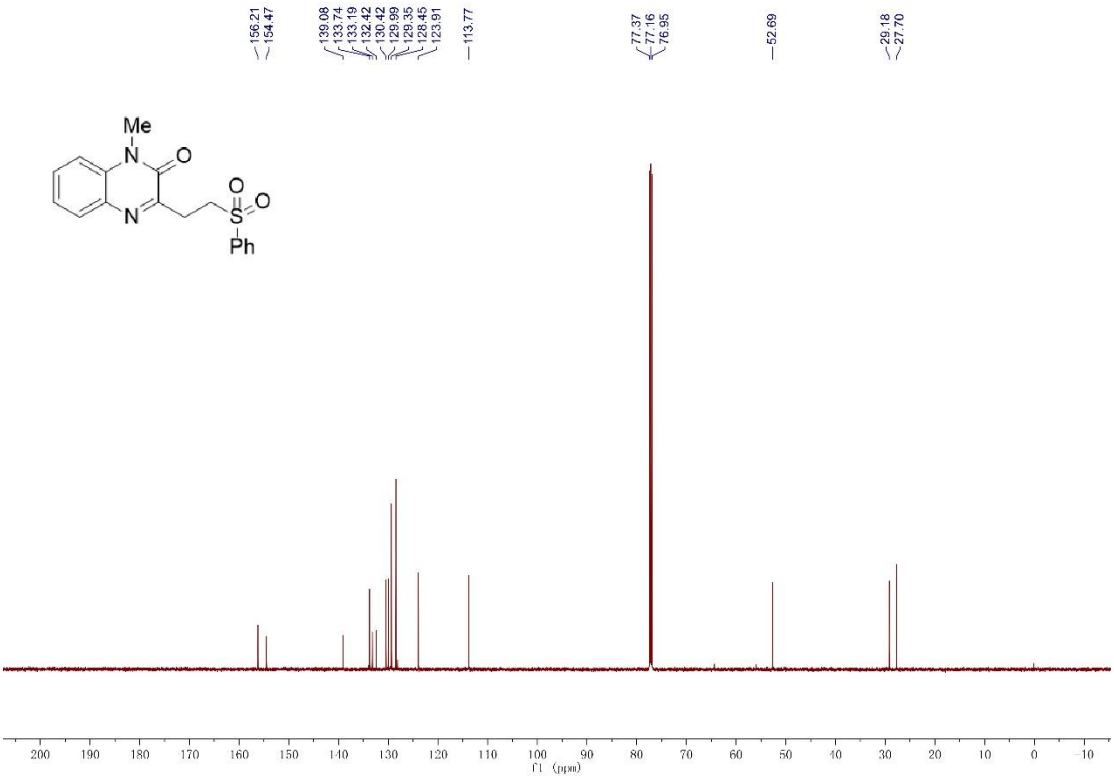
^{13}C NMR of **29**



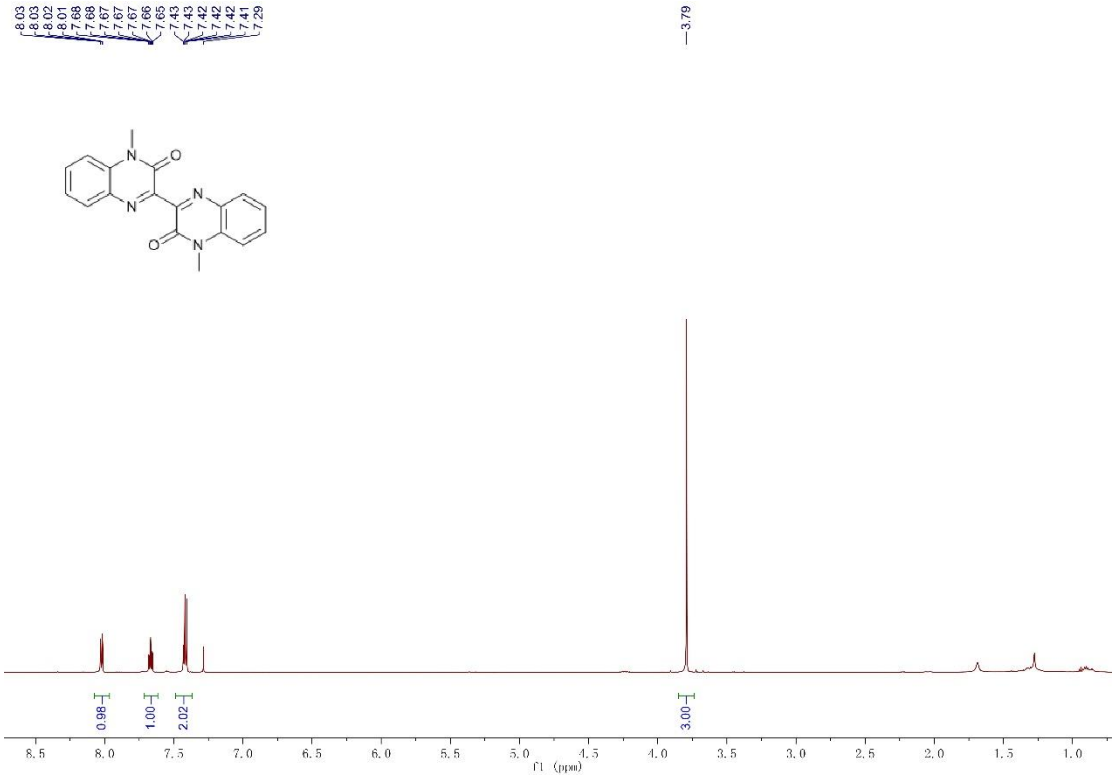
^{1}H NMR of **31**



^{13}C NMR of **31**



^{1}H NMR of **32**



^{13}C NMR of **32**