Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ring-opening C(sp^3)-C coupling of cyclobutanone oxime esters for the preparation of cyanoalkyl containing heterocycles enabled by photocatalysis

Wei Zhang,[a,b] Yu-Liang Pan,[a] Chen Yang,[a] Xin Li[a] and Bin Wang*[b]

[a] State Key Laboratory of Elemento-organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.

[b] Tianjin Key Laboratory of Structure and Performance for Functional Molecules, MOE Key Laboratory of Inorganic-Organic Hybrid Functional Material Chemistry, College of Chemistry, Tianjin Normal University, Tianjin 300387, P. R. China.

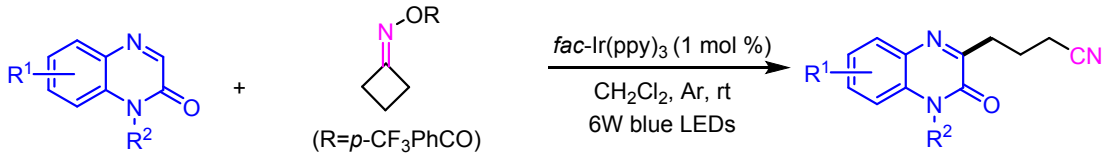
hxxywangb@tjnu.edu.cn (B. Wang)

Contents

General Information.

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. ^{1}H NMR were recorded on 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 101 MHz with complete proton decoupling spectrophotometer. Mass spectra were obtained using agilent 6520 Q-TOF electrospray ionization (ESI) mass spectrometer. Substrates 1 and 2 were synthesized according to the reported literature.[1-3]

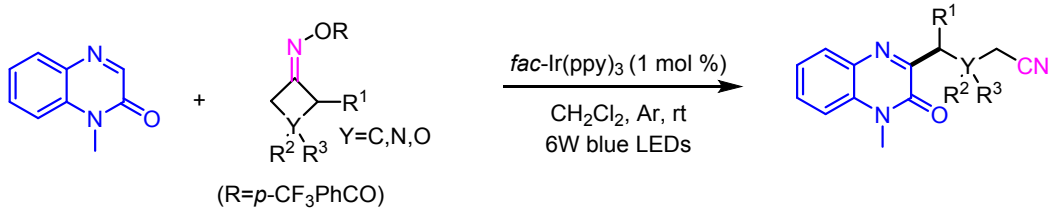
General procedure for synthesis of products 3aa-3aq



1a-1q **2a** **3aa-3aq**

1 (0.15 mmol), **2a** (0.1 mmol)，*fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at room temperature about 10-20 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 3:1~2:1) directly to give the desired product **3aa-3aq.**

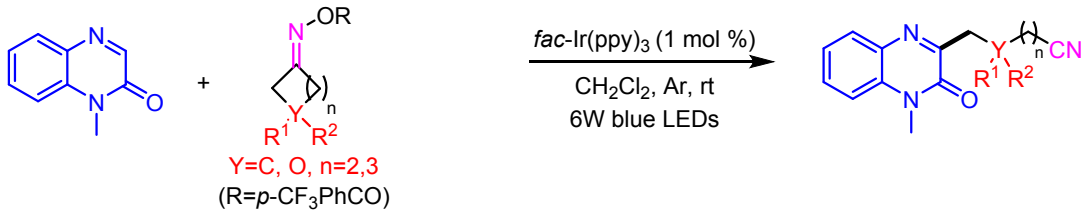
General procedure for synthesis of products 3ba-3pa



1a **2b-2p** **3ba-3pa**

1a (0.15 mmol), **2** (0.1 mmol)， *fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at room temperature about 10-20 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 3:1~2:1) directly to give the desired product **3ba-3pa.**

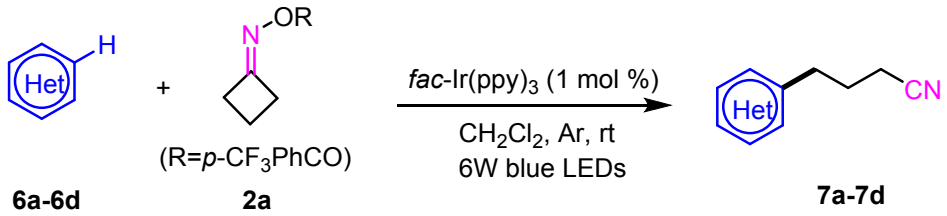
General procedure for synthesis of products 5a-5d



1a **4a-4d** **5a-5d**

1a (0.15 mmol), **4** (0.1 mmol)，*fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at room temperature until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1~2:1) directly to give the desired product **5.**

General procedure for synthesis of products 7a-7d

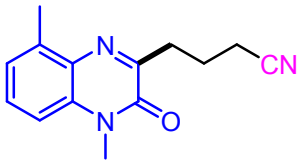


6a-6d **2a** **7a-7d**

6 (0.15 mmol), **2a** (0.1 mmol)，*fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6W blue LEDs (450-460 nm) at room temperature until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 5:1~3:1) directly to give the desired product **7.**

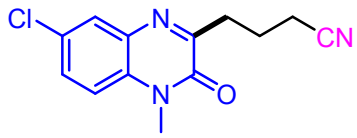
Spectral Data of Products

4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3aa***) yellow solid, 22 mg, 97% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.53 (m, 1H), 7.37-7.30 (m, 2H), 3.70 (s, 3H), 3.08 (t, *J* = 6.8 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.5, 154.7, 133.1, 132.5, 130.1, 129.8, 123.8, 119.6, 113.6, 32.3, 29.1, 22.0, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{13}N_3ONa$:250.0951, found:250.0954.

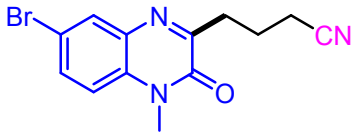


*4-(4,8-dimethyl-3-oxo-3,4-dihydroquinoxalin-2-yl)*butanenitrile (***3ab***) yellow solid, 21.7 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.43 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 3.69 (s, 3H), 3.10 (t, *J* = 6.8 Hz, 2H), 2.67 (s, 3H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ156.4, 154.7, 138.5, 133.1, 131.0, 129.7, 125.0, 119.7, 111.6, 32.1, 29.2, 21.9, 17.5, 16.6; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{15}N_3ONa$: 264.1107, found: 264.1110.

4-(7-fluoro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ac***) yellow solid, 24.5 mg, >99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.53 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.34-7.26 (m, 2H), 3.71 (s, 3H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ160.1, 158.7 (d, *J* = 244.8 Hz), 154.4, 133.1 (d, *J* = 11.1 Hz), 129.7 (d, *J* = 2.2 Hz), 119.5, 117.8 (d, *J* = 23.9 Hz), 115.3 (d, *J* = 22.7 Hz), 114.8 (d, *J* = 8.9 Hz), 32.4, 29.4, 21.8, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}FN_3ONa$: 268.0857, found:268.0860



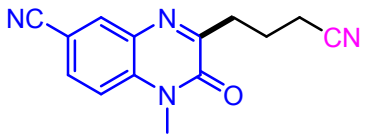
4-(7-chloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ad***) yellow solid, 23.8 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 (d, *J* = 2.4 Hz, 1H), 7.51 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.29 (d, *J* = 3.6 Hz, 1H), 3.71 (s, 3H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.57 (t, *J* = 7.2 Hz, 2H), 2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 154.4, 133.0, 131.8, 130.0, 129.2, 129.1, 119.5, 114.8, 32.3, 29.2, 21.8, 16.7; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}ClN_3ONa$: 284.0561, found:284.0565.



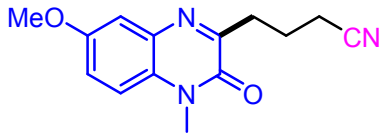
4-(7-bromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ae***) yellow solid, 30.5 mg, >99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.67-7.65 (m, 1H), 7.46-7.43 (m, 2H), 3.66 (s, 3H), 3.05 (t,

J = 6.8 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.9, 154.4, 134.1, 131.3, 131.0, 127.0, 124.1, 119.5, 116.8, 32.3, 29.2, 21.9, 16.7; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}BrN_3ONa$: 328.0056, found:328.0060.

4-(4-methyl-7-nitro-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3af***) yellow solid, 22.0mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.72 (d, *J* = 2.6 Hz, 1H), 8.41 (dd, *J* = 9.2, 2.6 Hz, 1H), 7.42 (d, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.28-2.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ161.3, 154.3, 143.4, 137.7, 131.6, 125.5, 124.6, 119.4, 114.3, 32.2, 29.7, 21.5, 16.7; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}N_4O_3Na$: 295.0802, found: 295.0804.



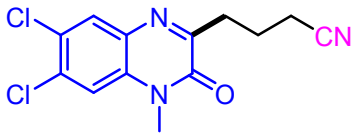
3-(3-cyanopropyl)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carbonitrile (***3ag***) yellow solid, 21.4 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.92-7.90 (m, 1H), 7.61-7.59 (m, 2H), 3.71 (s, 3H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.23 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.2, 154.2, 134.6, 133.5, 130.8, 126.7, 119.4, 118.1, 117.9, 113.2, 32.5, 29.3, 21.7, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{15}N_3O_2Na$: 275.0903, found:275.0906.



4-(7-methoxy-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ah***) yellow solid, 10.5 mg, 41% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.33 (d, *J* = 2.8 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.93 (s, 3H), 3.73 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ159.0, 156.0, 154.4, 133.3, 127.3, 119.6, 119.2, 114.6, 111.2, 55.8, 32.5, 29.2, 22.1, 16.7; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{15}N_3O_2Na$: 280.1056, found:280.1060.

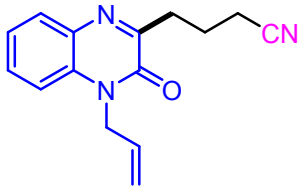
4-(6-bromo-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ai***) yellow solid, 22.6 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 1H), 7.47-7.44 (m, 2H), 3.66 (s, 3H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 2.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.9, 154.4, 134.1, 131.3, 131.0, 127.0, 124.1, 119.5, 116.8, 32.3, 29.2, 21.9, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}BrN_3ONa$: 328.0056, found:328.0058.

4-(4-methyl-6-nitro-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3aj***) yellow solid, 19.3 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.20 (m, 2H), 8.00 (d, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.18 (t, *J* = 7.2 Hz, 2H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ162.8, 154.2, 147.7, 135.8, 133.5, 130.9, 119.3, 118.3, 109.7, 32.6, 29.6, 21.6, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{12}N_4O_3Na$: 295.0802, found: 295.0804.

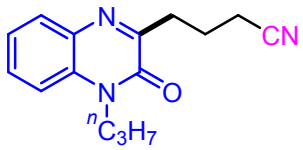


4-(6,7-dichloro-4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ak***) yellow solid, 23.6 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.39 (s, 1H), 3.65 (s, 3H), 3.07 (t, *J* = 6.8 Hz, 2H), 2.53 (t, *J* = 7.2 Hz, 2H), 2.19 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ160.1, 154.1, 134.1, 132.5, 131.5, 130.6, 127.5, 119.4, 115.2, 32.3, 29.4, 21.7, 16.7; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{13}H_{11}Cl_2N_3ONa$: 318.0171, found:318.0175.

4-(4-methyl-3-oxo-3,4-dihydrobenzo[g]quinoxalin-2-yl)butanenitrile (***3al***) yellow solid, 27.7mg, >99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.93 (dd, *J* = 26.4, 8.4 Hz, 2H), 7.63-7.53 (m, 2H), 7.51-7.47 (m, 1H), 3.75 (s, 3H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ159.0, 154.6, 133.5, 131.8, 131.6, 129.7, 128.9, 128.4, 127.9, 127.2, 125.4, 119.6, 110.1, 32.4, 29.1, 22.0, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{15}N_3ONa$: 300.1107, found:300.1111.

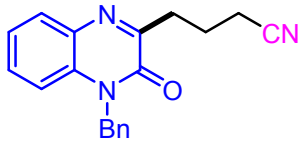


4-(4-allyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3am***) yellow solid, 24.3 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.53-7.49 (m, 1H), 7.36-7.32 (m, 1H), 7.29 (dd, *J* = 8.4, 0.4 Hz, 1H), 5.98-5.88 (m, 1H), 5.27 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.16 (dd, *J* = 17.2, 0.4 Hz, 1H), 4.90 (dt, *J* = 5.2, 1.8 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.5, 154.3, 132.7, 132.3, 130.5, 130.0, 129.9, 123.7, 119.6, 118.2, 114.3, 44.5, 32.3, 22.0, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{15}N_3ONa$: 276.1107, found:276.1112.

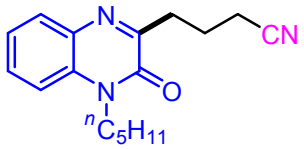


4-(3-oxo-4-propyl-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3an***) yellow solid, 25.5 mg, 99% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.53 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.36-7.30 (m, 2H), 4.23-4.19 (m, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.23 (m, 2H), 1.84-

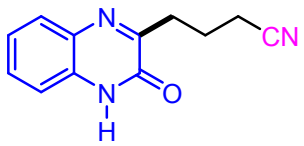
1.74 (m,2H), 1.05 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 154.5, 132.8, 132.3, 130.0, 129.9, 123.5, 119.6, 113.7, 43.9, 32.3, 22.1, 20.6, 16.8, 11.4; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{17}N_3ONa$: 278.1264, found:278.1266.



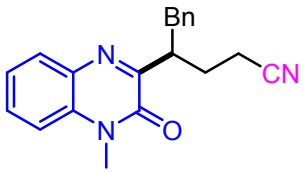
4-(4-benzyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ao***) yellow solid, 29.8 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.84 (d, *J* = 8.0, 1H), 7.45-7.40 (m, 1H), 7.34-7.22 (m, 7H), 5.50 (s, 2H), 3.15 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.27 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.6, 154.8, 135.1, 132.8, 132.4, 130.0, 129.9,129.0, 127.8, 126.9, 123.8, 119.7, 114.5, 46.0, 32.4, 22.1, 16.8; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{19}H_{17}N_3ONa$: 326.1264, found:326.1268.



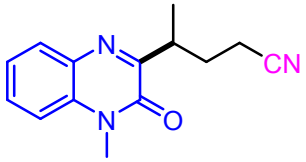
4-(3-oxo-4-pentyl-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ap***) yellow solid, 22.6 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 (ddd, *J* = 16.0, 7.3, 1.6 Hz, 1H), 7.35-7.30 (m, 2H), 4.25-4.18 (m, 2H), 3.08 (t, *J* = 7.2 Hz, 2H), 2.54 (t, *J* = 6.8 Hz, 2H), 2.22 (m, 2H), 1.79-1.71 (m, 2H), 1.47-1.35 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.5, 154.4, 132.8, 132.3, 130.0, 129.9, 123.5, 119.7, 113.6, 42.4, 32.2, 29.1, 27.0, 22.4, 22.1, 16.8, 14.0; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{17}H_{21}N_3ONa$: 306.1577, found:306.1579.



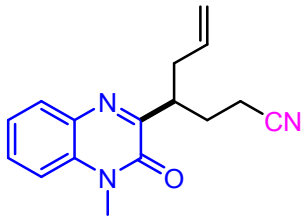
4-(3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3aq***) yellow solid, 17.0 mg, 78% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ12.37 (s, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.50 (td, *J* = 7.7, 1.4 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.1 Hz, 2H), 2.05 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.2, 154.6, 131.8, 131.5, 129.5, 128.1, 123.0, 120.6, 115.2, 31.3, 21.6, 15.9; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{12}H_{11}N_3ONa$: 236.0794, found:236.0797.



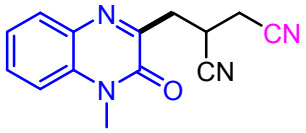
(R)-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-5-phenylpentanenitrile (***3ba***) yellow solid, 31.2 mg, 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 1H), 7.58-7.52 (m, 1H), 7.39-7.26 (m, 6H), 7.21-7.16 (m, 1H), 3.86-3.84 (m, 1H), 3.71 (s, 3H), 3.27-3.20 (m, 1H), 2.39-2.22 (m, 3H), 2.03-1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 154.6, 139.3, 133.0, 132.5, 130.3, 130.0, 129.2, 128.5, 126.4, 123.8, 119.7, 113.7, 42.6, 39.3, 29.2, 27.1, 15.1; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{20}H_{19}N_3O$: 340.1420, found:340.1425.



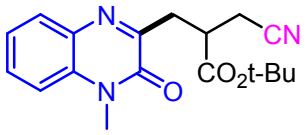
(S)-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)pentanenitrile (***3ca***) yellow solid, 23.2 mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 (ddd, *J* = 16.0, 7.3, 1.5 Hz, 1H), 7.38-7.30 (m, 2H), 3.71 (s, 3H), 3.67-3.58 (m, 1H), 2.47-2.32 (m, 3H), 2.04-1.94 (m, 1H), 1.32 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 154.5, 133.0, 132.5, 130.1, 130.0, 123.7, 119.8, 113.7, 35.5, 29.6, 29.2, 18.5, 15.2; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{14}H_{15}N_3O$: 242.1288, found: 242.1290.



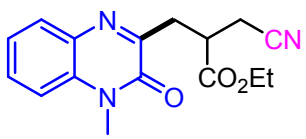
(R)-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)hept-6-enenitrile (**3da**) yellow oil, 20.8 mg, 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (ddd, *J* = 16.0, 7.3, 1.6 Hz, 1H), 7.38-7.33 (m, 2H), 5.83-5.75 (m, 1H), 5.08-4.99 (m, 2H), 3.71 (s, 3H), 3.69-3.62 (m, 1H), 2.66-2.58 (m, 1H), 2.41-2.30 (m, 4H), 2.13-2.04 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 154.6, 135.4, 132.9, 132.5, 130.2, 130.0, 123.7, 119.8, 117.4, 113.7, 40.2, 37.3, 29.3, 27.4, 15.1; HRMS (EI): m/z [M + Na]$^+$ calcd for $C_{16}H_{17}N_3O$: 290.1264, found: 290.1266.



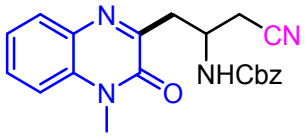
2-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)succinonitrile (***3ea***) yellow solid, 22.2 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.87 (d, *J* = 8.0, 1H), 7.61 (t, *J* = 7.6, 1H), 7.41-7.34 (m, 2H), 3.81 (m, 1H), 3.72 (s, 3H), 3.51-3.34 (m, 2H), 2.97 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ154.3, 153.8, 133.2, 132.1, 131.0, 130.1, 124.1, 118.9, 115.7, 113.9, 34.7, 29.3, 25.1, 20.7; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{14}H_{13}N_4O$: 253.1084, found:253.1087.



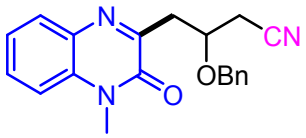
tert-butyl 3-cyano-2-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)propanoate (***3fa***) yellow solid, 26.8 mg, 82% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.78 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 (ddd, *J* = 8.5, 7.2, 1.2 Hz, 1H), 7.36-7.31 (m, 2H), 3.70 (s, 3H), 3.44-3.38 (m, 2H), 3.30-3.23 (m, 1H), 2.88-2.74 (m, 2H), 1.41 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ171.1, 156.7, 154.6, 133.1, 132.2, 130.2, 129.7, 123.8, 118.0, 113.7, 81.9, 39.3, 34.5, 29.1, 27.9,19.2; HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{21}N_3O_3Na$: 350.1475, found:350.1478.



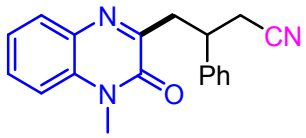
ethyl 3-cyano-2-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)propanoate (***3ga***) brown solid, 26.3 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56 (ddd, *J* = 16.0, 7.3, 1.6 Hz, 1H), 7.36-7.31 (m, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 3.70 (s, 3H), 3.51-3.45 (m, 2H), 3.31 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.93-2.80 (m, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ172.0, 156.4, 154.6, 133.1, 132.2, 130.3, 129.8, 123.8, 117.9, 113.7, 61.5, 38.5, 34.3, 29.1, 19.1, 14.1; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{18}N_3O_3$: 300.1343, found:300.1345.



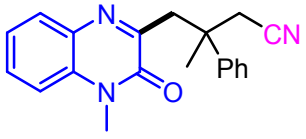
benzyl (1-cyano-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)propan-2-yl)carbamate (***3ha***) yellow solid, 34.1 mg, 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1H), 7.60-7.56 (m, 1H), 7.39-7.26 (m, 7H), 6.06 (d, *J* = 7.2 Hz, 1H), 5.05 (s, 2H), 4.53-4.46 (m,1H), 3.68 (s, 3H), 3.38-3.25 (m, 2H), 2.99-2.83 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 155.7, 155.2, 136.2, 133.1, 132.4, 130.6, 130.0, 128.5, 128.2, 128.1, 124.0, 117.2, 113.8, 66.9, 46.7, 37.0, 29.3, 23.4; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{21}H_{20}N_4O_3Na$: 399.1428, found:399.1431.



3-(benzyloxy)-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanenitrile (***3ia)*** brown oil, 16.7 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (ddd, *J* = 15.6, 8.4, 1.6 Hz, 1H), 7.39-7.35 (m, 1H), 7.31-7.26 (m, 3H), 7.22-7.19 (m, 3H), 4.73-4.66 (m, 2H), 4.43– 4.40 (m, 1H), 3.65 (s, 3H), 3.42 (dd, *J* = 15.2, 6.4 Hz, 1H), 3.18 (dd, *J* = 15.2, 6.5 Hz, 1H), 2.78 (qd, *J* = 16.8, 4.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ156.4, 154.7, 137.4, 133.2, 132.5, 130.3, 130.0, 128.3, 128.1, 127.8, 123.8, 117.7, 113.7, 72.4, 72.1, 38.6, 29.1, 23.7; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{19}N_3O_2Na$: 356.1369, found:356.1375.

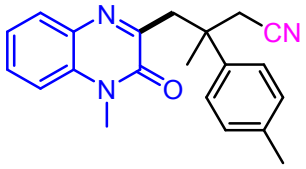


4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-3-phenylbutanenitrile (***3ja***) yellow solid, 16.7 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.53 (m, 1H), 7.40-7.29 (m, 6H), 7.27-7.23 (m, 1H), 3.92-3.85 (m, 1H), 3.69 (s, 3H), 3.48-3.34 (m, 2H), 2.88-2.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.4, 154.8, 141.6, 133.1, 132.5, 130.2, 129.9, 128.9, 127.5, 127.4, 123.8, 118.5, 113.7, 38.9, 38.6, 29.7, 29.2, 24.3; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{18}N_3O$: 304.1444, found:304.1448.

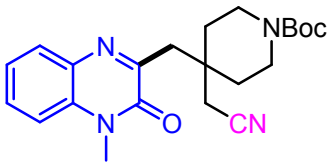


3-methyl-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-3-phenylbutanenitrile (***3ka***) yellow solid, 19.2 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.56-7.51 (m, 1H), 7.44-7.41 (m, 2H), 7.35-7.26 (m, 4H), 7.25-7.20 (m, 1H), 3.64 (s, 3H), 3.52-3.37 (m, 2H), 3.25-3.10

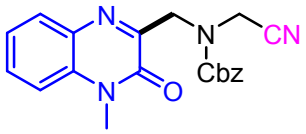
(m, 2H), 1.69 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 155.1, 144.6, 133.0, 132.2, 130.3, 129.9, 128.5, 126.9, 125.6, 123.7, 118.6, 113.6, 42.9, 41.1, 29.6, 29.3, 26.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{20}N_3O$: 318.1601, found:318.1605.



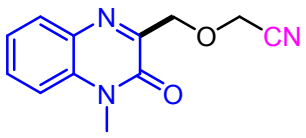
3-methyl-4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-3-(p-tolyl)butanenitrile (***3la***) yellow oil, 23.2 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.77 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.56-7.52 (m, 1H), 7.35-7.28 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.65 (s, 3H), 3.50-3.36 (m, 2H), 3.22-3.08 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 155.2, 141.8, 136.5, 133.0, 132.3, 130.2, 130.0, 129.2, 125.5, 123.7, 118.7, 113.6, 42.9, 40.8, 29.6, 29.3, 26.0, 20.9; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{21}H_{21}N_3ONa$: 354.1577, found:354.1581.



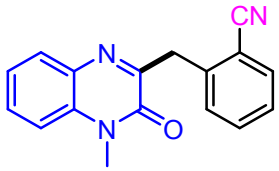
tert-butyl 4-(cyanomethyl)-4-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)piperidine-1-carboxylate (***3ma***) yellow oil, 26.6 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57 (ddd, *J* = 16.0, 7.2, 1.6 Hz, 1H), 7.38-7.30 (m, 2H), 3.71 (s, 3H), 3.63-3.50 (m, 4H), 3.19 (s, 2H), 2.78 (s, 2H), 1.77-1.72 (m, 2H), 1.67-1.61 (m, 2H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ157.2, 147.3, 133.0, 132.3, 130.9, 130.5, 130.0, 128.8, 123.8, 113.7, 79.7, 38.7, 37.7, 36.0, 34.4, 29.4, 28.4, 26.9; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{22}H_{29}N_4O_3$: 397.2234, found: 397.2237.



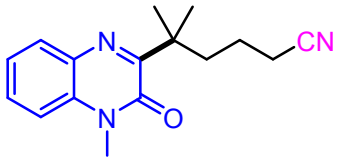
benzyl (cyanomethyl)((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)carbamate (***3na***) yellow solid, 33.5 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.81 (m, 1H), 7.62-7.56 (m, 1H), 7.45-7.32 (m, 4H), 7.20 (d, *J* = 0.8 Hz, 3H), 5.27-5.15 (m, 2H), 4.88-4.85 (m, 2H), 4.54-4.43 (m, 2H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 153.4, 135.8, 133.1, 132.2, 130.7, 130.3, 128.6, 128.4, 128.1, 127.8, 124.0, 115.7, 113.7, 68.1, 49.3, 37.0, 28.9; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{18}N_4O_3Na$: 385.1271, found:385.1275.



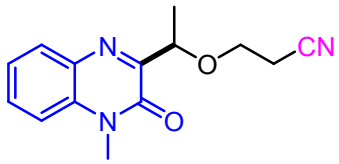
2-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methoxy)acetonitrile (***3oa***) yellow solid, 19.9 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 0.4 Hz, 1H), 7.64-7.60 (m, 1H), 7.42-7.35 (m, 2H), 4.97 (s, 2H), 4.59 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.1, 153.9, 133.2, 132.4, 131.0, 130.5, 124.1, 115.8, 113.8, 70.0, 56.6, 29.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{12}N_3O_2$: 230.0924, found:230.0927.



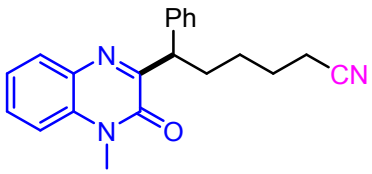
2-((4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)methyl)benzonitrile (***3pa***) white solid, 20.6 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.78 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.56-7.49 (m, 2H), 7.44-7.43 (m, 1H), 7.37-7.29 (m, 3H), 4.51 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 154.5, 140.9, 133.3, 133.0, 132.6, 132.6, 130.5, 130.3, 130.2, 127.1, 123.7, 118.2, 113.9, 113.6, 39.0, 29.2; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{14}N_3O$: 276.1131, found: 276.1135.



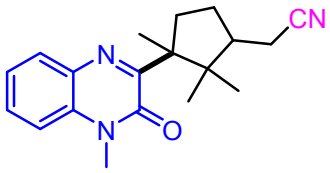
5-methyl-5-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)hexanenitrile (***5a***) colorless oil, 24.2 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.88-7.86 (m, 1H), 7.58-7.53 (m, 1H), 7.38-7.29 (m, 2H), 3.71 (s, 3H), 2.34 (td, *J* = 7.2, 1.8 Hz, 2H), 2.18-2.13 (m, 2H), 1.62-1.54 (m, 2H), 1.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 153.7, 133.2, 132.1, 130.2, 130.0, 123.4, 119.8, 113.4, 42.5, 39.3, 28.9, 26.1, 21.6, 17.7; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{19}N_3ONa$: 292.1420, found:292.1426.



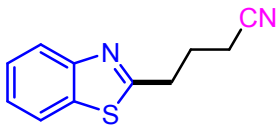
(R)-3-(1-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)ethoxy)propanenitrile (***5b***) yellow oil, 24.2mg, 96% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59 (ddd, *J* = 8.5, 7.2, 1.2 Hz, 1H), 7.40-7.32 (m, 2H), 5.14 (q, *J* = 6.5 Hz, 1H), 3.89-3.84 (m, 1H), 3.76-3.73 (m, 1H), 3.71 (s, 3H), 2.69 (td, *J* = 6.6, 3.2 Hz, 2H), 1.58 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ158.6, 154.2, 133.2, 132.5, 130.7, 130.5, 123.9, 117.8, 113.7, 74.4, 64.5, 29.0, 19.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{16}N_3O_2$: 258.1237, found:258.1240.



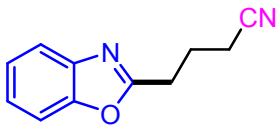
(R)-6-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)-6-phenylhexanenitrile (***5c***) yellow solid, 15.2mg, 46% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.55-7.51 (m, 1H), 7.45-7.43 (m, 2H), 7.38-7.34 (m, 1H), 7.30-7.25 (m, 3H), 7.21-7.17 (m, 1H), 4.67 (t, *J* = 7.6 Hz, 1H), 3.63 (s, 3H), 2.38-2.29 (m, 3H), 2.13-2.04 (m, 1H), 1.75-1.67 (m, 2H), 1.53-1.39 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 154.5, 141.1, 133.0, 132.7, 130.1, 129.9, 128.6, 128.5,126.8, 123.5, 119.7, 113.5; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{21}H_{21}N_3ONa$: 354.1577, found:354.1580.



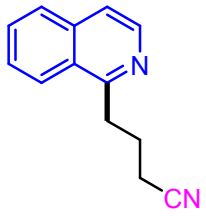
2-((3S)-2,2,3-trimethyl-3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)cyclopentyl)acetonitrile (***5d***) colorless oil, 13.2mg, 43% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.87(dd, *J* = 8.0, 1.5 Hz, 1H), 7.56-7.52 (m,1H), 7.37-7.27 (m,2H), 3.70 (s, 3H), 3.37 (dd, *J* = 13.1, 6.5 Hz, 1H), 2.45 (d, *J* = 14.2 Hz, 1H), 2.39-2.22 (m,2H), 2.00-1.95 (m,1H), 1.93-1.90 (m,2H), 1.58 (s, 3H), 1.02 (d, *J* = 2.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 153.8, 133.3, 131.8, 130.2, 129.8, 123.4, 119.8, 113.4, 53.5, 47.0, 45.3, 42.4, 41.0, 28.9, 28.8, 27.8, 23.8, 17.3; HRMS (ESI): m/z $[M + H]^+$ calcd for : $C_{19}H_{24}N_3O$: 310.1914, found: 310.1914.



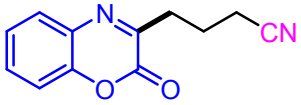
4-(benzo[d]thiazol-2-yl)butanenitrile (***7a***) colorless oil, 8.0mg, 40% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.50-7.46 (m,1H), 7.41-7.36(m,1H), 3.28 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.33-2.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 153.2, 135.0, 126.2, 125.1,122.7, 121.6, 119.0, 32.5, 24.8, 16.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{11}N_2S$: 203.0637, found:203.0640.



4-(benzo[d]oxazol-2-yl)butanenitrile (***7b***) colorless oil, 5.5mg, 30% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.65 (m, 1H), 7.52-7.48 (m, 1H), 7.35-7.31 (m, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 150.8, 141.1, 124.9, 124.4, 119.8, 118.8, 110.5, 27.1, 22.4, 16.6; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{11}H_{11}N_2O$: 187.0866, found:187.0863.



4-(isoquinolin-1-yl)butanenitrile (***7c***) yellow oil, 7.1mg, 36% ^{1}H NMR (400 MHz, $CDCl_3$) 8.45 (d, *J* = 5.6 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.74-7.70 (m, 1H), 7.67-7.63 (m,1H), 7.58 (d, *J* = 5.6 Hz, 1H), 3.49 (t, *J* = 7.2 Hz, 2H), 2.55 (t, *J* = 6.8 Hz, 2H), 2.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 141.2, 136.4, 130.4, 127.7, 127.6, 127.0, 124.8, 120.0, 119.7, 32.8, 24.4, 17.0; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{13}N_2$: 197.1073, found:197.1073.

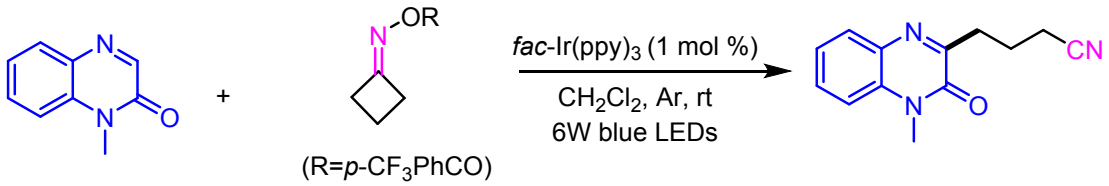


4-(2-oxo-2H-benzo[b][1,4]oxazin-3-yl)butanenitrile (***7d***) yellow solid, 14.4 mg, 67% yield; ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.50 (ddd, *J* = 16.0, 7.5, 1.2 Hz, 1H), 7.37 (td, *J* = 7.6, 1.2 Hz, 1H), 7.30 (dd, *J* = 8.0, 0.8 Hz, 1H), 3.06 (t, *J* = 7.2 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ155.5, 152.8, 146.3, 131.0, 130.9, 128.9, 125.6, 119.2, 116.5, 32.2, 21.6, 16.7; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{11}N_2O_2$: 215.0815, found:215.0818.

Synthetic Utility of the Methodology

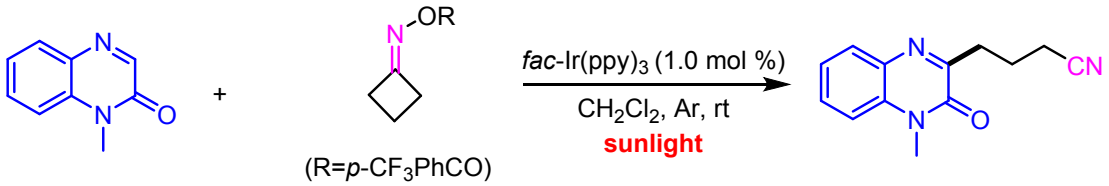
Large-scale Reaction



1a, 3 mmol **2a,** 2 mmol **3aa**, 0.41g, 90%

1a (3 mmol), **2a** (2 mmol), *fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 50 mL Schlenk tube. The reaction mixture was degassed three times. 20 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at room temperature about 20 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 3:1~2:1) directly to give the desired product **3aa.**

Sunlight-driven experiment

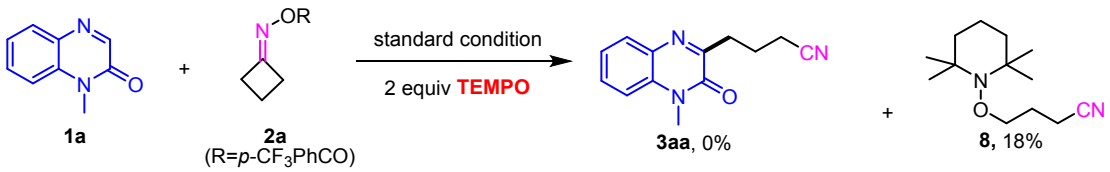


1a, 0.15 mmol **2a,** 0.1 mmol **3aa**, 87%

1a (0.15 mmol), **2a** (0.15 mmol), *fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an ovendried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. The solution was stirred under solar light for a day (Location: 39°6′2″ N, 117°9′51″ E). Afterward, the crude mixture was purified by column chromatography (eluent: petroleum ether/ethyl acetate 2:1) to give the product **3aa** in 87% yield as a yellow solid.

The Mechanism Studies and Spectral Data of Products

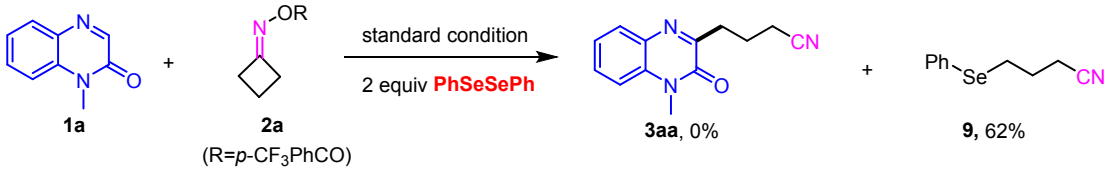
TEMPO trapping experiment



1 (0.15 mmol), **2a** (0.1 mmol), *fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at room temperature about 15 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 20:1) directly to give the desired product **8.**

4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanenitrile (***8***) colorless oil 4mg, 18% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.92-1.87 (m, 2H), 1.46-1.43 (m, 6H), 1.15 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.8，73.6，59.8，39.6，33.1，25.1, 20.1, 17.1, 4.5; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{25}N_2O$: 225.1961, found:225.1965.

PhSeSePh trapping experiment



1 (0.15 mmol), **2a** (0.1 mmol), *fac*-Ir(ppy)$_3$ (1 mol %) and a magnetic stir bar were added to an oven-dried 10 mL Schlenk tube. The reaction mixture was degassed three times. 1 mL of degassed dichloromethane was then added to the mixture in the presence of a flow of argon. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at room temperature about 15 h until the reaction was completed as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethylacetate 20:1) directly to give the desired product **9.**

4-(phenylselanyl)butanenitrile (***9***) colorless oil, 13.9mg, 62% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42(m,2H), 7.25-7.19(m, 3H), 2.92 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 7.2 Hz, 2H), 1.92 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.2, 128.3, 127.7, 126.5, 118.0, 25.0, 24.7, 16.0; HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{10}H_{11}NNaSe$: 247.9949, found: 247.9949.

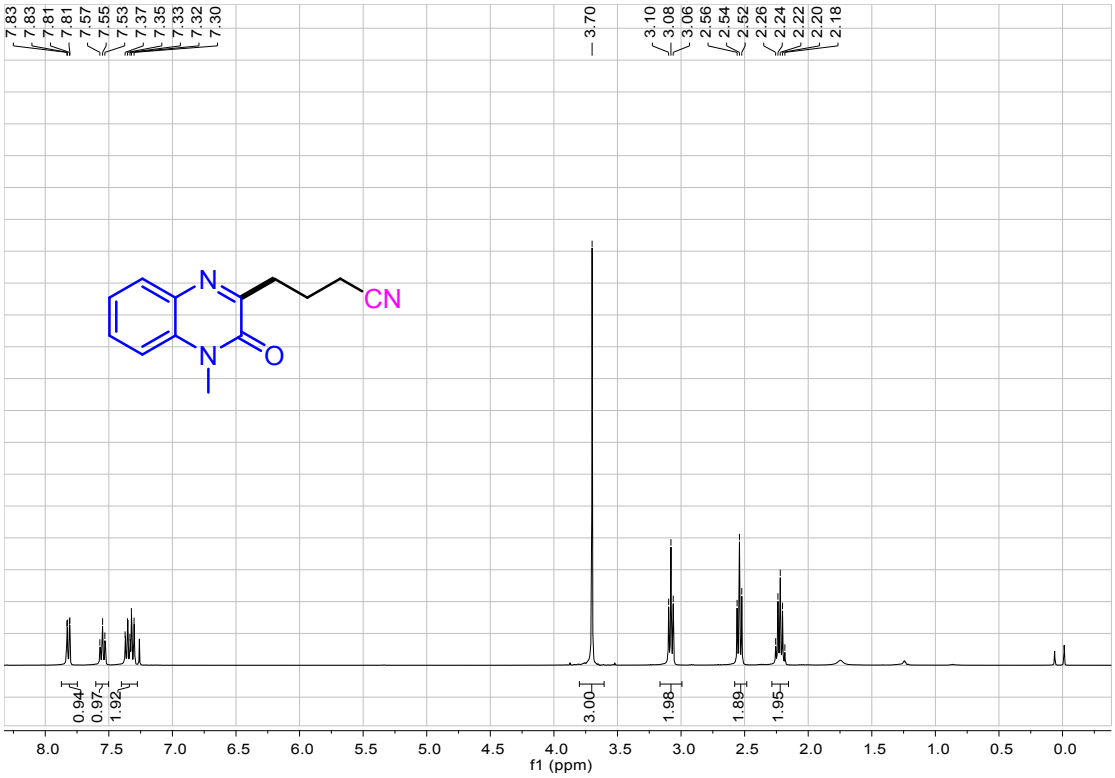
Reference:

1. L. Yang, P. Gao, X.-H. Duan, Y.-R. Gu and L.-N. Guo, *Org. Lett*., 2018, **20**, 1034.

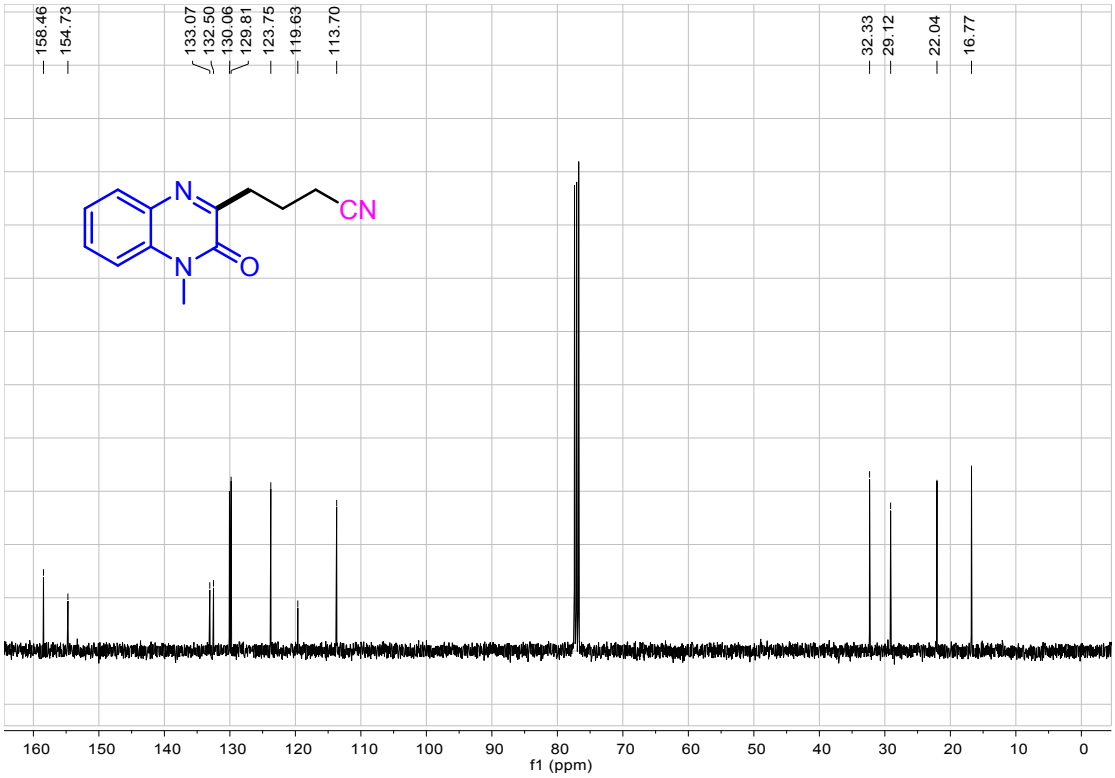
2. B. Zhao and Z. Shi, *Angew. Chem. Int. Ed.*, 2017, **56**, 12727.

3. X.-Y. Yu, J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang and W.-J. Xiao, *Angew. Chem. Int. Ed.*, 2018, **57**, 738.

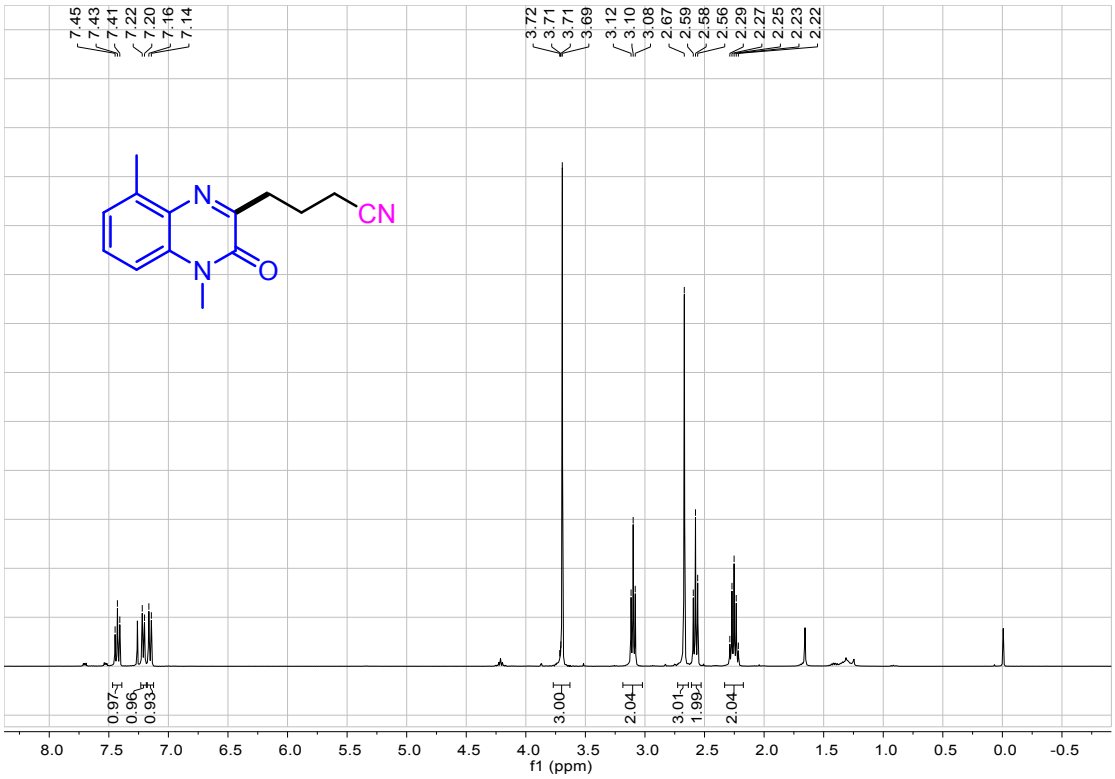
^{1}H NMR Spectrum of **3aa**



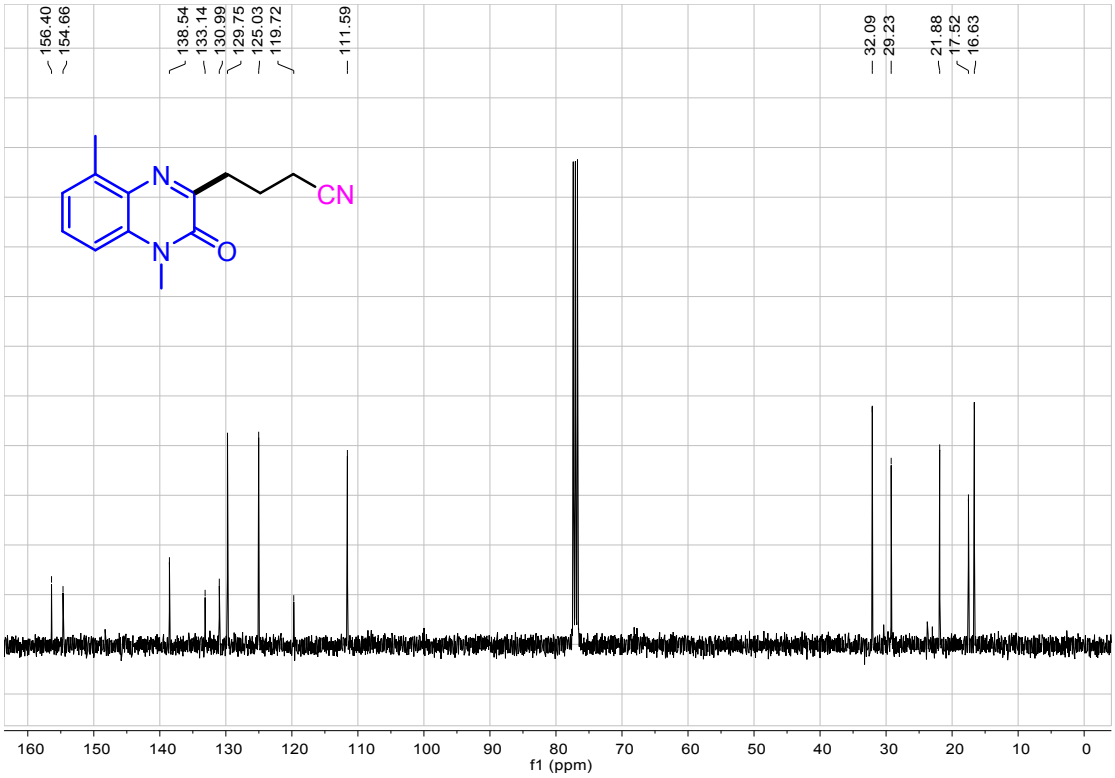
^{13}C NMR Spectrum of **3aa**



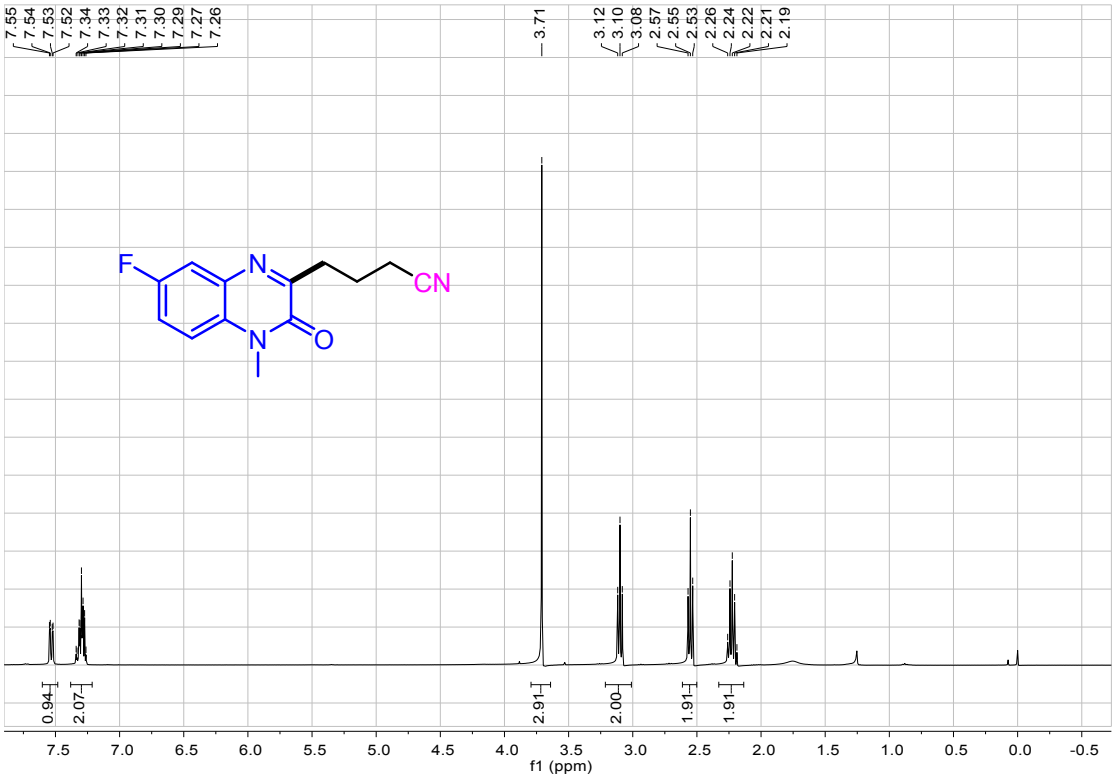
^{1}H NMR Spectrum of **3ab**



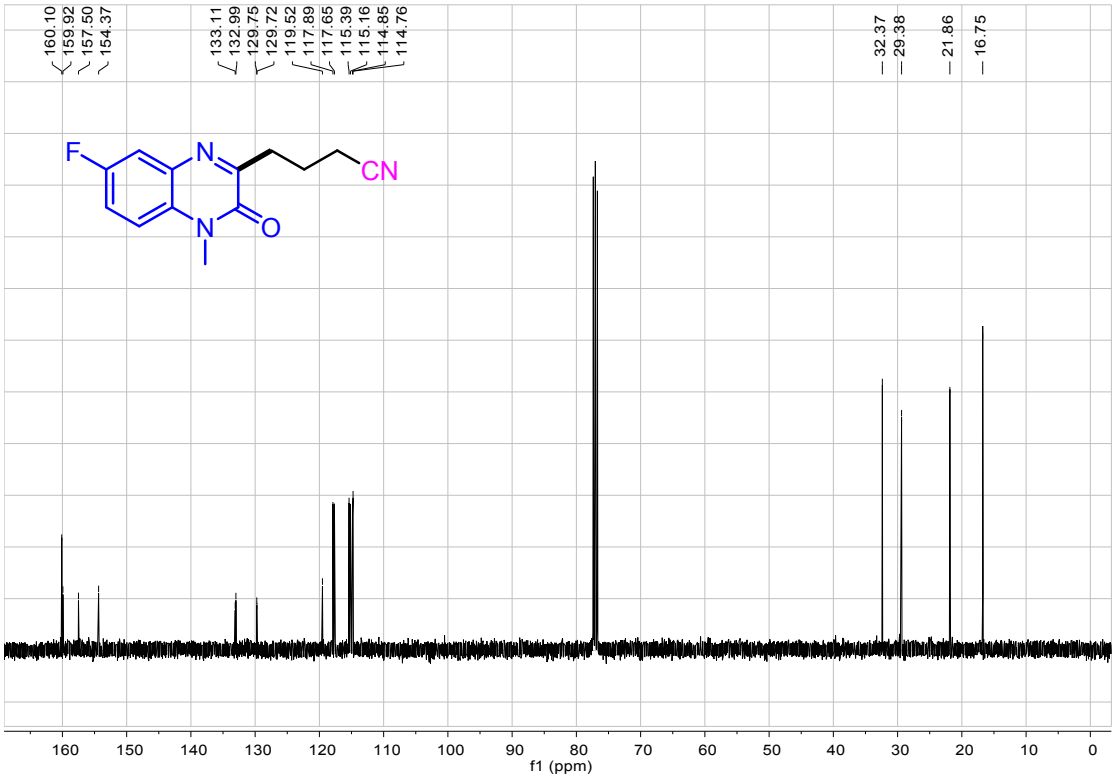
^{13}C NMR Spectrum of **3ab**



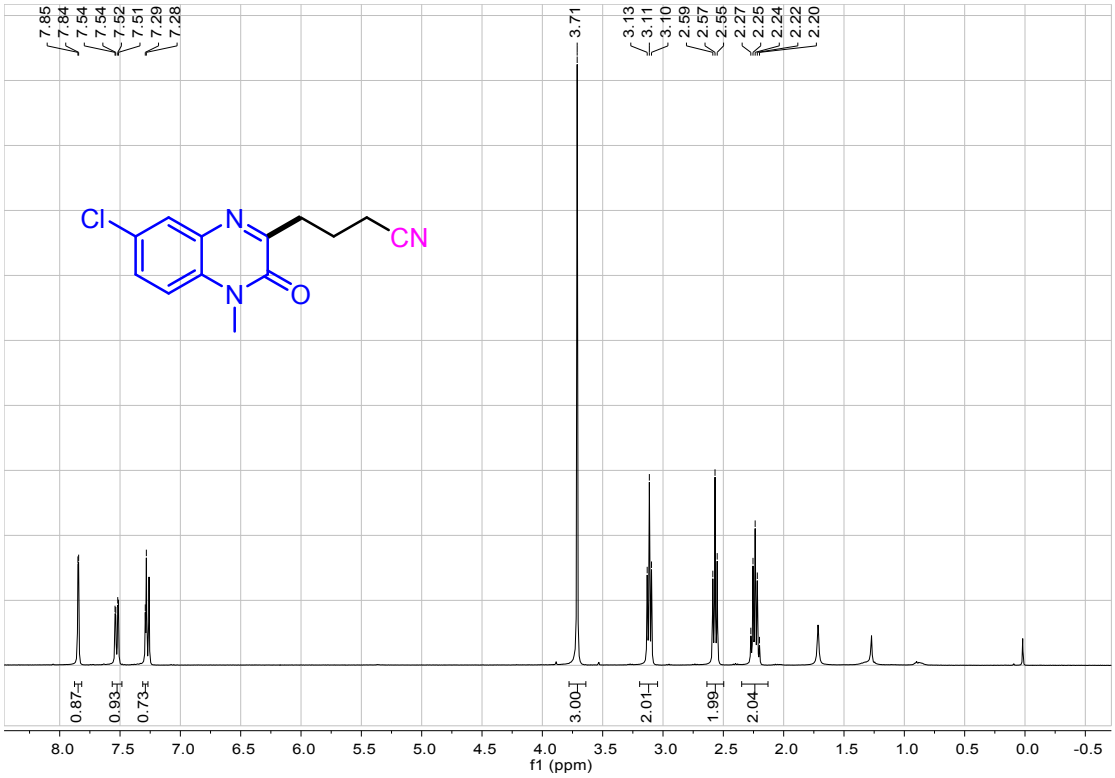
^{1}H NMR Spectrum of **3ac**



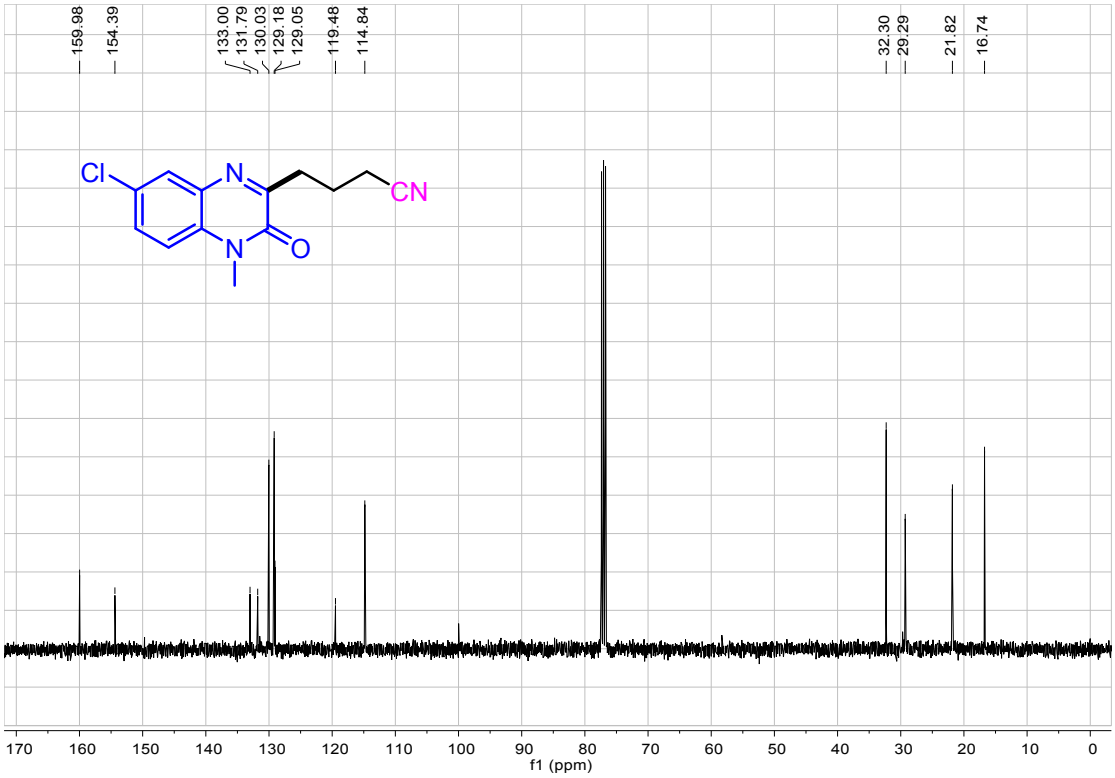
^{13}C NMR Spectrum of **3ac**



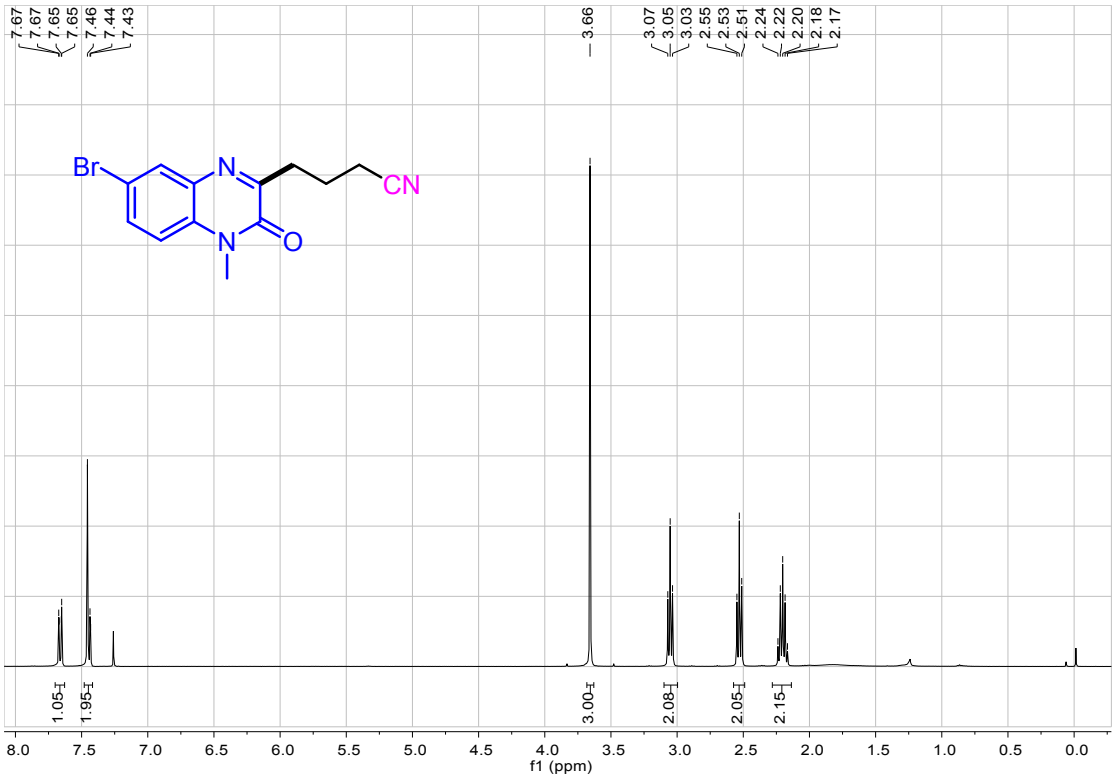
^{1}H NMR Spectrum of **3ad**



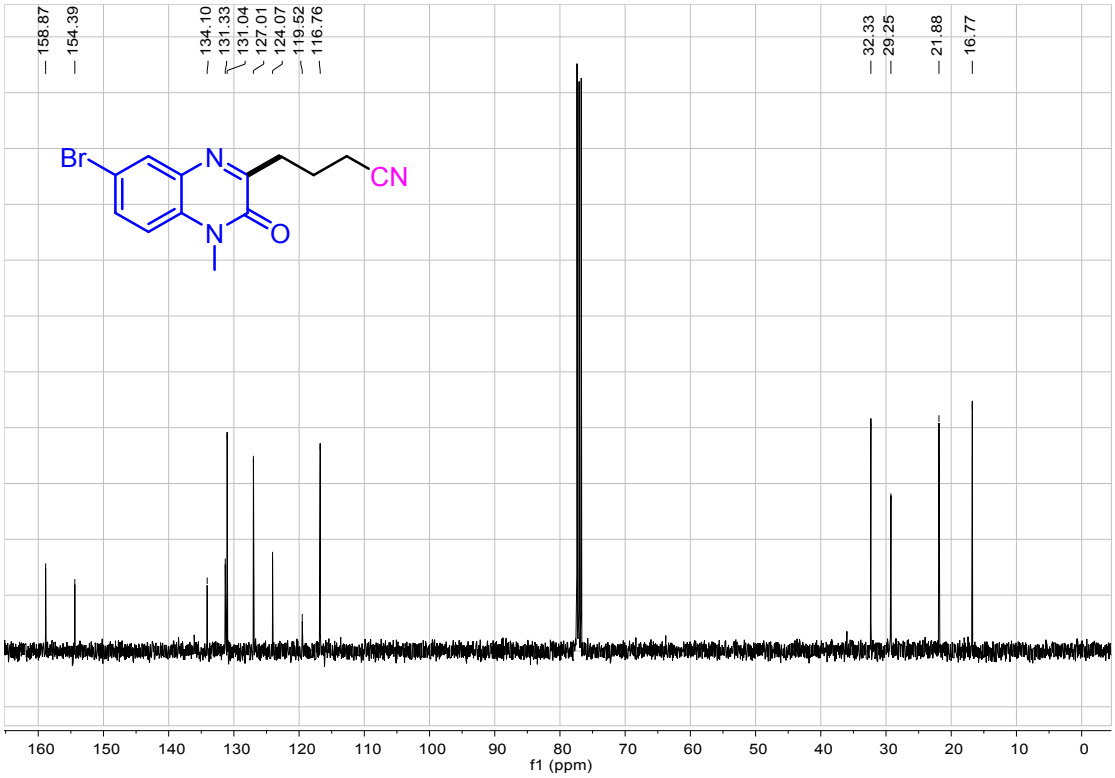
^{13}C NMR Spectrum of **3ad**



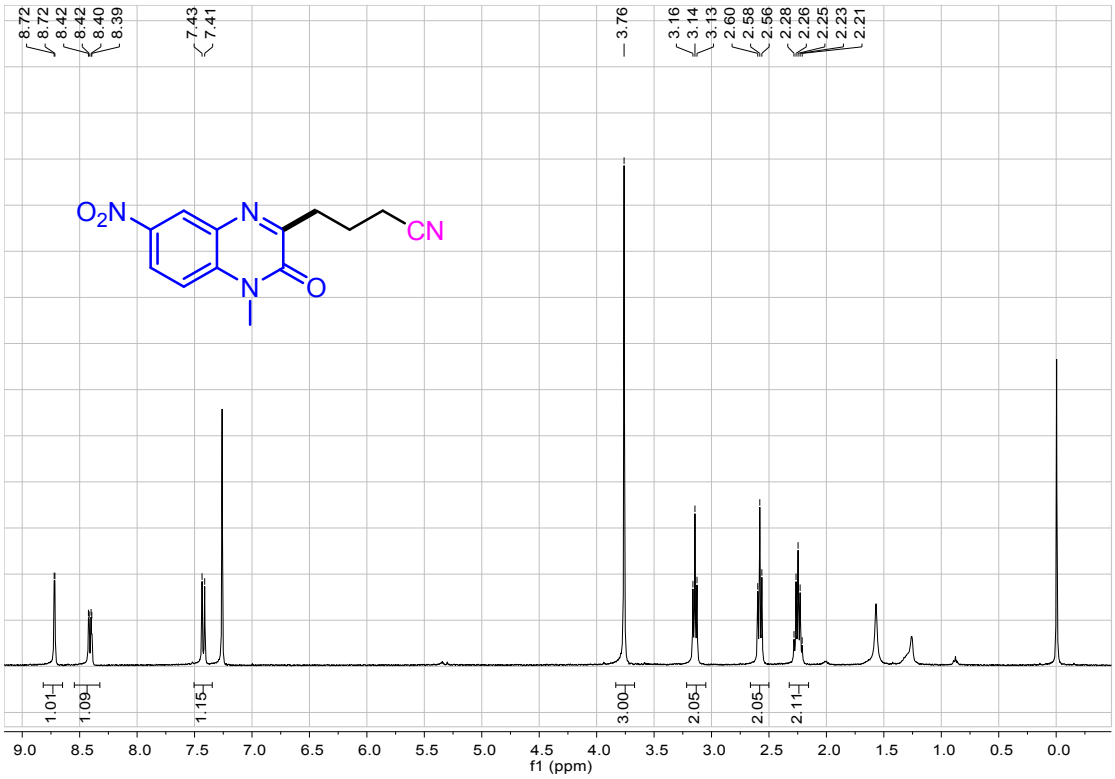
^{1}H NMR Spectrum of **3ae**



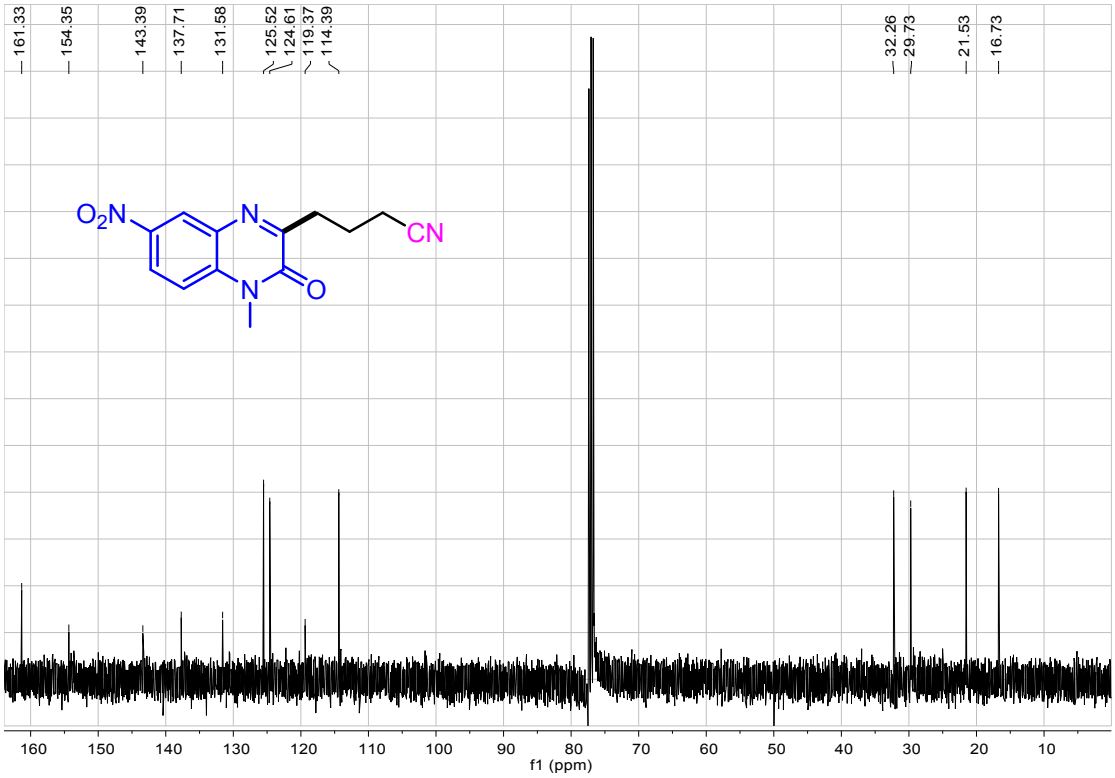
^{13}C NMR Spectrum of **3ae**



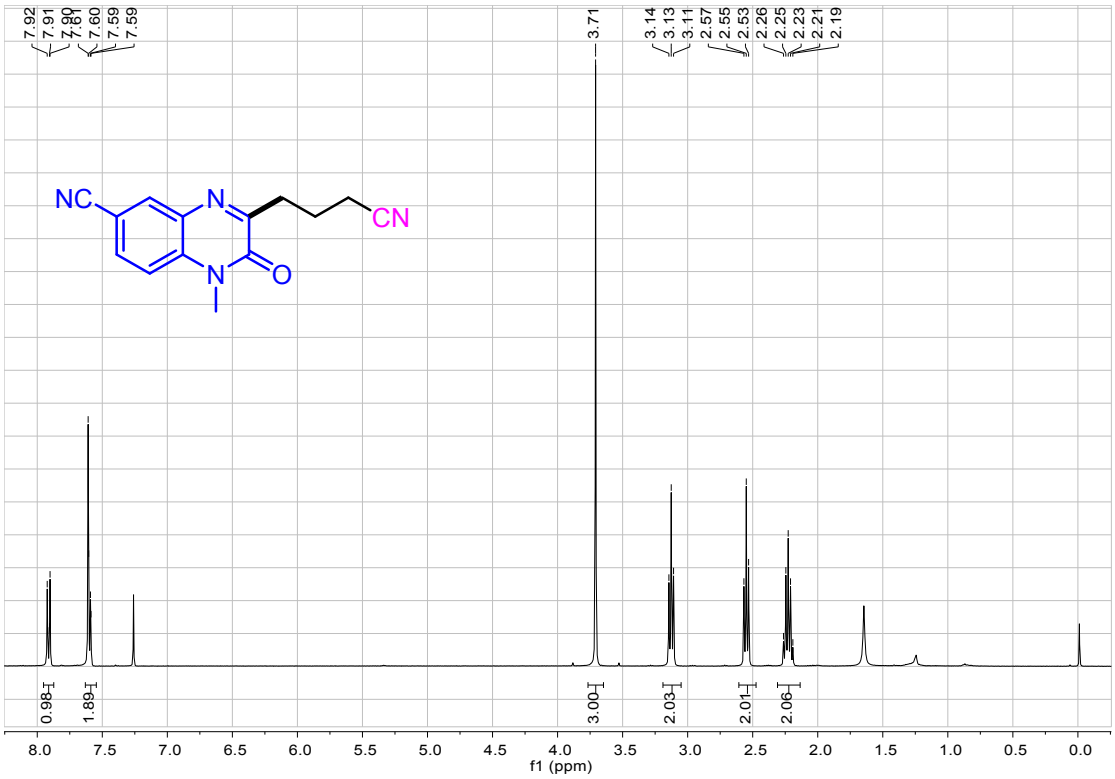
^{1}H NMR Spectrum of **3af**



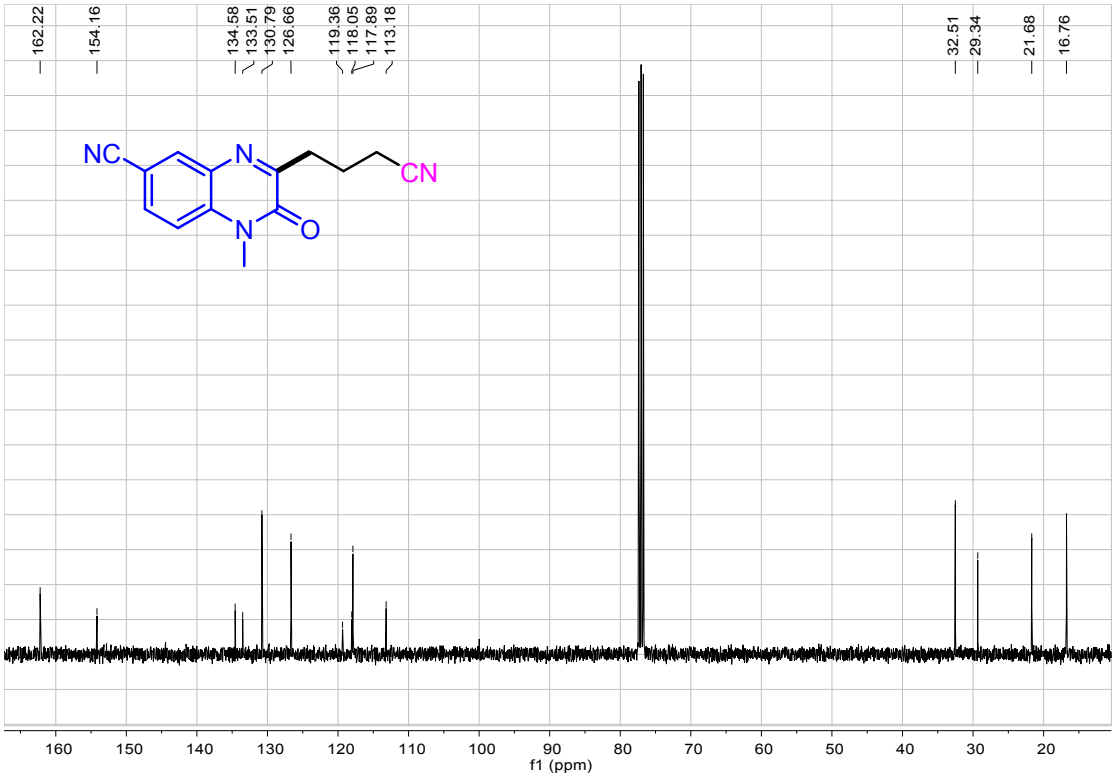
^{13}C NMR Spectrum of **3af**



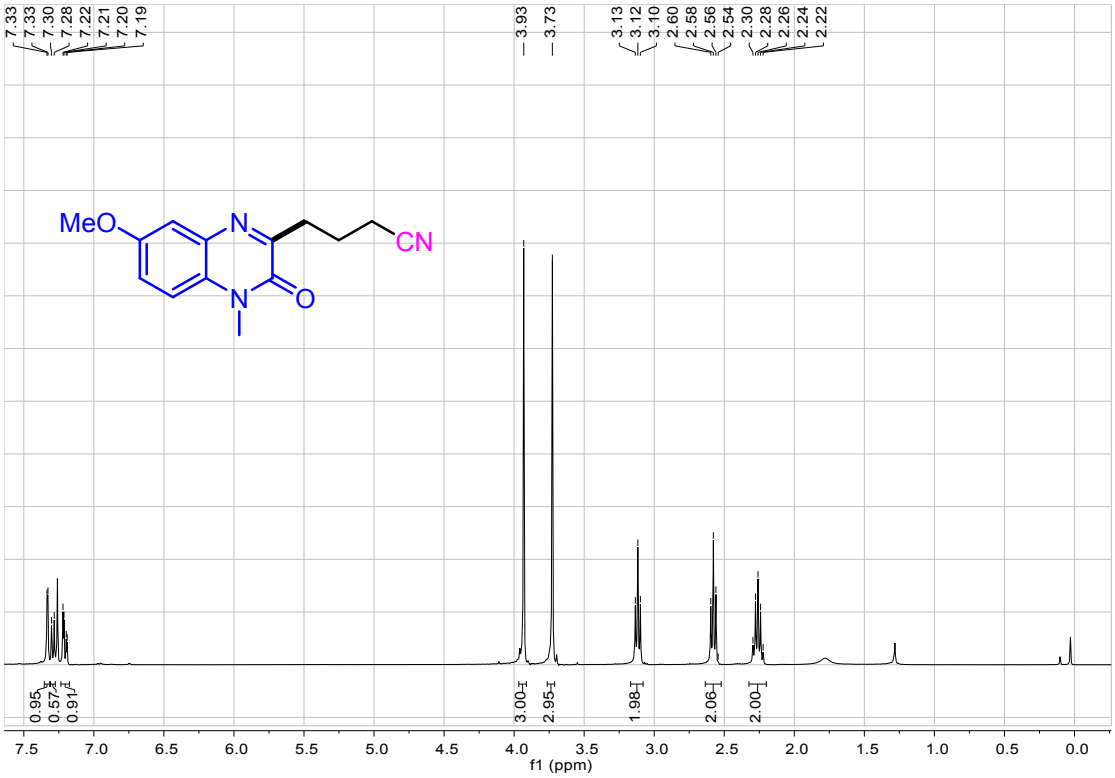
^{1}H NMR Spectrum of **3ag**



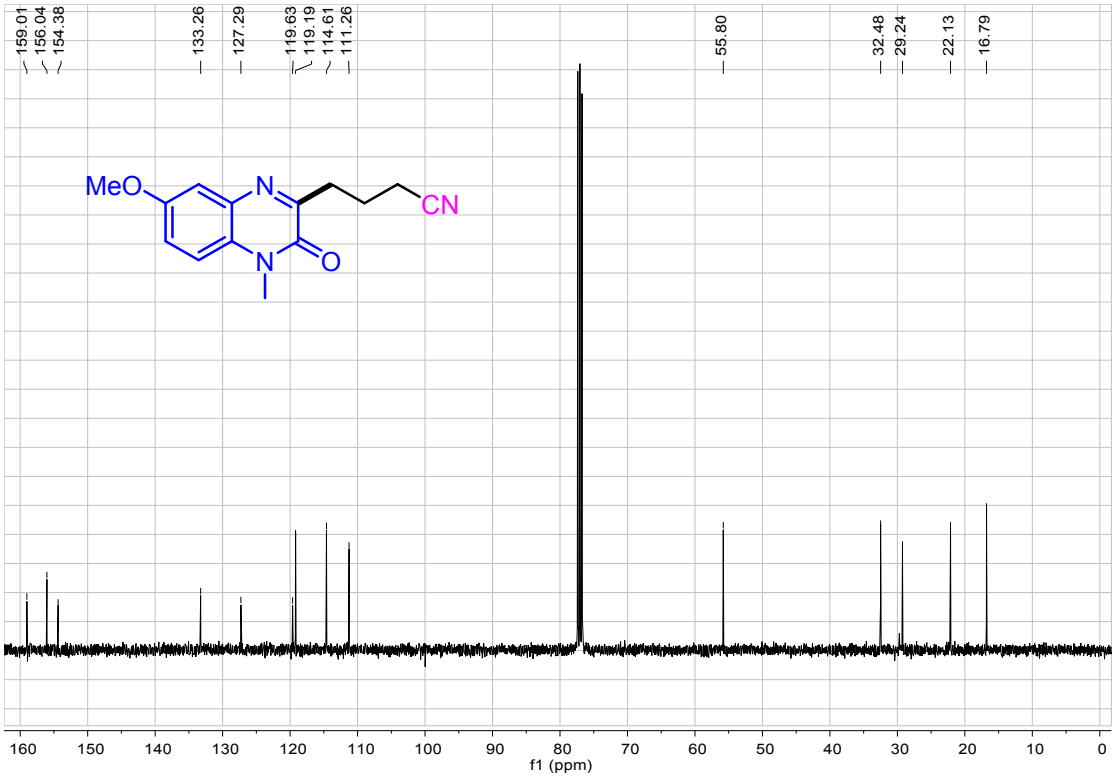
^{13}C NMR Spectrum of **3ag**



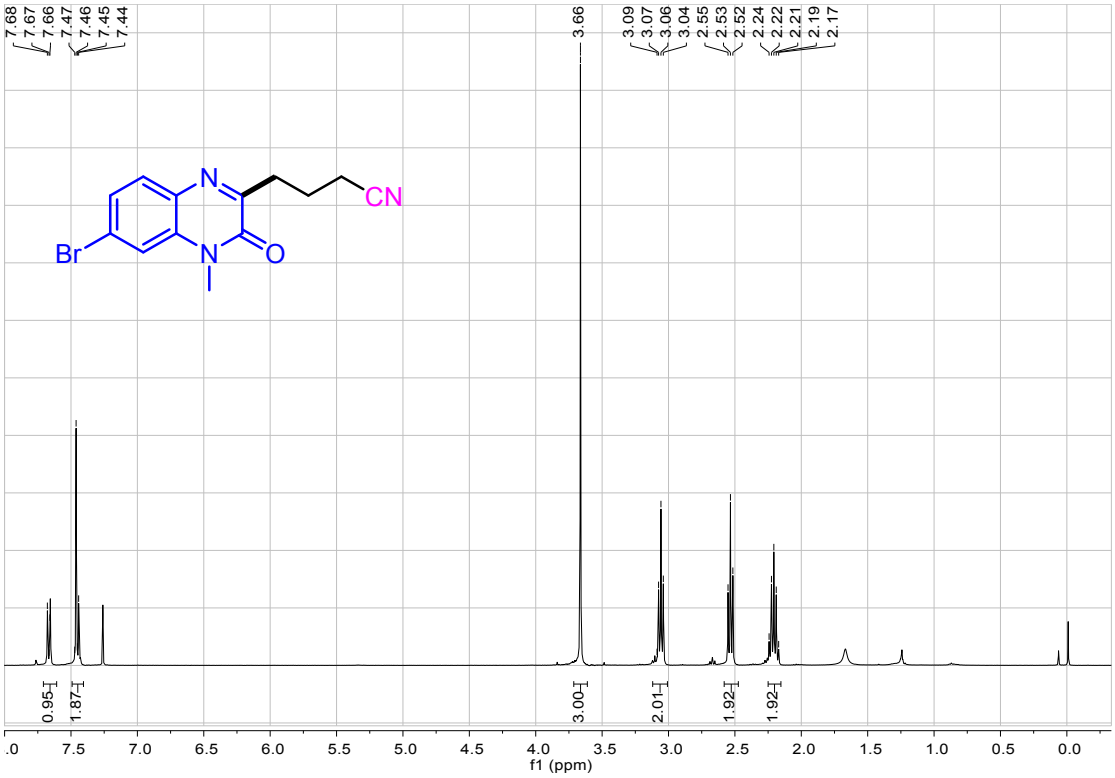
^{1}H NMR Spectrum of **3ah**



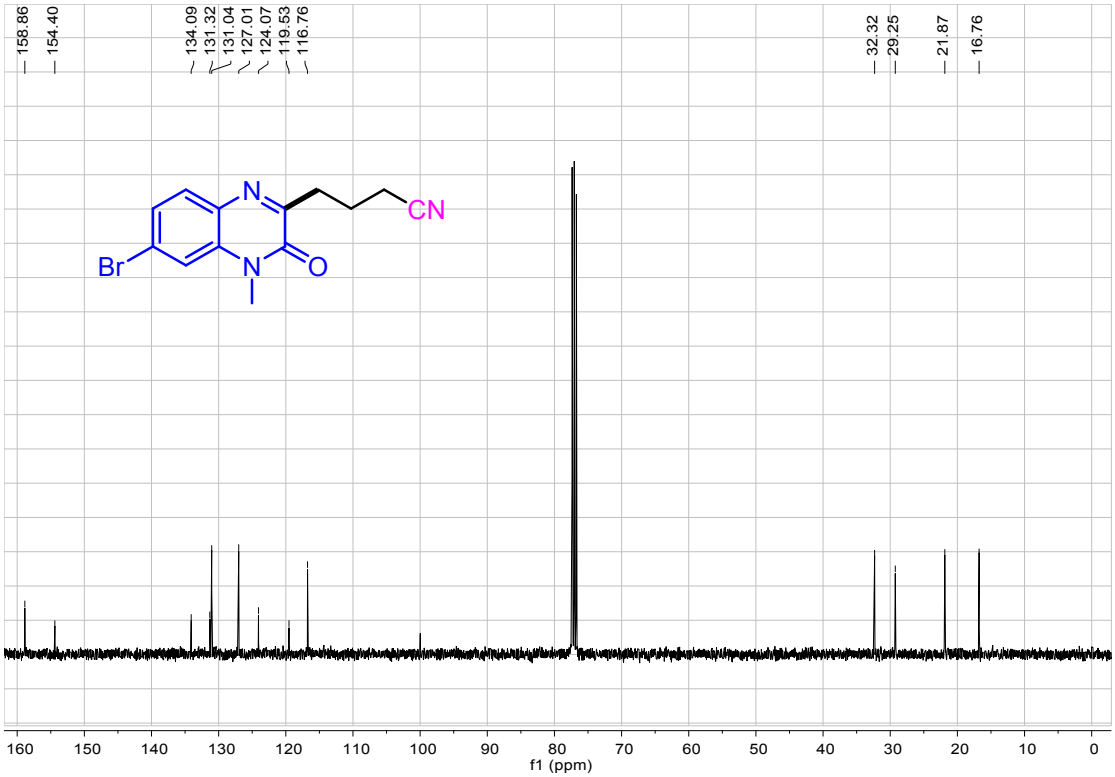
^{13}C NMR Spectrum of **3ah**



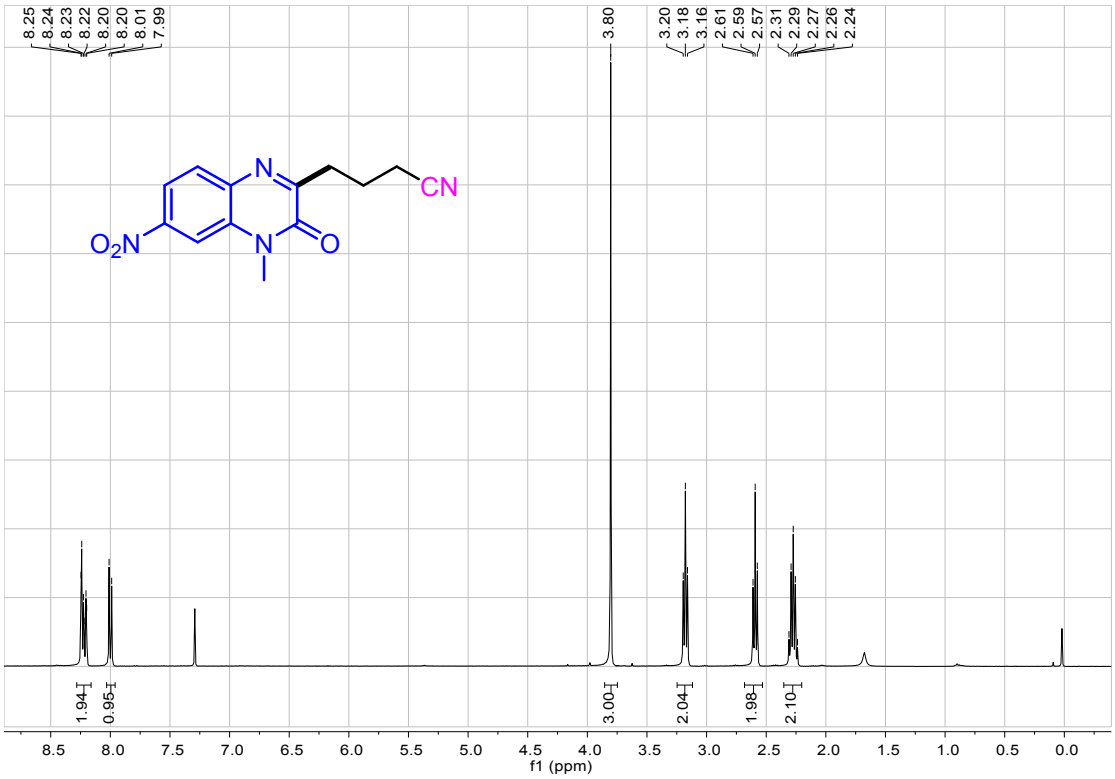
^{1}H NMR Spectrum of **3ai**



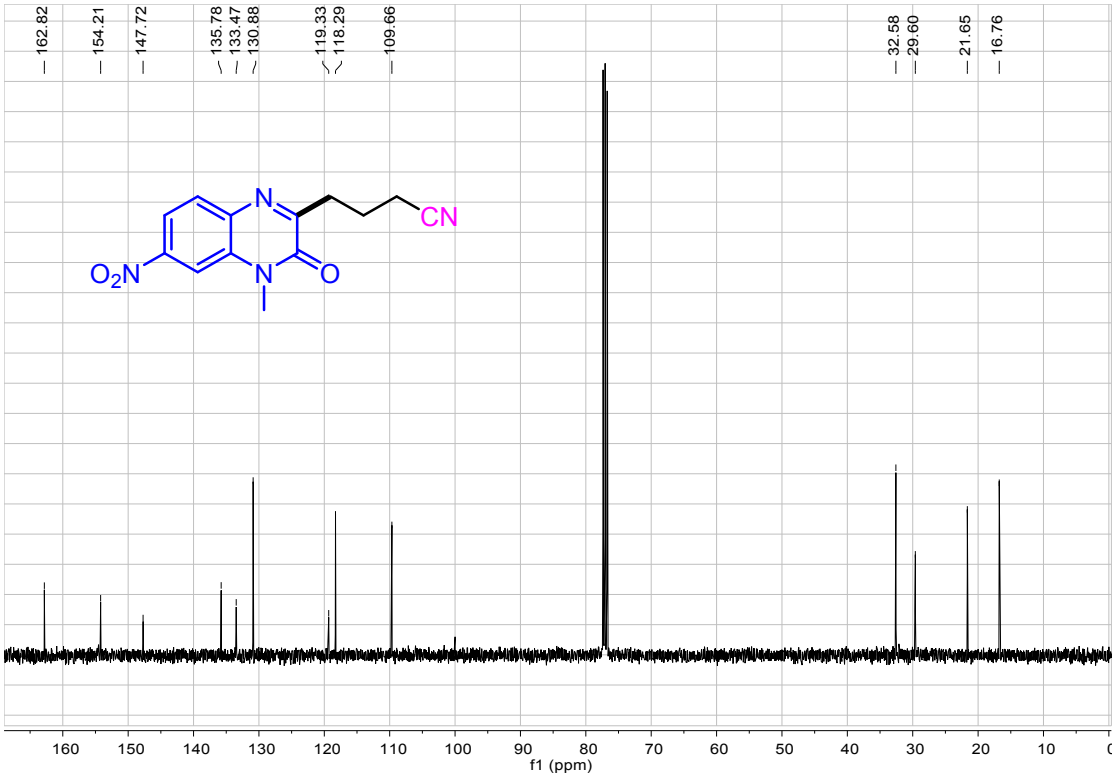
^{13}C NMR Spectrum of **3ai**



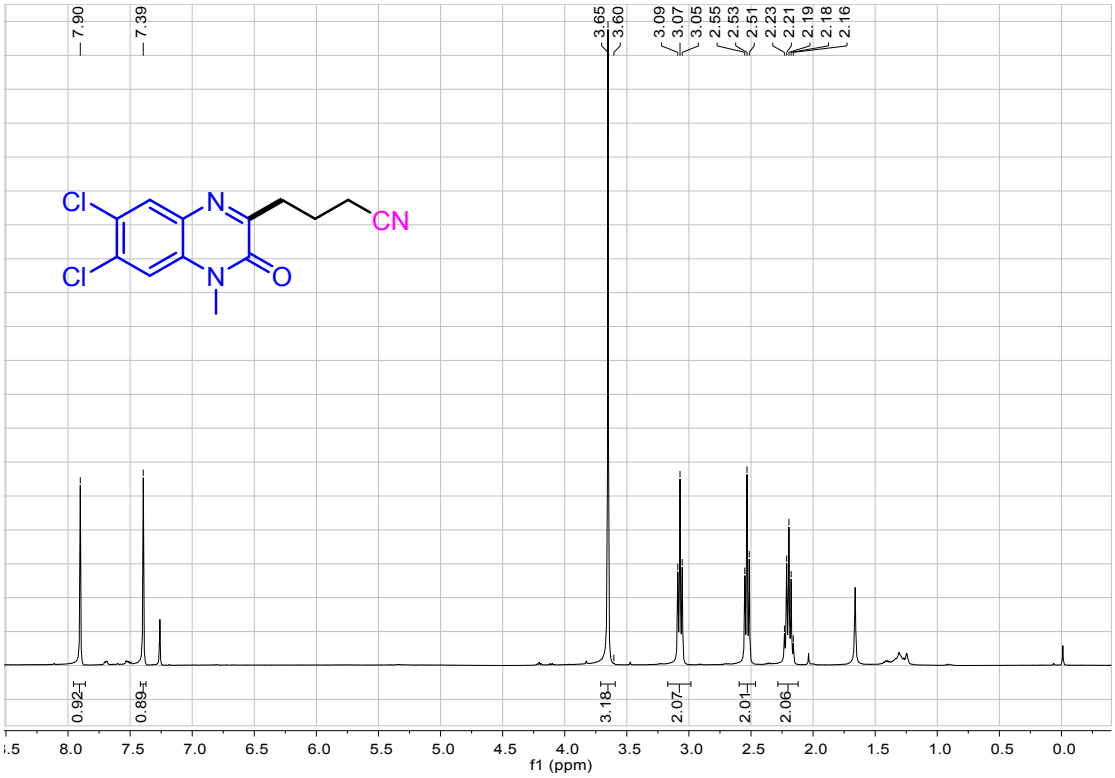
^{1}H NMR Spectrum of **3aj**



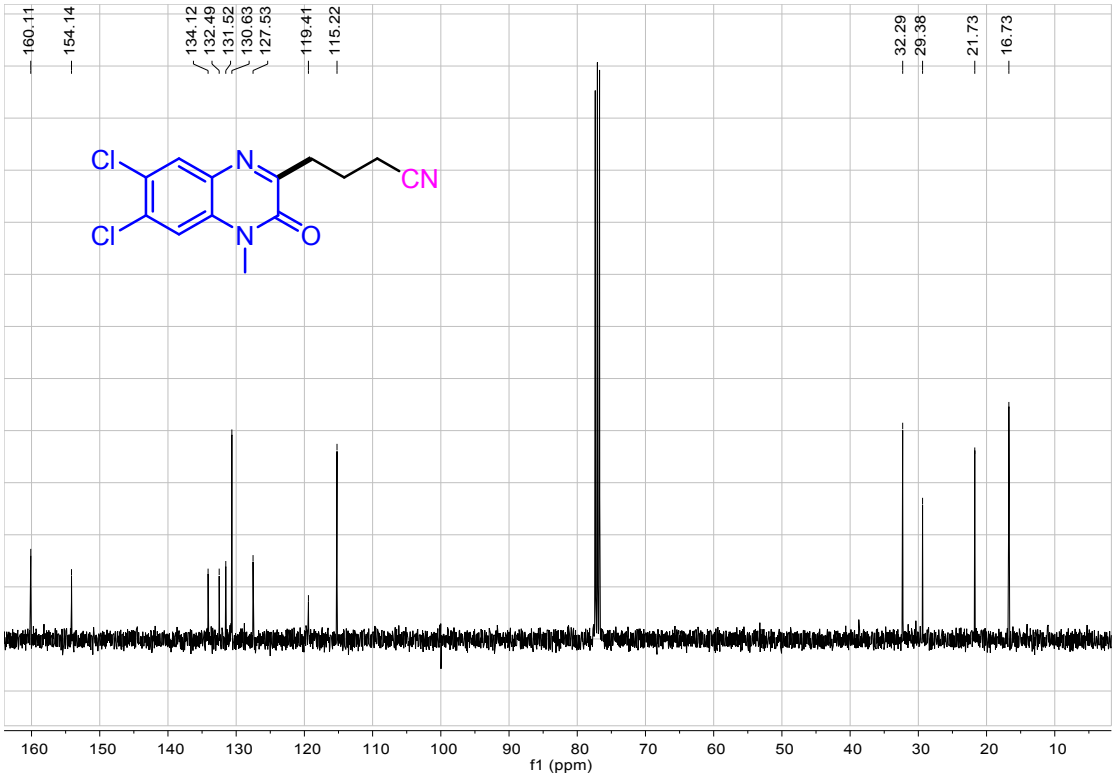
^{13}C NMR Spectrum of **3aj**



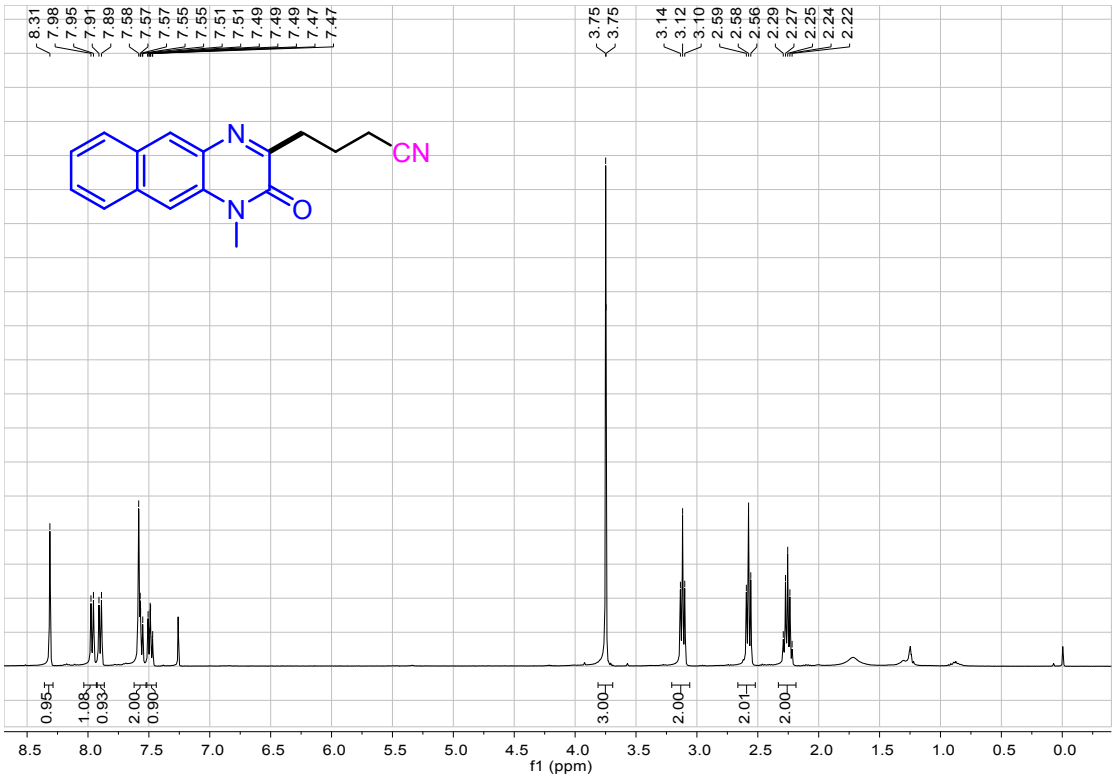
^{1}H NMR Spectrum of **3ak**



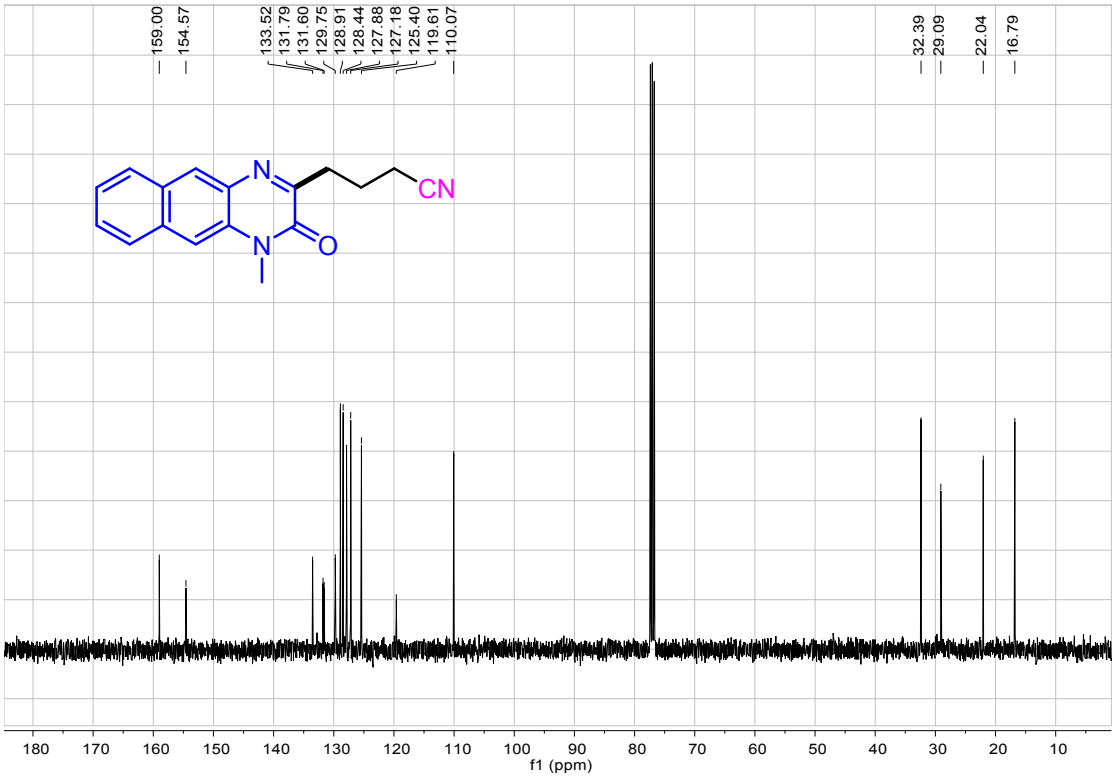
^{13}C NMR Spectrum of **3ak**



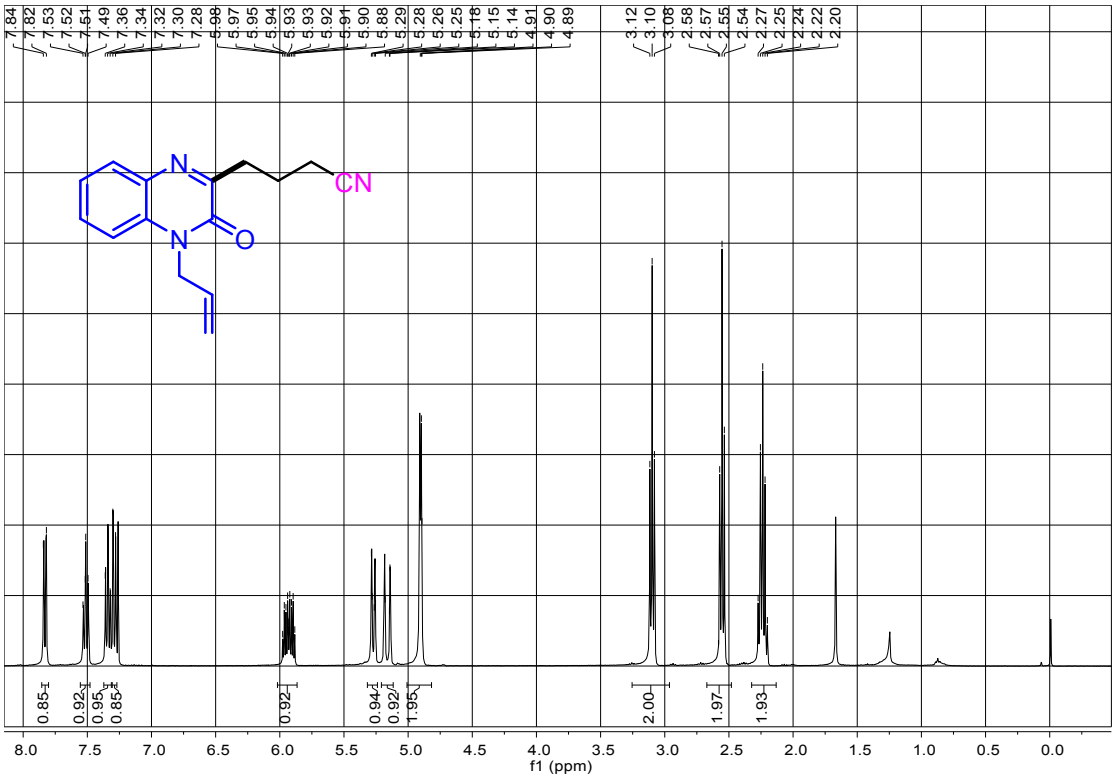
[1]H NMR Spectrum of **3al**



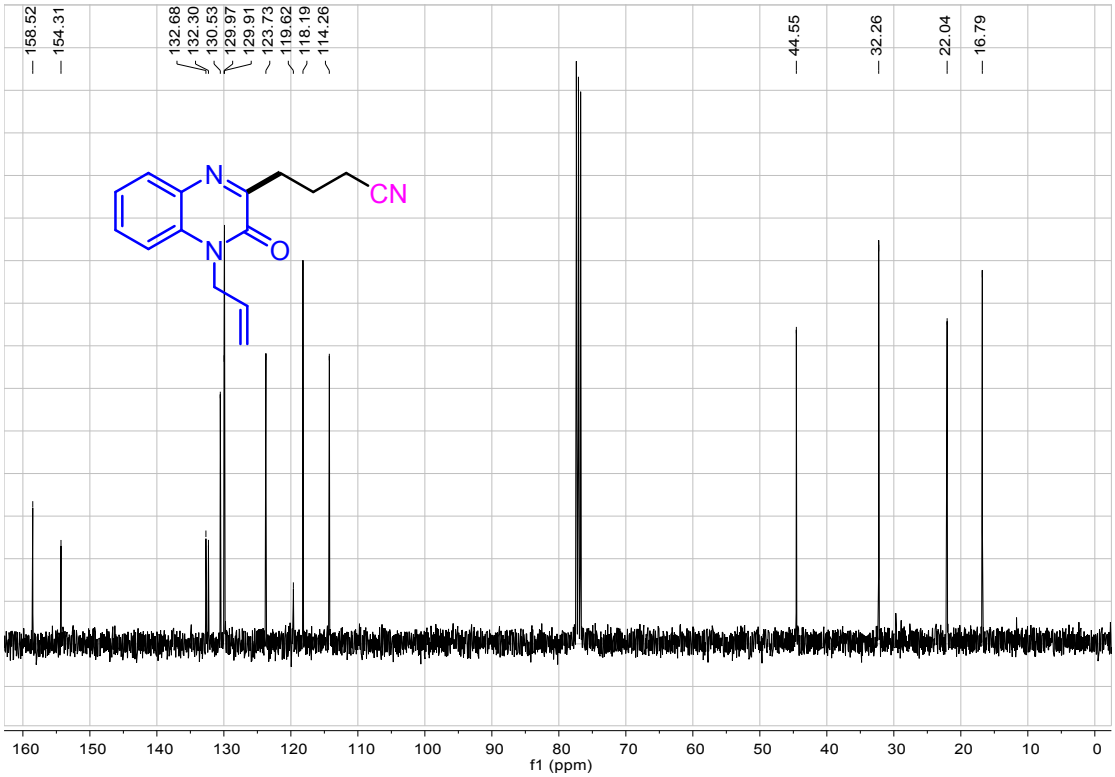
[13]C NMR Spectrum of **3al**



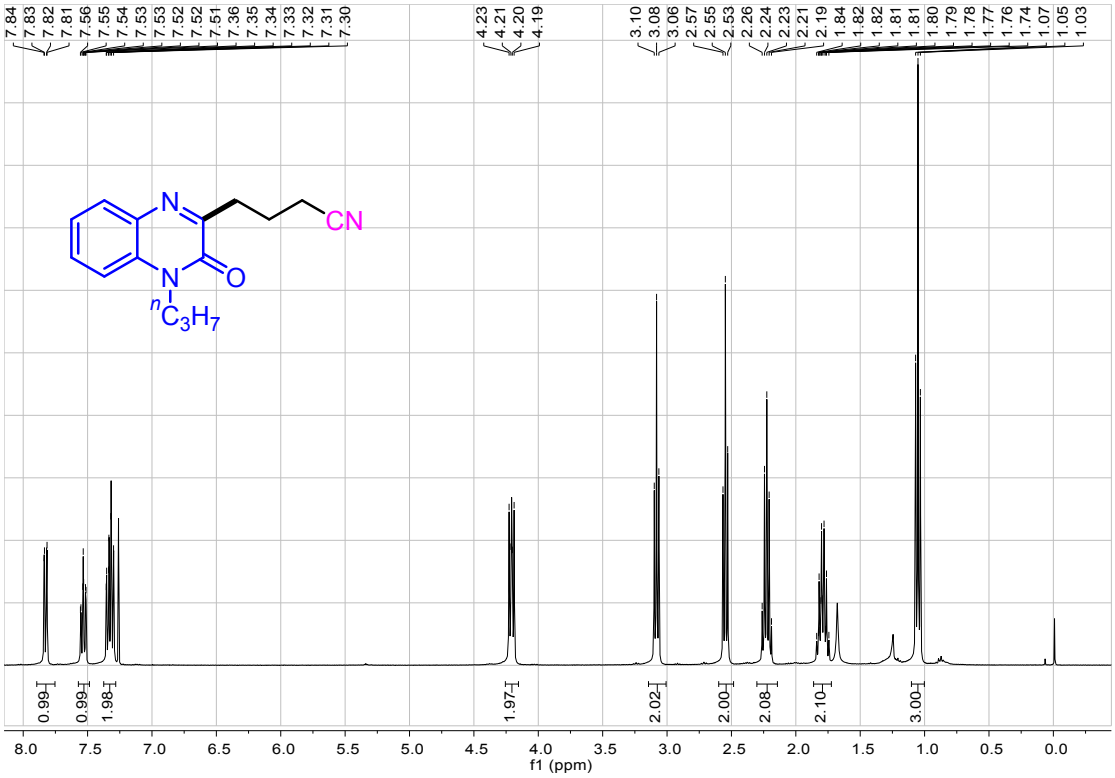
[1]H NMR Spectrum of **3am**



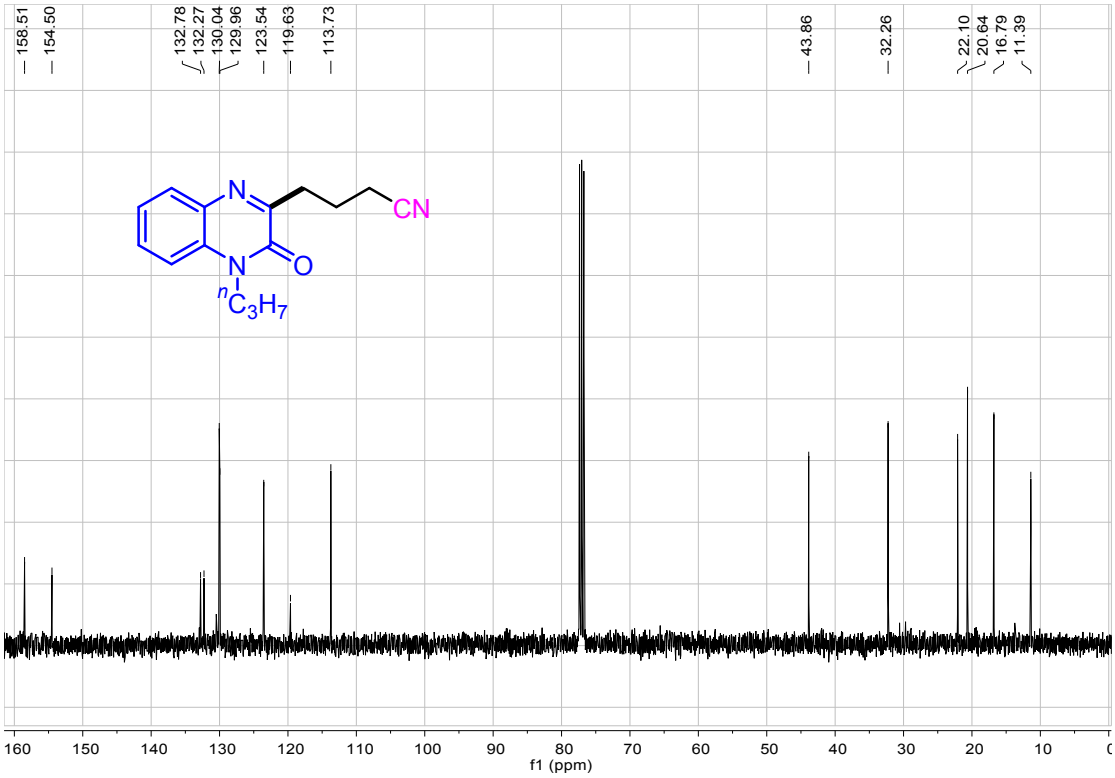
[13]C NMR Spectrum of **3l**



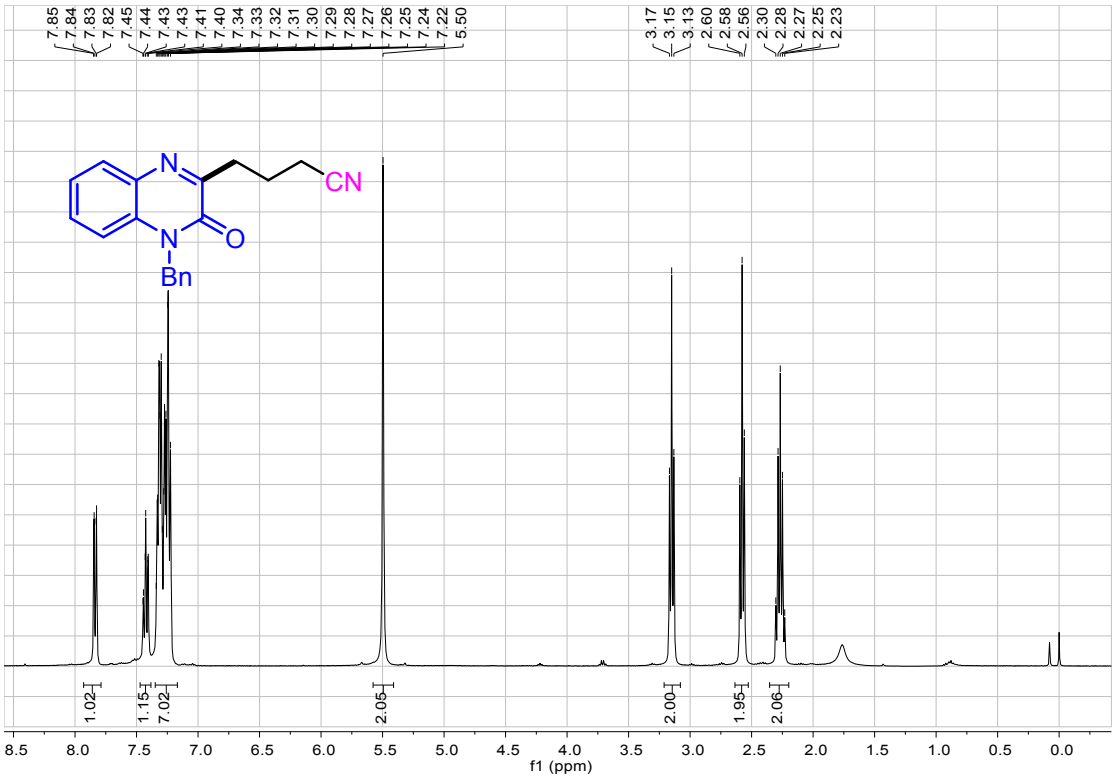
^{1}H NMR Spectrum of **3an**



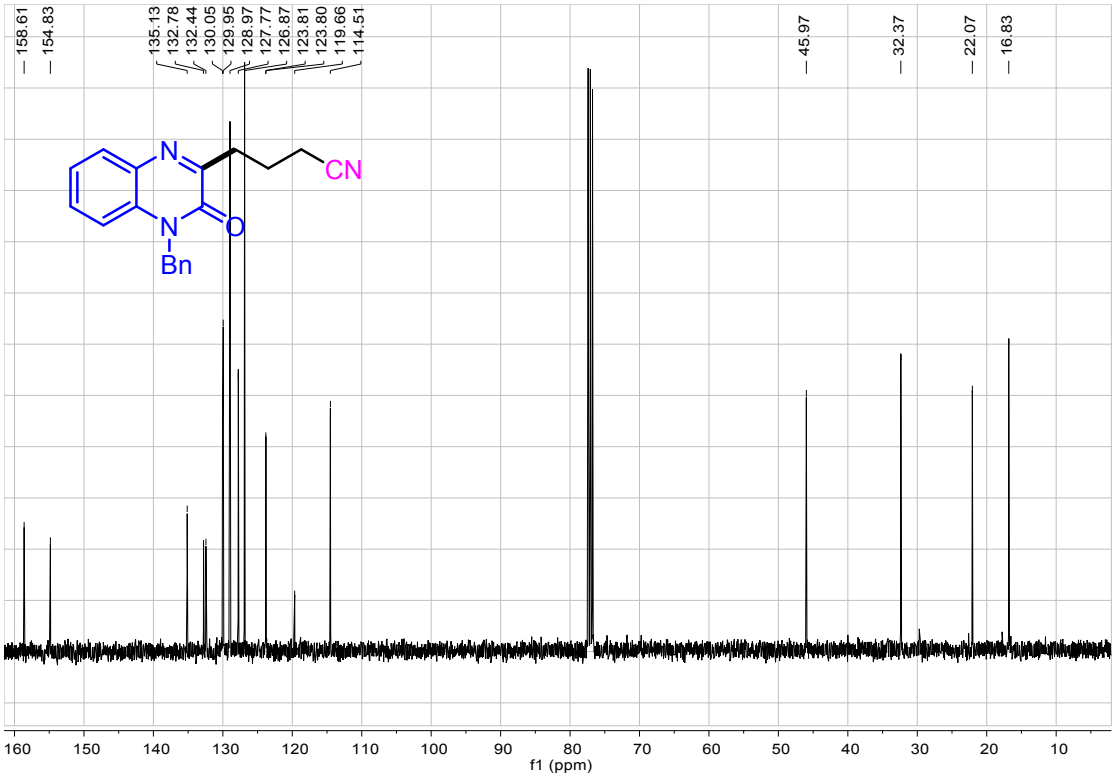
^{13}C NMR Spectrum of **3an**



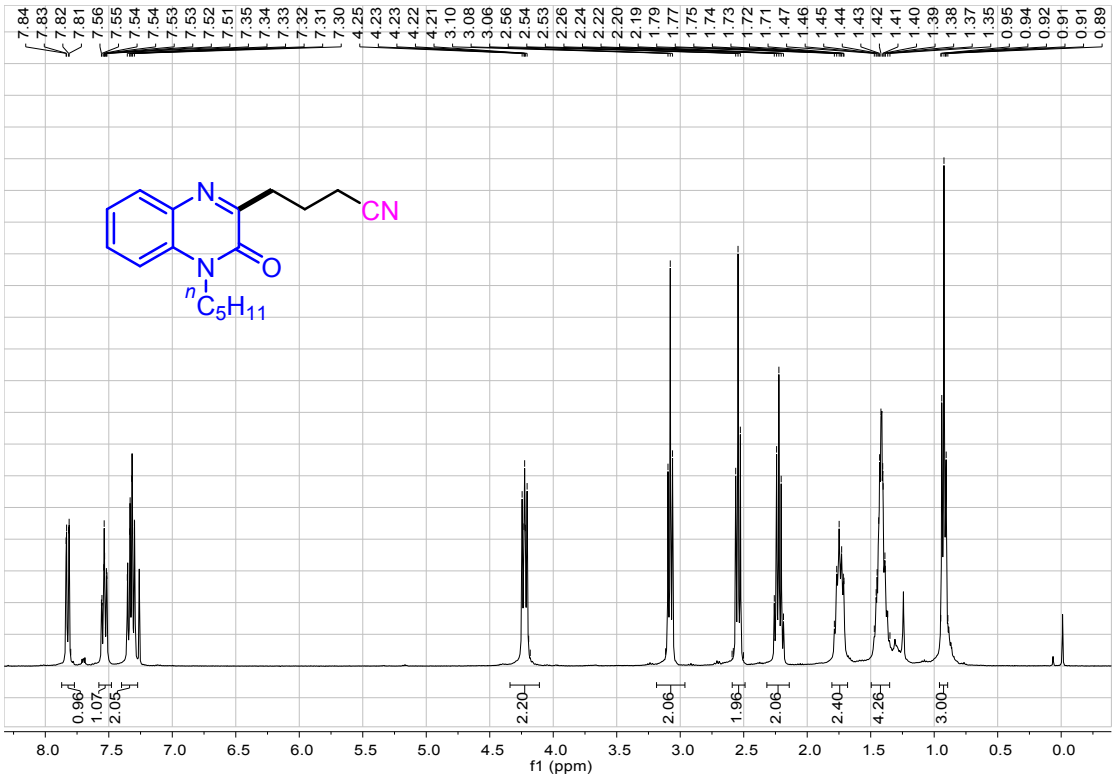
^{1}H NMR Spectrum of **3ao**



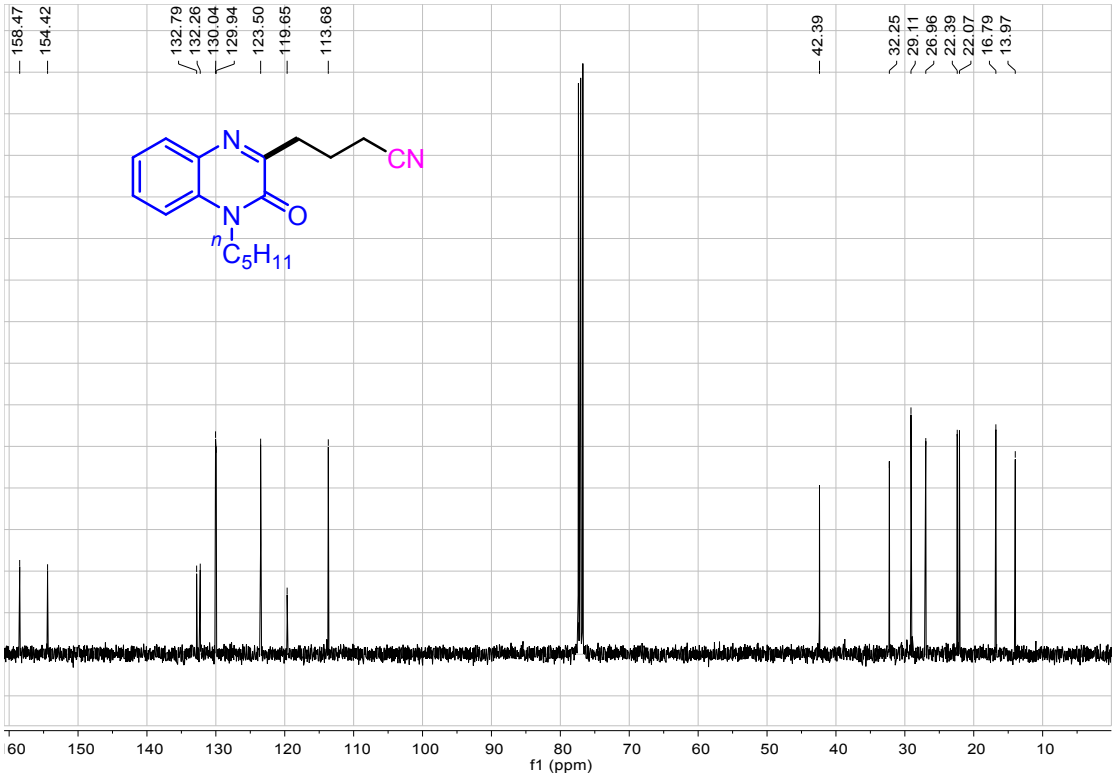
^{13}C NMR Spectrum of **3ao**



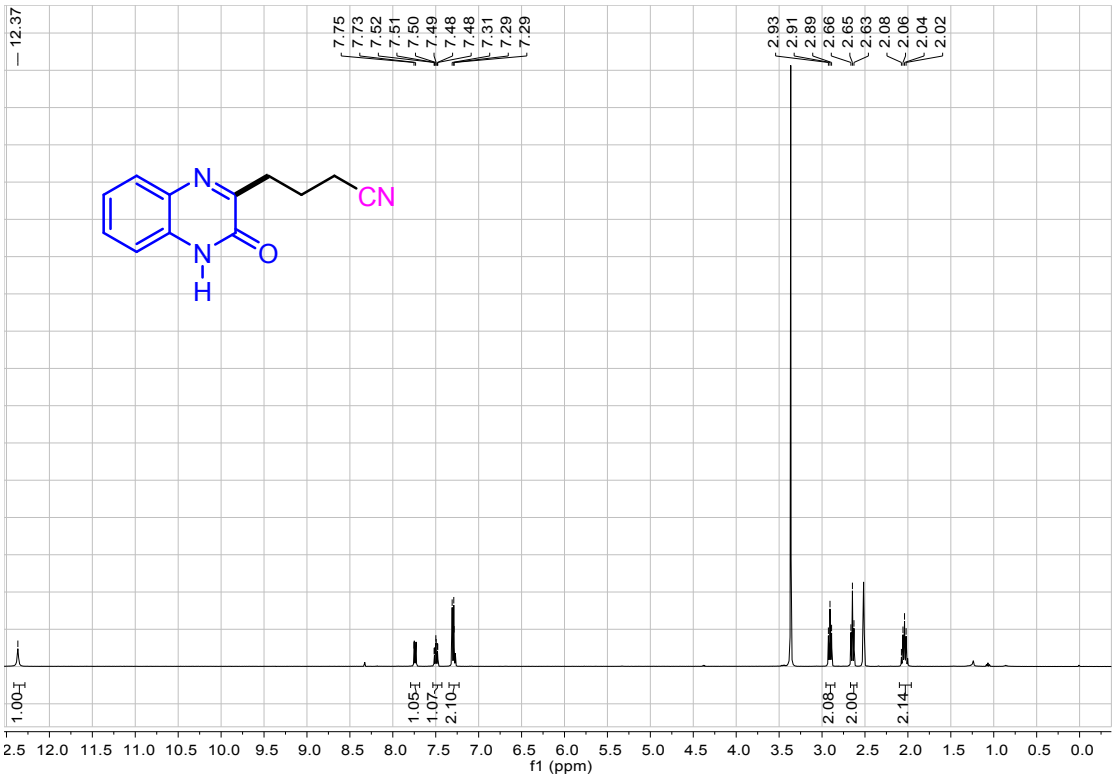
^{1}H NMR Spectrum of **3ap**



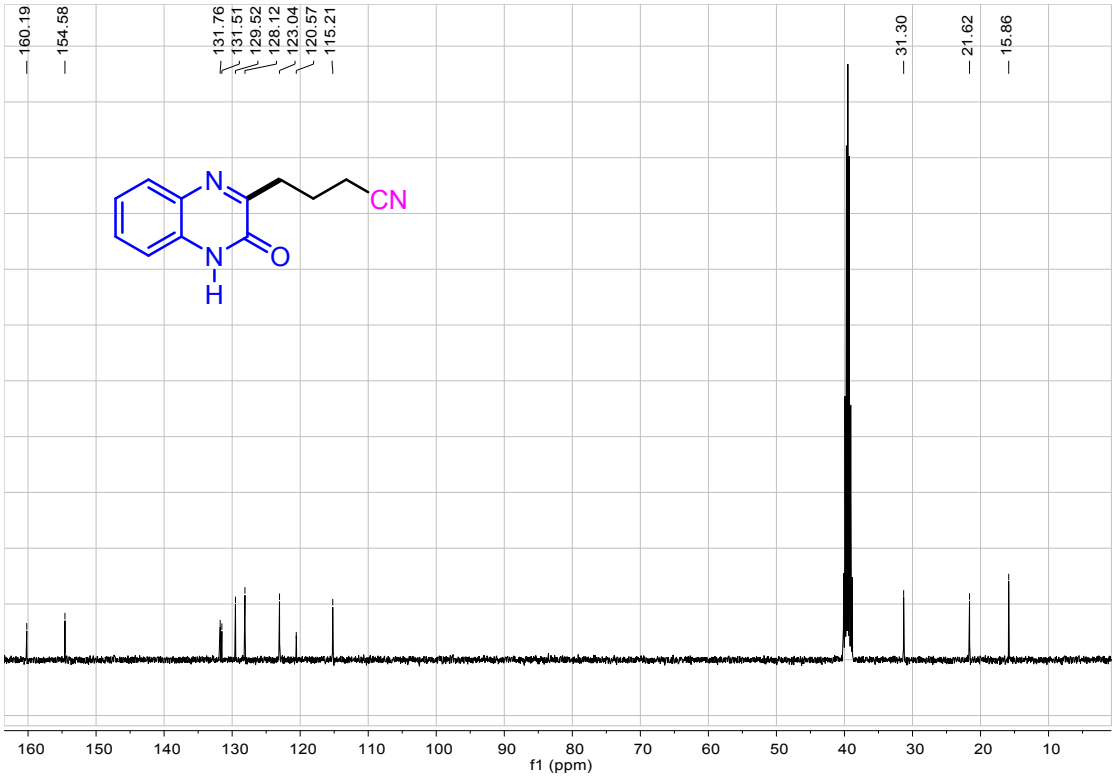
^{13}C NMR Spectrum of **3ap**



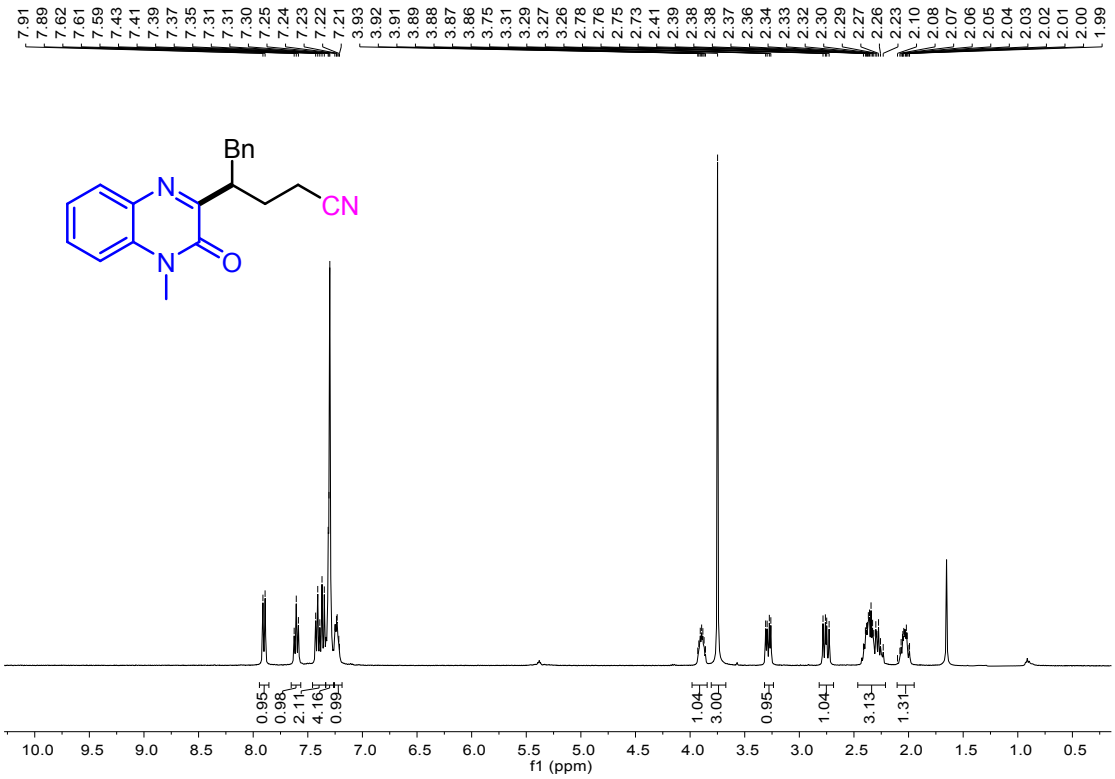
^{1}H NMR Spectrum of **3aq**



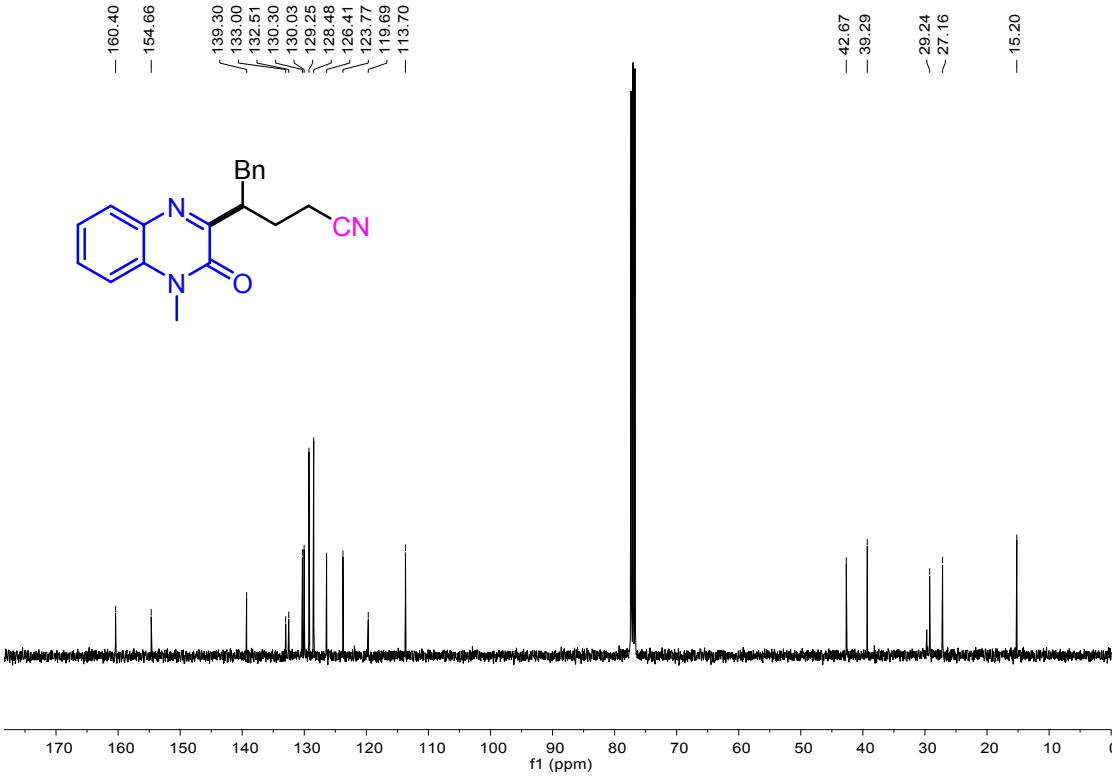
^{13}C NMR Spectrum of **3aq**



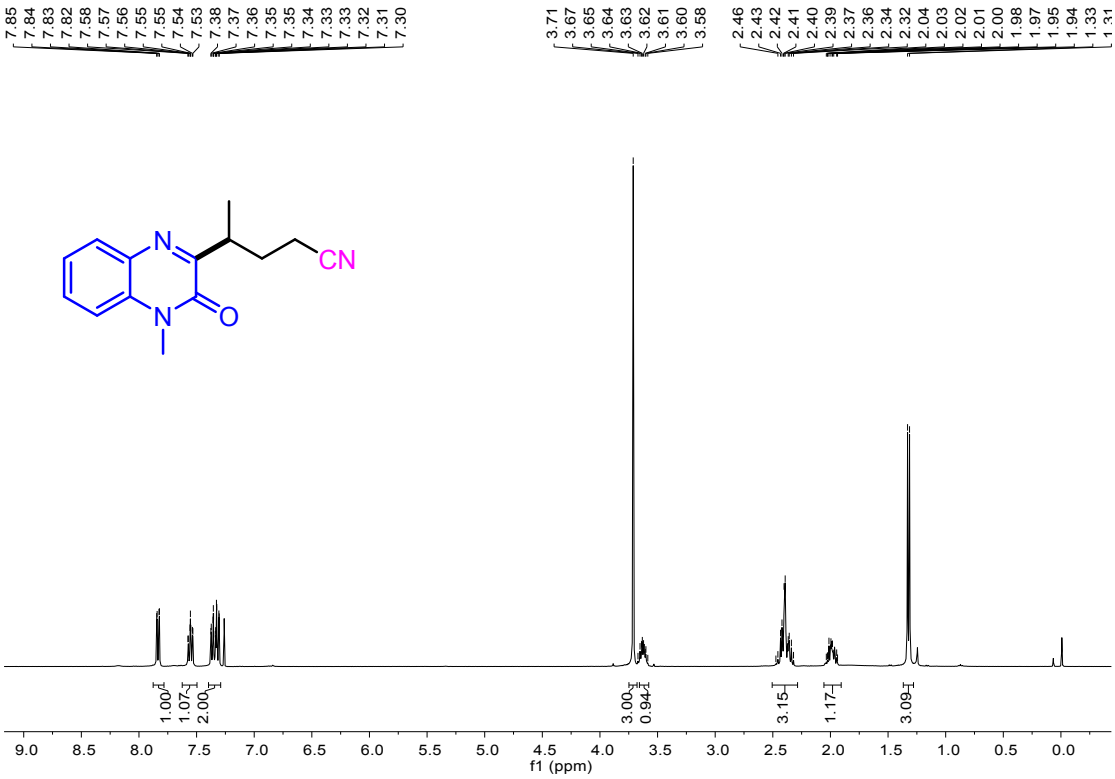
^{1}H NMR Spectrum of **3ba**



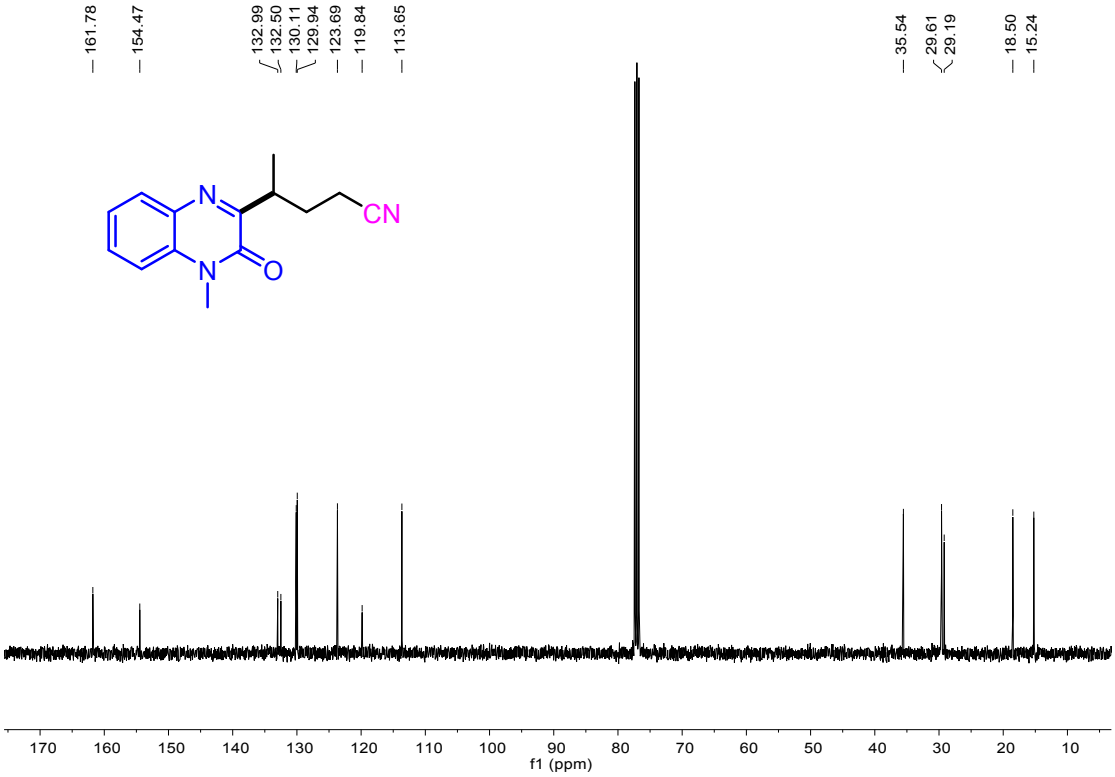
^{13}C NMR Spectrum of **3ba**



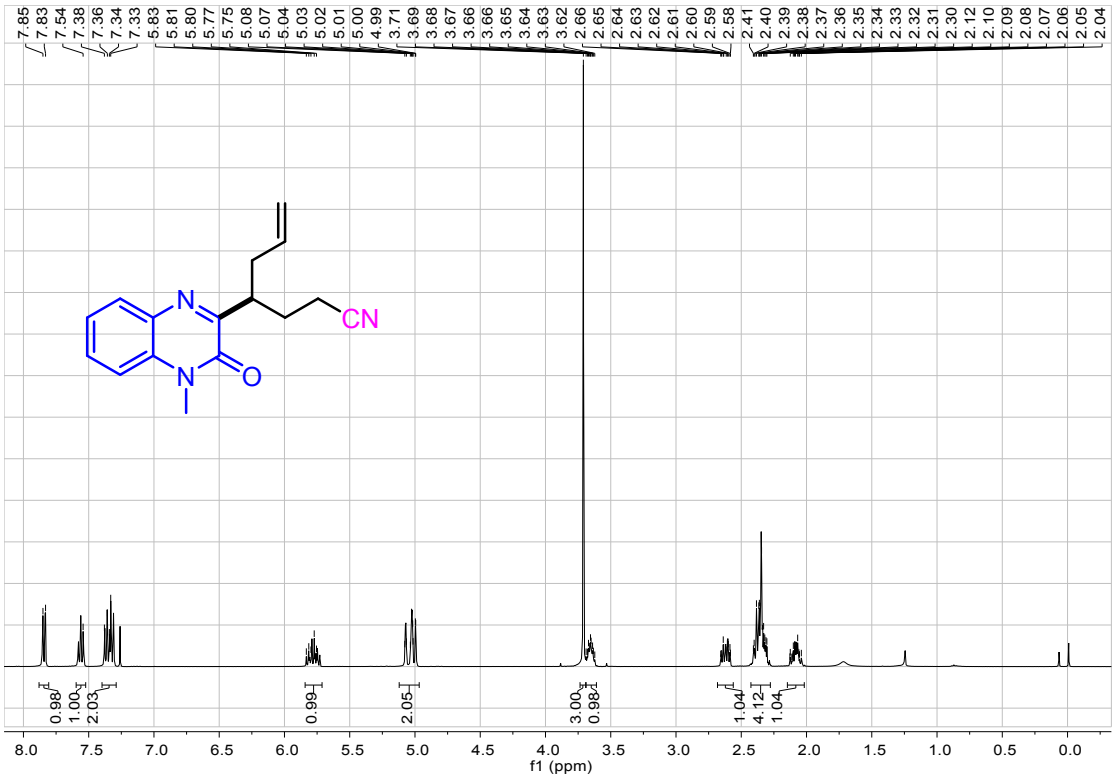
^{1}H NMR Spectrum of **3ca**



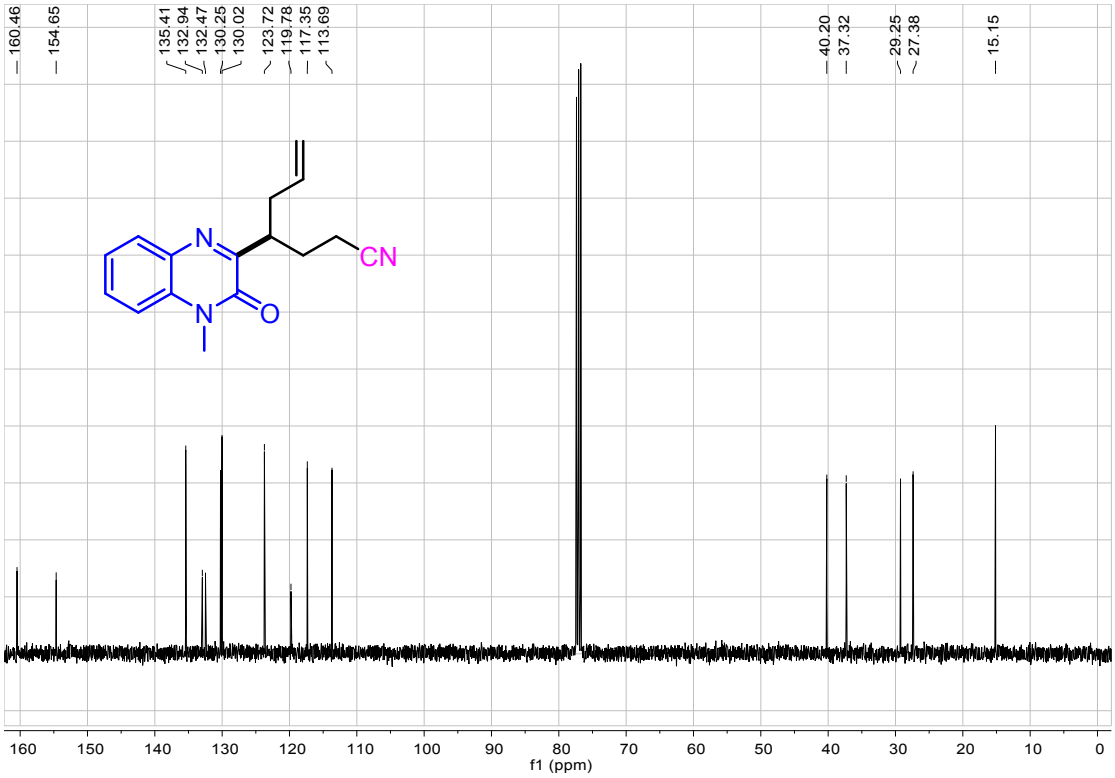
^{13}C NMR Spectrum of **3ca**



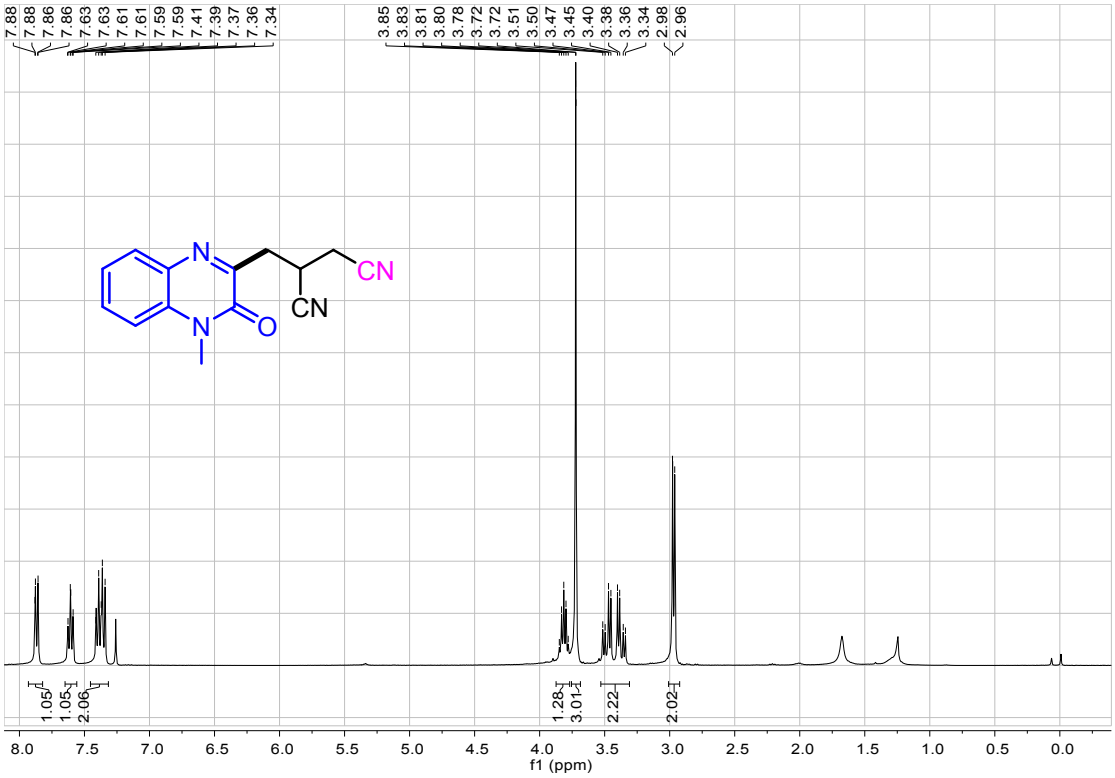
^{1}H NMR Spectrum of **3da**



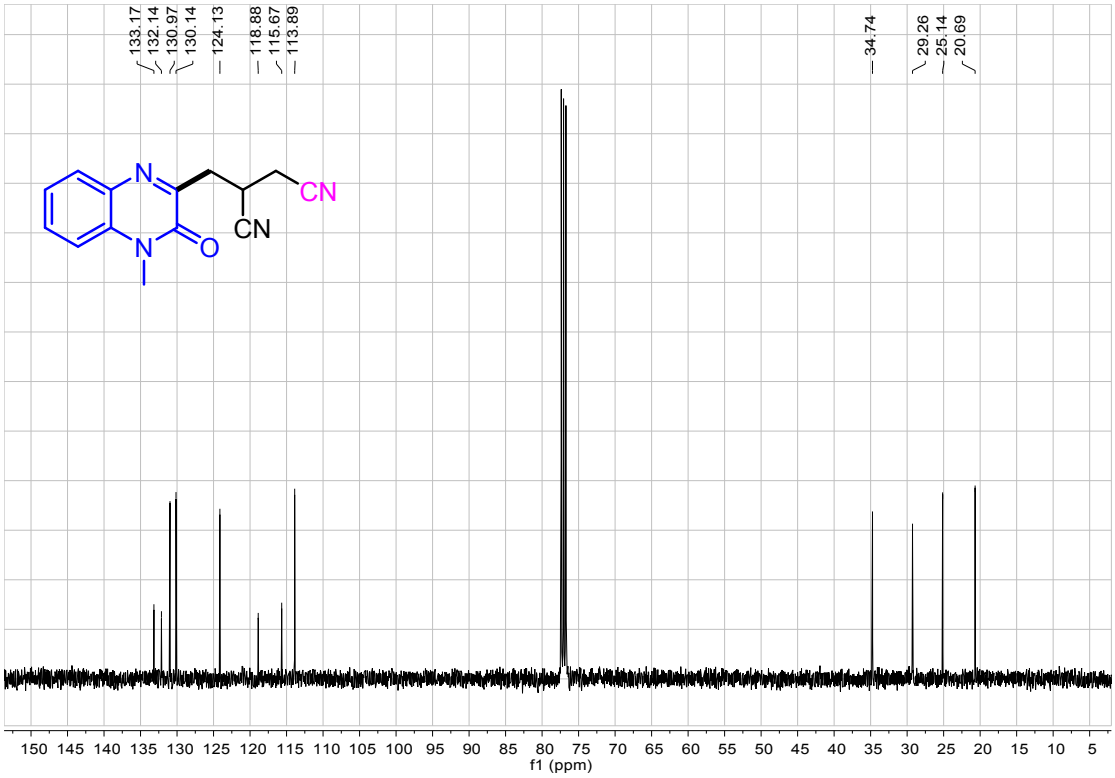
^{13}C NMR Spectrum of **3da**



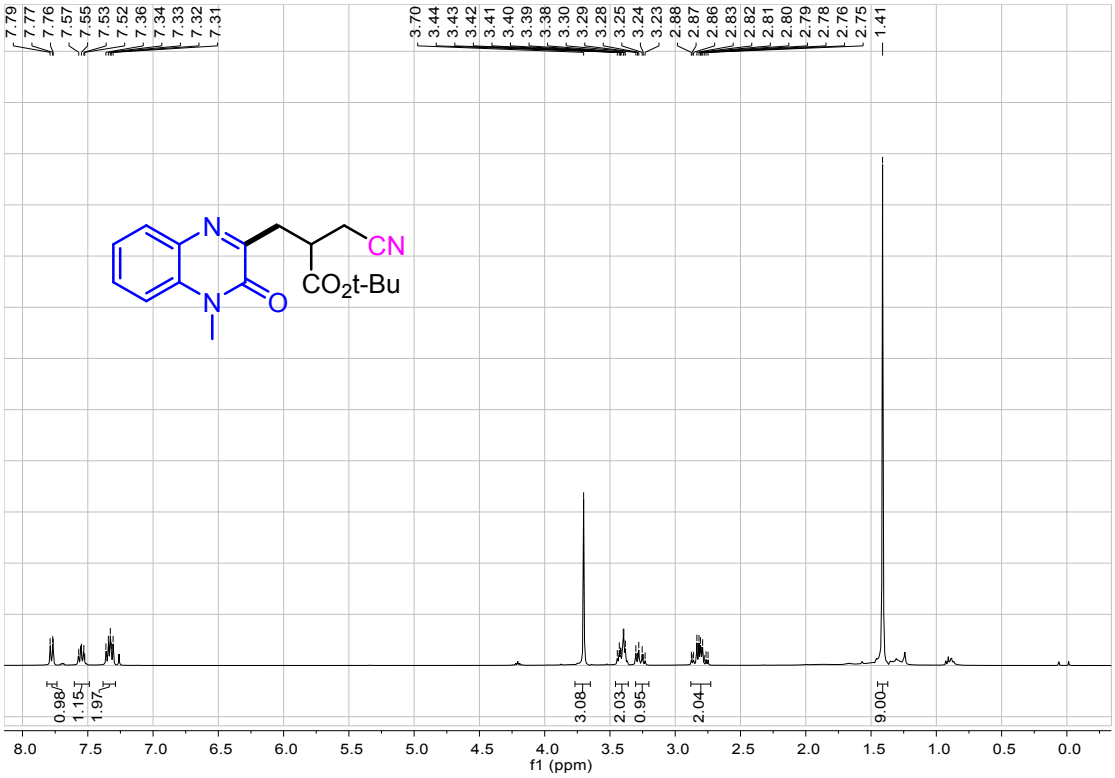
^{1}H NMR Spectrum of **3ea**



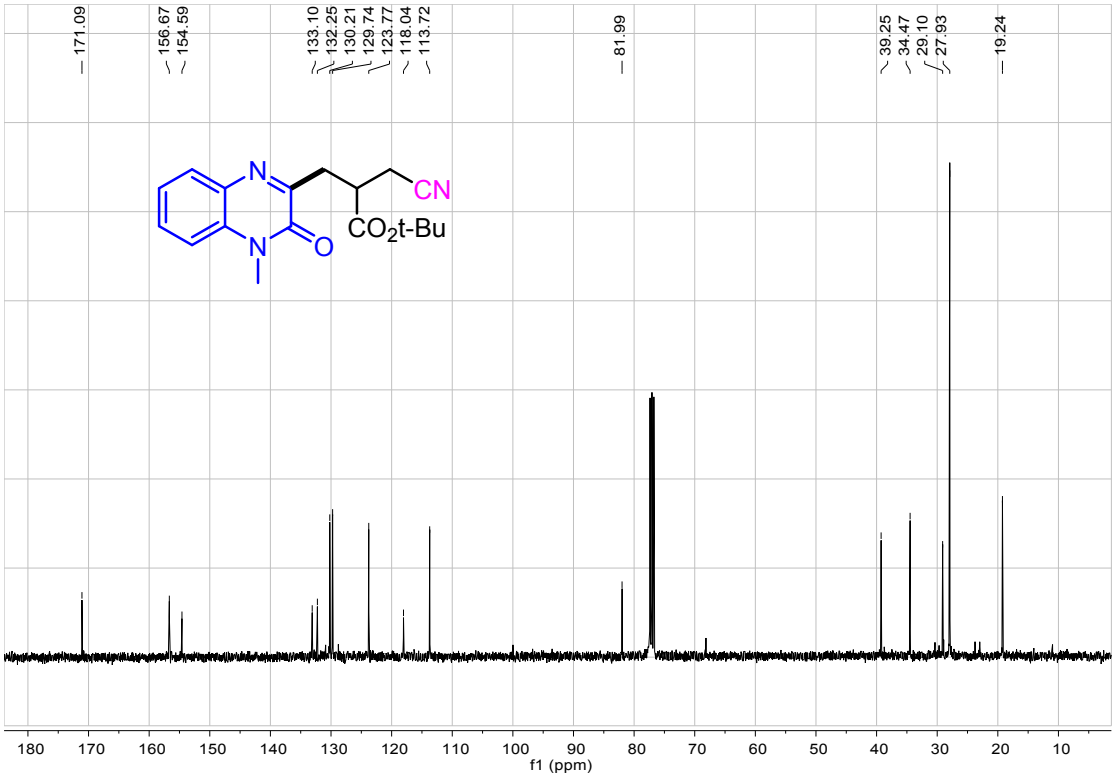
^{13}C NMR Spectrum of **3ea**



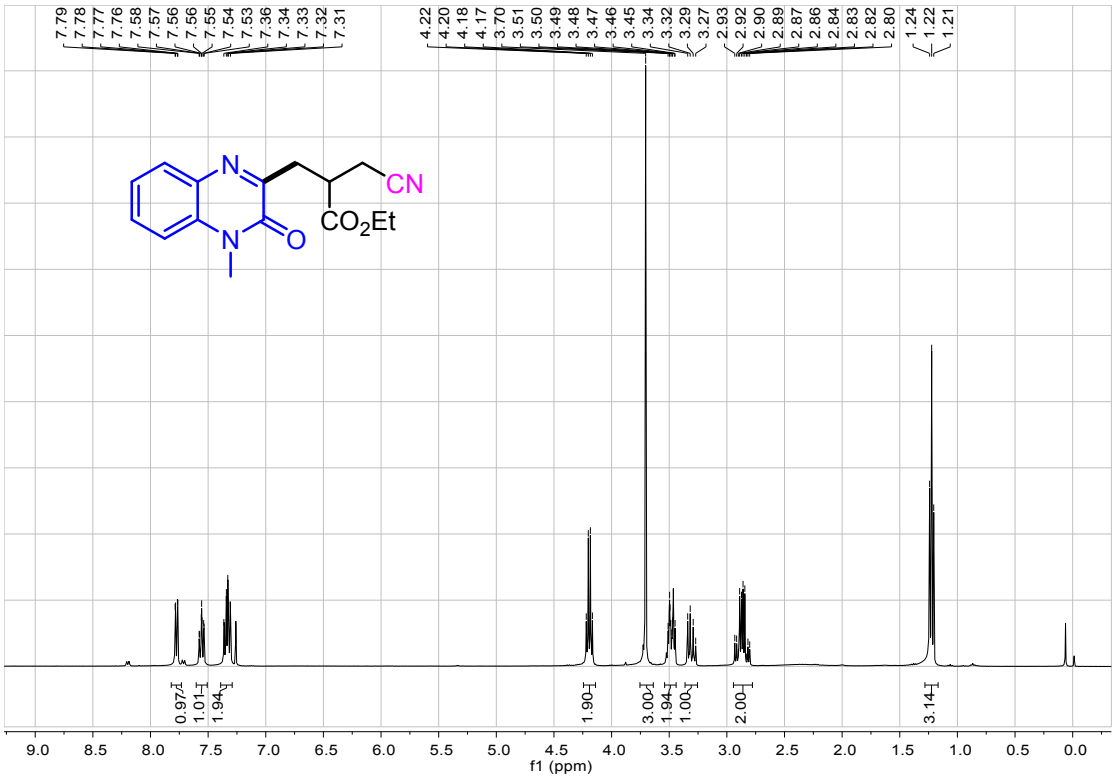
^{1}H NMR Spectrum of **3fa**



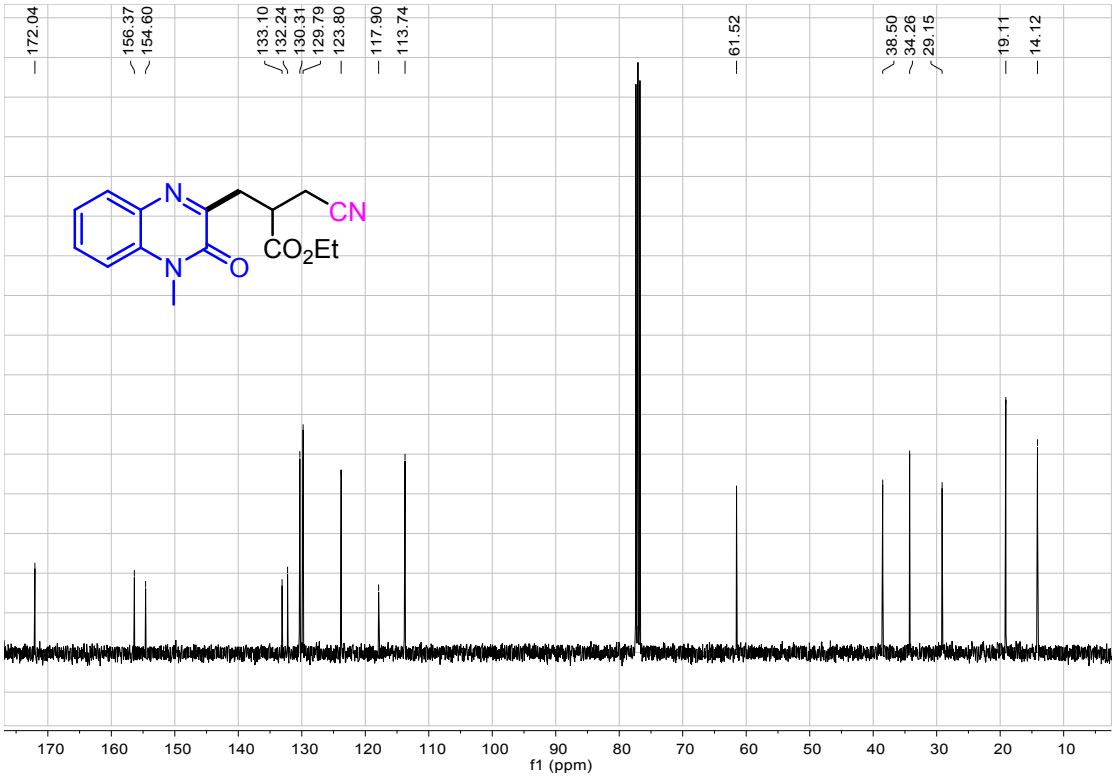
^{13}C NMR Spectrum of **3fa**



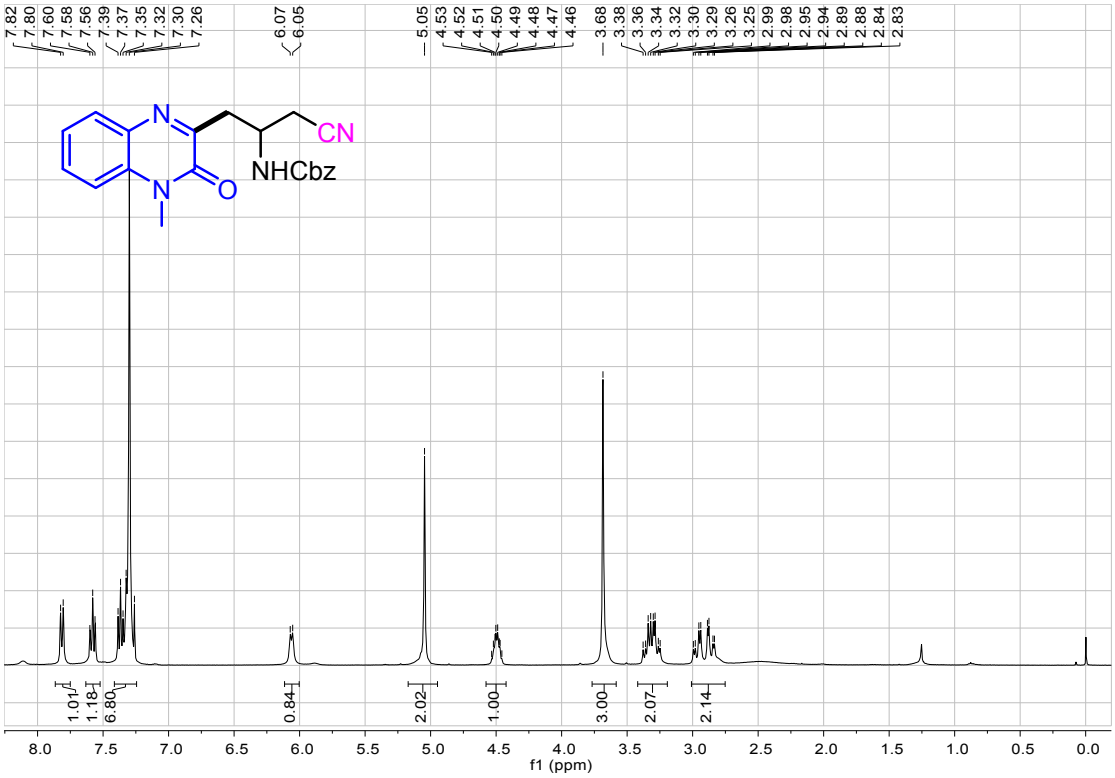
^{1}H NMR Spectrum of **3ga**



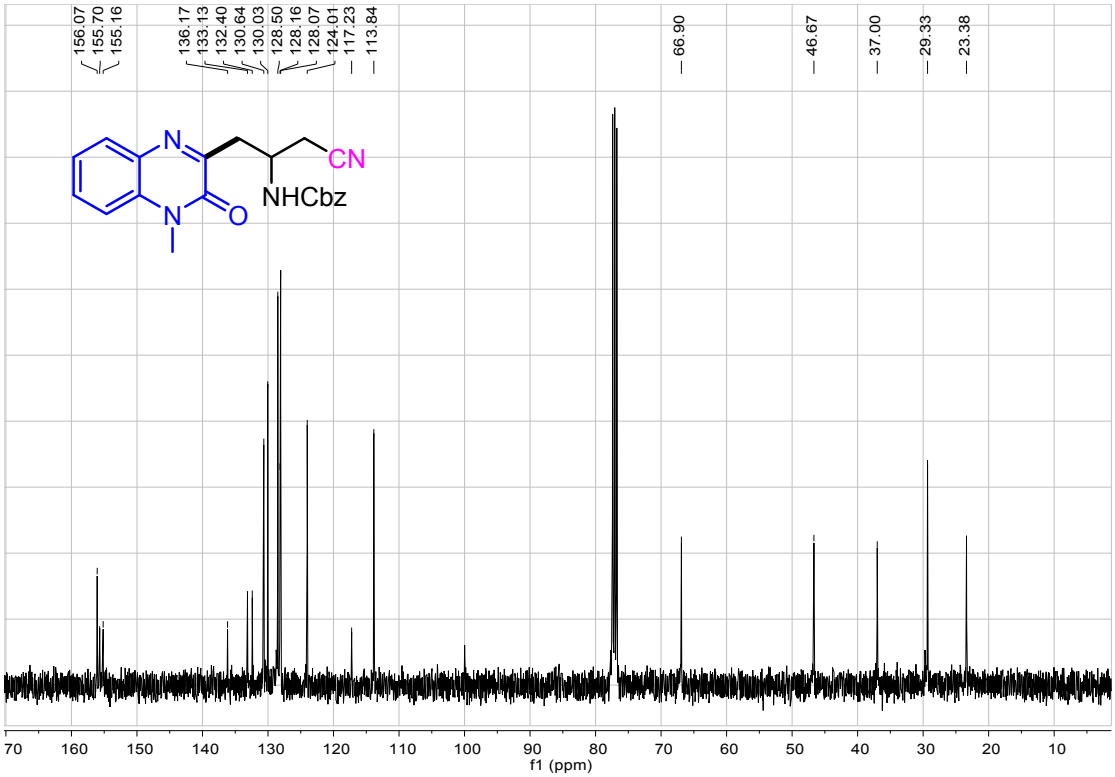
^{13}C NMR Spectrum of **3ga**



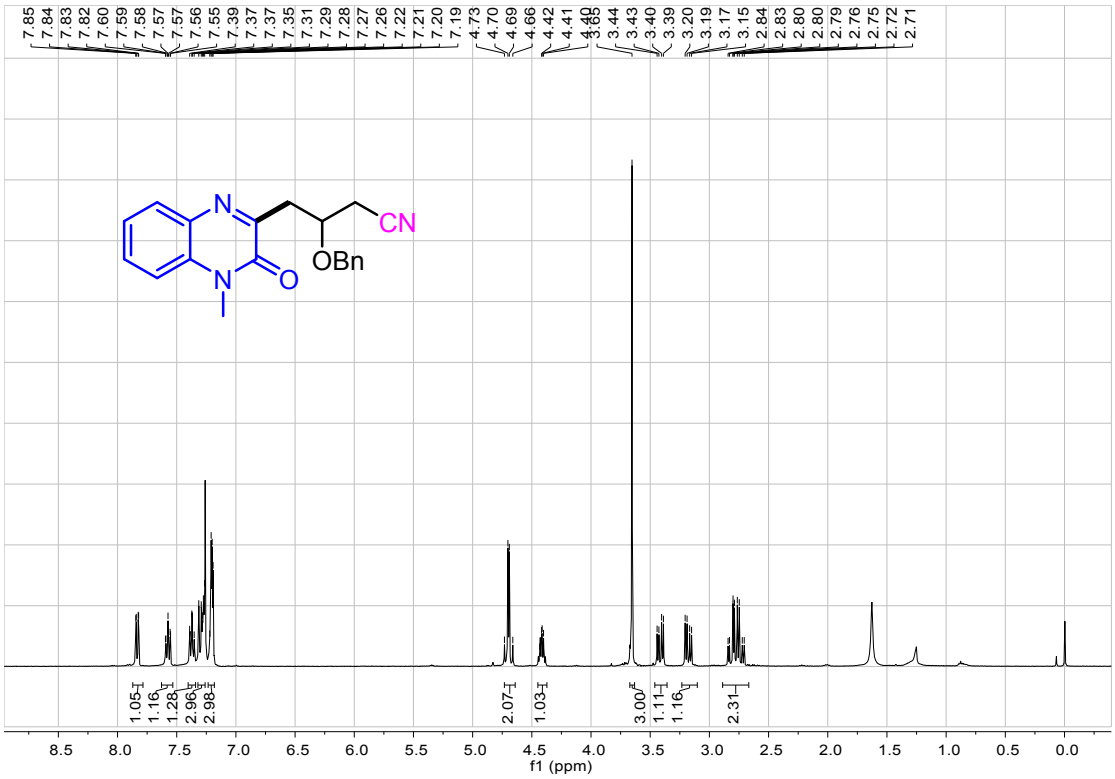
^{1}H NMR Spectrum of **3ha**



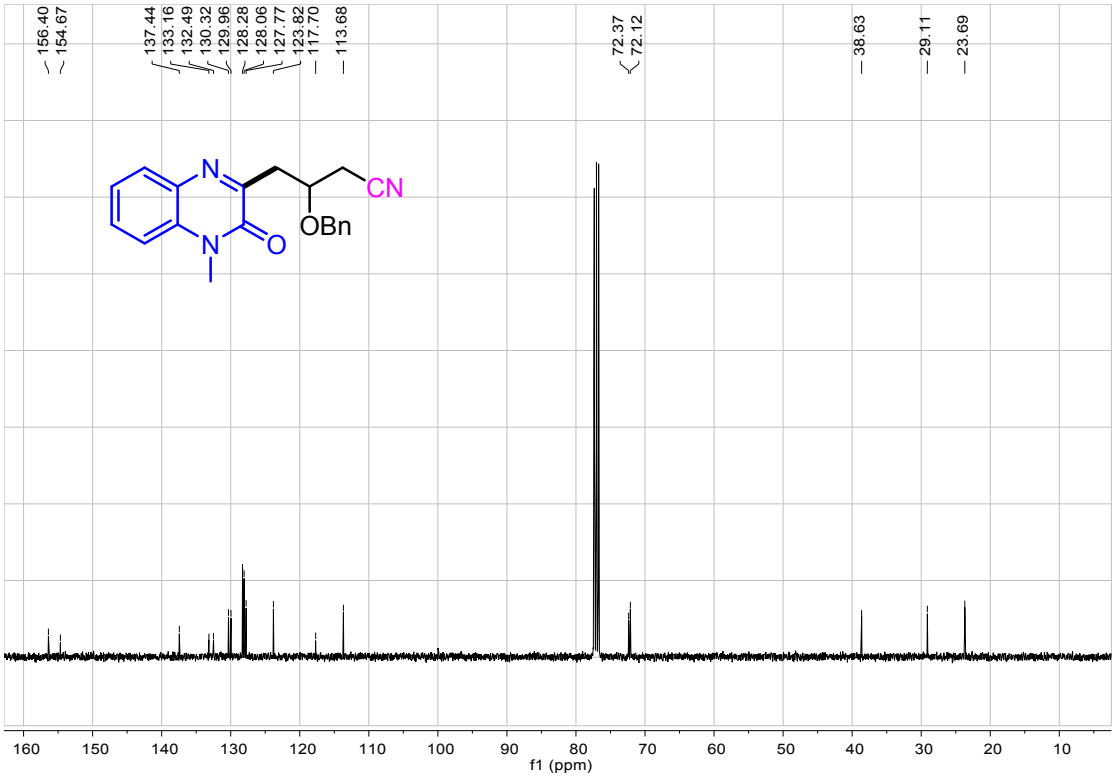
^{13}C NMR Spectrum of **3ha**



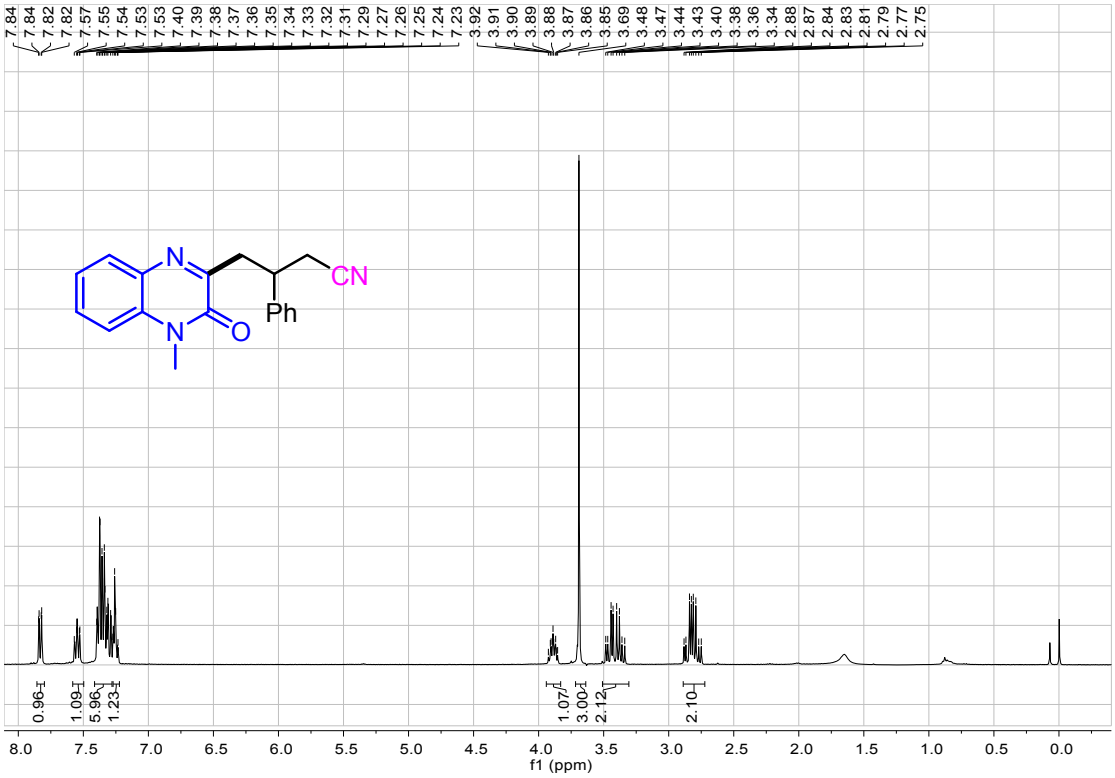
^{1}H NMR Spectrum of **3ia**



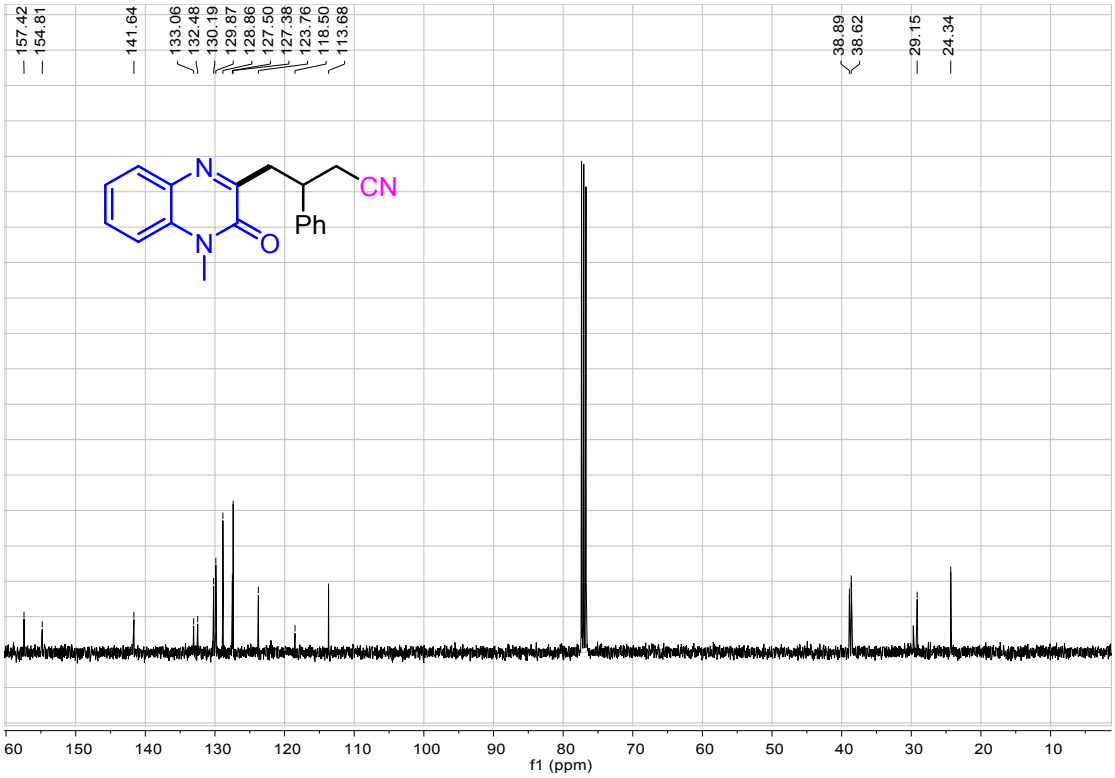
^{13}C NMR Spectrum of **3ia**



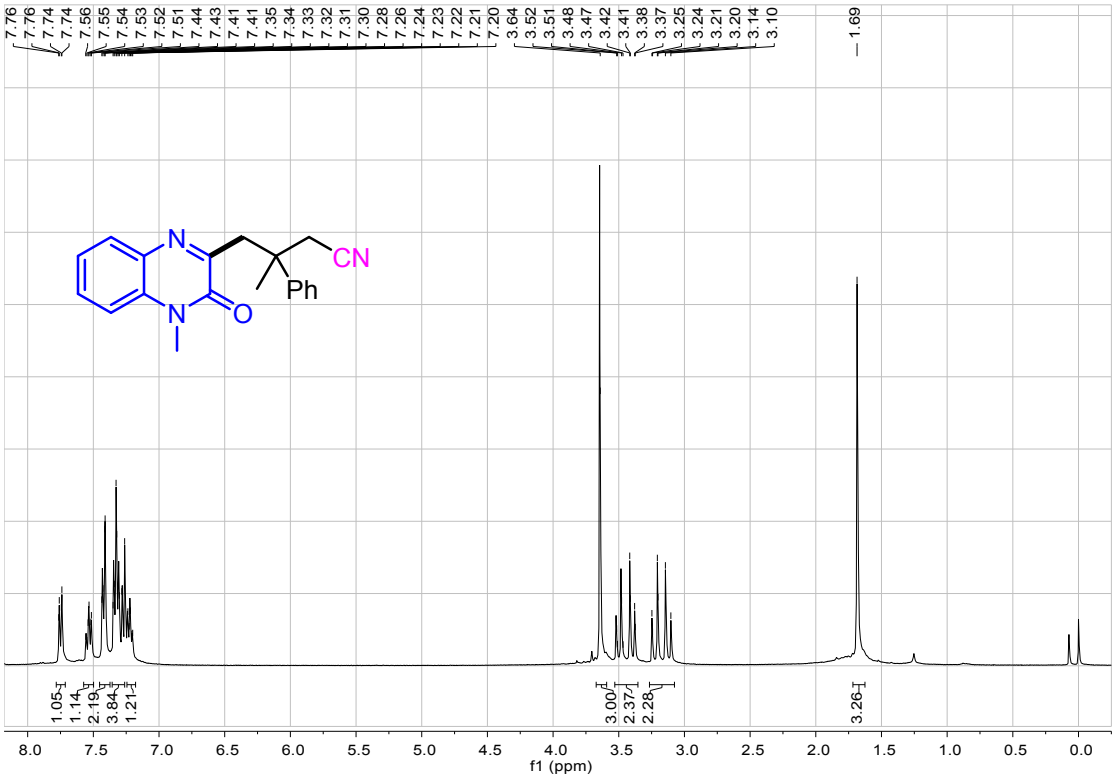
^{1}H NMR Spectrum of **3ja**



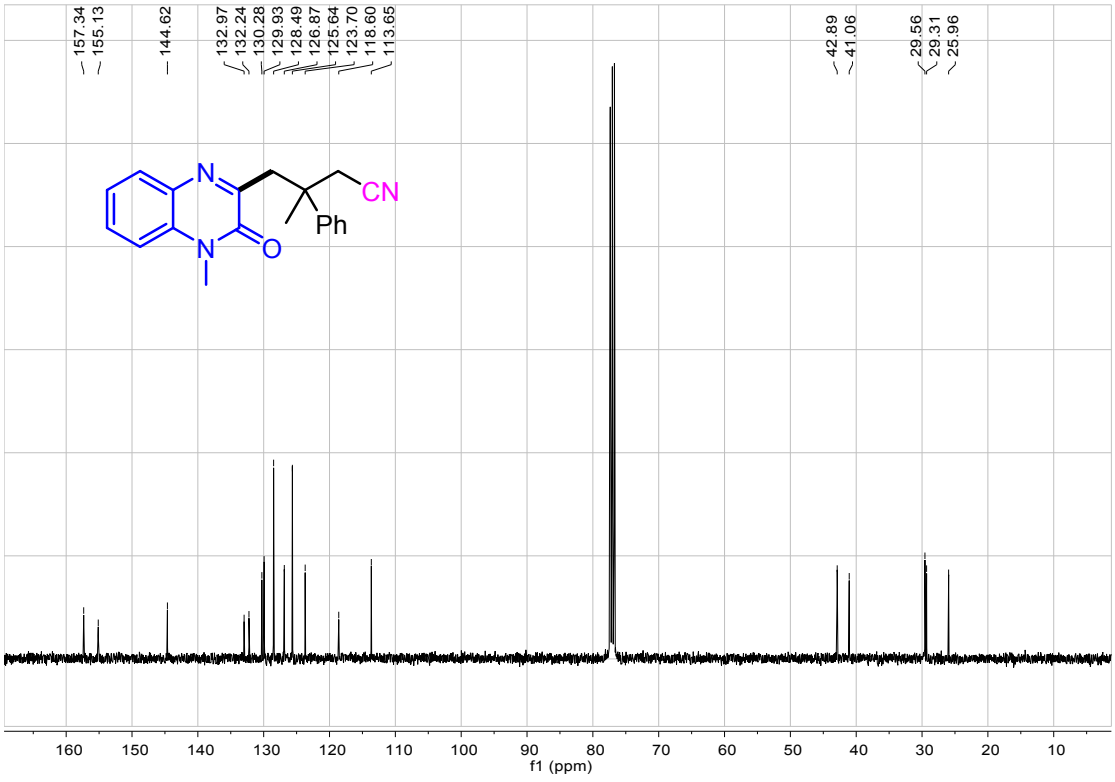
^{13}C NMR Spectrum of **3ja**



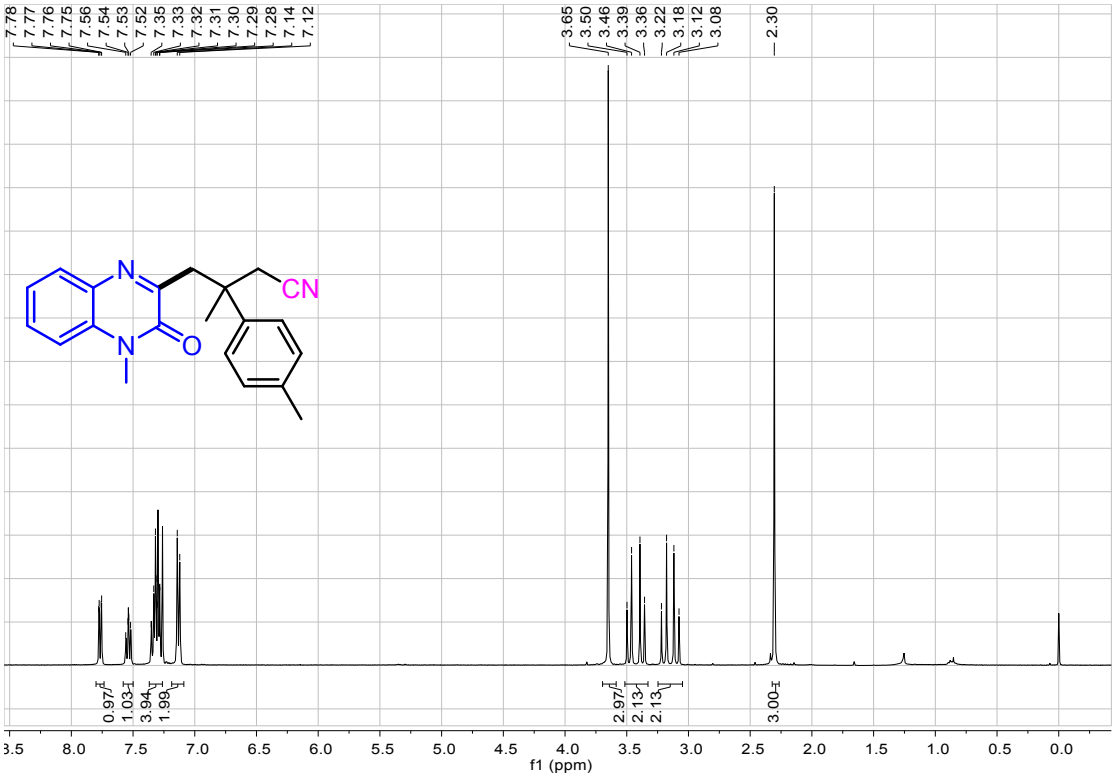
^{1}H NMR Spectrum of **3ka**



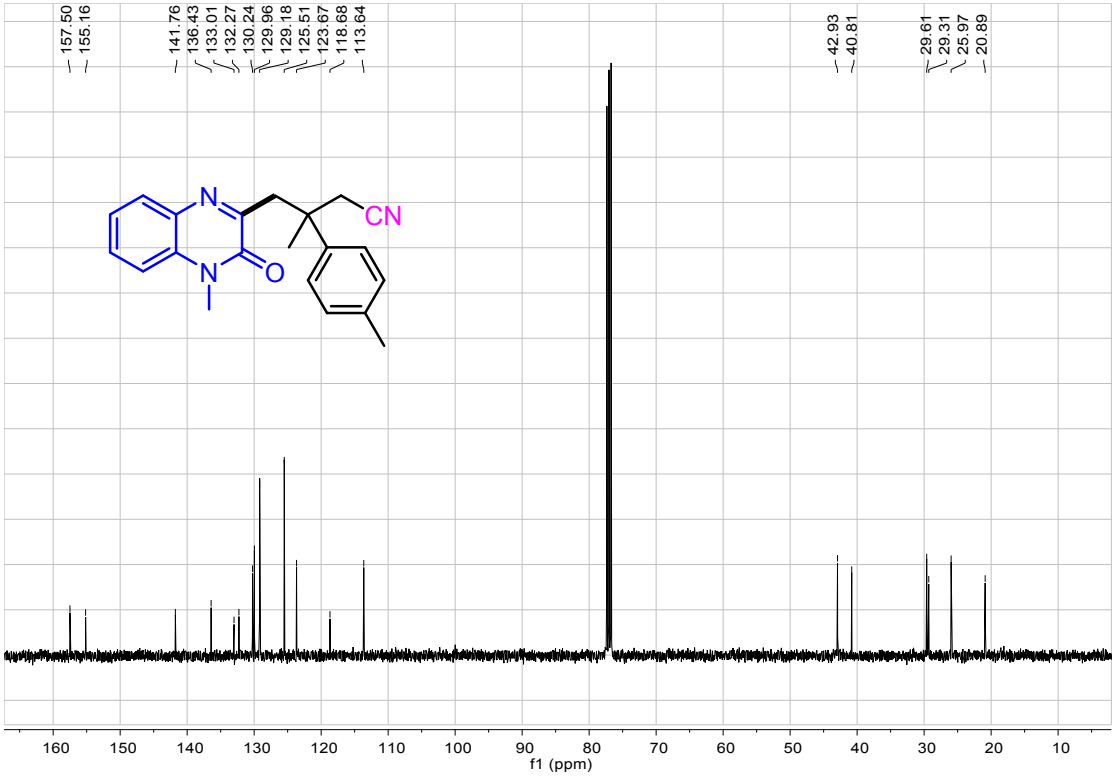
^{13}C NMR Spectrum of **3ka**



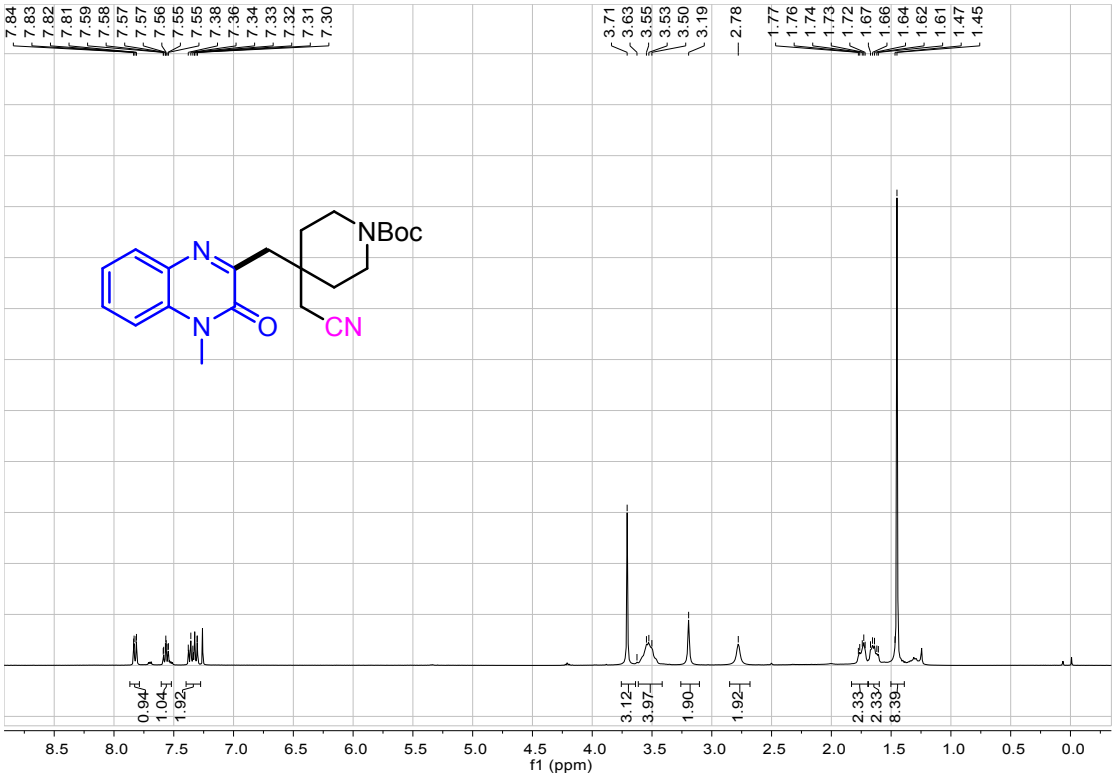
^{1}H NMR Spectrum of **3la**



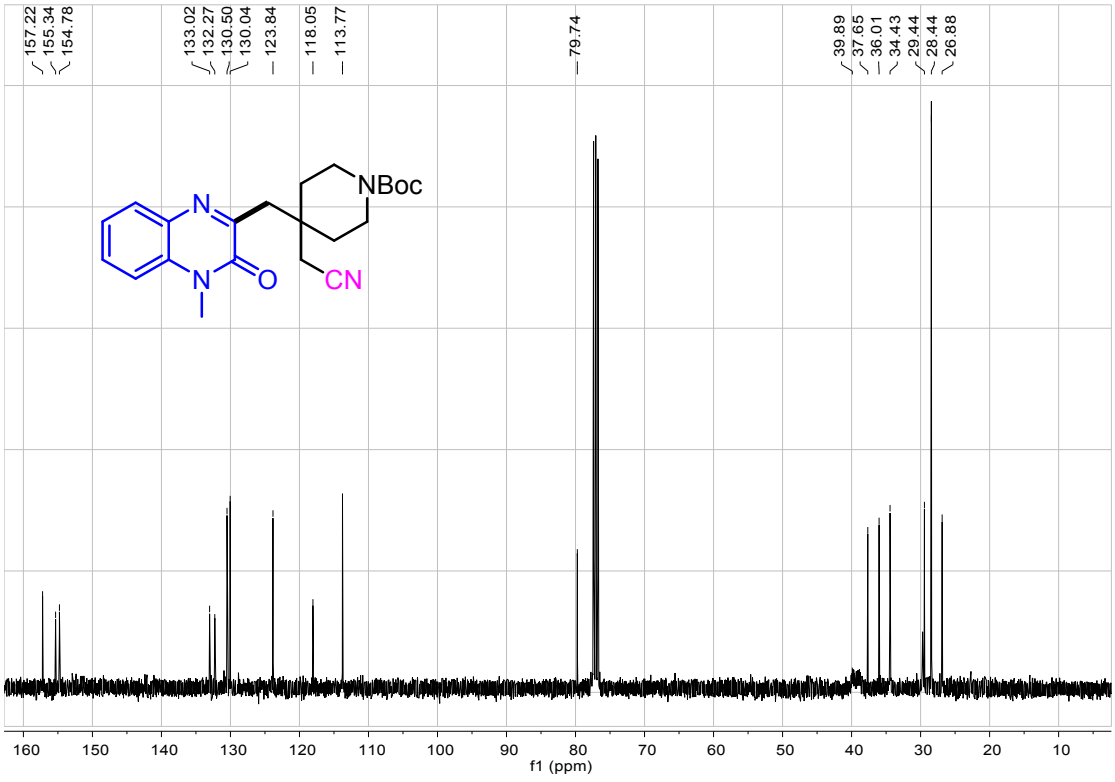
^{13}C NMR Spectrum of **3la**



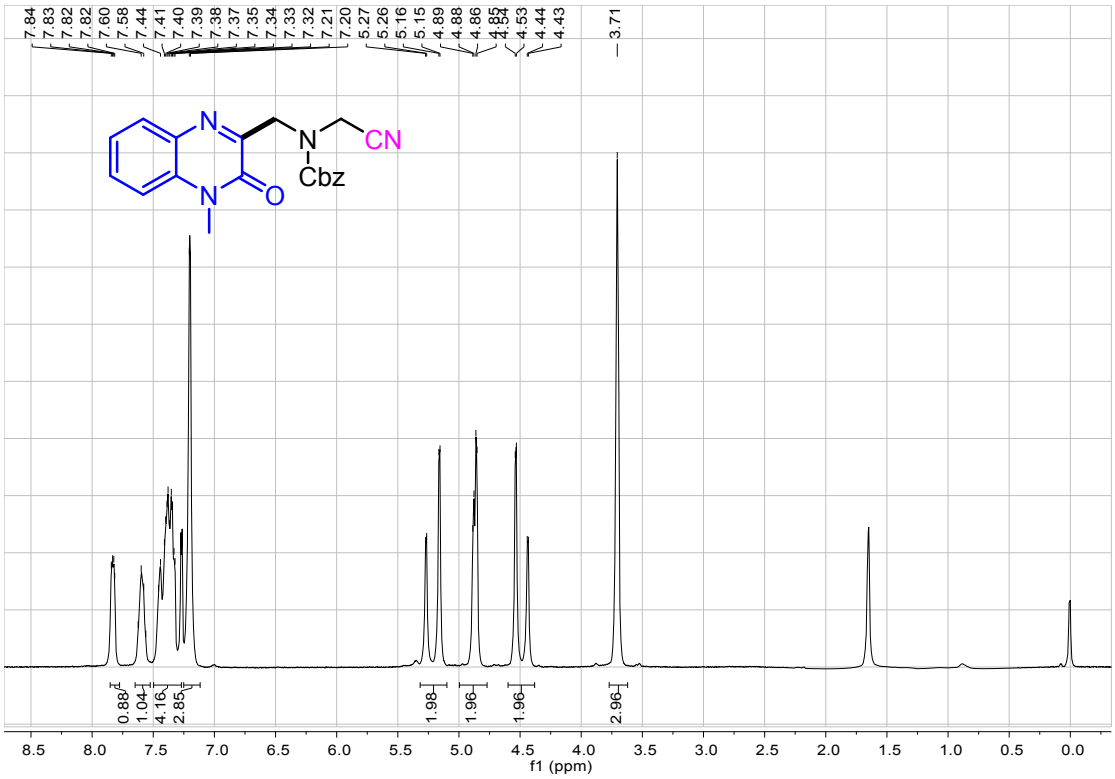
^{1}H NMR Spectrum of **3ma**



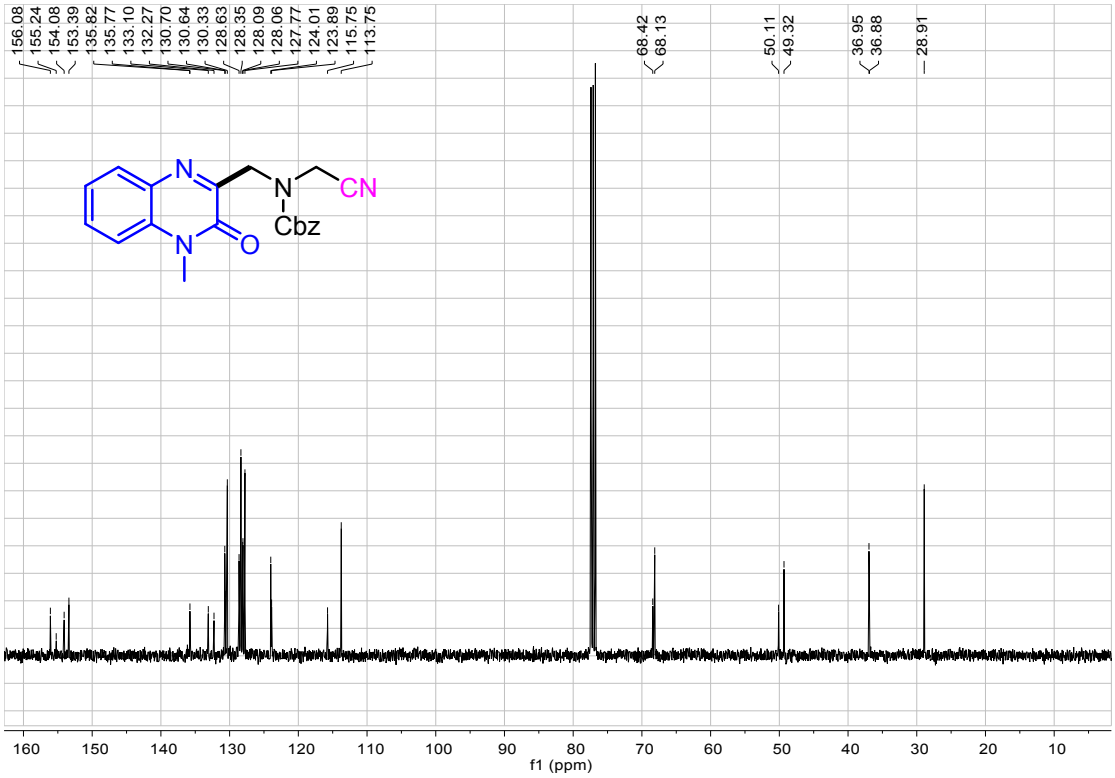
^{13}C NMR Spectrum of **3ma**



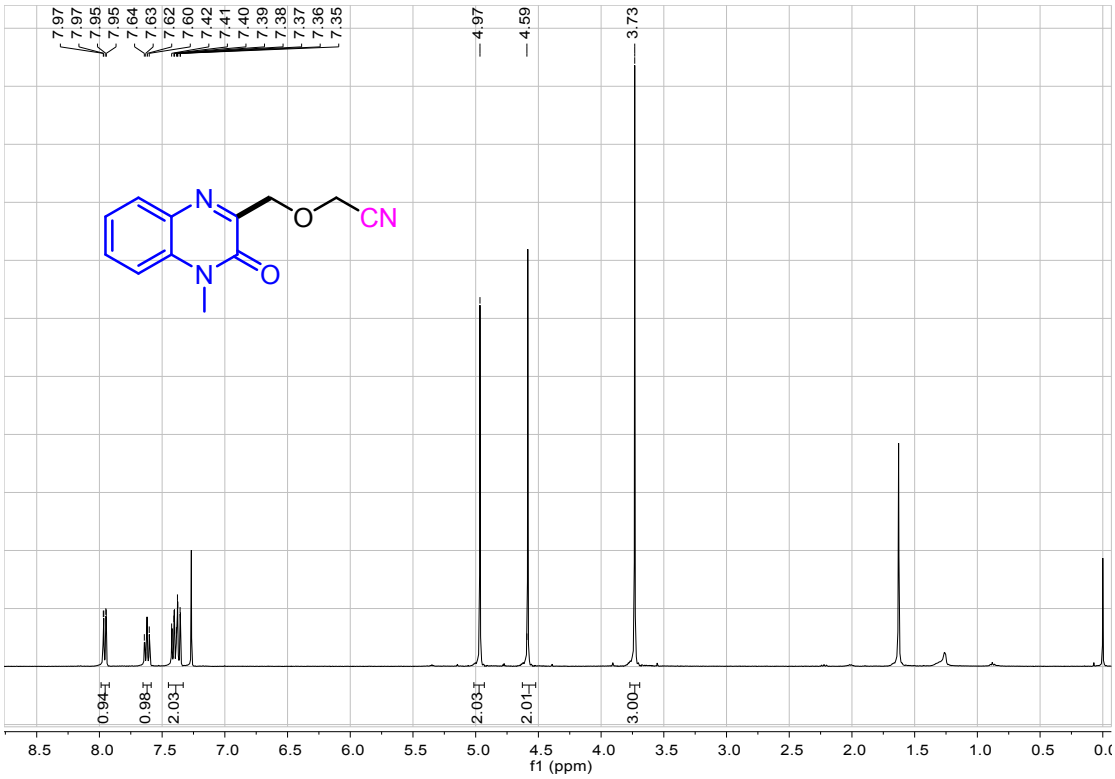
^{1}H NMR Spectrum of **3na**



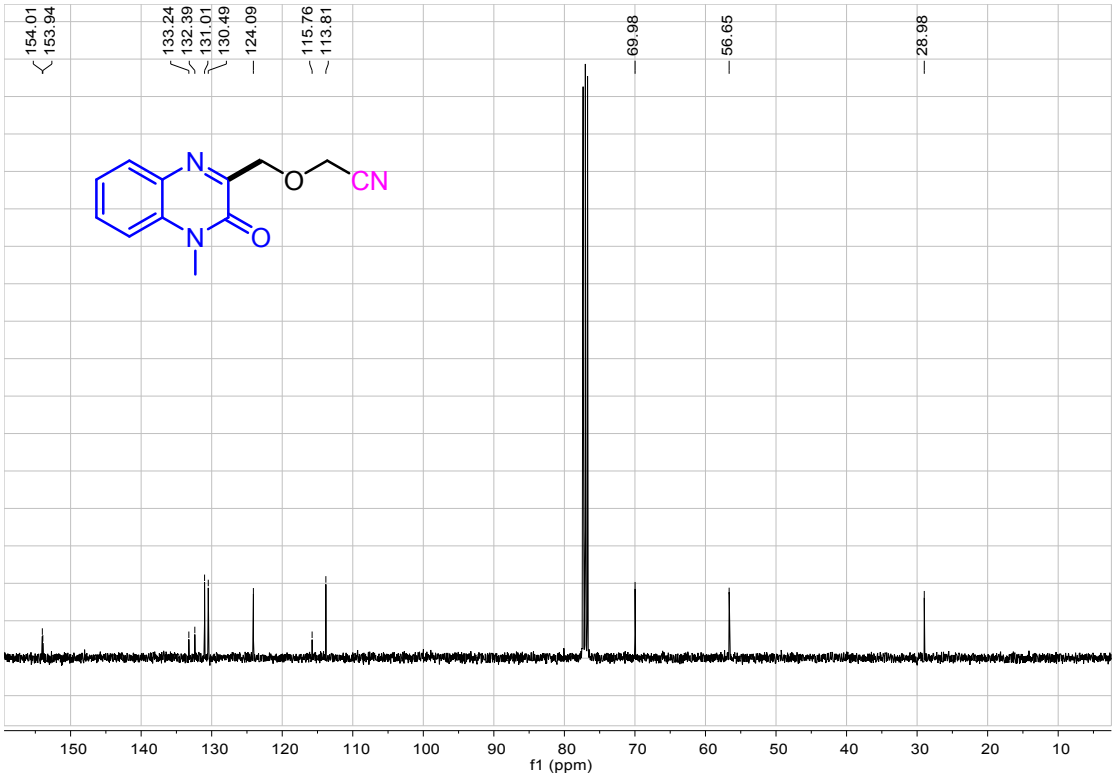
^{13}C NMR Spectrum of **3na**



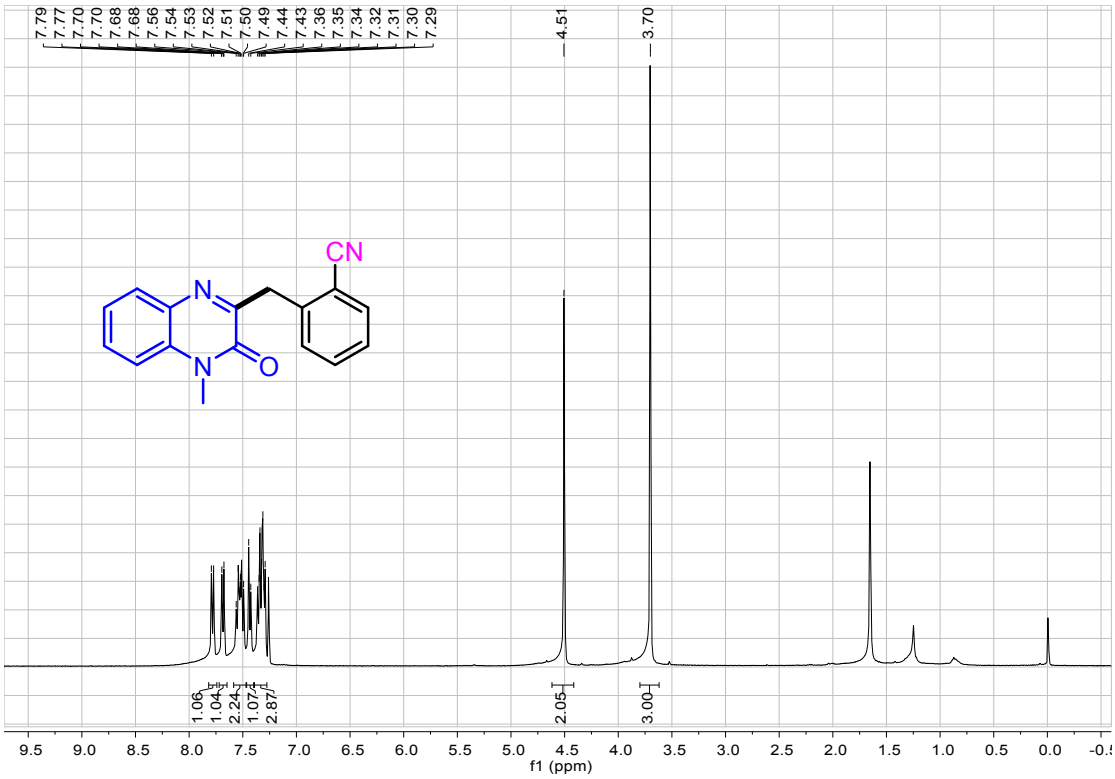
^{1}H NMR Spectrum of **3oa**



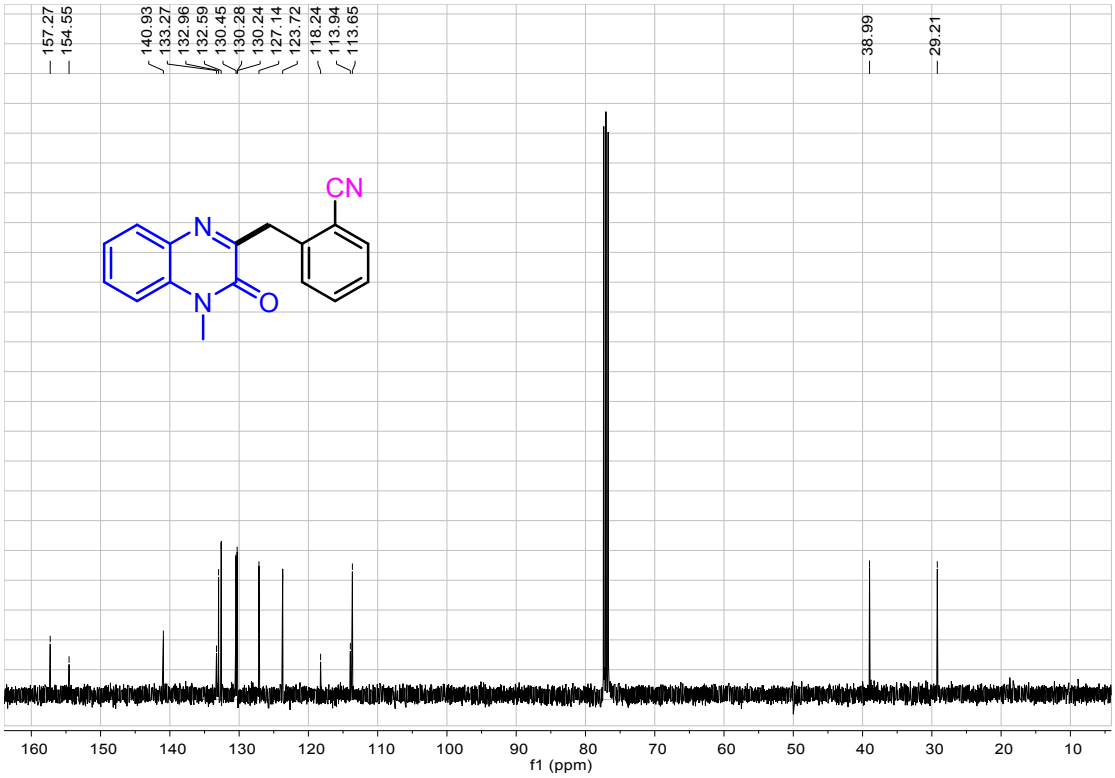
^{13}C NMR Spectrum of **4o**



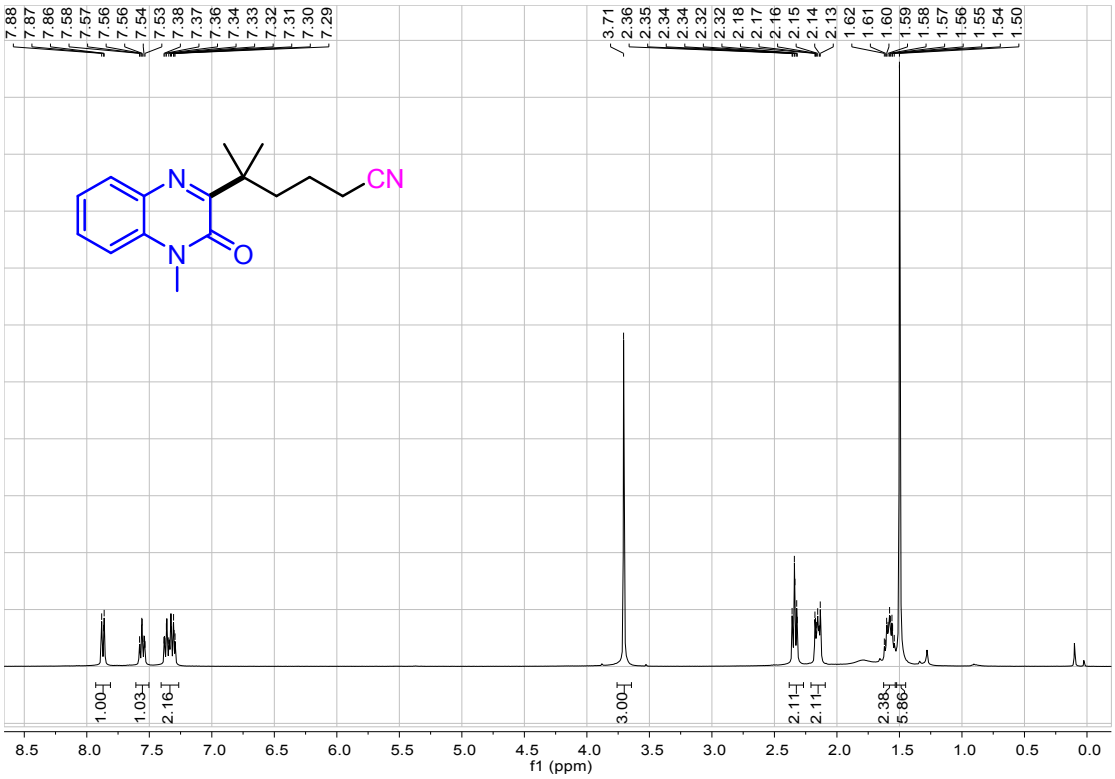
^{1}H NMR Spectrum of **3pa**



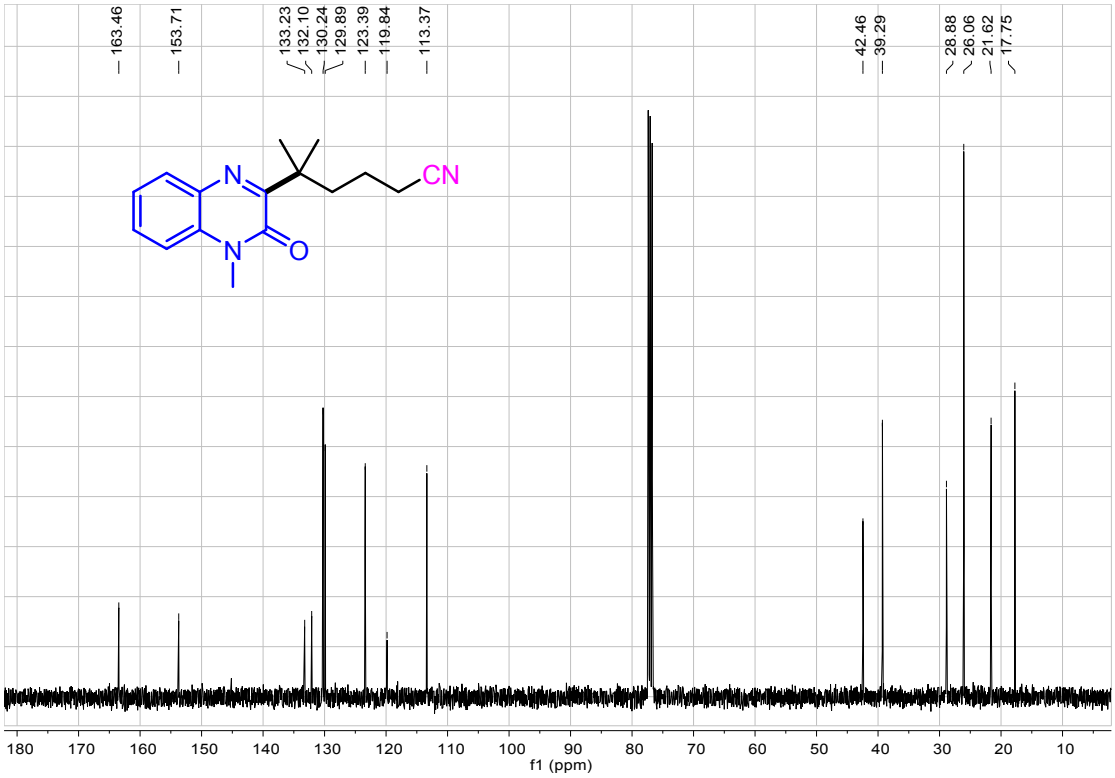
^{13}C NMR Spectrum of **4p**



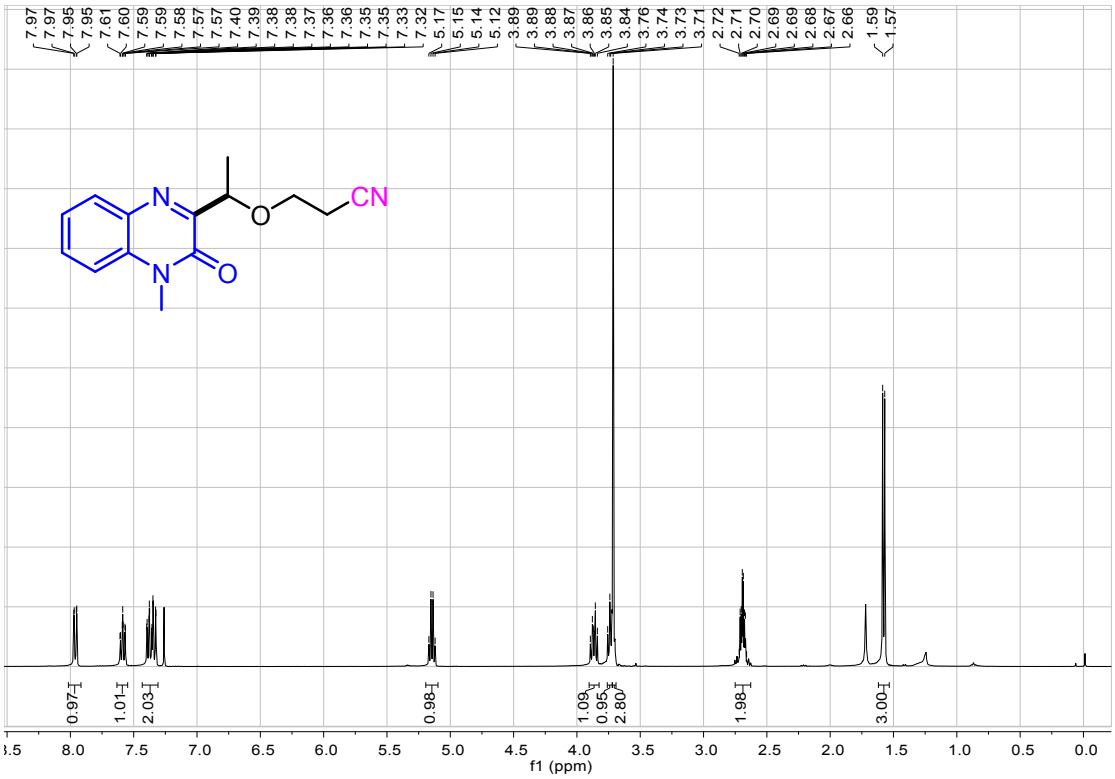
^{1}H NMR Spectrum of **5a**



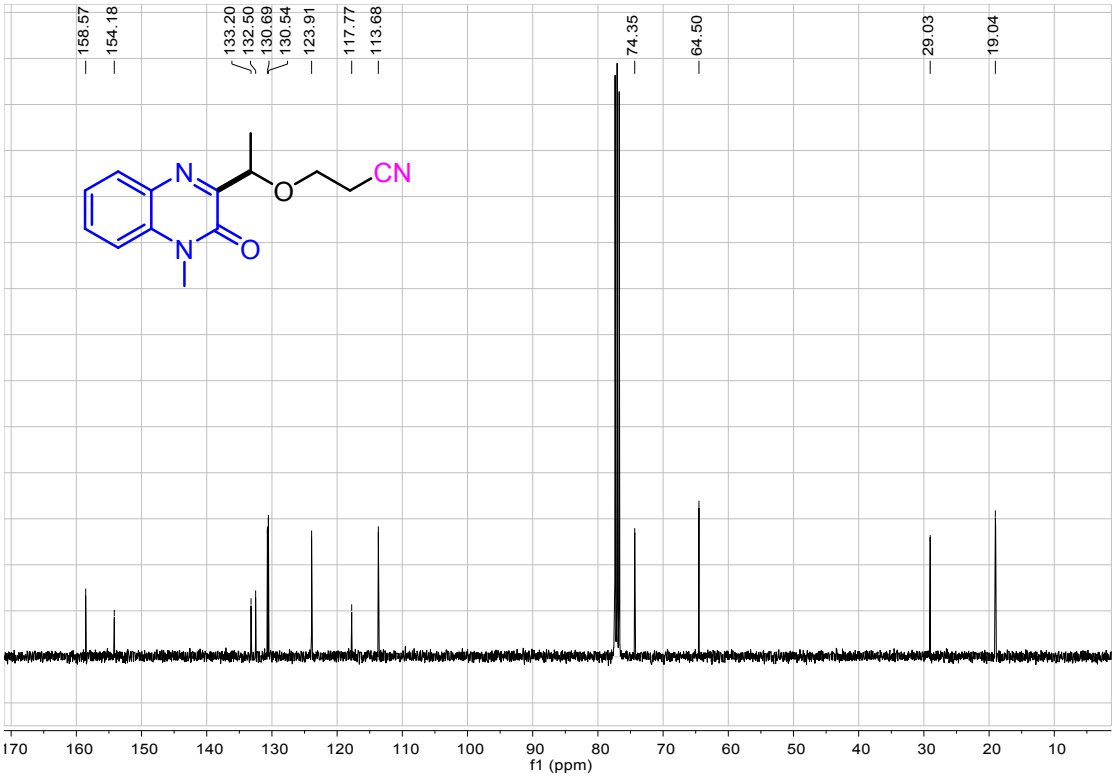
^{13}C NMR Spectrum of **5a**



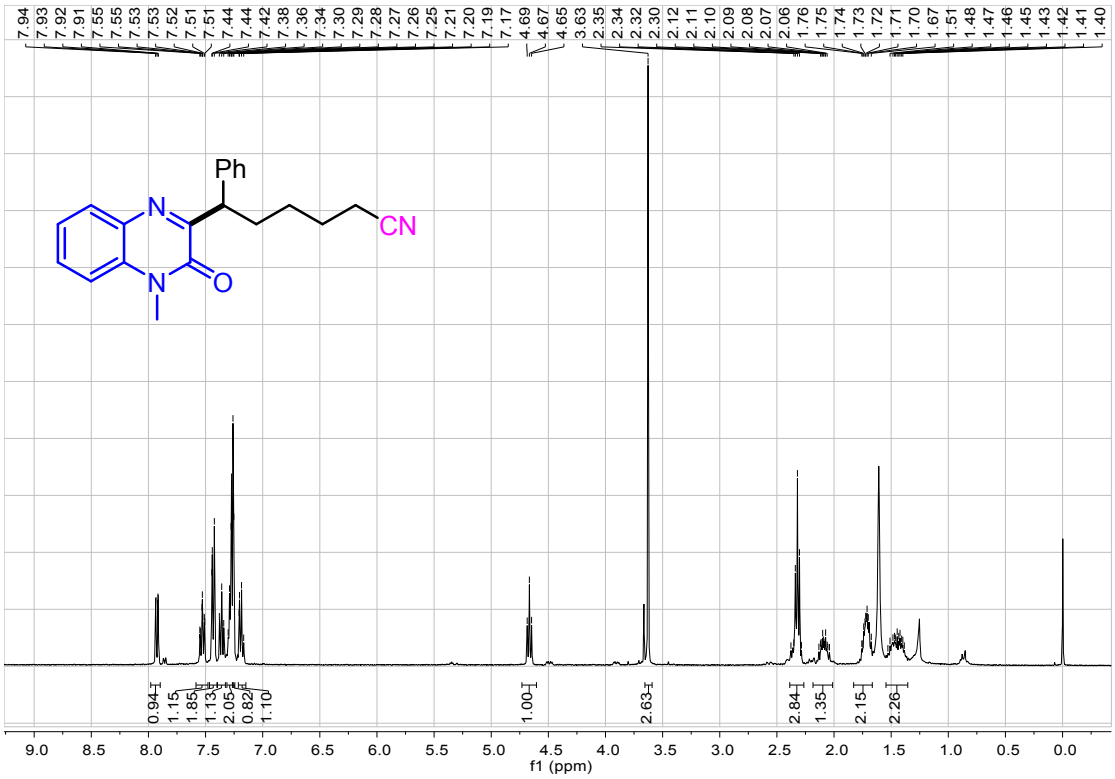
^{1}H NMR Spectrum of **5b**



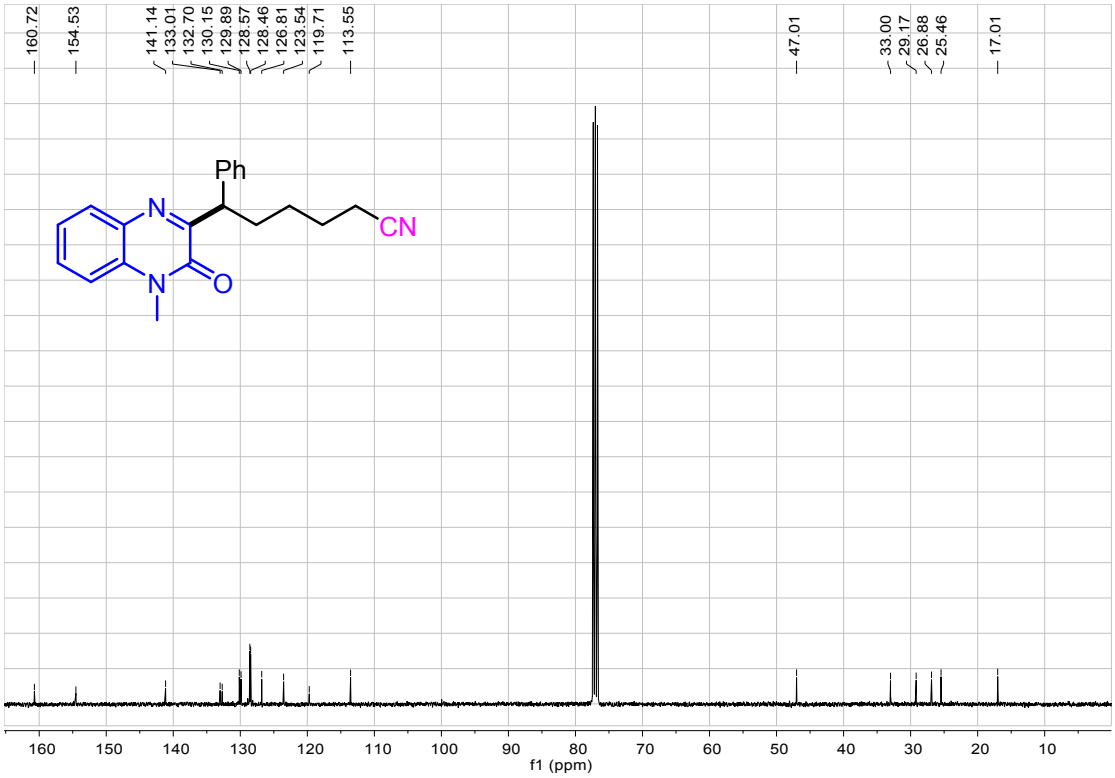
^{13}C NMR Spectrum of **5b**



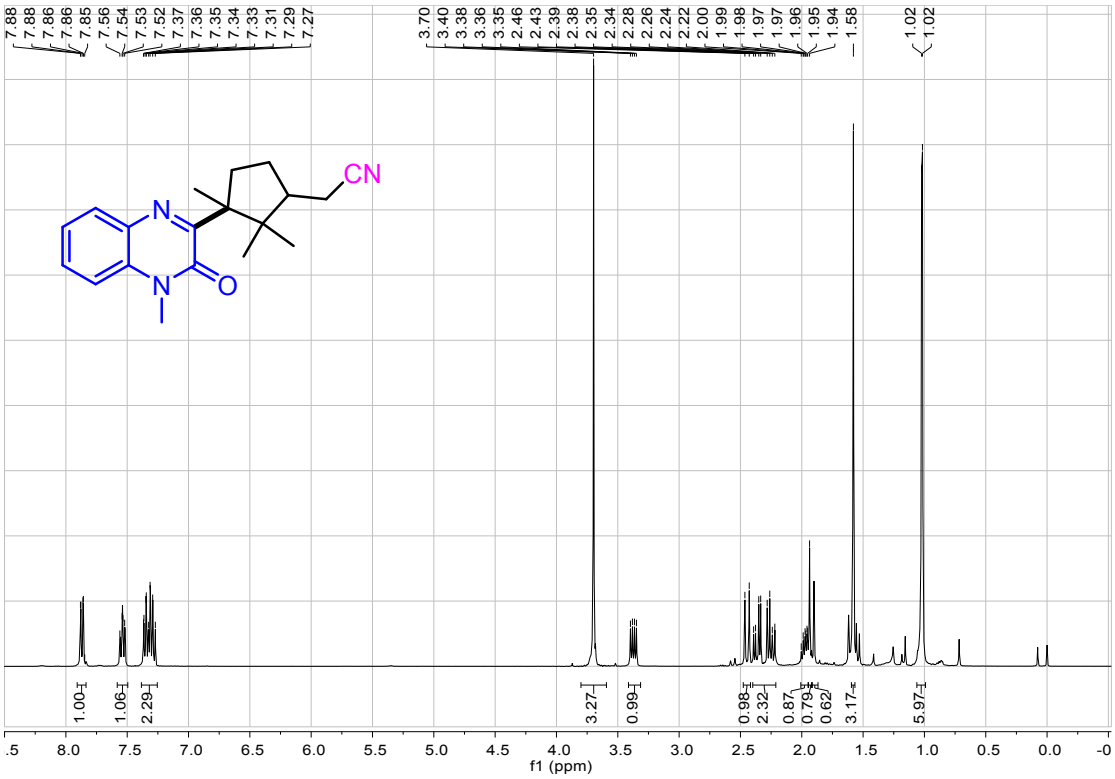
^{1}H NMR Spectrum of **5c**



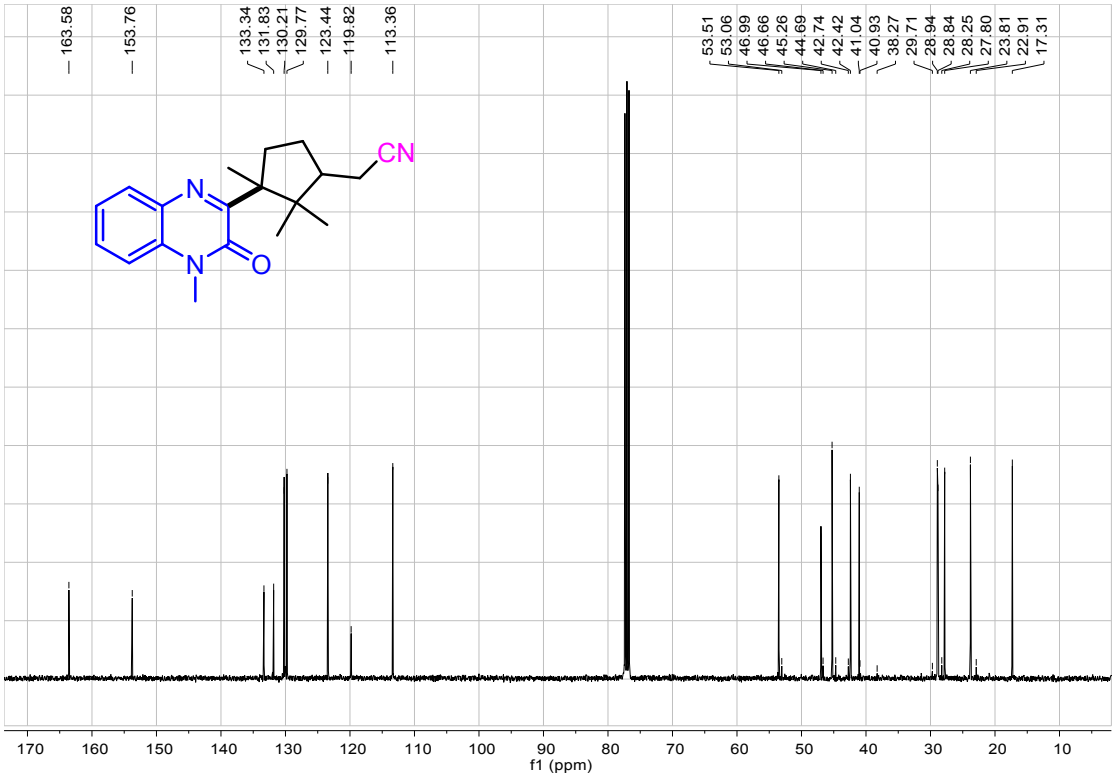
^{13}C NMR Spectrum of **5c**



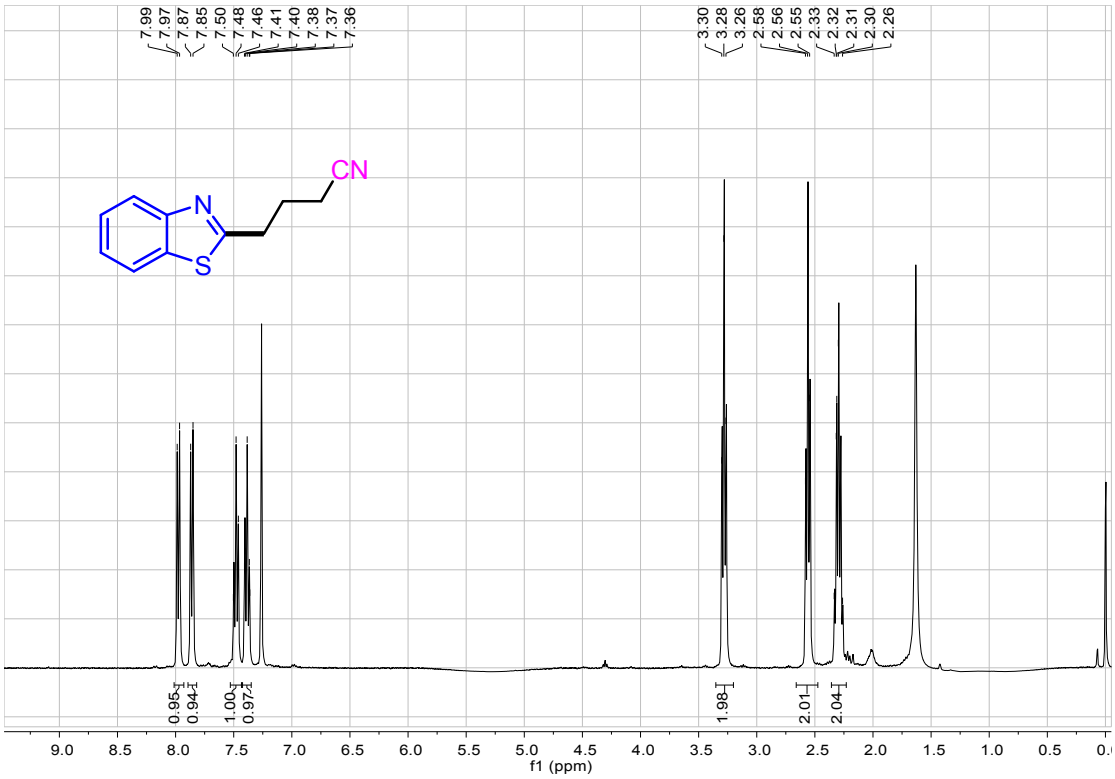
^{1}H NMR Spectrum of **5d**



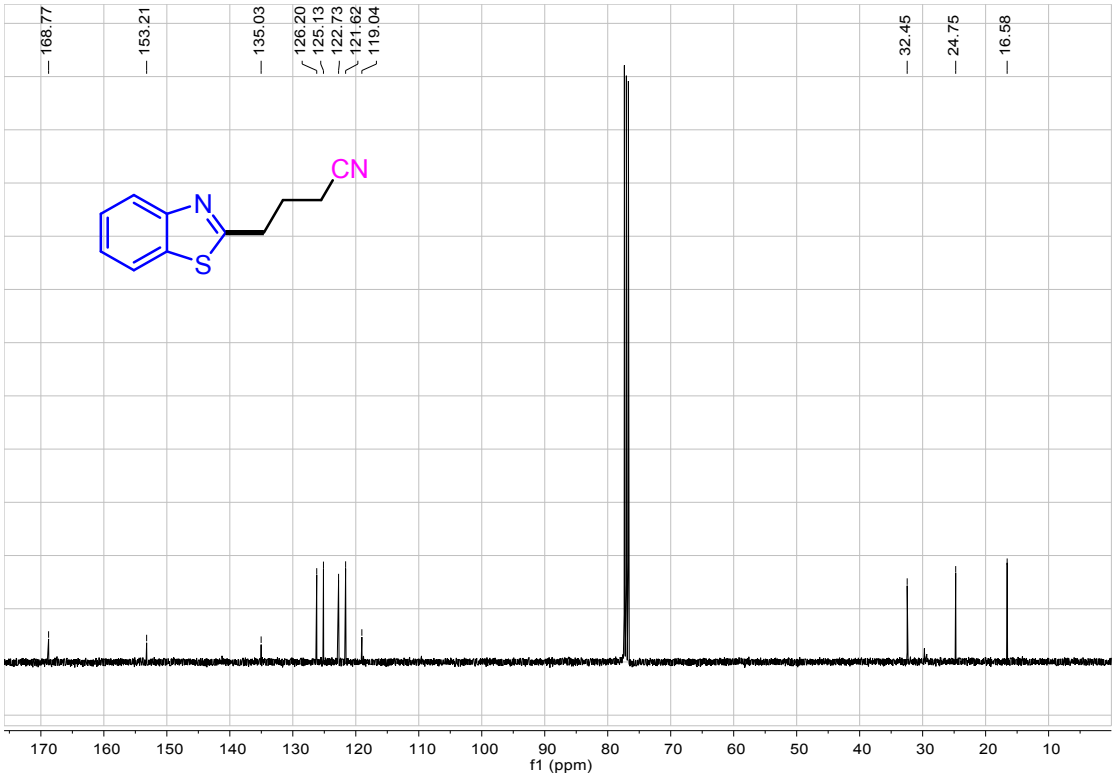
^{13}C NMR Spectrum of **5d**



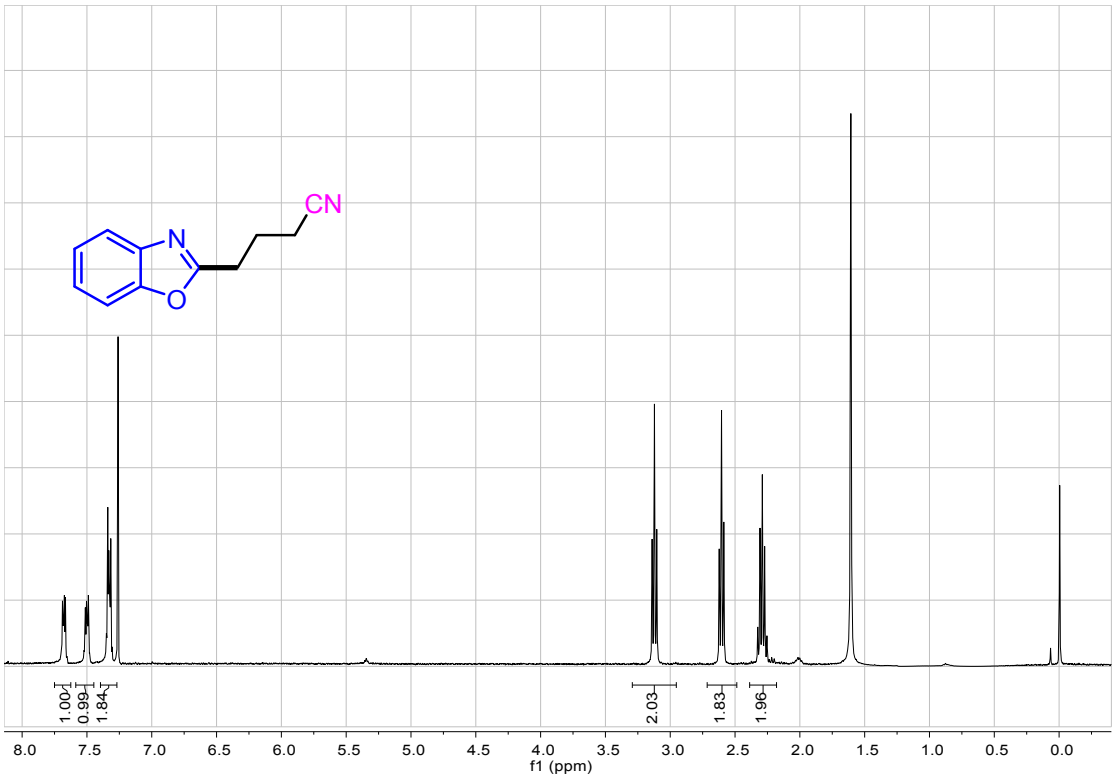
^{1}H NMR Spectrum of **7a**



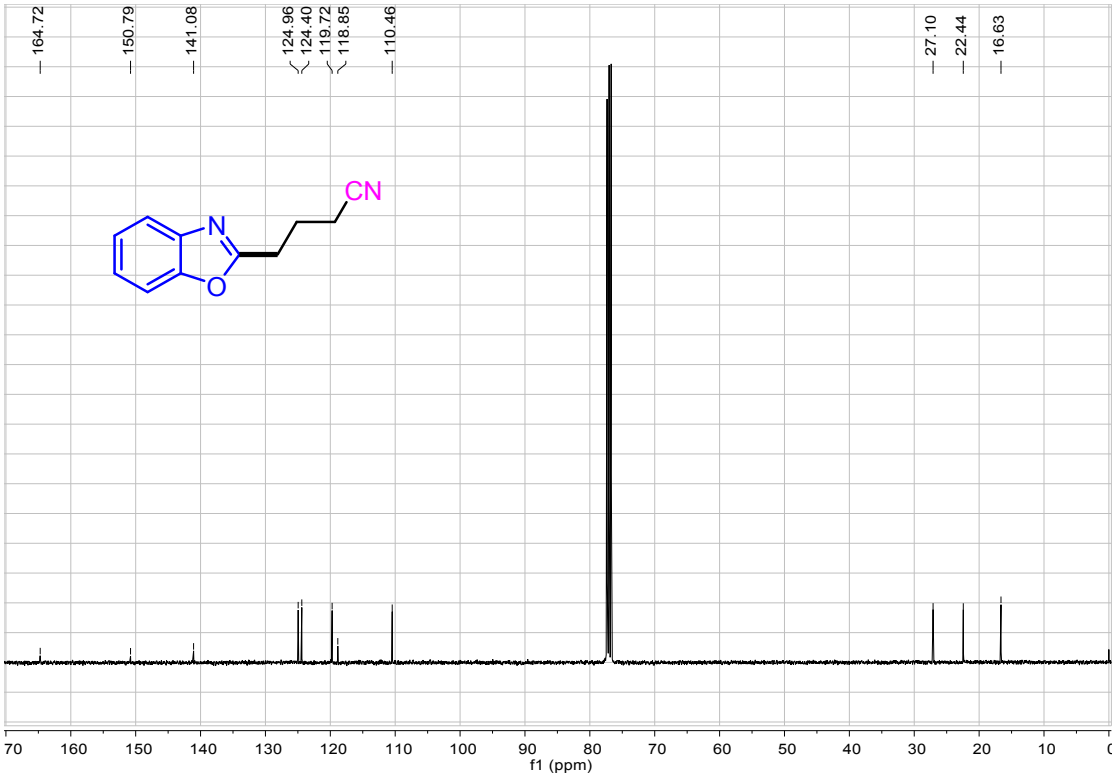
^{13}C NMR Spectrum of **7a**



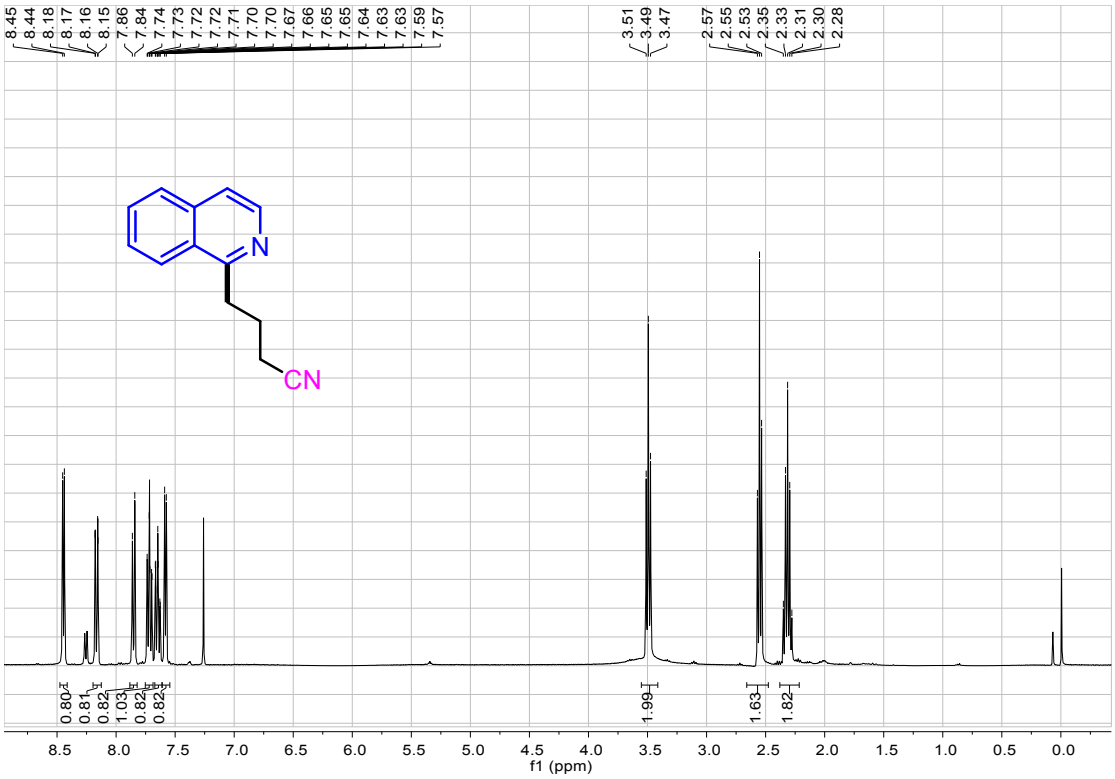
^{1}H NMR Spectrum of **7b**



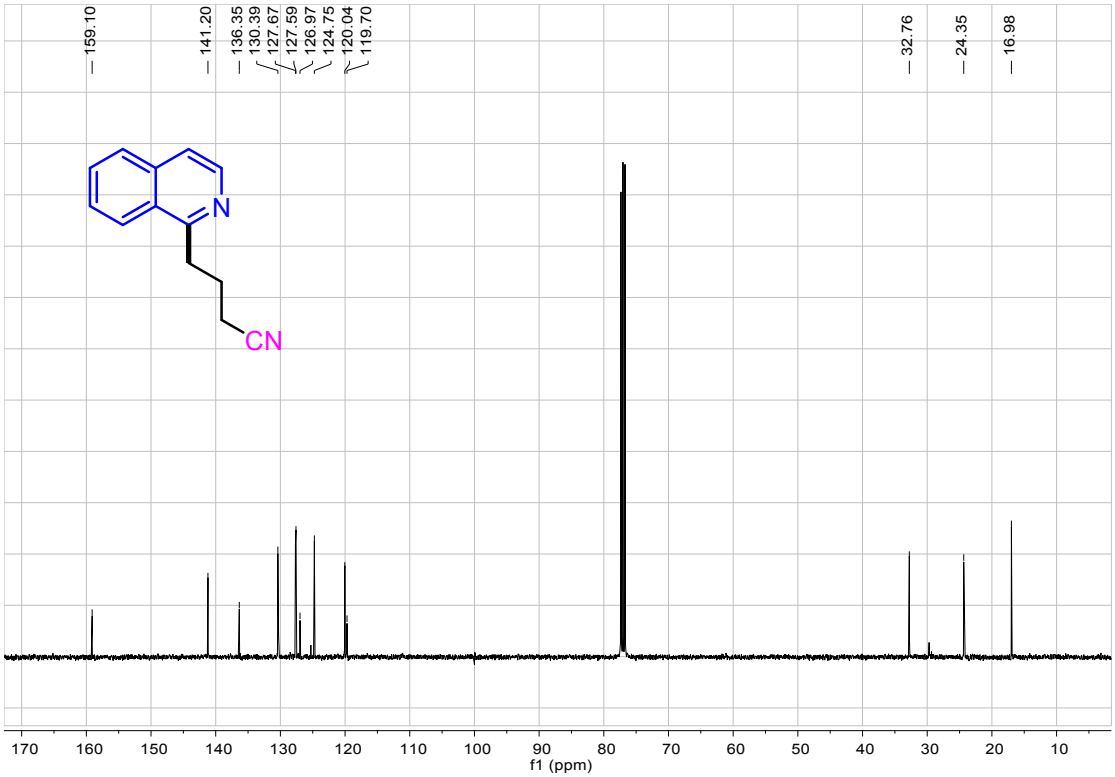
^{13}C NMR Spectrum of **7b**



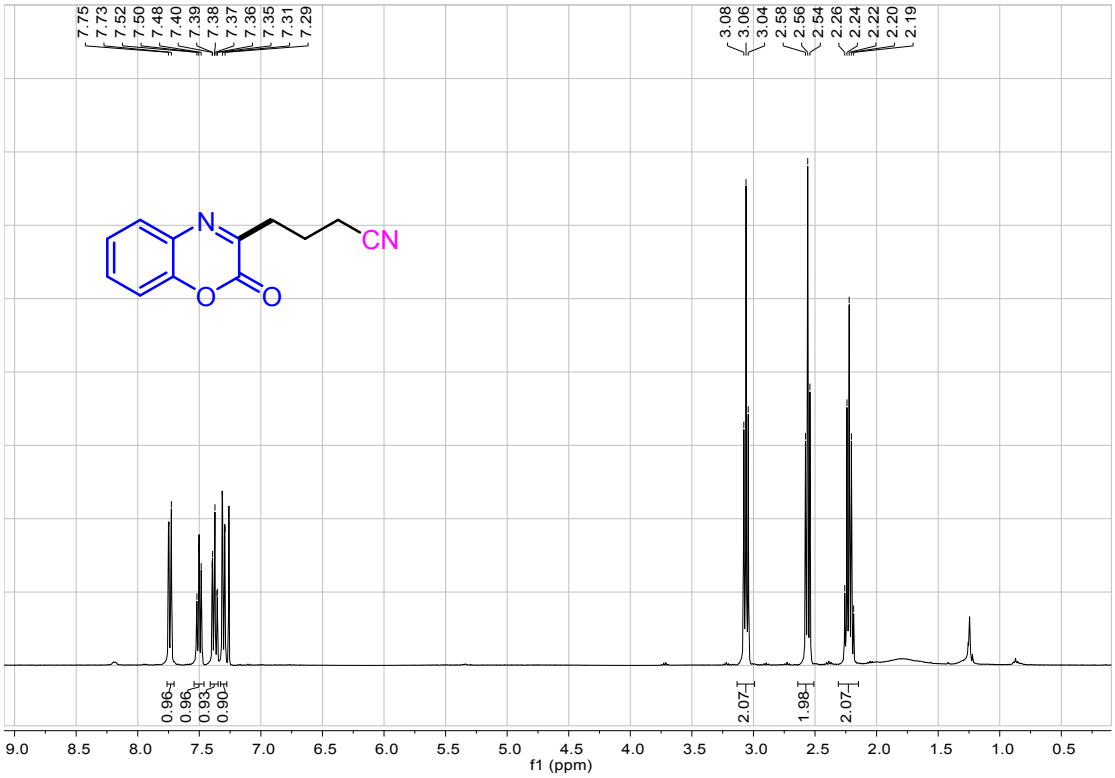
^{1}H NMR Spectrum of **7c**



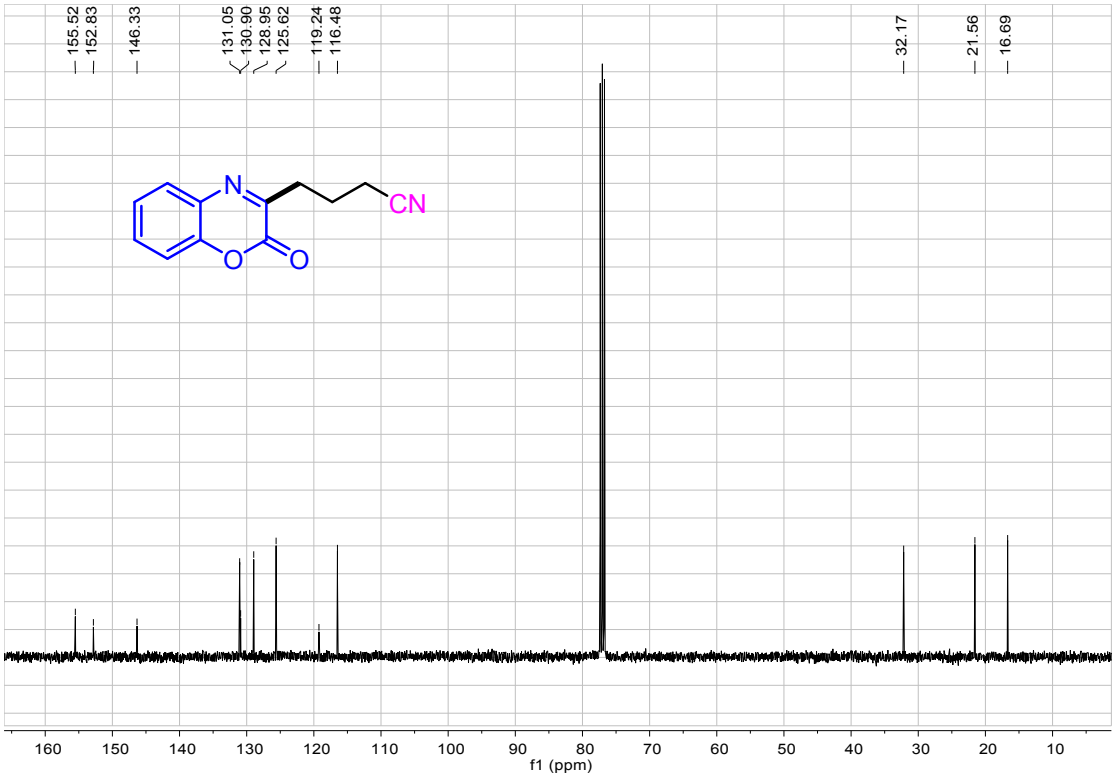
^{13}C NMR Spectrum of **7c**



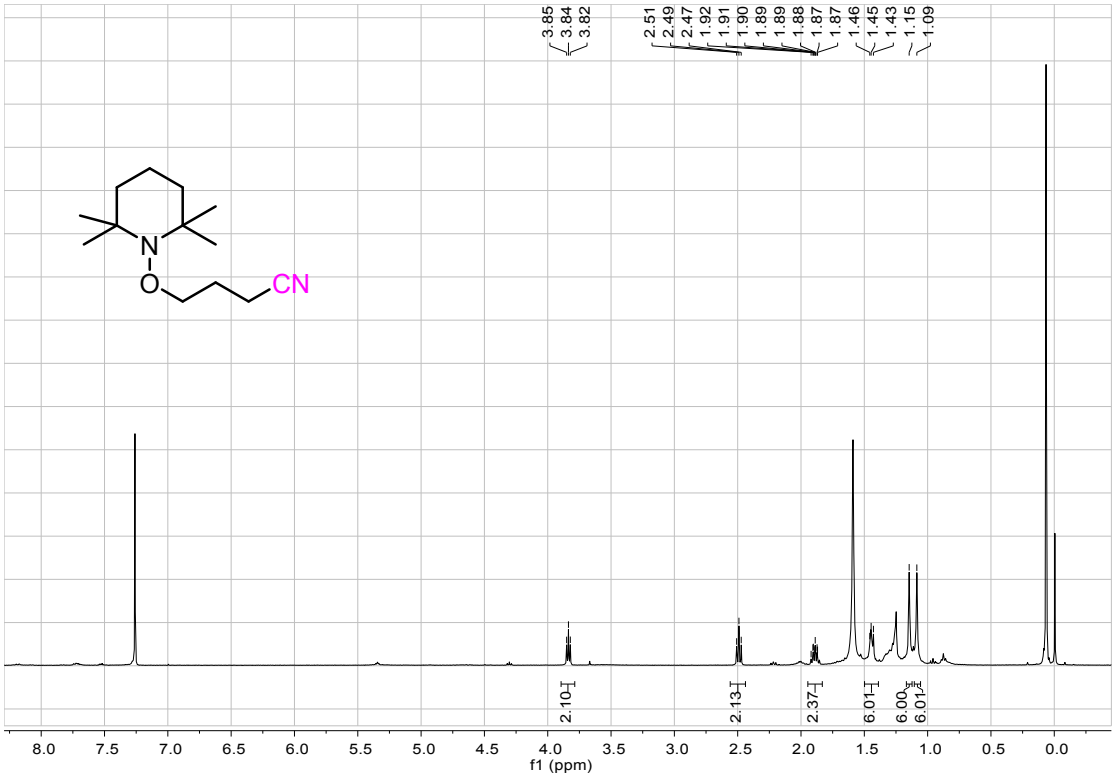
^{1}H NMR Spectrum of **7d**



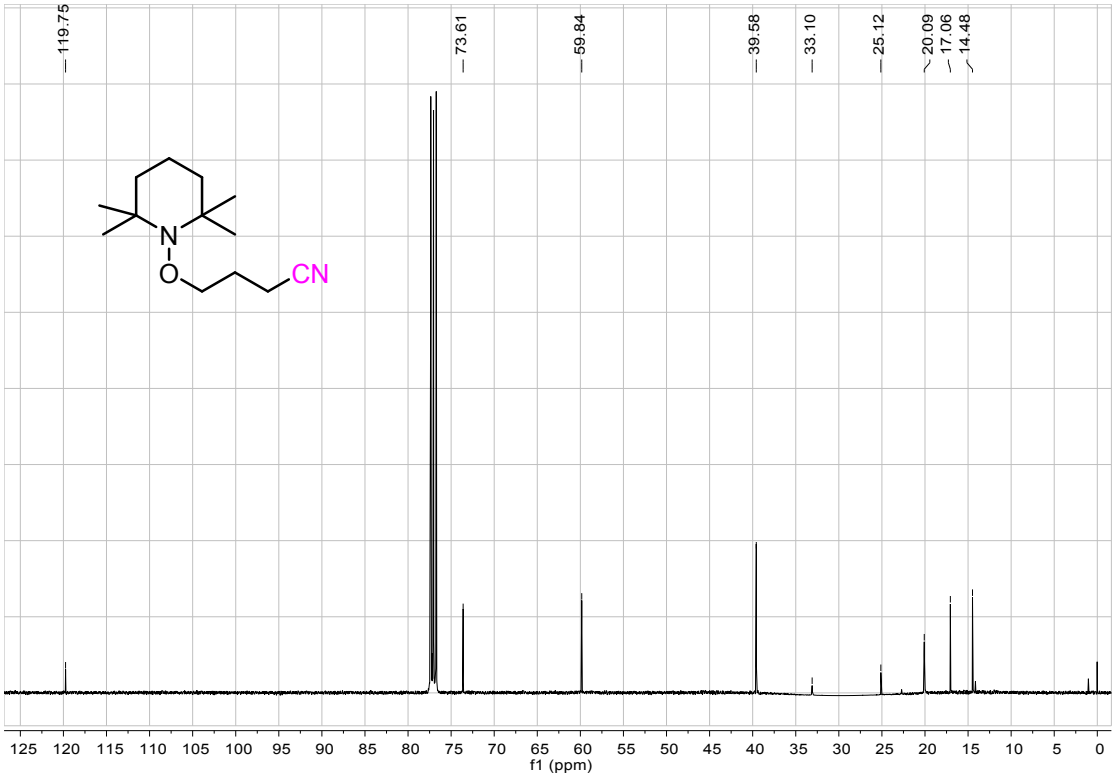
^{13}C NMR Spectrum of **7d**



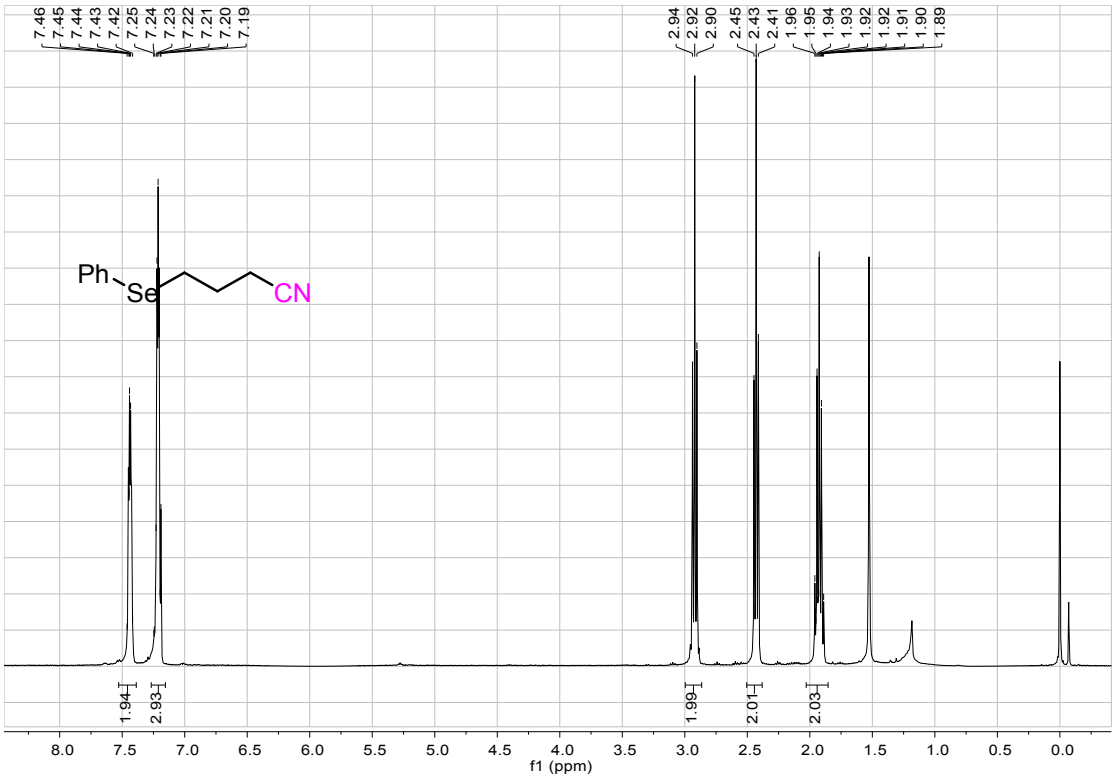
^{1}H NMR Spectrum of **8**



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



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



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