Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Direct C(sp^3)−H Difluoromethylation via Radical-Radical Cross-Coupling by Visible-Light Photoredox Catalysis

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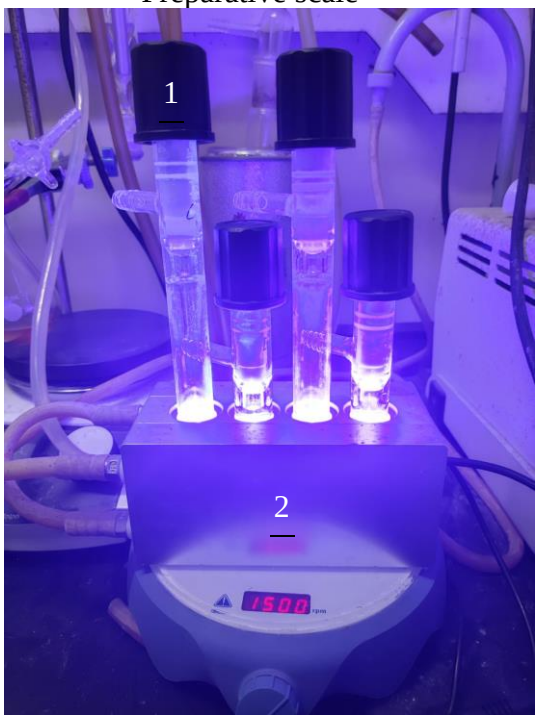
1. General Experimental Information

^{1}H NMR spectra were recorded on either a Bruker Ascend 400 MHz (400 MHz) spectrometer, a Bruker Ascend 500 MHz (500 MHz) spectrometer or a Bruker Ascend 600 MHz (600 MHz) spectrometer at ambient temperature unless otherwise indicated. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard in $CDCl_3$, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet-doublet, m = multiplet, br = broad), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on either a Bruker Ascend 500 MHz (126 MHz) spectrometer or a Bruker Ascend 600 MHz (151 MHz) spectrometer at ambient temperature and were proton decoupled. Chemical shifts are reported in ppm from tetramethylsilane on the scale with the solvent resonance employed as the internal standard. ^{19}F NMR spectra were recorded on a Bruker Ascend 400 MHz (377 MHz) spectrometer or a Bruker Ascend 500 MHz (471 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm from $CFCl_3$ as the internal standard. Single crystal X-ray diffraction data for compounds were collected on a Rigaku Oxford Diffraction Super nova Dual Source at 100 K using Cu-Kα radiation. ESI-MS analysis were performed in positive ionization mode on an Agilent 1260-Infinity LC/MSD resolution mass spectrometer. All high-resolution mass spectra were obtained on a Thermo Scientific Q-Exactive (HR/AM) Orbitrap mass spectrometer. Commercially available reagents were used as received. Reactions were monitored by TLC (detection with UV light). Flash chromatography: silica gel (300-400 mesh). Visible light irradiation was performed by Blue LED lamps (3 W × 4; λ = 450 nm) for preparative scale. Regent **2** was synthesized based on reported procedure and analytical data are in agreement with those reported in the literature.[1]

2. Reaction Apparatus

Preparative scale



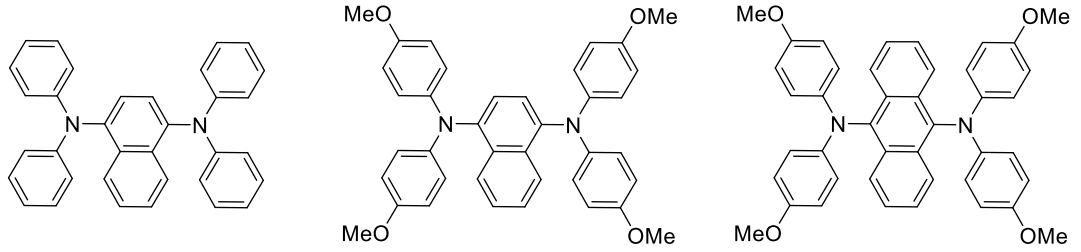
1. Schlenk tube (borosilicate glass)
2. Blue LED light source (Shanghai Zhaozhong Instrument Co., Ltd.)

Figure S1. Preparative scale reaction apparatus

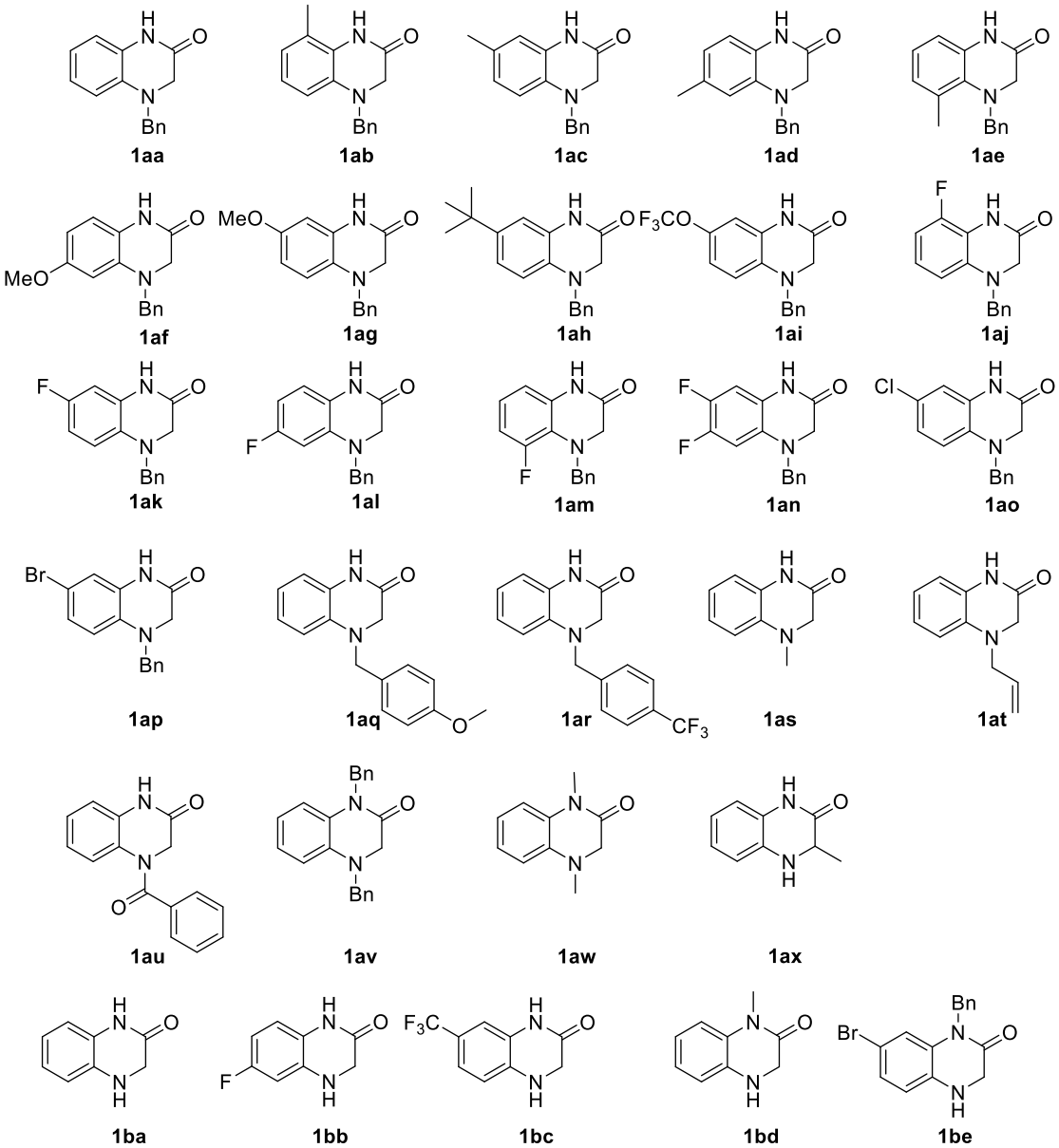
3. Synthesis of Organo-Photocatalysts and Substrates

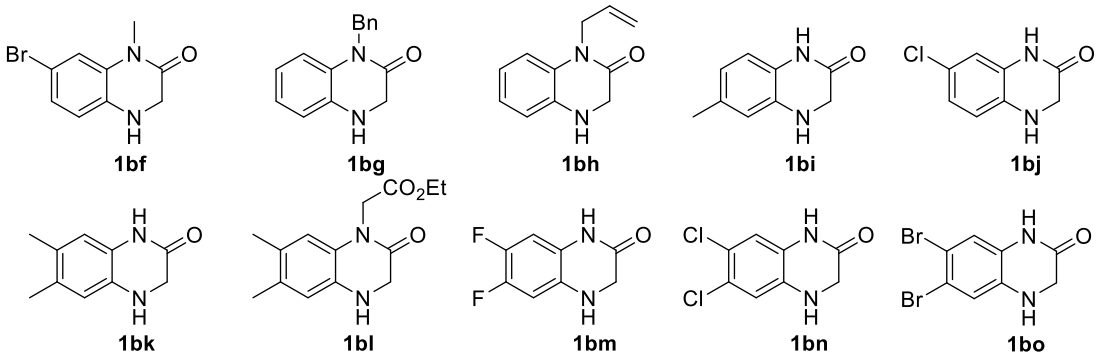
All organo-photocatalysts were known and prepared following a reported procedure,[2] all known dihydroquinoxalinones **1aa-1ac**,[3a] **1ag**,[3a] **1ak**,[3b] **1al**,[3a] **1ao**,[3b] **1ap-1ar**,[3a] **1as**,[4a] **1au**,[3b] **1av**,[3a] **1ba**,[3b] **1bb**,[3a] **1bc**,[4b] **1bd**,[4c] **1bh**,[4b] **1bi**,[4a] **1bj**,[4c] **1bk**,[4b]**1bm**,[4d] **1bn-1bo**[4e] were prepared following a reported procedure, and analytical data were in agreement with those reported in the literature. all new dihydroquinoxalinones were prepared following similar reported procedures[3,4] and were characterized by ^{1}H NMR and ^{13}C NMR and HRMS.

Organo-photocatalysts



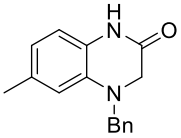
Dihydroquinoxalinones





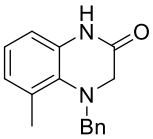
4. Characterization Data for 3,4-Dihydroquinoxalin-2(1H)-ones 1

4-benzyl-6-methyl-3,4-dihydroquinoxalin-2(1H)-one (1ad)



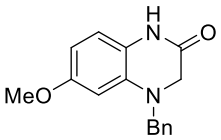
According to the literature procedure, **1ad** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 7.31 (tdd, *J* = 16.6, 16.0, 8.6, 4.1 Hz, 5H), 6.70 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.62 – 6.47 (m, 2H), 4.38 (s, 2H), 3.76 (d, *J* = 2.0 Hz, 2H), 2.24 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.4, 136.4, 135.3, 133.9, 128.9, 127.8, 127.6, 123.9, 119.5, 115.7, 112.8, 53.5, 52.0, 21.4. **ESI-HRMS**: Calcd for $C_{16}H_{17}N_2O+H^+$: 253.1335, found 253.1339.

4-benzyl-5-methyl-3,4-dihydroquinoxalin-2(1H)-one (1ae)



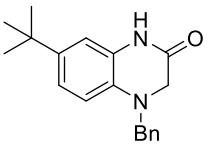
According to the literature procedure, **1ae** was isolated as a light yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.39 – 7.25 (m, 5H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 3.98 (s, 2H), 3.55 (s, 2H), 2.44 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 137.1, 134.3, 133.5, 133.0, 128.8, 128.6, 127.7, 125.9, 125.2, 114.3, 57.6, 51.43, 17.4. **ESI-HRMS**: Calcd for $C_{16}H_{17}N_2O+H^+$: 253.1335, found 253.1345.

4-benzyl-6-methoxy-3,4-dihydroquinoxalin-2(1H)-one (1af)



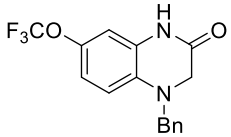
According to the literature procedure, **1af** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.30 (s, 1H), 7.38 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 6.30 – 6.24 (m, 2H), 4.40 (s, 2H), 3.69 (s, 2H), 3.60 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.5, 156.1, 137.7, 136.6, 129.1, 128.1, 127.6, 121.3, 115.8, 102.7, 99.8, 55.5, 53.1, 52.5. **ESI-HRMS**: Calcd for $C_{16}H_{17}N_2O_2+H^+$: 269.1258, found 269.1261.

4-benzyl-7-(tert-butyl)-3,4-dihydroquinoxalin-2(1H)-one (1ah)



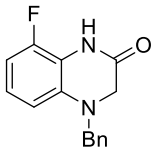
According to the literature procedure, **1ah** was isolated as a white solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.32 (s, 1H), 7.36 – 7.31 (m, 4H), 7.31 – 7.24 (m, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H), 4.37 (s, 2H), 3.65 (s, 2H), 1.20 (s, 9H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.5, 141.5, 137.9, 133.4, 129.0, 128.1, 127.6, 127.5, 119.8, 112.8, 112.1, 53.2, 52.8, 34.1, 31.8. **ESI-HRMS**: Calcd for $C_{19}H_{23}N_2O+H^+$: 295.1805, found 295.1805.

4-benzyl-7-(trifluoromethoxy)-3,4-dihydroquinoxalin-2(1H)-one (1ai)



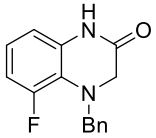
According to the literature procedure, **1ai** was isolated as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 7.45 – 7.28 (m, 5H), 6.82 (d, *J* = 8.3 Hz, 2H), 6.70 (d, *J* = 8.5 Hz, 1H), 4.42 (s, 2H), 3.88 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 141.5 (q, *J* = 2.1 Hz), 135.9, 134.1, 129.0, 127.8, 127.60, 126.9, 120.7 (q, *J* = 256.5 Hz), 116.6, 112.3, 109.6, 53.8, 52.0. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -58.27. **ESI-HRMS**: Calcd for $C_{16}H_{14}F_3N_2O_2$+H^+: 323.1002, found 323.1010.

4-benzyl-8-fluoro-3,4-dihydroquinoxalin-2(1H)-one (1aj)



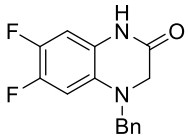
According to the literature procedure, **1aj** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.39 – 7.32 (m, 2H), 7.33 – 7.26 (m, 3H), 6.85 (td, *J* = 8.3, 6.2 Hz, 1H), 6.58 (t, *J* = 9.1 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 1H), 4.43 (s, 2H), 3.86 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 150.4 (d, *J* = 241.1 Hz), 136.8 (d, *J* = 4.4 Hz), 135.9, 128.9, 127.8, 127.5, 123.6 (d, *J* = 9.2 Hz), 114.4 (d, *J* = 15.0 Hz), 107.7 (d, *J* = 2.5 Hz), 105.6 (d, *J* = 18.6 Hz), 53.8, 52.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -135.0 (dd, *J* = 9.6, 6.3 Hz). **ESI-HRMS**: Calcd for $C_{15}H_{14}FN_2O$+H^+: 257.1085, found 257.1093.

4-benzyl-5-fluoro-3,4-dihydroquinoxalin-2(1H)-one (1am)



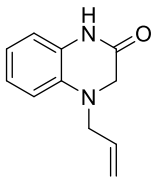
According to the literature procedure, **1am** was isolated as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.33 – 7.20 (m, 5H), 6.89 (td, *J* = 8.1, 5.2 Hz, 1H), 6.79 (ddd, *J* = 11.4, 8.3, 1.4 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 4.36 (s, 2H), 3.69 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 154.7 (d, *J* = 244.6 Hz), 137.1, 132.2 (d, *J* = 5.7 Hz), 128.6, 128.4, 127.8, 123.5 (d, *J* = 13.3 Hz), 122.8 (d, *J* = 9.4 Hz), 111.9 (d, *J* = 3.1 Hz), 111.4 (d, *J* = 20.9 Hz), 58.5 (d, *J* = 5.9 Hz), 51.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -125.6 (dd, *J* = 11.5, 5.3 Hz). **ESI-HRMS**: Calcd for $C_{15}H_{14}FN_2O$+H^+: 257.1085, found 257.1094.

4-benzyl-6,7-difluoro-3,4-dihydroquinoxalin-2(1H)-one (1an)



According to the literature procedure, **1an** was isolated as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.39 – 7.27 (m, 5H), 6.68 (dd, *J* = 10.3, 7.5 Hz, 1H), 6.54 (dd, *J* = 12.2, 7.1 Hz, 1H), 4.34 (s, 2H), 3.79 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 167.5, 146.6 (dd, *J* = 241.6, 13.2 Hz), 143.3 (dd, *J* = 239.4, 13.8 Hz), 135.4, 131.9 (dd, *J* = 8.0, 2.1 Hz), 129.1, 128.0, 127.6, 121.9 (dd, *J* = 7.8, 2.8 Hz), 105.0 (d, *J* = 22.1 Hz), 101.7 (d, *J* = 23.2 Hz), 54.1, 51.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -142.8 (ddd, *J* = 22.5, 12.3, 7.6 Hz), -149.8 (ddd, *J* = 22.3, 10.2, 7.1 Hz). **ESI-HRMS**: Calcd for $C_{15}H_{13}F_2N_2O$+H^+: 275.0990, found 275.0994.

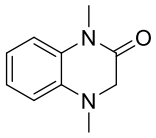
4-allyl-3,4-dihydroquinoxalin-2(1H)-one (1at)



According to the literature procedure, **1at** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.41 (s, 1H), 6.85 (td, *J* = 7.7, 1.6 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.66 (td, *J* = 7.5, 1.3 Hz, 1H), 5.91 – 5.83 (m, 1H), 5.29 (dd, *J* = 17.3, 1.7 Hz, 1H), 5.25 (dd, *J* = 10.2, 1.6 Hz, 1H), 3.85 (d, *J* = 5.8 Hz, 2H),

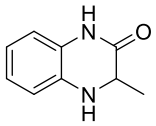
3.68 (s, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.4, 135.2, 132.9, 127.6, 123.4, 118.8, 118.7, 115.5, 112.4, 52.0, 51.7. **ESI-HRMS**: Calcd for $C_{11}H_{13}N_2O+H^+$: 189.1022, found 189.1020.

1,4-dimethyl-3,4-dihydroquinoxalin-2(1H)-one (1aw)



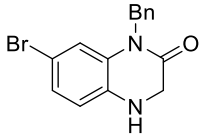
According to the literature procedure, **1aw** was isolated as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.03 (td, *J* = 7.6, 1.5 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.87 (td, *J* = 7.6, 1.3 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 3.71 (s, 2H), 3.34 (s, 3H), 2.81 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.1, 137.9, 130.0, 123.9, 119.3, 114.5, 111.7, 55.3, 37.5, 28.8. **ESI-HRMS**: Calcd for $C_{10}H_{13}N_2O+H^+$: 177.1022, found 177.1026.

3-methyl-3,4-dihydroquinoxalin-2(1H)-one (1ax)



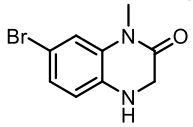
According to the literature procedure, **1ax** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.15 (s, 1H), 6.75 (td, *J* = 7.6, 1.5 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.59 (td, *J* = 7.5, 1.4 Hz, 1H), 5.98 (s, 1H), 3.75 (qd, *J* = 6.6, 1.7 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.9, 135.0, 126.7, 123.1, 118.3, 115.1, 113.9, 51.3, 17.9. **ESI-HRMS**: Calcd for $C_9H_{16}N_2O+H^+$: 163.0866, found 163.0867.

1-benzyl-7-bromo-3,4-dihydroquinoxalin-2(1H)-one (1be)



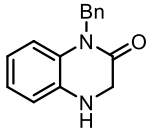
According to the literature procedure, **1be** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.19 (m, 3H), 6.89 (d, *J* = 1.8 Hz, 1H), 6.74 – 6.69 (m, 2H), 6.40 (s, 1H), 5.11 (s, 2H), 3.96 (d, *J* = 1.7 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.6, 139.2, 137.1, 129.1, 127.5, 127.1, 126.9, 120.5, 117.4, 116.3, 115.6, 46.7, 44.3. **ESI-HRMS**: Calcd for $C_{15}H_{14}BrN_2O+H^+$: 317.0285,319.0264 found 317.0287, 319.0268.

7-bromo-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (1bf)



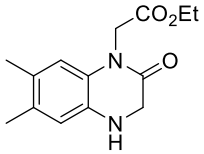
According to the literature procedure, **1bf** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.09 (d, *J* = 2.1 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.24 (s, 1H), 3.79 (d, *J* = 1.7 Hz, 2H), 3.22 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.52, 136.44, 130.44, 125.87, 117.58, 115.4, 109.2, 46.8, 28.7. **ESI-HRMS**: Calcd for $C_9H_{10}BrN_2O+H^+$: 240.9972, 242.9951, found 240.9975, 242.9956.

1-benzyl-3,4-dihydroquinoxalin-2(1H)-one (1bg)



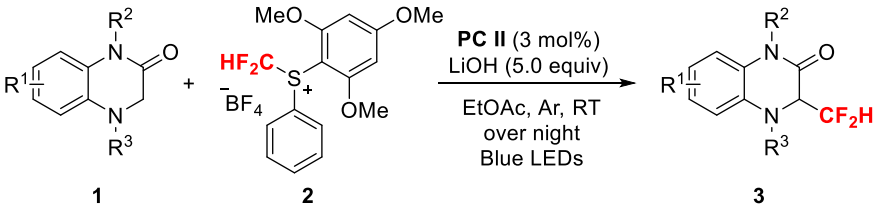
According to the literature procedure, **1bg** was isolated as a white solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.34 – 7.29 (m, 2H), 7.26 – 7.18 (m, 3H), 6.80 (ddd, *J* = 7.3, 6.4, 1.3 Hz, 2H), 6.74 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.58 (td, *J* = 7.6, 1.6 Hz, 1H), 6.13 (s, 1H), 5.12 (s, 2H), 3.91 (d, *J* = 1.9 Hz, 2H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.1, 137.5, 137.5, 129.0, 127.9, 127.4, 126.9, 123.7, 118.5, 115.7, 114.4, 47.3, 44.3. **ESI-HRMS**: Calcd for $C_{15}H_{15}BrN_2O+H^+$: 239.1179, found 239.1184.

Ethyl 2-(6,7-dimethyl-2-oxo-3,4-dihydroquinoxalin-1(2H)-yl)acetate (1bl)



According to the literature procedure, **1bl** was isolated as a light yellow solid. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 6.61 (s, 1H), 6.55 (s, 1H), 5.80 (s, 1H), 4.60 (s, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.73 (d, *J* = 1.9 Hz, 2H), 2.08 (d, *J* = 4.6 Hz, 6H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.9, 166.3, 134.7, 131.2, 126.1, 126.1, 116.2, 115.9, 61.3, 47.4, 43.5, 19.3, 19.3, 14.5. **ESI-HRMS**: Calcd for $C_{17}H_{16}N_2O$+H$^+$: 263.1390, found 263.1393.

5. General procedure for the visible-light photoredox catalyzed Direct C(sp^3)−H difluoromethylation of 3,4-dihydroquinoxalin-2(1H)-ones

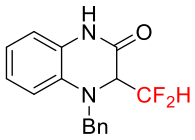


1 **2** **3**

The general procedure for difluoromethylation of dihydroquinoxalinones: To a 25 mL Schlenk tube equipped with a magnetic stir bar was added derivative of 3,4-dihydroquinoxalin-2(1H)-one **1** (0.1 mmol, 1.0 equiv.), **2** (83.0 mg,0.2 mmol, 2.0 equiv.), **PC II** (1.7 mg, 0.003 mmol, 3 mol%), LiOH (12.0 mg, 0.5 mmol, 5.0 equiv.). Then the flask was flushed with argon, followed by the addition of EtOAc (2 mL). The tube was placed at a distance of ~2 mm away from (3 W × 4) blue LED lamps (λ = 450 nm), the reaction mixture was stirred under irradiation of blue LEDs. After stirring overnight, the solvent was evaporated in vacuo; and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate) to afford the product **3**.

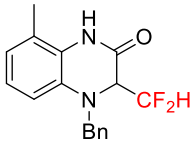
6. Characterization Data for Difluoromethylated 3,4-Dihydroquinoxalin-2(1H)-ones

4-benzyl-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3aa)



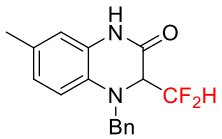
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3aa** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 21.4 mg, 74% yield, m.p. 123.1-124.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 7.45 – 7.31 (m, 5H), 7.07 – 7.00 (m, 1H), 6.93 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.90 – 6.82 (m, 2H), 6.00 (td, *J* = 54.6, 3.2 Hz, 1H), 4.89 (d, *J* = 15.0 Hz, 1H), 4.53 (d, *J* = 15.0 Hz, 1H), 4.32 (ddd, *J* = 18.3, 6.9, 3.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.6 (dd, *J* = 6.1, 4.1 Hz), 136.1, 133.6, 129.0, 127.9, 127.9, 125.3, 124.8, 119.7, 116.1, 115.1 (t, *J* = 250.6 Hz), 113.6, 63.0 (t, *J* = 21.5 Hz), 54.1. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -122.2 (ddd, *J* = 287.9, 54.3, 6.8 Hz, 1F), -124.5 (ddd, *J* = 288.1, 54.8, 18.3 Hz, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{14}F_2N_2O$+H$^+$: 289.1147, found 289.1152.

4-benzyl-3-(difluoromethyl)-8-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ab)



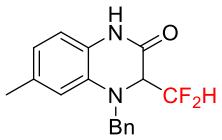
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ab** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 21.3 mg, 70% yield, m.p. 152.2-154.3 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 6.89 (t, *J* = 7.9 Hz, 1H), 6.70 (dd, *J* = 13.4, 7.8 Hz, 2H), 5.88 (td, *J* = 54.6, 3.5 Hz, 1H), 4.83 (d, *J* = 14.9 Hz, 1H), 4.46 (d, *J* = 14.9 Hz, 1H), 4.20 (ddd, *J* = 18.1, 6.6, 3.5 Hz, 1H), 2.27 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4 (t, *J* = 5.2 Hz), 136.10, 133.52, 128.92, 127.88, 127.88, 124.00, 123.57, 123.37, 121.72, 114.9 (t, *J* = 250.7 Hz), 111.94, 62.9 (t, *J* = 21.7 Hz), 54.3, 16.8. **^{19}F NMR** (377 MHz, $CDCl_3$ δ -122.4 (ddd, *J* = 289.0, 54.5, 6.9 Hz, 1F), -124.3 (ddd, *J* = 288.8, 54.8, 17.8 Hz, 1F). **ESI-HRMS**: Calcd for $C_{17}H_{16}F_2N_2O$+H$^+$: 303.1303, found 303.1306.

4-benzyl-3-(difluoromethyl)-7-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ac)



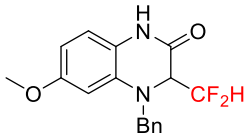
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ac** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 24.8 mg, 82% yield, m.p. 174.9-177.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.35 – 7.26 (m, 5H), 6.77 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.70 (d, *J* = 8.2 Hz, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 5.91 (td, *J* = 54.7, 3.3 Hz, 1H), 4.79 (d, *J* = 14.9 Hz, 1H), 4.43 (d, *J* = 14.9 Hz, 1H), 4.20 (ddd, *J* = 18.5, 6.8, 3.3 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.24 (dd, *J* = 6.1, 4.0 Hz), 136.2, 131.3, 129.4, 128.9, 128.0, 127.9, 127.8, 125.2, 116.5, 115.1 (t, *J* = 250.6 Hz), 113.72, 63.1 (t, *J* = 21.5 Hz), 54.3, 20.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.4 (ddd, *J* = 288.5, 54.5, 6.8 Hz, 1F), -124.5 (ddd, *J* = 288.4, 55.1, 18.7 Hz, 1F). **ESI-HRMS**: Calcd for $C_{17}H_{16}F_2N_2O+H^+$: 303.1303, found 303.1306.

4-benzyl-3-(difluoromethyl)-6-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ad)



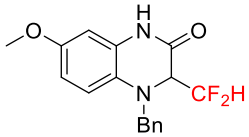
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ad** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 21.8 mg, 72% yield, m.p. 190.8-193.7 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.80 (s, 1H), 7.37 – 7.29 (m, 4H), 7.26 (t, *J* = 7.1 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.61 (s, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.20 (td, *J* = 54.1, 2.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 4.50 (d, *J* = 15.8 Hz, 1H), 4.43 (td, *J* = 14.4, 2.7 Hz, 1H), 2.13 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 161.7 (d, *J* = 3.7 Hz), 138.0, 133.2, 132.6, 129.0, 127.8, 127.7, 124.5, 119.6, 116.1 (t, *J* = 248.8 Hz), 115.5, 114.3, 63.6 (t, *J* = 20.8 Hz), 53.3, 21.4. **^{19}F NMR** (377 MHz, DMSO-d_6) δ -124.2 (dd, *J* = 54.2, 14.4 Hz, 2F). **ESI-HRMS**: Calcd for $C_{17}H_{16}F_2N_2O+H^+$: 303.1303, found 303.1306.

4-benzyl-3-(difluoromethyl)-6-methoxy-3,4-dihydroquinoxalin-2(1H)-one (3af)



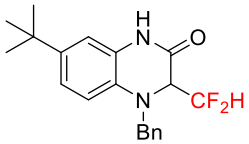
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3af** was isolated as a light yellow amorphous solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 11.8 mg, 37% yield; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.71 (s, 1H), 7.35 – 7.28 (m, 4H), 7.27 – 7.20 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.29 – 6.23 (m, 2H), 6.21 (td, *J* = 54.1, 2.6 Hz, 1H), 4.80 (d, *J* = 15.8 Hz, 1H), 4.50 (d, *J* = 15.8 Hz, 1H), 4.48 (td, *J* = 13.5, 12.3, 2.6 Hz, 1H), 3.58 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.9 (dd, *J* = 7.0, 3.3 Hz), 157.1, 135.8, 134.8, 129.0, 128.0, 127.9, 118.9, 116.0, 115.2 (t, *J* = 250.3 Hz), 103.5, 101.0, 62.9 (t, *J* = 21.4 Hz), 55.5, 54.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.1 (ddd, *J* = 287.8, 54.5, 6.2 Hz, 1F), -125.0 (ddd, *J* = 287.9, 54.7, 19.2 Hz, 1F). **ESI-HRMS**: Calcd for $C_{17}H_{16}F_2N_2O_2+H^+$: 319.1253, found 319.1257.

4-benzyl-3-(difluoromethyl)-7-methoxy-3,4-dihydroquinoxalin-2(1H)-one (3ag)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ag** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 18.5 mg, 58% yield, m.p. 135.4-137.5 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.00 (s, 1H), 7.62 (s, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 2.8 Hz, 1H), 6.43 (d, *J* = 8.9 Hz, 1H), 6.34 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.11 (t, *J* = 54.6 Hz, 1H), 4.91 (d, *J* = 16.5 Hz, 1H), 4.45 (d, *J* = 16.5 Hz, 1H), 3.59 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 162.9 (d, *J* = 2.8 Hz), 152.57, 139.5, 128.7, 127.3, 127.0, 126.2, 126.1, 116. 9 (d, *J* = 251.8 Hz), 113.9, 107.8, 102. 2, 83.1 (dd, *J* = 24.8, 21.9 Hz), 55.6, 47.0. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -128.2 (dd, *J* = 281.1, 54.3 Hz), -133.4 (dd, *J* = 281.1, 55.0 Hz). **ESI-HRMS**: Calcd for $C_{17}H_{16}F_2N_2O_2+H^+$: 319.1253, found 319.1254.

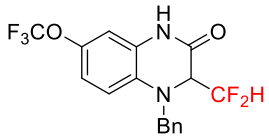
4-benzyl-7-(tert-butyl)-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ah)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ah** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 24.1 mg, 70% yield, m.p. 195.6-198.3 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.76 (s, 1H), 7.34 – 7.27 (m, 4H), 7.26 – 7.21 (m, 1H), 6.87 (d, *J* = 2.2 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.19 (td, *J* = 54.2, 2.7 Hz, 1H), 4.76 (d, *J* = 15.8 Hz, 1H), 4.50 (d, *J* = 15.8 Hz, 1H),

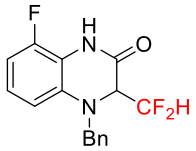
4.44 (dd, *J* = 14.4, 2.8 Hz, 1H), 1.18 (s, 9H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 162.0 (t, *J* = 4.1 Hz), 141.5, 138.2, 130.8, 129.0, 127.7, 127.7, 126.3, 120.3, 116.1 (t, *J* = 248.7 Hz), 113.1, 112.7, 63.9 (t, *J* = 20.9 Hz), 53.4, 34.1, 31.7. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.01 (dd, *J* = 54.2, 14.3 Hz). **ESI-HRMS**: Calcd for $C_{20}H_{22}F_2N_2O_2$+H^+: 345.1773, found 345.1777.

4-benzyl-3-(difluoromethyl)-7-(trifluoromethoxy)-3,4-dihydroquinoxalin-2(1H)-one (3ai)



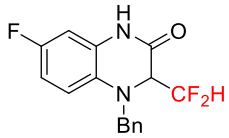
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ai** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 16.8 mg, 45% yield, m.p. 105.4-107.6 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.05 (s, 1H), 7.34 – 7.28 (m, 4H), 7.27 – 7.22 (m, 1H), 6.82 – 6.78 (m, 2H), 6.77 – 6.72 (m, 1H), 6.28 (td, *J* = 53.9, 2.4 Hz, 1H), 4.82 (d, *J* = 15.9 Hz, 1H), 4.61 (dt, *J* = 14.1, 2.5 Hz, 1H), 4.56 (d, *J* = 16.2 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 162.1, 140.7, 137.4, 132.4, 129.1, 127.9, 127.7, 127.6, 120.6 (q, *J* = 254.8 Hz), 116.0, 115.9 (t, *J* = 248.5 Hz), 114.1, 108.6, 63.5 (t, *J* = 21.1 Hz), 53.52. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -57.2 (s, 3F), -124.5 (dd, *J* = 14.5, 4.6 Hz, 1F), -124.6 (dd, *J* = 14.6, 4.7 Hz, 1F). **ESI-HRMS**: Calcd for $C_{17}H_{13}F_5N_2O_2$+H^+: 373.0970, found 373.0974.

4-benzyl-3-(difluoromethyl)-8-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3aj)



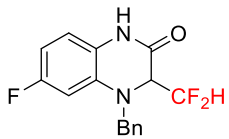
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3aj** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 16.3 mg, 53% yield, m.p. 119.1-120.8 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.38 – 7.27 (m, 5H), 6.89 (td, *J* = 8.3, 6.2 Hz, 1H), 6.61 (t, *J* = 9.6 Hz, 2H), 5.98 (td, *J* = 54.4, 2.6 Hz, 1H), 4.84 (d, *J* = 15.1 Hz, 1H), 4.48 (d, *J* = 15.0 Hz, 1H), 4.26 (ddd, *J* = 20.6, 6.3, 2.5 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.2 (dd, *J* = 7.7, 2.7 Hz), 150.1 (d, *J* = 241.9 Hz), 135.5, 135.2 (d, *J* = 4.0 Hz), 129.0, 128.1, 127.8, 124.0 (d, *J* = 9.1 Hz), 115.3 (t, *J* = 250.1 Hz), 113.6 (d, *J* = 1.7 Hz), 109.0 (d, *J* = 2.7 Hz), 106.1 (d, *J* = 18.3 Hz), 62.9 (t, *J* = 21.3 Hz), 54.3 (d, *J* = 2.2 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.1 (ddd, *J* = 287.2, 54.1, 6.1 Hz, 1F), -125.7 (ddd, *J* = 287.1, 54.6, 20.5 Hz, 1F), -135.1 – -135.2 (m, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{13}F_3N_2O$+H^+: 307.1053, found 307.1055.

4-benzyl-3-(difluoromethyl)-7-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3ak)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ak** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 27.0 mg, 88% yield, m.p. 132.1-134.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.37 – 7.27 (m, 5H), 6.77 – 6.65 (m, 2H), 6.60 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.93 (td, *J* = 54.5, 3.0 Hz, 1H), 4.77 (d, *J* = 14.9 Hz, 1H), 4.45 (d, *J* = 14.9 Hz, 1H), 4.21 (ddd, *J* = 18.9, 7.1, 3.0 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.6 (dd, *J* = 6.6, 3.4 Hz), 156.7 (d, *J* = 238.7 Hz), 135.8, 129.8 (d, *J* = 2.3 Hz), 129.0, 128.1, 127.9, 126.2 (d, *J* = 10.3 Hz), 115.1 (t, *J* = 250.5 Hz), 114.6 (d, *J* = 8.4 Hz), 110.6 (d, *J* = 22.2 Hz), 103.5 (d, *J* = 27.0 Hz), 63.0 (t, *J* = 21.6 Hz), 54.8. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -122.5 (ddd, *J* = 288.5, 54.3, 7.0 Hz, 1F), -123.6 – -123.7 (m, 1F), -124.8 (ddd, *J* = 288.5, 54.7, 19.1 Hz, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{13}F_3N_2O$+H^+: 307.1053, found 307.1059.

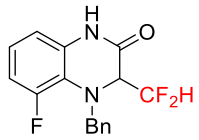
4-benzyl-3-(difluoromethyl)-6-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3al)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3al** was isolated as a white solid; R_f = 0.35 (4:1 petroleum ether/ethyl acetate); 17.5 mg, 57% yield, m.p. 132.2-135.0 °C; **1H NMR** (500 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.37 – 7.27 (m, 5H), 6.72 (dd, *J* = 8.6, 5.3 Hz, 1H), 6.55 (dd, *J* = 10.6, 2.6 Hz, 1H), 6.49 (td, *J* = 8.4, 2.6 Hz, 1H), 5.96 (td, *J* = 54.4, 2.7 Hz, 1H), 4.78 (d, *J* = 15.0 Hz, 1H), 4.47 (d, *J* = 15.0 Hz, 1H), 4.23 (ddd, *J* =

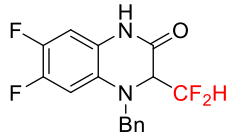
20.0, 6.3, 2.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4 (dd, *J* = 7.0, 2.8 Hz), 160.2 (d, *J* = 241.3 Hz), 135.3, 135.0 (d, *J* = 10.6 Hz), 129.1, 128.2, 127.9, 121.2 (d, *J* = 2.4 Hz), 116.2 (d, *J* = 10.0 Hz), 115.2 (t, *J* = 250.4 Hz), 105.6 (d, *J* = 23.5 Hz), 101.3 (d, *J* = 28.0 Hz), 62.6 (t, *J* = 21.3 Hz), 54.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -116.8 – -116.9 (m, 1F), -122.1 (ddd, *J* = 287.8, 54.4, 6.2 Hz, 1F), -125.4 (ddd, *J* = 287.7, 54.6, 20.0 Hz, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{13}F_3N_2O+H^+$: 307.1053, found 307.1054.

4-benzyl-3-(difluoromethyl)-5-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3am)



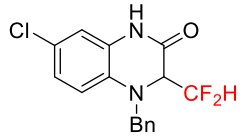
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3am** was isolated as a white solid; R_f = 0.4 (4:1 petroleum ether/ethyl acetate); 6.7 mg, 22% yield, m.p. 107.1-109.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.33 – 7.27 (m, 5H), 6.92 (td, *J* = 8.1, 5.3 Hz, 1H), 6.84 (ddd, *J* = 11.4, 8.4, 1.4 Hz, 1H), 6.56 (dt, *J* = 8.0, 1.3 Hz, 1H), 5.76 (td, *J* = 54.8, 2.9 Hz, 1H), 4.60 (d, *J* = 14.8 Hz, 1H), 4.39 (d, *J* = 14.8 Hz, 1H), 4.06 (ddd, *J* = 15.6, 12.2, 2.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.9 – 162.8 (m), 154.9 (d, *J* = 245.8 Hz), 136.5, 130.47 (d, *J* = 5.5 Hz), 128.8, 128.5, 128.2, 123.1 (d, *J* = 9.2 Hz), 121.7 (d, *J* = 13.1 Hz), 115.2 (d, *J* = 249.7 Hz), 112.0 (d, *J* = 20.5 Hz), 111.5 (d, *J* = 3.1 Hz), 63.1 (t, *J* = 22.7 Hz), 59.3 (d, *J* = 6.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -123.6 (ddd, *J* = 286.0, 54.6, 15.9 Hz, 1F), -124.1 (dd, *J* = 11.4, 5.3 Hz, 1F), -126.2 (ddd, *J* = 286.0, 54.8, 12.2 Hz, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{13}F_3N_2O+H^+$: 307.1053, found 307.1056.

4-benzyl-3-(difluoromethyl)-6,7-difluoro-3,4-dihydroquinoxalin-2(1H)-one (3an)



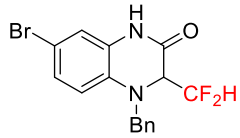
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3an** was isolated as a white solid; R_f = 0.3 (4:1 petroleum ether/ethyl acetate); 18.9 mg, 58% yield, m.p. 136.9-139.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.38 – 7.26 (m, 5H), 6.69 (dd, *J* = 10.1, 7.4 Hz, 1H), 6.62 (dd, *J* = 11.8, 7.0 Hz, 1H), 5.95 (td, *J* = 54.4, 2.7 Hz, 1H), 4.72 (d, *J* = 14.9 Hz, 1H), 4.46 (d, *J* = 14.9 Hz, 1H), 4.22 (ddd, *J* = 20.0, 6.6, 2.6 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.2 (dd, *J* = 7.4, 2.2 Hz), 146.9 (dd, *J* = 242.9, 13.1 Hz), 143.7 (dd, *J* = 240.2, 14.0 Hz), 135.1, 130.1 (dd, *J* = 8.3, 2.1 Hz), 129.1, 128.3, 127.8, 121.0 (dd, *J* = 7.9, 2.3 Hz), 115.1 (t, *J* = 250.3 Hz), 105.0 (d, *J* = 22.2 Hz), 103.1 (d, *J* = 23.0 Hz), 62.6 (t, *J* = 21.4 Hz), 54.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.3 (ddd, *J* = 288.2, 54.0, 6.5 Hz, 1F), -125.3 (ddd, *J* = 288.5, 54.6, 20.1 Hz, 1F), -141.7 (ddd, *J* = 22.2, 11.6, 7.2 Hz, 1F), -148.7 (ddd, *J* = 22.3, 10.1, 7.0 Hz, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{12}F_4N_2O+H^+$: 325.0959, found 325.0964.

4-benzyl-7-chloro-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ao)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ao** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 24.5 mg, 76% yield, m.p. 155.7-158.1 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.36 – 7.26 (m, 5H), 6.92 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.81 (d, *J* = 2.2 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 5.95 (td, *J* = 54.4, 2.6 Hz, 1H), 4.79 (d, *J* = 15.0 Hz, 1H), 4.46 (d, *J* = 15.0 Hz, 1H), 4.25 (ddd, *J* = 19.9, 6.6, 2.7 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 163.2 (dd, *J* = 6.9, 2.5 Hz), 135.5, 132.3, 129.0, 128.1, 127.8, 126.1, 124.5, 124.3, 115.8, 115.1 (t, *J* = 250.4 Hz), 114.5, 63.0 (t, *J* = 21.5 Hz), 54.3. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -122.3 (ddd, *J* = 287.9, 54.2, 6.6 Hz, 1F), -125.3 (ddd, *J* = 287.9, 54.6, 19.9 Hz, 1F). **ESI-HRMS**: Calcd for $C_{16}H_{13}ClF_2N_2O+H^+$: 323.0757, found 323. 0762.

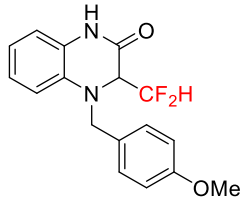
4-benzyl-7-bromo-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ap)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ap** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 21.7 mg, 59% yield, m.p. 137.7-140.2 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 11.01 (s, 1H), 7.35 – 7.28 (m, 2H), 7.30 – 7.20 (m, 3H), 6.97 – 6.91 (m, 2H), 6.64 (d, *J* = 9.2 Hz, 1H), 6.26 (td, *J* = 54.0, 2.5 Hz, 1H), 4.80 (d, *J* = 16.0 Hz, 1H), 4.63 – 4.56 (m, 2H), 4.54 (d, *J* = 16.0 Hz, 1H). **^{13}C NMR**

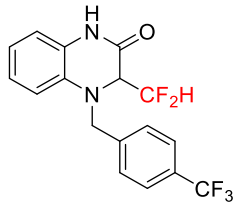
(151 MHz, DMSO-d_6) δ 161.9 (t, *J* = 3.4 Hz), 137.5, 132.6, 129.0, 128.5, 127.8, 127.6, 125.8, 117.7, 116.0 (d, *J* = 248.2 Hz), 115.4, 109.9, 63.7 (t, *J* = 20.8 Hz), 53.4. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.6 (ddd, *J* = 54.0, 14.7, 10.6 Hz, 2F). **ESI-HRMS**: Calcd for $C_{16}H_{13}BrF_2N_2O+H^+$: 367.0252, 369.0232, found 367.0255, 369.0235.

3-(difluoromethyl)-4-(4-methoxybenzyl)-3,4-dihydroquinoxalin-2(1H)-one (3aq)



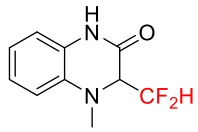
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3aq** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 19.8 mg, 62% yield, m.p. 134.9-137.6 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.00 (dt, *J* = 8.1, 4.5 Hz, 1H), 6.90 – 6.84 (m, 3H), 6.81 (d, *J* = 4.0 Hz, 2H), 5.90 (td, *J* = 54.6, 3.2 Hz, 1H), 4.76 (d, *J* = 14.4 Hz, 1H), 4.39 (d, *J* = 14.4 Hz, 1H), 4.20 (ddd, *J* = 18.8, 6.7, 3.2 Hz, 1H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.0 (dd, *J* = 6.3, 3.9 Hz), 159.3, 133.8, 129.4, 127.6, 125.2, 124.7, 119.6, 115.7, 115.1 (t, *J* = 250.6 Hz), 114.3, 113.6, 62.3 (t, *J* = 21.5 Hz), 55.3, 53.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.3 (ddd, *J* = 288.4, 54.5, 6.6 Hz, 1F), -124.5 (ddd, *J* = 288.4, 55.1, 18.9 Hz, 1F). **ESI-HRMS**: Calcd for $C_{17}H_{16}F_2N_2O_2+H^+$: 319.1253, found 319.1257.

3-(difluoromethyl)-4-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinoxalin-2(1H)-one (3ar)



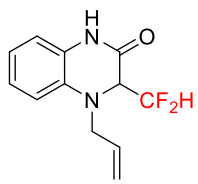
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ar** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 26.1 mg, 73% yield, m.p. 99.3-101.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 6.96 (ddd, *J* = 8.1, 5.5, 3.4 Hz, 1H), 6.86 – 6.80 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.99 (td, *J* = 54.5, 3.0 Hz, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 4.55 (d, *J* = 15.7 Hz, 1H), 4.24 (ddd, *J* = 19.7, 5.7, 3.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8 (dd, *J* = 7.0, 3.5 Hz), 140.4, 133.0, 130.1 (q, *J* = 32.6 Hz), 127.8, 125.9 (q, *J* = 3.8 Hz), 125.1, 124.8, 120.1, 115.9, 115.0 (t, *J* = 250.2 Hz), 113.8, 63.9 (t, *J* = 21.4 Hz), 53.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.56 (s, 3F), -122.0 (ddd, *J* = 288.4, 54.4, 6.0 Hz, 1F), -125.3 (ddd, *J* = 288.6, 54.7, 19.8 Hz, 1F). **ESI-HRMS**: Calcd for $C_{17}H_{13}F_5N_2O+H^+$: 357.1021, found 357.1030.

3-(difluoromethyl)-4-methyl-3,4-dihydroquinoxalin-2(1H)-one (3as)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3as** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 14.1 mg, 66% yield, m.p. 147.6-150.0 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.04 (ddd, *J* = 8.3, 6.4, 2.4 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.99 (td, *J* = 54.5, 2.7 Hz, 1H), 4.25 (ddd, *J* = 20.1, 5.8, 2.7 Hz, 1H), 3.12 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.4 (dd, *J* = 7.4, 3.0 Hz), 134.2, 124.9, 124.3, 118.9, 115.4, 115.3 (t, *J* = 250.3 Hz), 111.9, 65.9 (t, *J* = 21.4 Hz), 38.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -121.2 (ddd, *J* = 288.3, 54.6, 5.8 Hz, 1F), -126.0 (ddd, *J* = 287.5, 54.7, 20.0 Hz, 1F). **ESI-HRMS**: Calcd for $C_{10}H_{10}F_2N_2O+H^+$: 213.0834, found 213.0838.

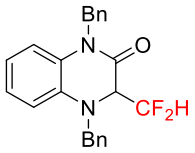
4-allyl-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3at)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3at** was isolated as a white amorphous solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 12.9 mg, 54% yield; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.82 (s, 1H), 6.87 (td, *J* = 7.7, 1.5 Hz, 1H), 6.80 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.69 (td, *J* = 7.5, 1.3 Hz, 1H), 6.17 (td, *J* =

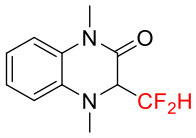
54.1, 2.4 Hz, 1H), 5.86 – 5.76 (m, 1H), 5.25 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.18 (dt, *J* = 10.2, 1.6 Hz, 1H), 4.42 (ddd, *J* = 15.8, 13.2, 2.5 Hz, 1H), 4.22 (dd, *J* = 16.2, 5.7 Hz, 1H), 3.91 (dd, *J* = 16.2, 5.6 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 161.6 (dd, *J* = 4.7, 2.6 Hz), 134.7, 133.4, 126.6, 123.7, 118.9, 118.0, 115.9 (t, *J* = 248.7 Hz), 115.6, 113.5, 63.4 (t, *J* = 20.7 Hz), 52.9. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -123.7 – -125.4 (m, 2F). **ESI-HRMS**: Calcd for $C_{12}H_{12}F_2N_2O+H^+$: 239.0990, found 239.0999.

1,4-dibenzyl-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3av)



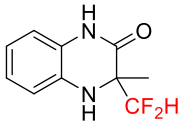
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3av** was isolated as a light yellow amorphous solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 20.8 mg, 55% yield; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 8H), 7.23 – 7.19 (m, 2H), 6.96 (td, *J* = 7.7, 1.4 Hz, 1H), 6.86 (td, *J* = 8.0, 1.4 Hz, 2H), 6.75 (td, *J* = 7.7, 1.4 Hz, 1H), 5.96 (td, *J* = 54.6, 3.3 Hz, 1H), 5.55 (d, *J* = 16.2 Hz, 1H), 4.91 (d, *J* = 16.2 Hz, 1H), 4.84 (d, *J* = 14.7 Hz, 1H), 4.47 (d, *J* = 14.8 Hz, 1H), 4.35 (ddd, *J* = 19.2, 6.2, 3.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.9 (dd, *J* = 6.0, 4.5 Hz), 136.0, 135.9, 135.0, 128.9, 128.9, 128.2, 128.0, 127.9, 127.4, 126.2, 124.4, 119.8, 115.8, 115.3 (d, *J* = 250.5 Hz), 113.8, 63.3 (t, *J* = 21.4 Hz), 54.1, 46.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -122.2 (ddd, *J* = 288.9, 54.3, 6.1 Hz), -123.9 (ddd, *J* = 288.9, 54.8, 19.2 Hz). **ESI-HRMS**: Calcd for $C_{23}H_{20}F_2N_2O+H^+$: 379.1616, found 379.1619.

3-(difluoromethyl)-1,4-dimethyl-3,4-dihydroquinoxalin-2(1H)-one (3aw)



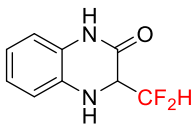
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3aw** was isolated as a white solid; Rf = 0.3 (5:1 petroleum ether/ethyl acetate); 8.9 mg, 39% yield, m.p. 77.8-78.9 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.07 (td, *J* = 7.7, 1.3 Hz, 1H), 6.95 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.87 (td, *J* = 7.7, 1.3 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 5.92 (td, *J* = 54.5, 2.9 Hz, 1H), 4.27 (ddd, *J* = 20.1, 5.6, 2.9 Hz, 1H), 3.42 (s, 3H), 3.10 (d, *J* = 2.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (dd, *J* = 7.3, 3.6 Hz), 135.52, 128.0, 124.5, 118.9, 115.44 (t, *J* = 250.4 Hz), 114.5, 111.8, 66.1 (t, *J* = 21.2 Hz), 37.9, 29.3. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -120.9 (dddd, *J* = 287.9, 54.7, 5.5, 2.3 Hz), -125.4 (ddd, *J* = 287.5, 54.8, 20.1 Hz). **ESI-HRMS**: Calcd for $C_{11}H_{13}F_2N_2O+H^+$: 227.0990, found 227.0998.

3-(difluoromethyl)-3-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ax)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ax** was isolated as a white solid; R_f = 0.3 (4:1 petroleum ether/ethyl acetate); 8.1 mg, 38% yield, m.p. 130.1-132.3 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.80 (s, 1H), 6.92 (td, *J* = 7.5, 1.8 Hz, 1H), 6.77 (td, *J* = 7.4, 1.2 Hz, 1H), 6.74 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 4.10 (s, 1H), 1.52 (t, *J* = 1.6 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 166.0 (dd, *J* = 4.5, 1.5 Hz), 131.4, 124.5, 123.8, 119.6, 115.4, 115. (dd, *J* = 249.6, 246.9 Hz), 114.0, 60.6 (t, *J* = 20.5 Hz), 19.5 (dd, *J* = 3.7, 2.1 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -129.22 (dd, *J* = 280.1, 55.0 Hz, 1F), -136.36 (dd, *J* = 280.0, 55.6 Hz, 1F). **ESI-HRMS**: Calcd for $C_{10}H_{10}F_2N_2O+H^+$: 213.0834, found 213.0837.

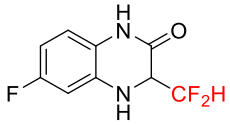
3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ba)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3ba** was isolated as a light yellow amorphous solid; R_f = 0.3 (4:1 petroleum ether/ethyl acetate); 10.0 mg, 50% yield; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 10.63 (s, 1H), 6.81 – 6.76 (m, 2H), 6.72 (d, *J* = 7.4 Hz, 1H), 6.57 (ddd, *J* = 7.8, 5.1, 3.7 Hz, 1H), 6.48 (d, *J* = 2.4 Hz, 1H), 6.25 (td, *J* = 54.7, 2.1 Hz, 1H), 4.39 (ddt, *J* = 21.5, 8.9, 2.2 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 162.0 (d, *J* = 8.0 Hz), 133.2, 124.7, 123.6, 118.0, 115.4, 115.4 (dd, *J* = 245.7, 242.4 Hz), 113.68, 57.6 (t, *J* = 21.2 Hz).

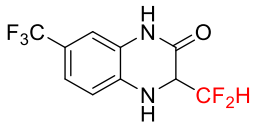
^{19}F NMR (377 MHz, DMSO-d_6) δ -127.47 (ddd, *J* = 278.9, 54.4, 9.3 Hz), -129.06 (ddd, *J* = 278.9, 54.9, 21.1 Hz). **ESI-HRMS**: Calcd for $C_9H_9F_2N_2O+H^+$: 199.0667, found 199.0660.

3-(difluoromethyl)-6-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3bb)



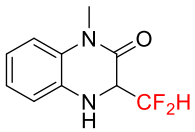
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3bb** was isolated as a white solid; R_f = 0.3 (4:1 petroleum ether/ethyl acetate); 7.8 mg, 36% yield, m.p. 169.6-171.3 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.69 (s, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.70 (dd, *J* = 8.6, 5.6 Hz, 1H), 6.59 (dd, *J* = 10.5, 2.8 Hz, 1H), 6.39 – 6.34 (m, 1H), 6.28 (td, *J* = 54.6, 2.0 Hz, 1H), 4.45 (ddt, *J* = 22.3, 8.3, 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 161.5 (d, *J* = 8.1 Hz), 159.1 (d, *J* = 236.1 Hz), 134.7 (d, *J* = 11.7 Hz), 121.1 (d, *J* = 2.0 Hz), 115.9 (d, *J* = 10.1 Hz), 115.3 (dd, *J* = 245.7, 242.0 Hz), 103.6 (d, *J* = 23.1 Hz), 100.4 (d, *J* = 27.1 Hz), 57.2 (t, *J* = 21.1 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ -119.90 – -119.98 (m, 1F), -127.6 (ddd, *J* = 279.1, 54.3, 8.5 Hz, 1F), -129.5 (ddd, *J* = 279.1, 55.0, 22.4 Hz, 1F). **ESI-HRMS**: Calcd for $C_9H_8F_3N_2O+H^+$: 217.0583, found 217.0590.

3-(difluoromethyl)-7-(trifluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3bc)



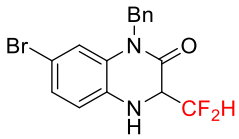
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3bc** was isolated as a white solid; R_f = 0.3 (3:1 petroleum ether/ethyl acetate); 13.8 mg, 52% yield, m.p. 159.2-160.8 °C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.91 (s, 1H), 7.21 (d, *J* = 2.2 Hz, 1H), 7.13 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.00 (d, *J* = 2.1 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.31 (td, *J* = 54.5, 1.9 Hz, 1H), 4.57 (dd, *J* = 22.3, 8.6 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 161.5 (d, *J* = 8.3 Hz), 136.8, 125.3 (q, *J* = 270.3 Hz), 124.4, 120.9 (q, *J* = 3.8 Hz), 117.7 (q, *J* = 32.2 Hz), 115.2 (dd, *J* = 245.3, 242.5 Hz), 113.1, 111.8 (q, *J* = 4.0 Hz), 57.28 (t, *J* = 21.2 Hz). **^{19}F NMR** (377 MHz, DMSO-d_6) δ -59.5 (s, 3F), -127.6 (ddd, *J* = 279.2, 54.0, 8.6 Hz, 1F), -129.5 (ddd, *J* = 279.0, 54.9, 22.3 Hz, 1F). **ESI-HRMS**: Calcd for $C_{10}H_8F_5N_2O+H^+$: 267.0551, found 267.0559.

3-(difluoromethyl)-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (3bd)



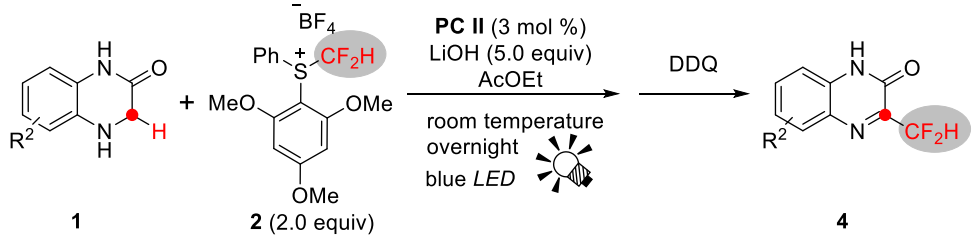
According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3bd** was isolated as a white solid; R_f = 0.3 (4:1 petroleum ether/ethyl acetate); 12.4 mg, 58% yield, m.p. 109.2-111.7 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (td, *J* = 7.5, 1.4 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.88 (td, *J* = 7.7, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.21 (td, *J* = 54.9, 2.5 Hz, 1H), 4.41 – 4.27 (m, 2H), 3.42 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.6 (dd, *J* = 7.9, 2.4 Hz), 133.2, 127.2, 124.3, 119.8, 114.8, 114.1, 114.0 (dd, *J* = 247.6, 241.9 Hz), 58.5 (dd, *J* = 23.1, 21.1 Hz, 29.1.**^{19}F NMR** (471 MHz, $CDCl_3$) δ -128.0 (ddd, *J* = 284.0, 55.0, 5.8 Hz), -131.2 (ddd, *J* = 284.2, 54.9, 21.0 Hz). **ESI-HRMS**: Calcd for $C_{10}H_{11}F_2N_2O+H^+$: 213.0834, found 213.0839.

1-benzyl-7-bromo-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3be)



According to the general procedure for difluoromethylation of dihydroquinoxalinones, **3be** was isolated as a white solid; R_f = 0.3 (4:1 petroleum ether/ethyl acetate); 21.5 mg, 70% yield, m.p. 178.0-180.5 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 1.9 Hz, 1H), 6.79 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 6.24 (td, *J* = 54.9, 2.2 Hz, 1H), 5.32 (d, *J* = 16.3 Hz, 1H), 5.03 (d, *J* = 16.3 Hz, 1H), 4.51 – 4.41 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.3 (d, *J* = 8.0 Hz), 135.3, 134.5, 129.0, 127.6, 126.2, 125.3, 122.4, 117.1, 117.0, 116.8, 114.1 (dd, *J* = 248.1, 243.3 Hz), 58.5 (t, *J* = 22.1 Hz), 45.8. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -127.9 (ddd, *J* = 284.5, 54.8, 5.5 Hz), -130.9 (ddd, *J* = 284.9, 55.0, 22.6 Hz). **ESI-HRMS**: Calcd for $C_{16}H_{13}F_3N_2O+H^+$: 367.0253, 369.0232, found 367.0252, 369.0230.

7. General Procedure for the Synthesis of 3-Difluoromethyl Quinoxalin-2-ones

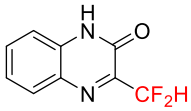


1 **2** (2.0 equiv) **4**

The general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones: To a 25 mL Schlenk tube equipped with a magnetic stir bar was added derivative of 3,4-dihydroquinoxalin-2(1H)-one **1** (0.1 mmol, 1.0 equiv.), **2** (83.0 mg, 0.2 mmol, 2.0 equiv.), **PC II** (1.7 mg, 0.003 mmol, 3 mol%), LiOH (12.0 mg, 0.5 mmol, 5.0 equiv.). Then flask was flushed with argon, followed by the addition of EtOAc (2 mL).The tube was placed at a distance of ~2 mm away from 3 W blue LED lamps (λ = 450 nm), the reaction mixture was stirred under irradiation of blue LEDs. After stirring overnight, DDQ (45.5 mg, 0.2 mmol, 2.0 equiv.) was added and the mixture was stirred at 80 °C for another 2 hours, then the solvent was evaporated in vacuo; and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate) to afford the product **4**.

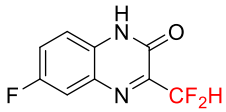
8. Characterization Data for 3-Difluoromethylated Quinoxalin-2(1H)-ones

3-(difluoromethyl)quinoxalin-2(1H)-one (4a)



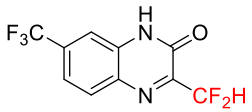
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4a** was isolated as a white solid, R_f = 0.3 (6:1 petroleum ether/ethyl acetate); 14.5 mg, 74% yield. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.84 (br, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 8.2 Hz, 2H), 7.06 (t, *J* = 53.3 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.7, 150.1 (d, *J* = 21.7 Hz), 133.4, 132.8, 131.2, 130.0, 124.5, 116.3, 110.8 (t, *J* = 239.5 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.3 (d, *J* = 53.1 Hz, 2F). Spectroscopic data were in accordance with previous reports.[5]

3-(difluoromethyl)-6-fluoroquinoxalin-2(1H)-one (4b)



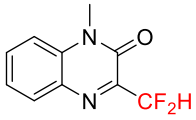
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4b** was isolated as a white solid, R_f = 0.3 (6:1 petroleum ether/ethyl acetate); 7.5 mg, 35% yield, m.p. 191.8-193.0 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 12.91 (s, 1H), 7.77 (dd, *J* = 9.2, 2.9 Hz, 1H), 7.59 (td, *J* = 8.8, 2.9 Hz, 1H), 7.40 (dd, *J* = 9.1, 5.2 Hz, 1H), 7.06 (t, *J* = 53.2 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 158.4 (d, *J* = 240.9 Hz), 153.4, 151.6 (t, *J* = 21.9 Hz), 131.4 (d, *J* = 11.9 Hz), 130.3, 121.0 (d, *J* = 24.4 Hz), 117.8 (d, *J* = 8.9 Hz), 115.0 (d, *J* = 23.0 Hz), 110.64 (t, *J* = 239.7 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -115.3 – -115.4 (m, 1F), -123.9 (d, *J* = 53.4 Hz, 2F). **ESI-HRMS**: Calcd for $C_9H_5F_3N_2O+H^+$: 215.0427, found 215.0432.

3-(difluoromethyl)-7-(trifluoromethyl)quinoxalin-2(1H)-one (4c)



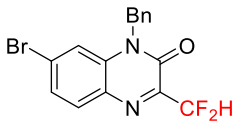
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4c** was isolated as a white solid. R_f = 0.4 (4:1 petroleum ether/ethyl acetate); 13.8 mg, 52% yield, m.p. 108.6-110.0 °C; **^{1}H NMR** (500 MHz, DMSO-d_6) δ 13.04 (s, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 7.65 (s, 1H), 7.09 (t, *J* = 53.0 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.5, 153.1 (t, *J* = 21.5 Hz), 133.6, 133.0, 131.7 (q, *J* = 32.6 Hz), 131.4, 124.0 (q, *J* = 272.9 Hz), 120.3 (q, *J* = 3.7 Hz), 113.4 (q, *J* = 2.9 Hz), 110.5 (t, *J* = 240.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -60.5 (s, 3F), -124.2 (d, *J* = 52.9 Hz, 2F). **ESI-HRMS**: Calcd for $C_{10}H_6F_5N_2O+H^+$: 265.0395, found 265.0340.

3-(difluoromethyl)-1-methylquinoxalin-2(1H)-one (4d)



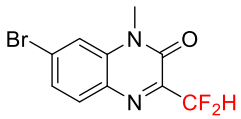
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4d** was isolated as a white solid, R_f = 0.4 (5:1 petroleum ether/ethyl acetate); 16.1 mg, 76% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.69 (td, *J* = 8.6, 1.5 Hz, 1H), 7.44 (td, *J* = 8.3, 1.2 Hz, 1H), 7.39 (d, *J* = 8.5 Hz, 1H), 6.96 (t, *J* = 53.7 Hz, 1H), 3.74 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.3, 148.7 (t, *J* = 22.3 Hz), 134.1, 132.7, 131.9, 131.5, 124.4, 114.0, 110.1 (t, *J* = 241.7 Hz), 29.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -124.4 (d, *J* = 53.8 Hz, 2F). Spectroscopic data were in accordance with previous reports.[5]

1-benzyl-7-bromo-3-(difluoromethyl)quinoxalin-2(1H)-one (4e)



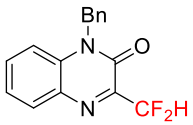
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4e** was isolated as a white solid, R_f = 0.4 (5:1 petroleum ether/ethyl acetate); 26.0 mg, 71% yield, m.p. 134.3-136.7 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.3 Hz, 1H), 7.63 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.31 – 7.28 (m, 1H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 9.0 Hz, 1H), 6.99 (t, *J* = 53.5 Hz, 1H), 5.49 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.0, 150.0 (t, *J* = 22.7 Hz), 135.4, 134.2, 133.9, 133.0, 132.5, 129.2, 128.3, 126.9, 117.1, 116.2, 109.9 (t, *J* = 242.3 Hz), 46.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -124.4 (d, *J* = 53.4 Hz, 2F). **ESI-HRMS**: Calcd for $C_{16}H_{11}BrF_2N_2O+H^+$: 365.0096, 367.0076, found 365.0100, 367.0079.

7-bromo-3-(difluoromethyl)-1-methylquinoxalin-2(1H)-one (4f)



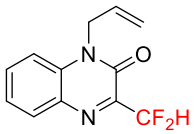
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4f** was isolated as a white solid, R_f = 0.3 (6:1 petroleum ether/ethyl acetate); 14.5 mg, 50% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.1 Hz, 1H), 7.60 – 7.52 (m, 2H), 6.95 (t, *J* = 53.6 Hz, 1H), 3.73 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.9, 148.9 (t, *J* = 22.6 Hz), 135.0, 132.6, 130.7, 127.9, 127.3, 117.1, 110.0 (t, *J* = 241.9 Hz), 29.2. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -124.5 (d, *J* = 53.7 Hz, 2F). Spectroscopic data were in accordance with previous reports.[5a,c]

1-benzyl-3-(difluoromethyl)quinoxalin-2(1H)-one (4g)



According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4g** was isolated as a white solid, Rf = 0.3 (6:1 petroleum ether/ethyl acetate); 18.3 mg, 64% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ8.03 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.58 (ddd, *J* = 8.7, 7.1, 1.6 Hz, 1H), 7.41 (td, *J* = 8.3, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.9, 6.2 Hz, 3H), 7.33 – 7.30 (m, 1H), 7.28 (d, *J* = 6.2 Hz, 2H), 7.05 (t, *J* = 53.7 Hz, 1H), 5.55 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 153.4 (t, *J* = 1.6 Hz), 148.8 (t, *J* = 22.5 Hz), 134.6, 133.4, 132.7, 132.2, 131.6, 129.1, 128.1, 127.0, 124.5, 114.8, 111.1 (t, *J* = 241.7 Hz), 45.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -124.2 (d, *J* = 53.9 Hz, 2F). Spectroscopic data were in accordance with previous reports.[5a,c]

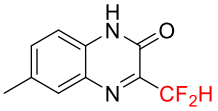
1-allyl-3-(difluoromethyl)quinoxalin-2(1H)-one (4h)



According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4h** was isolated as a white solid, R_f = 0.3 (6:1 petroleum ether/ethyl acetate); 10.2 mg, 43% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 6.98 (t, *J* = 53.7 Hz, 1H), 5.94 (ddt, *J* = 17.1, 10.4, 5.2 Hz, 1H), 5.32 (d, *J* = 10.4 Hz, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 4.94 (dt, *J* = 5.3, 1.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 152.9, 148.7 (t, *J* = 22.4 Hz), 133.3, 132.6, 132.1, 131.6, 130.0, 124.4, 118.8,

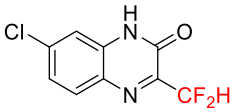
114.6, 110.0 (t, *J* = 241.7 Hz), 44.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -124.3 (d, *J* = 53.8 Hz, 2F). Spectroscopic data were in accordance with previous reports.[4a,c]

3-(difluoromethyl)-6-methylquinoxalin-2(1H)-one (4i)



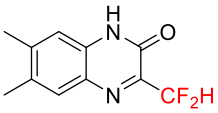
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4i** was isolated as a white solid, R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 11.2 mg, 53% yield, m.p. 253.2-255.7 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.78 (br, 1H), 7.70 (s, 1H), 7.50 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 53.4 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.6, 150.0 (t, *J* = 21.5 Hz), 134.1, 134.0, 131.2, 131.1, 129.4, 116.0, 110.9 (t, *J* = 239.3 Hz), 20.8. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.2 (d, *J* = 53.3 Hz, 2F). **ESI-HRMS**: Calcd for $C_{10}H_8F_2N_2O+H^+$: 211.0677, found 211.0686.

7-chloro-3-(difluoromethyl)quinoxalin-2(1H)-one (4j)



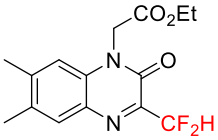
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4j** was isolated as a white solid, R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 12.5 mg, 54% yield, m.p. 115.8-117.7 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.89 (s, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.41 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.35 (d, *J* = 2.3 Hz, 1H), 7.04 (t, *J* = 53.2 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.5, 150.6 (t, *J* = 22.2 Hz), 136.9, 134.5, 131.7, 130.0, 124.5, 115.6, 110.7 (t, *J* = 239.6 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.5 (d, *J* = 53.2 Hz, 2F). **ESI-HRMS**: Calcd for $C_9H_5ClF_2N_2O+H^+$: 231.0131, found 231.0136.

3-(difluoromethyl)-6,7-dimethylquinoxalin-2(1H)-one (4k)



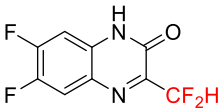
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4k** was isolated as a white solid, R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 14.9 mg, 66% yield. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.64 (s, 1H), 7.13 (s, 1H), 7.01 (t, *J* = 53.5 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.8, 148.7 (t, *J* = 21.1 Hz), 143.0, 133.5, 131.4, 129.8, 129.5, 116.1, 111.0 (t, *J* = 239.0 Hz), 20.4, 19.3. **^{19}F NMR** (471 MHz, DMSO-d_6) δ -123.7 (d, *J* = 53.3 Hz, 2F). **ESI-HRMS**: Calcd for $C_{11}H_{10}F_2N_2O+H^+$: 225.0834, found 225.0837. Spectroscopic data were in accordance with previous reports.[5d]

Ethyl 2-(3-(difluoromethyl)-6,7-dimethyl-2-oxoquinoxalin-1(2H)-yl)acetate (4l)



According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4l** was isolated as a white solid; R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 18.0 mg, 58% yield, m.p. 141.7-142.8 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 6.93 (t, *J* = 53.8 Hz, 1H), 6.88 (s, 1H), 5.02 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 2.36 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 152.9, 147.2 (t, *J* = 22.6 Hz), 143.4, 134.0, 131.6, 131.3, 130.5, 113.8, 110.1 (t, *J* = 241.4 Hz), 62.3, 43.3, 20.9, 19.2, 14.1. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -123.9 (d, *J* = 53.8 Hz, 2F). **ESI-HRMS**: Calcd for $C_{15}H_{17}F_2N_2O_3+H^+$: 311.1202, found 311.1206.

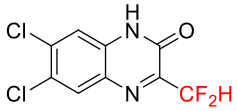
3-(difluoromethyl)-6,7-difluoroquinoxalin-2(1H)-one (4m)



According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4m** was isolated as a white solid, R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 10.3 mg, 44% yield. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 12.98 (br, 1H), 8.08 (dd, *J* = 10.8, 8.2 Hz, 1H), 7.29 (dd, *J* = 11.0, 7.5 Hz, 1H), 7.04 (t, *J* = 53.2 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.4, 153.1 (d, *J* = 14.7 Hz), 151.4 (d, *J* = 14.8 Hz), 147.4 (d, *J* = 14.4 Hz), 145.8 (d, *J* = 14.3 Hz), 131.3 (dd, *J* = 8.1, 3.0 Hz), 127.6 (d, *J* = 7.9 Hz), 110.6 (t, *J* = 239.7 Hz), 104.1 (d, *J* = 21.6 Hz). **^{19}F NMR** (471 MHz,

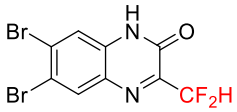
DMSO-d_6) δ -124.6 (d, J = 53.1 Hz, 2F), -129.8 (dt, J = 23.6, 9.8 Hz, 1F), -142.2 – -142.3 (m, 1F). **ESI-HRMS**: Calcd for $C_9H_4F_4N_2O+H^+$: 233.0333, found 233.0338. Spectroscopic data were in accordance with previous reports.[5d]

6,7-dichloro-3-(difluoromethyl)quinoxalin-2(1H)-one (4n)



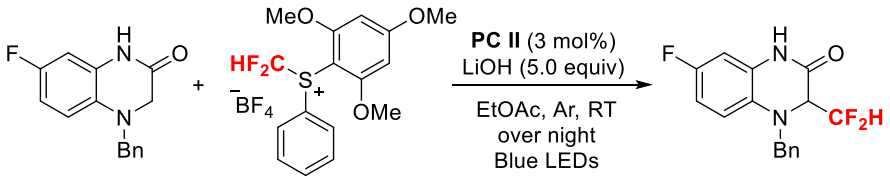
According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4n** was isolated as a white solid, R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 11.9 mg, 45% yield, m.p. 130.5-132.6 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.21 (s, 1H), 7.51 (s, 1H), 7.05 (t, J = 53.1 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.4, 151.9 (t, J = 19.7 Hz), 134.8, 133.4, 131.0, 130.6, 126.1, 117.4, 110.5 (t, J = 240.0 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.9 (d, J = 53.1 Hz, 2F). **ESI-HRMS**: Calcd for $C_9H_4Cl_2F_2N_2O+H^+$: 264.9742, found 264.9744.

6,7-dibromo-3-(difluoromethyl)quinoxalin-2(1H)-one (4o)



According to the general procedure for the Synthesis of 3-difluoromethyl quinoxalin-2-ones, **4o** was isolated as a white solid, R_f = 0.3 (5:1 petroleum ether/ethyl acetate); 10.6 mg, 30% yield, m.p. 109.6-110.8 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.91 (br, 1H), 8.27 (s, 1H), 7.66 (s, 1H), 7.03 (t, J = 53.1 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO-d_6) δ 153.3, 151.9 (t, J = 20.4 Hz), 133.9, 133.6, 131.2, 127.8, 120.5, 118.06, 110.6 (t, J = 240.0 Hz). **^{19}F NMR** (471 MHz, DMSO-d_6) δ -124.9 (d, J = 53.0 Hz, 2F). **ESI-HRMS**: Calcd for $C_9H_4Br_2F_2N_2O+H^+$: 352.8732, 354.8711, 356.8691, found 352.8730, 354.8707, 356.8685.

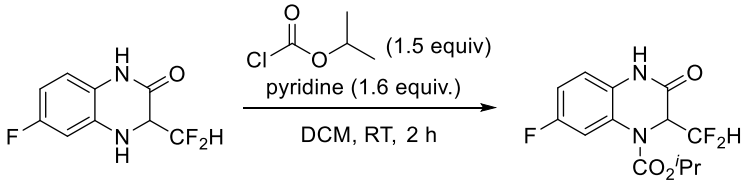
9. 2.0 mmol Scale Procedure for Radical Difluoromethylation of 1ak



1ak 512.0 mg, 2.0 mmol | **2** 1.656 g, 4.0 mmol | **3ak** 368.6 mg, 60%

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added 4-benzyl-7-fluoro-3,4-dihydroquinoxalin-2(1H)-one **1ak** (512.0 mg, 2.0 mmol, 1.0 equiv.), **2** (1.656 g, 4.0 mmol, 2.0 equiv.), **PC II** (34.8 mg, 0.06 mmol, 3 mol%), LiOH (240.0 mg, 10.0 mmol, 5.0 equiv.). Then the flask was flushed with argon, followed by the addition of EtOAc (10 mL). The tube was placed at a distance of ~2 mm away from (3 W × 4) blue LED lamps (λ = 450 nm), the reaction mixture was stirred under irradiation of blue LEDs. After stirring overnight, the solvent was evaporated in vacuo; and the residue was purified by flash column chromatography on silica gel (petrol ether/ethyl acetate) to afford the product **3ak** as a light yellow solid (368.6 mg, 60%).

10. Synthetic Application[6]



3bb | **5**, 82%

Isopropyl 2-(difluoromethyl)-7-fluoro-3-oxo-3,4-dihydroquinoxaline-1(2H)-carboxylate (5): To a solution of 3-(difluoromethyl)-6-fluoro-3,4-dihydroquinoxalin-2(1H)-one **3bb** (21.6 mg, 0.1 mmol, 1.0 equiv.) in DCM (2 mL) under nitrogen were added pyridine (13 μL, 0.16 mmol, 1.6 equiv.) and isopropyl chloroformate (20.6 μL, 0.15 mmol, 1.5 equiv.). The solution was stirred for 2 h at room temperature and diluted with chloroform (5 mL). The reaction mixture was washed with water and dried over magnesium sulfate. After evaporation of solvent in vacuo, the residue was purified via flash column chromatography (hexane/EtOAc=4/1) on silica gel to give **5** (24.9 mg, 82 %) as a white amorphous solid. **^{1}H NMR** (600 MHz, MeOD-d_4) δ 7.58 – 7.39 (m, 1H), 6.94 (dd, J = 8.5, 5.4 Hz, 1H), 6.90 (dt, J = 10.2, 5.2 Hz, 1H), 6.09 (td, J = 54.1, 3.6 Hz, 1H), 5.34 (t, J = 14.5 Hz, 1H), 5.08 (hept, J = 6.2 Hz, 1H), 1.35 (dd, J =

35.3, 6.3 Hz, 6H). **^{13}C NMR** (151 MHz, MeOD-d_4) δ 163.0 (br), 158.33 (d, J = 239.7 Hz), 152.9 (br), 128.42 (d, J = 241.7 Hz), 126.0 (d, J = 11.2 Hz), 125.7, 116.5 (d, J = 9.4 Hz), 113.8 (t, J = 247.8 Hz), 111.7 (d, J = 23.5 Hz), 71.8, 58.5 (t, J = 22.6 Hz), 20.6 (d, J = 12.5 Hz). **^{19}F NMR** (377 MHz, $CDCl_3$) δ -116.4 – -117.4 (m, 1F), -124.1 – -127.1 (m, 2F). **ESI-HRMS**: Calcd for $C_{13}H_{14}F_3N_2O_3$+H^+: 303.0951, found 303.0953.

11. Mechanistic Experiments

The reaction pathway design: generation and stability of C(sp^3) radical species

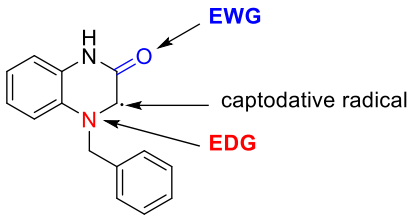


Figure S2. *C*-centered cyclic captodative radical

It is known that a radical is stabilized by electron-withdrawing groups (EWG) and electron-donating group (EDG). But, when a radical centre has both a EWG and a EDG attached (this radical is called captodative) it is even more stable. A rational explanation for this captodative effect comes from Molecular Orbital Theory (MOT). The Figure S3 scheme describes the orbital interactions in the formation of a sigma C-N bond between a α-carbonyl radical (stabilized radical due to the EWG) and a nitrogen (EDG)[7]. The interaction between N and α-EWG-radical provides a set of new MOs. As can be noted, there is a rise in energy of the SOMO, increasing the nucleophilicity of the radical while achieving an overall stabilization.

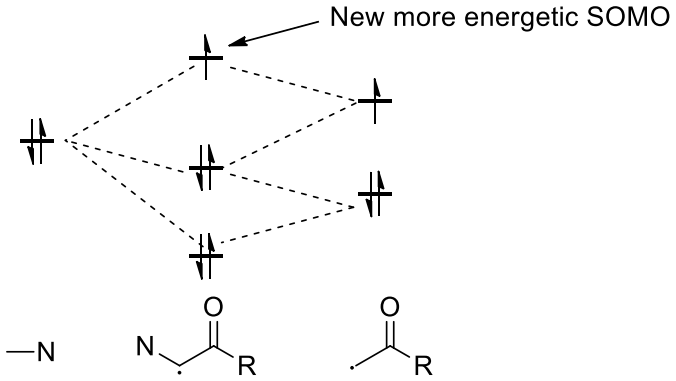


Figure S3. Molecular Orbitals Diagram for the formation of a sigma C-N bond between a N and a α-carbonyl radical

Additionally, within the resonance model, radicals featuring both EDG and EWG have additional charge-separate resonance structures (Figure S4) in comparison with radicals bearing either multiple EDG or EWG. This feature also supports its greater stability.

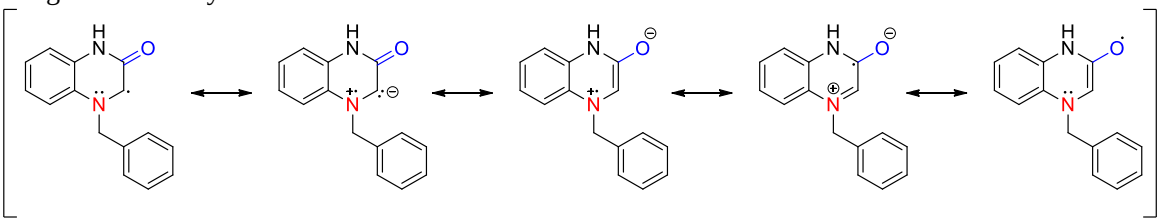
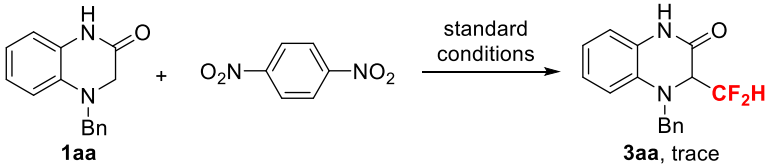


Figure S4. Resonance structures for the radical generated under photoredox conditions.

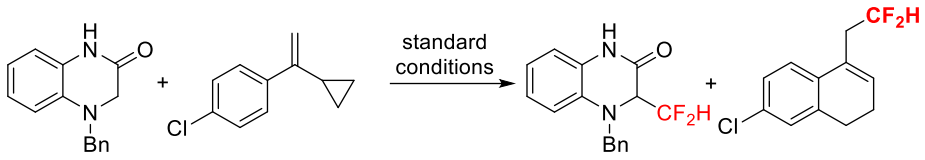
Evidence of difluoromethyl radical species



1aa **3aa**, trace

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added derivative of 4-benzyl-3,4-dihydroquinoxalin-2(1H)-one **1aa** (23.8 mg, 0.1 mmol, 1.0 equiv.), **2** (83.0 mg, 0.2 mmol, 2.0 equiv.), **PC II** (1.7 mg, 0.003 mol, 0.03 equiv), LiOH (12.0 mg, 0.5 mmol, 5.0 equiv.) and 1,4-dinitrobenzene (33.6 mg, 0.2 mmol, 2.0 equiv.). Then flask was flushed with argon, followed by the addition of EtOAc (2 mL). The tube was placed at a distance of ~2 mm away from (3 W × 4) blue LED lamps (λ = 450 nm), the reaction mixture was stirred under irradiation of blue LEDs. After stirring overnight, the reaction mixture was monitored by **^{19}F NMR** using PhF (0.1 mmol) as the internal standard, and no **3aa** was detected.

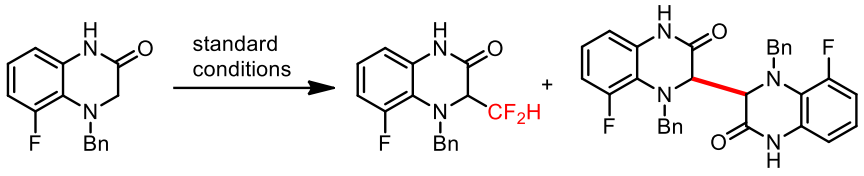
Radical-clock experiment



1aa **6**, 0.2 mmol **3aa**, 10% **7**, 24%

To a 25 mL Schlenk tube equipped with a magnetic stir bar was added 1-chloro-4-(1-cyclopropylvinyl)benzene **6** (0.1 mmol), **2** (2.0 equiv.), **PC II** (3 mol%), LiOH (2.0 equiv.), The flask was flushed with argon, followed by the addition of EtOAc (2 mL). The tube was placed at a distance of ~2 mm away from (3 W × 4) blue LED lamps (λ = 450 nm), the reaction mixture was stirred under irradiation of blue LEDs. After stirring overnight, the reaction mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel with hexane to afford **3aa** and **7** in 10% and 24 % respectively. **7-chloro-4-(2,2-difluoroethyl)-1,2-dihydronaphthalene (7)**[8], colorless oil, R_f = 0.35 (petroleum ether); 11.0 mg, 24% yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.11 (m, 3H), 6.10 – 6.05 (m, 1H), 5.92 (dt, *J* = 56.7, 4.8 Hz, 1H)2.98 (tdd, *J* = 16.5, 4.7, 1.3 Hz, 2H), 2.77 (t, *J* = 8.1 Hz, 2H), 2.37 – 2.25 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 132.6, 132.5, 130.3, 127.9, 127.9, 126.5, 123.7, 116.0 (t, *J* = 241.2 Hz), 37.7 (t, *J* = 22.5 Hz), 27.9, 22.9. **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.88 (dt, *J* = 56.7, 16.6 Hz, 2F). HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{12}H_{12}ClF_2^+$ 229.0590, found 229.0592.

Isolation of 4-benzyl-5-fluoro-3,4-dihydroquinoxalin-2(1H)-one dimer (8)



1am **3am**, 22% **Dimer 8**, 42%

In scope reaction of **1am**, a large amount of dimeric 4-benzyl-5-fluoro-3,4-dihydroquinoxalin-2-one (**8**) was obtained. It was isolated as a single diasteromer by removing the mother liquor and washing the solid with DCM. Dimer **8** was characterized by ^{1}H NMR and HRMS. The presence of this dimeric specie is consistent with the generation of the α-aminoradical under our photoredox conditions. **1,1'-dibenzyl-8,8'-difluoro-1,1',4,4'-tetrahydro-[2,2'-biquinoxaline]-3,3'(2H,2'H)-dione (8)**, whit solid, 10.7 mg, 42% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 7.29 – 7.20 (m, 3H), 7.10 (dd, *J* = 7.9, 1.7 Hz, 2H), 6.83 – 6.68 (m, 2H), 6.48 (d, *J* = 7.5 Hz, 1H), 4.37 (d, *J* = 15.3 Hz, 1H), 4.21 (d, *J* = 15.4 Hz, 1H), 3.86 (s, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 165.1, 154.3 (d, J = 242.8 Hz), 138.2, 132. 4 (d, J = 6.3 Hz), 128.9, 128.1, 127.9, 122.1 (d, J = 9.3 Hz), 121.3 (d, J = 12.3 Hz), 111.7, 110.5 (d, J = 20.4 Hz), 64.3, 58.1 (d, J = 7.2 Hz). ^{19}F NMR (377 MHz, DMSO-d_6) δ -125.4 (m, F). HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{30}H_{25}F_2N_4O_2^+$ 511.1940, found 511.1952.

12. Crystallographic Data

Crystal structure determination of 3aa

Crystal Data for $C_{16}H_{14}F_2N_2O$ (*M* =288.29 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 14.9886(8) Å, *b* = 13.3399(7) Å, *c* = 6.9690(3) Å, *β* = 90.812(4)°, *V* = 1393.29(12) Å^3, *Z* = 4, *T* = 180.00(10) K, μ(Mo Kα) = 0.105 mm^{-1}, *Dcalc* = 1.374 g/cm^3, 9617 reflections measured (4.088° ≤ 2Θ ≤ 49.986°), 2450 unique (R_{int} = 0.0377, R_{sigma} = 0.0320) which were used in all calculations. The final R_1 was 0.0378 (I > 2σ(I)) and wR_2 was 0.0933 (all data).

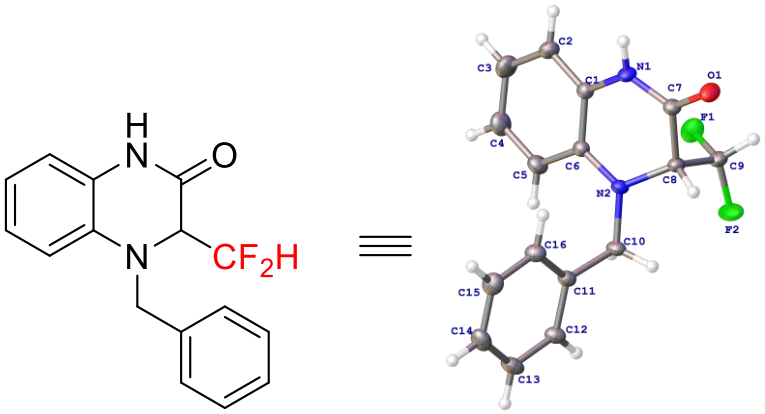


Figure S4. An ORTEP diagram of compound **3aa** with ellipsoids shown at the 30% counter percent probability level

The crystal was prepared by slow evaporation using petroleum ether and methane dichloride solvent mixture. A single crystal of **3aa** was mounted and the diffraction data was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. The data were collected and processed using CrysAlisPro22. The structures were solved by direct methods using Olex2 software24, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXL-201825 using a full-matrix least squares procedure based on F2. The weighted R factor, wR and goodness-of-fit S values were obtained based on F2.The hydrogen atom positions were fixed geometrically at the calculated distances and allowed to ride on their parent atoms. Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center and allocated with the deposition numbers: CCDC 2112795 for compound **3aa**.

Table 1 Crystal data and structure refinement for 3aa.

Identification code	**3aa**
Empirical formula	$C_{16}H_{14}F_2N_2O$
Formula weight	288.29
Temperature/K	180.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.9886(8)
b/Å	13.3399(7)
c/Å	6.9690(3)
α/°	90
β/°	90.812(4)
γ/°	90
Volume/Å^3	1393.29(12)
Z	4
ρ_{calc}g/cm^3	1.374
μ/mm^{-1}	0.105
F(000)	600.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.088 to 49.986
Index ranges	-17 ≤ h ≤ 15, -15 ≤ k ≤ 15, -6 ≤ l ≤ 8
Reflections collected	9617
Independent reflections	2450 [R_{int} = 0.0377, R_{sigma} = 0.0320]
Data/restraints/parameters	2450/0/191
Goodness-of-fit on F^2	1.055
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0888
Final R indexes [all data]	R_1 = 0.0454, wR_2 = 0.0933
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15

13. References

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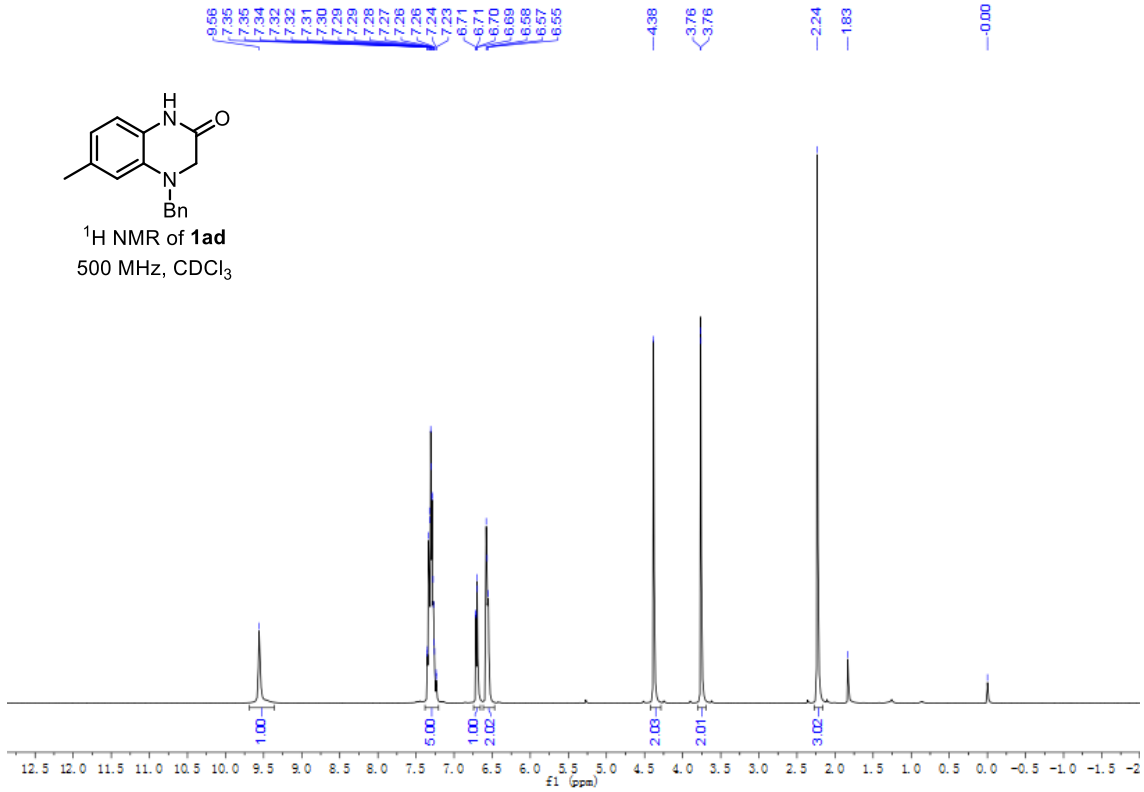
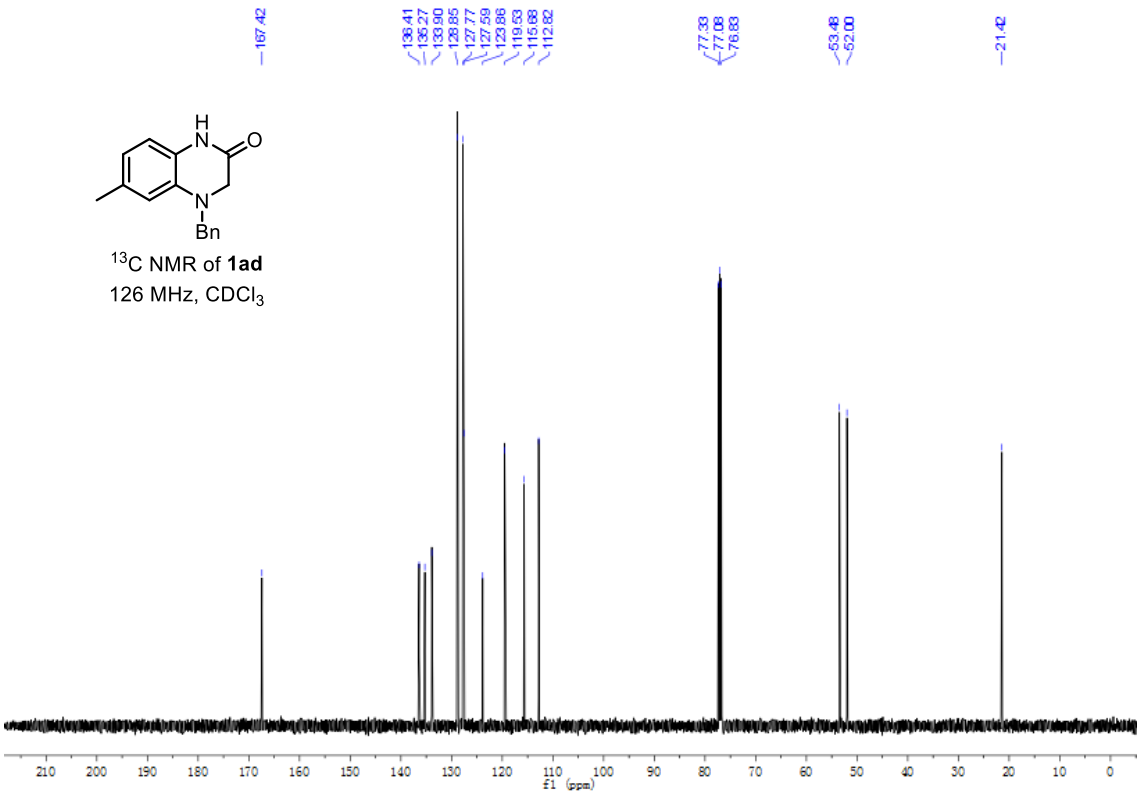
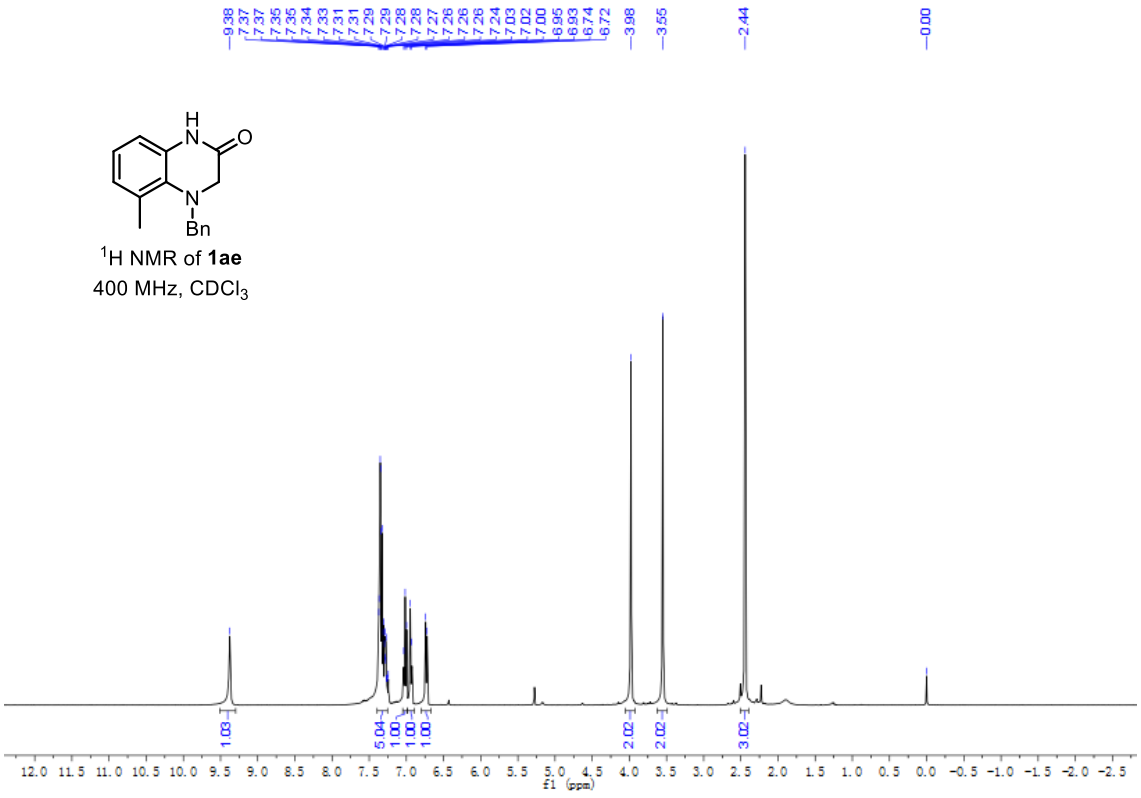
14. NMR Spectra for New Compound

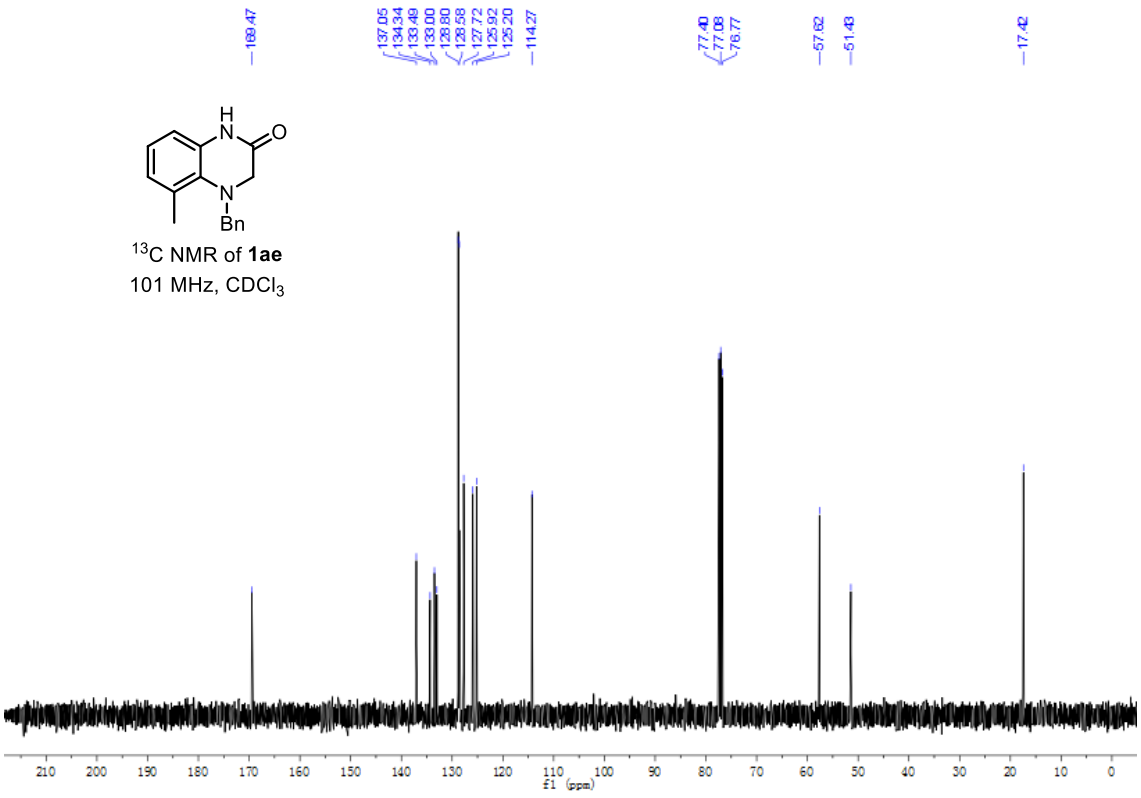
4-benzyl-6-methyl-3,4-dihydroquinoxalin-2(1H)-one (1ad)





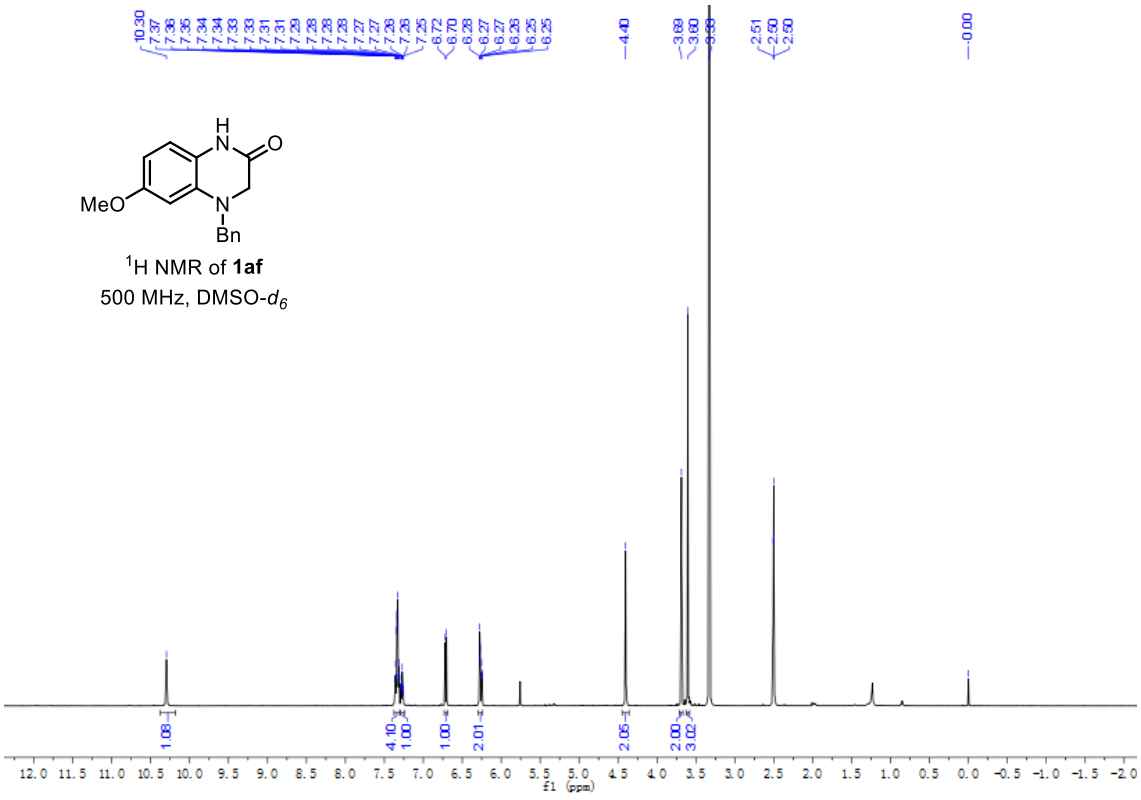
4-benzyl-5-methyl-3,4-dihydroquinoxalin-2(1H)-one (1ae)



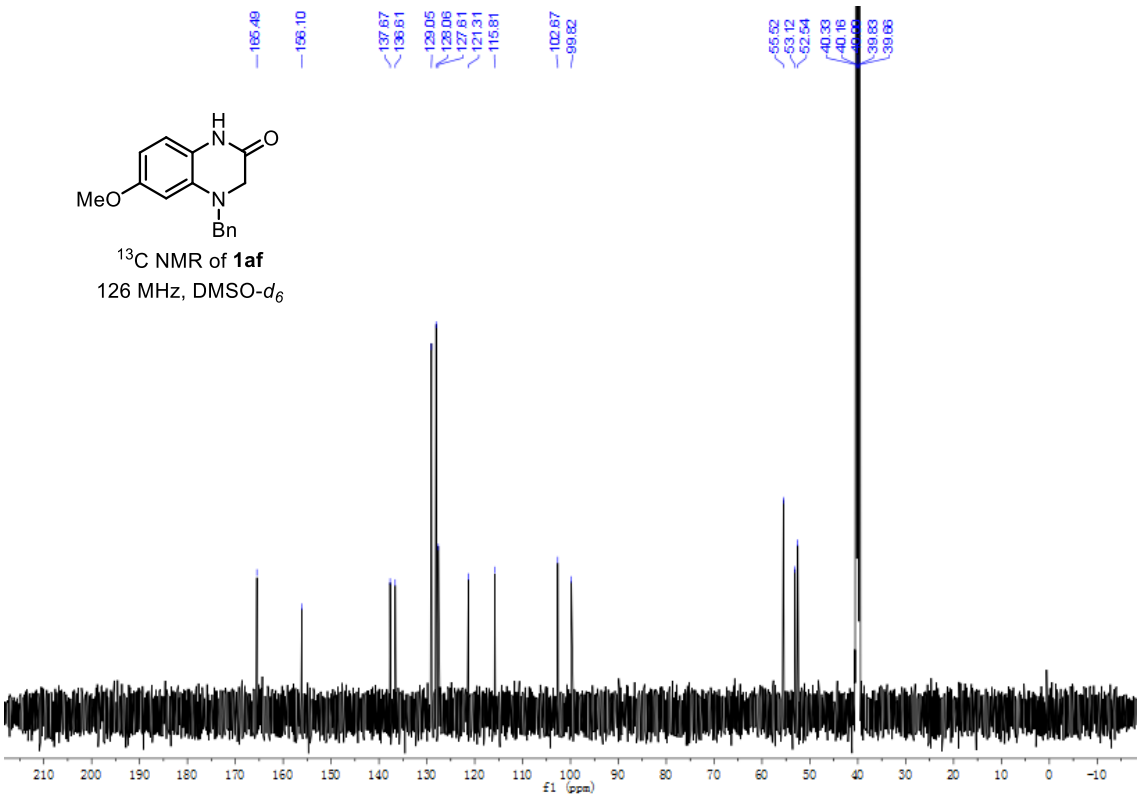


^{13}C NMR of **1ae**
101 MHz, $CDCl_3$

4-benzyl-6-methoxy-3,4-dihydroquinoxalin-2(1H)-one (1af)

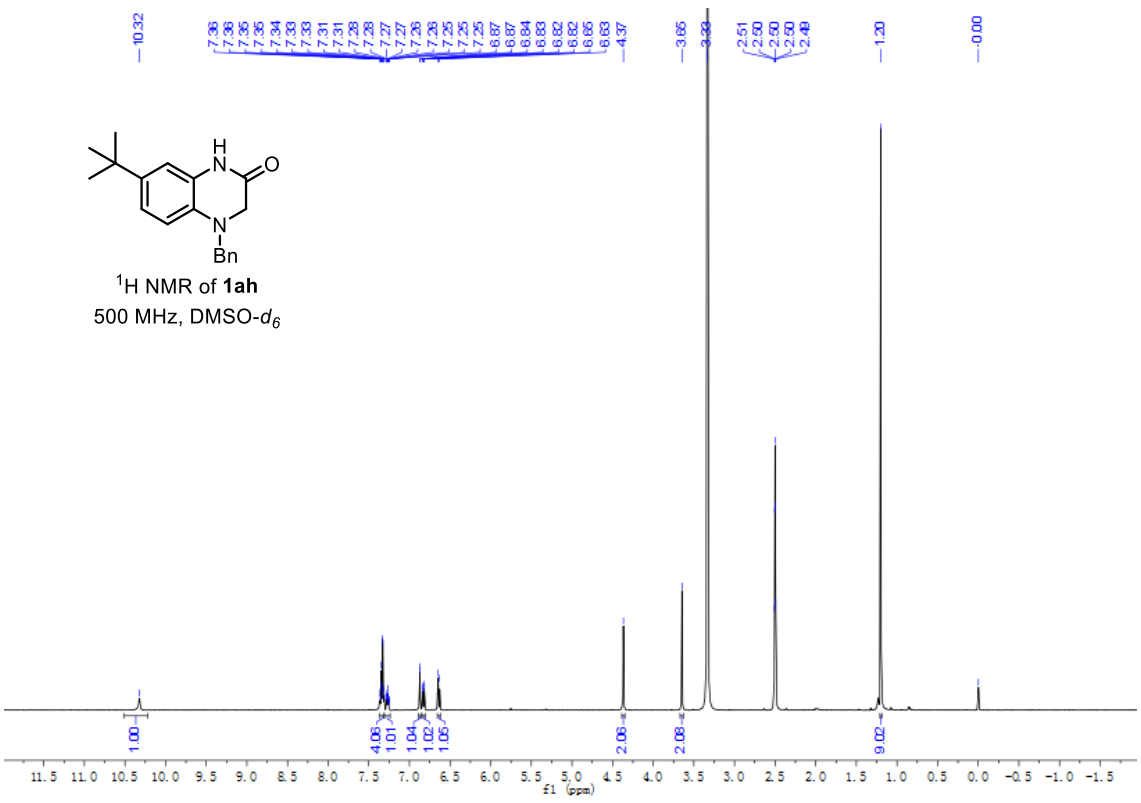


^{1}H NMR of **1af**
500 MHz, DMSO-d_6

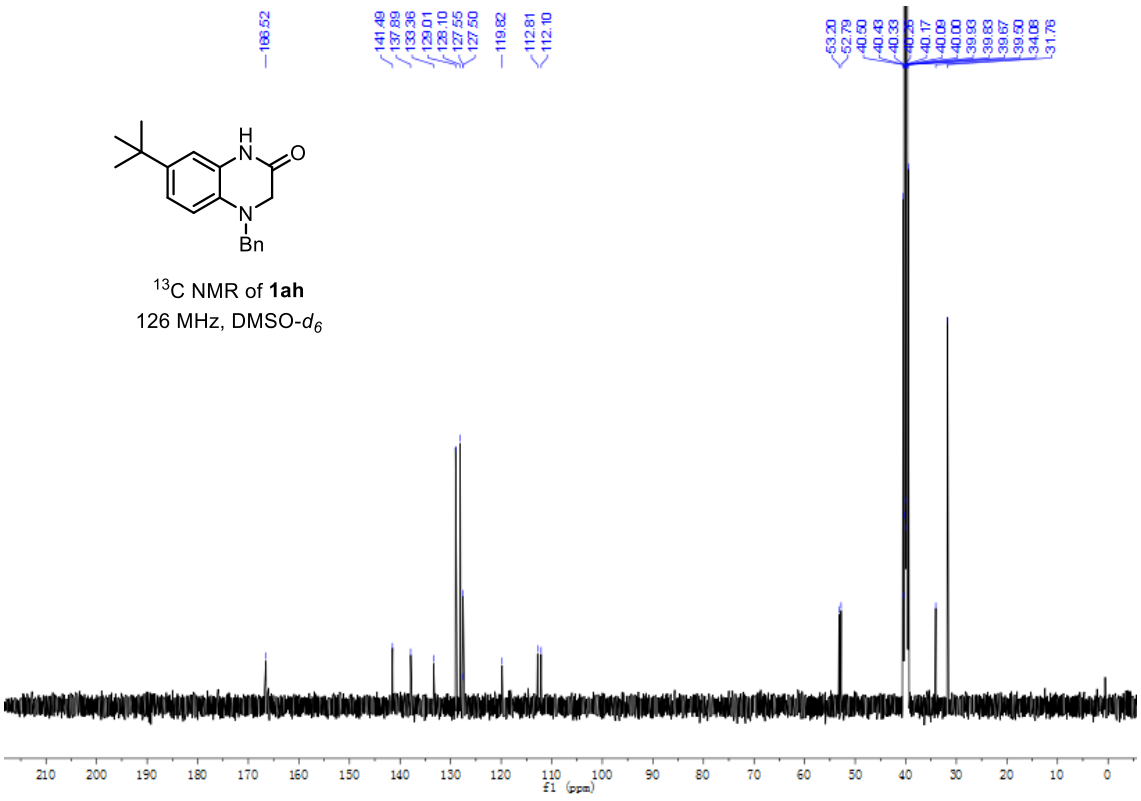


^{13}C NMR of **1af**
126 MHz, DMSO-d_6

4-benzyl-7-(tert-butyl)-3,4-dihydroquinoxalin-2(1H)-one (1ah)

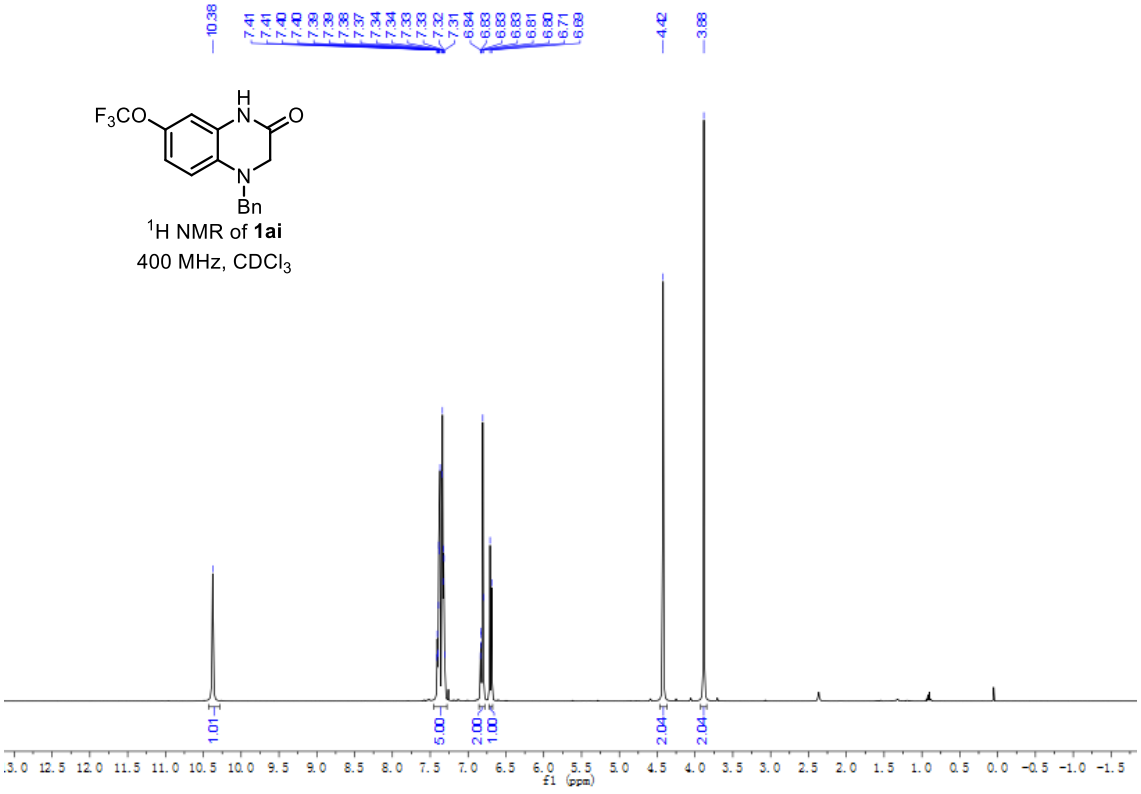


^{1}H NMR of **1ah**
500 MHz, DMSO-d_6

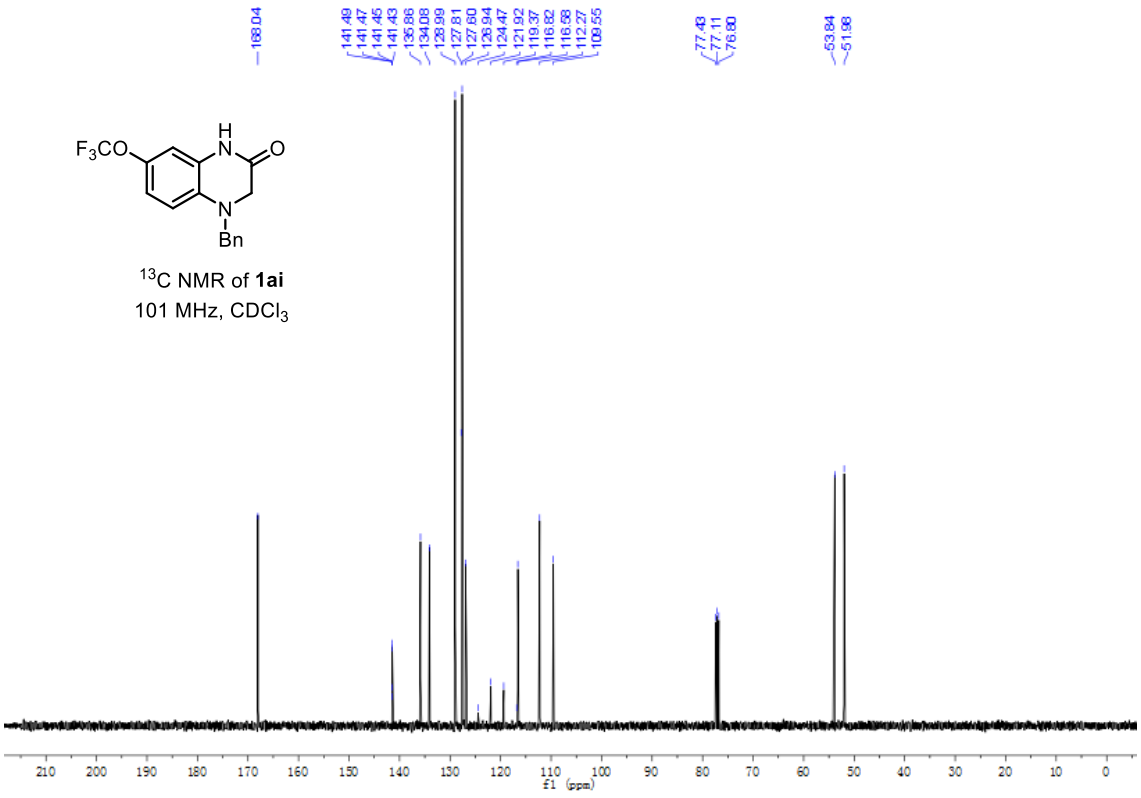


^{13}C NMR of **1ah**
126 MHz, DMSO-d_6

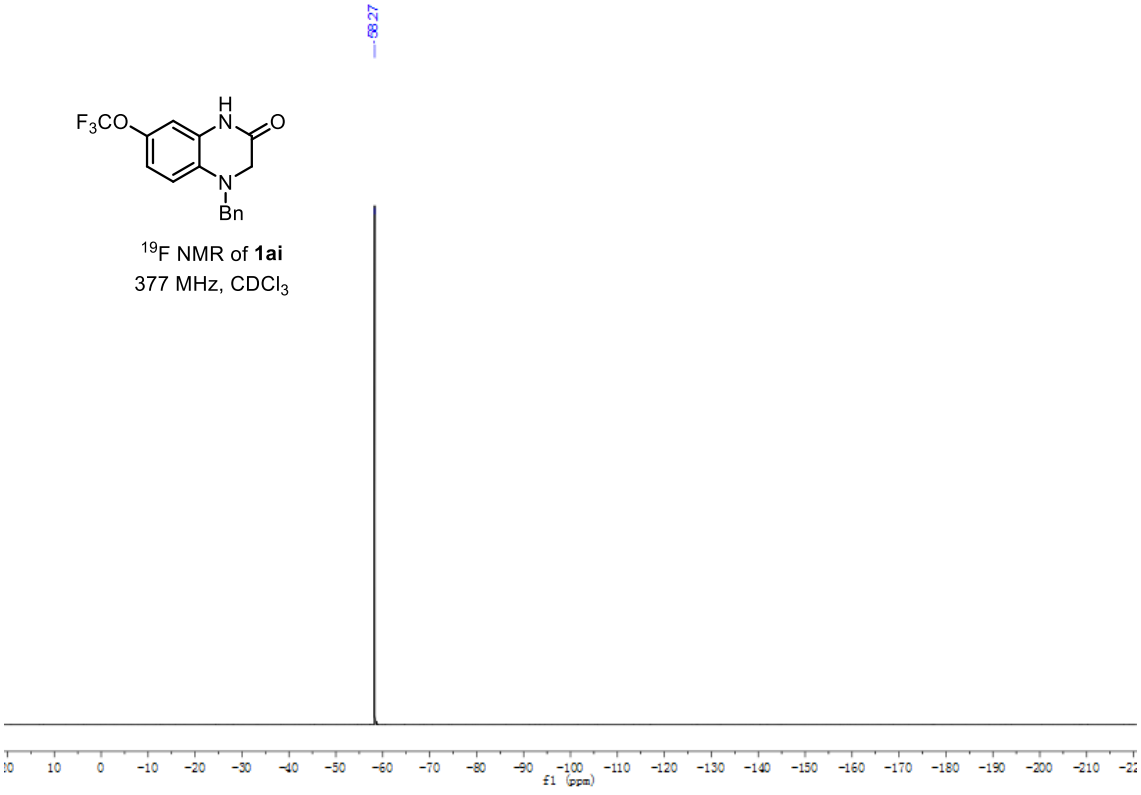
4-benzyl-7-(trifluoromethoxy)-3,4-dihydroquinoxalin-2(1H)-one (1ai)



^{1}H NMR of **1ai**
400 MHz, $CDCl_3$

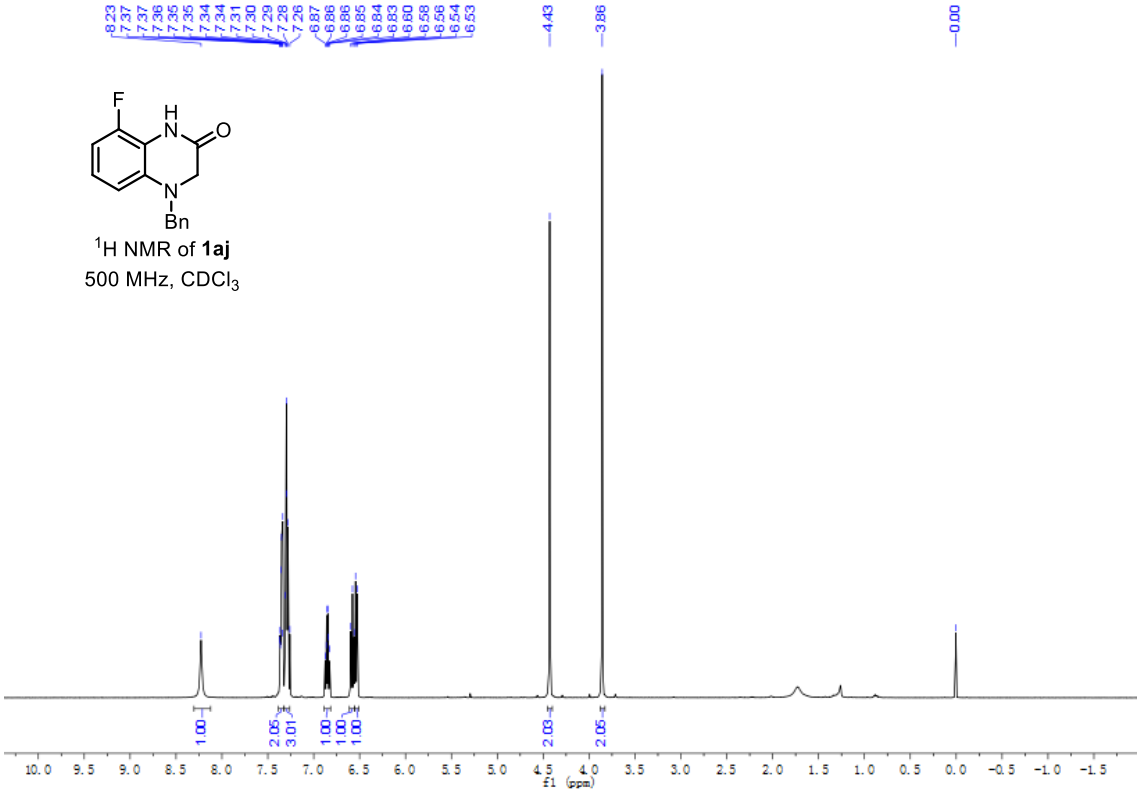


^{13}C NMR of **1ai**
101 MHz, $CDCl_3$

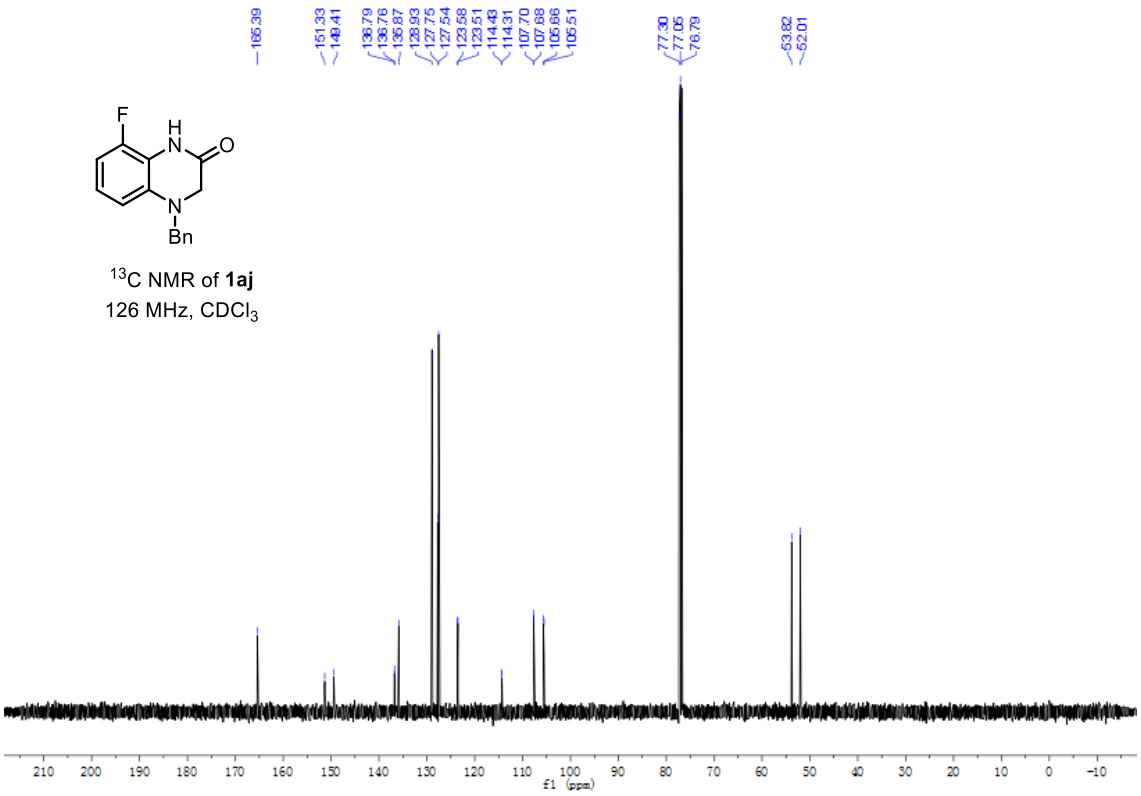


^{19}F NMR of **1ai**
377 MHz, $CDCl_3$

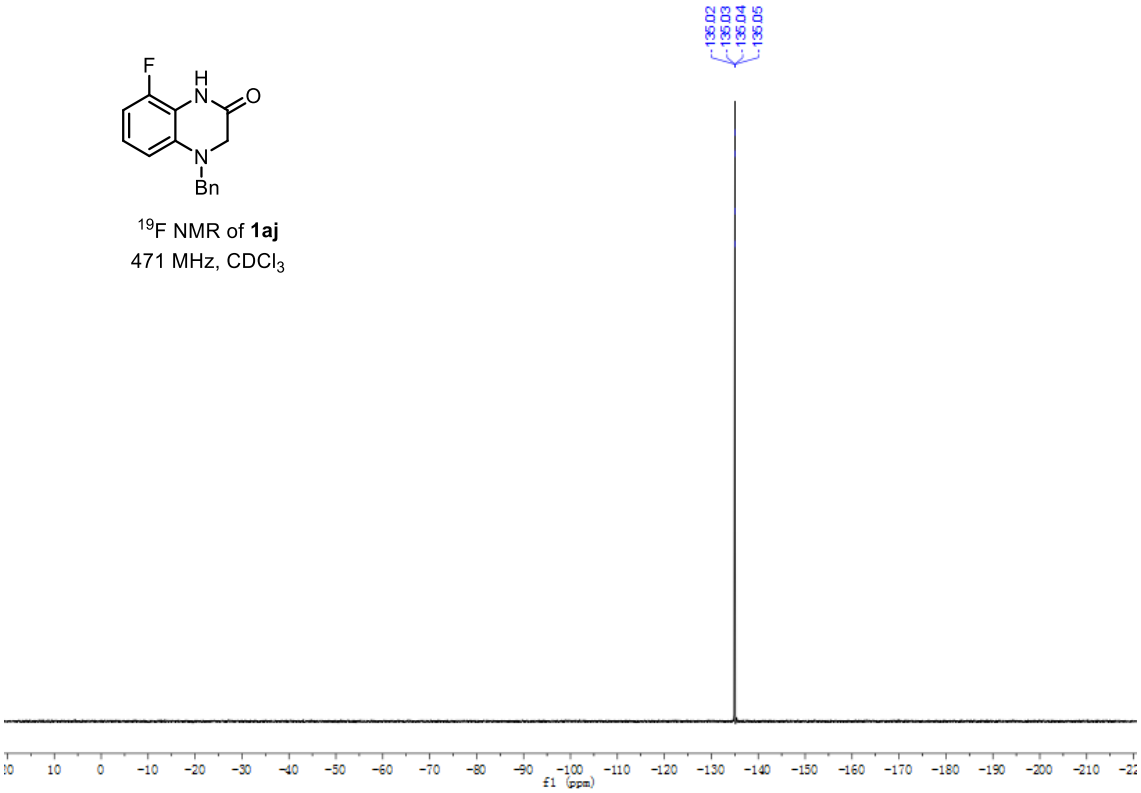
4-benzyl-8-fluoro-3,4-dihydroquinoxalin-2(1H)-one (1aj)



^{1}H NMR of **1aj**
500 MHz, $CDCl_3$

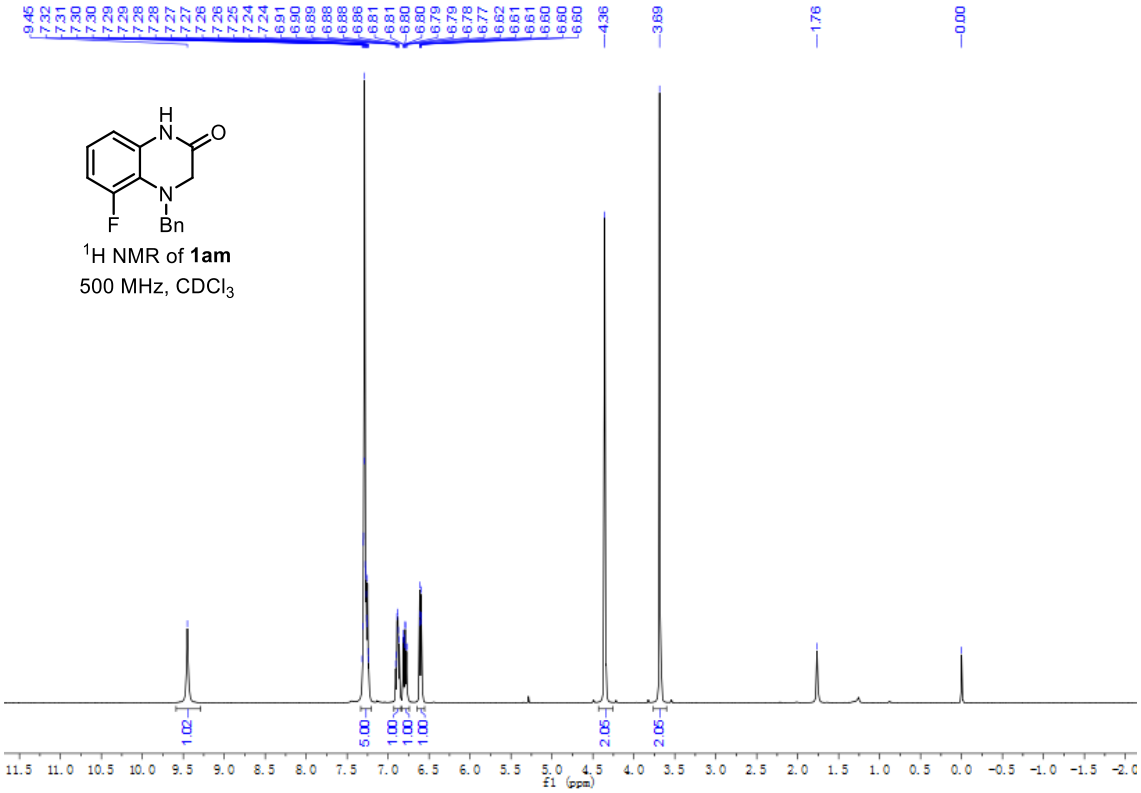


^{13}C NMR of **1aj**
126 MHz, $CDCl_3$

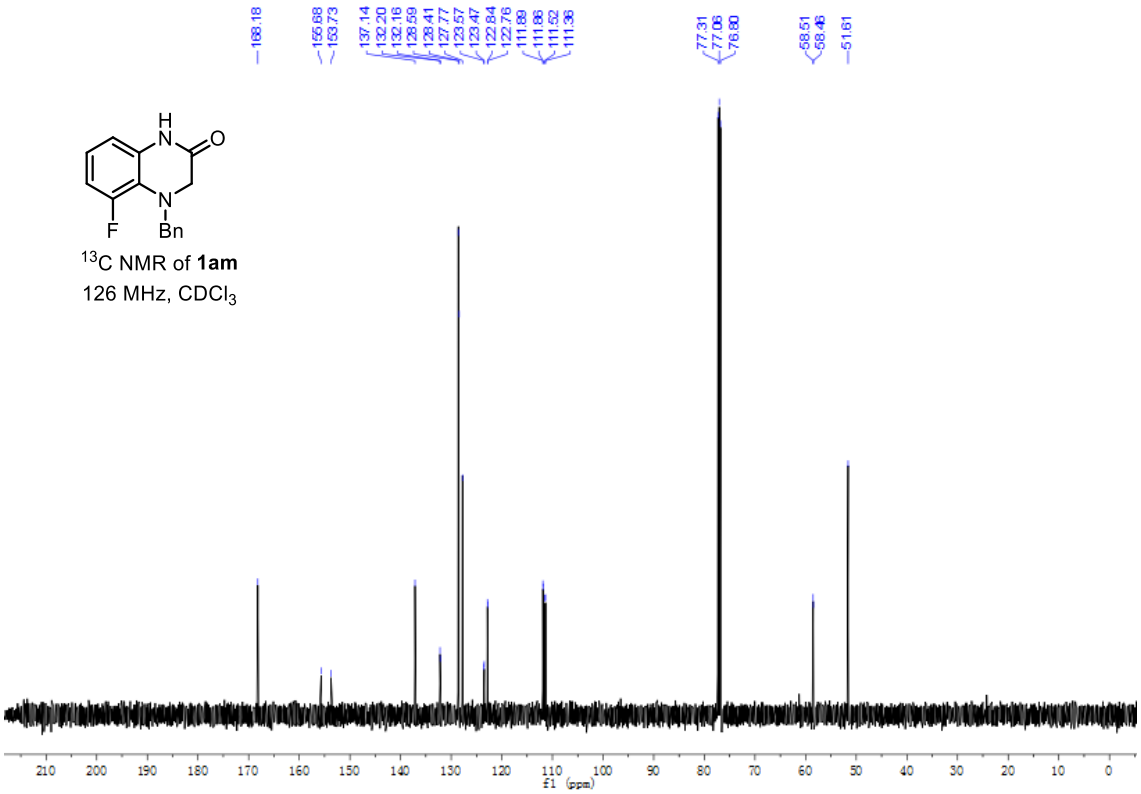


^{19}F NMR of **1aj**
471 MHz, $CDCl_3$

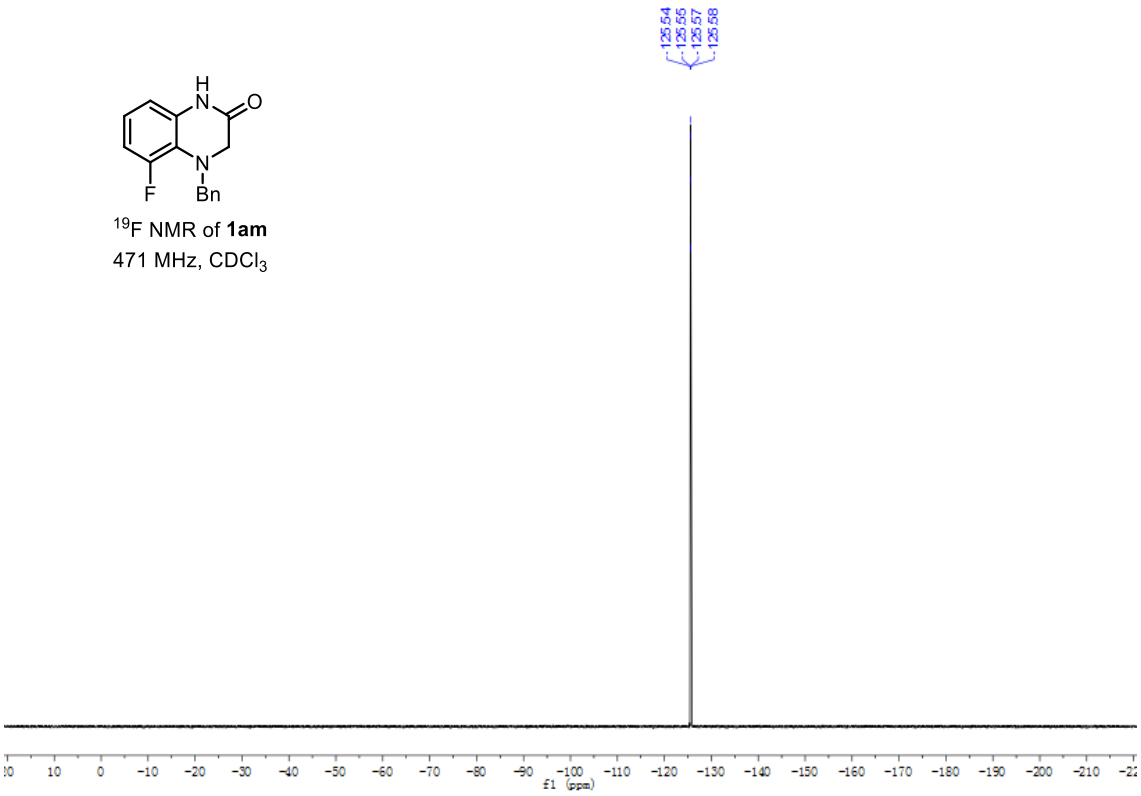
4-benzyl-5-fluoro-3,4-dihydroquinoxalin-2(1H)-one (1am)



^{1}H NMR of **1am**
500 MHz, $CDCl_3$

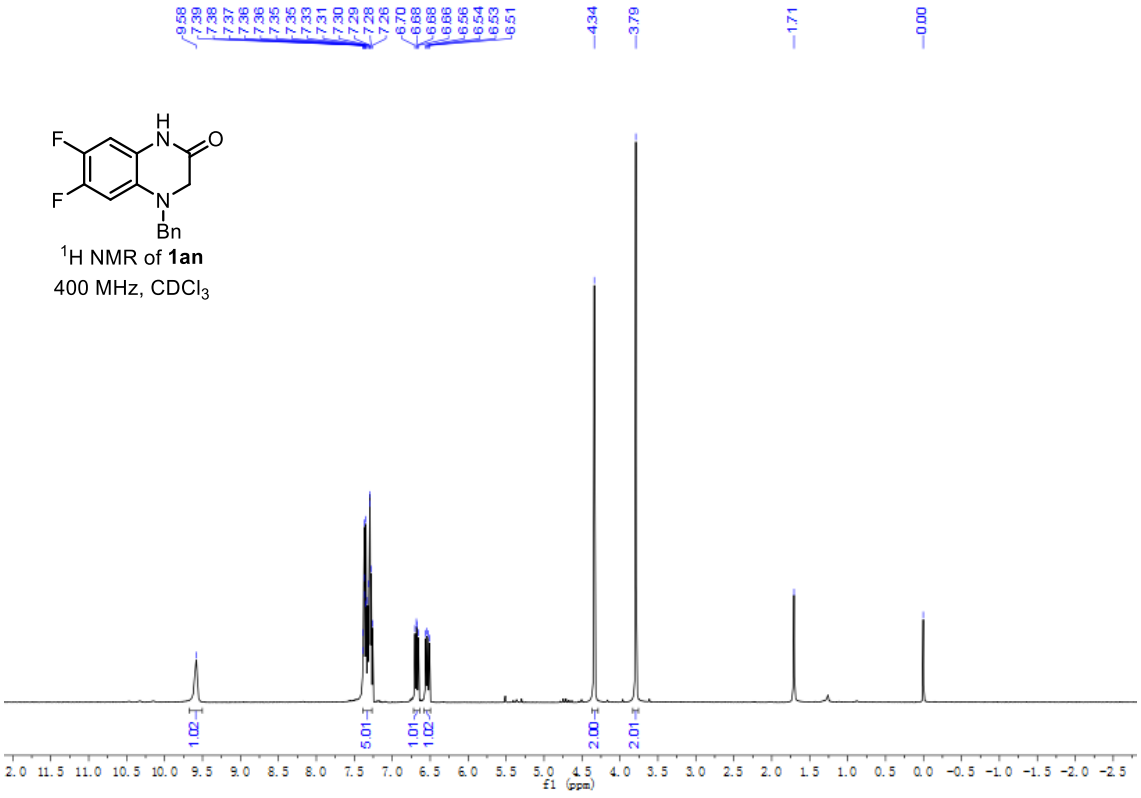


^{13}C NMR of **1am**
126 MHz, $CDCl_3$

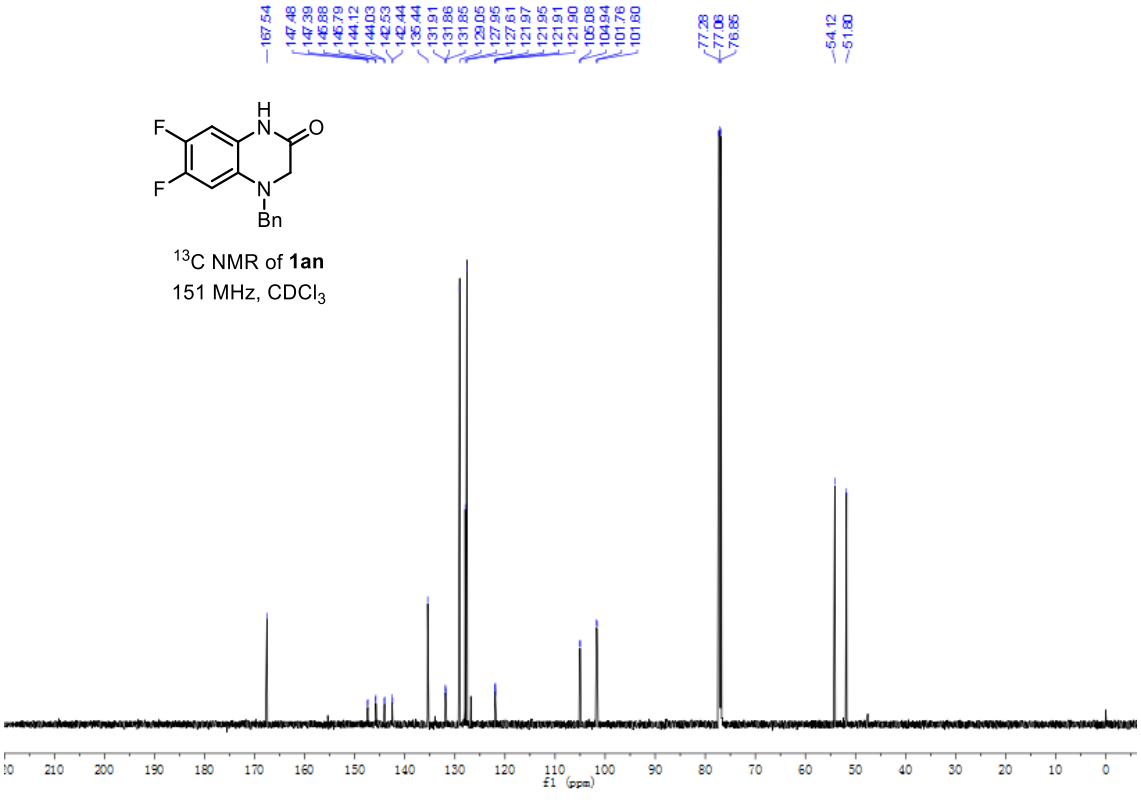


^{19}F NMR of **1am**
471 MHz, $CDCl_3$

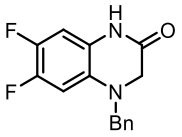
4-benzyl-6,7-difluoro-3,4-dihydroquinoxalin-2(1H)-one (1an)



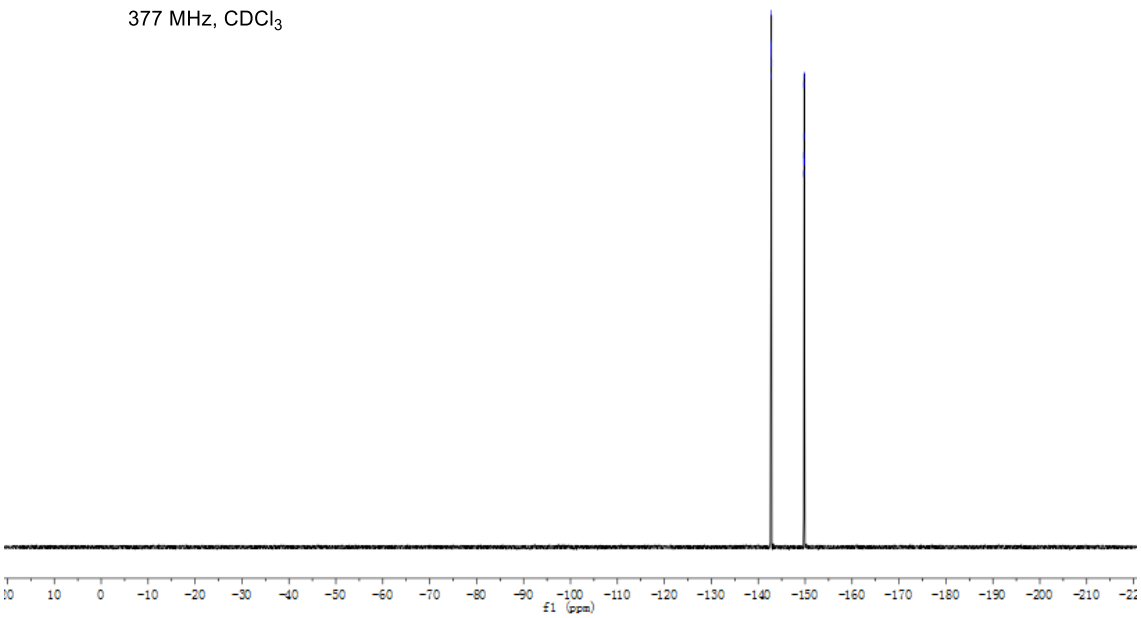
^{1}H NMR of **1an**
400 MHz, $CDCl_3$



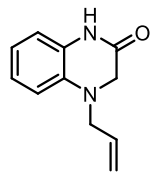
^{13}C NMR of **1an**
151 MHz, $CDCl_3$



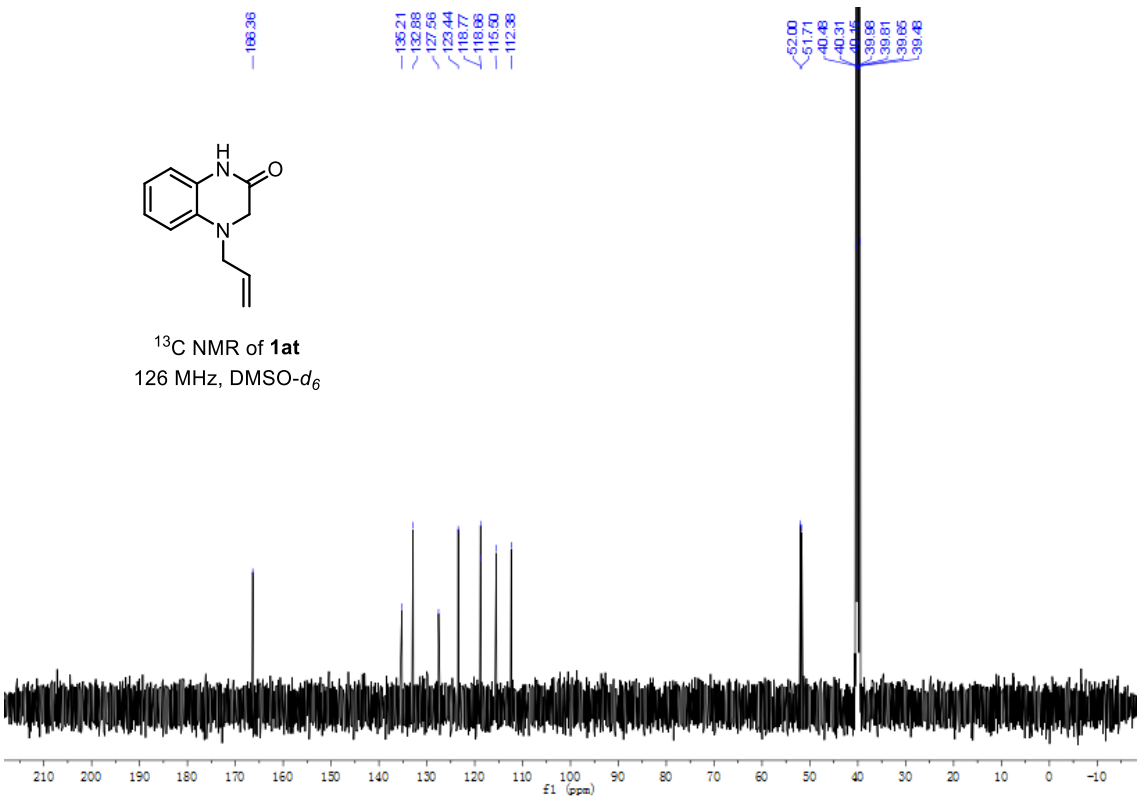
^{19}F NMR of **1an**
377 MHz, $CDCl_3$



4-allyl-3,4-dihydroquinoxalin-2(1H)-one (1at)

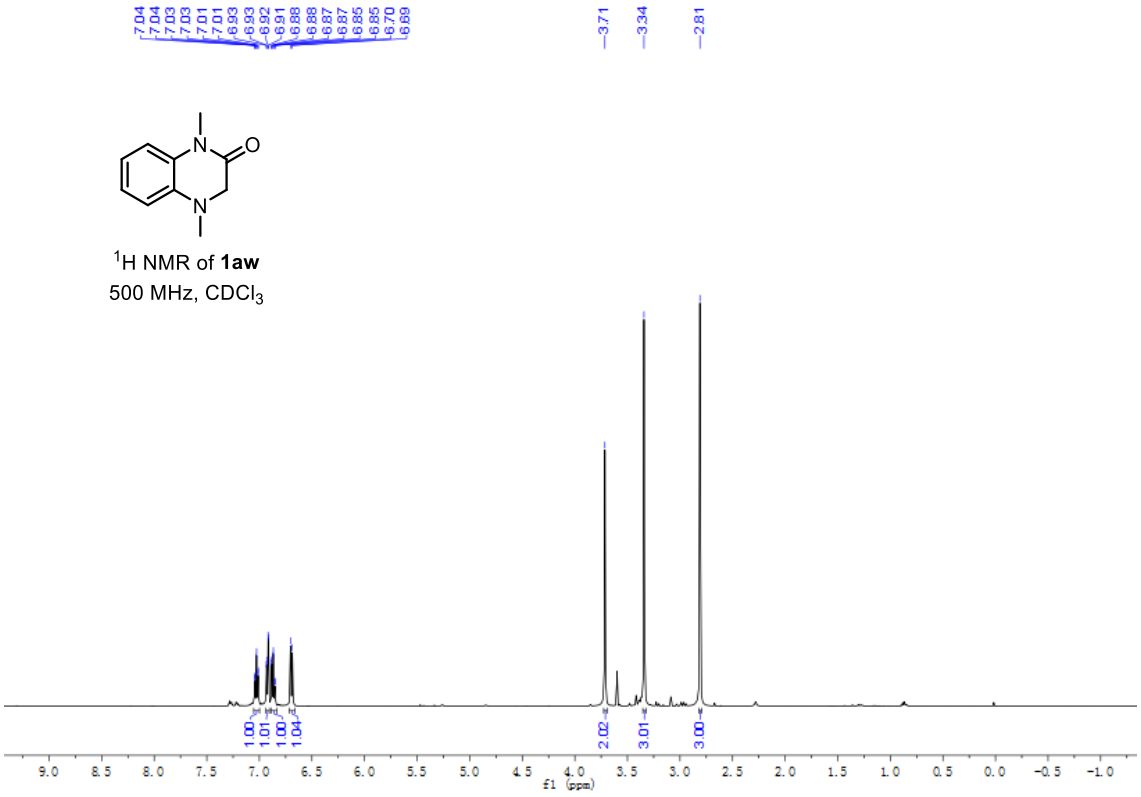


^{1}H NMR of **1at**
500 MHz, DMSO-d_6

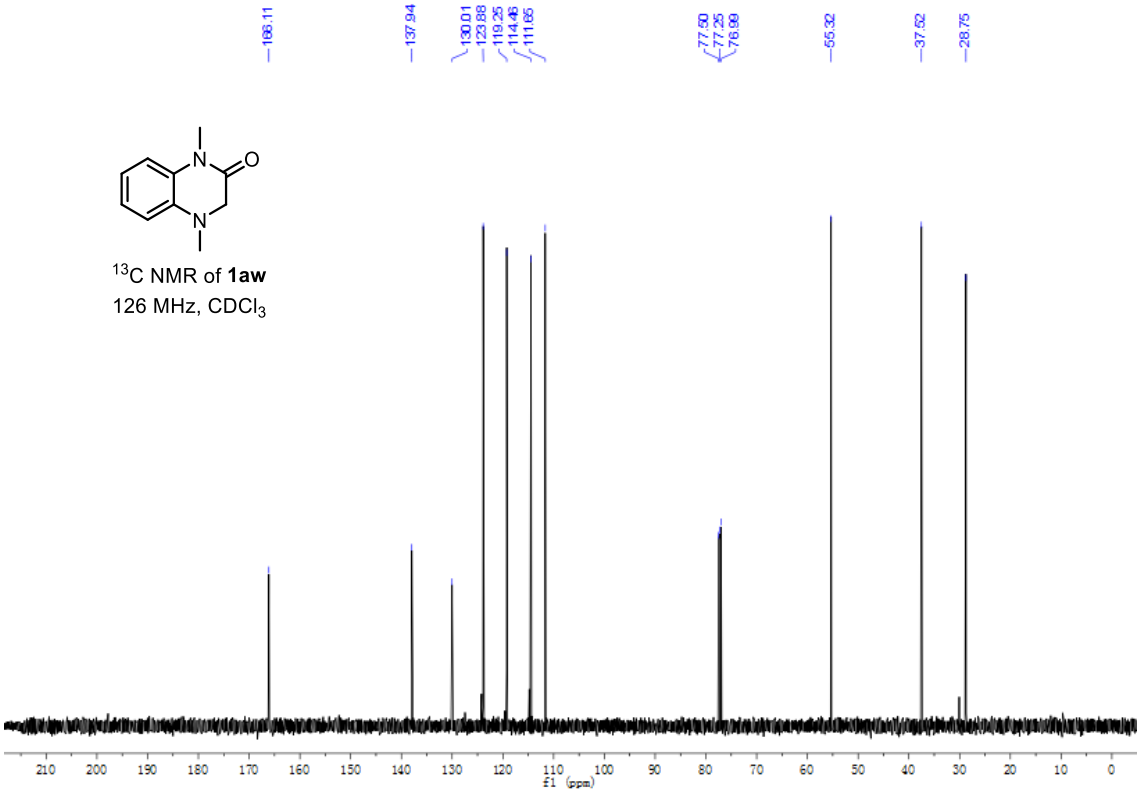


^{13}C NMR of **1at**
126 MHz, DMSO-d_6

1,4-dimethyl-3,4-dihydroquinoxalin-2(1H)-one (1aw)

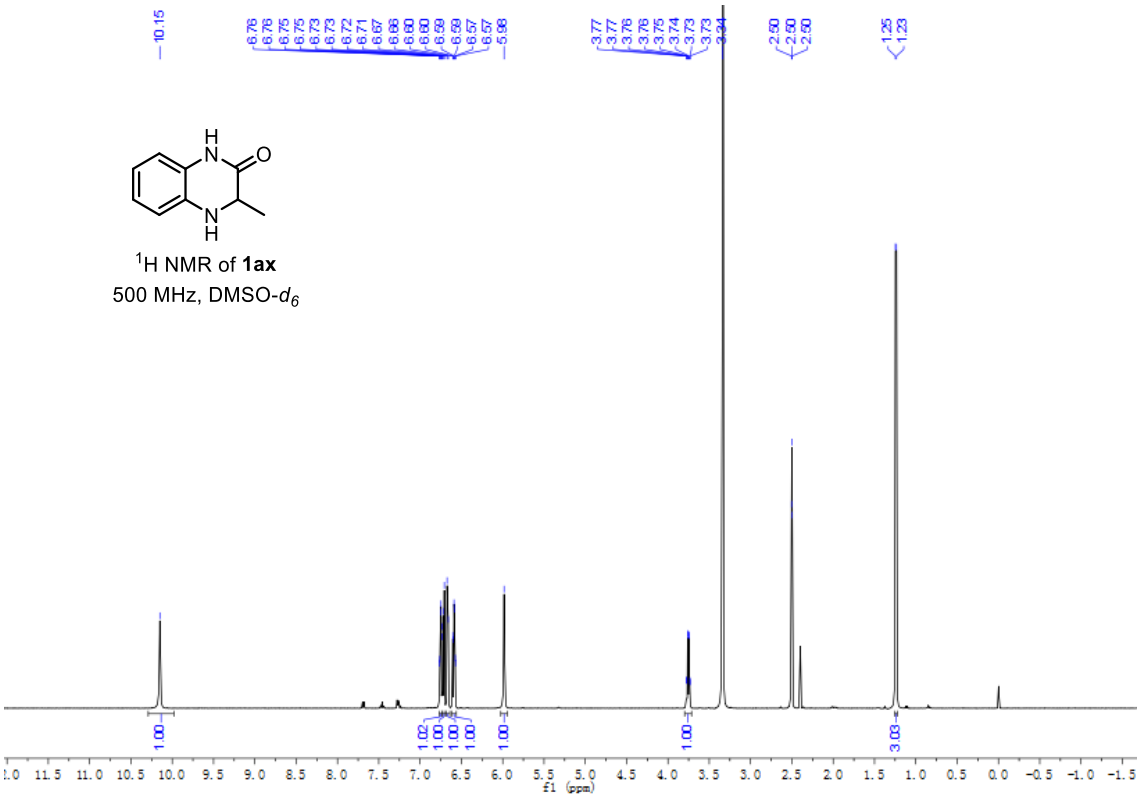


^{1}H NMR of **1aw**
500 MHz, $CDCl_3$

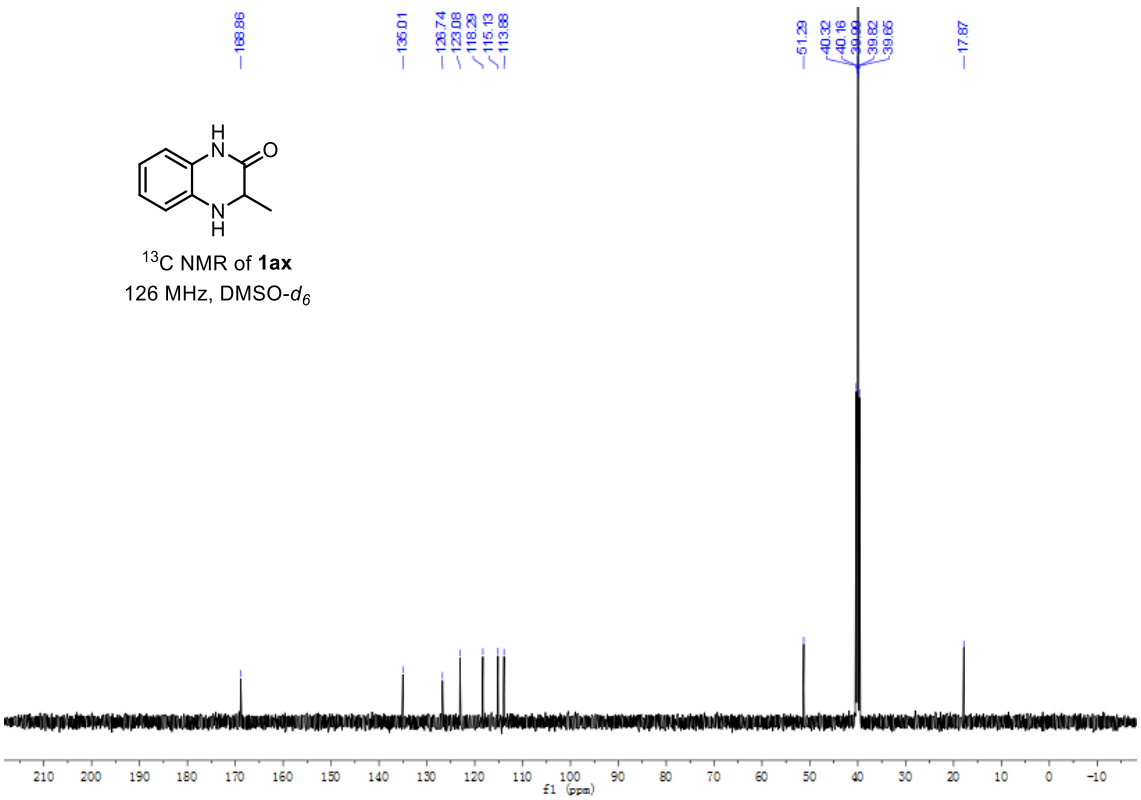


^{13}C NMR of **1aw**
126 MHz, $CDCl_3$

3-methyl-3,4-dihydroquinoxalin-2(1H)-one (1ax)

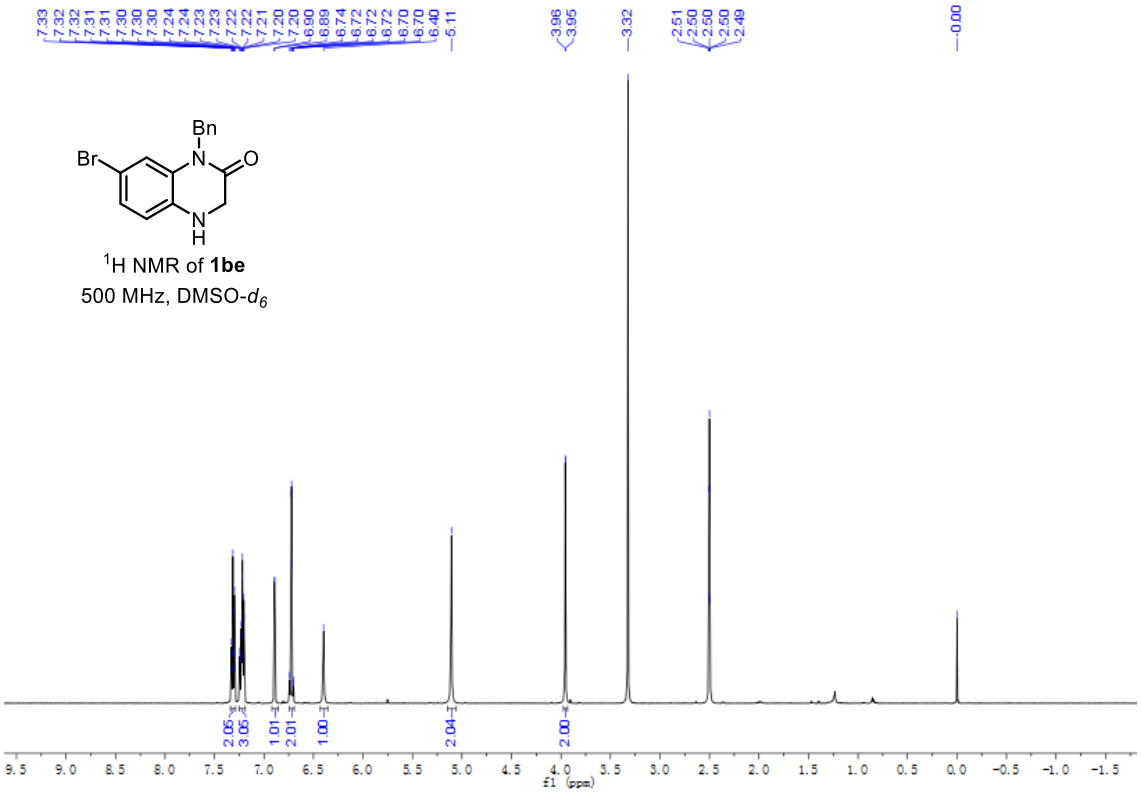


^{1}H NMR of **1ax**
500 MHz, DMSO-d_6

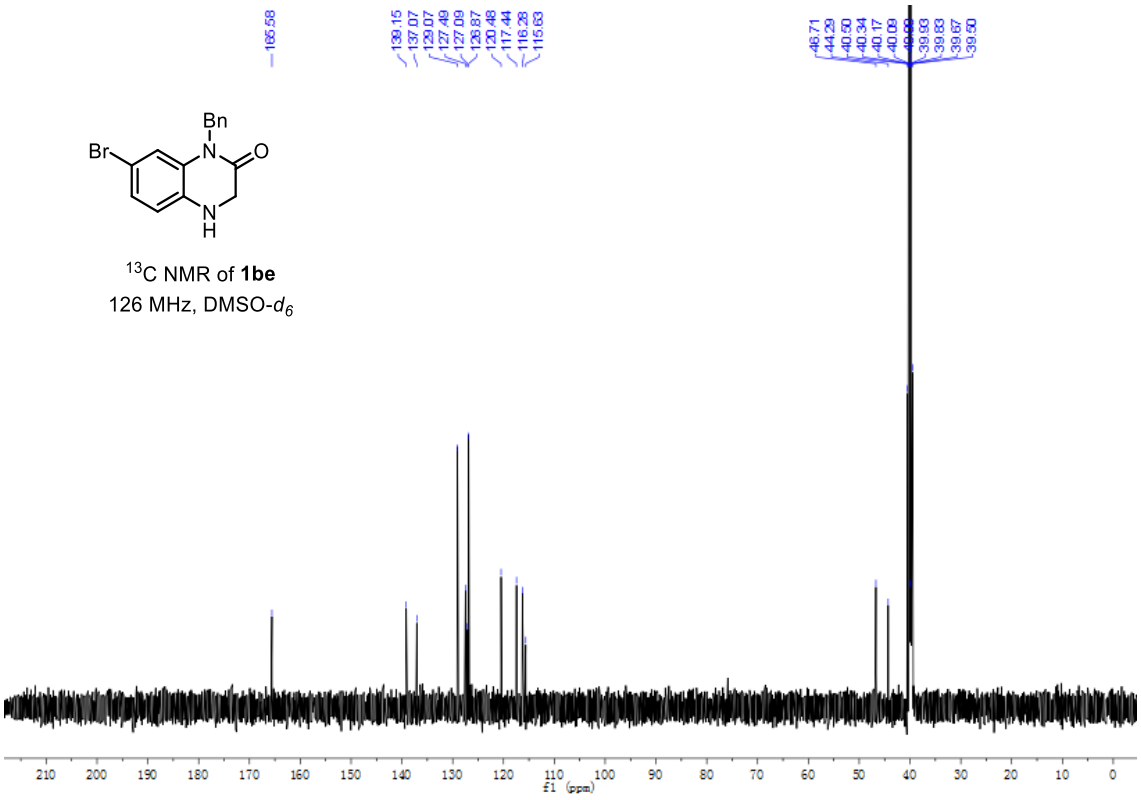


^{13}C NMR of **1ax**
126 MHz, DMSO-d_6

1-benzyl-7-bromo-3,4-dihydroquinoxalin-2(1H)-one (1be)

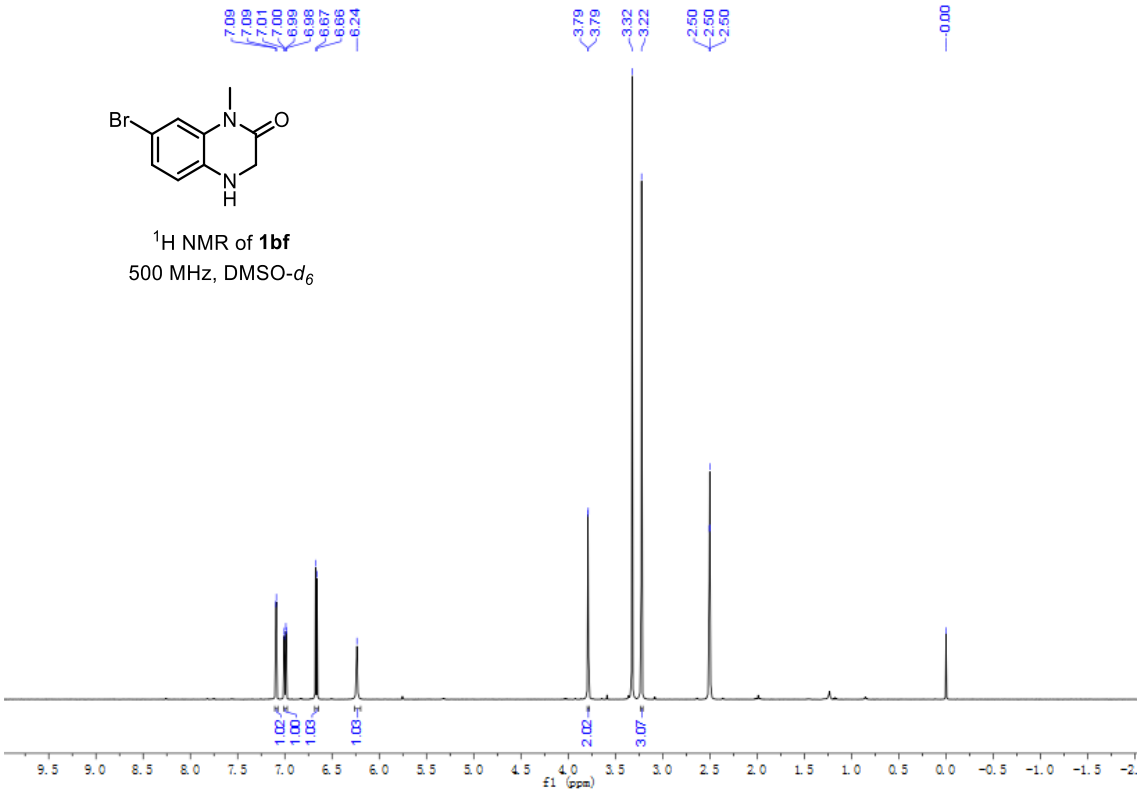


^{1}H NMR of **1be**
500 MHz, DMSO-d_6

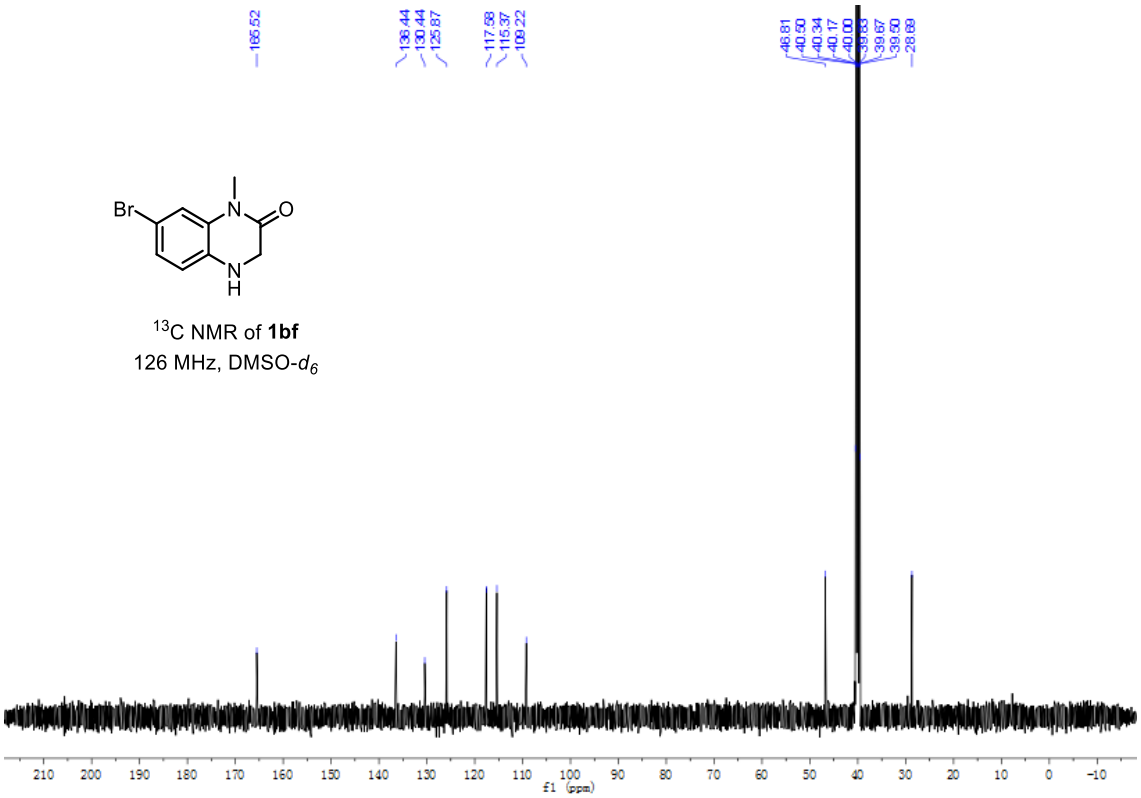


^{13}C NMR of **1be**
126 MHz, DMSO-d_6

7-bromo-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (1bf)

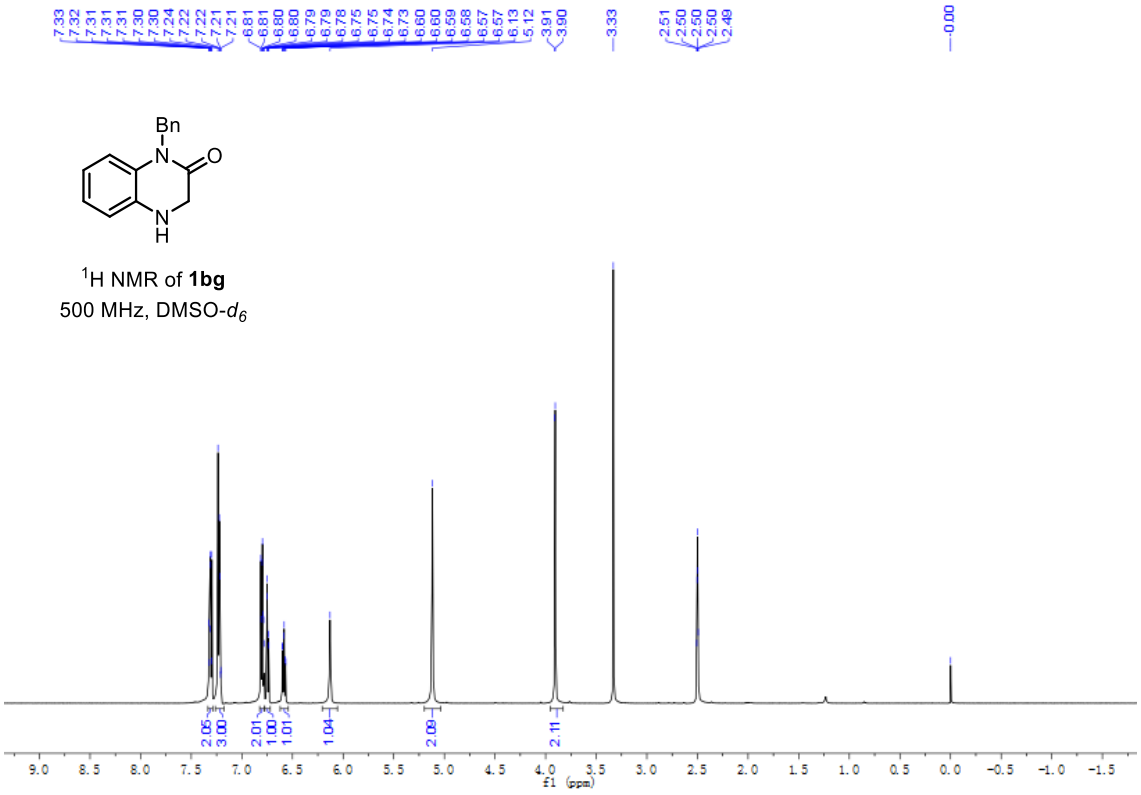


^{1}H NMR of **1bf**
500 MHz, DMSO-d_6

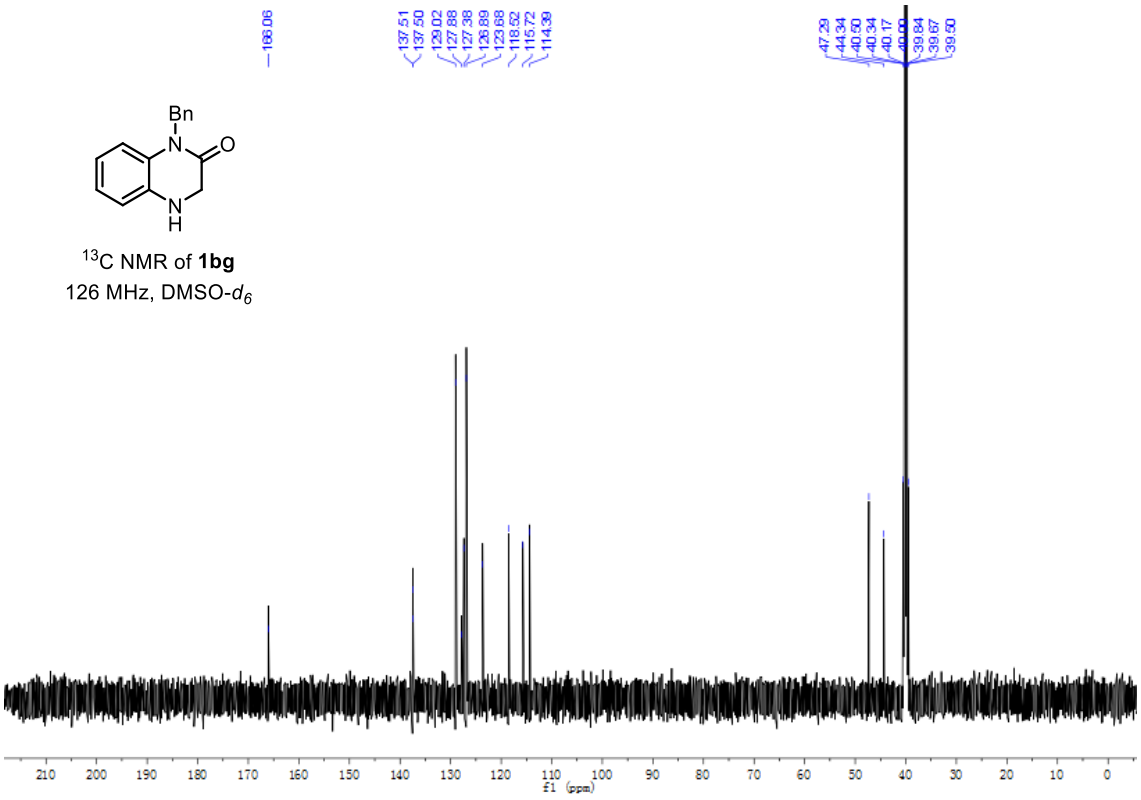


^{13}C NMR of **1bf**
126 MHz, DMSO-d_6

1-benzyl-3,4-dihydroquinoxalin-2(1H)-one (1bg)

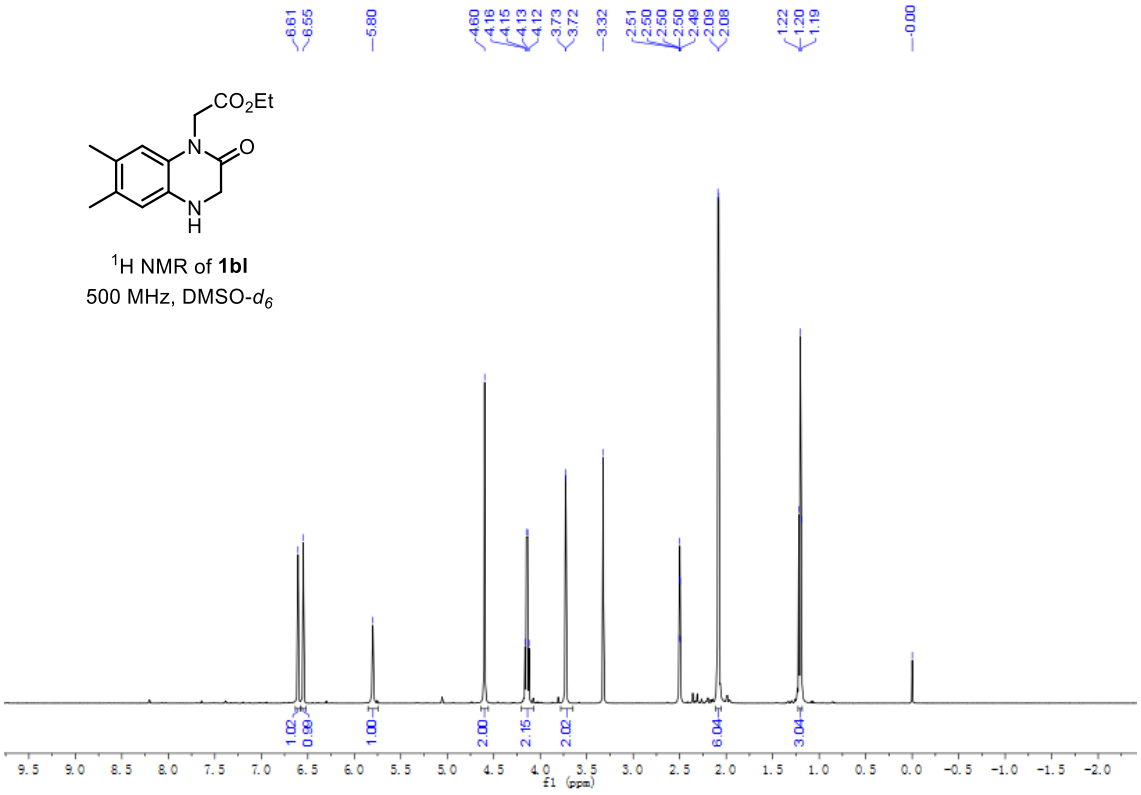


^{1}H NMR of **1bg**
500 MHz, DMSO-d_6

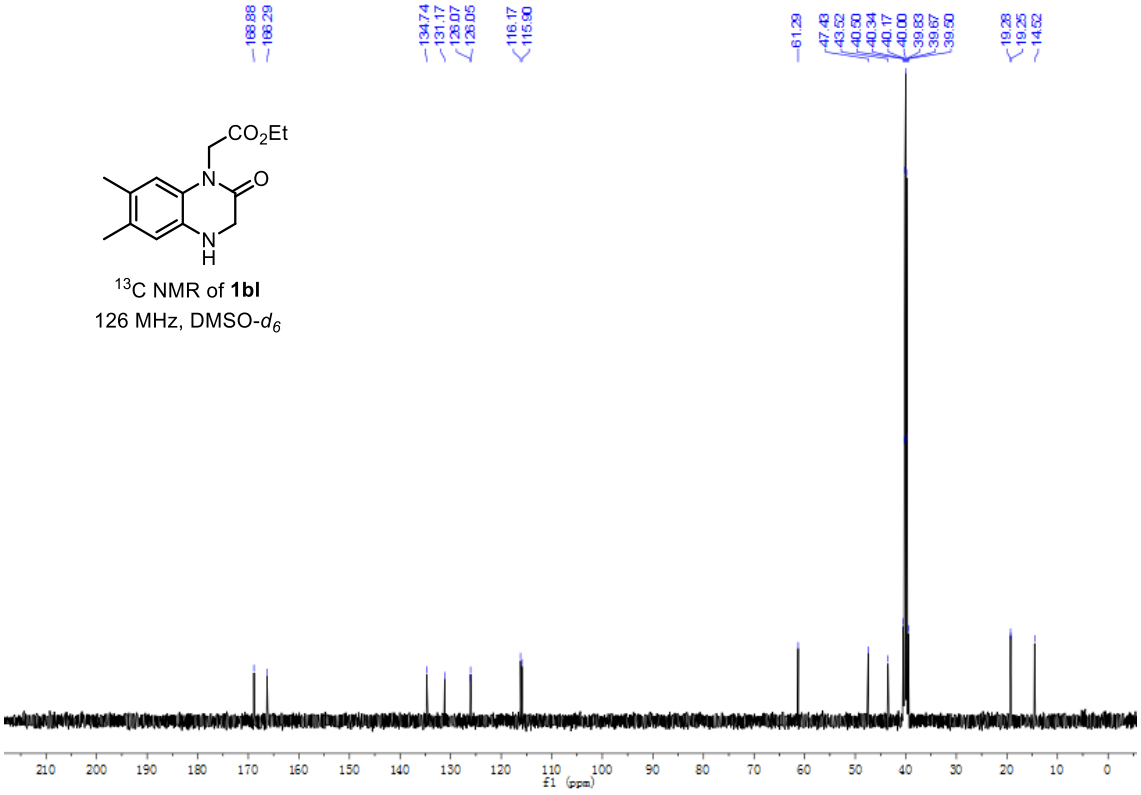


^{13}C NMR of **1bg**
126 MHz, DMSO-d_6

Ethyl 2-(6,7-dimethyl-2-oxo-3,4-dihydroquinoxalin-1(2H)-yl)acetate (1bl)

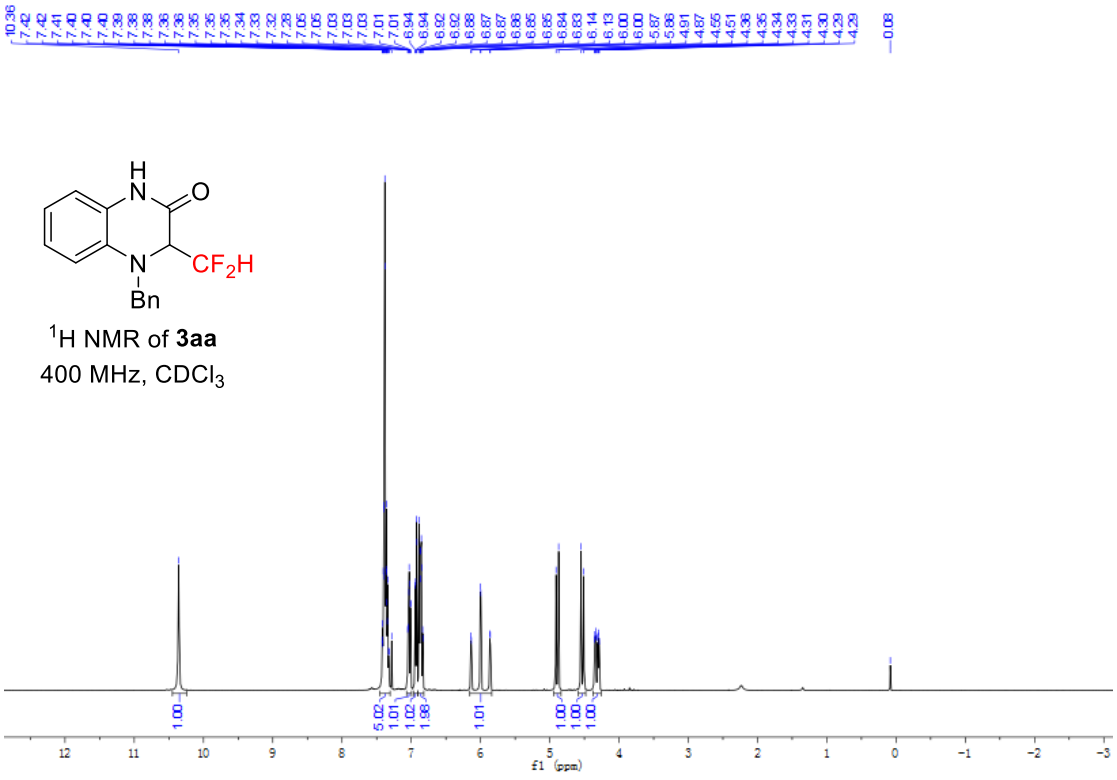


^{1}H NMR of **1bl**
500 MHz, DMSO-d_6

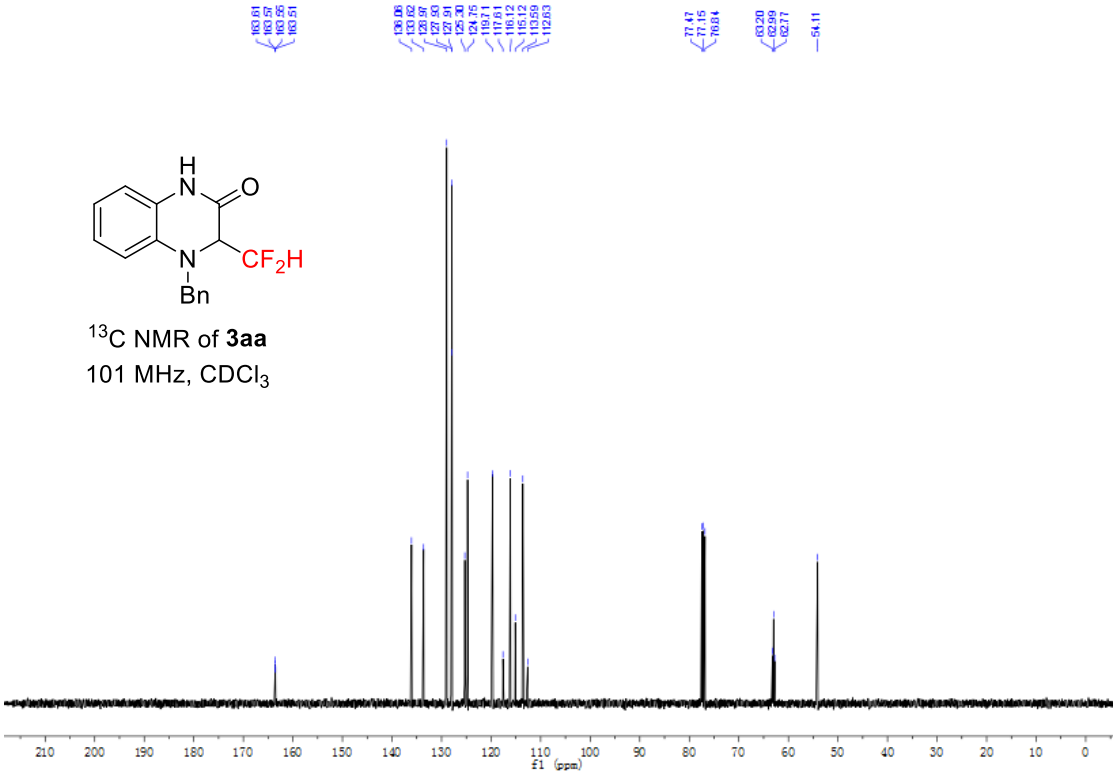


^{13}C NMR of **1bl**
126 MHz, DMSO-d_6

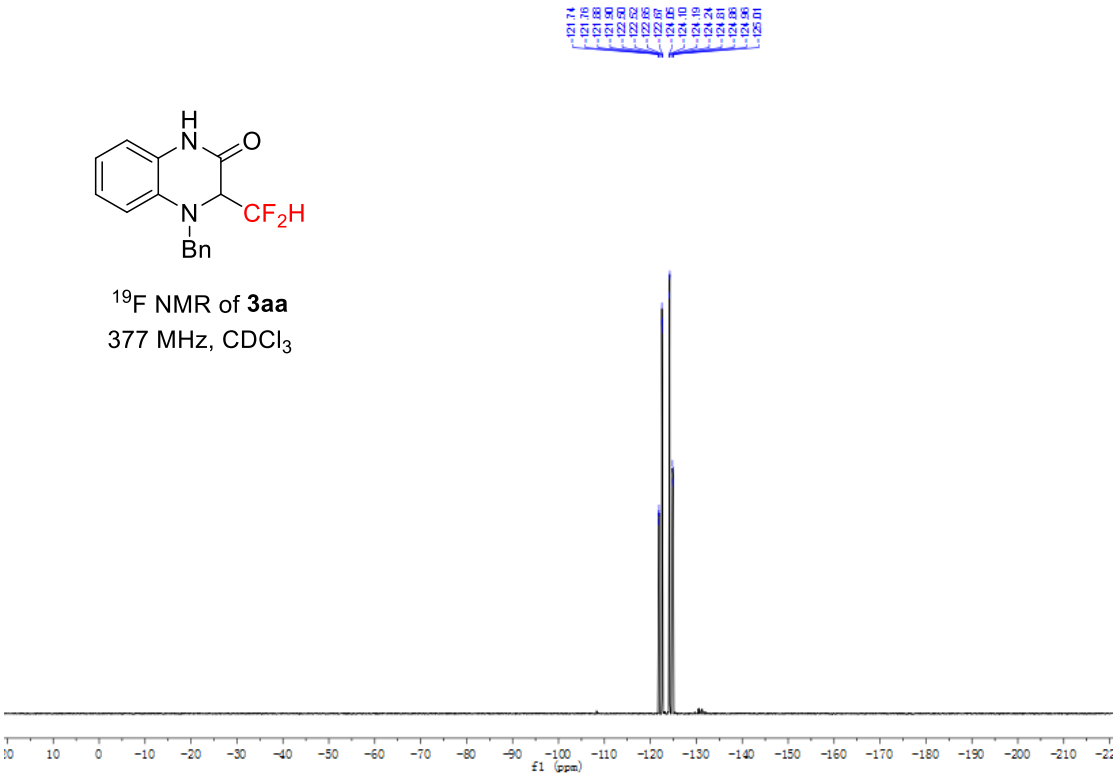
4-benzyl-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3aa)



^{1}H NMR of **3aa**
400 MHz, $CDCl_3$

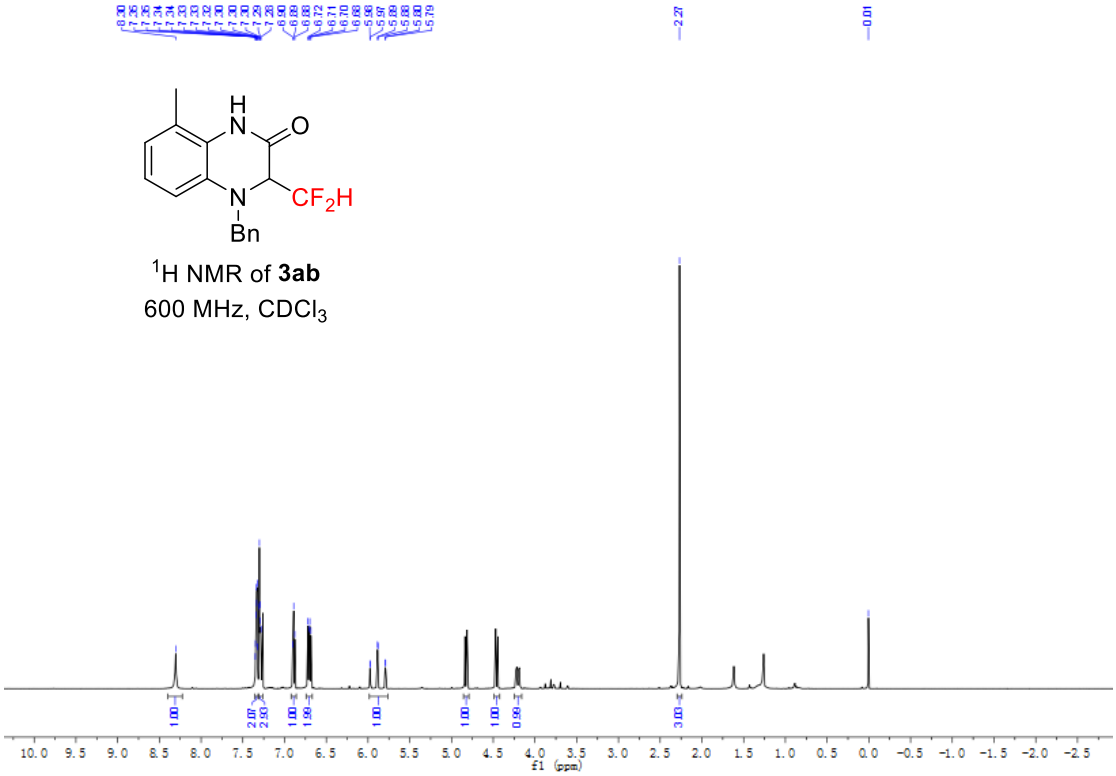


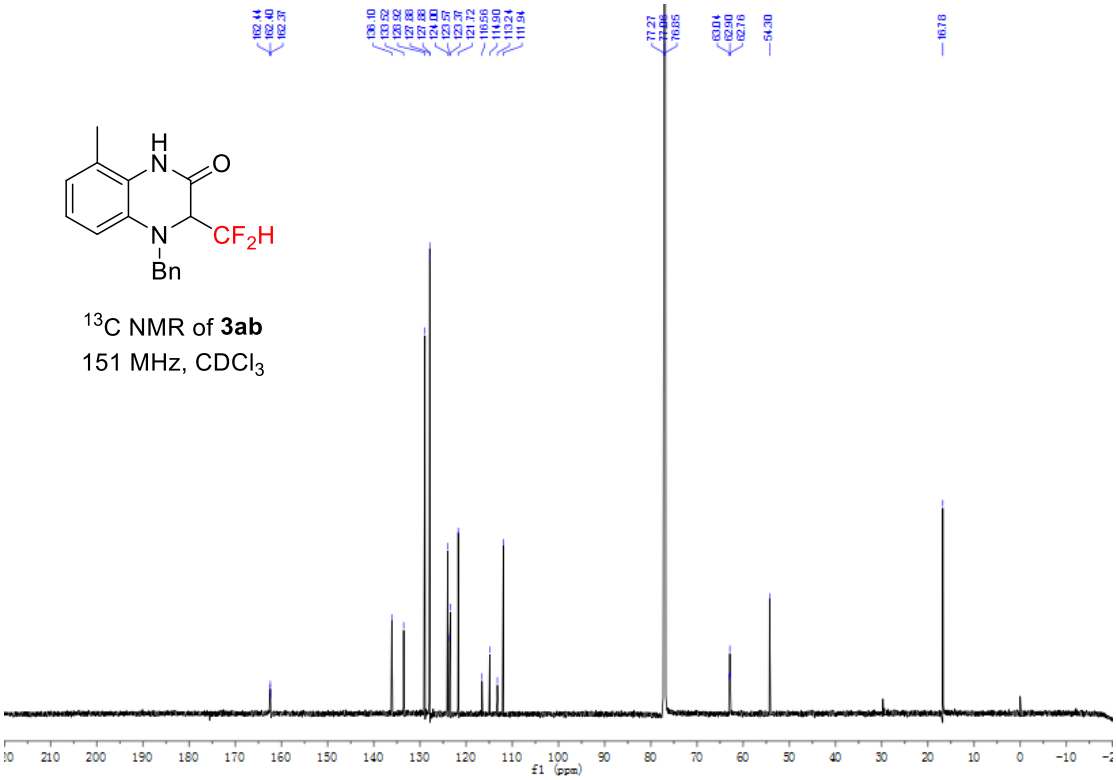
^{13}C NMR of **3aa**
101 MHz, $CDCl_3$

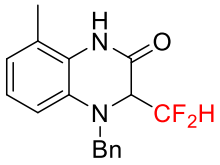


^{19}F NMR of **3aa**
377 MHz, $CDCl_3$

4-benzyl-3-(difluoromethyl)-8-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ab)

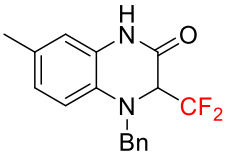




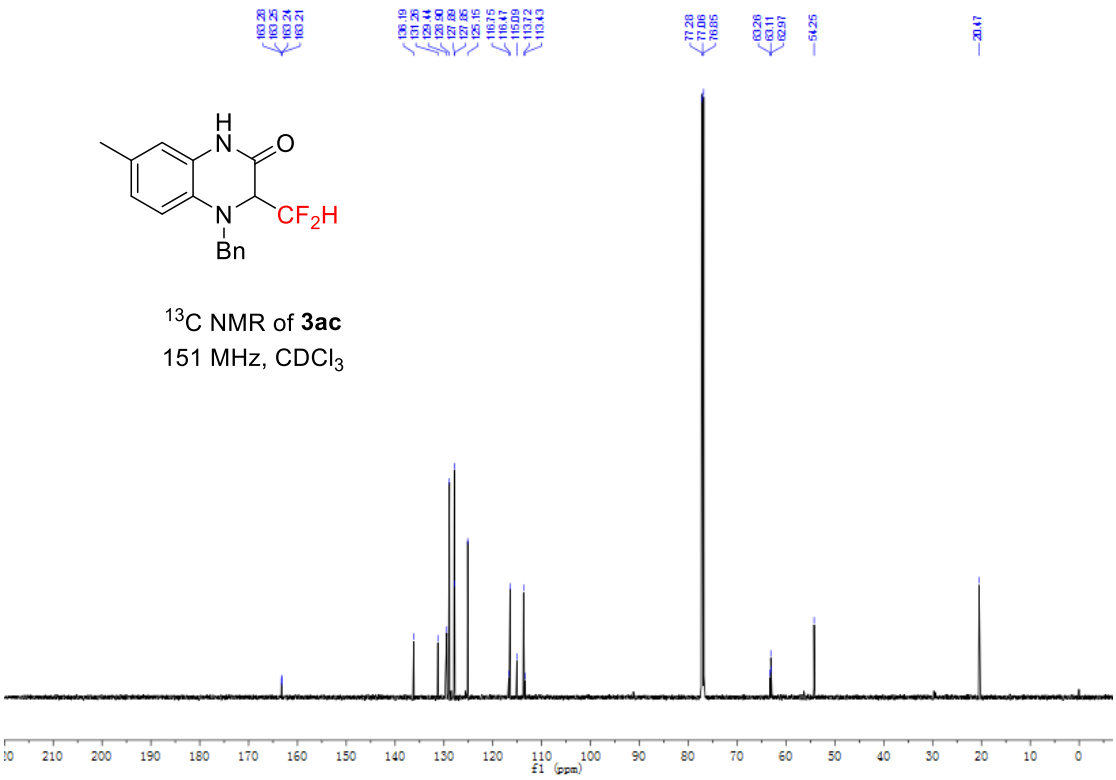


^{19}F NMR of **3ab**
377 MHz, $CDCl_3$

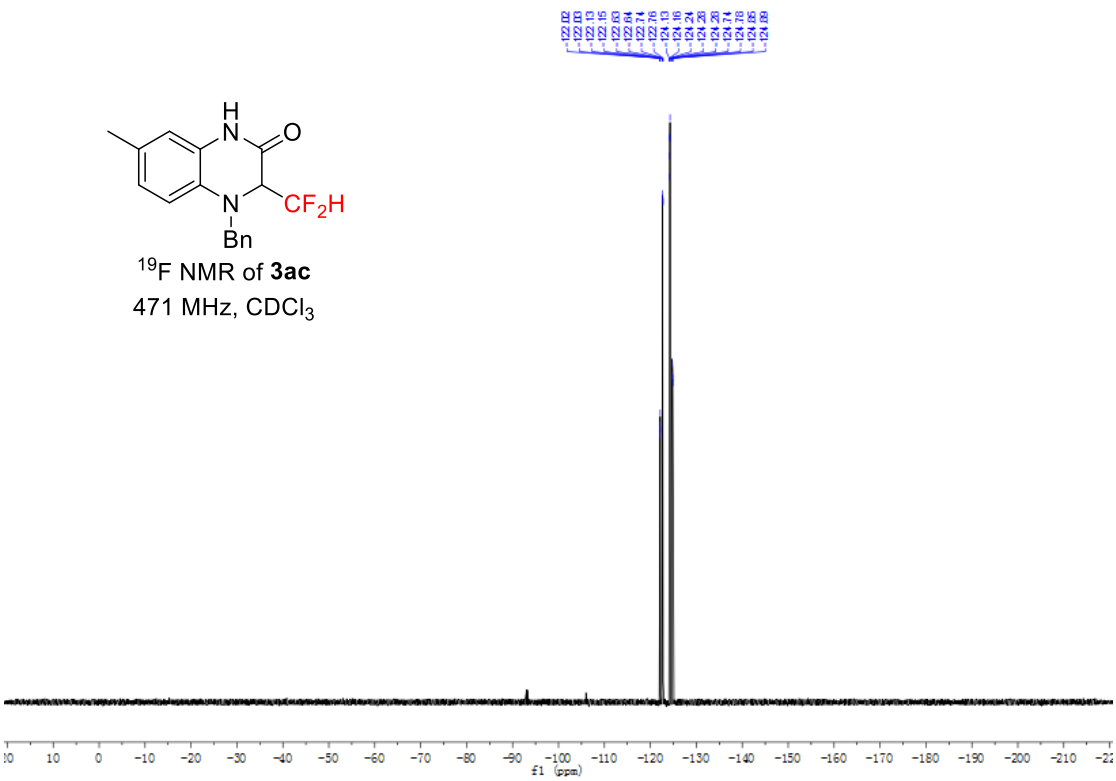
4-benzyl-3-(difluoromethyl)-7-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ac)



^{1}H NMR of **3ac**
500 MHz, $CDCl_3$

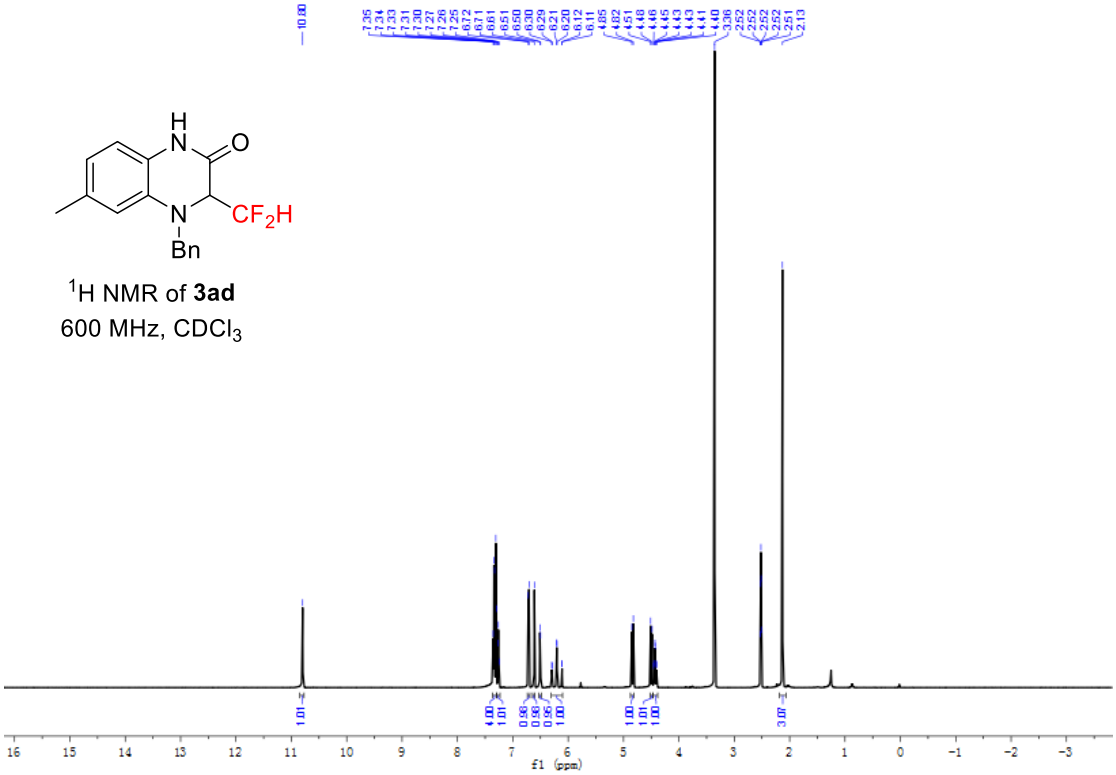


^{13}C NMR of **3ac**
151 MHz, $CDCl_3$

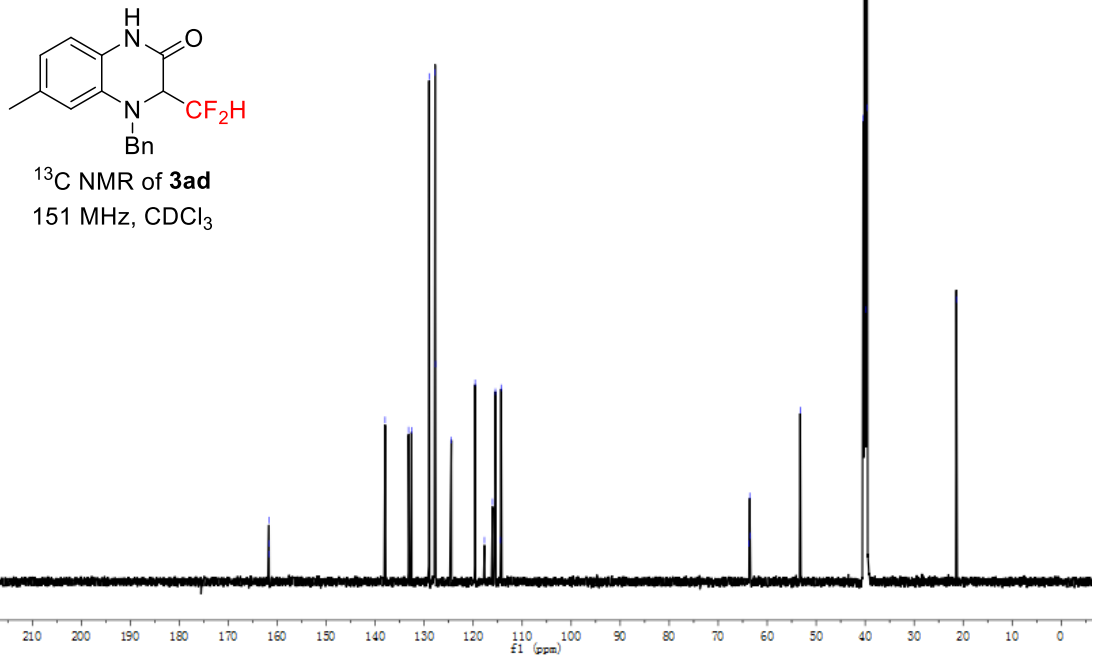


^{19}F NMR of **3ac**
471 MHz, $CDCl_3$

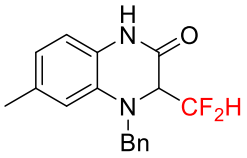
4-benzyl-3-(difluoromethyl)-6-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ad)



^{1}H NMR of **3ad**
600 MHz, $CDCl_3$

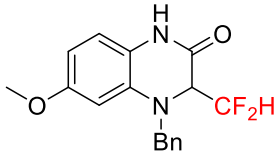


^{13}C NMR of **3ad**
151 MHz, $CDCl_3$

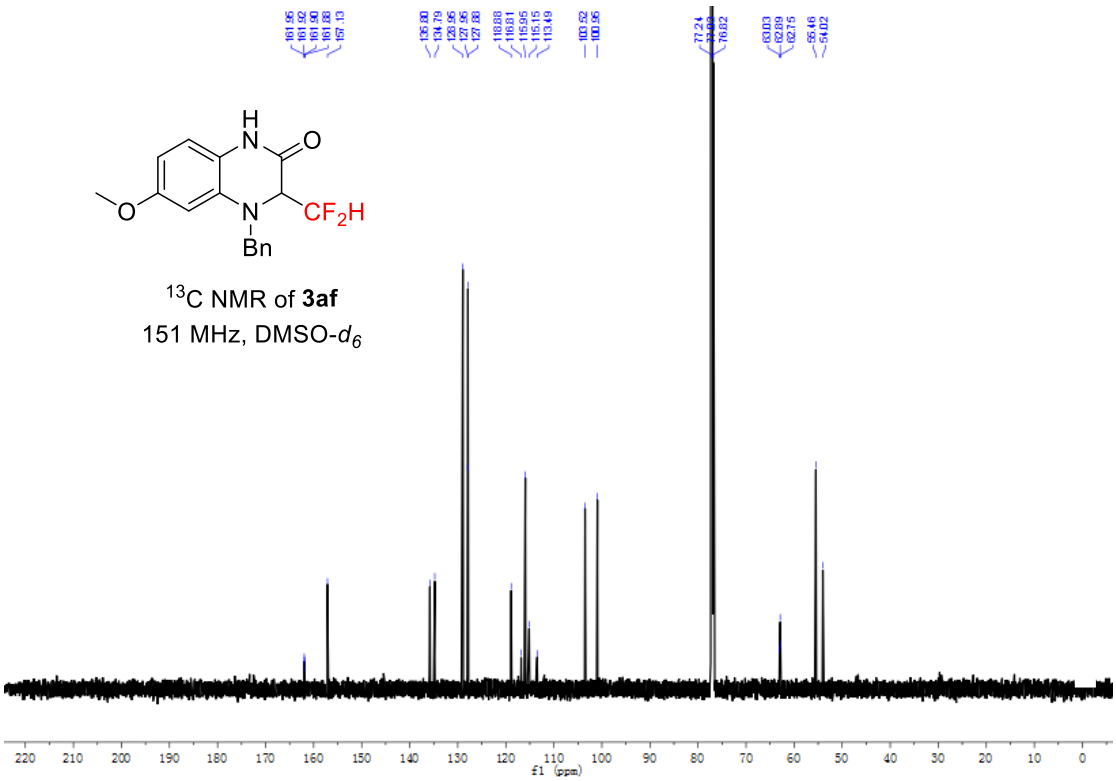


^{19}F NMR of **3ad**
377 MHz, $CDCl_3$

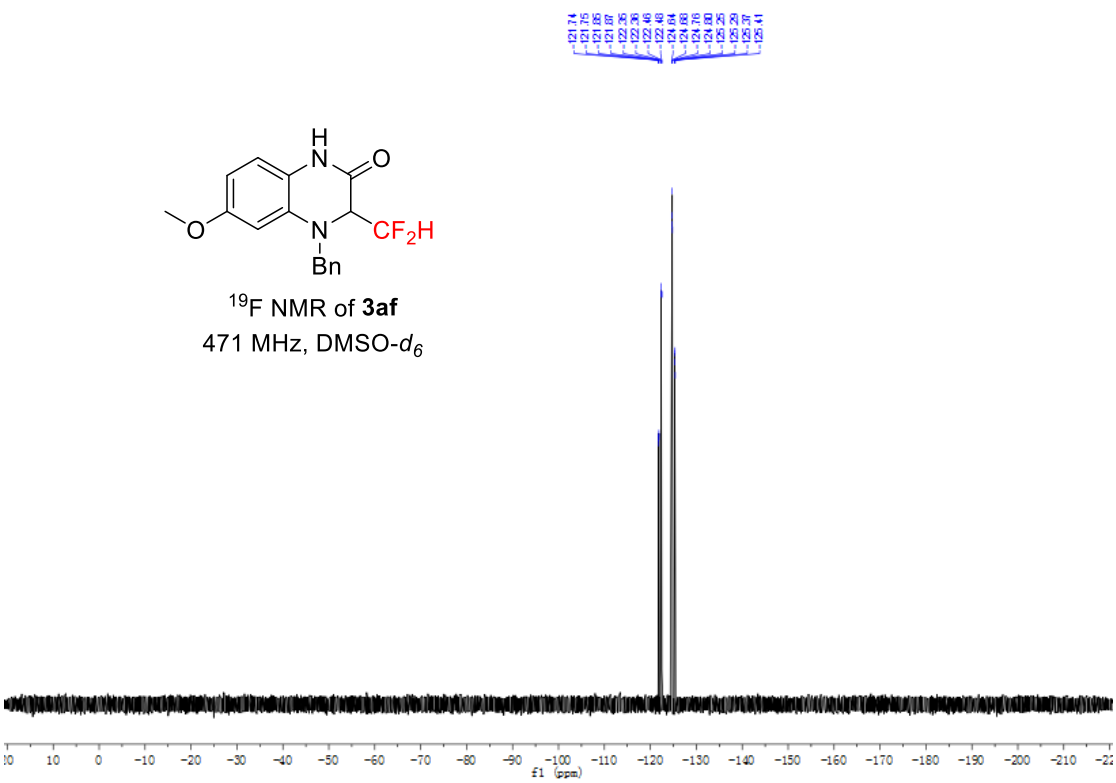
4-benzyl-3-(difluoromethyl)-6-methoxy-3,4-dihydroquinoxalin-2(1H)-one (3af)



^{1}H NMR of **3af**
500 MHz, DMSO-d_6

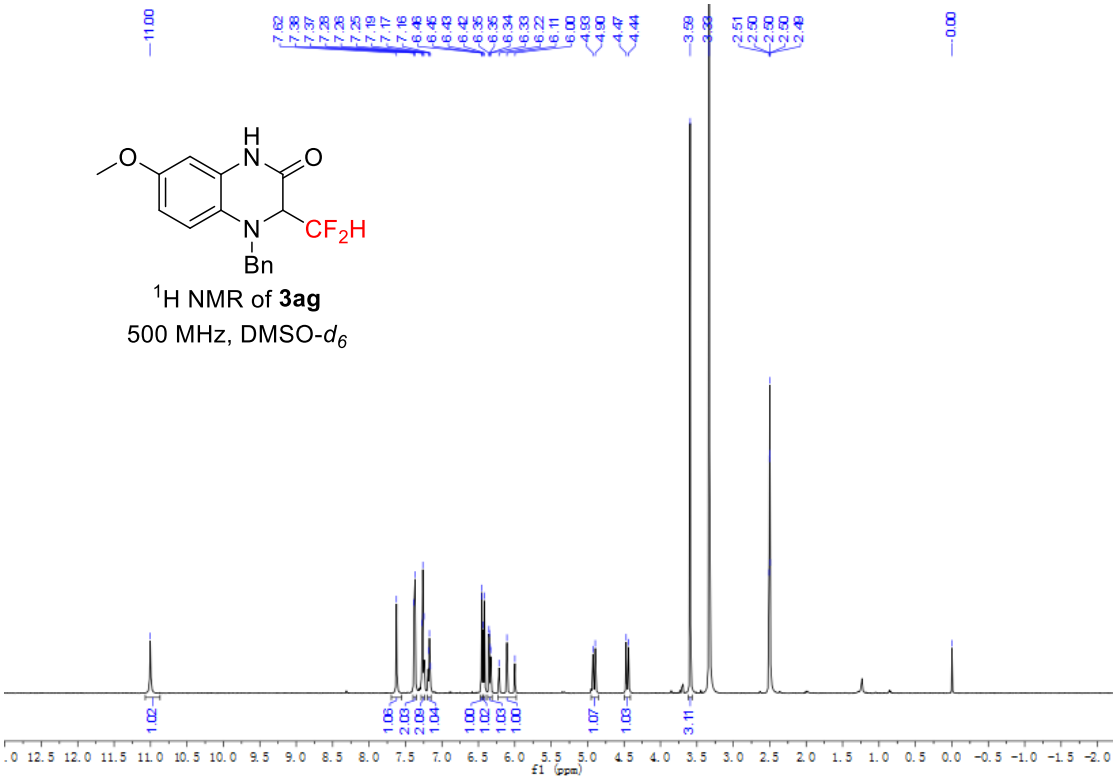


^{13}C NMR of **3af**
151 MHz, DMSO-d_6

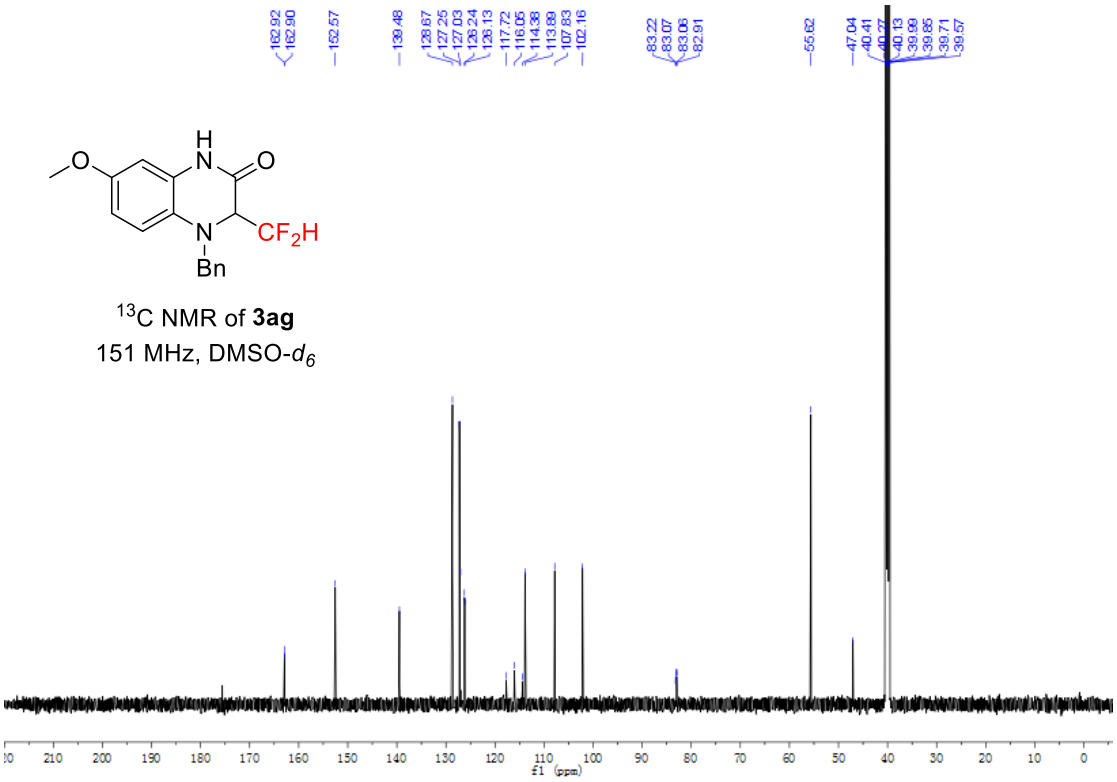


^{19}F NMR of **3af**
471 MHz, DMSO-d_6

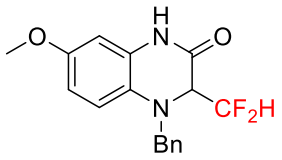
4-benzyl-3-(difluoromethyl)-7-methoxy-3,4-dihydroquinoxalin-2(1H)-one (3ag)



^{1}H NMR of **3ag**
500 MHz, DMSO-d_6

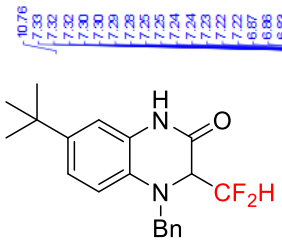


^{13}C NMR of **3ag**
151 MHz, DMSO-d_6

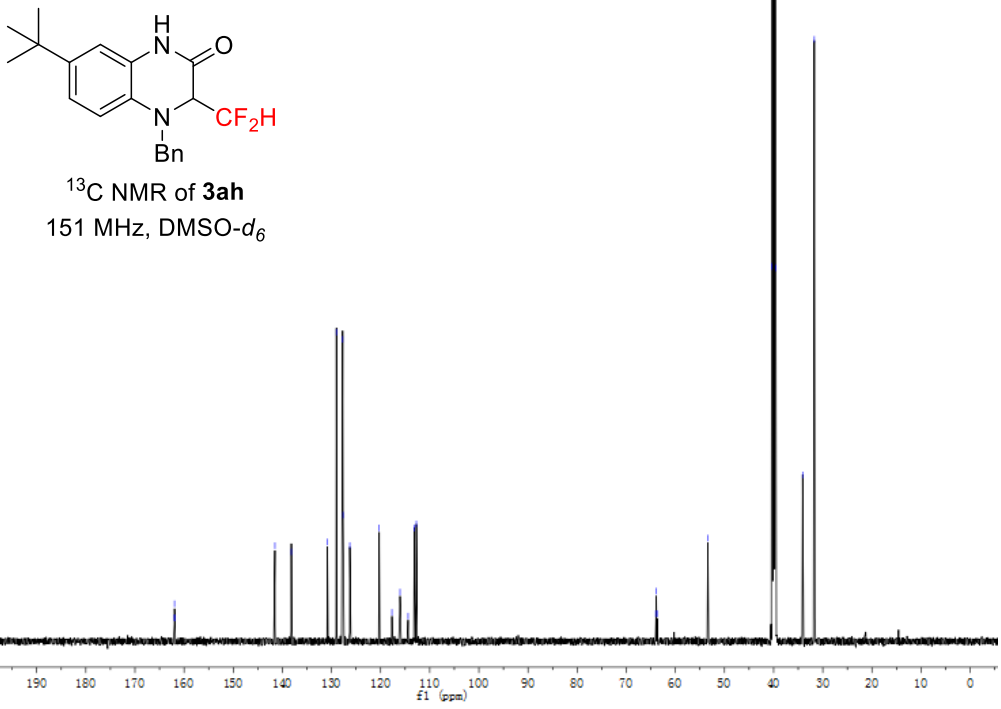


^{19}F NMR of **3ag**
471 MHz, DMSO-d_6

4-benzyl-7-(tert-butyl)-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ah)

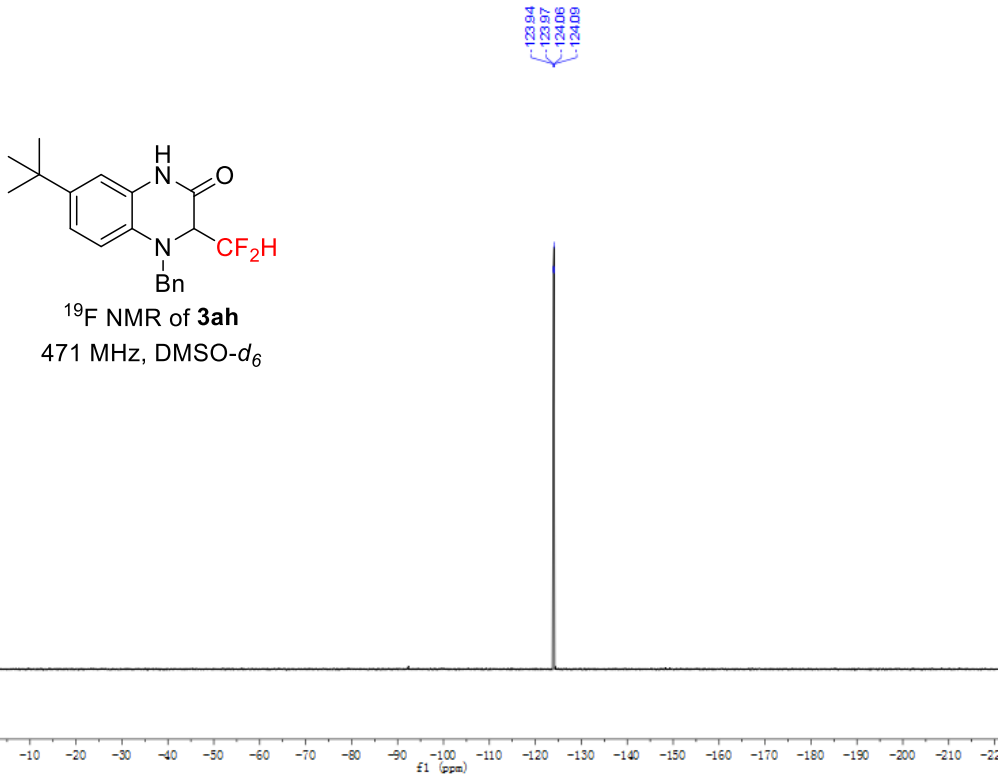


^{1}H NMR of **3ah**
500 MHz, DMSO-d_6



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

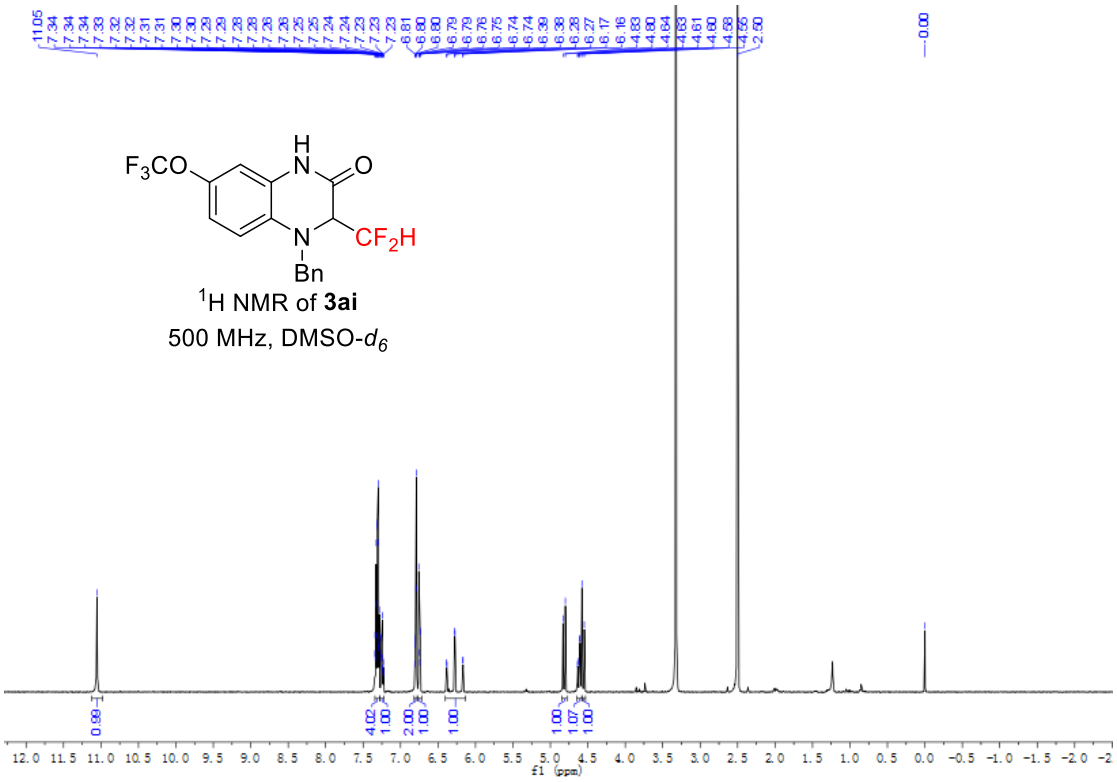
151 MHz, DMSO-d_6

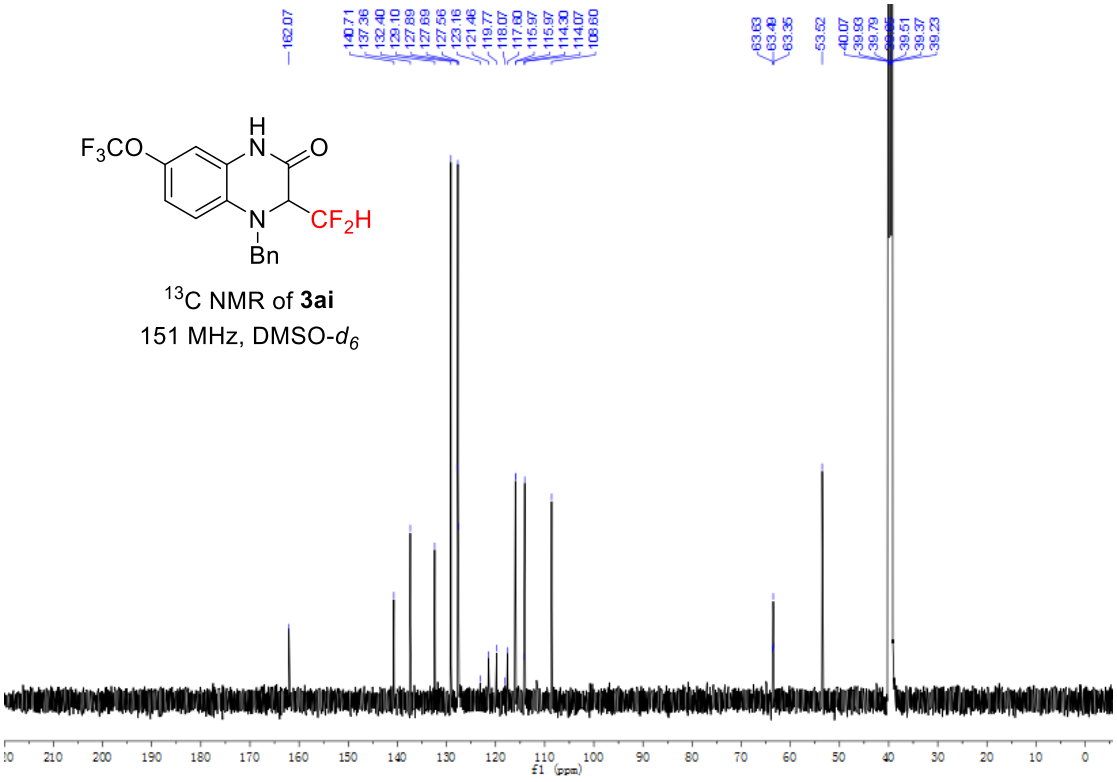


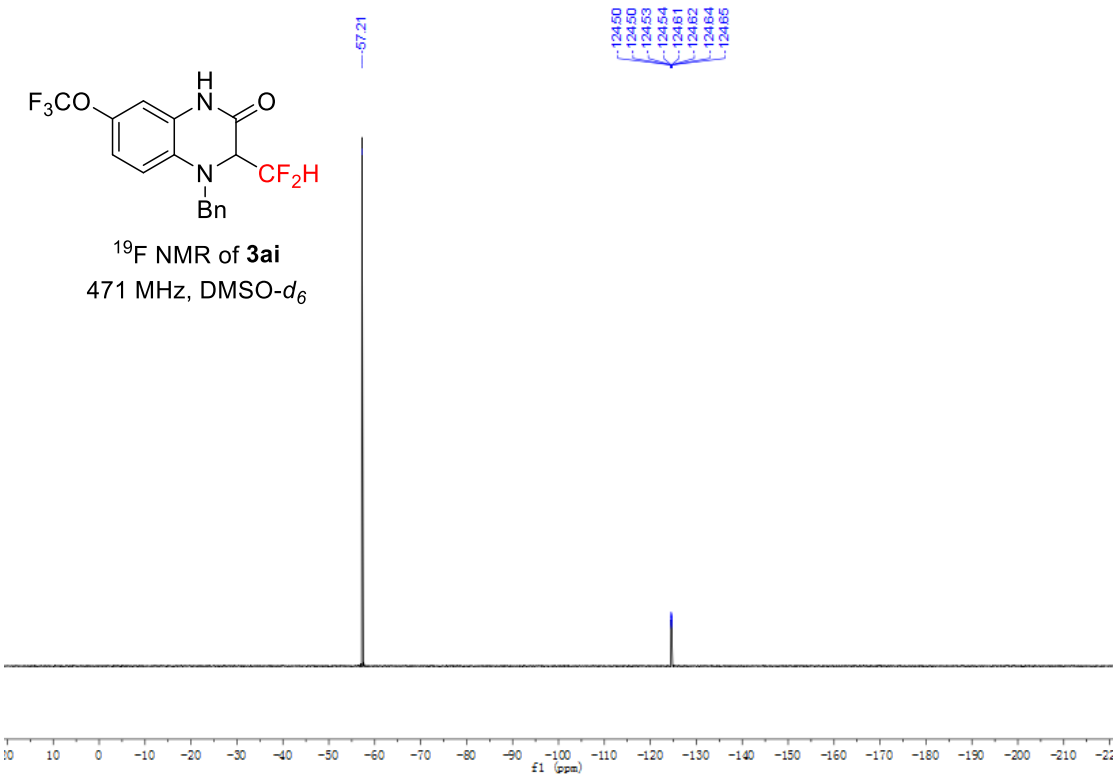
^{19}F NMR of **3ah**

471 MHz, DMSO-d_6

4-benzyl-3-(difluoromethyl)-7-(trifluoromethoxy)-3,4-dihydroquinoxalin-2(1H)-one (3ai)

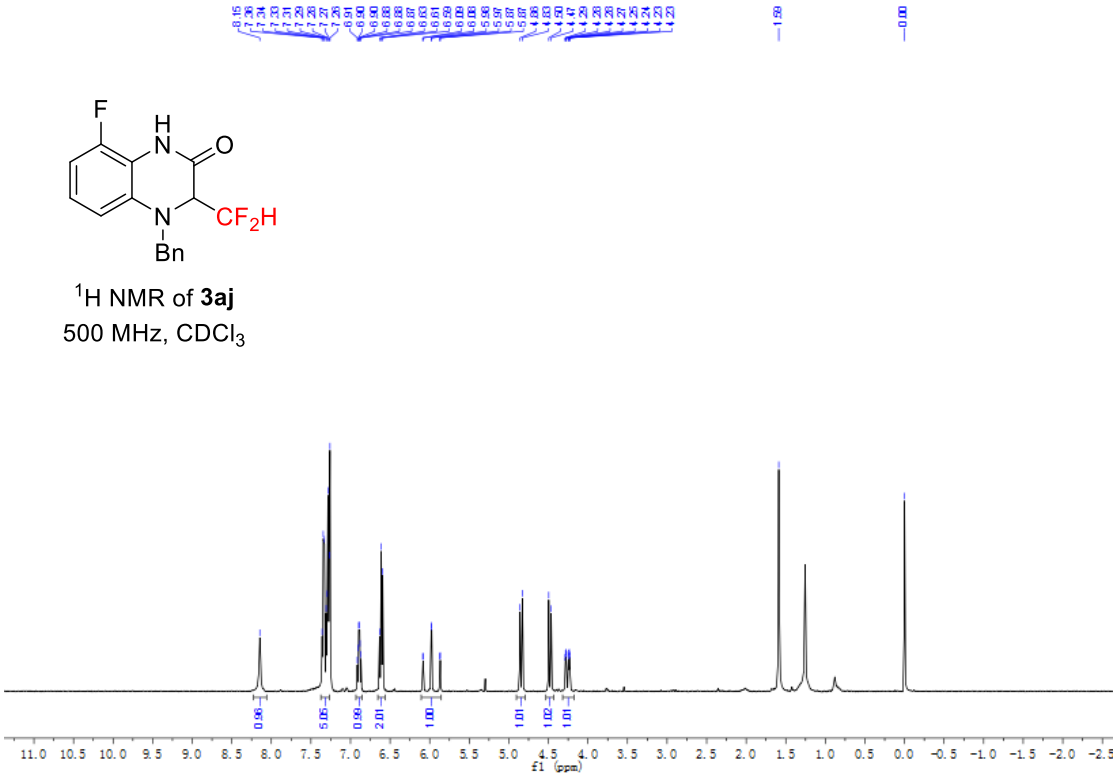






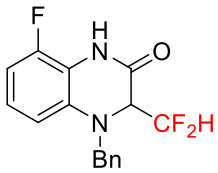
^{19}F NMR of **3ai**
471 MHz, DMSO-d_6

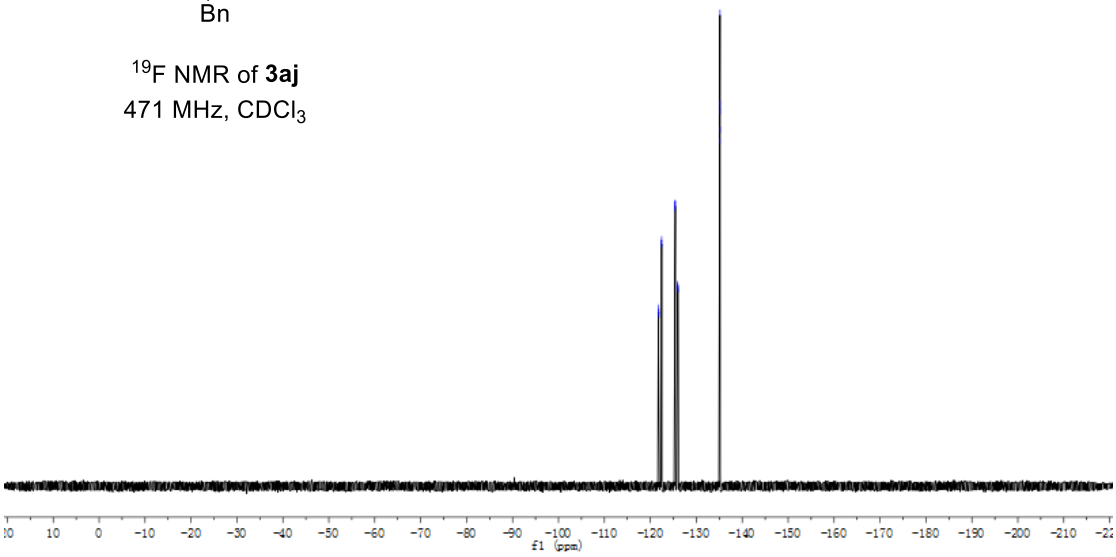
4-benzyl-3-(difluoromethyl)-8-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3aj)



^{1}H NMR of **3aj**
500 MHz, $CDCl_3$

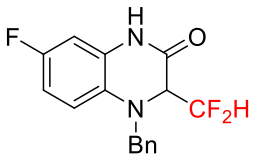
^{13}C NMR of **3aj**
151 MHz, $CDCl_3$



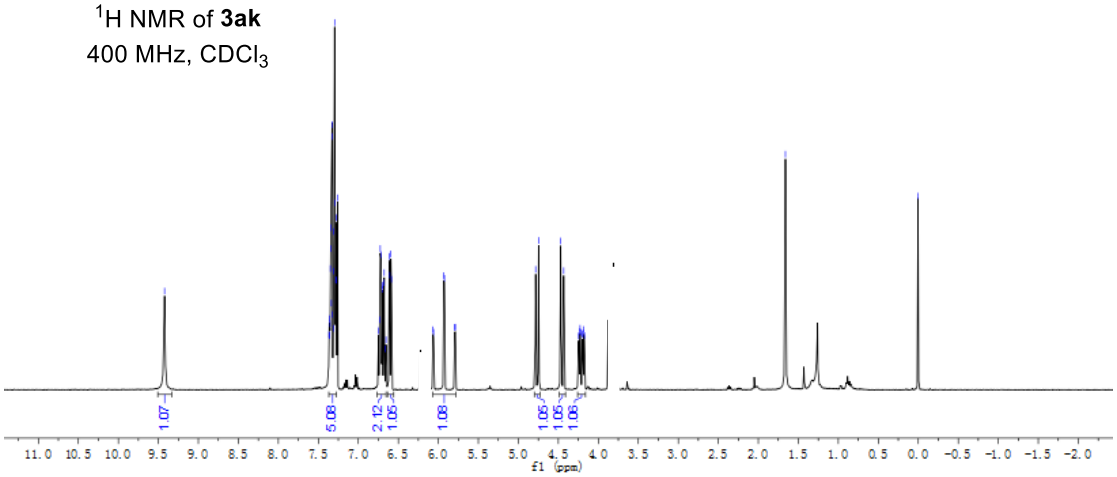


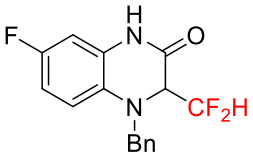
^{19}F NMR of **3aj**
471 MHz, $CDCl_3$

4-benzyl-3-(difluoromethyl)-7-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3ak)

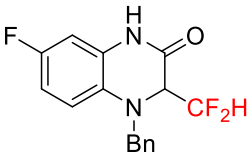


^{1}H NMR of **3ak**
400 MHz, $CDCl_3$



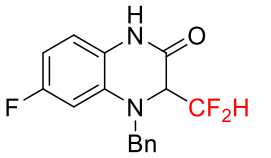


^{13}C NMR of **3ak**
151 MHz, $CDCl_3$

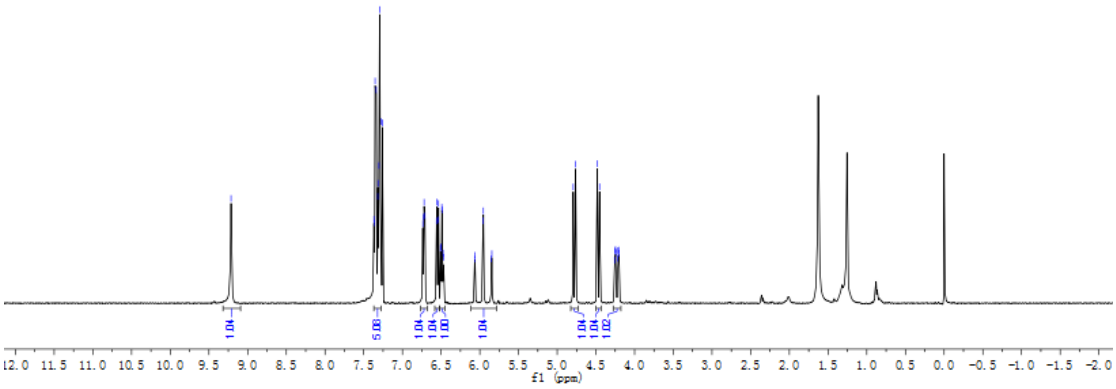


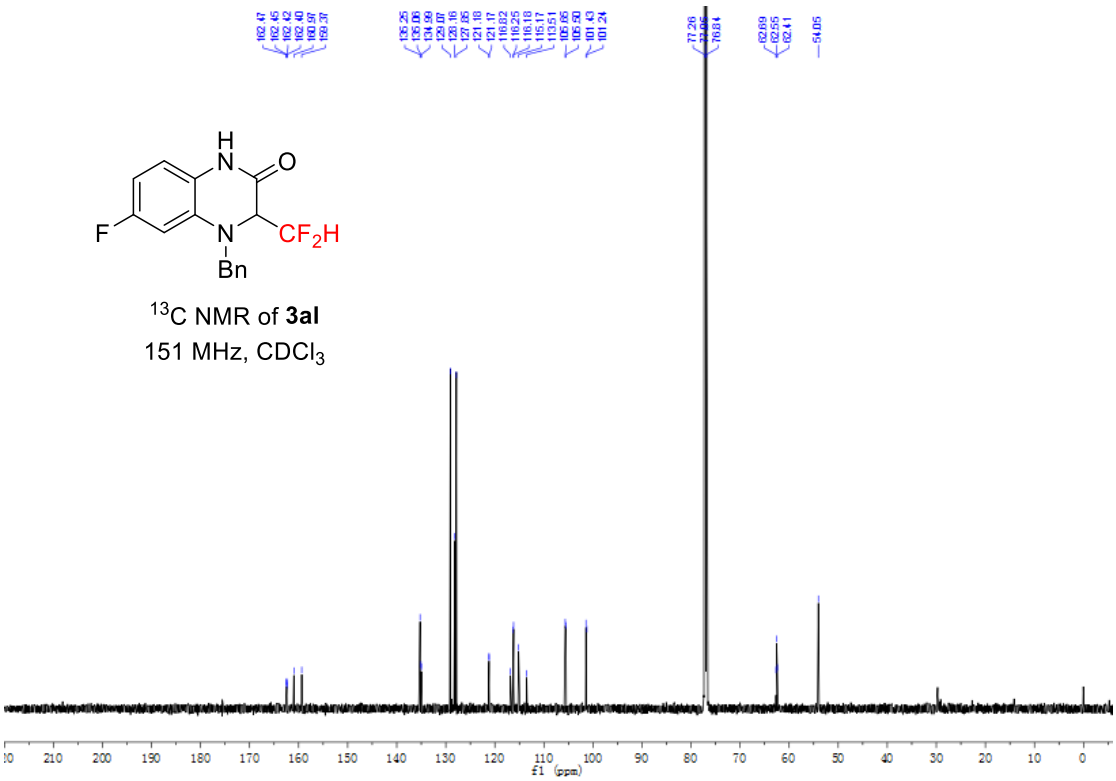
^{19}F NMR of **3ak**
377 MHz, $CDCl_3$

4-benzyl-3-(difluoromethyl)-6-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3al)

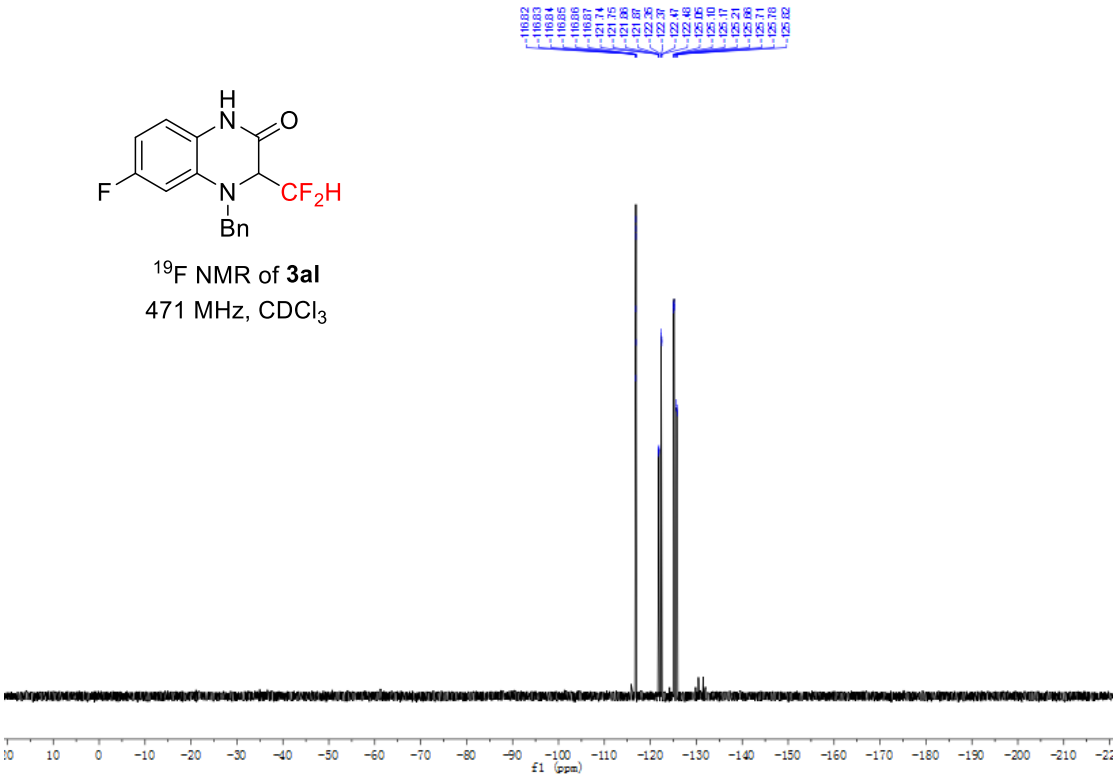


^{1}H NMR of **3al**
500 MHz, $CDCl_3$



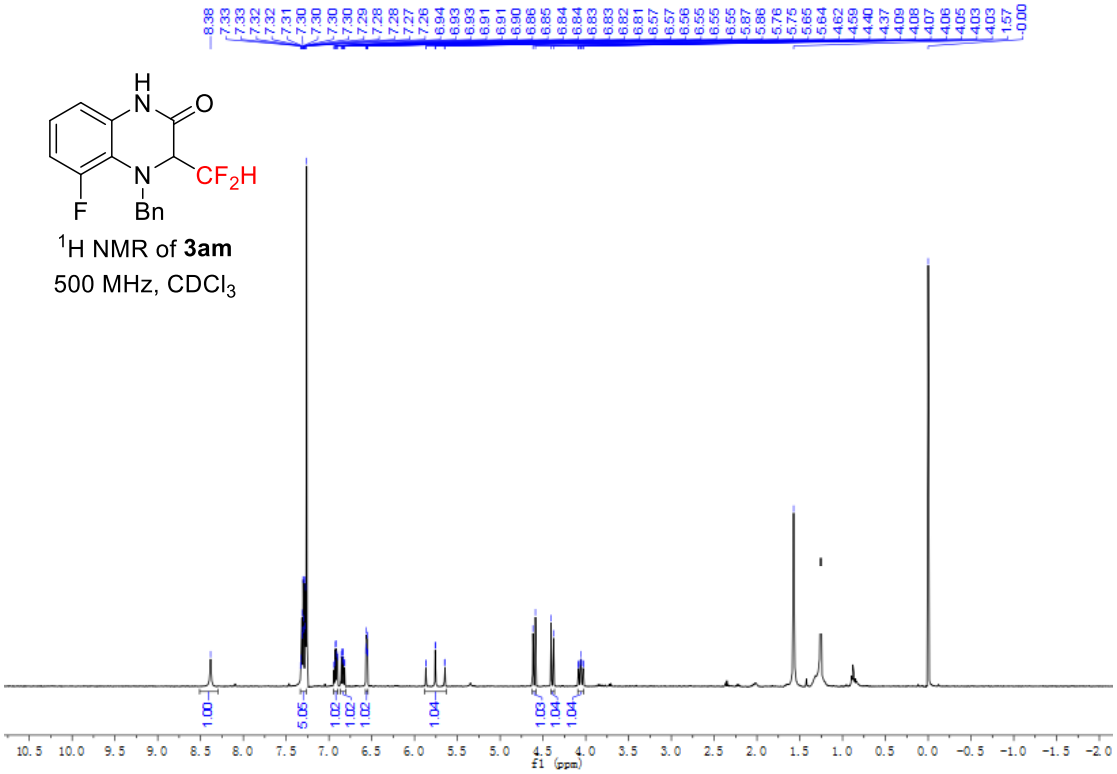


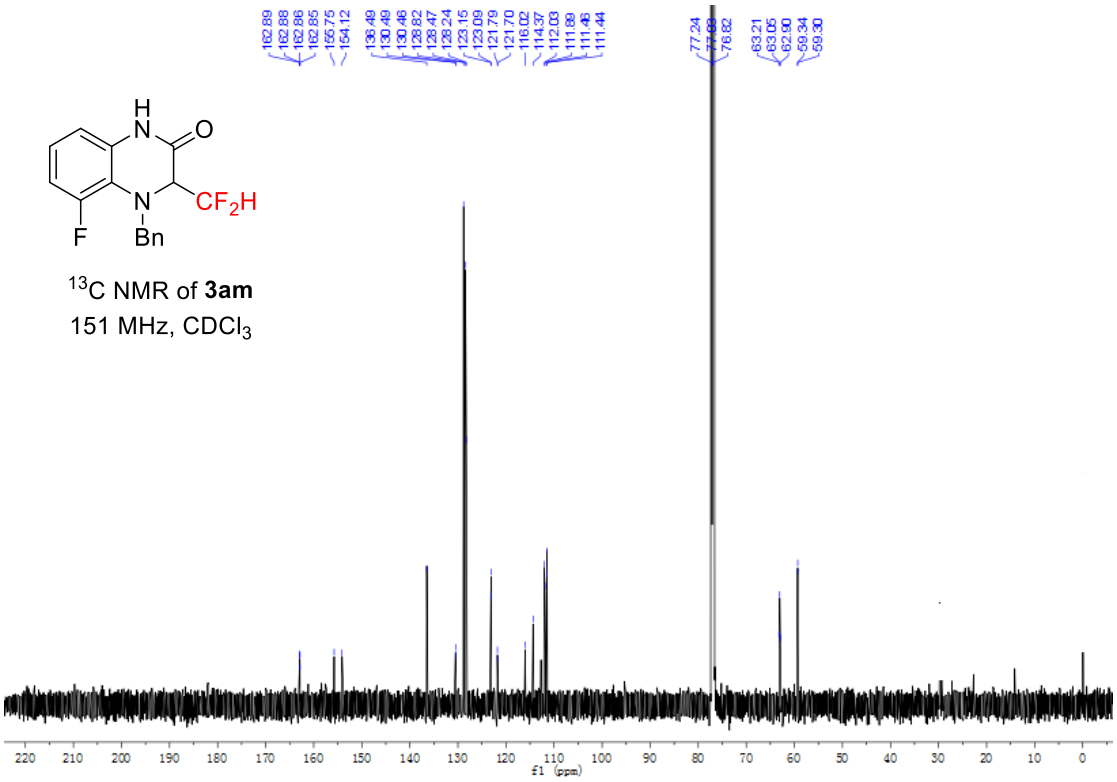
^{13}C NMR of **3al**
151 MHz, $CDCl_3$

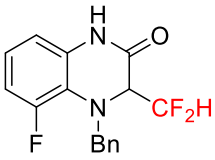


^{19}F NMR of **3al**
471 MHz, $CDCl_3$

4-benzyl-3-(difluoromethyl)-5-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3am)

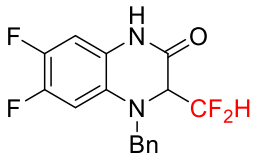




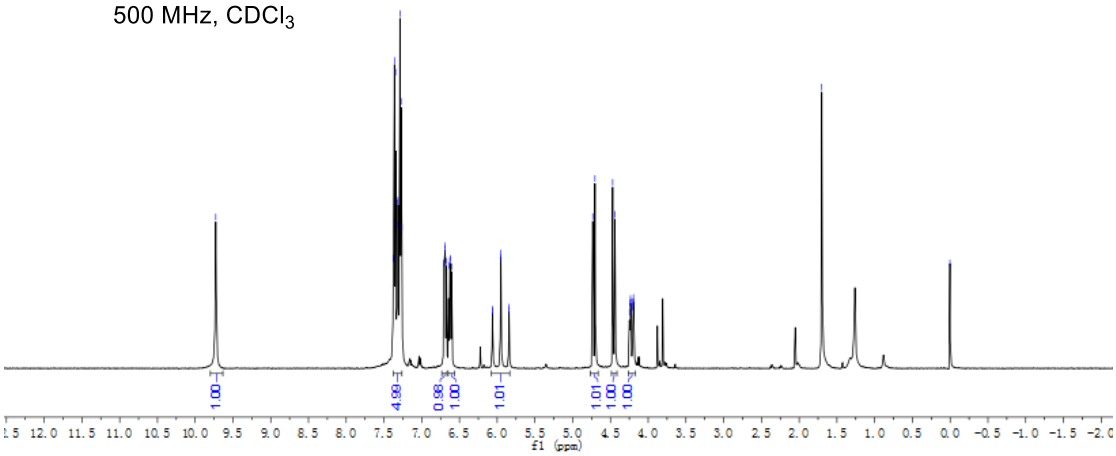


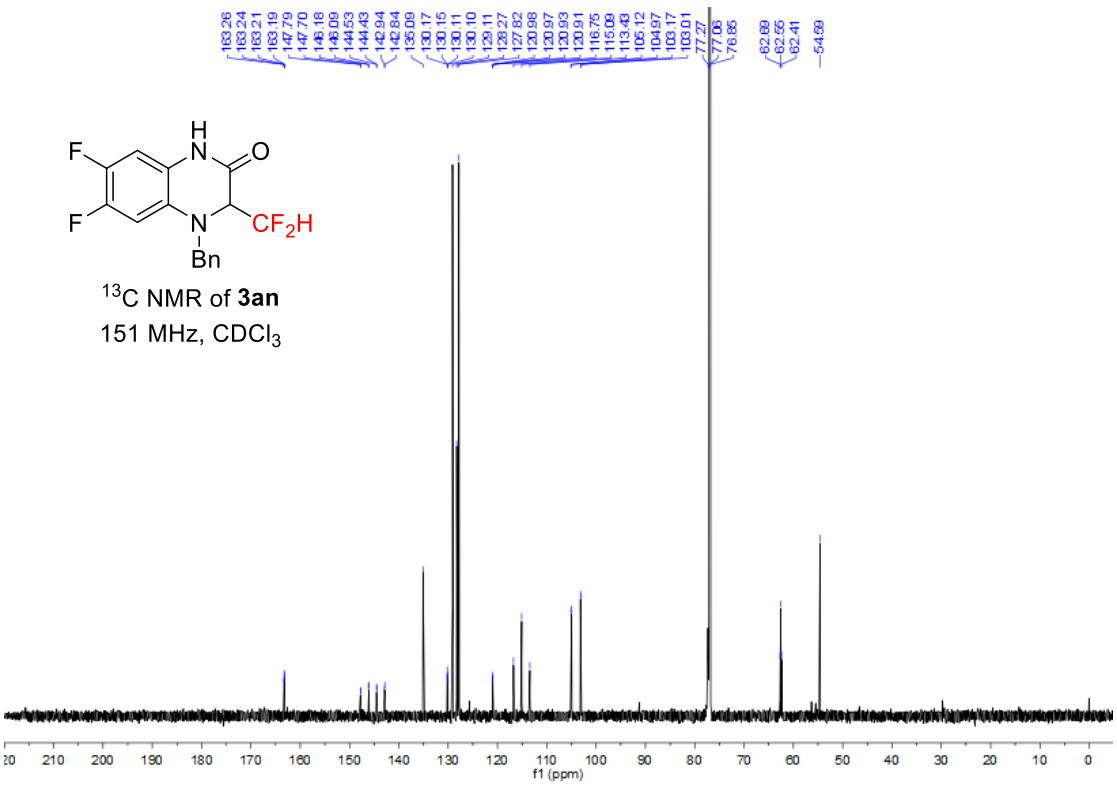
^{19}F NMR of **3am**
471 MHz, $CDCl_3$

4-benzyl-3-(difluoromethyl)-6,7-difluoro-3,4-dihydroquinoxalin-2(1H)-one (3an)

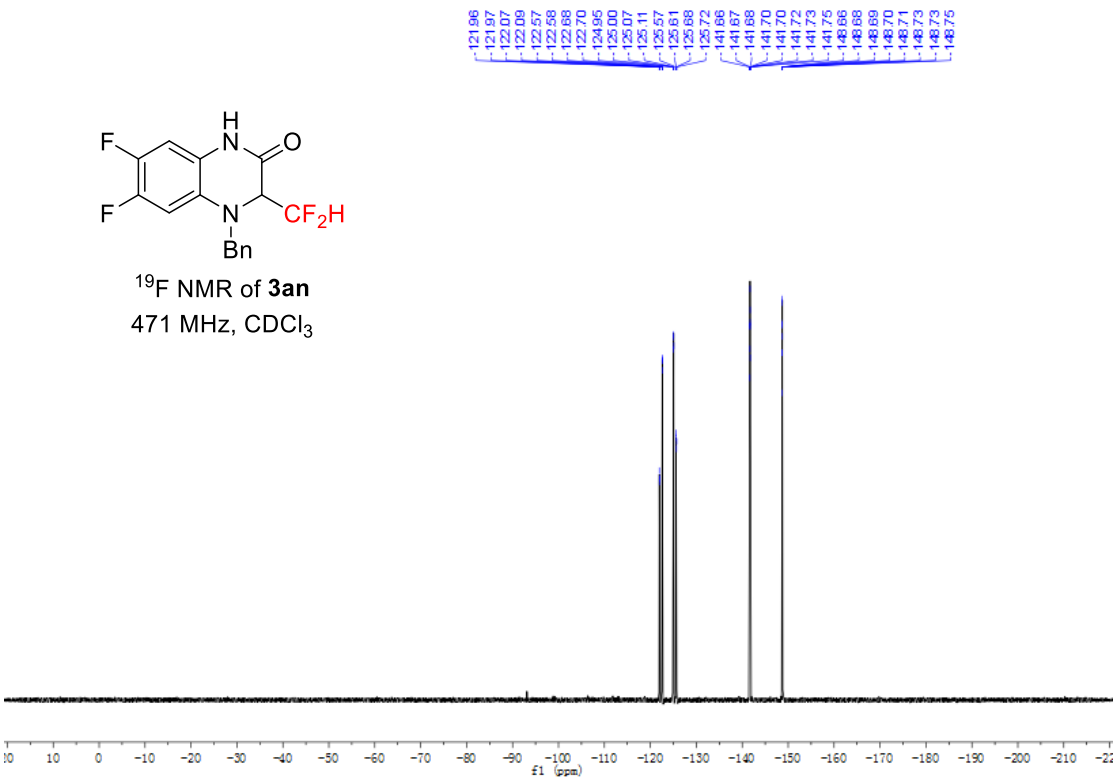


^{1}H NMR of **3an**
500 MHz, $CDCl_3$



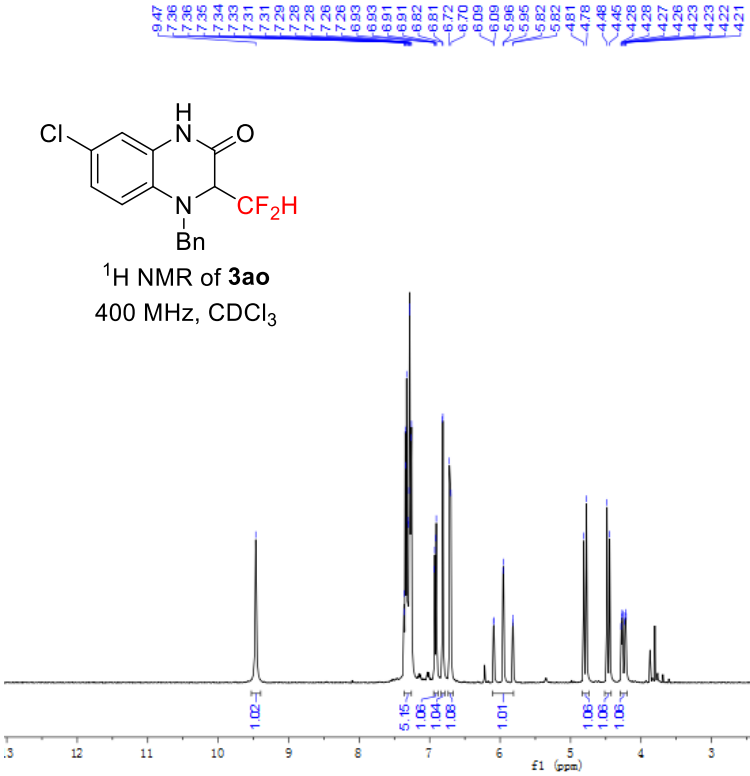


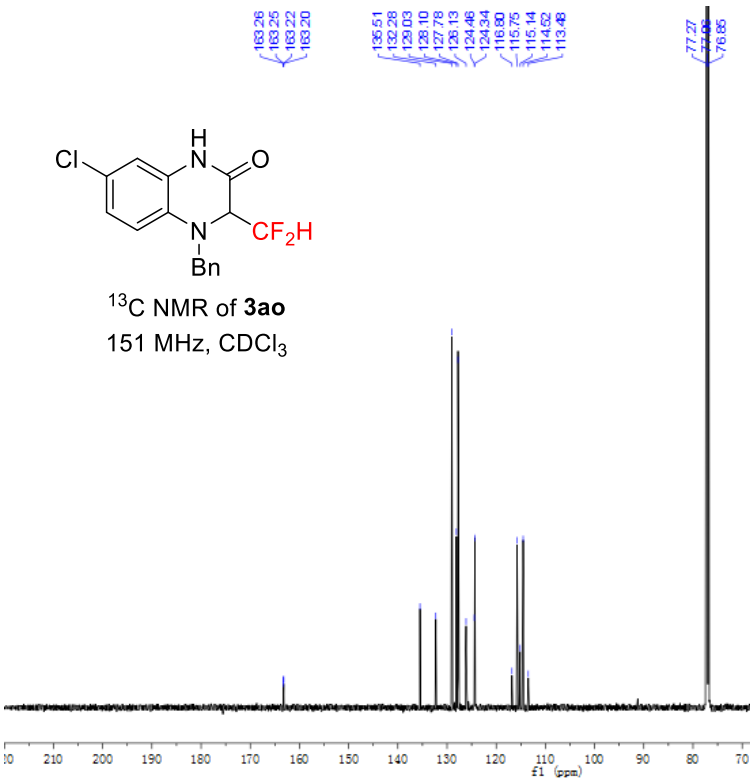
^{13}C NMR of **3an**
151 MHz, $CDCl_3$

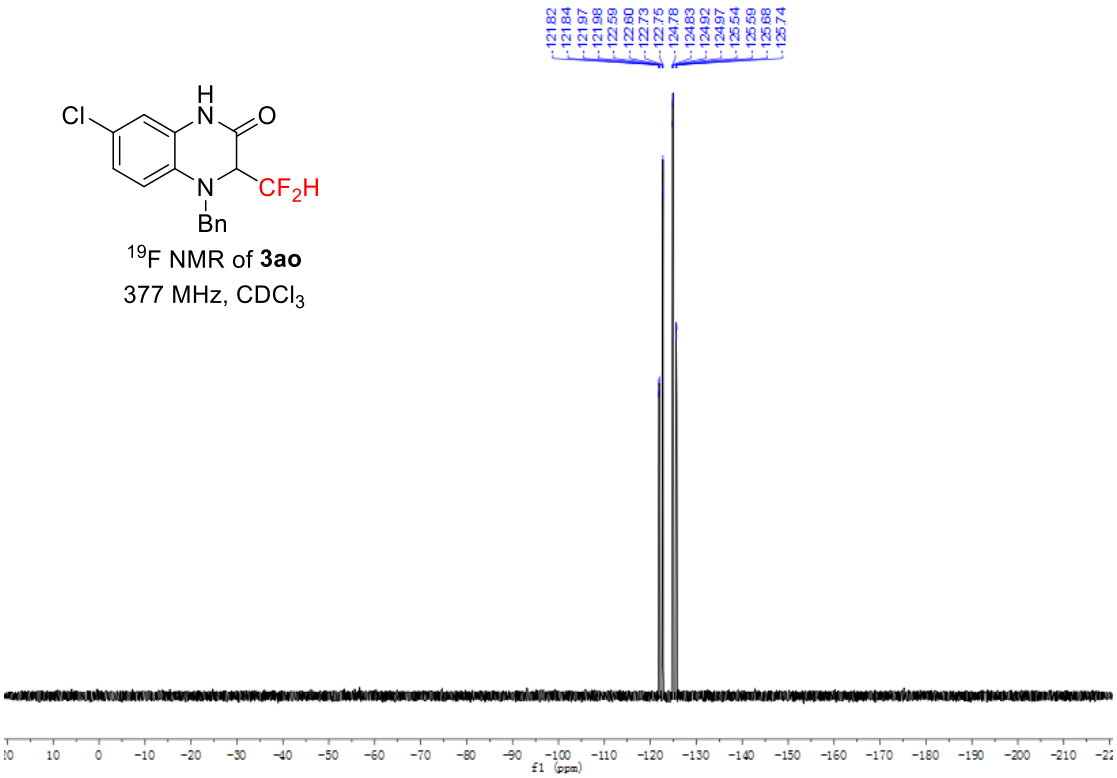


^{19}F NMR of **3an**
471 MHz, $CDCl_3$

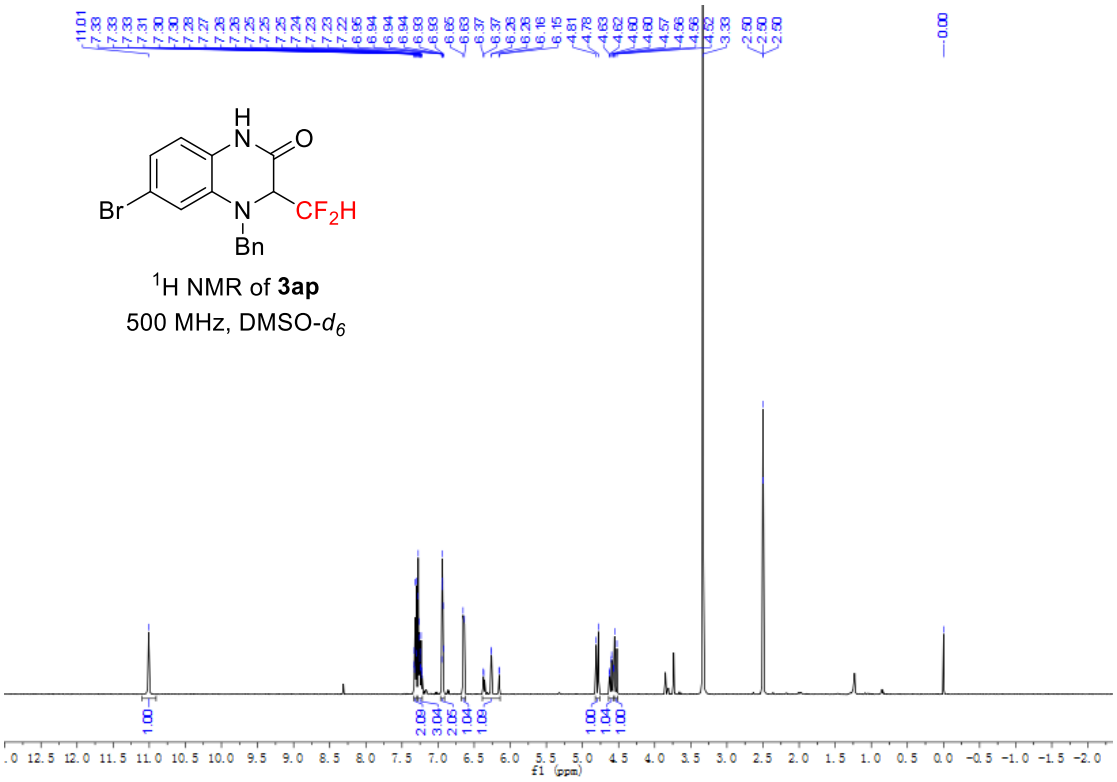
4-benzyl-7-chloro-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ao)

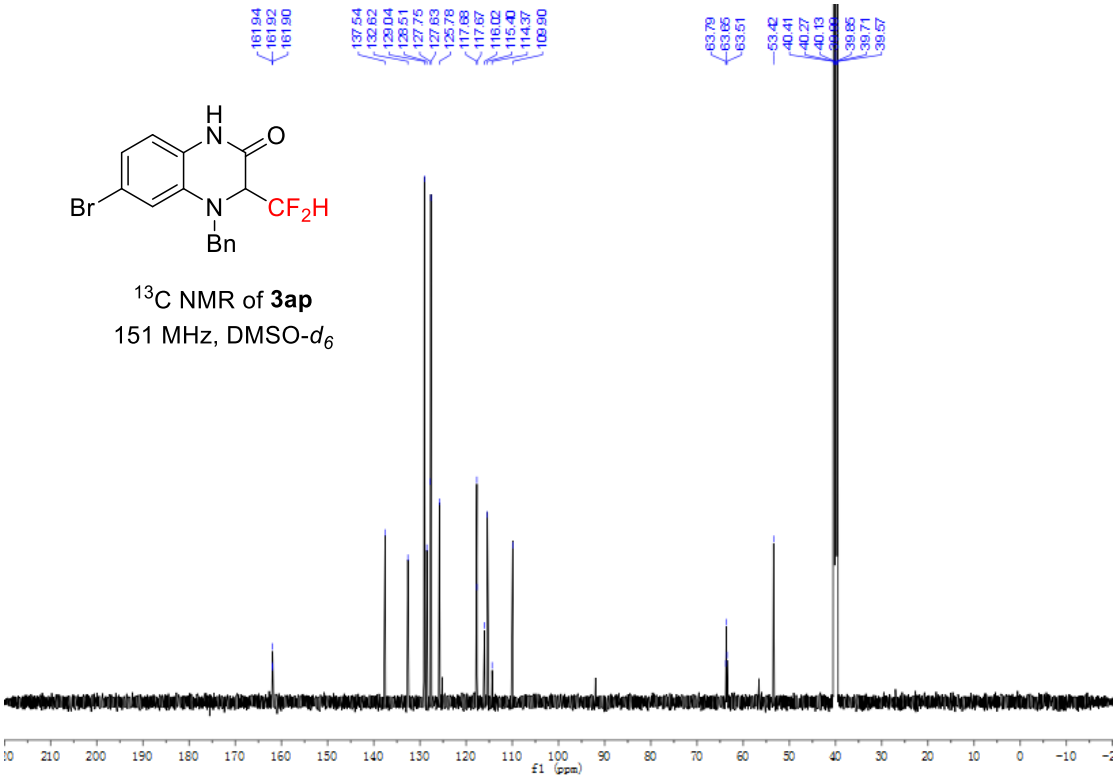




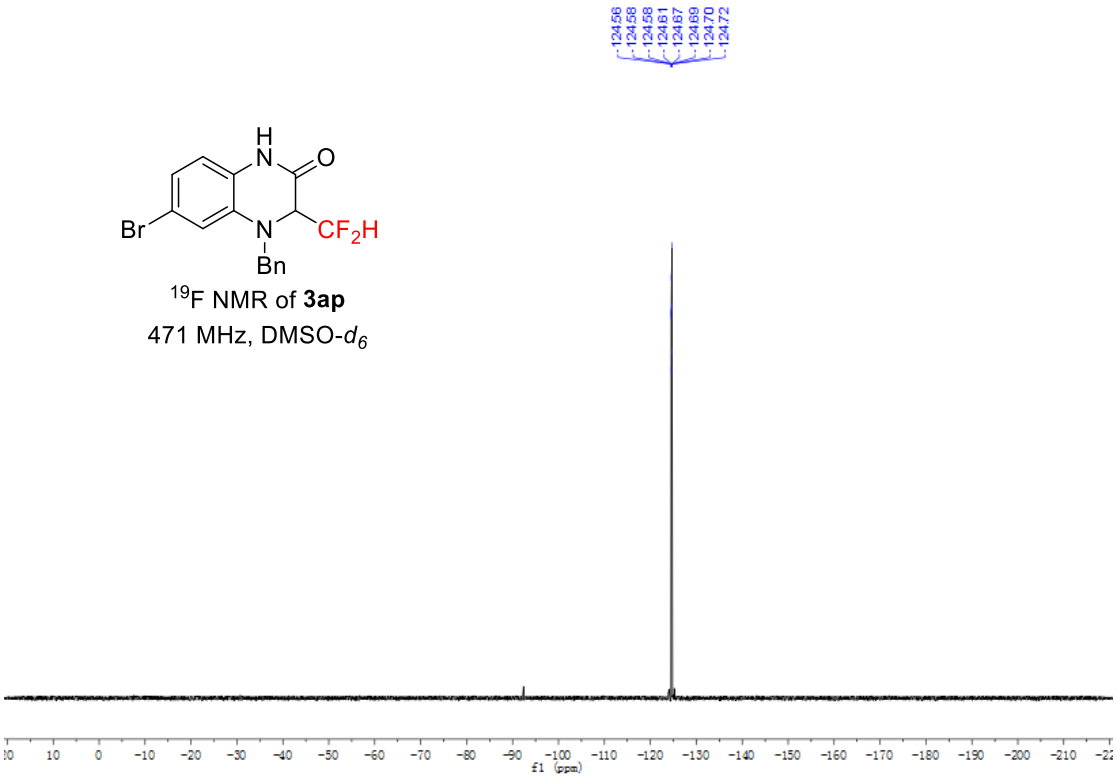


4-benzyl-7-bromo-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ap)



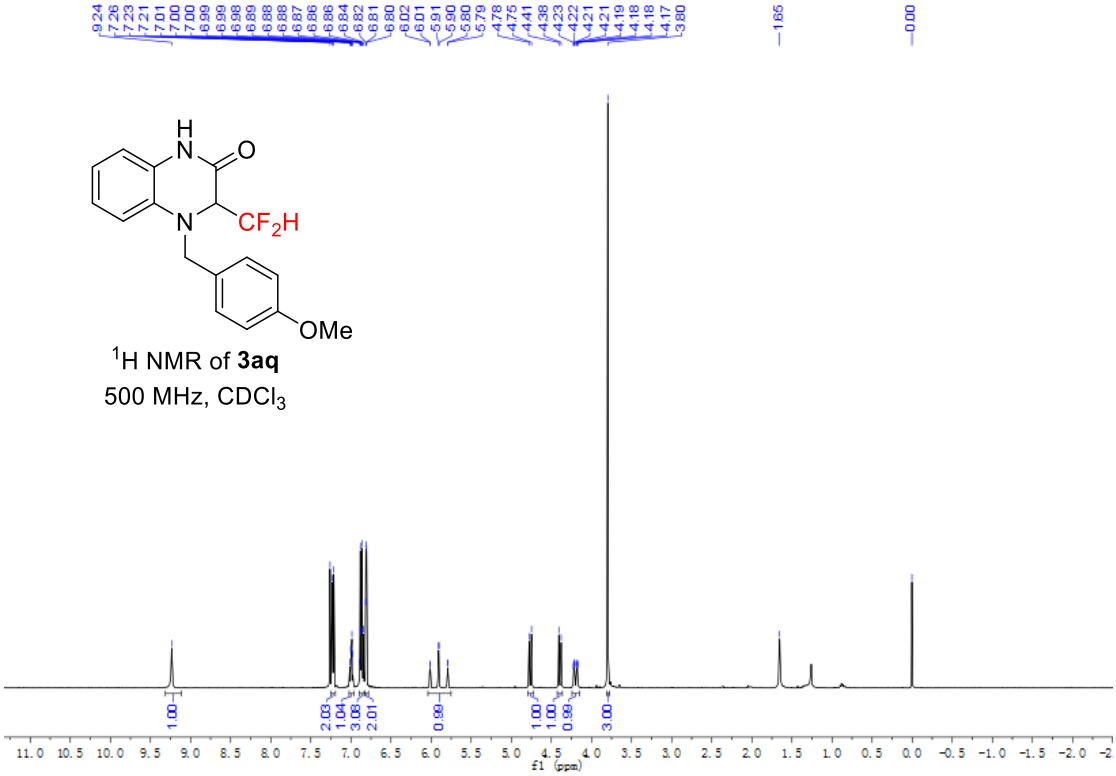


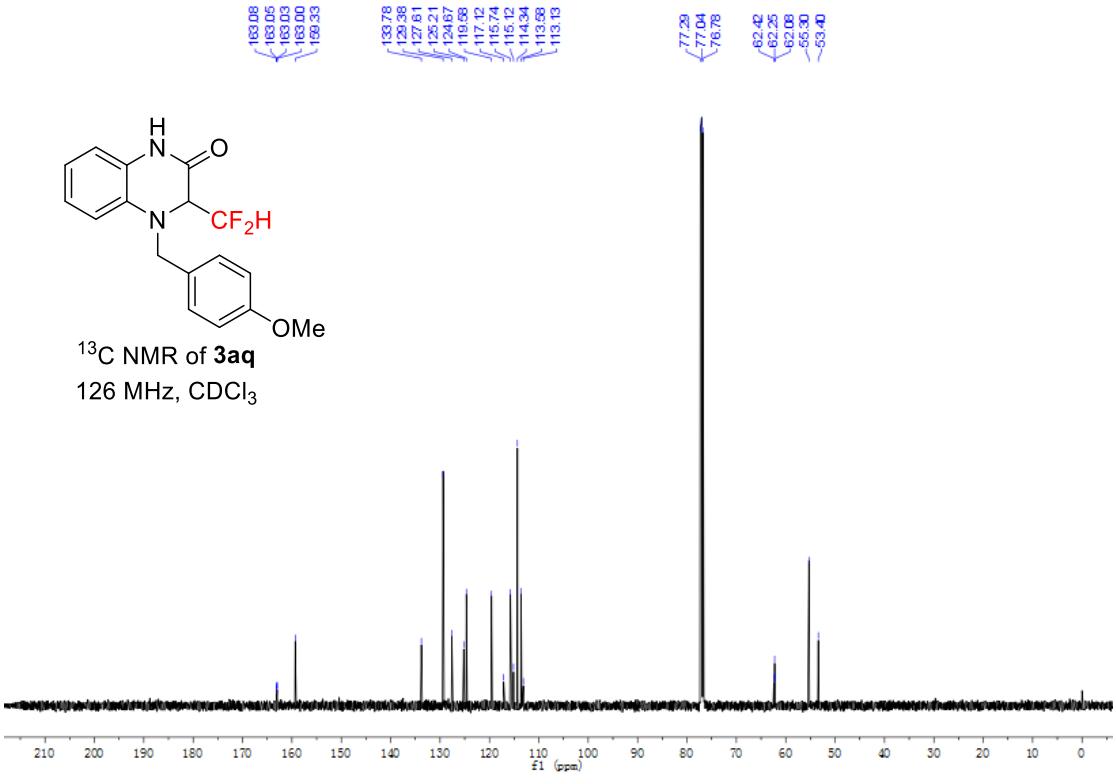
^{13}C NMR of **3ap**
151 MHz, DMSO-d_6

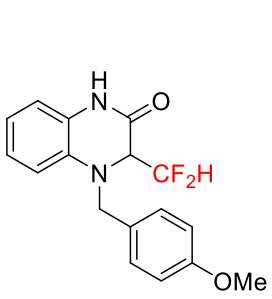


^{19}F NMR of **3ap**
471 MHz, DMSO-d_6

3-(difluoromethyl)-4-(4-methoxybenzyl)-3,4-dihydroquinoxalin-2(1H)-one (3aq)

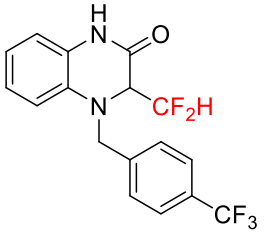




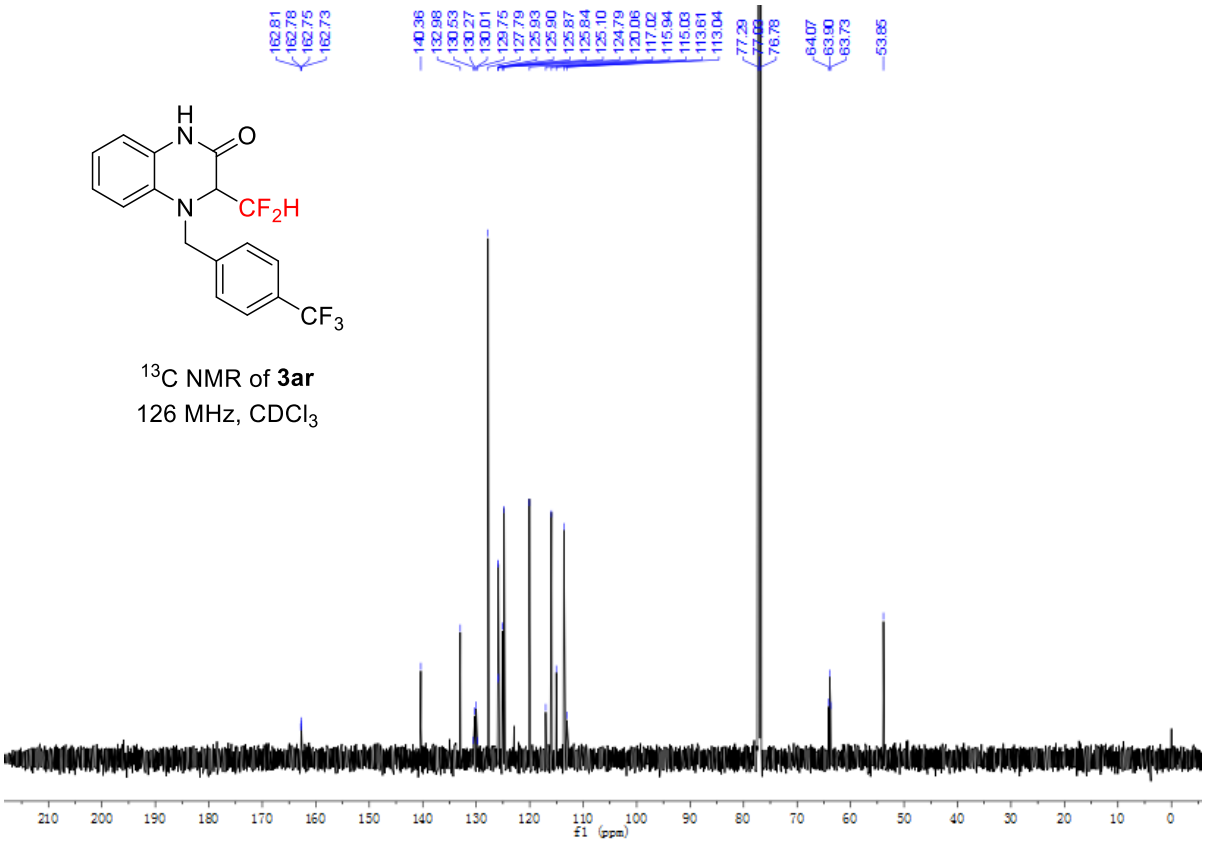


^{19}F NMR of **3aq**
471 MHz, $CDCl_3$

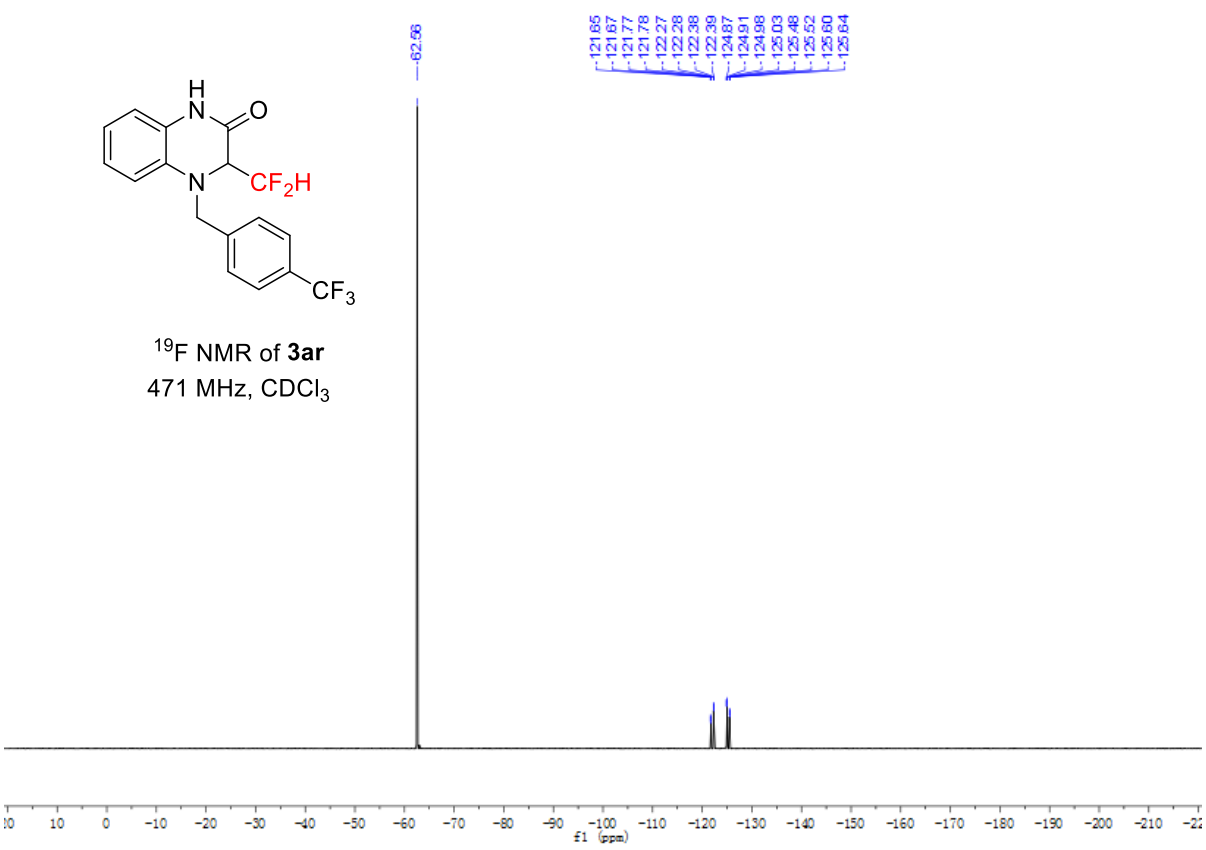
3-(difluoromethyl)-4-(4-(trifluoromethyl)benzyl)-3,4-dihydroquinoxalin-2(1H)-one (3ar)



^{1}H NMR of **3ar**
500 MHz, $CDCl_3$

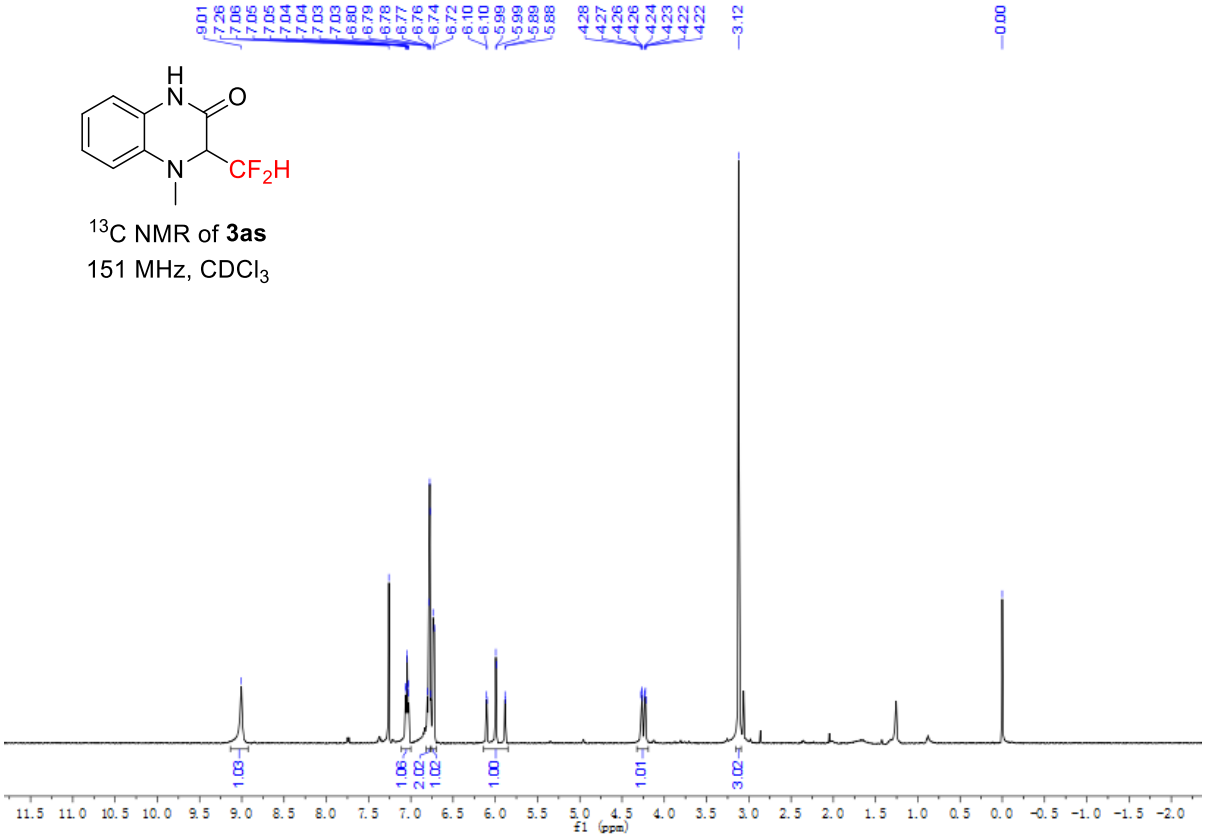


^{13}C NMR of **3ar**
126 MHz, $CDCl_3$

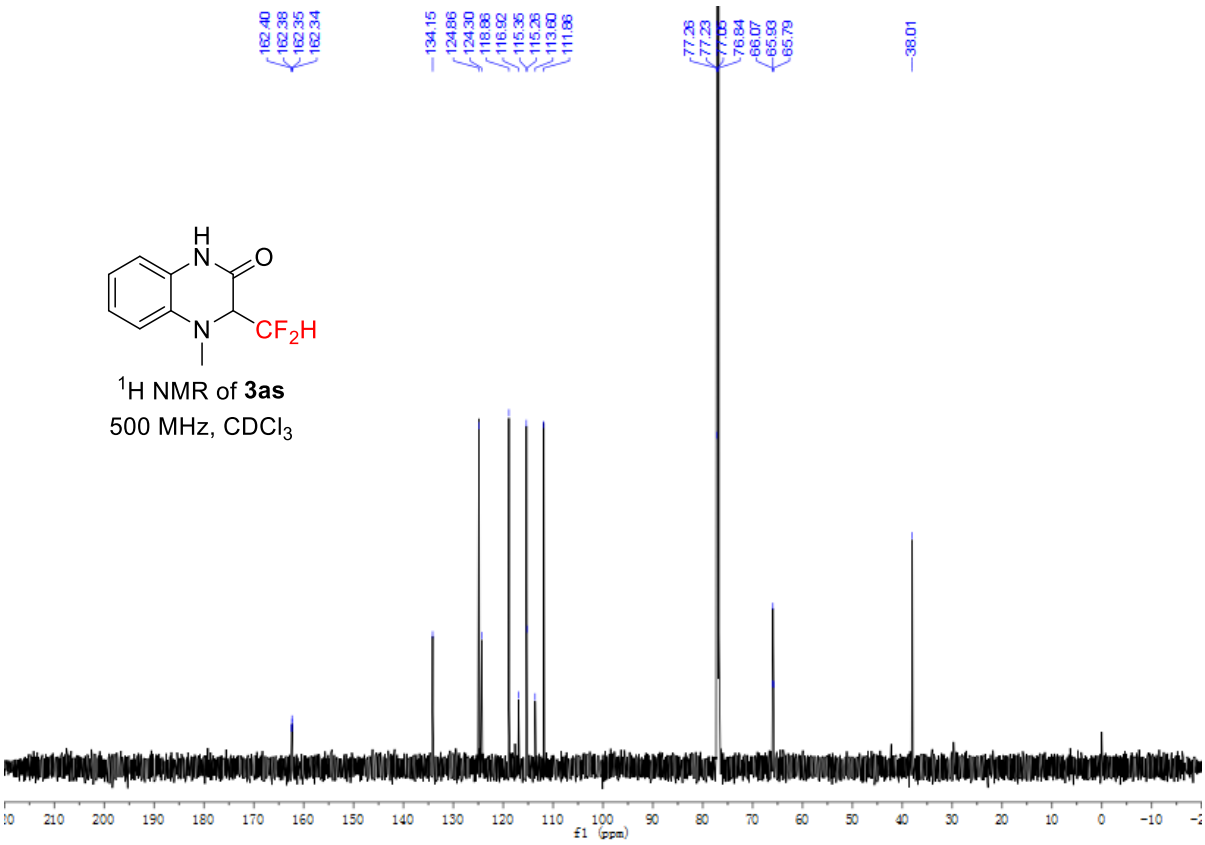


^{19}F NMR of **3ar**
471 MHz, $CDCl_3$

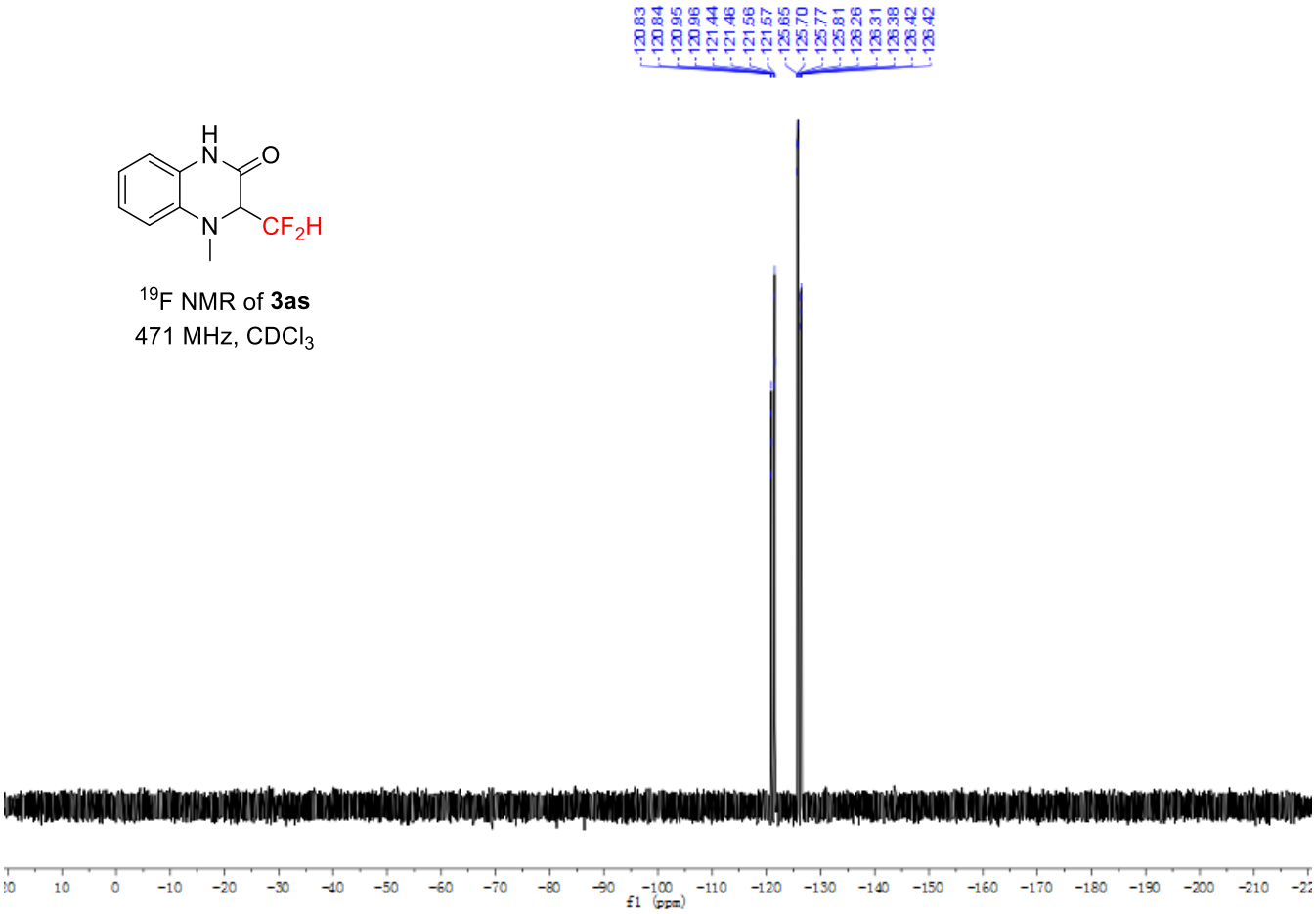
3-(difluoromethyl)-4-methyl-3,4-dihydroquinoxalin-2(1H)-one (3as)



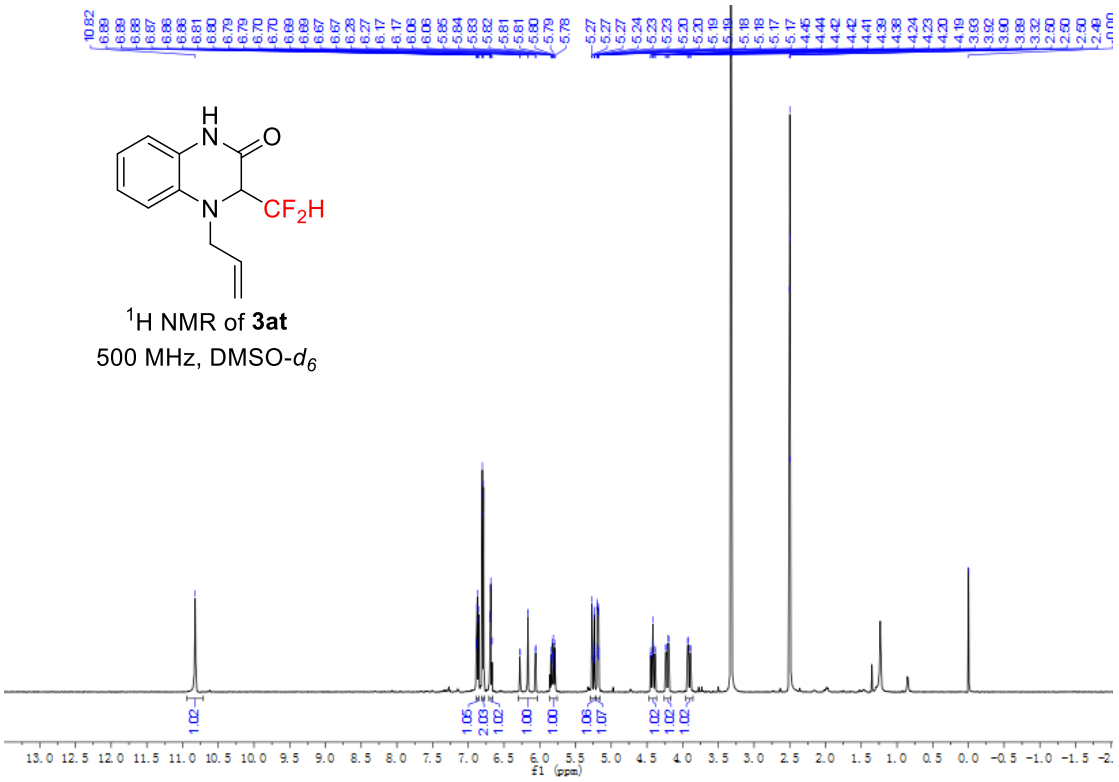
^{13}C NMR of **3as**
151 MHz, $CDCl_3$

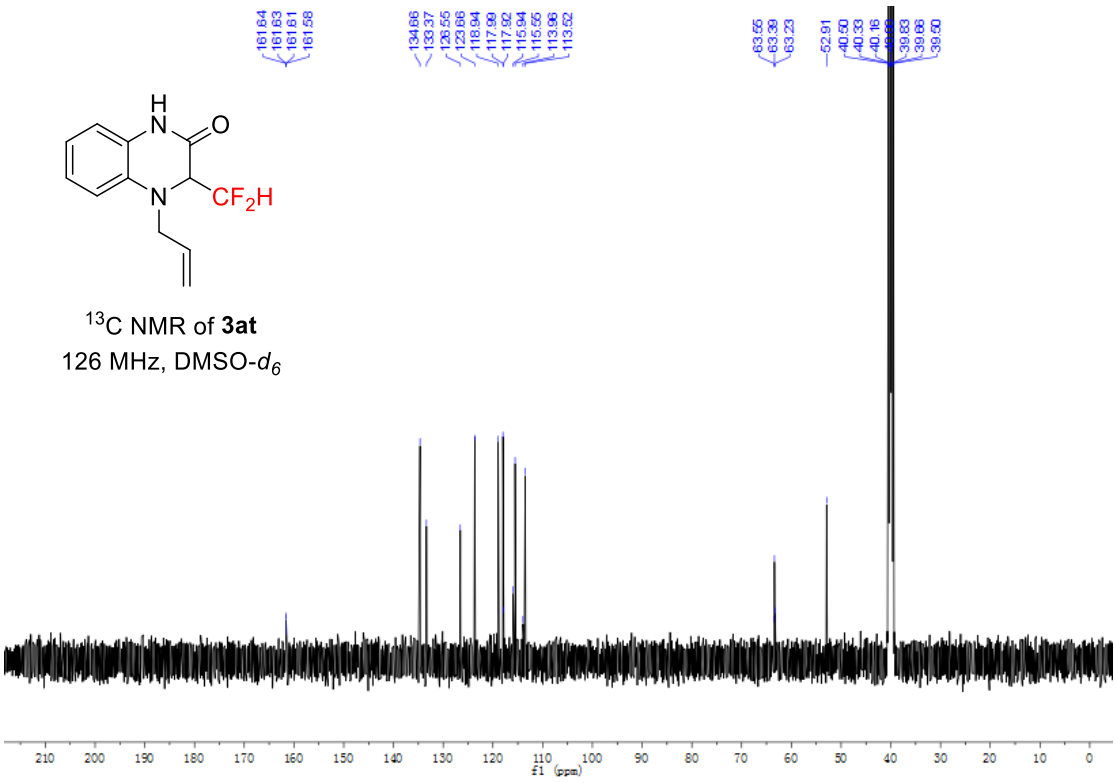


^{1}H NMR of **3as**
500 MHz, $CDCl_3$

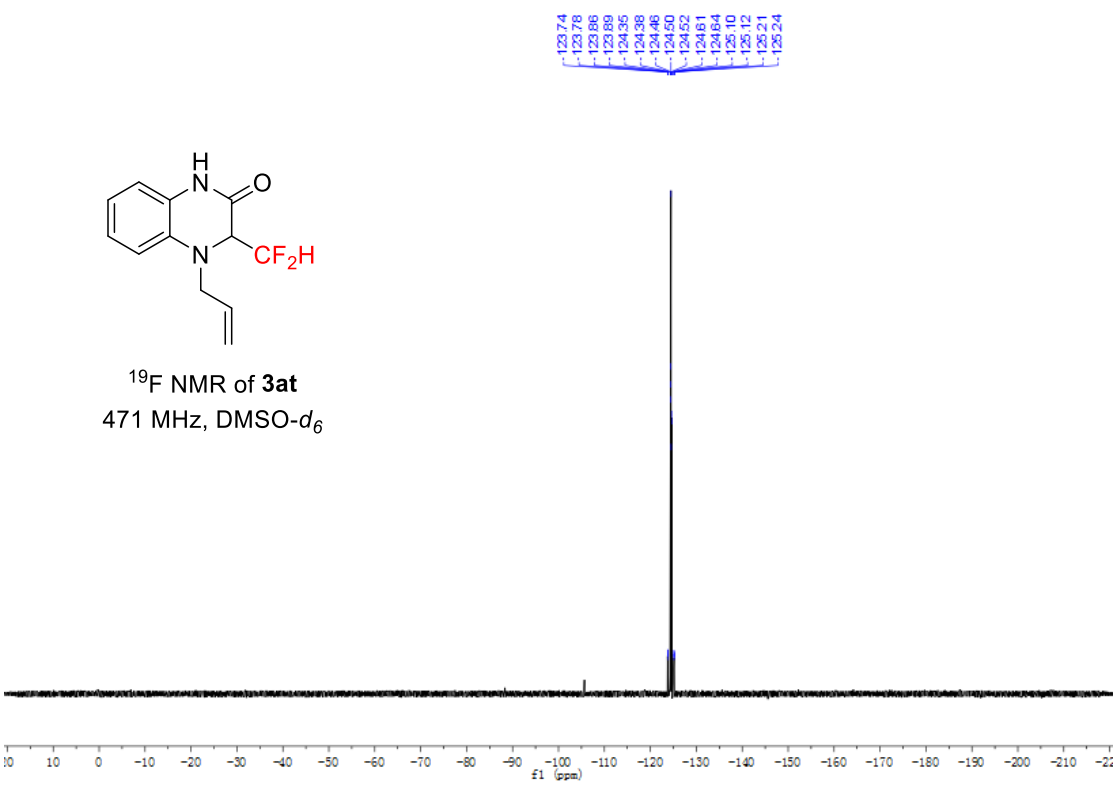


4-allyl-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3at)



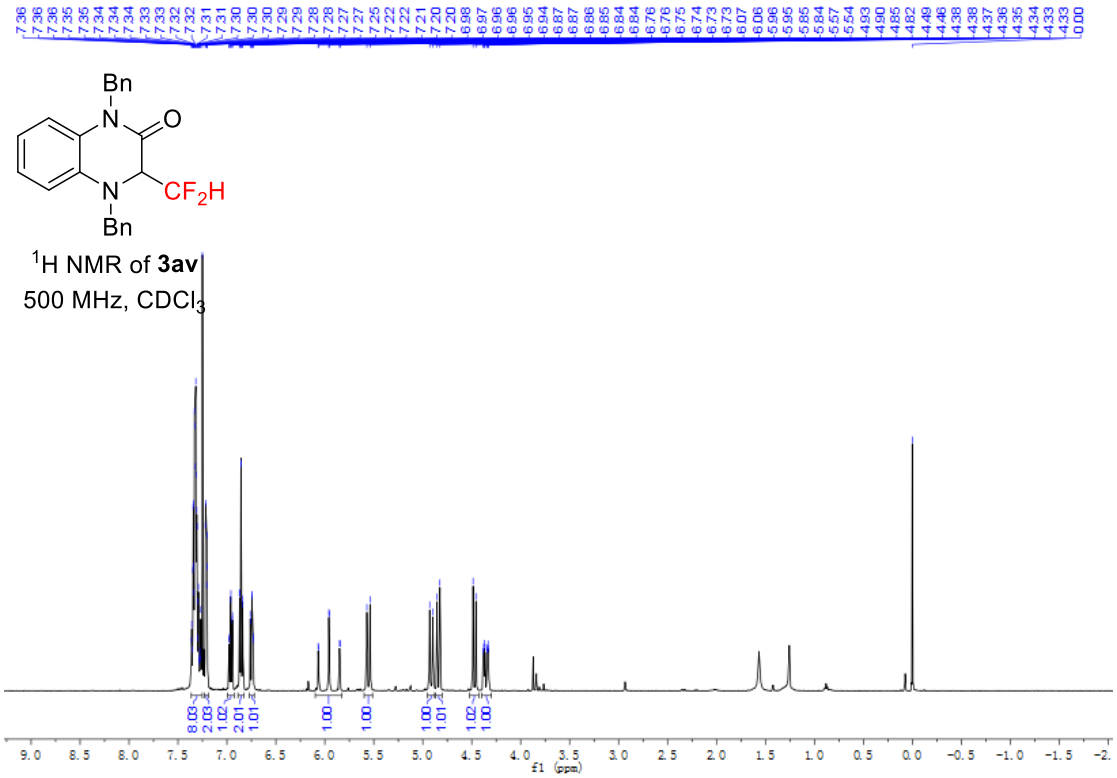


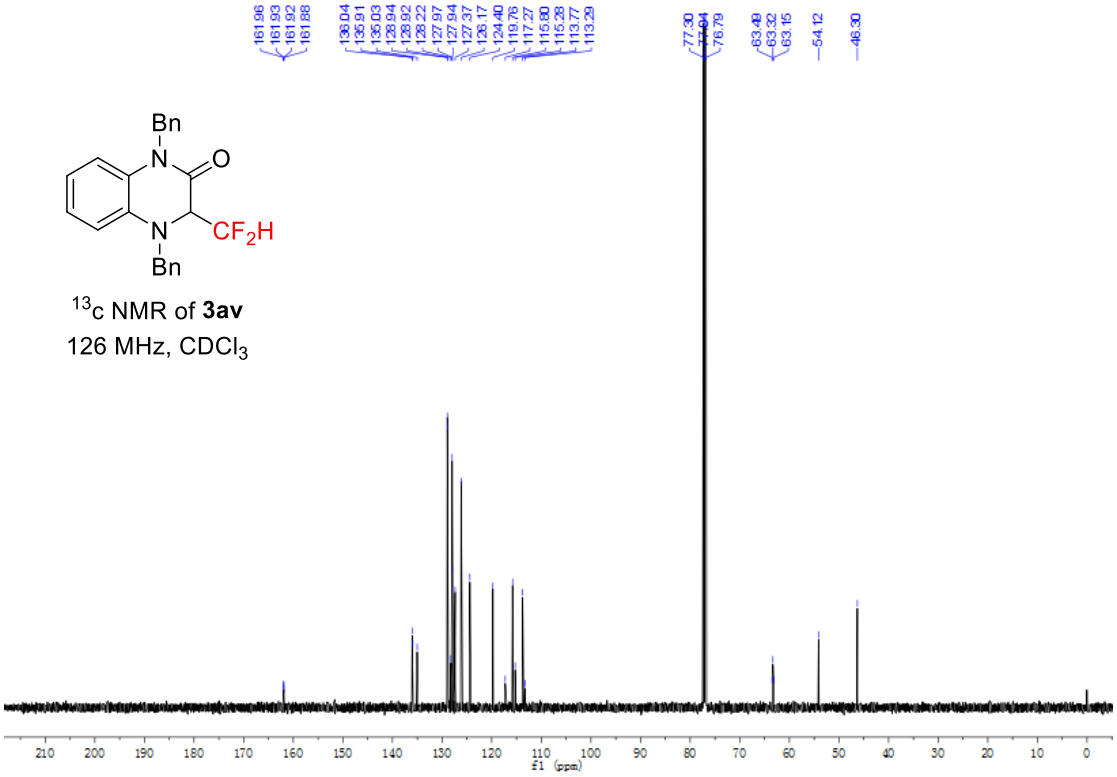
^{13}C NMR of **3at**
126 MHz, DMSO-d_6

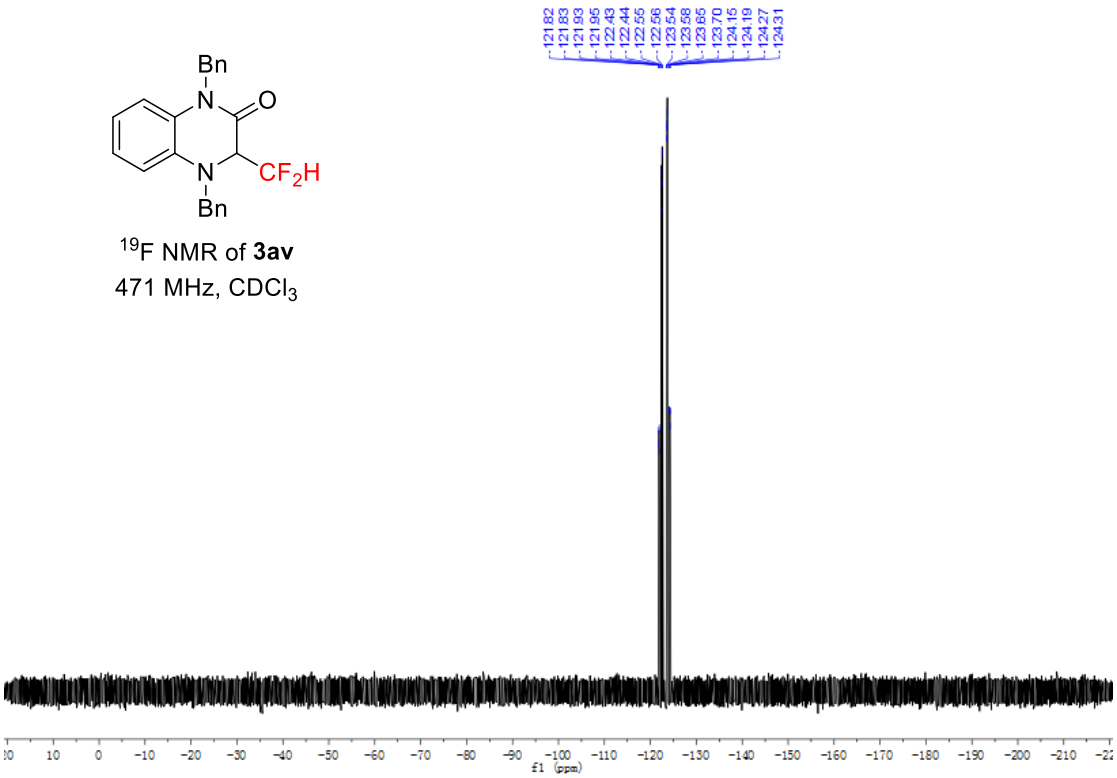


^{19}F NMR of **3at**
471 MHz, DMSO-d_6

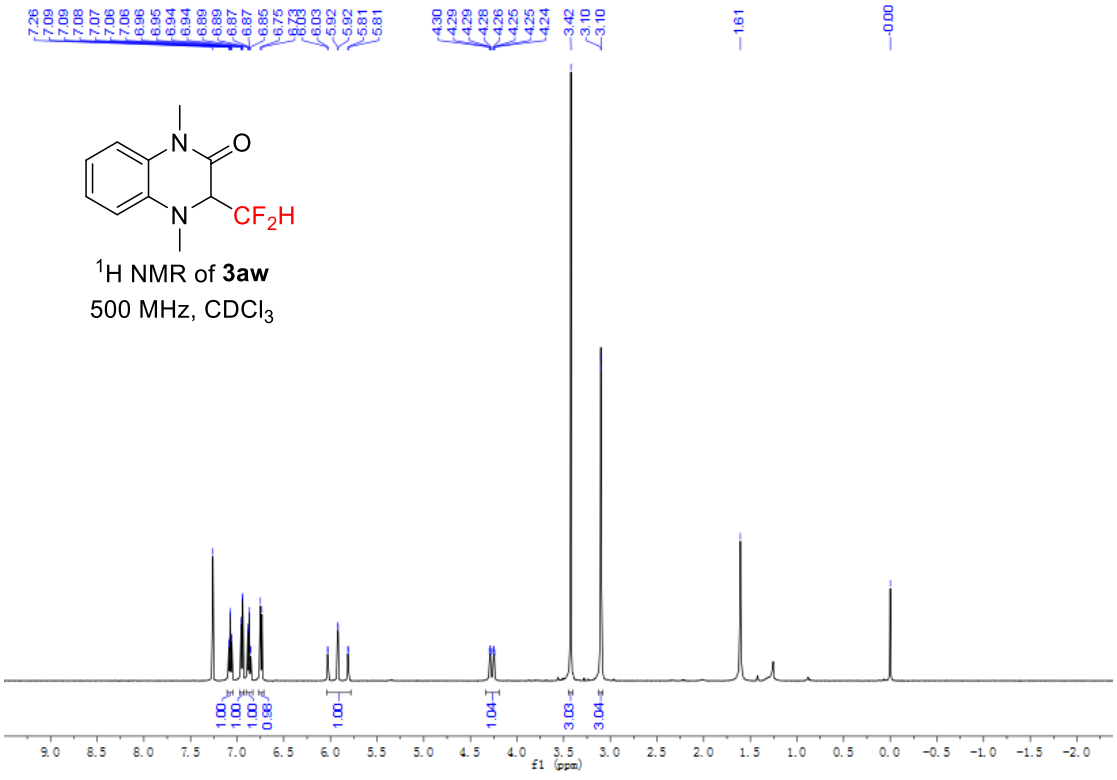
1,4-dibenzyl-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3av)

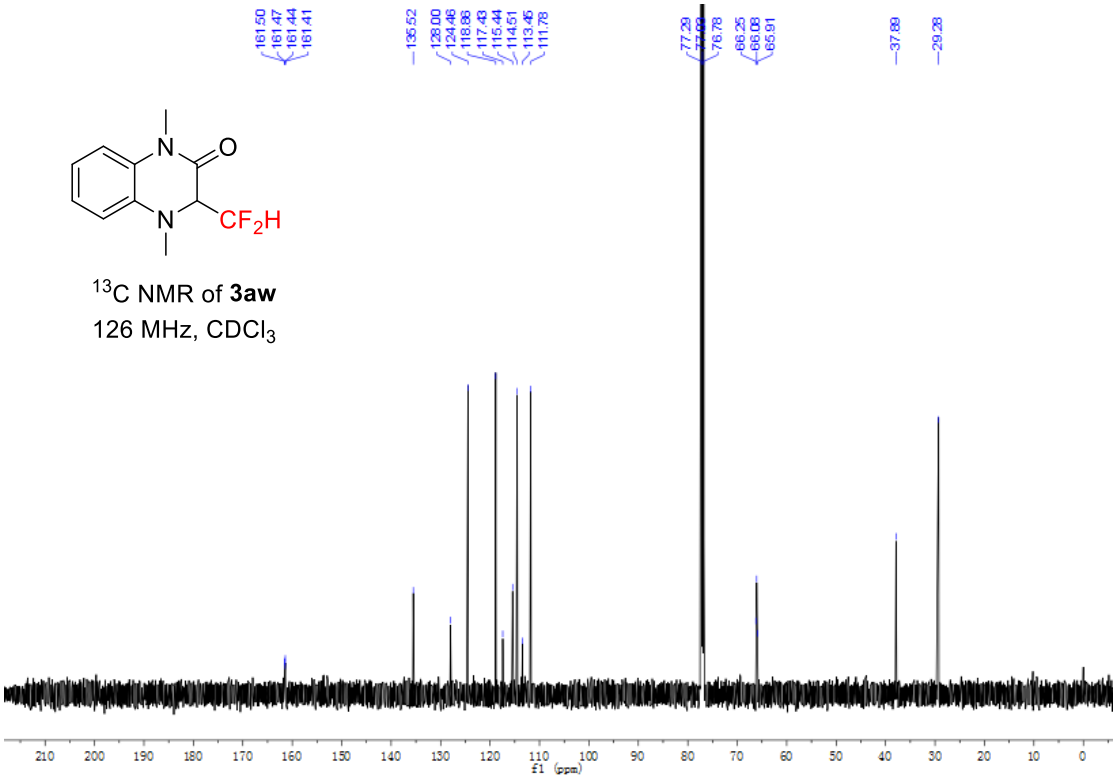




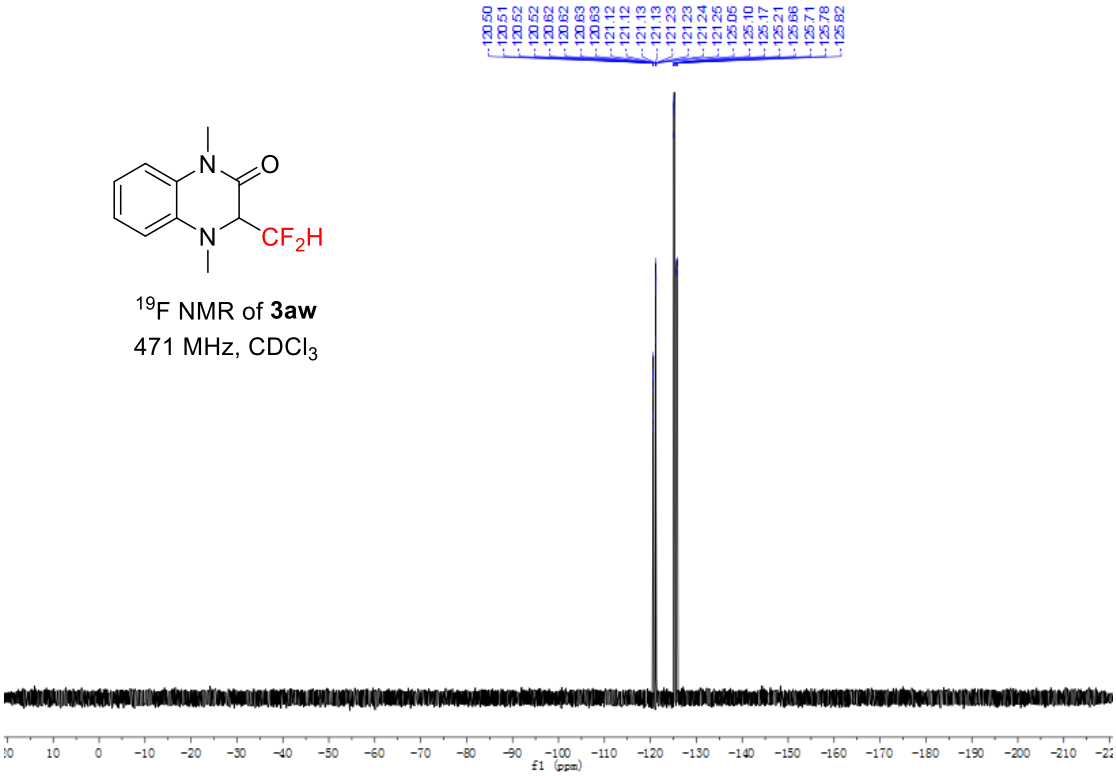


3-(difluoromethyl)-1,4-dimethyl-3,4-dihydroquinoxalin-2(1H)-one (3aw)



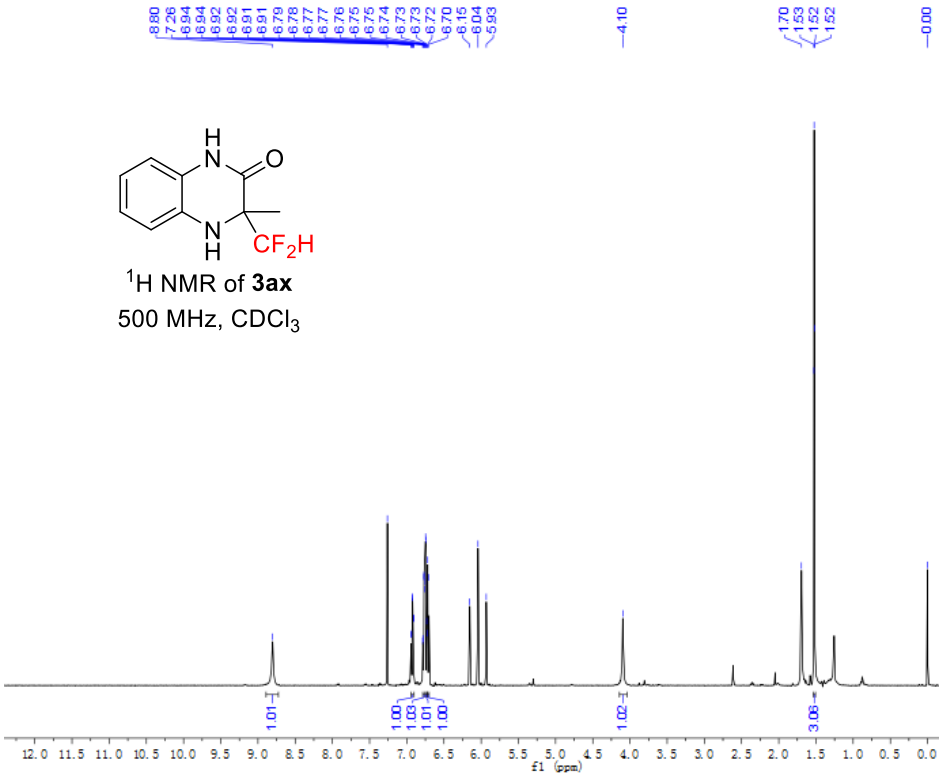


^{13}C NMR of **3aw**
126 MHz, $CDCl_3$

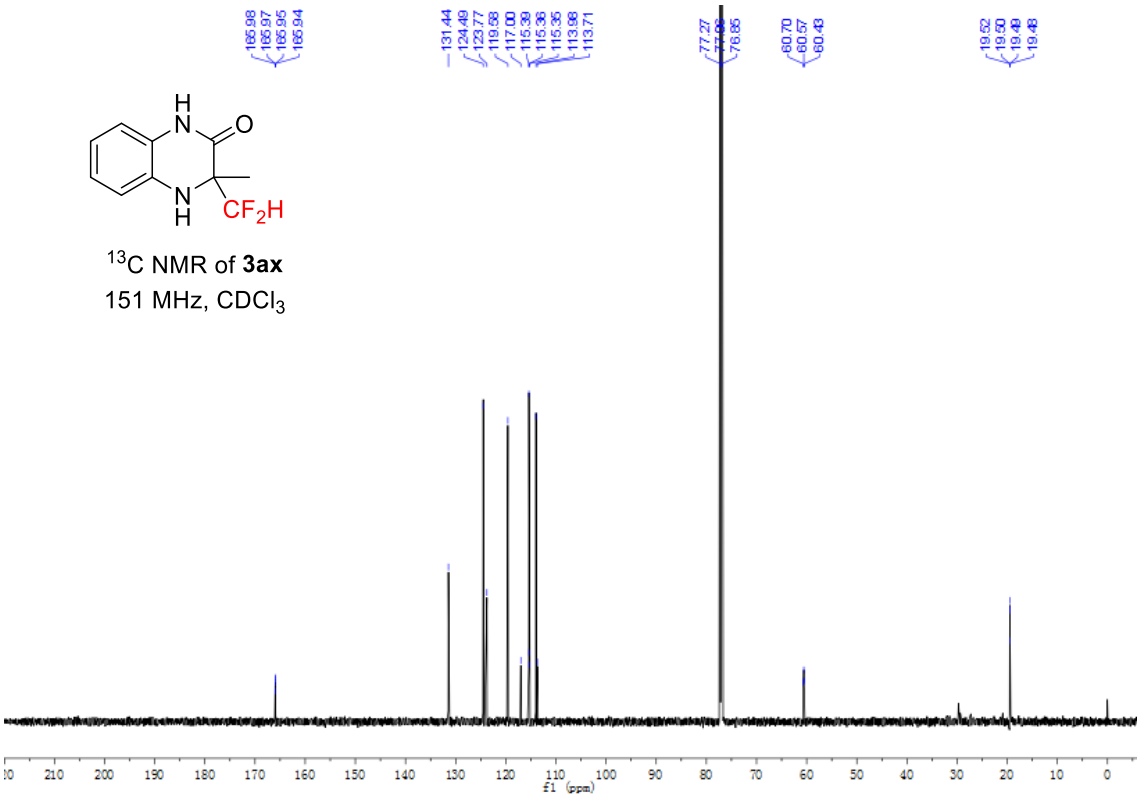


^{19}F NMR of **3aw**
471 MHz, $CDCl_3$

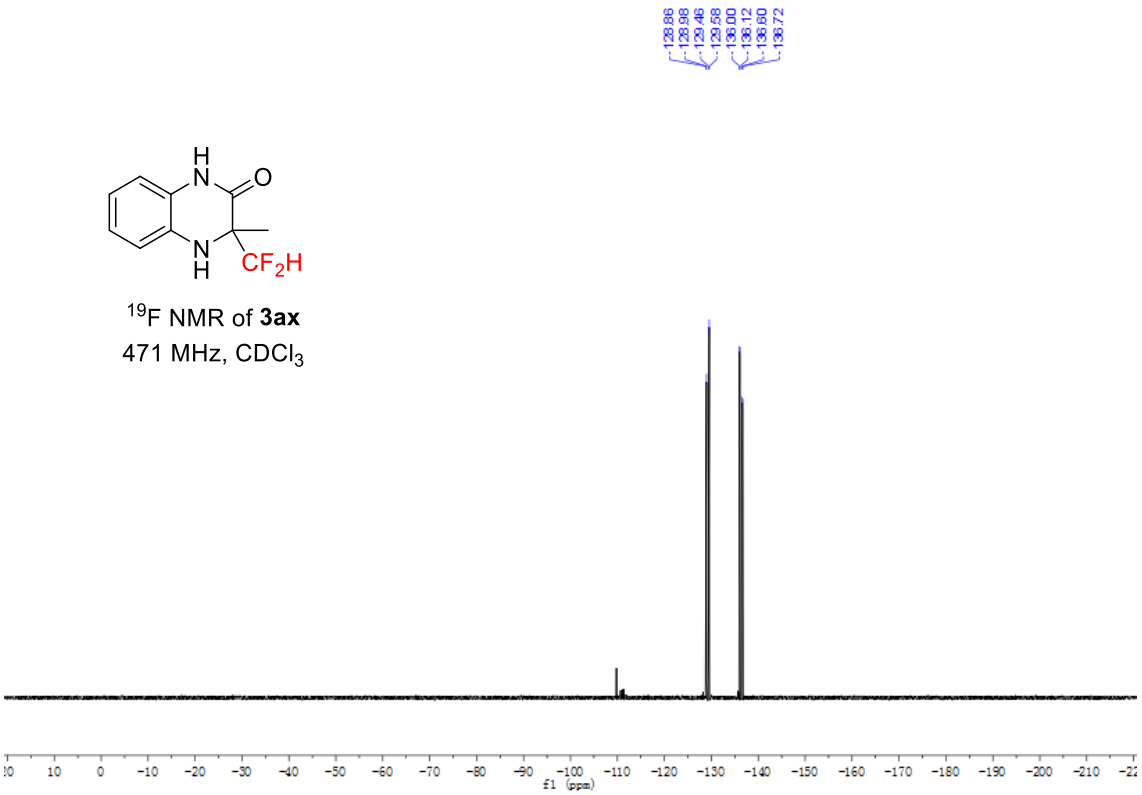
3-(difluoromethyl)-3-methyl-3,4-dihydroquinoxalin-2(1H)-one (3ax)



^{1}H NMR of **3ax**
500 MHz, $CDCl_3$

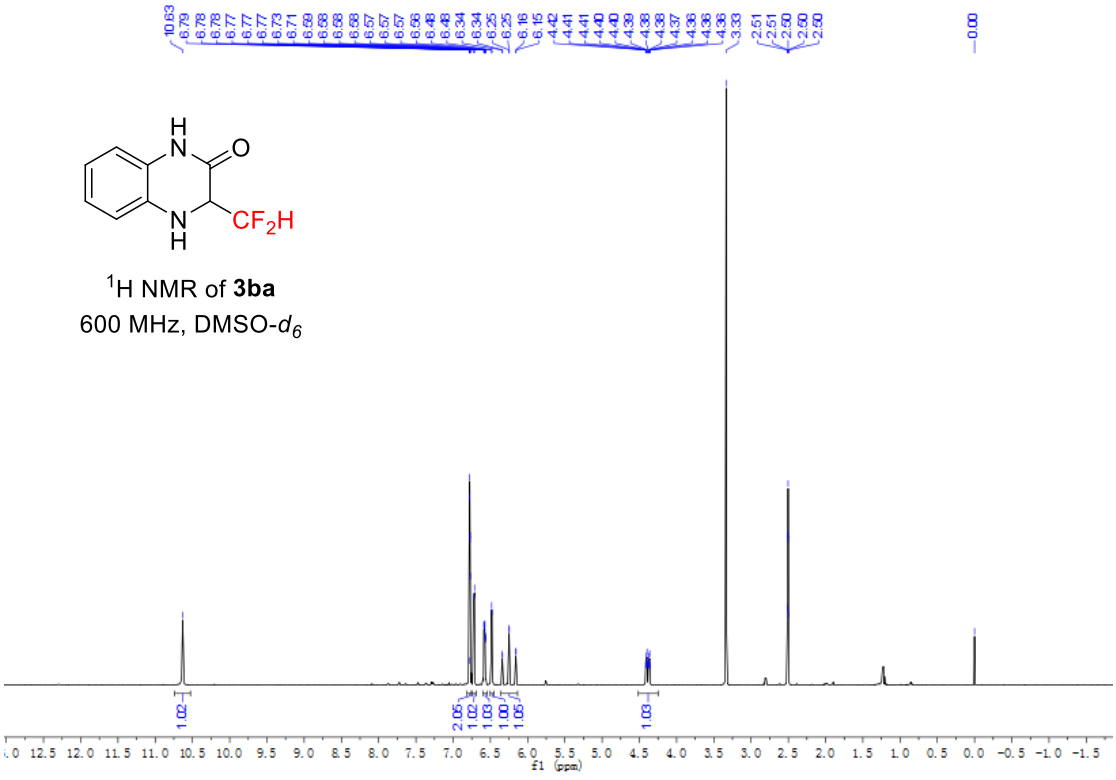


^{13}C NMR of **3ax**
151 MHz, $CDCl_3$

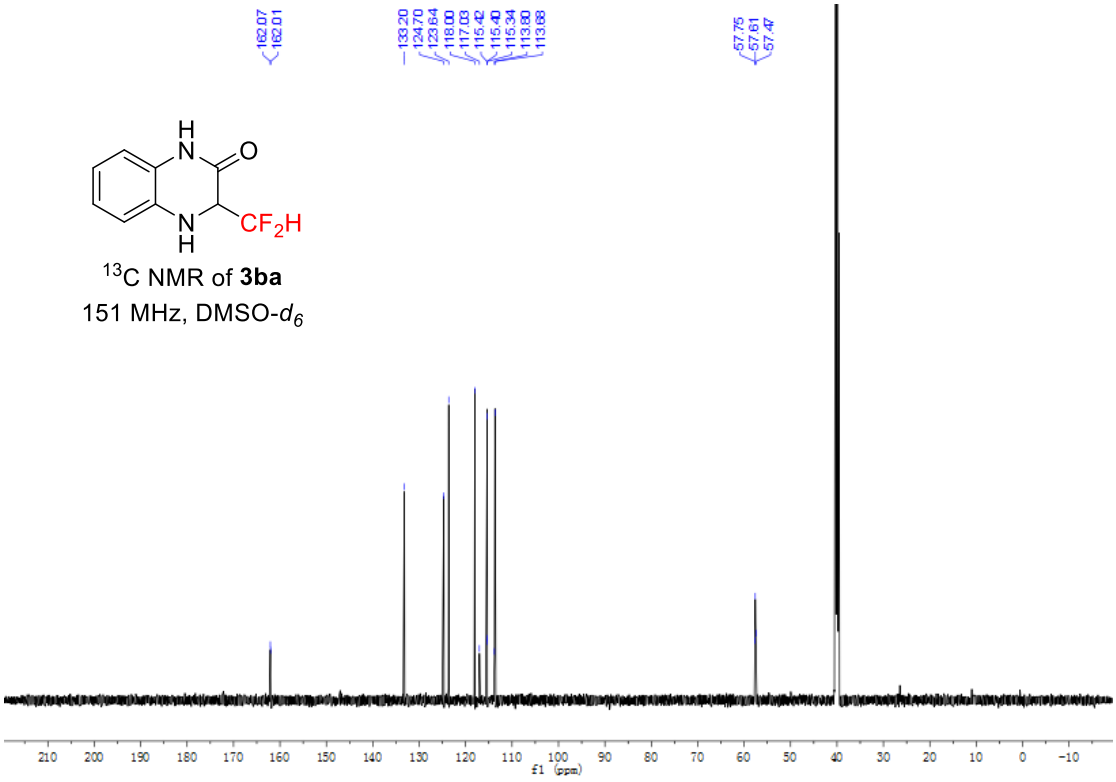


^{19}F NMR of **3ax**
471 MHz, $CDCl_3$

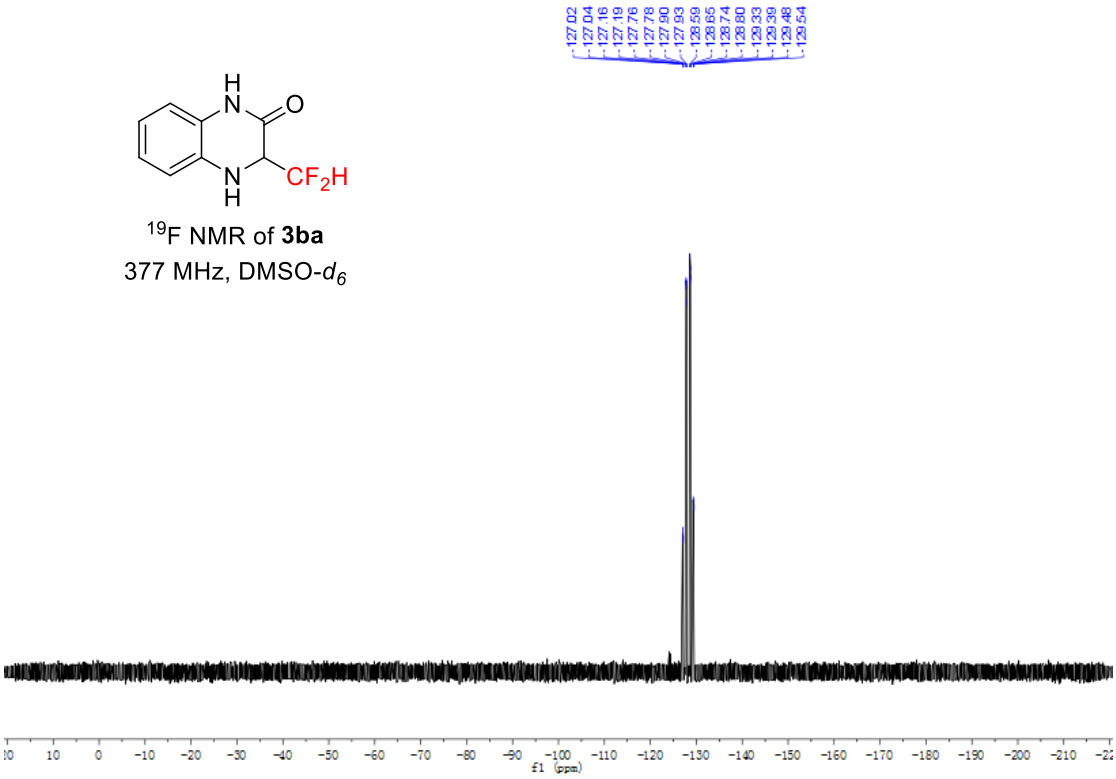
3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3ba)



^{1}H NMR of **3ba**
600 MHz, DMSO-d_6

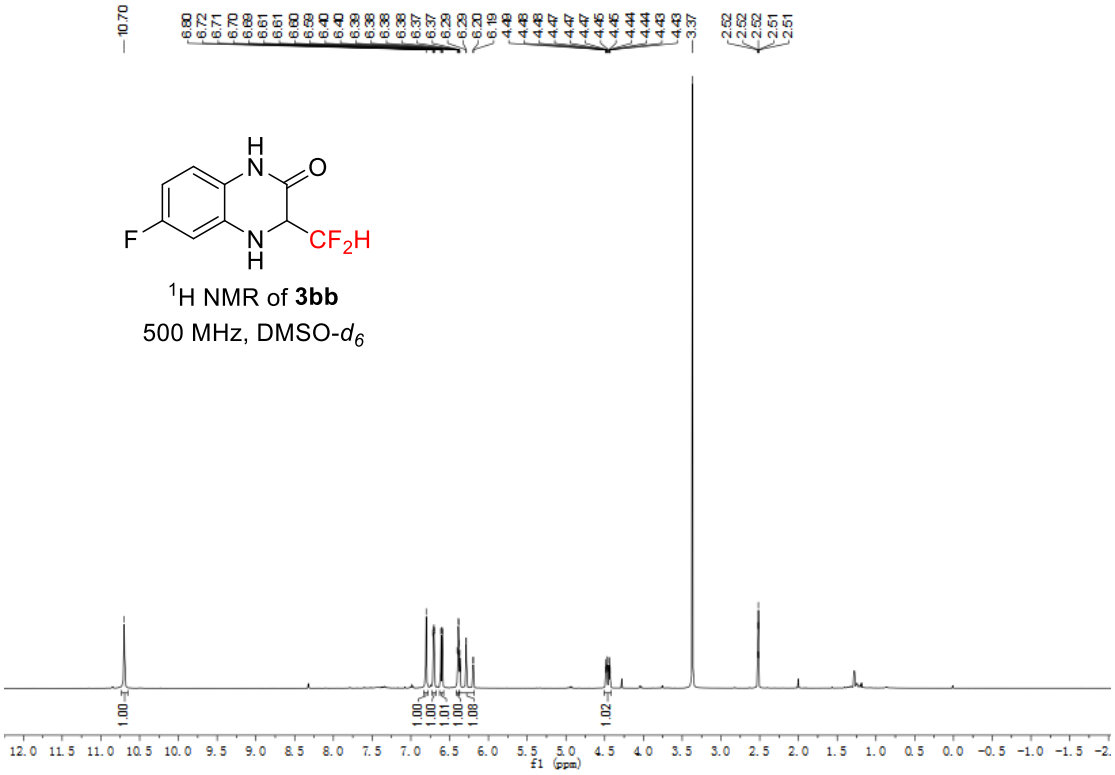


^{13}C NMR of **3ba**
151 MHz, DMSO-d_6

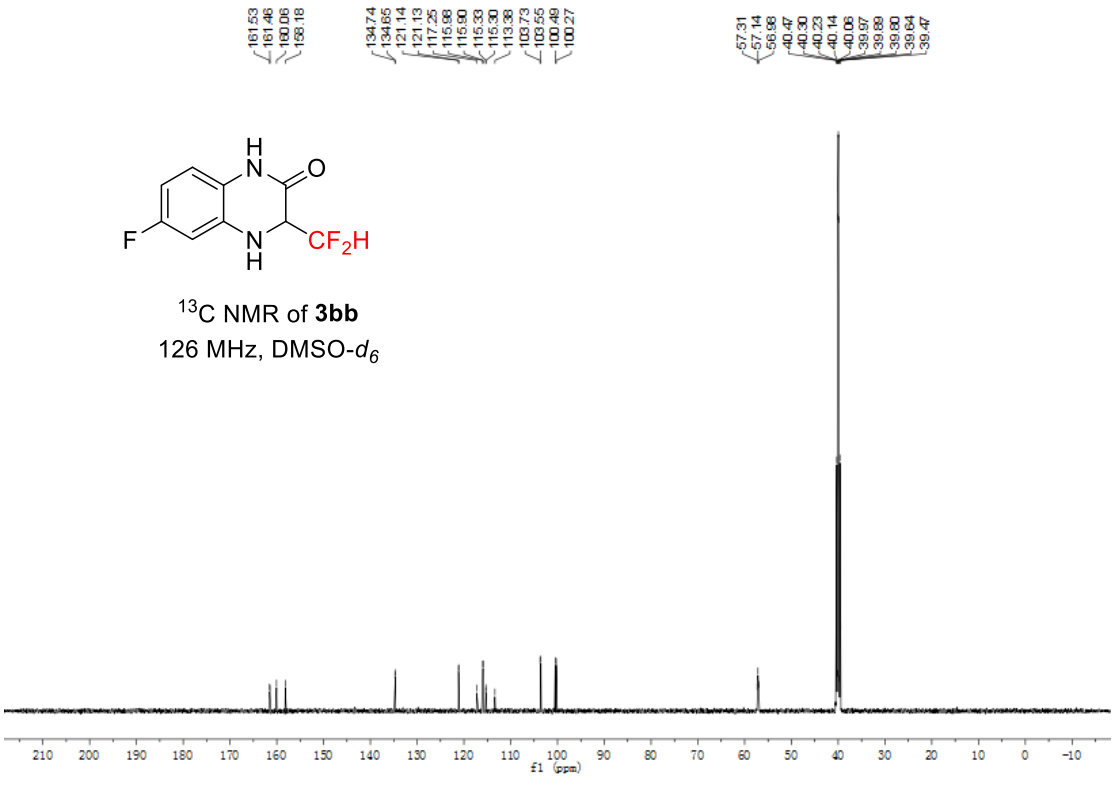


^{19}F NMR of **3ba**
377 MHz, DMSO-d_6

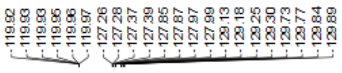
3-(difluoromethyl)-6-fluoro-3,4-dihydroquinoxalin-2(1H)-one (3bb)

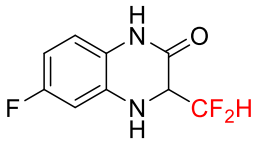


^{1}H NMR of **3bb**
500 MHz, DMSO-d_6

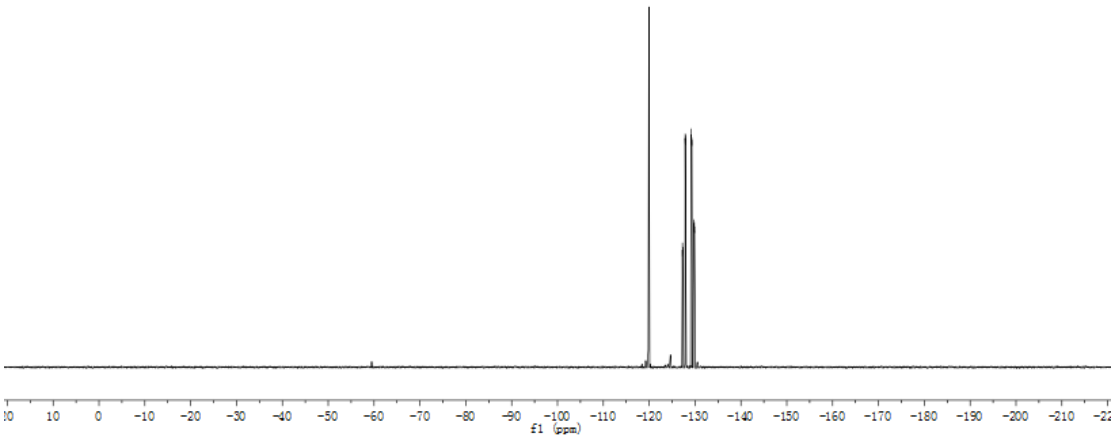


^{13}C NMR of **3bb**
126 MHz, DMSO-d_6

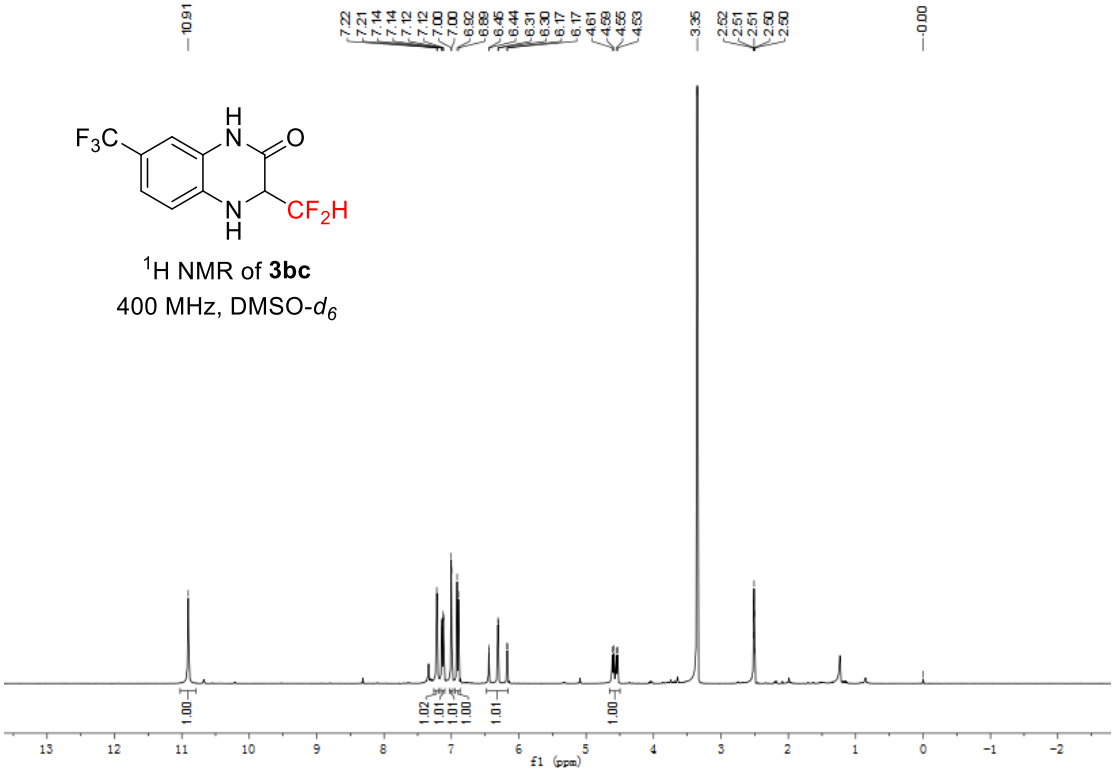




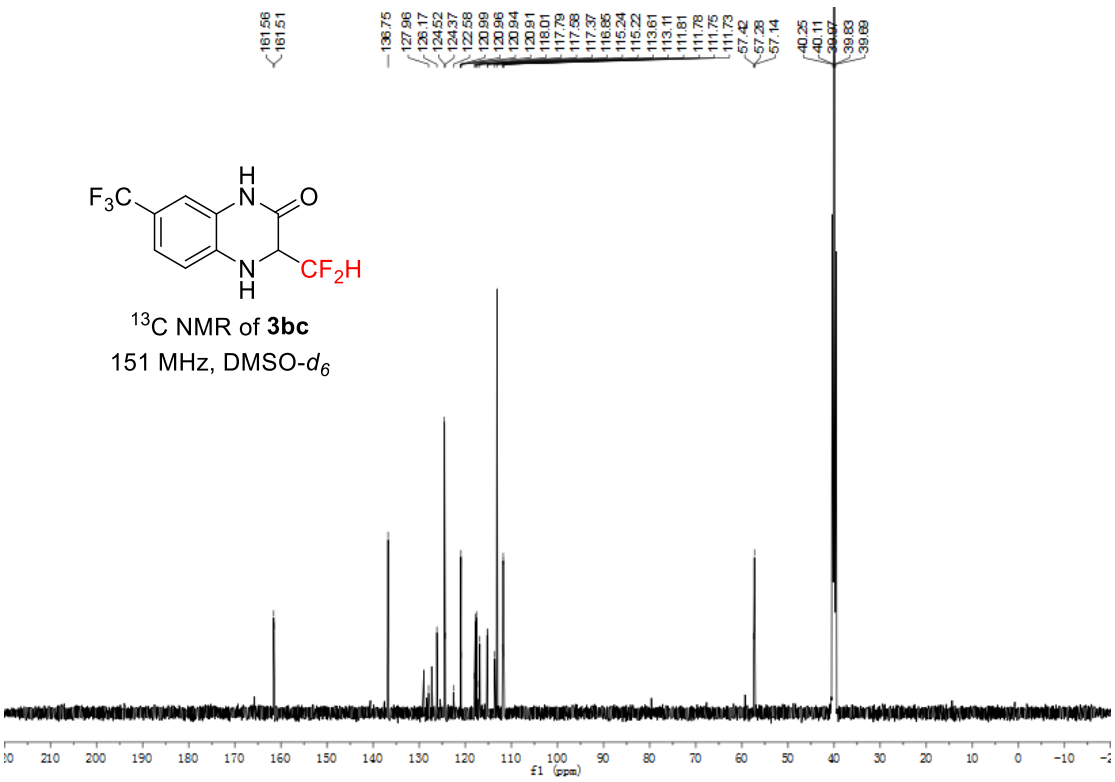
^{19}F NMR of **3bb**
471 MHz, DMSO-d_6



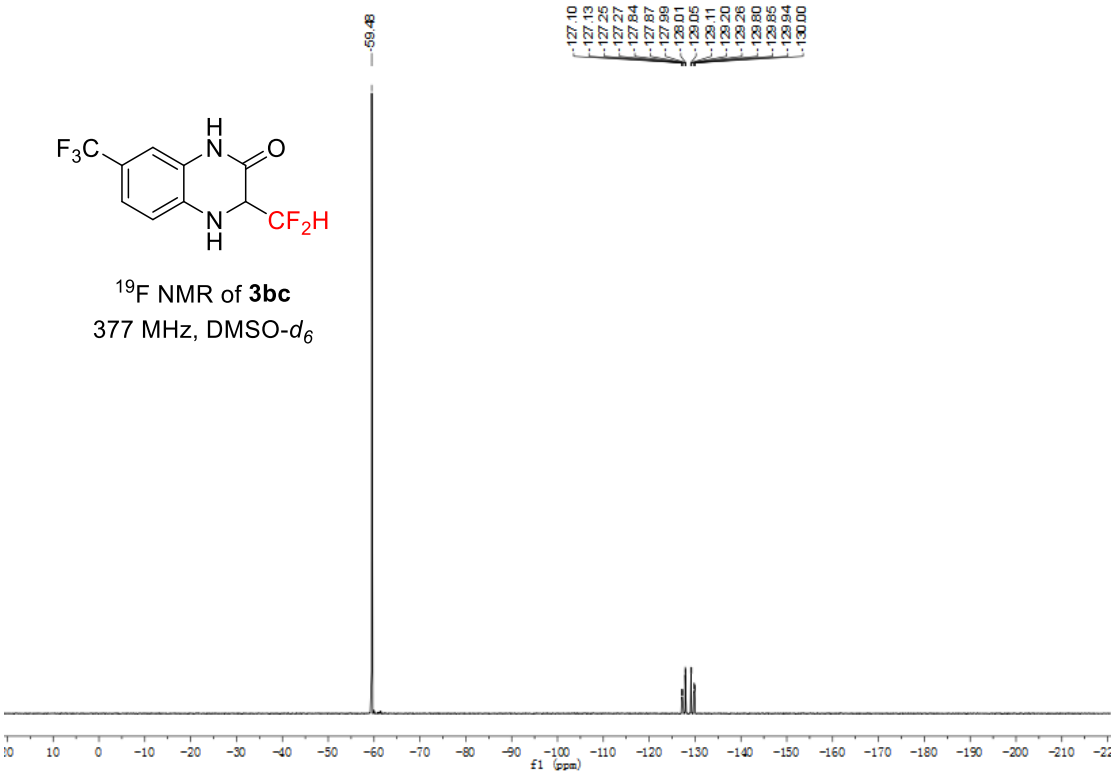
3-(difluoromethyl)-7-(trifluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3bc)



^{1}H NMR of **3bc**
400 MHz, DMSO-d_6

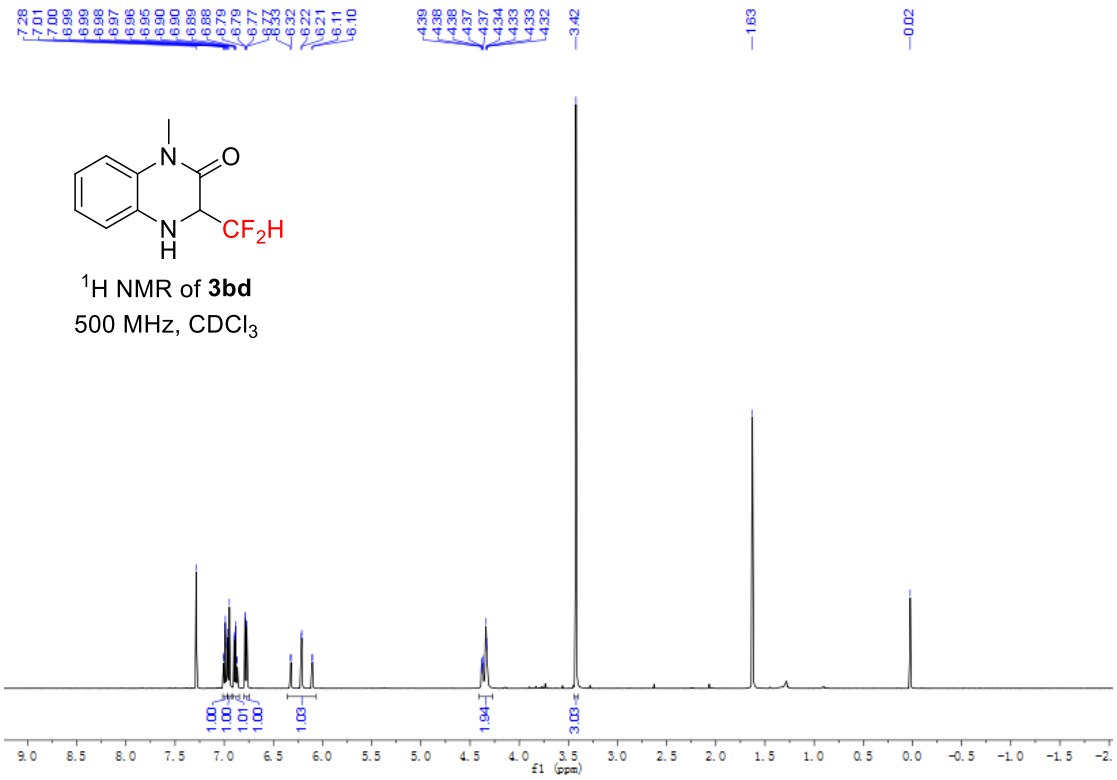


^{13}C NMR of **3bc**
151 MHz, DMSO-d_6

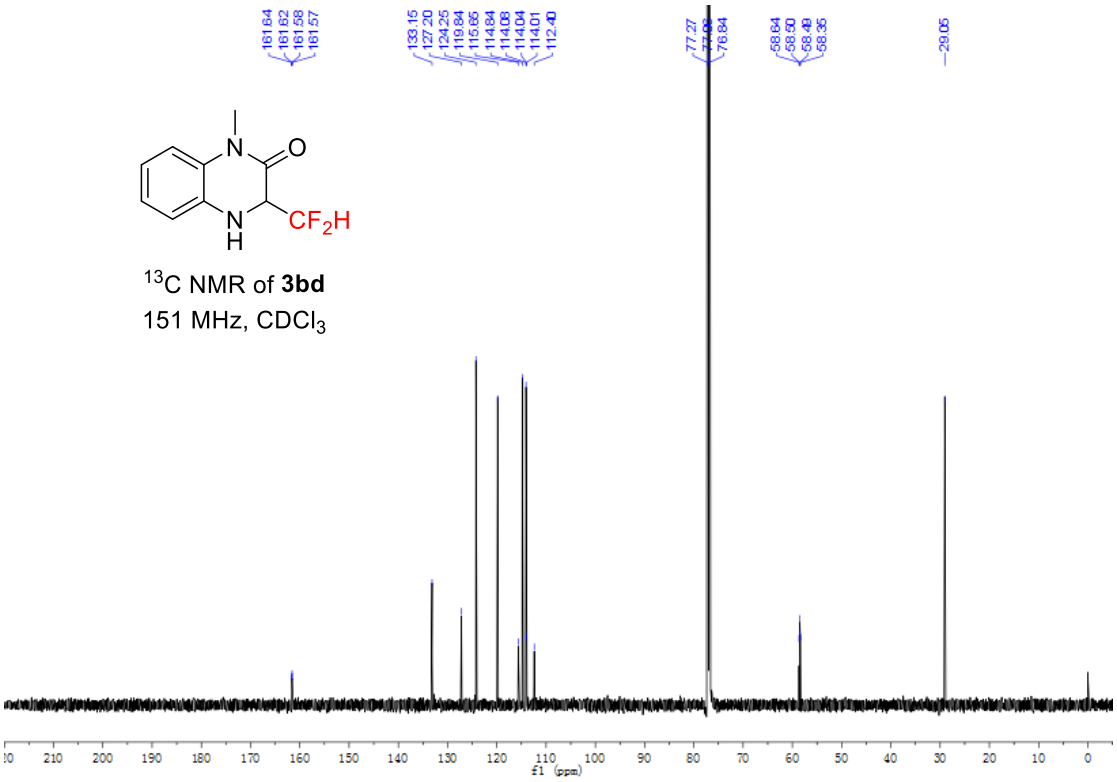


^{19}F NMR of **3bc**
377 MHz, DMSO-d_6

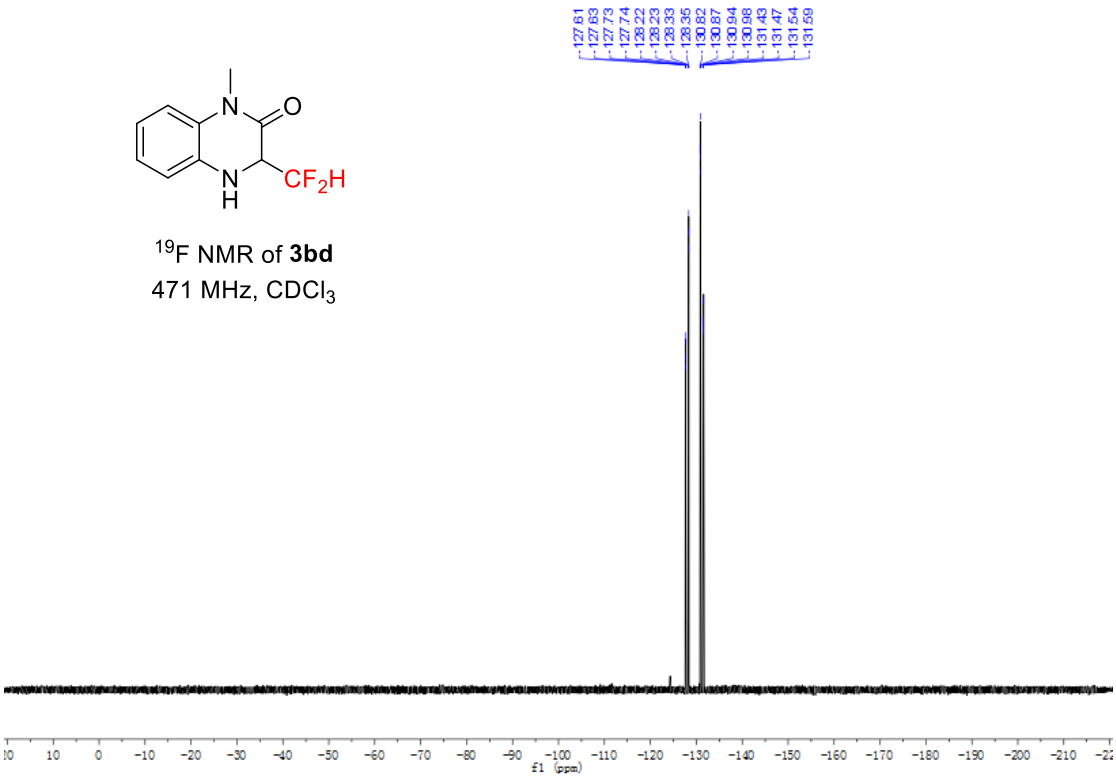
3-(difluoromethyl)-1-methyl-3,4-dihydroquinoxalin-2(1H)-one (3bd)



^{1}H NMR of **3bd**
500 MHz, $CDCl_3$

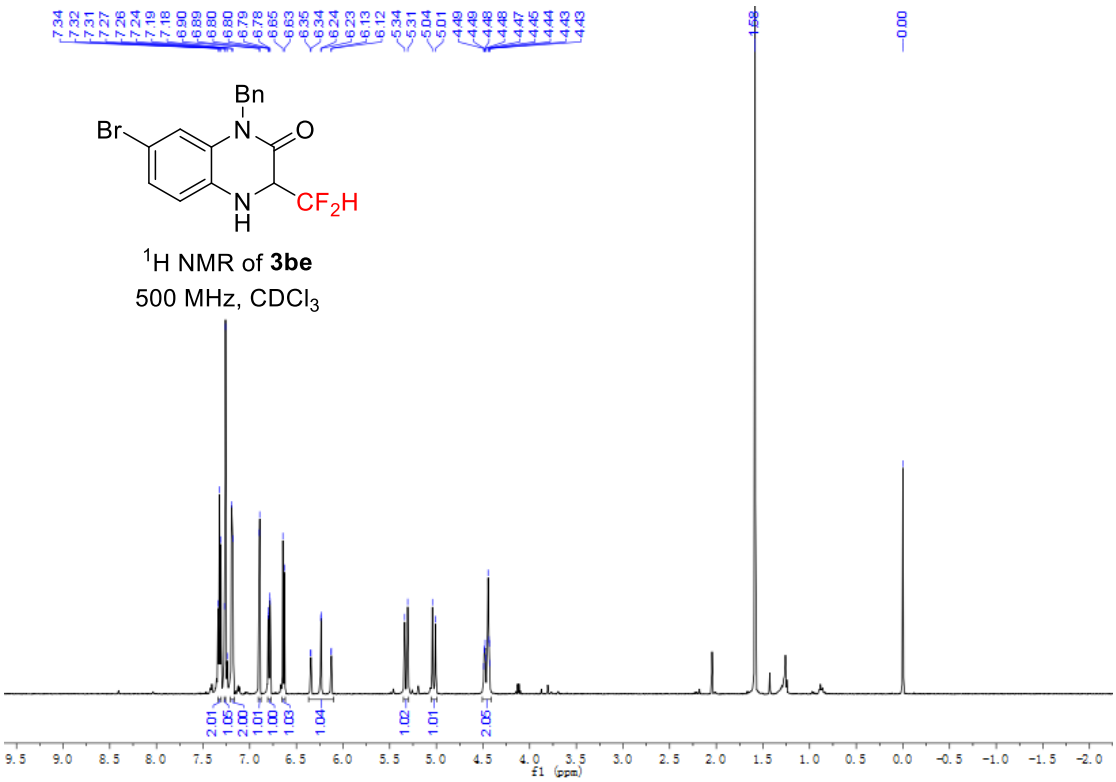


^{13}C NMR of **3bd**
151 MHz, $CDCl_3$

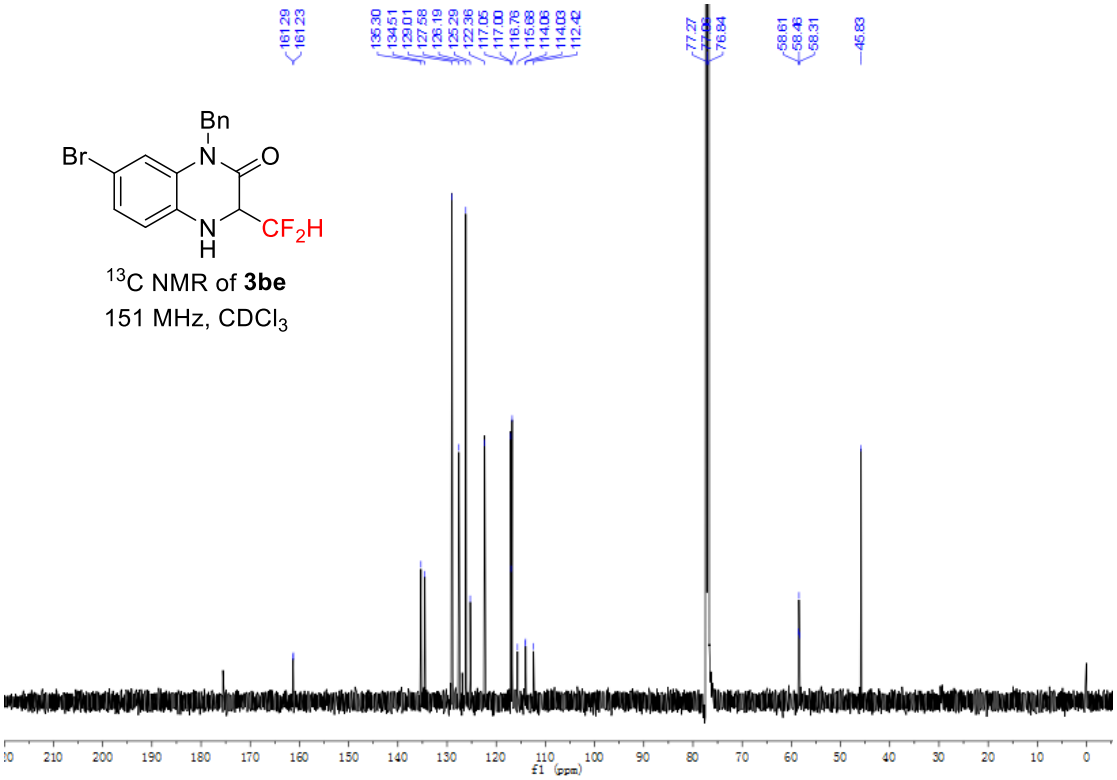


^{19}F NMR of **3bd**
471 MHz, $CDCl_3$

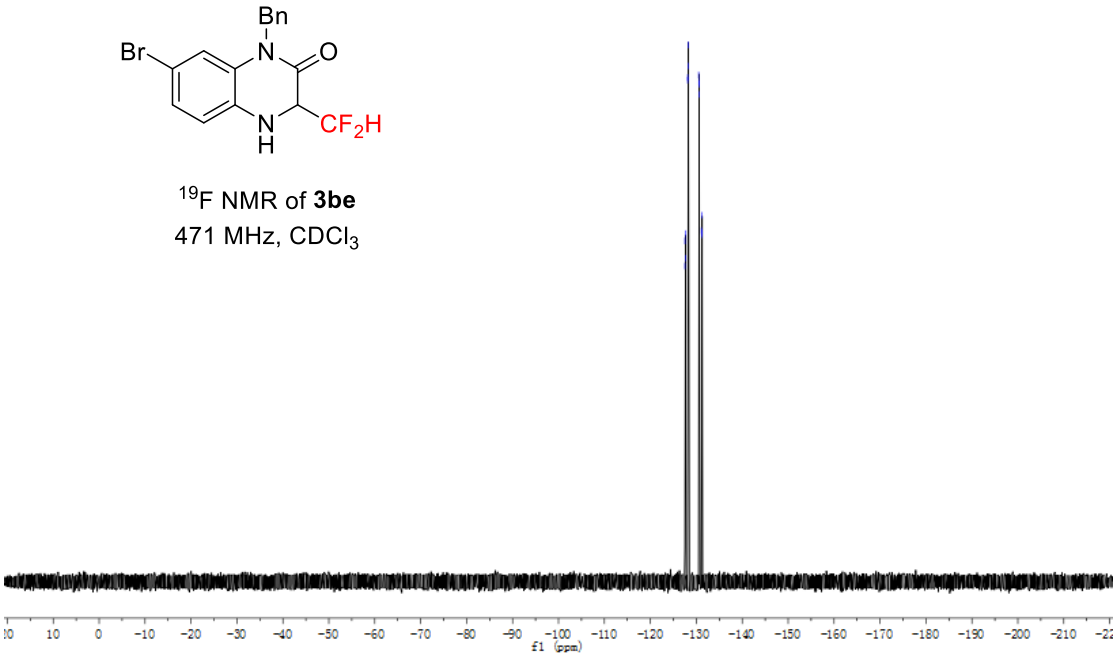
1-benzyl-7-bromo-3-(difluoromethyl)-3,4-dihydroquinoxalin-2(1H)-one (3be)



^{1}H NMR of **3be**
500 MHz, $CDCl_3$

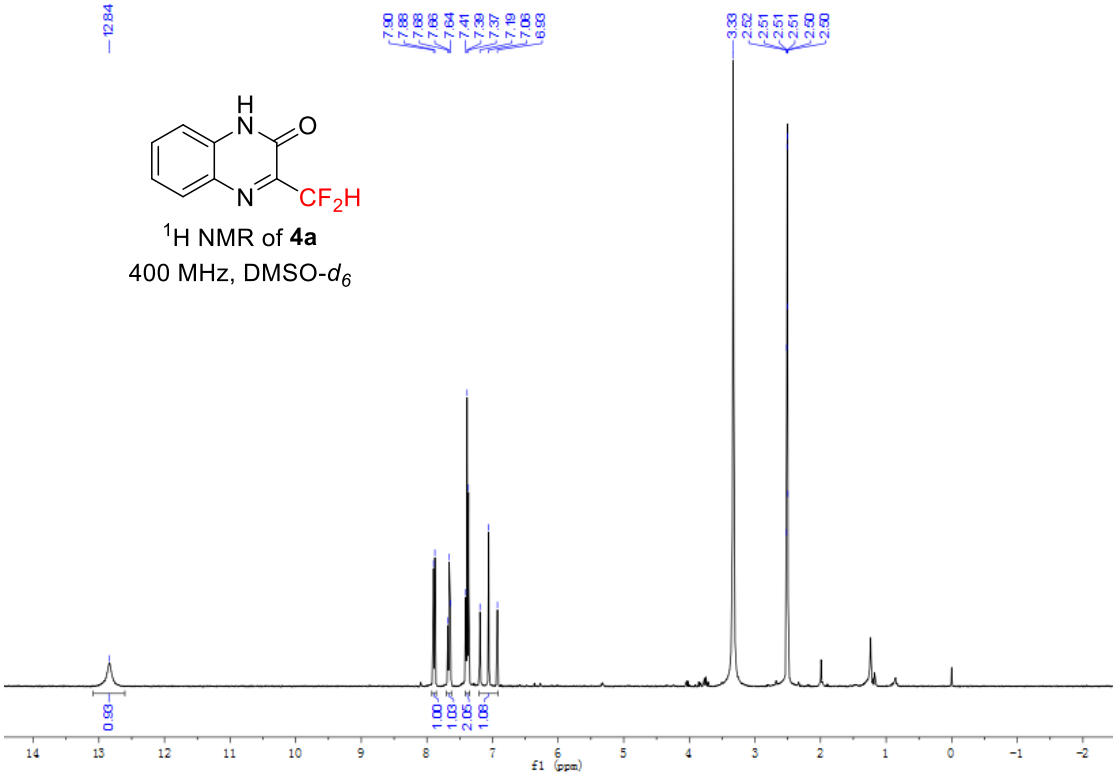


^{13}C NMR of **3be**
151 MHz, $CDCl_3$

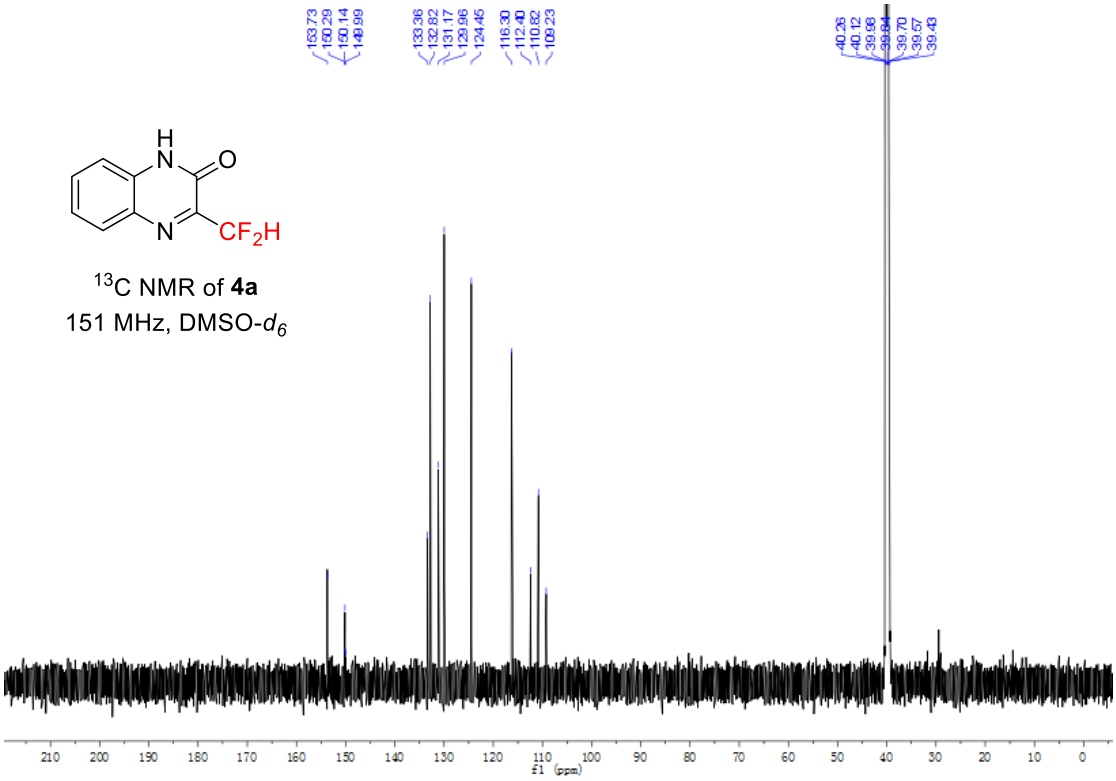


^{19}F NMR of **3be**
471 MHz, $CDCl_3$

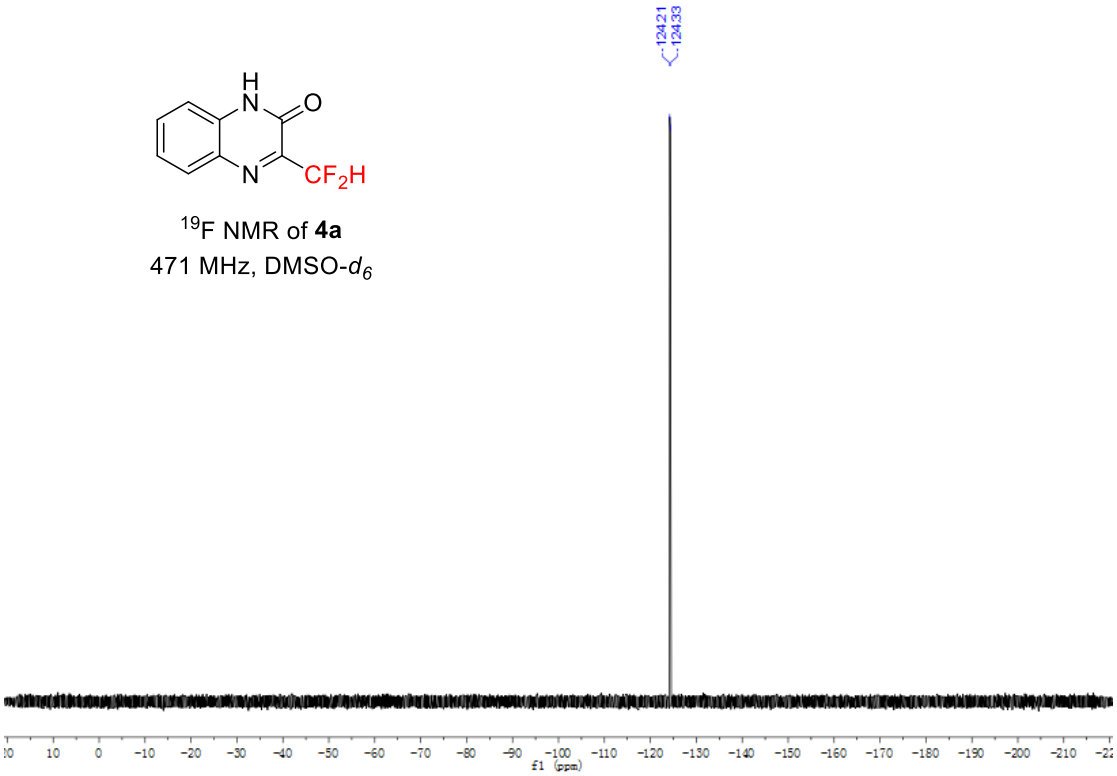
3-(difluoromethyl)quinoxalin-2(1H)-one (4a)



^{1}H NMR of **4a**
400 MHz, DMSO-d_6

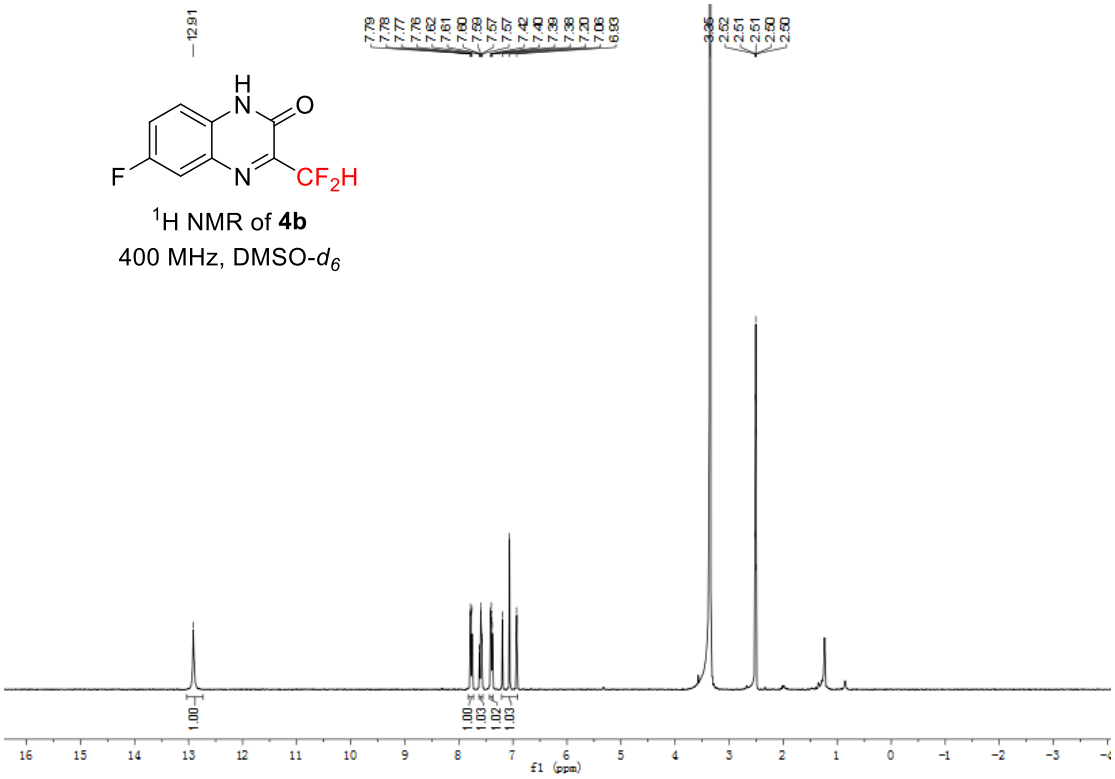


^{13}C NMR of **4a**
151 MHz, DMSO-d_6

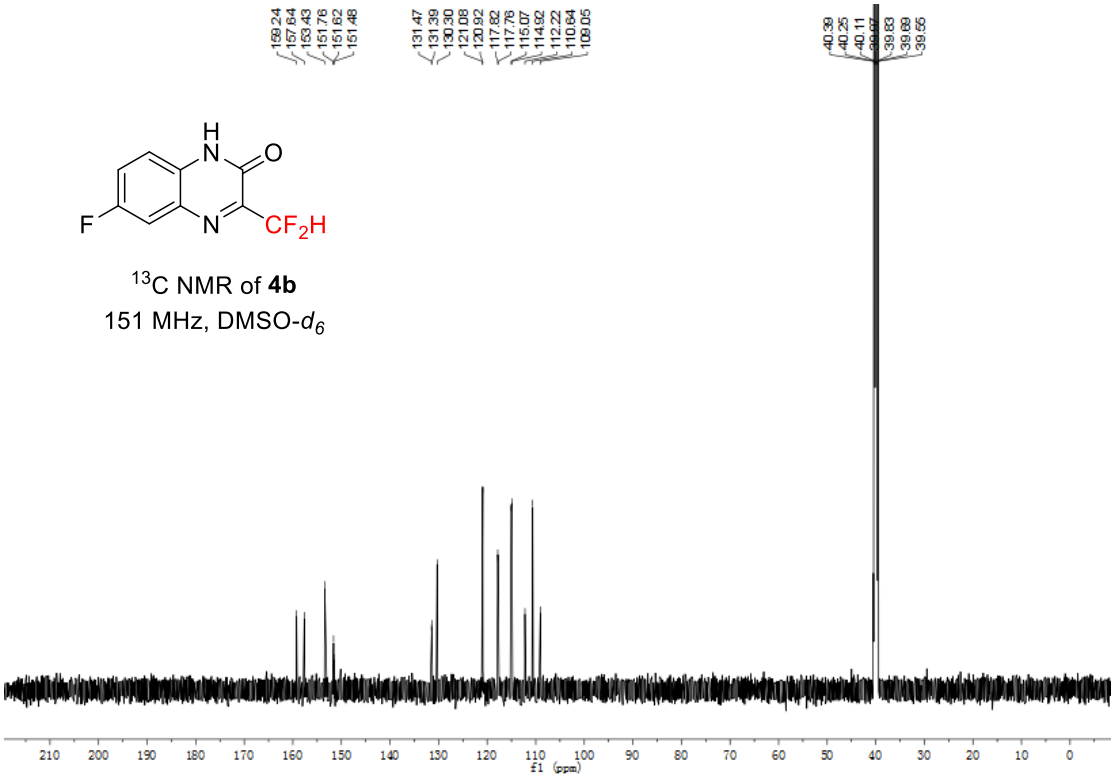


^{19}F NMR of **4a**
471 MHz, DMSO-d_6

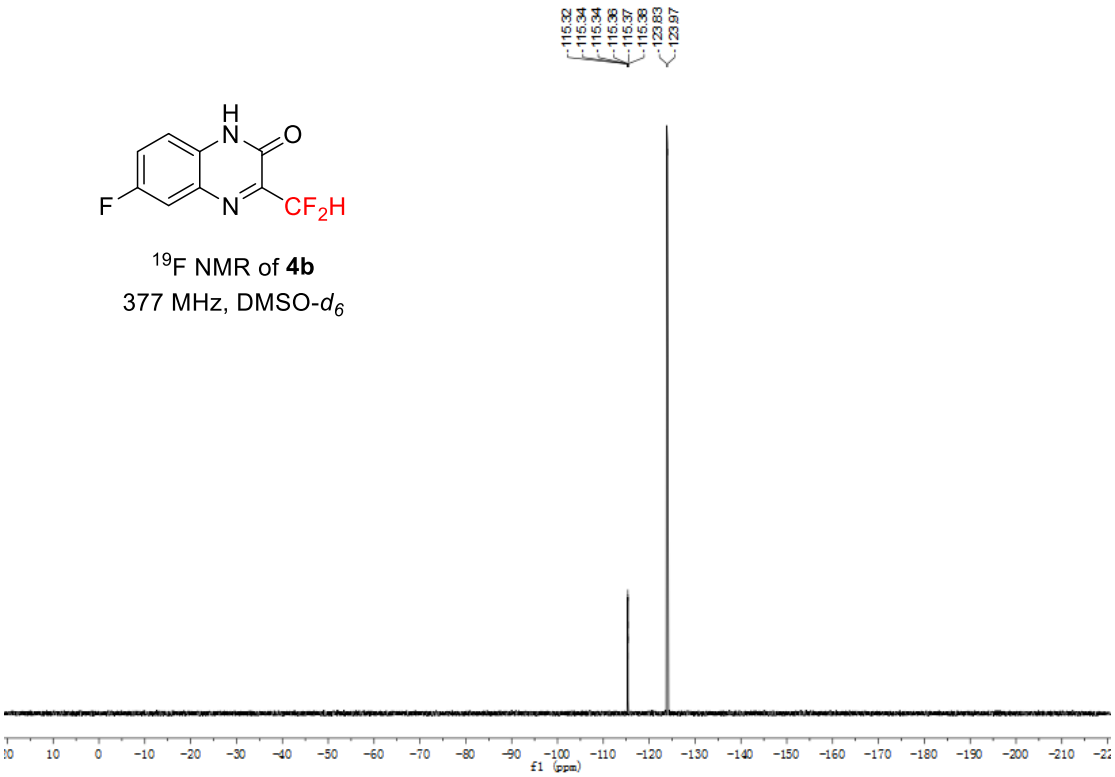
3-(difluoromethyl)-6-fluoroquinoxalin-2(1H)-one (4b)



^{1}H NMR of **4b**
400 MHz, DMSO-d_6

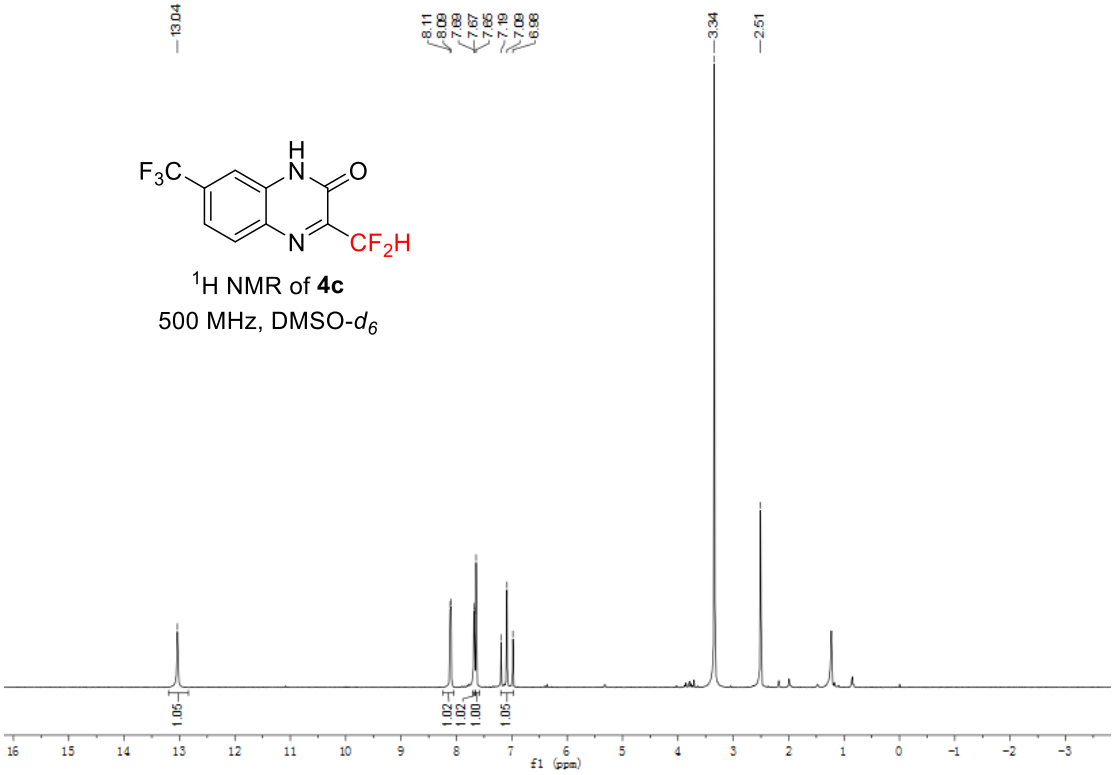


^{13}C NMR of **4b**
151 MHz, DMSO-d_6

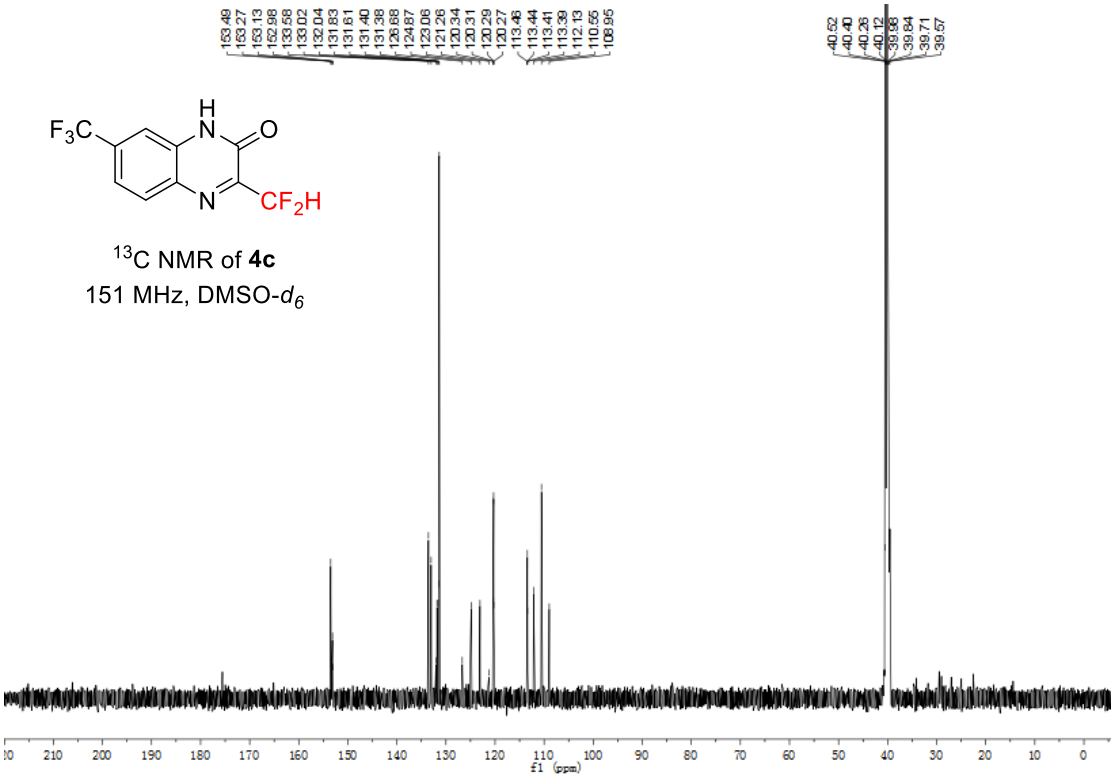


^{19}F NMR of **4b**
377 MHz, DMSO-d_6

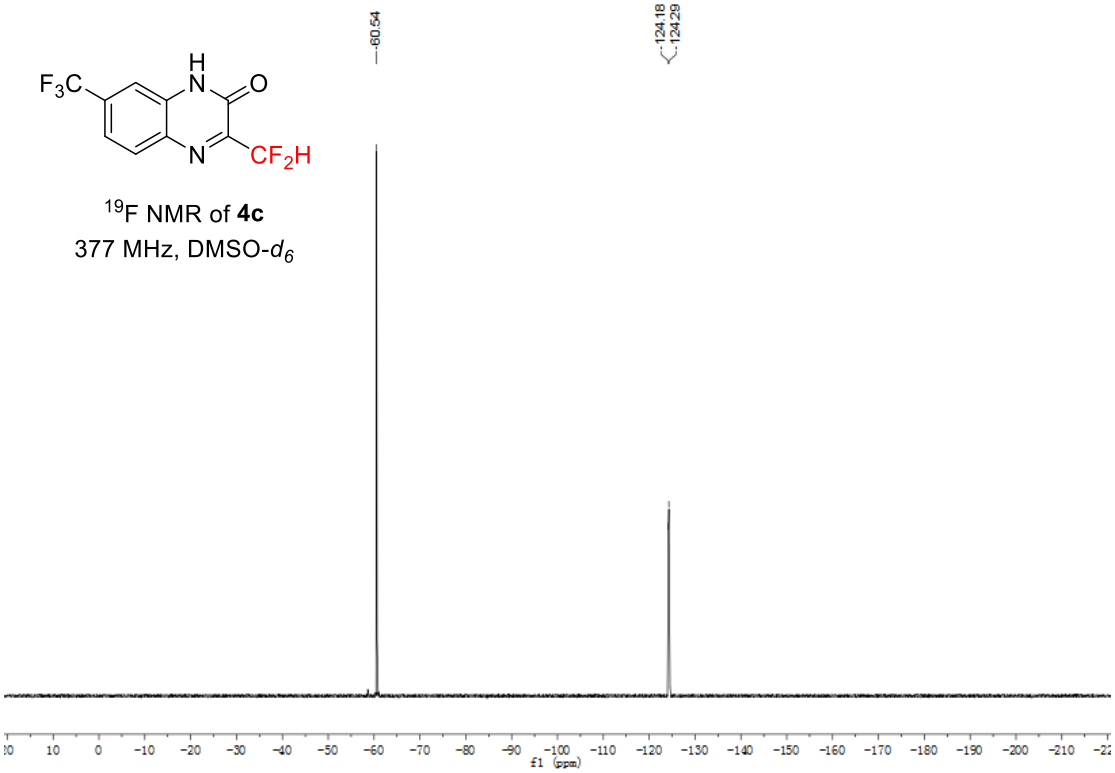
3-(difluoromethyl)-7-(trifluoromethyl)quinoxalin-2(1H)-one (4c)



^{1}H NMR of **4c**
500 MHz, DMSO-d_6

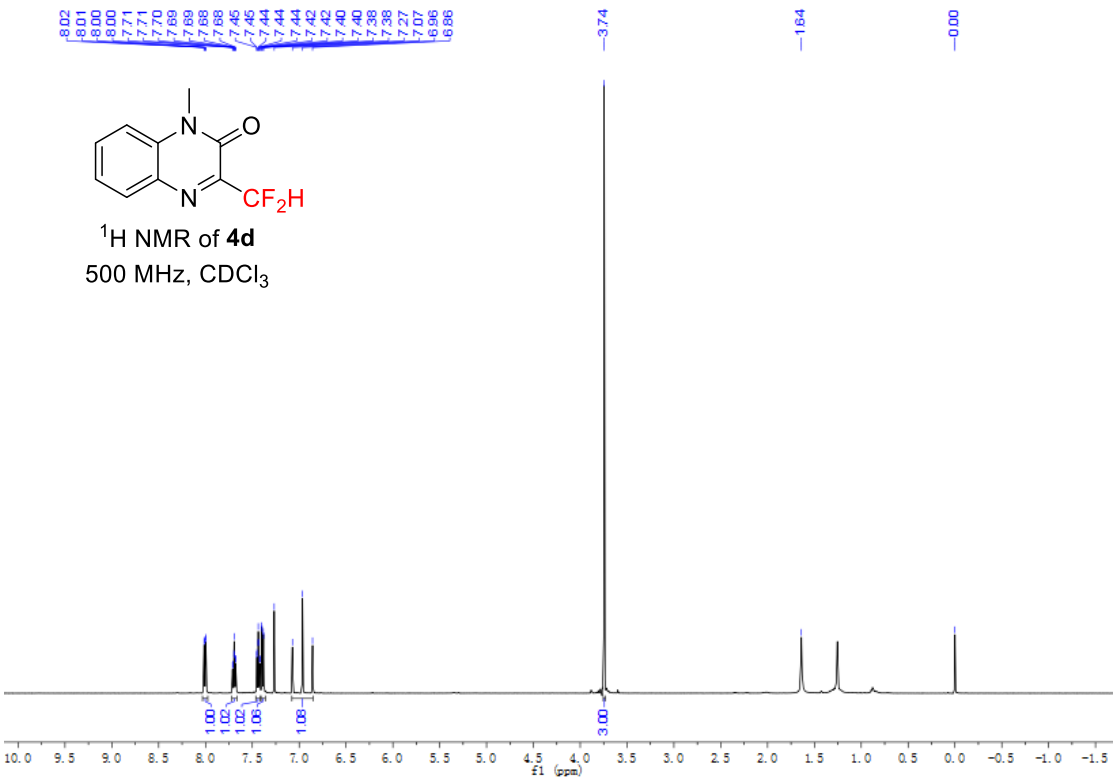


^{13}C NMR of **4c**
151 MHz, DMSO-d_6

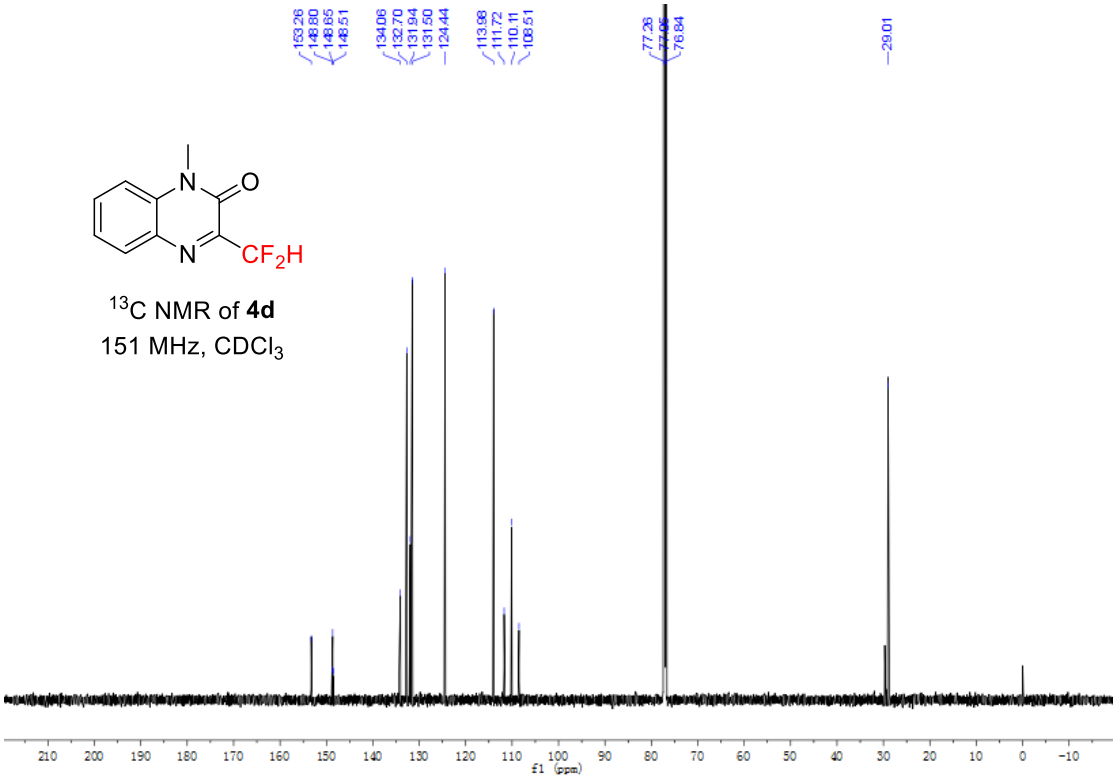


^{19}F NMR of **4c**
377 MHz, DMSO-d_6

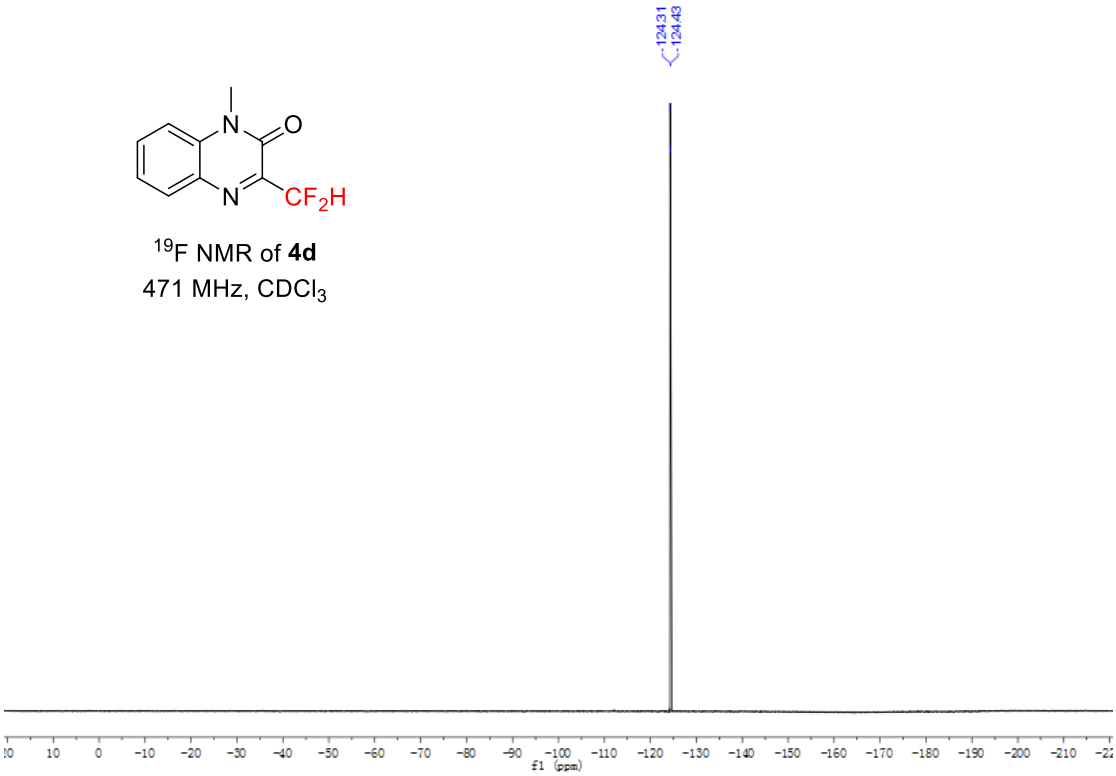
3-(difluoromethyl)-1-methylquinoxalin-2(1H)-one (4d)



^{1}H NMR of **4d**
500 MHz, $CDCl_3$

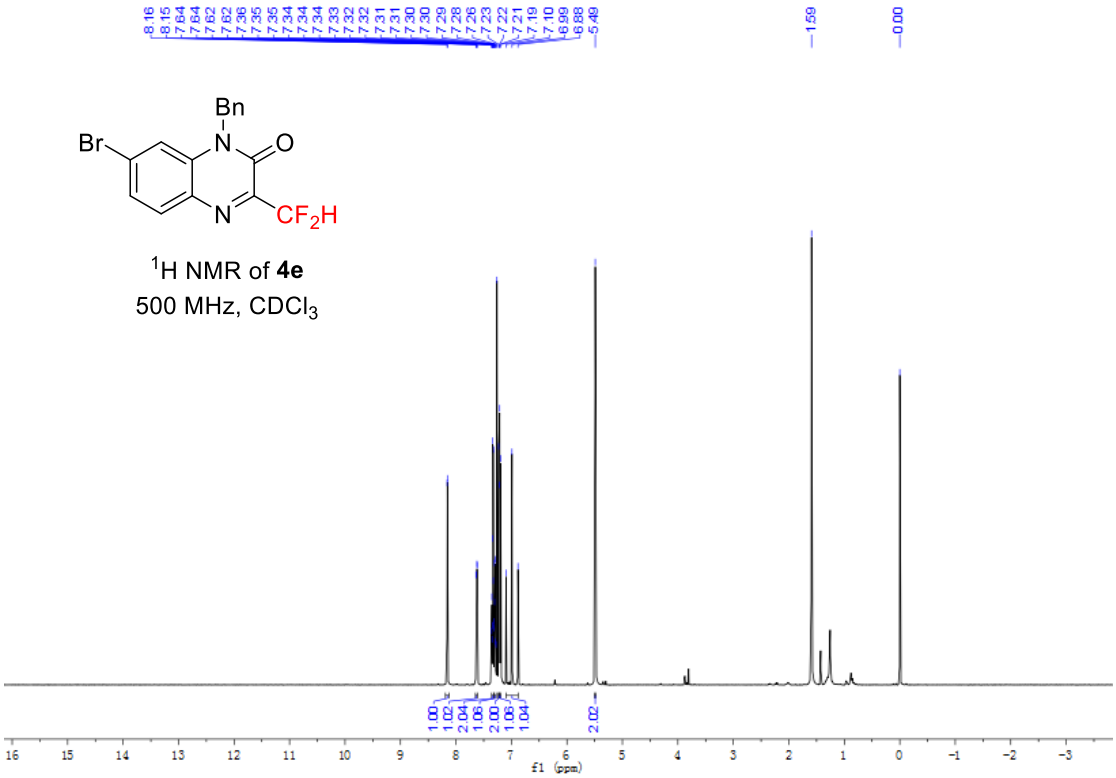


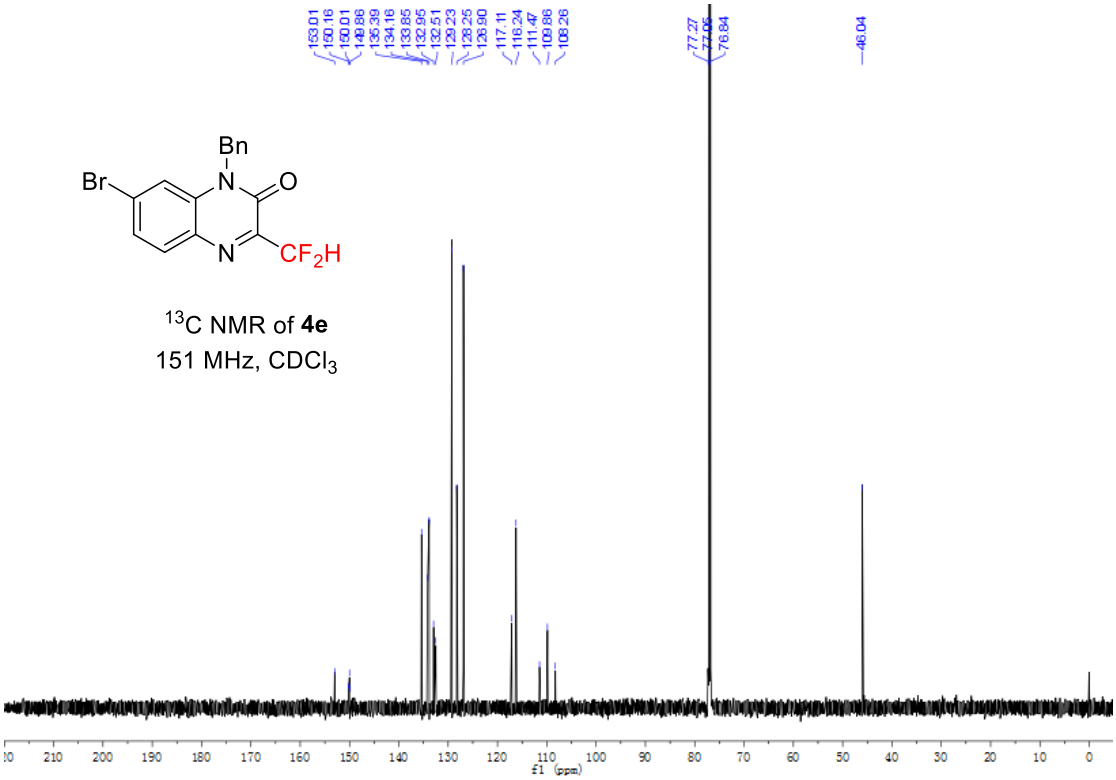
^{13}C NMR of **4d**
151 MHz, $CDCl_3$

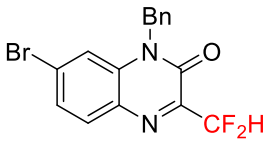


^{19}F NMR of **4d**
471 MHz, $CDCl_3$

1-benzyl-7-bromo-3-(difluoromethyl)quinoxalin-2(1H)-one (4e)



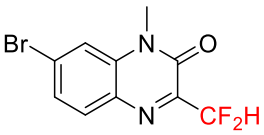




^{19}F NMR of **4e**

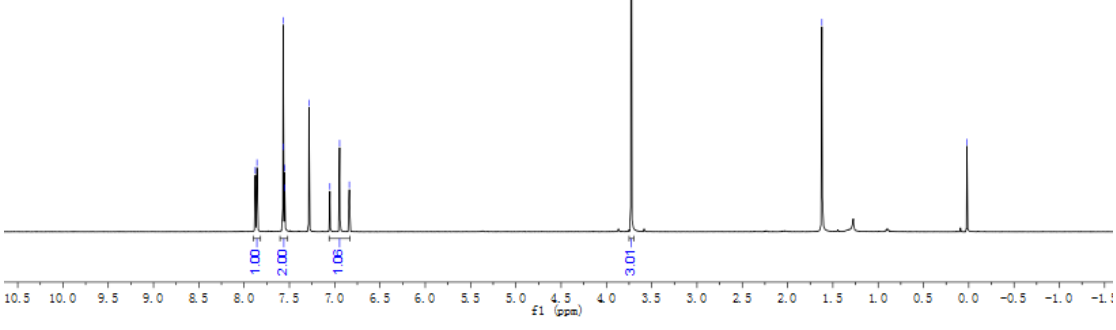
471 MHz, $CDCl_3$

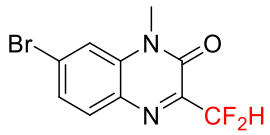
7-bromo-3-(difluoromethyl)-1-methylquinoxalin-2(1H)-one (4f)



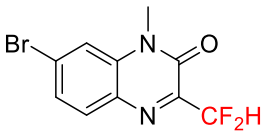
^{1}H NMR of **4f**

500 MHz, $CDCl_3$



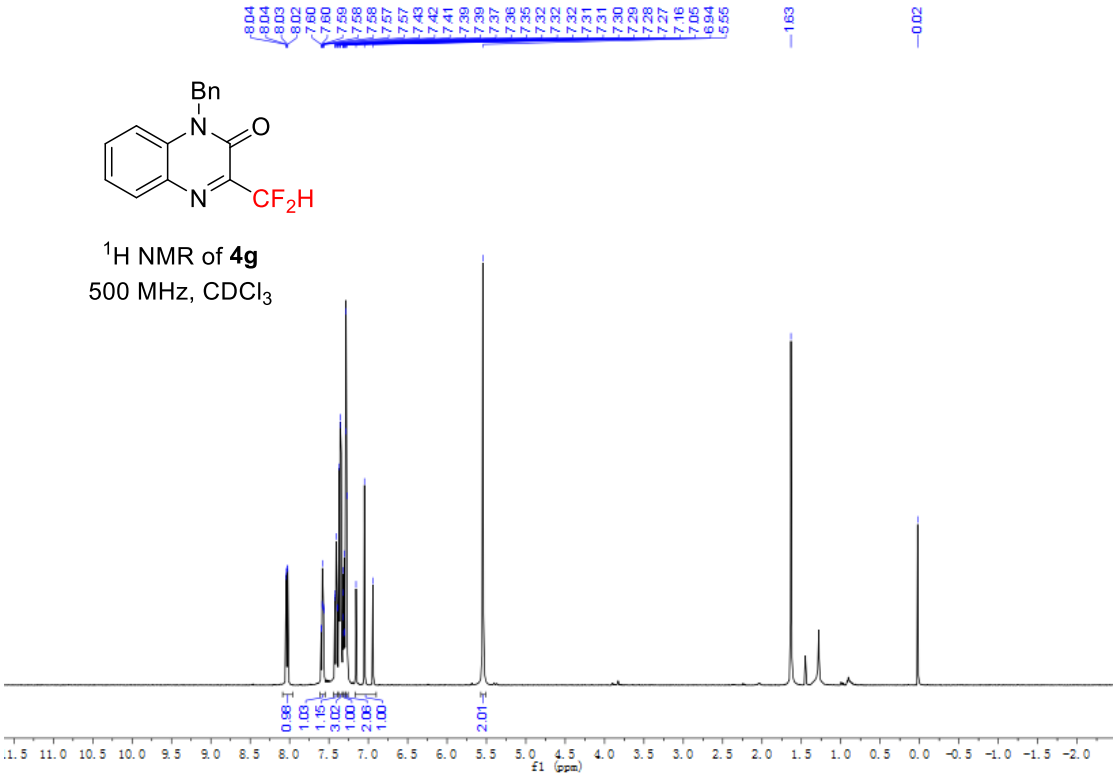


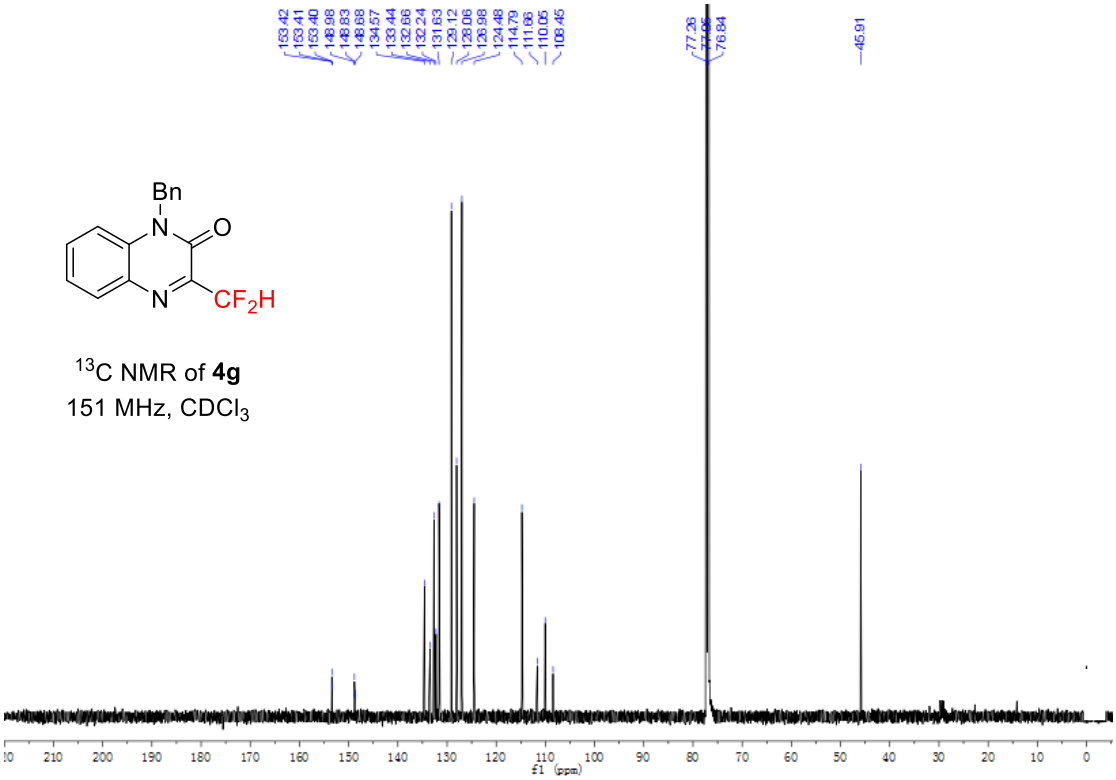
^{13}C NMR of **4f**
151 MHz, $CDCl_3$

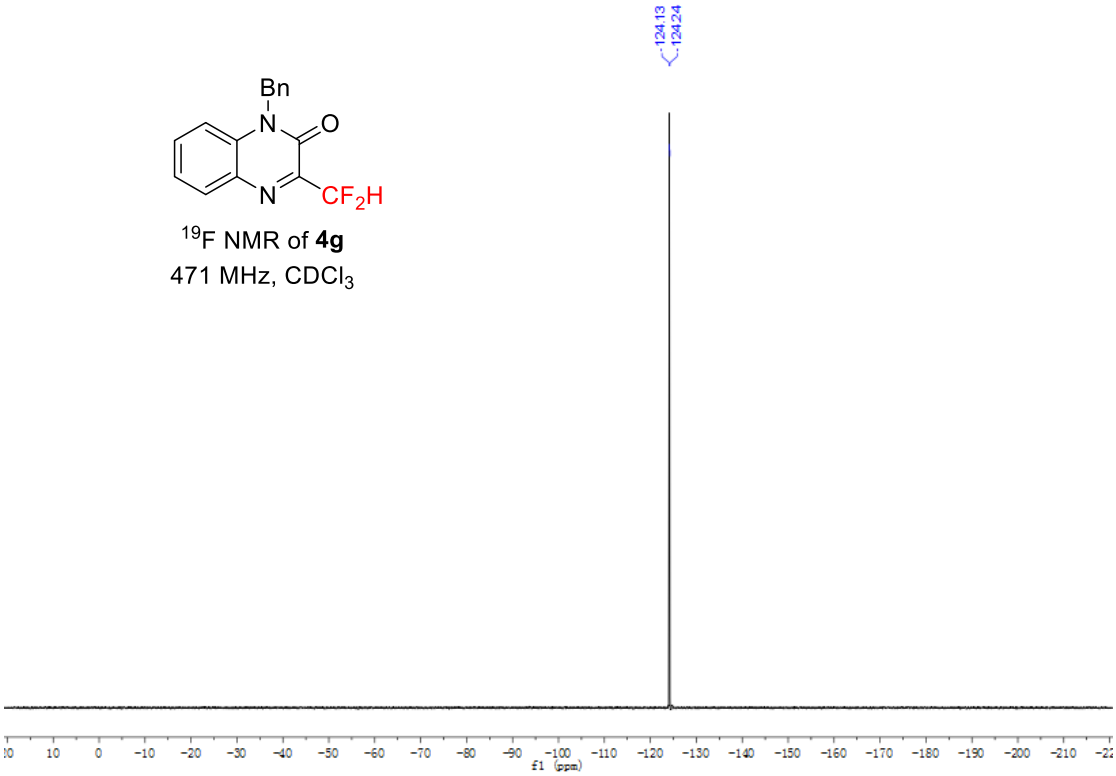


^{19}F NMR of **4f**
471 MHz, $CDCl_3$

1-benzyl-3-(difluoromethyl)quinoxalin-2(1H)-one (4g)

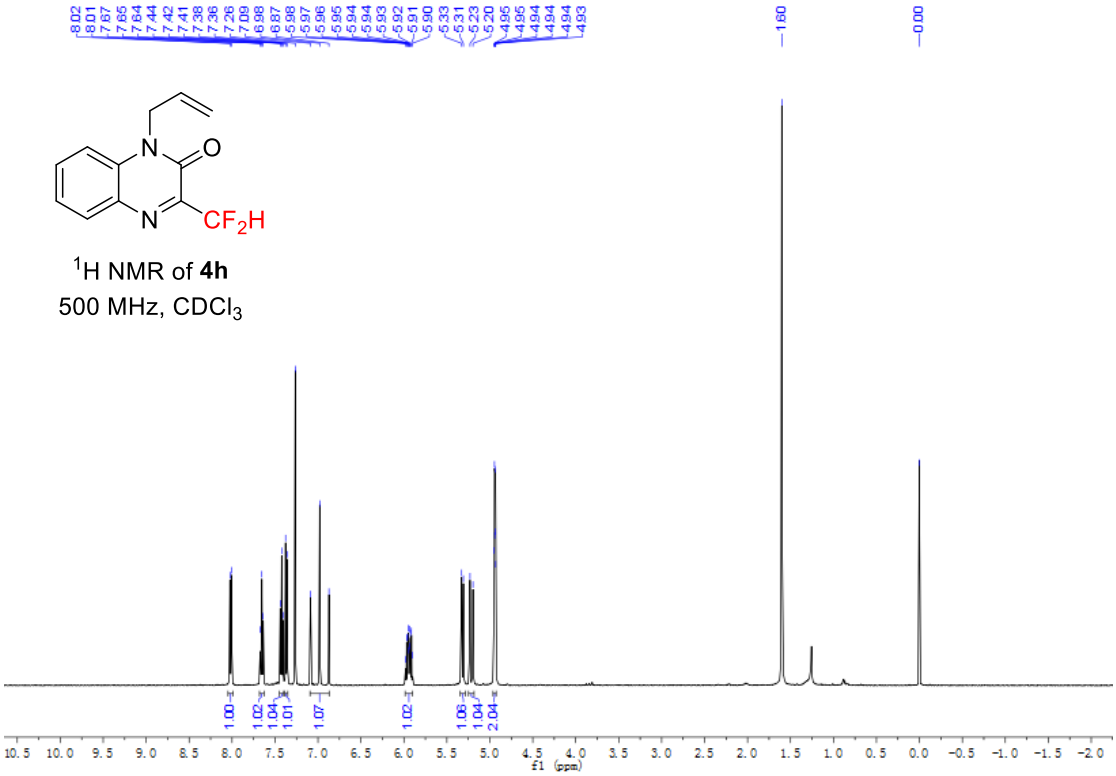




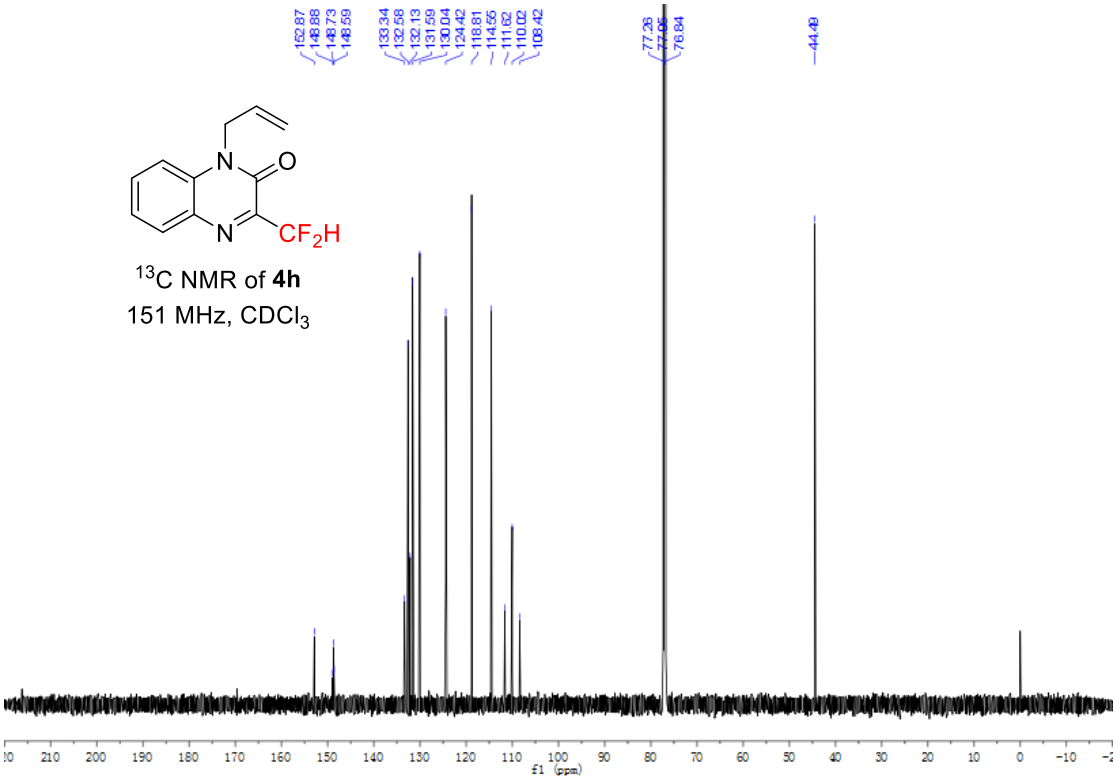


^{19}F NMR of **4g**
471 MHz, $CDCl_3$

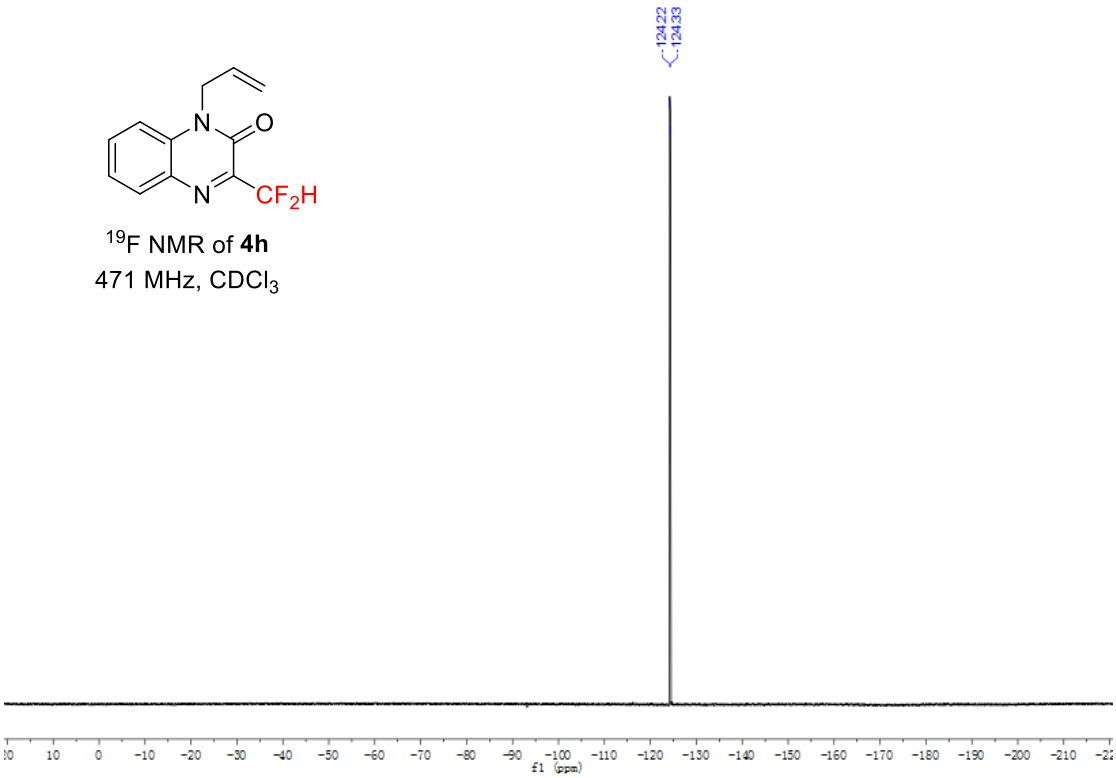
1-allyl-3-(difluoromethyl)quinoxalin-2(1H)-one (4h)



^{1}H NMR of **4h**
500 MHz, $CDCl_3$

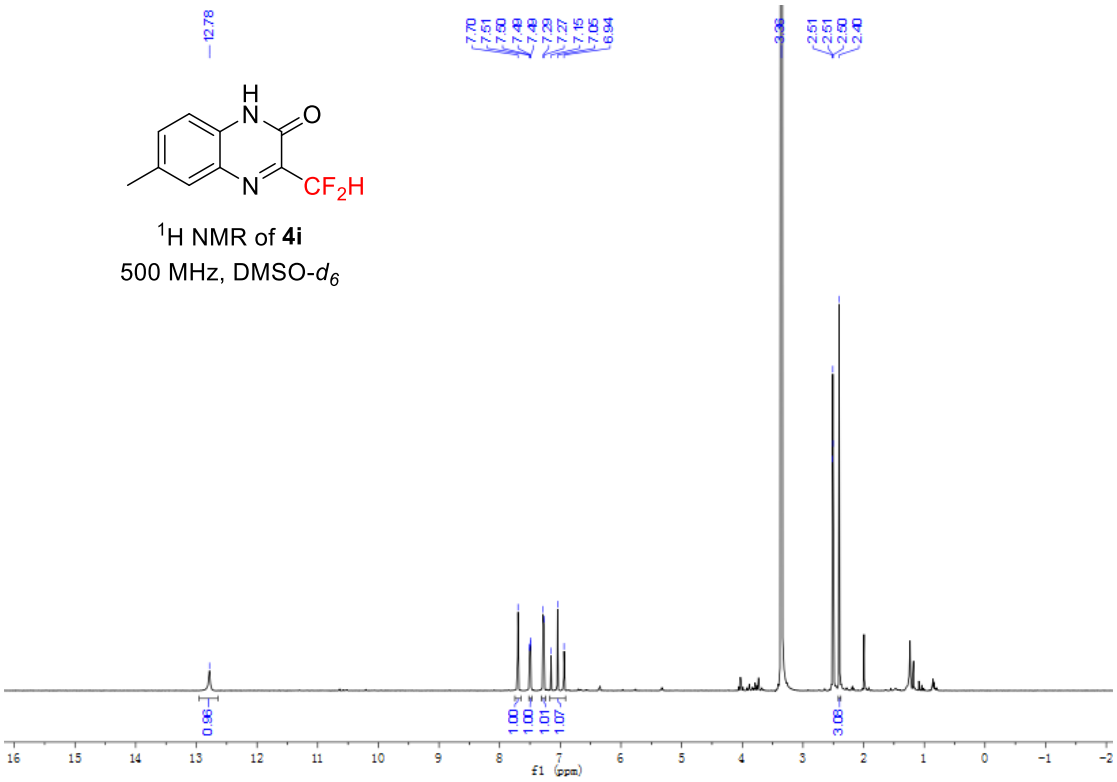


^{13}C NMR of **4h**
151 MHz, $CDCl_3$

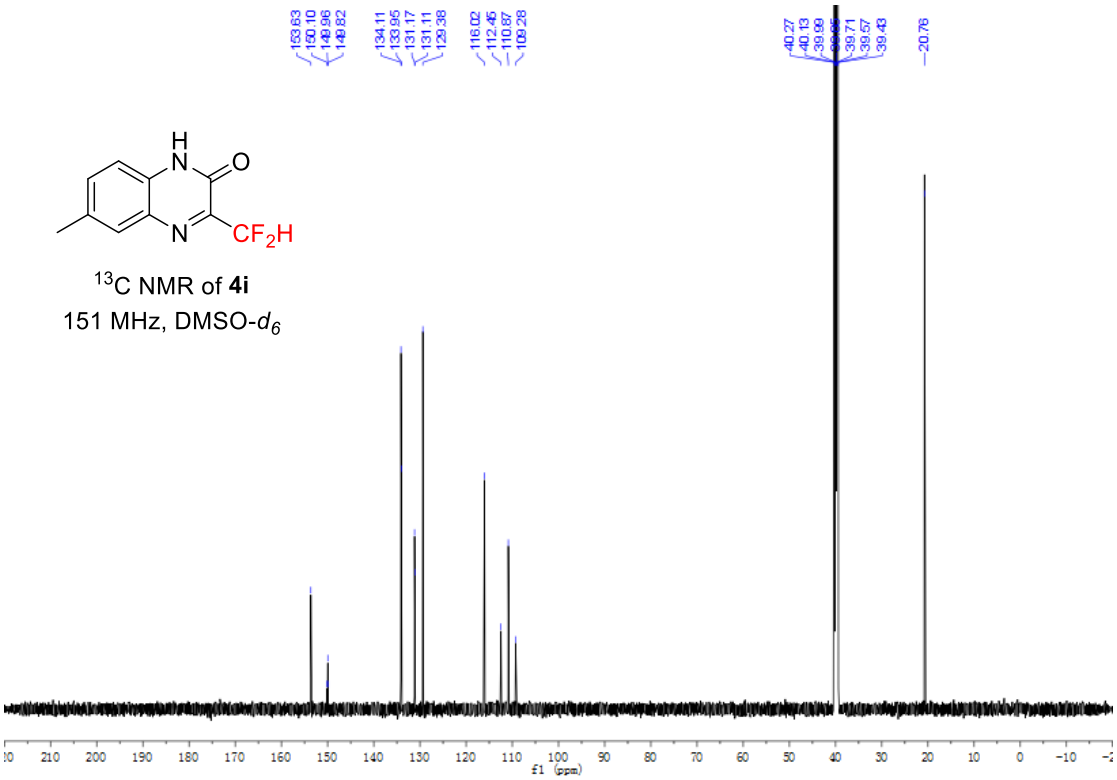


^{19}F NMR of **4h**
471 MHz, $CDCl_3$

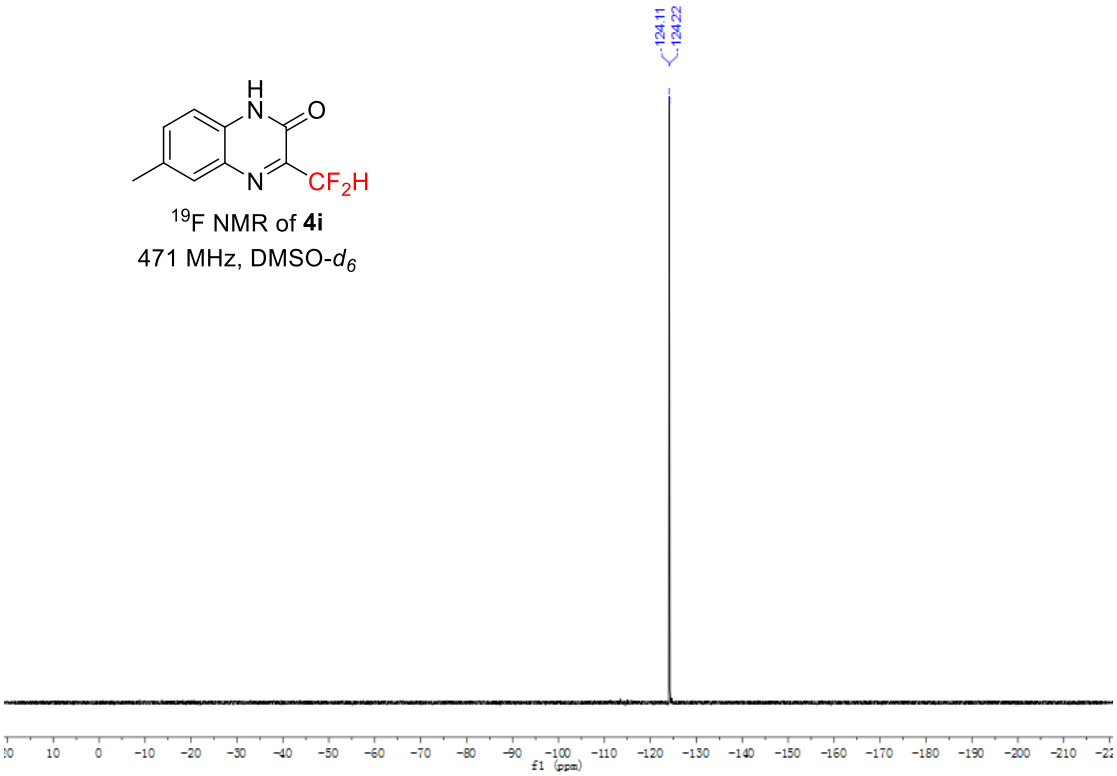
3-(difluoromethyl)-6-methylquinoxalin-2(1H)-one (4i)



^{1}H NMR of **4i**
500 MHz, DMSO-d_6

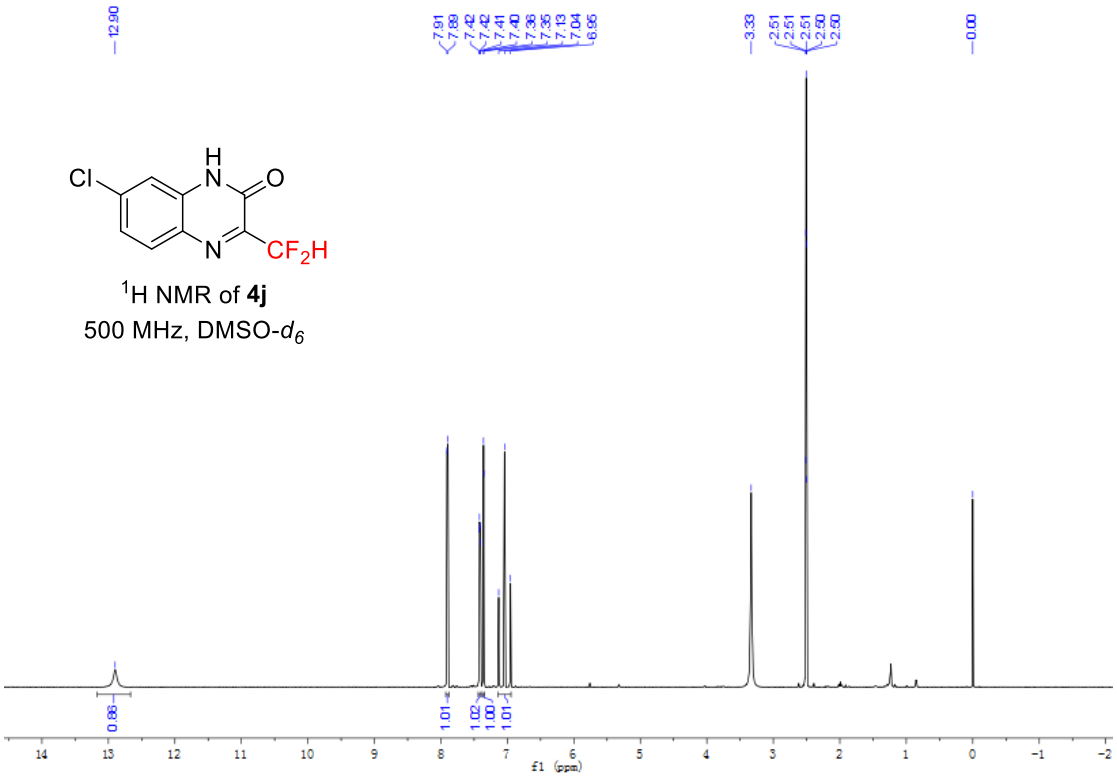


^{13}C NMR of **4i**
151 MHz, DMSO-d_6

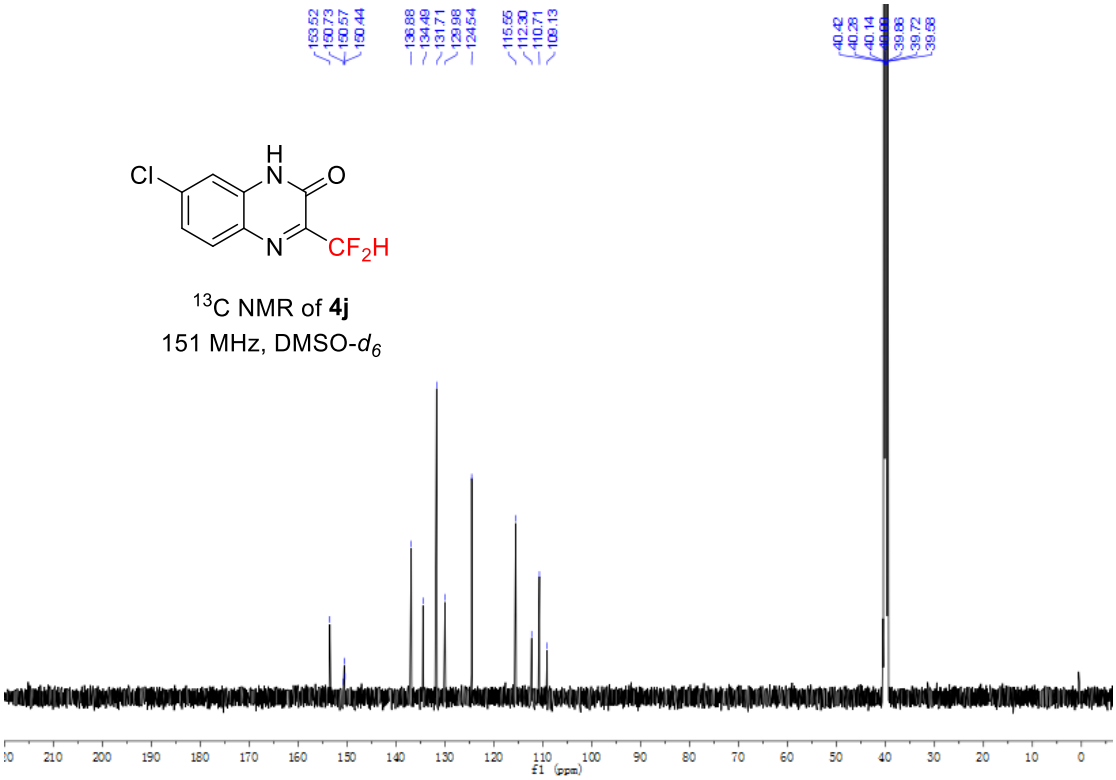


^{19}F NMR of **4i**
471 MHz, DMSO-d_6

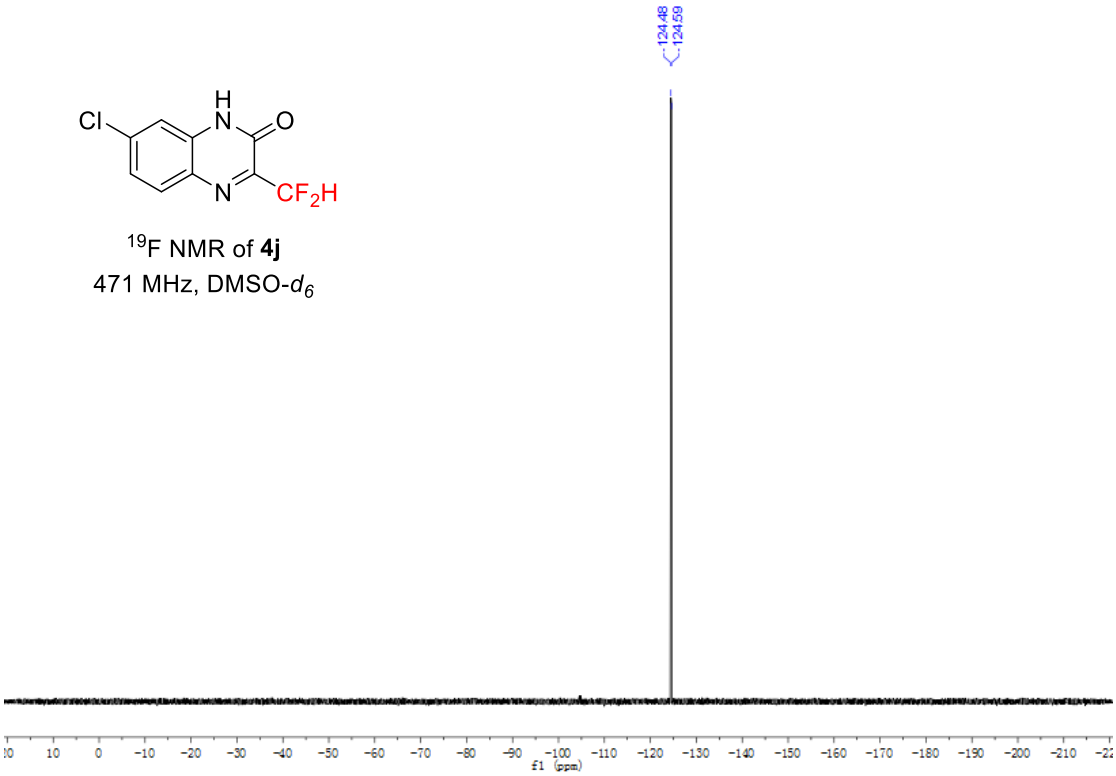
7-chloro-3-(difluoromethyl)quinoxalin-2(1H)-one (4j)



^{1}H NMR of **4j**
500 MHz, DMSO-d_6

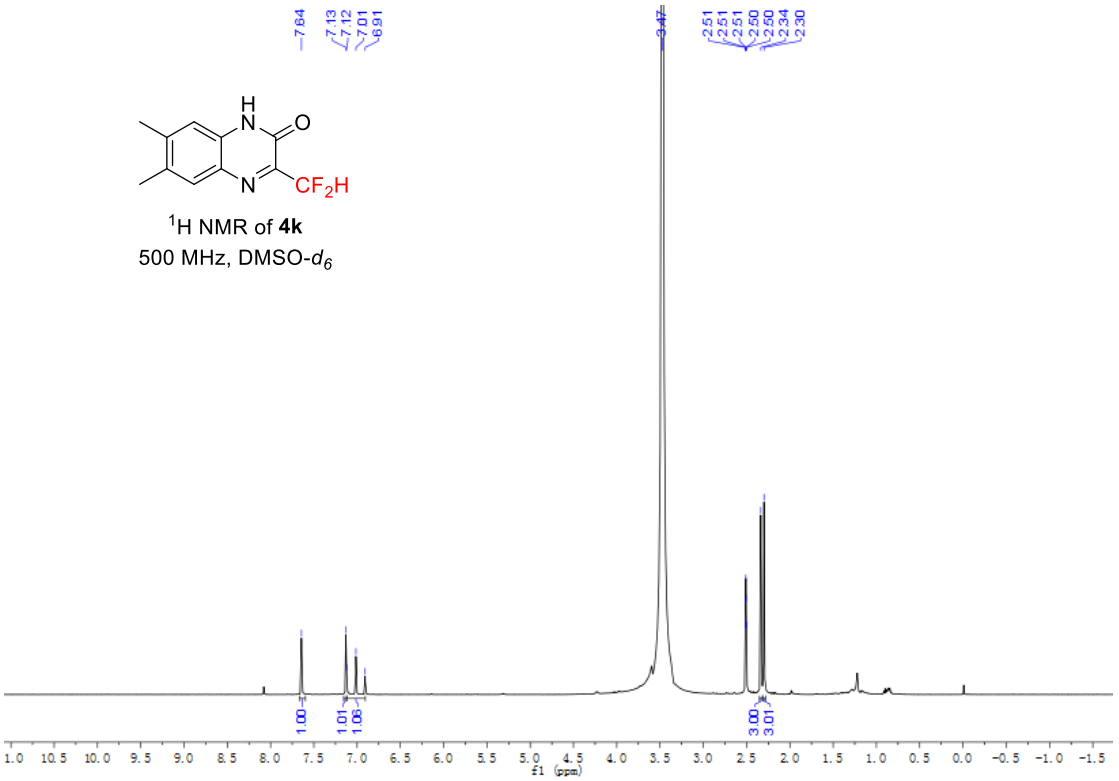


^{13}C NMR of **4j**
151 MHz, DMSO-d_6

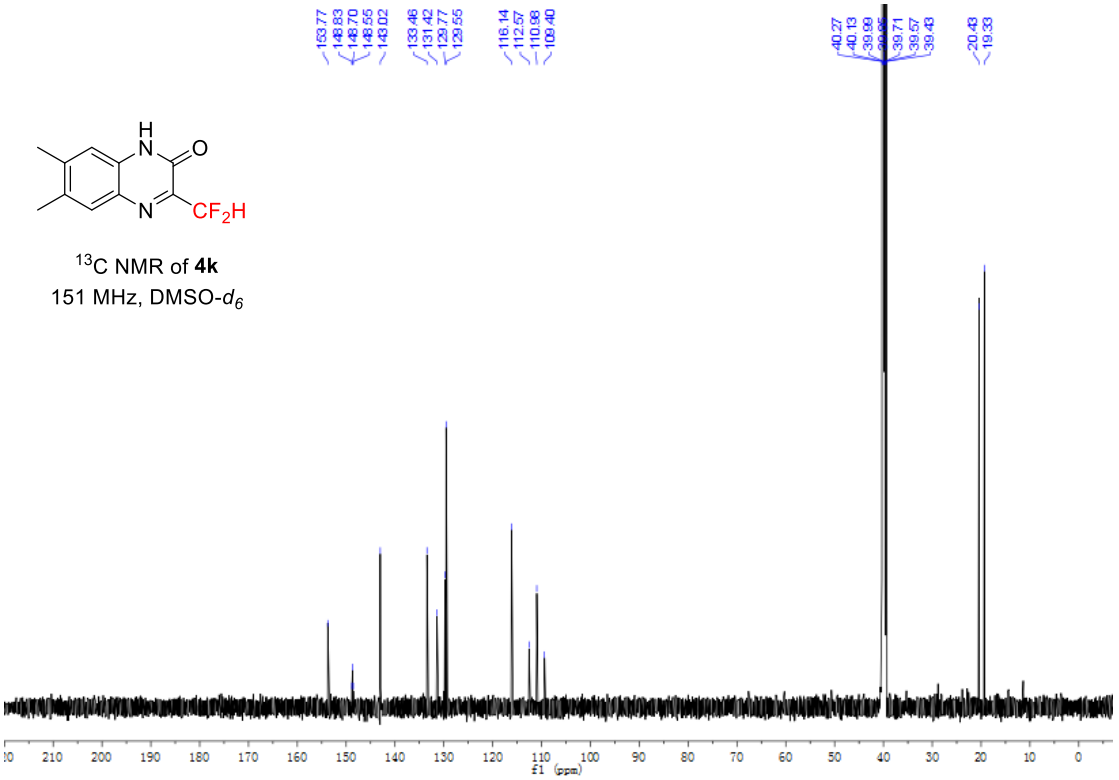


^{19}F NMR of **4j**
471 MHz, DMSO-d_6

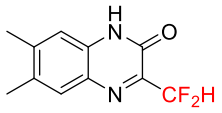
3-(difluoromethyl)-6,7-dimethylquinoxalin-2(1H)-one (4k)



^{1}H NMR of **4k**
500 MHz, DMSO-d_6

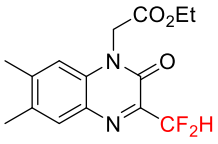


^{13}C NMR of **4k**
151 MHz, DMSO-d_6

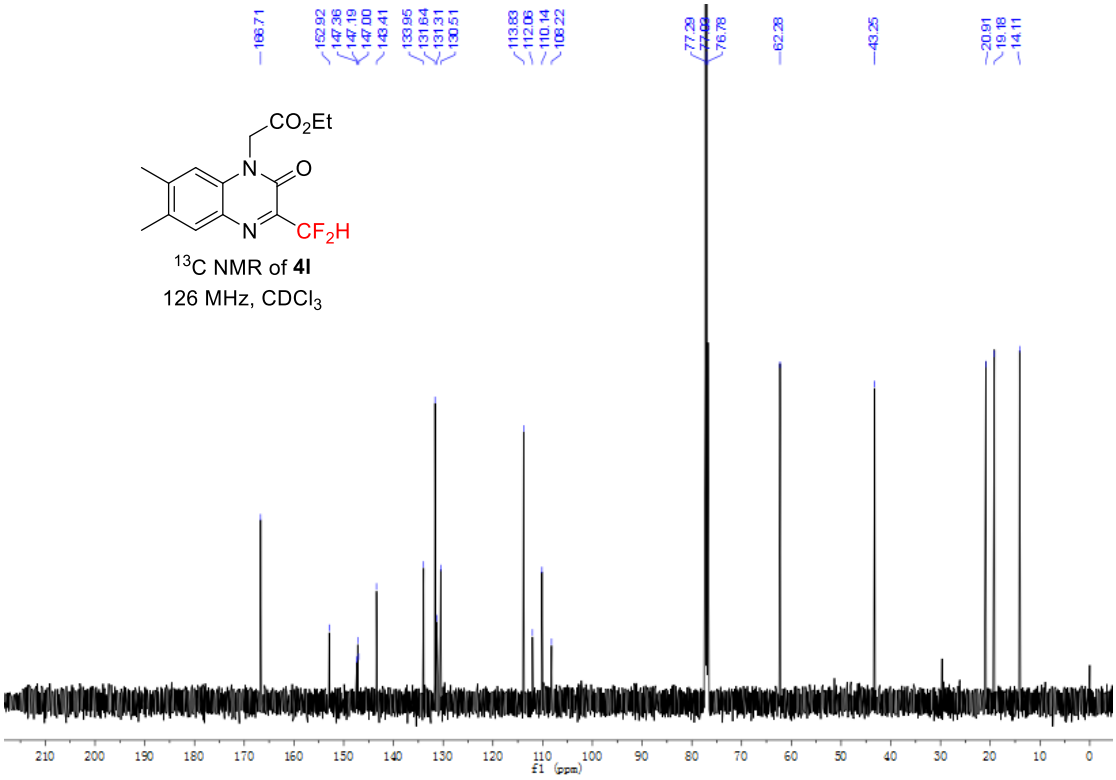


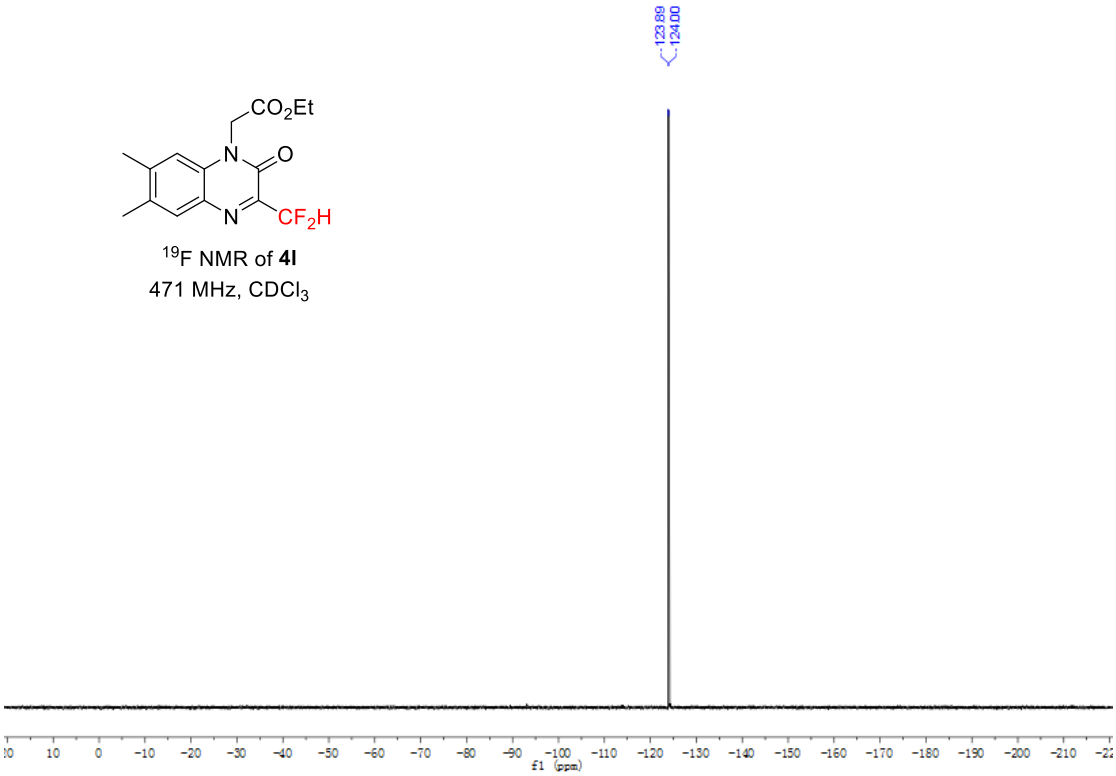
^{19}F NMR of **4k**
471 MHz, DMSO-d_6

Ethyl 2-(3-(difluoromethyl)-6,7-dimethyl-2-oxoquinoxalin-1(2H)-yl)acetate (4l)

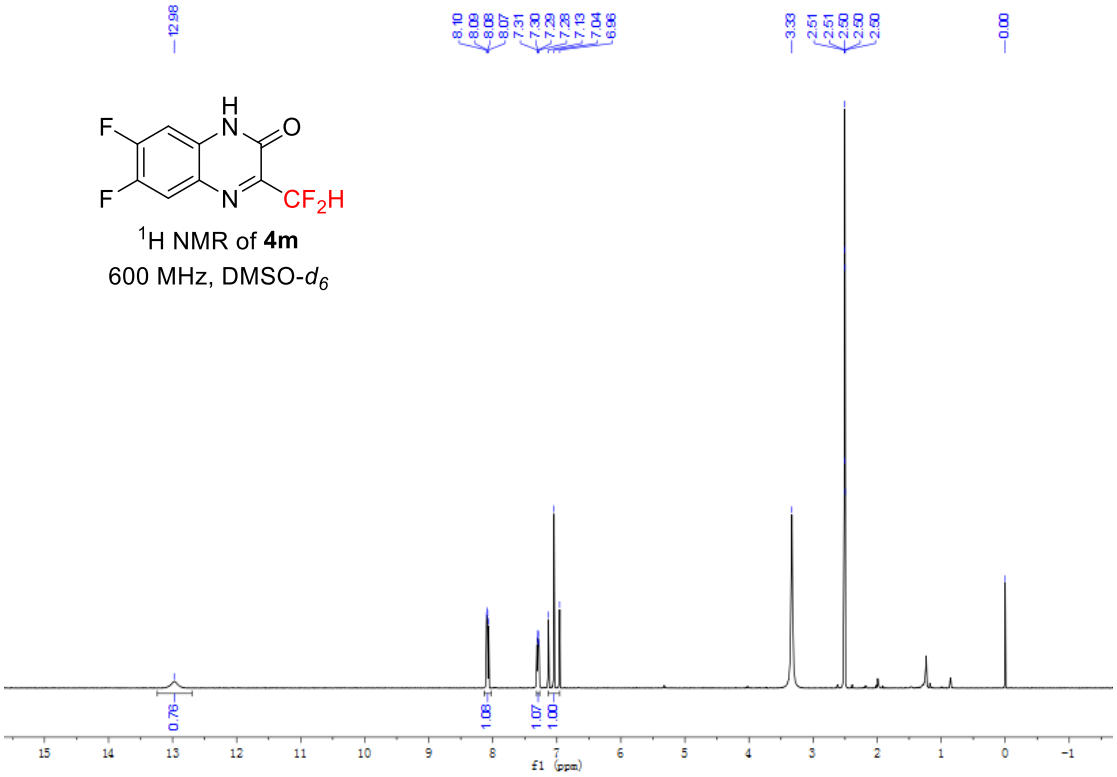


^{1}H NMR of **4l**
500 MHz, $CDCl_3$

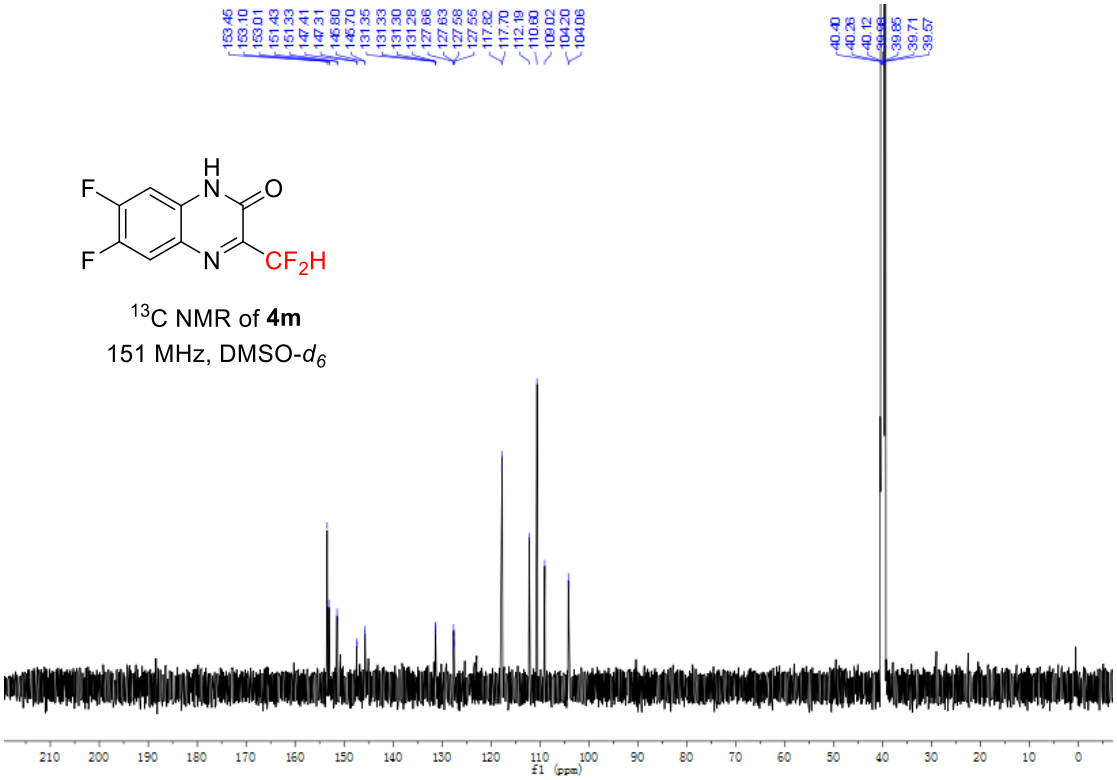

CO2Et
N
O
N
CF2H
13C NMR of 4l
126 MHz, CDCl3
f1 (ppm)


CO2Et
N
O
N
CF2H
19F NMR of 4l
471 MHz, CDCl3
f1 (ppm)

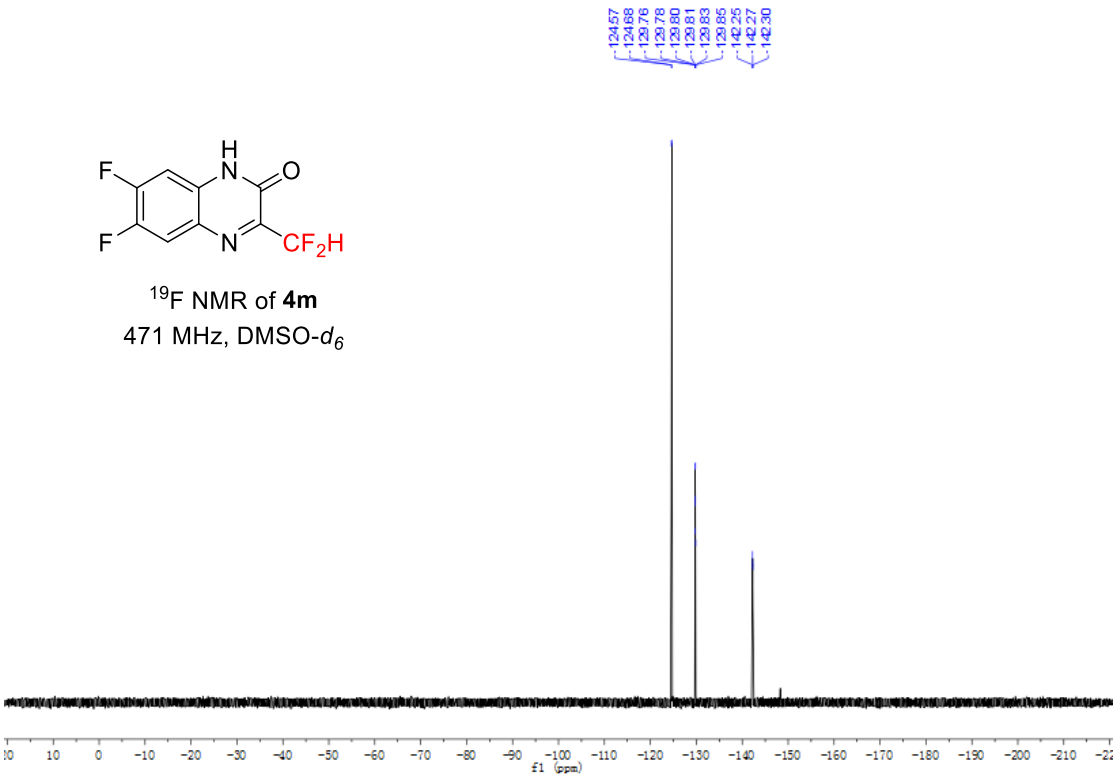
3-(difluoromethyl)-6,7-difluoroquinoxalin-2(1H)-one (4m)



^{1}H NMR of **4m**
600 MHz, DMSO-d_6

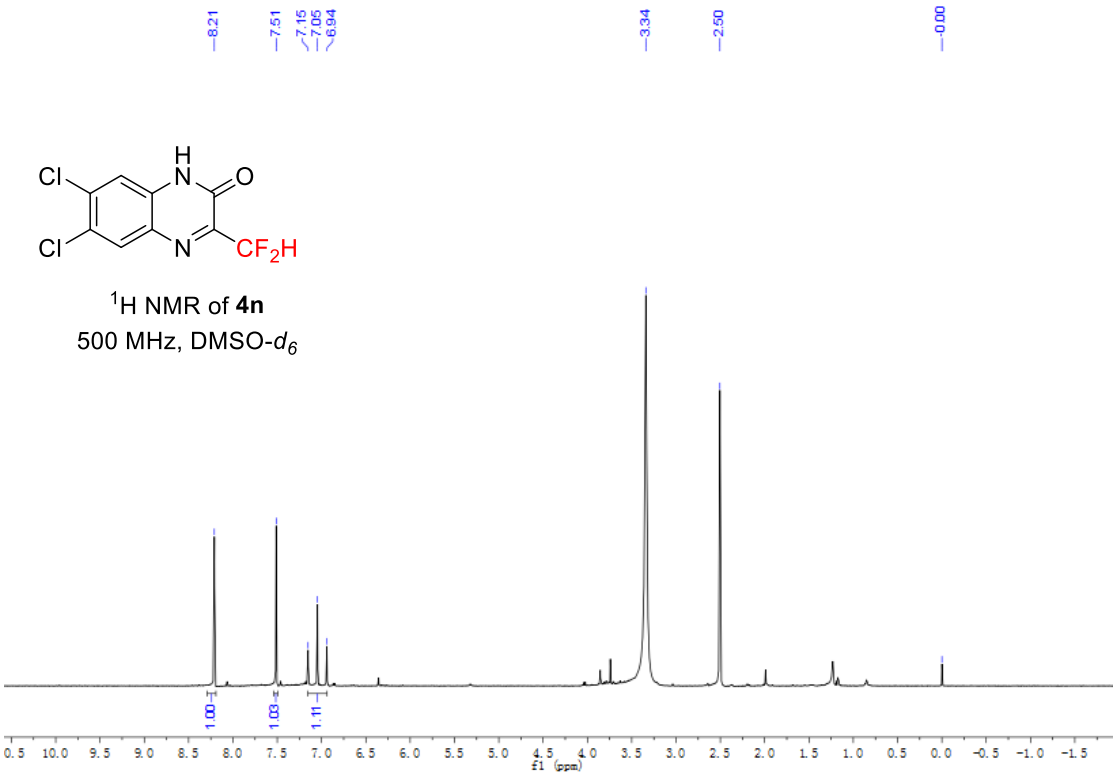


^{13}C NMR of **4m**
151 MHz, DMSO-d_6

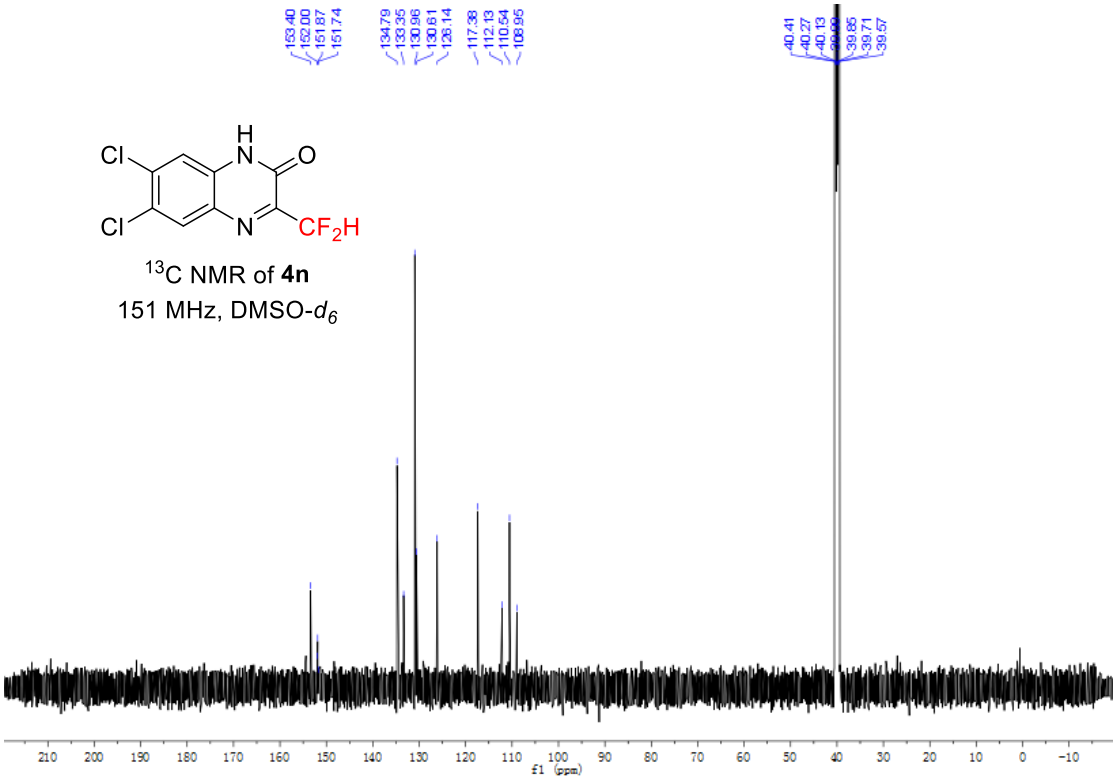


^{19}F NMR of **4m**
471 MHz, DMSO-d_6

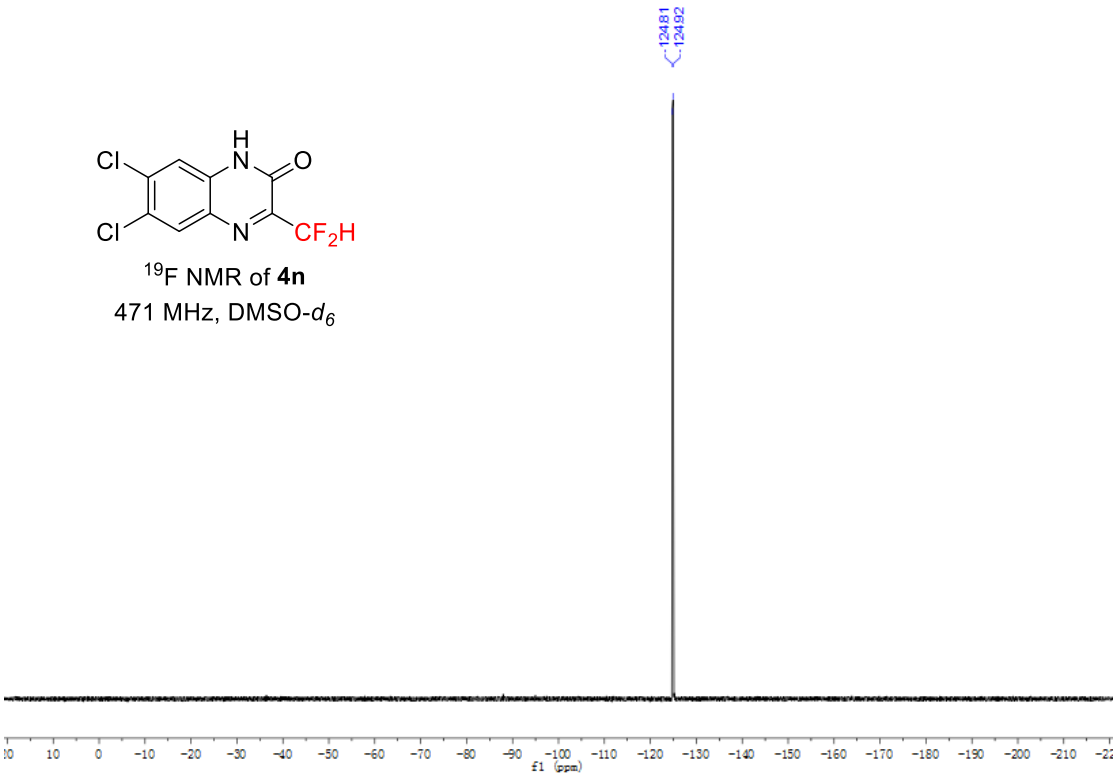
6,7-dichloro-3-(difluoromethyl)quinoxalin-2(1H)-one (4n)



^{1}H NMR of **4n**
500 MHz, DMSO-d_6

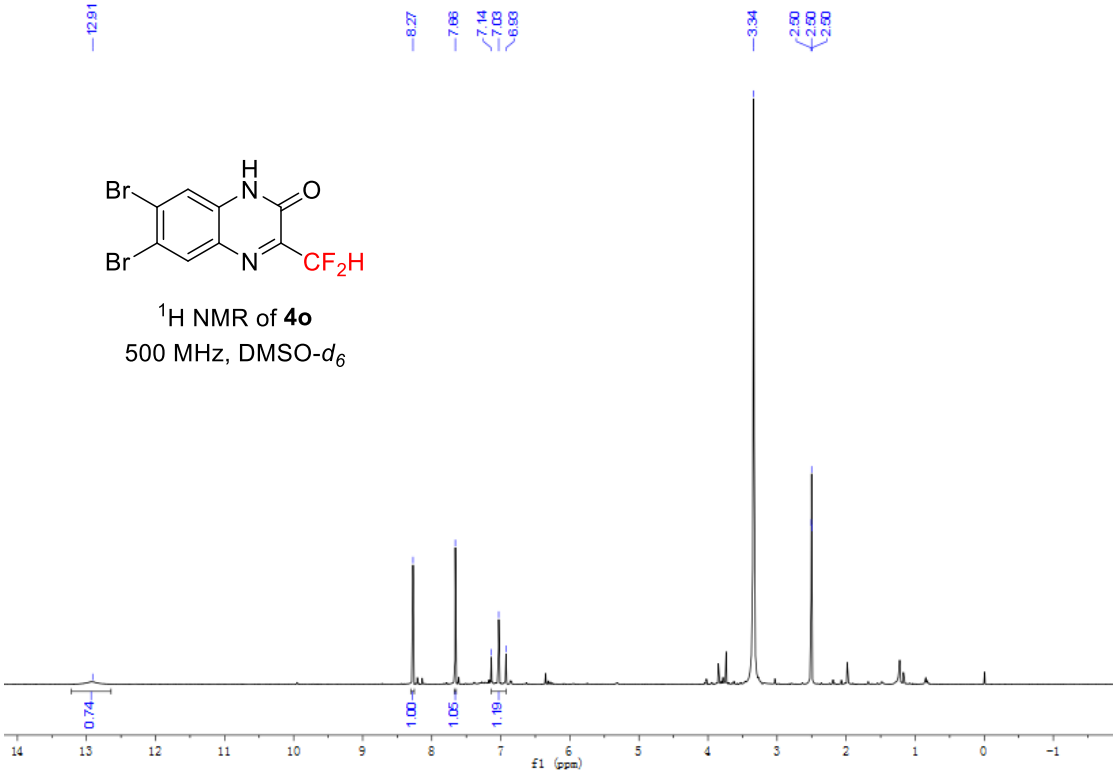


^{13}C NMR of **4n**
151 MHz, DMSO-d_6

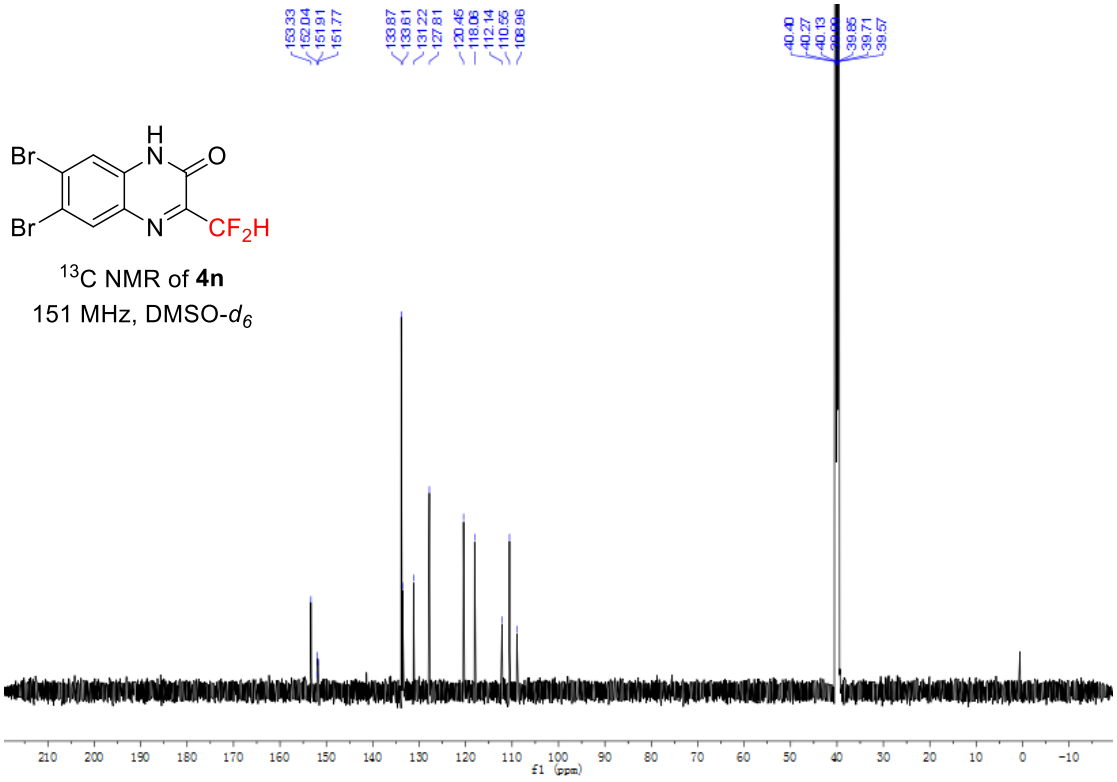


^{19}F NMR of **4n**
471 MHz, DMSO-d_6

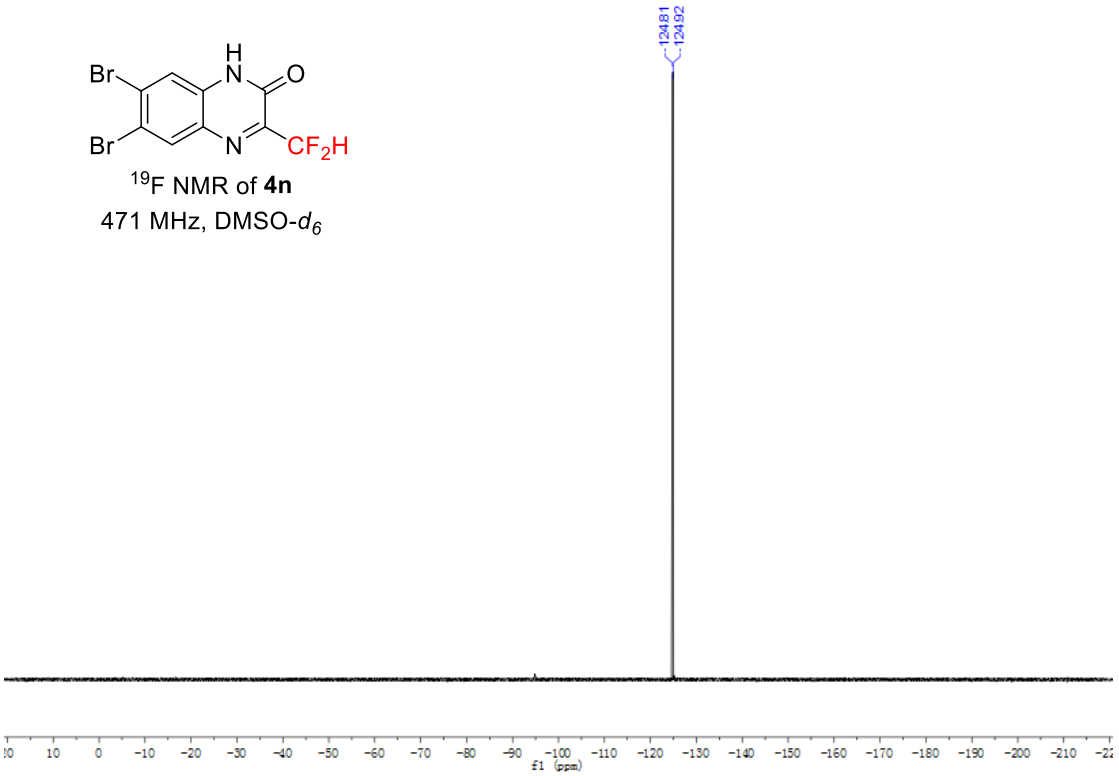
6,7-dibromo-3-(difluoromethyl)quinoxalin-2(1H)-one (4o)



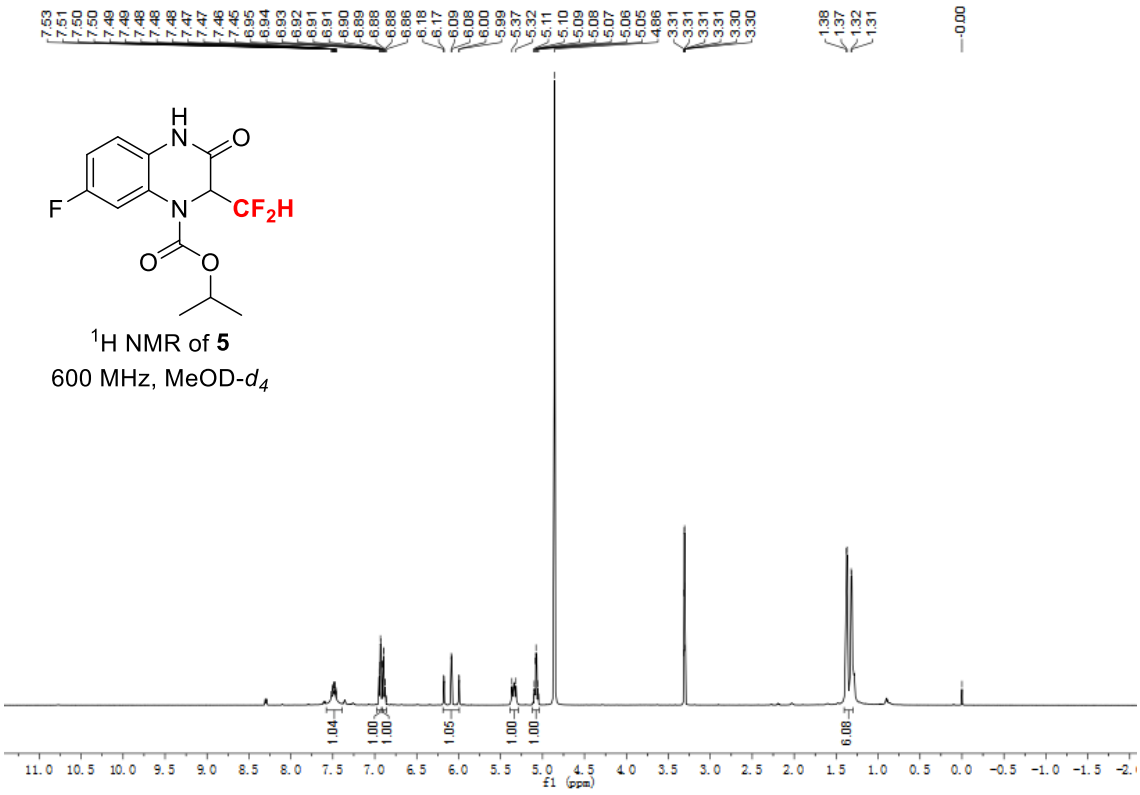
^{1}H NMR of **4o**
500 MHz, DMSO-d_6

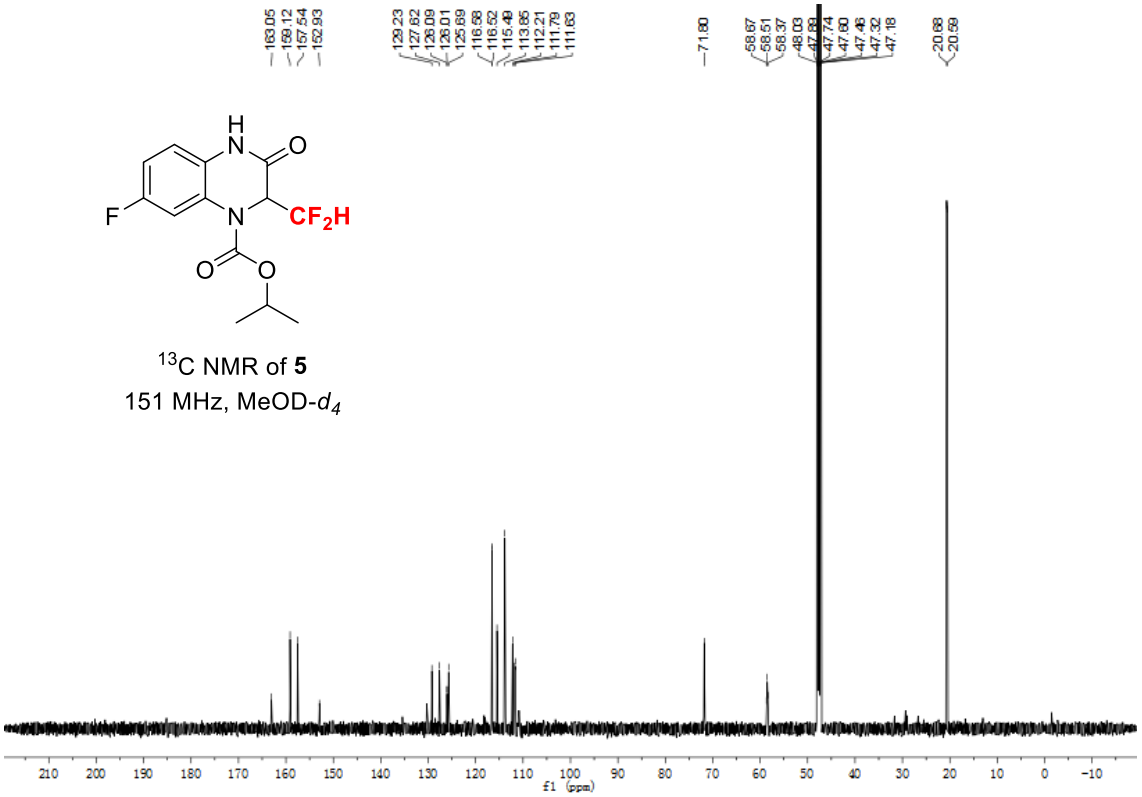


^{13}C NMR of **4n**
151 MHz, DMSO-d_6

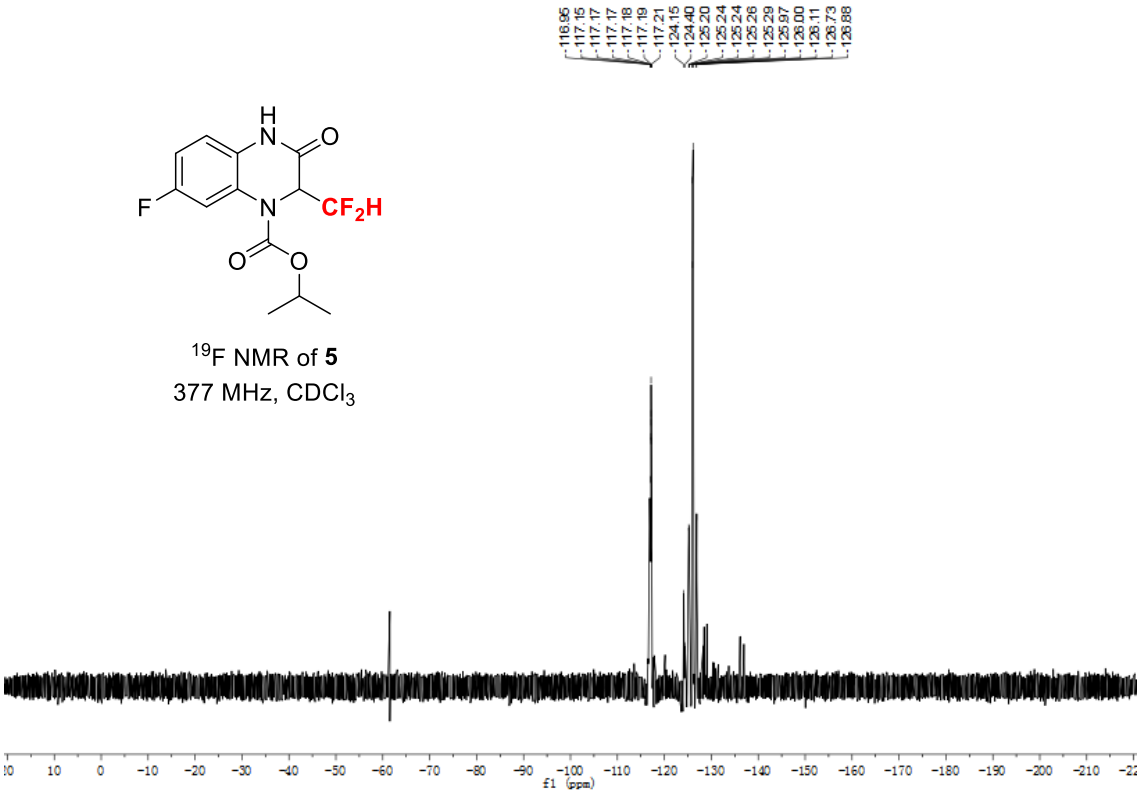


Isopropyl 2-(difluoromethyl)-7-fluoro-3-oxo-3,4-dihydroquinoxaline-1(2H)-carboxylate (5)



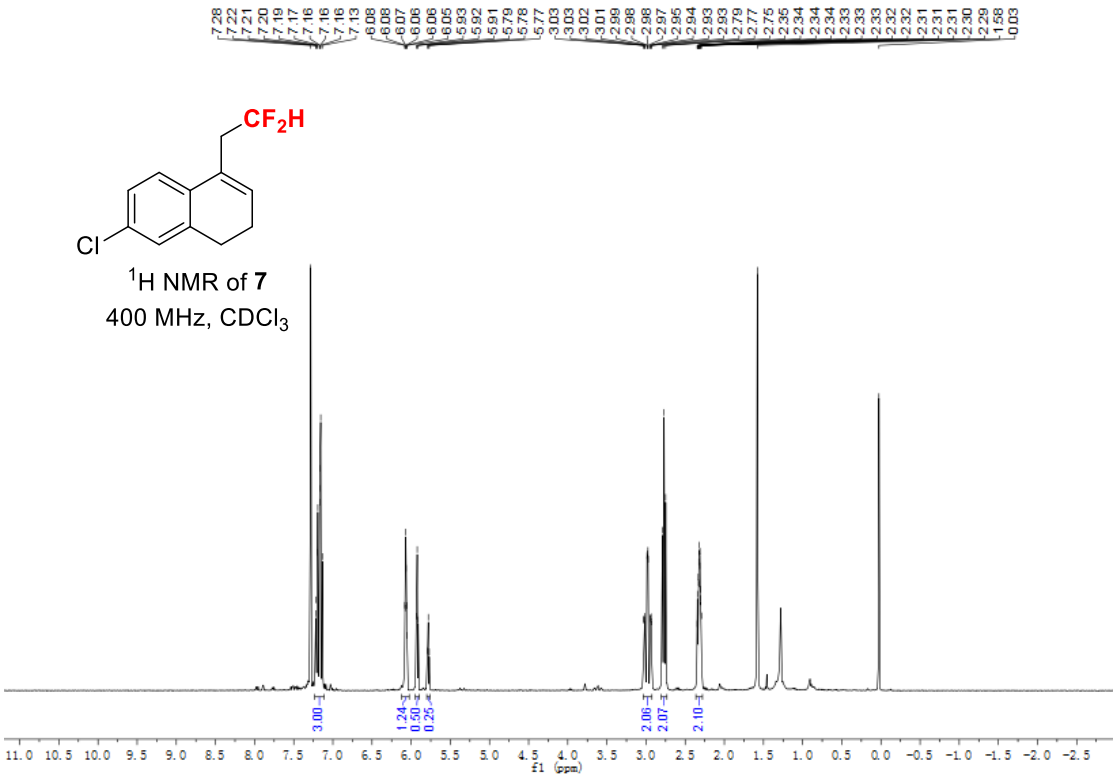


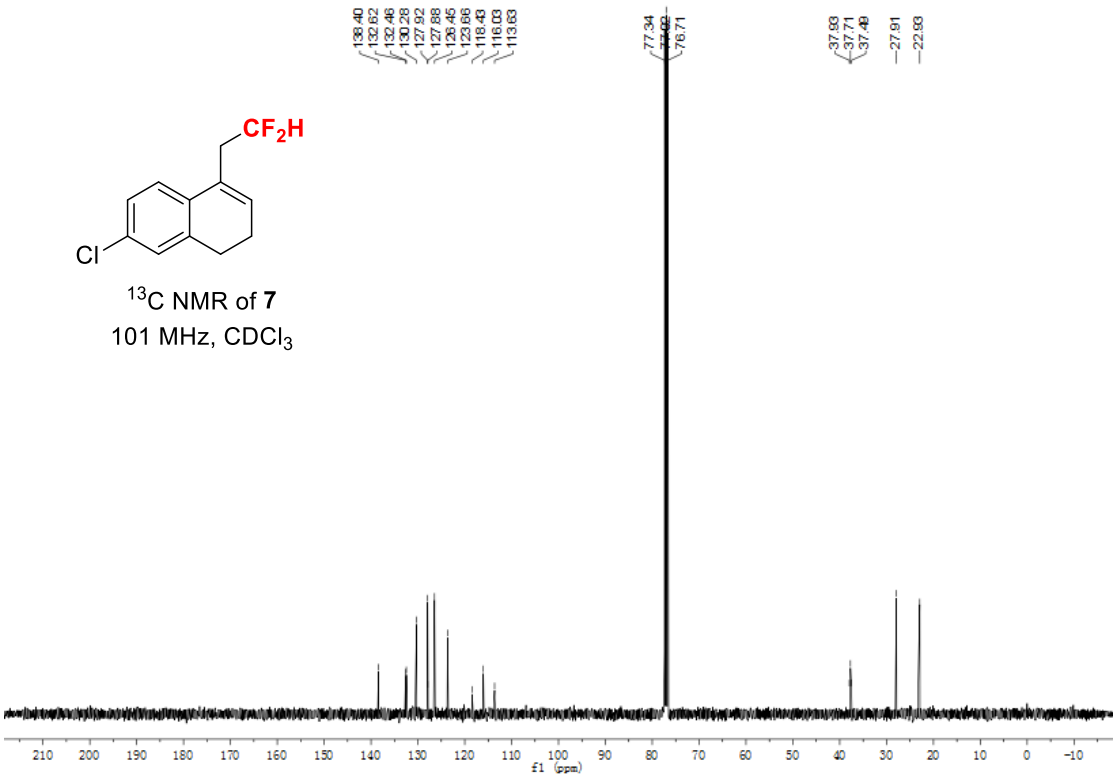
^{13}C NMR of **5**
151 MHz, MeOD-d_4

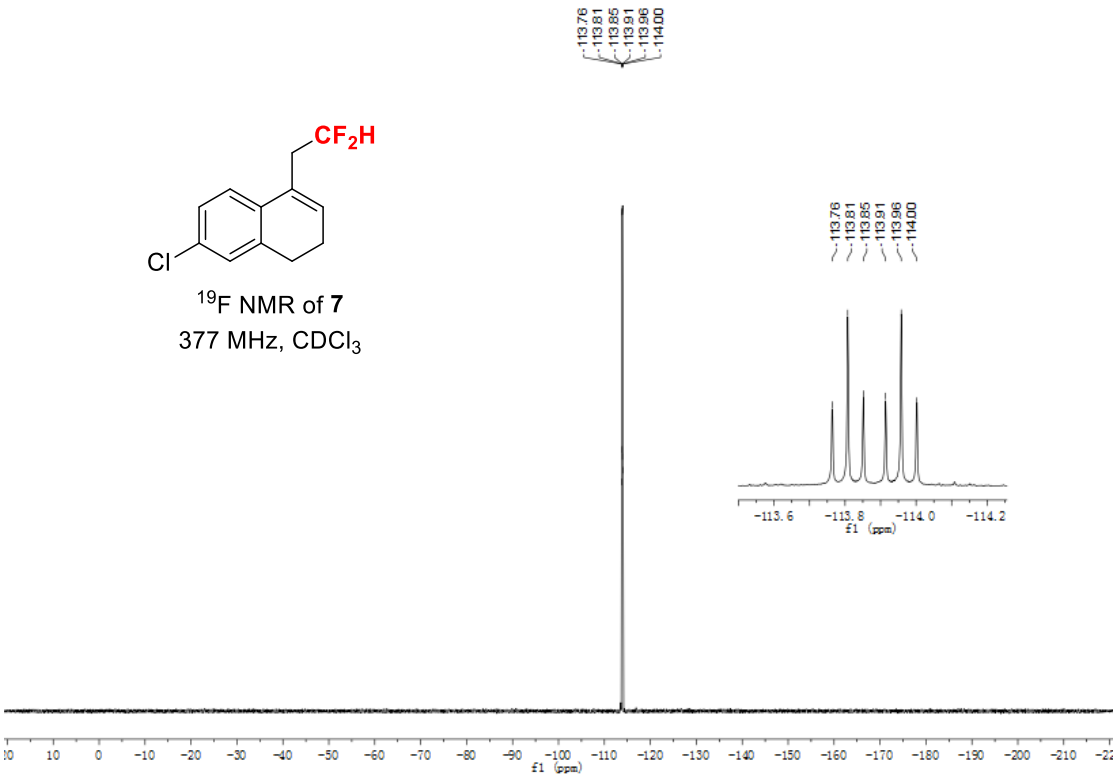


^{19}F NMR of **5**
377 MHz, $CDCl_3$

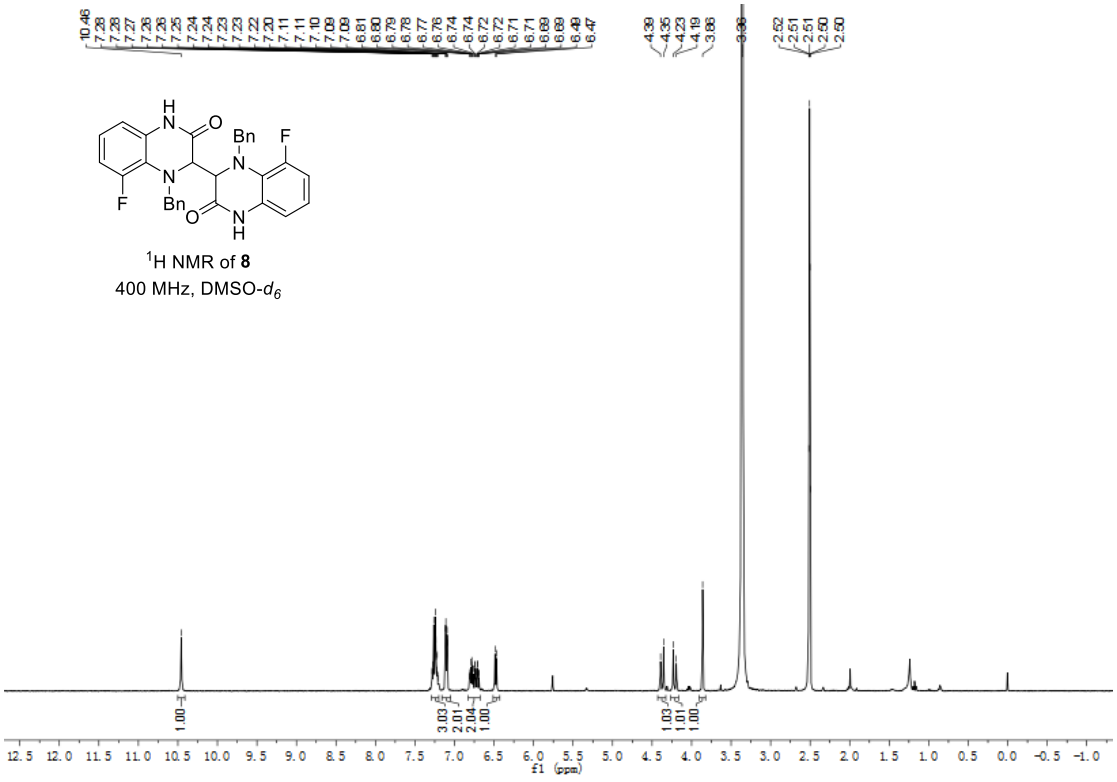
7-chloro-4-(2,2-difluoroethyl)-1,2-dihydronaphthalene (7)

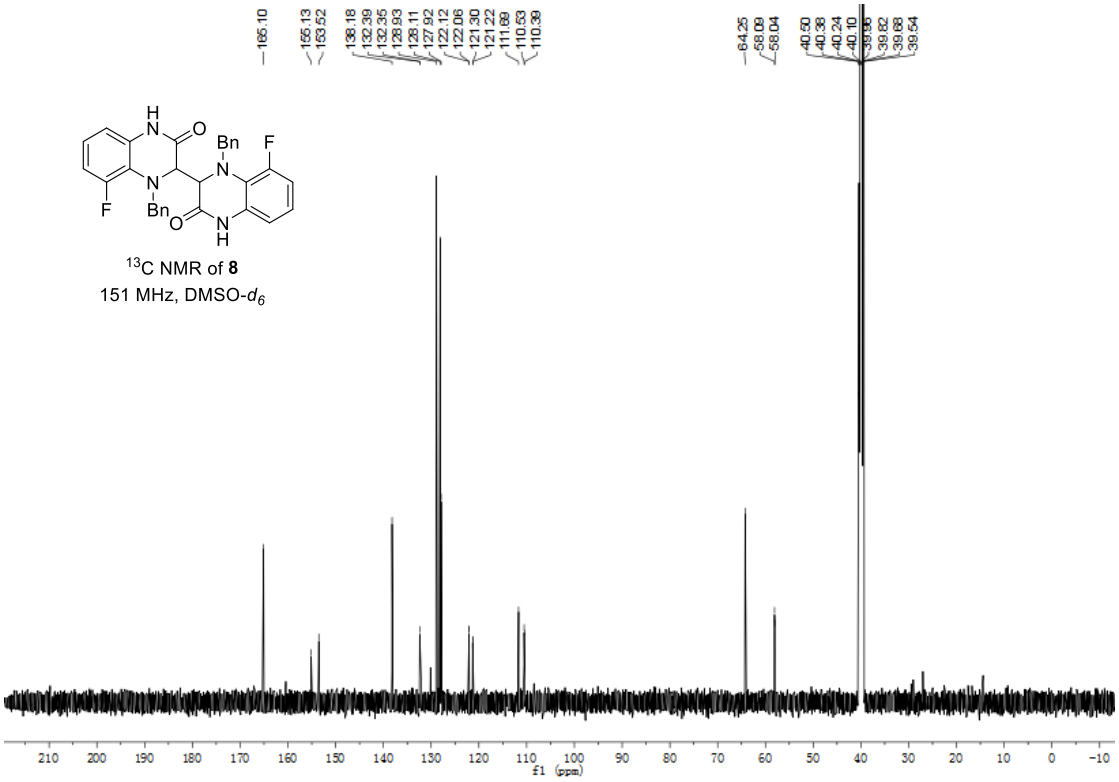




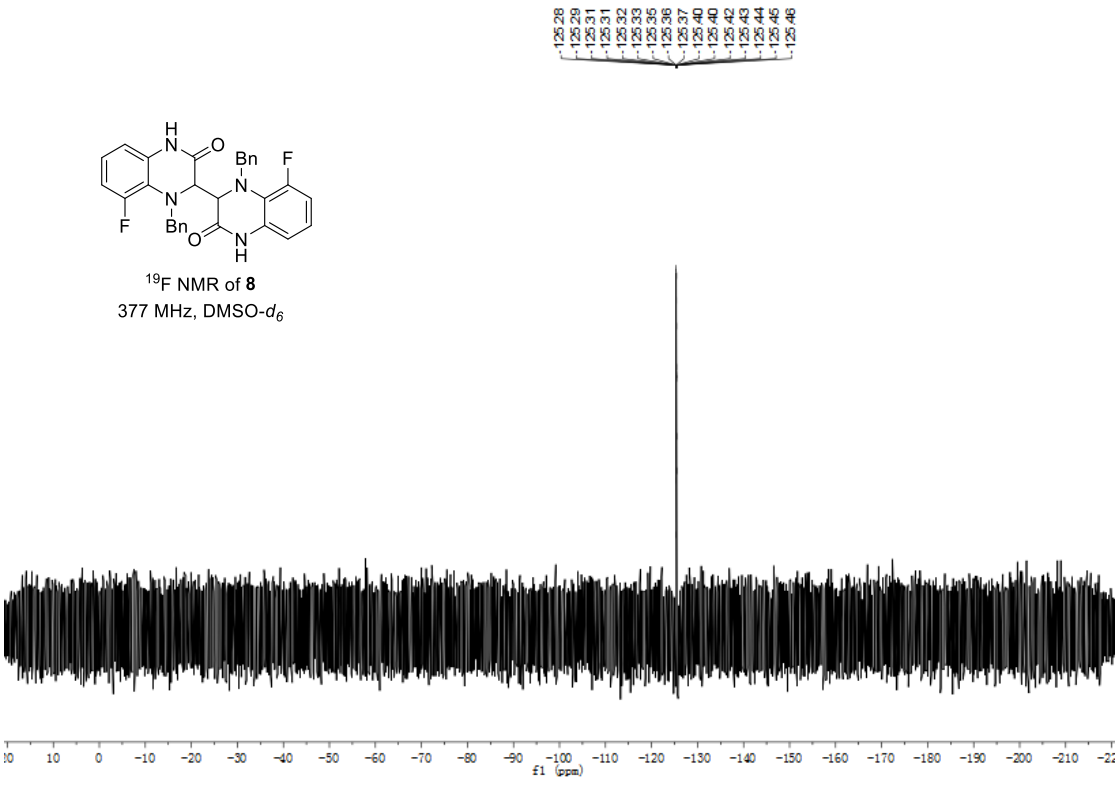


1,1'-dibenzyl-8,8'-difluoro-1,1',4,4'-tetrahydro-[2,2'-biquinoxaline]-3,3'(2H,2'H)-dione (8)





^{13}C NMR of **8**
151 MHz, DMSO-d_6



^{19}F NMR of **8**
377 MHz, DMSO-d_6