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Supporting Information

Electrocatalytic Minisci-type trifluoromethylation of electron-deficient heterocycles mediated by bromide ion

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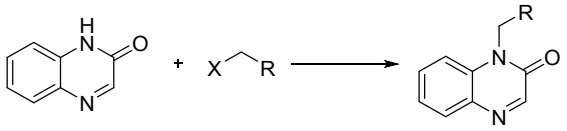
1 General information

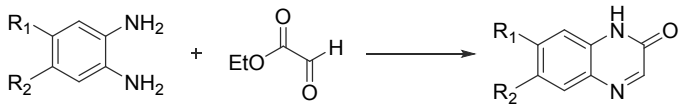
Unless otherwise special indicated, all the reagents were purchased from commercial supplies unless otherwise stated. And all the solvents were used without any purification. Thin-layer chromatography (TLC) was performed on plastic plates coated with silica gel GF254 with 0.2 mm thickness (Yantai Yuanbo Biological Technology Co., Ltd.) and all compounds were visualized with a UV light at 254nm. Flash column chromatography was performed using silica gel (300-400 mesh, Yantai Yuanbo Biological Technology Co., Ltd.). NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400 MHz or 300 MHz (^{1}H NMR) and 100 MHz or 75 MHz (^{13}C NMR). Chemical shifts were reported in ppm downfield and referenced as follows: ^{1}H: residual internal $CHCl_3$ (δ 7.26 ppm); ^{13}C: internal $CDCl_3$ (δ 77.2 ppm). Coupling constants were quoted in Hz(*J*). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

2 General procedure for the synthesis of starting materials (1b-1k) [1]



In a typical procedure, to a stirred solution of 2-quinoxalinone (5 mmol) in DMF (20 mL) was added the corresponding halide (1.6 equiv.) potassium and carbonate (1.2 equiv.) at room temperature overnight. Then resulting mixture was transferred to a separatory funnel. Ethanol and water were added to the reaction mixture, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were washed with a saturated solution of NH_4Cl and then with brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel to obtain product.

3 General procedure for the synthesis of starting materials (1l-1o) [2]



To ethanol (20 ml) suspension solution of *o*-arylenediamine (5 mmol) was added Ethyl 2-

oxoacetate (1.1 equiv.). The reaction system was stirred and heated to reflux at 85 °C for 1 h, then stirred at room temperature for 16 h. After the reaction was completed (as monitored by TLC), the precipitate was filtered and washed with ethanol (5 ml*3), and finally dried to give quinoxalinone.

4 General procedure for the synthesis of trifluoromethyl-substituted 2-Quinoxalinone

A undivided cell was equipped with a carbon anode (1 × 5 cm^2) and a Pt net cathode (1 × 3 cm^2) and connected to a DC regulated power supply. To the cell was added 2-Quinoxalinone (0.3 mmol), Zinc Trifluoromethanesulfinate (0.6 mmol), *n*-Et_4NBr (1 equiv.) and 3 mL of CH_3CN. The mixture was electrolyzed using constant current conditions (~5 mA cm^{-2}) at 50 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the 2-Quinoxalinone), the solvent was removed under reduced pressure. The residue was poured into a saturated aqueous solution of $Na_2S_2O_3$ and the product was then extracted with DCM (3×20 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired pure product.

5 Optimization of the reaction conditions

Table S1. Optimization of Reaction Condition [a]

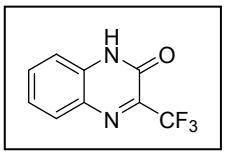
Entry	Solvent	Electrolyte (0.1 M)	Catalyst (equiv.)	Yield(%) [b]
1[cd]	CH_3CN	$LiClO_4$	NaBr (1 equiv.)	6
2[c]	CH_3CN	$LiClO_4$	NaBr (1 equiv.)	12
3[ce]	CH_3CN	$LiClO_4$	NaBr (1 equiv.)	10
4[c]	DMSO	$LiClO_4$	NaBr (1 equiv.)	trace
5[c]	DMF	$LiClO_4$	NaBr (1 equiv.)	trace
6[c]	CH_3OH	$LiClO_4$	NaBr (1 equiv.)	n.r.
7[c]	CH_3CN:DCE (v:v 5:1)	$LiClO_4$	NaBr (1 equiv.)	11
8[f]	CH_3CN	$LiClO_4$	NaBr (1 equiv.)	15

9	CH_3CN	$LiClO_4$	NaBr (1 equiv.)	24
10[g]	CH_3CN	$LiClO_4$	NaBr (1 equiv.)	22
11	CH_3CN	Et_4NClO_4	NaBr (1 equiv.)	19
12	CH_3CN	Et_4NBF_4	NaBr (1 equiv.)	33
13	CH_3CN	Bu_4NBF_4	NaBr (1 equiv.)	28
14	CH_3CN	Bu_4NPF_6	NaBr (1 equiv.)	23
15	CH_3CN	Bu_4NClO_4	NaBr (1 equiv.)	18
16	CH_3CN	Et_4NBF_4	NH_4Br (1 equiv.)	27
17	CH_3CN	Et_4NBF_4	KBr (1 equiv.)	31
18	CH_3CN	Et_4NBF_4	Et_4NBr (1 equiv.)	37
19	CH_3CN	Et_4NBF_4	Bu_4NBr (1 equiv.)	34
20	CH_3CN	/	Et_4NBr (1 equiv.)	40
21	CH_3CN	/	Et_4NBr (0.5 equiv.)	31
22	CH_3CN	/	Et_4NBr (0.2 equiv.)	27
23	CH_3CN	/	/	21

[a] Reaction conditions: **1a** (0.3 mmol) and **2b** (0.6 mmol) in 3 mL of solve, undivided cell, 50 °C, current density of 5 mA cm^{-2}, graphite plate anode and Pt net cathode (working area: 1 cm^2). [b] Isolated yield. [c] **2a**: CF_3SO_2Na. [d] 30 °C. [e] 80 °C. [f] Current density of 3 mA cm^{-2}. [g] Current density of 8 mA cm^{-2}.

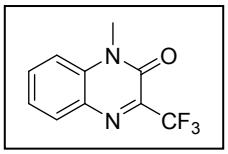
6 Characterization data of 3a-w

3-(trifluoromethyl)quinoxalin-2(1H)-one (3a) [3]



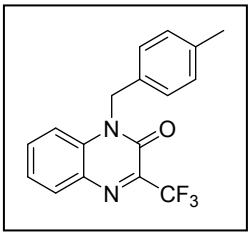
Following the general procedure, the desired compound was obtained as yellow solid, mp 148 – 150 °C, 25.6 mg, 40% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 7.40 (t, *J* = 8.2 Hz, 2H), 7.67-7.75 (m, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 13.06 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 116.3. 120.5 (q, *J* = 273.5 Hz), 124.6, 130.3, 130.3, 133.9, 134.1, 144.5 (q, *J* = 32.2 Hz), 152.1.

1-methyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (3b) [4]



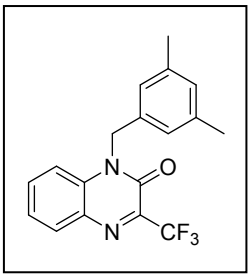
Following the general procedure, the title compound was obtained as yellow solid, mp 138 – 139 °C, 28.5 mg, 42% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 3.78 (s, 3H), 7.43 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.76 (ddd, *J* = 8.7, 7.3, 1.5 Hz, 1H), 8.01 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 29.2, 114.1, 119.9 (q, *J* = 273.6 Hz), 124.5, 130.9, 131.7, 133.6, 134.6, 143.8 (q, *J* = 33.6 Hz), 151.6.

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



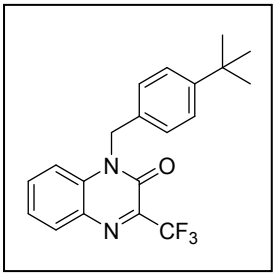
Following the general procedure, the desired compound was obtained as yellow solid, mp 141 – 142 °C, 31.5 mg, 33% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.31 (s, 3H), 5.49 (s, 2H), 7.12-7.20 (m, 4H), 7.37-7.41 (m, 2H), 7.60 (ddd, *J* = 8.8, 7.2, 1.5 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 21.1, 45.9, 114.8, 119.9 (q, *J* = 276.5 Hz), 124.5, 127.1, 129.7, 131.2, 131.5, 131.9, 133.4, 134.0, 137.9, 144.1 (q, *J* = 34.0 Hz), 151.8. HRMS (ESI) m/z calculated for $C_{17}H_{14}F_3N_2O^+$ 319.1053, Found 319.1046.

1-(3,5-dimethylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3d)



Following the general procedure, the desired compound was obtained as yellow solid, mp 155 – 156 °C, 23.7 mg, 24% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 2.20 (s, 6H), 5.45 (s, 2H) , 6.90 (d, *J* = 9.7 Hz, 3H) , 7.47 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H) , 7.52 (dd, *J* = 8.6, 1.1 Hz, 1H) , 7.74 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H) 8.00 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** (DMSO-d_6, 400 MHz) δ 21.3, 45.7, 116.1, 120.6 (q, *J* = 273.6 Hz), 124.8, 124.9, 129.4, 131.0, 131.4, 134.2, 134.6, 135.5, 138.3, 143.4 (q, *J* = 32.5 Hz), 151.9. HRMS (ESI) m/z calculated for $C_{18}H_{16}F_3N_2O^+$ 333.1209, Found 333.1208.

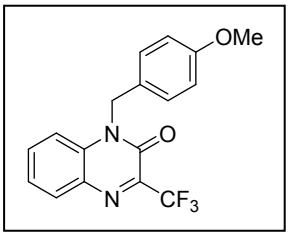
1-(4-(tert-butyl)benzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3e)



Following the general procedure, the desired compound was obtained as yellow solid, mp 154 – 155 °C, 51.0 mg, 47% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.30 (s, 9H), 5.53 (s, 2H), 7.24-7.26 (m, 2H), 7.36-7.40 (m, 2H), 7.41-7.46 (m, 2H), 7.65 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 8.02 (dd, *J* = 8.0, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ

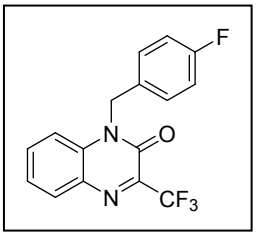
31.3, 34.6, 45.8, 114.9, 120.0 (q, *J* = 273.8 Hz), 124.5, 126.0, 126.9, 131.2, 131.4, 131.8, 133.5, 134.1, 144.1 (q, *J* = 33.7 Hz), 151.1, 151.8. HRMS (ESI) m/z calculated for $C_{20}H_{19}F_3N_2OK^+$ 399.1081, Found 399.1077.

1-(4-methoxybenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3f)



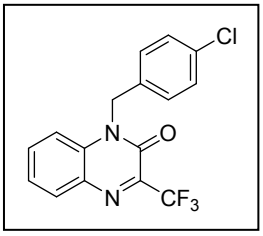
Following the general procedure, the desired compound was obtained as yellow solid, mp 118 – 120 °C, 23.0 mg, 23% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 3.70 (s, 3H) , 5.47 (s, 2H) , 6.87 - 6.91 (m, 2H) , 7.27-7.31 (m, 2H) , 7.46 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1H) , 7.62 (dd, *J* = 8.6, 1.1 Hz, 1H) , 7.75 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 7.99 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 45.0, 55.5, 114.6, 116.1, 120.5 (d, *J* = 273.6 Hz), 124.9, 127.5, 128.9, 131.1, 131.5, 134.2, 134.4, 143.4 (d, *J* = 32.7 Hz), 151.9, 159.1. HRMS (ESI) m/z calculated for $C_{17}H_{13}F_3N_2O_2K^+$ 373.0561, Found 373.0556.

1-(4-fluorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3g)



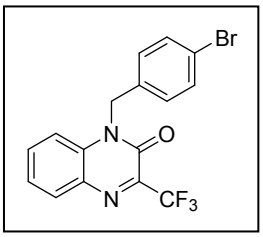
Following the general procedure, the desired compound was obtained as yellow solid, mp 138 – 139 °C, 38.5 mg, 40% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.52 (s, 2H) , 7.02-7.08 (m, 2H) , 7.28-7.33 (m, 2H) , 7.38 (dd, *J* = 8.5, 1.1 Hz, 1H) , 7.45 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H) , 7.66 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 8.04 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 45.4, 114.6, 116.1 (d, *J* = 21.6 Hz), 119.9 (q, *J* = 273.8 Hz), 124.7 (d, *J* = 2.3 Hz), 129.0 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 3.4 Hz), 131.2, 132.0, 133.6 (d, *J* = 2.6 Hz), 133.9, 144.1 (q, *J* = 33.8 Hz), 151.7, 162.4 (d, *J* = 244.9 Hz). HRMS (ESI) m/z calculated for $C_{16}H_{11}F_4N_2O^+$ 323.0802, Found 323.0803.

1-(4-chlorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3h)



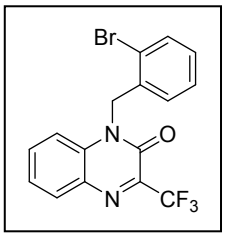
Following the general procedure, the desired compound was obtained as yellow solid, mp 132 – 133 °C, 42.6 mg, 42% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 5.53 (s, 2H), 7.36-7.41 (m, 4H), 7.45-7.49 (m, 1H), 7.54 (dd, *J* = 8.6, 1.1 Hz, 1H), 7.74 (ddd, *J* = 8.7, 7.1, 1.5 Hz, 1H), 8.00 (dd, *J* = 8.0, 1.5 Hz, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 45.1, 115.9, 120.5 (q, *J* = 273.5 Hz), 125.0, 129.1, 129.4, 131.1, 131.5, 132.6, 134.2, 134.4, 134.7, 143.5 (q, *J* = 32.6 Hz), 151.9. HRMS (ESI) m/z calculated for $C_{16}H_{10}ClF_3N_2OK^+$ 377.0065, Found 377.0072.

1-(4-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3i)



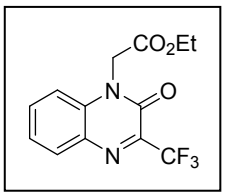
Following the general procedure, the desired compound was obtained as yellow solid, mp 156 – 157 °C, 46.0 mg, 40% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.50 (s, 2H), 7.18-7.20 (m, 2H), 7.33 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.43-7.47 (m, 1H), 7.48-7.50 (m, 2H), 7.65 (ddd, *J* = 8.7, 7.3, 1.5 Hz, 1H), 8.04 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 45.5, 114.5, 119.9 (q, *J* = 273.7 Hz), 122.1, 124.7, 128.9, 131.2, 132.1, 132.3, 133.5, 133.6, 133.8, 144.1 (q, *J* = 33.8 Hz) 151.7. HRMS (ESI) m/z calculated for $C_{16}H_{11}BrF_3N_2O^+$ 383.0001, Found 383.0006.

1-(2-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3j)



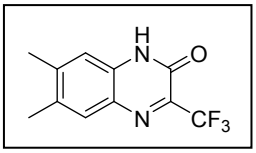
Following the general procedure, the desired compound was obtained as yellow solid, mp 138 – 140 °C, 33.1 mg, 29% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.62 (s, 2H) , 6.76-6.78 (m, 1H) , 7.15 (dd, *J* = 8.6, 1.1 Hz, 1H) , 7.18-7.21 (m, 2H) , 7.43-7.47 (m, 1H) , 7.63 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H) , 7.67-7.69 (m, 1H), 8.06 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 46.2, 114.9, 119.9 (q, *J* = 273.8 Hz), 122.6, 124.8, 126.9, 128.1, 129.5, 131.2, 131.9, 133.0, 133.2, 133.7 133.8, 144.1 (d, *J* = 34.4 Hz), 151.7. HRMS (ESI) m/z calculated for $C_{16}H_{11}Br\ F_3N_2O^+$ 383.0001, Found 383.0006.

ethyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(2H)-yl)acetate (3k)



Following the general procedure, the desired compound was obtained as yellow solid, mp 123 – 124 °C, 29.7 mg, 33% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.31 (t, *J* = 7.1 Hz, 3H), 4.29 (q, *J* = 7.1 Hz, 2H), 5.09 (s, 2H), 7.18 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.46-7. 50 (m, 1H), 7.73 (ddd, *J* = 8.6, 7.3, 1.5 Hz, 1H), 8.05 (dd, *J* = 8.1, 1.5 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.1, 43.4, 62.4, 113.6, 119.8 (q, *J* = 273.8 Hz), 124.8, 131.0, 132.1, 133.7, 133.8, 143.8 (q, *J* = 34.1 Hz), 151.2, 166.4. HRMS (ESI) m/z calculated for $C_{13}H_{12}F_3N_2O_3^+$ 301.0795, Found 301.0790.

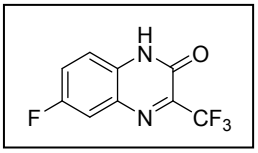
6,7-dimethyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (3l) [5]



Following the general procedure, the desired compound was obtained as yellow solid, mp 268 – 270 °C, 19.7 mg, 27% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 2.29 (s, 3H), 2.34 (s, 3H), 7.12 (s, 1H),

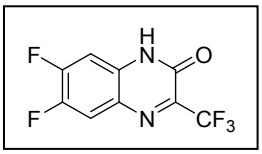
7.65 (s, 1H), 12.95 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 19.3, 20.5, 116.0, 120.7 (q, *J* = 273.1 Hz), 128.9, 129.7, 132.3, 133.7, 142.9 (q, *J* = 31.6 Hz), 144.4, 152.2.

6-fluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3m)



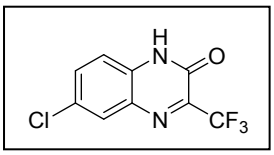
Following the general procedure, the desired compound was obtained as yellow solid, mp 222 – 224 °C, 20.2 mg, 29% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 7.38-7.43 (m, 1H), 7.64 (td, *J* = 8.4, 7.9, 4.3 Hz, 1H), 7.80 (dq, *J* = 9.8, 3.0 Hz, 1H), 13.14 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 115.2 (d, *J* = 22.8 Hz), 117.9 (d, *J* = 9.1 Hz), 120.4 (q, *J* = 273.7 Hz), 122.3 (d, *J* = 24.5 Hz), 130.5 (d, *J* = 11.8 Hz), 131.2, 145.8 (q, *J* = 32.2 Hz), 151.9, 158.5 (d, *J* = 238.8 Hz). HRMS (ESI) m/z calculated for $C_9H_5F_4N_2O^+$ 233.0333, Found 233.0332.

6,7-difluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3n)



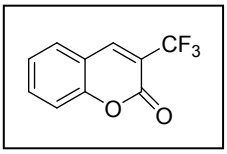
Following the general procedure, the desired compound was obtained as yellow solid, mp 152 – 154 °C, 27.5 mg, 37% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 7.31 (dd, *J* = 10.9, 7.5 Hz, 1H), 8.15 (dd, *J* = 10.8, 8.2 Hz, 1H), 13.21 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 104.1 (d, *J* = 21.8 Hz), 118.1 (d, *J* = 17.4 Hz), 120.4 (q, *J* = 273.5 Hz), 126.8 (d, *J* = 9.3 Hz), 132.3 (d, *J* = 10.1 Hz), 144.9 (q, *J* = 28.0 Hz), 146.7 (dd, *J* = 242.0, 14.4 Hz), 151.8, 153.0 (dd, *J* = 251.5, 14.9 Hz). HRMS (ESI) m/z calculated for $C_9H_4F_5N_2O^+$ 251.0238, Found 251.0238.

6-chloro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3o)



Following the general procedure, the desired compound was obtained as yellow solid, mp 158 – 161 °C, 21.1 mg, 28%. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 7.40 (d, *J* = 8.8 Hz, 1H), 7.77 (dd, *J* = 8.9, 2.4 Hz, 1H), 8.04 (d, *J* = 2.4 Hz, 1H), 13.18 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 118.0, 120.3 (q, *J* = 273.9 Hz), 128.2, 129.2, 130.9, 133.2, 133.8, 145.8 (q, *J* = 33.2 Hz), 152.0. HRMS (ESI) m/z calculated for $C_9H_5ClF_3N_2O^+$ 249.0037, Found 249.0022.

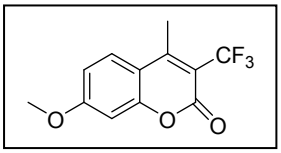
3-(trifluoromethyl)-2H-chromen-2-one (3p) [6]



Following the general procedure, the desired compound was obtained as white solid, mp 126 – 127 °C, 28.3 mg, 44% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.39-7.43 (m, 2H), 7.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.71 (ddd, *J* = 8.7, 7.3, 1.6 Hz, 1H), 8.19 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ116.8, 117.0, 117.7 (q, *J* =

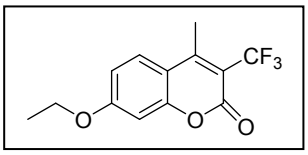
33.3 Hz), 121.4 (q, *J* = 272.1 Hz), 125.3, 129.5, 134.5, 143.3 (q, *J* = 4.9 Hz), 154.7, 155.9.

7-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3q) [6]



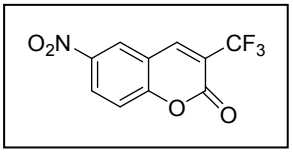
Following the general procedure, the desired compound was obtained as white solid, mp 138 – 139 °C, 40.6 mg, 52% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.65 (q, *J* = 2.2 Hz, 3H), 3.92 (s, 3H), 6.82 (d, *J* = 2.6 Hz, 1H), 6.94 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 15.7 (q, *J* = 4.1 Hz), 56.0, 100.4, 112.0 (q, *J* = 30.0 Hz), 112.5, 113.4, 123.2 (q, *J* = 272.1 Hz), 127.2, 155.1 (d, *J* = 1.8 Hz), 155.1, 156.4, 164.4.

7-ethoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3r)



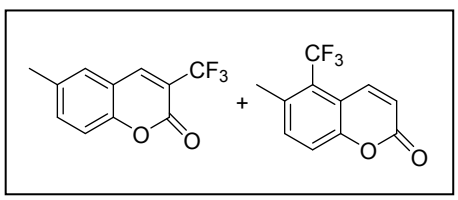
Following the general procedure, the desired compound was obtained as white solid, mp 99 – 100 °C, 53.4 mg, 65% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.49 (t, *J* = 7.0 Hz, 3H), 2.64 (q, *J* = 2.2 Hz, 3H), 4.13 (q, *J* = 7.0 Hz, 2H), 6.78 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.5, 15.7 (q, *J* = 4.1 Hz), 64.5, 100.8, 111.8 (q, *J* = 29.9 Hz), 112.3, 113.7, 123.2 (q, *J* = 272.0 Hz), 127.1, 155.1, 155.2 (d, *J* =1.5 Hz), 156.4, 163.8. HRMS (ESI) m/z calculated for $C_{13}H_{12}F_3O_3^+$ 273.0733, Found 273.0733.

6-nitro-3-(trifluoromethyl)-2H-chromen-2-one (3s) [7]



Following the general procedure, the desired compound was obtained as white solid, mp 188 – 190 °C, 13.8 mg, 18% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 7.73 (d, *J* = 9.1 Hz, 1H), 8.56 (dd, *J* = 9.2, 2.8 Hz, 1H) 8.91 (d, *J* = 2.8 Hz, 1H), 8.94 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 122.3, 122.8 (q, *J* = 32.7 Hz), 123.3, 126.6 (q, *J* = 269.3 Hz), 131.3 (d, *J* = 9.6 Hz), 134.1, 149.0, 149.4 (q, *J* = 4.9 Hz), 160.1, 163.0.

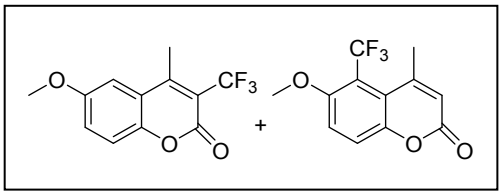
6-methyl-3-(trifluoromethyl)-2H-chromene (3t) [6] **and 6-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3t')**



Following the general procedure, the desired compound was obtained as white solid, mp 131 – 138 °C, 30.0 mg, 47% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) of **3q** δ 2.46 (s, 3H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 1H), 7.50 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.12 (s, 1H). **^{1}H NMR** ($CDCl_3$, 400 MHz)

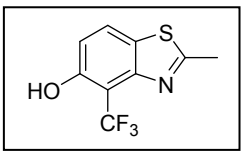
of **3q'** δ 2.58 (q, *J* = 3.8 Hz, 3H), 6.53 (d, *J* = 10.2 Hz, 1H), 7.43 (d, *J* = 3.5 Hz, 2H), 8.15 (d, *J* = 1.8 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 20.7, 21.27 (d, *J* = 4.4 Hz), 116.5, 116.7, 117.5 (q, *J* = 32.8 Hz), 117.9, 120.5, 121.5 (q, *J* = 269.3 Hz), 127.1 (q, *J* = 273.2 Hz), 129.1, 133.8, 135.2, 135.6, 135.8, 139.9 (q, *J* = 4.9 Hz), 143.3 (q, *J* = 4.9 Hz), 152.8, 153.3, 156.2, 159.2. HRMS (ESI) m/z calculated for $C_{11}H_8F_3O_2^+$ 229.0471, Found 229.0476.

6-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3u) and 6-methoxy-4-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3u')



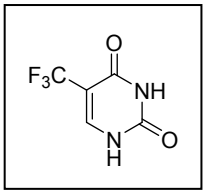
Following the general procedure, the desired compound was obtained as yellow solid, mp 103 – 106 °C, 31.4 mg, 41% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) of **3r** δ 2.68 (q, J = 2.2 Hz, 3H), 3.91 (s, 3H), 7.21 (d, J = 2.8 Hz, 1H), 7.26 (d, J = 2.8 Hz, 1H), 7.32 (d, J = 8.9 Hz, 1H). **^{1}H NMR** ($CDCl_3$, 400 MHz) of **3r'** δ 2.72 (q, *J* = 2.2 Hz, 3H), 4.02 (s, 3H), 7.23 (d, *J* = 2.8 Hz, 1H), 7.27 (s, 1H), 7.60 (s, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 156.4, 156.0, 155.0, 154.5, 153.9, 153.3, 147.5, 146.3, 124.2, 122.2, 121.5, 121.2, 121.2, 120.8, 119.5, 118.1, 116.62 (q, *J* = 5.4 Hz), 108.6, 108.6, 107.6, 107.6, 56.6, 55.9. HRMS (ESI) m/z calculated for $C_{19}H_{10}F_3O_3^+$ 259.0577, Found 259.0581.

2-methyl-4-(trifluoromethyl)benzo[d]thiazol-5-ol (3v) [3]



Following the general procedure, the desired compound was obtained as white solid, mp 190 – 192 °C, 18.5 mg, 26% yield. **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 2.80 (s, 3H), 7.11 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 10.62 (s, 1H). **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 20.5, 108.0 (q, *J* = 29.1 Hz), 115.9, 124.8 (q, *J* = 270.0 Hz), 126.6, 127.0, 150.9, 155.8, 170.0.

5-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3w)[3]

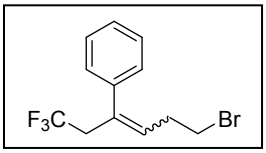


Following the general procedure, the desired compound was obtained as white solid, mp 99 – 100 °C, 53.4 mg, 65% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 1.49 (t, *J* = 7.0 Hz, 3H), 2.64 (q, *J* = 2.2 Hz, 3H), 4.13 (q, *J* = 7.0 Hz, 2H), 6.78 (d, *J* = 2.5 Hz, 1H), 6.92 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.70 (d, *J* = 9.1 Hz, 1H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 14.5, 15.7 (q, *J* = 4.1 Hz), 64.5, 100.8, 111.8 (q, *J* = 29.9 Hz), 112.3, 113.7, 123.2 (q, *J* = 272.0 Hz), 127.1, 155.1, 155.2 (d, *J* =1.5 Hz), 156.4, 163.8.

HRMS (ESI) m/z calculated for $C_{13}H_{12}F_3O_3^+$ 273.0733, Found 273.0733.

7 Characterization data of 6

(6-bromo-1,1,1-trifluorohex-3-en-3-yl)benzene



Colorless oil, 17% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 2.77 (q, *J* = 6.9 Hz, 2H), 2.87 (q, *J* = 7.0 Hz, 2H), 3.38 (q, *J* = 10.5, 2H), 3.38 (q, *J* = 10.5, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 3.67 (t, *J* = 6.7 Hz, 2H), 6.03 (t, *J* = 7.3 Hz, 2H), 6.03 (t, *J* = 7.3 Hz, 2H), 7.43-7.28 (m, 10H). **^{19}F NMR** (376 MHz, CDCl3) δ (ppm): -63.6, -63.6.

8 Reference

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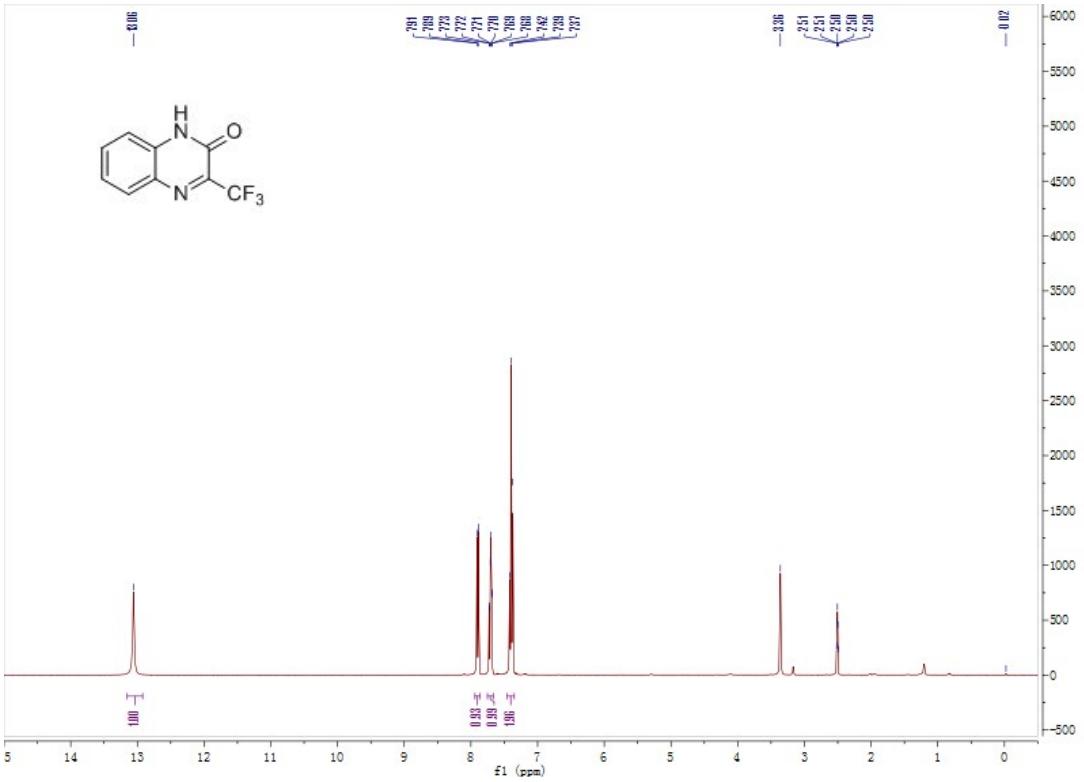
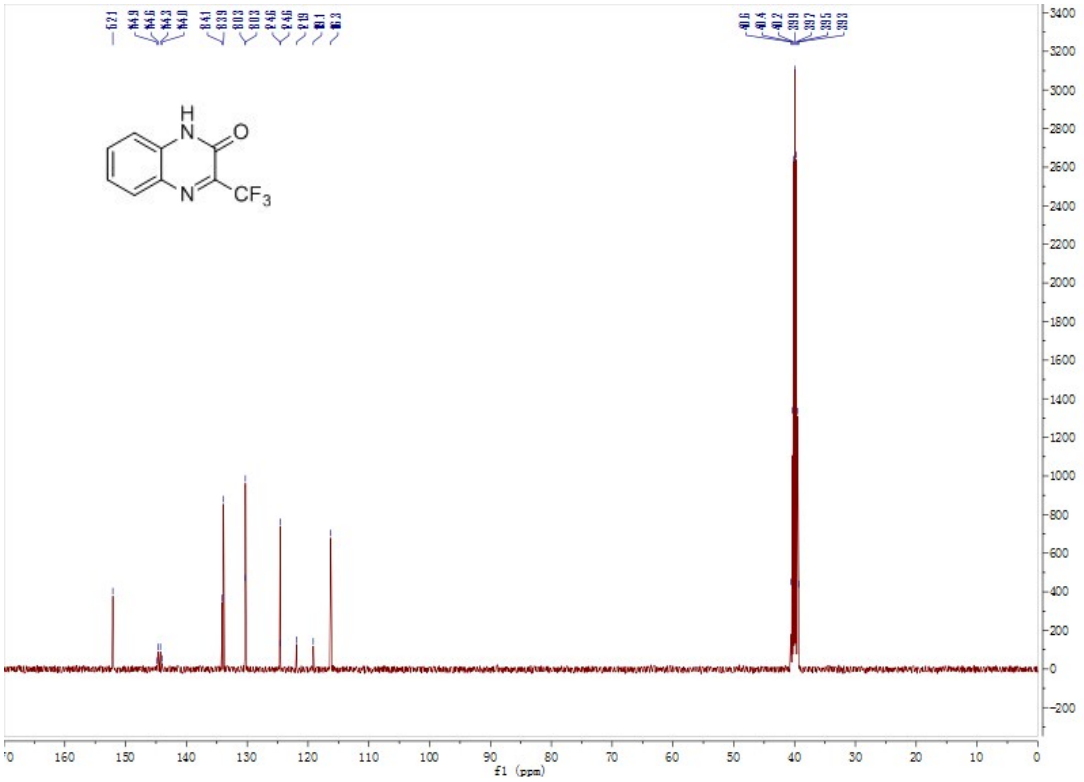
7 X. H. Cao, X. Q. Pan, P. J. Zhou, J. P. Zou, O. T. Asekun, *Chem. Commun.* **2014**, 50, 3359.

9 Copies of NMR spectra for prepared compounds

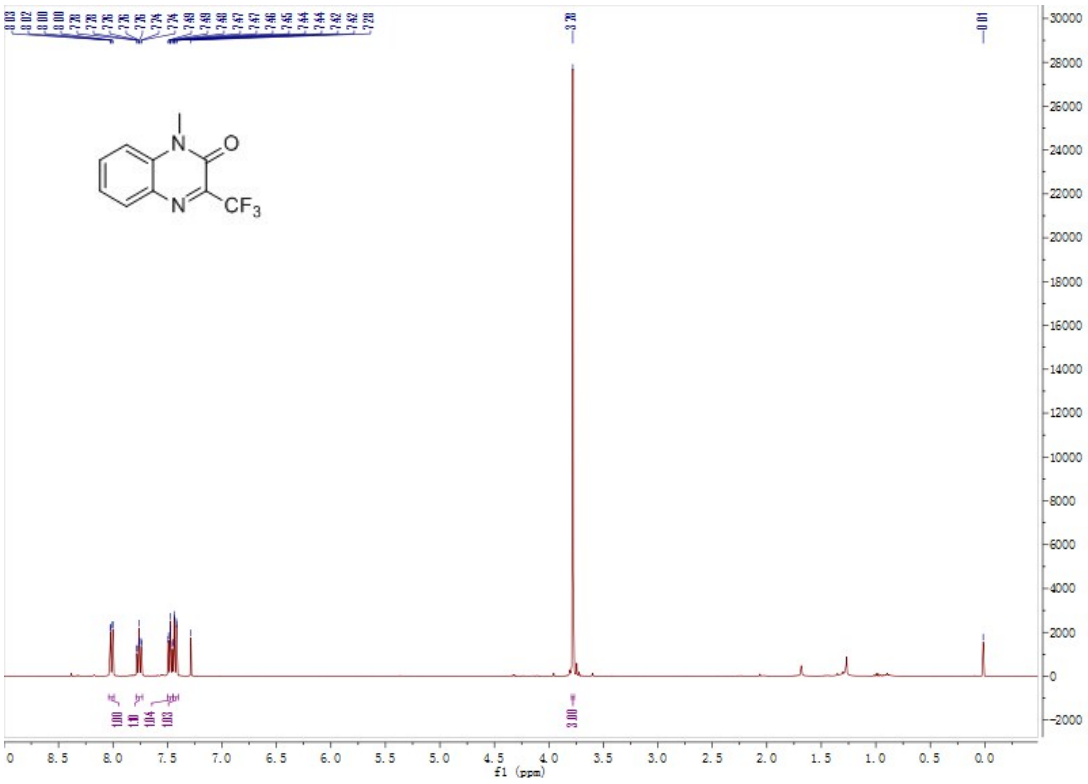
^{1} H NMR of 3-(trifluoromethyl)quinoxalin-2(1H)-one (3a)



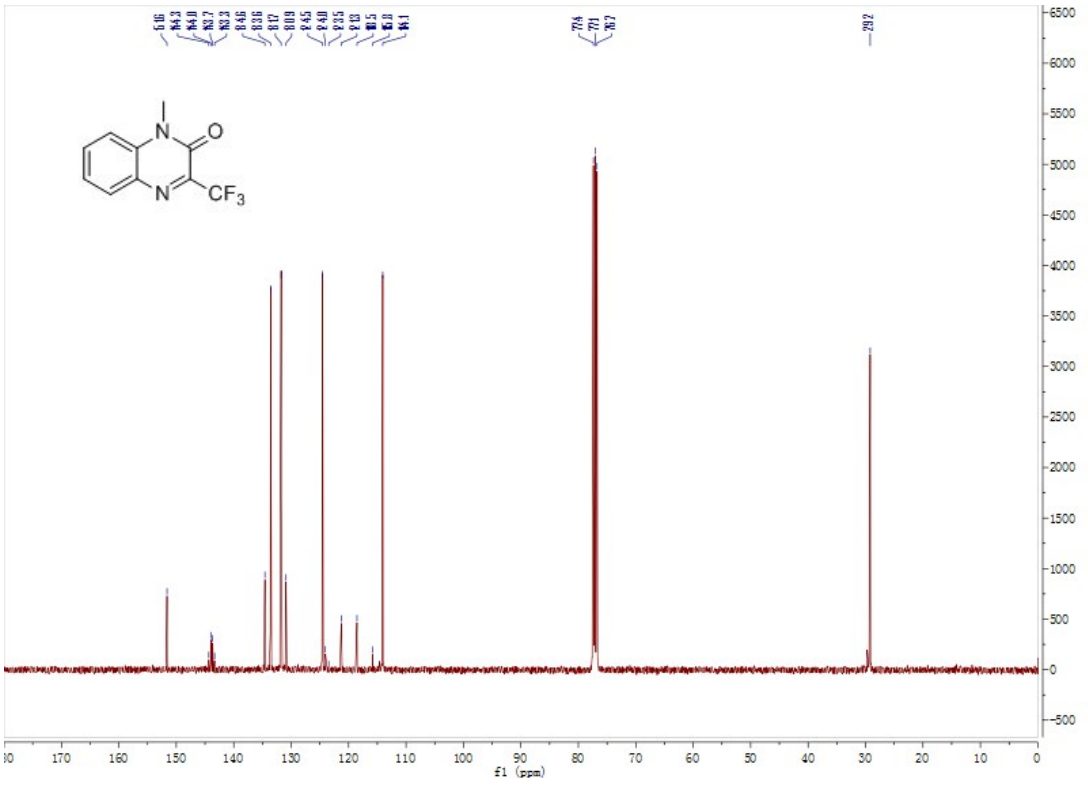
^{13} C NMR of 3-(trifluoromethyl)quinoxalin-2(1H)-one (3a)



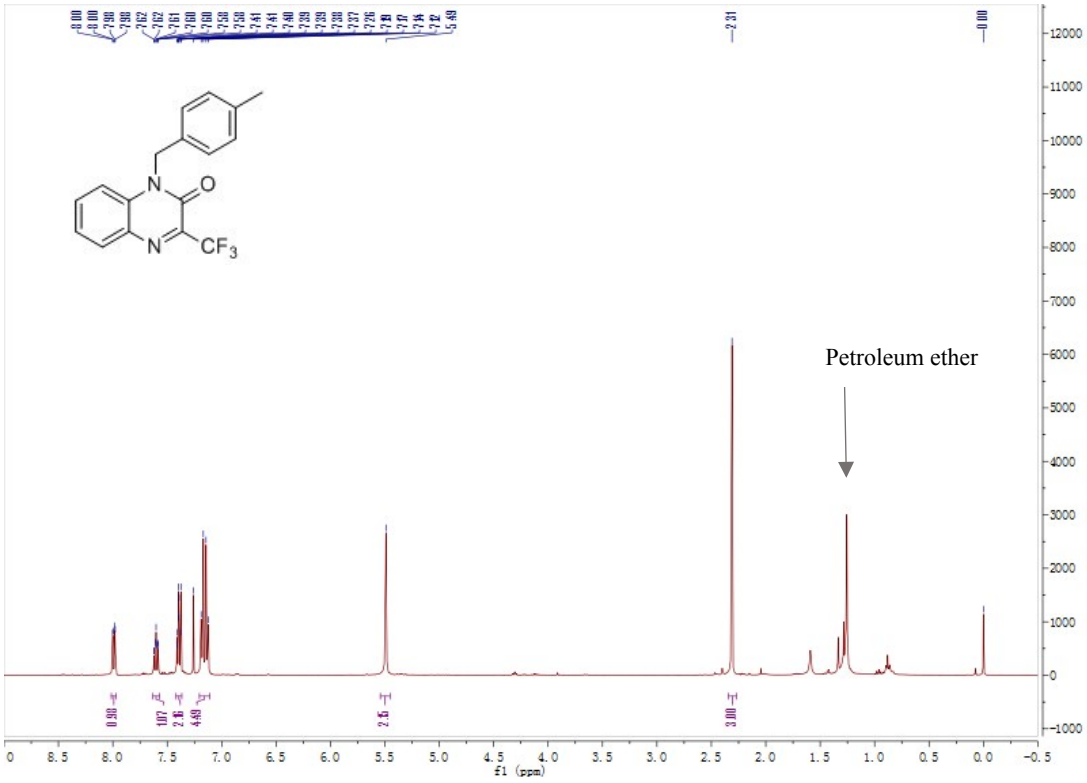
^{1} H NMR of 1-methyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (3b)



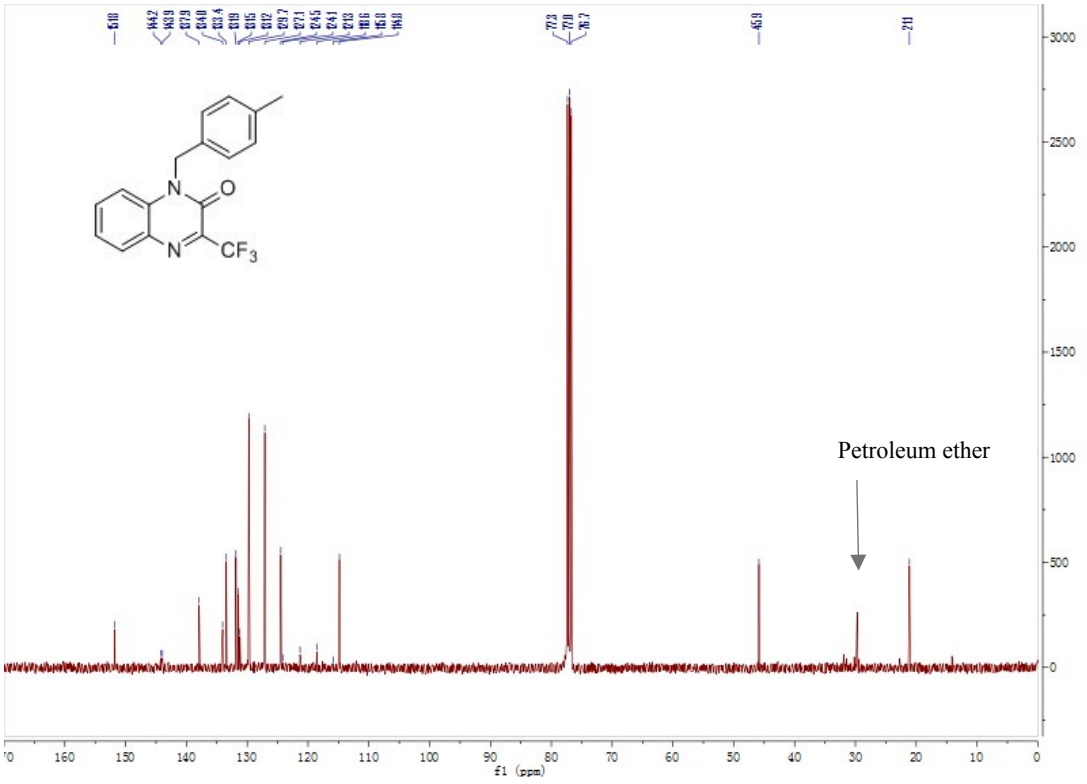
^{13} C NMR of 1-methyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (3b)



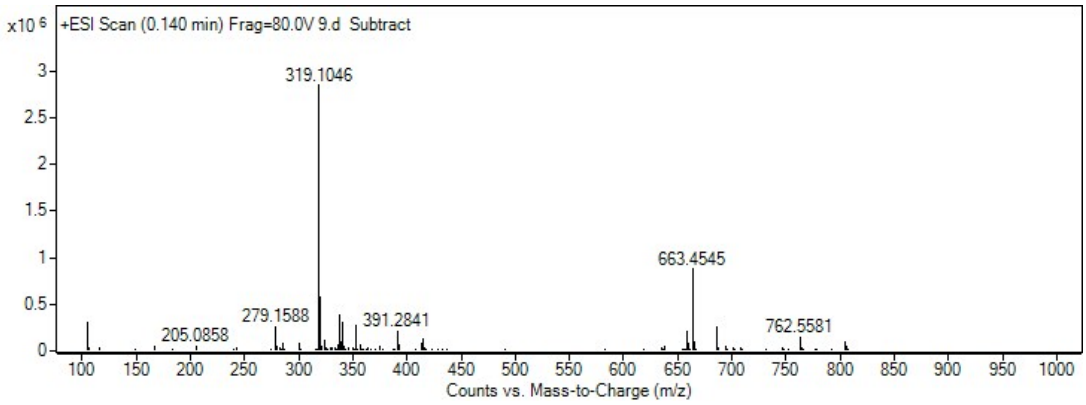
^{1} H NMR of 1-(4-methylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3c)



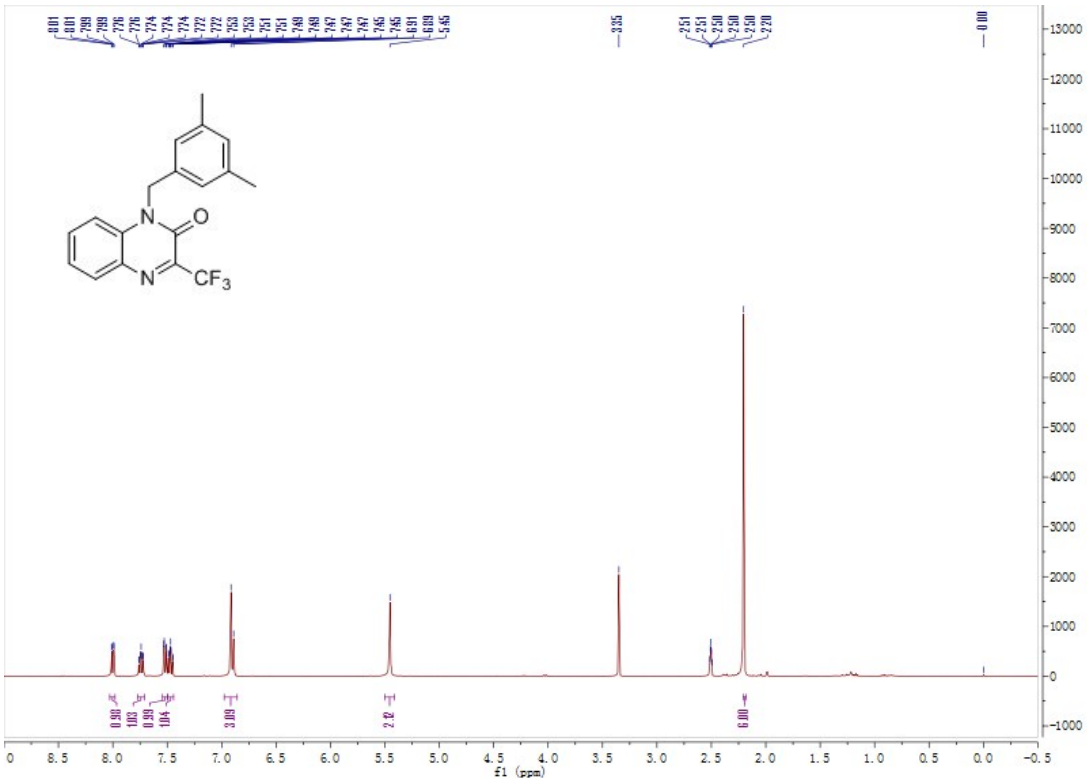
^{13} C NMR of 1-(4-methylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3c)



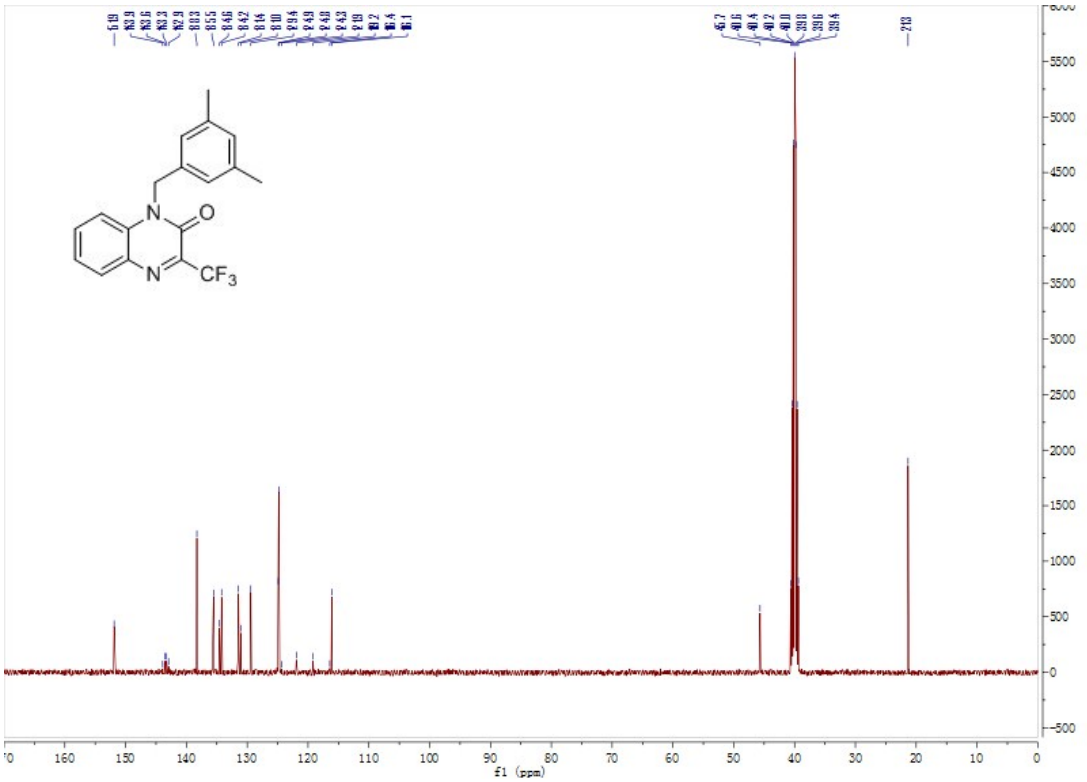
HRMS spectra of 1-(4-methylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3c)



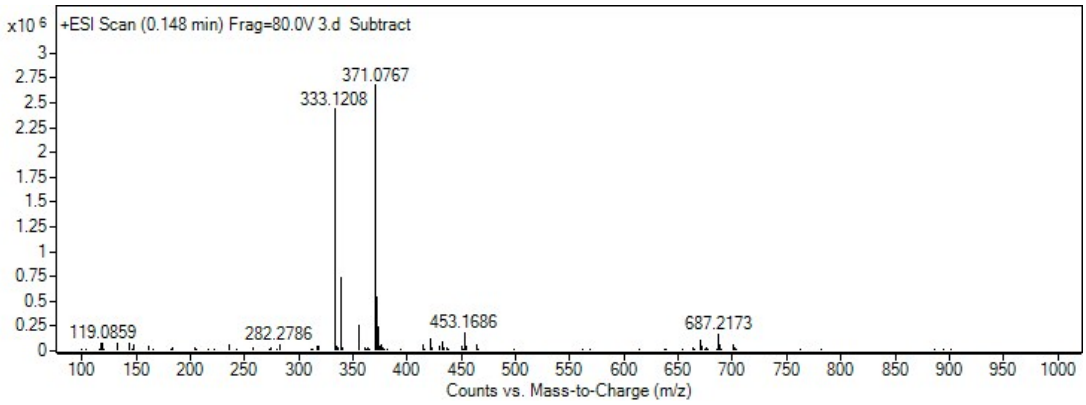
^{1} H NMR of 1-(3,5-dimethylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3d)



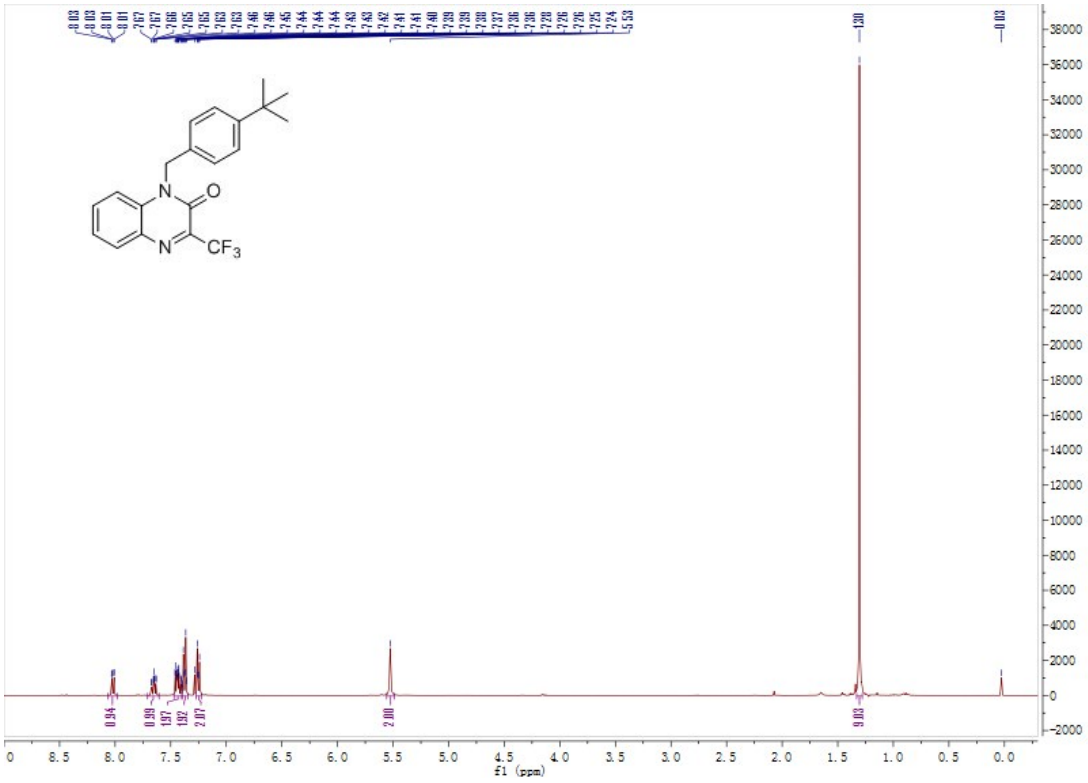
^{13} C NMR of 1-(3,5-dimethylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3d)



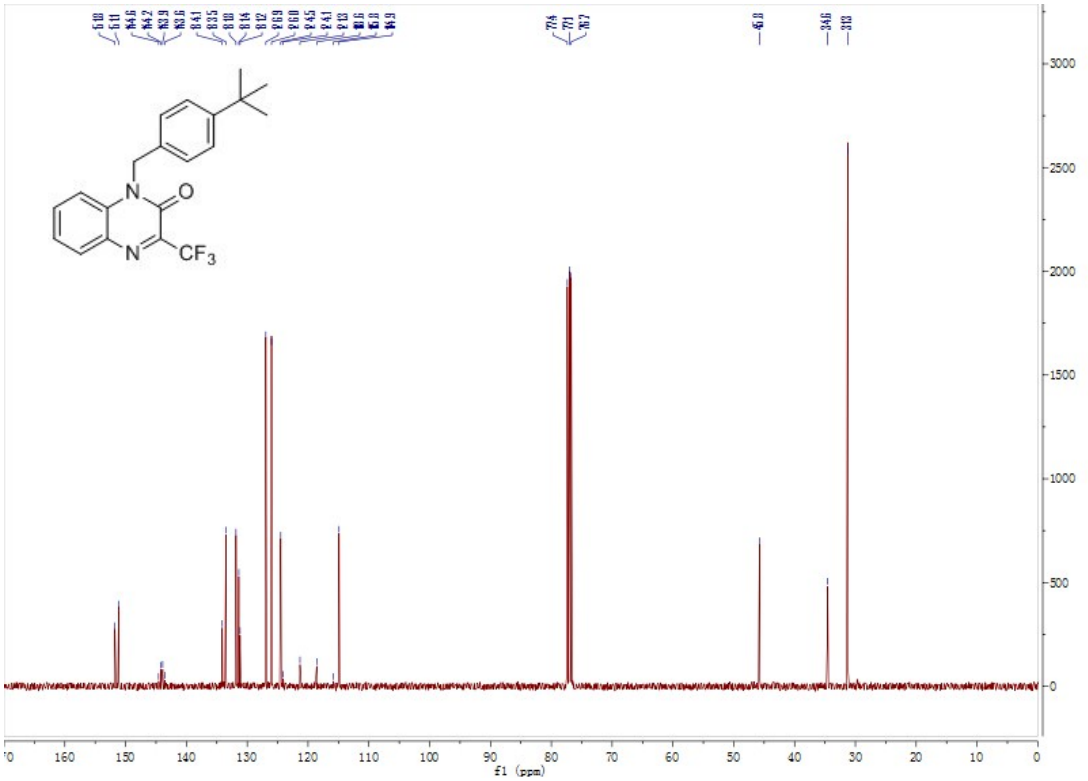
HRMS spectra of 1-(3,5-dimethylbenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3d)



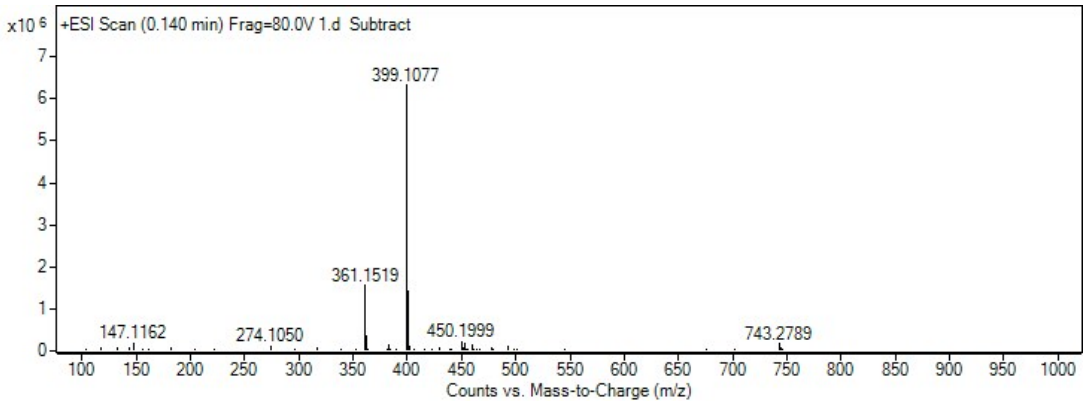
^{1} H NMR of 1-(4-(tert-butyl)benzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3e)



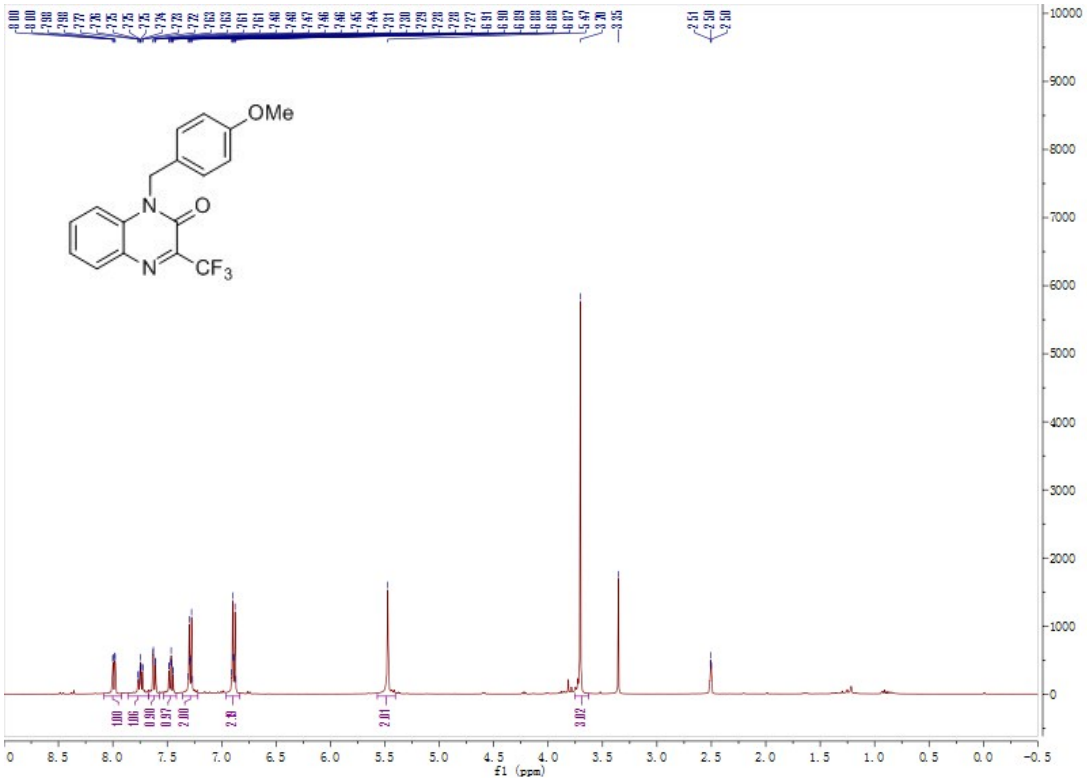
^{13} C NMR of 1-(4-(tert-butyl)benzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3e)



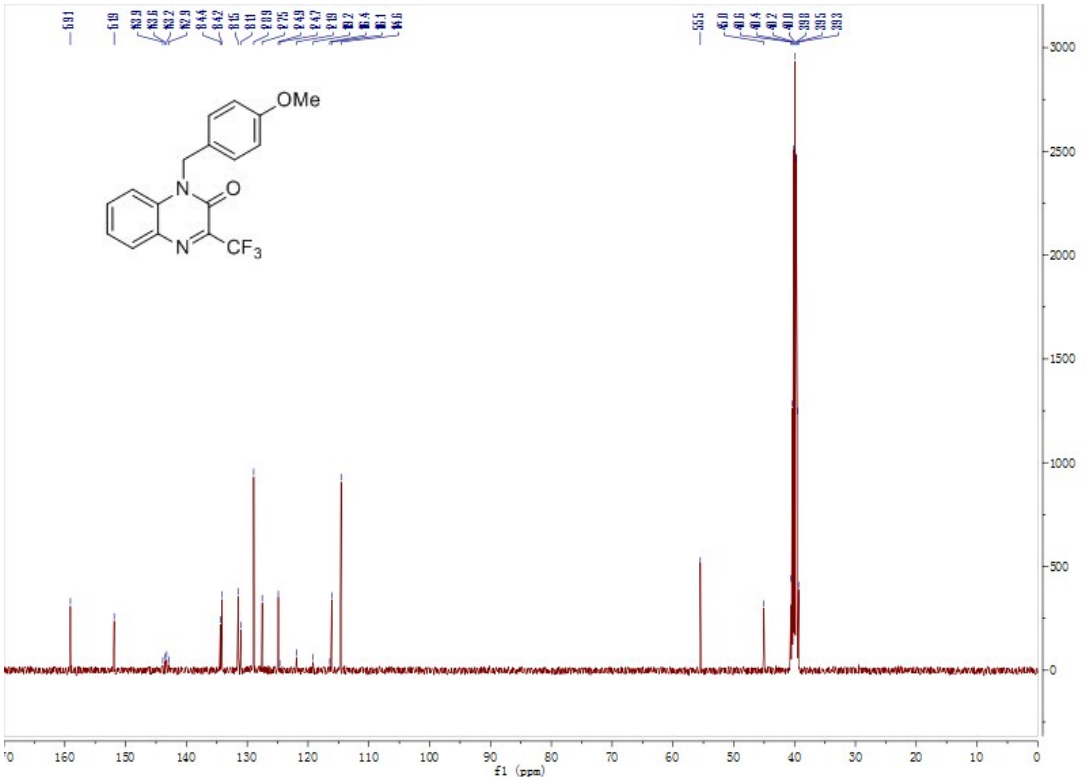
HRMS spectra of 1-(4-(tert-butyl)benzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3e)



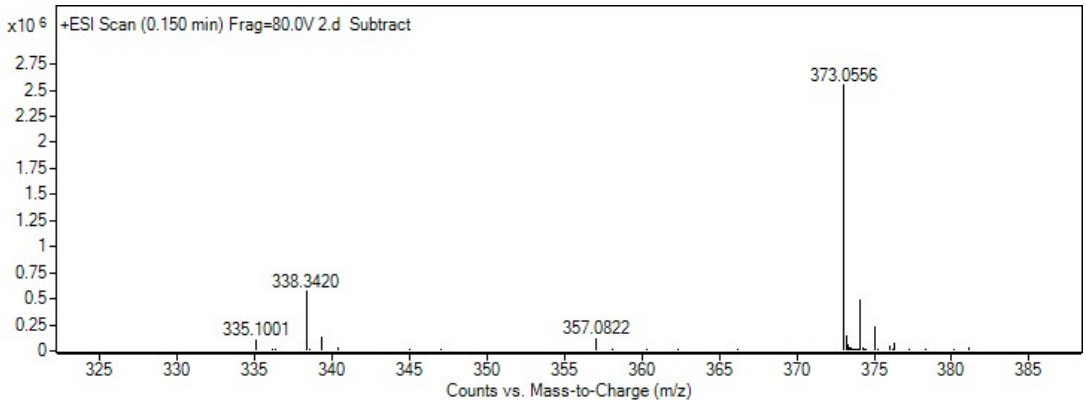
^{1} H NMR of 1-(4-methoxybenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3f)



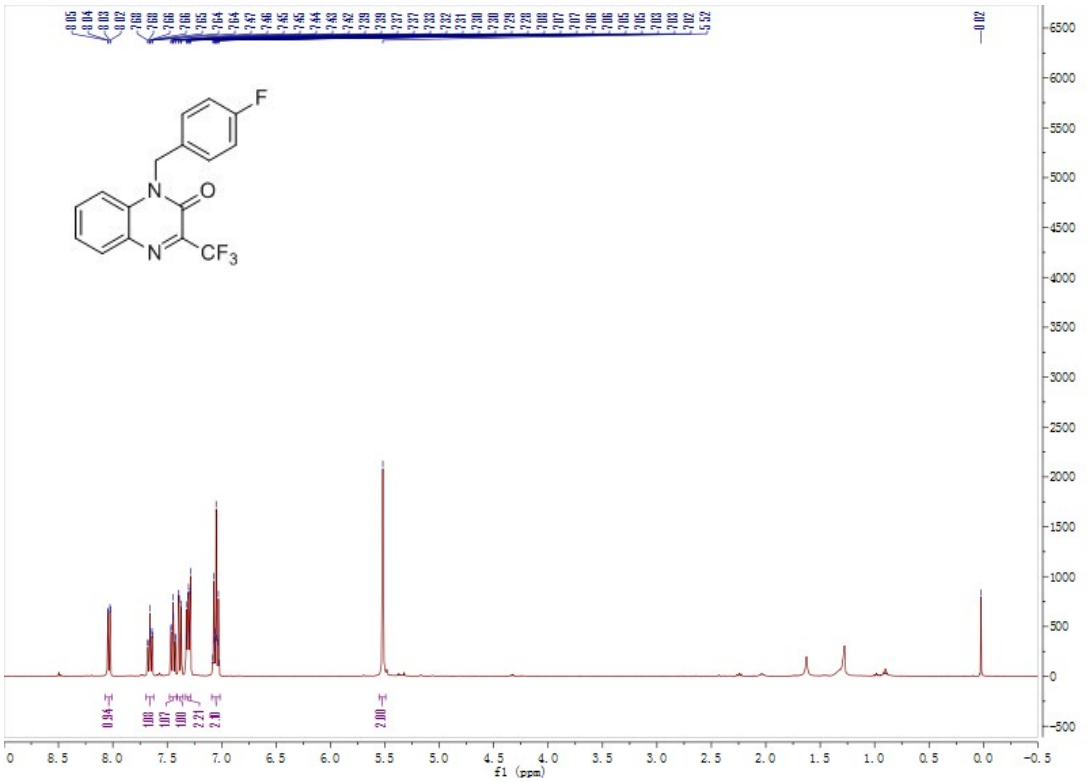
^{13} C NMR of 1-(4-methoxybenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3f)



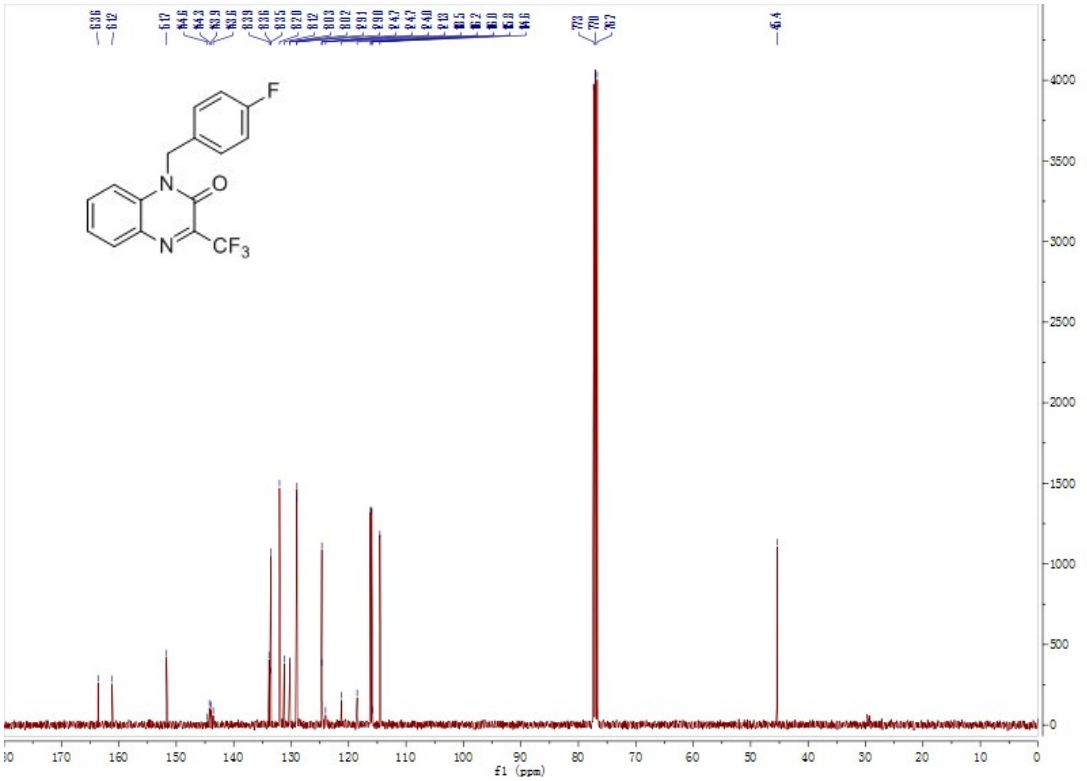
HRMS spectra of 1-(4-methoxybenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3f)



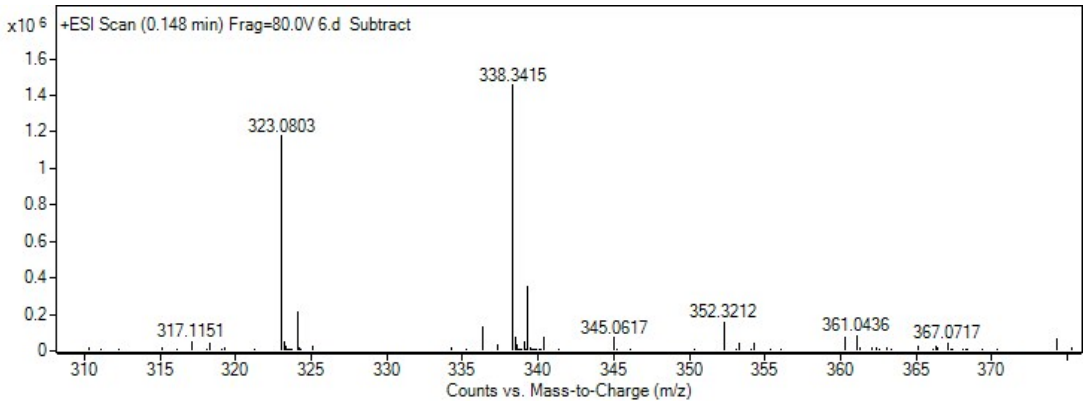
^{1} H NMR of 1-(4-fluorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3g)



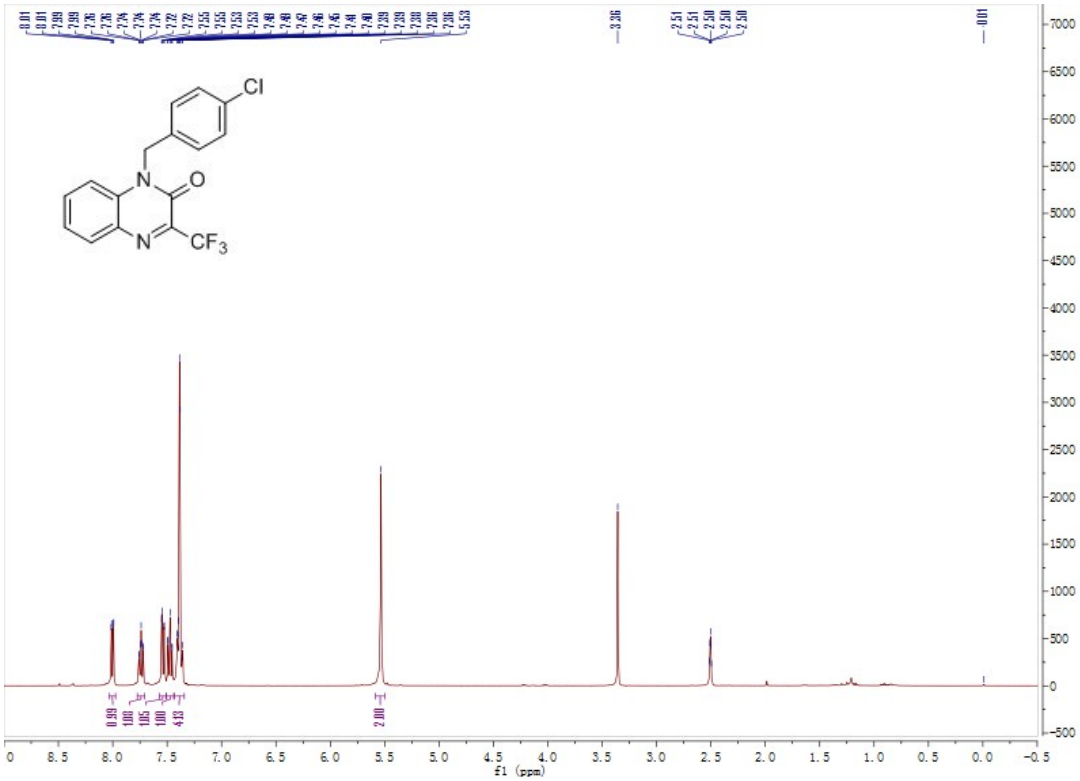
^{13} C NMR of 1-(4-fluorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3g)



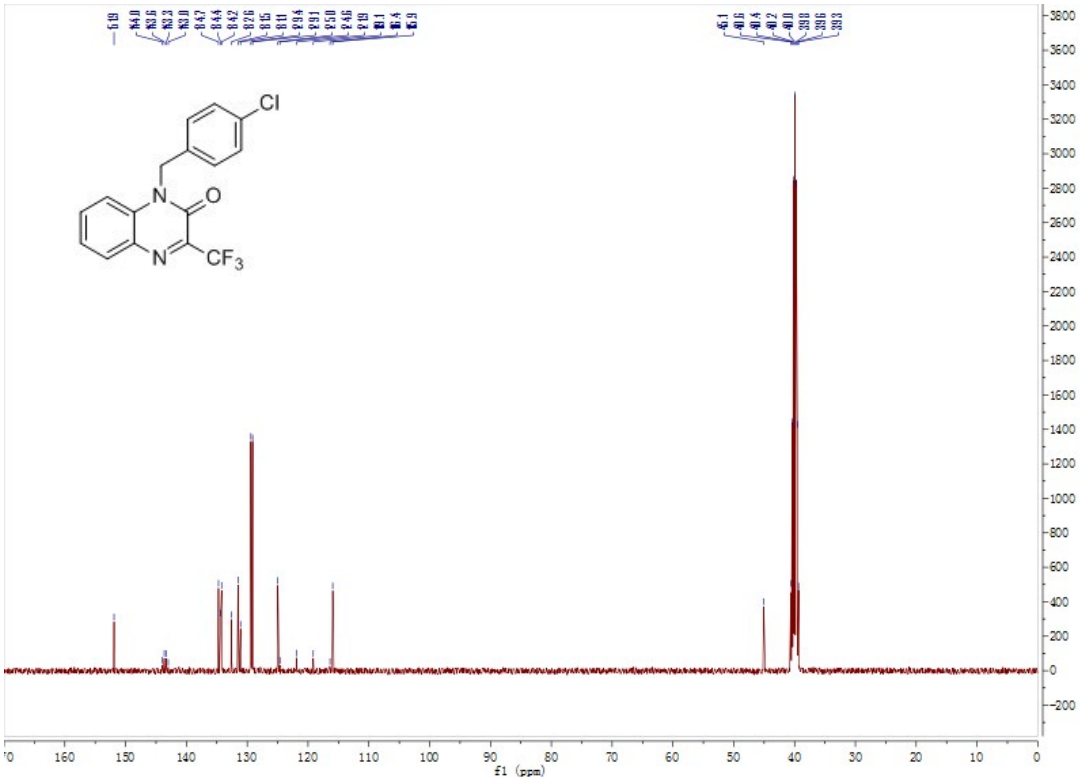
HRMS spectra of 1-(4-fluorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3g)



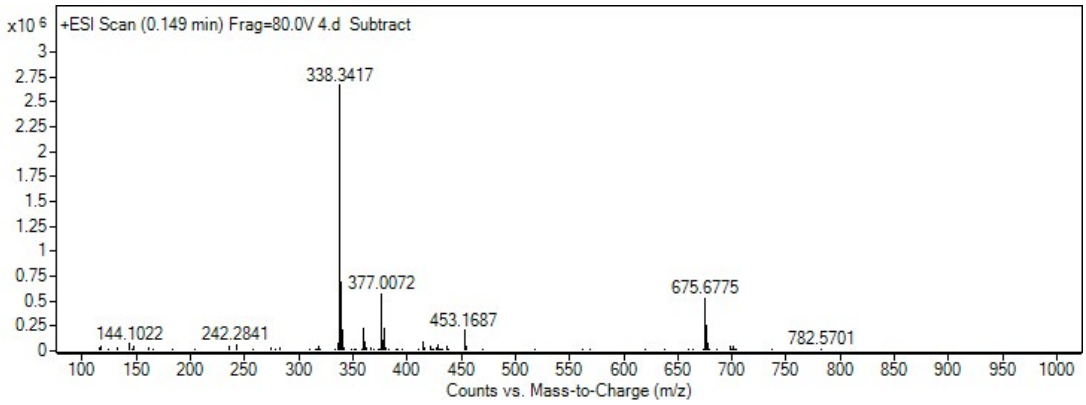
^{1} H NMR of 1-(4-chlorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3h)



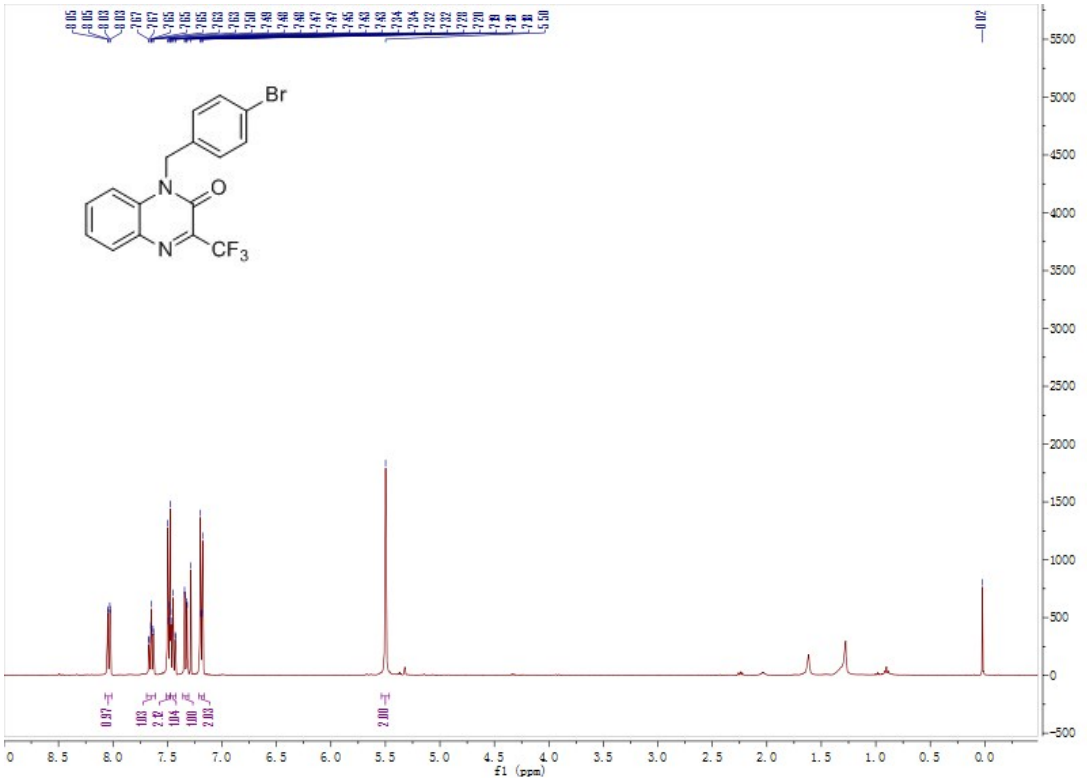
^{13} C NMR of 1-(4-chlorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3h)



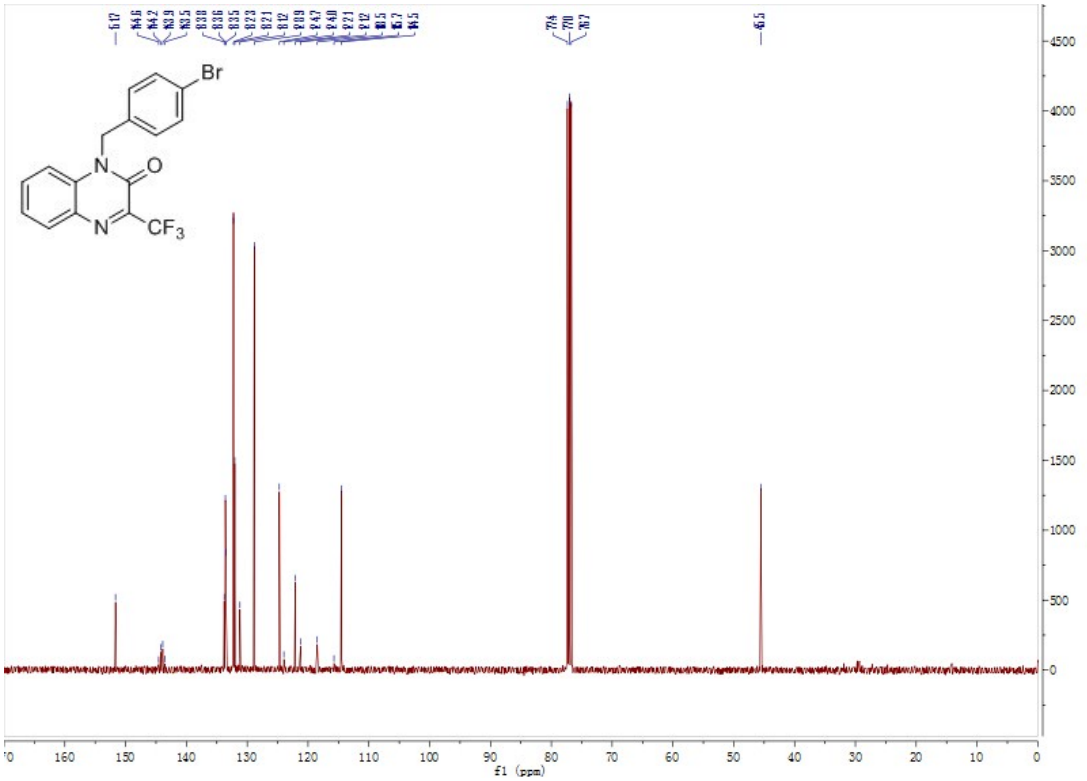
HRMS spectra of 1-(4-chlorobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3h)



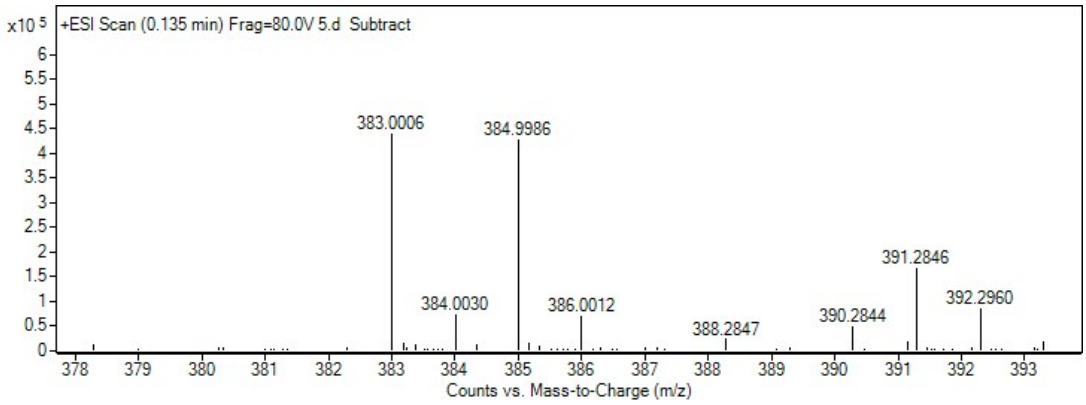
^{1} H NMR of 1-(4-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3i)



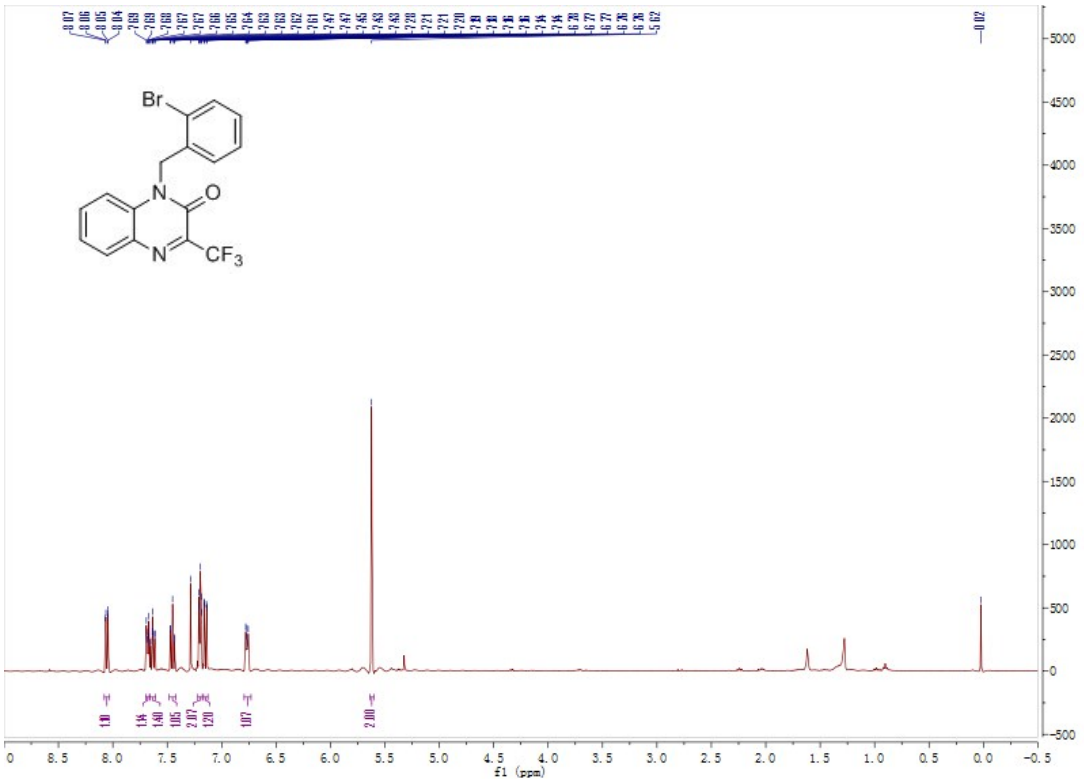
^{13} C NMR of 1-(4-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3i)



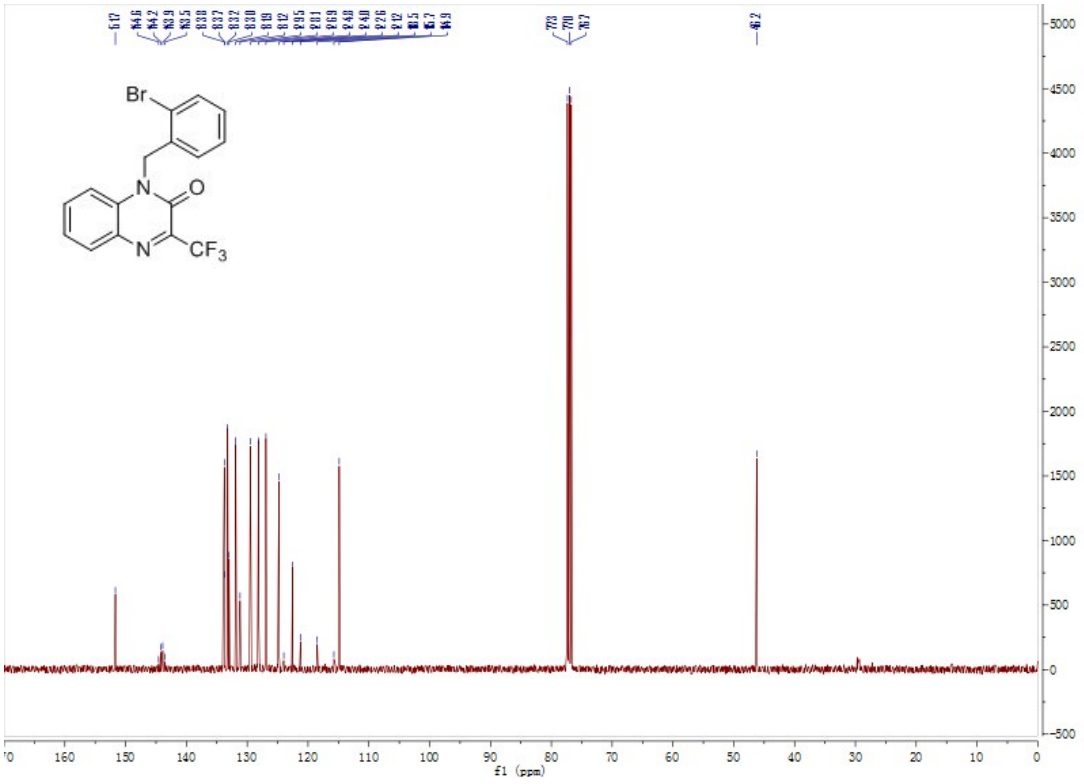
HRMS spectra of 1-(4-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3i)



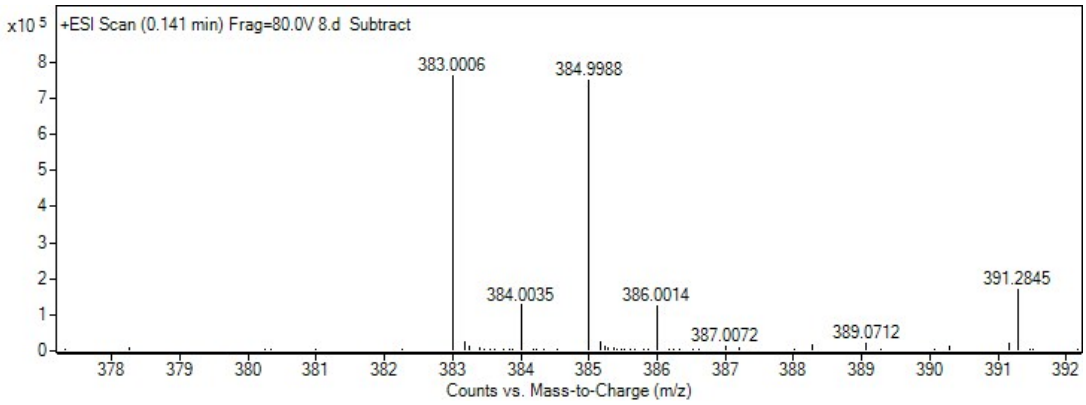
^{1} H NMR of 1-(2-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3j)



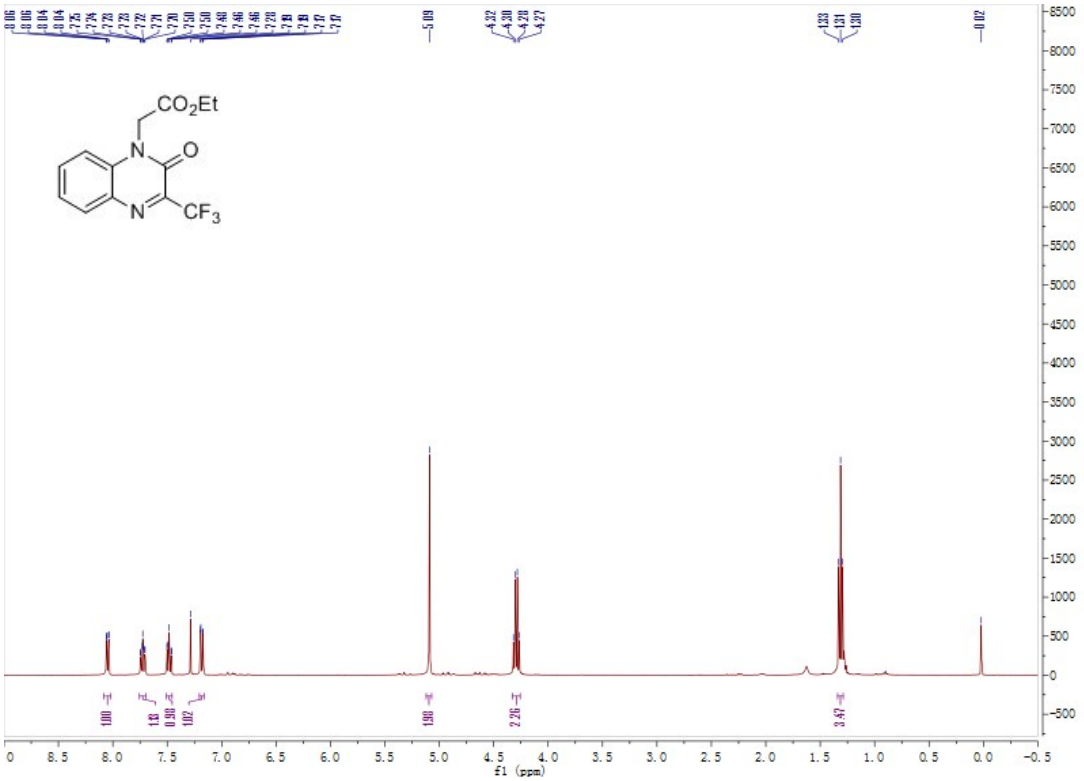
^{13} C NMR of 1-(2-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3j)



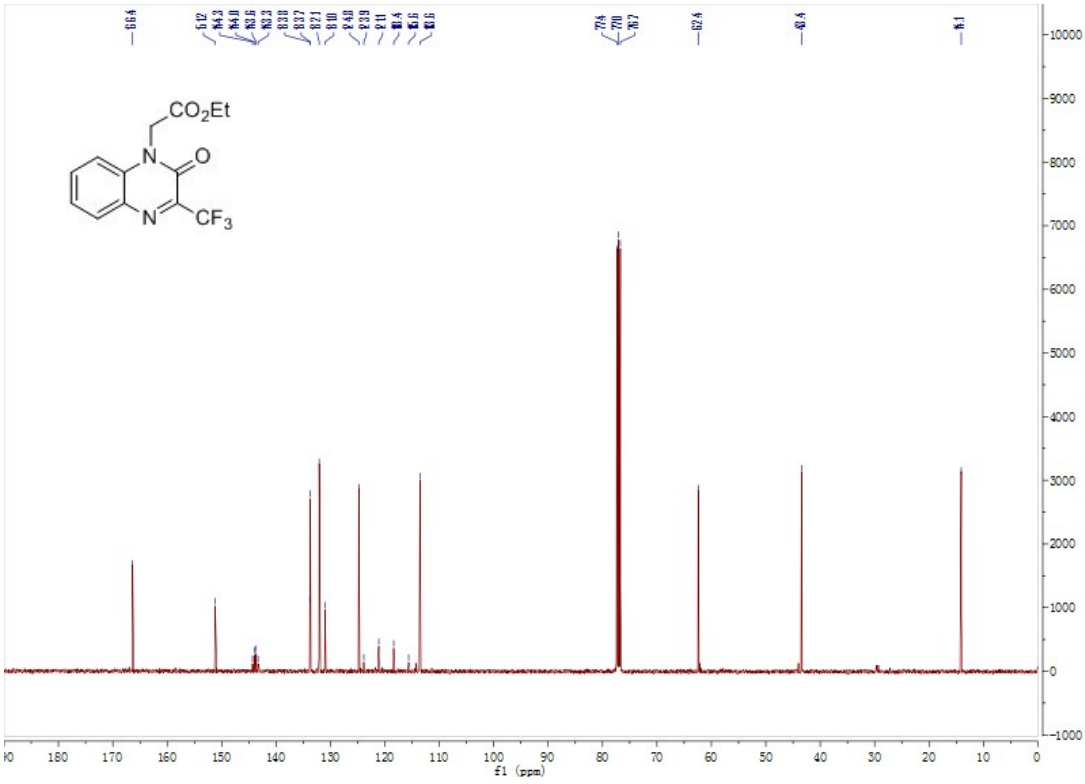
HRMS spectra of 1-(2-bromobenzyl)-3-(trifluoromethyl)quinoxalin-2(1H)-one (3j)



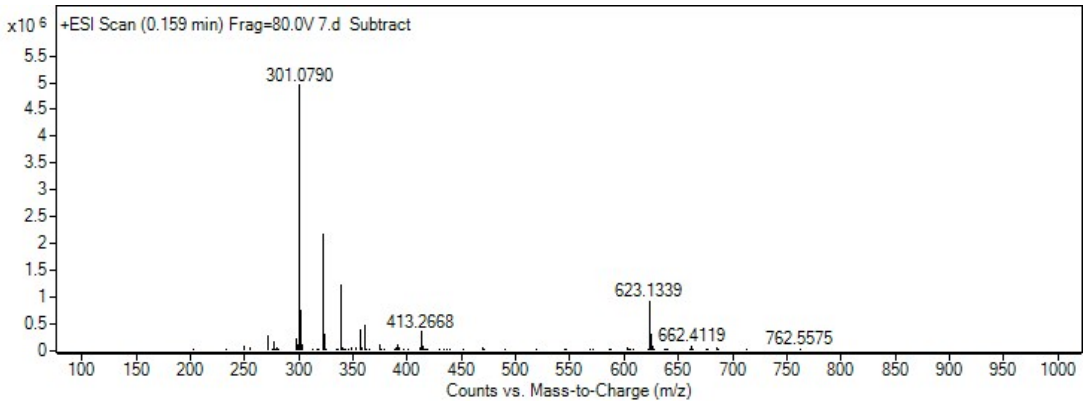
^{1} H NMR of ethyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(2H)-yl)acetate (3k)



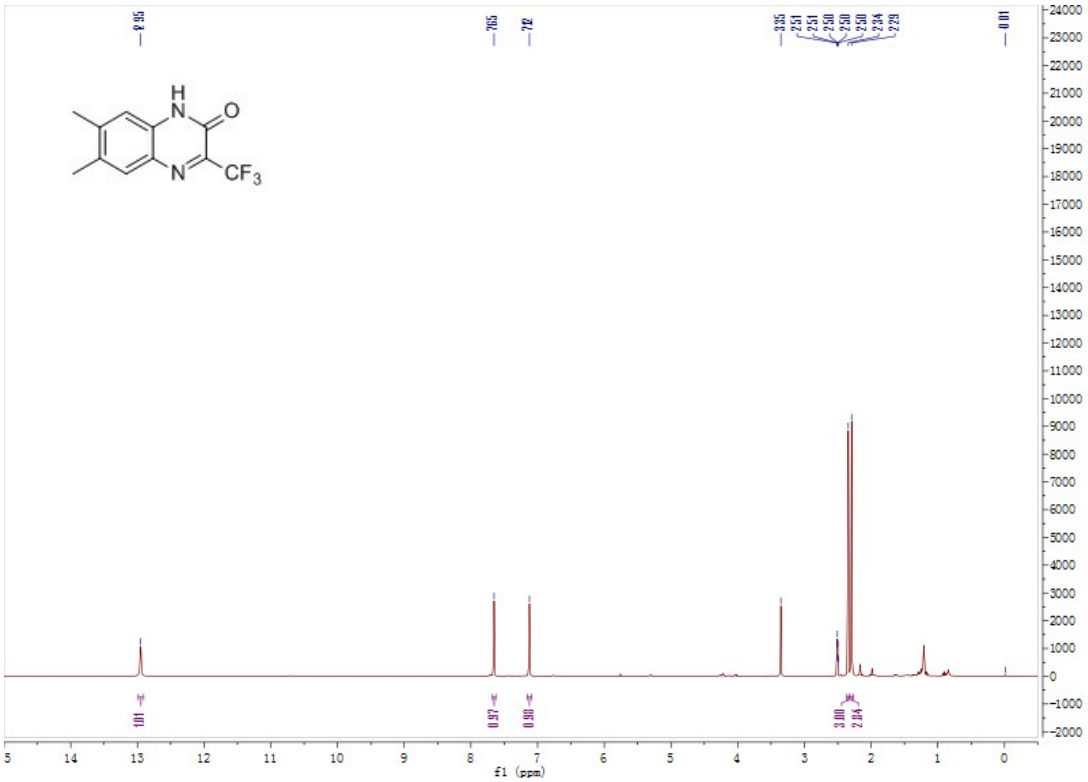
^{13} C NMR of ethyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(2H)-yl)acetate (3k)



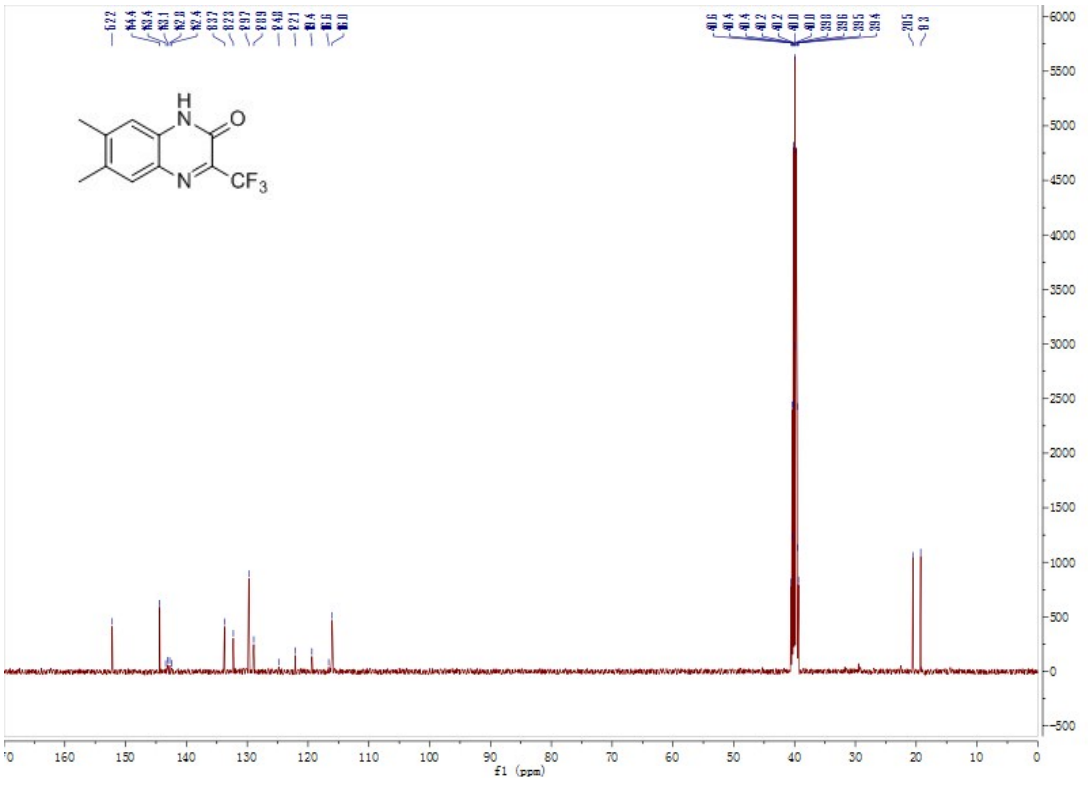
HRMS spectra of ethyl 2-(2-oxo-3-(trifluoromethyl)quinoxalin-1(2H)-yl)acetate (3k)



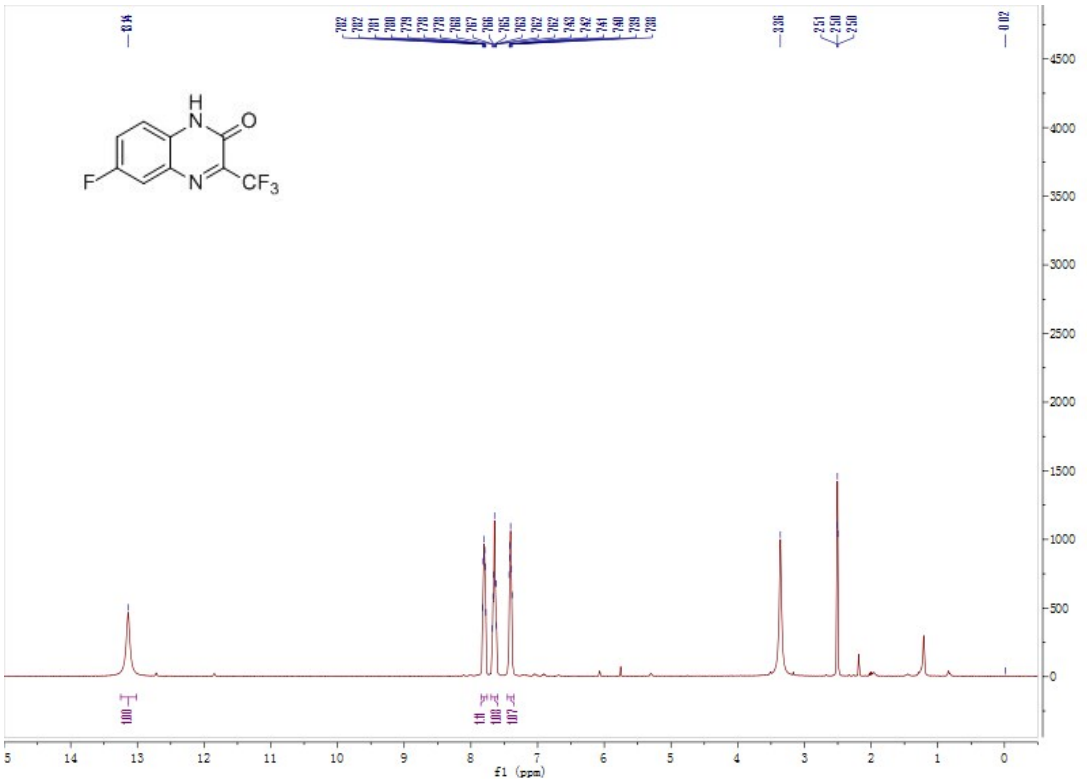
^{1} H NMR of 6,7-dimethyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (3l)



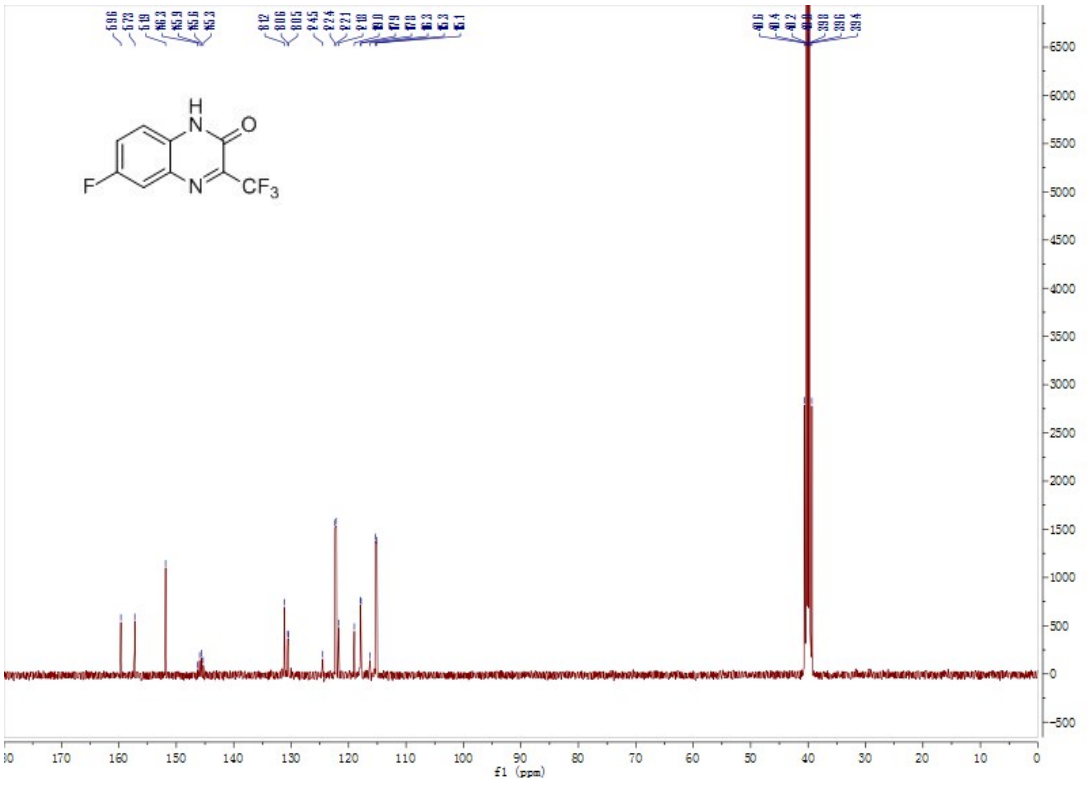
^{13} C NMR of 6,7-dimethyl-3-(trifluoromethyl)quinoxalin-2(1H)-one (3l)



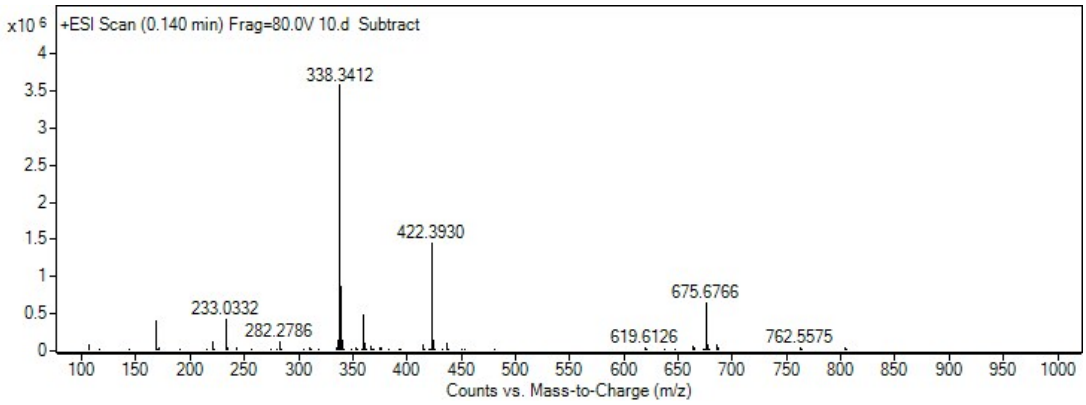
^{1} H NMR of 6-fluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3m)



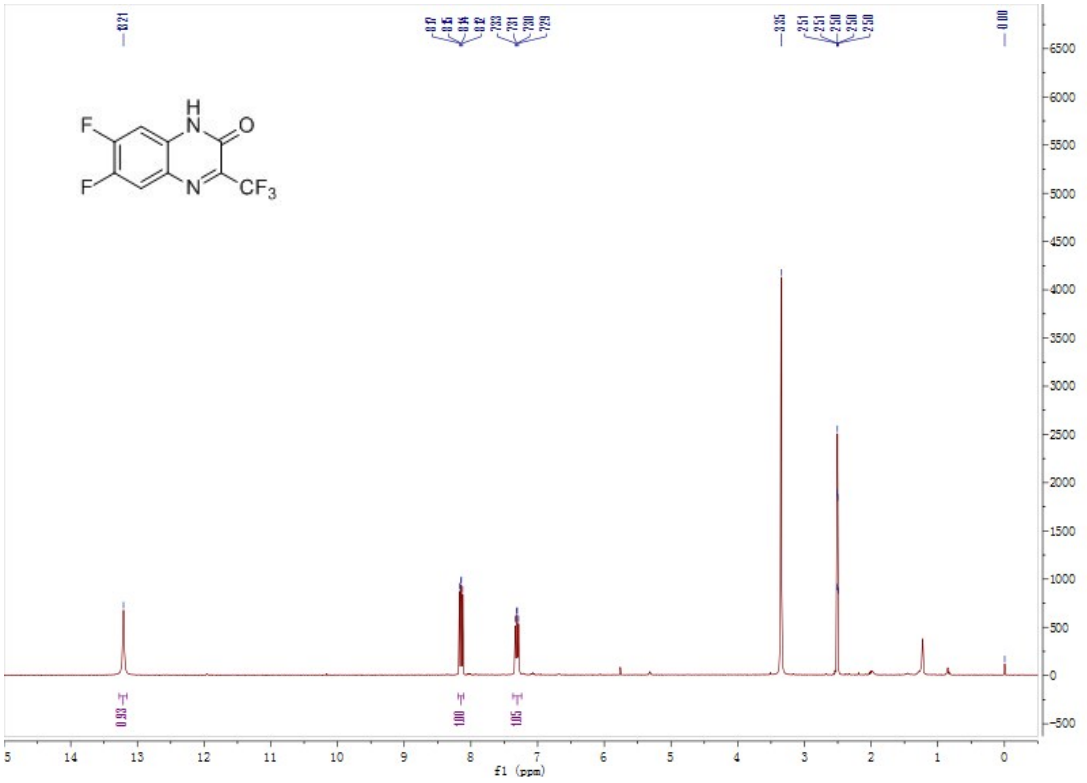
^{13} C NMR of 6-fluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3m)



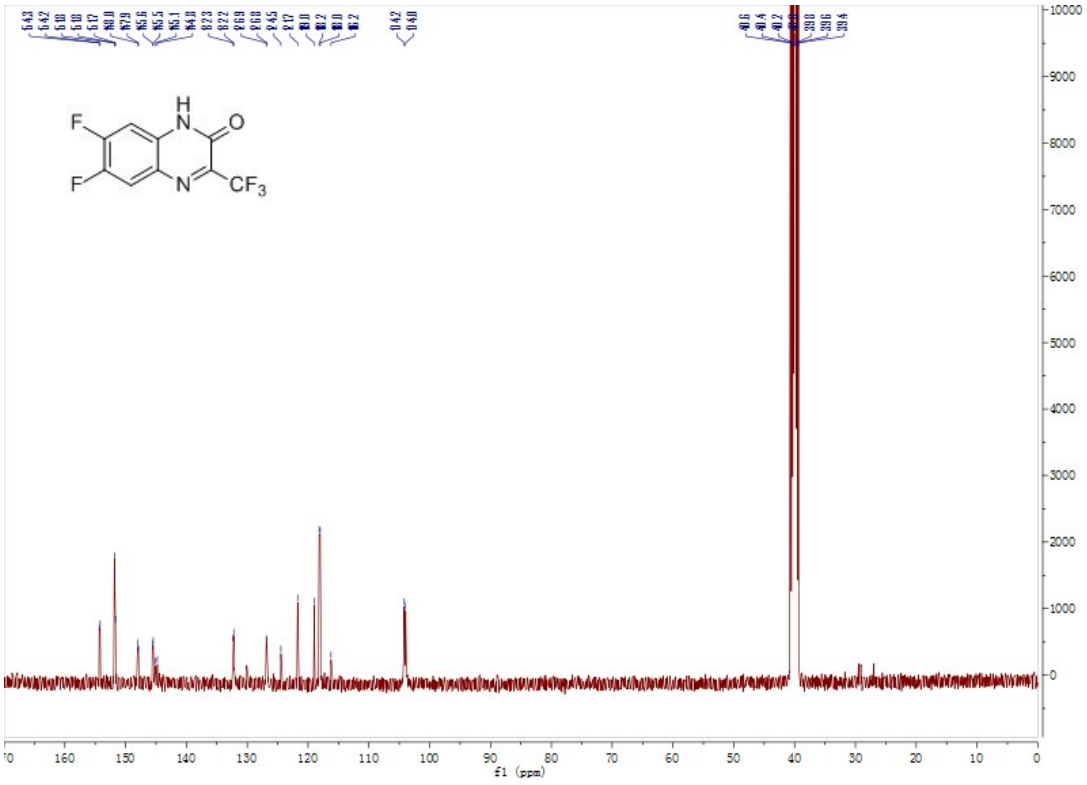
HRMS spectra of 6-fluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3m)



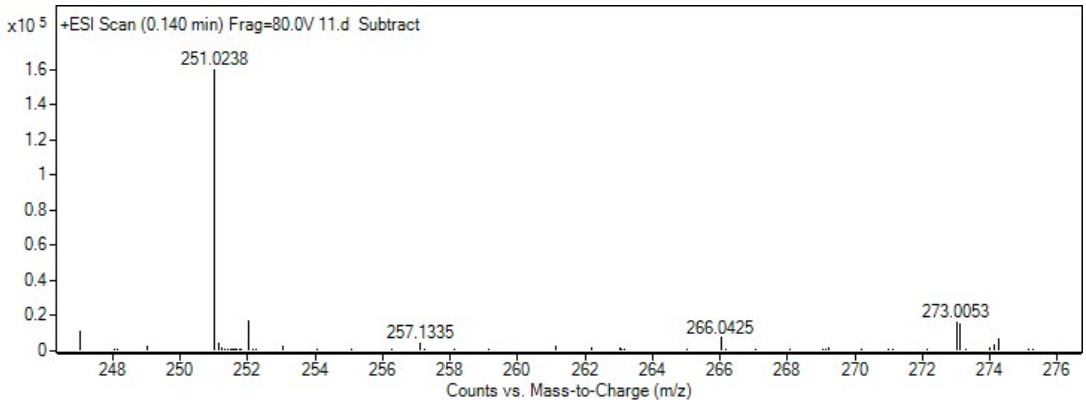
^{1} H NMR of 6,7-difluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3n)



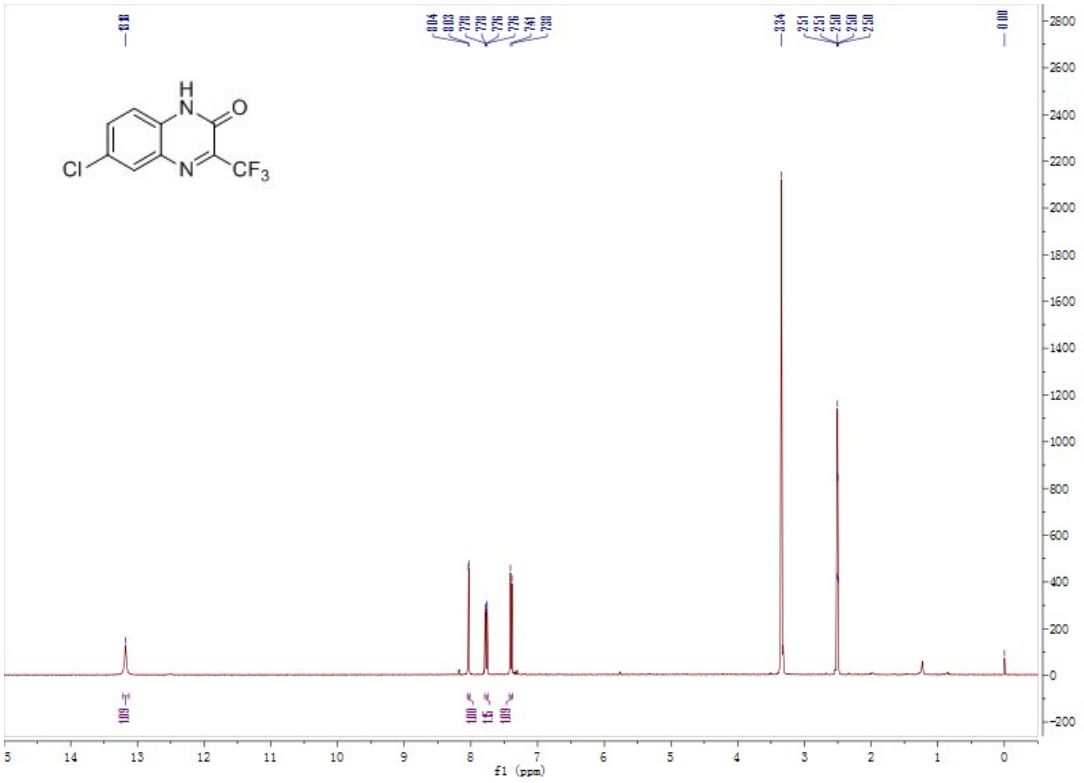
^{13} C NMR of 6,7-difluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3n)



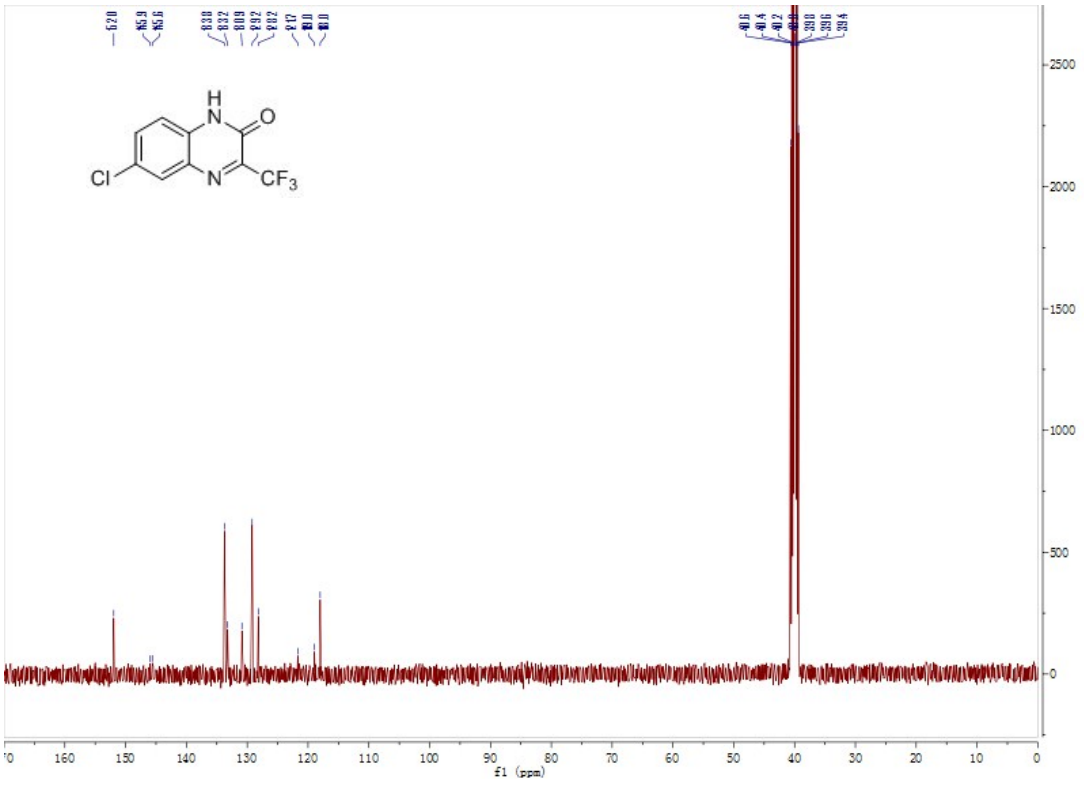
HRMS spectra of 6,7-difluoro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3n)



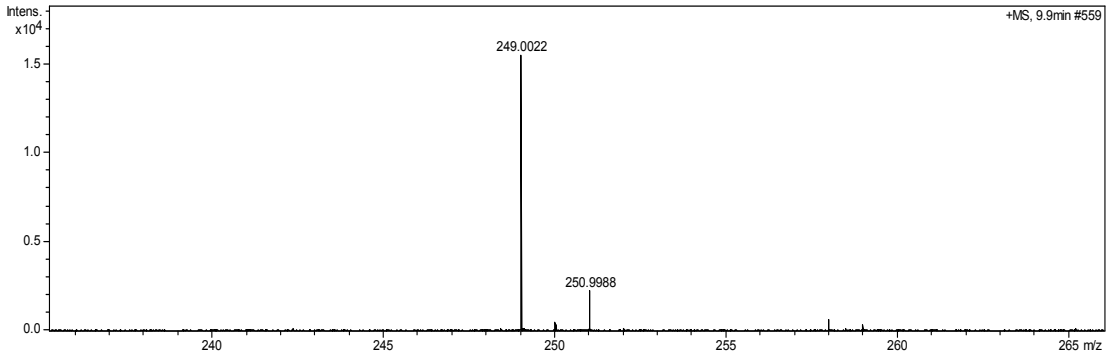
^{1} H NMR of 6-chloro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3o)



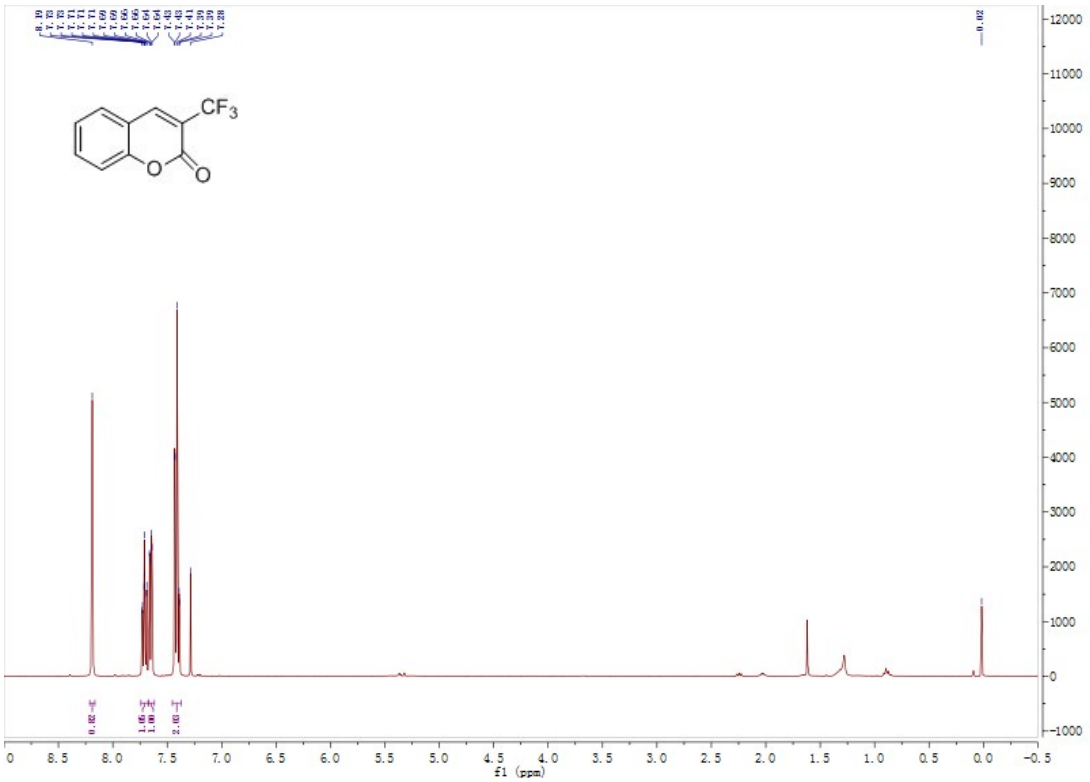
^{13} C NMR of 6-chloro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3o)



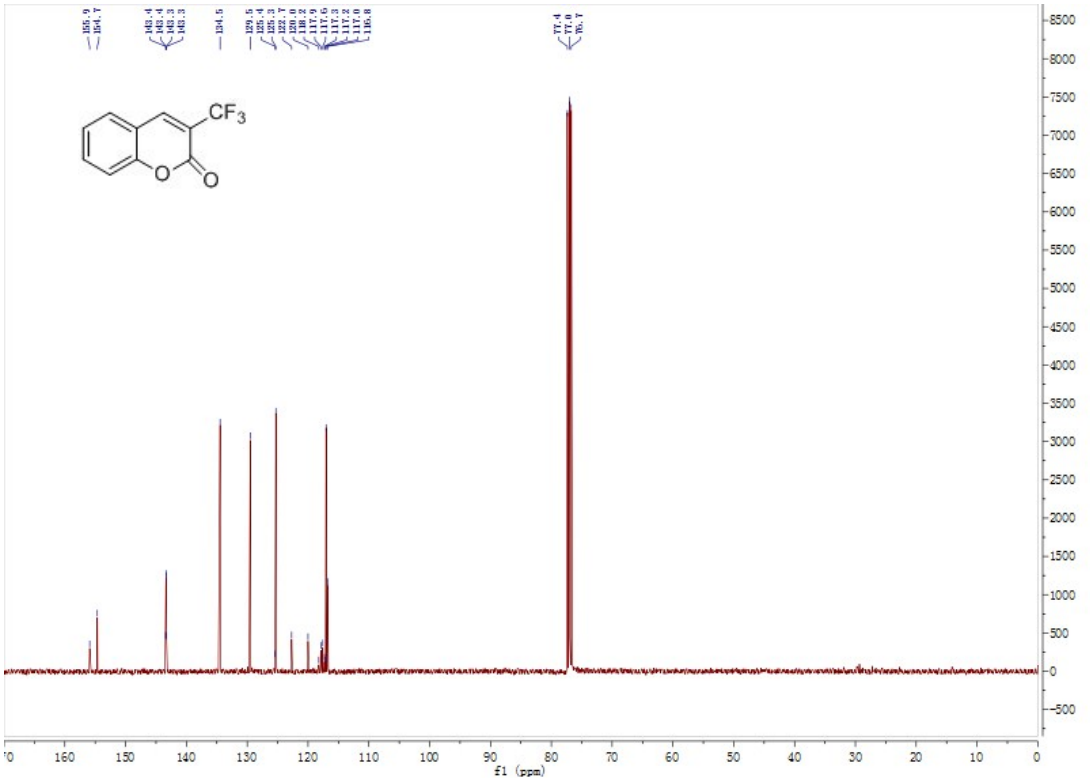
HRMS spectra of 6-chloro-3-(trifluoromethyl)quinoxalin-2(1H)-one (3o)



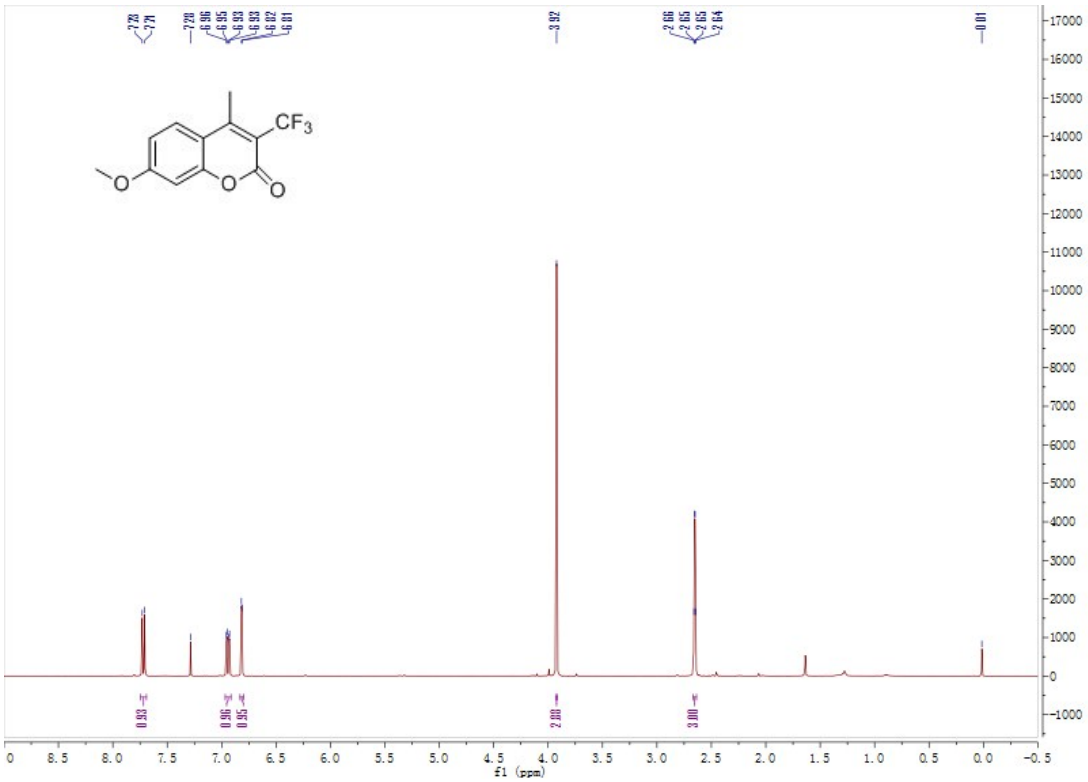
^{1} H NMR of 3-(trifluoromethyl)-2H-chromen-2-one (3p)



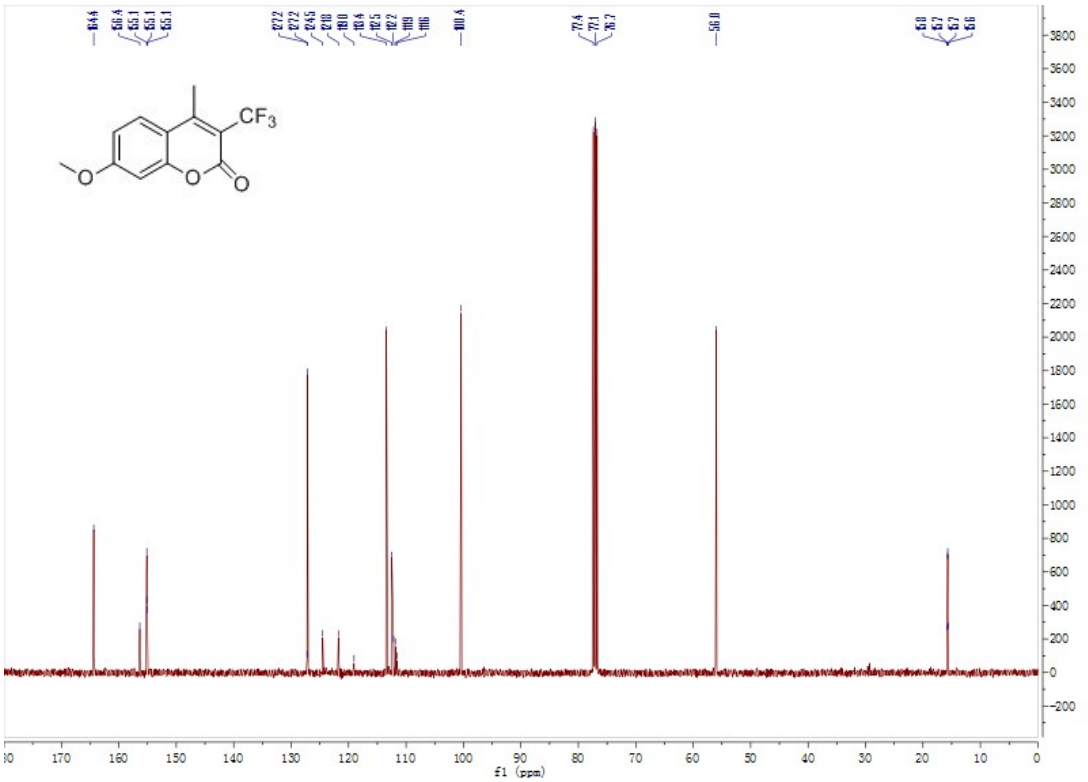
^{13} C NMR of 3-(trifluoromethyl)-2H-chromen-2-one (3p)



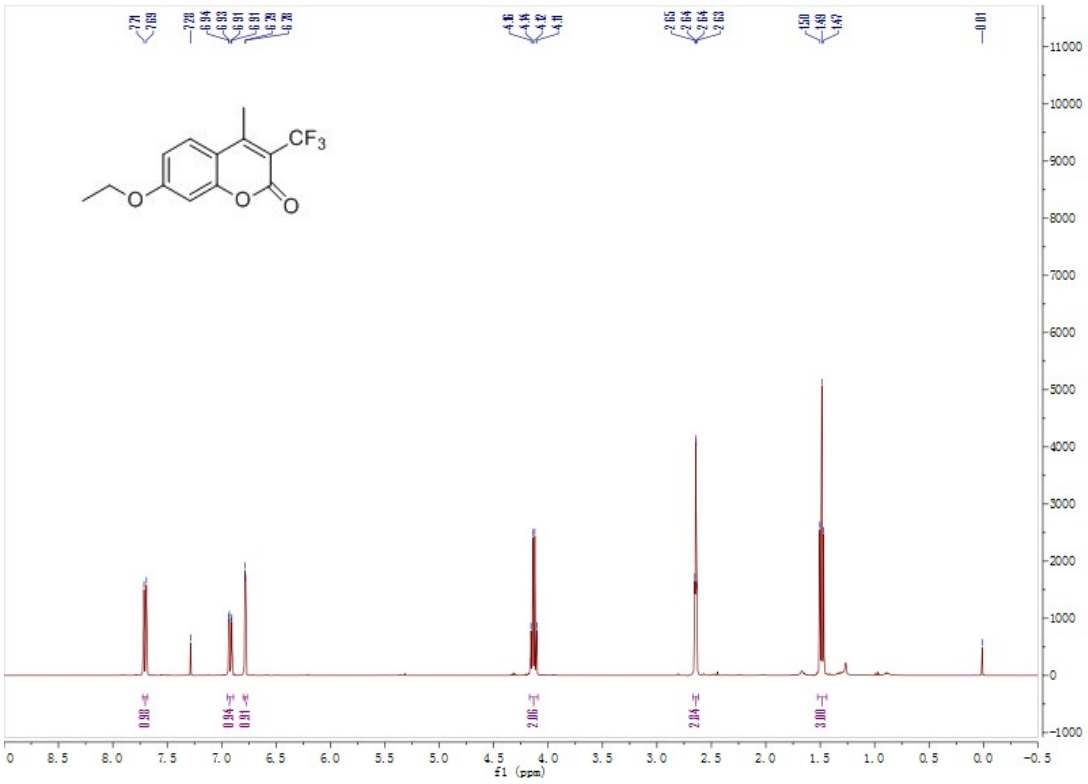
^{1} H NMR of 7-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3q)



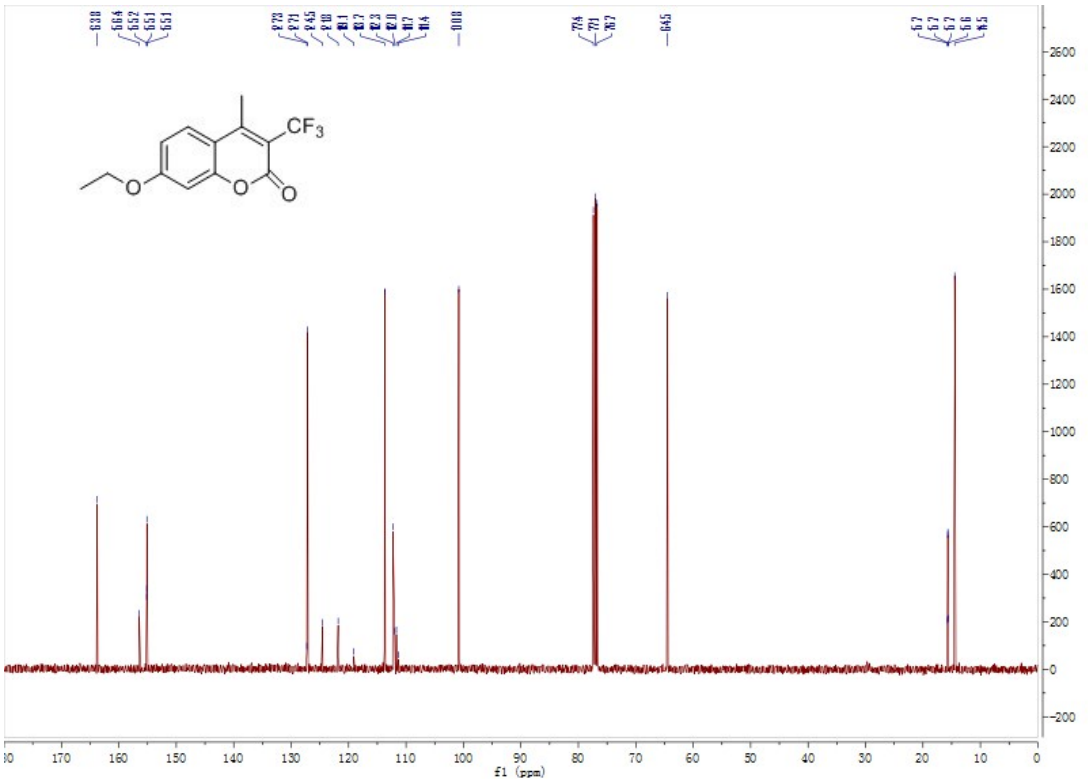
^{13} C NMR of 7-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3q)



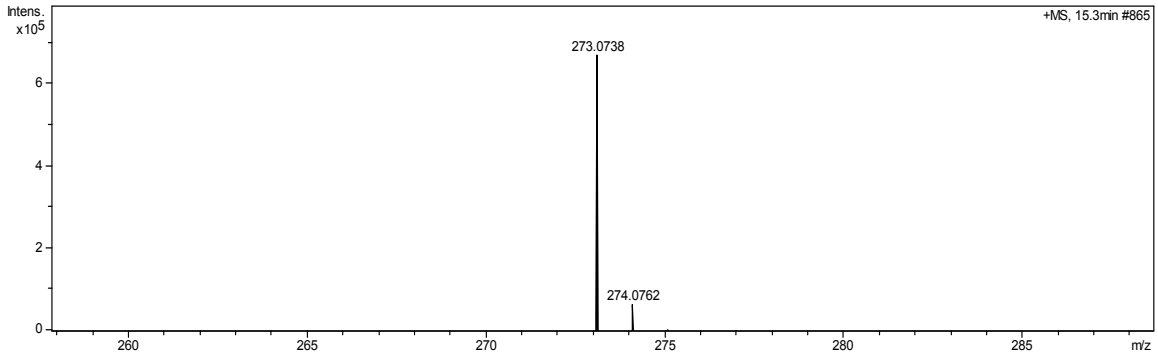
[1] H NMR of 7-ethoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3r)



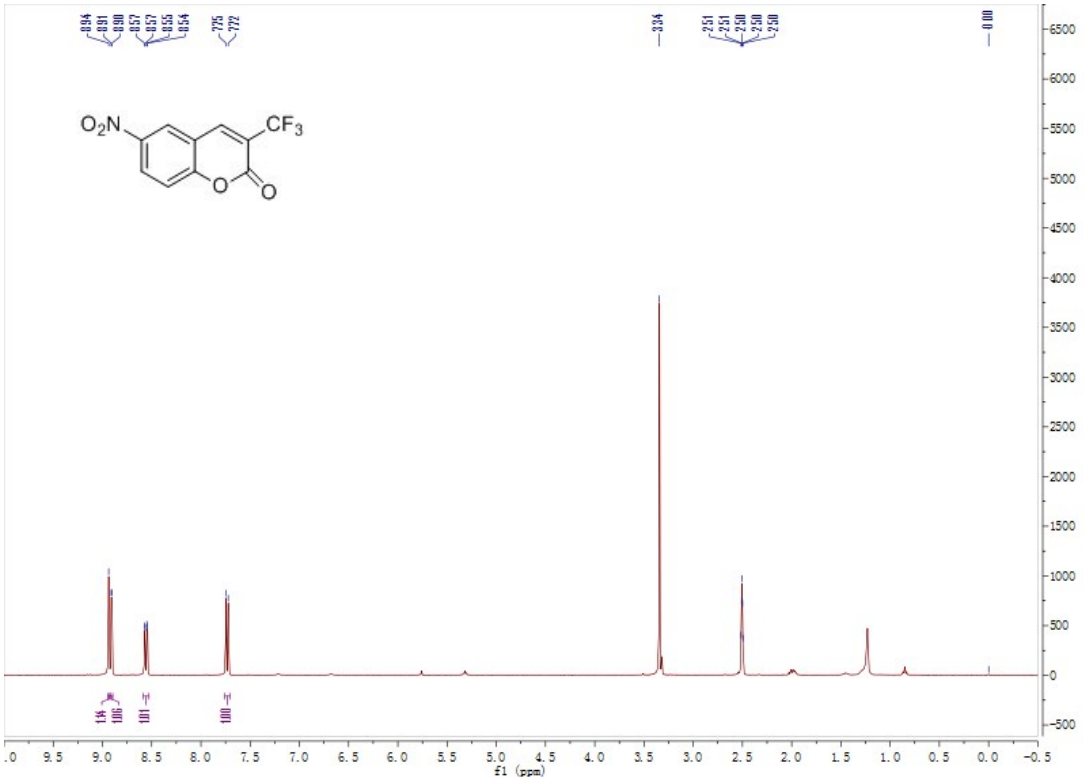
[13] C NMR of 7-ethoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3r)



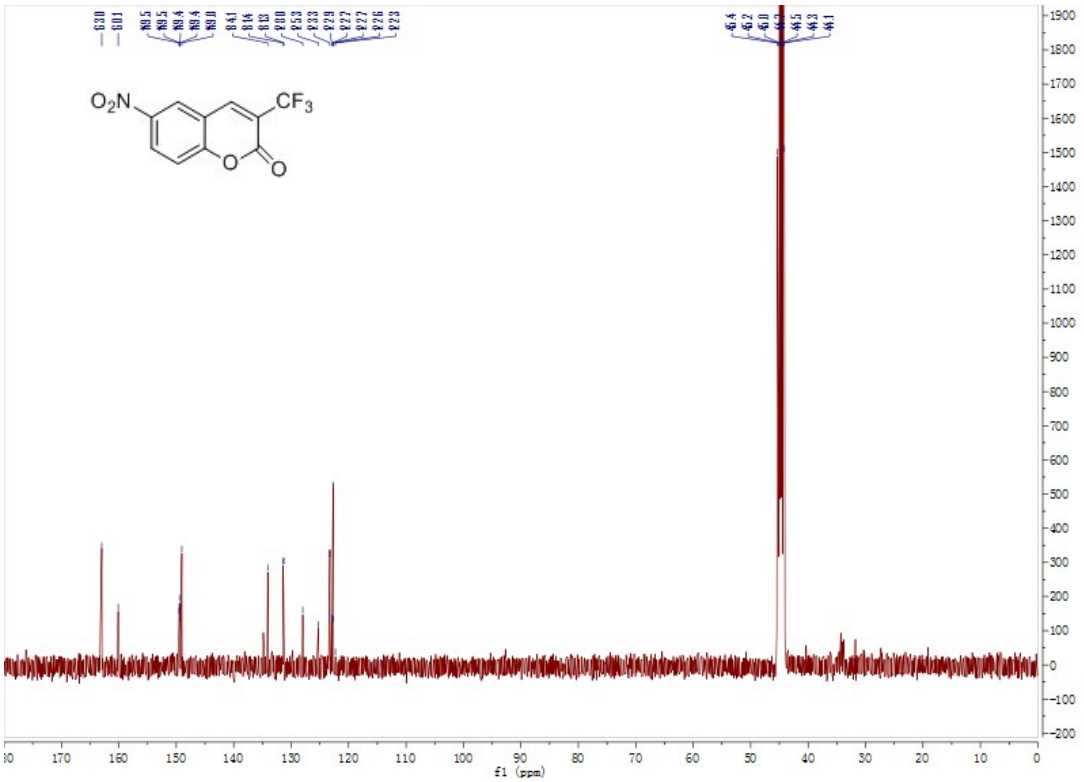
HRMS spectra of 7-ethoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3r)



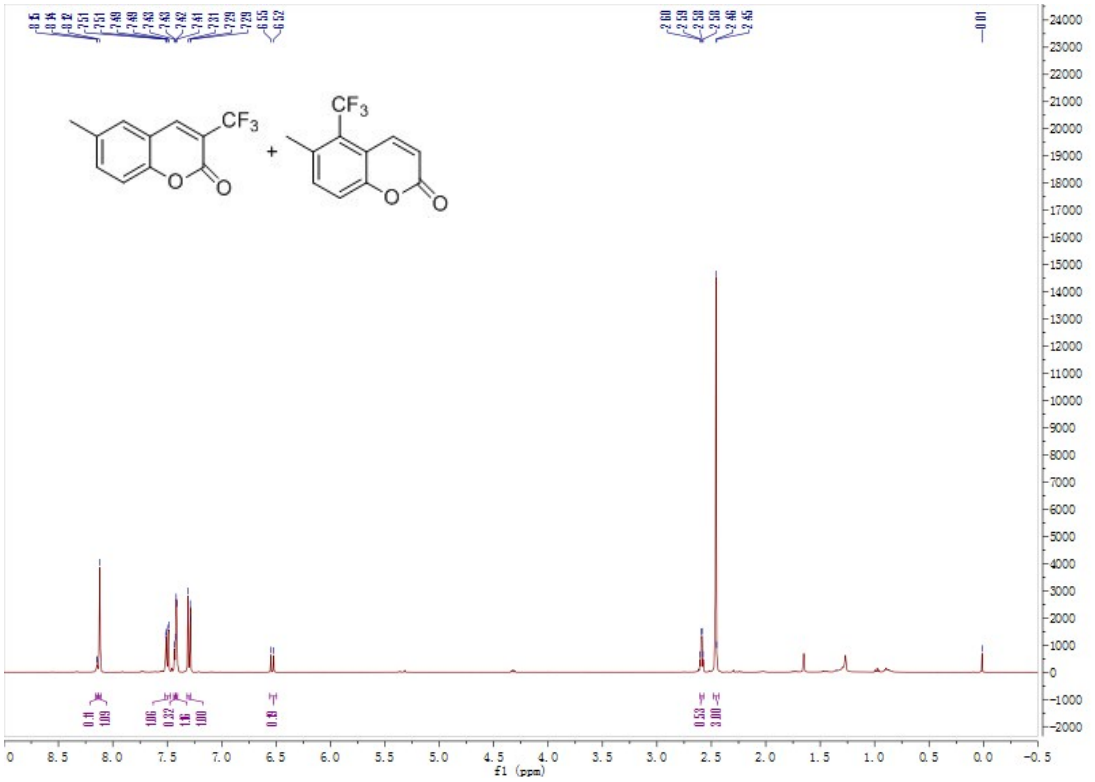
^{1} H NMR of 6-nitro-3-(trifluoromethyl)-2H-chromen-2-one (3s)



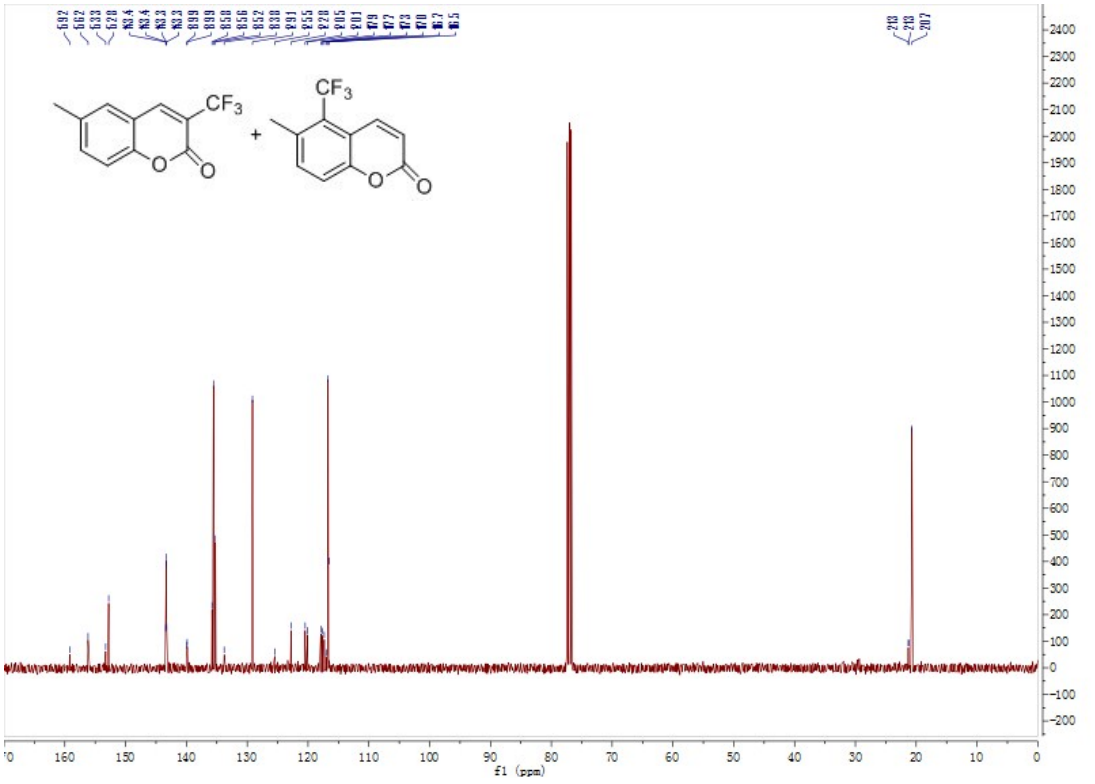
^{13} C NMR of 6-nitro-3-(trifluoromethyl)-2H-chromen-2-one (3s)



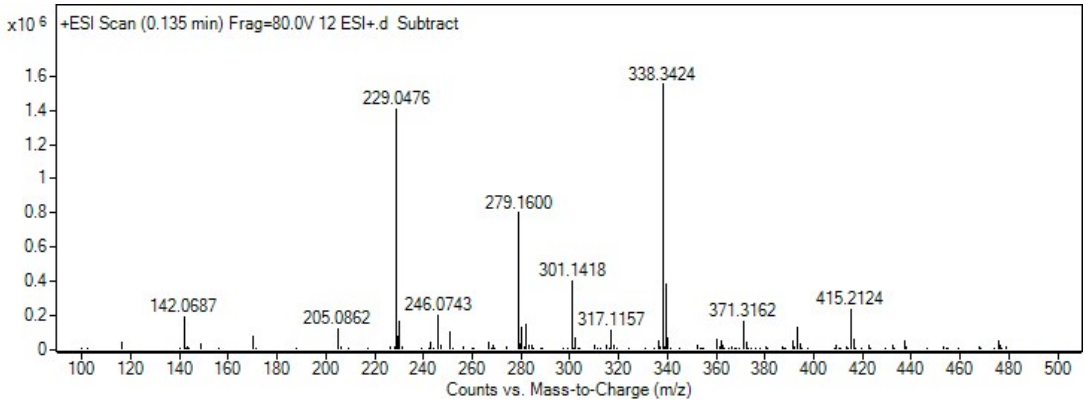
^{1} H NMR of 6-methyl-3-(trifluoromethyl)-2H-chromene (3t) and 6-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3t')



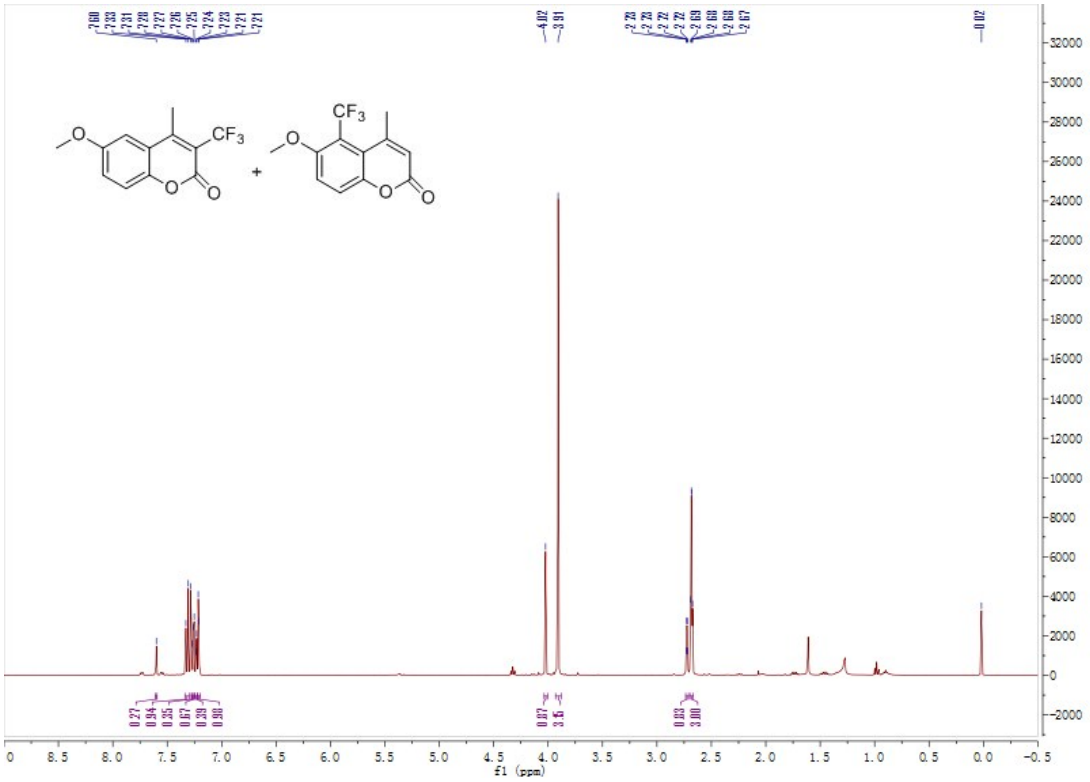
^{13} C NMR of 6-methyl-3-(trifluoromethyl)-2H-chromene (3t) and 6-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3t')



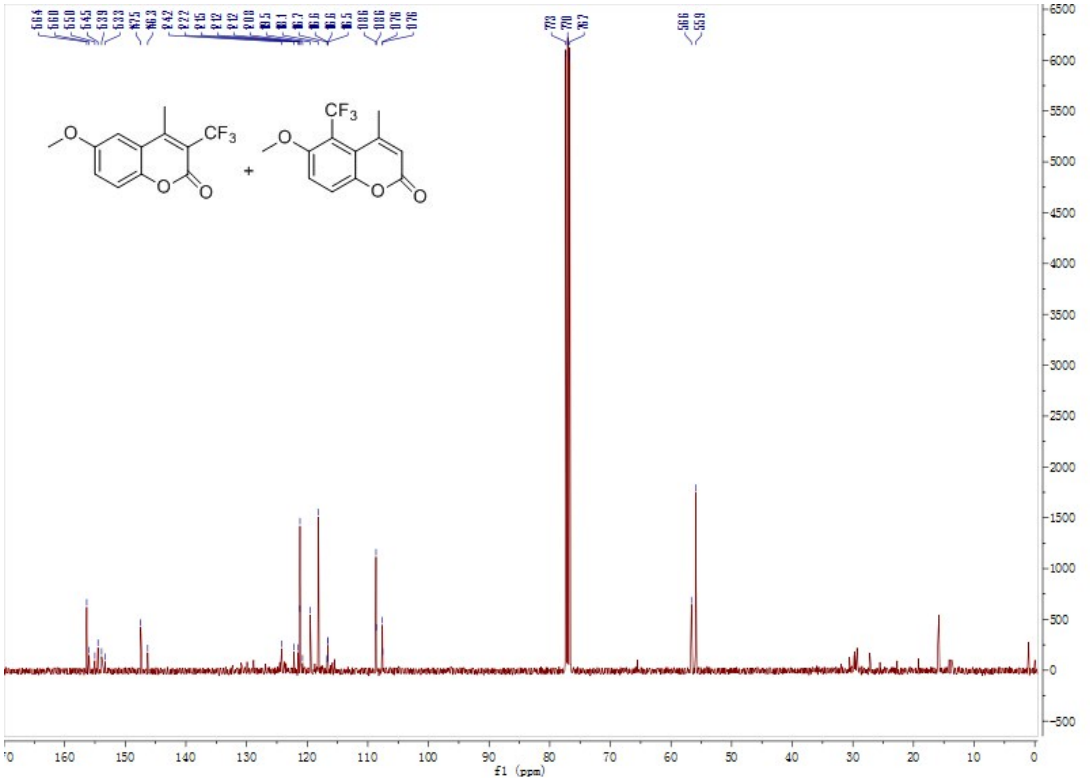
HRMS spectra of 6-methyl-3-(trifluoromethyl)-2H-chromene (3t) and 6-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3t')



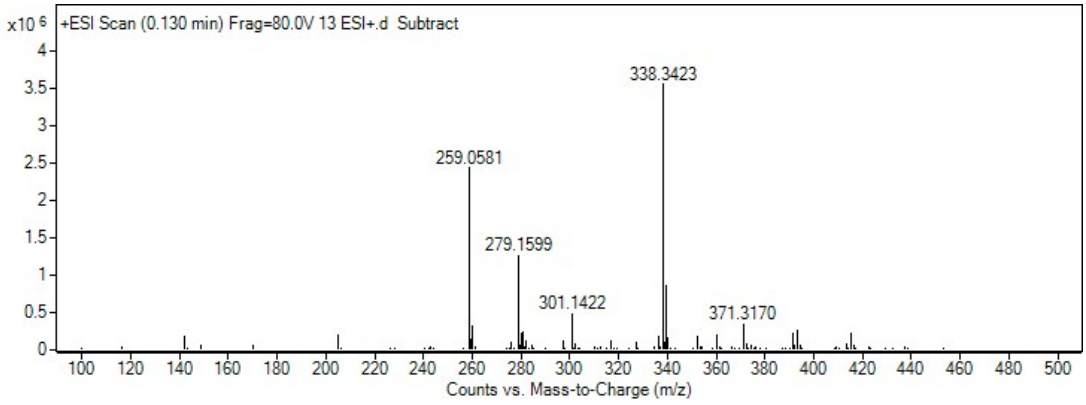
^{1} H NMR of 6-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3u) and 6-methoxy-4-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3u')



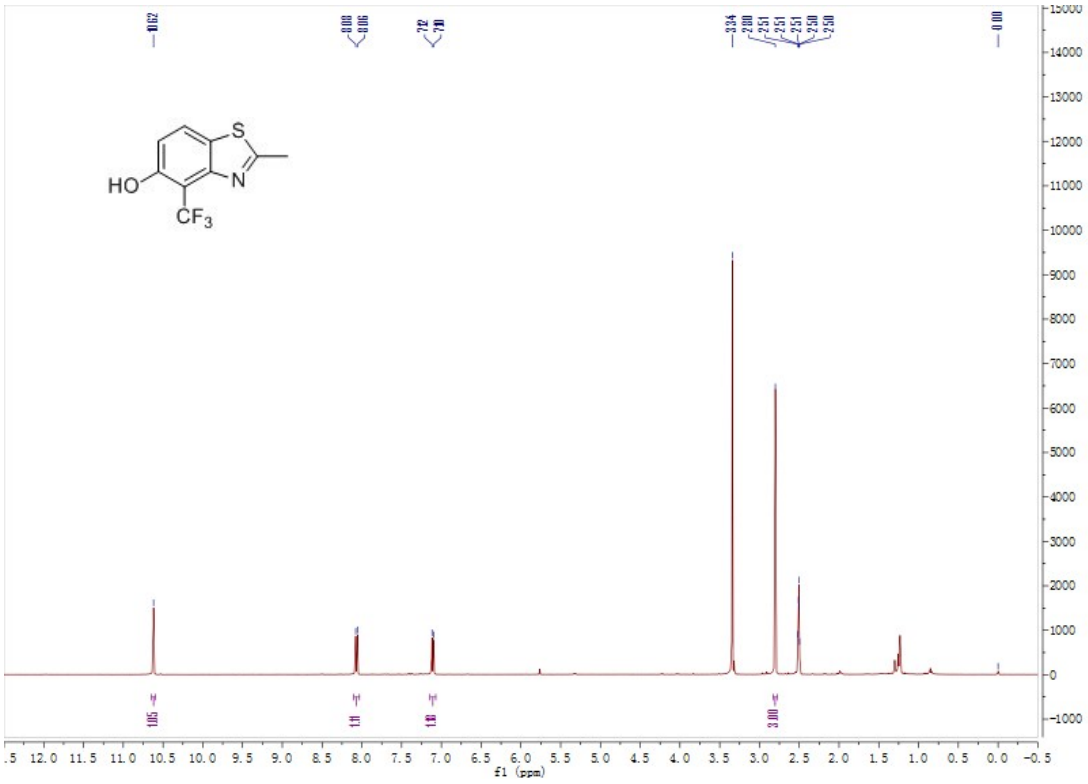
^{13} C NMR of 6-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3u) and 6-methoxy-4-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3u')



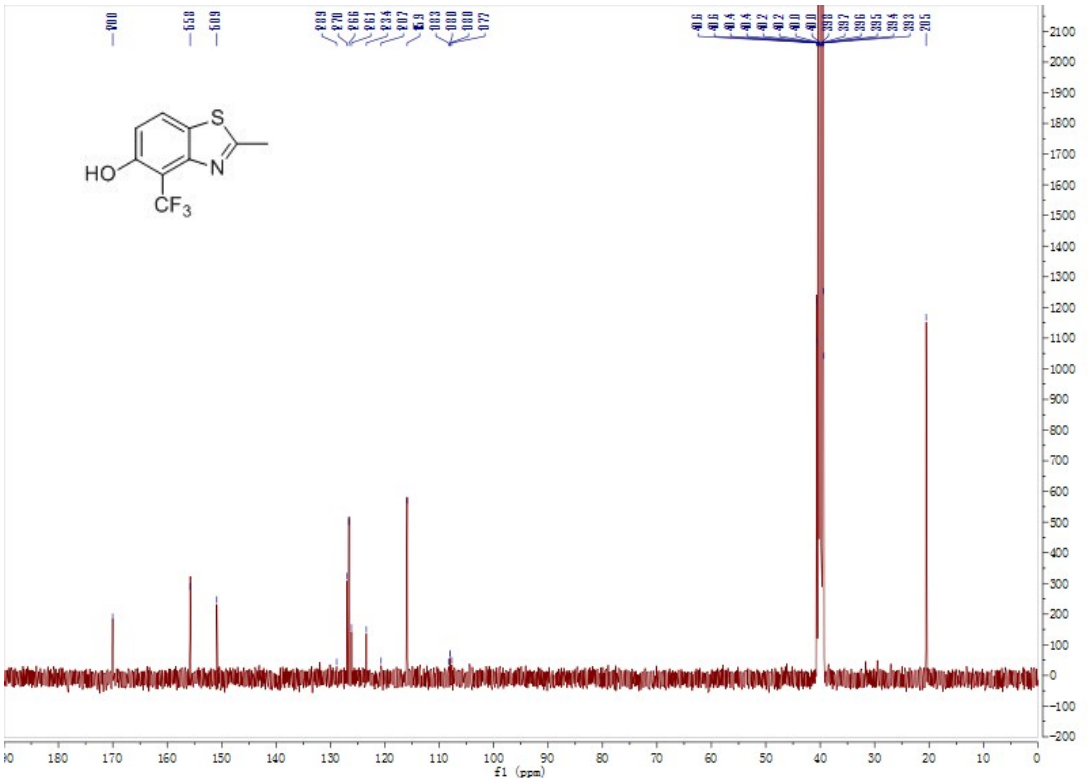
HRMS spectra of 6-methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3u) and 6-methoxy-4-methyl-5-(trifluoromethyl)-2H-chromen-2-one (3u')



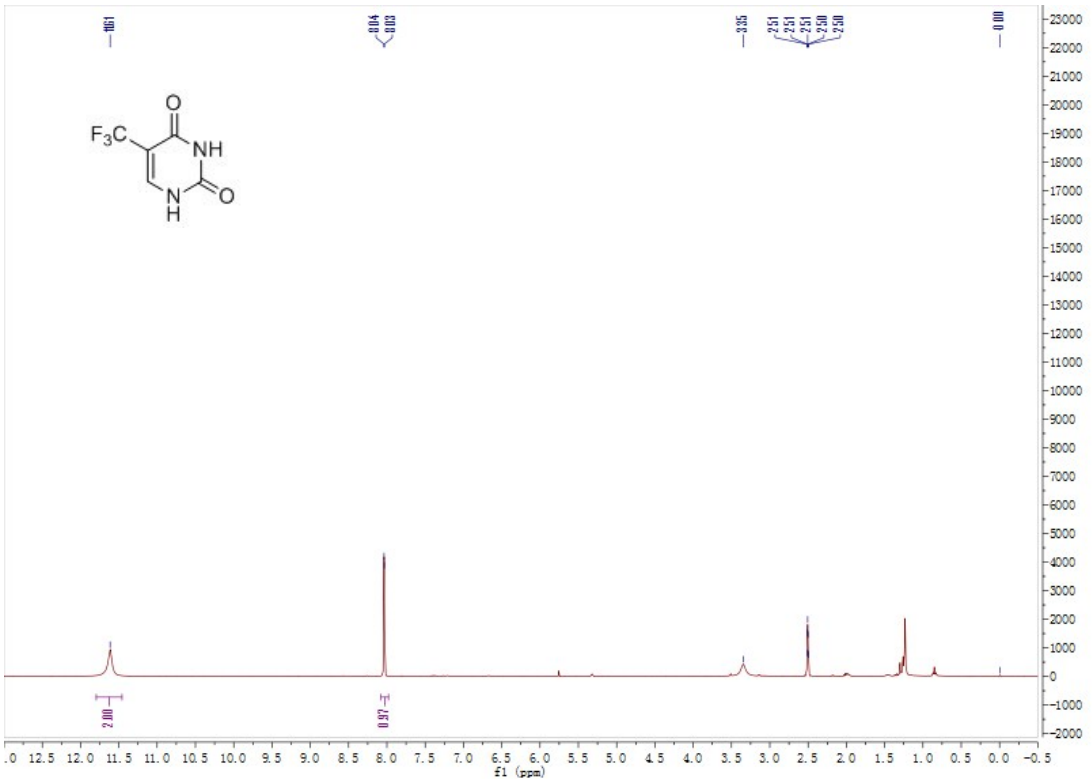
^{1} H NMR of 2-methyl-4-(trifluoromethyl)benzo[d]thiazol-5-ol (3v)



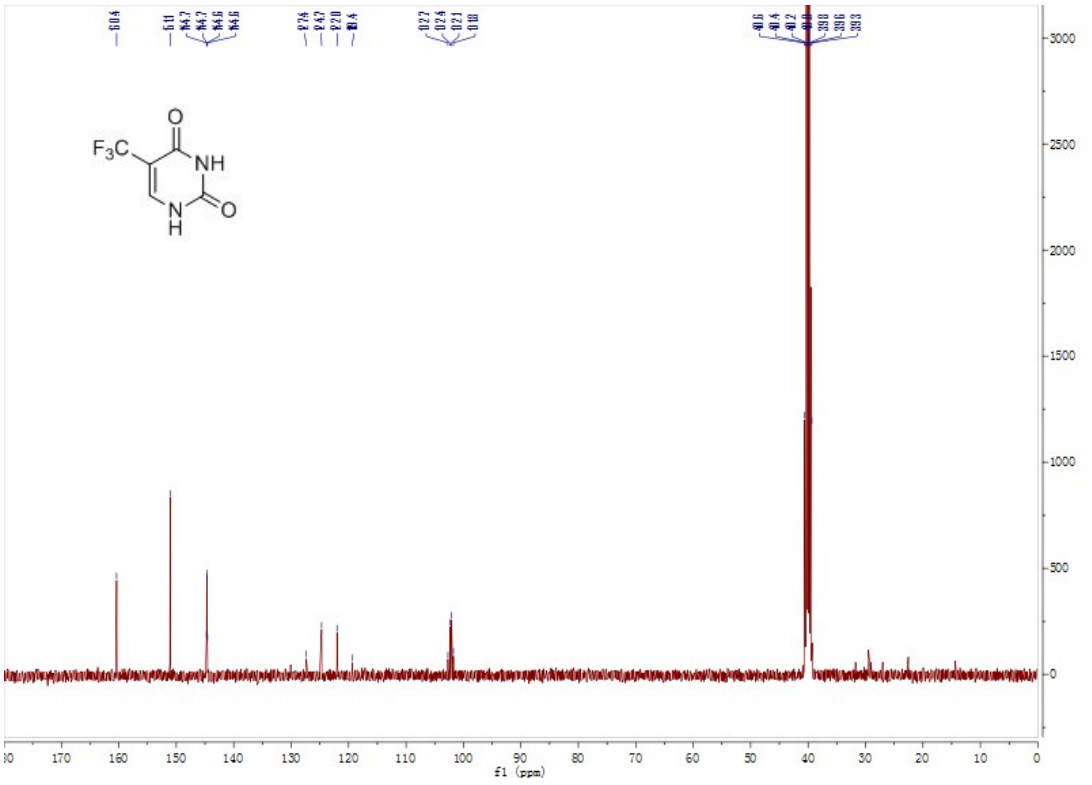
^{13} C NMR of 2-methyl-4-(trifluoromethyl)benzo[d]thiazol-5-ol (3v)



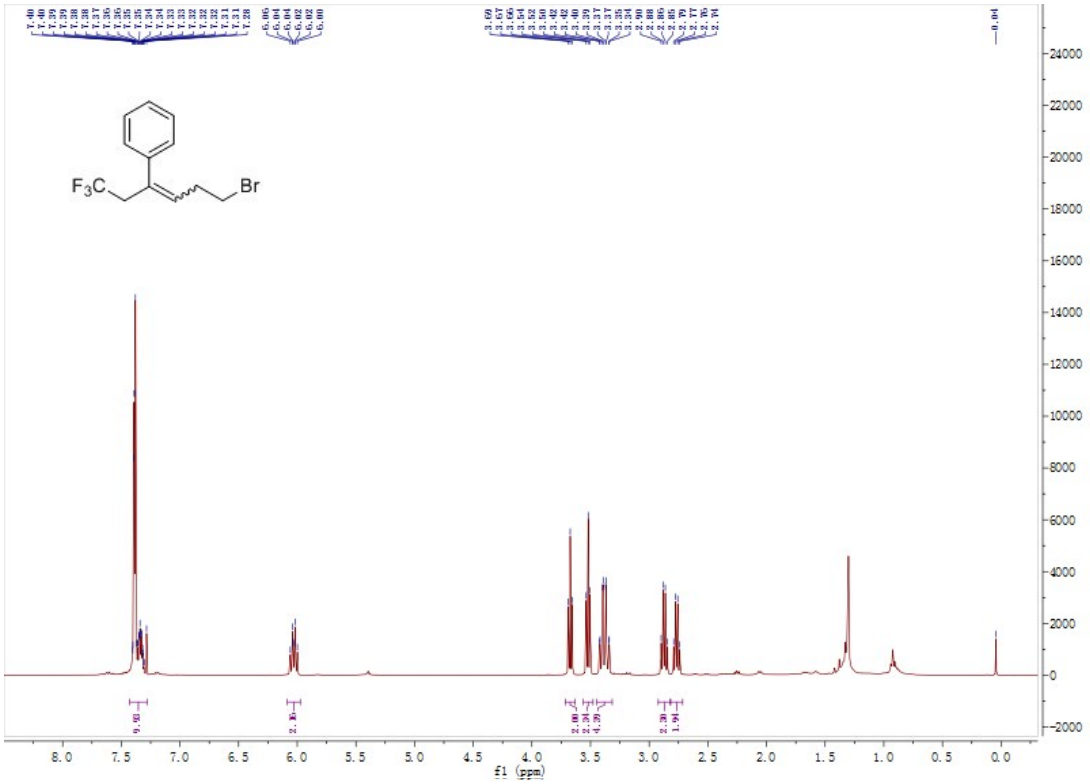
^{1} H NMR of 5-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3w)



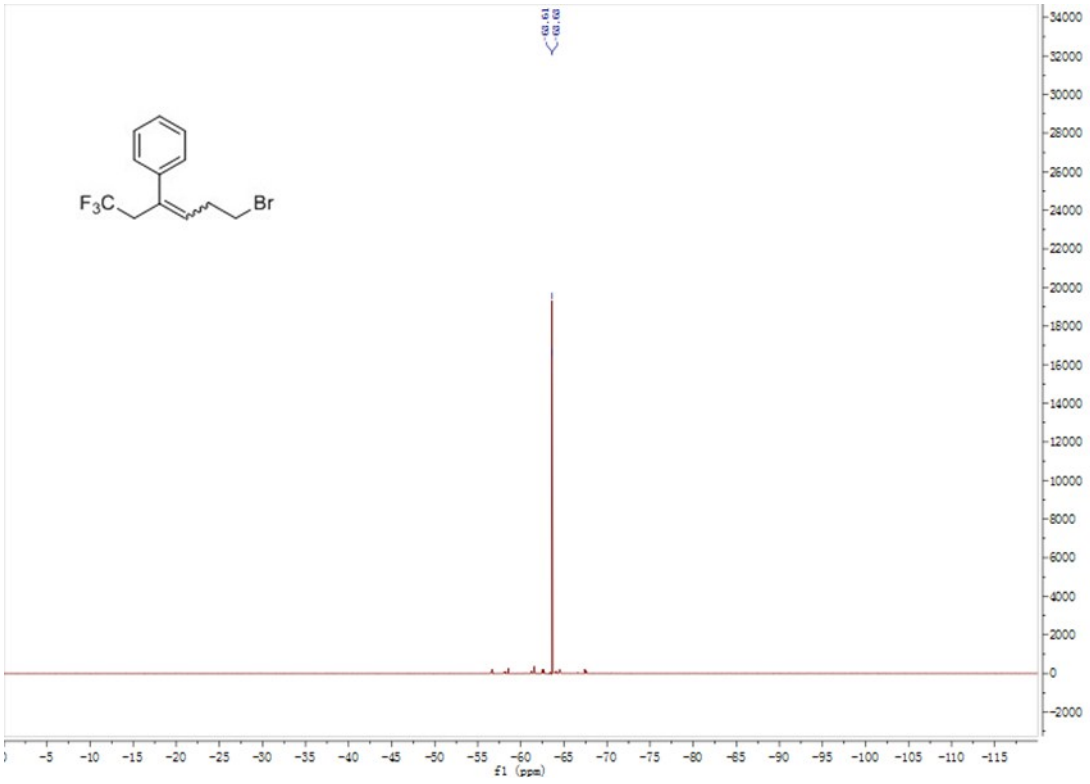
^{13} C NMR of 5-(trifluoromethyl)pyrimidine-2,4(1H,3H)-dione (3w)



^{1} H NMR of (6-bromo-1,1,1-trifluorohex-3-en-3-yl)benzene (6)



^{19} F NMR of (6-bromo-1,1,1-trifluorohex-3-en-3-yl)benzene (6)



GC-MS of (6-bromo-1,1,1-trifluorohex-3-en-3-yl)benzene (6)