Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Tandem trifluoromethylthiolation and cyclization of N-aryl-3-butenamides with $AgSCF_3$: divergent access to CF_3S-substituted 3,4-dihydroquinolin-2-ones and azaspiro[4,5]dienones

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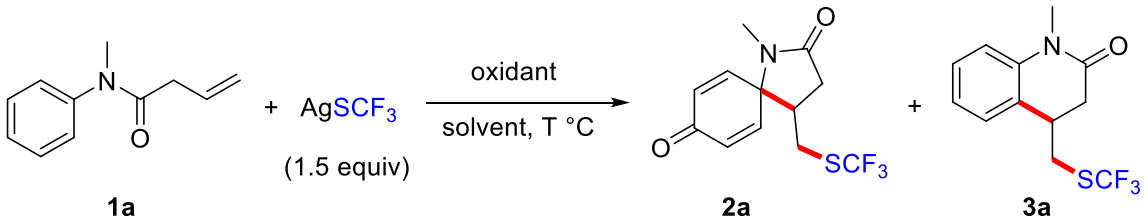
Supporting Information

Contents

Detailed Data for Optimization of Reaction Conditions



1a **2a** **3a**

Entry	Oxidant (1.5 equiv)	Solvent	Additive (1.5 equiv)	T (℃)	Time (h)	yield **2a**[b] (%)	yield **3a**[b] (%)
1	$K_2S_2O_8$	EtOAc	–	60	12	–	–
2	$K_2S_2O_8$	CH_2Cl_2	–	60	12	–	–
3	$K_2S_2O_8$	H_2O	–	60	12	14	–
4	$K_2S_2O_8$	MeCN	–	60	12	10	21
5	$K_2S_2O_8$	HFIP	–	60	12	–	–
6	$K_2S_2O_8$	PhCl	–	60	12	–	–
7	$K_2S_2O_8$	1,4-dioxane	–	60	12	–	–
8	$K_2S_2O_8$	DMF	–	60	12	–	–
9	$K_2S_2O_8$	THF	–	60	12	–	–
10	$K_2S_2O_8$	DCE	–	60	12	–	–
11	$K_2S_2O_8$	EtOH	–	60	12	–	–
12	$K_2S_2O_8$	EtOAc:H_2O(1:1)	–	60	12	–	–
13	$K_2S_2O_8$	CH_2Cl_2:H_2O(1:1)	–	60	12	27	10
14	$K_2S_2O_8$	MeCN:H_2O(1:1)	–	60	12	30	11
15	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	60	12	40	7
16	$K_2S_2O_8$	MeCN:H_2O(3:1)	–	60	12	22	13
17	$K_2S_2O_8$	HFIP:H_2O(1:1)	–	60	12	–	–
18	$K_2S_2O_8$	PhCl:H_2O(1:1)	–	60	12	–	–
19	$K_2S_2O_8$	1,4-dioxane:H_2O(1:1)	–	60	12	–	–
20	$K_2S_2O_8$	DMF:H_2O(1:1)	–	60	12	–	–
21	$K_2S_2O_8$	THF:H_2O(1:1)	–	60	12	–	–
22	$K_2S_2O_8$	DCE:H_2O(1:1)	–	60	12	20	3
23	$K_2S_2O_8$	EtOH:H_2O(1:1)	–	60	12	–	–
24	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	25	12	–	–
25	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	46	7
26	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	100	12	45	5
27	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	2	33	6
28	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	3	31	8
29	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	4	35	5
30	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	5	34	9
31	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	8	39	11
32	$Na_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	37	6
33	$(NH_4)_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	42	7
34	$PhI(OAc)_2$	MeCN:H_2O(1:3)	–	80	12	–	–
35	TBHP	MeCN:H_2O(1:3)	–	80	12	–	–

36	*m*CPBA	MeCN:H_2O(1:3)	–	80	12	–	–
37[c]	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	43	6
38[d]	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	45	4
39[e]	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	37	7
40[f]	$K_2S_2O_8$	MeCN:H_2O(1:3)	–	80	12	47	9
41[g]	$K_2S_2O_8$/TBHP	MeCN:H_2O(1:3)	–	80	12	61	–
38	$K_2S_2O_8$	MeCN:H_2O(1:3)	$NaHCO_3$	80	12	32	9
39	$K_2S_2O_8$	MeCN:H_2O(1:3)	PhCOOH	80	12	31	6
40	$K_2S_2O_8$	MeCN:H_2O(1:3)	$B(OH)_3$	80	12	34	7
41	$K_2S_2O_8$	MeCN:H_2O(1:3)	BF_3Et_2O	80	12	36	6
42	$K_2S_2O_8$	MeCN:H_2O(1:3)	CH_3COONa	80	12	35	7
43	$K_2S_2O_8$	MeCN:H_2O(1:3)	NaOH	80	12	32	5
44	$K_2S_2O_8$	MeCN:H_2O(1:3)	K_2CO_3	80	12	33	3
45	$K_2S_2O_8$	MeCN:H_2O(1:3)	K_2HPO_4	80	12	43	5
46[h]	$K_2S_2O_8$	MeCN:H_2O(1:3)	HMPA	80	12	40	11
47[h]	$K_2S_2O_8$	MeCN	HMPA	80	12	27	20
48[i]	$K_2S_2O_8$/TBHP	MeCN:H_2O(1:3)	–	80	12	61	–
49[i]	$K_2S_2O_8$	MeCN	HMPA	80	12	17	52

[a] Reaction conditions: **1a** (0.2 mmol), $AgSCF_3$ (1.5 equiv), oxidant (1.5 equiv) in solvent (2.0 mL). [b] Isolated yield. [c] 2 equiv $K_2S_2O_8$. [d] 3 equiv $K_2S_2O_8$. [e] 2 equiv $AgSCF_3$. [f] 3 equiv $AgSCF_3$. [g] 3 equiv TBHP. [h] 0.5 equiv HMPA. [i] under N_2.

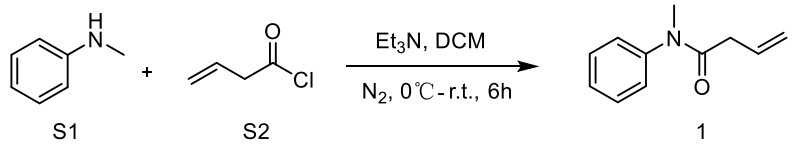
Experimental Section

Instrumentation and chemicals.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard, operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR and 376 MHz for ^{19}F NMR. Melting points were measured by SGW X-4A microscopic apparatus. HRMS was measured by Q Exactive Hybrid Quadrupole-Orbitrap LC/MS spectrometer.

Ethyl acetate and hexane for column chromatography were obtained from commercial sources and used without further purification. Other solvents were purified according to the standard methods. $AgSCF_3$ were prepared according to the reported literatures[1]. Other chemicals were obtained from commercial sources and used as received unless otherwise noted.

Preparation of Substrates:



S1 S2 1

The substrates **1** were synthesized according to the literature[2]. Into a 250 mL round-bottom flask equipped with a magnetic stir-bar was added solution of *N*-methylaniline **S1** (1.0 g, 1 equiv) in DCM (60 mL) and triethylamine (2 equiv). The mixture was stirred at 0 ℃. Then 3-butenoyl chloride **S2** (1.5 equiv) was added under nitrogen atmosphere. The resulting solution was allowed to warm up to room temperature and stirred for 6 hours, followed by the addition of H_2O (50 mL) to quench excess acyl chloride. The aqueous layer was further extracted by ethyl acetate

(2×50 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography.

Experimental procedures

General procedure for the the synthesis of azaspiro[4,5]dienones (2).

To a 4 mL round-bottomed flask was charged with *N*-aryl-3-butenamides (**1**, 0.2 mmol), $AgSCF_3$ (0.3 mmol), $K_2S_2O_8$ (0.3 mmol), TBHP (0.6 mmol), MeCN (0.5 mL) and H_2O (1.5 mL). The resulting mixture was stirred at 80 ℃ for 12 h. After the reaction was complete, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent *in vacuo*, the residue was purified by column chromatography (ethyl acetate/hexane) to afford the pure product **2**.

General procedure for the the synthesis of 3,4-dihydroquinolin-2-ones (3).

To a 4 mL round-bottomed flask was charged with *N*-aryl-3-butenamides (**1**, 0.2 mmol), $AgSCF_3$ (0.3 mmol), $K_2S_2O_8$ (0.3 mmol), HMPA (0.1 mmol), and MeCN (2 mL) under N_2 atmosphere. The resulting mixture was stirred at 80 ℃ for 12 h. After the reaction was complete, the mixture was added into H_2O (25 mL) and extracted with ethyl acetate (10 mL) three times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent *in vacuo*, the residue was purified by column chromatography (ethyl acetate/hexane) to afford the pure product **3**.

Characterization Data

1-Methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2a)

Yellow oil, 35.5 mg, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69–6.63 (m, 2H), 6.51–6.45 (m, 2H), 2.90–2.72 (m, 4H), 2.66 (s, 3H), 2.39–2.32 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.8, 171.6, 147.2, 142.9, 132.4, 131.8, 129.3 (q, J = 304.9 Hz), 63.7, 41.4, 34.1, 28.4 (q, J = 2.1 Hz), 25.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.1 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{13}F_3NO_2S$ $(M+H)^+$: 292.0614, found 292.0613.

1,7-Dimethyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2b)

Yellow oil, 38.4 mg, 63% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65–6.59 (m, 1H), 6.50–6.44 (m, 1H), 6.42–6.39 (m, 1H), 2.87–2.66 (m, 4H), 2.64 (s, 3H), 2.40–2.30 (m, 1H), 1.97 (dd, J_1 = 2.6 Hz, J_2 = 1.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 183.6, 171.6, 171.6, 147.1, 142.6, 142.2, 139.6, 139.0, 137.8, 132.1, 131.6, 129.3 (q, J = 304.8 Hz), 129.3 (q, J = 304.8 Hz), 64.0, 64.0, 41.5, 41.2, 34.2, 34.1, 28.4 (q, J = 2.1 Hz), 25.5, 25.5, 15.0, 14.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.2 (s), –41.2 (s). HRMS-ESI(m/z): calcd for $C_{13}H_{15}F_3NO_2S$ $(M+H)^+$: 306.0770, found 306.0773.

1,6-Dimethyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2c)

Yellow oil, 42.7 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.65–6.61 (m, 1H), 6.48–6.37 (m, 1H), 6.36–6.31 (m, 1H), 2.88–2.68 (m, 4H), 2.64 (s, 1H), 2.55 (s, 2H), 2.41–2.32 (m, 1H), 1.95 (d, J = 1.2 Hz, 2H), 1.86 (d, J = 1.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.2, 183.8, 173.0, 172.8, 155.6, 154.9, 149.8, 144.6, 133.0, 132.3, 132.1, 131.3, 130.4 (q, J = 304.9 Hz), 130.3 (q, J = 304.9 Hz), 67.5, 67.3, 41.7, 40.2, 35.3, 35.2, 29.7 (q, J = 2.1 Hz), 28.8 (q,

J = 2.1 Hz), 20.4, 18.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –41.2 (s). HRMS-ESI(m/z): calcd for $C_{13}H_{15}F_3NO_2S$ $(M+H)^+$: 306.0770, found 306.0765.

7-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2d)

Colorless oil, 40.8 mg, 66% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.70–6.64 (m, 1H), 6.49–6.42 (m, 1H), 6.22–6.16 (m, 1H), 2.82–2.79 (m, 1H), 2.76–2.70 (m, 2H), 2.62 (s, 3H), 2.37–2.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9 (d, *J* = 22.4 Hz), 175.9 (d, *J* = 22.4 Hz), 171.2, 154.2 (d, *J* = 270.4 Hz), 154.2 (d, *J* = 270.2 Hz), 148.4 (d, *J* = 2.5 Hz), 144.0 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 53.5 Hz), 130.8 (d, *J* = 53.6 Hz), 129.3 (q, *J* = 305.0 Hz), 129.2 (q, *J* = 304.9 Hz), 123.1 (d, *J* = 13.2 Hz), 118.5 (d, *J* = 11.3 Hz), 65.6 (d, *J* = 7.5 Hz), 65.5 (d, *J* = 7.5 Hz), 41.8 (d, *J* = 1.3 Hz), 41.3 (d, *J* = 1.3 Hz), 34.0, 33.9, 28.5 (q, *J* = 2.1 Hz), 28.3 (q, *J* = 2.3 Hz), 25.5, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.1 (s), –41.1 (s), –121.1~ –121.2 (m), –122.4~ –122.5 (m). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_4NO_2S$ $(M+H)^+$: 310.0519, found 310.0515.

6-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2e)

Colorless oil, 35.6 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.59–6.53 (m, 2H), 6.48–6.41 (m, 2H), 6.21–6.15 (m, 2H), 3.12–3.03 (m, 1H), 2.95–2.76 (m, 7H), 2.68 (s, 3H), 2.66 (s, 3H), 2.43–2.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.4 (d, *J* = 15.5 Hz), 184.1 (d, *J* = 15.5 Hz), 172.2, 171.2, 170.9 (d, *J* = 287.7 Hz), 170.3 (d, *J* = 288.7 Hz), 143.6 (d, *J* = 25.7 Hz), 139.3 (d, *J* = 3.6 Hz), 131.3 (d, *J* = 62.6 Hz), 131.2 (d, *J* = 62.6 Hz), 129.3 (q, *J* = 305.0 Hz), 129.2 (q, *J* = 305.0 Hz), 112.4 (d, *J* = 8.9 Hz), 112.3 (d, *J* = 10.2 Hz), 65.9 (d, *J* = 21.2 Hz), 64.6 (d, *J* = 21.4 Hz), 40.8 (d, *J* = 2.3 Hz), 38.0, 34.2 (d, *J* = 1.8 Hz), 33.8, 28.6 (q, *J* = 2.3 Hz), 28.3 (q, *J* = 1.7 Hz), 25.5, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –41.1 (s), –93.8~ –93.9 (m), –97.7~ –97.8 (m). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_4NO_2S$ $(M+H)^+$: 310.0519, found 310.0515.

7-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2f)

Yellow oil, 36.4 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (d, *J* = 2.6 Hz, 1H), 6.74–6.68 (m, 1H), 6.60–6.55 (m, 1H), 2.93–2.76 (m, 4H), 2.68 (s, 3H), 2.42–2.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 177.0, 172.2, 172.2, 148.7, 144.4, 144.1, 140.1, 136.4, 136.2, 132.1, 131.6, 130.2 (q, *J* = 305.0 Hz), 130.2 (q, *J* = 305.0Hz), 66.8, 66.6, 42.5, 42.4, 35.0, 34.9, 29.4 (q, *J* = 2.3 Hz), 29.3 (q, *J* = 2.2 Hz), 26.7, 26.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ–41.0 (s), –41.1 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}ClF_3NO_2S$ $(M+H)^+$: 326.0224, found 326.0227.

6-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2g)

Yellow oil, 46.8 mg, 72% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73–6.68 (m, 4H), 6.55–6.43 (m, 2H), 3.17–3.07 (m, 1H), 2.95–2.73 (m, 7H), 2.67 (s, 3H), 2.62 (s, 3H), 2.41–2.33 (m, 1H), 2.12–2.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.5, 181.2, 172.3, 171.2, 153.0, 151.9, 147.8, 142.9, 131.9, 131.7, 131.3, 130.0, 129.3 (q, *J* = 305.1 Hz), 129.2 (q, *J* = 305.0 Hz), 67.7, 67.4, 40.7, 39.7, 34.1, 33.9, 28.7 (q, *J* = 2.3 Hz), 27.7 (q, *J* = 2.0 Hz), 25.7, 25.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –41.1 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}ClF_3NO_2S$ $(M+H)^+$: 326.0224, found 326.0228.

7-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2h)

Yellow oil, 47.2 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14–7.11 (m, 1H), 6.75–6.69 (m, 1H), 6.63–6.58 (m,

1H), 2.93–2.74 (m, 4H), 2.70 (s, 3H), 2.42–2.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.9, 176.9, 172.2, 172.1, 148.6, 148.5, 144.6, 144.3, 132.7, 131.1, 130.2 (q, J = 305.2 Hz), 130.2 (q, J = 305.0Hz), 128.2, 128.2, 67.4, 67.3, 42.4, 42.2, 35.0, 34.9, 29.5 (q, J = 2.2 Hz), 29.3 (q, J = 2.2 Hz), 26.8, 26.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –41.0 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}BrF_3NO_2S$ $(M+H)^+$: 369.9719, found 369.9722.

6-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2i)

Yellow oil, 51.7 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98–6.92 (m, 2H), 6.80–6.75 (m, 2H), 6.57–6.46 (m, 2H), 3.17–3.07 (m, 1H), 3.00–2.72 (m, 7H), 2.67 (s, 3H), 2.63 (s, 3H), 2.42–2.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.7, 180.5, 172.1, 171.2, 148.5, 147.3, 144.6, 143.1, 136.2, 136.0, 131.2, 129.7, 129.3 (q, J = 305.1 Hz), 129.2 (q, J = 305.1Hz), 68.0, 67.8, 40.8, 40.7, 34.0, 33.9, 28.7 (q, J = 2.1 Hz), 27.6 (q, J = 2.2 Hz), 25.8, 25.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –41.1 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}BrF_3NO_2S$ $(M+H)^+$: 369.9719, found 369.9716.

1-methyl-7-(trifluoromethyl)-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2j)

Yellow oil, 25.1 mg, 35% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.13 (m, 2H), 6.75–6.70 (m, 1H), 6.60–6.54 (m, 1H), 2.93–2.77 (m, 4H), 2.69 (s, 3H), 2.47–2.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.2 (q, J = 2.1 Hz), 171.1, 148.0 (q, J = 5.2 Hz), 146.8, 143.9 (q, J = 4.9 Hz), 142.5, 132.4, 131.7 (q, J = 0.9 Hz), 129.1 (q, J = 305.2 Hz), 129.1 (q, J = 305.1 Hz), 119.6 (q, J = 272.9 Hz), 119.5 (q, J = 272.9 Hz), 63.3, 63.3, 41.7, 40.9, 33.9, 33.8, 28.6 (q, J = 2.3 Hz), 28.6 (q, J = 2.4 Hz), 25.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –41.1 (s), –65.9 (s), –66.2 (s). HRMS-ESI(m/z): calcd for $C_{13}H_{12}F_6NO_2S$ $(M+H)^+$: 360.0488, found 360.0485.

1'-Methyl-3'-(((trifluoromethyl)thio)methyl)-4H-spiro[naphthalene-1,2'-pyrrolidine]-4,5'-dione (2k)

Colorless oil, 46.4 mg, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–8.18 (m, 2H), 7.73–7.62 (m, 2H), 7.60–7.52 (m, 2H), 7.45 (dd, J_1 = 7.9 Hz, J_2 = 0.6 Hz, 1H), 7.12 (dd, J_1 = 7.9 Hz, J_2 = 0.7 Hz, 1H), 6.87 (d, J = 10.2 Hz, 1H), 6.77–6.69 (m, 2H), 6.63 (d, J = 10.2 Hz, 1H), 2.98–2.73 (m, 6H), 2.65 (s, 3H), 2.50 (s, 3H), 2.48–2.41 (m, 3H), 2.05–1.99 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.0, 182.7, 173.1, 172.9, 149.9, 144.3, 141.5, 138.5, 134.1, 133.5, 133.5, 132.4, 132.1, 131.4, 130.2 (q, J = 304.9 Hz), 130.1 (q, J = 304.8Hz), 129.6, 129.3, 128.3, 127.3, 126.3, 125.3, 66.5, 66.2, 47.1, 42.9, 35.6, 35.0, 29.6 (q, J = 2.2 Hz), 29.4 (q, J = 2.2 Hz), 26.9, 26.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.1 (s), –41.4 (s). HRMS-ESI(m/z): calcd for $C_{16}H_{15}F_3NO_2S$ $(M+H)^+$: 342.0770, found 342.0768.

1-benzyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2l)

Yellow oil, 37.4 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.22 (m, 2H), 7.17–7.13 (m, 2H), 6.52–6.44 (m, 2H), 4.45 (AB, J = 15.0 Hz, 1H), 4.17 (AB, J = 14.9 Hz, 1H),, 2.94–2.87 (m, 1H), 2.85–2.77 (m, 1H), 2.74–2.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.0, 171.5, 147.2, 143.2, 136.2, 131.2, 130.9, 145.5, 129.2 (q, J = 304.9 Hz), 127.6, 127.0, 64.9, 52.4, 44.0, 41.7, 34.0, 28.2 (q, J = 2.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.1 (s). HRMS-ESI(m/z): calcd for $C_{18}H_{17}F_3NO_2S$ $(M+H)^+$: 368.0927, found 368.0930.

1-Methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3a)

Colorless oil, 28.1 mg, 51% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 7.4 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 8.2 Hz, 1H), 3.37 (s, 3H), 3.23–3.16 (m, 1H), 3.12–3.05 (m, 1H), 3.00–2.93 (m,

1H), 2.87–2.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 138.6, 129.8 (q, J = 304.6 Hz), 127.7, 127.2, 125.1, 122.2, 114.2, 35.2, 34.5, 32.2 (q, J = 1.7 Hz), 28.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{13}F_3NOS$ $(M+H)^+$: 276.0664, found 276.0661.

1-Methyl-6-(trifluoromethyl)-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3b)

Yellow oil, 37.7 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, J_1 = 8.5 Hz, J_2 = 1.3 Hz 1H), 7.46 (d, J = 1.6 Hz, 1H), 7.11 (d, J = 8.5 Hz, 1H), 3.39 (s, 3H), 3.27–3.21 (m, 1H), 3.12–3.06 (m, 1H), 3.01–2.94 (m, 1H), 2.92–2.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 141.5, 138.6 (q, J = 304.8 Hz), 125.5, 124.1 (q, J = 16.0 Hz), 121.5, 114.2, 35.2, 34.1, 32.9 (q, J = 1.8 Hz), 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s), –62.1 (s). HRMS-ESI(m/z): calcd for $C_{13}H_{12}F_6NOS$ $(M+H)^+$: 344.0538, found 344.0536.

6-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3c)

Colorless oil, 33.4 mg, 57% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05–6.93 (m, 3H), 3.35 (s, 3H), 3.19–3.12 (m, 1H), 3.09–3.03 (m, 1H), 3.00–2.93 (m, 1H), 2.84 (d, J = 4.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 157.4 (d, J = 242.5 Hz), 134.9 (d, J = 2.7 Hz), 129.7 (q, J = 304.7 Hz), 127.0 (d, J = 7.2 Hz), 115.4 (d, J = 8.0 Hz), 114.3 (d, J = 23.1 Hz), 114.0 (d, J = 22.2 Hz), 35.2, 34.3, 31.9 (q, J = 1.6 Hz), 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s), –119.5~ –119.7 (m). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_4NO_2S$ $(M+H)^+$: 294.0570, found 294.0574.

6-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3d)

Yellow oil, 34 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, J_1 = 8.7 Hz, J_2 = 2.4 Hz 1H), 7.19 (d, J = 2.4 Hz, 1H), 6.95 (d, J = 8.7 Hz, 1H), 3.34 (s, 3H), 3.19–3.13 (m, 1H), 3.10–3.03 (m, 1H), 2.97–2.91 (m, 1H), 2.96–2.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 137.3, 129.7 (q, J = 304.7 Hz), 127.5, 127.4, 127.2, 126.8, 125.1, 35.1, 34.2, 31.9 (q, J = 1.8 Hz), 28.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.8 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}ClF_3NOS$ $(M+H)^+$: 310.0275, found 310.0271.

6-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3e)

Yellow oil, 36.7 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, J_1 = 8.7 Hz, J_2 = 2.3 Hz 1H), 7.33 (d, J = 2.3 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 3.33 (s, 3H), 3.19–3.12 (m, 1H), 3.10–3.04 (m, 1H), 2.97–2.88 (m, 1H), 2.86–2.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 137.8, 130.6 (q, J = 304.7 Hz), 130.5, 130.0, 127.1, 115.8, 114.8, 35.1, 34.2, 32.0 (q, J = 1.8 Hz), 28.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.8 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_3BrNOS$ $(M+H)^+$: 353.9770, found 353.9765.

1-Methyl-2-oxo-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydroquinoline-6-carbonitrile (3f)

Colorless oil, 31.8 mg, 53% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J_1 = 8.5 Hz, J_2 = 1.9 Hz, 1H), 7.45 (d, J = 1.9 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 3.32 (s, 3H), 3.22–3.15 (m, 1H), 3.02–2.89 (m, 2H), 2.85–2.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 142.3, 132.1, 130.9, 129.6 (q, J = 304.9 Hz), 125.9, 117.4, 114.7, 105.4, 35.0, 34.1, 31.8 (q, J = 1.9 Hz), 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.8 (s). HRMS-ESI(m/z): calcd for $C_{13}H_{12}F_3N_2OS$ $(M+H)^+$: 301.0617, found 301.0613.

1,6-Dimethyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3g)

Colorless oil, 28.9 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, J_1 = 8.2 Hz, J_2 = 1.4 Hz, 1H), 7.01 (d, J = 1.6 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 3.34 (s, 3H), 3.15–3.12 (m, 1H), 3.11–3.05 (m, 1H), 2.96–2.91 (m, 1H), 2.85–2.81 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 136.2, 129.9 (q, J = 304.5 Hz), 128.1, 127.8, 127.1, 125.0, 114.1, 35.3, 34.5, 32.2 (q, J = 1.8 Hz), 28.4, 19.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s). HRMS-ESI(m/z): calcd for $C_{13}H_{15}F_3NOS$ $(M+H)^+$: 290.0821, found 290.0825.

5-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3h)

Yellow oil, 21.5 mg, 37% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (dd, J_1 = 8.2 Hz, J_2 = 6.1 Hz, 1H), 6.80–6.73 (m, 2H), 3.34 (s, 3H), 3.22–3.15 (m, 1H), 3.07–3.01 (m, 1H), 2.98–2.92 (m, 1H), 2.87–2.85 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 161.8 (d, J = 244.2 Hz), 140.1 (d, J = 10.1 Hz), 129.8 (q, J = 304.7 Hz), 128.5 (d, J = 9.5 Hz), 120.6 (d, J = 3.2 Hz), 108.4 (d, J = 21.3 Hz), 102.2 (d, J = 26.7 Hz), 34.7, 34.5, 32.3 (q, J = 1.5 Hz), 28.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s), –111.8~ –112.0 (m). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_4NOS$ $(M+H)^+$: 294.0570, found 294.0566.

7-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3h')

Yellow oil, 15.4 mg, 26% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, J_1 = 8.3 Hz, J_2 = 2.0 Hz 1H), 6.87–6.80 (m, 2H), 3.62–3.56 (m, 1H), 3.37 (s, 3H), 3.13–3.07 (m, 1H), 3.01 (dd, J_1 = 16.7 Hz, J_2 = 1.6 Hz, 1H), 2.87–2.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 158.8 (d, J = 244.1 Hz), 140.3 (d, J = 6.3 Hz), 129.7 (q, J = 304.7 Hz), 128.7 (d, J = 9.7 Hz), 112.7 (d, J = 20.9 Hz), 108.4 (d, J = 3.1 Hz), 102.2 (d, J = 22.0 Hz), 33.2, 31.4 (q, J = 1.7 Hz), 28.7, 28.2 (d, J = 2.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –41.0 (s), –118.1~ –118.2 (m). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_4NOS$ $(M+H)^+$: 294.0570, found 294.0567.

5-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3i)

Yellow oil, 21.1 mg, 34% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 8.0 Hz, 1H), 7.05 (dd, J_1 = 10.0 Hz, J_2 = 2.0 Hz 1H), 7.02 (d, J = 1.9 Hz, 1H), 3.35 (s, 3H), 3.22–3.15 (m, 1H), 3.07–2.92 (m, 2H), 2.87–2.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 139.7, 133.5, 129.7 (q, J = 304.7 Hz), 128.3, 123.4, 121.9, 114.6, 34.8, 34.4, 32.1 (q, J = 1.8 Hz), 28.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.8 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_3ClNOS$ $(M+H)^+$: 310.0275, found 310.0271.

7-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3i')

Yellow oil, 14.1 mg, 23% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, J = 8.1 Hz, 1H), 7.14 (dd, J_1 = 8.1 Hz, J_2 = 0.9 Hz 1H), 6.90 (d, J = 8.1 Hz, 1H), 3.72–3.65 (m, 1H), 3.36 (s, 3H), 3.24–3.18 (m, 1H), 3.10 (dd, J_1 = 16.7 Hz, J_2 = 1.6 Hz 1H), 2.77–2.67 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 140.2, 132.6, 129.7 (q, J = 304.8 Hz), 128.3, 123.3, 123.3, 112.9, 32.6, 32.1, 30.1 (q, J = 1.8 Hz), 28.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.6 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_3ClNOS$ $(M+H)^+$: 310.0275, found 310.0273.

5-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3j)

Yellow oil, 23.1 mg, 33% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1H), 7.16 (d, J = 1.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 3.34 (s, 3H), 3.20–3.13 (m, 1H), 3.06–2.92 (m, 2H), 2.86–2.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 139.9, 129.7 (q, J = 304.7 Hz), 128.6, 124.9, 123.9, 121.4, 117.4, 34.9, 34.3, 32.0

(q, J = 1.8 Hz), 28.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.8 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_3BrNOS$ $(M+H)^+$: 353.9770, found 353.9768.

7-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-on (3j')

Yellow oil, 16.4 mg, 23% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (dd, J_1 = 8.0 Hz, J_2 = 0.9 Hz, 1H), 7.16 (t, J = 8.1 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 3.69–3.62 (m, 1H), 3.35 (s, 3H), 3.27–3.21 (m, 1H), 3.11 (dd, J_1 = 16.7 Hz, J_2 = 1.7 Hz 1H), 2.78–2.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 140.2, 129.7 (q, J = 304.9 Hz), 128.6, 126.6, 125.0, 122.9, 113.6, 34.7, 32.6, 30.0 (q, J = 1.8 Hz), 28.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.4 (s). HRMS-ESI(m/z): calcd for $C_{12}H_{12}F_3BrNOS$ $(M+H)^+$: 353.9770, found 353.9771.

7-(((Trifluoromethyl)thio)methyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-5-one (3k)

Yellow oil, 31.3 mg, 52% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.02 (m, 2H), 6.97 (t, J = 7.4 Hz, 1H), 4.20–4.13 (m, 1H), 3.64–3.57 (m, 1H), 3.21–3.14 (m, 1H), 3.11–3.04 (m, 1H), 2.98–2.91 (m, 1H), 2.85 (d, J = 4.6 Hz, 2H), 2.82–2.74 (m, 2H), 1.98–1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.3, 135.1, 130.9 (q, J = 304.5 Hz), 129.1, 126.2, 125.9, 125.5, 122.8, 40.9, 36.2, 35.3, 33.4 (q, J = 1.7 Hz), 27.3, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s). HRMS-ESI(m/z): calcd for $C_{14}H_{15}F_3NOS$ $(M+H)^+$: 302.0821, found 302.0818.

1-Methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydro-1,8-naphthyridin-2(1H)-one (3l)

Colorless oil, 37.0 mg, 67% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (dd, J_1 = 4.6 Hz, J_2 = 1.8 Hz, 1H), 7.54–7.51 (m, 1H), 7.00 (dd, J_1 = 7.4 Hz, J_2 = 5.0 Hz 1H), 3.47 (s, 3H), 3.23–3.16 (m, 1H), 3.03 (s, 1H), 3.01 (d, J = 1.9 Hz, 1H), 2.90 (d, J = 2.6 Hz, 1H), 2.89 (d, J = 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 150.5, 146.4, 135.3, 129.7 (q, J = 304.8 Hz), 119.7, 117.4, 34.4, 33.9, 32.1 (q, J = 1.9 Hz), 27.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.8 (s). HRMS-ESI(m/z): calcd for $C_{11}H_{12}F_3N_2OS$ $(M+H)^+$: 277.0617, found 277.0619.

1-benzyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3m)

Colorless oil, 29.5 mg, 42% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.29 (m, 2H), 7.25–7.20 (m, 4H), 7.20–7.16 (m, 1H), 7.04 (dt, J_1 = 7.5 Hz, J_2 = 1.0 Hz, 1H), 6.96 (d, J = 8.2 Hz, 1H), 5.35 (AB, J = 16.1 Hz, 1H), 5.03 (AB, J = 16.1 Hz, 1H), 3.29–3.22 (m, 1H), 3.14–3.08 (m, 1H), 3.04–2.99 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 137.8, 135.6, 129.8 (q, J = 303.4 Hz), 127.8, 127.7, 127.4, 126.3, 125.5, 125.3, 122.3, 115.1, 45.0, 35.4, 34.6, 32.2 (q, J = 1.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –40.9 (s). HRMS-ESI(m/z): calcd for $C_{18}H_{17}F_3NOS$ $(M+H)^+$: 352.0978, found 352.0980.

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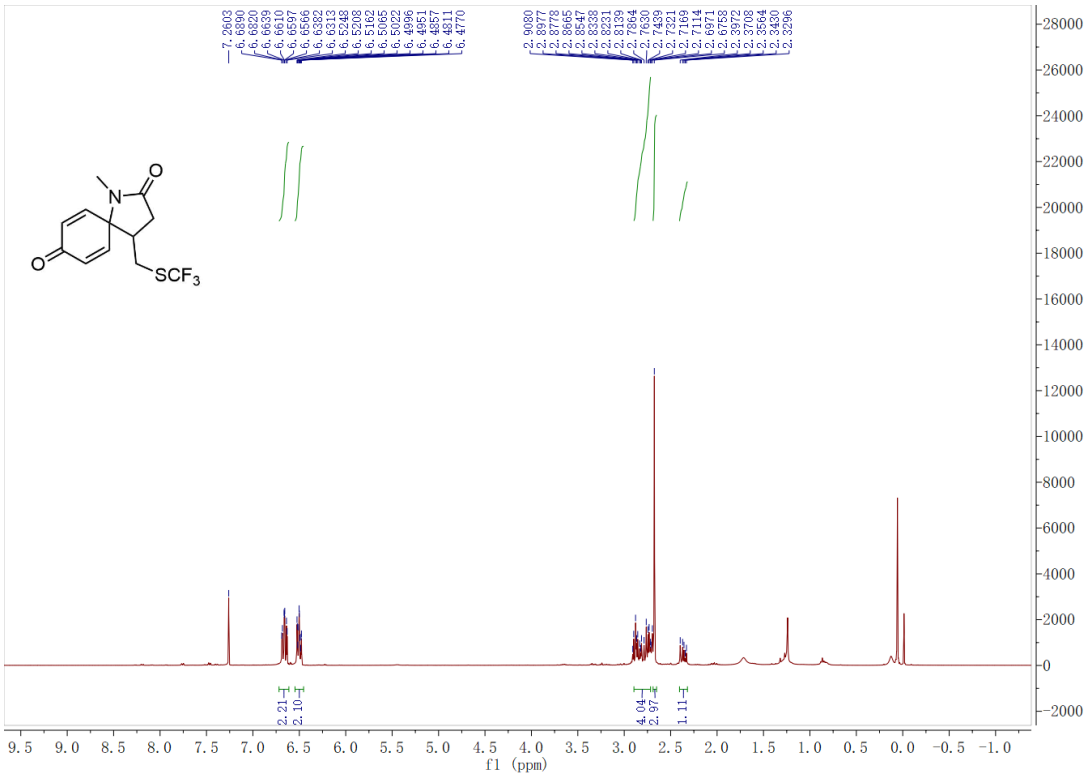
[1] Teverovskiy, G.; Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed*. **2011**, 50, 7312.

[2] Kilaru, P.; Acharya, S, P.; Zhao, P. *Chem. Commun*. **2018**, 54, 924.

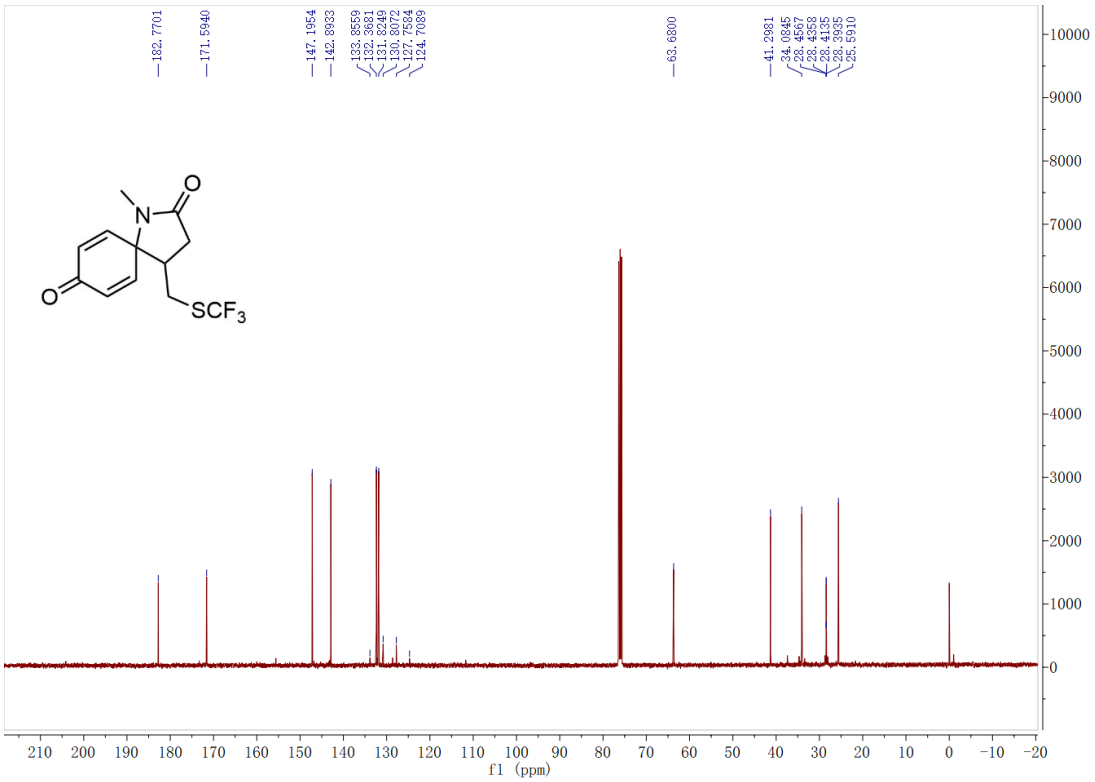
Copies of ^{1}H and ^{13}C NMR spectra

1-Methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2a)

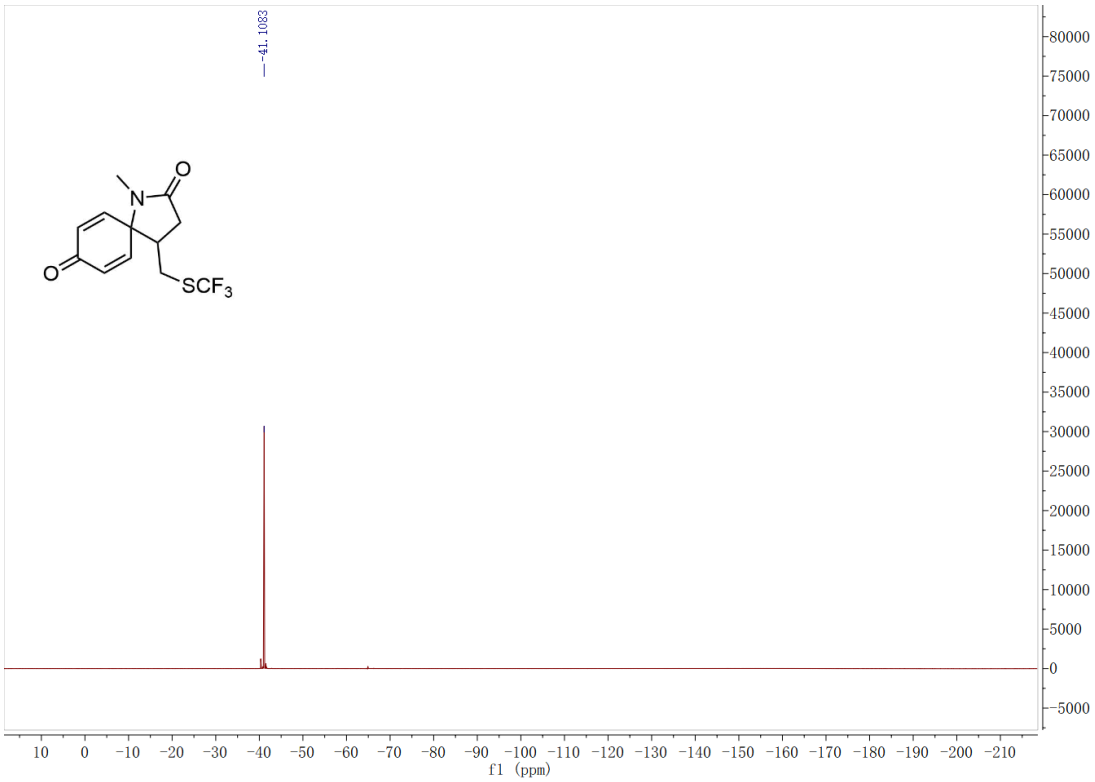
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

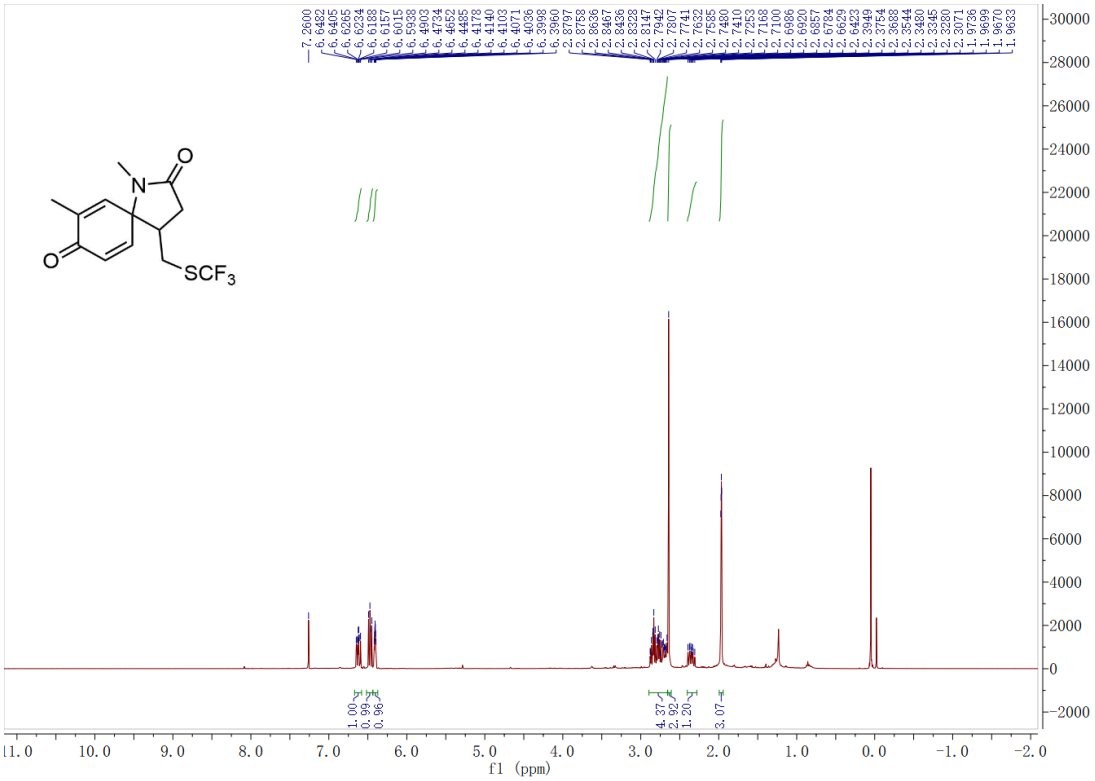


^{19}F NMR (376 MHz, $CDCl_3$)

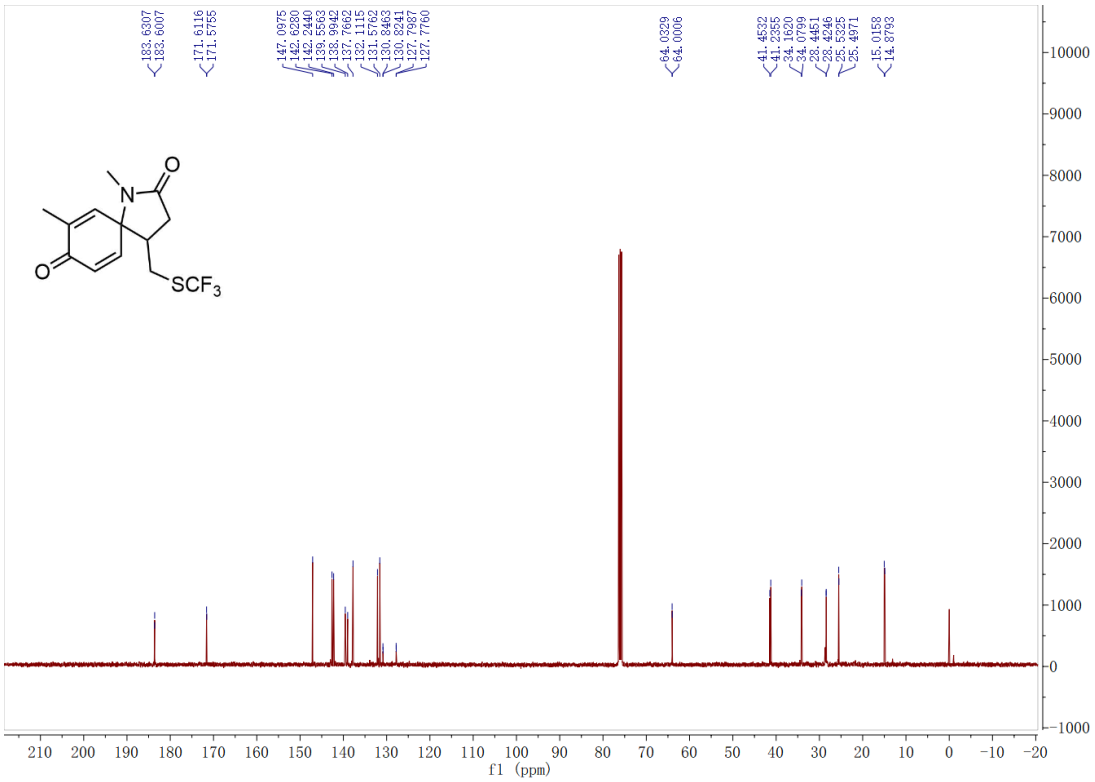


1,7-Dimethyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2b)

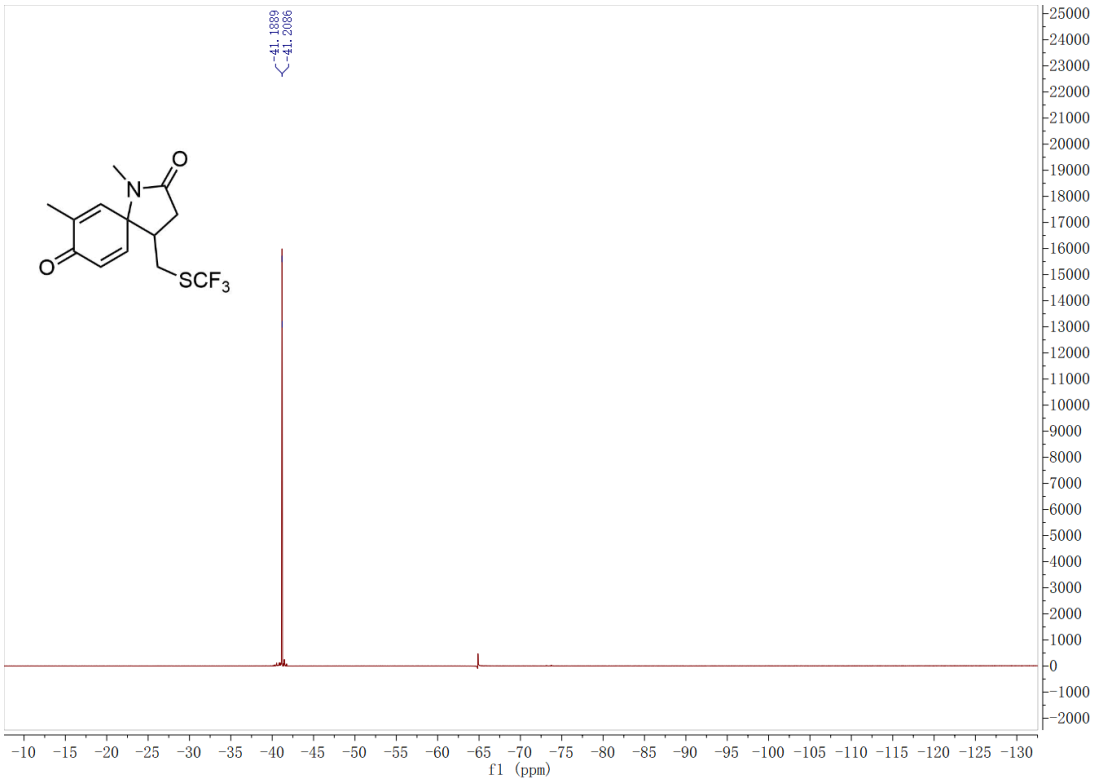
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

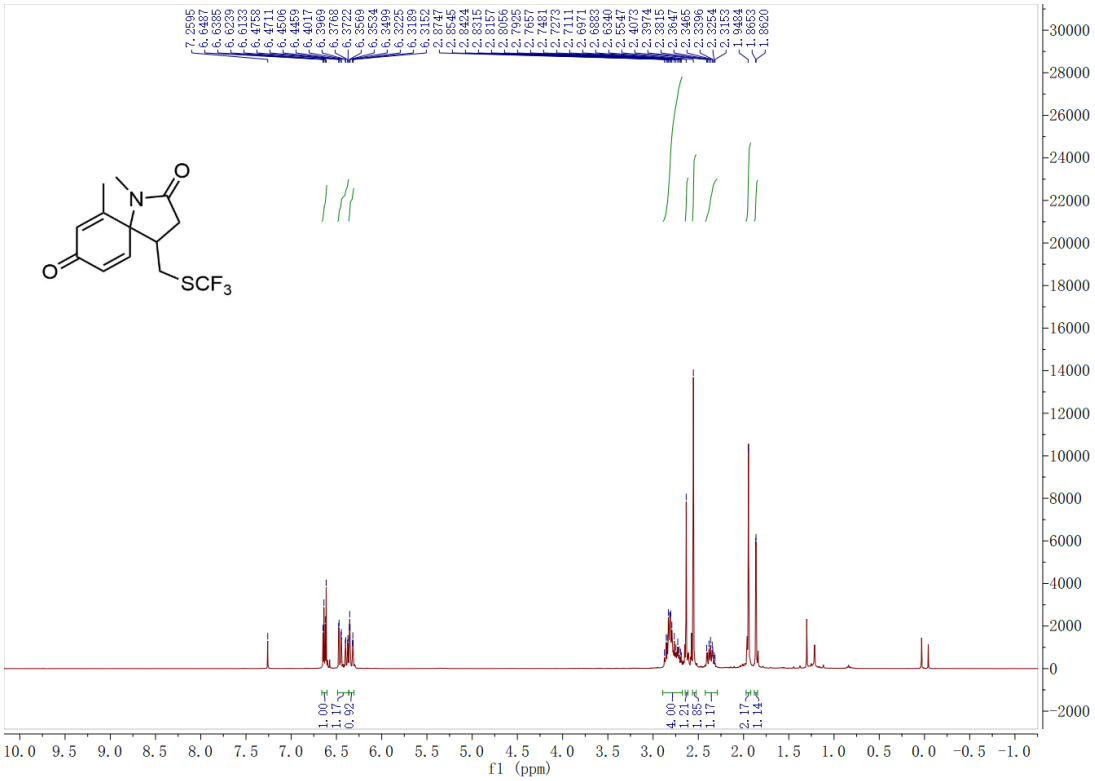


^{19}F NMR (376 MHz, $CDCl_3$)

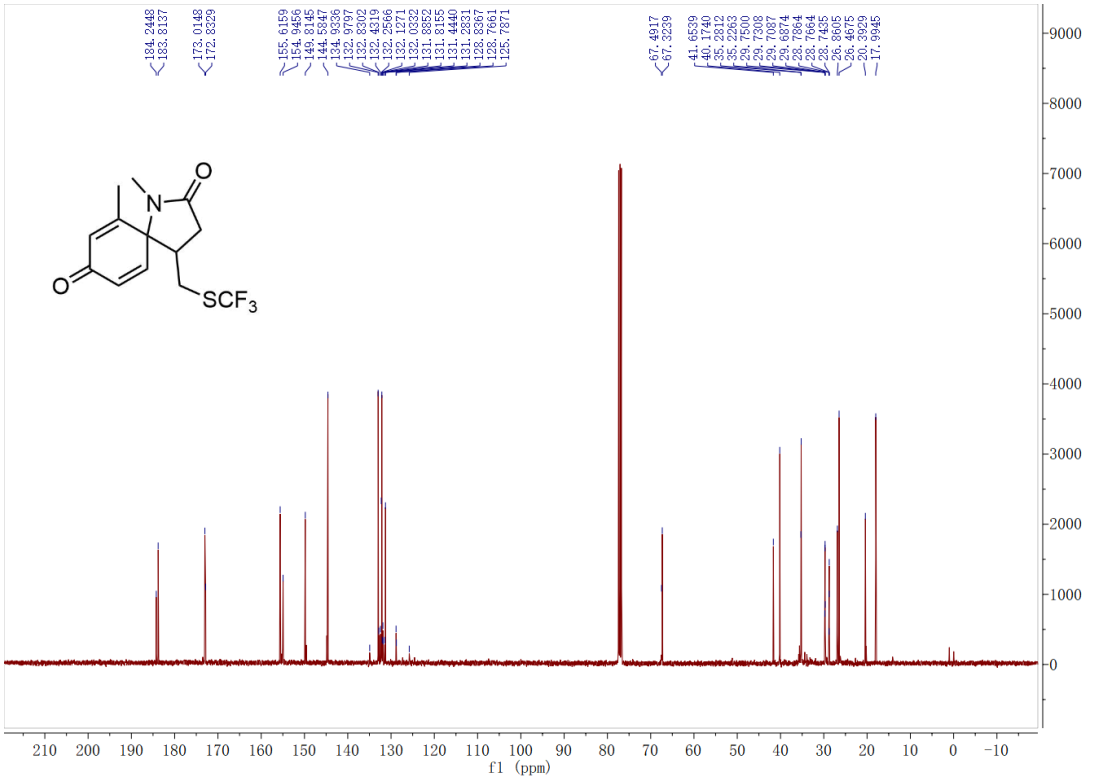


1,6-Dimethyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2c)

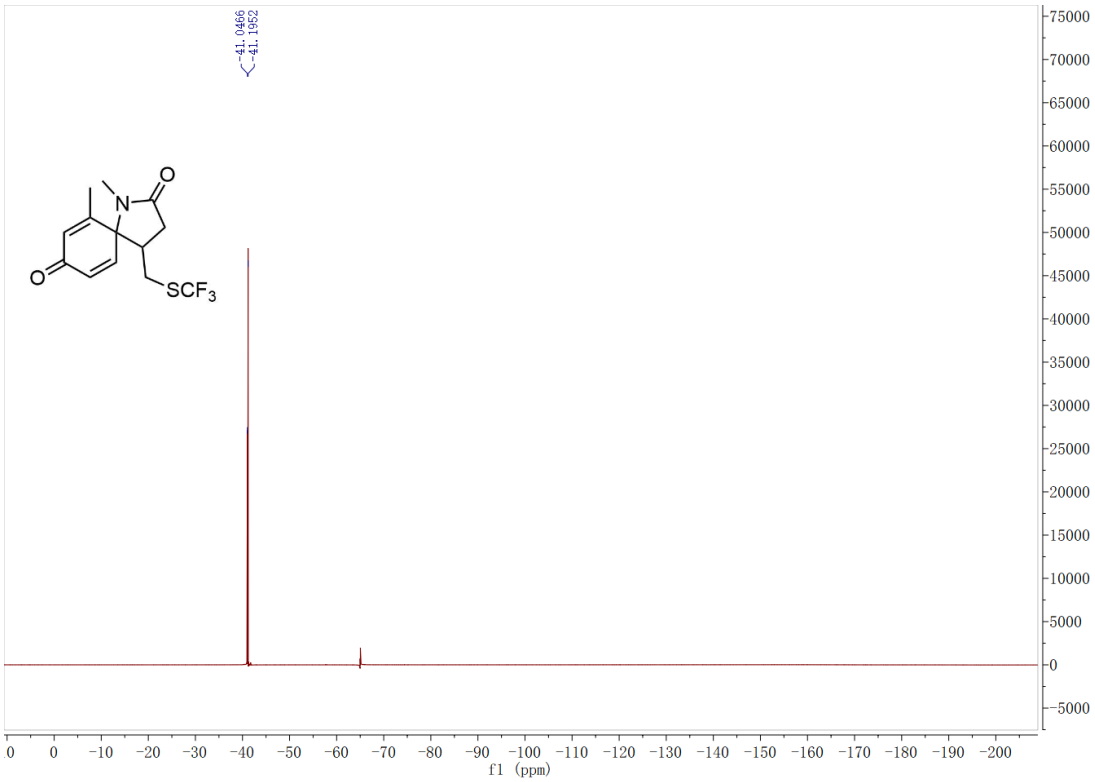
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

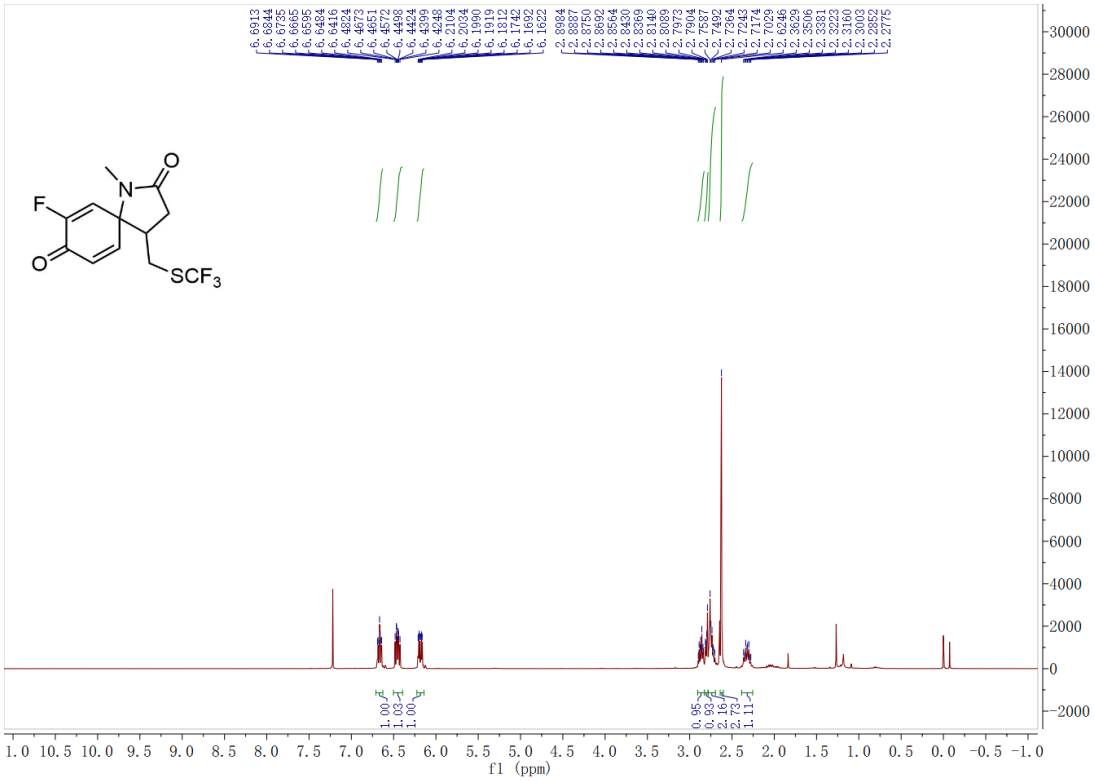


^{19}F NMR (376 MHz, $CDCl_3$)

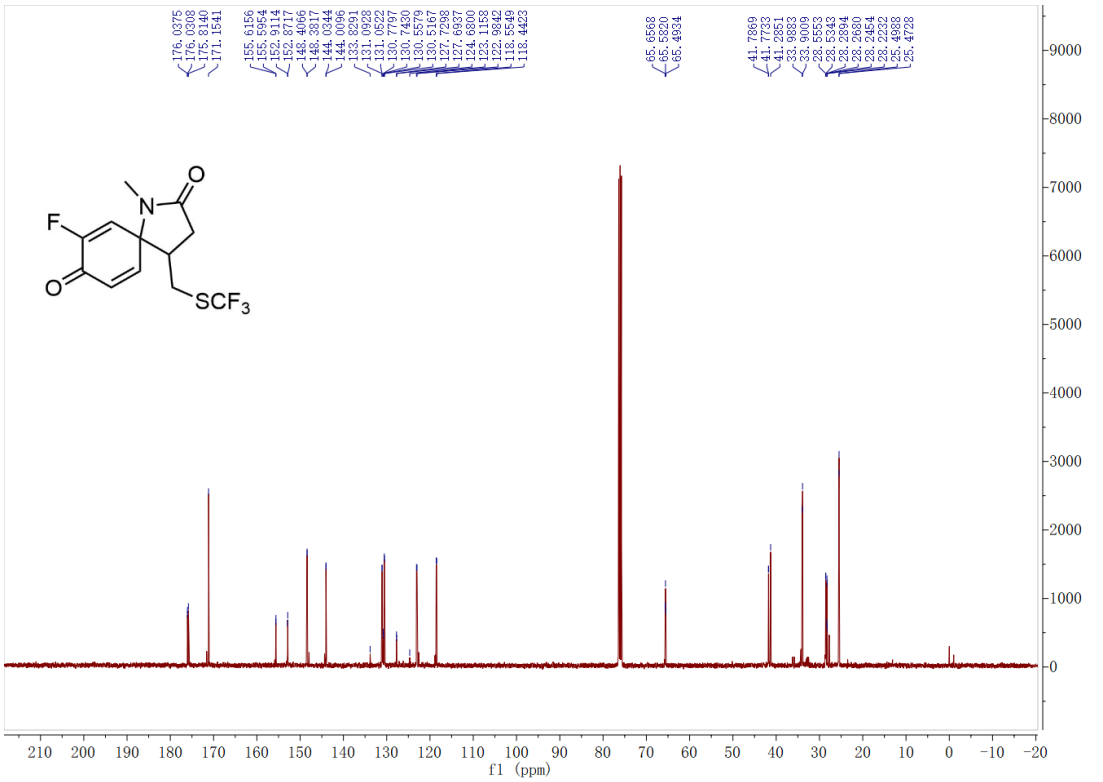


7-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2d)

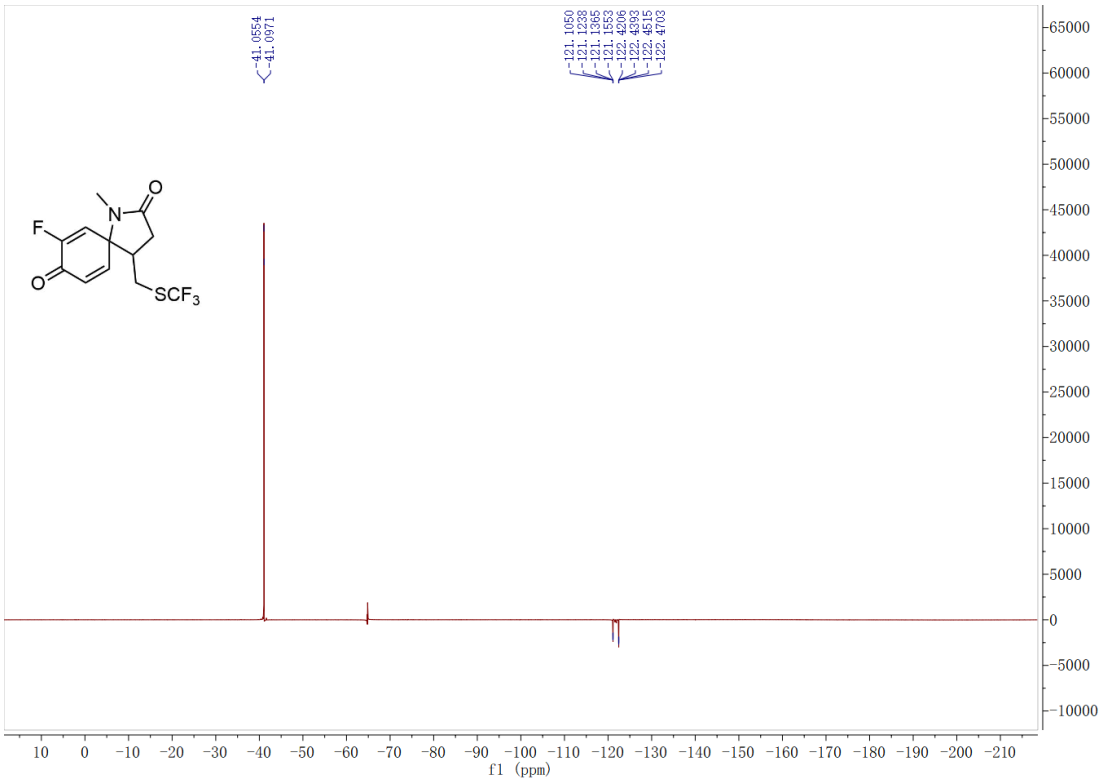
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

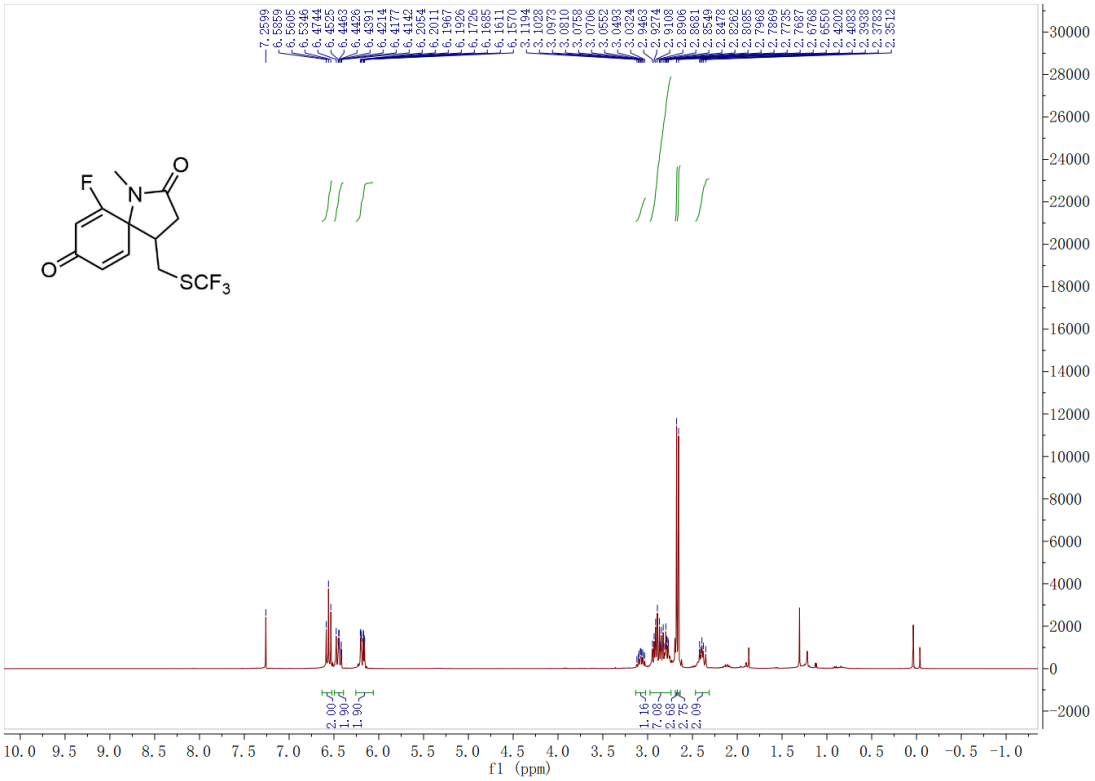


^{19}F NMR (376 MHz, $CDCl_3$)

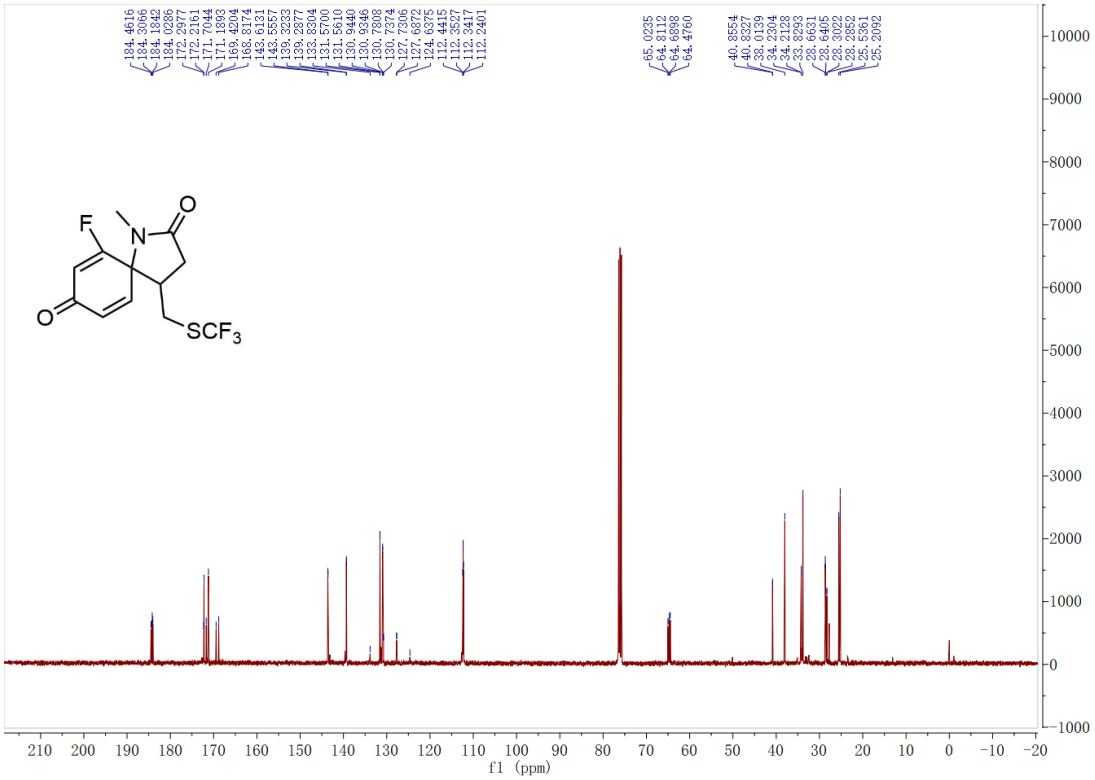


6-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2e)

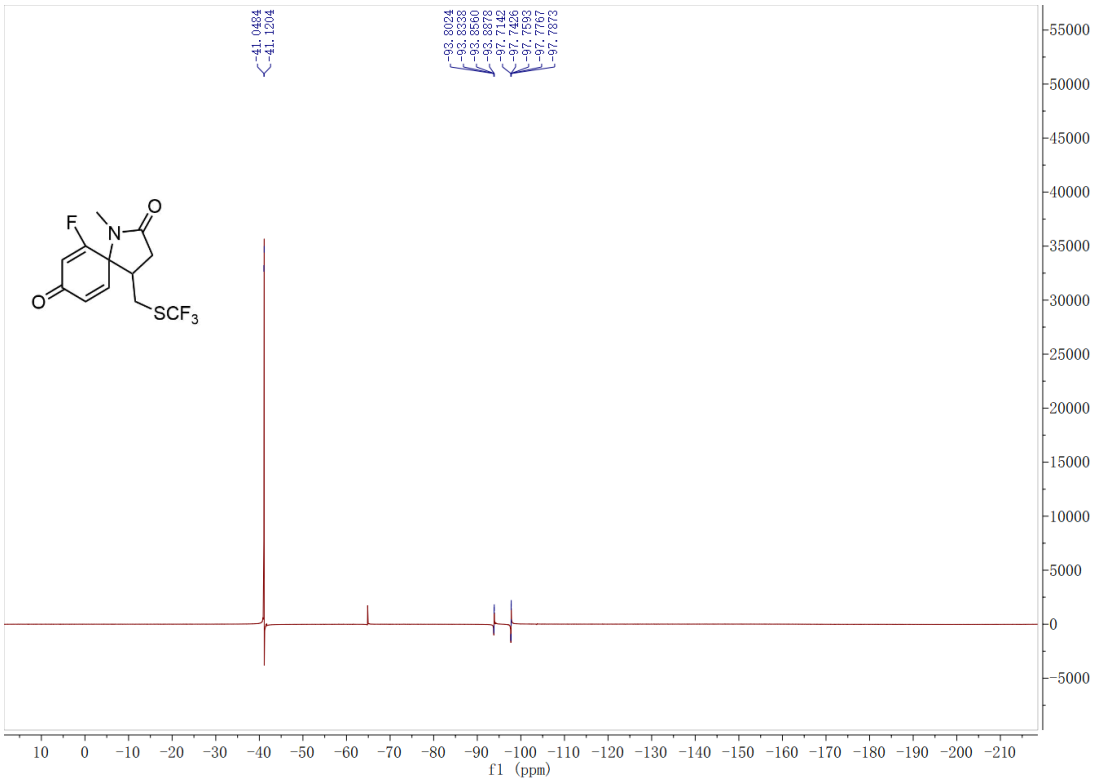
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

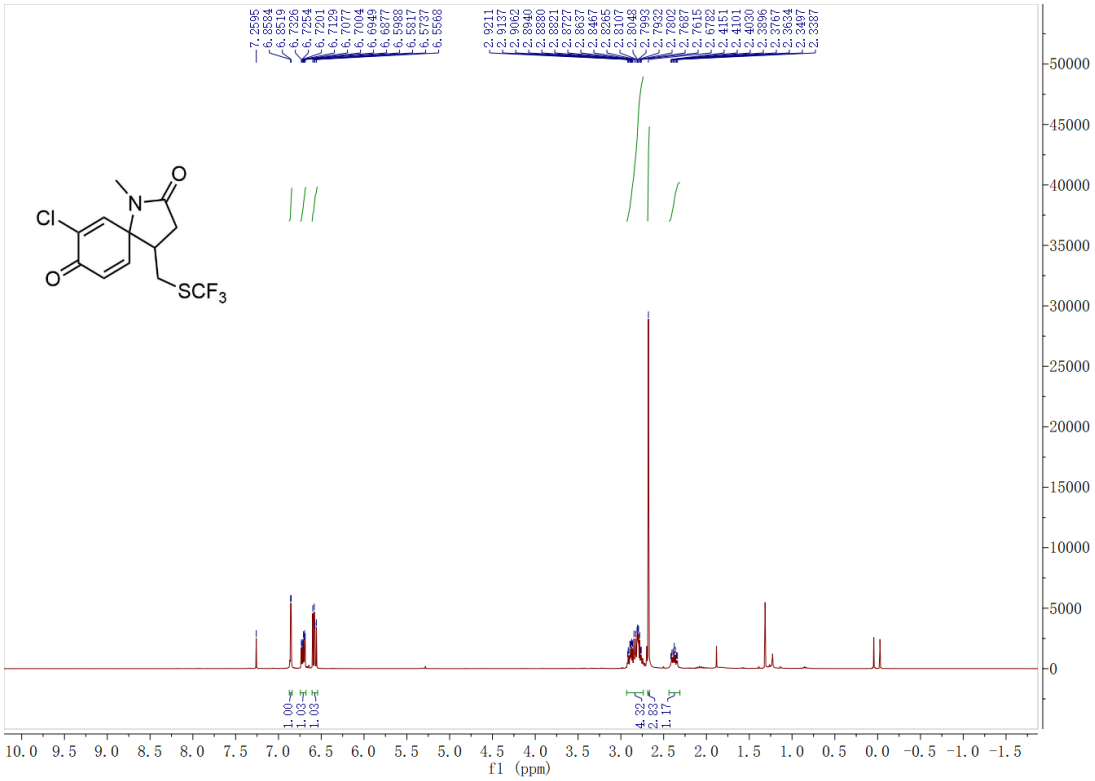


^{19}F NMR (376 MHz, $CDCl_3$)

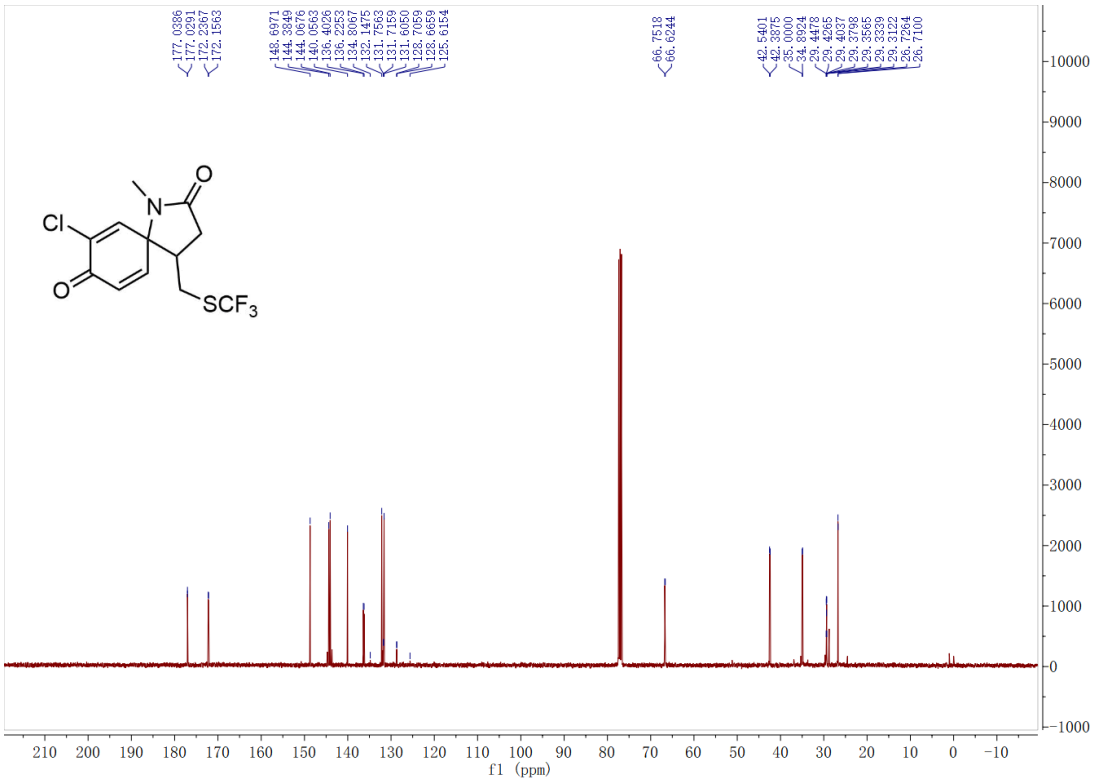


7-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2f)

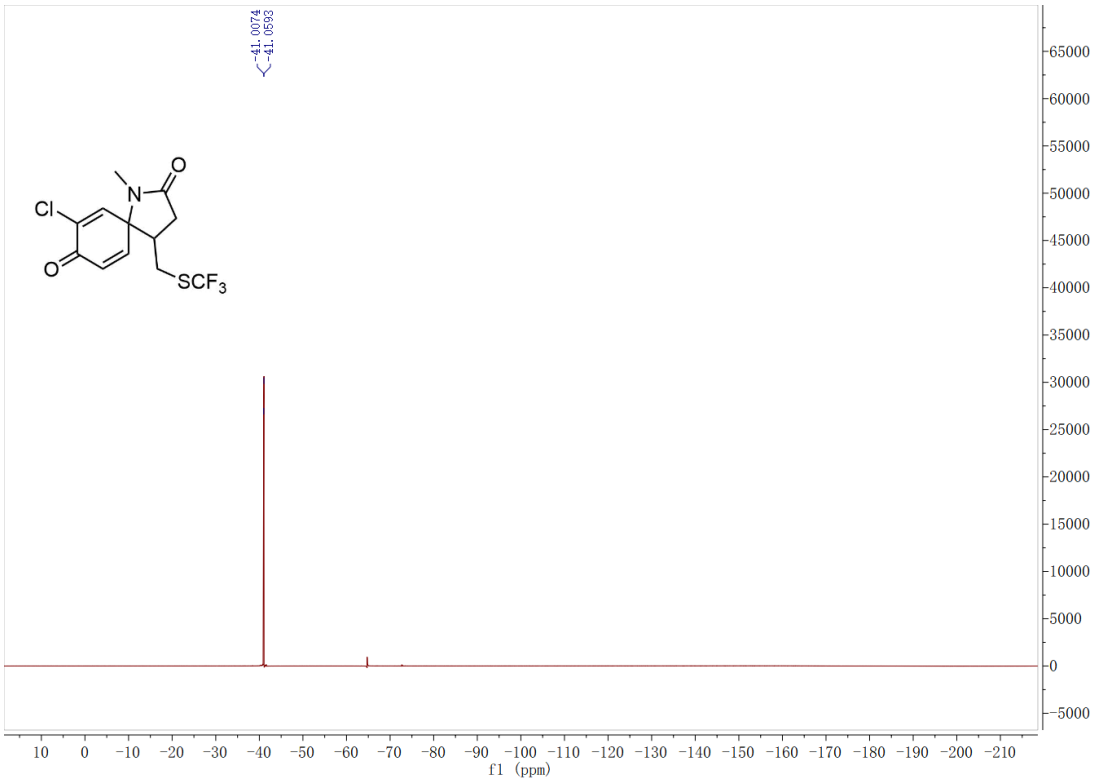
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

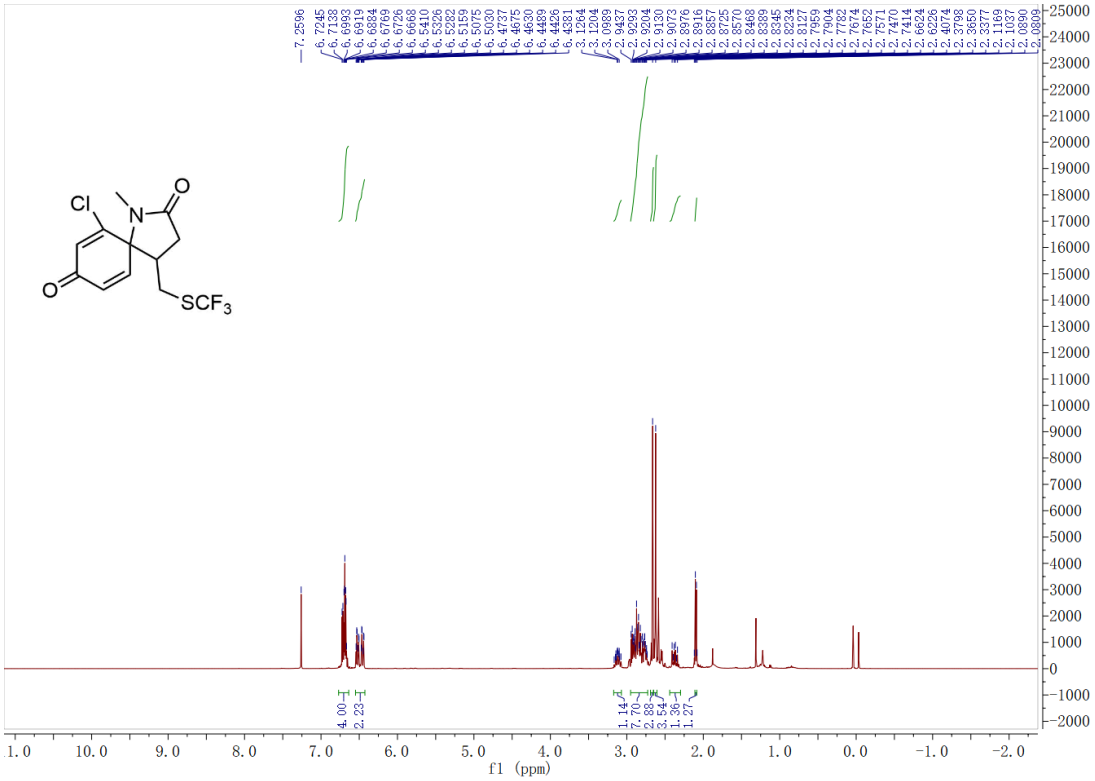


^{19}F NMR (376 MHz, $CDCl_3$)

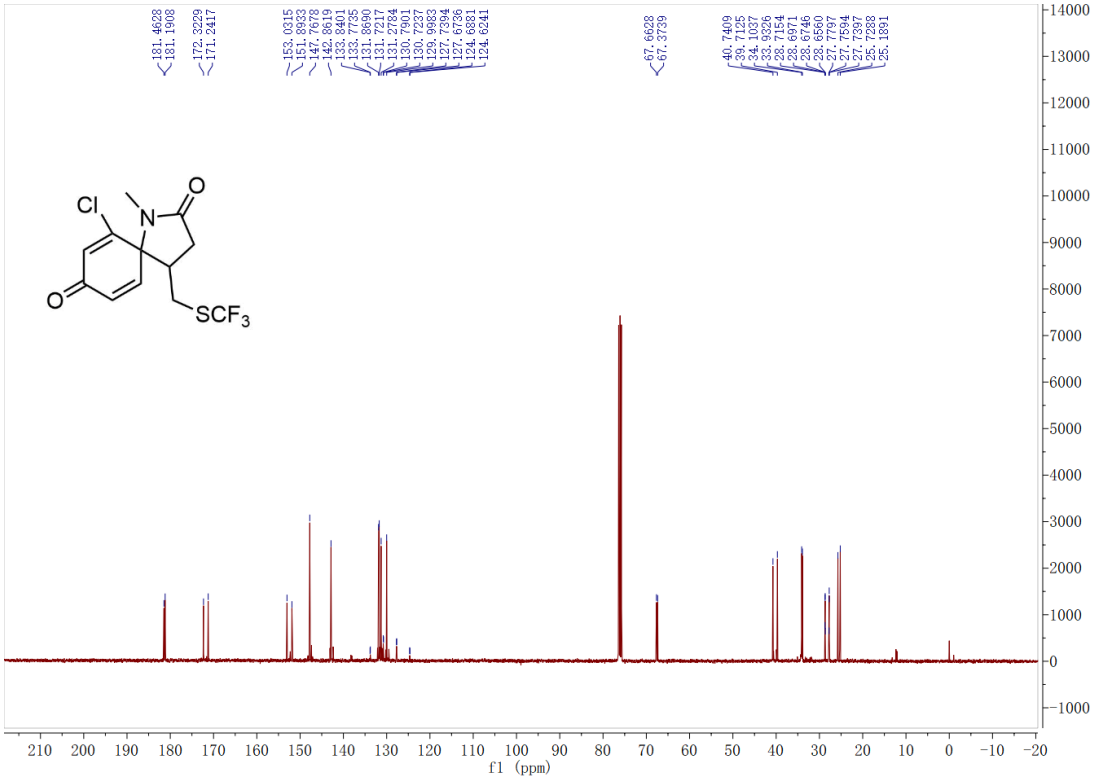


6-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2g)

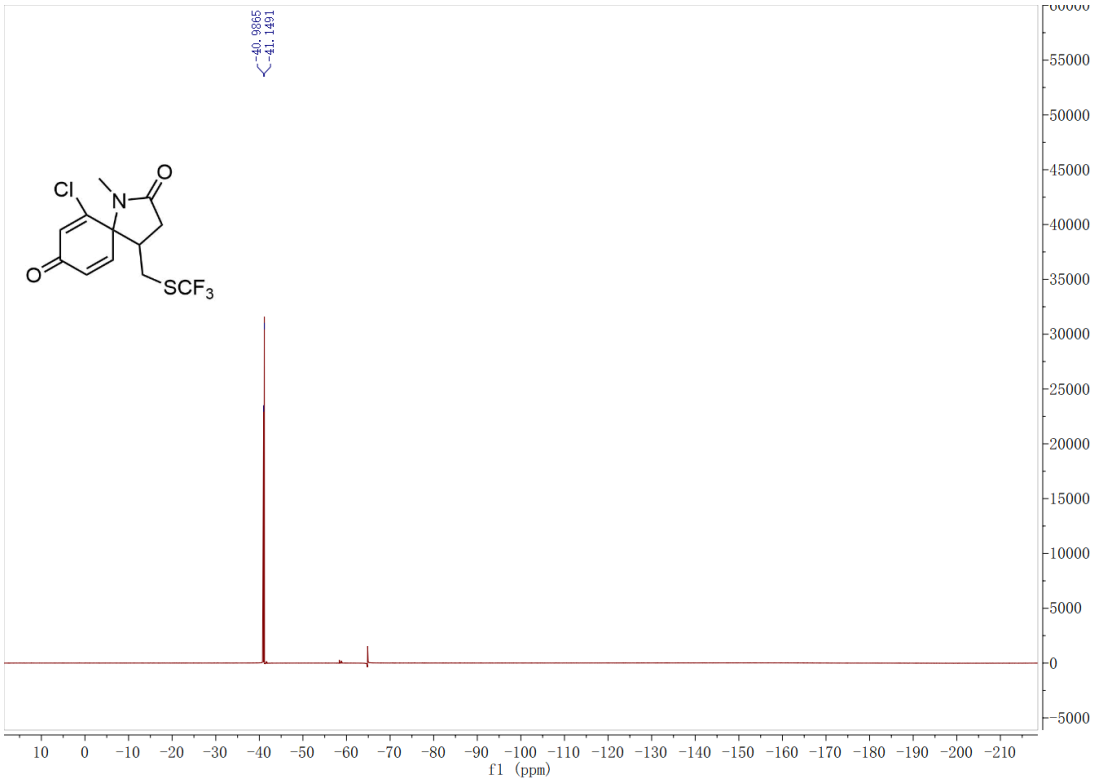
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

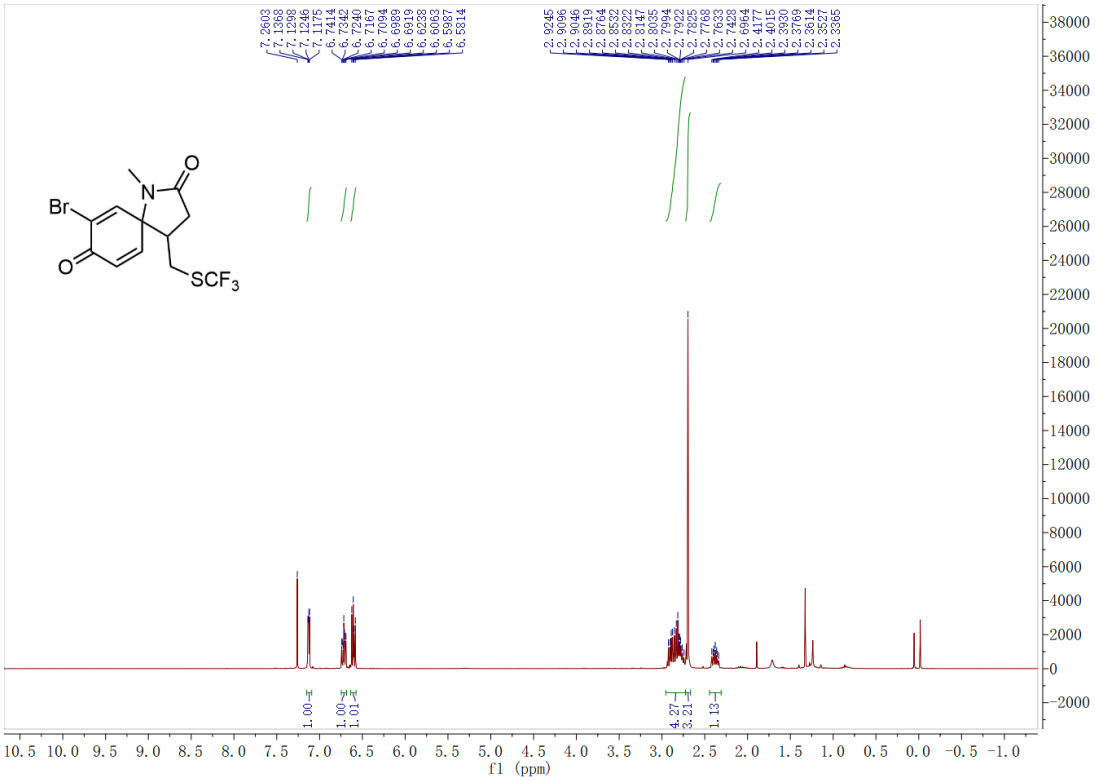


^{19}F NMR (376 MHz, $CDCl_3$)

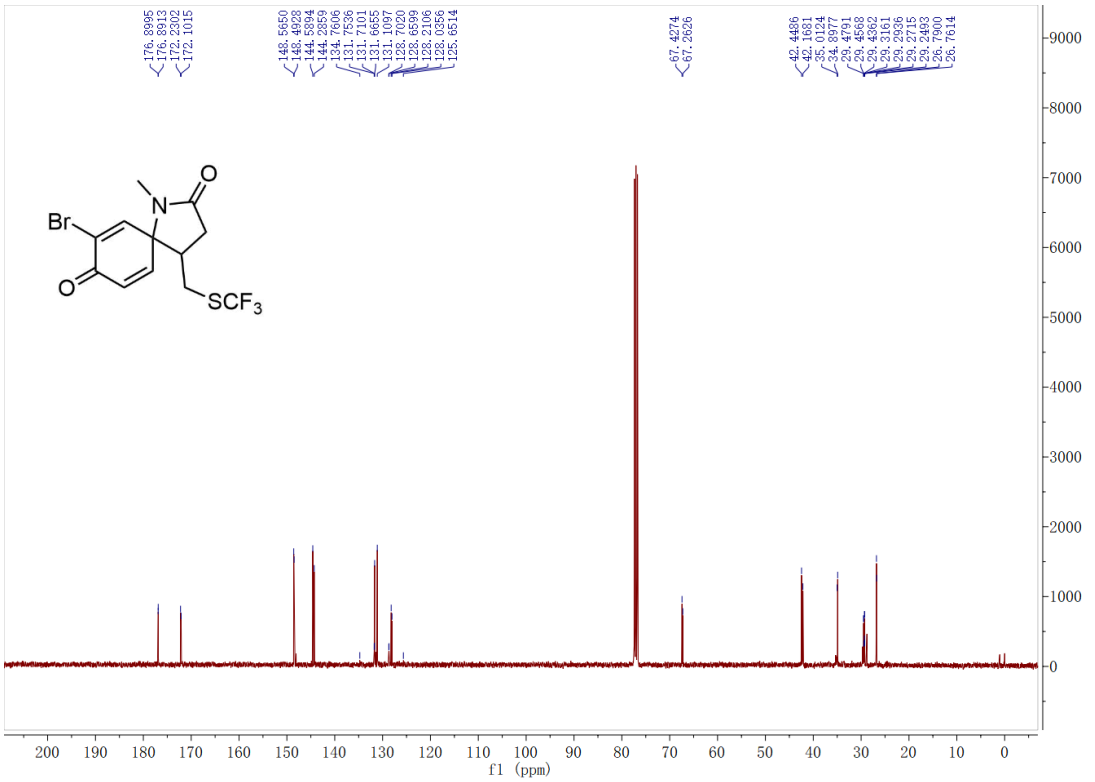


7-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2h)

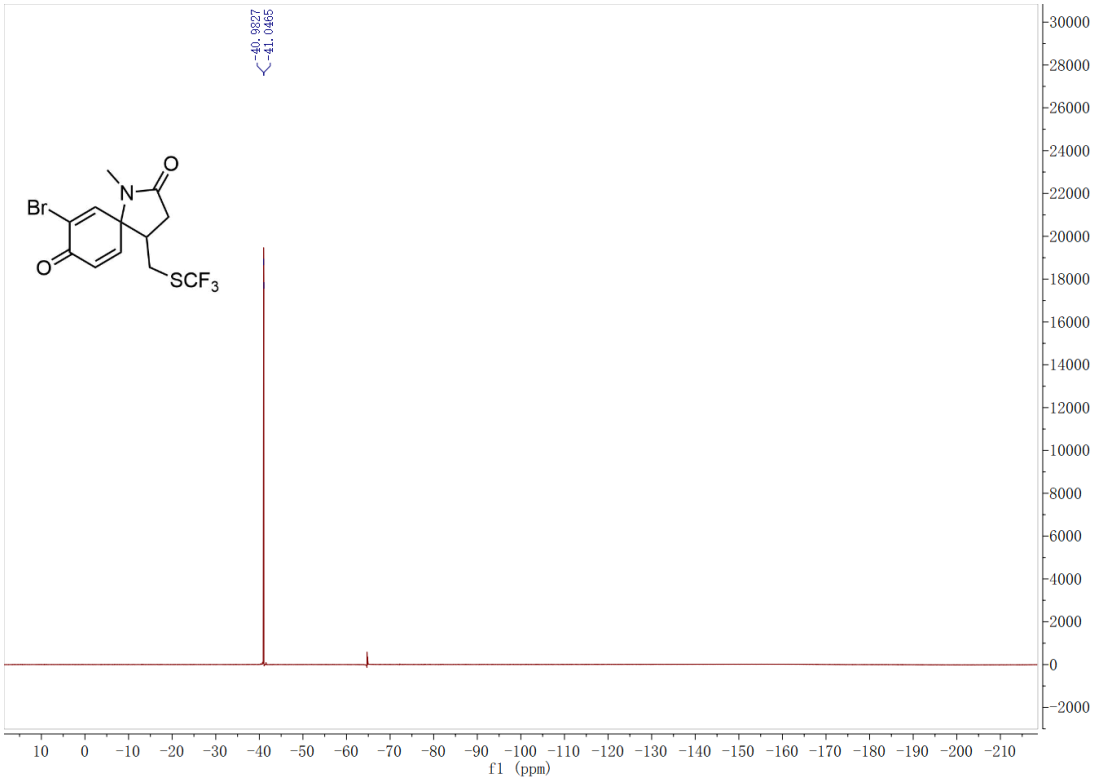
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

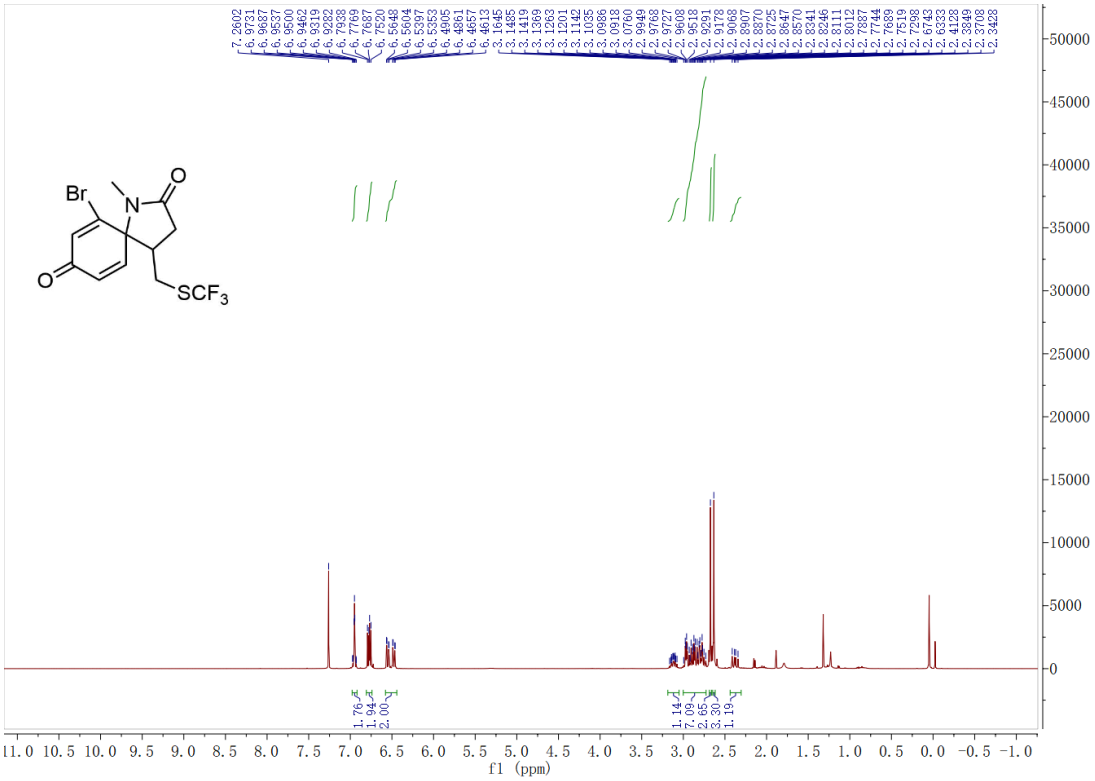


^{19}F NMR (376 MHz, $CDCl_3$)

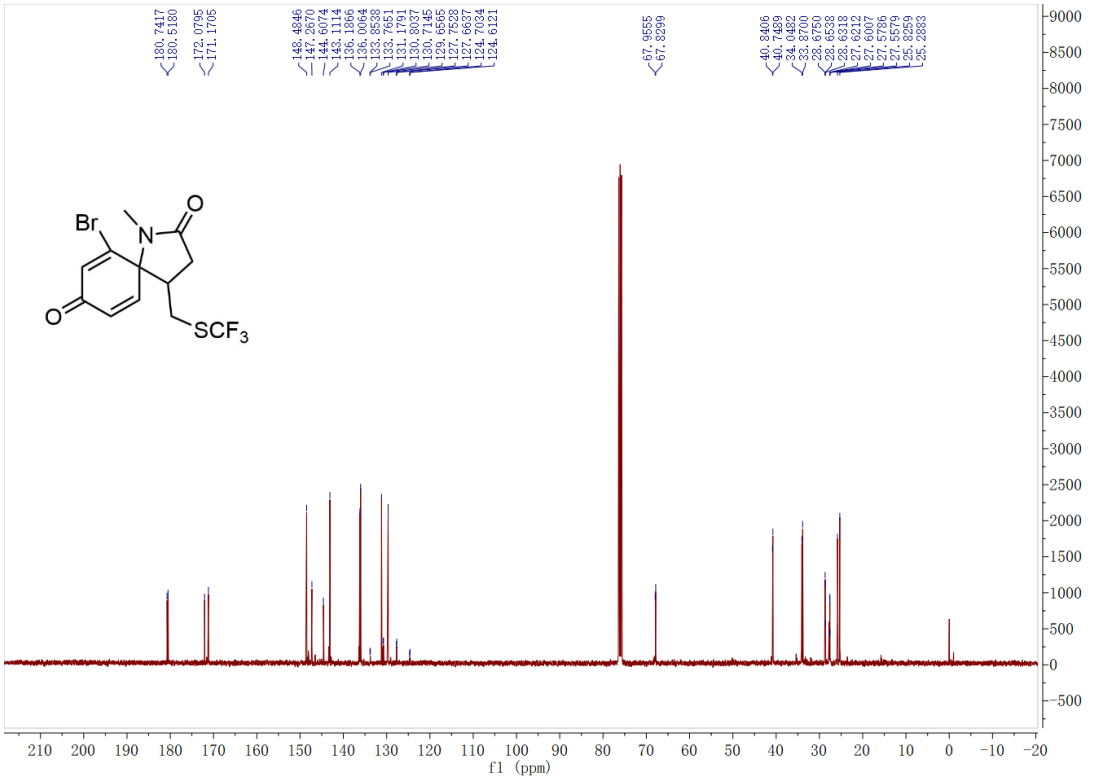


6-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2i)

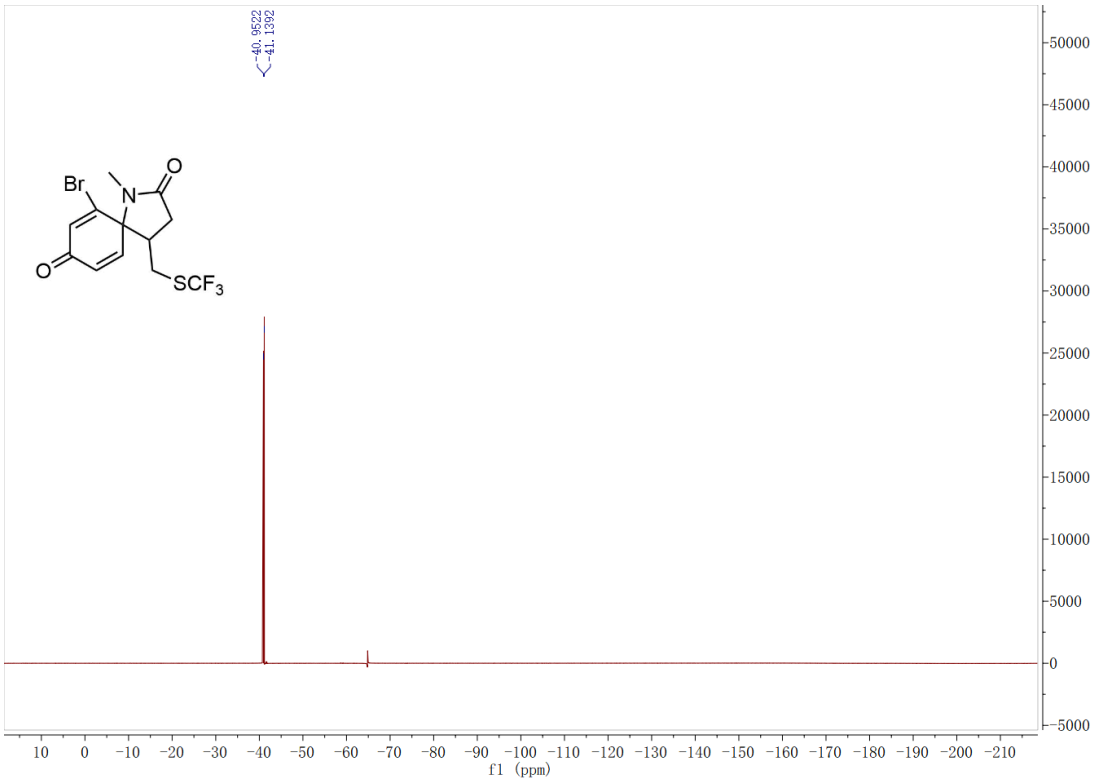
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

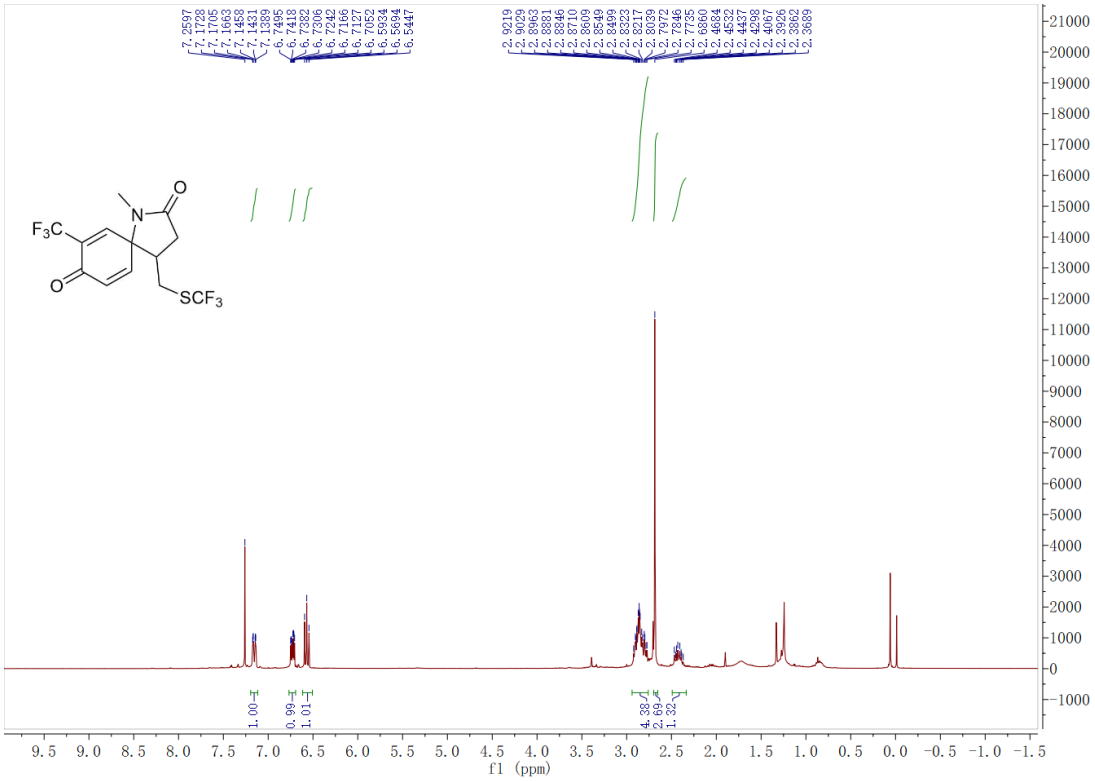


^{19}F NMR (376 MHz, $CDCl_3$)

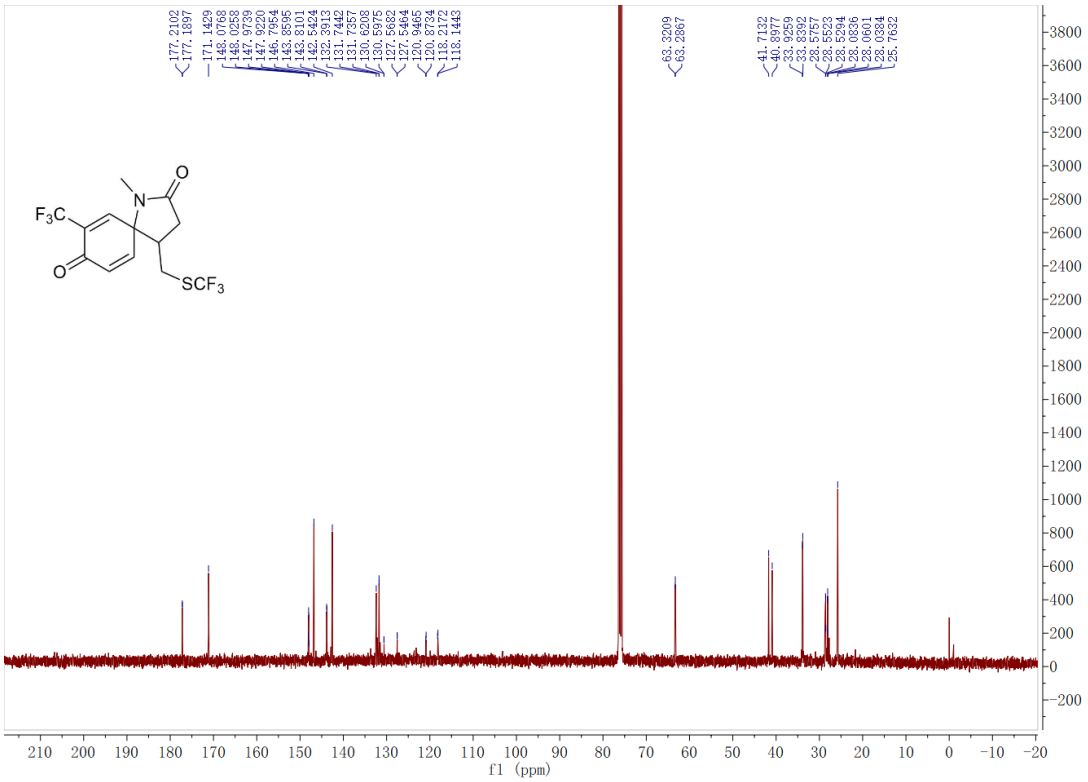


1-methyl-7-(trifluoromethyl)-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2j)

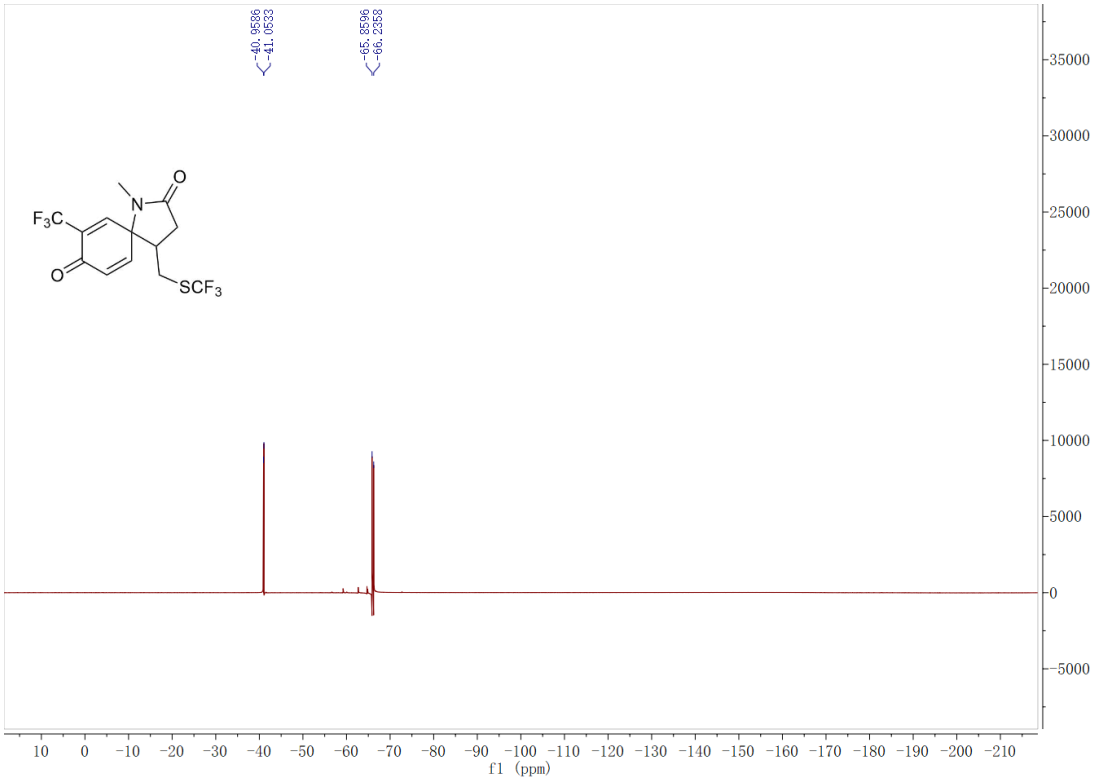
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

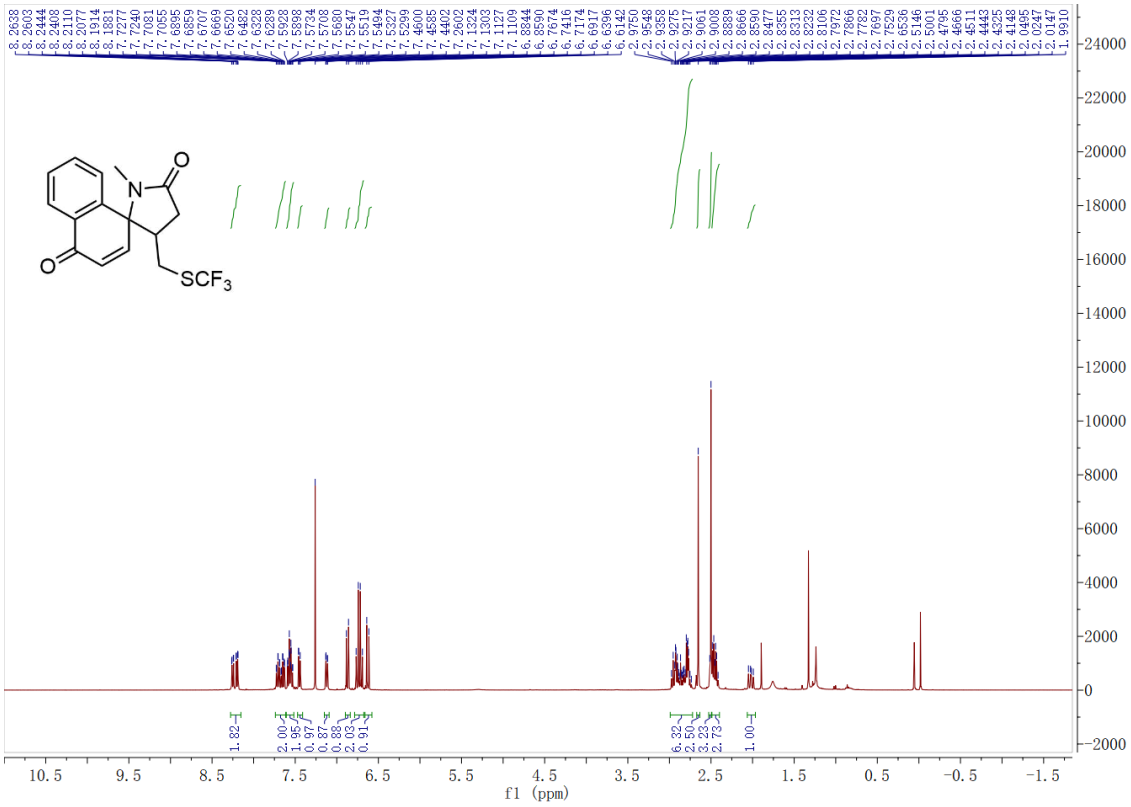


^{19}F NMR (376 MHz, $CDCl_3$)

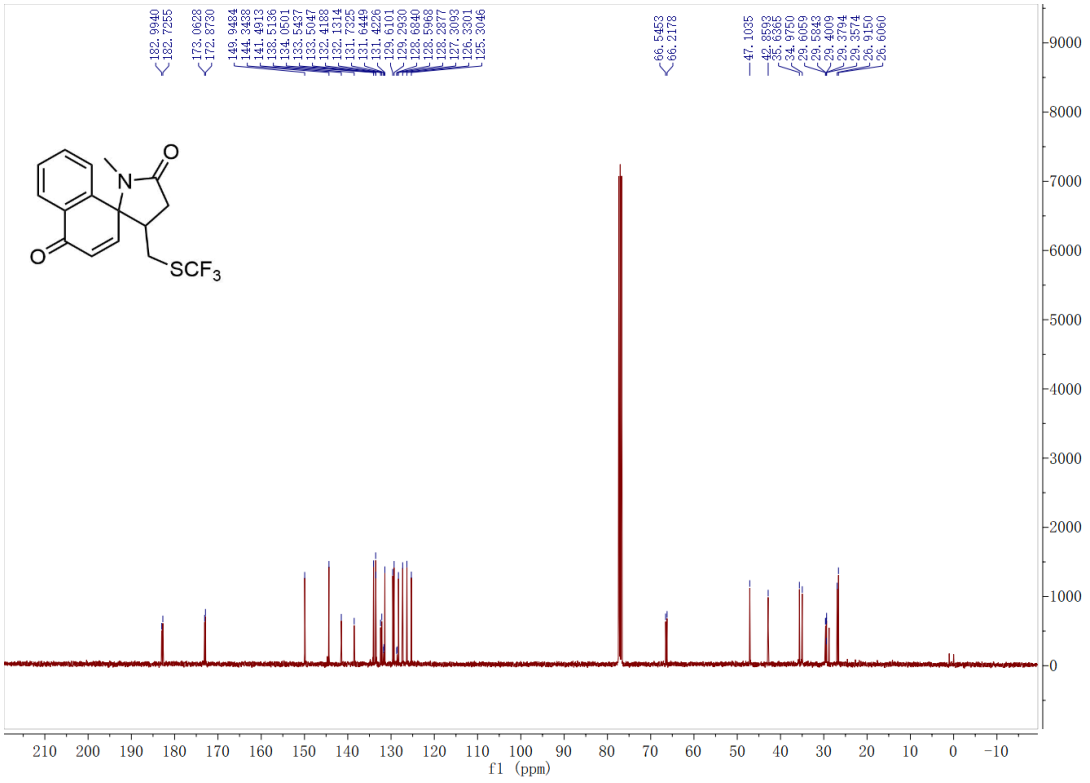


1'-Methyl-3'-(((trifluoromethyl)thio)methyl)-4H-spiro[naphthalene-1,2'-pyrrolidine]-4,5'-dione (2k)

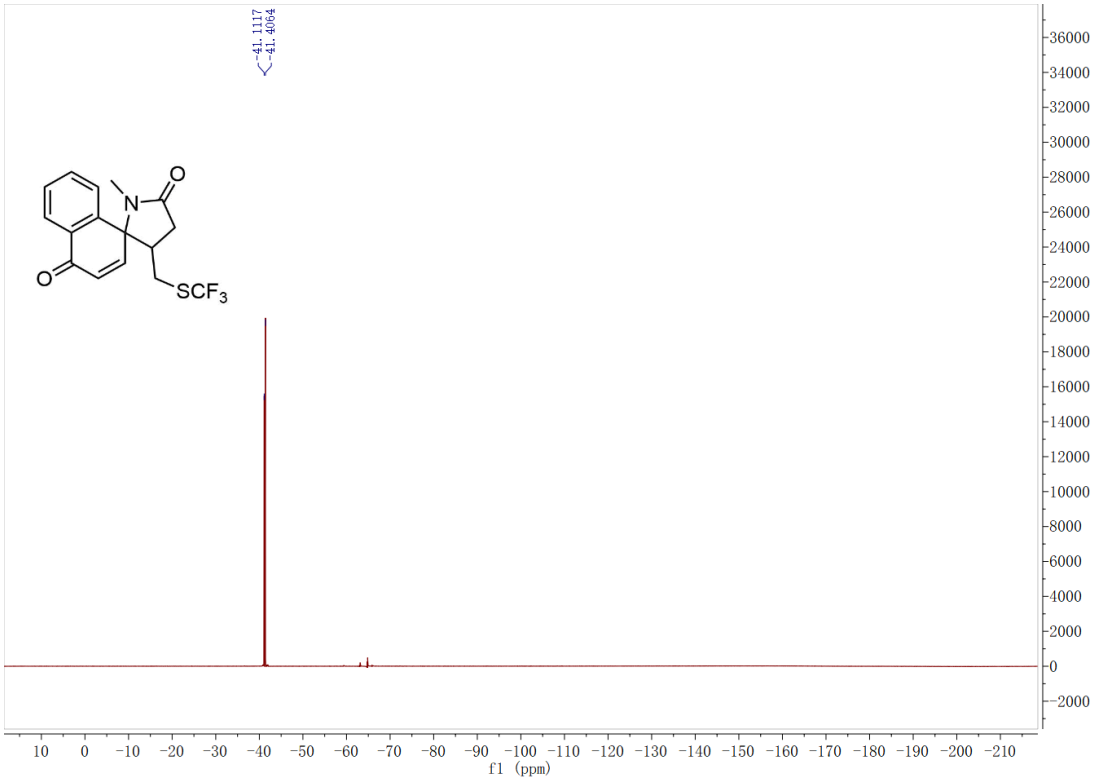
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

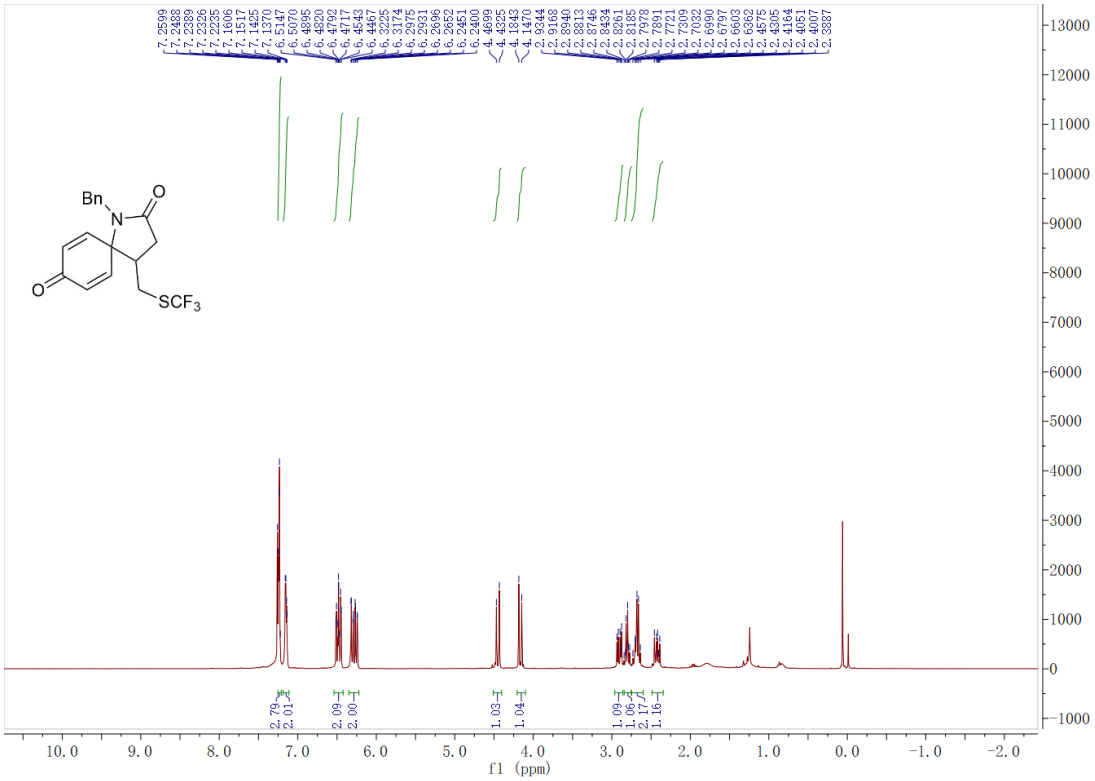


^{19}F NMR (376 MHz, $CDCl_3$)

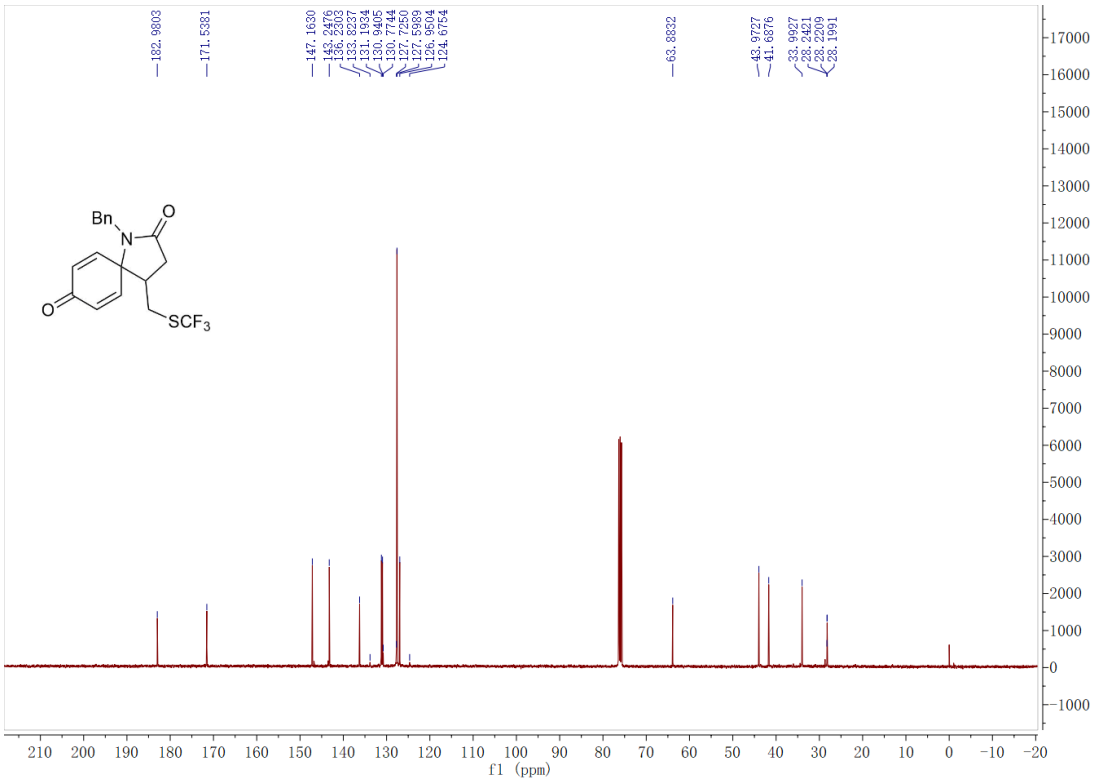


1-benzyl-4-(((trifluoromethyl)thio)methyl)-1-azaspiro[4.5]deca-6,9-diene-2,8-dione (2l)

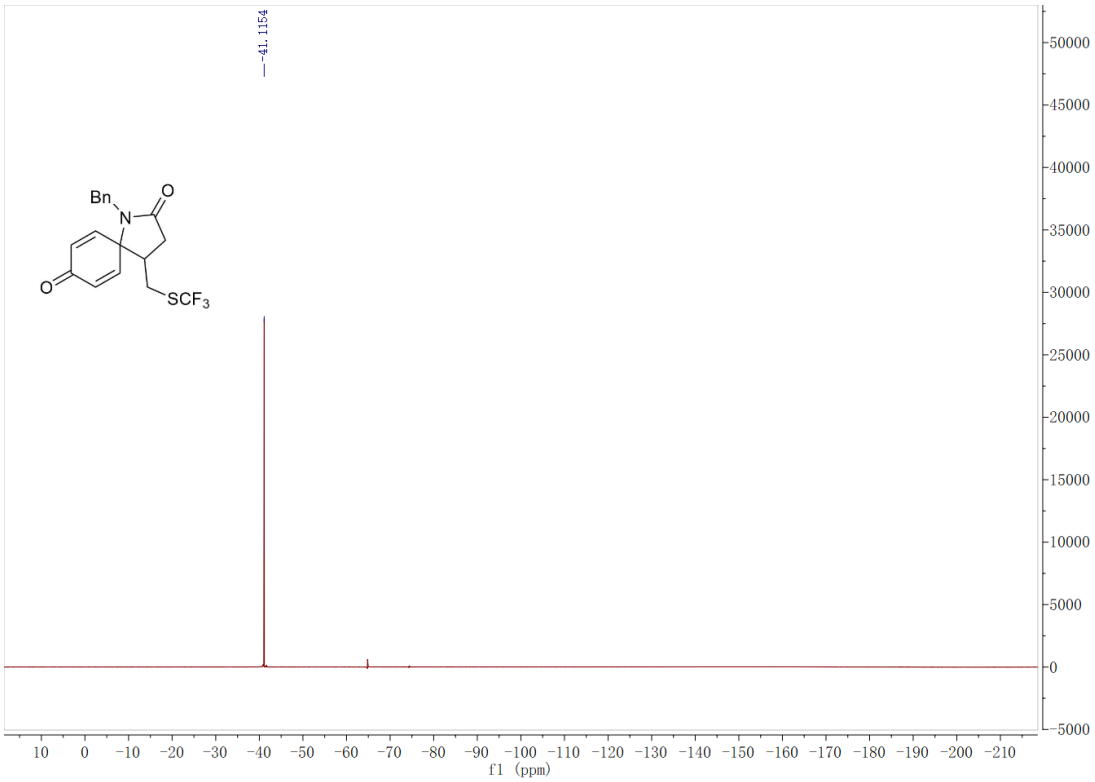
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

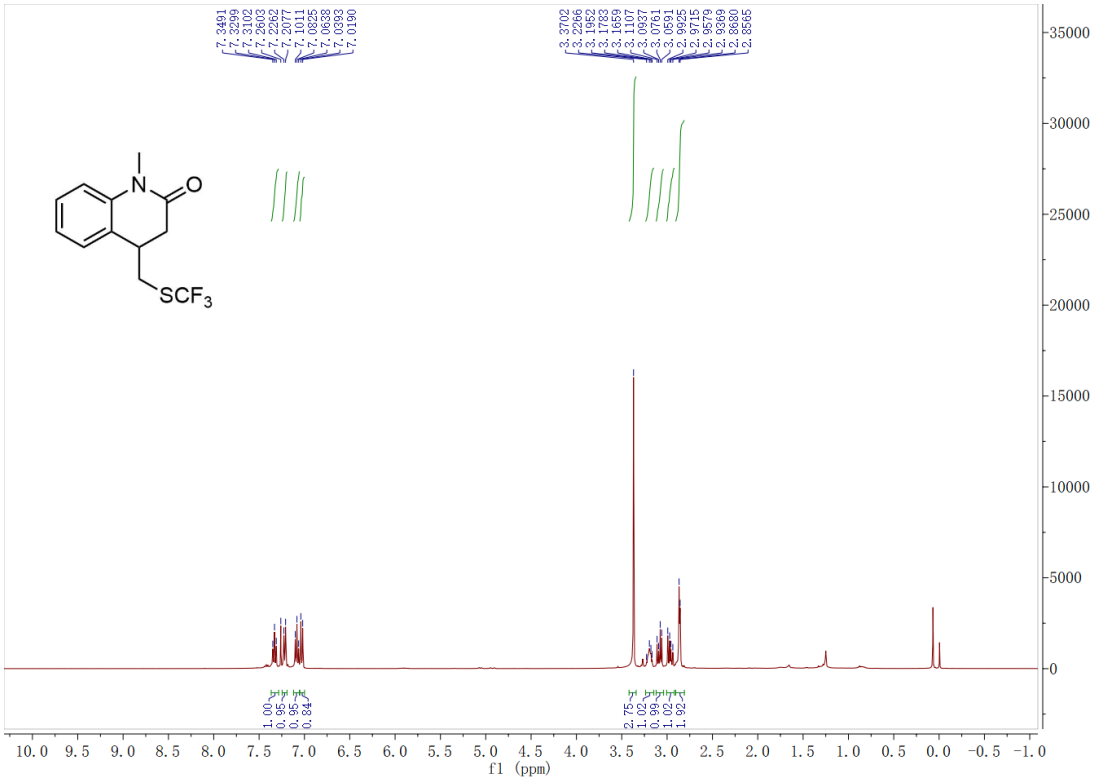


^{19}F NMR (376 MHz, $CDCl_3$)

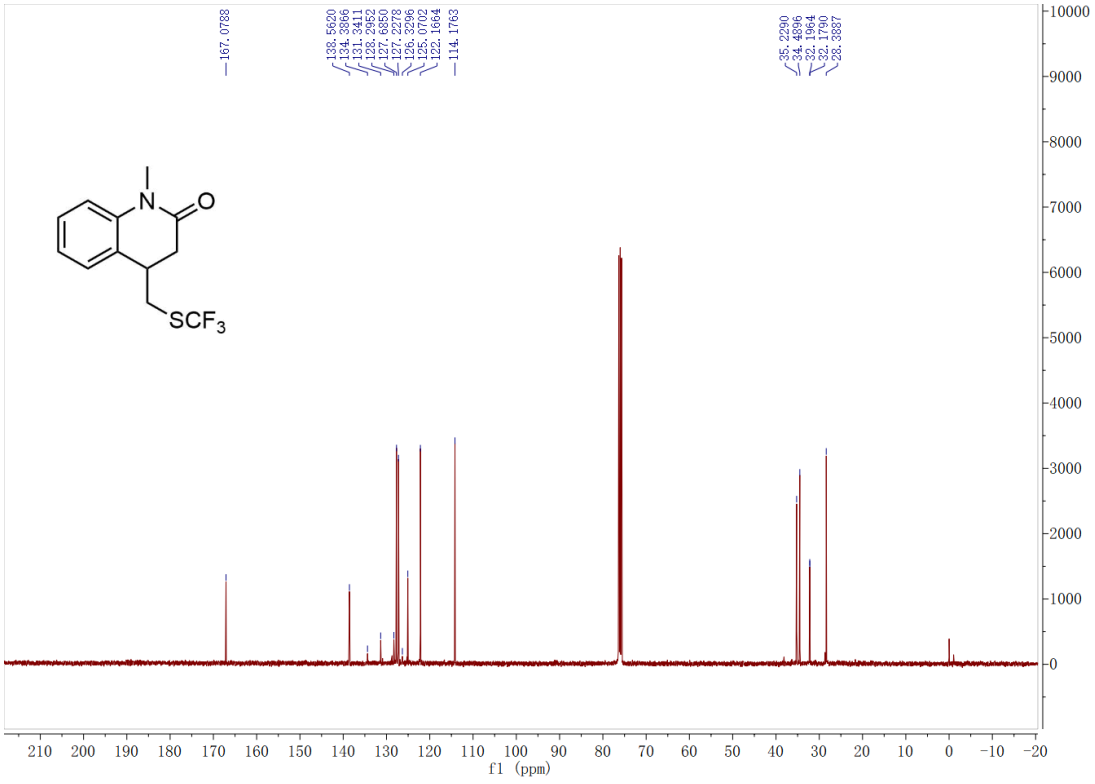


1-Methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3a)

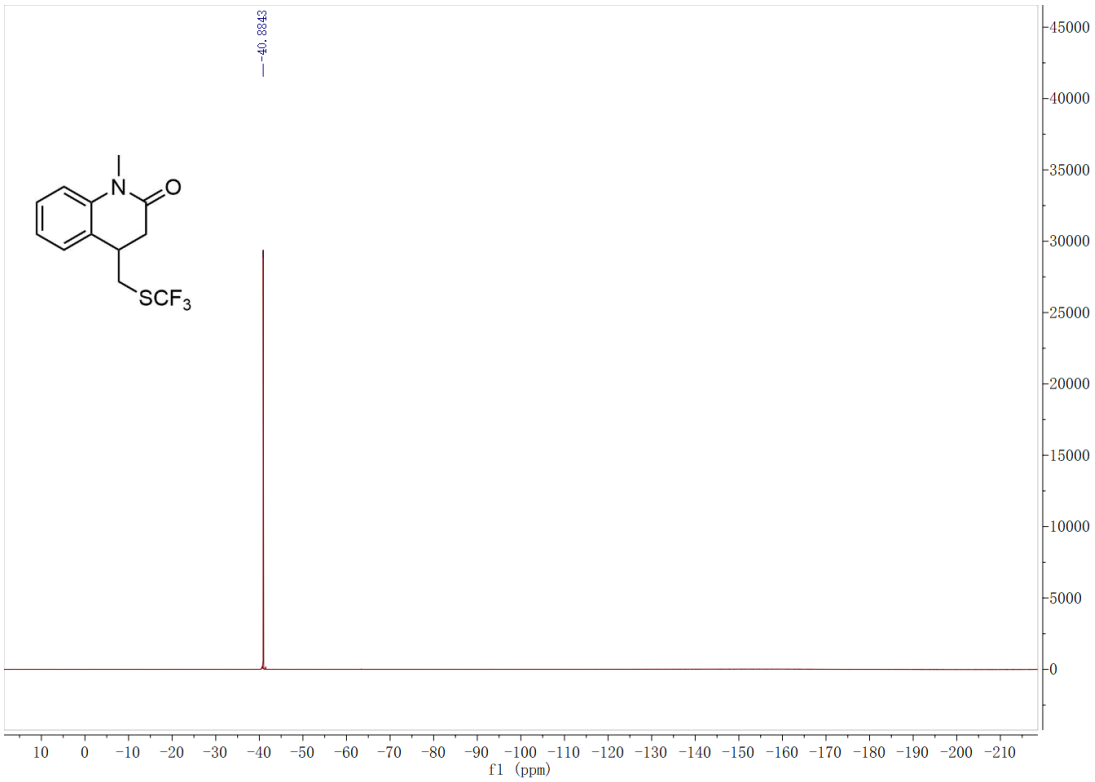
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

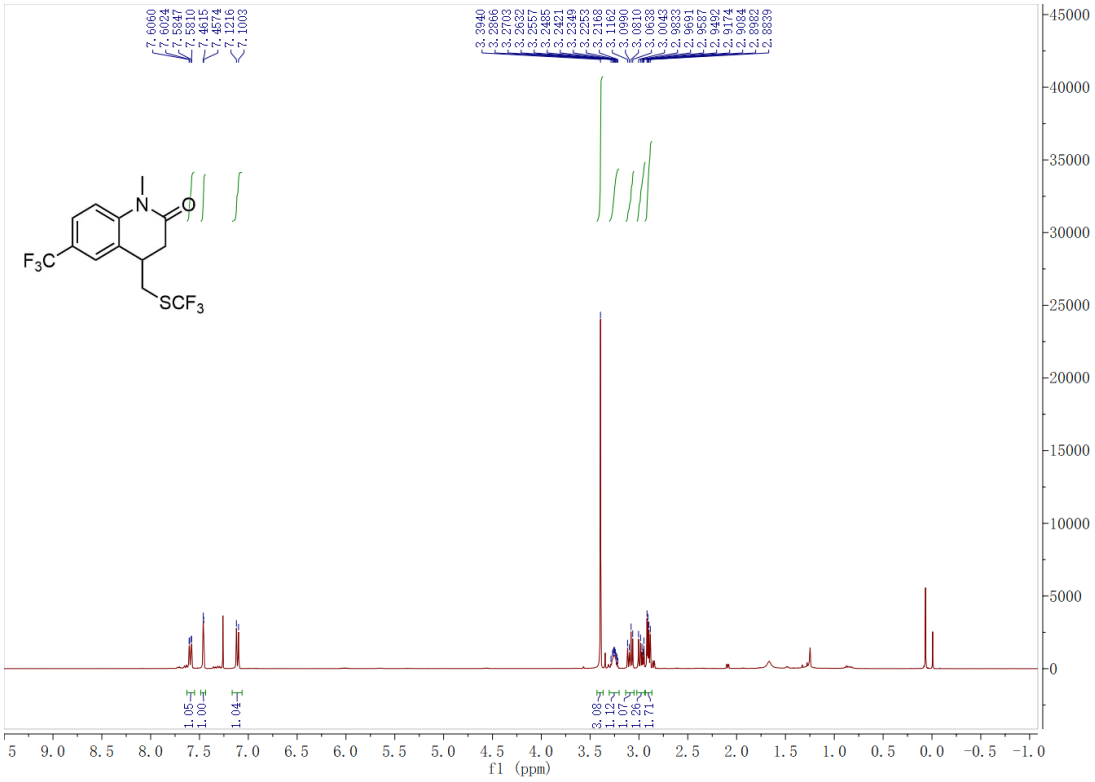


^{19}F NMR (376 MHz, $CDCl_3$)

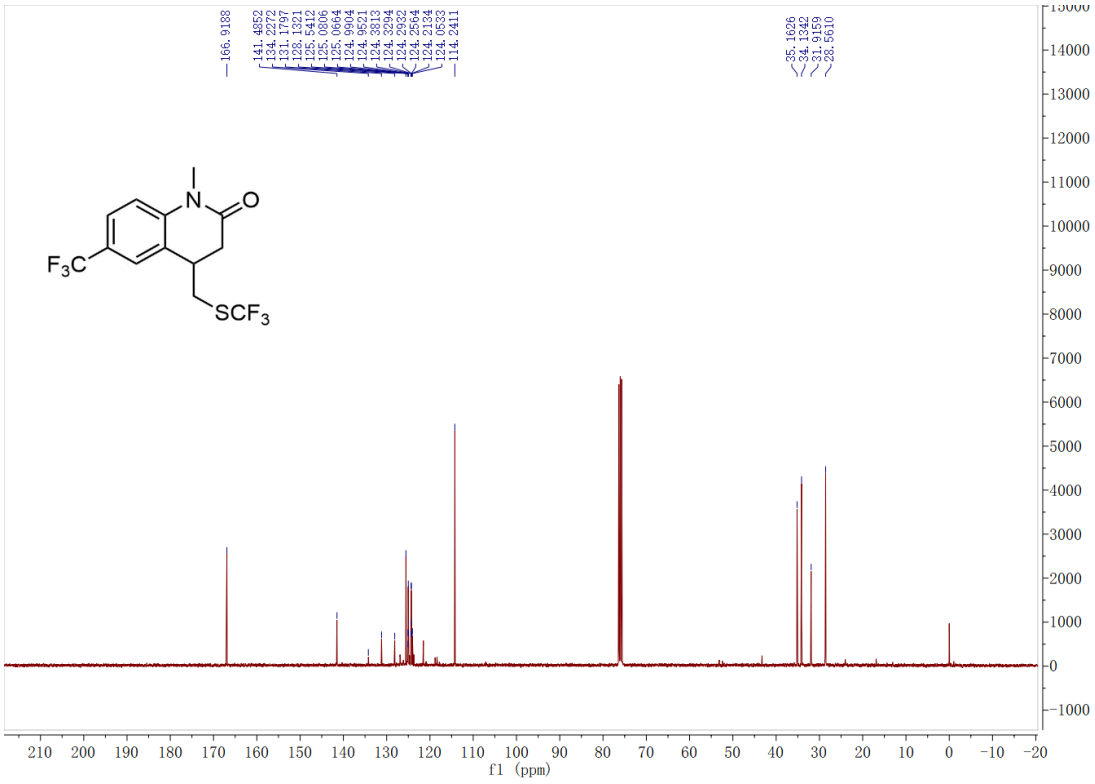


1-Methyl-6-(trifluoromethyl)-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3b)

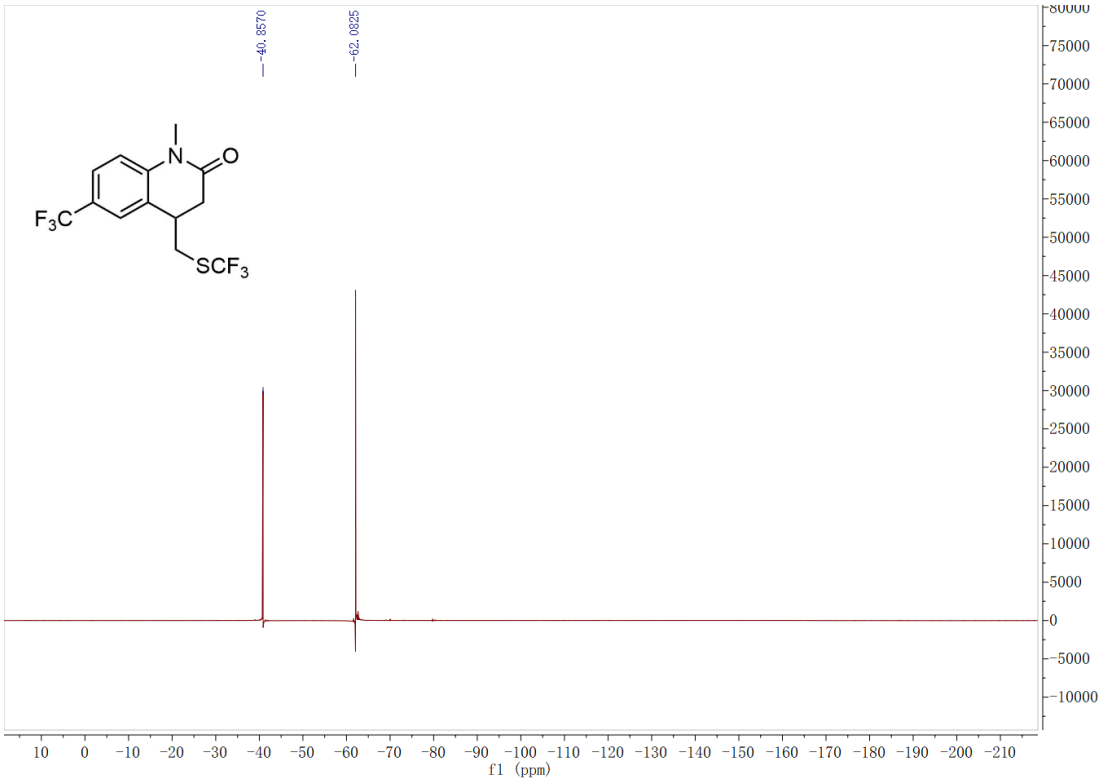
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

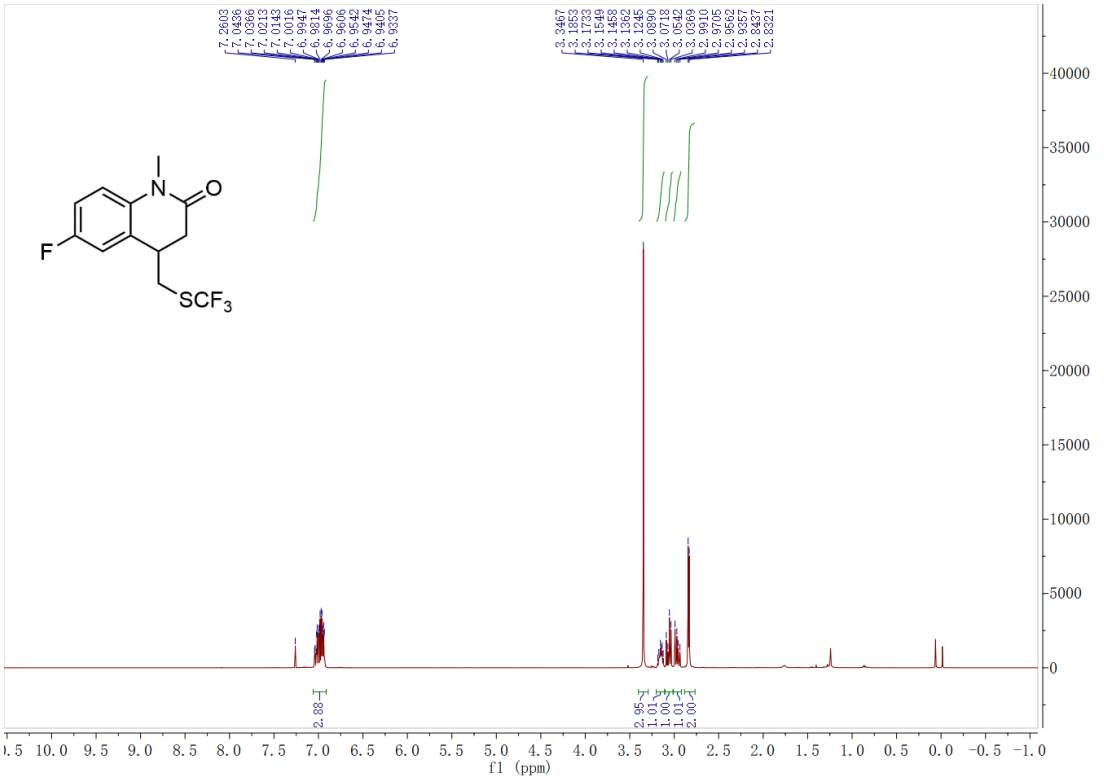


^{19}F NMR (376 MHz, $CDCl_3$)

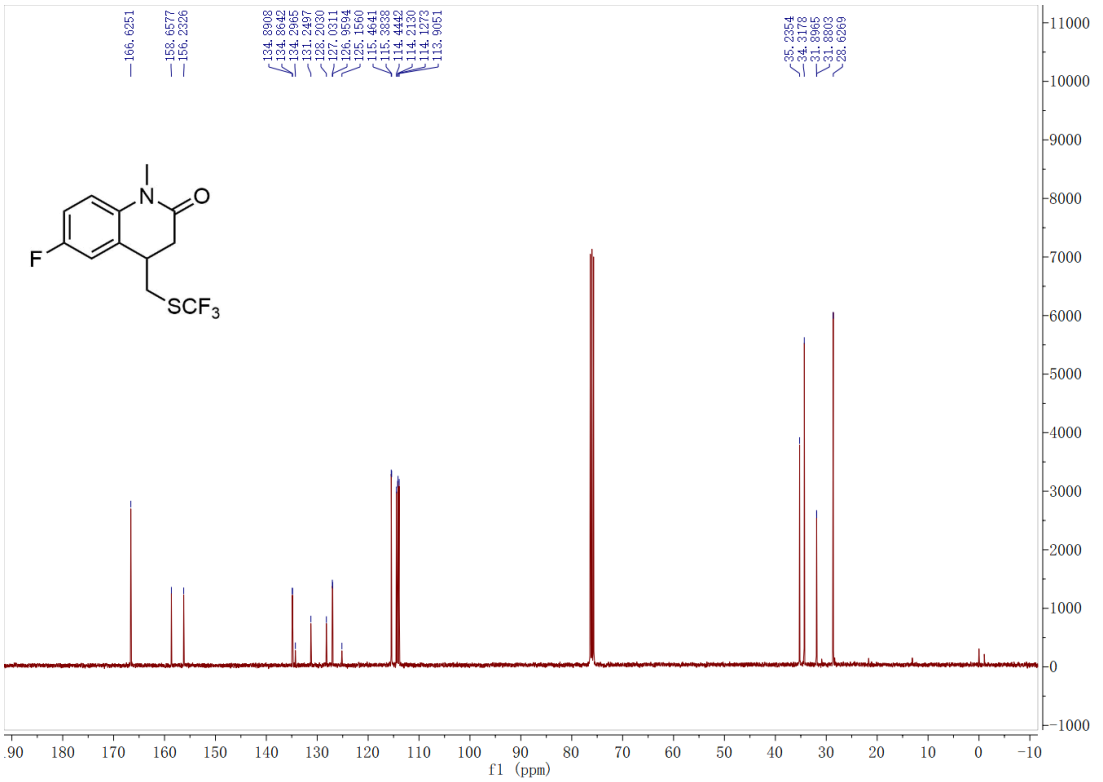


6-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3c)

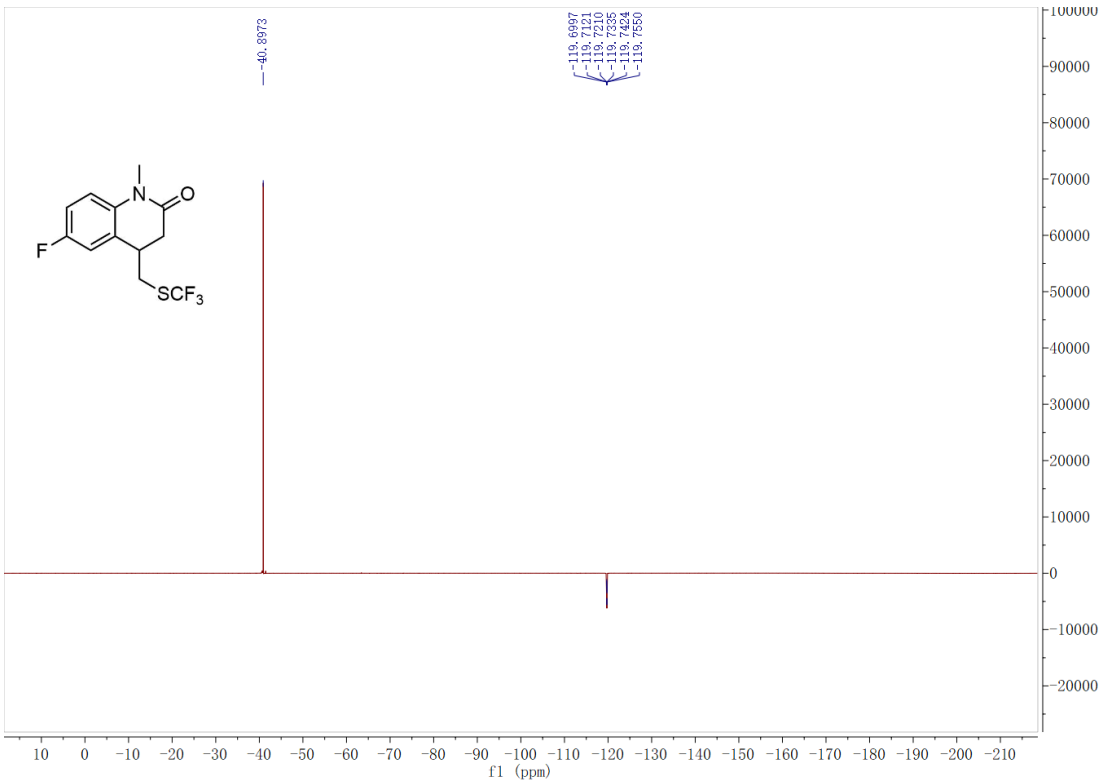
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

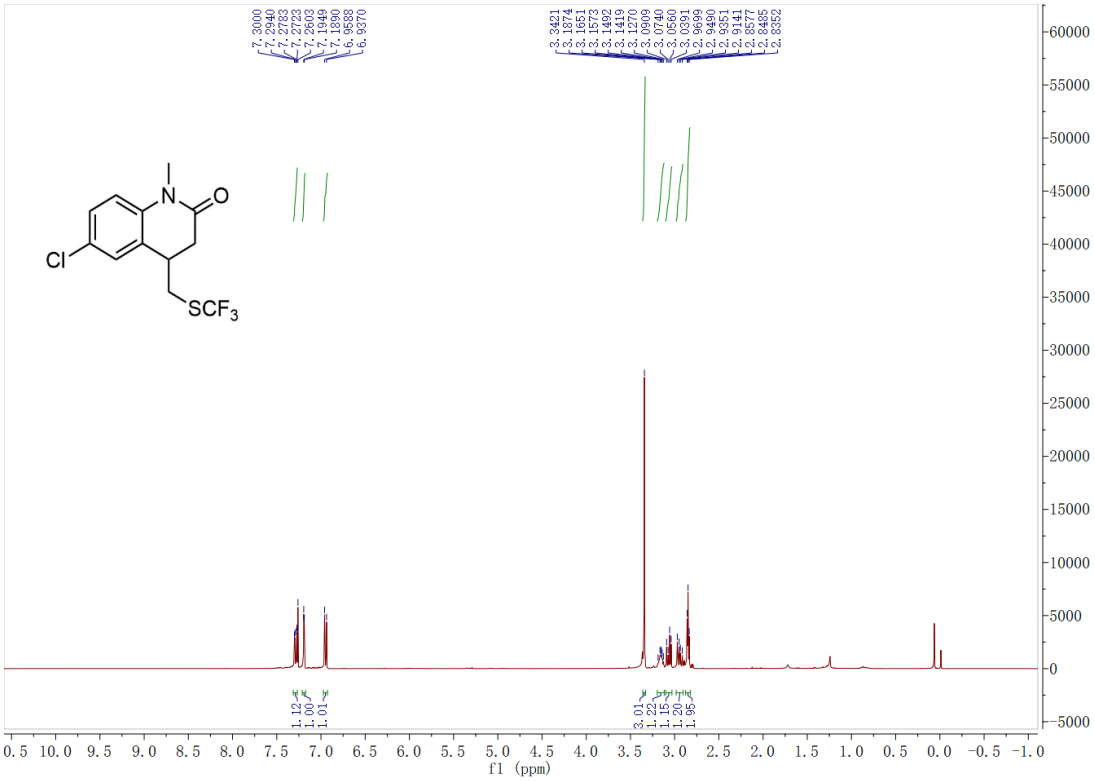


^{19}F NMR (376 MHz, $CDCl_3$)

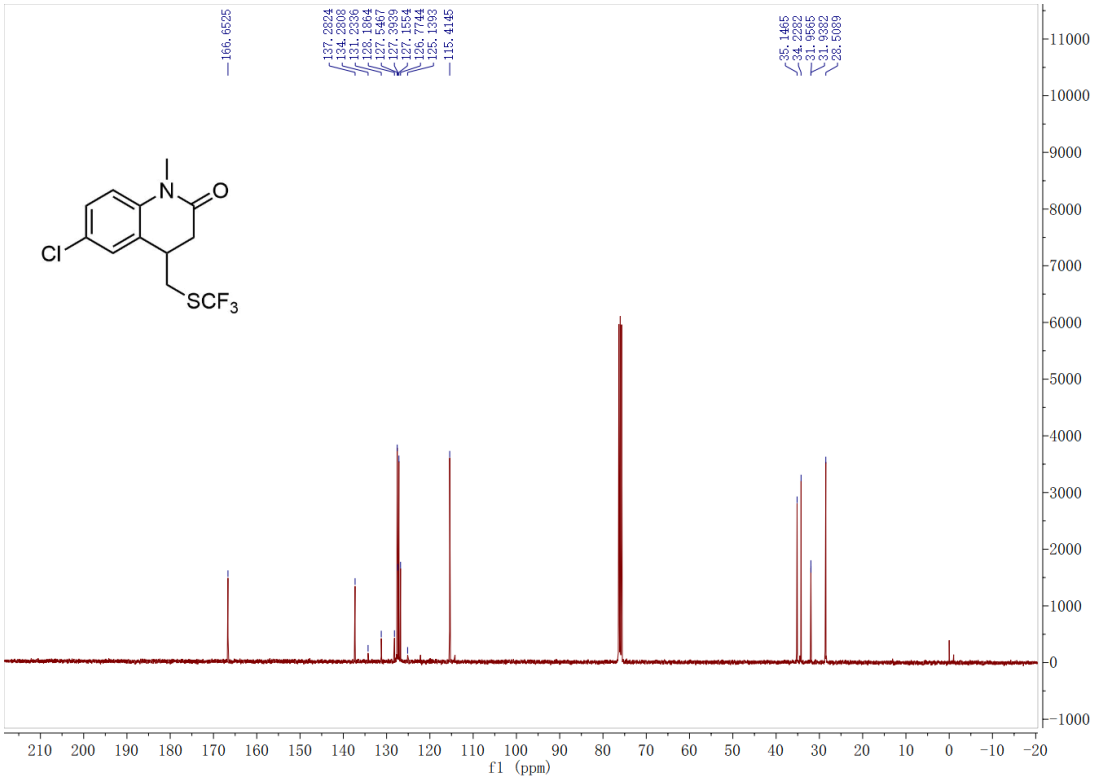


6-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3d)

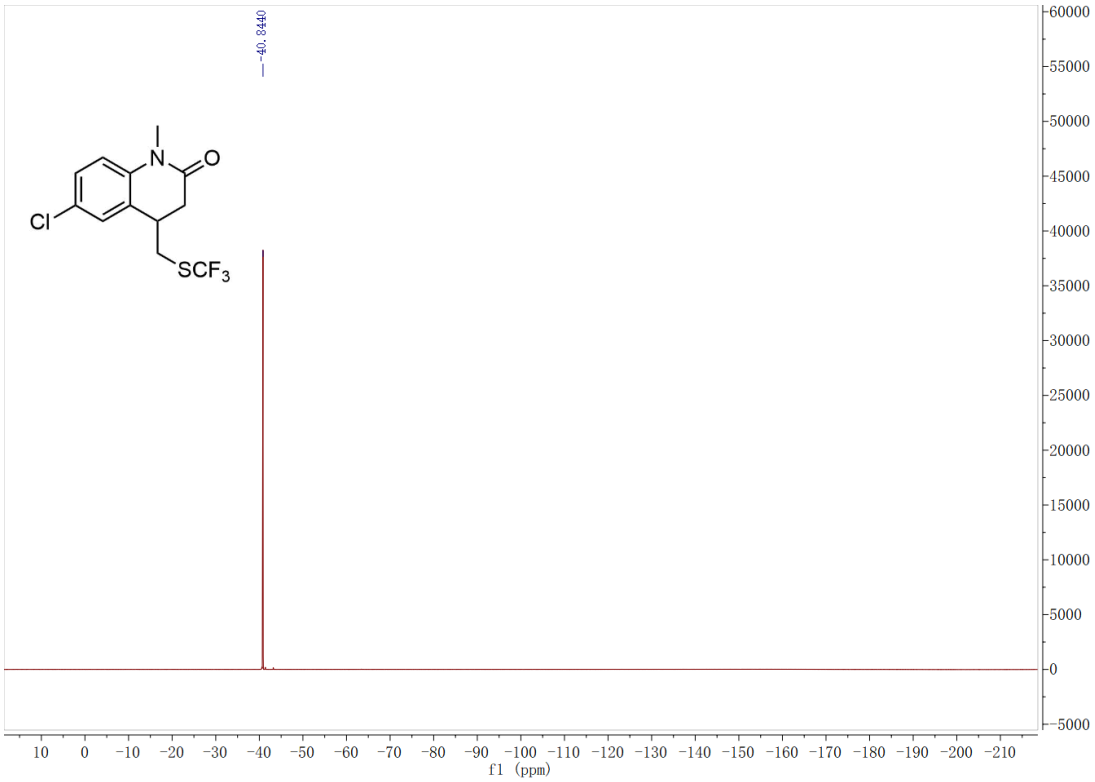
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

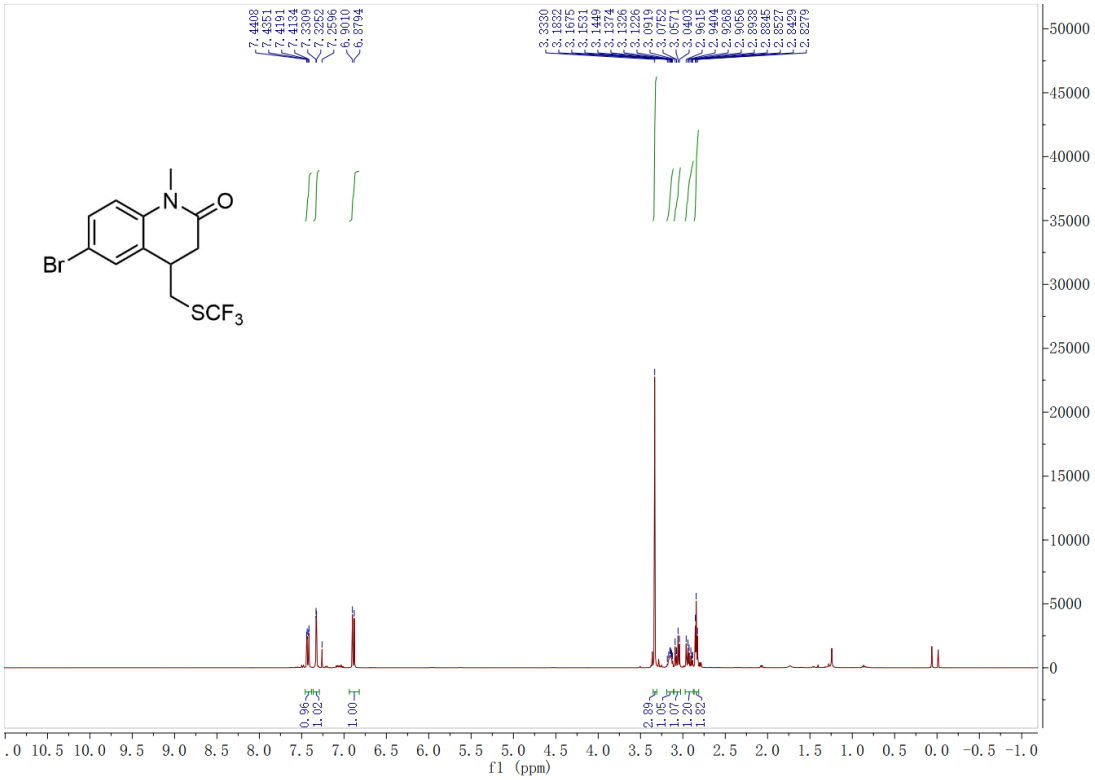


^{19}F NMR (376 MHz, $CDCl_3$)

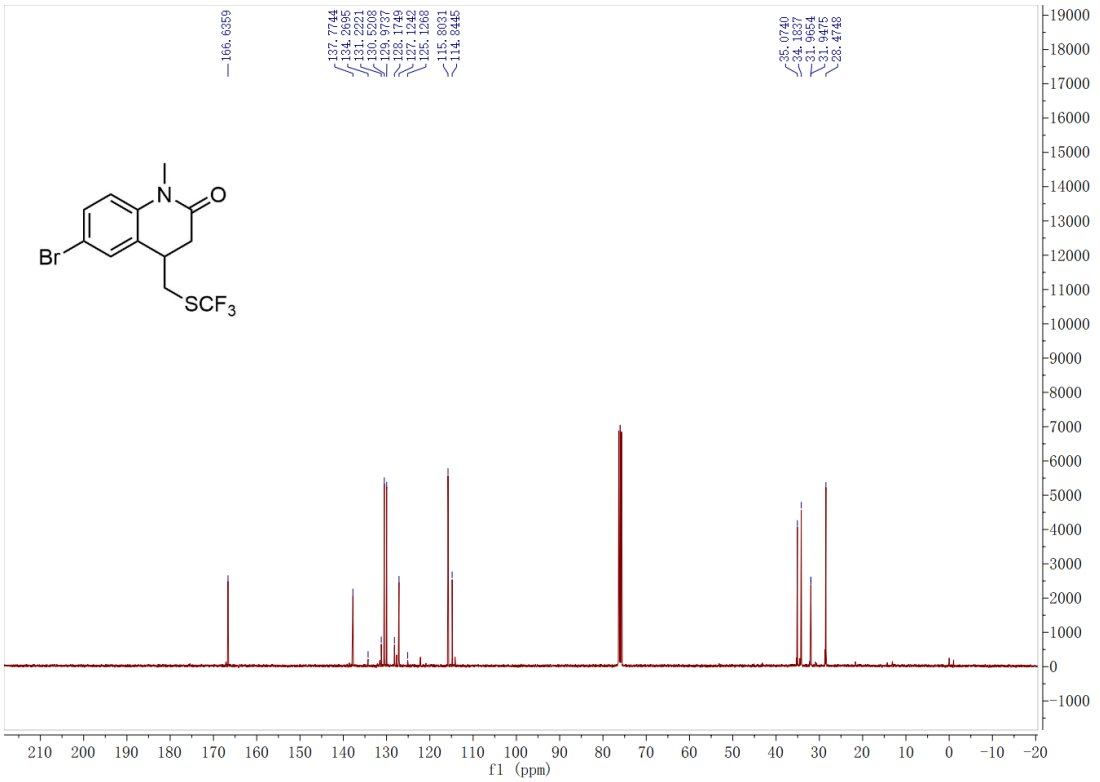


6-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3e)

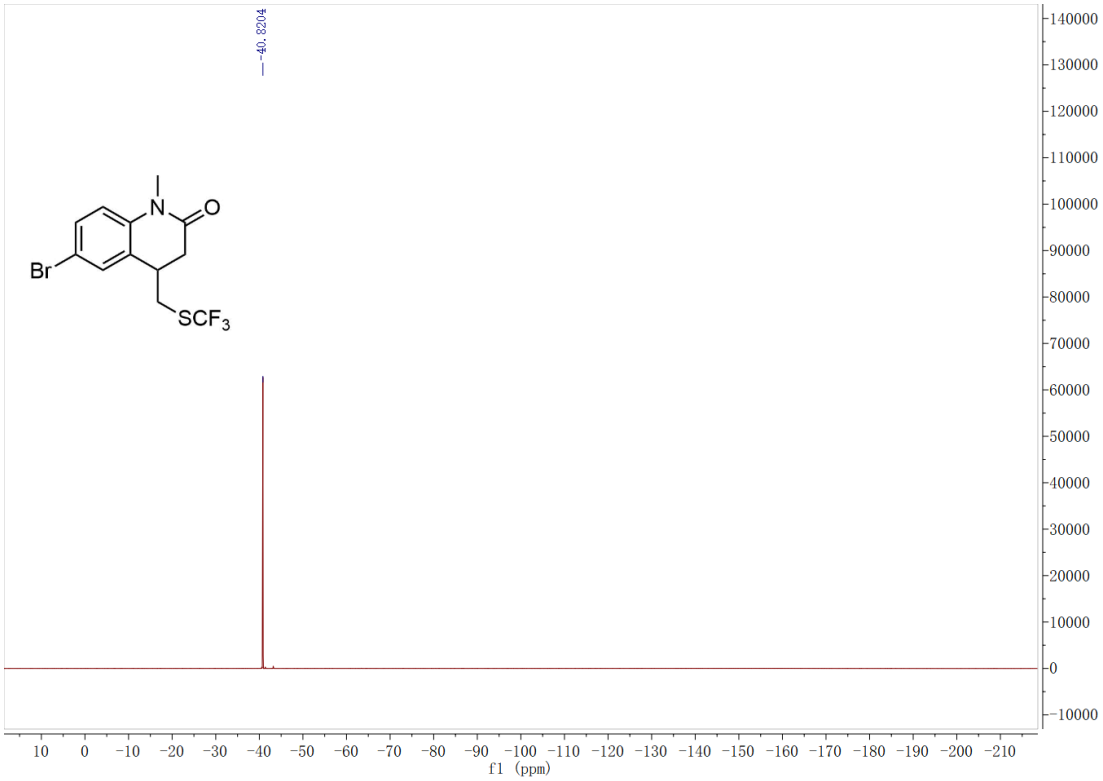
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

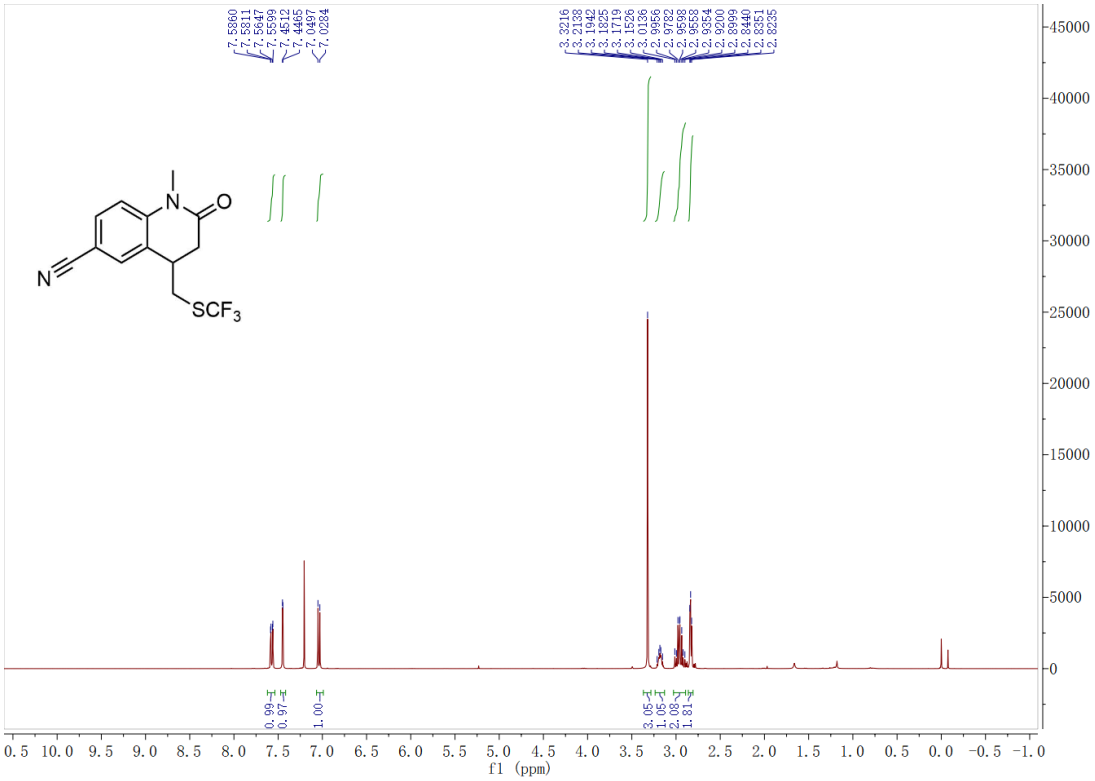


^{19}F NMR (376 MHz, $CDCl_3$)

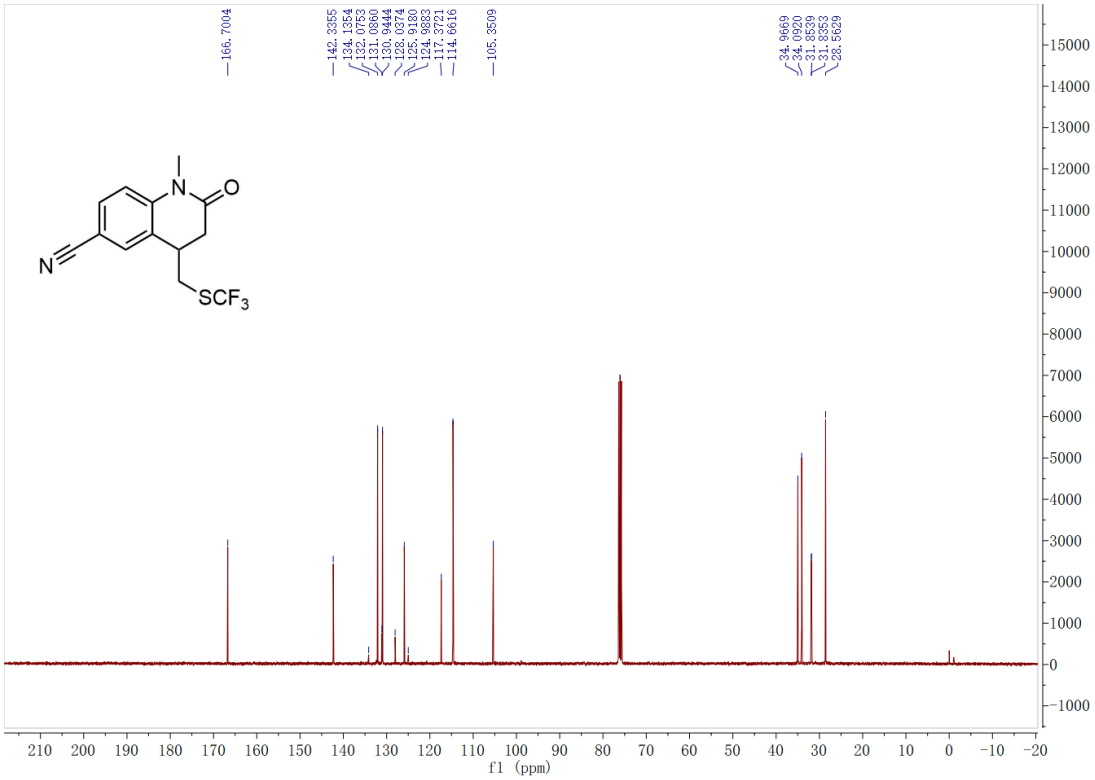


1-Methyl-2-oxo-4-(((trifluoromethyl)thio)methyl)-1,2,3,4-tetrahydroquinoline-6-carbonitrile (3f)

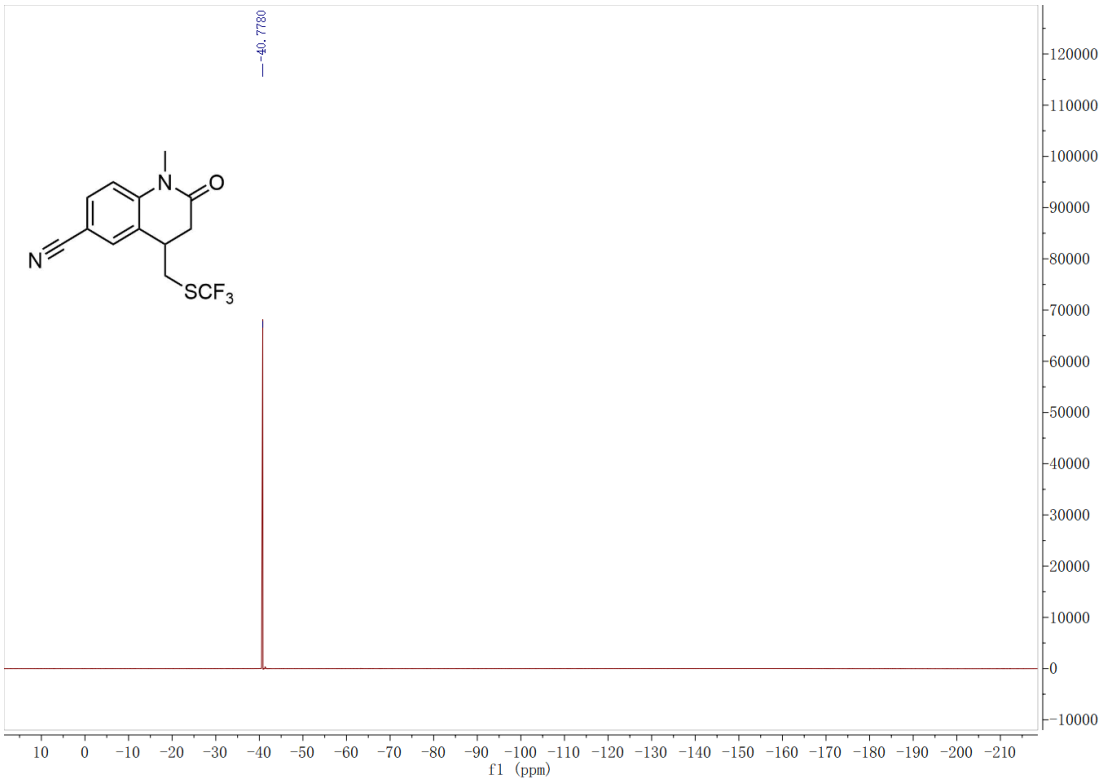
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

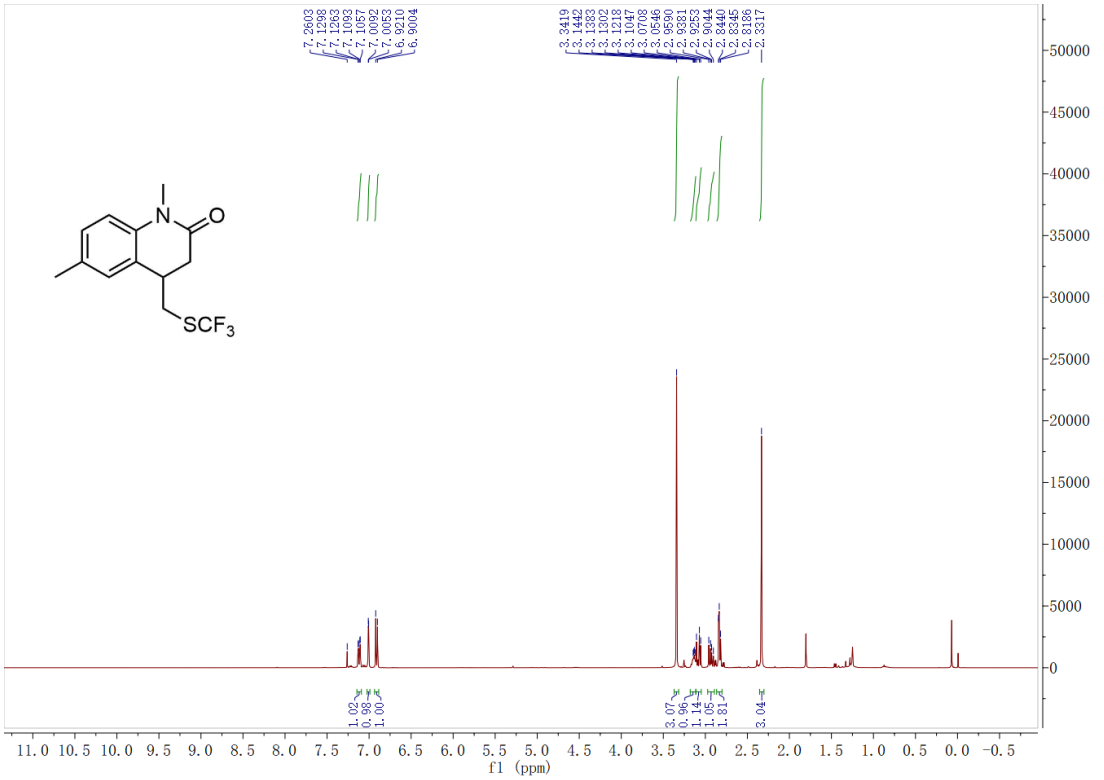


^{19}F NMR (376 MHz, $CDCl_3$)

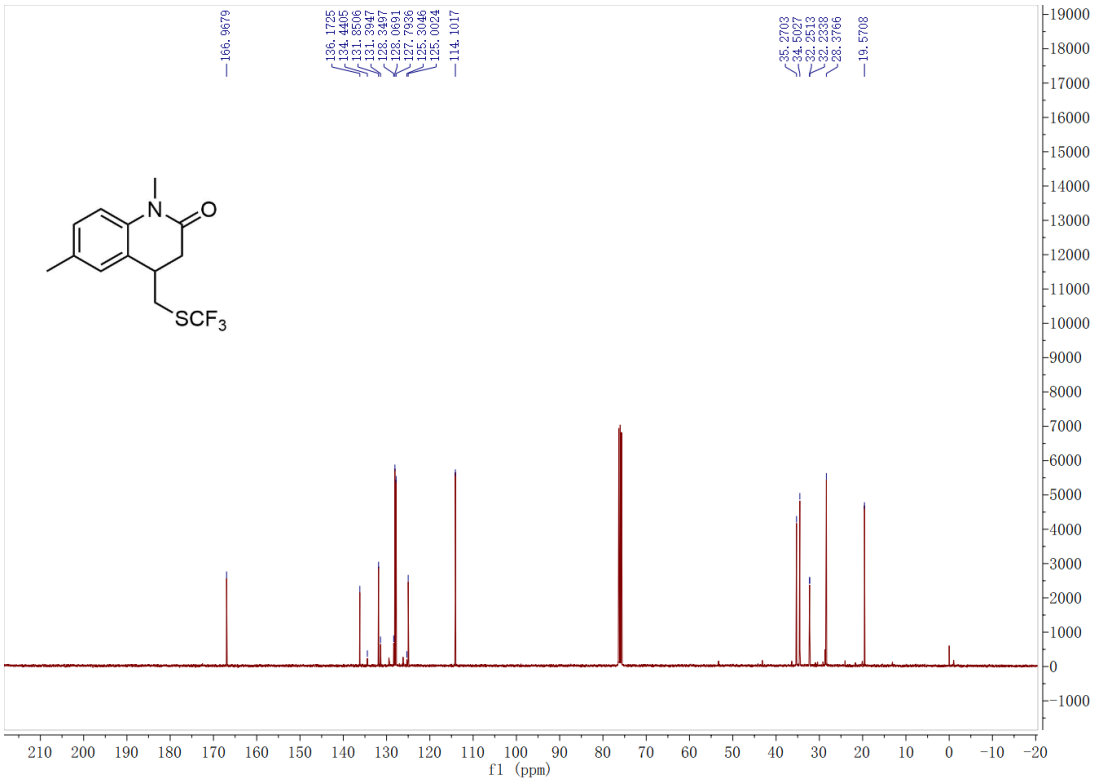


1,6-Dimethyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3g)

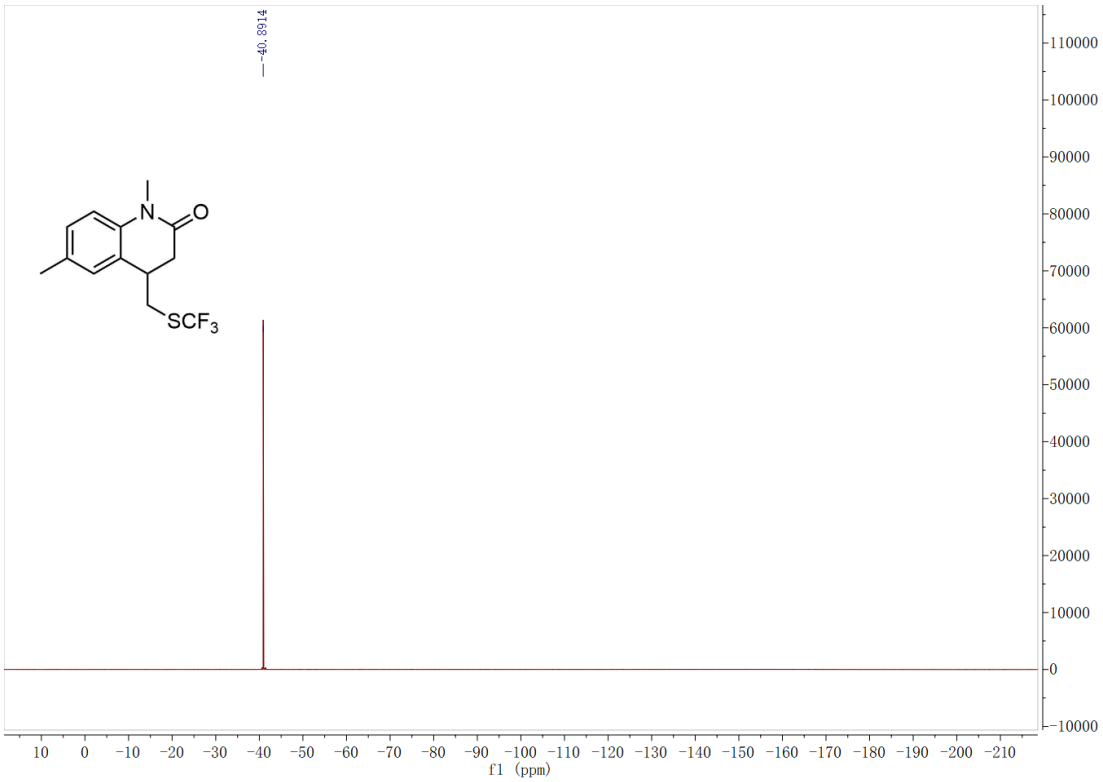
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

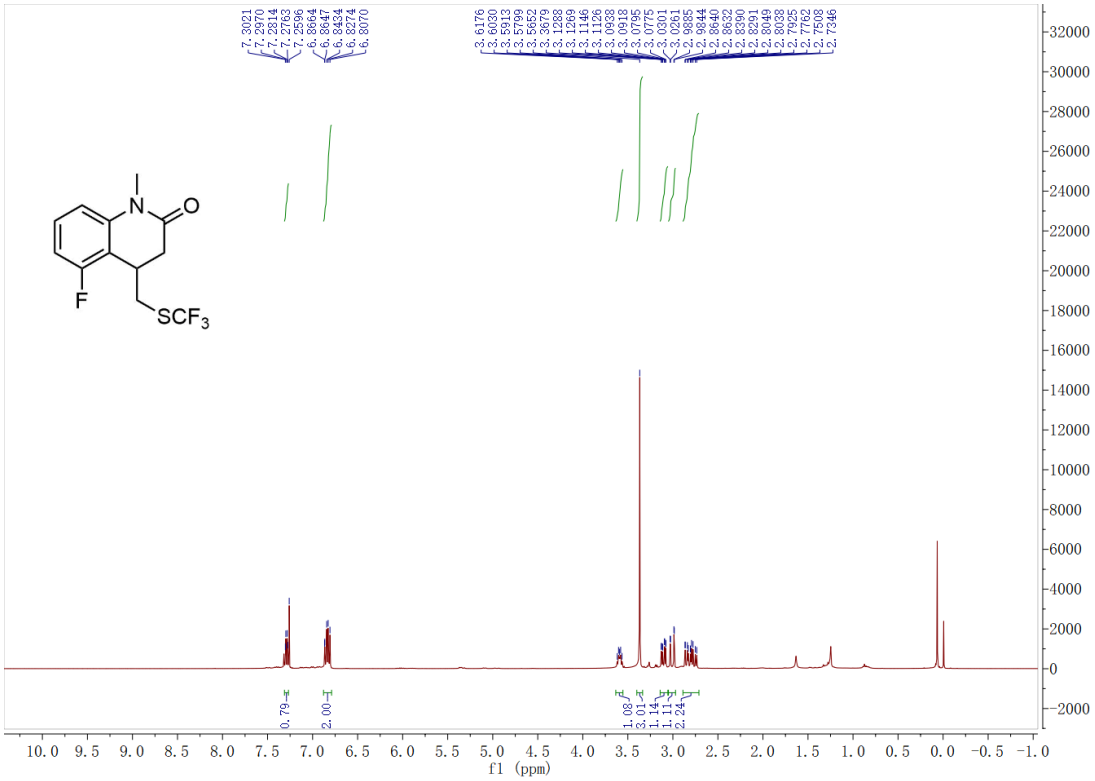


^{19}F NMR (376 MHz, $CDCl_3$)

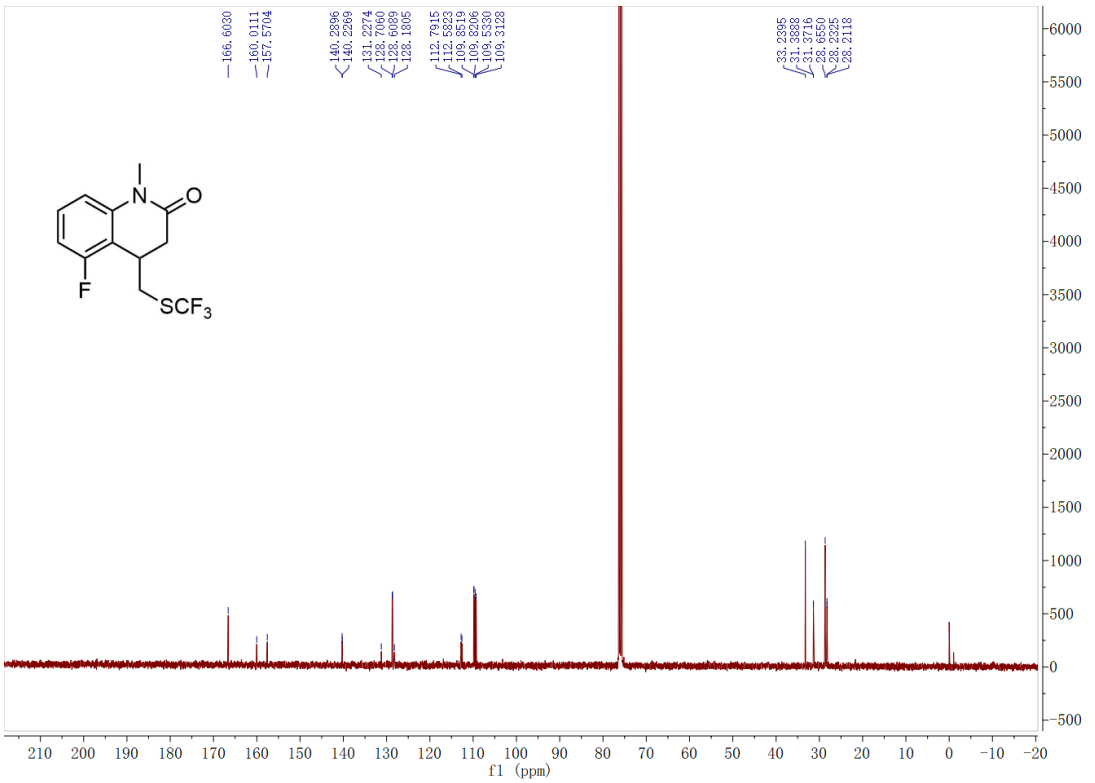


5-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3h)

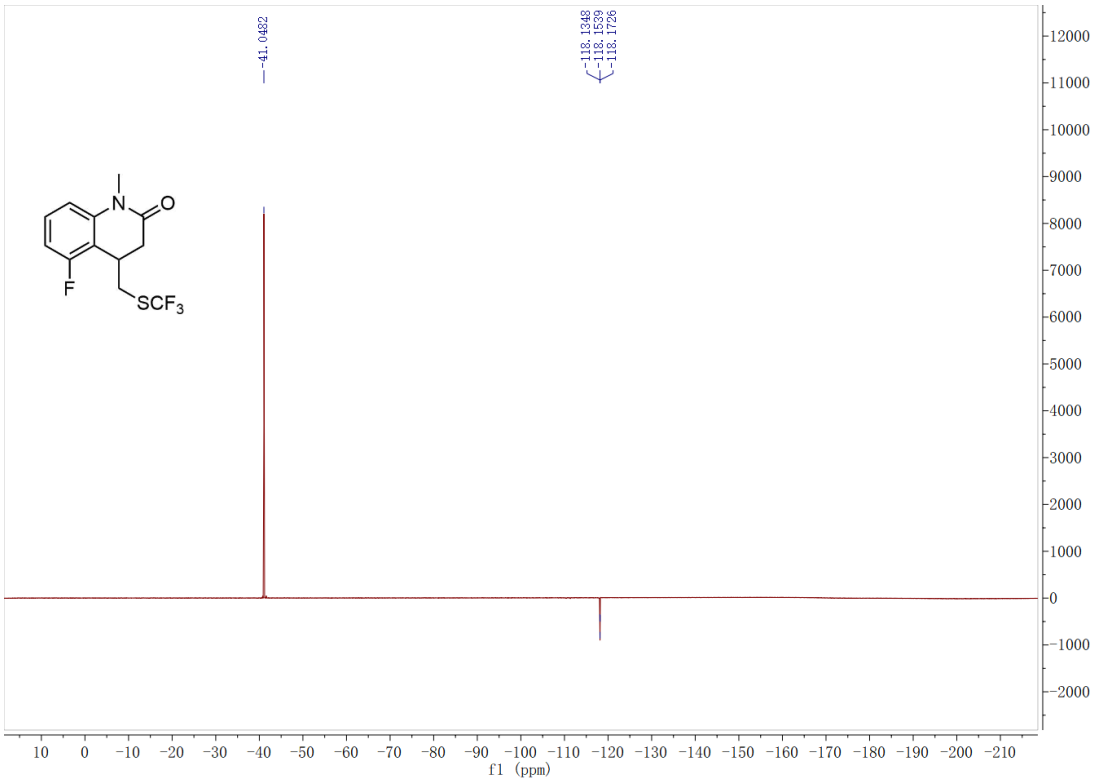
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

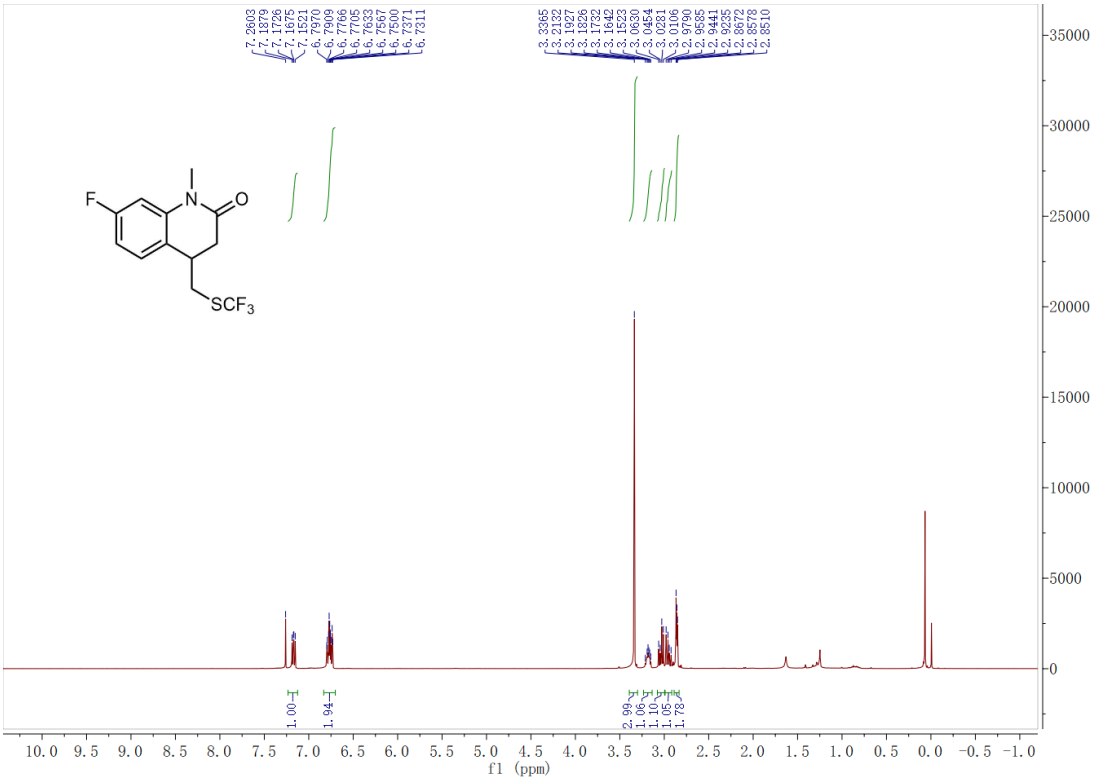


^{19}F NMR (376 MHz, $CDCl_3$)

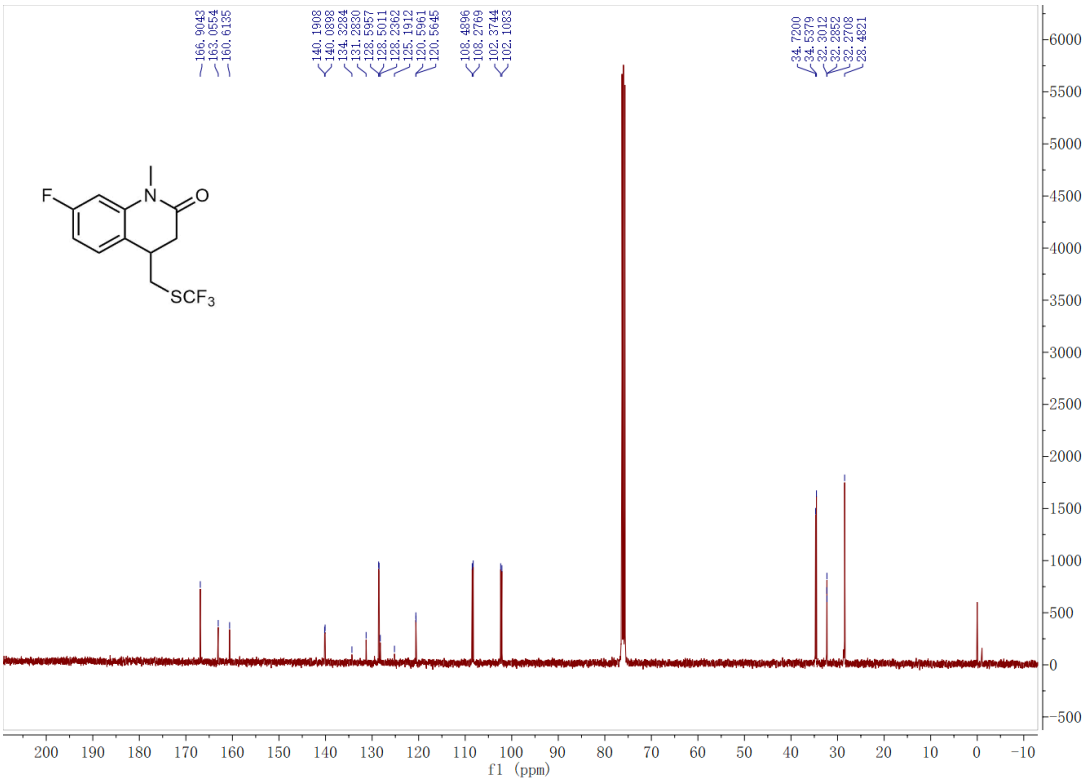


7-Fluoro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3h')

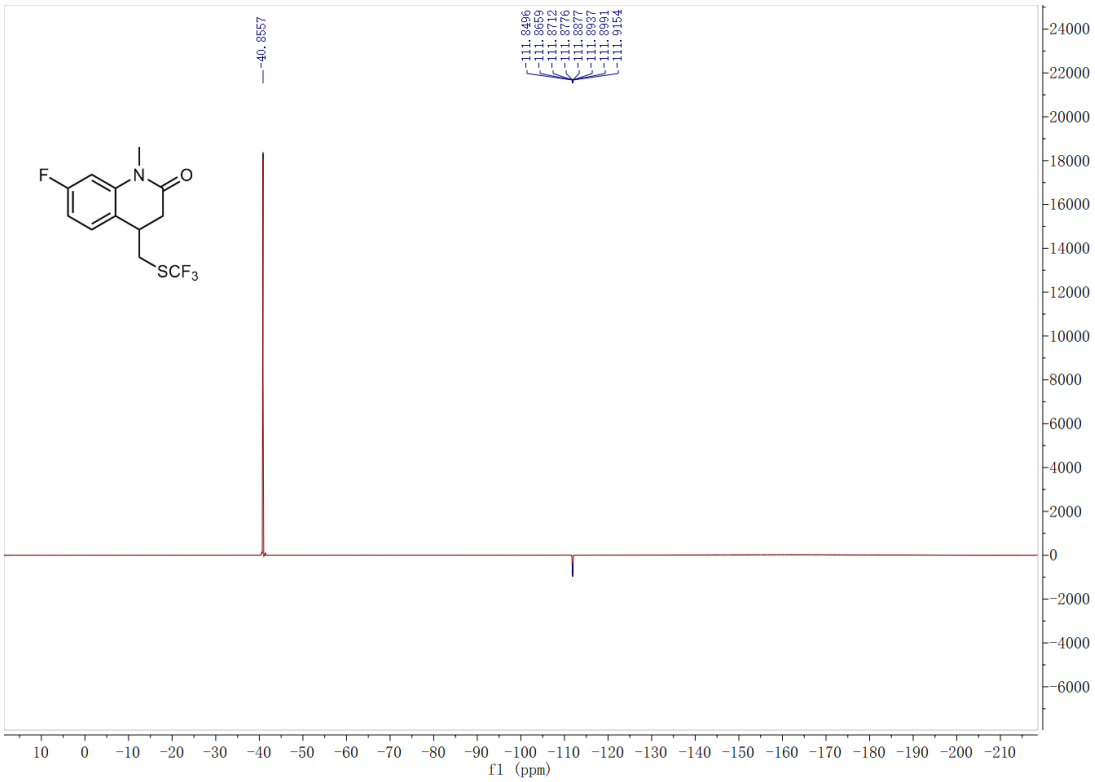
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

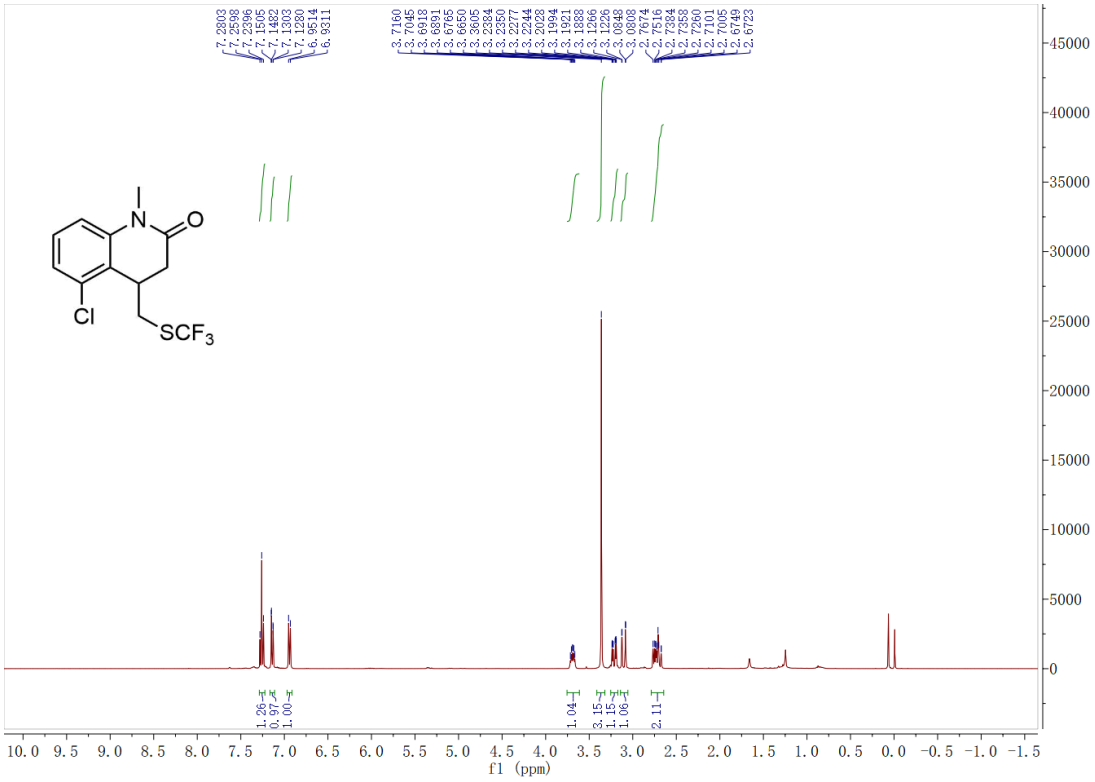


^{19}F NMR (376 MHz, $CDCl_3$)

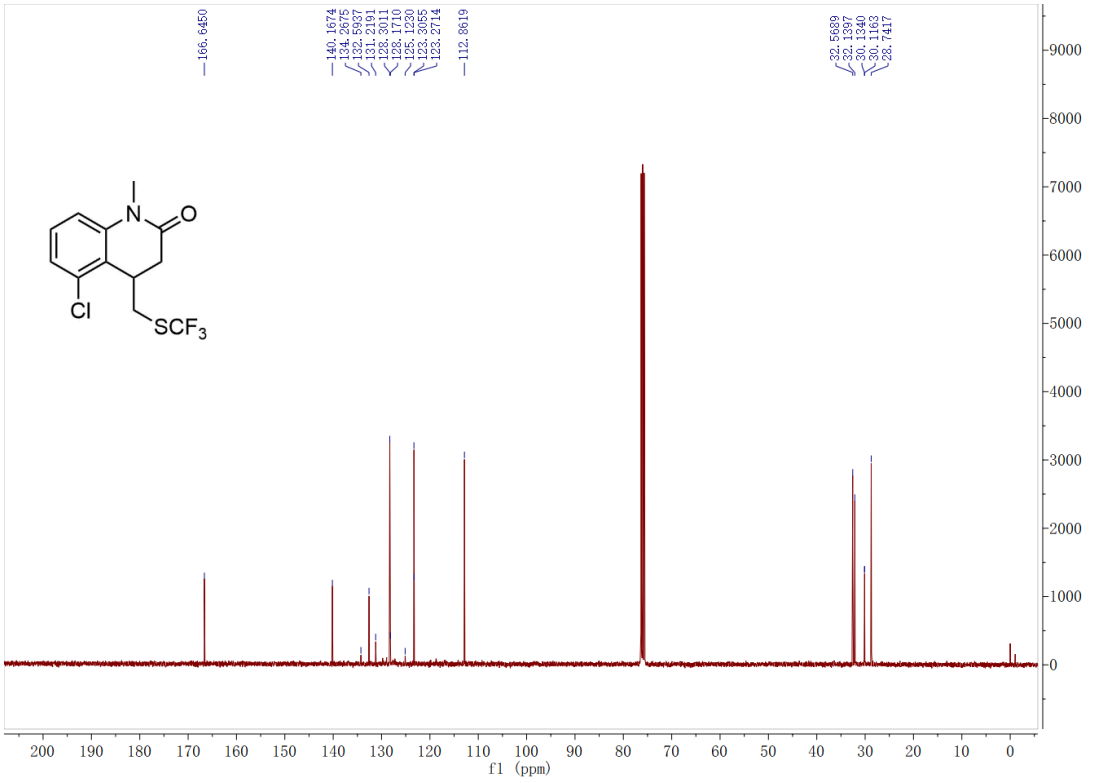


5-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3i)

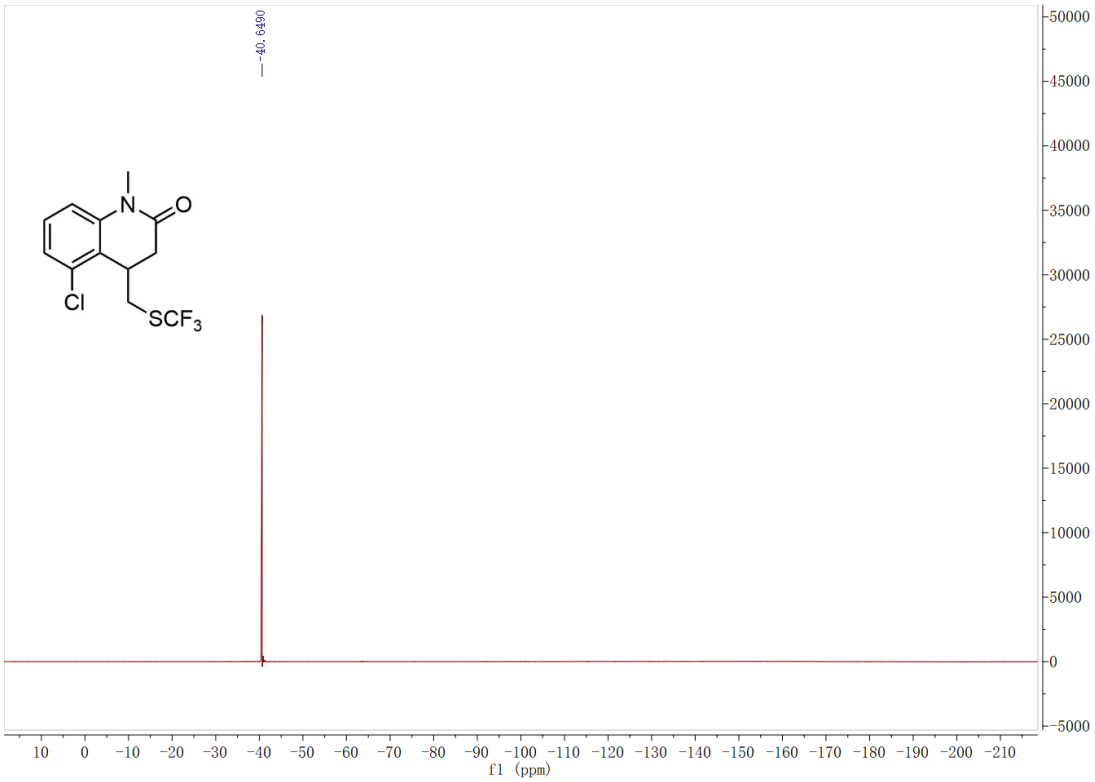
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

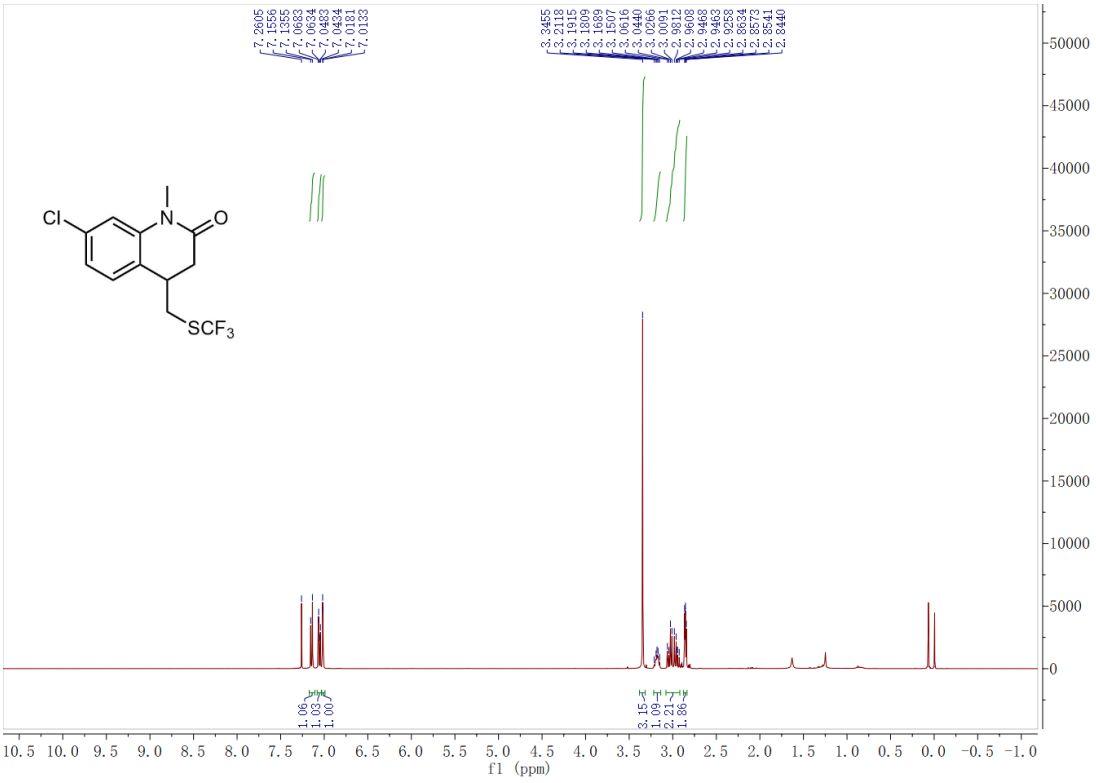


^{19}F NMR (376 MHz, $CDCl_3$)

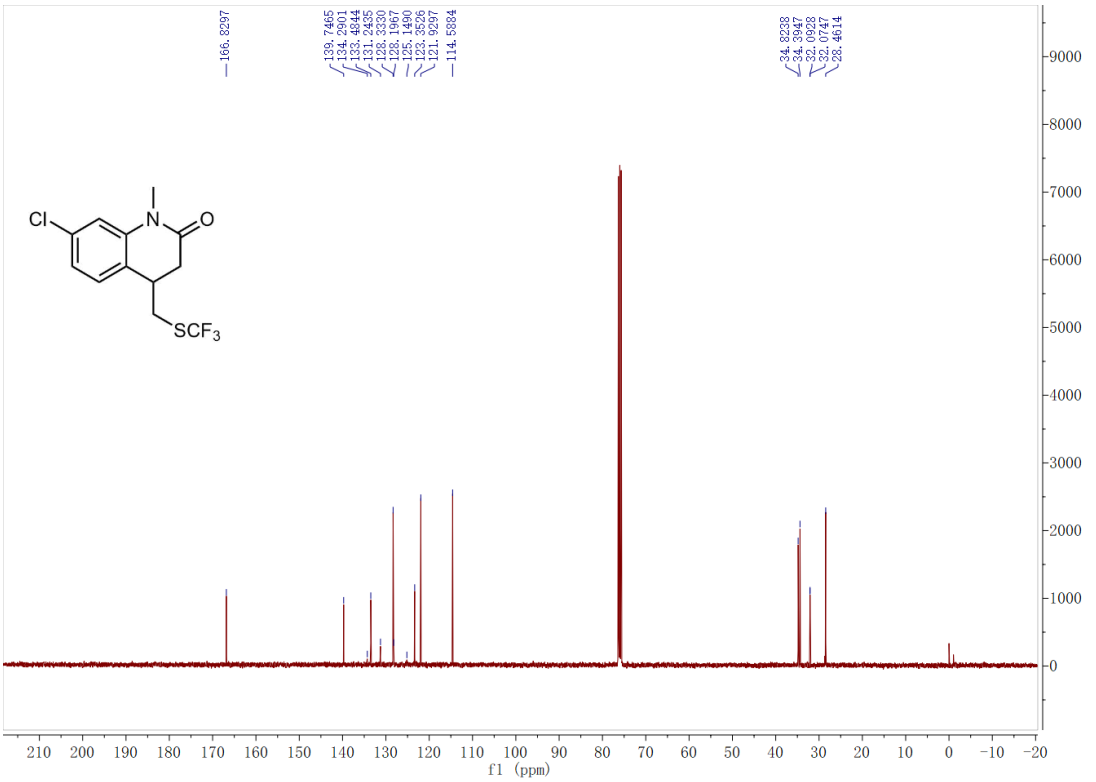


7-Chloro-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3i')

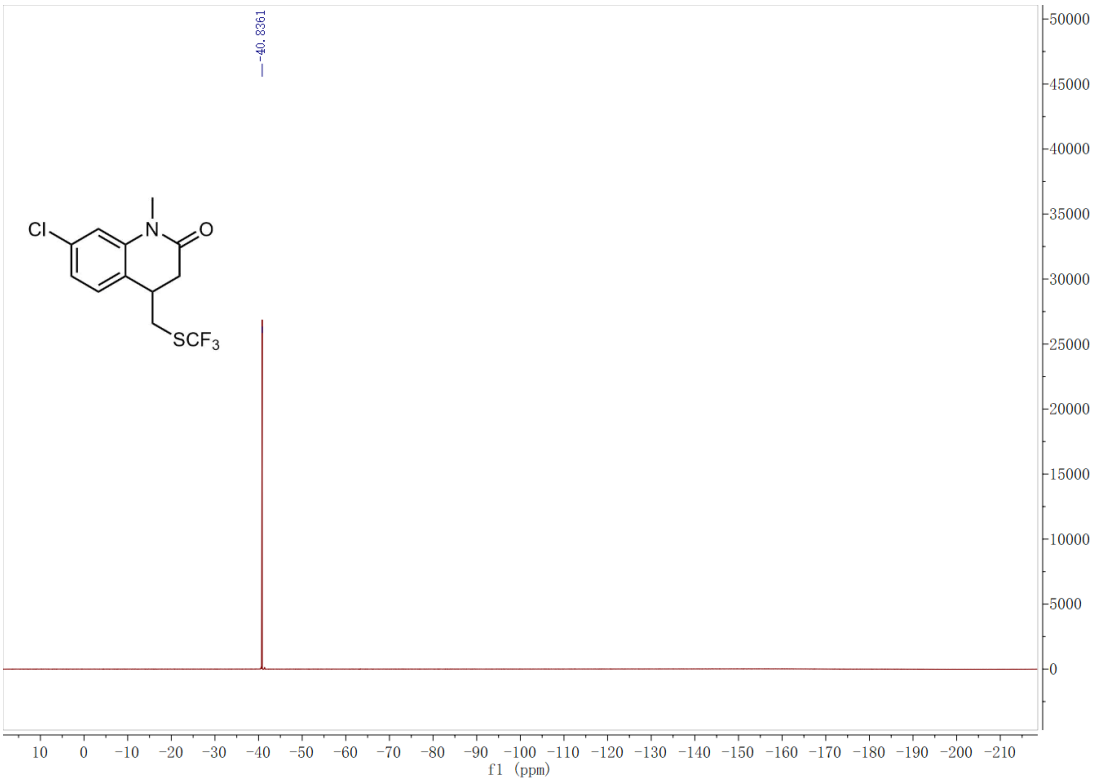
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

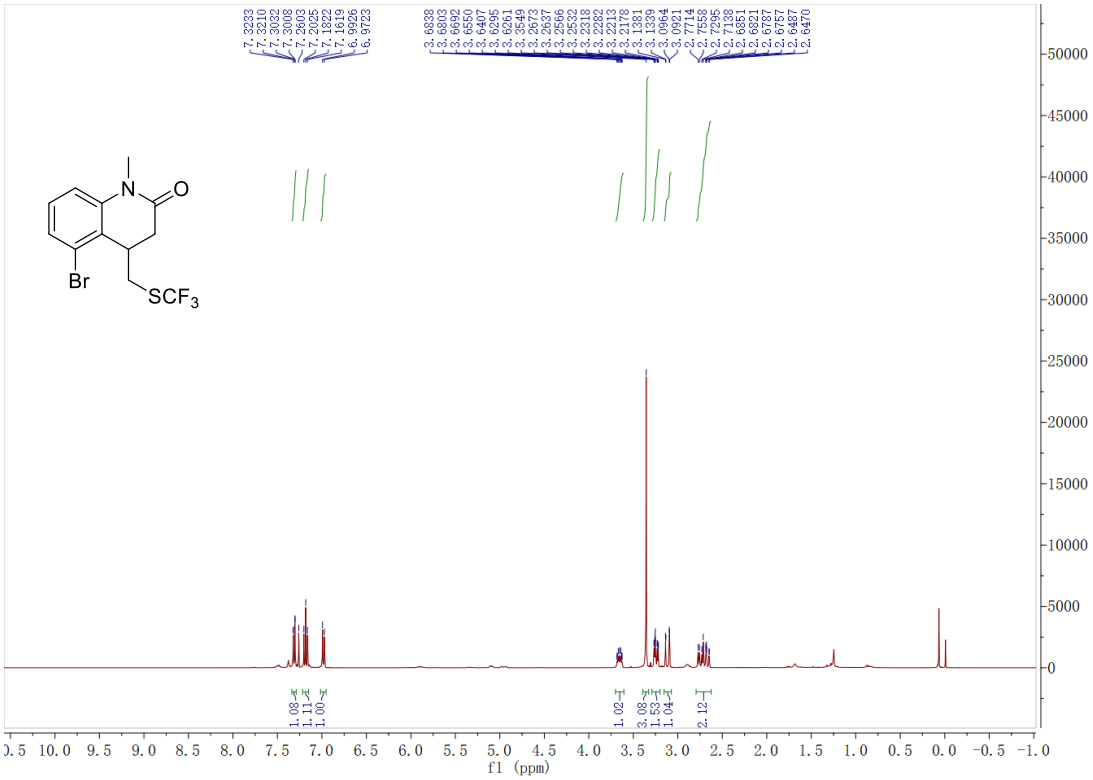


^{19}F NMR (376 MHz, $CDCl_3$)

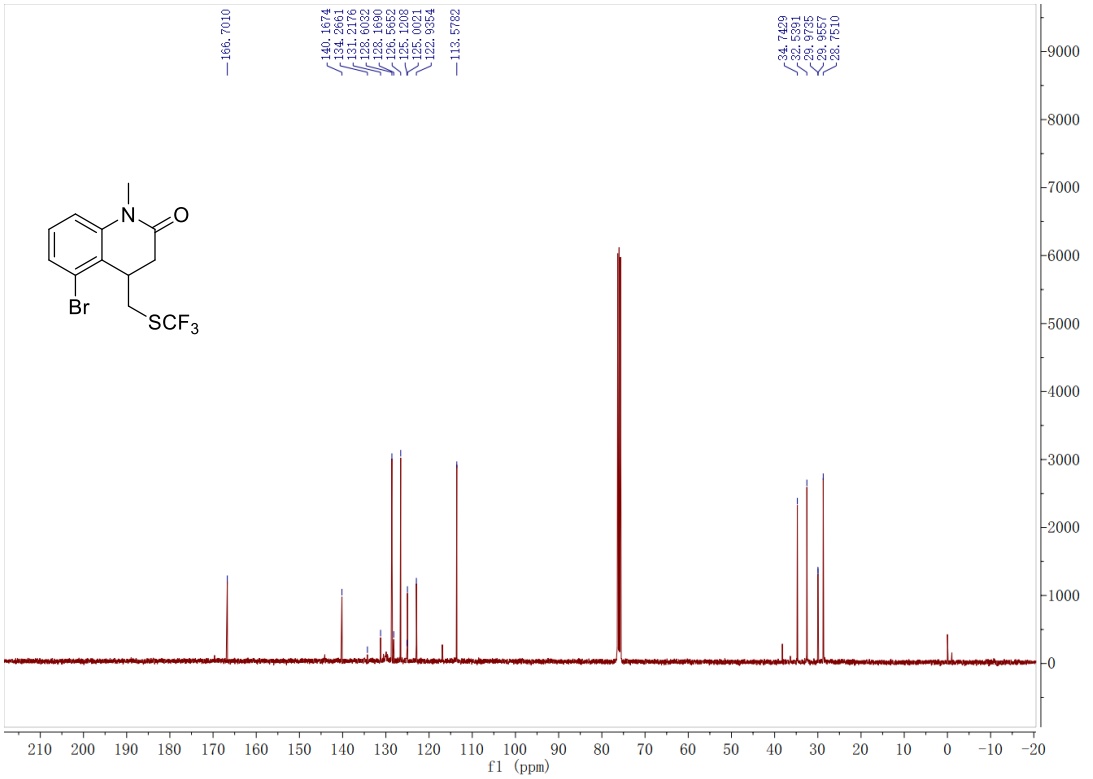


5-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3j)

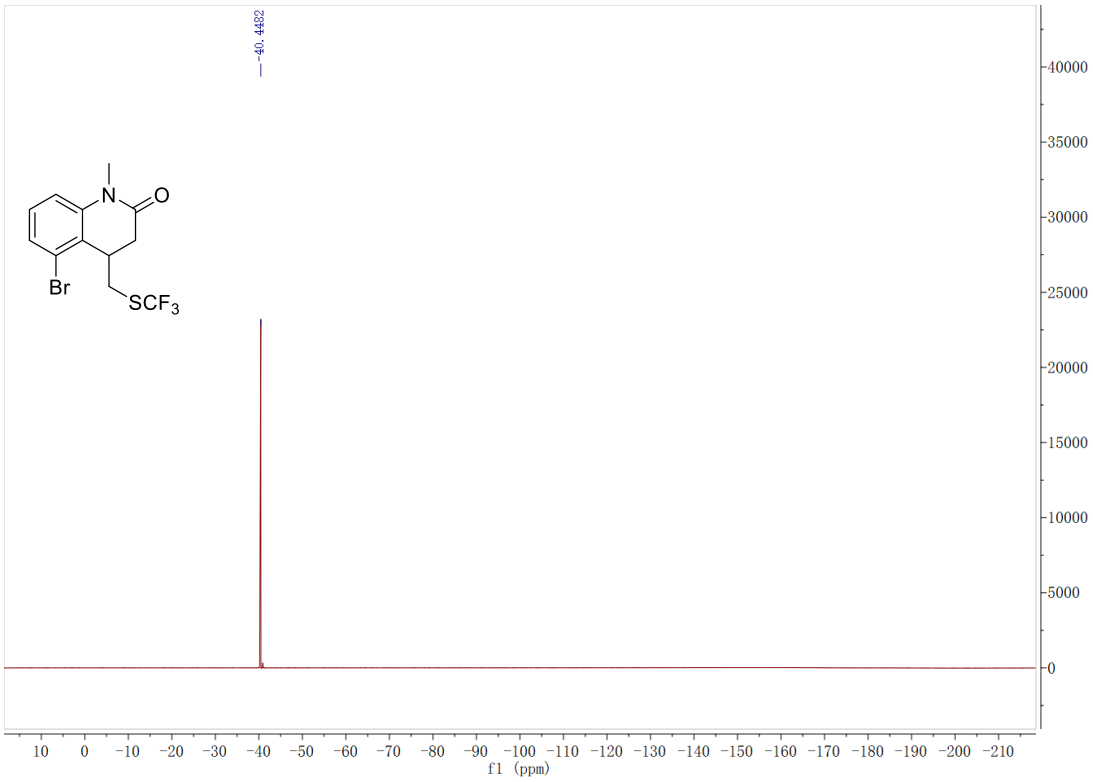
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

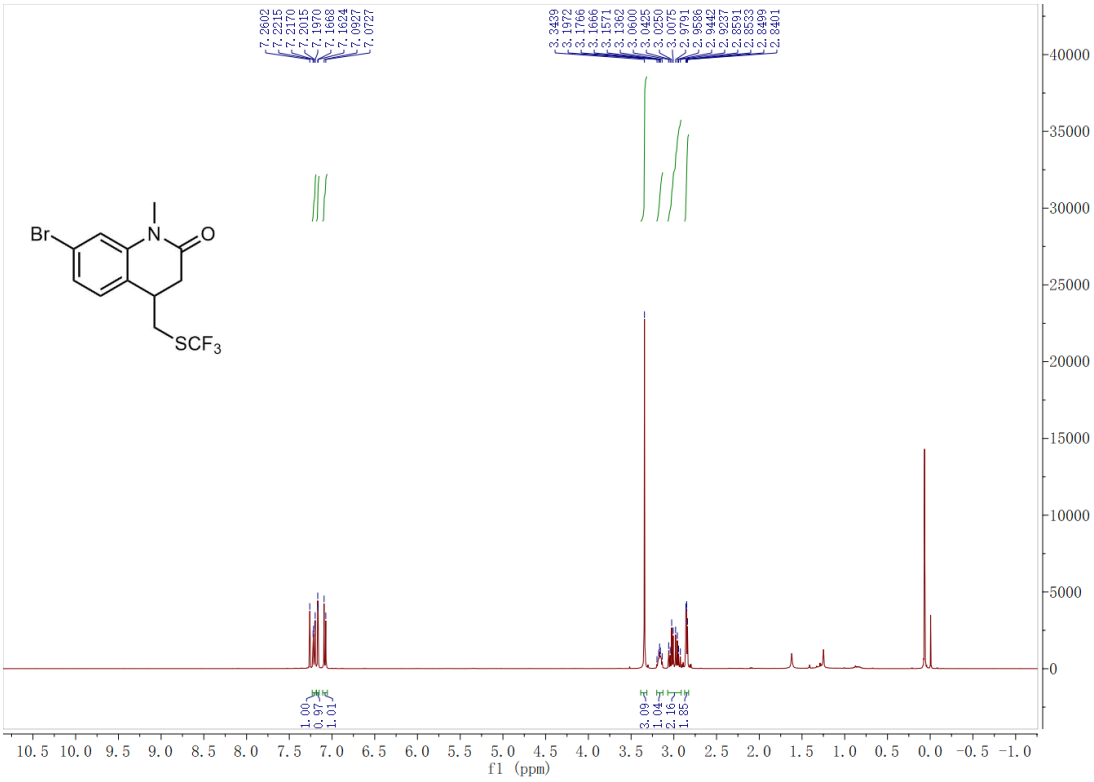


^{19}F NMR (376 MHz, $CDCl_3$)

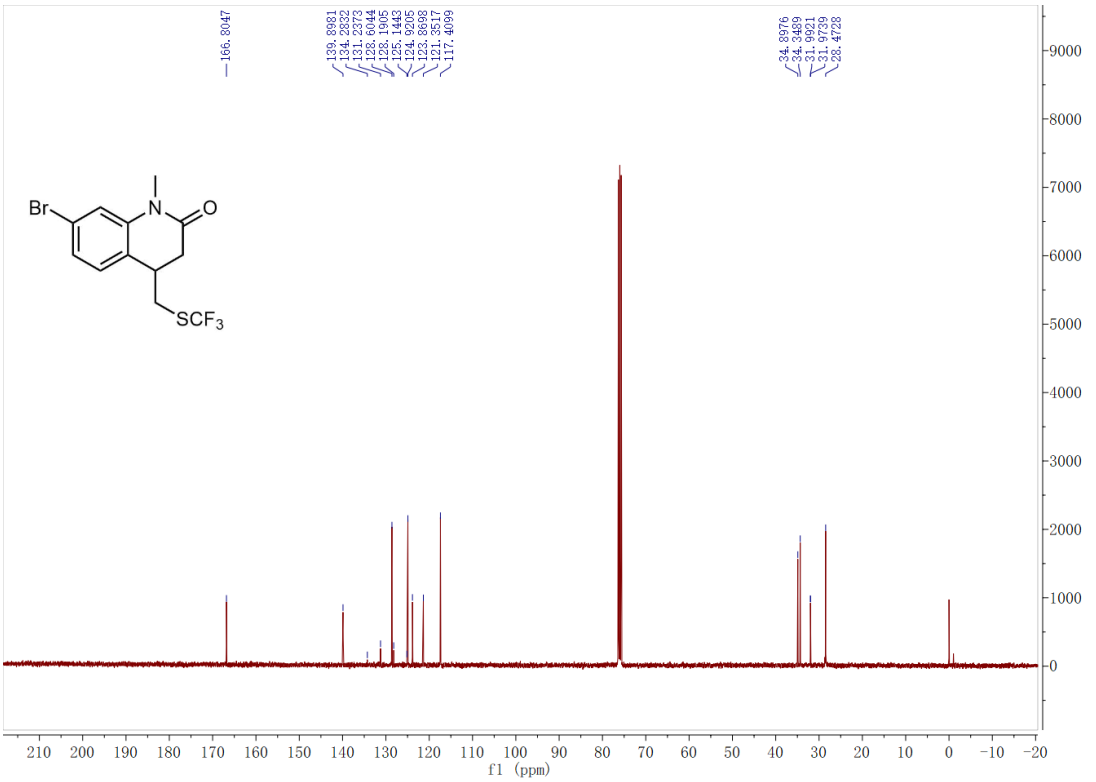


7-Bromo-1-methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-on (3j')

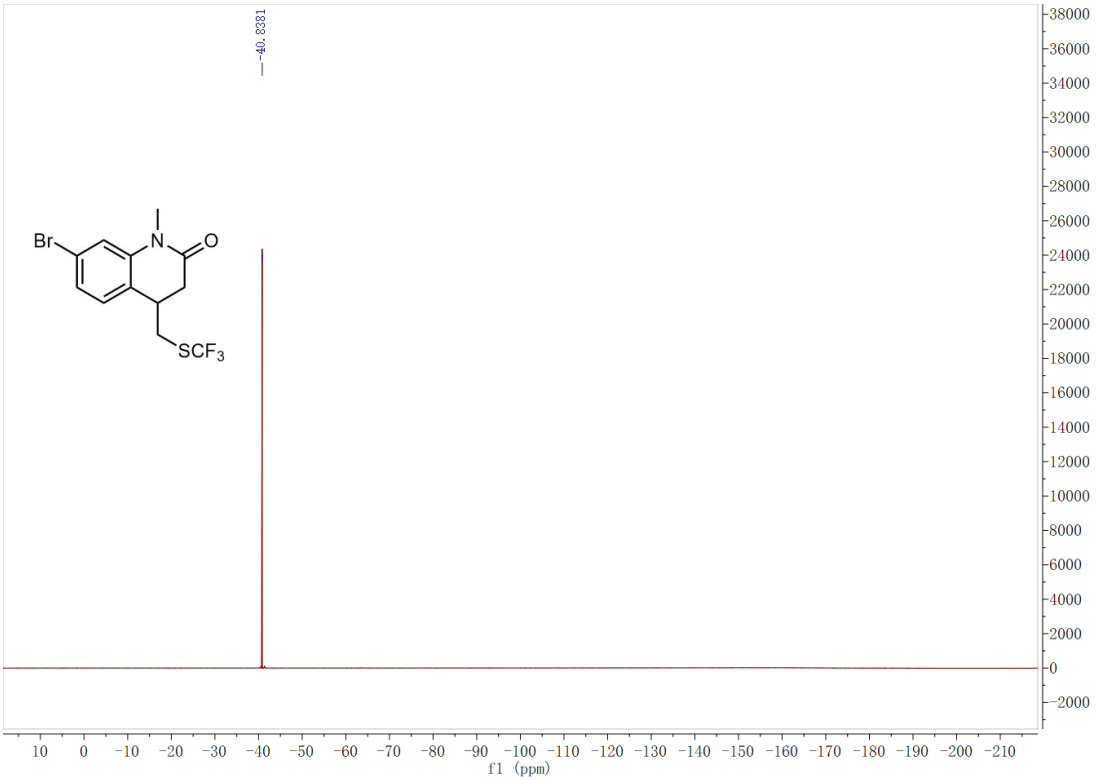
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

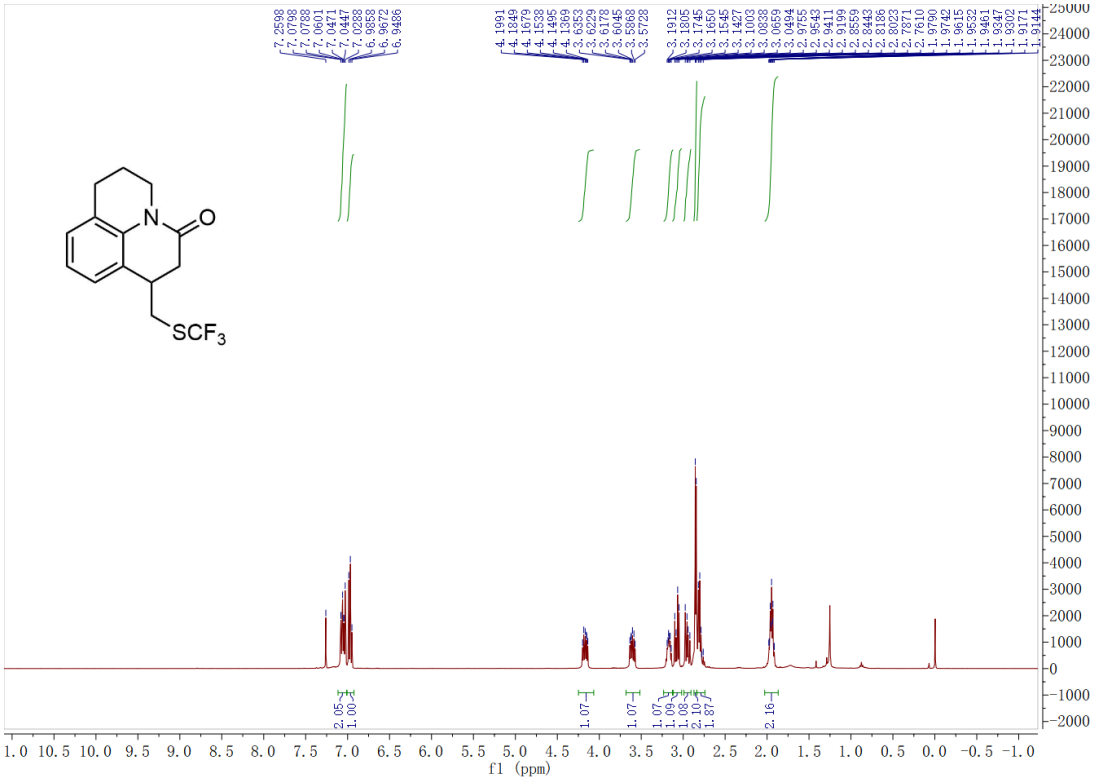


^{19}F NMR (376 MHz, $CDCl_3$)

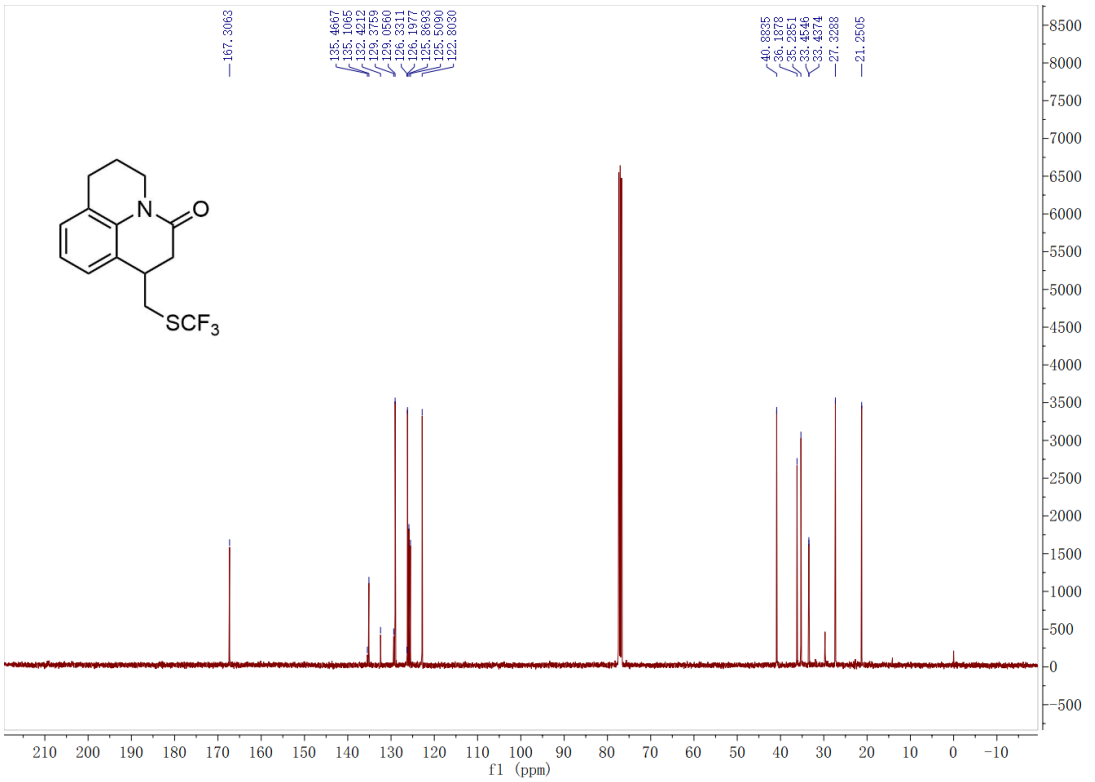


7-(((Trifluoromethyl)thio)methyl)-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-5-one (3k)

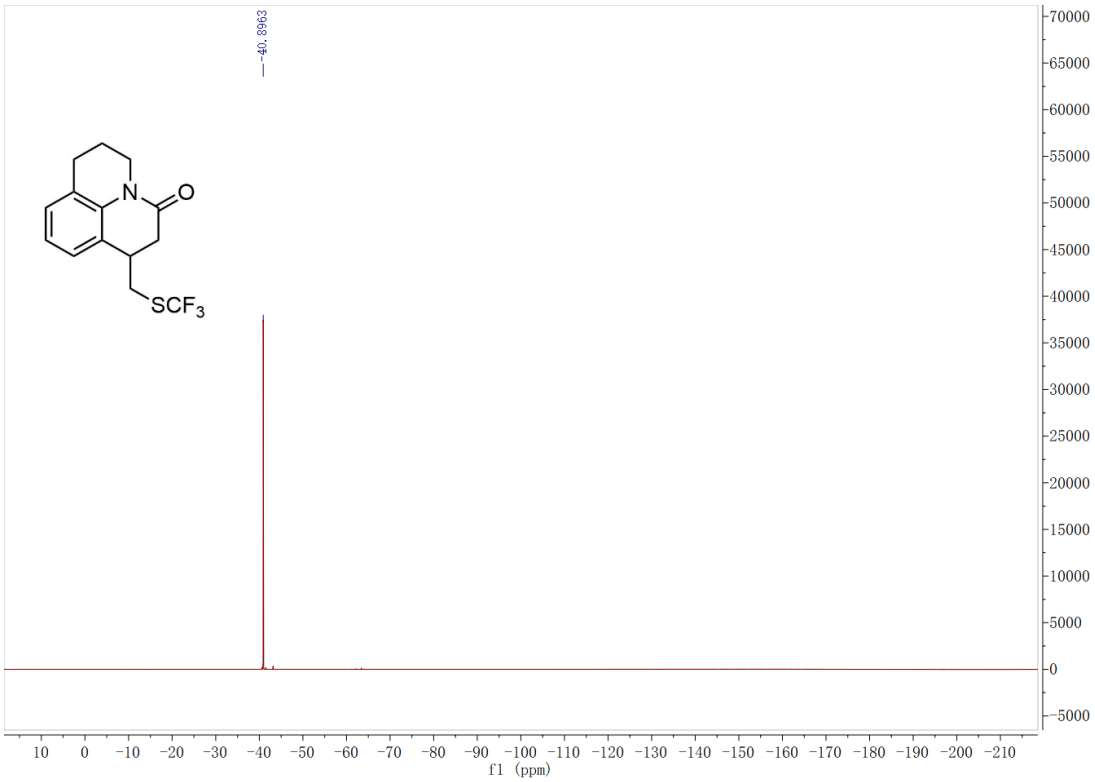
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

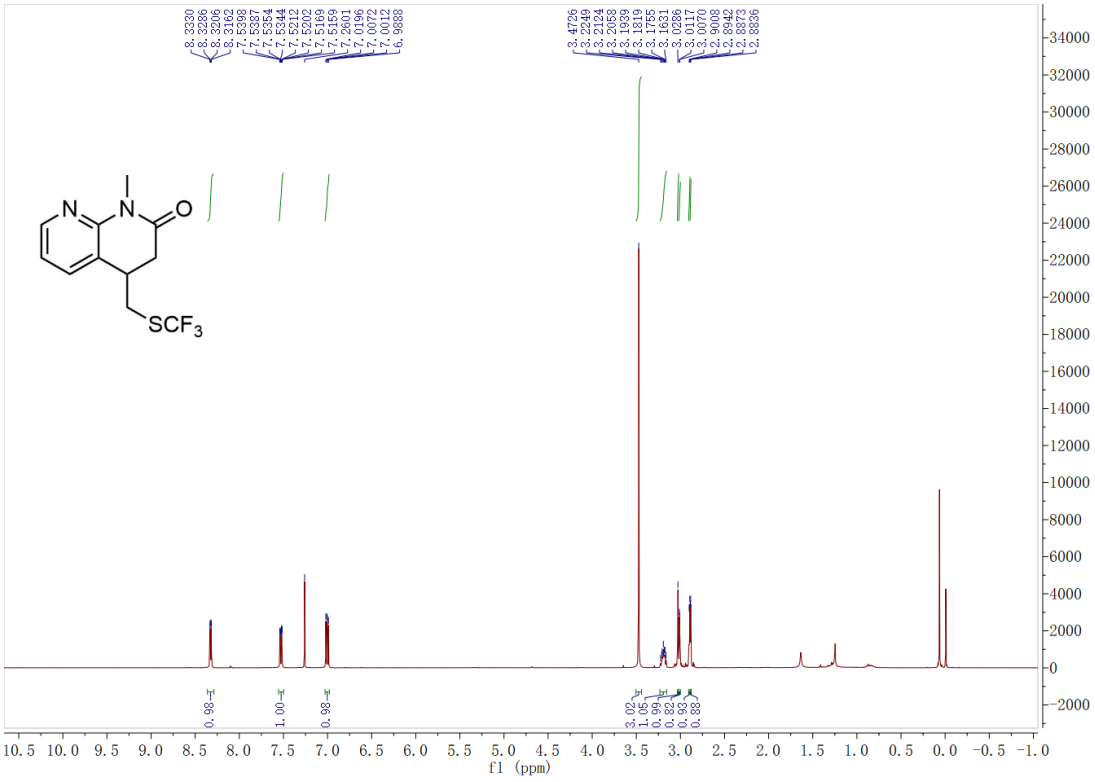


^{19}F NMR (376 MHz, $CDCl_3$)

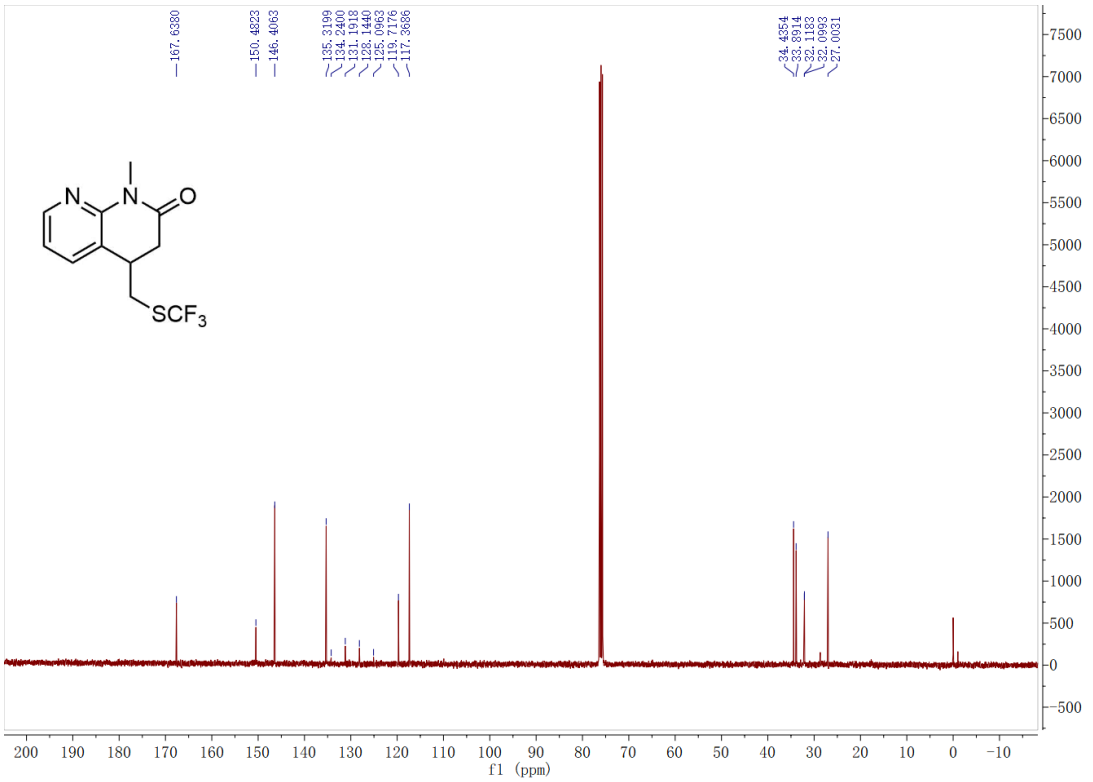


1-Methyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydro-1,8-naphthyridin-2(1H)-one (3l)

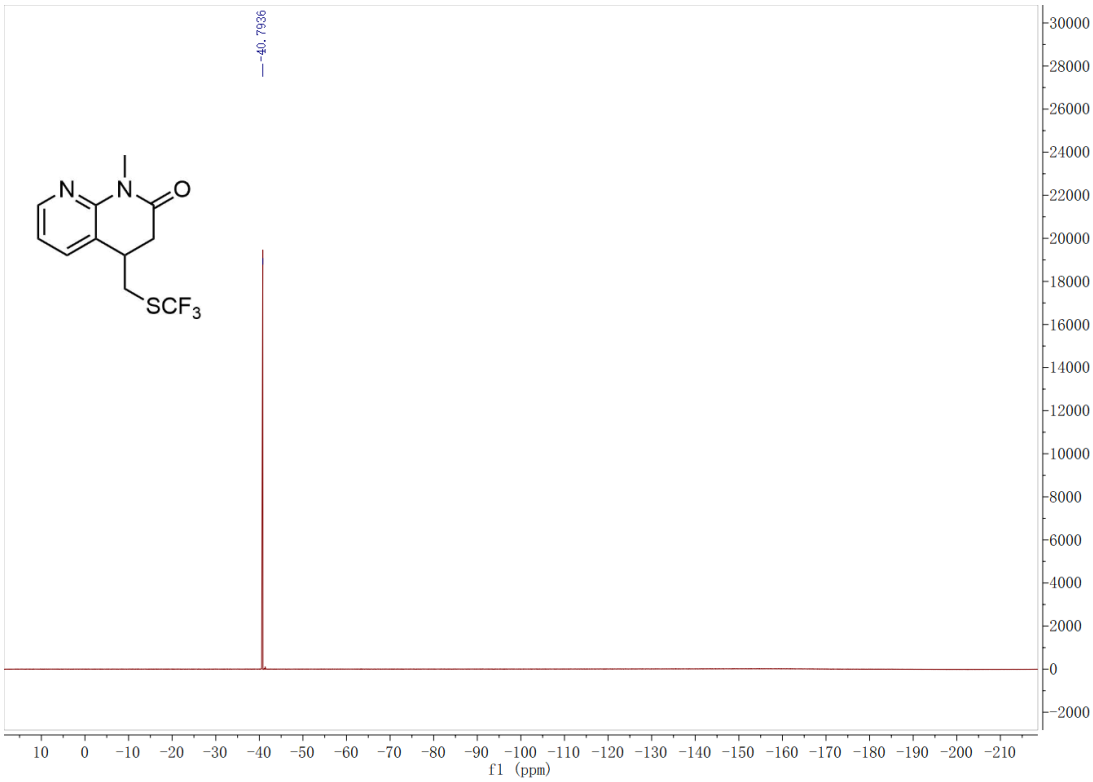
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

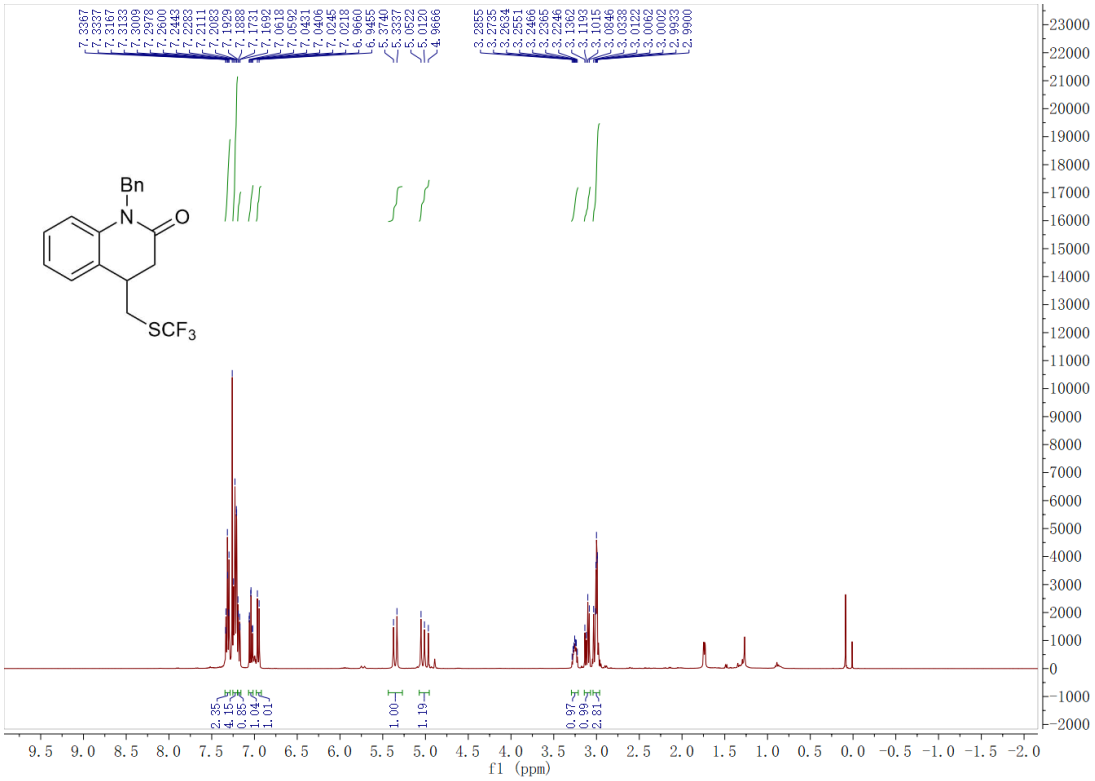


^{19}F NMR (376 MHz, $CDCl_3$)

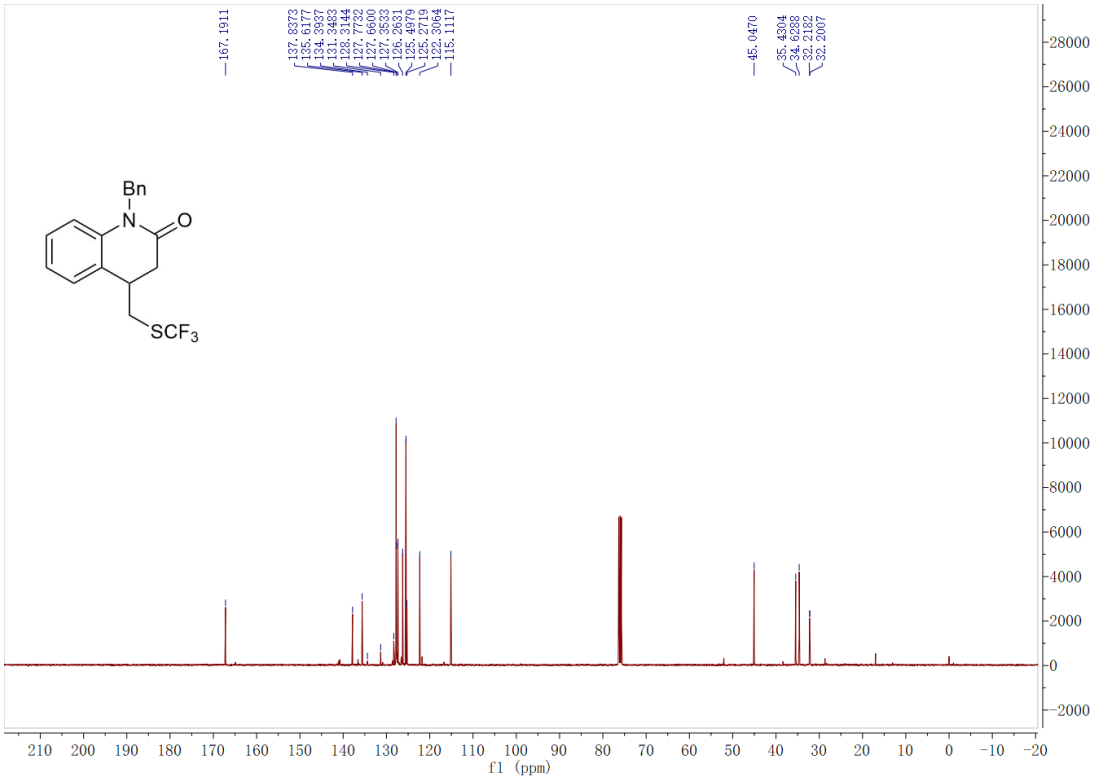


1-benzyl-4-(((trifluoromethyl)thio)methyl)-3,4-dihydroquinolin-2(1H)-one (3m)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)