Supporting Information

Solvent Dependent Fluorinative Cyclizations of *o*-Hydroxyarylenaminones Promoted by H_2O and NFSI: Switchable Access to Di- and Monofluorinated 2-Hydroxyl Chromanones

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(A) General Experimental Procedure

(a) General information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 500 MHz advance spectrometer at room temperature in $CDCl_3$ using TMS as internal standard or DMSO-d6. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra. High-resolution mass spectra (HRMS) was recorded on an electrospray ionization (ESI) apparatus using LTQ Orbitrap XL mass spectrometry. Unless otherwise noted, all reactions were carried out at at ambient temperature and atmospheric environment, and all starting materials and solvents were commercially available and were used without further purification. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE) / ethyl acetate (EA). All *o*-hydroxy-arylenaminones were synthesized according to the known procedures.[1]

(b) General procedure for the synthesis of difluorinated chromanones (2)

To a 10 mL tube was added substrate **1** (0.5 mmol), NFSI (1.2 mmol，2.4 equiv.), followed by THF(2 mL, extra dry) and H_2O (10 mmol, 20 equiv.). The content of the tube was stirred at room temperature under atmospheric environment for 20 h. Then, the reaction mixture was diluted in ethyl acetate and the solid was removed by filtration. The solvent was concentrated under reduced pressure. Purification by column chromatography (Hexanes/EtOAc: 5/1~3/1) afforded corresponding compounds **2**.

(c) Syntheis of difluorinated chromanone 2a on a gram scale.

To a 50 mL round bottom flask was added substrate **1a** (6 mmol), NFSI (14.4 mmol), followed by THF (20 mL, extra dry) and H_2O (120 mmol, 20 equiv.). The content of the flask was stirred at room temperature under atmospheric environment for 20 h. Then, the reaction mixture was diluted in ethyl acetate and the solid was removed by filtration. The solvent was concentrated under reduced pressure. Purification by column chromatography (Hexanes/EtOAc: 5/1~3/1) afforded corresponding compounds **2a**.

(d) General procedure for the synthesis of monofluorinated chromanones (3)

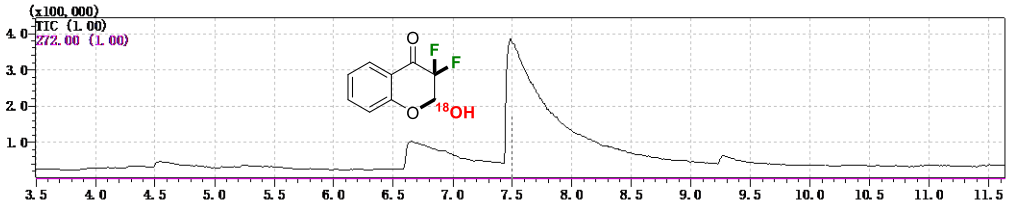
To a 10 mL tube was added substrate **1** (0.5 mmol), NFSI (0.6 mmol，1.2 equiv.) and EtOH (95%, 2 mL). The content of the tube was stirred at room temperature under atmospheric environment for 3 h. Then, the reaction mixture was diluted in ethyl acetate and the solid was removed by filtration. The solvent was concentrated under reduced pressure. Purification by column chromatography (Hexanes / EtOAc : 5/1~3/1) afforded corresponding compounds **3**.

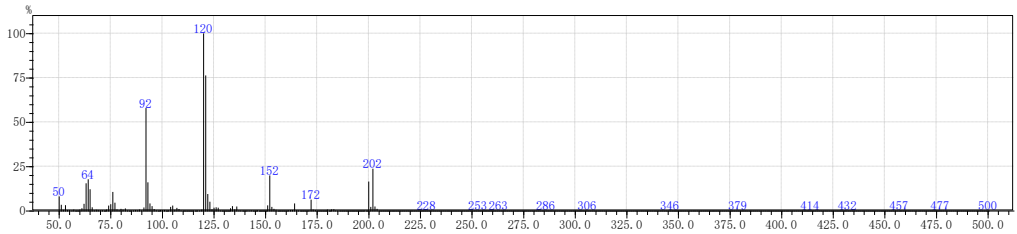
(e) Synthesis of 3,3-difluoro-4-oxochroman-2-yl acetate (4a) from 2a.

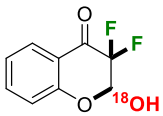
To a stirred solution of **2a** (0.5 mmol) in CH_2Cl_2 (10 mL) at room temperature was added acetyl chloride (1 mmol) and Et_3N (1 mol). The content of the tube was stirred at room temperature under atmospheric environment for 12 h. Then, the reaction mixture was concentrated under reduced pressure. Purification by column chromatography (Hexanes / EtOAc : 10/1) afforded corresponding compounds **4a**.

(B) ^{18}O -labeled experiment

Under the standard conditions, $H_2{}^{18}O$ was added to the reaction of **1a**, NFSI and dry THF. After the reaction was finished, the reaction mixture was monitored by GC-MS. The result indicated that ^{18}O-**2a** was generated from the reaction.







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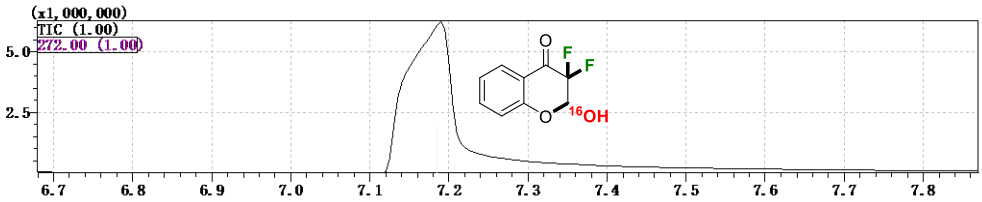
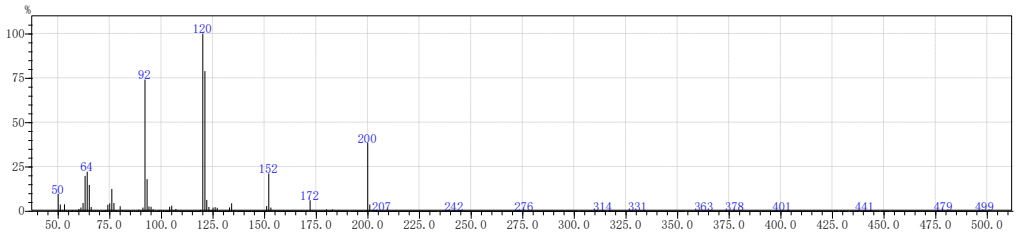
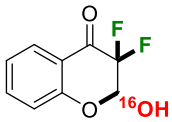
55.05 349 0.48
56.10 148 0.20
57.05 472 0.65
58.00 81 0.11
59.00 86 0.12

60.00	502	0.69	103.95	1587	2.17	148.00	70	0.10
61.00	1026	1.40	105.00	2158	2.95	149.00	92	0.13
62.00	2871	3.93	106.00	422	0.58	150.00	90	0.12
63.00	11319	15.49	107.00	1222	1.67	151.00	2241	3.07
64.00	12993	17.78	108.00	742	1.02	152.00	14574	19.95
65.00	8831	12.09	109.00	180	0.25	153.00	1546	2.12
66.00	1423	1.95	110.00	84	0.11	154.00	822	1.13
67.00	250	0.34	111.00	68	0.09	155.00	406	0.56
68.00	425	0.58	112.00	116	0.16	156.00	116	0.16
68.90	332	0.45	113.00	70	0.10	157.00	86	0.12
69.90	273	0.37	114.00	106	0.15	158.00	26	0.04
70.90	265	0.36	115.00	122	0.17	159.00	21	0.03
71.90	79	0.11	116.00	84	0.11	160.00	76	0.10
72.95	465	0.64	117.00	174	0.24	161.00	218	0.30
73.95	2171	2.97	118.00	127	0.17	162.00	334	0.46
75.00	2689	3.68	119.00	452	0.62	163.00	324	0.44
76.00	7770	10.64	119.95	73060	100.00	164.00	3015	4.13
77.00	3337	4.57	121.00	55775	76.34	165.00	353	0.48
78.00	543	0.74	122.00	6865	9.40	166.00	140	0.19
79.00	262	0.36	122.95	3683	5.04	167.00	41	0.06
79.95	817	1.12	124.00	617	0.84	168.00	81	0.11
80.95	457	0.63	125.00	1274	1.74	169.00	79	0.11
82.00	964	1.32	126.00	1396	1.91	170.00	111	0.15
83.00	172	0.24	127.00	1279	1.75	171.00	170	0.23
84.00	95	0.13	128.00	186	0.25	172.00	4578	6.27
85.00	148	0.20	129.00	76	0.10	173.00	473	0.65
86.00	183	0.25	130.00	62	0.08	174.00	292	0.40
87.00	294	0.40	131.00	49	0.07	175.00	95	0.13
88.00	234	0.32	132.00	44	0.06	176.00	33	0.05
88.95	489	0.67	133.00	1025	1.40	177.00	38	0.05
89.90	143	0.20	133.95	1914	2.62	178.00	66	0.09
91.00	1311	1.79	135.00	562	0.77	179.00	44	0.06
92.00	42340	57.95	136.00	1743	2.39	179.95	453	0.62
93.00	11742	16.07	137.00	159	0.22	180.90	65	0.09
93.95	3006	4.11	138.00	119	0.16	181.95	573	0.78
95.00	1926	2.64	139.00	54	0.07	183.00	641	0.88
96.00	708	0.97	140.00	74	0.10	184.00	154	0.21
97.00	204	0.28	141.00	129	0.18	185.00	146	0.20
98.00	65	0.09	142.00	196	0.27	186.00	33	0.05
99.00	284	0.39	143.00	233	0.32	187.00	55	0.08
100.00	241	0.33	144.00	65	0.09	188.00	47	0.06
101.00	297	0.41	145.00	78	0.11	189.00	27	0.04
102.00	90	0.12	146.00	238	0.33	190.00	58	0.08
103.00	135	0.18	147.00	62	0.08	191.00	58	0.08

192.00	34	0.05	197.00	54	0.07	**201.95**	**17344**	**23.74**
193.00	106	0.15	198.00	178	0.24	202.95	1730	2.37
194.00	62	0.08	198.90	42	0.06	203.95	786	1.08
195.00	95	0.13	**199.95**	**11992**	**16.41**	205.00	105	0.14
196.00	14	0.02	200.95	1556	2.13	206.00	36	0.05







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(scan : 738)
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(Inten : 1,196,897)
Event# 1
m/z Absolute Intensity
Relative Intensity

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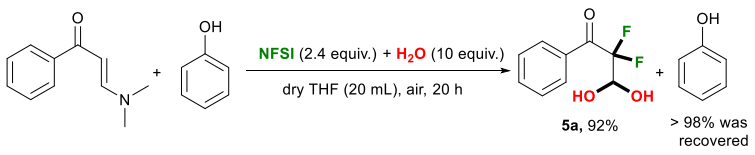
52.05	6177	0.52	65.00	175854	14.69	92.00	887577	74.16
53.00	45479	3.80	66.00	27337	2.28	93.00	214543	17.92
54.00	3127	0.26	67.00	3394	0.28	94.00	31119	2.60
55.00	3446	0.29	68.00	5188	0.43	95.00	28612	2.39
56.00	1289	0.11	69.00	5119	0.43	96.00	11762	0.98
57.00	5606	0.47	70.00	2830	0.24	97.00	2351	0.20
58.05	659	0.06	71.00	1217	0.10	98.00	591	0.05
59.05	530	0.04	72.00	473	0.04	98.95	5549	0.46
60.00	14370	1.20	73.00	6748	0.56	99.95	4001	0.33
61.00	22990	1.92	74.00	42804	3.58	101.00	5607	0.47
62.00	53990	4.51	75.00	51322	4.29	102.00	598	0.05
			76.00	148951	12.44	103.00	857	0.07
			77.00	54074	4.52	104.00	28114	2.35
			78.00	6562	0.55	105.00	36222	3.03
			79.00	2532	0.21	106.00	4300	0.36
			80.00	32258	2.70	107.00	14103	1.18
			81.00	5590	0.47	108.00	3458	0.29
			82.00	1044	0.09	109.00	644	0.05
			83.00	1207	0.10	110.00	178	0.01
			84.00	498	0.04	110.95	492	0.04
			85.00	1959	0.16	111.95	453	0.04
			86.00	2148	0.18	113.00	684	0.06
			87.00	2970	0.25	113.95	1726	0.14
			88.00	3058	0.26	115.00	1423	0.12
			89.00	8490	0.71	116.00	300	0.03

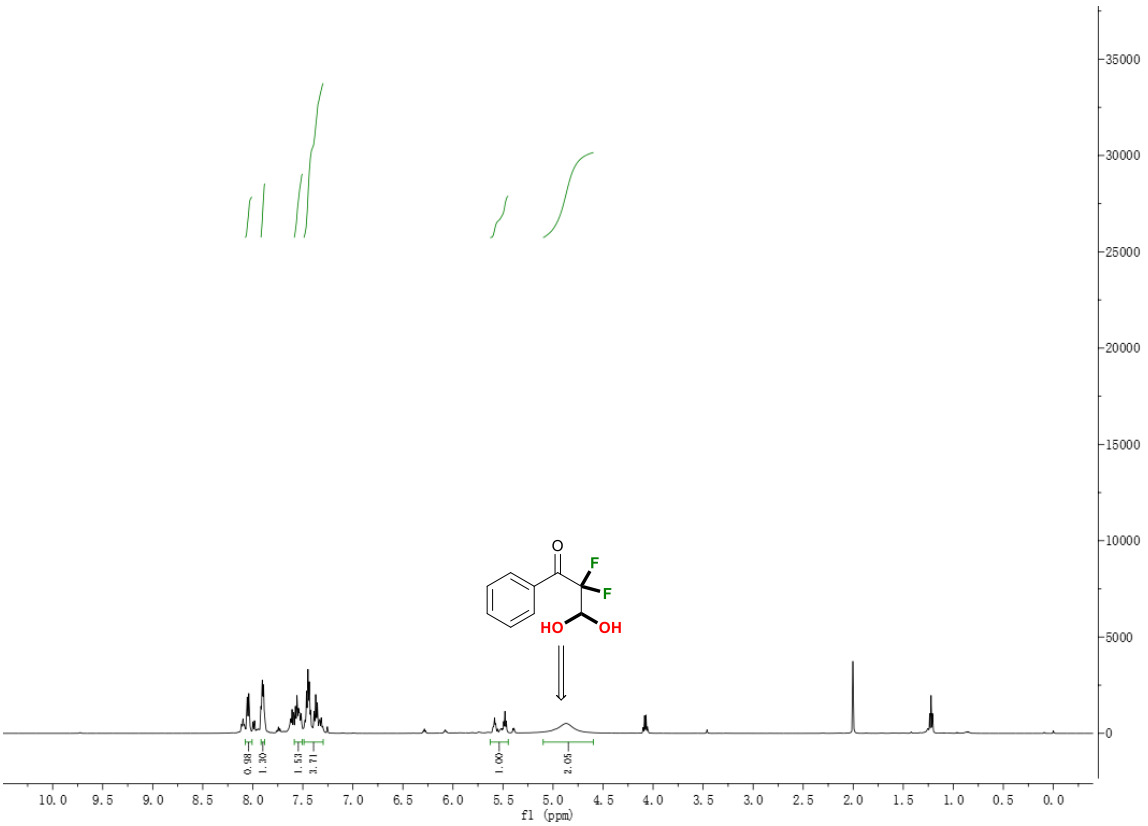
116.95	1859	0.16	147.00	70	0.01	177.00	44	0.00
118.00	455	0.04	148.00	217	0.02	178.00	27	0.00
119.00	7978	0.67	148.95	1752	0.15	178.90	169	0.01
120.00	1196897	100.00	150.00	254	0.02	179.95	12051	1.01
121.00	943967	78.87	150.95	34328	2.87	180.95	1159	0.10
122.00	75785	6.33	151.95	253552	21.18	181.95	839	0.07
123.00	27078	2.26	153.00	23710	1.98	182.95	11045	0.92
124.00	6962	0.58	154.00	3622	0.30	183.95	1151	0.10
125.00	23134	1.93	155.00	4886	0.41	184.90	142	0.01
126.00	25986	2.17	156.00	593	0.05	185.90	49	0.00
127.00	21959	1.83	157.00	90	0.01	186.90	58	0.00
128.00	1689	0.14	158.00	70	0.01	187.90	36	0.00
129.00	122	0.01	159.00	87	0.01	188.90	44	0.00
130.00	60	0.01	160.00	58	0.00	189.90	30	0.00
131.00	129	0.01	161.00	49	0.00	191.90	52	0.00
132.00	337	0.03	162.00	79	0.01	192.90	129	0.01
133.00	24014	2.01	163.00	433	0.04	193.90	29	0.00
134.00	51617	4.31	163.95	1809	0.15	194.90	44	0.00
135.00	5049	0.42	165.00	249	0.02	195.90	39	0.00
136.00	2534	0.21	166.00	38	0.00	196.90	86	0.01
137.00	300	0.03	167.00	95	0.01	197.95	987	0.08
138.00	142	0.01	168.00	121	0.01	198.95	888	0.07
138.90	484	0.04	169.00	108	0.01	**199.90**	**459810**	**38.42**
139.90	95	0.01	169.95	580	0.05	200.90	43924	3.67
140.95	844	0.07	171.00	2004	0.17	**201.90**	**4897**	**0.41**
142.00	660	0.06	172.00	72700	6.07	202.90	346	0.03
143.00	3425	0.29	173.00	6407	0.54	203.90	46	0.00
144.00	410	0.03	173.95	612	0.05	204.90	34	0.00
145.00	87	0.01	175.00	34	0.00	205.90	10	0.00
146.00	82	0.01	176.00	24	0.00	206.90	97	0.01

(C) The investigation of intermolecular reaction.

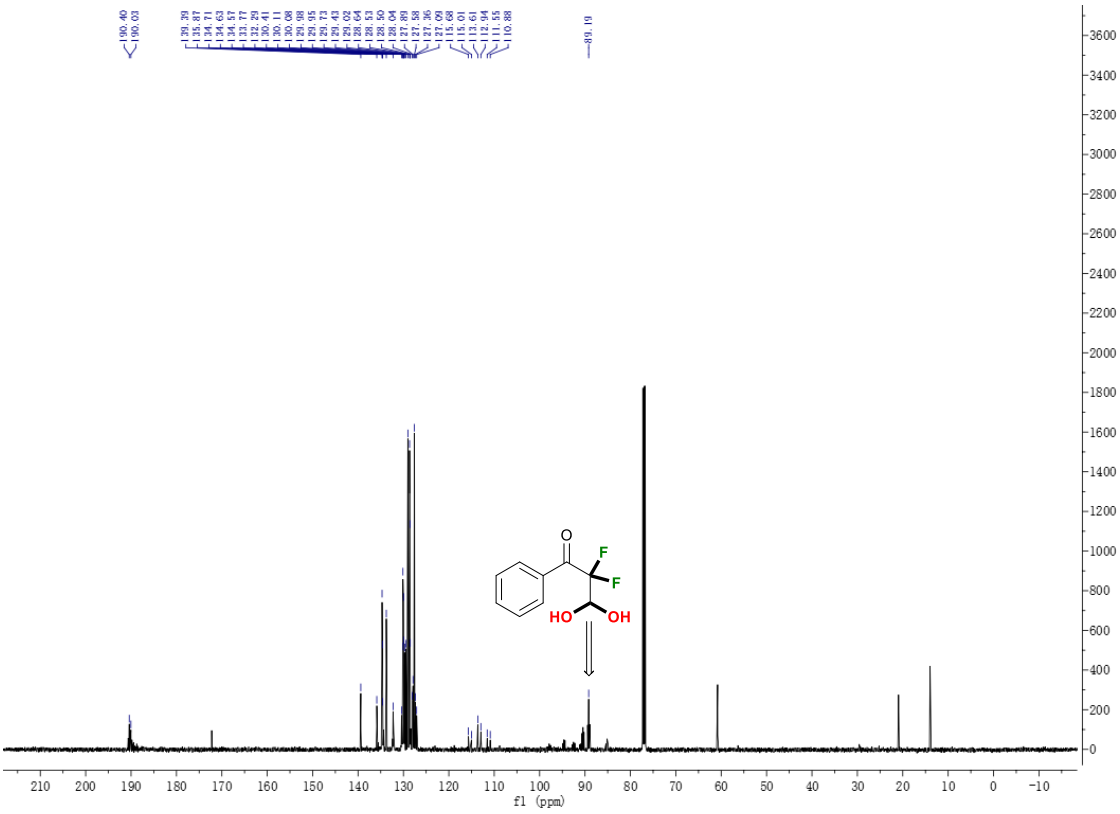
Under the standard conditions to difluorinated 2-hydroxyl chromanones, 2,2-difluoro-3,3-dihydroxy-1-phenylpropan-1-one (**5a**) was obtained from the intermolecular reaction of (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one with phenol. Although phenol did not participate in the reaction, the result indicates the dimethylamino group could transform to carbonyl group under present fluorinative reaction conditions. However, the structure of 2,2-difluoro-3,3-dihydroxy-1-phenylpropan-1-one is not very stable, resulting in difficulty in obtaining pure compound.



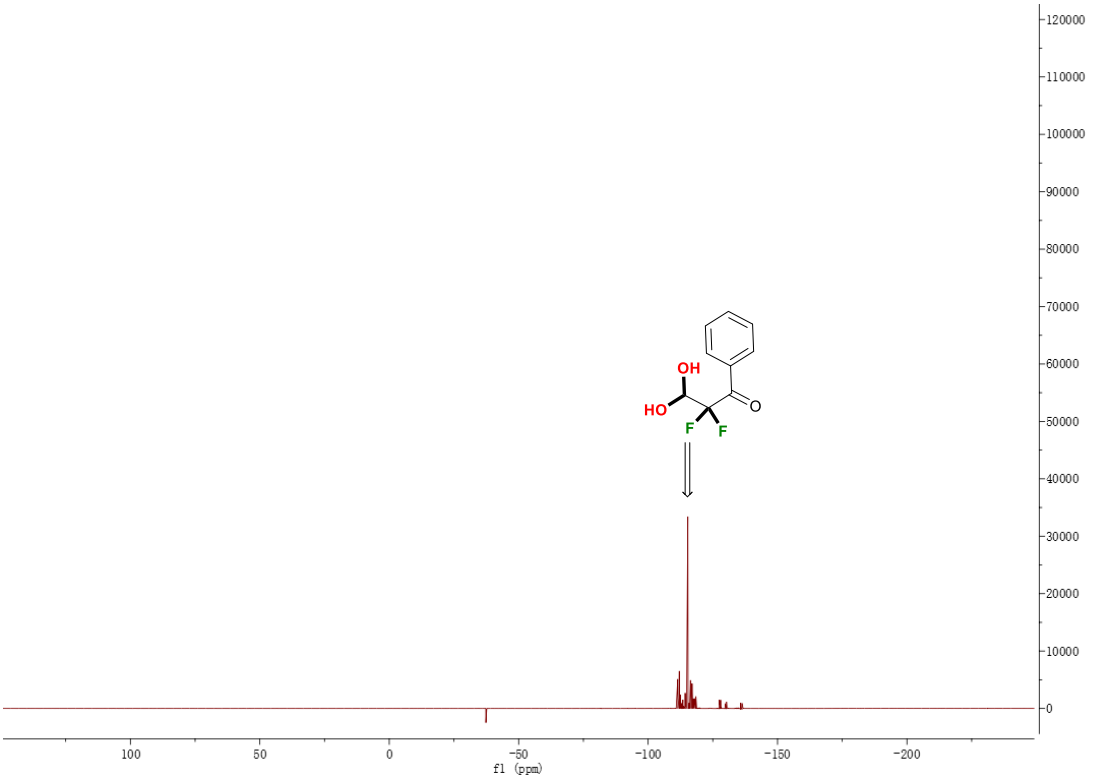
^{1}H NMR



^{13}C NMR

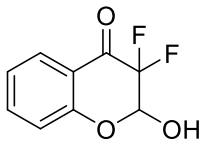


^{19}F NMR



(D) Analytical data for 2, 3, 4a and 6.

3,3-difluoro-2-hydroxychroman-4-one (**2a**)



90.2 mg, 90% yield; pale yellow oil.

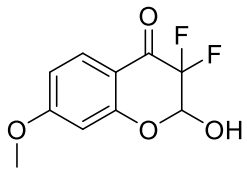
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.00 (dd, *J* = 10.0, 5.0 Hz, 1H), 6.91 (dd, *J* = 10.0, 5.0 Hz, 1H), 5.66 (s, 1H), 4.54 (br, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 181.7 (t, *J* = 25.0 Hz, 1C), 157.3 (d, *J* = 5.0 Hz, 1C), 138.5 (d, *J* = 8.8 Hz, 1C), 127.6, 123.1, 118.9, 118.7, 107.7 (dd, *J* = 258.8 Hz, 247.5 Hz, 1C), 94.1 (dd, *J* = 33.8 Hz, 27.5 Hz, 1C).

^{19}F NMR (471 MHz, Chloroform-d) δ -119.5 (d, *J* = 280.3 Hz), -134.7 (d, *J* = 280.3 Hz).

HRMS m/z (ESI) calcd for $C_9H_7F_2O_3$ $[M+H]^+$ 201.0358, found 201.0360.

3,3-difluoro-2-hydroxy-7-methoxychroman-4-one (**2b**)



86.3 mg, 75% yield; pale yellow oil.

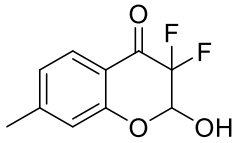
^{1}H NMR (500 MHz, DMSO-d6) δ 8.90 (d, *J* = 5.0 Hz, 1H), 7.77 (d, *J* = 10.0 Hz, 1H), 6.78 (d, *J* = 10.0 Hz, 1H), 6.66 (s, 1H), 5.95 (d, *J* = 2.5 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (125 MHz, DMSO-d6) δ 179.83 (t, *J* = 25.0 Hz, 1C), 168.21, 160.25, 129.48, 112.57, 111.99, 107.7 (dd, *J* = 257.5 Hz, 245.0 Hz, 1C), 102.85, 94.5 (dd, *J* = 35.0 Hz, 27.5 Hz, 1C), 56.77.

^{19}F NMR (471 MHz, DMSO-d6) δ -118.8 (d, *J* = 274.2 Hz), -133.4 (d, *J* = 274.1 Hz).

HRMS m/z (ESI) calcd for $C_{10}H_9F_2O_4$ $[M+H]^+$ 231.0463, found 231.0464.

3,3-difluoro-2-hydroxy-7-methylchroman-4-one (**2c**)



86.7 mg, 81% yield; pale yellow solid; m.p. 64.2 – 65.5 °C (uncorrected).

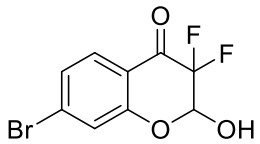
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 10.0 Hz, 1H), 6.87 (d, *J* = 5.0 Hz, 1H), 6.75 (s, 1H), 5.64 (t, *J* = 5.0 Hz, 1H), 4.16 (br, 1H), 2.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.90 (t, *J* = 25.0 Hz, 1C), 157.25, 150.61, 127.55, 124.56, 118.96, 116.47, 107.7 (dd, *J* = 258.8 Hz, 247.5 Hz, 1C), 94.1 (dd, *J* = 35.0 Hz, 27.5 Hz, 1C), 22.09.

^{19}F NMR (471 MHz, DMSO-d6) δ -119.2 (d, *J* = 273.7 Hz), -133.74 (d, *J* = 273.7 Hz).

HRMS m/z (ESI) calcd for $C_{10}H_9F_2O_3$ $[M+H]^+$ 215.0514, found 215.0515.

7-bromo-3,3-difluoro-2-hydroxychroman-4-one (**2d**)



113.9 mg, 82% yield; yellow solid; m.p. 68.4 – 69.9 °C (uncorrected).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 10.0 Hz, 1H), 7.28 (d, *J* = 10.0 Hz, 1H),

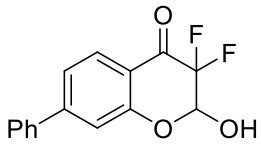
7.23 (d, *J* = 0.5 Hz, 1H), 5.79 (t, *J* = 3.0 Hz, 1H), 4.53 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 180.88 (t, *J* = 25.0 Hz, 1C), 157.33, 133.18, 128.62, 126.79, 122.22, 117.63, 107.5 (dd, *J* = 258.8 Hz, 246.3 Hz, 1C), 94.5 (dd, *J* = 35.0 Hz, 28.8 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d6) δ -119.8 (d, *J* = 274.3 Hz), -133.9 (d, *J* = 274.3 Hz).

HRMS m/z (ESI) calcd for $C_9H_5BrF_2O_3Na$ $[M+Na]^+$ 300.9282, found 300.9283.

3,3-difluoro-2-hydroxy-7-phenylchroman-4-one (**2e**)



103.5 mg, 75% yield; pale yellow solid; m.p. 49.7 – 51.2 °C (uncorrected)

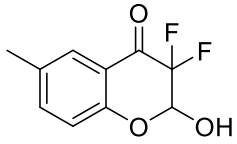
^{1}H NMR (500 MHz, DMSO-d6) δ 9.03 (d, *J* = 5.0 Hz, 1H), 7.92 (d, *J* = 10.0 Hz, 1H), 7.77 (d, *J* = 5.0 Hz, 2H), 7.61 – 7.38 (m, 5H), 6.07 (dd, *J* = 10.0, 5.0 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 181.31 (t, *J* = 25.0 Hz, 1C), 158.25, 150.67, 138.41, 129.88, 129.72, 128.30, 127.79, 122.11, 117.82, 117.05, 109.0 (dd, *J* = 257.5 Hz, 246.3 Hz, 1C), 94.5 (dd, *J* = 33.8 Hz, 27.5 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d6) δ -119.0 (d, *J* = 273.7 Hz), -133.7 (d, *J* = 273.6 Hz).

HRMS m/z (ESI) calcd for $C_{15}H_{11}F_2O_3$ $[M+H]^+$ 277.0671, found 277.0672.

3,3-difluoro-2-hydroxy-6-methylchroman-4-one (**2f**)



77.1 mg, 72% yield; pale yellow solid; m.p. 88.3 – 89.7 °C (uncorrected)

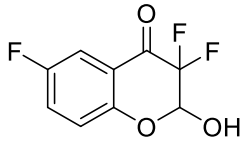
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.42 (d, *J* = 5.0 Hz, 1H), 6.94 (d, *J* = 5.0 Hz, 1H), 5.71 (t, *J* = 5.0 Hz, 1H), 3.96 (br, 1H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 181.13 (t, *J* = 25.0 Hz, 1C), 155.10, 141.53, 139.32, 133.05, 127.25, 118.64, 118.49, 107.6 (dd, J = 258.8 Hz, 247.5 Hz, 1C), 94.1 (dd, J = 35.0 Hz, 27.5 Hz, 1C), 20.31.

^{19}F NMR (471 MHz, DMSO-d6) δ -119.4 (d, *J* = 273.6 Hz), -133.9 (d, *J* = 273.5 Hz).

HRMS m/z (ESI) calcd for $C_{10}H_9F_2O_3$ $[M+H]^+$ 215.0514, found 215.0515.

3,3,6-trifluoro-2-hydroxychroman-4-one (**2g**)



101.4 mg, 93% yield; pale yellow oil.

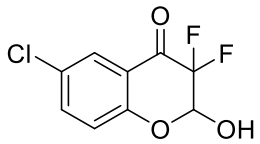
^{1}H NMR (500 MHz, DMSO-d6) δ 9.02 (s, 1H), 7.63 (d, *J* = 5.0 Hz, 1H), 7.58 (d, *J* = 10.0 Hz, 1H), 7.23 (d, *J* = 5.0 Hz, 1H), 6.02 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 181.27 (t, *J* = 25.0 Hz, 1C), 157.9 (d, *J* = 250.0 Hz, 1C), 154.28, 126.75 (d, *J* = 25.0 Hz, 1C), 121.92 (d, *J* = 7.5 Hz, 1C), 119.50 (d, *J* = 5.0 Hz, 1C), 112.5 (d, *J* = 25.0 Hz, 1C), 108.8 (dd, J = 258.8 Hz, 245.0 Hz, 1C), 94.5 (dd, J = 33.8 Hz, 27.5 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d6) δ -119.8 (d, *J* = 274.5 Hz), -119.7, -134.3 (d, *J* = 274.3 Hz).

HRMS m/z (ESI) calcd for $C_9H_6F_3O_3$ $[M+H]^+$ 219.0264, found 219.0265.

6-chloro-3,3-difluoro-2-hydroxychroman-4-one (**2h**)



100.6 mg, 86% yield; pale yellow oil.

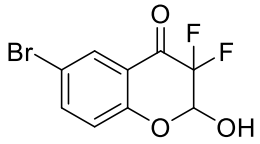
^{1}H NMR (500 MHz, DMSO-d6) δ 9.10 (d, *J* = 5.0 Hz, 1H), 7.80 – 7.77 (m, 2H), 7.22 (d, *J* = 5.0 Hz, 1H), 6.06 (d, *J* = 3.0 Hz, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 180.94 (t, *J* = 25.0 Hz, 1C), 156.53, 138.78, 127.82, 126.46, 121.91, 120.0 (d, *J* = 2.5 Hz, 1C), 108.8 (dd, *J* = 258.8 Hz, 246.3 Hz, 1C), 94.6 (dd, *J* = 33.8 Hz, 27.5 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d6) δ -119.7 (d, *J* = 274.3 Hz), -134.2 (d, *J* = 274.3 Hz).

HRMS m/z (ESI) calcd for $C_9H_6ClF_2O_3$ $[M+H]^+$ 234.9968, found 234.9970.

6-bromo-3,3-difluoro-2-hydroxychroman-4-one (**2i**)



116.7 mg, 84% yield; pale yellow solid; m.p. 76.5 – 77.4 °C (uncorrected)

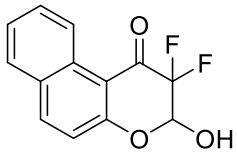
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 2.5 Hz, 1H), 7.69 (dd, *J* = 5.0, 2.5 Hz, 1H), 6.96 (d, *J* = 10.0 Hz, 1H), 5.77 (t, *J* = 5.0 Hz, 1H), 4.50 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 180.11 (t, *J* = 25.0 Hz, 1C), 155.96, 140.78, 129.95, 120.90, 120.11, 116.00, 107.3 (dd, *J* = 260.0 Hz, 247.5 Hz, 1C), 94.3 (dd, *J* = 35.0 Hz, 27.5 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d6) δ -120.0 (d, *J* = 274.1 Hz), -134.1 (d, *J* = 274.1 Hz).

HRMS m/z (ESI) calcd for $C_9H_5BrF_2O_3Na$ $[M+Na]^+$ 300.9282, found 300.9283.

2,2-difluoro-3-hydroxy-2,3-dihydro-1H-benzo[f]chromen-1-one (**2j**)



112.5 mg, 90% yield; red oil.

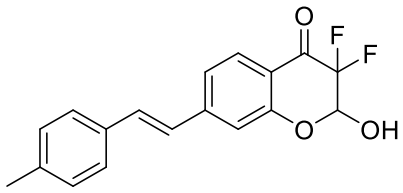
^{1}H NMR (500 MHz, DMSO-d6) δ 9.24 (s, 1H), 8.28 (d, *J* = 10.0 Hz, 1H), 7.98 (d, *J* = 10.0 Hz, 1H), 7.77 (t, *J* = 7.5 Hz, 2H), 7.69 – 7.66 (m, 2H), 6.30 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 181.40 (t, *J* = 25.0 Hz, 1C), 156.76, 138.42, 131.63, 128.82, 128.01, 124.69, 123.84, 123.35, 121.24, 113.50, 108.9 (dd, *J* = 257.5 Hz, 246.3 Hz, 1C), 95.2 (dd, *J* = 30.0 Hz, 28.8 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d_6) δ -120.3 (d, *J* = 275.1 Hz), -133.0 (d, *J* = 274.9 Hz).

HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{13}H_9F_2O_3^+$: 251.0514, found 251.0515.

(E)-3,3-difluoro-2-hydroxy-7-(4-methylstyryl)chroman-4-one (**2k**)



129.5 mg, 82% yield; yellow solid; m.p. 113.5 – 114.7 °C (uncorrected).

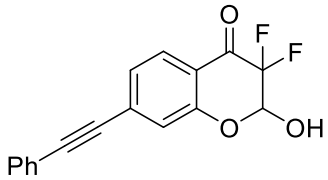
^{1}H NMR (500 MHz, DMSO-d6) δ 8.92 (s, 1H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.56 – 7.46 (m, 4H), 7.34 (s, 1H), 7.28 (d, *J* = 17.5 Hz, 1H), 7.23 (d, *J* = 5.0 Hz, 2H), 6.00 (s, 1H), 2.32 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ 180.72 (t, *J* = 25.0 Hz, 1C), 158.15, 148.14, 138.97, 134.19, 133.93, 129.92, 127.87, 127.65, 126.12, 121.35, 117.49, 116.42, 108.8 (dd, *J* = 258.8 Hz, 246.3 Hz, 1C), 94.3 (dd, *J* = 33.8 Hz, 27.5 Hz, 1C), 21.39.

^{19}F NMR (471 MHz, DMSO-d6) δ -118.9 (d, *J* = 273.9 Hz), -133.4 (d, *J* = 273.7 Hz).

HRMS m/z (ESI) calcd for $C_{18}H_{15}F_2O_3$ $[M+H]^+$ 317.0984, found 317.0984.

3,3-difluoro-2-hydroxy-7-(phenylethynyl)chroman-4-one (***2l***)



91.5 mg, 61% yield; yellow solid; m.p. 45.3 – 46.2 ºC (uncorrected).

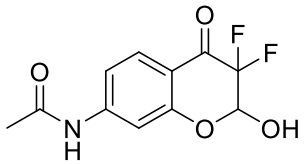
^{1}H NMR (500 MHz, DMSO-d6) δ 9.08 (d, *J* = 5.0 Hz, 1H), 7.88 (d, *J* = 10.0 Hz, 1H), 7.61 (d, *J* = 10.0 Hz, 2H), 7.47 – 7.46 (m, 3H), 7.37 (d, *J* = 5.0 Hz, 2H), 6.07 (s, 1H).

^{13}C NMR (126 MHz, DMSO-d6) δ 181.13 (t, *J* = 25.0 Hz, 1C), 157.64, 132.63, 132.32, 130.30, 129.43, 128.06, 126.41, 121.83, 121.80, 118.69, 108.9 (dd, *J* = 258.8 Hz, 245.0 Hz, 1C), 95.16, 94.5 (dd, *J* = 33.8 Hz, 27.5 Hz, 1C), 88.49.

^{19}F NMR (471 MHz, DMSO-*d*$_6$) δ -119.2 (d, *J* = 274.1 Hz), -133.7 (d, *J* = 274.1 Hz).

HRMS m/z (ESI) calcd for $C_{17}H_{11}F_2O_3$ $[M+H]^+$ 301.0671, found 301.0673

N-(3,3-difluoro-2-hydroxy-4-oxochroman-7-yl)acetamide (**2m**)



97.7 mg, 76% yield; brown solid; m.p. 128.2 – 129.5 ºC (uncorrected).

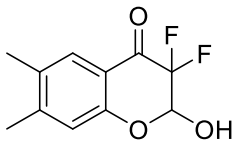
^{1}H NMR (500 MHz, DMSO-d6) δ 10.16 (s, 1H), 8.17 (d, *J* = 5.0 Hz, 1H), 7.83 (dd, *J* = 10.0, 5.0 Hz, 1H), 7.14 (d, *J* = 10.0 Hz, 1H), 5.98 (s, 1H), 4.04 (br, 1H), 2.06 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ 181.74 (t, *J* = 25.0 Hz, 1C), 169.04, 153.44, 135.12, 130.38, 128.48, 126.69, 119.95, 116.30, 109.0 (dd, *J* = 257.5 Hz, 245.0 Hz, 1C), 94.3 (dd, *J* = 32.5 Hz, 26.3 Hz, 1C), 24.40.

^{19}F NMR (471 MHz, DMSO-d6) δ -119.6 (d, J = 274.1 Hz), -133.8 (d, J = 274.1 Hz).

HRMS m/z (ESI) calcd for $C_{11}H_{10}F_2NO_4$ $[M+H]^+$ 258.0572, found 258.0574.

3,3-difluoro-2-hydroxy-6,7-dimethylchroman-4-one (**2n**)



91.2 mg, 80% yield; pale yellow solid; m.p. 44.7 – 45.6 °C (uncorrected).

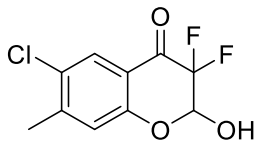
^{1}H NMR (500 MHz, DMSO-d6) δ 8.80 (s, 1H), 7.57 (s, 1H), 6.94 (s, 1H), 5.91 (s, 1H), 2.26 (s, 3H), 2.19 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ 181.21 (t, *J* = 25.0 Hz, 1C), 156.15, 150.08, 132.19, 127.13, 119.84, 116.69, 109.0 (dd, *J* = 257.5 Hz, 245.0 Hz, 1C), 94.3 (dd, *J* = 33.8 Hz, 27.5 Hz, 1C), 20.69, 18.77.

^{19}F NMR (471 MHz, DMSO-*d*$_6$) δ -119.1 (d, *J* = 273.8 Hz), -133.6 (d, *J* = 273.6 Hz).

HRMS m/z (ESI) calcd for $C_{11}H_{11}F_2O_3[M+H]^+$ 229.0671, found 229.0672.

6-chloro-3,3-difluoro-2-hydroxy-7-methylchroman-4-one (**2o**)



91.8 mg, 74% yield; pale yellow solid; m.p. 57.1 – 58.2 °C (uncorrected).

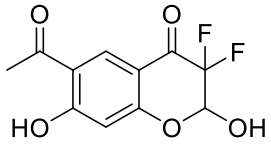
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 6.94 (s, 1H), 5.72 (s, 1H), 3.81 (br, 1H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.80 (t, *J* = 25.0 Hz, 1C), 155.33, 147.86, 129.62, 127.20, 120.96, 117.82, 107.4 (dd, *J* = 260.0 Hz, 247.5 Hz, 1C), 94.3 (dd, *J* = 35.0 Hz, 28.8 Hz, 1C), 21.04.

^{19}F NMR (471 MHz, DMSO-d6) δ -119.5 (dd, *J* = 274.5 Hz, 5.7 Hz), -134.0 (d, *J* = 274.3 Hz)

HRMS m/z (ESI) calcd for $C_{10}H_8ClF_2O_3$ $[M+H]^+$ 249.0125, found 249.0126.

6-acetyl-3,3-difluoro-2,7-dihydroxychroman-4-one (**2p**)



104.5 mg, 81% yield; white solid; m.p. 78.3 – 79.6 °C (uncorrected).

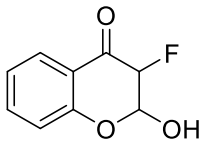
^{1}H NMR (500 MHz, DMSO-d6) δ 12.77 (s, 1H), 9.11 (s, 1H), 8.35 (s, 1H), 6.62 (s, 1H), 6.04 (t, *J* = 3.4 Hz, 1H), 2.65 (s, 3H).

^{13}C NMR (126 MHz, DMSO-d6) δ 202.76, 179.56 (t, *J* = 25.0 Hz, 1C), 168.77, 162.46, 133.27, 128.45, 126.69, 118.52, 112.0 (t, *J* = 2.5 Hz, 1C), 110.71, 107.6 (dd, *J* = 258.8 Hz, 95.0 Hz, 1C), 94.7 (dd, *J* = 35.0 Hz, 28.8 Hz, 1C), 28.54.

^{19}F NMR (471 MHz, DMSO-d_6) δ -118.6 (d, *J* = 274.0 Hz), -133.6 (d, *J* = 274.1 Hz).

HRMS m/z (ESI) calcd for $C_{11}H_9F_2O_5$ $[M+H]^+$ 259.0413, found 259.0414.

3-fluoro-4-oxochroman-2-yl acetate (**3a**, dr: 1:0.38)



82.8 mg, 91% yield; white solid; m.p. 71.1 – 71.9 °C (uncorrected).

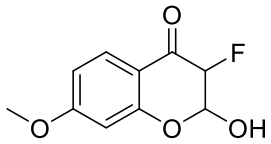
^{1}H NMR (500 MHz, DMSO-d6) δ 8.38 (d, *J* = 10.0 Hz, 1H), 8.05 (d, *J* = 5.0 Hz, 1H), 7.75 – 7.72(m, 1.33H), 7.65 – 7.59 (m, 1.4H), 7.14 – 7.03 (m, 2.69H), 5.94 (d, *J* = 5.0 Hz, 1H), 5.82 (s, 0.5H), 5.73 (s, 0.89H), 5.24 - 5.12 (m, 0.4H).

^{13}C NMR (126 MHz, DMSO-d6) δ 188.9 (d, *J* = 12.5 Hz, 1C), 188.6 (d, *J* = 12.5 Hz, 1C), 158.56, 157.59, 137.57, 137.08, 127.01, 126.18, 126.17, 122.56, 122.32, 120.55, 119.79, 118.74, 118.51, 96.2 (d, *J* = 25.0 Hz, 1C), 95.2 (d, *J* = 12.5 Hz, 1C), 89.6 (d, *J* = 187.5 Hz, 1C), 89.4 (d, *J* = 187.5 Hz, 1C).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -201.4 , -205.1.

HRMS m/z (ESI) calcd for $C_9H_8FO_3$ $[M+H]^+$ 183.0452, found 183.0454.

3-fluoro-2-hydroxy-7-methoxychroman-4-one (**3b**, dr: 1:0.49)



87.9 mg, 83% yield; white solid; m.p. 75.3 – 76.7 °C (uncorrected).

^{1}H NMR (500 MHz, DMSO-d6) δ 8.42 (s, 0.49H), 8.10 (s, 1H), 7.69 – 7.65 (m, 2H), 7.39 – 7.34 (m, 0.81H), 6.71 – 6.65 (m, 1.58H), 6.59 (s, 0.48H), 6.55 (s, 1H), 5.91 (s, 1H), 5.72 (s, 0.59H), 5.69 (s, 0.48H), 5.63 (s, 0.47H), 5.08 (dd, *J* = 47.5 Hz, 8.0 Hz, 0.48H), 3.82 (s, 4.33H).

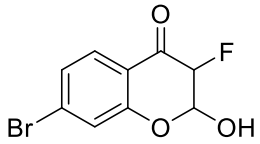
^{13}C NMR (126 MHz, DMSO-d6) δ 187.3 (d, *J* = 12.5 Hz, 1C), 186.9 (d, *J* = 12.5 Hz, 1C), 167.11, 166.73, 160.81, 159.88, 128.06, 126.64, 114.11, 113.43, 111.18, 110.37, 102.53, 101.89, 96.4 (d, *J* = 25.0 Hz, 1C), 95.30 (d, *J* = 25.0 Hz, 1C), 89.5 (d, *J* =

175.0 Hz, 1C), 89.0 (d, *J* = 187.5 Hz, 1C), 56.44.

^{19}F NMR (471 MHz, $CDCl_3$) δ -207.2, -211.1.

HRMS m/z (ESI) calcd for $C_{10}H_{10}FO_4$ $[M+H]^+$ 213.0558, found 213.0558.

7-bromo-3-fluoro-2-hydroxychroman-4-one (**3d**, dr: 1:0.33)



117.1 mg, 90% yield; white solid; m.p. 63.5.3 – 65.7 ºC (uncorrected).

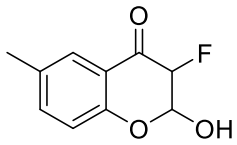
^{1}H NMR (500 MHz, DMSO-d6) δ 8.54 (s, 0.33H), 8.24 (s, 1H), 7.67 (d, *J* = 10.0 Hz, 0.41H), 7.65 (d, *J* = 10.0 Hz, 1H), 7.40 – 7.31 (m, 2.82H), 5.98 (s, 1H), 5.86 (d, *J* = 5.0 Hz, 0.52H), 5.80 (d, *J* = 5.0 Hz, 0.44H), 5.76 (d, *J* = 5.0 Hz, 0.51H), 5.23 (dd, *J* = 47.5 Hz, 8.0 Hz, 0.38H).

^{13}C NMR (126 MHz, DMSO-d6) δ 188.3 (d, *J* = 25.0 Hz, 1C), 188.0 (d, *J* = 12.5 Hz, 1C), 158.97, 158.08, 130.93, 130.36, 128.67, 127.91, 127.89, 125.94, 125.74, 121.67, 121.40, 119.84, 119.08, 96.6 (d, *J* = 25.0 Hz, 1C), 95.7 (d, *J* = 25.0 Hz, 1C), 89.5 (d, *J* = 175.0 Hz, 1C), 89.2 (d, *J* = 200 Hz, 1C).

^{19}F NMR (471 MHz, $CDCl_3$) δ -205.9, -210.5.

HRMS m/z (ESI) calcd for $C_9H_7BrFO_3$ $[M+H]^+$ 260.9557, found 260.9559.

3-fluoro-2-hydroxy-6-methylchroman-4-one (**3f**, dr: 1:0.40)



83.3 mg, 85% yield; white solid; m.p. 70.2 – 71.4 ºC (uncorrected).

^{1}H NMR (500 MHz, DMSO-d6) δ 8.33 (d, *J* = 5.0 Hz, 0.4H), 7.99 (d, *J* = 5.0 Hz, 1H), 7.54 (s, 0.45H), 7.52 (s, 1H), 7.46 (d, *J* = 10.0 Hz, 0.43H), 7.42 (d, *J* = 10.0 Hz, 1H), 6.99 (d, *J* = 10.0 Hz, 0.43H), 6.94 (d, *J* = 5.0 Hz, 1H), 5.90 (s, 1H), 5.81 (d, *J* = 5.0 Hz, 0.49H), 5.72 (d, *J* = 5.0 Hz, 0.51H), 5.69 – 5.66 (m, 0.4H), 5.16 (dd, *J* = 47.5 Hz, 8.0 Hz, 0.4H), 2.28 (s, 4.28H).

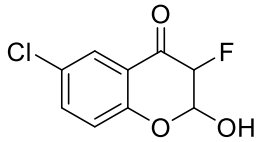
^{13}C NMR (126 MHz, DMSO-d6) δ 188.9 (d, *J* = 12.5 Hz, 1C), 188.3 (d, *J* = 12.5 Hz, 1C), 156.60, 155.56, 138.51, 137.89, 131.78, 131.46, 126.43, 125.74, 120.16, 119.42, 118.59, 118.36, 96.1 (d, *J* = 25.0 Hz, 1C), 95.1 (d, *J* = 25.0 Hz, 1C), 89.8 (d, *J* = 187.5

Hz, 1C), 89.4 (d, *J* = 200.0 Hz, 1C), 20.28.

^{19}F NMR (471 MHz, DMSO-d_6) δ -205.9 , -209.6.

HRMS m/z (ESI) calcd for $C_{10}H_{10}FO_3$ $[M+H]^+$ 197.0608, found 197.0610.

6-chloro-3-fluoro-2-hydroxychroman-4-one (**3h**, dr: 1:0.36)



95.1 mg, 88% yield; white solid; m.p. 85.4 – 86.3 ºC (uncorrected).

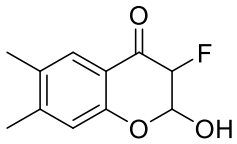
^{1}H NMR (500 MHz, DMSO-d6) δ 8.50 (d, *J* = 5.0 Hz, 0.36H), 8.21 (s, 1H), 7.69 – 7.66 (m, 2.62H), 7.14 (d, *J* = 5.0 Hz, 0.41H), 7.12 (d, *J* = 10.0 Hz, 1H), 5.97 (s, 1H), 5.89 (s, 0.51H), 5.80 (s, 1H), 5.26 (dd, J = 47.5 Hz, 8.0 Hz, 0.38H).

^{13}C NMR (126 MHz, DMSO-d6) δ 188.1 (d, *J* = 12.5 Hz, 1C), 187.8 (d, *J* = 25.0 Hz, 1C), 157.30, 156.28, 137.09, 136.64, 126.72, 126.61, 125.83, 125.13, 121.70, 121.11, 120.95, 120.88, 96.4 (d, *J* = 12.5 Hz, 1C), 95.5 (d, *J* = 25.0 Hz, 1C), 89.6 (d, *J* = 187.5 Hz, 1C), 89.3 (d, *J* = 200 Hz, 1C).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -205.4 , -210.7.

HRMS m/z (ESI) calcd for $C_9H_7ClFO_3$ $[M+H]^+$ 197.0608, found 197.0610.

3-fluoro-2-hydroxy-6,7-dimethylchroman-4-one (**3n**, dr: 1:0.46)



90.3 mg, 86% yield; white solid; m.p. 122.6 – 124.1 ºC (uncorrected).

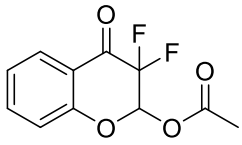
^{1}H NMR (500 MHz, DMSO-d6) δ 8.29 (d, *J* = 5.0 Hz, 0.45H), 7.93 (d, *J* = 5.0 Hz, 1H), 7.49 (s, 0.47H), 7.46 (s, 1H), 6.89 (s, 0.45H), 6.84 (s, 1H), 5.88 (s, 1H), 5.74 (d, *J* = 5.0 Hz, 0.52H), 5.65 – 5.61 (m, 1H), 5.10 (dd, *J* = 47.5 Hz, 8.0 Hz, 0.44H), 2.25 (s, 4.27H), 2.18 (s, 4.24H).

^{13}C NMR (126 MHz, DMSO-d6) δ 188.5 (d, *J* = 12.5 Hz, 1C), 188.1 (d, *J* = 12.5 Hz, 1C), 156.86, 155.86, 148.08, 147.30, 131.14, 130.68, 126.70, 126.05, 119.22, 118.89, 118.13, 117.45, 96.1 (d, *J* = 25.0 Hz, 1C), 95.1 (d, *J* = 25.0 Hz, 1C), 89.8 (d, *J* = 187.5 Hz, 1C), 89.3 (d, *J* = 187.5 Hz, 1C), 20.4 (d, *J* = 10.0 Hz, 1C), 18.7 (d, *J* = 3.75 Hz, 1C).

^{19}F NMR (471 MHz, DMSO-d_6) δ -205.4 , -209.5.

HRMS m/z (ESI) calcd for $C_{11}H_{12}FO_3$ $[M+H]^+$ 211.0765, found 211.0766.

3,3-difluoro-4-oxochroman-2-yl acetate (**4a**)



117.3 mg, 97% yield; pale yellow oil.

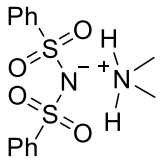
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 10.0, 5.0 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 10.0 Hz, 1H), 6.68 (dd, *J* = 5.0, 2.0 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.18 (t, *J* = 25.0 Hz, 1C), 167.81, 156.50, 138.24, 127.79, 123.81, 118.70, 118.6 (d, *J* = 2.5 Hz, 1C), 106.4 (dd, *J* = 261.3 Hz, 246.3 Hz, 1C), 90.5 (dd, *J* = 37.5 Hz, 30.0 Hz, 1C), 20.44.

^{19}F NMR (471 MHz, Chloroform-d) δ -117.2 (d, *J* = 285.8 Hz), -134.6 (d, *J* = 285.7 Hz).

HRMS m/z (ESI) calcd for $C_{11}H_9F_2O_4$ $[M+H]^+$ 243.0463, found 243.0464.

Dimethylammonium bis(phenylsulfonyl)amide (**5**)



124.8 mg, 73% yield; white solid; m.p. 135.7 – 136.6 ºC (uncorrected).

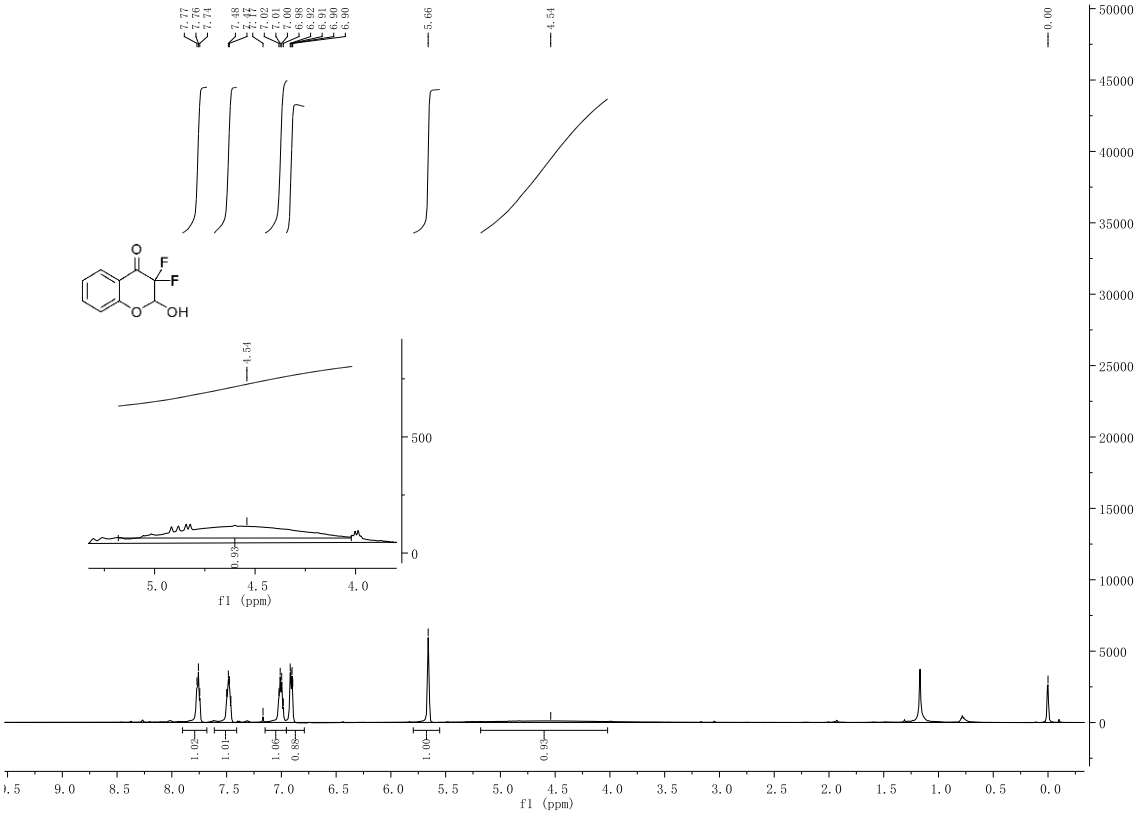
^{1}H NMR (500 MHz, DMSO-d6) δ 9.51 (br, 2H), 9.02 (d, *J* = 5.0 Hz, 3H), 8.74 – 8.69 (m, 5H), 4.82 (d, *J* = 15.0 Hz, 0.86 H), 3.87 (s, 6H).

^{13}C NMR (126 MHz, DMSO-d6) δ 146.68, 146.60, 130.58, 128.37, 126.56, 34.9.

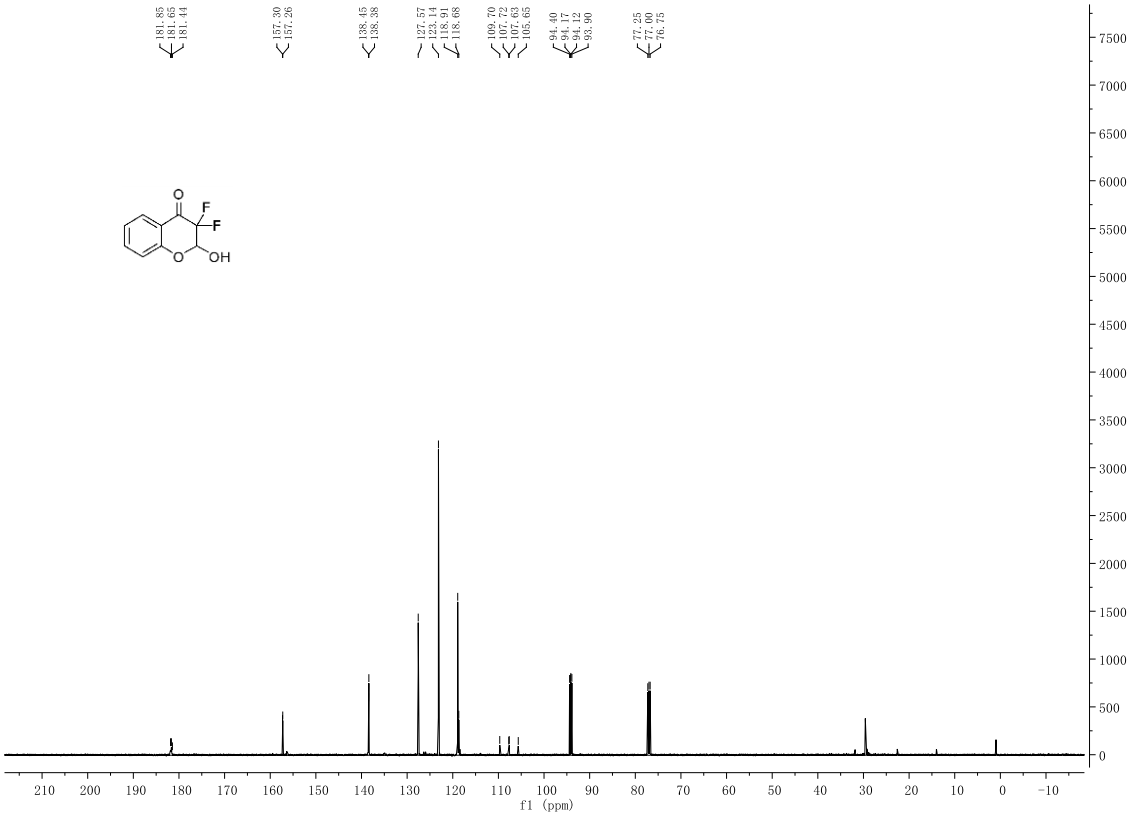
HRMS m/z (ESI) calcd for $C_{14}H_{19}N_2O_4S_2$ $[M+H]^+$ 343.0781, found 343.0783.

(E) Spectra of 2, 3, 4a and 8

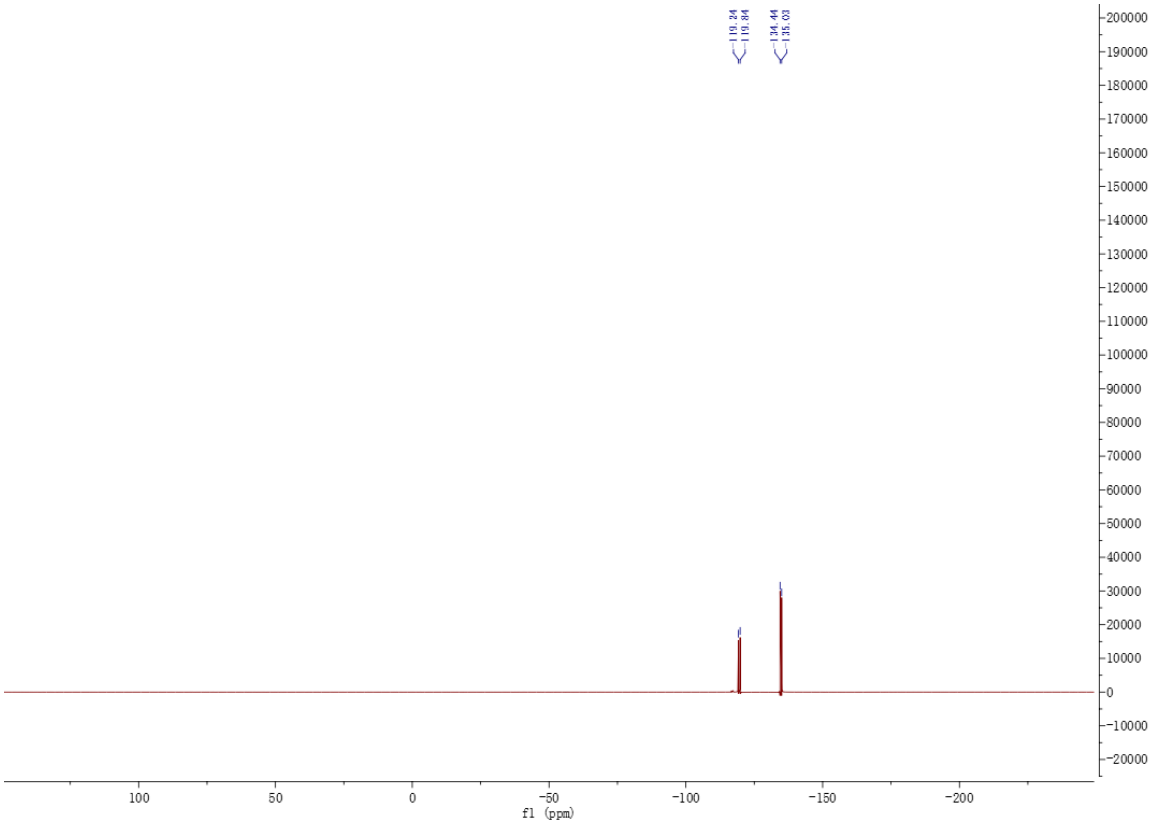
3,3-difluoro-2-hydroxychroman-4-one (2a, ^{1}H NMR, $DCCl_3$, 500 MHz)



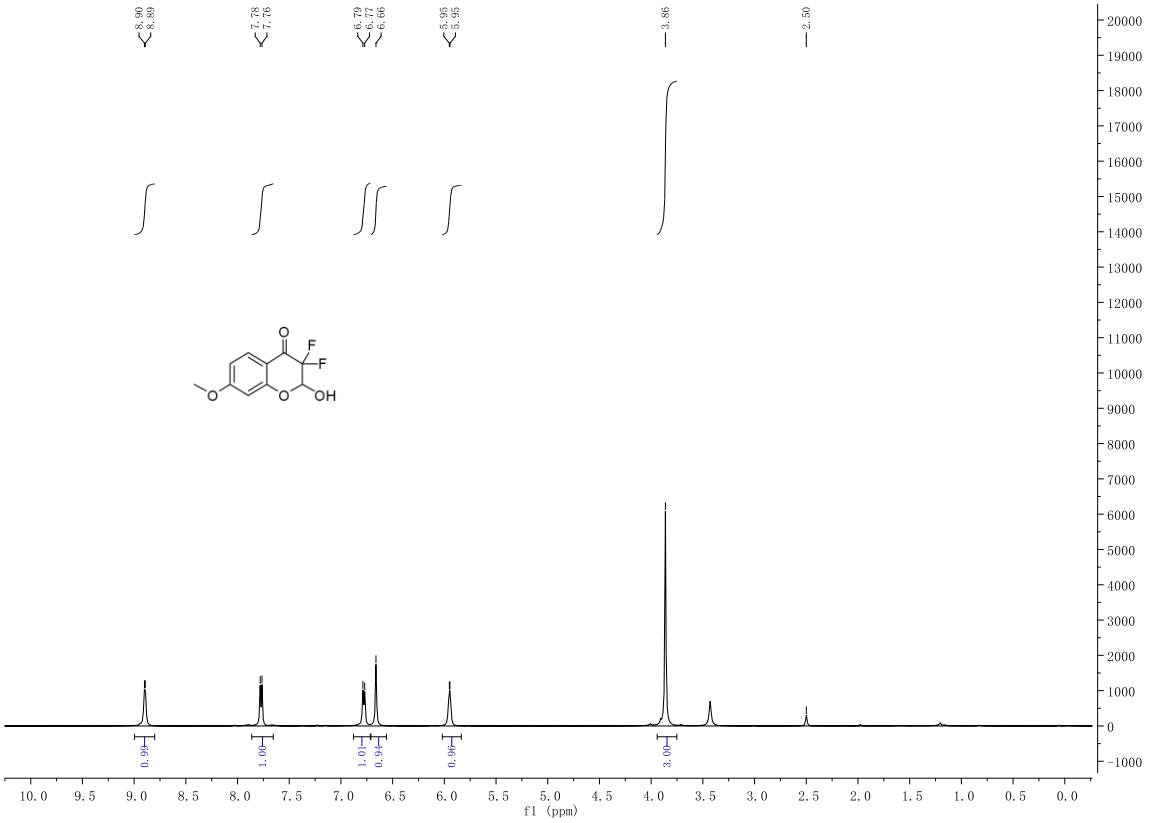
3,3-difluoro-2-hydroxychroman-4-one (2a, ^{13}C NMR, $DCCl_3$, 125 MHz)



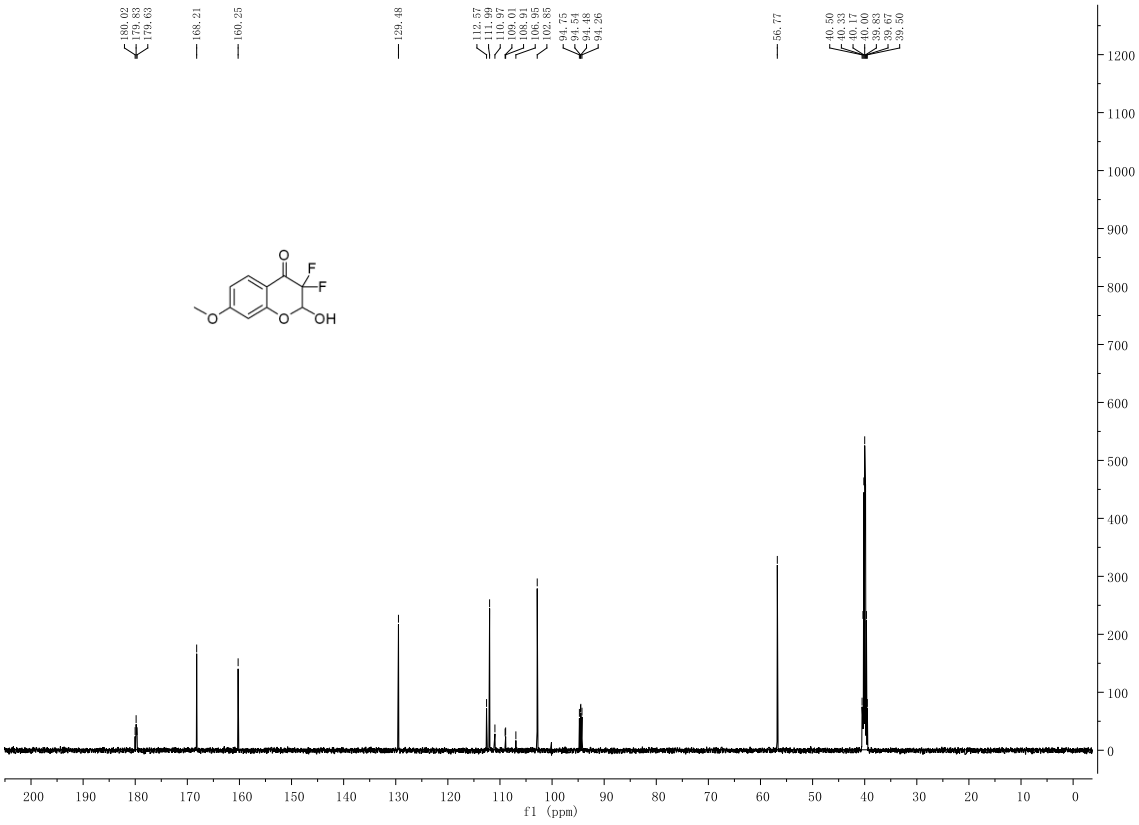
3,3-difluoro-2-hydroxychroman-4-one (2a, ^{19}F NMR, $DCCl_3$, 471 MHz)



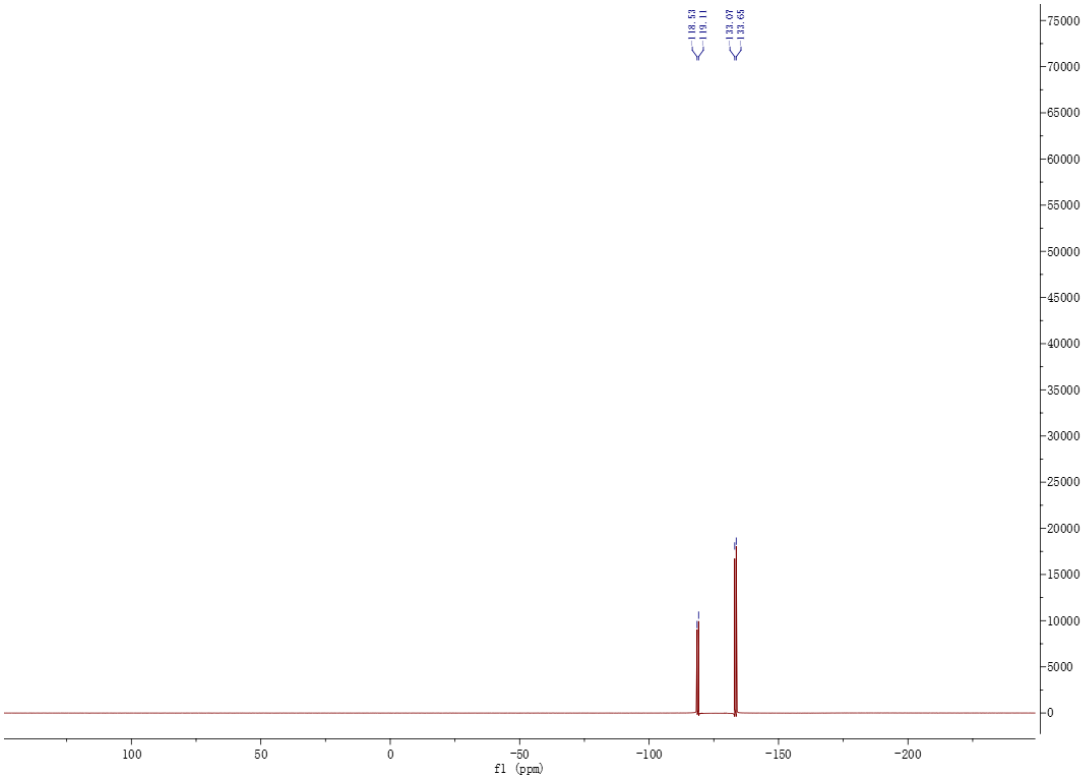
3,3-difluoro-2-hydroxy-7-methoxychroman-4-one (2b, ^{1}H NMR, DMSO-D_6, 500 MHz)



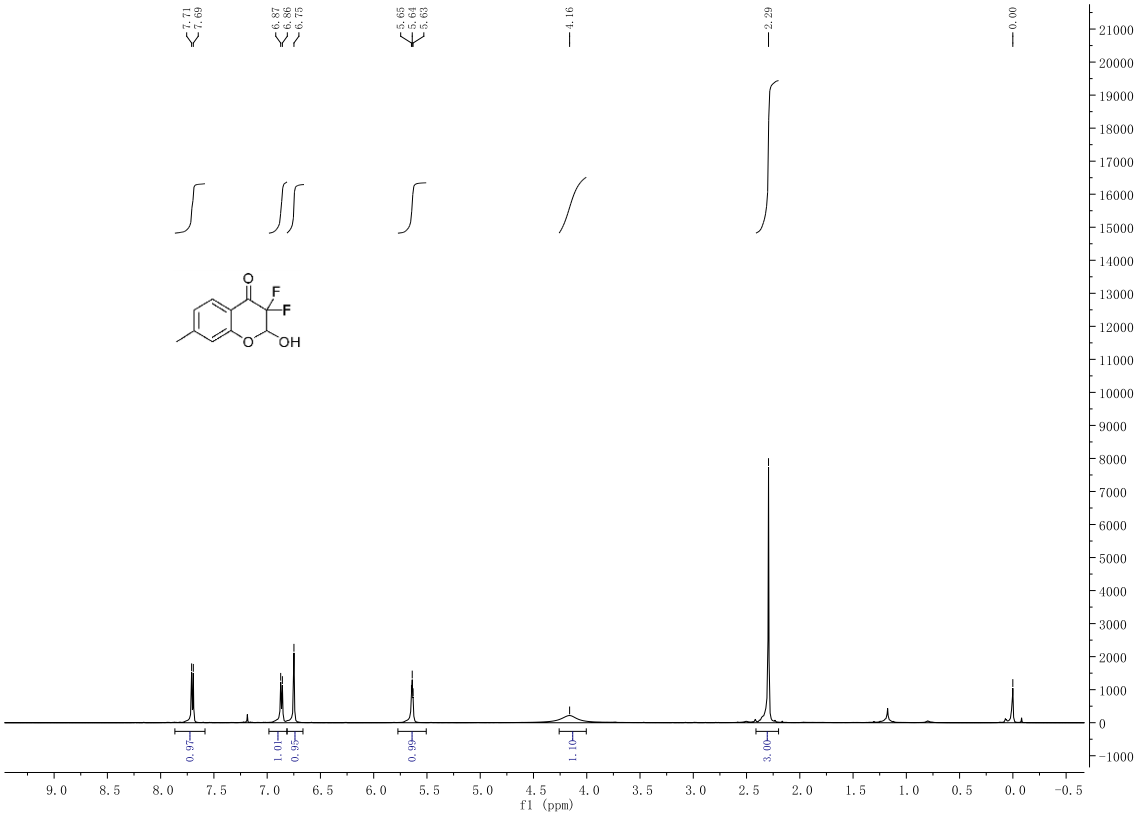
3,3-difluoro-2-hydroxy-7-methoxychroman-4-one (2b, ^{13}C NMR, DMSO-D_6, 125 MHz)



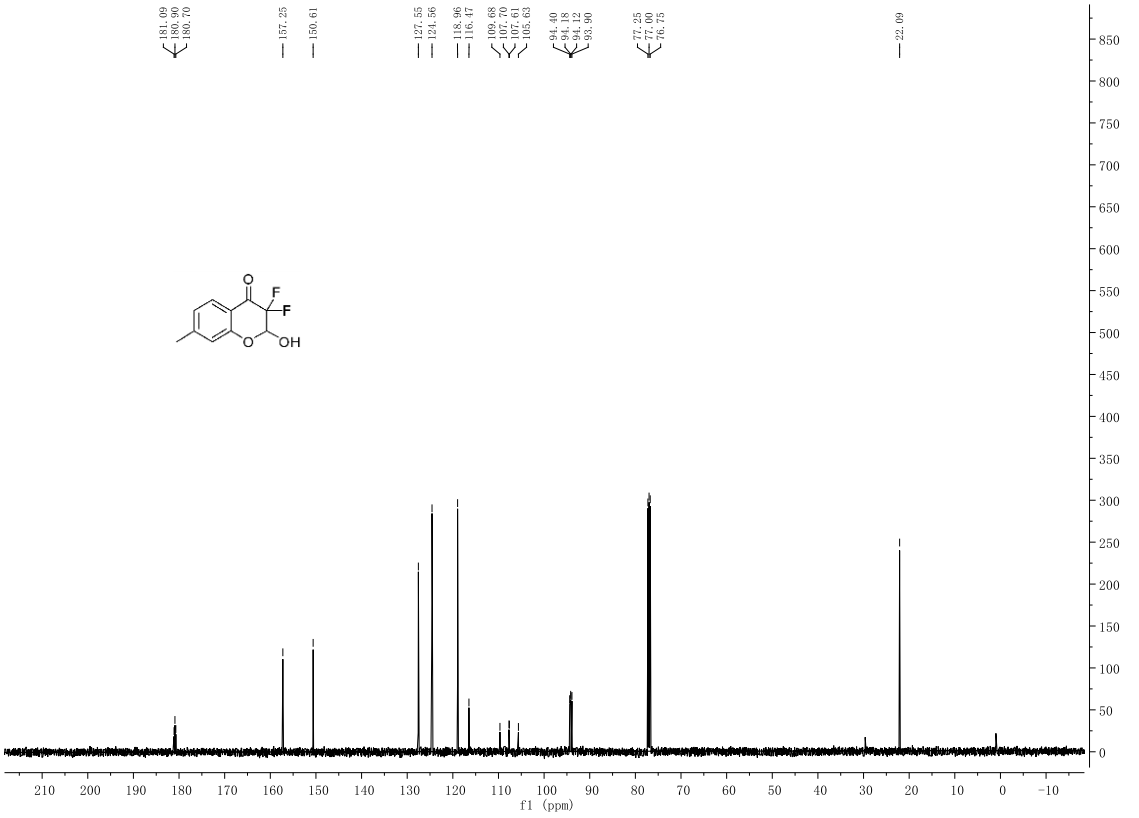
3,3-difluoro-2-hydroxy-7-methoxychroman-4-one (2b, ^{19}F NMR, DMSO-D_6, 471 MHz)



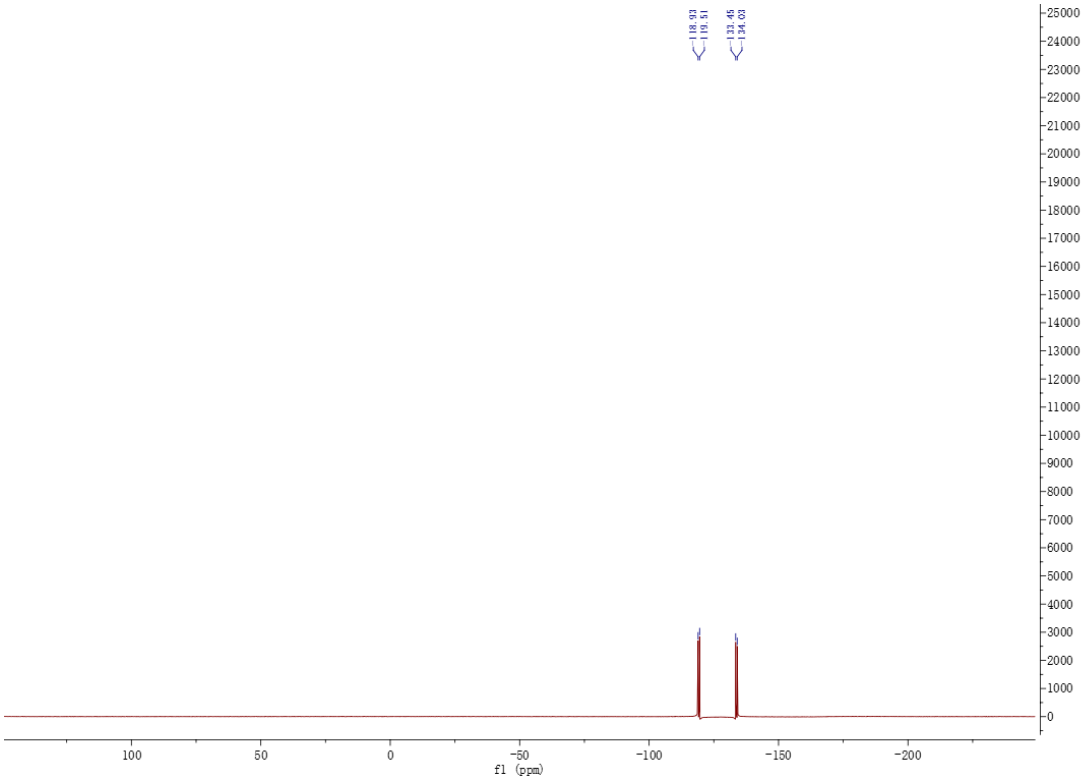
3,3-difluoro-2-hydroxy-7-methylchroman-4-one (2c, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



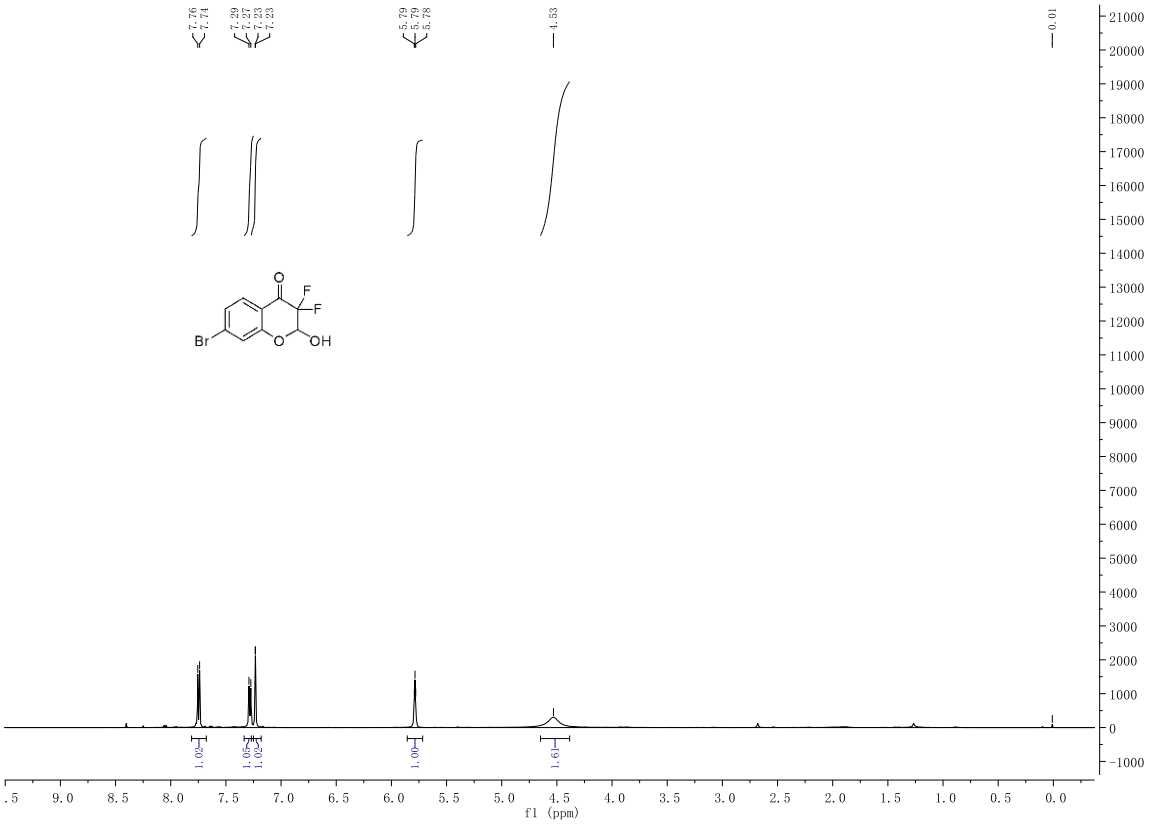
3,3-difluoro-2-hydroxy-7-methylchroman-4-one (2c, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



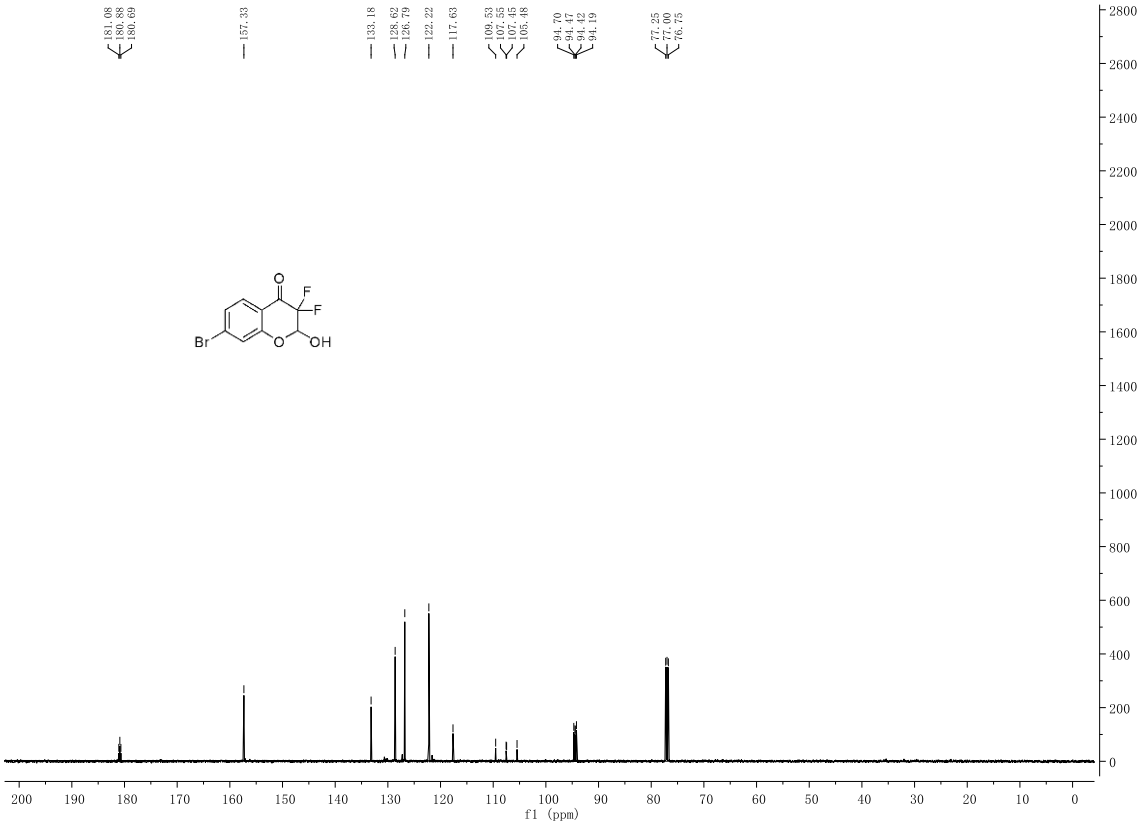
3,3-difluoro-2-hydroxy-7-methylchroman-4-one (2c, ^{19}F NMR, DMSO-D_6, 471 MHz)



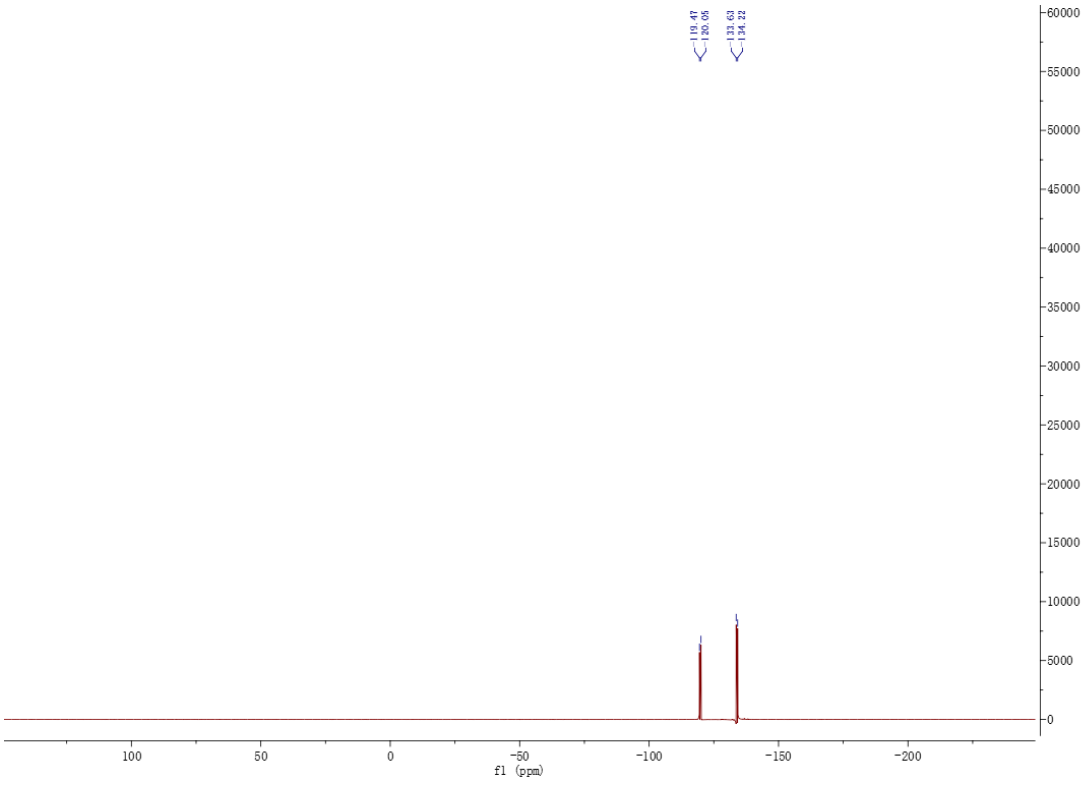
7-bromo-3,3-difluoro-2-hydroxychroman-4-one (2d, ^1H NMR, $DCCl_3$, 500 MHz)



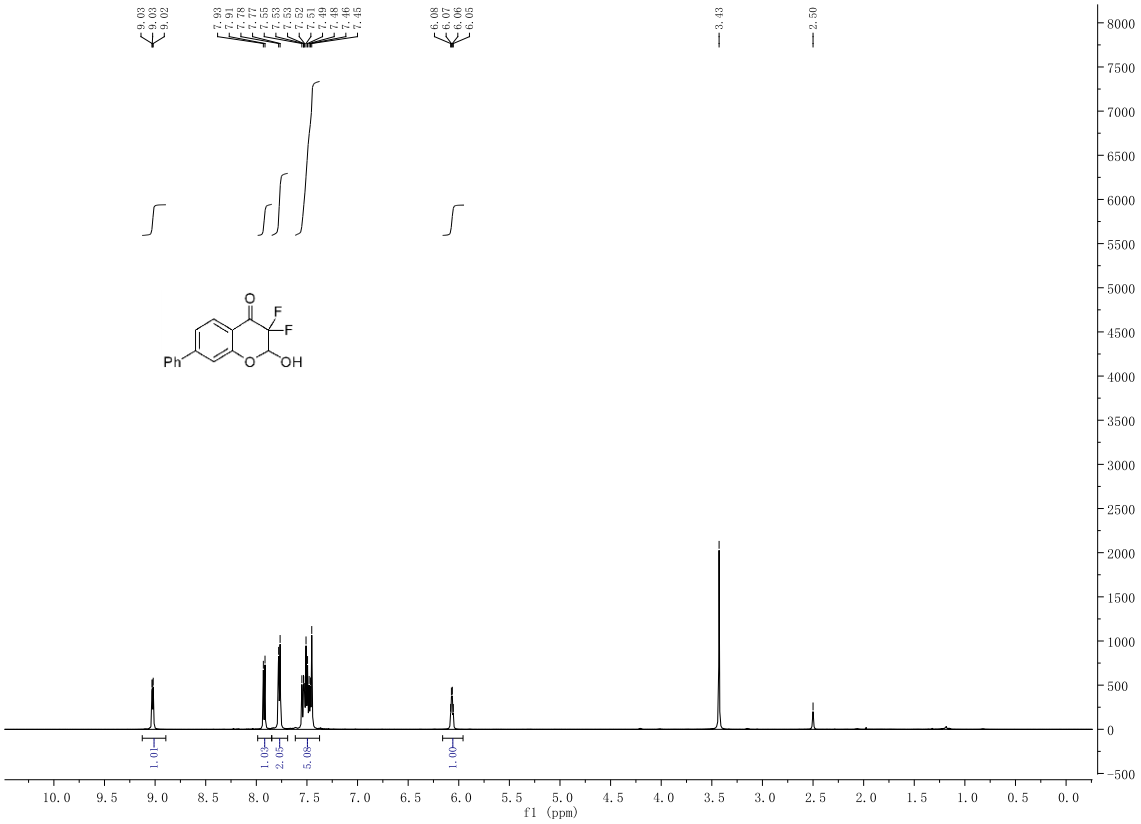
7-bromo-3,3-difluoro-2-hydroxychroman-4-one (2d, ^{13}C NMR, $DCCl_3$, 125 MHz)



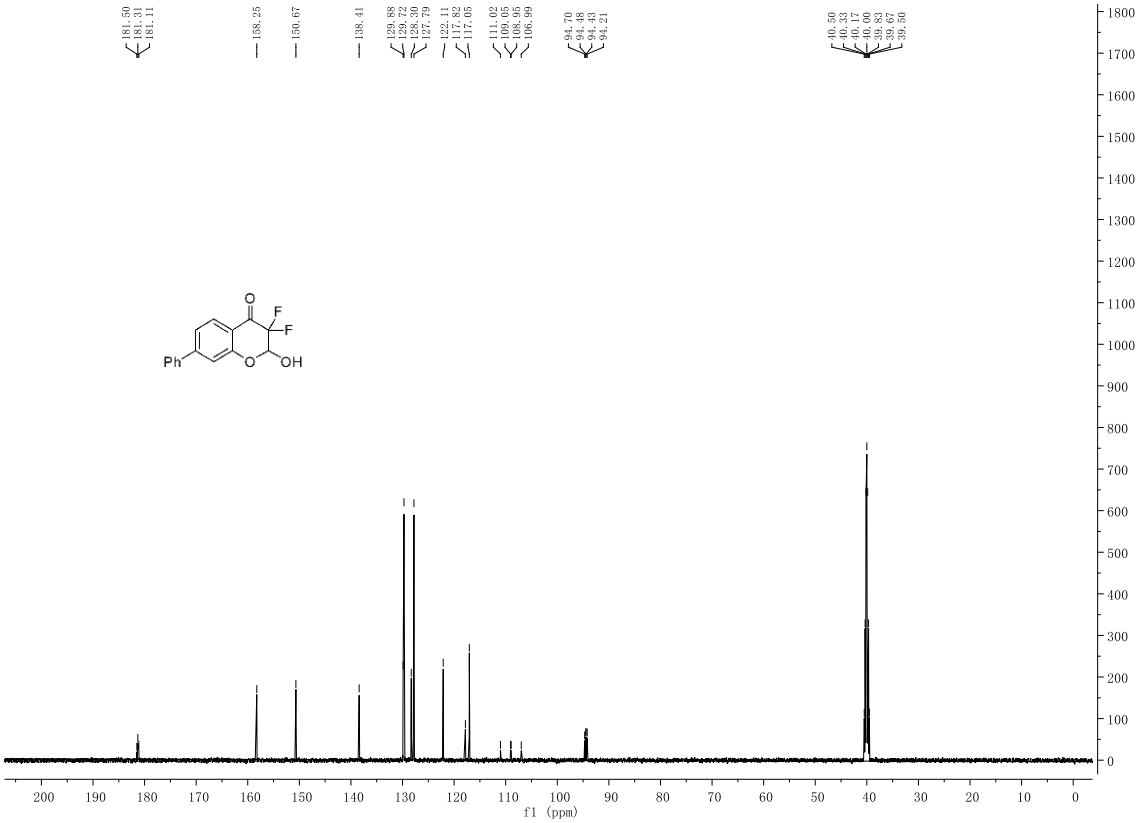
7-bromo-3,3-difluoro-2-hydroxychroman-4-one (2d, ^{19}F NMR, DMSO-D_6, 471 MHz)



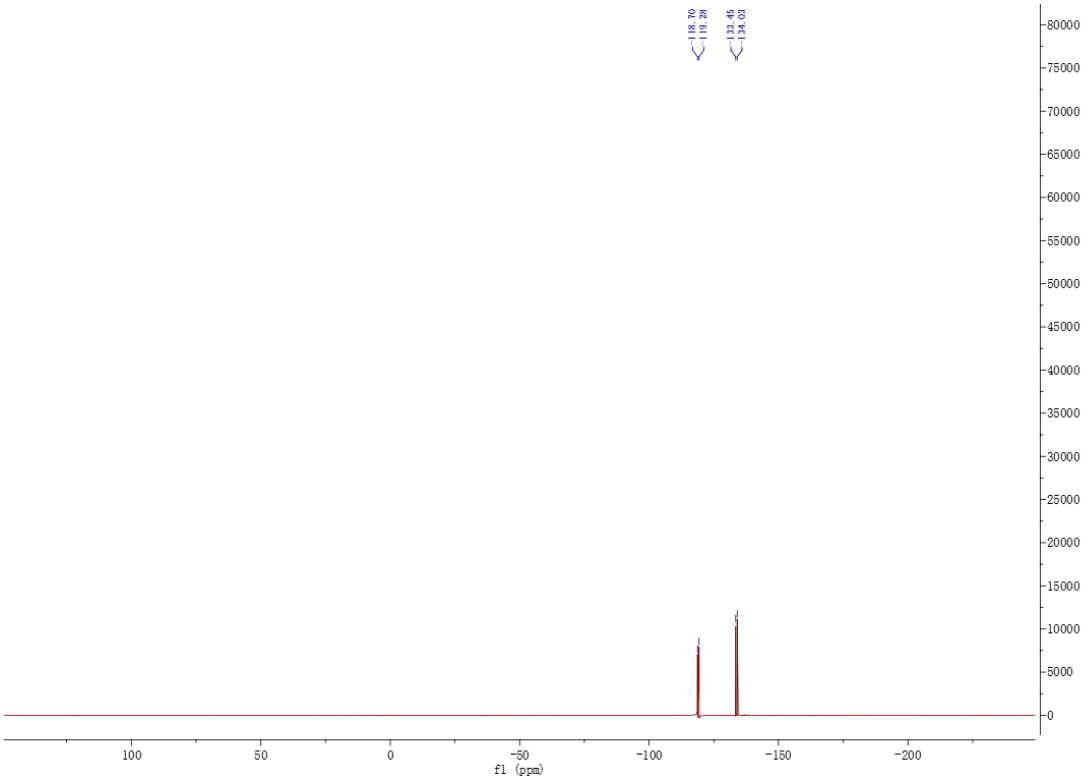
3,3-difluoro-2-hydroxy-7-phenylchroman-4-one (2e, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



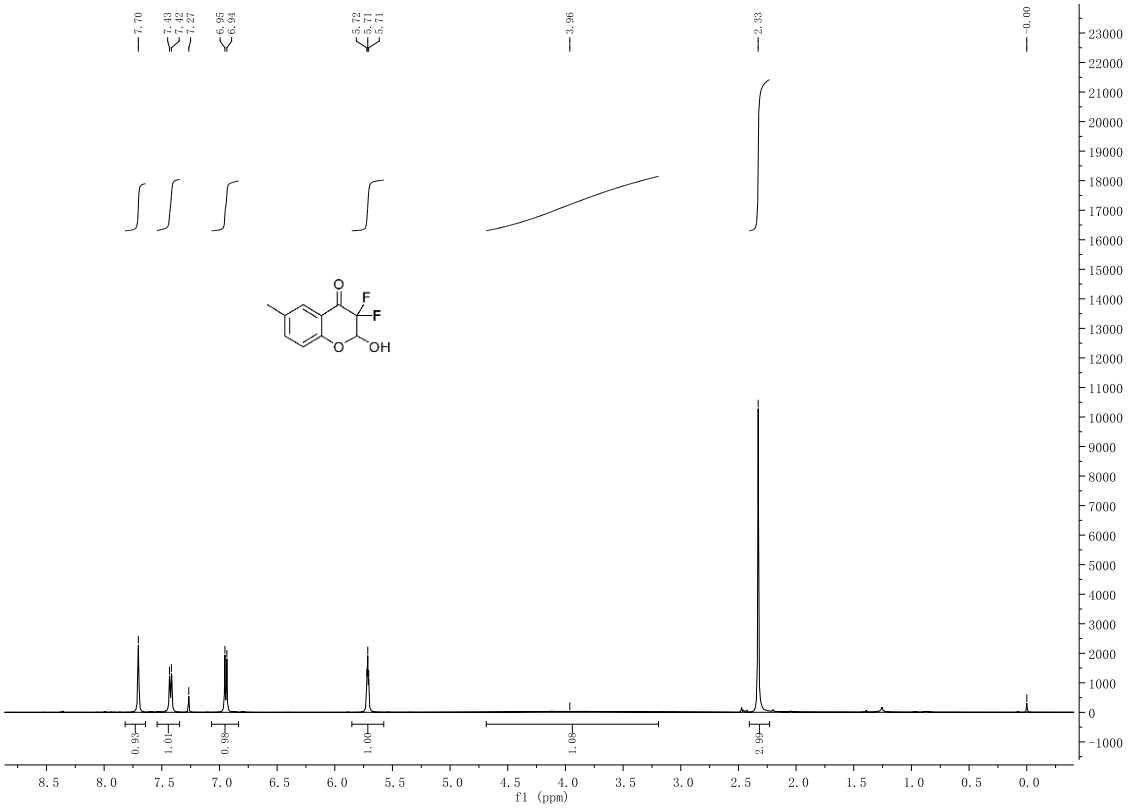
3,3-difluoro-2-hydroxy-7-phenylchroman-4-one (2e, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



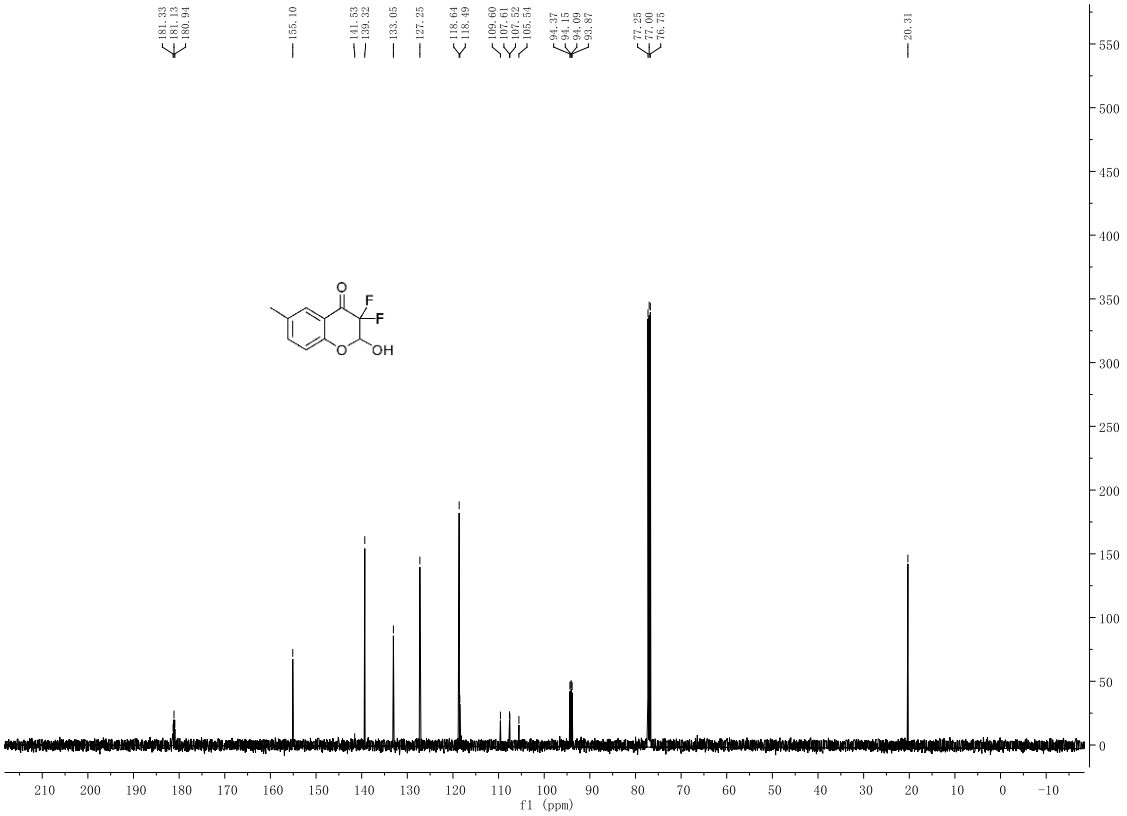
3,3-difluoro-2-hydroxy-7-phenylchroman-4-one (2e, ^{19}F NMR, DMSO-D_6, 471 MHz)



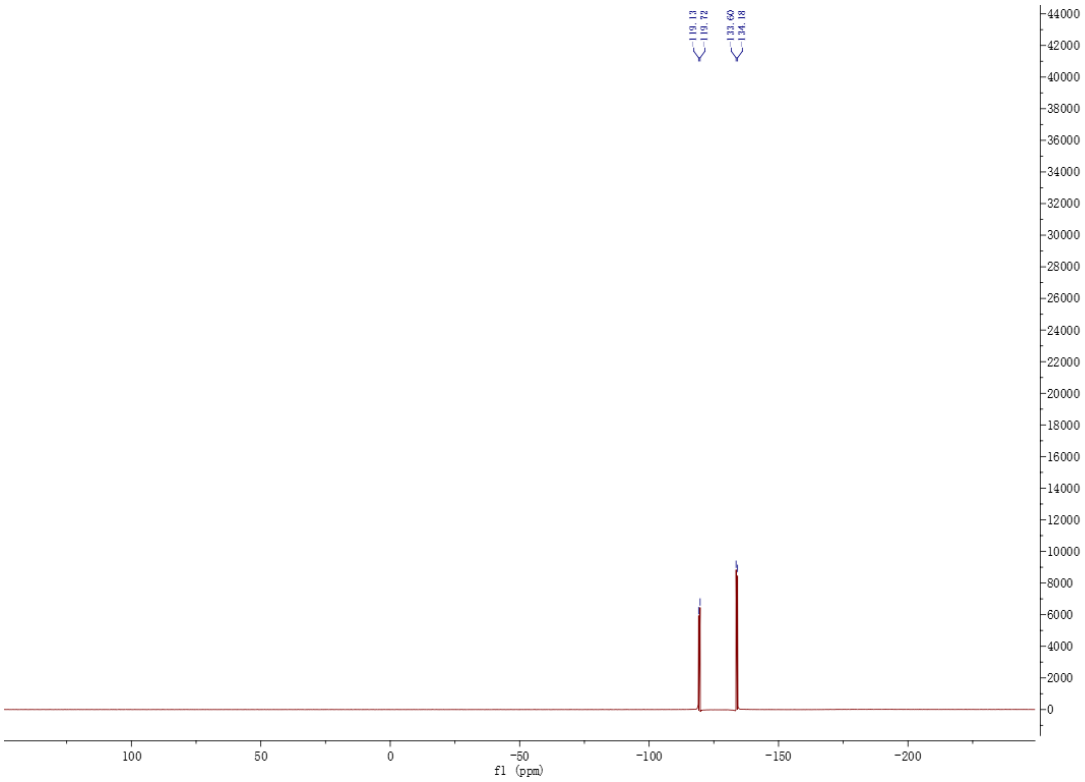
3,3-difluoro-2-hydroxy-6-methylchroman-4-one (2f, ^{1}H NMR, $DCCl_3$, 500 MHz)



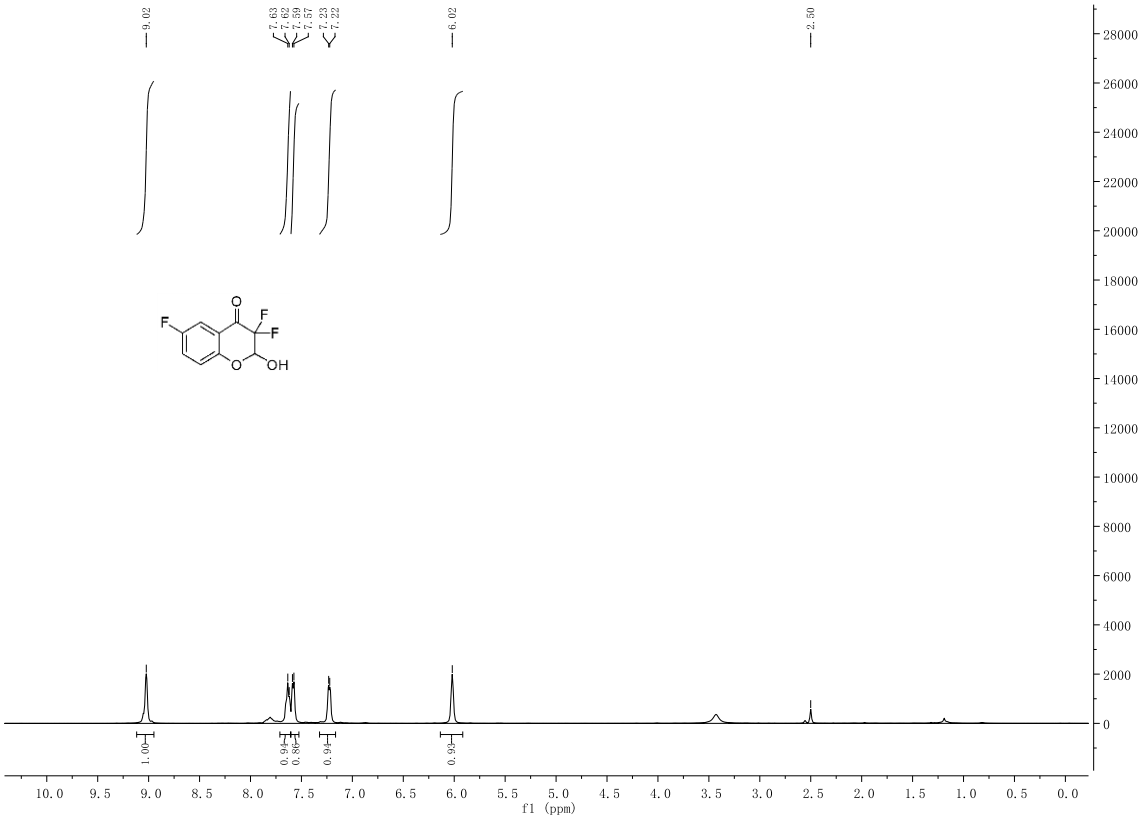
3,3-difluoro-2-hydroxy-6-methylchroman-4-one (2f, ^{13}C NMR, $DCCl_3$, 125 MHz)



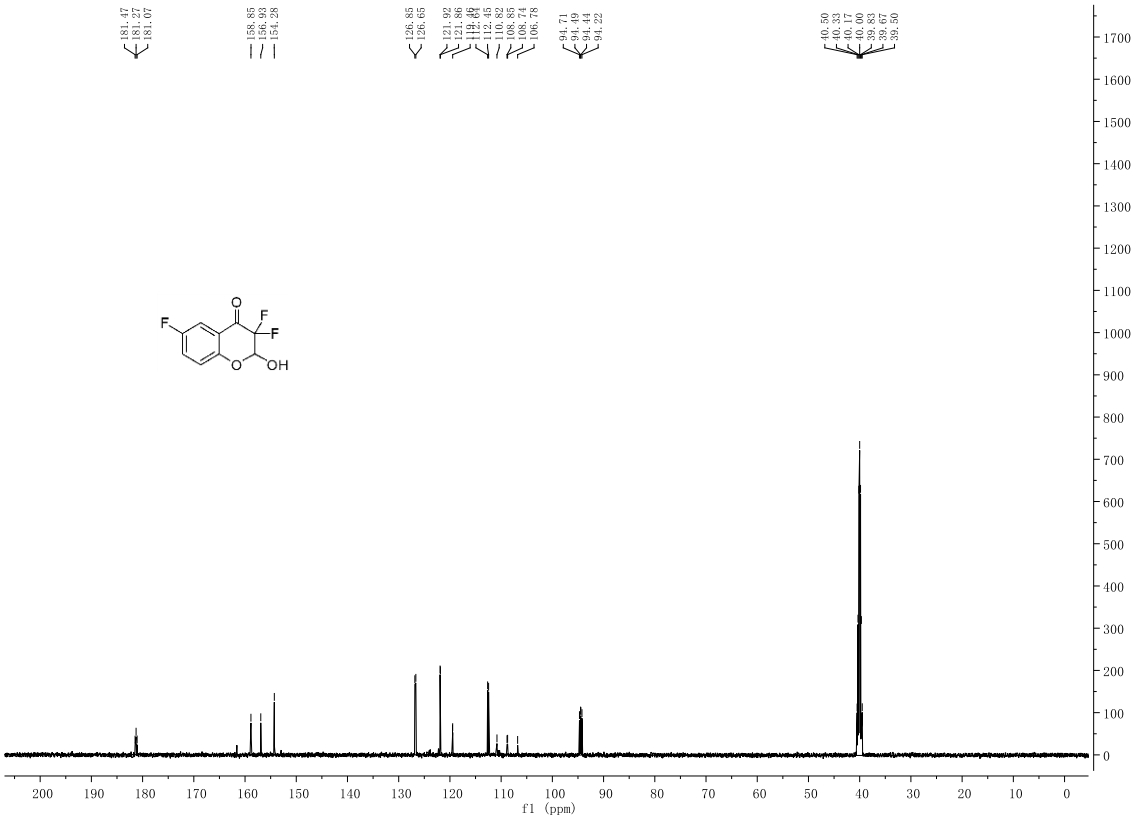
3,3-difluoro-2-hydroxy-6-methylchroman-4-one (2f, ^{19}F NMR, DMSO-D_6, 471 MHz)



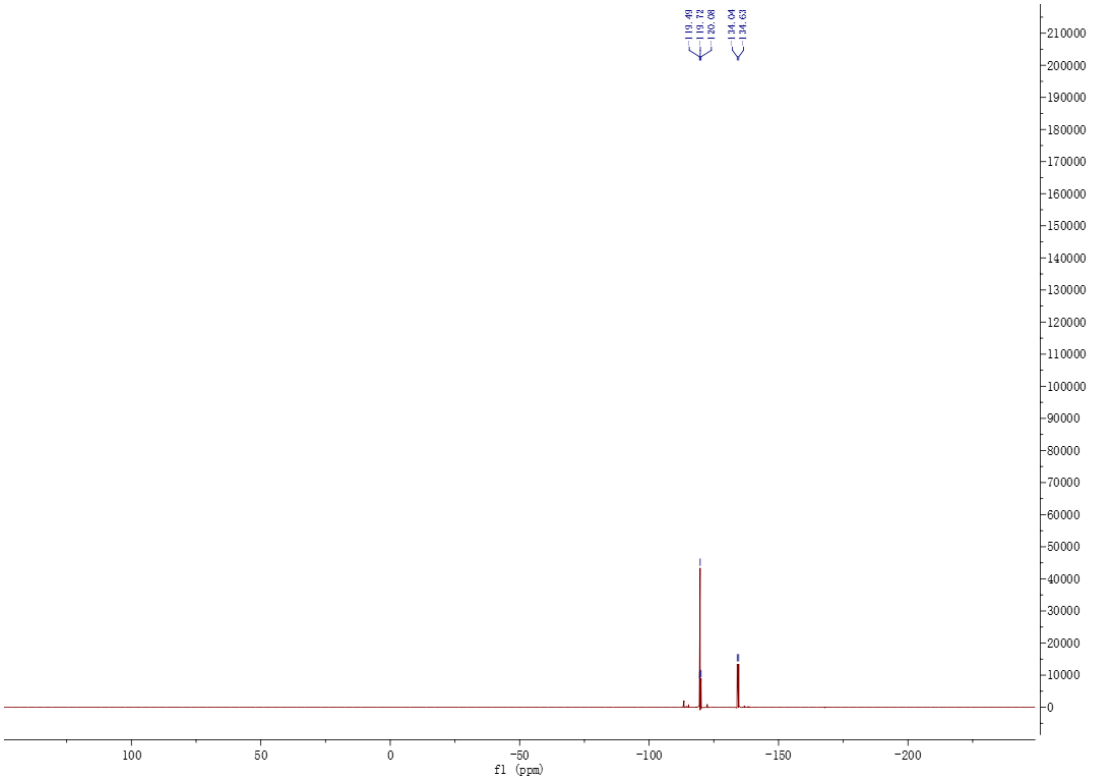
3,3,6-trifluoro-2-hydroxychroman-4-one (2g, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



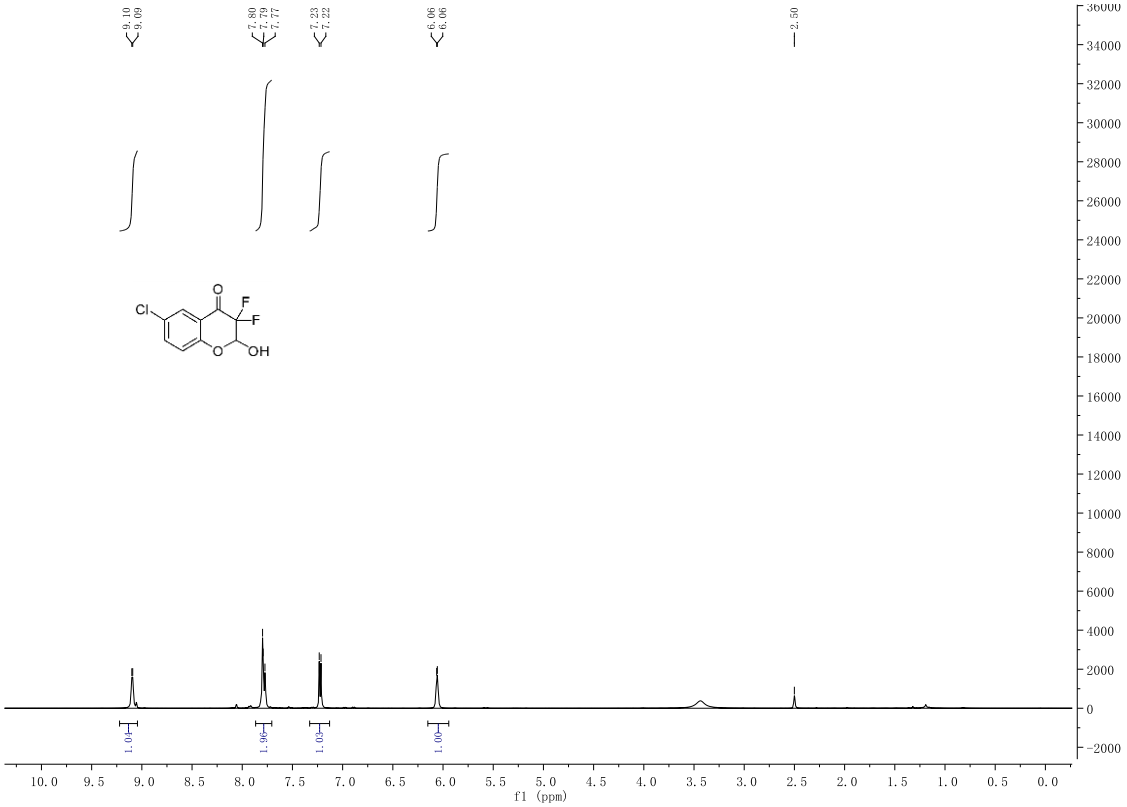
3,3,6-trifluoro-2-hydroxychroman-4-one (2g, ^{13}C NMR, DMSO-D$_6$, DCCl$_3$, 125 MHz)



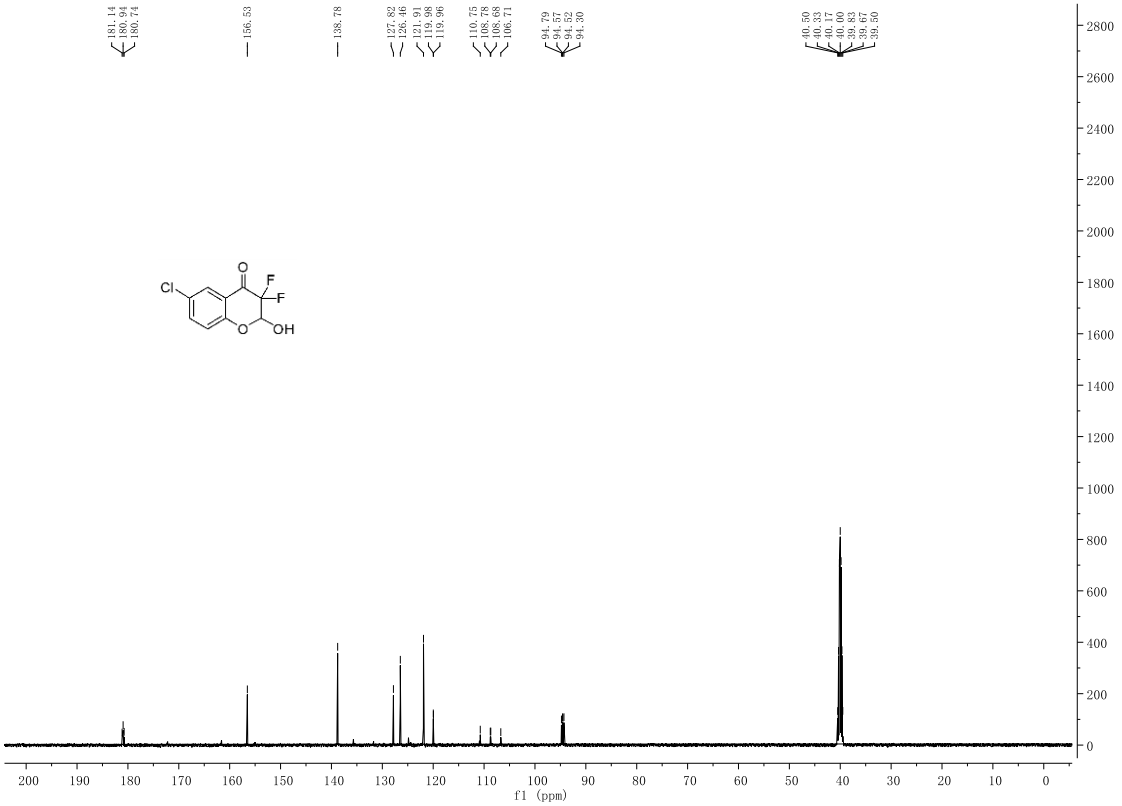
3,3,6-trifluoro-2-hydroxychroman-4-one (2g, ^{19}F NMR, DMSO-D_6, 471 MHz)



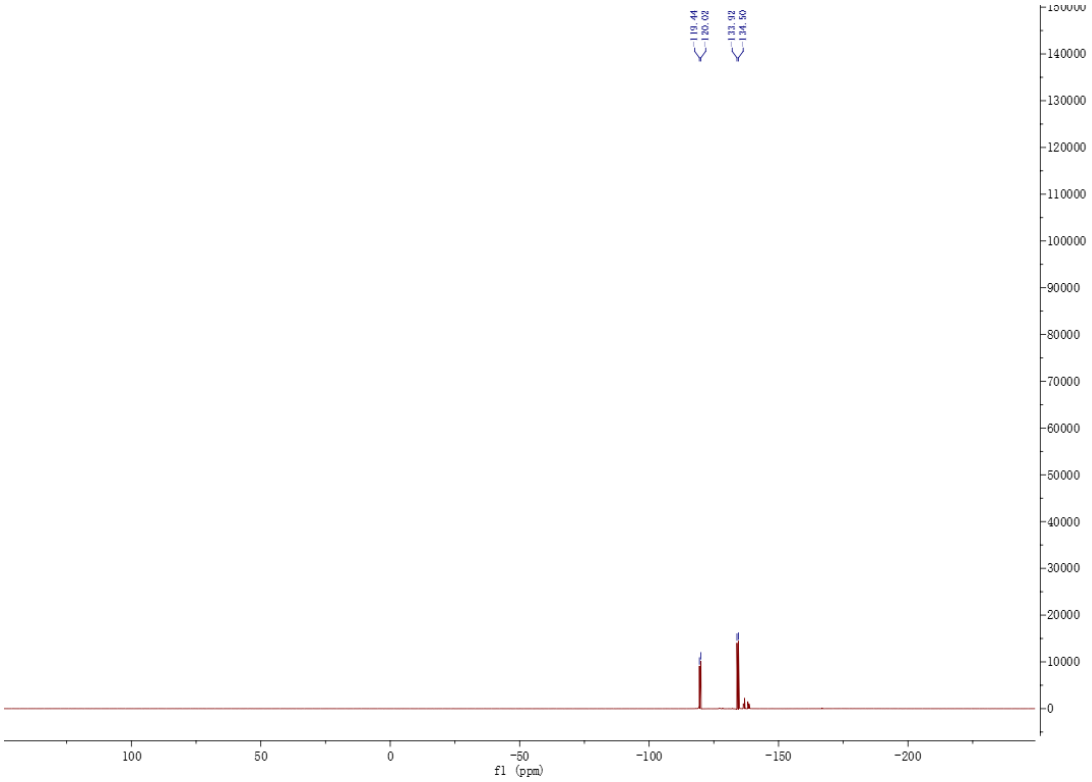
6-chloro-3,3-difluoro-2-hydroxychroman-4-one (2h, ^{1}H NMR, DMSO-D_6, 500 MHz)



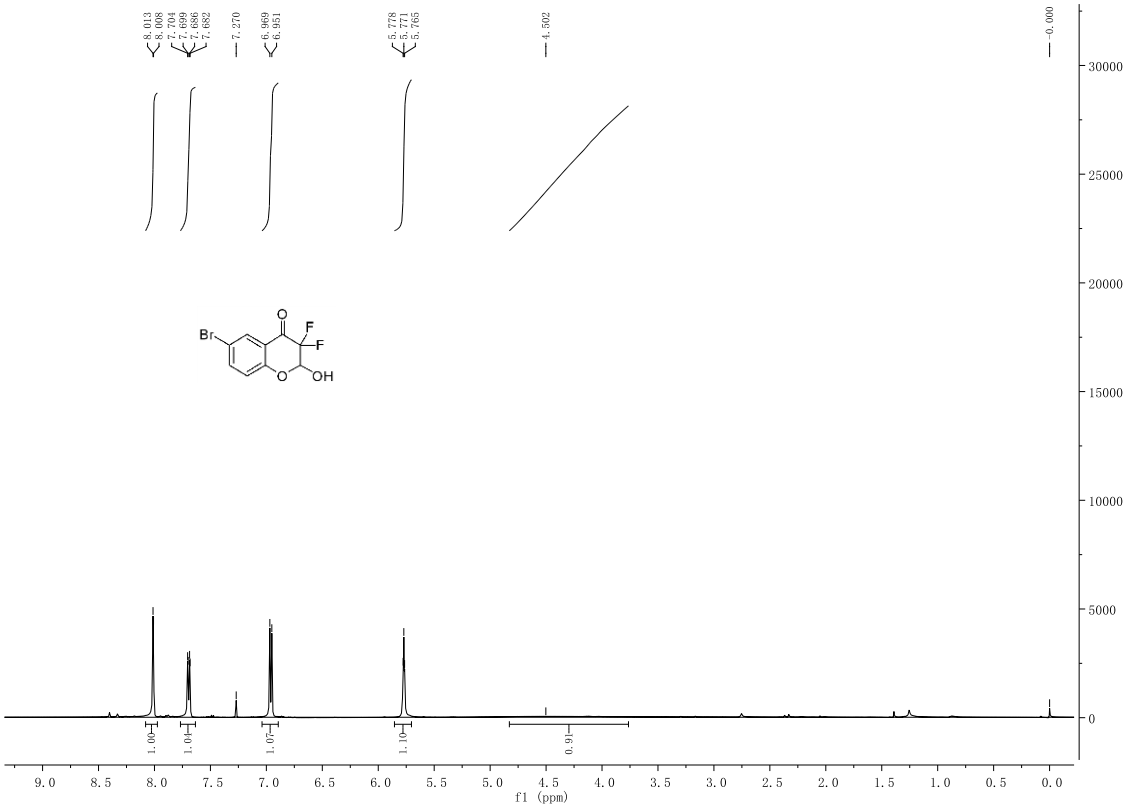
6-chloro-3,3-difluoro-2-hydroxychroman-4-one (2h, ^{13}C NMR, DMSO-D_6, $DCCl_3$, 125 MHz)



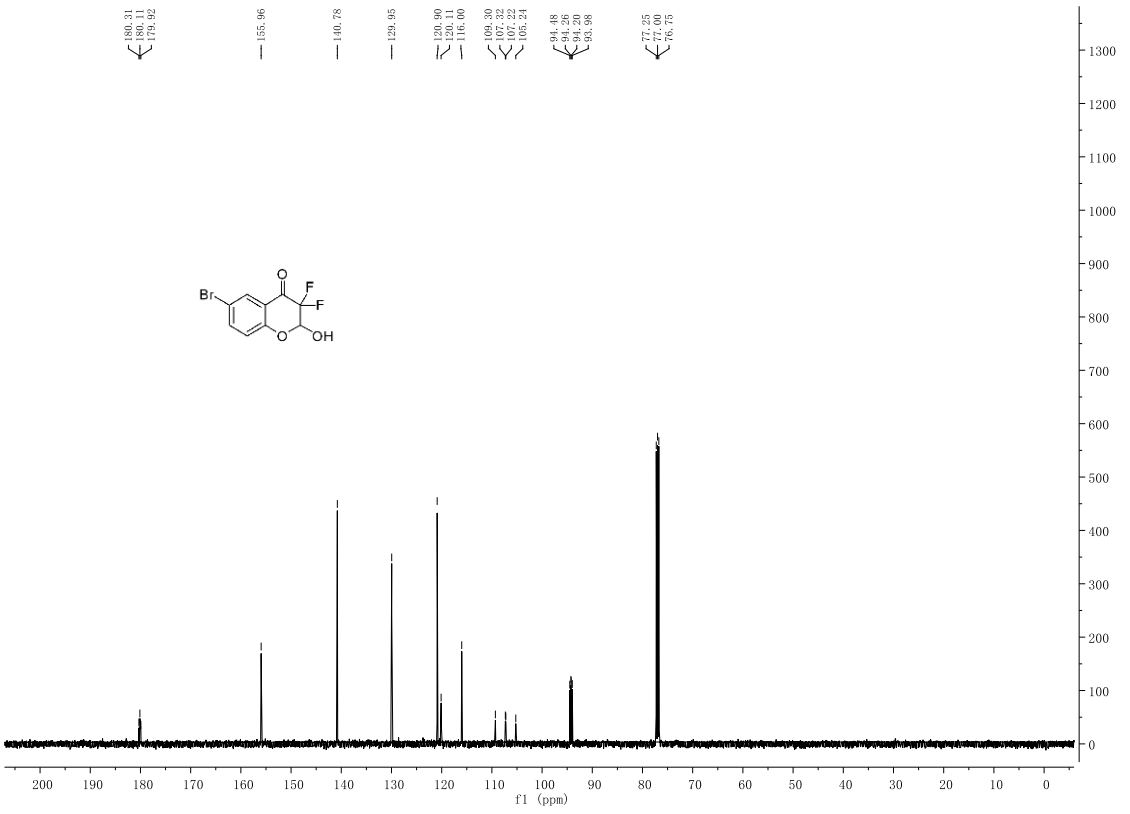
6-chloro-3,3-difluoro-2-hydroxychroman-4-one (2h, ^{19}F NMR, DMSO-D_6, 471 MHz)



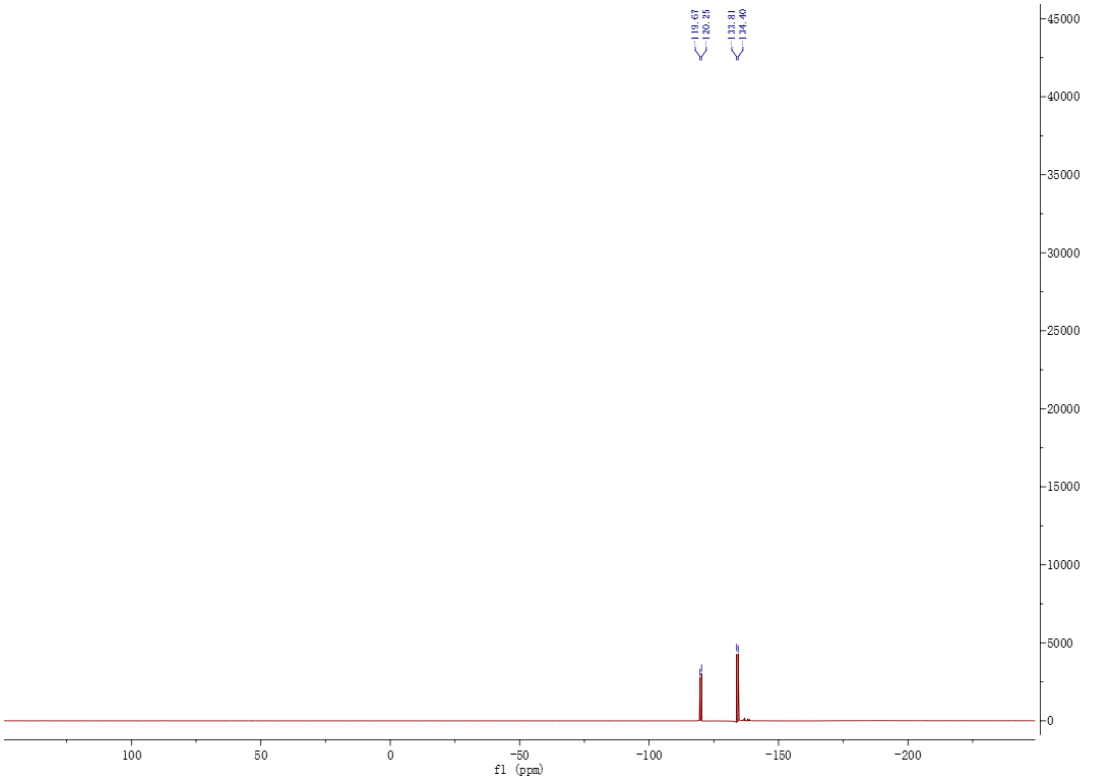
6-bromo-3,3-difluoro-2-hydroxychroman-4-one (2i, ^{1}H NMR, $DCCl_3$, 500 MHz)



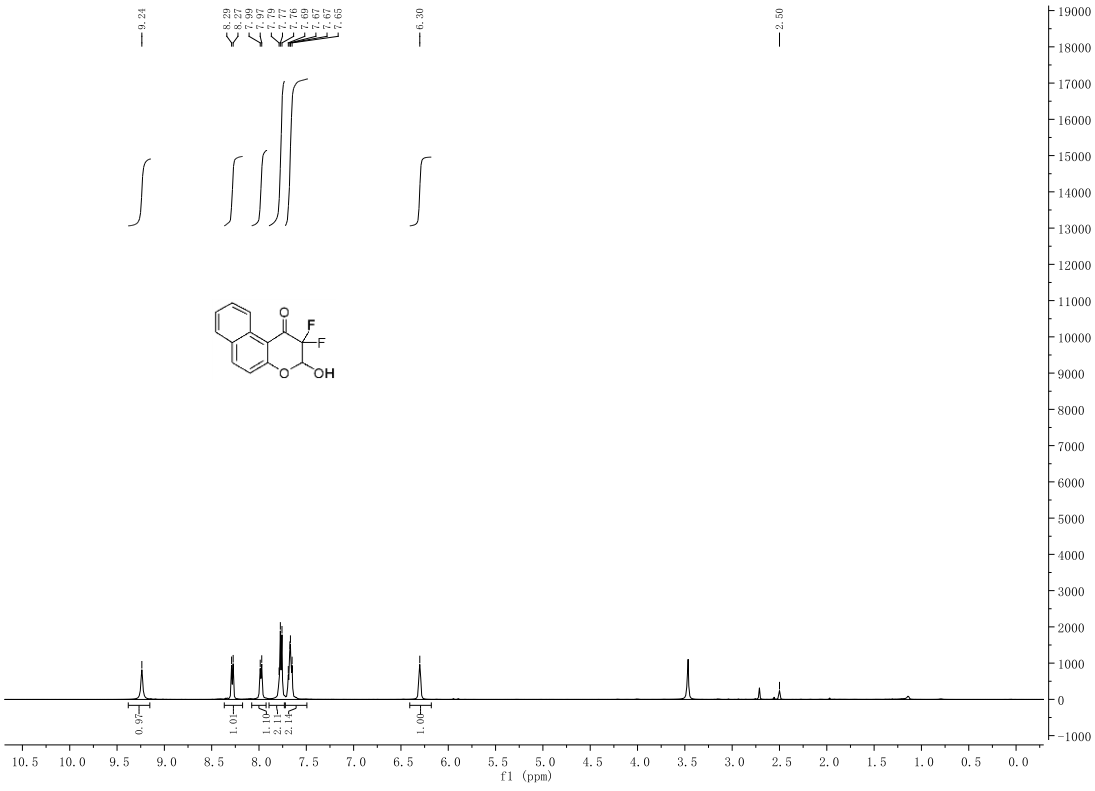
6-bromo-3,3-difluoro-2-hydroxychroman-4-one (2i, ^{13}C NMR, $DCCl_3$, 125 MHz)



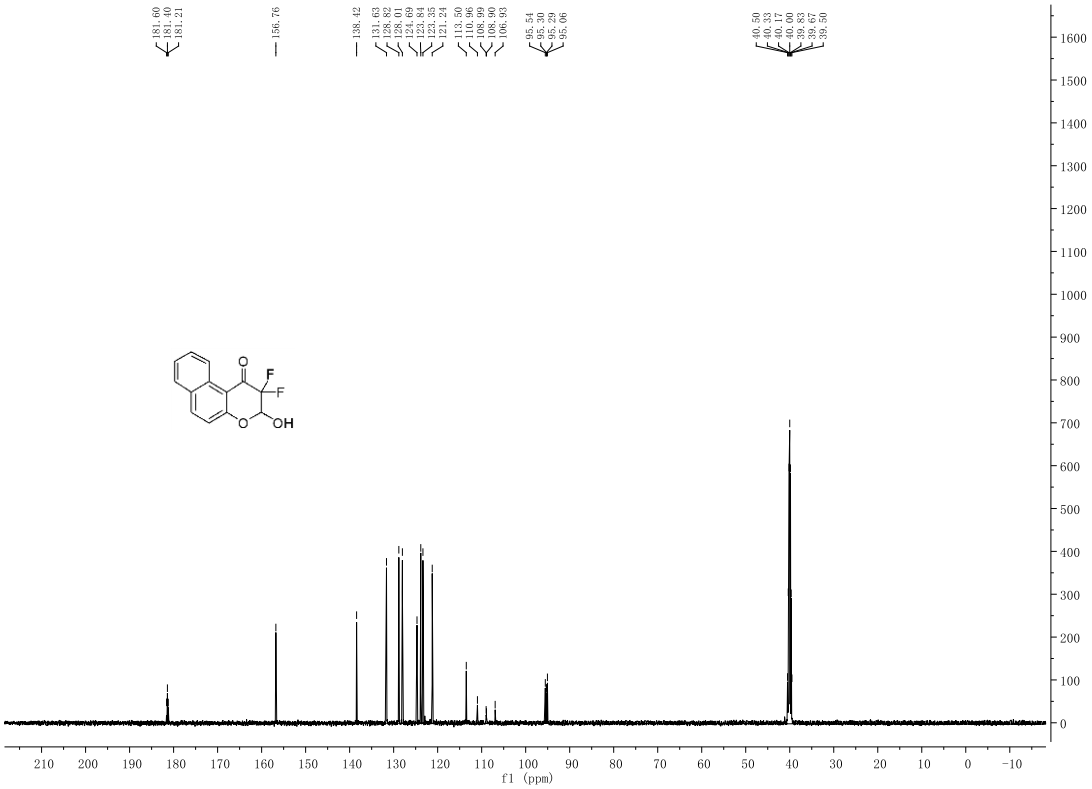
6-bromo-3,3-difluoro-2-hydroxychroman-4-one (2i, ^{19}F NMR, DMSO-D_6, 471 MHz)



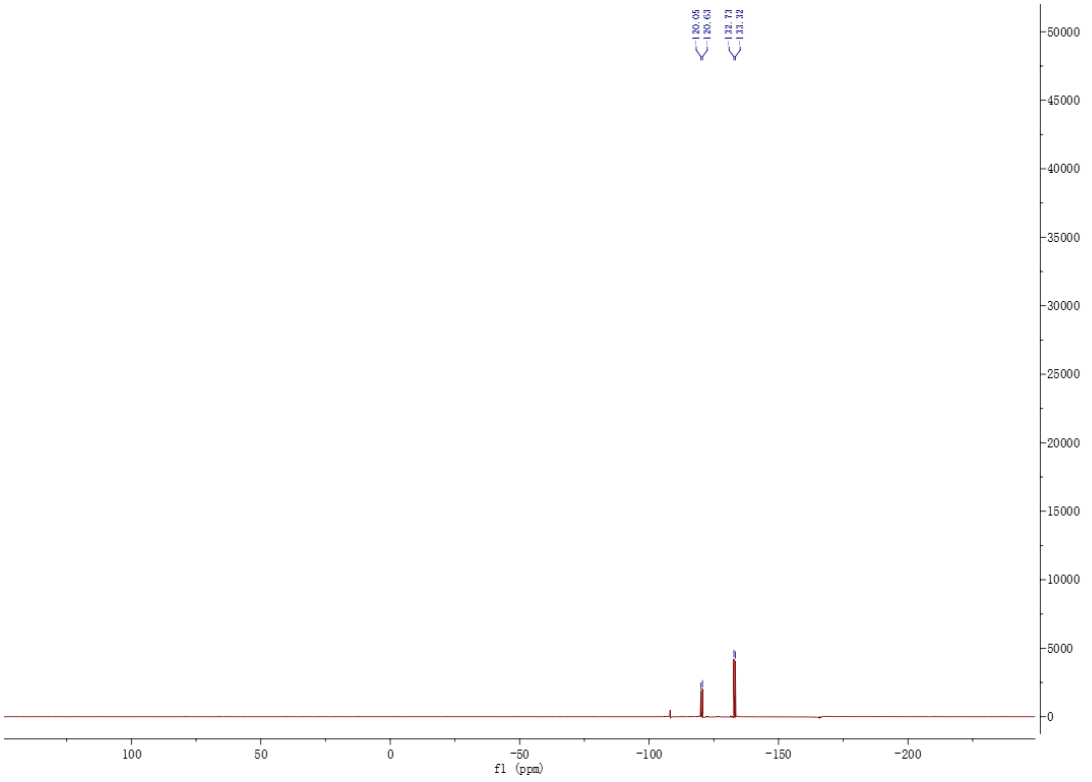
2,2-difluoro-3-hydroxy-2,3-dihydro-1H-benzo[f]chromen-1-one (2j, ^{1}H NMR, DMSO-D_6, 500 MHz)



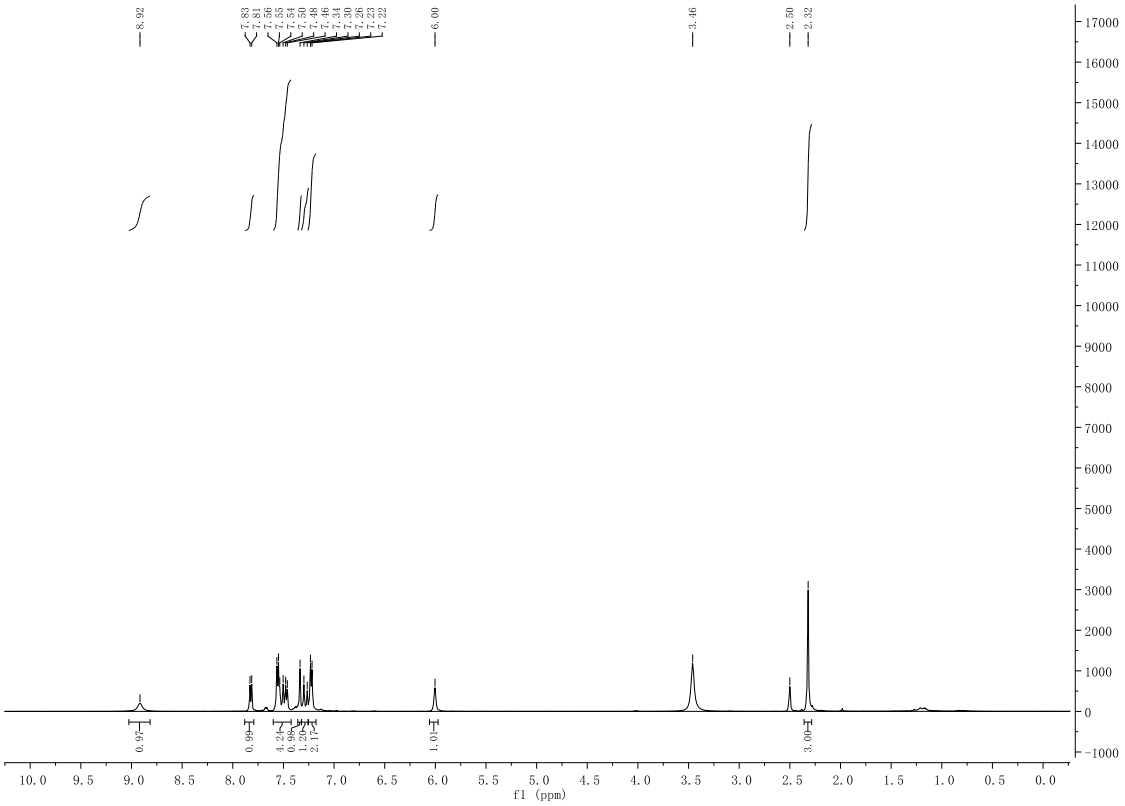
2,2-difluoro-3-hydroxy-2,3-dihydro-1H-benzo[f]chromen-1-one (2j, ^{13}C NMR, DMSO-D_6, 125 MHz)



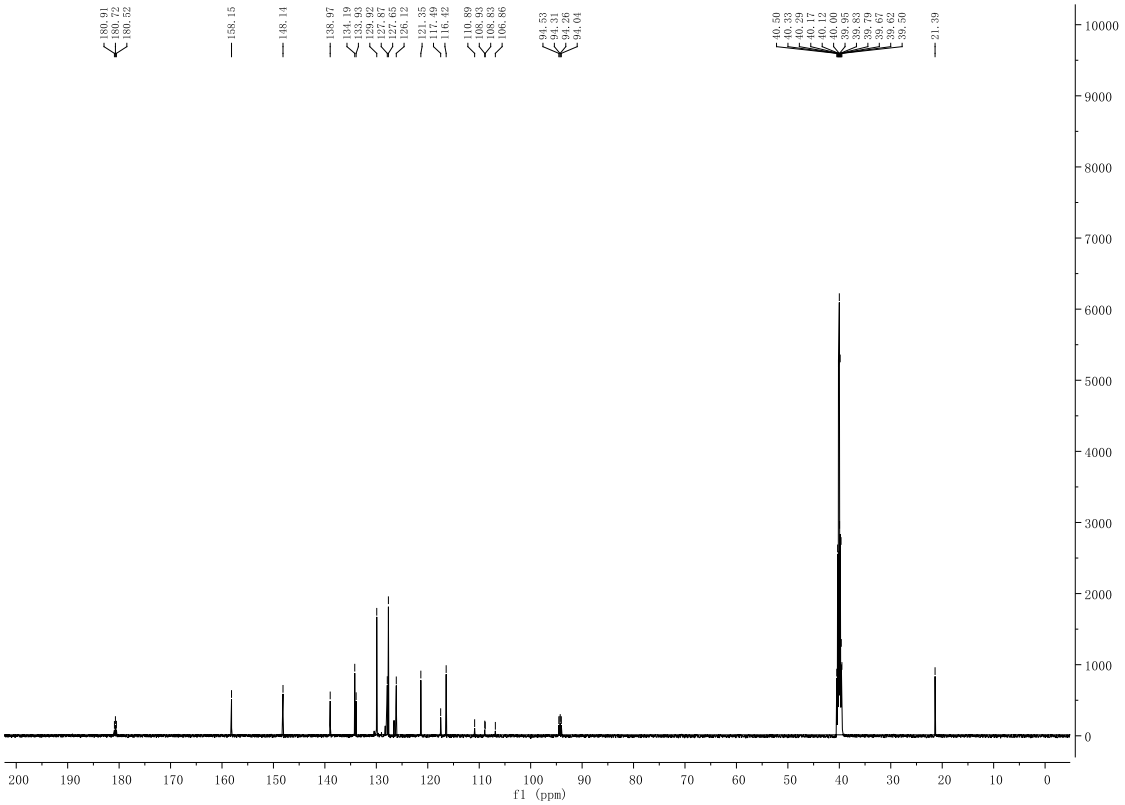
2,2-difluoro-3-hydroxy-2,3-dihydro-1H-benzo[f]chromen-1-one (2j, ^{19}F NMR, DMSO-D_6, 471 MHz)



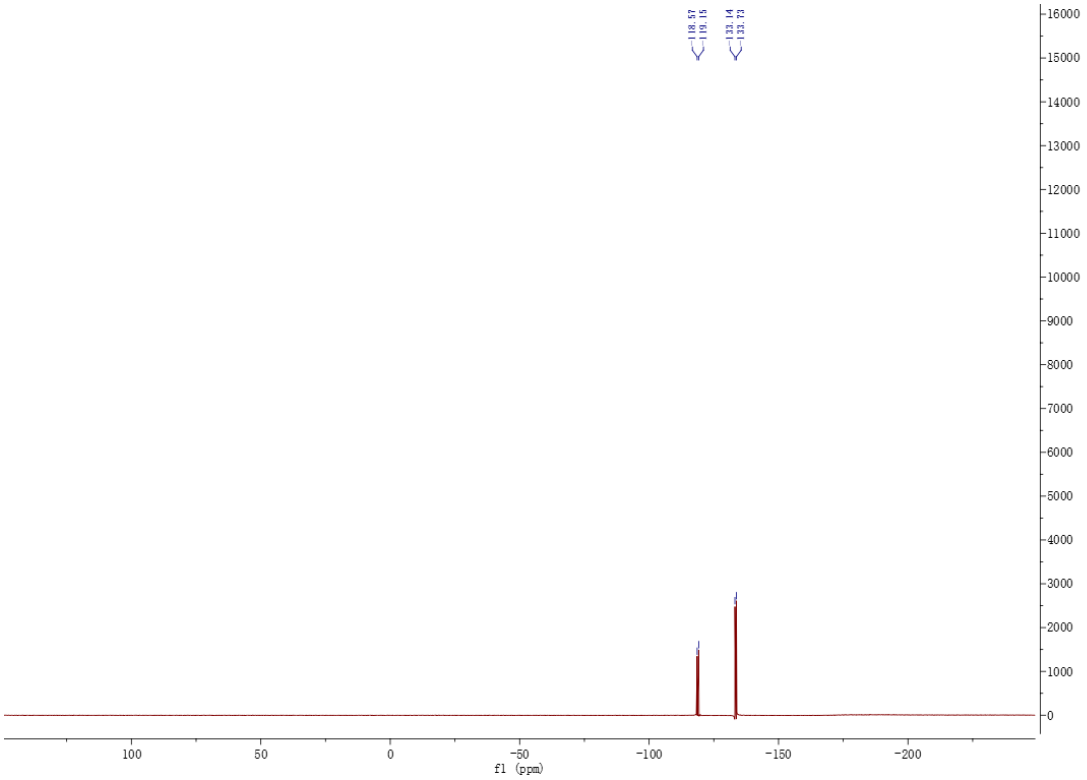
(E)-3,3-difluoro-2-hydroxy-7-(4-methylstyryl)chroman-4-one (2k, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



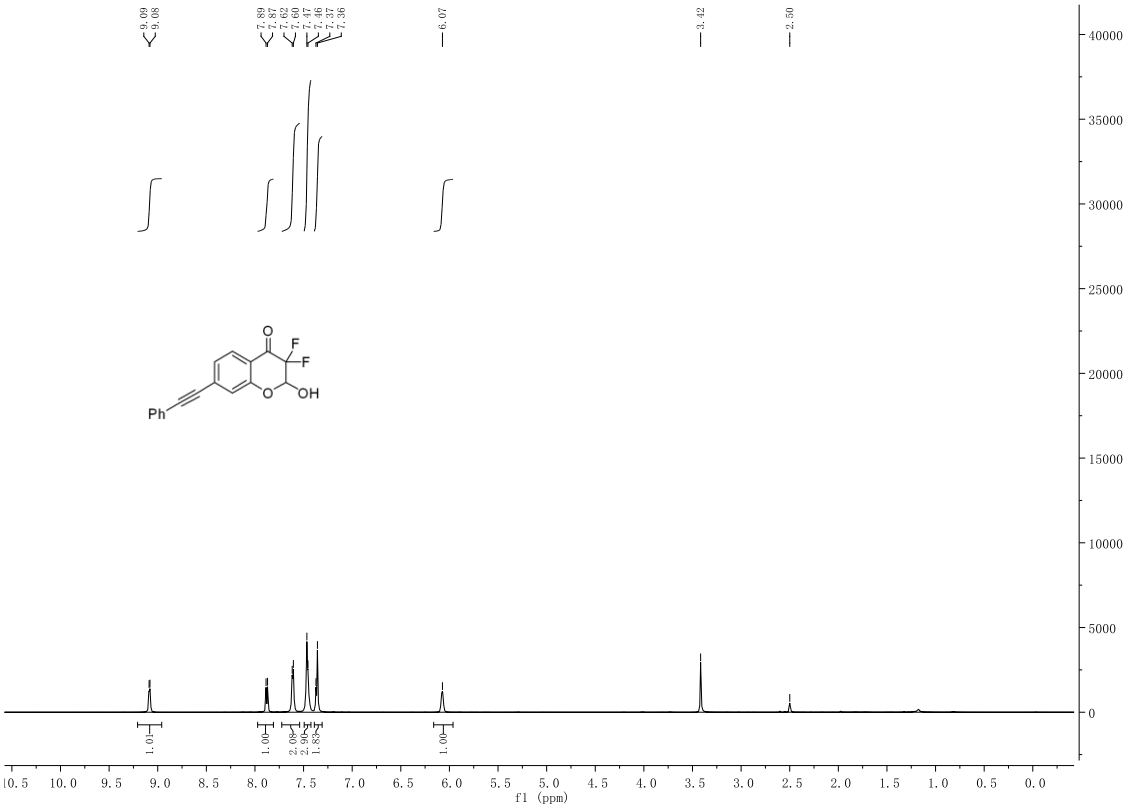
(E)-3,3-difluoro-2-hydroxy-7-(4-methylstyryl)chroman-4-one (2k, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



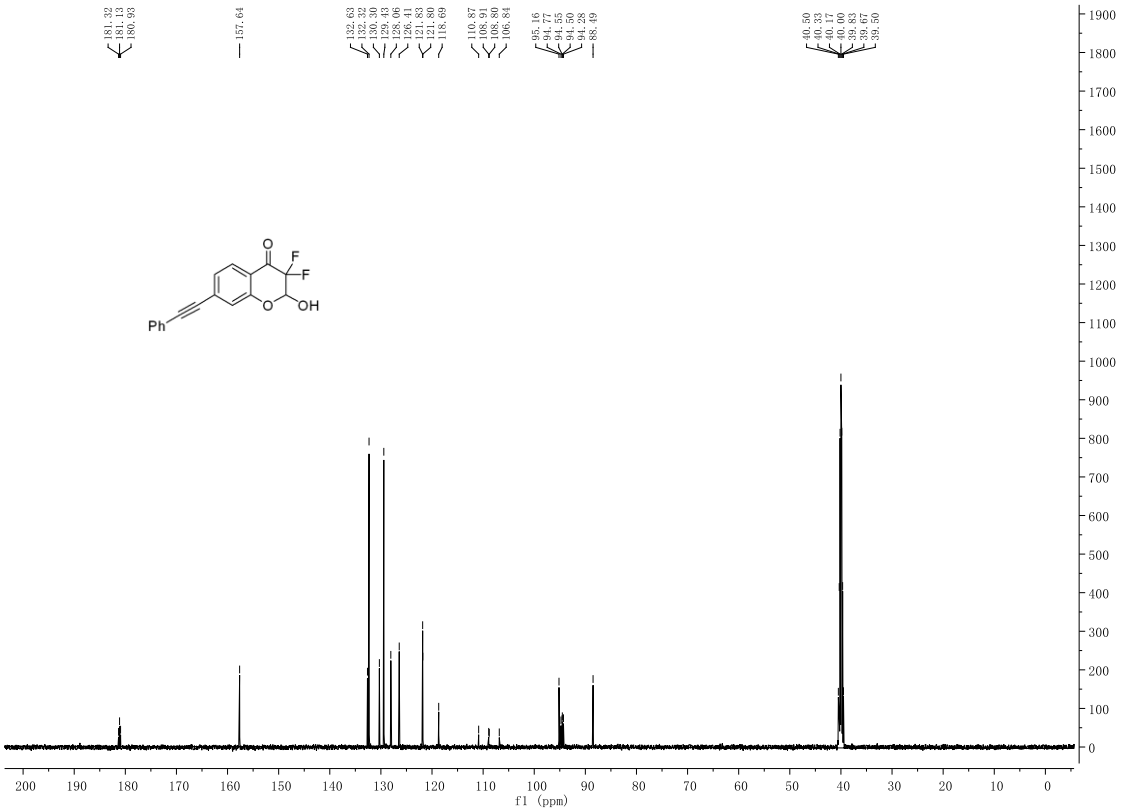
(E)-3,3-difluoro-2-hydroxy-7-(4-methylstyryl)chroman-4-one (2k, ^{19}F NMR, DMSO-D_6, 471 MHz)



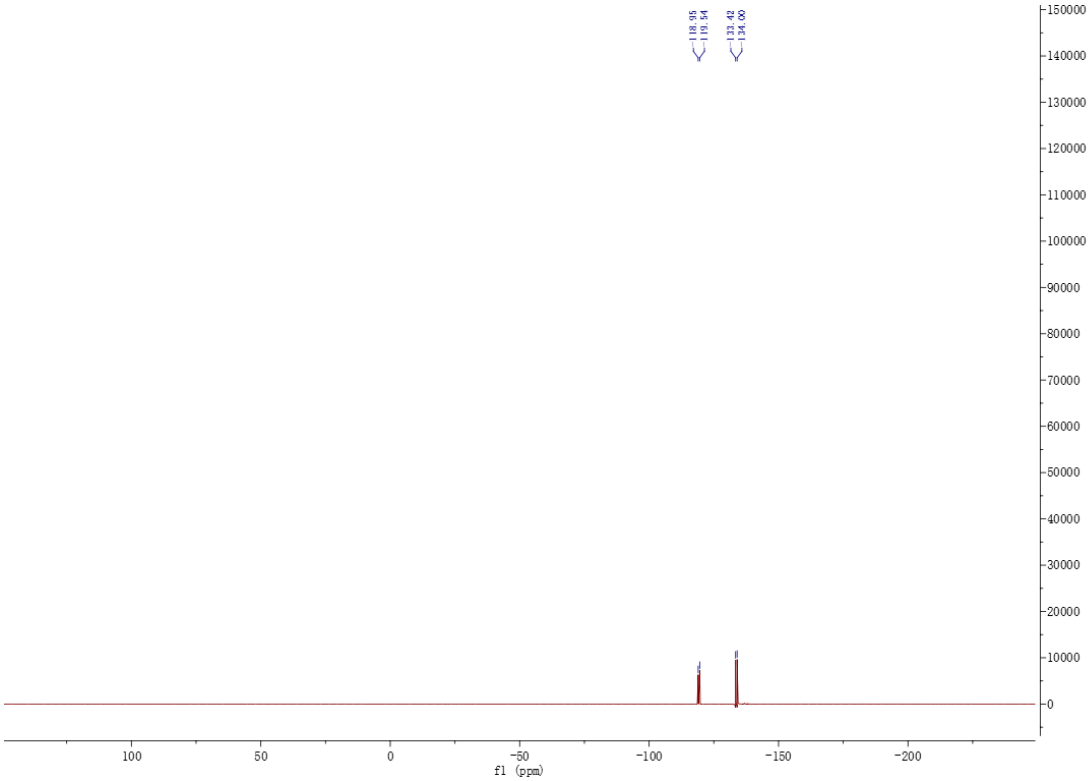
3,3-difluoro-2-hydroxy-7-(phenylethynyl)chroman-4-one (2l, ^{1}H NMR, DMSO-D_6, 500 MHz)



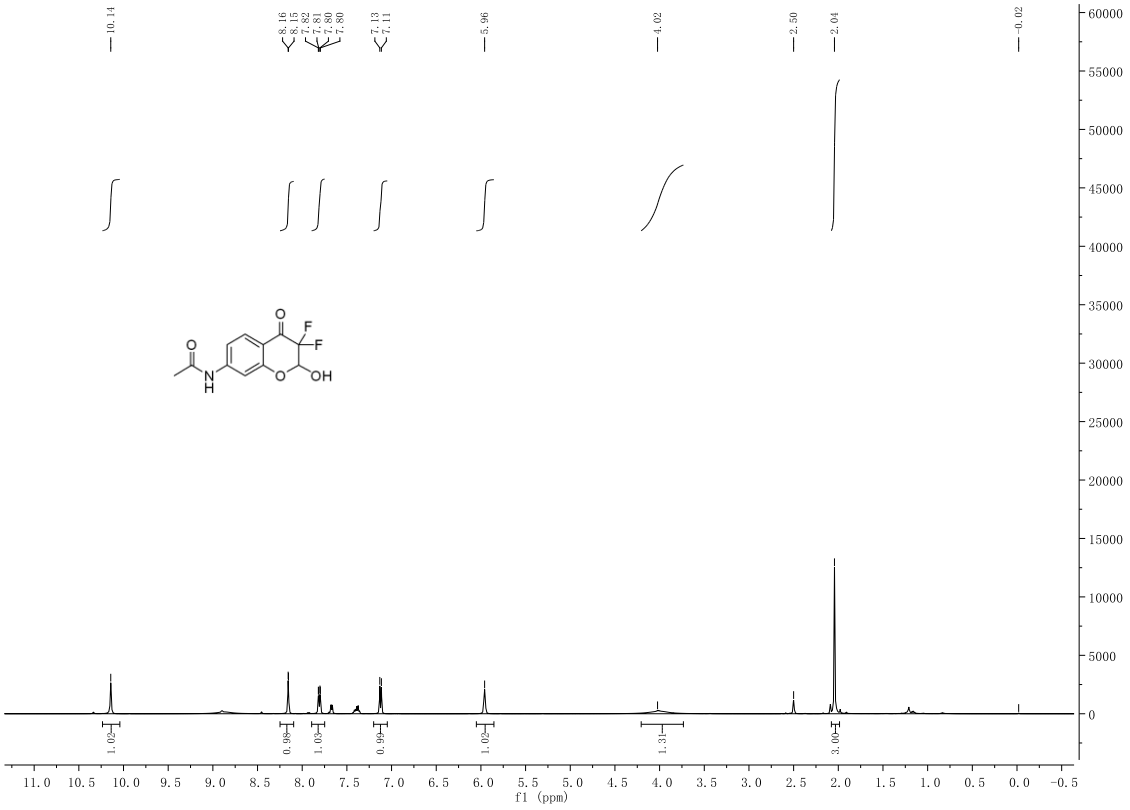
3,3-difluoro-2-hydroxy-7-(phenylethynyl)chroman-4-one (2l, ^{13}C NMR, DMSO-D_6, $DCCl_3$, 125 MHz)



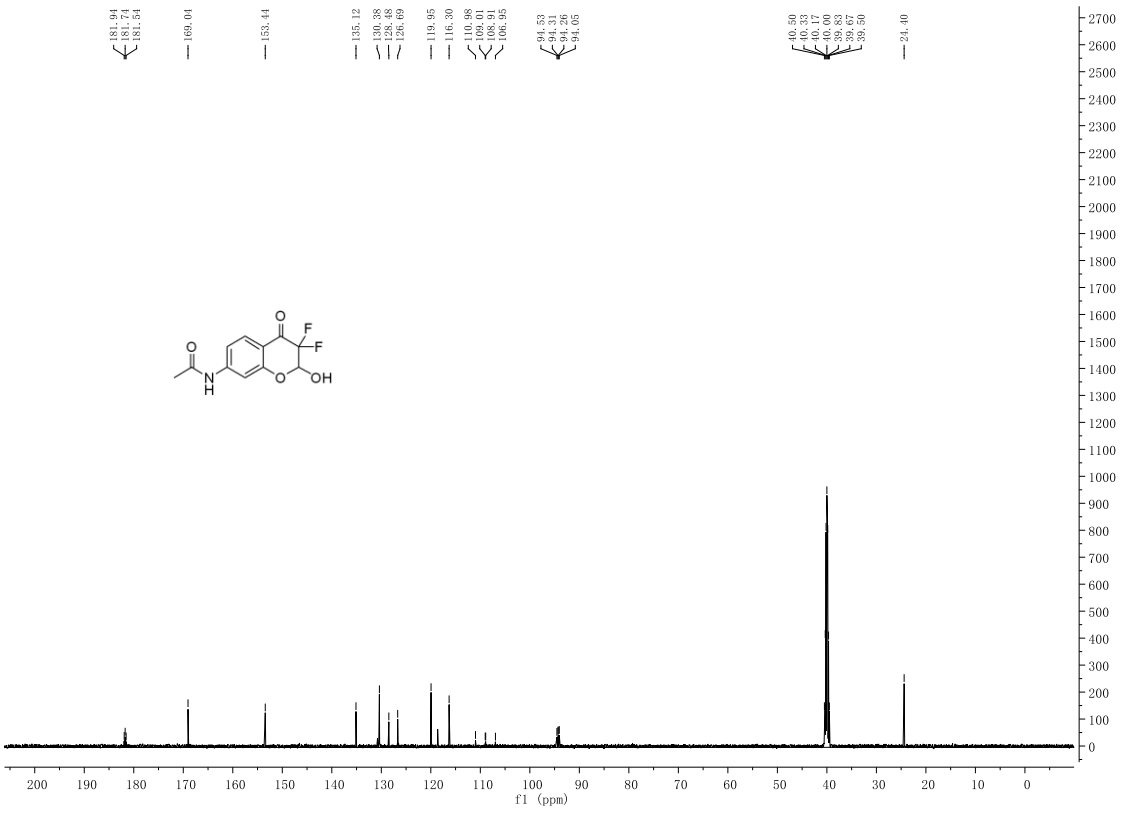
3,3-difluoro-2-hydroxy-7-(phenylethynyl)chroman-4-one (2l, ^{19}F NMR, DMSO-D_6, 471 MHz)



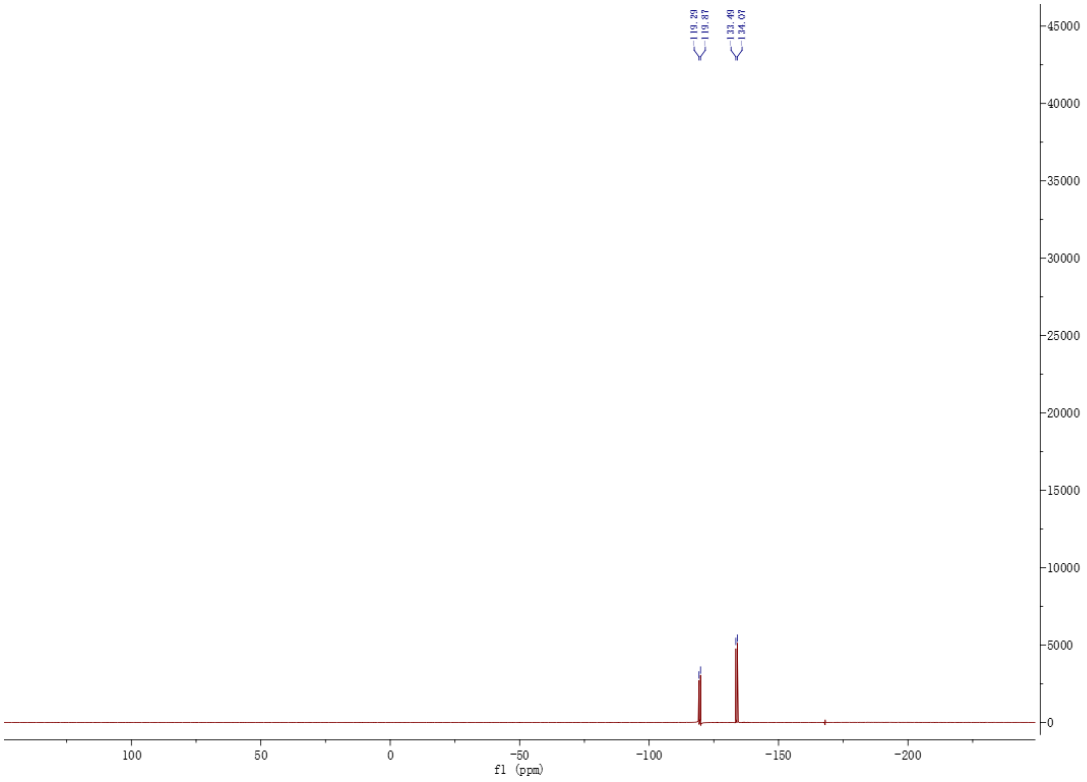
***N*-(3,3-difluoro-2-hydroxy-4-oxochroman-7-yl)acetamide (2m, ^{1}H NMR, DMSO-D$_6$, 500 MHz)**



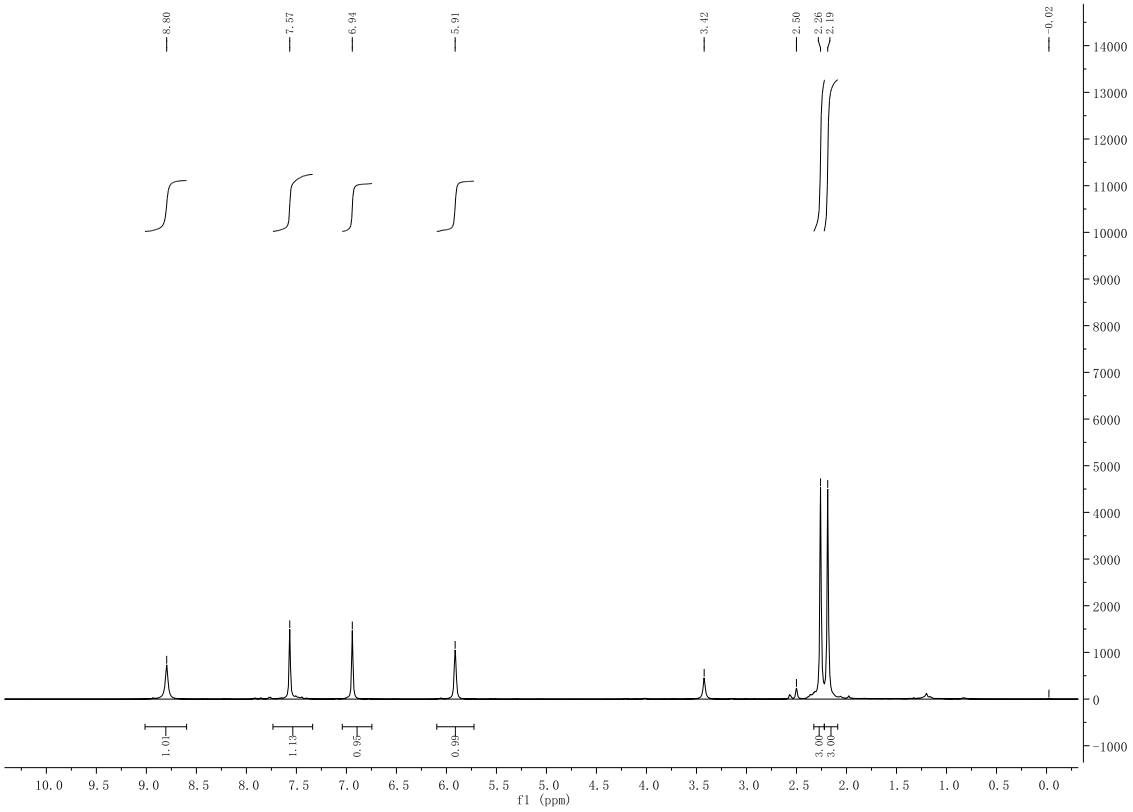
***N*-(3,3-difluoro-2-hydroxy-4-oxochroman-7-yl)acetamide (2m, ^{13}C NMR, DMSO-D$_6$, 125 MHz)**



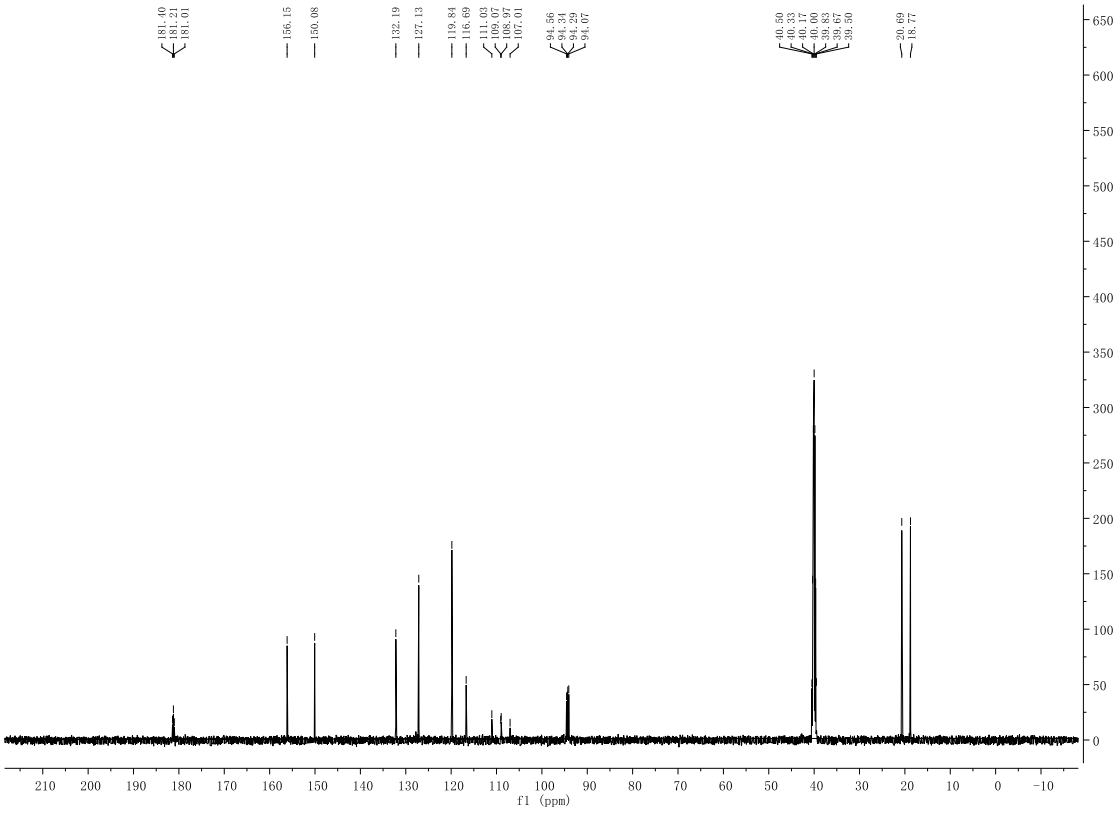
***N*-(3,3-difluoro-2-hydroxy-4-oxochroman-7-yl)acetamide (2m, ^{19}F NMR, DMSO-D$_6$, 471 MHz)**



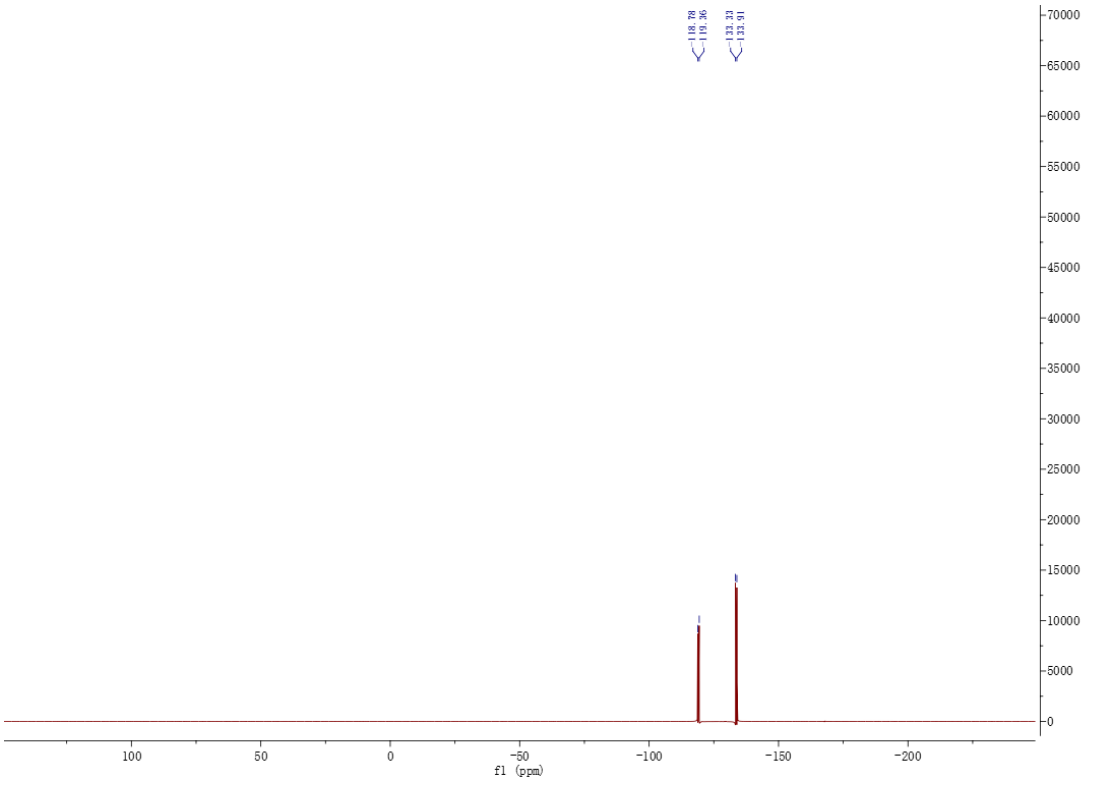
3,3-difluoro-2-hydroxy-6,7-dimethylchroman-4-one (2n, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



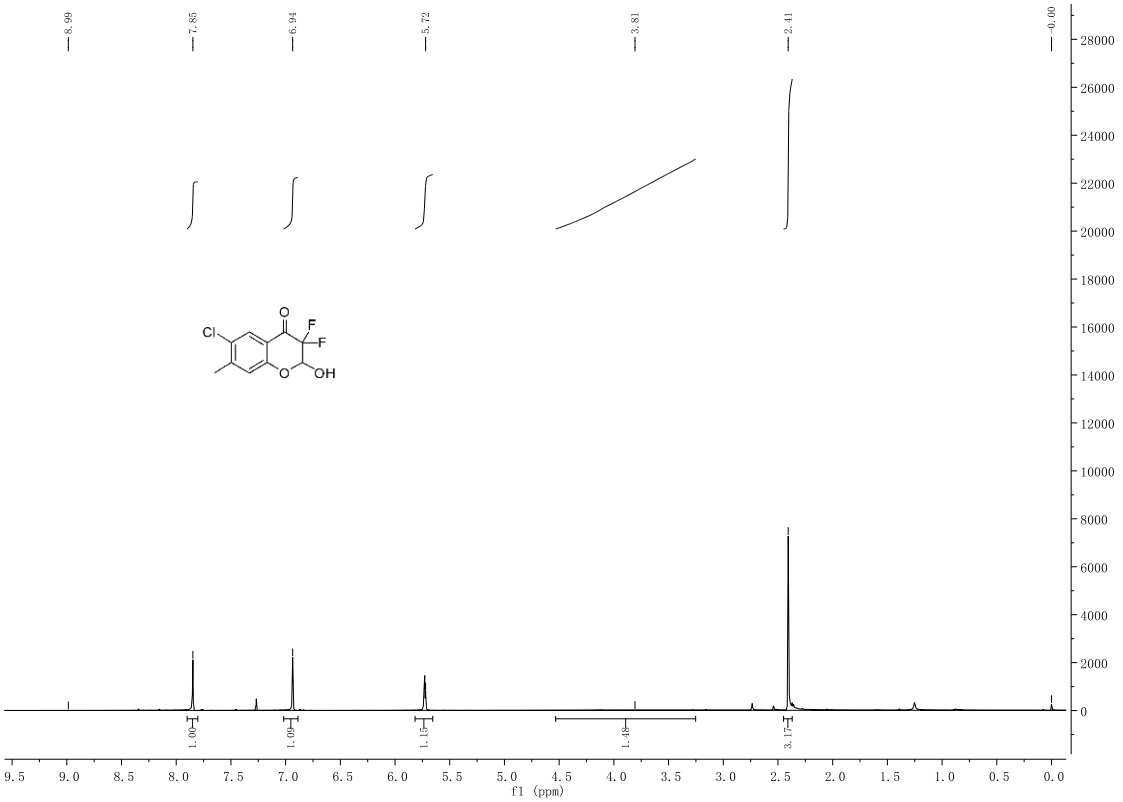
3,3-difluoro-2-hydroxy-6,7-dimethylchroman-4-one (2n, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



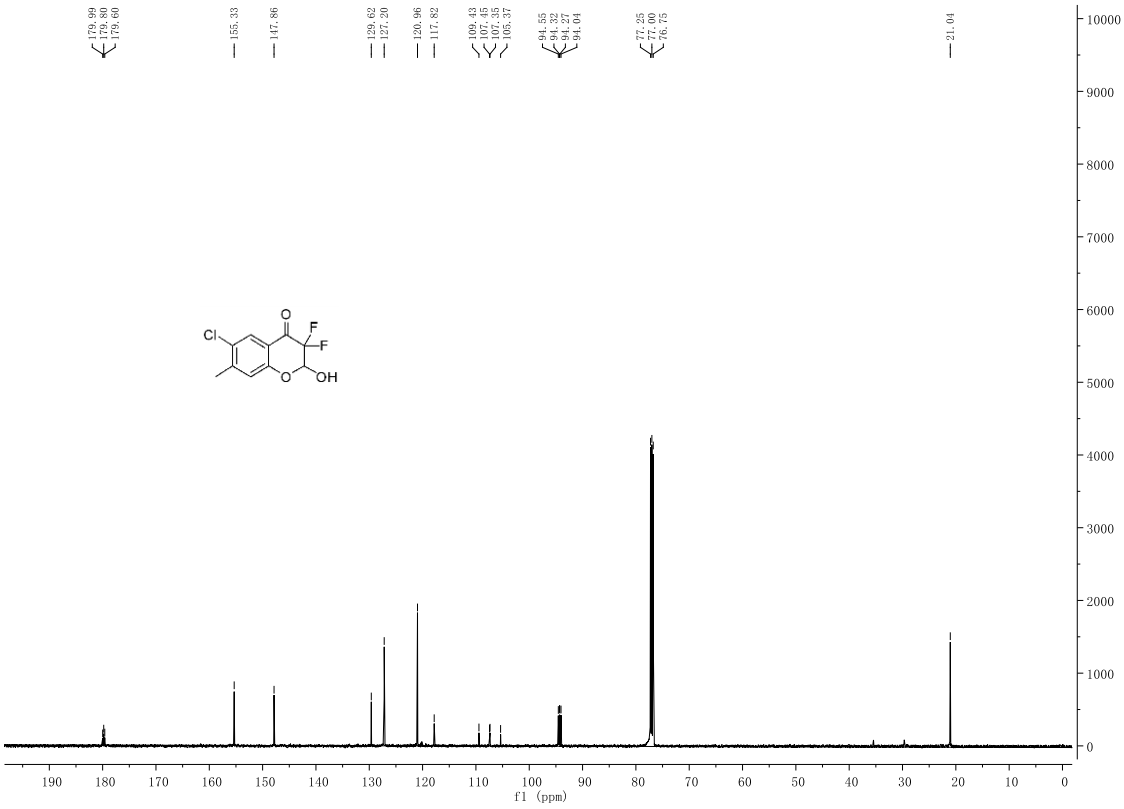
3,3-difluoro-2-hydroxy-6,7-dimethylchroman-4-one (2n, ^{19}F NMR, DMSO-D$_6$, 471 MHz)



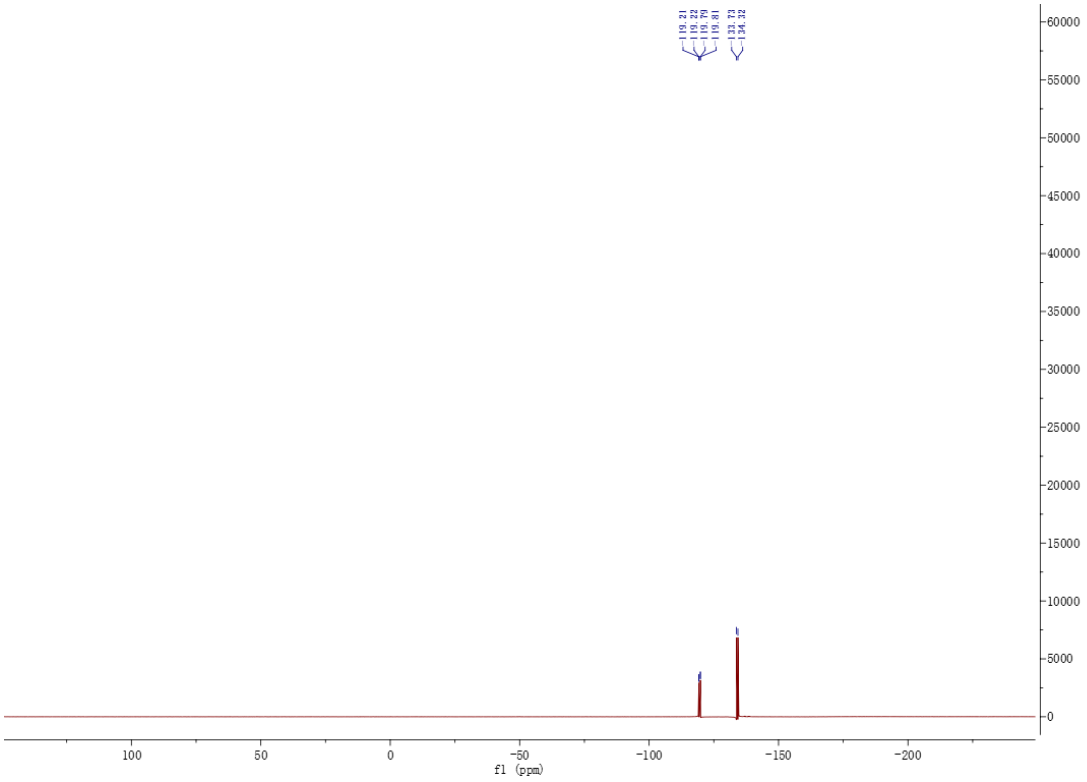
6-chloro-3,3-difluoro-2-hydroxy-7-methylchroman-4-one (2o, ^{1}H NMR, $DCCl_3$, 500 MHz)



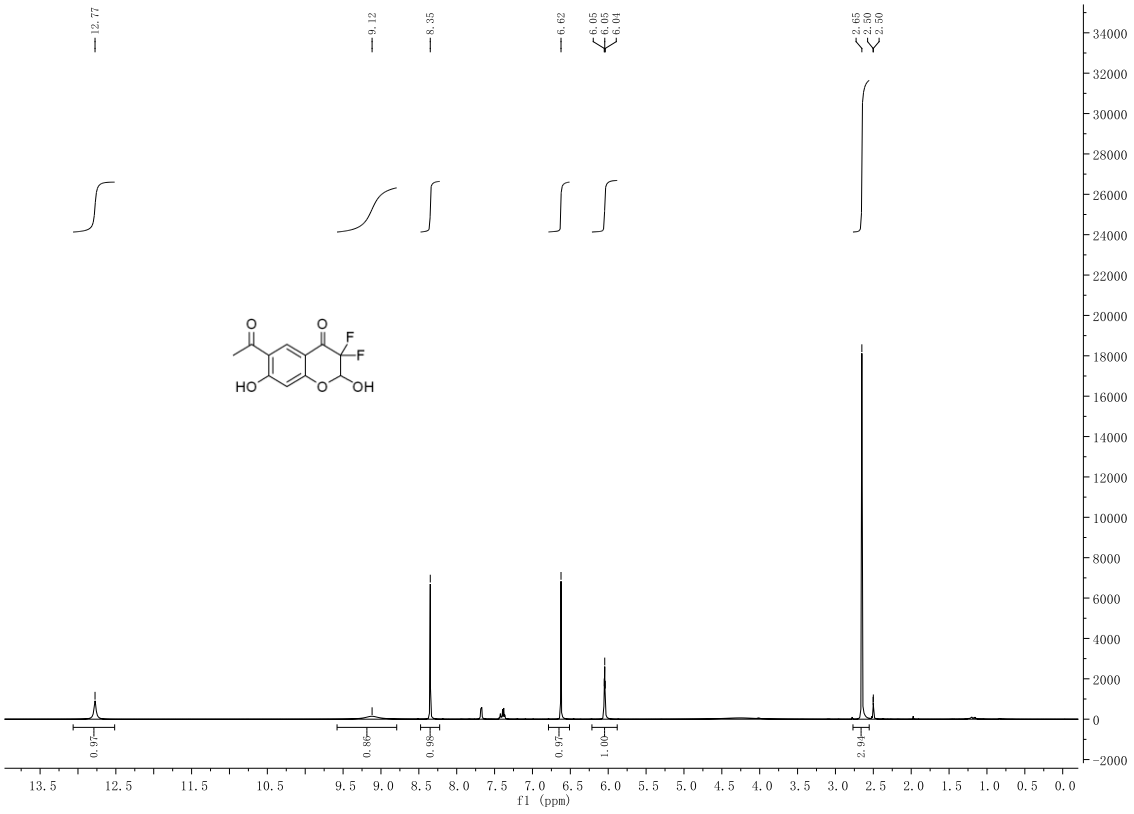
6-chloro-3,3-difluoro-2-hydroxy-7-methylchroman-4-one (2o, ^{13}C NMR, $DCCl_3$, 125 MHz)



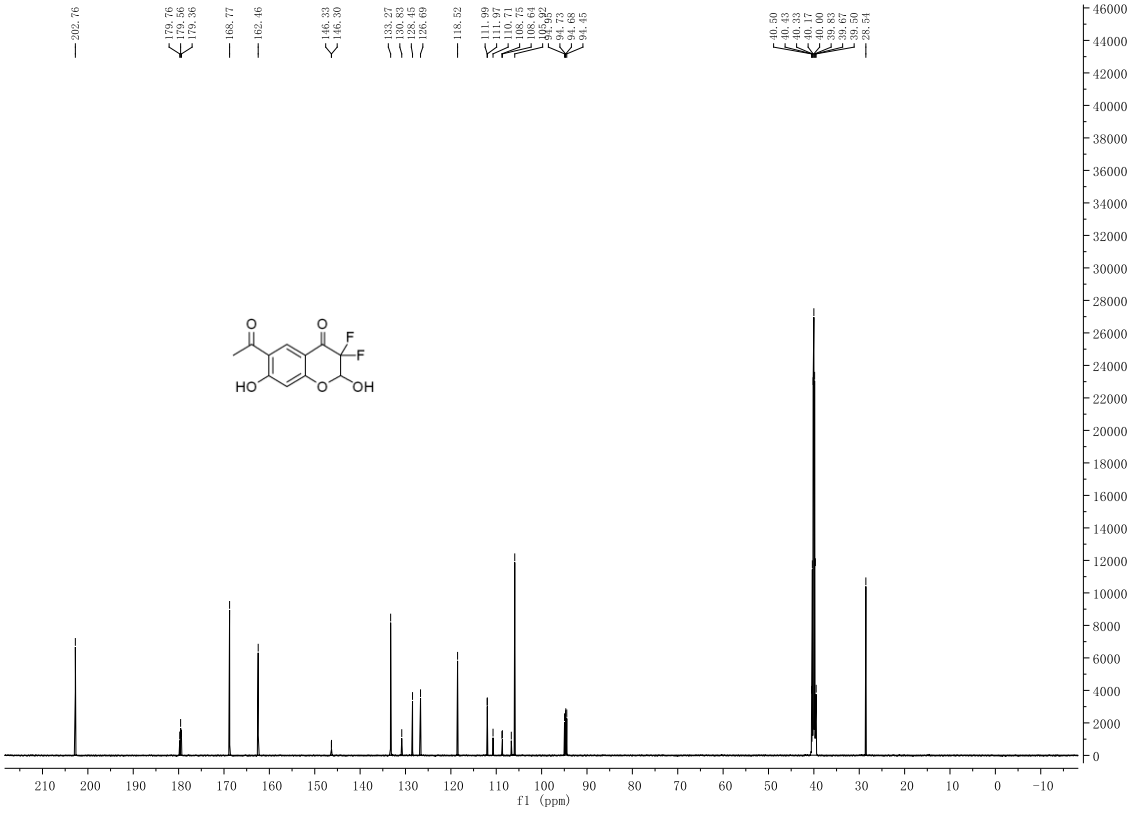
6-chloro-3,3-difluoro-2-hydroxy-7-methylchroman-4-one (2o, ^{19}F NMR, DMSO-D$_6$, 471 MHz)



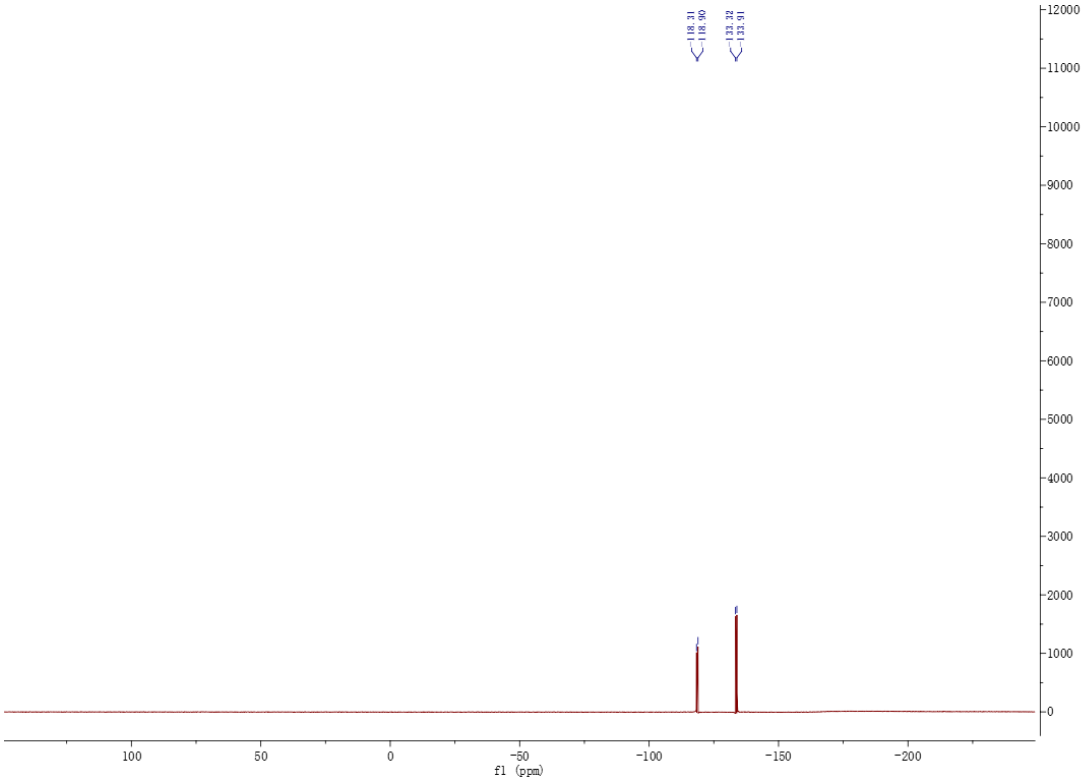
6-acetyl-3,3-difluoro-2,7-dihydroxychroman-4-one (2p, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



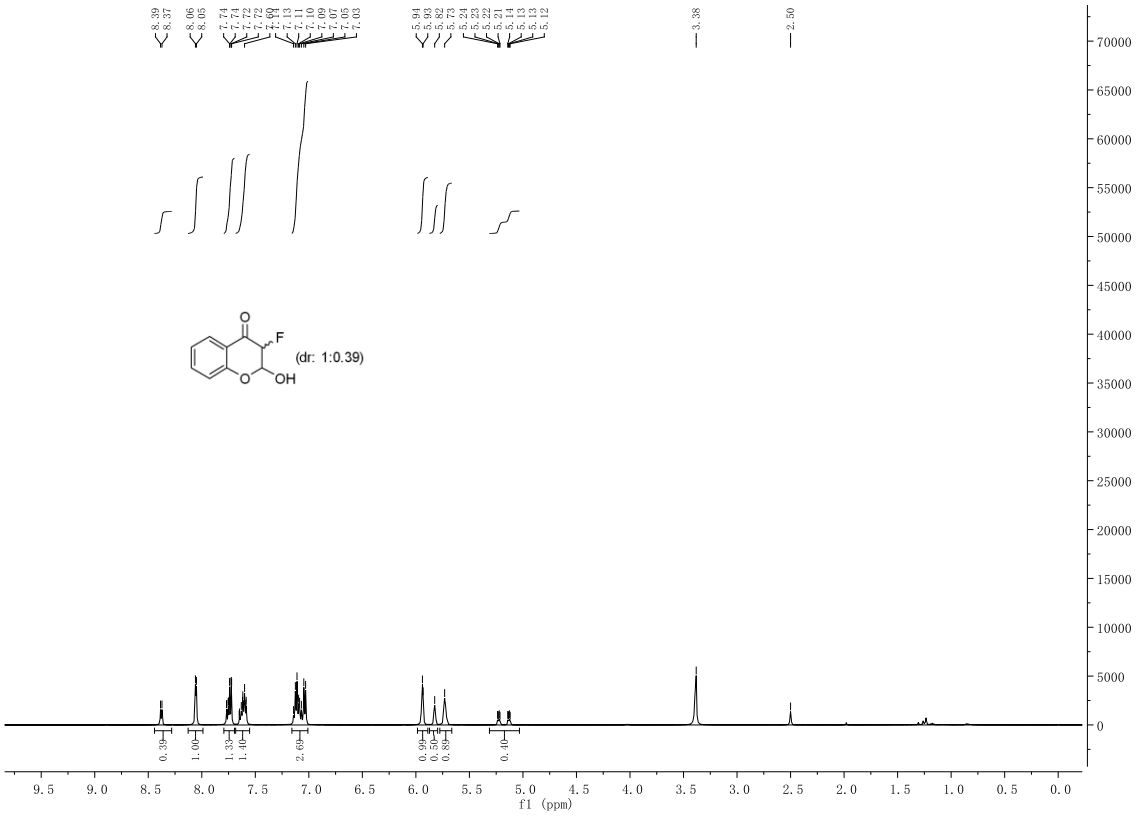
6-acetyl-3,3-difluoro-2,7-dihydroxychroman-4-one (2p, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



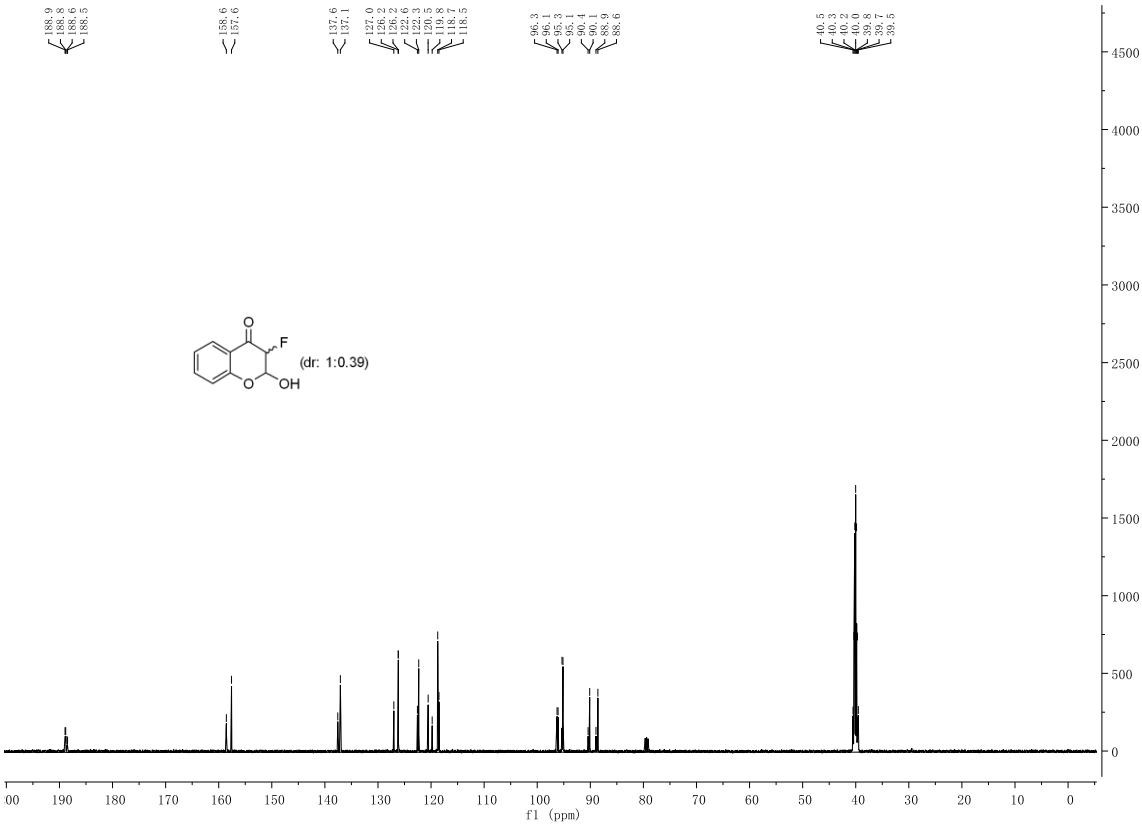
6-acetyl-3,3-difluoro-2,7-dihydroxychroman-4-one (2p, ^{19}F NMR, DMSO-D$_6$, 471 MHz)



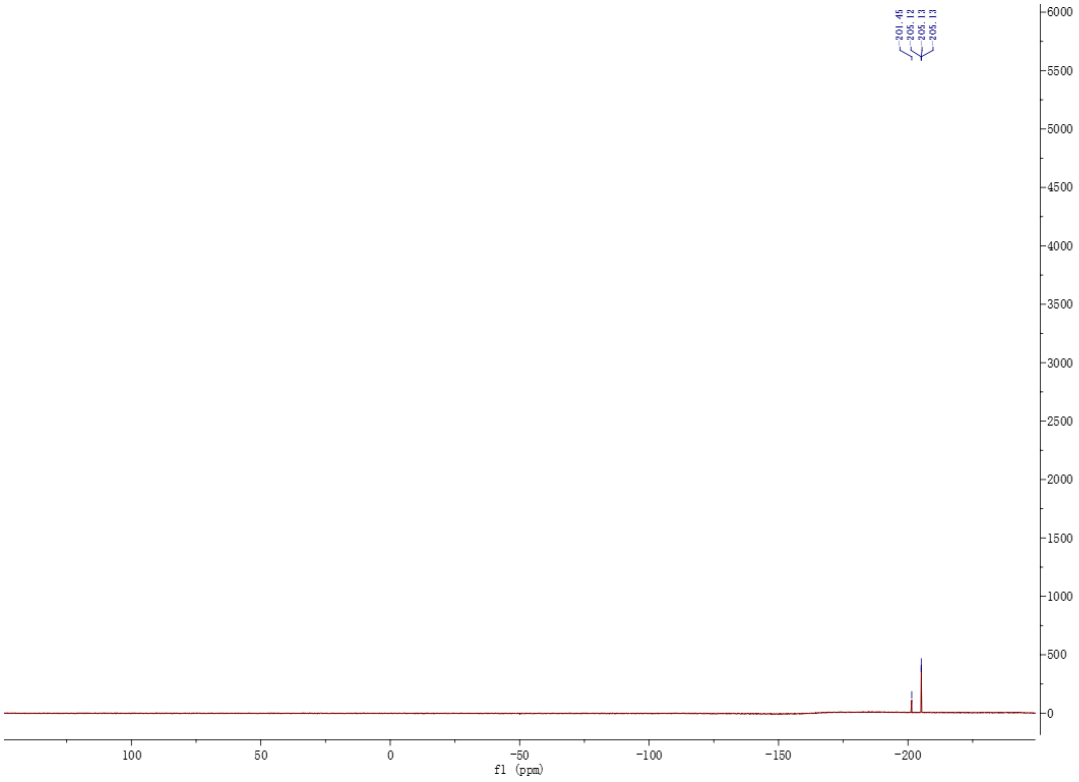
3-fluoro-4-oxochroman-2-yl acetate (3a, dr: 1:0.39, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



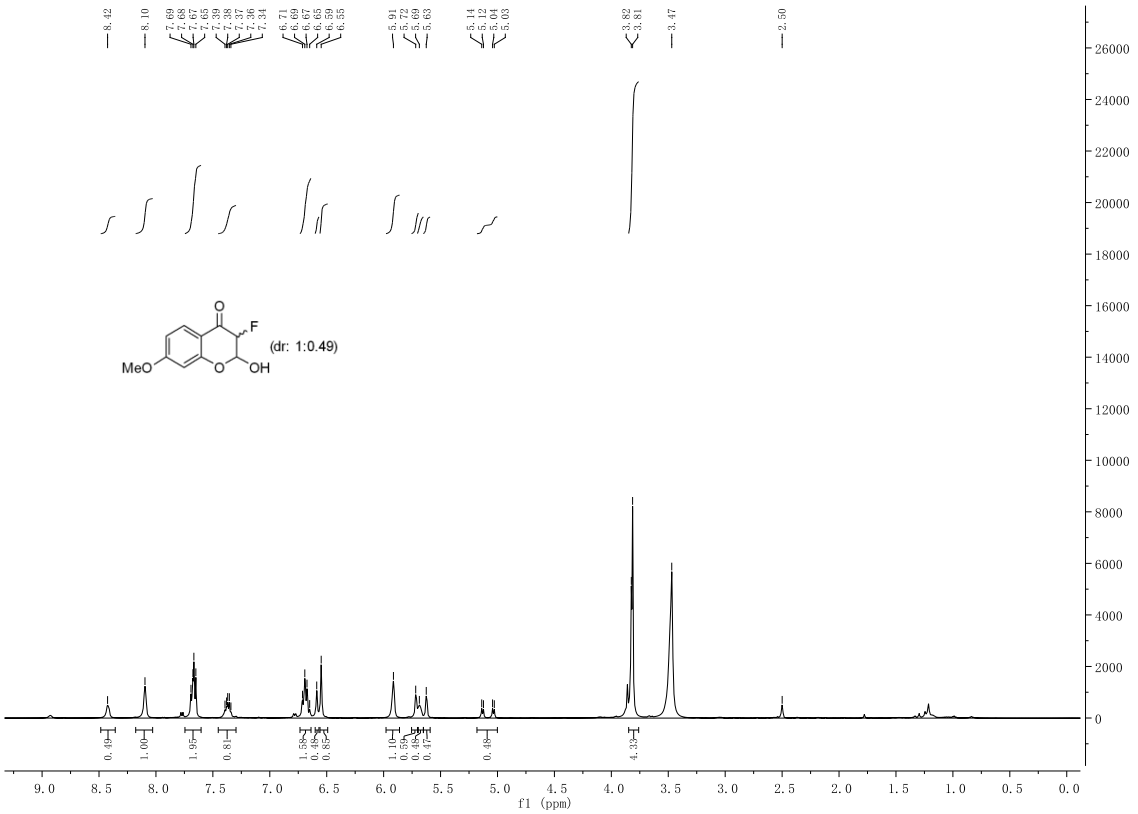
3-fluoro-4-oxochroman-2-yl acetate (3a, dr: 1:0.39, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



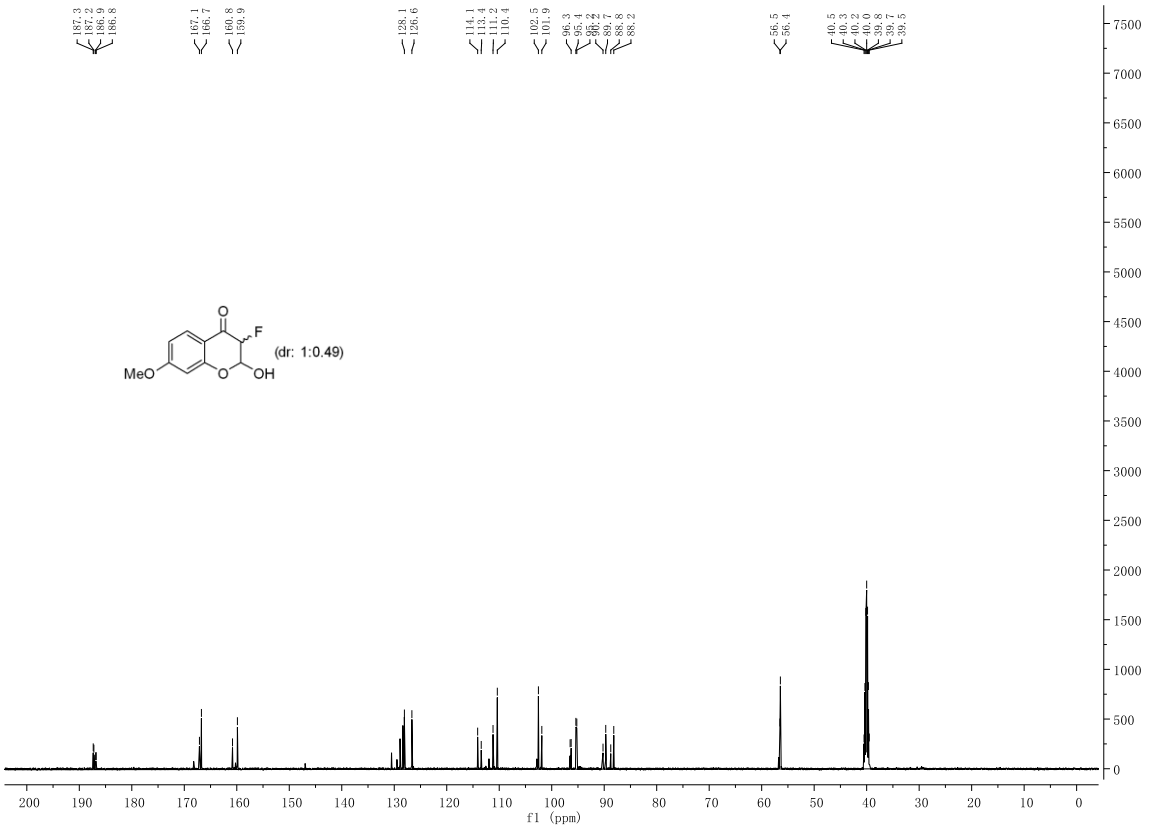
3-fluoro-4-oxochroman-2-yl acetate (3a, ^{19}F NMR, $DCCl_3$, 471 MHz)



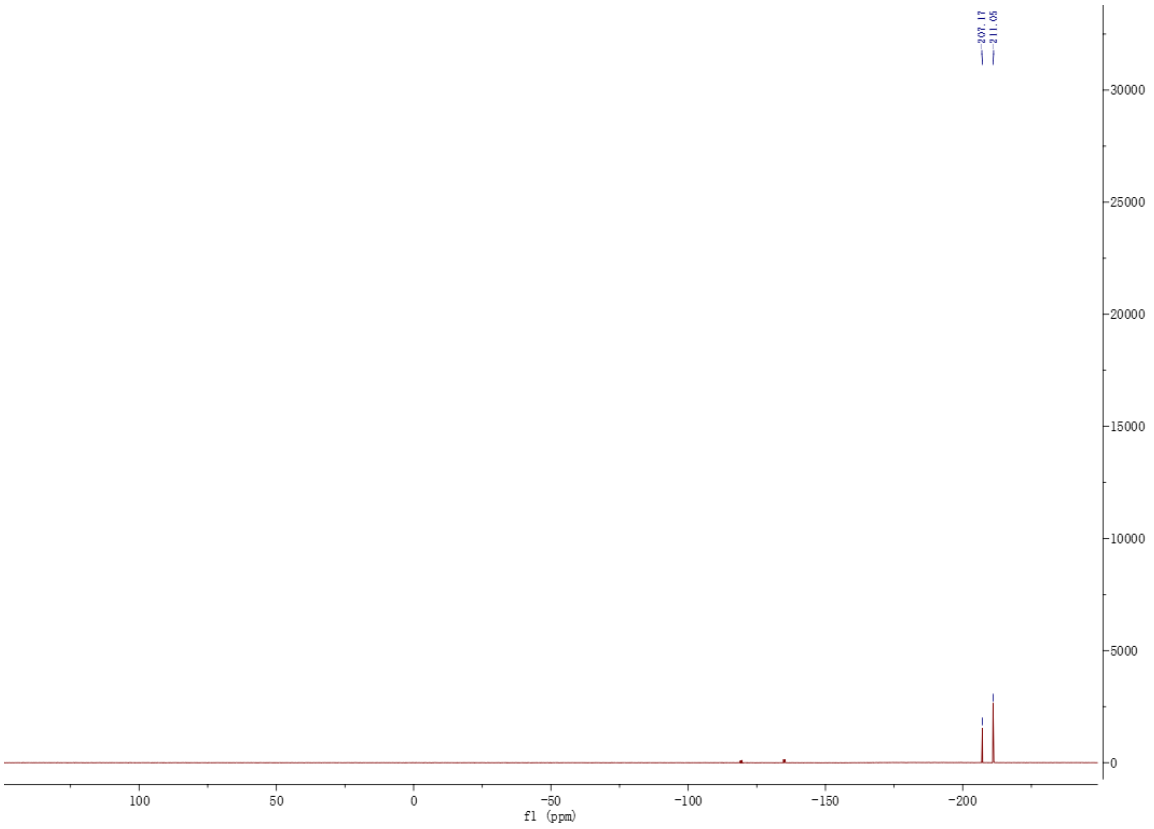
3-fluoro-2-hydroxy-7-methoxychromman-4-one (3b, dr: 1:0.49, ^1H NMR, DMSO-D_6, 500 MHz)



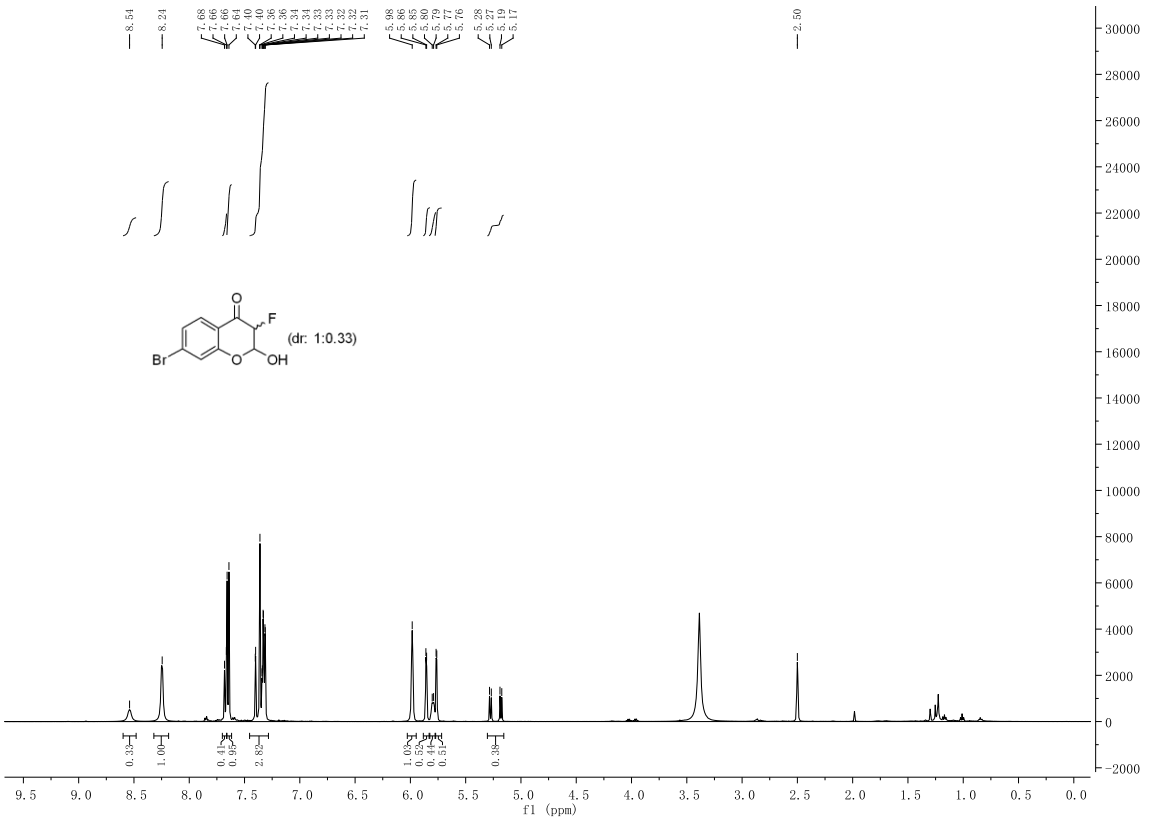
3-fluoro-2-hydroxy-7-methoxychroman-4-one (3b, dr: 1:0.49, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



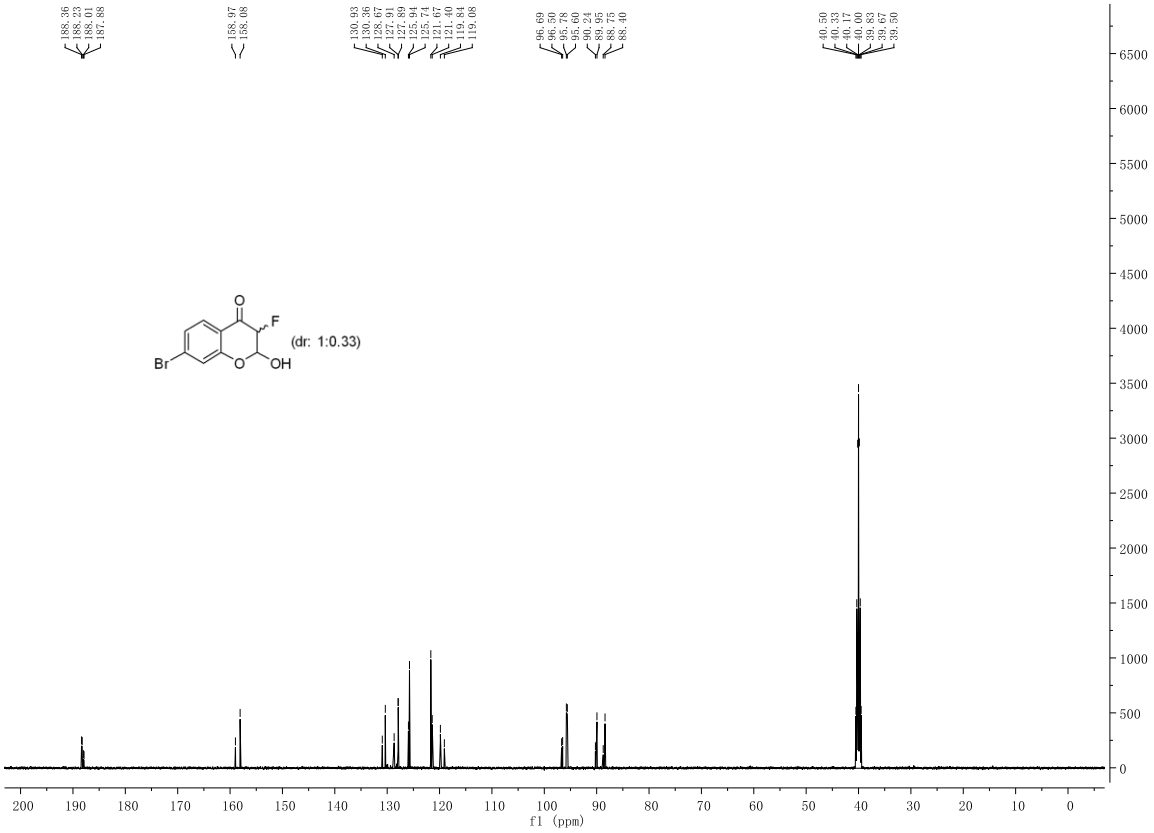
3-fluoro-2-hydroxy-7-methoxychroman-4-one (3b, ^{19}F NMR, DCCl$_3$, 471 MHz)



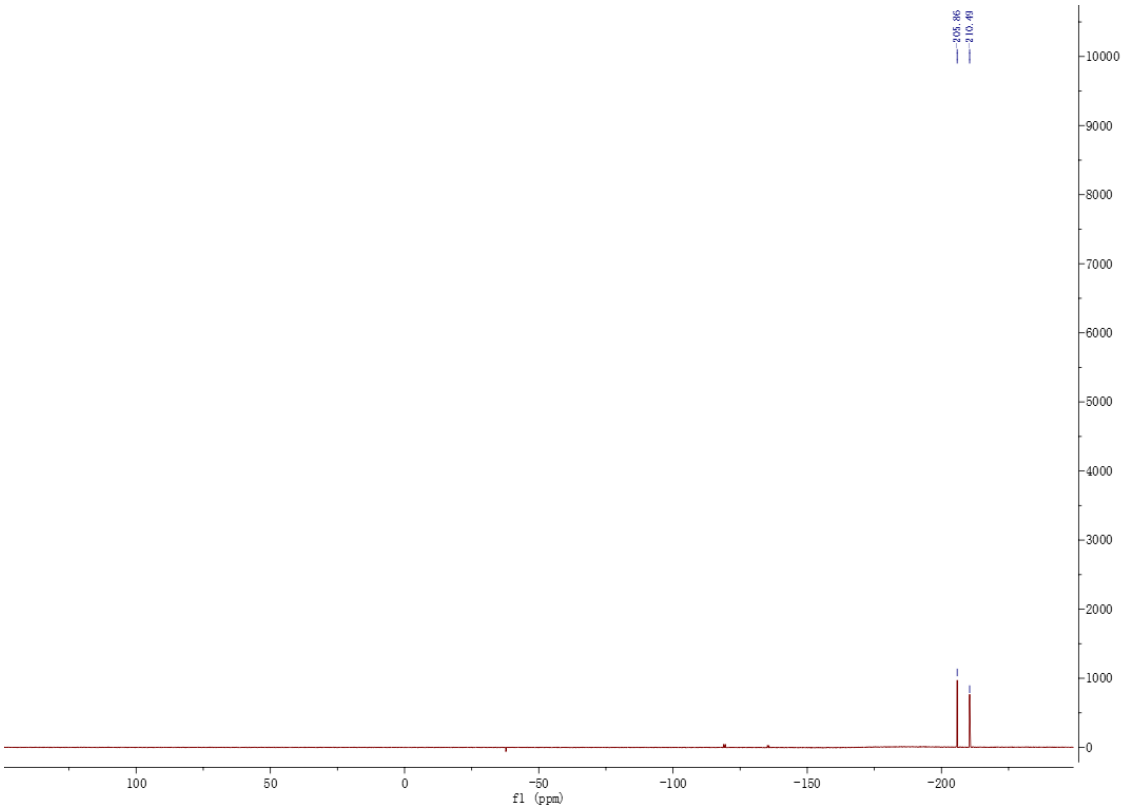
7-bromo-3-fluoro-2-hydroxychroman-4-one (3d, dr: 1:0.33, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



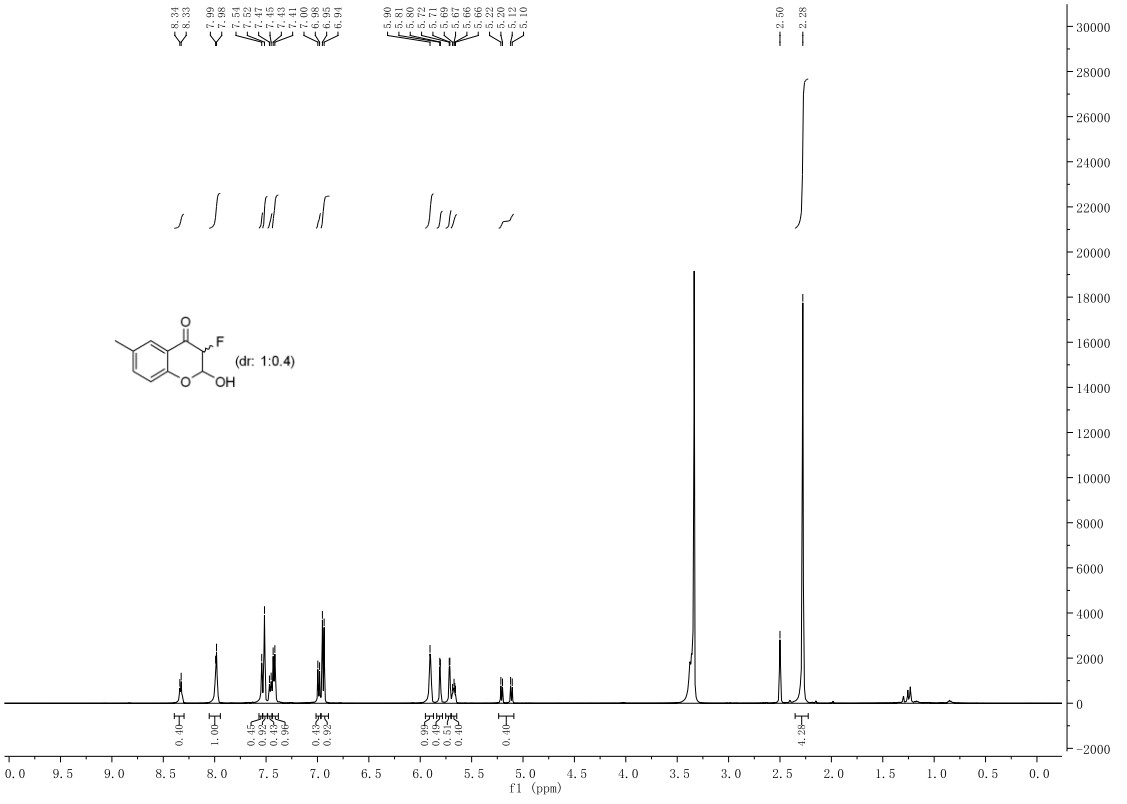
7-bromo-3-fluoro-2-hydroxychroman-4-one (3d, dr: 1:0.33, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



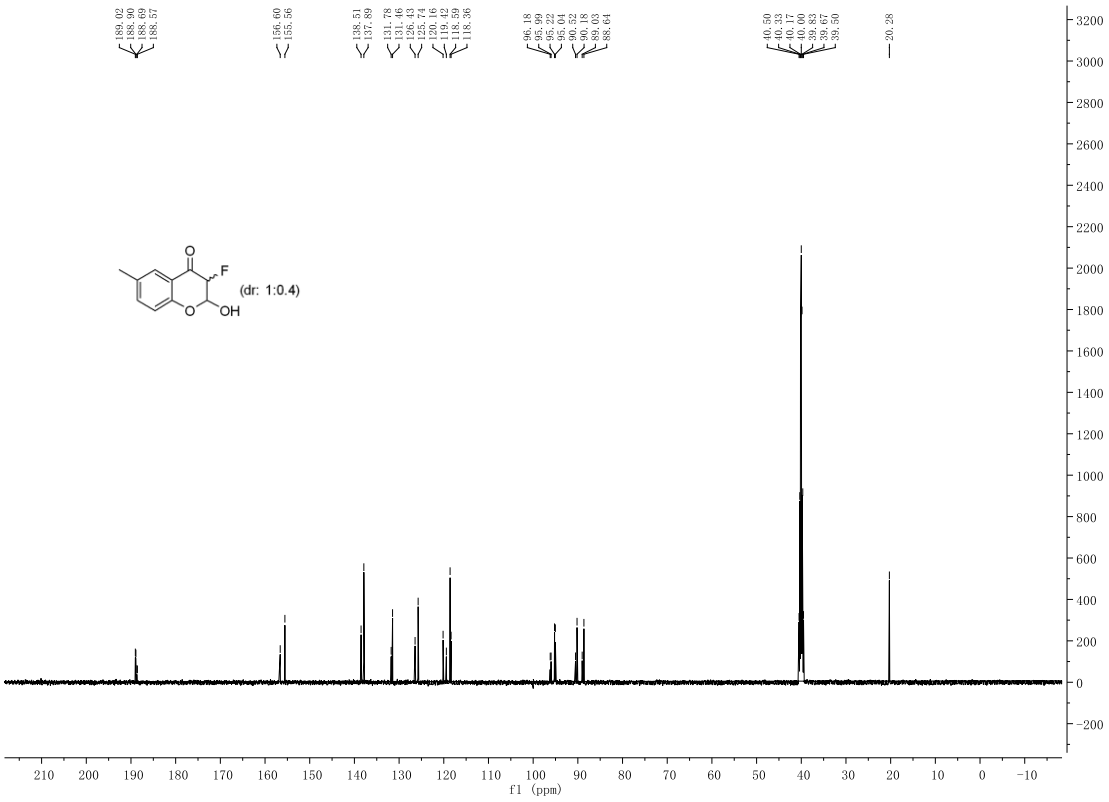
7-bromo-3-fluoro-2-hydroxychroman-4-one (3d, ^{19}F NMR, DCCl3, 471 MHz)



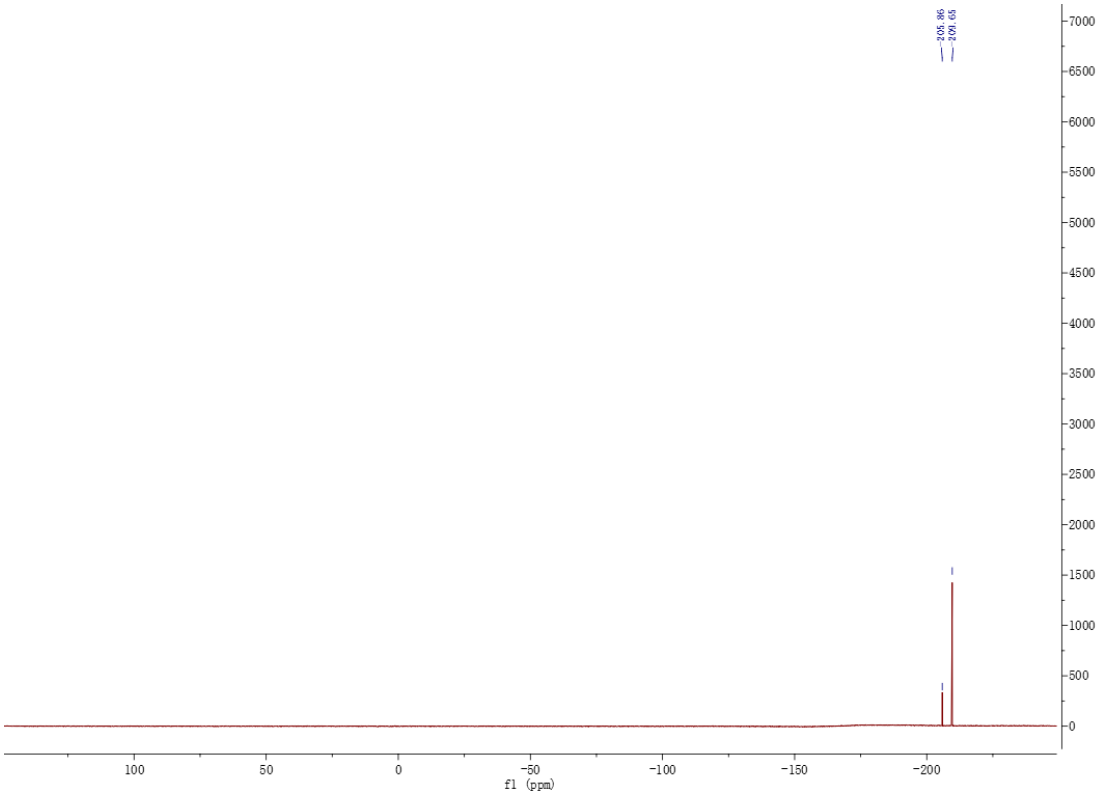
3-fluoro-2-hydroxy-6-methylchroman-4-one (3f, dr: 1:0.40, ^{1}H NMR, DMSO-D_6, 500 MHz)



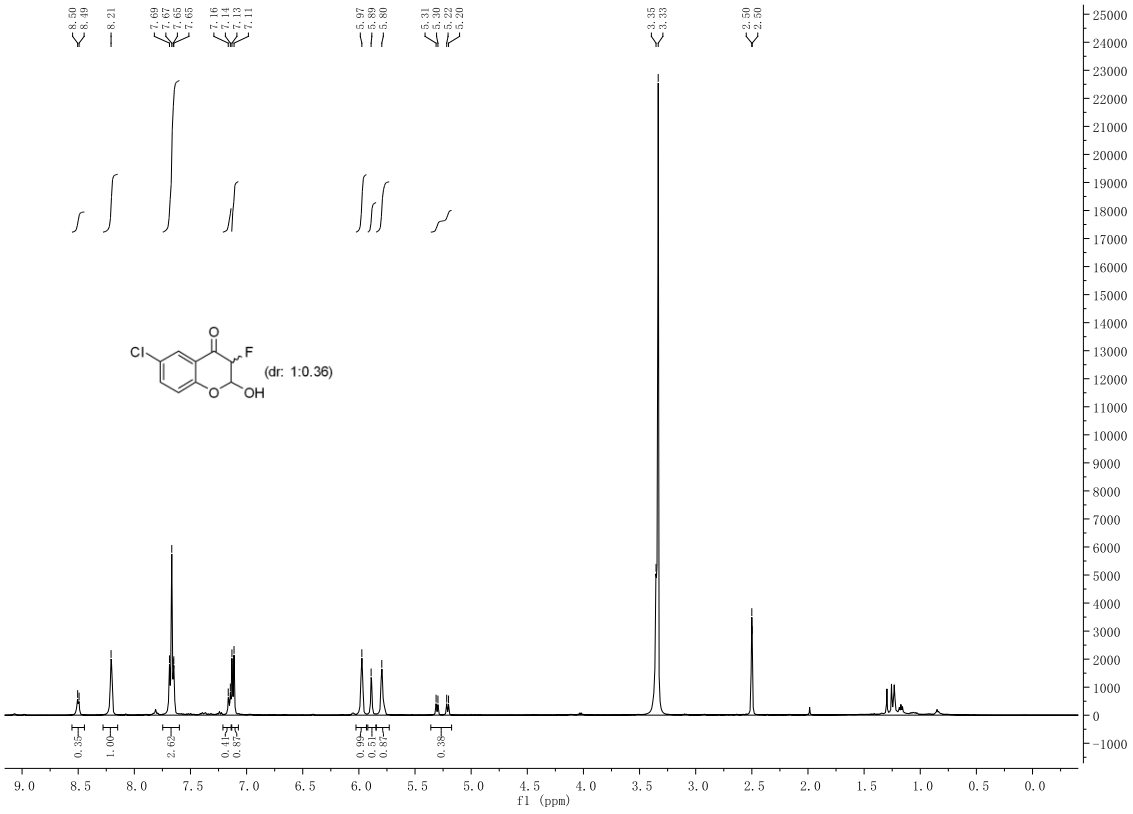
3-fluoro-2-hydroxy-6-methylchroman-4-one (3f, dr: 1:0.40, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



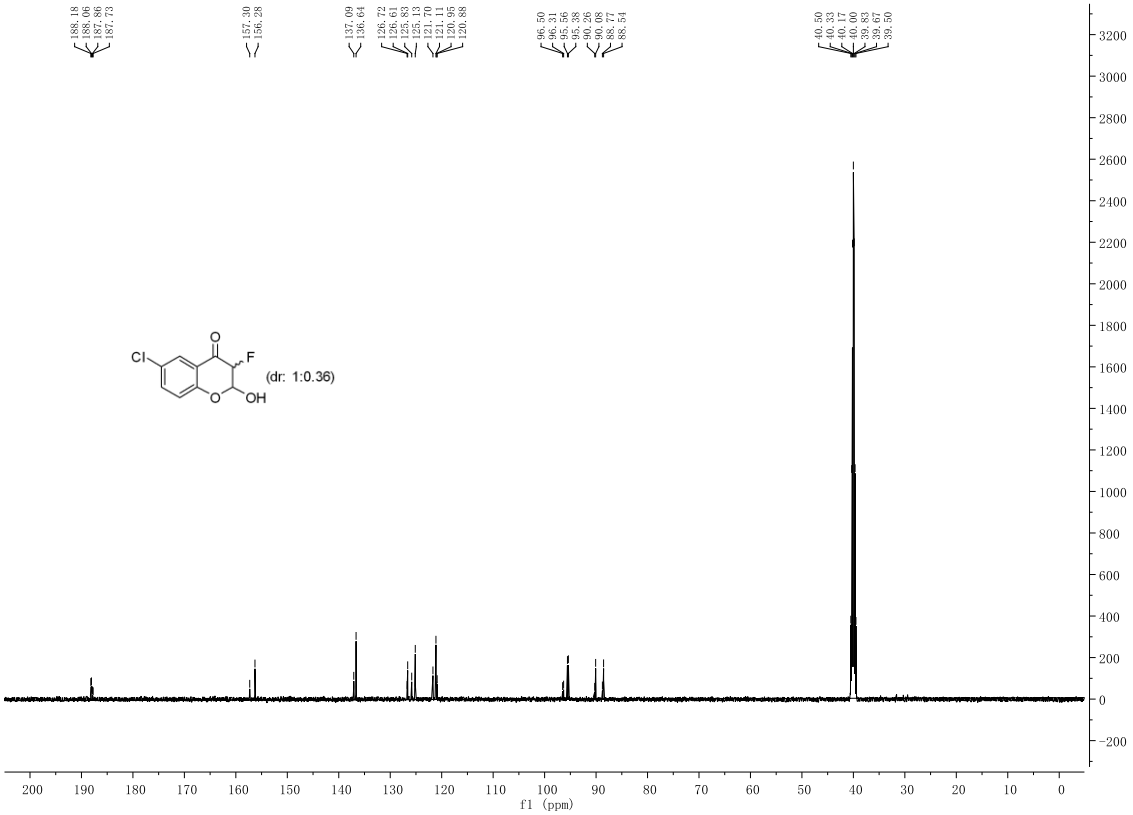
3-fluoro-2-hydroxy-6-methylchroman-4-one (3f, ^{19}F NMR, DMSO-D$_6$, 471 MHz)



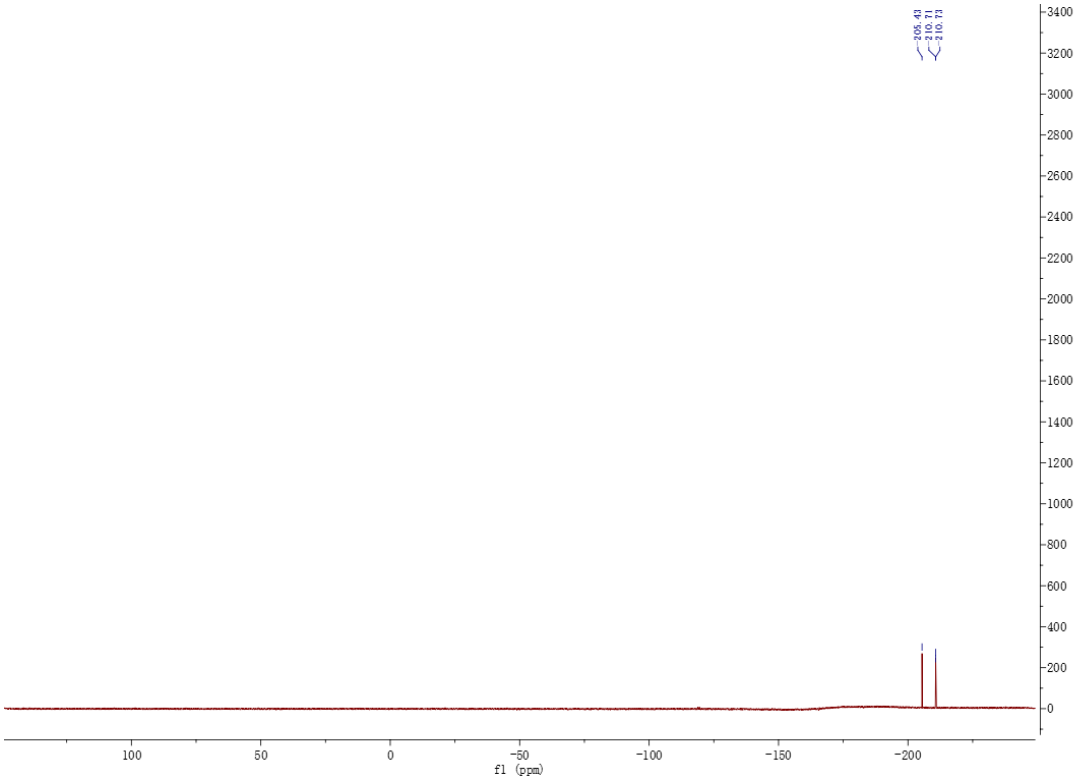
6-chloro-3-fluoro-2-hydroxychroman-4-one (3h, dr: 1:0.36, ^{1}H NMR, DMSO-D$_6$, 500 MHz)



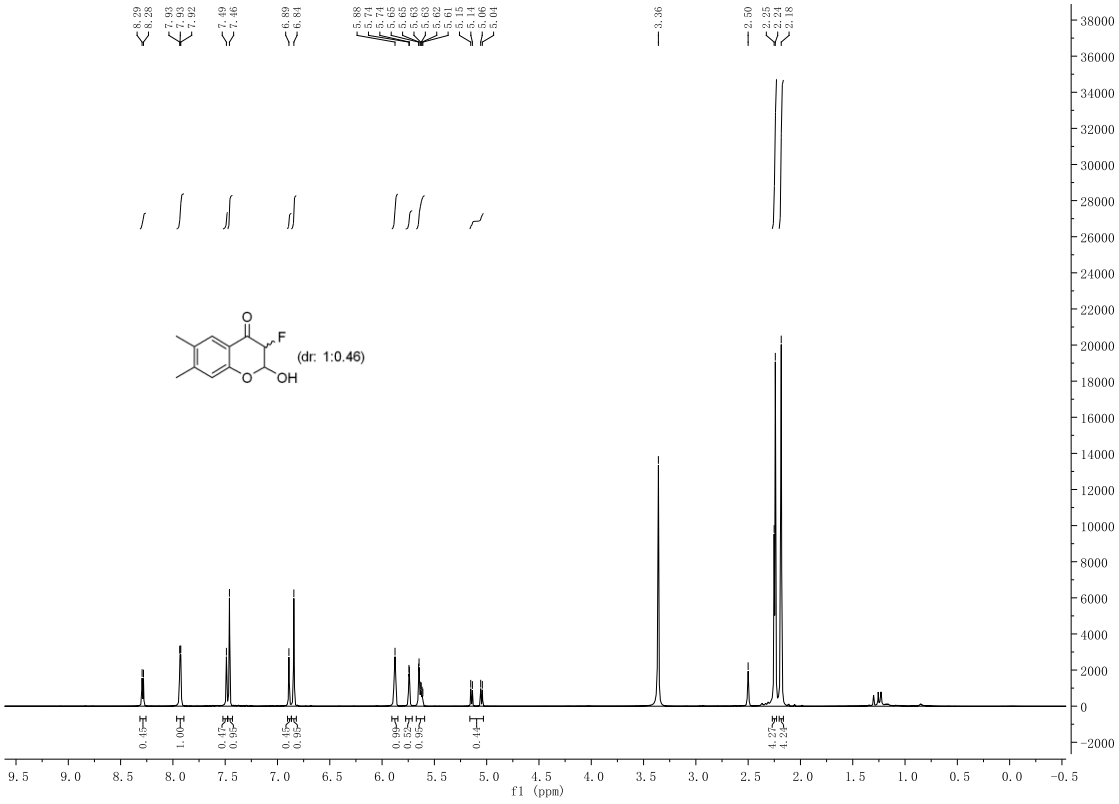
6-chloro-3-fluoro-2-hydroxychroman-4-one (3h, dr: 1:0.36, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



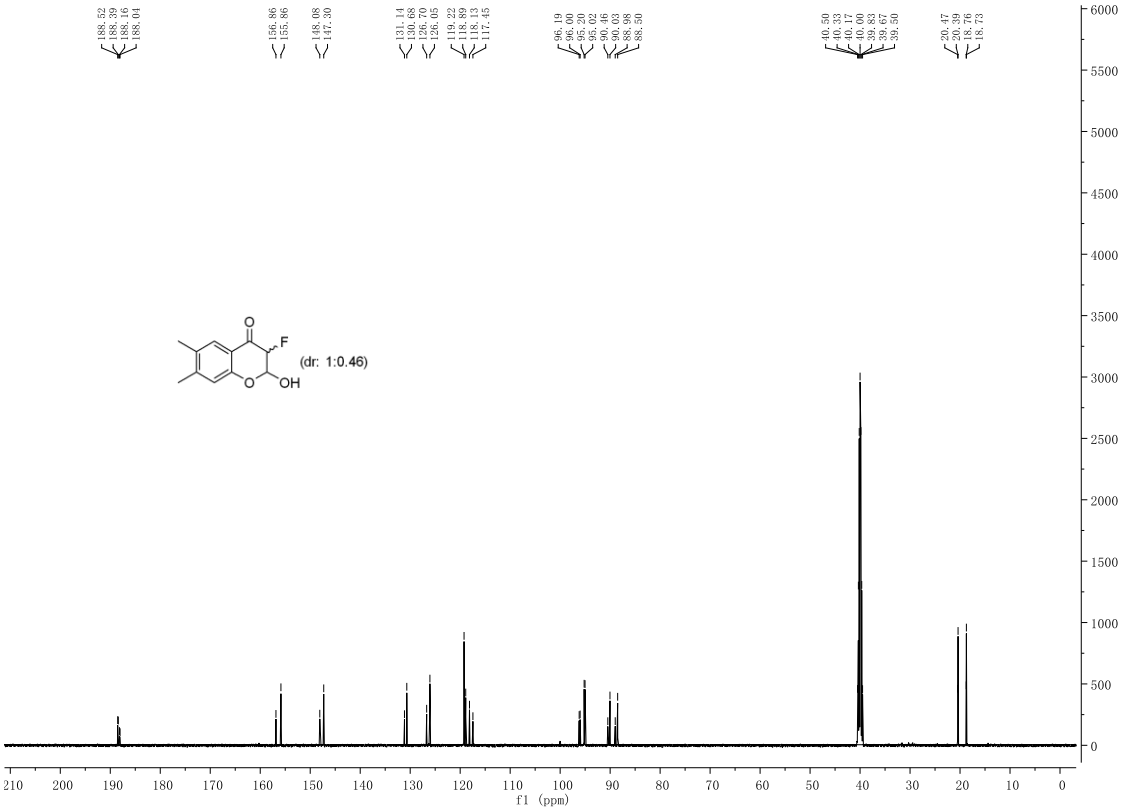
6-chloro-3-fluoro-2-hydroxychroman-4-one (3h, ^{19}F NMR, $DCCl_3$, 471 MHz)



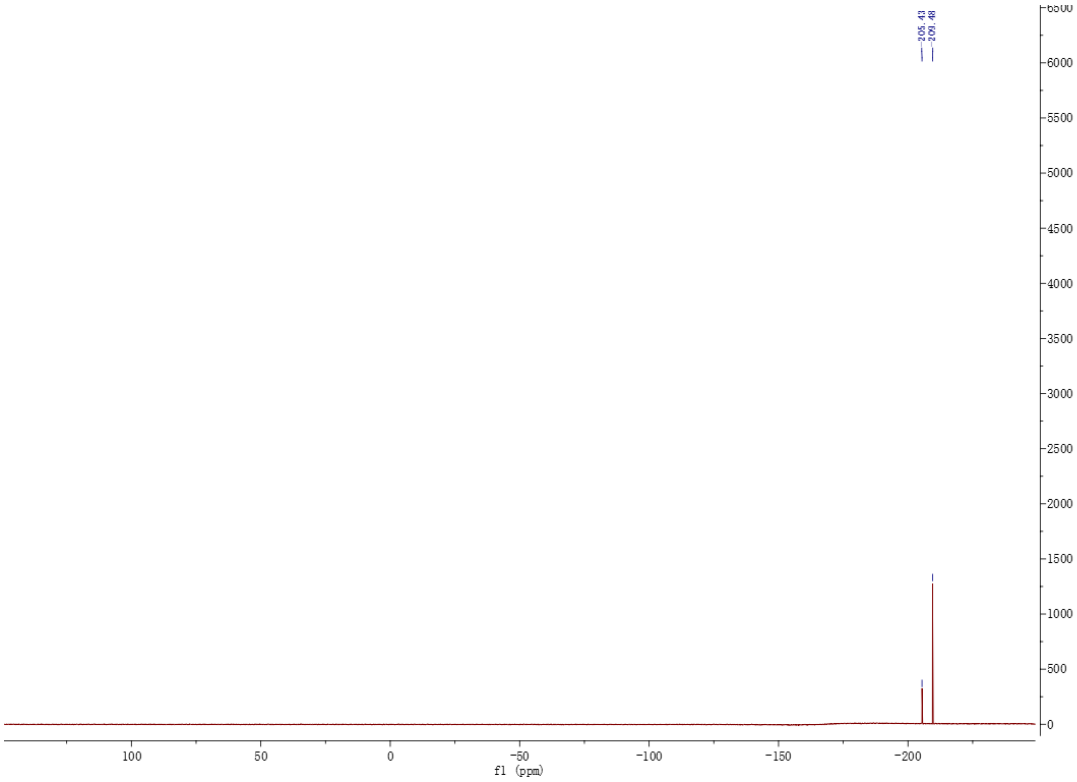
3-fluoro-2-hydroxy-6,7-dimethylchroman-4-one (3n, dr: 1:0.46, ^{1}H NMR, DMSO-D_6, 500 MHz)



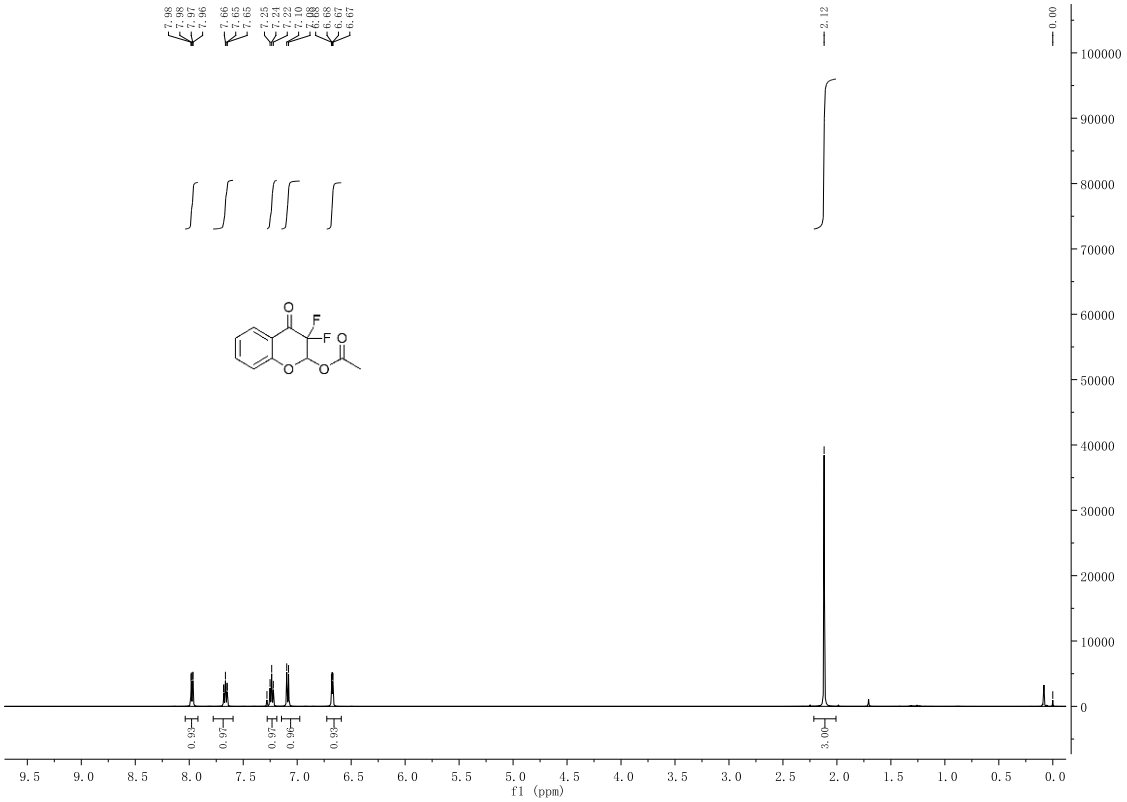
3-fluoro-2-hydroxy-6,7-dimethylchroman-4-one (3n, dr: 1:0.46, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



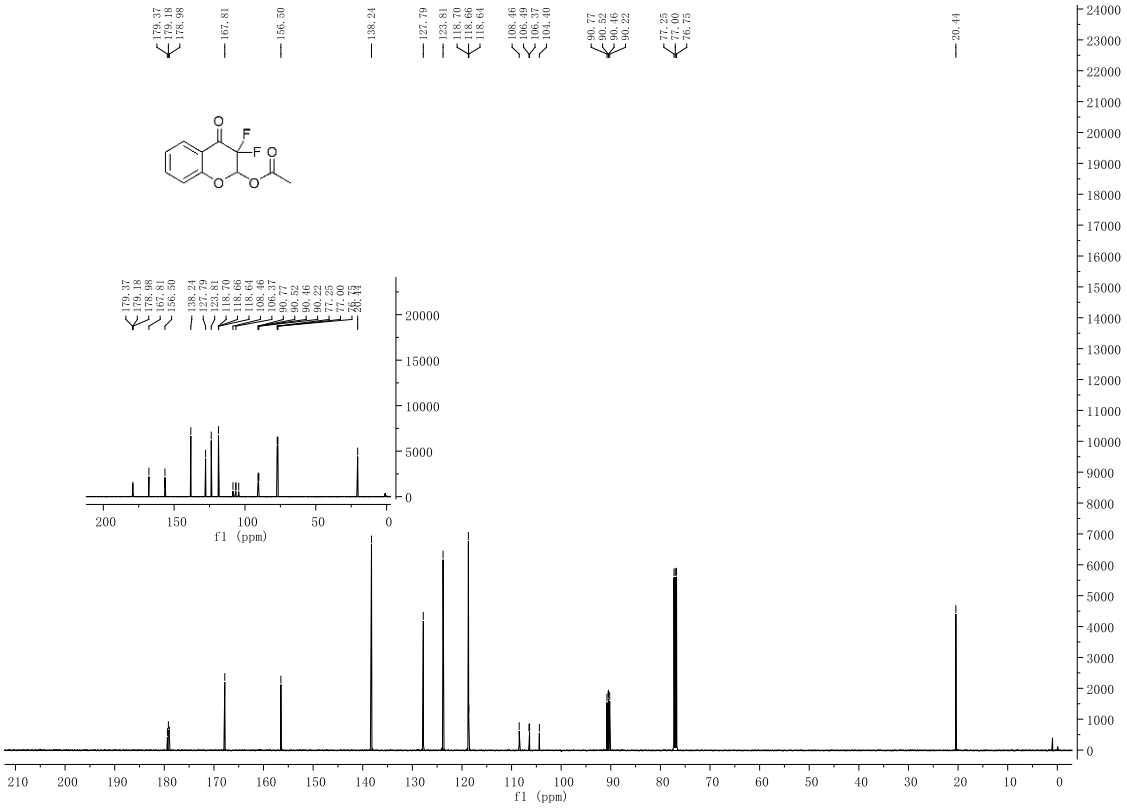
3-fluoro-2-hydroxy-6,7-dimethylchroman-4-one (3n, ^{19}F NMR, DMSO-D$_6$, 471 MHz)



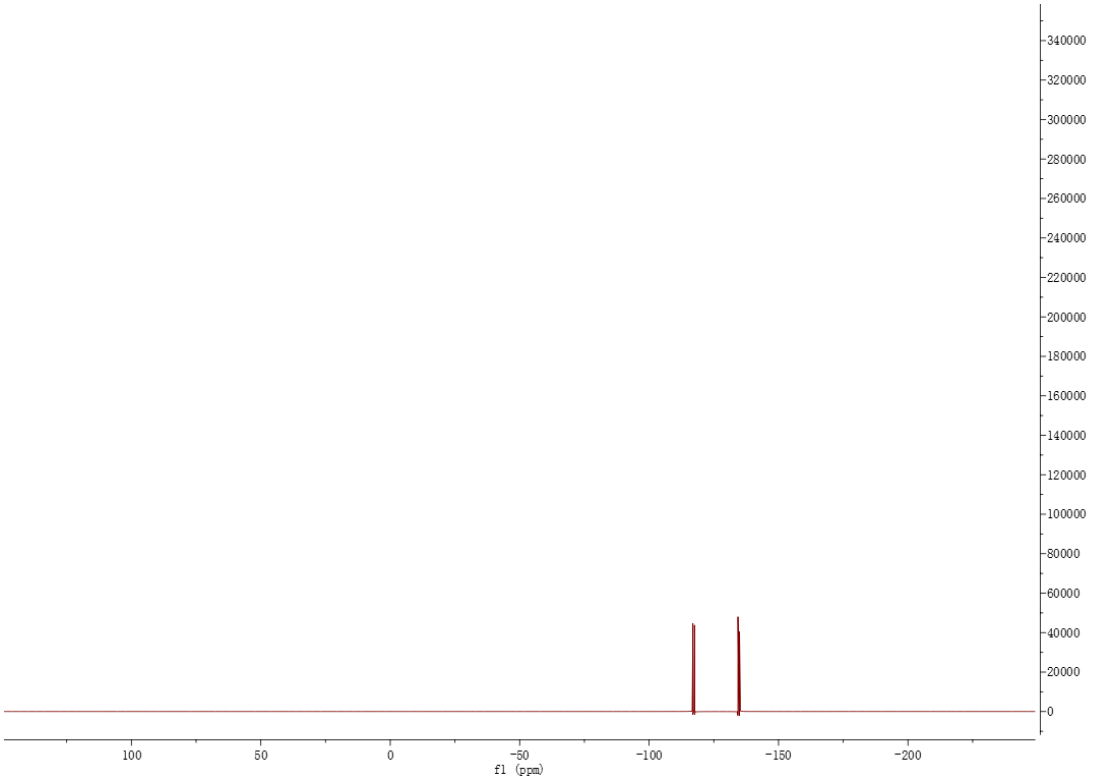
3,3-difluoro-4-oxochroman-2-yl acetate (4a, ^{1}H NMR, $DCCl_3$, 500 MHz)



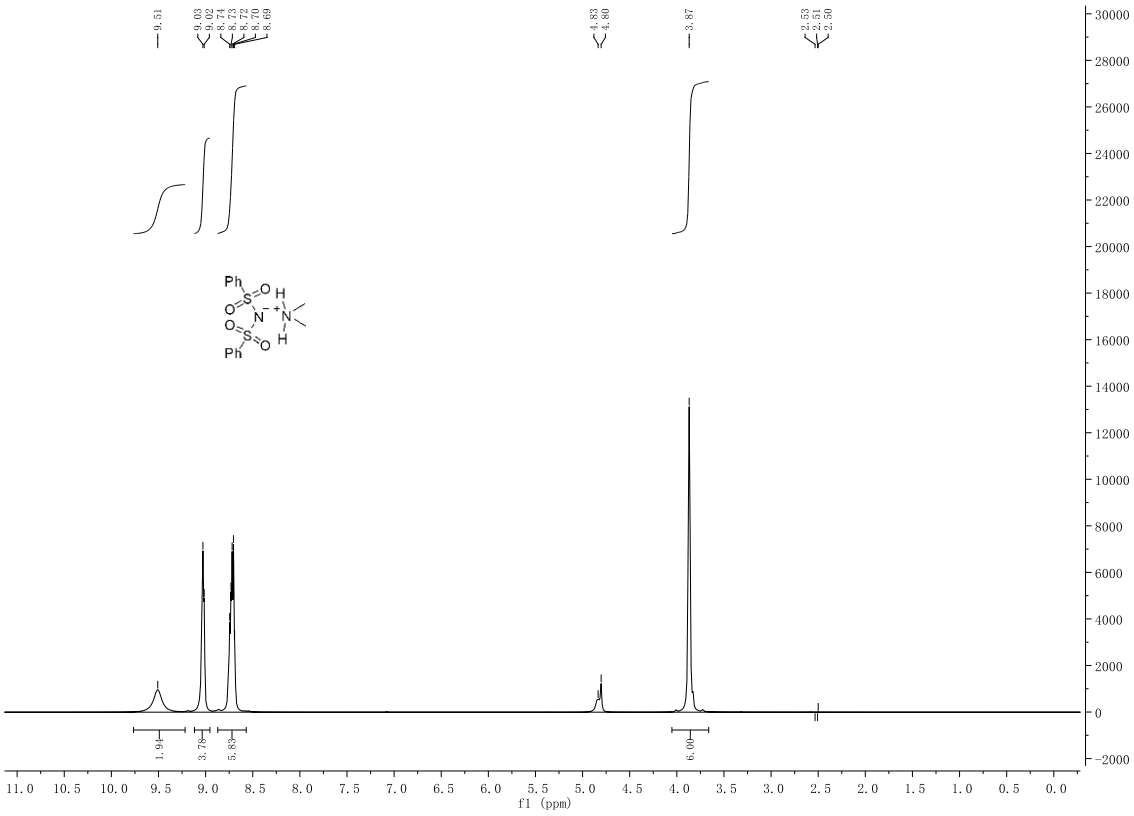
3,3-difluoro-4-oxochroman-2-yl acetate (4a, ^{13}C NMR, $DCCl_3$, 125 MHz)



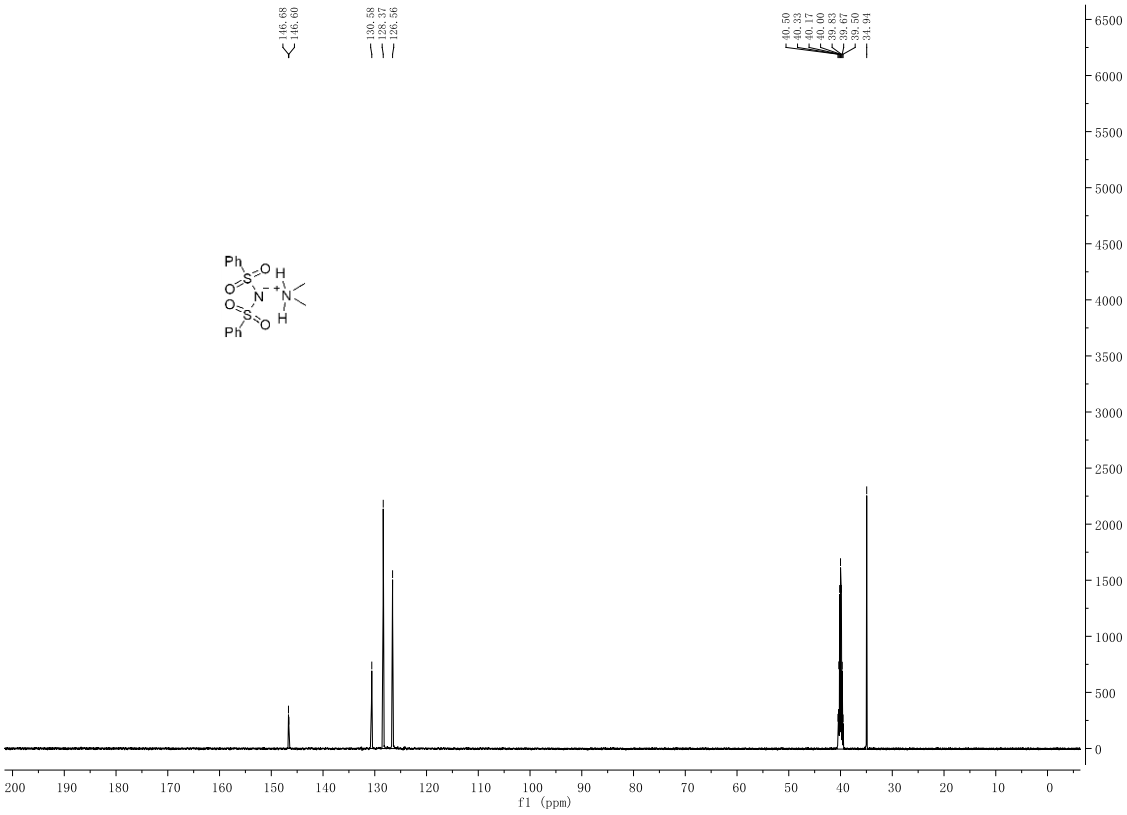
3,3-difluoro-4-oxochroman-2-yl acetate (4a, ^{19}F NMR, $DCCl_3$, 471 MHz)



Dimethylammonium bis(phenylsulfonyl)amide (5, ^{1}H NMR, DMSO-D_6, 500 MHz)



Dimethylammonium bis(phenylsulfonyl)amide (5, ^{13}C NMR, DMSO-D$_6$, 125 MHz)



(F) References

(1) S. K. Panja, S. Maiti, C. Bandyopadhyay, Synthesis of 3-allylchromones, homoisoflavones and bischromones from (*E*)-1-(2-hydroxyphenyl)-3-(*N*, *N*-dimethylamino)prop-2-en-1-one, *J. Chem. Res.*, 2010, **34**, 555.

(2) K. S. Levchenko, I. S. Semenova, V. N. Yarovenko, P. S. Shmelin, M. M. Krayushkin, Facile syntheses of 2-substituted 3-cyanochromones, *Tetrahedron Lett.*, 2012, **53**, 3630.