Cp*Ir(III) and Cp*Rh(III)-catalyzed Annulation of Salicylaldedydes with Fluorinated Vinyl Tosylates

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Supporting Information

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1. General Considerations

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. If reaction was not carried out at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under argon: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous DMF and MeOH were purchased from Acros Organics and stored under argon. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

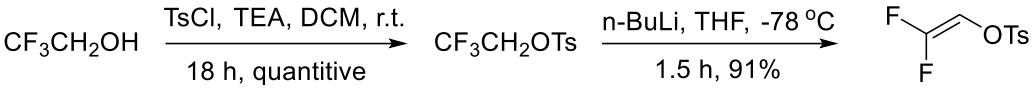
Analytical thin-layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (200-300 mesh) by standard technique.

^1H NMR were recorded on a Bruker AV 500 in solvents as indicate. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; d_6-DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm; d_4-MeOD: δ_H = 3.31 ppm, δ_C = 49.00 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR spectra were recorded on 125 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane (δ = 0). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

No attempts were made to optimize yields for substrate synthesis.

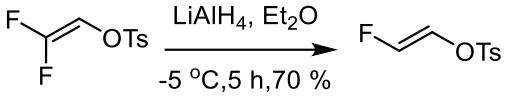
2. Preparation of Coupling reagents

(1) Preparation of 2, 2-Difluorovinyl tosylate



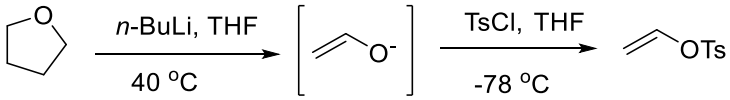
The title compound was prepared according to a known procedure.[1]

(2) Preparation of *E*-2 Fluorovinyl 4-methylbenzenesulfonate



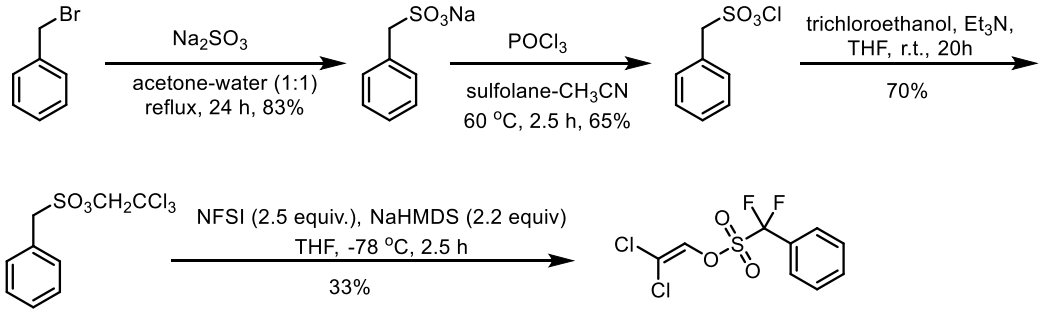
The title compound was prepared according to a known procedure.[2]

(3) Preparation of vinyl tosylate



The title compound was prepared according to a known procedure.[3]

(4) Preparation of 2,2-dichlorovinyl difluoro(phenyl)methanesulfonate



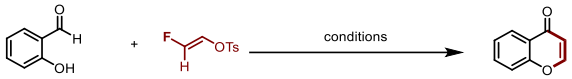
The title compound was prepared according to a known procedure.[4]

3. Optimization of the reaction

Initially, salicylaldehyde (**1a**) was subjected to react with monofluorovinyl tosylate (**2**) under the catalysis of $[Cp^*RhCl_2]_2$ (5 mol %) in HFIP (0.1 M) at 90 °C for 8 h. Delightedly, the desired product **3a** was obtained, albeit in a low yield (16%, Table 1, entry 1). Switching Cp*Rh(III) to Cp*Ir(III) gave a higher yield of 33% (entry 2). Of note, the base was crucial for the reaction as its omission or replacement with PivOH resulted in

trivial reactivity (entries 3 and 4). The use of K_2CO_3 was beneficial for the reaction, giving an improved 85% yield (entry 5). Nonfluorinated solvent MeOH or DCE turned out to be inferior to the reaction (entries 6 and 7). Probably because of HFIP formed hydrogen bonds between the substrate and solvent to facilitate not only the C-H activation step, but also the optimal geometry of the iridacycle. Decreasing the amount of the catalyst to 2.5 mol % reduced the yield due to incomplete conversion of salicylaldehyde (entry 8). Lowering the temperature from 90 °C to 60 °C led to incomplete conversion as well. Control experiments showed that $[Cp^*IrCl_2]_2$ was essential for the reaction (entry 10).

Table 1. Optimization of the Reaction Conditions[a].



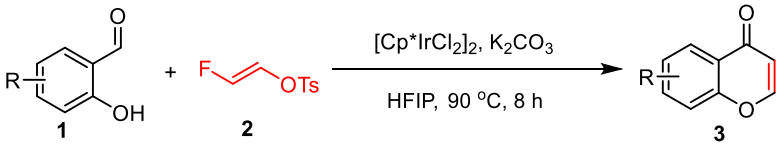
1a 2 3a

Entry	Cat.	Additive	solvent	*T* [°C]	Yield
1	$[Cp^*RhCl_2]_2$	CsOAc	HFIP	90	16%
2	$[Cp^*IrCl_2]_2$	CsOAc	HFIP	90	33%
3	$[Cp^*IrCl_2]_2$	PivOH	HFIP	90	trace
4	$[Cp^*IrCl_2]_2$	-	HFIP	90	trace
5	$[Cp^*IrCl_2]_2$	K_2CO_3	HFIP	90	85%
6	$[Cp^*IrCl_2]_2$	K_2CO_3	MeOH	90	14%
7	$[Cp^*IrCl_2]_2$	K_2CO_3	DCE	90	25%
8[b]	$[Cp^*IrCl_2]_2$	K_2CO_3	HFIP	90	54%
9	$[Cp^*IrCl_2]_2$	K_2CO_3	HFIP	60	23%
10	-	K_2CO_3	HFIP	90	0

[a] **1a** (0.1 mmol), **2** (0.2 mmol), cat. (5.0 mol %), additive (1.0 equiv.), HFIP (0.1 M), 8 h, isolated yield. [b] 2.5 mol % of $[Cp^*IrCl_2]_2$ was used.

4. General Procedure

General Procedure A:

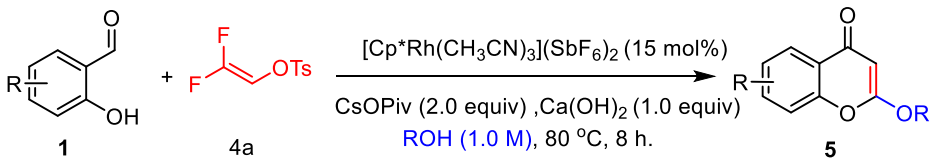


1 2 3

A 15 mL-schlenk tube charged with a stirring bar, was added salicylaldehyde **1** (0.2 mmol, 1 equiv) and **2** (0.4 mmol, 2 equiv)、$[Cp^*IrCl_2]_2$ (6.1 mg, 0.01 mmol, 5 mol%) and K_2CO_3 (138 mg, 0.3 mmol, 1.5 equiv), HFIP (2 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 90 °C until the complete consumption of **1** as monitored by TLC analysis (typically 8 hours). The reaction mixture was then diluted with DCM (20 mL) and washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined,

washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

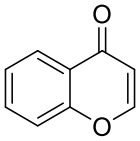
General Procedure B:



A 15 mL-schlenk tube charged with a stirring bar, was added salicylaldehyde **1** (0.2 mmol, 1 equiv) and **4a** (0.4 mmol, 2.0 equiv). $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$ (25 mg, 0.03 mmol, 15 mol%) 、CsOPiv (93.6 mg, 0.4 mmol, 2.0 equiv),、$Ca(OH)_2$ (14,8 mg, 0.2 mmol, 1 equiv) and ROH (2 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 80 °C until the complete consumption of **1** as monitored by TLC analysis (typically 8 hours). The reaction mixture was then diluted with DCM (20 mL) and washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5**.

5. Characterization of Products 3 and 5

4*H*-Chromen-4-one (3a)



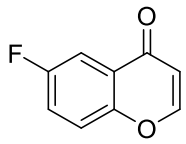
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3a** was obtained as a yellow oil (24.2 mg, 0.166 mmol, 83 %). R_f = 0.29 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.67 (ddd, *J* = 8.7, 7.2, 1.7 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.40 (td, *J* = 7.5, 0.9 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.8, 156.7, 155.5, 133.9, 125.9, 125.4, 125.0, 118.3, 113.1.

ESI-MS: calculated for $C_9H_6O_2[M+H]^+$: 147.0440, found: 147.0440.

6-Fluoro-4*H*-chromen-4-one (3b)



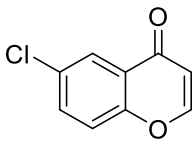
The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 6/1), **3b** was obtained as a yellow oil (28.5 mg, 0.174 mmol, 87 %). R_f = 0.29 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 6.0 Hz, 1H), 7.85 (dd, *J* = 8.3, 3.1 Hz, 1H), 7.48 (dd, *J* = 9.1, 4.2 Hz, 1H), 7.40 (m, *J* = 9.2, 7.6, 3.1 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.0 (d, J^4 = 2.0 Hz), 159.7, 158.7 (d, J^1 = 247.1 Hz), 155.6, 152.9, 126.2(d, J^3 = 7.3 Hz), 122.2 (d, J^2 = 25.4 Hz), 120.5 (d, J^3 = 8.0 Hz), 112.4, 110.9 (d, J^2 = 23.7 Hz).

ESI-MS: calculated for $C_9H_5FO_2[M+H]^+$: 165.0346, found: 165.0345.

6-Chloro-4*H*-chromen-4-one (3c)



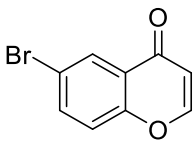
The title compound was prepared *via* the general procedure **A**, after purification by silica gel column chromatography (PE/EA = 6/1), **3c** was obtained as a white solid (31.1 mg, 0.172 mmol, 86 %). R_f = 0.32 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 2.6 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.59 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.5, 155.6, 154.9, 134.1, 131.3, 125.9, 125.3, 120.1, 113.0.

ESI-MS: calculated for $C_9H_5ClO_2$ $[M+H]^+$: 181.0050, found: 181.0049.

6-Bromo-4*H*-chromen-4-one (3d)



The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 4/1), **3d** was obtained as a white solid (36.2 mg, 0.162 mmol, 81 %).

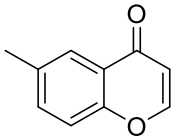
R_f = 0.29 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 2.5 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.74 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.35 (d, *J* = 8.9 Hz, 1H), 6.35 (d, *J* = 6.0 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.4, 155.6, 155.4, 136.9, 128.6, 126.2, 120.3, 118.8, 113.1.

ESI-MS: calculated for $C_9H_5BrO_2$ $[M+H]^+$: 224.9545, found: 224.9544.

6-Methyl-4H-chromen-4-one (3e)



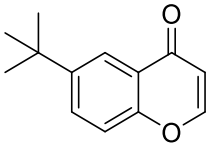
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3e** was obtained as a white solid (25 mg, 0.152 mmol, 76 %). R_f = 0.32 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.96 (m, 1H), 7.82 (d, *J* = 6.0 Hz, 1H), 7.46 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 6.31 (d, *J* = 6.0 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.9, 155.3, 154.8, 135.3, 135.1, 125.1, 124.5, 117.9, 112.8, 21.0.

ESI-MS: calculated for $C_{10}H_8O_2$ $[M+H]^+$: 161.0597, found:161.0596.

6-(*tert*-Butyl)-4H-chromen-4-one (3f)



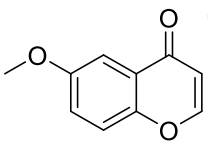
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3f** was obtained as a yellow oil (29.8 mg, 0.148 mmol, 74 %). R_f = 0.36 (PE/EA = 4/1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.5 Hz, 1H), 7.84 (d, *J* = 6.0 Hz, 1H), 7.75 (dd, *J* = 8.8, 2.5 Hz 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.2, 155.3, 154.9, 148.7, 131.9, 124.3, 121.6, 117.9, 112.9, 35.0, 31.4.

ESI-MS: calculated for $C_{13}H_{14}O_2$ $[M+H]^+$: 203.1066, found: 203.1065.

6-Methoxy-4*H*-chromen-4-one (3g)



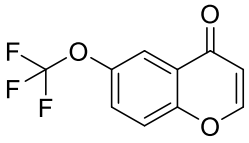
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3g** was obtained as a white solid (28.7 mg, 0.162 mmol, 81 %). R_f = 0.24 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 6.0 Hz, 1H), 7.57 (d, *J* = 3.1 Hz, 1H), 7.41 (d, *J* = 9.1 Hz, 1H), 7.27 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.34 (d, *J* = 6.0 Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.7, 157.1, 155.2, 151.5, 125.6, 124.1, 119.8, 112.2, 104.9, 56.1.

ESI-MS: calculated for $C_{10}H_8O_3$ $[M+H]^+$: 177.0546, found: 177.0545.

6-(Trifluoromethoxy)-4*H*-chromen-4-one (3h)



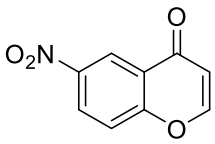
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 10/1), **3h** was obtained as a white solid (39.6 mg, 0.172 mmol, 86 %). R_f = 0.17 (PE/EA = 8/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (m, 1H), 7.89 (d, *J* = 6.1 Hz, 1H), 7.53 (d, *J* = 1.3 Hz, 2H), 6.38 (d, *J* = 6.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.7, 155.7, 154.6, 146.2, 127.3, 125.8, 120.5(q, J^1 = 258.3 Hz), 120.5, 117.5, 112.8.

ESI-MS: calculated for $C_{10}H_5F_3O_3$ $[M+H]^+$: 231.0263, found: 231.0262.

6-Nitro-4*H*-chromen-4-one (3i)



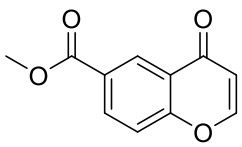
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 8/1), **3i** was obtained as a yellow solid (25.9 mg, 0.136 mmol, 69 %). R_f = 0.15 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.07 (d, *J* = 2.8 Hz, 1H), 8.50 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.93 (d, *J* = 6.1 Hz, 1H), 7.63 (d, *J* = 9.2 Hz, 1H), 6.44 (d, *J* = 6.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.1, 159.4, 155.8, 144.9, 128.3, 125.0, 122.7, 120.2, 113.7.

ESI-MS: calculated for $C_9H_5NO_4$ $[M+H]^+$: 192.0291, found: 192.0290.

Methyl 4-oxo-4*H*-chromene-6-carboxylate (3j)



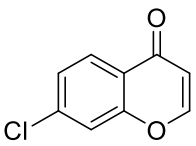
The title compound was prepared via the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3j** was obtained as a white solid (35.9 mg, 0.176 mmol, 88 %). Rf = 0.18 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*): δ 8.89 (d, *J* = 2.1 Hz, 1H), 8.33 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.89 (d, *J* = 6.1 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 6.40 (d, *J* = 6.1 Hz, 1H), 3.97 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.1, 165.8, 159.0, 155.6, 134.5, 128.5, 127.4, 124.6, 118.8, 113.6, 52.6.

ESI-MS: calculated for $C_{11}H_8O_4$ $[M+H]^+$: 205.0495, found: 205.0493.

7-Chloro-4*H*-chromen-4-one (3k)



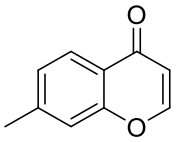
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3k** was obtained as a white solid (26.6 mg, 0.148 mmol, 74 %). R_f = 0.32 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 6.0 Hz, 1H), 7.47 (d, *J* = 1.9 Hz, 1H), 7.36 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.33 (d, *J* = 6.1 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.9, 156.7, 155.5, 140.0, 127.3, 126.3, 123.5, 118.4, 113.4.

ESI-MS: calculated for $C_9H_5ClO_2$ $[M+H]^+$: 181.0050:, found: 181.0050.

7-Methyl-4*H*-chromen-4-one (3l)



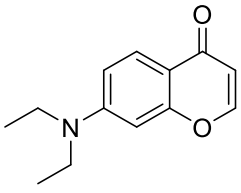
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3l** was obtained as a white solid (22 mg, 0.138 mmol, 69 %). R_f = 0.24 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 6.0 Hz, 1H), 7.28 – 7.21 (m, 2H), 6.32 (d, *J* = 6.0 Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.7, 156.7, 155.1, 145.2, 126.8, 125.6, 122.6, 117.9, 112.9, 21.8.

ESI-MS: calculated for $C_{10}H_8O_2$ $[M+H]^+$: 161.0597, found: 161.0596.

7-(Diethylamino)-4*H*-chromen-4-one (3m)



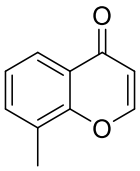
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 8/1), **3m** was obtained as a white solid (25 mg, 0.116 mmol, 58 %). R_f = 0.13 (PE/EA = 4/1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 6.0 Hz, 1H), 6.72 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.43 (d, *J* = 2.5 Hz, 1H), 6.18 (d, *J* = 6.0 Hz, 1H), 3.44 (q, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.1, 159.1, 154.2, 152.0, 127.1, 114.2, 112.6, 110.7, 96.5, 44.9, 12.6.

ESI-MS: calculated for $C_{13}H_{15}NO_2$ $[M+H]^+$: 218.1175, found: 218.1174.

8-Methyl-4*H*-chromen-4-one (3n)



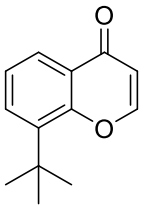
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3n** was obtained as a white solid (30.2 mg, 0.188 mmol, 94 %). R_f = 0.26 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 6.0 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.7 Hz, 1H), 6.32 (d, *J* = 6.0 Hz, 1H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.1, 155.2, 155.1, 134.7, 127.7, 124.8, 123.4, 112.8, 15.7.

ESI-MS: calculated for $C_{10}H_8O_2$ $[M+H]^+$: 161.0597, found: 161.0596 .

8-(*tert*-Butyl)-4*H*-chromen-4-one (3o)



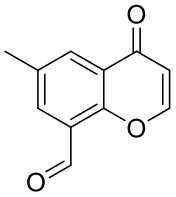
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3o** was obtained as a yellow oil (34.4 mg, 0.17 mmol, 85 %). R_f = 0.38 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.95 (d, *J* = 5.9 Hz, 1H), 7.65 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 5.9 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.2, 155.5, 154.5, 139.3, 131.1, 125.7, 125.0, 124.1, 112.7, 35.2, 30.1.

ESI-MS: calculated for $C_{13}H_{14}O_2$ $[M+H]^+$: 203.1066, found: 203.1066.

6-Methyl-4-oxo-4*H*-chromene-8-carbaldehyde (3p)



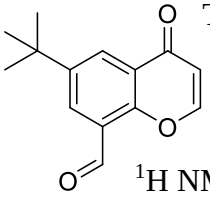
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 8/1), **3p** was obtained as a white solid (32.0 mg, 0.17 mmol, 85 %). R_f = 0.17 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.60 (s, 1H), 8.26 (d, *J* = 1.7 Hz, 1H), 8.04 (d, *J* = 2.2 Hz, 1H), 7.94 (d, *J* = 6.0 Hz, 1H), 6.42 (d, *J* = 6.0 Hz, 1H), 2.50 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.3, 176.6, 155.3, 155.0, 135.6, 134.6, 132.1, 125.4, 125.0, 113.7, 20.9.

ESI-MS: calculated for $C_{14}H_{14}O_3$ $[M+H]^+$: 189.0546, found: 189.0547.

6-(*tert*-Butyl)-4-oxo-4*H*-chromene-8-carbaldehyde (3q)



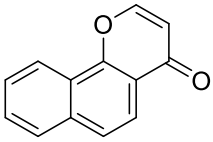
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 8/1), **3q** was obtained as a white solid (36.5 mg, 0.16 mmol, 80%). R_f = 0.11 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ10.64 (s, 1H), 8.48 (d, *J* = 2.6 Hz, 1H), 8.30 (d, *J* = 2.6 Hz, 1H), 7.96 (d, *J* = 6.0 Hz, 1H), 6.44 (d, *J* = 6.0 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.5, 176.8, 155.2, 155.0, 148.9, 131.4, 128.7, 125.1, 124.9, 113.7, 35.2, 31.3.

ESI-MS: calculated for $C_{14}H_{14}O_3$ $[M+H]^+$: 231.1015, found: 231.1014.

4*H*-Benzo[*h*]chromen-4-one (3r)



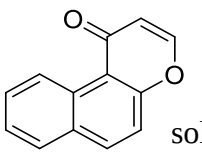
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 8/1), **3r** was obtained as a white solid (36mg, 0.184 mmol, 92%). R_f=0.22 (PE/EA = 4/1)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 8.2 Hz, 1H), 8.15 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 5.9 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.7 Hz, 1H), 7.72 (td, *J* = 7.6, 1.4 Hz, 1H), 7.68 (td, *J* = 7.7, 1.3 Hz, 1H), 6.53 (d, *J* = 5.9 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.6, 154.7, 154.2, 136.0, 129.5, 128.3, 127.3, 125.6, 124.2, 122.5, 121.4, 120.9, 114.5.

ESI-MS: calculated for $C_{13}H_8O_2$ $[M+H]^+$: 197.0597 found: 197.0596.

1*H*-Benzo[*f*]chromen-1-one (3s)



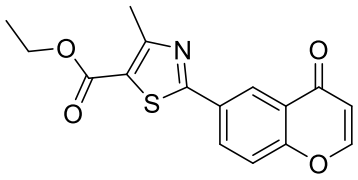
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 6/1), **3s** was obtained as a yellow solid (27.44 mg, 0.14 mmol, 70 %). R_f = 0.24 (PE/EA = 4/1).

^{1}H NMR (500 MHz, DMSO-d_6) δ 0.03 (d, J = 8.6 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.76 (ddd, J = 8.5, 7.0, 1.4 Hz, 1H), 7.62 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.50 (d, J = 9.0 Hz, 1H), 6.52 (d, J = 5.8 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.6, 157.9, 152.8, 135.7, 130.7, 130.6, 129.4, 128.3, 127.3, 126.8, 118.4, 117.7, 116.2.

ESI-MS: calculated for $C_{13}H_8O_2$ $[M+H]^+$: 197.0597, found: 197.0596.

Ethyl4-methyl-2-(4-oxo-4*H*-chromen-6-yl)thiazole-5-carboxylate (3t)



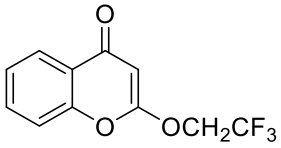
The title compound was prepared *via* the general procedure A, after purification by silica gel column chromatography (PE/EA = 8/1), **3t** was obtained as a yellow olid (18.9 mg, 0.06 mmol, 30 %). R_f = 0.18 (PE/EA = 4/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ8.70 (d, J = 2.2 Hz, 1H), 8.37 (dd, J = 8.8, 2.2 Hz, 1H), 7.89 (d, J = 6.0 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 6.40 (d, J = 6.0 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 2.79 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.1, 167.8, 162.2, 161.3, 157.8, 155.6, 131.9, 130.9, 125.2, 124.6, 122.8, 119.4, 113.5, 61.5, 17.6, 14.5.

ESI-MS: calculated for $C_{16}H_{14}NO_4S$ $[M-H]^-$: 316.0638, found: 316.0644.

2-(2,2,2-Trifluoroethoxy)-4*H*-chromen-4-one (5a)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5a** was obtained as a white solid (33 mg, 0.136 mmol, 68 %). R_f = 0.28 (PE/EA = 8/1).

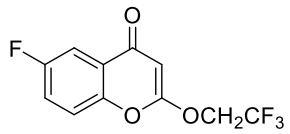
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 (dd, J = 8.4, 1.6 Hz, 1H), 7.68 (td, J = 8.2, 1.7 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 5.71 (s, 1H), 4.59 (q, J = 7.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.0, 165.0, 153.6, 133.9, 126.2, 126.1, 122.2(q, J^1 = 277.8 Hz), 123.0, 117.3, 89.6, 65.1(q, J^2 = 37.8 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.71 (t, J = 7.8 Hz).

ESI-MS: calculated for $C_{11}H_7F_3O_3$ $[M+H]^+$: 245.0420, found: 245.0418.

6-Fluoro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5b)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5b** was obtained as a white solid (28.3 mg, 0.108 mmol, 54 %). R_f = 0.39 (PE/EA = 8/1).

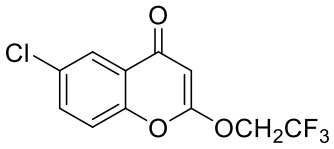
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 8.0, 3.1 Hz, 1H), 7.42 (dd, *J* = 9.1, 4.1 Hz, 1H), 7.39 – 7.33 (m, 1H), 5.70 (s, 1H), 4.60 (q, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.0, 165.2, 160.1 (d, J^1= 248.1 Hz), 149.5, 124.3 (d, J^3 = 7.4 Hz), 122.2 (q, J^1= 277.5 Hz), 121.7 (d, J^2 = 25.7 Hz), 119.3 (d, J^3 = 8.2 Hz), 111.3 (d, J^2 = 24.0 Hz), 89.1, 65.2 (q, J^2 = 37.7 Hz).

Decoupling ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.74, -114.34 .

ESI-MS: calculated for $C_{11}H_6F_4O_3$ $[M+H]^+$: 263.0325, found: 263.0324.

6-Chloro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5c)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5c** was obtained as a light yellow solid (28.3 mg, 0.102 mmol, 51 %). R_f = 0.4 (PE/EA = 8/1)

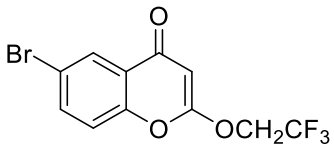
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.38 (d, *J* = 8.9 Hz, 1H), 5.70 (s, 1H), 4.59 (q, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.7, 165.1, 151.8, 134.0, 132.1, 125.7, 124.0, 122.1(q, J^1 = 277.7 Hz), 119.0, 89.5, 65.3(q, J^2 = 37.8 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.69 (t, *J* = 7.8 Hz).

ESI-MS: calculated for $C_{11}H_6ClF_3O_3$ $[M+K]^+$: 279.0030, found: 279.0029.

6-Bromo-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5d)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5d** was obtained as a white solid (20 mg, 0.062 mmol, 40 %). R_f = 0.47 (PE/EA = 4/1).

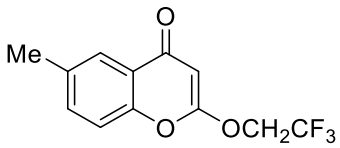
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 2.5 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 5.64 (s, 1H), 4.54 (q, *J* = 7.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.5, 165.1, 152.3, 136.8, 128.9, 124.4, 122.1(q, J^1 = 277.9 Hz), 119.5, 119.2, 89.5, 65.2(q, J^2 = 37.9 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.67 (t, *J* = 7.7 Hz).

ESI-MS: calculated for $C_{11}H_6BrF_3O_3$ $[M+H]^+$: 322.9525, found: 322.9523.

6-Methyl-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5e)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5e** was obtained as a white solid (25 mg, 0.096 mmol, 48 %). R_f = 0.31 (PE/EA = 4/1)

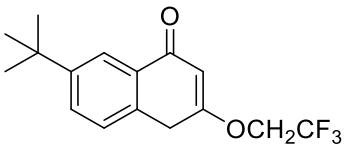
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.37 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H), 5.60 (s, 1H), 4.53 (q, *J* = 7.8 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 164.9, 151.7, 136.0, 134.8, 125.4, 122.5, 122.3 (q, J^1 = 277.8 Hz), 117.0, 89.3, 65.0 (q, J^2 = 37.6 Hz), 20.9.

Decoupling ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.78.

ESI-MS: calculated for $C_{12}H_9F_3O_3$ $[M+H]^+$: 259.0576, found: 259.0576.

7-(*tert*-Butyl)-3-(2, 2, 2-trifluoroethoxy)naphthalen-1(4*H*)-one (5f)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5f** was obtained as a white solid (25.2 mg, 0.086 mmol, 43%). R_f = 0.38 (PE/EA = 4/1)

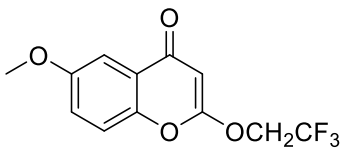
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 2.4 Hz, 1H), 7.70 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 5.68 (s, 1H), 4.59 (q, *J* = 7.7 Hz, 2H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.4, 165.0, 151.7, 149.4, 131.6, 122.3(q, J^1 = 277.8 Hz), 122.2, 122.0, 116.9, 89.4, 65.0(q, J^2 = 37.6 Hz), 35.0, 31.4.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.75(t, *J* = 8.6 Hz).

ESI-MS: calculated for $C_{15}H_{15}F_3O_3$ $[M+H]^+$: 301.1046, found: 301.1043.

6-Methoxy-2-(2, 2, 2-trifluoroethoxy)-4*H*-chromen-4-one (5g)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column

chromatography (PE/EA = 10/1), **5g** was obtained as a white solid (28.3 mg, 0.104 mmol, 52 %). R_f = 0.4 (PE/EA = 4/1).

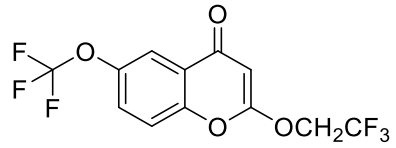
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 3.1 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.24 (dd, *J* = 9.1, 3.1 Hz, 1H), 5.70 (s, 1H), 4.59 (q, *J* = 7.7 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.0, 164.9, 157.6, 148.1, 123.7, 123.3, 122.3 (t, J^1 = 277.8 HZ), 118.6, 105.9, 89.1, 65.1 (q, J^2 = 37.7 Hz), 56.1.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.74 (t, *J* = 7.7 Hz).

ESI-MS: calculated for $C_{12}H_9F_3O_4$ $[M+H]^+$: 275.0525, found: 275.0522.

6-Nitro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5h)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5h** was obtained as a colorless oil (32.8 mg, 0.10 mmol, 50 %). R_f = 0.4 (PE/EA = 4/1)

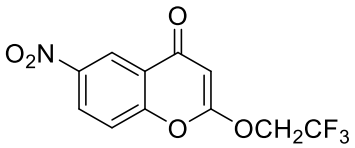
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 1.6 Hz, 1H), 7.52 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.49 (d, *J* = 8.9 Hz, 1H), 5.73 (s, 1H), 4.60 (q, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 177.8, 165.3, 151.4, 146.7, 127.0, 124.1, 122.1 (q, J^1 = 277.6 Hz,), 120.5 (q, J^1 = 259.8 Hz), 119.3, 117.9, 89.4, 65.3 (q, J^2 = 37.8 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -58.22 , -73.67 (t, *J* = 8.7 Hz).

ESI-MS: calculated for $C_{12}H_6F_6O_4$ $[M+H]^+$: 329.0243, found: 329.0240.

6-Nitro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5i)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5i** was obtained as a colorless oil (11 mg, 0.040 mmol, 20%). R_f = 0.4 (PE/EA = 4/1)

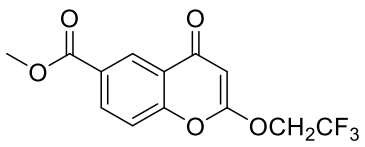
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.93 (d, *J* = 2.8 Hz, 1H), 8.44 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.55 (d, *J* = 9.1 Hz, 1H), 5.73 (s, 1H), 4.59 (q, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 176.9, 165.4, 156.3, 145.5, 128.3, 122.6, 122.0 (q, J^1 = 277.9 Hz),119.1, 89.8, 65.6 (q, J^2 = 37.9 Hz), 27.2.

Decoupling ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.60.

ESI-MS: calculated for $C_{11}H_6F_3NO_5$ $[M+H]^+$: 290.0270, found: 290.0274.

Methyl 4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromene-6-carboxylate (5j)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5j** was obtained as a white solid (28 mg, 0.092 mmol, 46%). R_f = 0.30 (PE/EA = 4/1).

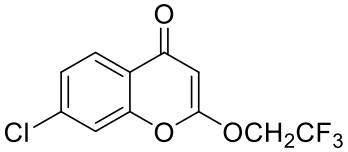
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.81 (d, *J* = 2.3 Hz, 1H), 8.30 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 1H), 5.72 (s, 1H), 4.61 (q, *J* = 7.6 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.0, 165.5, 165.1, 155.8, 134.5, 128.2, 128.0, 122.6, 122.0 (q, J^1 = 278.0 Hz), 117.7, 89.6, 65.2 (q, J^2 = 37.7 Hz), 52.5.

Decoupling ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.67.

ESI-MS: calculated for $C_{13}H_9F_3O_5$ $[M+H]^+$: 303.0474, found: 303.0472.

7-Chloro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5k)



The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 9/1), **5k** was obtained as a white solid (102.5 mg, 0.104 mmol, 52%). R_f = 0.32 (PE/EA = 4/1).

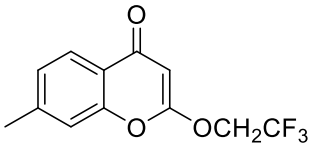
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 1.9 Hz, 1H), 7.39 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.69 (s, 1H), 4.59 (q, *J* = 7.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.0, 165.0, 153.6, 139.9, 127.3, 126.8, 122.1(d, J^1 = 277.8 Hz), 121.5, 117.6, 89.6, 65.3(q, J^2 = 37.7 Hz).

Decoupling ^{19}F NMR (471 MHz, $CDCl_3$) δ -73.69.

ESI-MS: calculated for $C_{11}H_6ClF_3O_3$ $[M+K]^+$: 316.9589, found: 316.9592.

7-Methyl-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5l)



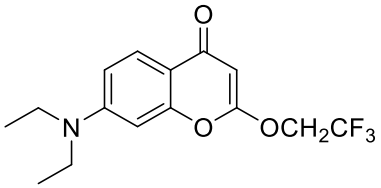
The title compound was prepared *via* the general procedure B using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 10/1), **5l** was obtained as a white solid (23.4 mg, 0.470 mmol, 45%). R_f = 0.28 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.15 (s, 1H), 5.62 (s, 1H), 4.57 (q, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.9, 164.8, 153.6, 145.2, 127.2, 125.6, 122.2 (q, J^1 = 276.3 Hz), 120.5, 117.1, 89.2, 64.9(q, J^2 = 37.7 Hz), 21.8.

ESI-MS: calculated for $C_{12}H_9F_3O_3$ $[M+H]^+$: 259.0576, found: 259.0576 .

7-(Diethylamino)-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5m)



Using TFE as solvent, the title compound was prepared *via* the general procedure B, after purification by silica gel column chromatography (PE/EA = 8/1), **5m** was obtained as a white solid (26.5 mg, 0.084 mmol, 42%). R_f = 0.20 (PE/EA = 4/1).

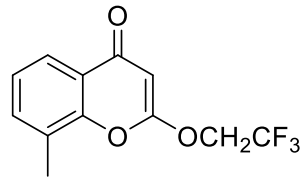
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 9.0 Hz, 1H), 6.70 (dd, *J* = 9.1, 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 5.50 (s, 1H), 4.51 (q, *J* = 7.7 Hz, 2H), 3.43 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.7, 164.5, 156.2, 152.1, 127.1, 122.4(d, J^1 = 277.6 Hz), 111.5, 110.5, 96.3, 88.3, 65.05 (q, J^2 = 38.5 Hz,), 44.9, 12.5.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.75 (t, *J* = 7.7 Hz).

ESI-MS: calculated for $C_{15}H_{16}F_3NO_3$ $[M+H]^+$: 316.1155, found: 316.1153.

8-Methyl-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5n)



Using TFE as solvent ,the title compound was prepared *via* the general procedure B by using TFE as solvent, after purification by silica gel column chromatography (PE/EA = 8/1), **5n** was obtained as a white solid (25.4 mg, 0.1 mmol, 50%). R_f = 0.28 (PE/EA = 4/1).

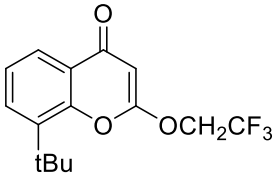
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 7.9, 3.6 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz,1H), 5.61 (s, 1H), 4.54 (q, *J* = 7.8 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.4, 164.8, 152.0, 134.9, 126.8, 125.4, 123.6, 122.8, 122.3 (q, J^1 = 277.8 Hz), 89.23, 65.0 (q, J^2 = 37.6 Hz), 15.45.

Decoupling ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.65.

ESI-MS: calculated for $C_{12}H_9F_3O_3$ $[M+H]^+$: 259.0576, found: 259.0575.

8-(*tert*-Butyl)-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5o)



Using TFE as solvent, the title compound was prepared *via* the general procedure B by using TFE as solvent, after purification by

silica gel column chromatography (PE/EA = 8/1), **5o** was obtained as a white solid (27 mg, 0.09 mmol, 45%). R_f = 0.26 (PE/EA = 4/1).

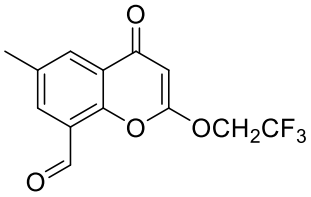
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.65 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 5.70 (s, 1H), 4.57 (q, *J* = 7.7 Hz, 2H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.5, 165.0, 152.5, 138.6, 131.4, 125.5, 124.3, 123.6, 122.2(q, J^1 = 276.0 Hz), 88.8, 65.5(q, J^2 = 37.6 Hz), 35.1, 30.2.

Decoupling ^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.63.

ESI-MS: calculated for $C_{15}H_{15}F_3O_3$ $[M+H]^+$: 301.1046, found: 301.1046.

6-Methyl-4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromene-8-carbaldehyde (5p)



Using TFE as solvent, the title compound was prepared *via* the general procedure B, after purification by silica gel column chromatography (PE/EA = 2/1), **5p** was obtained as a white solid (19.6 mg, 0.068 mmol, 34%). R_f = 0.16 (PE/EA = 2/1).

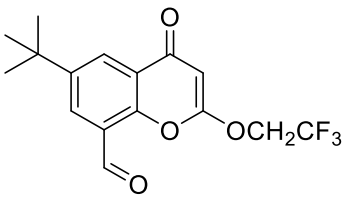
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 8.23 (d, *J* = 1.9 Hz, 1H), 7.98 (d, *J* = 2.0 Hz, 1H), 5.78 (s, 1H), 4.73 (q, *J* = 7.7 Hz, 2H), 2.52 (s, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.3, 177.8, 164.7, 151.3, 136.3, 136.3, 132.2, 124.5, 123.5, 122.3 (q, J^1 = 277.3 Hz), 90.1, 65.3 (q, J^2 = 37.6 Hz), 20.9.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.68 (t, *J* = 8.6 Hz,). .

ESI-MS: calculated for $C_{13}H_9F_3O_4$ $[M+H]^+$: 287.0525, found: 287.0523.

6-(*tert*-Butyl)-4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromene-8-carbaldehyde (5q)



Using TFE as solvent, the title compound was prepared *via* the general procedure B, after purification by silica gel column chromatography (PE/EA = 8/1), **5q** was obtained as a white solid (23 mg, 0.179 mmol, 35%). R_f = 0.19 (PE/EA = 8/1)

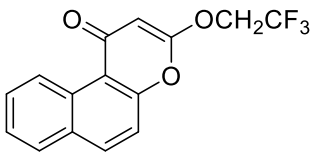
^{1}H NMR (500 MHz, Chloroform-*d*) δ 10.47 (s, 1H), 8.44 (d, *J* = 1.8 Hz, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 5.79 (s, 1H), 4.73 (q, *J* = 7.7 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 187.3, 177.9, 164.6, 151.1, 149.6, 132.8, 128.7, 124.3, 123.2, 122.1 (q, J^1 = 278.1 Hz), 90.0, 65.12 (q, J^2 = 37.6 Hz), 35.1 , 31.2.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.67 (t, *J* = 7.7 Hz).

ESI-MS: calculated for $C_{16}H_{15}F_3O$ $[M+H]^+$: 313.1046, found: 313.1043.

3-(2,2,2-Trifluoroethoxy)-1*H*-benzo[*f*]chromen-1-one (5r)



Using TFE as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 12/1), **5r** was obtained as a white solid (126.5 mg, 0.430 mmol, 86%). R_f = 0.33 (PE/EA = 8/1).

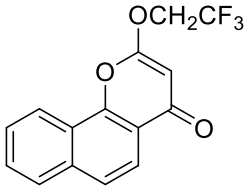
^{1}H NMR (500 MHz, DMSO-d_6) δ 9.91 (d, J = 8.4 Hz, 1H), 8.33 (d, J = 9.0 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.77 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.73 (d, J = 9.1 Hz, 1H), 7.68 (ddd, J = 8.1, 6.9, 1.3 Hz, 1H), 6.10 (s, 1H), 5.16 (q, J = 8.6 Hz, 2H).

^{13}C NMR (126 MHz, DMSO-d_6) δ 180.2, 163.5, 154.2, 135.5, 130.7, 129.6, 129.0, 128.6, 126.6, 125.8, 123.0 (q, J^1 = 277.4 Hz), 117.2, 114.8, 90.8, 65.0 (q, J^2 = 35.7 Hz).

Decoupling ^{19}F NMR (471 MHz, DMSO-d_6) δ -72.59.

ESI-MS: calculated for $C_{15}H_9F_3O_3$ $[M+H]^+$: 295.0576, found: 295.0575.

2-(2,2,2-Trifluoroethoxy)-4*H*-benzo[*h*]chromen-4-one (5s)



Using TFE as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 12/1), **5s** was obtained as a white solid (24.7 mg, 0.084 mmol, 42 %). R_f = 0.375 (PE/EA = 4/1).

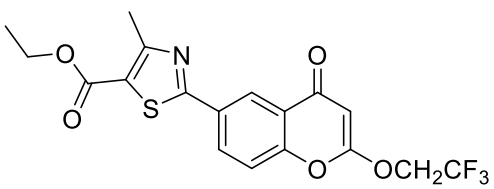
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.42 (d, J = 7.6 Hz, 1H), 8.13 (d, J = 8.7 Hz, 1H), 7.95 (dd, J = 7.1, 1.8 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.75 – 7.67 (m, 2H), 5.86 (s, 1H), 4.67 (q, J = 7.7 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.1, 164.9, 150.9, 136.2, 129.5, 128.4, 1276, 126.0, 123.4, 121.9, 122.3 (q, J^1 = 278.3 Hz,), 120.9, 119.2, 90.4, 65.5 (q, J^2 = 39.1 Hz,).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.50 (t, J = 8.7 Hz,).

ESI-MS: calculated for $C_{15}H_9F_3O_3$ $[M+H]^+$: 295.0576, found: 295.0576.

4-Methyl-2-(4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-6-yl)thiazole-5-carboxylate (5t)



Using TFE as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica

gel column chromatography (PE/EA = 8/1), **5t** was obtained as a white solid (35.7 mg, 0.086 mmol, 43%). R_f = 0.21 (PE/EA = 8/1)

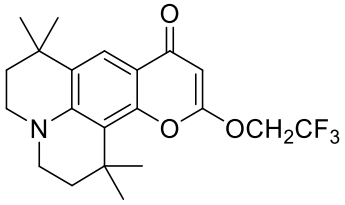
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 2.2 Hz, 1H), 8.35 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 5.73 (s, 1H), 4.61 (q, *J* = 7.7 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.78 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.1, 167.6, 165.1, 162.2, 161.3, 154.7, 131.8, 131.2, 124.7, 123.4, 123.3 (q, J^1 = 279.2 Hz), 123.0, 118.4, 89.8, 65.3 (q, J^2 = 37.7 Hz), 61.6, 17.6, 14.5.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.65 (t, *J* = 8.7 Hz).

ESI-MS: calculated for $C_{18}H_{14}F_3NO_5S$ $[M+H]^+$: 414.0617, found: 414.0615.

1,1,7,7-Tetramethyl-11-(2,2,2-trifluoroethoxy)-2,3,6,7-tetrahydro-1*H*,5*H*,9*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-one (5u)



Using TFE as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 8/1), **5u** was obtained as a white solid (30.7 mg, 0.078 mmol, 39%). R_f = 0.23 (PE/EA = 4/1)

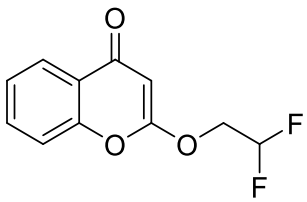
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 5.52 (s, 1H), 4.47 (q, *J* = 7.7 Hz, 2H), 3. 29 (t, *J* = 7.6 Hz, 2H), 3.22 (t, *J* = 7.6 Hz, 2H), 1.82 (t, *J* = 7.6 Hz, 2H), 1.74 (t, *J* = 7.6 Hz, 2H), 1.48 (s, 6H), 1.31 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.2, 164.5, 152.7, 146.9, 130.0, 123.5 (q, J^1 = 274.5 Hz), 121.0, 114.4, 111.4, 87.3, 65.5 (q, J^2 = 37.5 Hz), 47.4, 46.8, 39.6, 35.9, 32.6, 32.4, 30.8, 29.4.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.68 (t, *J* = 8.8 Hz).

ESI-MS: calculated for $C_{21}H_{24}F_3NO_3$ $[M+H]^+$: 396.1781, found: 396.1779.

2-(2,2-difluoroethoxy)-4H-chromen-4-one (5v)



Using CHF_2CH_2OH as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 8/1), **5v** was obtained as a white solid (20.7 mg, 0.078 mmol, 39%). R_f = 0.20 (PE/EA = 4/1).

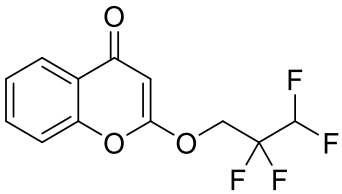
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.66 (td, *J* = 8.1, 1.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 6.14 (tt, *J* = 54.4, 3.9 Hz, 1H), 5.67 (s, 1H), 4.41 (td, *J* = 12.6, 3.9 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.1, 165.8, 153.6, 133.8, 126.1, 125.9, 122.9, 117.3, 112.2 (t, J^1 = 242.3 Hz), 88.9 , 67.1 (t, J^2 = 30.7 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -125.66 (dt, *J* = 54.9, 12.5 Hz).

ESI-MS: calculated for $C_{11}H_8F_2O_3[M+H]^+$: 227.0514, found: 227.0488.

2-(2,2,3,3-tetrafluoropropoxy)-4H-chromen-4-one (5w)



Using $CHF_2CF_2CH_2OH$ as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 8/1), **5w** was obtained as a white solid (24.3 mg, 0.088 mmol, 44%). R_f = 0.18 (PE/EA = 4/1).

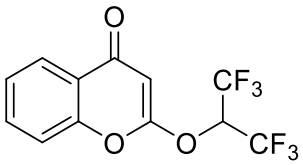
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 9.7 Hz, 1H), 7.68 (ddd, *J* = 9.0, 7.6, 1.7 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.03 (tt, *J* = 52.9, 3.8 Hz, 1H), 5.70 (s, 1H), 4.60 (t, *J* = 11.8 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 179.0, 165.3, 153.6, 133.9, 126.1, 126.0, 122.9, 117.3, 114.1 – 110.3(m), 109.9 – 106.8(m), 89.3, 64.6 (t, J^2 = 30.2 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -123.28 – -124.03 (m), -137.66 (d, *J* = 53.2 Hz).

ESI-MS: calculated for $C_{12}H_8F_4O_3[M+H]^+$: 277.0482, found:277.0438.

2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4H-chromen-4-one (5s)



Using HFIP as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 8/1), **5s** was obtained as a white solid (34.9 mg, 0.112 mmol, 56%). R_f = 0.17 (PE/EA = 4/1).

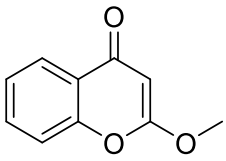
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.71(t, *J* = 7.8Hz 1H), 7.48 (t, *J* = 8.1 Hz, 2H), 5.93 (s, 1H), 5.50 (p, *J* = 5.5 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 178.8, 162.8, 153.4, 134.2, 126.6, 126.4, 123.1, 123.80 – 116.56 (m), 117.31, 92.18, 71.89 (p, J^2 = 35.0 Hz).

^{19}F NMR (471 MHz, Chloroform-*d*) δ -73.17 (d, *J* = 5.3 Hz).

ESI-MS: calculated for $C_{12}H_6F_6O_3[M+H]^+$: 313.0293, found: 313.0251.

2-methoxy-4H-chromen-4-one (5y)

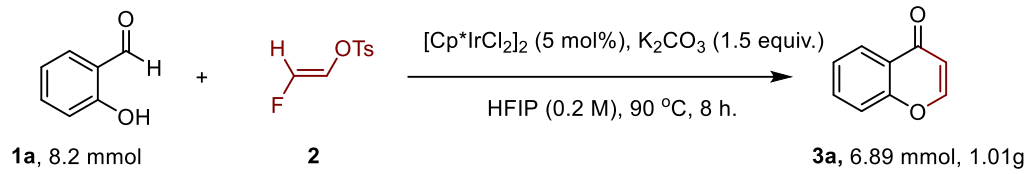


Using MeOH as solvent, the title compound was prepared *via* the general procedure **B**, after purification by silica gel column chromatography (PE/EA = 8/1), **5y** was obtained as a white solid (5.3 mg, 0.030 mmol, 15%). R_f = 0.14 (PE/EA = 4/1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.71(t, *J* = 7.8Hz 1H), 7.48 (t, *J* = 8.1 Hz, 2H), 5.93 (s, 1H), 5.50 (p, *J* = 5.5 Hz, 1H).

The characteristics data is consistent with the one reported before.[5]

6. Large Scale Reaction

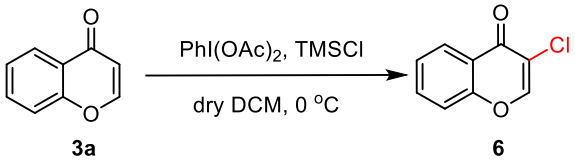


1a, 8.2 mmol　　**2**　　**3a,** 6.89 mmol, 1.01g

A 15 mL-schlenk tube charged with a stirring bar, was added salicylaldehyde **1** (8.2 mmol, 1 equiv) and **2** (16.4 mmol, 2 equiv)、$[Cp^*IrCl_2]_2$, (326 mg, 0.41 mmol, 5 mol%) and K_2CO_3 (12.3 mmol, 1.5 equiv), HFIP (2 mL) were added subsequently into the reaction vessel. The reaction was allowed to stir at 90 °C until the complete consumption of **1** as monitored by TLC analysis (8 hours). The reaction mixture was then diluted with DCM (20 mL) and washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3a** (84 %).

7. Derivatization of 3a

Synthetic Transformation of **3a** to **6**



3a　　**6**

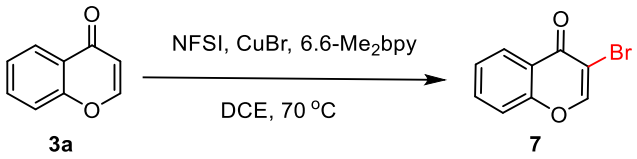
A 15 mL-schlenk tube was charged with $PhI(OAc)_2$ (0.15 mmol) in anhydrous DCM (0.5 mL), the solution was protected under Ar atmosphere and stirred in 0 °C. Then trimethyldilyl chloride (0.3 mmol) was added dropwise and the mixture was stirred in 0 °C for 30 min. The **3a** (0.1 mmol) in anhydrous DCM (0.5 mL) and pyridine (0.4 mmol) was added. The mixture was stirred in 0 °C for another 3.5 h. The mixture was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (12.1 mg, 67 % yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.16 (s, 1H), 7.72 (td, *J* = 8.0, 1.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.5, 156.2, 152.3, 134.3, 126.5, 126.0, 123.6, 121.0, 118.3.

The characteristics data is consistent with the one reported before.[6]

Synthetic Transformation of **3a** to **7**



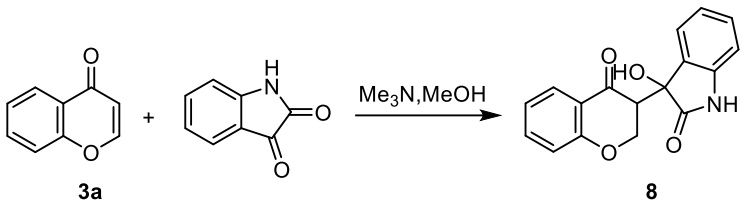
A 15 mL-schlenk tube was charged with **3a** (0.2 mmol), NFSI (0.21 mmol) and CuBr (1.1 equiv), 6,6'-Me_2bpy (12.0 mol%) in DCE (1.0 mL). Under an argon atmosphere, the reaction mixture was stirred at 70 °C for 11 h. The mixture was then cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **7** (15 mg, 33% yield)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.23 (s, 1H), 7.71 (td, *J* = 8.0, 1.7 Hz, 1H), 7.50 (t, *J* = 8.0, Hz 1H). 7.48 (d, *J* = 8.0 Hz, 1H),

^{13}C NMR (126 MHz, Chloroform-*d*) δ 172.4, 156.2, 153.9, 134.3, 126.6, 126.0, 123.2, 118.3, 110.8.

The characteristics data is consistent with the one reported before.[6]

Synthetic Transformation of **3a** to **8**



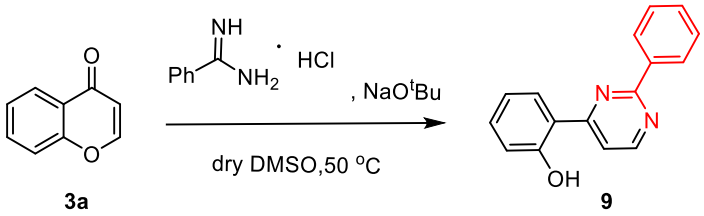
3a **8**

The compound was prepared according to a known procedure.[7]

Chromone **3a** (0.1 mmol), isatin (0.1 mmol, 1 equiv) and methanolic trimethylamine (25% w/w, 0.1 mmol) was stirred in methanol (2 mL) at room temperature for 12 h. An insoluble substance was formed. After completion of the reaction as indicated by TLC, the residue was concentrated in vacuo and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product **8** as white solid (15.6 mg, 53% yield).

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.60 (s, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.83 (td, J = 8.0, 1.7 Hz, 1H), 7.71 (d, J = 8.5 Hz, 1H), 7.46 (t, J = 7.5 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.04 (d, J = 7.3, Hz, 1H), 6.85 (q, J = 8.0 Hz, 2H), 6.66 (s, 1H). The characteristics data is consistent with the one reported before.[7]

Synthetic Transformation of **3a** to **9**



3a **9**

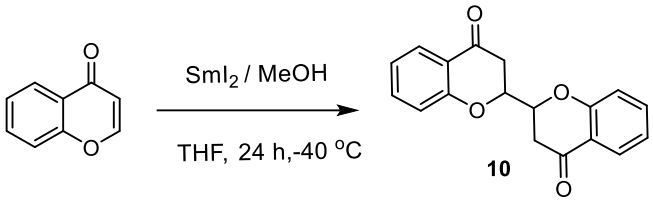
A 15 mL-schlenk tube was charged with **3a** (0.23 mmol, 1.0 equiv), benzamidine hydrochloride (0.29 mmol, 1.25 equiv), sodium *t*-butoxide (0.75 mmol, 3.25 equiv) in anhydrous DMSO (1.0 mL). Under Ar atmosphere, the reaction mixture was stirred at 50 °C for 15 min then immediately cooled to room temperature. The saturated ammonium chloride solution was added to the reaction mixture and extracted with EtOAc. The combined organic phase was washed with saturated brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding product (44.5 mg, 78 % yield), yellow solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 14.12 (s, 1H), 8.88 (d, J = 5.5 Hz, 1H), 8.35 (dd, J = 6.8, 3.0 Hz, 1H), 7.85 (dd, J = 8.0, 1.5 Hz, 1H), 7.70 (d, J = 5.6 Hz, 1H), 7.57 – 7.51 (m, 3H), 7.43 (m, J = 8.5, 7.3, 1.6 Hz, 1H), 7.08 (dd, J = 8.3, 0.9 Hz, 2H), 7.00 – 6.94 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 164.8, 162.9, 161.2, 158.4, 136.5, 133.8, 131.5, 129.1, 128.2, 127.2, 119.5, 119.1, 117.0, 113.1.

ESI-MS: calculated for $C_{16}H_{12}N_2O$ $[M+H]^+$: 249.1022.0617, found: 249.1021.

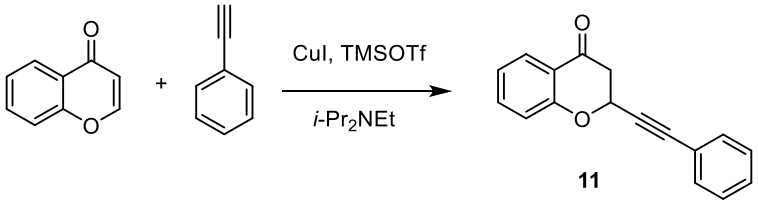
Synthetic Transformation of **3a** to **10**



Under nitrogen atmosphere, the chromone **3a** (0.4 mmol) was dissolved in dry THF (2.0 mL) in a 15 mL-schlenk tube. The mixture was cooled down to -40 ºC. Then, a 0.1 M solution of SmI_2 in THF (5.0 mL, 0.5 mmol) was slowly added, immediately followed by the addition of dry methanol (17 μL, 0.5 mmol). After stirring the mixture for 24 h at -40 ºC, the solution was hydrolyzed employing an aqueous 0.1 M HCl solution (10 mL). The desired biflavanone was extracted from the solution employing dichloromethane (3 x 10 mL) as solvent. The organic layers were combined, dried over Na_2SO_4, filtered and the solvent removed under reduced pressure. The residue was purified through flash column chromatography (silica gel) employing hexane/ ethyl acetate 10:1 as eluent (62.5mg, 53 % isolated yield)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.51 (td, *J* = 7.5, 1.8 Hz, 2H), 7.09 (td, *J* = 7.5, 1.0 Hz,2H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.71 – 4.62 (m, 2H), 3.31 (dd, *J* = 17.8, 12.8 Hz,2H), 2.79 (dd, *J* = 16.8, 2.8 Hz, 2H). The characteristics data is consistent with the one reported before.[8]

Synthetic Transformation of **3a** to **11**

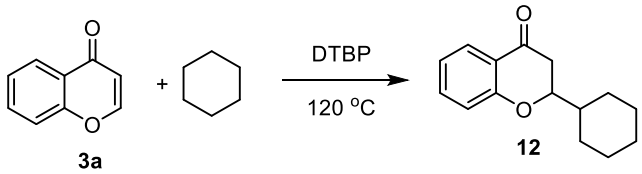


Copper iodide (1.3 mg, 0.0068 mmol), which was stored in a glovebox, was added to a 15 mL-schlenk tube equipped with a magnetic stirrer bar then removed from the box and dissolved in toluene (0.5 mL). The mixture was allowed to stir at room temperature for 0.5 hours and a pale-yellow solution resulted. Chromone **3a** (0.137 mmol, 1.0 equiv), phenylacetylene (0.178

mmol, 1.3 equiv), and N,N-diisopropylethylamine (38 µl, 0.219 mmol, 1.6 equiv) were then added sequentially and the reagents were washed down the test tube walls with an additional aliquot of toluene (0.9 mL). The mixture was then cooled to -78 °C, TMSOTf (32 µL, 0.178 mmol, 1.3 equiv) was added and the reaction mixture was then transferred to a - 20 °C bath and stirred for 18 h. The reaction was then quenched with 3 N HCl and allowed to stir for 2 h until the silyl enol ether was completely hydrolyzed as judged by TLC analysis. Saturated aqueous $NaHCO_3$ was then added to neutralize the solution, and then the reaction mixture was extracted with EtOAc. The organic layer was dried over $NaSO_4$, filtered and concentrated. The crude product was purified by flash column chromatography using EtOAc/hexanes. (25.5 mg, 75 % isolated yield)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54 (td, *J* = 8.0, 1.8 Hz,1H), 7.44 – 7.41 (dd, 2H), 7.37 – 7.28 (m, 3H), 7.07 (d, *J* = 7.6 Hz, 2H), 5.50 (dd, *J* = 8.3, 5.4 Hz, 1H), 3.10 (d, *J* = 6.8 Hz, 2H). The characteristics data is consistent with the one reported before.[9]

Synthetic Transformation of **3a** to **12**

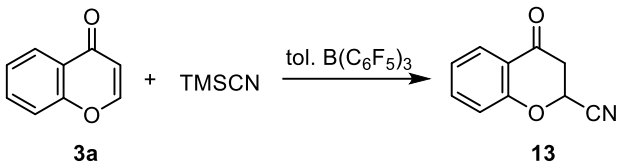


This compound was prepared according to a known procedure. [10]

A 15 mL-schlenk tube equipped with a magnetic stirrer bar was charged with chromone (29.2 mg, 0.2 mmol), DTBP (1.0 mmol), and cyclohexane (2.0 mL). The rubber septum was then replaced by a Teflon–coated screw cap, and the reaction vessel was placed in an oil bath at 120 °C. After stirring at this temperature for 24 h, it was cooled to room temperature and diluted with ethyl acetate, washed with water, dried over Na_2SO_4. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel (CH_2Cl_2/hexane = 2:1) to afford the corresponding product **12** (29.4 mg, 64% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 (td, *J* = 7.9, 1.7 Hz, 1H), 7.00 (dd, *J* = 13.7, 8.0 Hz, 1H), 4.23 (m, *J* = 12.7, 5.9, 3.2 Hz, 1H), 2..69 (qd, *J* = 17.4, 5.9 Hz, 2H), 2.01 (d, *J* = 12.5 Hz, 1H), 1.87 – 1.80 (m, 4H), 1.43 m, 1H), 1.33 – 1.26 (m, 4H). The characteristics data is consistent with the one reported before.[10]

Synthetic Transformation of **3a** to **13**



3a **13**

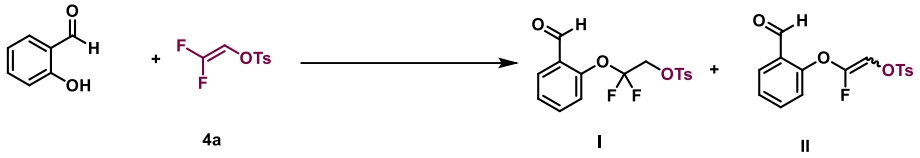
This compound was prepared according to a known procedure.[11]

To a 15 mL-schlenk tube were added chromones **3a** (0.2 mmol), $B(C_6F_5)_3$ (5.1 mg, 0.010 mmol), TMSCN (49.6 mg, 0.48 mmol, 0.064 mL) and dry toluene (2.0 mL) in a nitrogen atmosphere glovebox. After being sealed, the resulting mixture was stirred at 80 °C for 24 h. The reaction mixture was cooled to room temperature, and the solvent was removed under vacuum. The crude residue was purified by flash chromatography on silica gel using petroleum ether/ethyl acetate (10:1 v/v) as the eluent to give the desired product **13** (16.3 mg, 47% yield).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (td, *J* = 7.8, 1.7 Hz, 1H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 7.08 (d, *J* = 8.4 Hz,1H), 5.42 (dd, *J* = 6.8, 5.1 Hz, 1H), 3.16 (dd, *J* = 17.3, 5.1 Hz, 1H). 3.08 (dd, *J* = 17.5, 6.8 Hz, 1H). The characteristics data is consistent with the one reported before.[11]

8. Mechanistic Studies

8.1 Nucleophilic addition reaction of difluorovinyl tosylate



conditions A:	DBU (1.1 equiv), DMF, rt, overnight	23%	28% (*E*/*Z* = 1/9)
conditions A:	$Pd(OAc)_2$ (5 mol%), Ph_3P=S (10 mol%) Na_2CO_3 (3equiv), TEBAC (2 equiv.), NMP, 110 °C, N_2, 24 h	18%	25% (*E*/*Z* = 1/5)

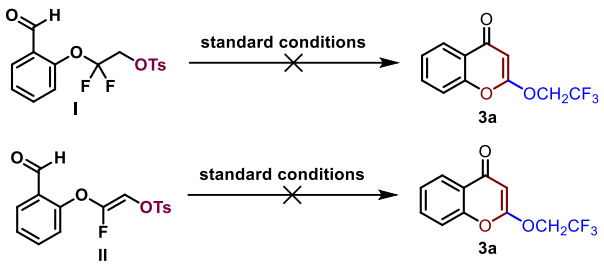
Procedure C

To a solution of salicylaldehyde **1a** (0.2 mmol) in DMF (5 mL) was added 4a (1.5 equiv.) and DBU (1.1 equiv.) at ambient temperature, the reaction was stirred overnight. Then, water was added to quench the reaction. After neutralization to pH = 7 using 1 M HCl, the mixture was extracted with EA (3 x 30 mL). The combined organic layer washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacum. The crude product was purified by thin layer chromatography (PE/EA = 16/1), gave **I** (16.4 mg, 0.046 mmol) and **II** (18.8 mg, 0.056 mmol) as colorless oil. It should note that compound **I** is difficult to seperate from **II**. The peak of compound **II** is interspersed in the spectrum of **I**

Procedure D

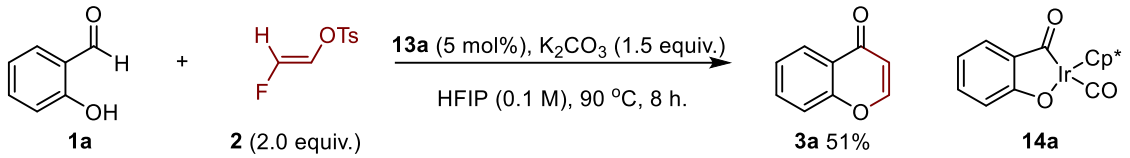
A mixture of salicylaldehyde **1a** (0.5 mmol), $Pd(OAc)_2$ (5 mol%), Ph_3P=S (10 mol%) Na_2CO_3 (3 equiv.), TEBAC (2 equiv.) and NMP (2.0 mL) was stirred at 110°C under N_2 atomosphere for 24 h. After cooling to room temperature, EA (30 mL) was added and aqueous phase was extracted by H_2O (3 x 30 mL). The organic phase was dried over Na2SO4, and concentrated in vacuum. The residue was purified by thin layer chromatography (PE/EA = 16/1), gave **I** (32.0 mg, 0.09 mmol) and **II** (42.0 mg, 0.125 mmol) as colorless oil.

8.2 Reaction of Compound I or II under standard conditions



Compound **I** or **II** was reacted under standard conditions, giving no chromone **3a** detected by GC-MS.

8.3 Reaction with Iridacycle as Catalyst

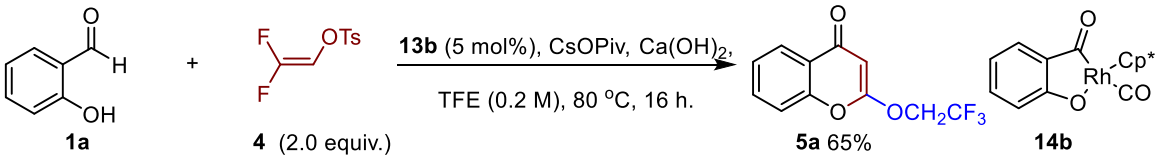


The iridacycle **13a** was prepared according to the known procedure.[12]

A mixture of sodium 2-formylphenolate (0.15 mmol, 22 mg), $[Cp^*IrCl_2]_2$ (0.075 mmol, 60 mg), and DBU (0.15 mmol, 17 mg) was stirred in toluene-d8 (5.0 mL) under Ar at 100 °C for 3 d. After evaporation of the solvents under vacuum, complex **13a** (10 mg, 13%) was isolated by thin-layer chromatography on silica gel using hexane-ethyl acetate (1:1, v/v) as eluant.

A 15 mL-schlenk tube charged with a stirring bar, was added K_2CO_3 (20.7 mg, 0.15 mmol). **13a** (2.4 mg, 5 mol%), and HFIP (1 mL). After one minute of ultrasound, and **1a** (0.1 mmol). The reaction was allowed to stir at 90 °C for 8 h. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica gel to afford the pure product **3a**, 51 % yield.

8.4 Reaction with Rhodacycle as Catalyst



The rhodacycle **13b** was prepared according to Ackermann's procedure.[13]

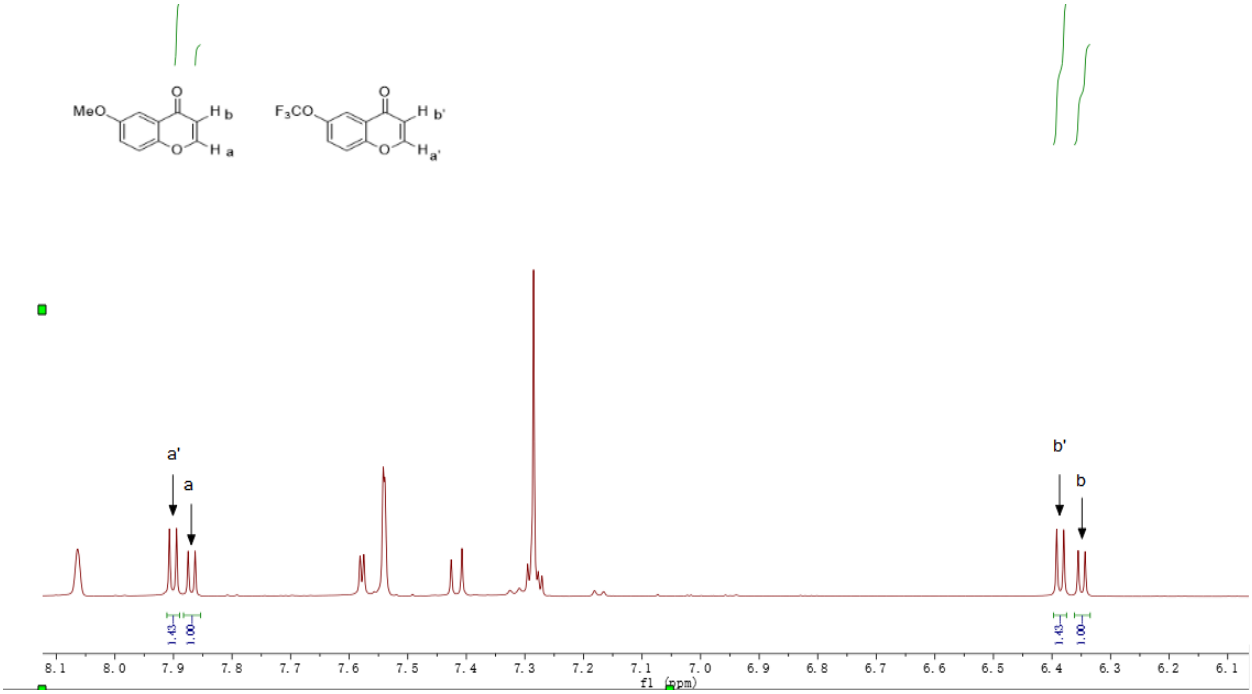
A 15 mL-schlenk tube charged with a stirring bar, was added NaOPiv (20.8 mg, 0.168 mmol). [Cp*$IrCl_2$] (800 mg, 1.3 mmol), and DCM (2 mL). After one minute of ultrasound, add **1a** (4.4 μL, 42 μmol, 1 equiv). The reaction was allowed to stir at 30 ^oC for 24 h. The reaction mixture was then diluted with EtOAc (20 mL) and washed with brine. The aqueous phase was extracted with EtOAc again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica gel to afford the pure product **13b**, 34 % yield.

Reaction with rhodacycle **13b** as catalyst.

A 15 mL-schlenk tube charged with a stirring bar, was added salicylaldehyde **1a** (0.2 mmol, 1 equiv) and **2** (0.4 mmol, 2 equiv). **13b** (3.9 mg, 0.01 mmol, 5 mol%), CsOPiv (93.6 mg, 0.4 mmol, 2 equiv), $Ca(OH)_2$(14,8 mg, 0.2 mmol, 1 equiv), TFE (2 mL). The reaction was allowed to stir at 80 ^oC until the complete consumption of **1** as monitored by TLC analysis (8 hours). The reaction mixture was then diluted with DCM (20 mL) and washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5a** (65 %).

8.5 Intermolecular competitive experiment

A 15 mL-schlenk tube charged with a stirring bar, was added the starting materials **1g** (0.2 mmol, 1 equiv) and **1h** (0.2 mmol, 1 equiv) and 2 (0.8 mmol), [Cp*$IrCl_2$]$_2$ (12.2 mg, 0.02 mmol, 5 mol%) and K_2CO_3 (276 mg, 0.6 mmol), HFIP (4 mL). The reaction was allowed to stir at 90 ^oC for 8 hours. The reaction mixture was cooled to room temperature, then diluted with DCM (20 mL) washed with brine. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4, purified by flash column chromatography on silica with an appropriate solvent to afford the mixture products 3g and 3h. The ratio of **3g** and **3h** was determined by NMR.



8.6 Kinetic isotope effect

To a 15 mL pressure tube was added salicylaldehyde **1a** (24.4 mg, 0.2 mmol), monofluorovinyl tosylate **2** (43.2 mg, 0.4 mmol), [Cp*$IrCl_2$] (8 mg, 5 mol%), anhydrous potassium carbonate 41.4 mg (0.3 mmol) and HFIP (2 mL). After a certain time of reaction at 80 ℃, an appropriate amount of water was added to quench the reaction. To the reaction mixture was added P-iodoanisole (46.8 mg, 0.2 mmol, 1.0 equiv) as internal standard. The reaction flask and internal standard solution was filtered with EtOAc in a short silica gel. The filtrate was evaporated under reduced pressure, and the the yield was determined by NMR by integration of the product peaks relative to the P-iodoanisole.

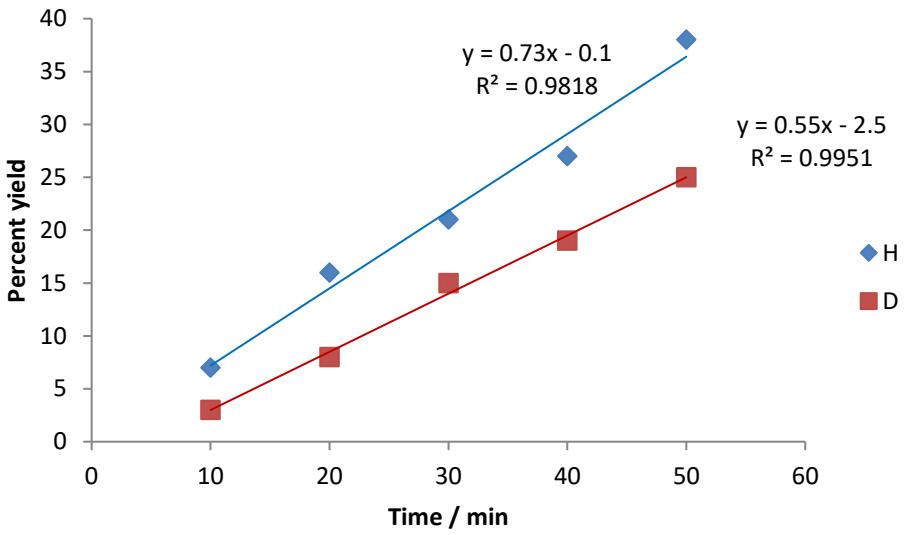


Figure 1 NMR yield mechanism diagram

With deuterium salicylic aldehyde as raw material, the yield of every 10 min is 3，9，15，19，23%. And with deuterium salicylic aldehyde as raw material, the yield of every 10 min is 8, 16, 21, 26, 37%.

9 X-ray crystal structure of compound 5c

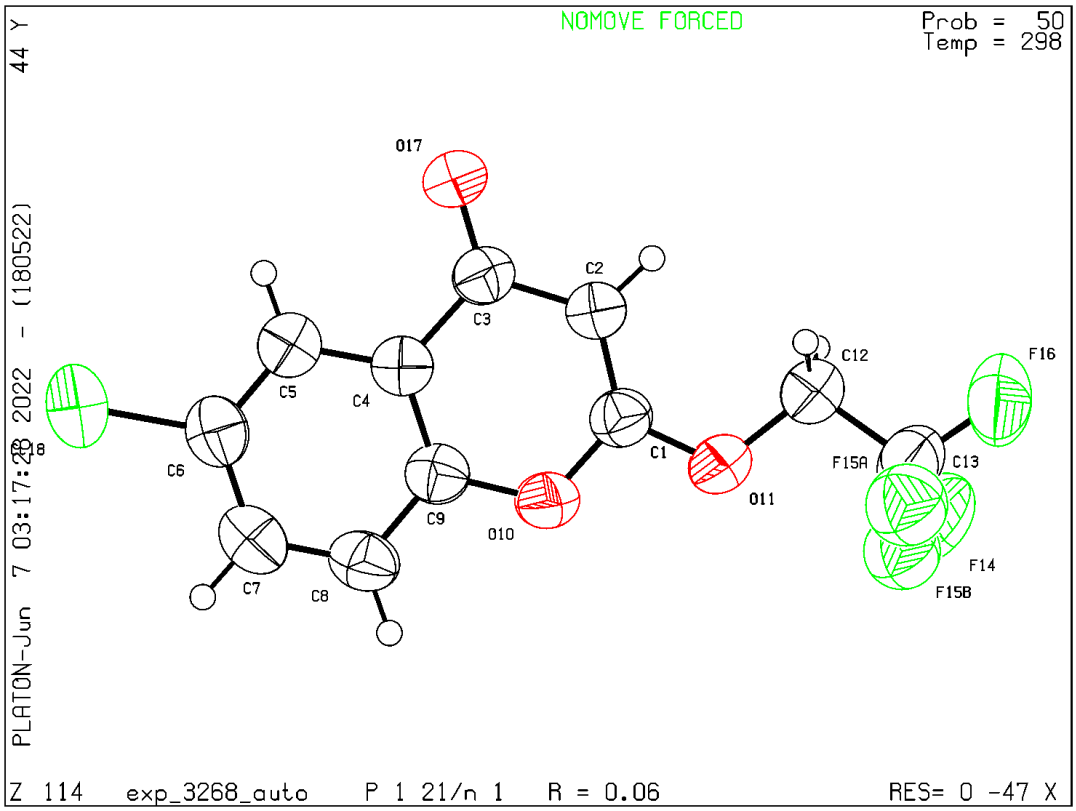


Figure 1 ORTEP drawing of compound **5c(**Deposition Number 2177415**)**

Supplementary:

Identification code	**5c**
Empirical formula	C11H6ClF3O3
Formula weight	278.61
Temperature/K	297.56(10)
Crystal System	Monoclinic
Space group	$P2_1/n$
a/Å	4.72550(10)
b/Å	22.4433(7)
c/Å	10.8444(3)
α/°	90

β/°	94.625(3)
γ/°	90
Volume，V/Å	1146.37(5)
Z	4
Calculated density，g cm^{-3}	1.614
Absorption coefficient，μ/mm^{-1}	3.363
F(000)	560.0
Crystal size/mm^3	0.15 × 0.11 ×0.12
Radiation	CuKa(λ = 1.54184)
2θ range for data collection/°	7.878 to 152.804
Index ranges	-4 ≤ h ≤ 5，26 ≤ k ≤ 27，-13≤l≤13
Reflections collected	7225
Independent reflections	2253[R_{int} = 0.0326，R_{sigma} = 0.0363]
Data/restraints/parameters	2253/0/163
Goodness-of-fit on F^2	1.091
Final R indexes[I ≥ 2σ(I)]	R1 = 0.0639, wR2 = 0.1869
Final R indexes[all data]	R1 = 0.0724, wR2 = 0.1962
Largest diff.peak/hole/e$Å^{-3}$	0.63/-0.41

10. References

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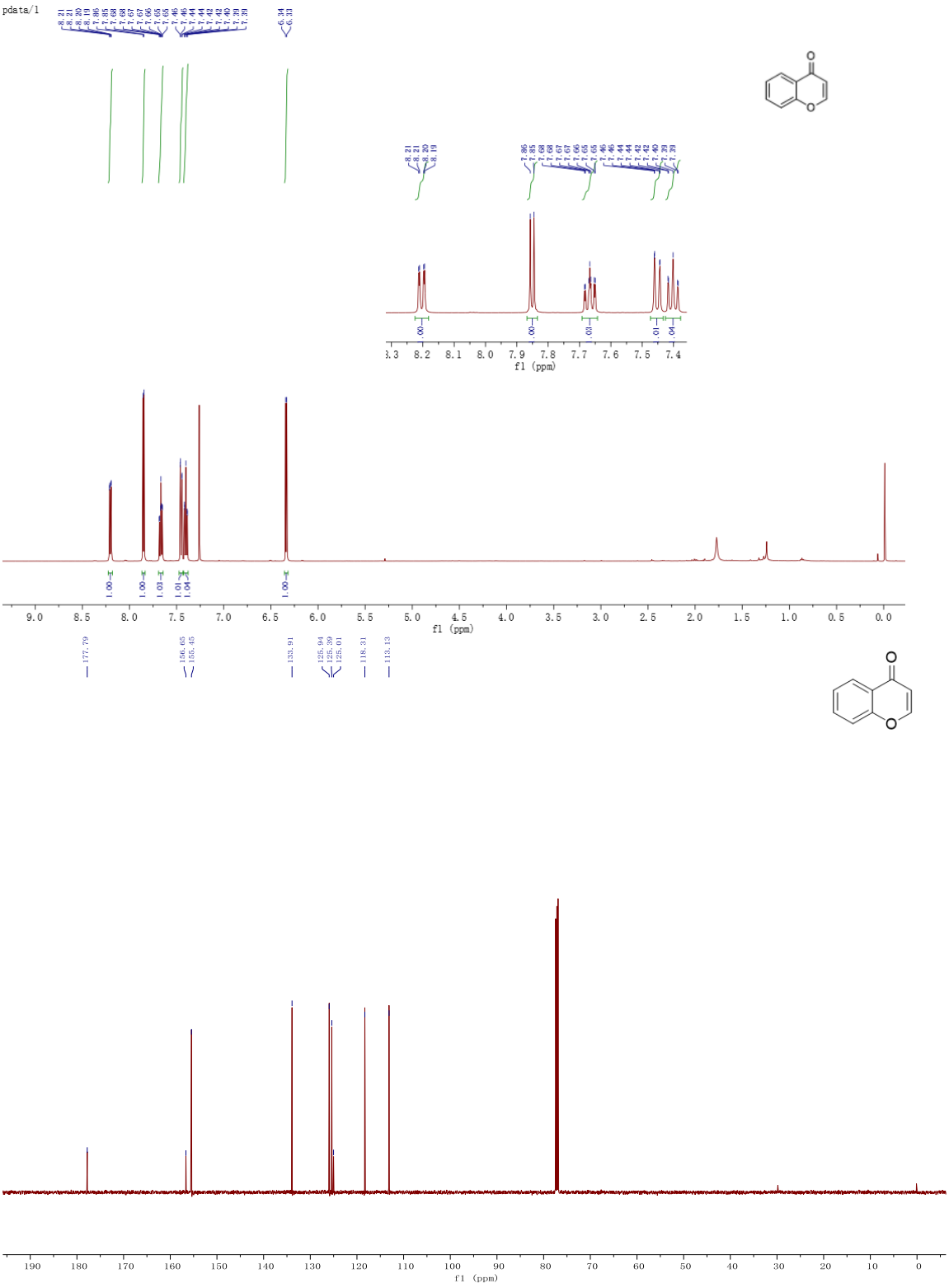
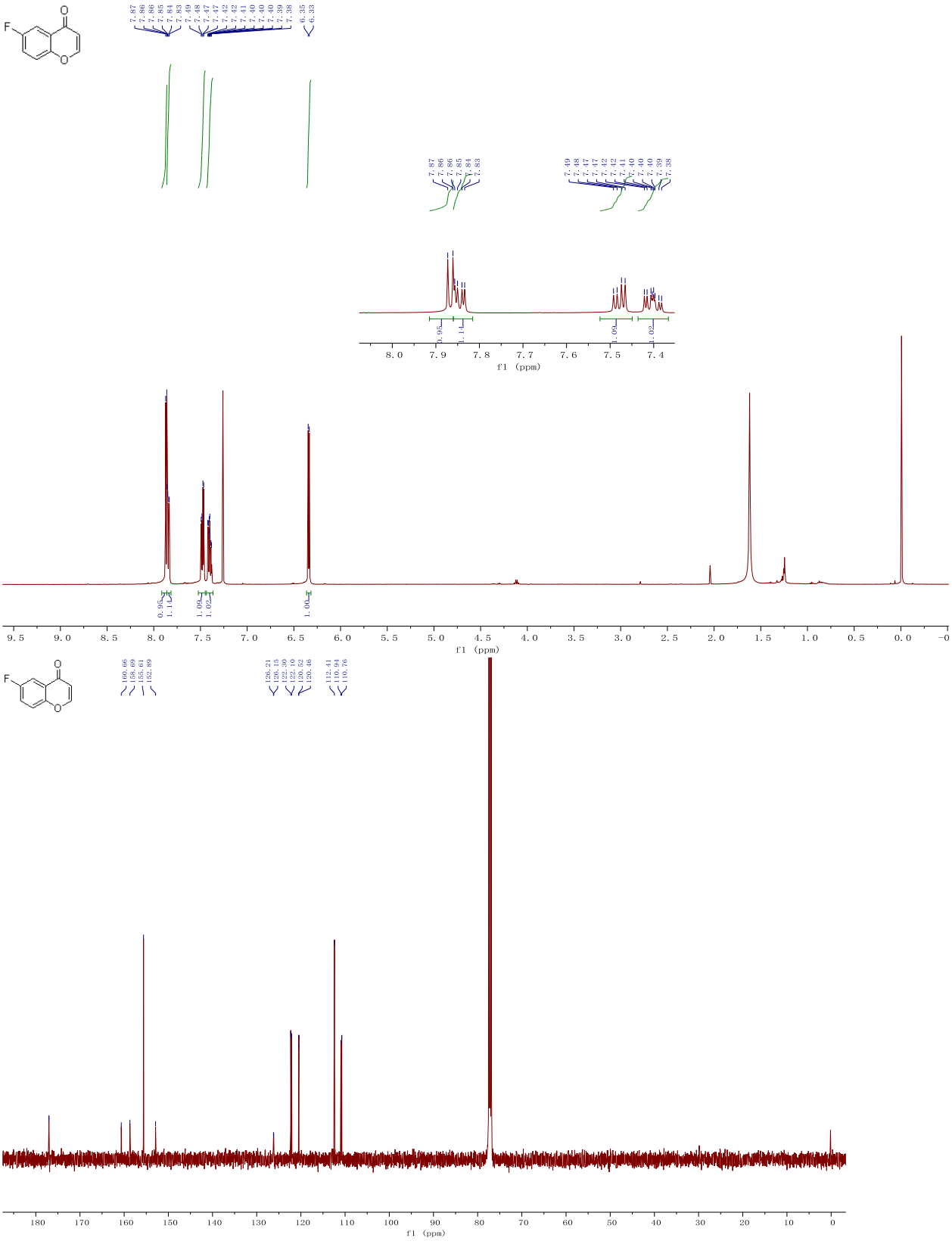
11. ^{1}H NMR and ^{13}C NMR spectra of Products

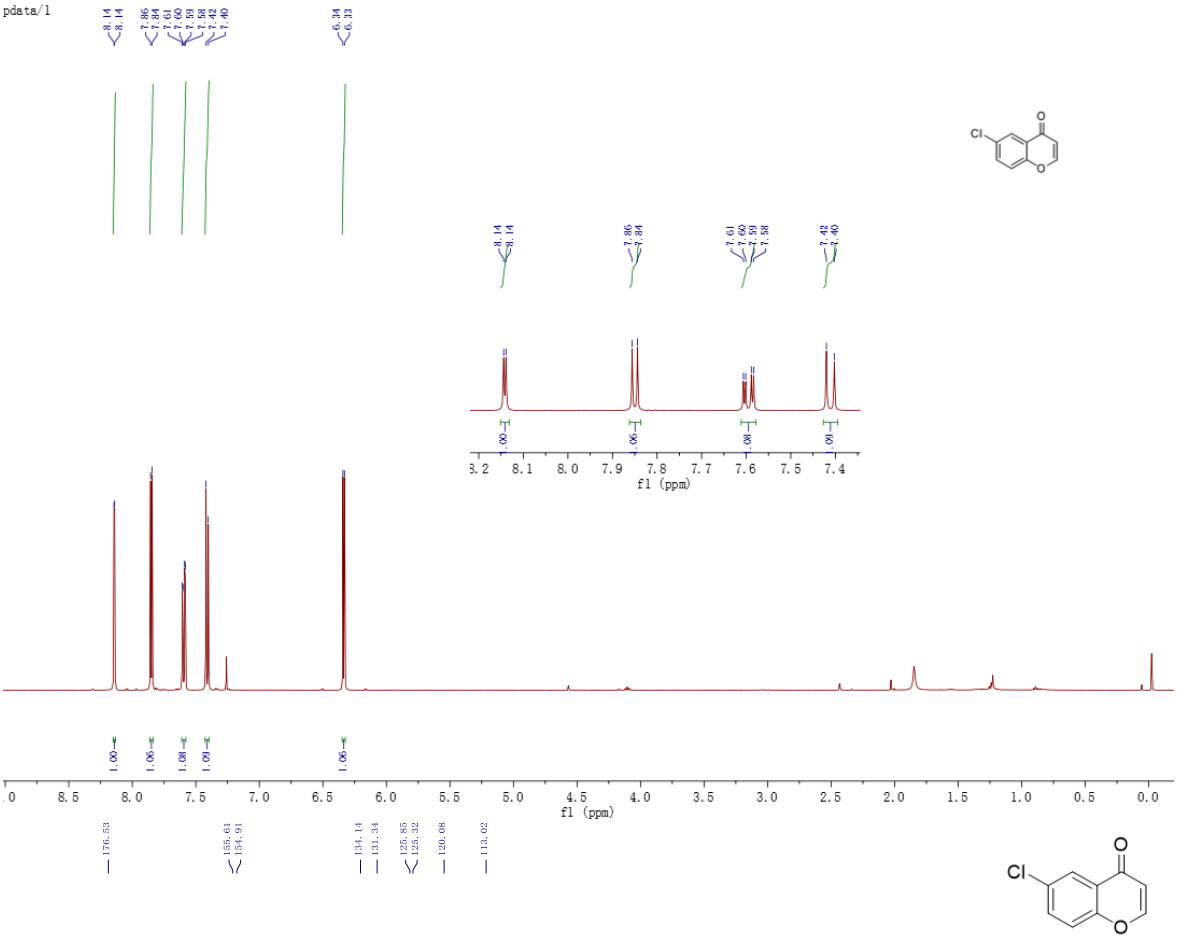
4*H*-Chromen-4-one (3a)

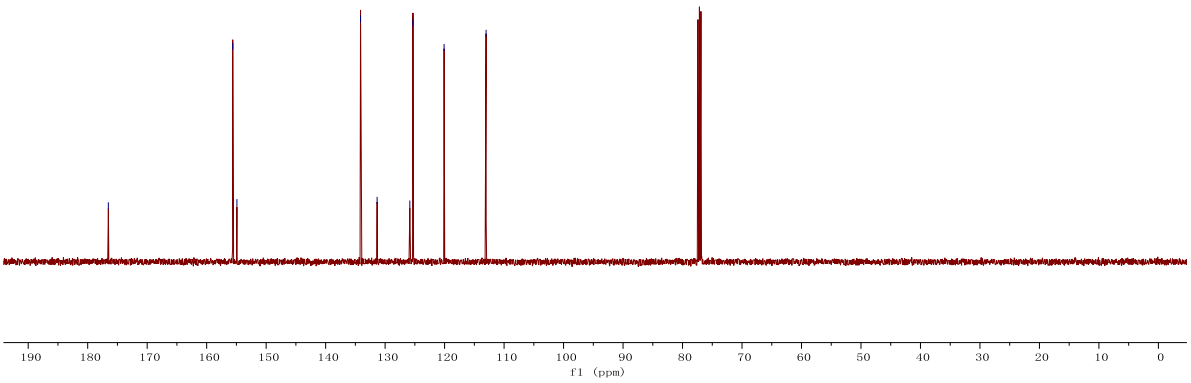


6-Fluoro-4*H*-chromen-4-one (3b)

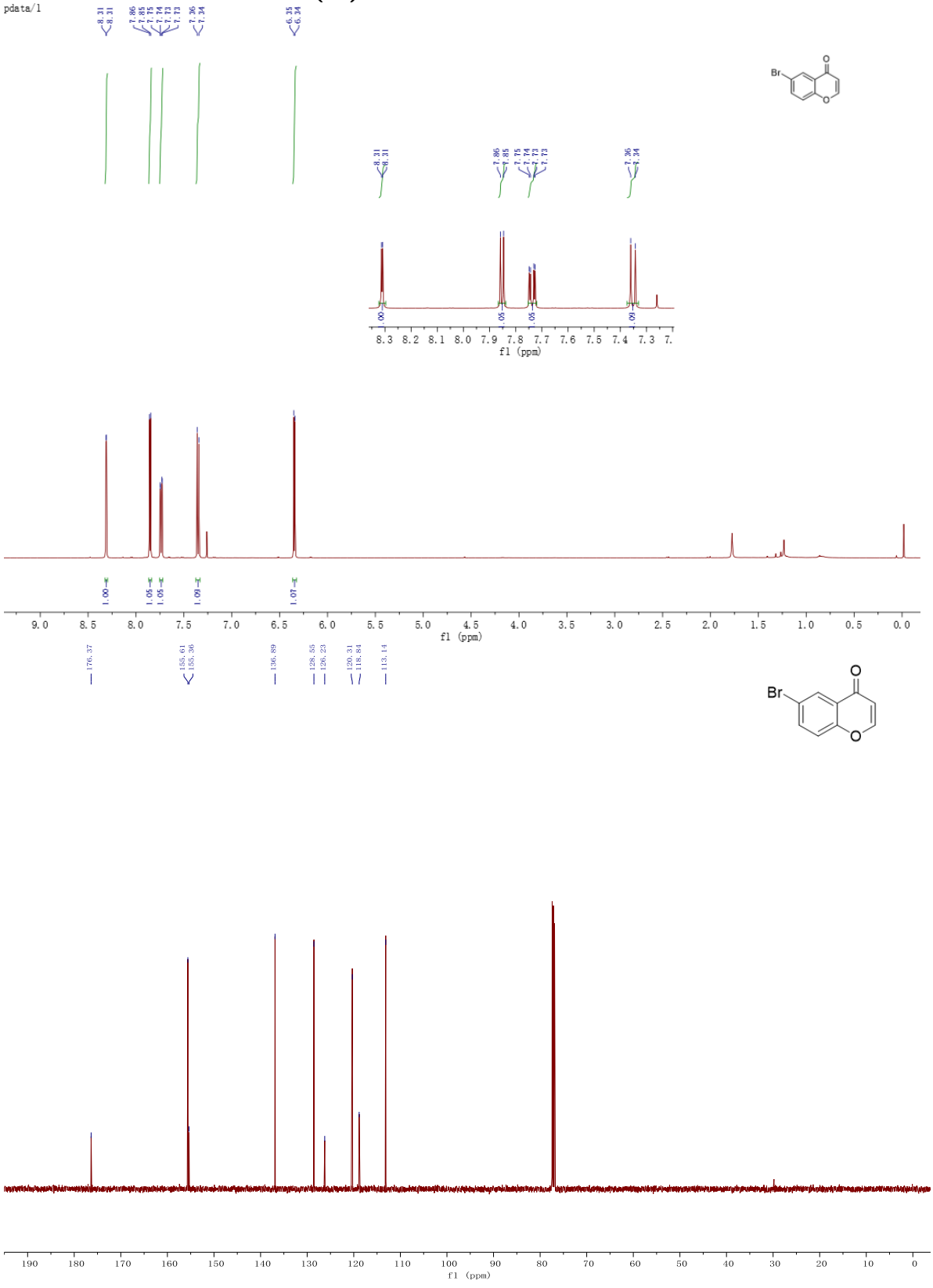


6-Chloro-4*H*-chromen-4-one (3c)

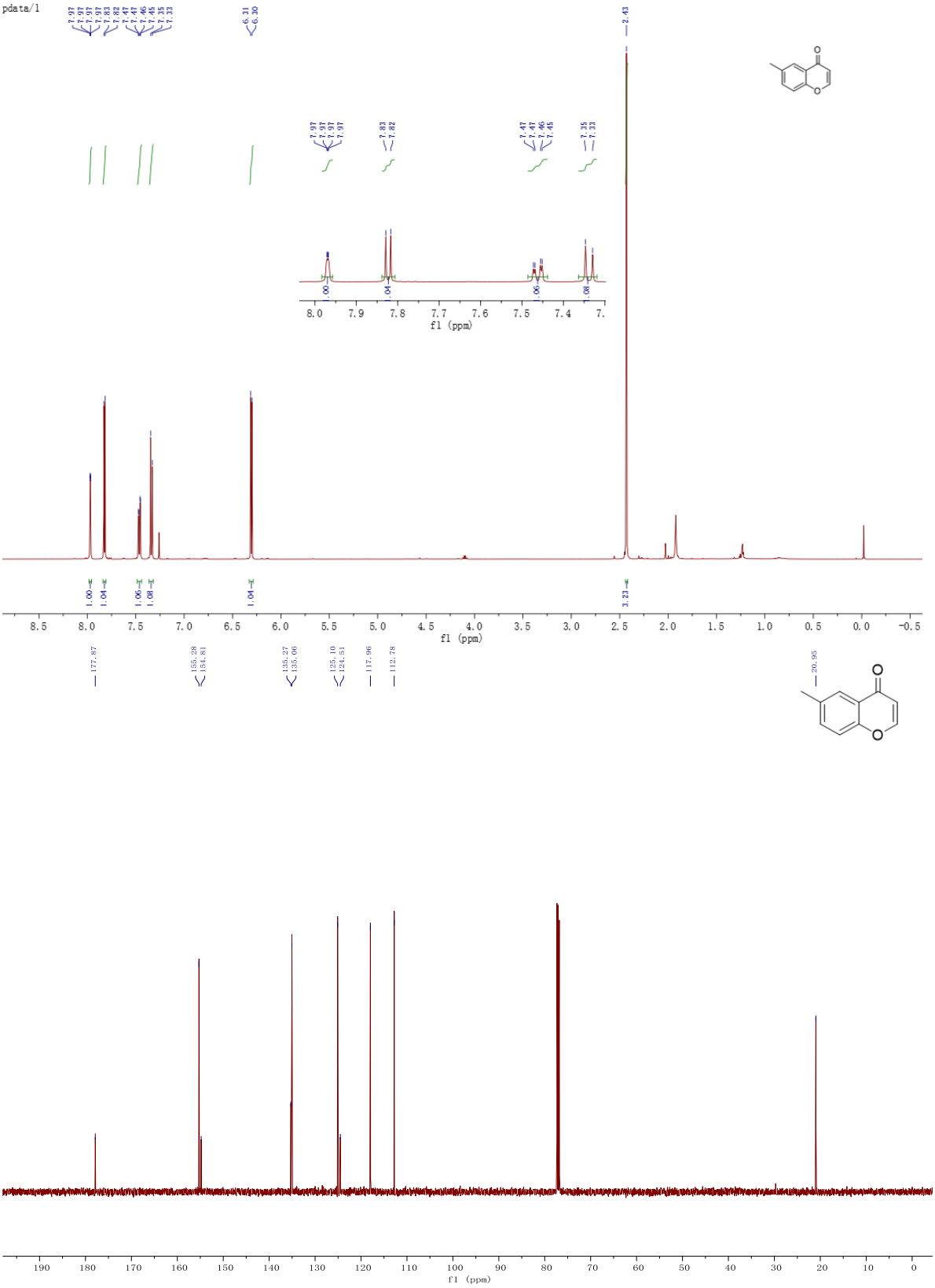




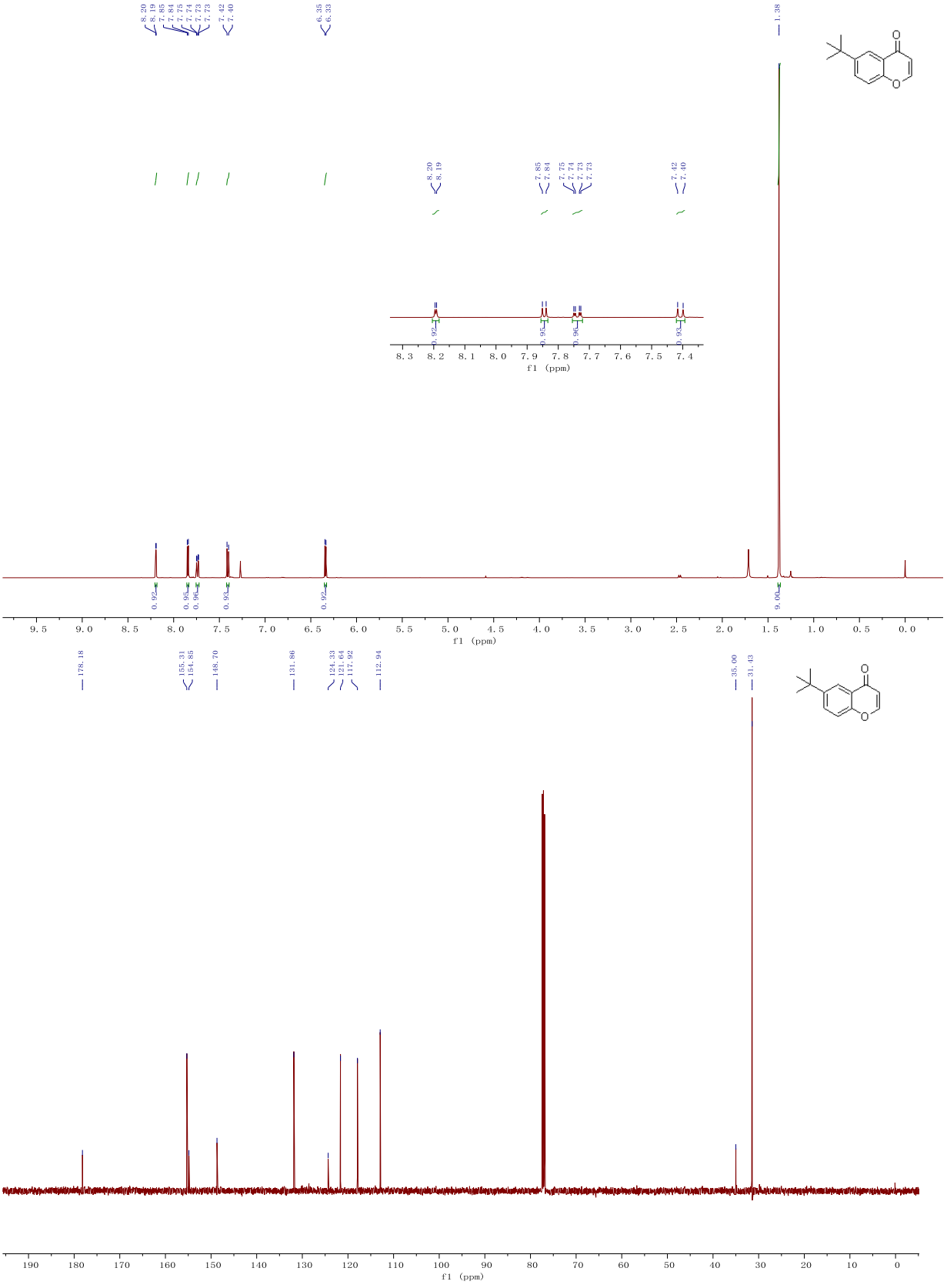
6-Bromo-4*H*-chromen-4-one (3d)



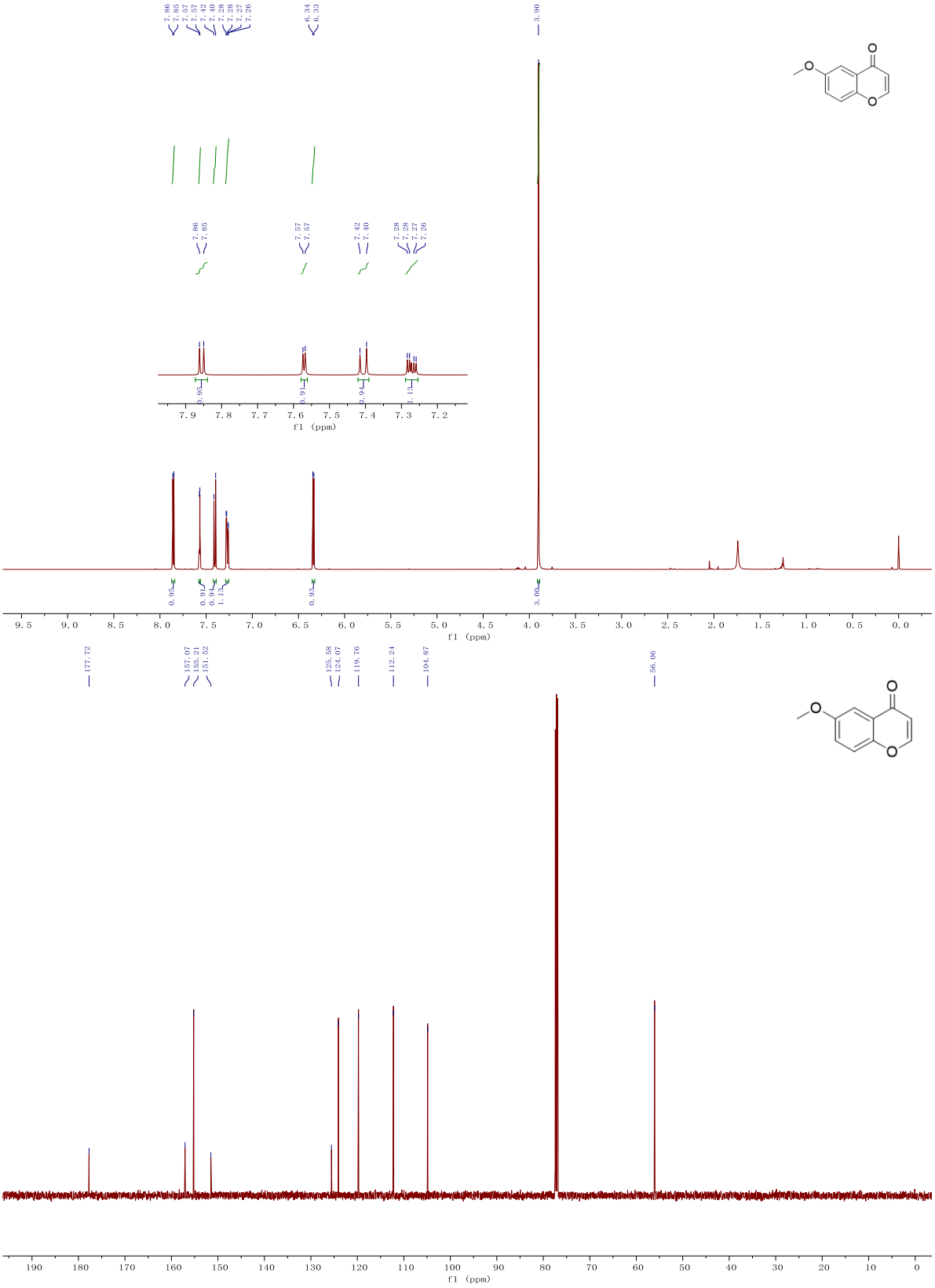
6-Methyl-4*H*-chromen-4-one (3e)



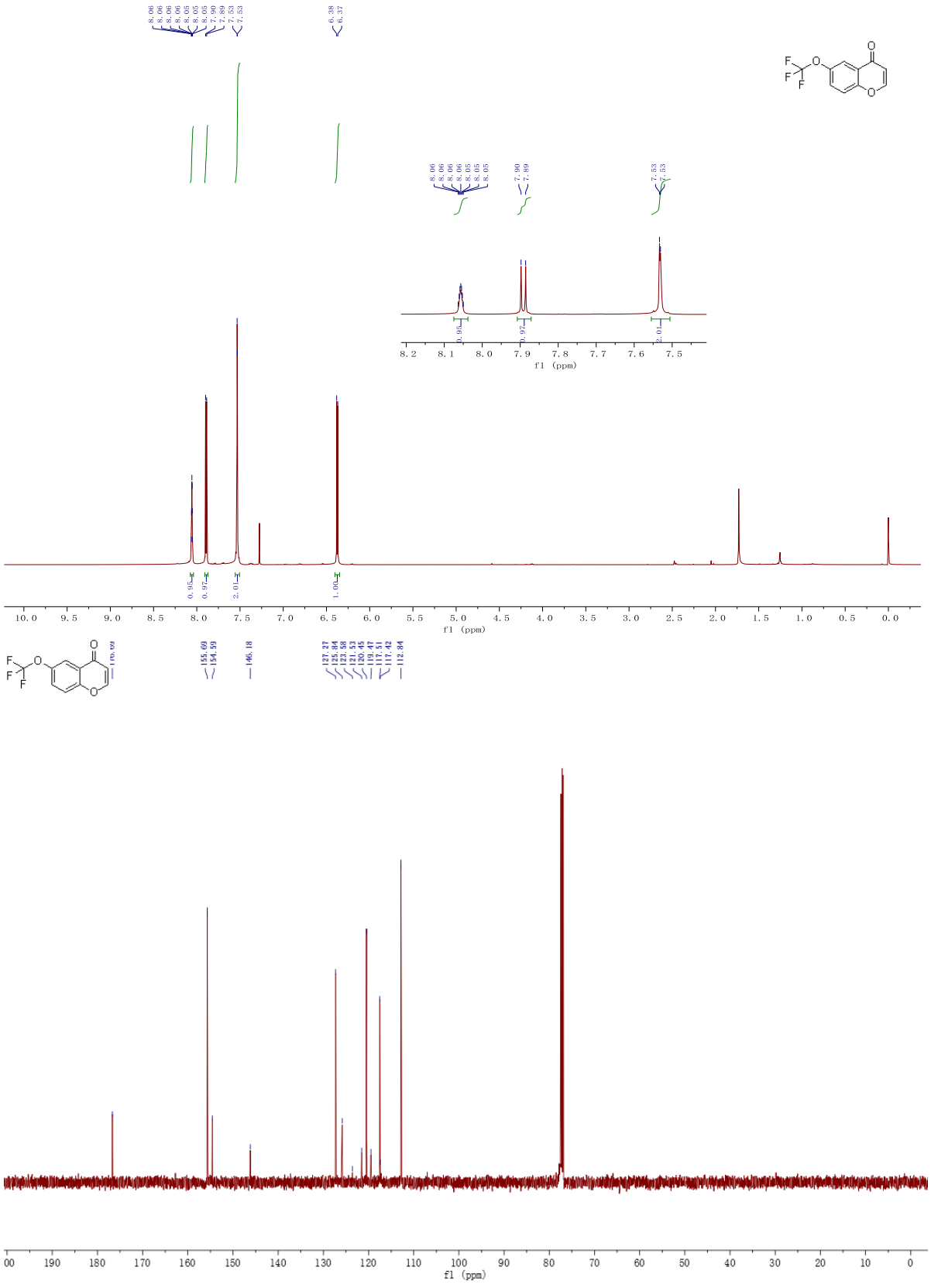
6-(*tert*-Butyl)-4H-chromen-4-one (3f)



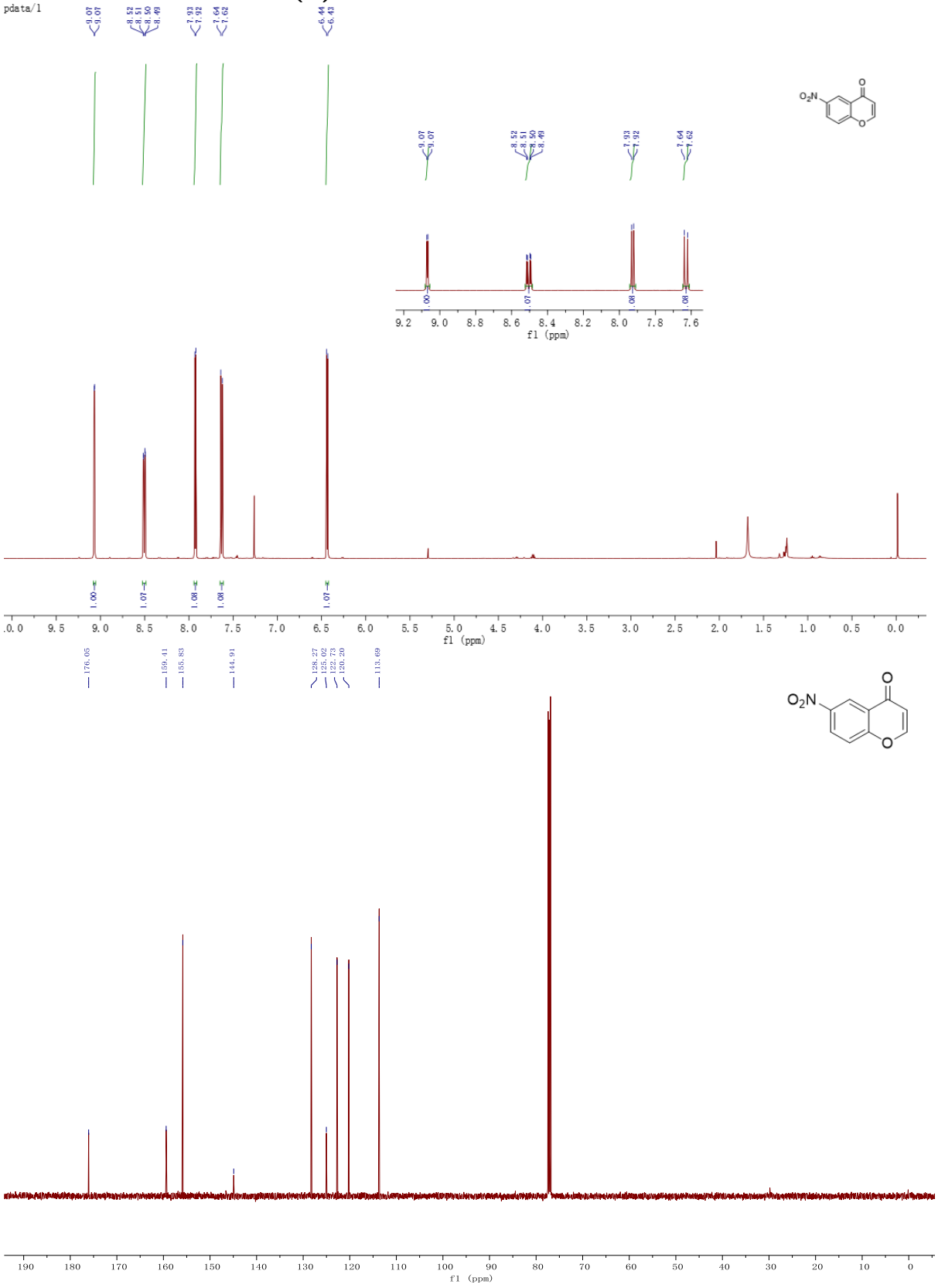
6-Methoxy-4*H*-chromen-4-one (3g)



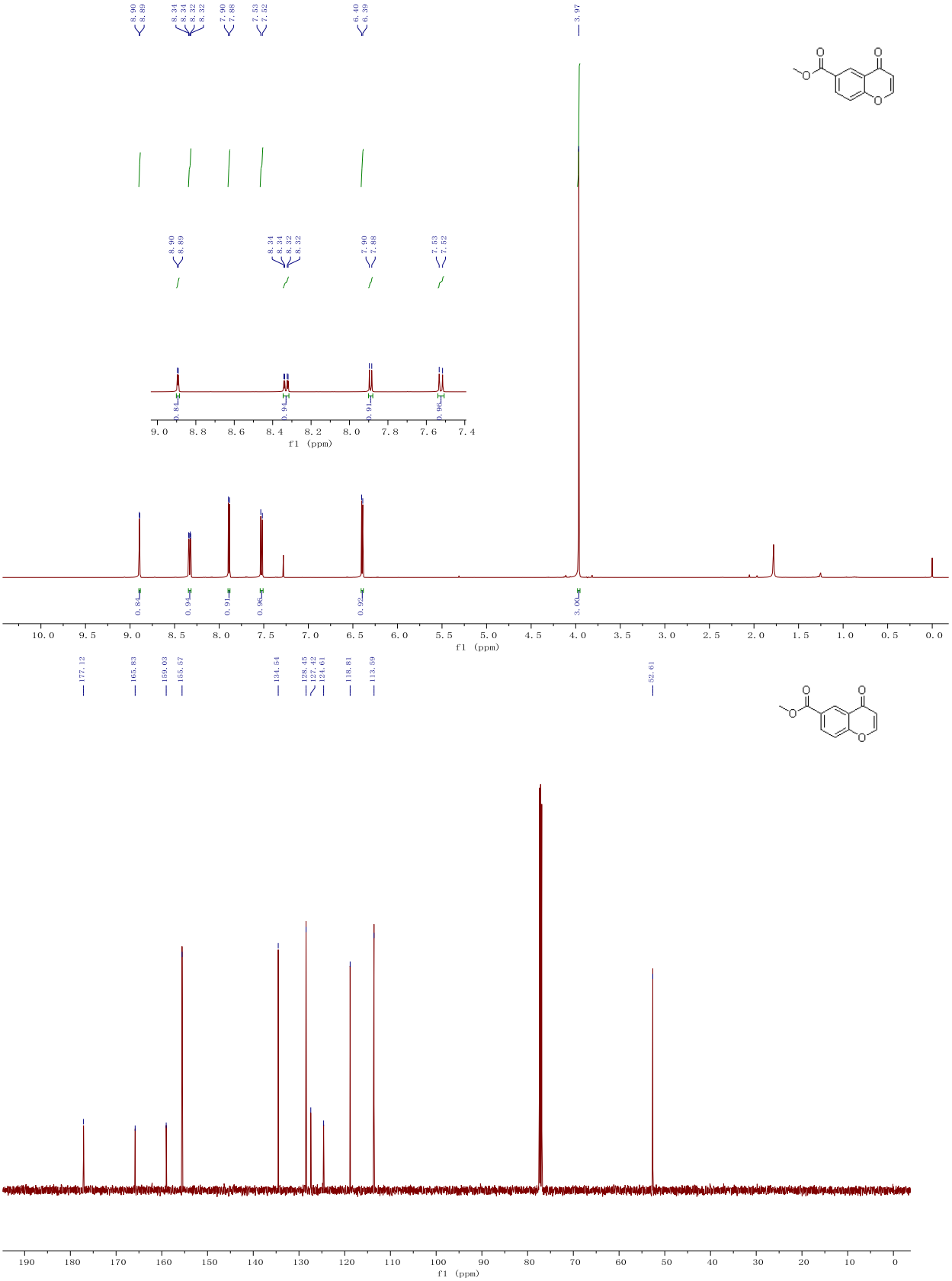
6-(Trifluoromethoxy)-4*H*-chromen-4-one (3h)



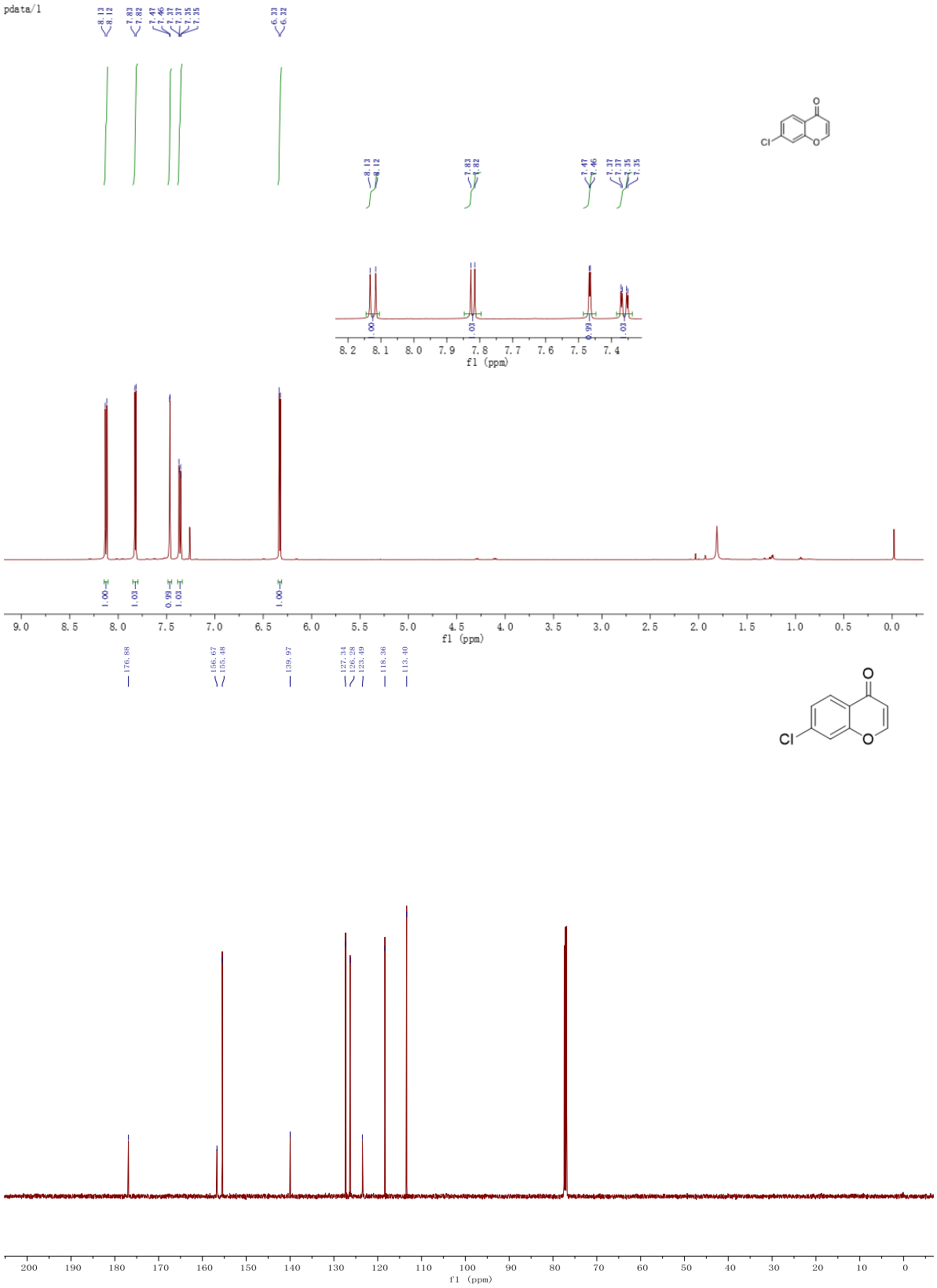
6-Nitro-4*H*-chromen-4-one (3i)



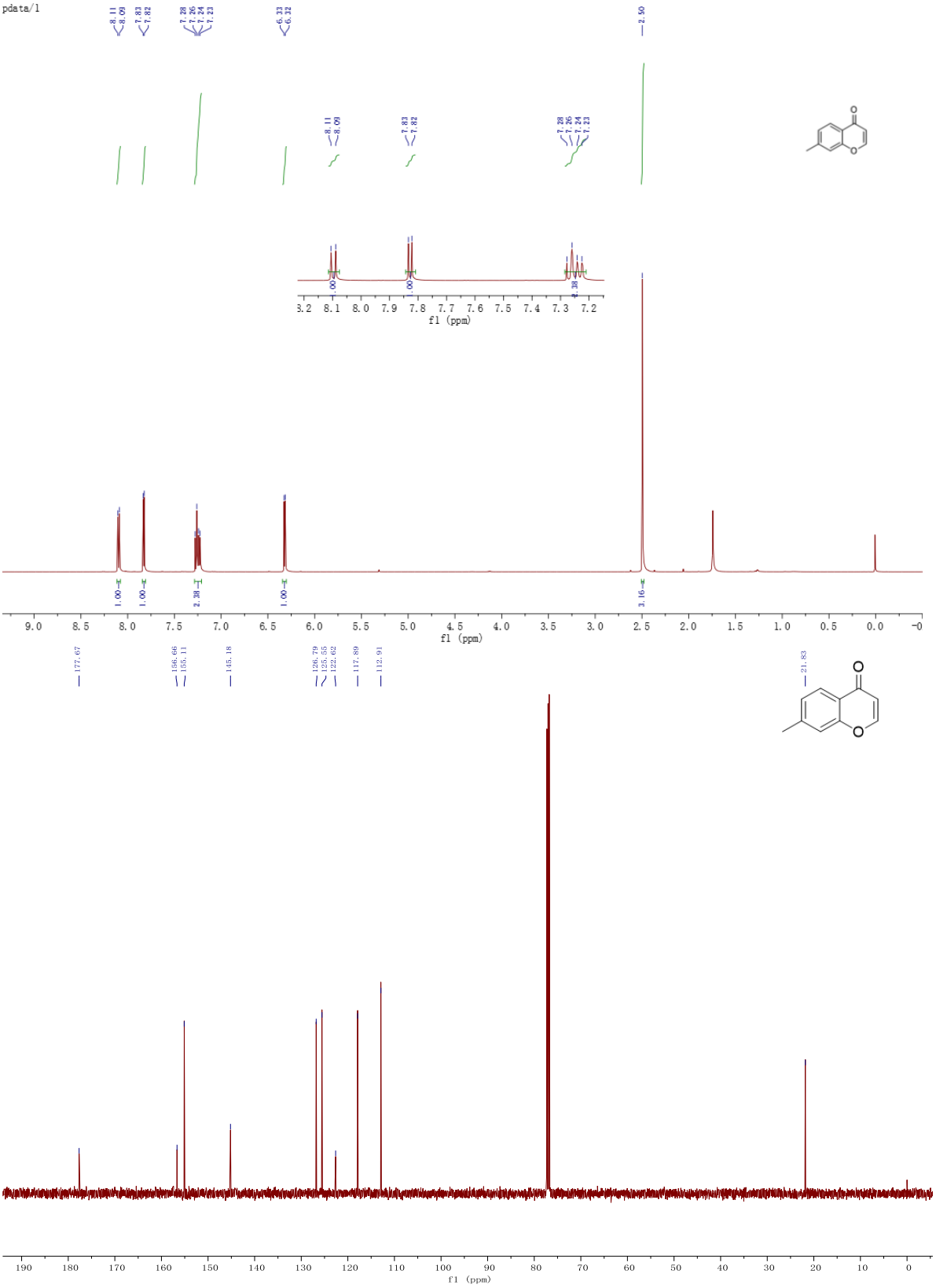
Methyl 4-oxo-4*H*-chromene-6-carboxylate (3j)



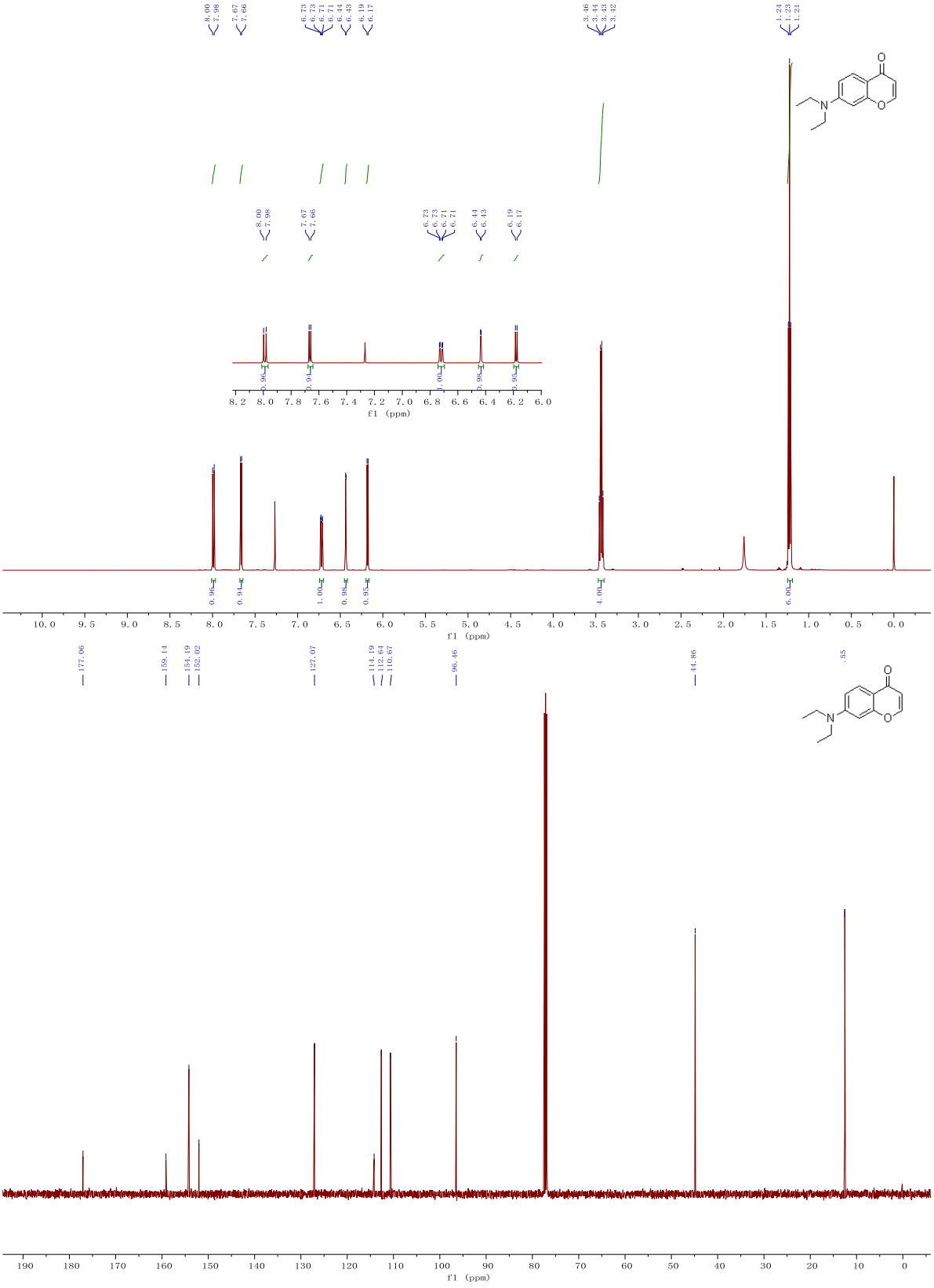
7-Chloro-4*H*-chromen-4-one (3k)



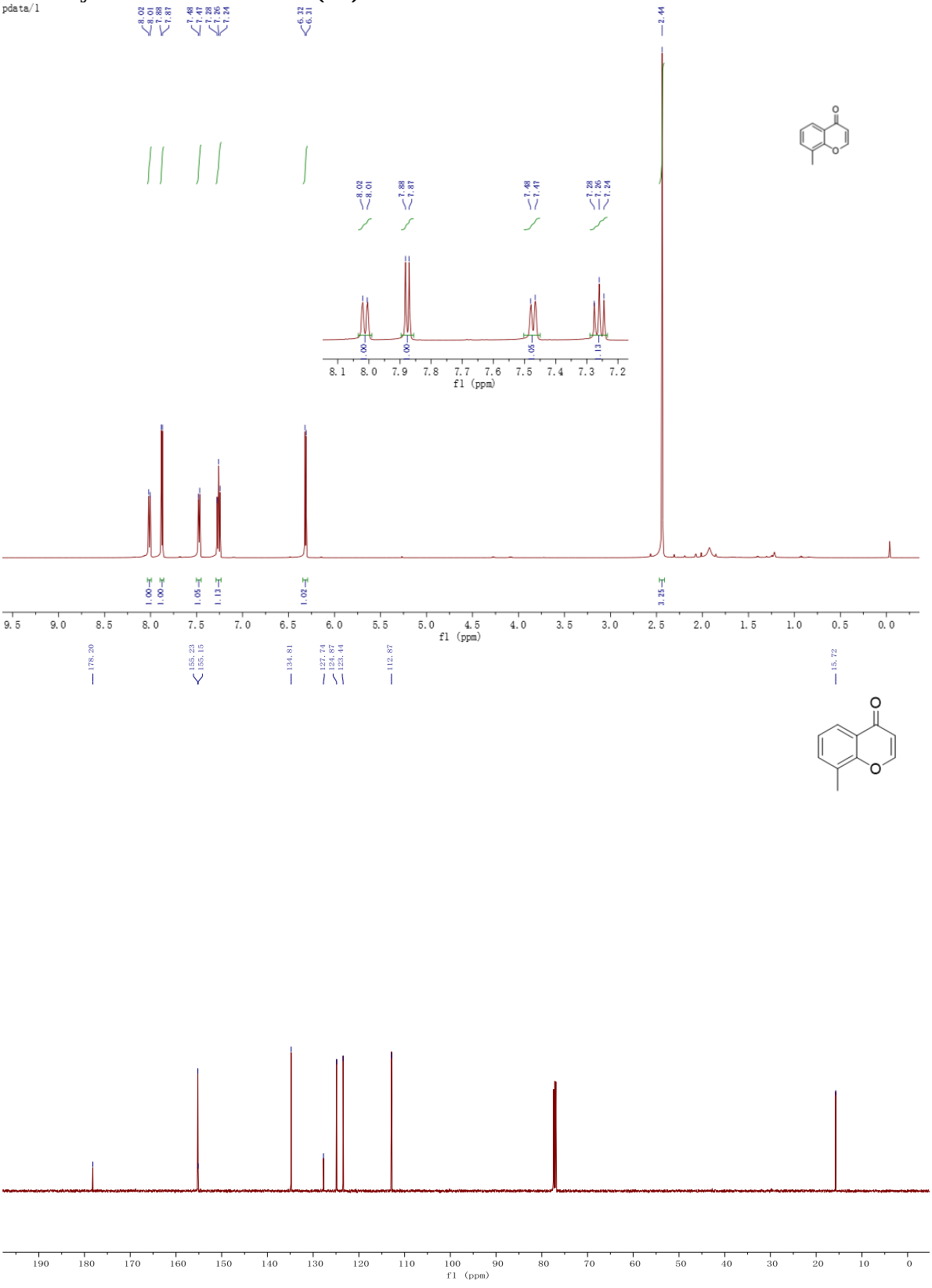
7-Methyl-4*H*-chromen-4-one (3l)



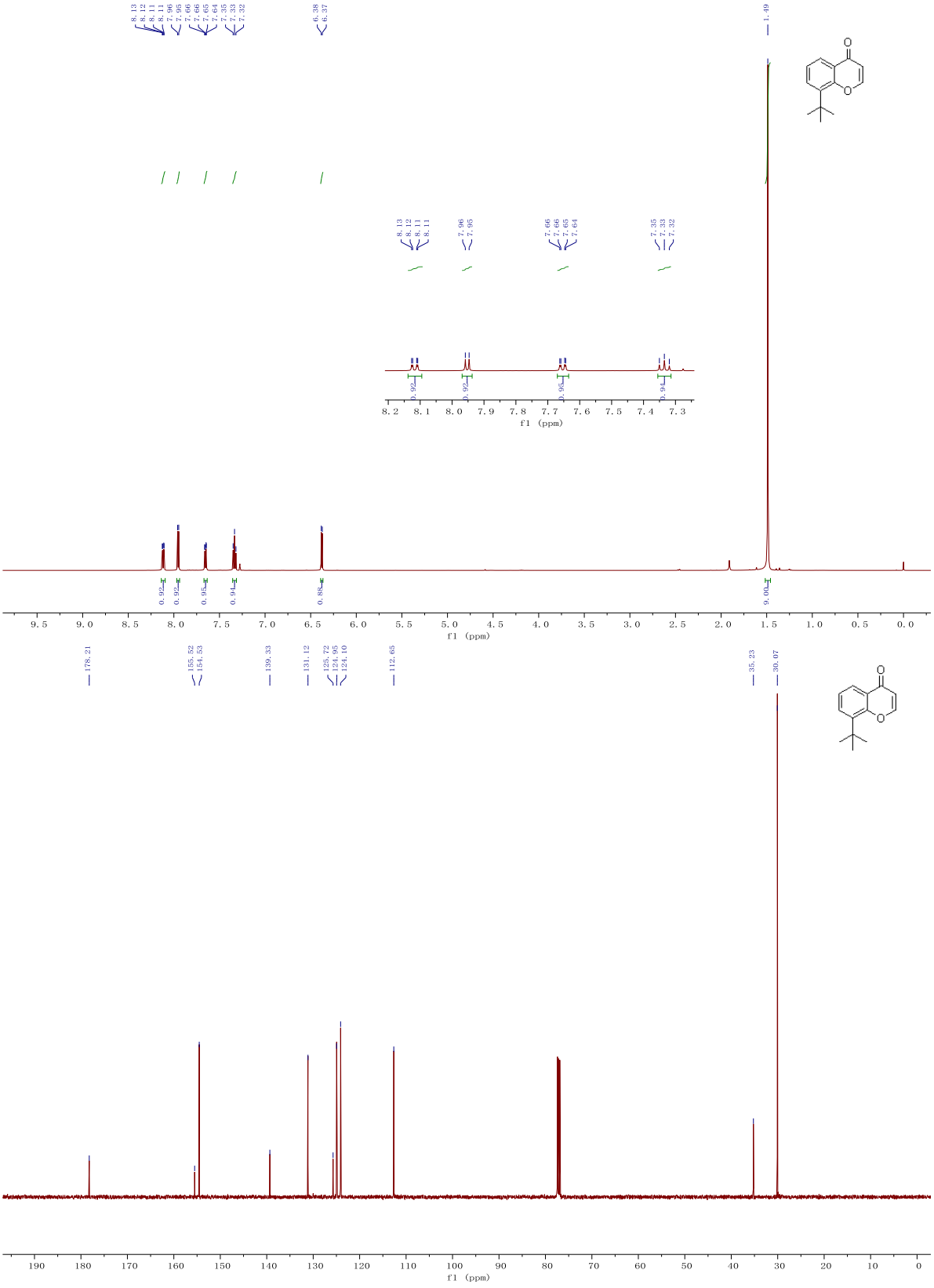
7-(Diethylamino)-4*H*-chromen-4-one (3m)



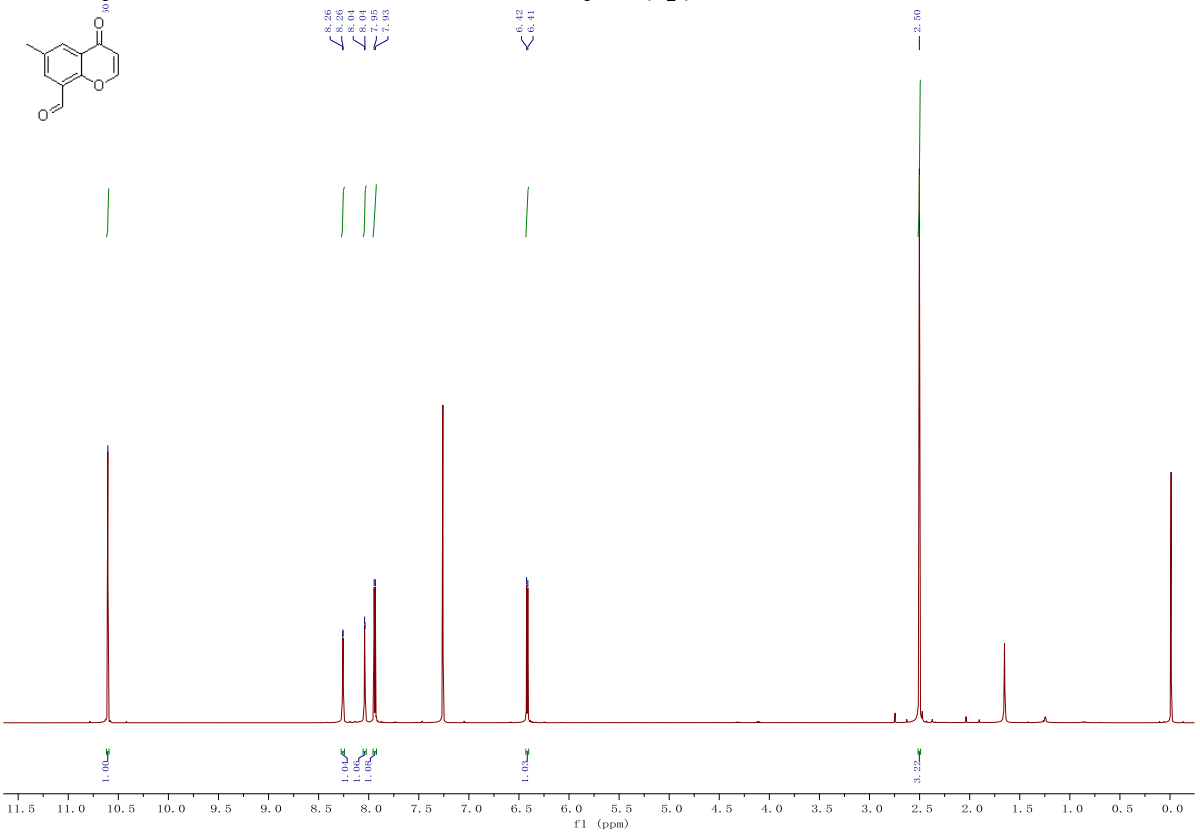
8-Methyl-4*H*-chromen-4-one (3n)

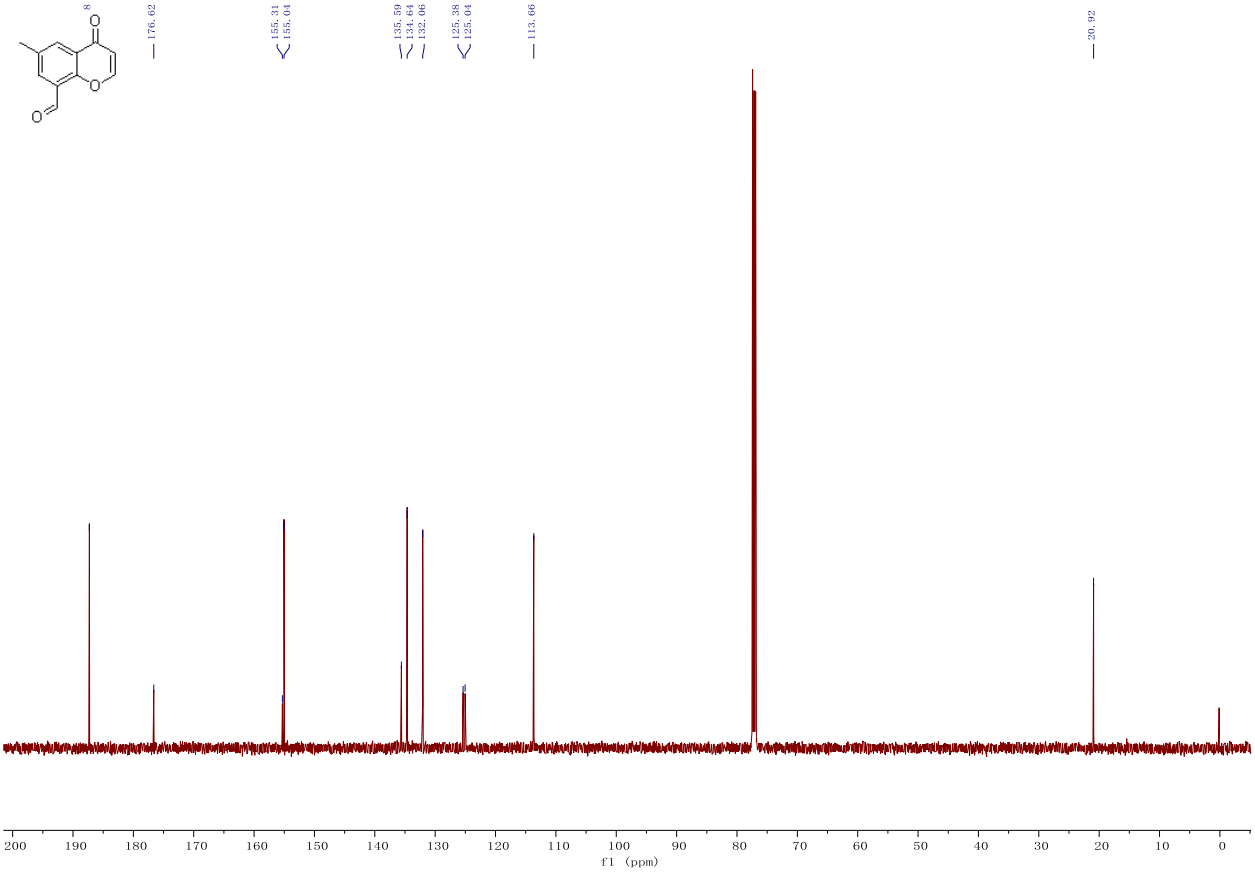


8-(*tert*-Butyl)-4*H*-chromen-4-one (3o)

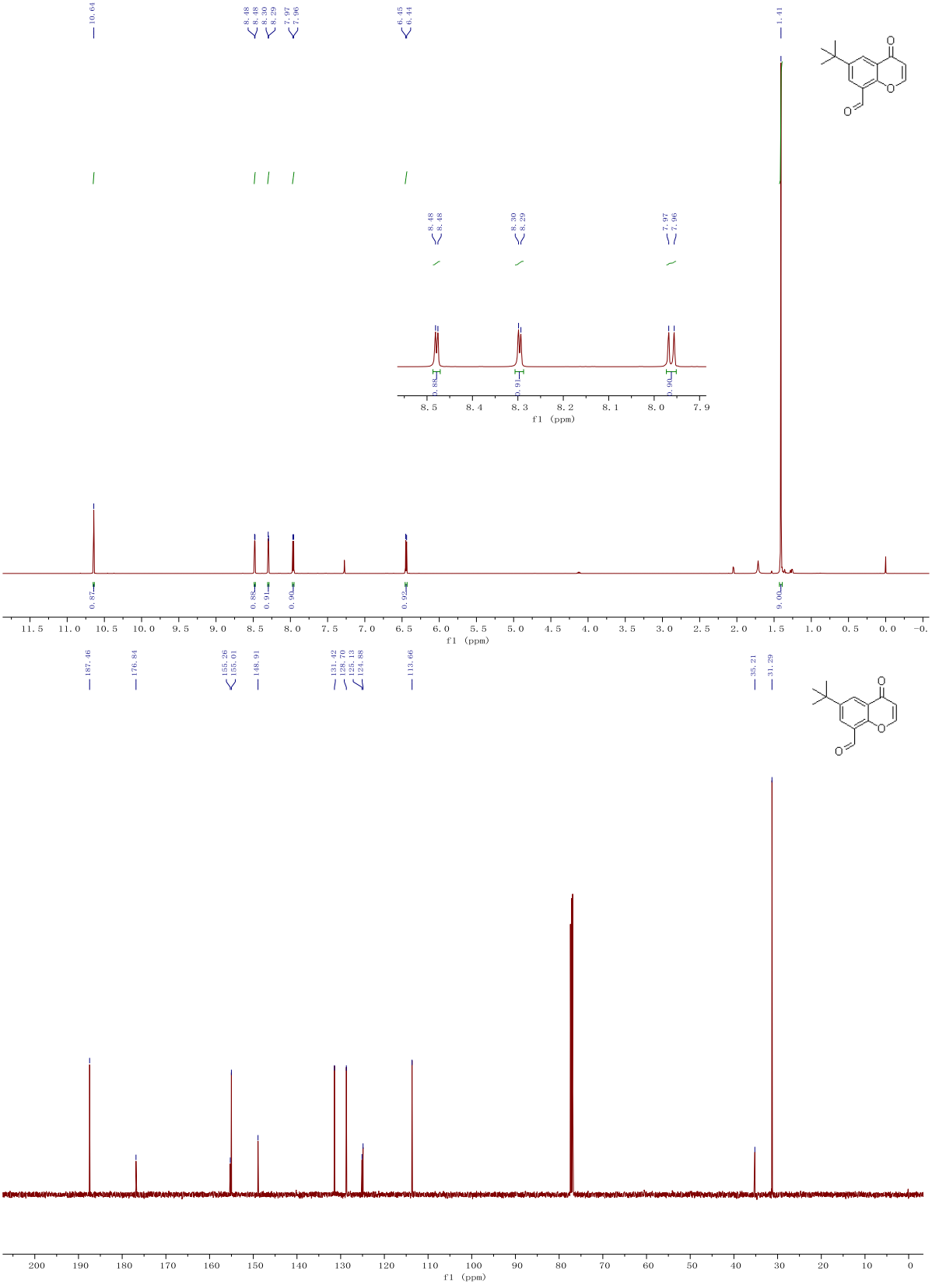


6-Methyl-4-oxo-4*H*-chromene-8-carbaldehyde (3p)

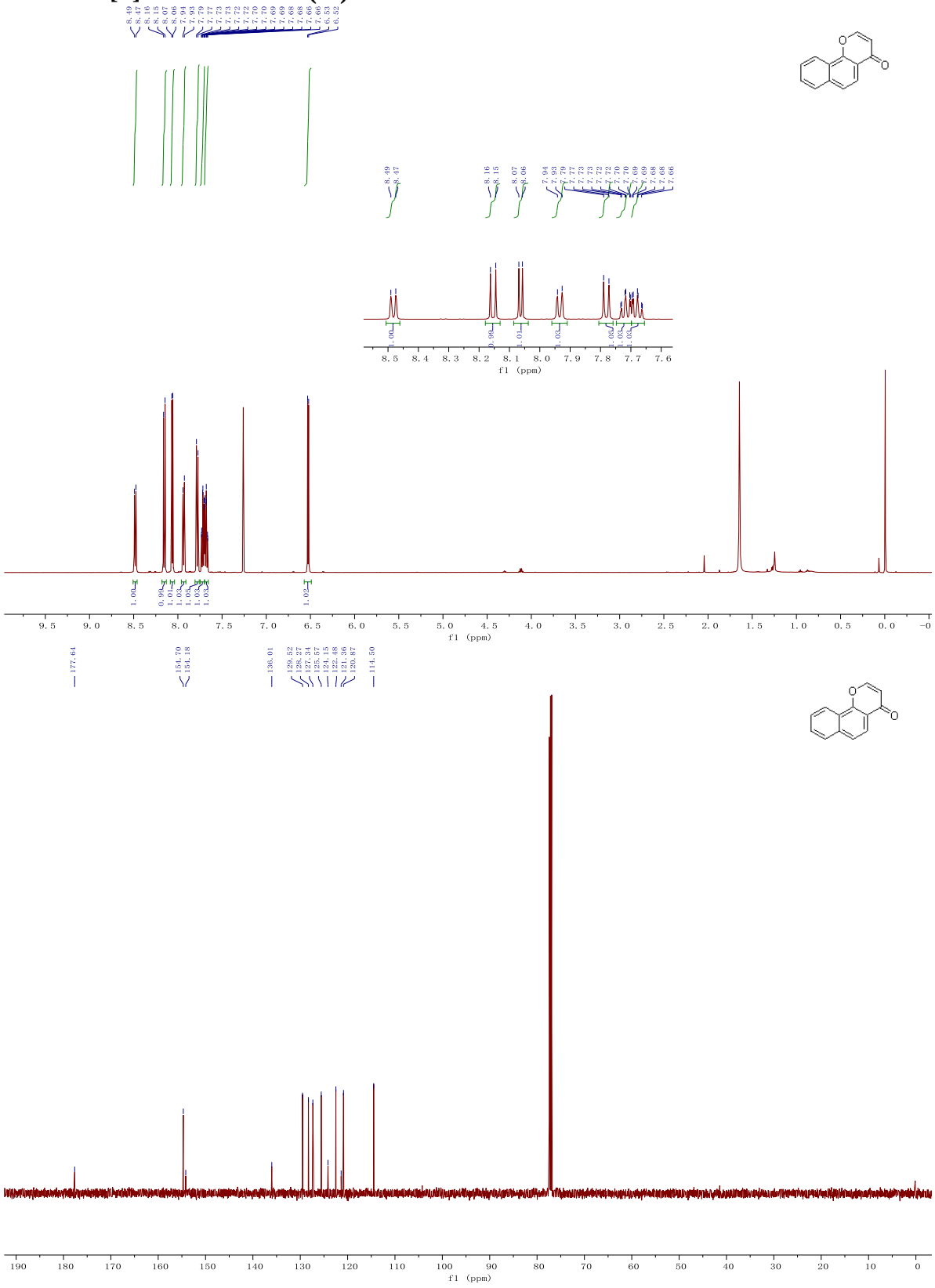




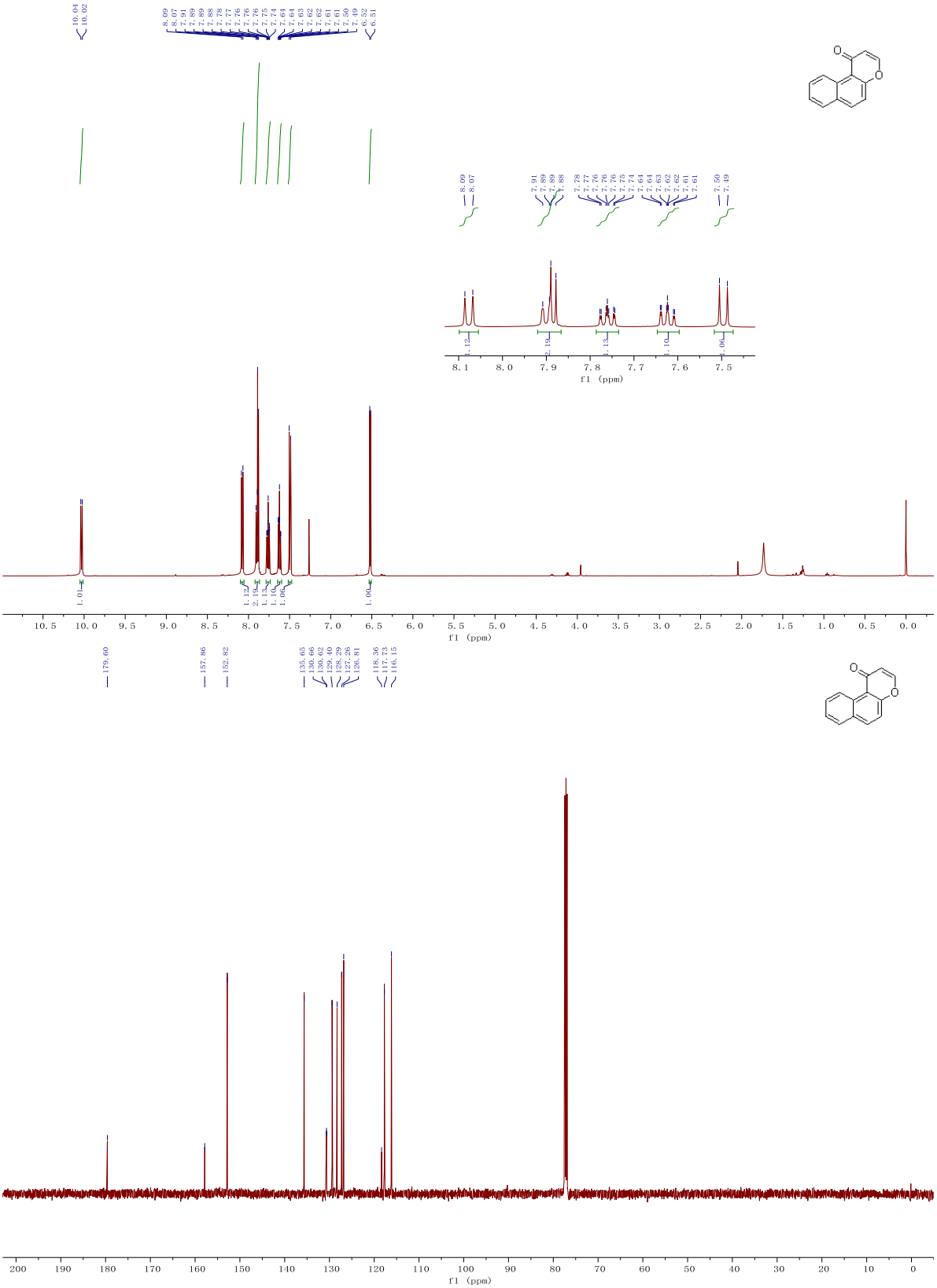
6-(*tert*-Butyl)-4-oxo-4*H*-chromene-8-carbaldehyde (3q)



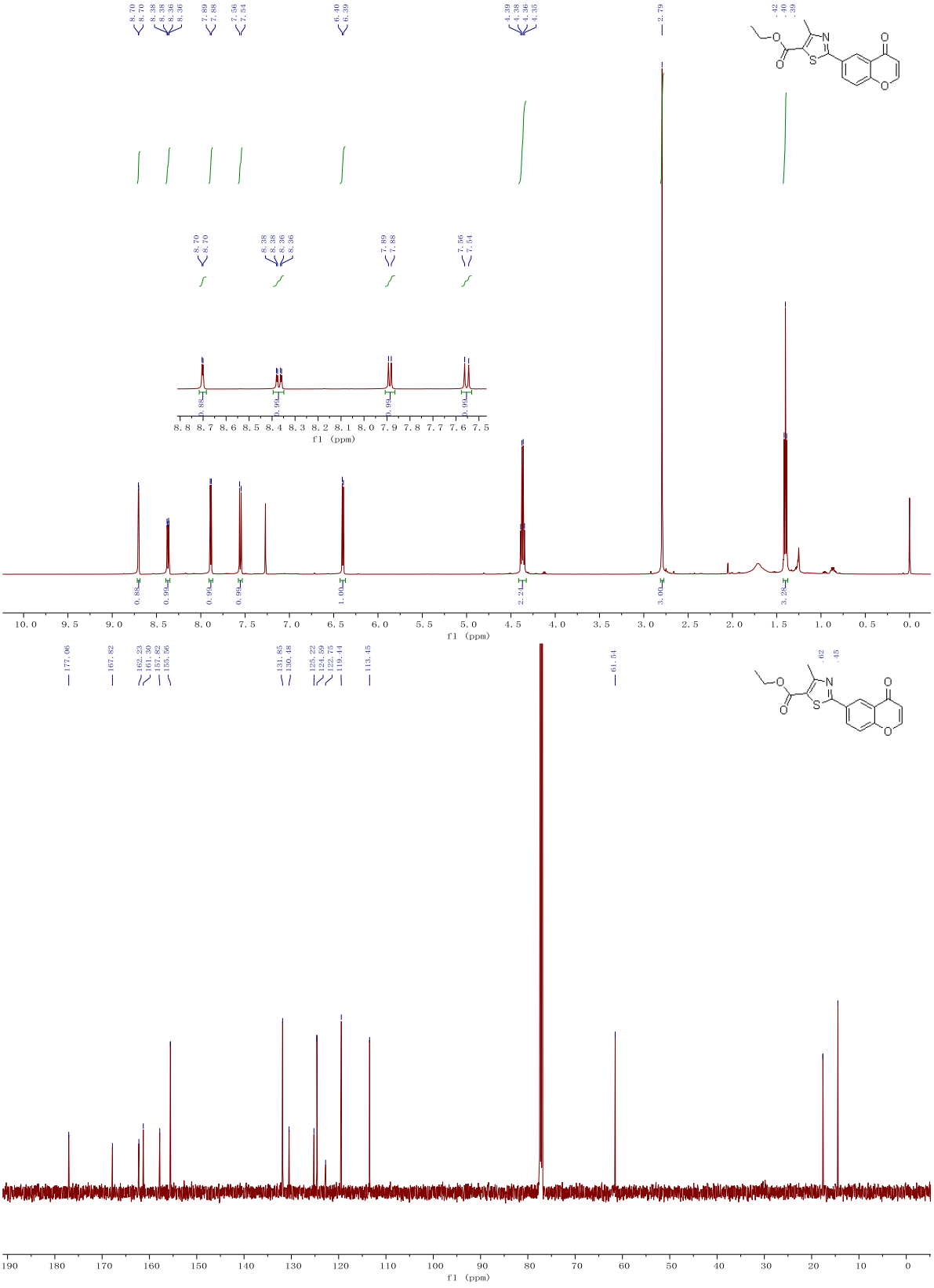
4*H*-Benzo[*h*]chromen-4-one (3r)



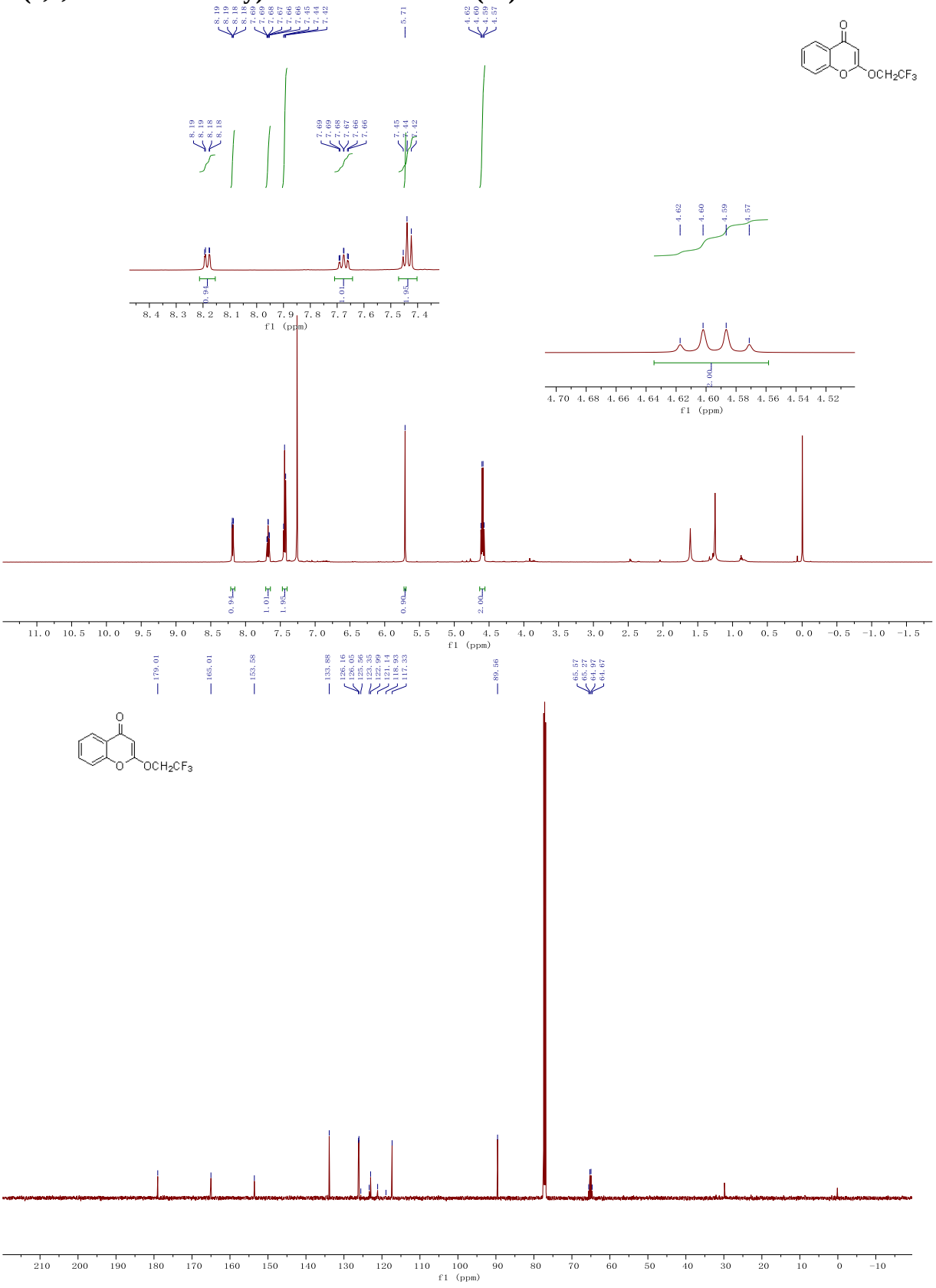
1*H*-benzo[*f*]chromen-1-one (3s)

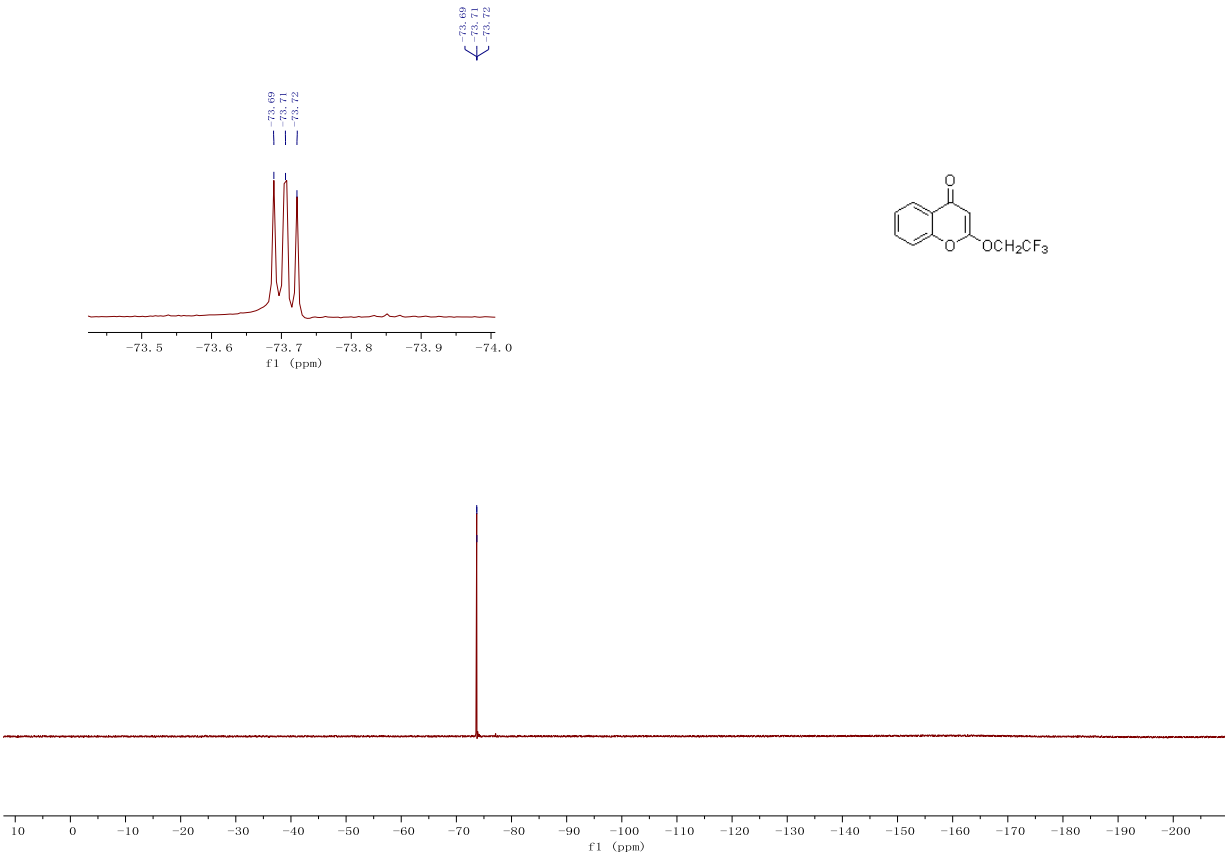


Ethyl 4-methyl-2-(4-oxo-4*H*-chromen-6-yl)thiazole-5-carboxylate (3t)



2-(2,2,2-Trifluoroethoxy)-4*H*-chromen-4-one (5a)

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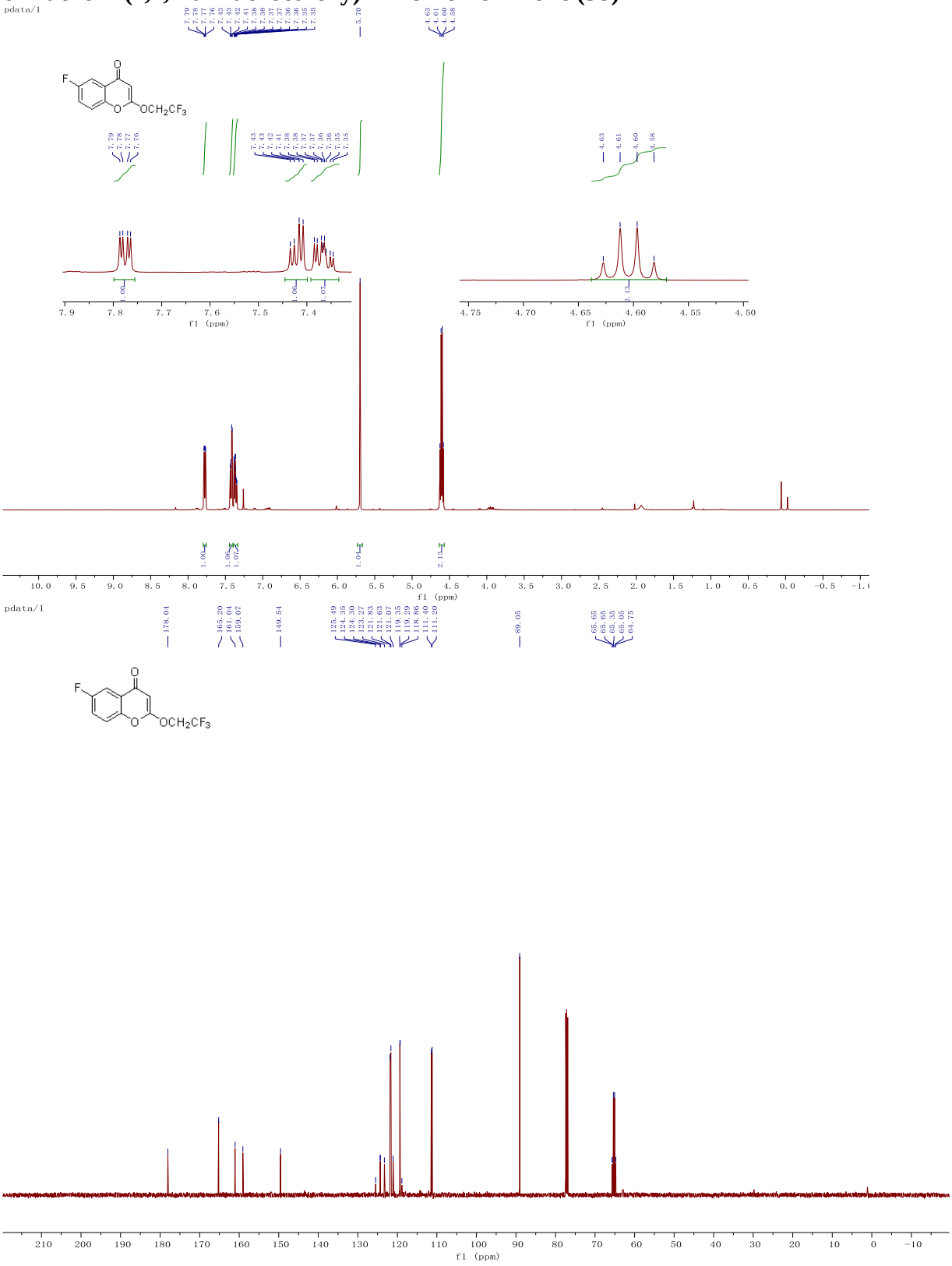
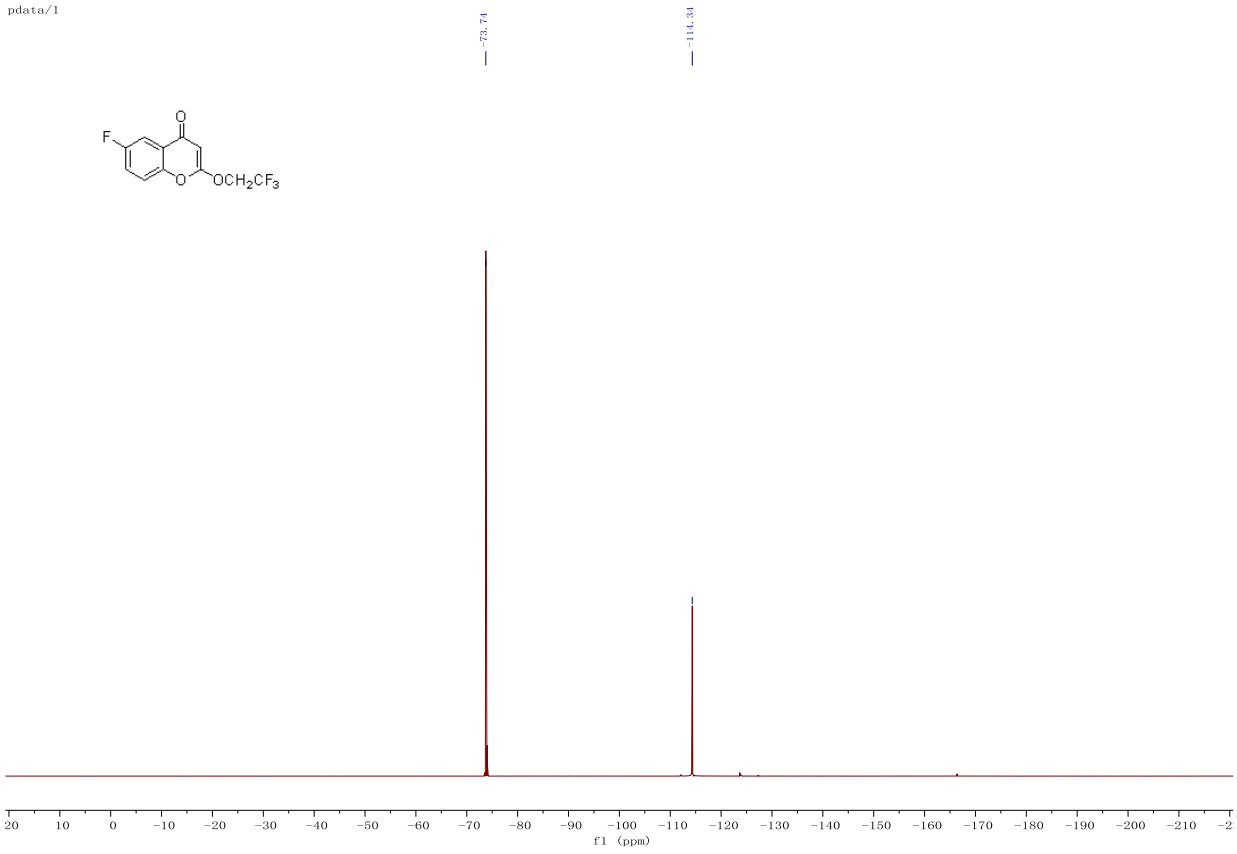
-73.9
-74.0
f1 (ppm)
O
O
OCH2CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

6-Fluoro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5b)

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O
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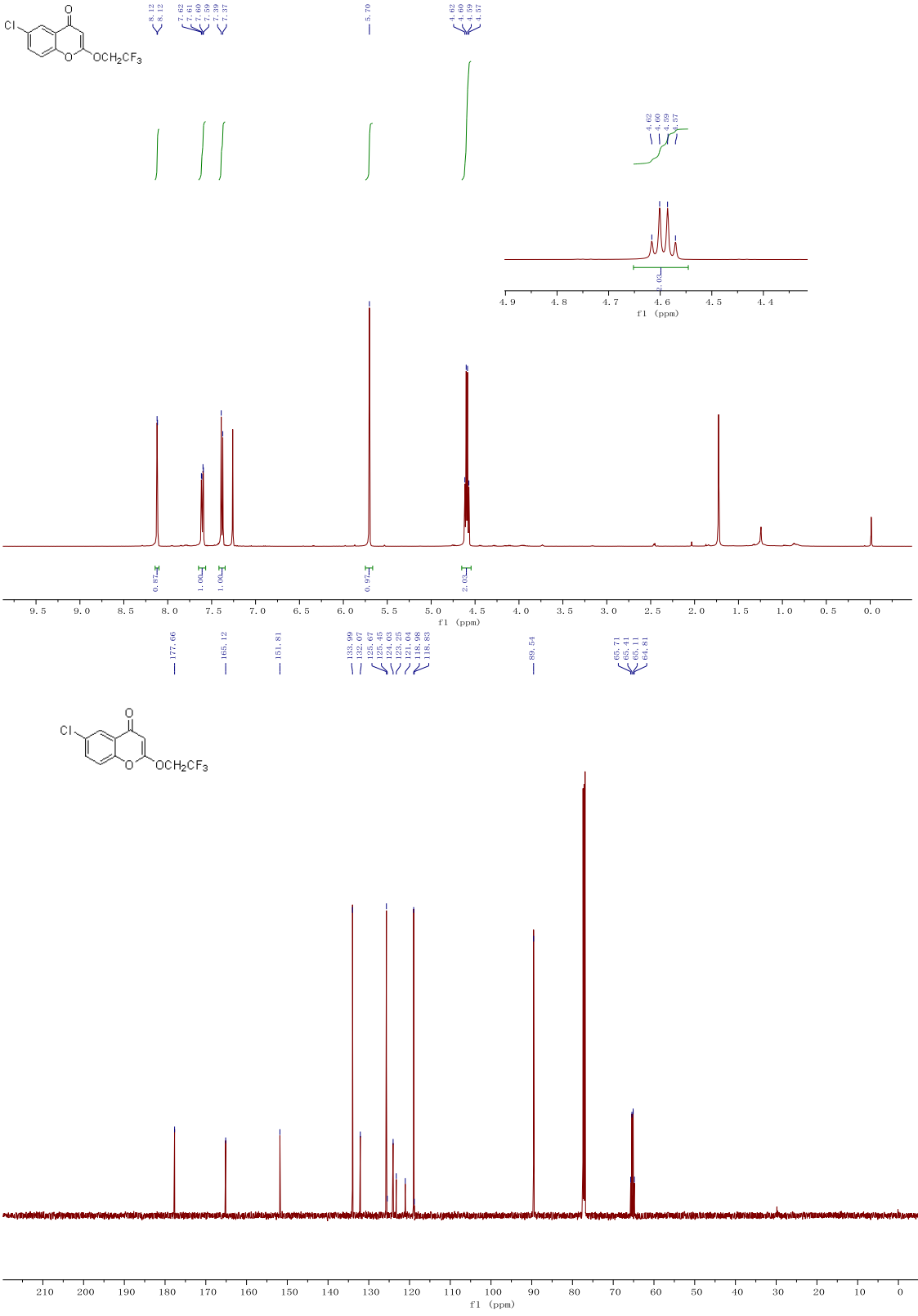
f1 (ppm)

6-Chloro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5c)

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-73.70
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-73.9
f1 (ppm)
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-10
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-30
-40
-50
-60
-70
-80
-90
-100
-110
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-130
-140
-150
-160
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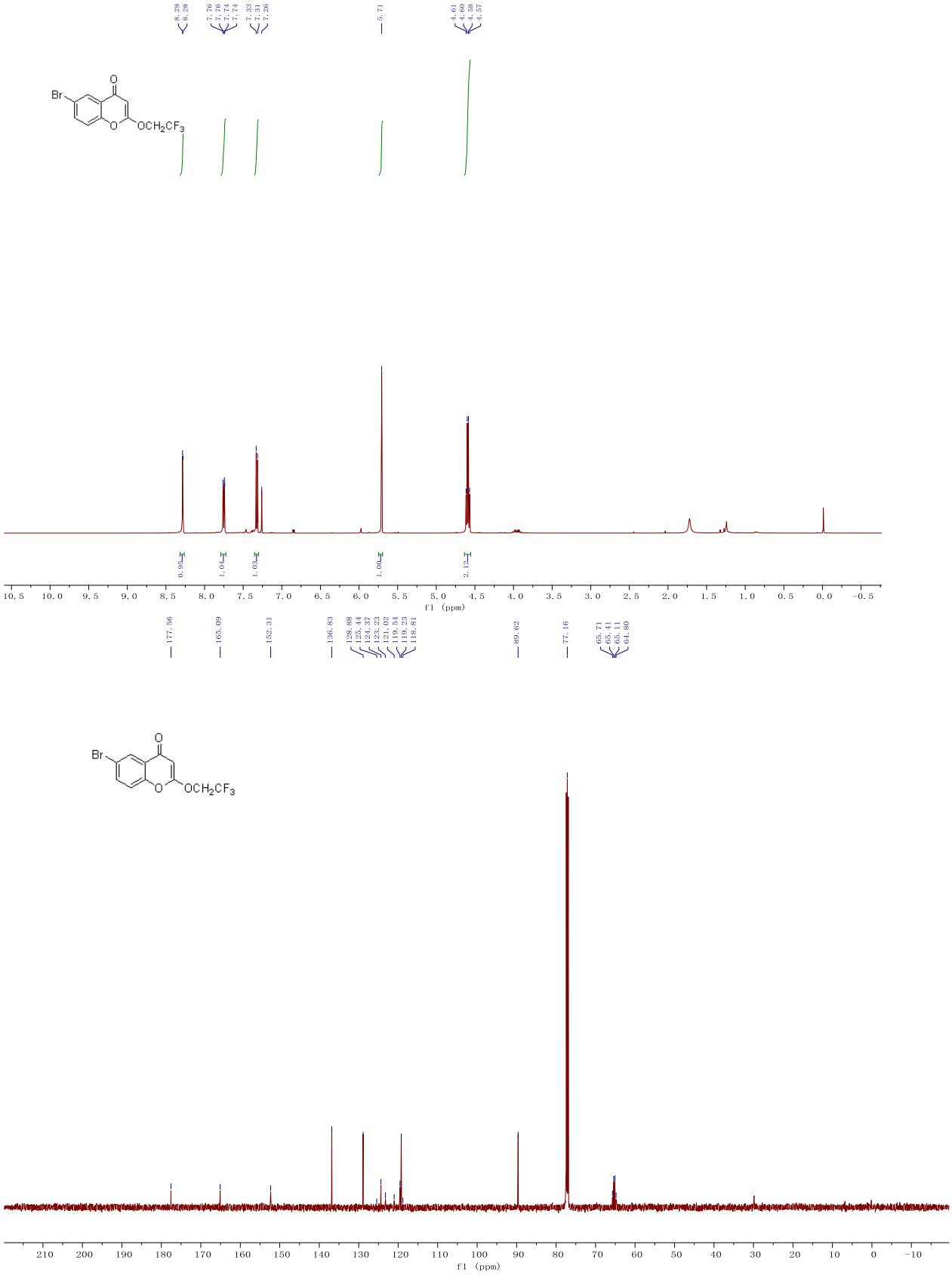
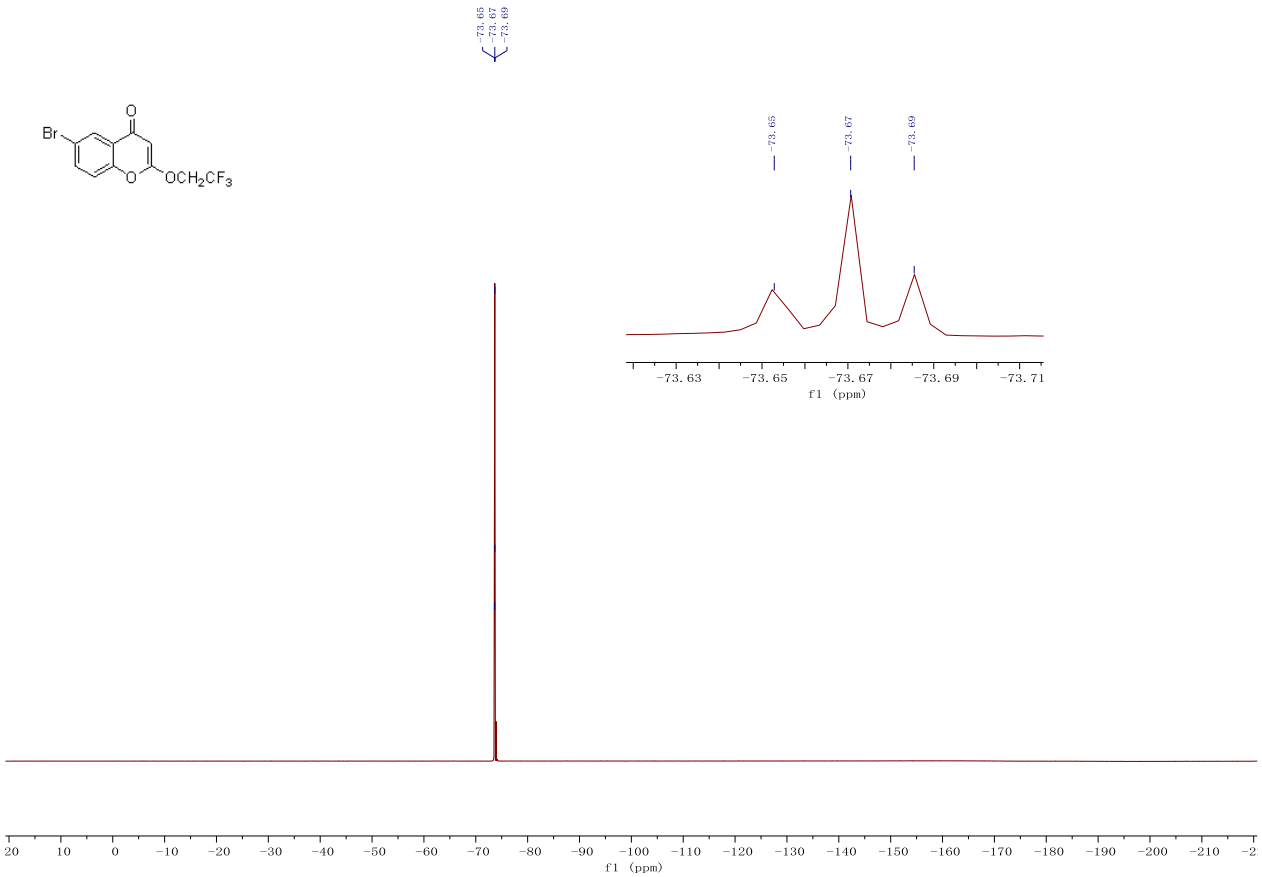
f1 (ppm)

6-Bromo-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5d)

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O
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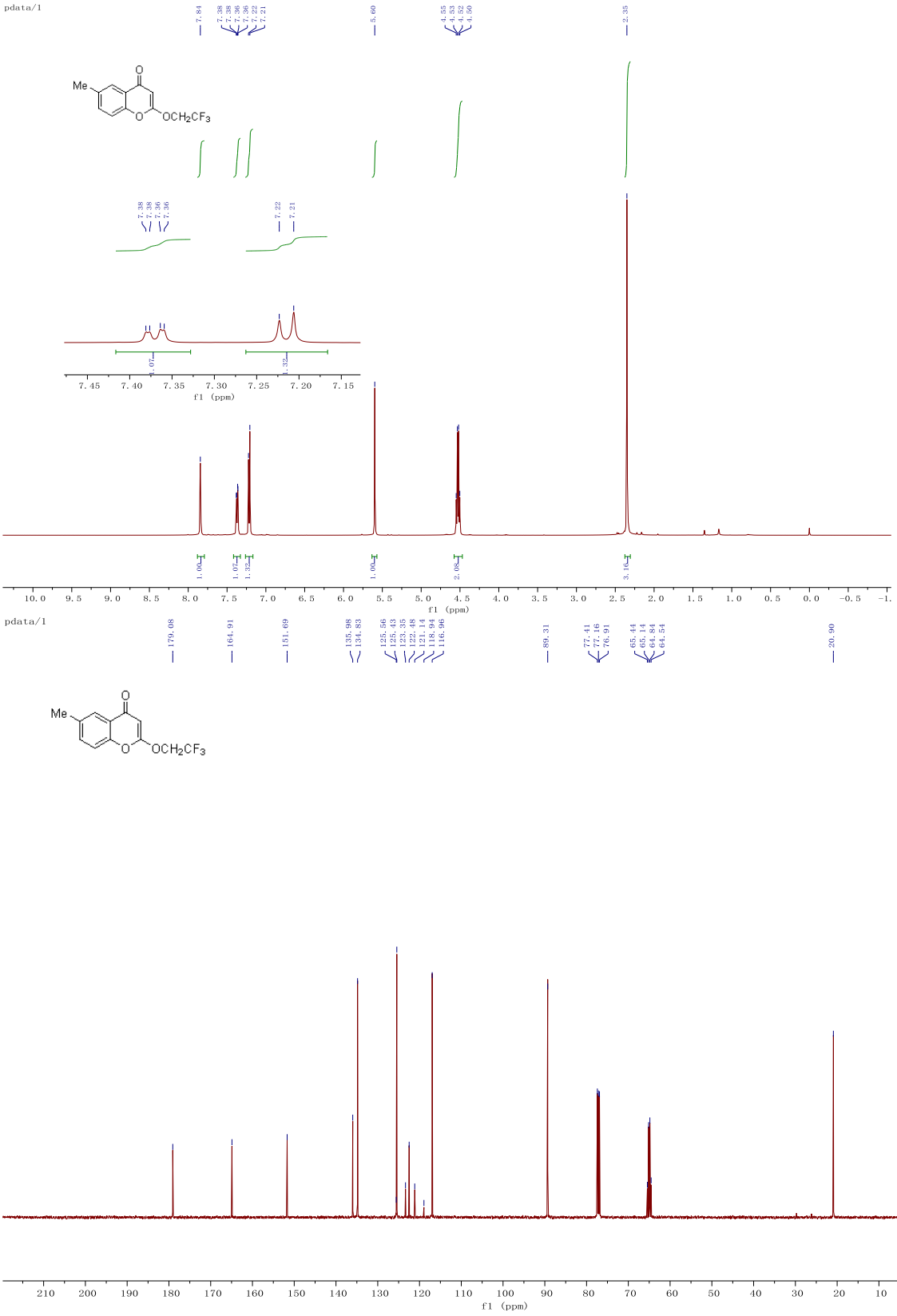
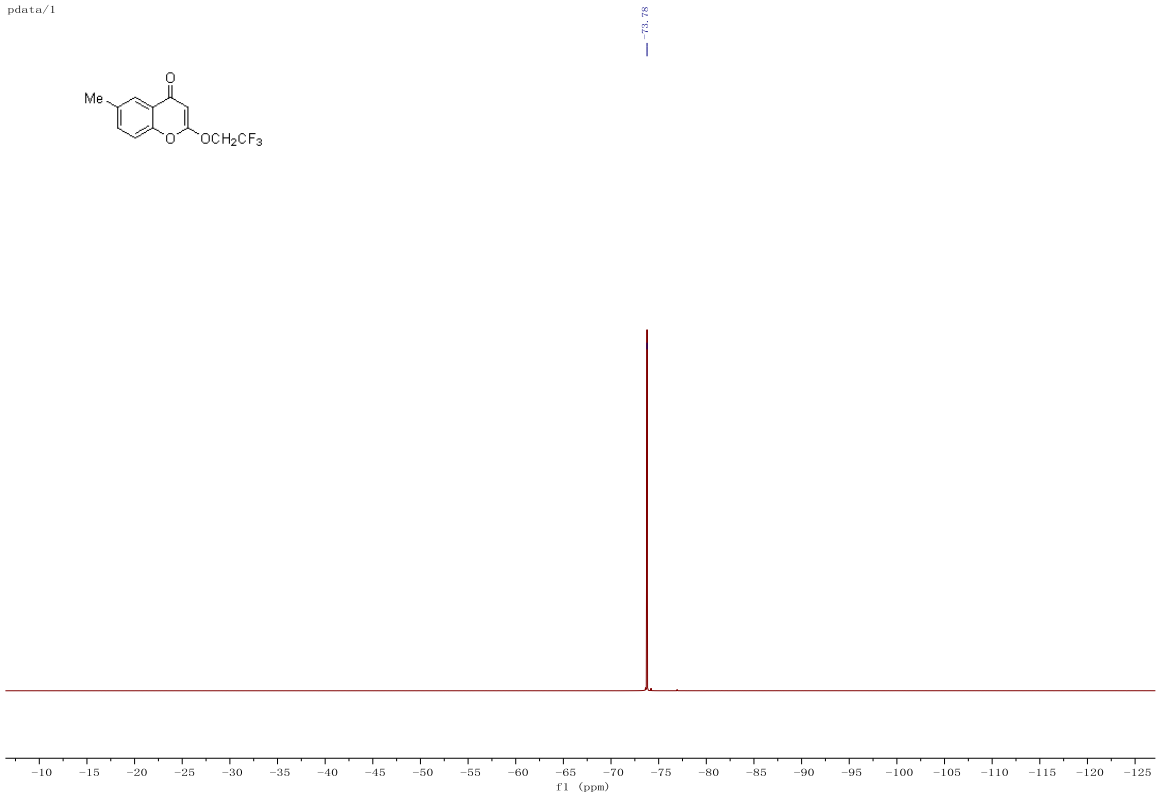
-73.69
-73.71
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

6-Methyl-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5e)

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Me
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O
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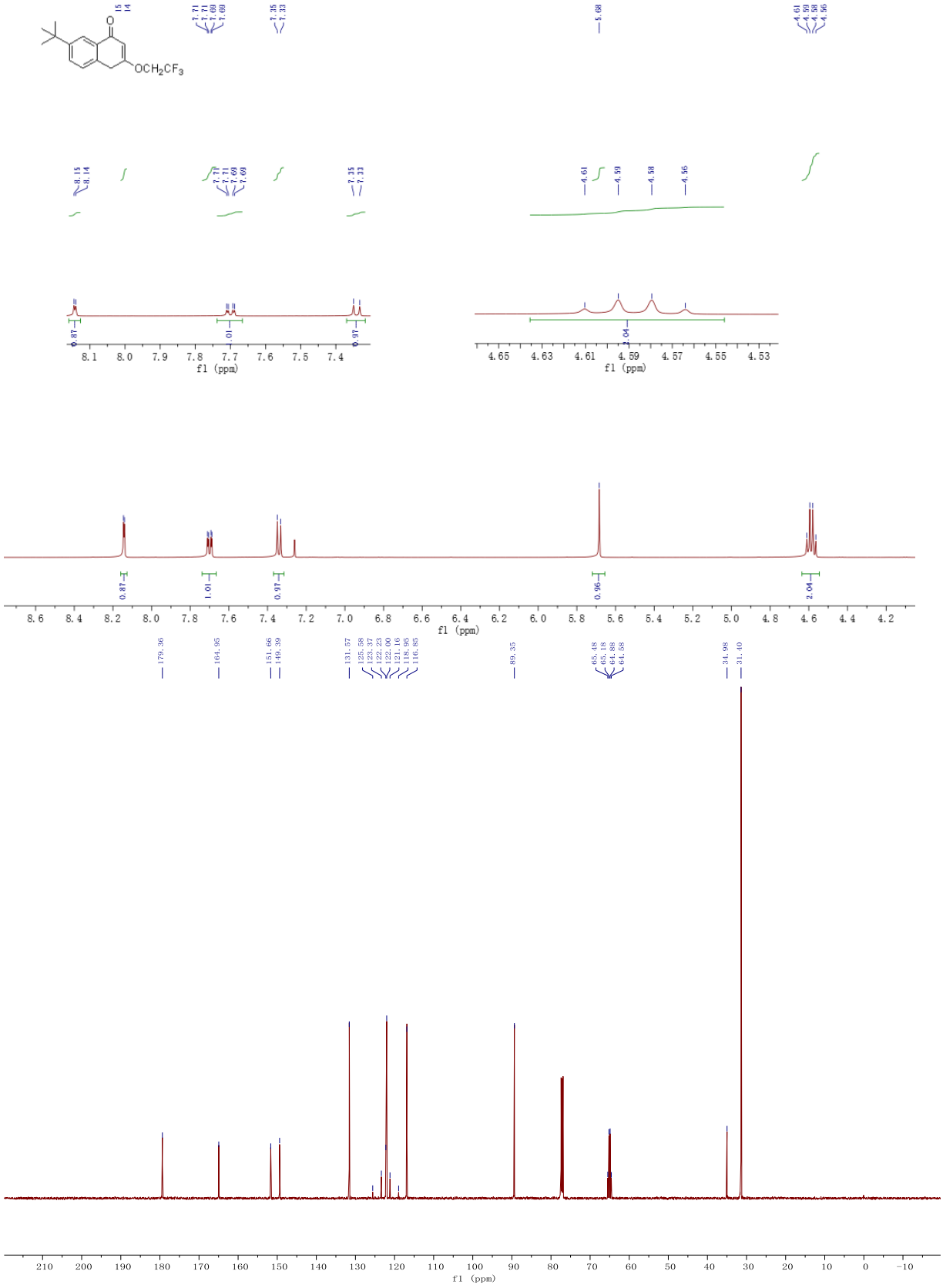
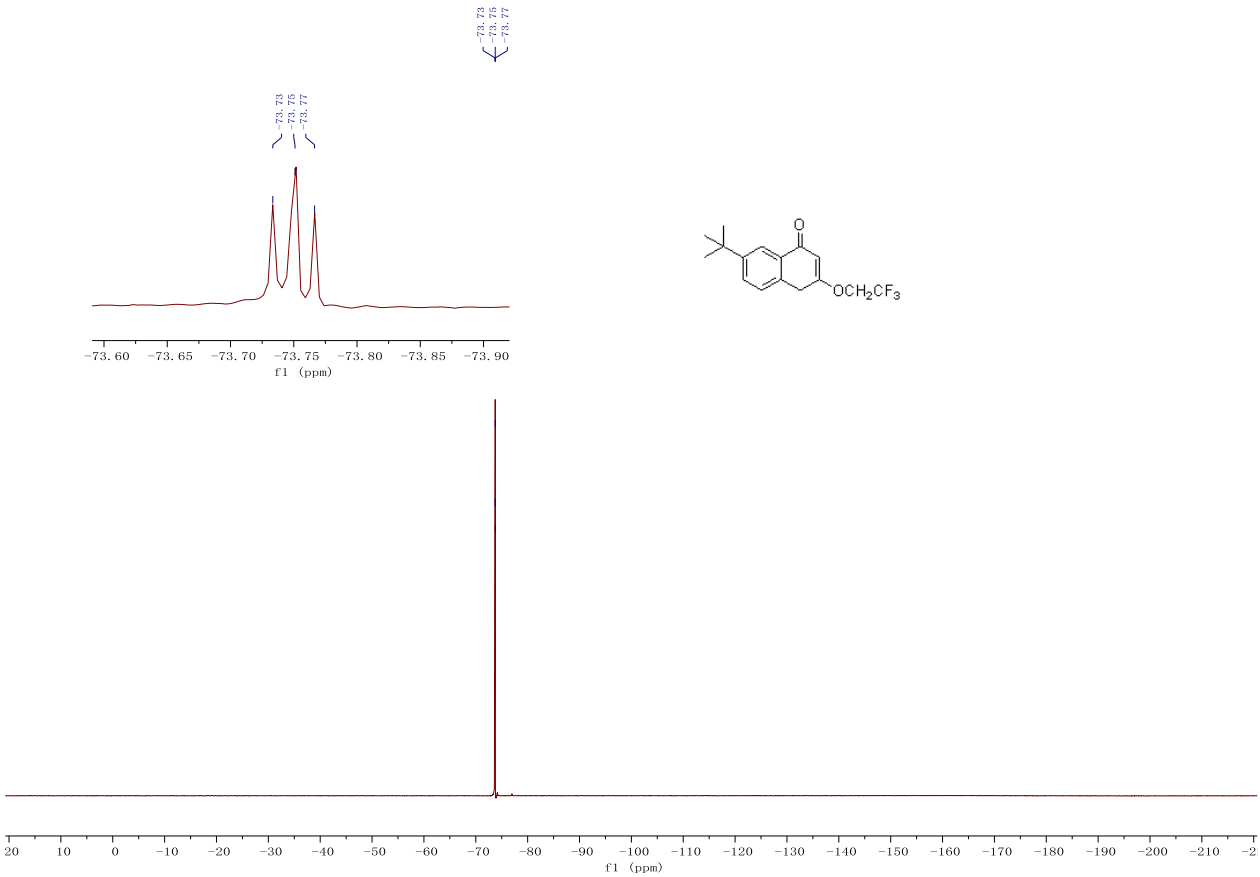
-10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125
f1 (ppm)

7-(*tert*-Butyl)-3-(2,2,2-trifluoroethoxy)naphthalen-1(4H)-one (5f)

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f1 (ppm)
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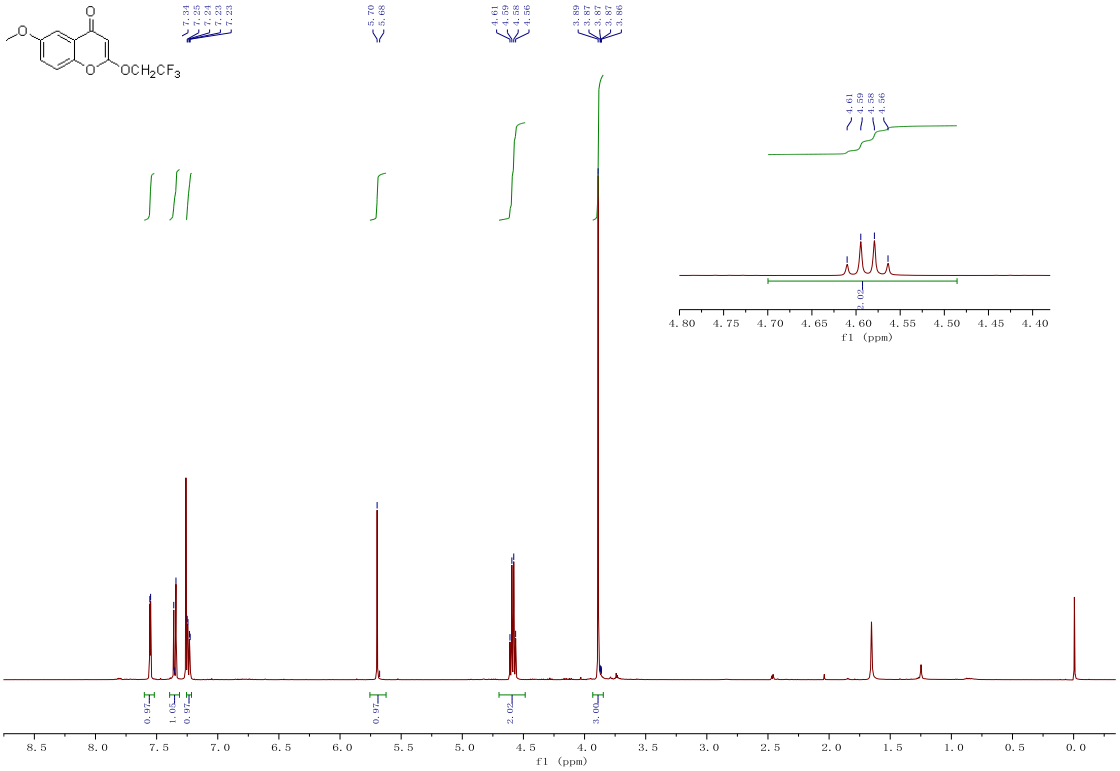
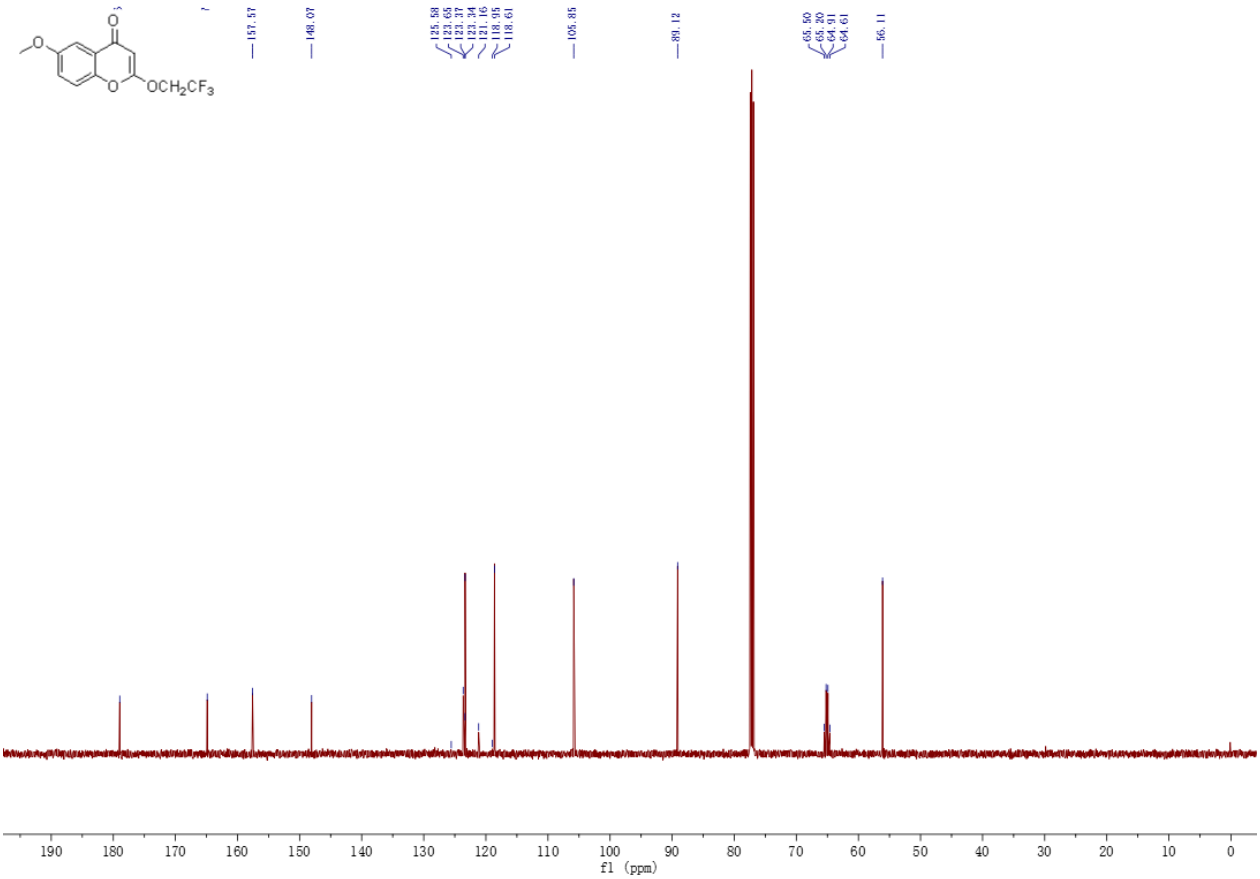
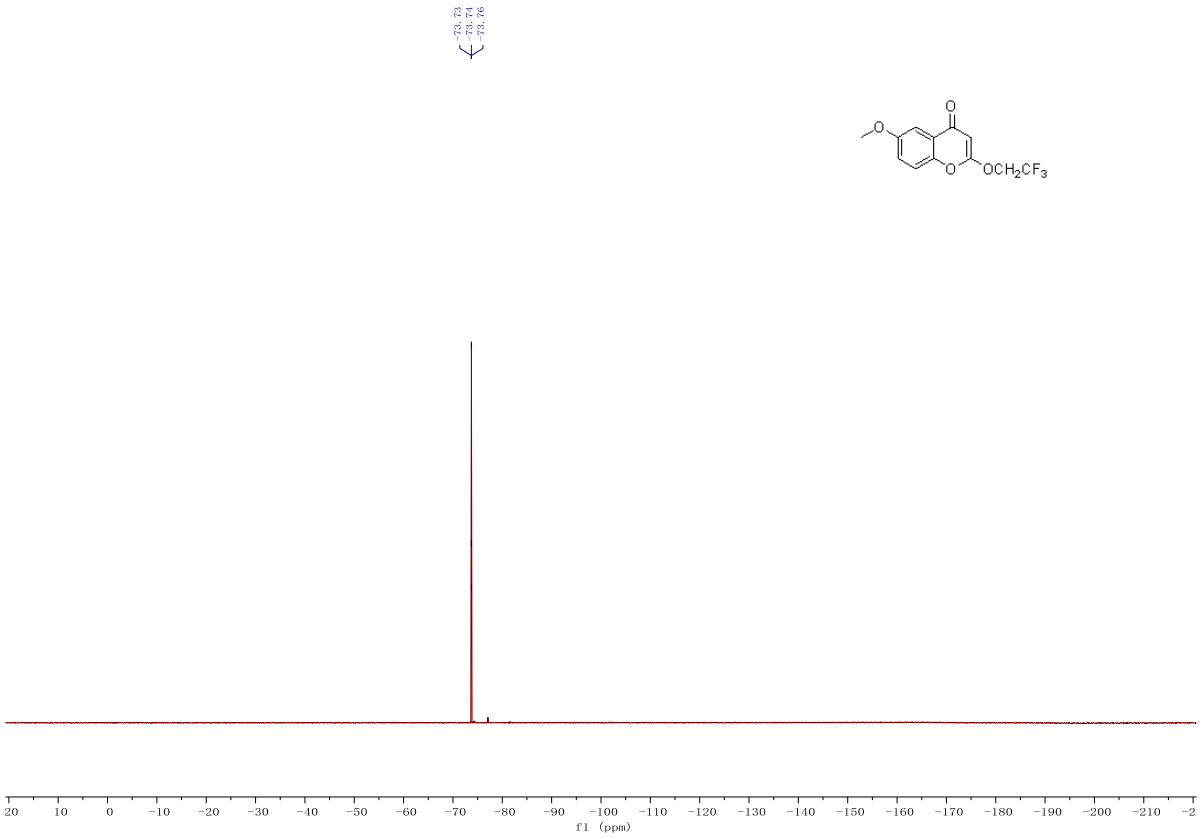
f1 (ppm)

6-Methoxy-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5g)



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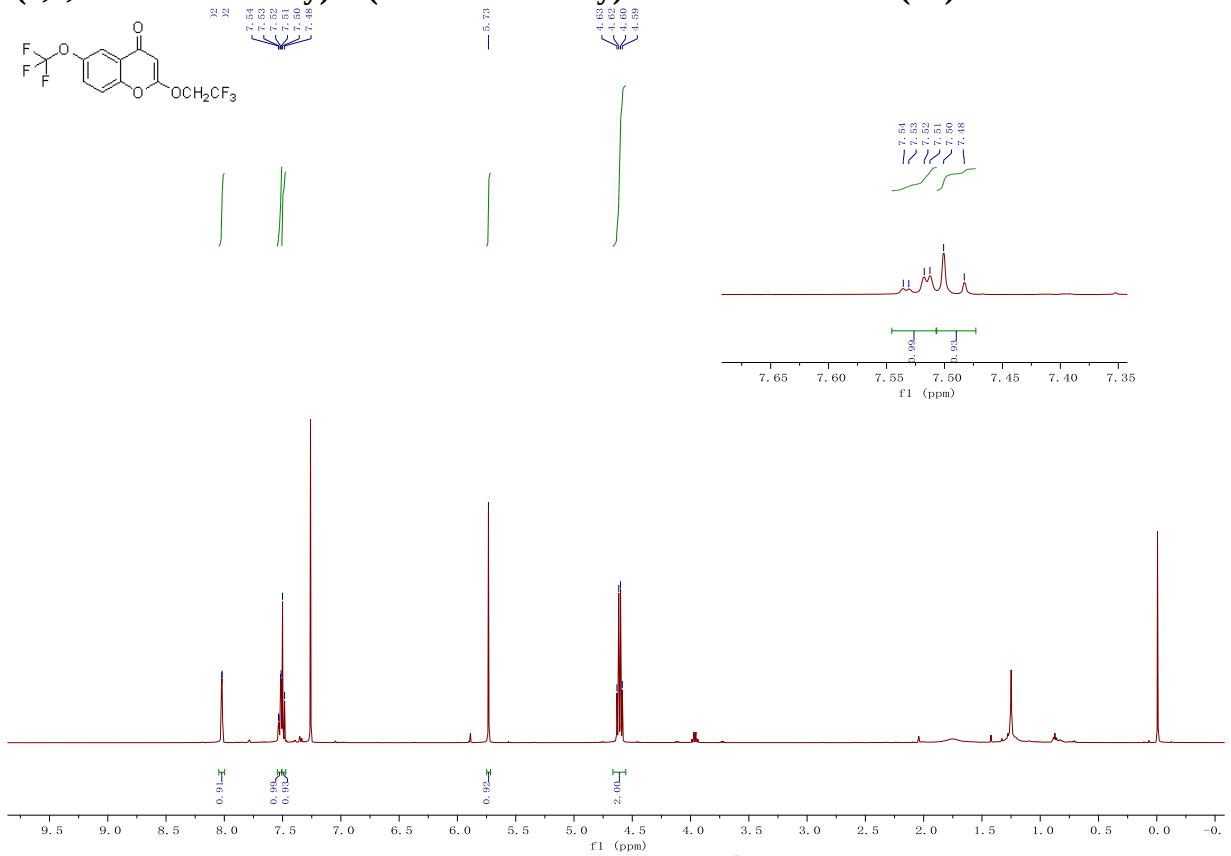
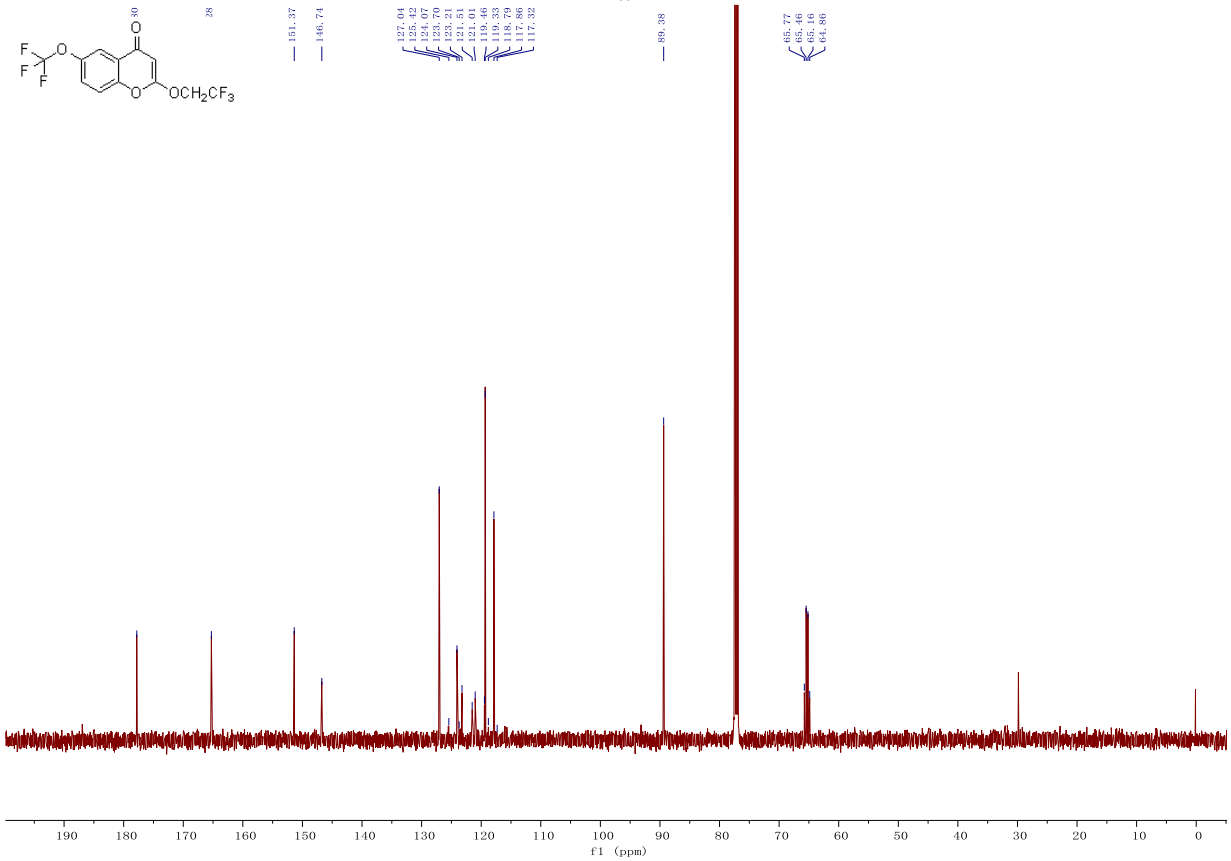
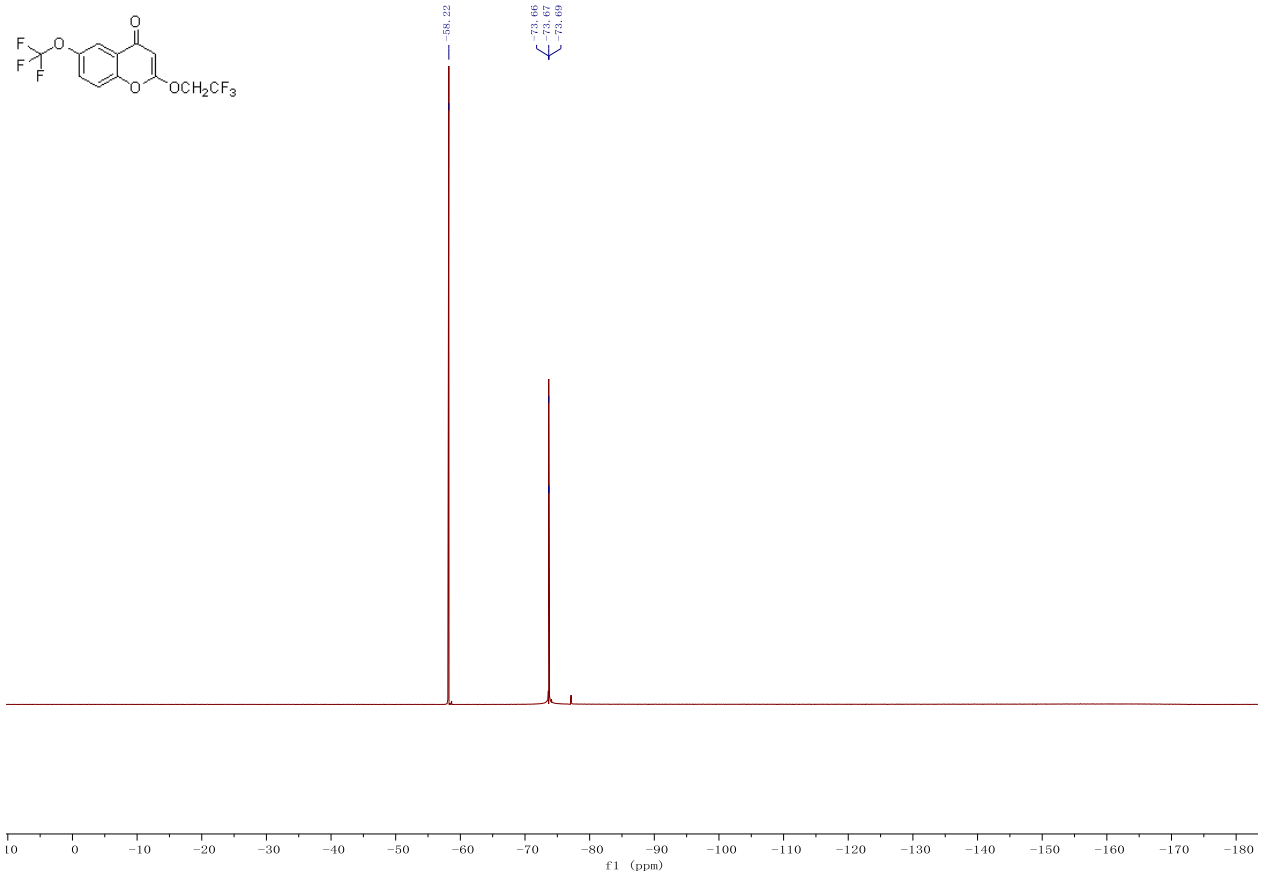
-73.74
-73.76
O
O
O
OCH2CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

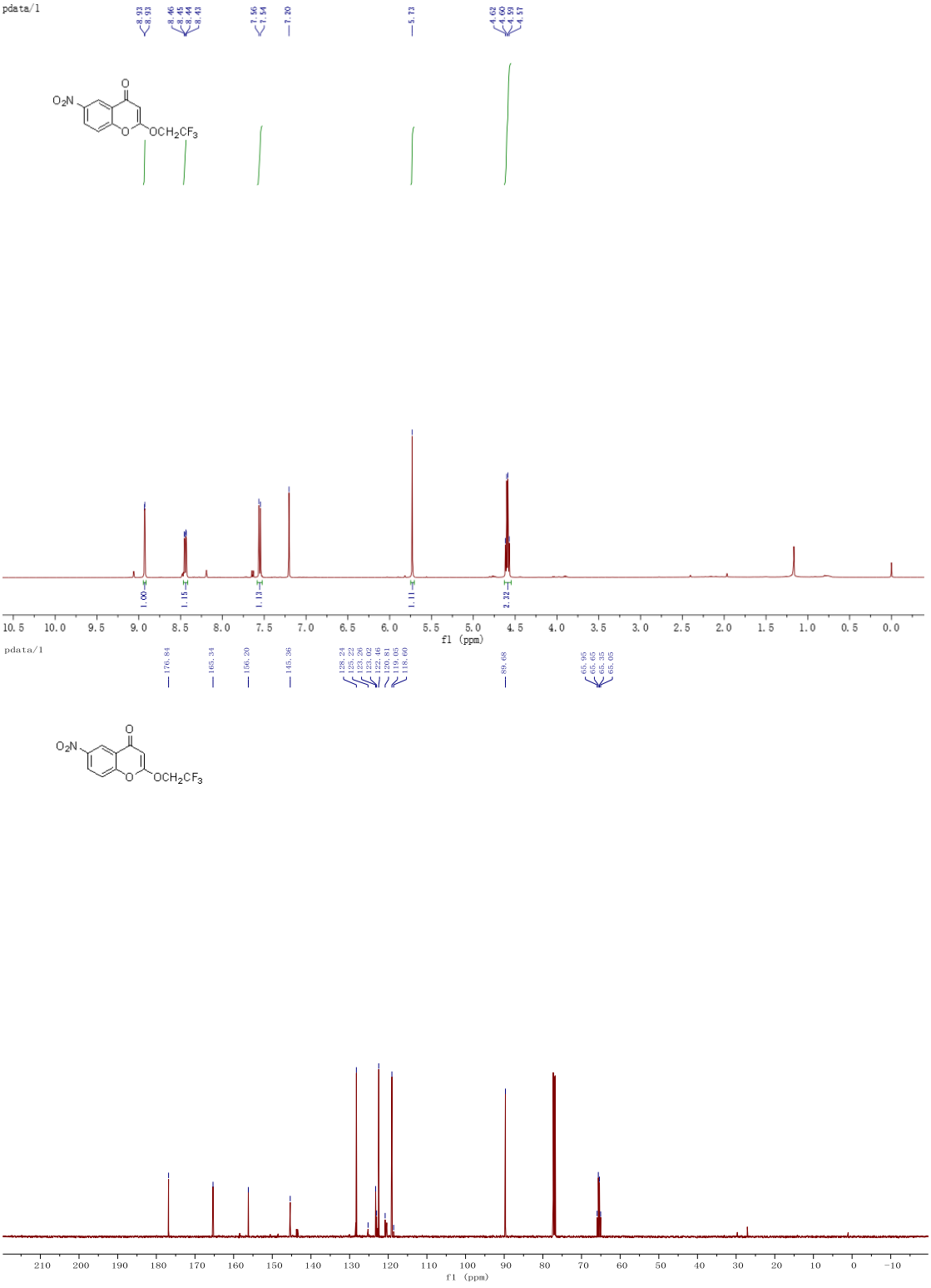
2-(2,2,2-Trifluoroethoxy)-6-(trifluoromethoxy)-4*H*-chromen-4-one (5h)



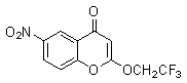


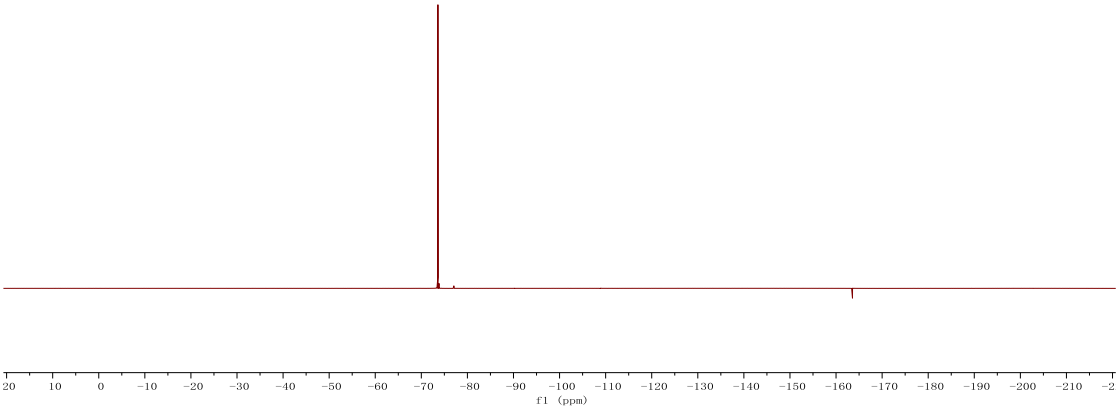

O
F
F
F
O
O
OCH2CF3
-58.22
-73.66
-73.67
-73.69
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

6-Nitro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5i)

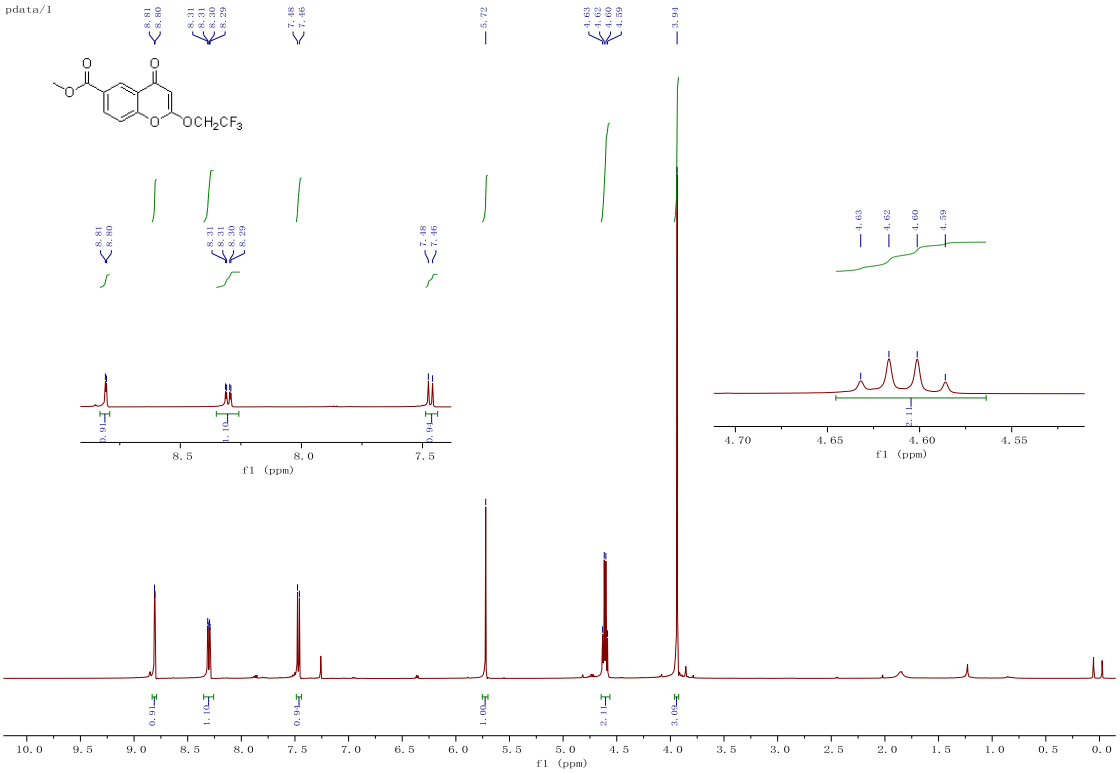


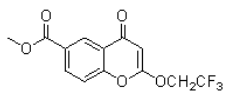
pdata/1

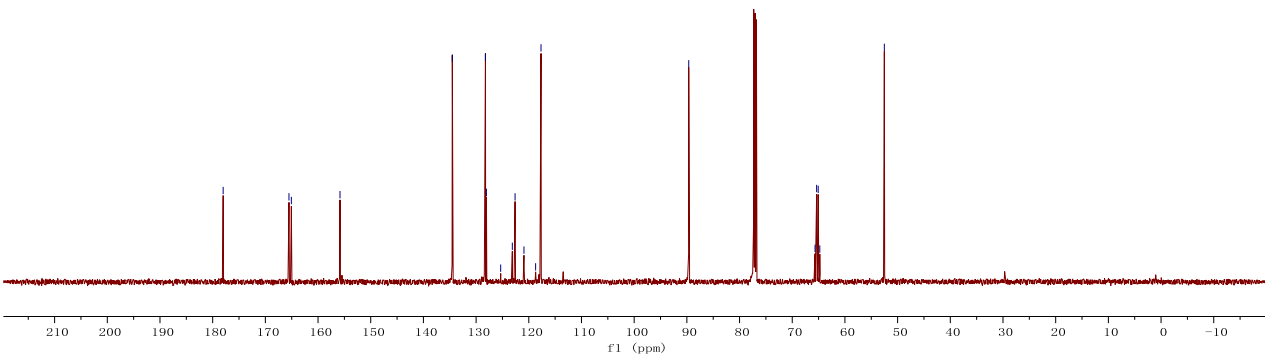

O
O2N
O
OCH2CF3


20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −2
f1 (ppm)

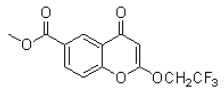
Methyl 4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromene-6-carboxylate (5j)





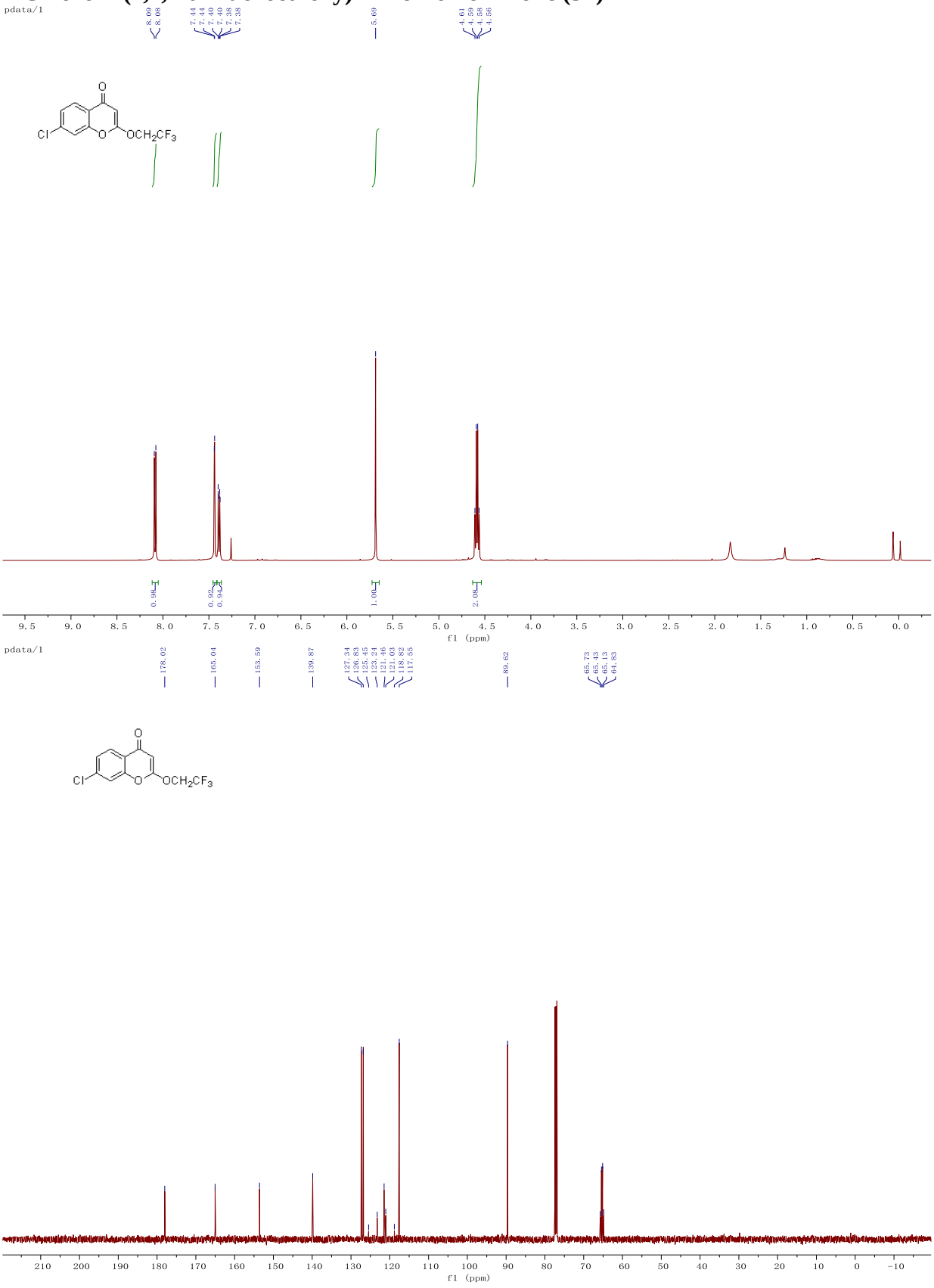


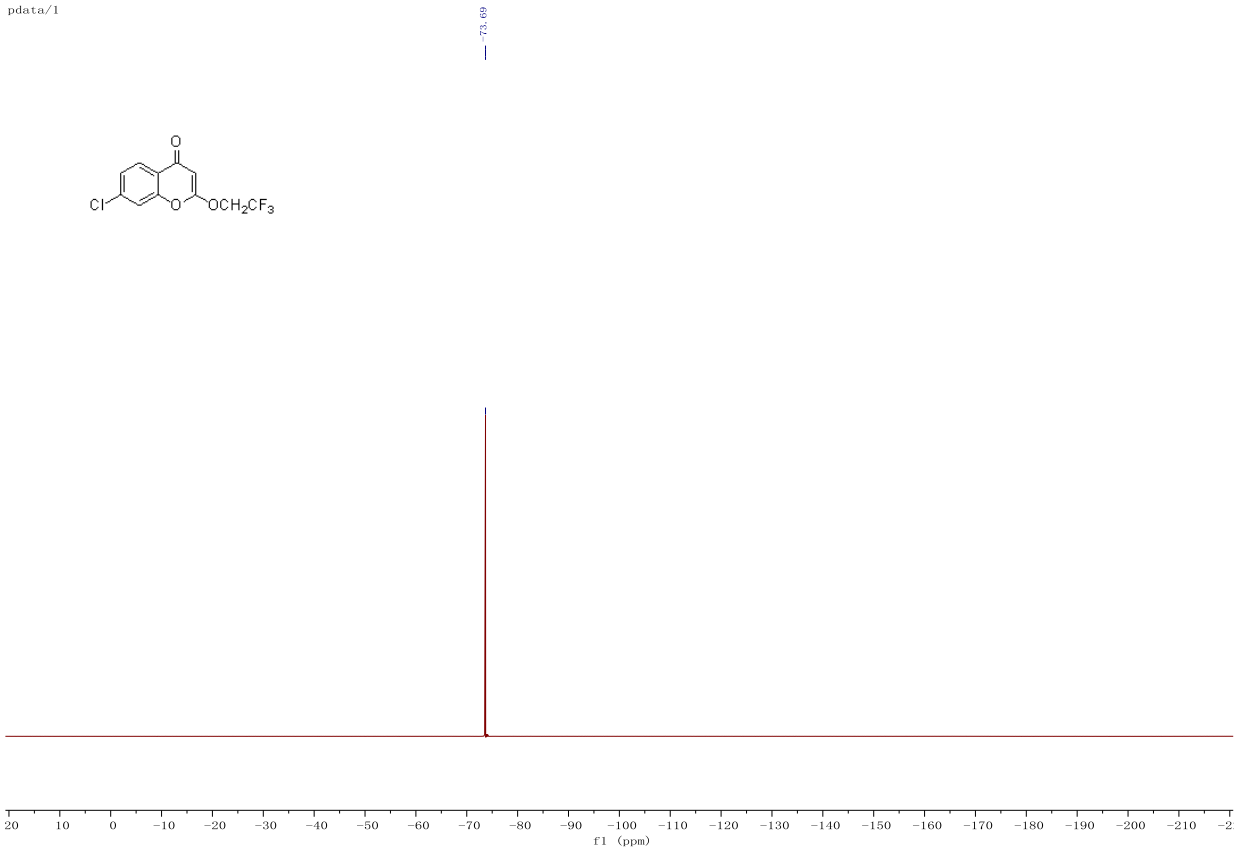
pdata/1


O
O
O
O
OCH2CF3

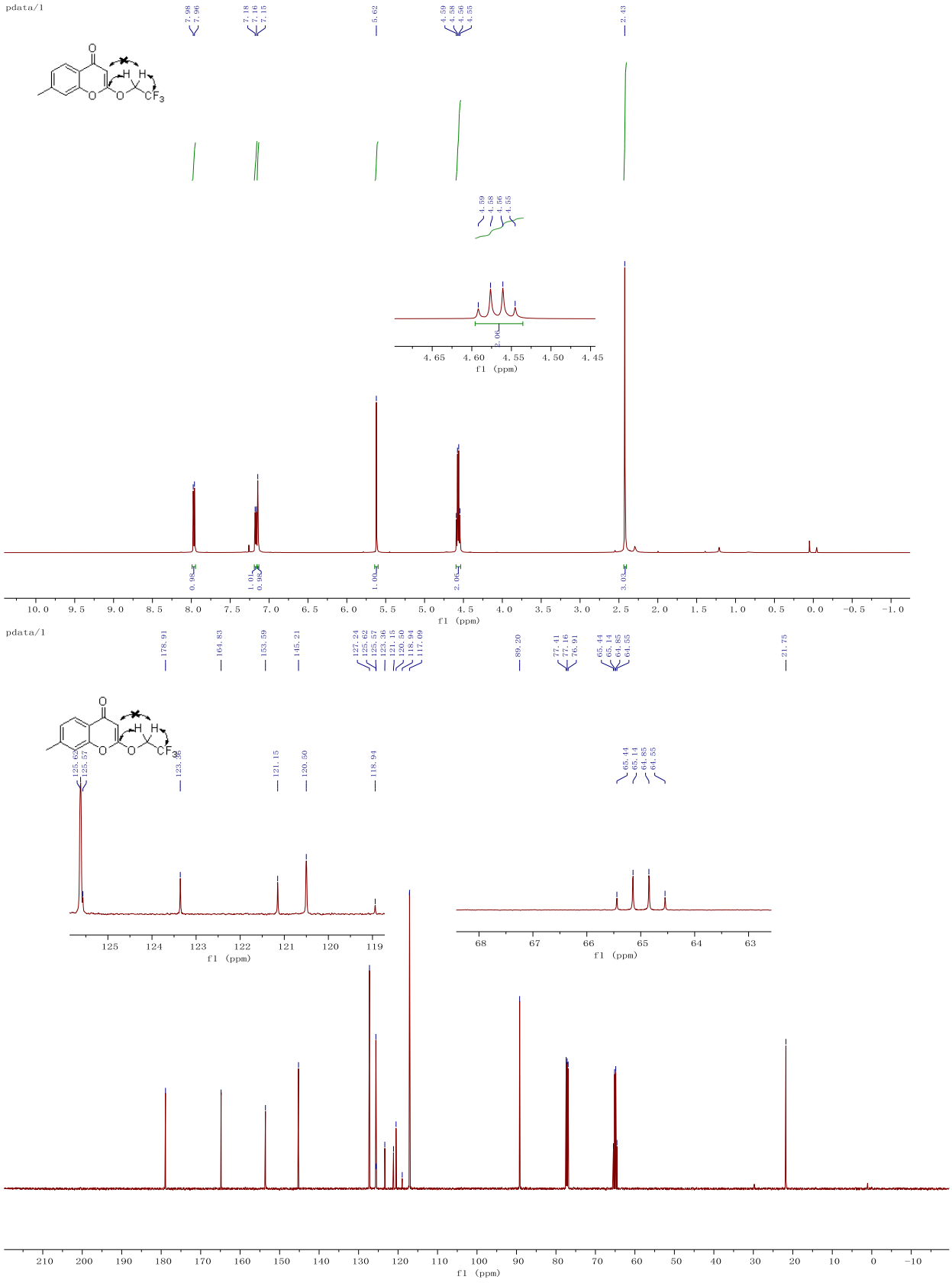
-73.67
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-2
f1 (ppm)

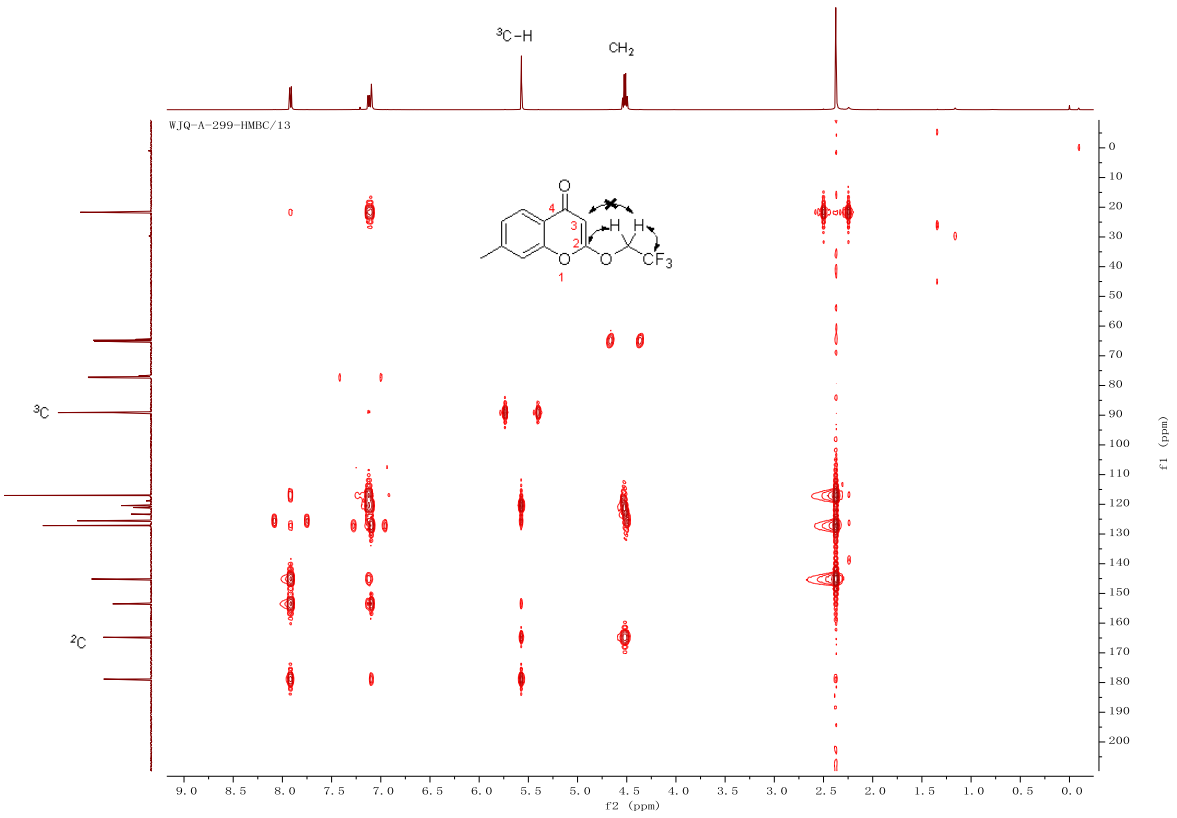
7-Chloro-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5k)



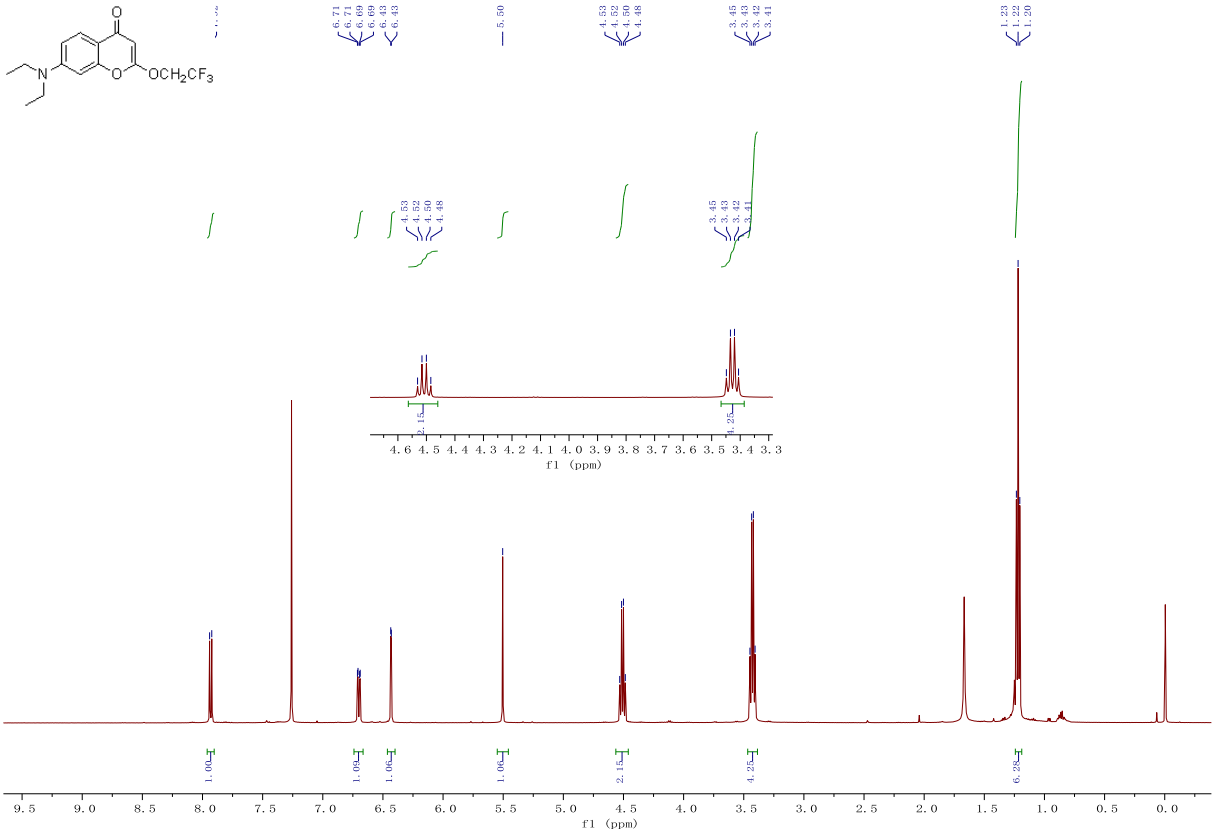

pdata/1
-73.69
O
Cl
O
OCH2CF3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

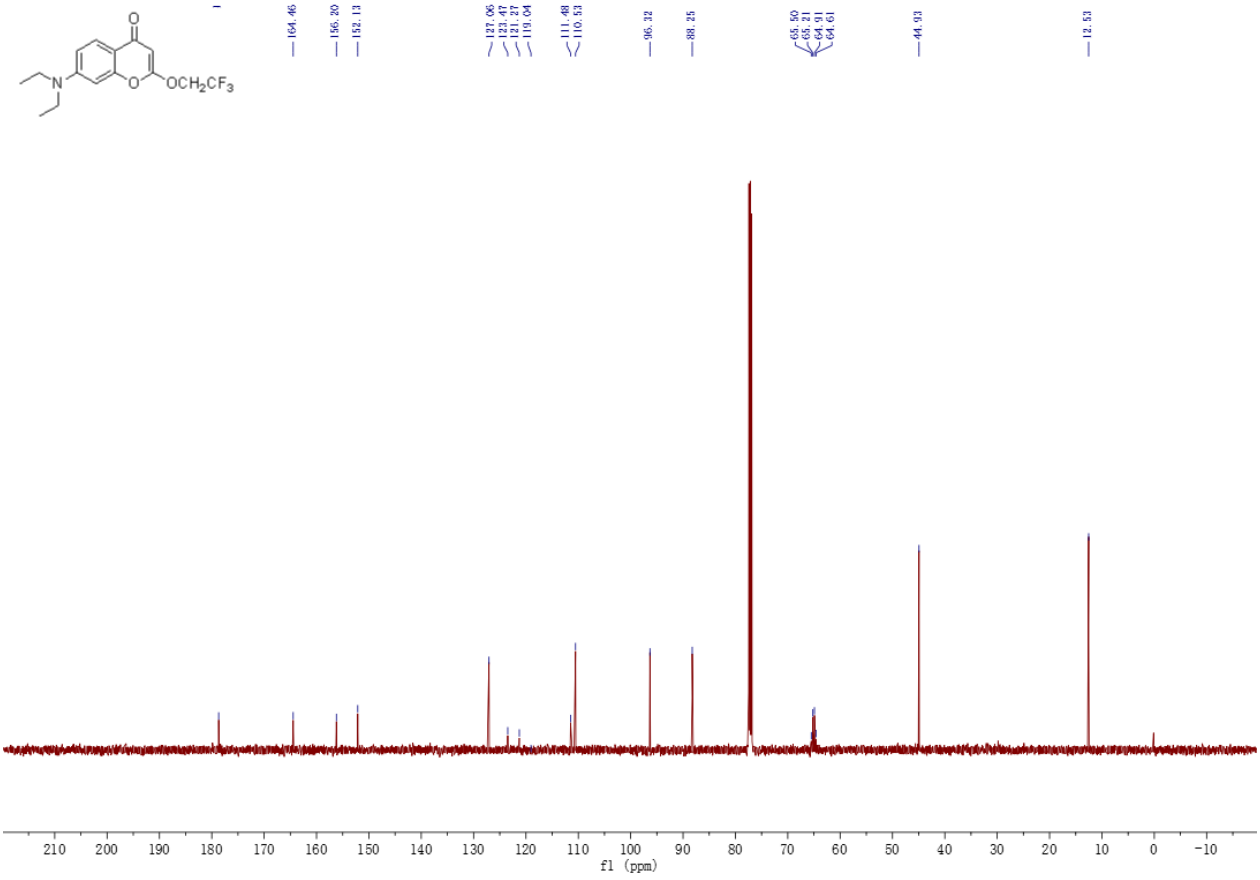
7-Methyl-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5l)

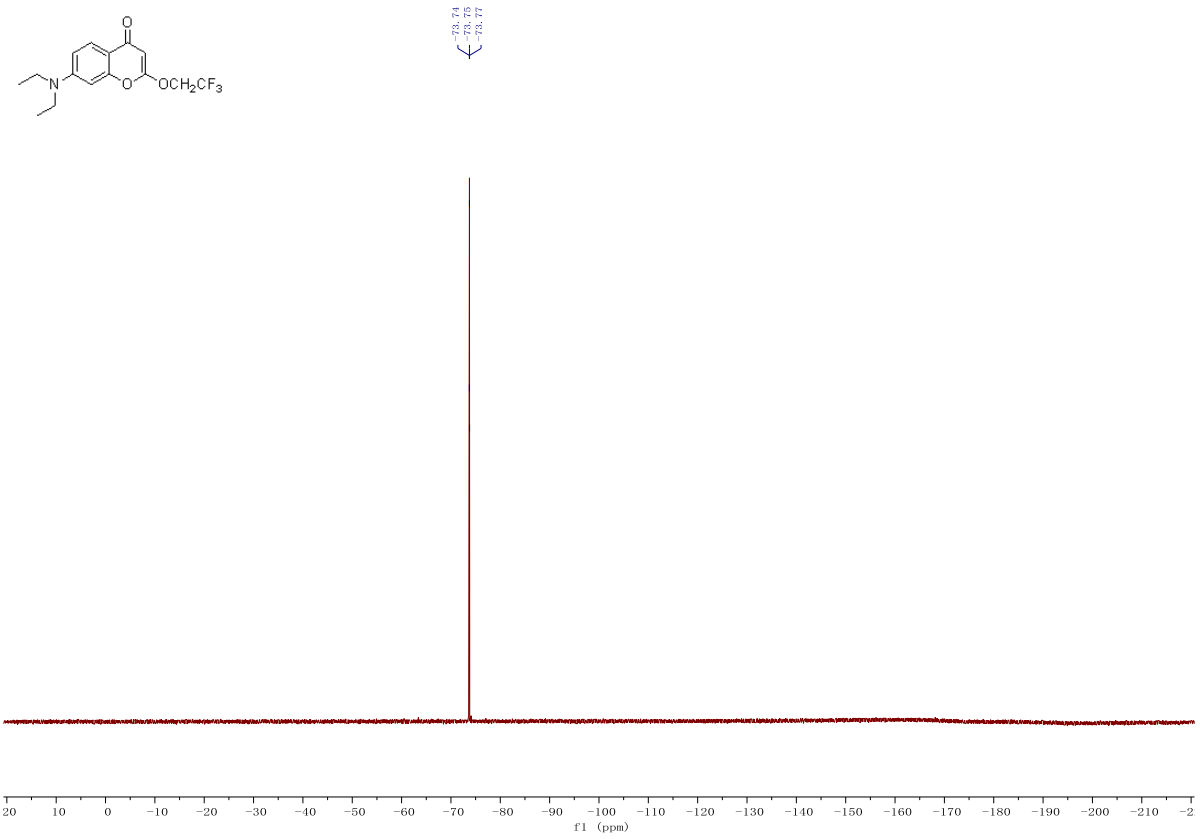



^{3}C-H
CH$_2$
WJQ-A-299-HMBC/13
^{3}C
^{2}C
f2 (ppm)
f1 (ppm)

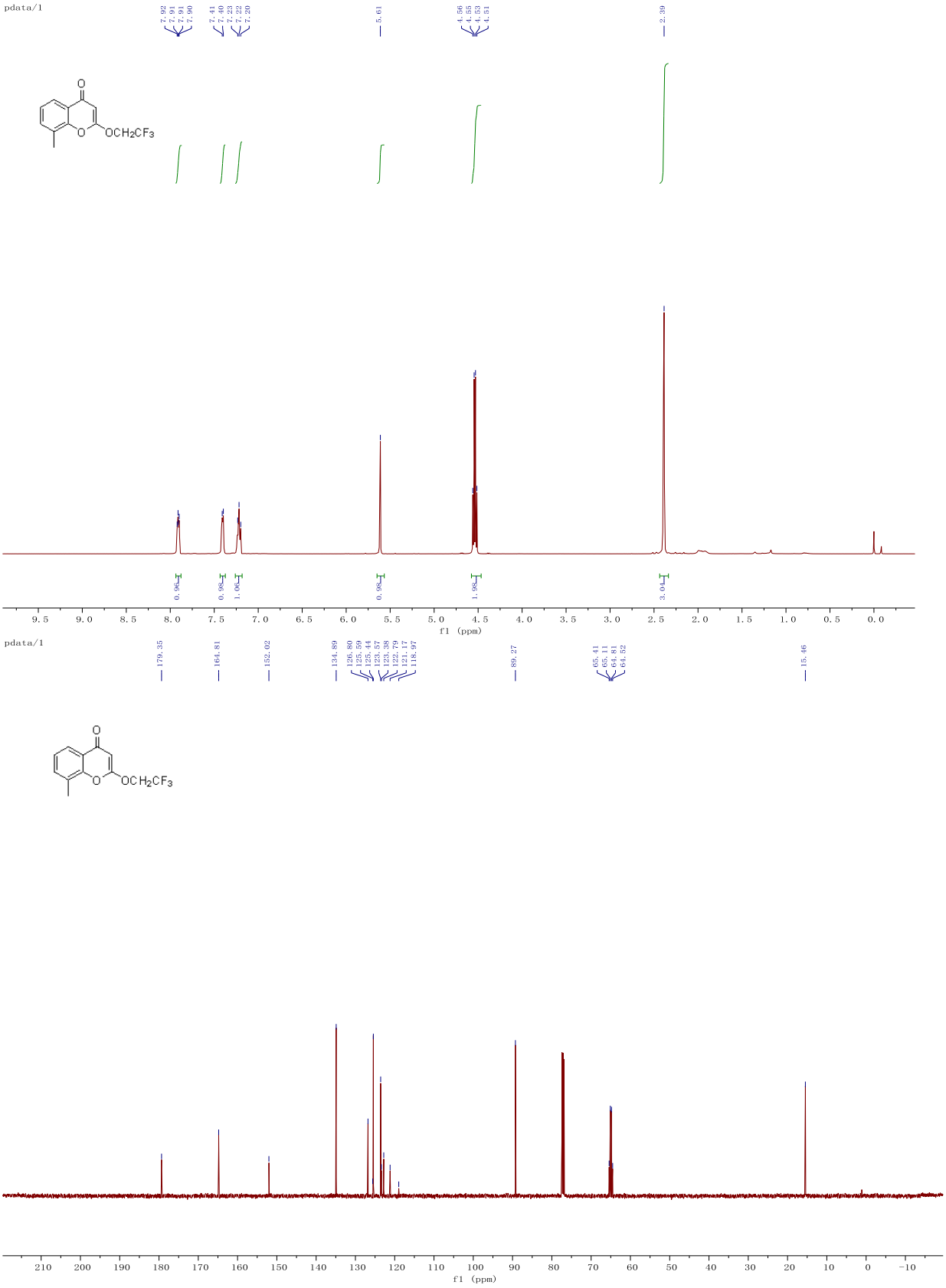
7-(Diethylamino)-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5m)

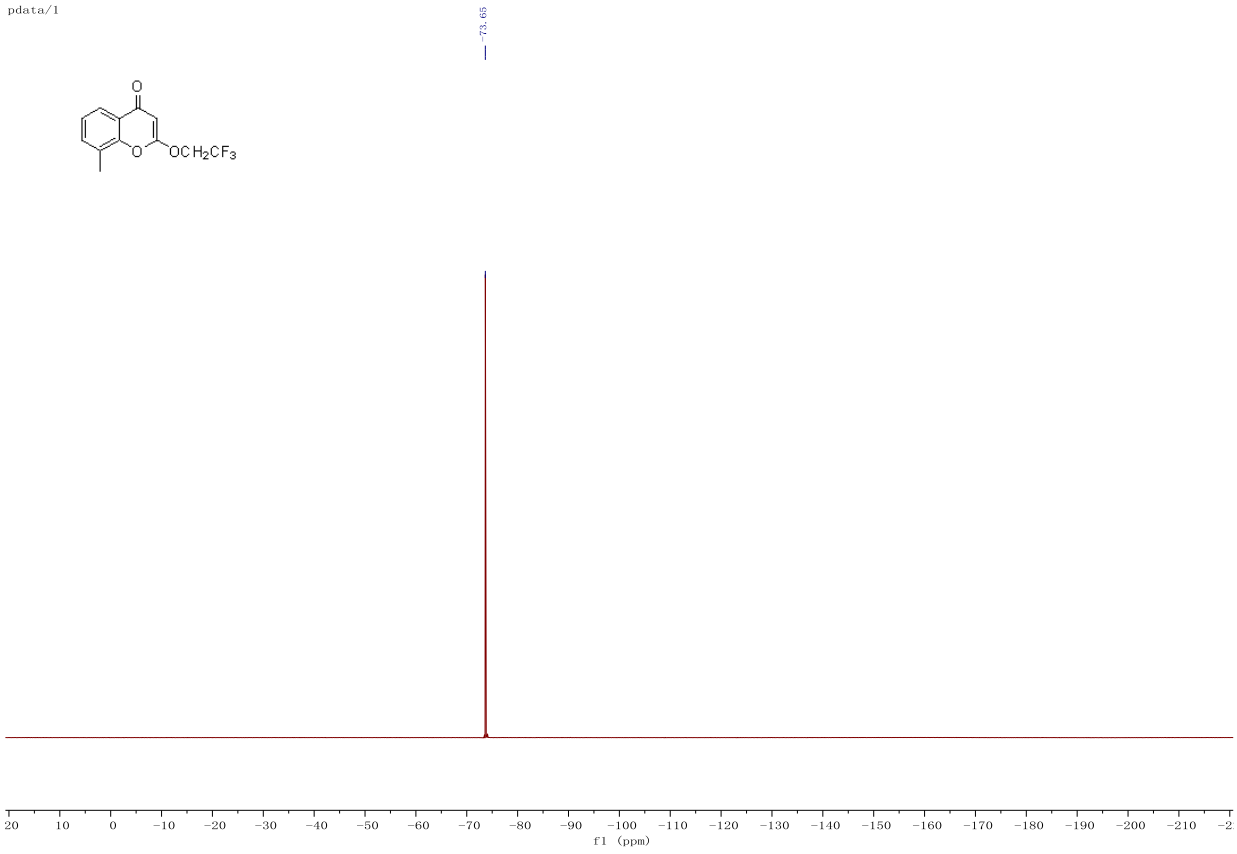




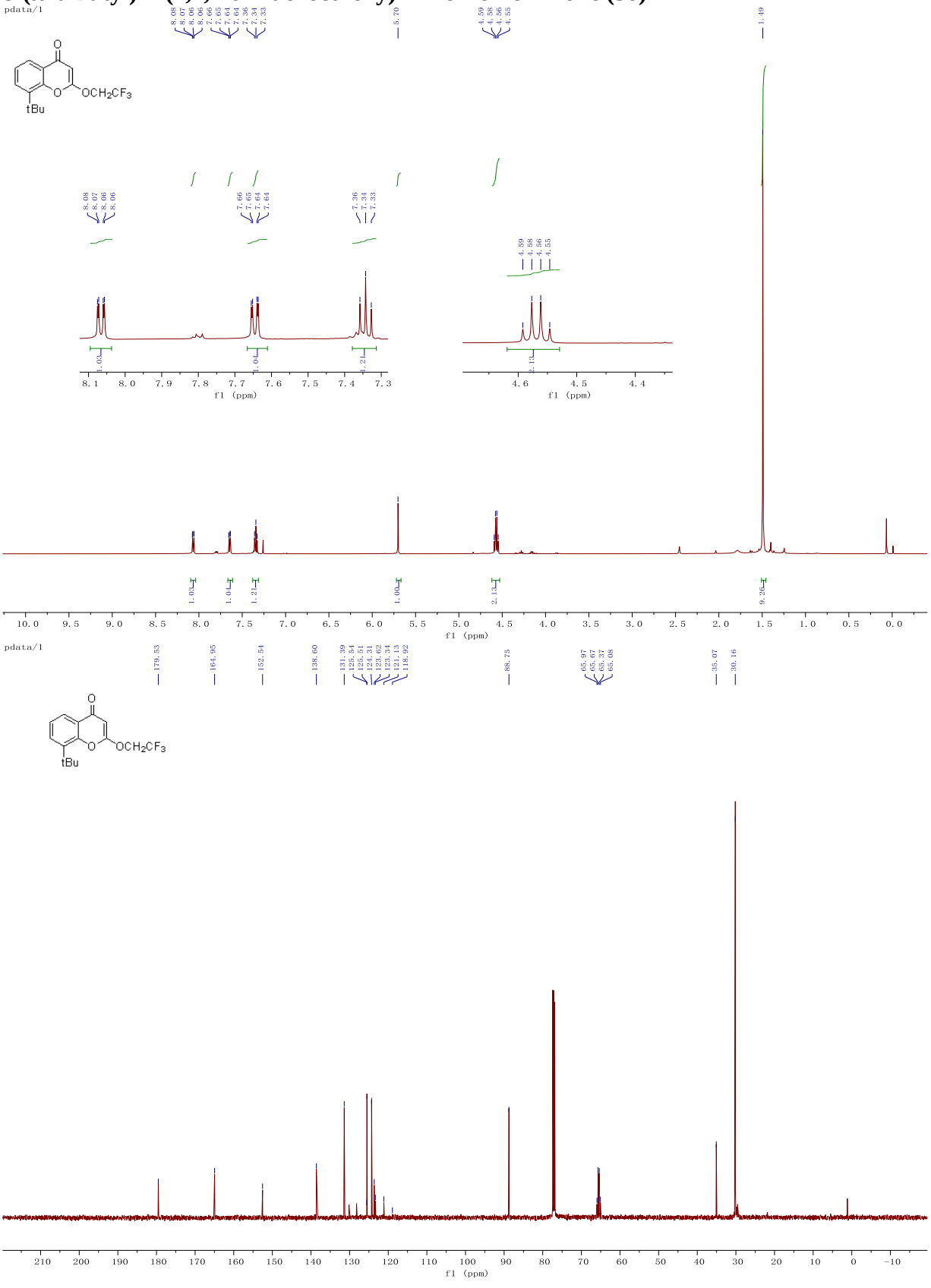

-73.74
-73.75
-73.77
O
N
O
OCH2CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

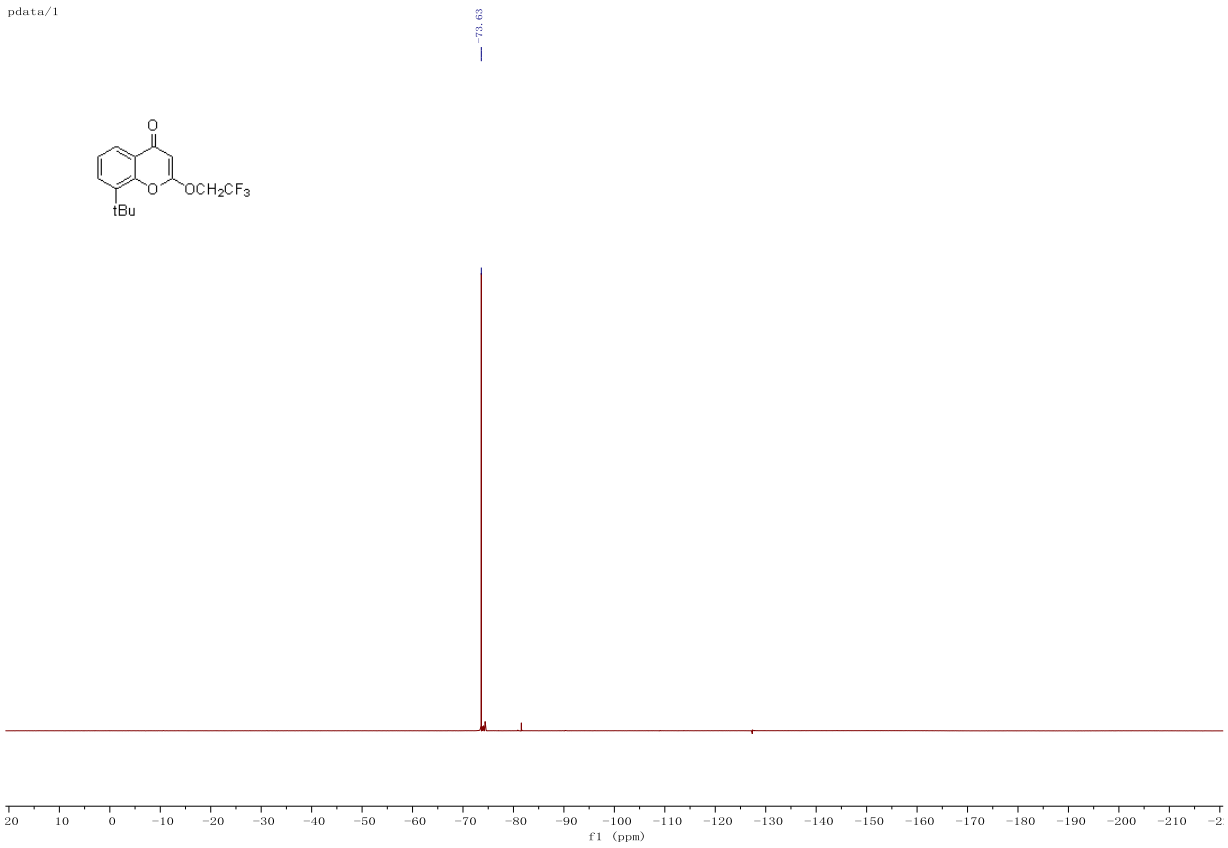
8-Methyl-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5n)



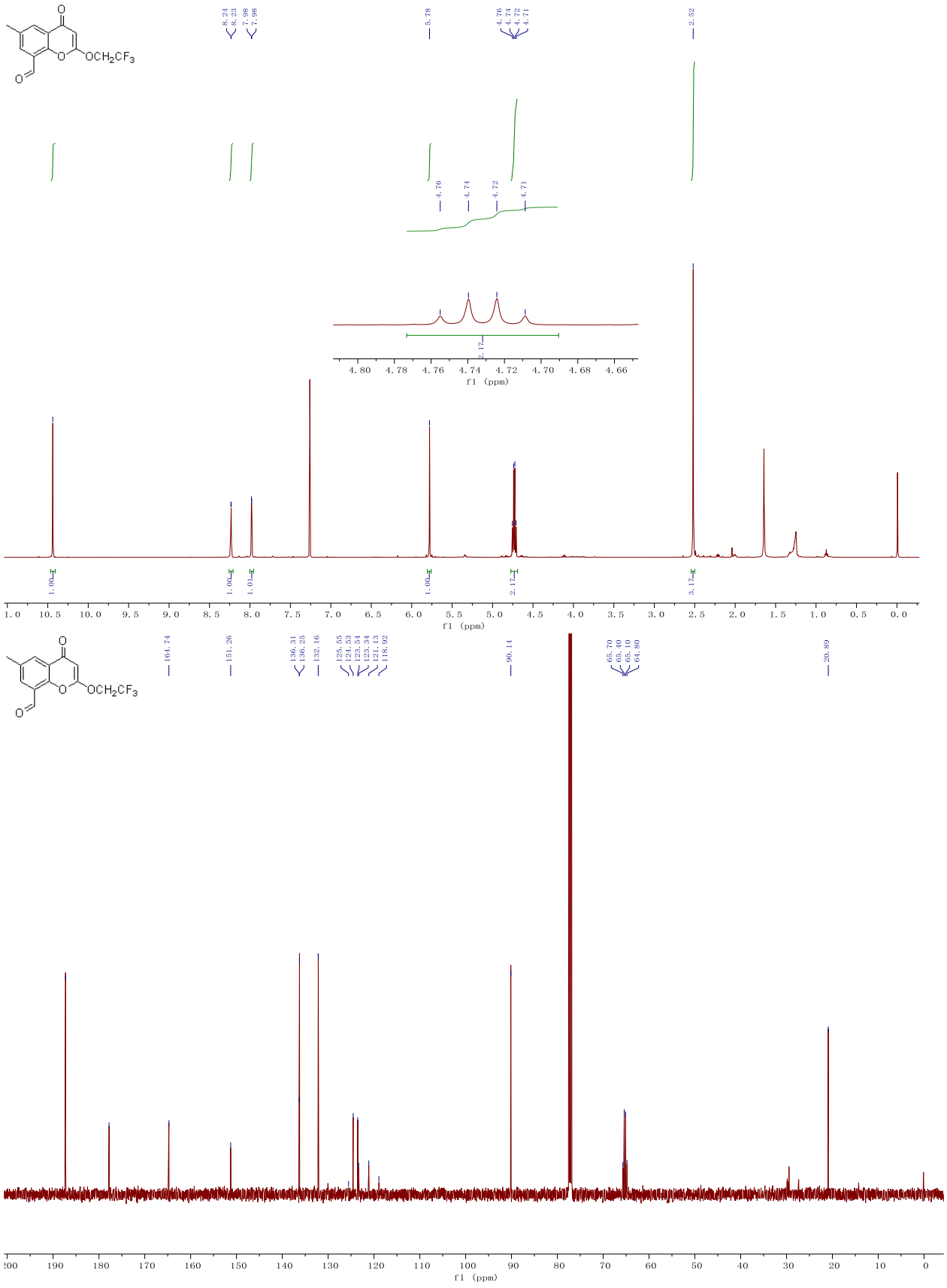

pdata/1
-73.65
O
O
OCH2CF3
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

8-(*tert*-Butyl)-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-4-one (5o)



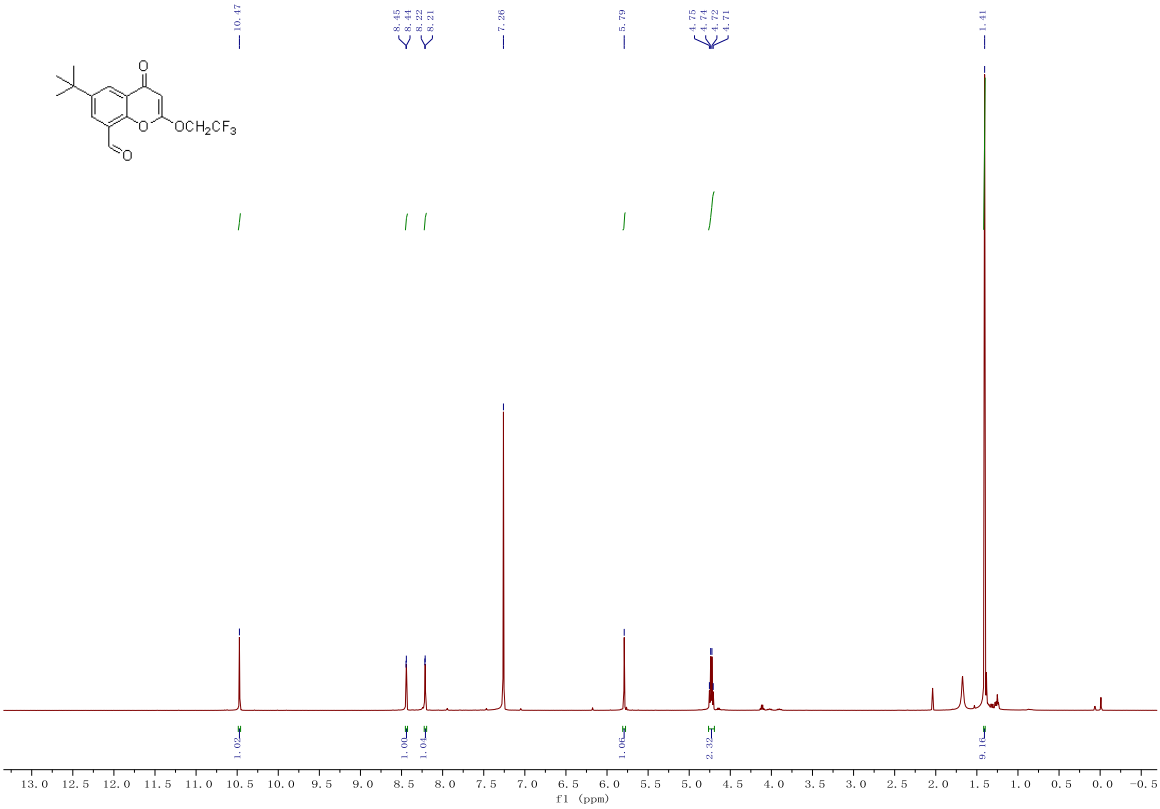

pdata/1
-73.63
O
O
OCH2CF3
tBu
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

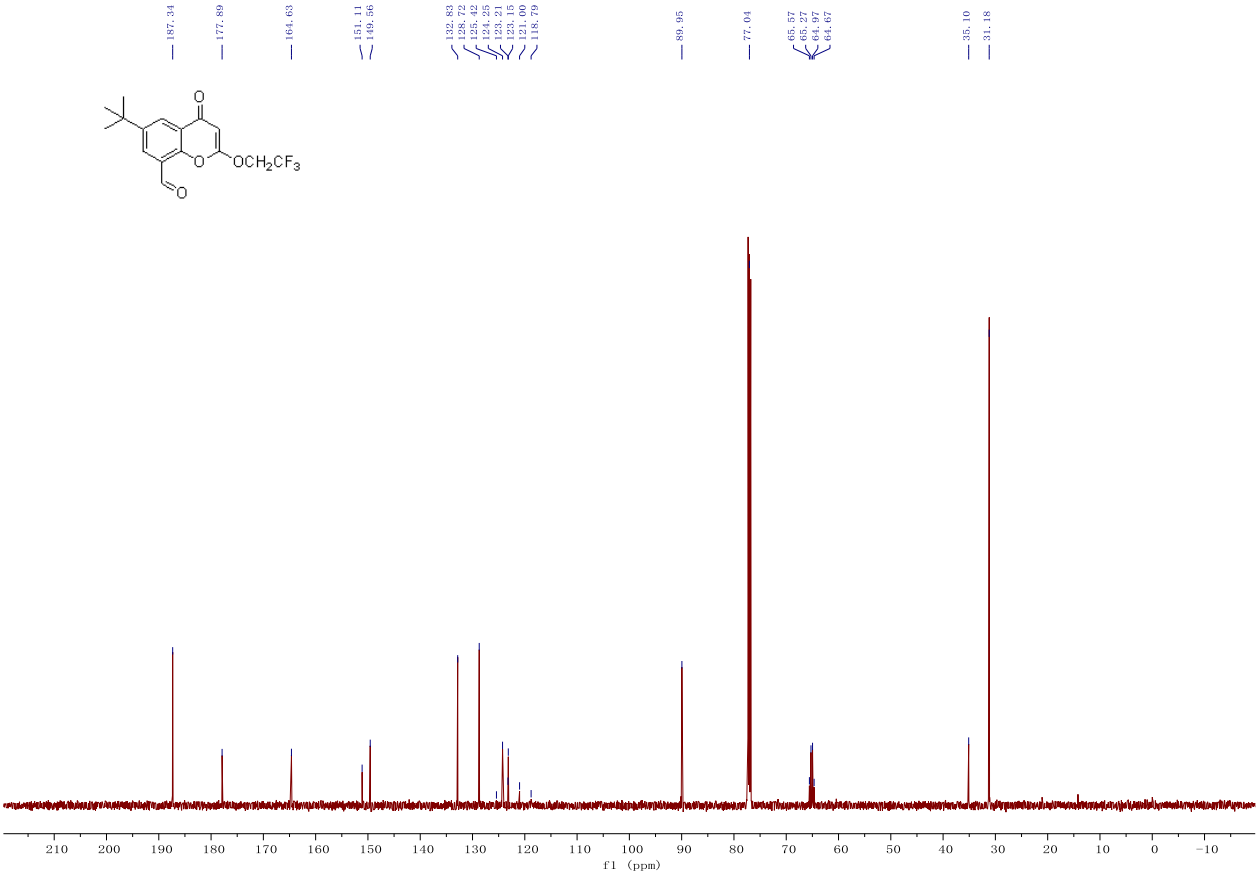
6-Methyl-4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromene-8-carbaldehyde (5p)

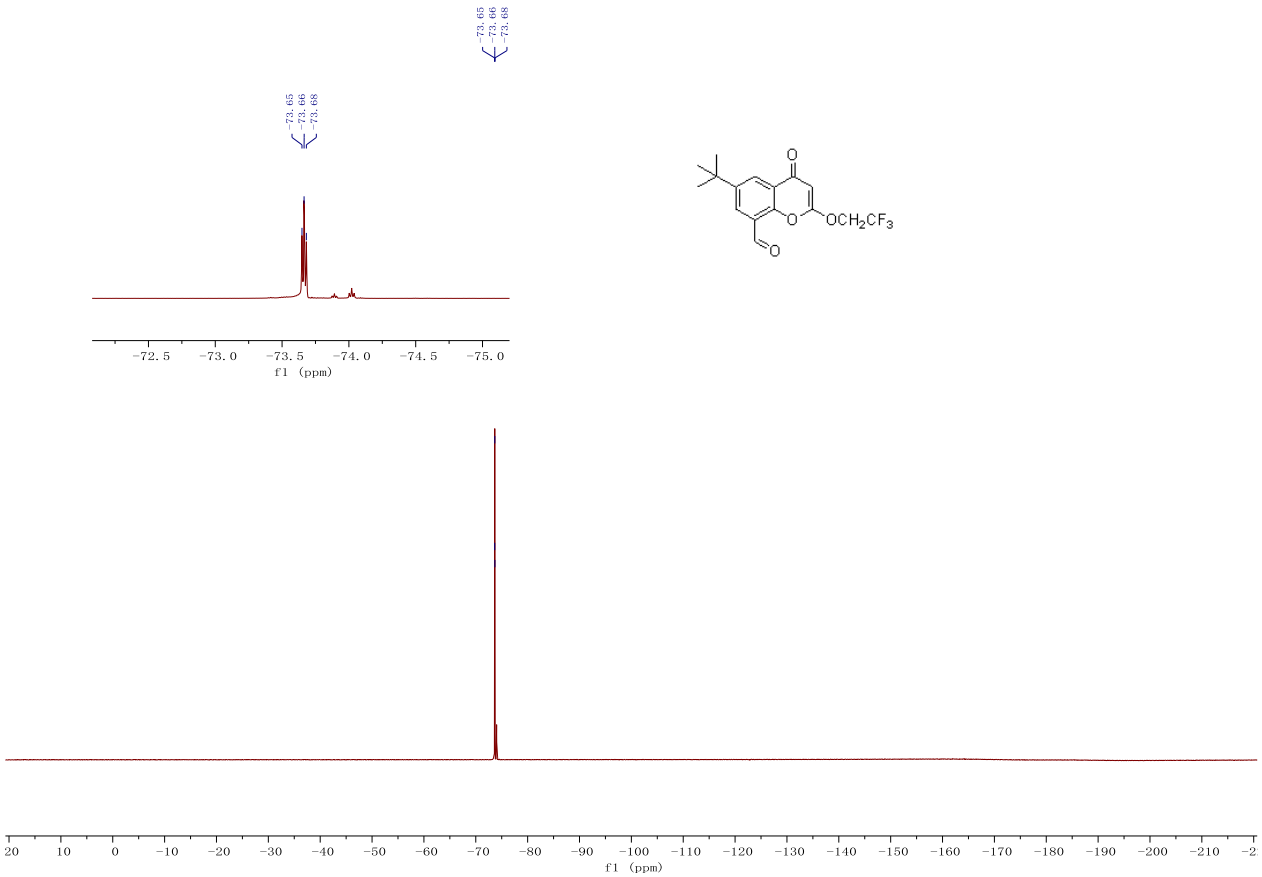



-73.65
-73.66
-73.68
O
O
OCH2CF3
O
-72.5
-73.0
-73.5
-74.0
-74.5
-75.0
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

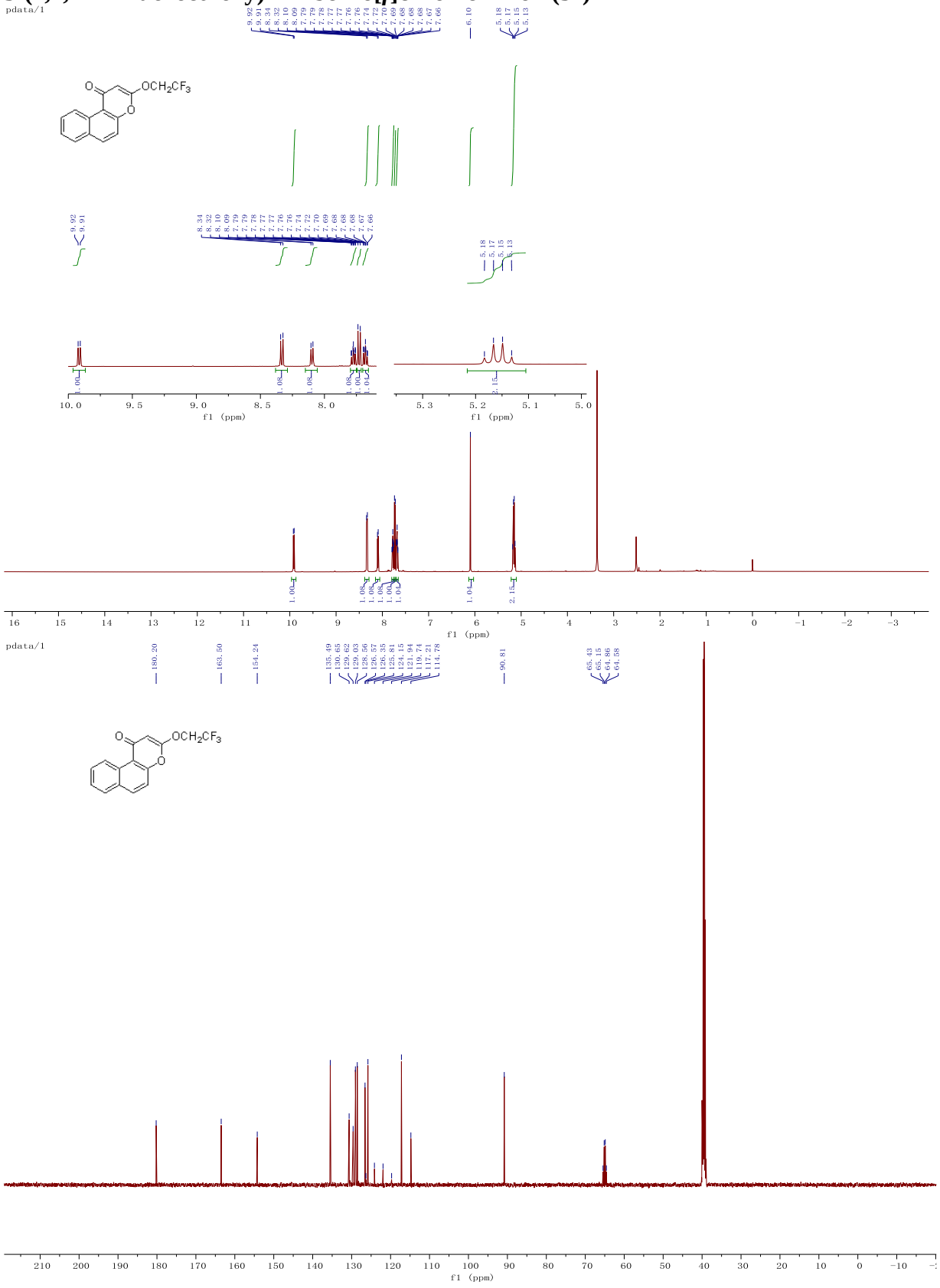
6-(*tert*-Butyl)-4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromene-8-carbaldehyde (5q)

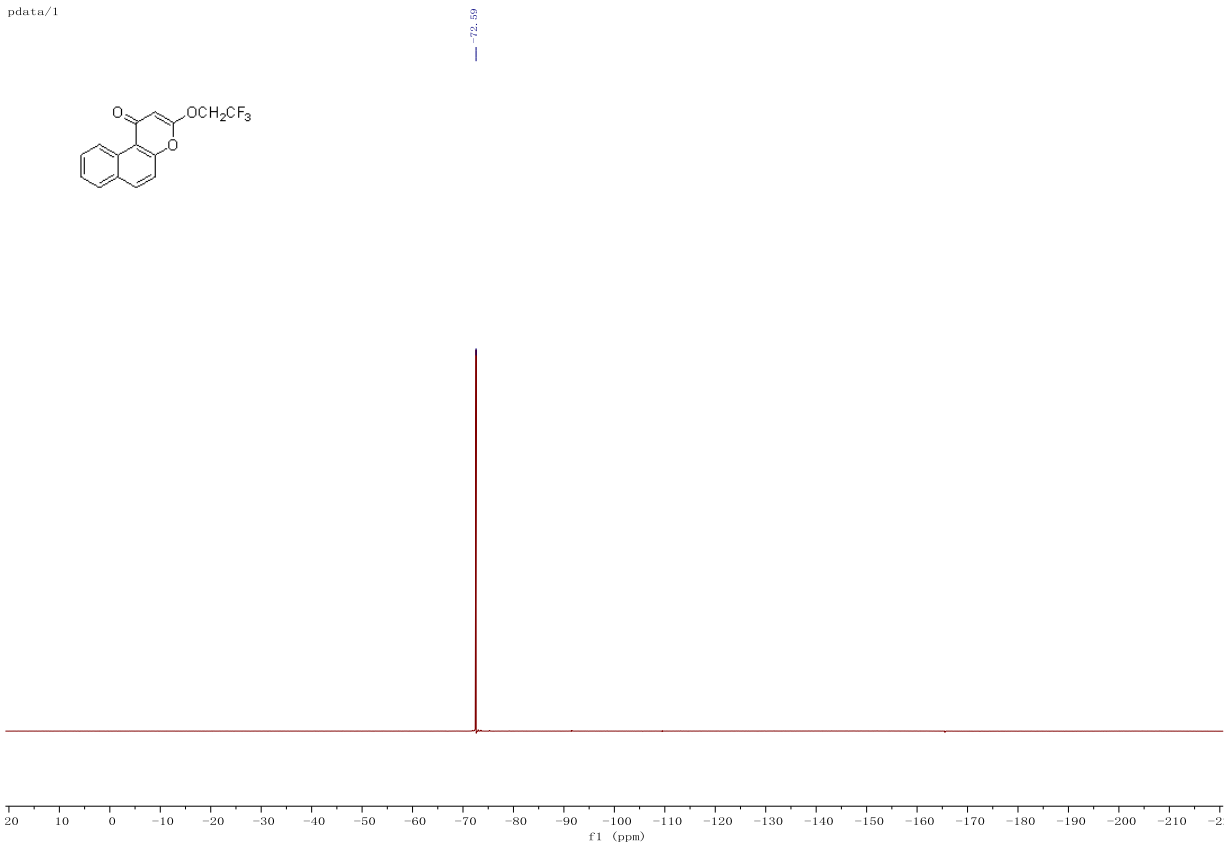




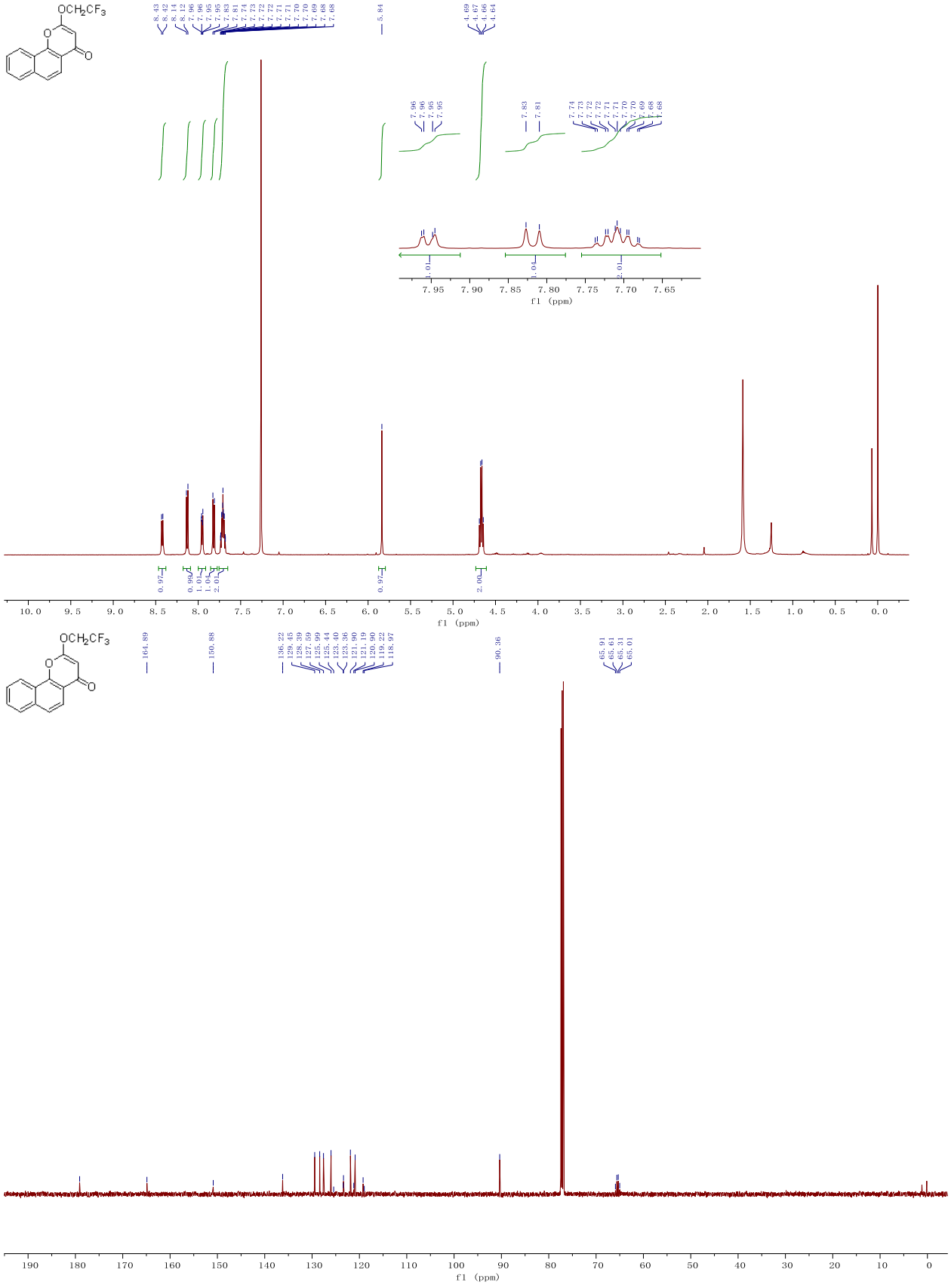

-73.65
-73.66
-73.68
-73.65
-73.66
-73.68
O
O
OCH2CF3
O
-72.5
-73.0
-73.5
-74.0
-74.5
-75.0
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

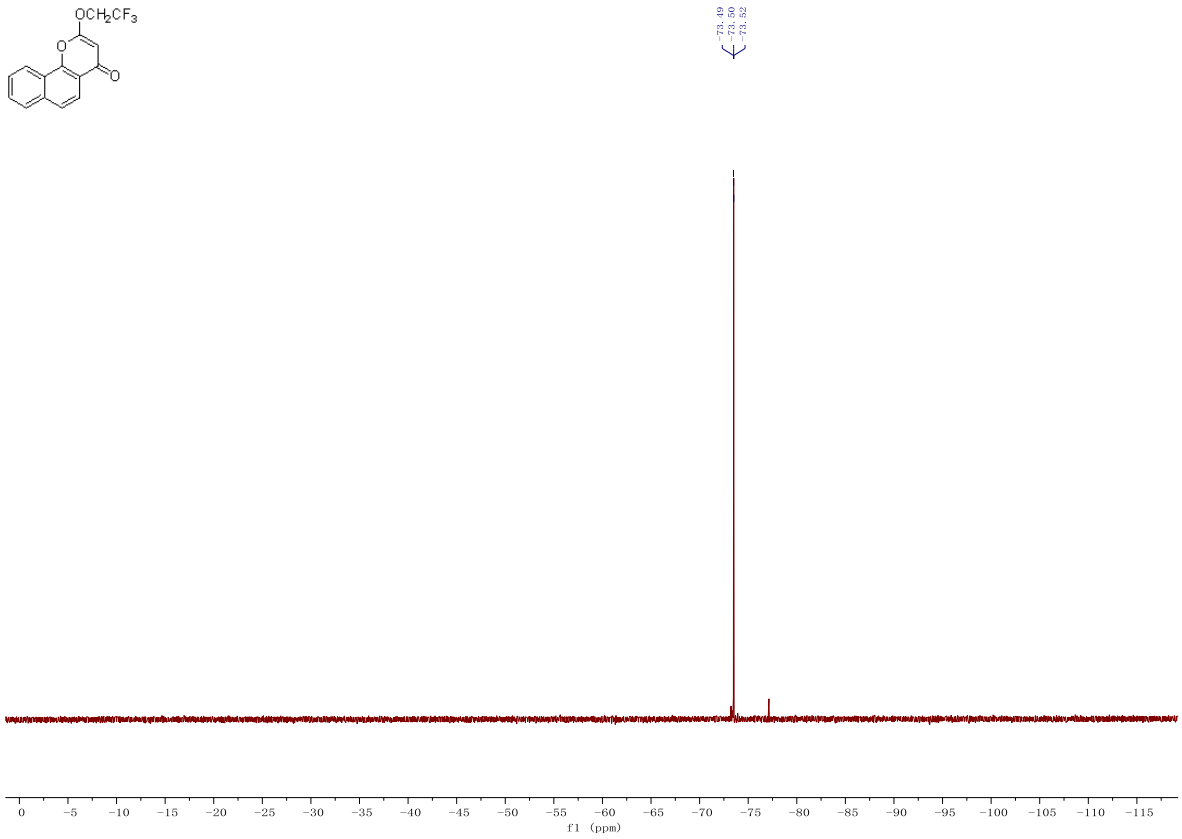
3-(2,2,2-Trifluoroethoxy)-1*H*-benzo[*f*]chromen-1-on (5r)



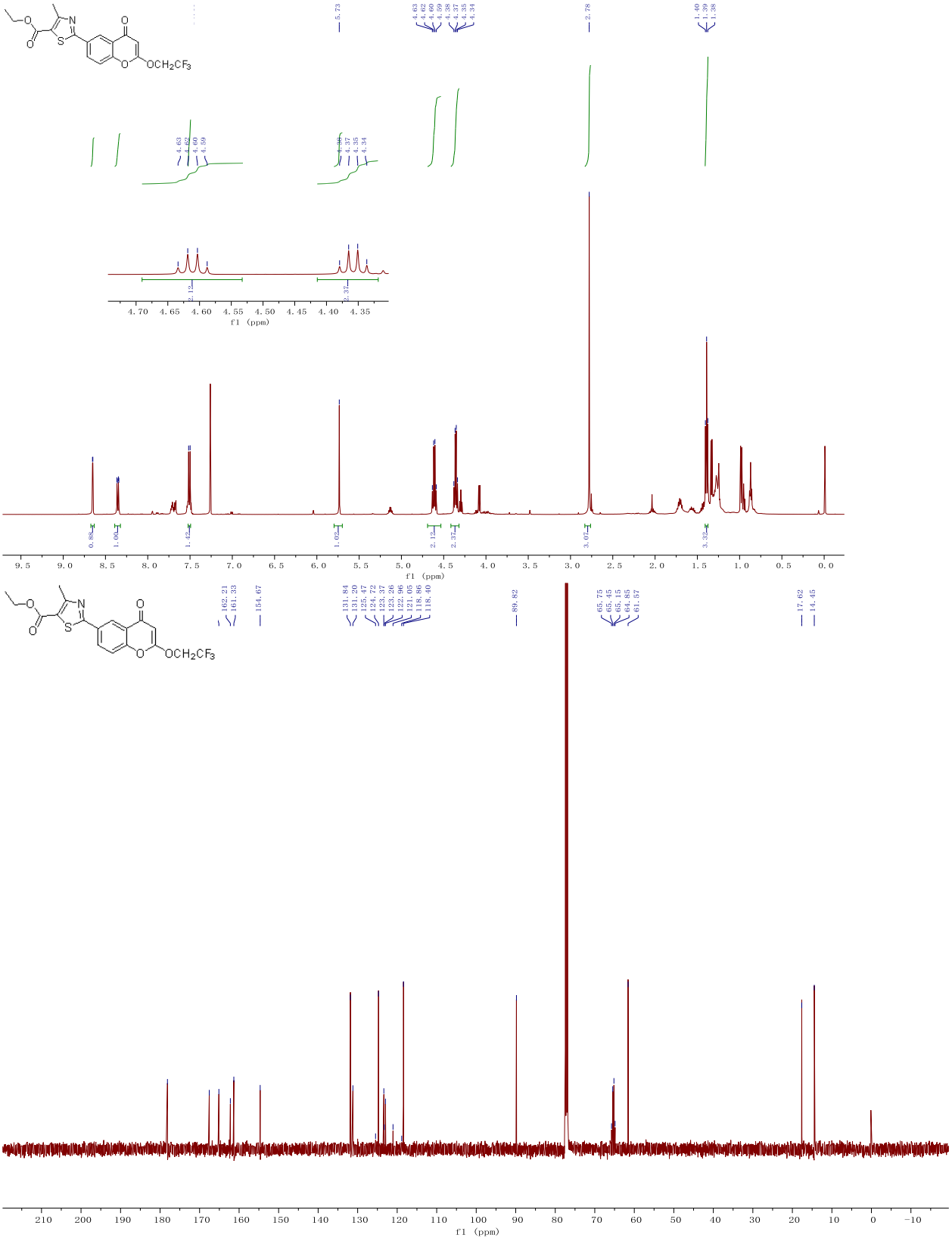

pdata/1
-72.59
OCH2CF3
O
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

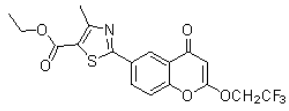
2-(2,2,2-Trifluoroethoxy)-4*H*-benzo[*h*]chromen-4-one (5s)




OCH2CF3
O
O
-73.49
-73.50
-73.52
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
f1 (ppm)

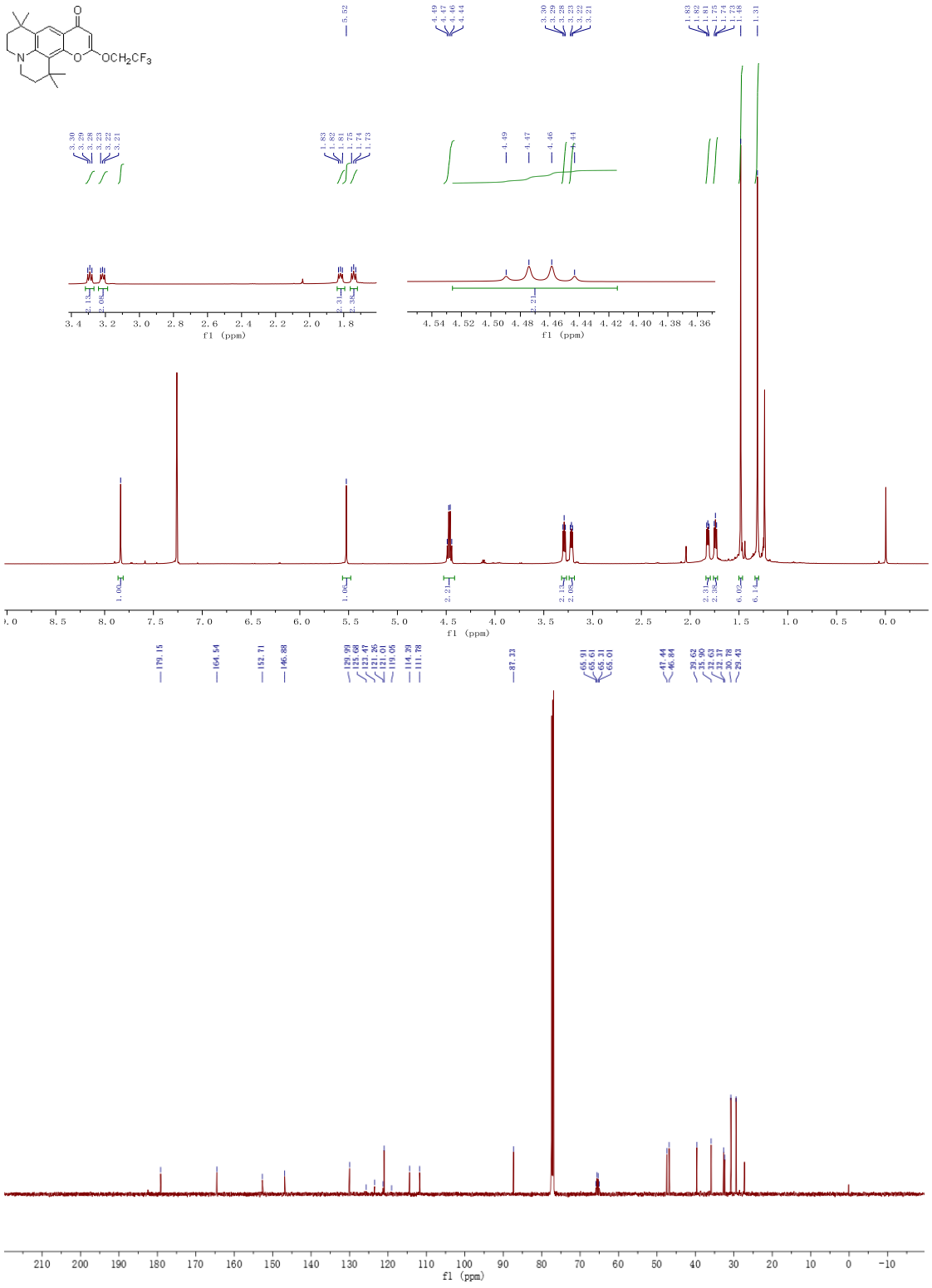
4-Methyl-2-(4-oxo-2-(2,2,2-trifluoroethoxy)-4*H*-chromen-6-yl)thiazole-5-carboxylate (5t)

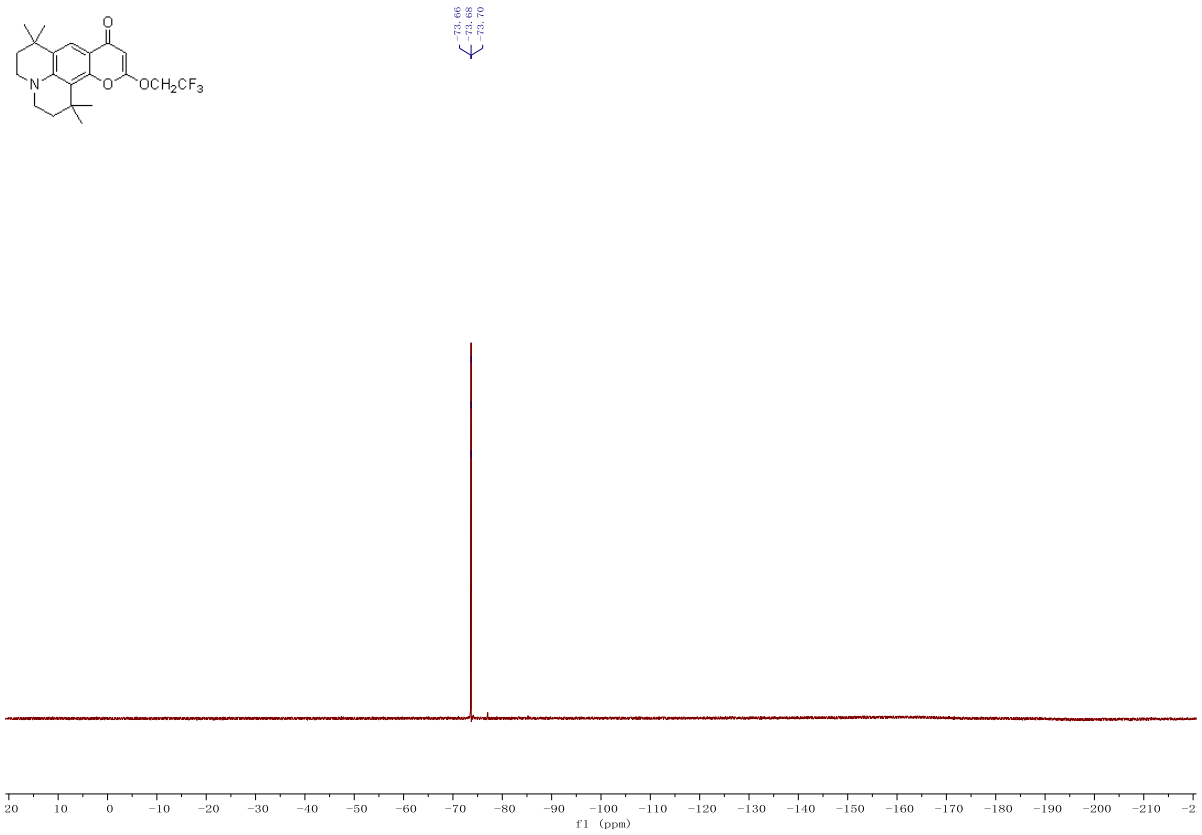



O
N
S
O
O
O
OCH2CF3

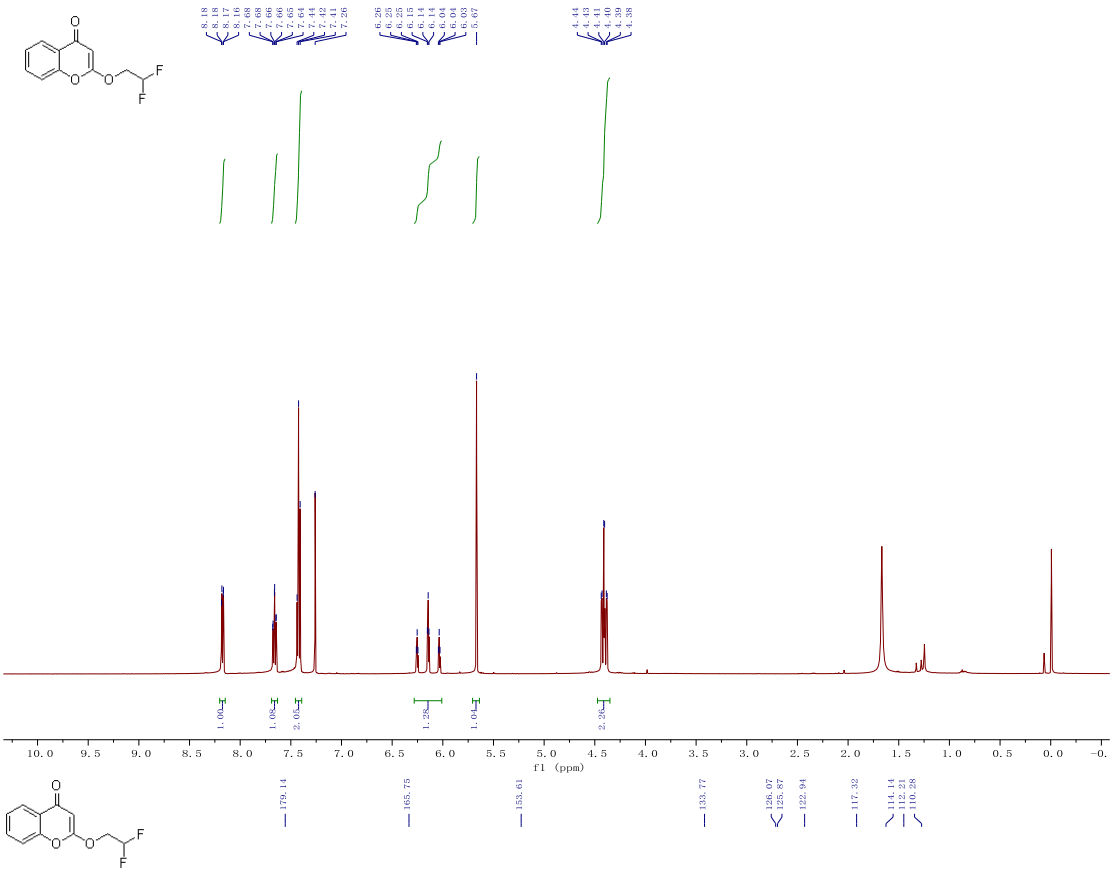
-73.64
-73.65
-73.67
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)

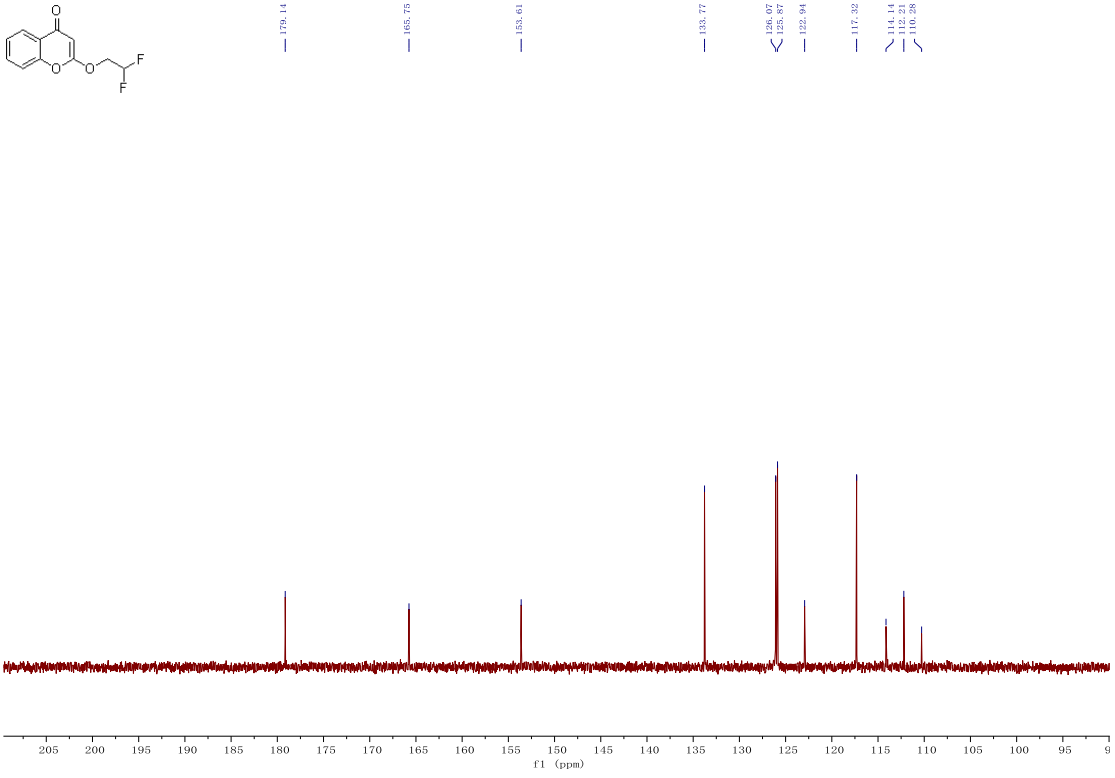
1,1,7,7-Tetramethyl-11-(2,2,2-trifluoroethoxy)-2,3,6,7-tetrahydro-1*H*,5*H*,9*H*-pyrano[2,3-*f*]pyrido[3,2,1-*ij*]quinolin-9-one (5u)

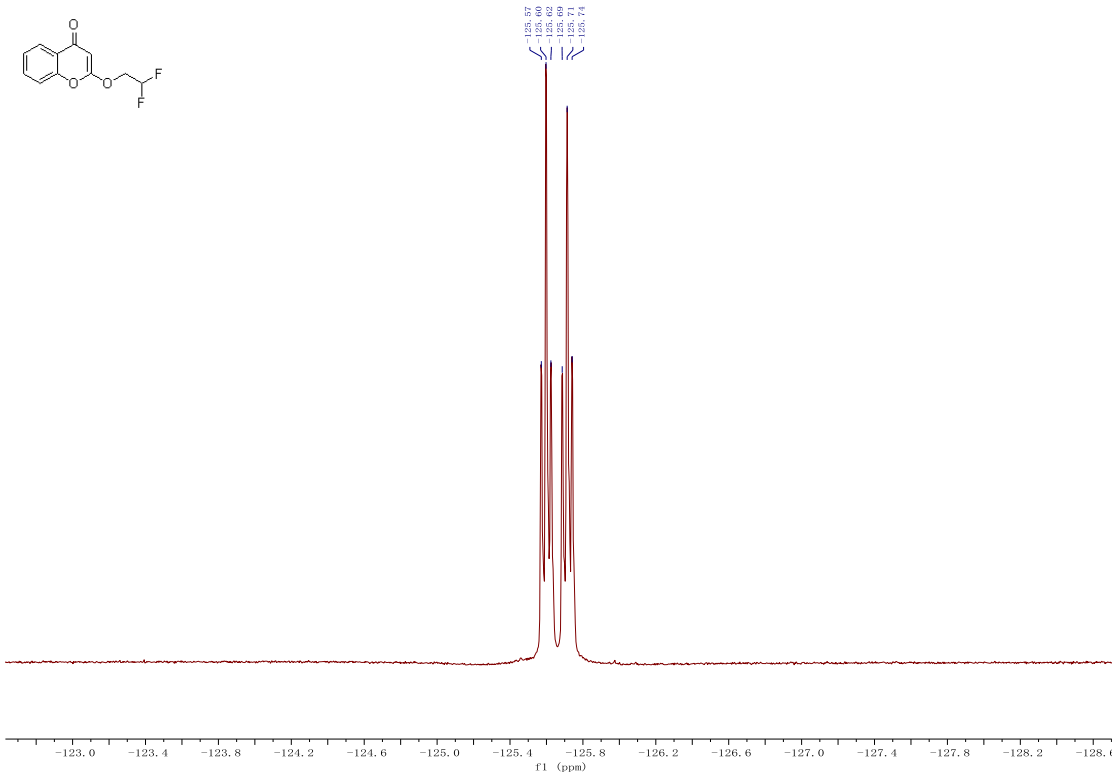



O
N
O
OCH2CF3
-73.66
-73.68
-73.70
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

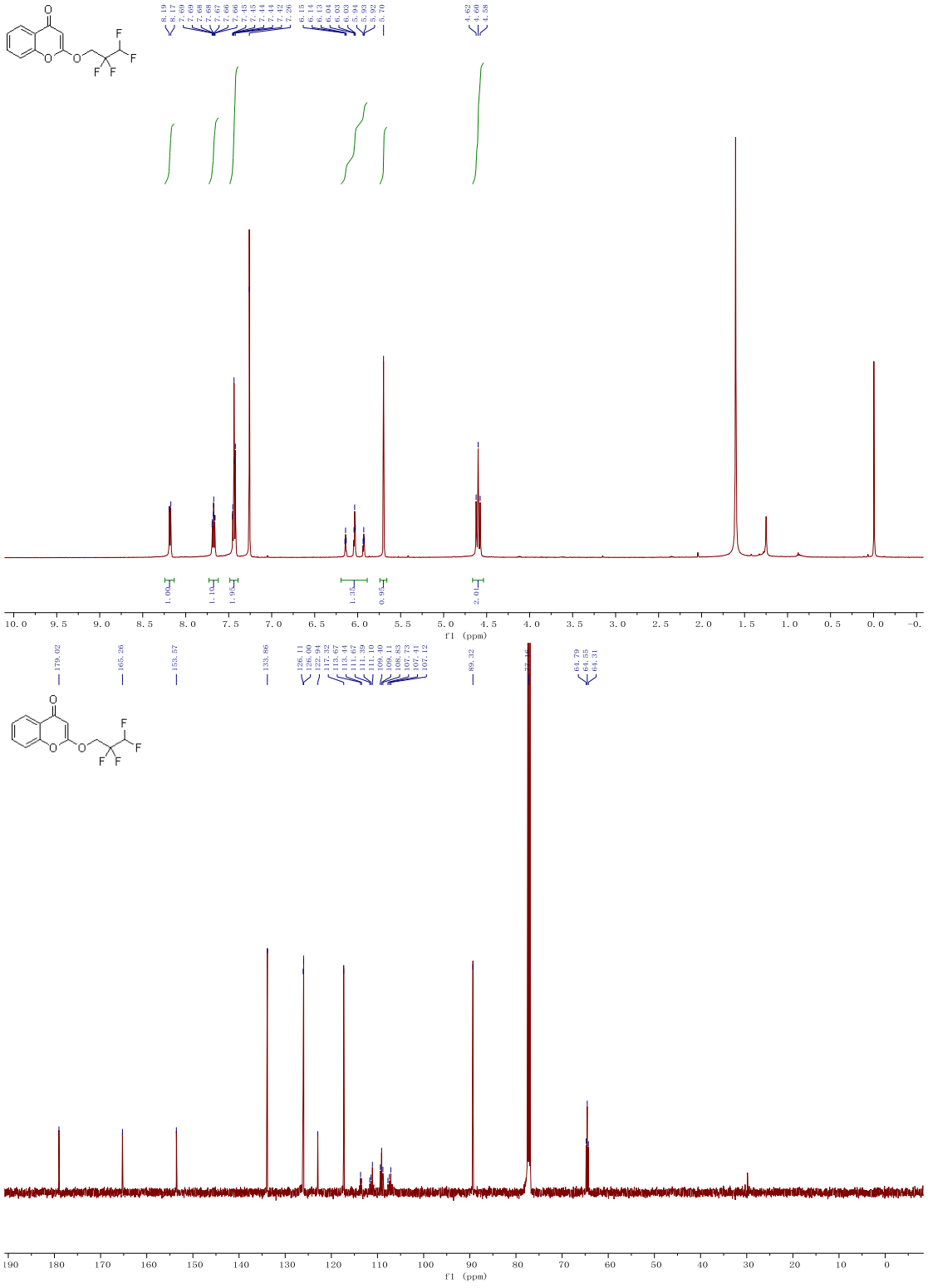
2-(2,2-difluoroethoxy)-4H-chromen-4-one (5v)

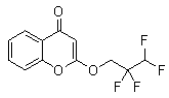


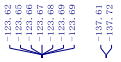


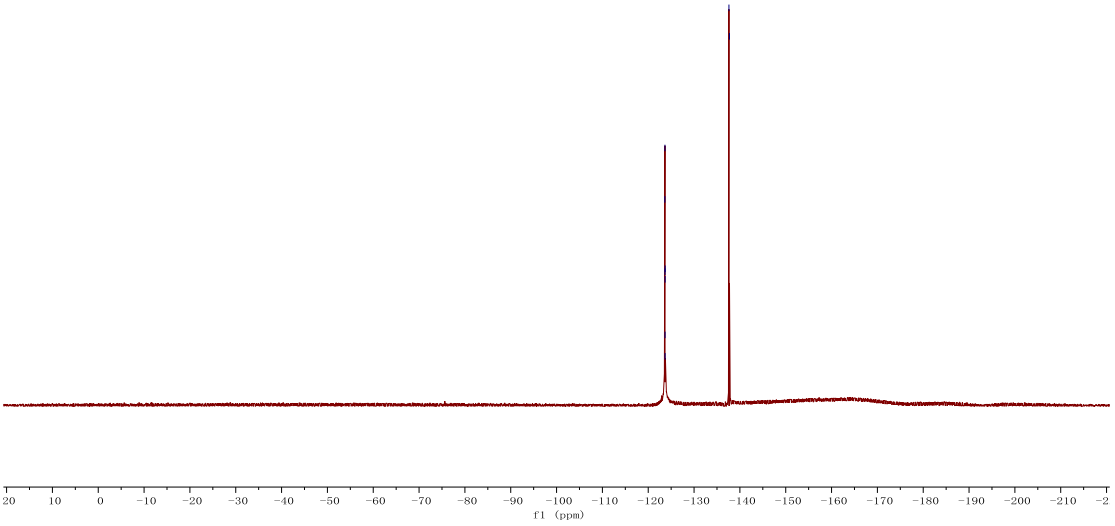

O
O
O
F
F
-123.57
-123.60
-125.62
-125.69
-125.71
-125.74
-123.0
-123.4
-123.8
-124.2
-124.6
-125.0
-125.4
-125.8
-126.2
-126.6
-127.0
-127.4
-127.8
-128.2
f1 (ppm)

2-(2,2,3,3-tetrafluoropropoxy)-4H-chromen-4-one (5w)

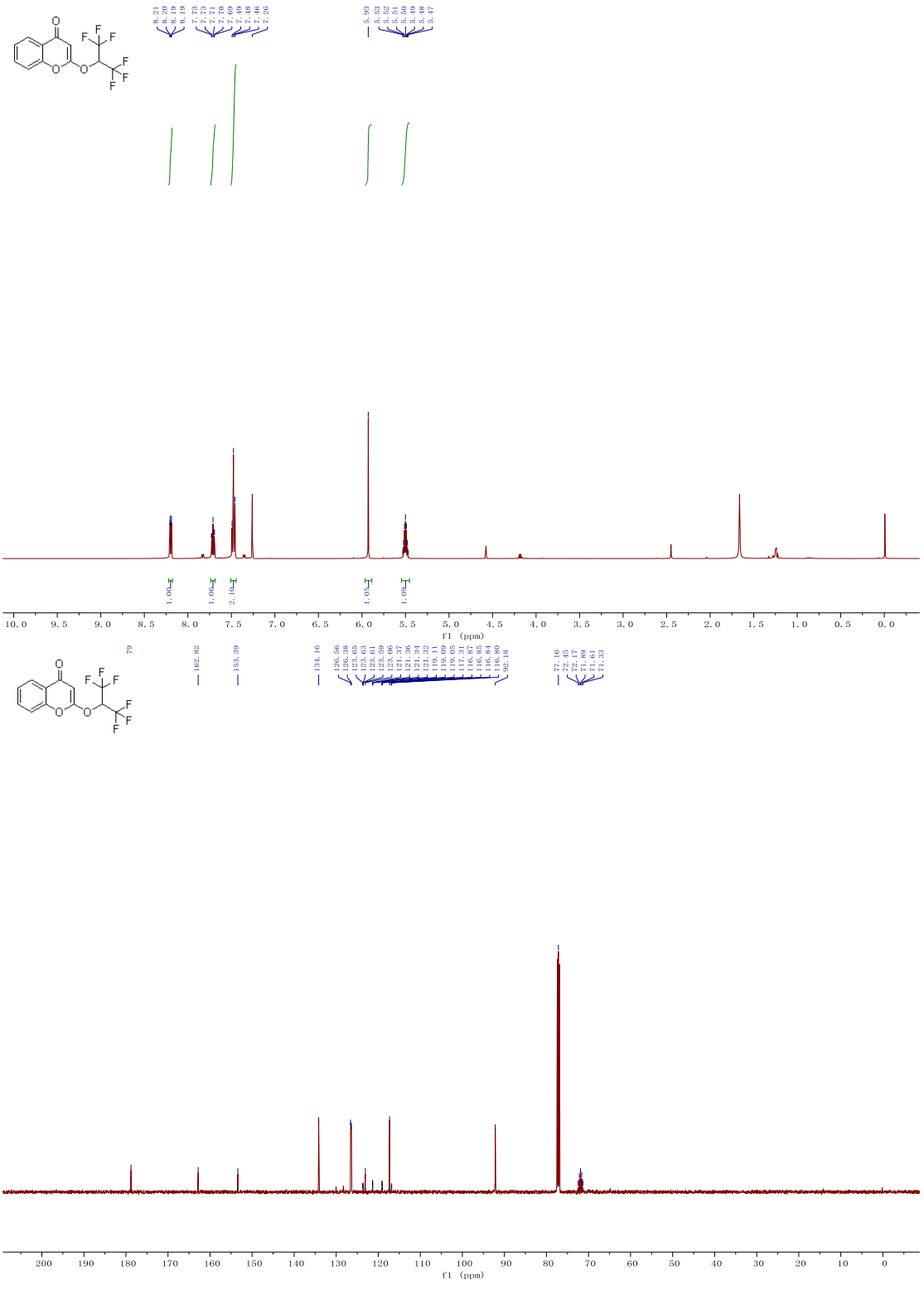


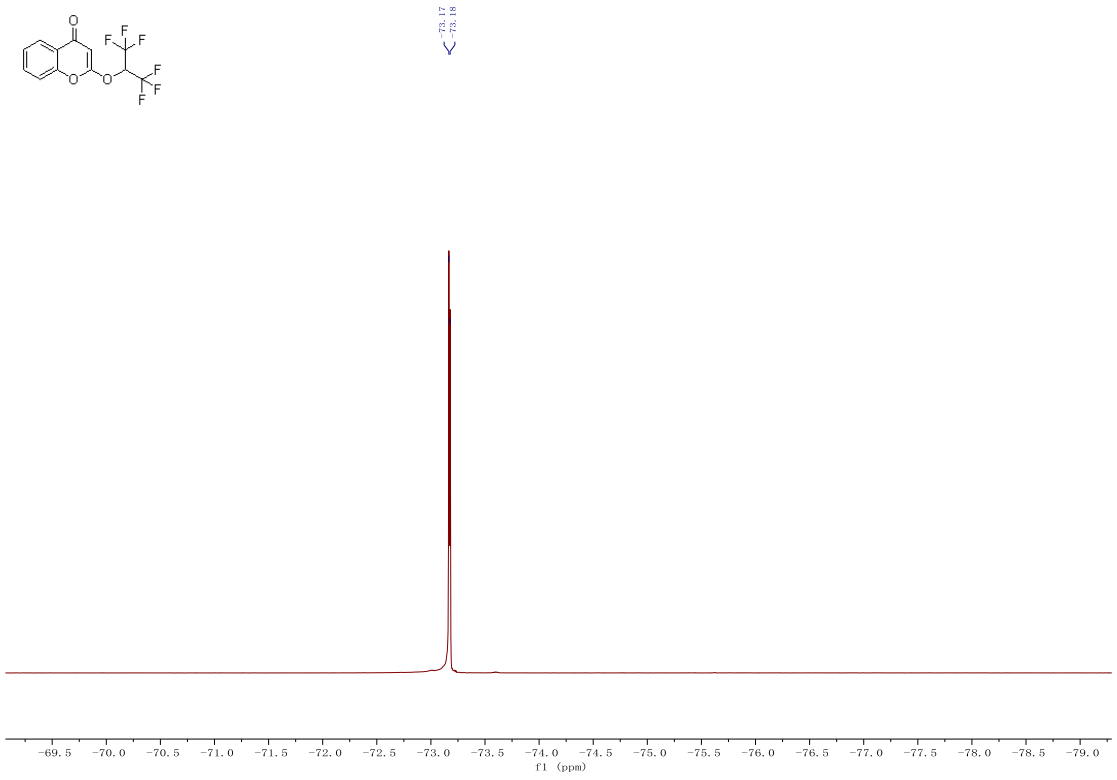

O
O
O
F
F
F


-123.62
-123.65
-123.66
-123.67
-123.68
-123.69
-123.69
-132.61
-137.72

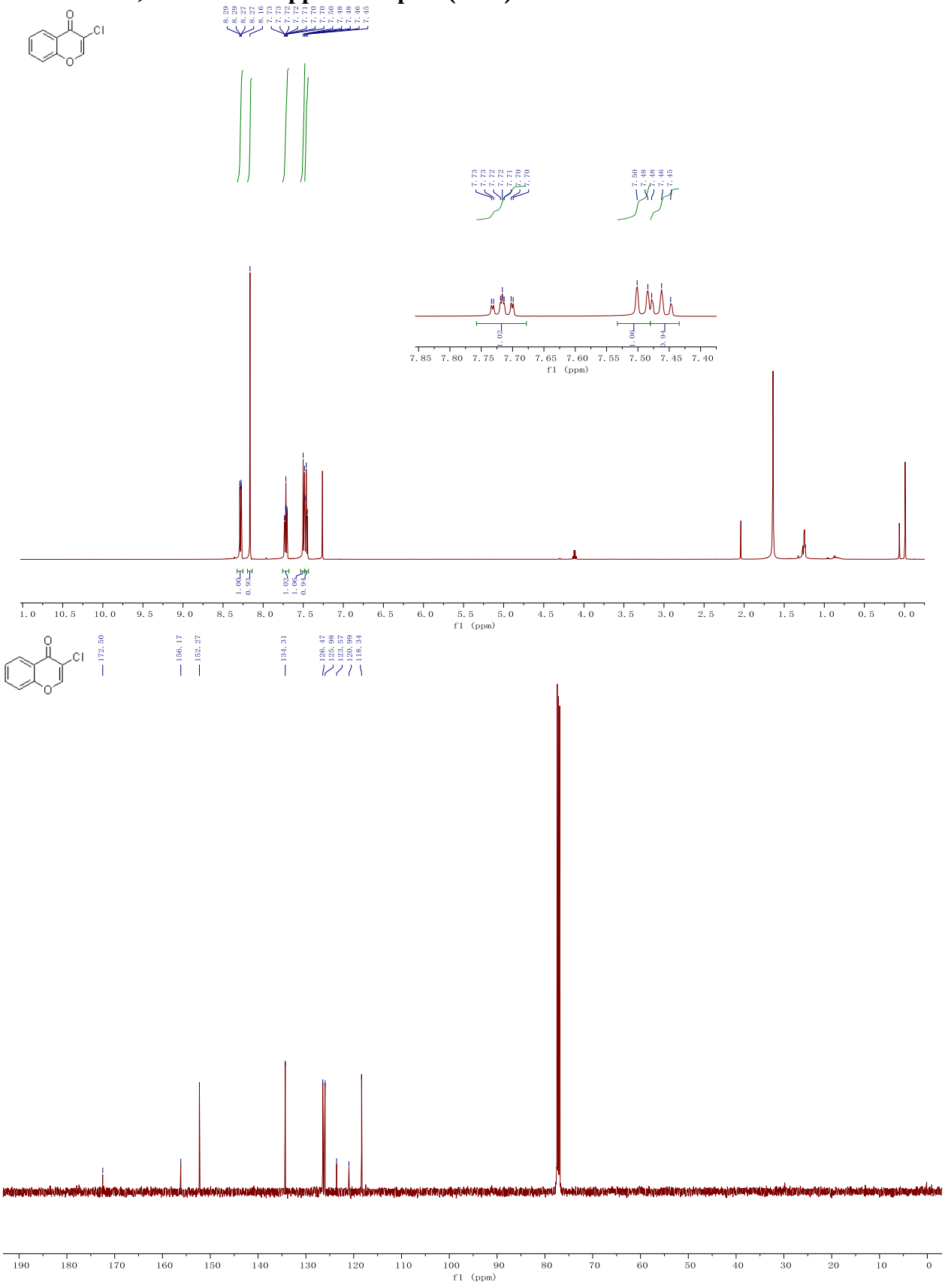

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

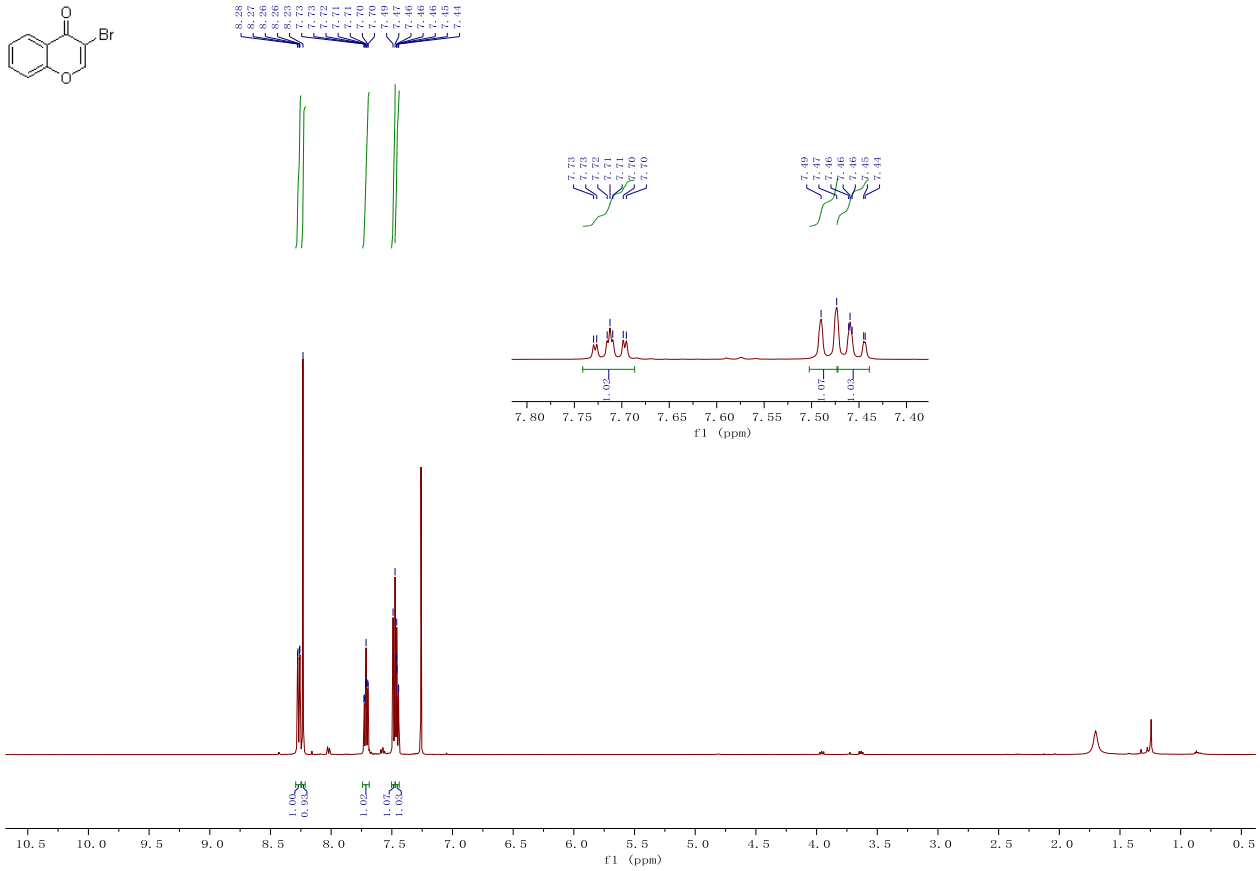
2-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-4H-chromen-4-one (5s)

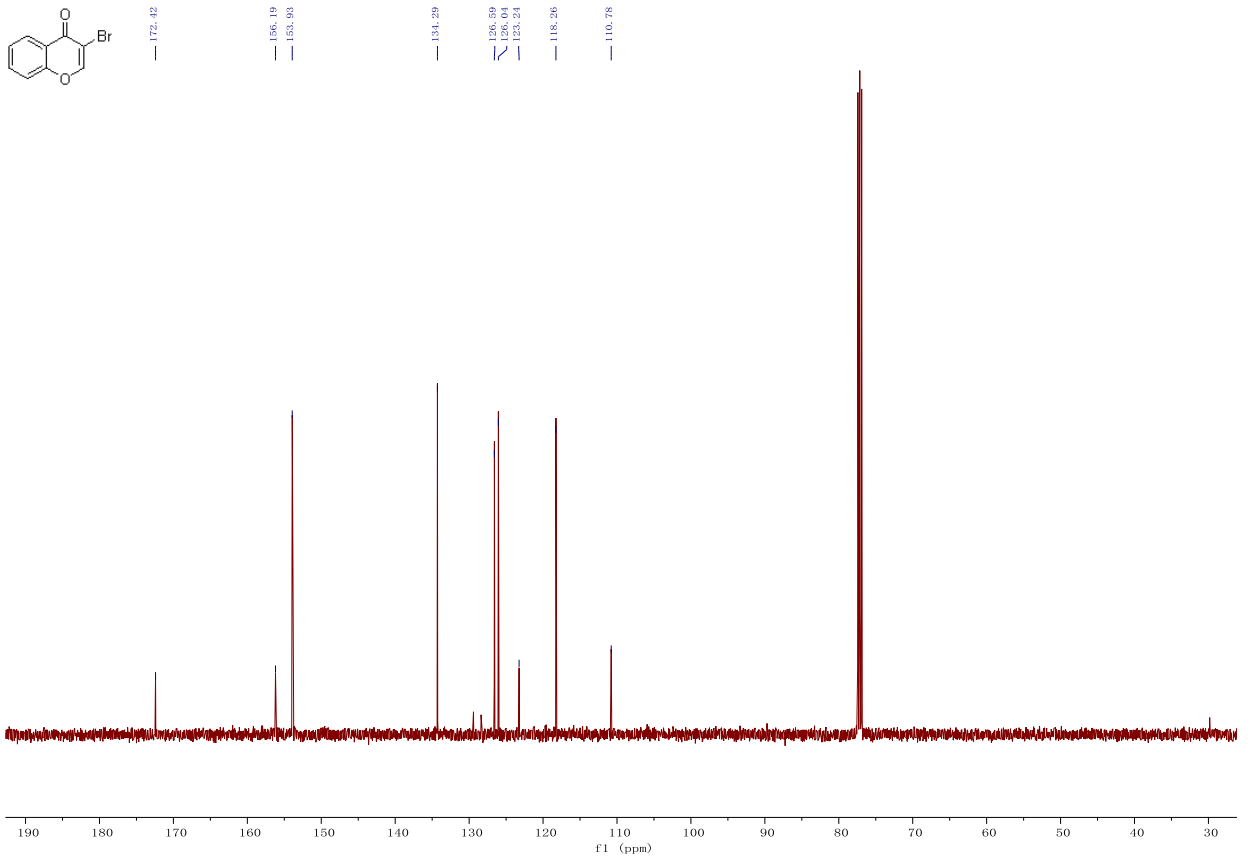


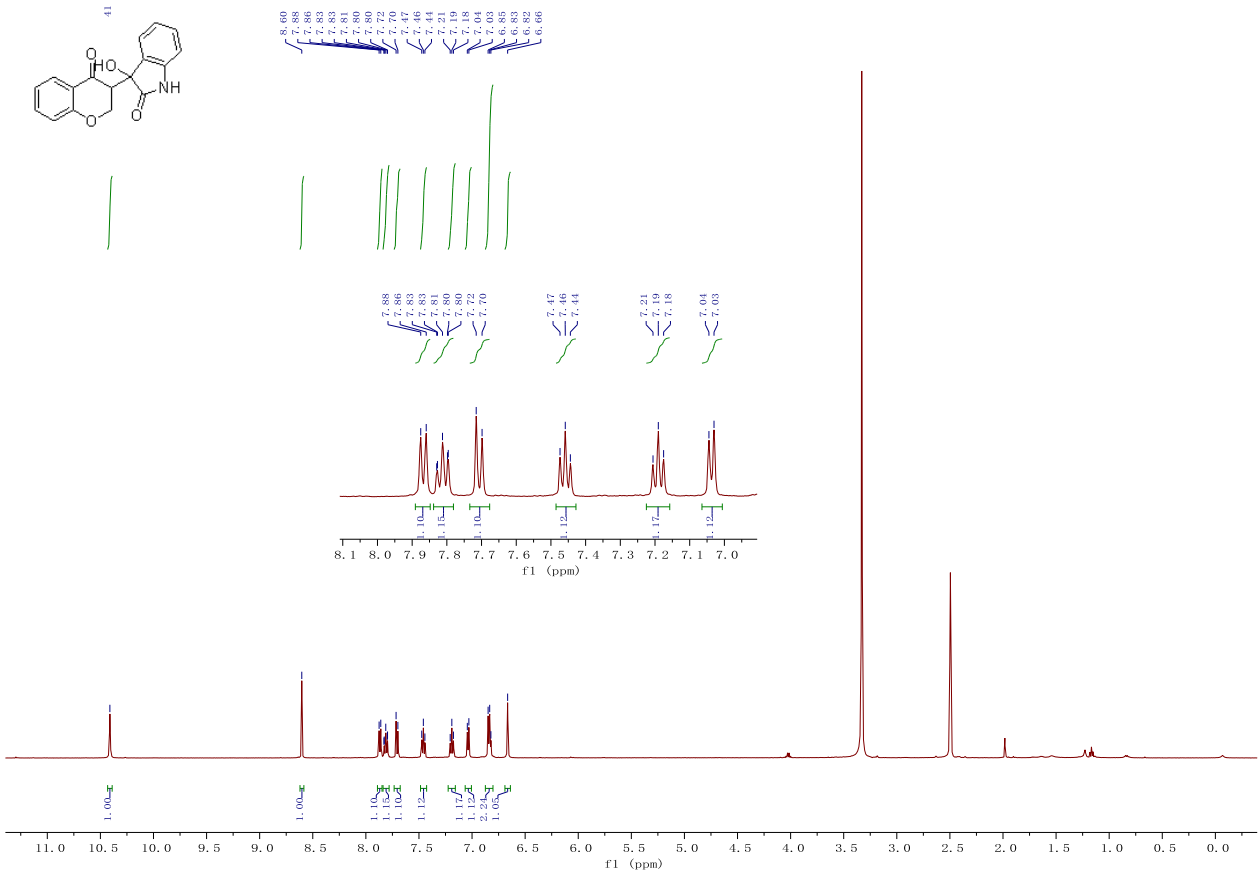

-73.17
-73.18
-69.5
-70.0
-70.5
-71.0
-71.5
-72.0
-72.5
-73.0
-73.5
-74.0
-74.5
-75.0
-75.5
-76.0
-76.5
-77.0
-77.5
-78.0
-78.5
-79.0
f1 (ppm)

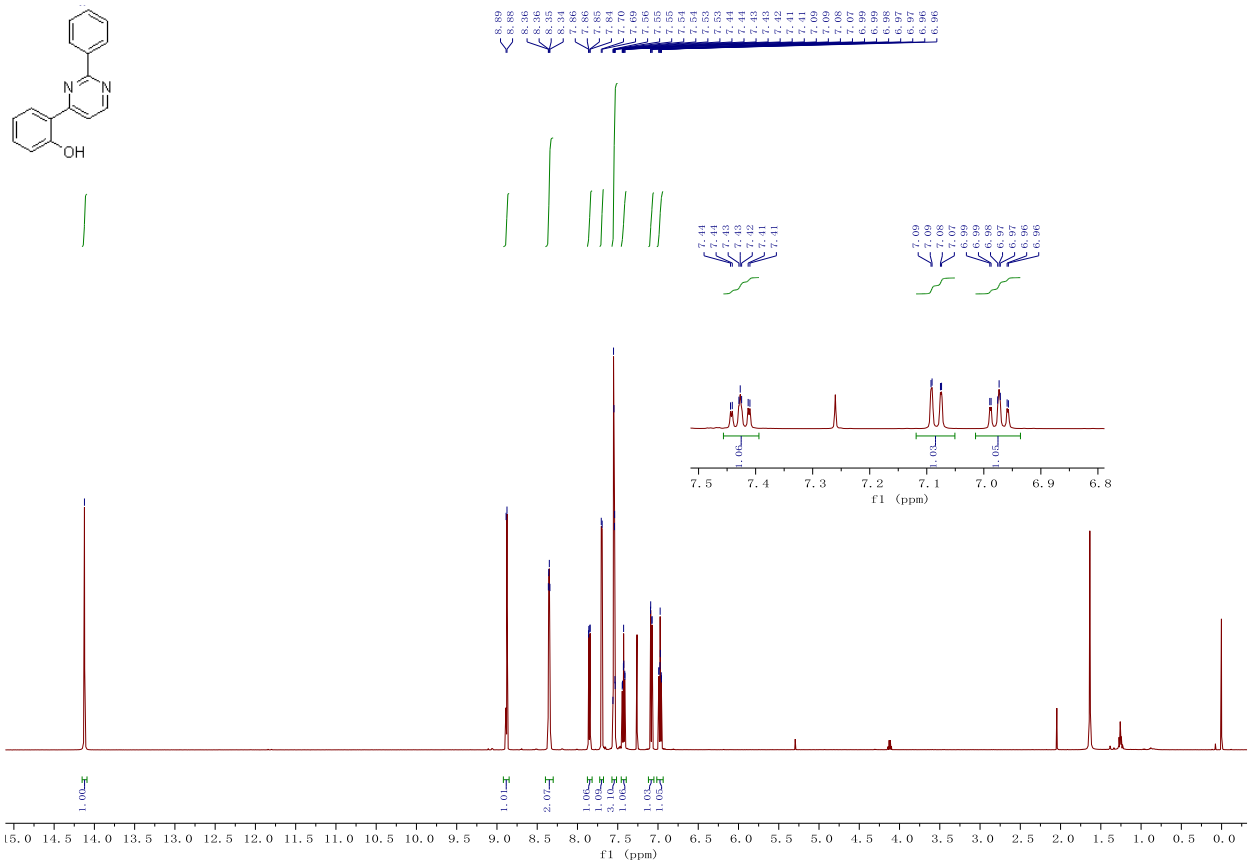
The ^{1}H NMR, ^{13}C NMR of application part (6~13)

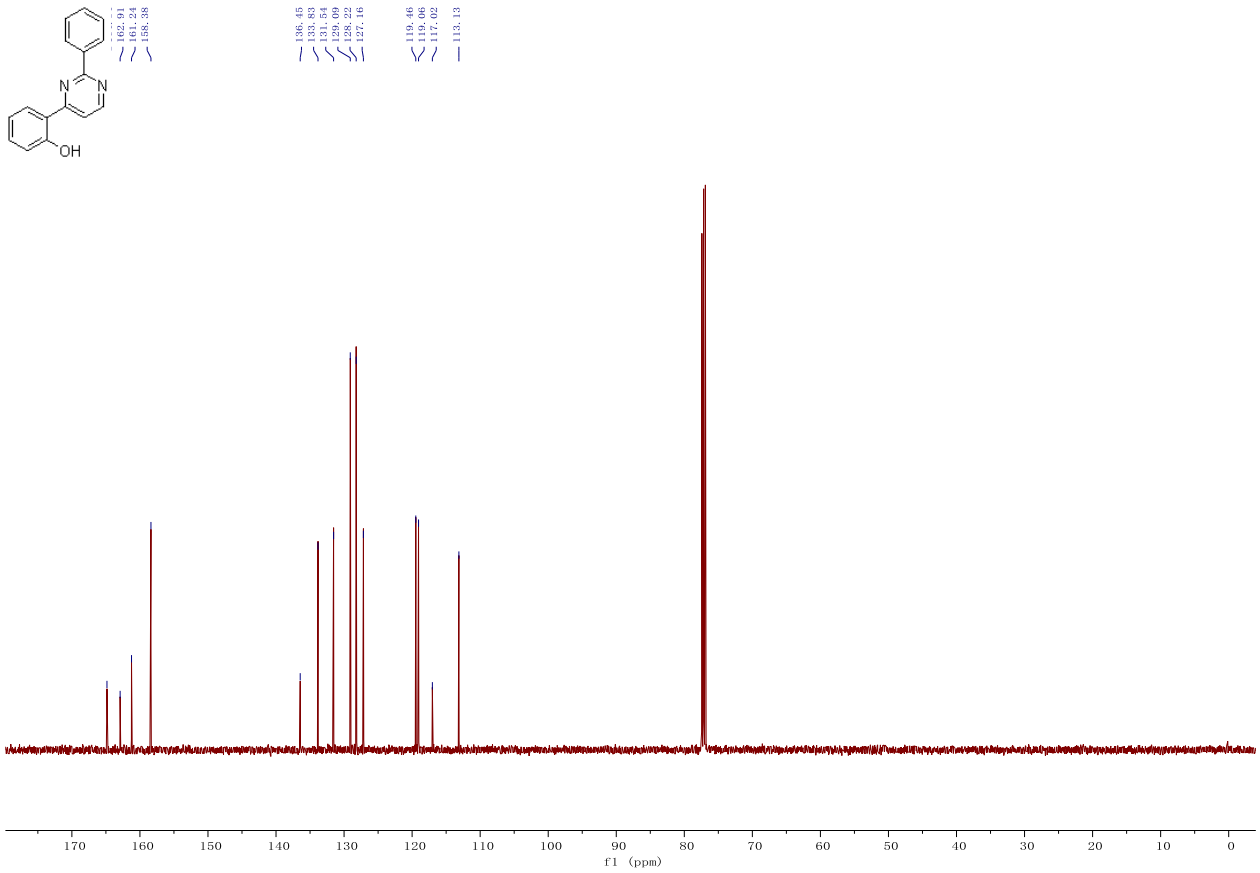


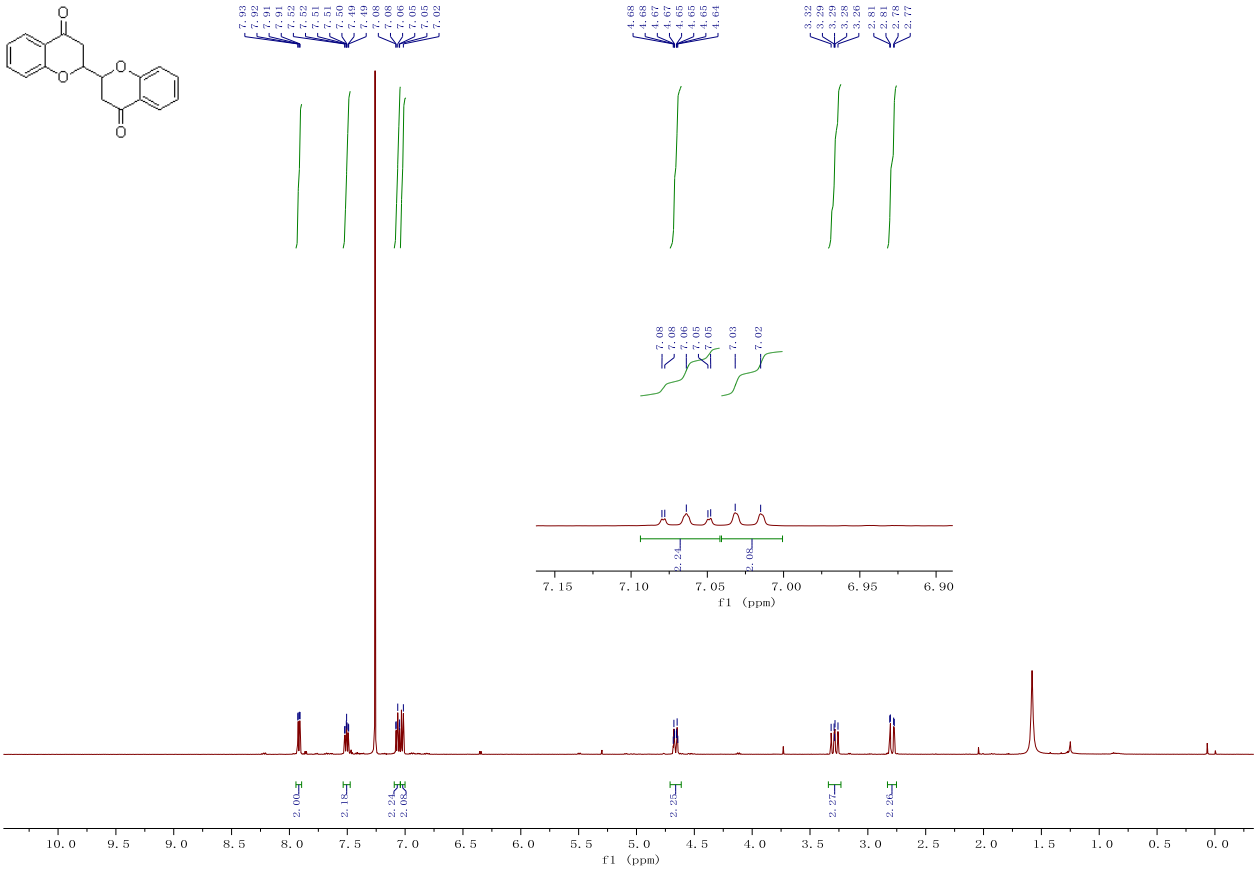

8.28
8.27
8.26
8.26
8.23
7.73
7.73
7.72
7.71
7.71
7.70
7.70
7.49
7.47
7.46
7.46
7.46
7.45
7.44
1.00
0.93
1.02
1.07
1.03
f1 (ppm)

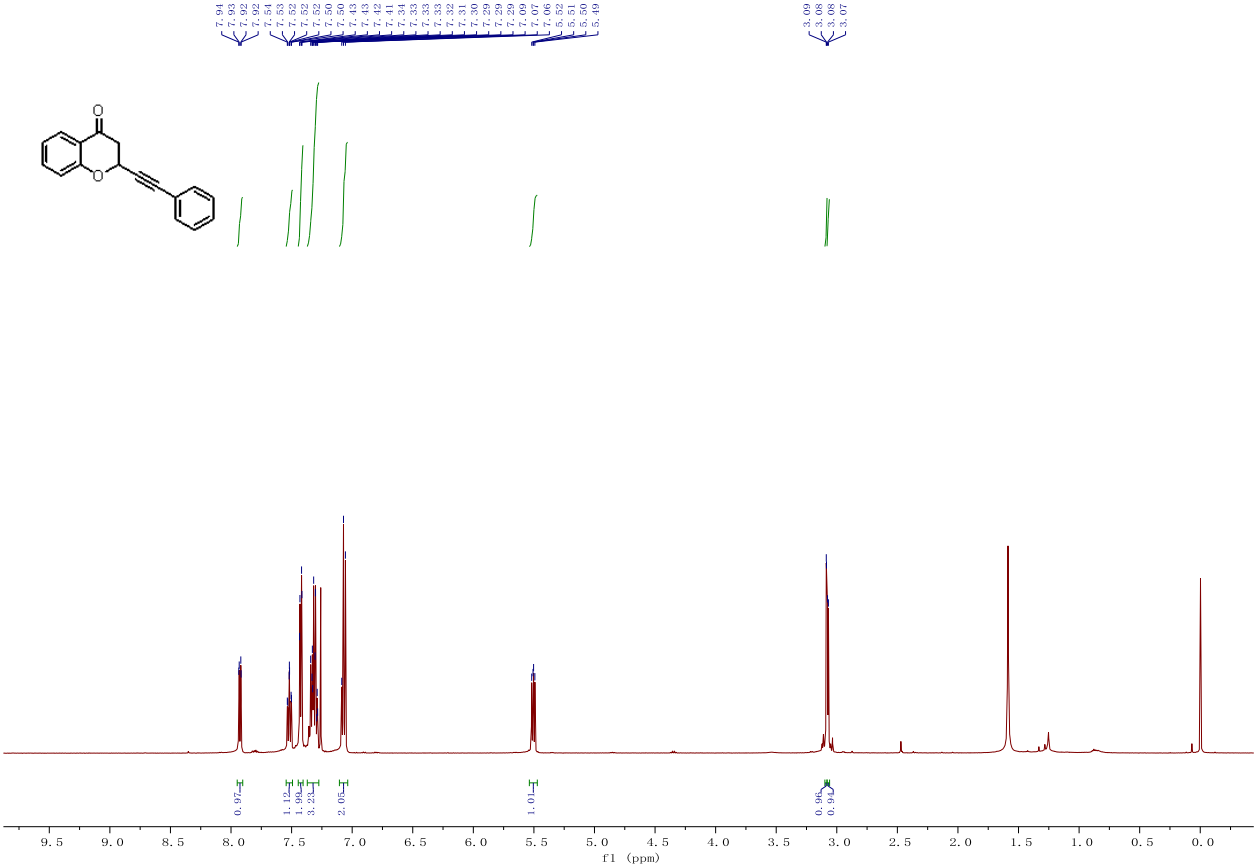

172.42
156.19
153.93
134.29
126.59
126.04
123.24
118.26
110.78
f1 (ppm)

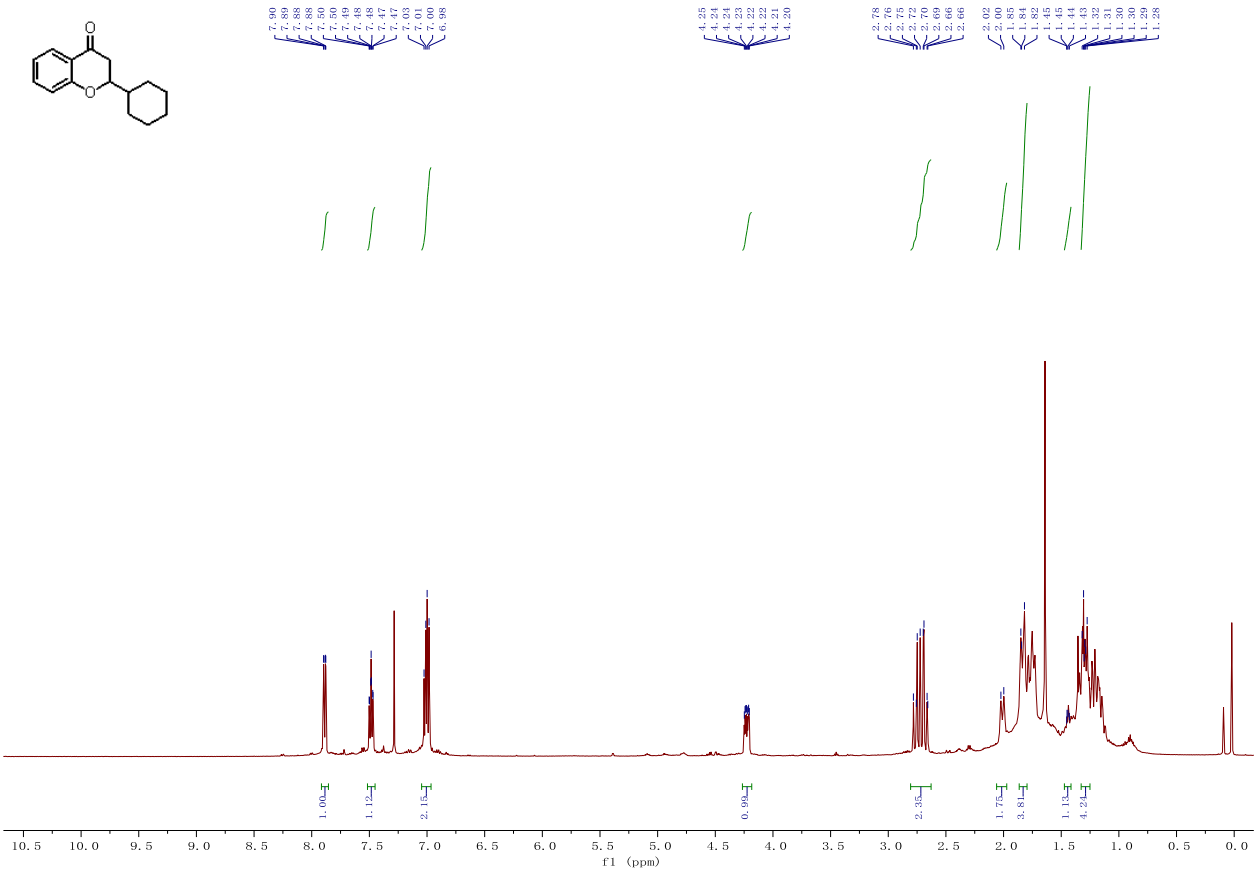

41
O
HO
NH
O
O
8.60
7.88
7.86
7.83
7.83
7.81
7.80
7.80
7.72
7.70
7.47
7.46
7.44
7.21
7.19
7.18
7.04
7.03
6.85
6.83
6.82
6.66
1.00
1.00
1.10
1.15
1.10
1.12
1.17
1.12
2.24
1.05
f1 (ppm)

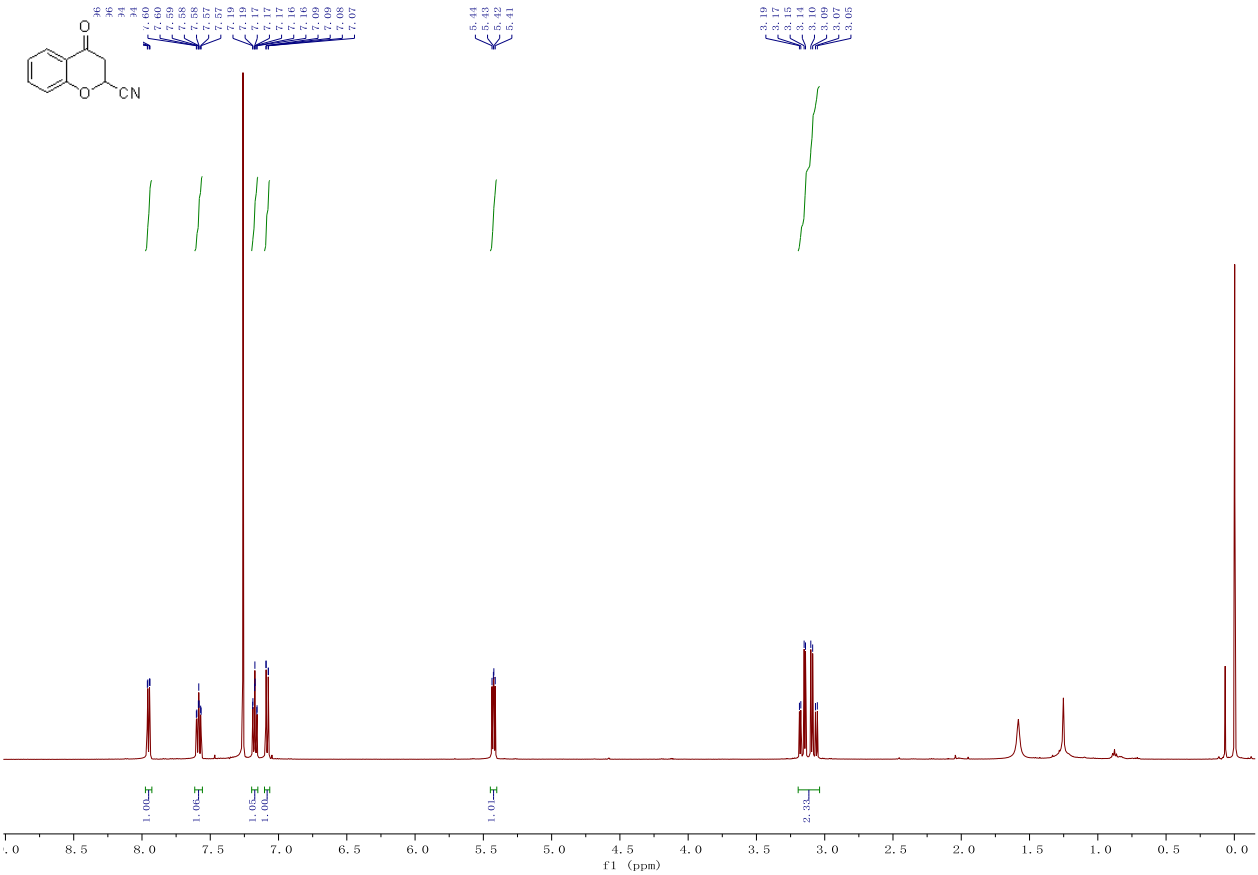

8.89
8.88
8.36
8.36
8.35
8.34
7.86
7.86
7.85
7.84
7.70
7.69
7.56
7.55
7.55
7.54
7.54
7.53
7.53
7.44
7.44
7.43
7.43
7.42
7.43
7.42
7.41
7.41
7.41
7.09
7.09
7.08
7.07
6.99
6.99
6.98
6.98
6.97
6.97
6.96
6.96
6.96
1.06
1.03
1.05
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
1.01
2.07
1.06
1.09
3.10
1.06
1.02
1.05
15.0 14.5 14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.91
161.24
158.38
136.45
133.83
131.54
129.09
128.22
127.16
119.46
119.06
117.02
113.13
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.93 7.92 7.91 7.91 7.52 7.52 7.51 7.50 7.49 7.49 7.08 7.06 7.05 7.02
4.68 4.68 4.67 4.67 4.65 4.65 4.65 4.64
3.32 3.29 3.29 3.28 3.26 2.81 2.81 2.78 2.77
7.08 7.08 7.06 7.05 7.05 7.03 7.02
2.24 2.08
7.15 7.10 7.05 7.00 6.95 6.90
f1 (ppm)
2.00 2.18 2.24 2.08 2.25 2.27 2.26
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.94 7.93 7.92 7.92 7.54 7.53 7.52 7.52 7.52 7.50 7.50 7.43 7.43 7.42 7.41 7.34 7.34 7.33 7.33 7.32 7.31 7.30 7.29 7.29 7.29 7.09 7.07 7.06 5.52 5.51 5.50 5.49
3.09 3.08 3.08 3.07
0.97 1.12 1.99 3.23 2.05 1.01 0.96 0.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.90
7.89
7.88
7.88
7.50
7.50
7.48
7.48
7.47
7.47
7.03
7.01
7.00
6.98
4.25
4.24
4.24
4.23
4.22
4.22
4.21
4.20
2.78
2.76
2.75
2.72
2.70
2.69
2.66
2.66
2.02
2.00
1.85
1.84
1.82
1.45
1.45
1.44
1.43
1.32
1.31
1.30
1.30
1.29
1.28
1.00
1.12
2.15
0.99
2.35
1.75
3.81
1.13
4.24
f1 (ppm)


CN
7.60
7.59
7.58
7.58
7.57
7.57
7.19
7.17
7.17
7.16
7.16
7.09
7.08
7.07
5.44
5.43
5.42
5.41
3.19
3.17
3.15
3.14
3.10
3.09
3.07
3.05
1.00
1.06
1.05
1.00
1.01
2.33
f1 (ppm)