Supporting Information for

An Efficient Approach for the Synthesis of 1,2-Dihydroxanthones Enabled by One-pot Claisen Condensation/Cyclization Reactions

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Contents

General Information

All glassware was dried with a hot air gun and all reactions were carried out under an atmosphere of dry N_2 unless otherwise stated. All reagents and dry solvents were used as received from the supplier. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated aluminum plates. Compounds were visualized by use of UV light, 2.5% phosphomolybdic acid in ethanol or vanillin with acetic and sulfuric acid in ethanol or potassium permanganate in sodium hydroxide aqueous solution with heating. Anhydrous sodium sulfate was used for drying solutions. ^{1}H and ^{13}C NMR were performed on Bruker AV-400, AV-600 or Agilent 400 NMR spectrometers in $CDCl_3$, CD_3OD or DMSO-d_6. Chemical shifts (δ) are quoted in ppm, coupling constants (J) in Hz. All spectra are calibrated based on the solvent peak used unless otherwise stated. The following abbreviations apply: (br) broad, (s) singlet, (d) doublet, (t) triplet, (q) quartet and (m) multiplet. Mass spectrometry was performed on a SYNAPT G2-Si HDMS (Waters Corp., Manchester, UK). A Waters 2535 series machine equipped with an Xbridge C_{18} column (4.6 × 250 mm, 5 mm) was used for HPLC analysis, and a preparative Xbridge Prep C_{18} OBD column (19 × 250 mm, 5 mm) was used for the sample preparation. Flash column chromatography was performed using silica gel (300-400 mesh).

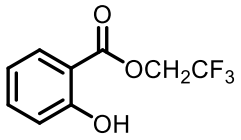
General procedure for the synthesis of trifluoroethyl salicylates

A mixture of salicylic acids (10.0 mmol), CF_3CH_2OH (10.0 mL) were placed in a 50mL round-bottomed flask equipped with a magnetic stirrer. Then thionyl chloride (7.0 eq.) was added to the flask. The mixture was stirred under reflux for 6h. The progress was monitored by TLC. After the reaction, the mixture was concentrated to remove CF_3CH_2OH and thionylchloride, which was purified by column to give the desired products in good yields.

General procedure for the one-pot synthesis of 1,2-dihydroxanthones

To a dried Schlenk tube under N_2 were added trifluoroethyl salicylates **1** (0.25 mmol) and cyclohexenones **2** (0.30 mmol, 1.2 equiv.). To the above mixture at room temperature, LiHMDS (1.0 M in THF or solid, 0.75 mmol, 3.0 equiv) was added in one-portion. The mixture was then stirred vigorously for 3-5 minutes, which was then quenched by addition of 1.0 mL of water. The suspension was kept stirring overnight and monitored by TLC until completion. The aqueous phase was extracted with EtOAc (2 x 5 mL) and the combined organic phases was dried over $MgSO_4$, filtered and the solvent removed in vacuo to give a crude product. The following column chromatography using EtOAc/petroleum ether to give the product **3** mostly as a solid.

Characterization data for the products



1a

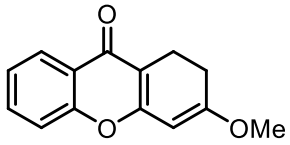
White solid, 76% yield. m.p. = 44 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.28 (s, 1H), 7.91 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.53 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.95 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 4.74 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.3, 162.0, 136.7, 130.1, 122.9 (q, *J* = 277.3 Hz), 119.6, 117.8, 111.0, 60.7 (q, *J* = 37.3, 36.9 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.7.

HRESIMS calcd for $C_9H_6F_3O_3$ $[M - H]^-$ 219.0269, found 219.0267.



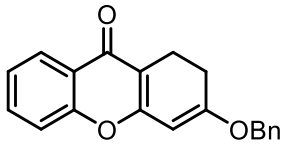
3a

Yellow solid, 98% yield. m.p. = 132 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.41 – 7.33 (m, 2H), 5.39 (s, 1H), 3.82 (s, 3H), 2.93 (t, *J* = 8.9 Hz, 2H), 2.53 (t, *J* = 8.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 170.5, 162.6, 155.6, 132.3, 125.7, 124.5, 124.0, 117.5, 108.8, 91.2, 56.0, 27.3, 18.6.

HRESIMS calcd for $C_{14}H_{13}O_3$ $[M + H]^+$ 229.0865, found 229.0864.



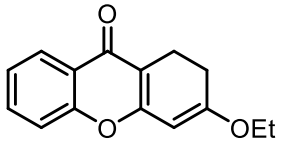
3b

Yellow solid, 92% yield. m.p. = 167 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59 (ddd, *J* = 8.5, 7.0, 1.7 Hz, 1H), 7.47 – 7.34 (m, 8H), 5.50 (s, 1H), 5.04 (s, 2H), 2.96 (t, *J* = 9.0 Hz, 2H), 2.61 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 169.3, 162.5, 155.6, 135.2, 132.3, 128.8, 128.6, 127.8, 125.7, 124.5, 124.1, 117.5, 109.0, 92.3, 70.8, 29.7, 27.5, 18.6.

HRESIMS calcd for $C_{20}H_{17}O_3$ $[M + H]^+$ 305.1178, found 305.1181.



3c

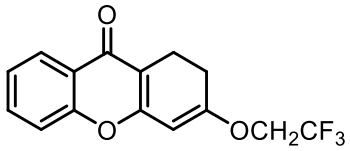
Yellow solid, 95% yield. m.p. = 104 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.40 – 7.33 (m, 2H), 5.36 (s, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 2.92 (t, *J* = 8.9 Hz, 2H), 2.52 (t, *J* = 8.9 Hz,

2H), 1.44 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 169.7, 162.9, 155.5, 132.2, 125.7, 124.4, 124.0, 117.5, 108.7, 91.4, 64.5, 27.5, 18.5, 14.2.

HRESIMS calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1022.



3d

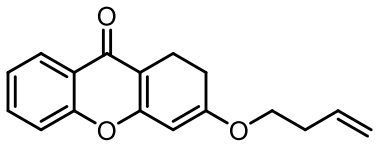
White solid, 81% yield. m.p. = 154 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.61 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.41 – 7.38 (m, 3H), 5.40 (s, 1H), 4.32 (q, *J* = 7.9 Hz, 2H), 2.97 (t, *J* = 9.0 Hz, 2H), 2.62 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 175.7, 167.1, 160.8, 155.6, 132.6, 125.8, 124.8, 124.0, 122.6 (q, *J* = 277.3 Hz), 117.6, 109.8, 93.2, 65.3 (q, *J* = 36.3 Hz), 26.7, 18.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.5.

HRESIMS calcd for $C_{15}H_{12}F_3O_3$ $[M + H]^+$ 297.0739, found 297.0741.



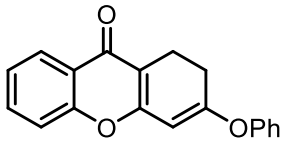
3e

Yellow solid, 89% yield. m.p. = 81 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.40 – 7.33 (m, 2H), 5.88 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.37 (s, 1H), 5.25 – 5.12 (m, 2H), 4.00 (t, *J* = 6.7 Hz, 2H), 2.92 (t, *J* = 9.0 Hz, 2H), 2.58 – 2.51 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.5, 169.6, 162.7, 155.5, 133.7, 132.3, 125.7, 124.5, 124.1, 117.6, 117.5, 108.7, 91.6, 67.9, 33.0, 27.4, 18.5.

HRESIMS calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1178, found 269.1185.



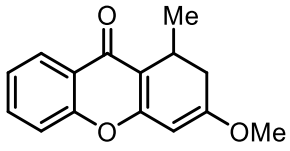
3f

Yellow solid, 56% yield. m.p. = 116 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.56 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.37 – 7.29 (m, 4H), 7.19 – 7.15 (m, 2H), 5.19 (d, *J* = 1.0 Hz, 1H), 3.04 (t, *J* = 9.1 Hz, 2H), 2.80 – 2.75 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.6, 169.7, 162.0, 155.5, 153.4, 132.4, 130.1, 126.0, 125.7, 124.6, 124.0, 121.4, 117.5, 109.1, 95.7, 26.8, 18.7.

HRESIMS calcd for $C_{19}H_{15}O_3$ $[M + H]^+$ 291.1021, found 291.1021.



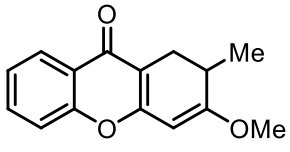
3g

Yellow solid, 53% yield. m.p. = 111 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.40 – 7.34 (m, 2H), 5.39 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H), 3.49 (p, *J* = 7.4 Hz, 1H), 2.86 (ddd, *J* = 17.0, 8.3, 2.1 Hz, 1H), 2.19 (d, *J* = 17.0 Hz, 1H), 1.14 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 168.9, 161.8, 155.6, 132.3, 125.7, 124.4, 124.3, 117.5, 114.2, 90.4, 56.0, 34.8, 24.4, 18.1.

HRESIMS calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1025.



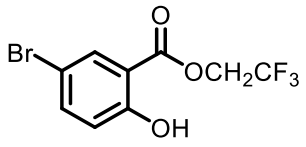
3h

Yellow solid, 91% yield. m.p. = 121 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.1, 1.8 Hz, 1H), 7.40 – 7.32 (m, 2H), 5.33 (s, 1H), 3.80 (s, 3H), 2.93 (dd, *J* = 16.4, 7.8 Hz, 1H), 2.78 (dd, *J* = 16.4, 6.2 Hz, 1H), 2.69 – 2.58 (m, 1H), 1.15 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 174.6, 162.0, 155.5, 132.3, 125.6, 124.5, 124.0, 117.5, 107.7, 90.1, 56.1, 32.6, 26.5, 17.3.

HRESIMS calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1020.



1aa

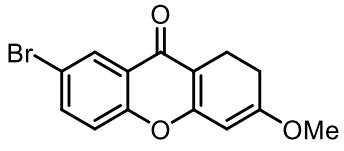
White solid, 72% yield. m.p. = 47 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.22 (s, 1H), 7.99 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.94 (d, *J* = 8.9 Hz, 1H), 4.75 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.4, 161.0, 139.6, 132.2, 122.6 (q, *J* = 277.2 Hz), 119.9, 112.4, 111.3, 61.0 (q, *J* = 37.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.5.

HRESIMS calcd for $C_9H_7F_3BrO_3$ $[M + H]^+$ 298.9531, found 298.9526.



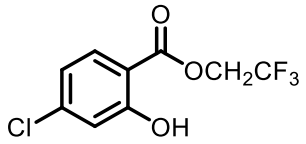
3aa

White solid, 74% yield. m.p. = 189 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 2.5 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.27 (s, 0H), 5.37 (s, 1H), 3.82 (s, 3H), 2.91 (t, *J* = 9.0 Hz, 2H), 2.53 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.1, 171.0, 163.0, 154.3, 135.2, 128.3, 125.4, 119.4, 117.8, 108.9, 91.0, 56.0, 27.2, 18.5.

HRESIMS calcd for $C_{14}H_{12}BrO_3$ $[M + H]^+$ 306.9970, found 306.9973.



1ab

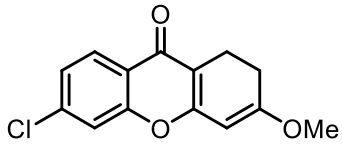
White solid, 91% yield. m.p. = 40 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.36 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 2.1 Hz, 1H), 6.94 (dd, *J* = 8.6, 2.0 Hz, 1H), 4.74 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 162.4, 142.8, 131.1, 122.7 (q, *J* = 277.3 Hz), 120.4, 118.0, 109.6, 60.9 (q, *J* = 37.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6.

HRESIMS calcd for $C_9H_5F_3ClO_3$ $[M - H]^-$ 252.9879, found 252.9879.



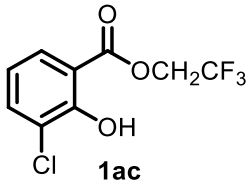
3ab

White solid, 58% yield. m.p. = 123 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.14 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.39 (d, *J* = 2.2 Hz, 1H), 7.32 (dt, *J* = 8.5, 2.1 Hz, 1H), 5.35 (s, 1H), 3.82 (d, *J* = 2.1 Hz, 2H), 2.90 (td, *J* = 9.0, 2.2 Hz, 2H), 2.52 (td, *J* = 9.0, 2.1 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.7, 170.9, 162.9, 155.6, 138.1, 127.0, 125.3, 122.6, 117.5, 109.0, 91.0, 56.0, 27.2, 18.5.

HRESIMS calcd for $C_{14}H_{12}ClO_3$ $[M + H]^+$ 263.0475, found 263.0474.



1ac

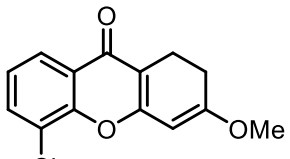
White solid, 82% yield. m.p. = 56 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.79 (s, 1H), 7.85 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.64 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.92 (t, *J* = 8.0 Hz, 1H), 4.76 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 157.6, 136.9, 128.6, 122.7 (q, *J* = 277.3 Hz), 122.6, 119.7, 112.3, 61.1 (q, *J* = 37.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6.

HRESIMS calcd for $C_9H_5F_3ClO_3$ $[M - H]^-$ 252.9879, found 252.9909.



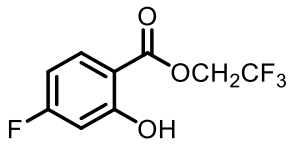
3ac

Yellow solid, 42% yield. m.p. = 164 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.12 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 5.46 (s, 1H), 3.83 (s, 3H), 2.91 (t, *J* = 9.0 Hz, 2H), 2.53 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 171.0, 162.8, 151.2, 132.6, 125.4, 124.5, 124.3, 122.3, 108.9, 91.1, 56.1, 27.2, 18.5.

HRESIMS calcd for $C_{14}H_{12}ClO_3$ $[M + H]^+$ 263.0475, found 263.0456.



1ad

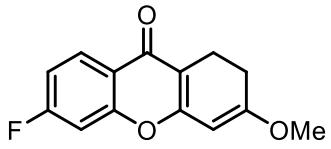
Colorless oil, 89% yield..

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.49 (d, *J* = 1.5 Hz, 1H), 7.96 – 7.89 (m, 1H), 6.76 – 6.62 (m, 2H), 4.74 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.2 , 167.2 (d, *J* = 109.2 Hz), 164.1 (d, *J* = 14.4 Hz), 132.4 (d, *J* = 11.7 Hz), 122.8 (q, *J* = 277.1 Hz), 108.0 (d, *J* = 22.8 Hz), 107.7 (d, *J* = 2.4 Hz), 104.7 (d, *J* = 24.3 Hz), 60.8 (q, *J* = 37.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.7, -99.0.

HRESIMS calcd for $C_9H_5F_4O_3$ $[M - H]^-$ 237.0175, found 237.0170.



3ad

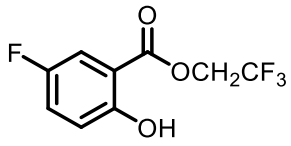
Yellow solid, 73% yield. m.p. = 138 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.08 – 7.03 (m, 2H), 5.34 (s, 1H), 3.79 (s, 3H), 2.88 (t, *J* = 9.0 Hz, 2H), 2.50 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 170.6, 165.7, 164.0, 163.0, 156.4 (d, *J* = 12.1 Hz), 128.0 (d, *J* = 10.7 Hz), 120.9 (d, *J* = 2.2 Hz), 113.1 (d, *J* = 22.7 Hz), 108.7, 104.2 (d, *J* = 25.0 Hz), 91.0, 56.0, 27.2, 18.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -105.5.

HRESIMS calcd for $C_{14}H_{12}FO_3$ $[M + H]^+$ 247.0770, found 247.0772.



1ae

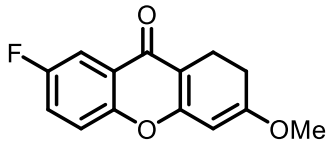
White solid, 88% yield. m.p. = 53 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 7.57 (dd, *J* = 8.5, 3.2 Hz, 1H), 7.32 – 7.25 (m, 1H), 7.01 (dd, *J* = 9.2, 4.4 Hz, 1H), 4.75 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 167.6 (d, *J* = 3.1 Hz), 158.3 , 155.2 (d, *J* = 239.8 Hz), 124.5 (d, *J* = 23.4 Hz), 122.7 (q, *J* = 277.3 Hz), 119.3 (d, *J* = 6.8 Hz), 115.1 (d, *J* = 24.2 Hz), 110.8 (d, *J* = 7.7 Hz), 61.0 (q, *J* = 37.3 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.6, -123.3.

HRESIMS calcd for $C_9H_5F_4O_3$ [M - H]$^-$ 237.0175, found 237.0176.



3ae

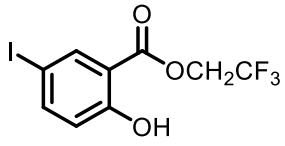
Yellow solid, 83% yield. m.p. = 136 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.38 (dd, *J* = 9.1, 4.2 Hz, 1H), 7.32 – 7.29 (m, 1H), 5.38 (s, 1H), 3.82 (s, 3H), 2.92 (t, *J* = 8.9 Hz, 2H), 2.53 (t, *J* = 8.9 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.7 (d, *J* = 1.9 Hz), 171.0 , 163.1 , 159.3 (d, *J* = 245.4 Hz), 151.7 , 125.2 (d, *J* = 6.9 Hz), 120.3 (d, *J* = 26.1 Hz), 119.4 (d, *J* = 8.6 Hz), 110.6 (d, *J* = 23.2 Hz), 108.3 , 91.1 , 56.0 , 27.2 , 18.5 .

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.5.

HRESIMS calcd for $C_{14}H_{12}FO_3$ [M + H]$^+$ 247.0770, found 247.0771.



1af

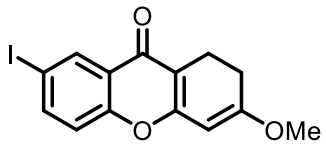
White solid, 90% yield. m.p. = 60 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.24 (s, 1H), 8.16 (d, *J* = 2.4 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 4.75 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 161.6, 145.2, 138.2, 122.6 (q, *J* = 277.3 Hz), 120.2, 113.1, 80.5, 61.0 (q, *J* = 37.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.4.

HRESIMS calcd for $C_9H_5F_3IO_3$ [M + H]$^+$ 344.9235, found 344.9235.



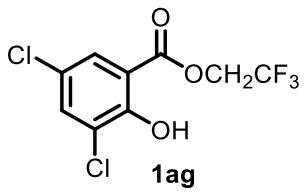
3af

White solid, 68% yield. m.p. = 178 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 2.2 Hz, 1H), 7.83 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 1H), 5.36 (s, 1H), 3.82 (s, 3H), 2.90 (t, *J* = 9.0 Hz, 2H), 2.52 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 171.0, 163.0, 155.0, 140.8, 134.6, 125.7, 119.6, 109.0, 91.0, 88.3, 56.1, 27.2, 18.6.

HRESIMS calcd for $C_{14}H_{12}IO_3$ [M + H]$^+$ 354.9831, found 354,9837.



1ag

White solid, 87% yield. m.p. = 51 °C.

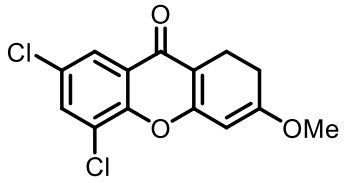
^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.72 (s, 1H), 7.80 (d, *J* = 2.6 Hz, 1H), 7.63 (d, *J* = 2.6 Hz, 1H),

4.77 (q, *J* = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.3, 156.4, 136.5, 127.8, 124.3, 123.8, 122.5 (q, *J* = 277.3 Hz), 112.7, 61.4 (q, *J* = 37.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.5.

HRESIMS calcd for $C_9H_4Cl_2F_3O_3$ $[M - H]^-$ 286.9490, found 286.9493.



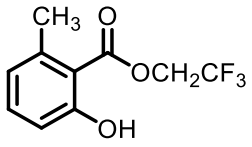
3ag

Yellow solid, 41% yield. m.p. = 175 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 2.6 Hz, 1H), 7.63 (d, *J* = 2.6 Hz, 1H), 5.46 (s, 1H), 3.85 (s, 4H), 2.91 (t, *J* = 9.0 Hz, 2H), 2.55 (t, *J* = 9.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 171.5, 163.2, 149.8, 132.4, 130.0, 125.9, 123.9, 123.5, 109.0, 91.0, 56.2, 27.2, 18.5.

HRESIMS calcd for $C_{14}H_{11}Cl_2O_3$ $[M + H]^+$ 297.0085, found 297.0085.



1ah

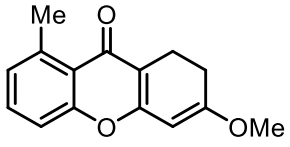
White solid, 90% yield. m.p. = 89 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.85 (s, 1H), 7.35 (dd, *J* = 8.4, 7.5 Hz, 1H), 6.92 – 6.87 (m, 1H), 6.78 (dt, *J* = 7.5, 1.0 Hz, 1H), 4.75 (q, *J* = 8.3 Hz, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 163.4, 141.7, 135.3, 122.7 (q, *J* = 277.2 Hz), 123.4, 115.8, 110.9, 61.0 (q, *J* = 36.8 Hz), 24.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.3.

HRESIMS calcd for $C_{10}H_8F_3O_3$ $[M - H]^-$ 233.0426, found 233.0415.



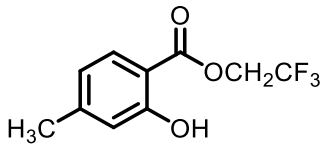
3ah

Yellow solid, 56% yield. m.p. = 153 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.41 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.33 (s, 1H), 3.80 (s, 3H), 2.91 (s, 3H), 2.87 (t, *J* = 9.0 Hz, 2H), 2.51 (t, *J* = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 169.9, 161.0, 157.0, 140.7, 131.3, 127.2, 122.3, 115.7, 109.6, 90.7, 55.9, 27.3, 22.9, 18.6.

HRESIMS calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1021.



1ai

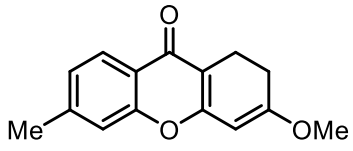
White solid, 92% yield. m.p. = 42 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.23 (s, 1H), 7.78 (d, J = 8.2 Hz, 1H), 6.85 (s, 1H), 6.76 (dd, J = 8.2, 1.6 Hz, 1H), 4.72 (q, J = 8.3 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 162.0, 148.4, 129.9, 122.9 (q, J = 277.3 Hz), 120.9, 117.9, 108.4, 60.6 (q, J = 36.8 Hz), 21.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6.

HRESIMS calcd for $C_{10}H_8F_3O_2$ $[M - H]^-$ 233.0426, found 233.0423.



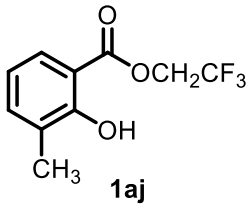
3ai

Yellow solid, 73% yield. m.p. = 127 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.4 Hz, 1H), 7.15 (t, J = 3.5 Hz, 2H), 5.34 (s, 1H), 3.79 (s, 3H), 2.90 (t, J = 8.9 Hz, 2H), 2.50 (t, J = 9.0 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 170.3, 162.5, 155.7, 143.4, 126.0, 125.4, 121.7, 117.3, 108.6, 91.2, 55.9, 27.3, 21.7, 18.5.

HRESIMS calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1023.



1aj

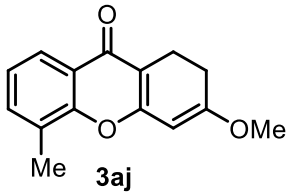
Colorless oil, 91% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.53 (s, 1H), 7.77 (dd, J = 8.0, 1.7 Hz, 1H), 7.40 (ddt, J = 7.3, 1.7, 0.8 Hz, 1H), 6.85 (t, J = 7.7 Hz, 1H), 4.74 (q, J = 8.3 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 160.4, 137.5, 127.6, 127.0, 122.9 (q, J = 277.3 Hz), 118.9, 110.2, 60.7 (q, J = 37.3 Hz), 15.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6.

HRESIMS calcd for $C_{10}H_8F_3O_3$ $[M - H]^-$ 233.0426, found 233.0423.



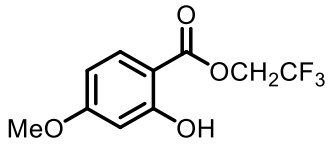
3aj

Yellow solid, 85% yield. m.p. = 145 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (dd, J = 8.0, 1.6 Hz, 1H), 7.43 (d, J = 6.9 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H), 5.42 (s, 1H), 3.83 (s, 3H), 2.93 (t, J = 8.9 Hz, 2H), 2.53 (t, J = 9.0 Hz, 2H), 2.49 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 170.3, 162.3, 154.0, 133.3, 126.7, 124.0, 123.9, 123.3, 108.6, 91.3, 56.0, 27.3, 18.6, 15.6.

HRESIMS calcd for $C_{15}H_{15}O_3$ $[M + H]^+$ 243.1021, found 243.1022.



1ak

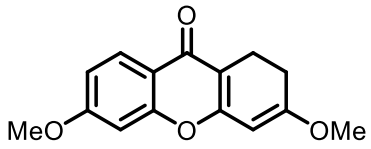
White solid, 94% yield. m.p. = 72 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.49 (s, 1H), 7.89 – 7.72 (m, 1H), 6.53 – 6.46 (m, 2H), 4.71 (q, *J* = 8.3 Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 166.5, 164.3, 131.5, 122.9 (q, *J* = 277.3 Hz), 108.2, 103.9, 100.8, 60.5 (q, *J* = 37.1 Hz), 55.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.7.

HRESIMS calcd for $C_{10}H_8F_3O_4$ $[M - H]^-$ 249.0375, found 249.0377.



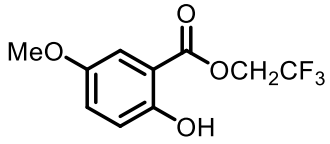
3ak

White solid, 53% yield. m.p. = 161 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.8 Hz, 1H), 6.94 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 5.35 (s, 1H), 3.90 (s, 3H), 3.81 (s, 3H), 2.90 (t, *J* = 9.0 Hz, 2H), 2.52 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.3, 170.0, 163.1, 162.2, 157.1, 127.0, 117.9, 113.3, 108.4, 100.2, 91.1, 77.2, 77.2, 77.0, 76.8, 55.9, 55.7, 27.3, 18.5.

HRESIMS calcd for $C_{15}H_{15}O_4$ $[M + H]^+$ 259.0970, found 259.0968.



1al

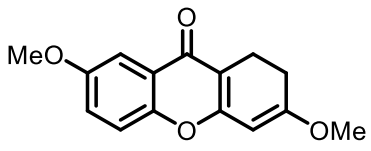
White solid, 87% yield. m.p. = 46 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 7.31 (d, *J* = 3.1 Hz, 1H), 7.16 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.96 (d, *J* = 9.1 Hz, 1H), 4.74 (q, *J* = 8.3 Hz, 2H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 156.5, 152.2, 125.1, 122.8 (q, *J* = 277.2 Hz), 118.8, 111.8, 110.4, 60.7 (q, *J* = 37.3 Hz), 55.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6.

HRESIMS calcd for $C_{10}H_8F_3O_4$ $[M - H]^-$ 249.0375, found 249.0373.



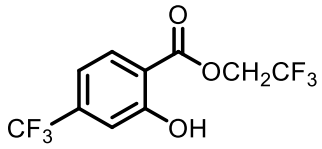
3al

Yellow solid, 86% yield. m.p. = 182 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 3.1 Hz, 1H), 7.30 (d, *J* = 9.0 Hz, 1H), 7.16 (dd, *J* = 9.1, 3.1 Hz, 1H), 5.35 (s, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 2.91 (t, *J* = 8.9 Hz, 2H), 2.51 (t, *J* = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 170.2, 162.5, 156.5, 150.3, 124.5, 122.0, 118.8, 108.2, 105.2, 91.2, 55.9, 55.9, 27.3, 18.6.

HRESIMS calcd for $C_{15}H_{15}O_4$ $[M + H]^+$ 259.0970, found 259.0970.



1am

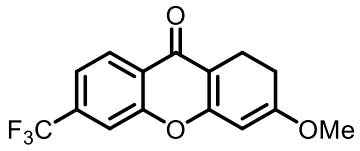
White solid, 86% yield. m.p. = 34 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.39 (s, 1H), 8.05 – 8.01 (m, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 7.19 (dd, *J* = 8.3, 1.7 Hz, 1H), 4.78 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.6, 161.8, 137.9 (q, *J* = 33.1 Hz), 131.0, 123.0 (q, *J* = 273.4 Hz), 122.6 (q, *J* = 277.3 Hz), 116.0 (q, *J* = 3.4 Hz), 115.3 (q, *J* = 4.2 Hz), 113.6, 61.1 (q, *J* = 37.4 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -64.1, -73.6.

HRESIMS calcd for $C_{10}H_5F_6O_3$ $[M - H]^-$ 287.0143, found 287.0145.



3am

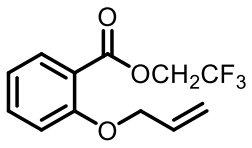
Yellow solid, 73% yield. m.p. = 134 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.68 (s, 1H), 7.62 – 7.55 (m, 1H), 5.40 (s, 1H), 3.84 (s, 4H), 2.94 (t, *J* = 9.0 Hz, 2H), 2.56 (t, *J* = 9.0 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.4, 171.4, 163.5, 154.9, 133.9 (q, *J* = 33.2 Hz), 126.9, 126.3, 123.3 (q, *J* = 272.9 Hz), 120.9 (q, *J* = 3.8 Hz), 115.3 (q, *J* = 4.3 Hz), 109.5, 90.9, 56.1, 27.2, 18.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.9.

HRESIMS calcd for $C_{15}H_{12}F_3O_2$ $[M + H]^+$ 297.0739, found 297.0741.



S1

A mixture of **1a** (5 mmol, 1.0 equiv), potassium carbonate (10 mmol, 2.0 equiv), and allyl bromide (6 mmol, 1.2 equiv) in 8 mL of DMF was heated to 80 °C for 2 h. TLC analysis indicated that the reaction

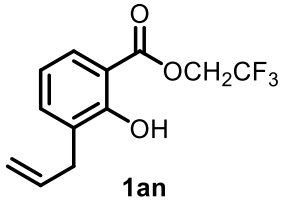
had ceased. After cooling to room temperature, the solution was diluted with EtOAc (50 mL) and washed with water (50 mL × 2) and brine (50 mL × 2). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to give **S1** as colorless oil in 86% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.51 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.09 (ddt, *J* = 17.2, 10.4, 5.1 Hz, 1H), 5.52 (dq, *J* = 17.3, 1.7 Hz, 1H), 5.33 (dq, *J* = 10.6, 1.5 Hz, 1H), 4.72 – 4.64 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 164.2, 158.8, 134.5, 132.5, 132.2, 123.3 (q, *J* = 277.3 Hz), 120.4, 118.3, 117.8, 113.6, 69.6, 60.6 (q, *J* = 36.4 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.5.

HRESIMS calcd for $C_{12}H_{12}F_3O_3$ $[M + H]^+$ 541.4049, found 531.4053.



1an

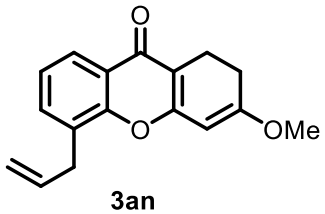
Compound **S1** (1.00 g, 3.85 mmol) was neatly heated at 200 °C for 12 h, which resulted in the crude brownish oil that was purified by flash chromatography to get compound **1an** as pale-yellow oil (0.87 g, 87% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 10.56 (s, 1H), 7.81 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.42 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.13 – 5.95 (m, 1H), 5.12 (dq, *J* = 13.8, 1.9 Hz, 2H), 4.74 (q, *J* = 8.3 Hz, 2H), 3.47 (d, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 159.9, 136.9, 135.9, 128.9, 128.1, 122.9 (q, *J* = 277.3 Hz), 119.2, 116.1, 110.5, 60.8 (q, *J* = 36.9 Hz), 33.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6.

HRESIMS calcd for $C_{12}H_{10}F_3O_3$ $[M - H]^-$ 259.0582, found 259.0579.



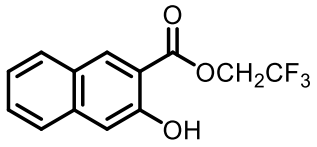
3an

Yellow solid, 88% yield. m.p. = 123 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 6.02 (ddt, *J* = 20.0, 9.7, 6.6 Hz, 1H), 5.36 (s, 1H), 5.16 – 5.08 (m, 2H), 3.80 (s, 3H), 3.61 (d, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 8.9 Hz, 2H), 2.50 (t, *J* = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 170.4, 162.3, 153.4, 135.6, 132.5, 128.7, 124.1, 124.0, 123.8, 116.6, 108.6, 91.1, 56.0, 33.6, 27.3, 18.5.

HRESIMS calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1178, found 269.1179.



1ao

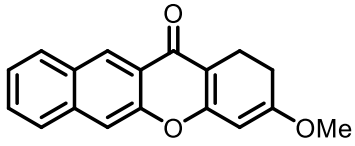
Yellow solid, 83% yield. m.p. = 78 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.90 (s, 1H), 8.56 (s, 1H), 7.86 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.41 – 7.35 (m, 2H), 4.82 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 156.1, 138.4, 133.0, 129.8, 129.4, 127.1, 126.4, 124.3, 122.9 (d, *J* = 277.3 Hz), 112.7, 112.1, 61.0 (q, *J* = 37.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -73.4.

HRESIMS calcd for $C_{13}H_8O_3F_3$ $[M - H]^-$ 269.0426, found 269.0431.



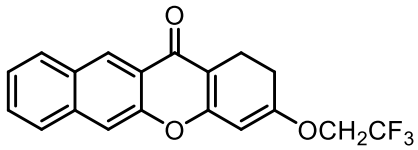
3ao

Yellow solid, 78% yield. m.p. = 150 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.79 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.81 (s, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.46 (m, 1H), 5.42 (s, 1H), 3.84 (s, 3H), 2.97 (t, *J* = 8.9 Hz, 2H), 2.56 (t, *J* = 8.9 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.0, 171.2, 163.6, 152.2, 135.2, 130.2, 129.5, 128.1, 127.1, 126.4, 125.5, 123.2, 113.5, 107.3, 91.6, 56.0, 27.4, 18.6.

HRESIMS calcd for $C_{18}H_{15}O_3$ $[M + H]^+$ 279.1021, found 279.1006.



3i

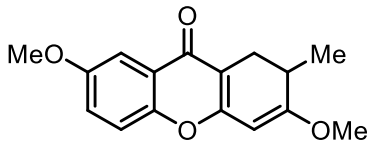
Yellow solid, 76% yield. m.p. = 128 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.80 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.83 (s, 1H), 7.60 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 1H), 7.52 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 5.45 (s, 1H), 4.35 (q, *J* = 7.8 Hz, 2H), 3.01 (t, *J* = 9.1 Hz, 2H), 2.66 (t, *J* = 9.1 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.3, 167.7, 161.8, 152.2, 135.3, 130.3, 129.6, 128.3, 127.1, 126.6, 125.7, 123.0, 122.6 (q, *J* = 277.3 Hz), 113.7, 108.2, 93.5, 65.4 (q, *J* = 36.7 Hz), 26.8, 18.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.4.

HRESIMS calcd for $C_{19}H_{14}F_3O_3$ $[M + H]^+$ 347.0895, found 347.0902.



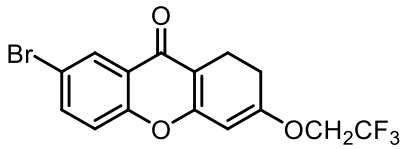
3j

Yellow solid, 84% yield. m.p. = 123 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 3.1 Hz, 1H), 7.32 (d, *J* = 9.1 Hz, 1H), 7.18 (dd, *J* = 9.1, 3.1 Hz, 1H), 5.33 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 2.94 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.79 (dd, *J* = 16.3, 6.2 Hz, 1H), 2.64 (dt, *J* = 13.9, 7.0 Hz, 1H), 1.15 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 174.5, 161.9, 156.5, 150.3, 124.5, 122.1, 118.8, 107.1, 105.2, 90.2, 56.1, 55.9, 32.6, 26.6, 17.3.

HRESIMS calcd for $C_{16}H_{17}O_4$ $[M + H]^+$ 273.1127, found 273.1129.



3k

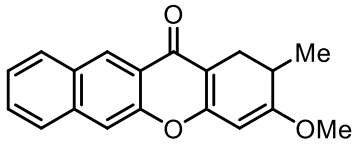
White solid, 53% yield. m.p. = 180 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 2.5 Hz, 1H), 7.66 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 5.36 (s, 1H), 4.32 (q, *J* = 7.8 Hz, 2H), 2.92 (t, *J* = 9.1 Hz, 2H), 2.60 (t, *J* = 9.1 Hz, 2H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.2, 167.5, 161.2, 154.3, 135.5, 128.3, 125.3, 122.6 (q, *J* = 277.6 Hz), 119.5, 118.1, 109.8, 93.0, 65.4 (q, *J* = 36.4 Hz), 26.6, 18.4.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.5.

HRESIMS calcd for $C_{15}H_{11}BrF_3O_2$ $[M + H]^+$ 374.9844, found 374.9846.



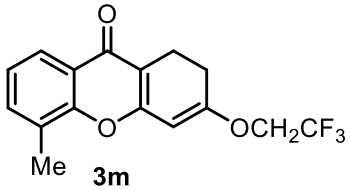
3l

Yellow solid, 86% yield. m.p. = 112 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 2.6 Hz, 1H), 8.06 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.90 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.52 – 7.48 (m, 1H), 5.41 (d, *J* = 2.6 Hz, 1H), 3.85 (d, *J* = 2.6 Hz, 3H), 3.00 (ddd, *J* = 16.2, 7.8, 2.7 Hz, 1H), 2.84 (ddd, *J* = 16.2, 6.3, 2.7 Hz, 1H), 2.69 (tt, *J* = 7.1, 3.6 Hz, 1H), 1.20 (dd, *J* = 7.2, 2.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.5, 175.4, 163.0, 152.3, 135.2, 130.2, 129.5, 128.1, 127.1, 126.4, 125.5, 123.2, 113.5, 106.2, 90.5, 56.2, 32.8, 26.6, 17.3.

HRESIMS calcd for $C_{19}H_{17}O_3$ $[M + H]^+$ 293.1178, found 293.1120.



3m

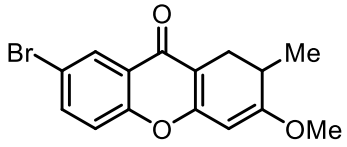
White solid, 57% yield. m.p. = 168 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.07 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.44 (ddd, *J* = 7.2, 1.8, 0.9 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 5.43 (s, 1H), 4.34 (q, *J* = 7.8 Hz, 2H), 2.95 (t, *J* = 9.1 Hz, 2H), 2.66 – 2.56 (m, 2H), 2.47 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 176.0, 166.9, 160.6, 154.1, 133.6, 126.8, 124.3, 123.8, 123.4, 122.7 (q, *J* = 277.5 Hz), 109.5, 93.2, 65.4 (q, *J* = 36.4 Hz), 26.7, 18.4, 15.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.5.

HRESIMS calcd for $C_{16}H_{14}F_3O_3$ $[M + H]^+$ 311.0895, found 311.0898.



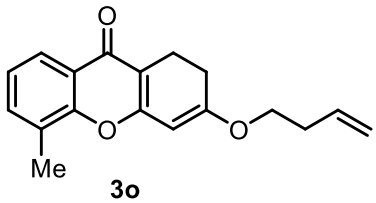
3n

Yellow solid, 58% yield. m.p. = 196 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 5.28 (s, 1H), 3.77 (s, 3H), 2.88 (dd, *J* = 16.4, 7.8 Hz, 1H), 2.71 (dd, *J* = 16.4, 6.2 Hz, 1H), 2.61 – 2.58 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 175.1, 174.4, 162.3, 154.2, 135.1, 128.2, 125.4, 119.5, 117.7, 107.8, 90.0, 56.2, 32.6, 26.5, 17.3.

HRESIMS calcd for $C_{15}H_{14}BrO_3$ $[M + H]^+$ 321.0126, found 321.0130.



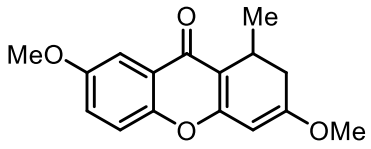
3o

Yellow solid, 72% yield. m.p. = 99 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.39 (dt, *J* = 7.2, 1.3 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 5.87 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.37 (s, 1H), 5.22 – 5.12 (m, 2H), 4.00 (t, *J* = 6.7 Hz, 2H), 2.90 (t, *J* = 8.9 Hz, 2H), 2.57 – 2.48 (m, 4H), 2.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 169.4, 162.4, 154.0, 133.7, 133.2, 126.7, 123.9, 123.8, 123.2, 117.6, 108.5, 91.6, 67.9, 33.0, 27.4, 18.5, 15.6.

HRESIMS calcd for $C_{18}H_{19}O_3$ $[M + H]^+$ 283.1334, found 283.1336.



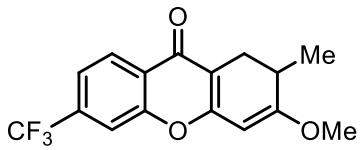
3p

Yellow solid, 76% yield. m.p. = 153 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 3.1 Hz, 1H), 7.32 (d, *J* = 9.1 Hz, 1H), 7.18 (dd, *J* = 9.1, 3.1 Hz, 1H), 5.33 (s, 1H), 3.91 (s, 3H), 3.80 (s, 3H), 2.94 (dd, *J* = 16.3, 7.8 Hz, 1H), 2.79 (dd, *J* = 16.3, 6.2 Hz, 1H), 2.64 (dt, *J* = 13.9, 7.0 Hz, 1H), 1.15 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 174.5, 161.9, 156.5, 150.3, 124.5, 122.1, 118.8, 107.1, 105.2, 90.2, 56.1, 55.9, 32.6, 26.6, 17.3.

HRESIMS calcd for $C_{16}H_{17}O_4$ $[M + H]^+$ 273.1127, found 273.1131.



3q

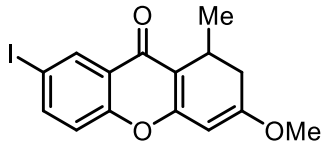
White solid, 59% yield. m.p. = 139 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 8.2 Hz, 1H), 7.63 (s, 1H), 7.55 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.32 (s, 1H), 3.80 (s, 3H), 2.91 (dd, *J* = 16.4, 7.8 Hz, 1H), 2.76 (dd, *J* = 16.4, 6.3 Hz, 1H), 2.63 (h, *J* = 7.0 Hz, 1H), 1.14 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.5 , 174.7 , 162.8 , 154.9 , 133.8 (q, *J* = 33.3 Hz), 126.8 , 126.2 , 123.3 (q, *J* = 272.8 Hz), 120.7 (q, *J* = 3.6 Hz), 115.3 (q, *J* = 4.3 Hz), 108.3 , 89.8 , 56.2 , 32.6 , 26.4 , 17.2 .

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9.

HRESIMS calcd for $C_{16}H_{14}F_3O_3$ $[M + H]^+$ 311.0895, found 311.0898.



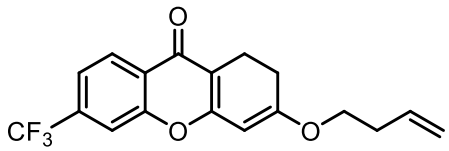
3r

White solid, 63% yield. m.p. = 178 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 2.2 Hz, 1H), 7.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.12 (d, *J* = 8.7 Hz, 1H), 5.35 (d, *J* = 2.1 Hz, 1H), 3.81 (s, 3H), 3.48 – 3.40 (m, 1H), 2.84 (ddd, *J* = 17.2, 8.4, 2.1 Hz, 1H), 2.18 (dd, *J* = 17.1, 1.2 Hz, 1H), 1.11 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 169.4, 162.1, 155.0, 140.8, 134.6, 126.0, 119.6, 114.3, 90.2, 88.2, 56.1, 34.7, 24.4, 18.1.

HRESIMS calcd for $C_{15}H_{14}IO_3$ $[M + H]^+$ 368.9988, found 368.9993.



3s

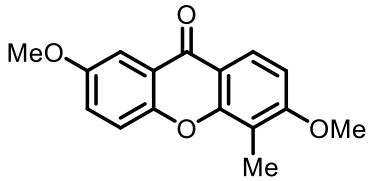
Yellow solid, 71% yield. m.p. = 140 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.34 (d, *J* = 8.2 Hz, 1H), 7.67 (s, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 5.93 – 5.84 (m, 1H), 5.38 (s, 1H), 5.24 – 5.14 (m, 2H), 4.05 – 4.01 (m, 2H), 2.93 (td, *J* = 9.0, 1.5 Hz, 2H), 2.56 (q, *J* = 9.1, 7.6 Hz, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.3, 170.6, 163.6, 154.9, 133.9 (q, *J* = 33.5 Hz), 133.5, 126.9, 126.3, 123.3 (q, *J* = 273.0 Hz), 120.8 (q, *J* = 3.4 Hz), 117.7, 115.3 (q, *J* = 3.9 Hz), 109.4, 91.3, 68.2, 32.9, 27.3, 18.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.9.

HRESIMS calcd for $C_{18}H_{16}F_3O_3$ $[M + H]^+$ 337.1052, found 337.1051.



3t

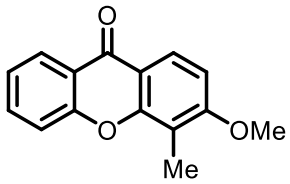
Yellow solid, 83% yield. m.p. = 168 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.9 Hz, 1H), 7.72 (d, *J* = 3.2 Hz, 1H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.32 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.9, 162.2, 155.8, 155.3, 151.2, 125.4, 124.2, 121.7, 119.2, 115.4, 113.5,

107.4, 105.9, 56.1, 55.9, 8.2.

HRESIMS calcd for $C_{16}H_{15}O_4$ $[M + H]^+$ 271.0970, found 271.0974.

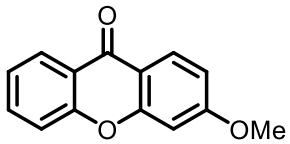


3u

Yellow solid,[1] 78% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.35 (dd, *J* = 7.9, 1.8 Hz, 1H), 8.25 (dd, *J* = 9.0, 0.7 Hz, 1H), 7.72 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.54 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.38 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.00 (d, *J* = 8.9 Hz, 1H), 4.01 (s, 3H), 2.42 (s, 3H).

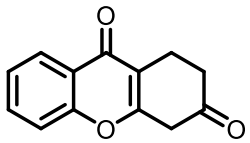
Procedures for the transformation of 3a



4

To a solution of **3a** (57 mg, 0.25 mmol) in toluene (2 mL) was added DDQ (68.1 mg, 0.3 mmol), the suspension was heated at reflux for 3 hours. After cooling, the reaction mixture was filtered, Then the filtrate was concentrated by rotary evaporator and the residue was purified by column chromatography on silica gel to afford **2h** in 97% yield as a white solid.[2]

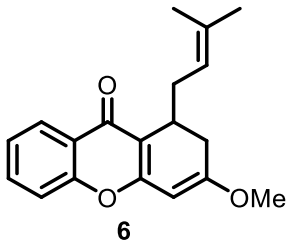
^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.33 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.25 (d, *J* = 8.9 Hz, 1H), 7.70 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.46 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.38 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.95 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 3H).



5

2 mL of HCl (1N) was added to **3a** (57 mg, 0.25 mmol) in a 25 mLof flask. The reaction mixture was heated to 70 °C for 1 h. On cooling, the mixture was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic phases were washed with an aqueous saturated $NaHCO_3$ solution (10 mL), dried (MgSO4), filtered and the solvent was removed in vacuo to give **5** (49 mg, 92%) as a white solid.[3]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.69 (ddd, *J* = 8.6, 7.0, 1.7 Hz, 1H), 7.47 – 7.41 (m, 2H), 3.59 (d, *J* = 1.2 Hz, 2H), 3.01 (tt, *J* = 6.9, 1.3 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H).



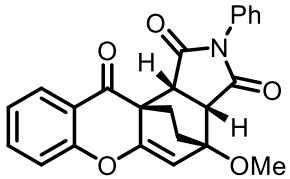
6

A 25 mL of flame-dried flask charged with compound **3a** (57 mg, 0.25 mmol) and THF (2 mL) was cooled to -78 °C. A solution of lithium diisopropylamide (2 M in THF, 0.3 mL, 0.6 mmol) was added dropwise. The solution was stirred for 30 min at -78 °C and then 3, 3-dimethylallyl bromide (95%, 69 μL, 0.6 mmol) in THF (2 mL) was added dropwise. The reaction mixture was slowly warm to 0 °C and stirred at 0 °C for another 5 hours, and then quenched with saturated solution of NH_4Cl. The aqueous phase was extracted with AcOEt (3 × 5 mL), and the combined organic layers were dried over Na_2SO_4. Column chromatography yielded **6** as an oil in 63% yield.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.23 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59 (ddd, *J* = 8.6, 7.1, 1.7 Hz, 1H), 7.41 – 7.35 (m, 2H), 5.37 (s, 1H), 5.14 (dddt, *J* = 8.5, 6.8, 3.1, 1.5 Hz, 1H), 3.81 (s, 3H), 3.02 (dd, *J* = 16.5, 4.4 Hz, 1H), 2.76 (dd, *J* = 16.6, 7.8 Hz, 1H), 2.49 (ddt, *J* = 9.1, 7.8, 4.6 Hz, 1H), 2.26 – 2.13 (m, 2H), 1.71 (s, 4H), 1.56 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.9, 173.7, 162.0, 155.5, 134.6, 132.2, 125.7, 124.4, 124.0, 120.9, 117.5, 107.7, 90.7, 56.0, 38.3, 29.8, 25.8, 23.1, 17.7.

HRESIMS calcd for $C_{19}H_{21}O_3$ $[M + H]^+$ 297.1491, found 297.1490.



7

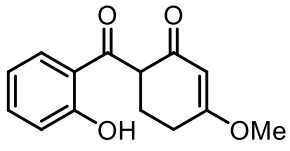
The DHX **3a** (0.3 mmol) and *N*-phenyl maleimide (1.8 mmol, 6 equiv.) in a sealed tube was heated to 100 °C for 24 hours. After cooling. The mixture was purified directly by column chromatography to furnish the product **7** as a white solid in 71% yield.

m.p. = 219 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.56 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.43 – 7.31 (m, 3H), 7.20 – 7.13 (m, 3H), 7.03 (dd, *J* = 8.4, 1.1 Hz, 1H), 5.79 (s, 1H), 4.00 (d, *J* = 8.4 Hz, 1H), 3.61 (s, 3H), 3.40 (d, *J* = 8.5 Hz, 1H), 2.28 (ddd, *J* = 12.9, 9.9, 4.9 Hz, 1H), 2.12 – 2.05 (m, 1H), 1.83 (td, *J* = 12.6, 3.6 Hz, 1H), 1.67 – 1.57 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 174.9, 173.4, 156.9, 149.8, 136.8, 131.4, 129.0, 128.7, 127.1, 126.3, 123.1, 118.2, 117.4, 106.3, 80.1, 51.5, 50.1, 46.3, 45.0, 28.9, 27.9.

HRESIMS calcd for $C_{24}H_{20}NO_5$ $[M + H]^+$ 402.1341, found 402.1340.



8

White solid, quantitative. m.p. = 135 °C.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 12.15 (s, 1H), 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.6, 7.2, 1.6 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.93 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 5.47 (s, 1H), 4.38 (dd, *J* = 8.6, 5.1 Hz, 1H), 3.75 (s, 3H), 2.74 – 2.68 (m, 1H), 2.56 – 2.44 (m, 2H), 2.26 – 2.19 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 204.3, 194.6, 178.8, 162.9, 136.7, 131.5, 119.7, 119.1, 118.5, 102.2, 56.0, 53.0, 27.3, 24.3.

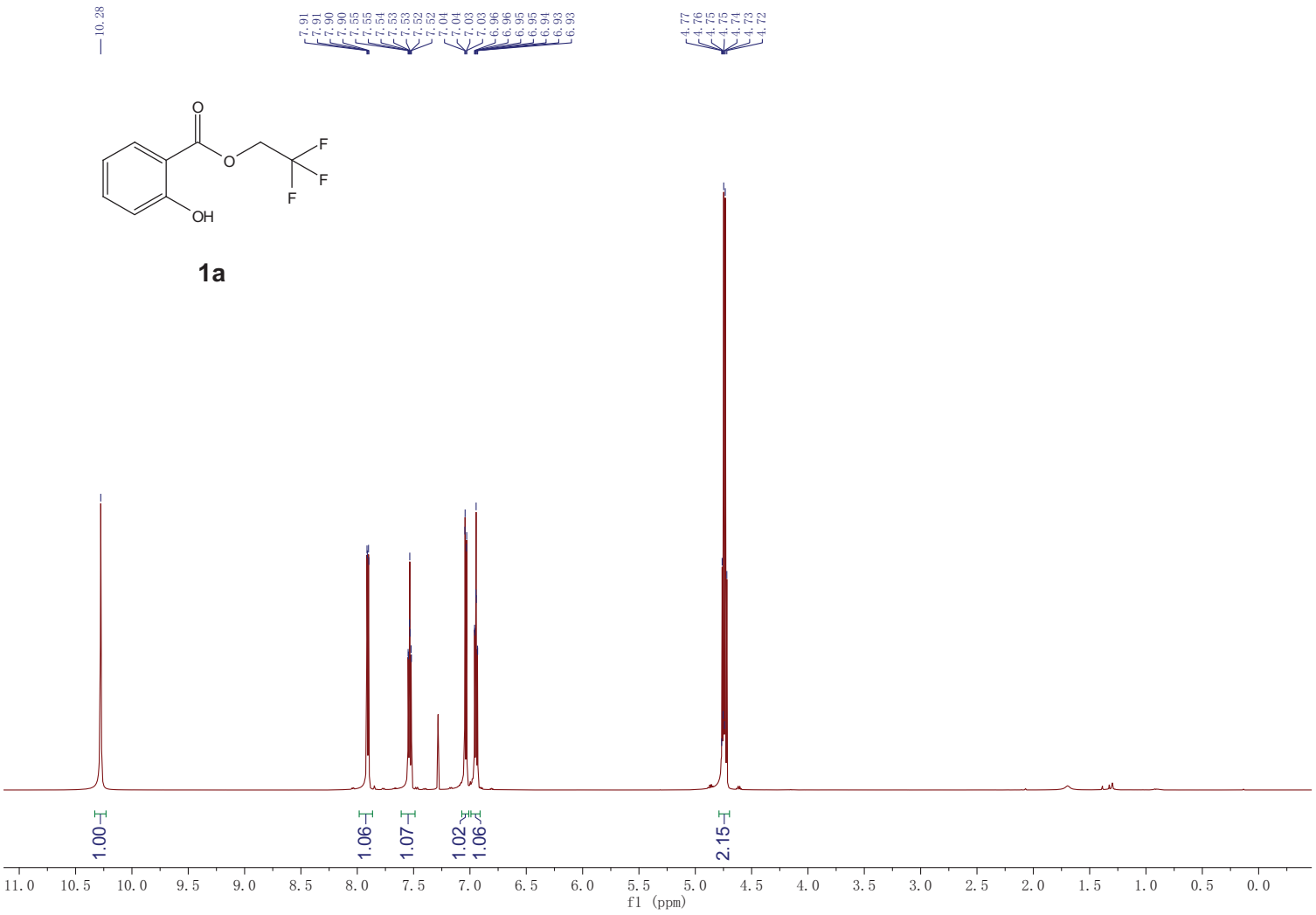
HRESIMS calcd for $C_{14}H_{13}O_4$ $[M - H]^-$ 245.0814, found 245.0816.

References

[1] Cavitt, S. B.; J. Org. Chem. 1962, 1211-1216

[2] Zhao, Jian; J. Org. Chem. **2007**, 72, 583-588.

[3] P. A. Turner a, S. a, J. L. Whatmore, M. Shipman, *Tetrahedron Lett.* **2013,** 54, 6538–6540.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6.94
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6.93
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4.76
4.75
4.75
4.74
4.73
4.72
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O
F
F
F
OH
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1.06
1.07
1.02
1.06
2.15
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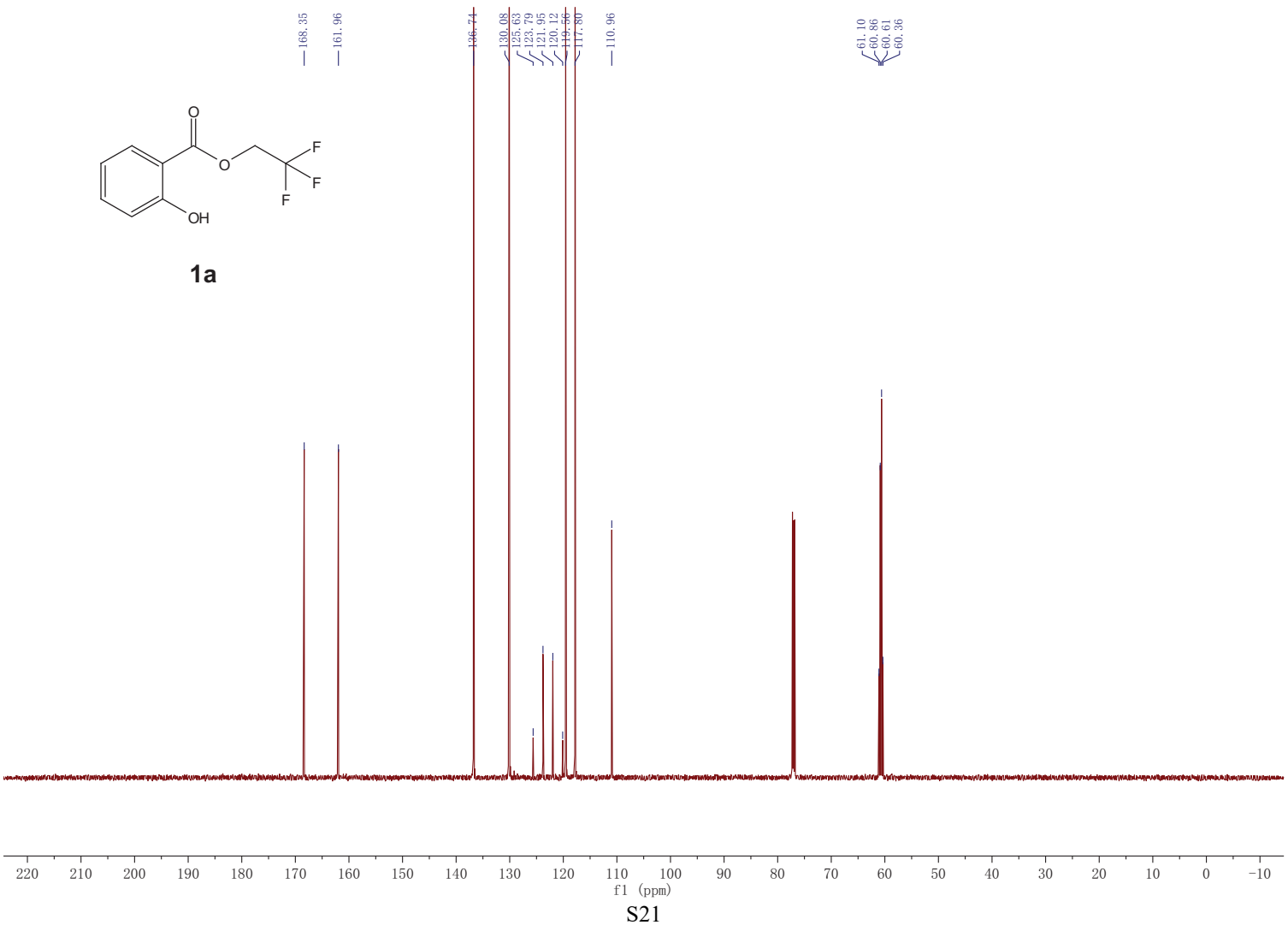
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^{19}FNMR

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F
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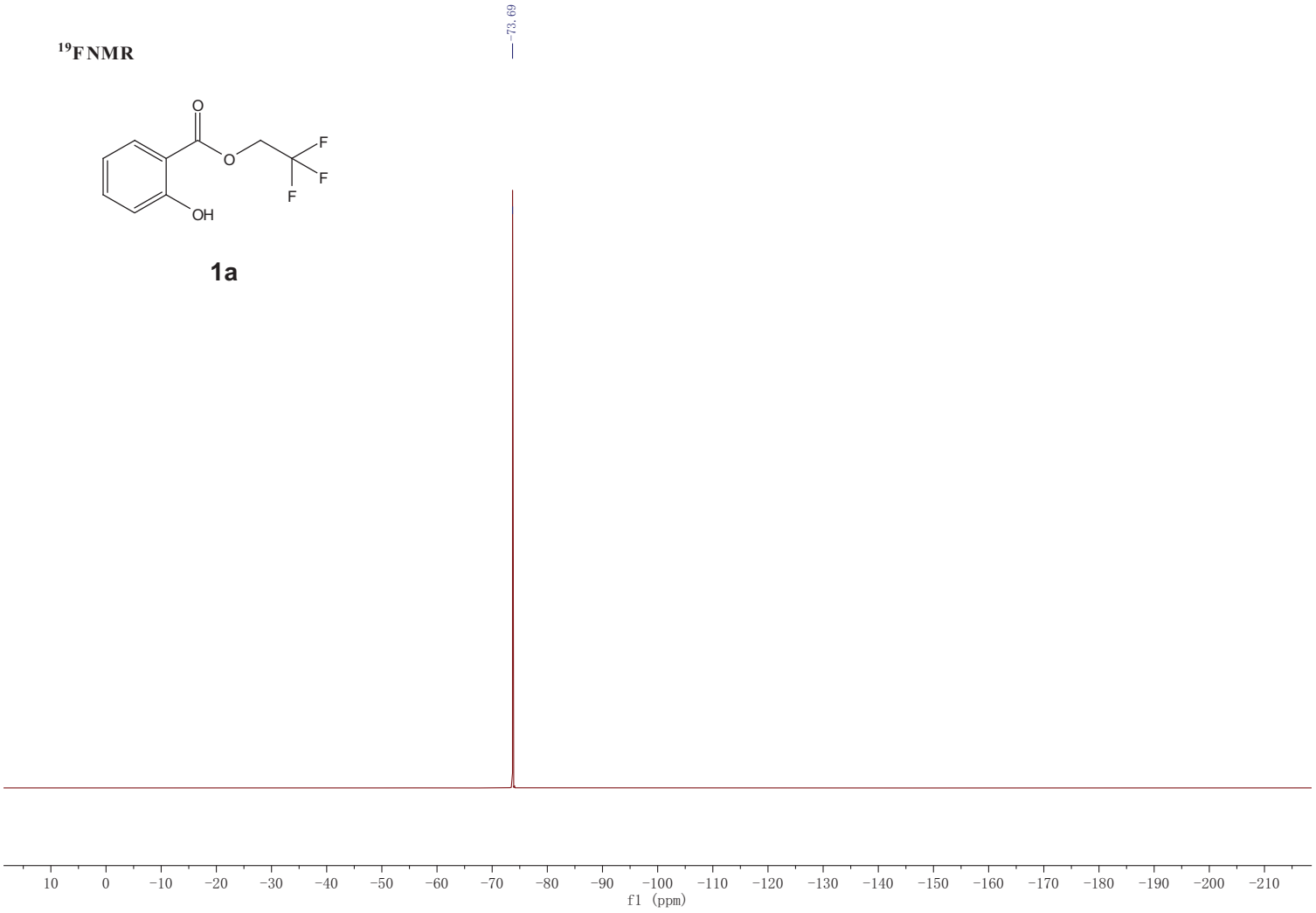
OH

1a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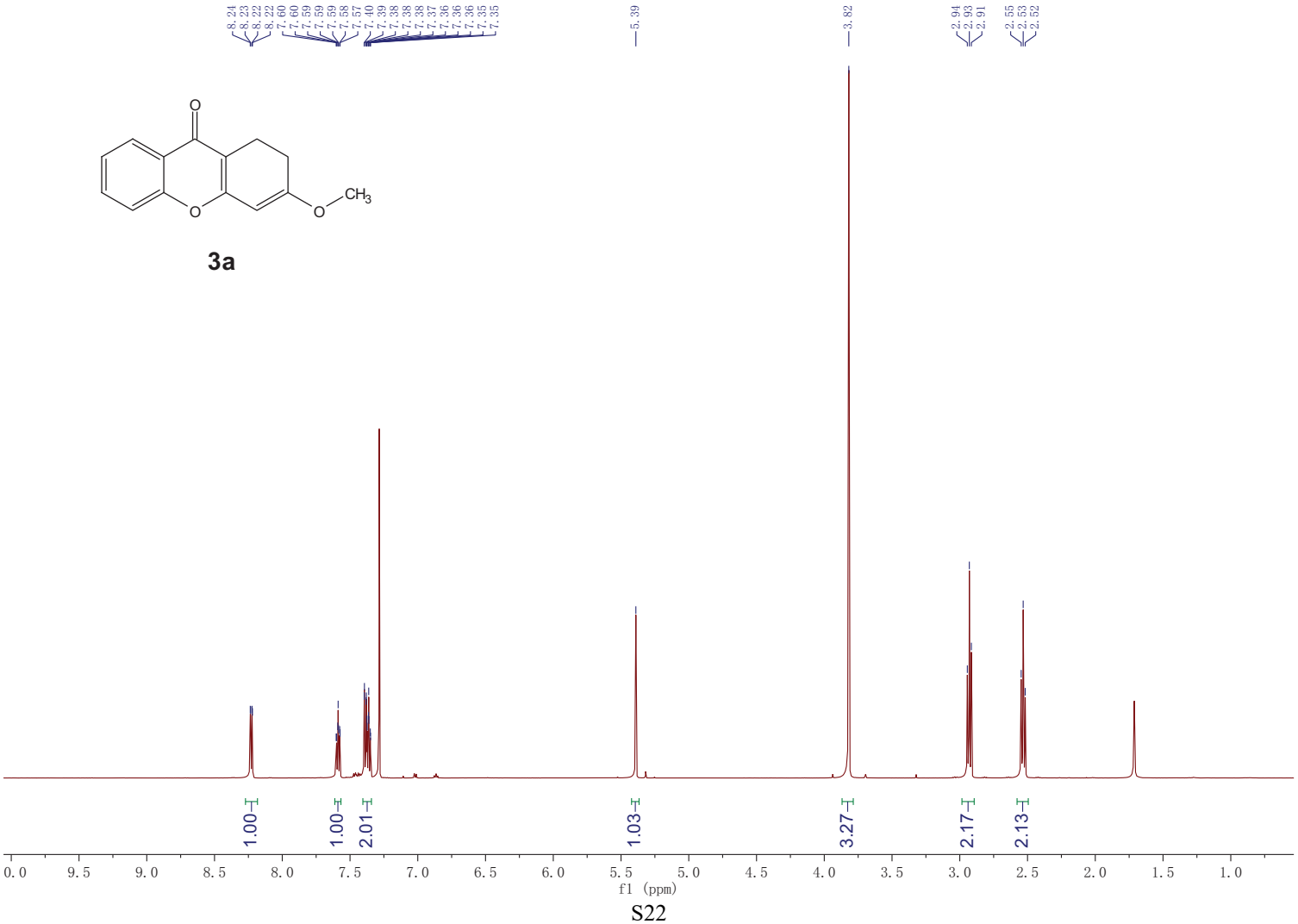
3a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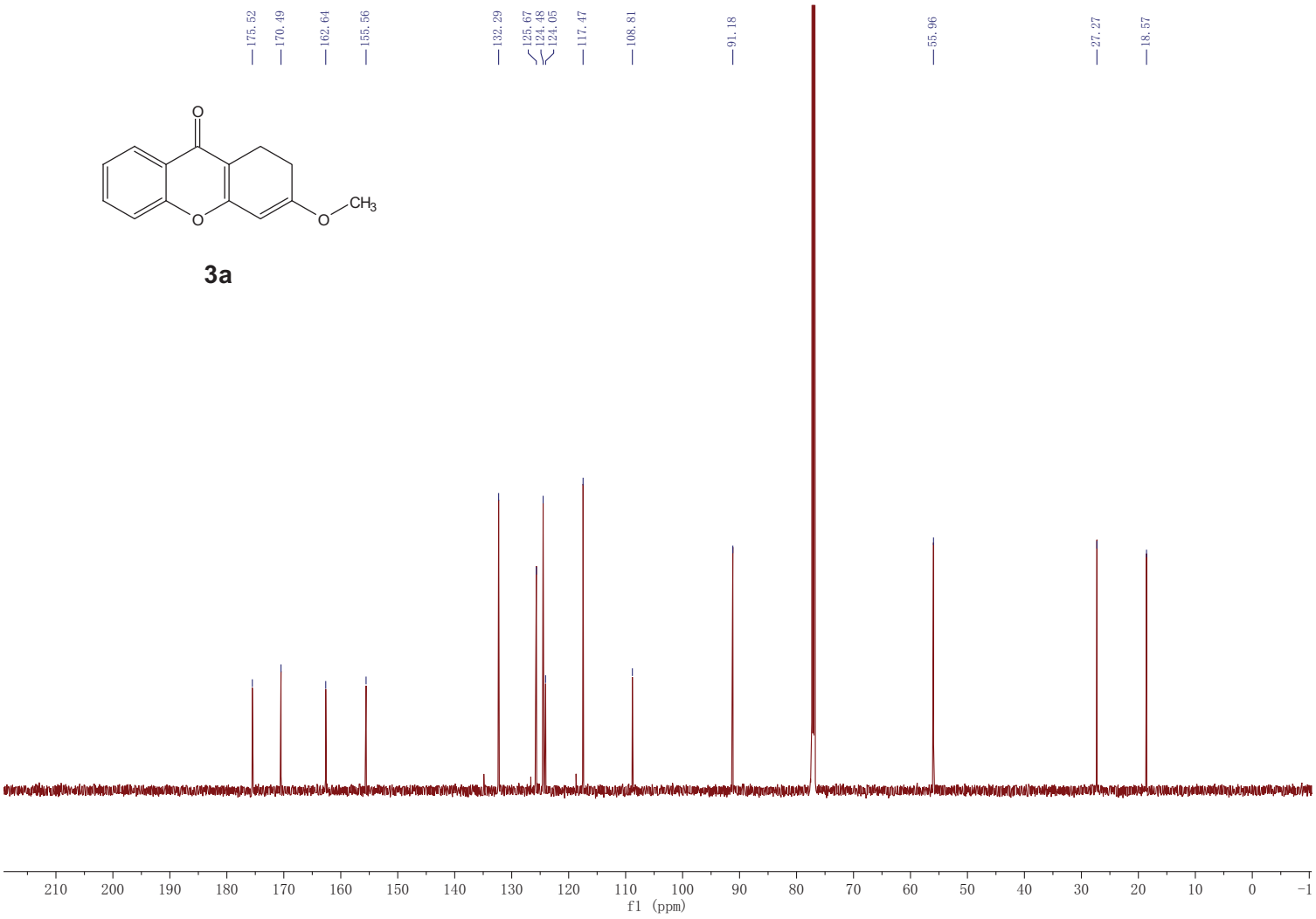
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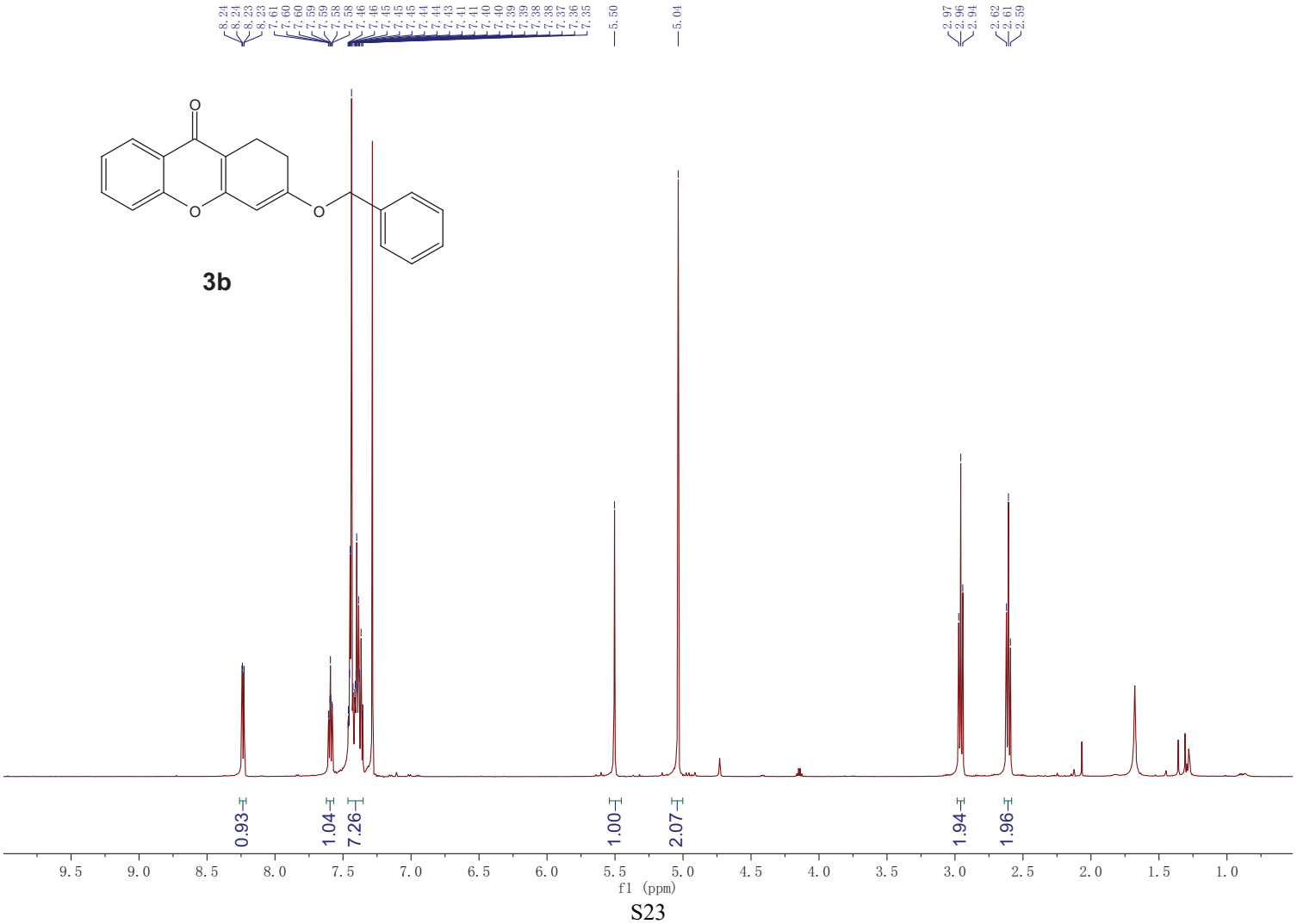
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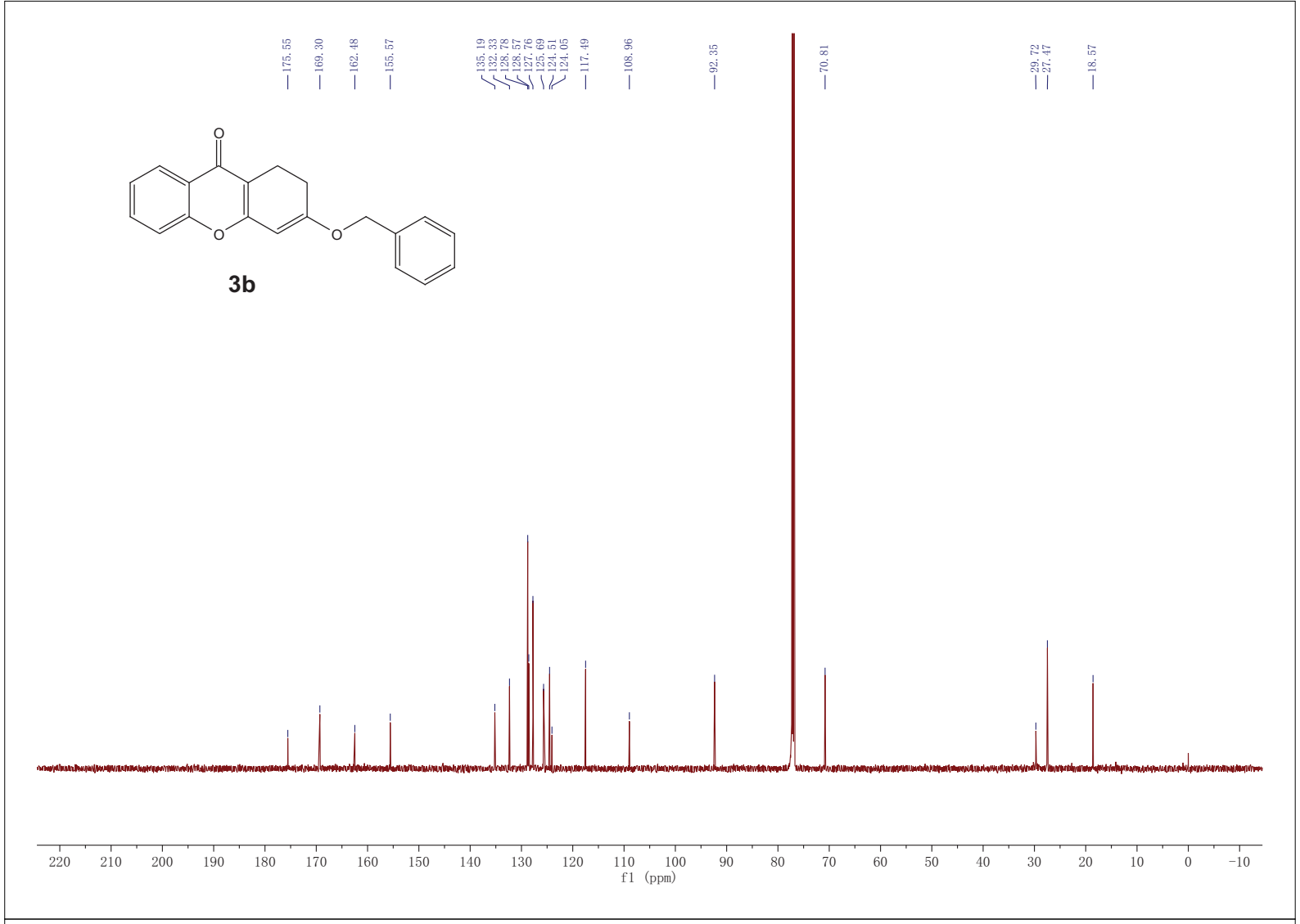
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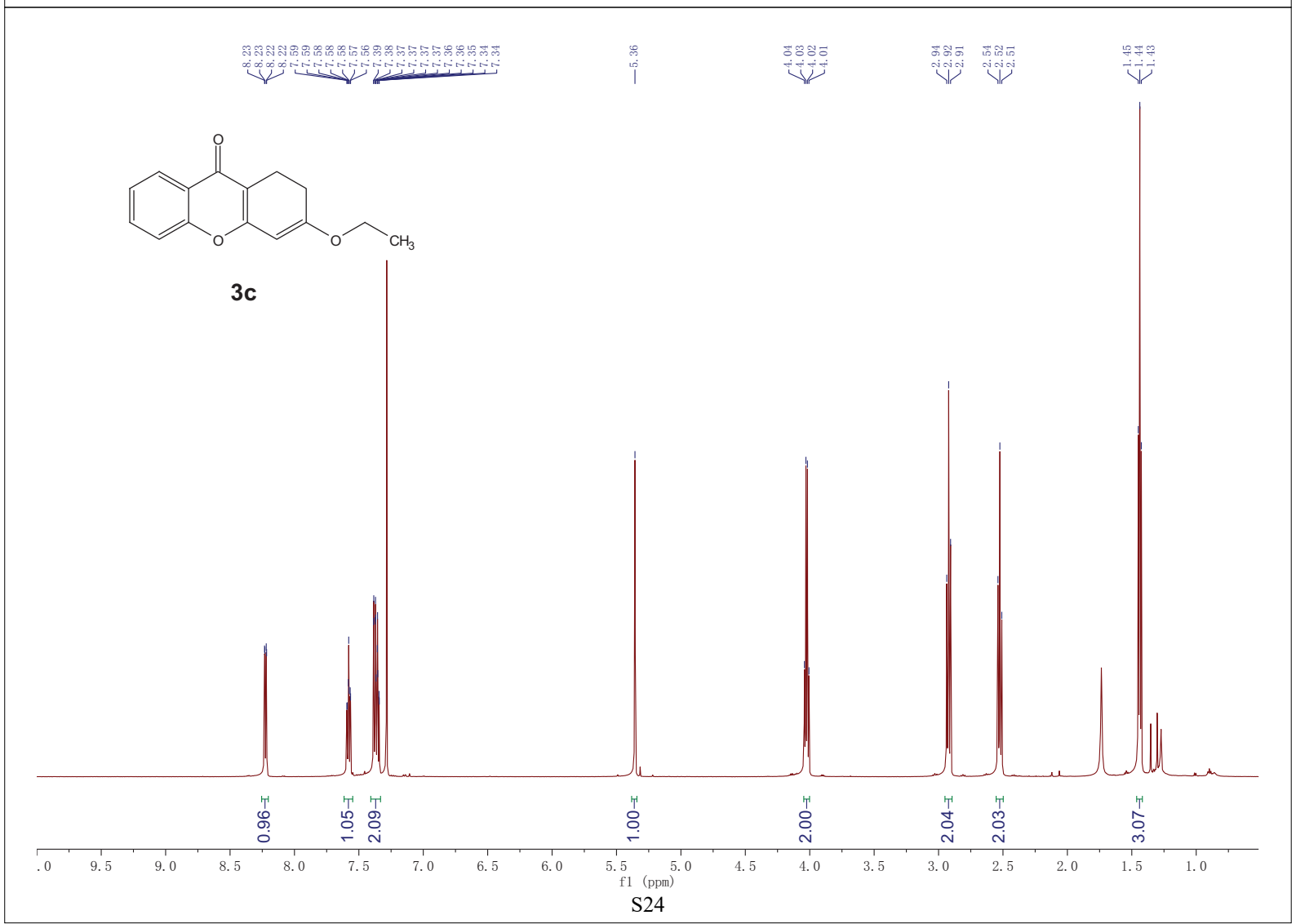
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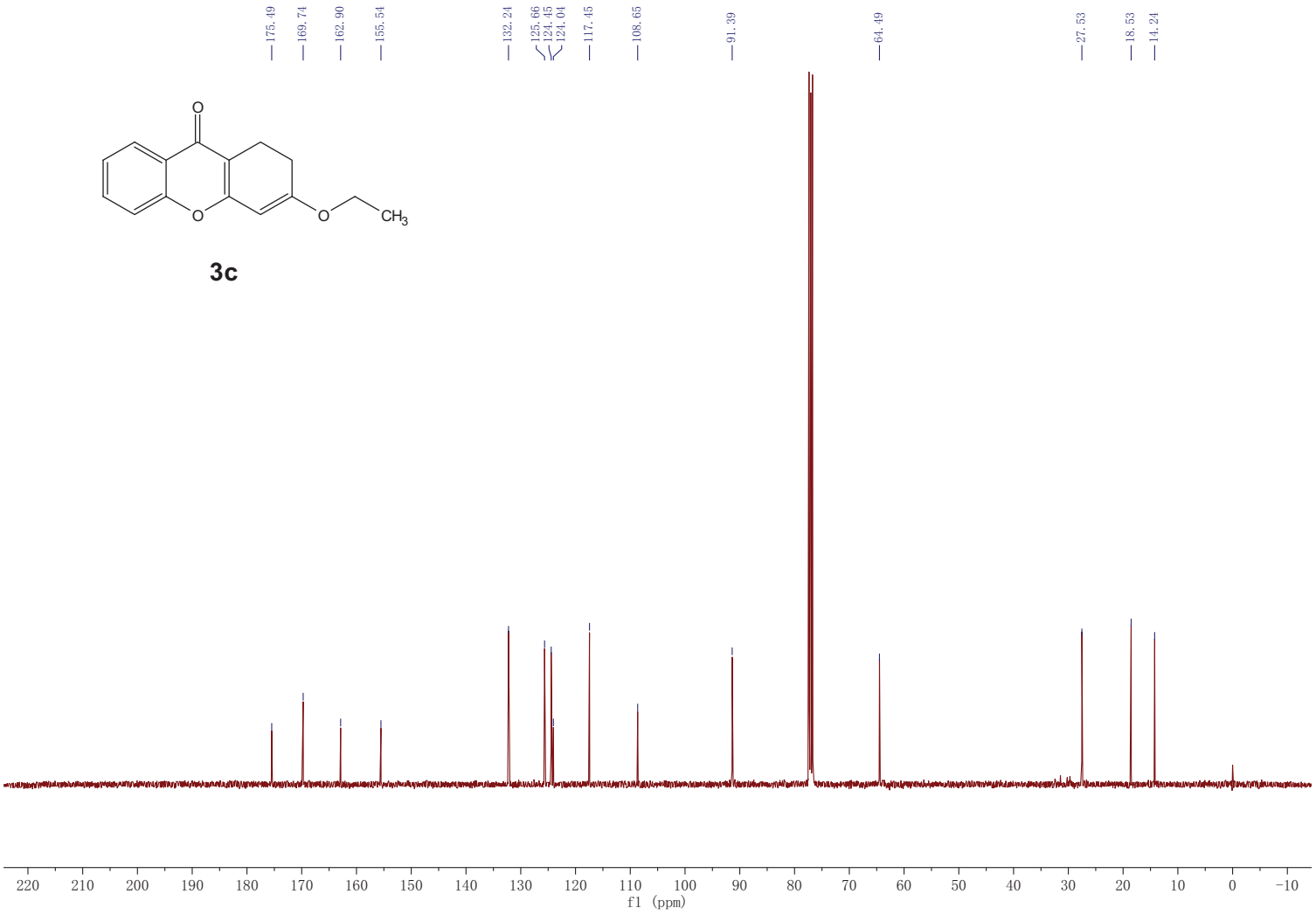
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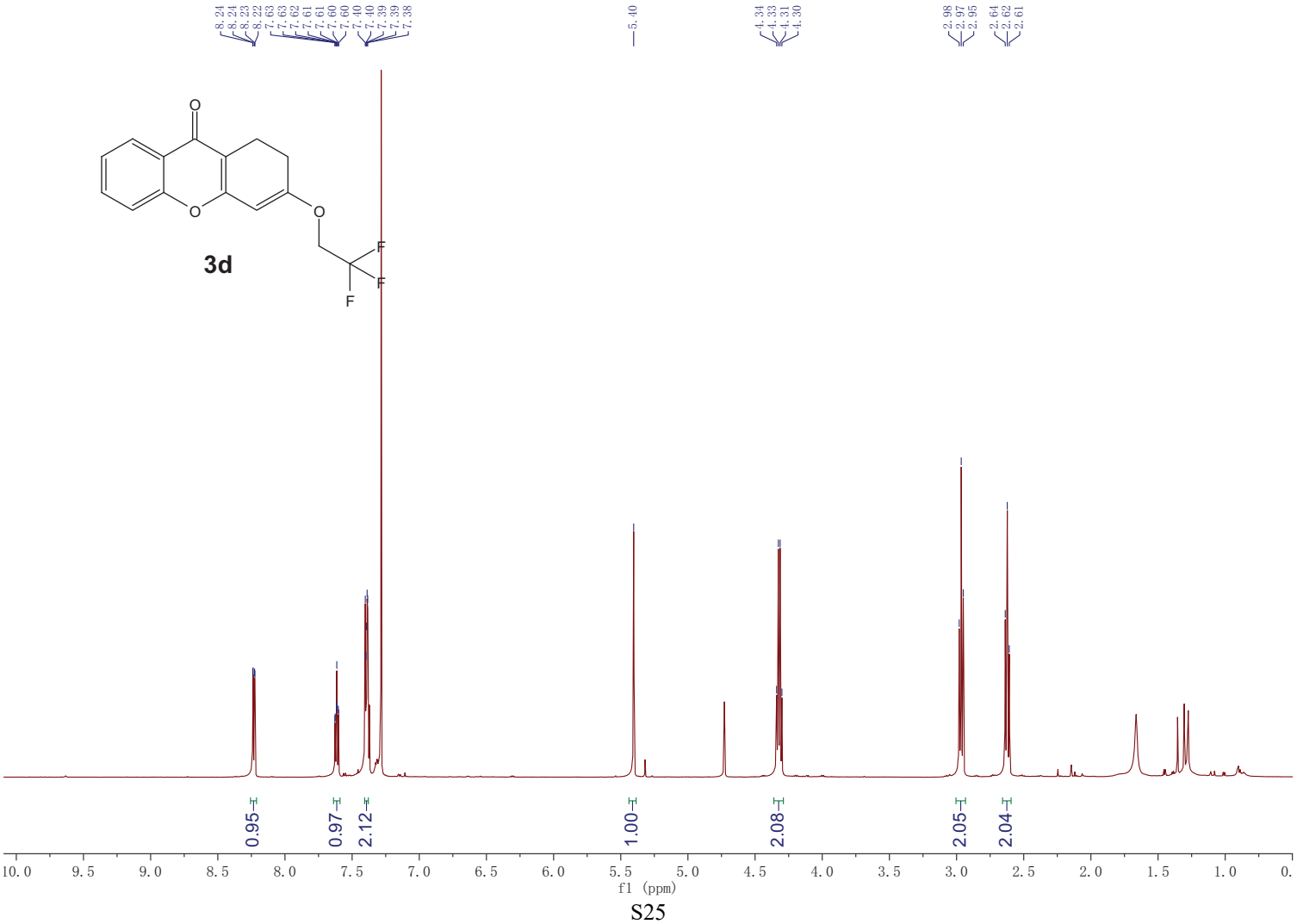
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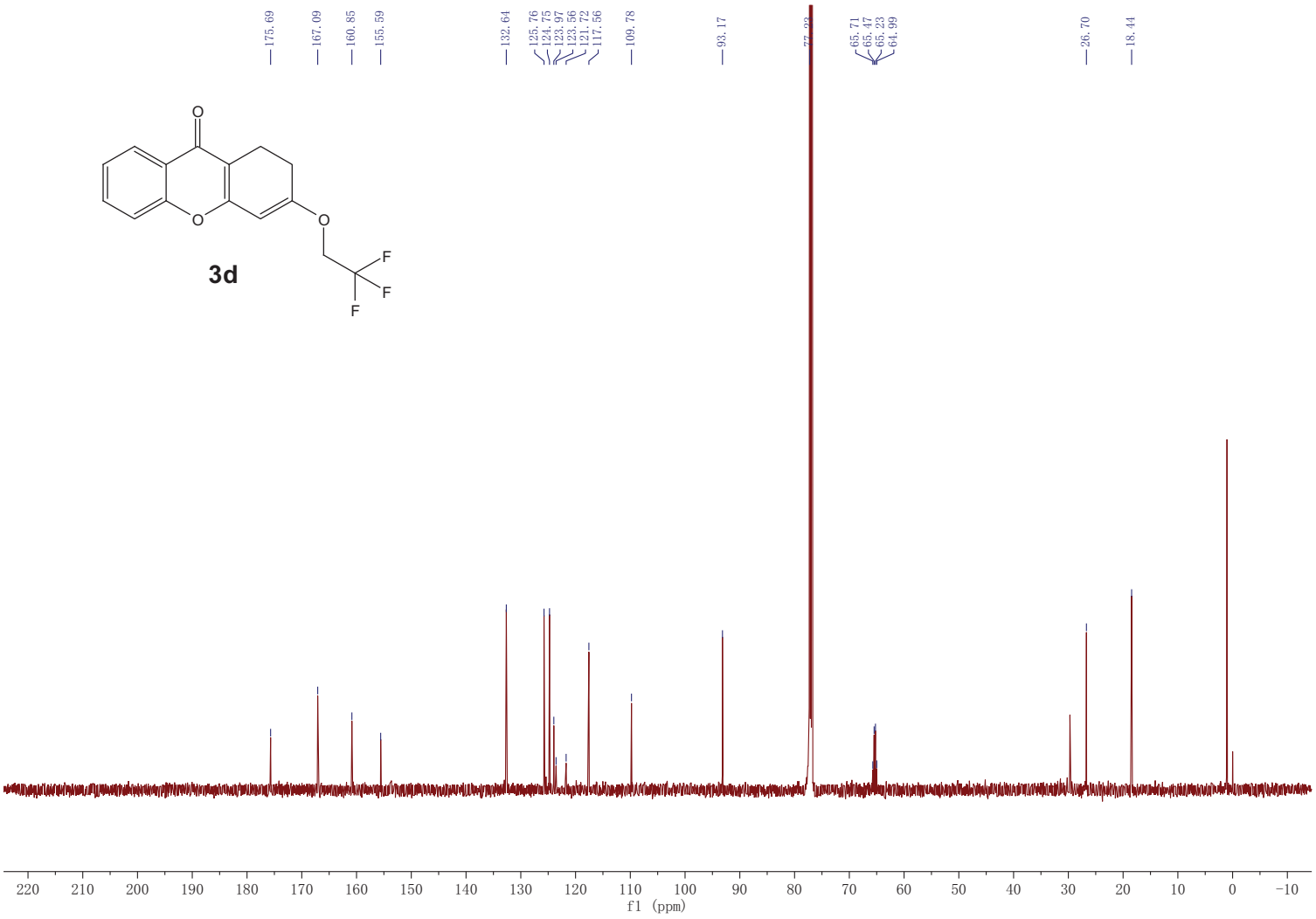
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f1 (ppm)

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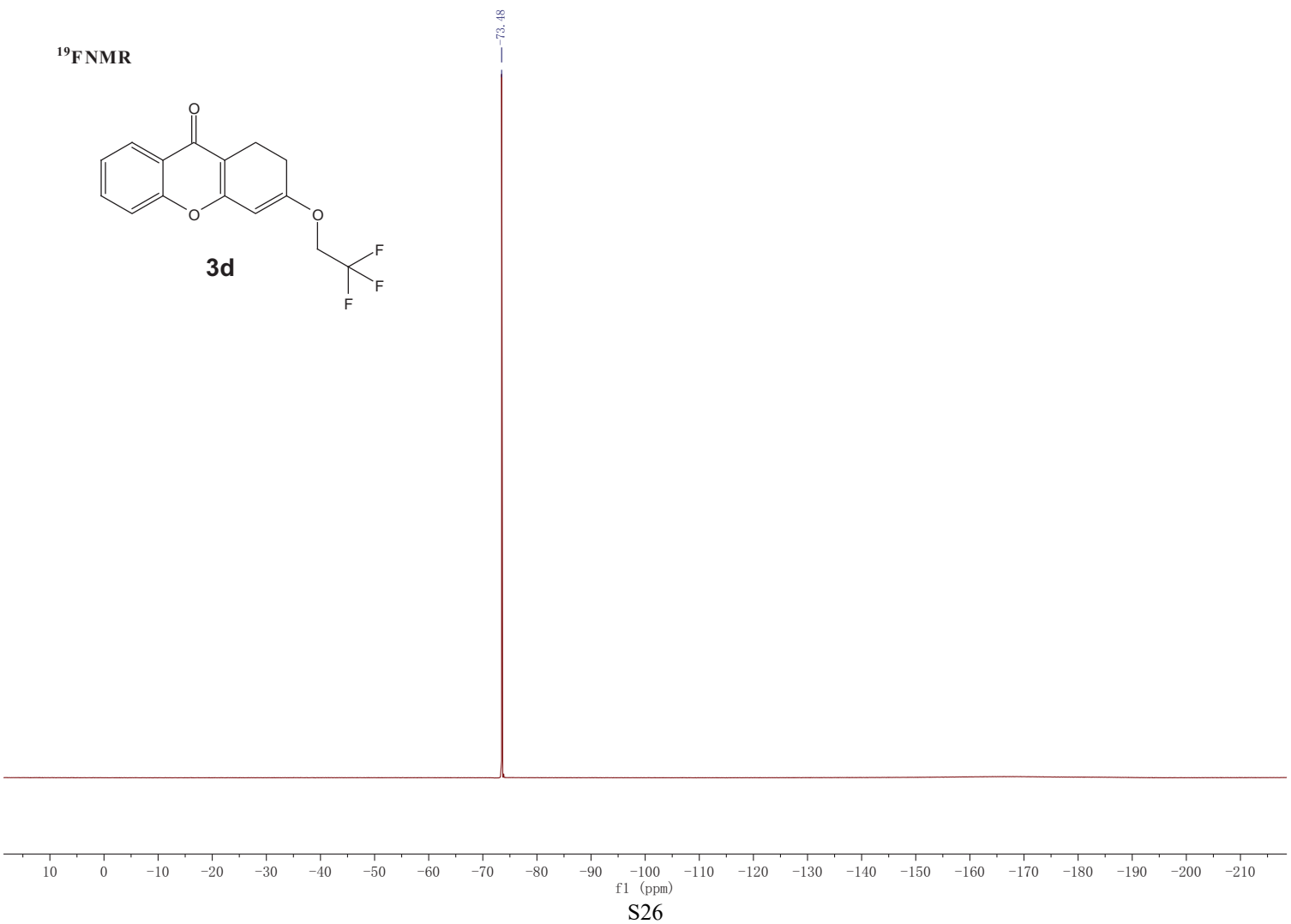
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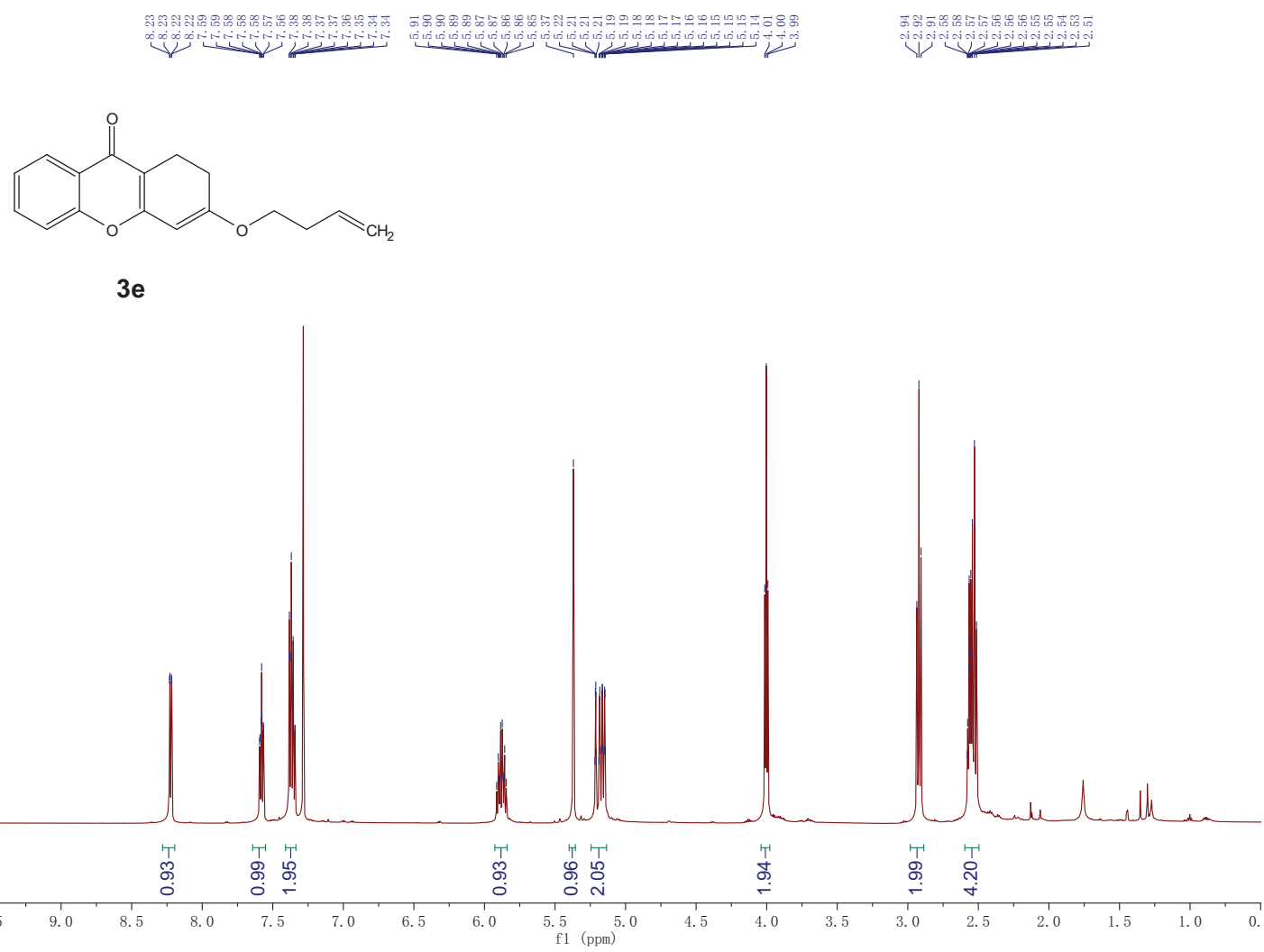
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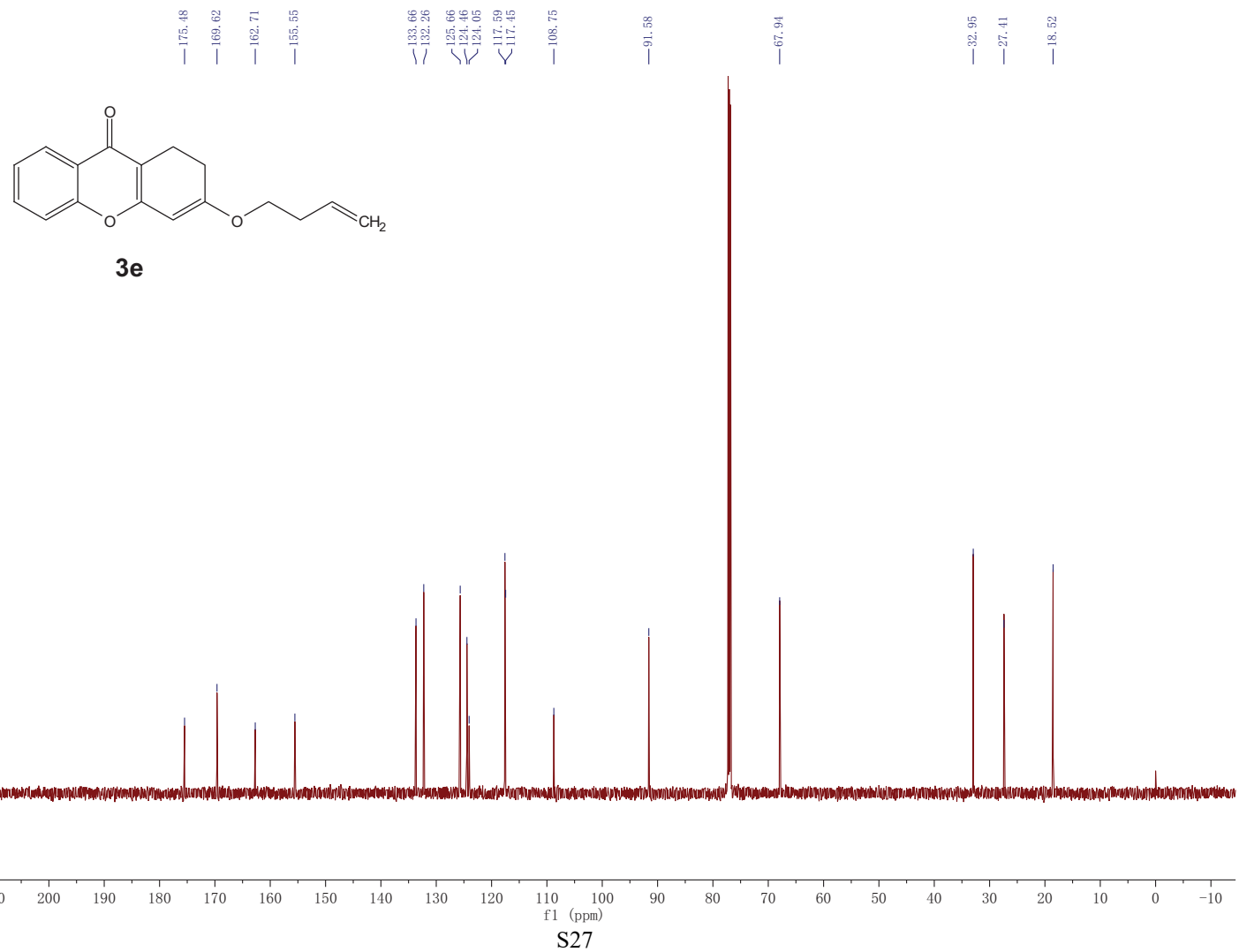
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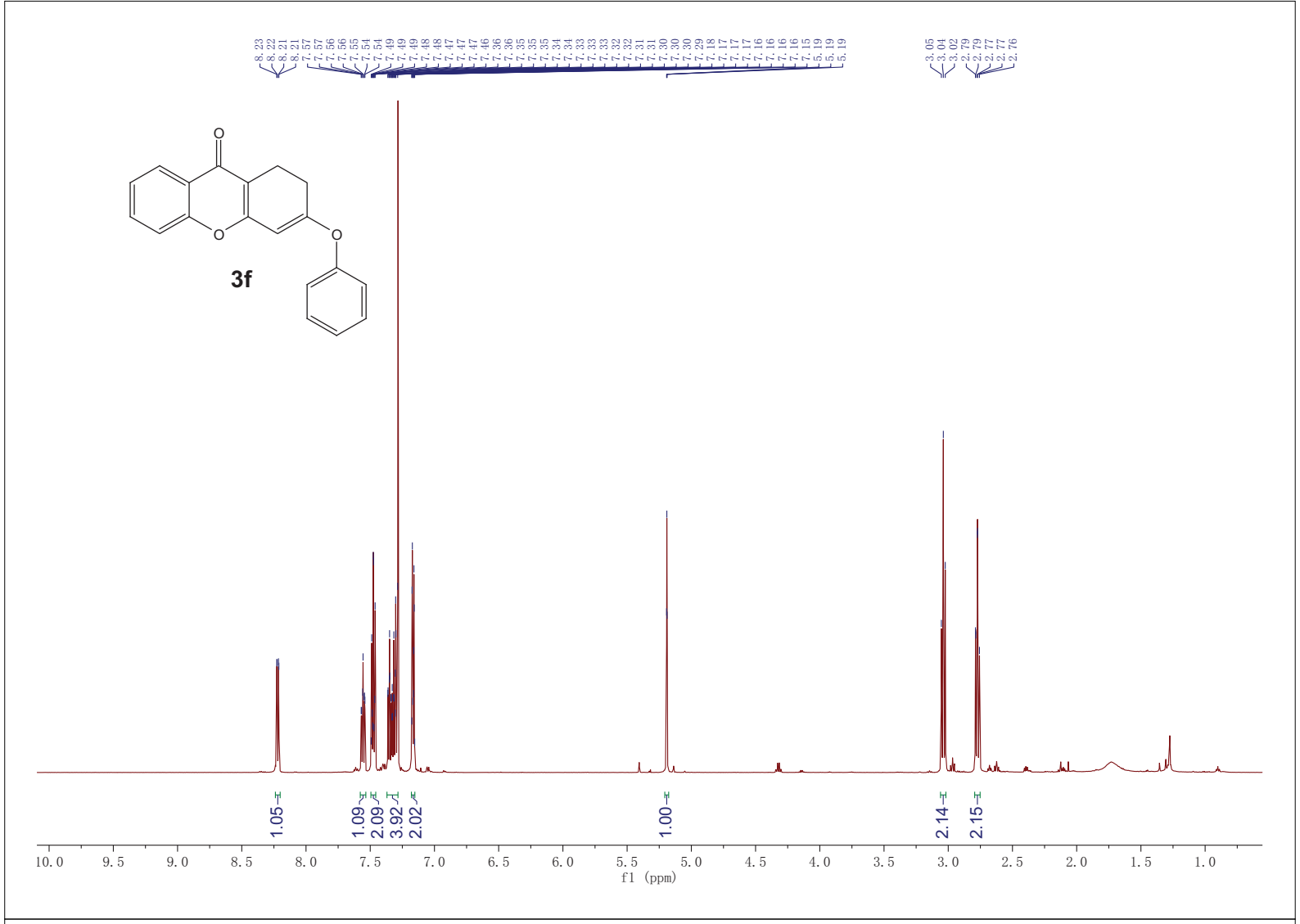
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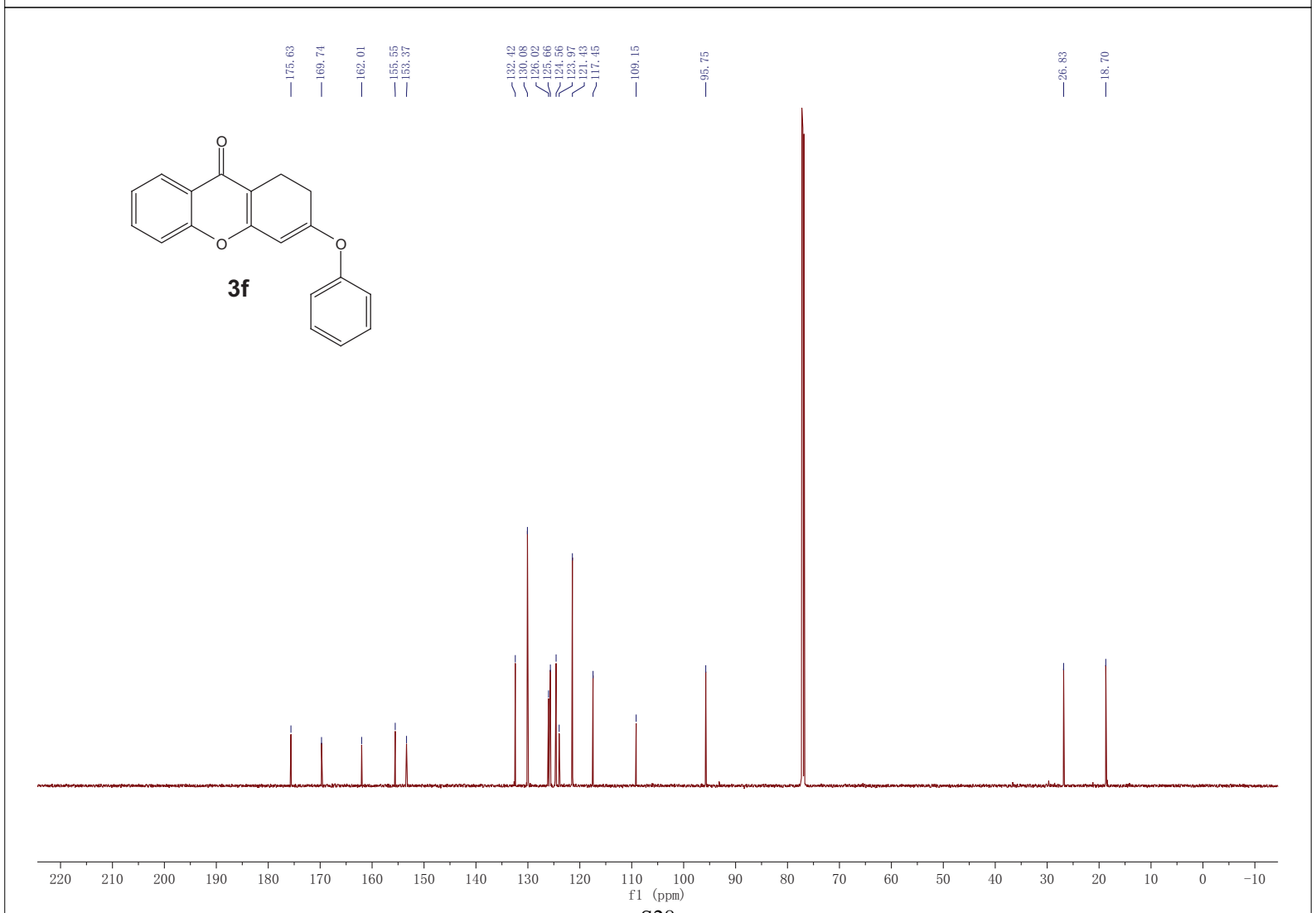
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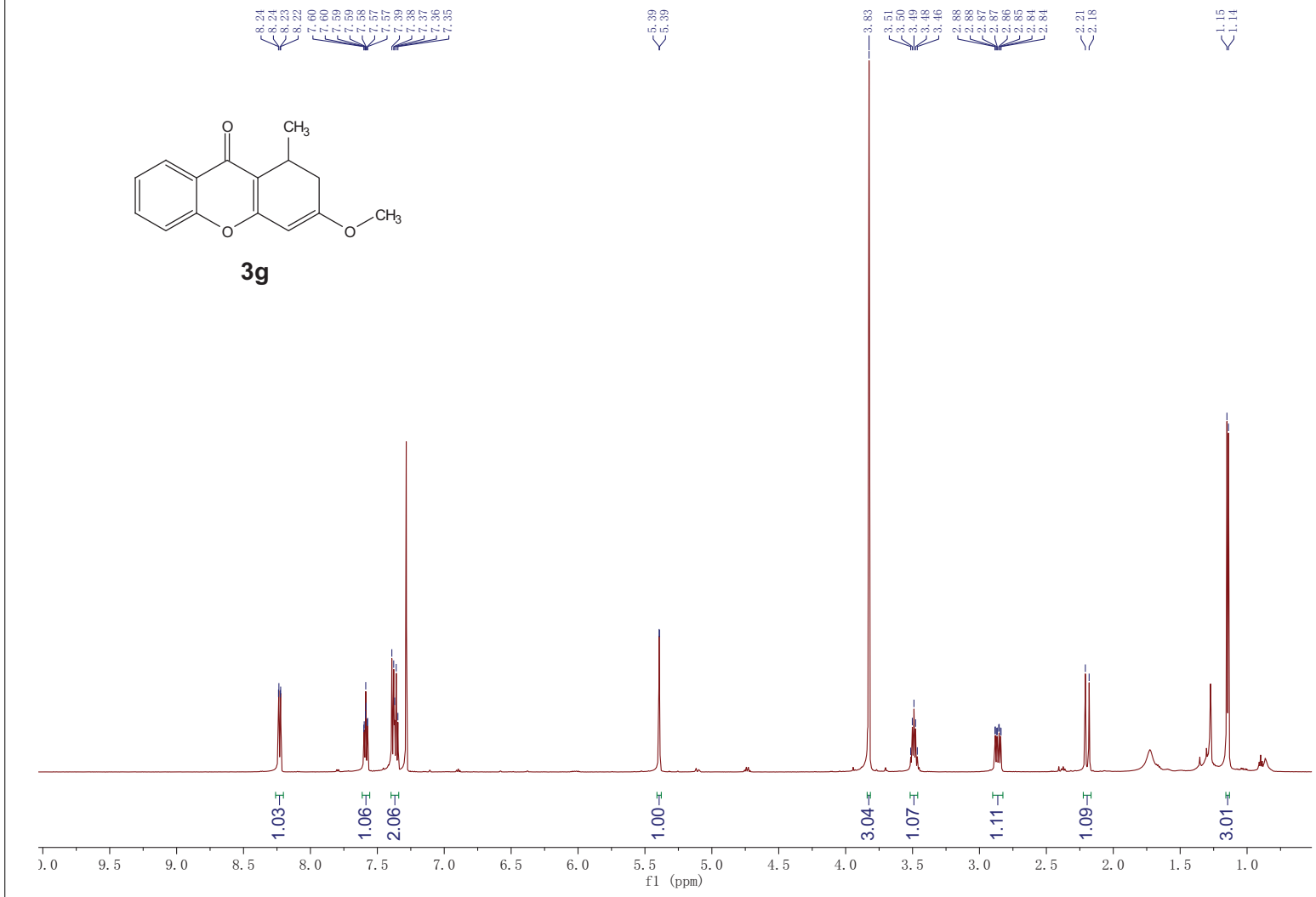
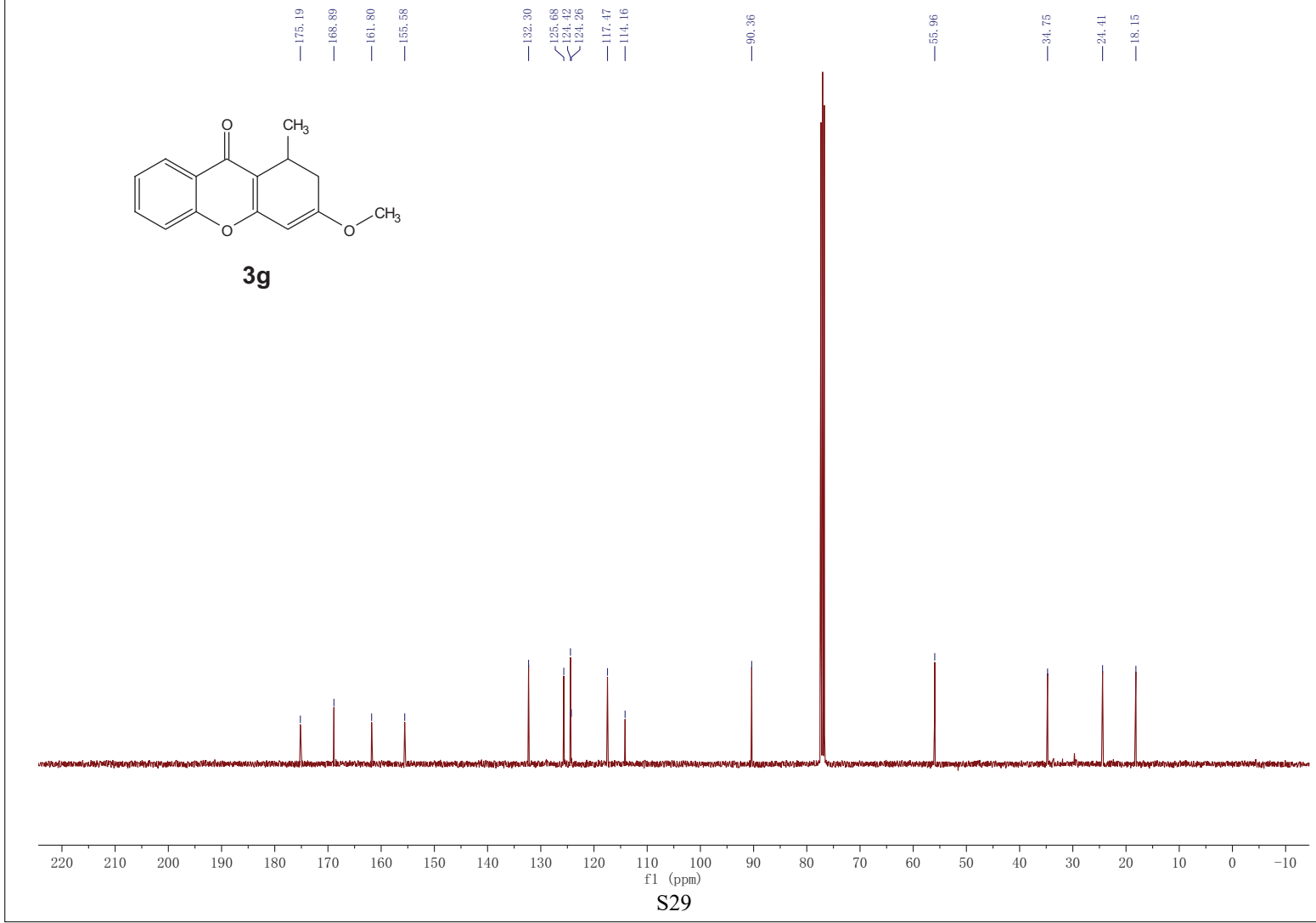
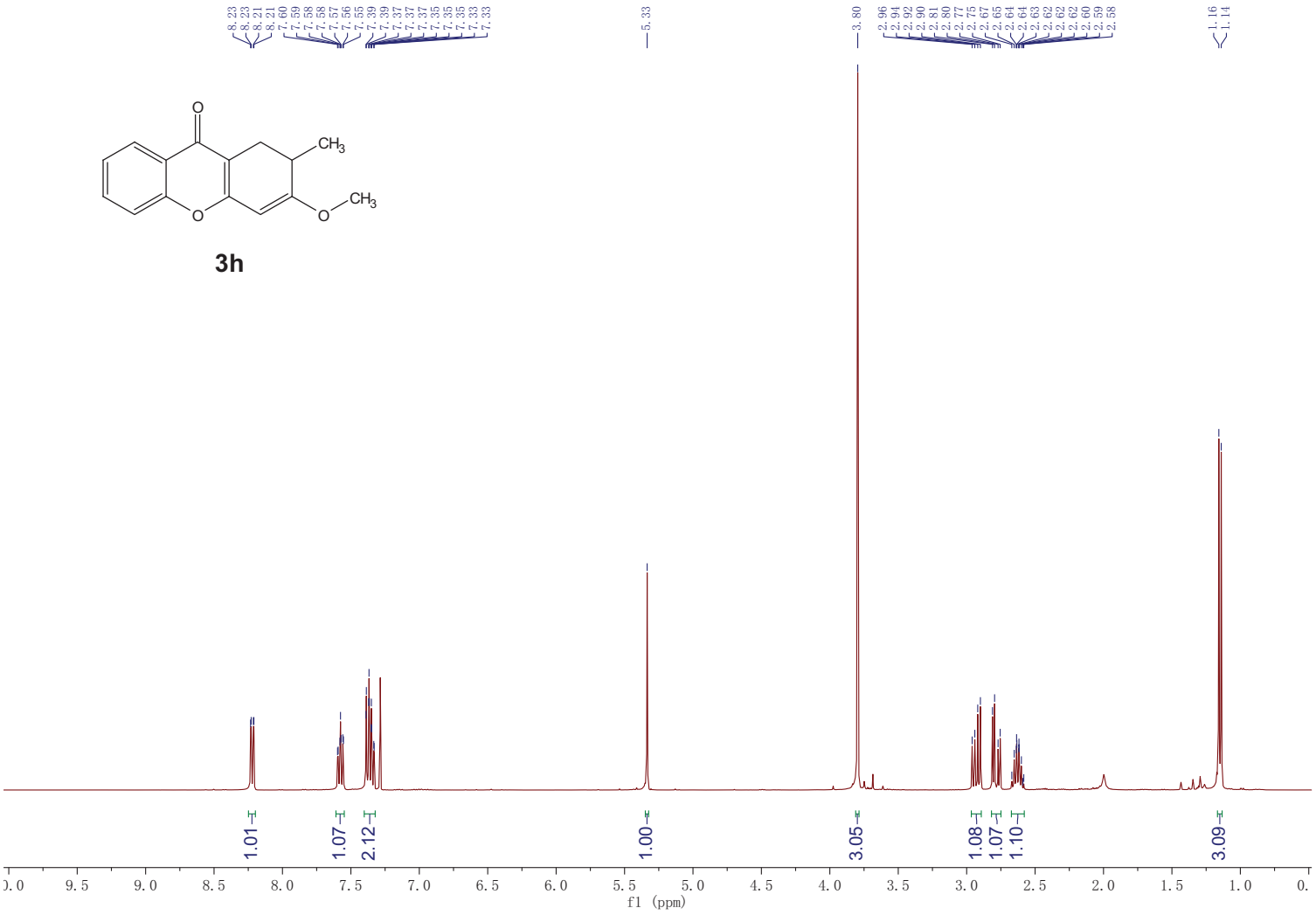
0
-10
f1 (ppm)


8.24
8.24
8.23
8.22
7.60
7.60
7.59
7.59
7.58
7.57
7.57
7.39
7.38
7.37
7.36
7.35
5.39
5.39
3.83
3.51
3.50
3.49
3.48
3.46
2.88
2.88
2.87
2.87
2.86
2.85
2.84
2.84
2.21
2.18
1.15
1.14
O
CH3
O
CH3
1.03
1.06
2.06
1.00
3.04
1.07
1.11
1.09
3.01
f1 (ppm)

3g


175.19
168.89
161.80
155.58
132.30
125.68
124.42
124.26
117.47
114.16
90.36
55.96
34.75
24.41
18.15
O
CH3
O
CH3
f1 (ppm)

3g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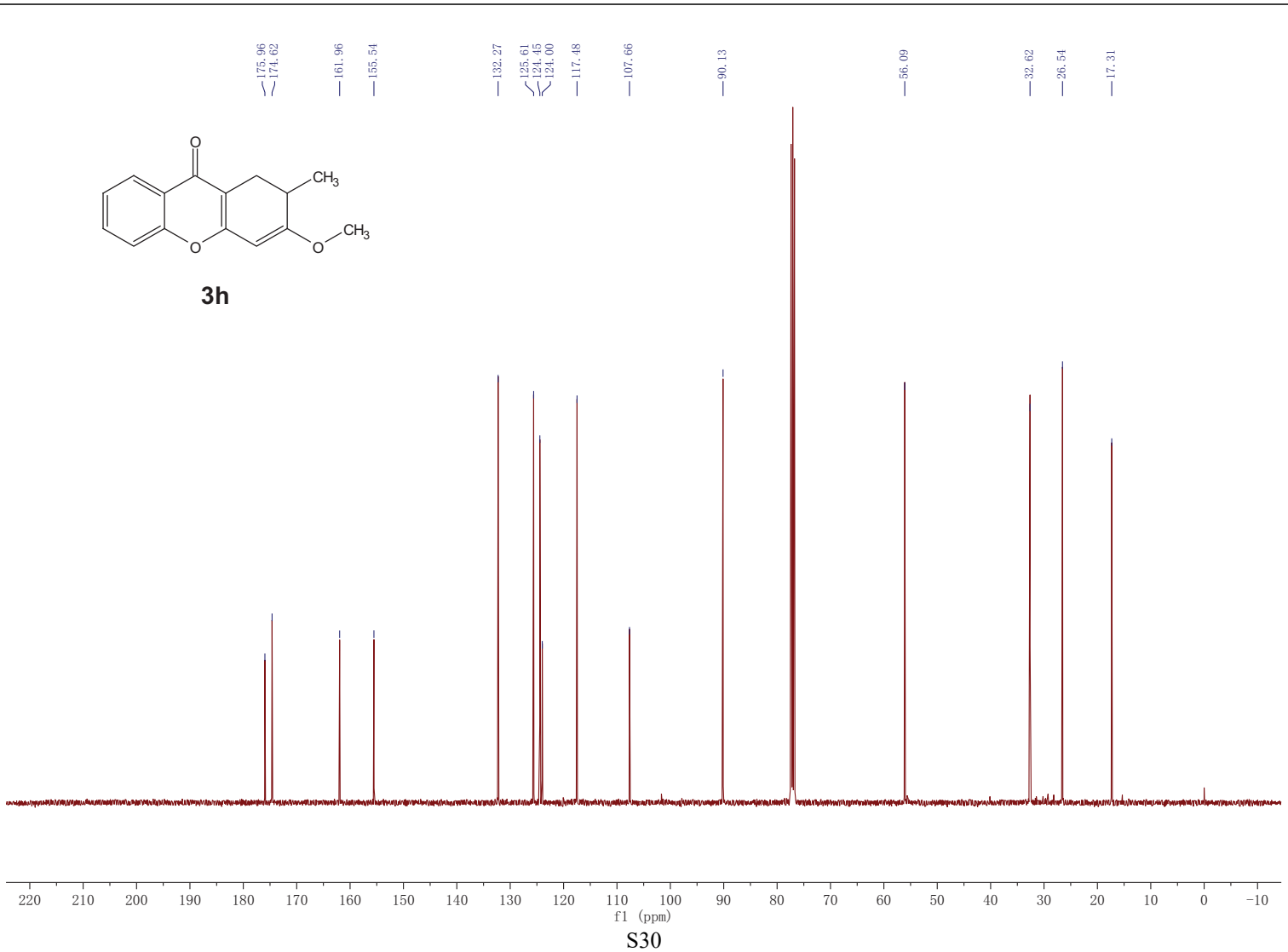
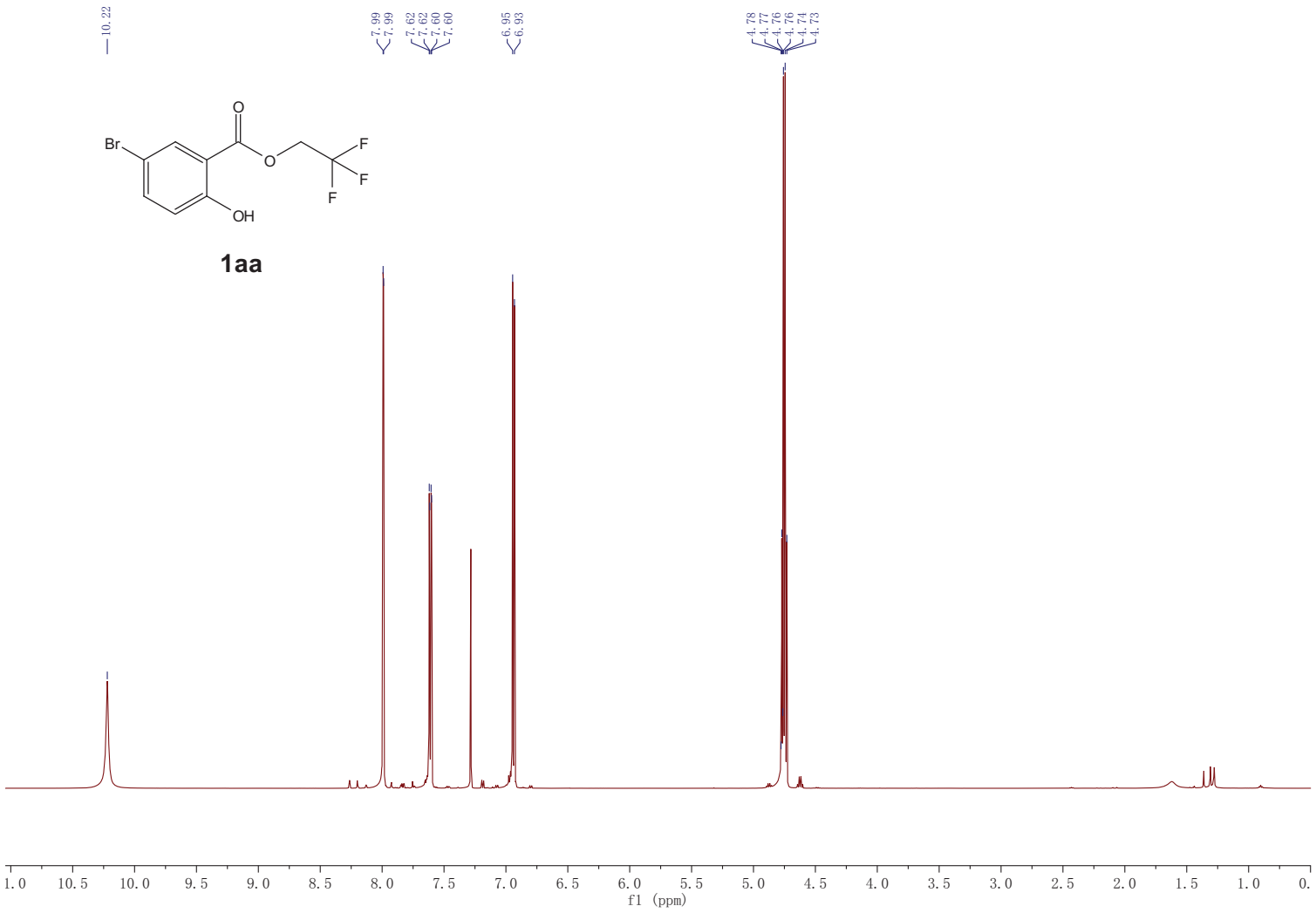
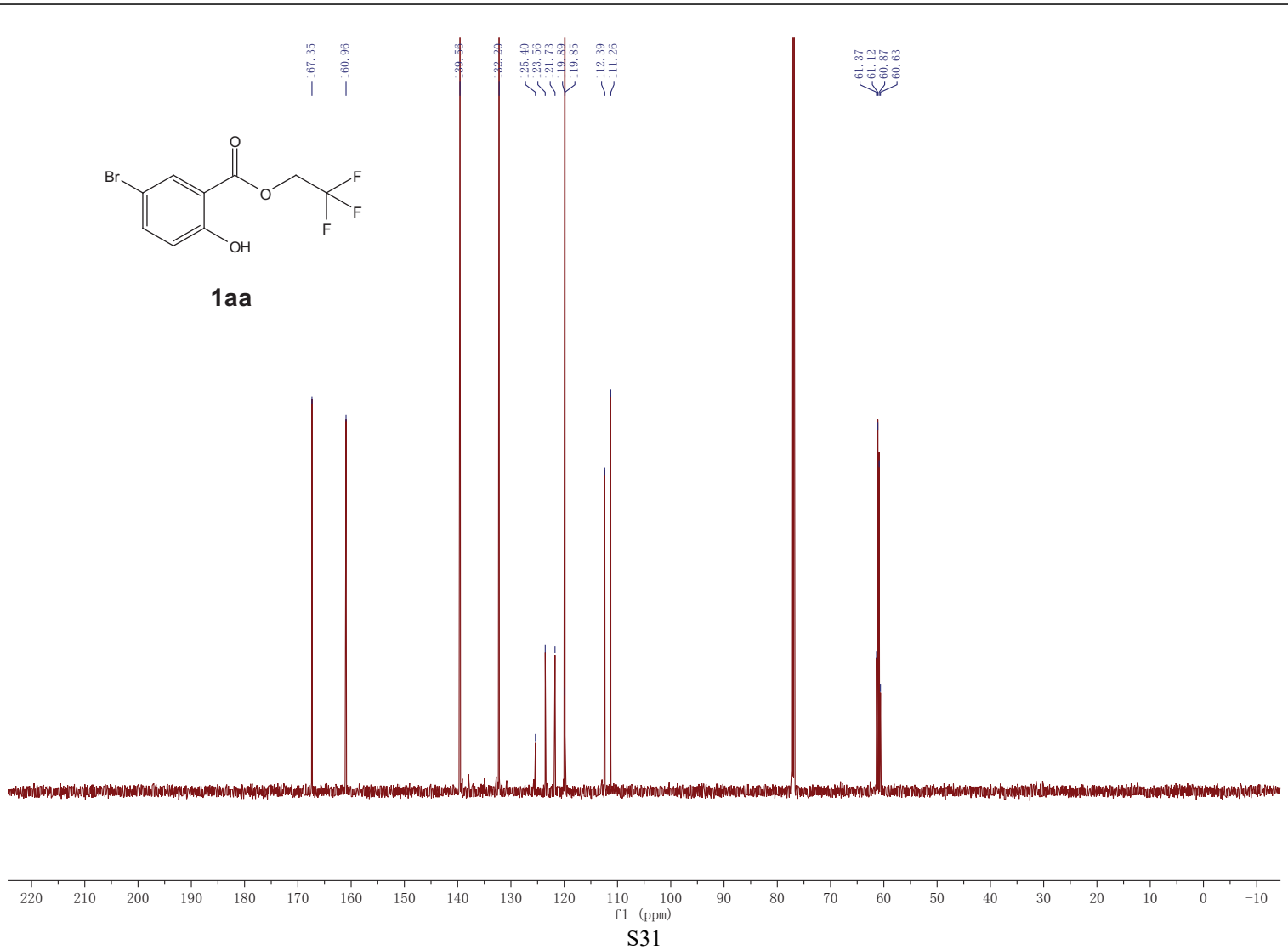
8.23
8.21
8.21
7.60
7.59
7.58
7.58
7.57
7.56
7.55
7.39
7.37
7.37
7.37
7.35
7.35
7.33
7.33
5.33
3.80
2.96
2.94
2.92
2.90
2.81
2.80
2.77
2.75
2.67
2.65
2.64
2.64
2.63
2.62
2.62
2.62
2.60
2.59
2.58
1.16
1.14
O
CH3
O
CH3
1.01
1.07
2.12
1.00
3.05
1.08
1.07
1.10
3.09
f1 (ppm)

3h


175.96
174.62
161.96
155.54
132.27
125.61
124.45
124.00
117.48
107.66
90.13
56.09
32.62
26.54
17.31
O
CH3
O
CH3
f1 (ppm)

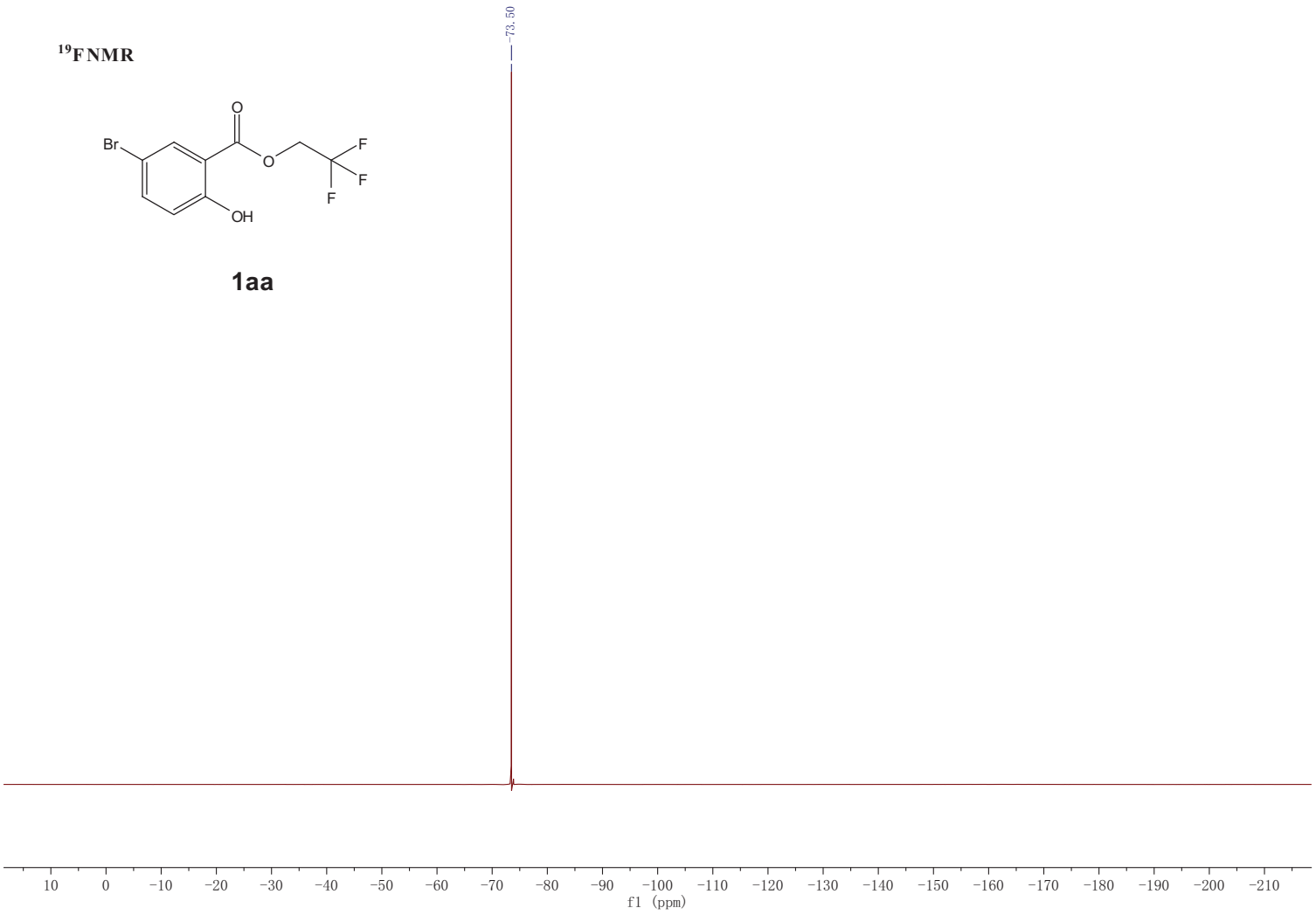
3h


10.22
7.99
7.99
7.62
7.62
7.60
7.60
6.95
6.93
4.78
4.77
4.76
4.76
4.74
4.73
Br
O
O
F
F
F
OH
1aa
1.0
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.
f1 (ppm)

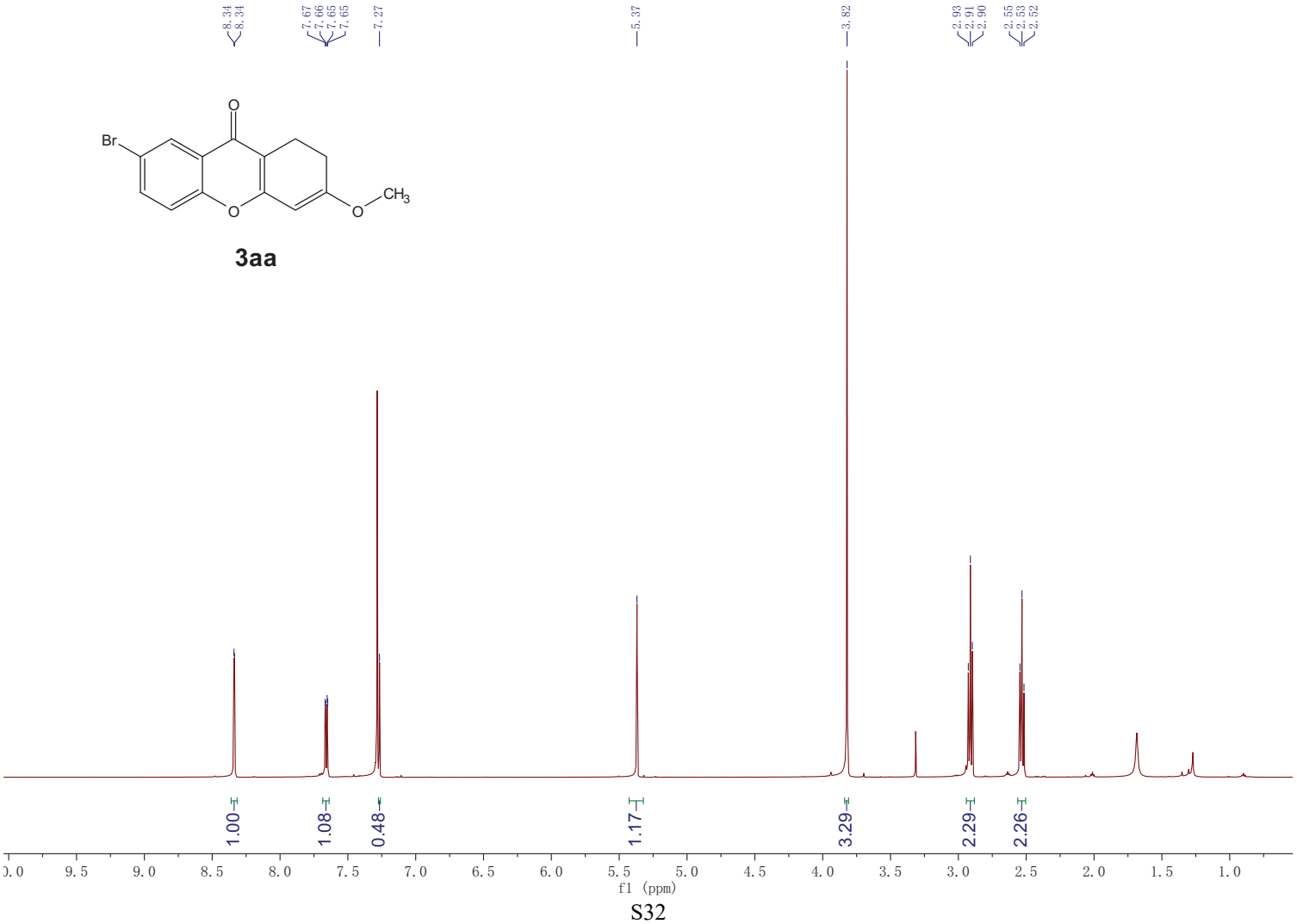

167.35
160.96
139.56
132.20
125.40
123.56
121.73
119.89
119.85
112.39
111.26
61.37
61.12
60.87
60.63
Br
O
O
F
F
F
OH
1aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

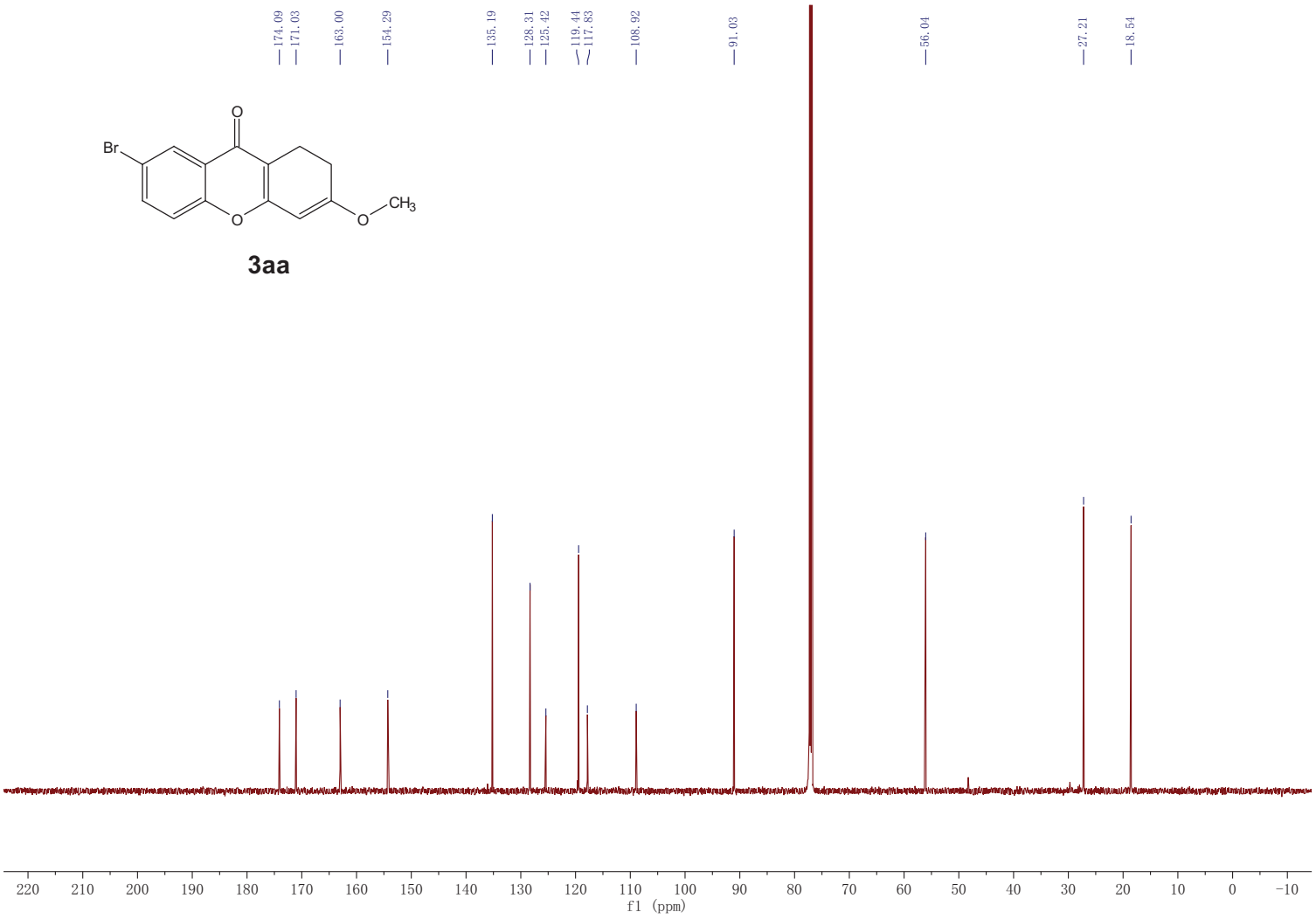
^{19}FNMR

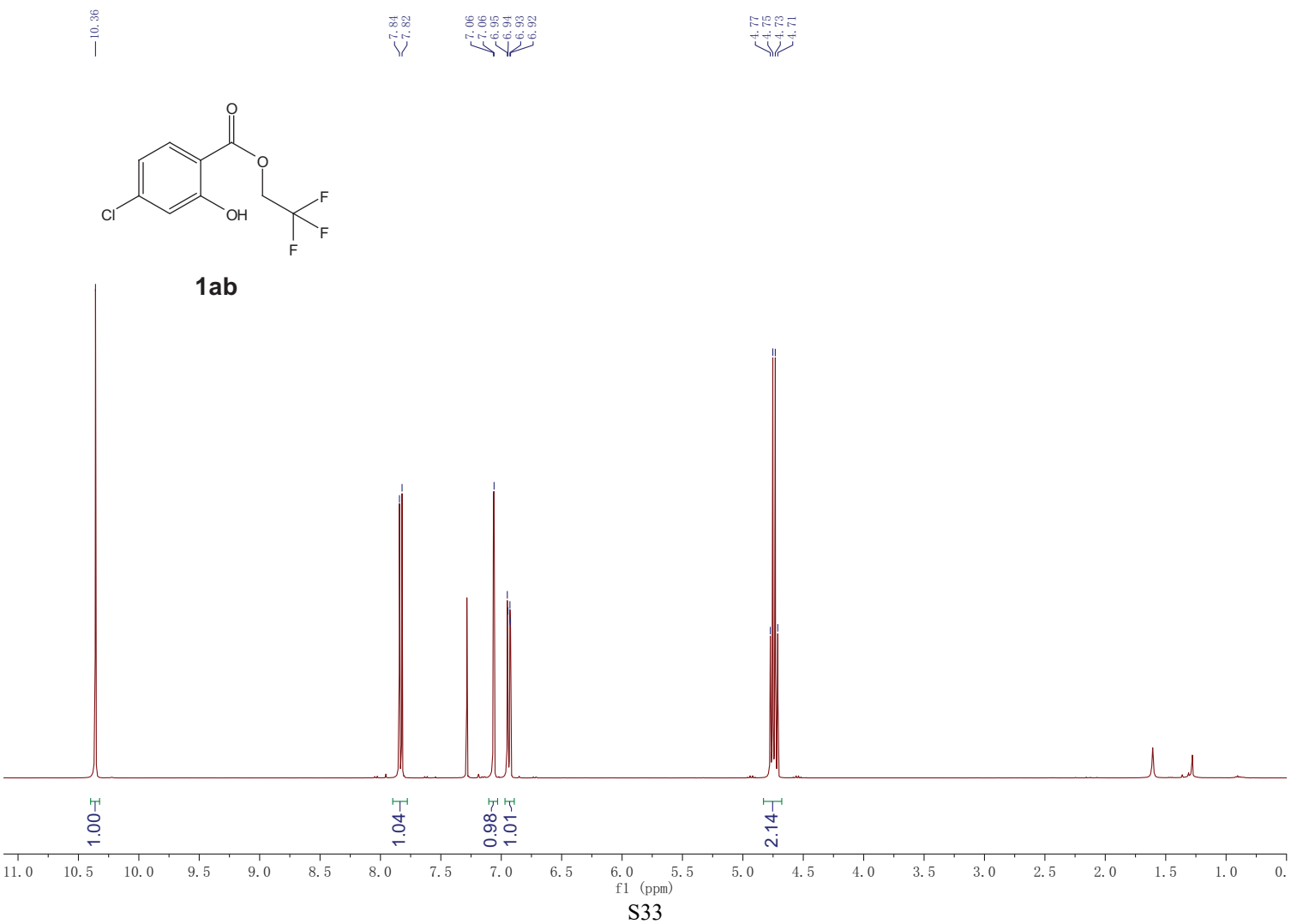
1aa

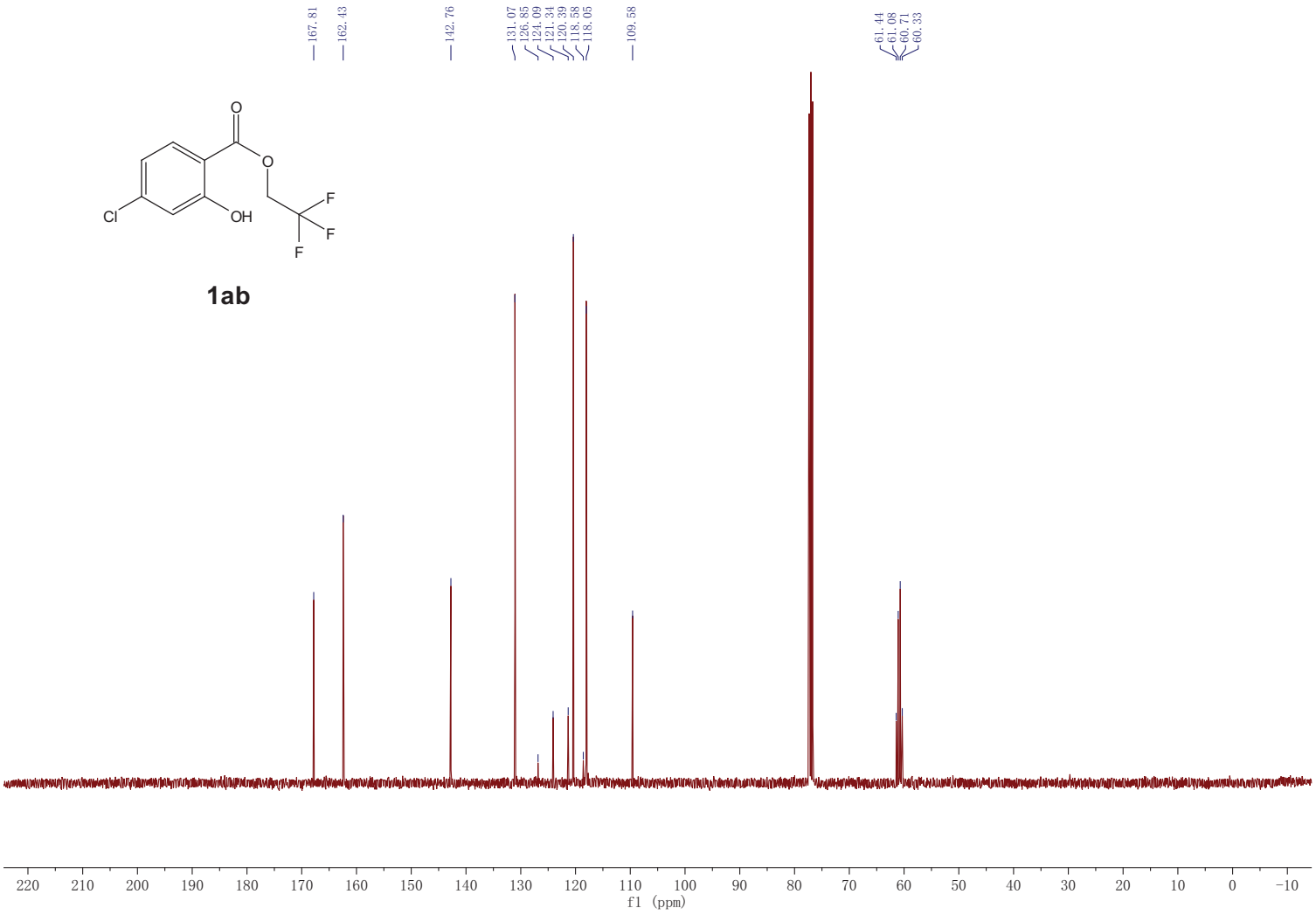


3aa



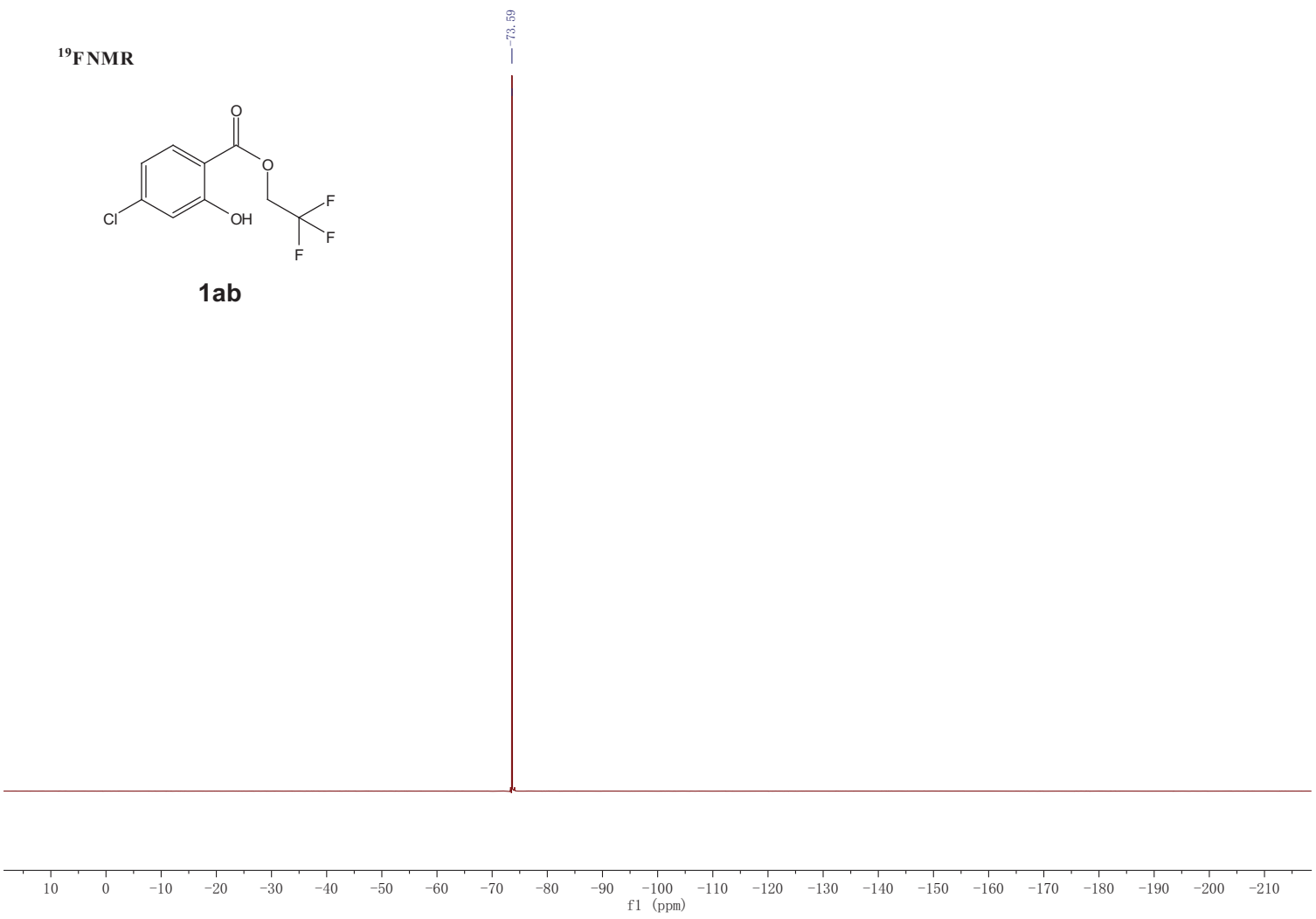

174.09
171.03
163.00
154.29
135.19
128.31
125.42
119.44
117.83
108.92
91.03
56.04
27.21
18.54
Br
O
O
O
CH3
3aa
f1 (ppm)


10.36
7.84
7.82
7.06
7.06
6.95
6.94
6.93
6.92
4.77
4.75
4.73
4.71
Cl
OH
O
O
F
F
F
1ab
1.00
1.04
0.98
1.01
2.14
f1 (ppm)

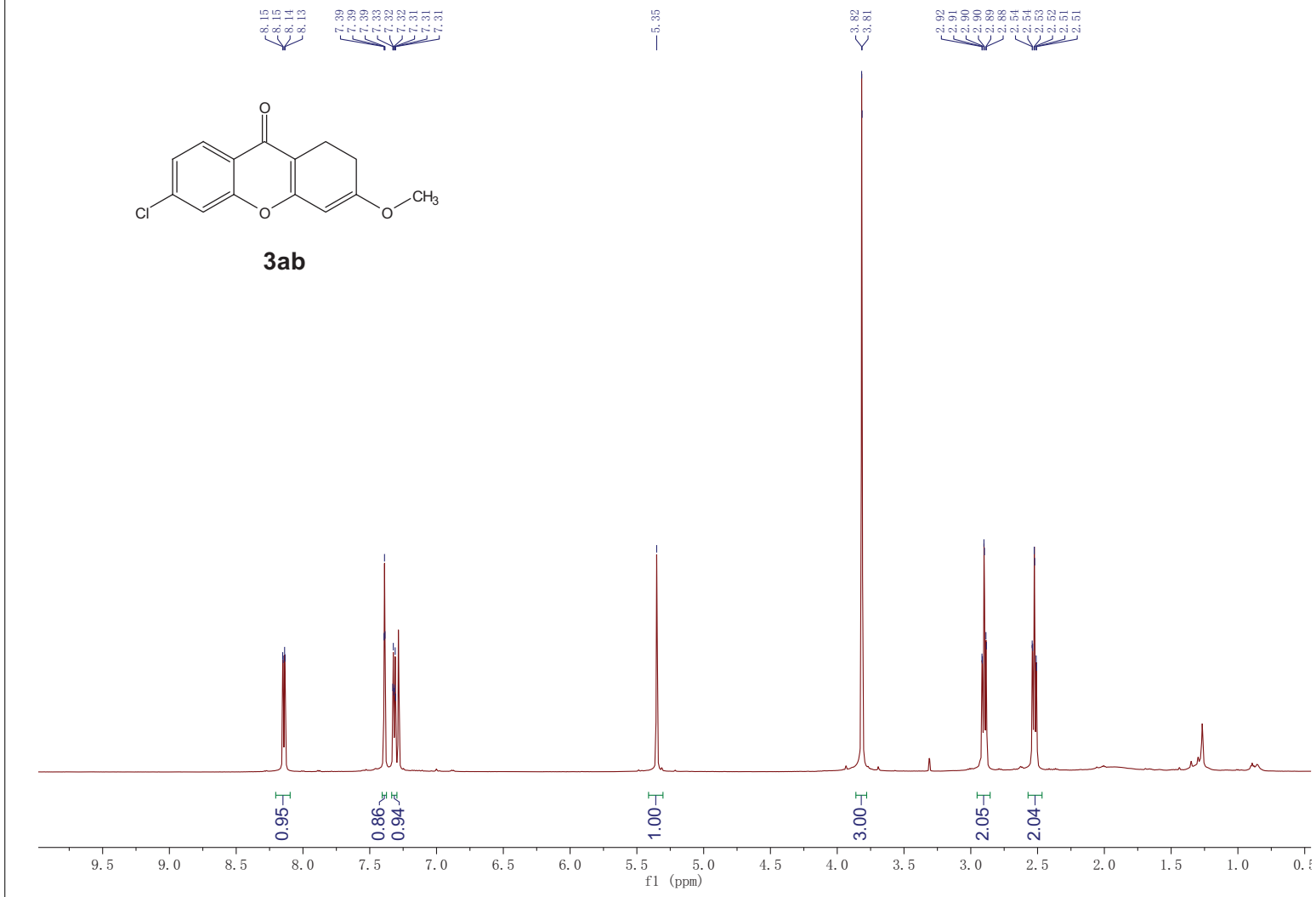


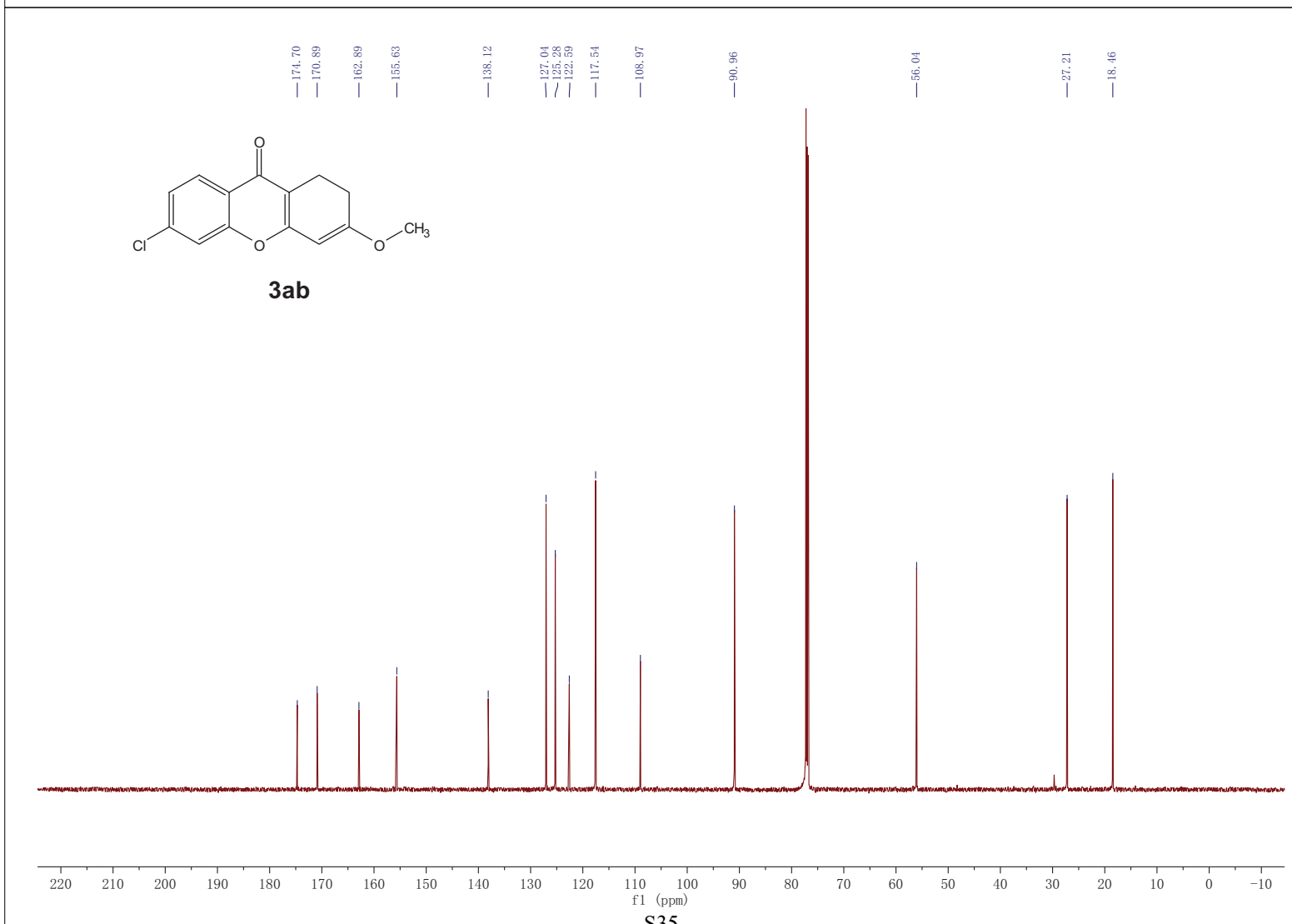
1ab

^{19}FNMR



1ab


8.15
8.15
8.14
8.13
7.39
7.39
7.39
7.33
7.32
7.32
7.31
7.31
7.31
5.35
3.82
3.81
2.92
2.91
2.90
2.90
2.89
2.88
2.54
2.54
2.53
2.52
2.51
2.51
O
Cl
O
O
CH3
3ab
0.95
0.86
0.94
1.00
3.00
2.05
2.04
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
f1 (ppm)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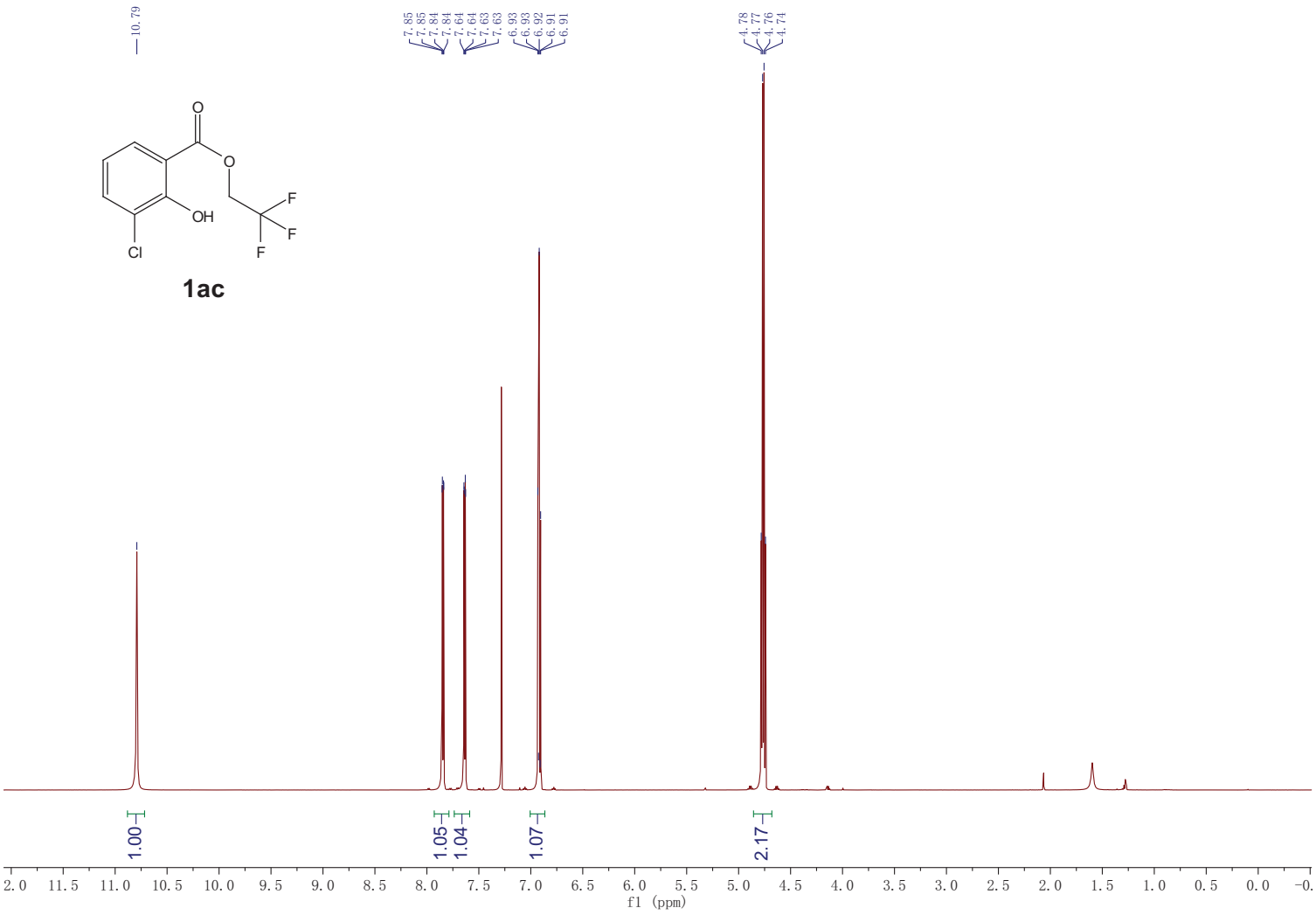
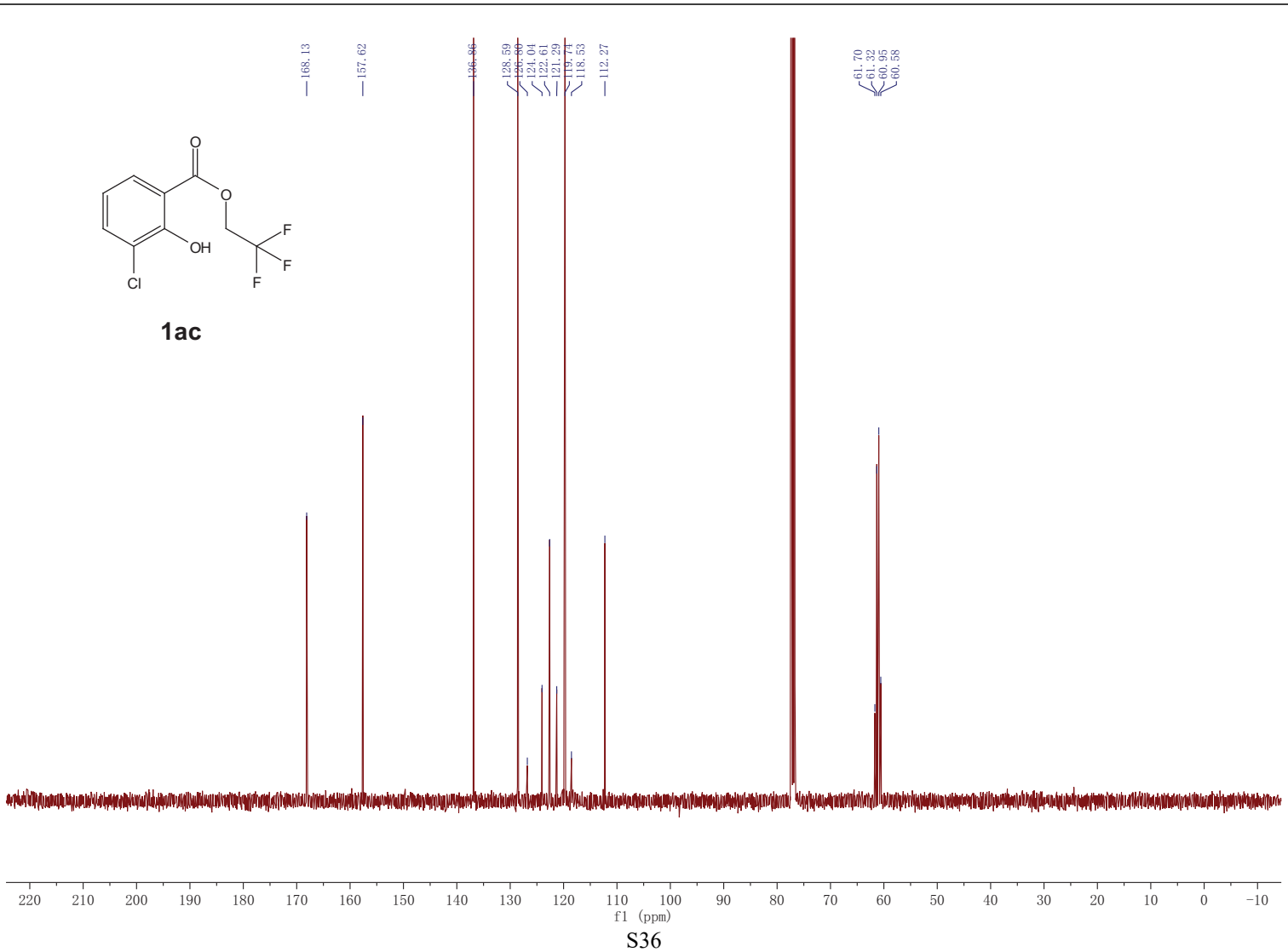
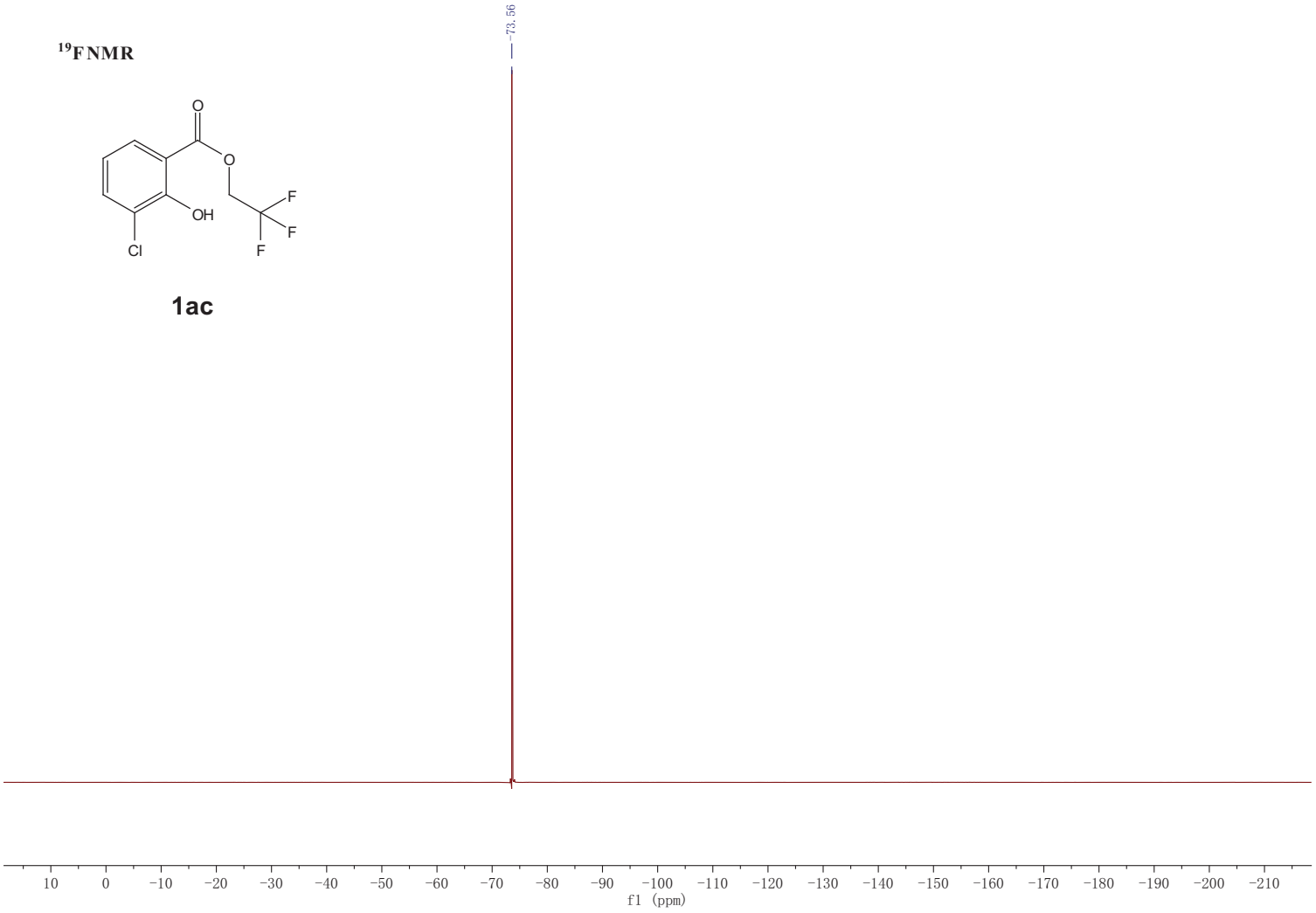
170.89
162.89
155.63
138.12
127.04
125.28
122.59
117.54
108.97
90.96
56.04
27.21
18.46
O
Cl
O
O
CH3
3ab
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


10.79
7.85
7.85
7.84
7.84
7.64
7.64
7.63
7.63
6.93
6.93
6.92
6.91
6.91
4.78
4.77
4.76
4.74
O
O
OH
Cl
F
F
F
1ac
1.00
1.05
1.04
1.07
2.17
f1 (ppm)

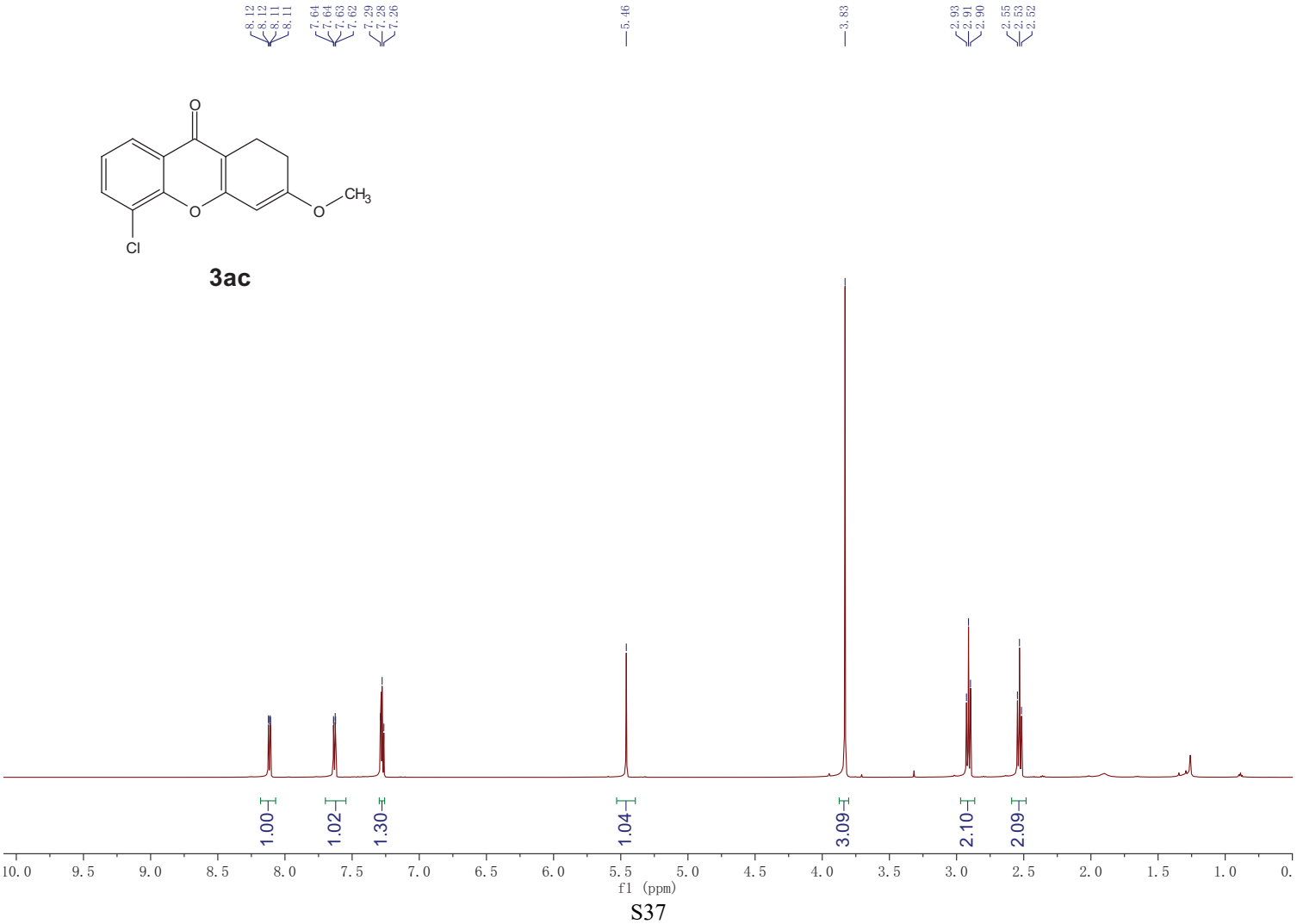

168.13
157.62
136.86
128.59
126.80
124.04
122.61
121.29
119.74
118.53
112.27
61.70
61.32
60.95
60.58
O
O
OH
Cl
F
F
F
1ac
f1 (ppm)

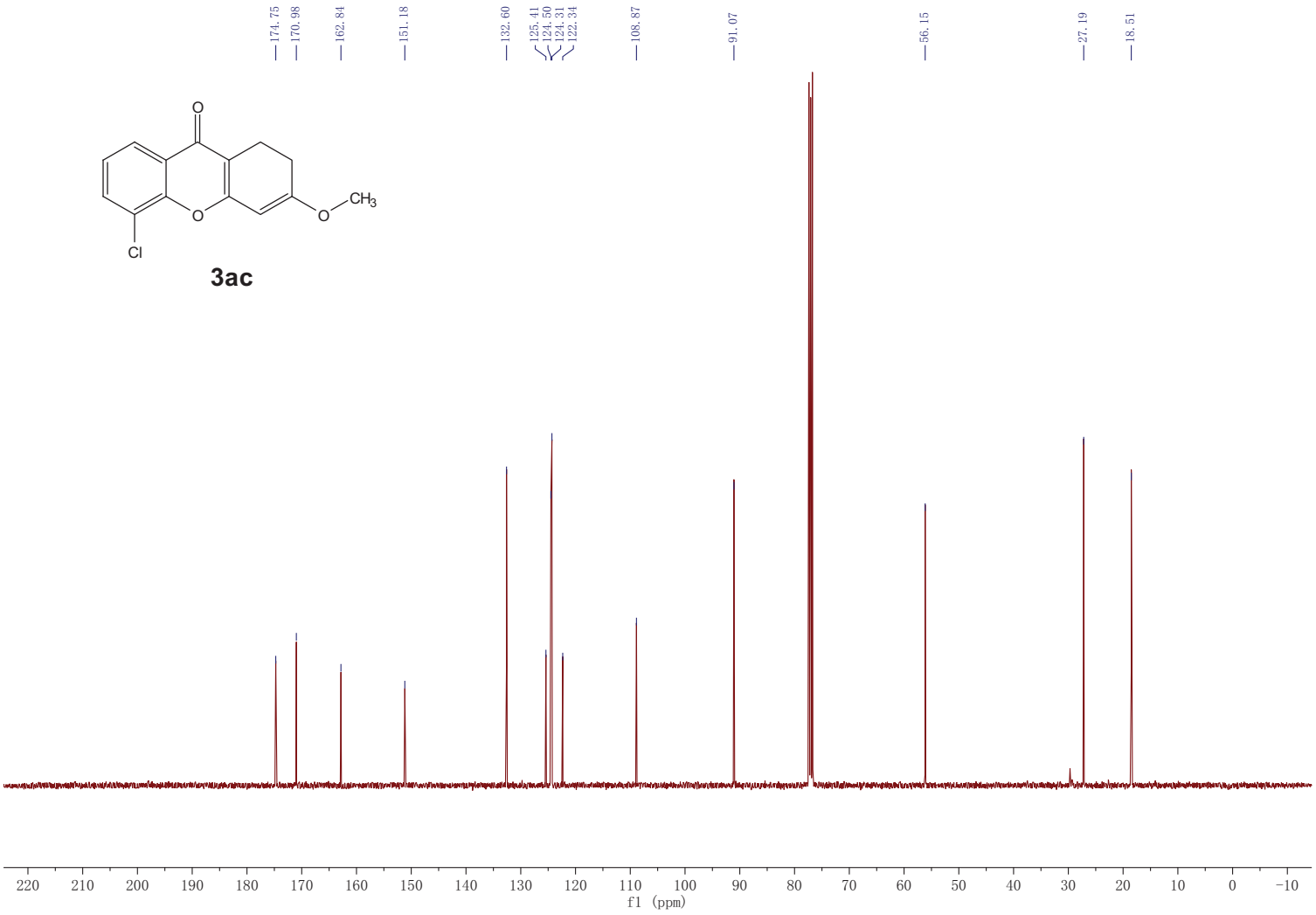
^{19}FNMR

1ac



3ac

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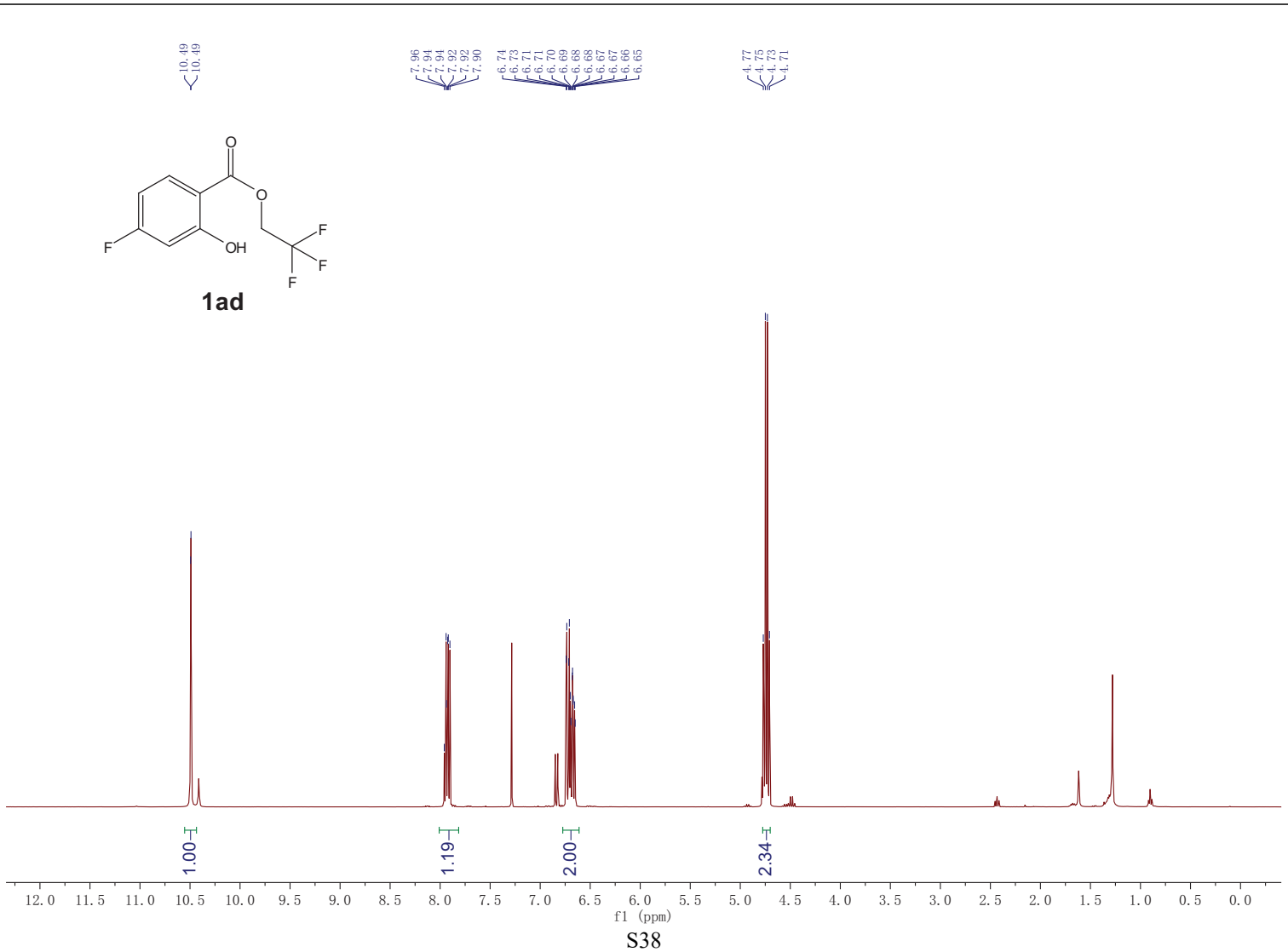
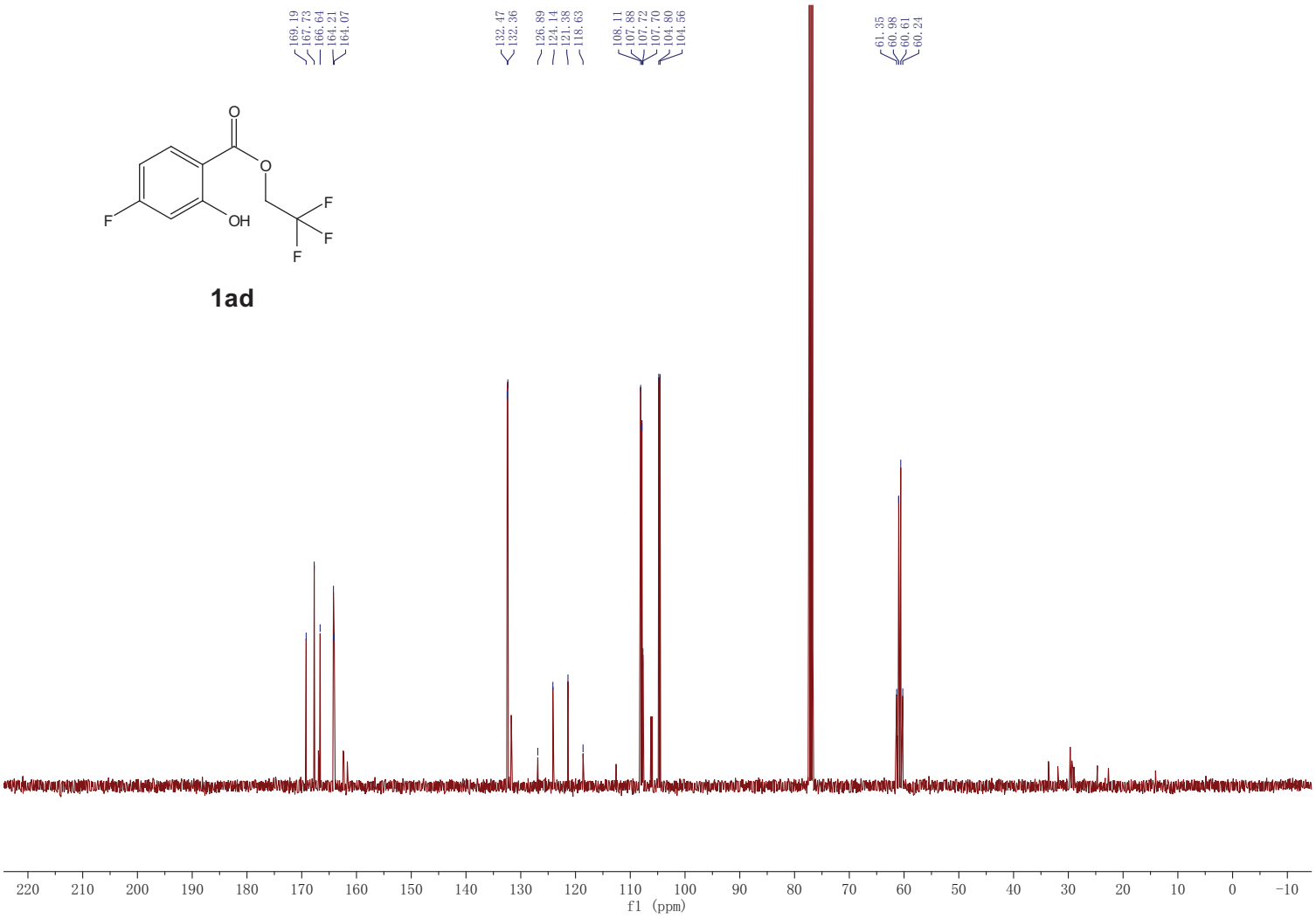
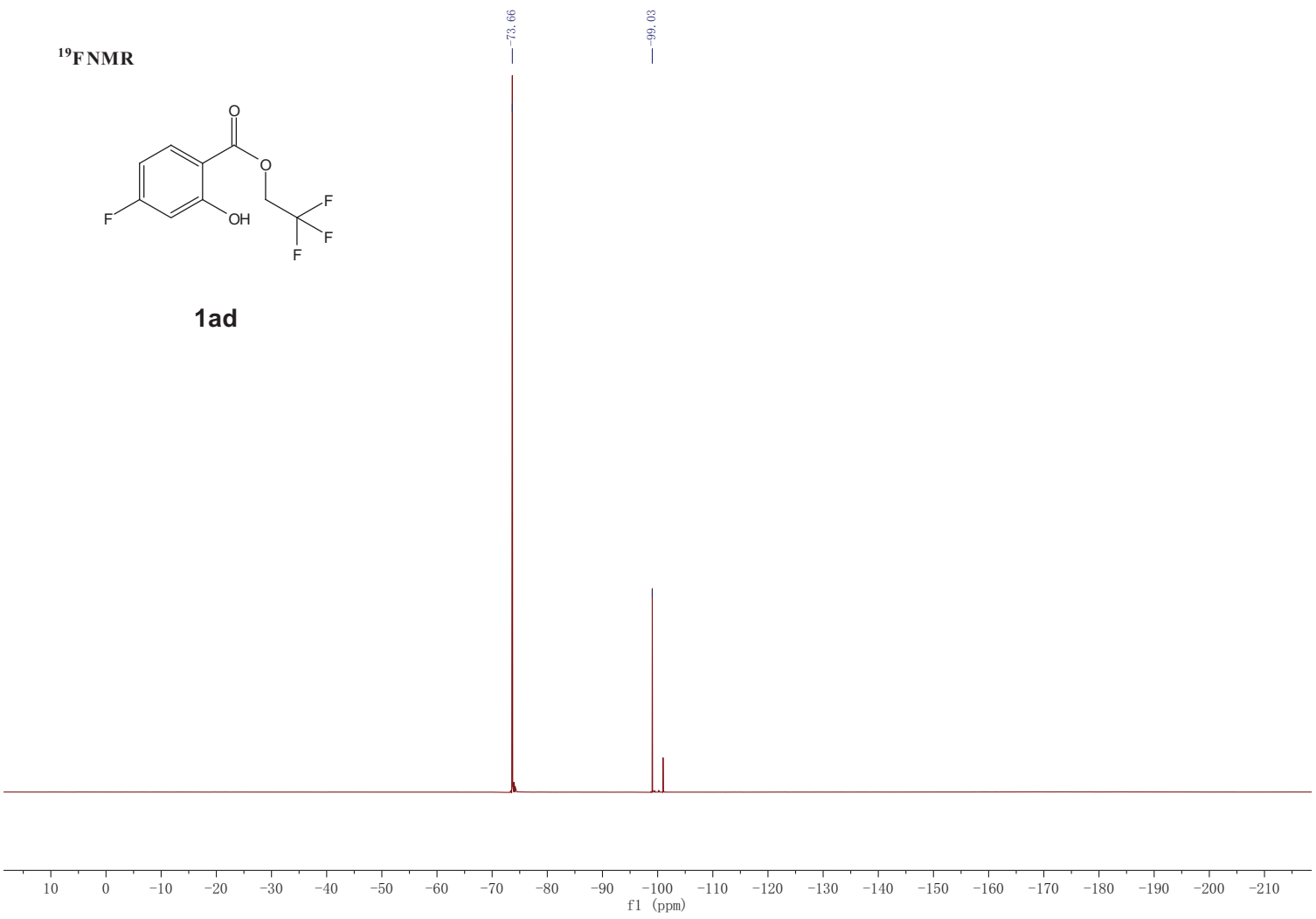
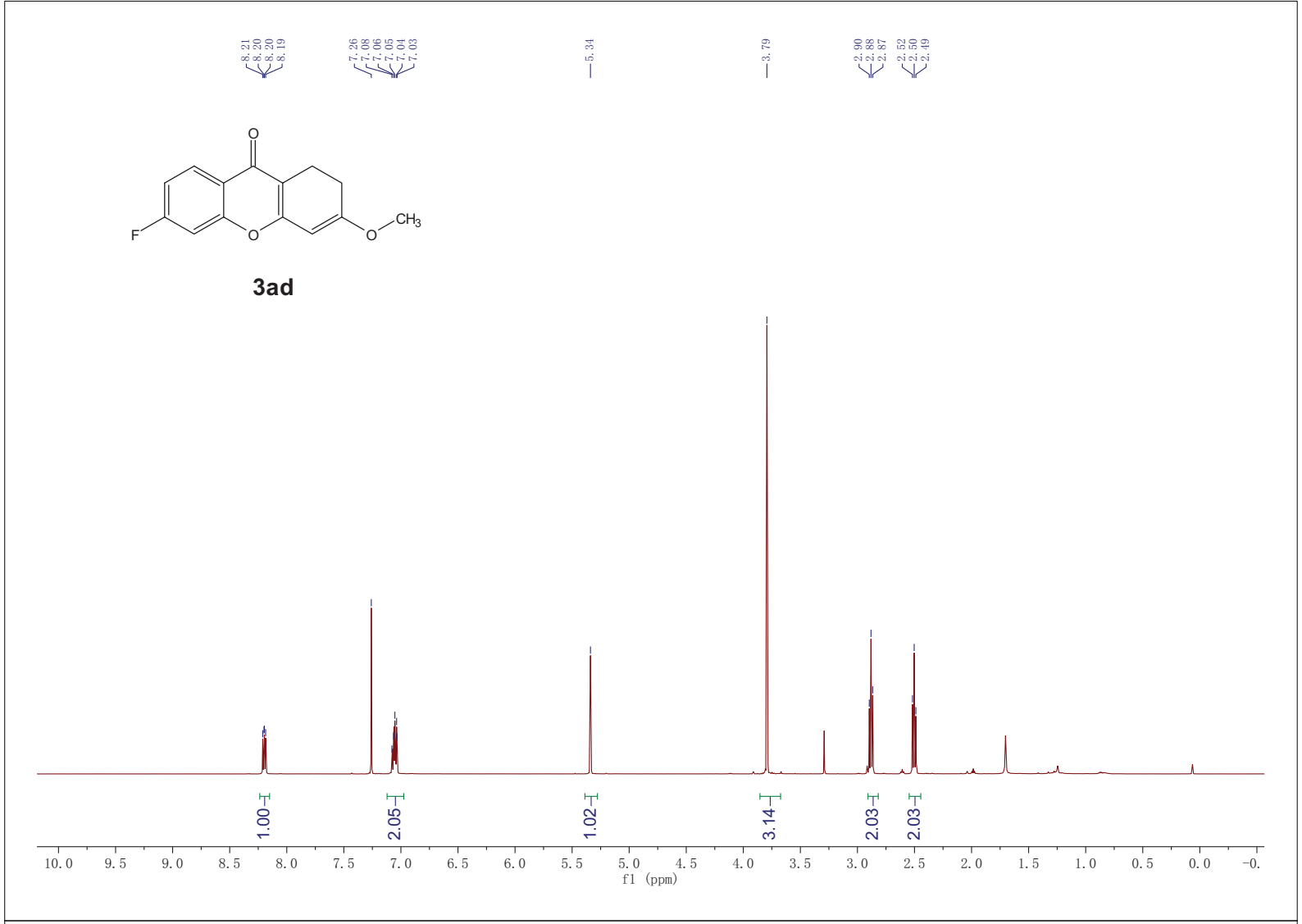
170.98
162.84
151.18
132.60
125.41
124.50
124.31
122.34
108.87
91.07
56.15
27.19
18.51
O
O
O
CH3
Cl
3ac
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.49
10.49
7.96
7.94
7.94
7.92
7.92
7.90
6.74
6.73
6.71
6.71
6.70
6.69
6.68
6.68
6.67
6.67
6.66
6.65
4.77
4.75
4.73
4.71
O
O
F
OH
F
F
F
1ad
1.00
1.19
2.00
2.34
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)

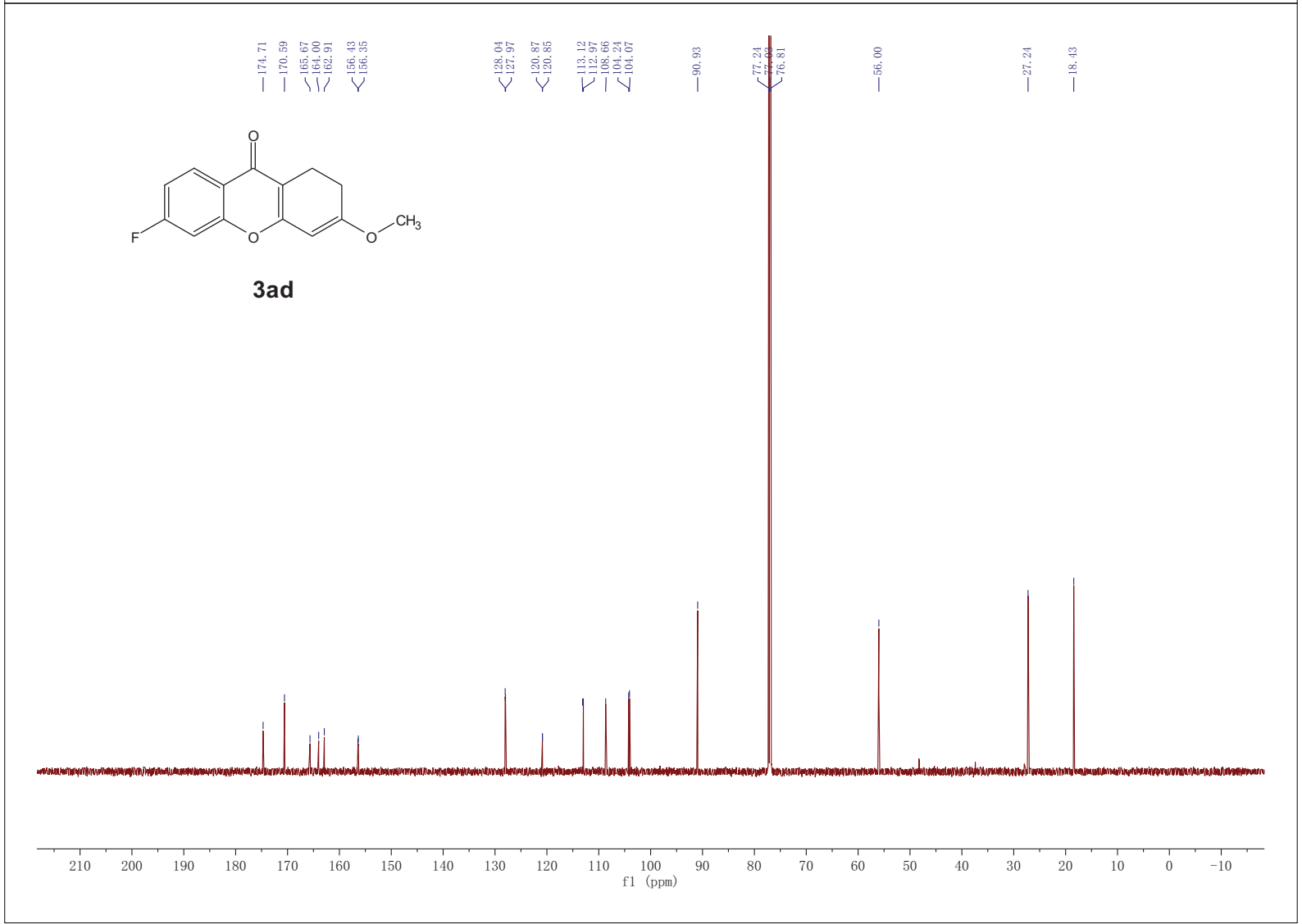

169.19
167.73
166.64
164.21
164.07
132.47
132.36
126.89
124.14
121.38
118.63
108.11
107.88
107.72
107.70
104.80
104.56
61.35
60.98
60.61
60.24
O
O
F
OH
F
F
F
1ad
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{19}FNMR


−73.66
−99.03
O
O
F
OH
F
F
F
1ad
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)


8.21
8.20
8.20
8.19
7.26
7.08
7.06
7.05
7.04
7.03
5.34
3.79
2.90
2.88
2.87
2.52
2.50
2.49
O
F
O
O
CH3
1.00
2.05
1.02
3.14
2.03
2.03
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 -0.
f1 (ppm)

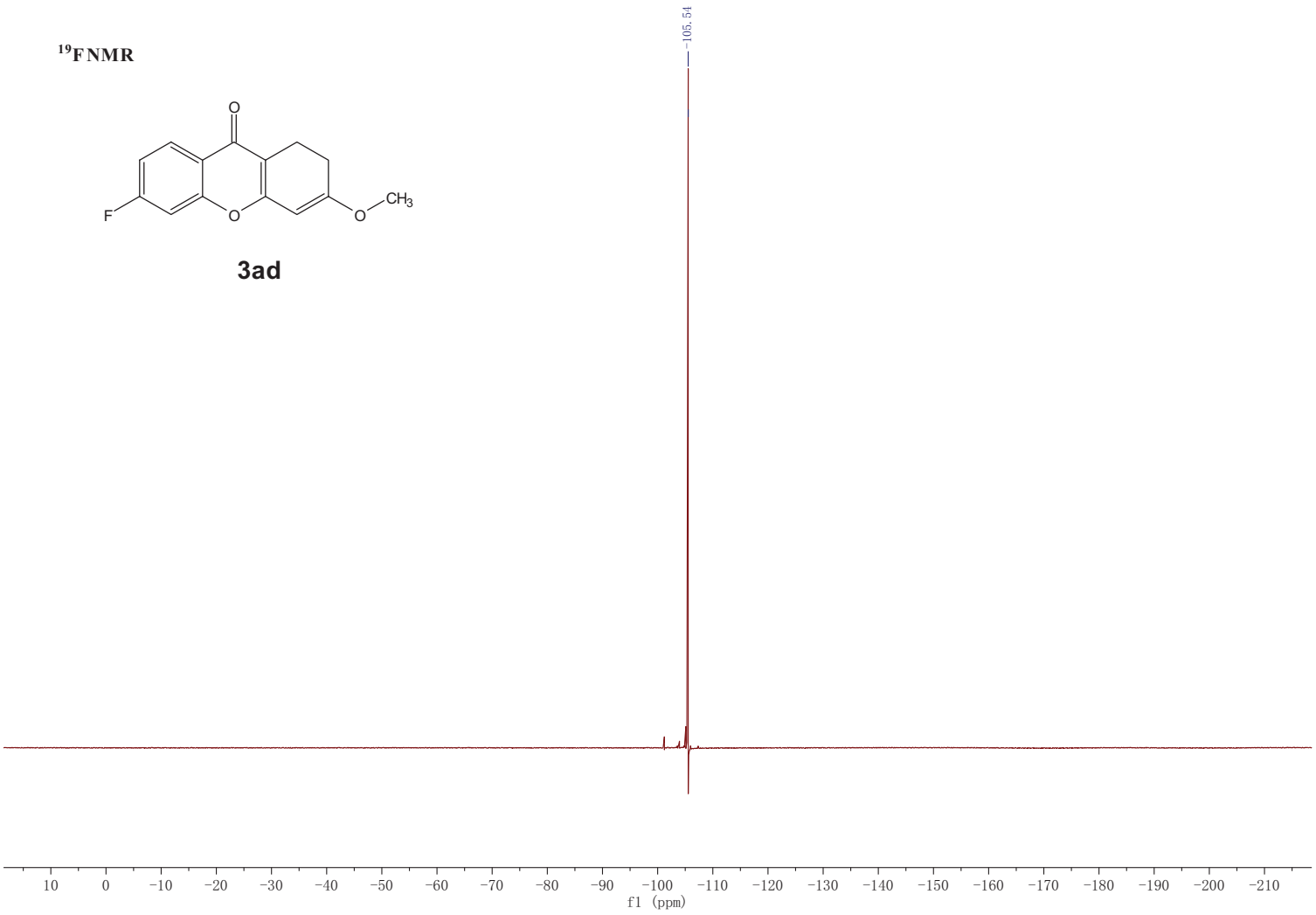
3ad


174.71
170.59
165.67
164.00
162.91
156.43
156.35
128.04
127.97
120.87
120.85
113.12
112.97
108.66
104.24
104.07
90.93
77.24
77.03
76.81
56.00
27.24
18.43
O
F
O
O
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

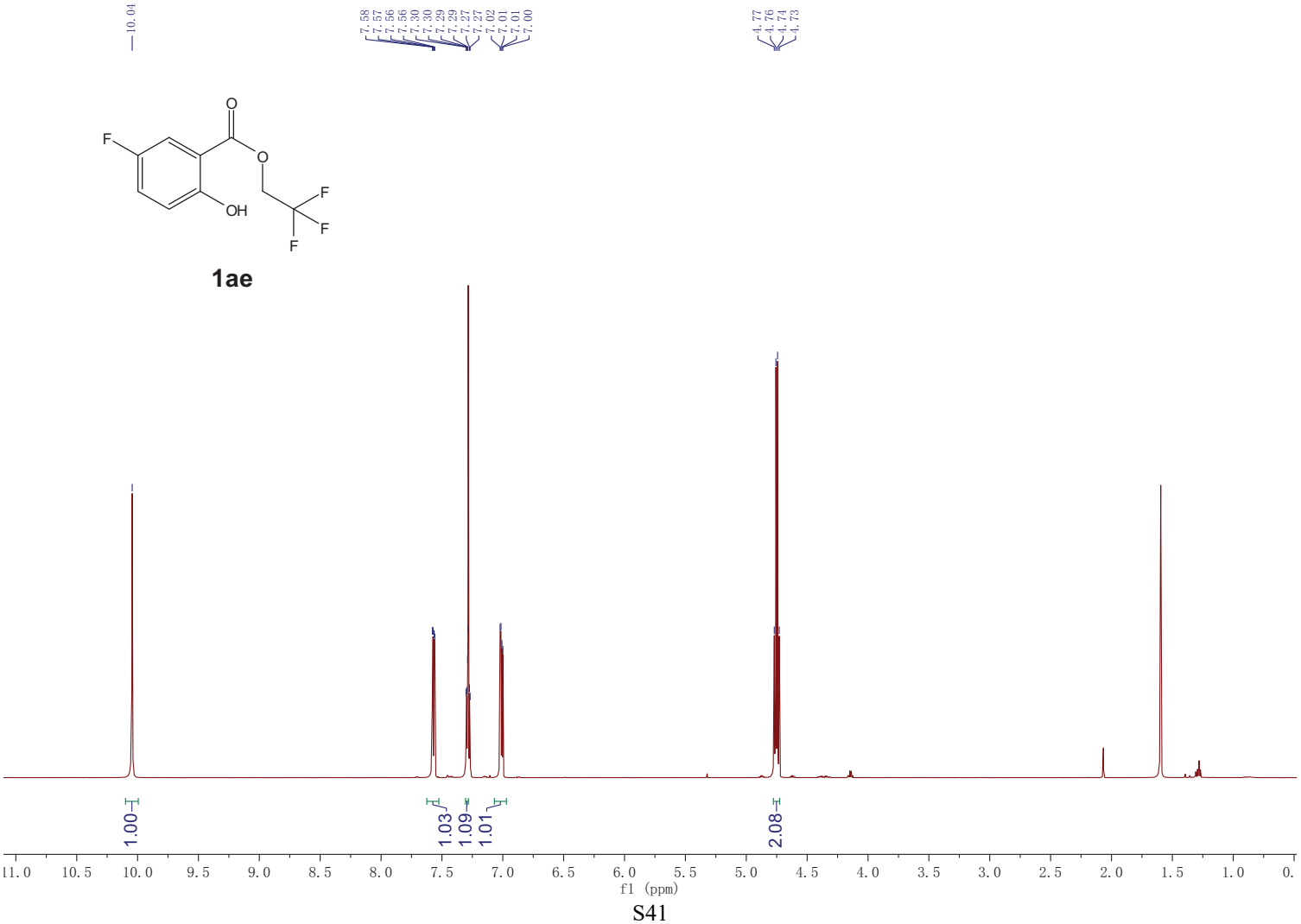
3ad

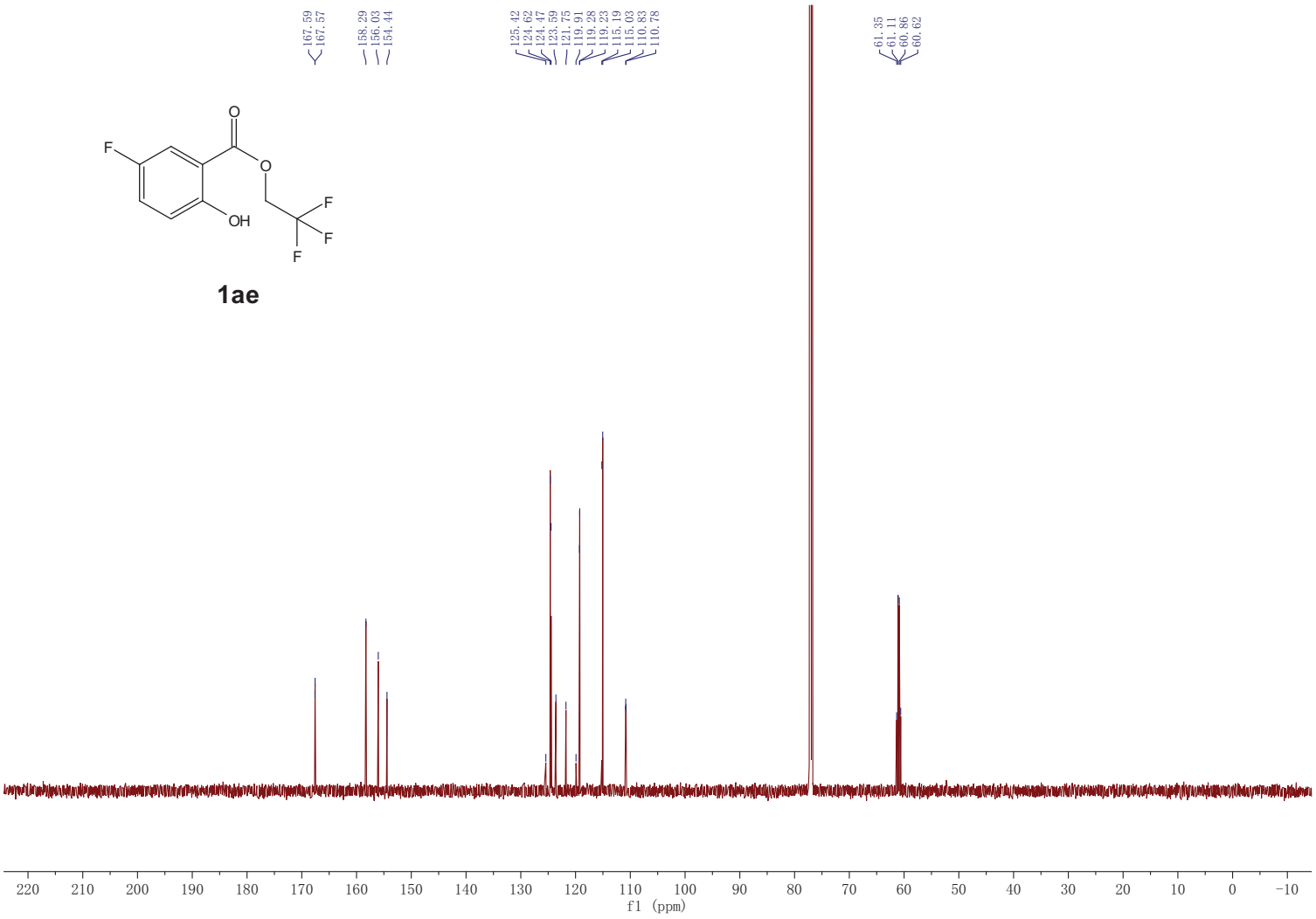
^{19}FNMR

3ad

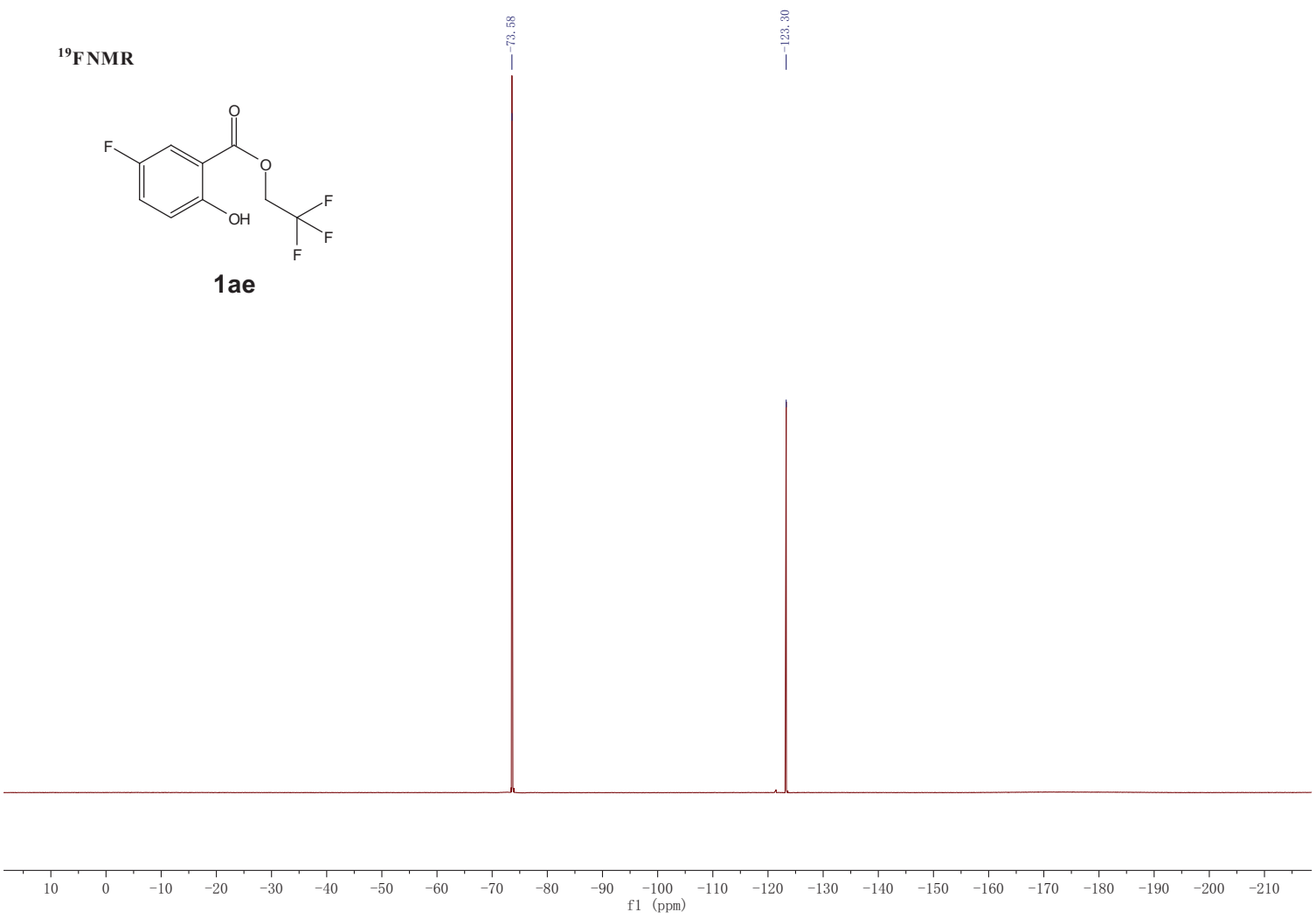


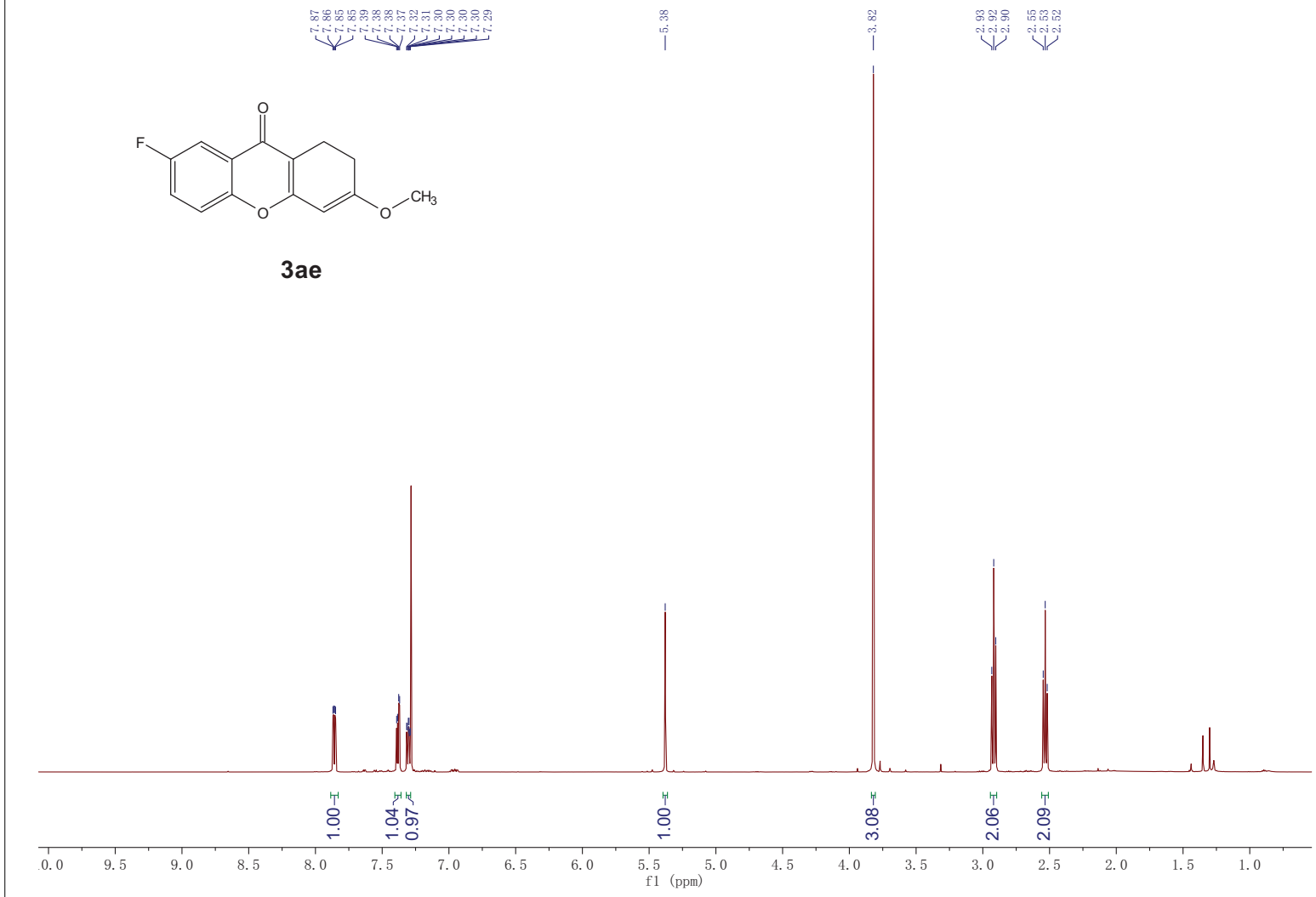
1ae



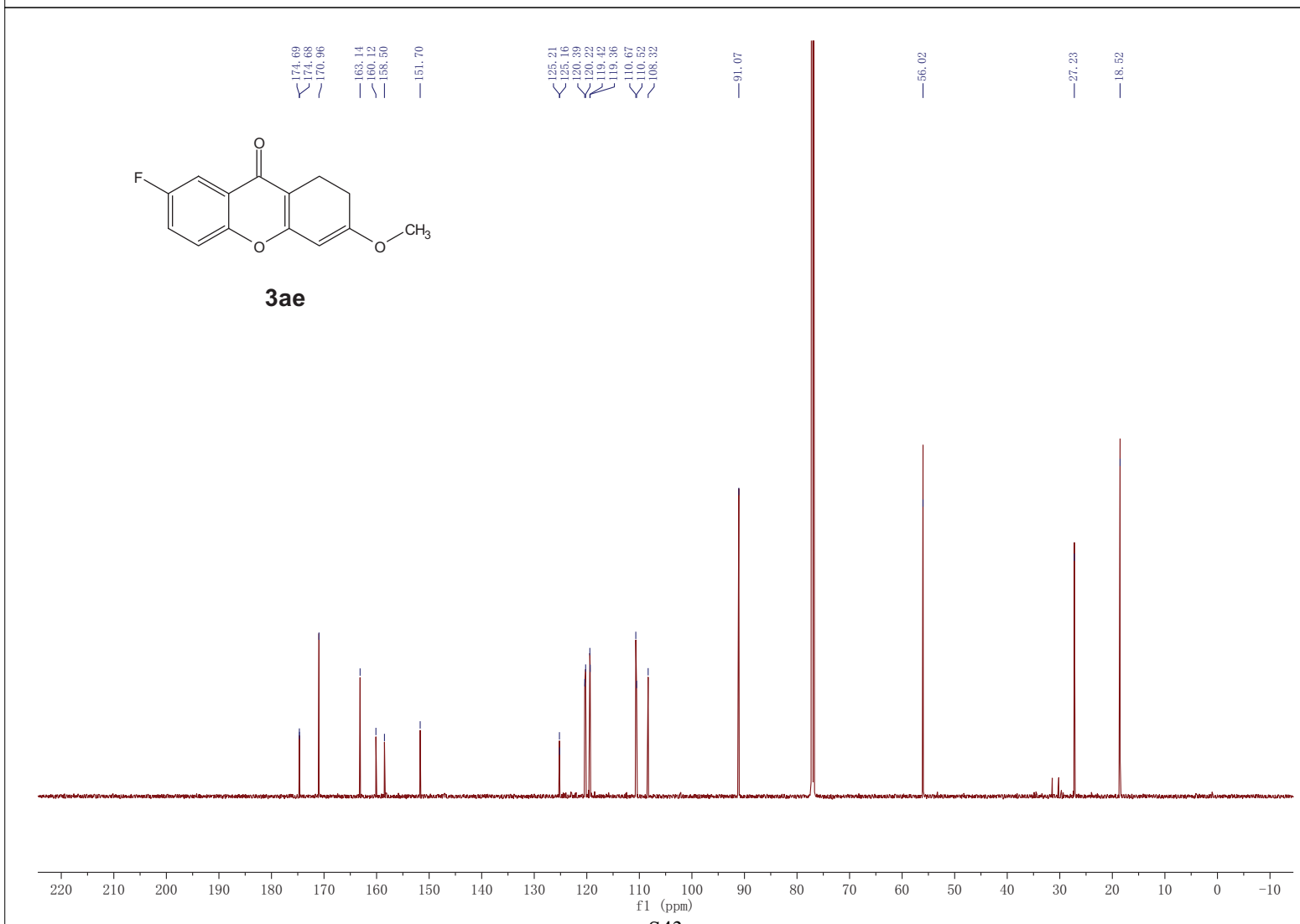

167.59
167.57
158.29
156.03
154.44
125.42
124.62
124.47
123.59
121.75
119.91
119.28
119.23
115.19
115.03
110.83
110.78
61.35
61.11
60.86
60.62
F
O
O
OH
F
F
F
1ae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{19}FNMR


−73.58
−123.30
F
O
O
OH
F
F
F
1ae
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)


7.87
7.86
7.85
7.85
7.39
7.38
7.38
7.37
7.32
7.31
7.30
7.30
7.30
7.29
5.38
3.82
2.93
2.92
2.90
2.55
2.53
2.52
F
O
O
O
CH3
1.00
1.04
0.97
1.00
3.08
2.06
2.09
f1 (ppm)

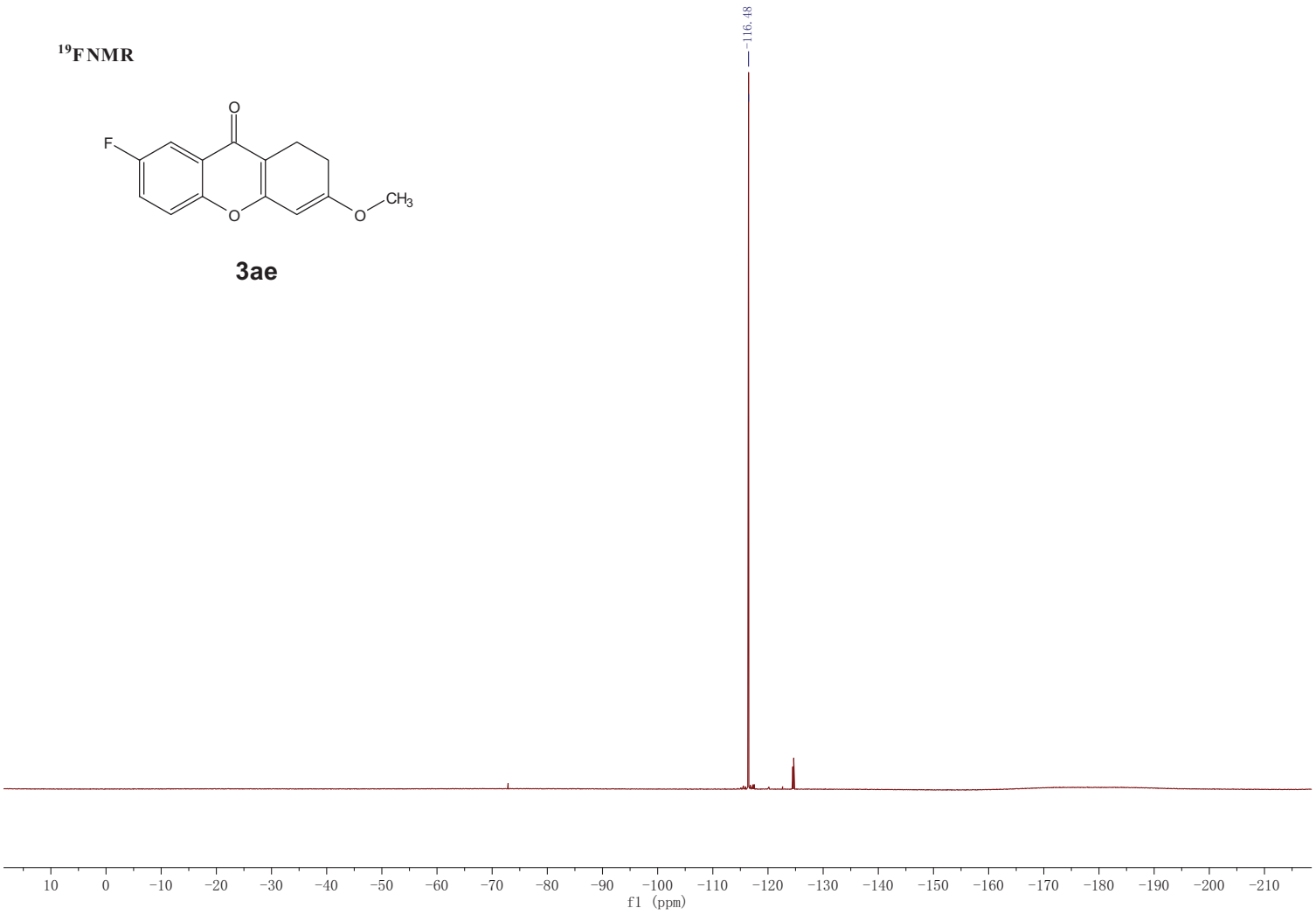
3ae


174.69
174.68
170.96
163.14
160.12
158.50
151.70
125.21
125.16
120.39
120.22
119.42
119.36
110.67
110.52
108.32
91.07
56.02
27.23
18.52
F
O
O
O
CH3
f1 (ppm)

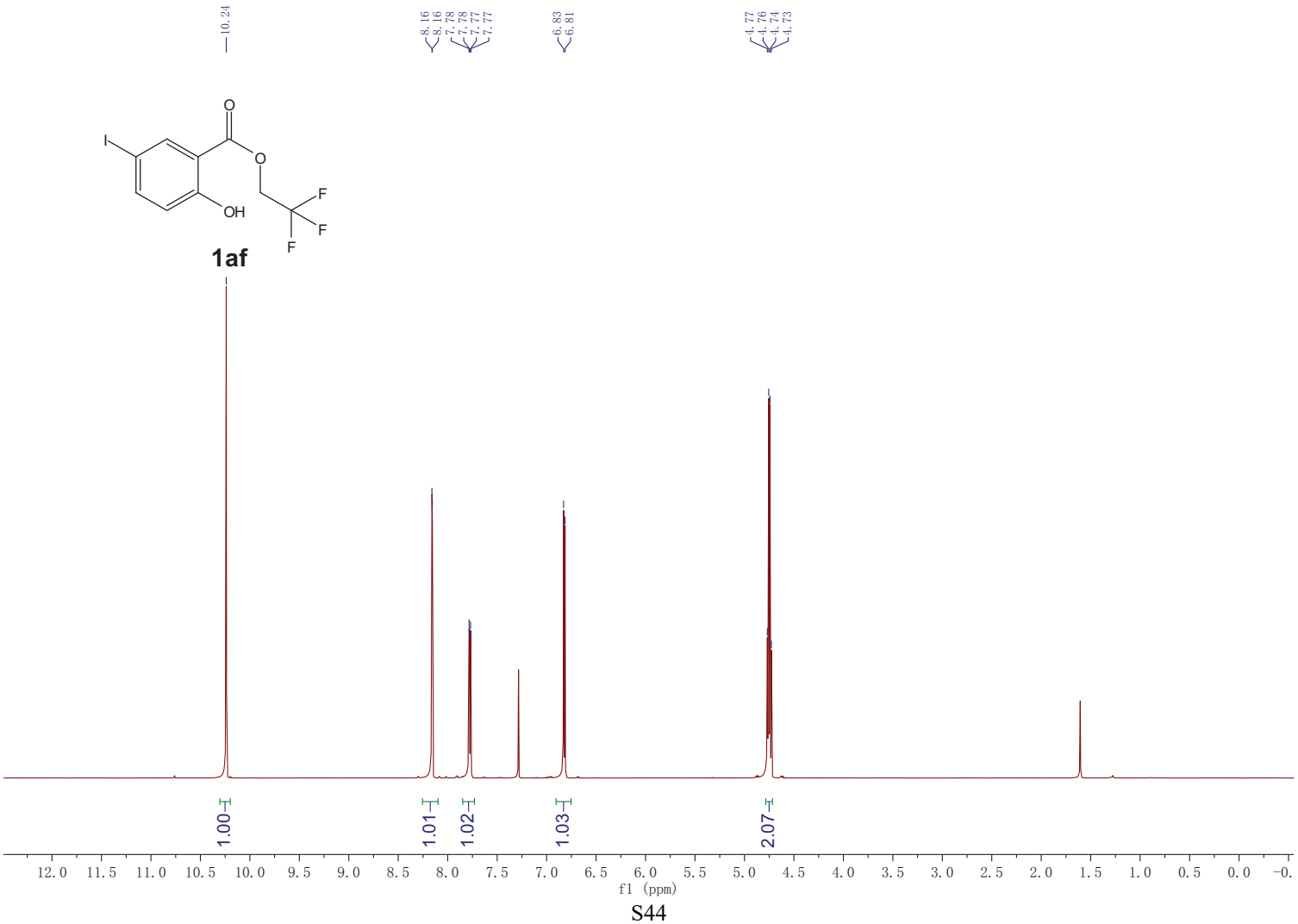
3ae

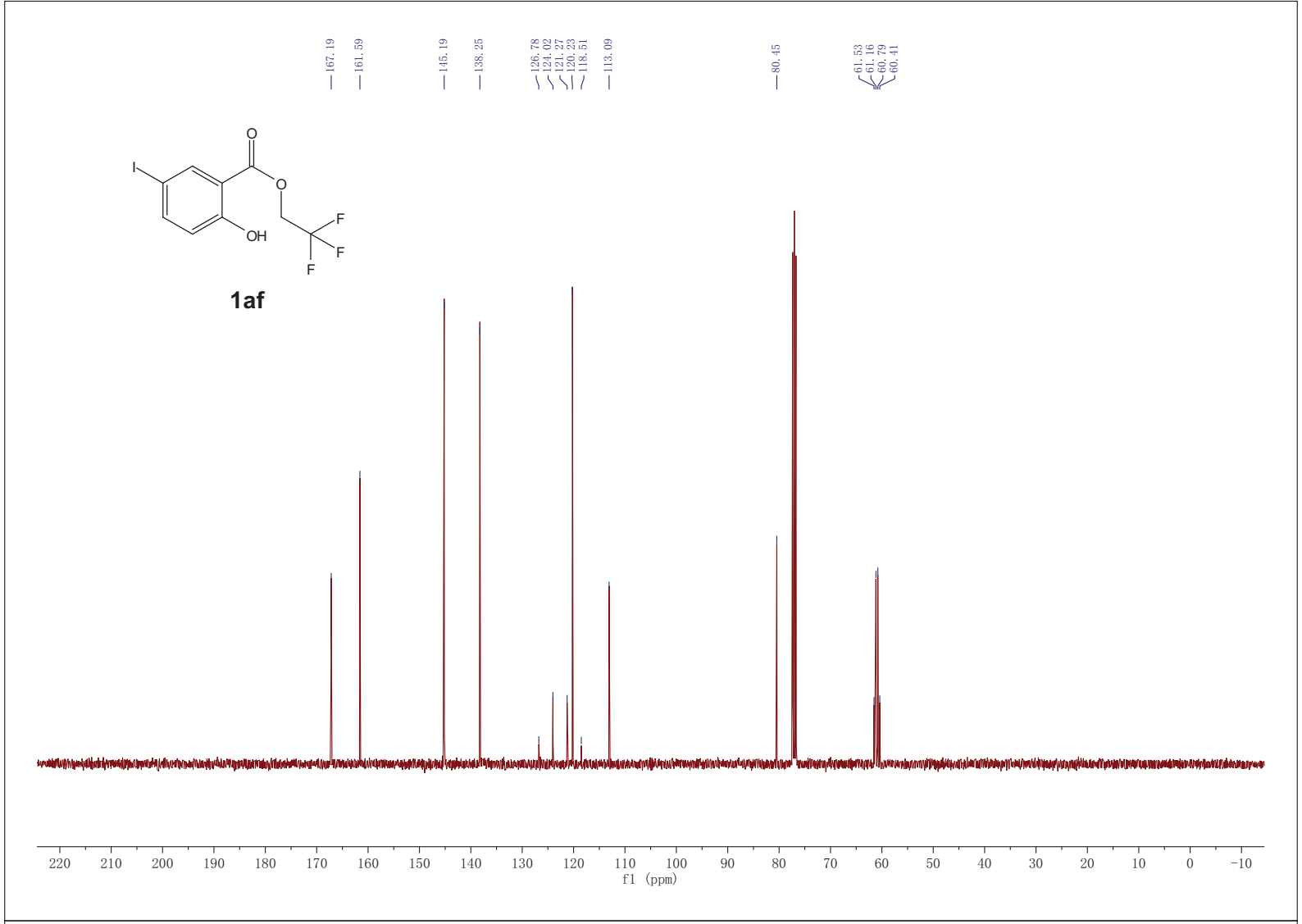
^{19}FNMR

3ae

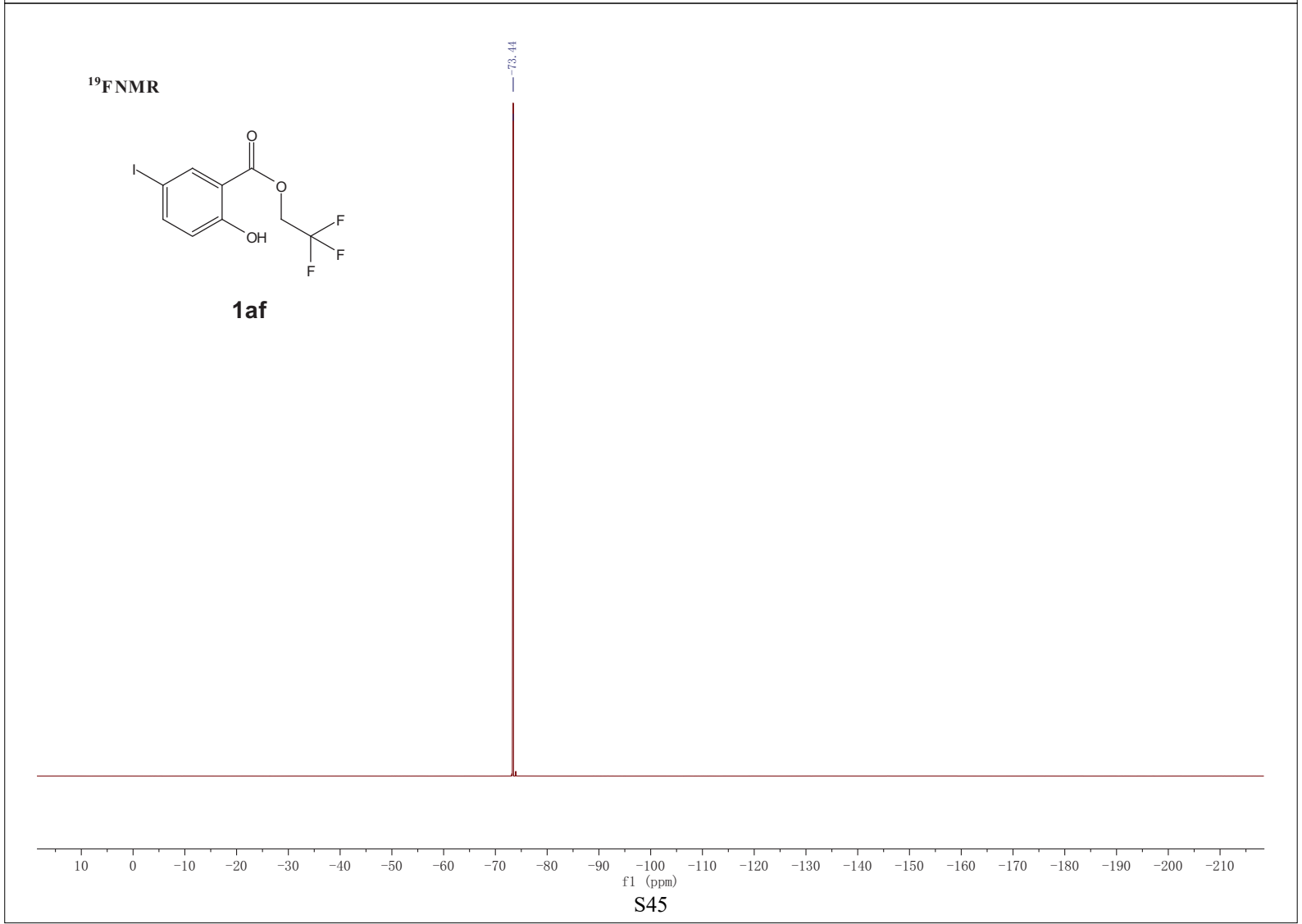


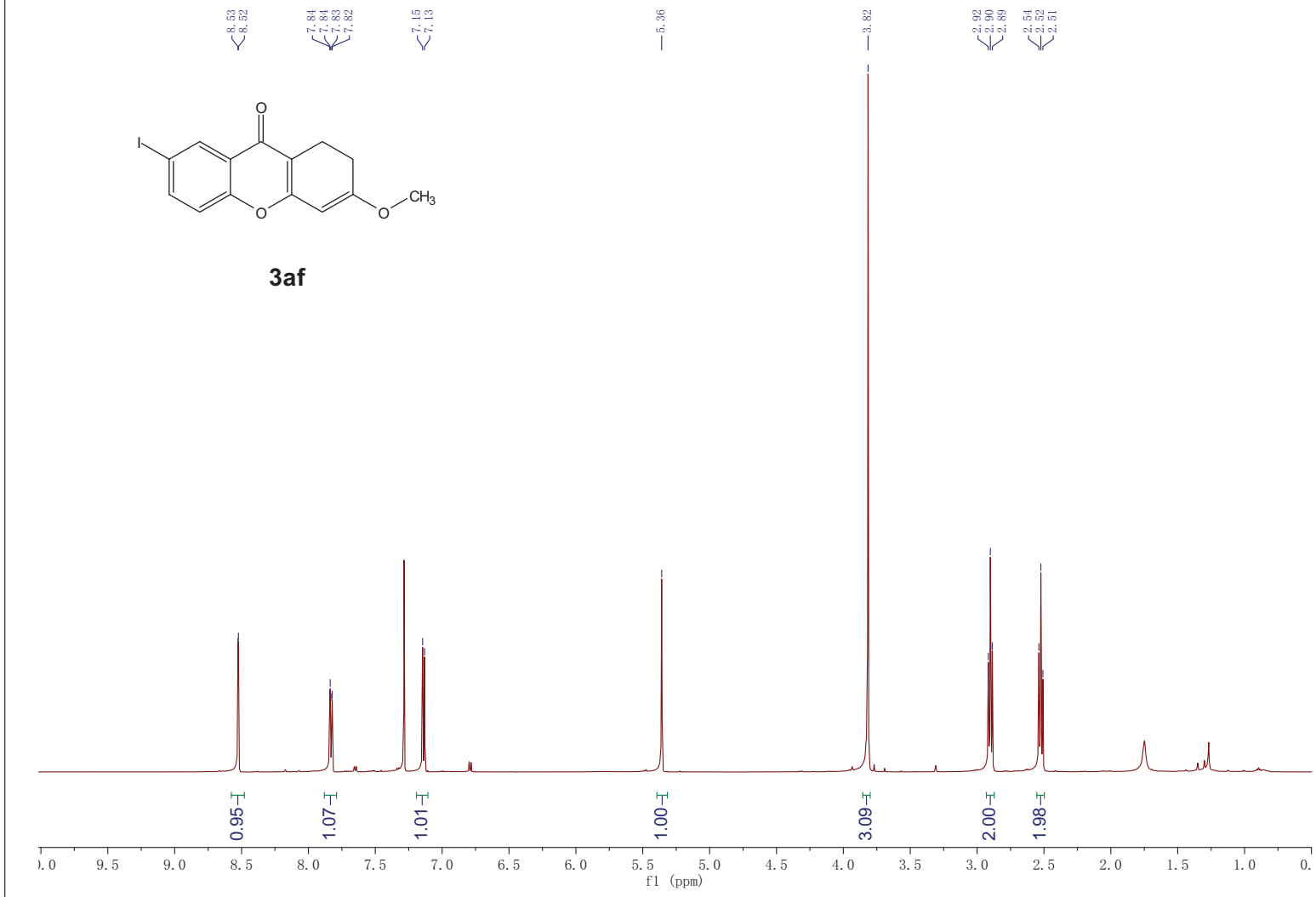
1af



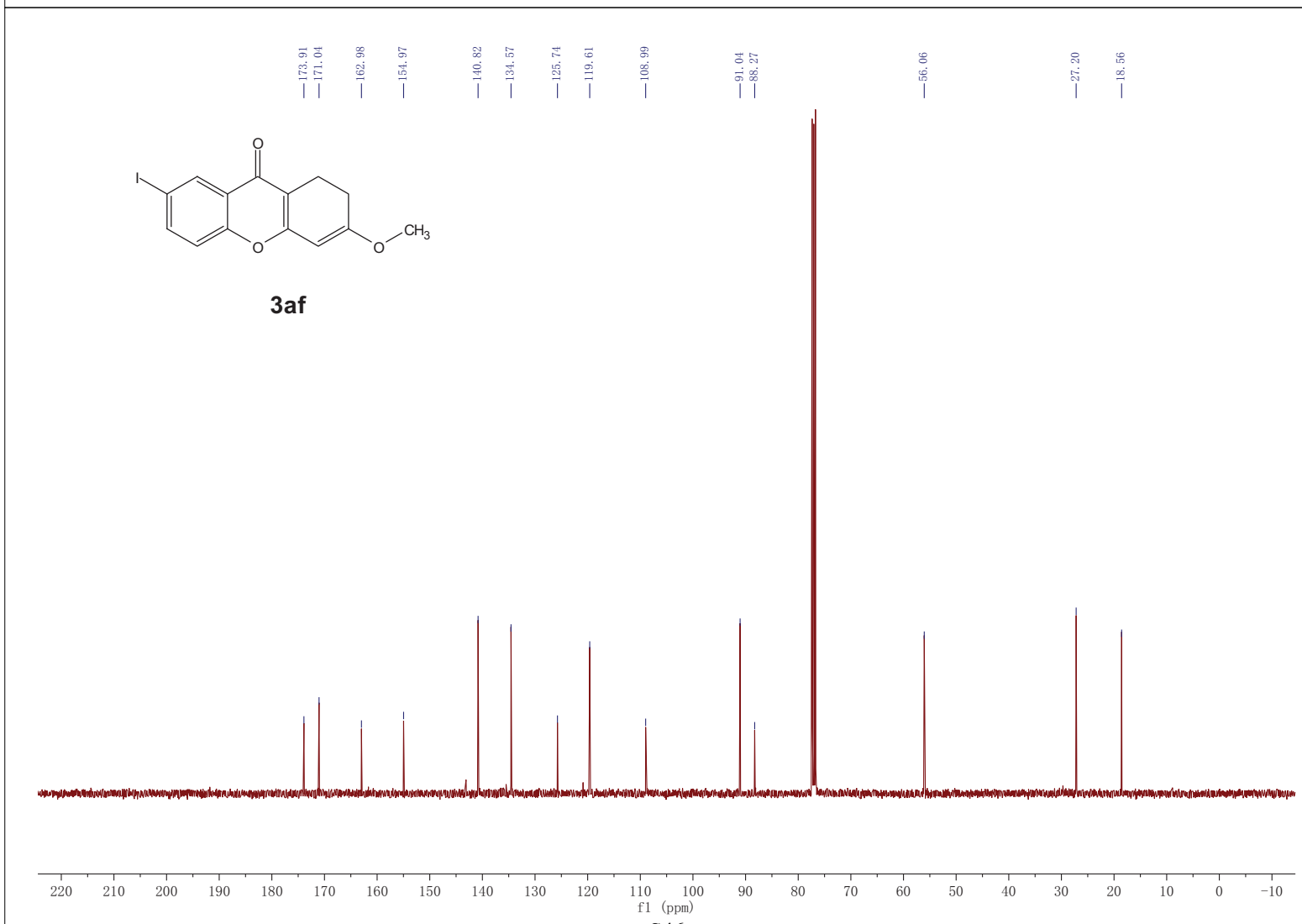

167.19
161.59
145.19
138.25
126.78
124.02
121.27
120.23
118.51
113.09
80.45
61.53
61.16
60.79
60.41
O
I
O
F
F
F
OH
1af
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{19}FNMR

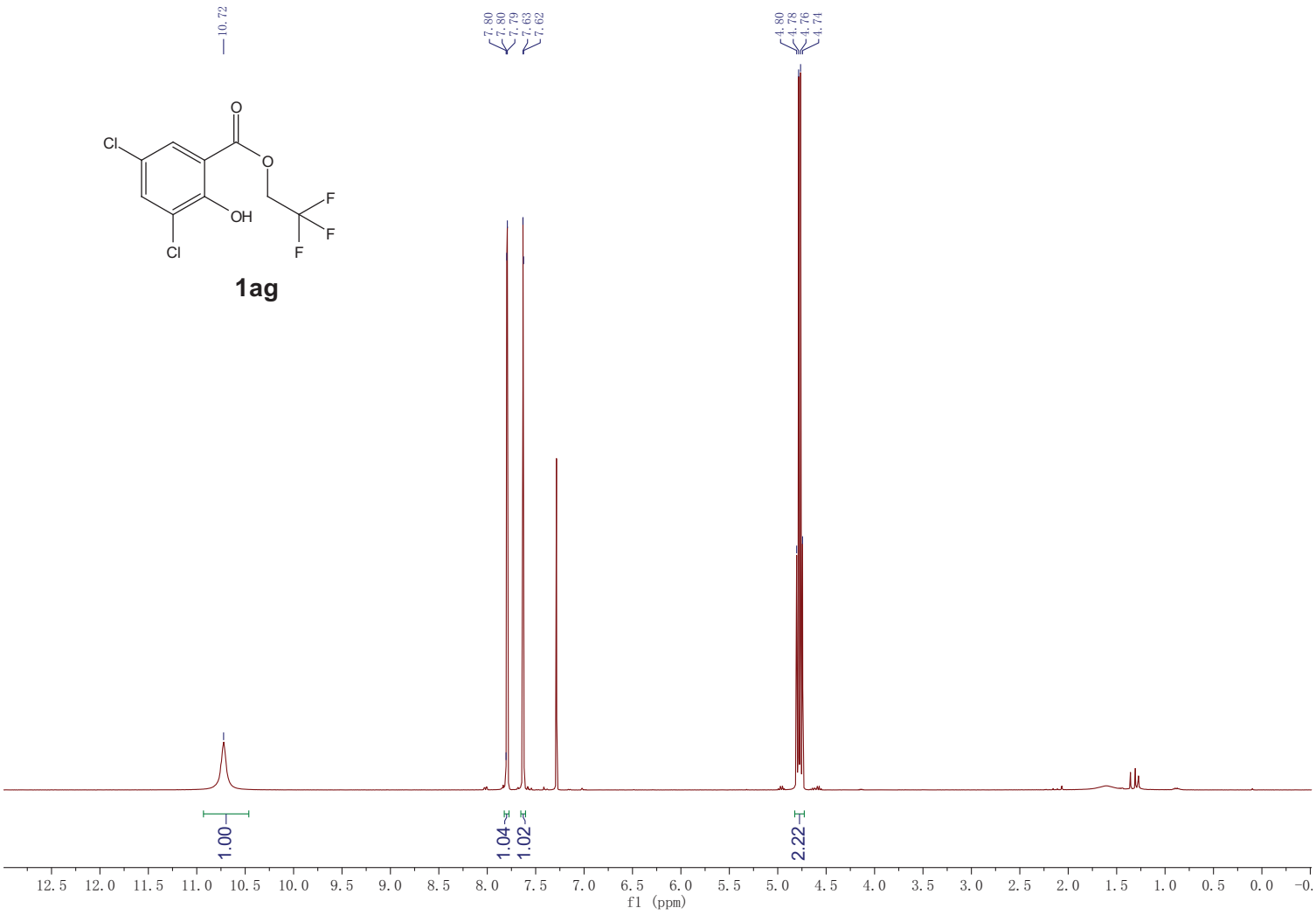

−73.44
O
I
O
F
F
F
OH
1af
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

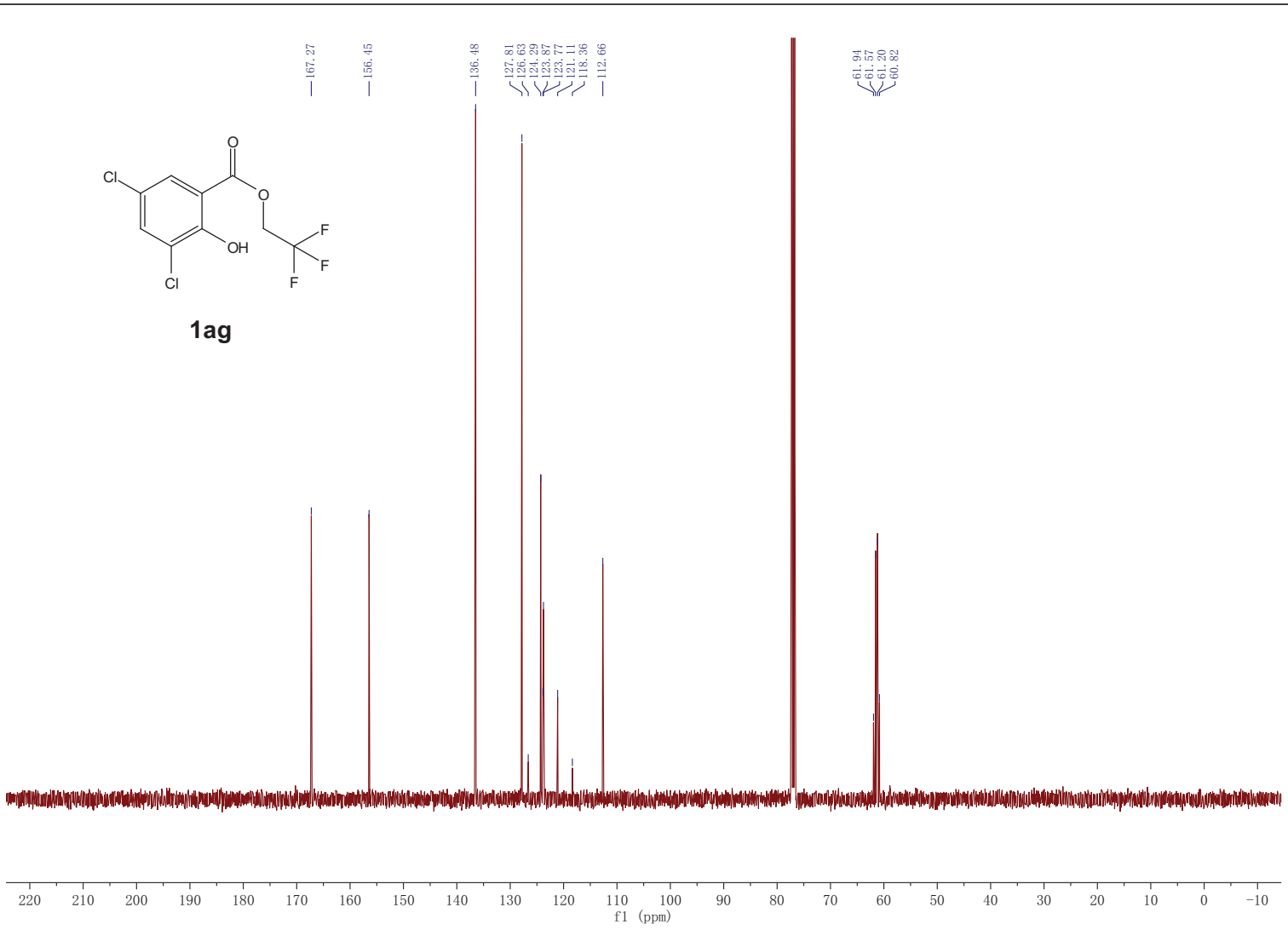

8.53
8.52
7.84
7.84
7.83
7.82
7.15
7.13
5.36
3.82
2.92
2.90
2.89
2.54
2.52
2.51
O
I
O
O
CH3
0.95
1.07
1.01
1.00
3.09
2.00
1.98
f1 (ppm)

3af


173.91
171.04
162.98
154.97
140.82
134.57
125.74
119.61
108.99
91.04
88.27
56.06
27.20
18.56
O
I
O
O
CH3
f1 (ppm)

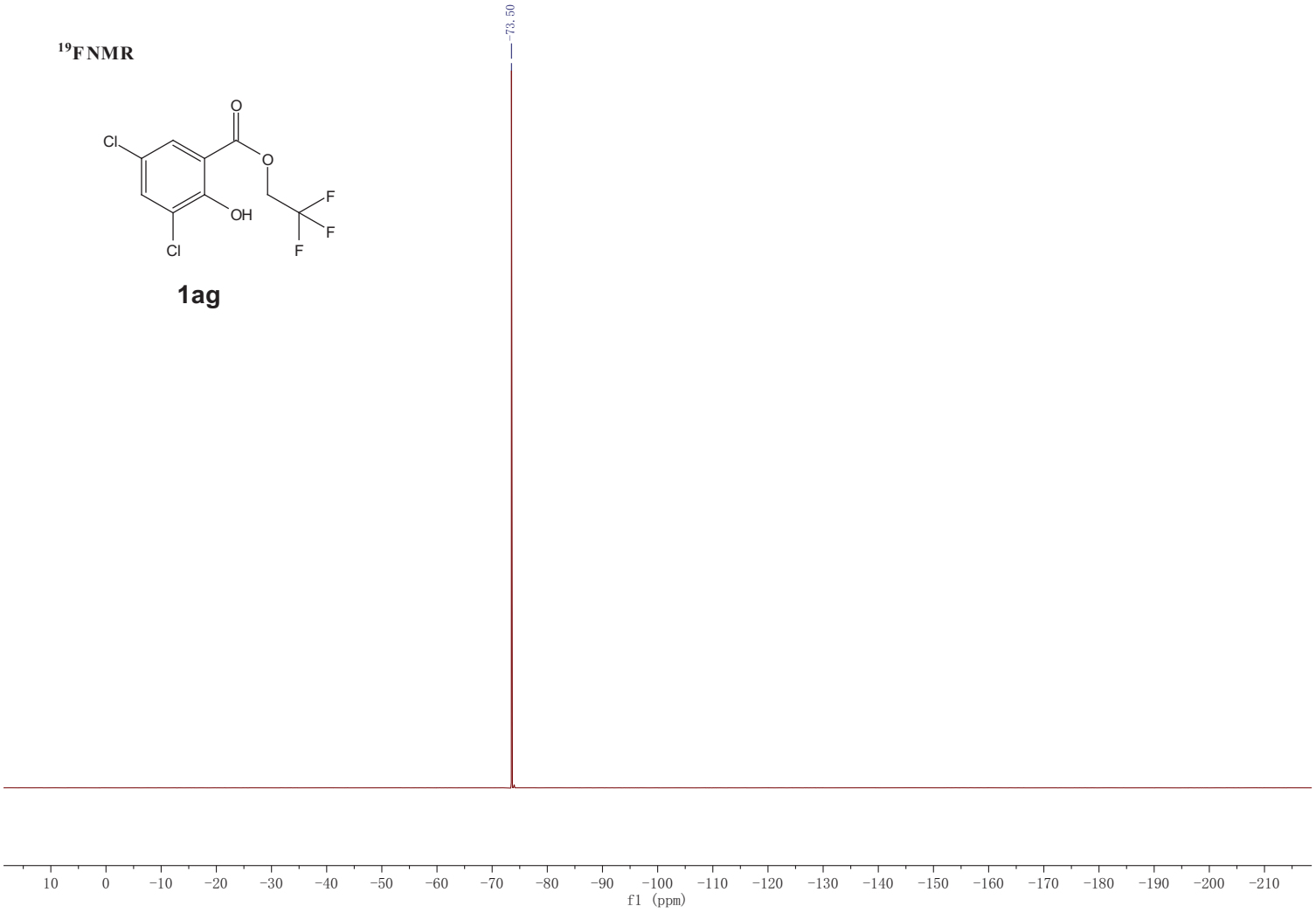
3af


10.72
7.80
7.80
7.79
7.63
7.62
4.80
4.78
4.76
4.74
Cl
O
O
OH
Cl
F
F
F
1ag
1.00
1.04
1.02
2.22
f1 (ppm)

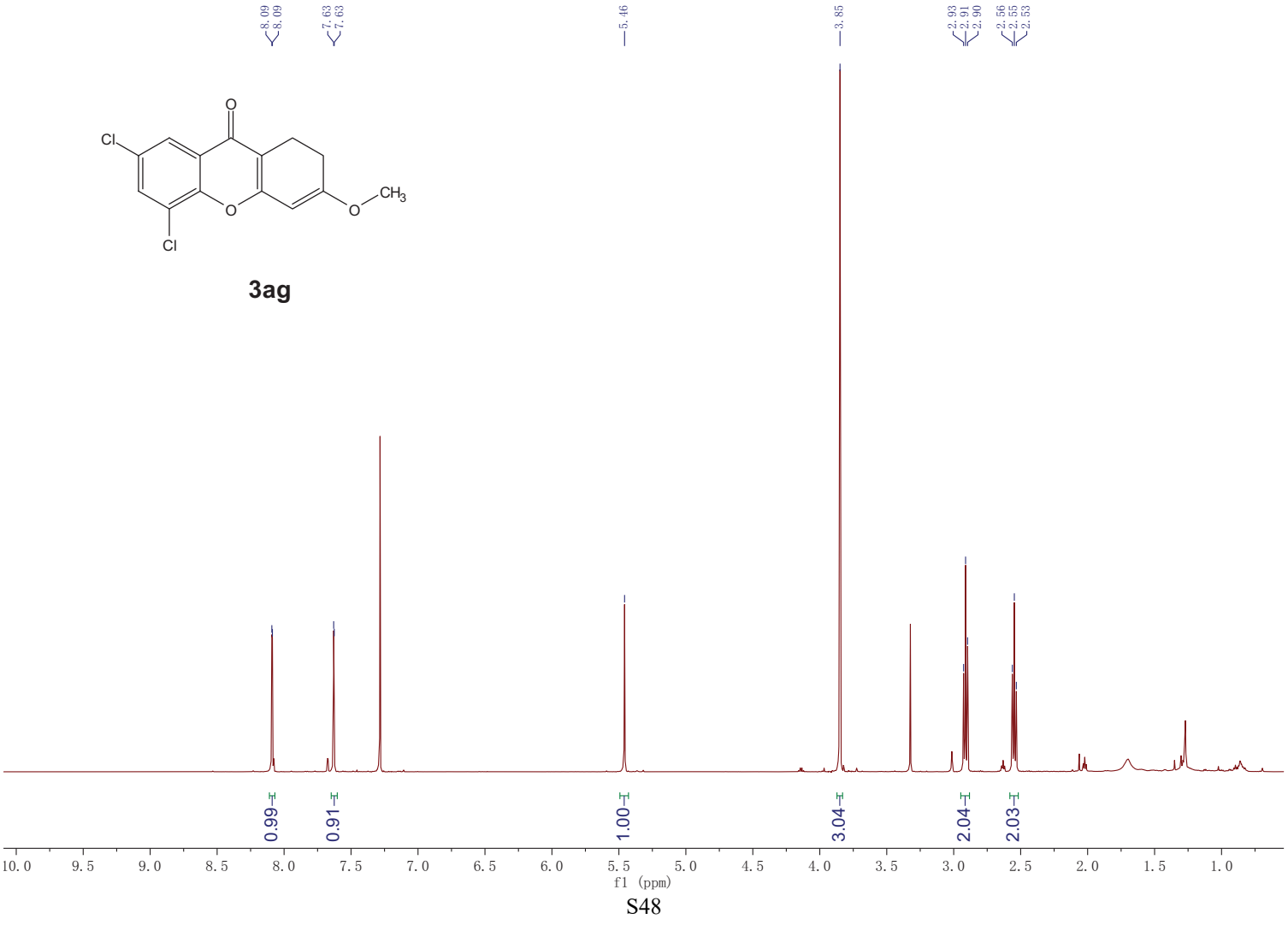

167.27
156.45
136.48
127.81
126.63
124.29
123.87
123.77
121.11
118.36
112.66
61.94
61.57
61.20
60.82
Cl
O
O
OH
Cl
F
F
F
1ag
f1 (ppm)

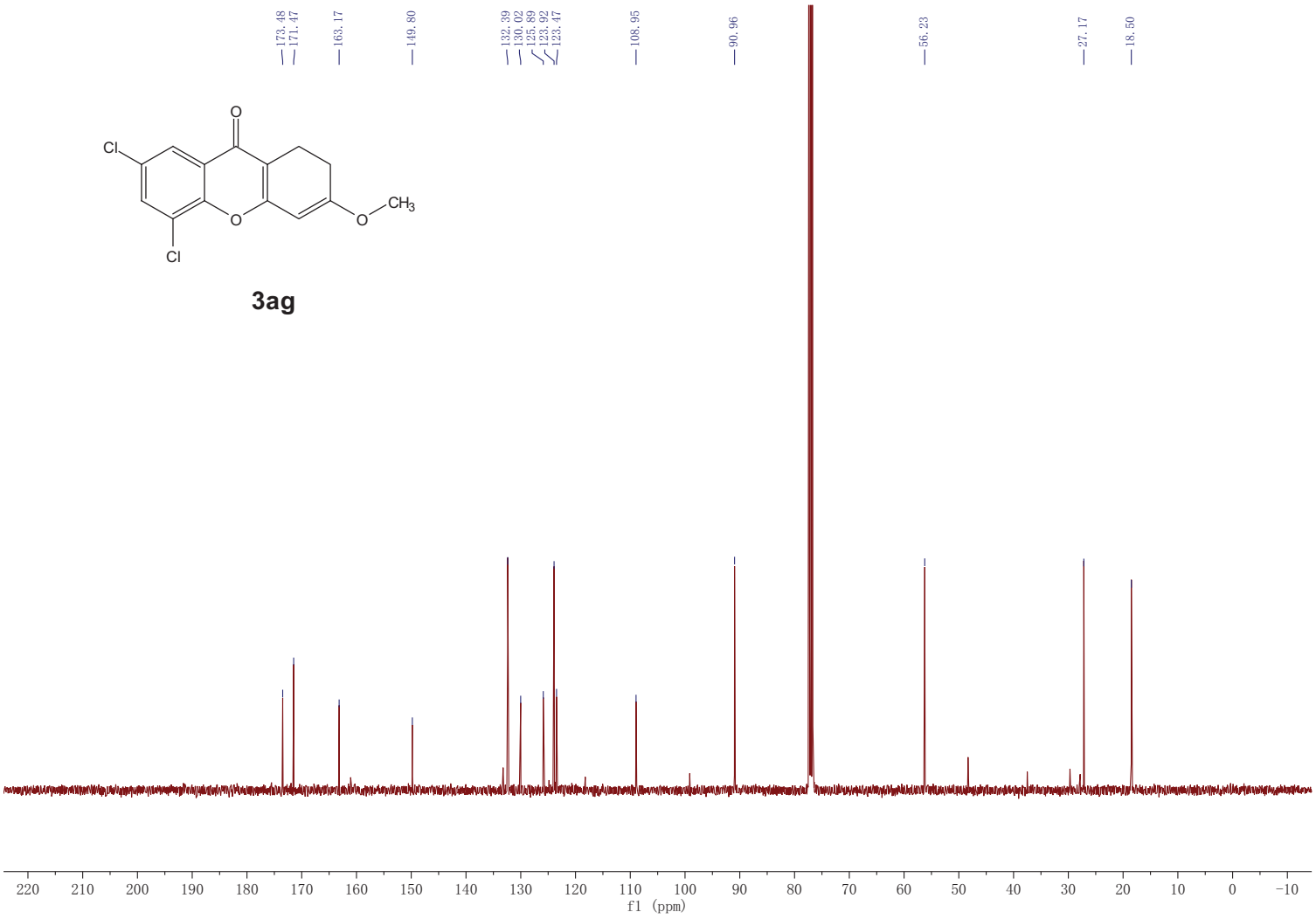
^{19}FNMR

1ag

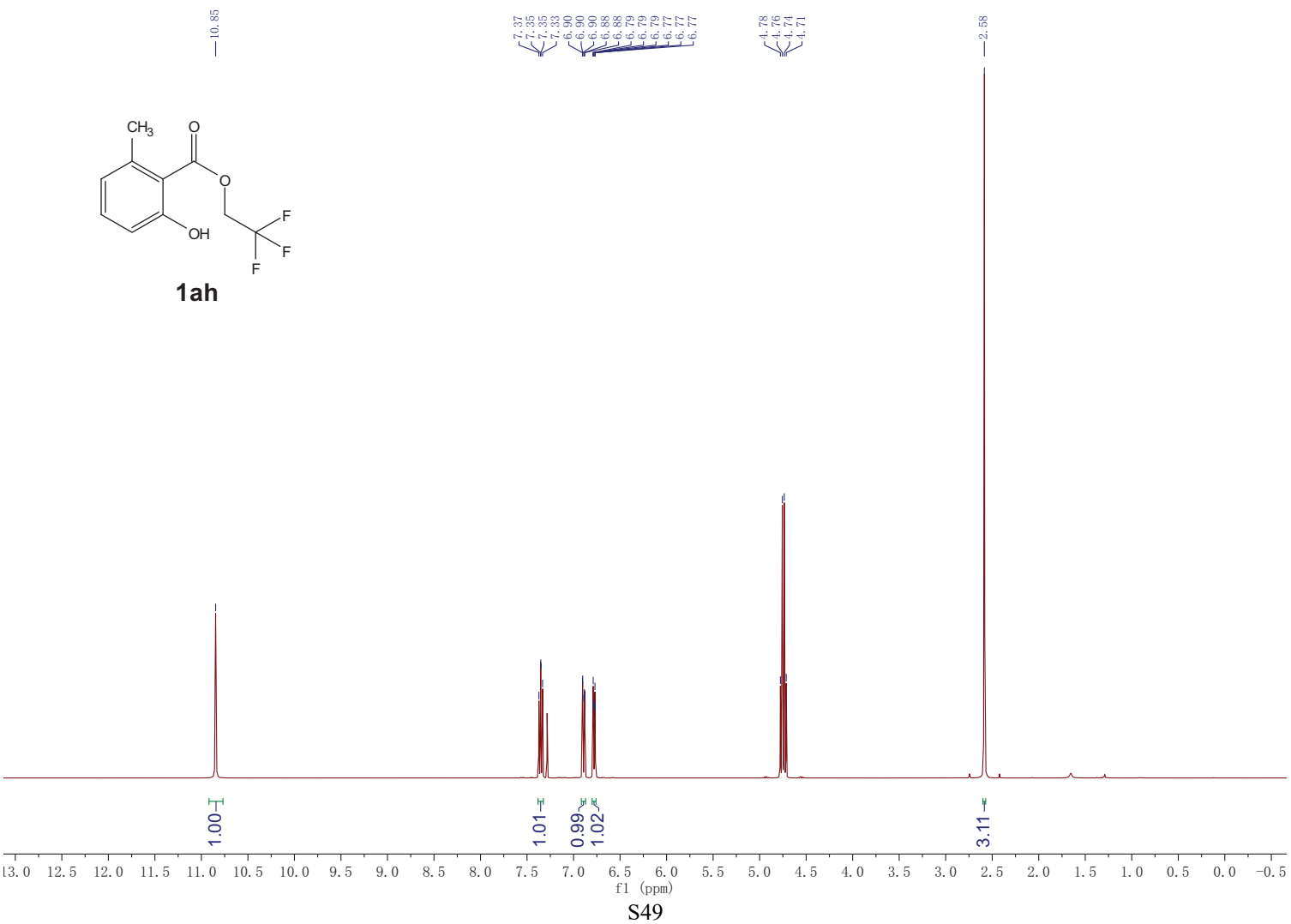


3ag

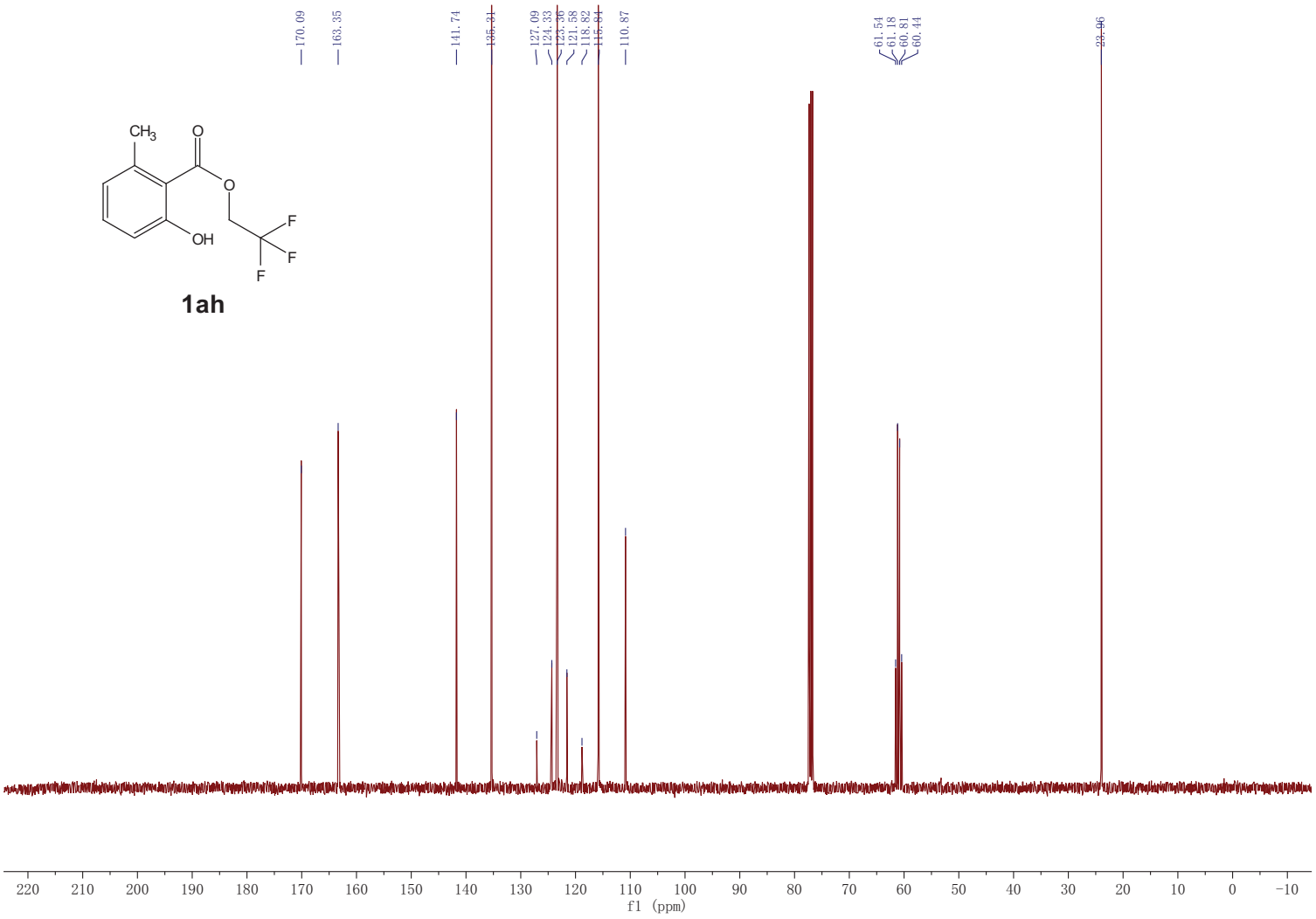



173.48
171.47
163.17
149.80
132.39
130.02
125.89
123.92
123.47
108.95
90.96
56.23
27.17
18.50
Cl
O
O
O
CH3
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

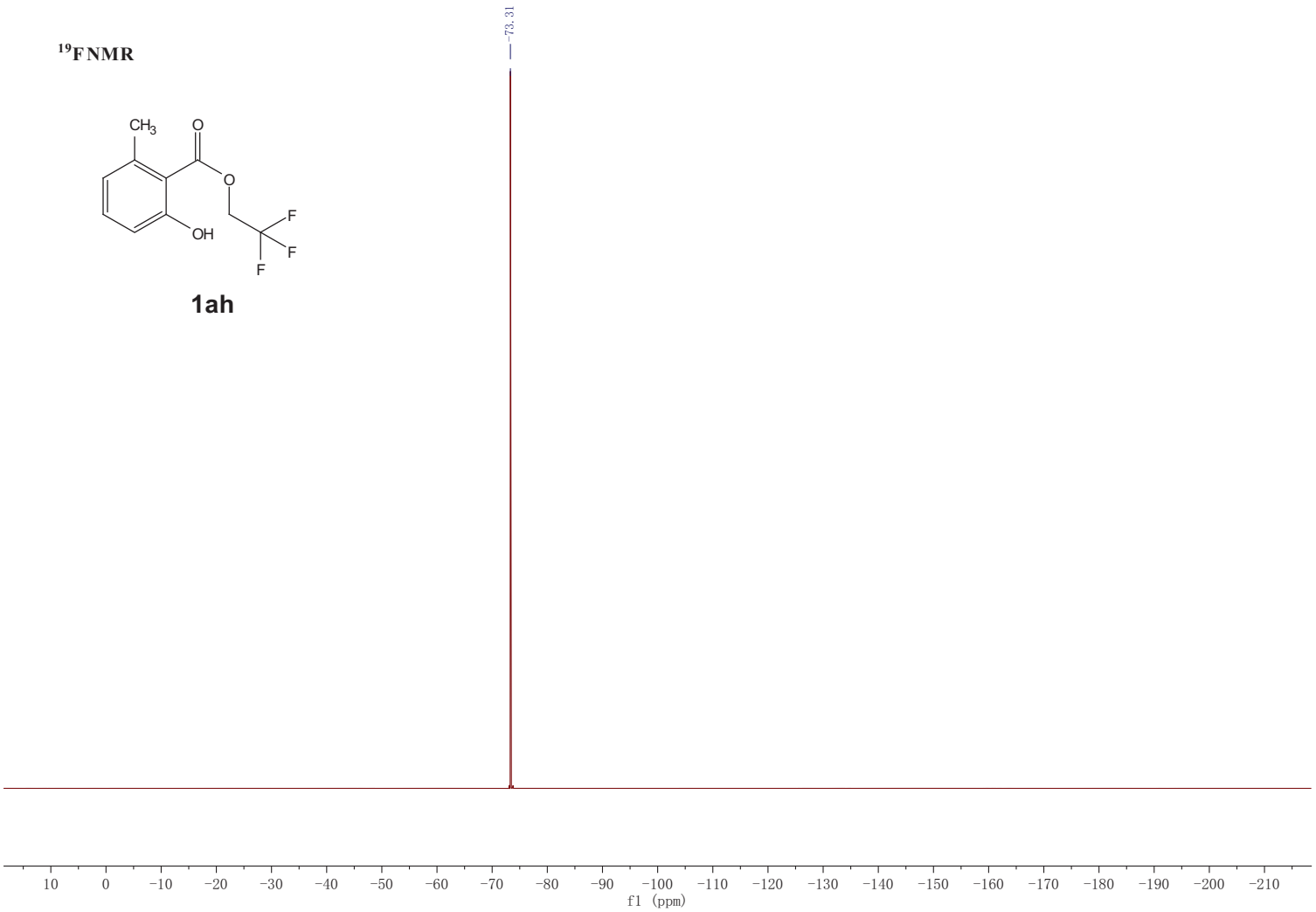
3ag

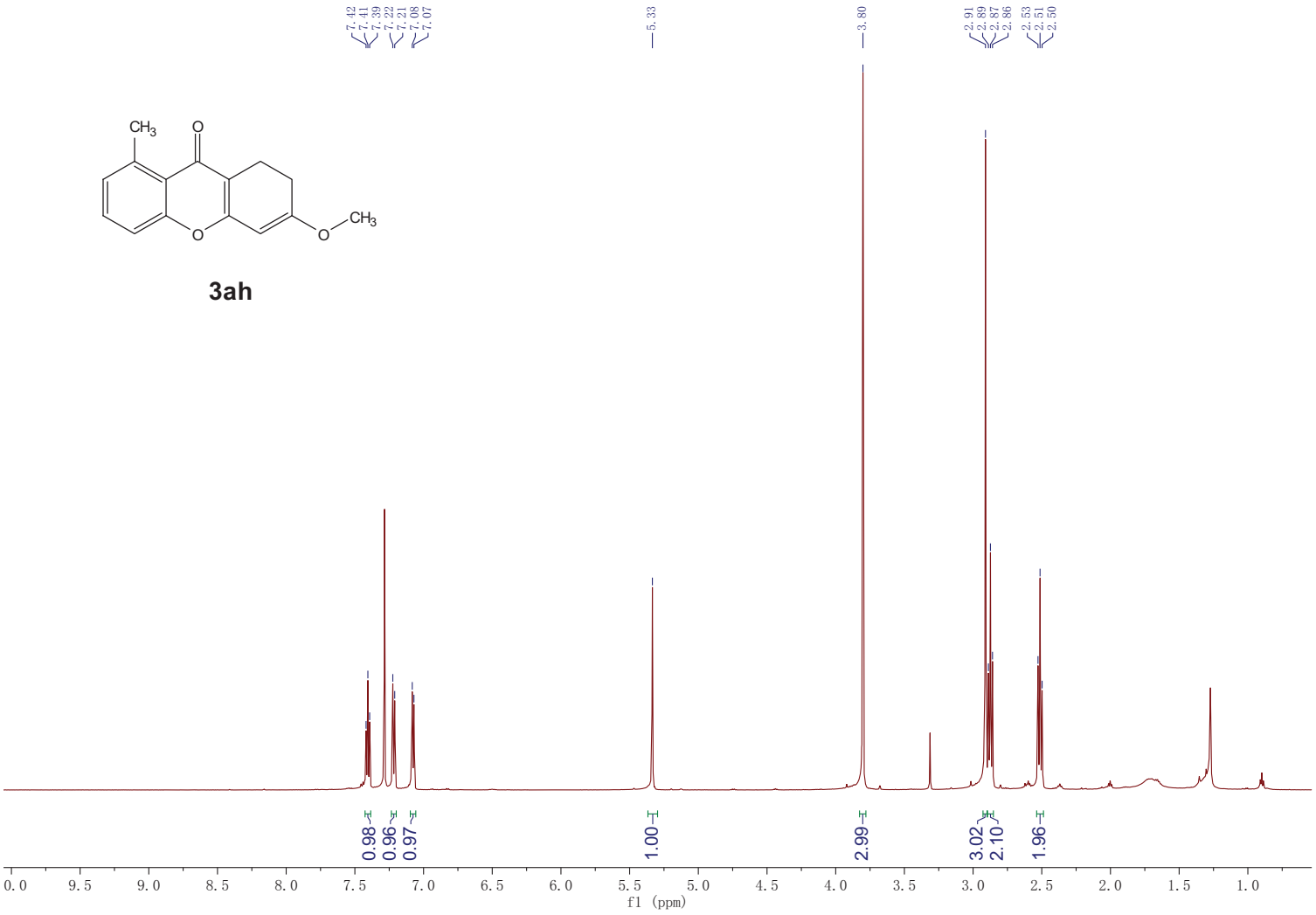

10.85
7.37
7.35
7.35
7.33
6.90
6.90
6.90
6.88
6.88
6.79
6.79
6.79
6.77
6.77
6.77
6.77
4.78
4.76
4.74
4.71
2.58
CH3
O
O
OH
F
F
F
1.00
1.01
0.99
1.02
3.11
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

1ah

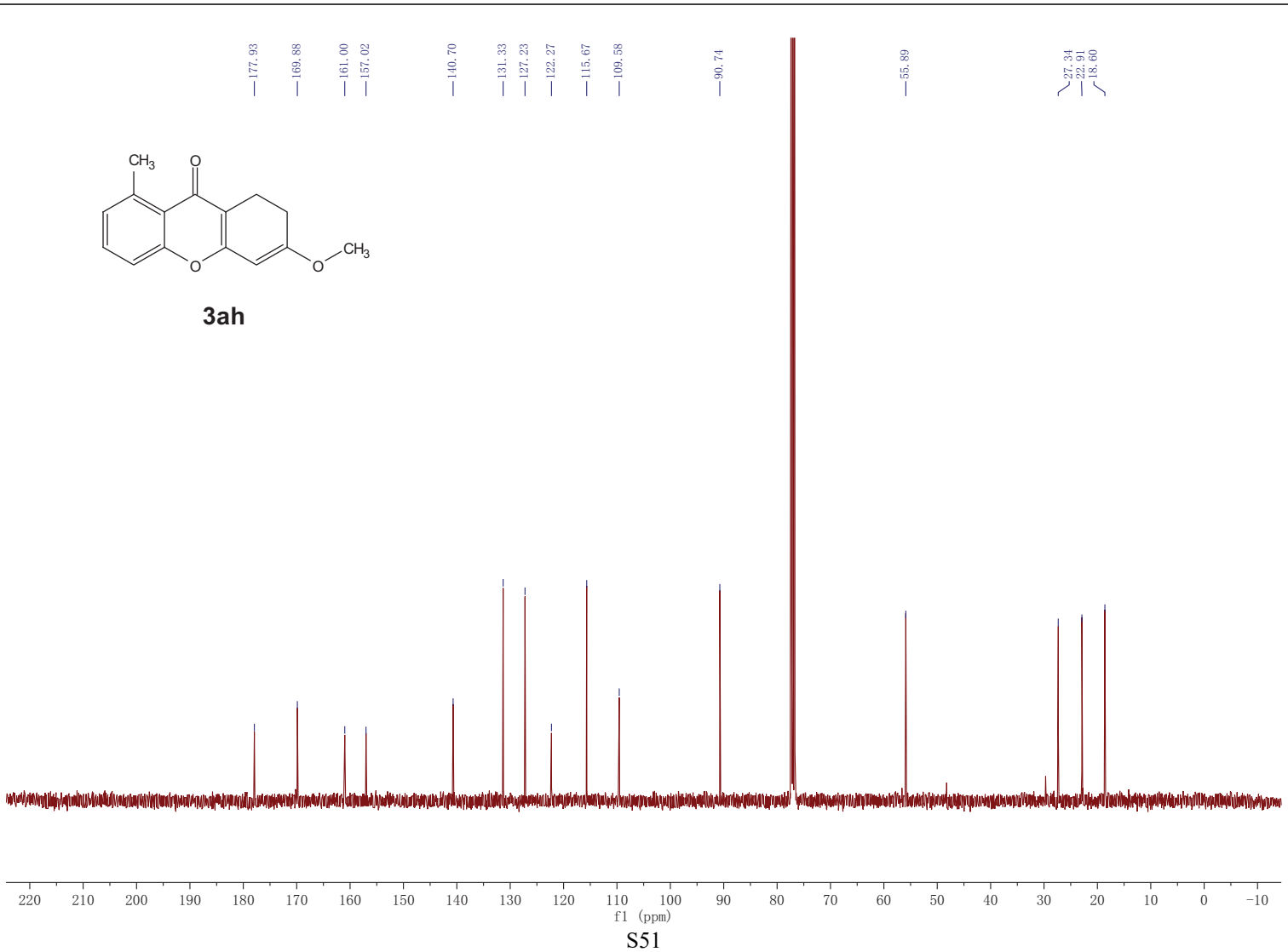

170.09
163.35
141.74
135.31
127.09
124.33
123.36
121.58
118.82
116.84
110.87
61.54
61.18
60.81
60.44
23.96
CH3
O
O
OH
F
F
F
1ah
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{19}FNMR

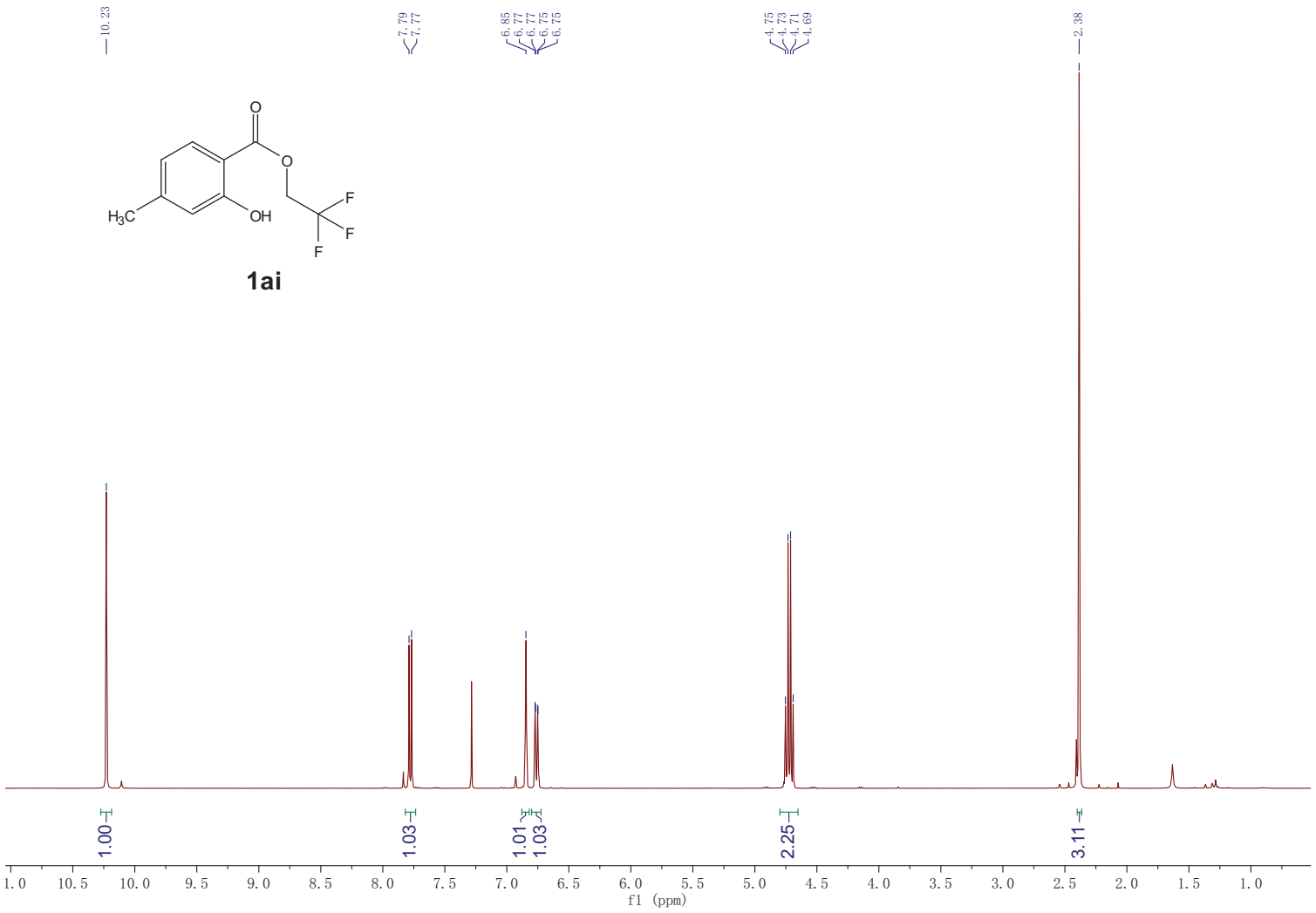

−73.31
CH3
O
O
OH
F
F
F
1ah
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

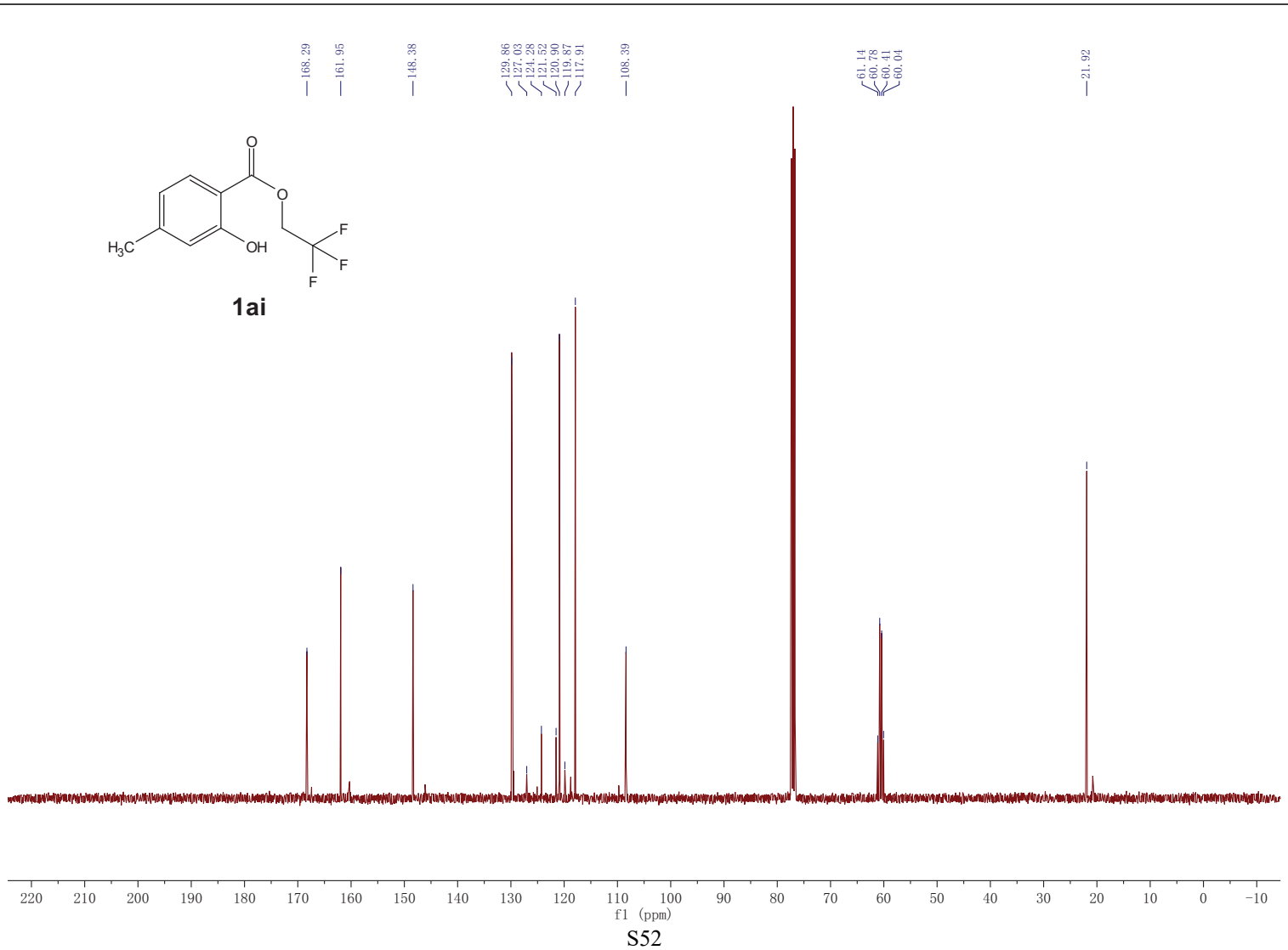

7.42
7.41
7.39
7.22
7.21
7.08
7.07
5.33
3.80
2.91
2.89
2.87
2.86
2.53
2.51
2.50
CH3
O
O
CH3
0.98
0.96
0.97
1.00
2.99
3.02
2.10
1.96
f1 (ppm)

3ah


177.93
169.88
161.00
157.02
140.70
131.33
127.23
122.27
115.67
109.58
90.74
55.89
27.34
22.91
18.60
CH3
O
O
CH3
f1 (ppm)

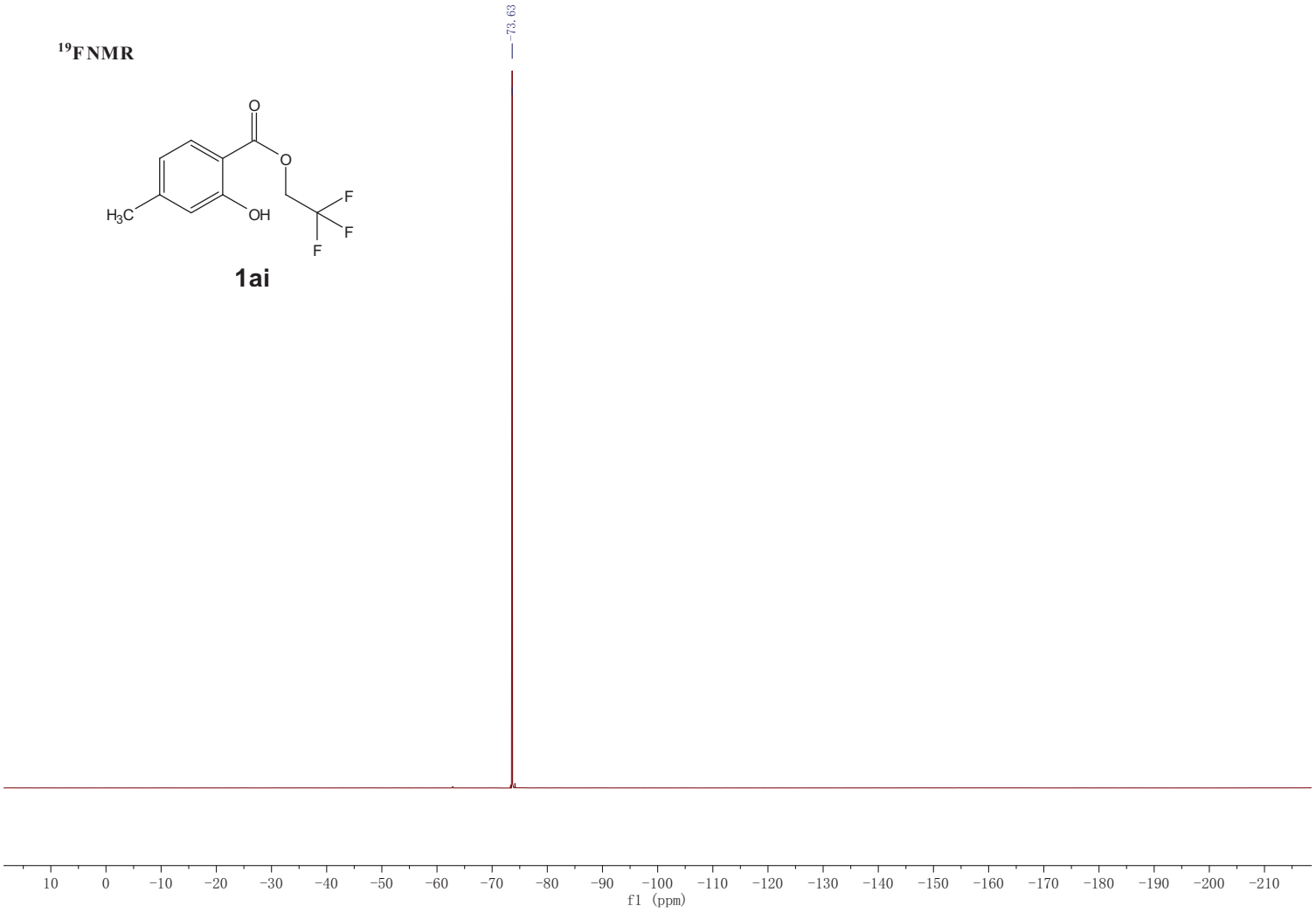
3ah


10.23
7.79
7.77
6.85
6.77
6.77
6.75
6.75
4.75
4.73
4.71
4.69
2.38
O
O
F
F
F
H3C
OH
1ai
1.00
1.03
1.01
1.03
2.25
3.11
f1 (ppm)

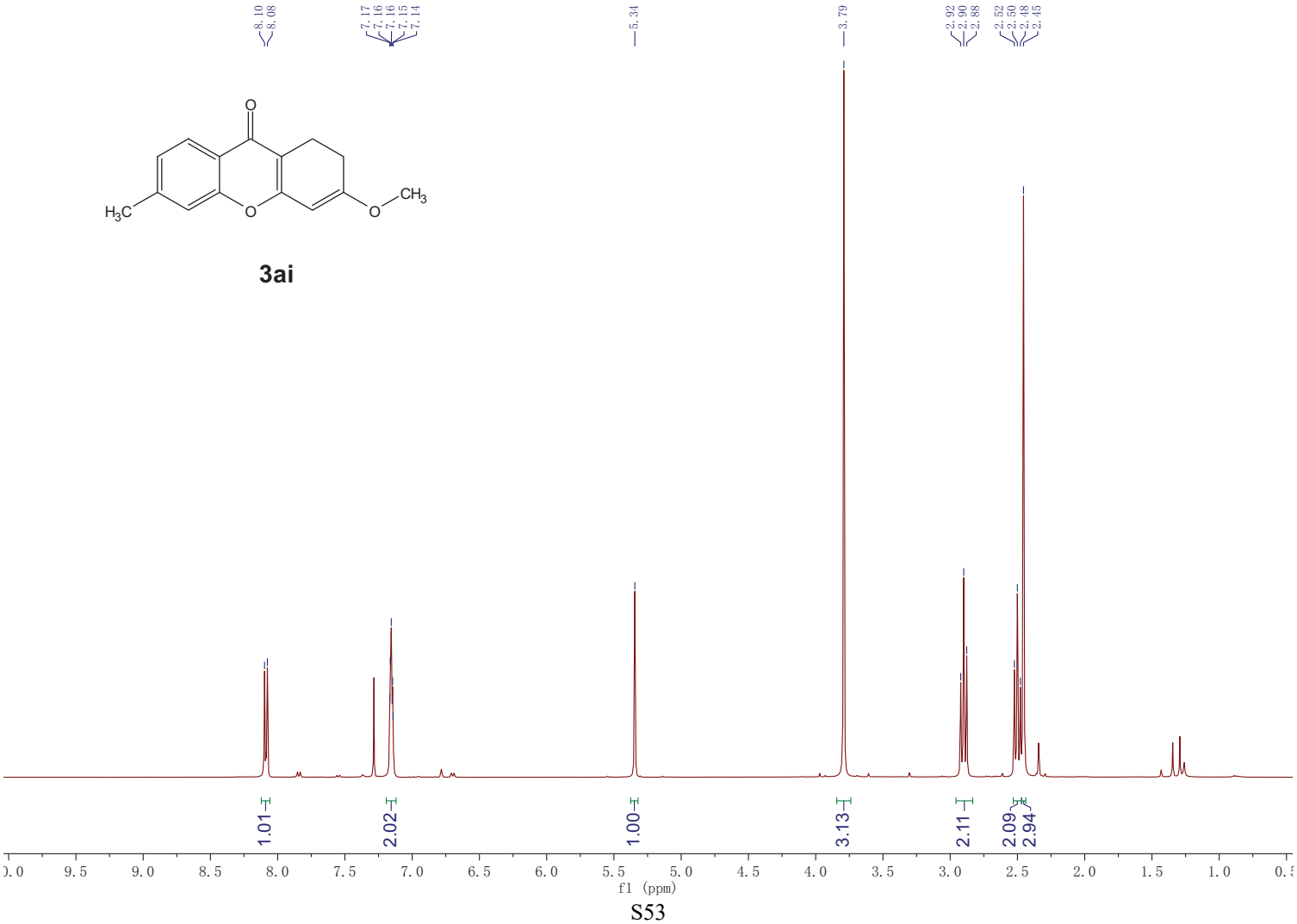

168.29
161.95
148.38
129.86
127.03
124.28
121.52
120.90
119.87
117.91
108.39
61.14
60.78
60.41
60.04
21.92
O
O
F
F
F
H3C
OH
1ai
f1 (ppm)

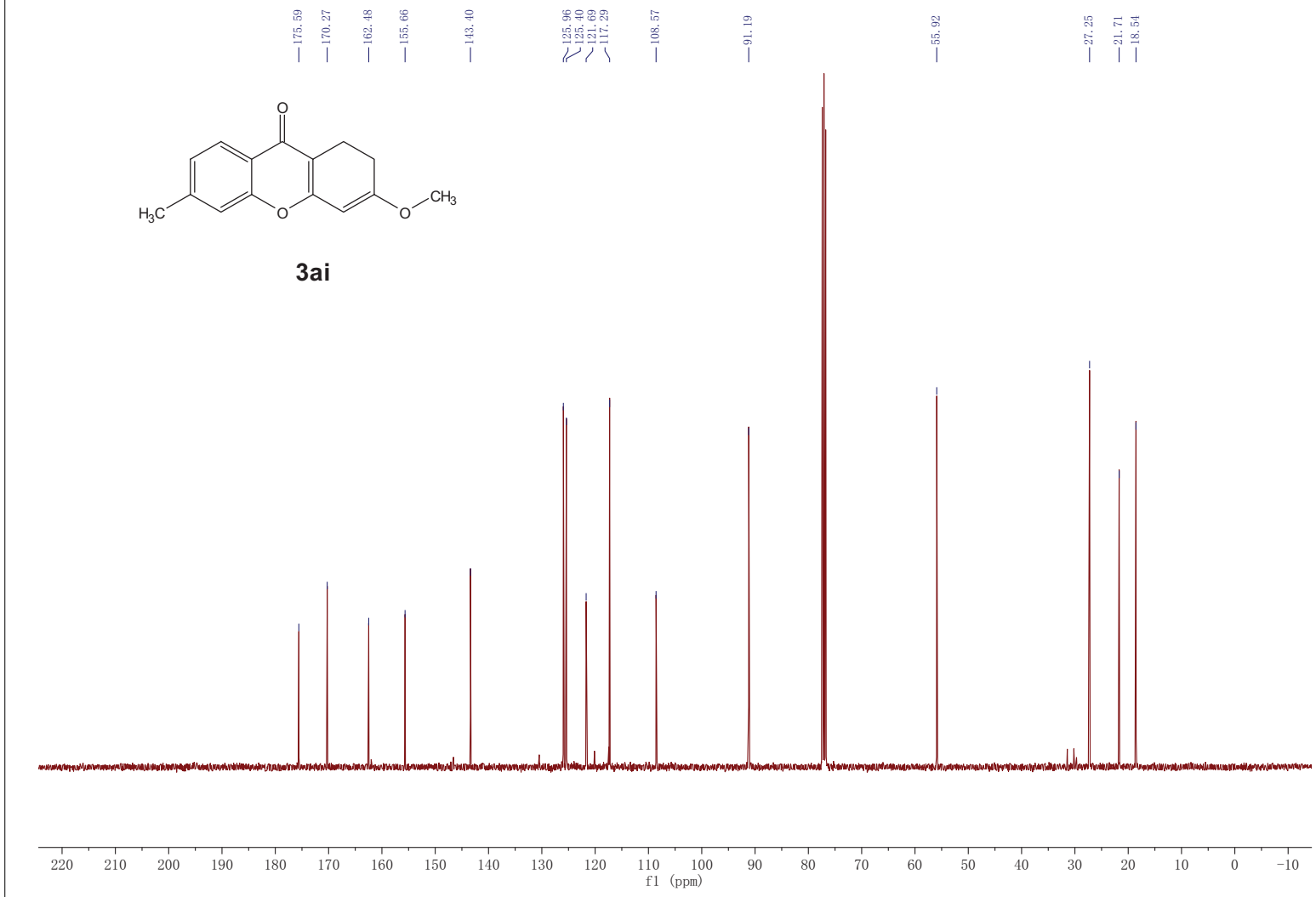
^{19}FNMR

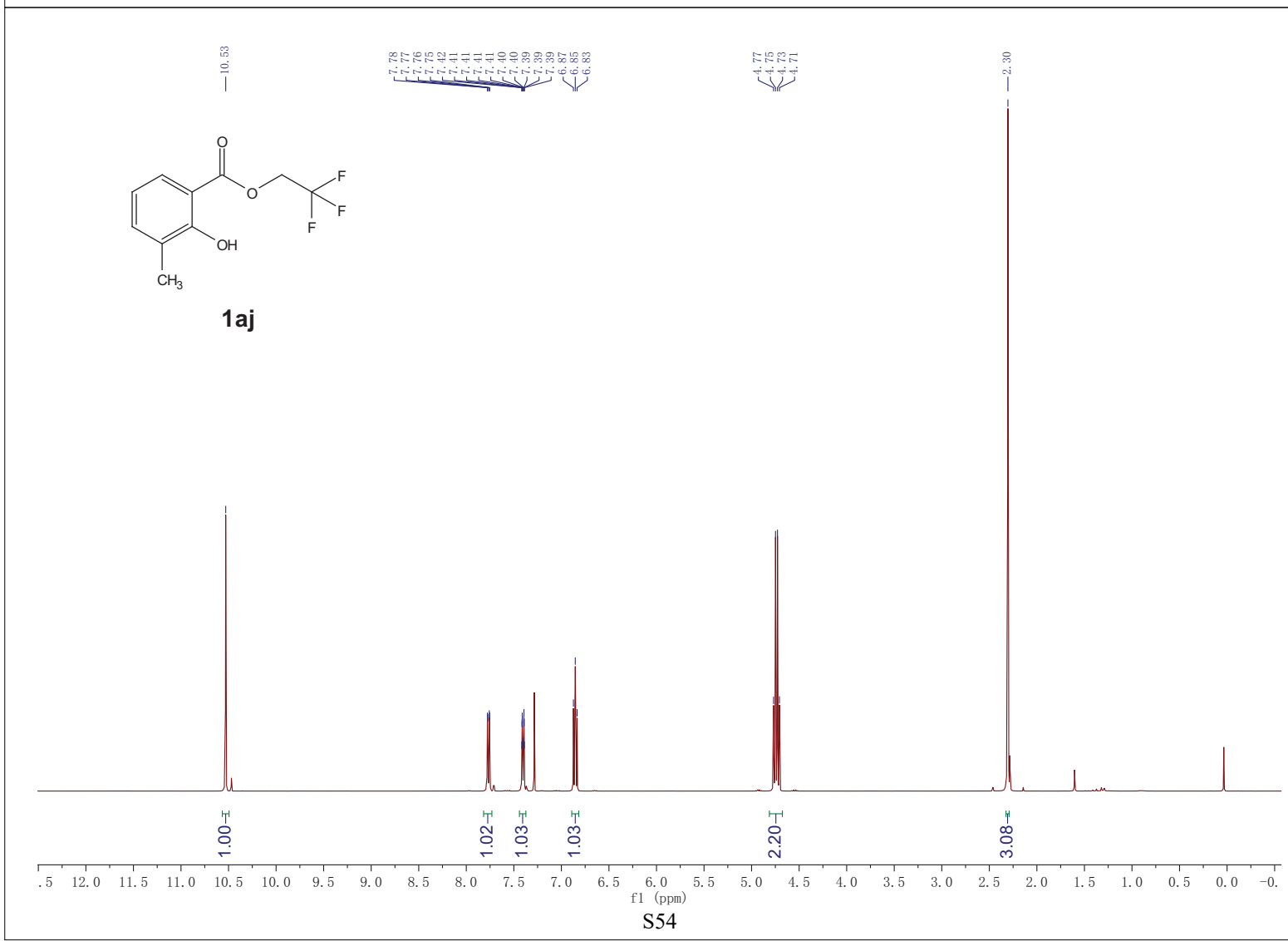
1ai

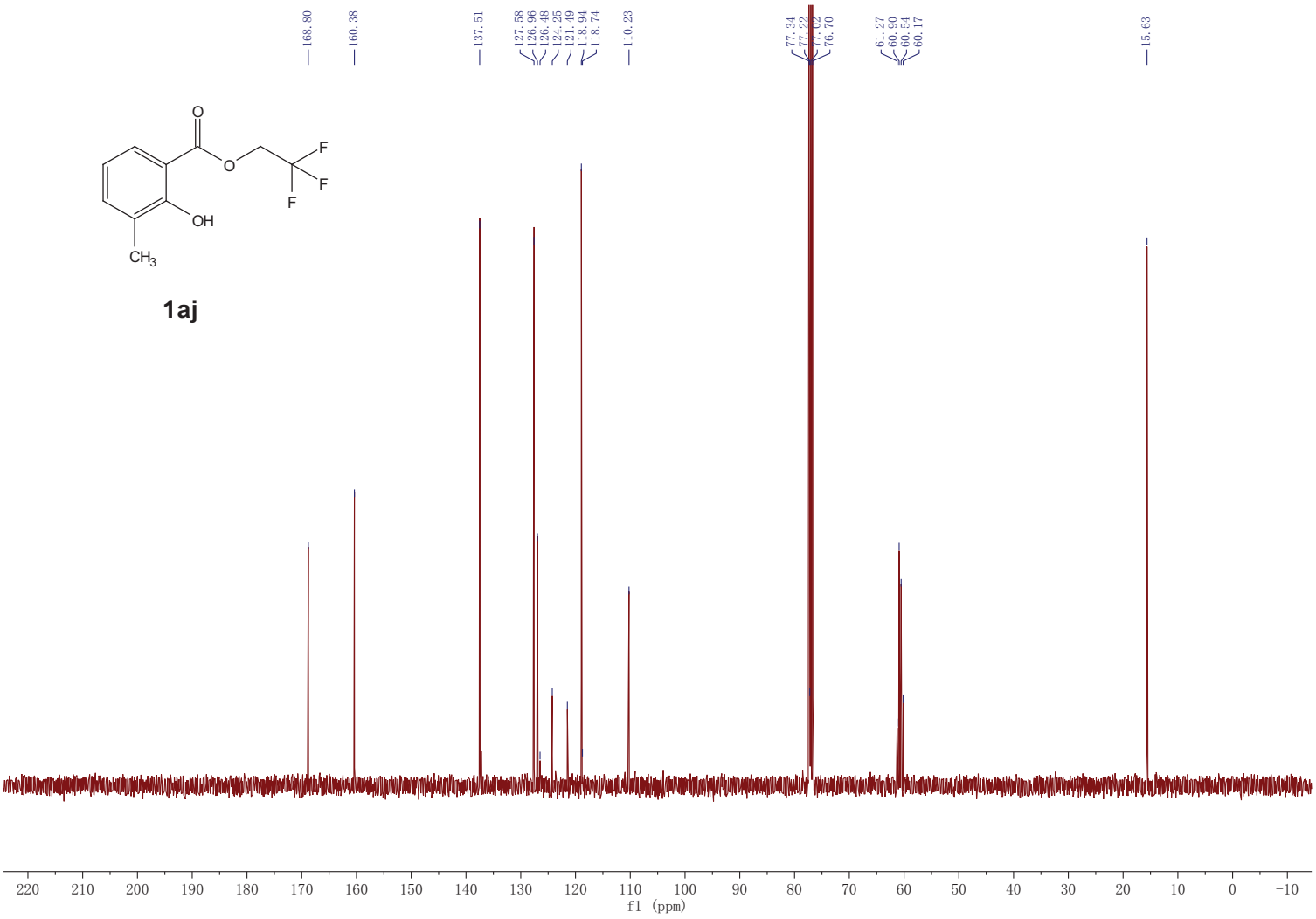


3ai



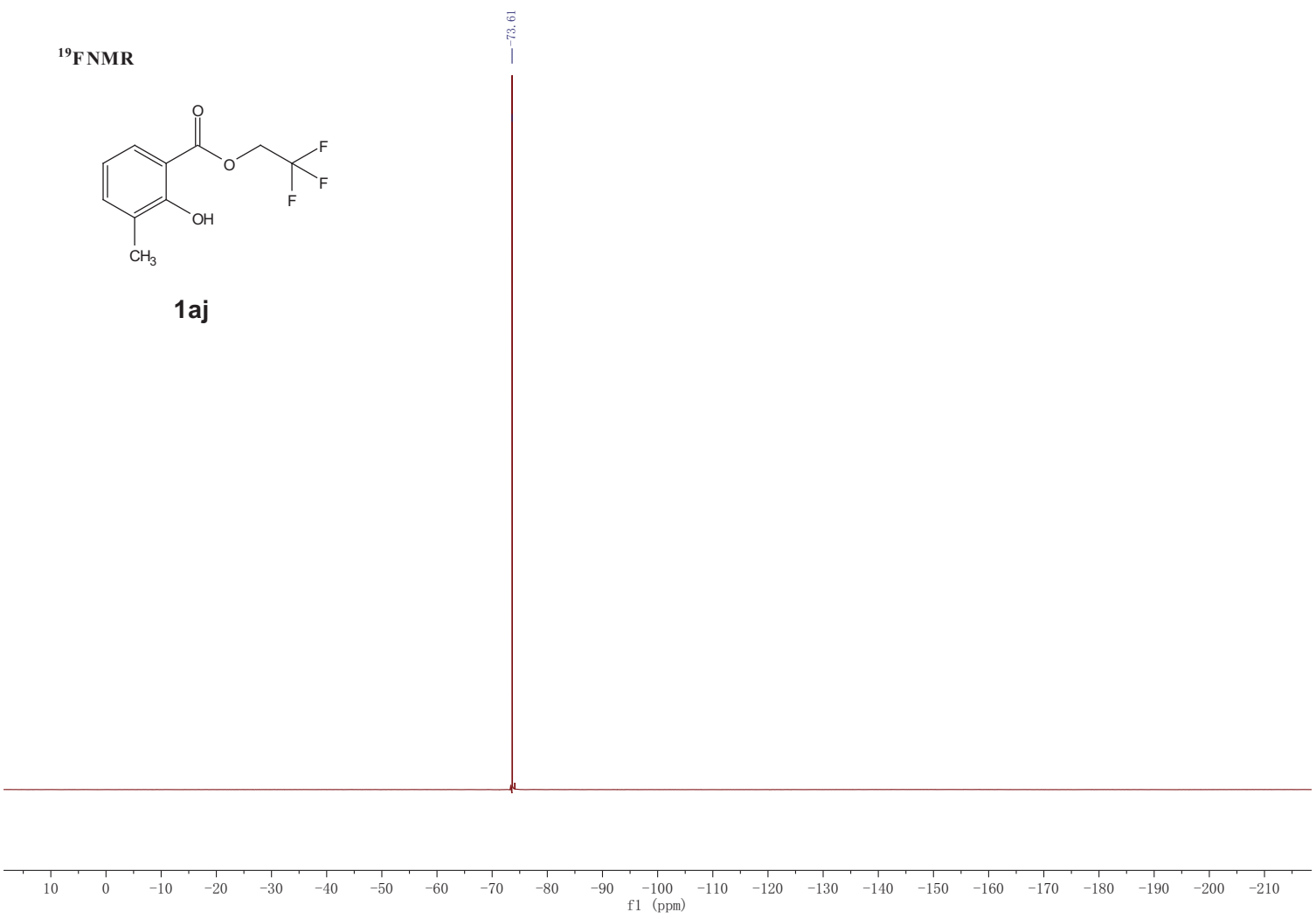

175.59
170.27
162.48
155.66
143.40
125.96
125.40
121.69
117.29
108.57
91.19
55.92
27.25
21.71
18.54
O
H3C
O
O
CH3
3ai
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.53
7.78
7.77
7.76
7.75
7.42
7.41
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.39
6.87
6.85
6.83
4.77
4.75
4.73
4.71
2.30
O
O
F
F
F
OH
CH3
1aj
1.00
1.02
1.03
1.03
2.20
3.08
f1 (ppm)

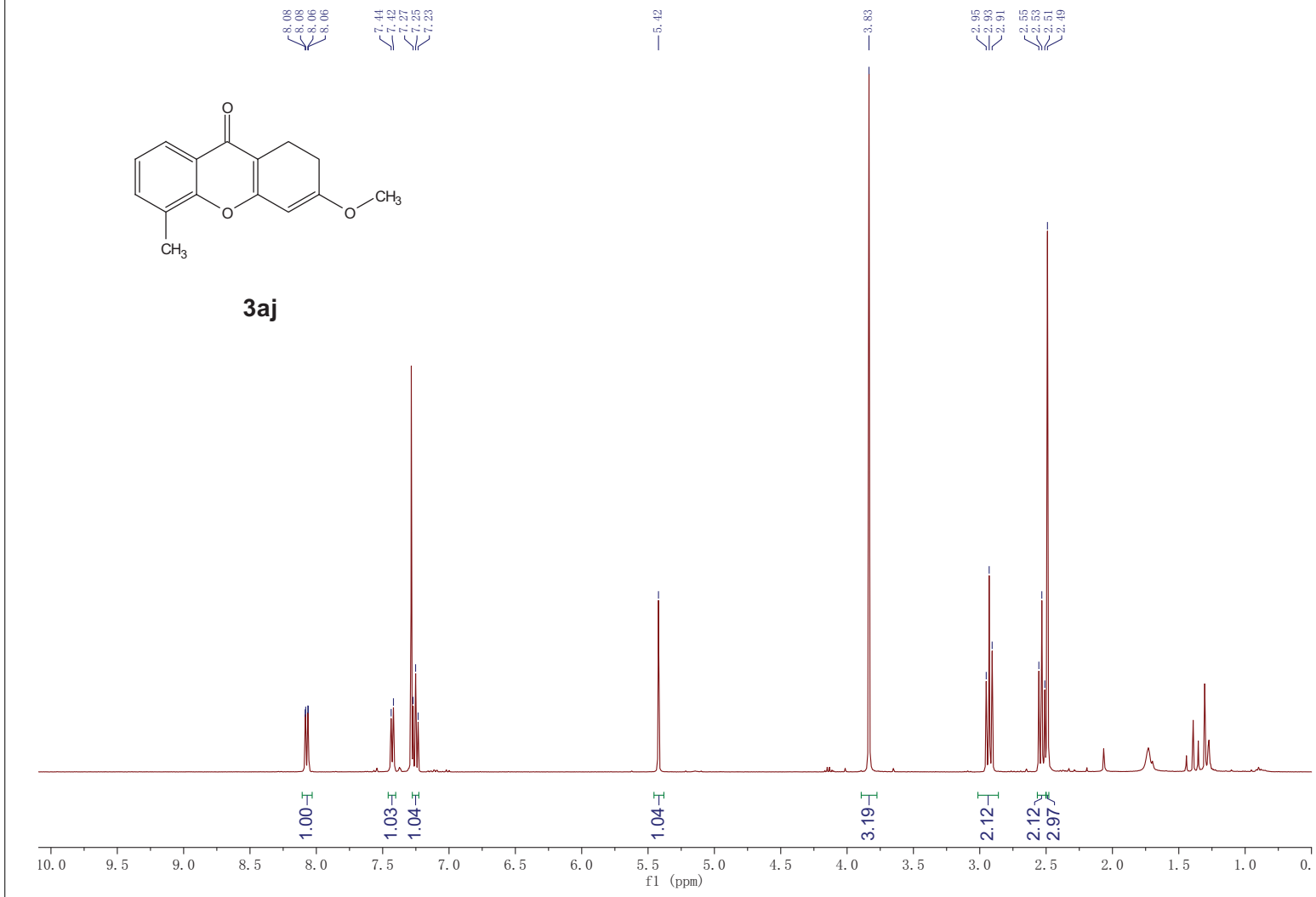


1aj

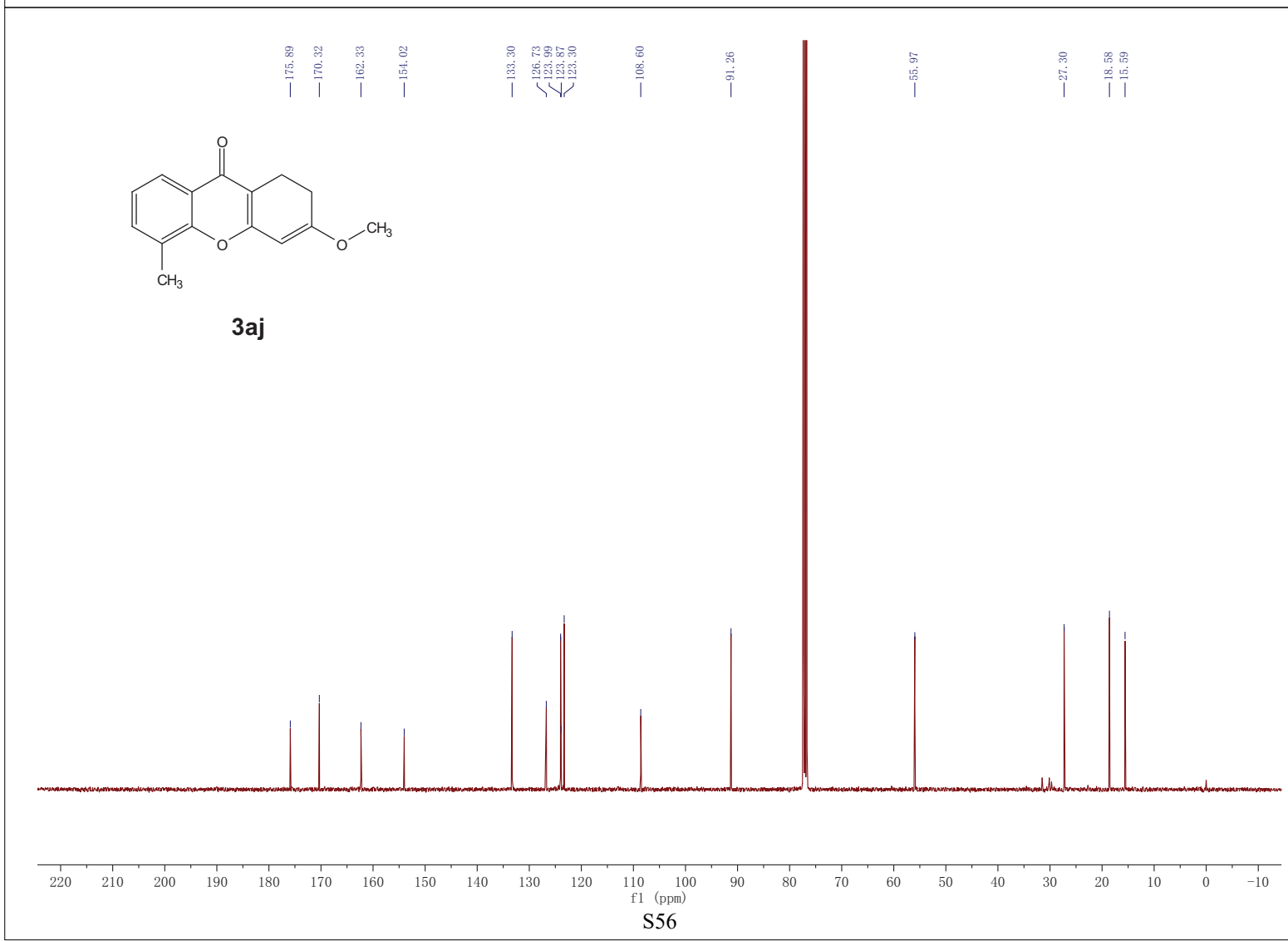
^{19}FNMR



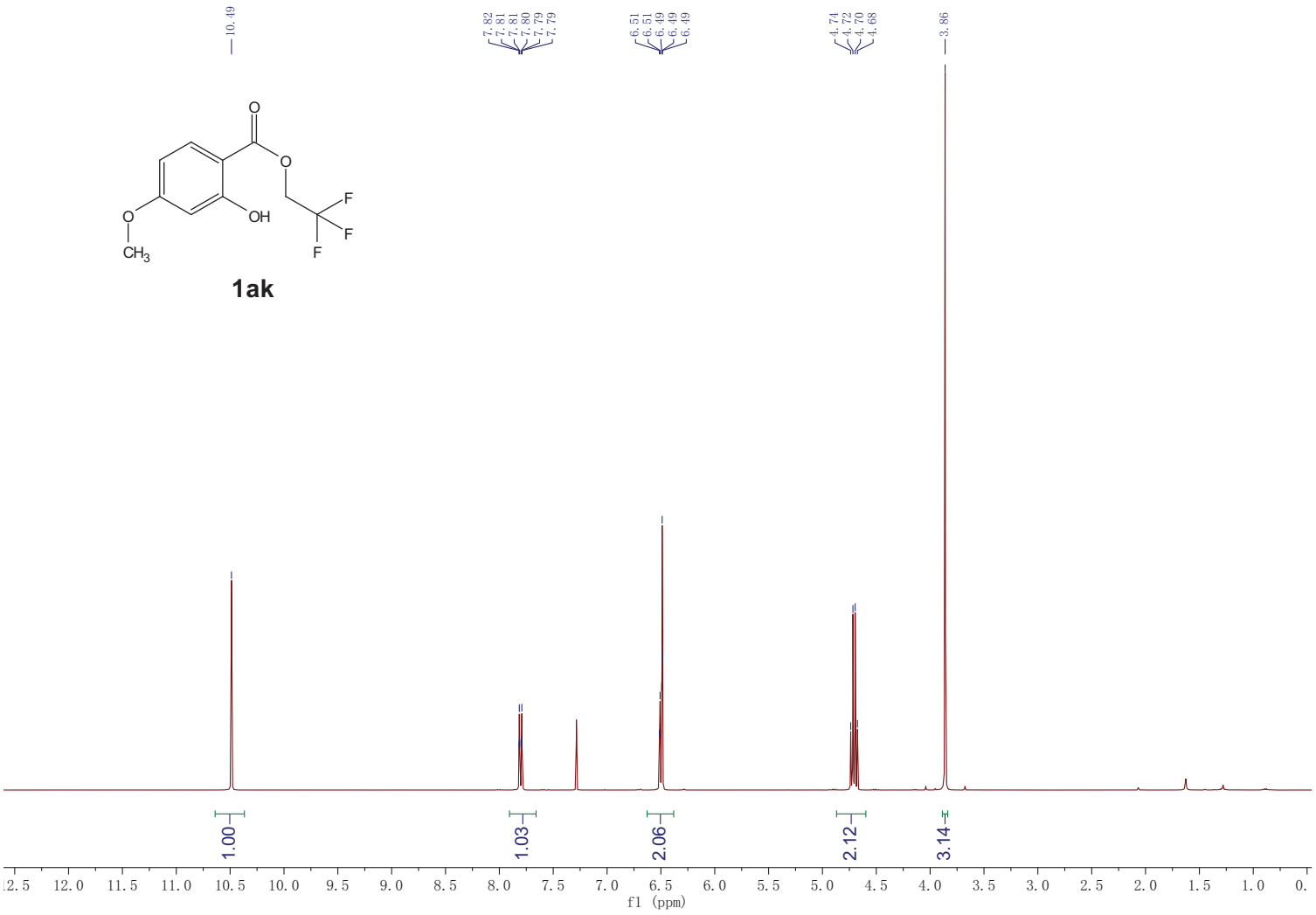
1aj

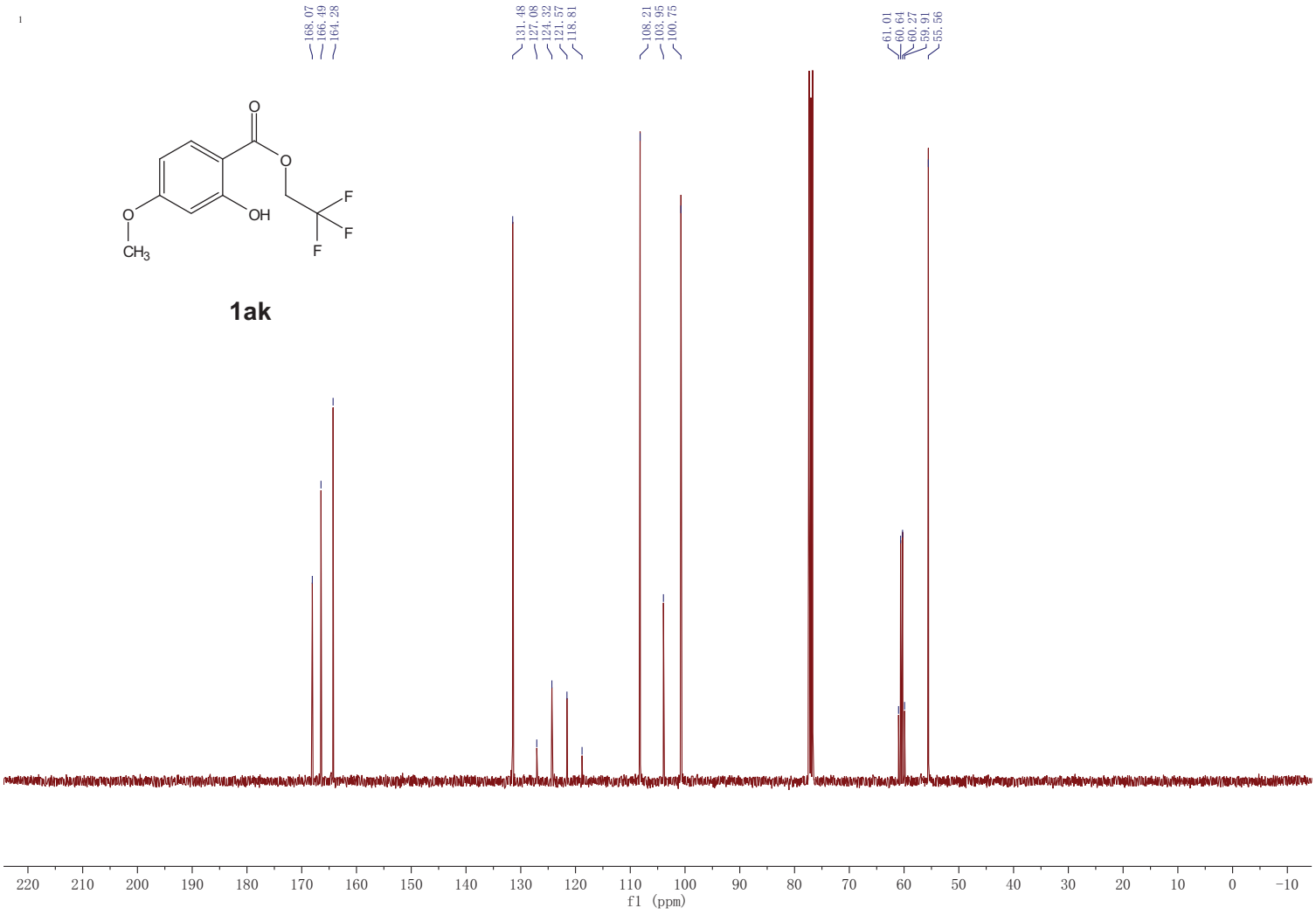

8.08
8.08
8.06
8.06
7.44
7.42
7.27
7.25
7.23
5.42
3.83
2.95
2.93
2.91
2.55
2.53
2.51
2.49
O
O
O
CH3
CH3
1.00
1.03
1.04
1.04
3.19
2.12
2.12
2.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.
f1 (ppm)

3aj


175.89
170.32
162.33
154.02
133.30
126.73
123.99
123.87
123.30
108.60
91.26
55.97
27.30
18.58
15.59
O
O
O
CH3
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

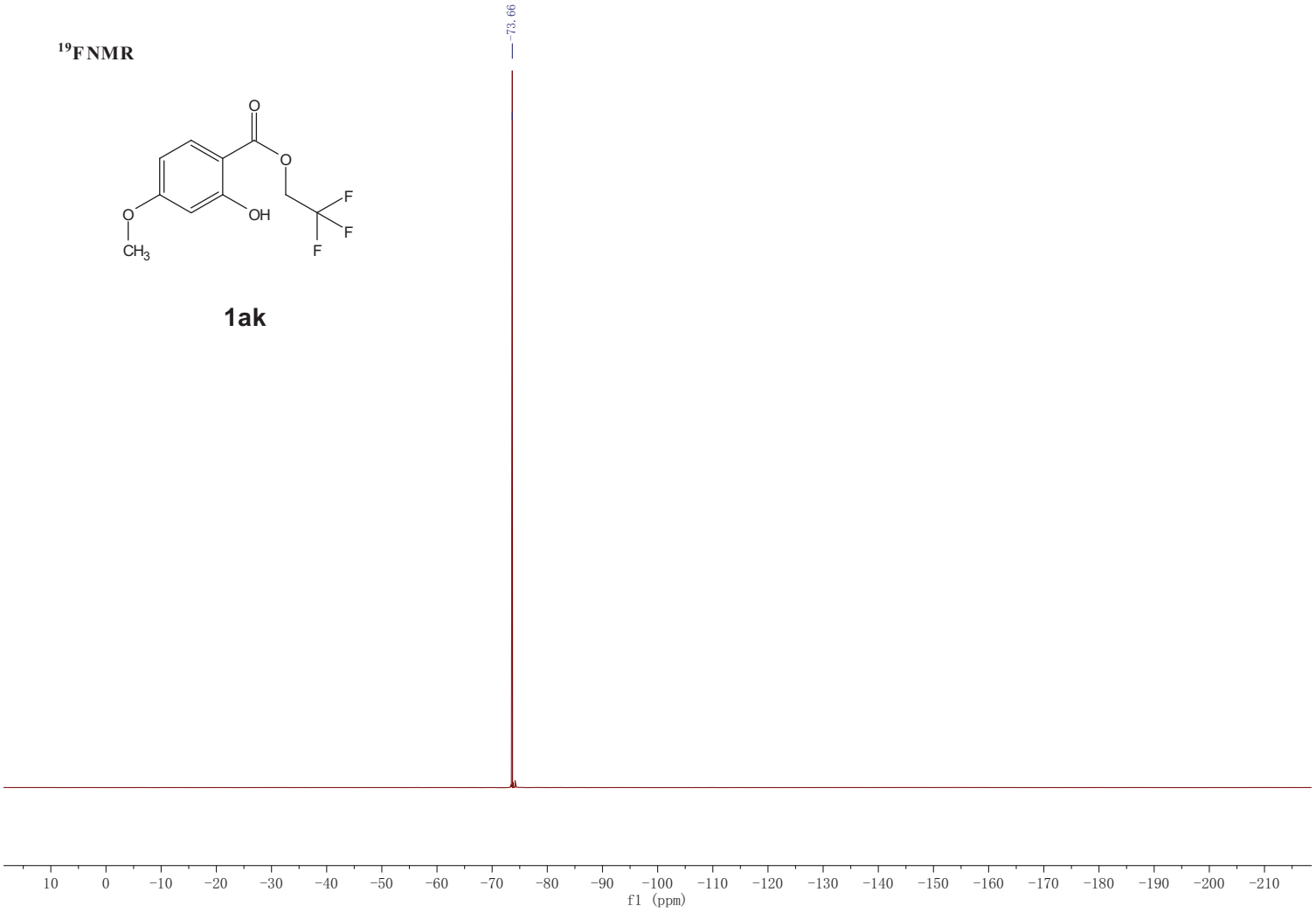
3aj


10.49
7.82
7.81
7.81
7.80
7.79
7.79
6.51
6.51
6.49
6.49
6.49
4.74
4.72
4.70
4.68
3.86
O
O
O
OH
CH3
F
F
F
1ak
1.00
1.03
2.06
2.12
3.14
f1 (ppm)

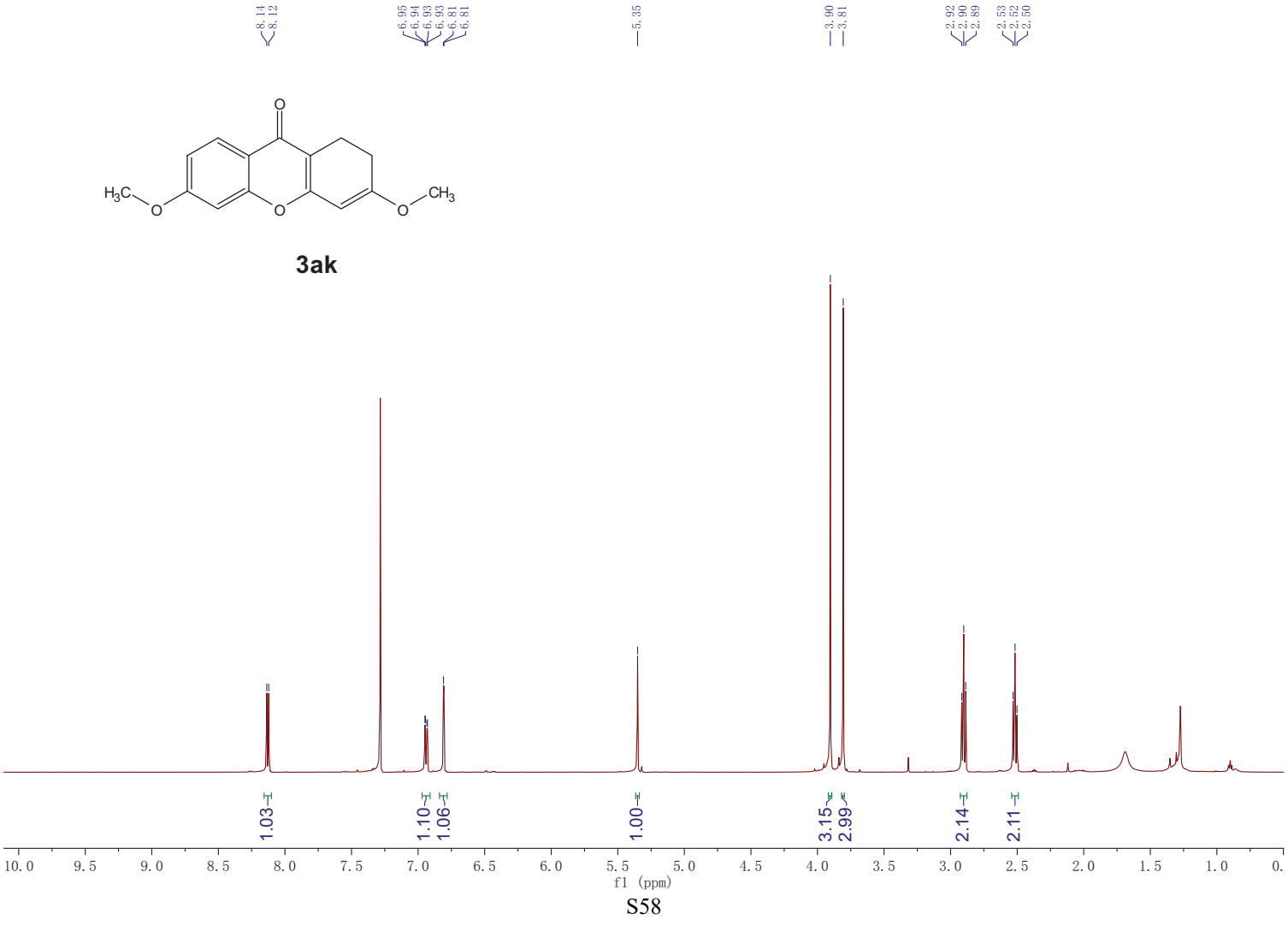

168.07
166.49
164.28
131.48
127.08
124.32
121.57
118.81
108.21
103.95
100.75
61.01
60.64
60.27
59.91
55.56
O
O
O
OH
CH3
F
F
F
1ak
f1 (ppm)

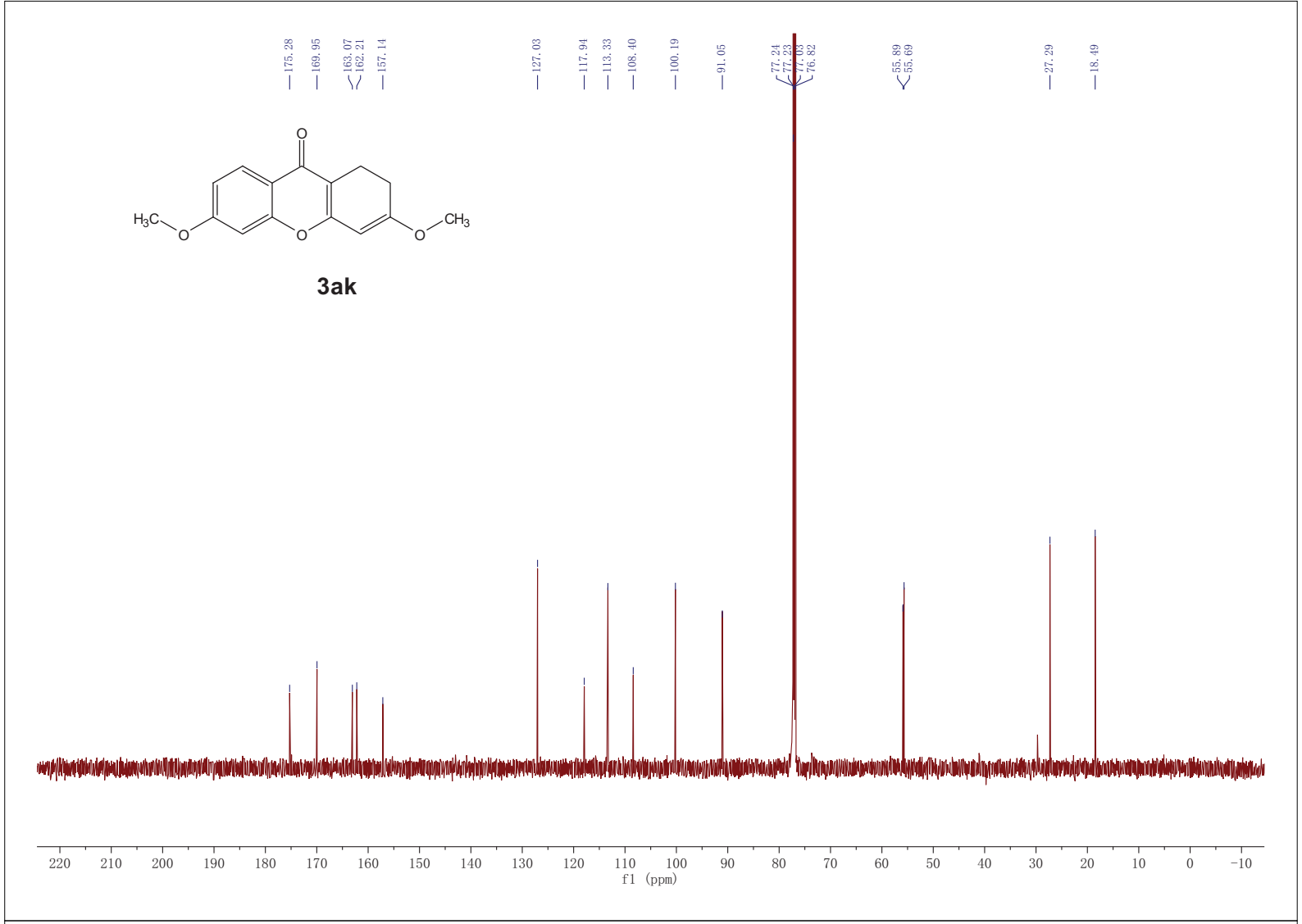
^{19}FNMR

1ak

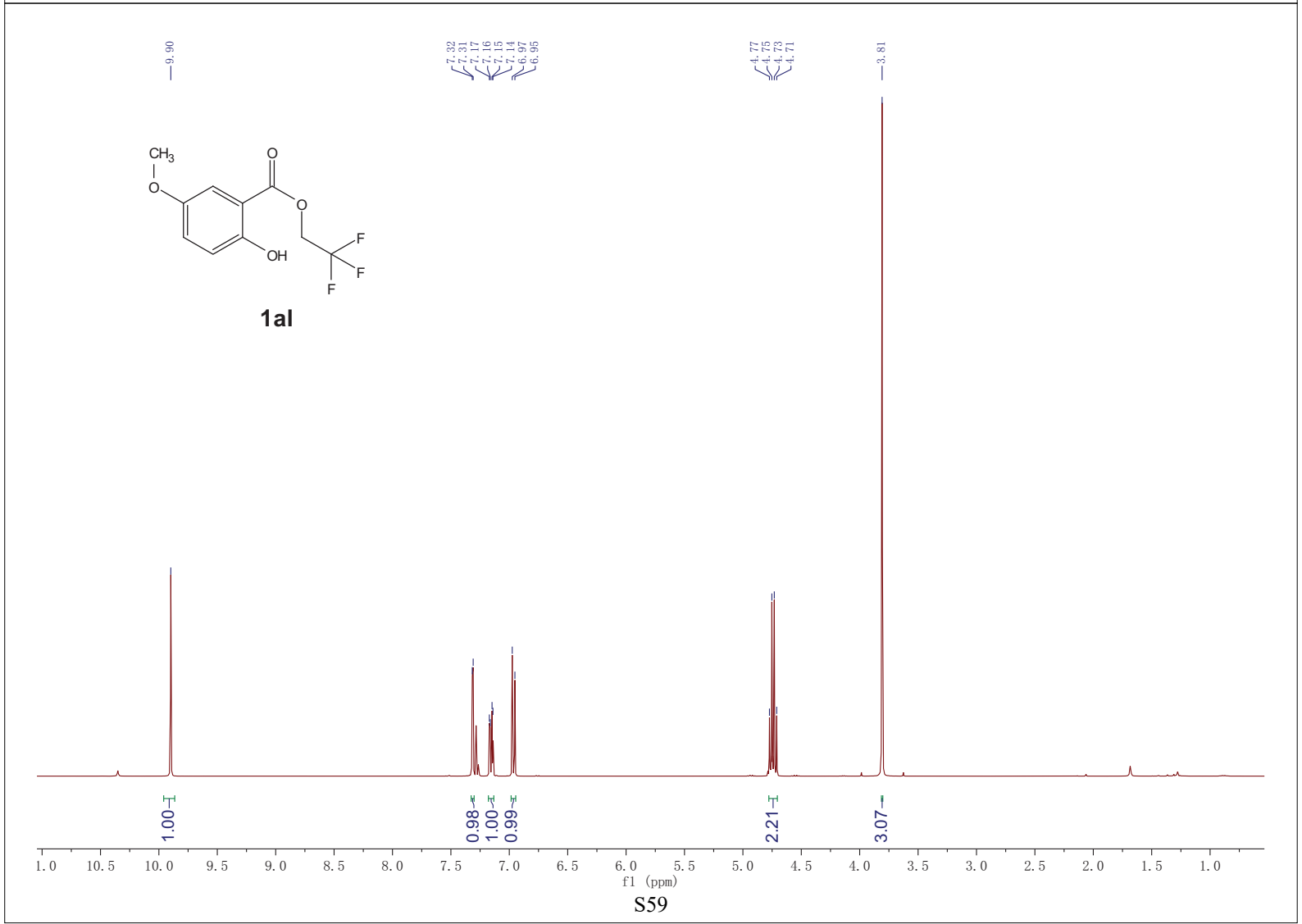


3ak

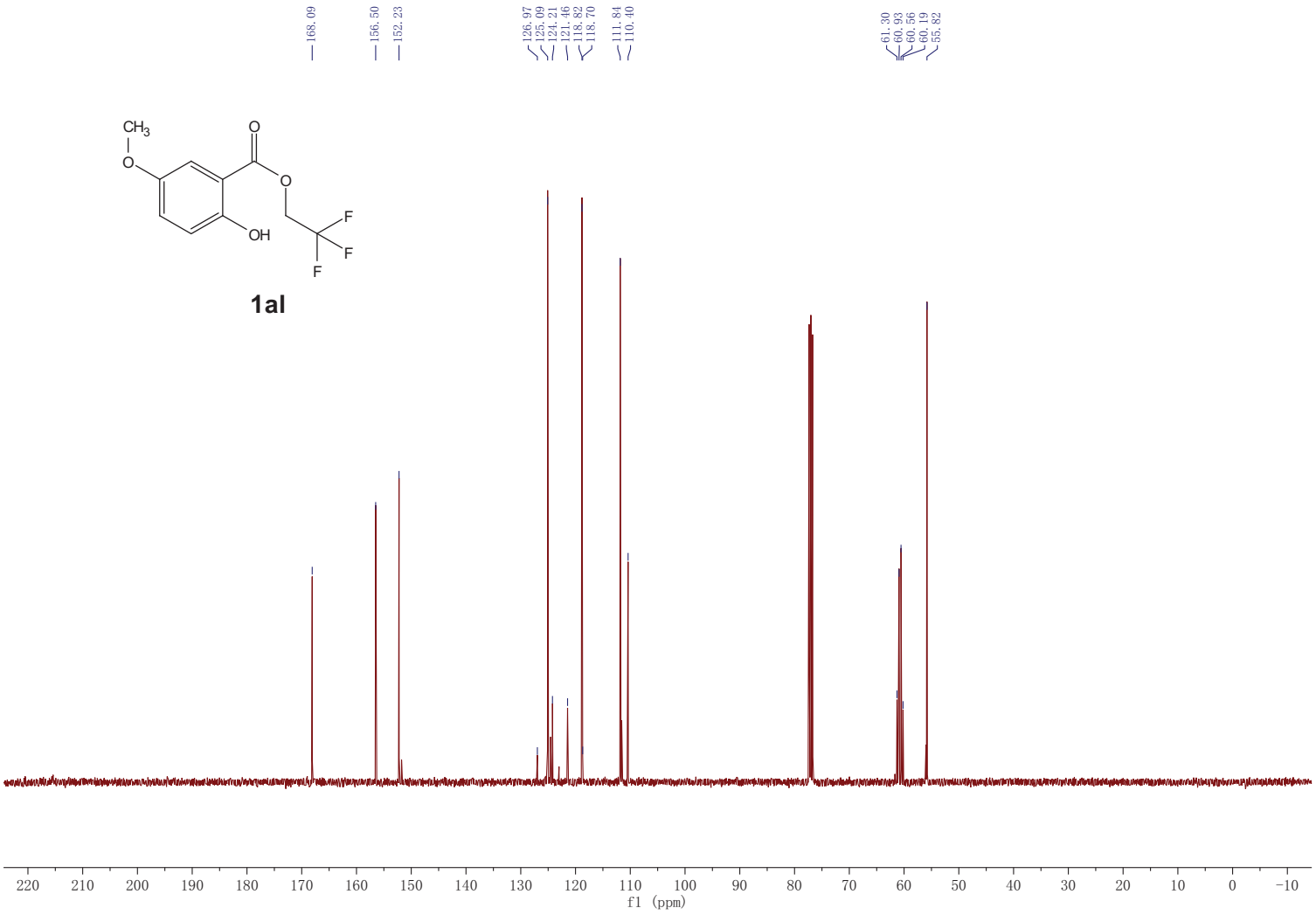



175.28
169.95
163.07
162.21
157.14
127.03
117.94
113.33
108.40
100.19
91.05
77.24
77.23
77.03
76.82
55.89
55.69
27.29
18.49
O
H3C
O
O
O
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ak

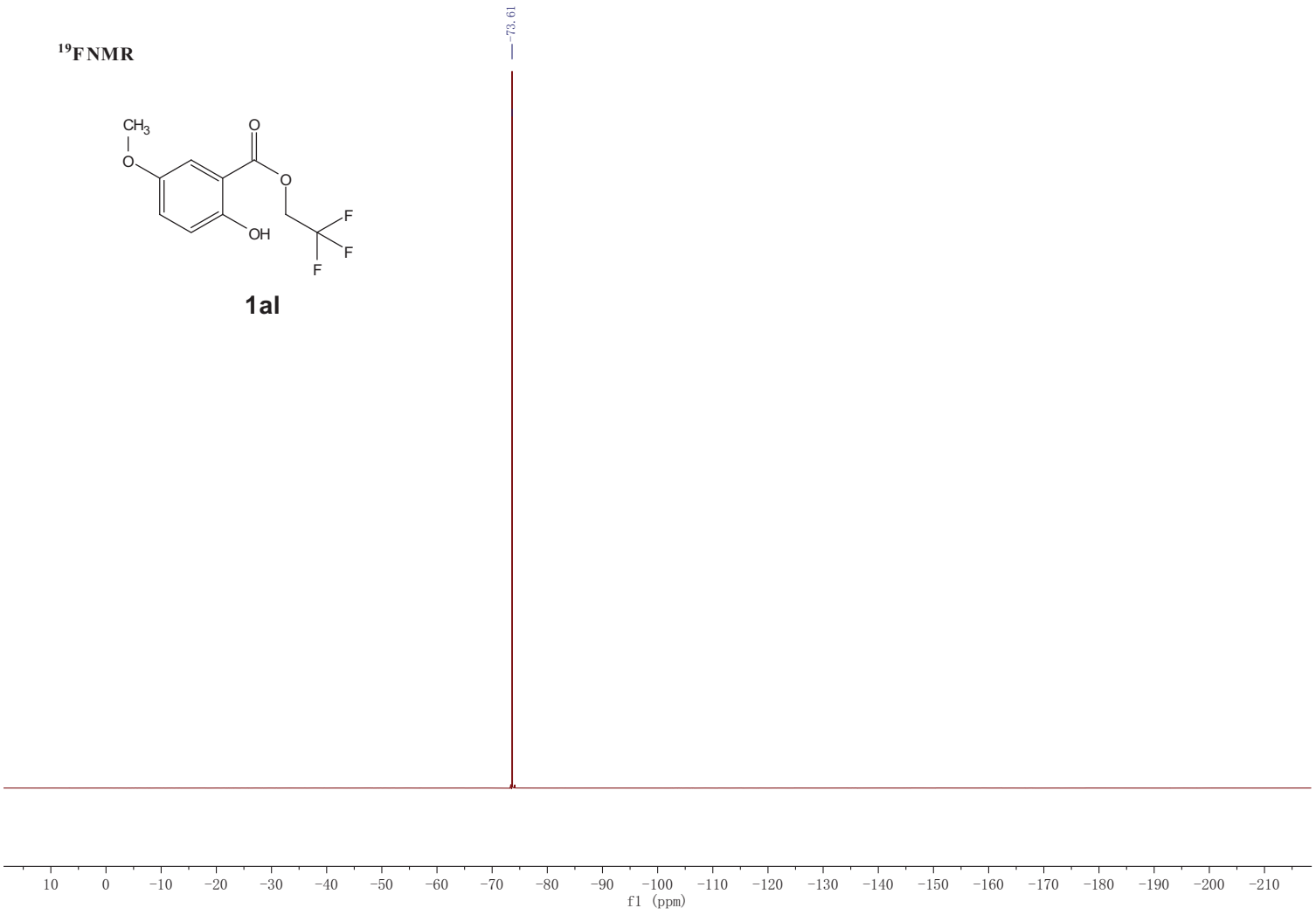

9.90
7.32
7.31
7.17
7.16
7.15
7.14
6.97
6.95
4.77
4.75
4.73
4.71
3.81
CH3
O
O
O
OH
F
F
F
1.00
0.98
1.00
0.99
2.21
3.07
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

1al

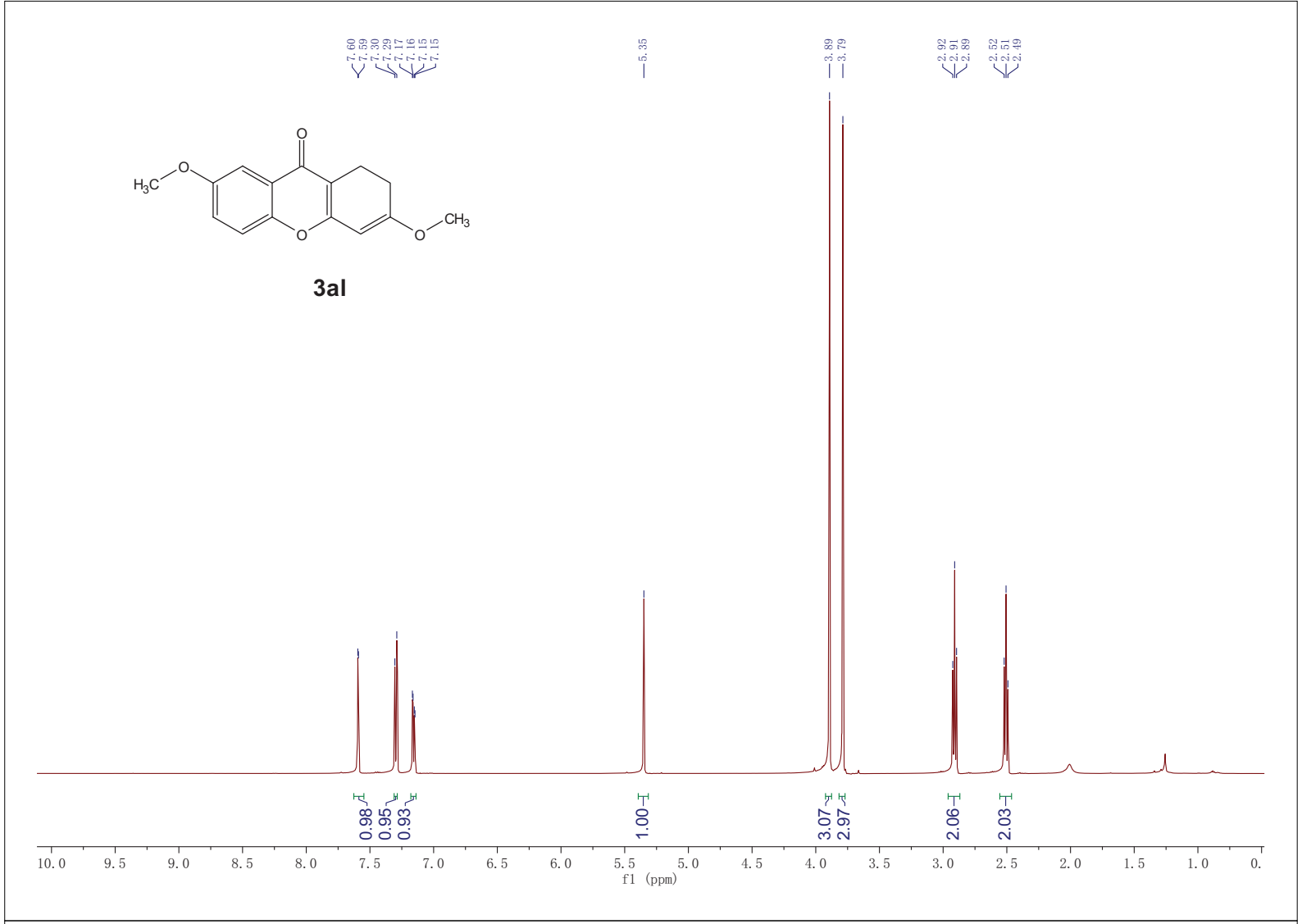


1al

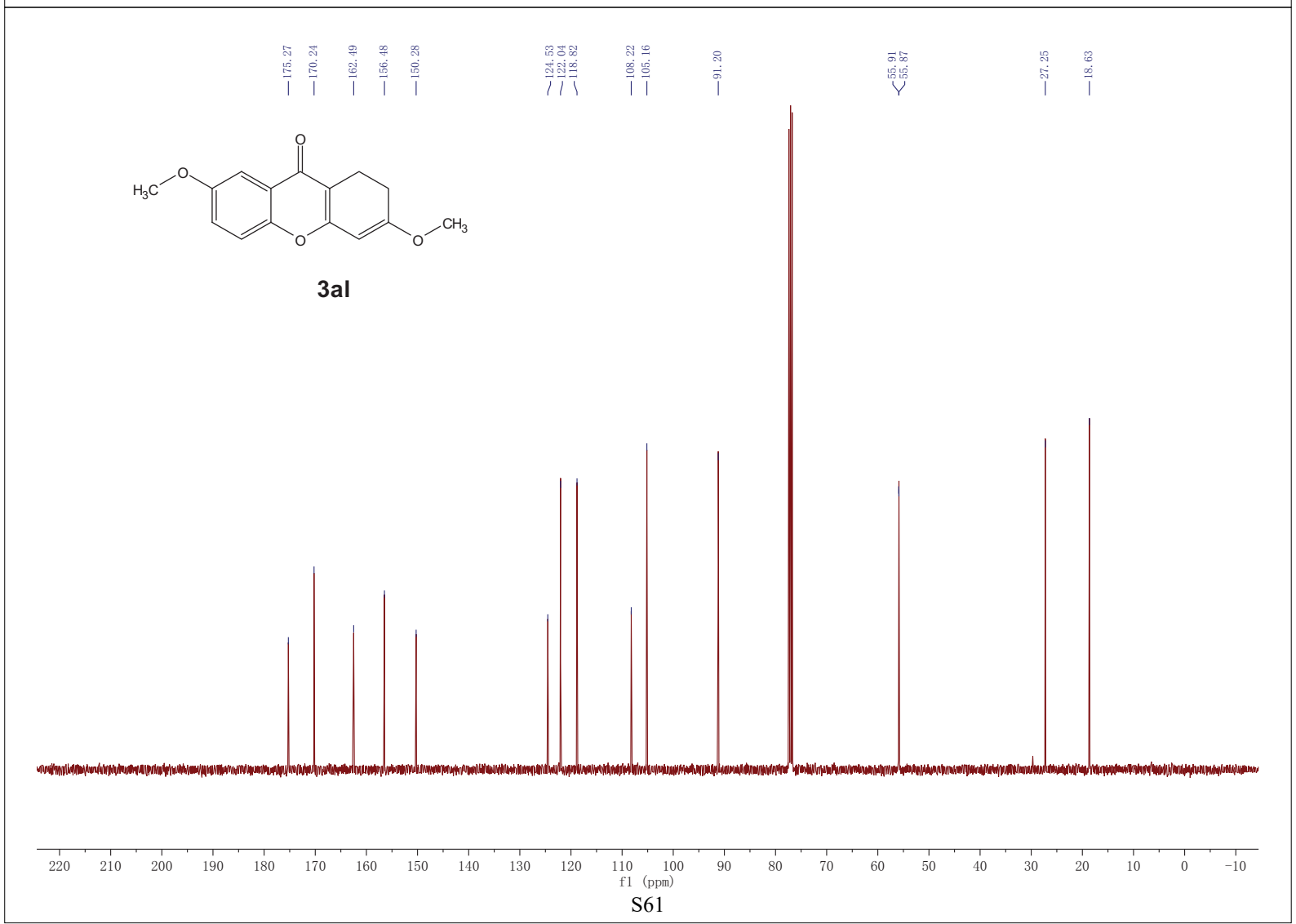
^{19}FNMR



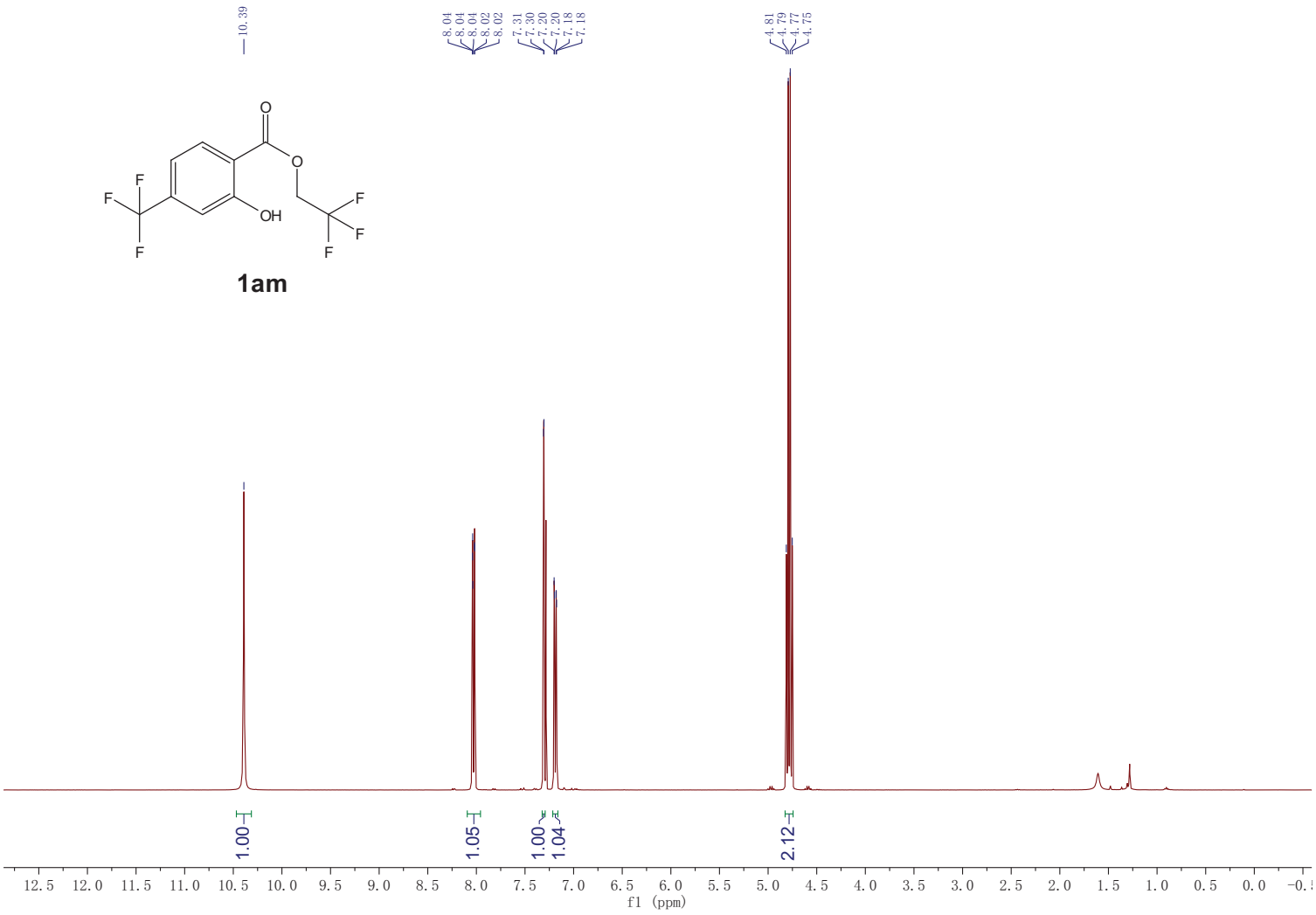
1al


7.60
7.59
7.30
7.29
7.17
7.16
7.15
7.15
5.35
3.89
3.79
2.92
2.91
2.89
2.52
2.51
2.49
O
H3C
O
O
O
CH3
0.98
0.95
0.93
1.00
3.07
2.97
2.06
2.03
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.
f1 (ppm)

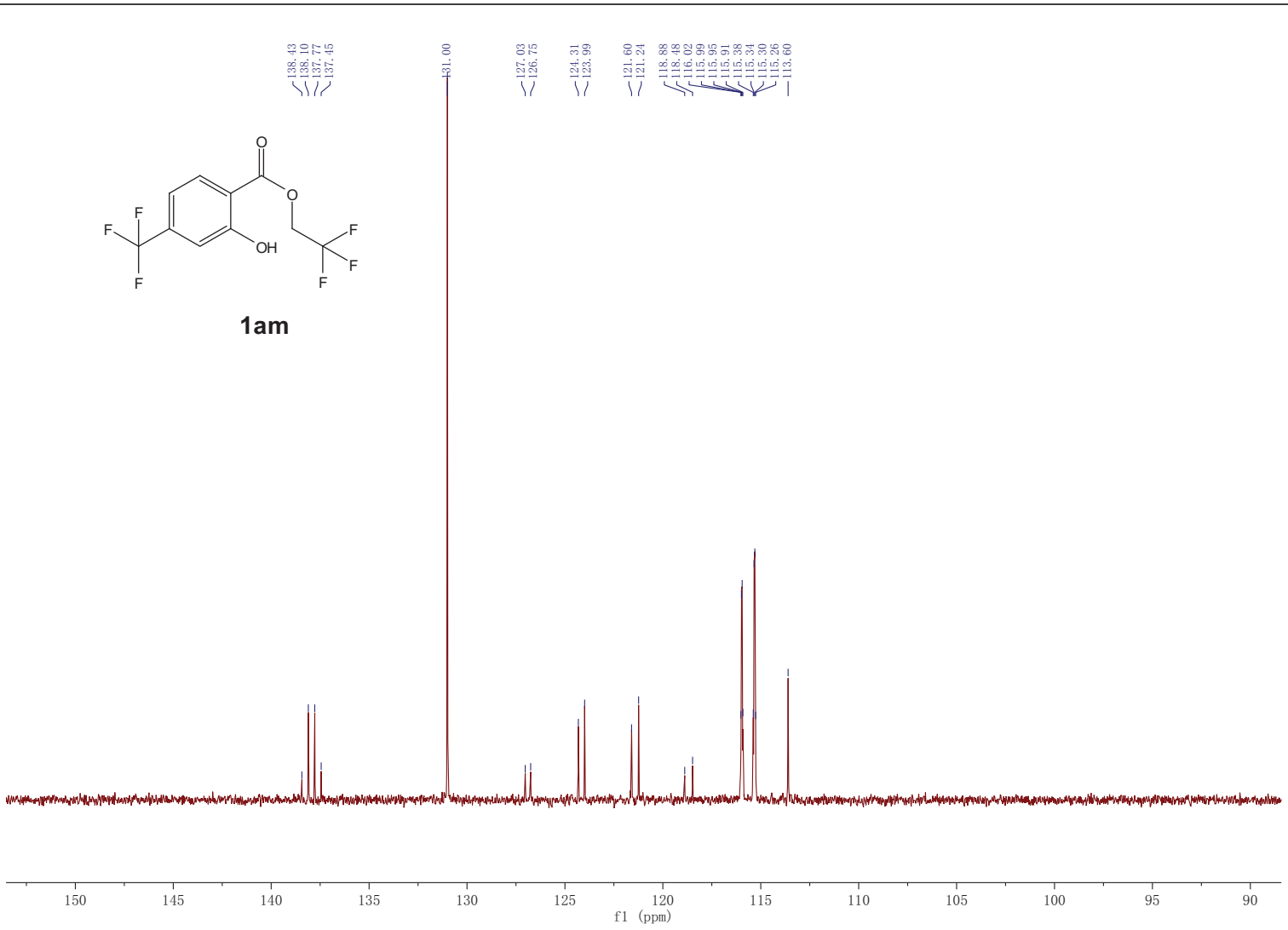
3al


175.27
170.24
162.49
156.48
150.28
124.53
122.04
118.82
108.22
105.16
91.20
55.91
55.87
27.25
18.63
O
H3C
O
O
O
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

3al


10.39
8.04
8.04
8.04
8.02
8.02
7.31
7.30
7.20
7.20
7.18
7.18
4.81
4.79
4.77
4.75
1.00
1.05
1.00
1.04
2.12
f1 (ppm)

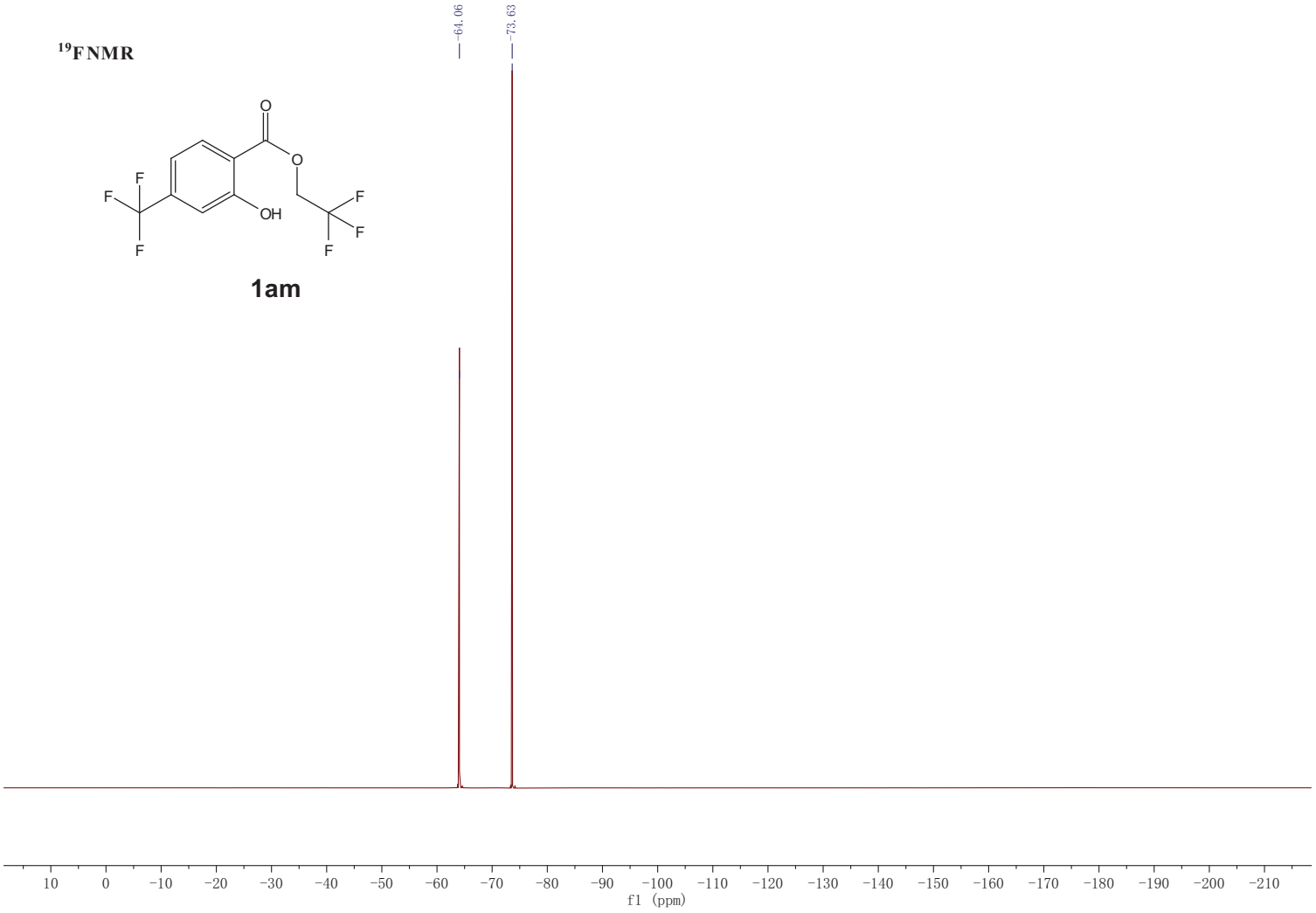
1am


138.43
138.10
137.77
137.45
131.00
127.03
126.75
124.31
123.99
121.60
121.24
118.88
118.48
116.02
115.99
115.95
115.91
115.38
115.34
115.30
115.26
113.60
f1 (ppm)

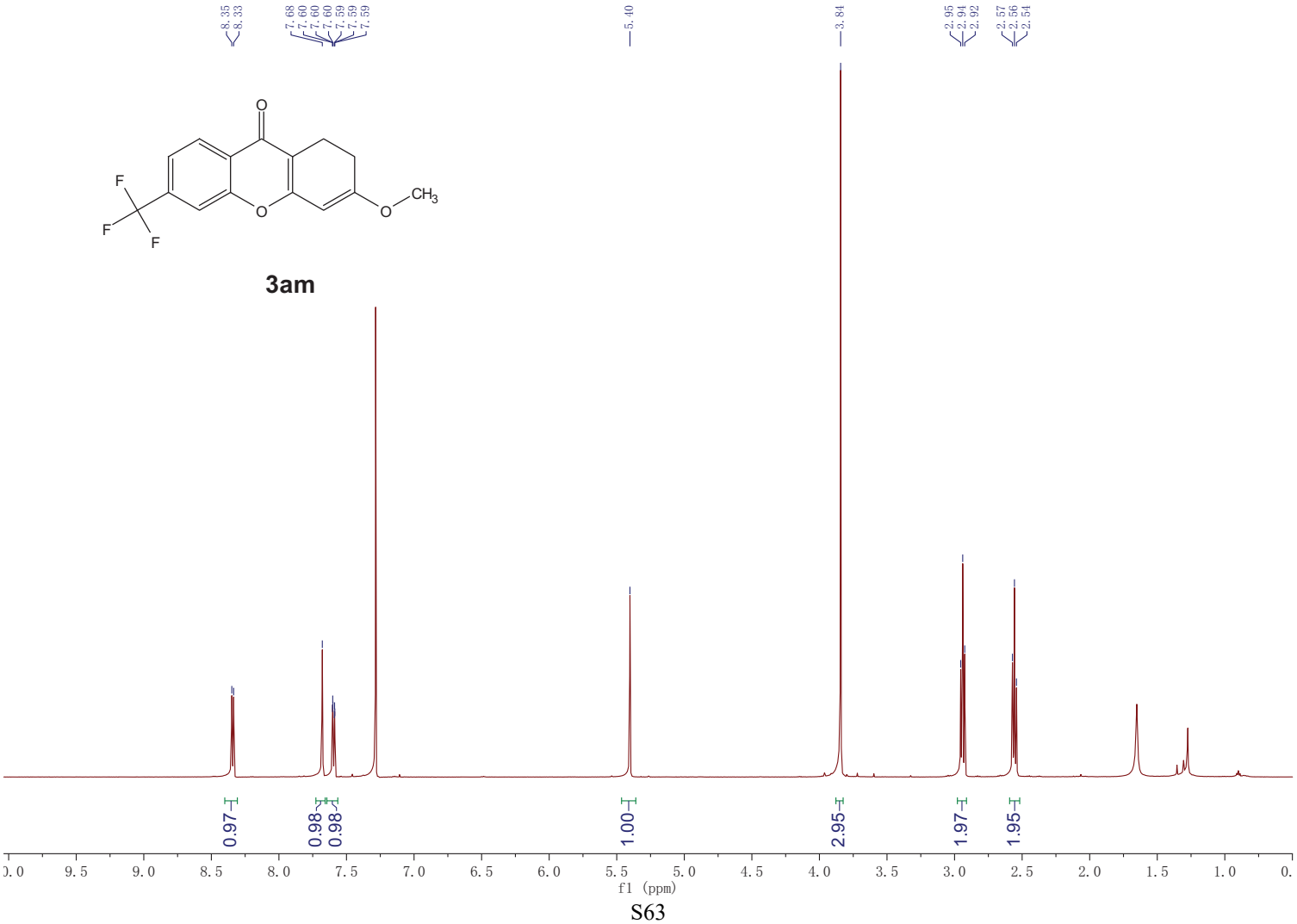
1am

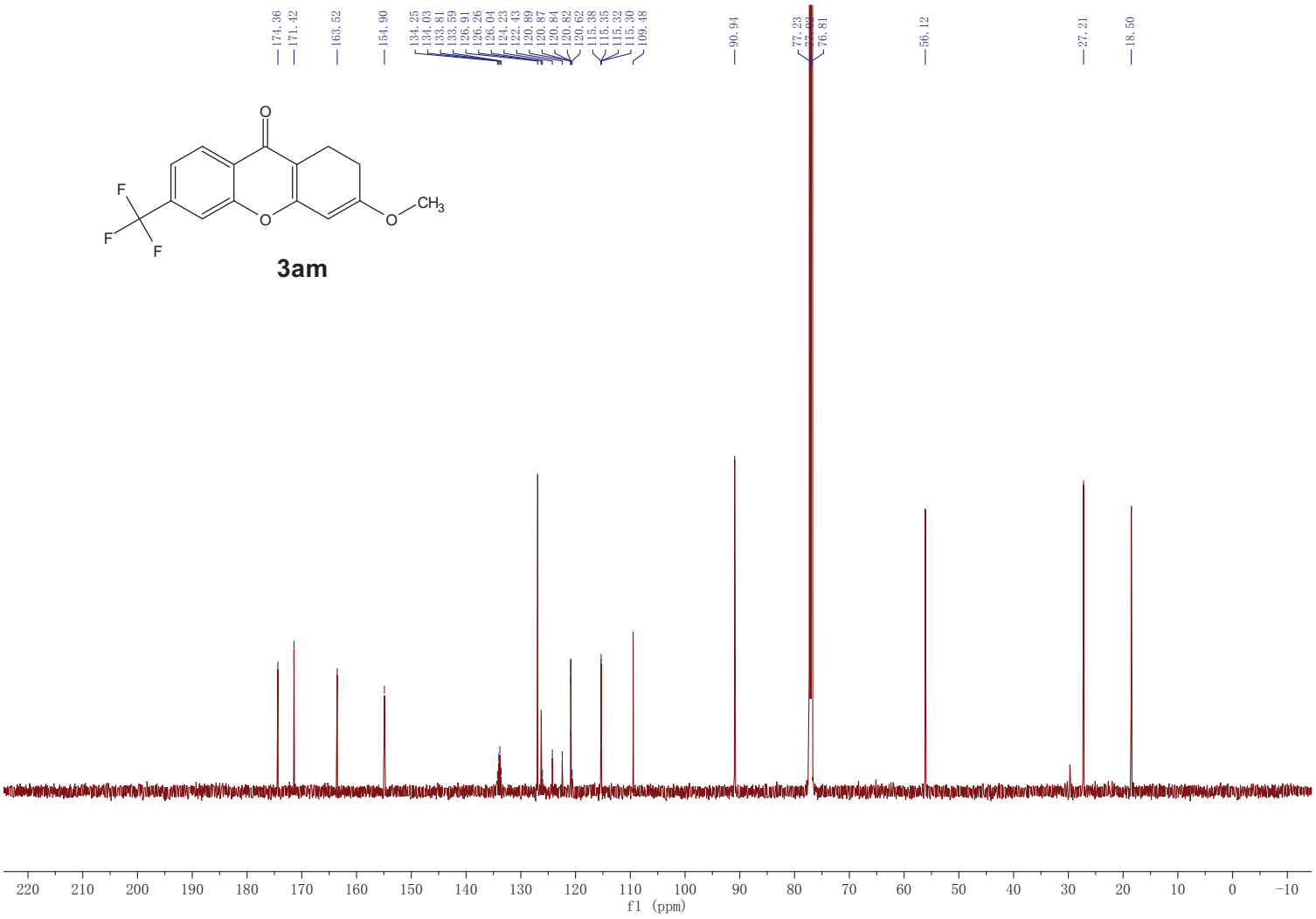
^{19}FNMR

1am

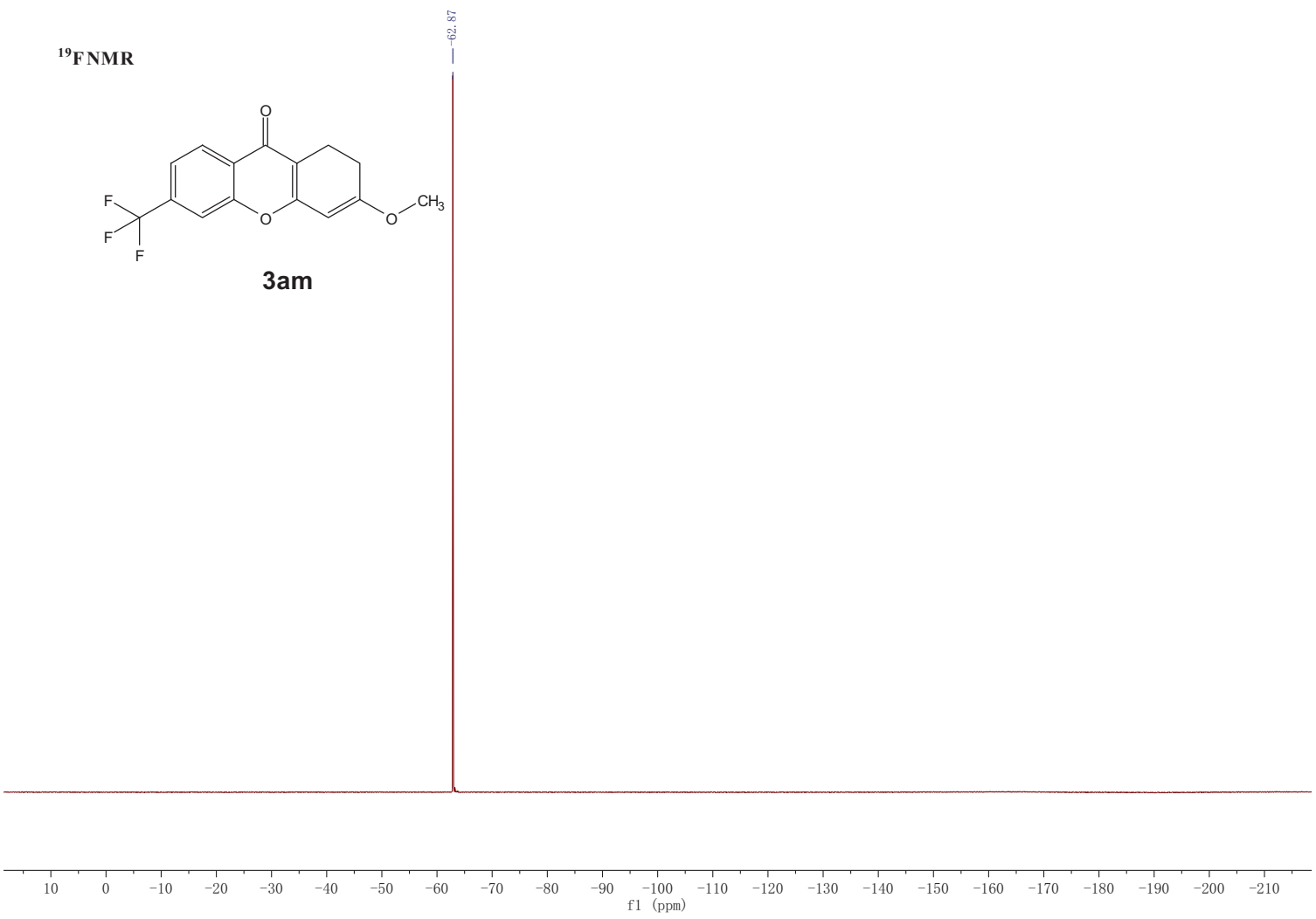


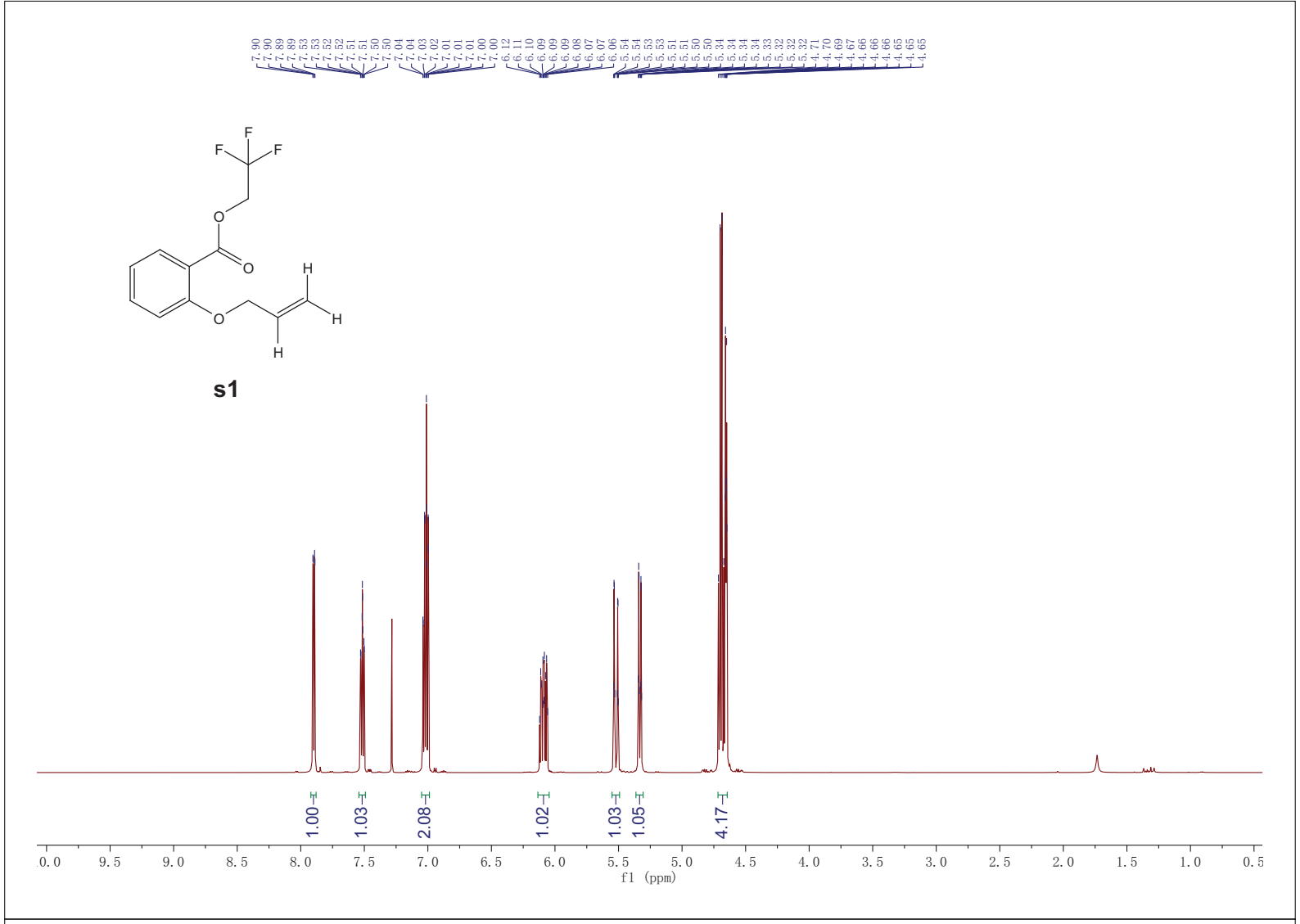
3am

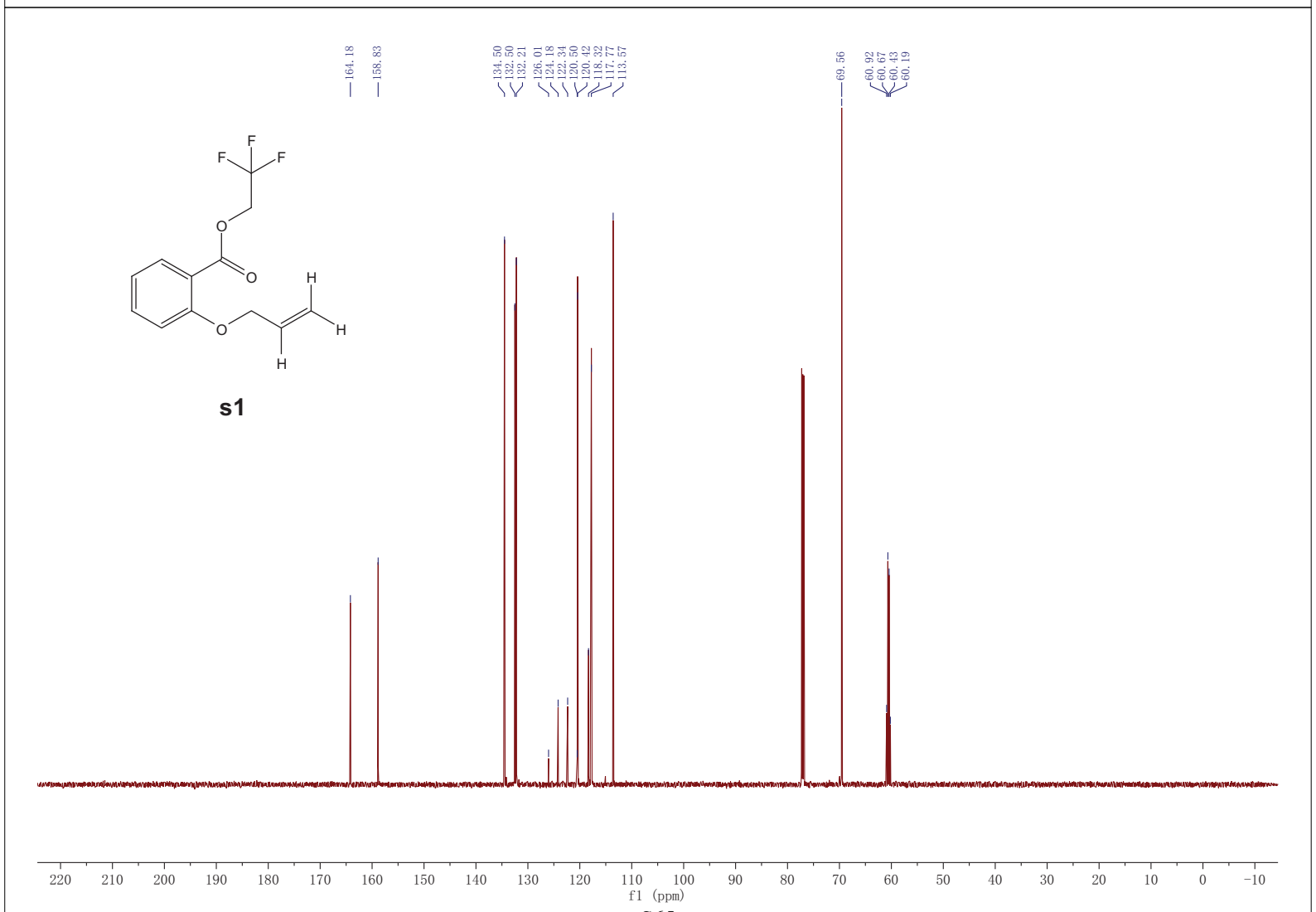



174.36
171.42
163.52
154.90
134.25
134.03
133.81
133.59
126.91
126.26
126.04
124.23
122.43
120.89
120.87
120.84
120.82
120.62
115.38
115.35
115.32
115.30
109.48
90.94
77.23
76.81
56.12
27.21
18.50
O
F
F
F
O
O
CH3
3am
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

^{19}FNMR

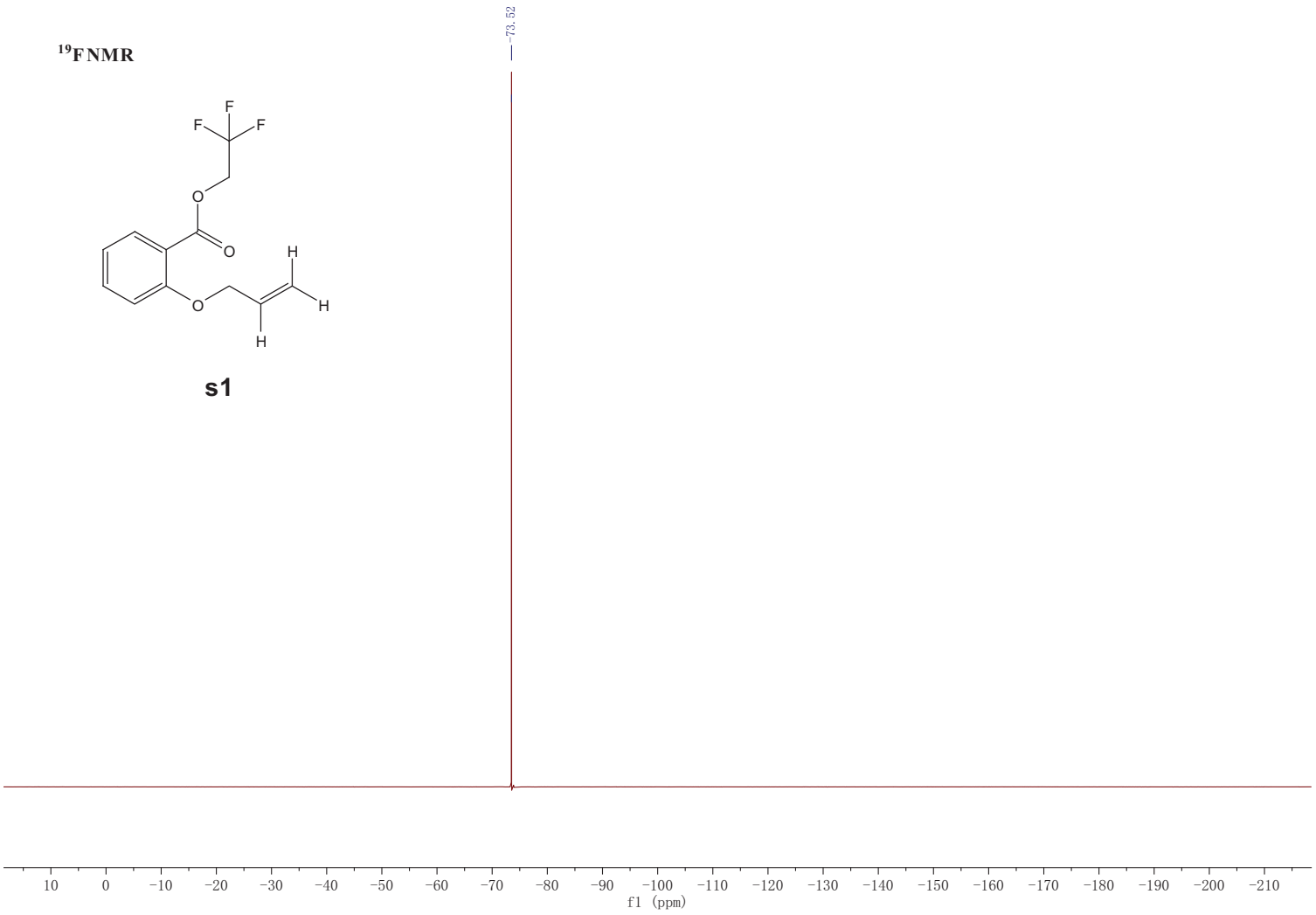

−62.87
O
F
F
F
O
O
CH3
3am
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)


7.90
7.90
7.89
7.89
7.53
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.04
7.04
7.03
7.02
7.01
7.01
7.00
7.00
6.12
6.11
6.10
6.09
6.09
6.09
6.08
6.07
6.06
5.54
5.54
5.53
5.53
5.51
5.51
5.50
5.50
5.34
5.34
5.33
5.33
5.32
5.32
4.71
4.70
4.69
4.67
4.66
4.66
4.66
4.65
4.65
4.65
F
F
F
O
O
O
H
H
H
s1
1.00
1.03
2.08
1.02
1.03
1.05
4.17
0.0
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
f1 (ppm)

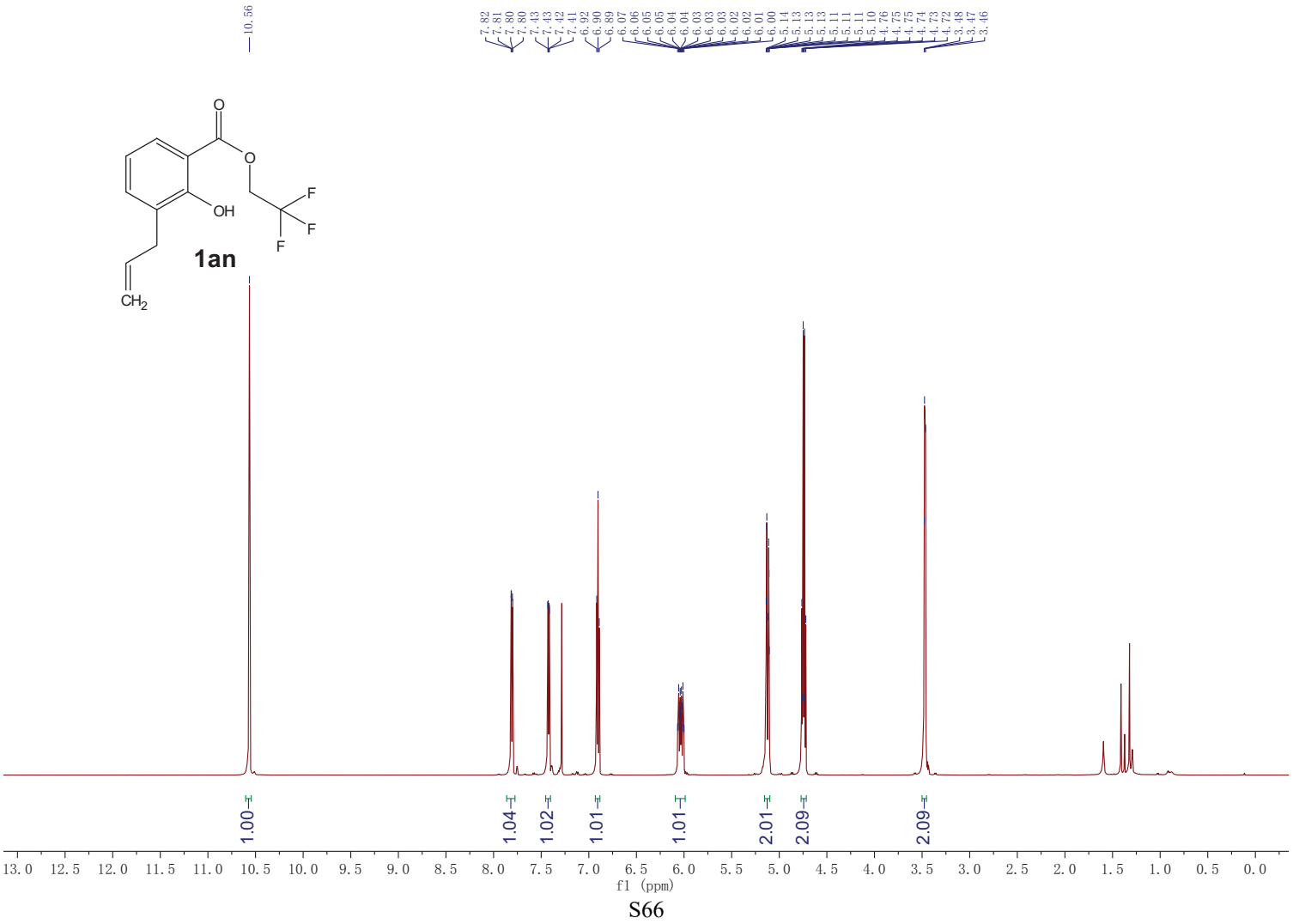

164.18
158.83
134.50
132.50
132.21
126.01
124.18
122.34
120.50
120.42
118.32
117.77
113.57
69.56
60.92
60.67
60.43
60.19
F
F
F
O
O
O
H
H
H
s1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

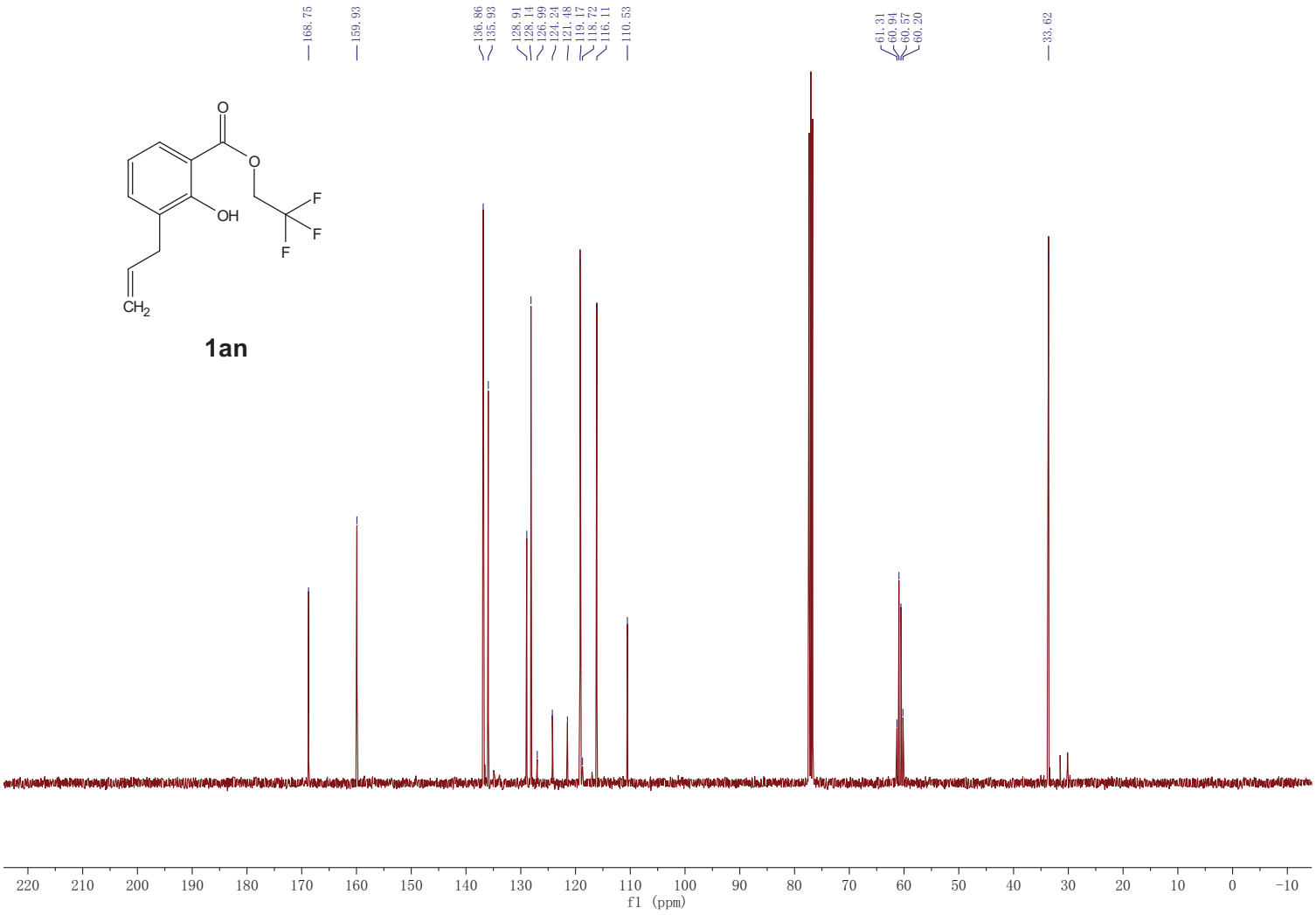
^{19}FNMR

s1

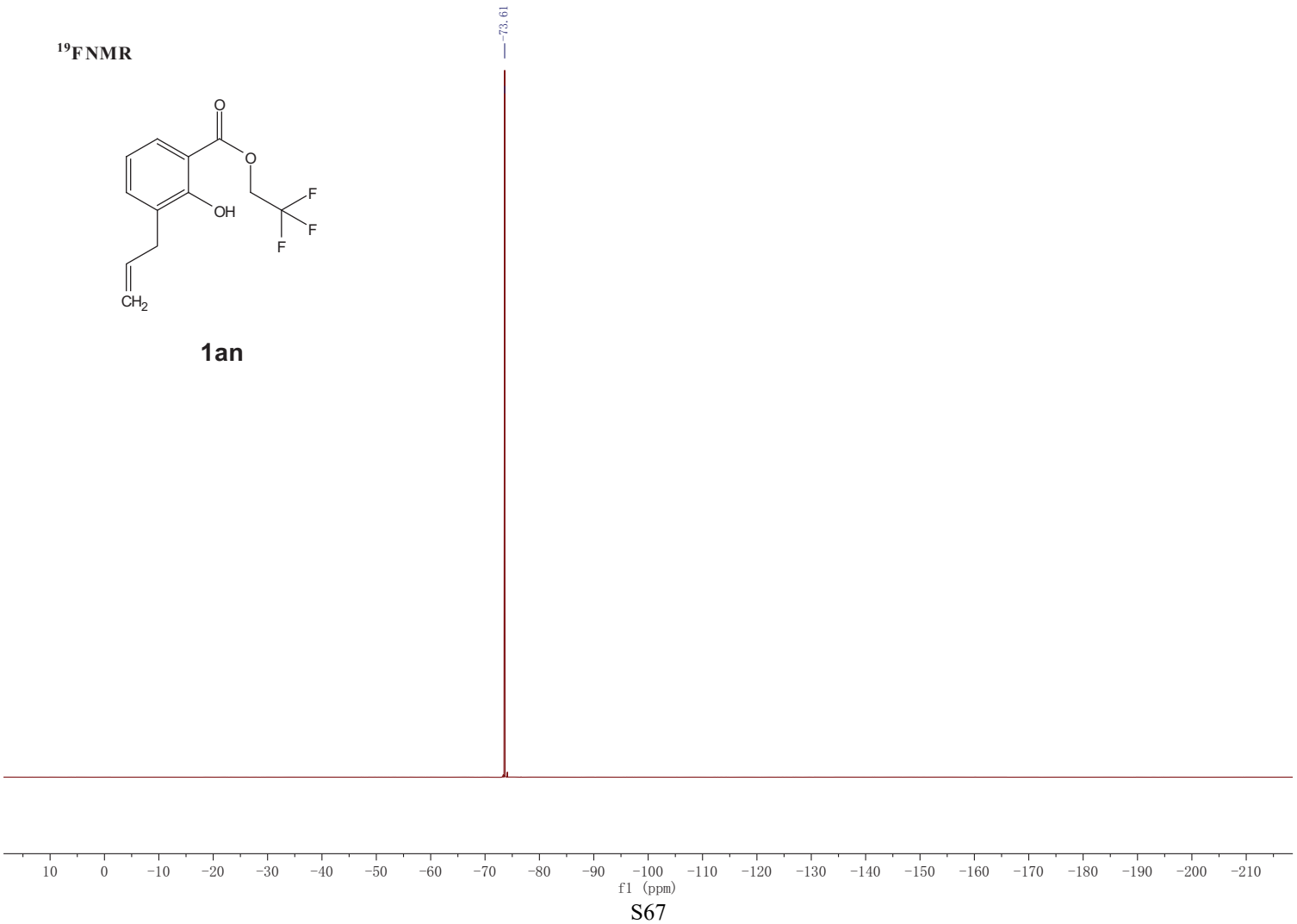


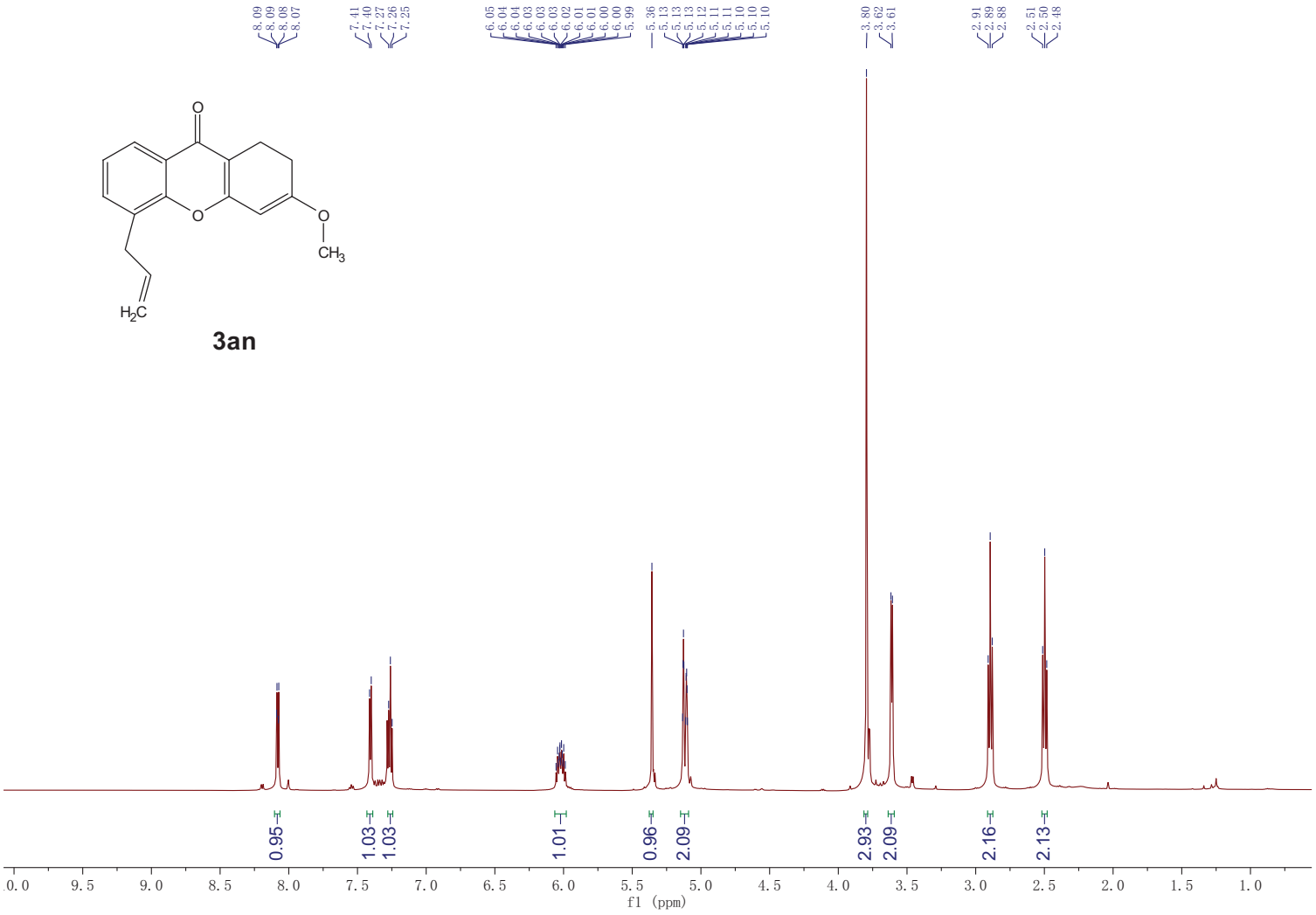
1an

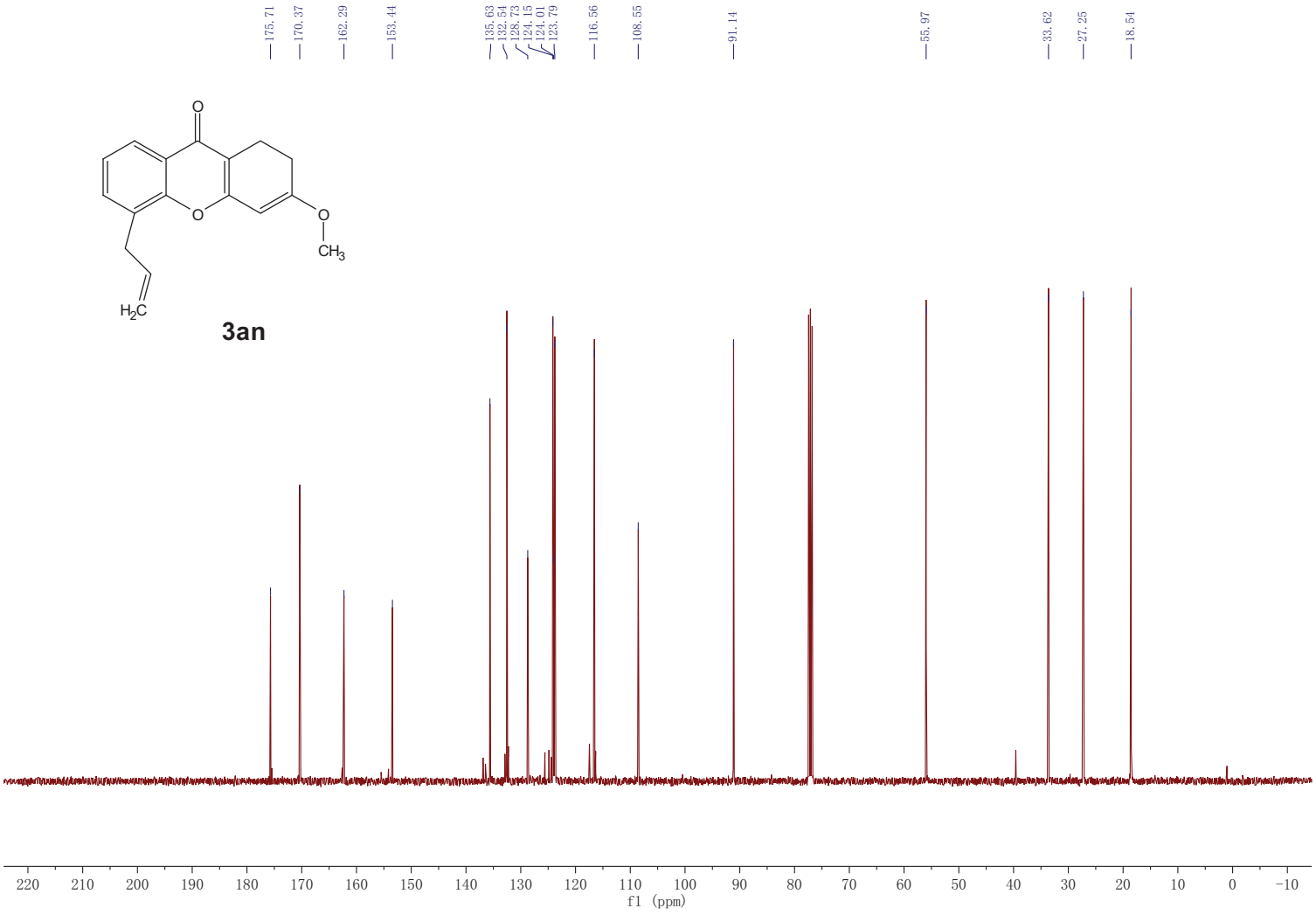


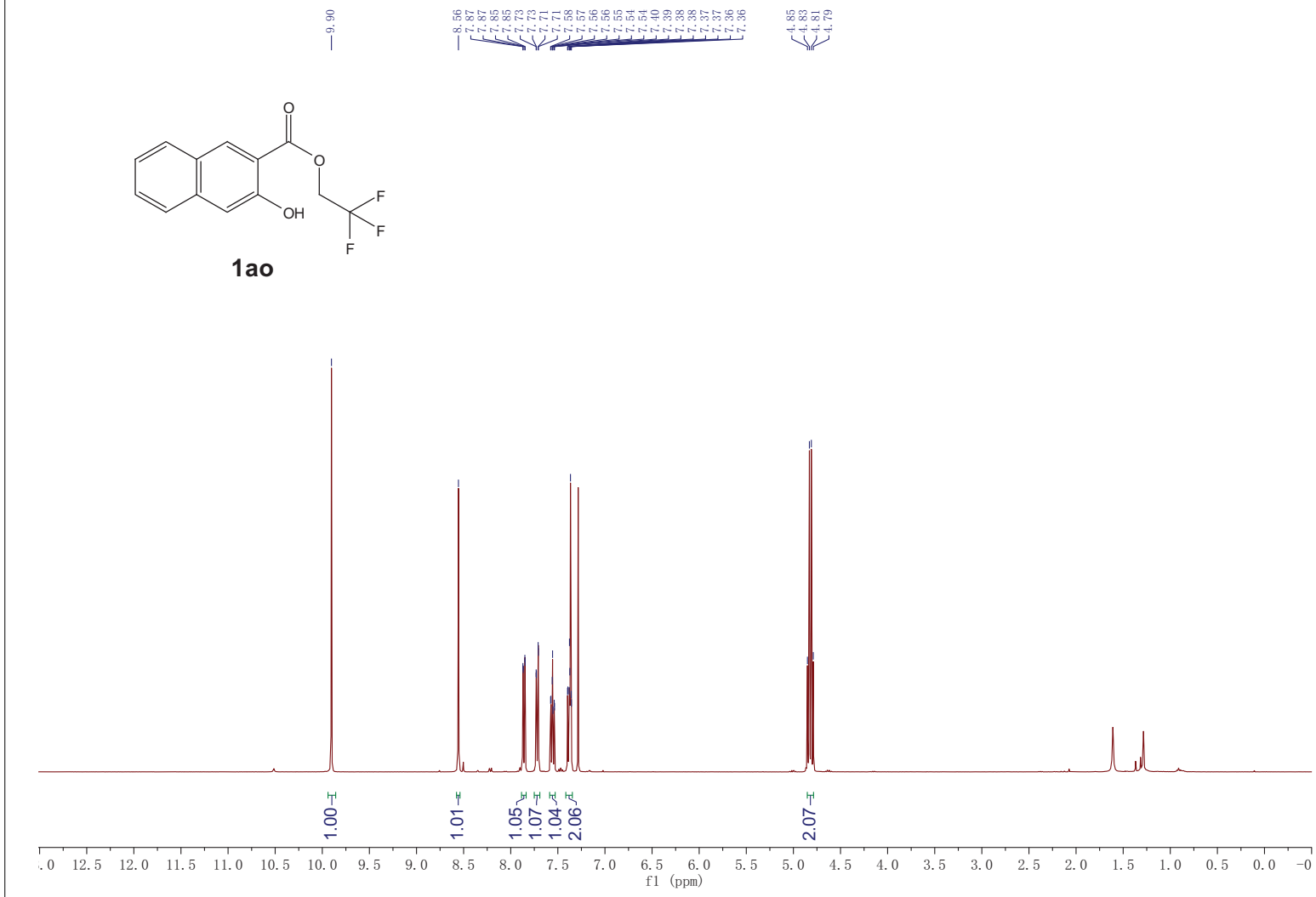

168.75
159.93
136.86
135.93
128.91
128.14
126.99
124.24
121.48
119.17
118.72
116.11
110.53
61.31
60.94
60.57
60.20
33.62
O
O
OH
F
F
F
CH2
1an
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

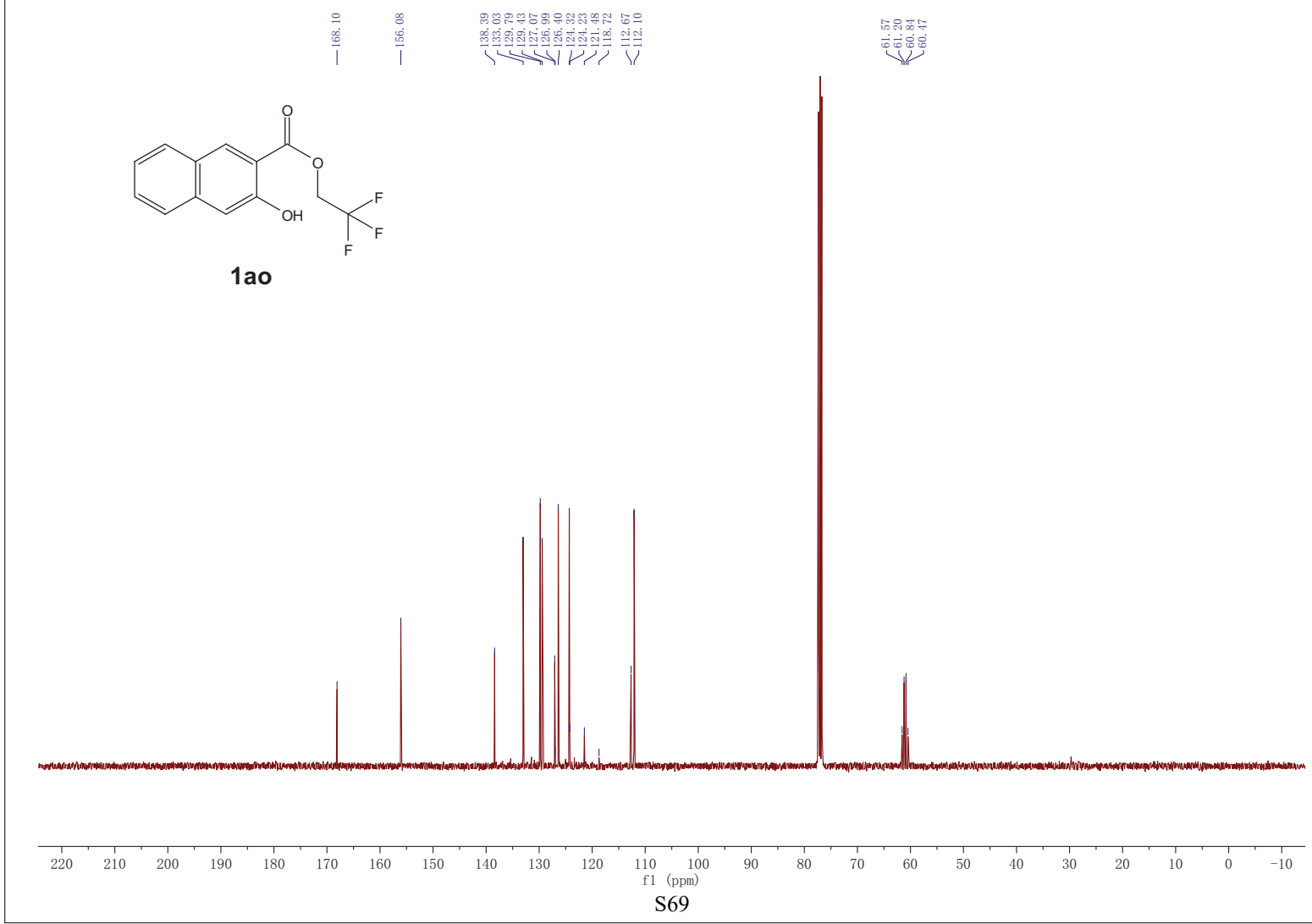
^{19}FNMR


−73.61
O
O
OH
F
F
F
CH2
1an
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)


8.09
8.09
8.08
8.07
7.41
7.40
7.27
7.26
7.25
6.05
6.04
6.04
6.03
6.03
6.02
6.01
6.01
6.00
6.00
5.99
5.36
5.13
5.13
5.12
5.11
5.10
5.10
5.10
3.80
3.62
3.61
2.91
2.89
2.88
2.51
2.50
2.48
O
O
O
CH3
H2C
3an
0.95
1.03
1.03
1.01
0.96
2.09
2.93
2.09
2.16
2.13
f1 (ppm)

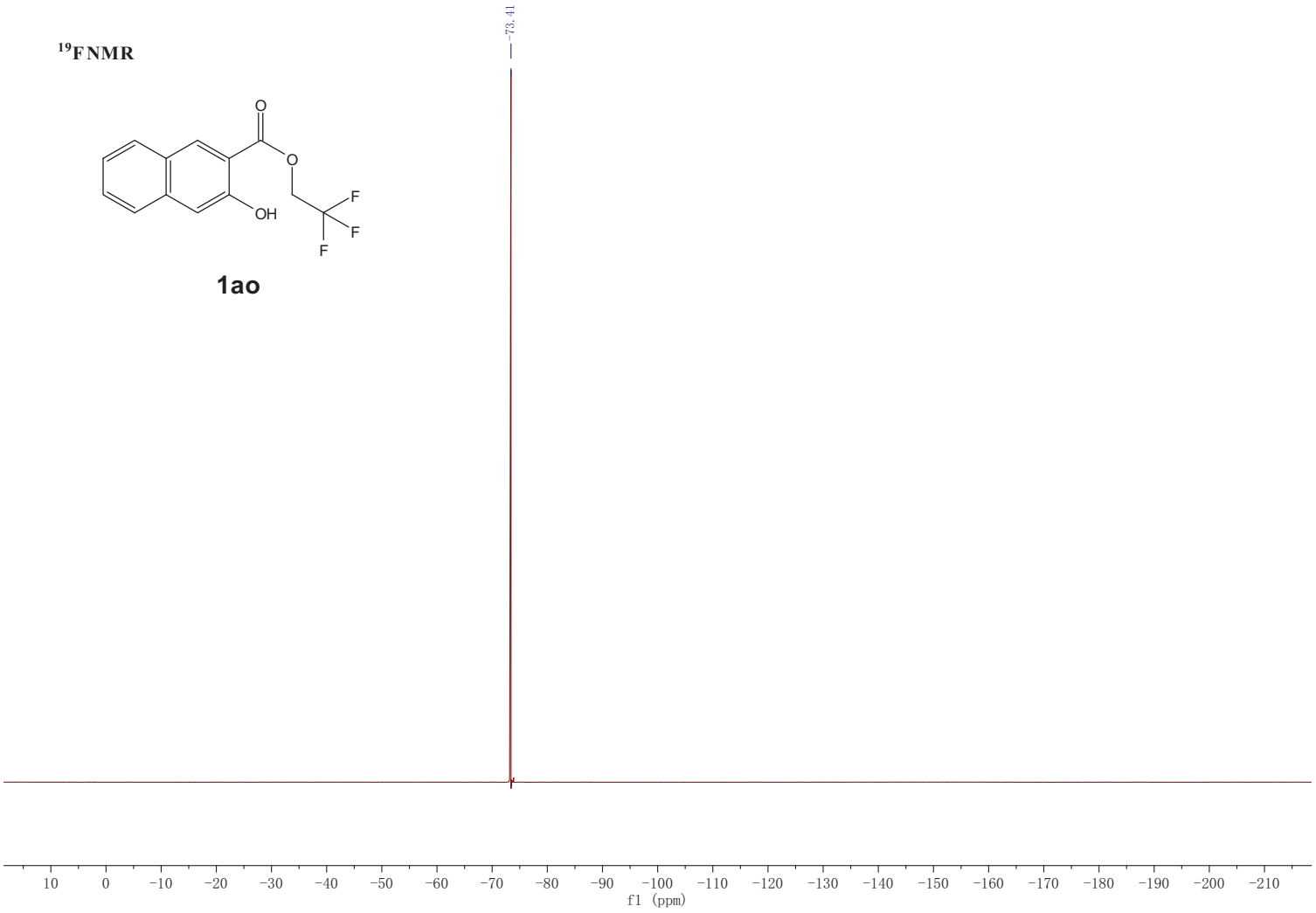

175.71
170.37
162.29
153.44
135.63
132.54
128.73
124.15
124.01
123.79
116.56
108.55
91.14
55.97
33.62
27.25
18.54
O
O
O
CH3
H2C
3an
f1 (ppm)


9.90
8.56
7.87
7.87
7.85
7.85
7.73
7.73
7.71
7.71
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.36
4.85
4.83
4.81
4.79
O
O
OH
F
F
F
1ao
1.00
1.01
1.05
1.07
1.04
2.06
2.07
f1 (ppm)

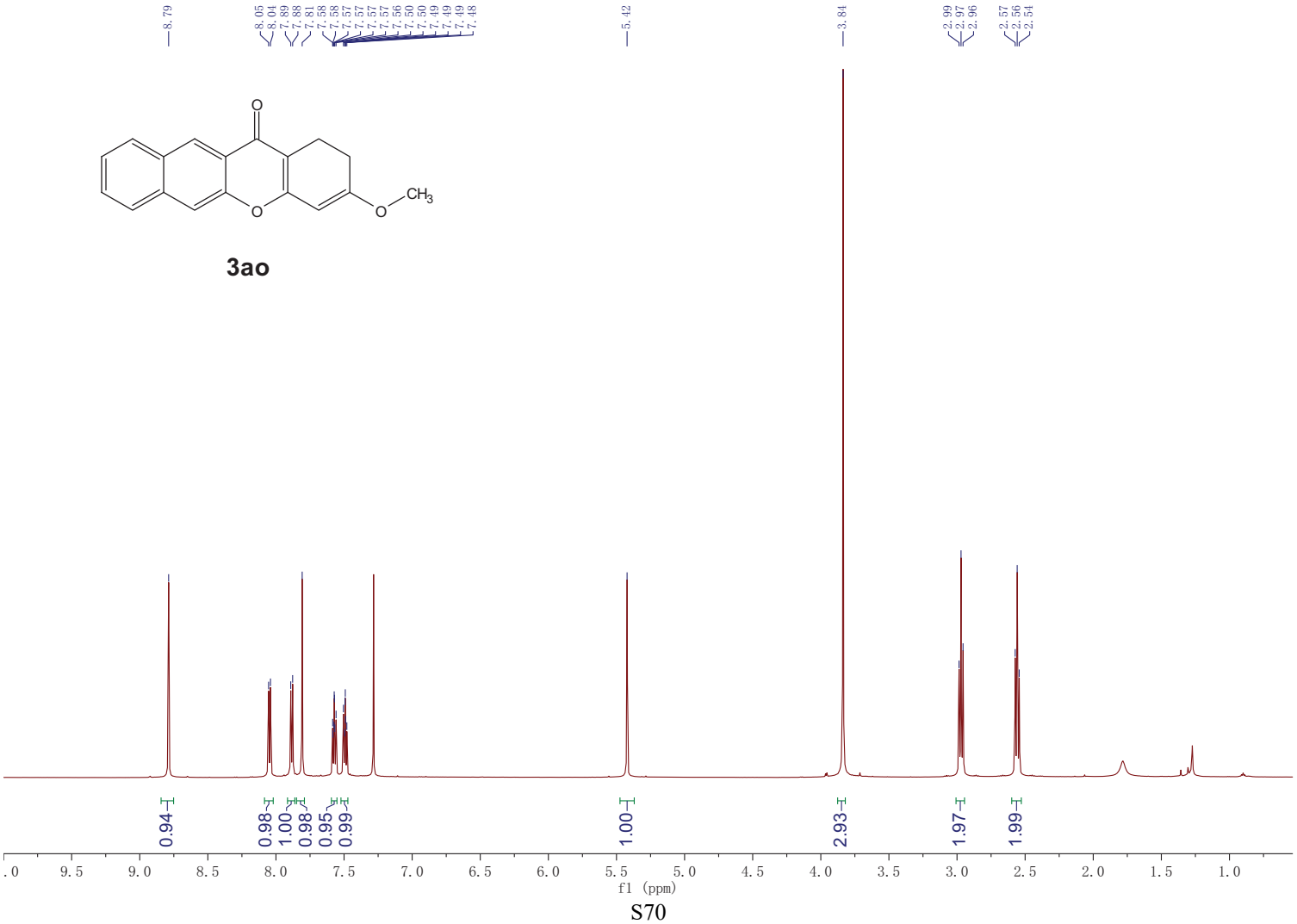

168.10
156.08
138.39
133.03
129.79
129.43
127.07
126.99
126.40
124.32
124.23
121.48
118.72
112.67
112.10
61.57
61.20
60.84
60.47
O
O
OH
F
F
F
1ao
f1 (ppm)

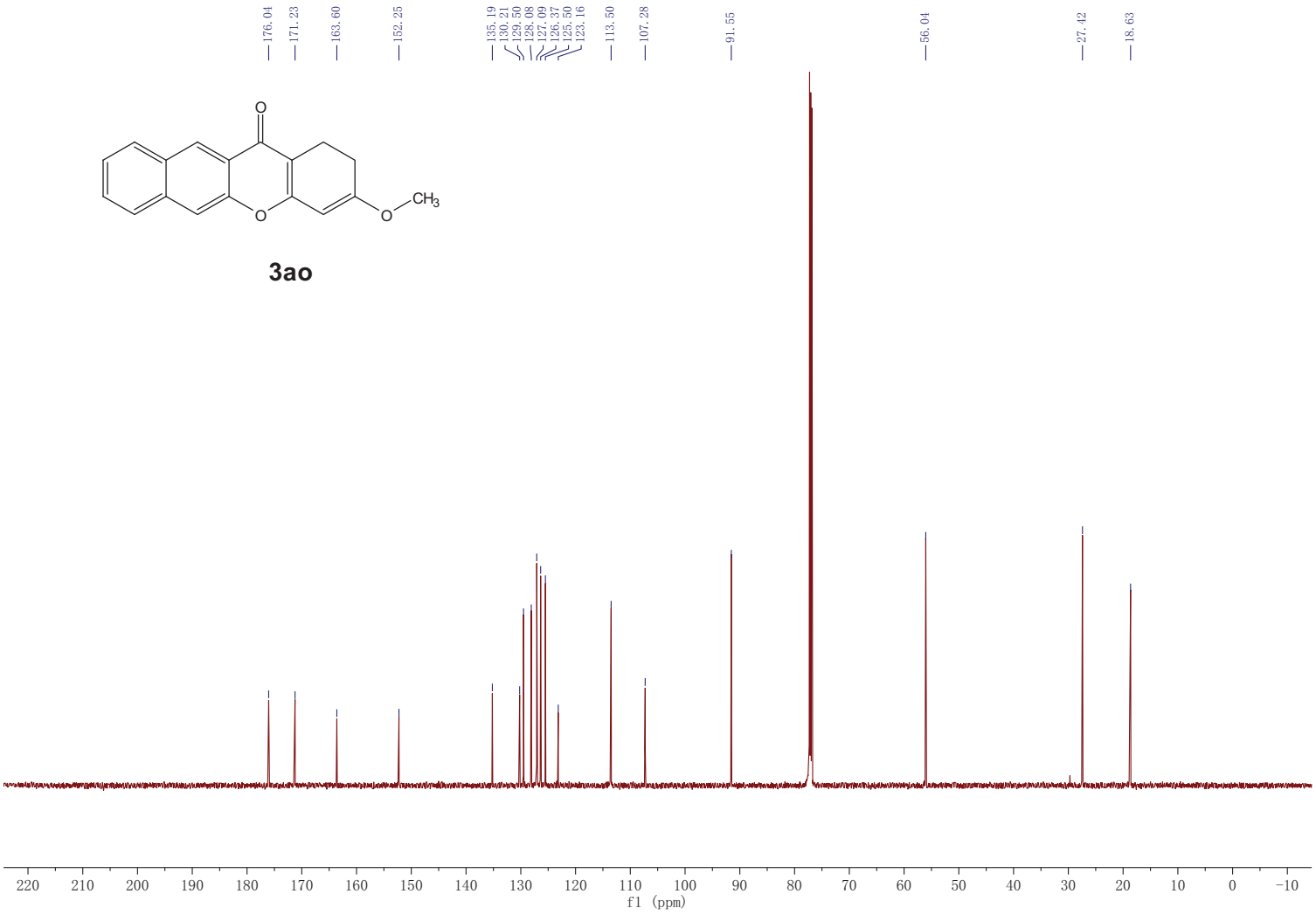
^{19}FNMR

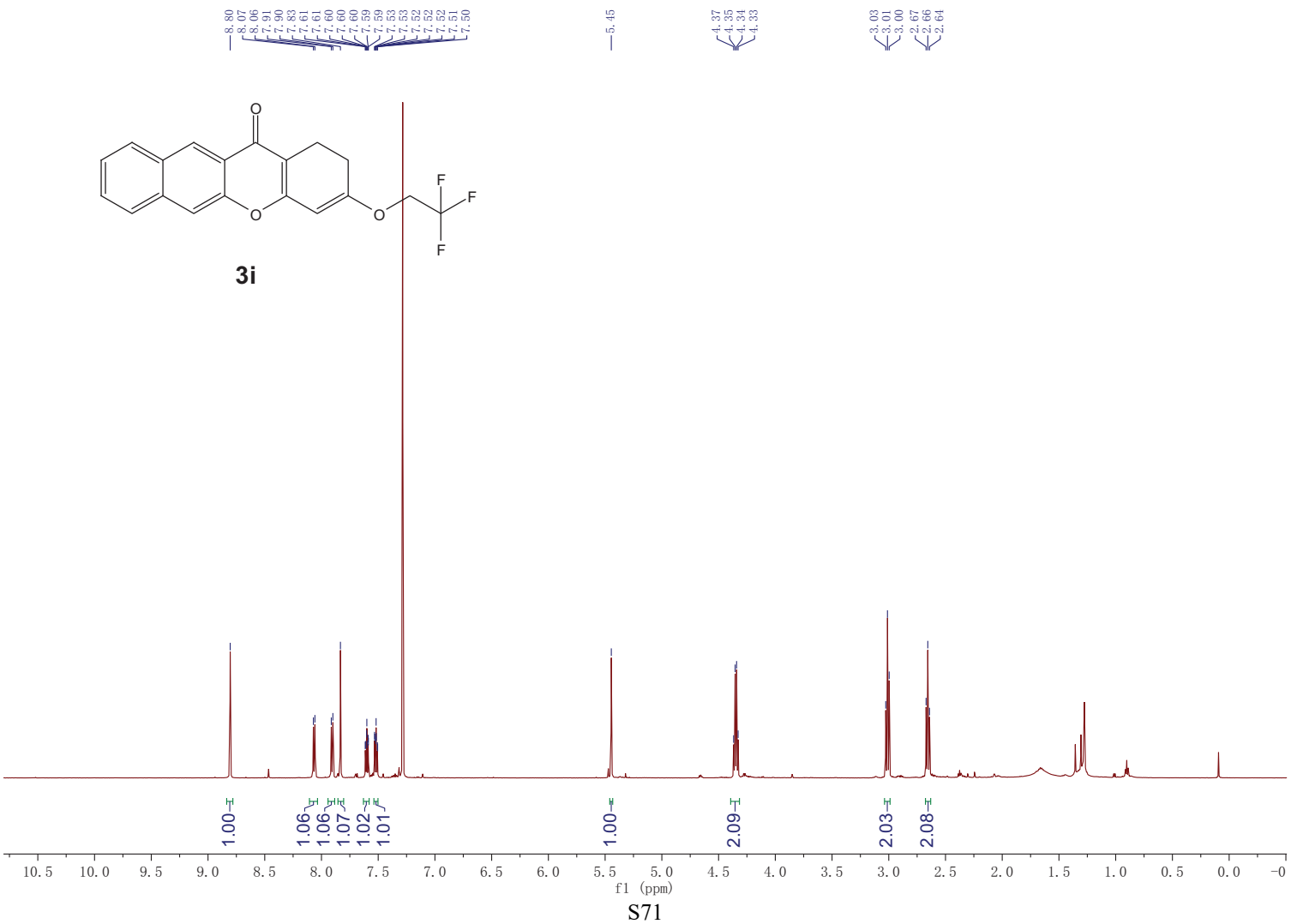
1ao

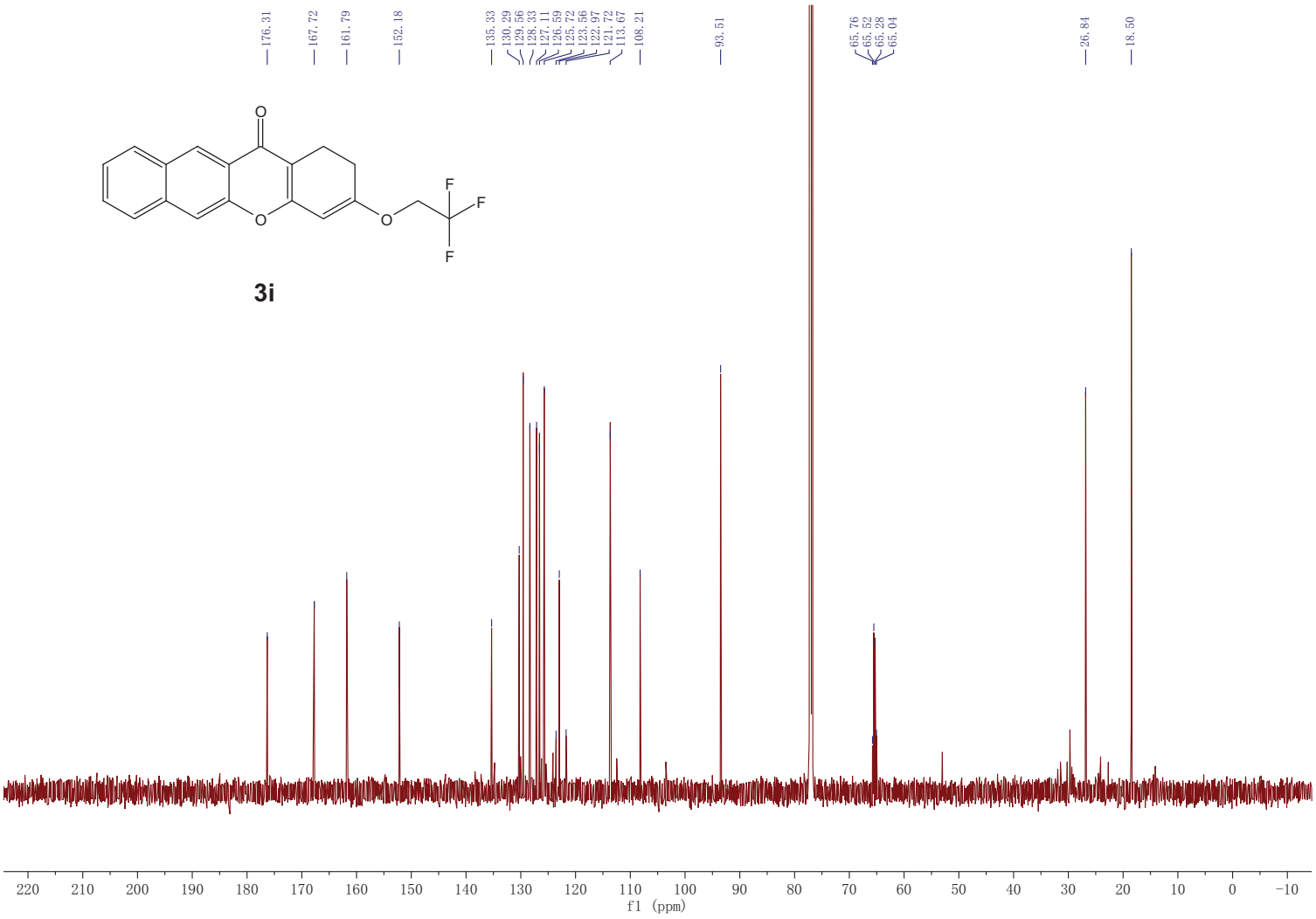


3ao



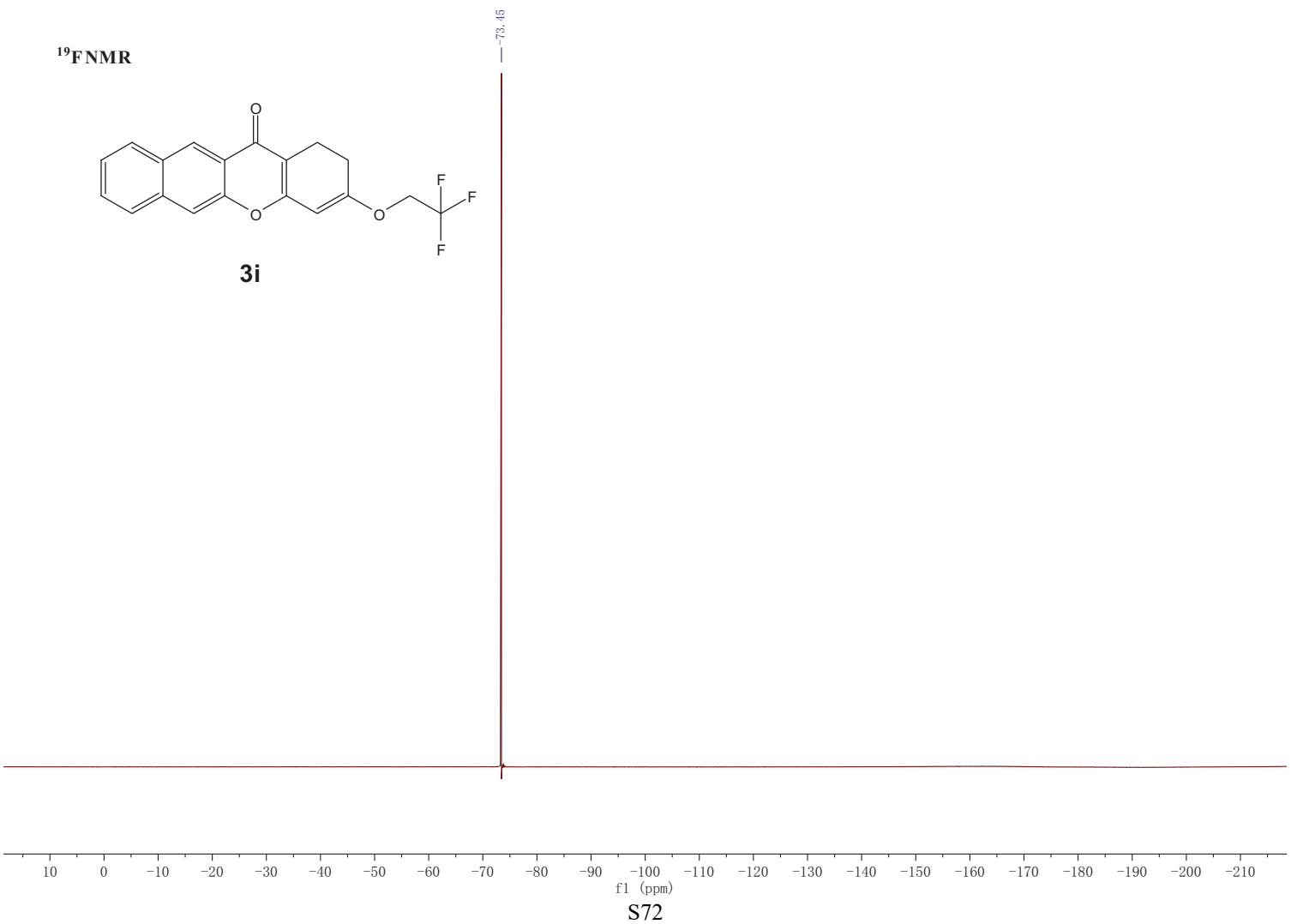

176.04
171.23
163.60
152.25
135.19
130.21
129.50
128.08
127.09
126.37
125.50
123.16
113.50
107.28
91.55
56.04
27.42
18.63
O
O
O
CH3
3ao
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


8.80
8.07
8.06
7.91
7.90
7.83
7.61
7.61
7.60
7.60
7.60
7.59
7.59
7.53
7.53
7.52
7.52
7.52
7.51
7.50
5.45
4.37
4.35
4.34
4.33
3.03
3.01
3.00
2.67
2.66
2.64
O
O
O
F
F
F
3i
1.00
1.06
1.06
1.07
1.02
1.01
1.00
2.09
2.03
2.08
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 −0
f1 (ppm)

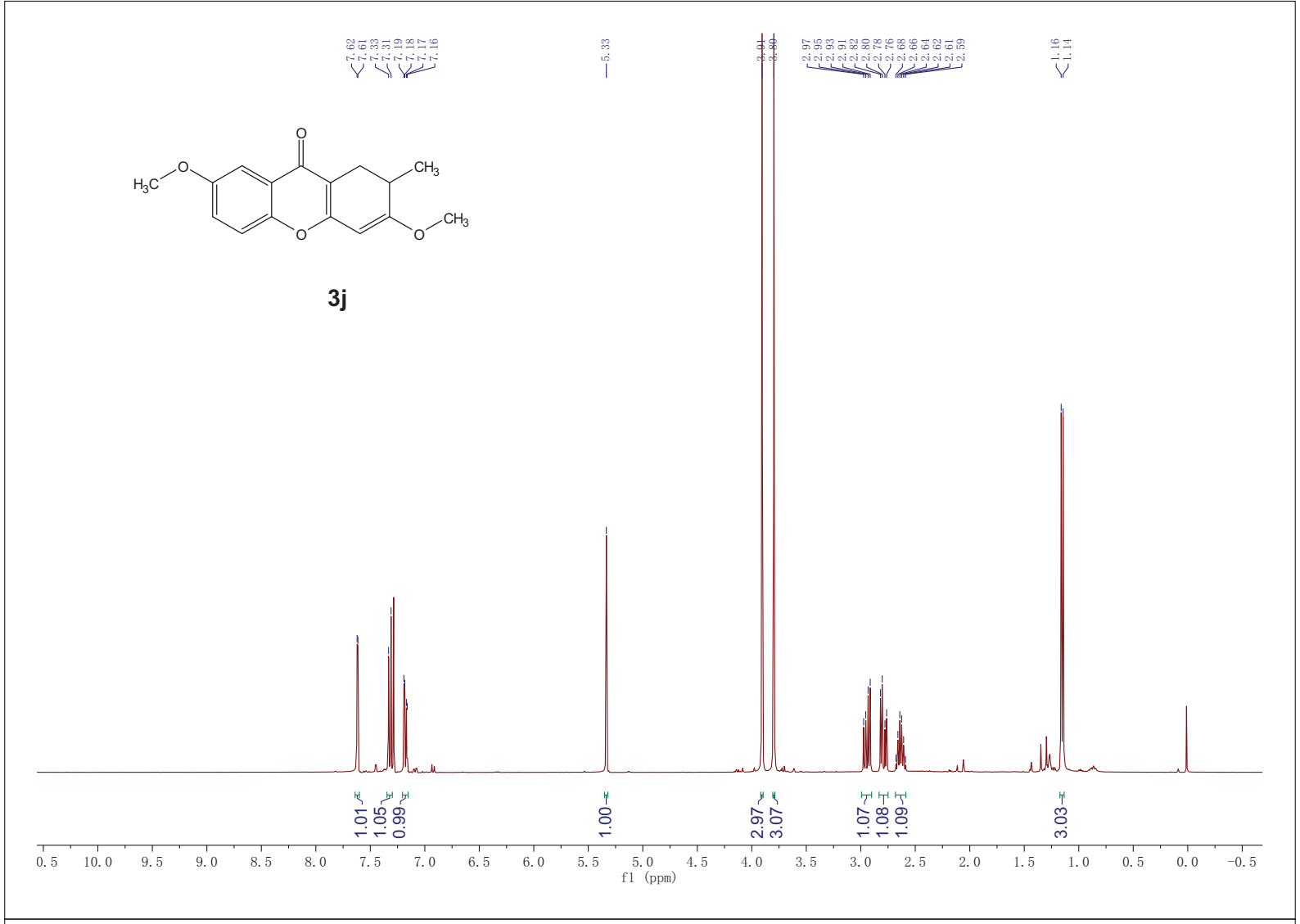

176.31
167.72
161.79
152.18
135.33
130.29
129.56
128.33
127.11
126.59
125.72
123.56
122.97
121.72
113.67
108.21
93.51
65.76
65.52
65.28
65.04
26.84
18.50
O
O
O
F
F
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

3i

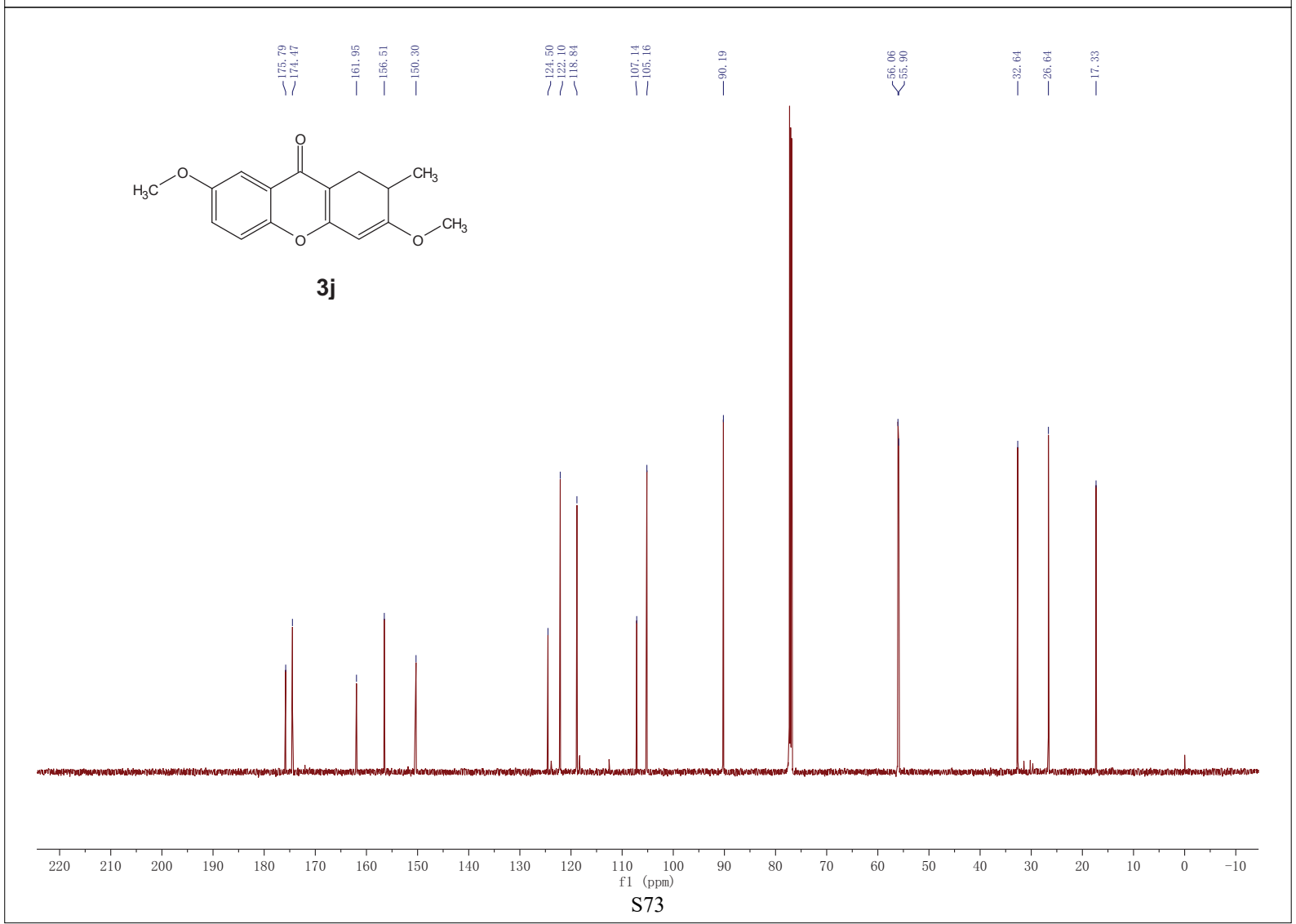
^{19}FNMR


−73.45
O
O
O
F
F
F
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)

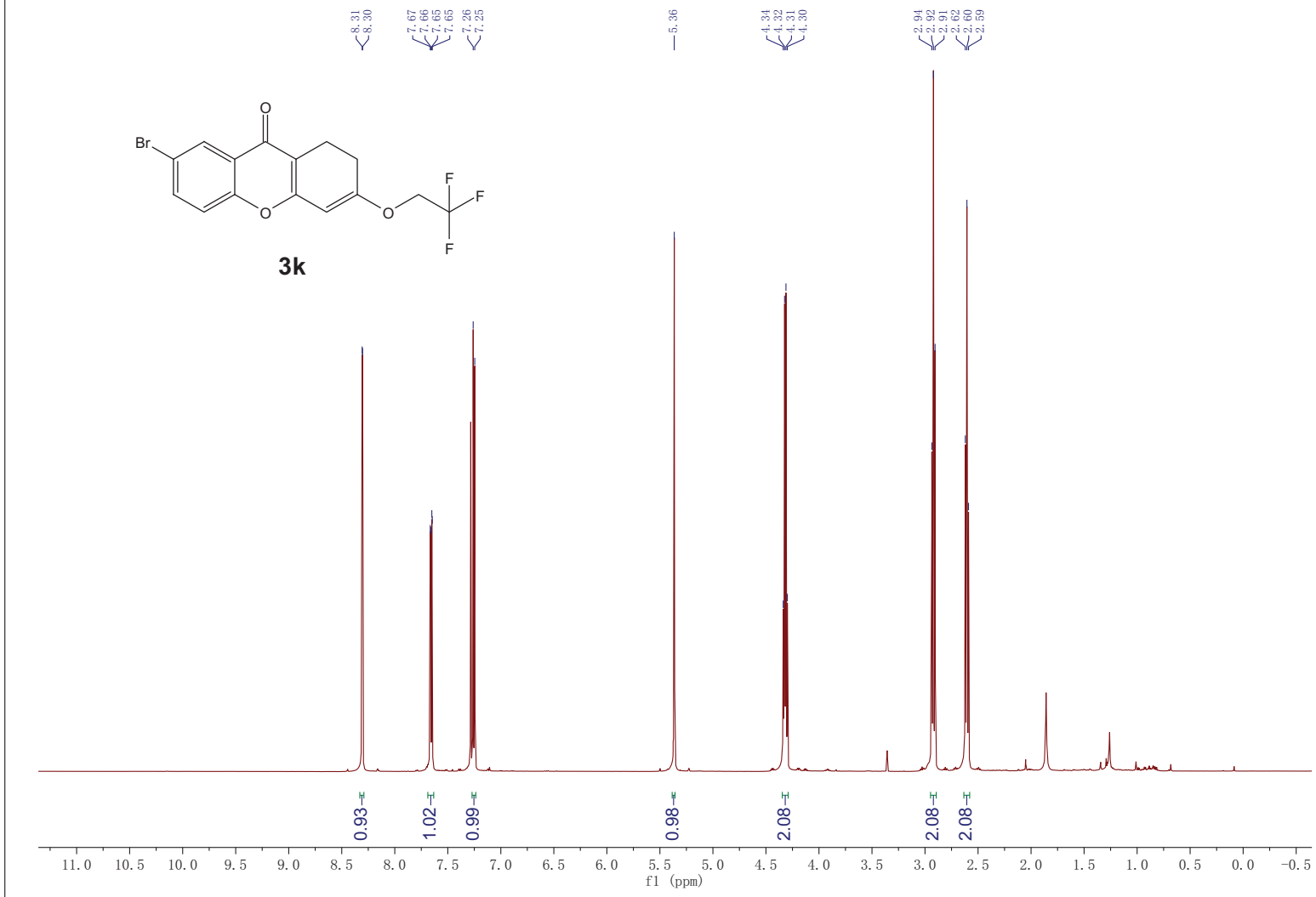
3i

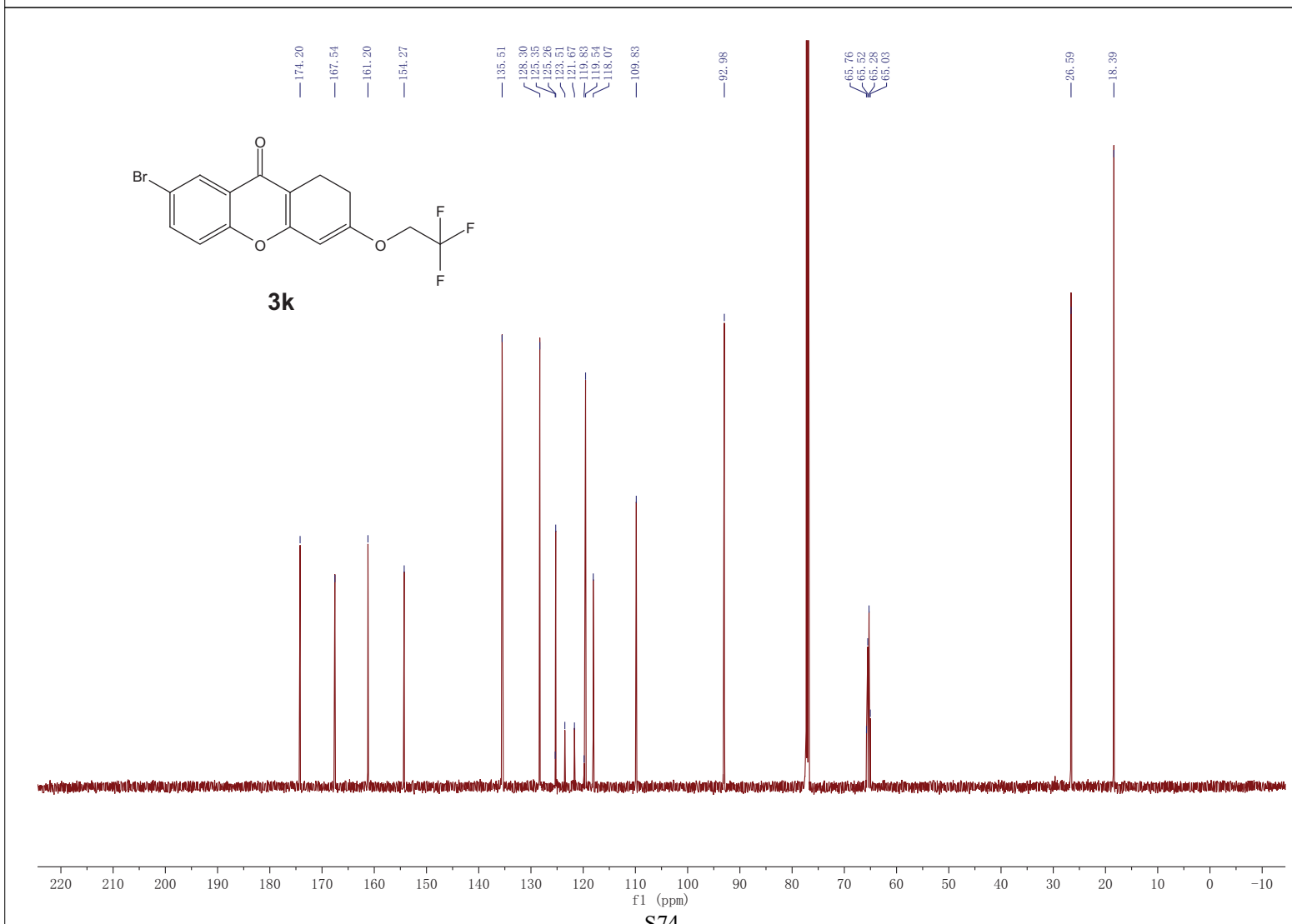

7.62
7.61
7.33
7.31
7.19
7.18
7.17
7.16
5.33
3.91
3.80
2.97
2.95
2.93
2.91
2.82
2.80
2.78
2.76
2.68
2.66
2.64
2.62
2.61
2.59
1.16
1.14
O
H3C
O
CH3
O
CH3
1.01
1.05
0.99
1.00
2.97
3.07
1.07
1.08
1.09
3.03
f1 (ppm)

3j


175.79
174.47
161.95
156.51
150.30
124.50
122.10
118.84
107.14
105.16
90.19
56.06
55.90
32.64
26.64
17.33
O
H3C
O
CH3
O
CH3
f1 (ppm)

3j

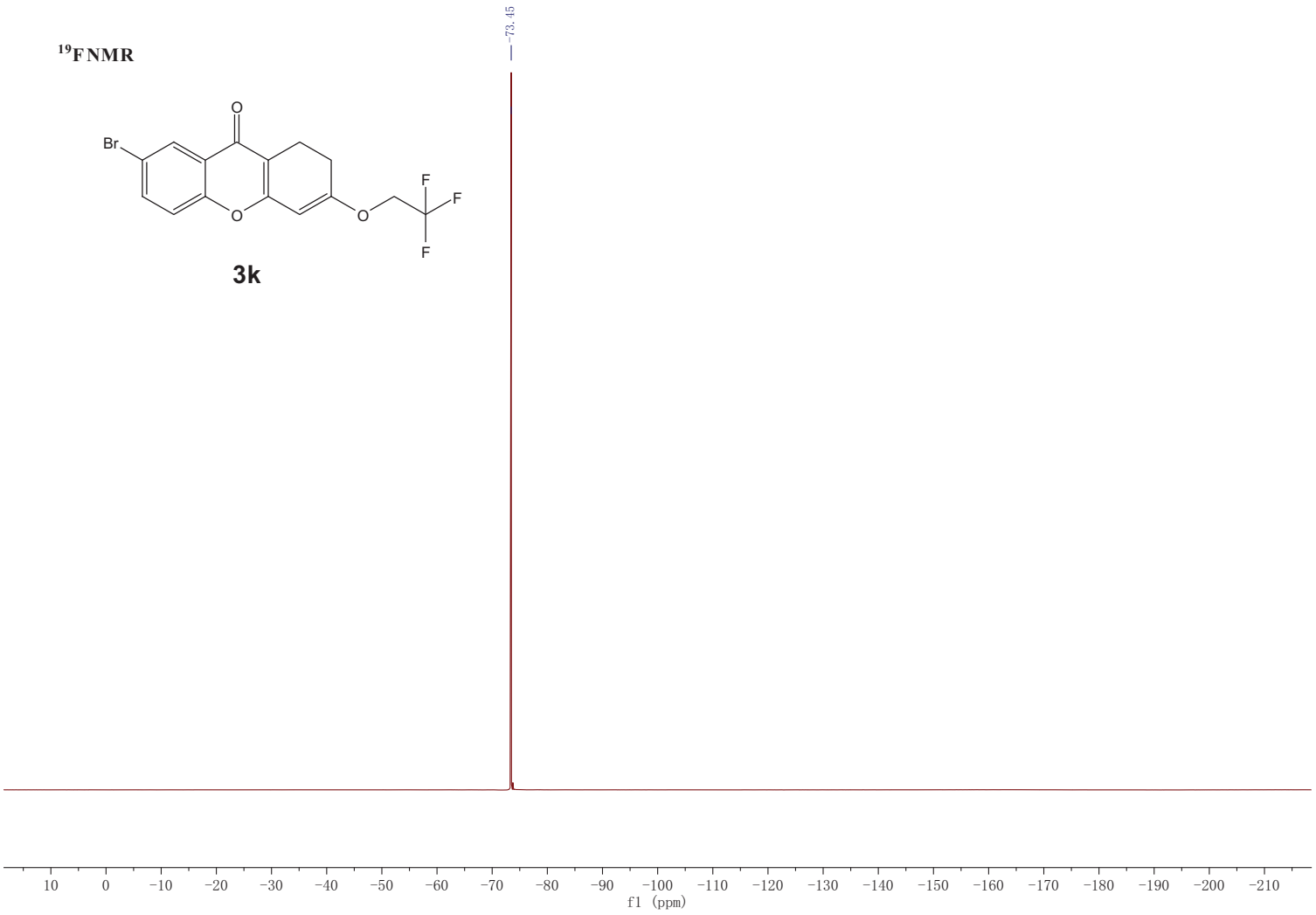

8.31
8.30
7.67
7.66
7.65
7.65
7.26
7.25
5.36
4.34
4.32
4.31
4.30
2.94
2.92
2.91
2.62
2.60
2.59
Br
O
O
O
F
F
F
3k
0.93
1.02
0.99
0.98
2.08
2.08
2.08
f1 (ppm)


174.20
167.54
161.20
154.27
135.51
128.30
125.35
125.26
123.51
121.67
119.83
119.54
118.07
109.83
92.98
65.76
65.52
65.28
65.03
26.59
18.39
Br
O
O
O
F
F
F
3k
f1 (ppm)

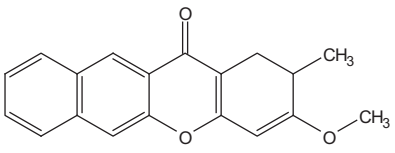
^{19}FNMR

O
Br
O
O
F
F
F

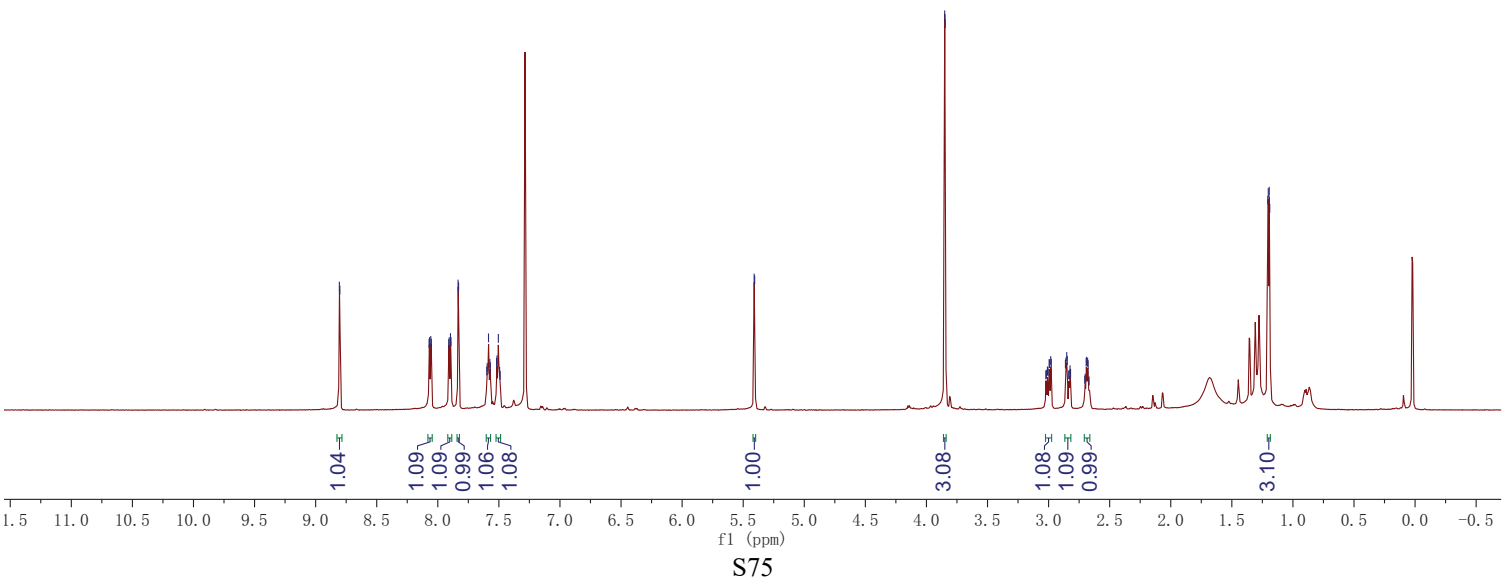
3k

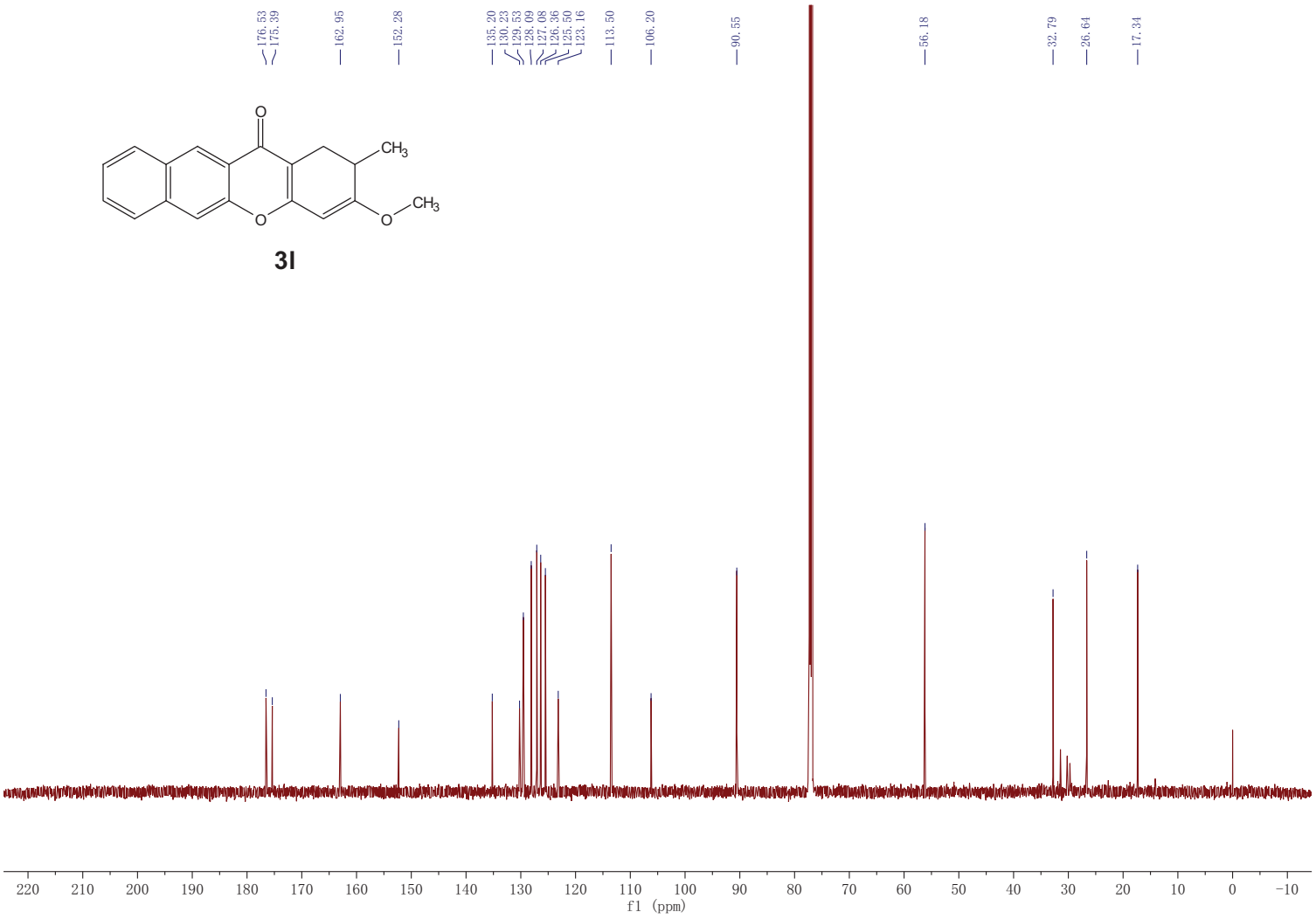

-73.45
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.81 8.80 8.07 8.07 8.06 8.05 7.91 7.90 7.89 7.83 7.83 7.60 7.60 7.58 7.57 7.57 7.52 7.51 7.50 7.49 7.49
5.41 5.41
3.85 3.85 3.02 3.01 3.00 3.00 2.99 2.98 2.98 2.86 2.86 2.85 2.85 2.83 2.83 2.82 2.82 2.70 2.70 2.69 2.69 2.68 2.68 2.67 1.21 1.20 1.19 1.19

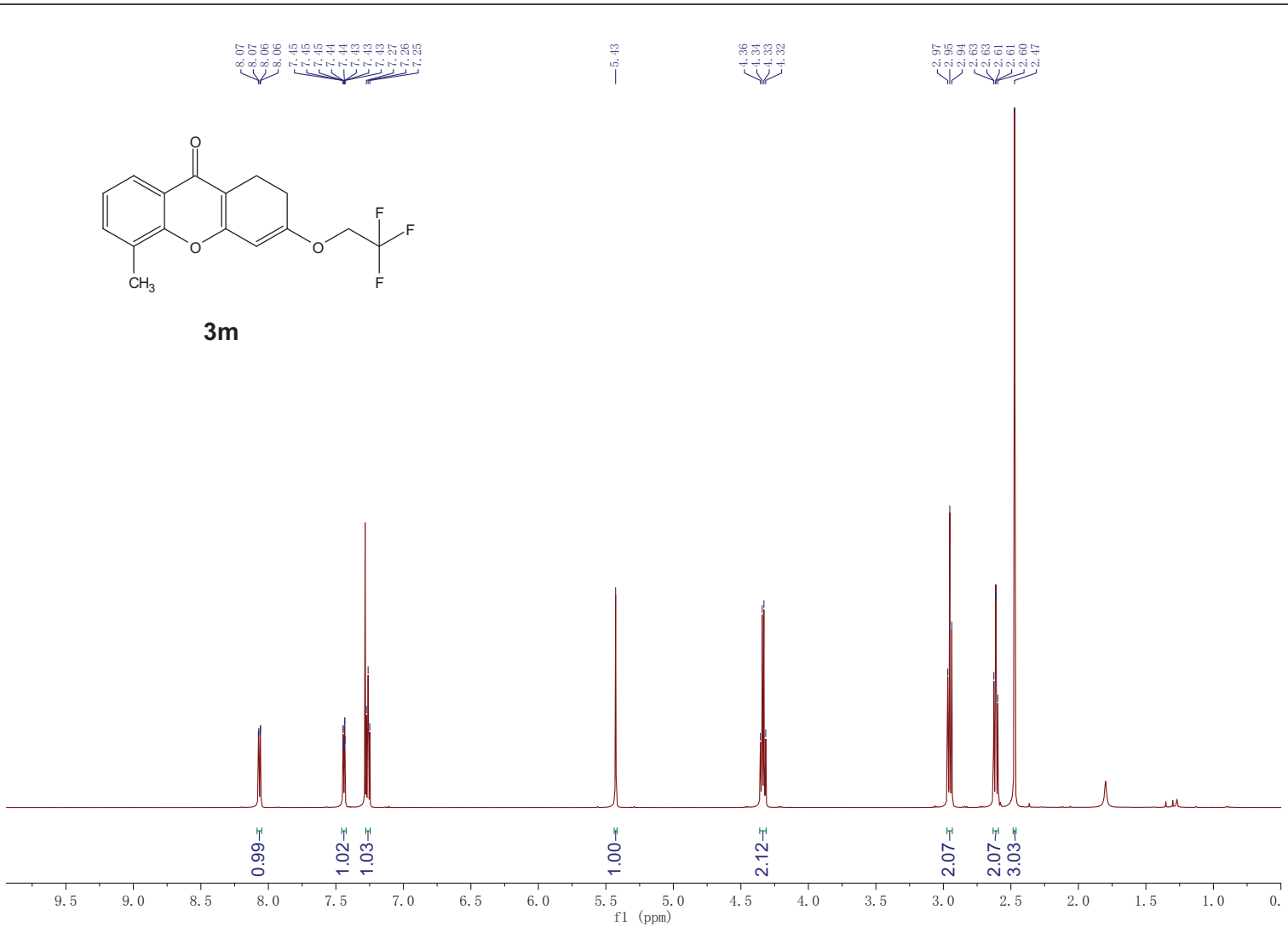

O
CH3
O
CH3

3l

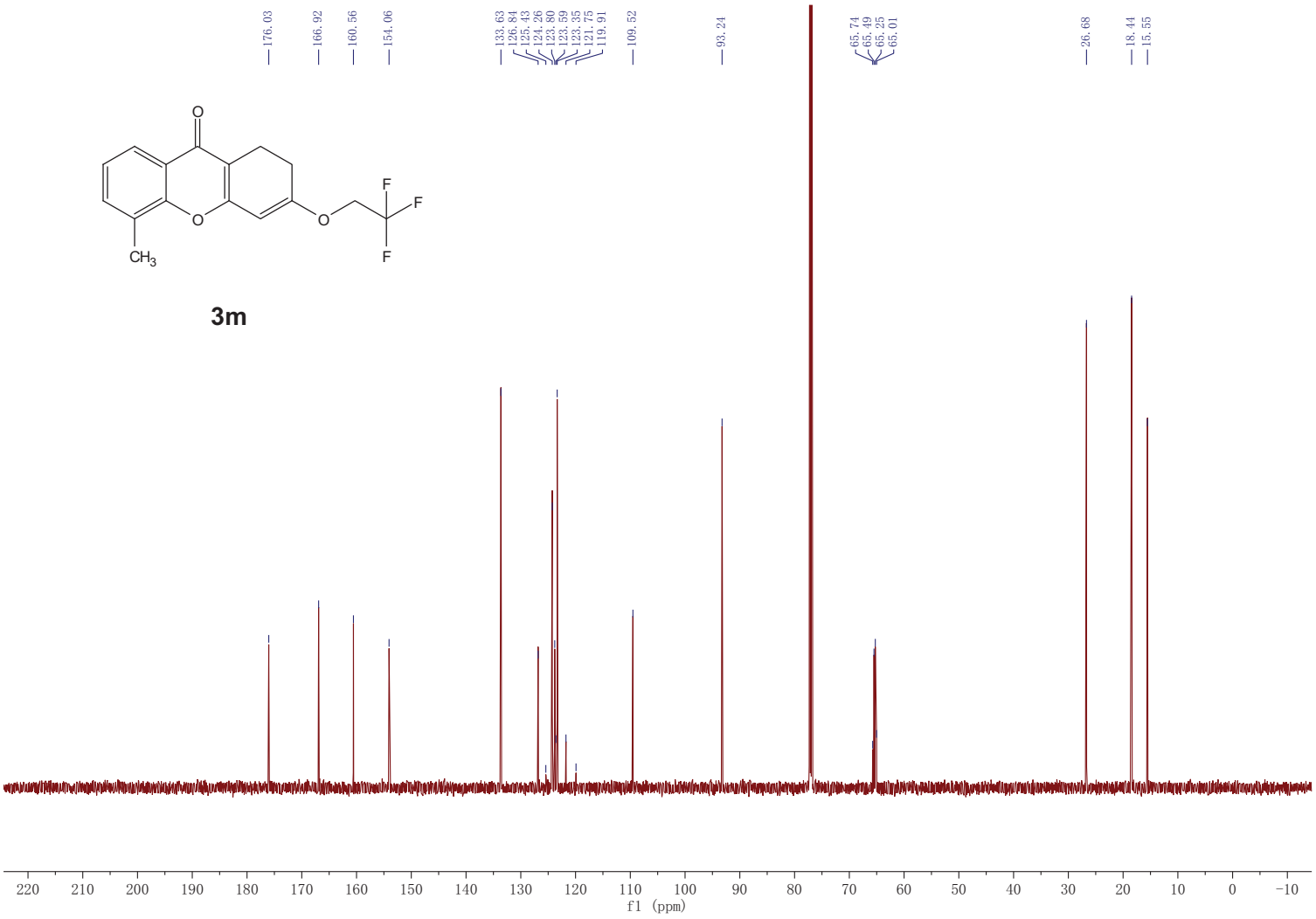

1.04 1.09 1.09 0.99 1.06 1.08 1.00 3.08 1.08 1.09 0.99 3.10
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


176.53
175.39
162.95
152.28
135.20
130.23
129.53
128.09
127.08
126.36
125.50
123.16
113.50
106.20
90.55
56.18
32.79
26.64
17.34
O
CH3
O
O
CH3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

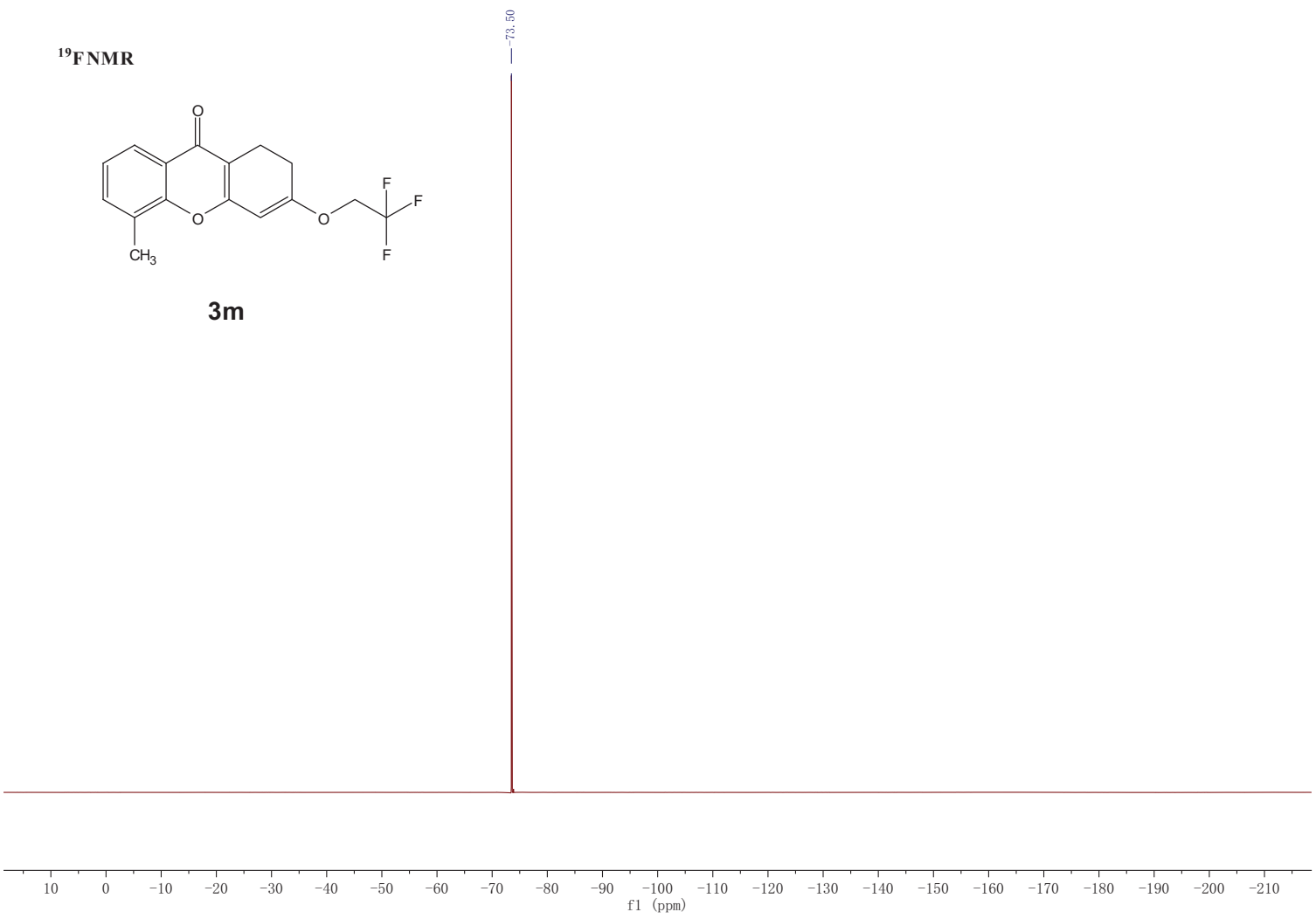
3l

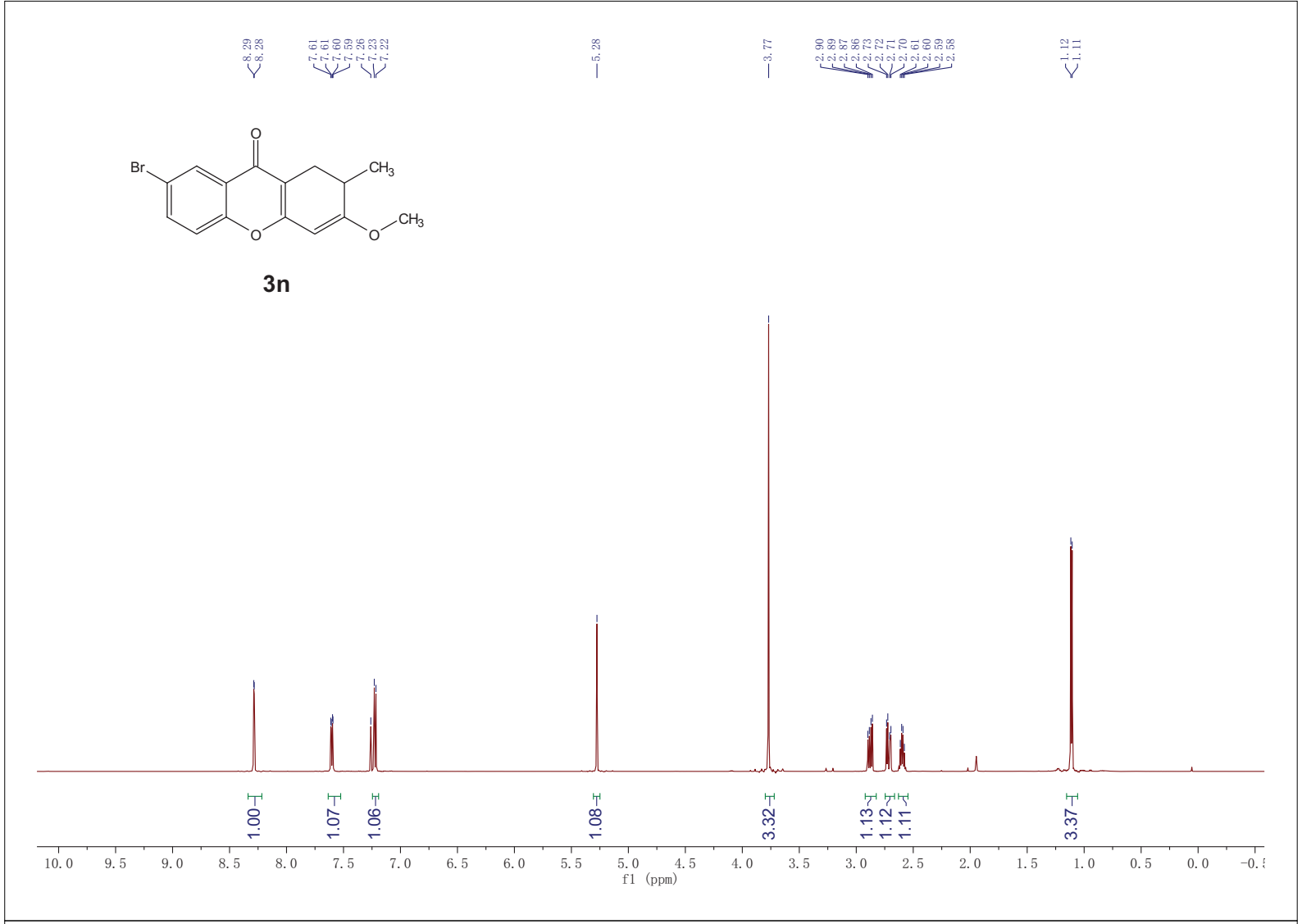

8.07
8.07
8.06
8.06
7.45
7.45
7.45
7.44
7.44
7.43
7.43
7.43
7.27
7.26
7.25
5.43
4.36
4.34
4.33
4.32
2.97
2.95
2.94
2.63
2.63
2.61
2.61
2.60
2.47
O
F
F
F
O
O
CH3
0.99
1.02
1.03
1.00
2.12
2.07
2.07
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.
f1 (ppm)

3m

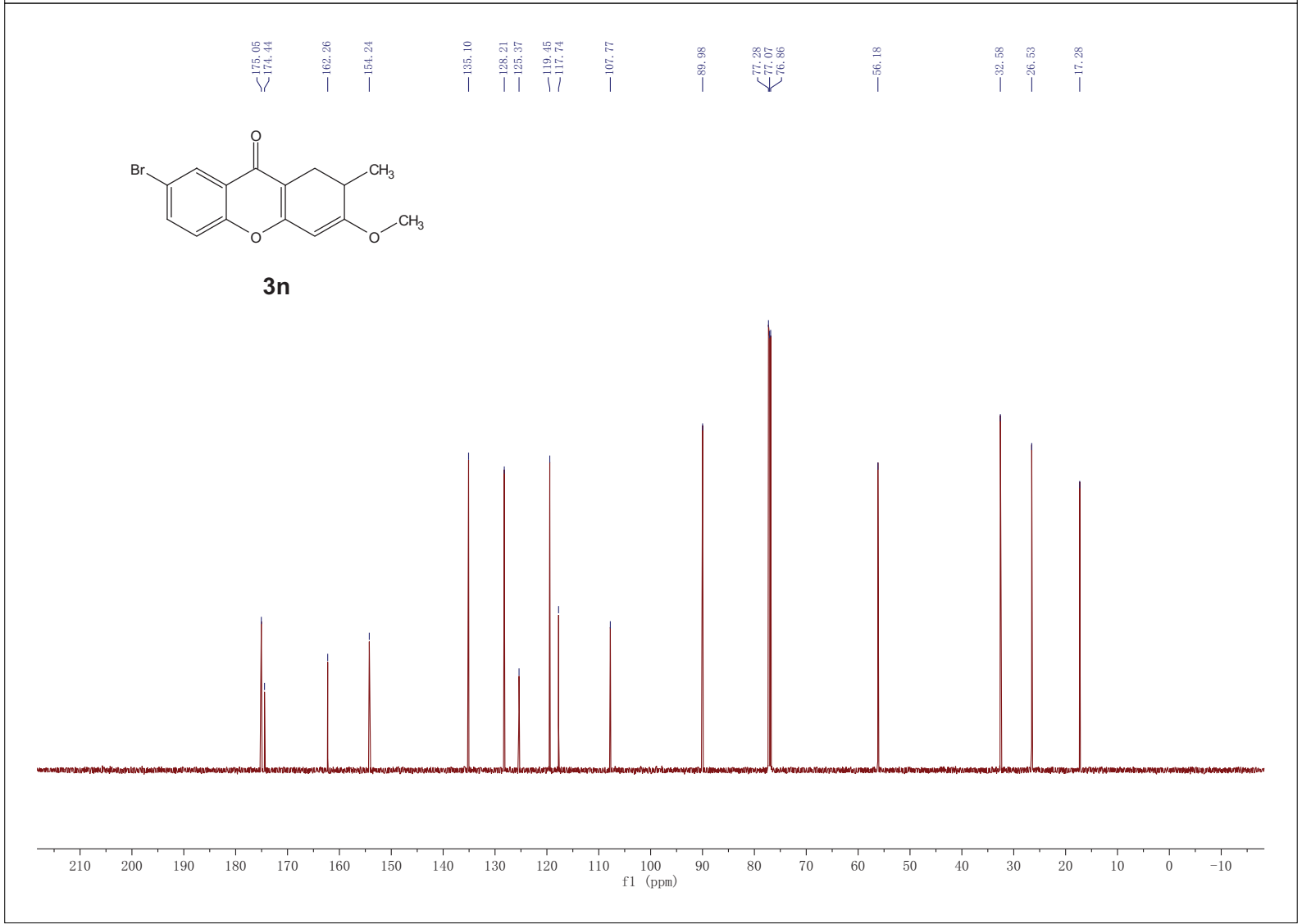

176.03
166.92
160.56
154.06
133.63
126.84
125.43
124.26
123.80
123.59
123.35
121.75
119.91
109.52
93.24
65.74
65.49
65.25
65.01
26.68
18.44
15.55
O
O
O
F
F
F
CH3
3m
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

^{19}FNMR

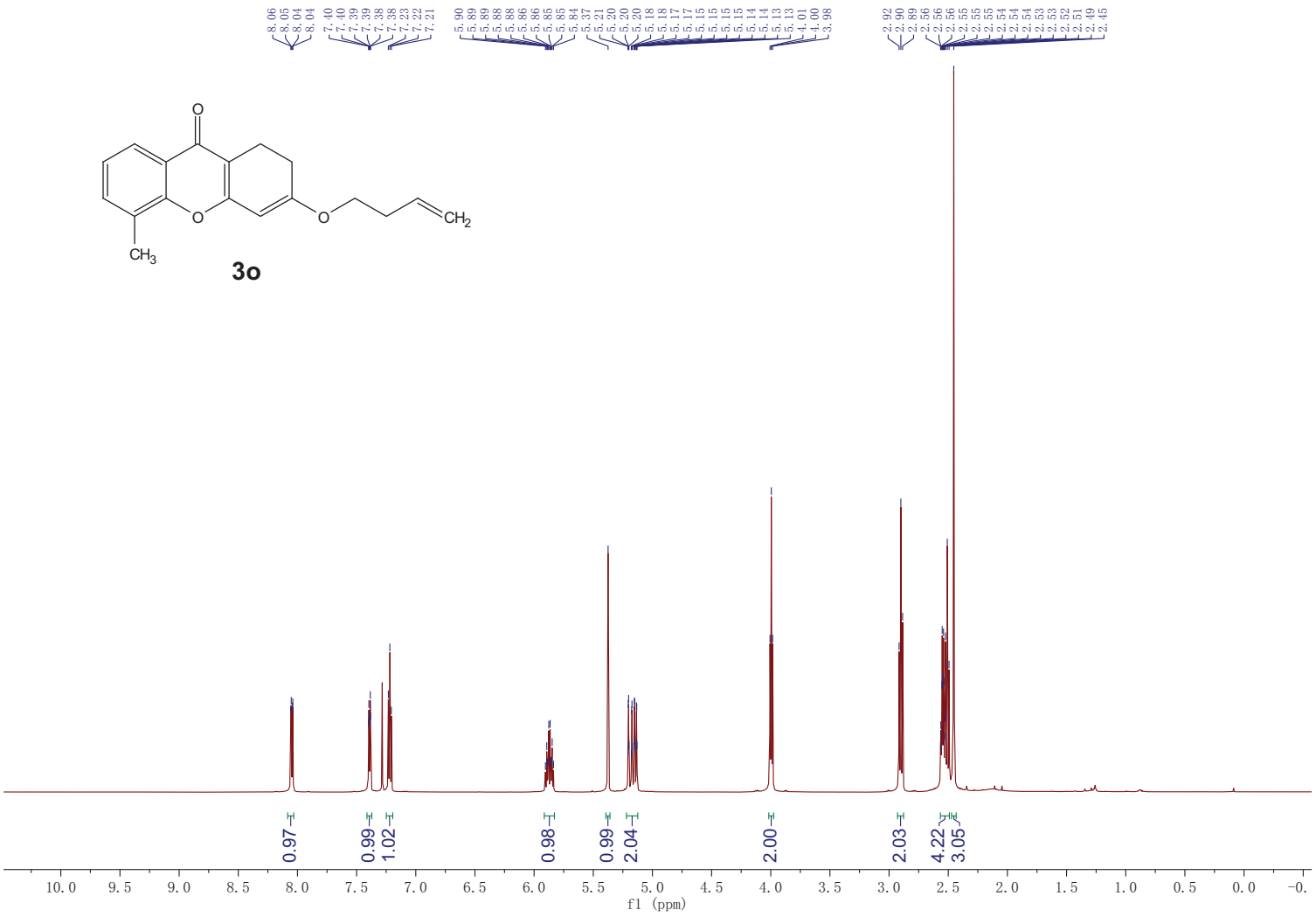

−73.50
O
O
O
F
F
F
CH3
3m
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)

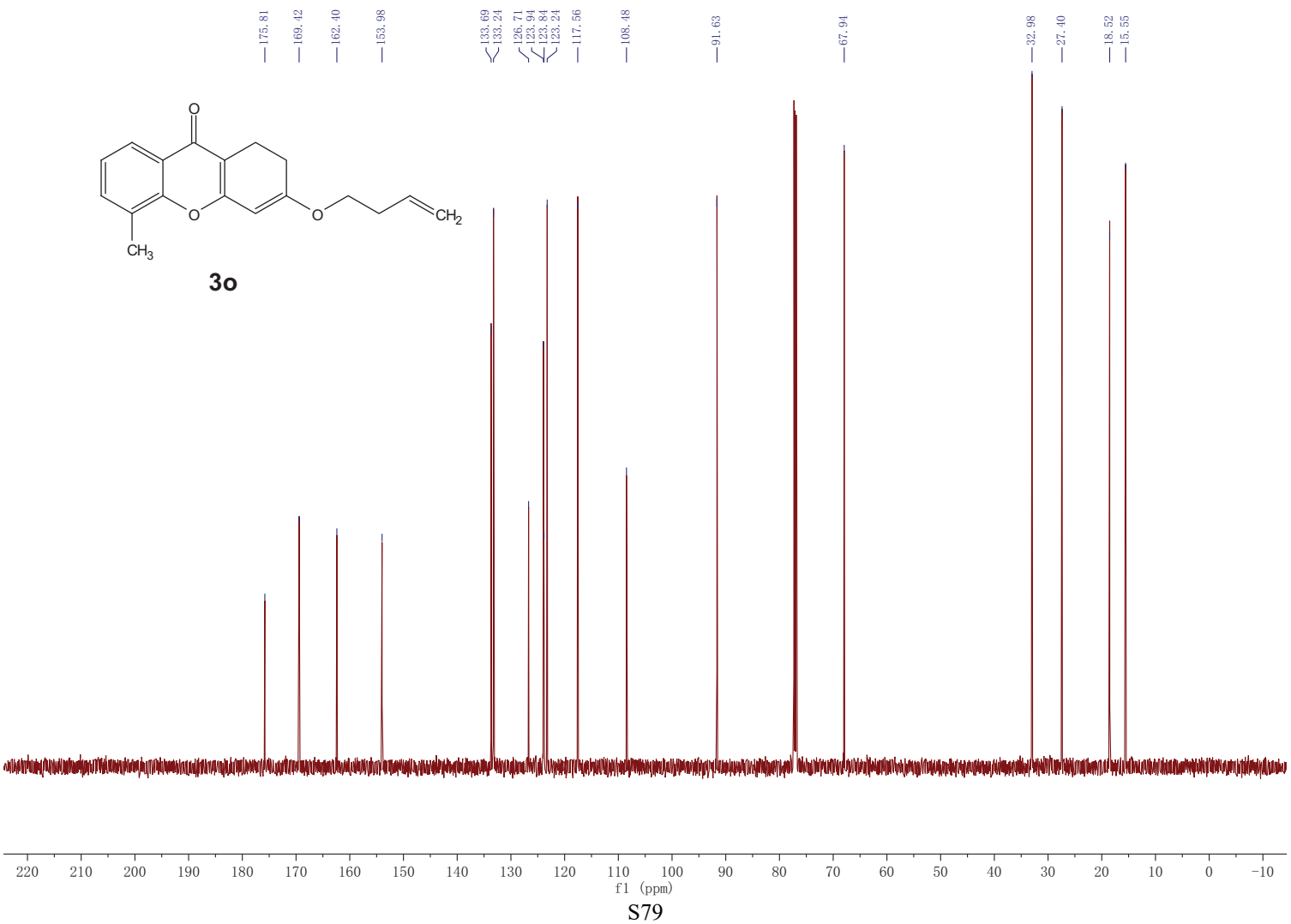

8.29
8.28
7.61
7.61
7.60
7.59
7.26
7.23
7.22
5.28
3.77
2.90
2.89
2.87
2.86
2.73
2.72
2.71
2.70
2.61
2.60
2.59
2.58
1.12
1.11
Br
O
CH3
O
O
CH3
1.00
1.07
1.06
1.08
3.32
1.13
1.12
1.11
3.37
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3n

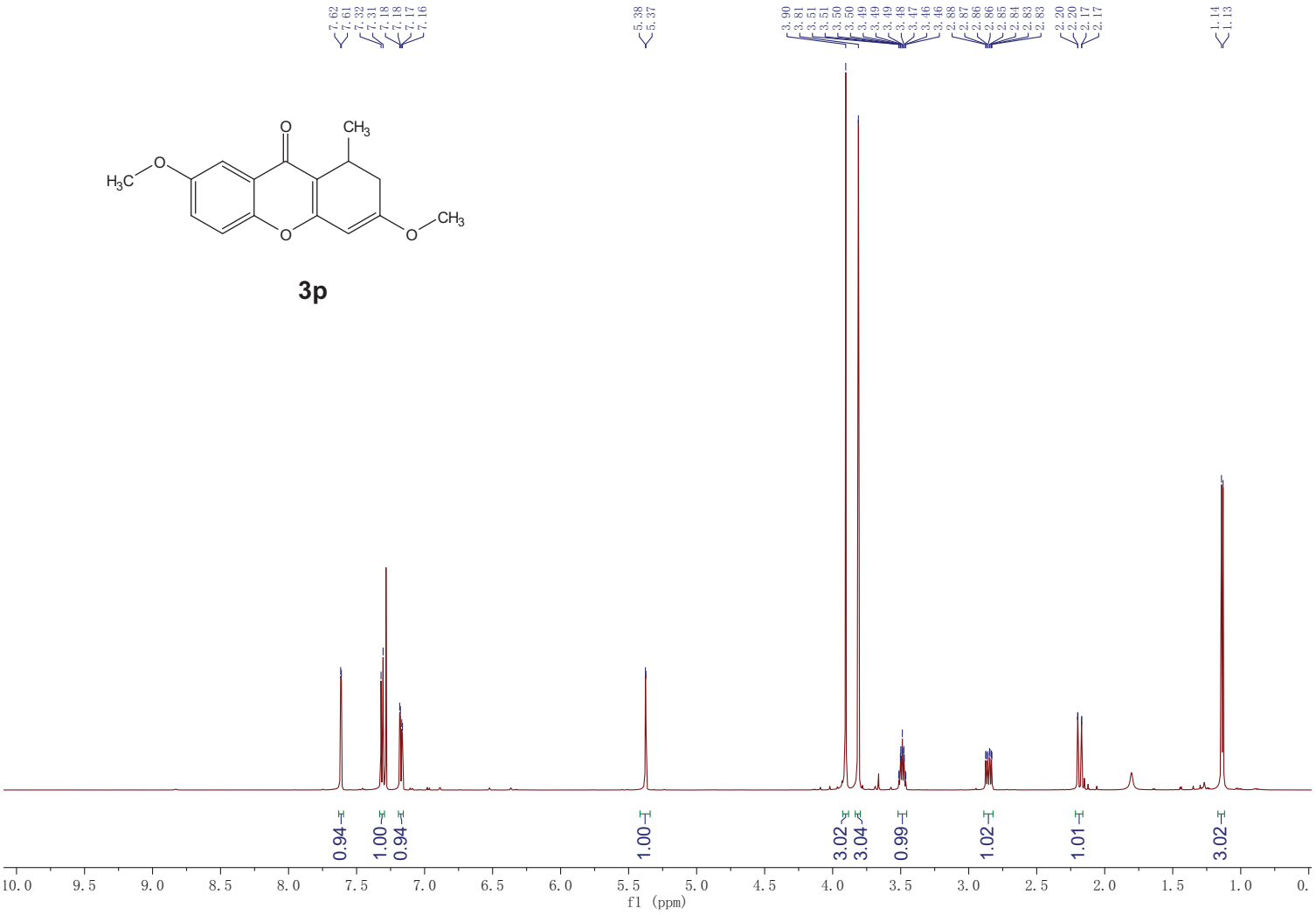

175.05
174.44
162.26
154.24
135.10
128.21
125.37
119.45
117.74
107.77
89.98
77.28
77.07
76.86
56.18
32.58
26.53
17.28
Br
O
CH3
O
O
CH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3n

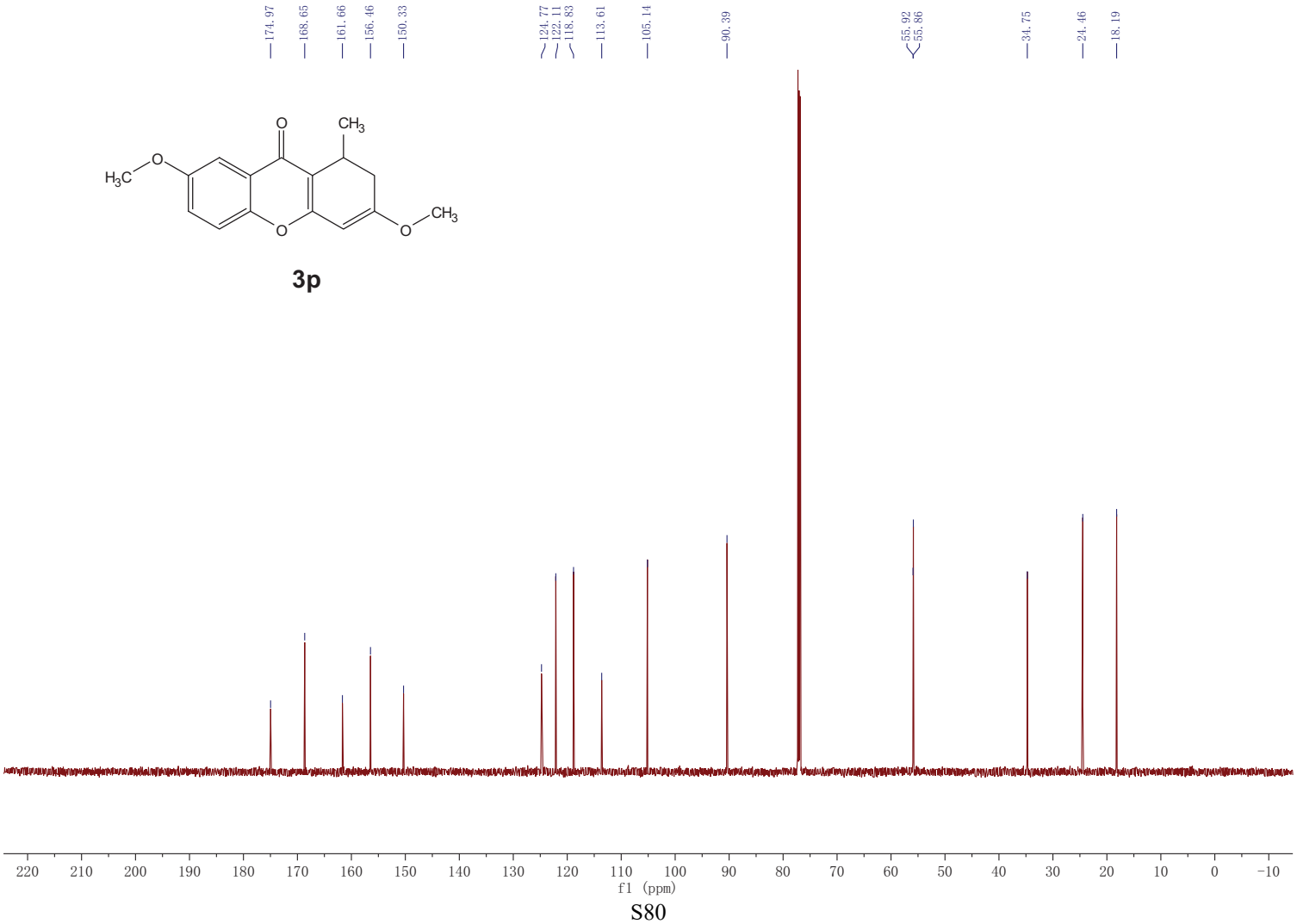

8.06
8.05
8.04
8.04
7.40
7.40
7.39
7.39
7.38
7.38
7.23
7.22
7.21
5.90
5.89
5.89
5.88
5.88
5.86
5.86
5.85
5.85
5.84
5.37
5.21
5.20
5.20
5.18
5.18
5.17
5.17
5.15
5.15
5.15
5.15
5.14
5.14
5.13
5.13
4.01
4.00
3.98
2.92
2.90
2.89
2.56
2.56
2.56
2.55
2.55
2.55
2.54
2.54
2.54
2.53
2.53
2.52
2.51
2.49
2.45
O
O
O
CH3
CH2
3o
0.97
0.99
1.02
0.98
0.99
2.04
2.00
2.03
4.22
3.05
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
-0.
f1 (ppm)

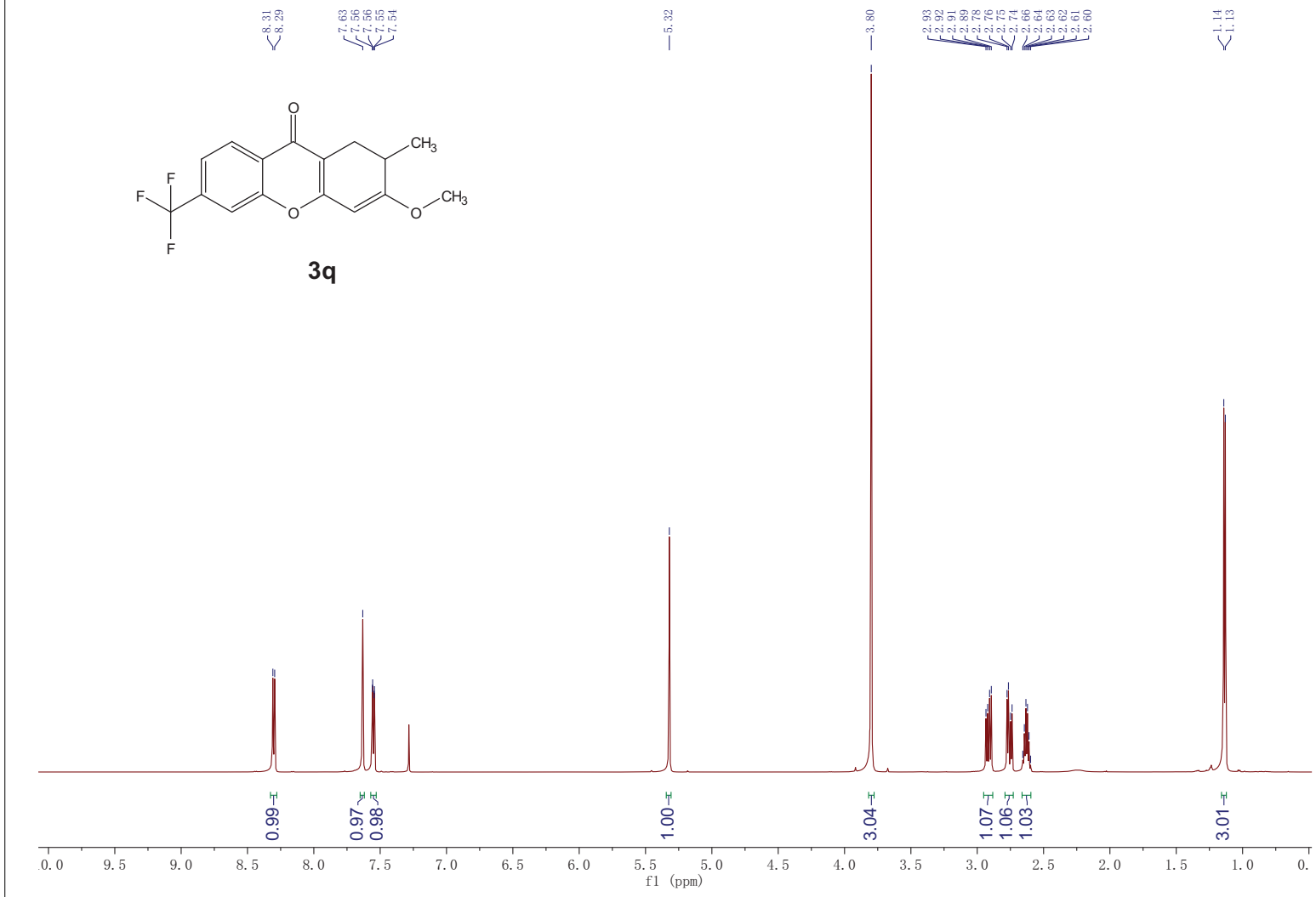

175.81
169.42
162.40
153.98
133.69
133.24
126.71
123.94
123.84
123.24
117.56
108.48
91.63
67.94
32.98
27.40
18.52
15.55
O
O
O
CH3
CH2
3o
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

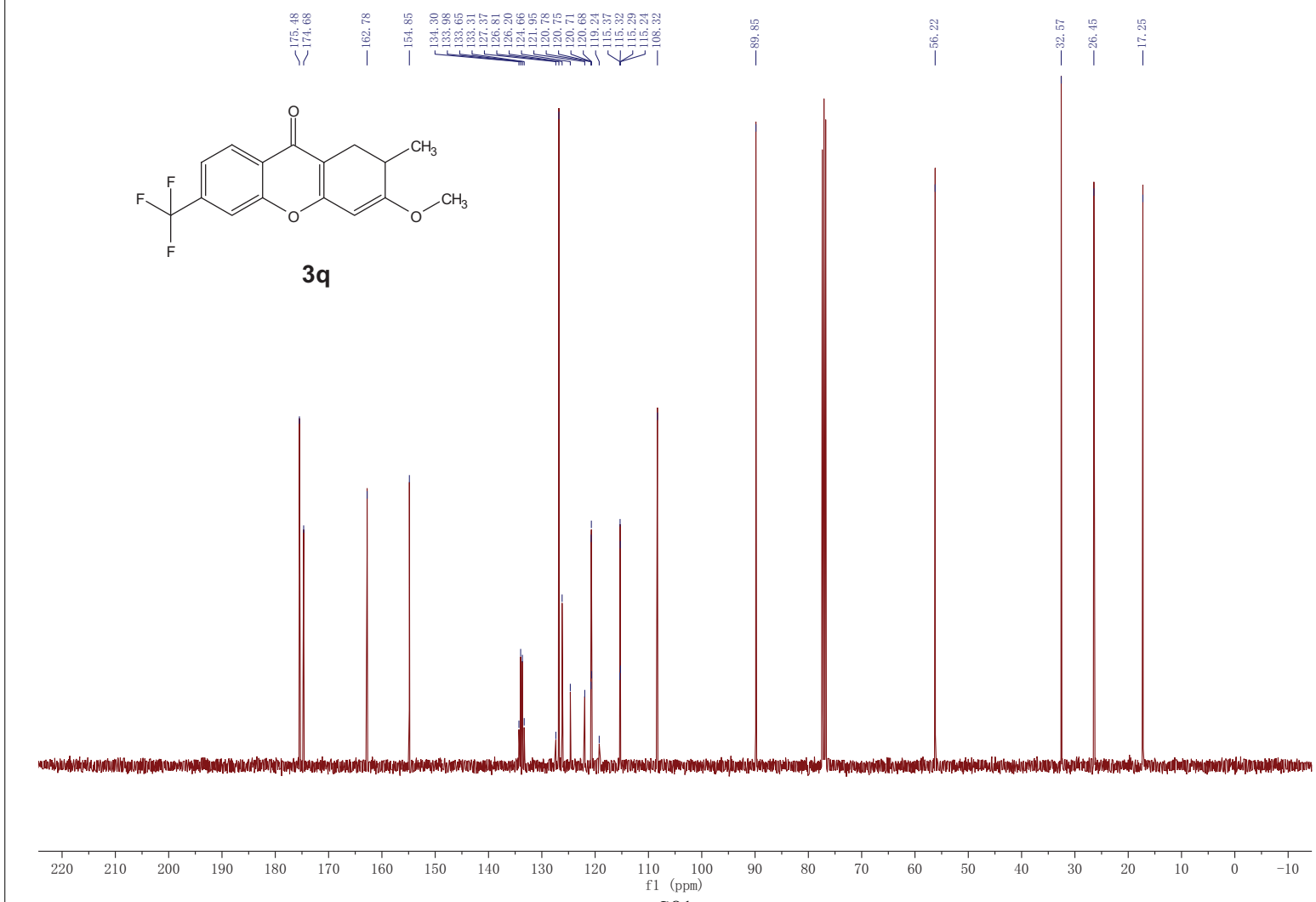
3p


7.62
7.61
7.32
7.31
7.18
7.18
7.17
7.16
5.38
5.37
3.90
3.81
3.51
3.51
3.50
3.50
3.49
3.49
3.49
3.48
3.47
3.46
3.46
2.88
2.87
2.86
2.86
2.85
2.84
2.83
2.83
2.20
2.20
2.17
2.17
1.14
1.13
0.94
1.00
0.94
1.00
3.02
3.04
0.99
1.02
1.01
3.02
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.
f1 (ppm)

3p

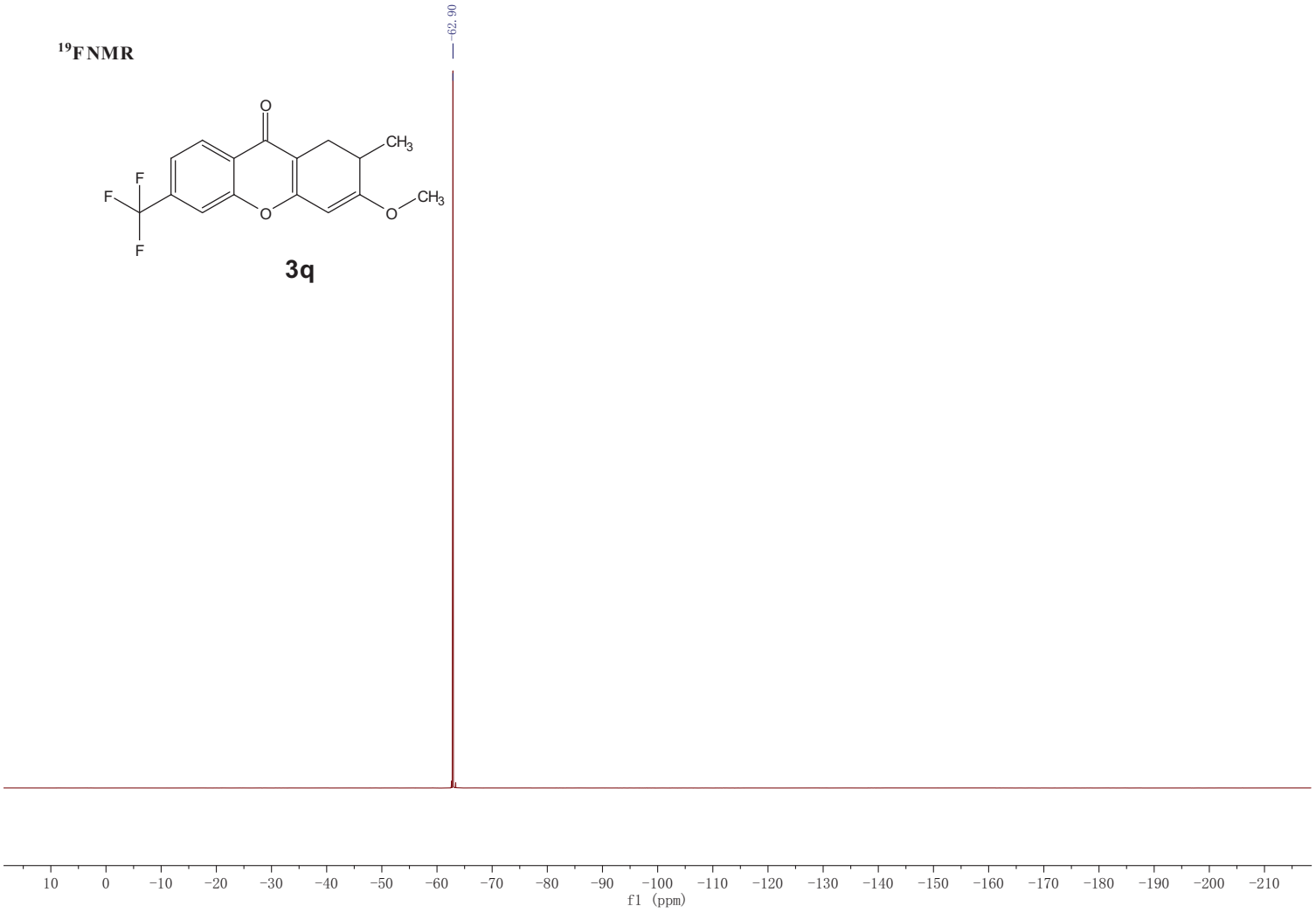

174.97
168.65
161.66
156.46
150.33
124.77
122.11
118.83
113.61
105.14
90.39
55.92
55.86
34.75
24.46
18.19
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.31
8.29
7.63
7.56
7.56
7.55
7.54
5.32
3.80
2.93
2.92
2.91
2.89
2.78
2.76
2.75
2.74
2.66
2.64
2.63
2.62
2.61
2.60
1.14
1.13
O
CH3
F
F
F
O
O
CH3
3q
0.99
0.97
0.98
1.00
3.04
1.07
1.06
1.03
3.01
f1 (ppm)

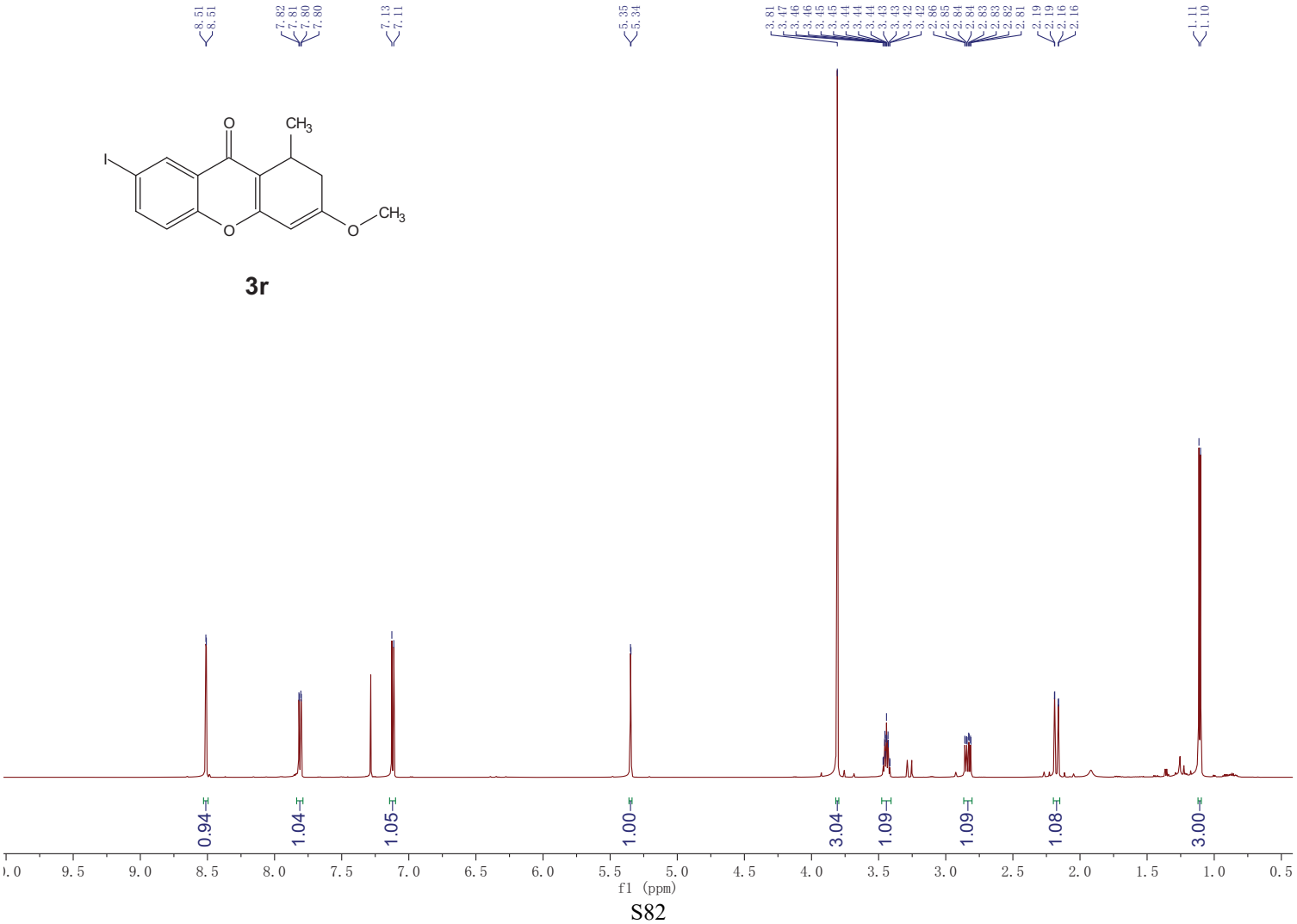

175.48
174.68
162.78
154.85
134.30
133.98
133.65
133.31
127.37
126.81
126.20
124.66
121.95
120.78
120.75
120.71
120.68
119.24
115.37
115.32
115.29
115.24
108.32
89.85
56.22
32.57
26.45
17.25
O
CH3
F
F
F
O
O
CH3
3q
f1 (ppm)

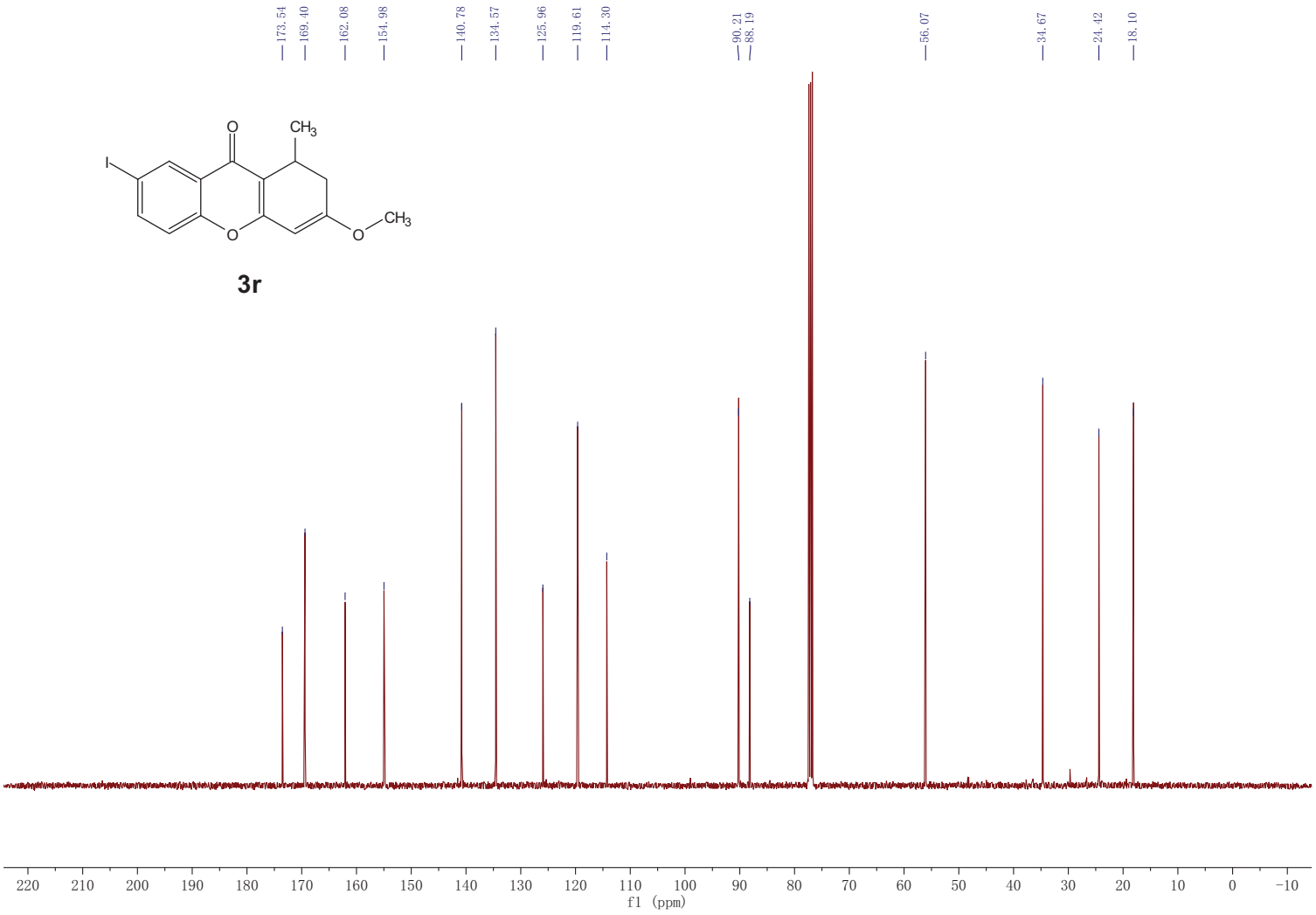
^{19}FNMR

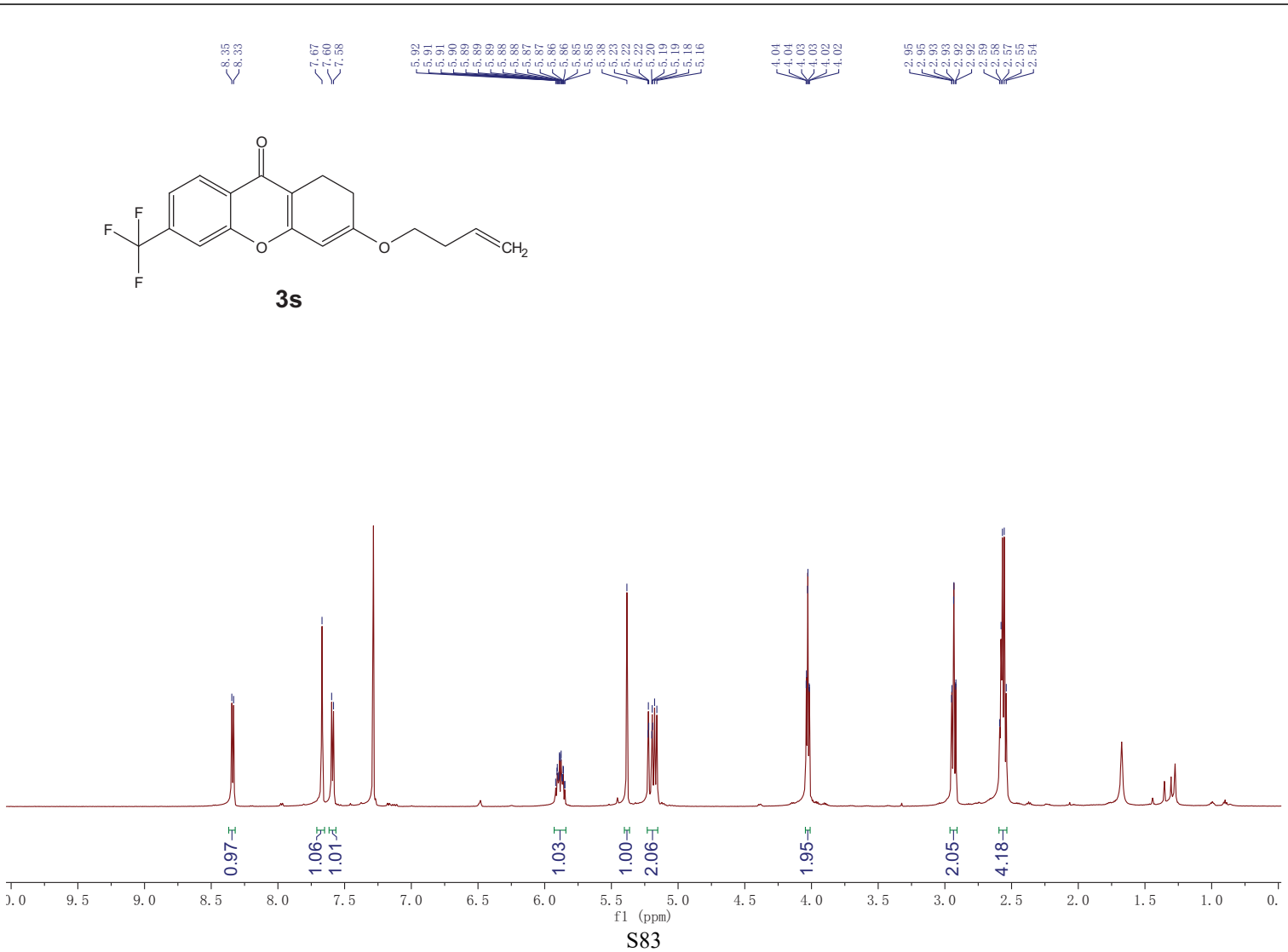
3q

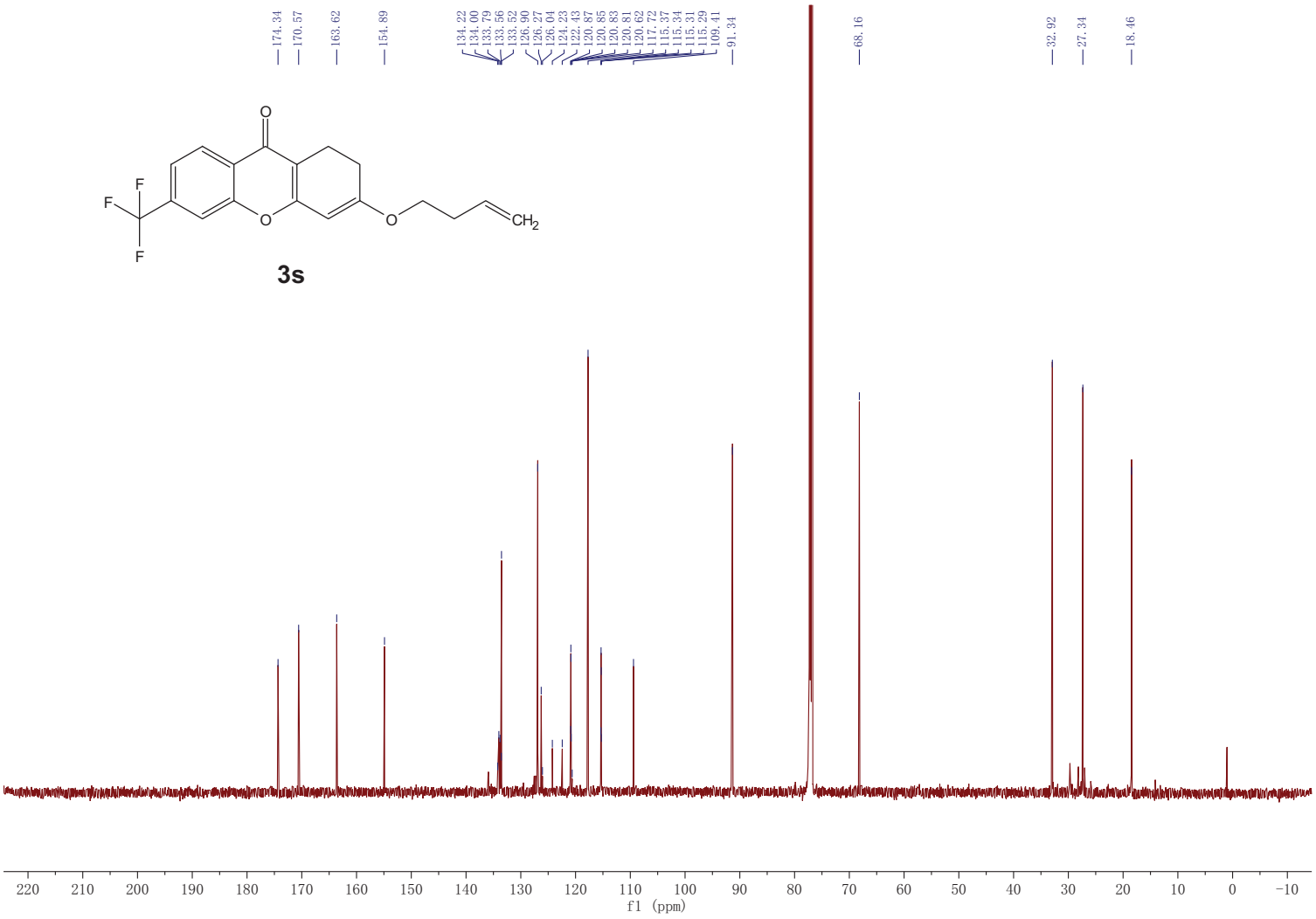

-62.90
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3r

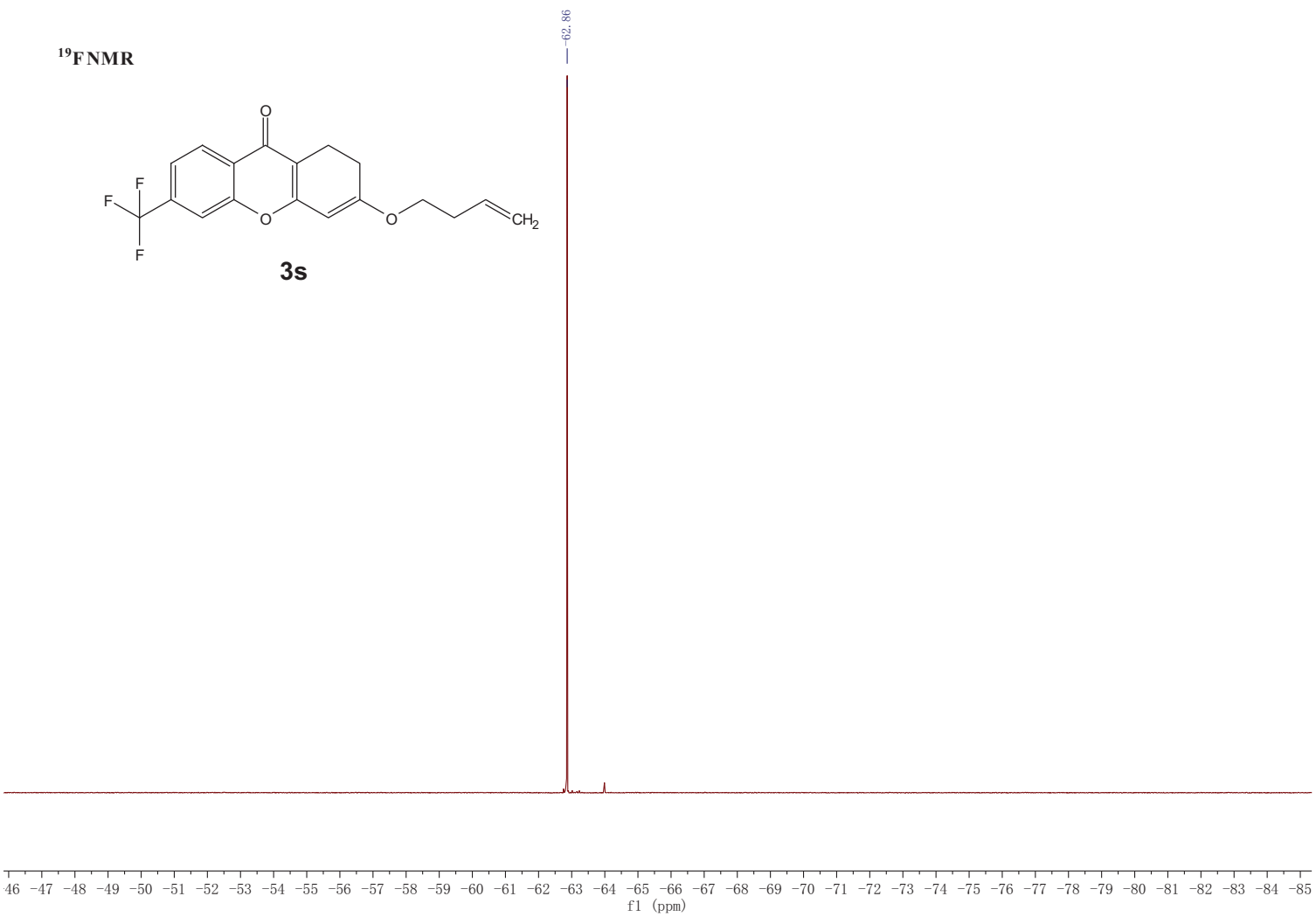

8.51
8.51
7.82
7.81
7.80
7.80
7.13
7.11
5.35
5.34
3.81
3.47
3.46
3.46
3.45
3.44
3.44
3.43
3.43
3.42
3.42
2.86
2.85
2.84
2.84
2.83
2.83
2.82
2.81
2.19
2.19
2.16
2.16
1.11
1.10
0.94
1.04
1.05
1.00
3.04
1.09
1.09
1.08
3.00
f1 (ppm)

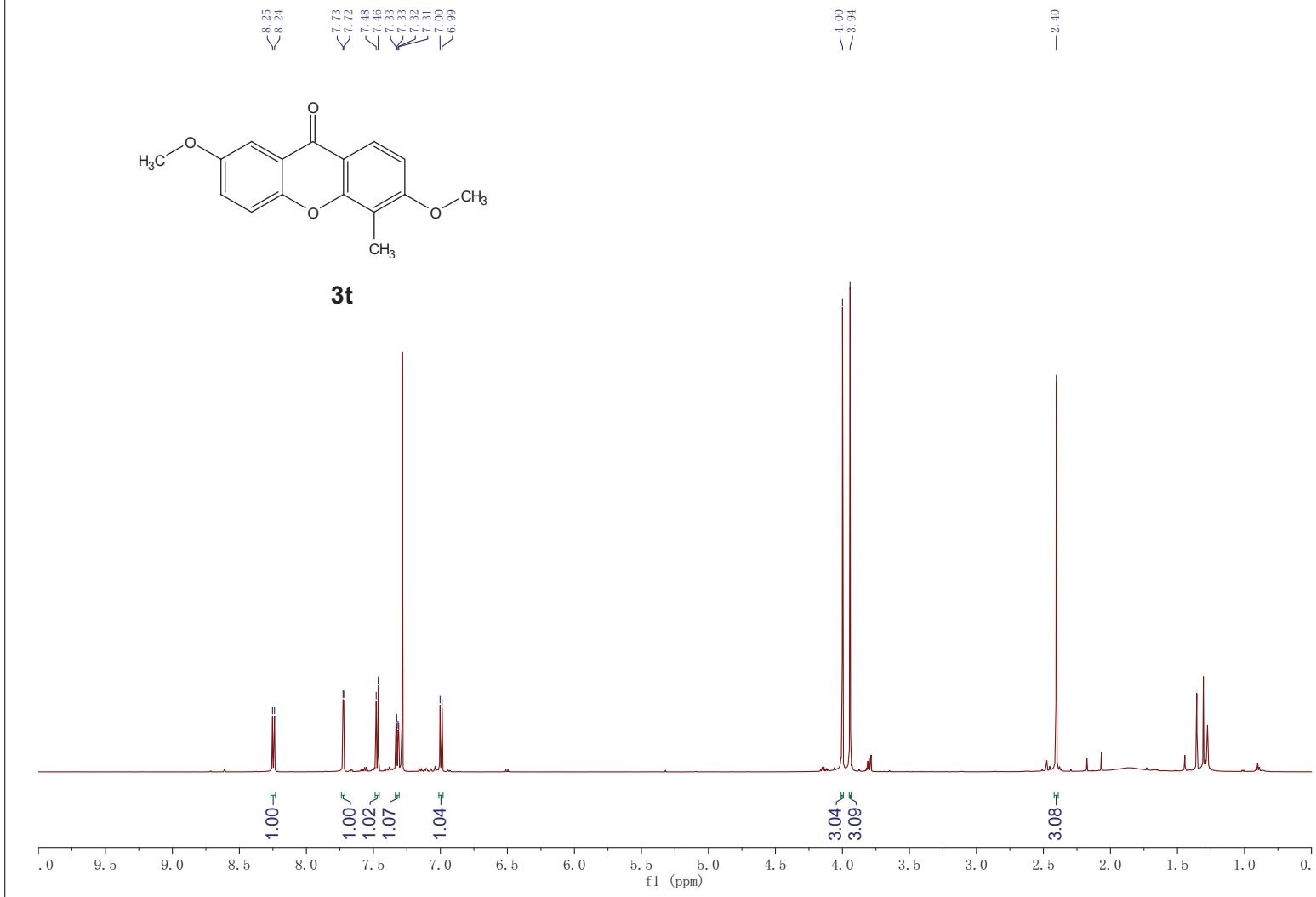

173.54
169.40
162.08
154.98
140.78
134.57
125.96
119.61
114.30
90.21
88.19
56.07
34.67
24.42
18.10
O
CH3
I
O
O
CH3
3r
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.35
8.33
7.67
7.60
7.58
5.92
5.91
5.91
5.90
5.89
5.89
5.88
5.88
5.87
5.87
5.86
5.86
5.85
5.85
5.38
5.23
5.22
5.22
5.20
5.19
5.19
5.18
5.16
4.04
4.04
4.03
4.03
4.02
4.02
2.95
2.95
2.93
2.93
2.92
2.92
2.59
2.58
2.57
2.55
2.54
O
F
F
F
O
O
CH2
3s
0.97
1.06
1.01
1.03
1.00
2.06
1.95
2.05
4.18
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.
f1 (ppm)

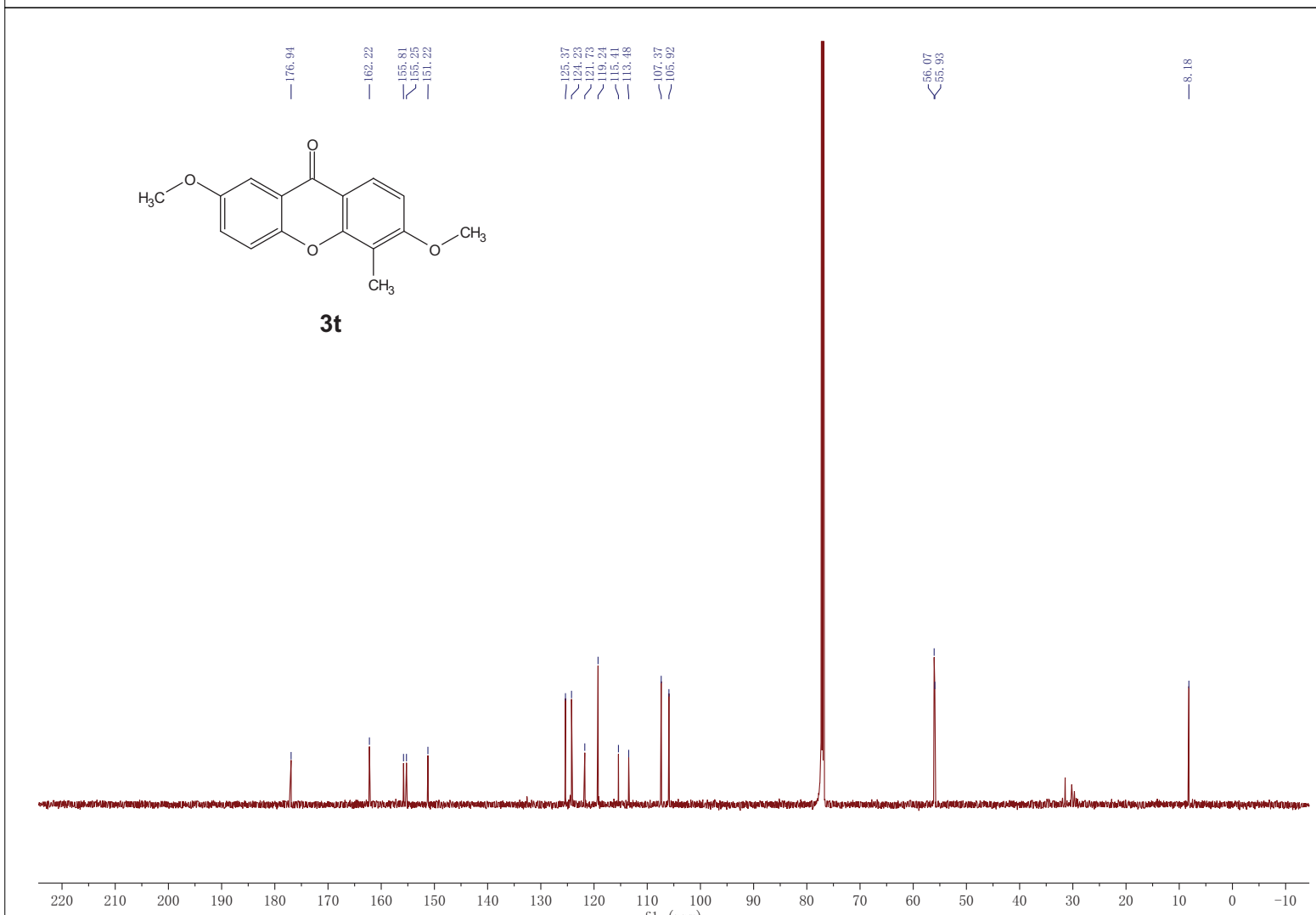

174.34
170.57
163.62
154.89
134.22
134.00
133.79
133.56
133.52
126.90
126.27
126.04
124.23
122.43
120.87
120.85
120.83
120.81
120.62
117.72
115.37
115.34
115.31
115.29
109.41
91.34
68.16
32.92
27.34
18.46
O
F
F
F
O
O
CH2
3s
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

^{19}FNMR

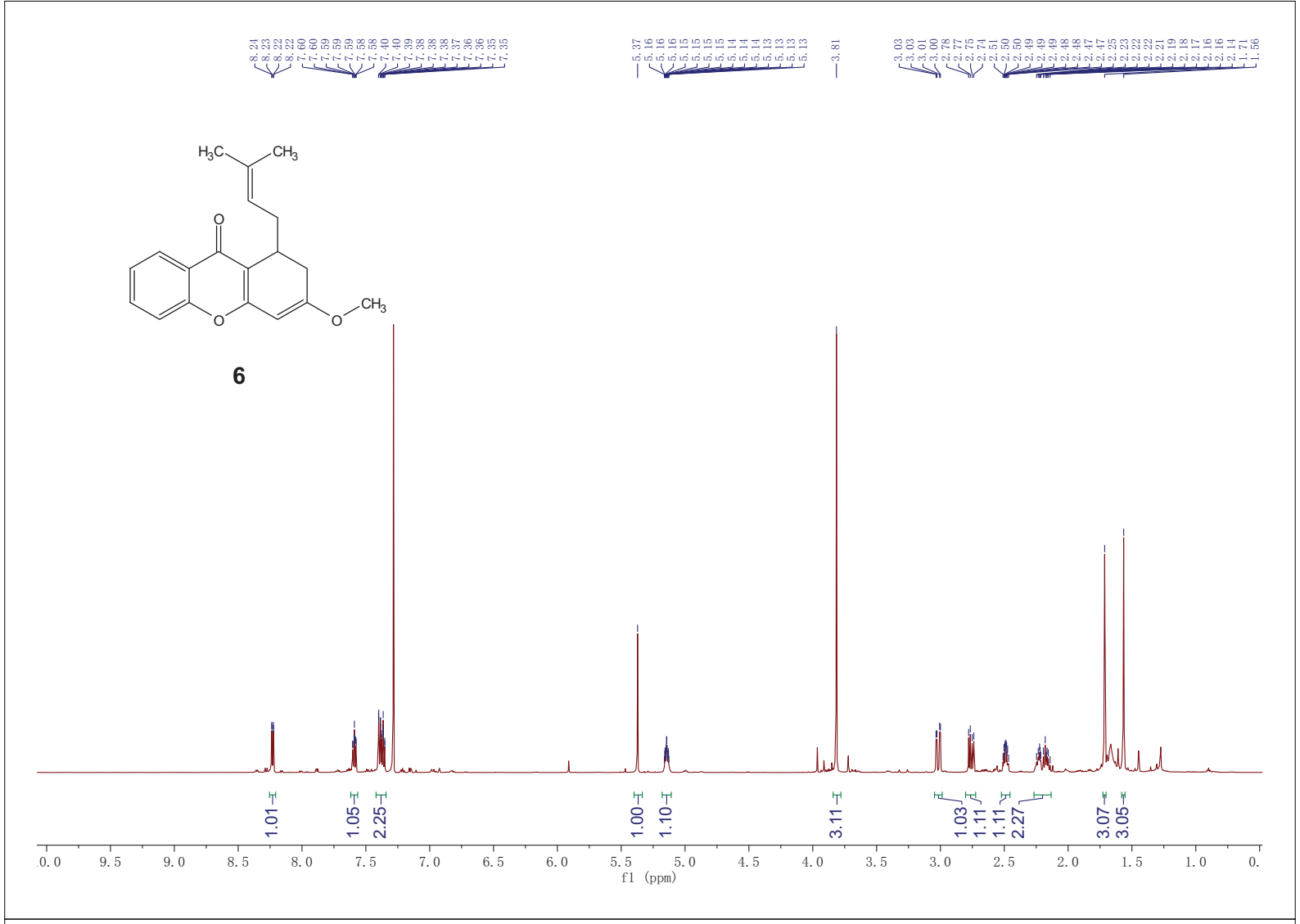

-62.86
O
F
F
F
O
O
CH2
3s
-46 -47 -48 -49 -50 -51 -52 -53 -54 -55 -56 -57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85
f1 (ppm)

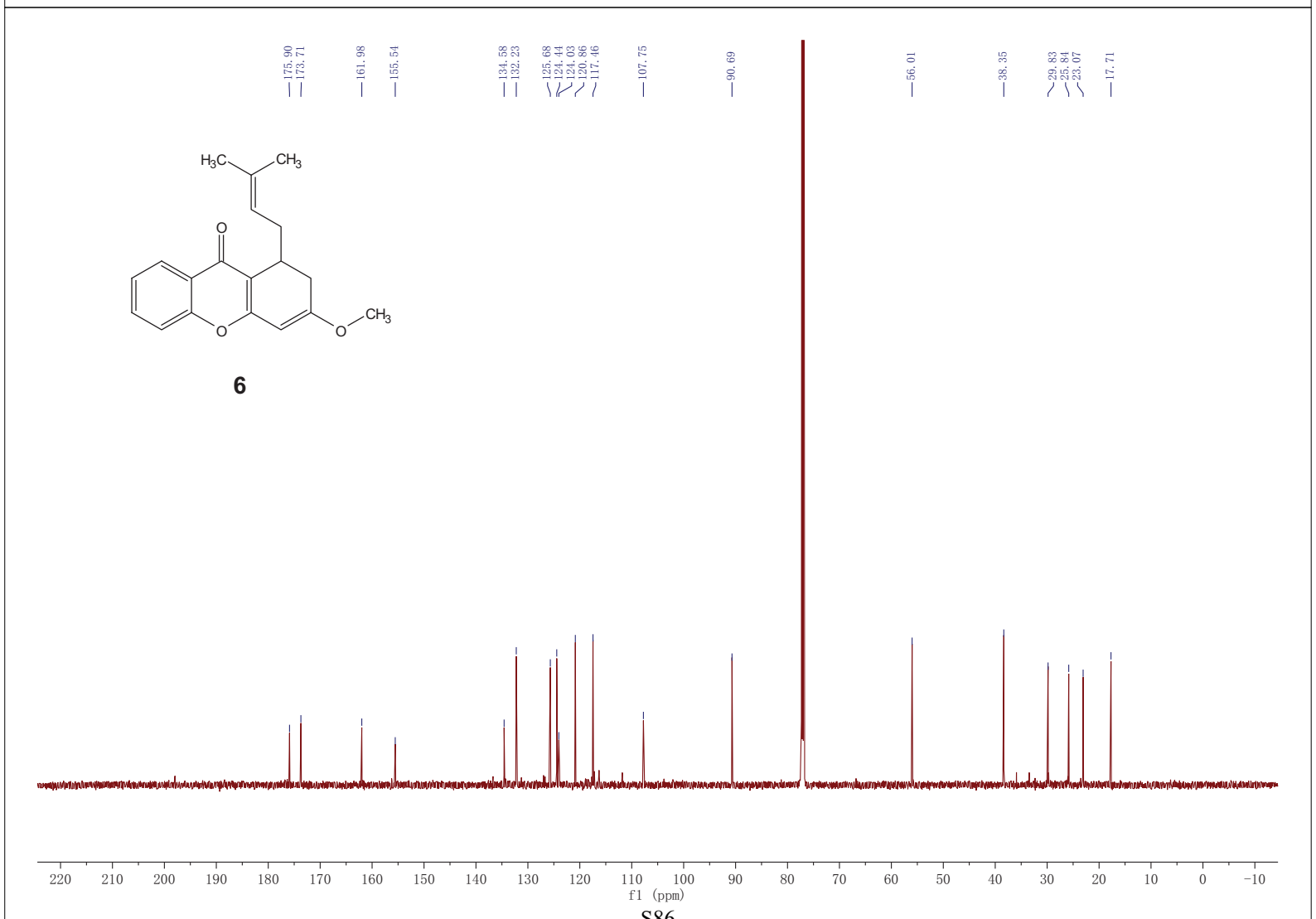

8.25
8.24
7.73
7.72
7.48
7.46
7.33
7.32
7.31
7.00
6.99
4.00
3.94
2.40
O
H3C
O
O
O
CH3
CH3
1.00
1.00
1.02
1.07
1.04
3.04
3.09
3.08
f1 (ppm)

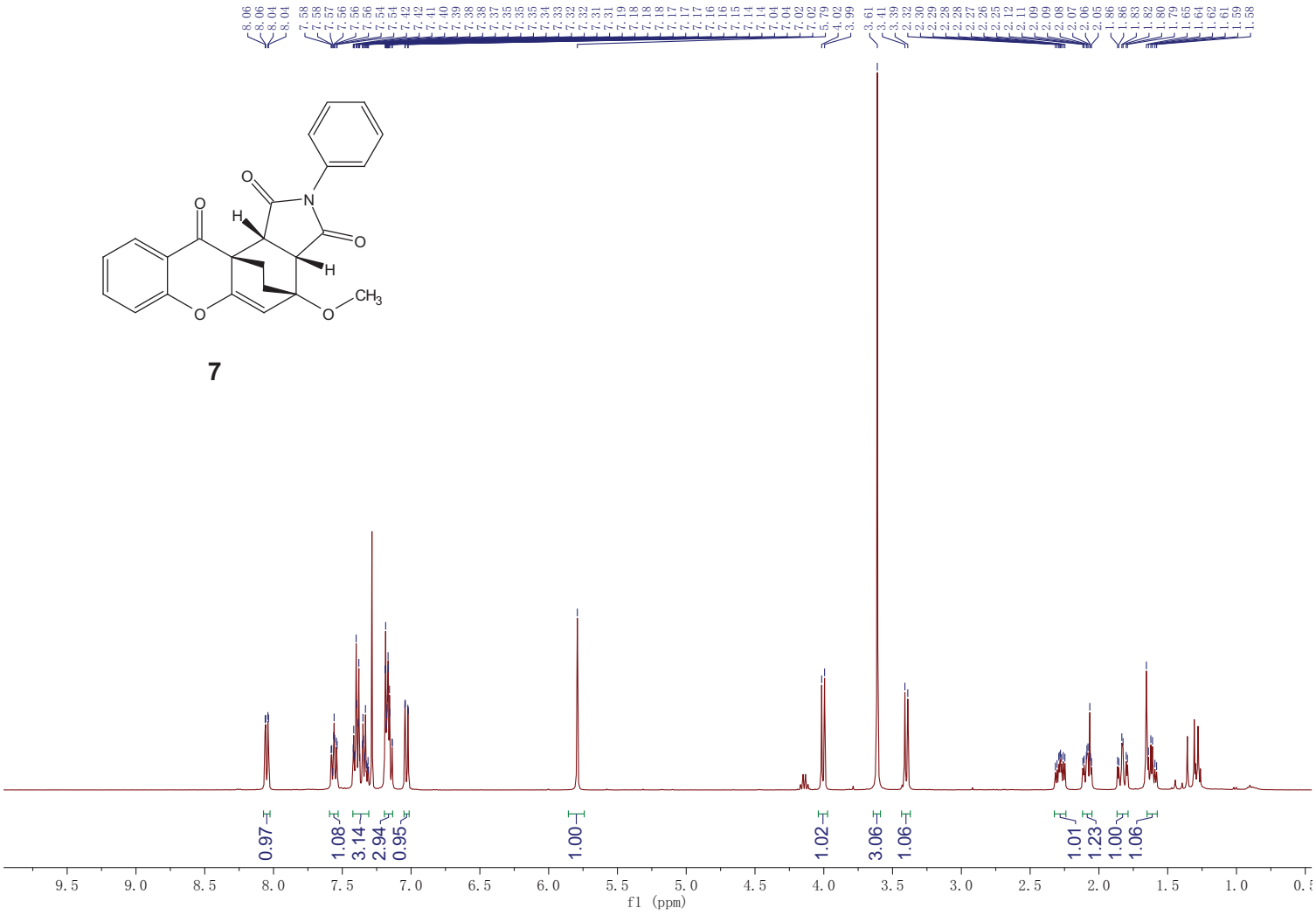
3t

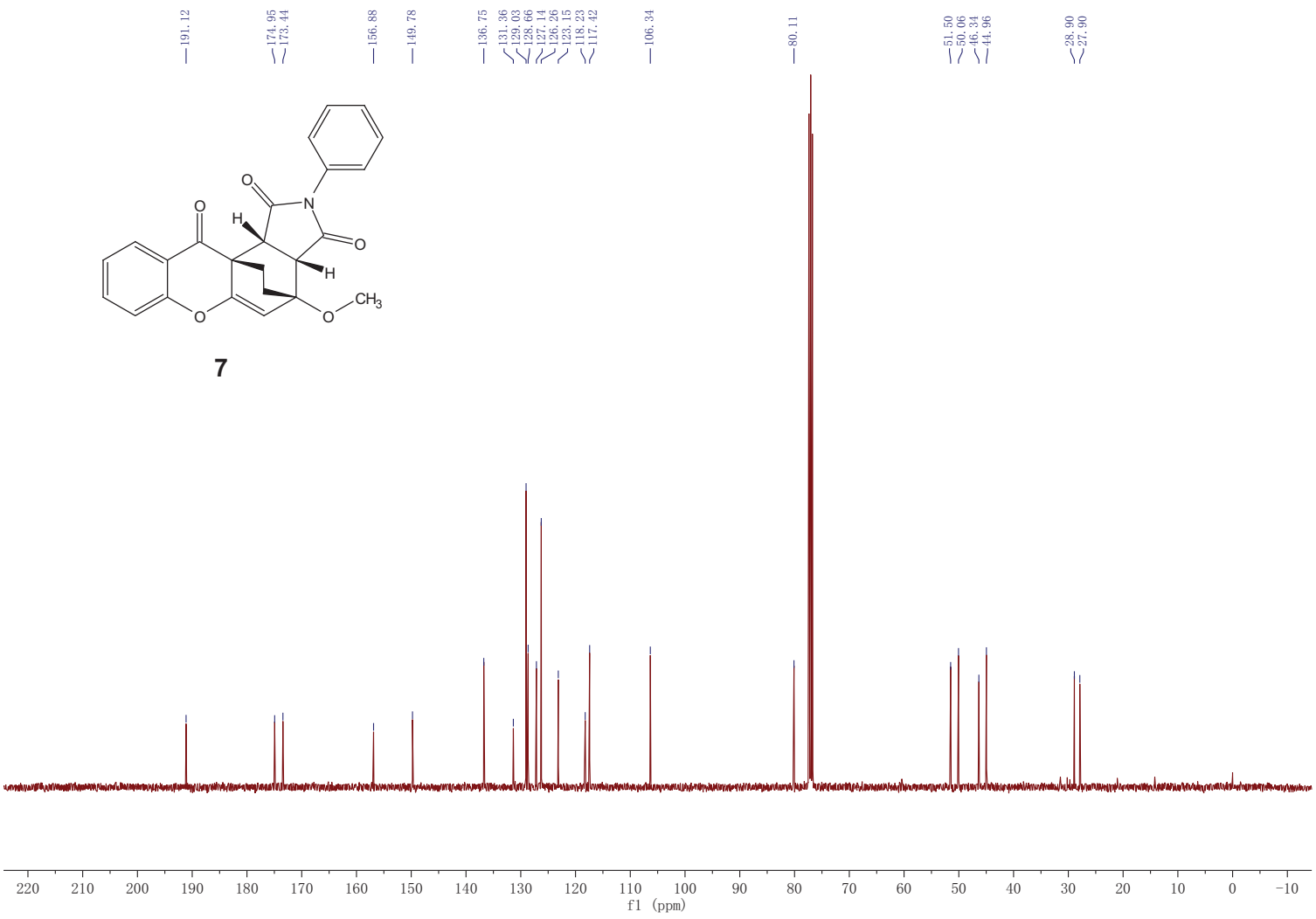

176.94
162.22
155.81
155.25
151.22
125.37
124.23
121.73
119.24
115.41
113.48
107.37
105.92
56.07
55.93
8.18
O
H3C
O
O
O
CH3
CH3
f1 (ppm)

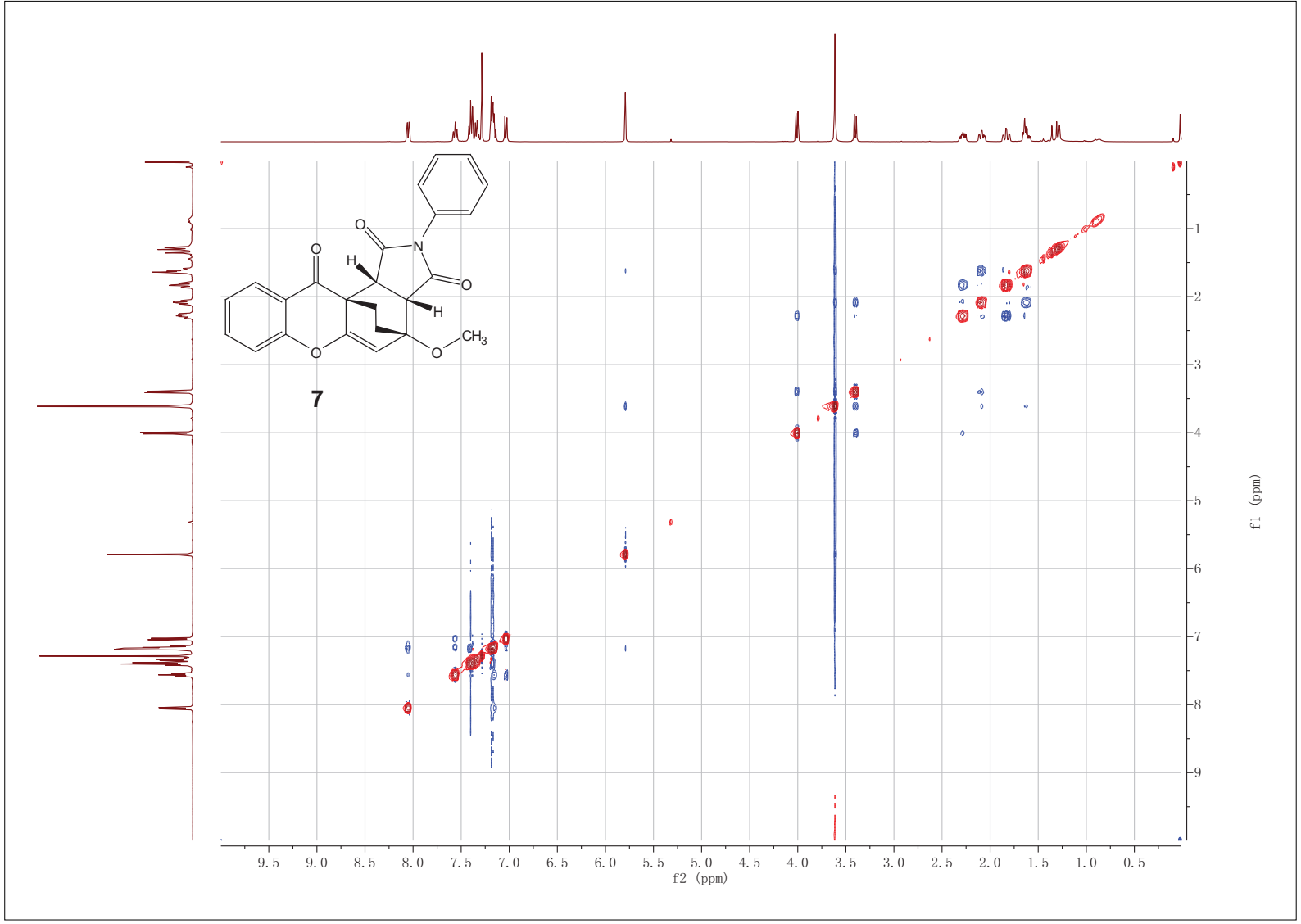
3t


8.24
8.23
8.22
8.22
7.60
7.60
7.59
7.59
7.59
7.58
7.58
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
5.37
5.16
5.16
5.15
5.15
5.15
5.15
5.14
5.14
5.13
5.13
5.13
5.13
3.81
3.03
3.03
3.01
3.00
2.78
2.77
2.75
2.74
2.51
2.50
2.50
2.49
2.49
2.48
2.48
2.47
2.25
2.23
2.22
2.22
2.21
2.19
2.18
2.17
2.16
2.16
2.14
1.71
1.56
H3C
CH3
O
O
O
CH3
6
1.01
1.05
2.25
1.00
1.10
3.11
1.03
1.11
1.11
2.27
3.07
3.05
f1 (ppm)


175.90
173.71
161.98
155.54
134.58
132.23
125.68
124.44
124.03
120.86
117.46
107.75
90.69
56.01
38.35
29.83
25.84
23.07
17.71
H3C
CH3
O
O
O
CH3
6
f1 (ppm)


8.06 8.06 8.04 8.04 7.58 7.58 7.57 7.56 7.56 7.56 7.54 7.54 7.42 7.42 7.41 7.40 7.39 7.38 7.38 7.37 7.35 7.35 7.34 7.33 7.32 7.32 7.31 7.31 7.19 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.15 7.14 7.14 7.04 7.04 7.02 7.02 5.79 4.02 3.99 3.61 3.41 3.39 3.32 2.30 2.29 2.28 2.28 2.27 2.26 2.25 2.12 2.11 2.09 2.09 2.08 2.07 2.06 2.05 1.86 1.86 1.83 1.82 1.80 1.79 1.65 1.64 1.62 1.61 1.59 1.58
O
N
O
H
O
H
O
CH3
O
7
0.97 1.08 3.14 2.94 0.95 1.00 1.02 3.06 1.06 1.01 1.23 1.00 1.06
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
f1 (ppm)


191.12
174.95 173.44
156.88
149.78
136.75
131.36 129.03 128.66 127.14 126.26 123.15 118.23 117.42
106.34
80.11
51.50 50.06 46.34 44.96
28.90 27.90
O
N
O
H
O
H
O
CH3
O
7
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
N
O
H
O
H
O
O
CH3
7
f2 (ppm)
f1 (ppm)