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Photochemical synthesis of 3-trifluoromethyl-2,3-dihydrobenzofuran-3-ols

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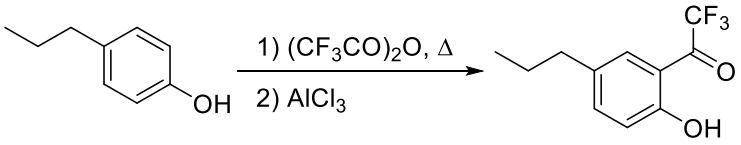
General

Commercially available reagents were used without additional purification. Compounds **1a**, **1b**, **1d-f** were synthesized according to literature.[S1–S3] E. Merck Kieselgel 60 was used for column chromatography.
Thin-layer chromatography (TLC) was performed on silica gel 60 F254 glass-backed plates (Merck). Visualization was performed using UV light (254 or 312 nm) or staining with $KMnO_4$.
NMR spectra were recorded on a Avance III 800 (with a 5-mm CPTXI cryoprobe) at 303 K and Bruker DPX 300. Chemical shifts were reported relative to residue peaks $CDCl_3$ (7.27 ppm for ^1H and 77.5 ppm for ^{13}C) or DMSO-d_6 (2.51 ppm for ^1H and 39.5 ppm for ^{13}C).
Melting points were measured on a SMP 30 apparatus without correction.
High-resolution mass spectra (HRMS) spectra were recorded on AB Sciex TripleTOF® 5600+ System using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage – 5500 V); mass range from *m/z* 50 to 3000; external or internal calibration was done with ESI Tuning Mix, Agilent. A syringe injection was used for solutions in acetonitrile, methanol, or water (flow rate 20 μl/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.
IUPAC compound names were generated using ChemDraw Software.
Photoinduced processes were performed on Evoluchem™ PhotoRedOx box. 365 nm (LG, HCK1012-01-006, 25 mW/cm^2) LED lamps from Evoluchem™ were used. This device is equipped with a fan to maintain room temperature during the irradiation process.

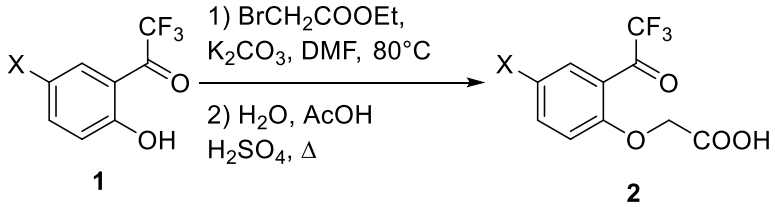
Synthesis of the starting material

2,2,2-Trifluoro-1-(2-hydroxy-5-propylphenyl)ethan-1-one (1c).



4-Propylphenol (4.08 g, 30 mmol) and $(CF_3CO)_2O$ (6.93 g, 33 mmol) were stirred at 100 °C on oil bath for 24 h. The resulted mixture was distilled *in vacuo* and then mixed with powdered $AlCl_3$ (6 g, 45 mmol) and stirred at 100 °C in oil bath in argon atmosphere for 24 h. Hydrochloric acid (10% aq, 50 mL) was added carefully to the resulted solids, the resulted mixture was extracted with CH_2Cl_2 (5×50 mL), the combined organic layers were washed with brine (3×50 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed *in vacuo*, and the residue was purified by flash-chromatography (eluent: mixture of hexane and EtOAc 100:1 v/v). Yield 1.53 g (22%), viscous yellowish oil. ^1H NMR (800 MHz, $CDCl_3$) δ ppm: 0.96 (t, *J*=7.3 Hz, 3H), 1.64 (sx, *J*=7.5 Hz, 2H), 2.58 (t, *J*=7.6 Hz, 2H), 7.02 (d, *J*=8.6 Hz, 1H), 7.47 (dd, *J*=8.6, 1.9 Hz, 1H), 7.58 (br. s., 1H), 10.95 (s, 1H). $^{13}C\{^1H\}$ NMR (201 MHz, $CDCl_3$) δ ppm: 13.5, 24.4, 37.0, 113.6, 116.5 (q, *J*=289.8 Hz), 118.8, 129.5 (q, *J*=3.7 Hz), 134.2, 139.7, 162.9, 184.3 (q, *J*=35.3 Hz). Found, m/z: 233.0782 $[M+H]^+$. $C_{11}H_{12}F_3O_2^+$. Calculated, m/z: 233.0784.

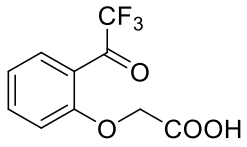
Synhtesis of 2-[2-(trifluoroacetyl)phenoxy]acetic acids 2.



General method
The corresponding phenol **1** (5 mmol), ethyl 2-bromoacetate (920 mg, 5.5 mmol) and K_2CO_3 (830 mg, 6 mmol) were dissolved in DMF (20 mL), and this was stirred at 80 °C for 24 h. To the resulting reaction mixture was added EtOAc (200 mL) and washed with brine (3×50 mL) and dried over anhydrous Na_2SO_4. The solvents were evaporated *in vacuo*, the residue was dissolved in a mixture of H_2O (10 mL), H_2SO_4 (3 mL) and CH_3COOH (15 mL) and refluxed for 4 h. To the resulting reaction mixture was added saturated NaCl solution (100 mL) and extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with brine (3×50 mL) and dried over anhydrous Na_2SO_4. All volatiles were removed *in*

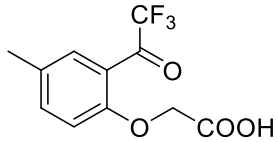
vacuo, and the residue was purified with flash-chromatography (eluent: mixture of hexane and EtOAc 100:1 v/v).

2-[2-(Trifluoroacetyl)phenoxy]acetic acid (2a).



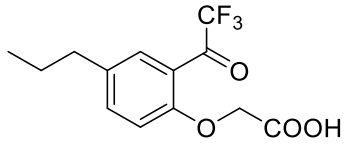
Yield 768 mg (62%), white powder, m.p. 100-102° C. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 4.78 (br. s., 2H), 7.02 (d, *J*=8.2 Hz, 1H), 7.23 (t, *J*=7.6 Hz, 1H), 7.69 (t, *J*=7.6 Hz, 1H), 7.89 (d, *J*=7.7 Hz, 1H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ ppm: 77.2, 113.9, 116.1 (q, *J*=291.5 Hz), 121.1, 122.3, 131.9, 136.4, 157.9, 181.8 (q, *J*=36.6 Hz). Found, m/z: 249.0374 $[M+H]^+$. $C_{10}H_8F_3O_4^+$. Calculated, m/z: 249.0369.

2-[4-Methyl-2-(trifluoroacetyl)phenoxy]acetic acid (2b).



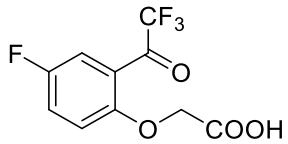
Yield 642 mg (49%), beige powder, m.p. 86-88° C. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 2.39 (s, 3H), 4.74 (br. s., 2H), 6.90 (d, *J*=8.2 Hz, 1H), 7.46 (d, *J*=7.9 Hz, 1H), 7.62 (br. s., 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm: 20.3, 77.2, 113.9, 116.1 (q, *J*=291.6 Hz), 121.0, 131.8 (q, *J*=2.2 Hz), 132.0, 136.9, 156.0, 182.0 (q, *J*=36.3 Hz). Found, m/z: 263.0531 $[M+H]^+$. $C_{11}H_{10}F_3O_4^+$. Calculated, m/z: 263.0526.

2-[4-Propyl-2-(trifluoroacetyl)phenoxy]acetic acid (2c).



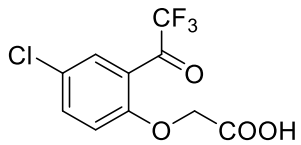
Yield 825 mg (57%), beige powder, m.p. 67-69° C. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 0.95 (t, *J*=7.3 Hz, 4H), 1.64 (sx, *J*=7.5 Hz, 2H), 2.60 (t, *J*=7.6 Hz, 2H), 4.74 (s, 2H), 6.91 (d, *J*=8.5 Hz, 1H), 7.44 (d, *J*=8.4 Hz, 1H), 7.58 (s, 1H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ ppm: 13.5, 24.3, 36.8, 66.1, 114.0 (q, *J*=4.8 Hz), 116.2 (q, *J*=291.3 Hz), 120.8, 131.4, 136.5, 136.9, 156.2, 171.4, 181.9 (q, *J*=36.0 Hz). Found, m/z: 289.0696 $[M-H]^-$. $C_{13}H_{12}F_3O_4^-$. Calculated, m/z: 289.0693.

2-(4-Fluoro-2-(2,2,2-trifluoroacetyl)phenoxy) acetic acid (2d).



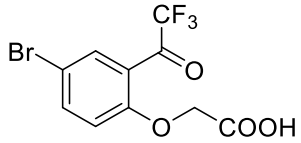
Yield 918 mg (69%), beige powder, m.p. 63-65° C. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 4.76 (br. s., 2H), 6.99 (br. s., 1H), 7.36 (br. s., 1H), 7.51 (d, *J*=6.2 Hz, 1H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ ppm: 77.2, 115.7 (d, *J*=3.3 Hz), 115.9 (q, *J*=291.0 Hz), 117.8 (d, *J*=25.0 Hz), 122.3 (d, *J*=3.2 Hz), 122.9 (d, *J*=22.9 Hz), 154.1, 156.9 (d, *J*=244.2 Hz), 181.1 (q, *J*=38.3 Hz). Found, m/z: 267.0276 $[M+H]^+$. $C_{10}H_7F_4O_4^+$. Calculated, m/z: 267.0275.

2-[4-Chloro-2-(trifluoroacetyl)phenoxy]acetic acid (2e).



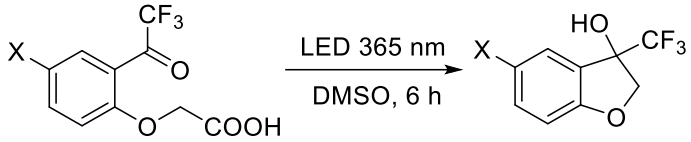
Yield 725 mg (52%), white powder, m.p. 71-73° C. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 4.78 (s, 2H), 6.95 (d, *J*=8.9 Hz, 1H), 7.61 (dd, *J*=8.9, 2.5 Hz, 1H), 7.77 (s, 1H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ ppm: 65.8, 115.1, 115.8 (q, *J*=290.9 Hz), 123.0, 127.7, 131.1, 135.6 (q, *J*=4.4 Hz), 156.1, 172.0, 181.3 (q, *J*=37.4 Hz). Found, m/z: 280.9838 $[M+H]^+$. $C_{10}H_5ClF_3O_4^+$. Calculated, m/z: 280.9834.

2-[4-Bromo-2-(trifluoroacetyl)phenoxy]acetic acid (2f).



Yield 732 mg (45%), beige powder, m.p. 85-87° C. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 4.77 (s, 2H), 6.88 (d, *J*=8.9 Hz, 1H), 7.73 (dd, *J*=8.9, 2.4 Hz, 1H), 7.87 (d, *J*=1.2 Hz, 1H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ ppm: 65.8, 114.6, 115.8 (q, *J*=290.9 Hz), 123.3, 134.0, 138.5, 156.6, 171.7, 181.2 (q, *J*=37.4 Hz). Found, m/z: 324.9323 $[M-H]^-$. $C_{10}H_5BrF_3O_4^-$. Calculated, m/z: 324.9329.

Synthesis of 3-trifluoromethyl-2,3-dihydrobenzofuran-3-ols 3

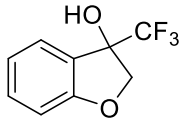


2 **3**

General method

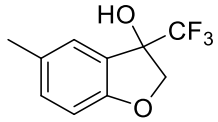
Corresponding compound **2** (1.0 mmol) was dissolved in freshly distilled DMSO (20 mL) in a Schlenk vessel. The mixtures were degassed under vacuum and filled with argon three times. The obtained solutions were irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box with stirring. The progress of the reaction was monitored by TLC and ^{1}H NMR. After the reaction completion (six hours or less was sufficient in all cases), reaction mixtures were dissolved in EtOAc (200 mL), washed with saturated KCl solution (10×30 mL) and dried over Na_2SO_4. All volatiles were removed in vacuo. At this stage the residue was fairly pure product.

3-Trifluoromethyl-2,3-dihydrobenzofuran-3-ol (3a).



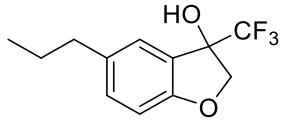
Yield 191 mg (94%), viscous yellowish oil. ^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 4.42 (dd, *J*=10.9, 1.4 Hz, 1H), 4.73 (d, *J*=10.8 Hz, 1H), 6.95 (d, *J*=8.2 Hz, 1H), 7.01 (td, *J*=7.5, 0.8 Hz, 1H), 7.24 (s, 1H), 7.37 (td, *J*=7.8, 1.4 Hz, 1H), 7.43 (d, *J*=7.5 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 77.2 (q, *J*=1.2 Hz, C1), 79.7 (q, *J*=30.2 Hz, C2), 110.2 (C7), 120.8 (C5), 123.9 (C3), 125.01 (C4), 125.02 (q, *J*=283.8 Hz, CF_3), 131.4 (C6), 160.4 (C8). ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm: -81.7 (s). Found, m/z: 205.0468 $[M+H]^+$. $C_9H_8F_3O_2^+$. Calculated, m/z: 205.0471.

5-Methyl-3-trifluoromethyl-2,3-dihydrobenzofuran-3-ol (3b).



Yield 203 mg (93%), viscous yellowish oil. ^{1}H NMR (800 MHz, DMSO-d_6) δ ppm: 2.28 (s, 3H), 4.39 (d, *J*=11.7 Hz, 1H), 4.69 (d, *J*=10.8 Hz, 1H), 6.83 (d, *J*=8.2 Hz, 1H), 7.14 - 7.20 (m, 2H), 7.22 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6) δ ppm: 20.0 (CH_3), 77.3 (C1), 79.8 (q, *J*=30.1 Hz, C2), 109.8 (C7), 125.02 (C4), 125.03 (q, *J*=283.9 Hz, CF_3), 129.8 (C6), 131.9 (C5), 158.4 (C8). ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm: -81.6 (s). Found, m/z: 219.0620 $[M+H]^+$. $C_{10}H_{10}F_3O_2^+$. Calculated, m/z: 219.0627.

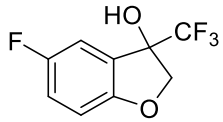
5-Propyl-3-trifluoromethyl-2,3-dihydrobenzofuran-3-ol (3c).



Yield 220 mg (90%), viscous yellowish oil. ^{1}H NMR (800 MHz, $CDCl_3$) δ ppm: 0.95 (t, *J*=7.2 Hz, 3H), 1.60 - 1.66 (m, 2H), 2.54 - 2.60 (m, 2H), 4.52 (d, *J*=10.7 Hz, 1H), 4.74 (d, *J*=10.8 Hz, 1H), 6.84 (d, *J*=8.3

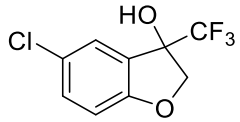
Hz, 1H), 7.18 (d, *J*=8.3 Hz, 1H), 7.24 – 7.28 (m, 2H, intersect with $CHCl_3$) $^{13}C\{^1H\}$ NMR (201 MHz, DMSO-d_6) δ ppm: 13.4 (CH_3), 24.4 ($\underline{C}H_2CH_3$), 36.5 (Ar$\underline{C}H_2$), 77.5 (C1), 79.9 (q, *J*=30.1 Hz, C2), 110.1 (C7), 123.9 (C3), 124.7 (C4), 125.2 (q, *J*=283.8 Hz, CF_3), 131.6 (C6), 134.9 (C5), 158.7 (C8). ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm: -81.6 (s). Found, m/z: 247.0944 $[M+H]^+$. $C_{12}H_{14}F_3O_2^+$. Calculated, m/z: 247.0940.

5-Fluoro-3-trifluoromethyl-2,3-dihydrobenzofuran-3-ol (3d).



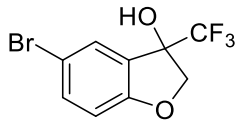
Yield 180 mg (81%), viscous yellowish oil. ^1H NMR (800 MHz, DMSO-d_6) δ ppm: 4.46 (dd, *J*=11.0, 1.4 Hz, 1H), 4.78 (d, *J*=11.0 Hz, 1H), 6.98 (dd, *J*=8.8, 4.0 Hz, 1H), 7.19 - 7.25 (m, 2H), 7.40 (s, 1H). $^{13}C\{^1H\}$ NMR (201 MHz, DMSO-d_6) δ ppm: 78.0 (C1), 79.8 (q, *J*=31.2 Hz, C2), 111.5 (d, *J*=8.5 Hz, C7), 111.8 (d, *J*=25.2 Hz, C4), 118.5 (d, *J*=24.4 Hz, C6), 124.9 (q, *J*=283.9 Hz, CF_3), 125.1 (d, *J*=8.5 Hz, C3), 156.7 (C8), 156.6 (d, *J*=236.7 Hz, C5). ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm: -125.2 (s), -81.8 (s). Found, m/z: 223.0967 $[M+H]^+$. $C_9H_7F_4O_2^+$. Calculated, m/z: 223.0377.

5-Chloro-3-trifluoromethyl-2,3-dihydrobenzofuran-3-ol (3e).



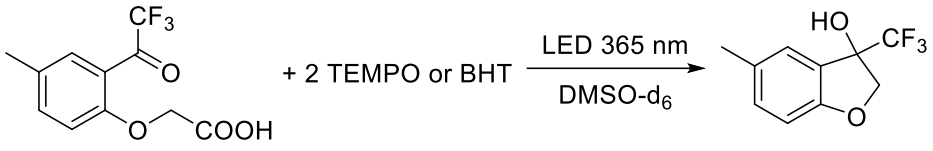
Yield 222 mg (94%), viscous yellowish oil. ^1H NMR (800 MHz, DMSO-d_6) δ ppm: 4.40 - 4.54 (m, 1H), 4.80 (d, *J*=11.0 Hz, 1H), 7.01 (d, *J*=8.6 Hz, 1H), 7.39 - 7.41 (m, 1H), 7.42 - 7.45 (m, 2H). $^{13}C\{^1H\}$ NMR (201 MHz, DMSO-d_6) δ ppm: 78.0 (C1), 79.6 (q, *J*=30.2, C2), 112.3 (C7), 124.6 (C4), 124.86 (q, *J*=284.0, CF_3) 124.93 (C5), 126.0 (C3), 131.7 (C6), 159.3 (C8). ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm: -81.8 (s). Found, m/z: 236.9935 $[M-H]^-$. $C_9H_5ClF_3O_2^-$. Calculated, m/z: 236.9936.

5-Bromo-3-trifluoromethyl-2,3-dihydrobenzofuran-3-ol (3f).



Yield 246 mg (88%), viscous yellowish oil. ^1H NMR (800 MHz, DMSO-d_6) δ ppm: 4.47 (dd, *J*=11.0, 0.9 Hz, 1H), 4.79 (d, *J*=11.0 Hz, 1H), 6.97 (d, *J*=8.6 Hz, 1H), 7.43 (s, 1H), 7.52 (d, *J*=1.6 Hz, 1H), 7.55 (dd, *J*=8.6, 2.2 Hz, 1H). $^{13}C\{^1H\}$ NMR (201 MHz, DMSO-d_6) δ ppm: 78.0 (C1), 79.6 (q, *J*=30.4 Hz, C2) 111.9 (C5), 112.9 (C7), 124.9 (q, *J*=283.8 Hz, CF_3), 126.5 (C3), 127.8 (C4), 134.5 (C6), 159.8 (C8). ^{19}F NMR (282 MHz, DMSO-d_6) δ ppm: -81.7 (s). Found, m/z: 280.9433 $[M-H]^-$. $C_9H_5BrF_3O_2^-$. Calculated, m/z: 280.9431.

Experiments with radical quenching reagents



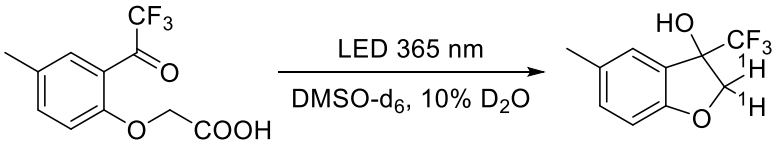
2b **3b**

Compound **2b** (23 mg, 0.09 mmol) was dissolved in 3 mL of DMSO-d_6 in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, parts of the solution (0.65 mL) were transferred to three argon-filled NMR tubes and sealed. (2,2,6,6-Tetramethylpiperidin-1-yl)oxidanyl (TEMPO, 6 mg, 0.04 mmol) was added to one tube, butylated hydroxytoluene (BHT, 8 mg, 0.04 mmol) was added to the second, and the last tube was used without additives. NMR tubes with these solutions were sealed and irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. The mixtures were analyzed by ^{1}H NMR. Results presented in Table S1.

Table S1.

Time, min	Conversion, %		
	from pure **2b**	TEMPO added	BHT added
30	78	75	79
60	100	100	100

Experiment with D_2O



2b **3b**

Compound **2b** (8 mg, 0.03 mmol) was dissolved in DMSO-d_6 (1 mL) in a Schlenk vessel. The mixture was degassed under vacuum and filled with argon three times. Next, part of the solution (0.65 mL) was transferred to argon-filled NMR tube and sealed. Deuterium oxide (65 μL) was added to the NMR tube. Then this tube was sealed and irradiated with 365 nm LED lamp in Evoluchem™ PhotoRedOx box. The mixture was analyzed by ^{1}H NMR.

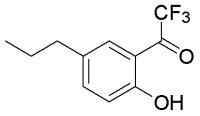
References

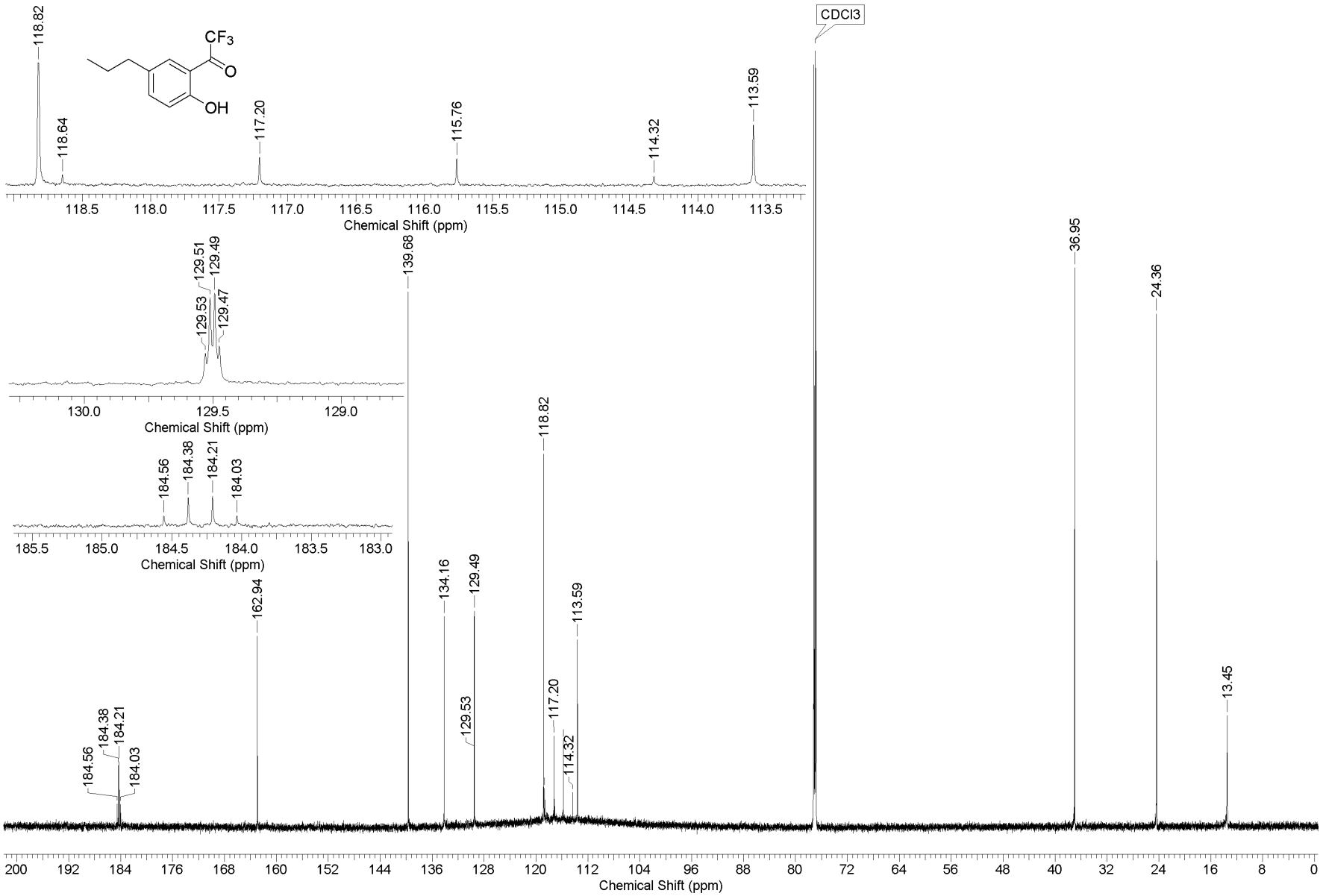
[S1] D. V. Sevenard, M. Vorobyev, V. Y. Sosnovskikh; H. Wessel, O. Kazakova, V. Vogel, N. E. Shevchenko, V. G. Nenajdenko, E. Lork, G.-V. Röschenthaler, *Tetrahedron*, 2009, **65**, 7538; https://doi.org/10.1016/j.tet.2009.06.122.

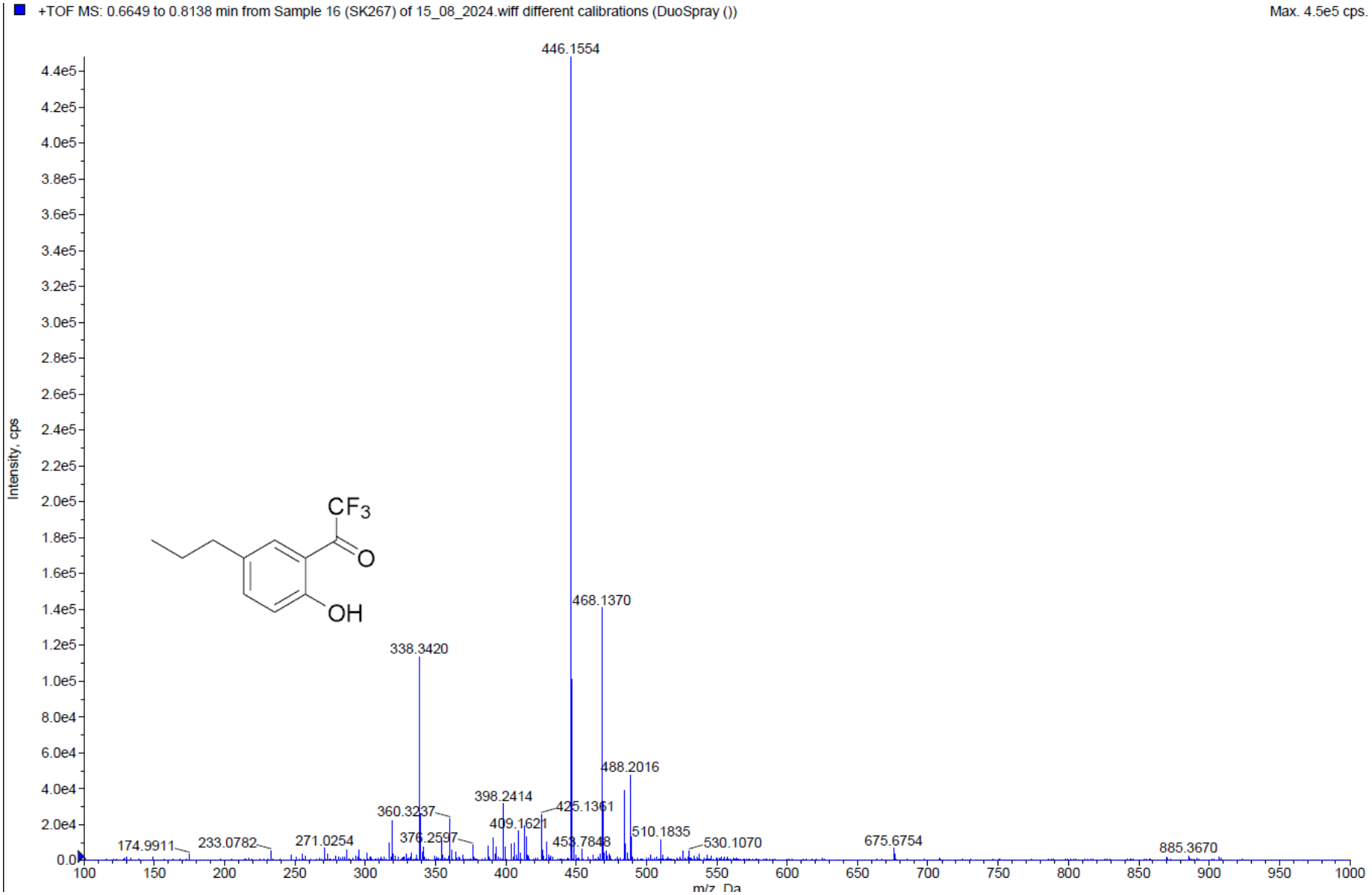
[S2] A. F. Shidlovskii, A. S. Golubev, D. V. Gusev, K. Yu. Suponitsky, A. S. Peregudov and N. D. Chkanikov, *J. Fluorine Chem.*, 2012, **143**, 272; https://doi.org/10.1016/j.jfluchem.2012.07.002.

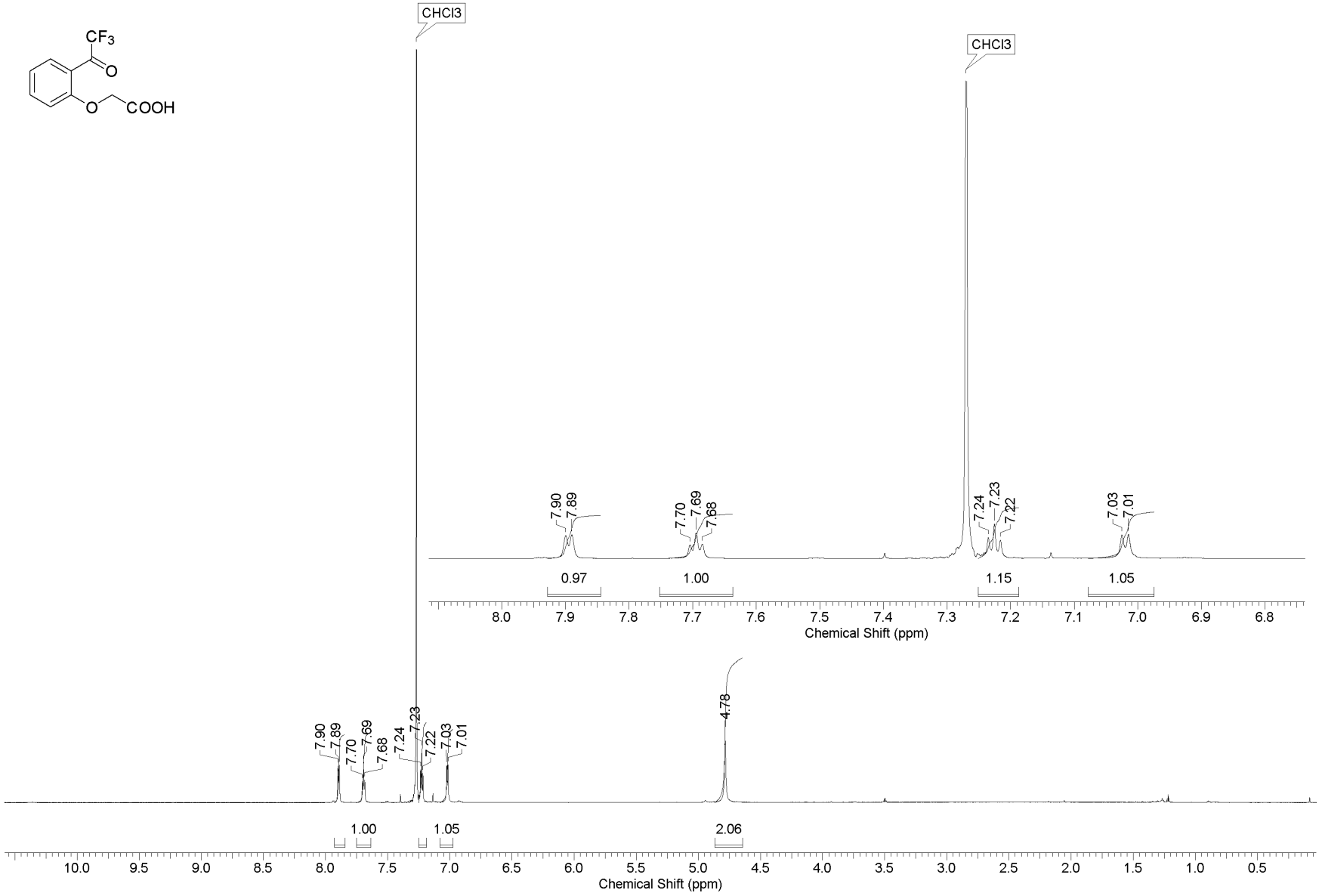
[S3] A. S. Golubev, P. N. Ostapchuk, T. V. Strelkova, N. D. Kagramanov, K. Yu. Suponitsky, R. U. Takazova and N. D. Chkanikov, *Org. Biomol. Chem.*, 2022, **20**, 6809; https://doi.org/10.1039/D2OB01177H.

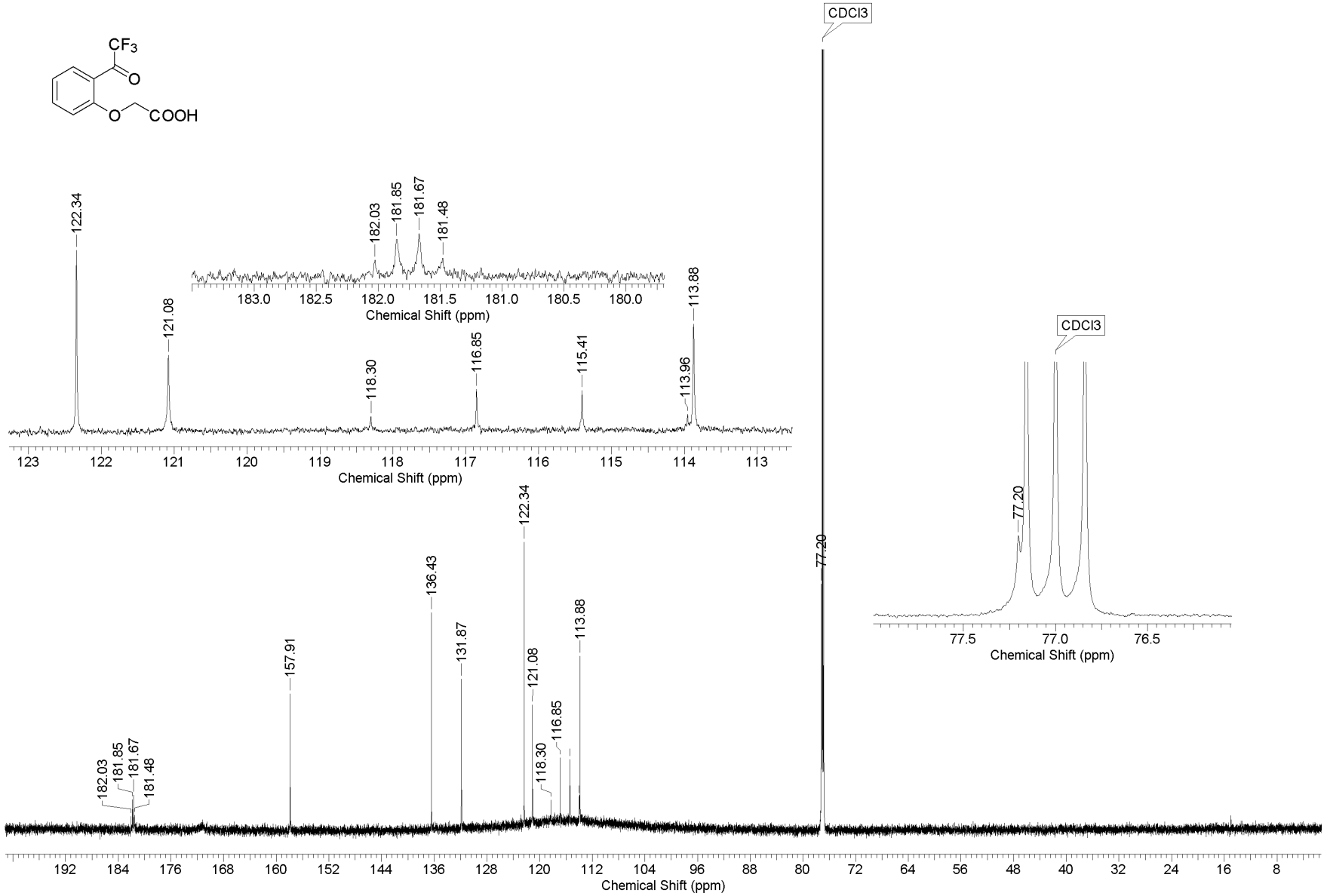
Copies of NMR spectra

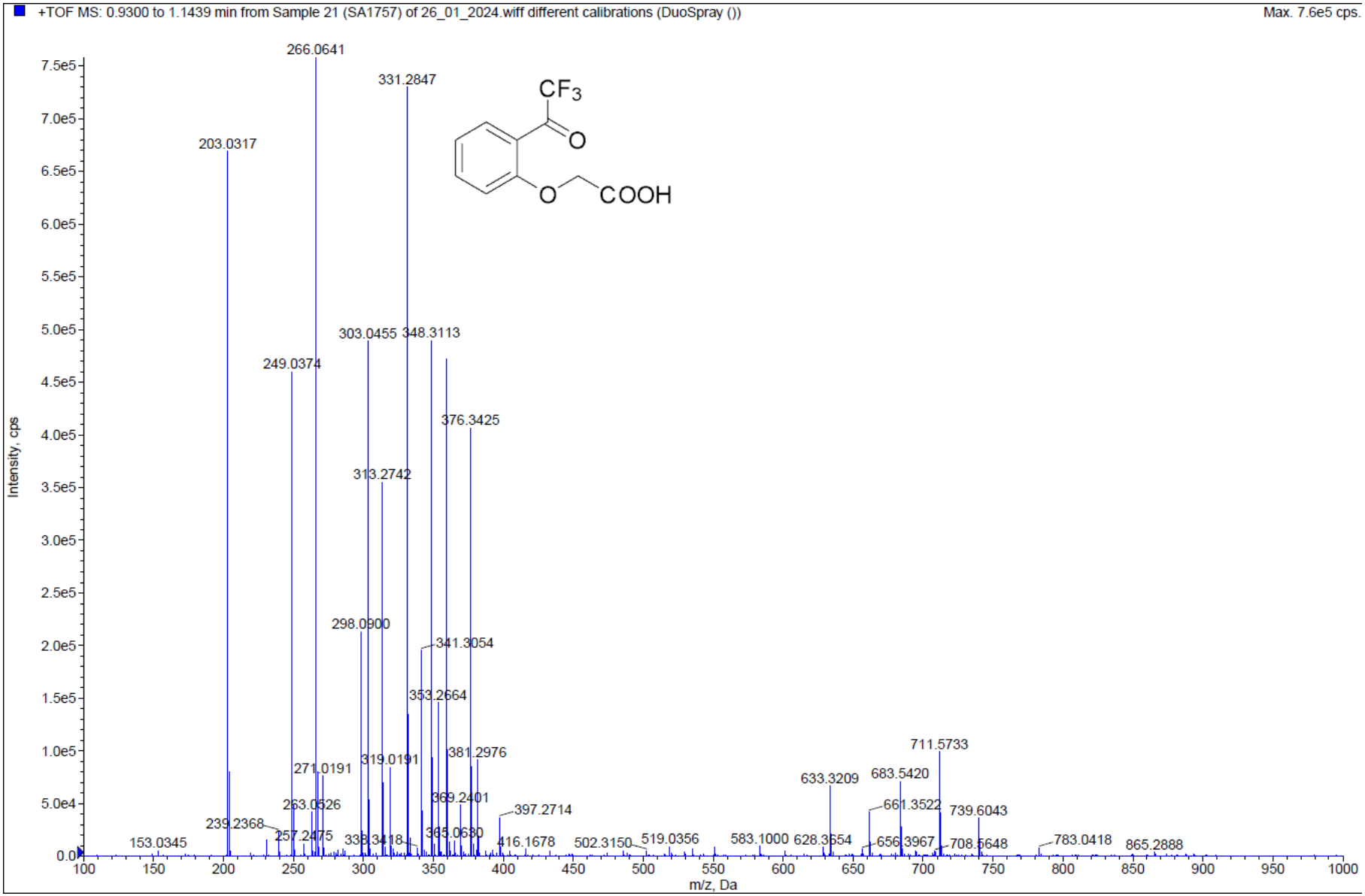


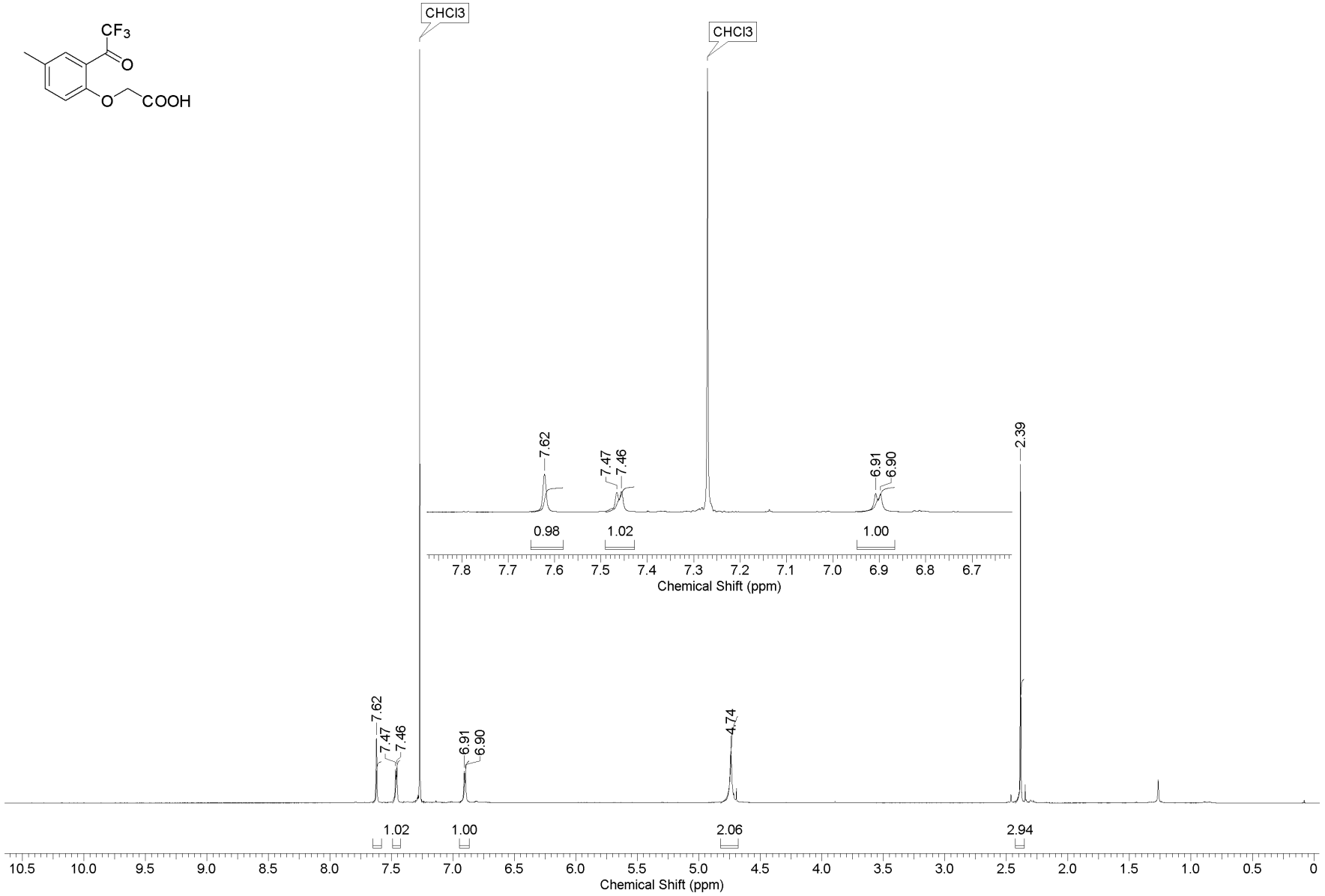

CDCl3
118.82
118.64
117.20
115.76
114.32
113.59
36.95
24.36
13.45
139.68
134.16
129.49
129.53
118.82
117.20
114.32
113.59
162.94
184.56
184.38
184.21
184.03
129.51
129.49
129.53
129.47
CF3
O
OH
Chemical Shift (ppm)

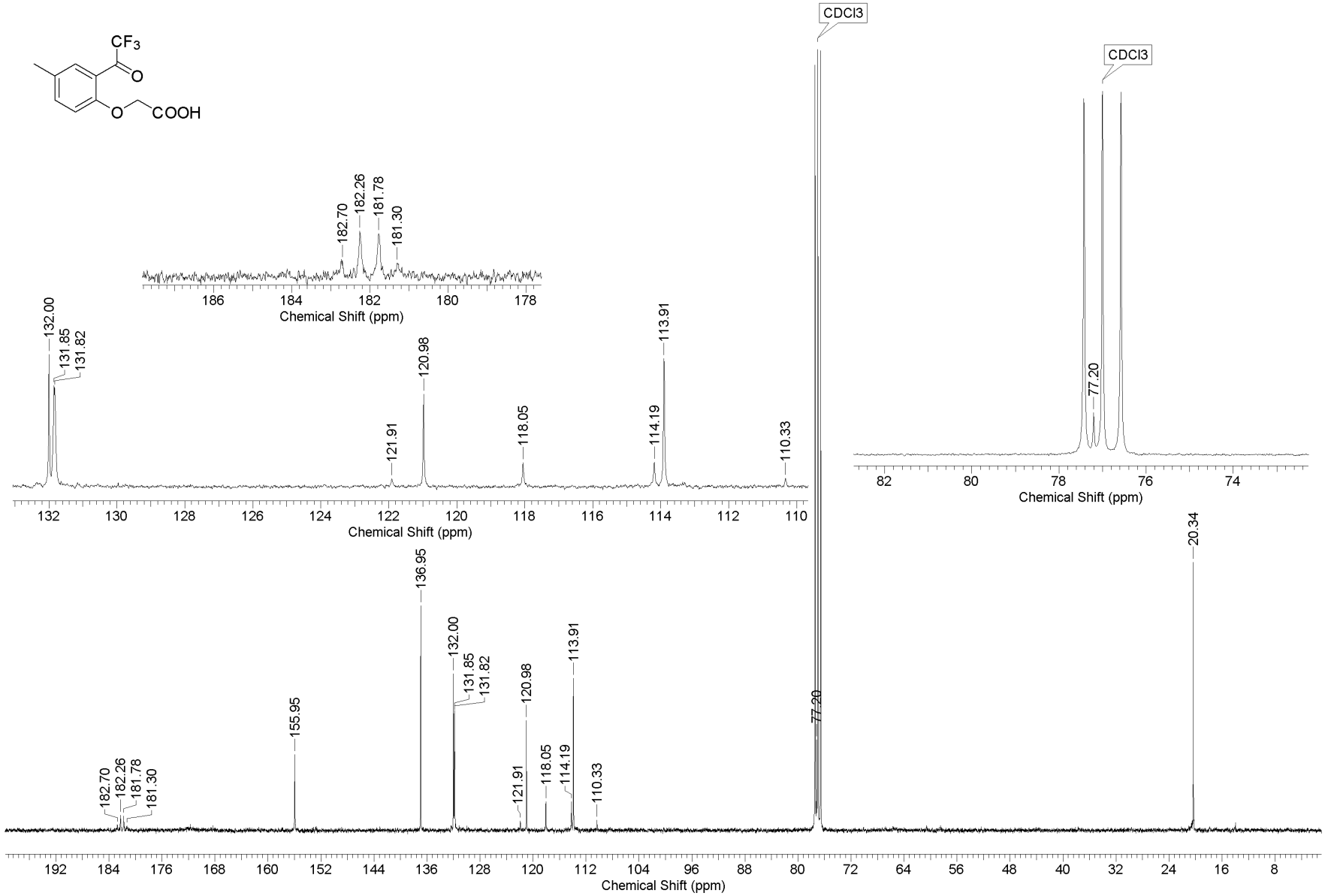

+TOF MS: 0.6649 to 0.8138 min from Sample 16 (SK267) of 15_08_2024.wiff different calibrations (DuoSpray ())
Max. 4.5e5 cps.
Intensity, cps
m/z, Da
446.1554
468.1370
338.3420
488.2016
398.2414
425.1361
360.3237
409.1621
376.2597
453.7848
510.1835
530.1070
675.6754
885.3670
174.9911
233.0782
271.0254
CF3
O
OH

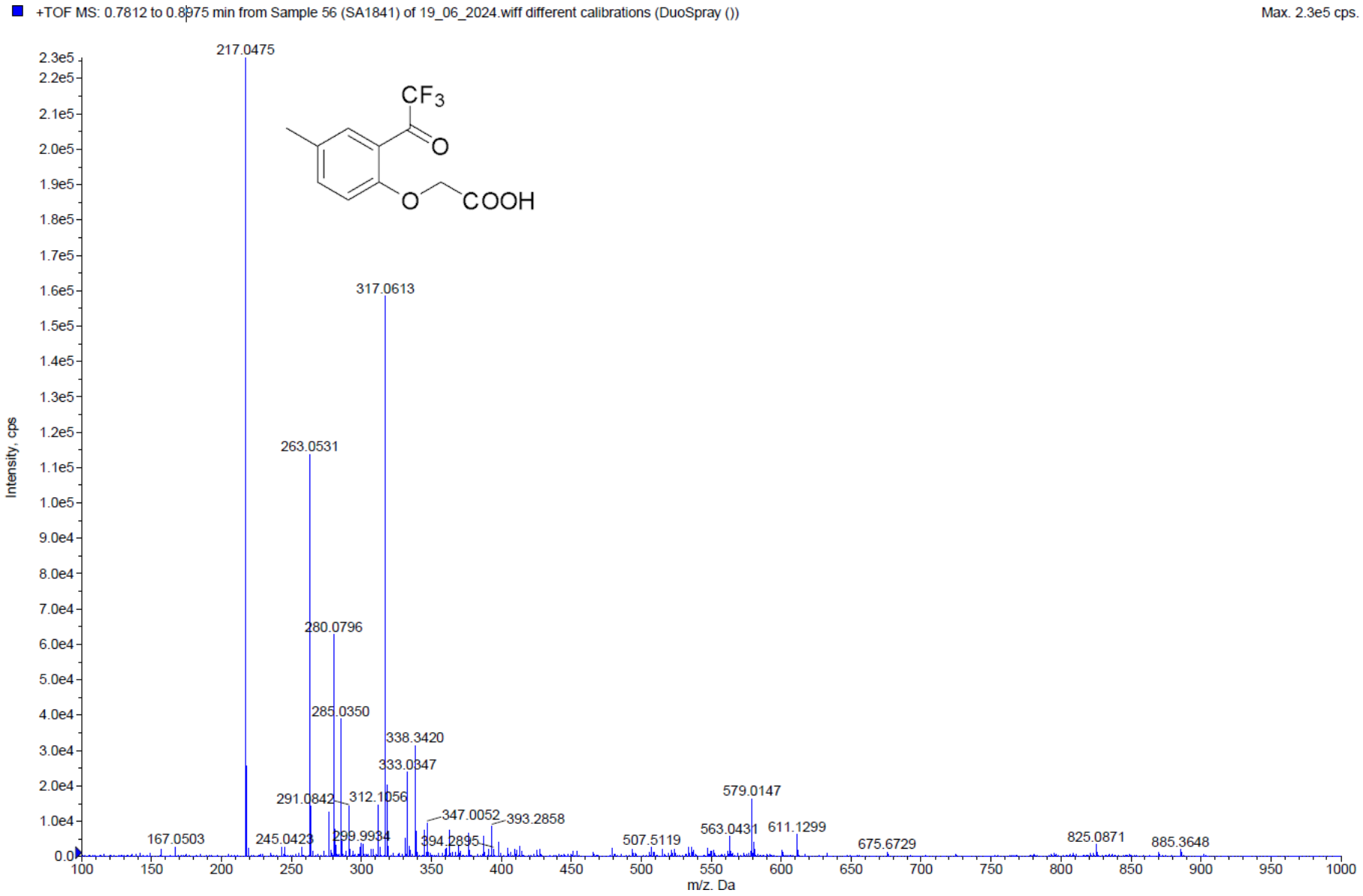

CF3
O
O
COOH
CHCl3
CHCl3
7.90
7.89
7.70
7.69
7.68
7.24
7.23
7.22
7.03
7.01
0.97
1.00
1.15
1.05
Chemical Shift (ppm)
4.78
1.00
1.05
2.06
Chemical Shift (ppm)

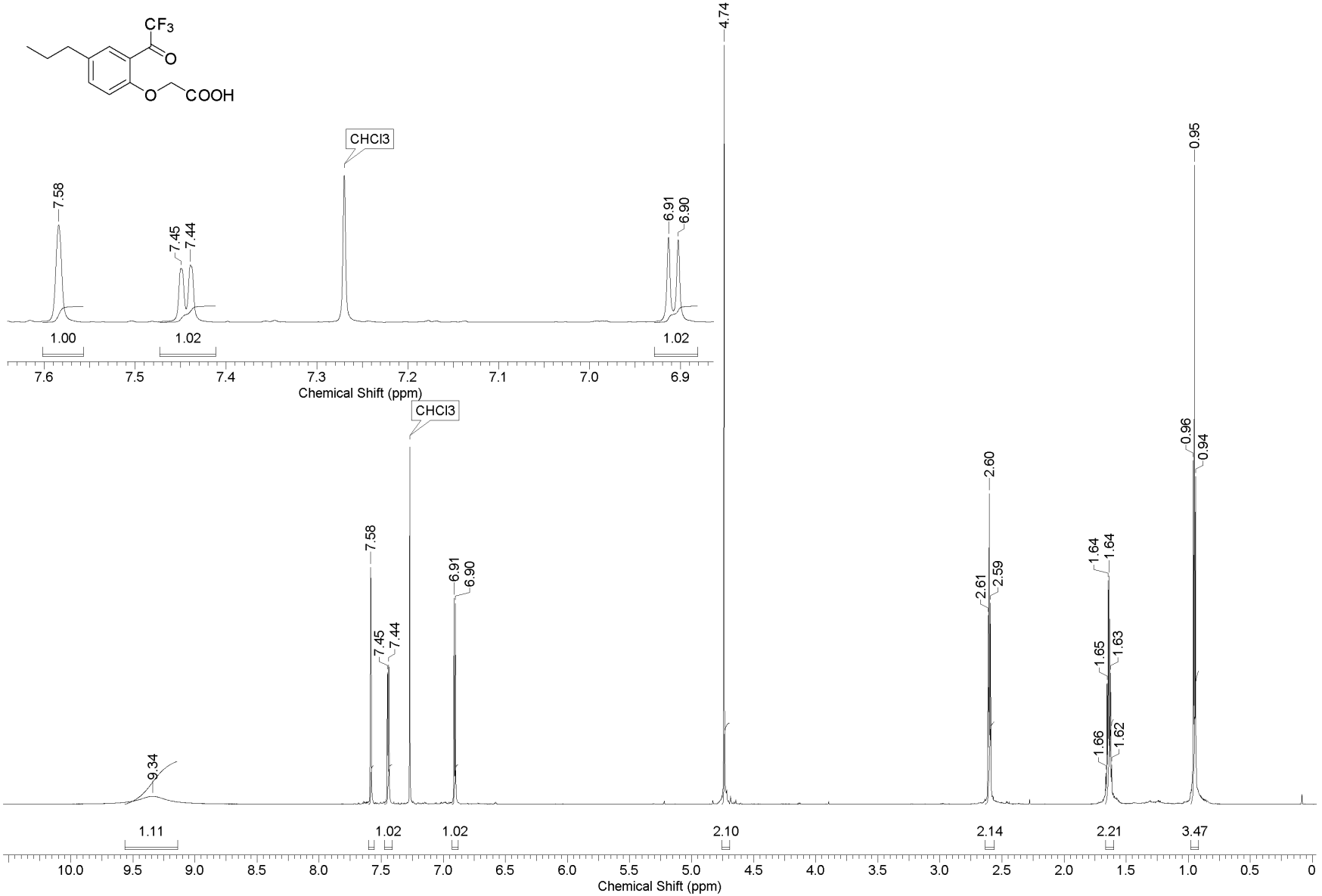

CF3
O
O
COOH
CDCl3
122.34
121.08
118.30
116.85
115.41
113.96
113.88
182.03
181.85
181.67
181.48
183.0
182.5
182.0
181.5
181.0
180.5
180.0
Chemical Shift (ppm)
123
122
121
120
119
118
117
116
115
114
113
Chemical Shift (ppm)
77.20
77.5
77.0
76.5
Chemical Shift (ppm)
157.91
136.43
131.87
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

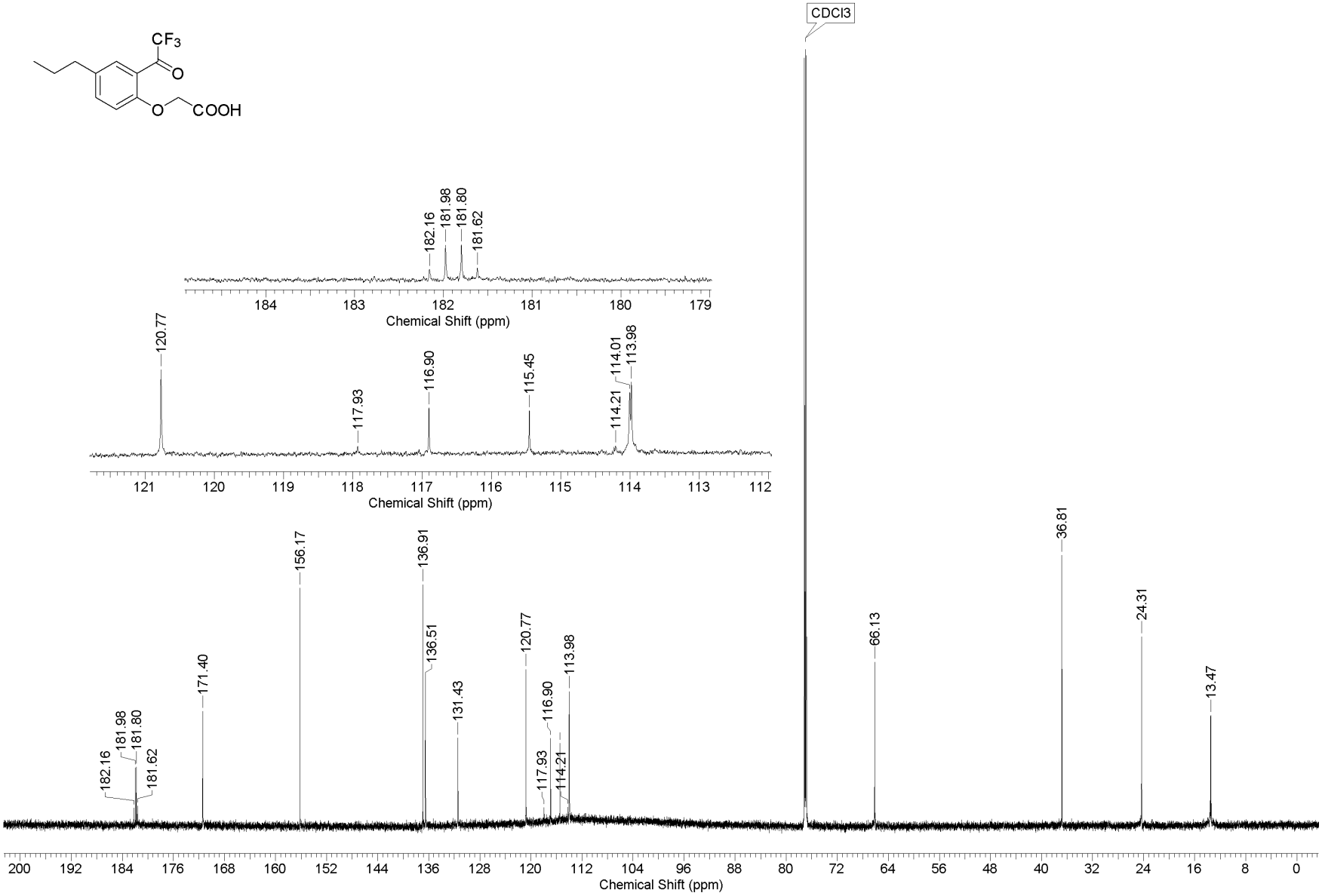

+TOF MS: 0.9300 to 1.1439 min from Sample 21 (SA1757) of 26_01_2024.wiff different calibrations (DuoSpray ())
Max. 7.6e5 cps.
Intensity, cps
m/z, Da
CF3
O
O
COOH
266.0641
331.2847
203.0317
303.0455
348.3113
249.0374
376.3425
313.2742
298.0900
341.3054
353.2664
381.2976
319.0191
271.0191
369.2401
263.0626
397.2714
239.2368
257.2475
338.3418
365.0630
153.0345
416.1678
502.3150
519.0356
583.1000
628.3654
633.3209
683.5420
711.5733
661.3522
739.6043
656.3967
708.5648
783.0418
865.2888

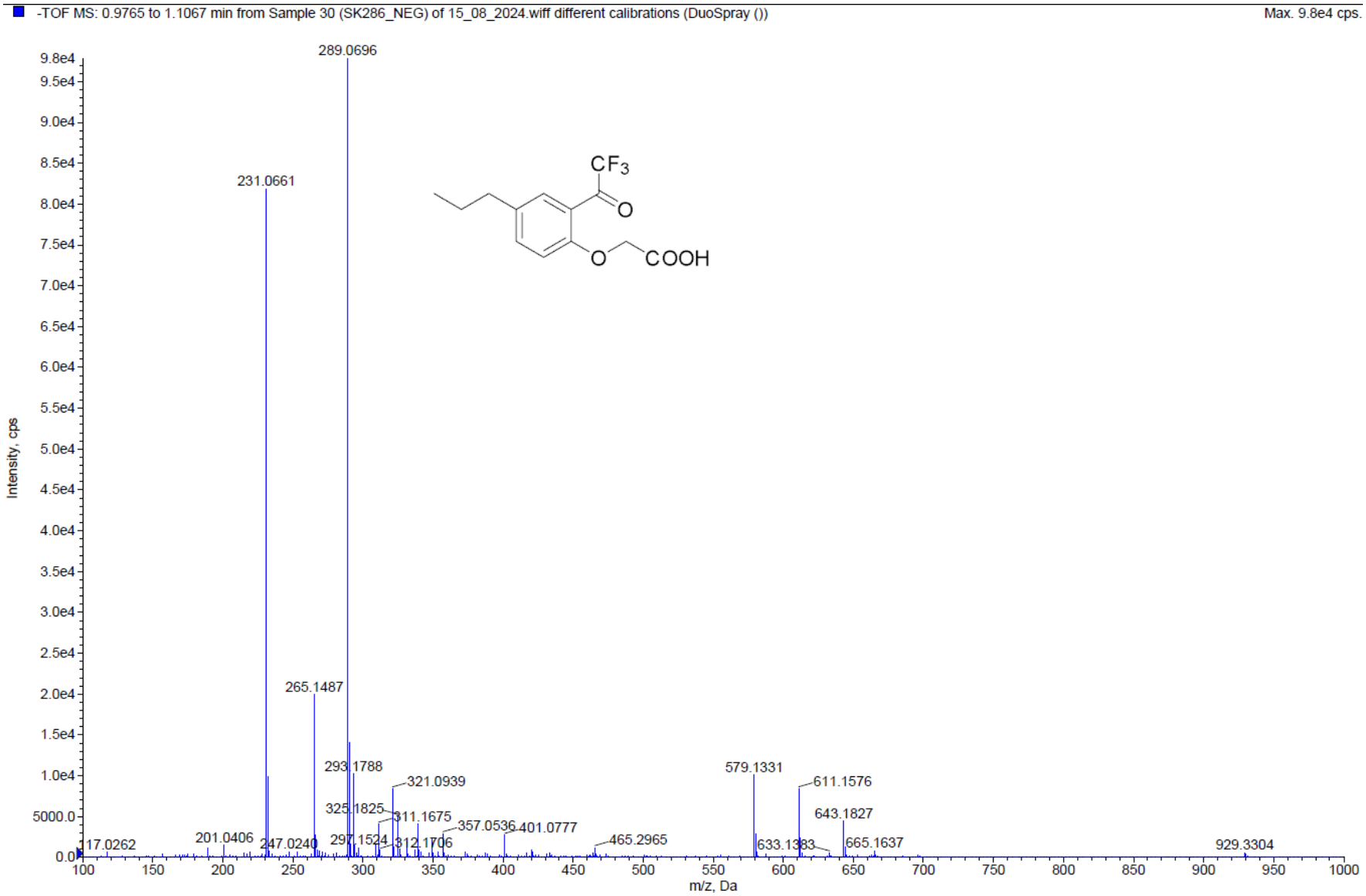

CF3
O
O
COOH
CHCl3
CHCl3
7.62
7.47
7.46
6.91
6.90
2.39
0.98
1.02
1.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
Chemical Shift (ppm)
7.62
7.47
7.46
6.91
6.90
4.74
2.39
1.02
1.00
2.06
2.94
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

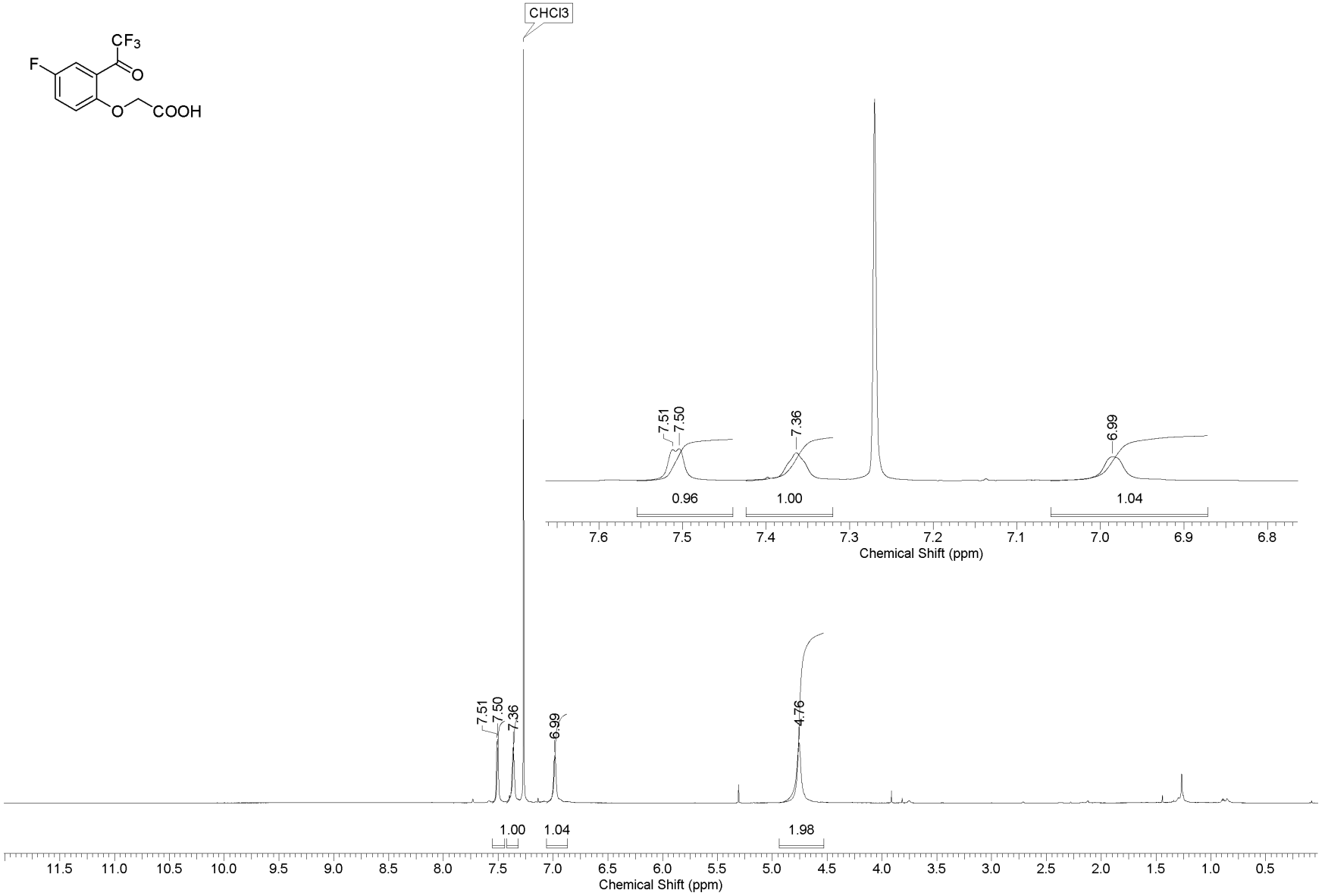

CF3
O
O
COOH
CDCl3
CDCl3
77.20
Chemical Shift (ppm)
182.70
182.26
181.78
181.30
132.00
131.85
131.82
121.91
120.98
118.05
114.19
113.91
110.33
136.95
155.95
20.34

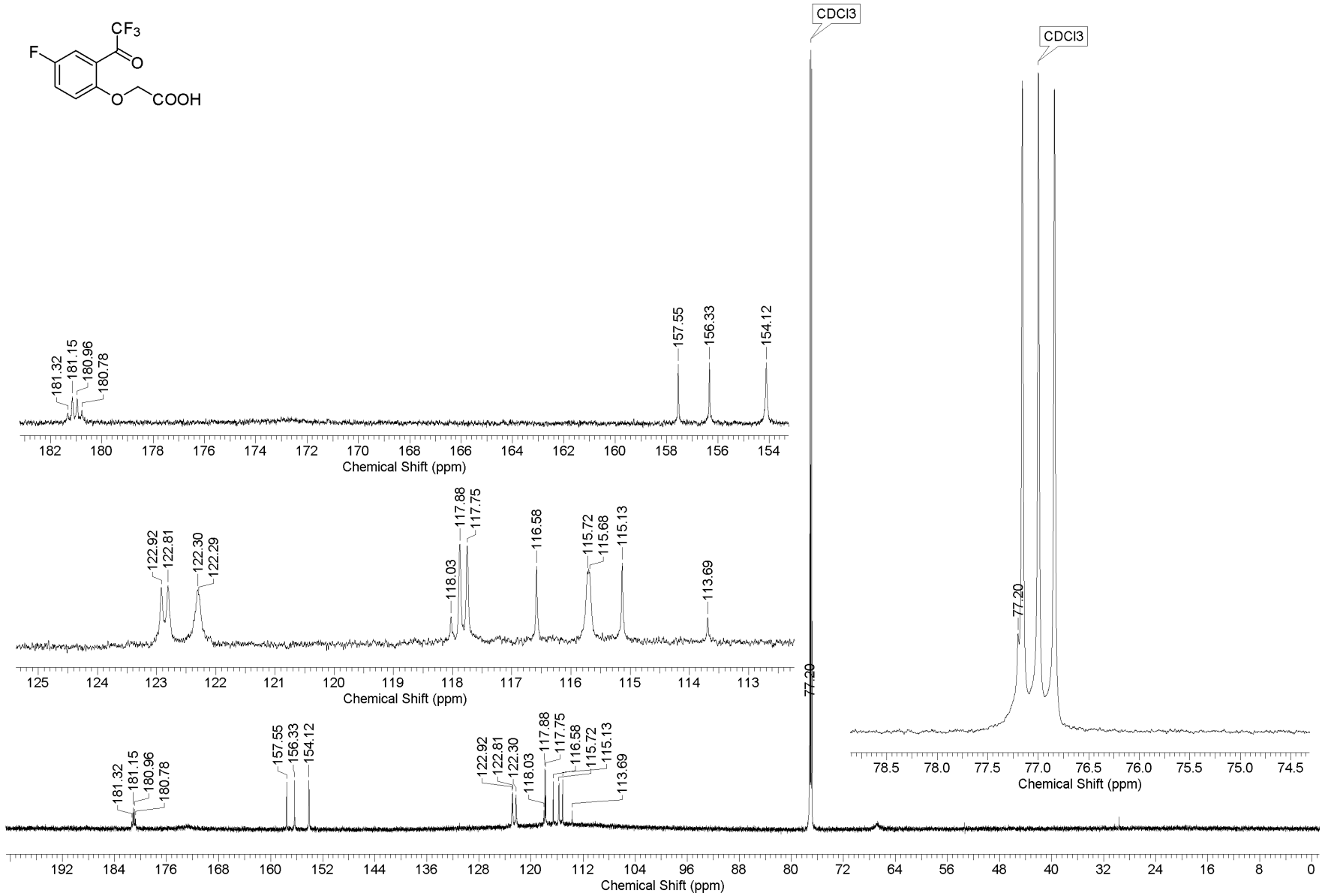

+TOF MS: 0.7812 to 0.8975 min from Sample 56 (SA1841) of 19_06_2024.wiff different calibrations (DuoSpray ())
Max. 2.3e5 cps.
Intensity, cps
m/z, Da
CF3
O
O
COOH
217.0475
317.0613
263.0531
280.0796
285.0350
338.3420
333.0847
291.0842
312.1056
347.0052
393.2858
579.0147
563.0431
611.1299
167.0503
245.0423
299.9934
394.2895
507.5119
675.6729
825.0871
885.3648

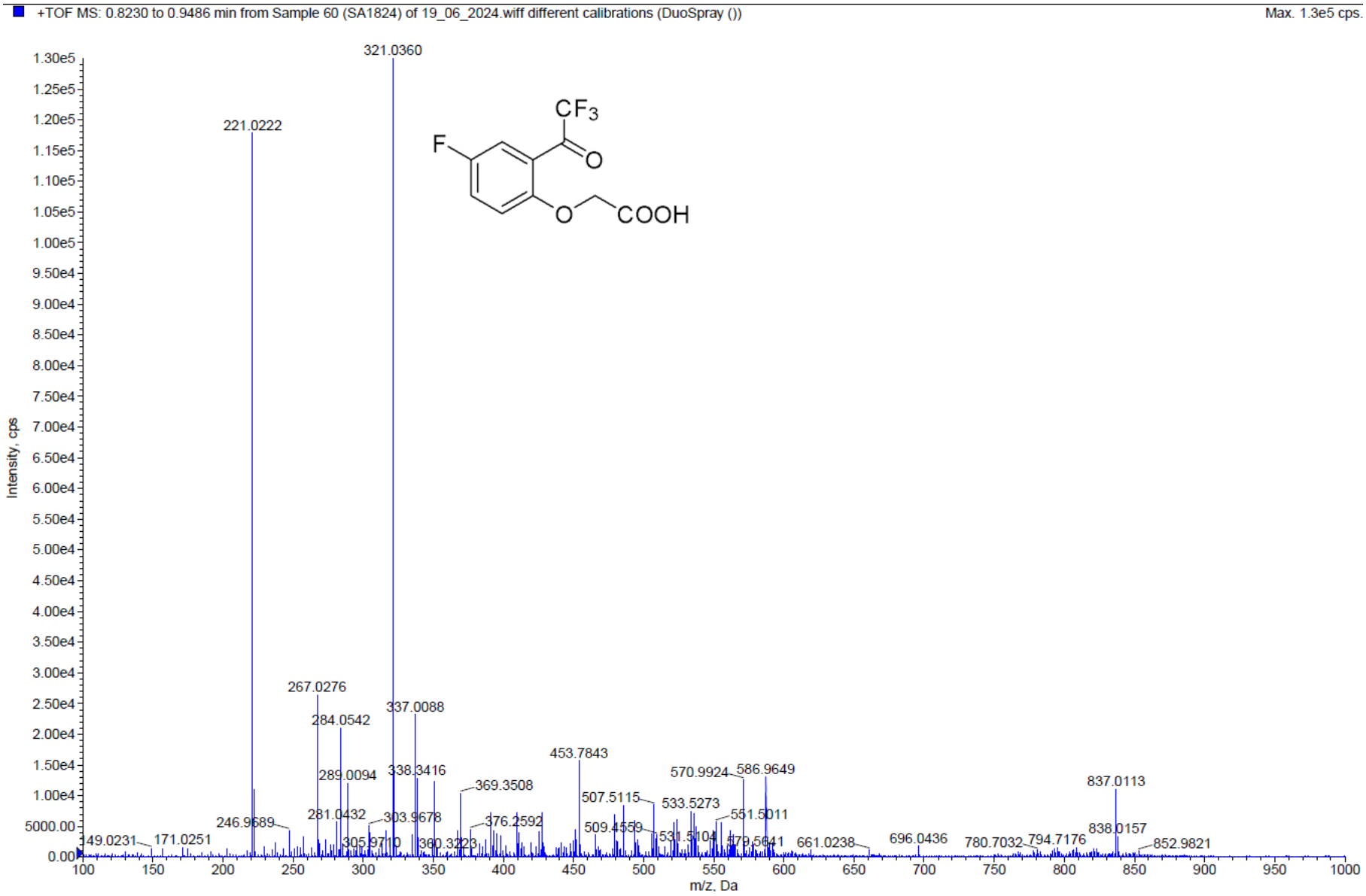

CF3
O
O
COOH
CHCl3
7.58
7.45
7.44
6.91
6.90
4.74
0.95
0.96
0.94
2.60
2.61
2.59
1.64
1.64
1.65
1.63
1.66
1.62
9.34
1.00
1.02
1.02
1.11
1.02
1.02
2.10
2.14
2.21
3.47
Chemical Shift (ppm)
Chemical Shift (ppm)

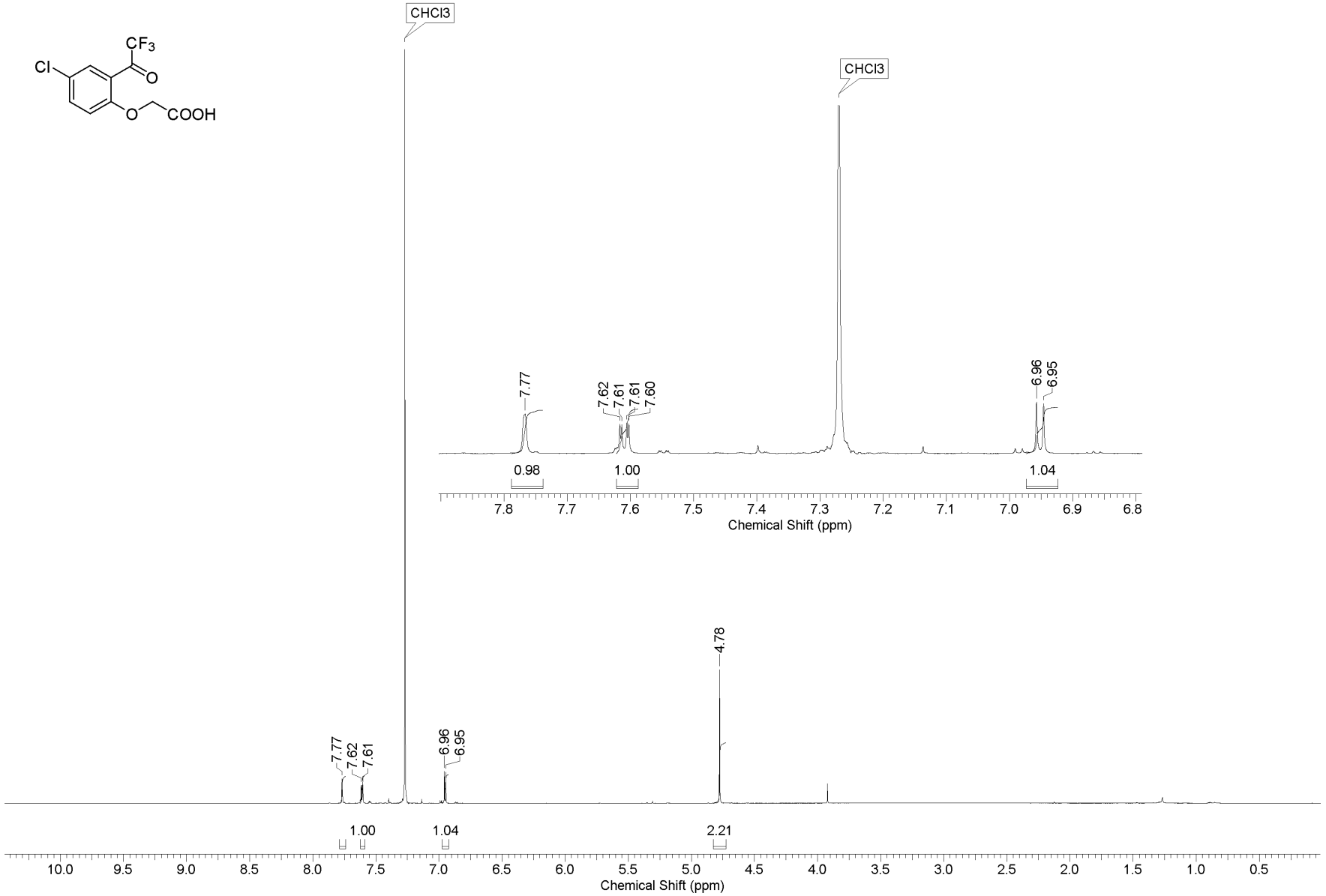

CF3
O
O
COOH
CDCl3
182.16
181.98
181.80
181.62
184
183
182
181
180
179
Chemical Shift (ppm)
120.77
117.93
116.90
115.45
114.21
114.01
113.98
121
120
119
118
117
116
115
114
113
112
Chemical Shift (ppm)
156.17
136.91
136.51
131.43
171.40
120.77
116.90
117.93
114.21
113.98
66.13
36.81
24.31
13.47
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

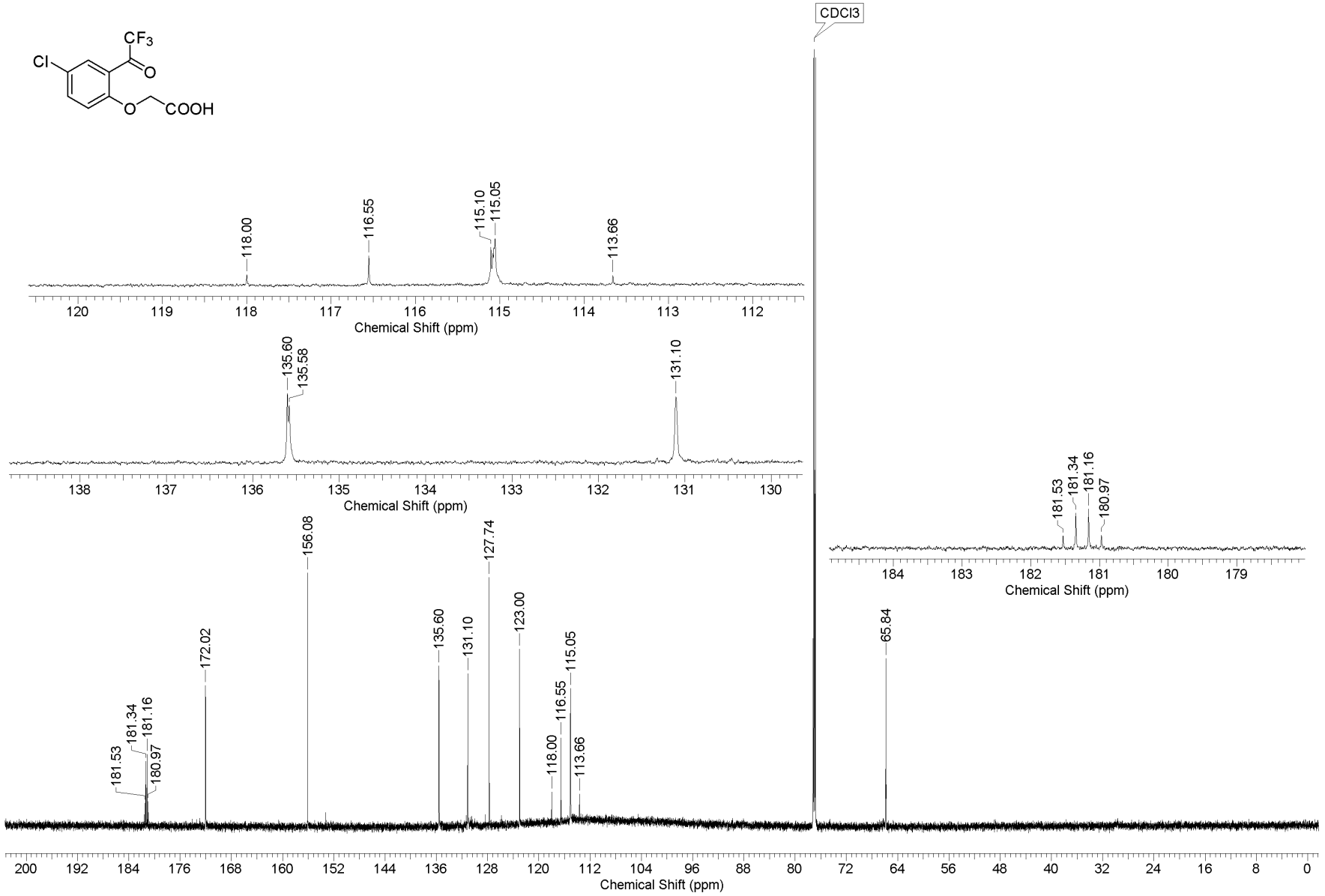

-TOF MS: 0.9765 to 1.1067 min from Sample 30 (SK286_NEG) of 15_08_2024.wiff different calibrations (DuoSpray ())
Max. 9.8e4 cps.
Intensity, cps
m/z, Da
289.0696
231.0661
265.1487
293.1788
321.0939
325.1825
311.1675
357.0536
401.0777
465.2965
579.1331
611.1576
643.1827
665.1637
929.3304
633.1383
117.0262
201.0406
247.0240
297.1524
312.1706
CF3
O
O
COOH

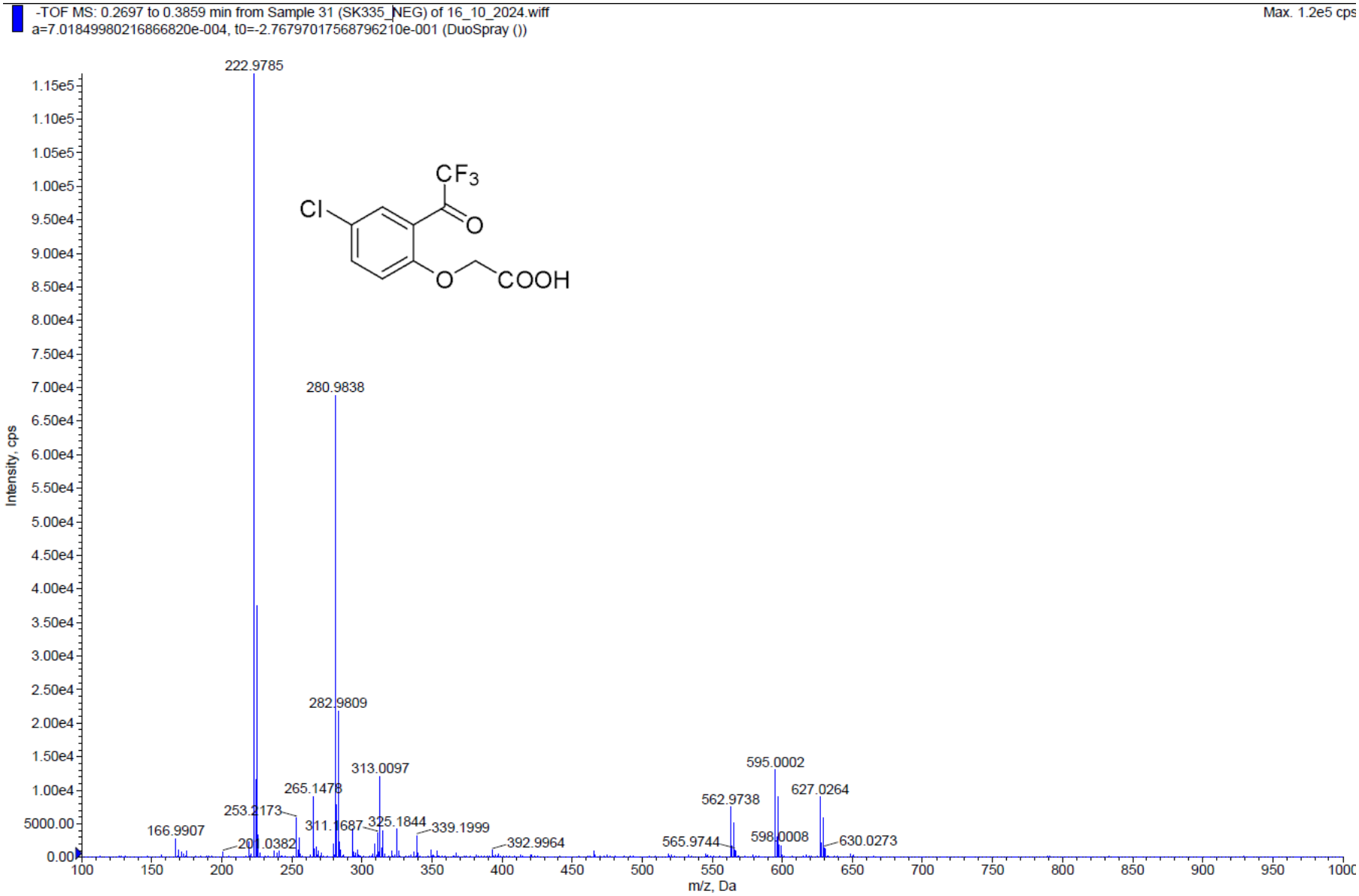

CHCl3
7.51
7.50
7.36
6.99
4.76
0.96
1.00
1.04
1.98
Chemical Shift (ppm)


CF3
O
F
O
COOH
CDCl3
CDCl3
181.32
181.15
180.96
180.78
157.55
156.33
154.12
Chemical Shift (ppm)
122.92
122.81
122.30
122.29
118.03
117.88
117.75
116.58
115.72
115.68
115.13
113.69
Chemical Shift (ppm)
77.20
77.20
Chemical Shift (ppm)
Chemical Shift (ppm)


+TOF MS: 0.8230 to 0.9486 min from Sample 60 (SA1824) of 19_06_2024.wiff different calibrations (DuoSpray ())
Max. 1.3e5 cps.
Intensity, cps
m/z, Da
321.0360
221.0222
267.0276
284.0542
337.0088
289.0094
338.3416
453.7843
369.3508
570.9924
586.9649
507.5115
533.5273
837.0113
281.0432
303.9678
376.2592
551.5011
246.9689
509.4559
838.0157
49.0231
171.0251
305.9710
360.3223
579.5641
661.0238
696.0436
780.7032
794.7176
852.9821
F
CF3
O
O
COOH


CF3
Cl
O
O
COOH
CHCl3
CHCl3
7.77
7.62
7.61
7.61
7.60
6.96
6.95
0.98
1.00
1.04
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
Chemical Shift (ppm)
4.78
7.77
7.62
7.61
6.96
6.95
1.00
1.04
2.21
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
Chemical Shift (ppm)


CF3
O
Cl
O
COOH
CDCl3
118.00
116.55
115.10
115.05
113.66
Chemical Shift (ppm)
135.60
135.58
131.10
Chemical Shift (ppm)
181.53
181.34
181.16
180.97
Chemical Shift (ppm)
156.08
127.74
135.60
131.10
123.00
115.05
116.55
118.00
113.66
172.02
65.84
181.53
181.34
181.16
180.97
Chemical Shift (ppm)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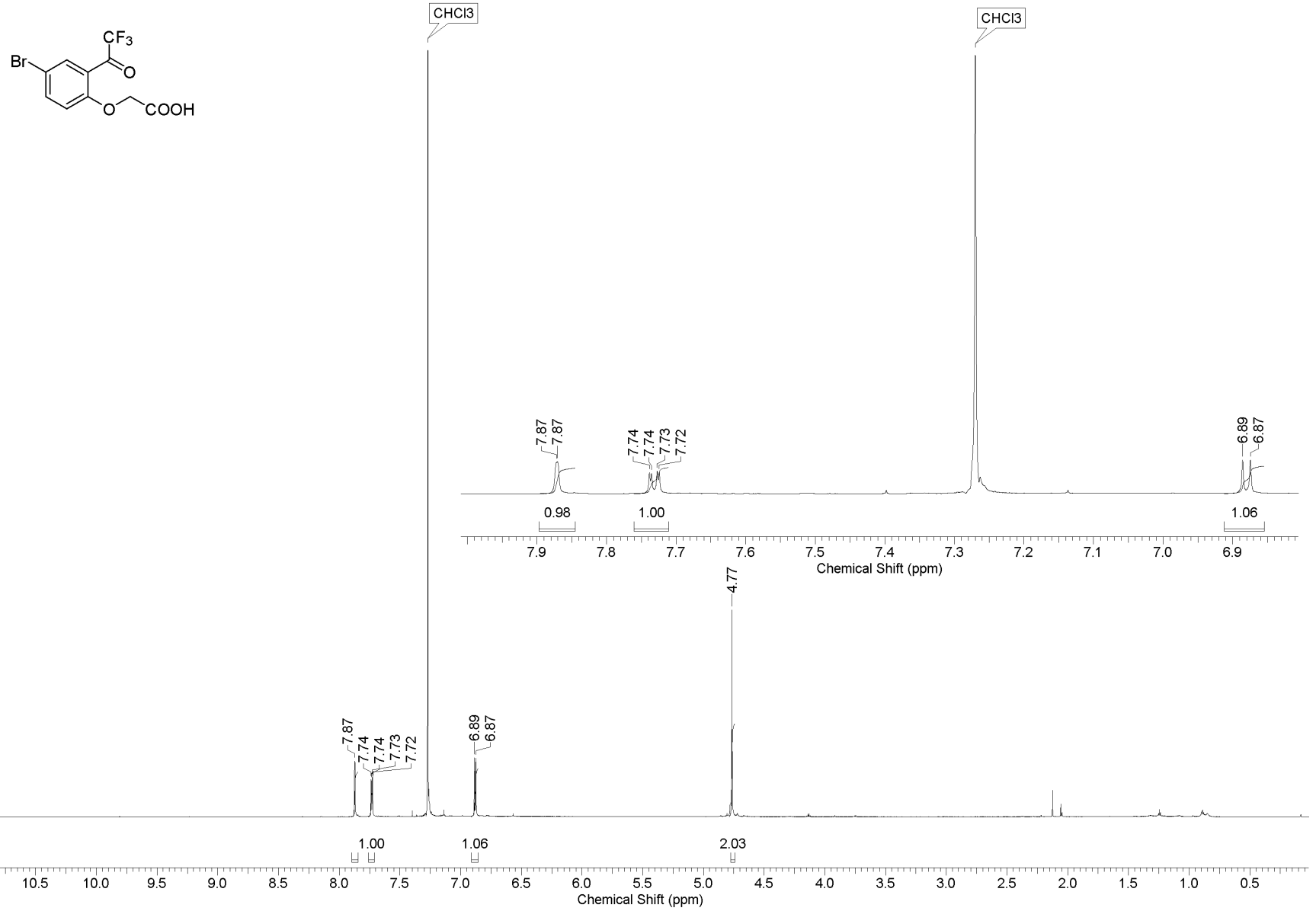
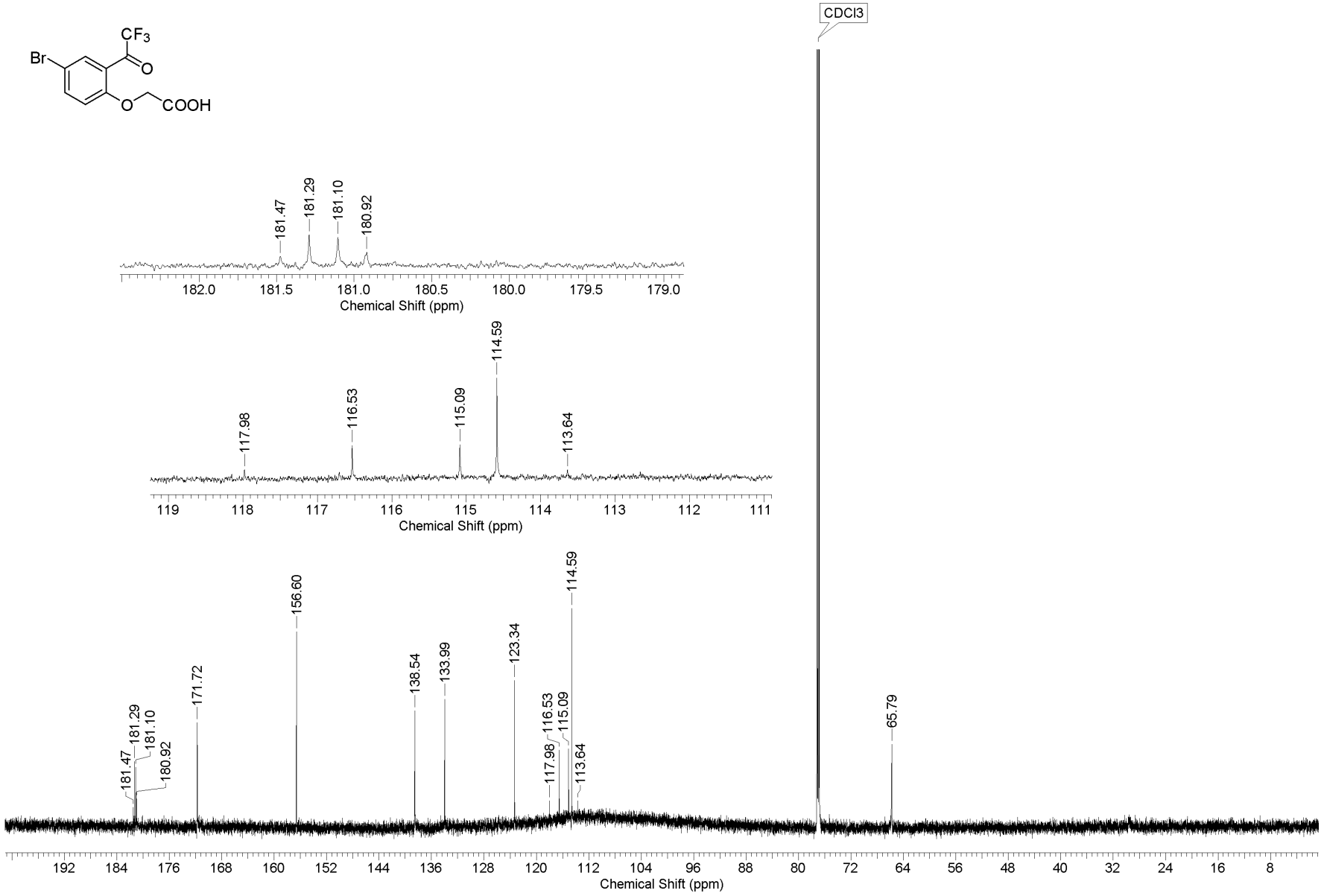
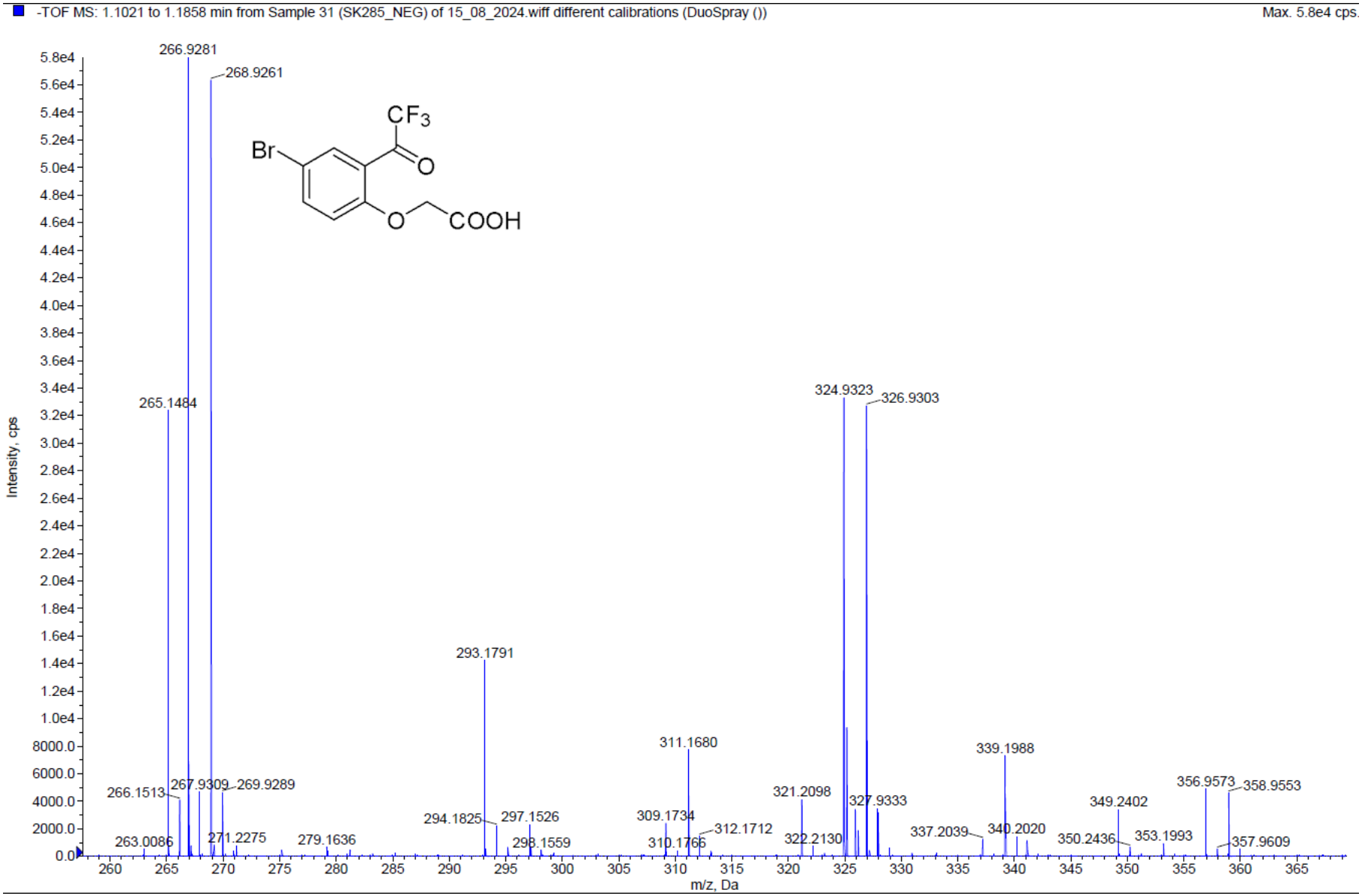
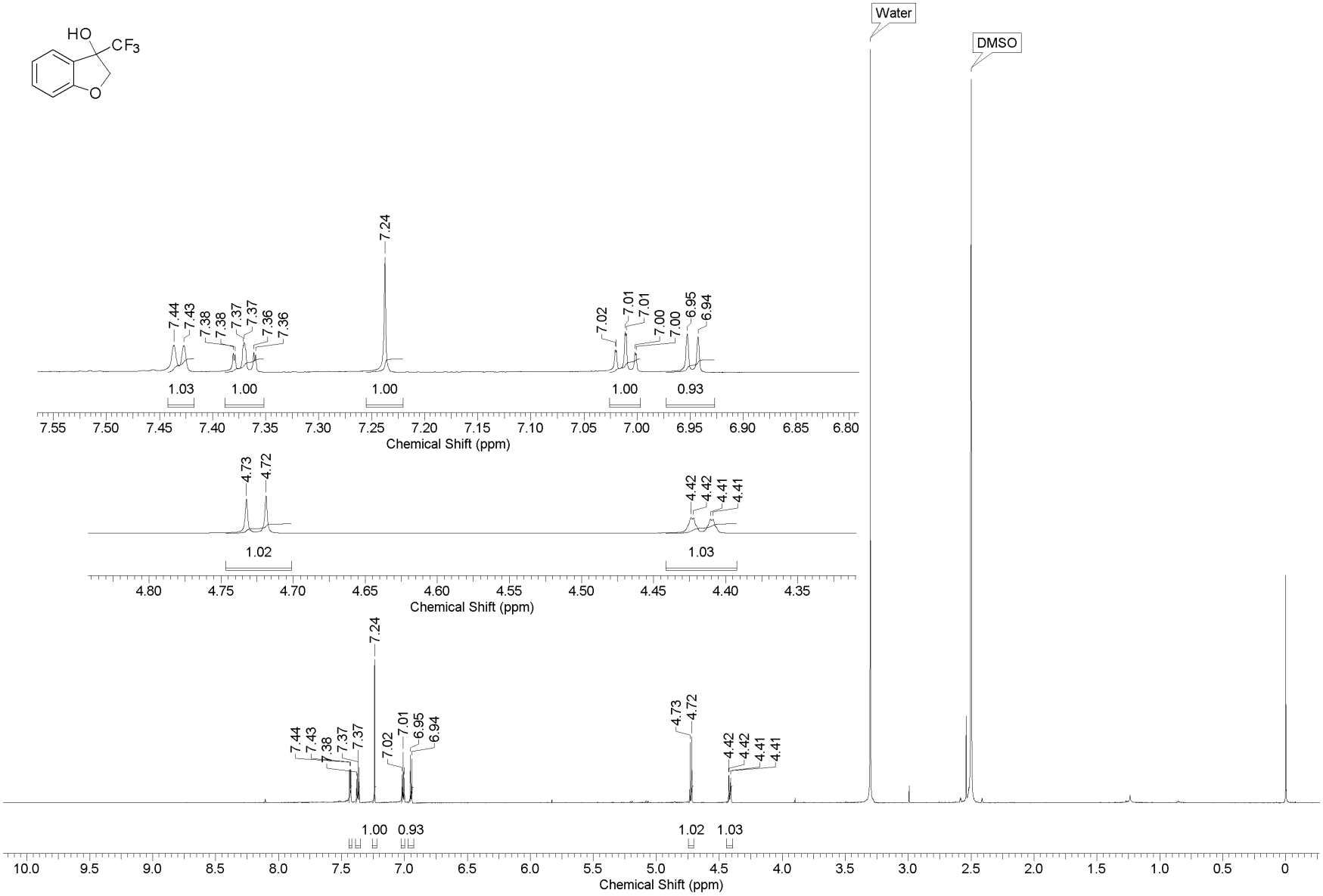
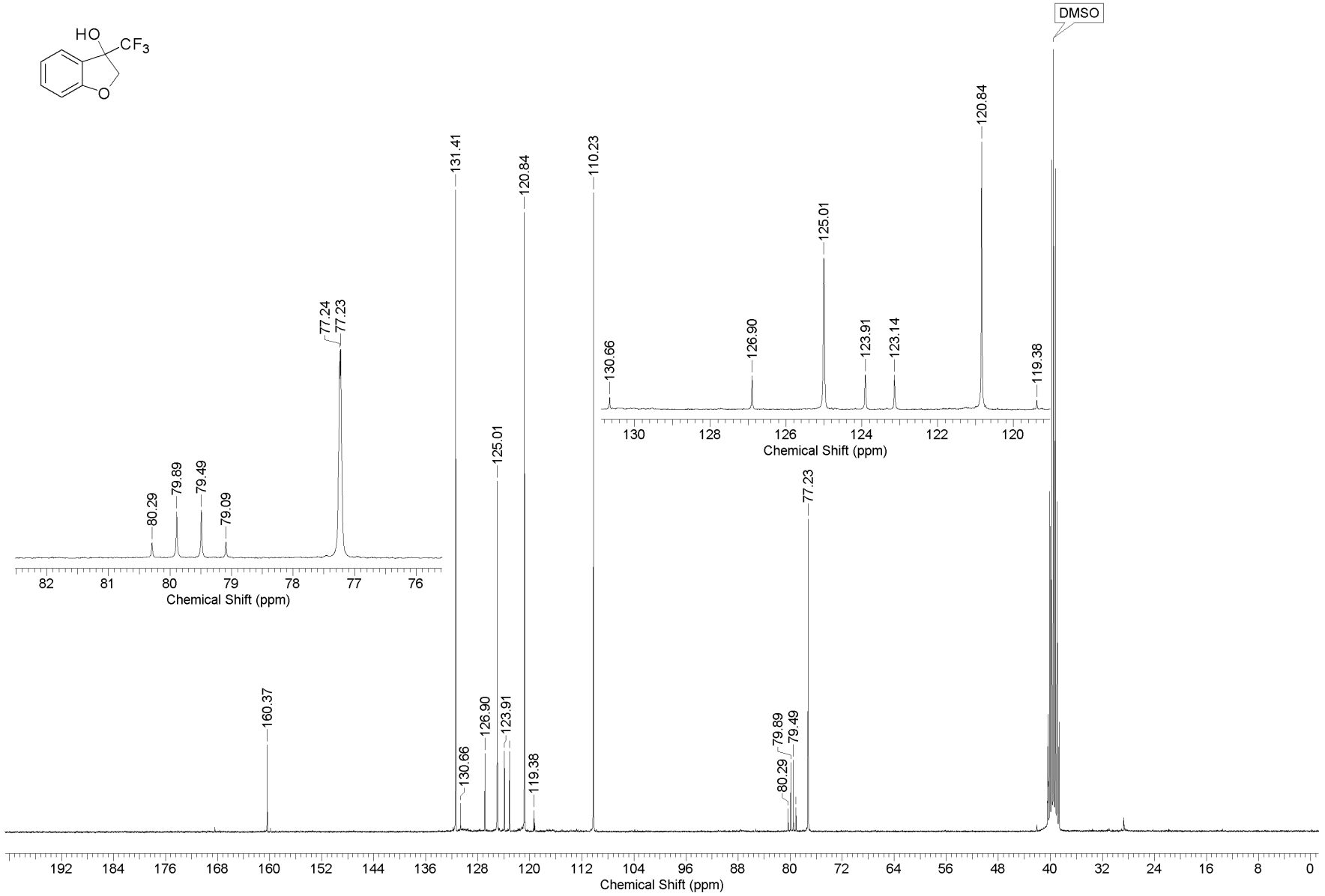
a=7.01849980216866820e-004, t0=-2.76797017568796210e-001 (DuoSpray ())
Max. 1.2e5 cps
Intensity, cps
m/z, Da
222.9785
280.9838
282.9809
313.0097
595.0002
627.0264
265.1478
562.9738
253.2173
325.1844
339.1999
166.9907
565.9744
630.0273
392.9964
CF3
Cl
O
O
COOH

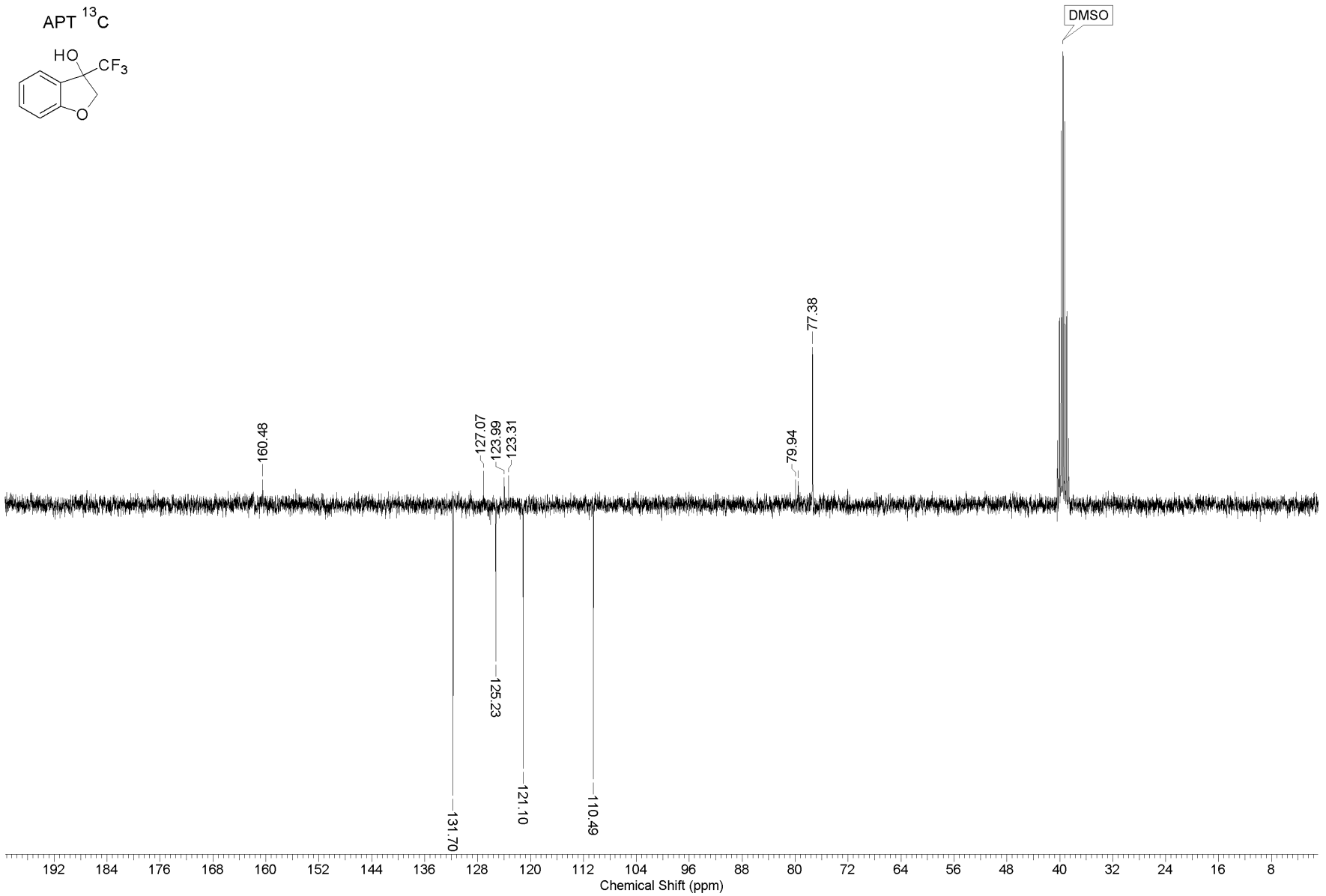

CF3
O
Br
O
COOH
CHCl3
CHCl3
7.87
7.87
7.74
7.74
7.73
7.72
6.89
6.87
0.98
1.00
1.06
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
Chemical Shift (ppm)
4.77
7.87
7.74
7.74
7.73
7.72
6.89
6.87
1.00
1.06
2.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

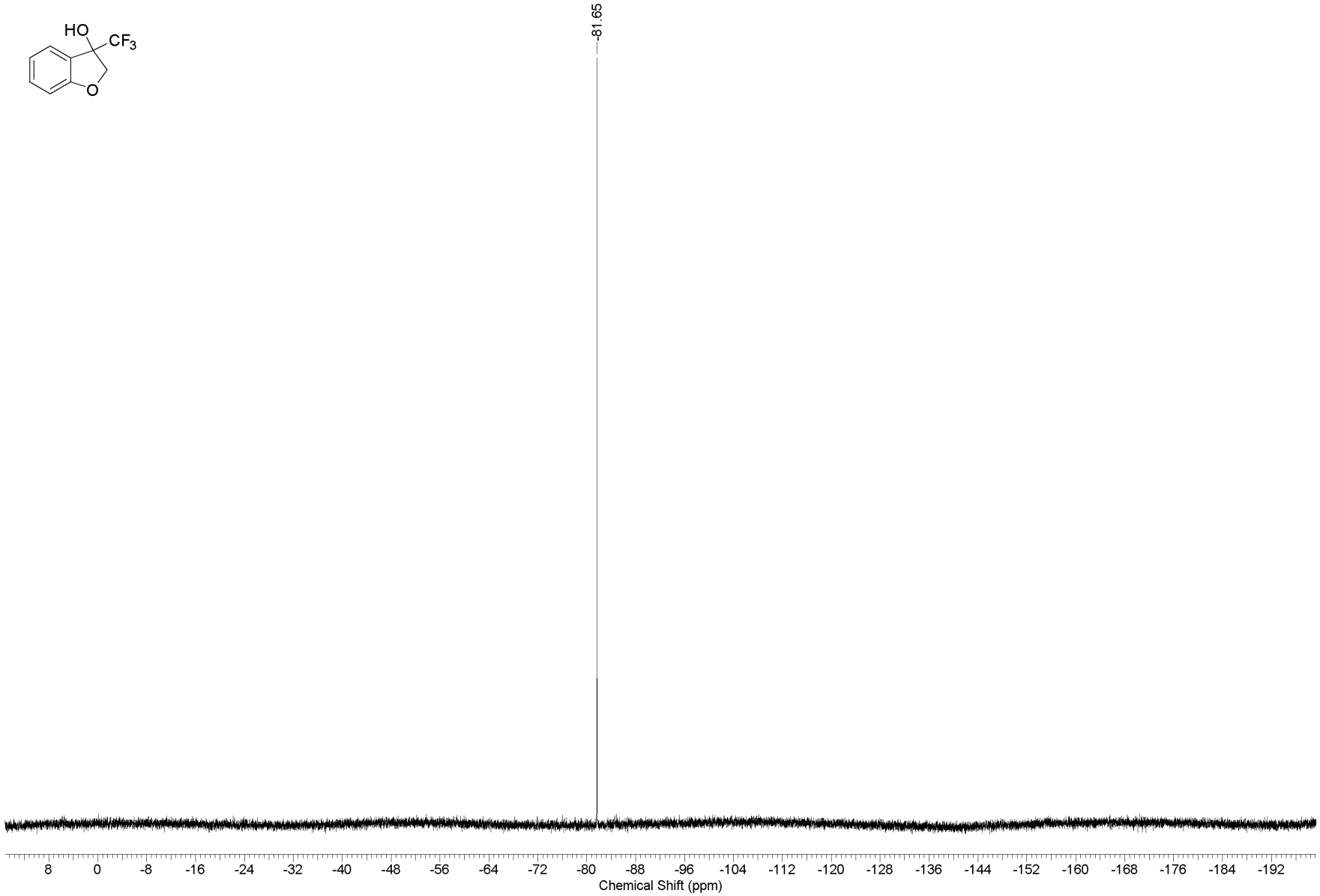

Br
CF3
O
O
COOH
CDCl3
181.47
181.29
181.10
180.92
182.0
181.5
181.0
180.5
180.0
179.5
179.0
Chemical Shift (ppm)
114.59
116.53
115.09
117.98
113.64
119
118
117
116
115
114
113
112
111
Chemical Shift (ppm)
156.60
114.59
138.54
133.99
123.34
171.72
65.79
181.47
181.29
181.10
180.92
116.53
115.09
117.98
113.64
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

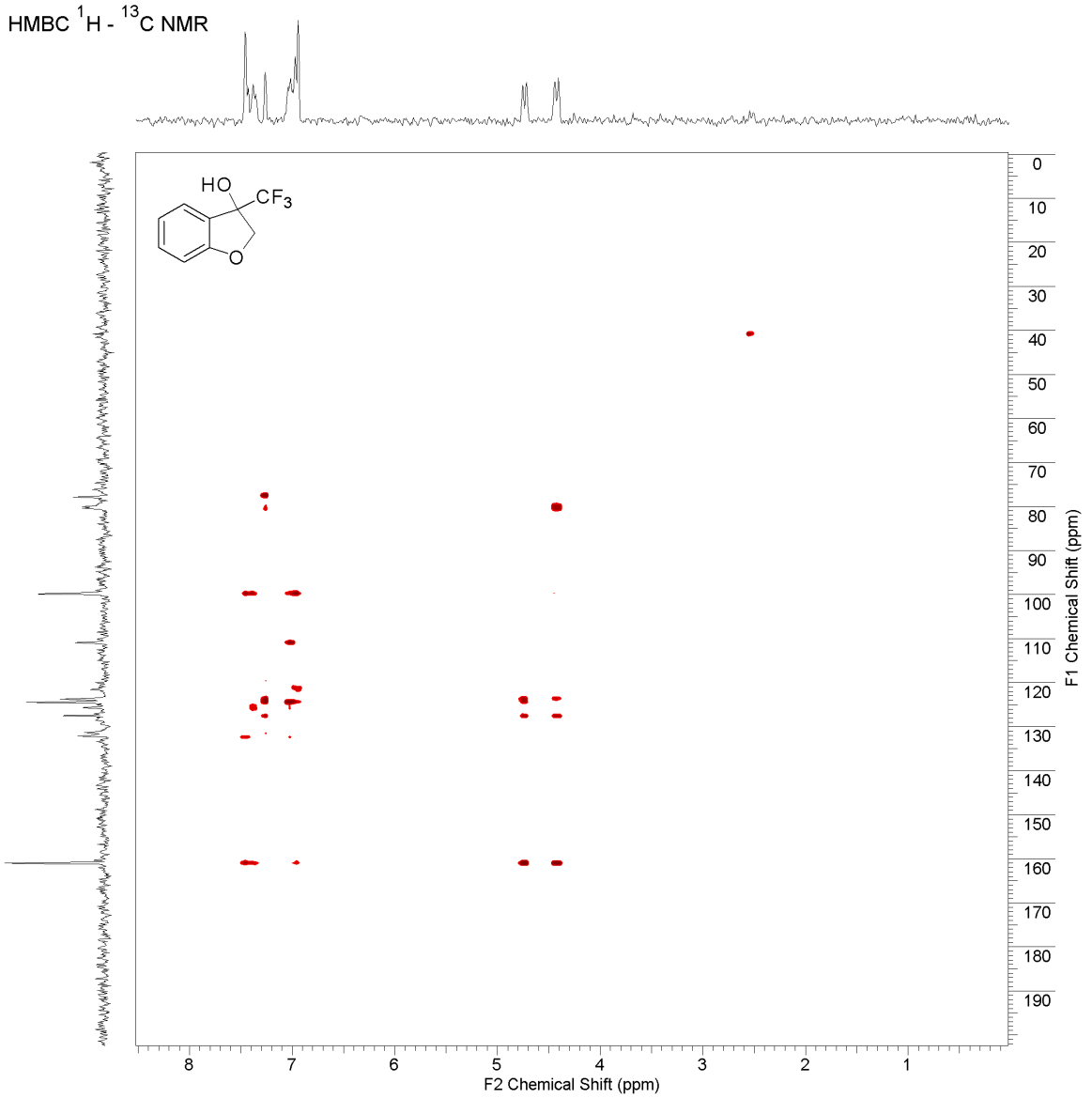

-TOF MS: 1.1021 to 1.1858 min from Sample 31 (SK285_NEG) of 15_08_2024.wiff different calibrations (DuoSpray ())
Max. 5.8e4 cps.
Intensity, cps
m/z, Da
CF3
Br
O
O
COOH
266.9281
268.9261
265.1484
324.9323
326.9303
293.1791
311.1680
339.1988
356.9573
358.9553
321.2098
327.9333
349.2402
266.1513
267.9309
269.9289
294.1825
297.1526
309.1734
312.1712
337.2039
340.2020
350.2436
353.1993
263.0086
271.2275
279.1636
298.1559
310.1766
322.2130
357.9609

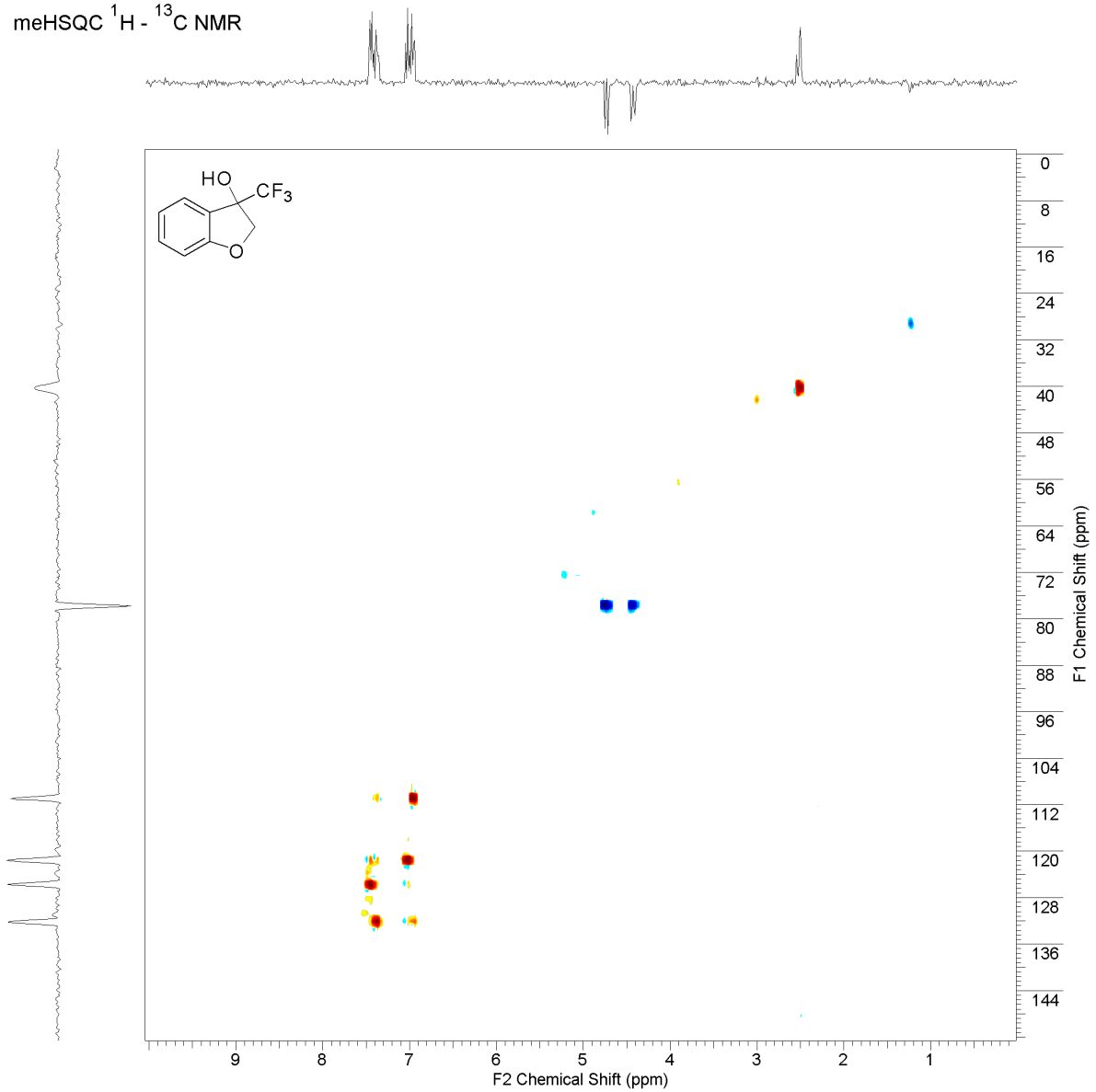

HO
CF3
O
Water
DMSO
7.24
7.44
7.43
7.38
7.38
7.37
7.37
7.36
7.36
7.02
7.01
7.01
7.00
7.00
6.95
6.94
1.03
1.00
1.00
1.00
0.93
Chemical Shift (ppm)
4.73
4.72
4.42
4.42
4.41
4.41
1.02
1.03
Chemical Shift (ppm)
1.00
0.93
1.02
1.03
Chemical Shift (ppm)

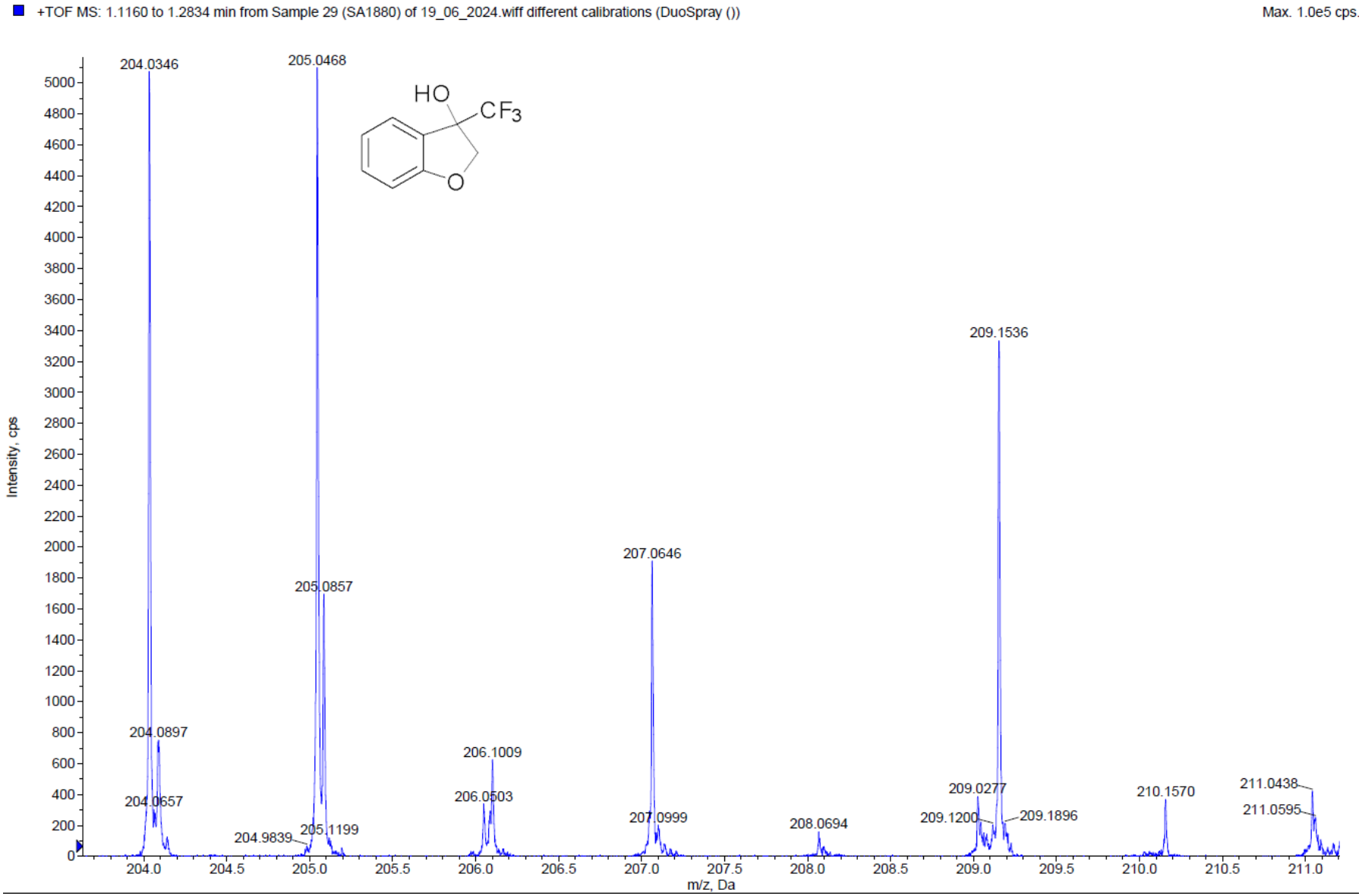

HO
CF3
O
DMSO
131.41
120.84
110.23
125.01
120.84
77.24
77.23
80.29
79.89
79.49
79.09
130.66
126.90
123.91
123.14
119.38
160.37
Chemical Shift (ppm)

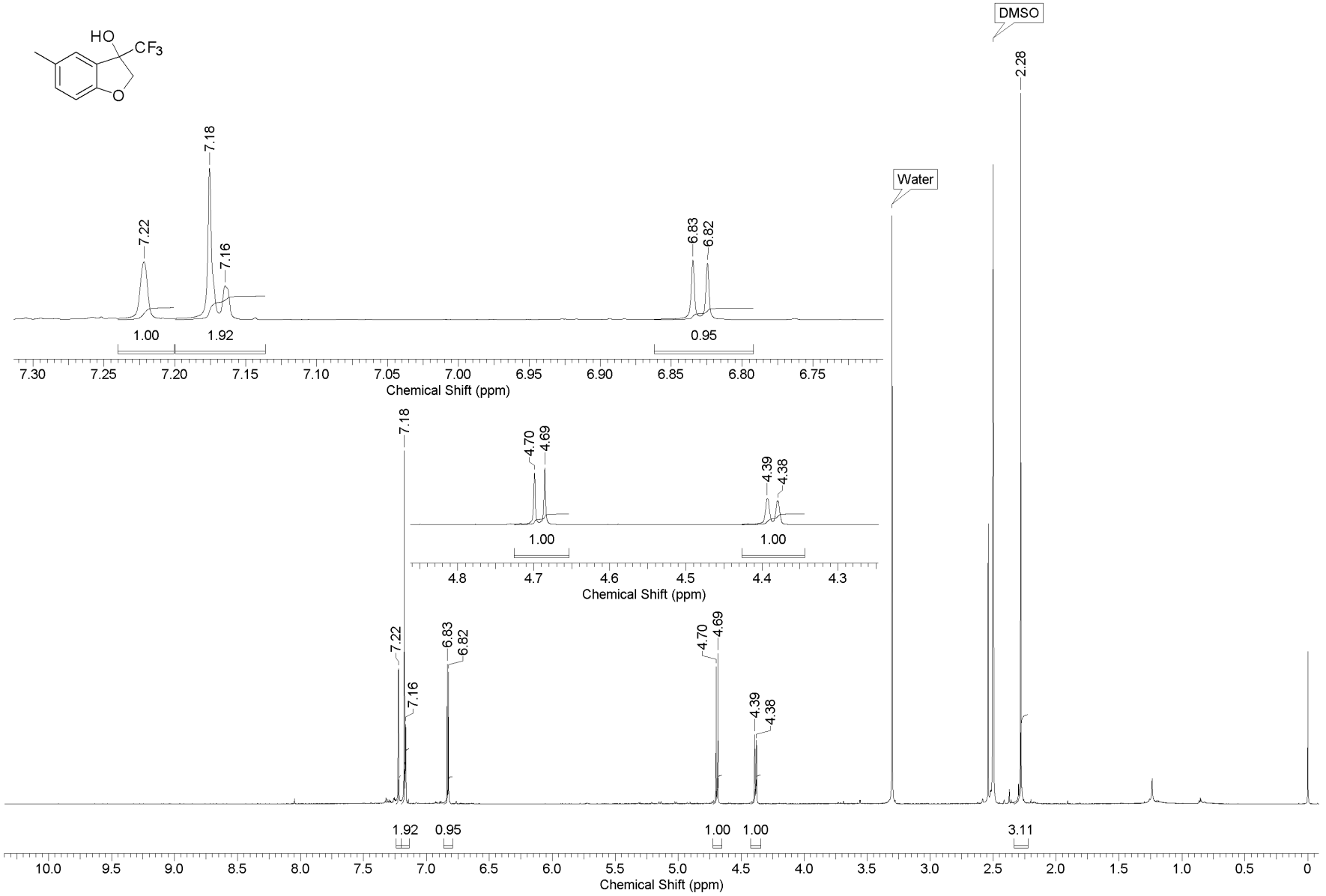

APT ^{13}C
HO
CF_3
O
DMSO
160.48
127.07
123.99
123.31
79.94
77.38
131.70
125.23
121.10
110.49
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

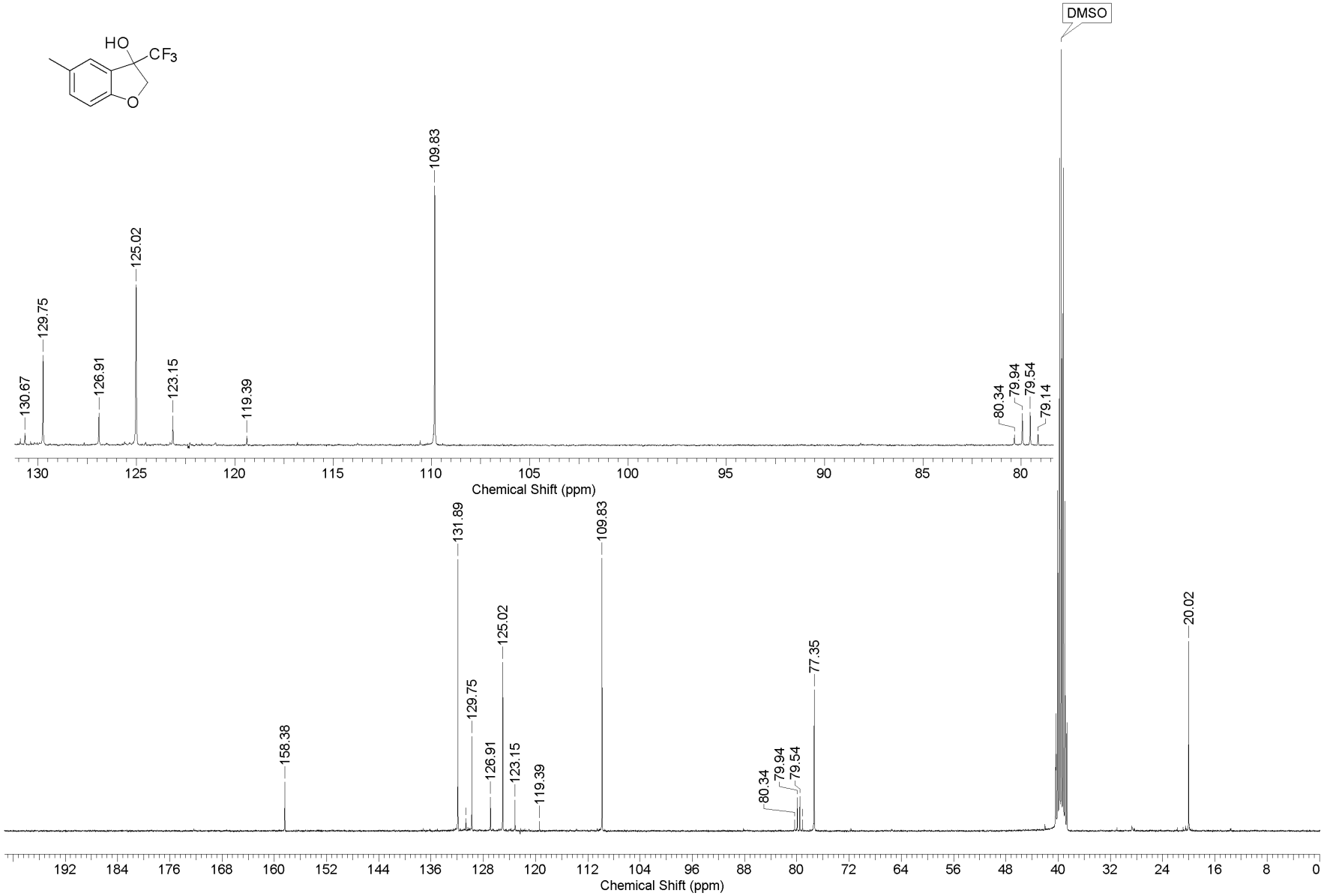

HO
CF3
O
-81.65
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

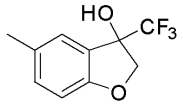

HMBC ^{1}H - ^{13}C NMR
HO
CF3
O
F2 Chemical Shift (ppm)
F1 Chemical Shift (ppm)


meHSQC ^{1}H - ^{13}C NMR
HO
CF3
O
0
8
16
24
32
40
48
56
64
72
80
88
96
104
112
120
128
136
144
F1 Chemical Shift (ppm)
9
8
7
6
5
4
3
2
1
F2 Chemical Shift (ppm)

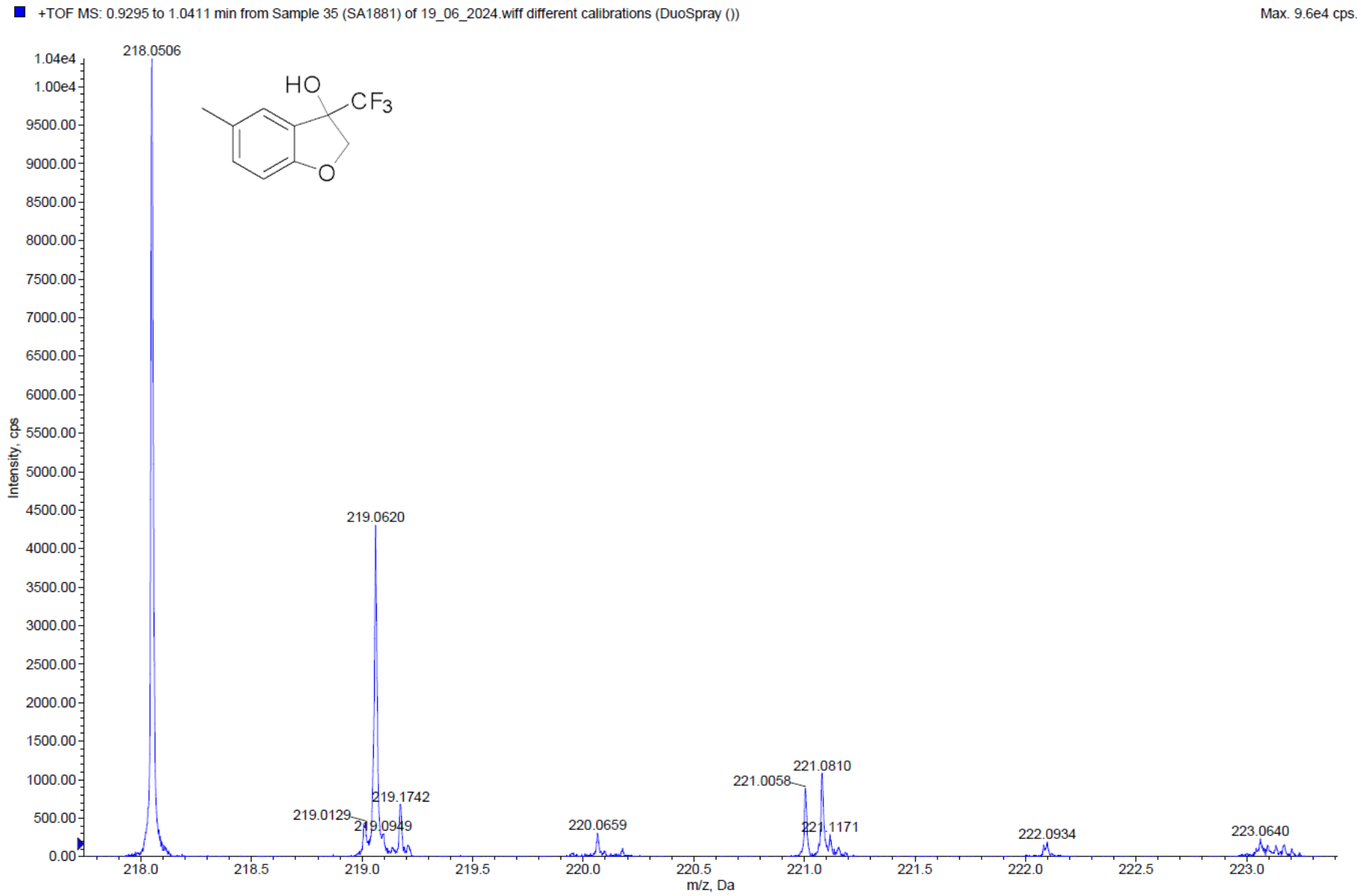

+TOF MS: 1.1160 to 1.2834 min from Sample 29 (SA1880) of 19_06_2024.wiff different calibrations (DuoSpray ())
Max. 1.0e5 cps.
HO
CF3
O
Intensity, cps
m/z, Da
204.0346
205.0468
205.0857
207.0646
209.1536
204.0897
204.0657
206.1009
206.0503
204.9839
205.1199
207.0999
208.0694
209.0277
209.1200
209.1896
210.1570
211.0438
211.0595

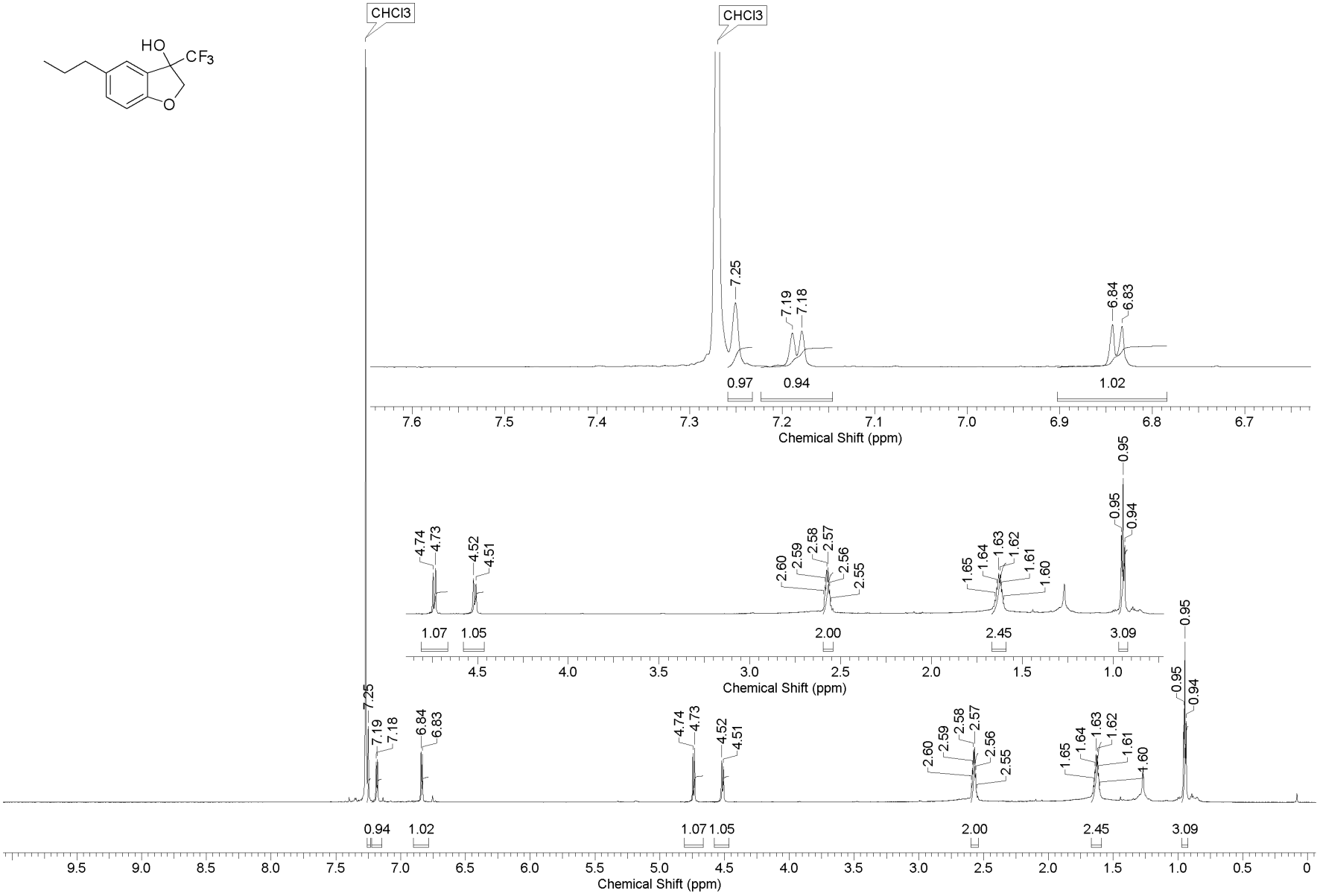

HO
CF3
O
DMSO
2.28
Water
7.18
7.22
7.16
6.83
6.82
1.00
1.92
0.95
7.30
7.25
7.20
7.15
7.10
7.05
7.00
6.95
6.90
6.85
6.80
6.75
Chemical Shift (ppm)
7.18
4.70
4.69
4.39
4.38
1.00
1.00
4.8
4.7
4.6
4.5
4.4
4.3
Chemical Shift (ppm)
7.22
7.16
6.83
6.82
4.70
4.69
4.39
4.38
1.92
0.95
1.00
1.00
3.11
10.0
9.5
9.0
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
Chemical Shift (ppm)

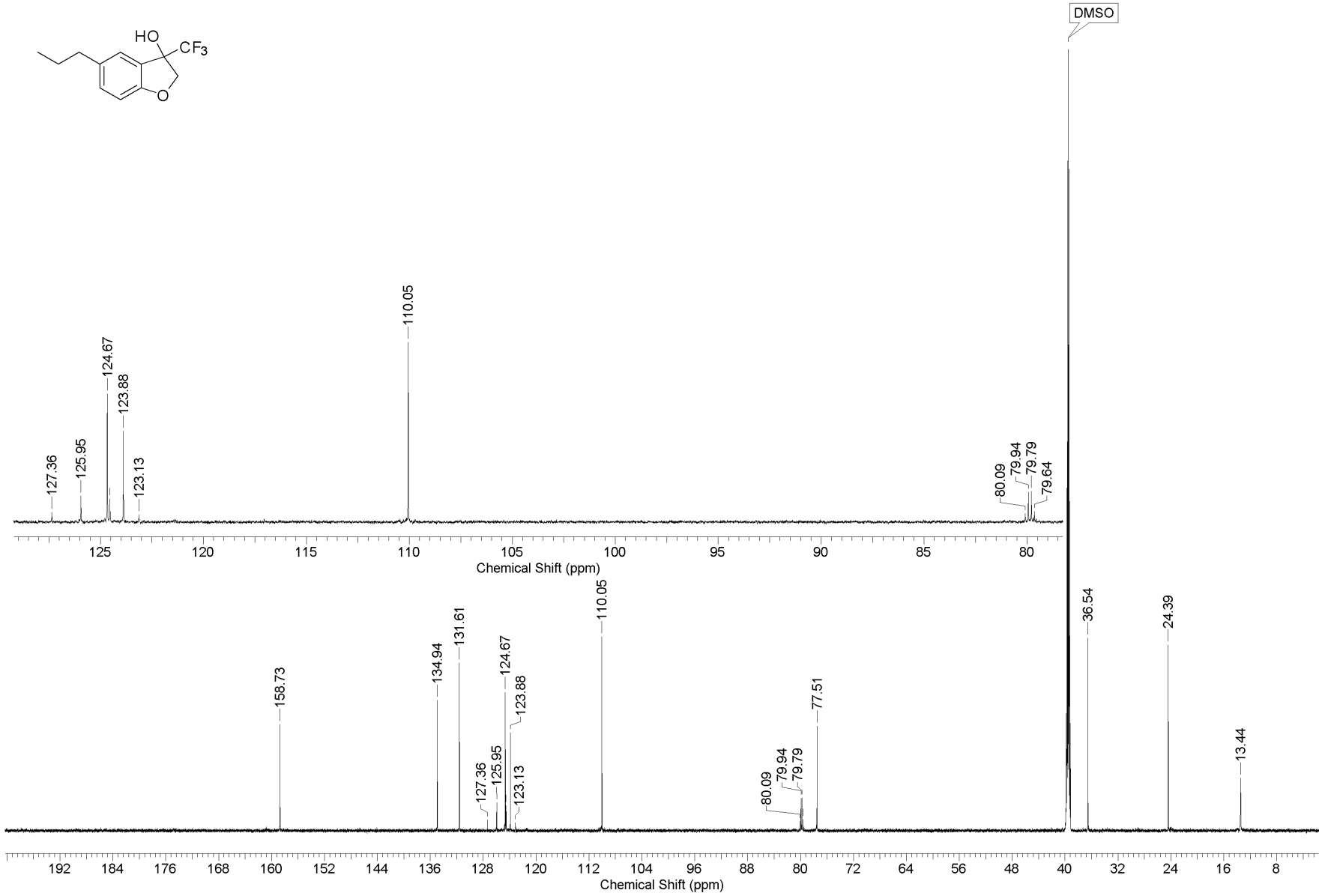

HO
CF3
O
DMSO
109.83
125.02
129.75
130.67
126.91
123.15
119.39
80.34
79.94
79.54
79.14
Chemical Shift (ppm)
131.89
109.83
125.02
20.02
77.35
158.38
129.75
126.91
123.15
119.39
80.34
79.94
79.54
Chemical Shift (ppm)

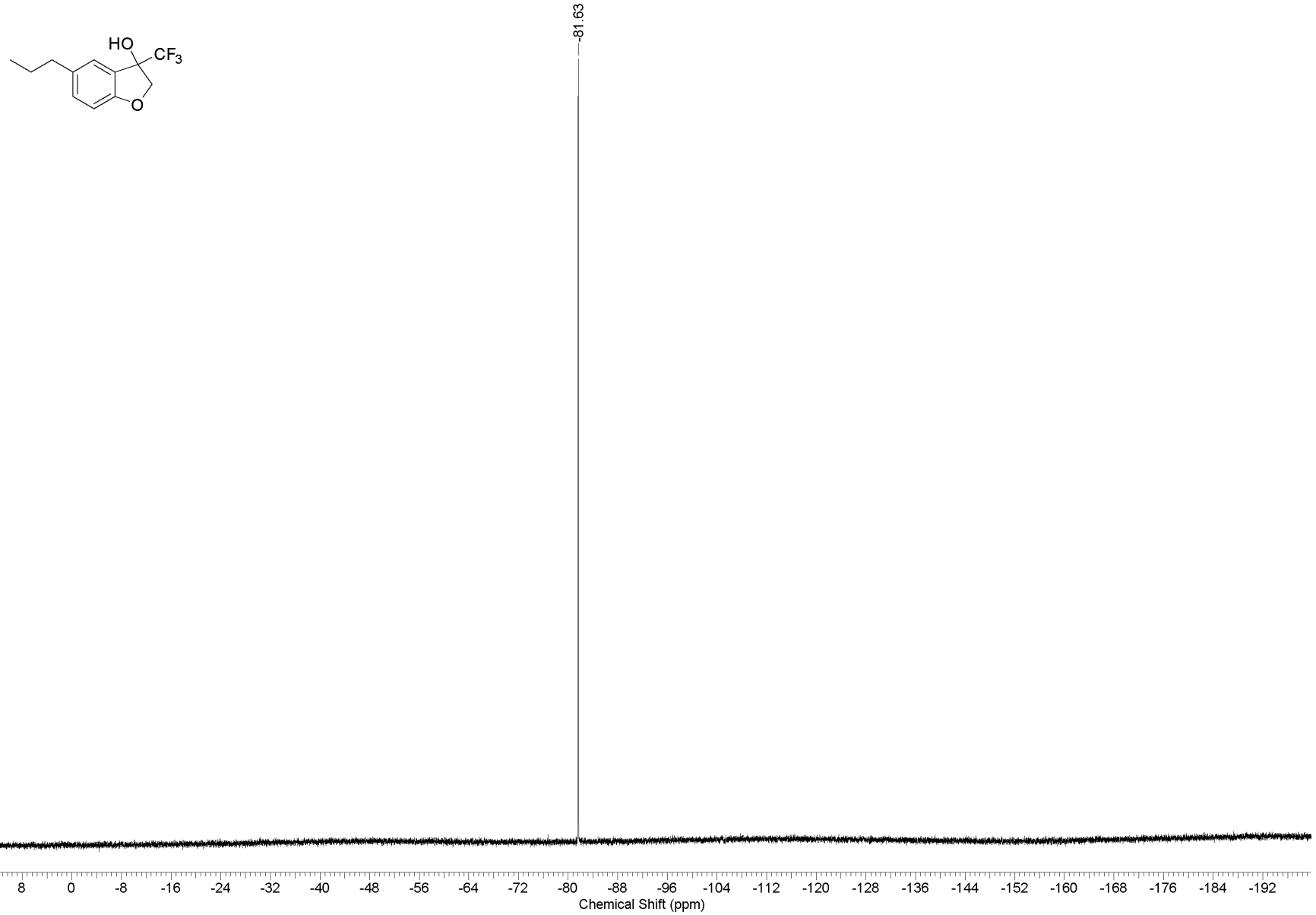

HO
CF3
O

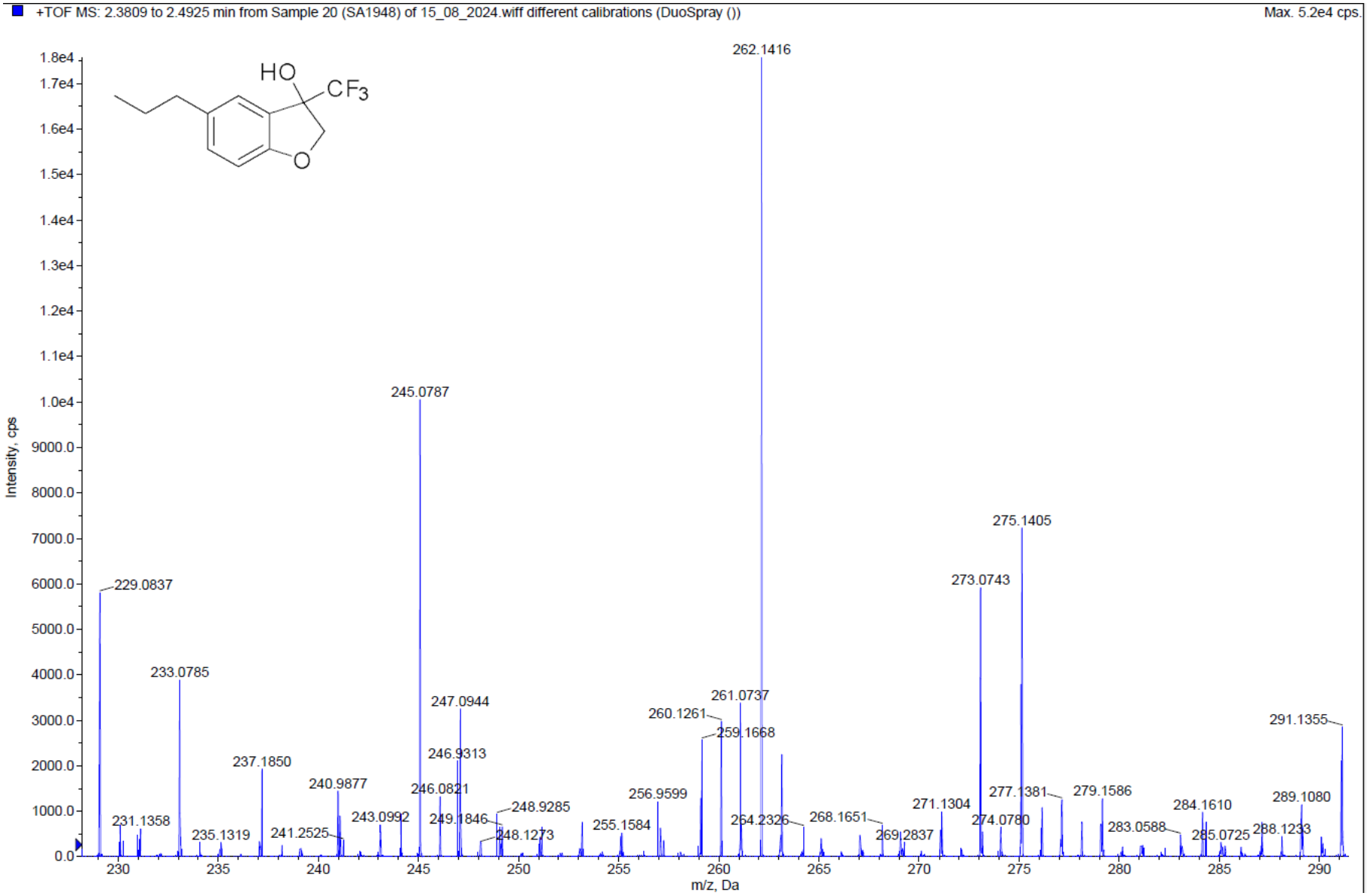
-81.63
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
-200
Chemical Shift (ppm)

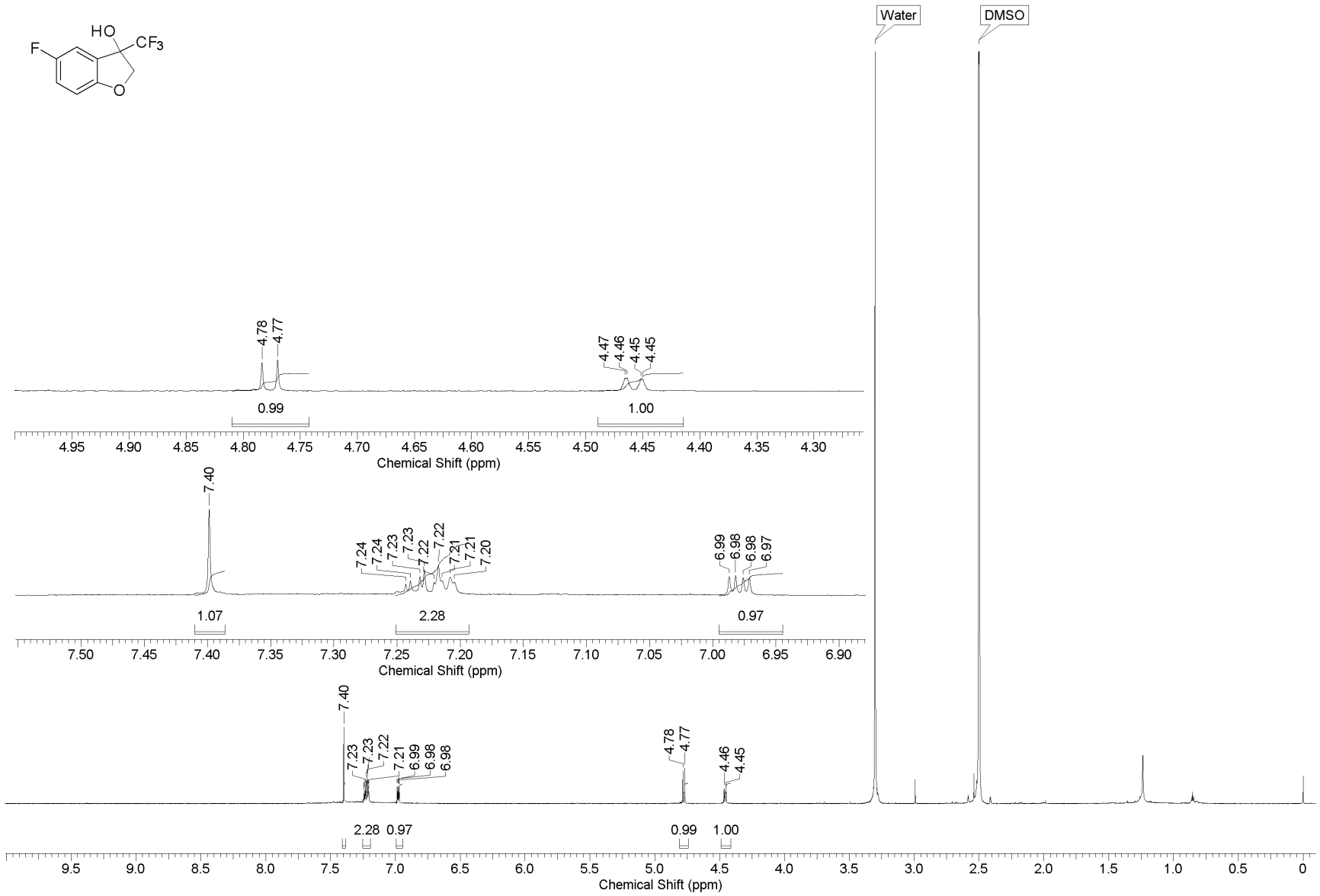

+TOF MS: 0.9295 to 1.0411 min from Sample 35 (SA1881) of 19_06_2024.wiff different calibrations (DuoSpray ())
Max. 9.6e4 cps.
HO
CF3
O
218.0506
219.0620
219.1742
219.0129
219.0949
220.0659
221.0810
221.0058
221.1171
222.0934
223.0640
Intensity, cps
m/z, Da

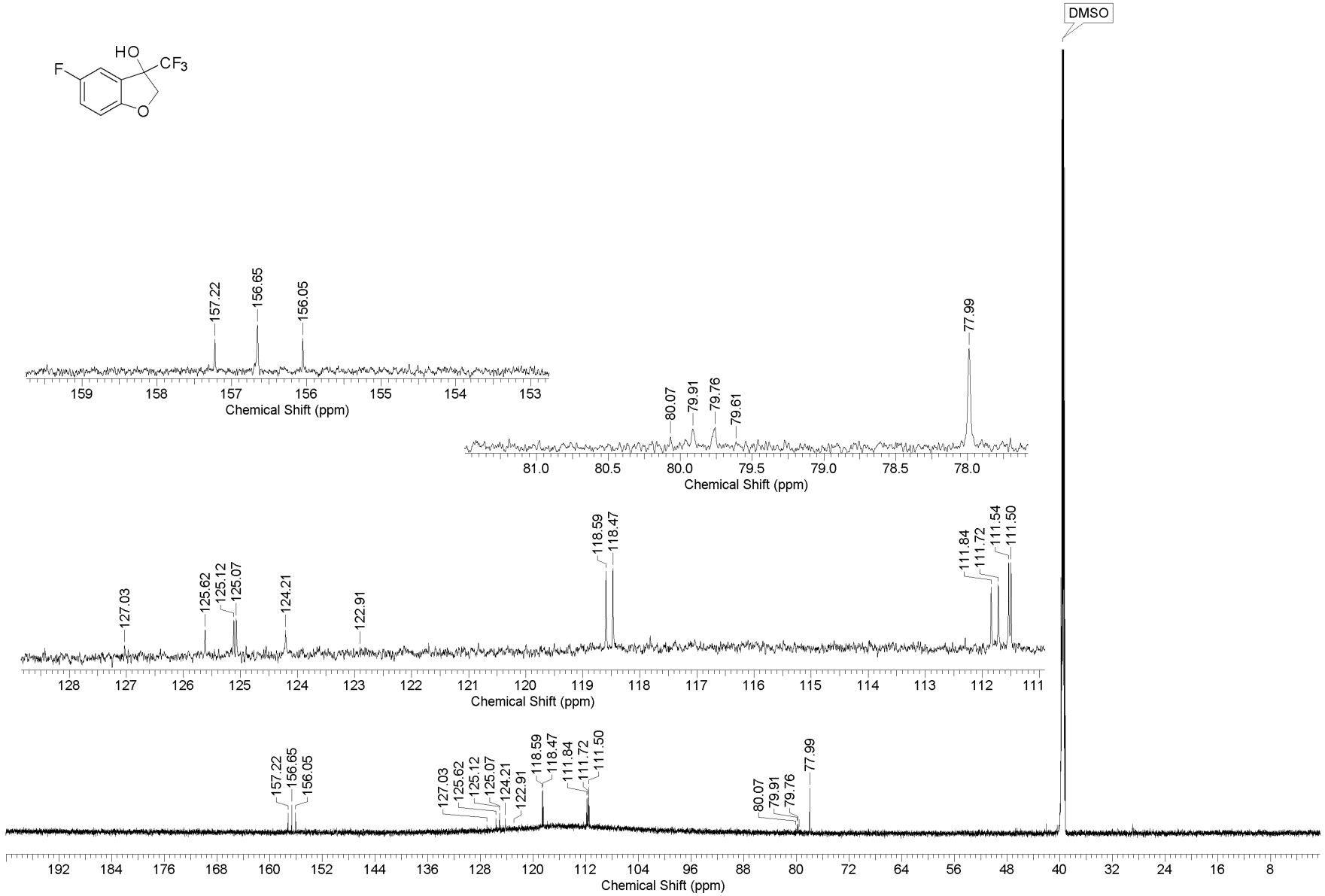

HO
CF3
O
CHCl3
CHCl3
7.25
7.19
7.18
6.84
6.83
0.97
0.94
1.02
Chemical Shift (ppm)
4.74
4.73
4.52
4.51
2.60
2.59
2.58
2.57
2.56
2.55
1.65
1.64
1.63
1.62
1.61
1.60
0.95
0.95
0.94
1.07
1.05
2.00
2.45
3.09
Chemical Shift (ppm)
Chemical Shift (ppm)

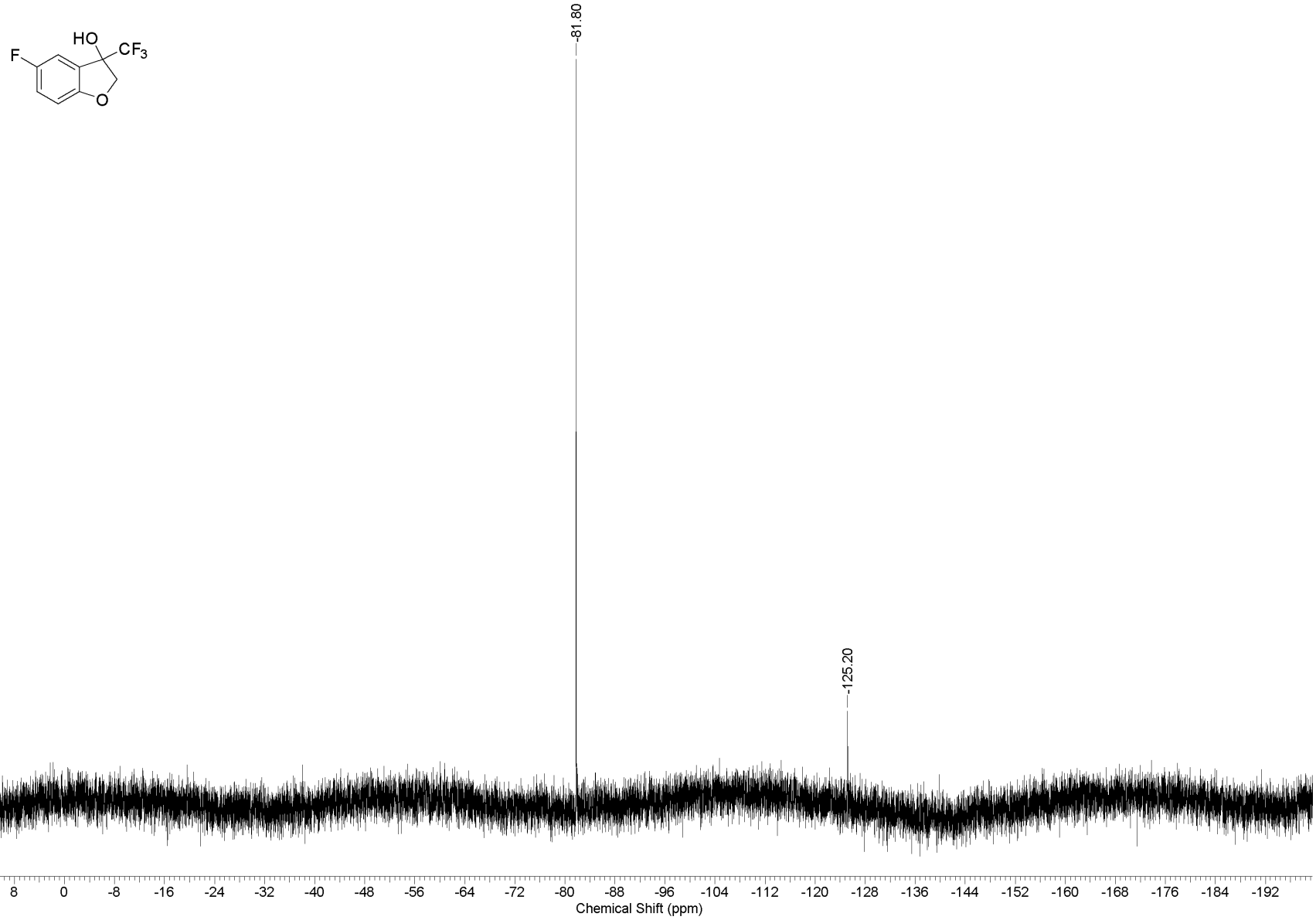

HO
CF3
O
DMSO
127.36
125.95
124.67
123.88
123.13
110.05
80.09
79.94
79.79
79.64
Chemical Shift (ppm)
158.73
134.94
131.61
124.67
123.88
110.05
77.51
36.54
24.39
13.44
Chemical Shift (ppm)

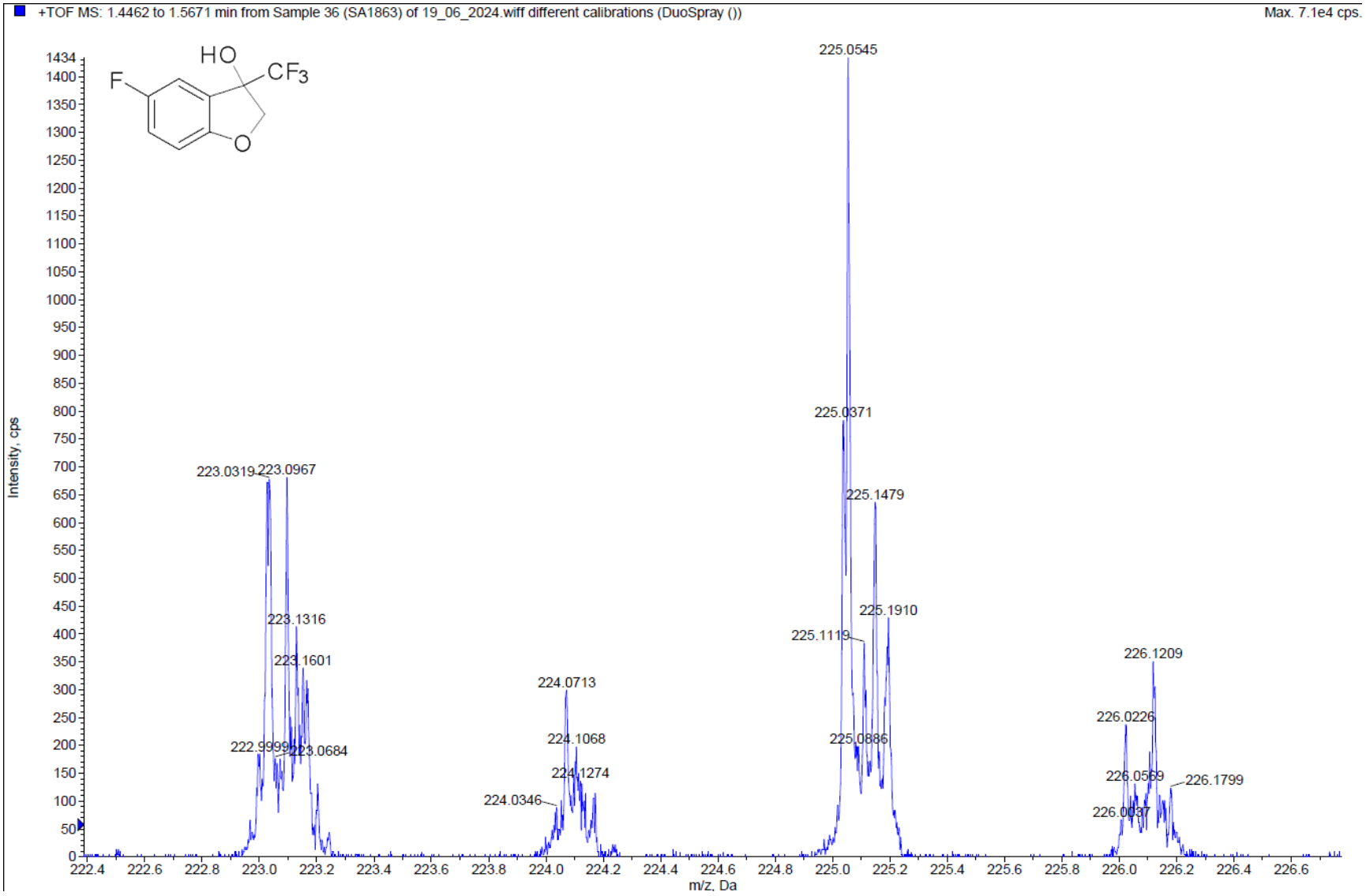

HO
CF3
O
-81.63
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

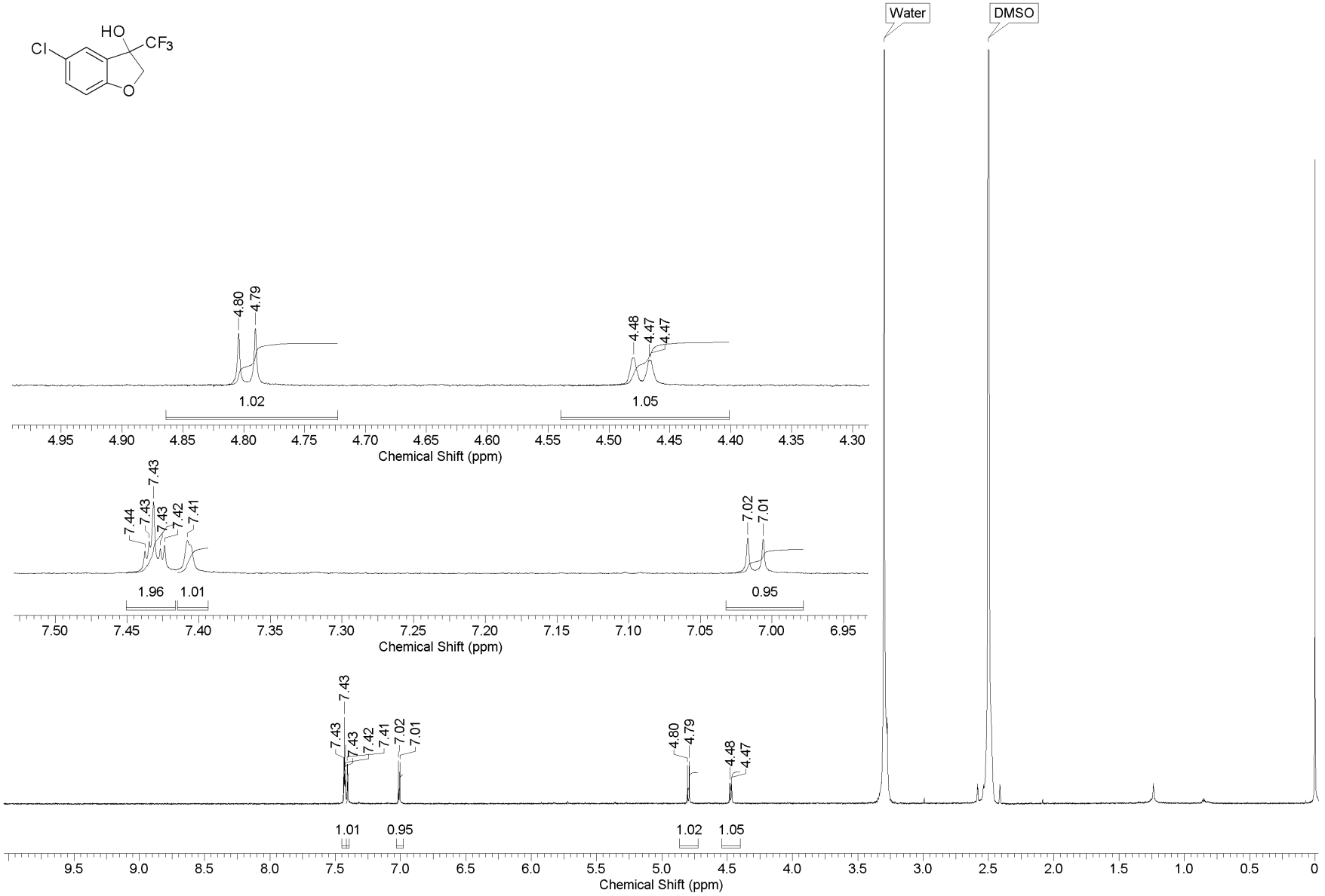

+TOF MS: 2.3809 to 2.4925 min from Sample 20 (SA1948) of 15_08_2024.wiff different calibrations (DuoSpray ())
Max. 5.2e4 cps.
HO
CF3
O
Intensity, cps
m/z, Da
262.1416
245.0787
275.1405
229.0837
273.0743
233.0785
247.0944
261.0737
260.1261
259.1668
246.9313
237.1850
240.9877
246.0821
256.9599
291.1355
248.9285
271.1304
277.1381
279.1586
289.1080
284.1610
231.1358
243.0992
249.1846
255.1584
264.2326
268.1651
274.0780
283.0588
235.1319
241.2525
248.1273
269.2837
285.0725
288.1233

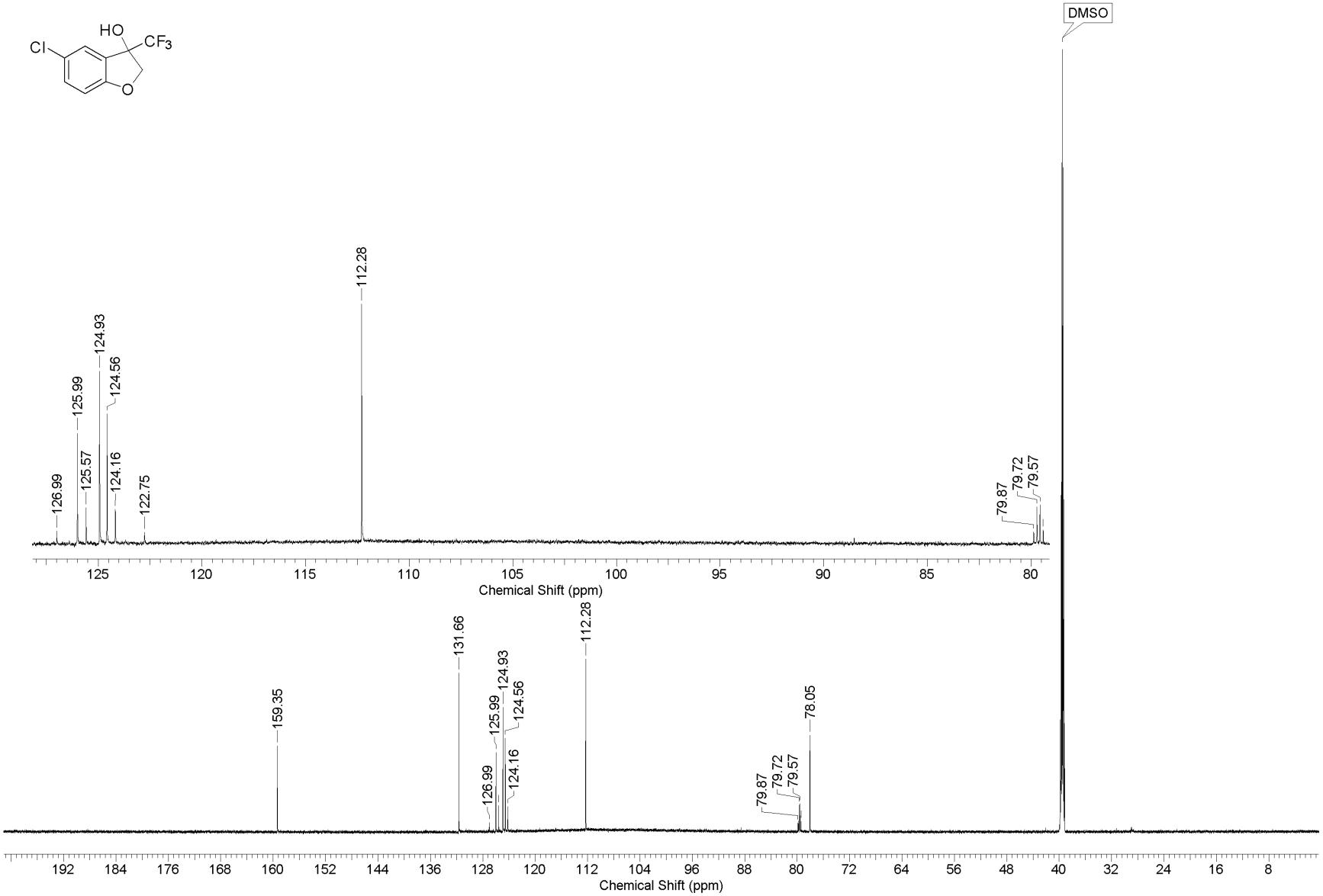

HO
CF3
F
O
Water
DMSO
4.78
4.77
4.47
4.46
4.45
4.45
0.99
1.00
Chemical Shift (ppm)
7.40
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
6.99
6.98
6.98
6.97
1.07
2.28
0.97
Chemical Shift (ppm)
7.40
7.23
7.23
7.22
7.21
6.99
6.98
6.98
4.78
4.77
4.46
4.45
2.28
0.97
0.99
1.00
Chemical Shift (ppm)

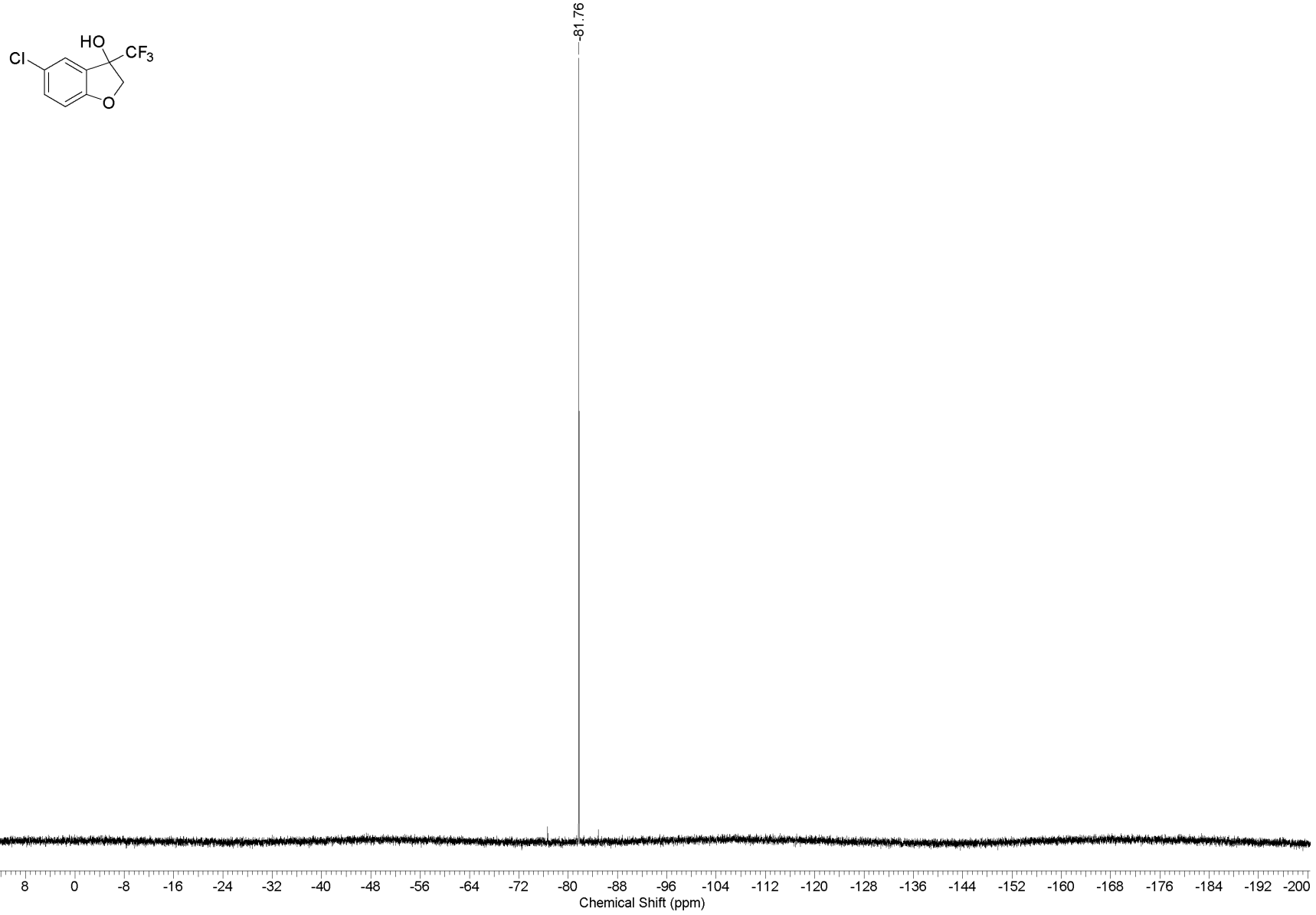

HO
CF3
F
O
DMSO
157.22
156.65
156.05
159
158
157
156
155
154
153
Chemical Shift (ppm)
77.99
80.07
79.91
79.76
79.61
81.0
80.5
80.0
79.5
79.0
78.5
78.0
Chemical Shift (ppm)
118.59
118.47
111.84
111.72
111.54
111.50
127.03
125.62
125.12
125.07
124.21
122.91
128
127
126
125
124
123
122
121
120
119
118
117
116
115
114
113
112
111
Chemical Shift (ppm)
157.22
156.65
156.05
127.03
125.62
125.12
125.07
124.21
122.91
118.59
118.47
111.84
111.72
111.50
80.07
79.91
79.76
77.99
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

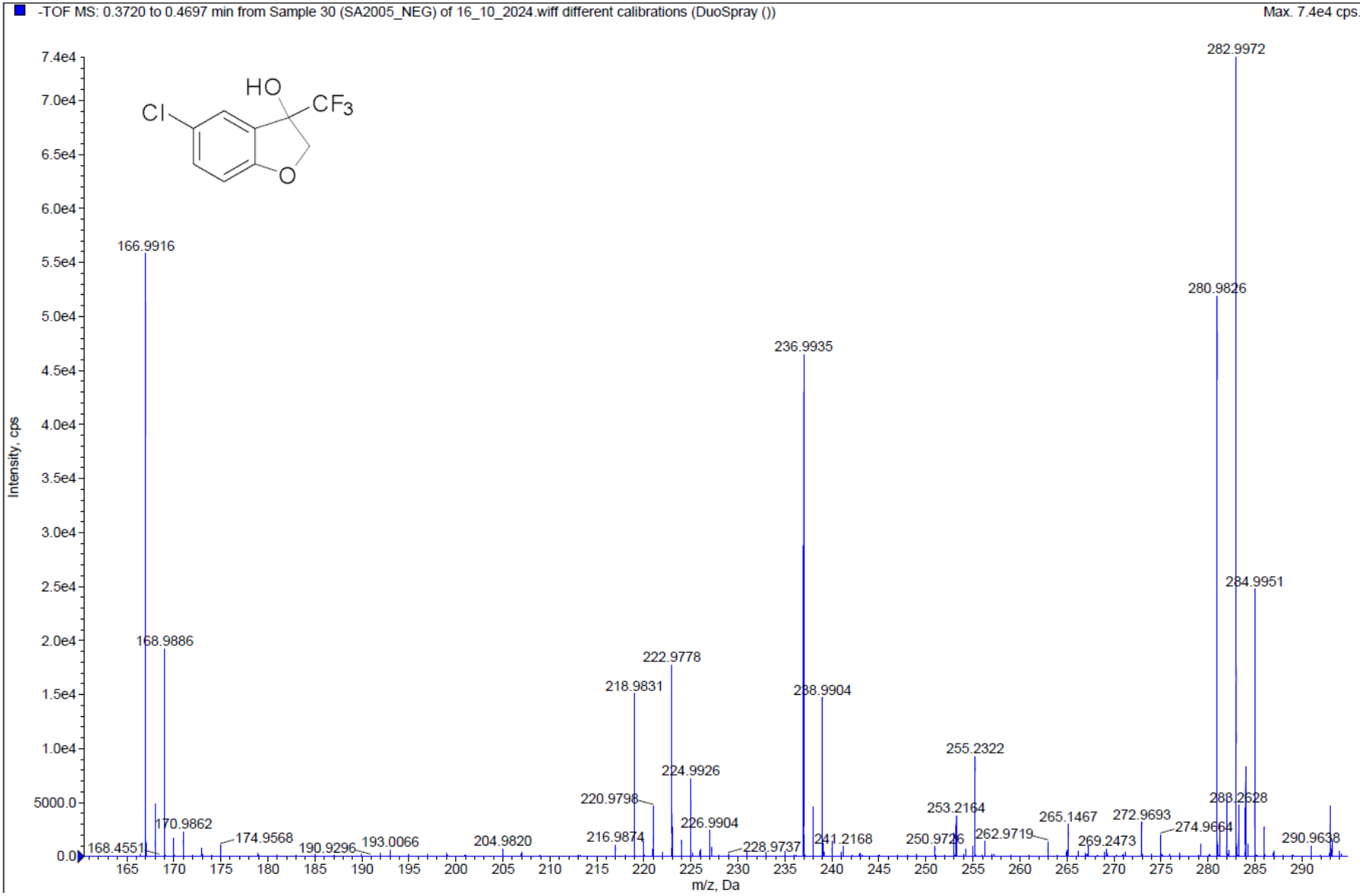

HO
CF3
F
O
-81.80
-125.20
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
Chemical Shift (ppm)

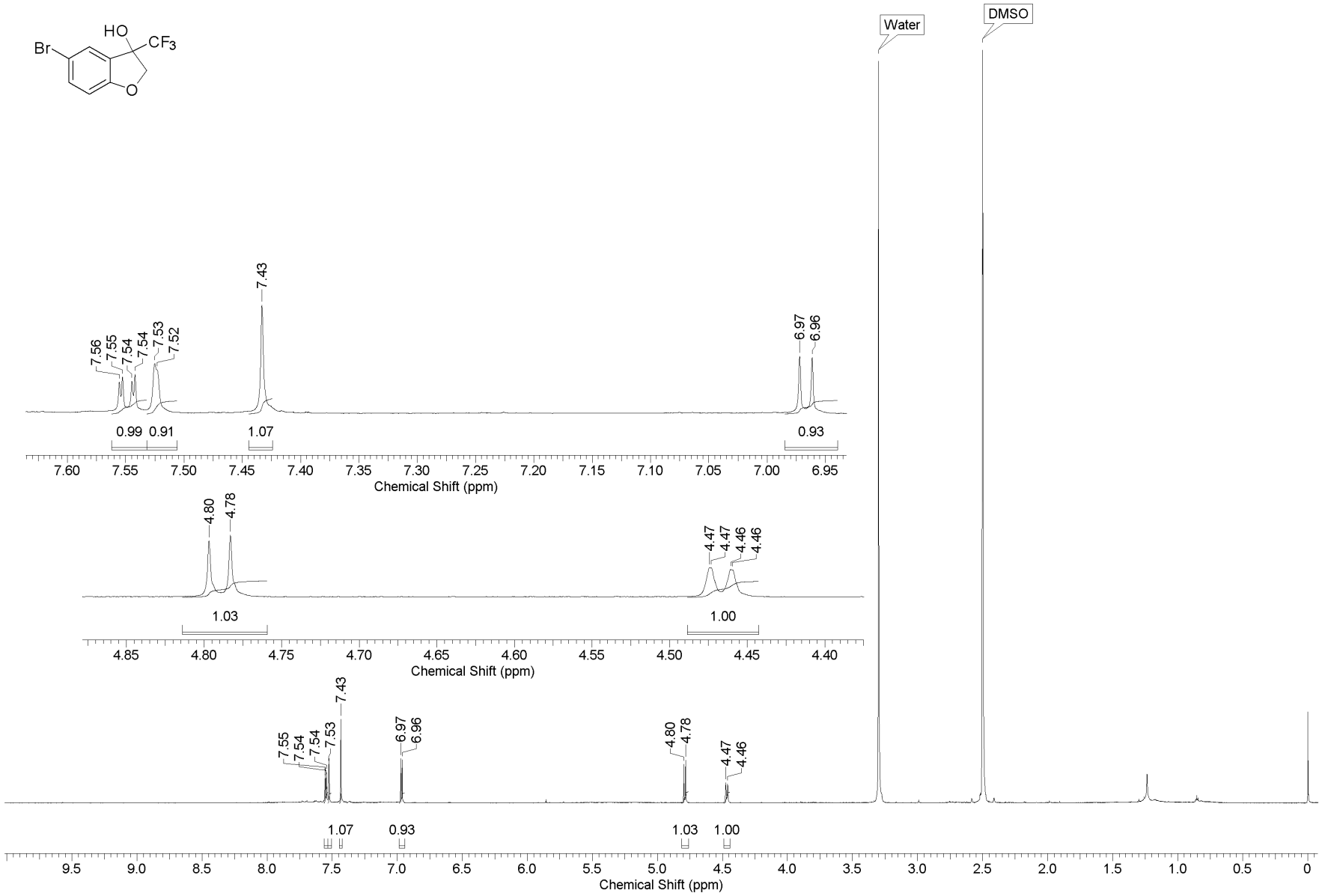

+TOF MS: 1.4462 to 1.5671 min from Sample 36 (SA1863) of 19_06_2024.wiff different calibrations (DuoSpray ())
Max. 7.1e4 cps.
HO
CF3
F
O
Intensity, cps
m/z, Da
225.0545
225.0371
225.1479
225.1910
225.1119
225.0886
223.0319
223.0967
223.1316
223.1601
222.9999
223.0684
224.0713
224.1068
224.1274
224.0346
226.1209
226.0226
226.0569
226.1799
226.0037

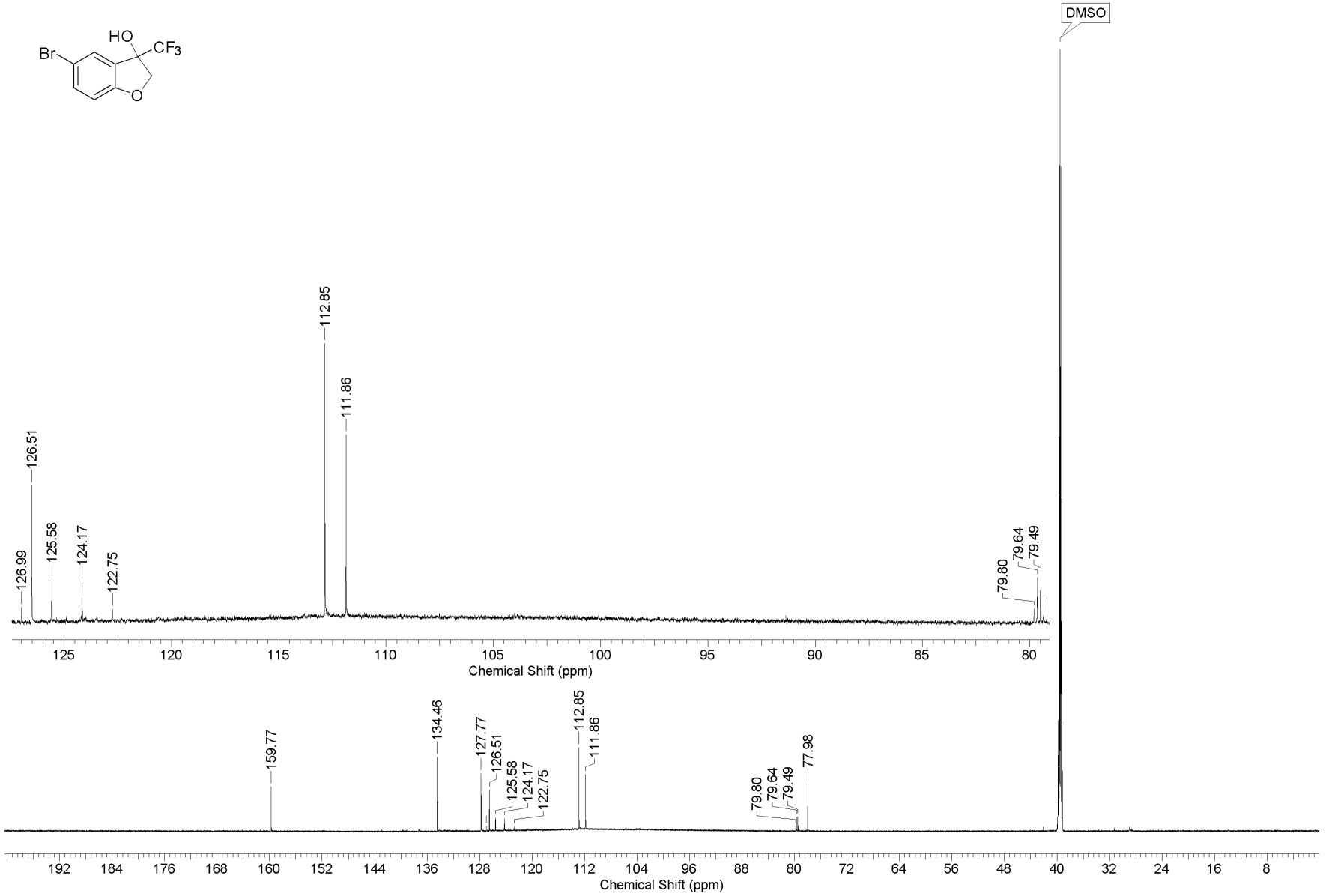

HO
CF3
Cl
O
Water
DMSO
4.80
4.79
4.48
4.47
4.47
1.02
1.05
Chemical Shift (ppm)
7.44
7.43
7.43
7.43
7.42
7.41
7.02
7.01
1.96
1.01
0.95
Chemical Shift (ppm)
7.43
7.43
7.43
7.42
7.41
7.02
7.01
4.80
4.79
4.48
4.47
1.01
0.95
1.02
1.05
Chemical Shift (ppm)

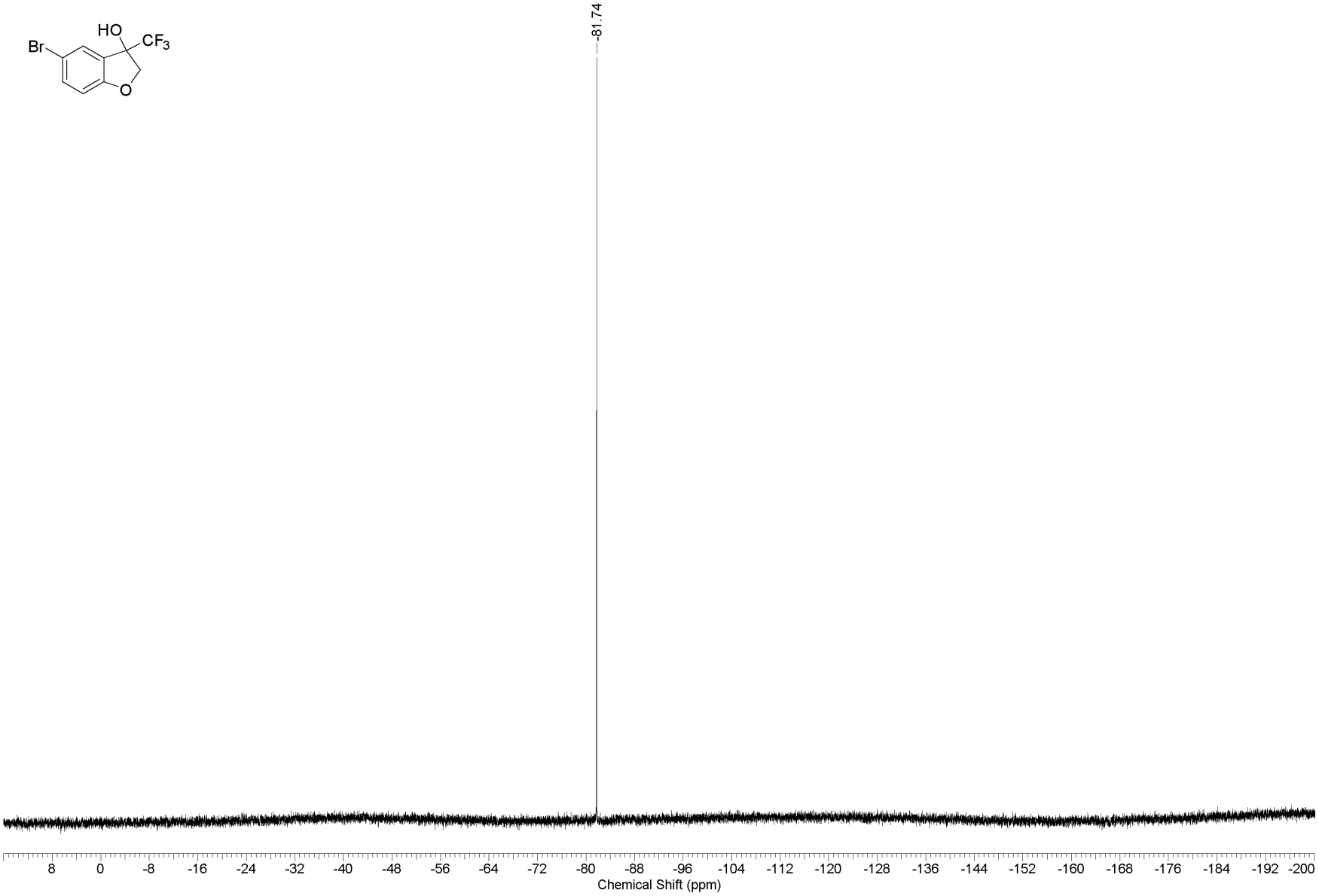

HO
CF3
Cl
O
DMSO
112.28
124.93
125.99
124.56
124.16
126.99
125.57
122.75
79.87
79.72
79.57
Chemical Shift (ppm)
131.66
159.35
112.28
124.93
125.99
124.56
124.16
126.99
78.05
79.87
79.72
79.57
Chemical Shift (ppm)

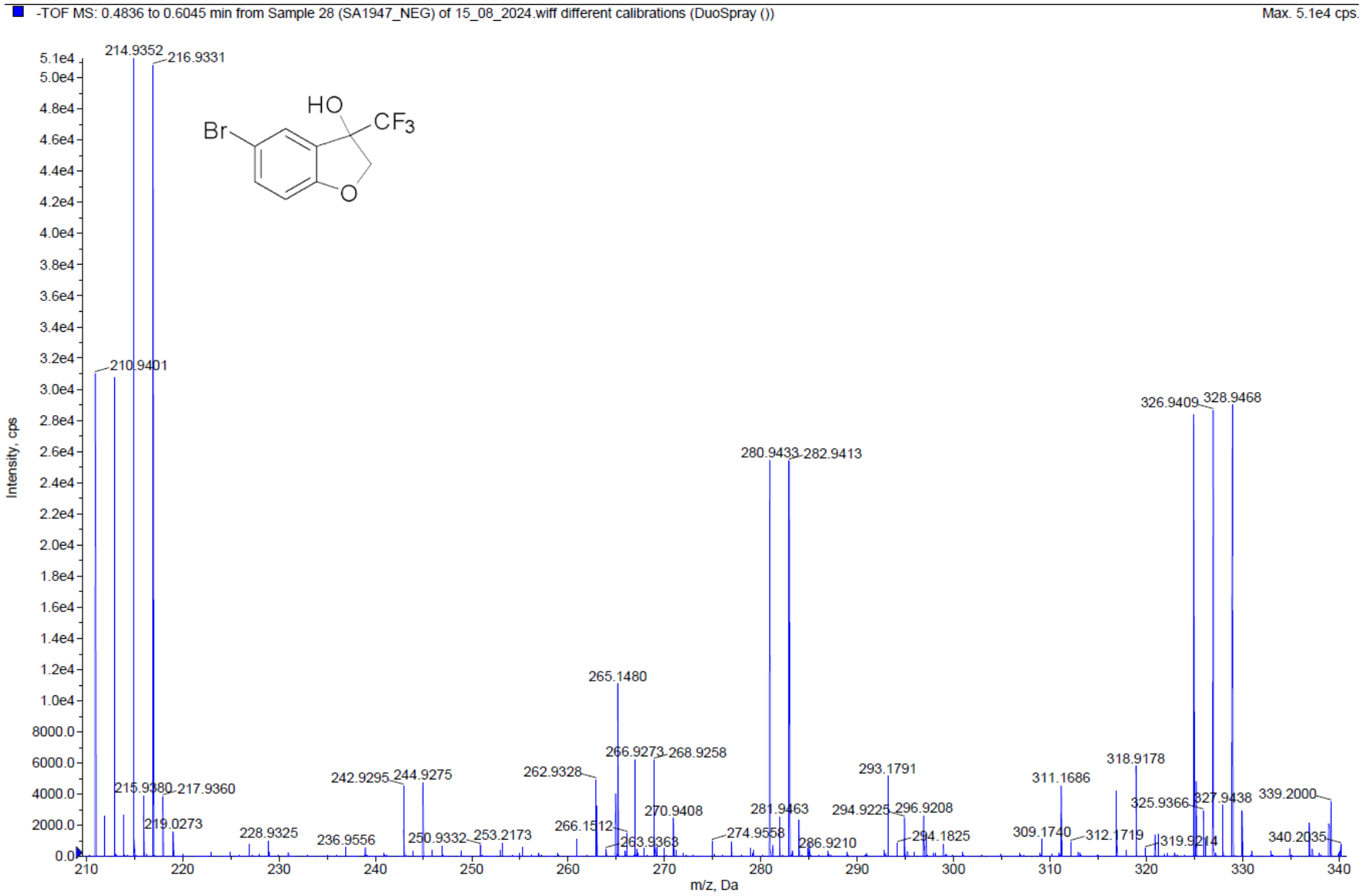

HO
CF3
Cl
O
-81.76
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
-200
Chemical Shift (ppm)


-TOF MS: 0.3720 to 0.4697 min from Sample 30 (SA2005_NEG) of 16_10_2024.wiff different calibrations (DuoSpray ())
Max. 7.4e4 cps.
Intensity, cps
m/z, Da
HO
CF3
Cl
O
282.9972
166.9916
280.9826
236.9935
284.9951
168.9886
222.9778
218.9831
238.9904
255.2322
224.9926
220.9798
253.2164
288.2628
226.9904
265.1467
272.9693
170.9862
274.9664
216.9874
262.9719
290.9638
174.9568
269.2473
168.4551
190.9296
193.0066
204.9820
228.9737
241.2168
250.9726


HO
CF3
Br
O
Water
DMSO
7.56
7.55
7.54
7.54
7.53
7.52
7.43
6.97
6.96
0.99
0.91
1.07
0.93
Chemical Shift (ppm)
4.80
4.78
4.47
4.47
4.46
4.46
1.03
1.00
Chemical Shift (ppm)
7.55
7.54
7.54
7.53
7.43
6.97
6.96
4.80
4.78
4.47
4.46
1.07
0.93
1.03
1.00
Chemical Shift (ppm)


HO
CF3
Br
O
DMSO
112.85
111.86
126.51
125.58
124.17
122.75
126.99
79.80
79.64
79.49
125
120
115
110
105
100
95
90
85
80
Chemical Shift (ppm)
159.77
134.46
127.77
126.51
125.58
124.17
122.75
112.85
111.86
79.80
79.64
79.49
77.98
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


HO
CF3
Br
O
-81.74
8
0
-8
-16
-24
-32
-40
-48
-56
-64
-72
-80
-88
-96
-104
-112
-120
-128
-136
-144
-152
-160
-168
-176
-184
-192
-200
Chemical Shift (ppm)


-TOF MS: 0.4836 to 0.6045 min from Sample 28 (SA1947_NEG) of 15_08_2024.wiff different calibrations (DuoSpray ())
Max. 5.1e4 cps.
Intensity, cps
m/z, Da
HO
CF3
Br
O
214.9352
216.9331
210.9401
326.9409
328.9468
280.9433
282.9413
265.1480
266.9273
268.9258
242.9295
244.9275
262.9328
293.1791
318.9178
311.1686
215.9380
217.9360
219.0273
228.9325
236.9556
250.9332
253.2173
266.1512
263.9363
270.9408
281.9463
294.9225
296.9208
274.9558
286.9210
294.1825
309.1740
312.1719
319.9214
325.9366
327.9438
339.2000
340.2035