Supporting Information

Facile Friedel-Crafts alkylation of arenes under solvent-free conditions

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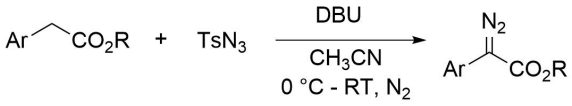
1. General information

^{1}H, ^{13}C, ^{19}F NMR spectra were recorded on Bruker advance III 400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 376 MHz for ^{19}F). All chemical shifts were reported in units with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts. The data contained properties such as chemical shift, multiplicity, peaks and coupling constants. High Resolution Mass Spectra (HRMS-ESI) were obtained on an Ultra-high-resolution electro-spray time-of-flight mass spectrometer. GC-MS analysis was performed on the agilent GC-MS 2010 spectrometer or GC-MS-QP2020 NX. The starting materials were purchased from J&K Chemicals, Macklin, Energy Chemical or TCI and used as received. Thin-layer chromatography (TLC) was performed using 300 mesh silica gel plates visualized with short-wavelength UV light (254 nm).

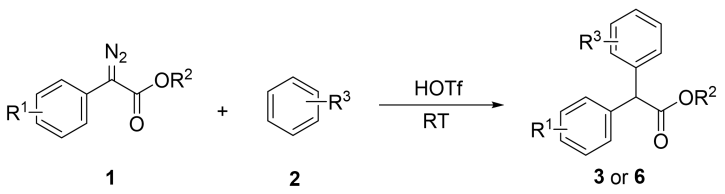
2. Experimental details

Preparation of Starting Aryldiazoacetates



Under N_2 conditions, aryl acetate (1.0 equiv, 10 mmol) and *p*-toluenesulfonate azide (1.2 equiv, 12 mmol) were dissolved in 30 mL of anhydrous acetonitrile. Stir the solution under an ice water bath and add DBU (1.2 equiv, 12 mmol). The solution gradually turns orange, is transferred to room temperature for the reaction overnight, and quenches the reaction with saturated NH_4Cl (100 mL). The organic phase was extracted with EA (30 mL x 3), the organic phase was combined, the organic phase was dried with anhydrous Na_2SO_4, and then concentrated to obtain an orange oily crude product, and then quickly passed through the silica gel column with PE/EA = 15 : 1 to obtain aryl diazoacetate.[1] **Caution**: On this scale and under these conditions no explosions occurred. Nevertheless, it should be emphasized that diazo compounds are generally unstable in nature and are potentially explosive.

Preparation of diaryl acetate 3 or 6.



First, the aryl diazoacetate **1** (1.0 equiv, 0.3 mmol) and aromatic hydrocarbons **2** (3.0 equiv, 0.9 mmol) are weighed into a glass reaction tube, then HOTf (2.0 equiv, 0.6 mmol) is carefully and slowly added, the reaction is stirred at room temperature for 30 minutes, 1 mL of EA is added to the reaction tube for dilution, then saturated $NaHCO_3$ is added to neutralize to pH = 6 - 7, and then extracted with EA (20 mL × 3). The organic phase was collected and dried with Na_2SO_4, the

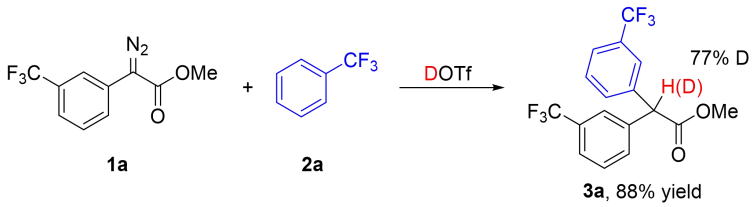
organic phase was concentrated to obtain a crude product, and the purified diaryl acetate **3 or 6** was further obtained with PE/EA = 20 : 1 over the silica gel column.

Synthesis of DOTf.[6]

Add Tf_2O (1.05 equiv, 92.9 mmol, 15.6 mL) to a Schlenk tube under a nitrogen atmosphere, and then transfer the vial to an ice water bath and add D_2O dropwise (88.5 mmol, 1.6 mL). After that, reflux (85 °C) was carried out under anhydrous and oxygen-free, nitrogen protected conditions, reacted for 15 h, and then distilled at 120 °C under reduced pressure (50 mbar) to obtain DOTf as a colorless liquid.

3. Mechanism experiment

Deuterium experiment



1a (1.0 equiv, 0.3 mmol) and **2a** (3 equiv, 0.9 mmol) are weighed into a glass reaction tube, then DOTf (2.0 equiv, 0.6 mmol) is carefully and slowly added, the reaction is stirred at room temperature for 30 minutes, 1 mL of EA is added to the reaction tube for dilution, then saturated $NaHCO_3$ is added to neutralize to pH = 6 - 7, and then extracted with EA (20 mL × 3). The organic phase was collected and dried with Na_2SO_4, the organic phase was concentrated to obtain a crude product.The mixture was purified by column chromatography on silica gel using PE/EA = 20 : 1 as the eluent to afford the product **3a** in 88% yield (figure S1).

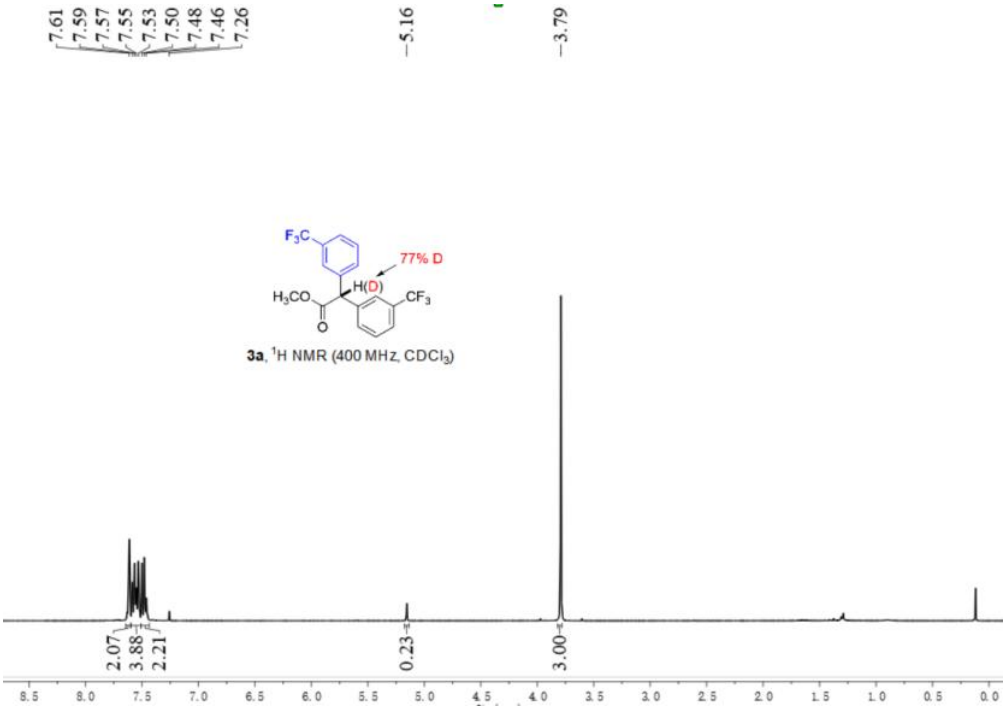
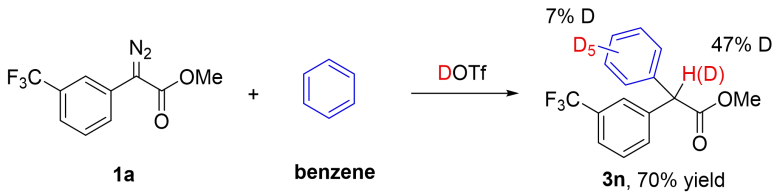


Figure S1. ^1H NMR spectrum of **3a-D**.



1a (1.0 equiv, 0.3 mmol) and **benzene** (3.0 equiv, 0.9 mmol) are weighed into a glass reaction tube, then DOTf (2.0 equiv, 0.6 mmol) is carefully and slowly added, the reaction is stirred at room temperature for 30 minutes, 1 mL of EA is added to the reaction tube for dilution, then saturated $NaHCO_3$ is added to neutralize to pH = 6 - 7, and then extracted with EA (20 mL × 3). The organic phase was collected and dried with Na_2SO_4, the organic phase was concentrated to obtain a crude product.The mixture was purified by column chromatography on silica gel using PE/EA = 20:1 as the eluent to afford the product **3m** in 70% yield (figure S2).

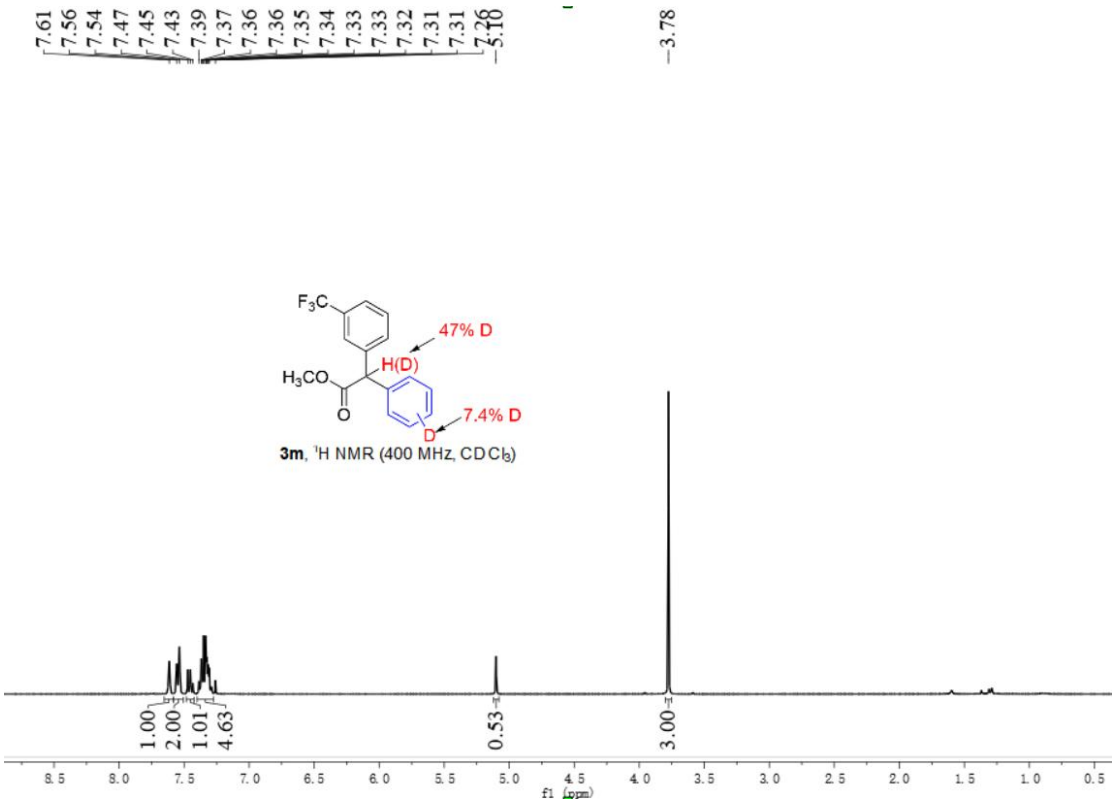
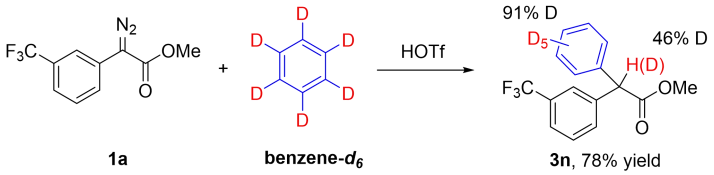


Figure S2. ^{1}H NMR spectrum of **3m-D**.



1a (1.0 equiv, 0.3 mmol) and **benzene-*d*$_6$** (3.0 equiv, 0.9 mmol) are weighed into a glass reaction tube, then DOTf (2.0 equiv, 0.6 mmol) is carefully and slowly added, the reaction is stirred at

room temperature for 30 minutes, 1 mL of EA is added to the reaction tube for dilution, then saturated $NaHCO_3$ is added to neutralize to pH = 6 - 7, and then extracted with EA (20 mL × 3). The organic phase was collected and dried with Na_2SO_4, the organic phase was concentrated to obtain a crude product.The mixture was purified by column chromatography on silica gel using PE/EA = 20 : 1 as the eluent to afford the product **3m** in 78% yield (figure S3).

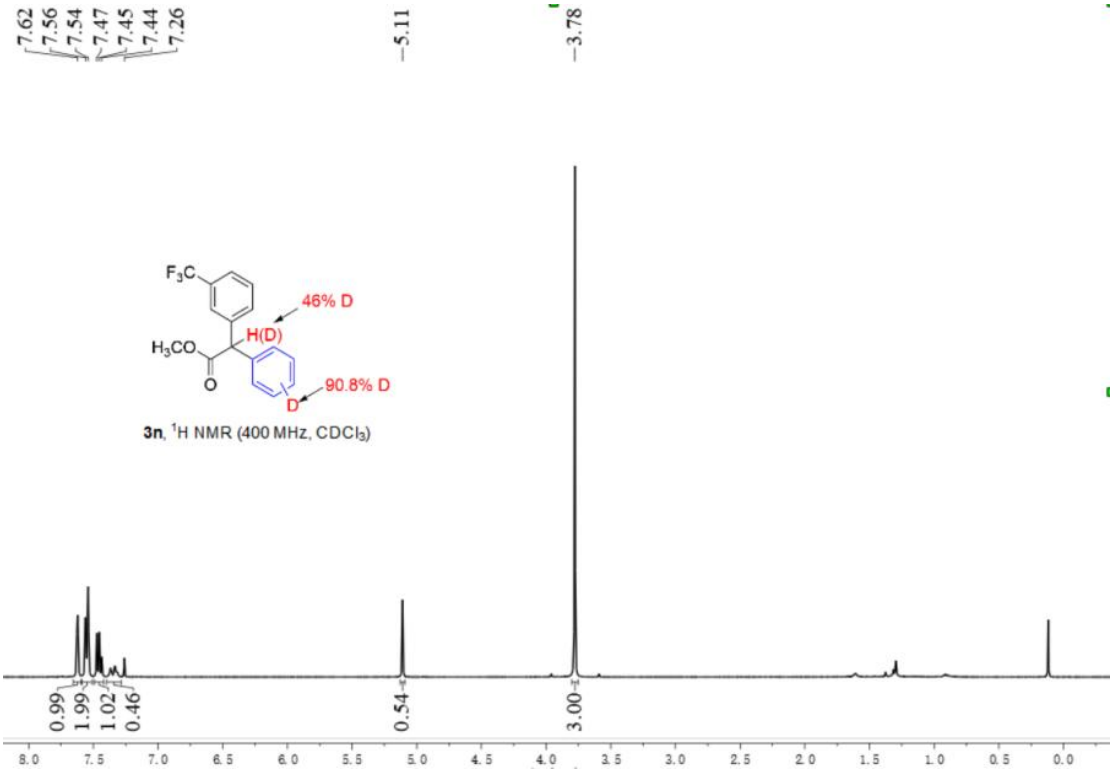
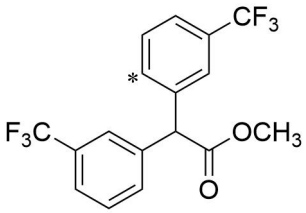


Figure S3. ^{1}H NMR spectrum of **3m-D**.

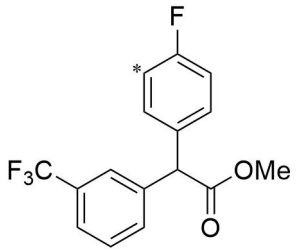
4. Characterization data



3a (*m* : *p* = 7 : 1): Yield 88 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (s, 2H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 5.16 (s, 1H), 3.65 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 171.9, 138.9, 132.1, 131.4 (q, *J* = 32.5 Hz), 129.5, 125.5 (q, *J* = 3.8 Hz), 124.8 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 273.71 Hz), 56.5, 52.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.82, -62.84.

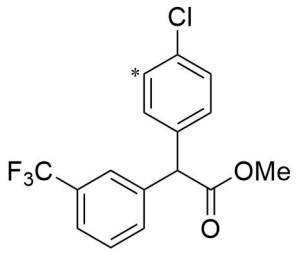
HRMS (ESI): m/z calcd for $C_{17}H_{12}O_2F_6$ $[M+ Na]^+$: 385.0633, found 385.0631.



3b (*p* : *o* = 2.7 : 1): Yield 77 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 - 7.43 (m, 5H), 7.31 - 7.23 (m, 3H), 7.14 - 7.07 (m, 1H), 7.06 - 7.99 (m, 2H), 5.05 (s, 1H), 3.77 (s, 1H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.4, 163.6, 161.1, 139.6, 133.7 (d, J = 3.2 Hz), 132.3, 132.1, 131.2 (q, J = 32.32 Hz), 131.1 (q, J = 32.32 Hz), 130.3 (d, J = 8.1 Hz), 129.7 (d, J = 3.4 Hz), 129.6 (d, J = 8.4 Hz), 129.3, 125.8 (q, J = 3.8 Hz), 125.4 (q, J = 3.9 Hz), 124.6 (tt, J_1 = 7.5 Hz, J_2 = 3.7 Hz), 124.1 (q, J = 273.71 Hz), 116.0, 115.8, 56.0, 52.7, 49.7 . **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.59, -62.60, -114.60, -116.68.

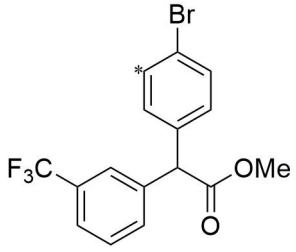
HRMS (ESI): m/z calcd for $C_{16}H_{12}O_2F_4$ $[M+ NH_4]^+$: 330.1116, found 330.1111.



3c (*p* : *o* = 2.4 : 1): Yield 70 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (d, J = 8.9 Hz, 1H), 7.50-7.44 (m, 3H), 7.43-7.38 (m, 1H), 7.33-7.30 (m, 2H), 7.28-7.21 (m, 3H), 5.04 (s, 1H), 3.77 (s, 2H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.1, 139.3, 136.4, 133.9, 132.5, 132.1, 131.2 (q, J = 32.32 Hz), 131.1 (q, J = 32.32 Hz), 130.0, 129.8, 129.4, 129.2, 127.3, 125.9 (q, J = 3.8 Hz), 125.4 (q, J = 4.04 Hz), 124.6 (q, J = 3.03 Hz), 124.1 (q, J = 273.71 Hz), 124.0 (q, J = 273.71 Hz), 56.11, 53.51, 52.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.58, -62.60.

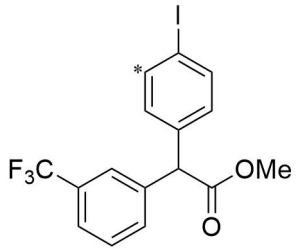
HRMS (ESI): m/z calcd for $C_{16}H_{12}O_2ClF_3$ $[M+ H]^+$: 329.0550, found 329.0557.



3d (*p* : *o* = 2.6 : 1) : Yield 76 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 - 7.54 (m, 3H), 7.51 - 7.44 (m, 5H), 7.33 - 7.27 (m, 1H), 7.19 - 7.16 (m, 2H), 5.03 (s, 1H), 3.78 (s, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.0, 139.2, 136.9, 133.4, 132.5, 132.1, 132.0, 131.2 (q, *J* = 32.32 Hz), 131.1 (q, *J* = 32.32 Hz), 130.3, 130.0, 129.4, 129.2, 128.0, 125.9 (q, *J* = 3.7 Hz), 125.5 (q, *J* = 4.40 Hz), 125.1, 124.6 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 273.7 Hz), 124.0 (q, *J* = 273.71 Hz), 124.1 (q, *J* = 273.71 Hz), 122.0, 56.2, 52.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.56, -62.58.

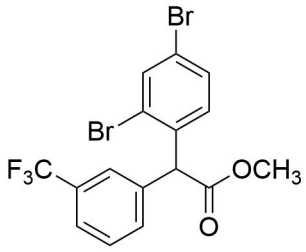
HRMS (ESI): m/z calcd for $C_{16}H_{12}O_2BrF_3$ $[M+ NH_4]^+$: 390.0311, found 390.0307.



3e (*p* : *o* = 2.9 : 1) : Yield 80 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 6.8 Hz, 2H), 7.58 - 7.55 (m, 2H), 7.51 - 7.46 (m, 2H), 7.37 - 7.29 (m, 1H), 7.07 (d, *J* = 7.1 Hz, 2H), 5.03 (s, 1H), 3.78 (s, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.0, 140.3, 139.1, 138.1, 137.6, 137.0, 132.5, 131.2 (q, *J* = 32.32 Hz), 131.1 (q, *J* = 32.32 Hz), 130.6, 129.5, 129.2, 128.8, 126.0 (q, *J* = 3.8 Hz), 125.4 (q, *J* = 3.03 Hz), 124.6 (q, *J* = 4.04 Hz), 124.0 (q, *J* = 273.71 Hz), 124.1 (q, *J* = 273.71 Hz), 101.7, 93.5, 60.7, 56.3, 52.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.49, -62.51.

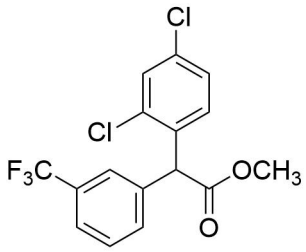
HRMS (ESI): m/z calcd for $C_{16}H_{12}O_2F_3I$ $[M+ Na]^+$: 442.9726, found 442.9725.



3f: Yield 78 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, *J* = 2.0 Hz, 1H), 7.58 (d, *J* = 6.9 Hz, 1H), 7.54 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.46 (s, 1H), 7.43 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 5.49 (s, 1H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 171.2, 137.9, 136.6, 135.7, 132.3, 131.4 (q, *J* = 31.31 Hz), 131.2, 131.1, 129.5, 125.8 (q, *J* = 3.8 Hz), 125.7, 124.8 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 273.71 Hz), 122.4, 55.5, 53.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.59.

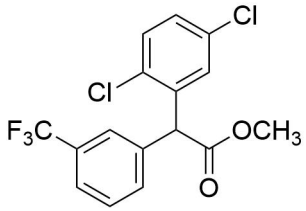
HRMS (ESI): m/z calcd for $C_{16}H_{11}O_2Br_2F_3$ $[M+ NH_4]^+$: 469.9396, found 469.9406.



3g: Yield 77 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 - 7.54 (m, 2H), 7.48 - 7.42 (m, 3H), 7.25 - 7.19 (m, 2H), 5.49 (s, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 171.6, 137.8, 136.1, 135.0, 134.5, 132.3, 131.4 (q, *J* = 32.32 Hz), 130.7, 129.8, 129.5, 127.7, 126.7 (q, *J* = 273.7 Hz), 125.8 (q, *J* = 3.03 Hz), 124.9 (q, *J* = 3.03 Hz), 53.0 52.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.61.

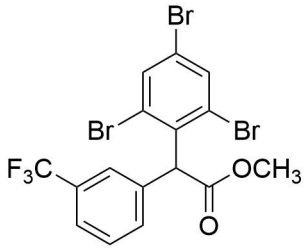
HRMS (ESI): m/z calcd for $C_{16}H_{11}O_2Cl_2F_3$ $[M+ Na]^+$: 384.9980, found 384.9976.



3h: Yield 86 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 - 7.58 (m, 1H), 7.55 (s, 1H), 7.52 - 7.47 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.25 - 7.21 (m, 2H), 5.48 (s, 1H), 3.78 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 171.4, 137.5, 133.3, 132.6, 132.3, 131.5 (q, *J* = 30.3 Hz), 131.0, 129.9, 129.6, 129.3, 125.9 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 273.71 Hz), 53.4, 53.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.59.

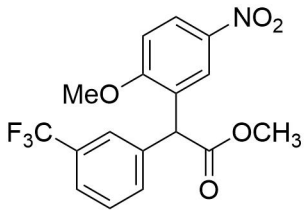
HRMS (ESI): m/z calcd for $C_{16}H_{11}O_2Cl_2F_3$ $[M+ Na]^+$: 384.9980, found 384.9980.



3i: Yield 53 %; Yellow liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (s, 2H), 7.67 (s, 1H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.48 - 7.41 (m, 2H), 5.84 (s, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 170.2, 136.6, 135.8, 135.2, 132.6, 130.7 (q, *J* = 32.3 Hz), 128.8, 126.7, 126.4, 124.5, 124.2 (q, *J* = 273.71 Hz), 122.6, 56.0, 53.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.54.

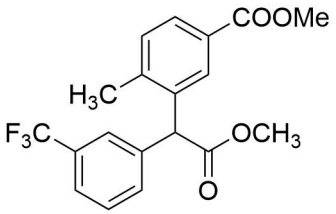
HRMS (ESI): m/z calcd for $C_{16}H_{10}O_2Br_3F_3$ $[M+ NH_4]^+$: 549.8657, found 549.8476.



3j: Yield 85 %; Yellow liquid; **Eluent**: PE/EA = 3 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (dd, J_1 = 9.1 Hz, J_2 = 2.8 Hz, 1H), 7.99 (d, J = 2.7 Hz, 1H), 7.60 - 7.49 (m, 4H), 6.97 (d, J = 9.1 Hz, 1H), 5.36 (s, 1H), 3.95 (s, 3H), 3.76 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 171.7, 161.8, 141.6, 137.5, 132.3, 131.4 (q, J = 32.32 Hz), 129.6, 128.2, 126.0 (q, J = 3.8 Hz), 125.5, 125.0, 124.9 (q, J = 3.7 Hz), 124.0 (q, J = 273.71 Hz), 110.5, 56.7, 52.9, 50.6. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.57.

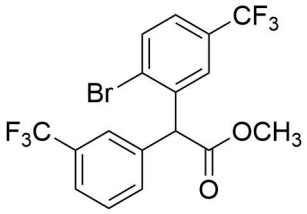
HRMS (ESI): m/z calcd for $C_{17}H_{14}O_5F_3N$ $[M+ Na]^+$: 392.0716, found 392.0714.



3k: Yield 45 %; White solid; **m.p.**: 112 - 114 ℃; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.93 (d, J = 1.6 Hz, 1H), 7.90 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1H), 7.54 (d, J = 7.3 Hz, 1H), 7.49 (s, 1H), 7.47 - 7.41 (m, 2H), 7.27 (d, J =7.9 Hz, 1H), 5.28 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.2, 166.9, 142.1, 138.4, 136.5, 132.4, 131.2, 131.1 (q, J = 32.32 Hz), 129.3, 129.2, 129.1, 128.8, 125.9 (q, J = 3.8 Hz), 124.6 (q, J = 3.7 Hz), 124.1 (q, J = 273.71 Hz), 53.8, 53.5, 53.2, 20.2. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.57.

HRMS (ESI): m/z calcd for $C_{19}H_{17}O_4F_3$ $[M+ Na]^+$: 389.0971, found 389.0972.

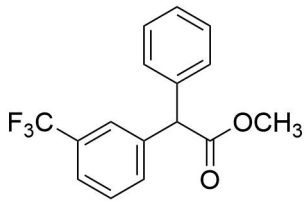


3l: Yield 70 %; White solid; **m.p.**: 84 - 86 ℃; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 8.3 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.57 (s, 1H), 7.55 (d, J = 1.7 Hz, 1H), 7.53 - 7.47 (m, 2H), 7.43 (dd, J_1 = 8.3 Hz, J_2 = 1.9 Hz, 1H), 5.59 (s, 1H), 3.80 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 171.3, 138.6, 137.4, 134.0, 132.2, 131.5 (q, J =

32.6 Hz), 130.5 (q, *J* = 32.9 Hz), 129.7, 129.1, 126.8 (q, *J* = 3.8 Hz), 126.1 (q, *J* = 3.6 Hz), 126.0 (q, *J* = 3.8 Hz), 125.1 (q, *J* = 3.03 Hz), 124.0 (q, *J* = 237.71 Hz), 123.7 (q, *J* = 273.71 Hz), 55.9, 53.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.70, -62.80.

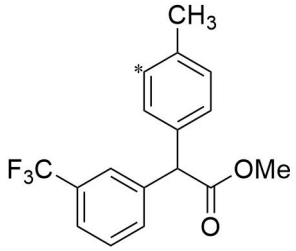
HRMS (ESI): m/z calcd for $C_{17}H_{11}O_2BrF_6$ $[M+ NH_4]^+$: 458.0184, found 458.0204.



3m: Yield 70 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.39 - 7.28 (m, 5H), 5.10 (s, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.5, 139.7, 137.9, 132.2, 131.0 (q, *J* = 32.3 Hz), 129.2, 129.0, 128.6, 127.8, 125.6 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.7 Hz), 56.8, 52.7. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.54.

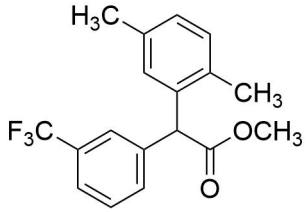
HRMS (ESI): m/z calcd for $C_{16}H_{13}F_3O_2$ $[M+ H]^+$: 295.0940, found 295.0940.[3]



3n (*p* : *o* = 1 : 1.2): Yield 80 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 (s, 1H), 7.53 (d, *J* = 9.3 Hz, 3H), 7.46 - 7.42 (m, 3H), 7.25 - 7.15 (m, 6H), 7.11 (d, *J* = 5.8 Hz, 1H), 5.28 (s, 1H), 5.05 (s, 1H), 3.77 (s, 3H), 3.76(s, 2H), 2.34 (s, 3H), 2.29 (s, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.8, 139.9, 139.0, 137.6, 136.5, 136.2, 134.9, 132.5, 132.1, 131.1, 131.0 (q, *J* = 32.32 Hz), 129.7, 129.3, 129.2, 129.1, 128.9, 128.6, 128.4, 128.0, 127.9, 126.6, 125.8 (q, *J* = 3.8 Hz), 125.5 (q, *J* = 3.03 Hz), 124.2 (m), 124.1 (q, *J* = 273.71 Hz), 56.5, 53.5, 52.7, 52.6, 21.2, 19.9 . **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.54.

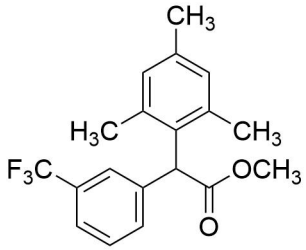
HRMS (ESI): m/z calcd for $C_{17}H_{15}O_2F_3$ $[M+ Na]^+$: 331.0916, found 331.0915.



3o: Yield 77 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 - 7.51 (m, 2H) , 7.46 - 7.41 (m, 2H), 7.09 (d, *J* = 7.7 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 5.24 (s, 1H), 3.77 (s, 3H), 2.32 (s, 3H), 2.23 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.9, 139.1, 136.2, 135.9, 133.3, 132.5, 131.0, 130.9 (q, *J* = 32.32 Hz), 129.1 , 128.7, 128.6, 125.9 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.7 Hz), 53.5, 52.6, 21.3, 19.5. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.52.

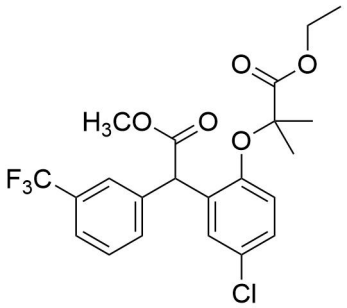
HRMS (ESI): m/z calcd for $C_{18}H_{17}O_2F_3$ [M+ Na]$^+$: 345.1072, found 345.1073.



3p: Yield 79 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (s, *J* = 7.9 Hz, 1H), 7.50 (s, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 7.8 Hz, 1H), 6.96 (s, 2H), 5.44 (s, 1H), 3.77 (s, 3H), 2.34 (s, 3H), 2.19 (s, 6H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 173.3, 137.9, 137.5, 137.4, 132.2, 131.5, 130.6 (q, *J* = 32.0 Hz), 130.2, 128.7, 125.9 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 272.3 Hz), 123.8 (q, *J* = 3.7 Hz), 52.6, 50.5, 21.0, 20.8. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.46.

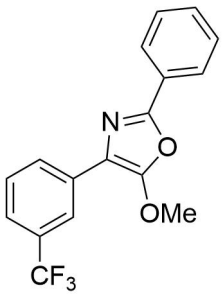
HRMS (ESI): m/z calcd for $C_{19}H_{19}O_2F_3$ [M+ Na]$^+$:359.1229 , found 359.1229.



3q: Yield 46 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.59 - 7.45 (m, 4H), 7.12 (dd, J_1 = 8.8 Hz, J_2 = 2.6 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 5.29 (s, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 1.58 (s, 3H), 1.49 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 173.8, 172.2, 151.7, 138.4, 132.6, 131.1, 130.6, 129.5, 129.2, 128.1, 126.5, 126.2 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 3.6 Hz), 124.2 (q, *J* = 273.71 Hz), 116.2, 79.6, 61.8, 52.6, 51.5, 25.2, 25.1, 14.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.54.

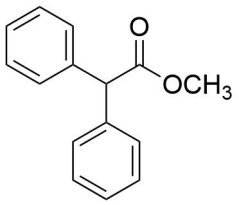
HRMS (ESI): m/z calcd for $C_{22}H_{22}O_5ClF_3$ [M+ Na]$^+$: 481.1000, found 481.1004.



5: Yield 73 %; White solid; **m.p.**: 50 - 52 ℃; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.16 (s, 1H), 8.06 (d, J = 7.2 Hz, 1H), 8.02 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 7.53 - 7.41 (m, 5H), 4.30 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 155.2, 152.0, 132.5, 131.0 (q, J =32.1 Hz), 130.0, 129.0, 128.9, 128.2, 127.4, 125.7, 124.5 (q, J =273.71 Hz), 122.9 (q, J = 3.7 Hz), 121.8 (q, J = 3.9 Hz), 114.6, 60.0. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.65.

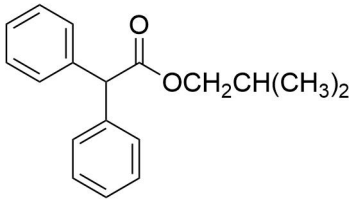
HRMS (ESI): m/z calcd for $C_{17}H_{13}O_2F_3N$ $[M+H]^+$: 320.0893, found 320.0894.



6a: Yield 58 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 - 7.24 (m, 10H), 5.00 (s, 1H), 3.74 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 173.1, 138.8, 128.8, 128.7, 127.4, 57.2, 52.5.

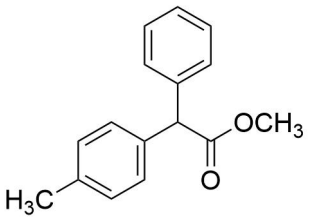
HRMS (ESI): m/z calcd for $C_{15}H_{14}O_2$ $[M+H]^+$: 227.1067, found 227.1006.[1]



6b: Yield 48 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (d, J = 4.5 Hz, 8H), 7.28 - 7.23 (m, 2H), 5.03 (s, 1H), 3.94 - 3.92 (m, 2H), 1.96 - 1.86 (m, 1H), 0.86 (d, J = 6.7 Hz, 6H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.6, 138.9, 128.8, 128.7, 127.3, 71.4, 57.4, 27.8, 19.1.

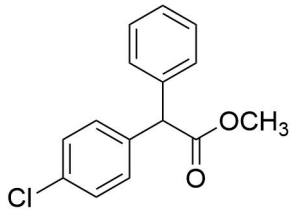
HRMS (ESI): m/z calcd for $C_{18}H_{20}O_2$ $[M+H]^+$: 269.1536, found 269.1537.



6c: Yield 27 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 - 7.28 (m, 4H), 7.27 - 7.25 (m, 1H), 7.21 - 7.18 (m, 2H), 7.14 (s, 1H), 7.12 (s, 1H), 5.00 (s, 1H), 3.73 (s, 3H), 2.32 (s, 3H) . **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 173.3, 140.0, 137.1, 135.8, 129.5, 128.7, 128.6, 128.5, 127.4, 56.8, 52.4, 21.2.

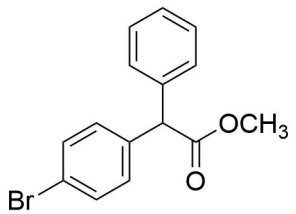
HRMS (ESI): m/z calcd for $C_{16}H_{16}O_2$ $[M+H]^+$: 241.1223, found 241.1221.[1]



6e: Yield 75 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 - 7.23 (m, 9H), 4.99 (s, 1H), 3.72 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.7, 138.3, 137.2, 133.4, 130.1, 128.9, 128.8, 128.6, 127.6, 56.4, 52.5.

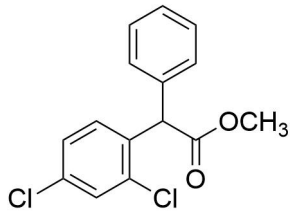
HRMS (ESI): m/z calcd for $C_{15}H_{13}ClO_2$ $[M+H]^+$: 261.0677, found 261.0674.[1]



6f: Yield 57 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 - 7.42 (m, 2H), 7.34 - 7.24 (m, 5H), 7.20 - 7.16 (m, 2H), 4.97 (s, 1H), 3.73 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.6, 138.2, 137.8, 131.8, 130.5, 128.9, 128.6, 127.6, 121.5, 56.5, 52.6.

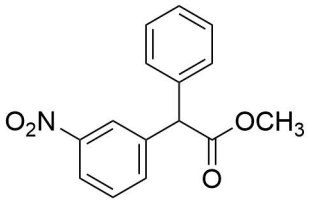
HRMS (ESI): m/z calcd for $C_{15}H_{13}BrO_2$ $[M+H]^+$: 305.0172, found: 305.0170.[1]



6g: Yield 73 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 1.7 Hz, 1H), 7.38 - 7.29 (m, 3H), 7.28 - 7.24 (m, 2H), 7.20 - 7.14 (m, 2H), 5.42 (s, 1H), 3.75 (s, 3H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.1, 136.8, 135.4, 133.9, 131.1, 129.5, 129.0, 128.9, 127.9, 127.4, 53.4, 52.7.

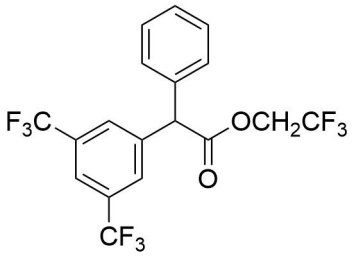
HRMS (ESI): m/z calcd for $C_{15}H_{13}Cl_2O_2$ $[M+H]^+$: 295.0287, found 295.0288.[3]



6h: Yield 85 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (t, *J* = 1.8 Hz, 1H), 8.13 (ddd, J_1 = 8.2 Hz, J_2 =2.2 Hz, J_3 = 1.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.39 - 7.29 (m, 5H), 5.14 (s, 1H), 3.78 (s, 3H) . **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 172.0, 148.5, 140.8, 137.4, 134.9, 129.6, 129.1, 128.5, 128.0, 123.8, 122.5, 56.5, 52.7.

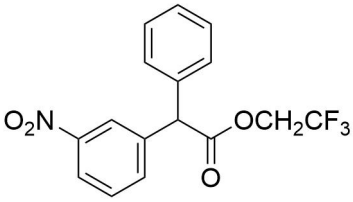
HRMS (ESI): m/z calcd for $C_{15}H_{13}NO_4$ $[M+Na]^+$: 294.0742, found 294.0737.[2]



6i: Yield 77 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.84 (s, 1H), 7.83 (s, 2H), 7.44 - 7.36 (m, 3H), 7.33 - 7.31 (m, 2H), 5.25 (s, 1H), 4.65 - 4.52 (m, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 170.0, 140.3, 136.1, 132.3 (q, *J* = 33.5 Hz), 129.5, 129.1 (d, *J* = 4.04 Hz), 128.6, 128.4, 123.3 (q, *J* = 273.7 Hz), 122.8 (q, *J* = 277.8 Hz), 122.1 - 121.9 (m), 61.2 (q, *J* = 36.9 Hz), 56.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -63.02, -73.80.

HRMS (ESI): m/z calcd for $C_{18}H_{11}O_2F_9$ $[M+H]^+$: 431.0688, found 431.0698.

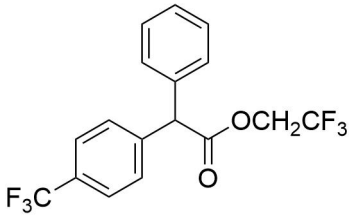


6j: Yield 75 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.21 (t, *J* = 2.0 Hz, 1H), 8.16 (ddd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, J_3 = 1.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.39 - 7.31 (m, 5H), 5.23 (s, 1H) , 4.64 - 4.50 (m, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 170.2, 148.6, 139.9, 136.4, 134.8, 129.8,

129.3, 128.5, 128.4, 123.8, 122.9, 122.8 (q, J = 278.76 Hz), 61.1 (q, J = 36.9 Hz), 56.1. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -73.59.

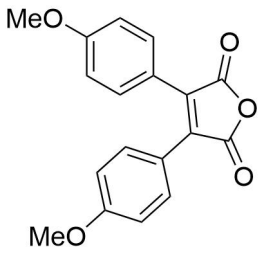
HRMS (ESI): m/z calcd for $C_{16}H_{12}O_4F_3N$ $[M+ Na]^+$: 362.0610, found 362.0607.



6k: Yield 62 %; Colorless liquid; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.38 - 7.31 (m, 5H), 5.19 (s, 1H), 4.63 - 4.49 (m, 2H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 170.6, 141.7, 136.9, 130.1 (q, J = 32.6 Hz), 129.2, 129.1, 128.6, 128.2, 125.8 (q, J = 3.7 Hz), 124.0 (q, J = 272.7 Hz), 122.9 (q, J = 278.76 Hz), 61.0 (q, J = 36.8 Hz), 56.4. **^{19}F NMR (376 MHz, $CDCl_3$)** δ: -62.64, -73.59.

HRMS (ESI): m/z calcd for $C_{17}H_{12}O_2F_6$ $[M+ Na]^+$: 385.0639, found 385.0638.[4]



7: Yield 91 %; Yellow powder; **Eluent**: PE/EA = 20 : 1

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.58 - 7.54 (m, 4H), 6.93 - 6.89 (m, 4H), 3.82 (s, 6H). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$)** δ: 165.6, 161.8, 135.8, 131.6, 120.1, 114.6, 55.4.

HRMS (ESI): m/z calcd for $C_{18}H_{14}O_5$ $[M+ H]^+$: 310.0841, found 310.0834.[7]

5. Tables of crystal data and structure refinements

	5
CCDC number	2329085
Empirical formula	$C_{17}H_{12}F_3NO_2$
Formula weight	319.28
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	34.085(2)
b/Å	11.9376(5)
c/Å	15.8740(12)
α /°	90
β /°	112.316(8)
γ /°	90
Volume/Å^3	5975.3(7)
Z	16
ρ_{calc}g/cm^3	1.420
μ /mm^{-1}	1.021
F(000)	2624.0
Crystal size/mm^3	0.16 × 0.11 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.92 to 134.156
Index ranges	-40 ≤ h ≤ 32, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	11015
Independent reflections	5333 [R_{int} = 0.0369, R_{sigma} = 0.0547]
Data/restraints/parameters	5333/97/437
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0739, wR_2 = 0.1964
Final R indexes [all data]	R_1 = 0.1073, wR_2 = 0.2384
Largest diff. peak/hole / e Å^{-3}	0.41/-0.29

6. References

[1] A. F. D. Silva, M. A. S. Afonso, R. A. Cormanich and I. D. Jurberg, *Chemistry – A European Journal*, 2020, **25**.

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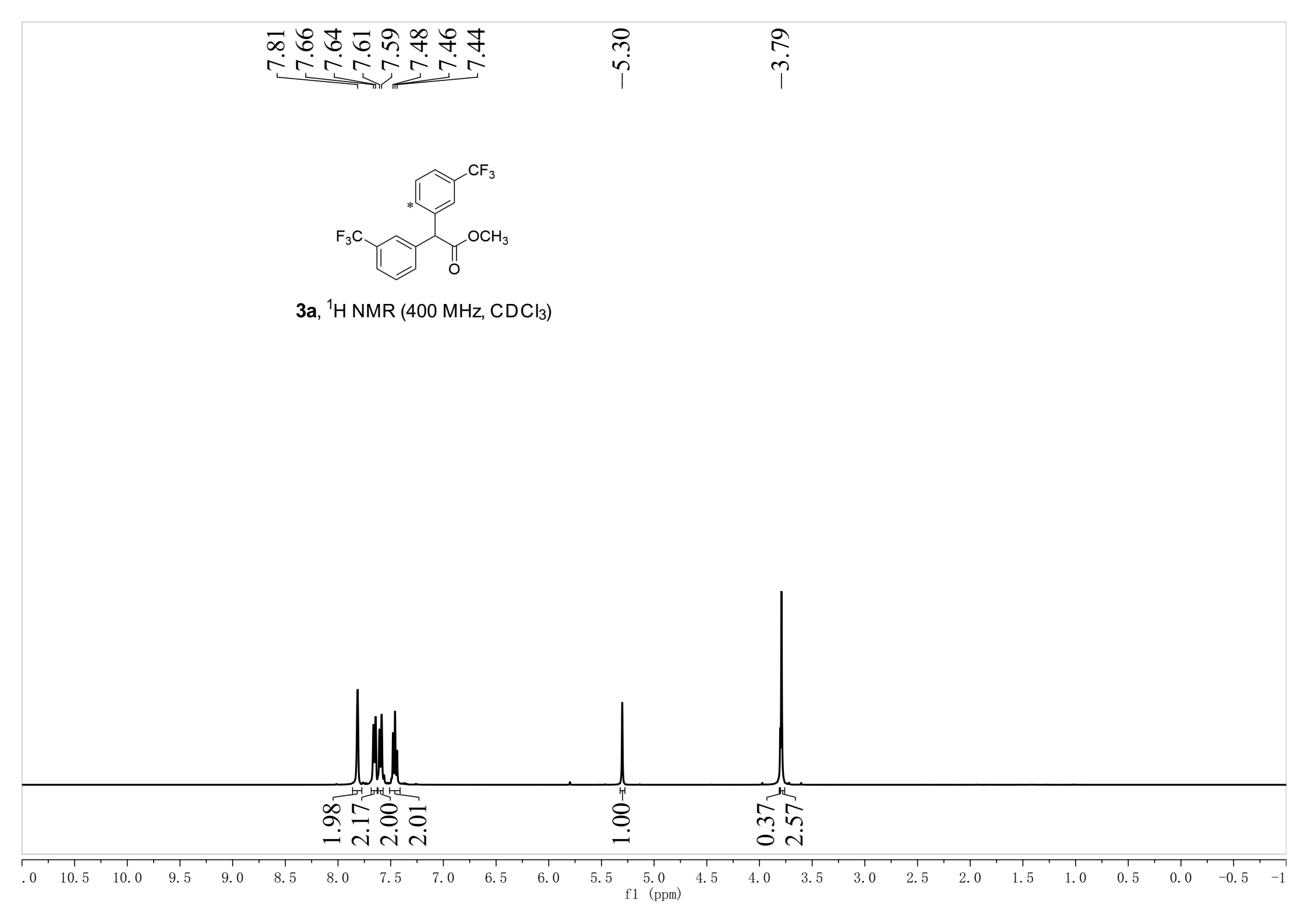
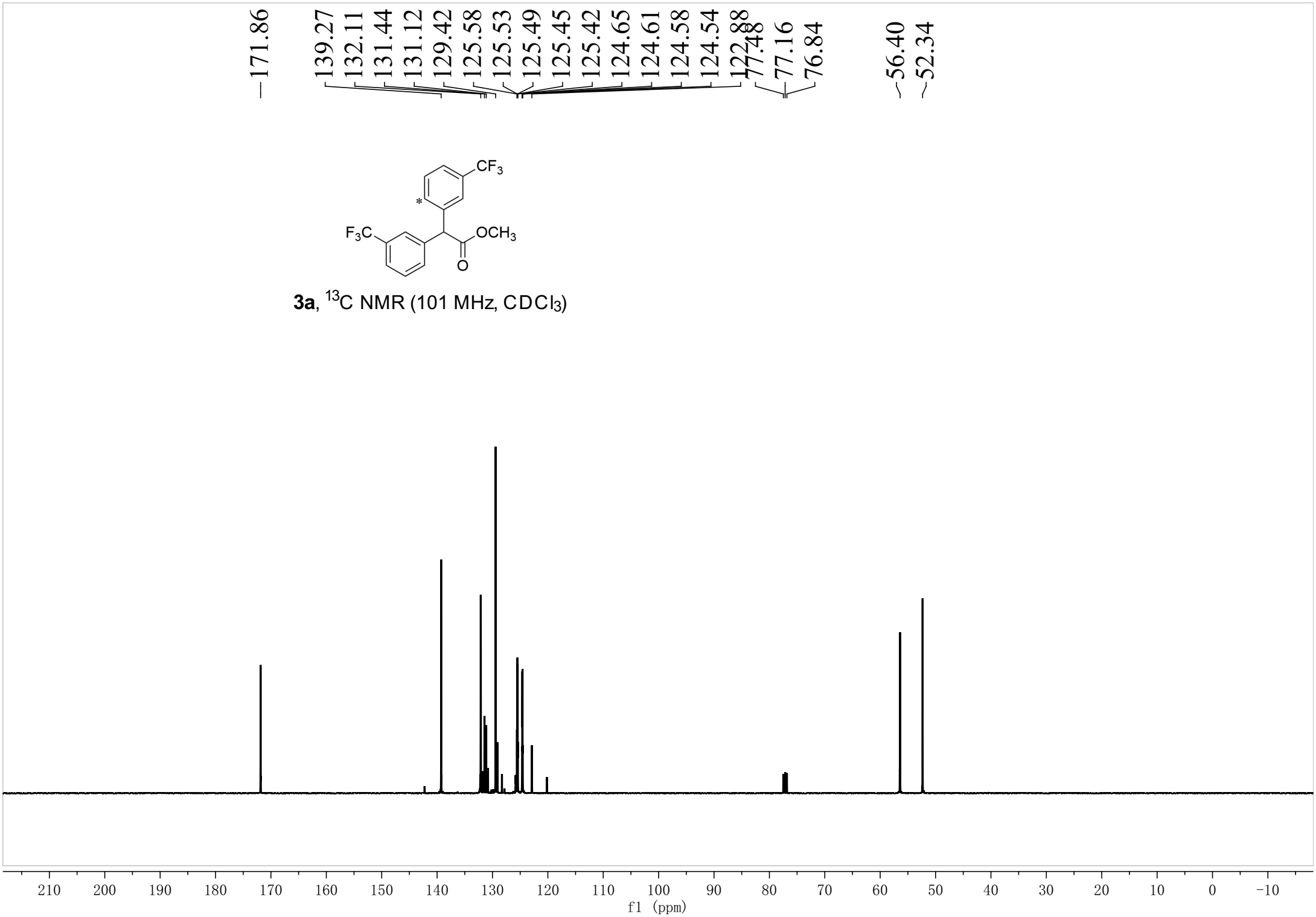
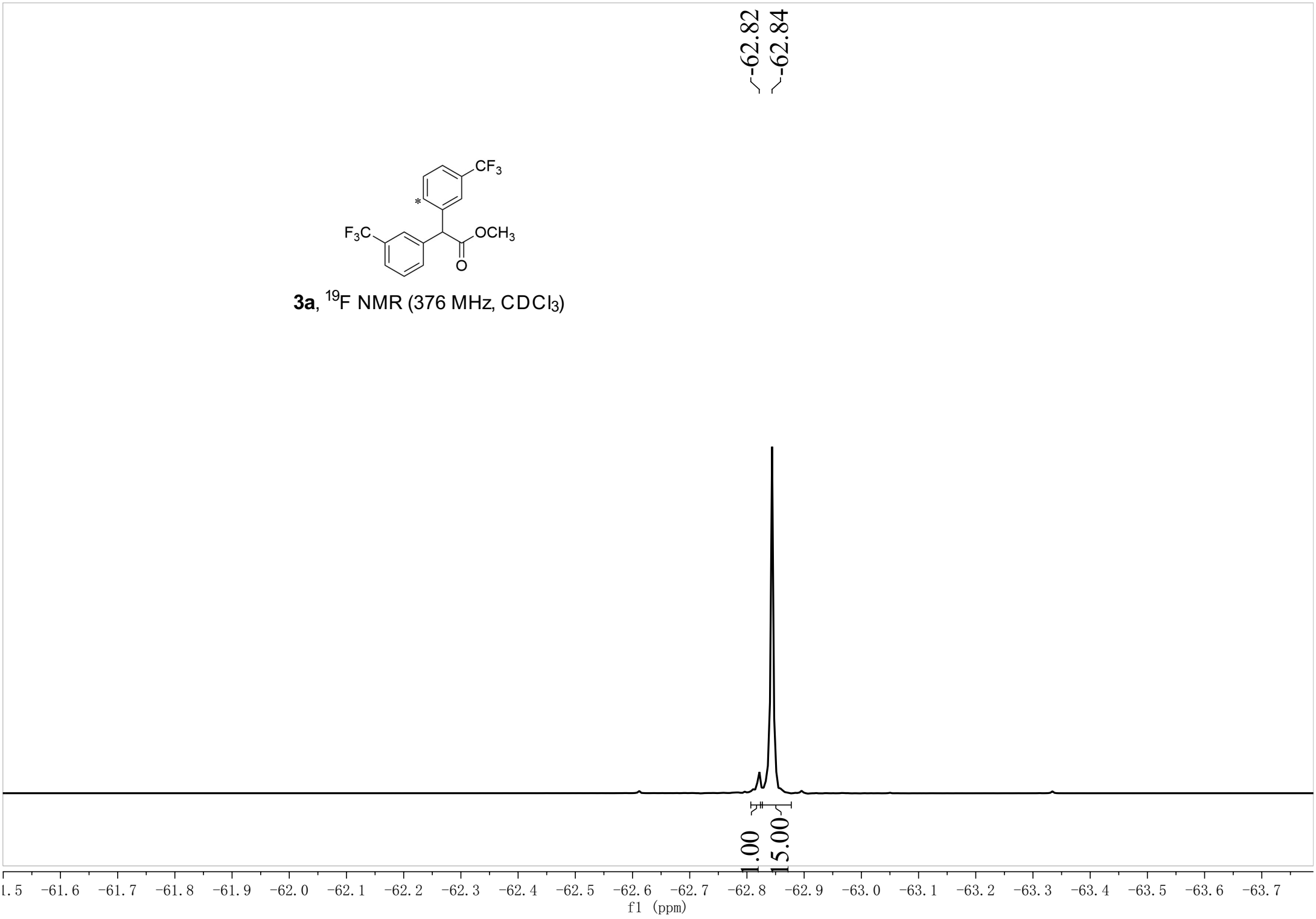
[7] X. -F. Mei, J. -W. Wang, Z. -G. Zhou, S. -Y. Wu, L. M. Huang, Z. H. Lin and Q. D. Ling, *J. Mater. Chem. C.*, 2017, **5**, 2135 - 2141.



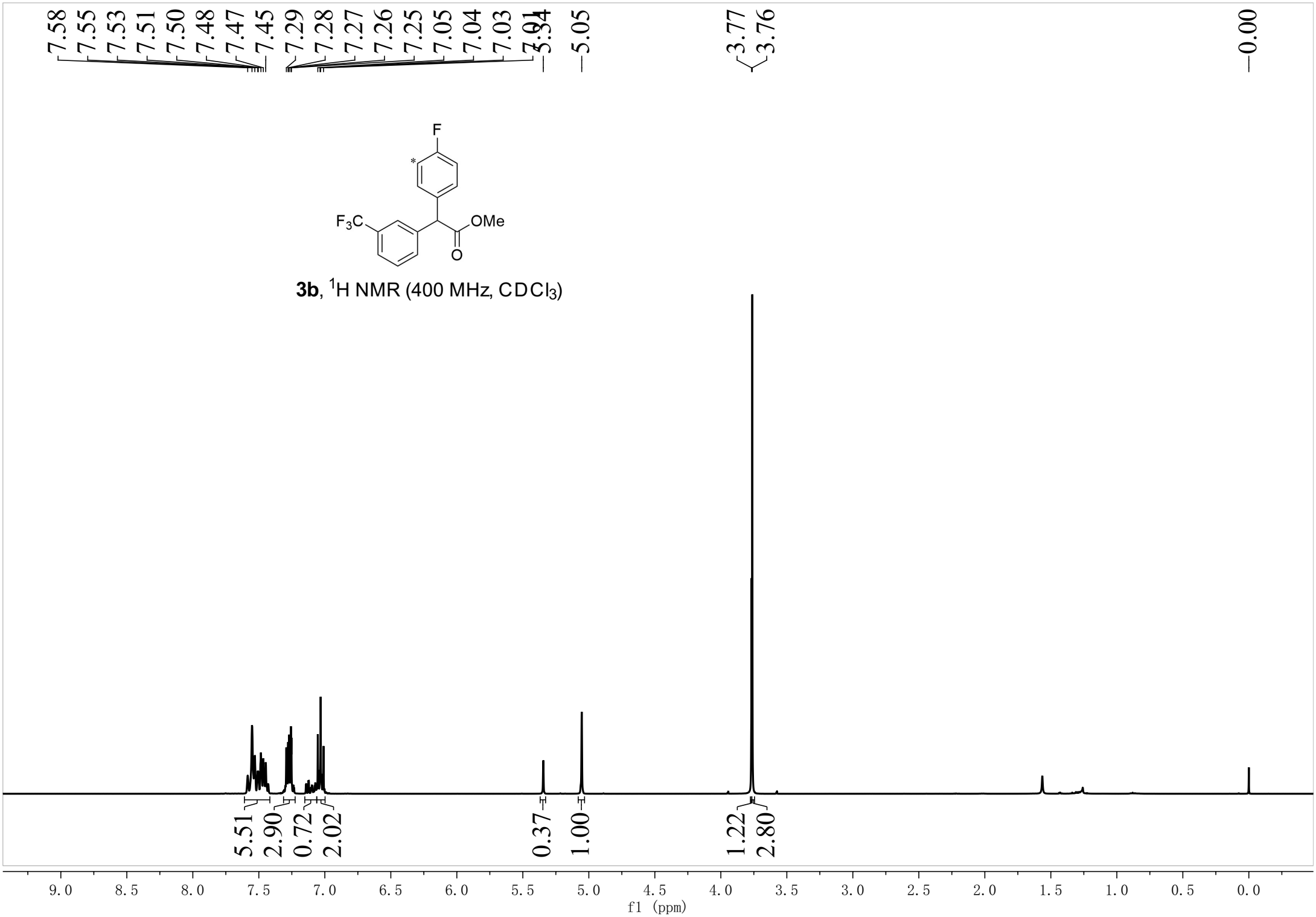
3a, ^{1}H NMR (400 MHz, $CDCl_3$)



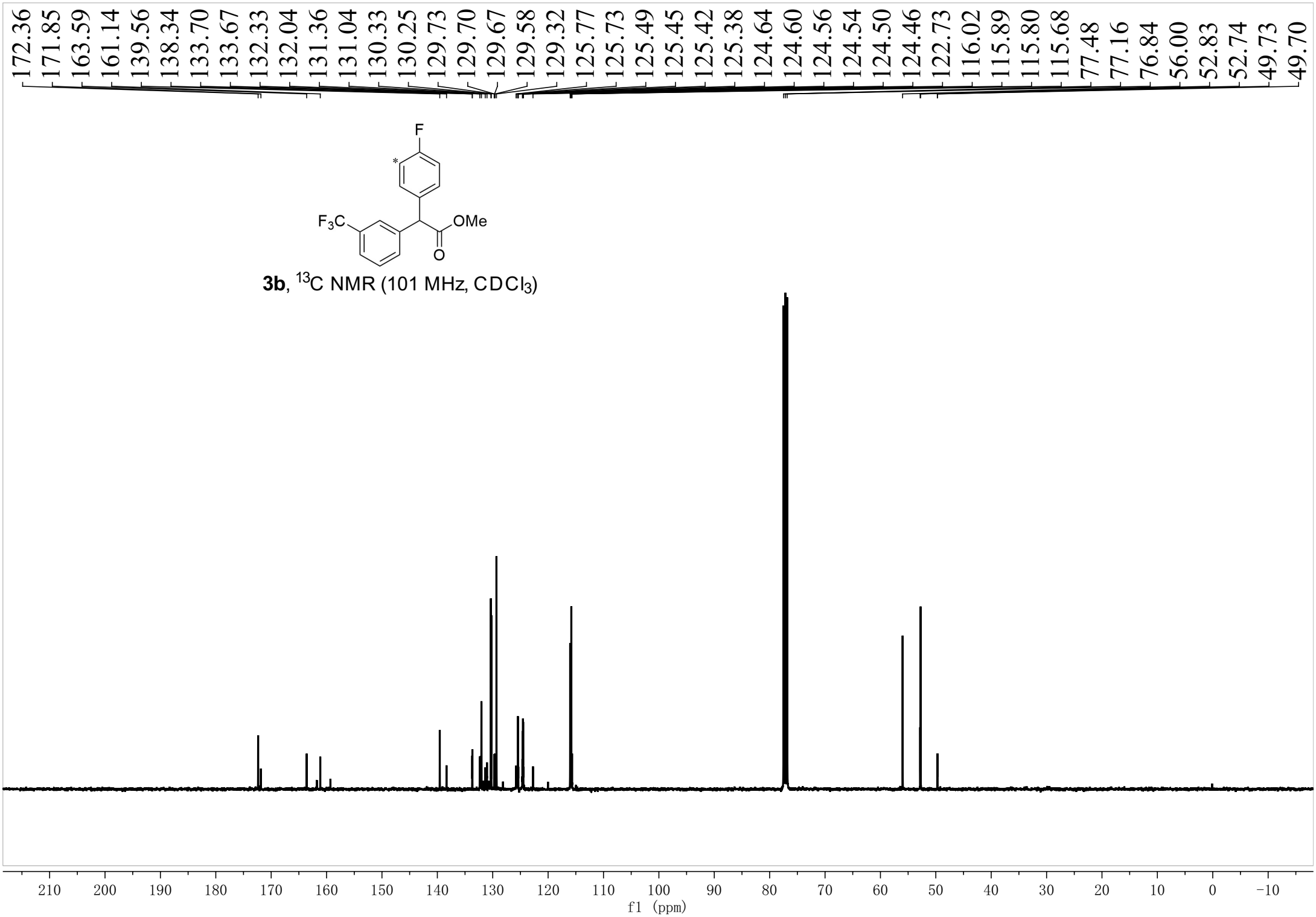
3a, ^{13}C NMR (101 MHz, $CDCl_3$)

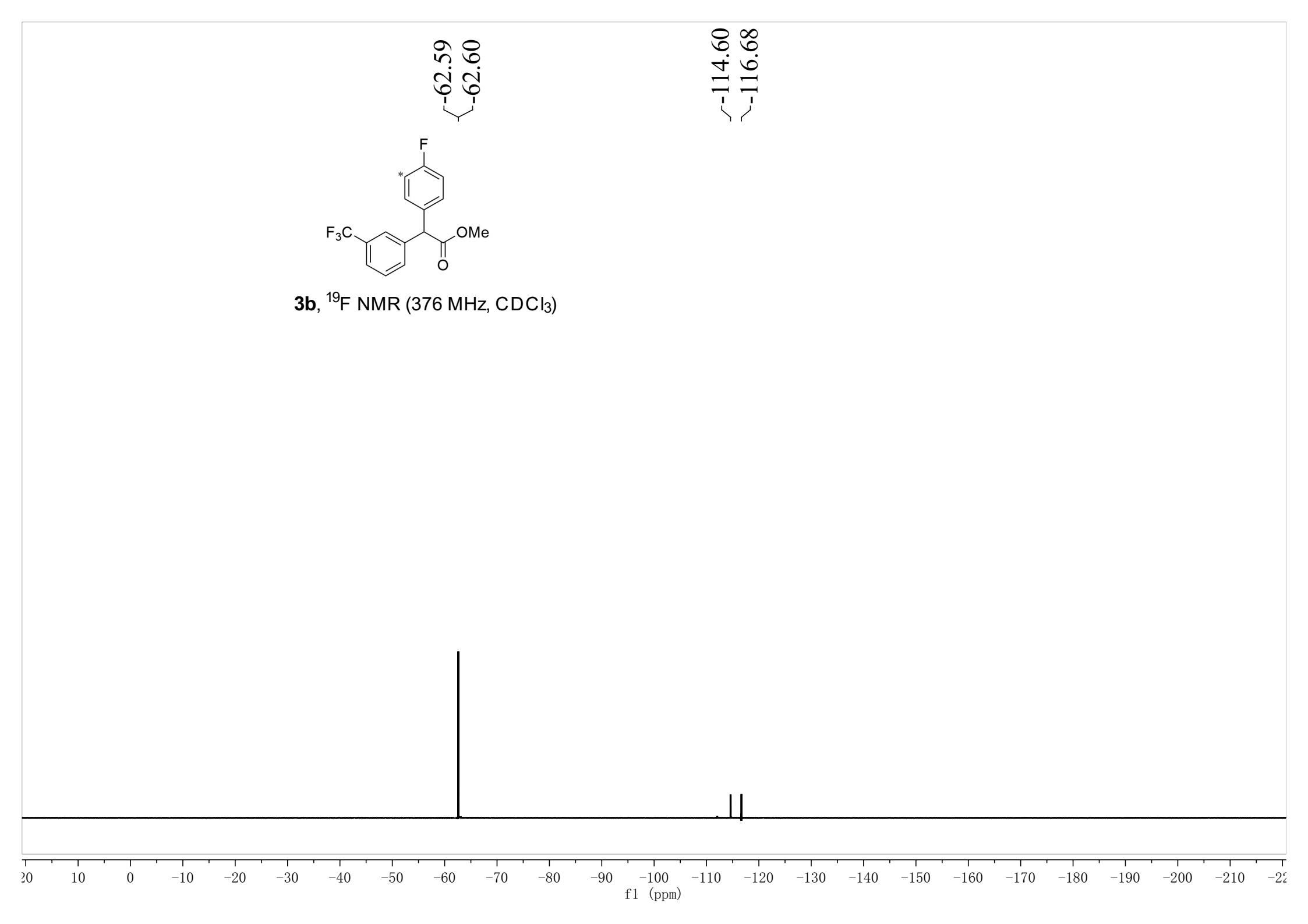


3a, ^{19}F NMR (376 MHz, $CDCl_3$)

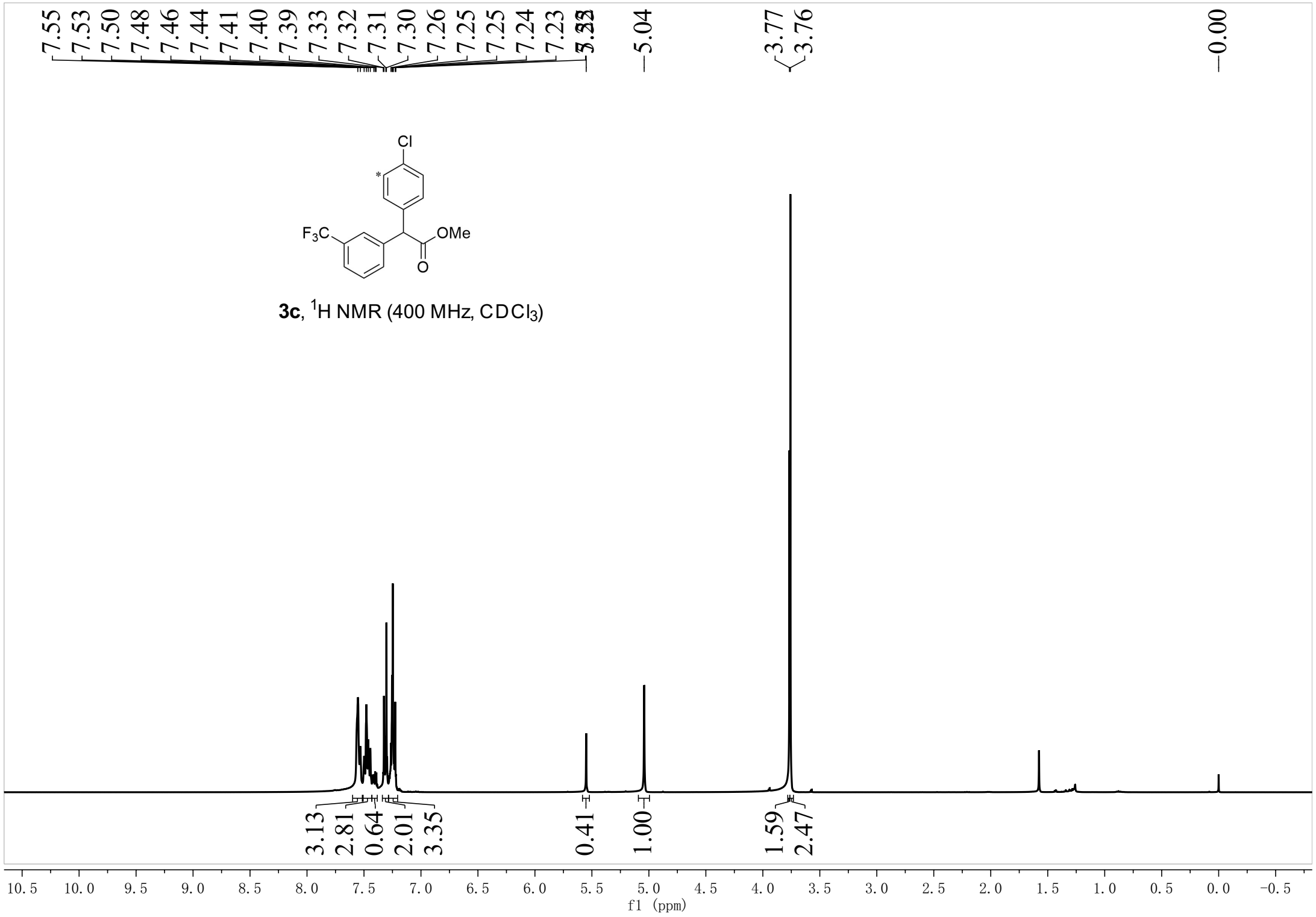


3b, ^{1}H NMR (400 MHz, $CDCl_3$)

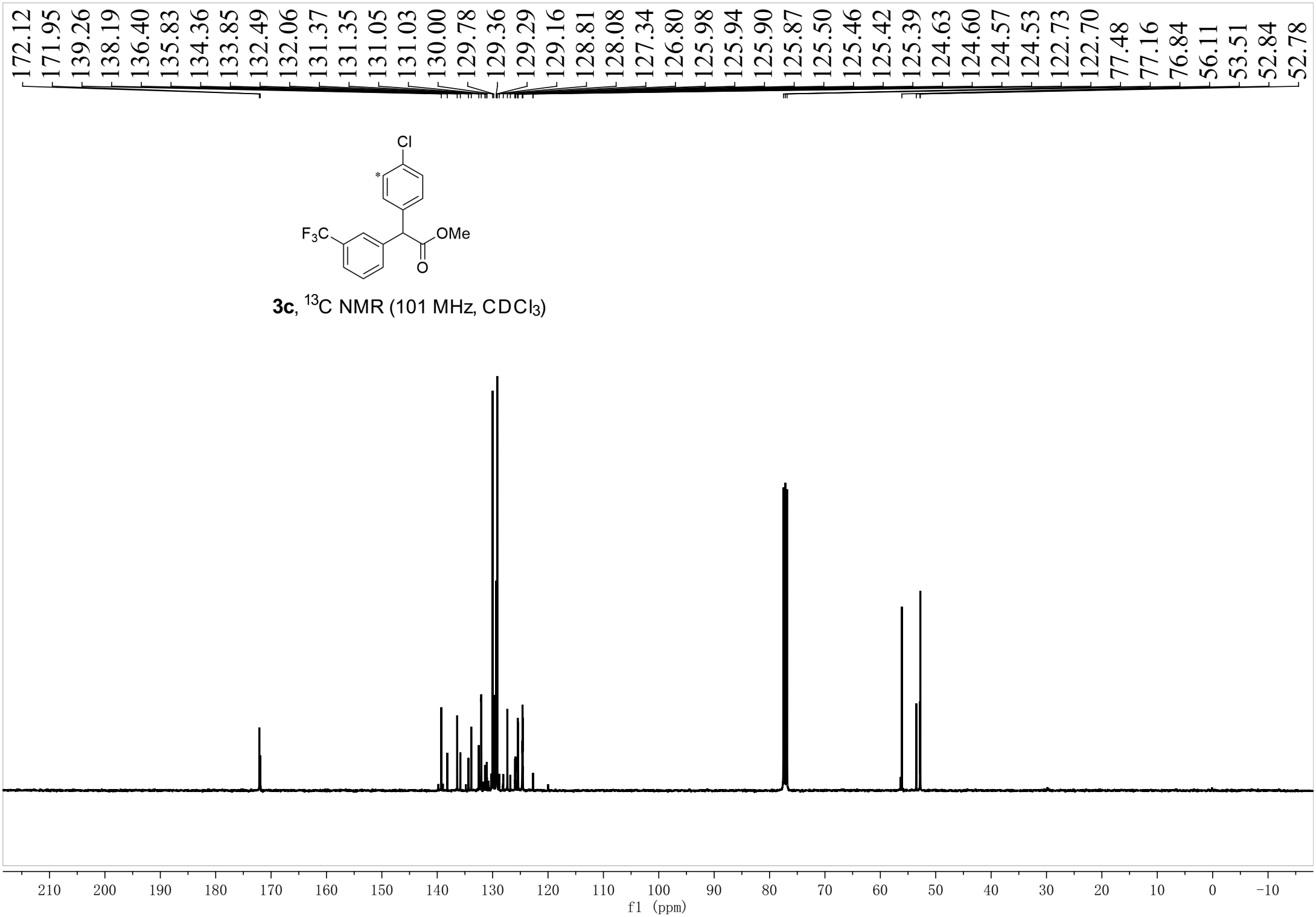

172.36
171.85
163.59
161.14
139.56
138.34
133.70
133.67
132.33
132.04
131.36
131.04
130.33
130.25
129.73
129.70
129.67
129.58
129.32
125.77
125.73
125.49
125.45
125.42
125.38
124.64
124.60
124.56
124.54
124.50
124.46
122.73
116.02
115.89
115.80
115.68
77.48
77.16
76.84
56.00
52.83
52.74
49.73
49.70
F
*
F3C
OMe
O
3b, 13C NMR (101 MHz, CDCl3)
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)



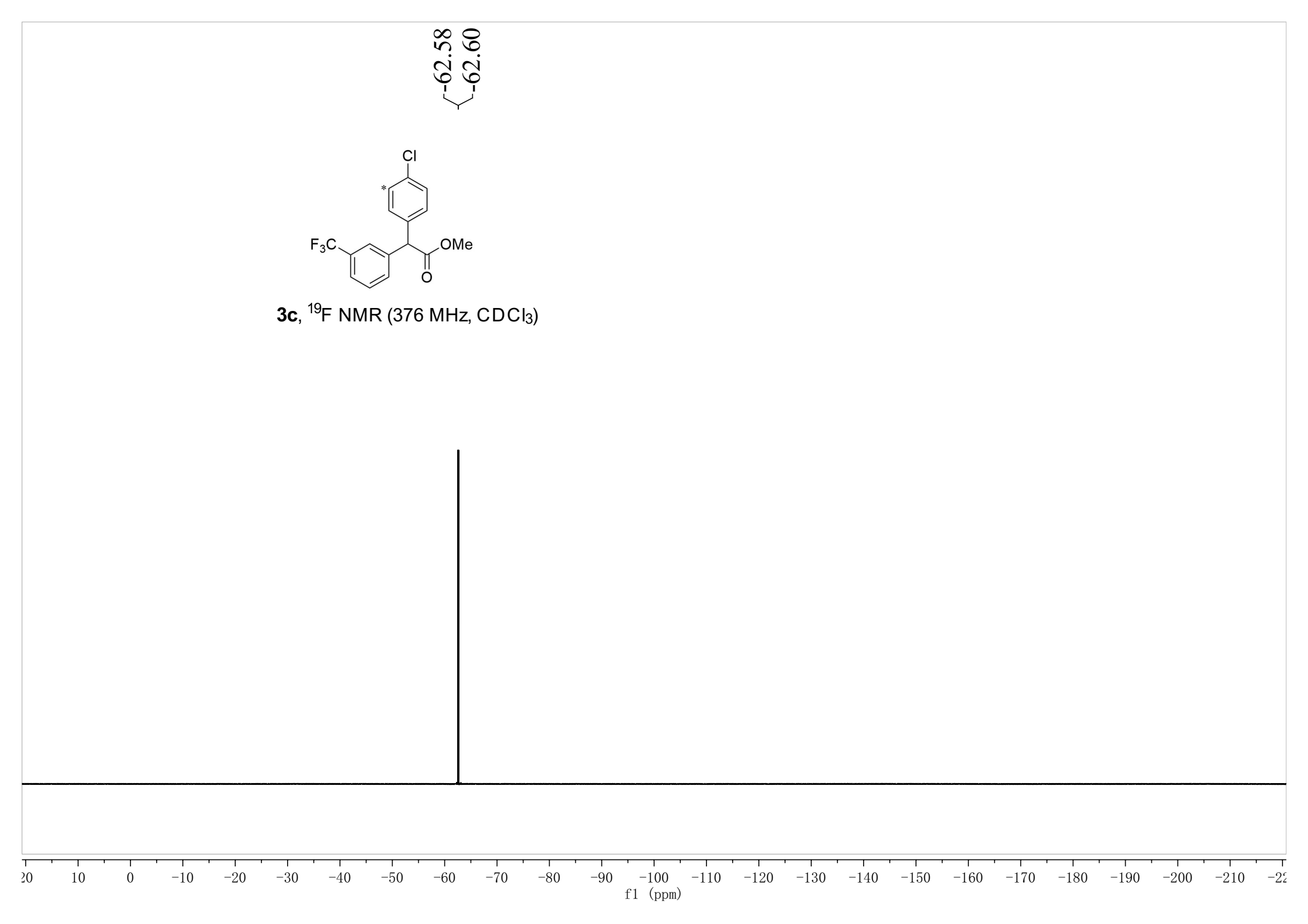
3b, ^{19}F NMR (376 MHz, $CDCl_3$)



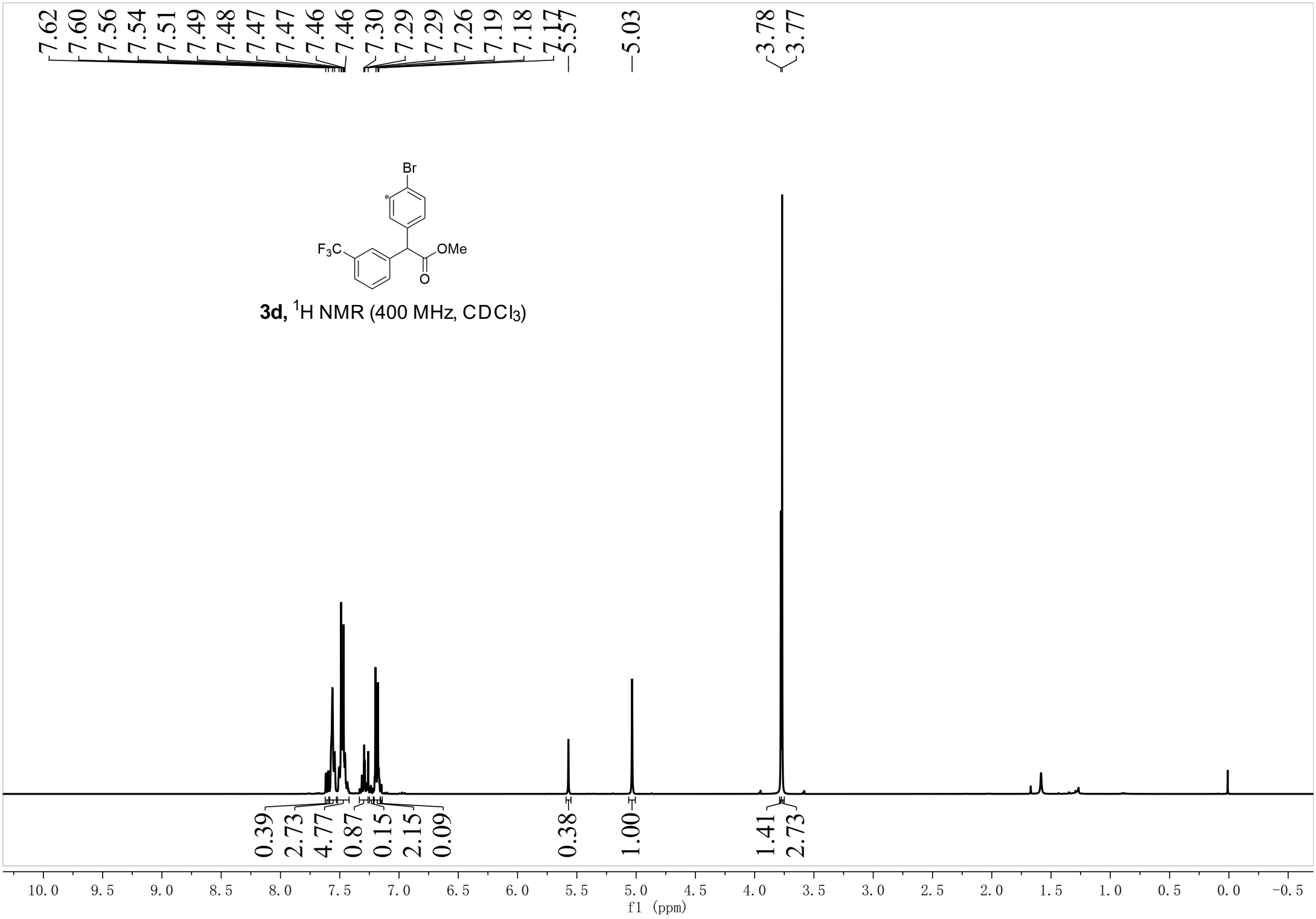
3c, ^{1}H NMR (400 MHz, $CDCl_3$)



3c, ^{13}C NMR (101 MHz, $CDCl_3$)

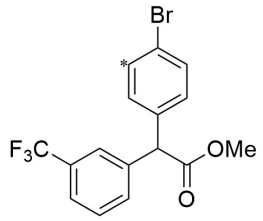


3c, ^{19}F NMR (376 MHz, $CDCl_3$)

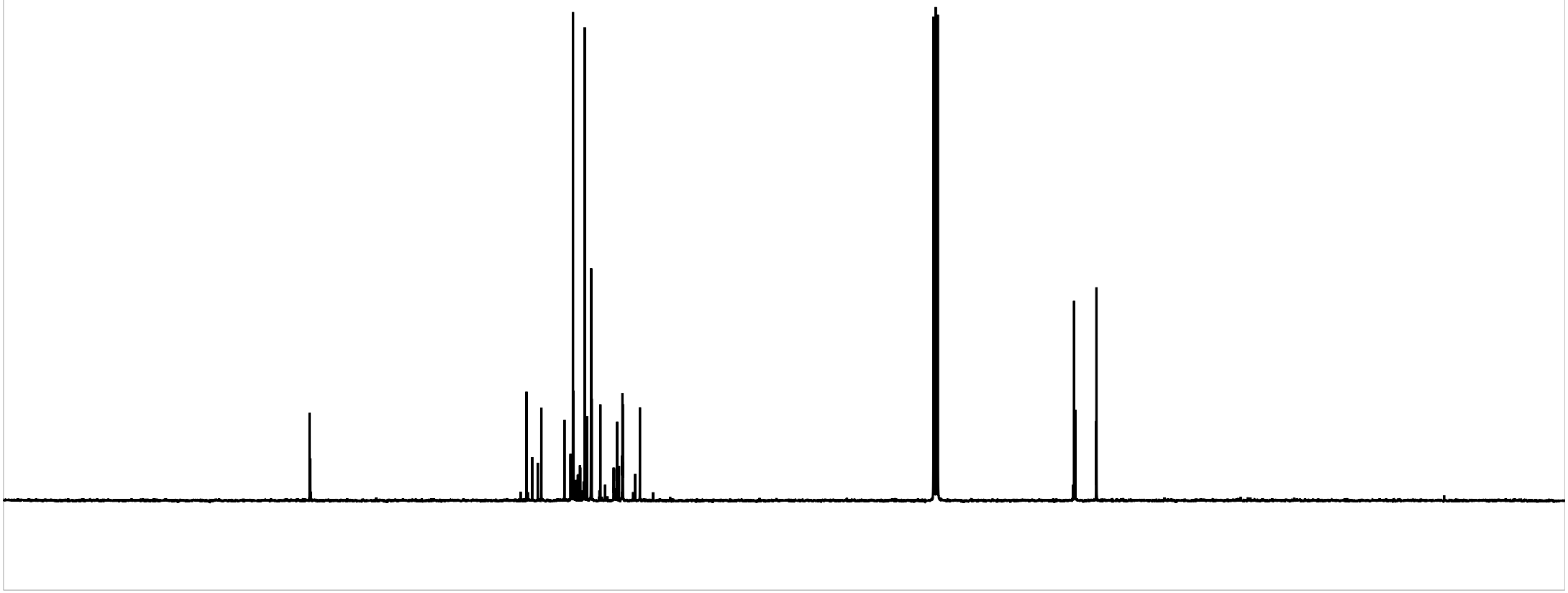


3d, ^{1}H NMR (400 MHz, $CDCl_3$)

172.03 171.93 139.16 138.30 137.45 136.92 133.41 132.49 132.12 132.05 131.69 131.38 131.34 131.06 131.02 130.34 129.99 129.39 129.36 129.28 127.97 127.25 125.99 125.95 125.92 125.50 125.46 125.42 125.40 125.39 125.15 124.66 124.62 124.58 124.54 122.69 121.98 77.48 77.16 76.84 56.19 56.01 52.86 52.79



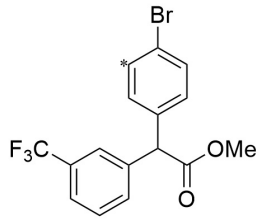
3d, ^{13}C NMR (101 MHz, $CDCl_3$)



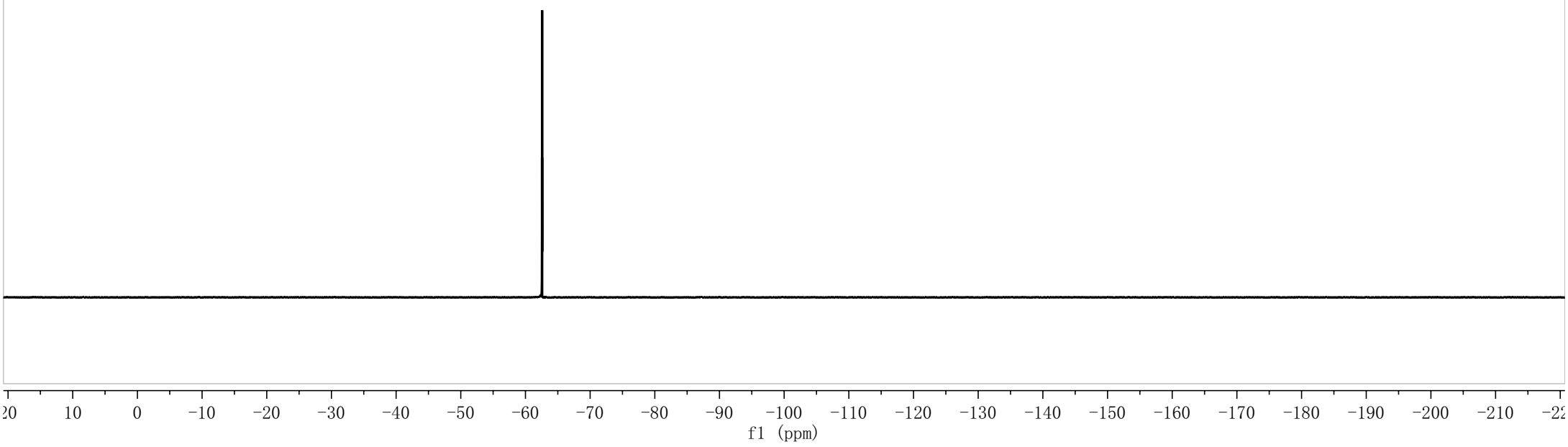
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

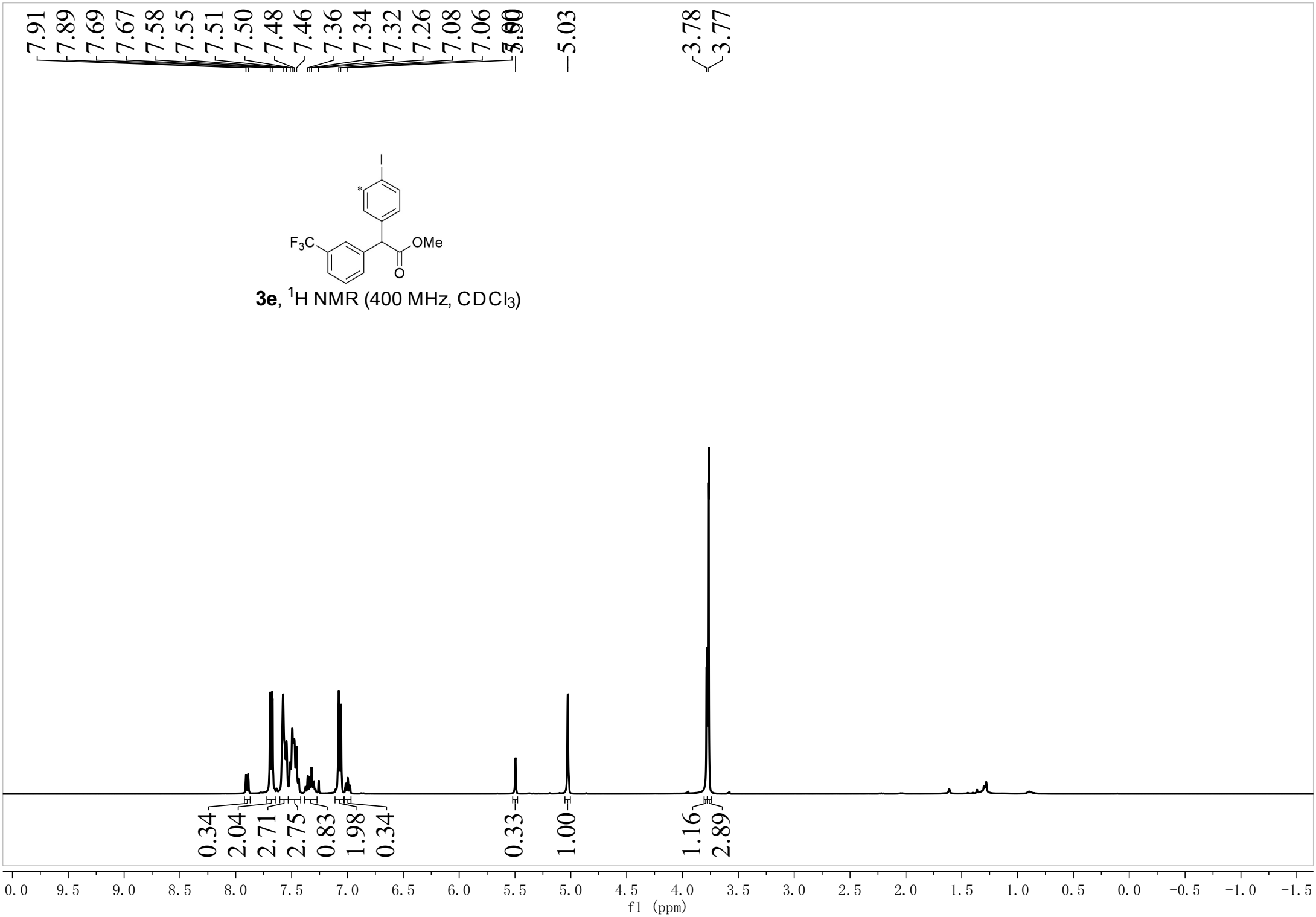
f1 (ppm)

-62.56
-62.58

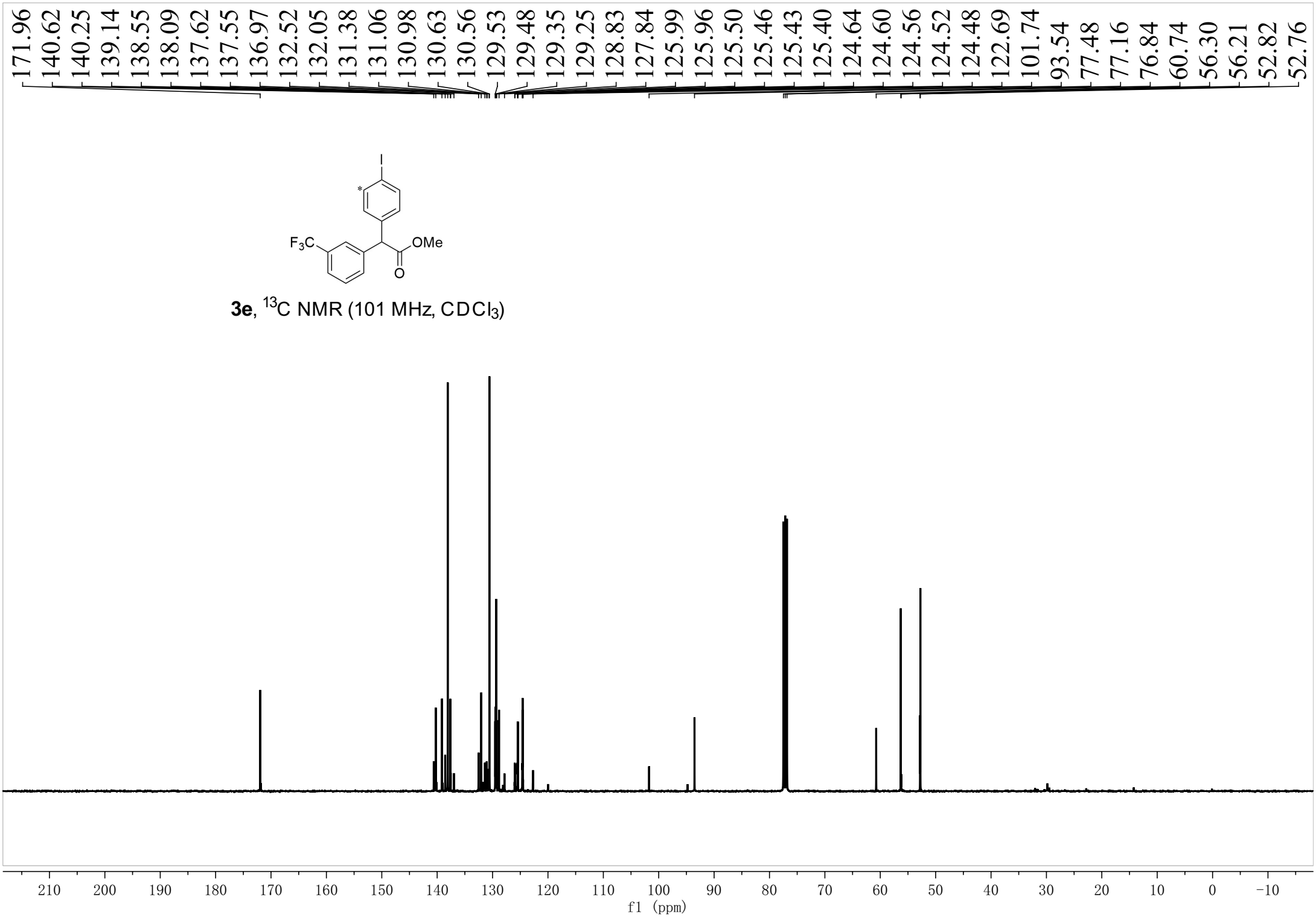


3d, ^{19}F NMR (376 MHz, $CDCl_3$)



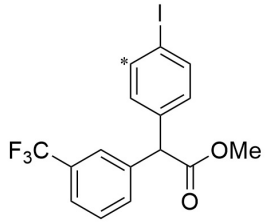


3e, ^{1}H NMR (400 MHz, $CDCl_3$)

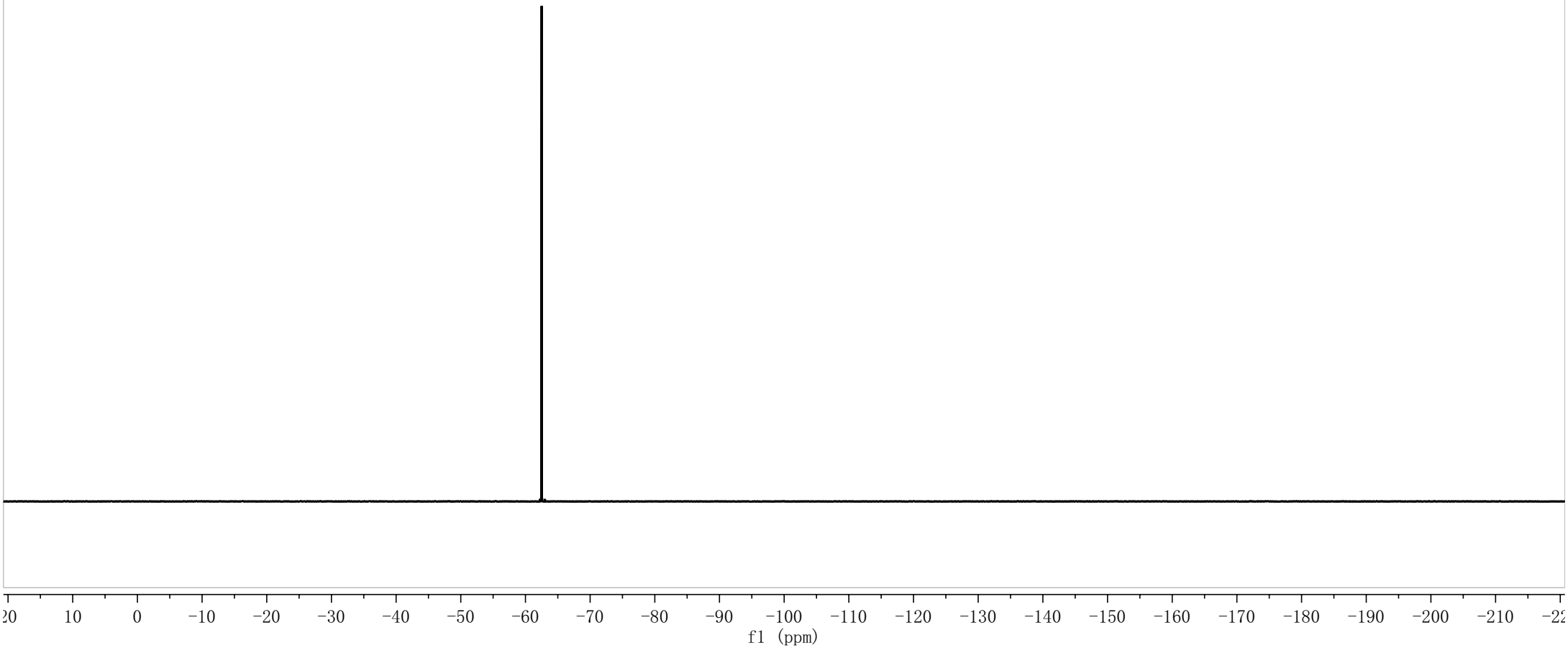


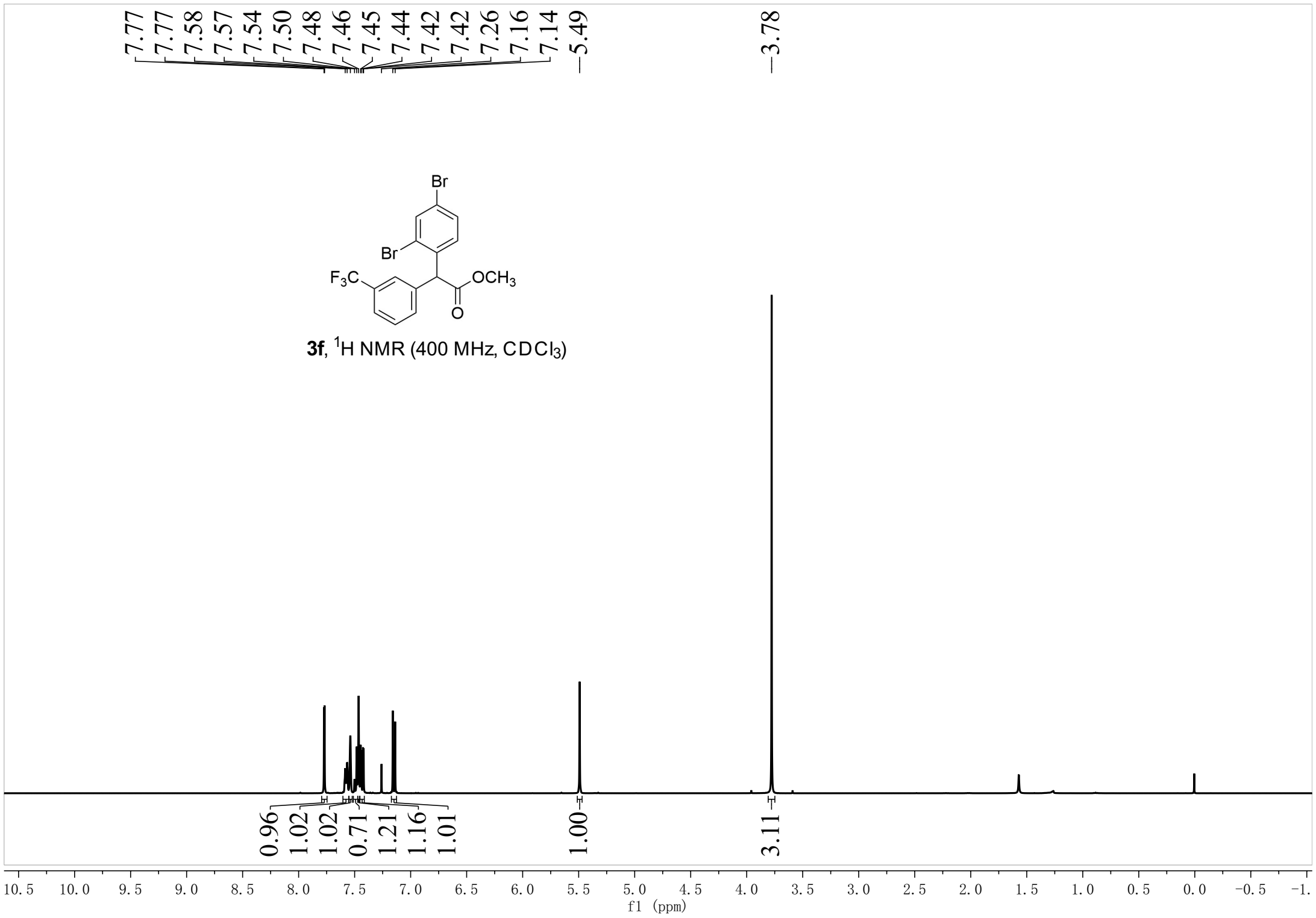
3e, ^{13}C NMR (101 MHz, $CDCl_3$)

-62.49
-62.51

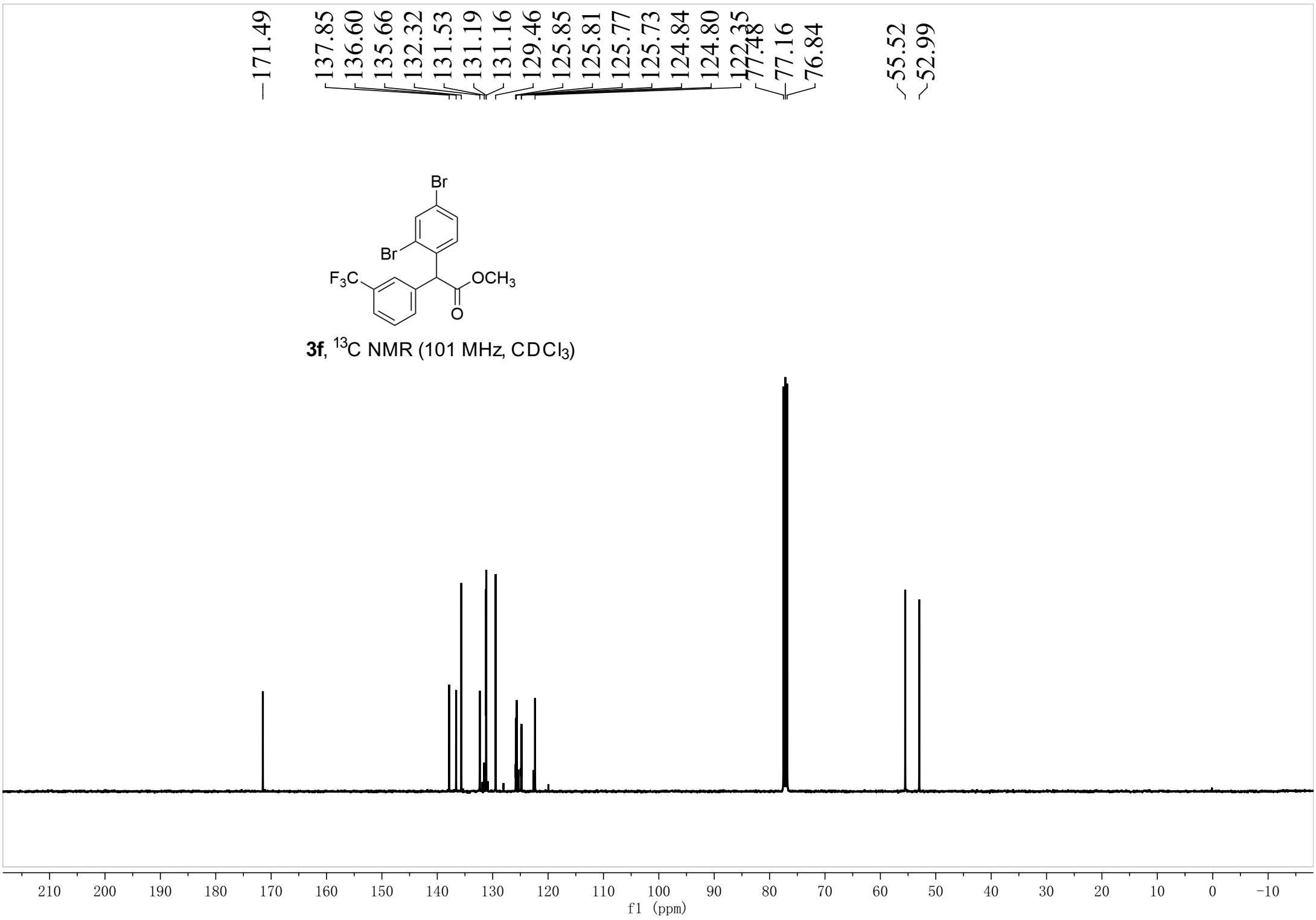


3e, ^{19}F NMR (376 MHz, $CDCl_3$)





3f, ^{1}H NMR (400 MHz, $CDCl_3$)


171.49
137.85
136.60
135.66
132.32
131.53
131.19
131.16
129.46
125.85
125.81
125.77
125.73
124.84
124.80
122.35
77.48
77.16
76.84
55.52
52.99
Br
Br
F3C
OCH3
O
3f, 13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
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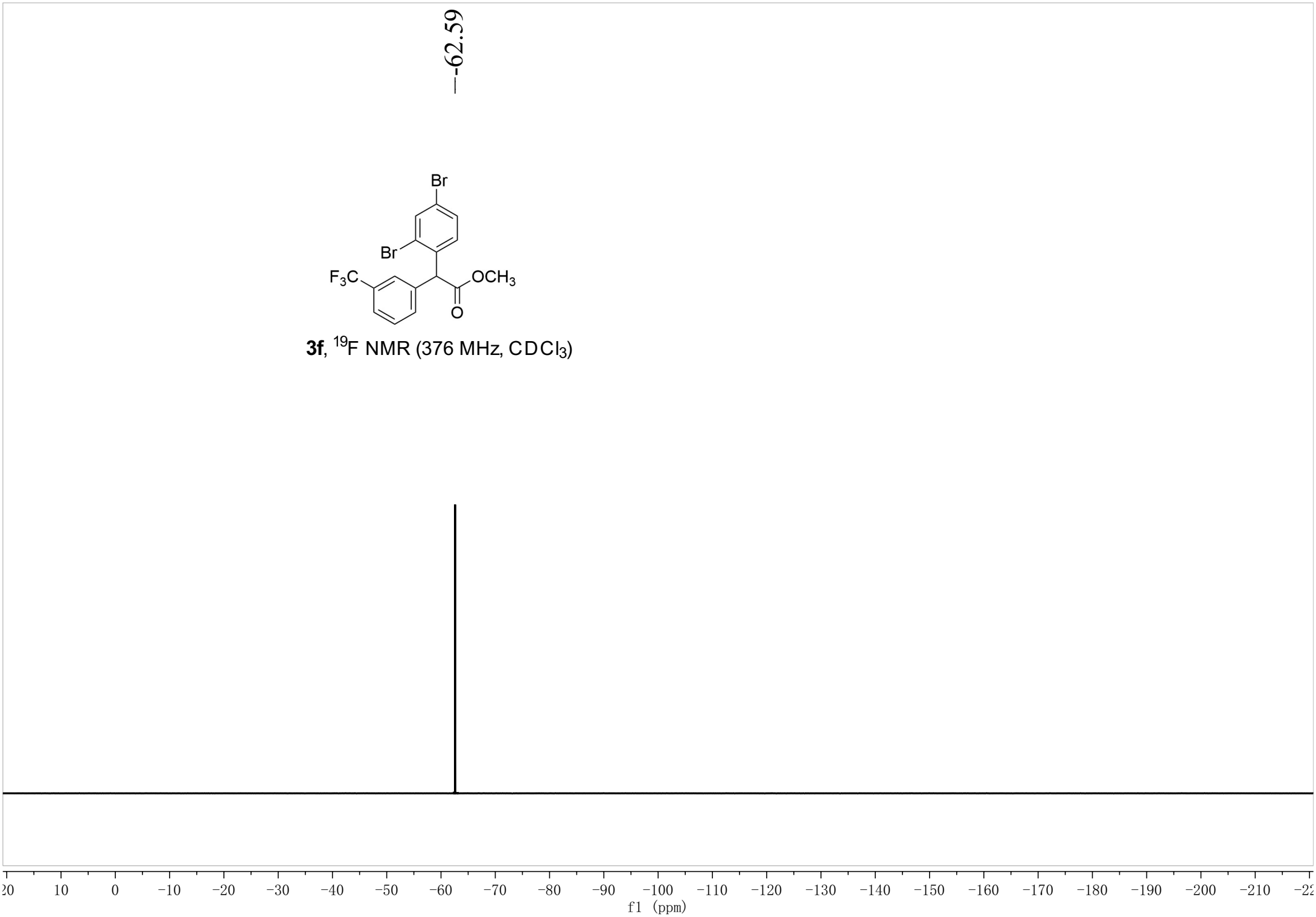
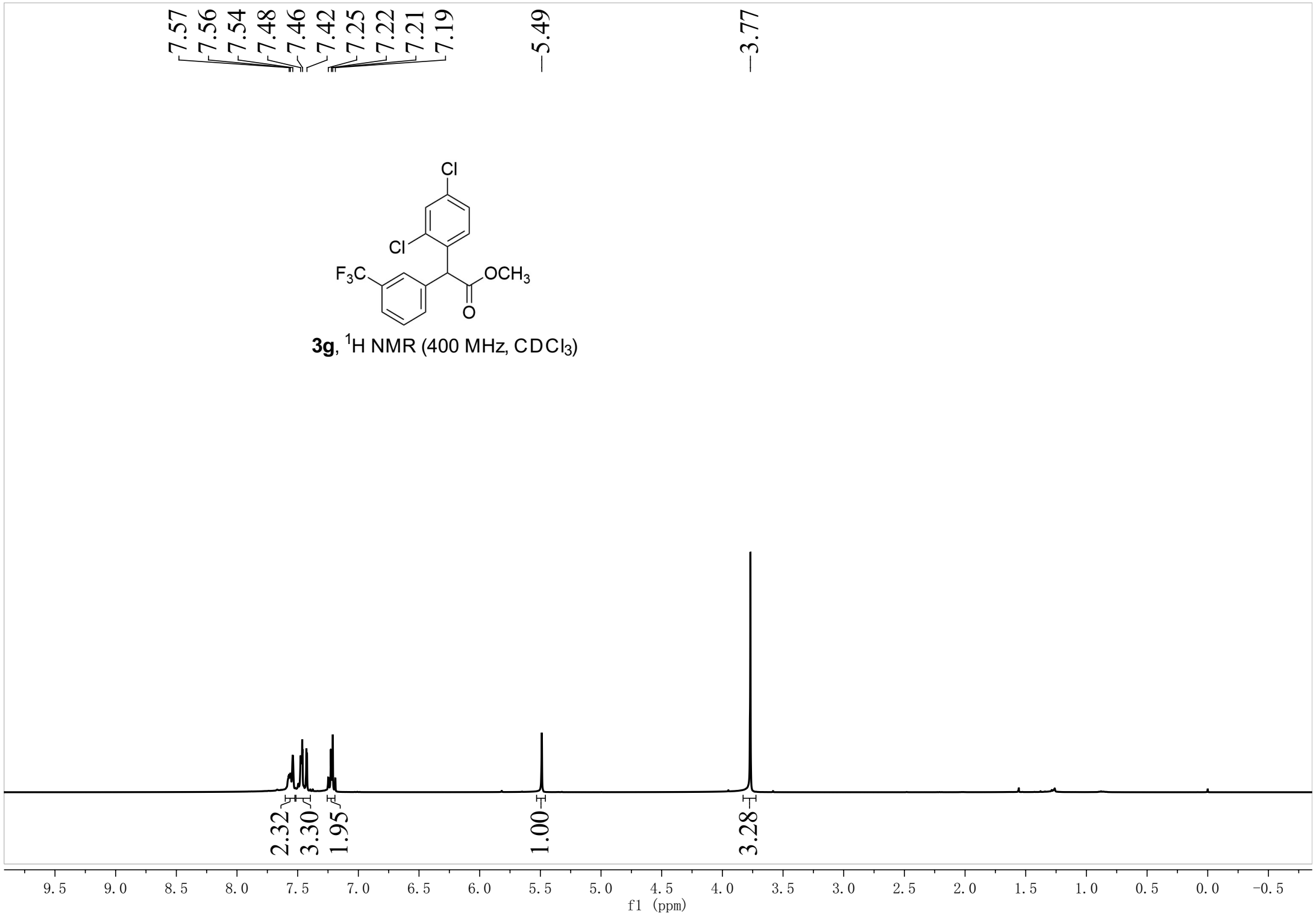
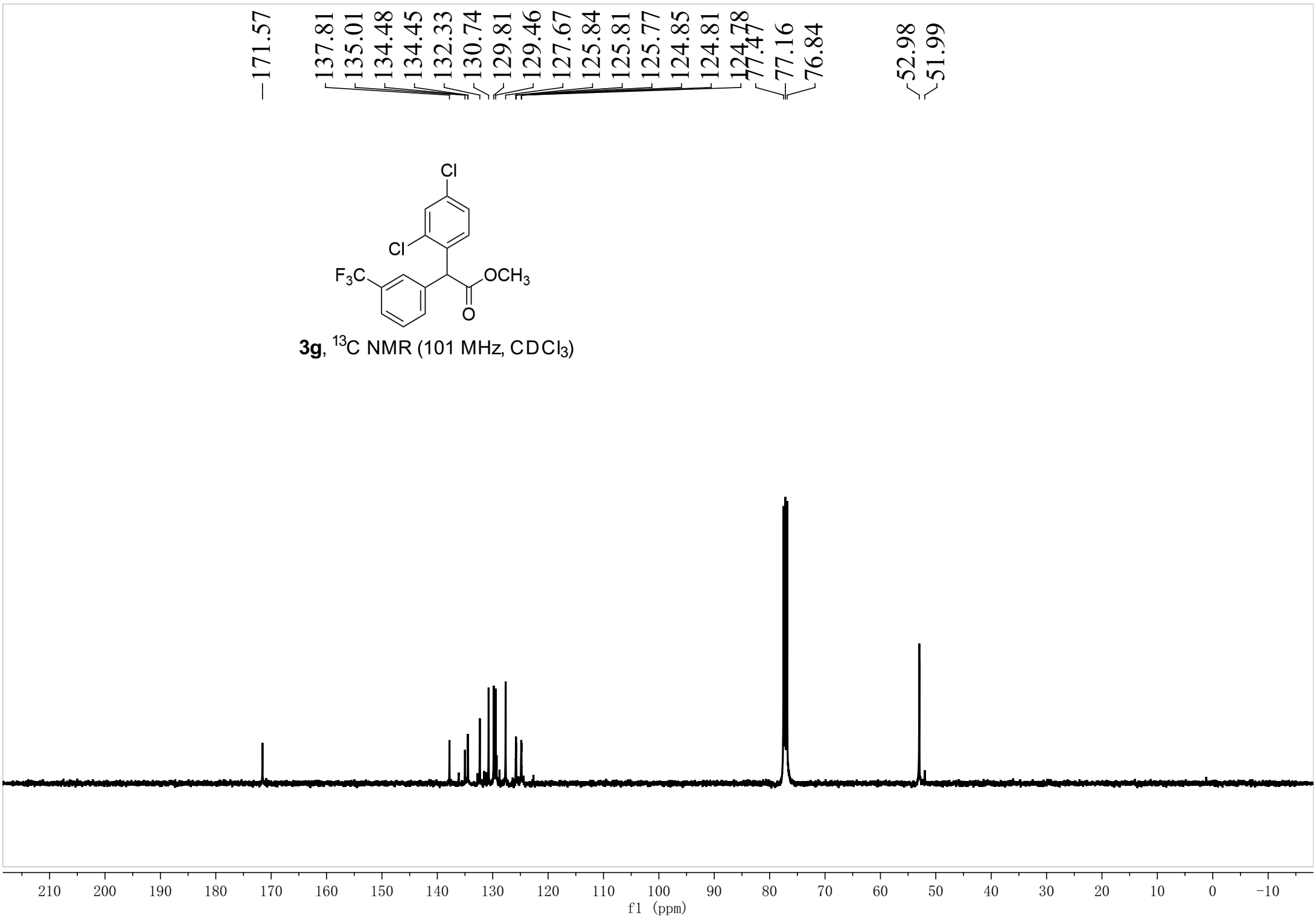
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



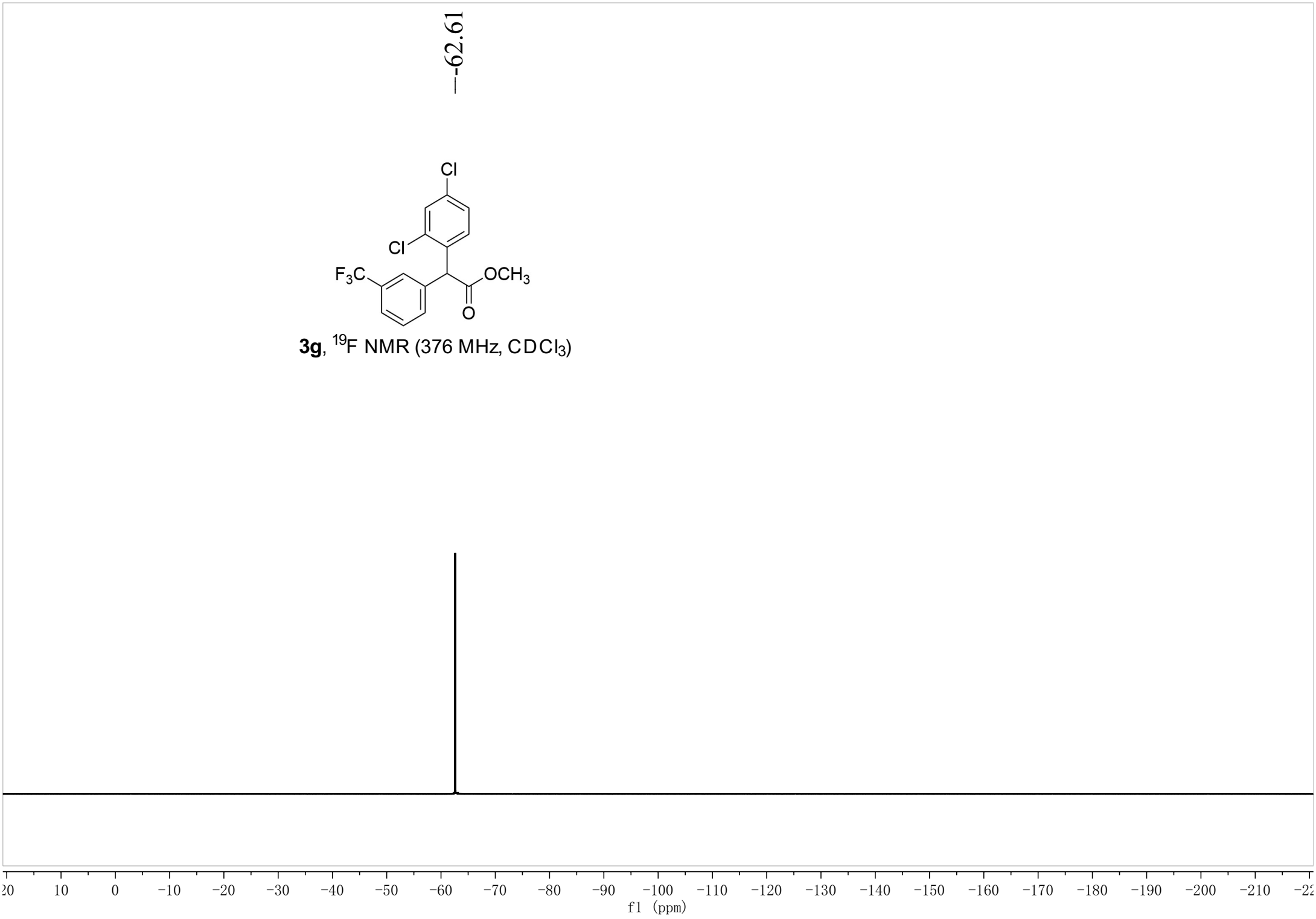
3f, ^{19}F NMR (376 MHz, $CDCl_3$)



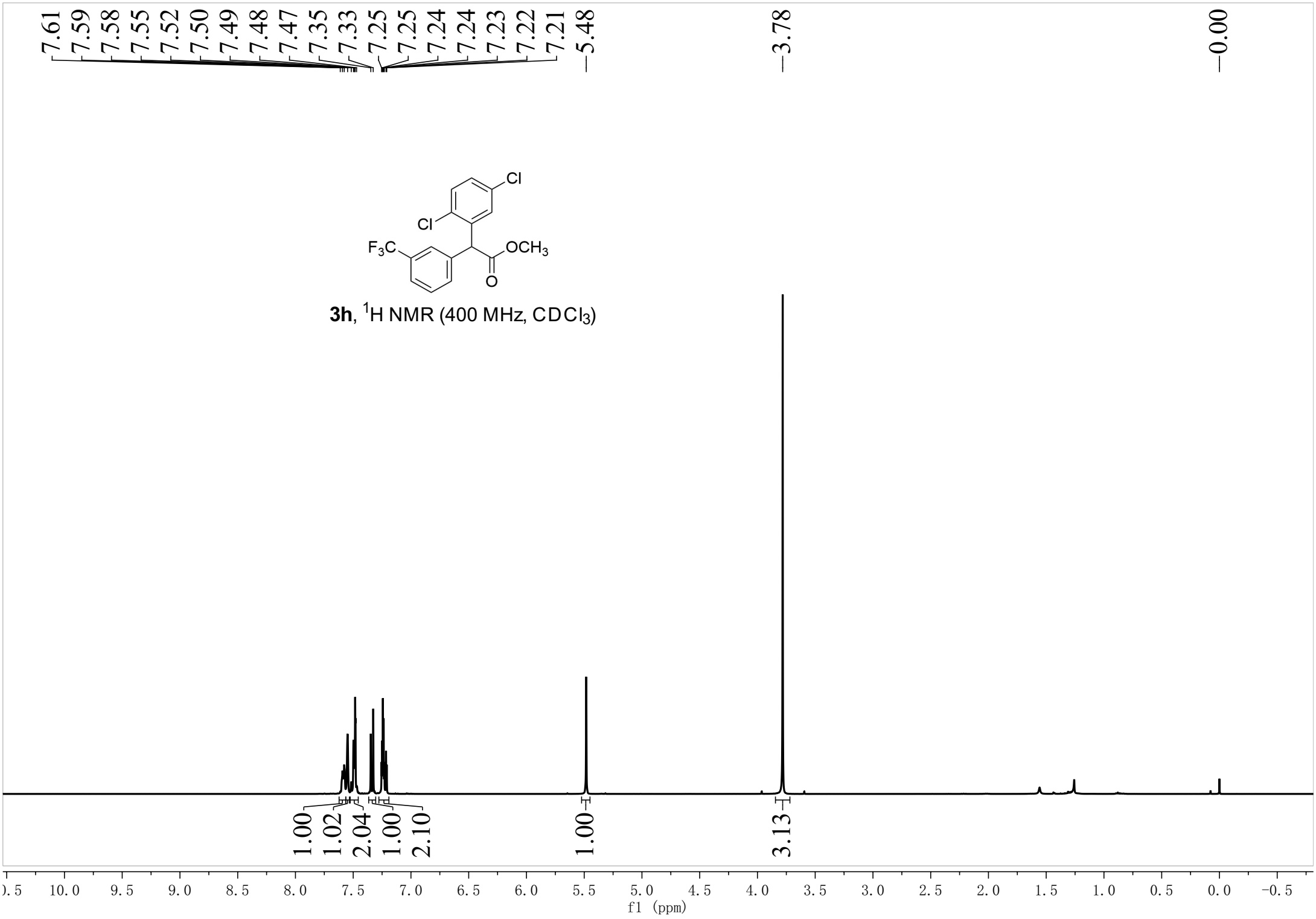
3g, ^{1}H NMR (400 MHz, $CDCl_3$)



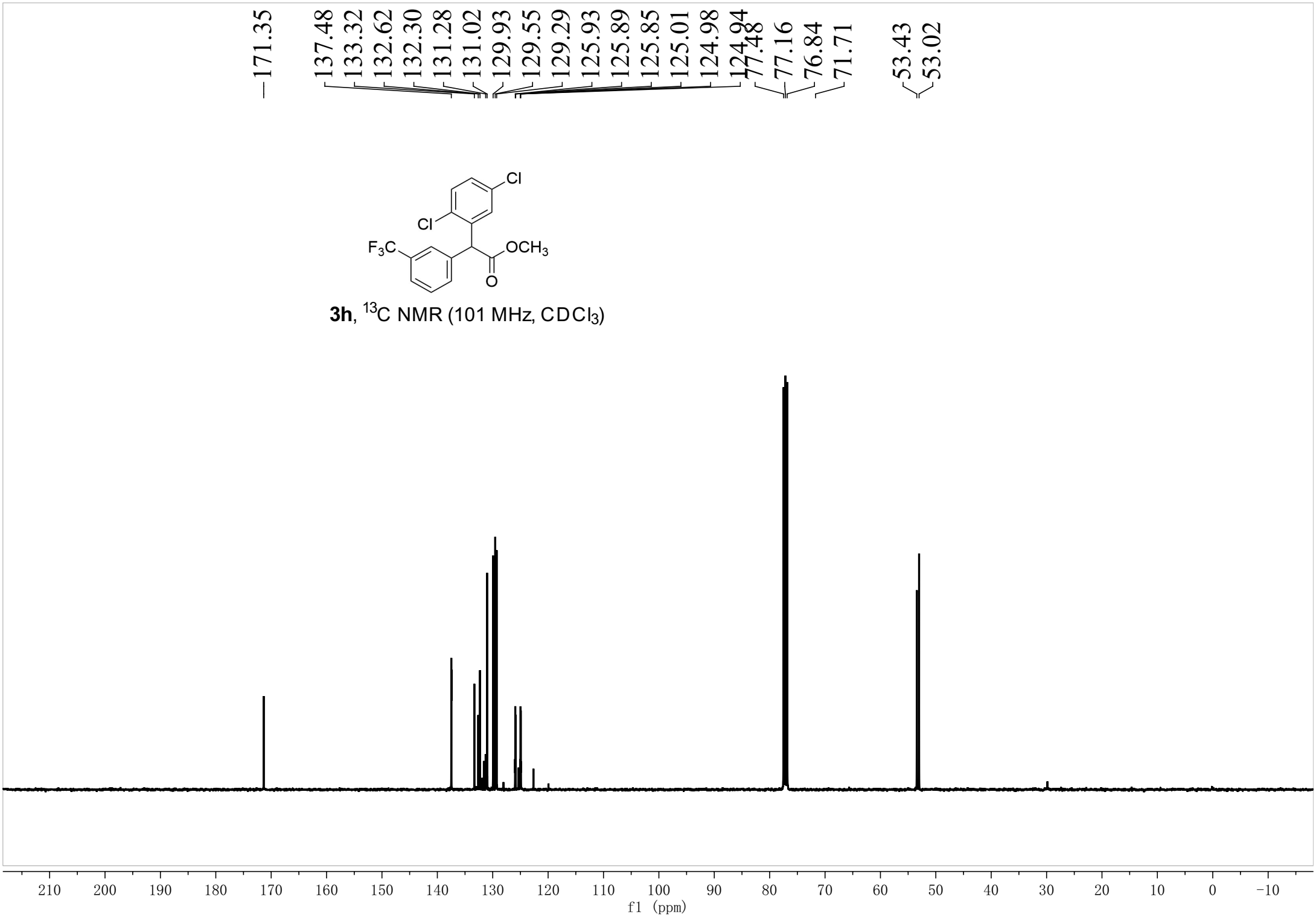
3g, ^{13}C NMR (101 MHz, $CDCl_3$)

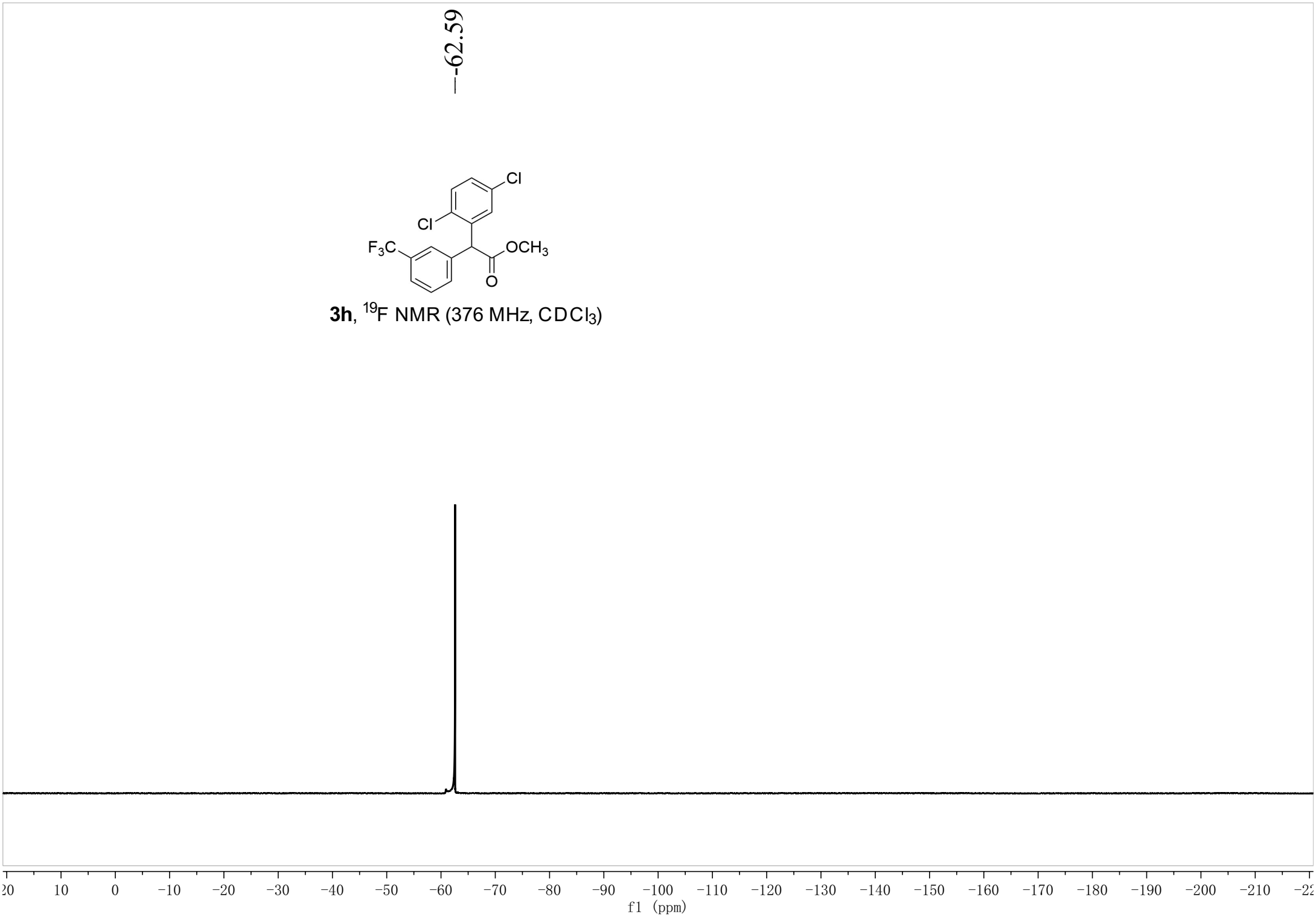


3g, ^{19}F NMR (376 MHz, $CDCl_3$)

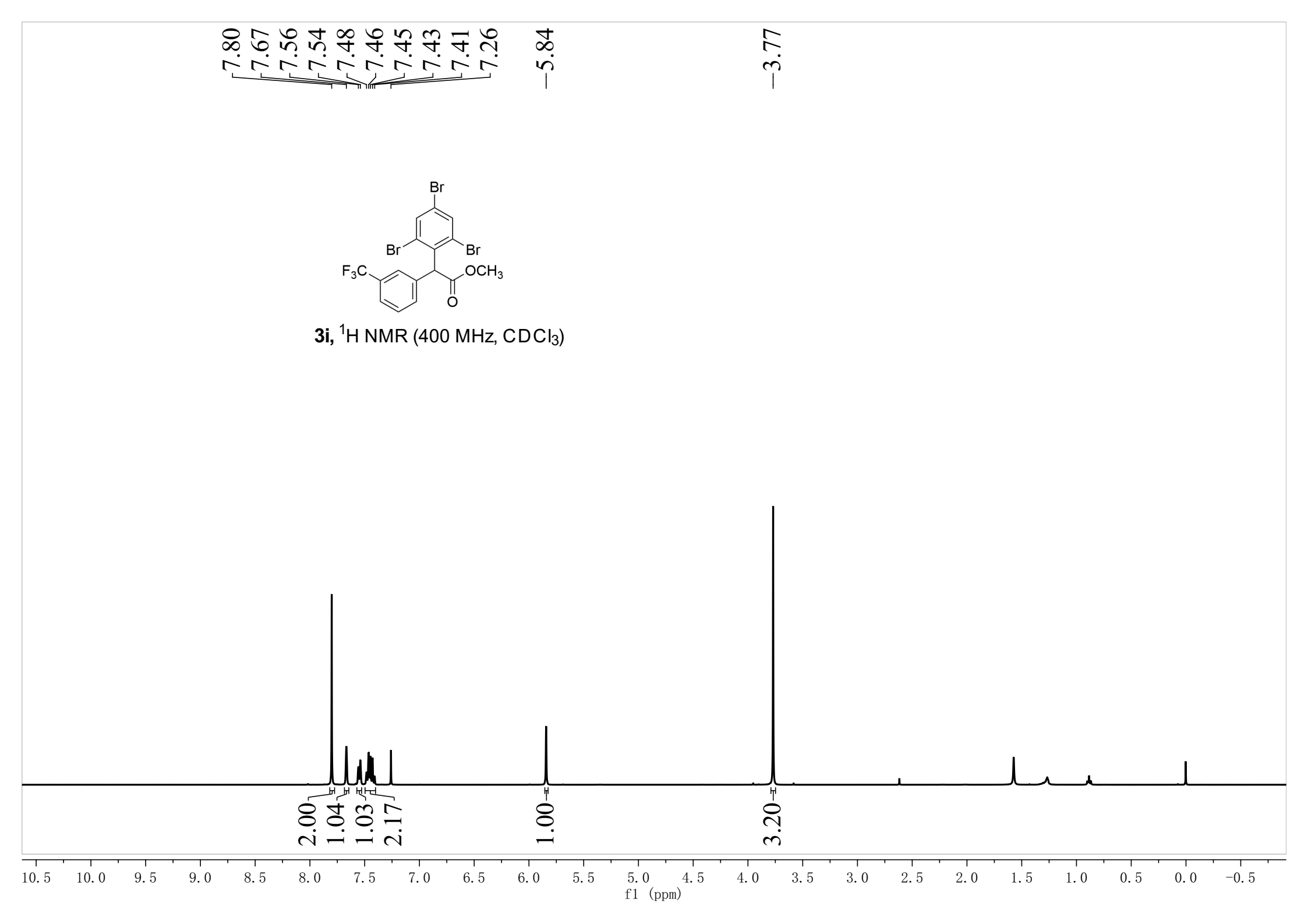


3h, ^{1}H NMR (400 MHz, $CDCl_3$)

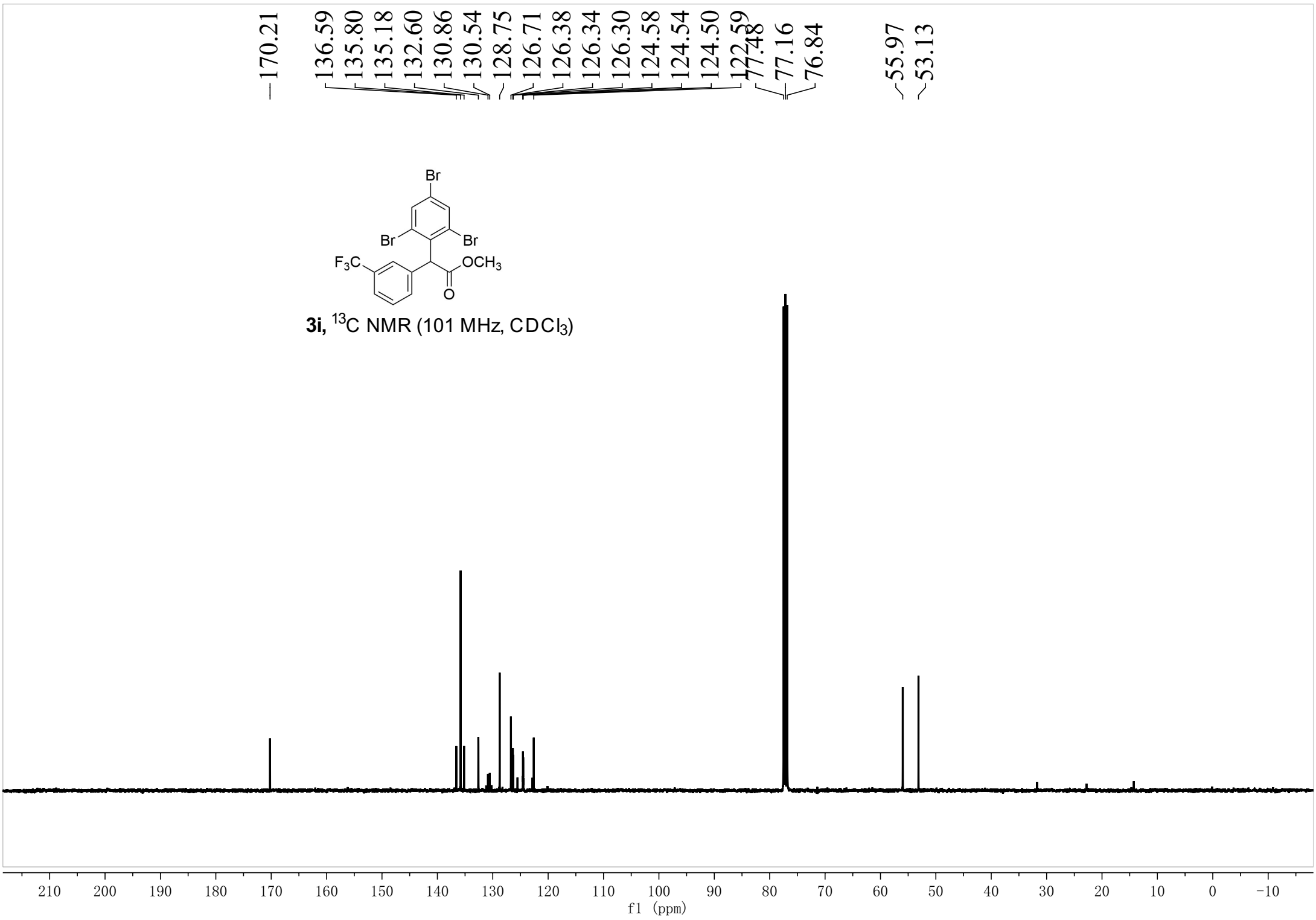

171.35
137.48
133.32
132.62
132.30
131.28
131.02
129.93
129.55
129.29
125.93
125.89
125.85
125.01
124.98
124.94
77.48
77.16
76.84
71.71
53.43
53.02
Cl
Cl
F3C
OCH3
O
3h, 13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

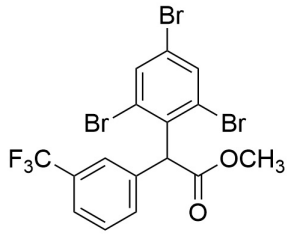


3h, ^{19}F NMR (376 MHz, $CDCl_3$)

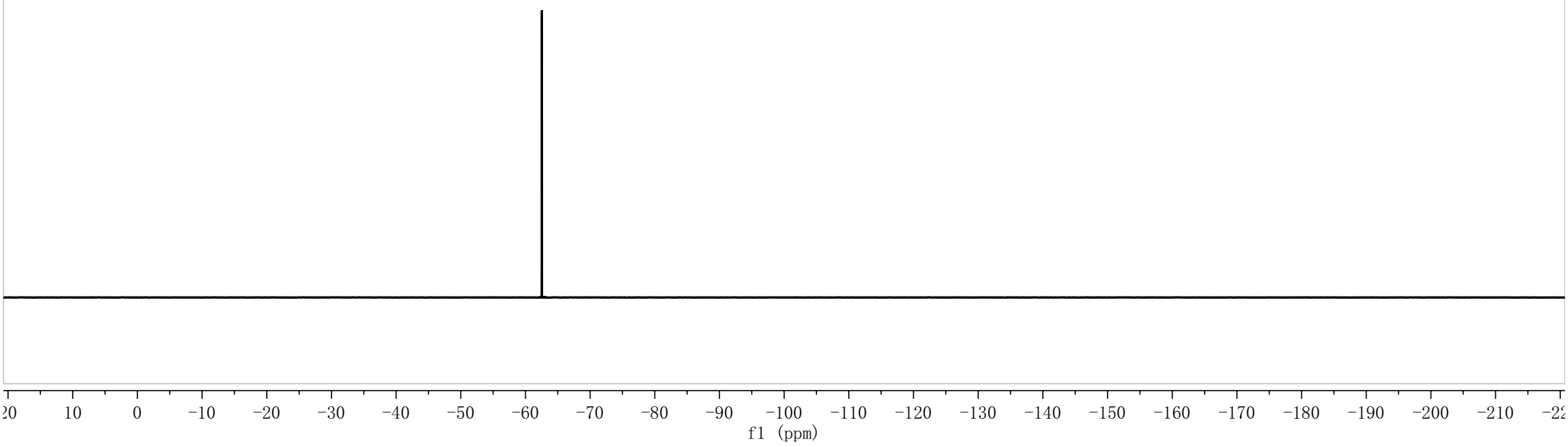


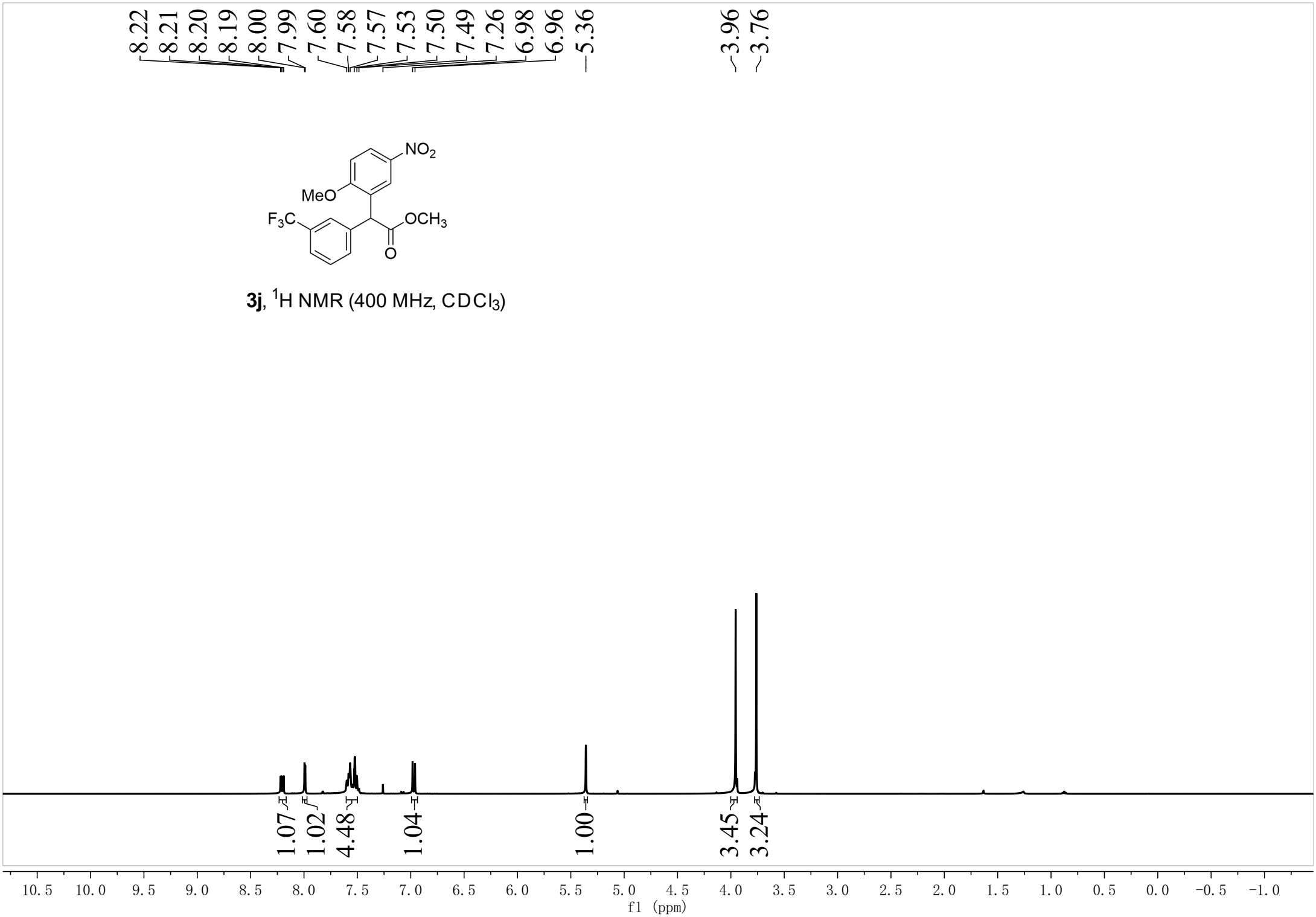
3i, ^{1}H NMR (400 MHz, $CDCl_3$)


170.21
136.59
135.80
135.18
132.60
130.86
130.54
128.75
126.71
126.38
126.34
126.30
124.58
124.54
124.50
122.59
77.48
77.16
76.84
55.97
53.13
Br
Br
Br
F3C
OCH3
O
3i, 13C NMR (101 MHz, CDCl3)
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)

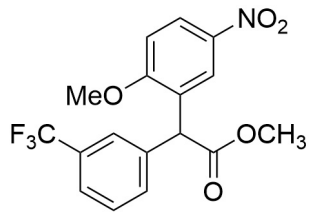


3i, ^{19}F NMR (376 MHz, $CDCl_3$)

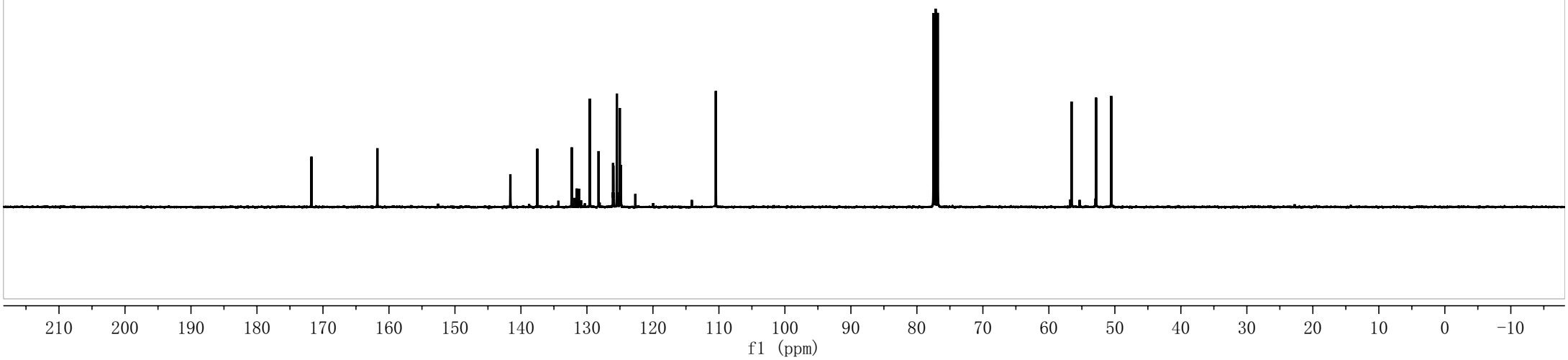


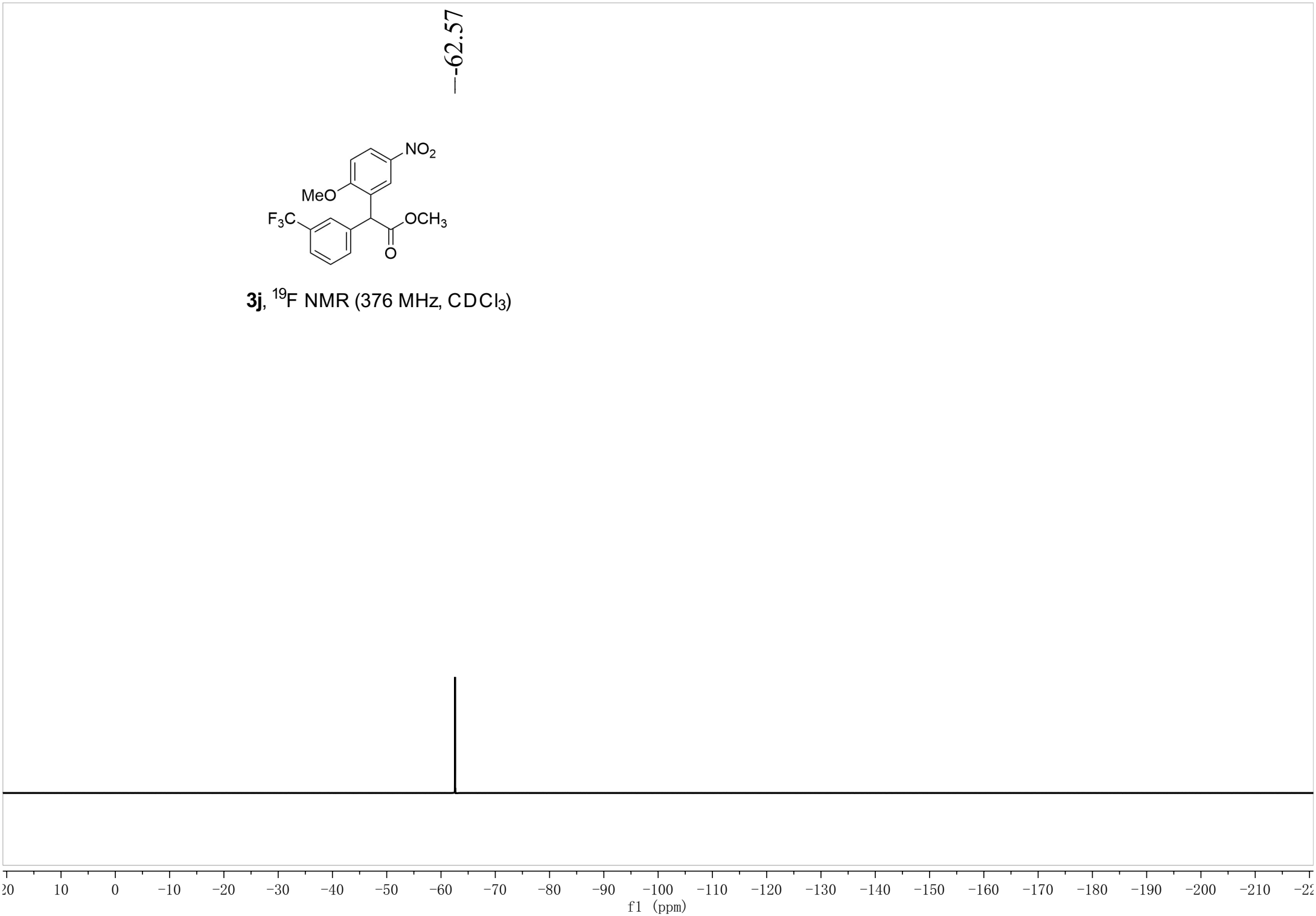


3j, ^{1}H NMR (400 MHz, $CDCl_3$)

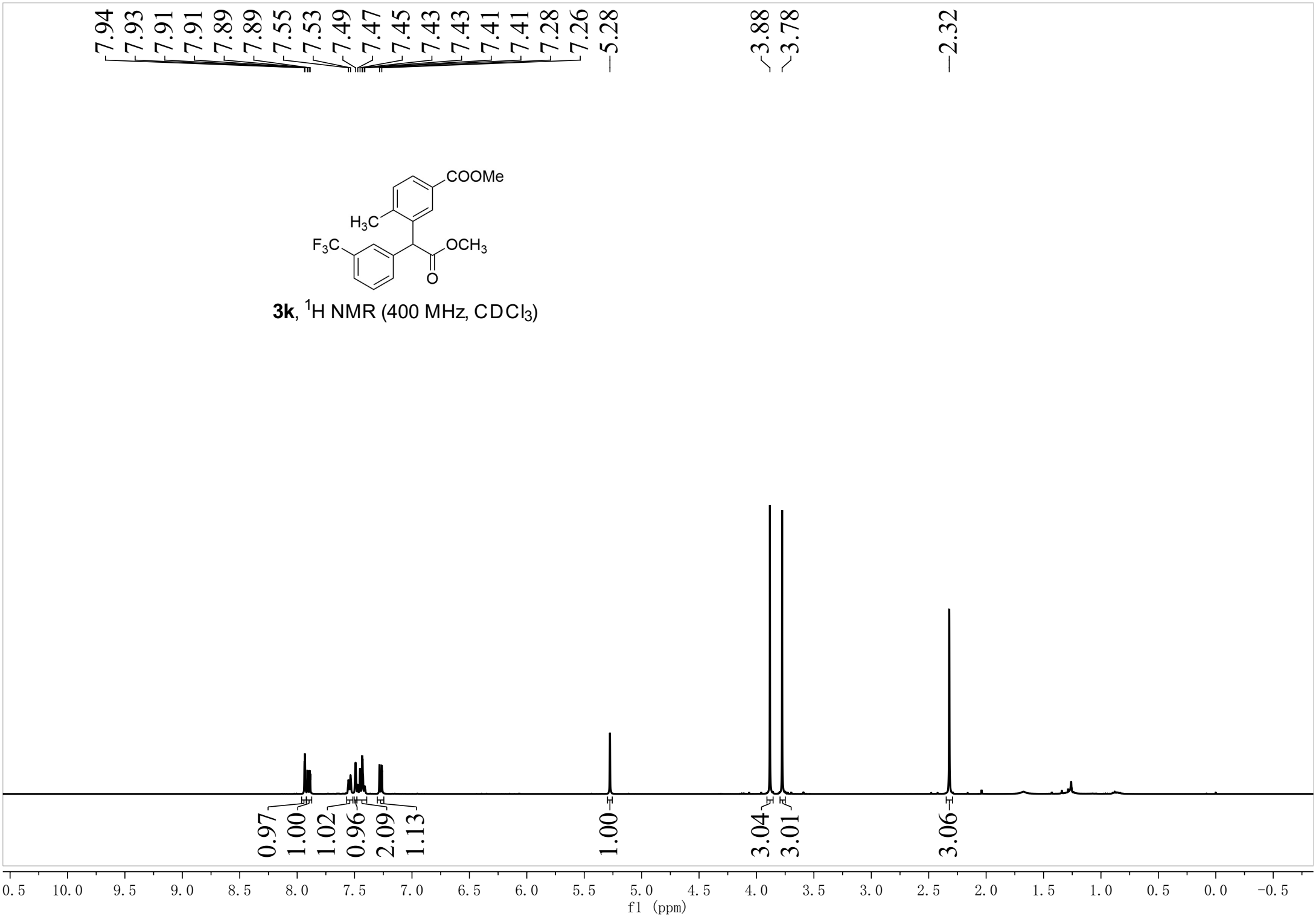


3j, ^{13}C NMR (101 MHz, $CDCl_3$)

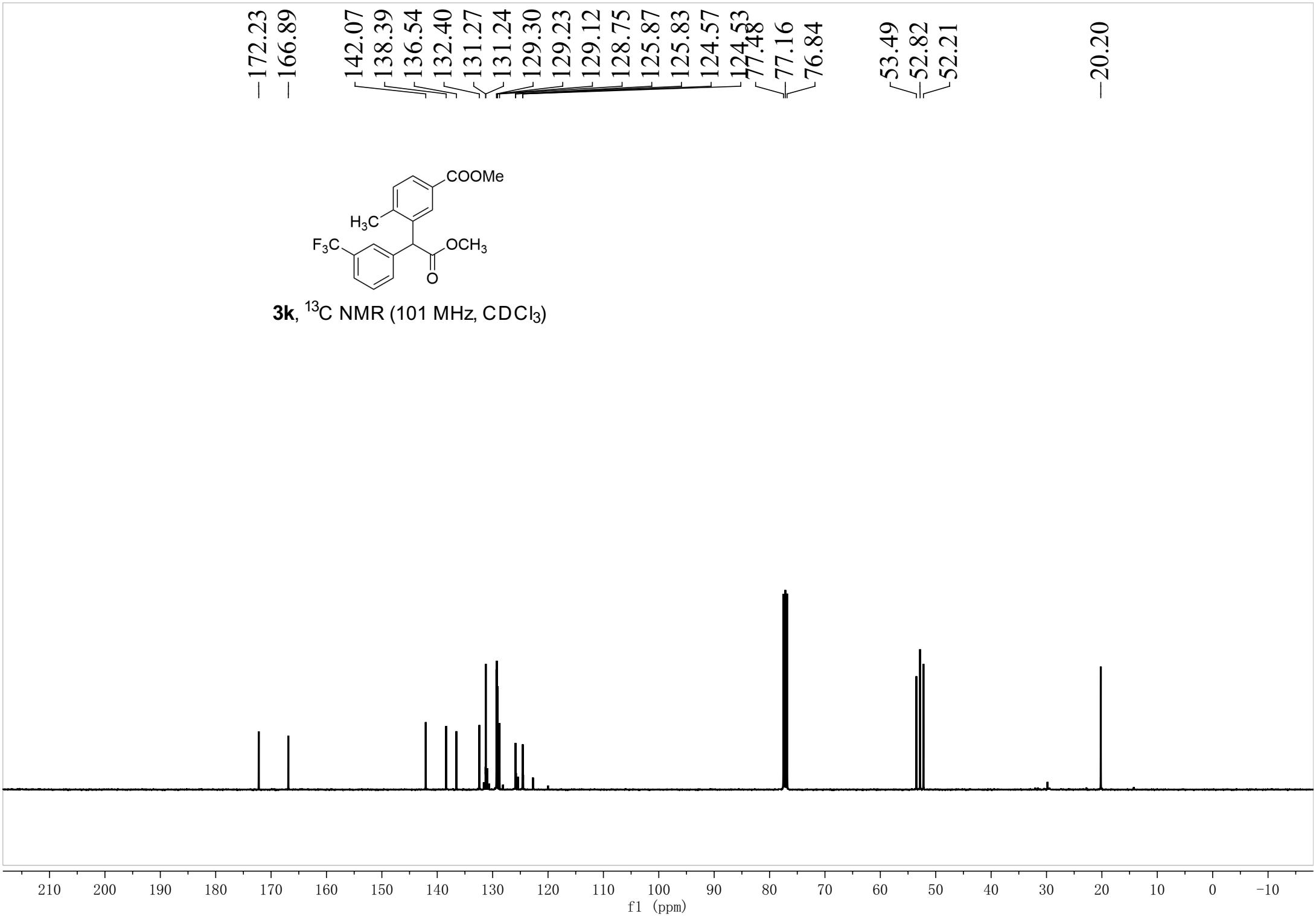




3j, ^{19}F NMR (376 MHz, $CDCl_3$)

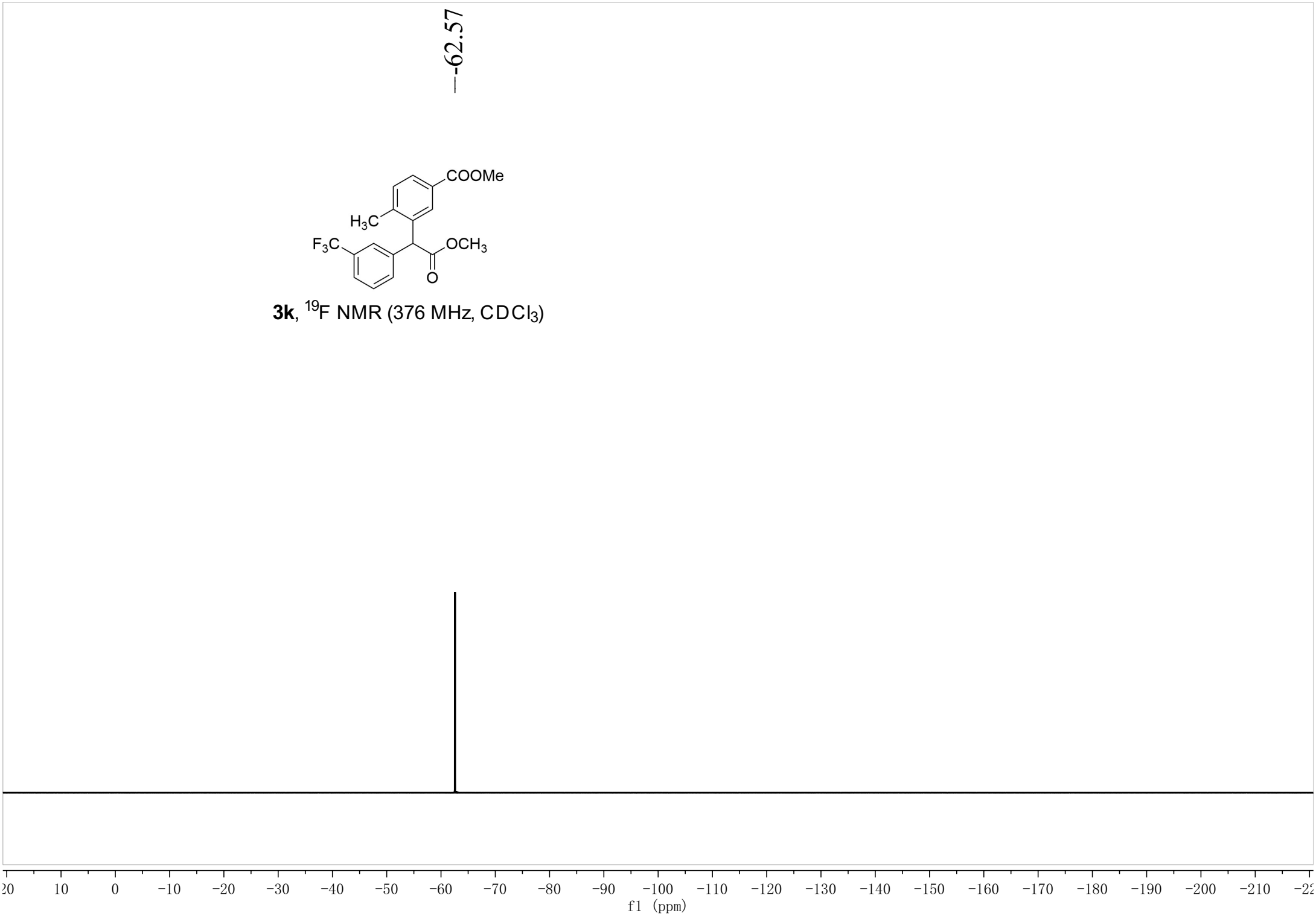


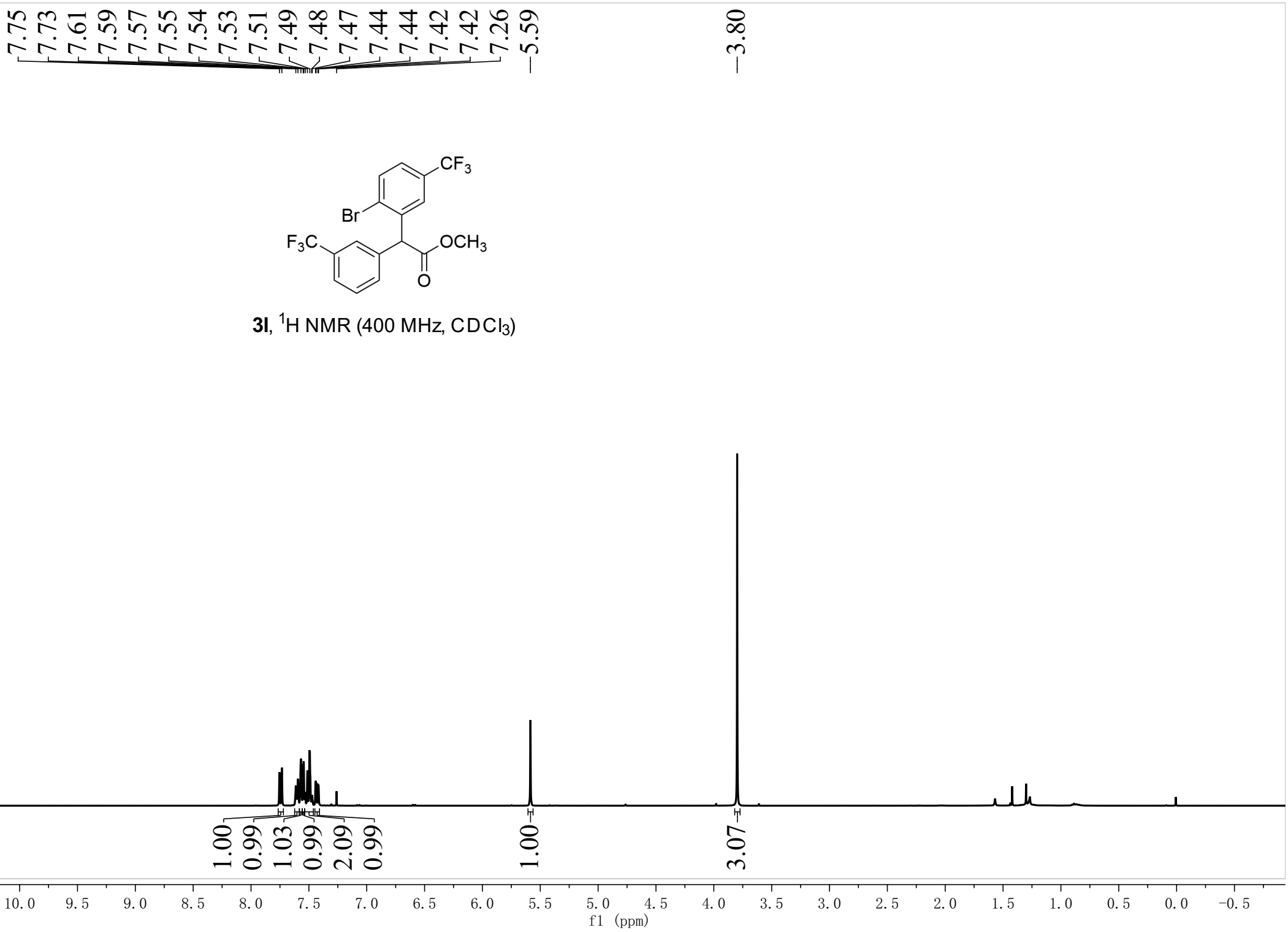
3k, ^{1}H NMR (400 MHz, $CDCl_3$)



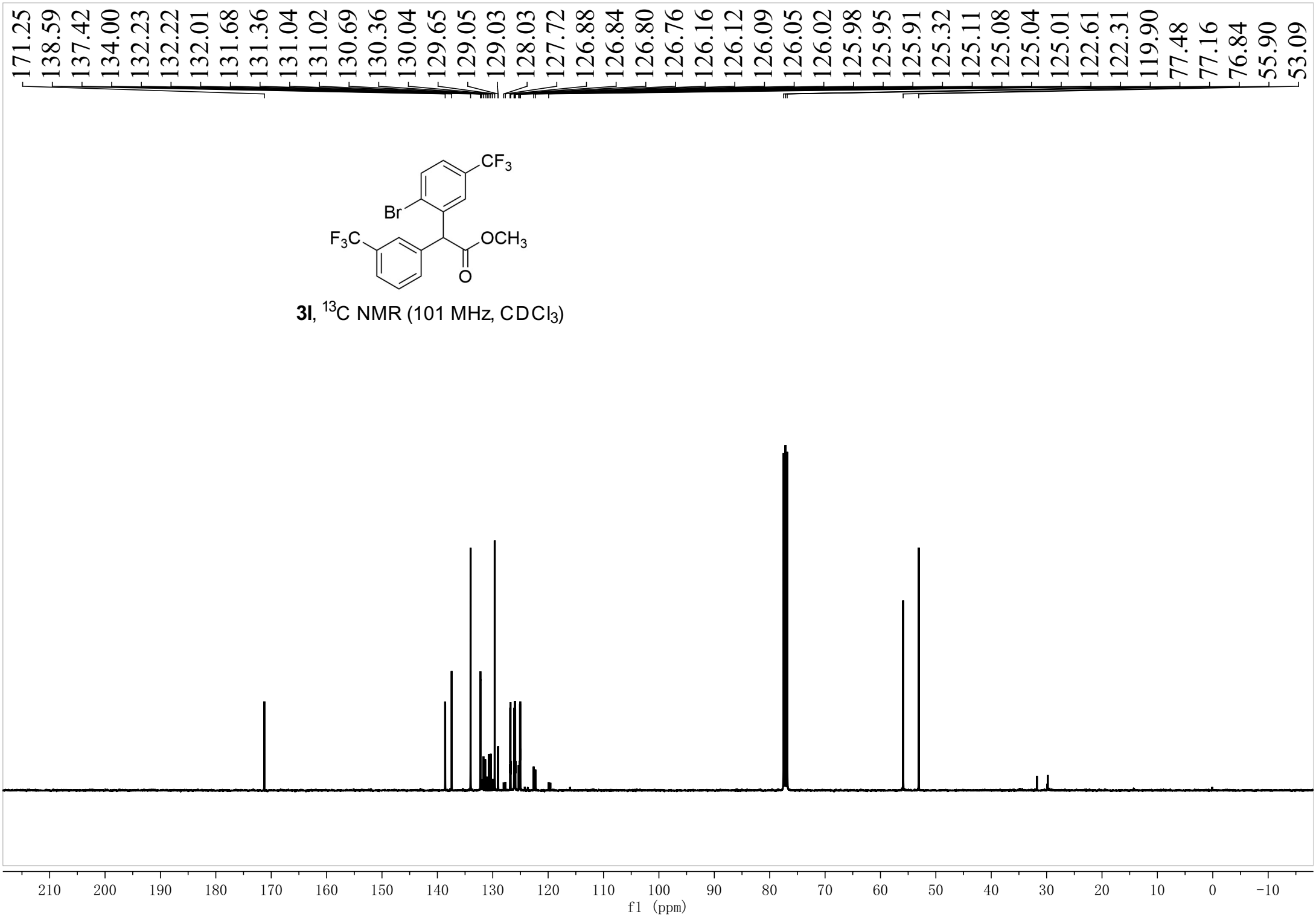
3k, ^{13}C NMR (101 MHz, $CDCl_3$)

3k, ^{19}F NMR (376 MHz, $CDCl_3$)



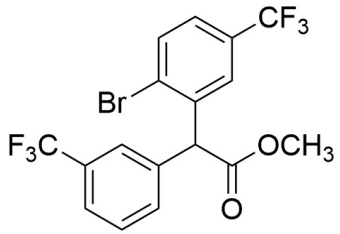


3l, ^{1}H NMR (400 MHz, $CDCl_3$)

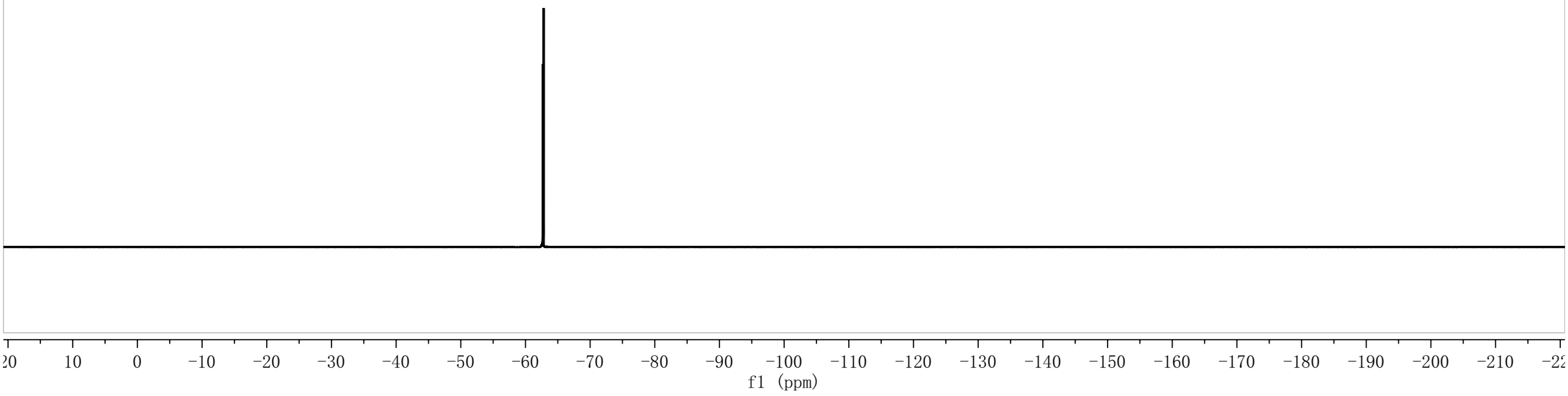


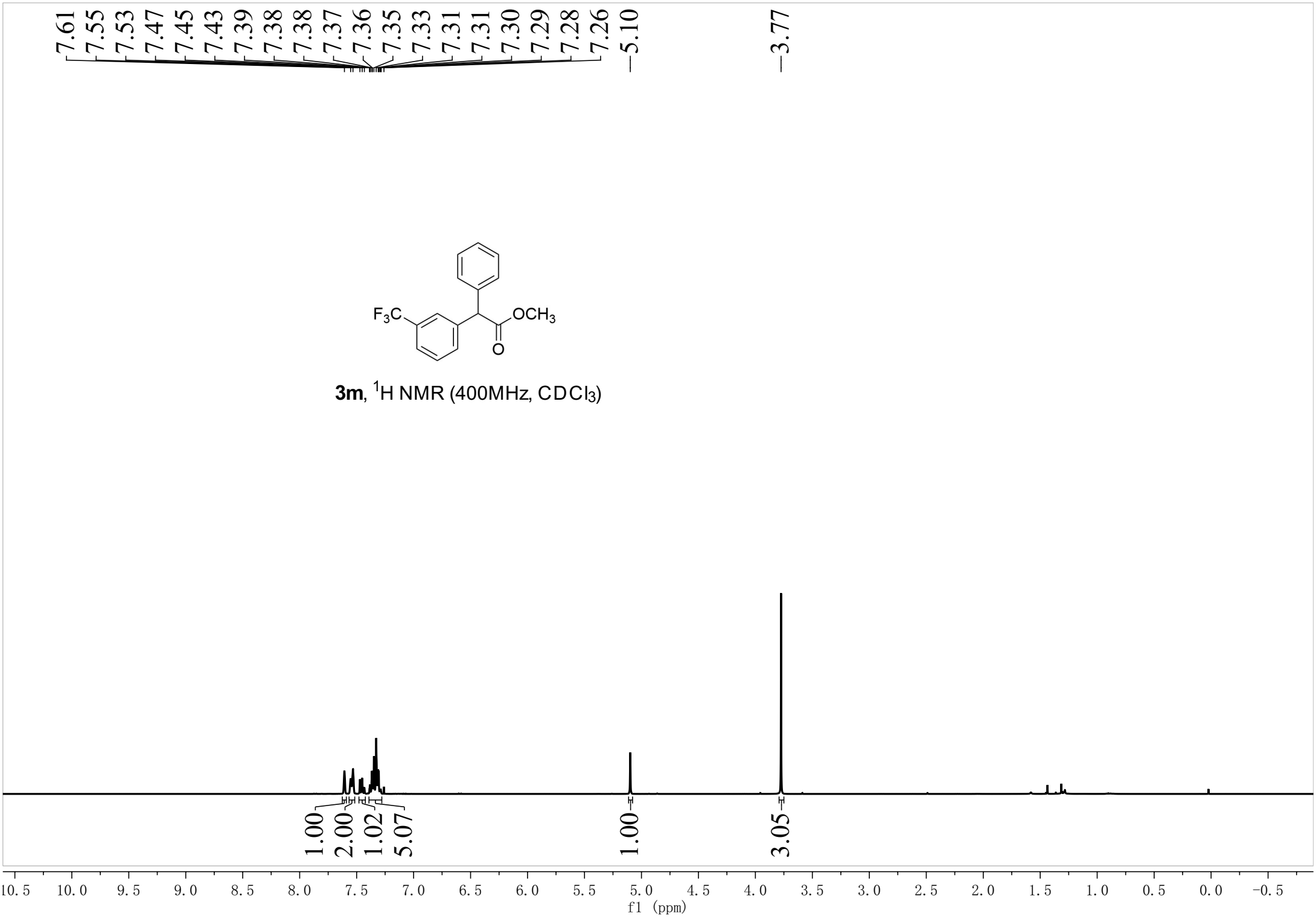
3l, ^{13}C NMR (101 MHz, $CDCl_3$)

-62.70
-62.80

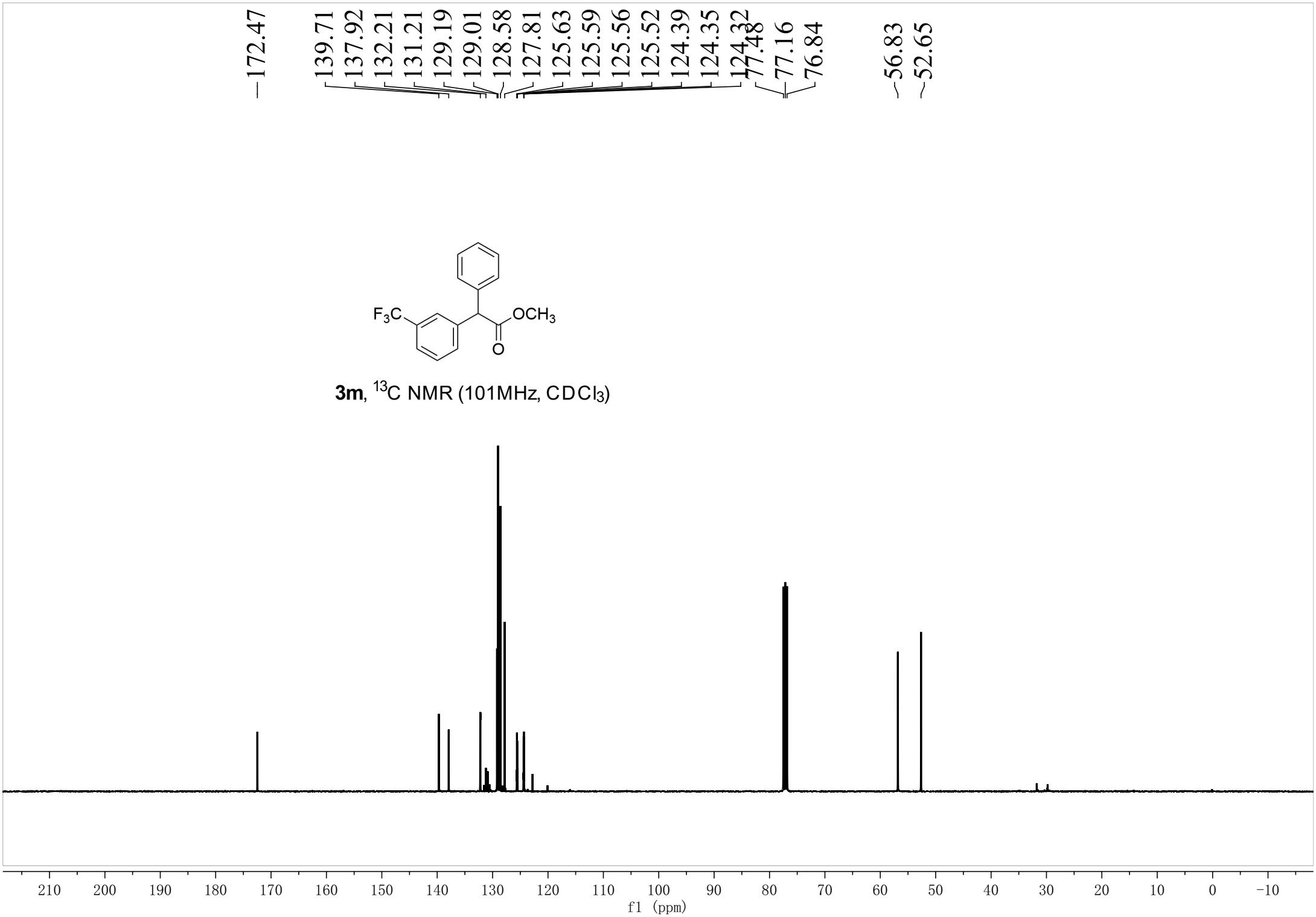


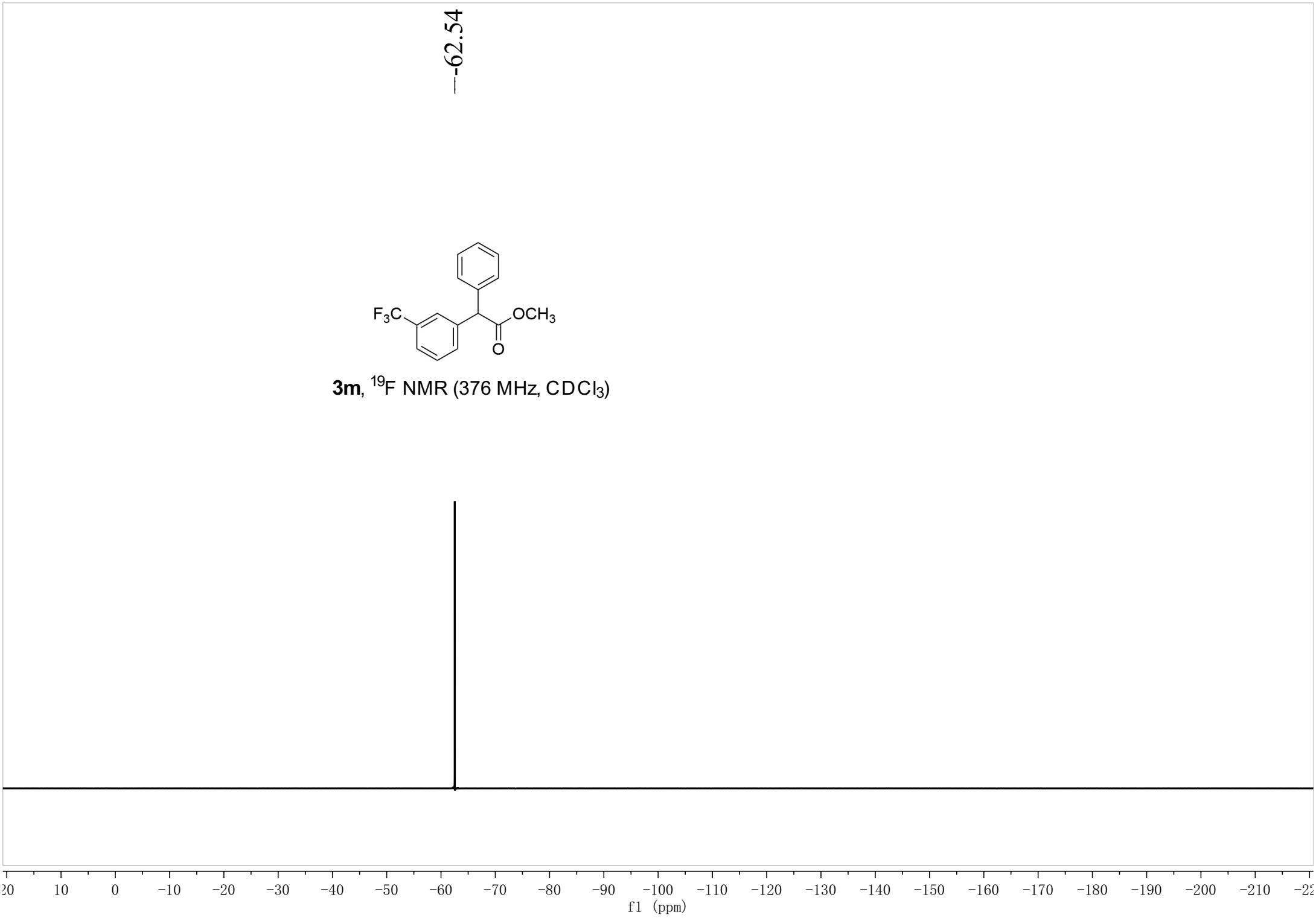
3l, ^{19}F NMR (376 MHz, $CDCl_3$)



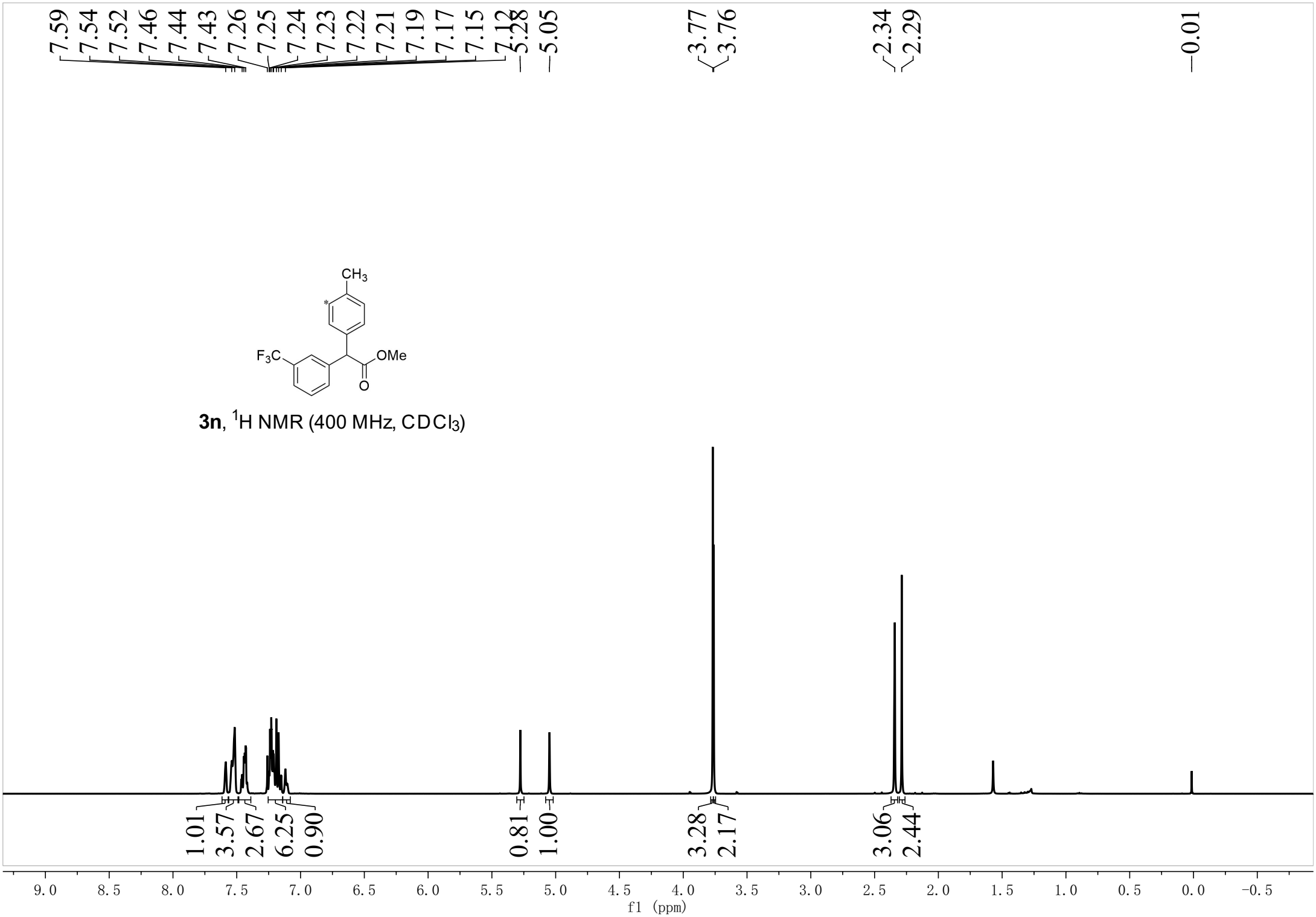


3m, ^{1}H NMR (400MHz, $CDCl_3$)

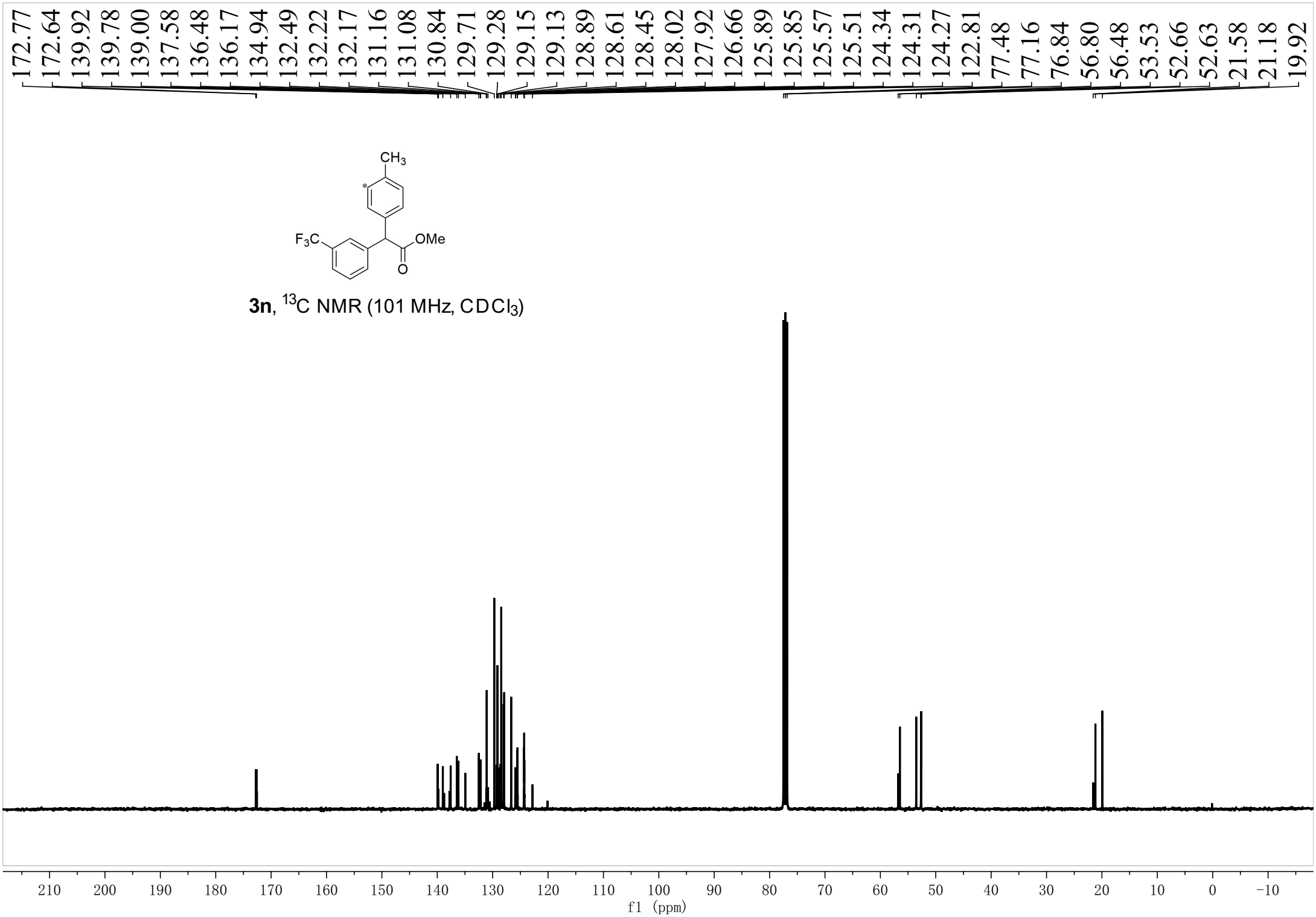

172.47
139.71
137.92
132.21
131.21
129.19
129.01
128.58
127.81
125.63
125.59
125.56
125.52
124.39
124.35
124.32
77.48
77.16
76.84
56.83
52.65
F3C
OCH3
O
3m, 13C NMR (101MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

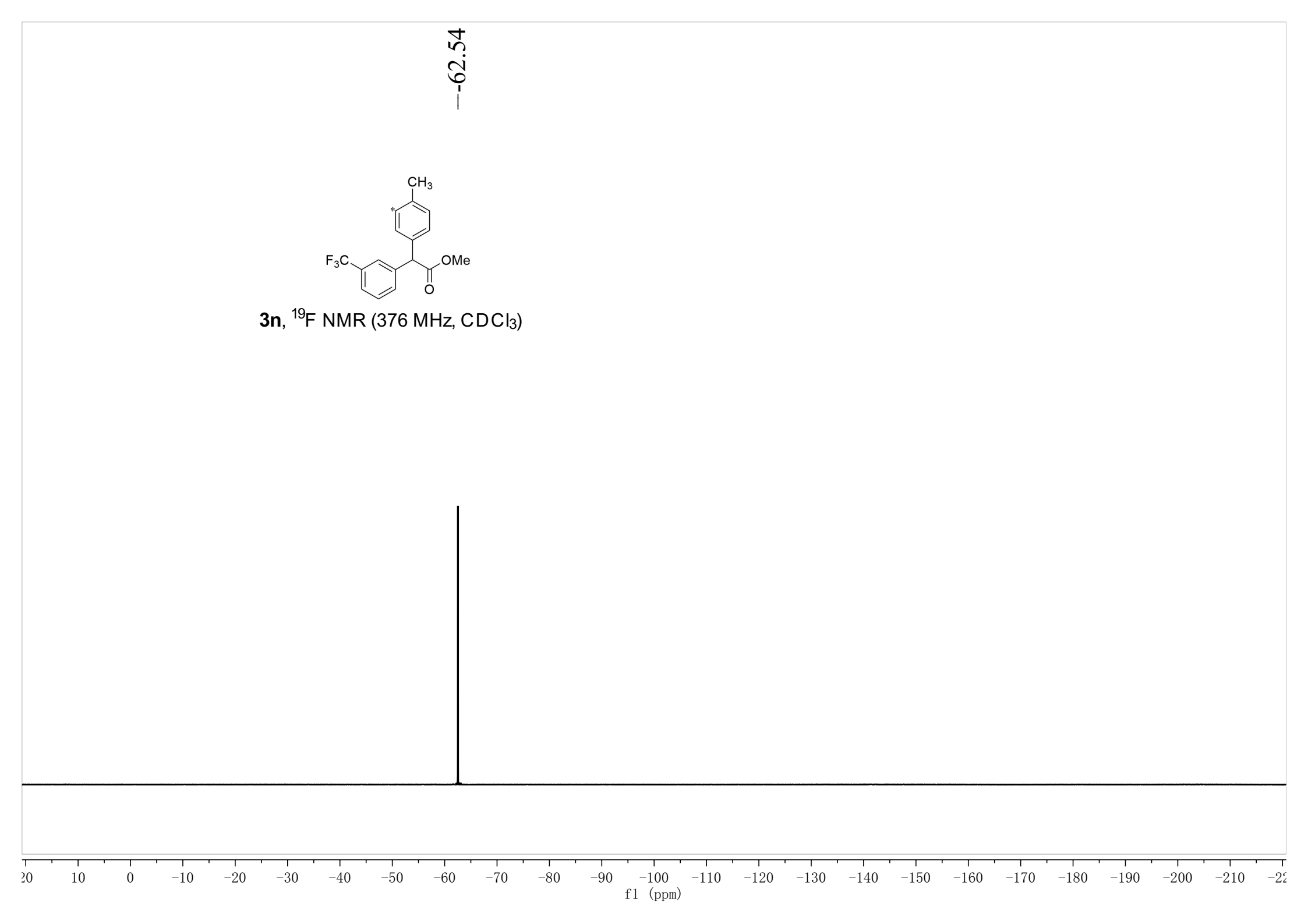


3m, ^{19}F NMR (376 MHz, $CDCl_3$)

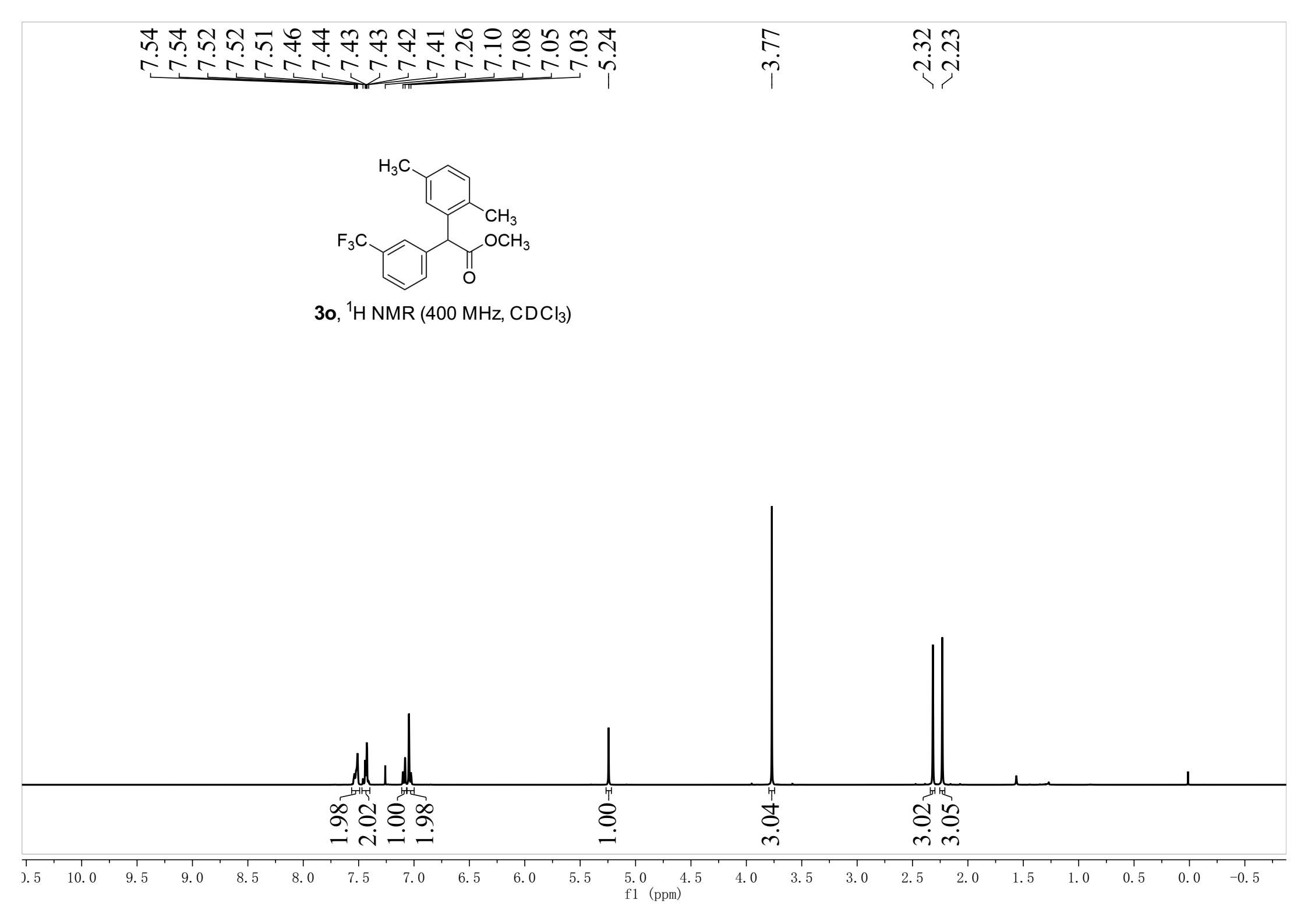


3n, ^{1}H NMR (400 MHz, $CDCl_3$)

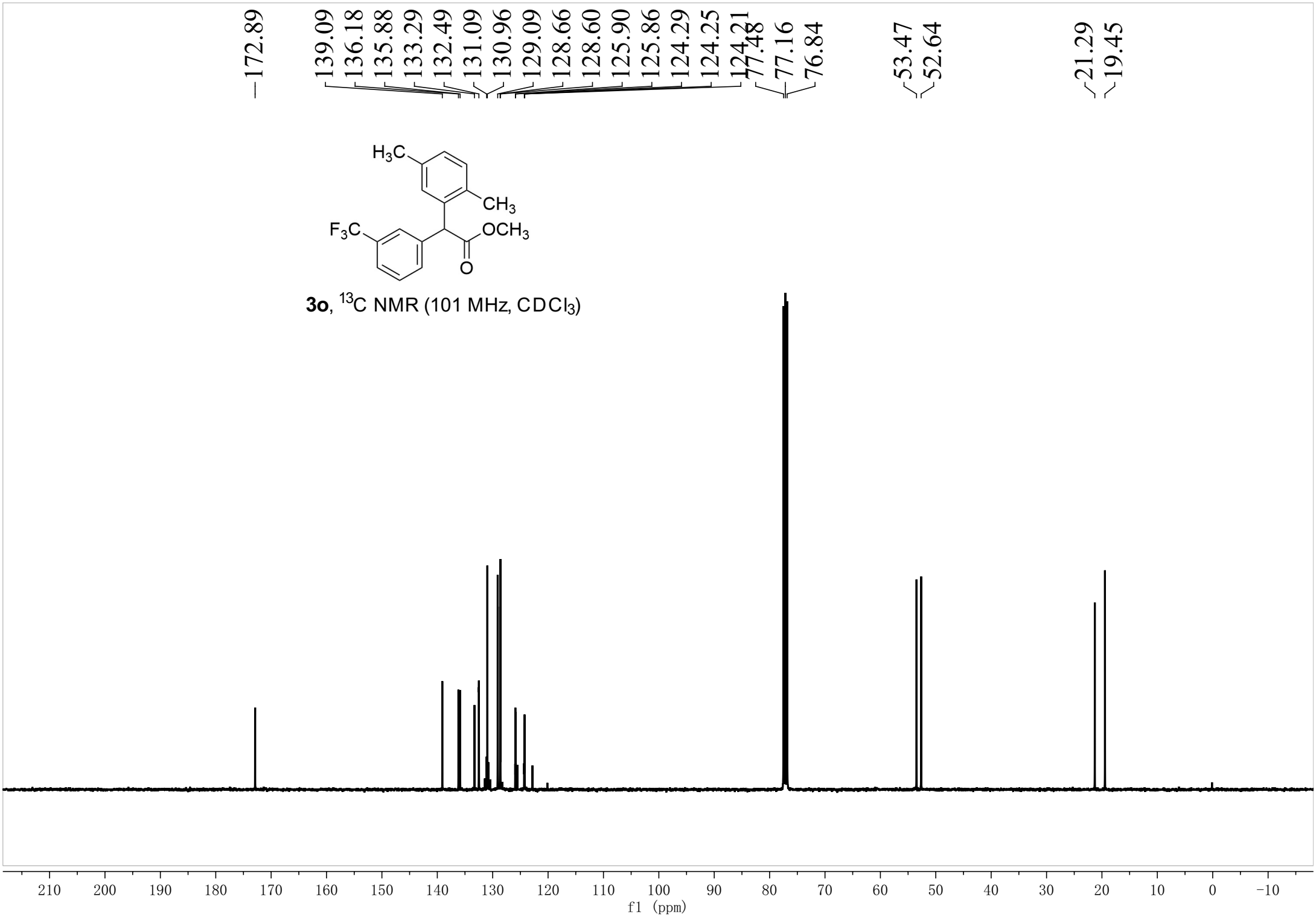

172.77
172.64
139.92
139.78
139.00
137.58
136.48
136.17
134.94
132.49
132.22
132.17
131.16
131.08
130.84
129.71
129.28
129.15
129.13
128.89
128.61
128.45
128.02
127.92
126.66
125.89
125.85
125.57
125.51
124.34
124.31
124.27
122.81
77.48
77.16
76.84
56.80
56.48
53.53
52.66
52.63
21.58
21.18
19.92
CH3
F3C
OMe
O
3n, 13C NMR (101 MHz, CDCl3)
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)

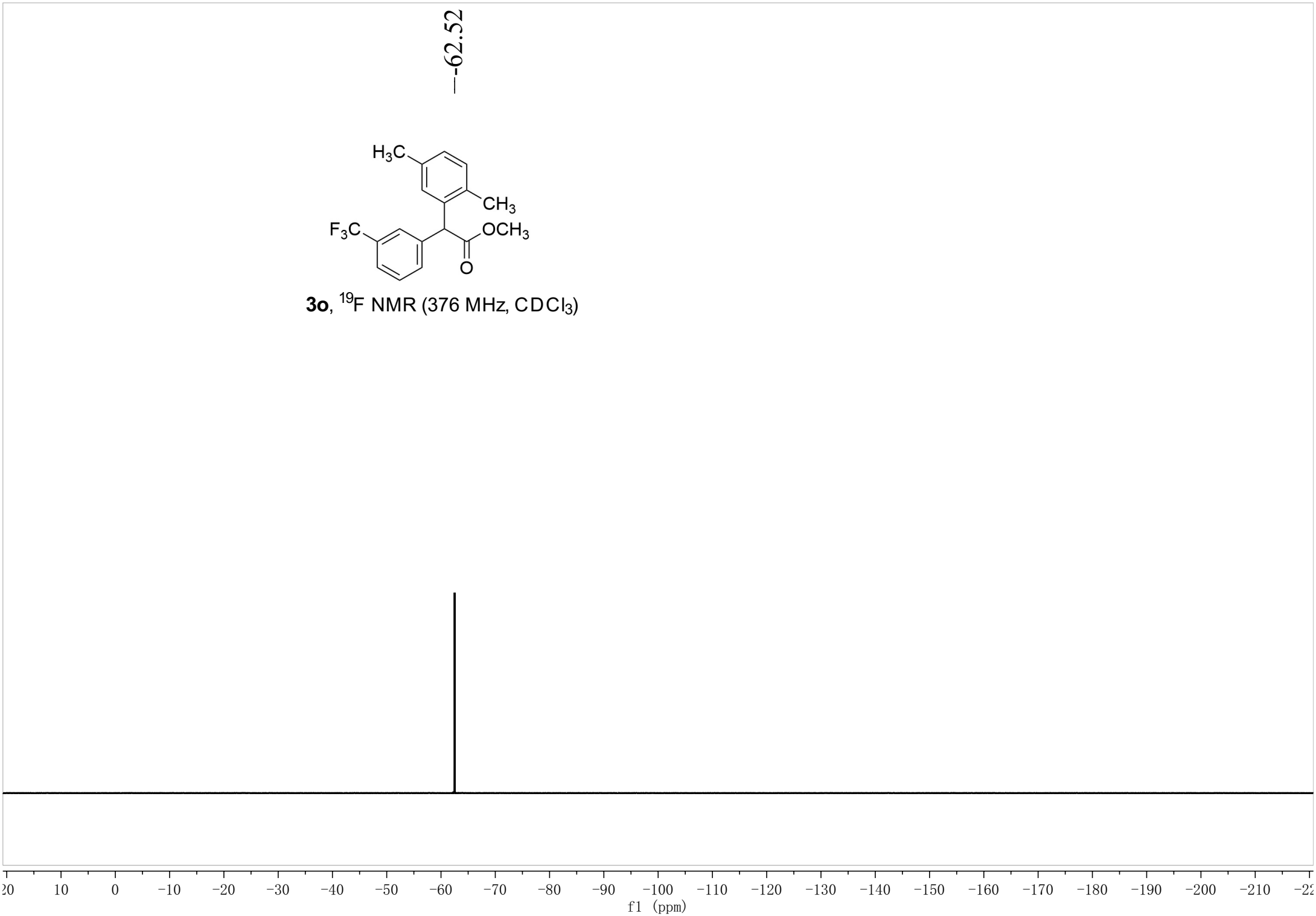


3n, ^{19}F NMR (376 MHz, $CDCl_3$)

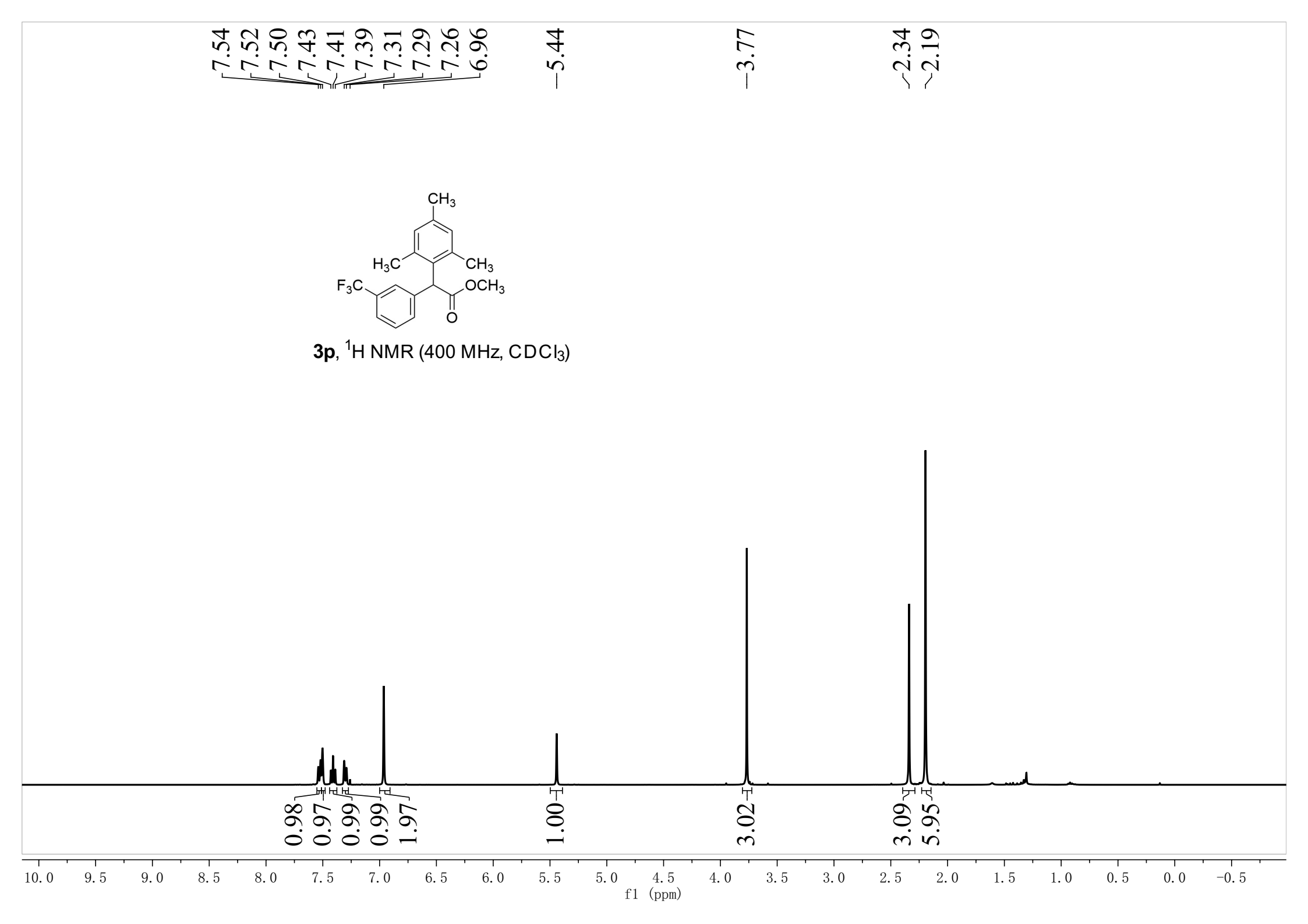


3o, ^{1}H NMR (400 MHz, $CDCl_3$)

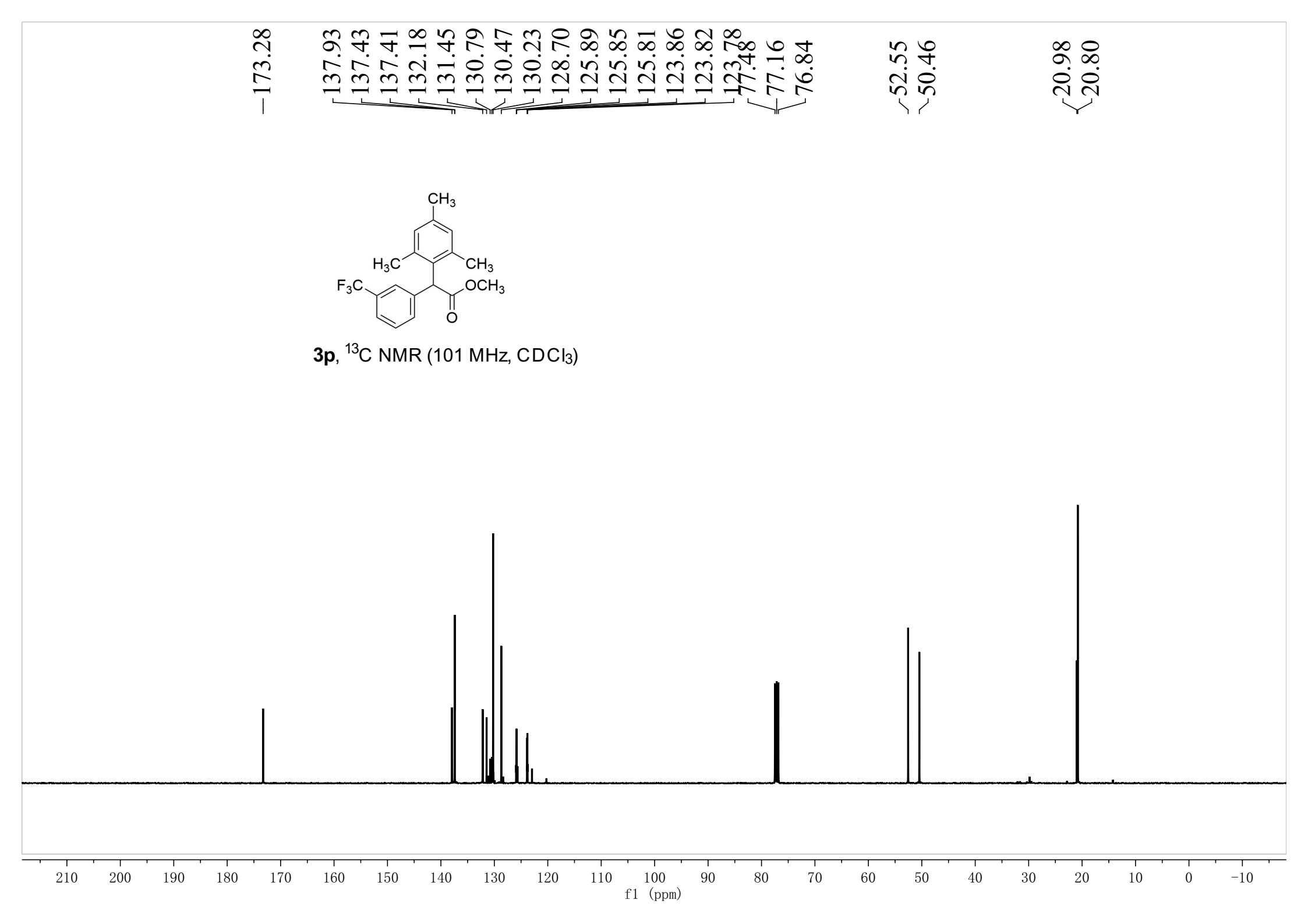

172.89
139.09
136.18
135.88
133.29
132.49
131.09
130.96
129.09
128.66
128.60
125.90
125.86
124.29
124.25
124.21
77.48
77.16
76.84
53.47
52.64
21.29
19.45
H3C
CH3
F3C
OCH3
O
3o, 13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



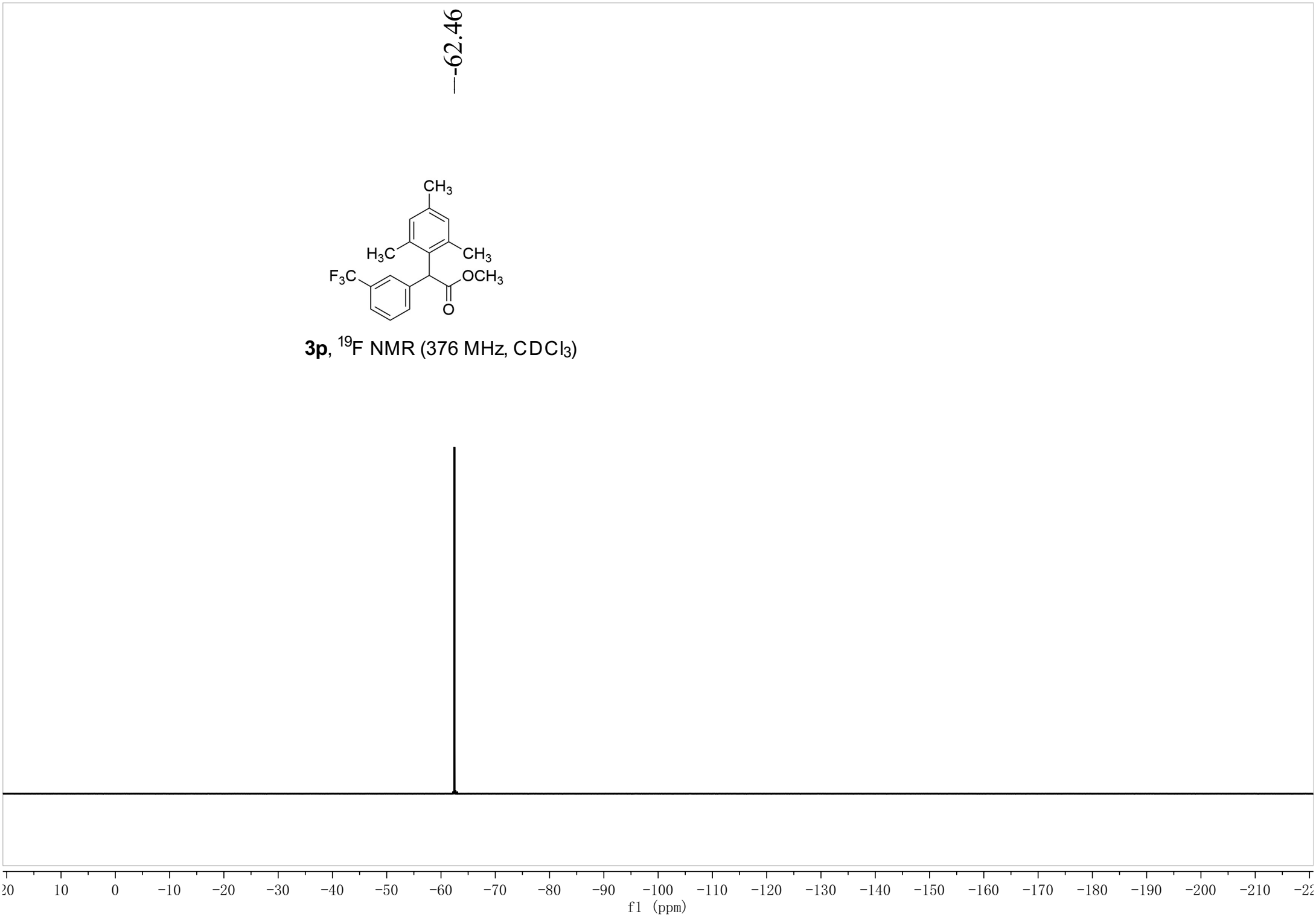
3o, ^{19}F NMR (376 MHz, $CDCl_3$)

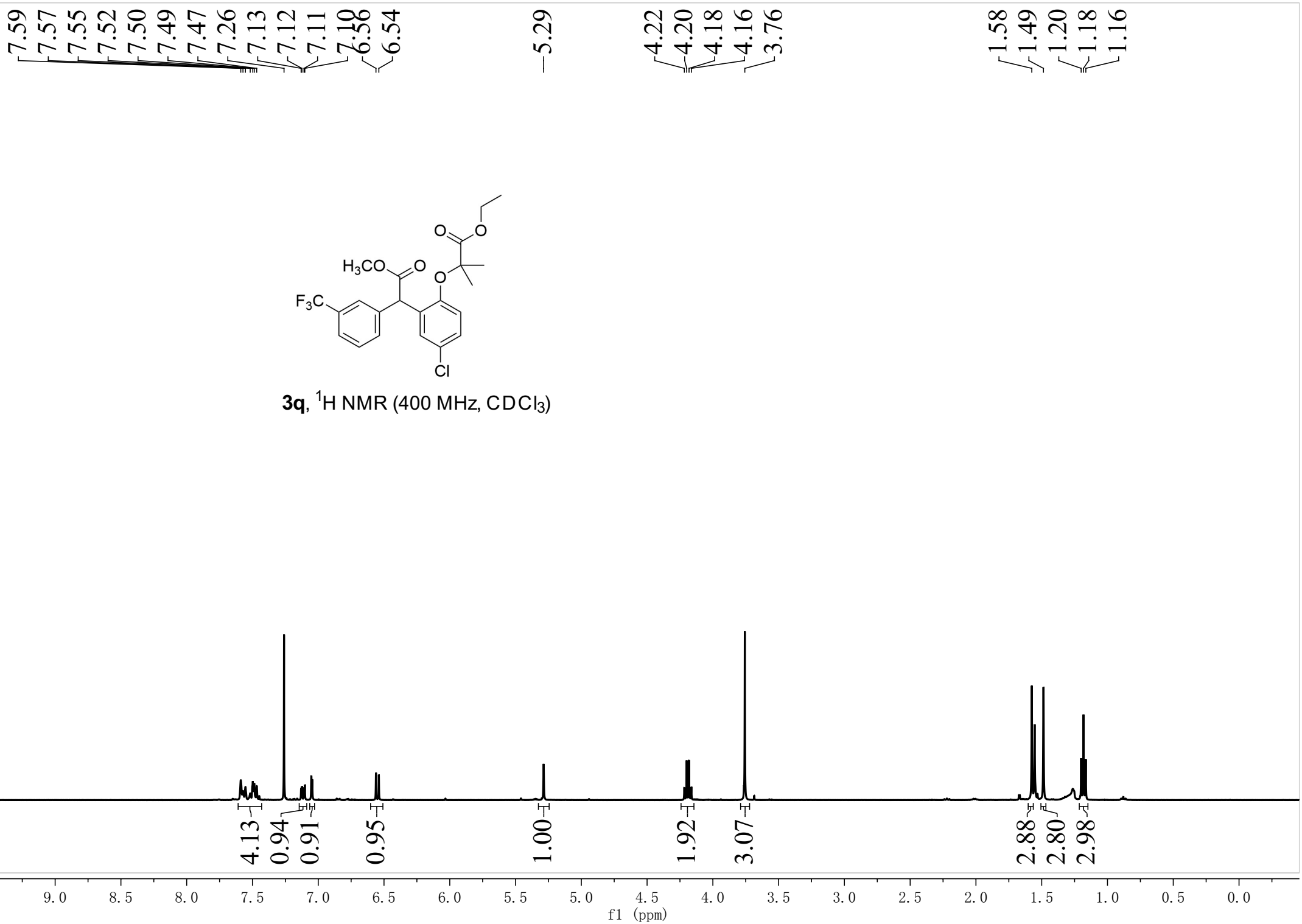


3p, ^{1}H NMR (400 MHz, $CDCl_3$)

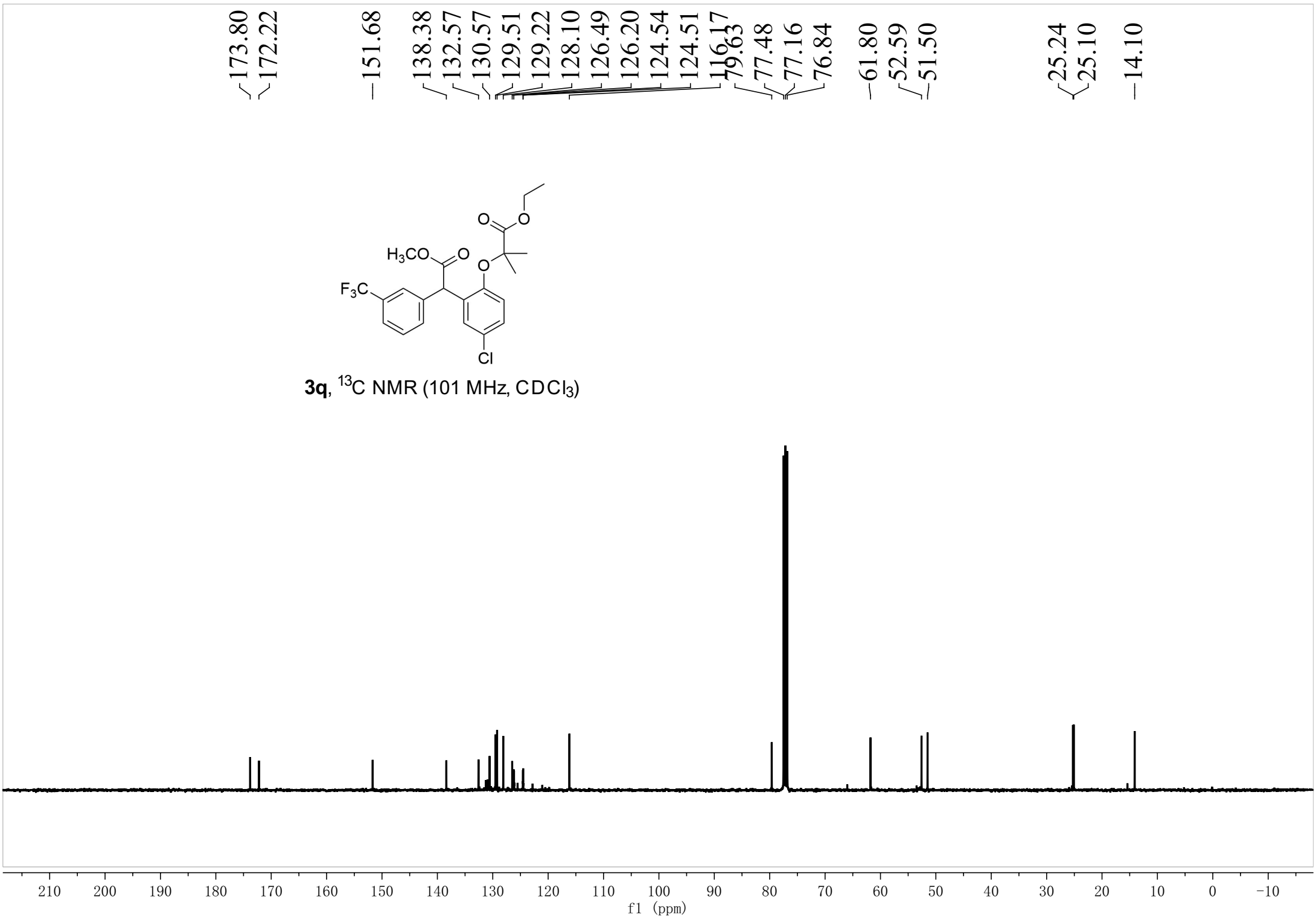


3p, ^{13}C NMR (101 MHz, $CDCl_3$)

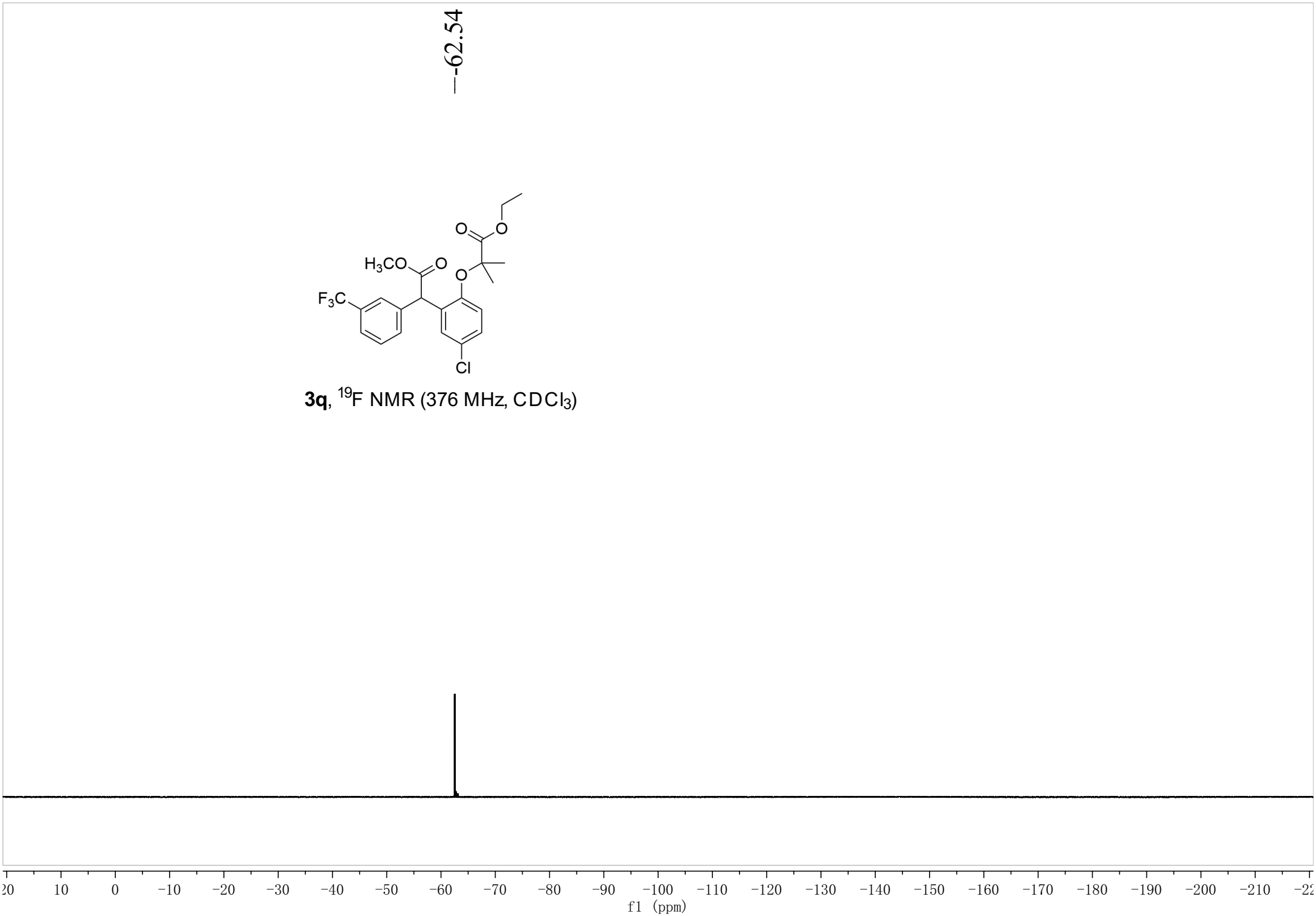

-62.46
CH3
H3C
CH3
F3C
OCH3
O
3p, 19F NMR (376 MHz, CDCl3)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



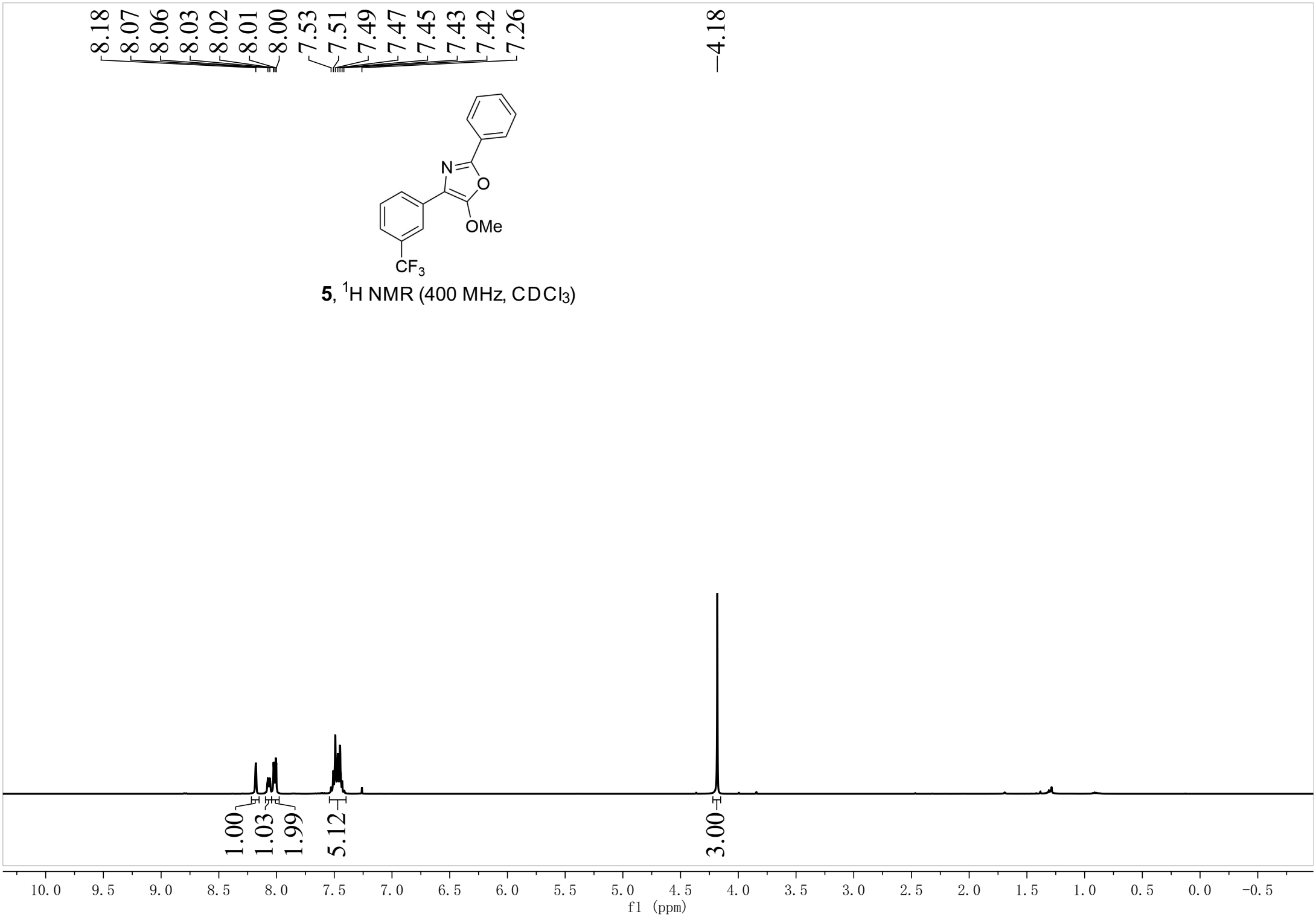
3q, ^{1}H NMR (400 MHz, $CDCl_3$)



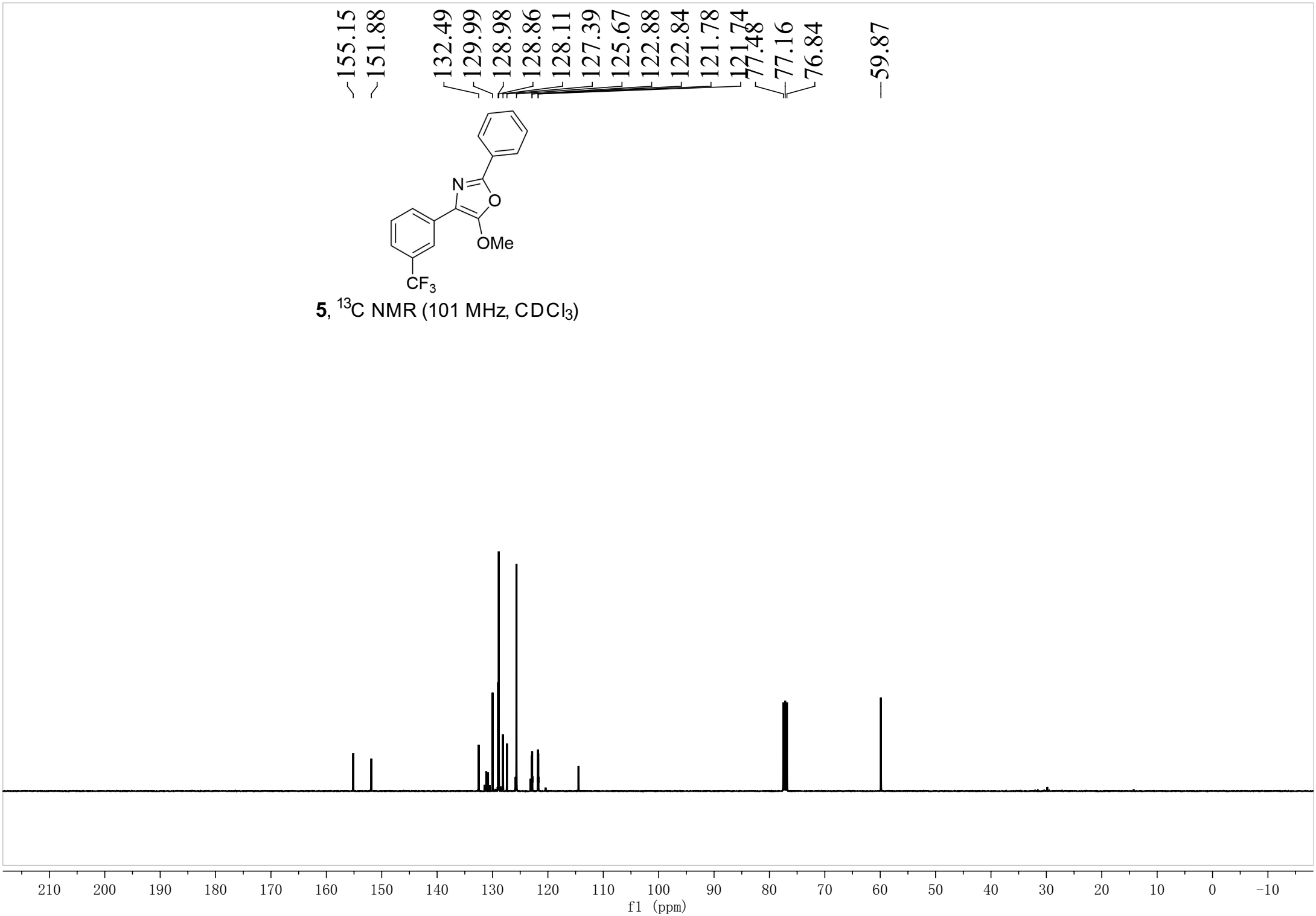
3q, ^{13}C NMR (101 MHz, $CDCl_3$)



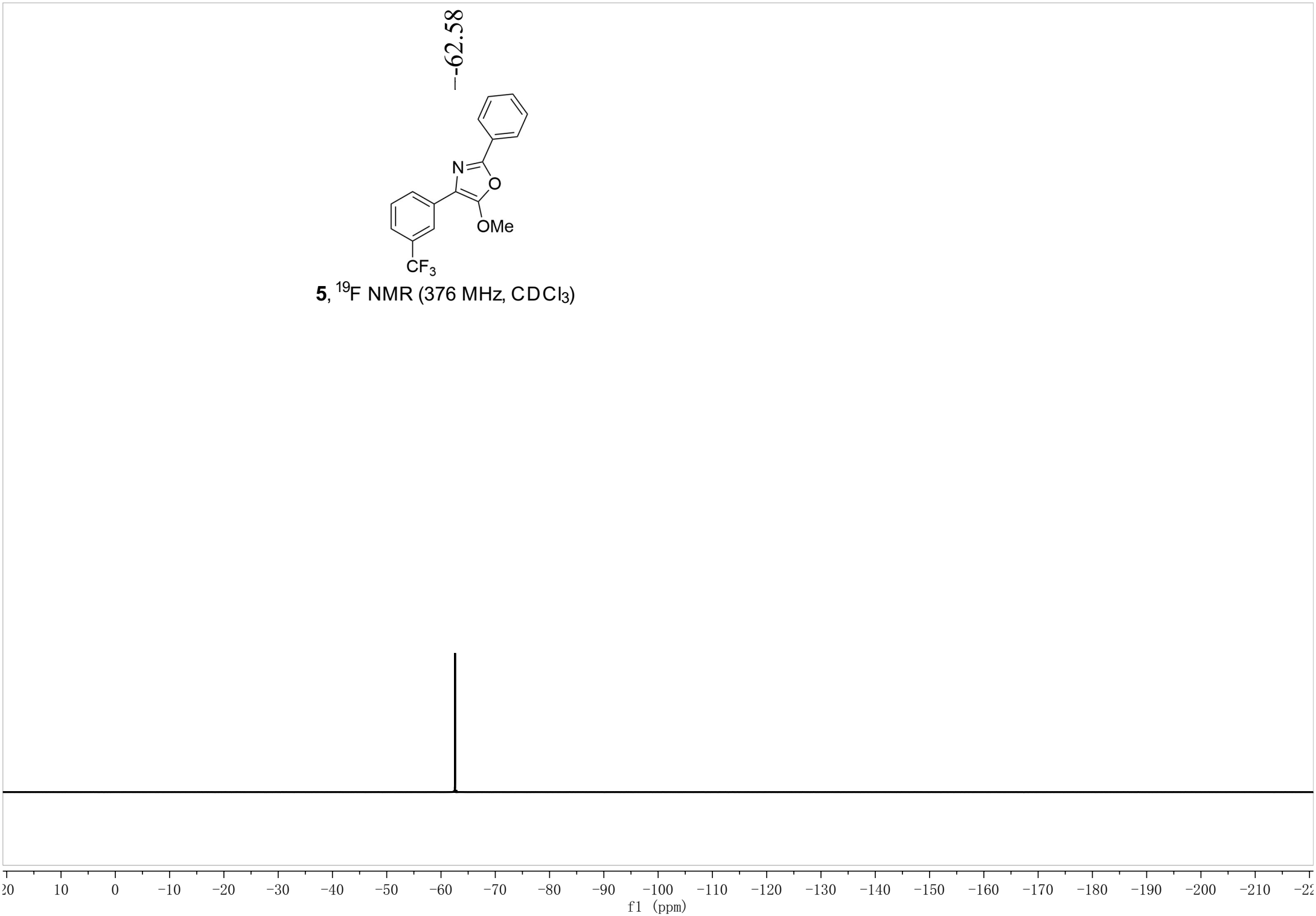
3q, ^{19}F NMR (376 MHz, $CDCl_3$)



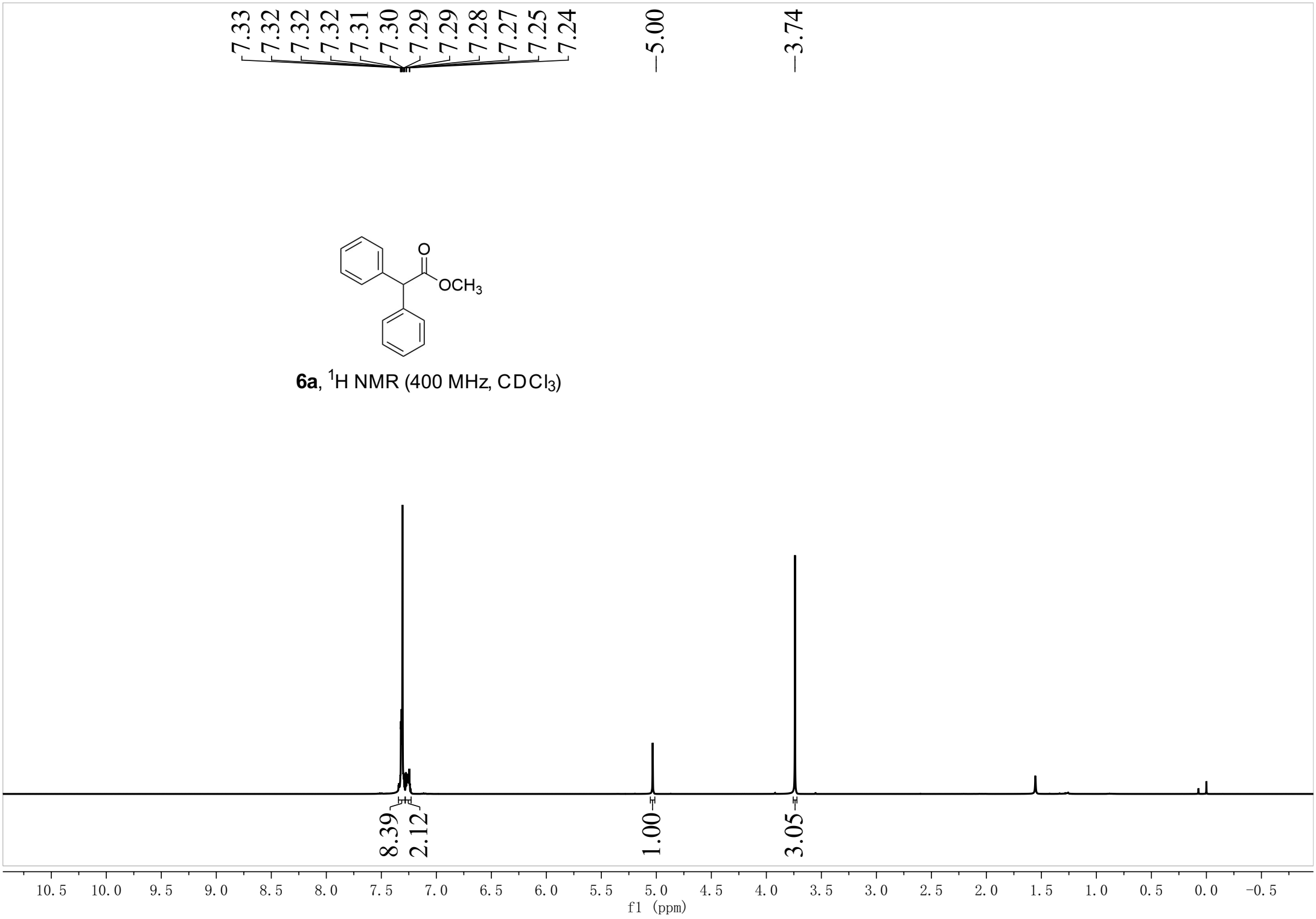
5, ^{1}H NMR (400 MHz, $CDCl_3$)



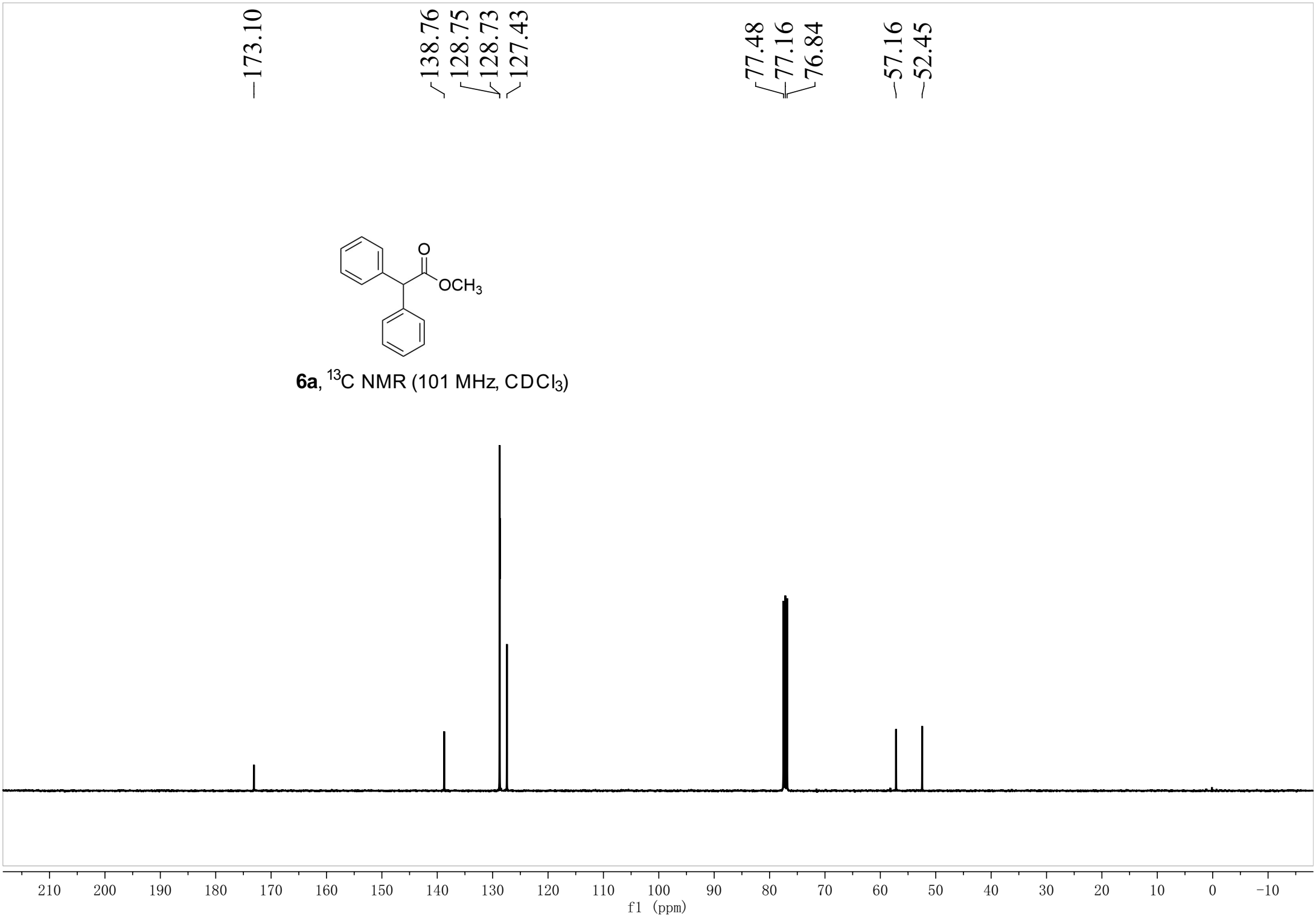
5, ^{13}C NMR (101 MHz, $CDCl_3$)



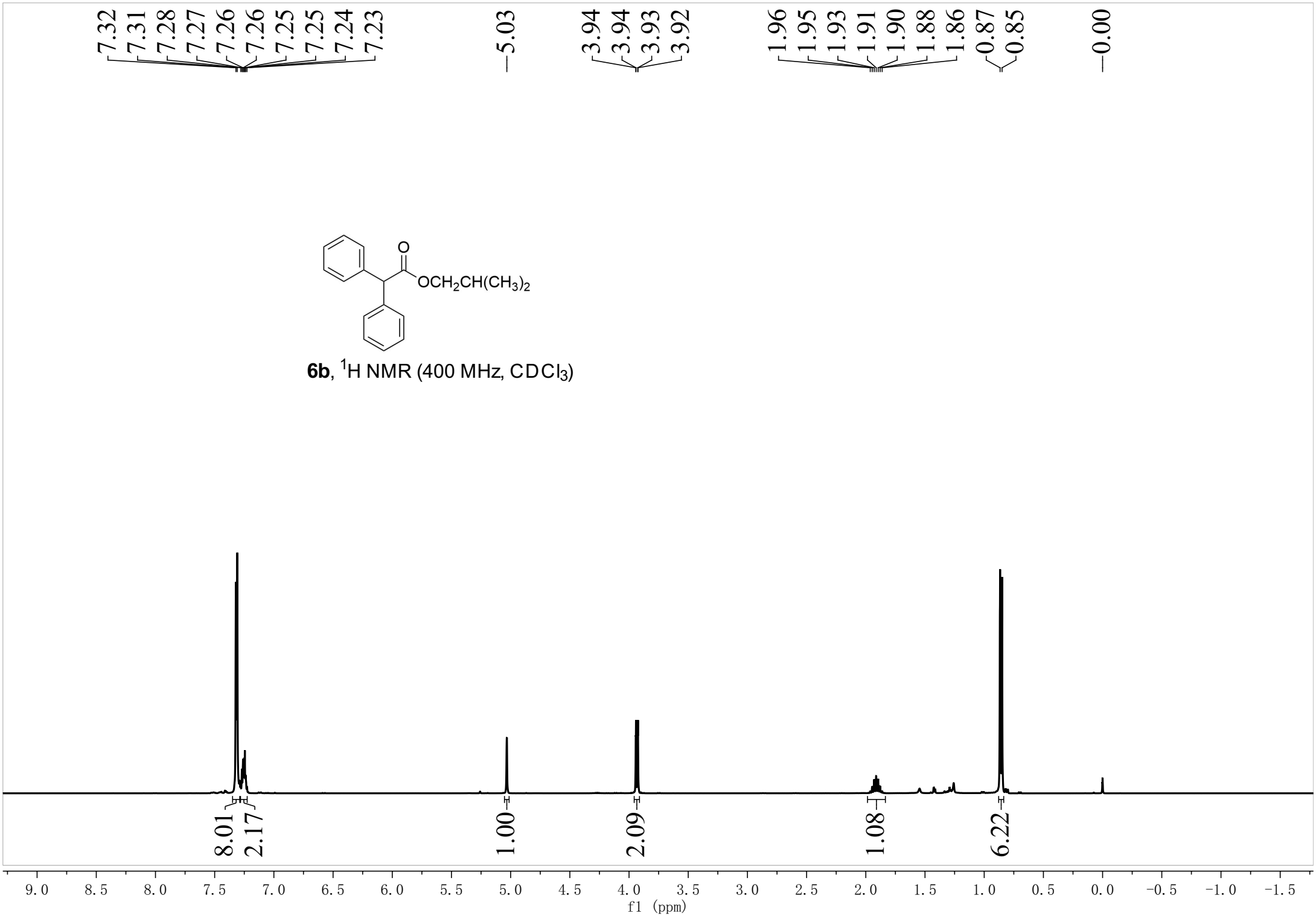
5, ^{19}F NMR (376 MHz, $CDCl_3$)



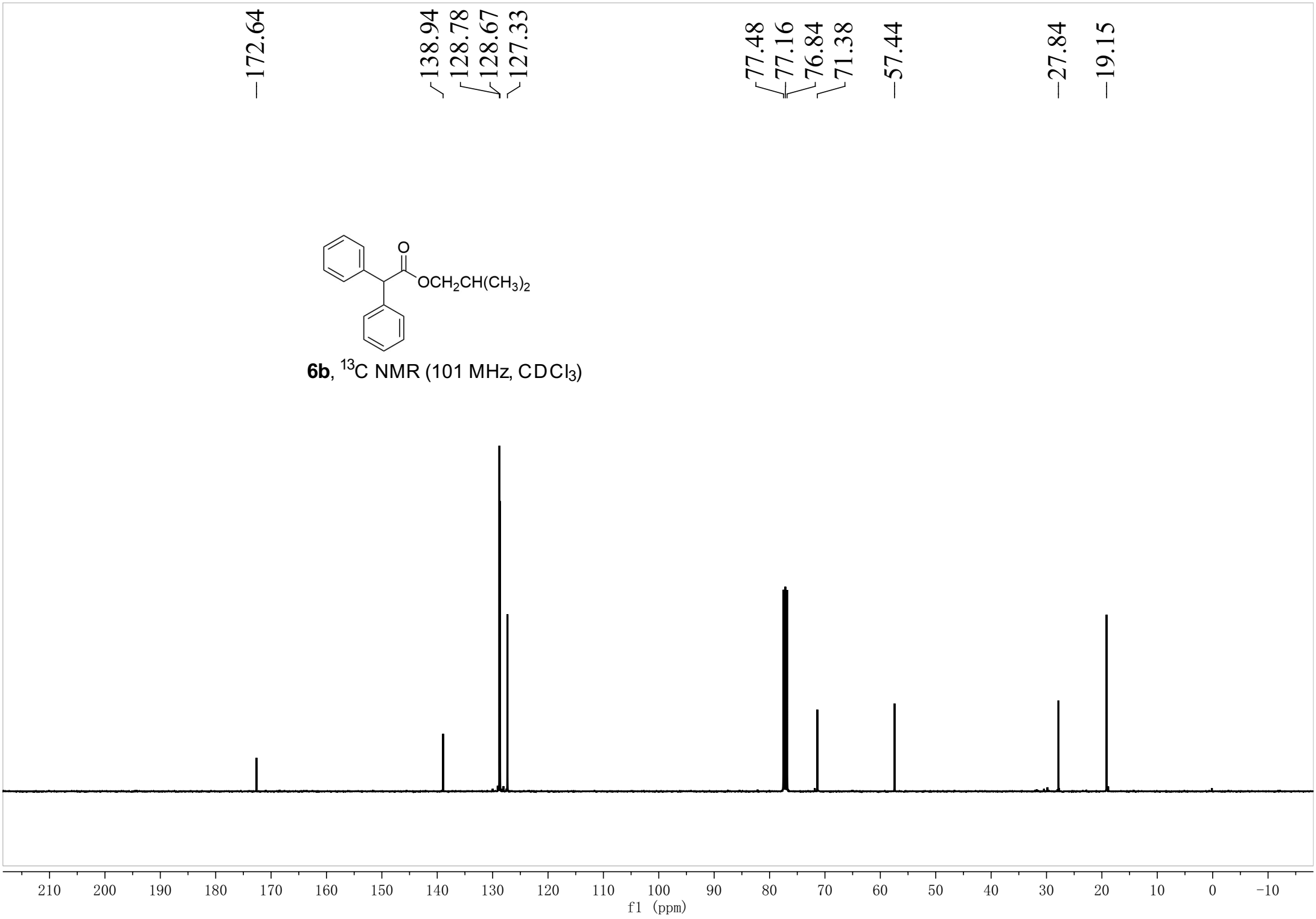
6a, ^{1}H NMR (400 MHz, $CDCl_3$)



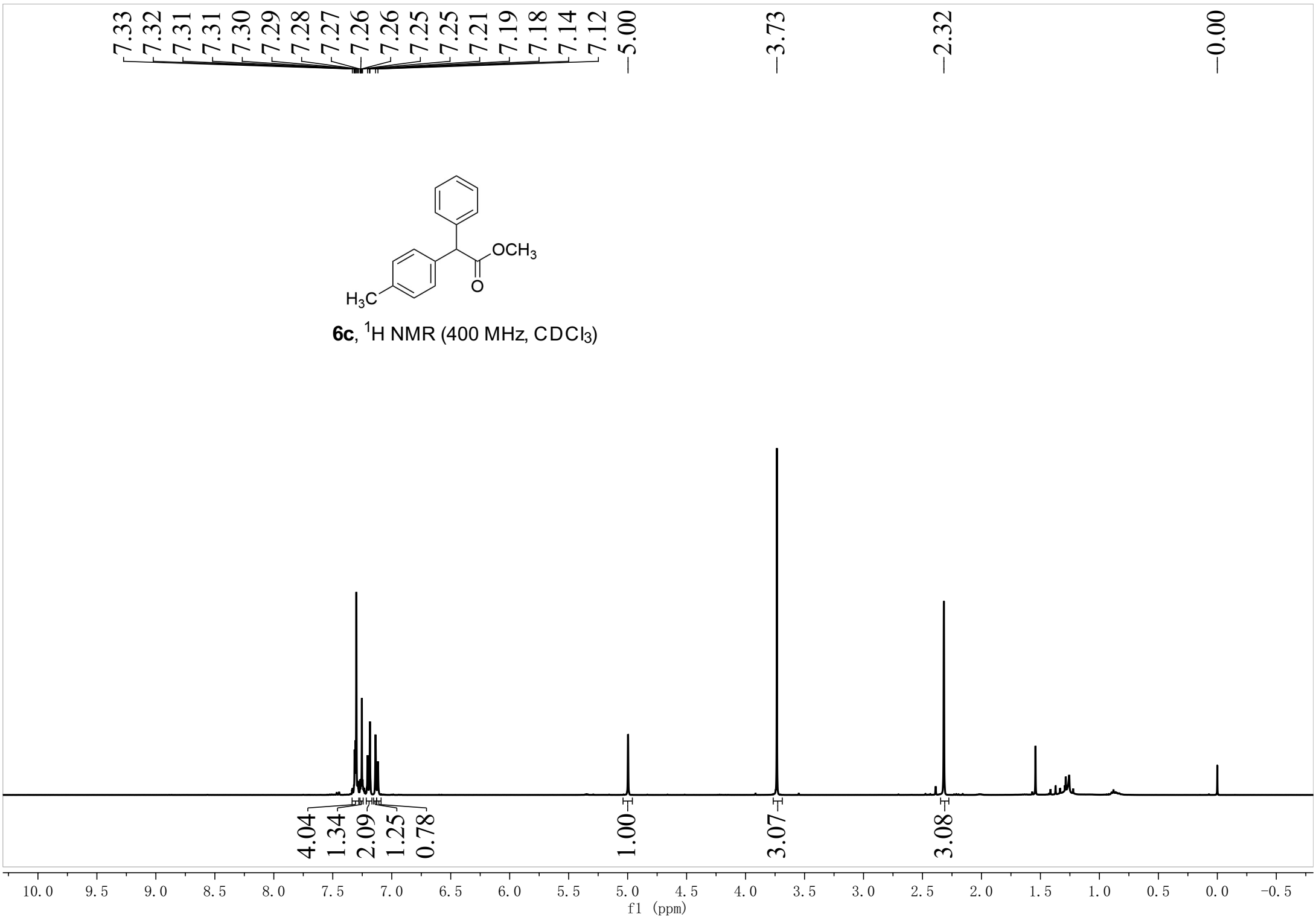
6a, ^{13}C NMR (101 MHz, $CDCl_3$)



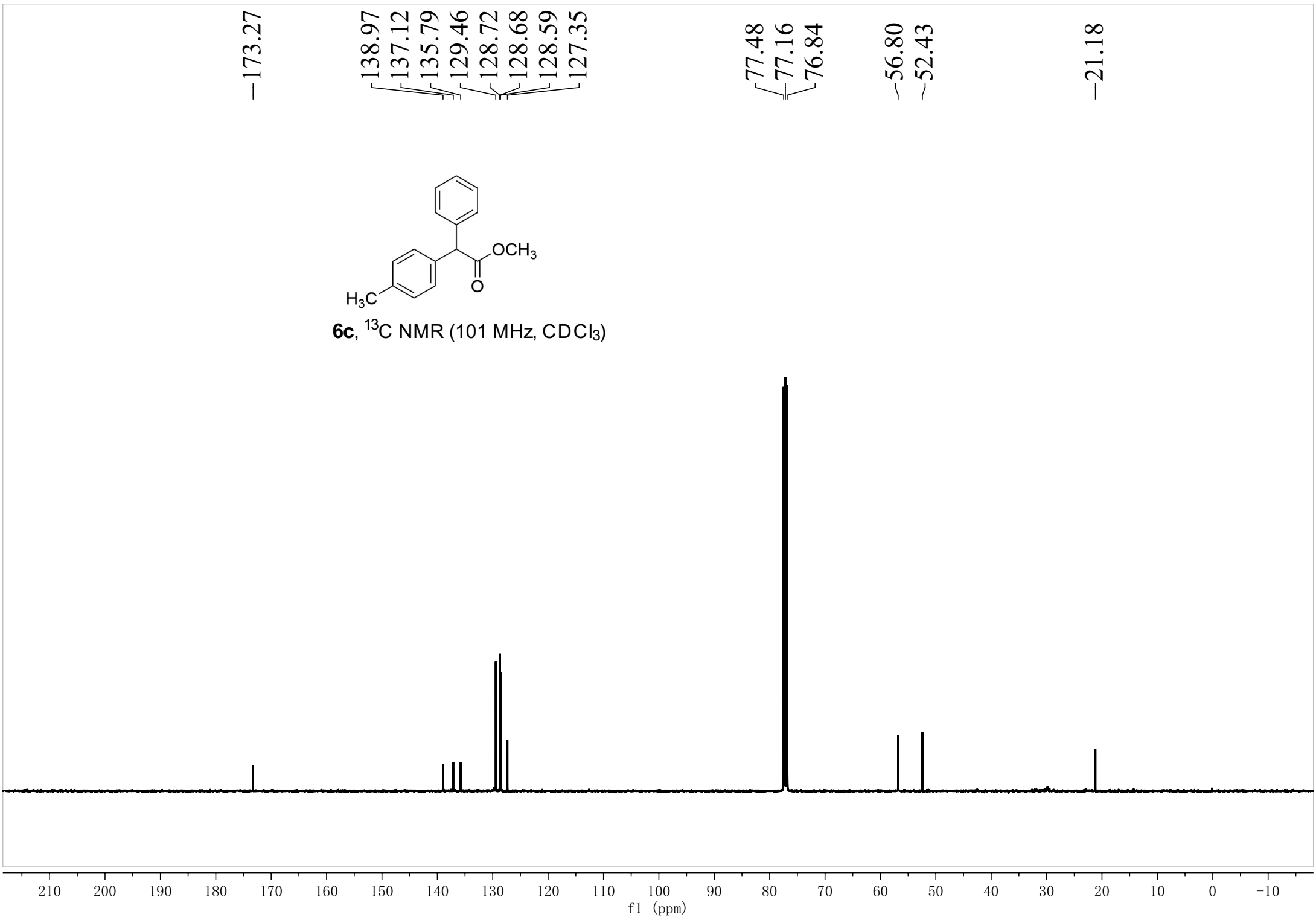
6b, ^{1}H NMR (400 MHz, $CDCl_3$)

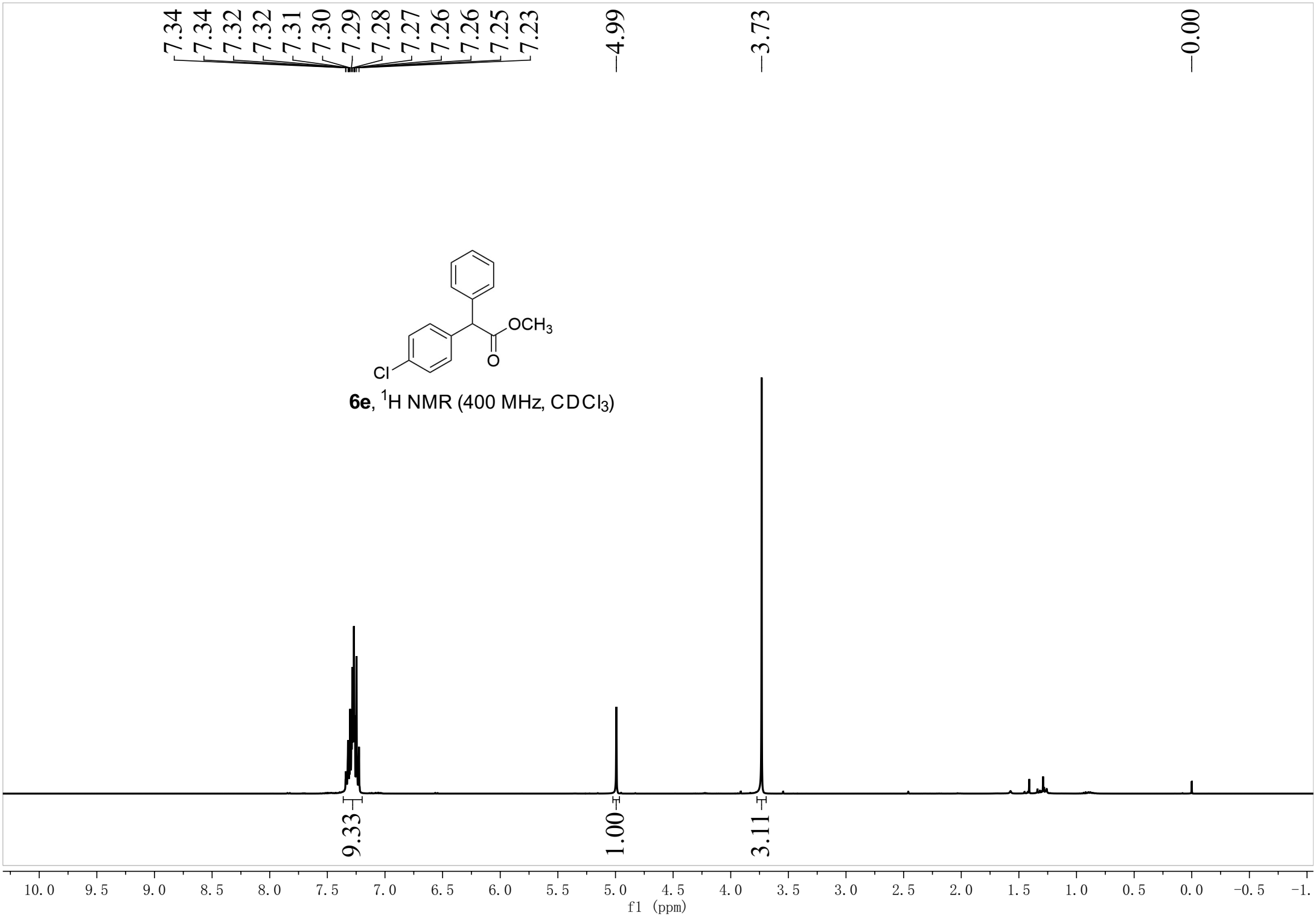


6b, ^{13}C NMR (101 MHz, $CDCl_3$)

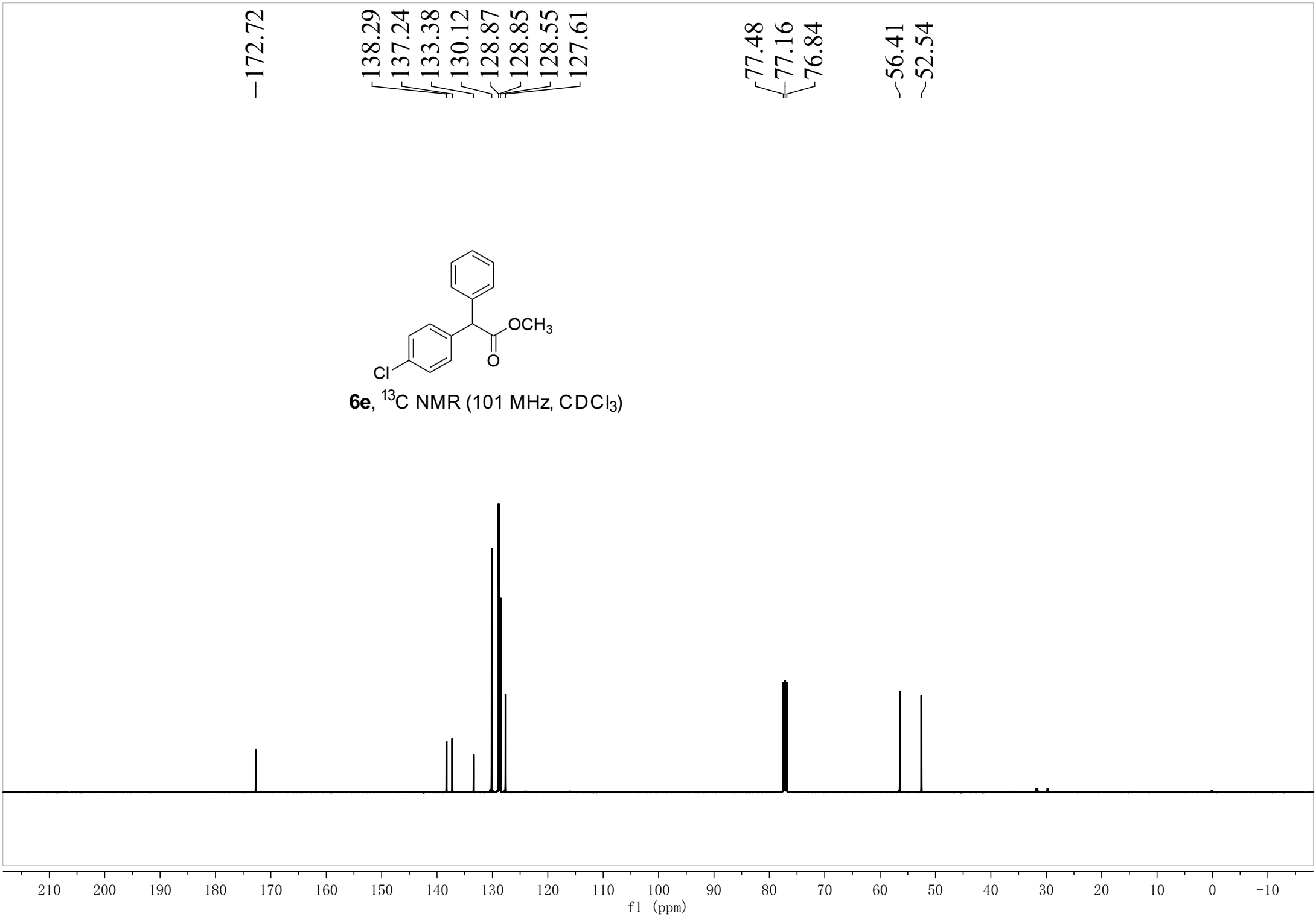


6c, ^{1}H NMR (400 MHz, $CDCl_3$)

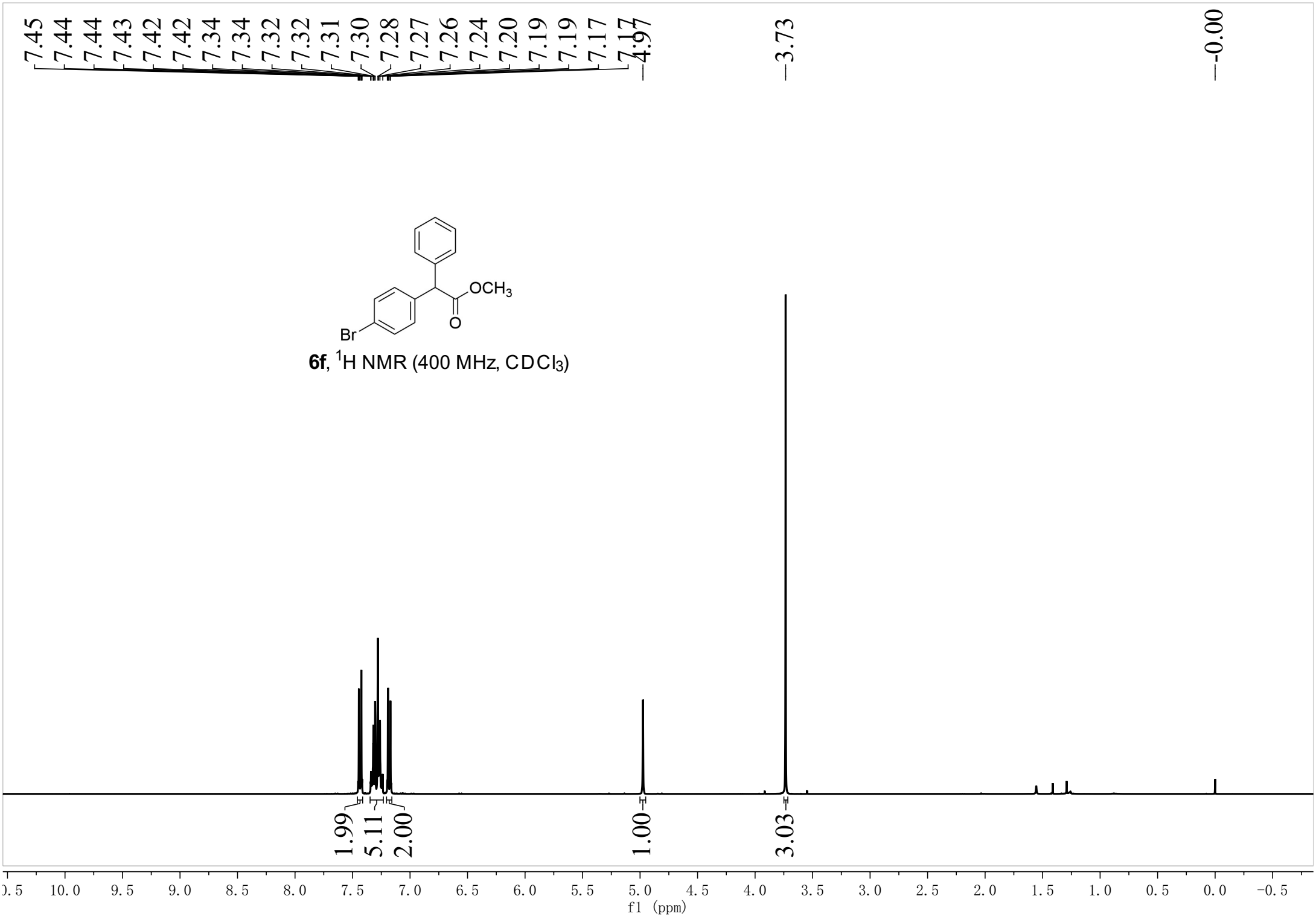

173.27
138.97
137.12
135.79
129.46
128.72
128.68
128.59
127.35
77.48
77.16
76.84
56.80
52.43
21.18
OCH3
O
H3C
6c, 13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



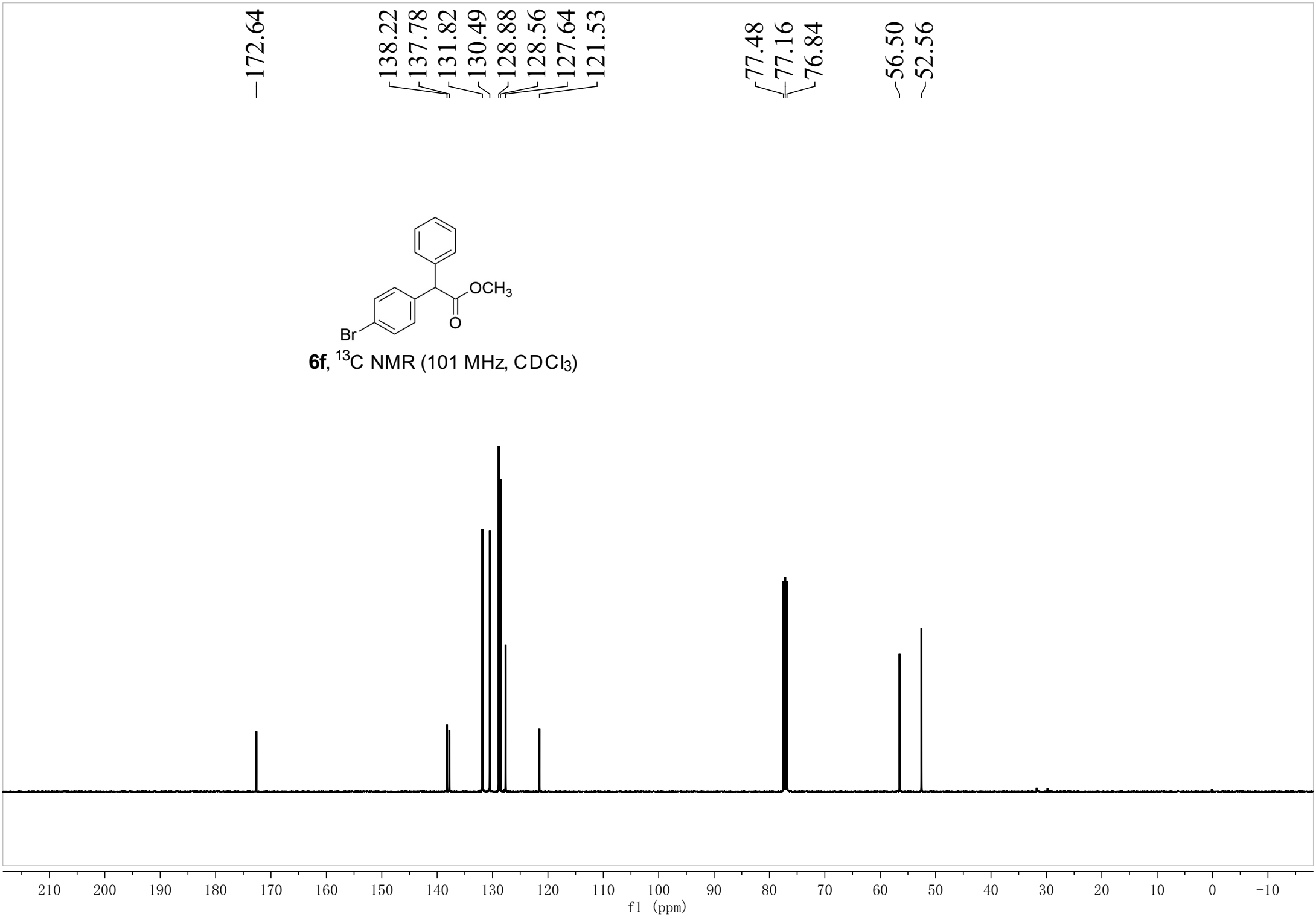
6e, ^{1}H NMR (400 MHz, $CDCl_3$)

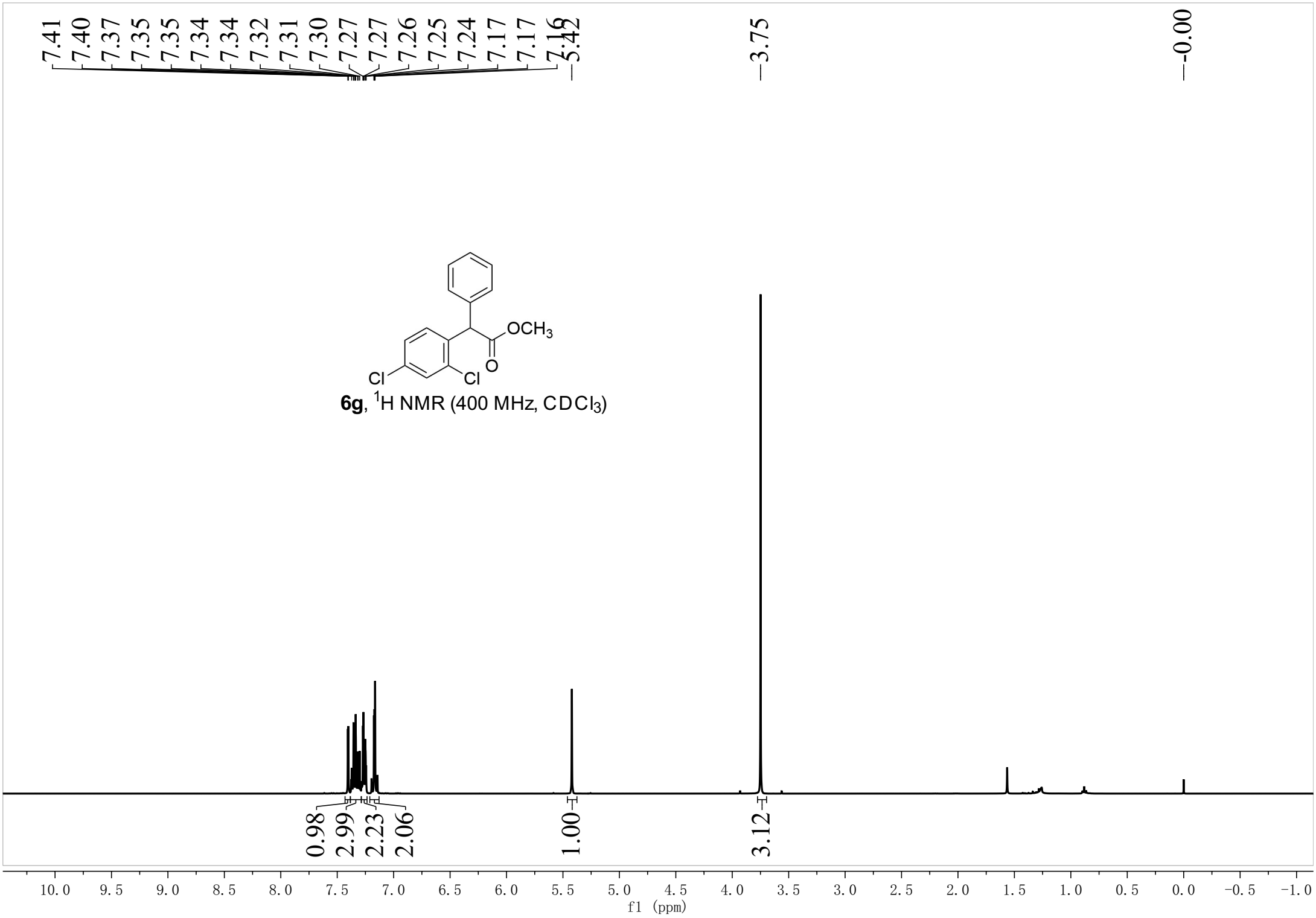


6e, ^{13}C NMR (101 MHz, $CDCl_3$)

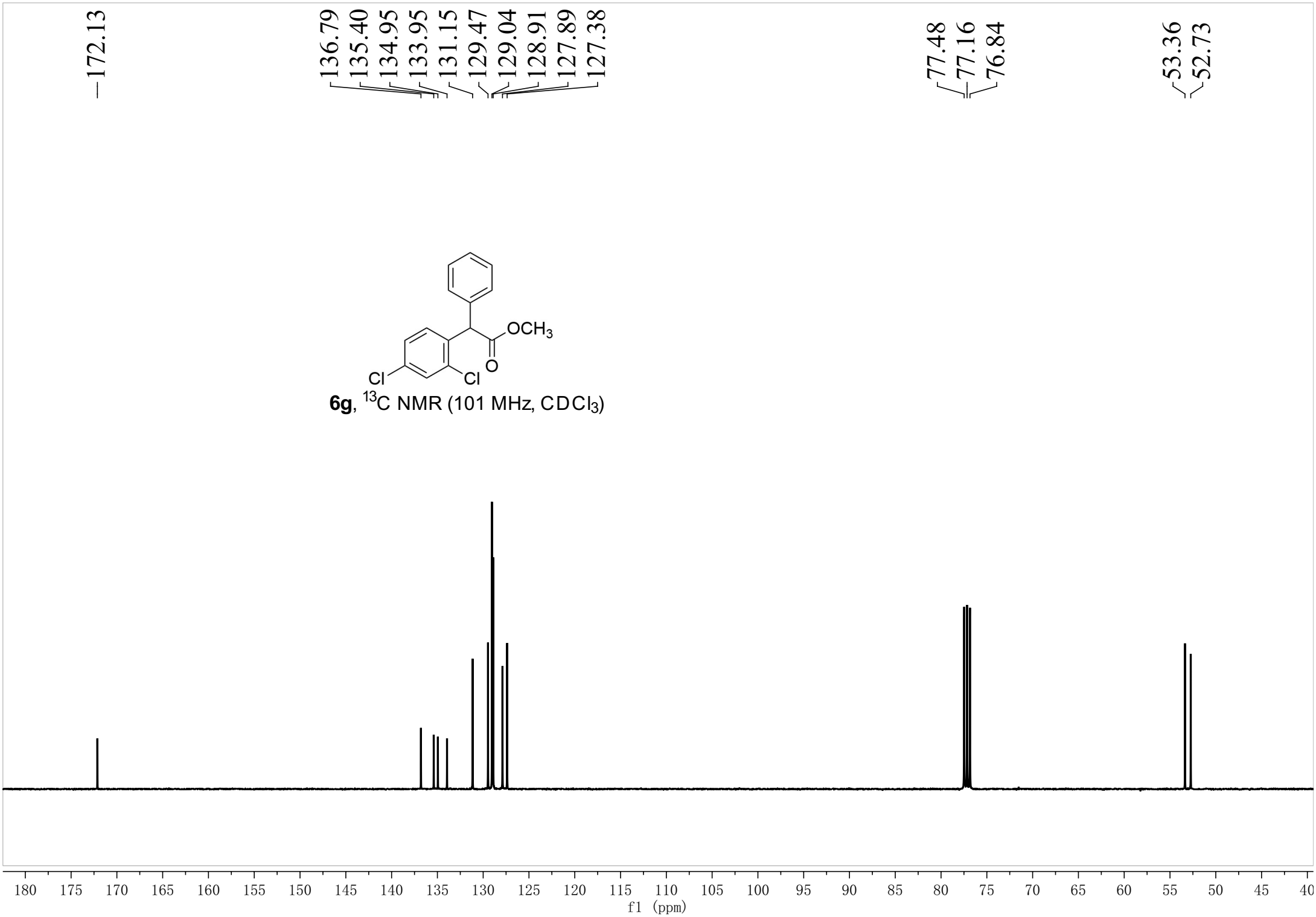


6f, ^{1}H NMR (400 MHz, $CDCl_3$)

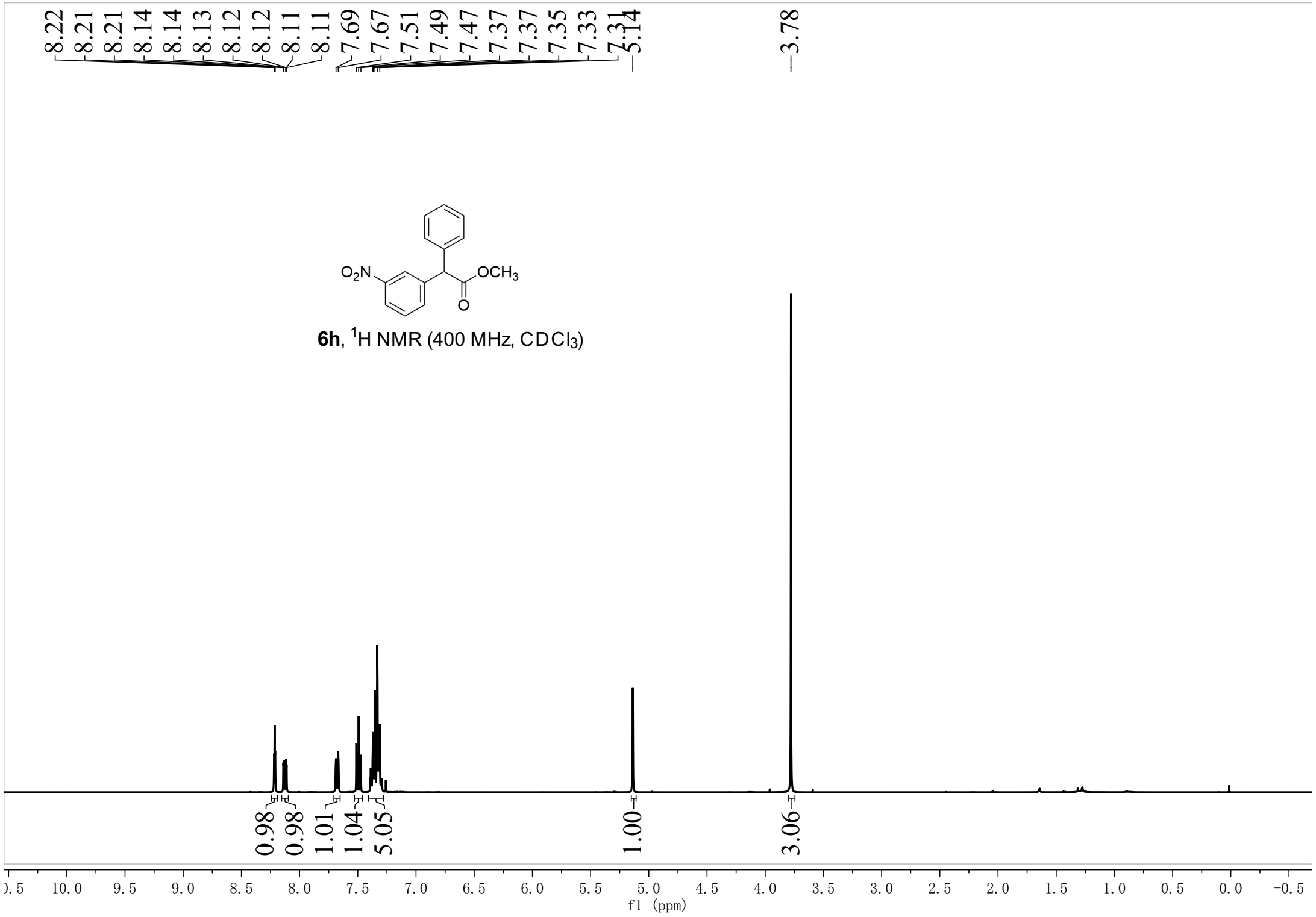

172.64
138.22
137.78
131.82
130.49
128.88
128.56
127.64
121.53
77.48
77.16
76.84
56.50
52.56
OCH3
O
Br
6f, 13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



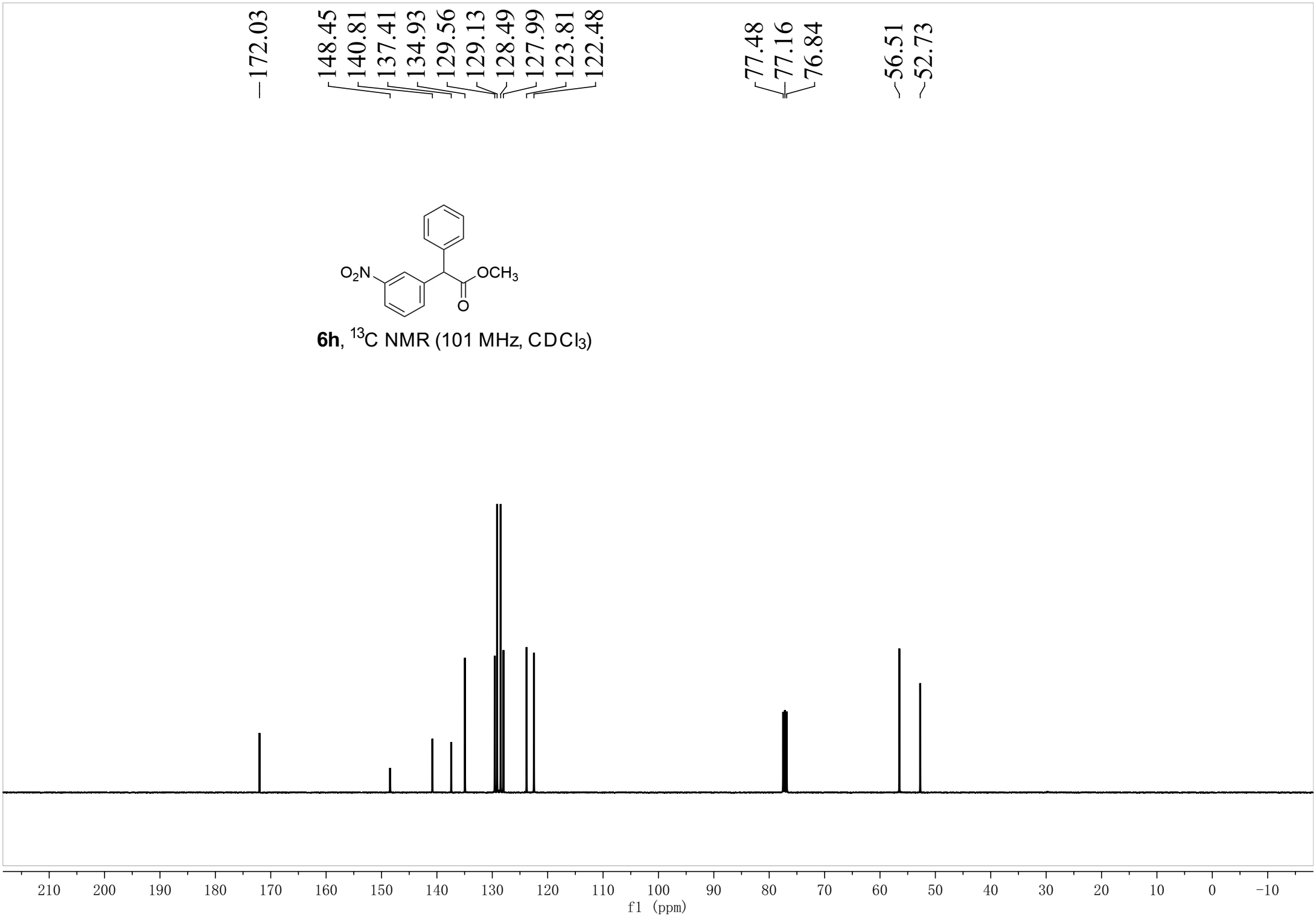
6g, ^{1}H NMR (400 MHz, $CDCl_3$)



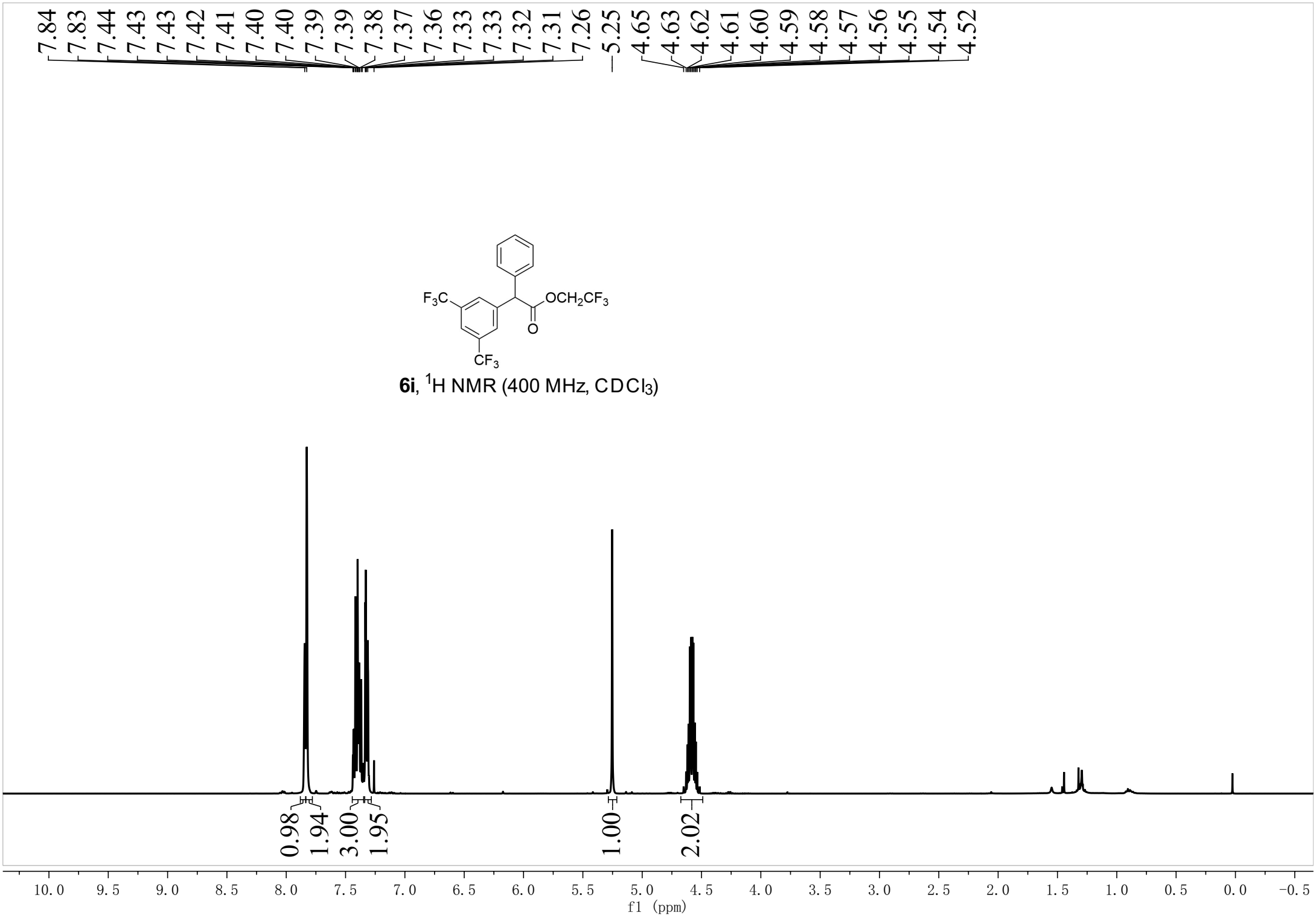
6g, ^{13}C NMR (101 MHz, $CDCl_3$)



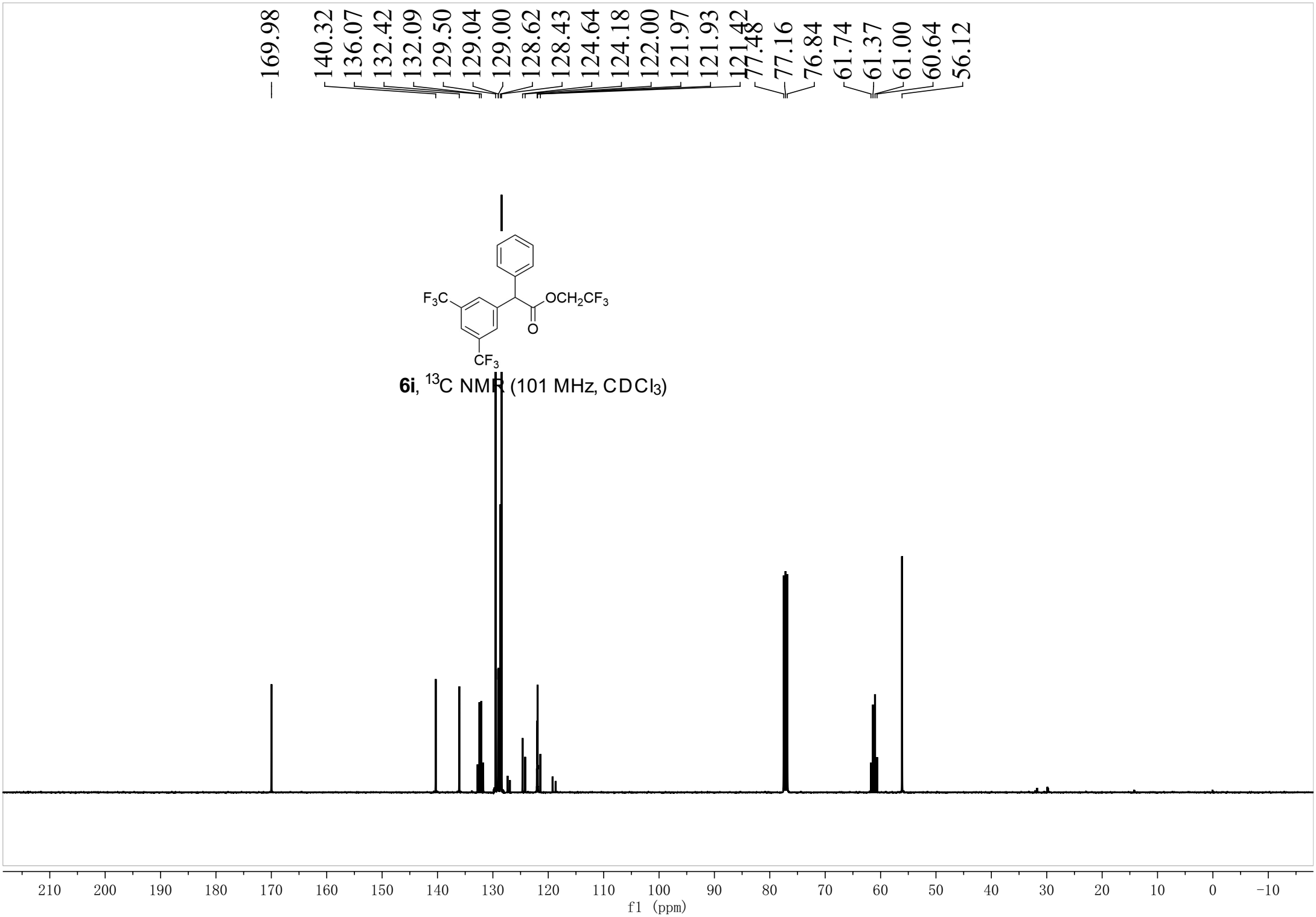
6h, ^{1}H NMR (400 MHz, $CDCl_3$)



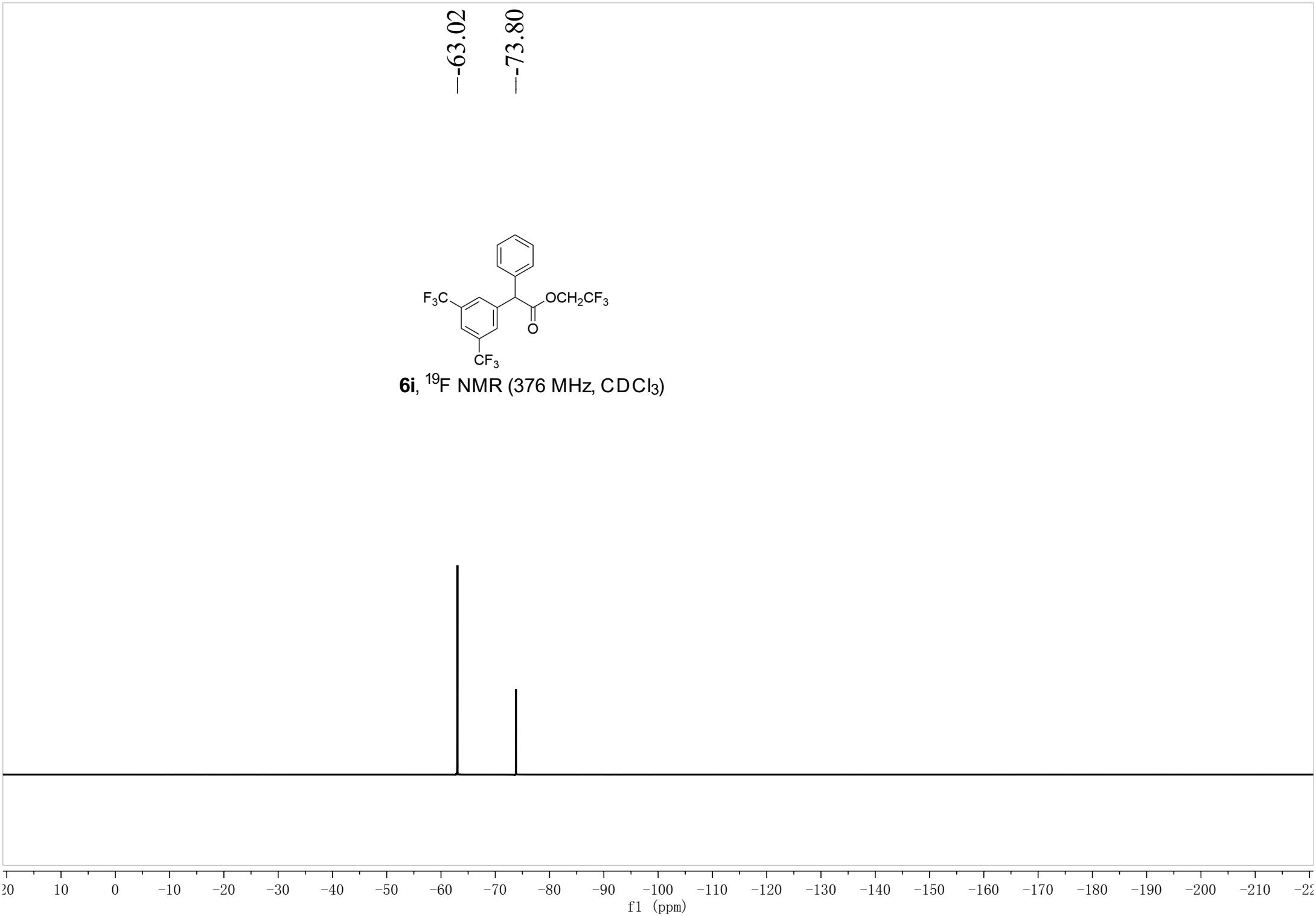
6h, ^{13}C NMR (101 MHz, $CDCl_3$)



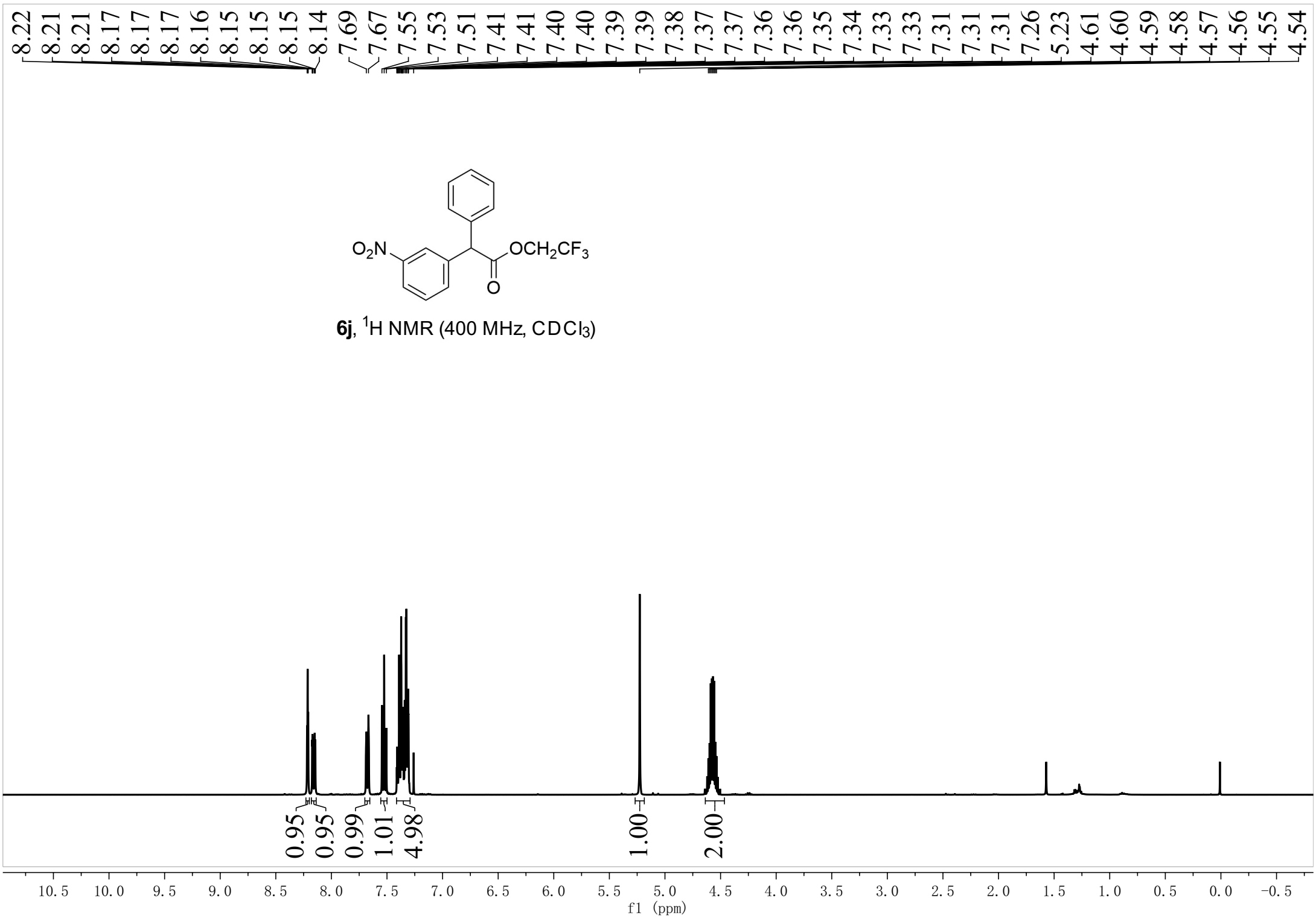
6i, ^{1}H NMR (400 MHz, $CDCl_3$)



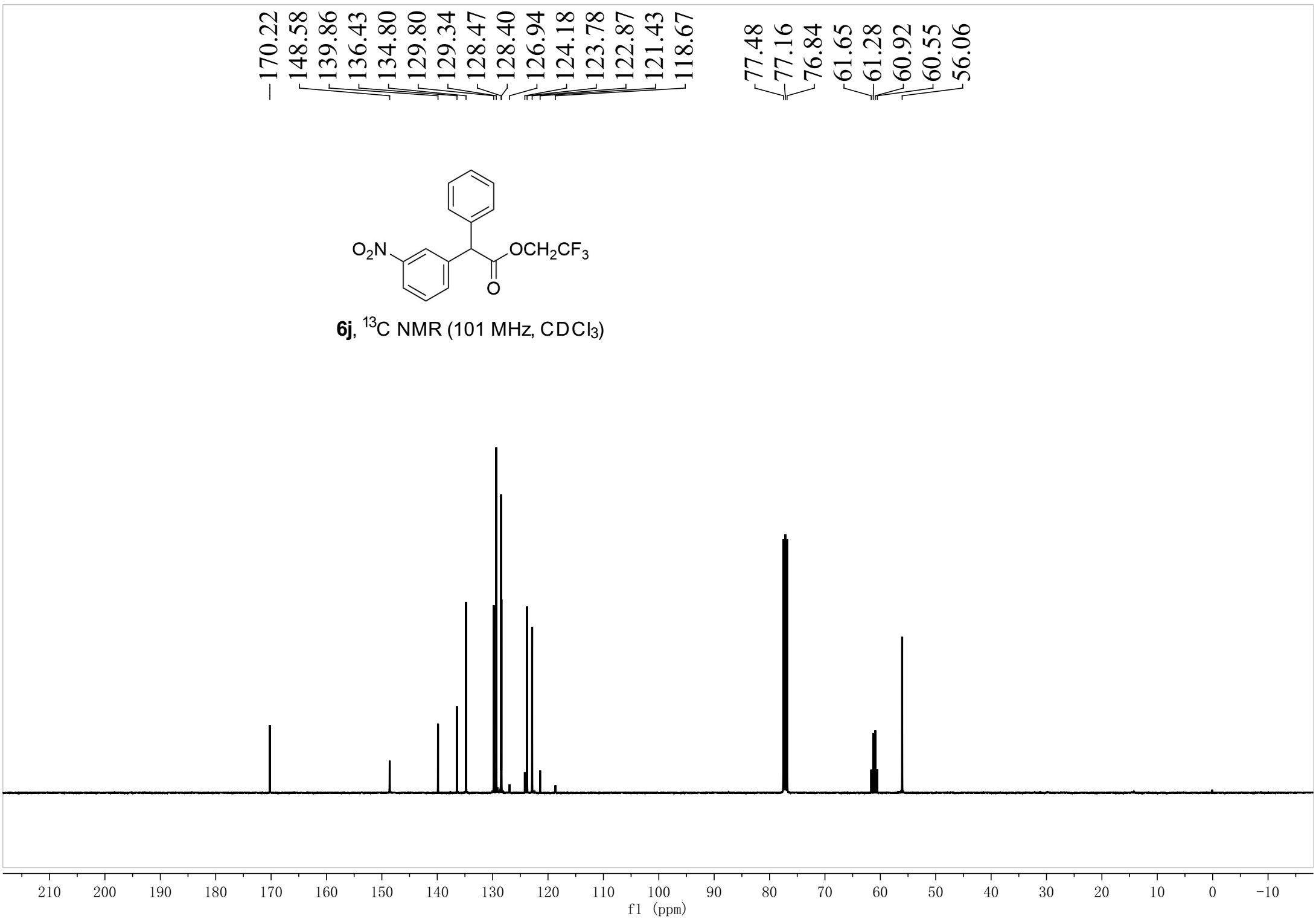
6i, ^{13}C NMR (101 MHz, $CDCl_3$)



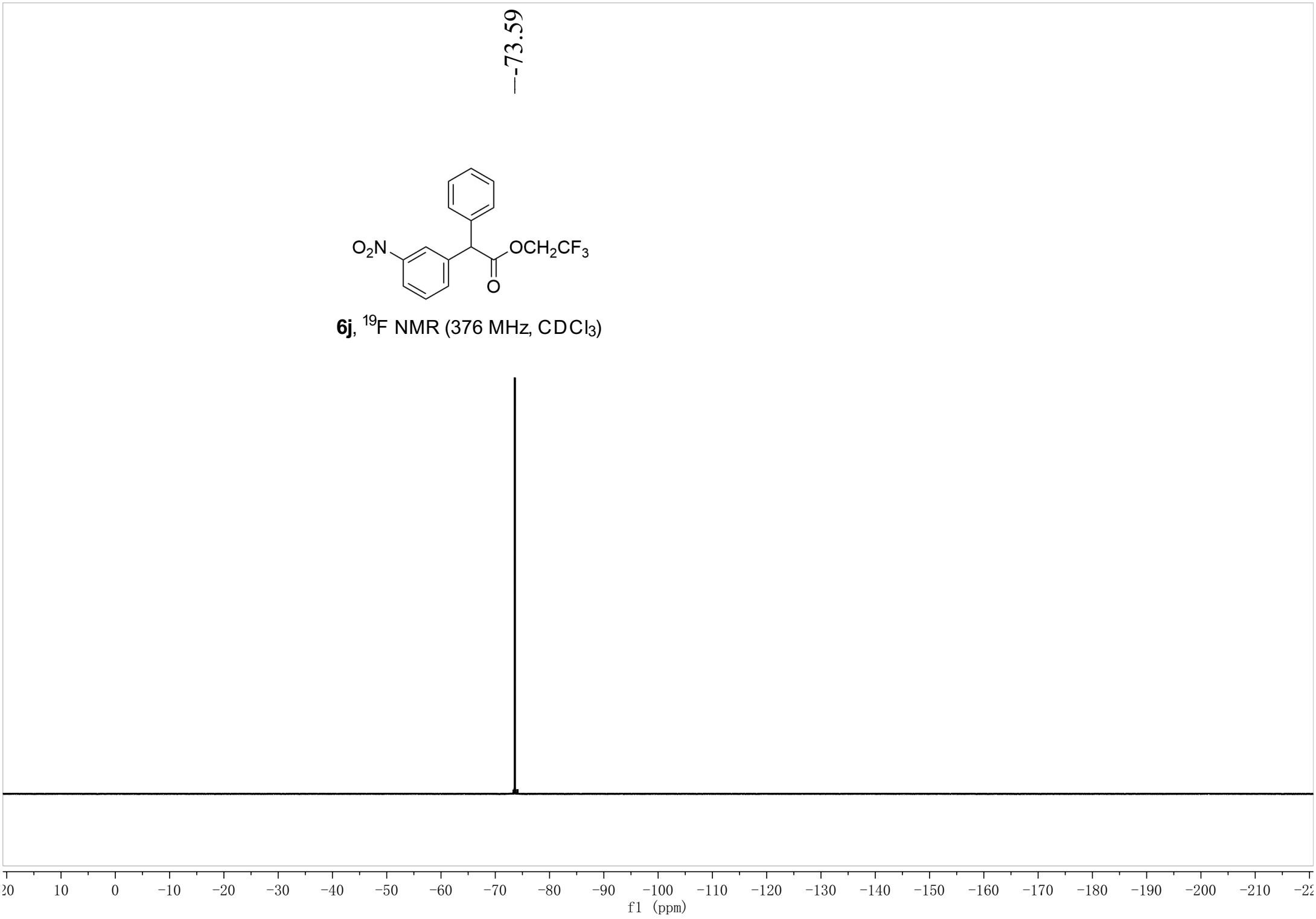
6i, ^{19}F NMR (376 MHz, $CDCl_3$)



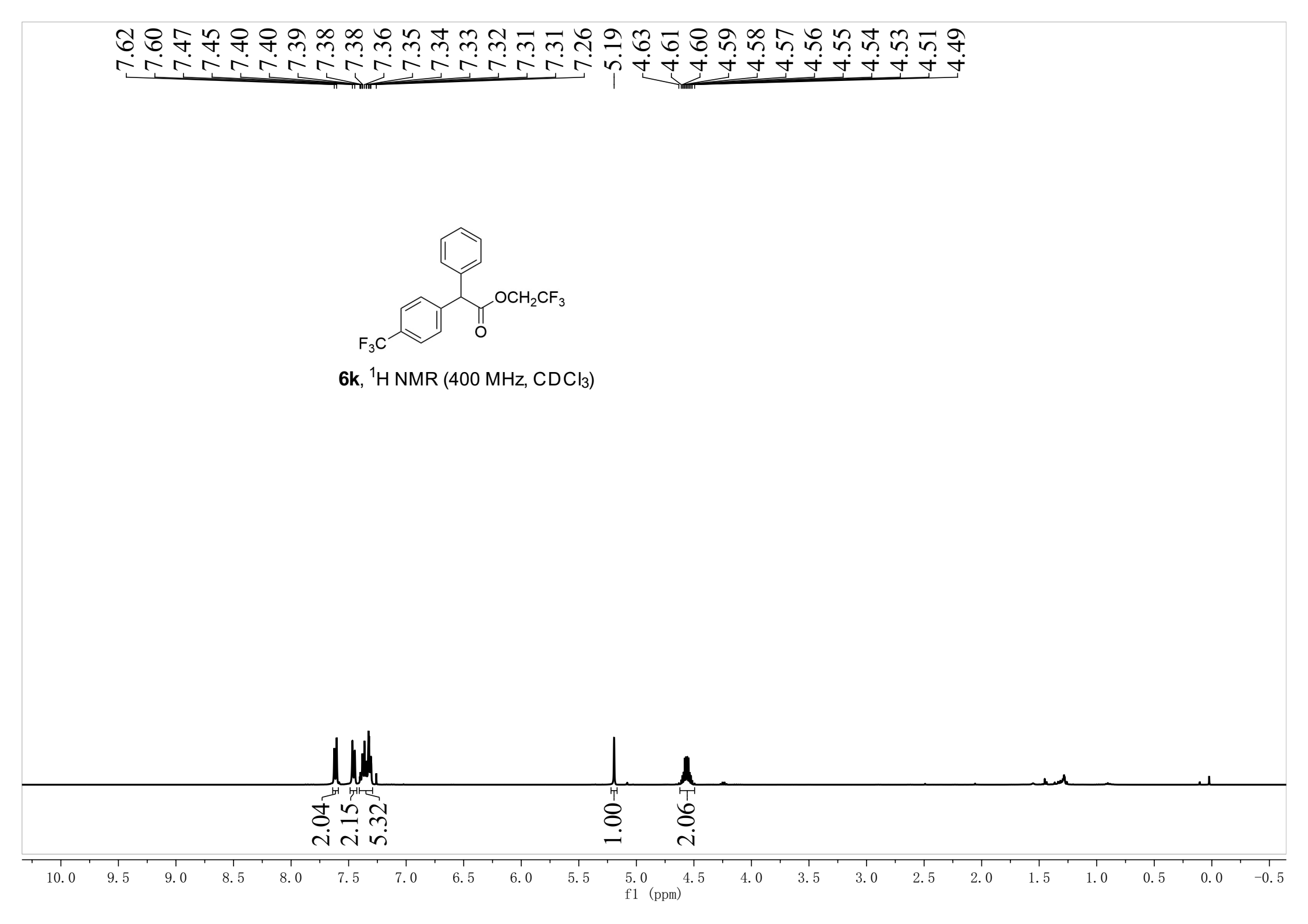
6j, ^{1}H NMR (400 MHz, $CDCl_3$)



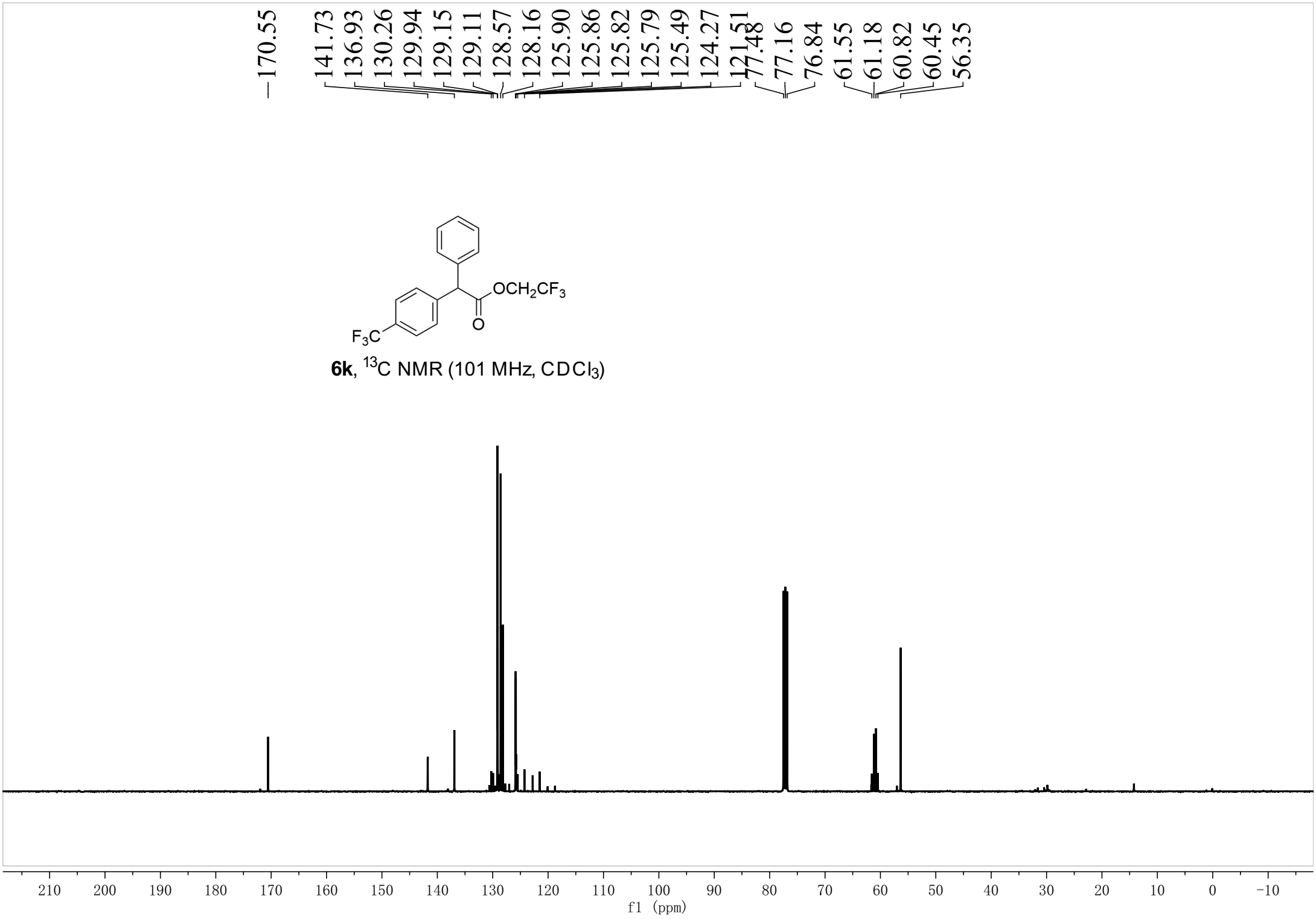
6j, ^{13}C NMR (101 MHz, $CDCl_3$)



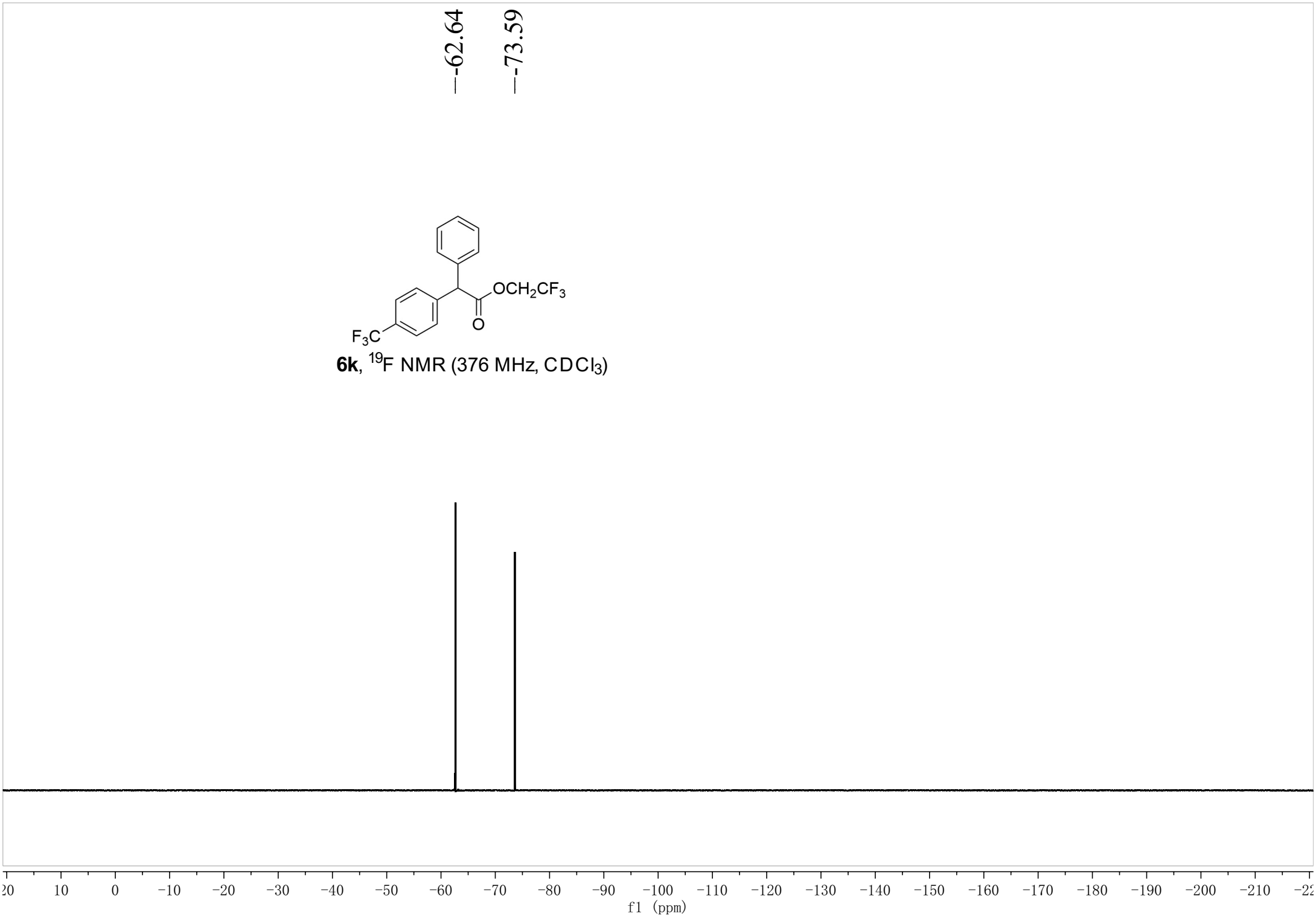
6j, ^{19}F NMR (376 MHz, $CDCl_3$)



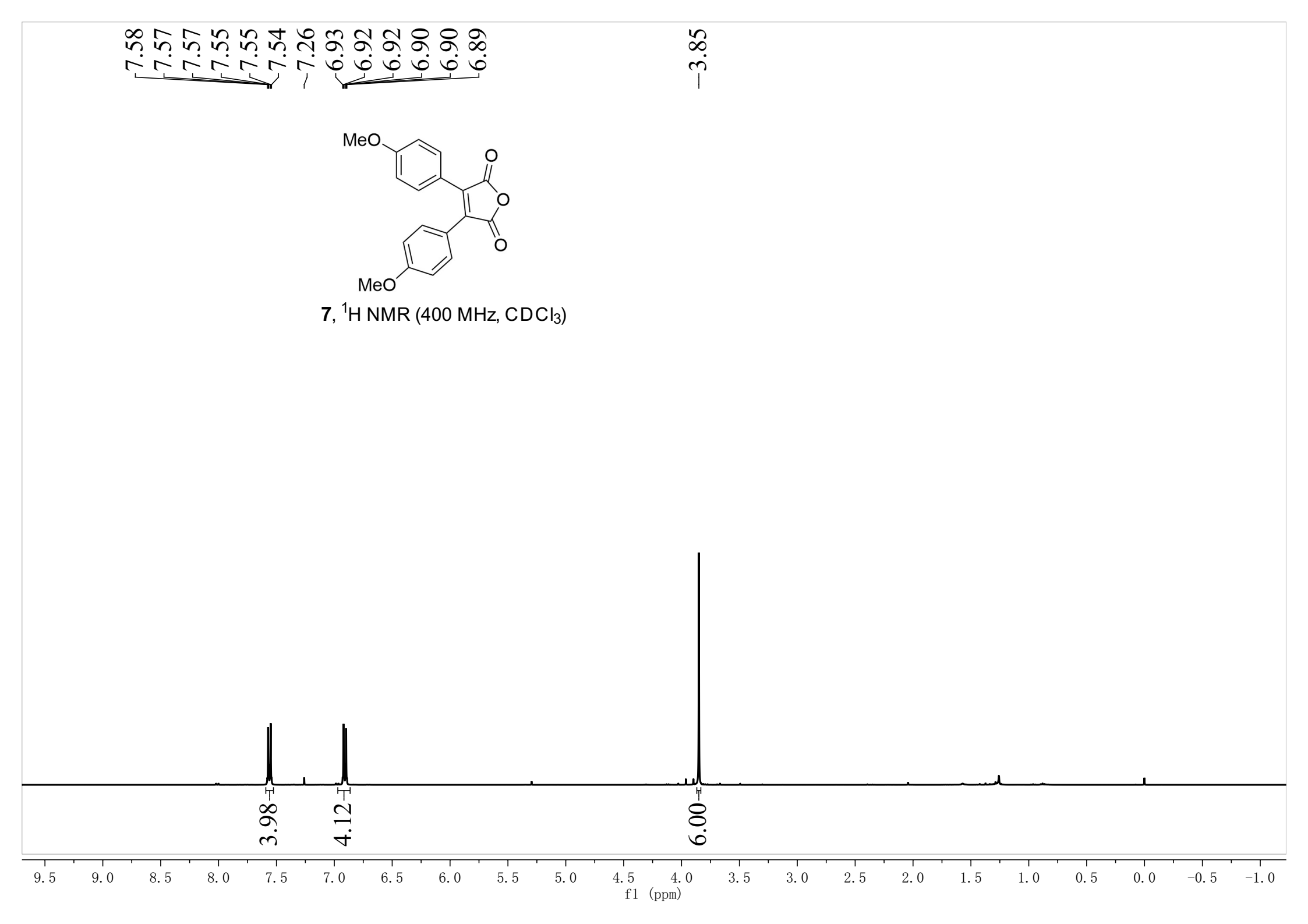
6k, ^{1}H NMR (400 MHz, $CDCl_3$)



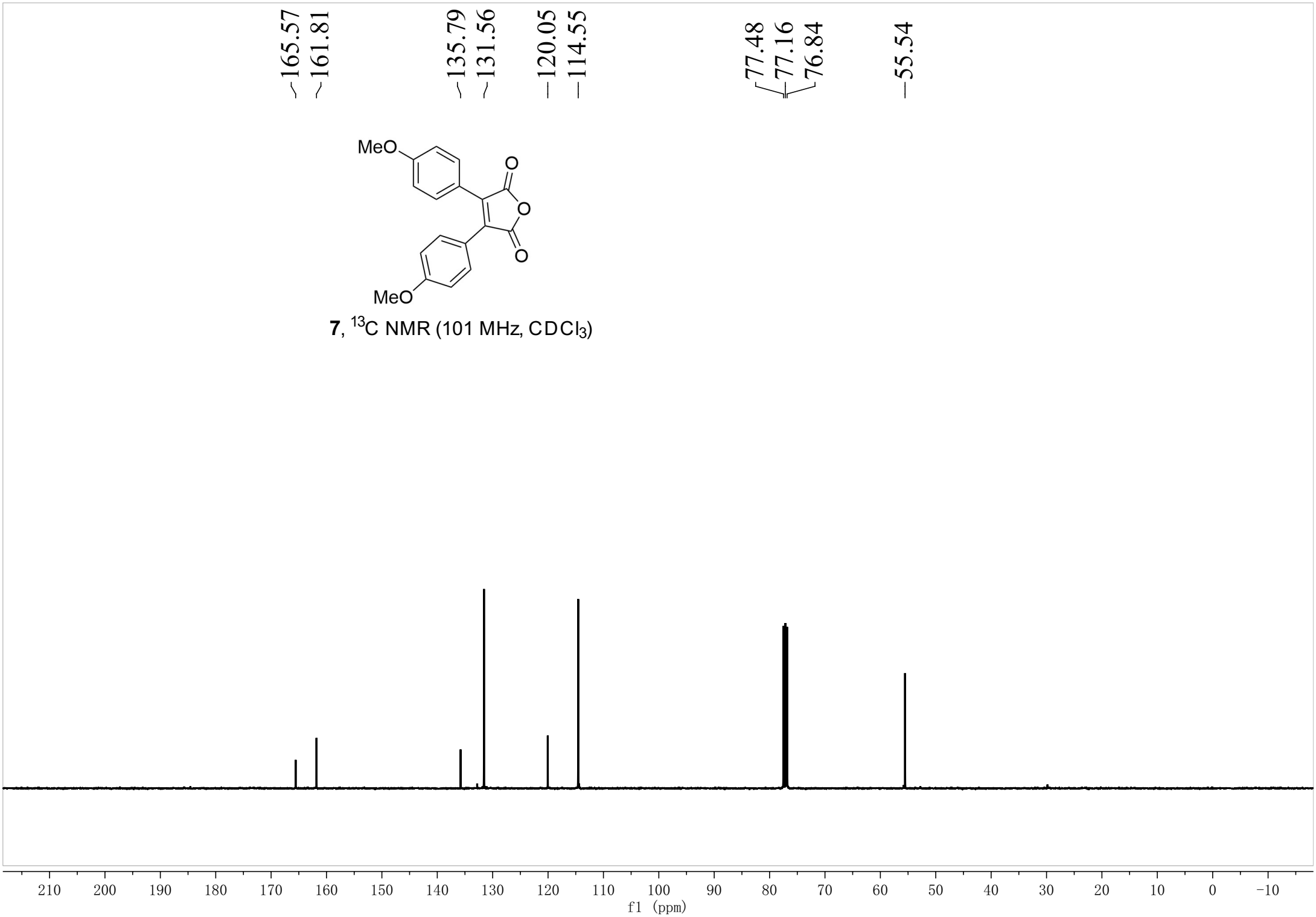
6k, ^{13}C NMR (101 MHz, $CDCl_3$)



6k, ^{19}F NMR (376 MHz, $CDCl_3$)



7, ^{1}H NMR (400 MHz, $CDCl_3$)



7, ^{13}C NMR (101 MHz, $CDCl_3$)