

A Nickel/Organoboron Catalyzed Coupling of Aryl Bromides with Sodium Sulfinates: Synthesis of Sulfones under Visible Light

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1. General considerations

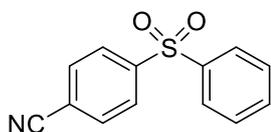
General. Unless otherwise noted, all reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

Structural analysis. NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts (δ) are reported in parts per million (ppm). ^1H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were acquired on Thermo Scientific LTQ Orbitrap XL with an ESI source.

Materials. Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

2. Characterization data

(3a) 4-(phenylsulfonyl)benzonitrile (CAS: 28525-13-5)¹

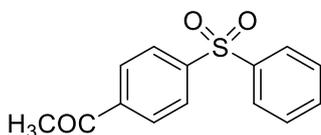


4-(phenylsulfonyl)benzonitrile
Chemical Formula: C₁₃H₉NO₂S
Exact Mass: 243.0354
Molecular Weight: 243.2800

Following the General Procedure with 4-Bromobenzonitrile (36.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3a** was obtained as white solid (41.3 mg, 85%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).
¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 145.9, 140.2, 134.1, 133.1, 129.7, 128.3, 128.0, 117.2, 116.9.

(3b) (4-(phenylsulfonyl)phenyl)ethan-1-one (CAS: 65085-83-8)¹



1-(4-(phenylsulfonyl)phenyl)ethan-1-one
Chemical Formula: C₁₄H₁₂O₃S
Exact Mass: 260.0507
Molecular Weight: 260.3070

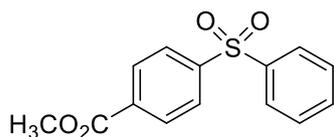
Following the General Procedure with 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3b** was obtained as white solid (41.6 mg, 80%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 4H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 6.0 Hz, 1H), 7.54 (d, *J* = 6.8

Hz, 2H), 2.62 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.7, 145.4, 140.8, 140.4, 133.7, 129.5, 129.1, 128.0, 127.9, 26.9.

(3c) methyl 4-(phenylsulfonyl)benzoate (CAS: 38337-00-7)¹



methyl 4-(phenylsulfonyl)benzoate
Chemical Formula: C₁₄H₁₂O₄S
Exact Mass: 276.0456
Molecular Weight: 276.3060

Following the General Procedure with methyl 4-bromobenzoate (42.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3c** was obtained as white solid (22.1 mg, 40%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J*

= 7.2 Hz, 1H), 7.52 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H).

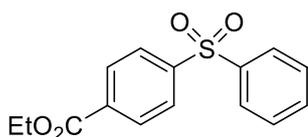
¹³C NMR (101 MHz, CDCl₃) δ 165.5, 145.5, 140.8, 134.3, 133.6, 130.5, 129.5, 127.8, 127.7, 52.7.

(3d) (4-(phenylsulfonyl)phenyl)propan-1-one (CAS: 69567-00-6)

Following the General Procedure with methyl 1-(4-bromophenyl)propan-1-one (45.6 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3d** was obtained as white solid (42.7 mg, 78%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 5.2 Hz, 4H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.97 (d, *J* = 7.2 Hz, 2H), 1.18 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 199.5, 145.2, 140.8, 140.3, 133.7, 129.5, 128.8, 128.0, 127.8, 32.3, 8.0.



ethyl 4-(phenylsulfonyl)benzoate

Chemical Formula: C₁₅H₁₄O₄S

Exact Mass: 290.0613

Molecular Weight: 290.3330

HRMS (ESI) *m/z* calcd for C₁₅H₁₅O₃S⁺ M+H⁺ 275.3415, found 275.3415.

IR: 3070, 2978, 2935, 1697, 1582, 1448, 1155, 730, 600.

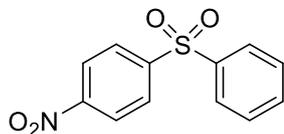
Melting point (°C): 57.9-59.1

(3e) ethyl 4-(phenylsulfonyl)benzoate (CAS: 101094-06-8)¹

Following the General Procedure with ethyl 4-bromobenzoate (45.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3e** was obtained as white solid (24.4 mg, 42%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 4.38 (d, *J* = 7.2 Hz, 2H), 1.38 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 165.0, 145.4, 140.9, 134.7, 133.6, 130.4, 129.5, 129.3, 127.8, 127.7, 61.7, 14.2.



1-nitro-4-(phenylsulfonyl)benzene

Chemical Formula: C₁₂H₉NO₄S

Exact Mass: 263.0252

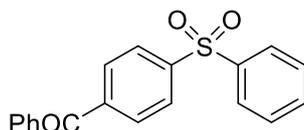
Molecular Weight: 263.2670

(3f) nitro-4-(phenylsulfonyl)benzene (CAS: 1146-39-0)¹

Following the General Procedure with methyl 1-bromo-4-nitrobenzene (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3f** was obtained as white solid (38.3 mg, 73%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 6.7 Hz, 2H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 6.4 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 150.4, 147.4, 140.0, 134.2, 129.7, 129.0, 128.1, 124.6.



phenyl(4-(phenylsulfonyl)phenyl)methanone

Chemical Formula: C₁₉H₁₄O₃S

Exact Mass: 322.0664

Molecular Weight: 322.3780

C₂H₅OC

1-(4-(phenylsulfonyl)phenyl)propan-1-one

Chemical Formula: C₁₅H₁₄O₃S

Exact Mass: 274.0664

Molecular Weight: 274.3340

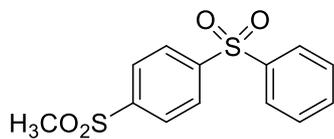
(3g) phenyl(4-(phenylsulfonyl)phenyl)methanone (CAS: 54687-39-7)²

Following the General Procedure with (4-bromophenyl)(phenyl)methanone (52.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3g** was obtained as white solid (32.8 mg, 51%). This product of interest

is purified by silica gel flash chromatography (PE: EA = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 6.4$ Hz, 2H), 7.99 (d, $J = 7.6$ Hz, 2H), 7.88 (d, $J = 6.8$ Hz, 2H), 7.77 (d, $J = 7.6$ Hz, 2H), 7.66 – 7.59 (m, 2H), 7.56 (d, $J = 6.8$ Hz, 2H), 7.49 (s, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.2, 144.7, 141.7, 140.9, 136.4, 133.7, 133.3, 130.5, 130.1, 129.5, 128.6, 127.9, 127.7.



1-(methylsulfonyl)-4-(phenylsulfonyl)benzene

Chemical Formula: $\text{C}_{13}\text{H}_{12}\text{O}_4\text{S}_2$

Exact Mass: 296.0177

Molecular Weight: 296.3550

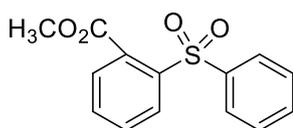
(3h) (methylsulfonyl)-4-(phenylsulfonyl)benzene (CAS: 3112-84-3)³

Following the General Procedure with 1-bromo-4-(methylsulfonyl)benzene (46.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3h** was

obtained as white solid (26.6 mg, 45%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.4$ Hz, 2H), 8.08 (d, $J = 8.4$ Hz, 2H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.63 (d, $J = 6.8$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 2H), 3.07 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.8, 144.8, 140.2, 134.1, 129.7, 128.7, 128.5, 128.0, 44.3.



methyl 2-(phenylsulfonyl)benzoate

Chemical Formula: $\text{C}_{14}\text{H}_{12}\text{O}_4\text{S}$

Exact Mass: 276.0456

Molecular Weight: 276.3060

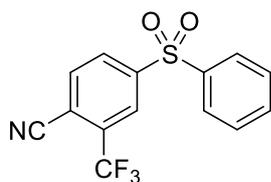
(3i) methyl 2-(phenylsulfonyl)benzoate (CAS: 67373-14-2)¹

Following the General Procedure with methyl 2-iodobenzoate (52.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3i** was obtained as white solid (35.3 mg, 64%). This product of interest is purified by silica gel flash chromatography (PE:

EA = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.15 (m, 1H), 7.97 (d, $J = 7.2$ Hz, 2H), 7.62 (m, 2H), 7.57 (m, 2H), 7.51 (t, $J = 7.4$ Hz, 2H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.7, 141.5, 139.0, 133.3, 130.9, 130.2, 129.2, 129.0, 127.8, 53.0.



4-(phenylsulfonyl)-2-(trifluoromethyl)benzonitrile

Chemical Formula: $\text{C}_{14}\text{H}_8\text{F}_3\text{NO}_2\text{S}$

Exact Mass: 311.0228

Molecular Weight: 311.2782

(3j) 4-(phenylsulfonyl)-2-(trifluoromethyl)benzonitrile (CAS: 2383030-86-0)¹

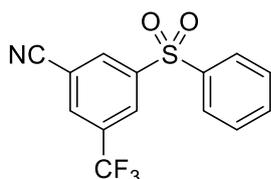
Following the General Procedure with 4-bromo-2-(trifluoromethyl)benzonitrile (49.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3j** was obtained as white solid (51.0

mg, 82%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

^1H NMR (400 MHz, CDCl_3) δ 8.34 (s, 1H), 8.25 (d, $J = 8.0$ Hz, 1H), 8.04 – 7.95 (m, 3H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 146.6, 139.3, 135.9, 134.6, 134.2 (d, $J = 34.0$ Hz), 131.3, 130.0, 128.2, 125.8 (q, $J = 4.7$ Hz), 121.5 (d, $J = 275.8$ Hz), 114.5, 114.0.

^{19}F NMR (376 MHz, CDCl_3) δ -62.10 (s).



3-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile

Chemical Formula: C₁₄H₈F₃NO₂S

Exact Mass: 311.0228

Molecular Weight: 311.2782

(3k) 3-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile¹

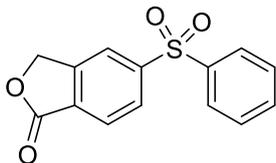
Following the General Procedure with 3-bromo-5-(trifluoromethyl)benzonitrile (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3k** was obtained as white solid (34.8 mg, 56%). This product of interest is

purified by silica gel flash chromatography (PE: EA = 5:1).

¹H NMR (400 MHz, CDCl₃) δ 8.40 (d, *J* = 10.4 Hz, 2H), 8.08 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.68 (m, 1H), 7.60 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 145.1, 139.3, 134.6, 134.3, 133.5 (d, *J* = 35.0 Hz), 133.0 (d, *J* = 3.6 Hz), 130.2, 128.3 (q, *J* = 3.6), 128.2, 127.7, 122.0 (d, *J* = 274.8 Hz), 115.7, 115.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.06 (s).



5-(phenylsulfonyl)isobenzofuran-1(3H)-one

Chemical Formula: C₁₄H₁₀O₄S

Exact Mass: 274.0300

Molecular Weight: 274.2900

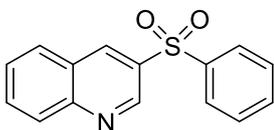
(3l) 5-(phenylsulfonyl)isobenzofuran-1(3H)-one (CAS: 2232133-50-3)³

Following the General Procedure with 5-bromoisobenzofuran-1(3H)-one (42.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3l** was obtained as white solid (27.4 mg, 50%). This product of interest is purified by silica gel flash

chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.99 – 7.96 (m, 2H), 7.64 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 5.39 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.1, 147.3, 147.2, 140.3, 134.0, 129.8, 129.7, 128.6, 128.0, 126.9, 122.0, 69.6.



3-(phenylsulfonyl)quinoline

Chemical Formula: C₁₅H₁₁NO₂S

Exact Mass: 269.0510

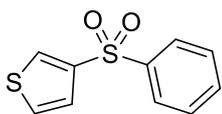
Molecular Weight: 269.3180

(3m) 3-(phenylsulfonyl)quinoline (CAS: 117620-35-6)¹

Following the General Procedure with methyl 1-bromo-4-nitrobenzene (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3m** was obtained as white solid (22.6 mg, 42%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 9.28 (d, *J* = 2.0 Hz, 1H), 8.83 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.87 (m, 1H), 7.68 (m, 1H), 7.63 – 7.57 (m, 1H), 7.54 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 149.4, 147.1, 141.0, 137.0, 134.7, 133.8, 132.8, 129.6, 129.2, 128.4, 127.8, 126.4.

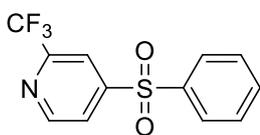


3-(phenylsulfonyl)thiophene
 Chemical Formula: C₁₀H₈O₂S₂
 Exact Mass: 223.9966
 Molecular Weight: 224.2920

(3n) 3-(phenylsulfonyl)thiophene (CAS: 89770-30-9) ⁴

Following the General Procedure with 3-iodothiophene (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (44.6 mg, 0.4 mmol, 2.0 equiv), **3n** was obtained as white solid (25.0 mg, 56%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.13 – 8.08 (m, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.59 (t, *J* = 6.8 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.36 – 7.32 (m, 1H).
¹³C NMR (101 MHz, CDCl₃) δ 142.0, 141.6, 133.3, 131.6, 129.3, 128.4, 127.5, 125.9.

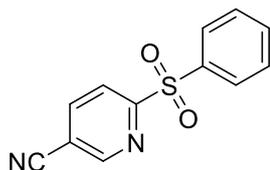


4-(phenylsulfonyl)-2-(trifluoromethyl)pyridine
 Chemical Formula: C₁₂H₈F₃NO₂S
 Exact Mass: 287.0228
 Molecular Weight: 287.2562

(3o) 4-(phenylsulfonyl)-2-(trifluoromethyl)pyridine ⁵ (CAS: 2412989-04-7)

Following the General Procedure with 4-bromo-2-(trifluoromethyl)pyridine (44.9 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3o** was obtained as white solid (46.5 mg, 81%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.93 (d, *J* = 4.8 Hz, 1H), 8.13 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 3H), 7.74 – 7.63 (m, 1H), 7.63 – 7.53 (m, 2H).
¹³C NMR (101 MHz, CDCl₃) δ 152.2, 151.7, 150.0 (d, *J* = 36.1 Hz), 138.8, 134.7, 130.0, 128.3, 123.7, 120.7 (d, *J* = 275.8 Hz), 117.79 (d, *J* = 2.7 Hz).
¹⁹F NMR (376 MHz, CDCl₃) δ -68.06 (s).



6-(phenylsulfonyl)nicotinonitrile
 Chemical Formula: C₁₂H₈N₂O₂S
 Exact Mass: 244.0306
 Molecular Weight: 244.2680

(3p) 6-(phenylsulfonyl)nicotinonitrile (205514-29-0)

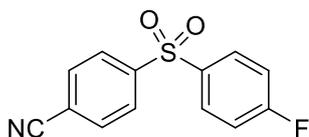
Following the General Procedure with 2-Bromo-4-cyanopyridine (36.6 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3p** was obtained as white solid (20.5 mg, 42%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.89 (d, *J* = 1.1 Hz, 1H), 8.34 (d, *J* = 8.0 Hz, 1H), 8.23 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 6.8 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H).
¹³C NMR (101 MHz, CDCl₃) δ 161.7, 152.7, 141.9, 137.5, 134.6, 129.4, 129.4, 121.9, 115.1, 113.0.

HRMS (ESI) *m/z* calcd for C₁₂H₉N₂O₂S⁺ M+H⁺ 245.0371, found 245.0371.

IR: 3065, 2243, 1452, 325, 1161, 628.

Melting point (°C): 119.1-120.1



4-((4-fluorophenyl)sulfonyl)benzonitrile
 Chemical Formula: $C_{13}H_8FNO_2S$
 Exact Mass: 261.0260
 Molecular Weight: 261.2704

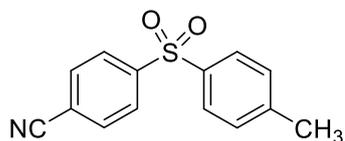
(3q) 4-((4-fluorophenyl)sulfonyl)benzonitrile¹ (CAS: 1268049-80-4)

Following the General Procedure with 4-Bromobenzonitrile (36.4 mg, 0.2 mmol, 1.0 equiv), 4-Fluorobenzenesulfinic acid sodium salt (91.0 mg, 0.4 mmol, 2.0 equiv), **3q** was obtained as white solid (20.8 mg, 40%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.4 Hz, 2H), 8.02 – 7.95 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 16.0, 8.0 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 166.0 (d, *J* = 258.7 Hz), 145.7, 136.2, 133.2, 130.9 (d, *J* = 9.8 Hz), 128.2, 117.2, 117.1 (d, *J* = 3.7 Hz), 117.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -102.34 (s).



4-tosylbenzonitrile
 Chemical Formula: $C_{14}H_{11}NO_2S$
 Exact Mass: 257.0510
 Molecular Weight: 257.3070

(3r) 4-tosylbenzonitrile¹ (CAS: 38111-56-7)

Following the General Procedure with 4-Bromobenzonitrile (36.4 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfinic acid sodium salt (71.2 mg, 0.4 mmol, 2.0 equiv), **3r** was obtained as white solid (27.8 mg, 54%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 6.8 Hz, 2H), 7.83 (d, *J* = 6.8 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H).

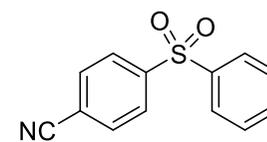
¹³C NMR (101 MHz, CDCl₃) δ 146.3, 145.3, 137.1, 133.1, 130.3, 128.1, 128.0, 117.2, 116.7, 21.7.

3. References

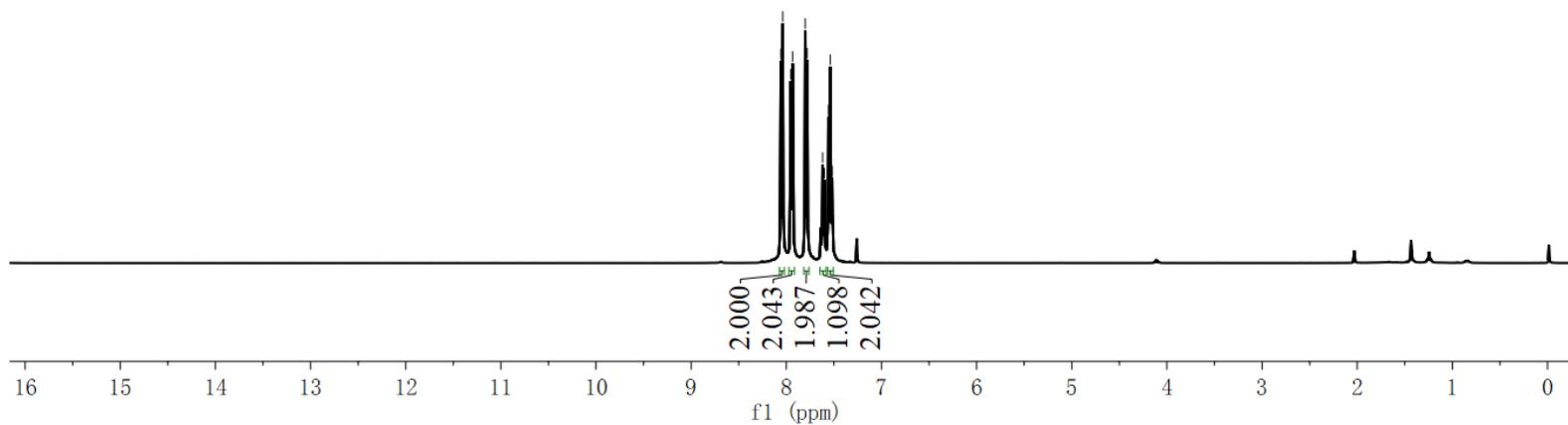
1. Jiang, S.; Zhang, Z.-T.; Young, D. J.; Chai, L.-L.; Wu, Q.; Li, H.-X., Visible-light mediated cross-coupling of aryl halides with sodium sulfinates via carbonyl-photoredox/nickel dual catalysis. *Organic Chemistry Frontiers* **2022**, *9* (5), 1437-1444.
2. Nandi, G. C., An efficient Cu-catalyzed microwave-assisted synthesis of diaryl sulfones. *Synthetic Communications* **2017**, *47* (4), 319-323.
3. Cabrera-Afonso, M. a. J. s.; Lu, Z.-P.; Kelly, C. B.; Lang, S. B.; Dykstra, R.; Gutierrez, O.; Molander, G. A., Engaging sulfinate salts via Ni/photoredox dual catalysis enables facile Csp²–SO₂R coupling. *Chemical Science* **2018**, *9* (12), 3186-3191.
4. Liu, N.-W.; Liang, S.; Margraf, N.; Shaaban, S.; Luciano, V.; Drost, M.; Manolikakes, G., Nickel-Catalyzed Synthesis of Diaryl Sulfones from Aryl Halides and sodium Sulfinates. *European Journal of Organic Chemistry* **2018**, *2018* (10), 1208-1210.
5. Zhu, D. L.; Wu, Q.; Li, H. Y.; Li, H. X.; Lang, J. P., Hantzsch Ester as a Visible-Light Photoredox Catalyst for Transition-Metal-Free Coupling of Arylhalides and Arylsulfinates. *Chemistry* **2020**, *26* (16), 3484-3488.

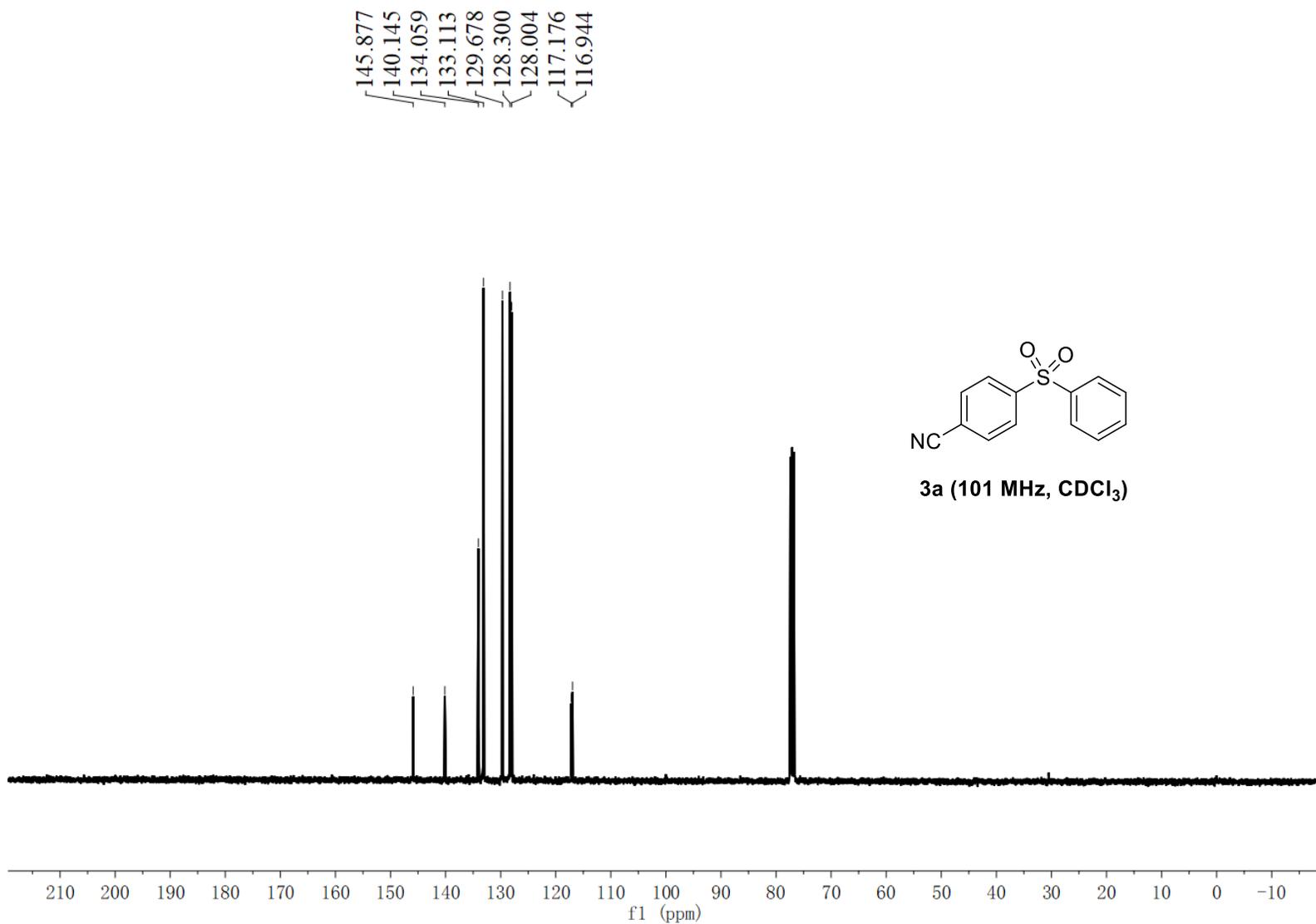
4. Copies of NMR spectra

8.058
8.037
7.953
7.934
7.801
7.781
7.618
7.600
7.557
7.537
7.519



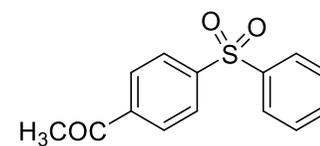
3a (400 MHz, CDCl₃)



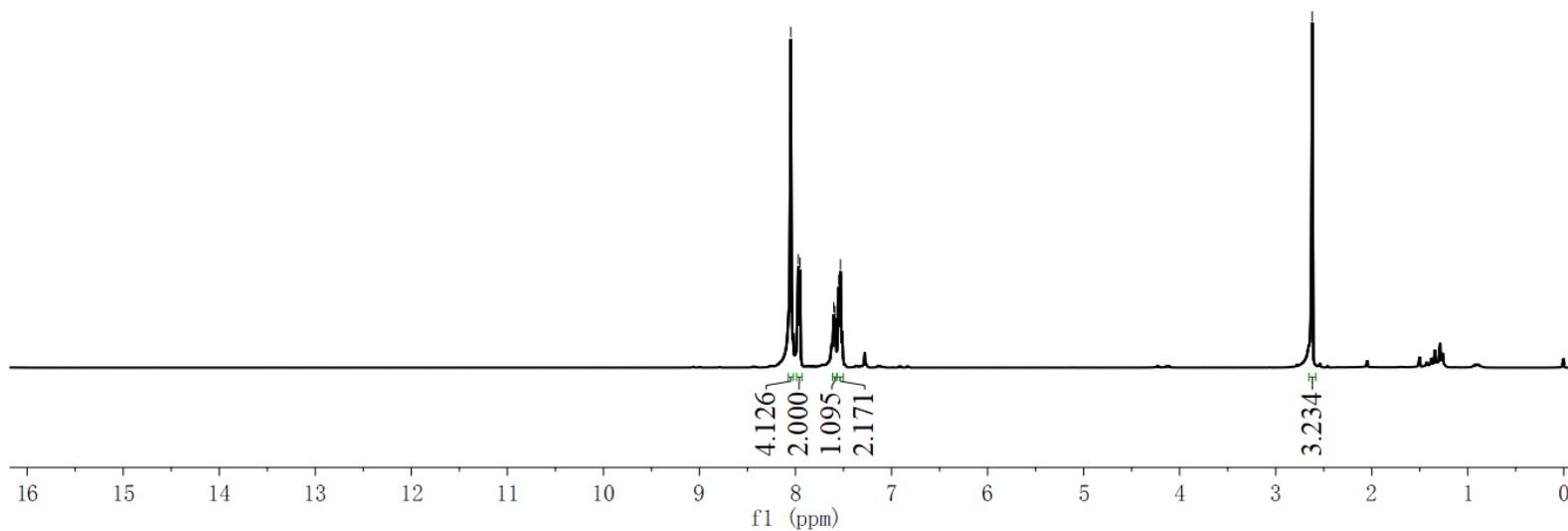


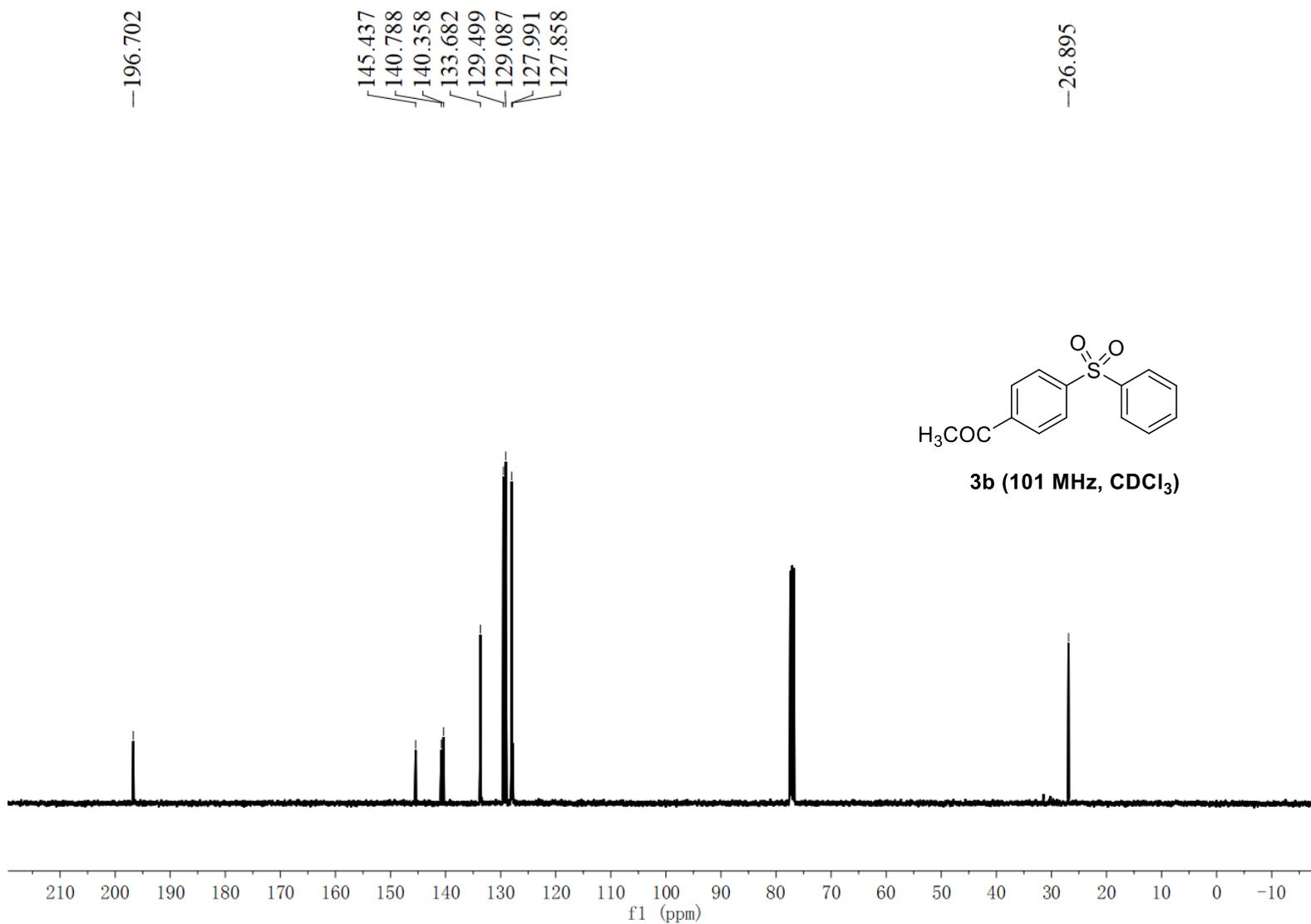
8.048
7.972
7.952
7.601
7.586
7.549
7.532

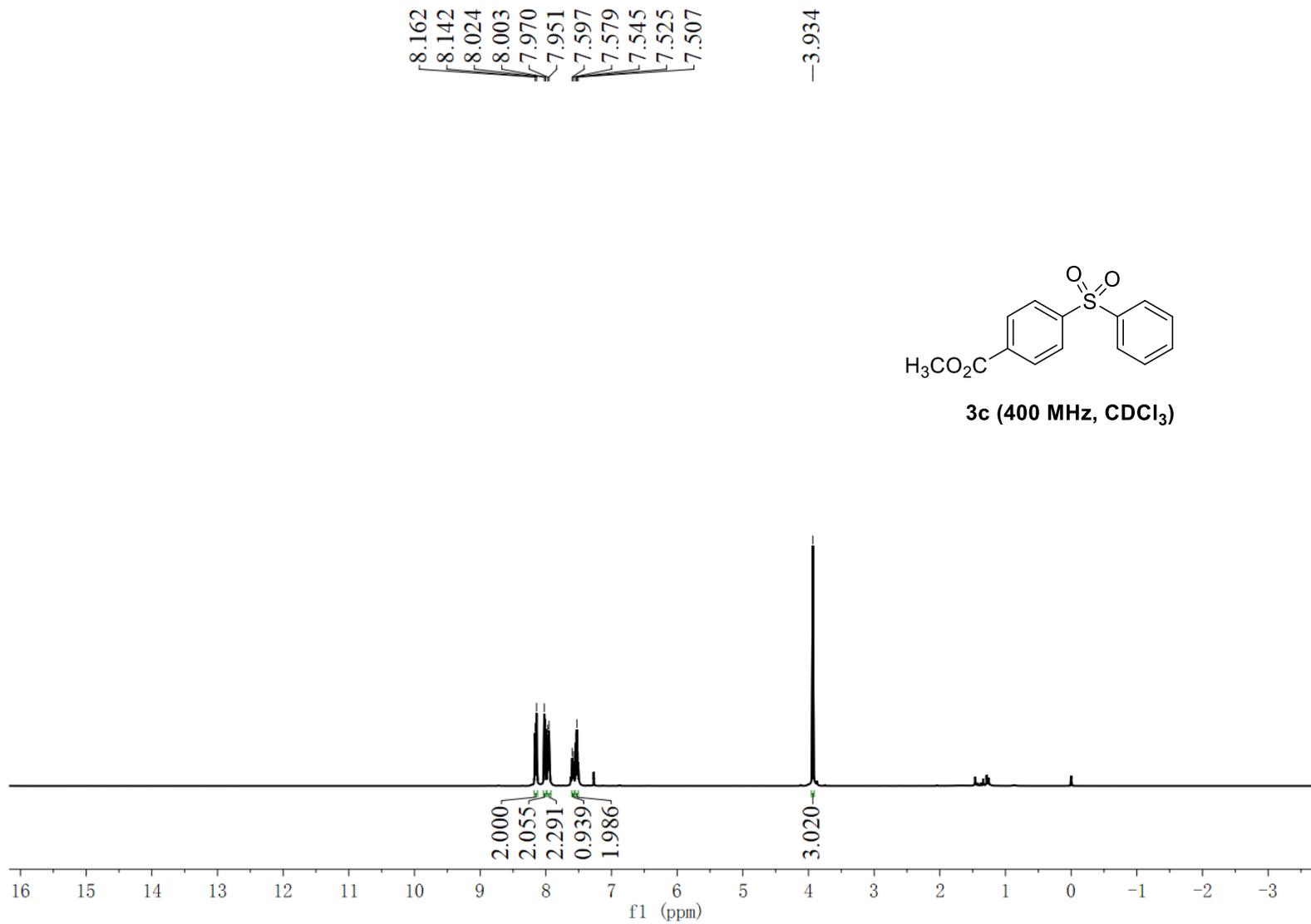
-2.620

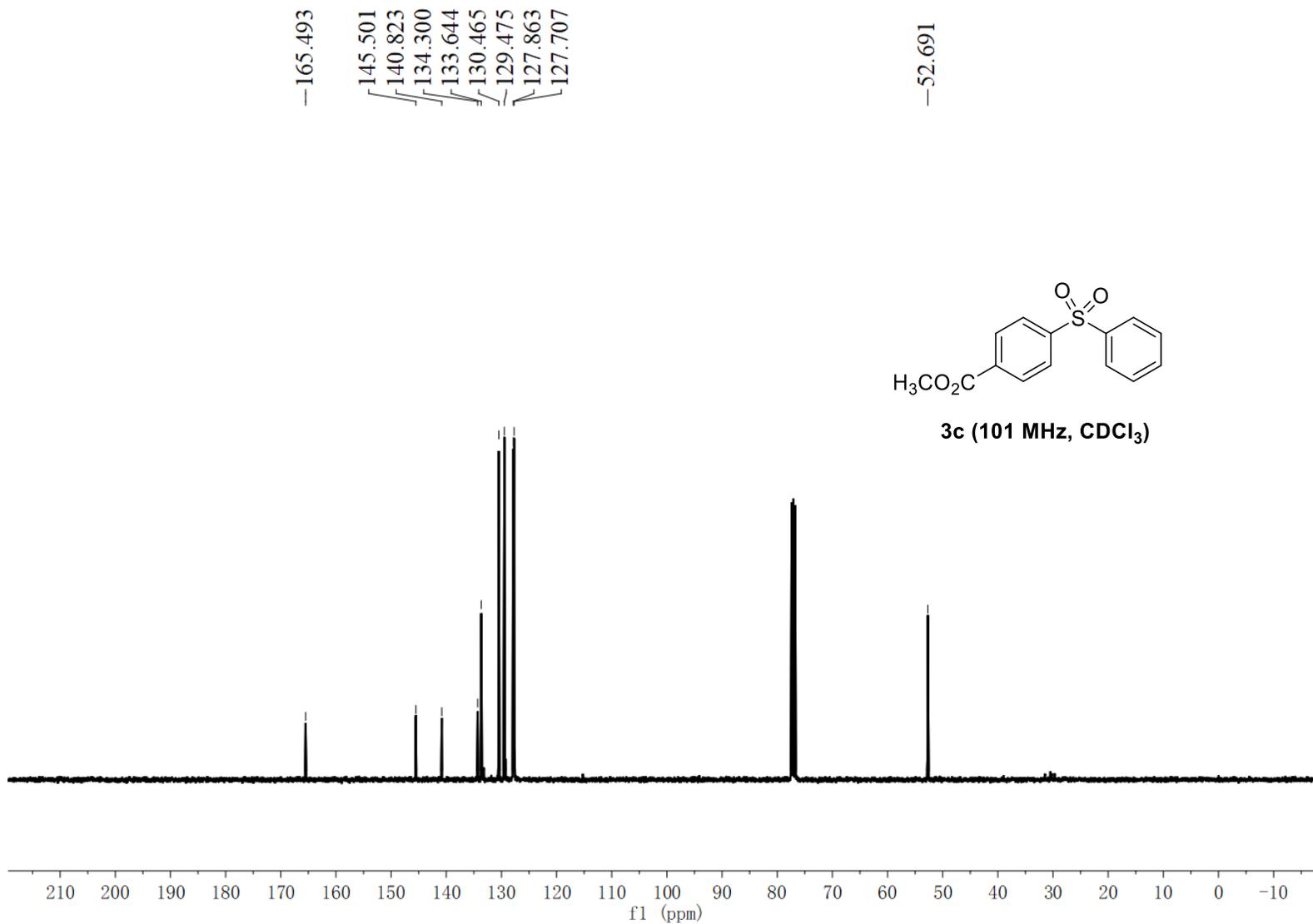


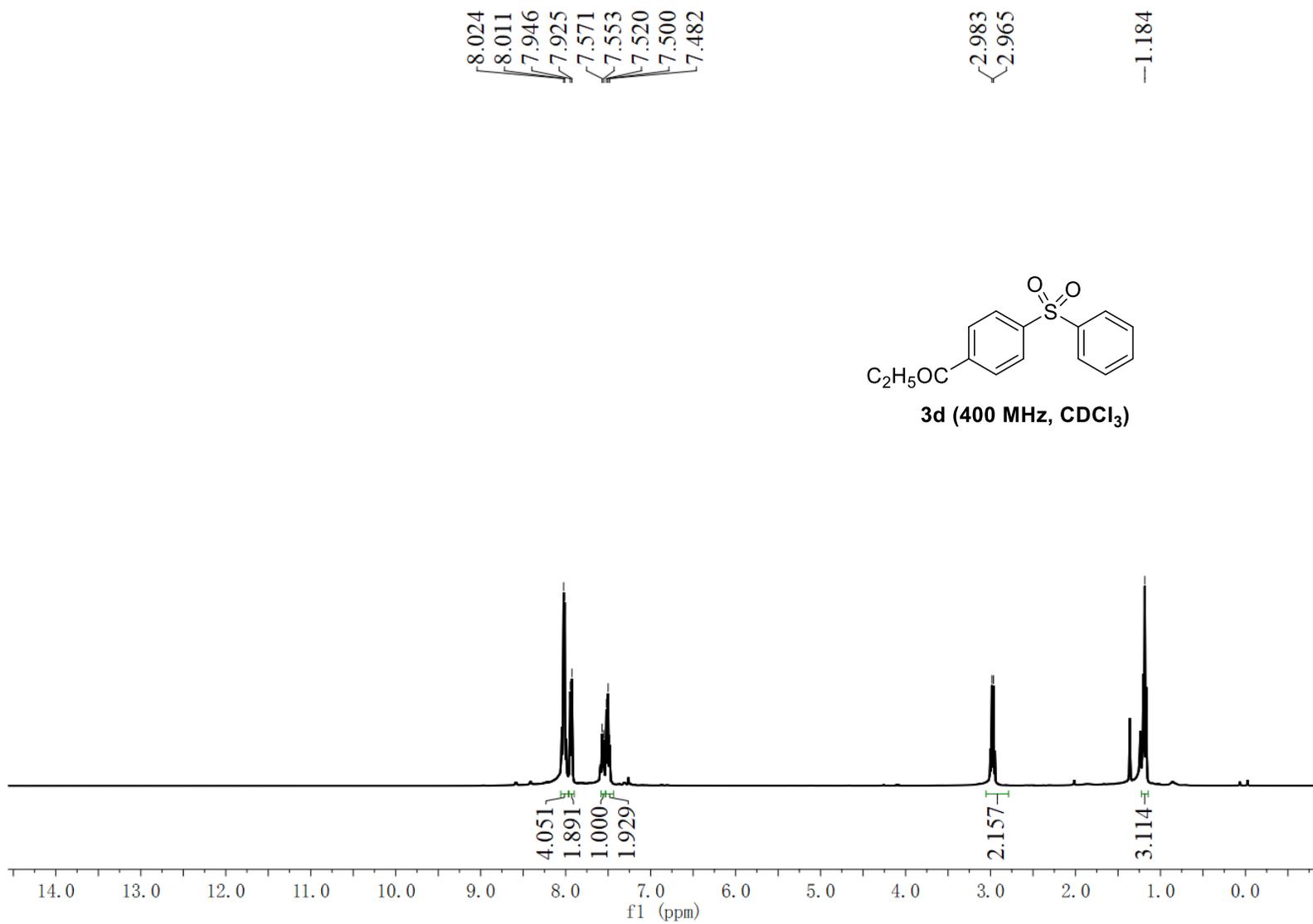
3b (400 MHz, CDCl₃)

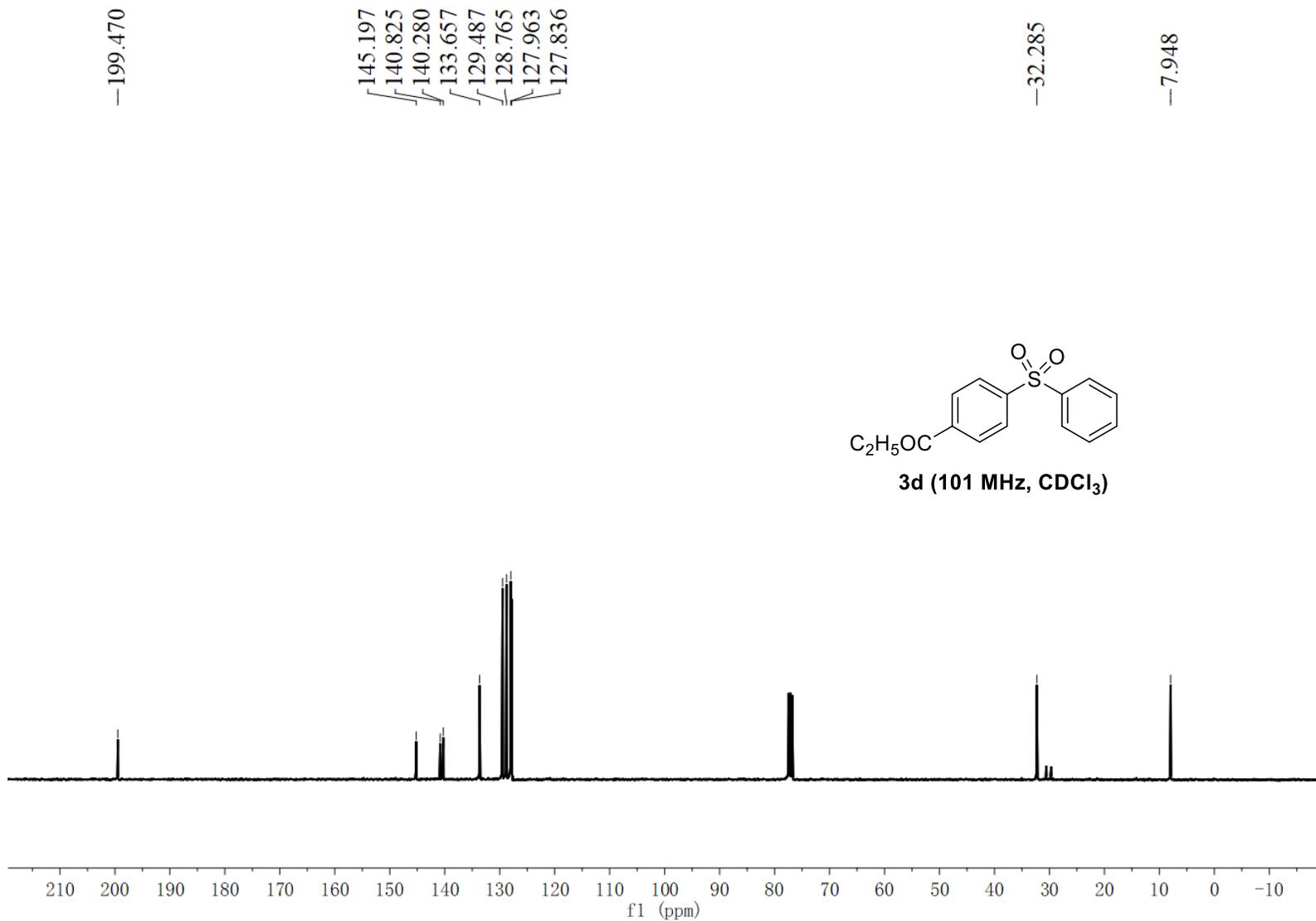


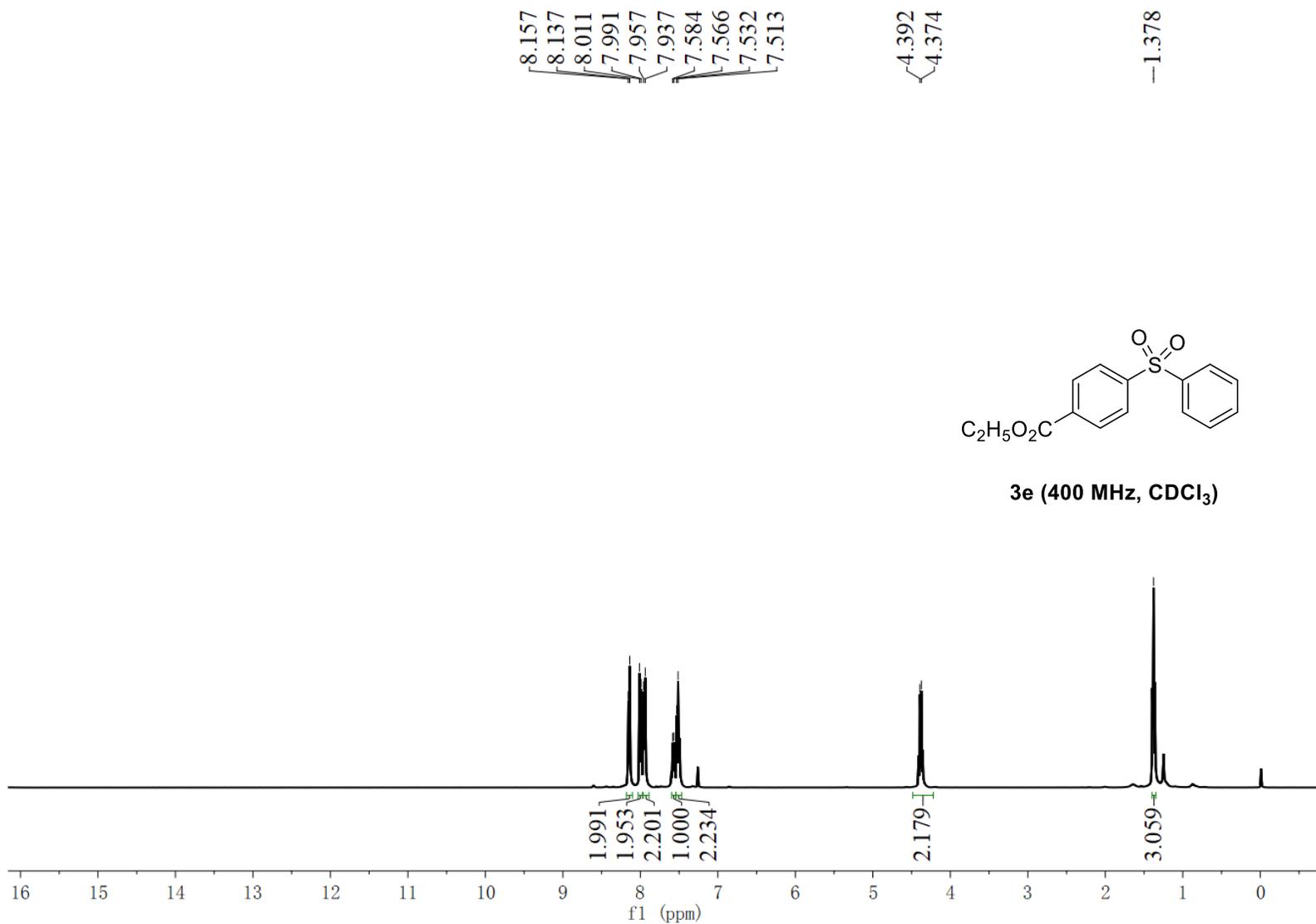


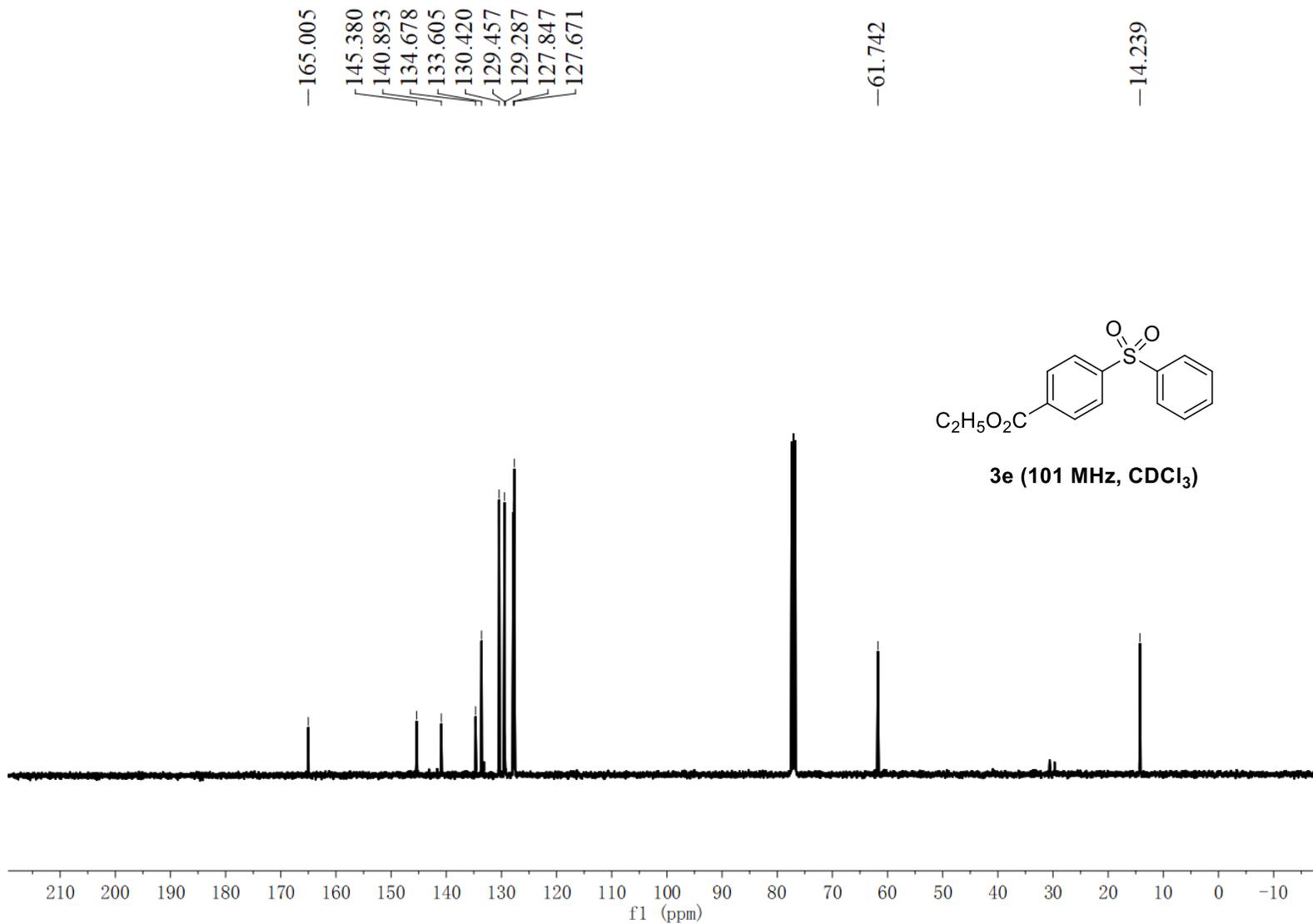




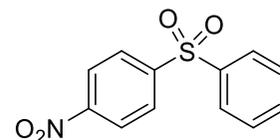




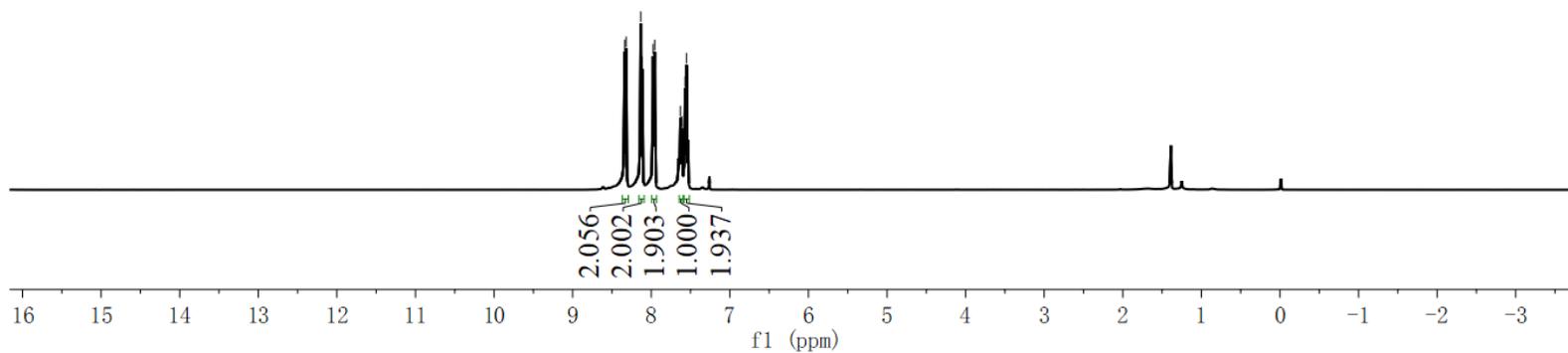




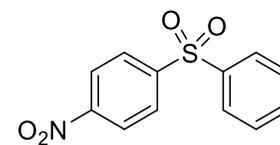
8.339
8.317
8.134
8.117
7.975
7.955
7.629
7.613
7.569
7.552



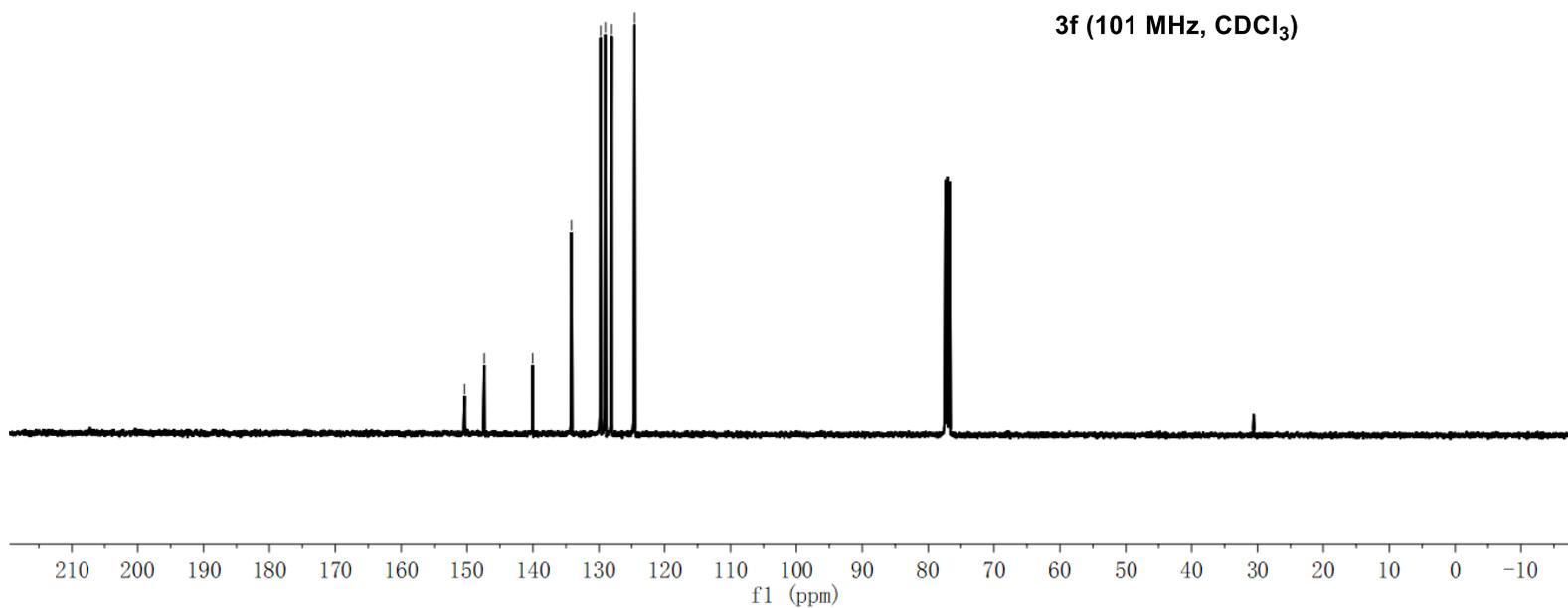
3f (400 MHz, CDCl₃)



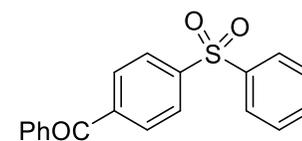
150.373
147.385
140.040
134.155
129.725
129.007
128.053
124.553



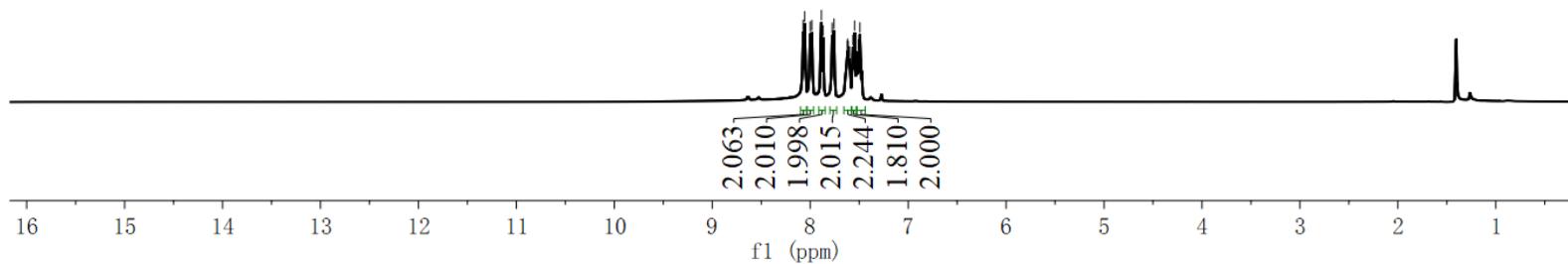
3f (101 MHz, CDCl₃)

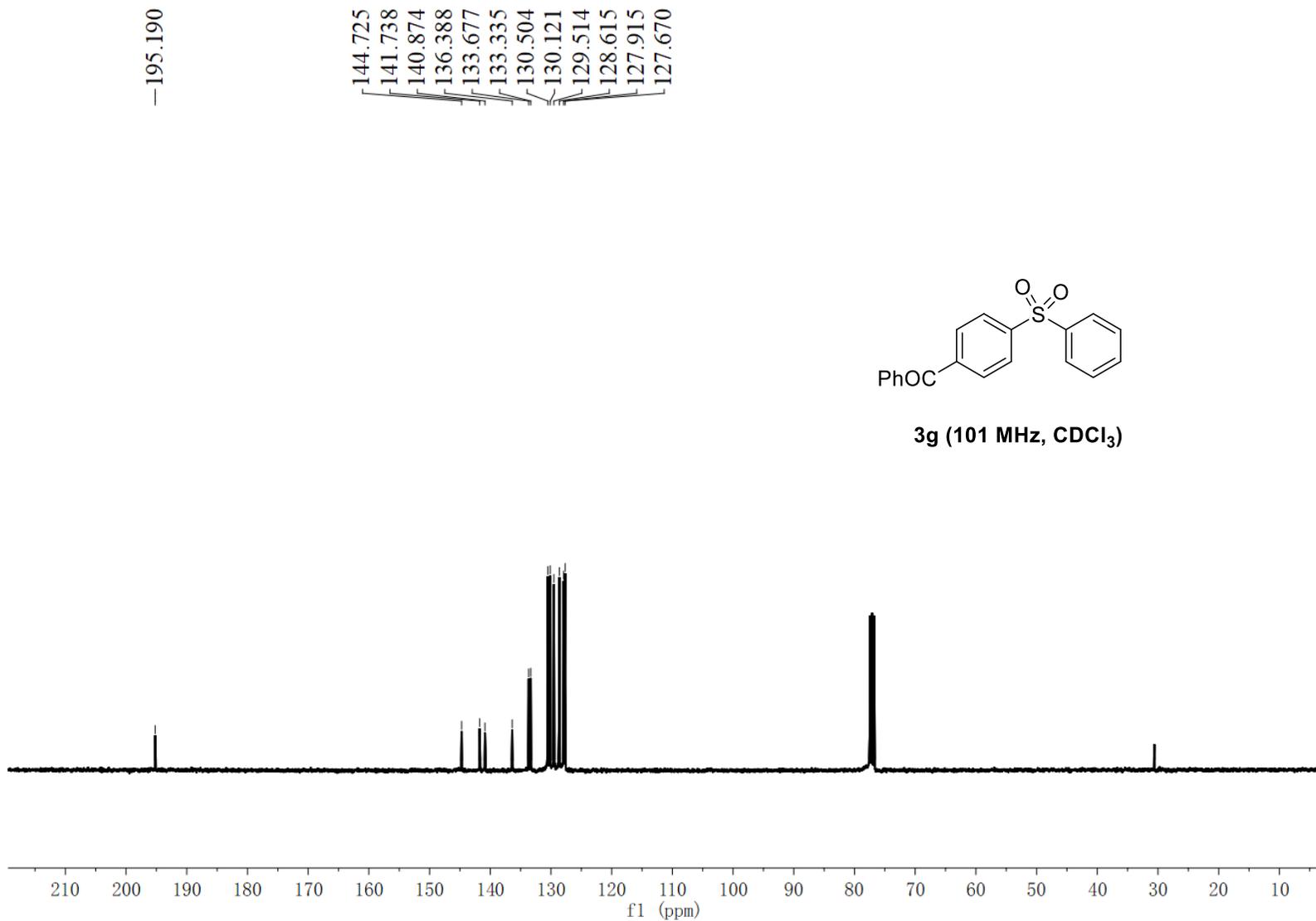


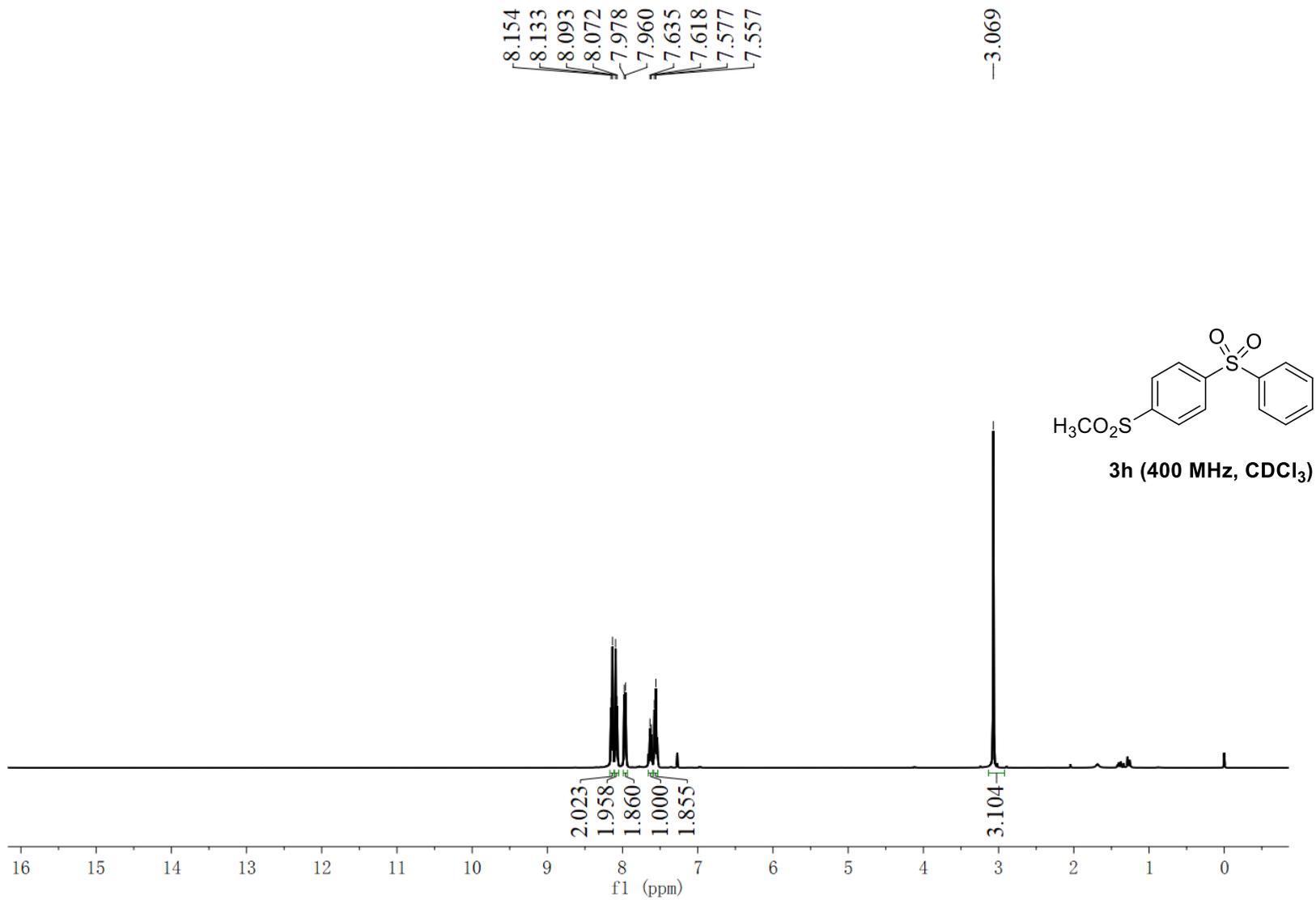
8.072
8.056
8.001
7.982
7.886
7.869
7.776
7.757
7.621
7.618
7.612
7.606
7.603
7.600
7.564
7.547
7.509
7.493
7.474

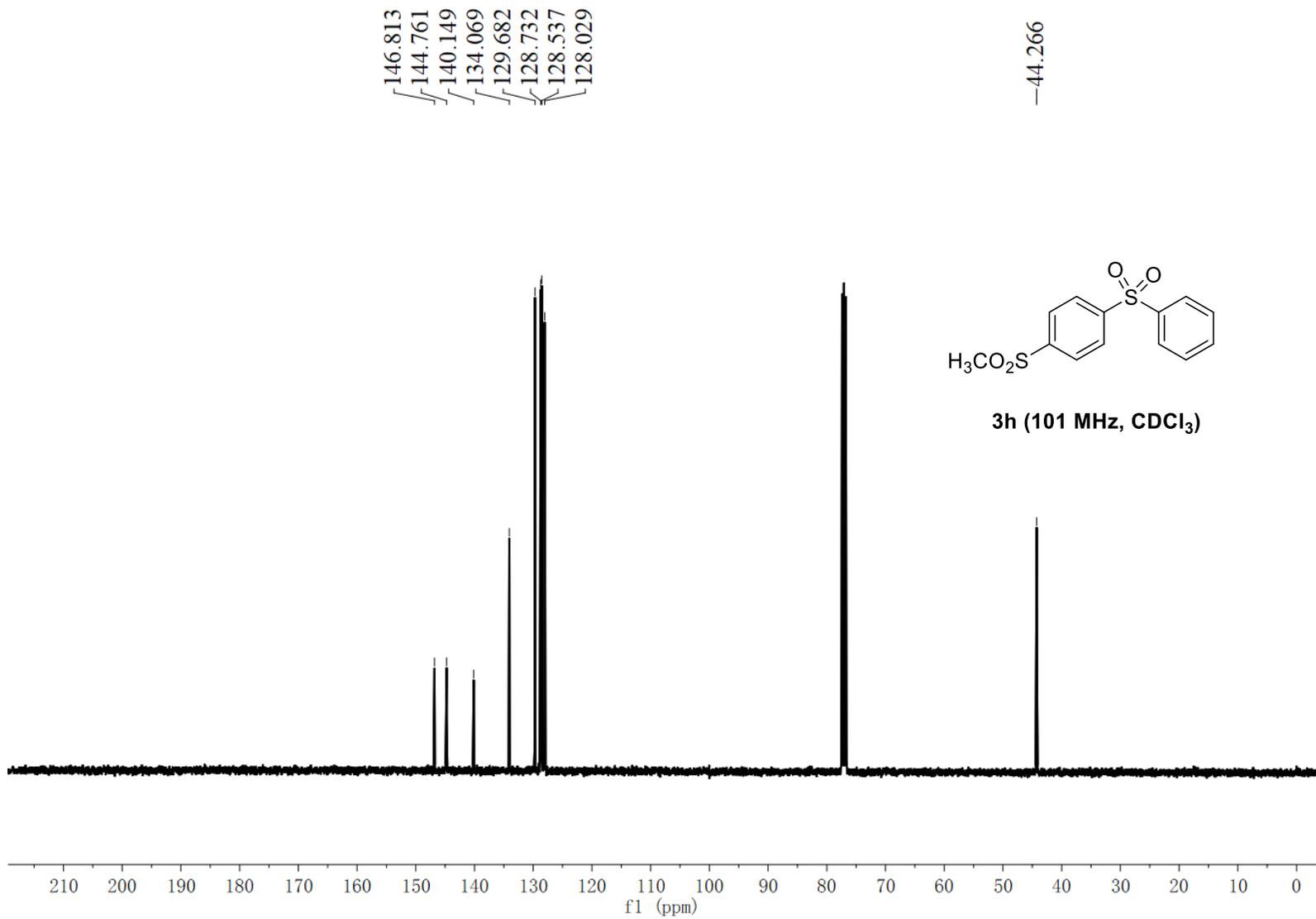


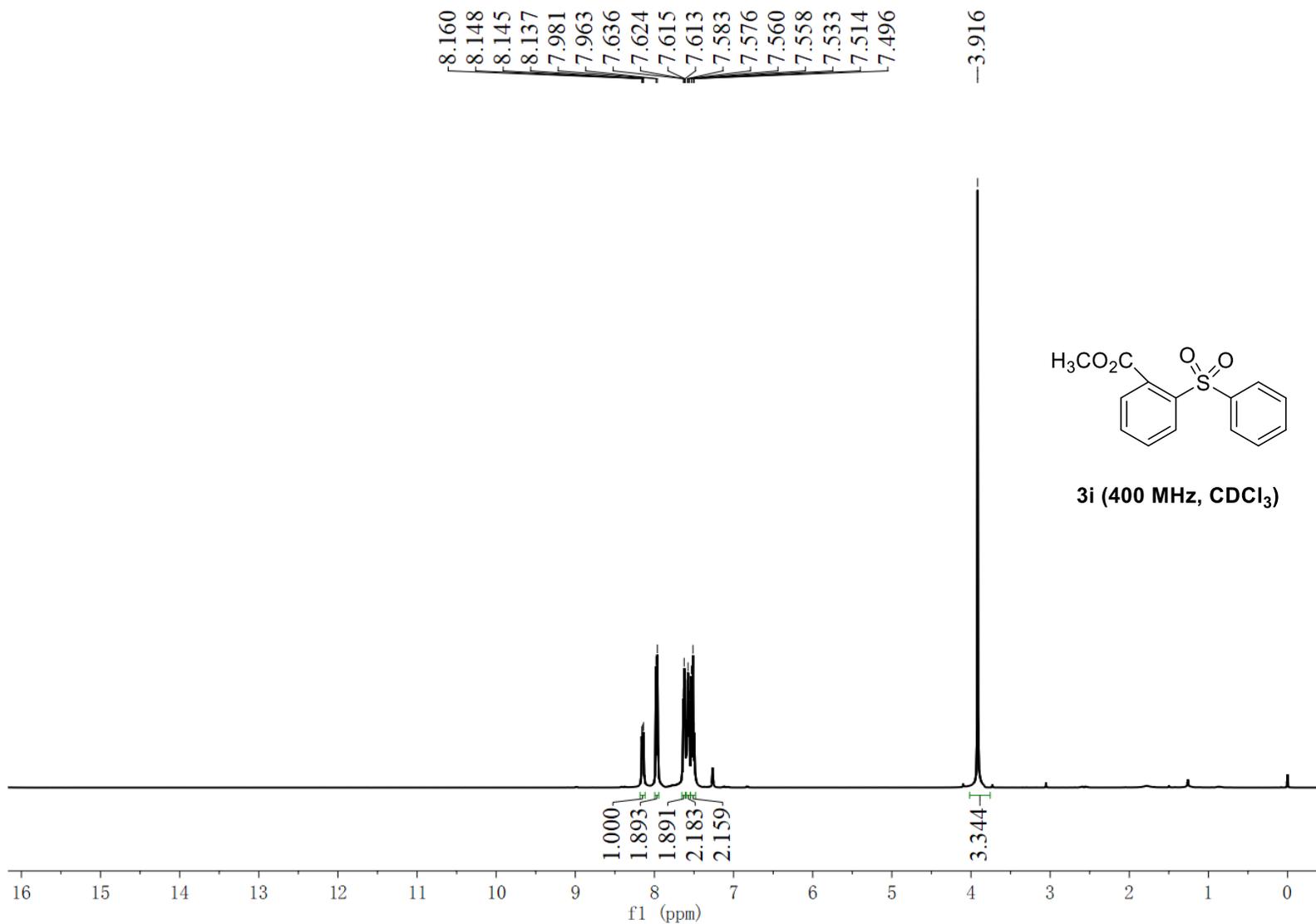
3g (400 MHz, CDCl₃)

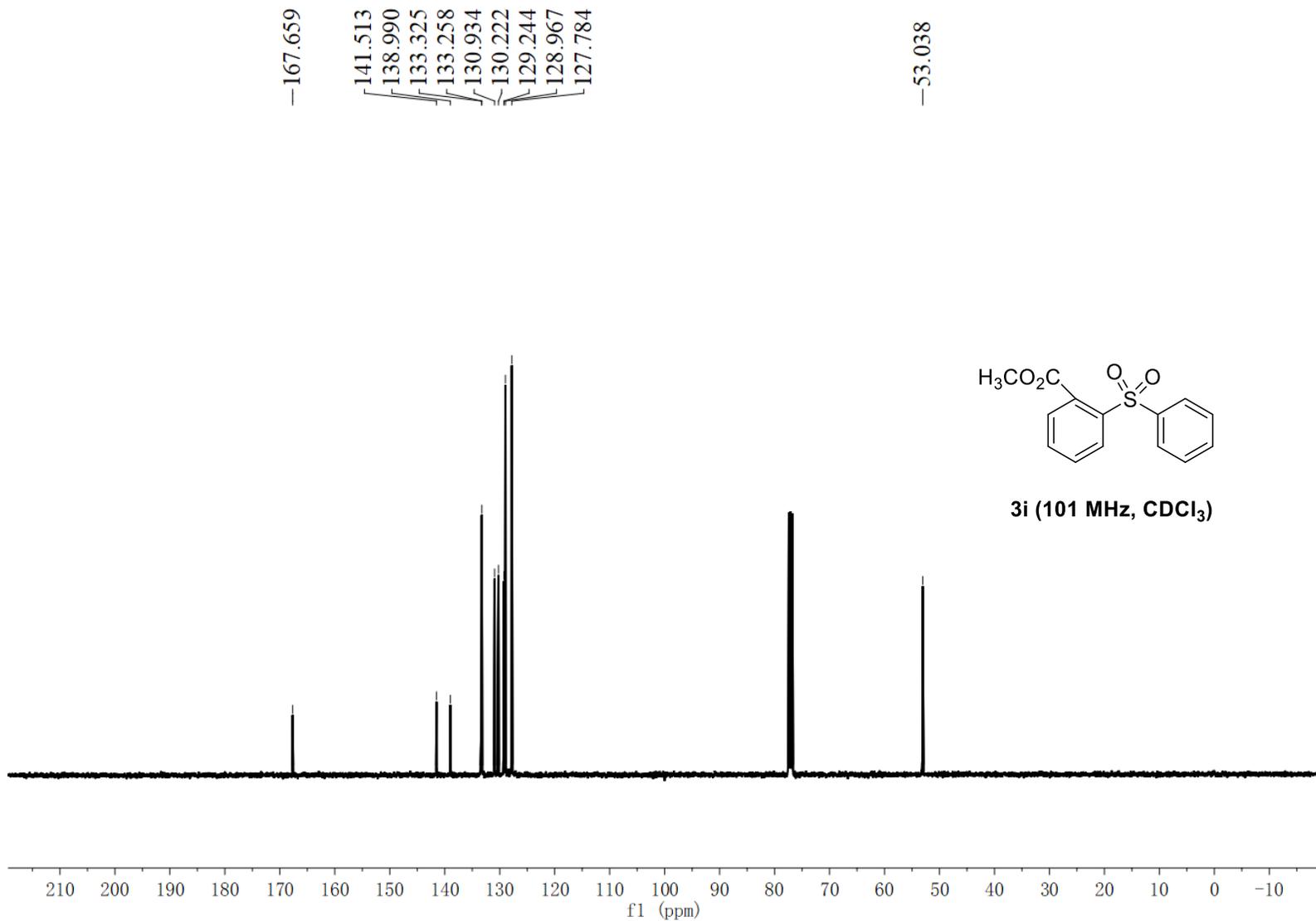




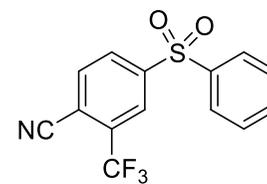




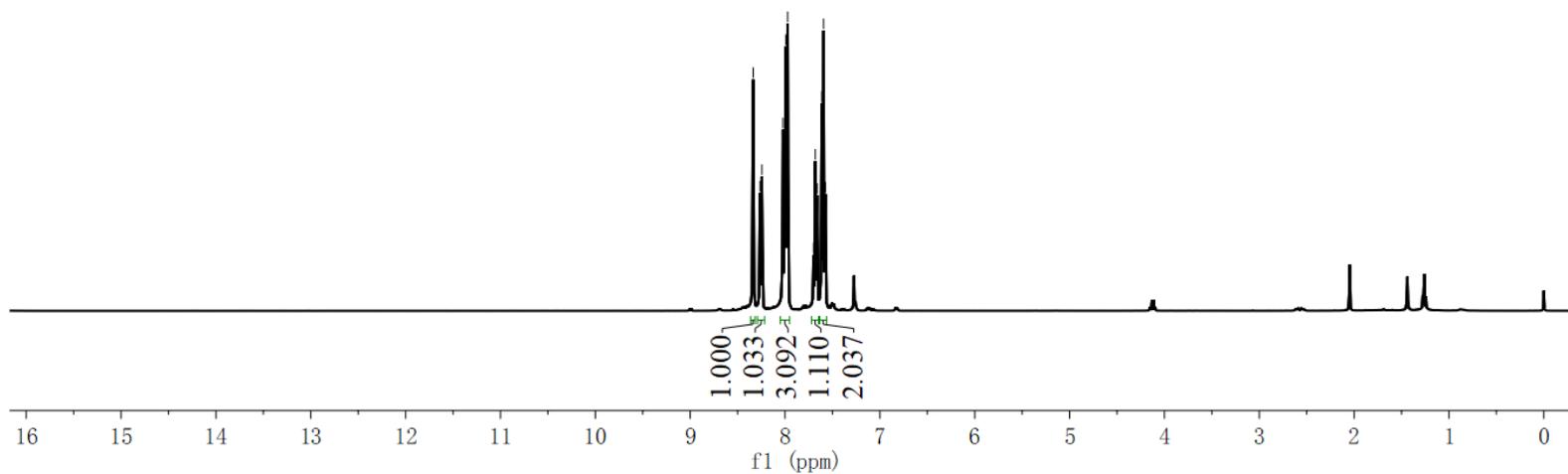




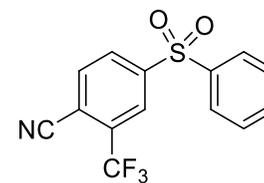
8.336
8.264
8.244
8.022
8.002
7.992
7.973
7.969
7.699
7.681
7.662
7.613
7.593
7.575



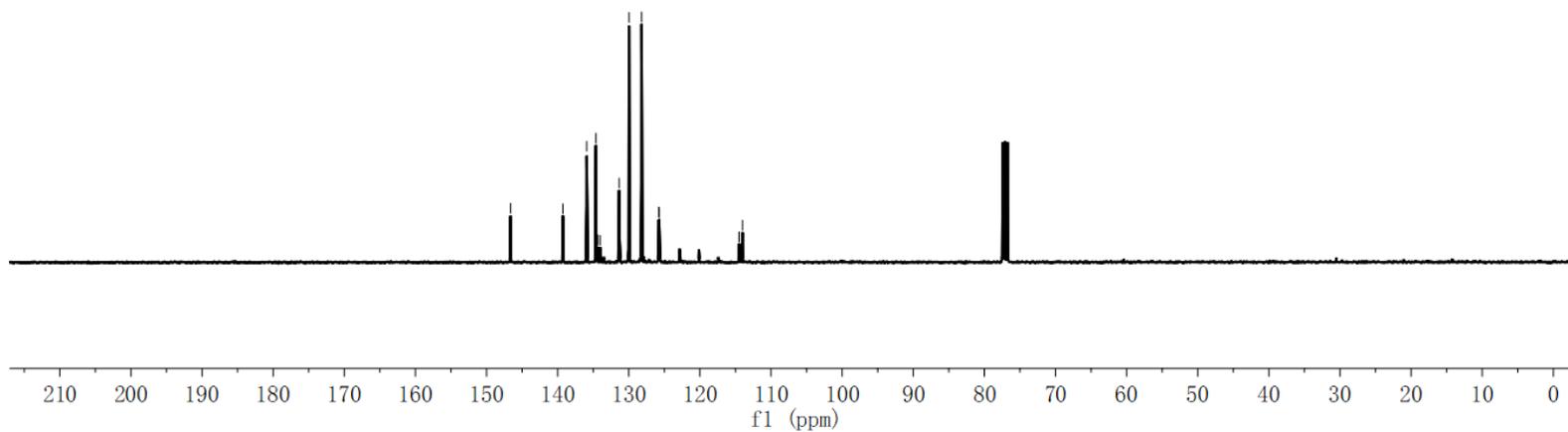
3j (400 MHz, CDCl₃)

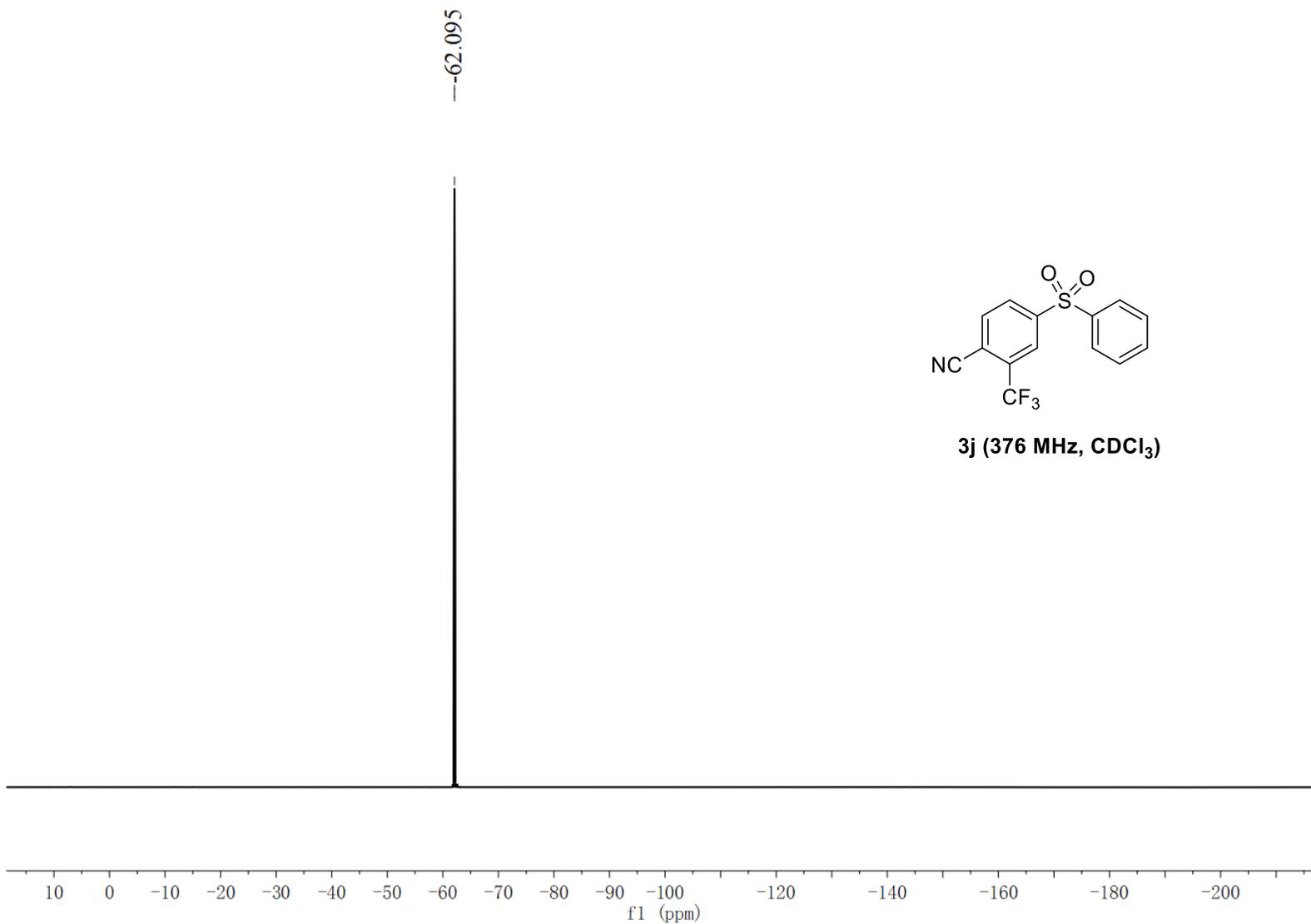


146.612
139.267
135.912
134.615
134.372
134.035
131.339
129.968
128.195
125.823
125.777
125.730
125.683
114.493
114.473
114.016

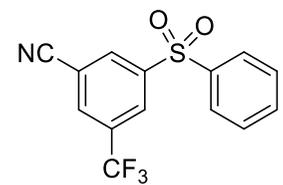


3j (101 MHz, CDCl₃)

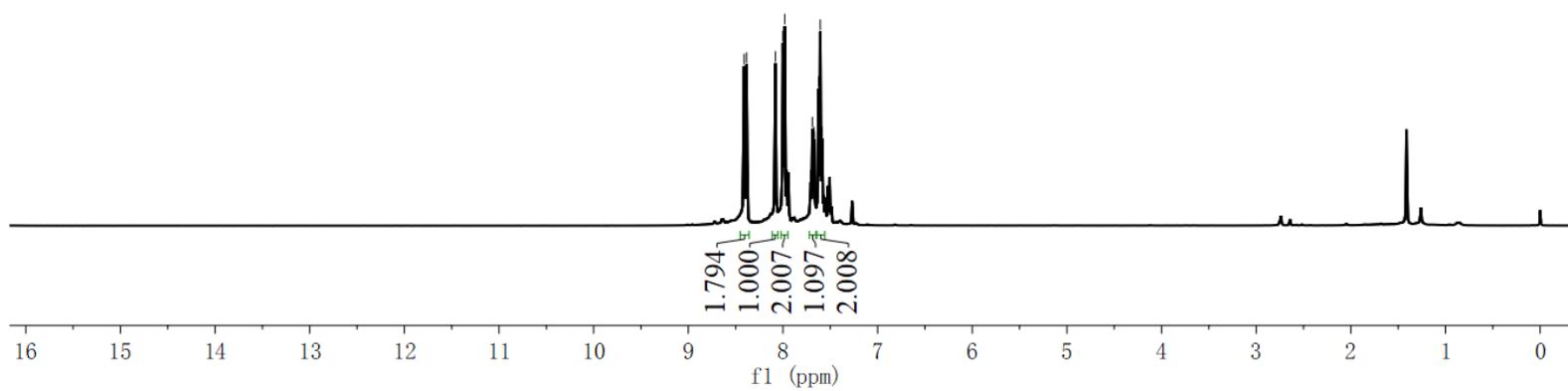




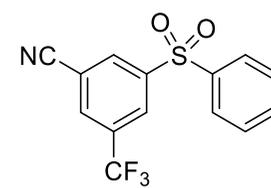
8.410
8.384
8.080
8.001
7.980
7.708
7.706
7.689
7.671
7.669
7.624
7.606
7.588
7.586



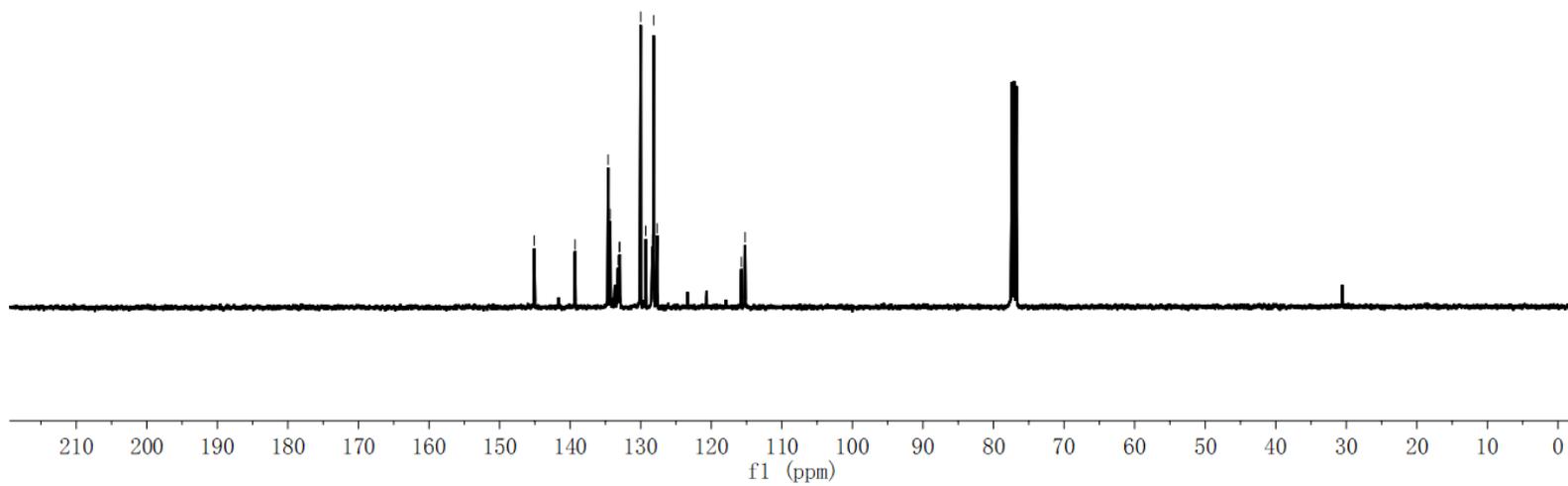
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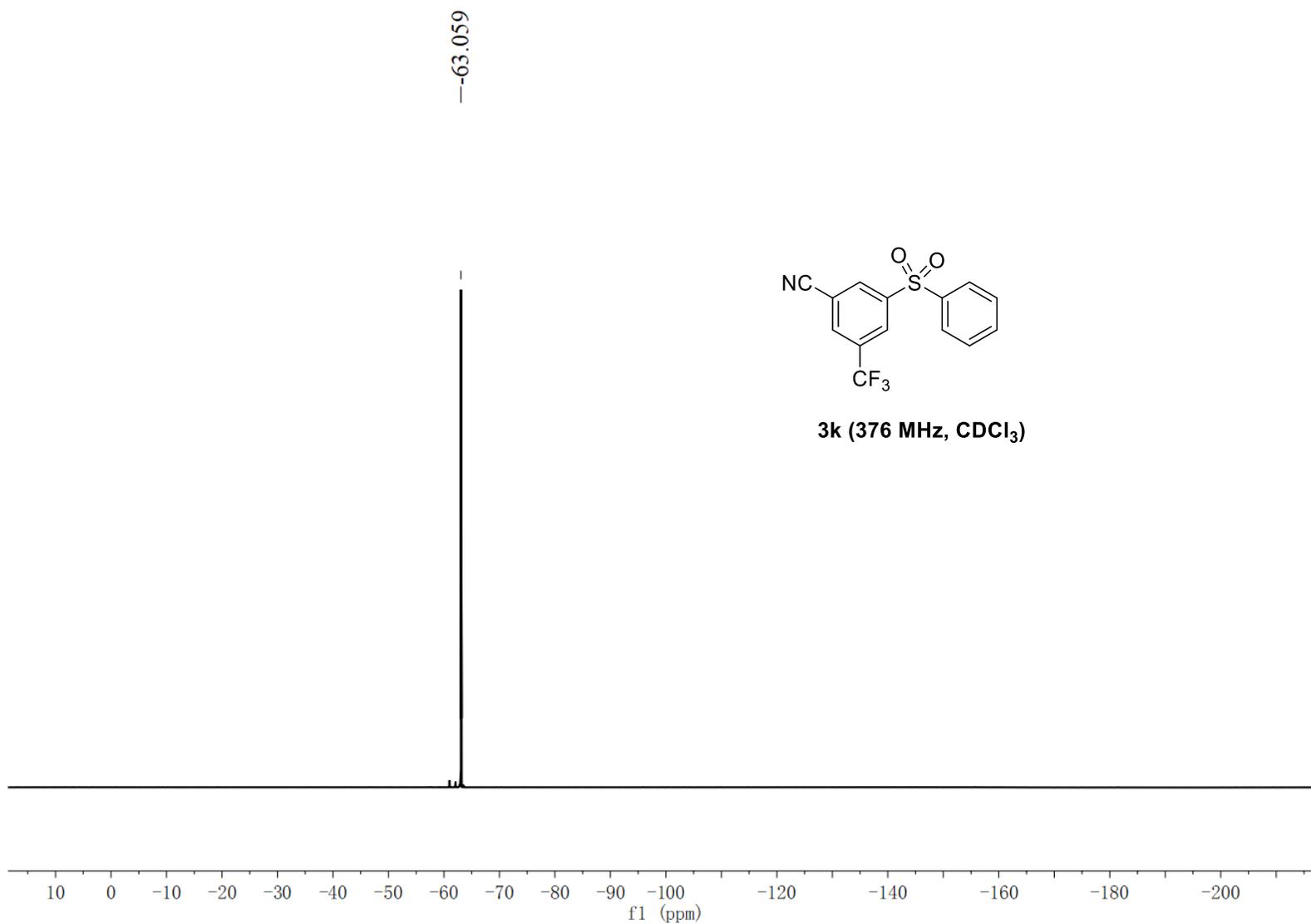


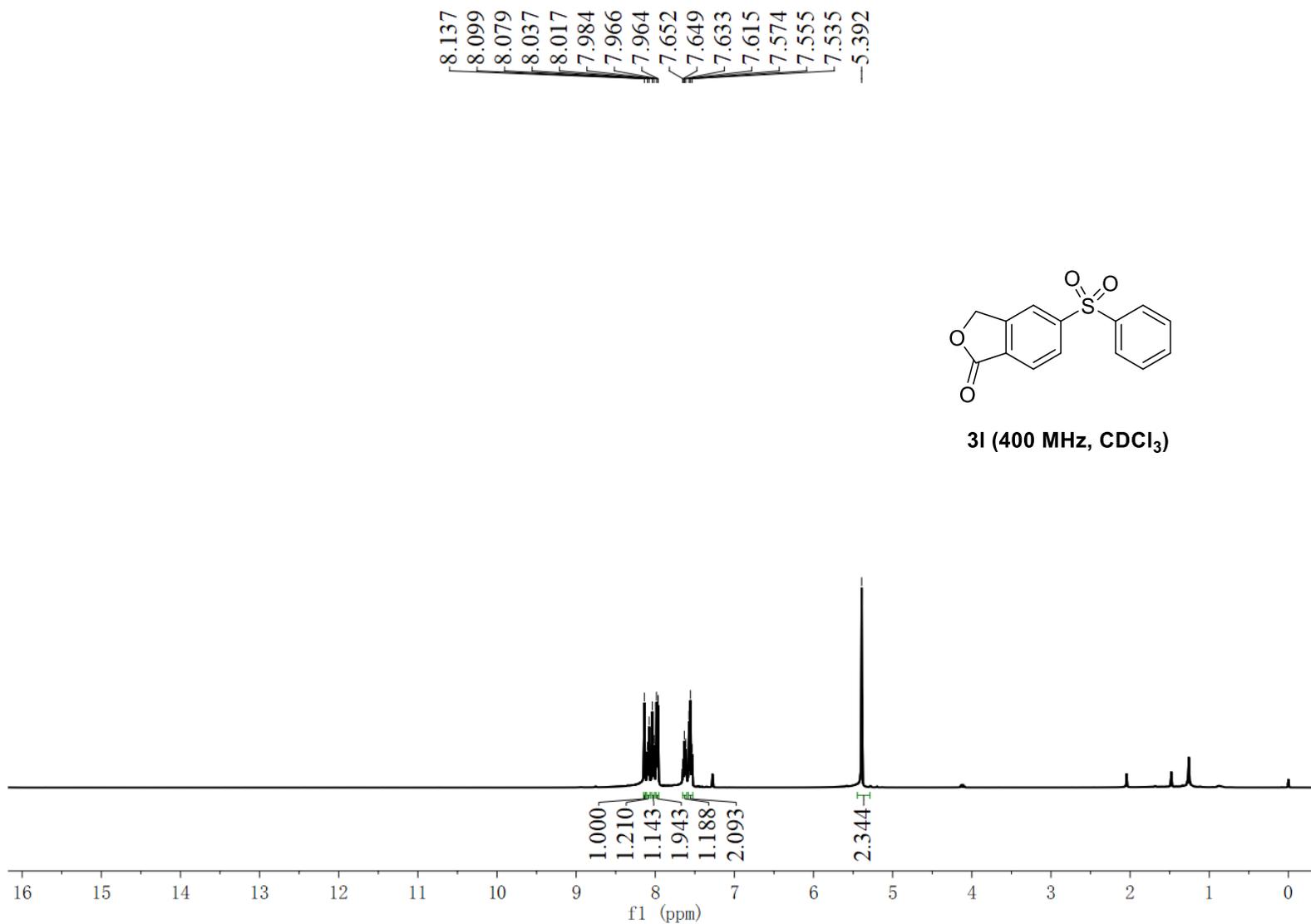
145.087
139.304
134.625
134.326
133.196
133.017
132.981
130.008
129.294
128.335
128.299
128.172
127.674
115.734
115.210

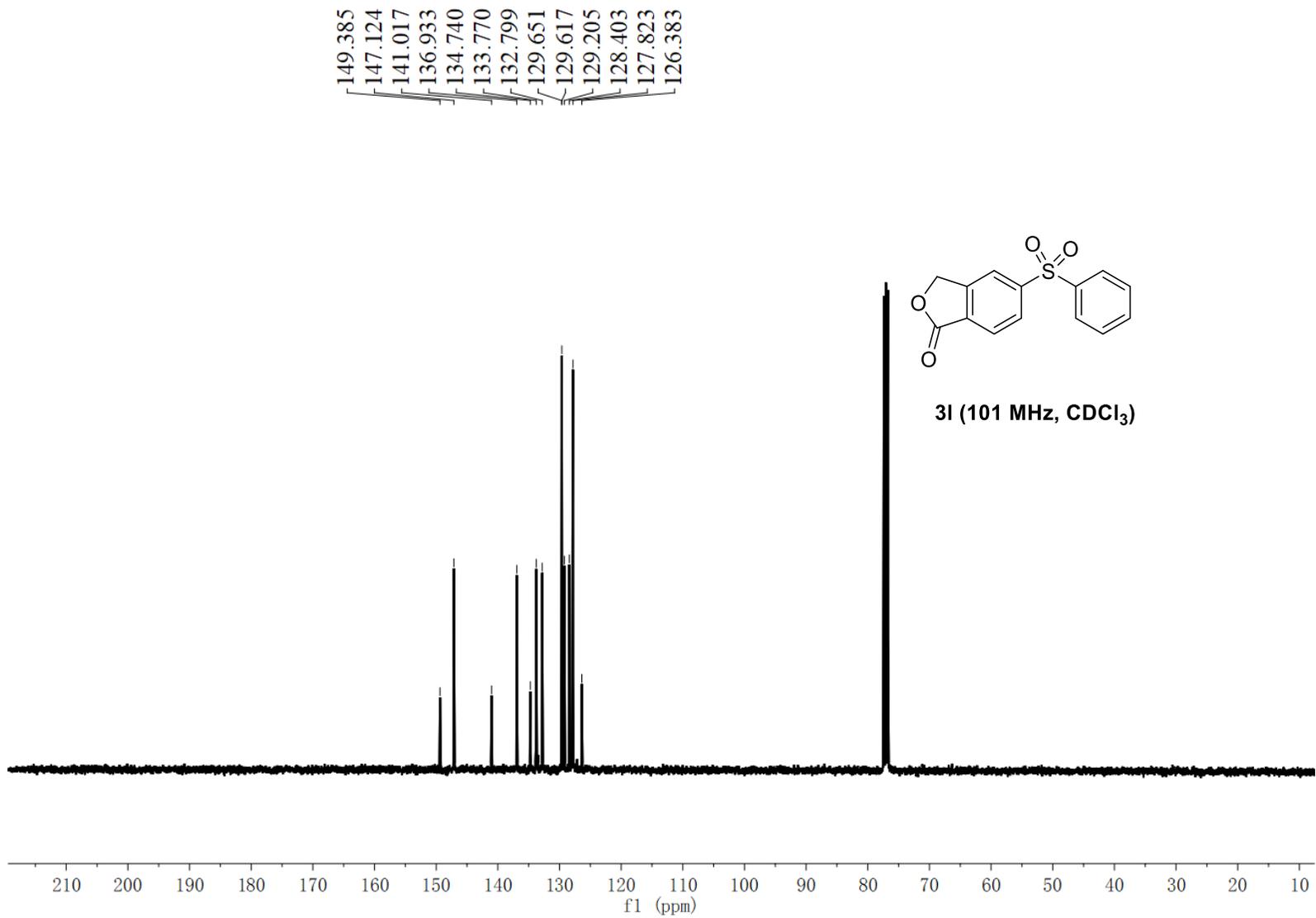


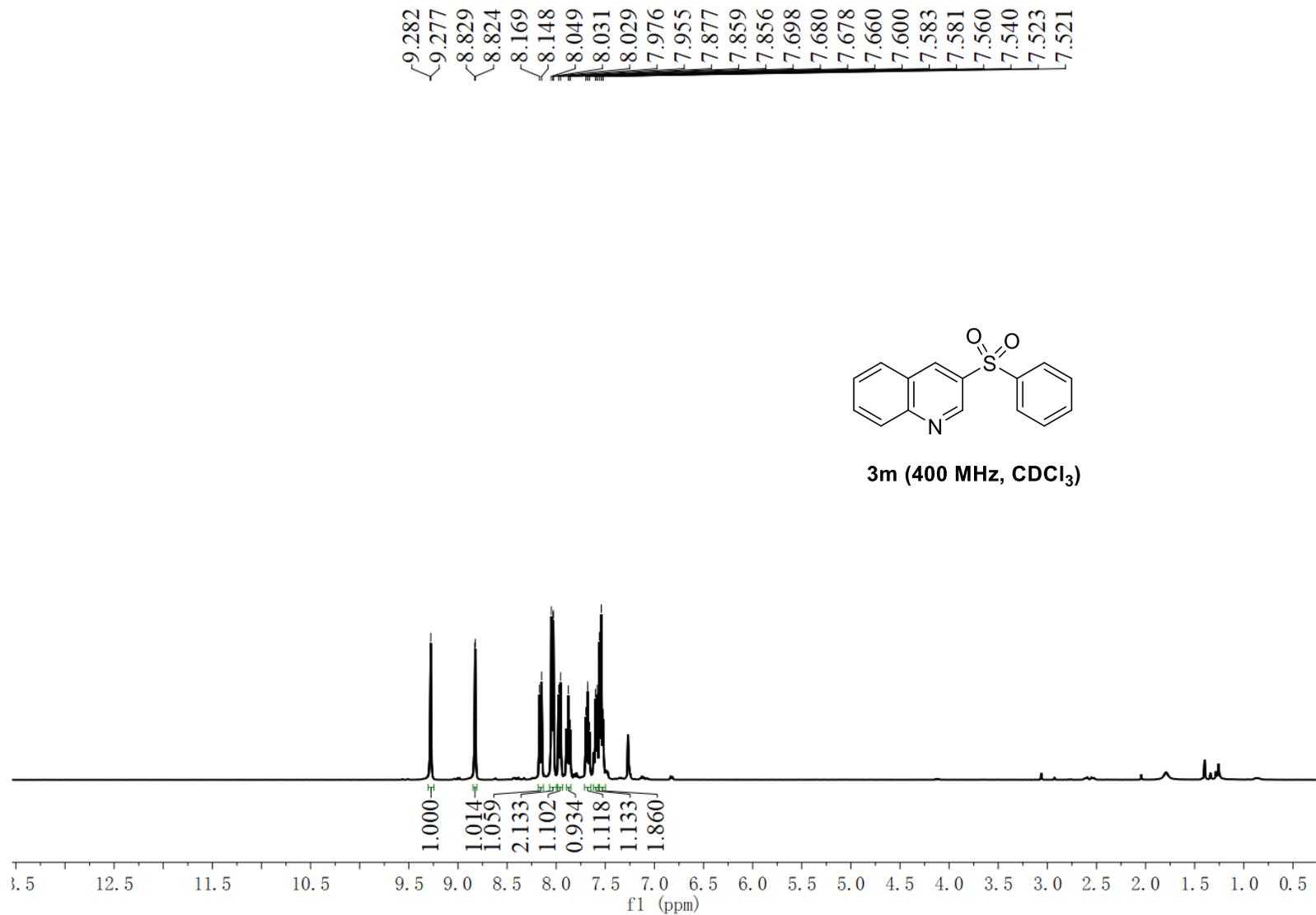
3k (101 MHz, CDCl₃)

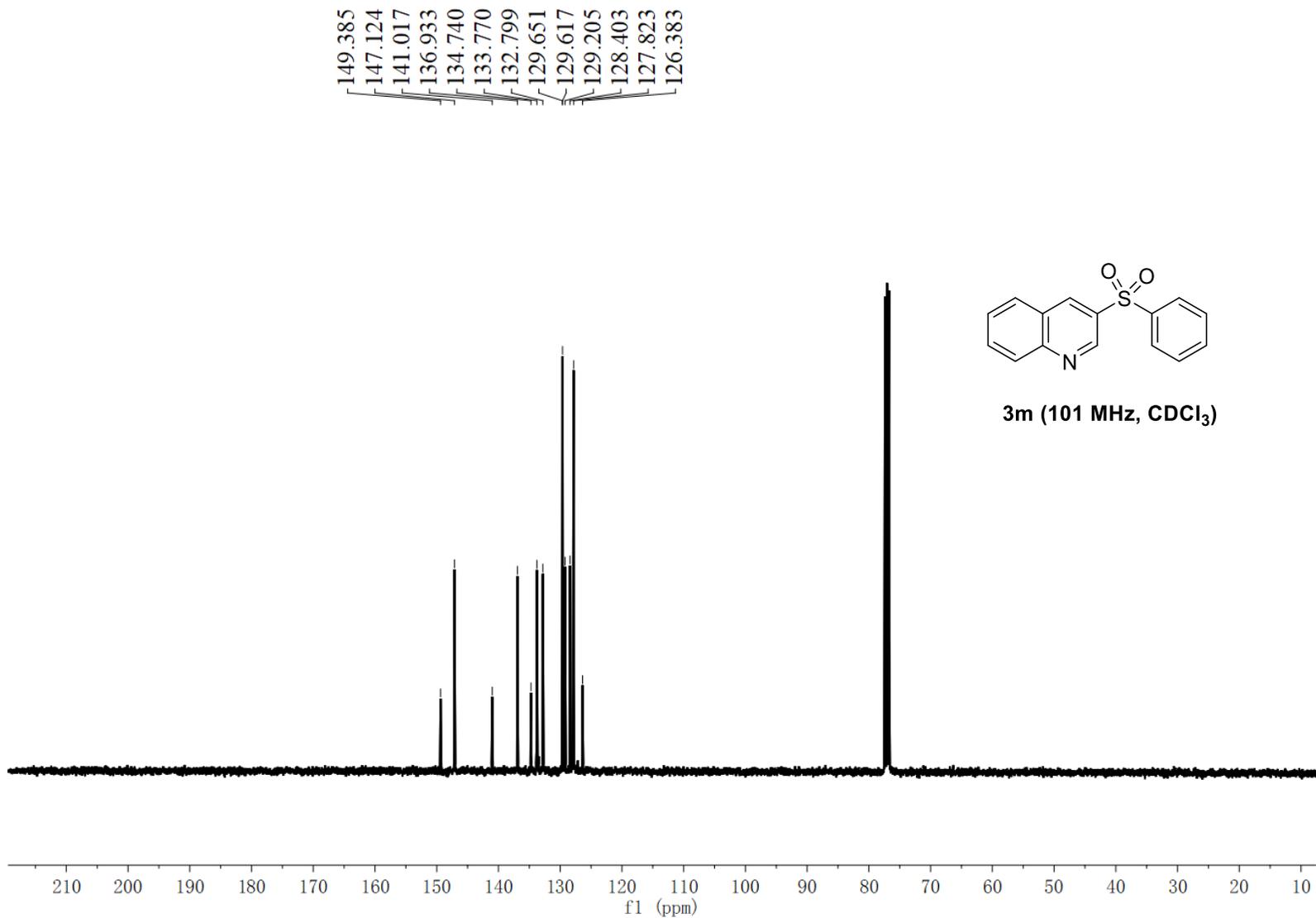




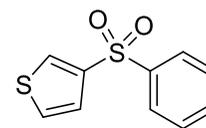




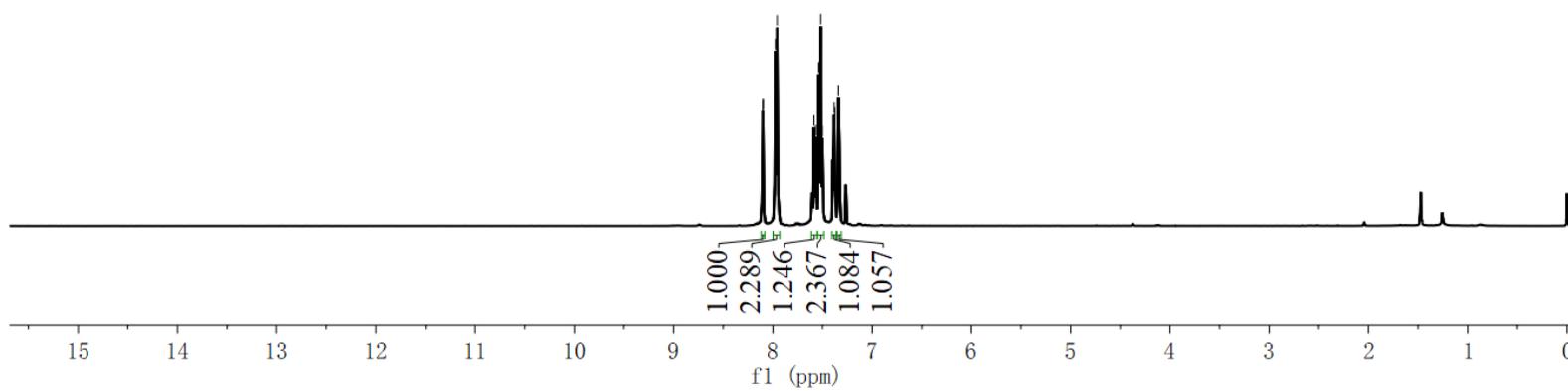




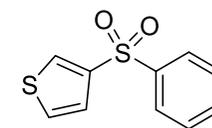
8.104
8.100
8.098
7.976
7.958
7.586
7.568
7.538
7.518
7.501
7.395
7.387
7.382
7.375
7.340
7.330
7.328



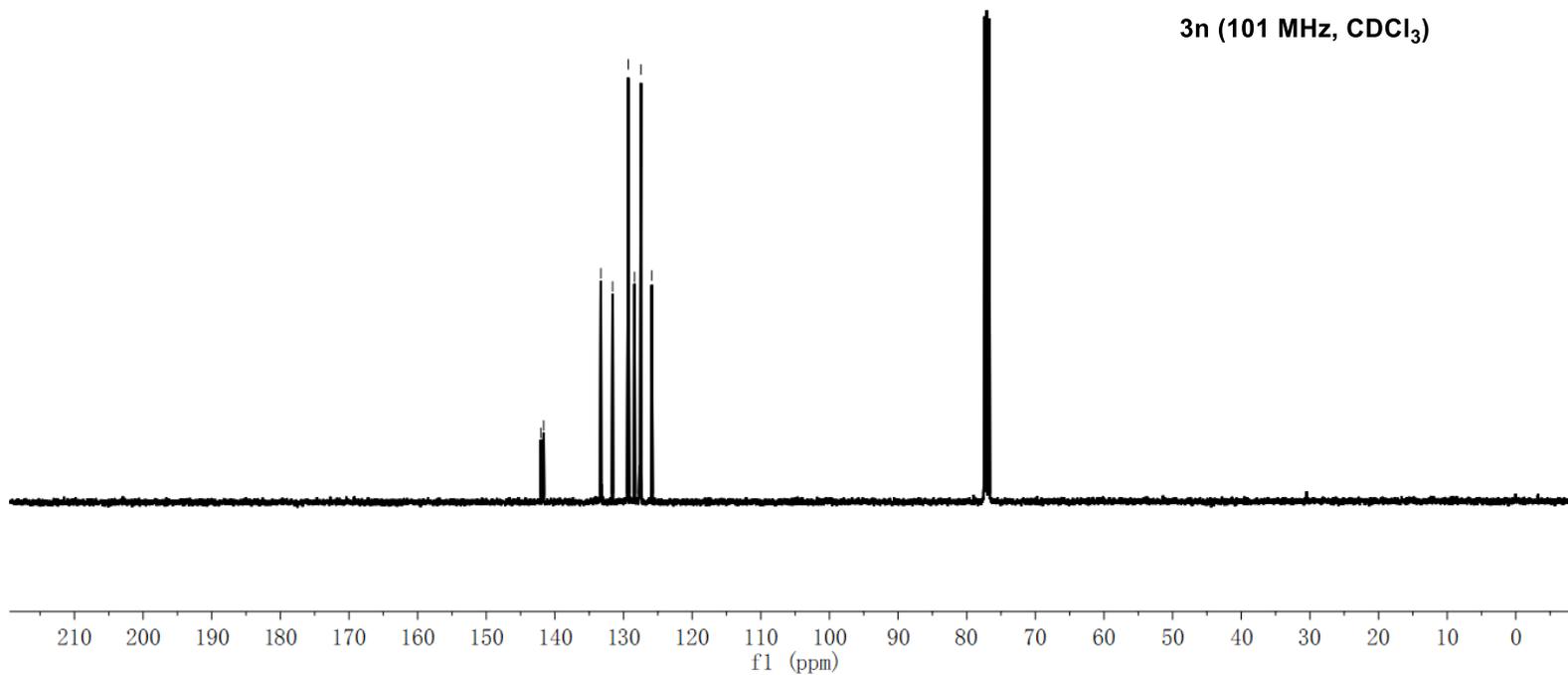
3n (400 MHz, CDCl₃)

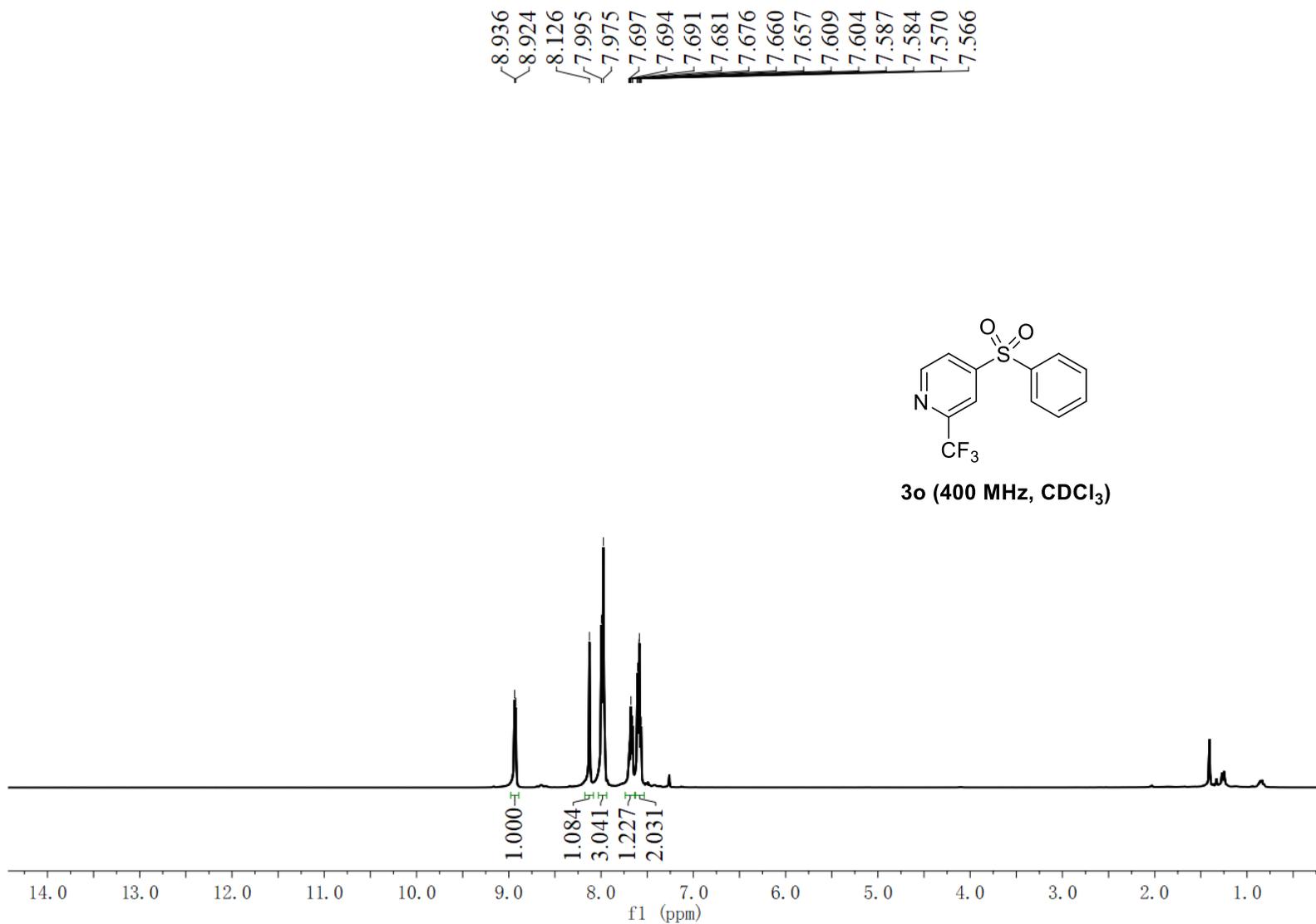


142.034
141.640
133.303
131.593
129.321
128.392
127.472
125.880

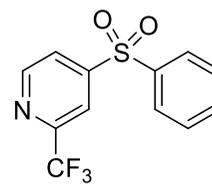


3n (101 MHz, CDCl₃)

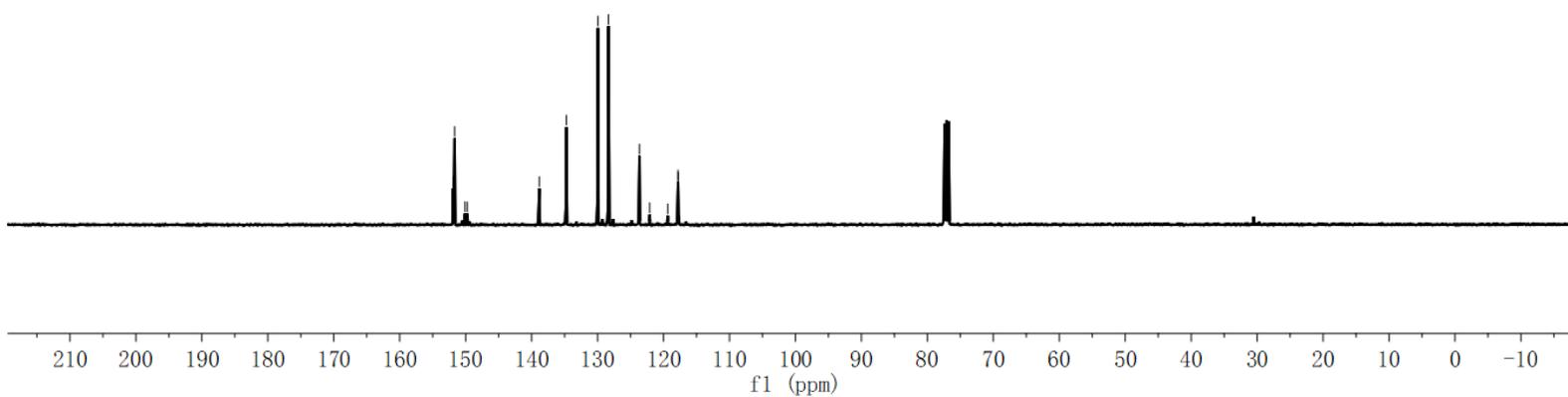


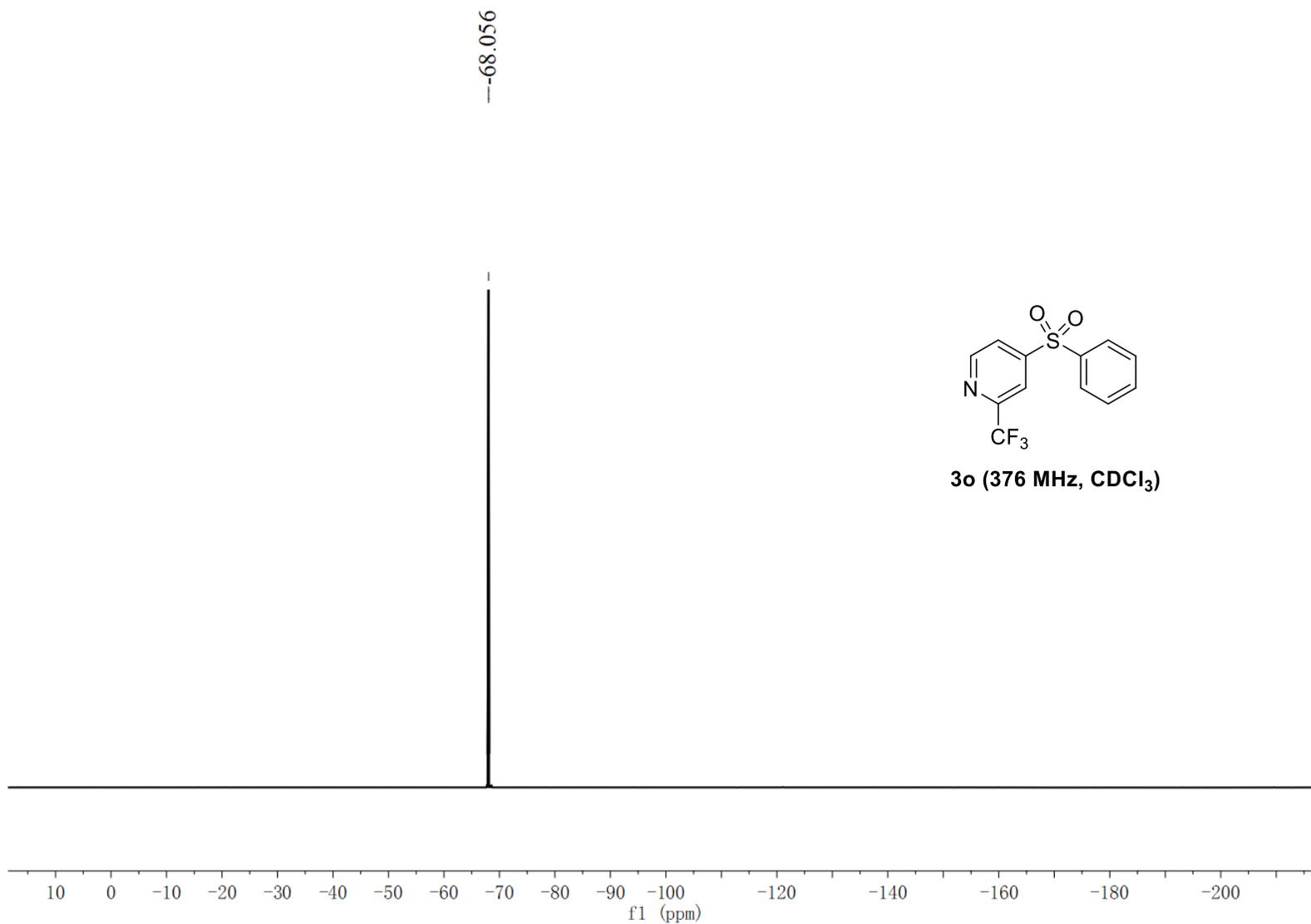


151.890
151.671
150.107
149.750
138.843
134.737
129.946
128.341
123.650
122.095
119.364
117.803
117.776

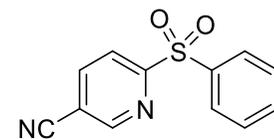


3o (101 MHz, CDCl₃)

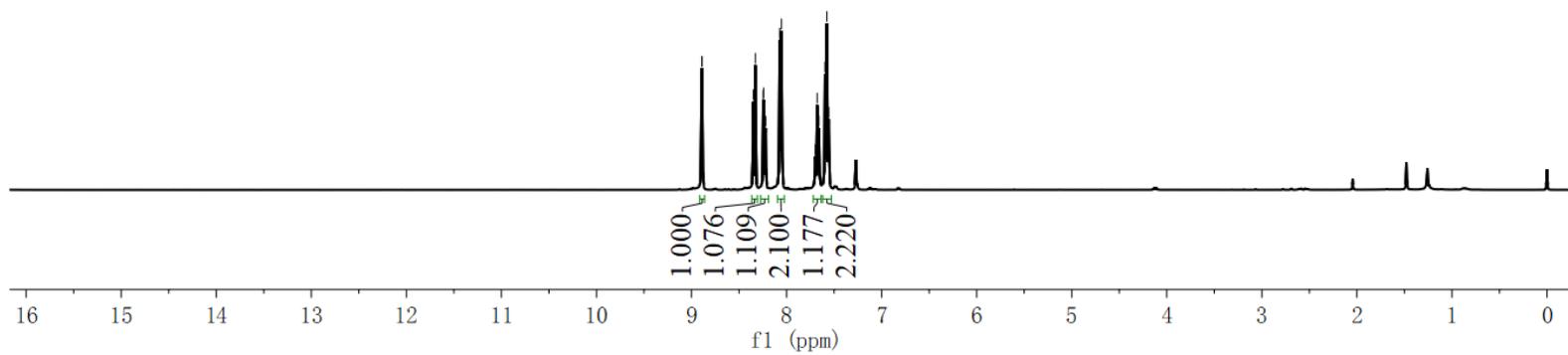




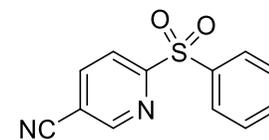
8.892
8.889
8.349
8.329
8.246
8.241
8.225
8.220
8.072
8.054
7.697
7.678
7.660
7.595
7.576
7.557



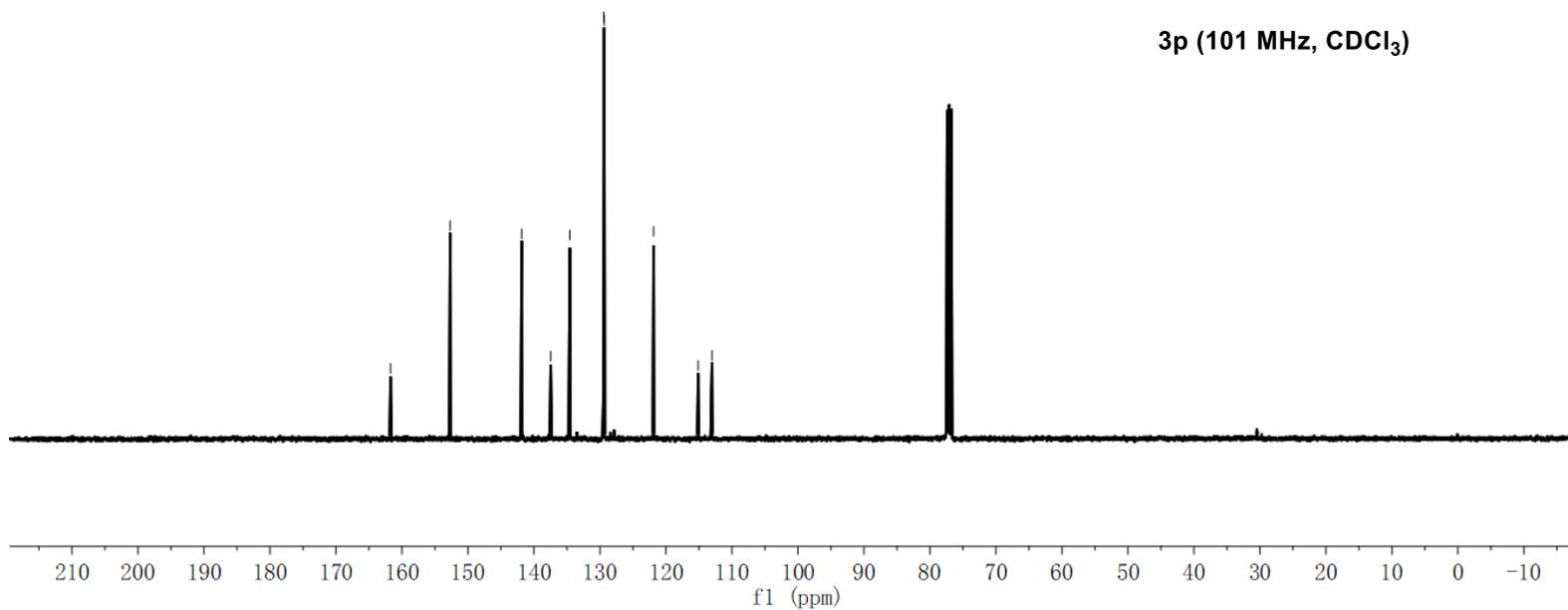
3p (400 MHz, CDCl₃)



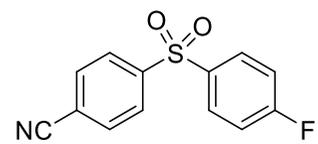
-161.730
-152.701
/ 141.870
/ 137.472
- 134.577
/ 129.418
/ 129.358
/ 121.872
- 115.128
/ 113.015



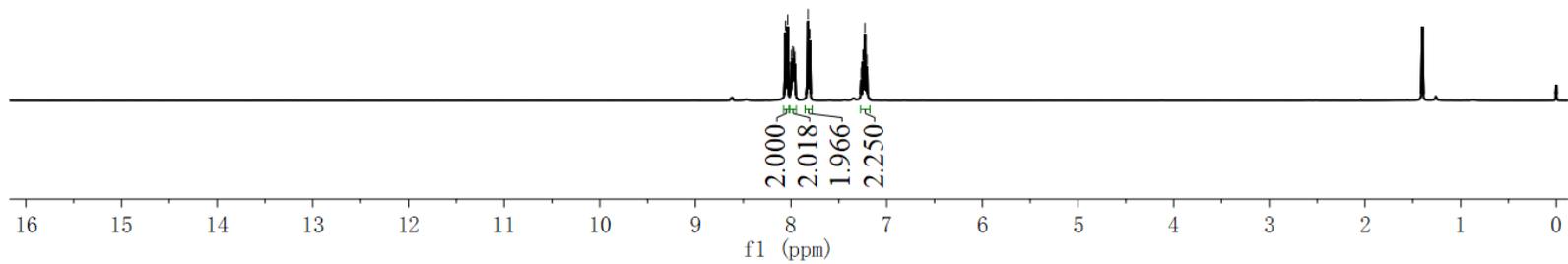
3p (101 MHz, CDCl₃)



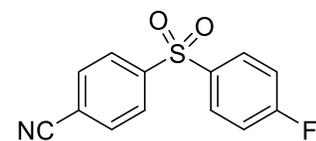
8.056
8.035
7.994
7.982
7.976
7.972
7.960
7.824
7.804
7.267
7.249
7.229
7.207



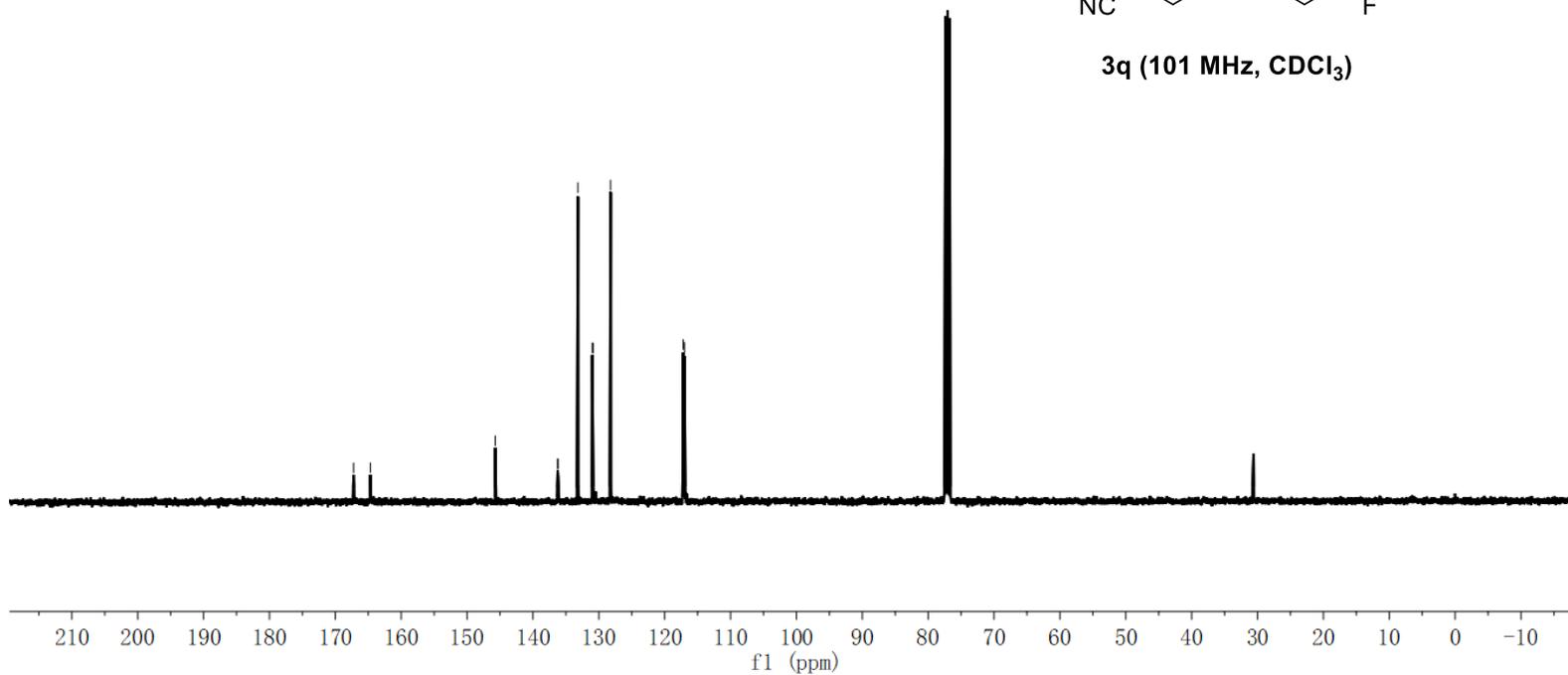
3q (400 MHz, CDCl₃)

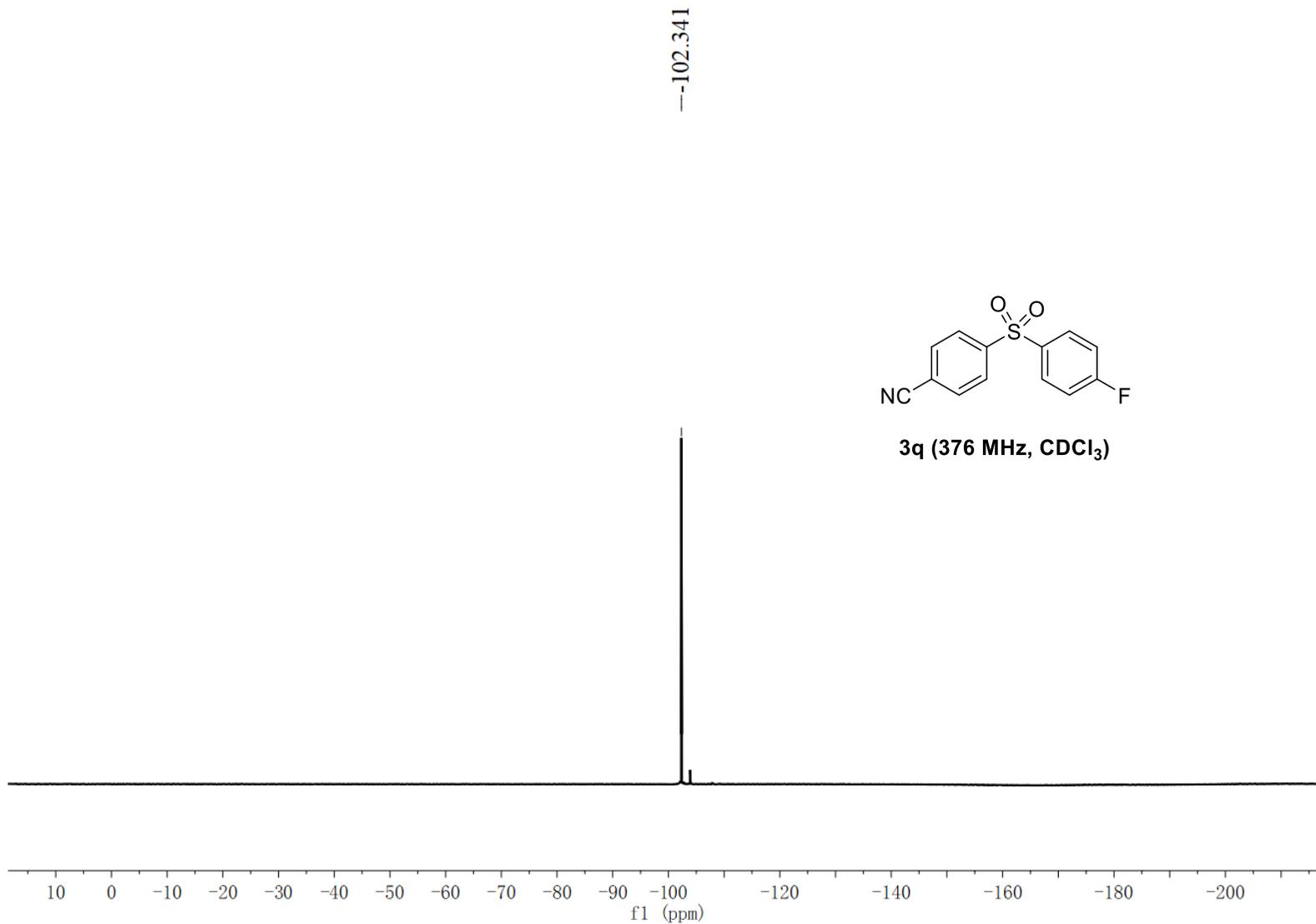


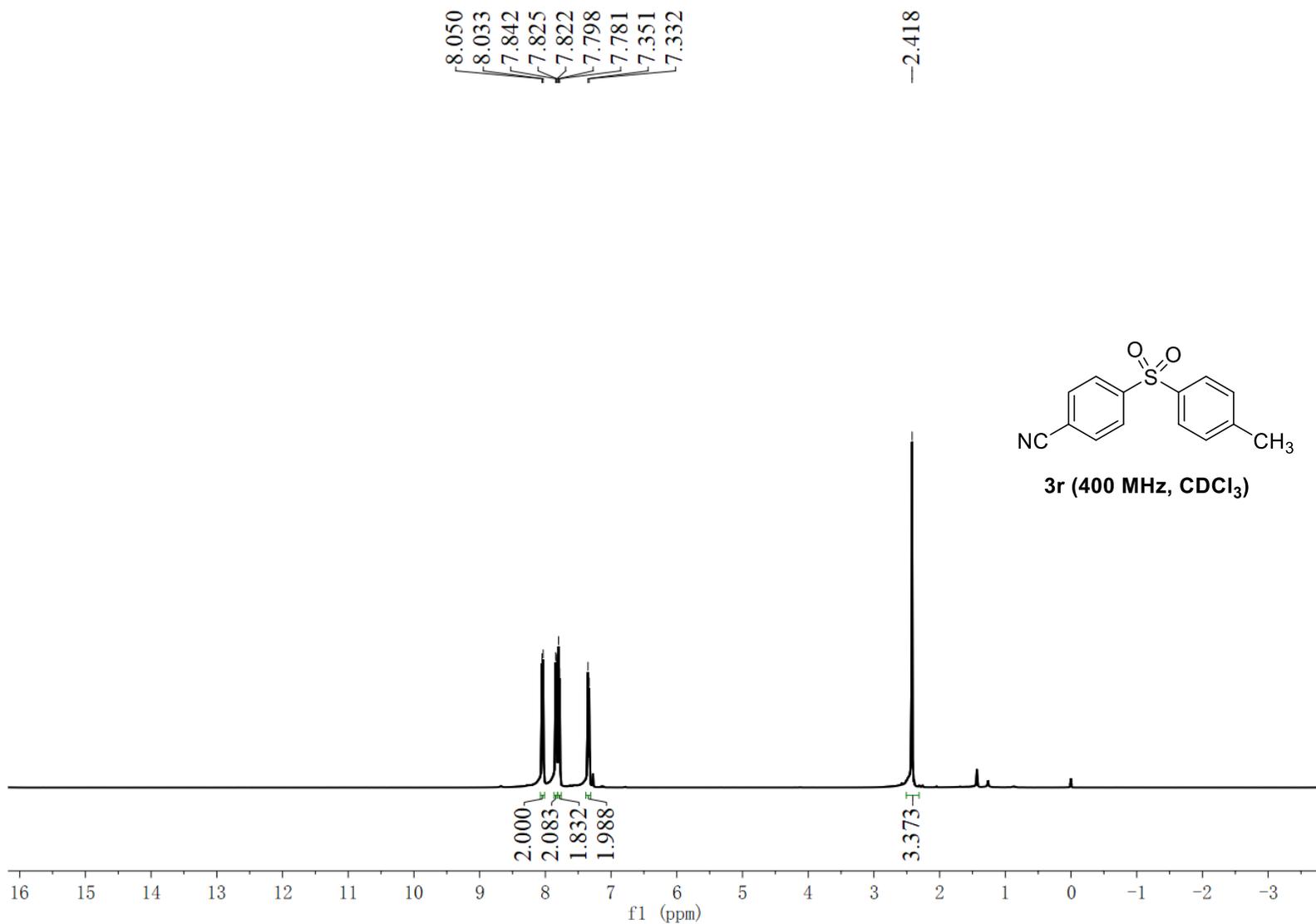
167.233
164.671
145.720
136.241
136.210
133.187
130.974
130.877
128.228
117.199
117.116
117.079
116.973



3q (101 MHz, CDCl₃)

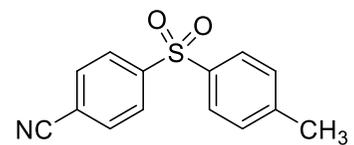






146.267
145.286
137.142
133.058
130.311
128.144
128.058
117.237
116.721

-21.660



3r (101 MHz, CDCl₃)

