

Supporting Information

Photochemical acridone-mediated direct arylation of (hetero)arenes with aryl diazonium salts

Zhenhua Li*, Lijun Chen, Dayou Rong, Longfeng Yuan, Yuanyuan, Xie*

*Key Laboratory for Green Pharmaceutical Technologies and Related Equipment of
Ministry of Education, College of Pharmaceutical Sciences, Zhejiang University of
Technology, Chao Wang Road 18, Hangzhou, P. R. China.*

Email: lizhenhua@zjut.edu.cn

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1. Experimental Section

1.1 General information

The aryl diazonium tetrafluoroborates were synthesized according to the previously described methods.¹ Other chemicals were purchased from commercial sources and used without further purification. Melting points (m.p.) were obtained on a digital melting point apparatus and uncorrected. Column chromatography was performed on silica gel (200-300 mesh) by standard technique. Thin-layer chromatography was performed using silica gel plates F254. Visualization was accomplished with short wavelength UV light (254 nm) sources. UV-Vis and fluorescence measurements were performed with UV-2600 UV-visible spectrophotometer and F-7000 FL spectrofluorometer. Melting points were determined using a digital melting point apparatus and uncorrected. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) were recorded with CDCl₃. Chemical shifts (δ) were referenced relative to residual solvent signal (CDCl₃: ¹H NMR: δ 7.26 ppm, ¹³C NMR: 77.16 ppm). All chemical shifts were reported as δ values (ppm) relative to TMS and observed coupling constants (*J*) are given in Hertz (Hz). The followed abbreviations are used to describe peak patterns where appropriate: (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublets of doublets, td = triplet of doublets, m = multiplet). High-resolution mass spectra were measured with HRMS-ESI-Q-TOF.

1.2 Synthesis of 4-bromobenzenediazonium tetrafluoroborate 1

Sodium nitrite (0.76 g, 11 mmol) dissolved in 1 mL of water was slowly added to the cold mixture of the appropriate aniline (1.27 g, 10 mmol) and 50% of HBF₄ (5 mL, 40 mmol) in 2 mL of water. The mixture was stirred for 1.5 h at 0°C and the precipitate was collected by filtration and redissolved in the least amount of acetone. Then the diazonium salt was recrystallized and washed several times using diethyl ether and dried under vacuum. The same procedure was followed by preparation of other

diazonium salts.

1.3 Reaction procedure for C-H arylation of benzene, furan and thiophene.

In a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with acridone (0.1 equiv), aryl diazonium tetrafluoroborate **1** (0.5 mmol) and (hetero)arene (5 mmol) dissolved in dry DMSO (2 mL). The reaction mixture was stirred under irradiation of 10 W blue LEDs at room temperature for 6 h, then washed with brine and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using petroleum ether to afford the desired products.

1.4 Reaction procedure for C-H arylation of mesitylene.

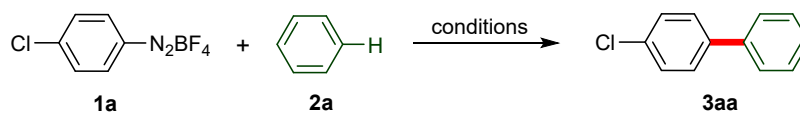
In a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with acridone (0.1 equiv), aryl diazonium tetrafluoroborate **1** (0.5 mmol) and mesitylene (2.5 mmol) dissolved in dry DMSO (2 mL). The reaction mixture was stirred under irradiation of 10 W blue LEDs at room temperature for 6 h, then washed with brine and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using petroleum ether to afford the desired products.

1.5 Reaction procedure for C-H arylation of pyrrole and benzofuran

In a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with acridone (0.1 equiv), aryl diazonium tetrafluoroborate **1** (0.5 mmol) and heteroarene (2.5 mmol) dissolved in dry DMSO (2 mL). The reaction mixture was stirred under irradiation of 10 W blue LEDs at room temperature for 6 h, then washed with brine and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue

was purified by flash column chromatography on silica gel using petroleum ether to afford the desired products.

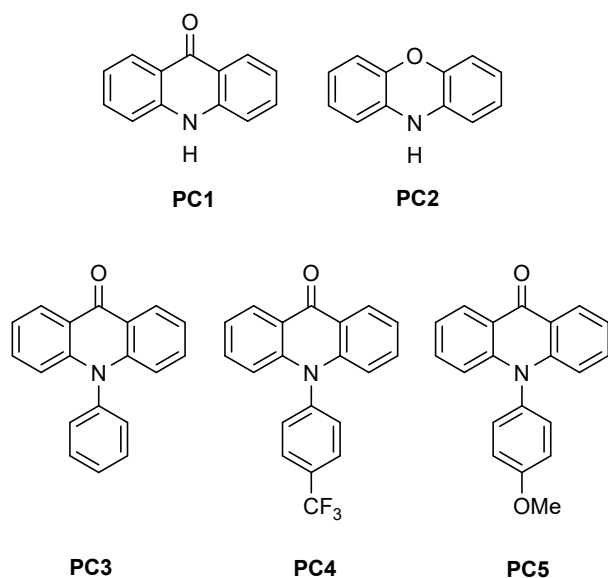
1.6 Screening of reaction conditions^a



Entry	Cat. (mol%)	Solvent	Time (h)	Yield ^b (%)
1	PC 1(10.0)	DMSO	12	76
2	PC 1(10.0)	DMSO	10	77
3	PC 1(10.0)	DMSO	8	77
4	PC 1(10.0)	DMSO	6	77
5	PC 1(0)	DMSO	6	N.D.
6 ^c	PC 1(10.0)	DMSO	6	N.D.
7 ^d	PC 1(10.0)	DMSO	6	77
8 ^e	PC 1(10.0)	DMSO	6	35
9 ^f	PC 1(10.0)	DMSO	6	72
10	PC 1(5.0)	DMSO	6	65
11	PC 1(3.0)	DMSO	12	50
12	PC 1(20.0)	DMSO	6	75
13	PC 2(10.0)	DMSO	6	45
14	PC 3(10.0)	DMSO	6	63
15	PC 4(10.0)	DMSO	6	60
16	PC 5(10.0)	DMSO	6	52
17	PC 1(10.0)	DMF	6	49
18	PC 1(10.0)	THF	6	30
19	PC 1(10.0)	MeCN	6	52

^aReaction conditions: **1a** (0.5 mmol), **2a** (5 mmol), **PC** (10 mol%), DMSO (2 ml), blue LEDs, rt, 6h, air. ^bIsolated yields. ^cReaction was conducted in the dark. ^dBenzene (20 equiv) was used. ^eWith a 10 W green LEDs irradiation.

^fWith a 10 W white LEDs irradiation.



1.7 Radical Capturing Experiments



In a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with acridone (0.1 equiv), aryl diazonium tetrafluoroborate **1a** (0.5 mmol), benzene (**2a**) (5 mmol) and TEMPO (2 equiv) dissolved in dry DMSO (2 mL). The reaction mixture was stirred under irradiation of 10 W blue LEDs at room temperature for 6 h, then washed with brine and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using petroleum ether to afford the desired products.

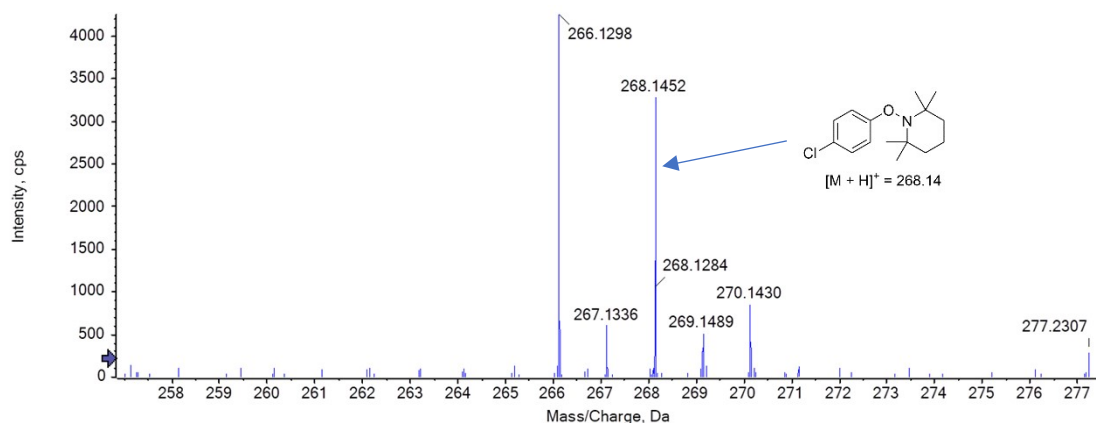
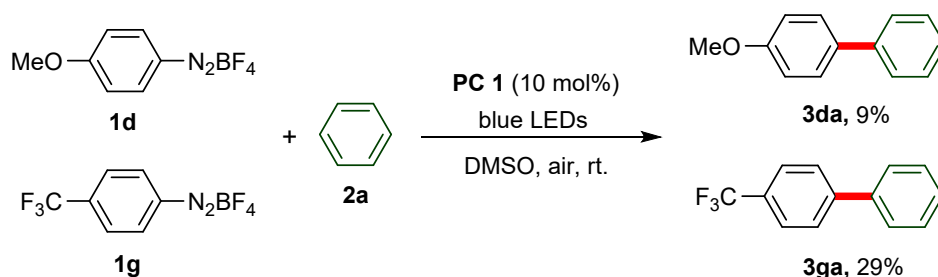


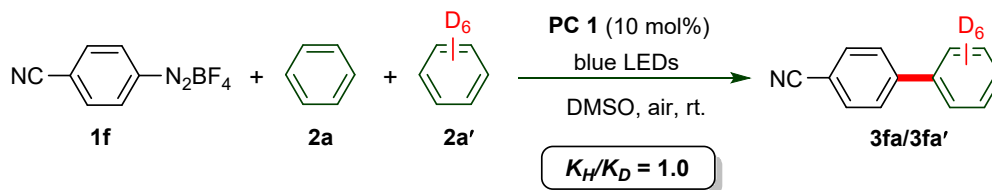
Figure S1. Mass spectra of radical trapped compounds with TEMPO.

1.8 Intermolecular Competition Experiments



In a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with acridone (0.1 equiv), 4-methoxyphenyl diazonium tetrafluoroborate (**1d**) (75 mg, 0.25 mmol), 4-(trifluoromethyl)phenyl diazonium tetrafluoroborate (**1g**) (50.5 mg, 0.25 mmol) and benzene (**2a**) (10 mmol) dissolved in dry DMSO (2 mL). The reaction mixture was stirred under irradiation of 10 W blue LEDs at room temperature for 6 h, then washed with brine and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using petroleum ether to afford the desired products **3da** (4 mg, 9%) and **3ga** (16 mg, 29%) .

1.9 Intermolecular Competition Experiments



In a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with acridone (0.1 equiv), 4-cyanophenyl diazonium tetrafluoroborate (**1f**) (0.5 mmol), benzene (**2a**) (5 mmol), benzene (**2a**) - d_6 (5 mmol) dissolved in dry DMSO (2 mL). The reaction mixture was stirred under irradiation of 10 W blue LEDs at room temperature for 6 h, then washed with brine and extracted with ethyl acetate. The organic layers were combined and dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using petroleum ether to afford the desired products **3fa**/[**D**]**5-3fa** (31 mg, 35%).

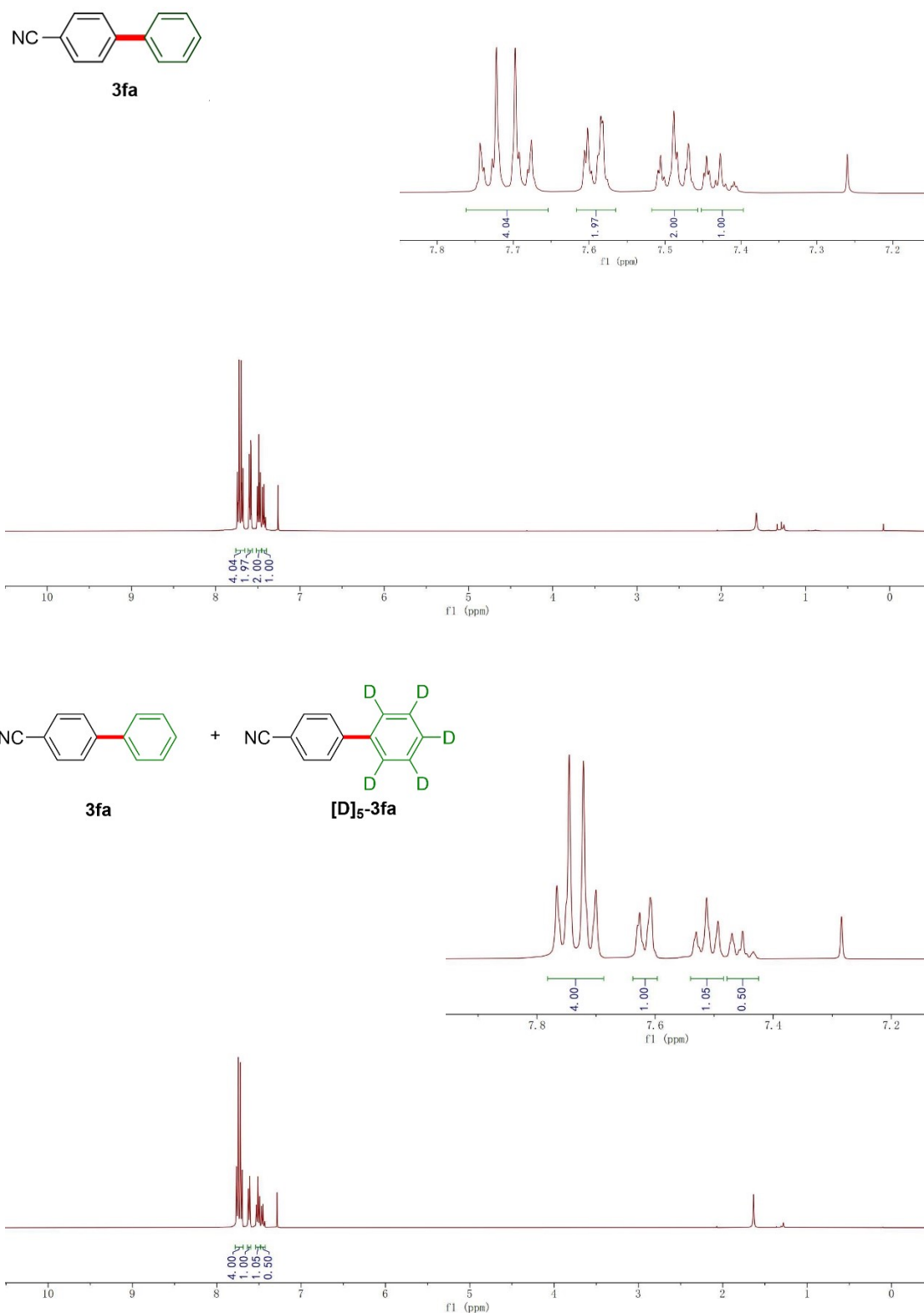


Figure S2. ^1H NMR of **3fa** and **3fa+[D]₅-3fa**.

1.10 The UV-visible absorption experiment:

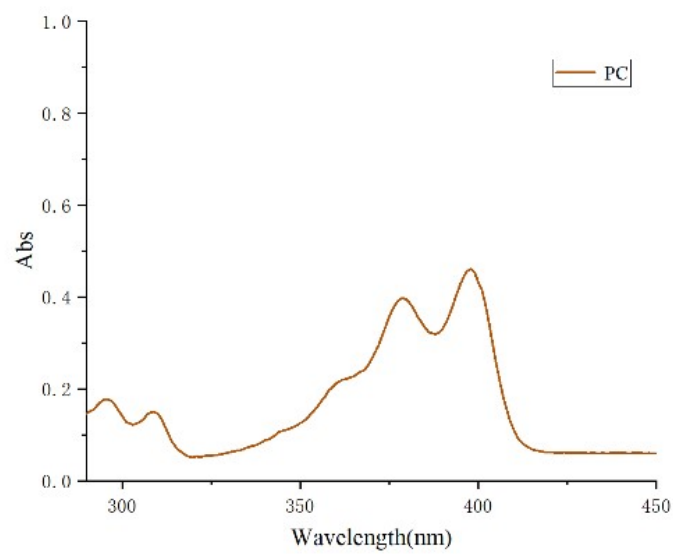
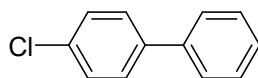


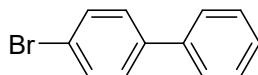
Figure S3. UV-visible spectra of acridone in DMSO.

2. Characterization data of products



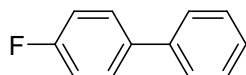
4-chloro-1,1'-biphenyl (3aa)²

Colorless solid; 77% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 78 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.59-7.49 (m, 4H), 7.48-7.36 (m, 5H). **¹³C NMR** (101 MHz, CDCl₃) δ 13C NMR (101 MHz, Chloroform-d) δ 140.01, 139.69, 133.40, 128.93, 128.91, 128.42, 127.61, 127.01.



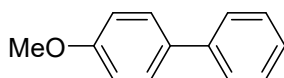
4-bromo-1,1'-biphenyl (3ba)³

Colorless solid; 67% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 91 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.59-7.53 (m, 4H), 7.49-7.42 (m, 4H), 7.40-7.34 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.16, 140.03, 131.89, 128.93, 128.77, 127.67, 126.97, 121.56.



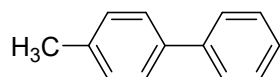
4-fluoro-1,1'-biphenyl (3ca)²

White solid; 69% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 74 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.56 (dd, $J = 8.2, 3.9$ Hz, 4H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.39-7.33 (m, 1H), 7.14 (t, $J = 8.6$ Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 163.71, 161.27, 140.28, 137.35, 128.84, 128.75, 128.67, 127.28, 127.04, 115.74, 115.52.



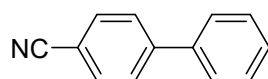
4-methoxy-1,1'-biphenyl (3da)²

Colorless solid; 34% yield. $R_f = 0.6$ (Petroleum ether), m.p. = 90 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.61-7.50 (m, 4H), 7.47-7.38 (m, 2H), 7.35-7.28 (m, 1H), 7.04-6.95 (m, 2H), 3.86 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.16, 140.85, 133.80, 128.75, 128.18, 126.76, 126.68, 114.22, 55.37.



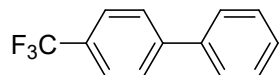
4-methyl -1,1'-biphenyl (3ea)⁴

White solid; 44% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 50 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.70-7.53 (m, 4H), 7.52-7.45 (m, 2H), 7.38 (td, $J = 7.2, 1.6$ Hz, 1H), 7.31 (dd, $J = 7.7, 4.7$ Hz, 2H), 2.46 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.26, 138.57, 138.46, 138.34, 137.08, 129.57, 128.80, 127.87, 127.81, 127.08, 127.06, 124.18, 121.17.



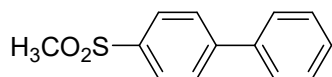
[1,1'-biphenyl]-4-carbonitrile (3fa)⁵

Off white solid; 65% yield. $R_f = 0.2$ (Petroleum ether), m.p. = 85 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.76-7.65 (m, 4H), 7.62-7.57 (m, 2H), 7.52-7.46 (m, 2H), 7.45-7.40 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 145.70, 139.20, 132.61, 129.13, 128.67, 127.75, 127.24, 118.94, 110.95.



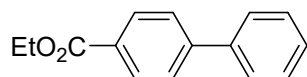
4-trifluoromethyl -1,1'-biphenyl (3ga)³

Colorless solid; 72% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 70 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.70 (s, 4H), 7.63-7.58 (m, 2H), 7.48 (t, $J = 7.4$ Hz, 2H), 7.44-7.38 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 144.75, 139.79, 129.52, 129.20, 129.00, 128.38, 128.20, 127.44, 127.30, 125.78, 125.74, 125.70, 125.67, 122.98.



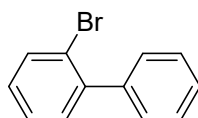
4-methylsulfonyl -1,1'-biphenyl (3ha)⁶

Colorless solid; 60% yield. $R_f = 0.5$ (10% of Ethyl acetate in Petroleum ether), m.p. = 145 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.07-8.01 (m, 2H), 7.83-7.77 (m, 2H), 7.67-7.61 (m, 2H), 7.55-7.49 (m, 2H), 7.49-7.43 (m, 1H), 3.12 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 146.75, 139.15, 139.10, 129.14, 128.72, 128.02, 127.94, 127.42, 44.66.



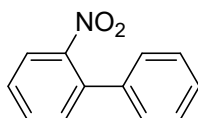
ethyl [1,1'-biphenyl]-4-carboxylate (3ia)⁷

Colorless solid; 70% yield. $R_f = 0.3$ (Petroleum ether), m.p. = 93 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.17-8.07 (m, 2H), 7.70-7.60 (m, 4H), 7.51-7.44 (m, 2H), 7.43-7.37 (m, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), 1.42 (t, $J = 7.1$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 166.66, 145.67, 140.21, 130.19, 129.40, 129.05, 128.23, 127.41, 127.13, 61.09, 14.49.



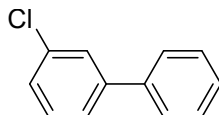
2-bromo-1,1'-biphenyl (3ka)⁸

Colorless oil; 65% yield. $R_f = 0.9$ (Petroleum ether). **¹H NMR** (400 MHz, CDCl₃) δ 7.71 (d, $J = 7.5$ Hz, 1H), 7.50-7.41 (m, 5H), 7.41-7.35 (m, 2H), 7.24 (ddd, $J = 8.8, 6.6, 2.4$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.63, 141.15, 133.14, 131.31, 129.41, 128.74, 127.99, 127.63, 127.39, 122.67.



2-nitro-1,1'-biphenyl (3la)⁹

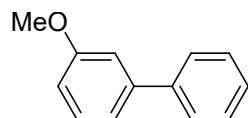
Yellow solid; 69% yield. $R_f = 0.2$ (Petroleum ether), m.p. = 37 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.86 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.62 (td, $J = 7.5, 1.3$ Hz, 1H), 7.52-7.40 (m, 5H), 7.33 (dd, $J = 7.4, 2.0$ Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.33, 137.40, 136.37, 132.30, 131.98, 128.71, 128.26, 128.18, 127.91, 124.10.



3-chloro-1,1'-biphenyl (3ma)¹⁰

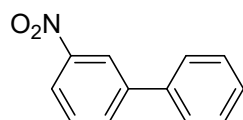
Colorless oil; 45% yield. $R_f = 0.9$ (Petroleum ether). **¹H NMR** (400 MHz, CDCl₃) δ 7.53-7.43 (m, 5H), 7.41 (dt, $J = 5.7, 3.3$ Hz, 1H), 7.33 (dtd, $J = 16.1, 7.2, 2.3$ Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 140.56, 139.44, 132.54, 131.41, 129.97, 129.48,

128.56, 128.07, 127.63, 126.85.



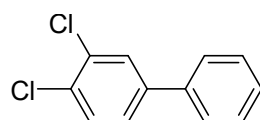
3-methoxy-1,1'-biphenyl (3na)¹¹

White solid; 60% yield. R_f = 0.6 (Petroleum ether), m.p. = 89 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.59-7.50 (m, 4H), 7.42 (t, J = 7.7 Hz, 2H), 7.34-7.28 (m, 1H), 7.03-6.95 (m, 2H), 3.86 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 159.15, 140.84, 133.80, 128.74, 128.18, 126.76, 126.68, 114.21, 55.37.



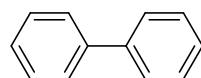
3-nitro-1,1'-biphenyl (3oa)¹²

Yellow solid; 65% yield. R_f = 0.2 (Petroleum ether), m.p. = 62 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.46 (t, J = 2.0 Hz, 1H), 8.20 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 7.92 (dt, J = 7.8, 1.4 Hz, 1H), 7.66-7.58 (m, 3H), 7.54-7.47 (m, 2H), 7.47-7.41 (m, 1H). **¹³C NMR** (151 MHz, CDCl₃) δ 146.88, 146.56, 143.07, 130.31, 129.95, 129.86, 125.21, 124.13, 119.27, 116.32.



3,4-dichloro-1,1'-biphenyl (3pa)¹³

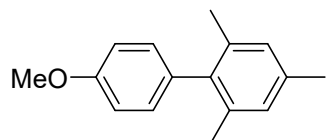
Little yellow solid; 60% yield. R_f = 0.8 (Petroleum ether), m.p. = 46 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (s, 1H), 7.60-7.34 (m, 8H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.26, 138.79, 132.84, 131.44, 130.70, 129.03, 128.14, 126.98, 126.39.



1,1'-biphenyl (3qa)¹⁴

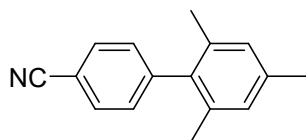
Colorless solid; 75% yield. R_f = 0.9 (Petroleum ether). **¹H NMR** (400 MHz, CDCl₃) δ

7.72-7.66 (m, 4H), 7.53 (t, $J = 7.6$ Hz, 4H), 7.46-7.40 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.34, 128.87, 127.37, 127.28.



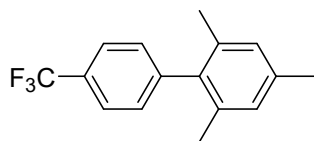
4'-methoxy-2,4,6-trimethyl-1,1'-biphenyl (3db)²

White solid; 32% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 74 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.10-7.05 (m, 2H), 7.00-6.94 (m, 4H), 3.87 (s, 3H), 2.35 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 158.21, 138.70, 136.46, 133.32, 130.34, 128.05, 113.78, 55.23, 21.05, 20.84.



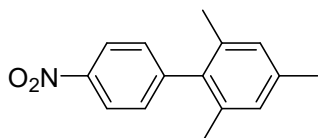
2',4',6'-trimethyl-[1,1'-biphenyl]-4-carbonitrile (3fb)¹⁵

White oil; 81% yield. $R_f = 0.2$ (Petroleum ether). ^1H NMR (400 MHz, CDCl_3) δ 7.75-7.71 (m, 2H), 7.28 (d, $J = 8.3$ Hz, 2H), 6.97 (s, 2H), 2.35 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.45, 137.60, 137.17, 135.33, 132.34, 130.38, 128.39, 119.05, 110.67, 21.07, 20.64.



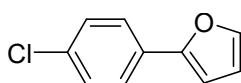
2,4,6-trimethyl-4'-(trifluoromethyl)-1,1'-biphenyl (3gb)⁷

White solid; 69% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 59 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 7.9$ Hz, 2H), 6.99 (s, 2H), 2.37 (s, 3H), 2.02 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.08, 137.65, 137.28, 135.65, 129.81, 129.09, 128.77, 128.28, 125.76, 125.49, 125.45, 125.41, 125.37, 123.06, 21.05, 20.69.



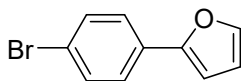
2,4,6-trimethyl-4'-nitro-1,1'-biphenyl (3jb)¹⁶

Yellow solid; 80% yield. $R_f = 0.3$ (Petroleum ether), m.p. = 94 °C. **¹H NMR** (400 MHz, CDCl₃) δ 8.36-8.26 (m, 2H), 7.38-7.29 (m, 2H), 6.97 (s, 2H), 2.35 (s, 3H), 1.99 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 148.59, 146.87, 137.75, 136.79, 135.28, 130.49, 128.43, 123.78, 21.06, 20.65.



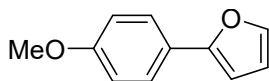
2-(4-chlorophenyl) furan (3ac)¹⁷

Colorless solid; 70% yield. $R_f = 0.8$ (Petroleum ether), m.p. = 67 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.63-7.57 (m, 2H), 7.47 (d, $J = 1.3$ Hz, 1H), 7.38-7.33 (m, 2H), 6.64 (d, $J = 2.7$ Hz, 1H), 6.48 (dd, $J = 3.4, 1.8$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 152.95, 142.35, 132.97, 129.39, 128.89, 125.03, 111.80, 105.44.



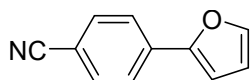
2-(4-bromophenyl) furan (3bc)⁷

Colorless solid; 76% yield. $R_f = 0.8$ (Petroleum ether), m.p. = 85 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.57-7.44 (m, 5H), 6.65 (d, $J = 3.4$ Hz, 1H), 6.47 (dd, $J = 3.4, 1.8$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 152.96, 142.40, 131.81, 129.81, 125.30, 121.07, 111.81, 105.54.



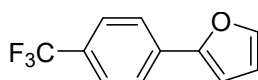
2-(4-methoxyphenyl) furan (3dc)¹⁸

Colorless solid; 33% yield. $R_f = 0.5$ (Petroleum ether), m.p. = 58 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.66-7.55 (m, 2H), 7.43 (dd, $J = 1.9, 0.8$ Hz, 1H), 6.97-6.87 (m, 2H), 6.48 (ddd, $J = 28.0, 3.4, 1.3$ Hz, 2H), 3.84 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ 159.06, 154.08, 141.38, 125.26, 124.09, 114.15, 103.37, 55.32.



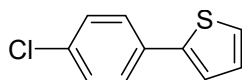
4-(furan-2-yl) benzonitrile (3fc)¹⁷

Pale orange solid; 80% yield. $R_f = 0.2$ (Petroleum ether), m.p. = 49 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.77-7.72 (m, 2H), 7.68-7.63 (m, 2H), 7.54 (d, $J = 1.7$ Hz, 1H), 6.81 (dd, $J = 3.4, 0.7$ Hz, 1H), 6.53 (dd, $J = 3.4, 1.8$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 151.98, 143.71, 134.66, 132.61, 123.95, 118.99, 112.27, 110.27, 108.19.



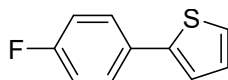
2-(4-(trifluoromethyl) phenyl) furan (3gc)¹⁷

Colorless solid; 74% yield. $R_f = 0.8$ (Petroleum ether), m.p. = 88 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.76 (d, $J = 8.2$ Hz, 2H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.52 (d, $J = 1.7$ Hz, 1H), 6.77 (d, $J = 3.4$ Hz, 1H), 6.51 (dd, $J = 3.4, 1.8$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 152.52, 143.10, 133.97, 129.12, 128.80, 125.77, 125.74, 125.70, 125.66, 125.54, 123.77, 122.84, 111.97, 106.98.



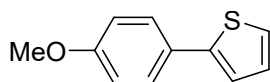
2-(4-chlorophenyl) thiophene (3ad)⁷

Colorless solid; 66% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 83 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.56-7.52 (m, 2H), 7.36-7.33 (m, 2H), 7.31-7.28 (m, 2H), 7.10-7.06 (m, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 143.11, 133.22, 132.95, 129.05, 128.18, 127.13, 125.23, 123.48.



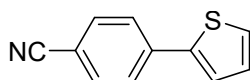
2-(4-fluorophenyl) thiophene (3cd)⁷

Colorless solid; 65% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 48 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.61 (t, $J = 6.9$ Hz, 2H), 7.36-7.26 (m, 2H), 7.13 (d, $J = 8.6$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 163.57, 161.12, 143.36, 130.76, 130.73, 128.09, 127.68, 127.60, 124.81, 123.13, 115.95, 115.74.



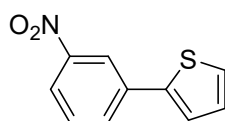
2-(4-methoxyphenyl) thiophene (3dd)¹⁸

Colorless solid; 40% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 103 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.58-7.49 (m, 2H), 7.25-7.18 (m, 2H), 7.06 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.95-6.89 (m, 2H), 3.84 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 159.19, 144.35, 127.95, 127.32, 127.25, 123.86, 122.10, 114.29, 55.38.



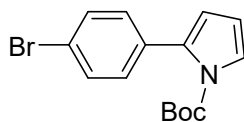
4-(thiophen-2-yl) benzonitrile (3fd)¹⁹

Colorless solid; 66% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 85 °C. **¹H NMR** (400 MHz, CDCl₃) δ 7.71-7.63 (m, 4H), 7.43-7.38 (m, 2H), 7.13 (dd, $J = 5.1, 3.7$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.08, 138.67, 132.76, 128.57, 127.10, 126.10, 125.14, 118.88, 110.56.



2-(3-nitrophenyl) thiophene (3od)¹⁹

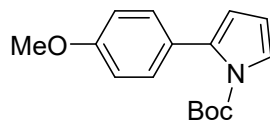
Yellow oil; 72% yield. $R_f = 0.9$ (Petroleum ether). **¹H NMR** (400 MHz, CDCl₃) δ 8.45 (t, $J = 2.1$ Hz, 1H), 8.14-8.08 (m, 1H), 7.91 (dt, $J = 7.9, 1.5$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.45-7.37 (m, 2H), 7.14 (dd, $J = 5.1, 3.6$ Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 146.88, 146.56, 143.07, 130.31, 129.95, 129.86, 125.21, 124.13, 119.27, 116.32.



tert-butyl 2-(4-bromophenyl)-1H-pyrrole-1-carboxylate (3be)²⁰

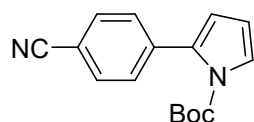
Colorless oil; 45% yield. $R_f = 0.5$ (5% of Ethyl acetate in Petroleum ether). **¹H NMR** (400 MHz, CDCl₃) δ 7.49-7.45 (m, 2H), 7.34 (dd, $J = 3.3, 1.8$ Hz, 1H), 7.24-7.19 (m, 2H), 6.22 (t, $J = 3.3$ Hz, 1H), 6.18 (dd, $J = 3.3, 1.8$ Hz, 1H), 1.39 (s, 9H). **¹³C NMR**

(101 MHz, CDCl₃) δ 133.79, 133.27, 130.79, 130.72, 122.89, 121.29, 114.81, 110.70, 83.92, 27.69.



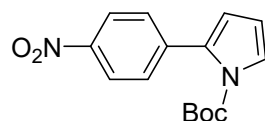
tert-butyl 2-(4-methoxyphenyl)-1H-pyrrole-1-carboxylate (3de)²¹

Colorless oil; 63% yield. R_f = 0.3 (5% of Ethyl acetate in Petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.33 (dd, J = 3.3, 1.8 Hz, 1H), 7.30-7.26 (m, 2H), 6.92-6.87 (m, 2H), 6.21 (t, J = 3.3 Hz, 1H), 6.14 (dd, J = 3.3, 1.8 Hz, 1H), 3.83 (s, 3H), 1.39 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 158.91, 149.43, 134.88, 130.41, 126.90, 122.18, 114.01, 113.05, 110.48, 83.44, 55.29, 27.72.



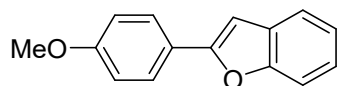
tert-butyl 2-(4-cyanophenyl)-1H-pyrrole-1-carboxylate (3fe)²²

Colorless oil; 75% yield. R_f = 0.2 (5% of Ethyl acetate in Petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.60 (m, 2H), 7.48-7.43 (m, 2H), 7.39 (dd, J = 3.2, 1.8 Hz, 1H), 6.29-6.24 (m, 2H), 1.41 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 148.96, 138.82, 133.12, 131.41, 129.59, 123.99, 119.02, 116.12, 111.07, 110.53, 84.40, 27.71.



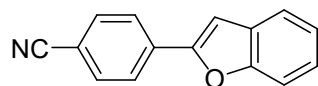
tert-butyl 2-(4-nitrophenyl)-1H-pyrrole-1-carboxylate (3je)²²

Colorless oil; 66% yield. R_f = 0.2 (5% of Ethyl acetate in Petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 8.26-8.17 (m, 2H), 7.56-7.48 (m, 2H), 7.41 (dd, J = 3.3, 1.8 Hz, 1H), 6.32 (dd, J = 3.4, 1.7 Hz, 1H), 6.27 (t, J = 3.4 Hz, 1H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 148.92, 146.62, 140.71, 132.79, 129.56, 124.32, 122.96, 111.17, 84.55, 27.74.



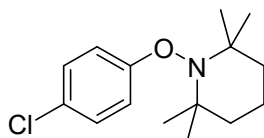
2-(4-methoxyphenyl) benzofuran (3df)²³

Colorless solid; 40% yield. $R_f = 0.2$ (Petroleum ether), m.p. = 152 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86-7.80 (m, 2H), 7.61-7.56 (m, 1H), 7.53 (d, $J = 8.2$ Hz, 1H), 7.31-7.22 (m, 2H), 7.04-6.98 (m, 2H), 6.92 (d, $J = 0.9$ Hz, 1H), 3.89 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.00, 156.07, 154.71, 129.51, 126.44, 123.76, 123.36, 122.85, 120.59, 114.27, 111.01, 99.70, 55.39.



4-(benzofuran-2-yl) benzonitrile (3ff)²⁴

Colorless solid; 71% yield. $R_f = 0.3$ (Petroleum ether), m.p. = 143 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.2$ Hz, 2H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.68-7.63 (m, 1H), 7.57 (d, $J = 8.2$ Hz, 1H), 7.44-7.24 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 155.27, 153.57, 134.49, 132.66, 128.68, 125.58, 125.14, 123.47, 121.53, 118.78, 111.53, 111.46, 104.37.



1-(4-chlorophenoxy)-2,2,6,6-tetramethylpiperidine (5).

Colorless oil; 51% yield. $R_f = 0.9$ (Petroleum ether), m.p. = 320 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.18-7.09 (m, 4H), 1.64-1.53 (m, 5H), 1.45-1.38 (m, 1H), 1.22 (s, 6H), 0.99 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 162.22, 128.57, 124.33, 115.20, 60.47, 39.74, 32.50, 20.43, 17.00.

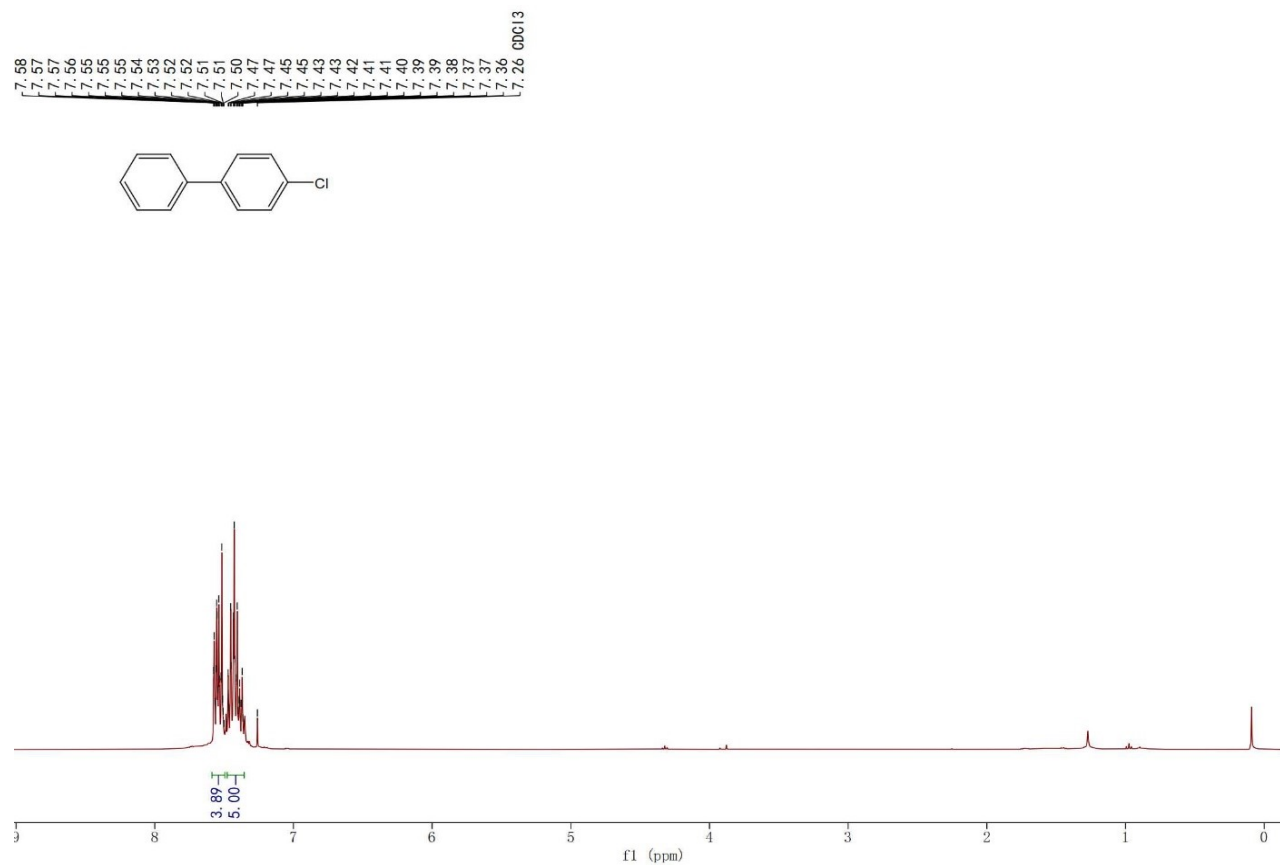
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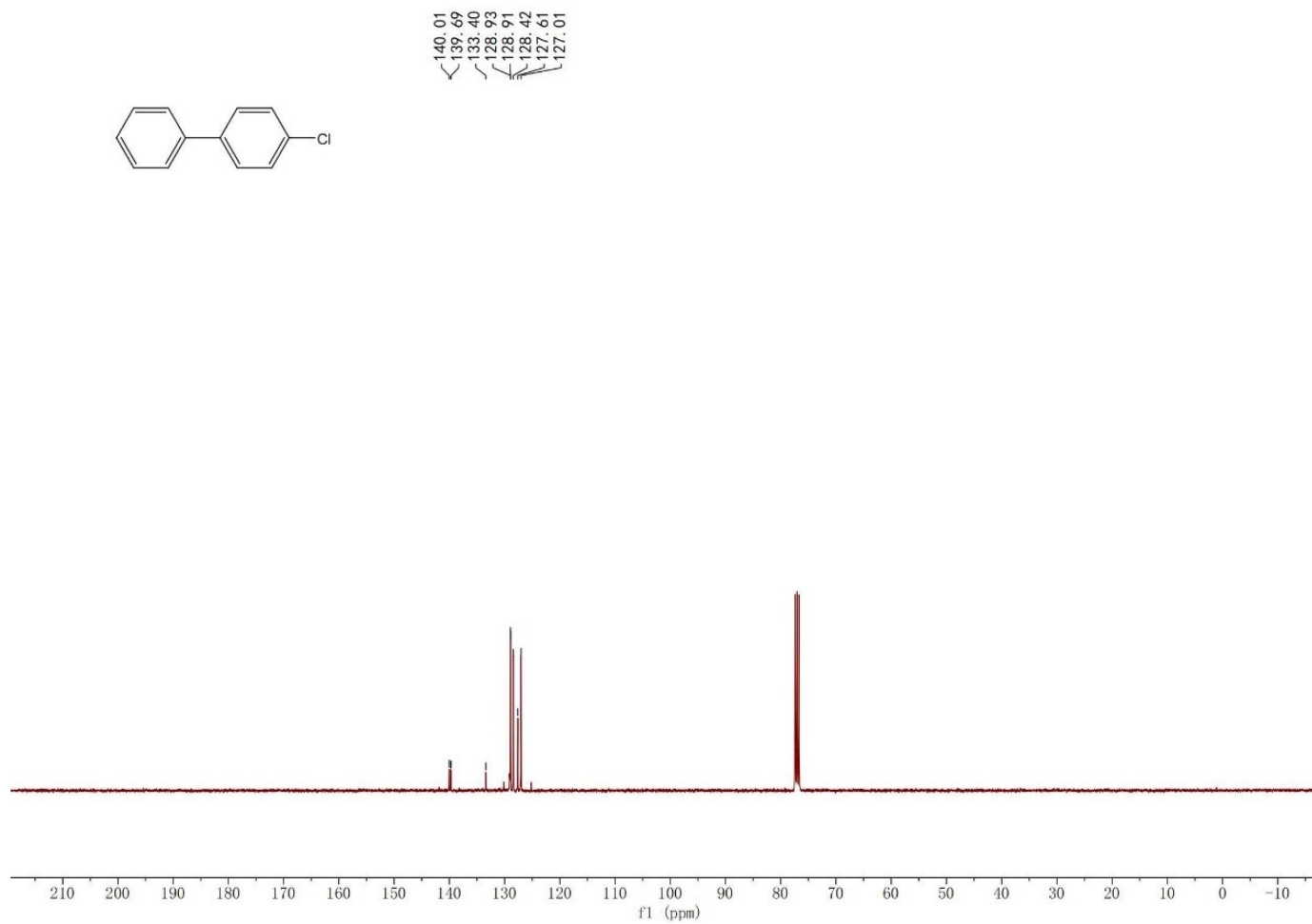
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4. Copies of NMR spectra of 3aa-3ff

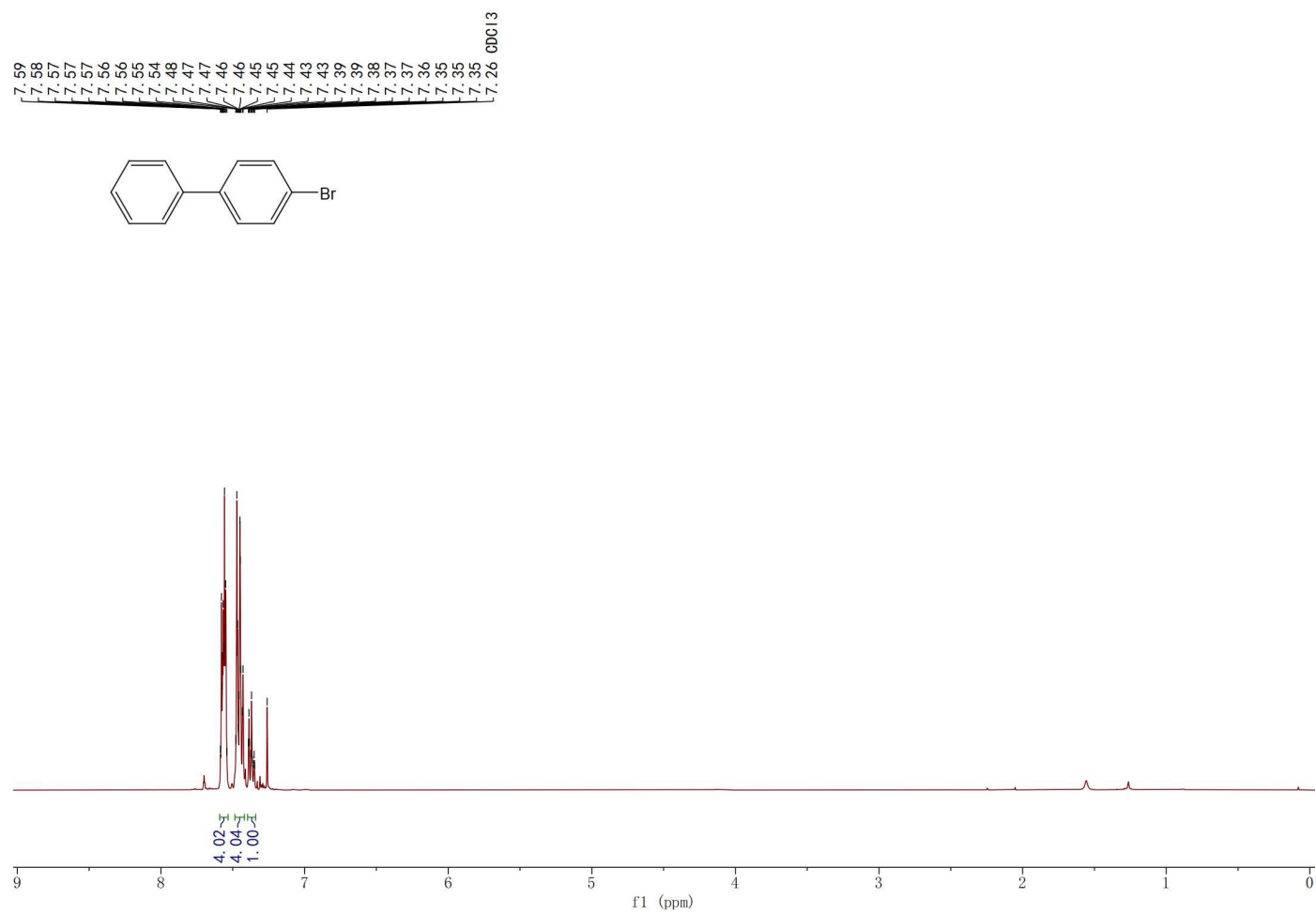
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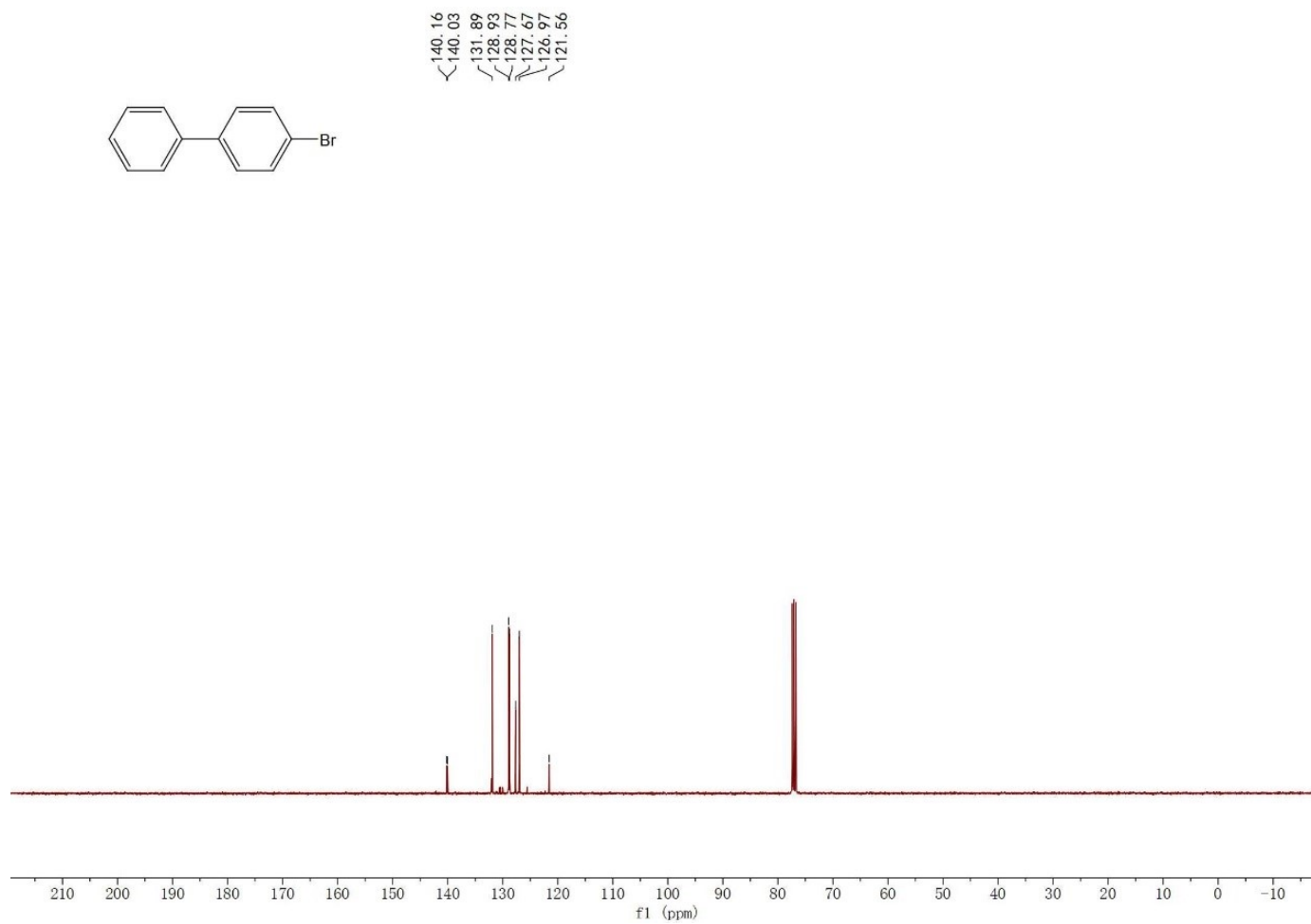
3aa ^{13}C NMR



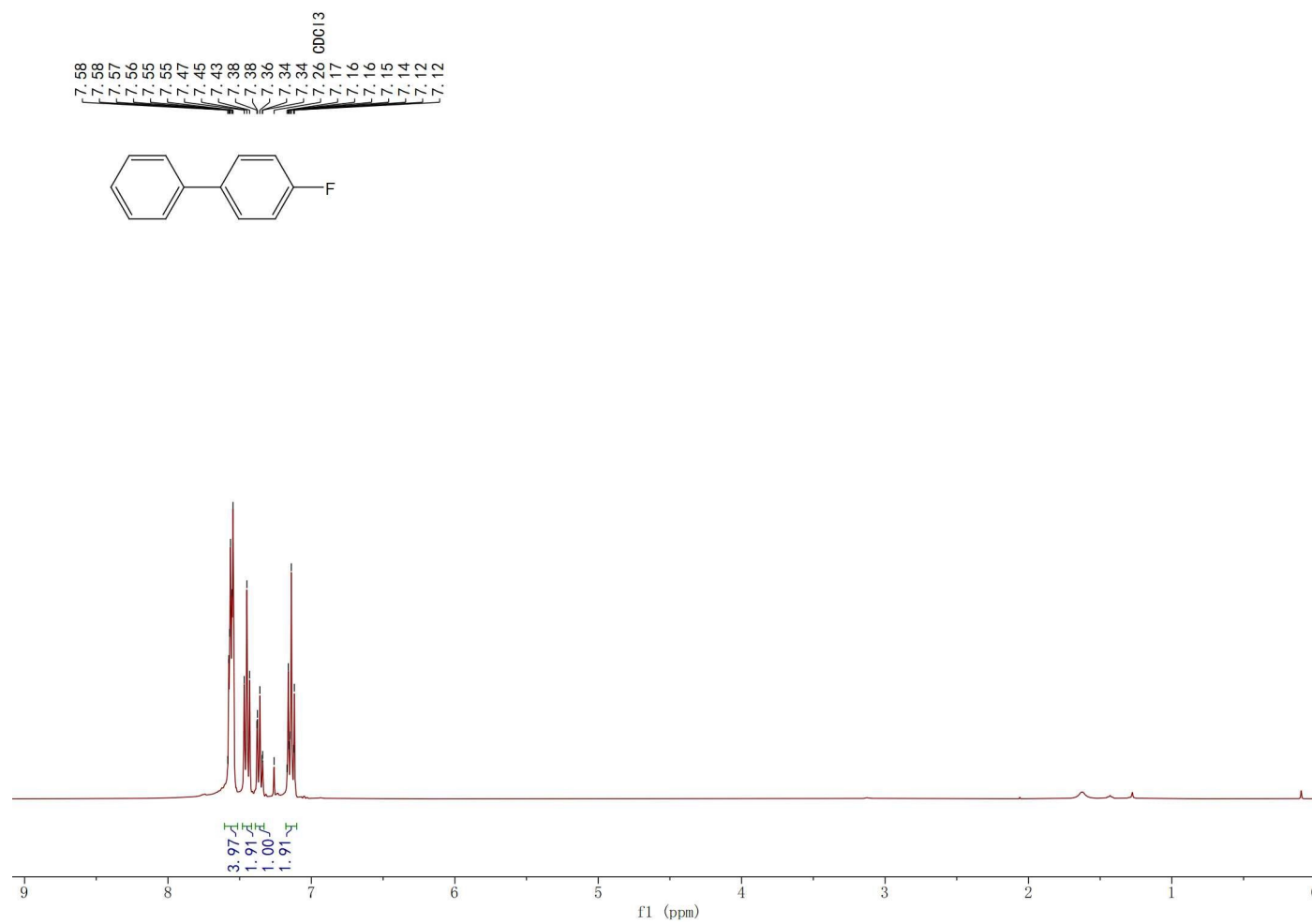
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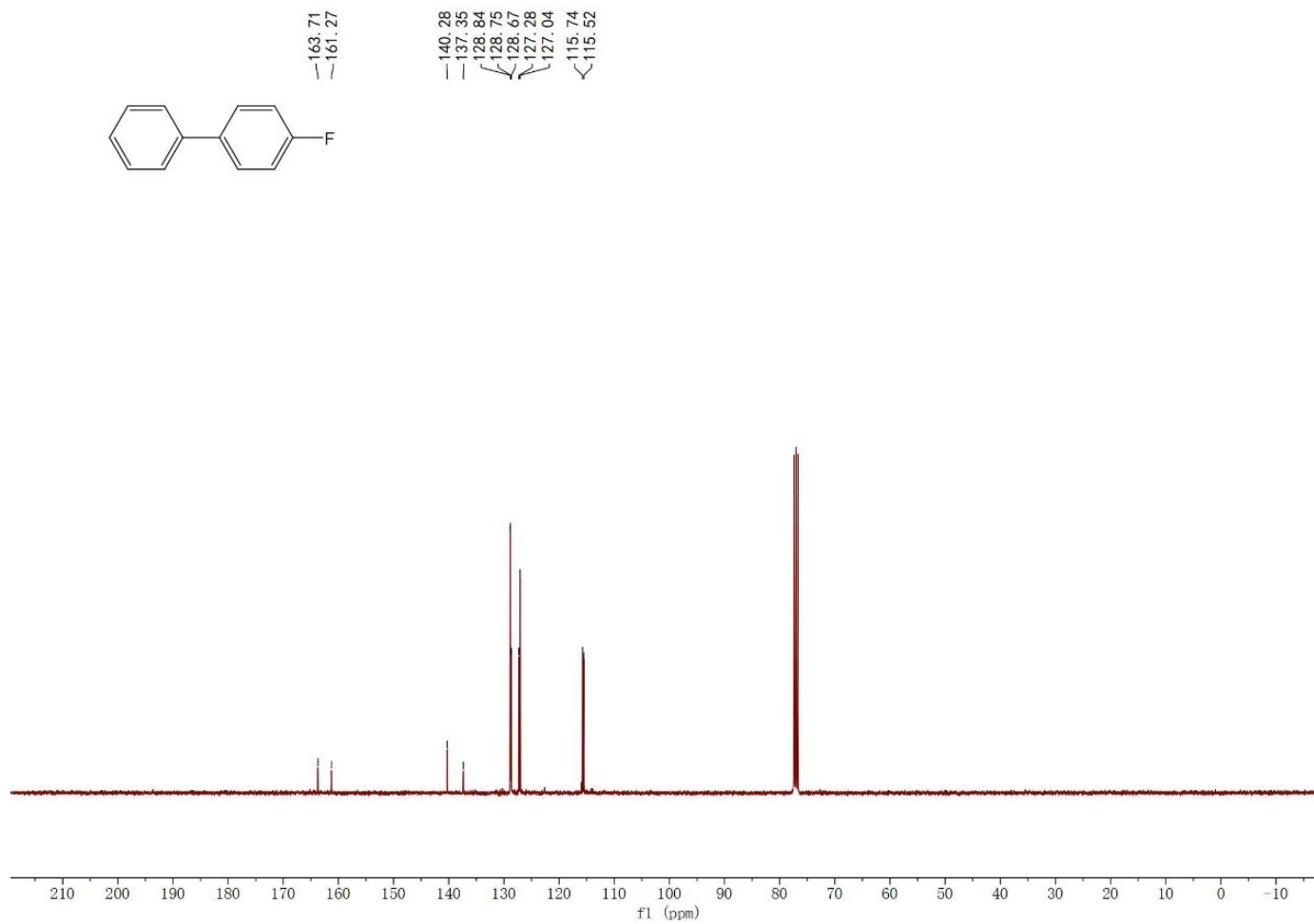
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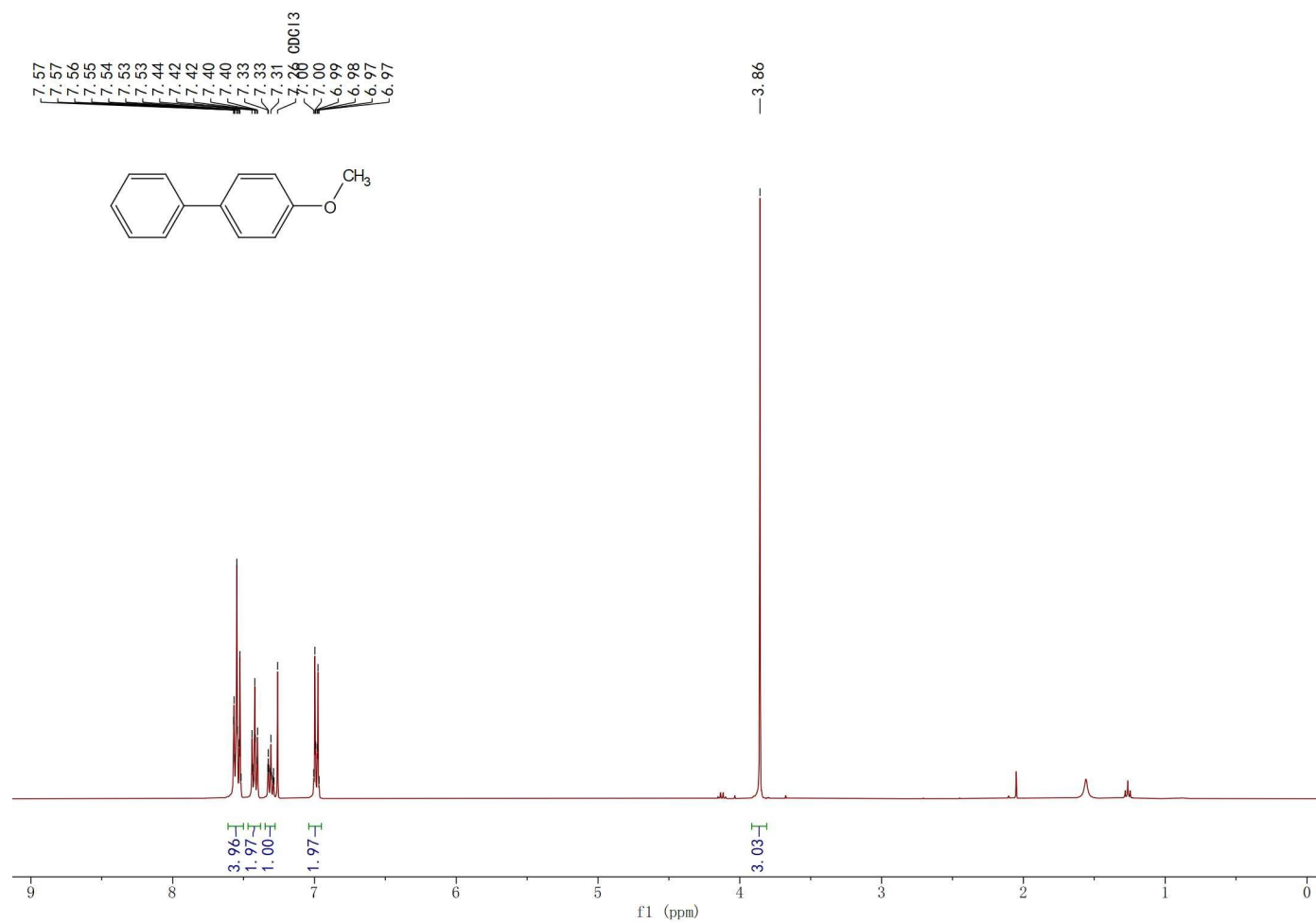
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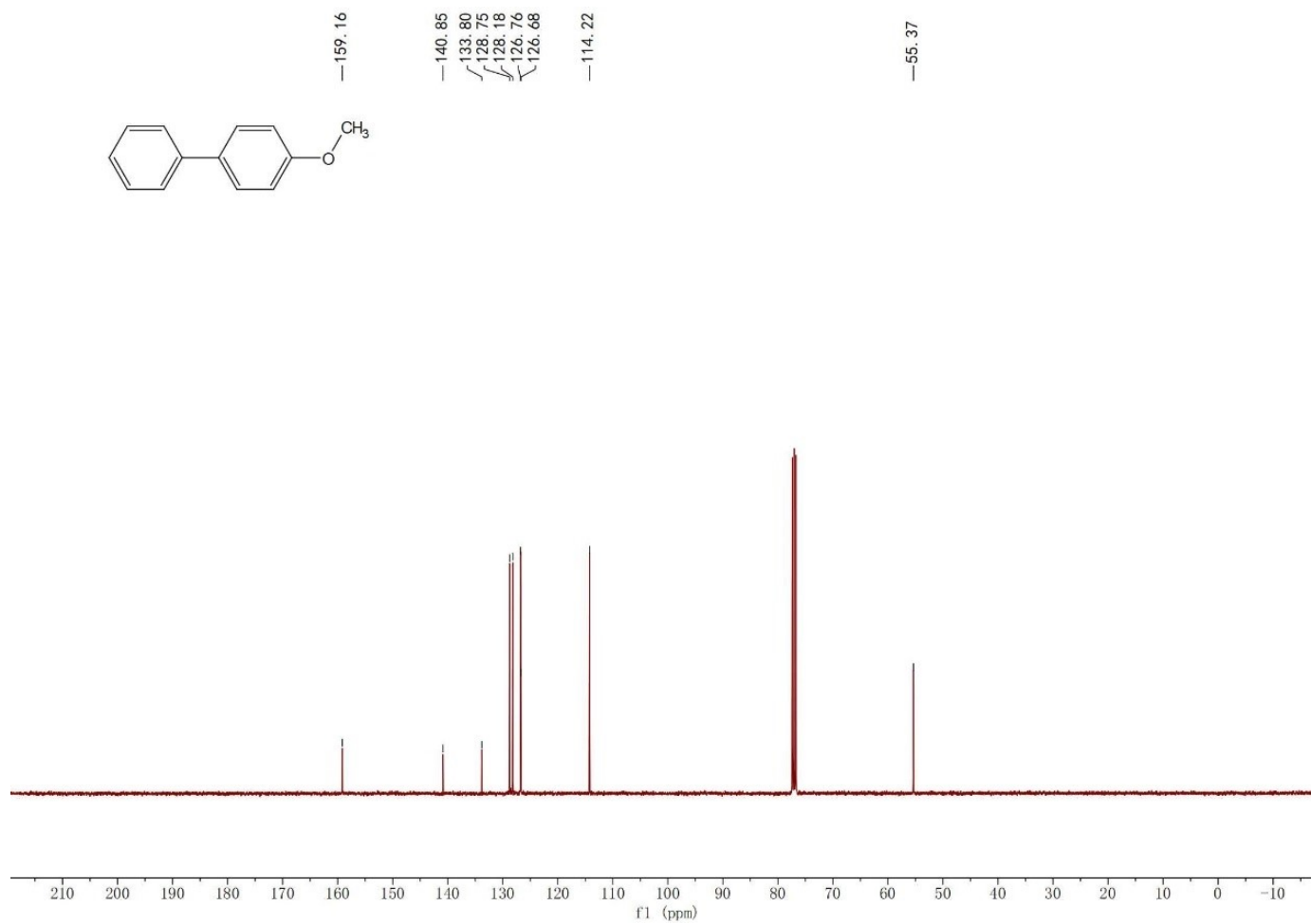
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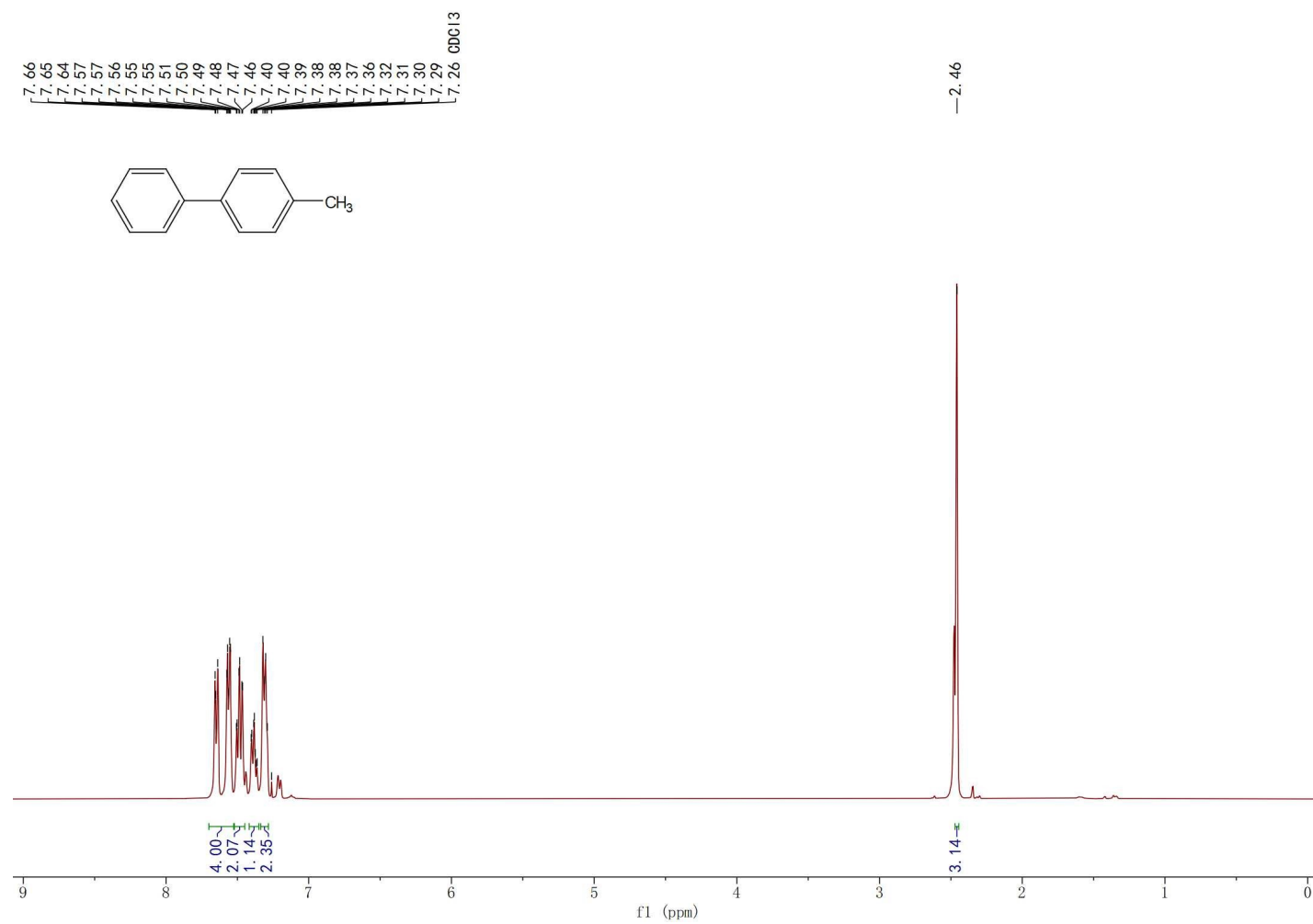
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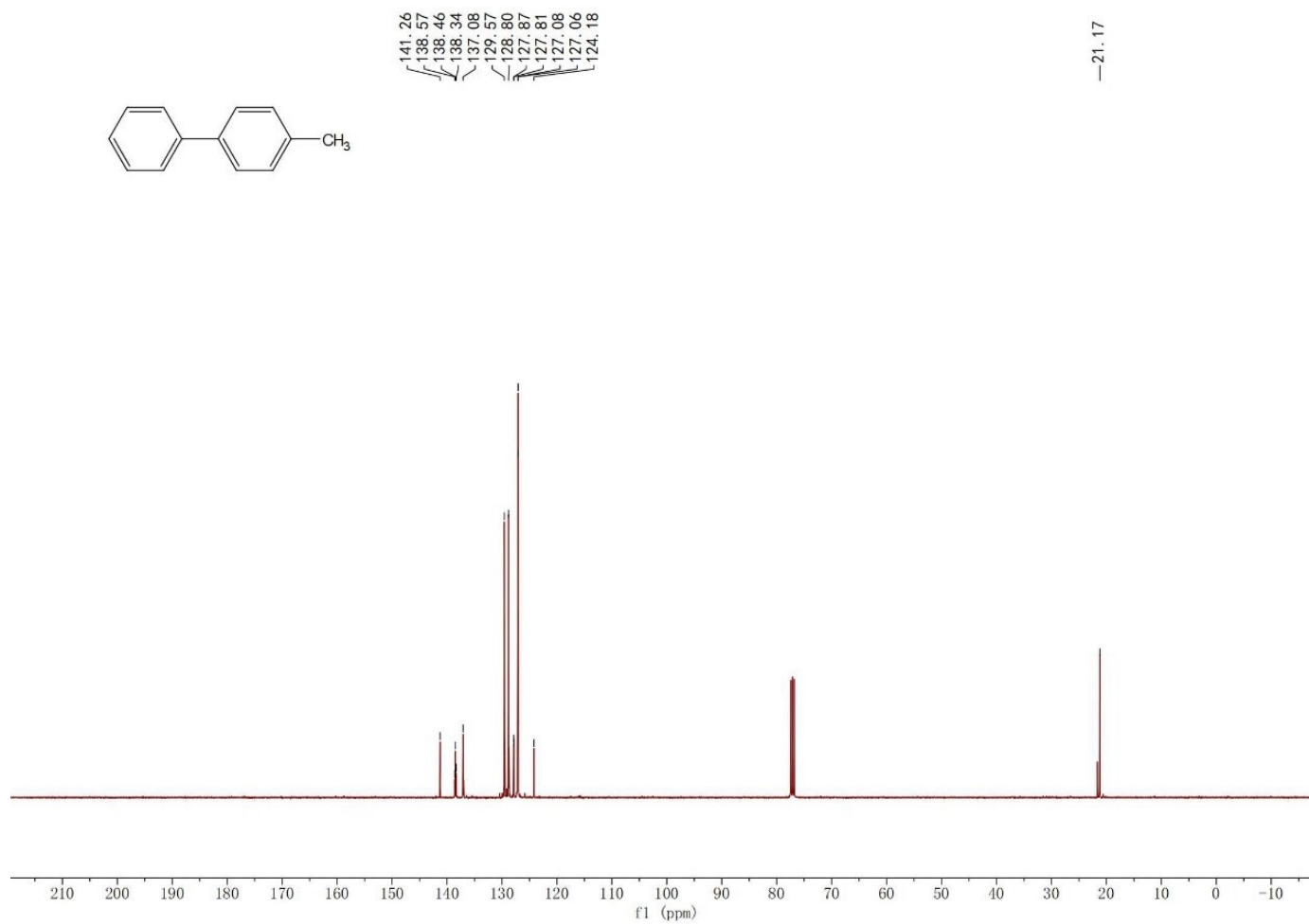
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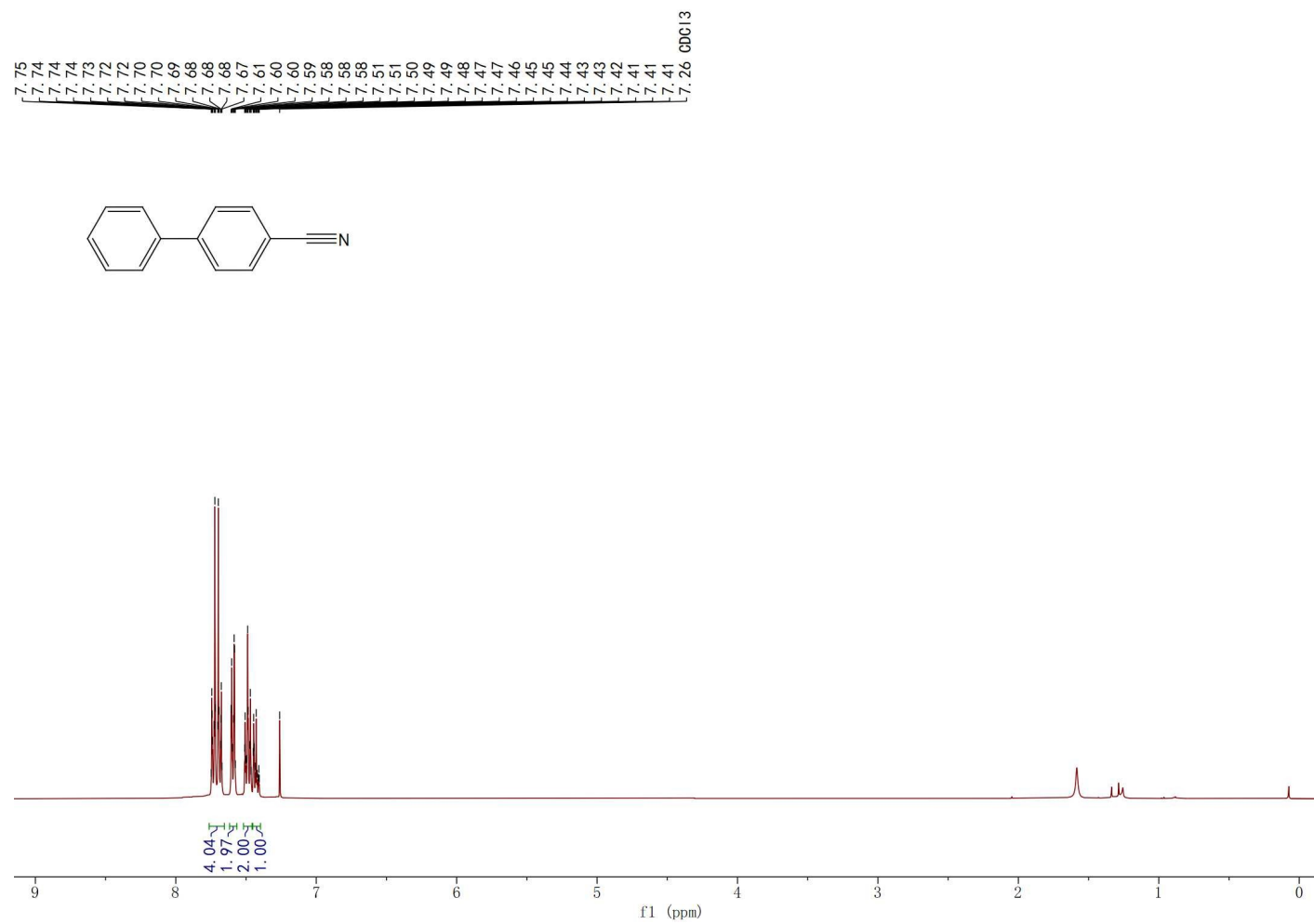
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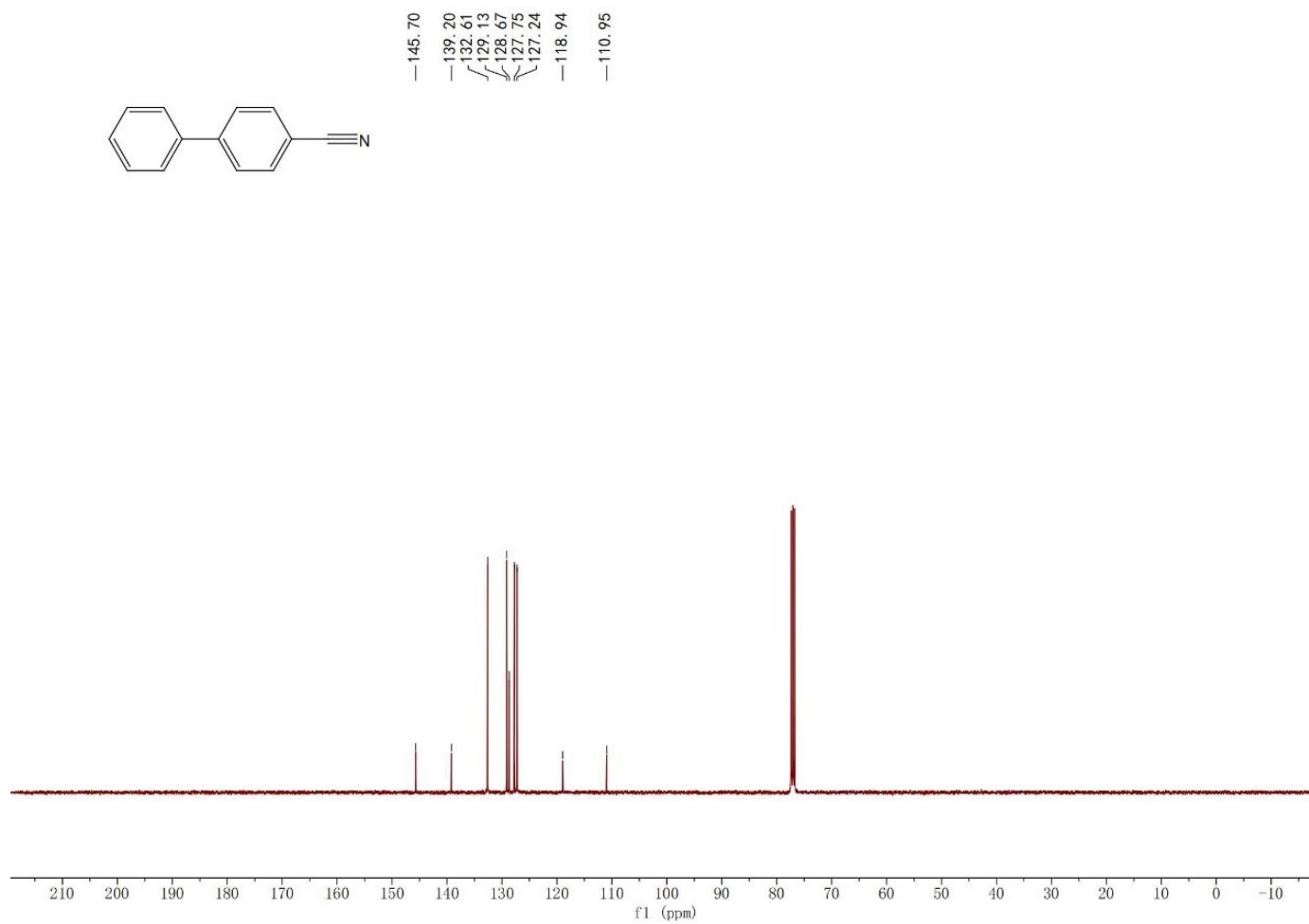
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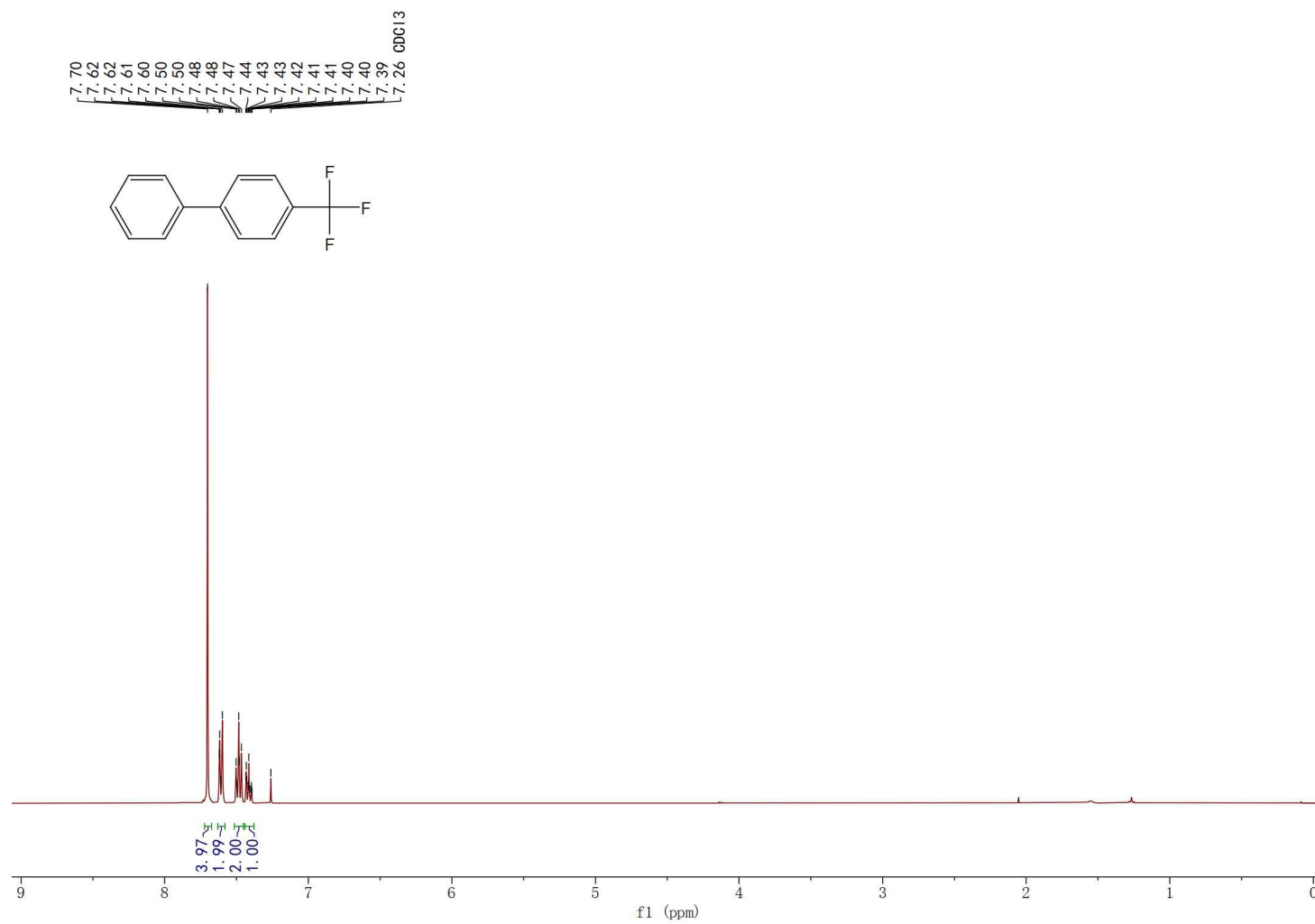
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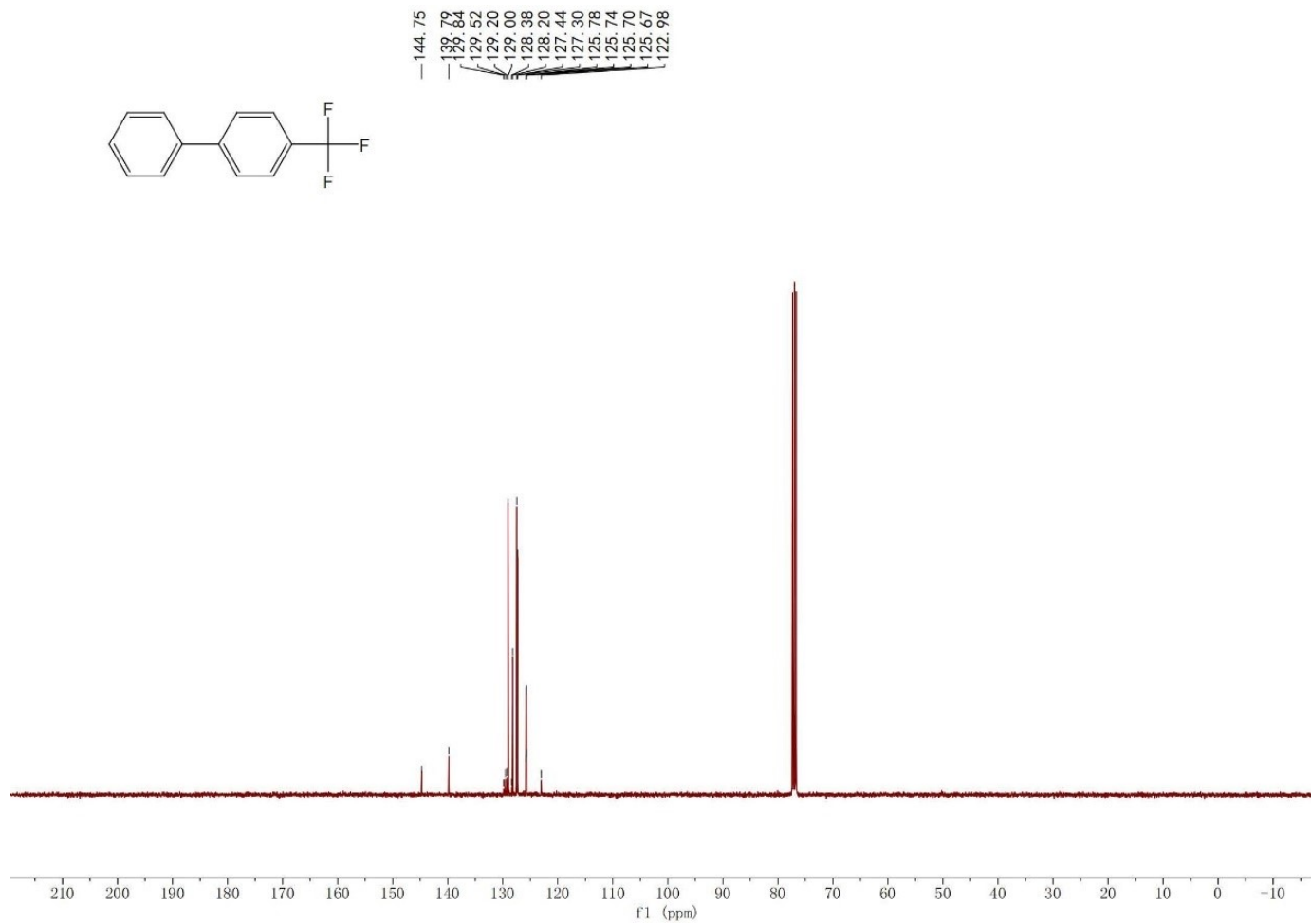
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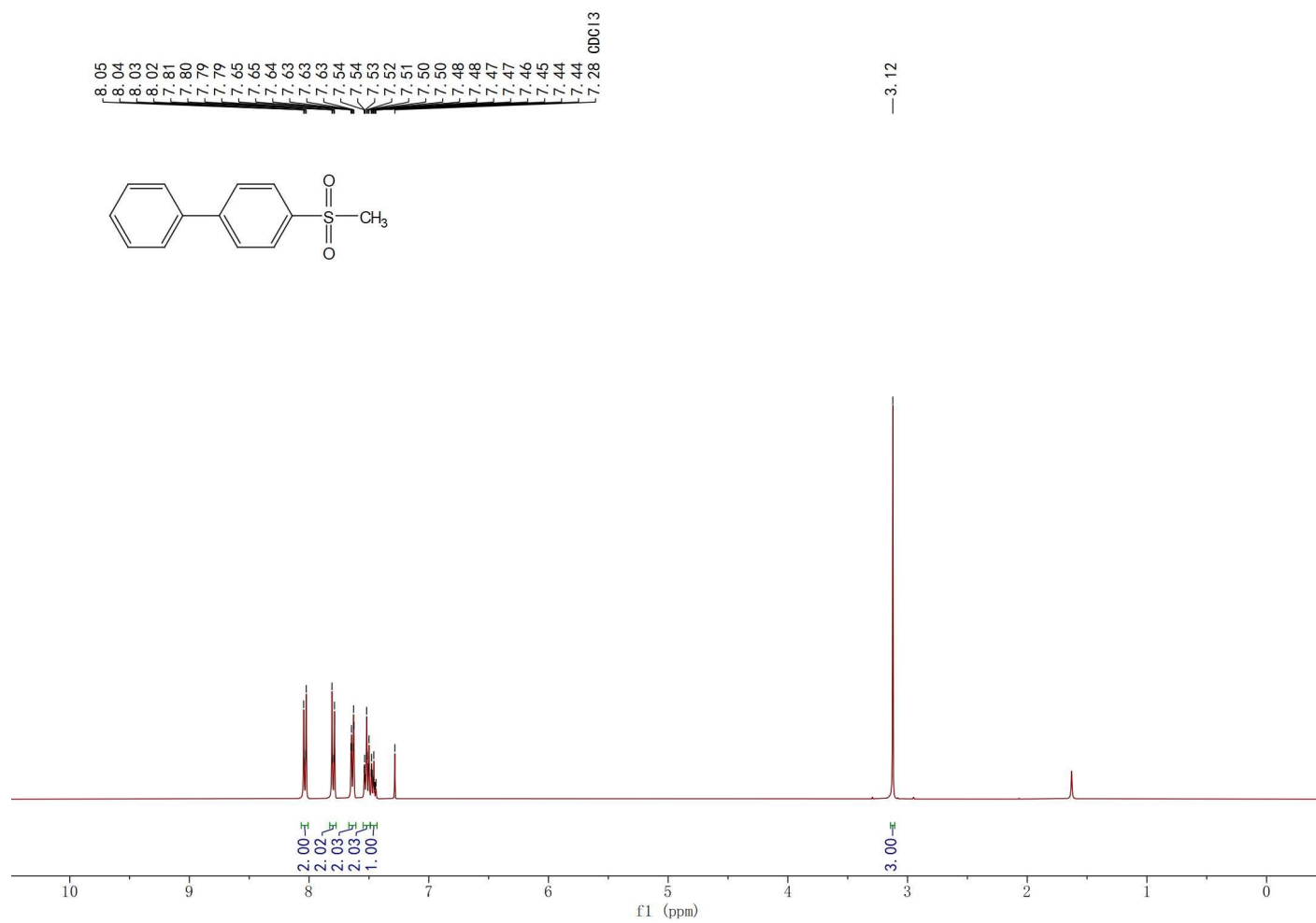
3ga ^1H NMR



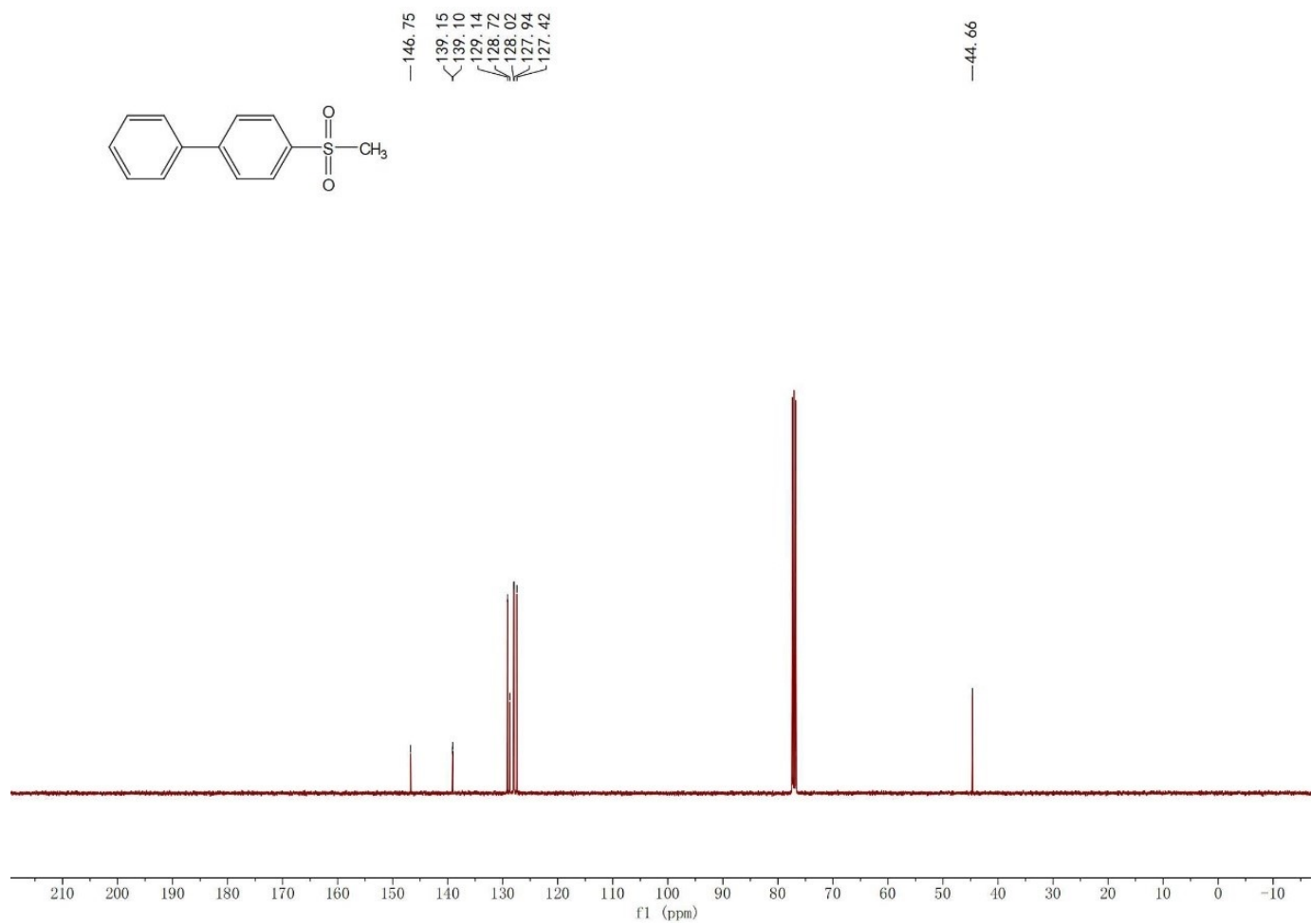
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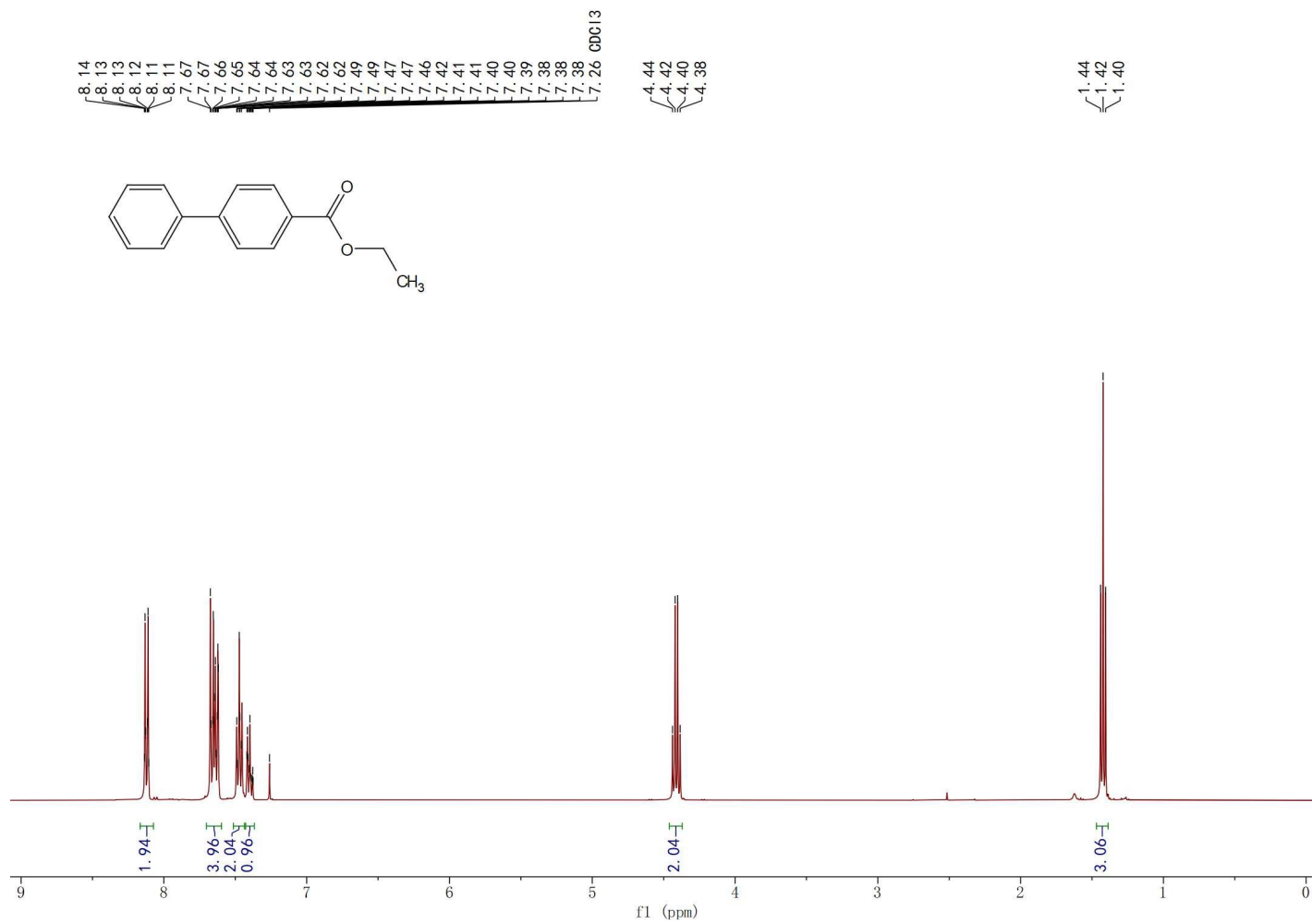
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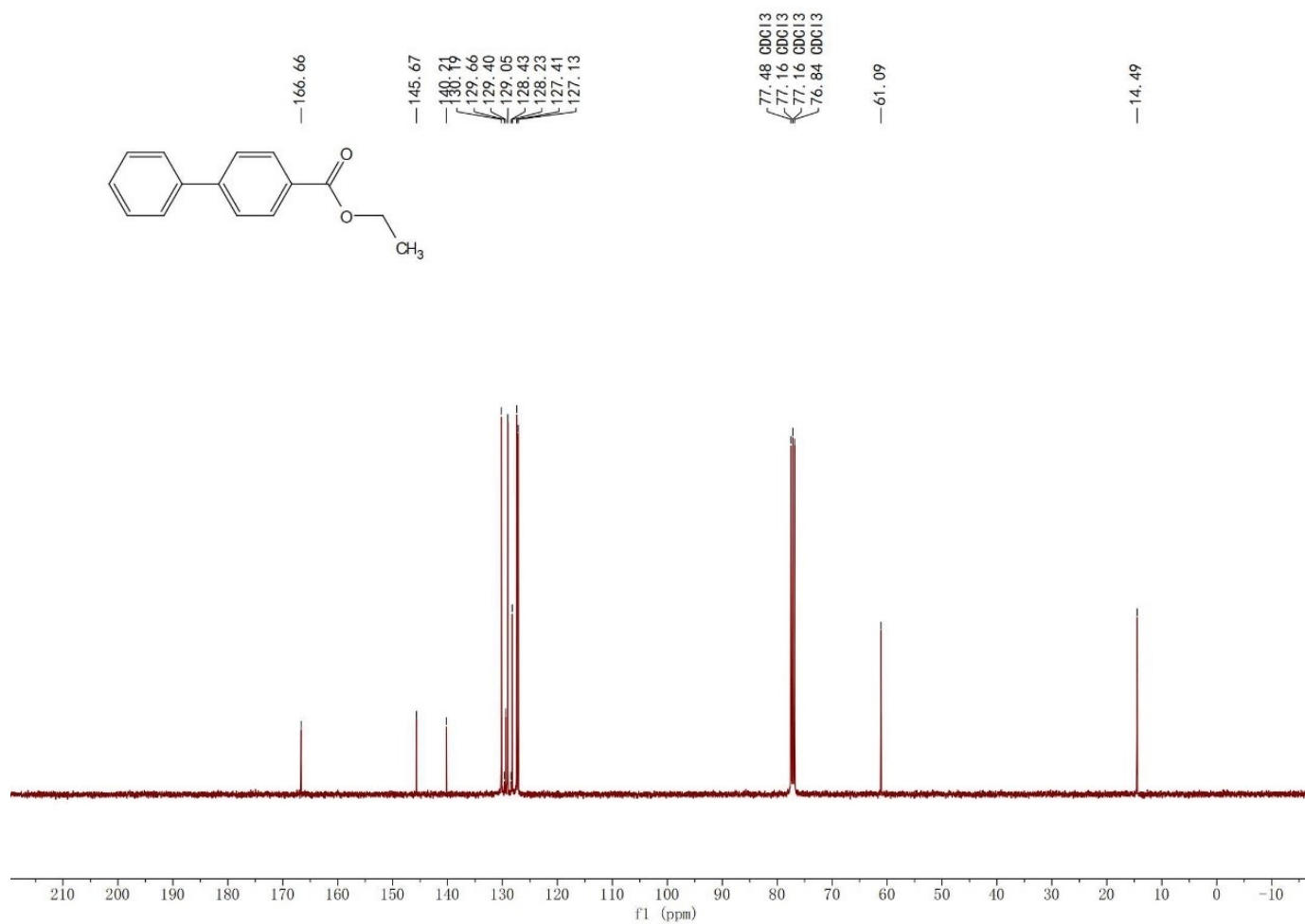
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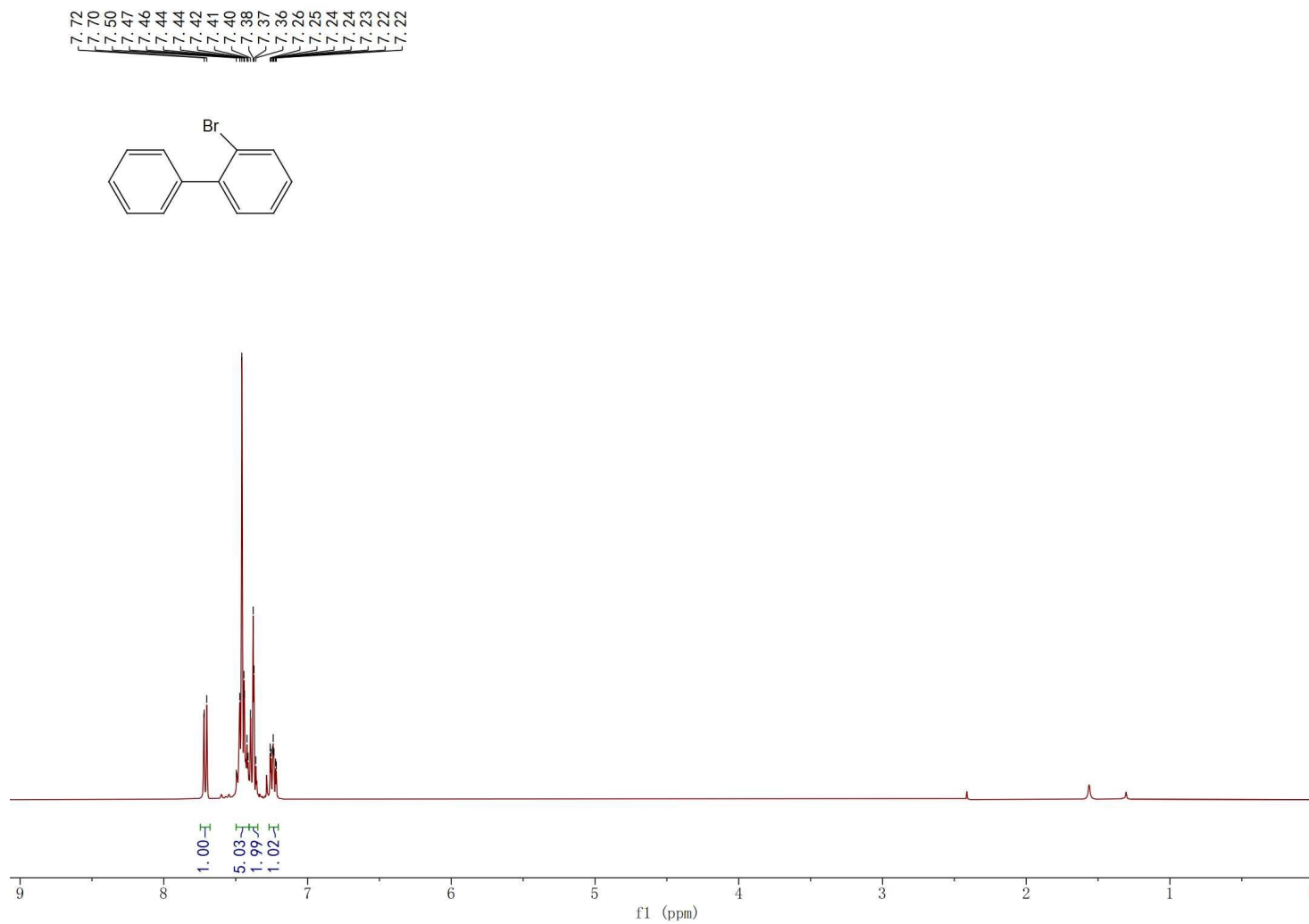
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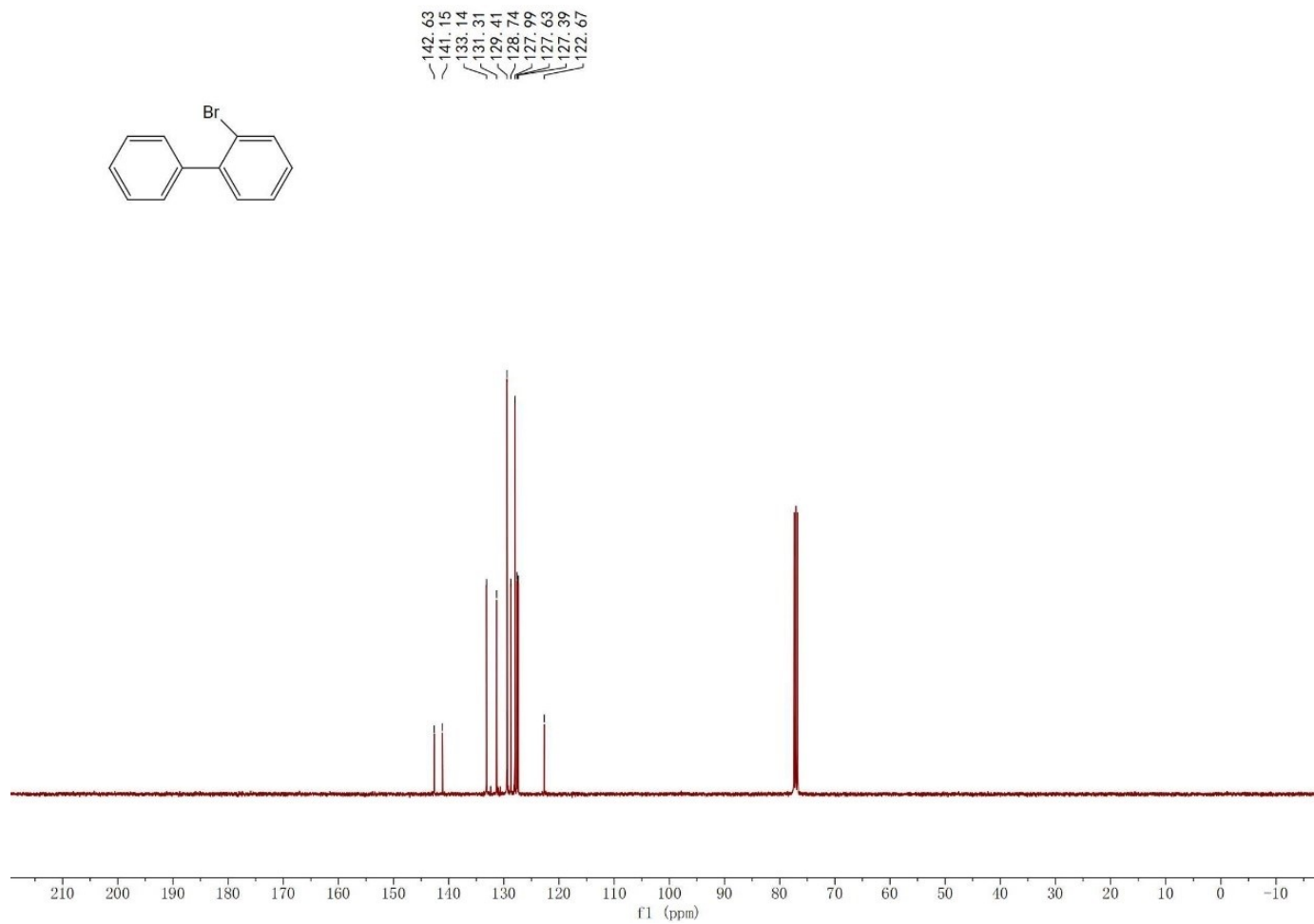
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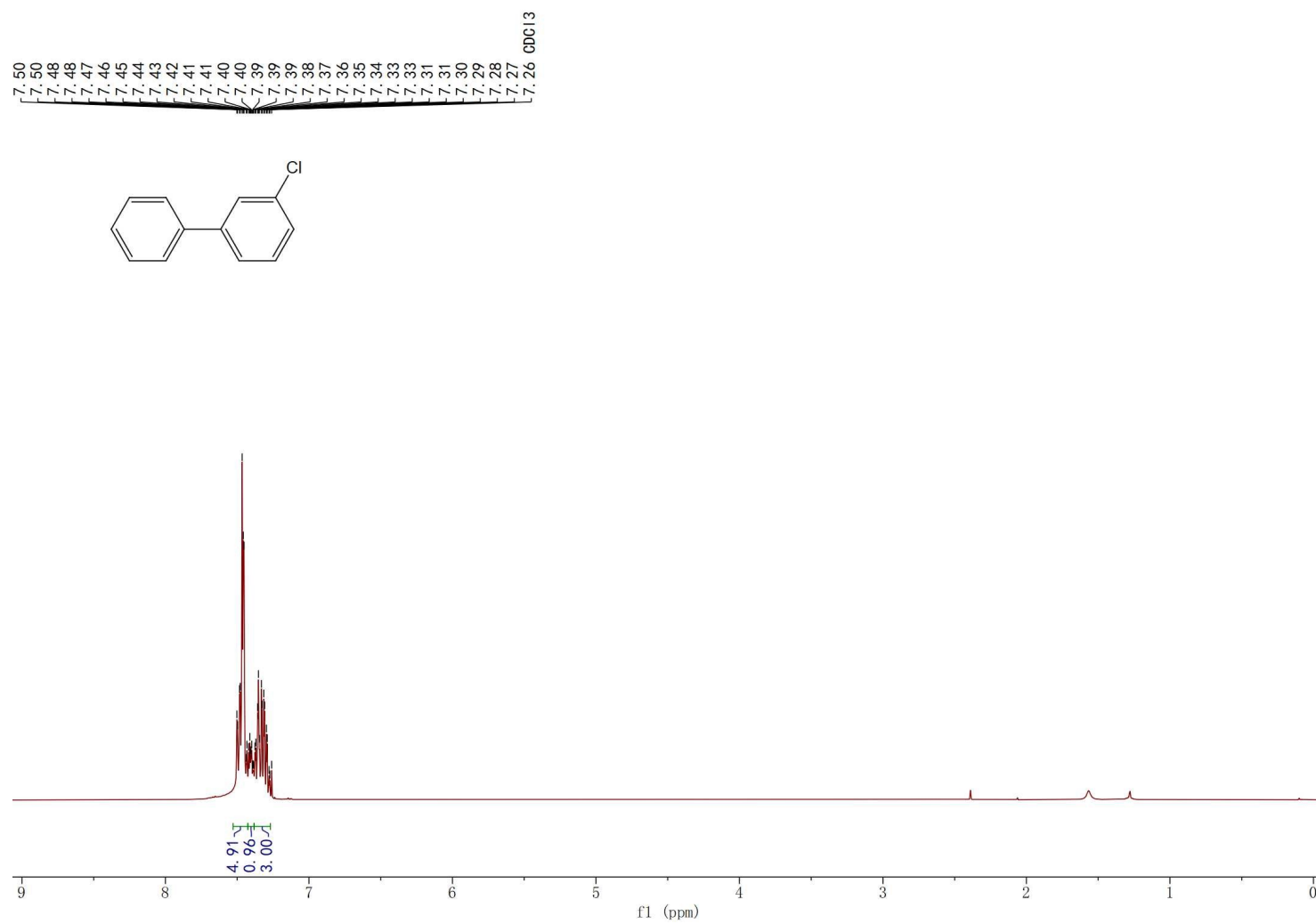
3ka ^1H NMR



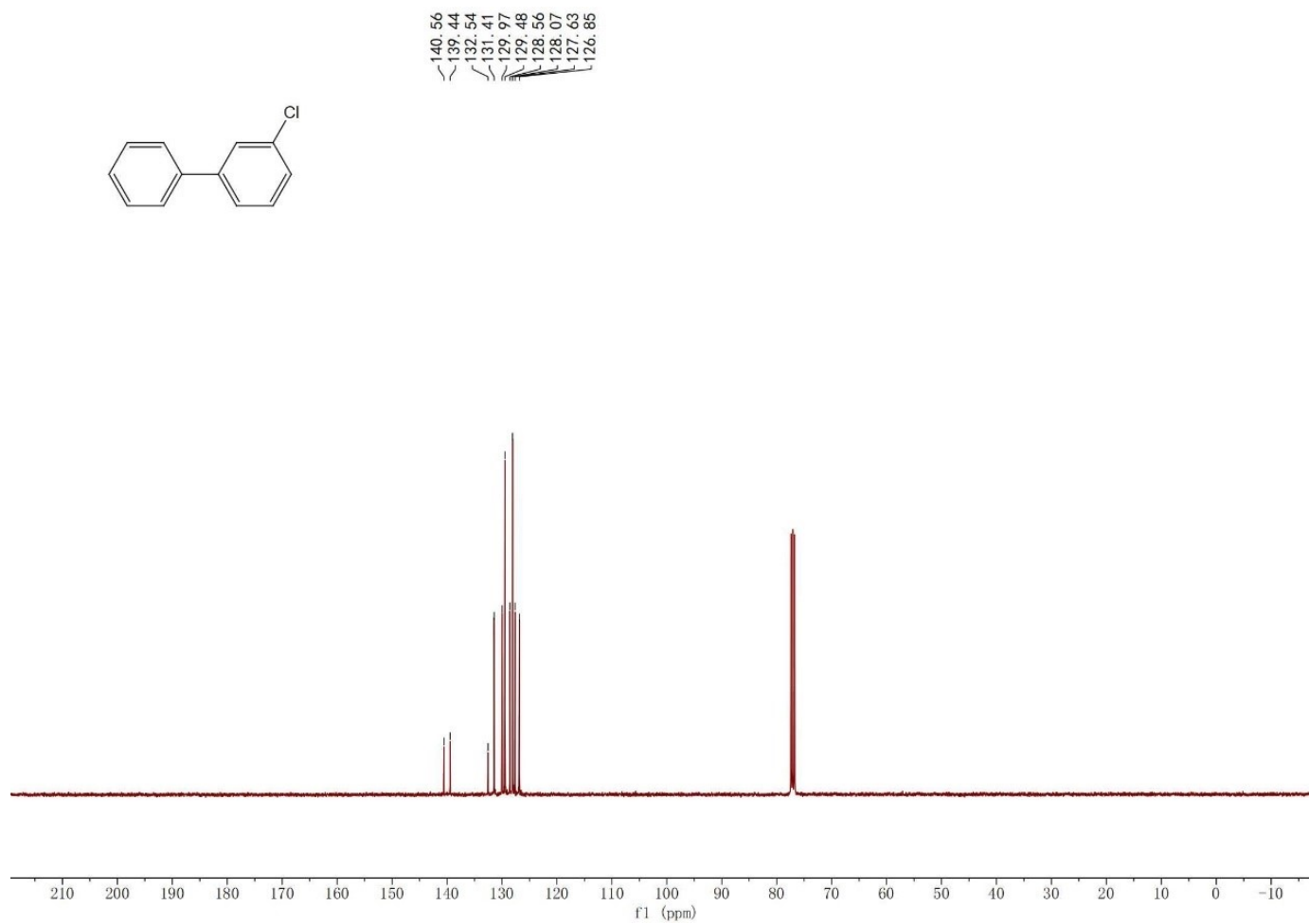
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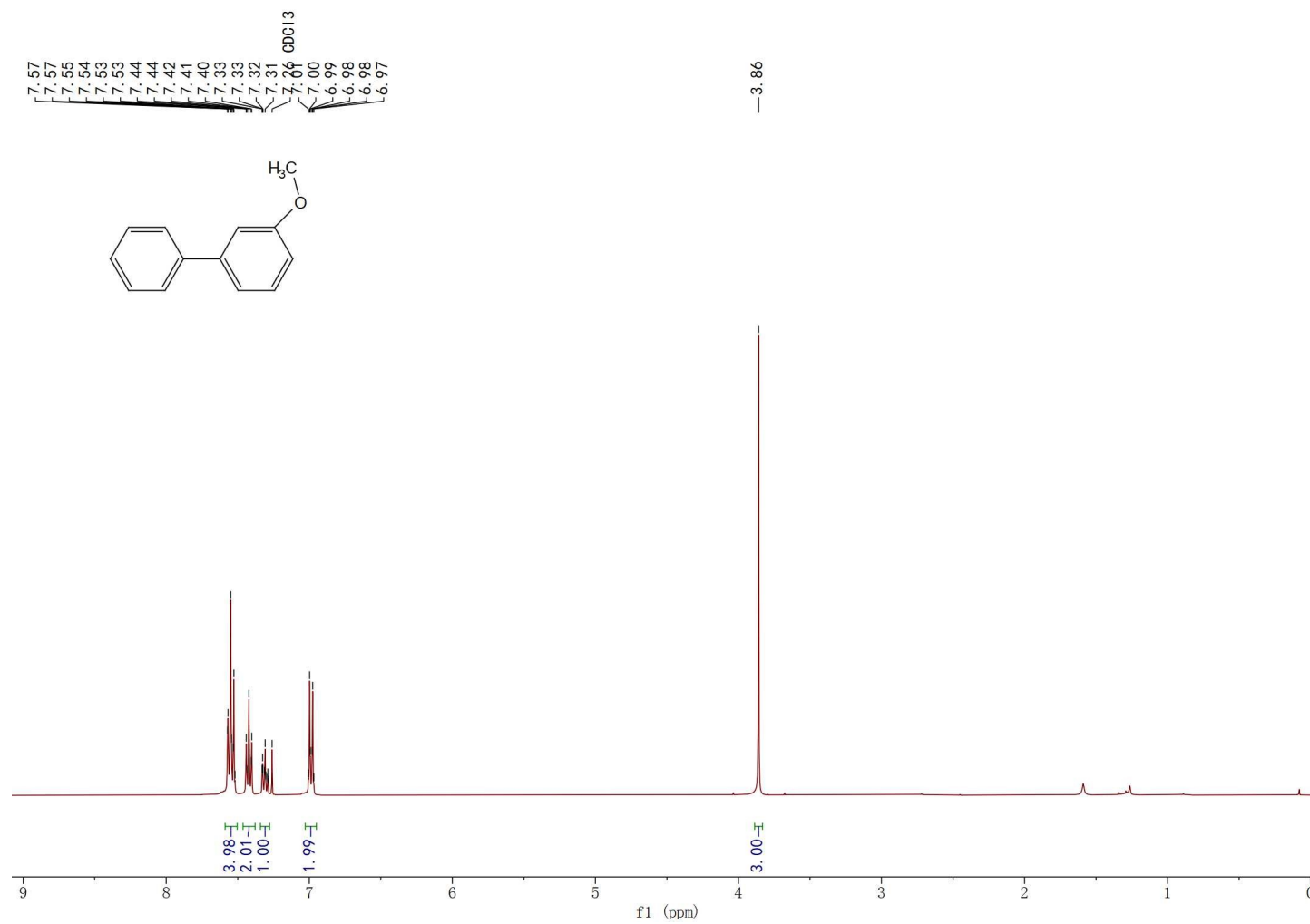
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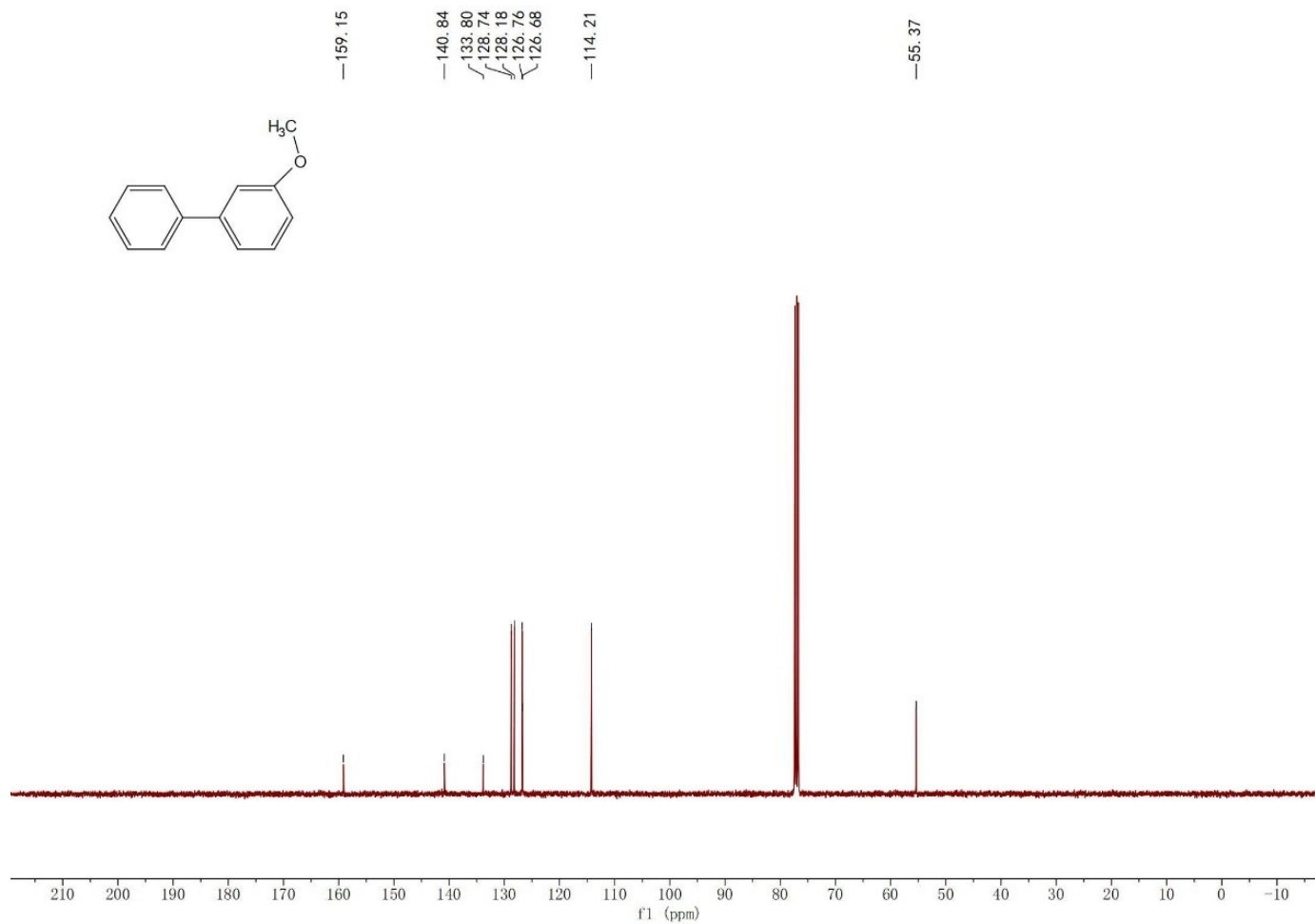
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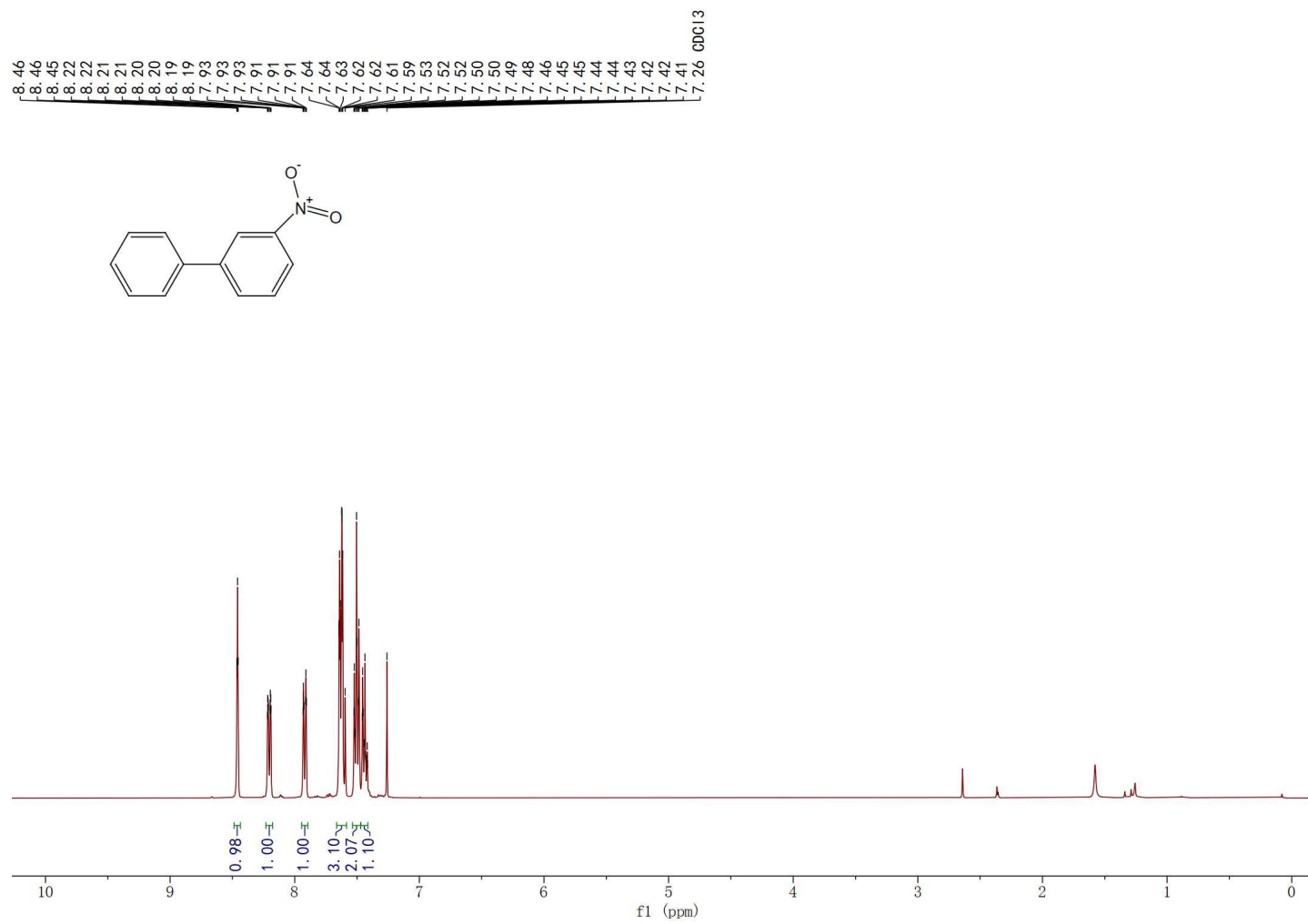
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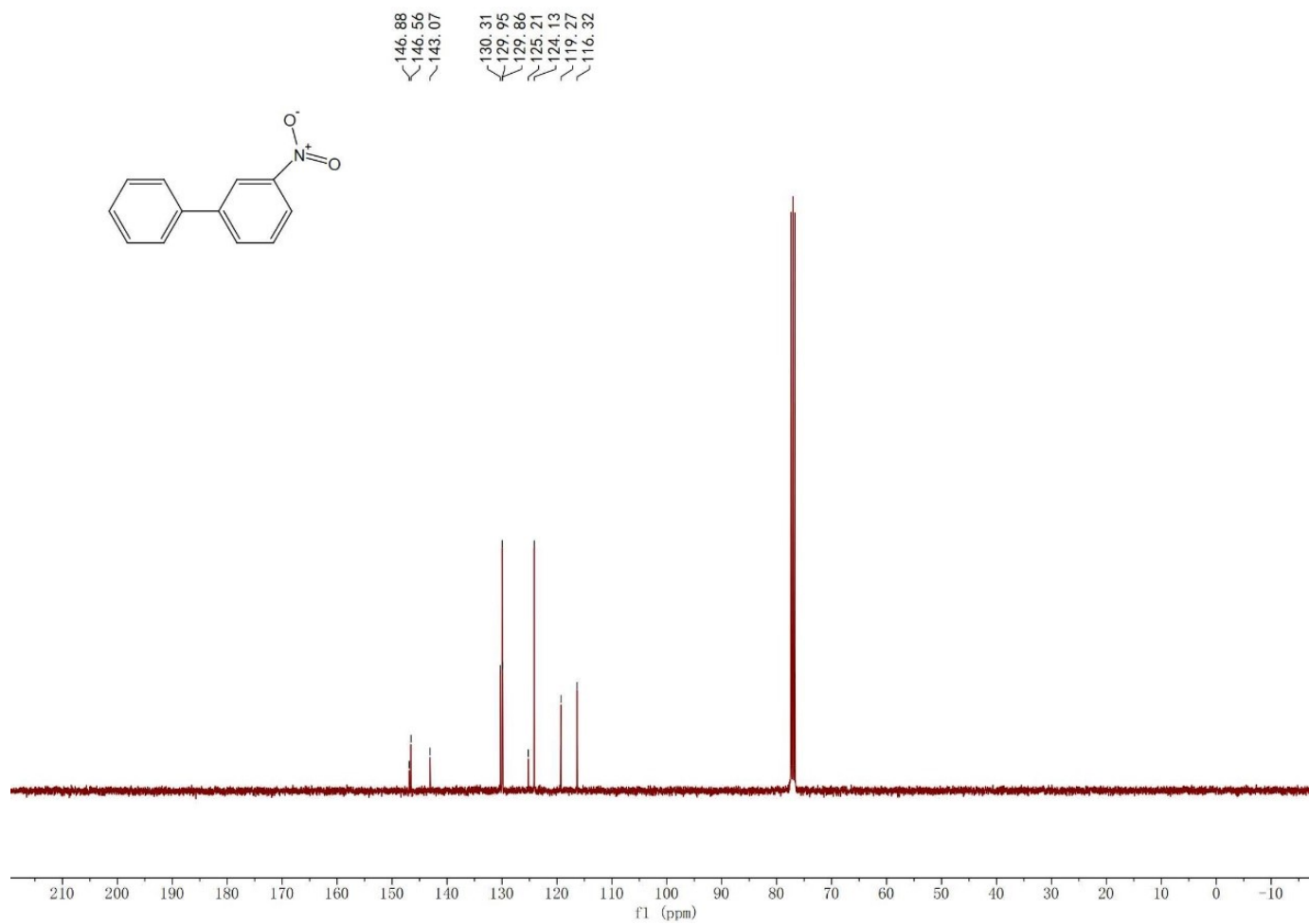
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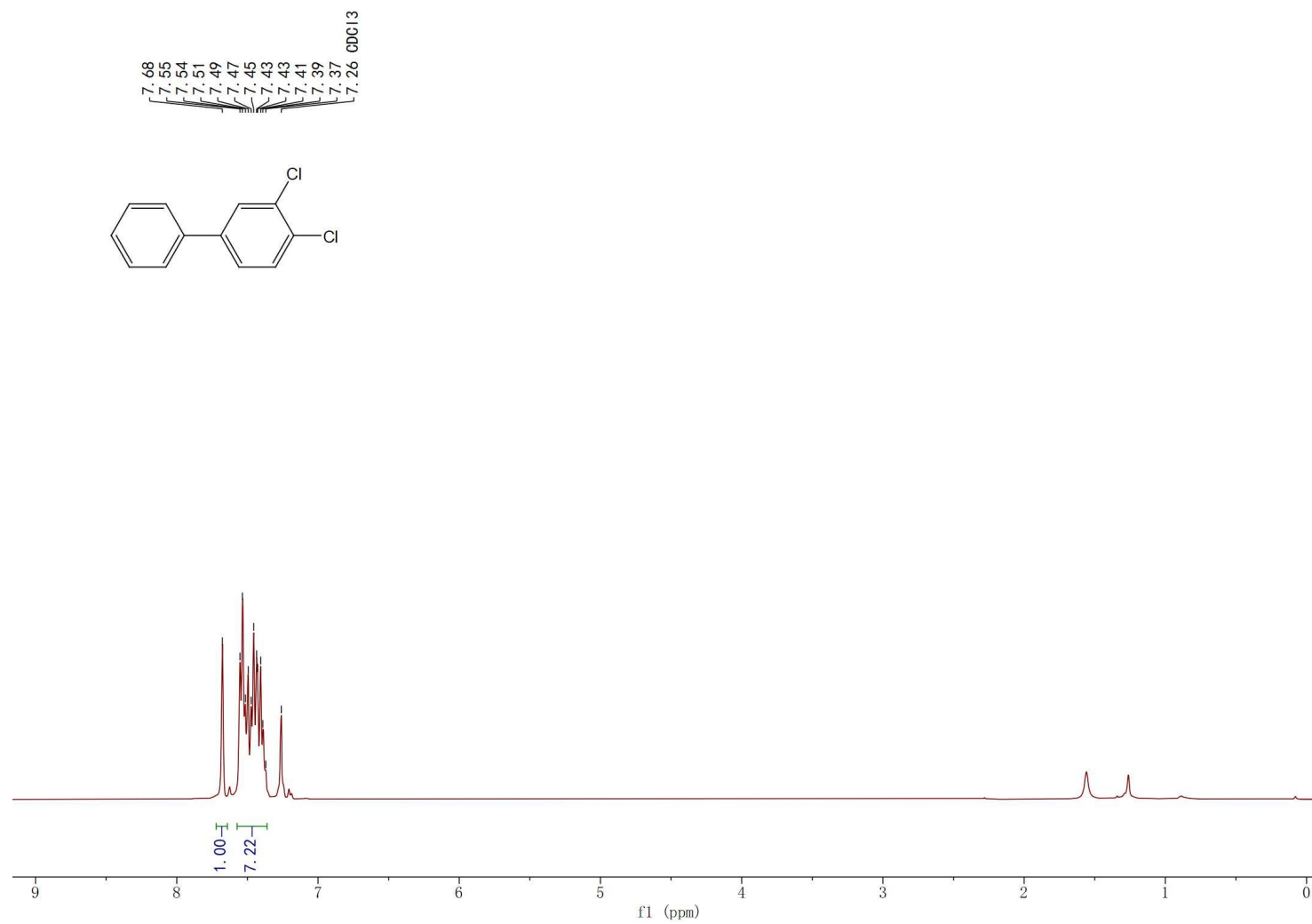
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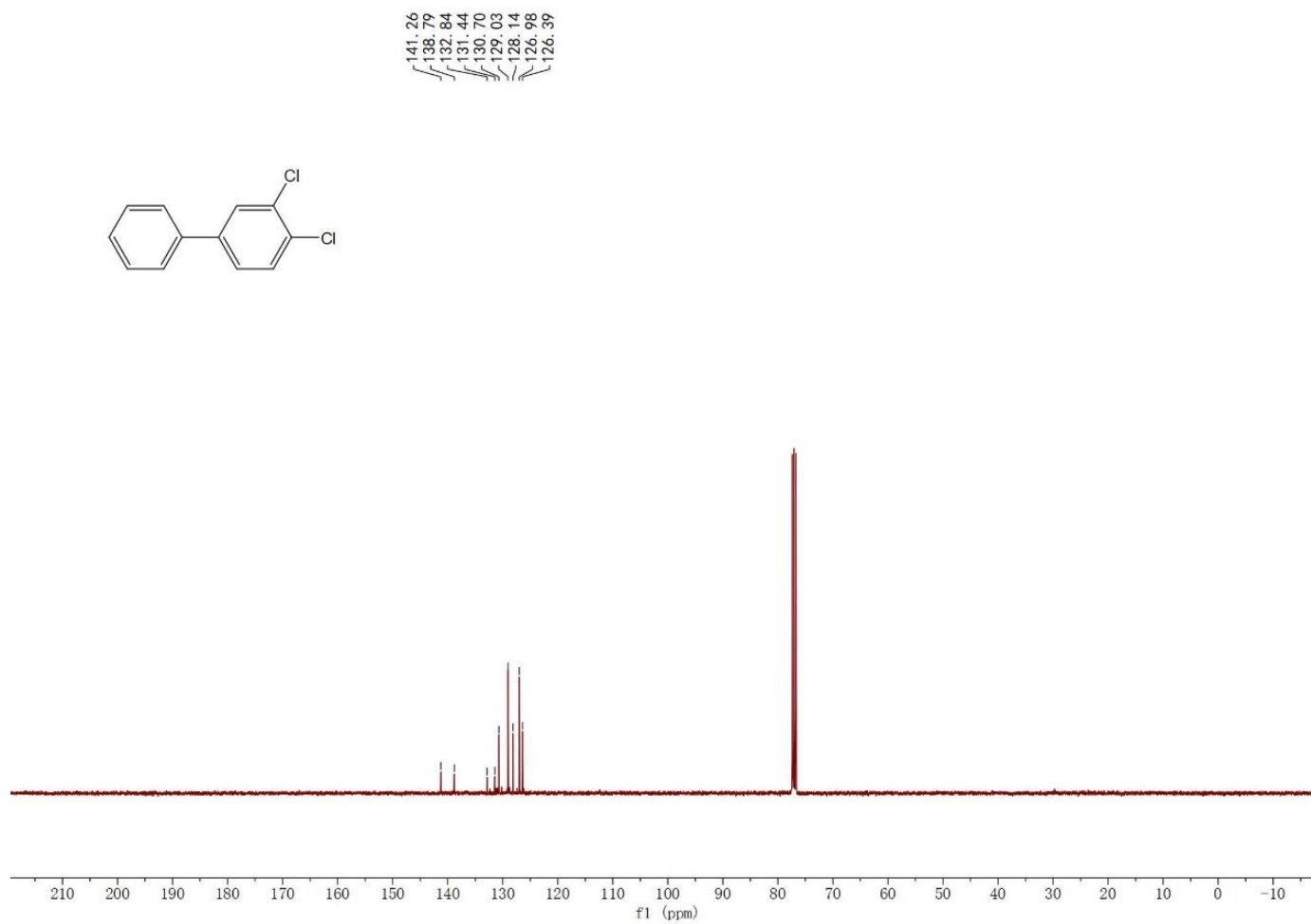
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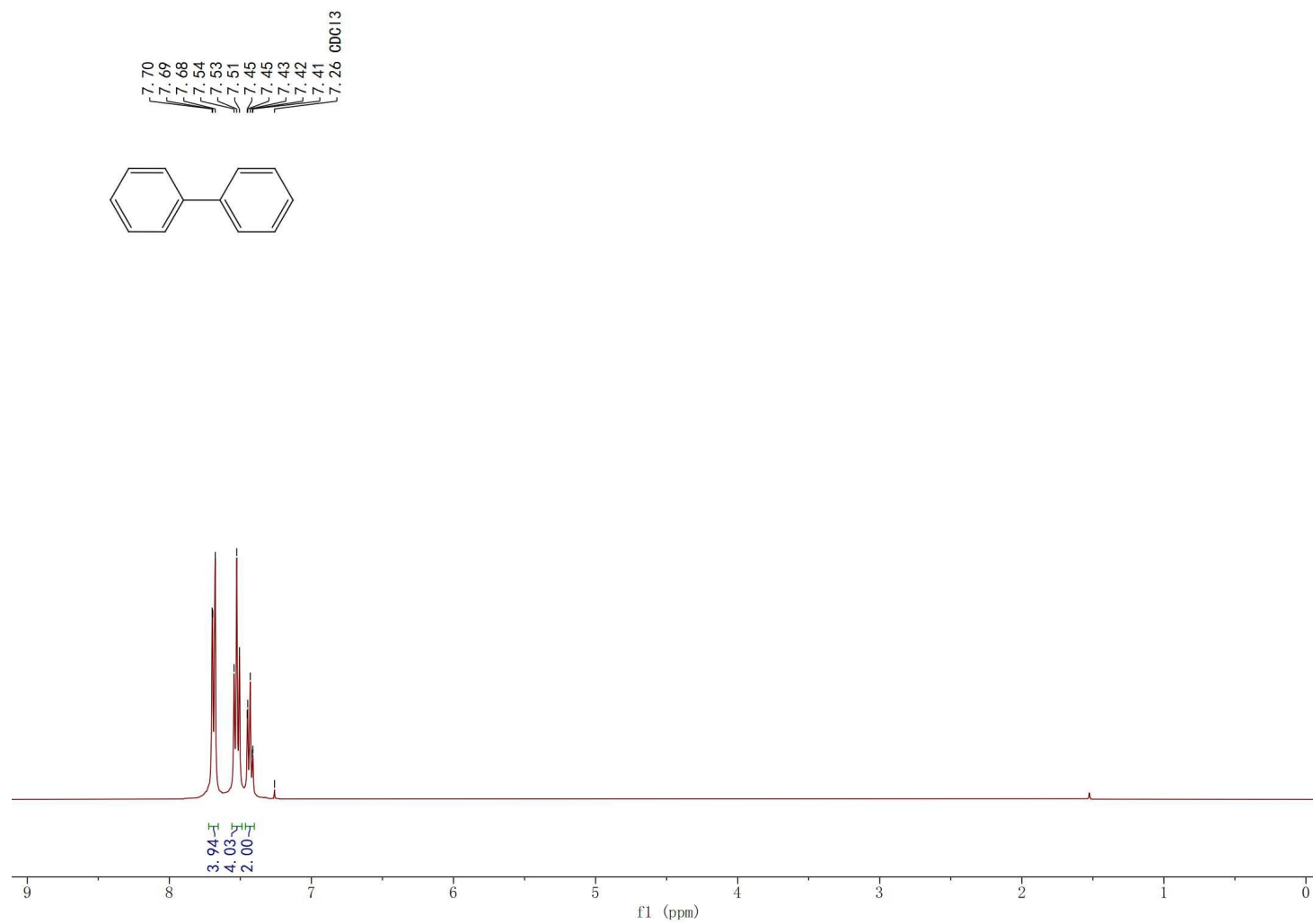
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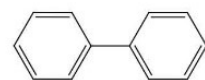
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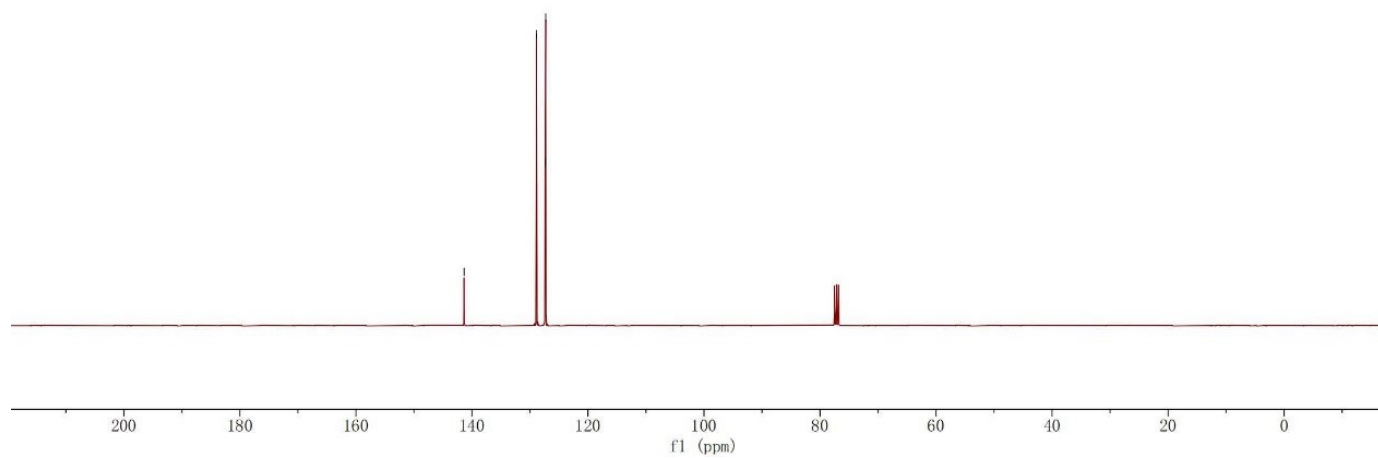
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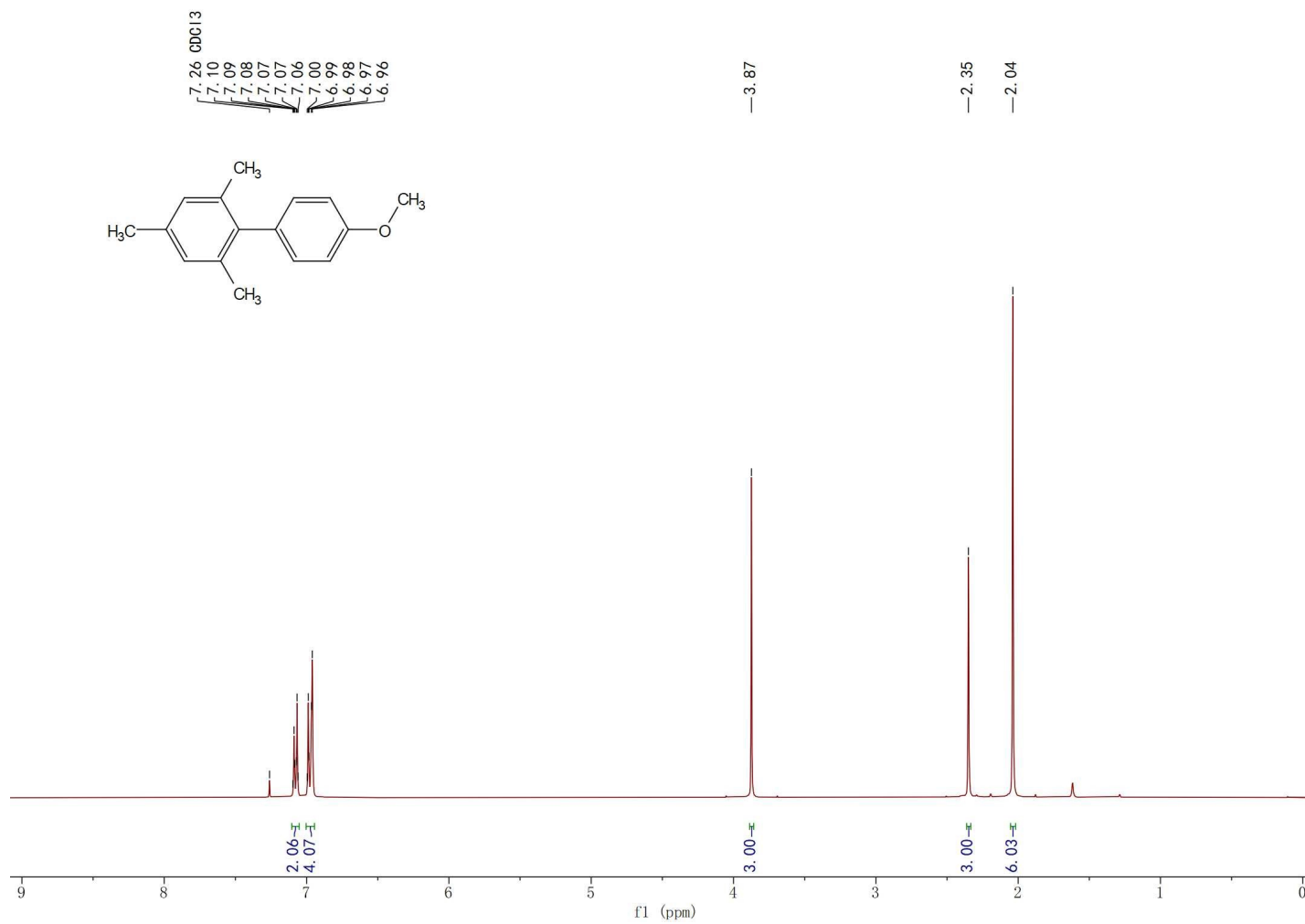
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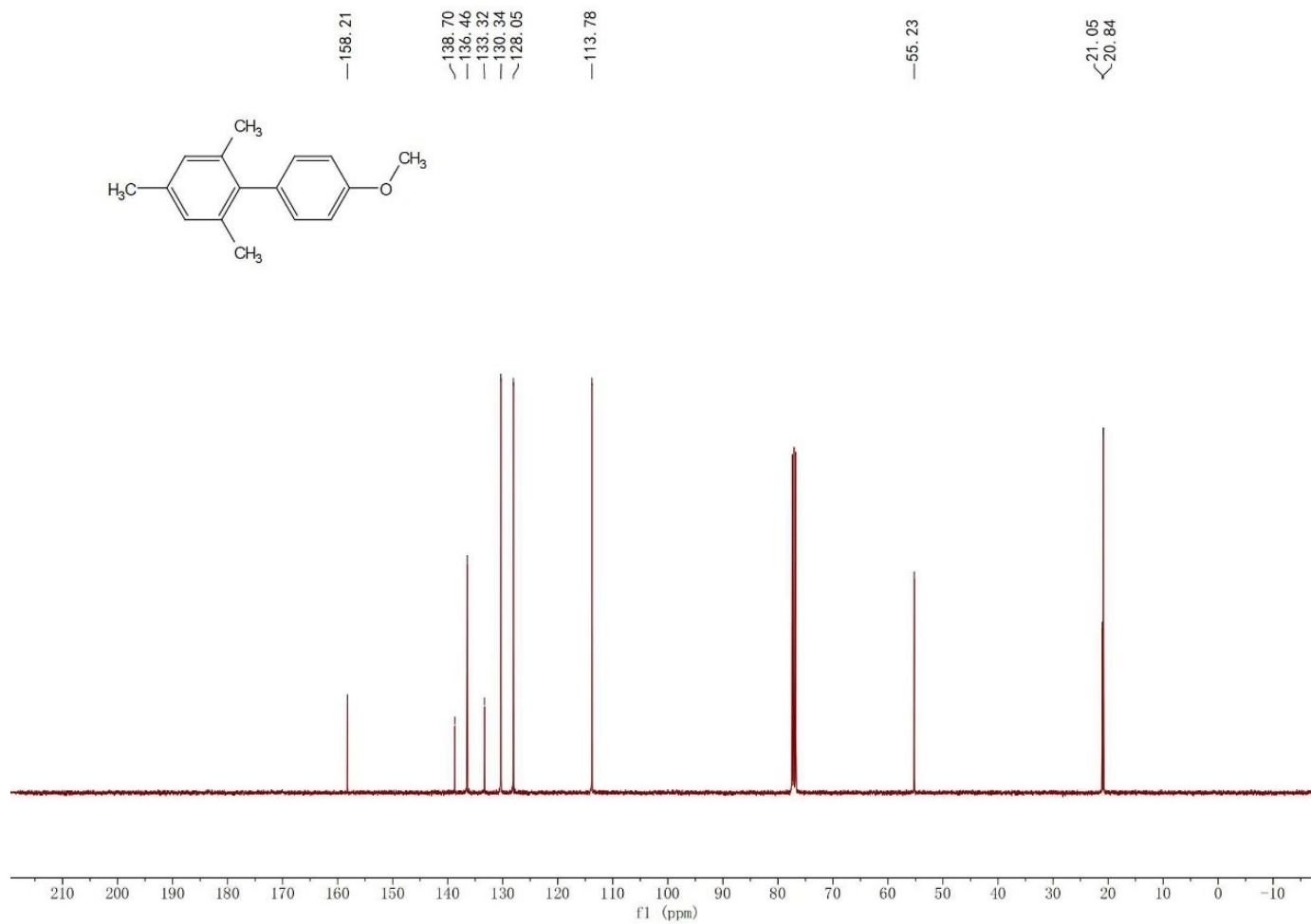
—141.34
128.87
127.37
127.28



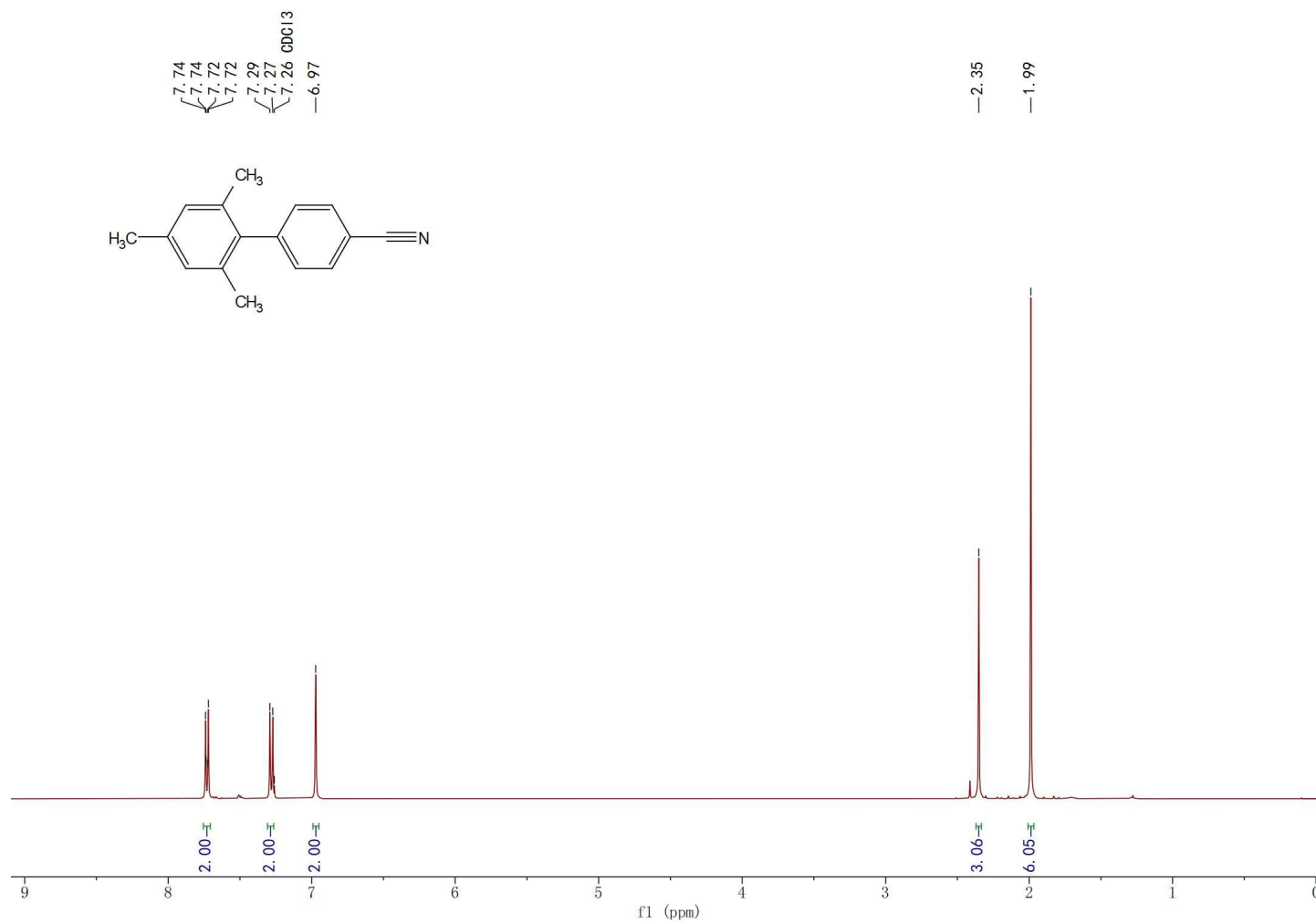
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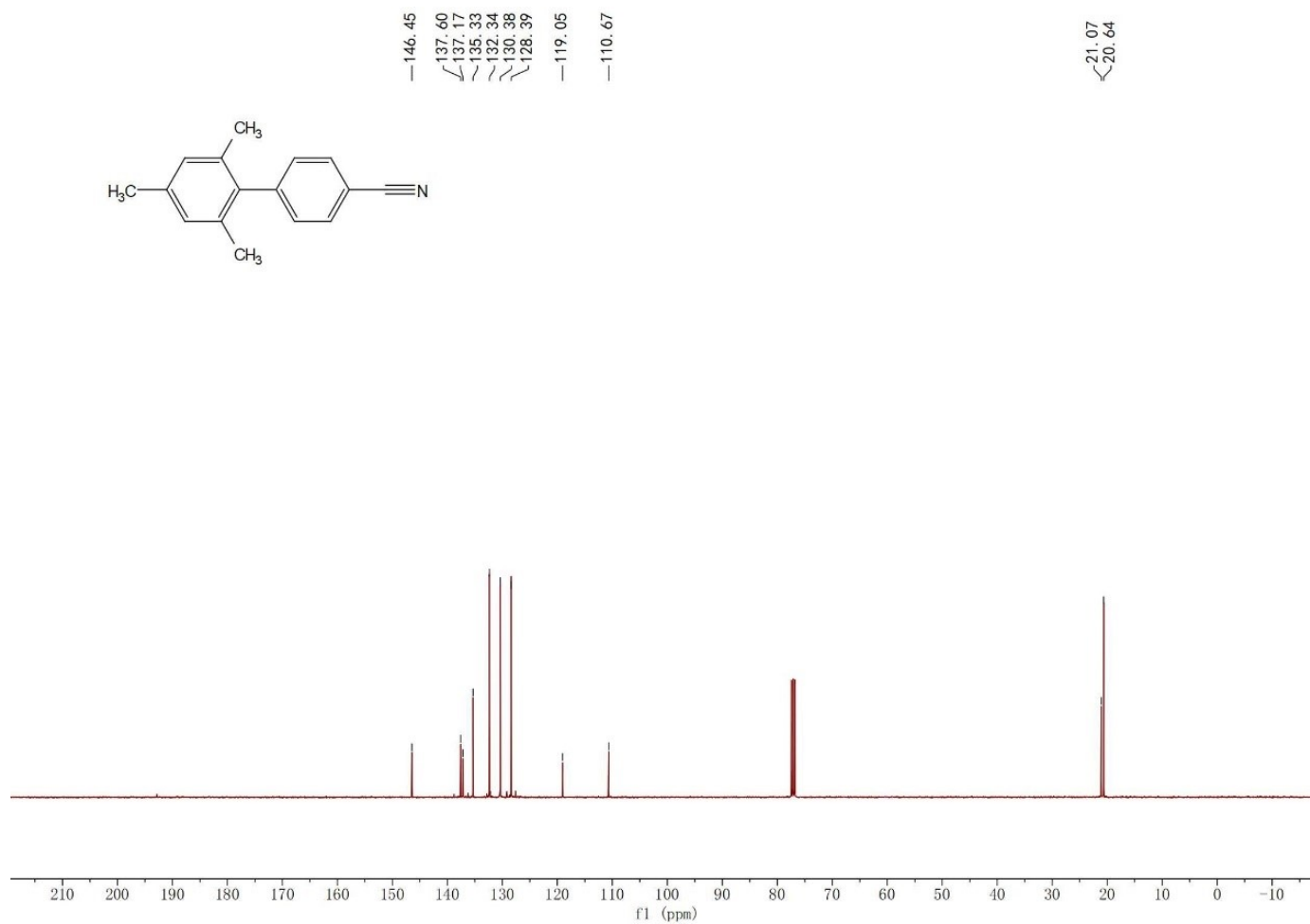
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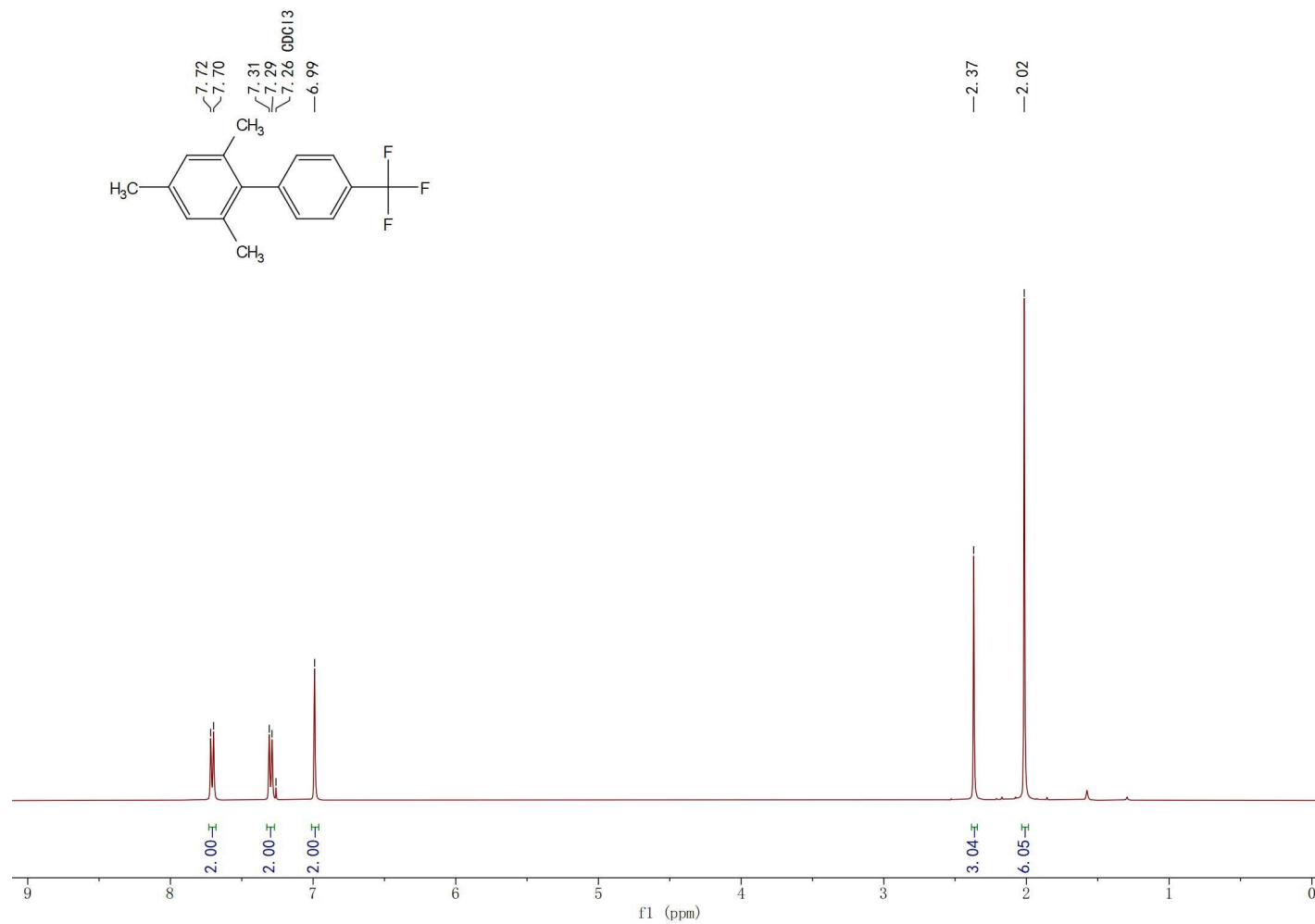
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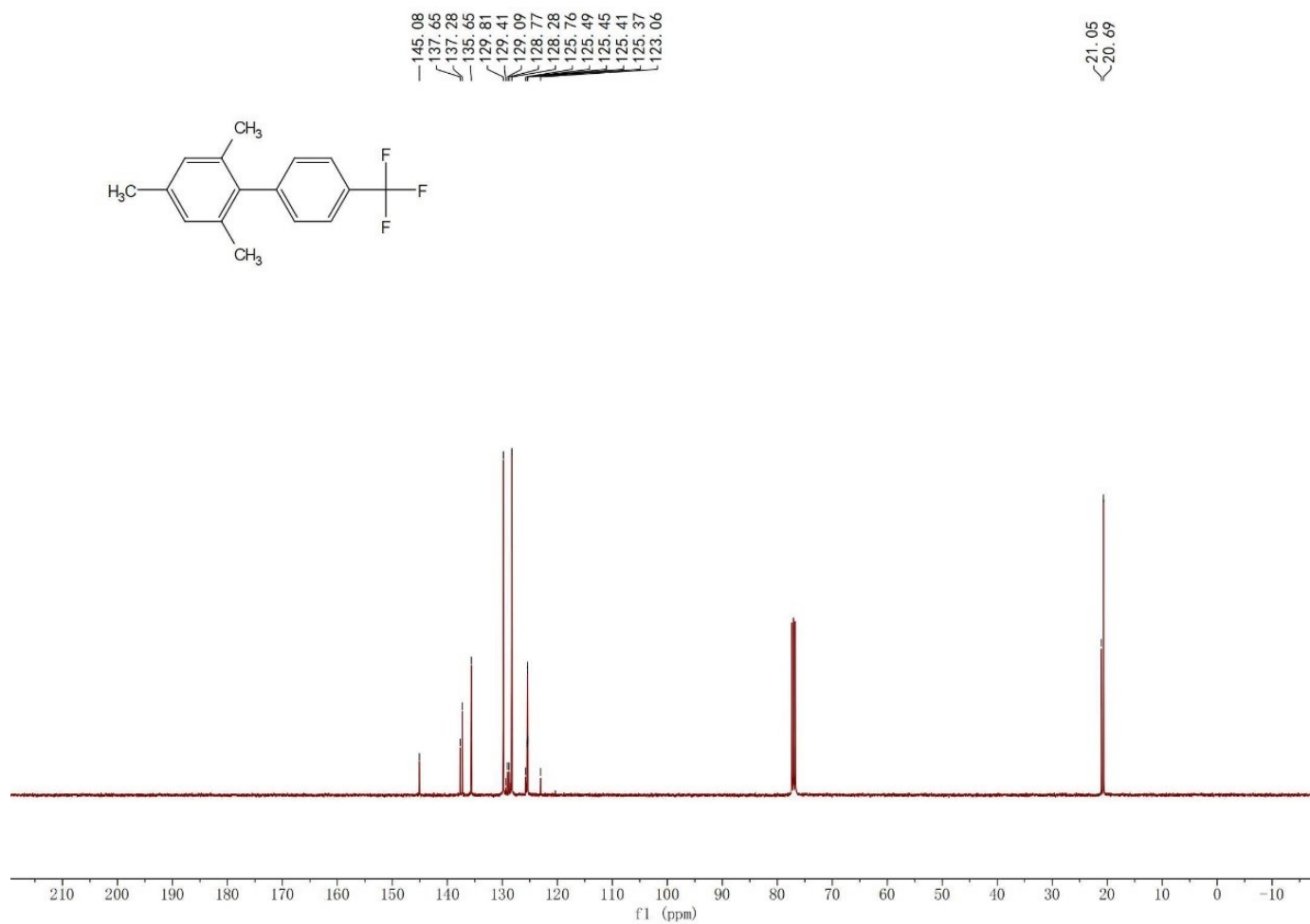
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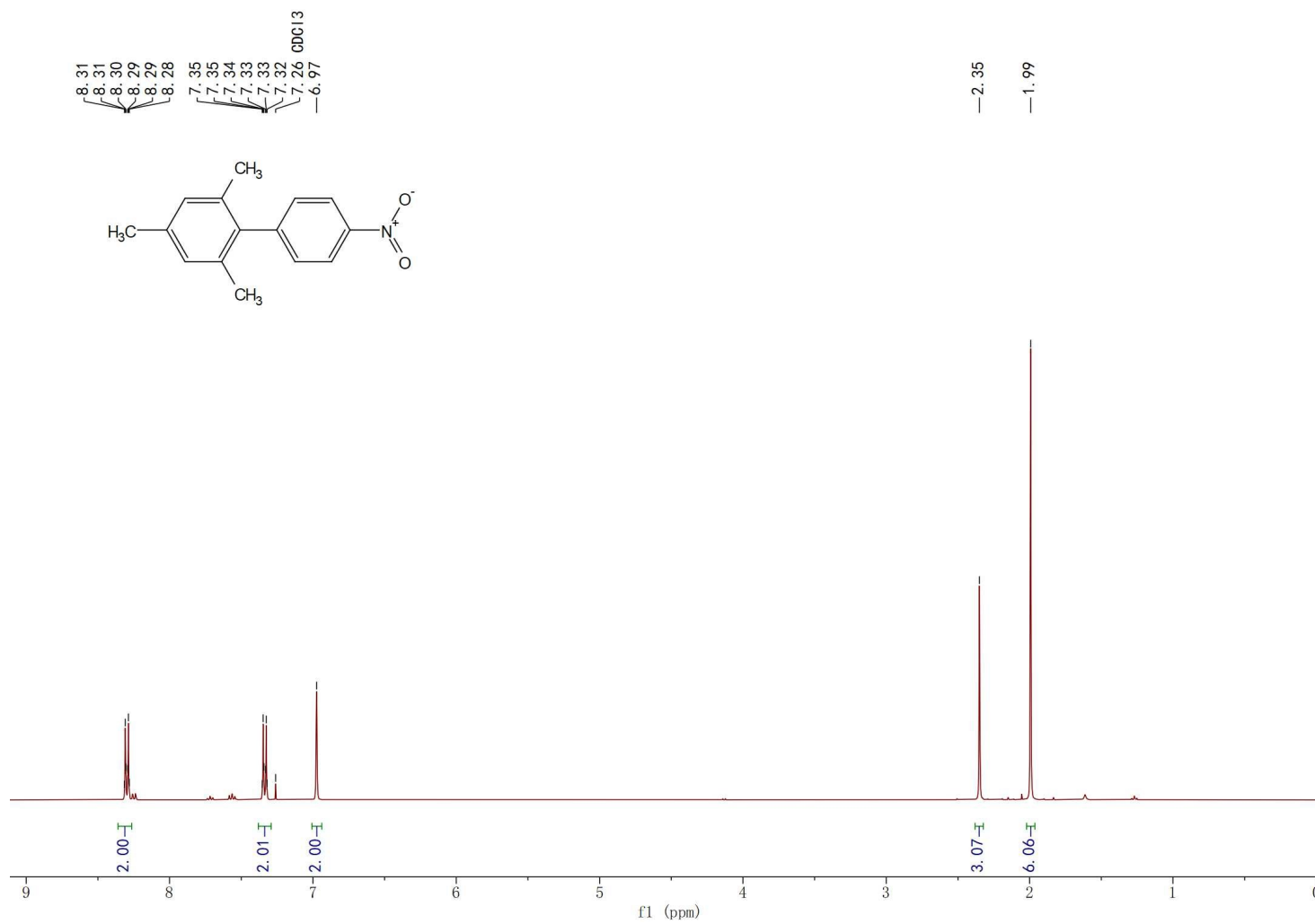
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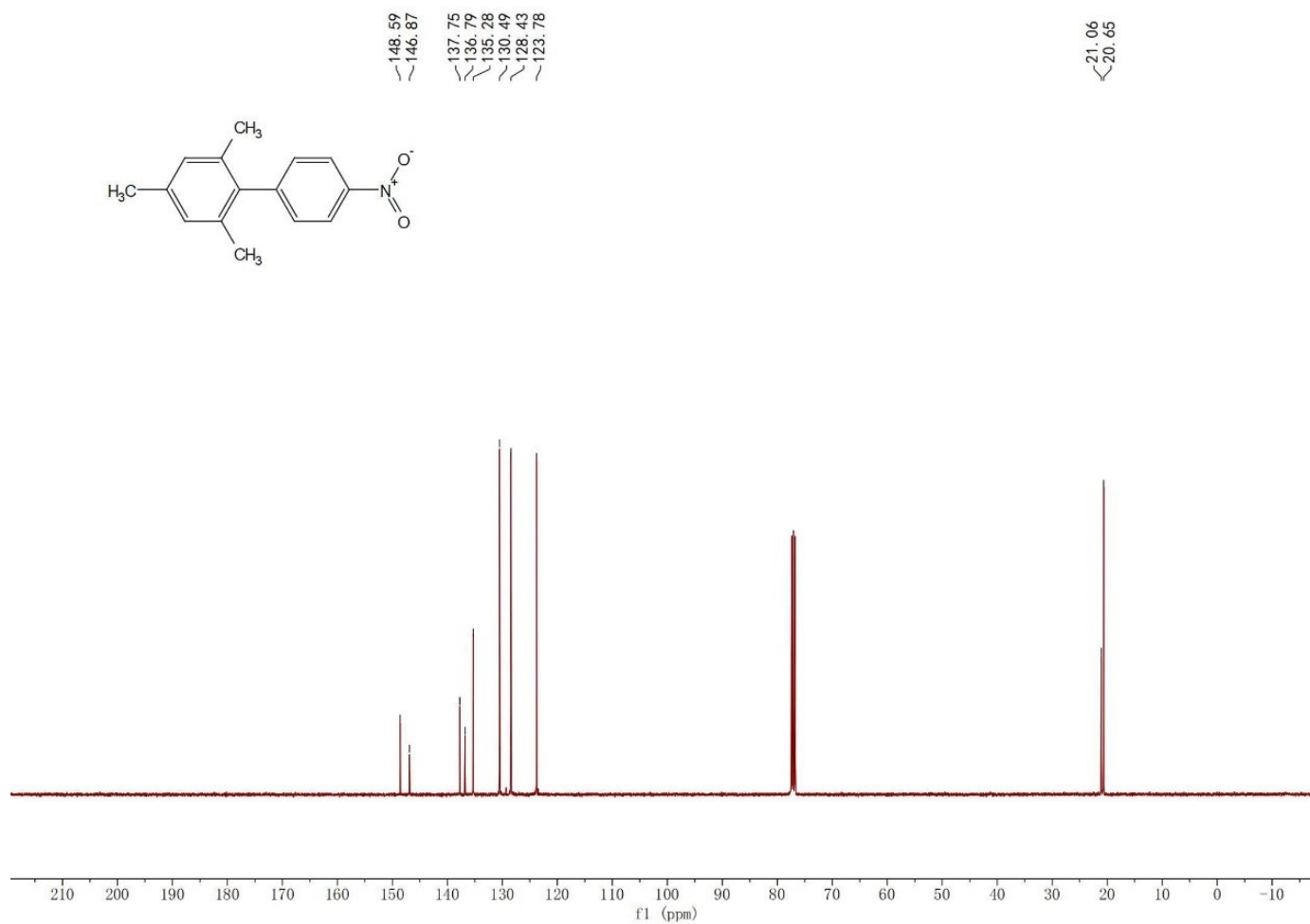
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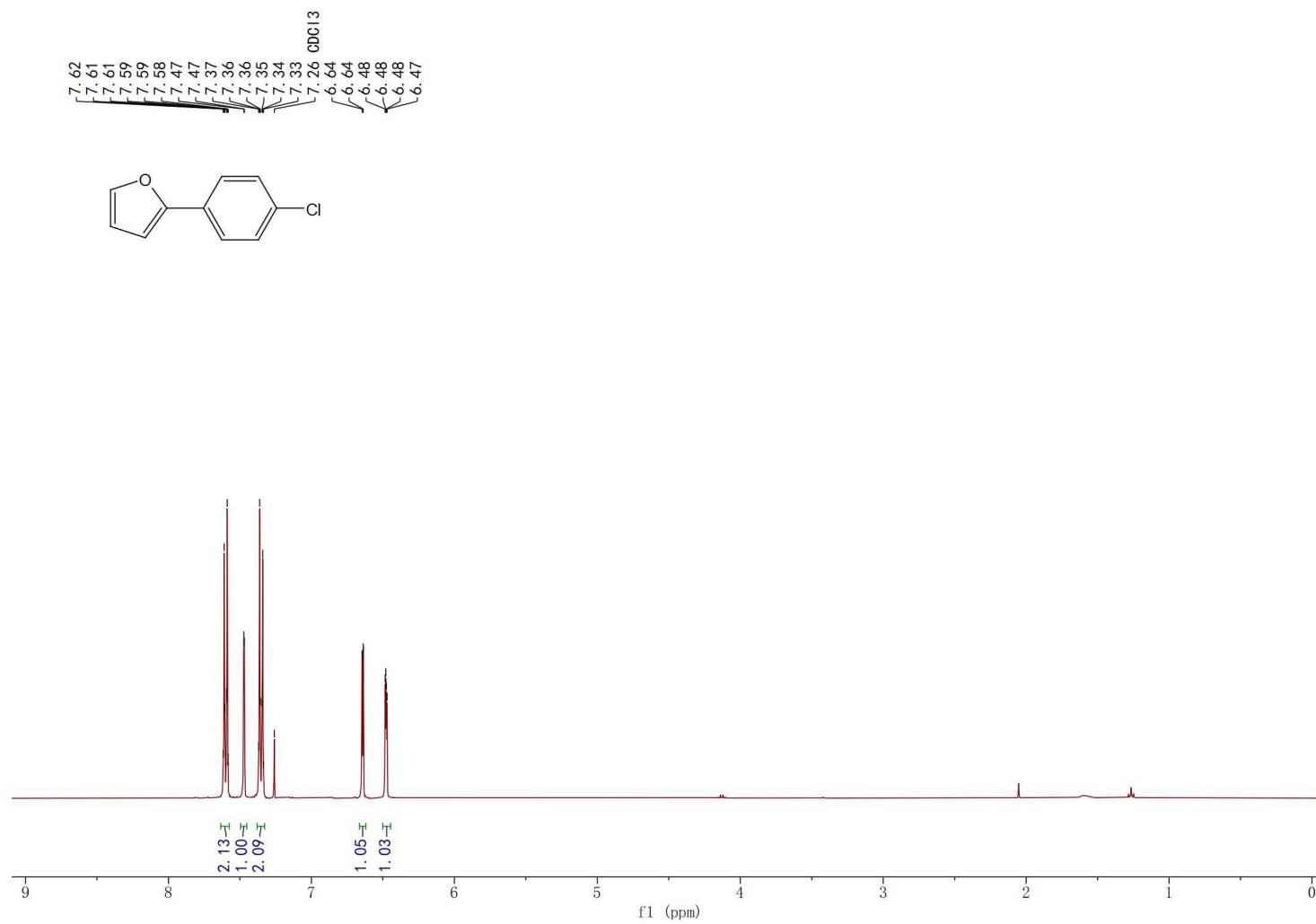
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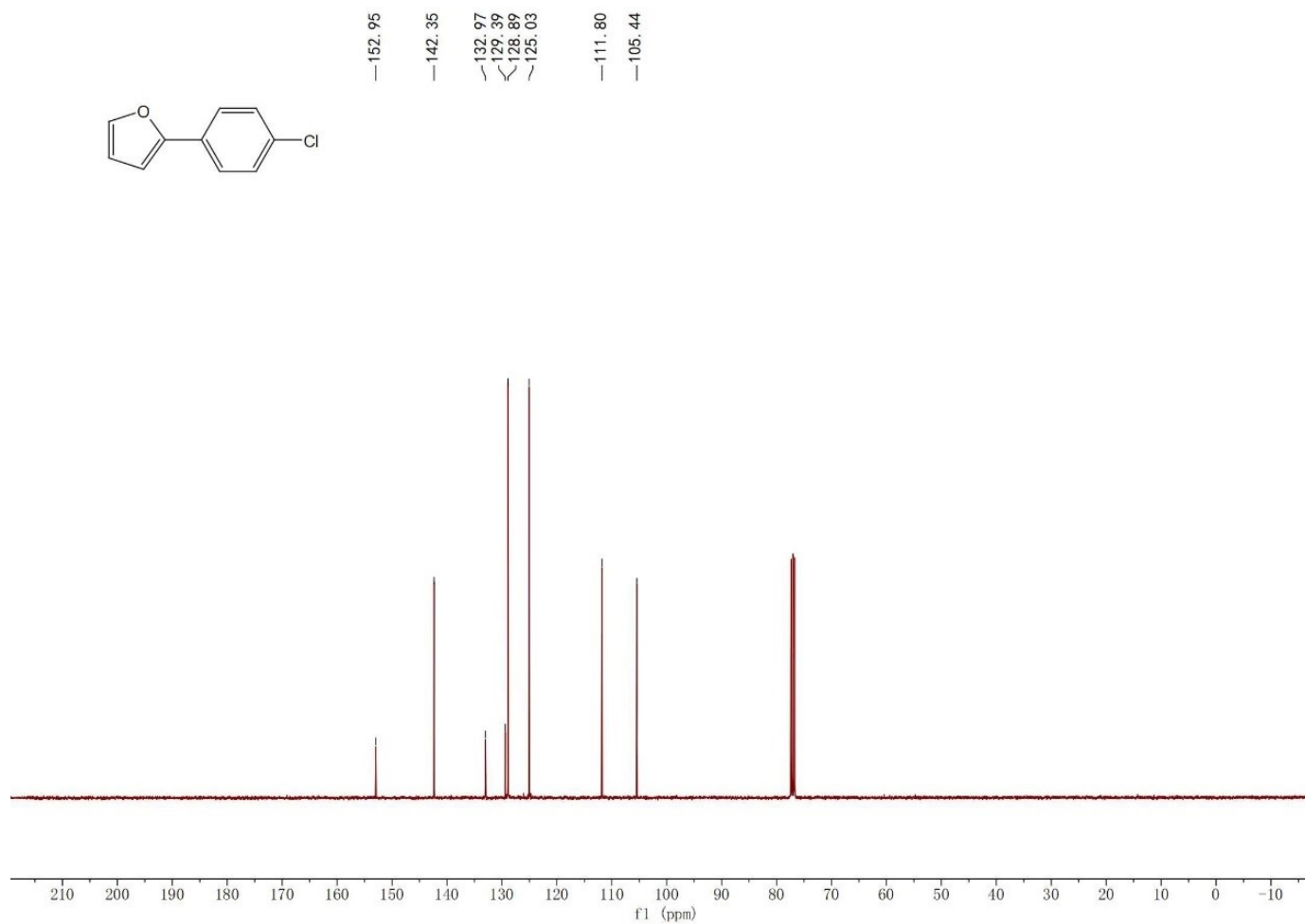
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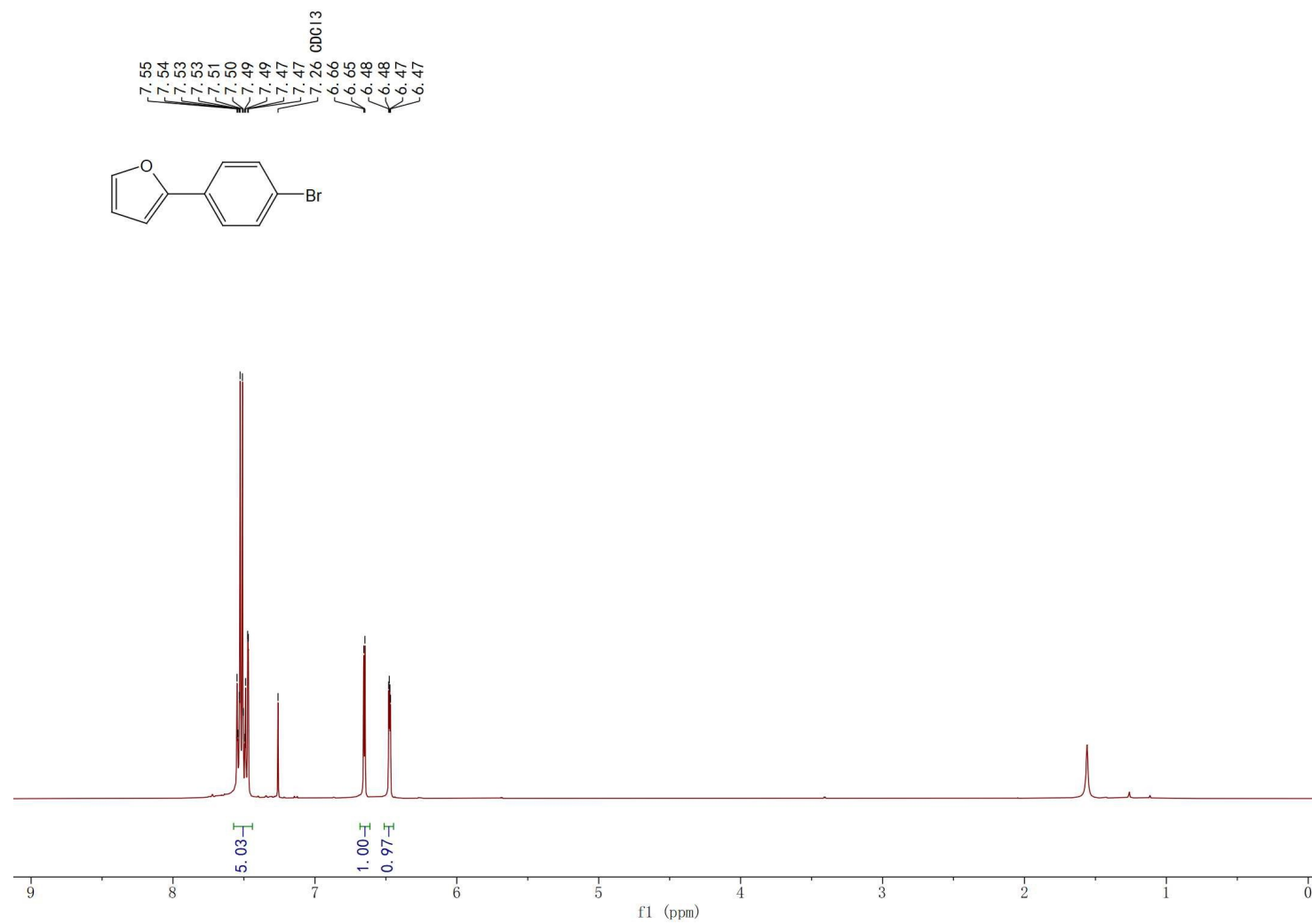
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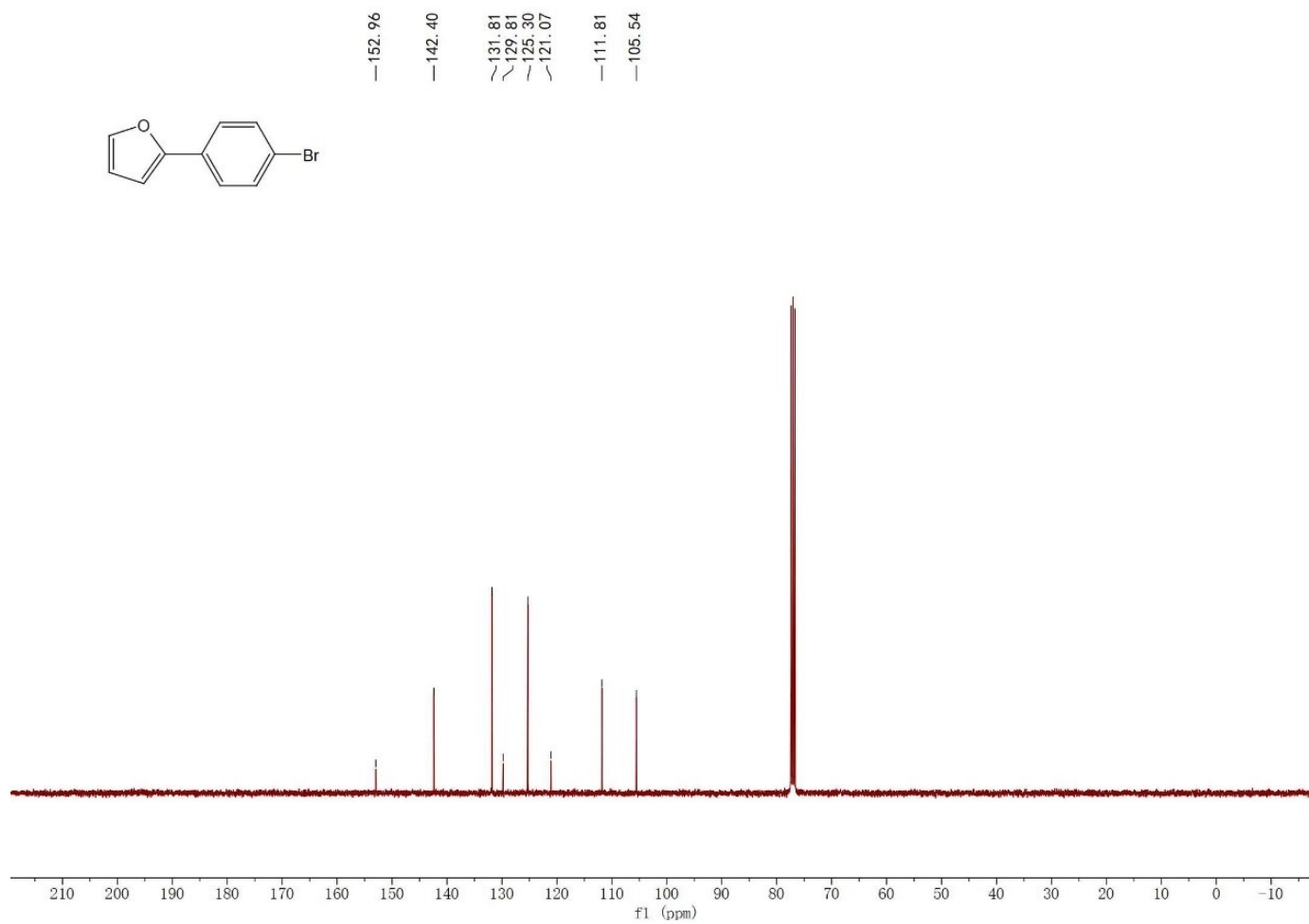
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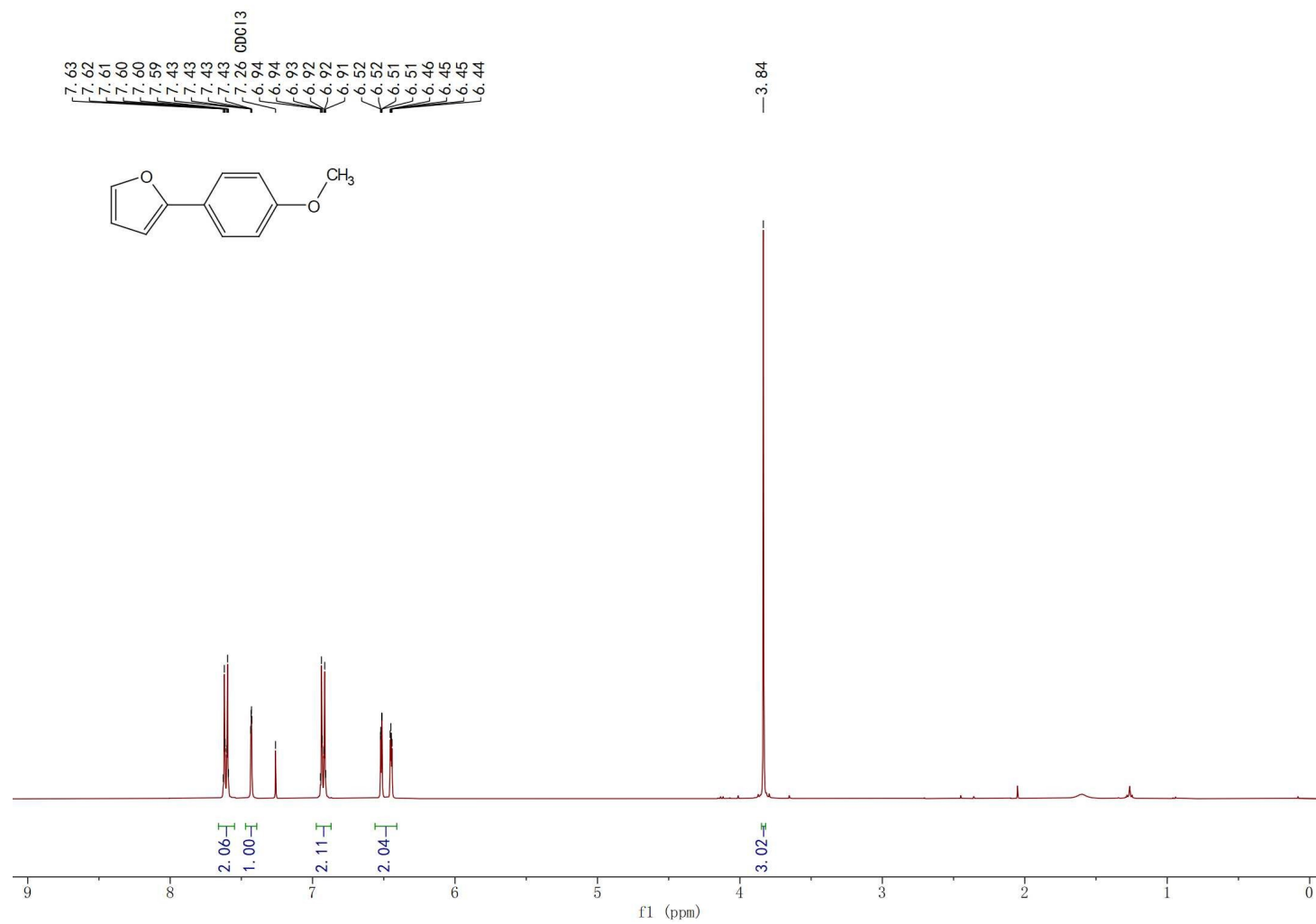
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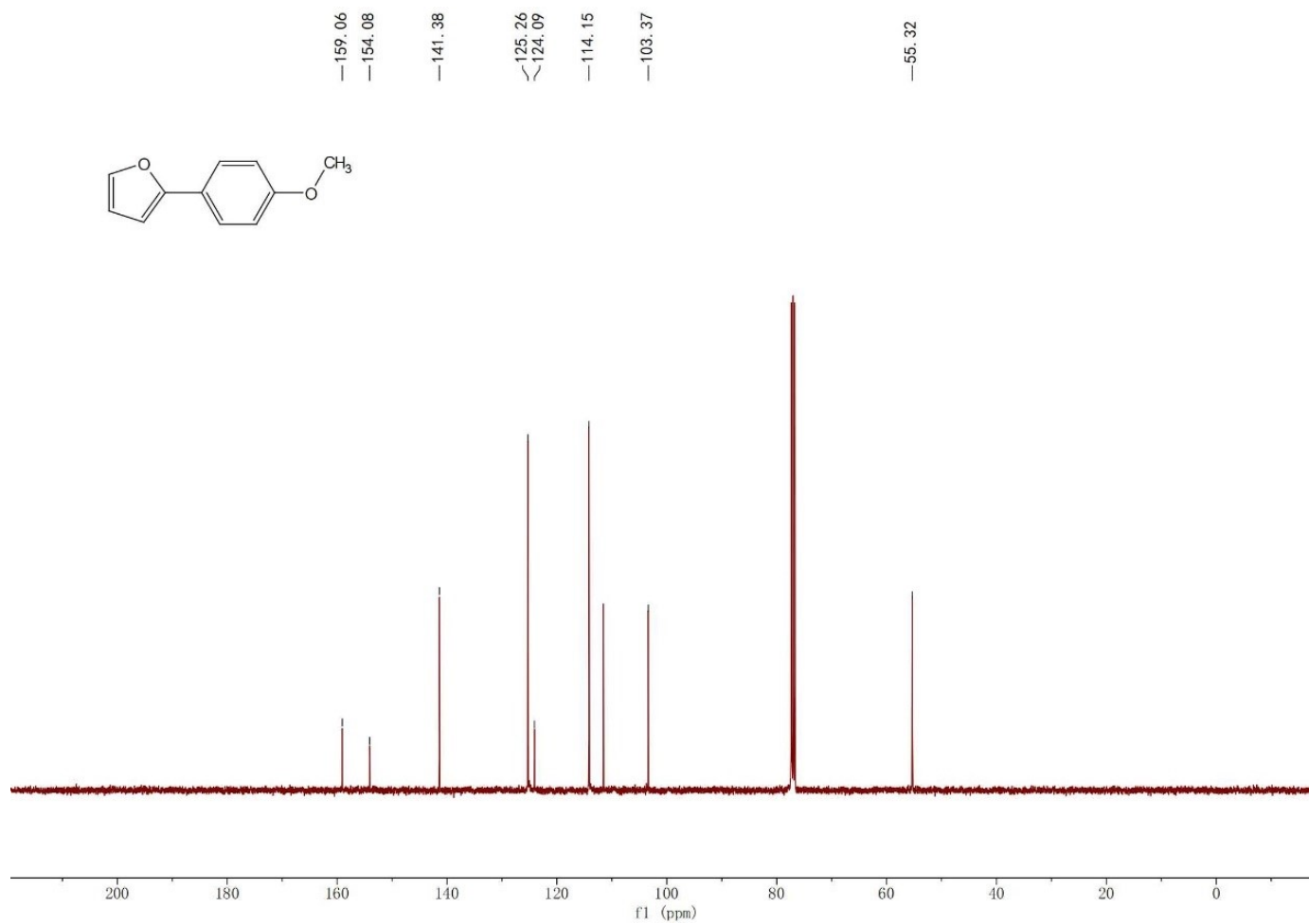
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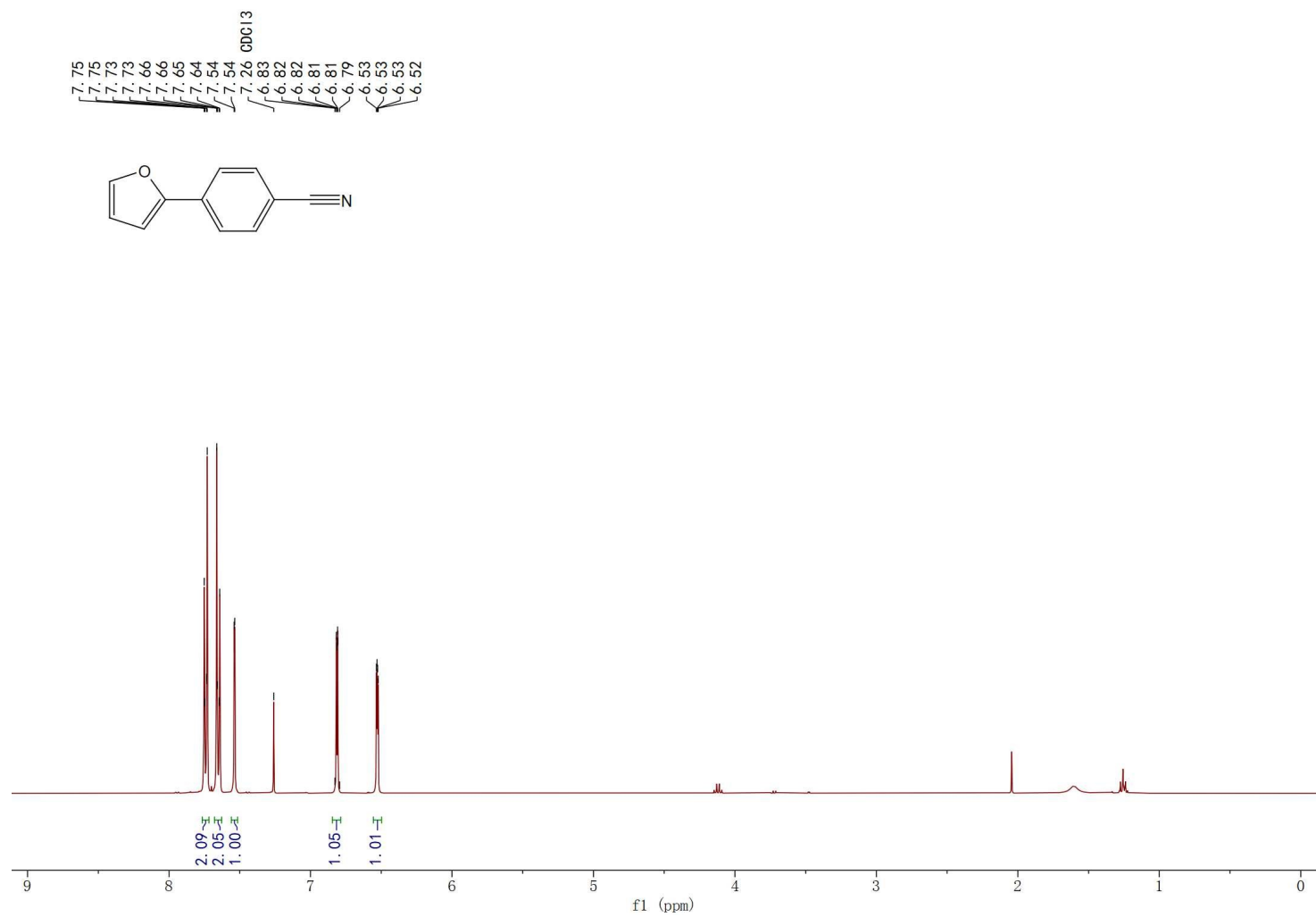
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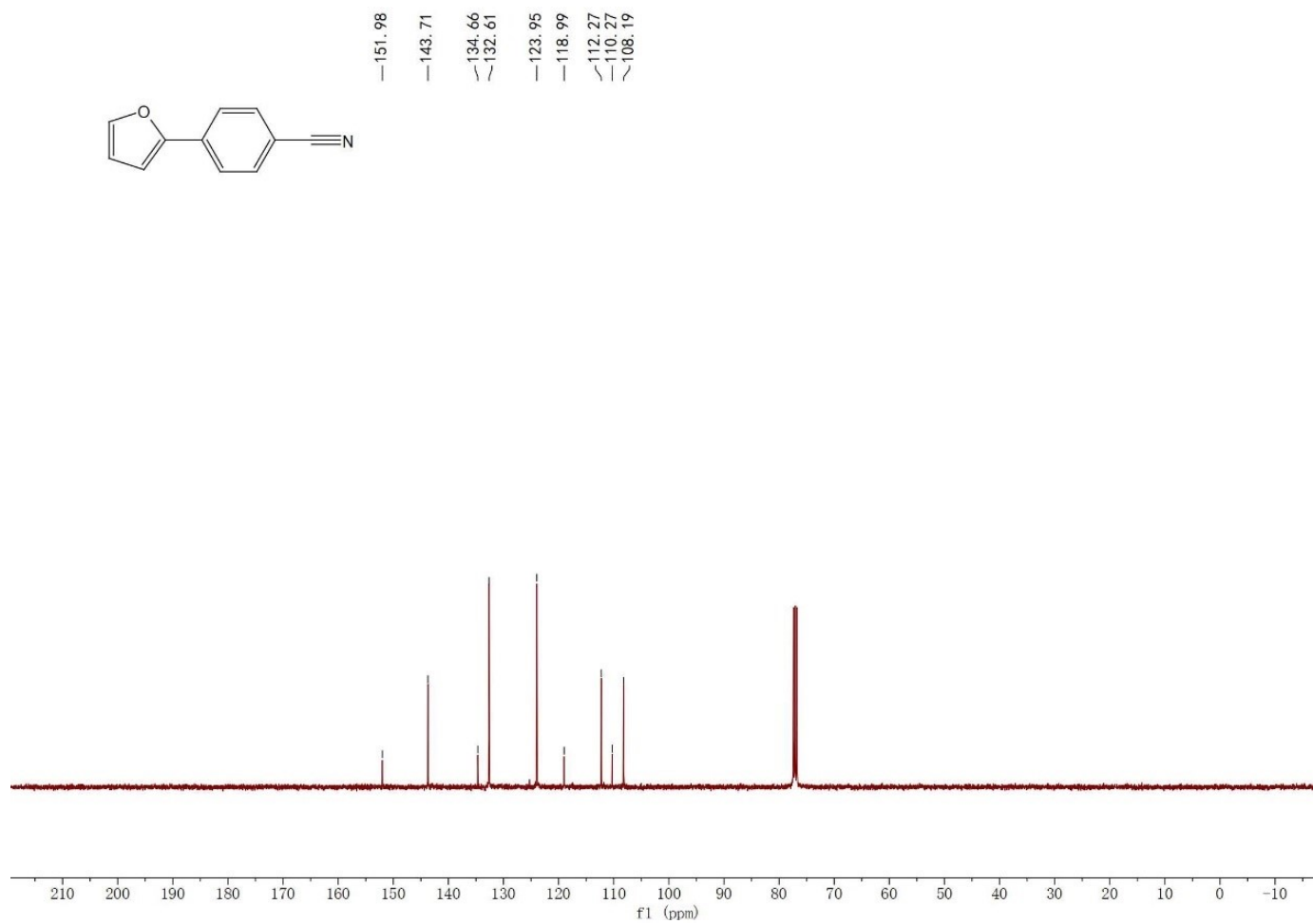
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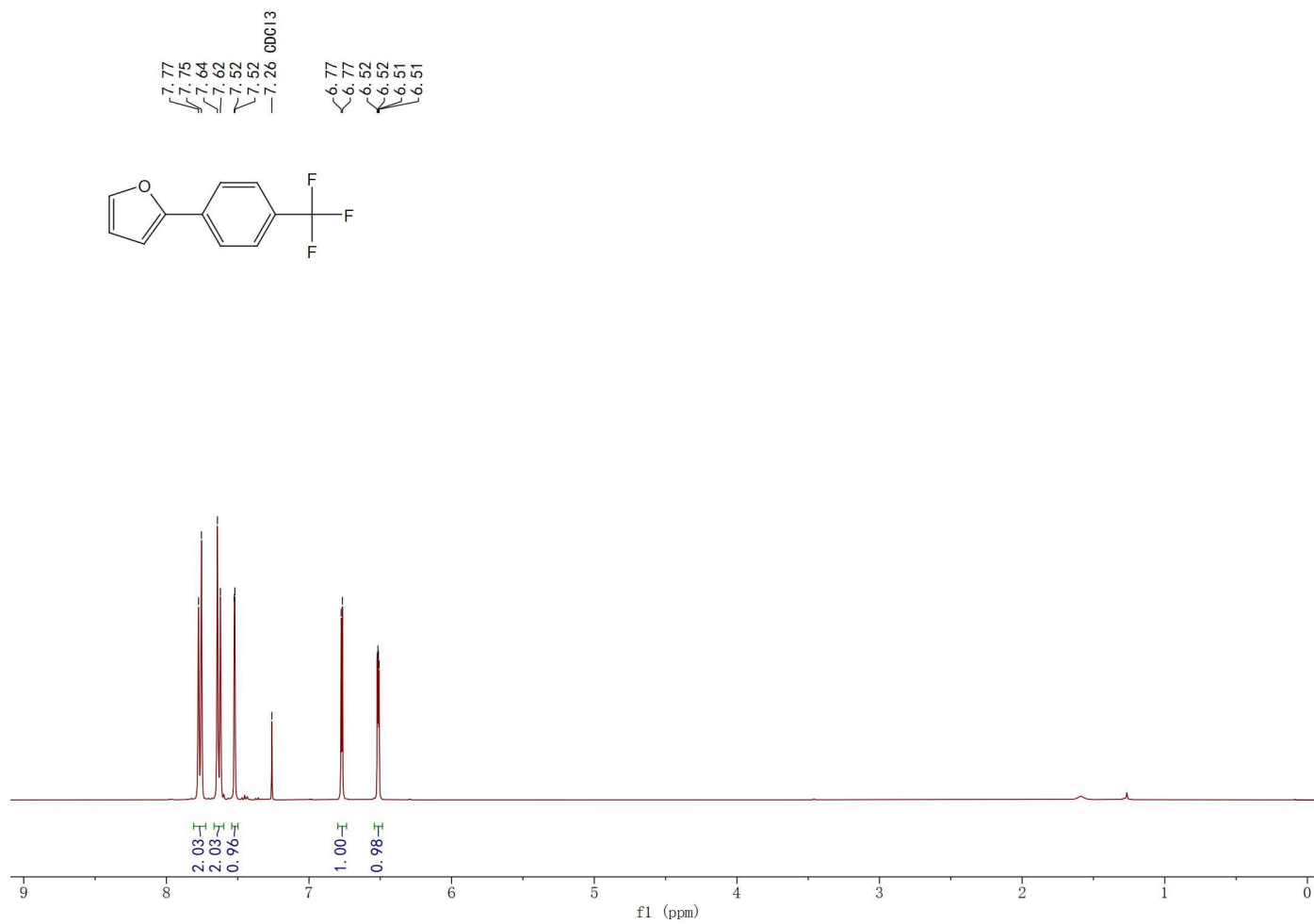
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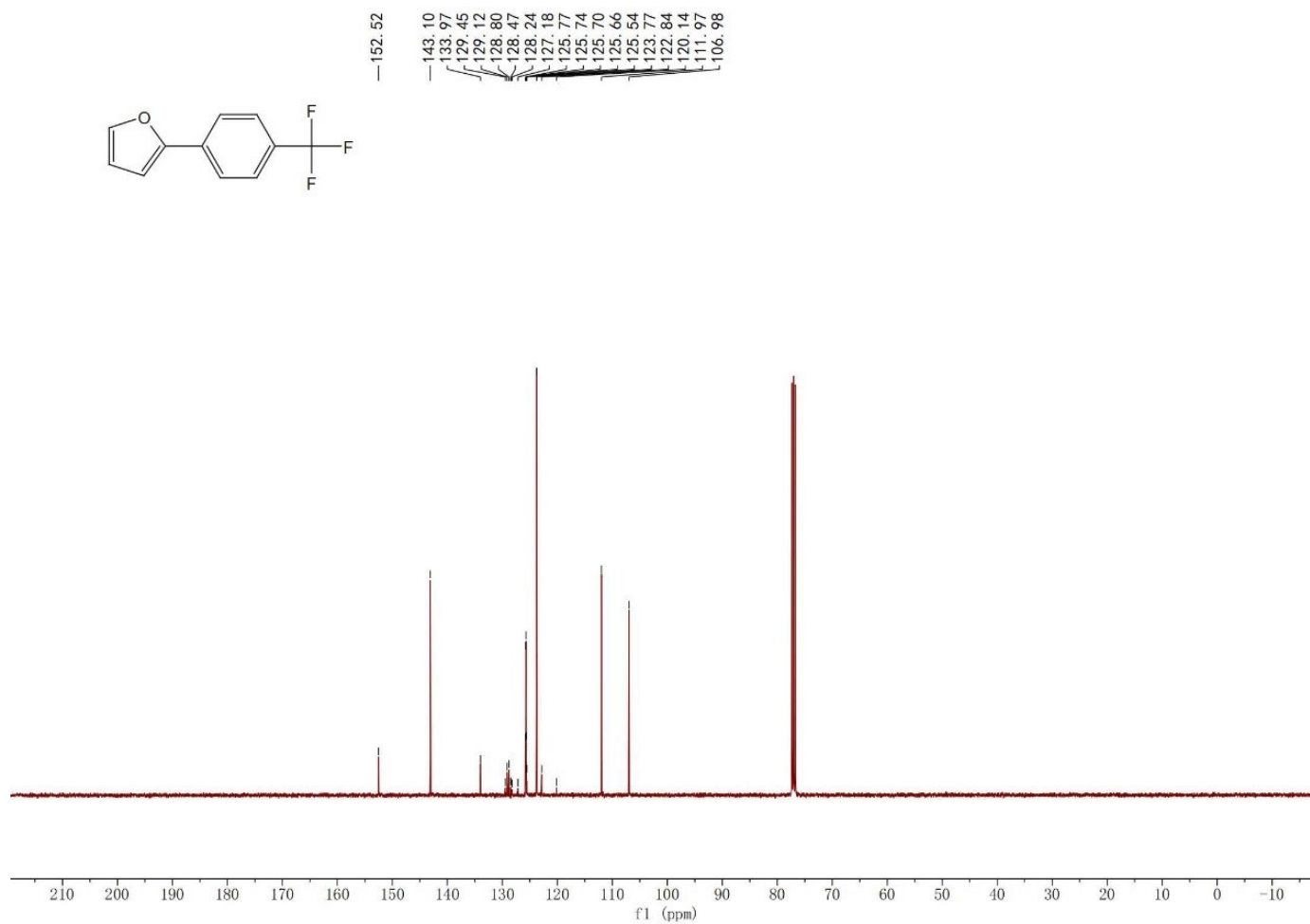
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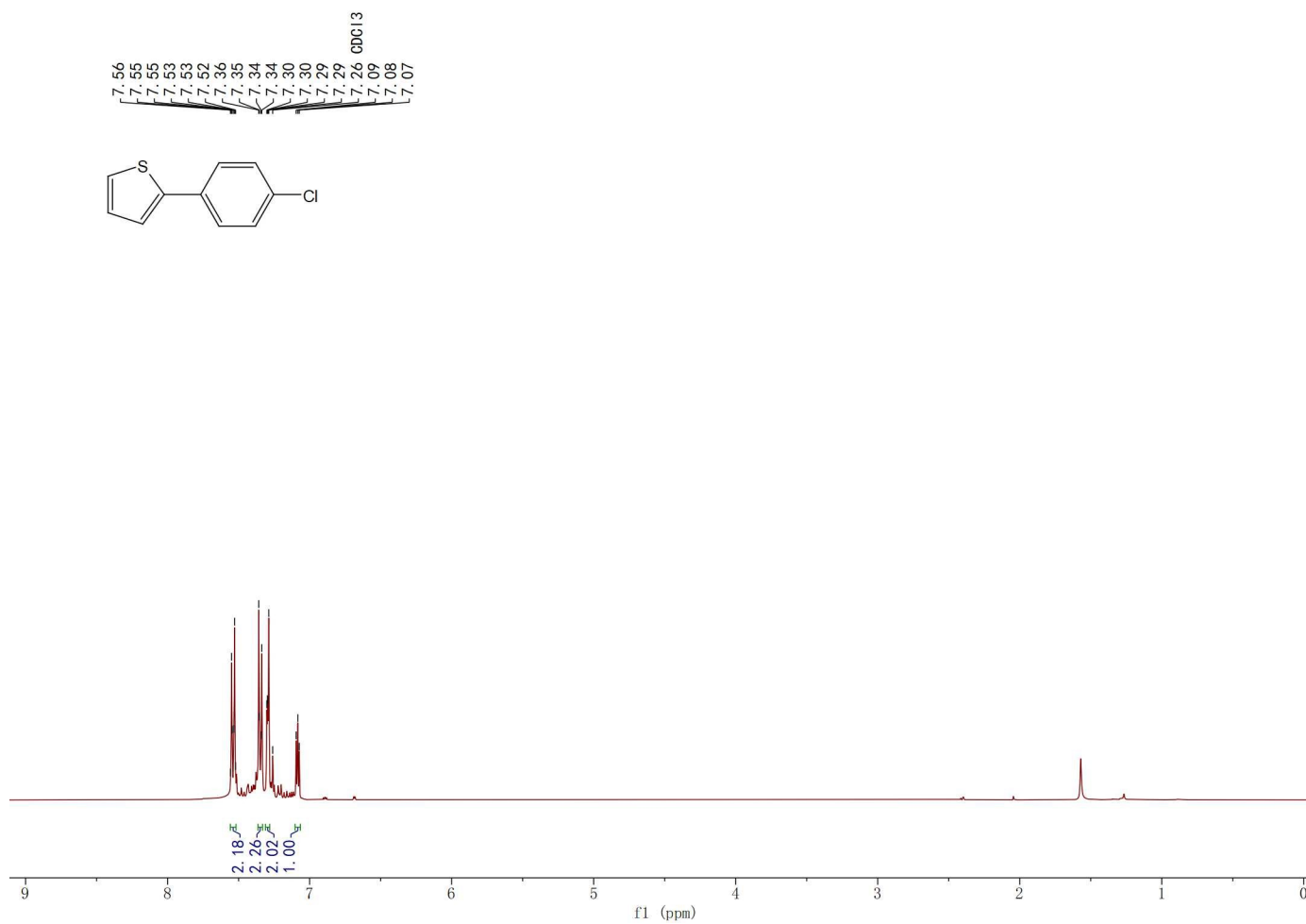
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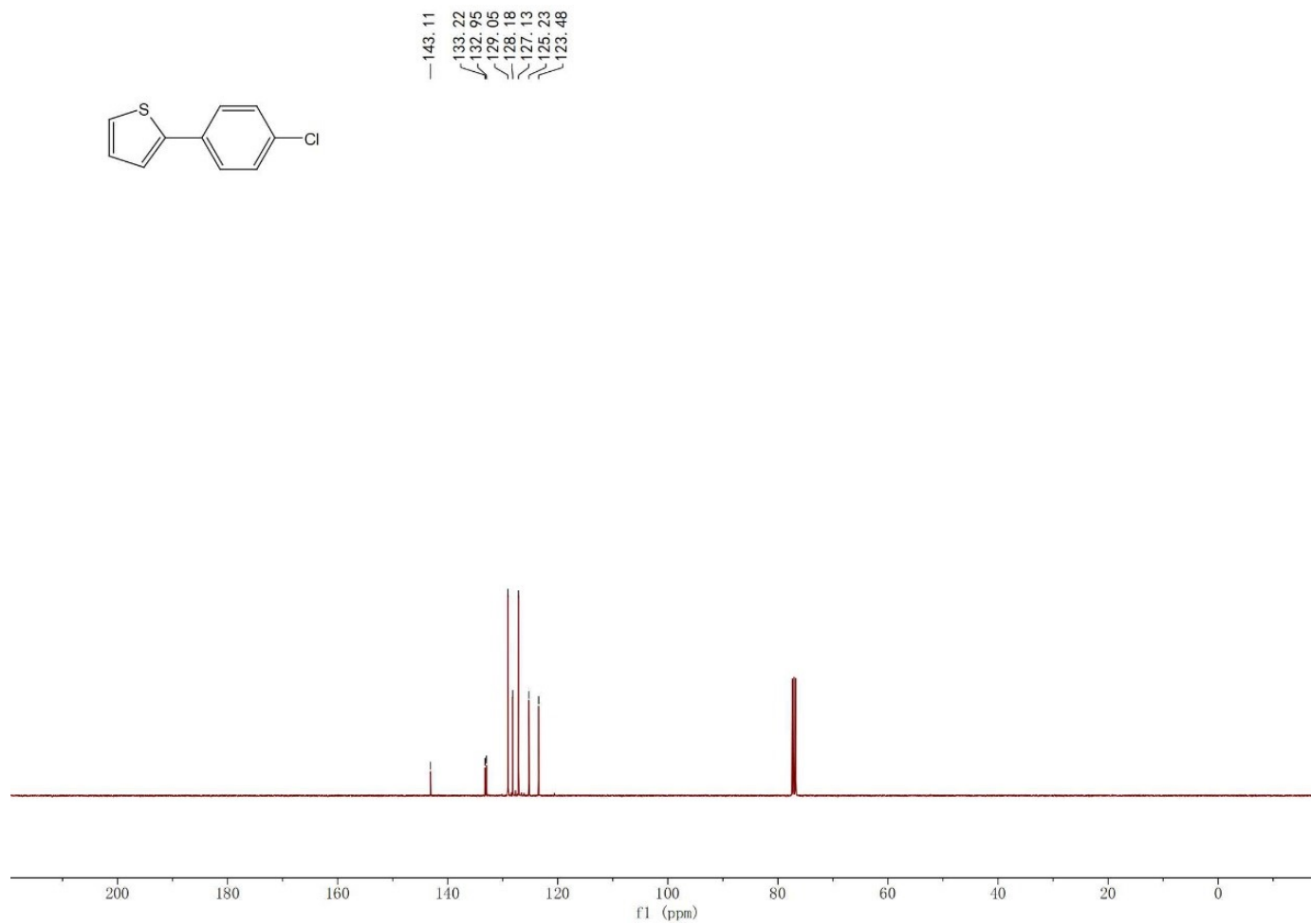
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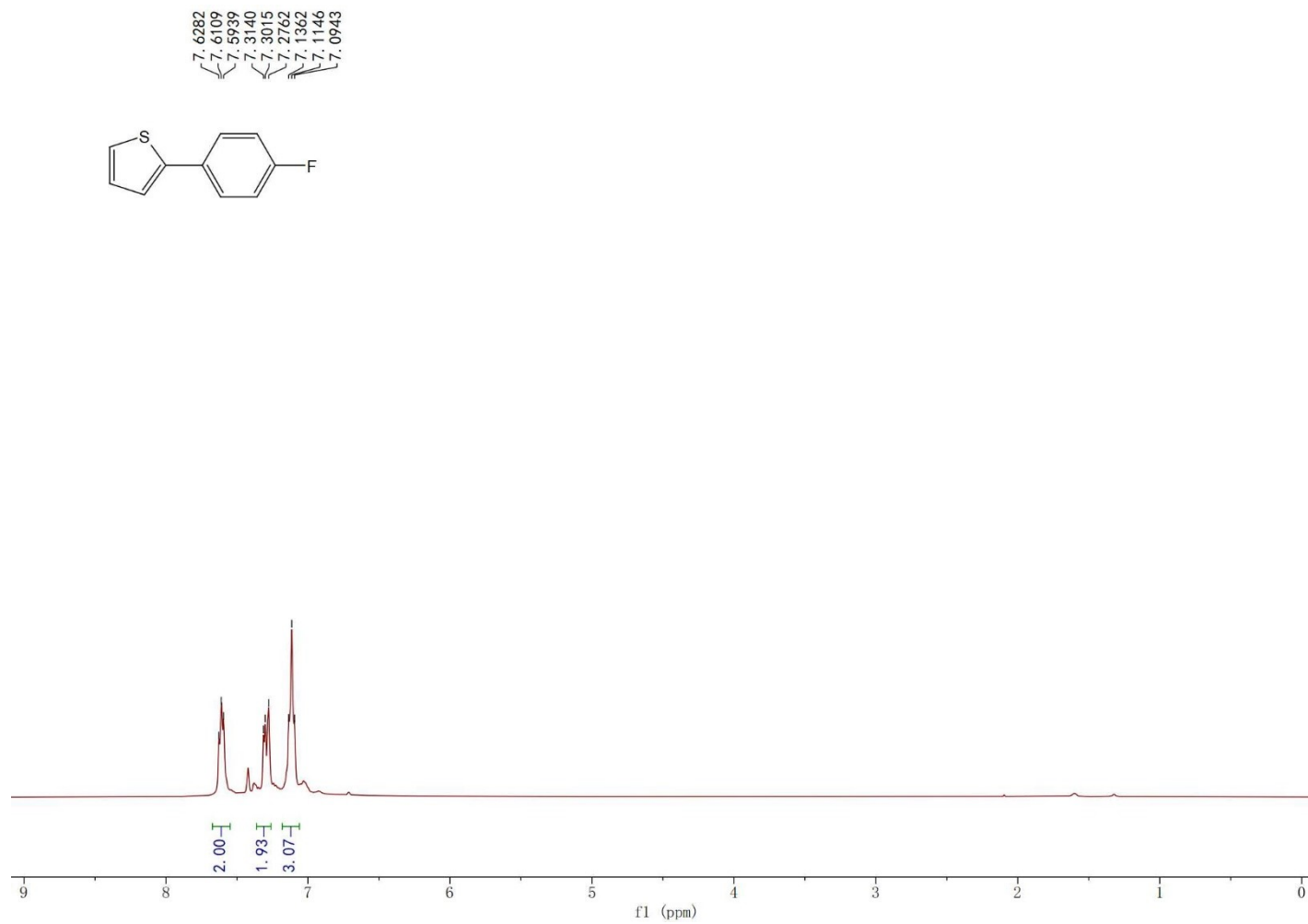
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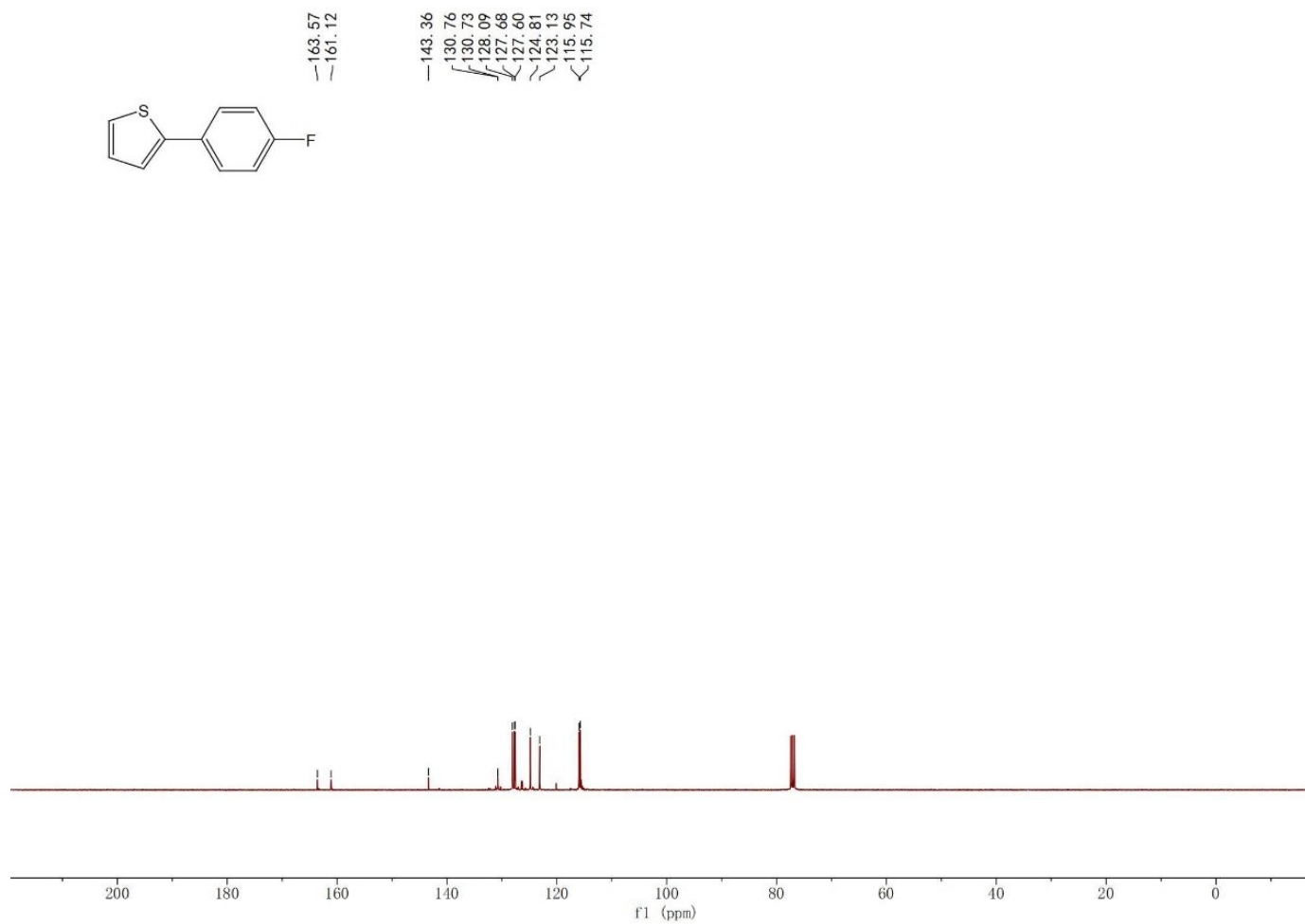
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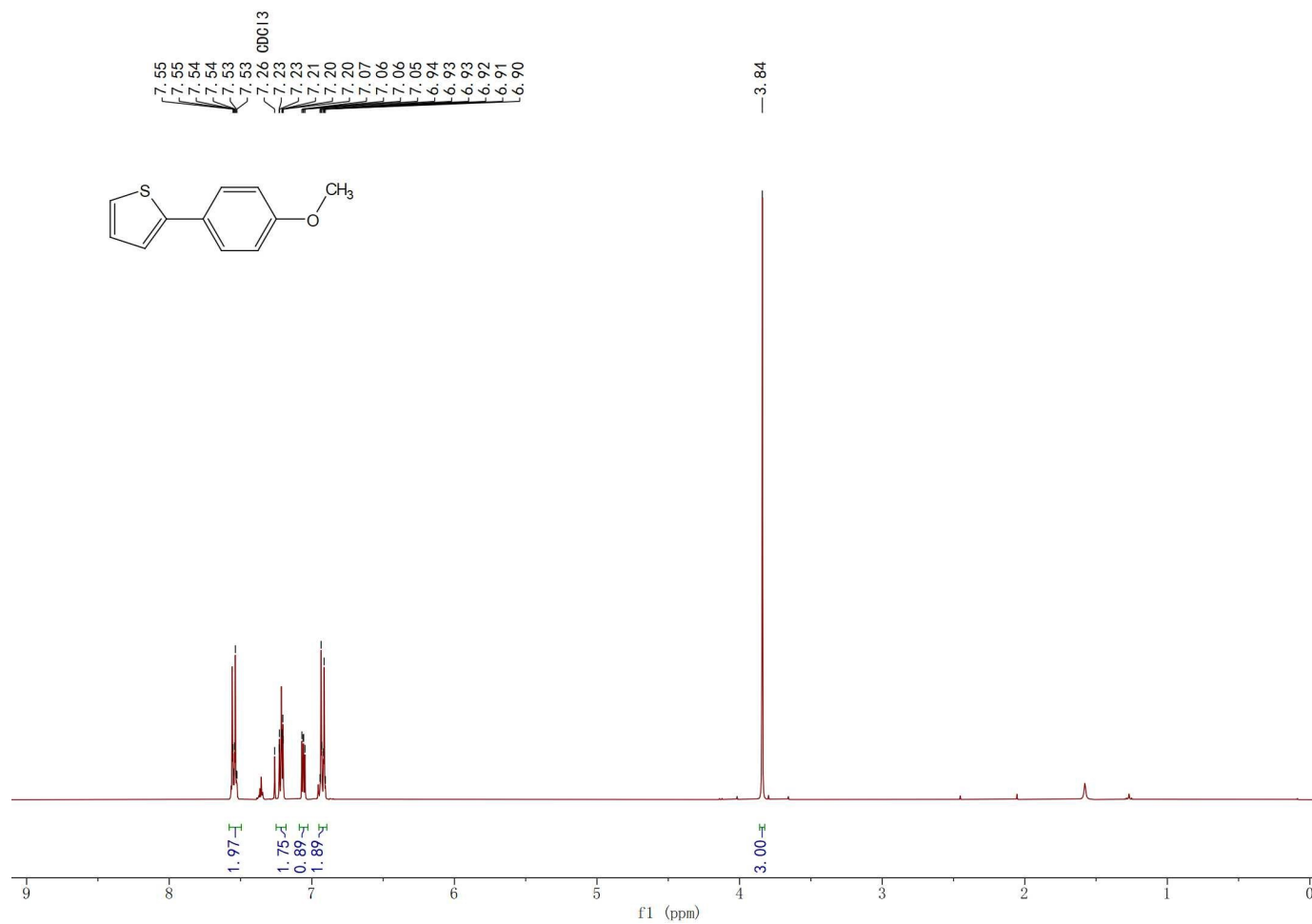
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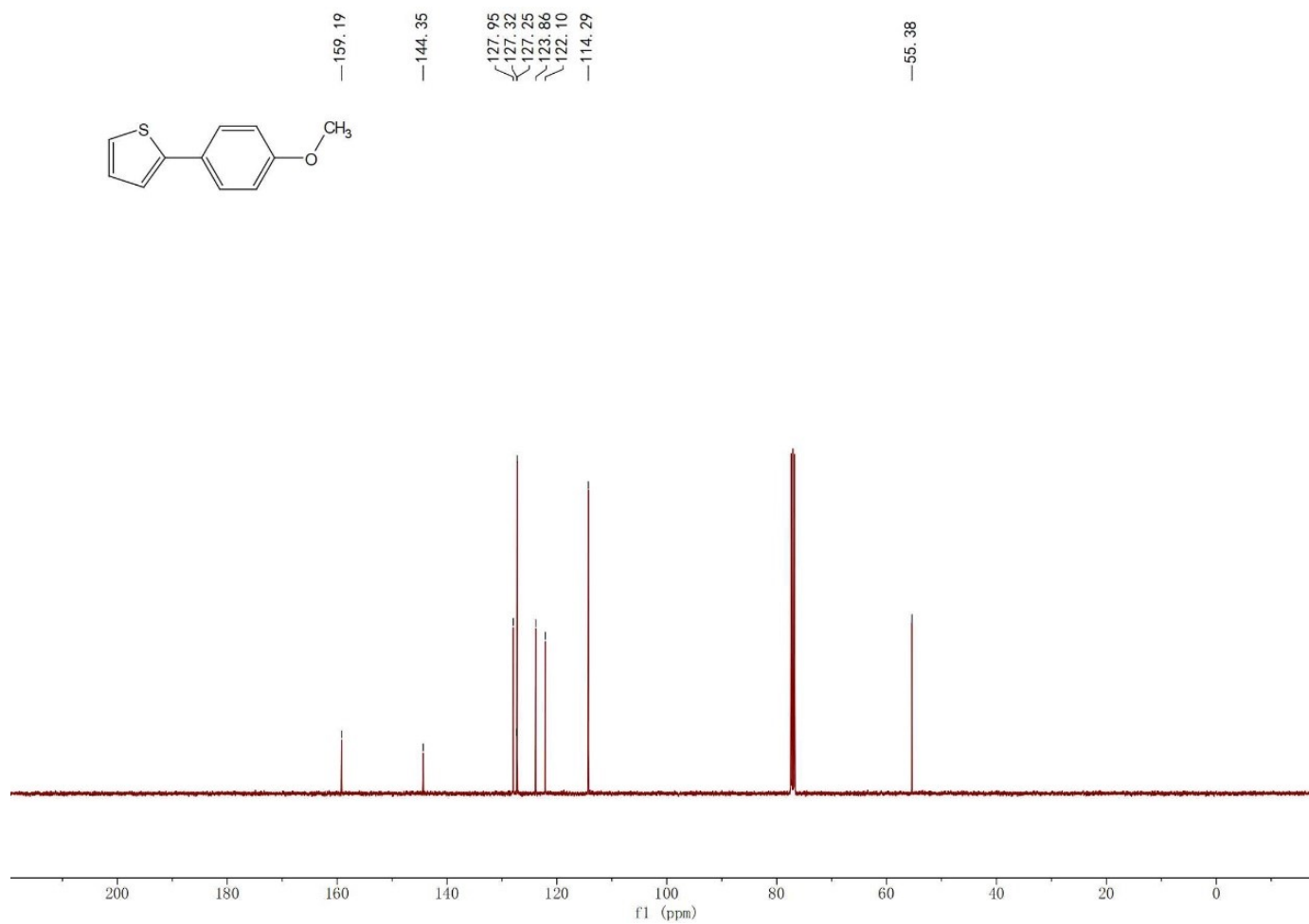
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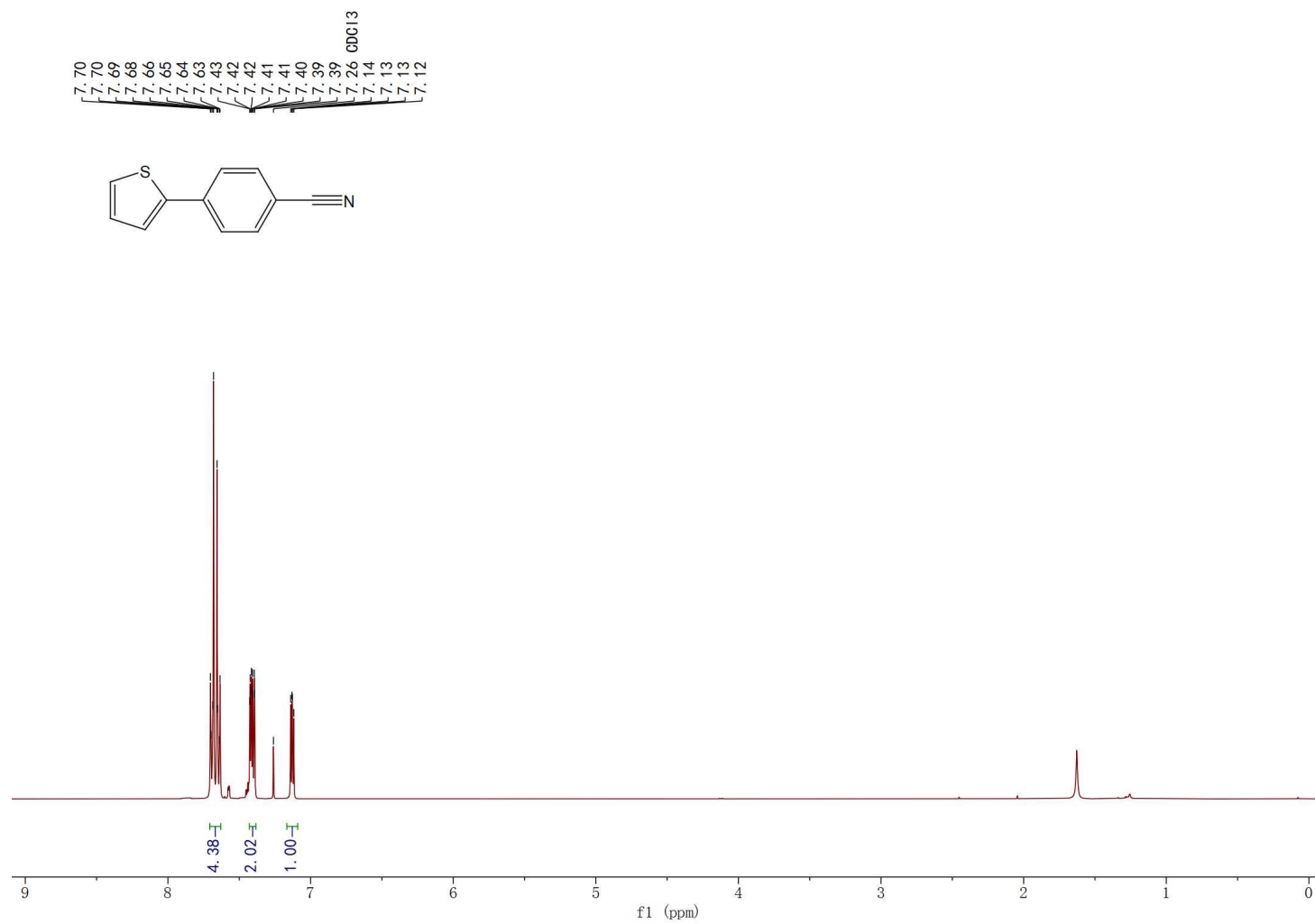
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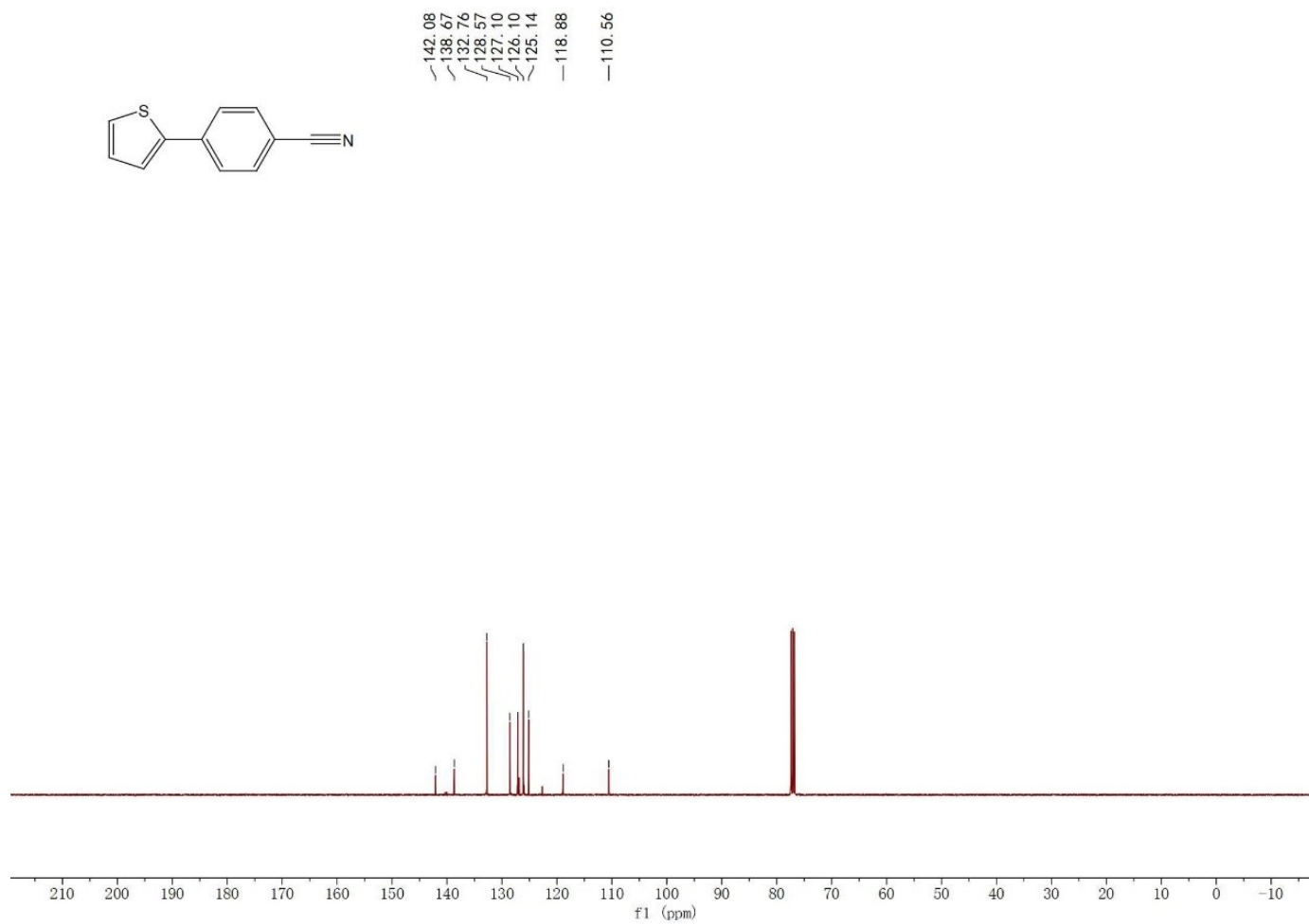
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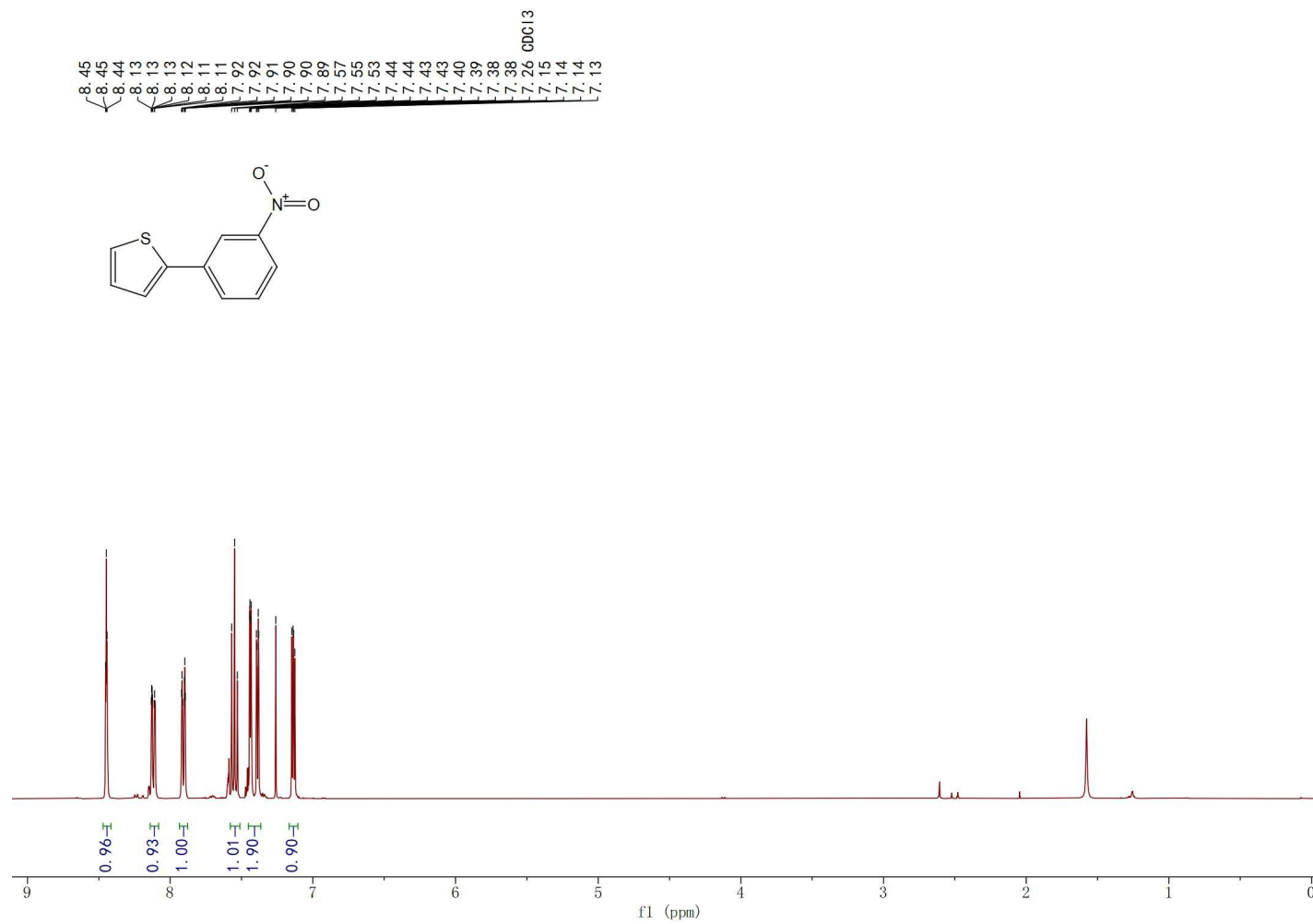
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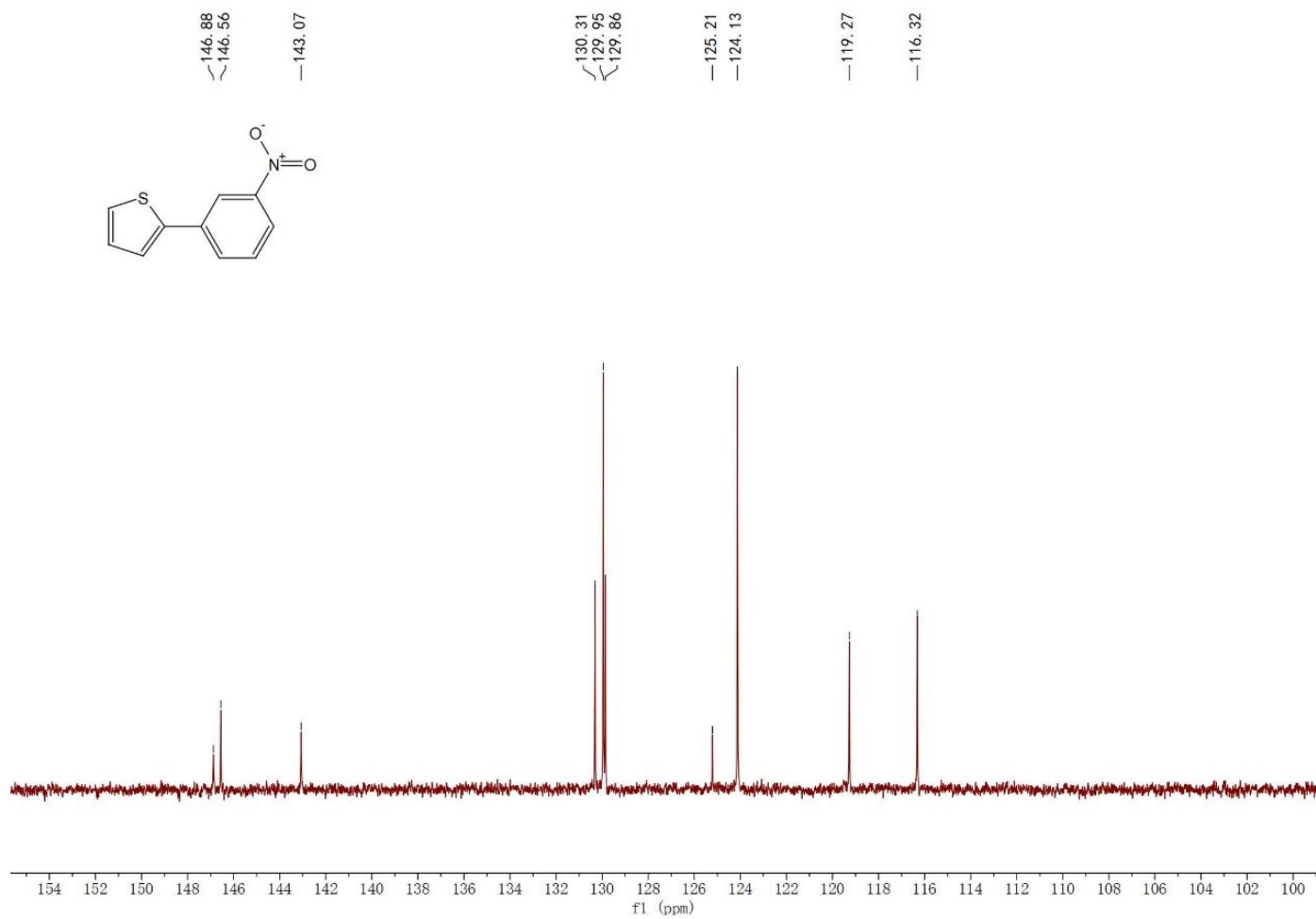
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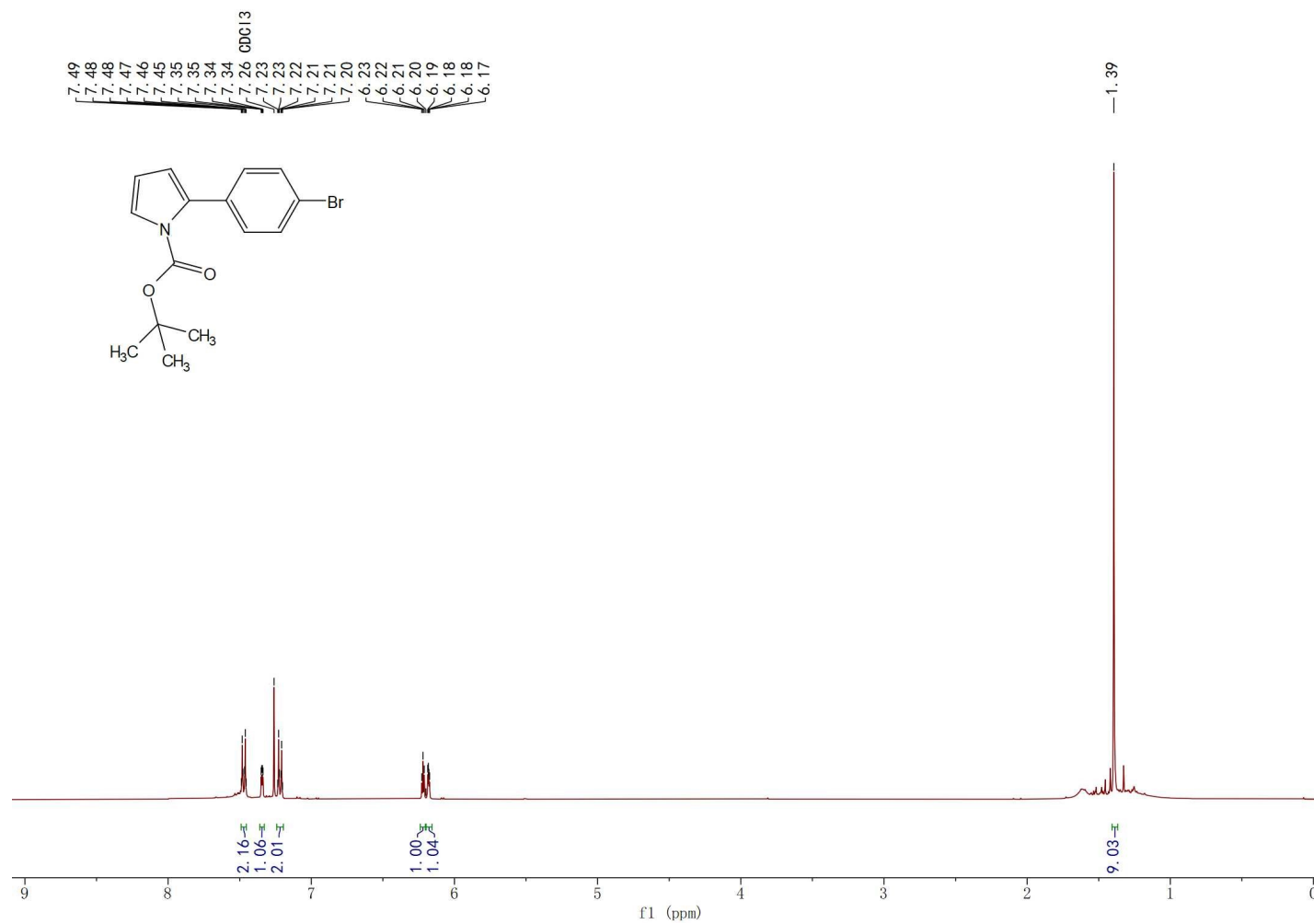
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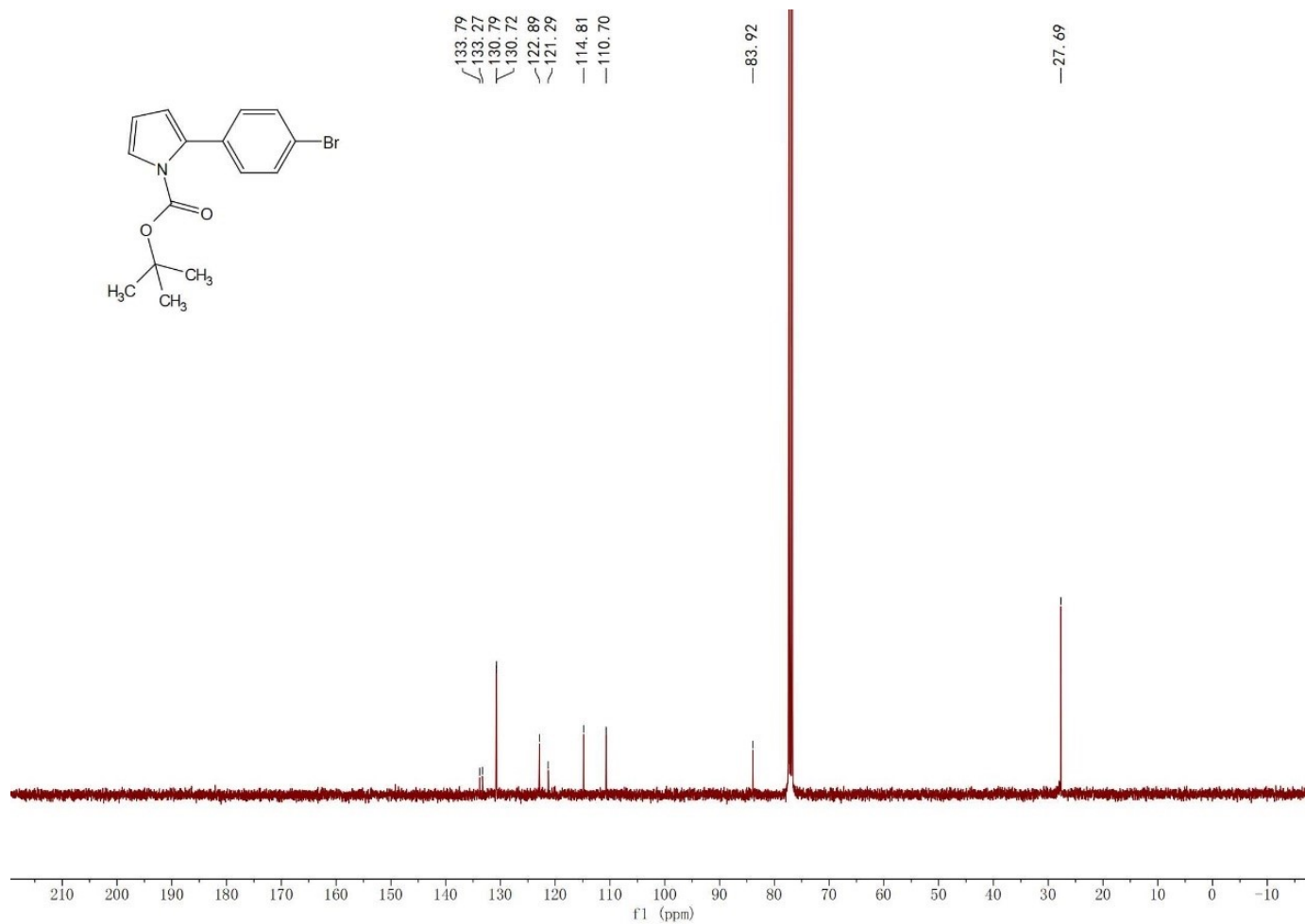
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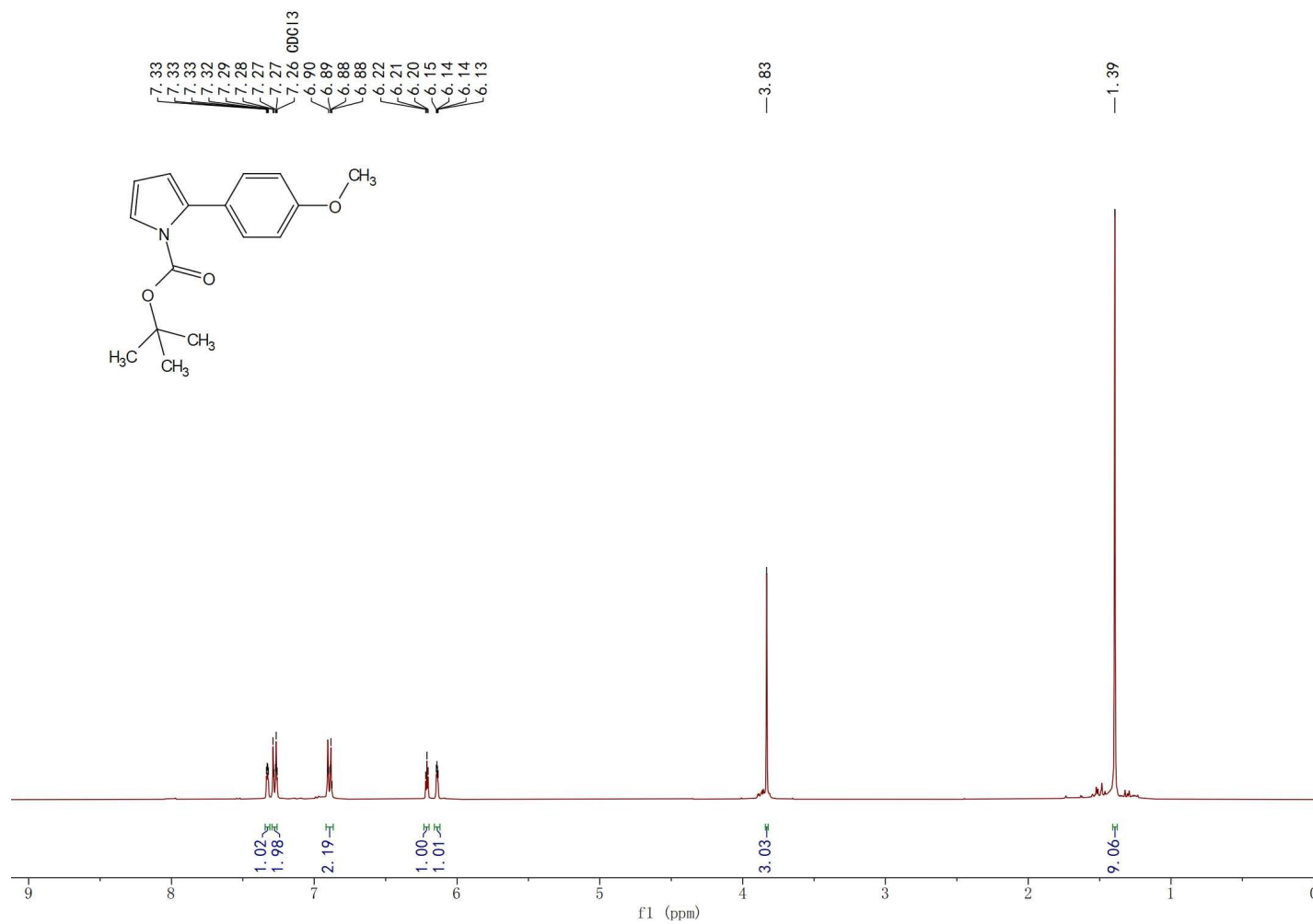
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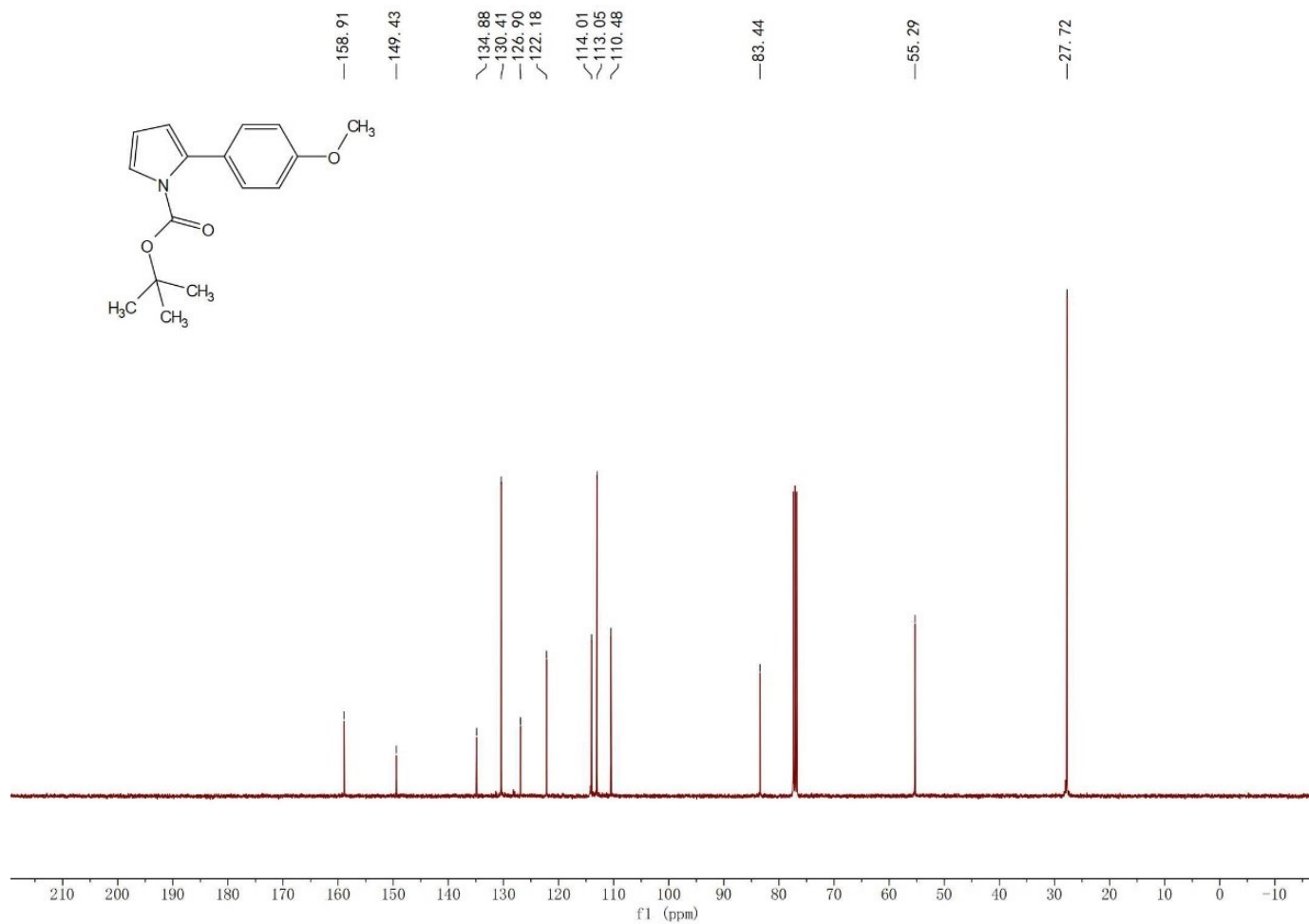
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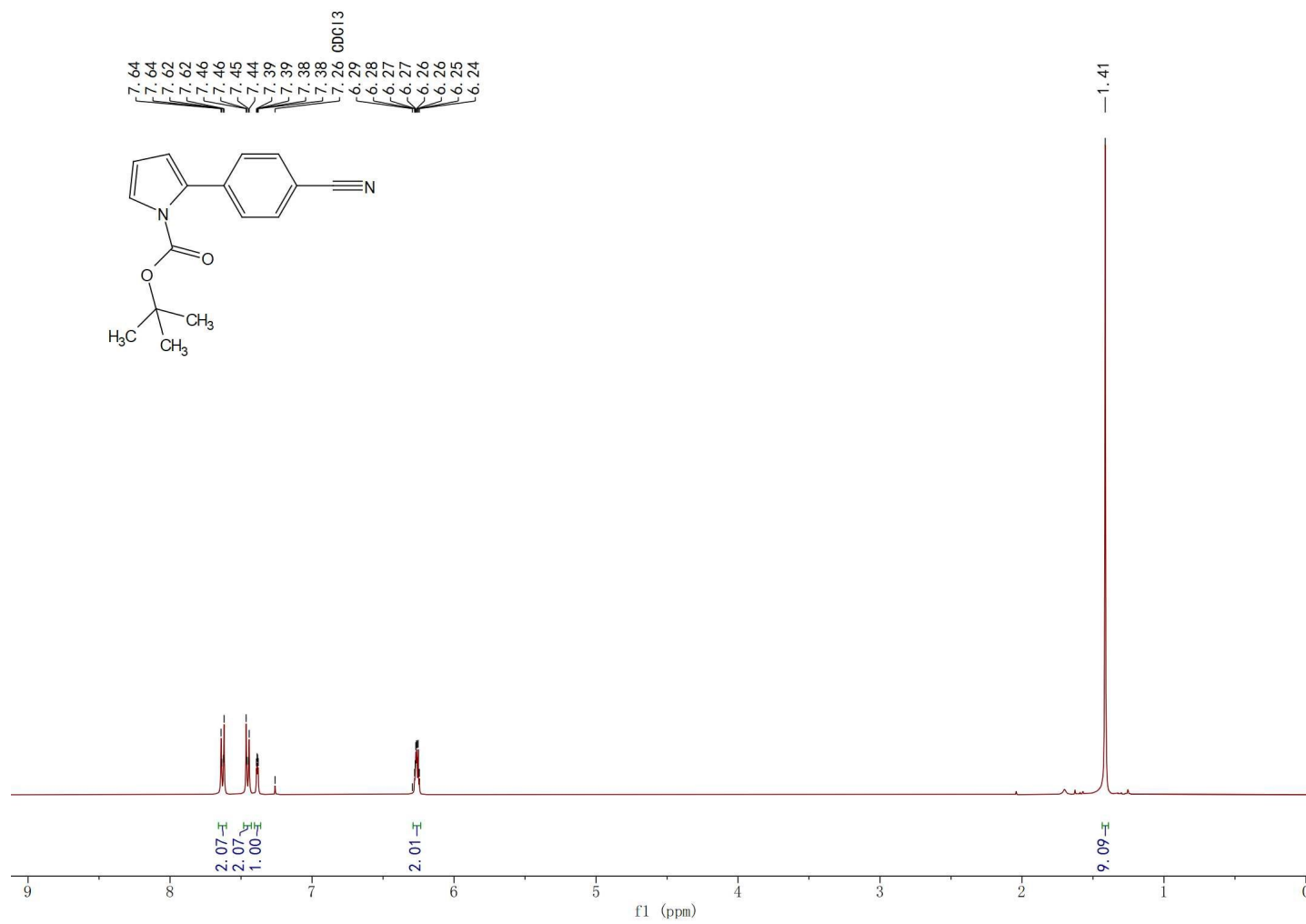
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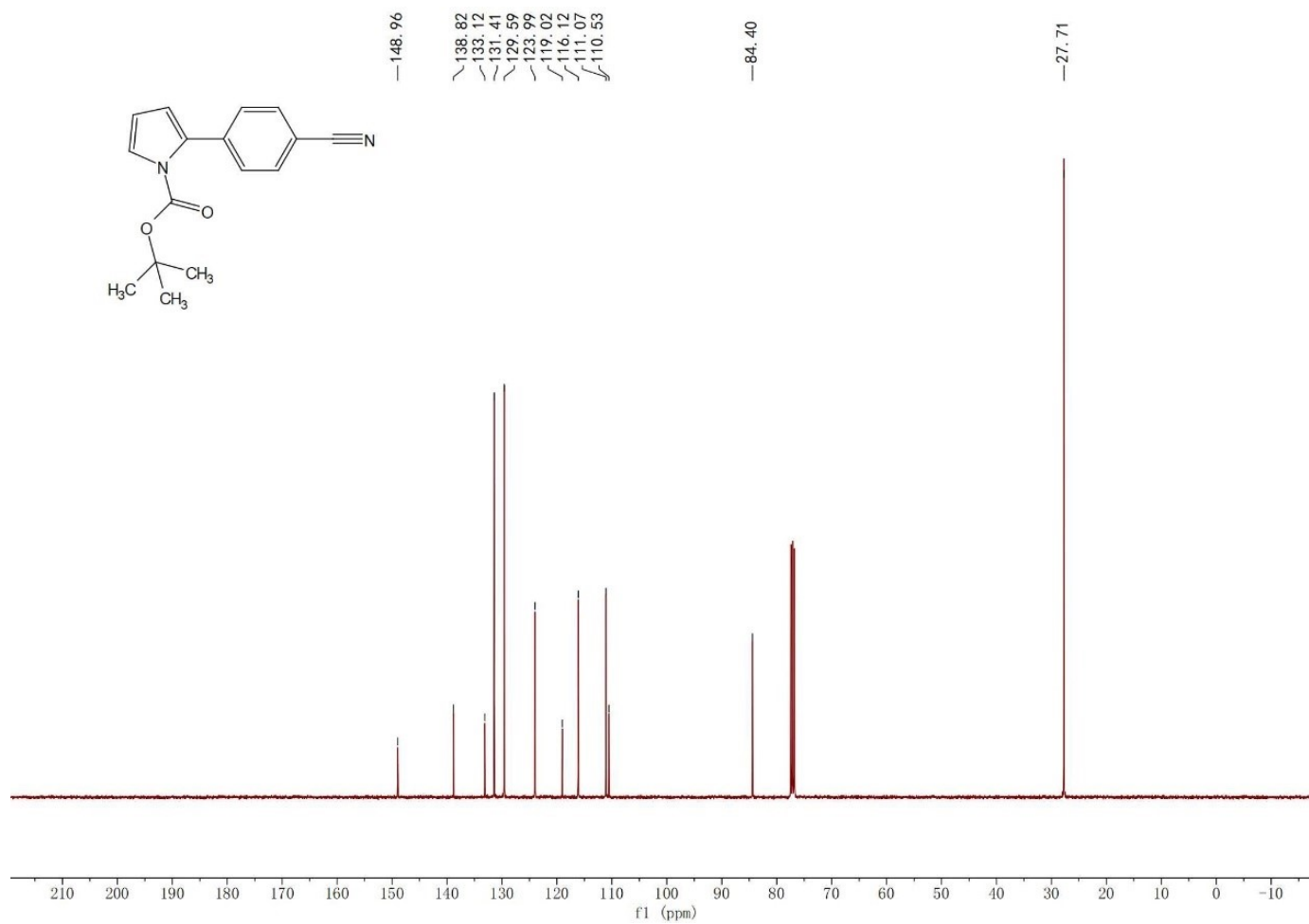
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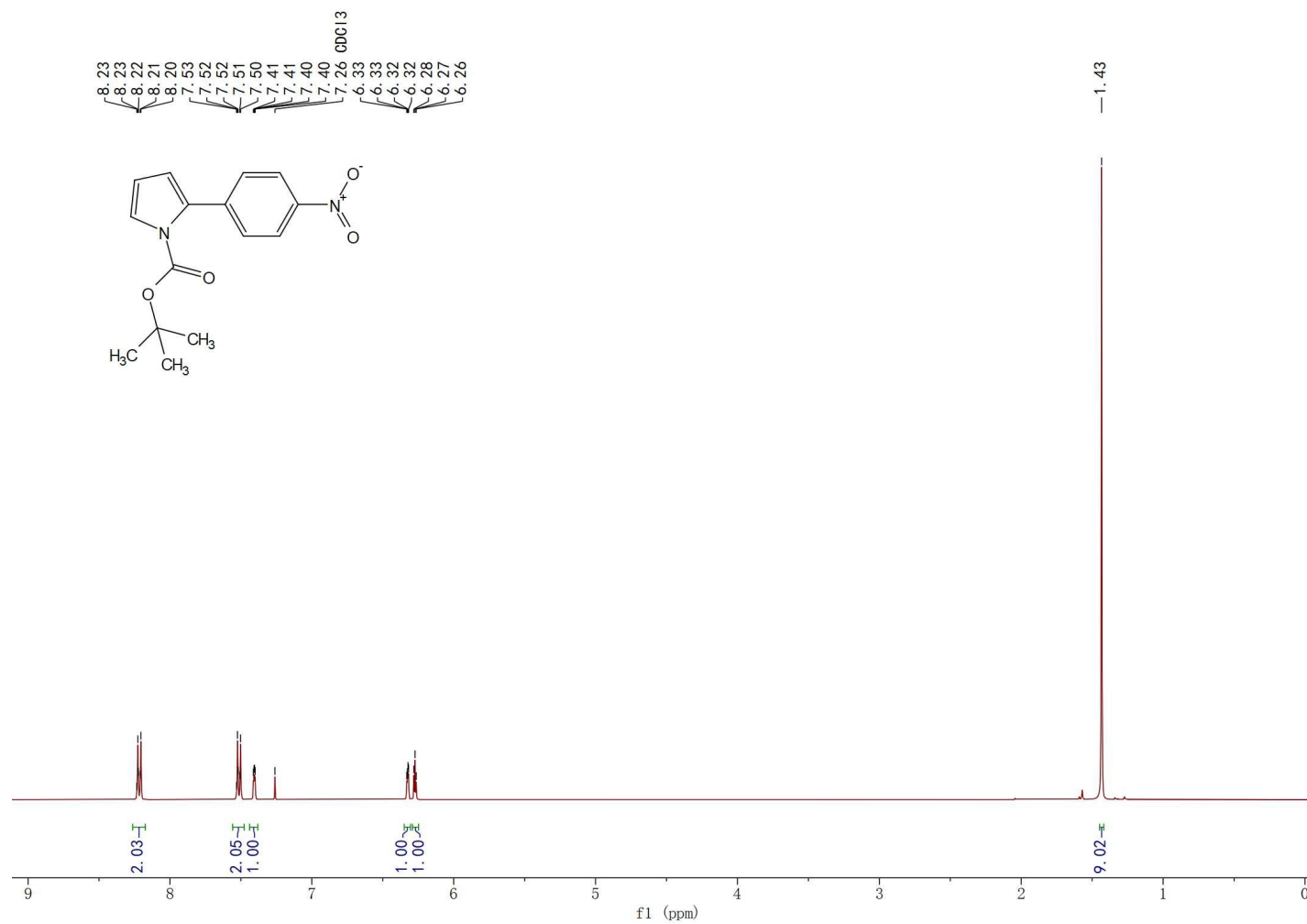
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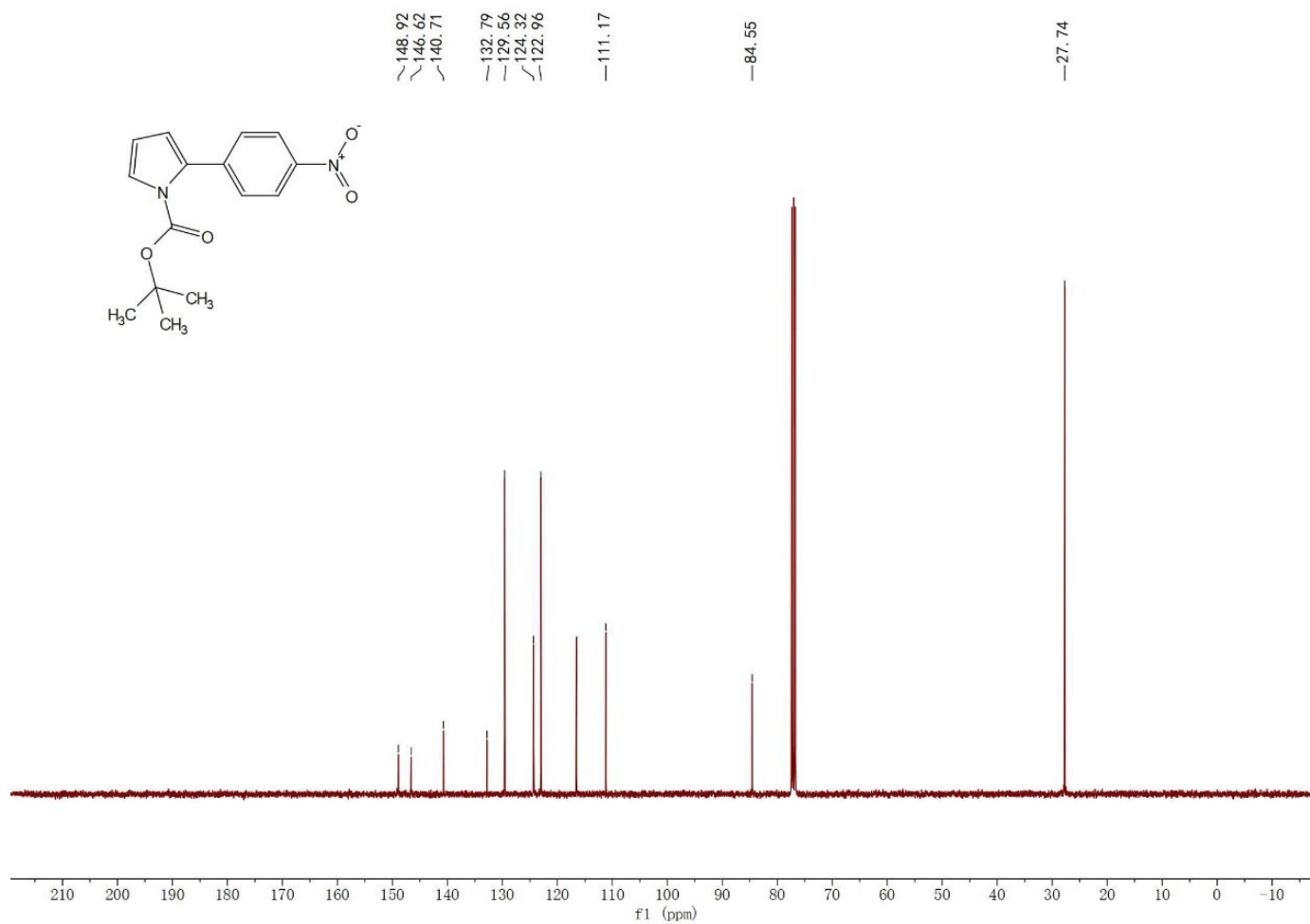
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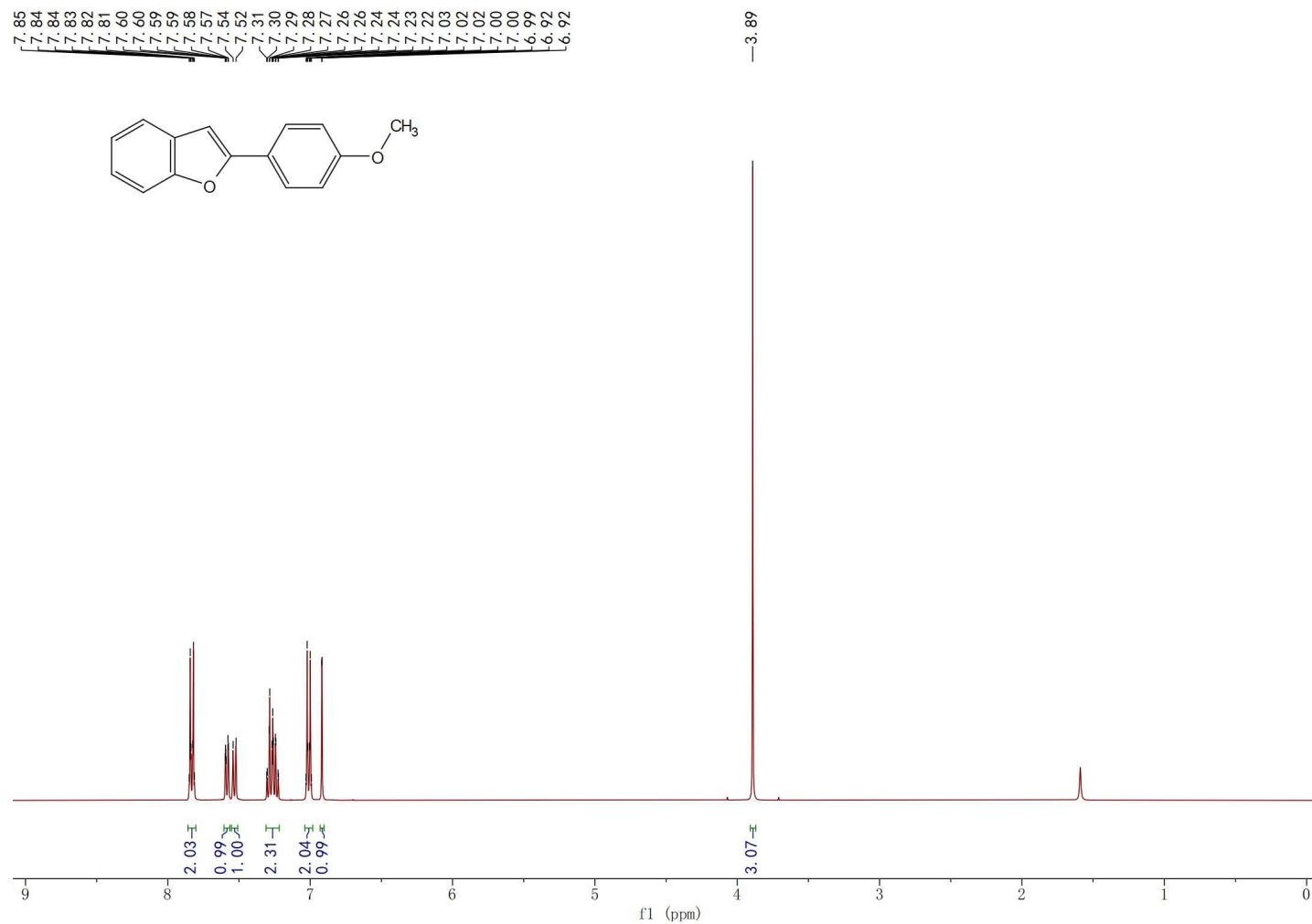
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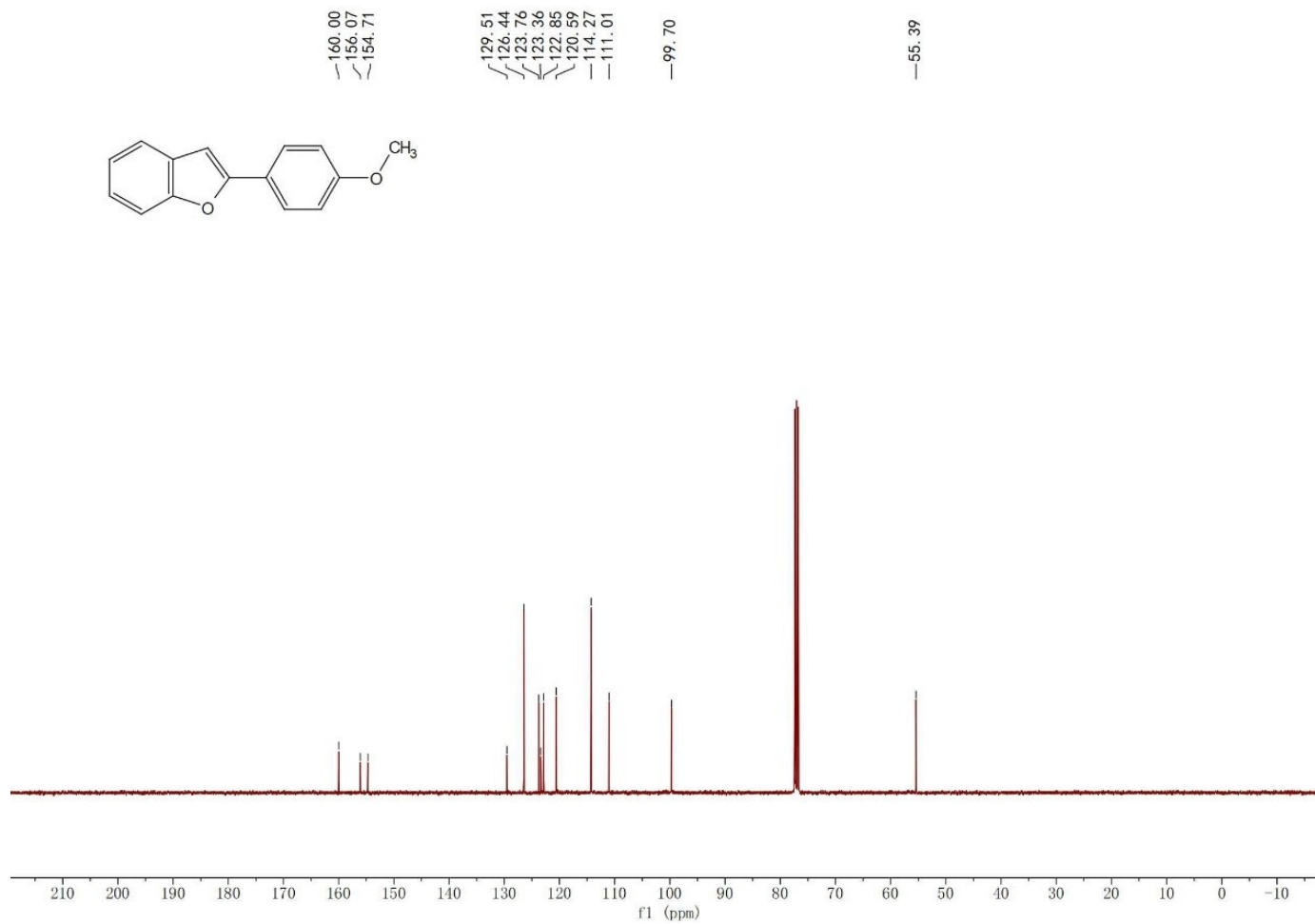
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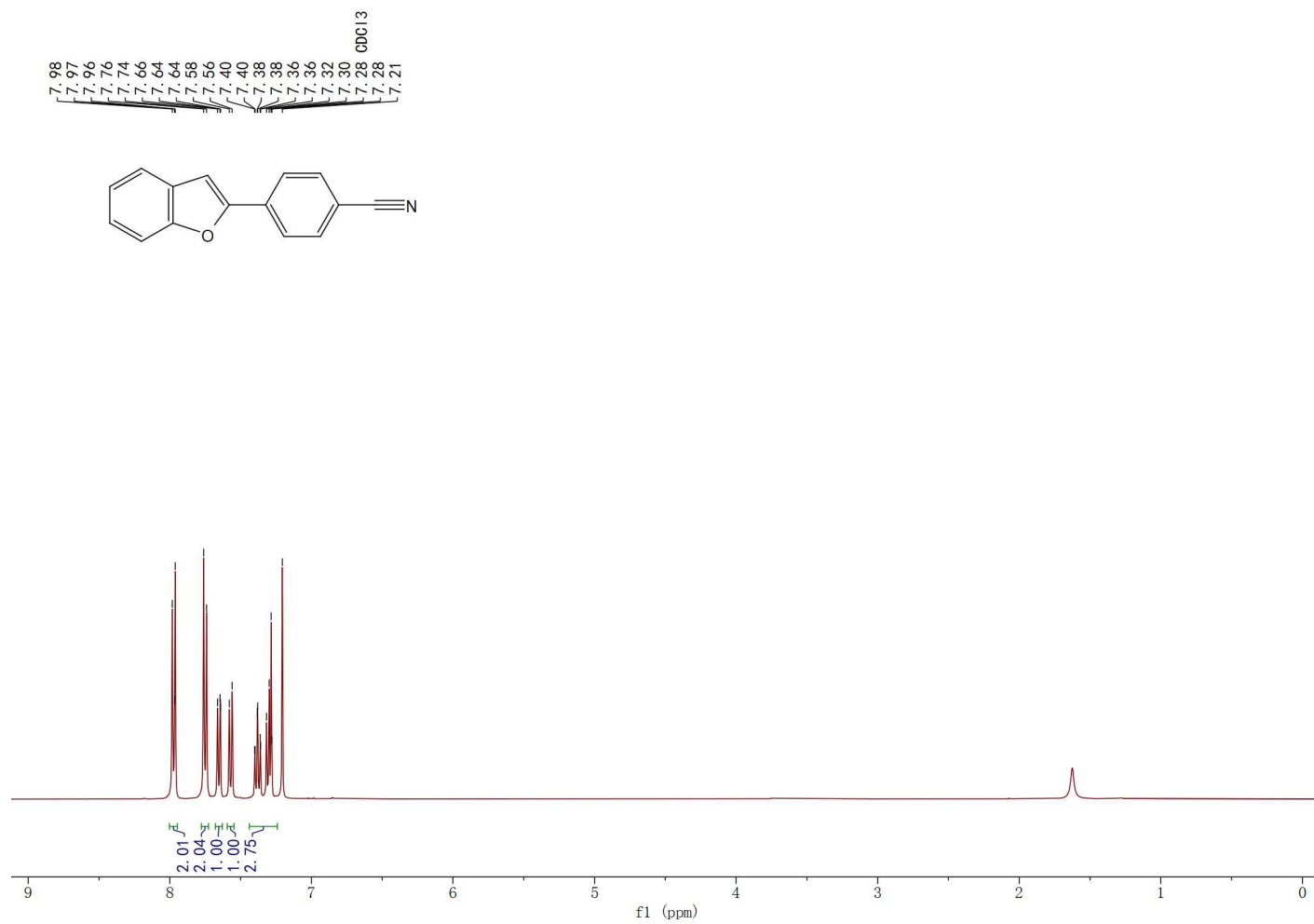
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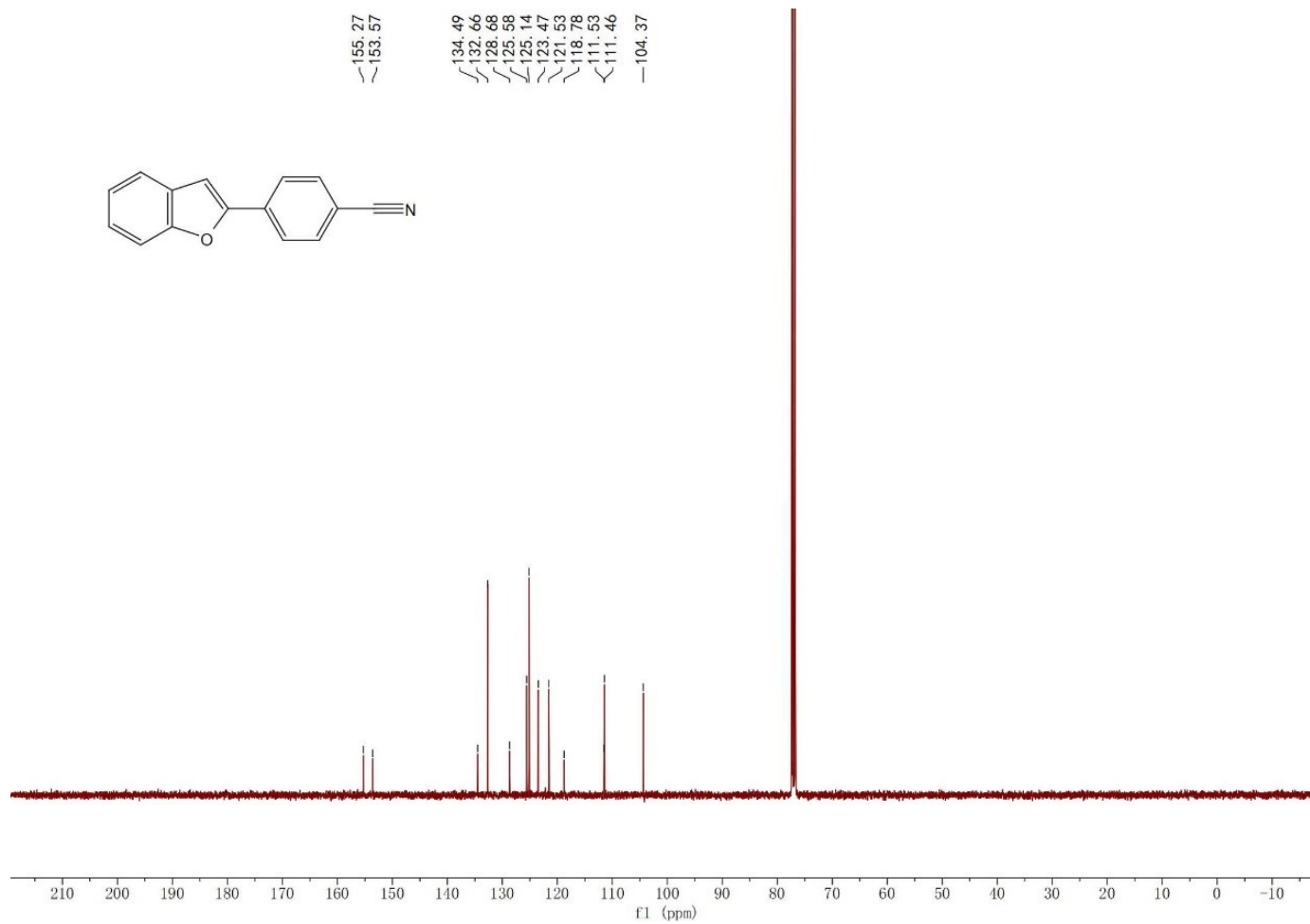
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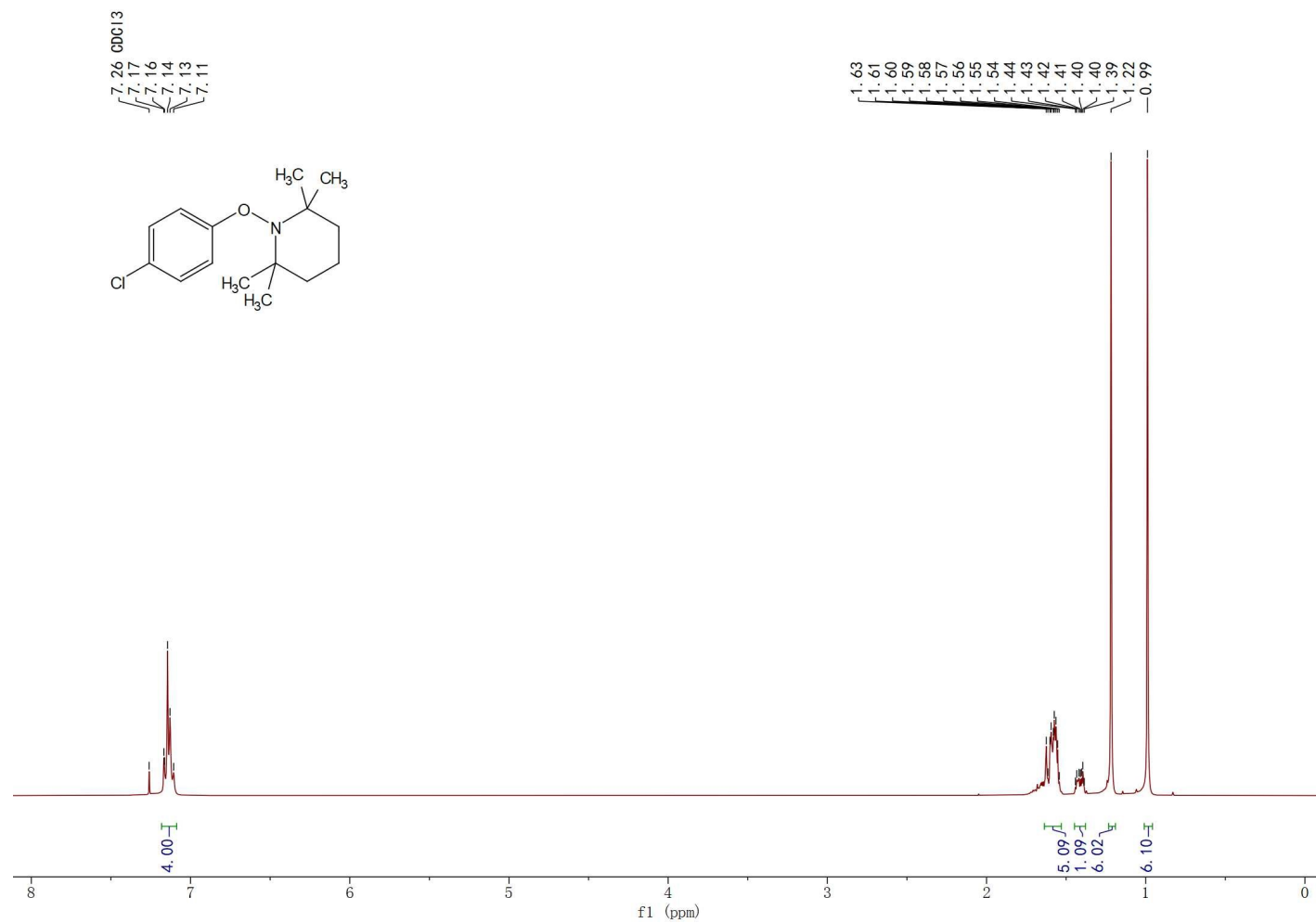
3ff ^1H NMR



3ff ^{13}C NMR



5 ¹H NMR



5 ¹³C NMR

