

Supporting Information

Photoredox/Copper-Catalyzed Formal Cyclopropanation of Olefins

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1. General Information

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of argon in oven-dried glassware equipped with a rubber septum inlet. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reaction mixtures were stirred in 10 mL sample vial with Teflon-coated magnetic stirring bars unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high vacuo by means of an oil pump and subsequent purging with nitrogen. Solvents were removed in vacuo under ~30 mmHg and heated with a water bath at 40 – 45 ° C using rotary evaporator with aspirator. The condenser was cooled with running water at 0 ° C. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, 60 F254. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining $\text{Ce}(\text{SO}_4)_2$ and phosphomolybdic acid solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

All the products were purified by *SepaBean*® Machine. *SepaFlash*® column were purchased from *Santaitech* Company. All commercial reagents were purchased with the highest purity grade. They were used without further purification unless specified.

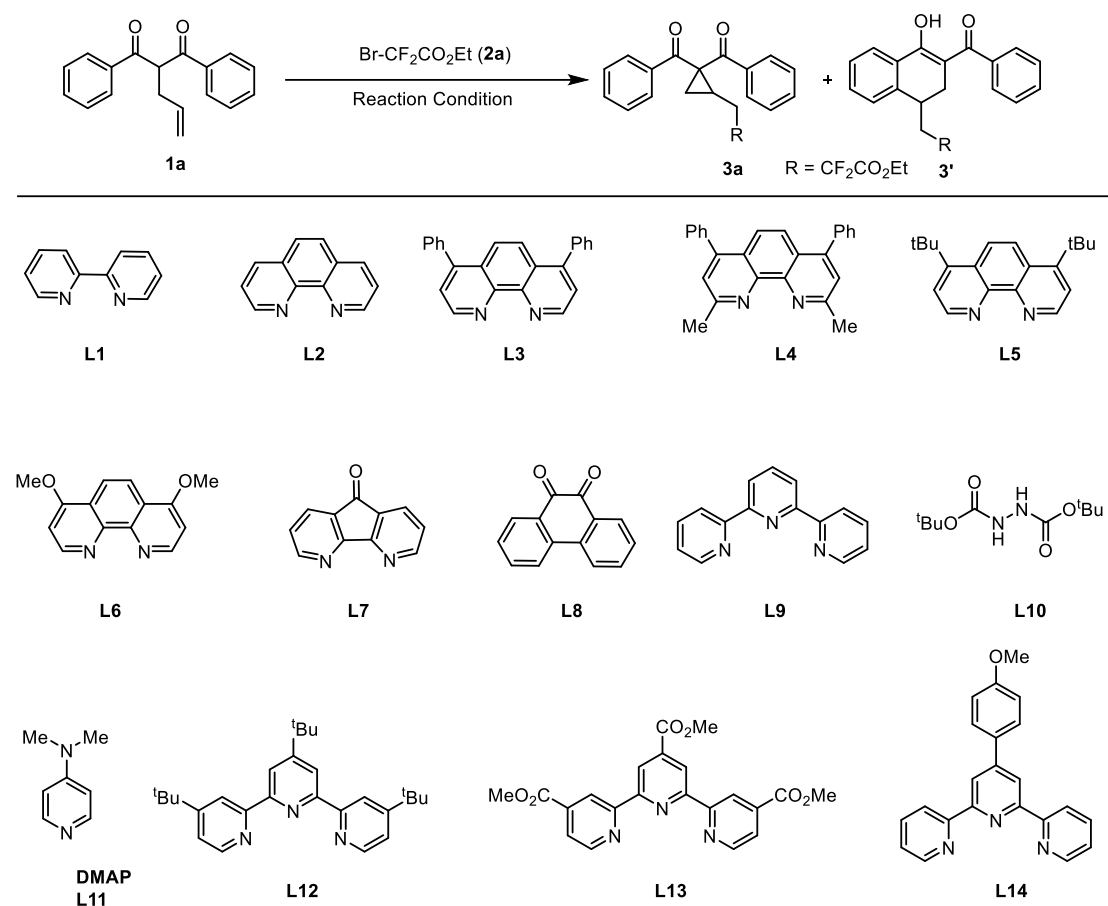
All solvents used, mainly petroleum ether (PE) and ethyl acetate (EtOAc) were distilled. Anhydrous dichloromethane (DCM), CH_3CN , CHCl_3 were freshly distilled from CaH_2 and stored under Ar atmosphere. Tetrahydrofuran (THF), Et_2O , 1,2-dimethoxyethane, mesitylene and toluene were freshly distilled from sodium/benzophenone before use. All compounds synthesized were stored in a -20 ° C freezer and light-sensitive compounds were protected with aluminium foil.

^1H and ^{13}C NMR spectra were recorded on a Bruker advance III400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C) and III600 spectrometer (600 MHz for ^1H and 150 MHz for ^{13}C) in CDCl_3 , DMSO-d_6 and DMF-d_7 . Chemical shifts (δ) were measured in ppm relative to TMS $\delta = 0$ for ^1H , or to chloroform $\delta = 77.0$ for ^{13}C as internal standard. ^{19}F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, J , are reported in hertz. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals Adamas-beta or TCI and used without

further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm).

2. Optimization of Reaction Conditions

2.1 Reaction conditions screening ^{a,b}



Entry	PC	[Cu]	Ligand	Base	Solvent	Yield of 3a (%)	Yield of 3' (%)
1	Ir(ppy) ₃	--	--	K ₂ CO ₃	DCM	ND	85
2	Ir(ppy) ₃	--	--	KOAc	DCM	ND	77
3	Ir(ppy) ₃	--	--	K ₃ PO ₄	DCM	ND	82
4	Ir(ppy) ₃	--	--	NEt ₃	DCM	ND	68
5	Ir(ppy) ₃	--	--	TMEDA	DMSO	ND	90
6	Ir(ppy) ₃	--	--	DMAP	DCM	ND	ND
7	Ir(ppy) ₃	--	--	2,6-lutidine	DCM	ND	ND
8	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L1	K ₂ CO ₃	DCM	messy	<10

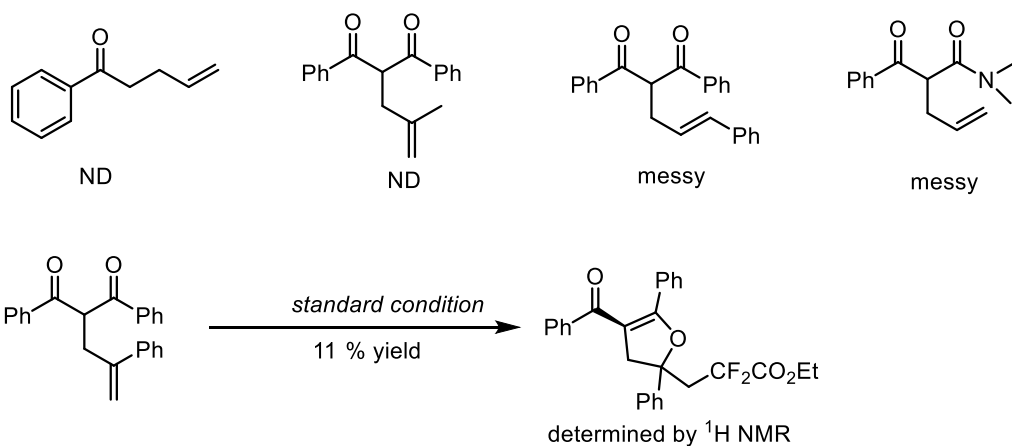
9	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L2	K ₂ CO ₃	DCM	22	<10
10	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L3	K ₂ CO ₃	DCM	23	<10
11	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L4	K ₂ CO ₃	DCM	15	<10
12	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L5	K ₂ CO ₃	DCM	27	<10
13	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L6	K ₂ CO ₃	DCM	36	<10
14	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L7	K ₂ CO ₃	DCM	trace	<10
15	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L8	K ₂ CO ₃	DCM	14	32
16	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L9	K ₂ CO ₃	DCM	67	25
17	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L10	K ₂ CO ₃	DCM	trace	<10
18	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L11 (DMAP)	K ₂ CO ₃	DCM	72	nd
19	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L12	K ₂ CO ₃	DCM	52	20
20	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L13	K ₂ CO ₃	DCM	trace	<10
21	Ir(ppy) ₃	Cu(MeCN) ₄ PF ₆	L14	K ₂ CO ₃	DCM	45	11
22	Ir(ppy)₃	CuI	DMAP	K₂CO₃	DCM	88	ND
23	Ir(ppy) ₃	CuCN	DMAP	K ₂ CO ₃	DCM	78	<10
24	Ir(ppy) ₃	CuTc	DMAP	K ₂ CO ₃	DCM	61	<10
25	Ir(ppy) ₃	CuBr ₂	DMAP	K ₂ CO ₃	DCM	52	<10
26	Ir(ppy) ₃	Cu(OAc) ₂	DMAP	K ₂ CO ₃	DCM	47	<10
27	Ir(ppy) ₃	Cu(acac) ₂	DMAP	K ₂ CO ₃	DCM	37	<10
28	Ir(ppy) ₃	Cu(acac-F) ₂	DMAP	K ₂ CO ₃	DCM	44	<10
29	Ir(ppy) ₃	Cu(acac- ^t Bu) ₂	DMAP	K ₂ CO ₃	DCM	51	<10
30	Ir(ppy) ₃	CuI	DMAP	KOAc	DCM	81	<10
31	Ir(ppy) ₃	CuI	DMAP	CsOH	DCM	NR	<10
32	Ir(ppy) ₃	CuI	DMAP	^t BuOLi	DCM	ND	<10
33	Ir(ppy) ₃	CuI	DMAP	Li ₂ CO ₃	DCM	61	<10
34	Ir(ppy) ₃	CuI	DMAP	Na ₂ CO ₃	DCM	67	<10
35	Ir(ppy) ₃	CuI	DMAP	NaOAc	DCM	66	<10
36	Ir(ppy) ₃	CuI	DMAP	Cs ₂ CO ₃	DCM	54	<10
37	Ir(ppy) ₃	CuI	DMAP	TMEDA	DCM	46	<10

38	Ir(ppy) ₃	CuI	DMAP	NEt ₃	DCM	22	<10
39	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	DCE	69	<10
40	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	MeCN	28	<10
41	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	THF	trace	<10
42	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	Dioxane	trace	<10
43	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	DMF	trace	<10
44	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	DMSO	12	<10
45	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	Toluene	trace	--
46	--	CuI	DMAP	K ₂ CO ₃	DCM	NR	ND
47 ^c	Ir(ppy) ₃	CuI	DMAP	K ₂ CO ₃	DCM	NR	ND
48	Ir(ppy) ₃	CuI	--	K ₂ CO ₃	DCM	17	56
50	Ir(ppy) ₃	--	DMAP	K ₂ CO ₃	DCM	nd	45

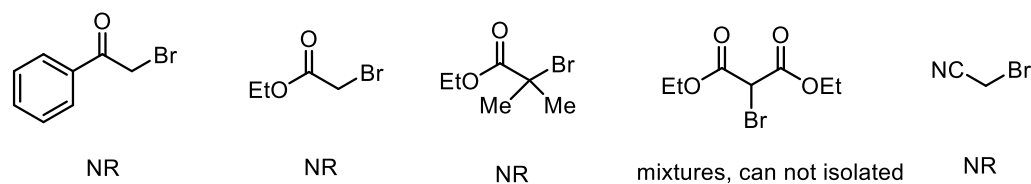
^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Ir(ppy)₃ (1 mol%), CuI (10 mol%), DMAP (20 mol%), K₂CO₃ (0.4 mmol), DCM (2.0 mL), 25 °C, 450 nm blue LEDs. ^b Yield of isolated product. ^c no light. NR is no reaction. ND is no detected.

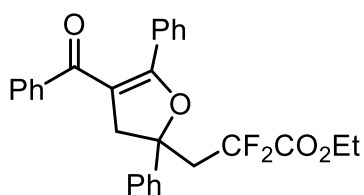
2.2 Limited substrate scopes.

Alkenes

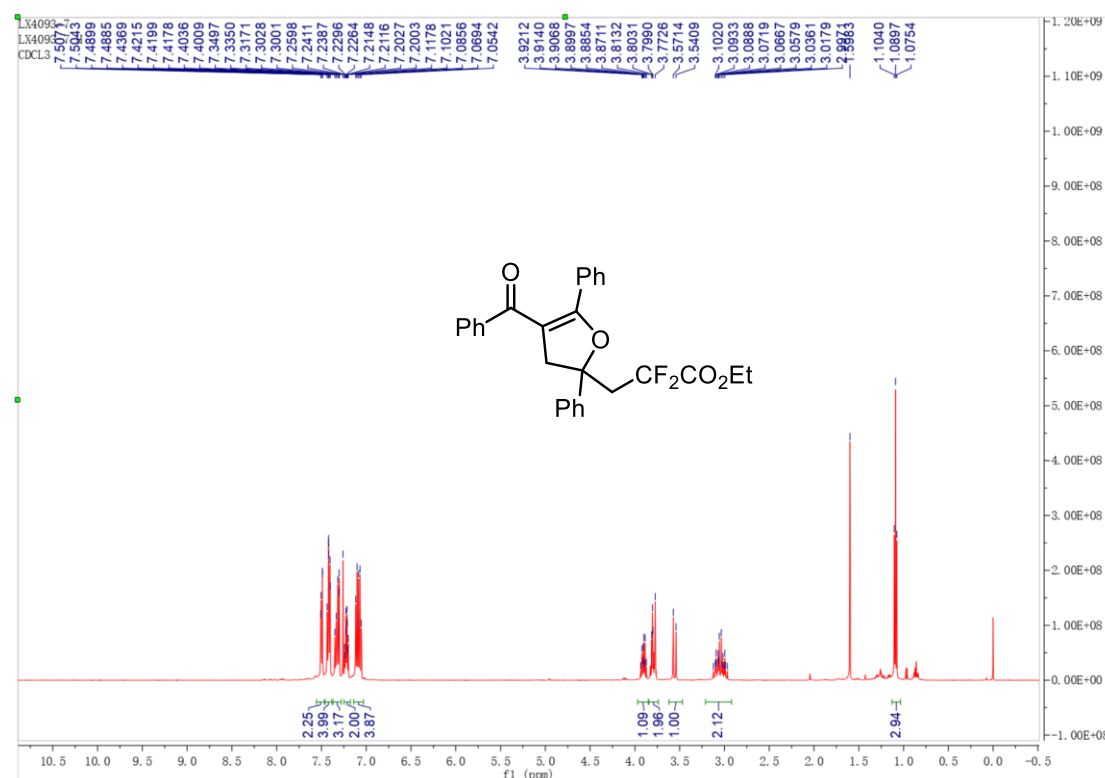


Halides

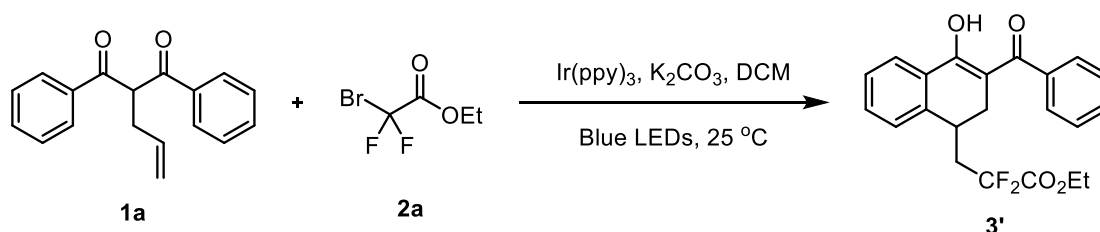




^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.48 (m, 2H), 7.42 – 7.40 (m, 4H), 7.34 – 7.30 (m, 3H), 7.24 – 7.20 (m, 2H), 7.15 – 7.05 (m, 4H), 3.93 – 3.87 (m, 1H), 3.81 – 3.77 (m, 2H), 3.57 – 3.54 (m, 1H), 3.12 – 2.96 (m, 2H), 1.08 (t, $J = 5.7$ Hz, 3H).

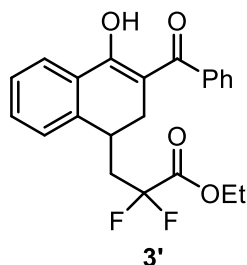


3. General procedure for products and Data.



To a 10 mL Schlenk tube was added Ir(ppy)_3 (1 mol%), K_2CO_3 (2.0 equiv.) under Argon atmosphere. Subsequently, DCM (2.0 mL), **1a** (0.2 mmol) and **2a** (0.4 mmol) was sequentially added into the tube, degassed three times (10 minutes every time) by freeze-pump-thaw method. The reaction mixture was stirred under Argon atmosphere at 25 °C in an incubator with 450 nm blue LEDs for 24 hours. After reaction completed, the reaction mixture was transfer into a 100 mL round-bottom

flask, follow by *silica gel* (about 20-50 mg) was added into, then the solvent was removed under reduced conditions. The residue was directly loaded onto a short SepaFlash® column, and the pure products **3'** were purified by SepaBean® Machine in 85% yield.



Ethyl 3-(3-benzoyl-4-hydroxy-1,2-dihydronaphthalen-1-yl)-2,2-difluoropropanoate (3'**):**

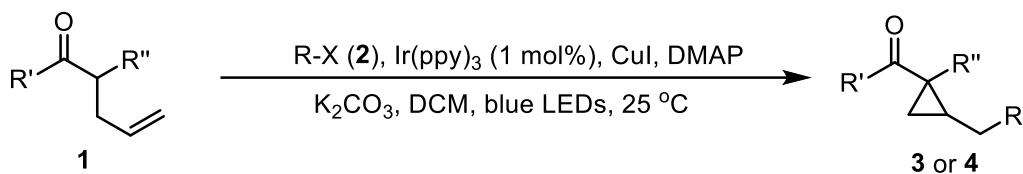
Yield: 65.5 mg, 85%, colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.04 – 8.02 (m, 1H), 7.57 – 7.55 (m, 2H), 7.49 – 7.45 (m, 4H), 7.42 – 7.40 (m, 1H), 7.25 – 7.23 (m, 1H), 4.08 – 4.04 (m, 2H), 3.25 – 3.23 (m, 1H), 3.02 -2.97 (m, 1H), 2.82 -2.77 (m, 1H), 2.33 (dt, *J* = 6.8 Hz, 15.8 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -102.00 (d, *J* = 263.2 Hz, 1F), -105.86 (d, *J* = 263.3 Hz, 1F).

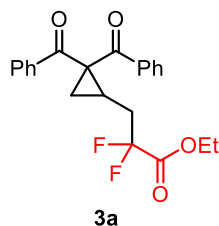
¹³C NMR (100 MHz, CDCl₃) δ -186.76, 183.21, 163.69 (t, *J* = 32.5 Hz), 143.00, 136.00, 132.93, 131.25, 130.75, 128.33, 127.86, 127.81, 127.64, 126.75, 115.65 (t, *J* = 250.3 Hz), 105.99, 62.93, 38.36 (t, *J* = 22.5 Hz), 32.24, 29.84, 13.82.

HRMS (ESI) *m/z* calcd for C₂₂H₂₀F₂O₄Na [*M*+Na⁺] 409.1222, found 409.1224.



To a 10 mL Schlenk tube was added Ir(ppy)₃ (1 mol%), CuI (10 mol%), DMAP (20 mol%), K₂CO₃ (2.0 equiv.) under Argon atmosphere. Subsequently, DCM (2.0 mL), **1** (1.0 equiv.) and **2** (2.0 equiv.) was sequentially added into the tube, degassed three times (10 minutes every time) by freeze-pump-thaw method. The reaction mixture was stirred under Argon atmosphere at 25 °C in an incubator with 450 nm blue LEDs for 12 - 24 hours. After reaction completed, the reaction mixture was transfer into a 100 mL round-bottom flask, follow by *silica gel* (about 20-50 mg) was added into, then the solvent was removed under reduced conditions. The residue was directly loaded onto a

short SepaFlash® column, and the crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent.



Ethyl 3-(2,2-dibenzoylcyclopropyl)-2,2-difluoropropanoate (3a) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and ethyl bromodifluoroacetate (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 67.9 mg, 88% yield.

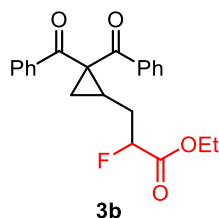
Gram scale: using alkene **1a** (10.0 mmol) and ethyl bromodifluoroacetate (15.0 mmol) in DCM (30.0 mL) with 0.5 mmol% Ir(ppy)₃ as photocatalyst, the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 3.32 g, 86% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.72 - 7.70 (m, 4H), 7.41 - 7.35 (m, 2H), 7.29 - 7.24 (m, 4H), 4.35 (q, *J* = 6.8 Hz, 2H), 2.83 - 2.76 (m, 1H), 2.37 - 2.33 (m, 1H), 2.13 (dd, *J* = 4.5 Hz, 7.2 Hz, 1H), 1.94 - 1.80 (m, 1H), 1.49 (dd, *J* = 4.5 Hz, 8.7 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -103.91 (d, *J* = 260.6 Hz, 1F), -106.01 (d, *J* = 260.8 Hz, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 196.54, 196.12, 163.80 (t, *J* = 32.3 Hz), 137.94, 137.35, 133.31, 133.07, 128.66, 128.61, 128.51, 115.59 (t, *J* = 250.3 Hz), 63.07, 44.09, 32.85 (t, *J* = 23.7 Hz), 20.86, 20.17 (t, *J* = 6.8 Hz), 13.97.

HRMS (ESI) *m/z* calcd for C₂₂H₂₀F₂O₄Na [*M*+Na⁺] 409.1222, found 409.1223.



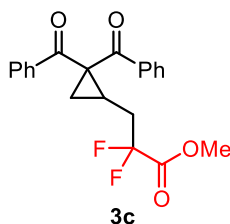
Ethyl 3-(2,2-dibenzoylcyclopropyl)-2-fluoropropanoate (3b) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 39.7 mg, 54% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.74 - 7.70 (m, 4H), 7.39 - 7.35 (m, 2H), 7.30 - 7.23 (m, 4H), 5.05 - 4.90 (m, 1H), 4.29 - 4.21 (m, 2H), 2.86 - 2.78 (m, 1H), 2.21 - 2.05 (m, 1H), 1.82 - 1.57 (m, 1H), 1.46 (ddd, *J* = 1.6 Hz, 4.2 Hz, 8.5 Hz, 1H), 1.30 (dt, *J* = 6.1 Hz, 7.1 Hz 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -191.19 (d, *J* = 385.6 Hz, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 196.83, 196.36, 169.28 (d, *J* = 23.5 Hz), 138.03, 137.53, 133.23, 132.97, 129.16, 128.93, 128.63, 128.48, 89.43 (d, *J* = 184.7 Hz), 61.77, 45.27, 30.89 (d, *J* = 20.8 Hz), 23.29 (d, *J* = 4.4 Hz), 20.90, 14.12.

HRMS (ESI) *m/z* calcd for C₂₂H₂₁FO₄Na [*M*+Na⁺] 391.1316, found 391.1315.



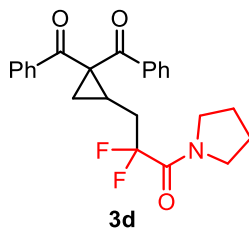
Methyl 3-(2,2-dibenzoylcyclopropyl)-2,2-difluoropropanoate (3c) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 61.0 mg, 82% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.72 - 7.70 (m, 4H), 7.41 - 7.35 (m, 2H), 7.30 - 7.24 (m, 4H), 3.88 (s, 3H), 2.83 - 2.75 (m, 1H), 2.38 - 2.30 (m, 1H), 2.11 (dd, *J* = 4.5 Hz, 7.2 Hz, 1H), 1.95 - 1.80 (m, 1H), 1.48 (dd, *J* = 4.5 Hz, 8.2 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -104.06 (d, *J* = 261.7 Hz, 1F), -105.83 (d, *J* = 261.4 Hz).

¹³C NMR (100 MHz, CDCl₃) δ 196.54, 196.11, 164.26 (t, *J* = 32.0 Hz), 137.90, 137.33, 133.33, 133.09, 128.67, 128.61, 128.52, 115.60 (t, *J* = 250.3 Hz), 53.46, 44.05, 32.88 (t, *J* = 23.6 Hz), 20.79, 20.10 (t, *J* = 6.3 Hz).

HRMS (ESI) *m/z* calcd for C₂₁H₁₈F₂O₄Na [*M*+Na⁺] 395.1065, found 395.1069.



(2-(2,2-difluoro-3-oxo-3-(pyrrolidin-1-yl)propyl)cyclopropane-1,1-diyl)bis(phenylmethanone) (3d) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl bromide (0.4 mmol),

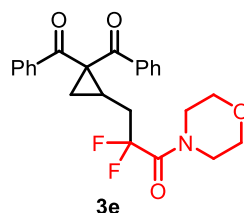
the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give white solid, 63.3 mg, 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.73 - 7.70 (m, 4H), 7.39 - 7.33 (m, 2H), 7.27 - 7.22 (m, 4H), 3.66 (t, *J* = 6.7 Hz), 3.50 (t, *J* = 7.0 Hz), 2.94 – 2.86 (m, 1H), 2.50 – 2.36 (m, 1H), 2.16 (dd, *J* = 4.4 Hz, 7.3 Hz), 1.98 – 1.91 (m, 3H), 1.88 – 1.83 (m, 2H), 1.48 (dd, *J* = 4.4 Hz, 8.8Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -102.80 - -102.81 (m, 2F).

¹³C NMR (100 MHz, CDCl₃) δ 197.02, 196.34, 161.03 (t, *J* = 29.5 Hz); 138.10, 137.61, 133.12, 132.89, 128.68, 128.55, 128.49, 128.45, 118.57 (t, *J* = 253.0 Hz), 47.41, 46.52 (t, *J* = 6.3 Hz), 44.32, 32.48 (t, *J* = 23.5 Hz), 26.50, 23.28, 21.38, 20.95 (t, *J* = 5.8 Hz).

HRMS (ESI) *m/z* calcd for C₂₄H₂₃F₂NO₃Na [M+Na⁺] 434.1538, found 434.1539.



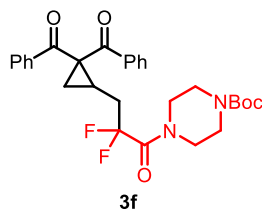
(2-(2,2-difluoro-3-morpholino-3-oxopropyl)cyclopropane-1,1-diyl)bis(phenylmethanone) (3e) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give white solid, 63.2 mg, 74% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.73 - 7.70 (m, 4H), 7.39 - 7.33 (m, 2H), 7.28 - 7.22 (m, 4H), 3.73 – 3.59 (m, 8H), 2.94 – 2.89 (m, 1H), 2.48 – 2.39 (m, 1H), 2.17 (dd, *J* = 4.4 Hz, 7.3 Hz), 2.05 – 1.90 (m, 1H), 1.49 (m, 4.4 Hz, 8.8 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ - 98.76 (s, 1F), - 99.07 (s, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 196.98, 196.36, 161.53 (t, *J* = 28.8 Hz), 138.10, 137.56, 133.15, 132.92, 128.64, 128.56, 128.48, 128.46, 121.60, 119.06, 116.52, 66.75, 66.69, 46.45 (t, *J* = 6.0 Hz), 44.39, 43.34, 32.78 (t, *J* = 23.0 Hz), 21.39, 20.95 (t, *J* = 6.0 Hz).

HRMS (ESI) *m/z* calcd for C₂₄H₂₃F₂NO₄Na [M+Na⁺] 450.1487, found 450.1489.



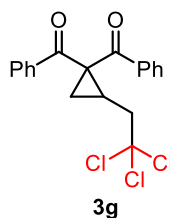
tert-butyl 4-(3-(2,2-dibenzoylcyclopropyl)-2,2-difluoropropanoyl)piperazine-1-carboxylate (3f) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give white solid, 63.1 mg, 60% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.73 - 7.70 (m, 4H), 7.39 - 7.33 (m, 2H), 7.28 - 7.22 (m, 4H), 3.66 - 3.65 (m, 2H), 3.59 - 3.57 (m, 2H), 3.49 - 3.45 (m, 4H), 2.95 - 2.88 (m, 1H), 2.51 - 2.38 (m, 1H), 2.16 (dd, *J* = 4.4 Hz, 7.3 Hz), 2.05 - 1.91 (m, 1H), 1.50 - 1.46 (m, 10H).

¹⁹F NMR (376 MHz, CDCl₃) δ - 98.67 (s, 1F), - 98.94 (s, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 196.97, 196.35, 161.65 (t, *J* = 28.7 Hz), 154.45, 138.09, 137.55, 133.15, 132.92, 128.64, 128.56, 128.48, 128.46, 119.04 (t, *J* = 254.4 Hz), 80.45, 45.63 (t, *J* = 6.3 Hz), 44.30, 42.98, 32.78 (t, *J* = 23.0 Hz), 28.36, 26.91, 21.38, 20.94 (t, *J* = 5.9 Hz), 18.44.

HRMS (ESI) *m/z* calcd for C₂₉H₃₂F₂N₂O₅Na [M+Na⁺] 549.2171, found 549.2170.



(2-(2,2,2-trichloroethyl)cyclopropane-1,1-diyl)bis(phenylmethanone) (3g) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl bromide (0.6 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 65.5 mg, 86% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.75 - 7.72 (m, 4H), 7.43 - 7.39 (m, 2H), 7.37 - 7.25 (m, 4H), 3.08 - 2.98 (m, 2H), 2.42 - 2.34 (m, 2H), 1.66 (dd, *J* = 4.7 Hz, 9.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 196.50, 196.08, 137.79, 136.38, 133.45, 137.30, 133.46, 133.15, 128.78, 128.64, 128.56, 128.54, 98.87, 52.75, 43.85, 24.46, 22.10.

HRMS (ESI) *m/z* calcd for C₁₉H₁₆Cl₃O₂ [M+H⁺] 381.0210, found 381.0212.



(3h) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl iodide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 55.3 mg, 64% yield.

¹⁹F NMR (376 MHz, CDCl₃) δ - 75.33 - -75.42 (m, 3F), -76.36 – 76.45 (m, 3F), -183.38 - -183.45 (m, 1F). **¹³C NMR** (100 MHz, CDCl₃) δ 196.28, 196.07, 137.91, 137.16, 133.47, 133.20, 128.76, 128.58, 128.52, 44.50, 27.60 (d, *J* = 20.1 Hz), 21.44, 20.15 (t, *J* = 5.2 Hz).

3i

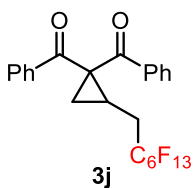
-thanone) (3i) was prepared via typical procedure, using alkene **1a** (0.2 mmol) and alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 80.0 mg, 83% yield.

¹⁹F NMR (376 MHz, CDCl₃) δ -81.04 (dt, *J* = 3.5 Hz, 7.0 Hz, 3F), -113.35 – 113.67(m, 2F), -123.94 -124.02 (m, 2F), -125.96 – 126.64 (m, 2F).

¹³C NMR (100 MHz, CDCl₃) δ 196.38, 196.13, 137.89, 137.18, 133.39, 133.17, 128.69, 128.56, 128.54, 128.53, 43.89, 29.49 (t, *J* = 21.86 Hz), 20.91, 19.31, (t, *J* = 4.9 Hz).

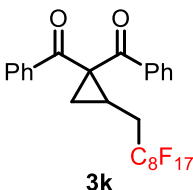
3j

Chemical structure of compound **3j** is shown, which is a cyclopropane ring substituted with two benzoyl groups and a (6-fluorohexyl)ethyl group.



¹H NMR (400 MHz, CDCl₃) δ 7.73 - 7.69 (m, 4H), 7.42 - 7.36 (m, 2H), 7.30 - 7.24 (m, 4H), 2.92 - 2.84 (m, 1H), 2.44 - 2.30 (m, 1H), 2.17 (dd, *J* = 4.6 Hz, 7.2 Hz, 1H), 2.03 - 1.88 (m, 1H), 1.56 (dd, *J* = 4.6 Hz, 8.8 Hz, 1H).

HRMS (ESI) m/z calcd for $C_{24}H_{16}F_{13}O_2$ $[M+H]^+$ 583.0937, found 583.0934.



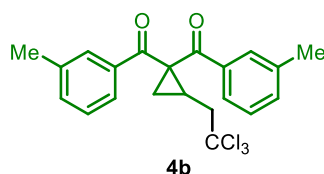
¹H NMR (400 MHz, CDCl₃) δ 7.73 - 7.70 (m, 4H), 7.42 - 7.36 (m, 2H), 7.30 - 7.25 (m, 4H), 2.92 - 2.85 (m, 1H), 2.44 - 2.30 (m, 1H), 2.17 (dd, *J* = 4.6 Hz, 7.2 Hz, 1H), 2.04 - 1.88 (m, 1H), 1.57 (dd, *J* = 4.6 Hz, 8.8 Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -80.79 (t, *J* = 10.2 Hz, 3F), -113.12 – 113.43 (m, 2F), -121.66 - 126.16 (m, 12F).

¹⁹F NMR (376 MHz, CDCl₃) δ -106.24 - -106.25 (m, 2F).

¹³C NMR (100 MHz, CDCl₃) δ 198.05, 197.87, 163.63 (t, *J* = 32.1 Hz), 142.49, 141.58, 135.03, 134.99, 122.65, 122.55, 115.19 (t, *J* = 250.2 Hz), 63.03, 37.82, 31.35 (t, *J* = 23.6 Hz), 27.76 (t, *J* = 5.7 Hz), 23.82, 13.88.

HRMS (ESI) *m/z* calcd for C₁₆H₁₄F₂O₄Na [M+Na⁺] 331.0752, found 331.0755.

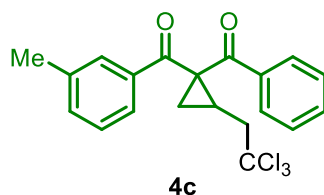


(2-(2,2,2-trichloroethyl)cyclopropane-1,1-diyl)bis(m-tolylmethanone) (4b) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.6 mmol), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 68.5 mg, 84% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.70- 7.68 (m, 4H), 7.11 - 7.07 (m, 4H), 7.30 - 7.24 (m, 4H), 3.00 – 2.94 (m, 2H), 2.34 – 2.31 (m, 1H), 2.30 (s, 3H), 2.29 (s, 3H), 1.58 – 1.55 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 195.86, 195.40, 144.53, 144.12, 135.18, 134.58, 129.50, 129.28, 128.92, 128.83, 99.01, 52.84, 43.66, 23.77, 21.67, 21.63, 21.51.

HRMS (ESI) *m/z* calcd for C₂₁H₁₉Cl₃O₂Na [M+Na⁺] 431.0343, found 431.0358.



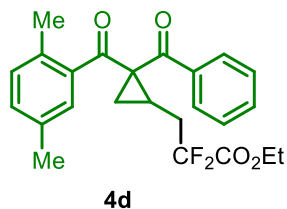
(1-benzoyl-2-(2,2,2-trichloroethyl)cyclopropyl)(m-tolyl)methanone 4c was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.6 mmol), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 64.6 mg, 84% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.75- 7.73 (m, 2H), 7.55 – 7.53 (m, 2H), 7.41 – 7.37 (m, 1H), 7.32 – 7.26 (m, 2H), 7.21 – 7.15 (m, 2H), 3.07 – 2.97 (m, 2H), 2.40 -2.31 (m, 2H), 2.28 – 2.27 (m, 3H), 1.64 – 1.61 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 196.56, 196.53, 196.10, 138.69, 138.44, 137.83, 137.75, 137.32,

137.27, 134.34, 133.98, 133.40, 133.09, 129.00, 128.95, 128.77, 128.62, 128.56, 128.53, 128.41, 126.04, 125.89, 98.92, 52.75, 43.85, 26.92, 24.40, 24.36, 22.07, 21.25.

HRMS (ESI) m/z calcd for $C_{20}H_{17}Cl_3O_2Na$ $[M+Na^+]$ 417.0186, found 417.0205.



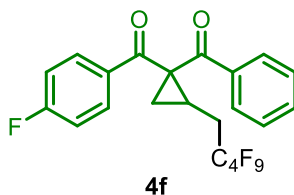
Ethyl 3-(2-benzoyl-2-(2,5-dimethylbenzoyl)cyclopropyl)-2,2-difluoropropanoate (4d) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 66.2 mg, 80% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.57- 7.55 (m, 2H), 7.40 – 7.33 (m, 1H), 7.29 – 7.22 (m, 3H), 6.99 – 6.93 (m, 1H), 6.84 – 6.80 (m, 1H), 4.38 – 4.31 (m, 2H), 2.84 – 2.77 (m, 1H), 2.43 – 2.34 (m, 1H), 2.26 – 2.18 (m, 6H), 2.15 – 2.10 (m, 1H), 2.04 – 1.79 (m, 1H), 1.59 – 1.46 (m, 1H), 1.40 – 1.35 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.81 - -104.55 (m, 1F), -105.92 - -106.62 (m, 1F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.15, 198.11, 196.89, 196.37, 163.89 (t, J = 32.2 Hz), 163.79 (t, J = 32.3 Hz), 138.60, 138.13, 137.95, 137.74, 135.29, 135.22, 134.93, 134.54, 132.93, 132.69, 132.52, 132.17, 131.59, 131.40, 129.31, 128.91, 128.49, 128.35, 127.95, 127.82, 115.74 (t, J = 250.4 Hz), 115.58 (t, J = 250.6 Hz), 63.07, 45.04, 45.00, 33.18 (t, J = 23.6 Hz), 32.49 (t, J = 23.6 Hz), 22.65, 21.69, 21.31 (t, J = 5.2 Hz), 21.13 (t, J = 5.4 Hz), 20.87, 20.80, 19.79, 19.63, 13.99, 13.97.

HRMS (ESI) m/z calcd for $C_{24}H_{24}F_2O_4Na$ $[M+Na^+]$ 437.1535, found 437.1536.



(1-benzoyl-2-(5,5,5,5,5,5,5,5,5-nonafluoro-5H12-penta-2,4-diyn-1-yl)cyclopropyl)(4-fluorophenyl)methanone (4f) was prepared via typical procedure, using alkene (0.2 mmol) and

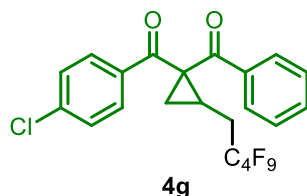
alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 75.0 mg, 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.79 - 7.72 (m, 4H), 7.44 - 7.39 (m, 1H), 7.32 - 7.29 (m, 2H), 6.97 - 6.93 (m, 2H), 2.90 - 2.84 (m, 1H), 2.40 - 2.28 (m, 1H), 2.17 - 2.16 (m, 1H), 2.03 - 1.92 (m, 1H), 1.58-1.53 (m, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -81.11 - -81.17 (m, 3F), -103.79 (d, *J* = 164.9 Hz), -124.03 - -126.11 (m, 4F).

¹³C NMR (100 MHz, CDCl₃) δ 196.21, 195.97, 194.68, 194.41, 166.94 (d, *J* = 254.7 Hz), 166.83 (d, *J* = 254.2 Hz), 137.74, 137.02, 134.27 (d, *J* = 77.01 Hz), 134.24, (d, *J* = 77.2 Hz), 133.55, 133.33, 131.30 (d, *J* = 9.3 Hz), 131.22 (d, *J* = 9.2 Hz), 128.77, 128.64, 128.53, 116.03 (d, *J* = 21.9 Hz), 115.90 (d, *J* = 21.8 Hz), 43.87, 43.81, 29.68, (t, *J* = 26.9 Hz), 29.62 (t, *J* = 21.7 Hz), 20.76, 20.68, 19.29 (t, *J* = 5.0 Hz).

HRMS (ESI) *m/z* calcd for C₂₂H₁₄F₁₀O₂Na [M+Na⁺] 523.0726, found 523.0701.



(1-benzoyl-2-(5,5,5,5,5,5,5,5,5,5-nonafuoro-5H12-penta-2,4-diyn-1-yl)cyclopropyl)(4-chlorophenyl)methanone (4g) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 80.4 mg, 78% yield.

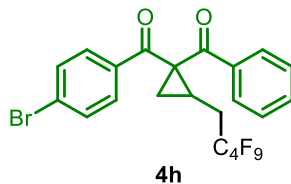
¹H NMR (400 MHz, CDCl₃) δ 7.74 (t, *J* = 5.7 Hz, 2H), 7.61 - 7.56 (m, 2H), 7.42 (t, *J* = 6.1 Hz), 7.33 - 7.27 (m, 2H), 2.89 - 2.84 (m, 1H), 2.39 - 2.30 (m, 1H), 2.16 - 2.15 (m, 1H), 2.01 - 1.91 (m, 1H), 1.65-1.53 (m, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -81.05 - -81.11 (m, 3F), -113.37 - -113.68 (m, 2F), -124.00 - -126.07 (m, 4F).

¹³C NMR (100 MHz, CDCl₃) δ 196.03, 195.77, 195.30, 195.07, 137.69, 136.95, 136.53, 135.81, 133.66, 133.44, 132.05, 133.33, 131.94, 129.97, 129.96, 128.84, 128.71, 128.57, 43.88, 43.81,

29.45 (t, $J = 21.7$ Hz), 29.36, (m, $J = 21.5$ Hz), 20.83, 19.49, 19.36.

HRMS (ESI) m/z calcd for $C_{22}H_{14}F_{10}ClO_2Na$ [$M+Na^+$] 539.0431, found 539.0480.



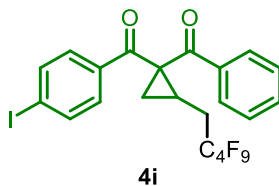
(1-benzoyl-2-(5,5,5,5,5,5,5,5,5,5-nonafluoro-5H12-penta-2,4-diyne-1-yl)cyclopropyl)(4-bromophenyl)methanone (4h) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 82.8 mg, 74% yield.

1H NMR (400 MHz, $CDCl_3$) δ 7.74 - 7.66 (m, 4H), 7.43 - 7.30 (m, 1H), 7.33 - 7.24 (m, 4H), 2.90 - 2.84 (m, 1H), 2.39 - 2.27 (m, 1H), 2.16 - 2.14 (m, 1H), 2.05 - 1.93 (m, 1H), 1.58 - 1.53 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.02 - -81.09 (m, 3F), -113.34 - -113.69 (m, 2F), -124.01 - -126.05 (m, 4F).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.07, 195.82, 195.10, 194.85, 139.96, 139.70, 136.97, 136.13, 135.40, 133.64, 133.43, 129.91, 129.88, 129.06, 128.95, 128.83, 128.70, 128.55, 43.87, 43.83, 29.47 (t, $J = 23.6$ Hz), 29.38 (t, $J = 21.5$ Hz), 20.83, 19.46 (t, $J = 4.8$ Hz), 19.35 (t, $J = 5.0$ Hz).

HRMS (ESI) m/z calcd for $C_{22}H_{14}F_9BrO_2Na$ [$M+Na^+$] 582.9926, found 582.9927.



(1-benzoyl-2-(5,5,5,5,5,5,5,5,5,5-nonafluoro-5H12-penta-2,4-diyne-1-yl)cyclopropyl)(4-iodophenyl)methanone (4i) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 78.9 mg, 65% yield.

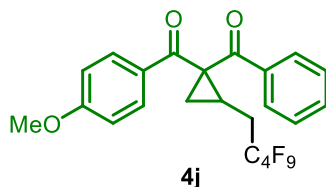
1H NMR (400 MHz, $CDCl_3$) δ 7.80 - 7.62 (m, 4H), 7.54 - 7.26 (m, 5H), 2.89 - 2.81 (m, 1H), 2.41 - 2.24 (m, 1H), 2.15 - 2.12 (m, 1H), 2.04 - 1.89 (m, 1H), 1.62 - 1.51 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -81.00 - -81.06 (m, 3F), -111.77 - -113.66 (m, 2F), -122.94 - -126.03

(m, 4F).

¹³C NMR (100 MHz, CDCl₃) δ 195.98, 195.73, 195.58, 195.36, 138.04, 137.93, 137.67, 137.04, 136.94, 136.31, 133.68, 133.46, 129.79, 128.84, 128.71, 128.58, 101.71, 101.35, 43.84, 43.77, 29.46 (t, *J* = 21.9 Hz), 29.38 (t, *J* = 21.8 Hz), 20.81, 19.46, 19.36.

HRMS (ESI) *m/z* calcd for C₂₂H₁₅F₉IO₂ [M+H⁺] 608.9968, found 608.9979.



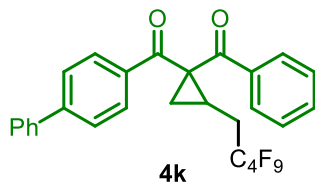
(1-benzoyl-2-(5,5,5,5,5,5,5,5,5,5-nonafluoro-5H12-penta-2,4-diyn-1-yl)cyclopropyl)(4-methoxyphenyl)methanone (4j) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 73.7 mg, 72% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.79 - 7.74 (m, 4H), 7.42 - 7.38 (m, 1H), 7.32 - 7.27 (m, 2H), 6.78 - 6.74 (m, 2H), 3.76 - 3.75 (m, 3H), 2.86 - 2.79 (m, 1H), 2.89 - 2.30 (m, 1H), 2.14 - 2.11 (m, 1H), 1.95-1.83 (m, 1H), 1.50 (dd, *J* = 3.7 Hz, 6.9Hz, 1H).

¹⁹F NMR (376 MHz, CDCl₃) δ -81.13 (t, *J* = 10.4 Hz, 3F), -113.43 - -113.68 (m, 2F) -124.03 - -126.11 (m, 4F).

¹³C NMR (100 MHz, CDCl₃) δ 196.52, 196.28, 194.32, 193.88, 163.75, 163.56, 137.81, 137.08, 133.29, 133.17, 131.08, 131.01, 130.78, 129.92, 128.68, 128.62, 128.54, 113.95, 113.81, 55.34, 55.32, 43.65, 29.74 (t, *J* = 21.6 Hz, major), 29.45 (t, *J* = 29.8 Hz, minor), 20.42, 20.17, 18.84 (t, *J* = 4.8 Hz), 18.49 (t, *J* = 5.2 Hz).

HRMS (ESI) *m/z* calcd for C₂₃H₁₇F₉NaO₃ [M+Na⁺] 535.0926, found 535.0917.



(1-([1,1'-biphenyl]-4-carbonyl)-2-(5,5,5,5,5,5,5,5,5,5-nonafluoro-5H12-penta-2,4-diyn-1-yl)cyclopropyl)(phenyl)methanone (4k) was prepared via typical procedure, using alkene (0.2

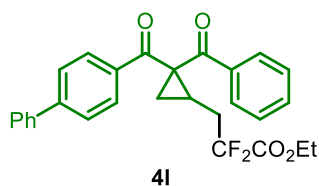
mmol) and alkyl iodine (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 85.9 mg, 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.83 - 7.76 (m, 4H), 7.52 - 7.49 (m, 4H), 7.43 - 7.26 (m, 6H), 2.92 - 2.86 (m, 1H), 2.43 – 2.35 (m, 1H), 2.18 (dd, *J* = 4.5 Hz, 7.2 Hz, 1H), 2.12 (dd, *J* = 4.5 Hz, 7.2 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.48 (dd, *J* = 3.8 Hz, 5.5 Hz, 1H), 2.03 - 1.91 (m, 1H), 1.58 - 1.55 (m, 1H);

¹⁹F NMR (376 MHz, CDCl₃) δ -81.06 (t, *J* = 10.6 Hz, 3F), - 113.34 - -113.66 (m, 2F), - 123.94 - -126.05 (m, 4F);

¹³C NMR (100 MHz, CDCl₃) δ 196.36, 196.11, 195.72, 195.46, 146.03, 145.81, 139.47, 139.39, 137.88, 137.16, 135.77, 133.49, 133.26, 129.22, 129.93, 129.21, 128.75, 128.64, 128.41, 128.35, 127.28, 127.17, 127.15, 43.94, 27.58 (t, *J* = 21.48 Hz, minor) 29.54 (t, *J* = 21.5 Hz, major) 20.77, 20.72, 19.21, 19.16.

HRMS (ESI) *m/z* calcd for C₂₈H₁₉F₉O₂Na [*M*+Na⁺] 581.1134, found 581.1140.



Ethyl 3-(2-([1,1'-biphenyl]-4-carbonyl)-2-benzoylcyclopropyl)-2,2-difluoropropanoate (4I)

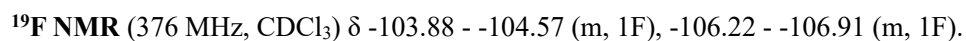
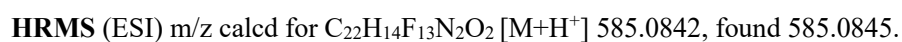
was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 67.4 mg, 73% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.82 - 7.76 (m, 4H), 7.52 - 7.48 (m, 4H), 7.43 - 7.35 (m, 4H), 7.31 - 7.27 (m, 2H), 4.35 (q, *J* = 5.6 Hz, 2H), 2.84 – 2.78 (m, 1H), 2.39 - 2.35 (m, 1H), 2.13 (q, *J* = 3.8 Hz, 1H), 1.94 - 1.83 (m, 1H), 1.49 - 1.47 (m, 1H), 1.37 (t, *J* = 5.7 Hz, 3H);

¹⁹F NMR (376 MHz, CDCl₃) δ -103.85 (d, *J* = 260.6 Hz, 1F), - 105.96 (d, *J* = 260.7 Hz, 1F).

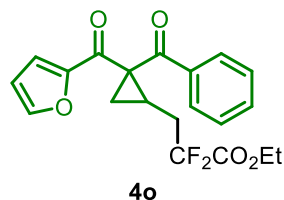
¹³C NMR (100 MHz, CDCl₃) δ 196.53, 196.11, 195.89, 195.47, 163.83 (t, *J* = 32.3 Hz), 145.94, 145.71, 139.51, 139.44, 137.91, 137.31, 136.56, 135.92, 133.42, 133.18, 129.29, 129.19, 128.94, 128.73, 128.62, 128.58, 128.39, 128.33, 127.26, 127.18, 127.16, 127.13, 115.63 (t, *J* = 250.4 Hz), 63.09 44.14, 32.94 (t, *J* = 23.2 Hz, minor), 32.91 (t, *J* = 23.44 Hz, major); 20.74, 20.68, 20.08, 20.02,

HRMS (ESI) m/z calcd for $C_{28}H_{25}F_2O_4$ $[M+H]^+$ 463.1715, found 463.1791.



¹³C NMR (100 MHz, CDCl₃) δ 194.01, 193.69, 163.93 (t, *J* = 32.17 Hz), 153.70, 152.97, 147.94, 147.69, 136.74, 136.70, 125.95, 125.91, 122.26, 121.79, 115.76 (t, *J* = 249.7 Hz), 62.89, 40.66, 32.30 (t, *J* = 23.7 Hz), 26.91, 22.00, 21.35 (t, *J* = 6.6 Hz), 13.94.

HRMS (ESI) *m/z* calcd for C₂₀H₁₈F₂N₂O₄Na [M+Na⁺] 411.1127, found 411.1129.



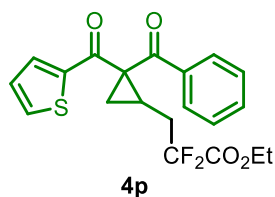
ethyl 3-(2-benzoyl-2-(furan-2-carbonyl)cyclopropyl)-2,2-difluoropropanoate (4o) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give yellow oil as inseparable 1:1 mixture of diastereomers, 48.1 mg, 64% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.81 (m, 2H), 7.47 – 7.31 (m, 4H), 7.09 (m, *J* = 3.6 Hz, 1H), 6.35 (dt, *J* = 1.6 Hz, 3.8 Hz, 1H), 4.34 (q, *J* = 7.0 Hz, 2H), 2.79 -2.67 (m, 1H), 2.40 -2.20 (m, 1H), -2.67 (m, 1H), 2.09 -1.97 (m, 1H), 1.98 -1.74 (m, 1H), 1.42 (dd, *J* = 4.6 Hz, 8.7 Hz, 1H), 1.36 (dt, *J* = 2.1 Hz, 7.1 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -103.93 – -104.94 (m, 1F), -106.06 – -106.94 (m, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 195.18, 194.68, 183.62, 183.02, 163.79 (t, *J* = 32.1 Hz), 163.77 (t, *J* = 32.0 Hz), 152.68, 151.71, 146.99, 146.78, 137.82, 137.26, 133.11, 133.05, 128.79, 128.62, 128.48, 128.38, 119.07, 118.89, 118.04 (t, *J* = 217.3 Hz), 117.98 (t, *J* = 219.4 Hz), 112.57, 112.47, 63.03, 42.26, 42.99, 32.84 (t, *J* = 24.0 Hz), 32.57 (t, *J* = 23.8 Hz), 29.70, 20.87, 20.14, 20.07 (t, *J* = 5.6 Hz); 19.81, 13.95.

HRMS (ESI) *m/z* calcd for C₂₀H₁₈F₂O₅Na [M+Na⁺] 399.1015, found 399.1013.



Ethyl 3-(2-benzoyl-2-(thiophene-2-carbonyl)cyclopropyl)-2,2-difluoropropanoate (4p) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction

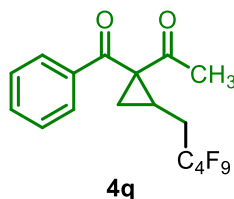
was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give yellow oil as inseparable 1:1 mixture of diastereomers, 44.6 mg, 57% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.86 (m, 2H), 7.60 – 7.58 (m, 1H), 7.54 – 7.45 (m, 2H), 7.38 – 7.34 (m, 2H), 6.97 – 6.94 (m, 1H), 4.34 (q, *J* = 7.2 Hz), 2.72–2.64 (m, 1H), 2.41 – 2.29 (m, 1H), 2.06 – 1.99 (m, 1H), 1.92 – 1.72 (m, 1H), 1.47 – 1.42 (m, 1H), 1.37 (dt, *J* = 2.0 Hz, 7.2 Hz, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -103.93 – -104.64 (m, 1F), -105.95 – -106.68 (m, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 195.76, 195.38, 187.85, 187.35, 163.80 (t, *J* = 32.3 Hz), 163.78 (t, *J* = 32.3 Hz), 144.25, 143.23, 137.56, 136.95, 134.84, 134.44, 133.89, 133.60, 133.55, 133.34, 128.87, 128.85, 128.26, 128.71, 128.37, 128.18, 115.56 (t, *J* = 249.6 Hz), 63.06, 44.21, 44.09, 33.06 (t, *J* = 23.7 Hz), 32.94 (t, *J* = 23.5 Hz), 20.28, 20.09, 19.70 (t, *J* = 6.8 Hz), 19.48 (t, *J* = 6.8 Hz), 13.96.

HRMS (ESI) *m/z* calcd for C₂₀H₁₈F₂SO₄Na [M+Na⁺] 415.0786, found 415.0787.



1-(1-benzoyl-2-(5,5,5,5,5,5,5,5,5,5-nonafluoro-5-iodopenta-2,4-dien-1-yl)cyclopropyl)ethan-1-one (4q)

was prepared via typical procedure, using alkene (0.2 mmol) and alkyl iodide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as major product, 35.3 mg, 42% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 5.9 Hz, 2H), 7.62 (t, *J* = 6.0 Hz, 1H), 7.49 (t, *J* = 6.3 Hz, 2H), 2.53 – 2.47 (m, 1H), 2.37 – 2.28 (m, 1H), 2.25 – 2.18 (m, 1H), 2.06 (s, 3H), 1.94 (dd, *J* = 3.7 Hz, 6.0 Hz, 1H), 1.41 (dd, *J* = 3.8 Hz, 7.2 Hz).

¹⁹F NMR (376 MHz, CDCl₃) δ -81.00 – -81.07 (m, 3F), -114.17 – -114.26 (m, 2F), -124.28 – -126.04 (m, 4F); **¹³C NMR** (100 MHz, CDCl₃) δ 202.47, 195.21, 136.29, 133.90, 129.12, 128.79, 45.49, 139.51, 30.86, 28.04 (t, *J* = 21.4 Hz), 20.14, 19.85 (t, *J* = 4.7 Hz).

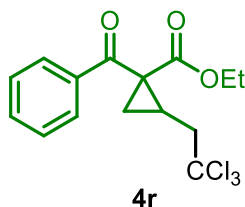
Minor products, 23.5 mg, 28% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.91 (t, *J* = 6.0 Hz, 2H), 7.52 (t, *J* = 6.2 Hz, 2H), 2.56 – 2.50 (m, 1H), 2.45 – 2.34 (m, 1H), 2.08 (s, 3H), 1.73 (dd, *J* = 3.7 Hz, 1H), 1.67 – 1.60 (m, 1H), 1.53 (m, dd, *J* = 3.7 Hz, 7.2 Hz, 1H).

= 3.7 Hz, $J_2 = 7.0$ Hz, 1H).

^{19}F NMR (376 MHz, CDCl_3) δ -81.05 - -81.12(m, 3F), -113.68 - -113.81 (m, 2F), -123.99 - -126.12 (m, 4F); **^{13}C NMR** (100 MHz, CDCl_3) δ 202.58, 195.10, 136.92, 134.15, 129.26, 128.80, 44.73, 30.47 (t, $J = 21.4$ Hz), 29.54, 21.85, 20.43 (t, $J = 5.5$ Hz).

HRMS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{13}\text{F}_9\text{O}_2\text{Na}$ [$\text{M}+\text{Na}^+$] 443.0664, found 443.0664.

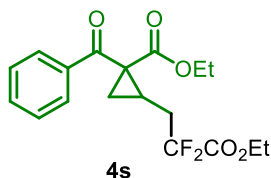


Ethyl 1-benzoyl-2-(2,2,2-trichloroethyl)cyclopropane-1-carboxylate (4r) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 61.0 mg, 88% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.90 – 7.87 (m, 2H), 7.61 – 7.53 (m, 1H), 7.50 – 7.43 (m, 2H), 4.13 – 3.97 (m, 2H), 3.11 – 3.05 (m, 1H), 2.97 – 2.91 (m, 0.5H), 2.67 – 2.57 (m, 1H), 2.13 – 2.06 (m, 0.5H), 1.95 – 1.91 (m, 1H), 1.74 – 1.58 (m, 1H), 0.97 – 0.88 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ 193.78, 193.41, 170.95, 169.71, 137.16, 136.83, 133.37, 132.99, 128.76, 128.56, 128.43, 128.18, 98.81, 98.60, 61.78, 61.73, 53.42, 52.02, 37.52, 35.82, 25.48, 23.16, 21.37, 21.20, 13.68, 13.66.

HRMS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{O}_3\text{Na}$ [$\text{M}+\text{Na}^+$] 370.9979, found 371.0002.



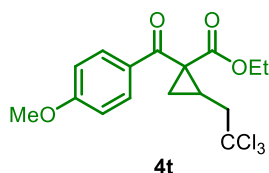
Ethyl 1-benzoyl-2-(3-ethoxy-2,2-difluoro-3-oxopropyl)cyclopropane-1-carboxylate (4s) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 3:1 mixture of diastereomers, 50.3 mg, 71% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.85 (m, 2H), 7.59 – 7.44 (m, 3H), 4.35 – 4.28 (m, 2H), 4.11 – 3.97 (m, 2H), 2.40 – 2.34 (m, 2H), 1.71 – 1.68 (m, 1H), 1.55 – 1.52 (m, 2H), 1.42 – 1.32 (m, 3H), 0.96 – 0.89 (m, 3H).

¹⁹F NMR (376 MHz, CDCl₃) δ -104.07 - -105.03 (m, 1F), -106.10 - -106.81 (m, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 193.99(minor), 193.51, 170.96, 169.65(minor), 163.67 (t, *J* = 32.2 Hz), 137.29, 136.93(minor), 133.26, 132.91(minor), 128.66, 128.51(minor), 128.40, 128.16(minor), 115.40 (t, *J* = 250.4 Hz), 63.07, 63.03(minor), 61.68, 37.40(minor), 36.21, 33.69 (t, *J* = 23.7 Hz), 32.35 (t, *J* = 23.7 Hz, minor), 21.30 (t, *J* = 6.7 Hz), 20.79(minor), 19.81, 19.02 (t, *J* = 5.9 Hz, minor), 13.94(minor), 13.92, 13.65, 13.61(minor).

HRMS (ESI) *m/z* calcd for C₁₈H₂₀F₂O₅Na [M+Na⁺] 377.1171, found 377.1171.

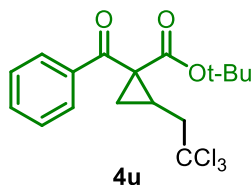


Ethyl 1-(4-methoxybenzoyl)-2-(2,2,2-trichloroethyl)cyclopropane-1-carboxylate (4t) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.6 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 3:2 mixture of diastereomers, 56.7 mg, 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.89 - 7.88 (m, 2H), 6.97 – 6.93 (m, 2H), 4.15 – 4.04 (m, 2H), 3.89 - 3.87 (m, 3H), 3.10 - 3.03 (m, 1H), 2.95 – 2.91 (m, 0.42H, minor), 2.60 - 2.52 (m, 1H), 2.07 – 2.02 (m, 0.55H, major), 1.72 - 1.69 (m, 0.63H, major), 1.57 - 1.54 (m, 0.47H, minor), 1.05 - 0.97 (m, 3H, major), 1.72 - 1.69 (m, 0.63H, major).

¹³C NMR (100 MHz, CDCl₃) δ 192.02, 191.55, 171.25, 170.03, 163.80, 163.52, 130.96, 130.68, 129.92, 129.39, 113.97, 113.79, 98.89, 61.79, 61.75, 55.56, 55.51, 53.65 52.06, 37.25, 35.53, 24.99, 23.02, 21.18, 20.96, 13.85.

HRMS (ESI) *m/z* calcd for C₁₆H₁₇Cl₃O₄Na [M+Na⁺] 401.0085, found 401.0098.

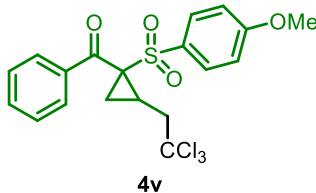


tert-butyl 1-benzoyl-2-(2,2,2-trichloroethyl)cyclopropane-1-carboxylate (4u) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.6 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 57.9 mg, 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.89 - 7.87 (m, 4H), 7.61 - 7.55 (m, 2H), 7.49 - 7.45 (m, 4H), 3.10 - 3.04 (m, 2H), 2.94 - 2.89 (m, 1H), 2.61 - 2.56 (m, 2H), 2.11 (dd, *J* = 8.8 Hz, 11.7 Hz, 1H), 1.93 - 1.85 (m, 2H), 1.66 - 1.63 (m, 1H), 1.58 - 1.54 (m, 1H), 1.19 (s, 9H), 1.17 (s, 9H).

¹³C NMR (100 MHz, CDCl₃) δ 194.53, 194.06, 169.83, 168.56, 137.72, 137.69, 133.15, 132.77, 128.66, 128.47, 128.31, 128.09, 98.94, 98.70, 82.77, 82.60, 53.36, 51.92, 38.38, 36.84, 27.57, 27.54, 25.26, 22.68, 22.18, 20.74.

HRMS (ESI) *m/z* calcd for C₁₇H₁₉Cl₃O₃Na [M+Na⁺] 399.0292, found 399.0289.

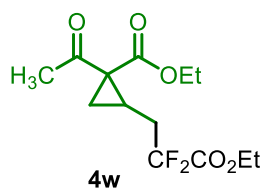


(1-((4-methoxyphenyl)sulfonyl)-2-(2,2,2-trichloroethyl)cyclopropyl)(phenyl)methanone (4v) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.6 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 5:1 mixture of diastereomers, 40.0 mg, 45% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.05 - 8.04 (m, 2H), 7.64 - 7.61 (m, 2H), 7.51 - 7.48 (m, 2H), 6.97 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 3.21 (dd, *J* = 1.8 Hz, 11.8 Hz, 1H), 2.52 - 2.43 (m, 2H), 1.86 (dd, *J* = 8.6 Hz, 11.9 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 190.58, 164.15, 135.48, 134.38, 130.98, 130.61, 129.46, 128.60, 114.38, 98.05, 55.69, 54.57, 51.37, 22.63, 20.66.

HRMS (ESI) *m/z* calcd for C₁₉H₁₇Cl₃O₄SNa [M+Na⁺] 469.9805, found 469.9804.



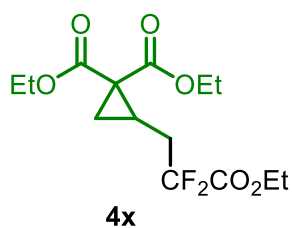
Ethyl 1-acetyl-2-(3-ethoxy-2,2-difluoro-3-oxopropyl)cyclopropane-1-carboxylate (4w) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 1:1 mixture of diastereomers, 51.3 mg, 88% yield.

¹H NMR (400 MHz, CDCl₃) δ 4.33 (q, t, *J* = 7.1 Hz, 2H), 4.28 – 4.17 (m, 2H), 2.43 – 2.40 (m, 3H), 2.20 – 2.03 (m, 3H), 1.66 – 1.62 (m, 1H), 1.48 – 1.41 (m, 1H), 1.37 – 1.28 (m, 6H).

¹⁹F NMR (376 MHz, CDCl₃) δ -104.60 - -105.32 (m, 3F), -106.27 – 107.45 (m, 1F).

¹³C NMR (100 MHz, CDCl₃) δ 201.82(minor), 201.66, 170.33, 169.08(minor), -163.76 (t, *J* = 29.7 Hz, minor), 163.65 (t, *J* = 32.1 Hz), 115.37 (t, *J* = 249.8 Hz, minor), 115.24 (t, *J* = 249.7 Hz), 63.05, 61.77(minor), 61.64, 39.83(minor), 39.17, 32.77 (t, *J* = 23.7 Hz, minor), 31.90 (t, *J* = 23.6 Hz), 30.76, 29.39(minor), 23.60 (t, *J* = 6.4 Hz), 22.54 (t, *J* = 5.6 Hz), 21.94 (minor), 20.26, 14.11(minor), 14.04, 13.90.

HRMS (ESI) *m/z* calcd for C₁₃H₁₈F₂O₅Na [*M*+Na⁺] 315.1015, found 315.0910.



diethyl 2-(3-ethoxy-2,2-difluoro-3-oxopropyl)cyclopropane-1,1-dicarboxylate (4x) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 12 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 52.8 mg, 81% yield.

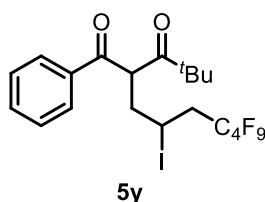
Gram scale: using alkene (10.0 mmol) and alkyl bromide (15.0 mmol) with 0.5 mol% Ir(ppy)₃ as the photocatalyst in DCM (30.0 mL), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil, 2.99 g, 93% yield.

¹H NMR (400 MHz, CDCl₃) δ 4.34 (q, t, *J* = 7.1 Hz, 2H), 4.29 – 4.12 (m, 4H), 2.50 – 2.37 (m, 1H), 2.02 – 2.00 (m, 1H), 1.99 – 1.85 (m, 1H), 1.48 – 1.42 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.31 – 1.25 (m, 6H).

¹⁹F NMR (376 MHz, CDCl₃) δ -104.39 - -106.69 (m, 2F).

¹³C NMR (100 MHz, CDCl₃) δ 169.39, 167.71, 163.75 (t, *J* = 32.2 Hz), 115.36 (t, *J* = 250.0 Hz), 63.02, 61.75, 61.71, 33.48 (t, *J* = 24.0 Hz), 32.85, 20.16 (t, *J* = 6.2 Hz), 20.08, 14.00 (t, *J* = 7.9 Hz).

HRMS (ESI) *m/z* calcd for C₁₄H₂₀F₂O₆Na [M+Na⁺] 345.1120, found 345.1120.



4,4-dimethyl-2-(7,7,7,7,7,7,7,7-nonafluoro-2-iodo-7H-hepta-4,6-diyn-1-yl)-1-

phenylpentane-1,3-dione (5y) was prepared via typical procedure, using alkene (0.2 mmol) and alkyl bromide (0.4 mmol), the reaction was stirred for 24 hours. The crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give colorless oil as inseparable 3:1 mixture diastereomers, 108.5 mg, 92% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.12 – 8.00 (m, 2H), 7.68 – 7.51 (m, 3H), 5.32 – 5.29 (m, 1H), 4.21 – 4.14 (m, 1H), 2.96 – 2.75 (m, 2H), 2.59 – 2.53 (m, 1H), 2.35 – 1.97 (m, 1H), 1.17 – 1.64 (m, 9H).

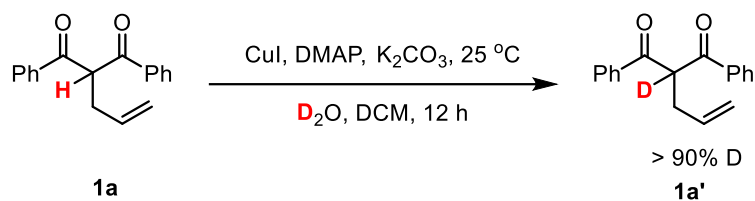
¹⁹F NMR (376 MHz, CDCl₃) δ -80.99 - -81.06 (m, 3F), -111.37 - -114.41 (m, 2F), -124.54 - -125.94 (m, 4F).

¹³C NMR (100 MHz, CDCl₃) δ 209.29, 208.64(minor), 195.21, 194.85(minor), 136.67(minor), 134.65, 134.12, 133.76(minor), 129.18, 128.97(minor), 128.82, 128.62(minor), 56.80, 56.64(minor), 45.64(minor), 44.58, 42.05 (t, *J* = 20.8 Hz), 41.09(minor), 39.85, 26.87(minor), 26.61, 20.05, 18.35(minor).

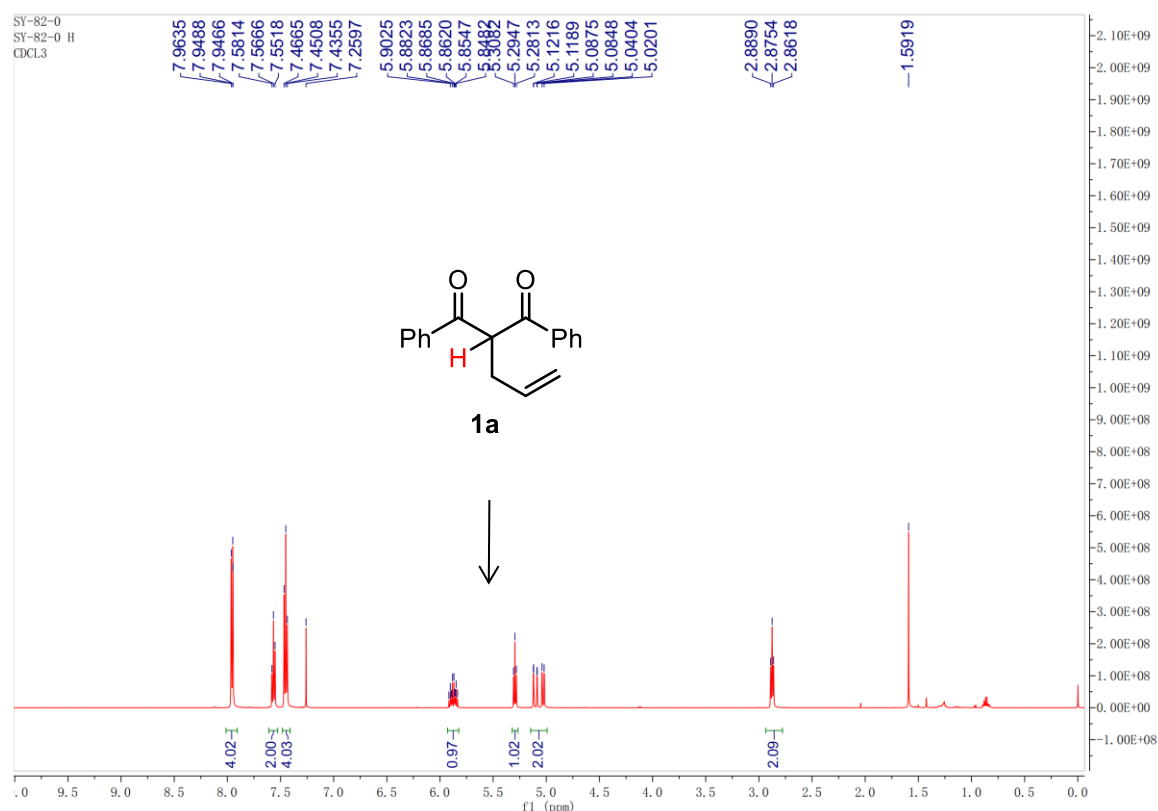
HRMS (ESI) *m/z* calcd for C₂₀H₂₀F₉O₂NaI [M+Na⁺] 613.0256, found 613.0261.

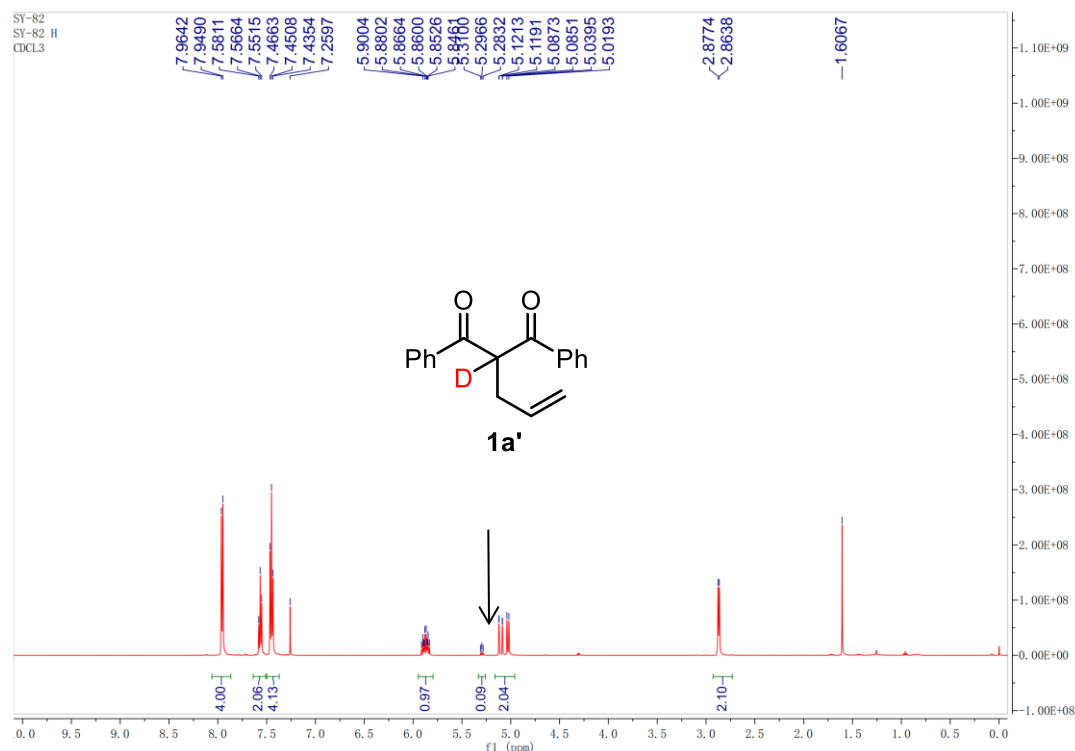
4. Mechanism studies

Deuterium experiment

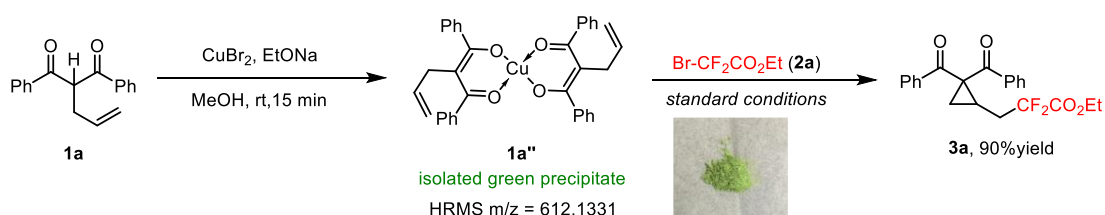


To a dried Schlenk tube was added CuI (10 mol%), DMAP (20 mol%), K₂CO₃ (2.0 equiv.), followed by DCM (1.0 mL), **1a** (0.2 mmol) and D₂O (0.5 mL) was injected into mixture. The mixture was shanked three times, degassed three times (10 minutes every time) by freeze-pump-thaw method. The reaction mixture was stirred under Argon atmosphere at 25 °C in an incubator for 12 hours. After reaction completed, the reaction mixture was transfer into a 100 mL round-bottom flask, follow by *silica gel* (about 20-50 mg) was added into, then the solvent was removed under reduced conditions. The residue was directly loaded onto a short SepaFlash® column, and the crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give desired product as white solid in quantitative yield, the structure of **1a'** was checked by ¹H NMR.

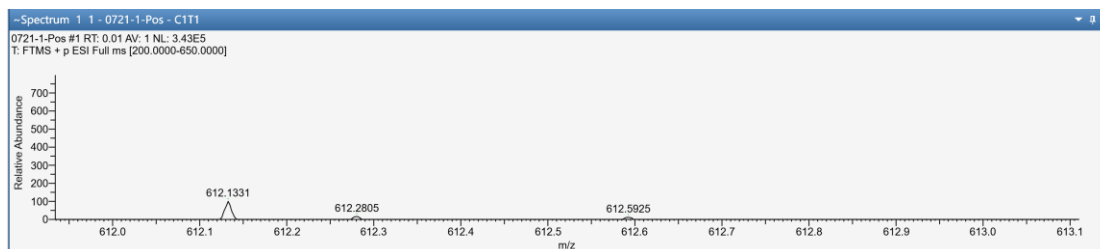




Preparation of Copper complex



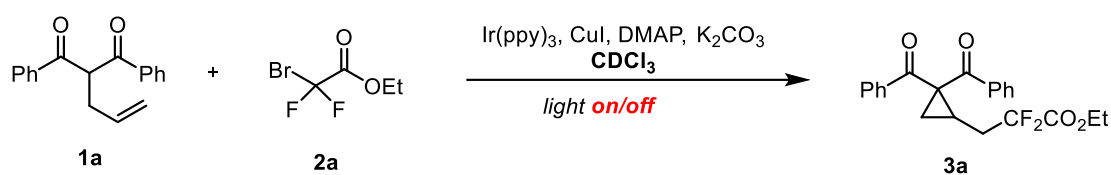
To a 25 mL seal tube was added **1a** (2.2 mmol) and MeOH (10.0 mL) under open air, then mixture was stirred at room temperature until the solid was completely dissolved. Subsequently, CuBr_2 (1.0 mmol) was added in one portion, then EtONa (2.2 mmol) was added slowly (green solids will slowly precipitate). The reaction mixture was stirred about 15 minutes, filter to give a green precipitate, and rinse with MeOH to obtain a pure product **1a''**, 420 mg, 68% yield.



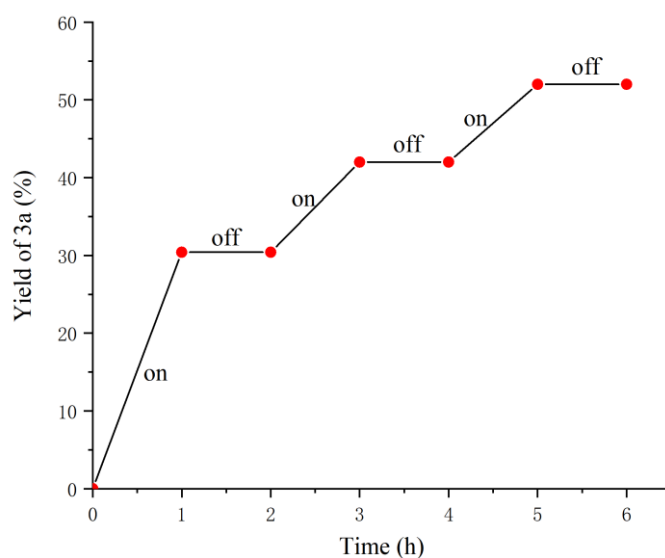
To a dried 10 mL Schlenk tube was added **1a''** (122.4 mg, 0.2 mmol), DMAP (20 mol%), K_2CO_3 (2.0 equiv.) and Ir(ppy)_3 (1 mol%) under Argon atmosphere. Subsequently, DCM (2.0 mL), **2a** (0.4 mmol) was added, the mixture was degassed three times (10 minutes every time) by freeze-

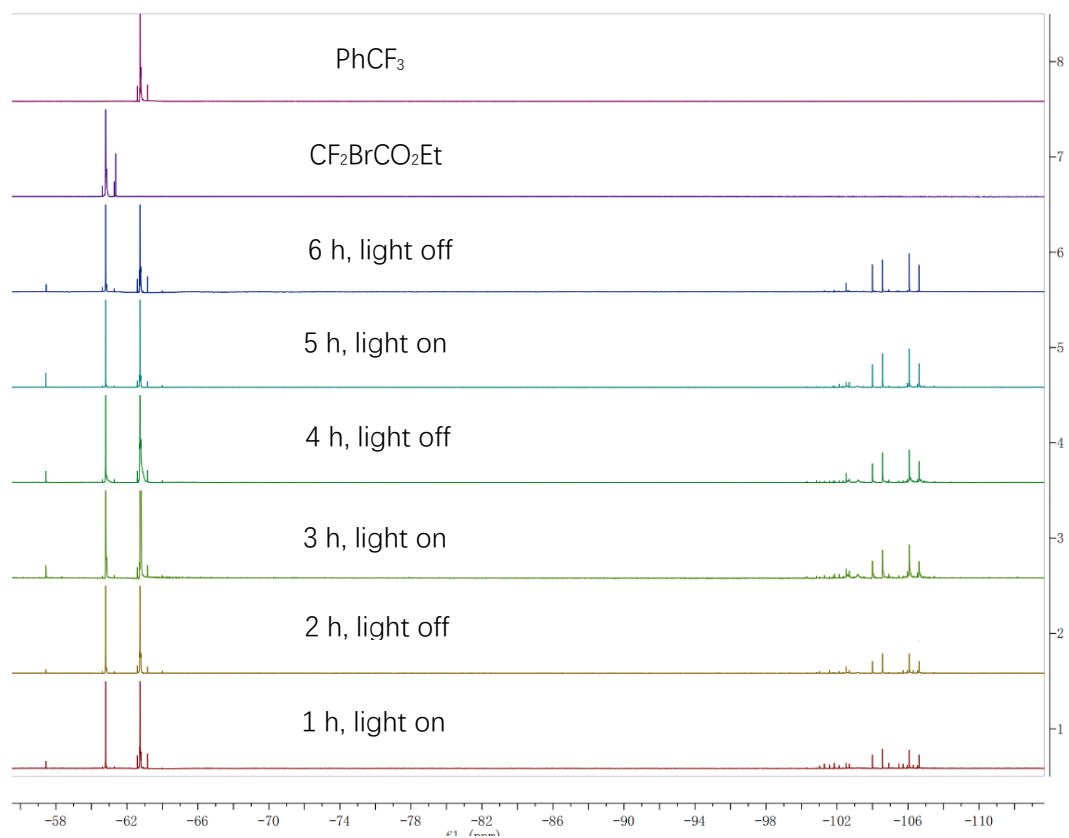
pump-thaw method. The reaction mixture was stirred under Argon atmosphere at 25 °C in an incubator under 450 nm blue LEDs for 12 hours. After reaction completed, the reaction mixture was transfer into a 100 mL round-bottom flask, follow by *silica gel* (about 20-50 mg) was added into, then the solvent was removed under reduced conditions. The residue was directly loaded onto a short SepaFlash® column, and the crude products were purified by SepaBean® Machine with petroleum ether and ethyl acetate as eluent to give desired product as colorless oil in 90% yield.

Light on/off experiment



To a dried 10 mL Schlenk tube was added **1a** (0.05 mmol), DMAP (20 mol%), K_2CO_3 (2.0 equiv.) and Ir(ppy)_3 (1 mol%) under Argon atmosphere. Subsequently, CDCl_3 (0.5 mL), **2a** (0.1 mmol) was added, the mixture was degassed three times (10 minutes every time) by freeze-pump-thaw method. Reaction mixture was stirred under Argon atmosphere at 25 °C in an incubator under 450 nm blue LEDs for one hour. The product yield was then measured by ^{19}F -NMR with PhCF_3 as an internal standard. After which the reaction mixture was kept in dark for another one hour and further analyzed by ^{19}F -NMR analysis. These on-off measurements were repeated, which showed that the product is formed only upon constant irradiation and the reaction was not a chain reaction.





Luminescence quenching experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CHI600E. A solution of sample in MeCN (0.001M) was tested with 0.1 M Bu₄NP₆ as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, an a saturated calomel electrode reference electrode. Scan rate = 0.05 V/s, 2 sweep segments, a sample interval of 0.001 V.

UV-vis absorption spectra

UV-vis absorption spectroscopy was conducted using a spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in 1.5 mL quartz cuvettes fitted with a PTFE stopper. **1a**, **2a**, CuI, *fac*-Ir, DMAP, and their mixture were prepared as a 0.1 mM solution with fresh MeCN as the solvent for measurement.

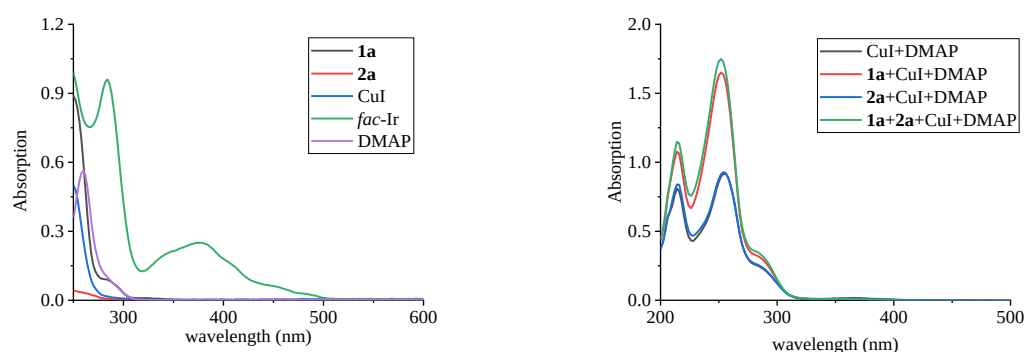


Figure S1. UV-vis absorption spectra.

Stern-Volmer Fluorescence Quenching Experiments

Emission intensities were recorded using Microplate Accessory 5JO-0139 spectrometer for all experiments. All *fac*-Ir(ppy)₃ solutions were excited at 380 nm and the emission intensity was collected at 528 nm. In a typical experiment, the solution of *fac*-Ir(ppy)₃ in MeCN (3.33×10^{-5}) was added the appropriate amount of quencher in a screw-up 3.0 cm quartz cuvette. After degassing with Argon for 10 min, the emission spectra of the samples were collected.

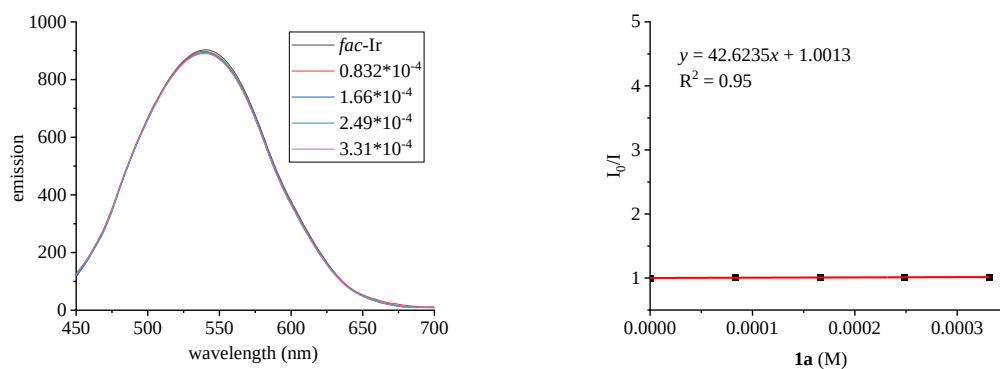


Figure S2. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of **1a** in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

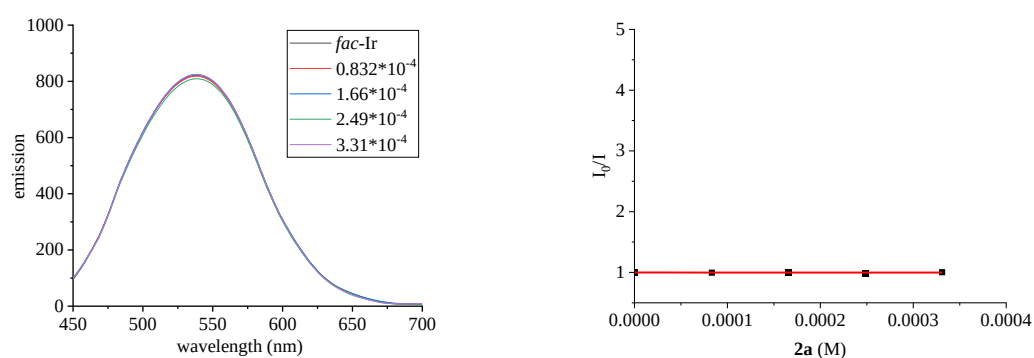


Figure S3. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of **2a** in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

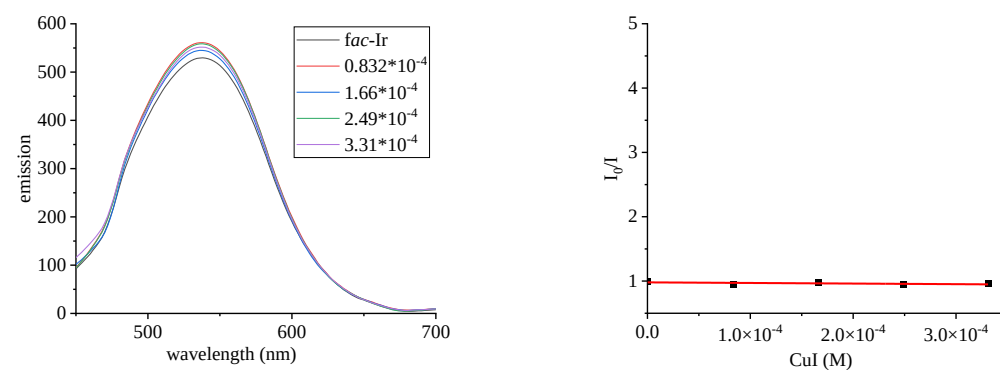


Figure S4. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of CuI in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

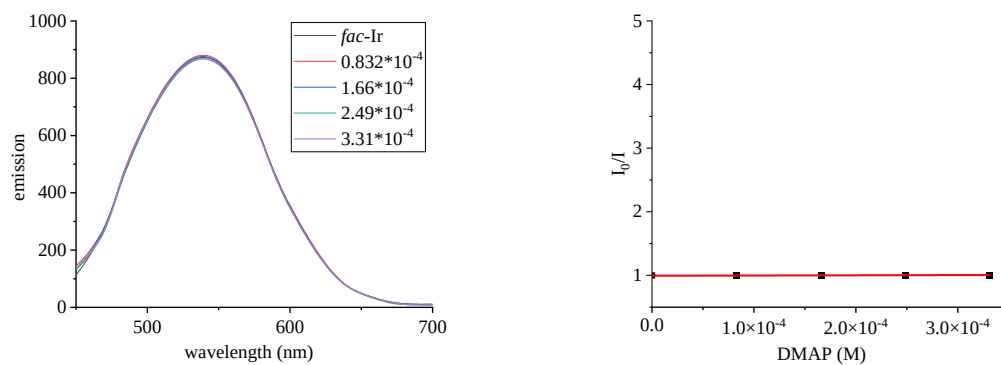


Figure S5. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of DMAP in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

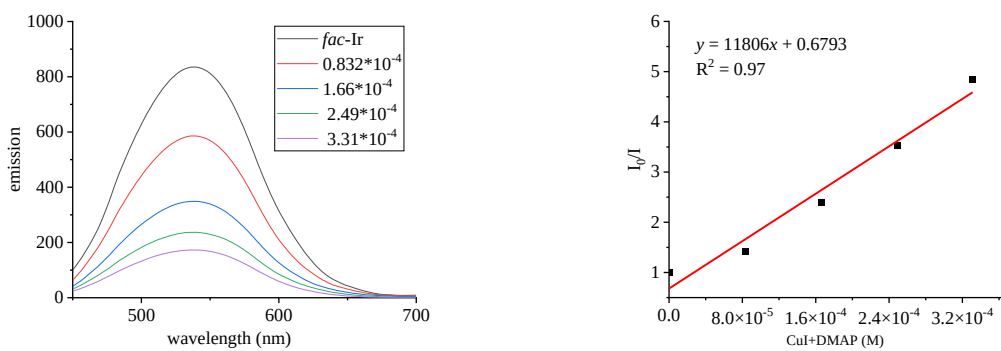


Figure S6. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of the combination of 1.0 equiv CuI and 1.0 equiv DMAP in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

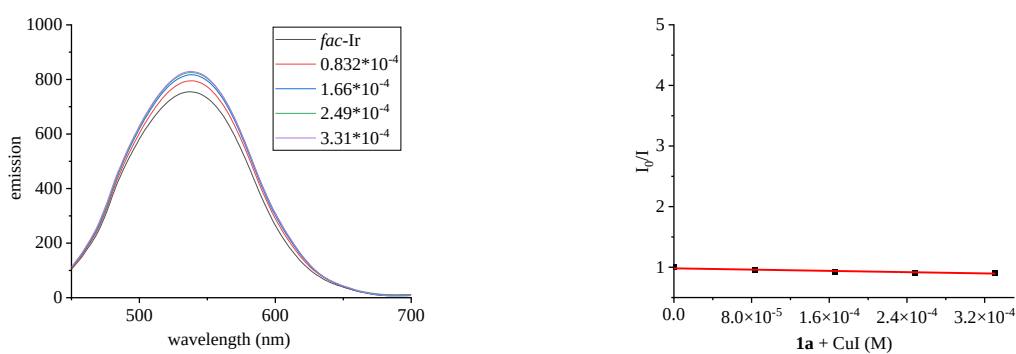


Figure S7. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of the combination of 1.0 equiv **1a** and 1.0 equiv CuI in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

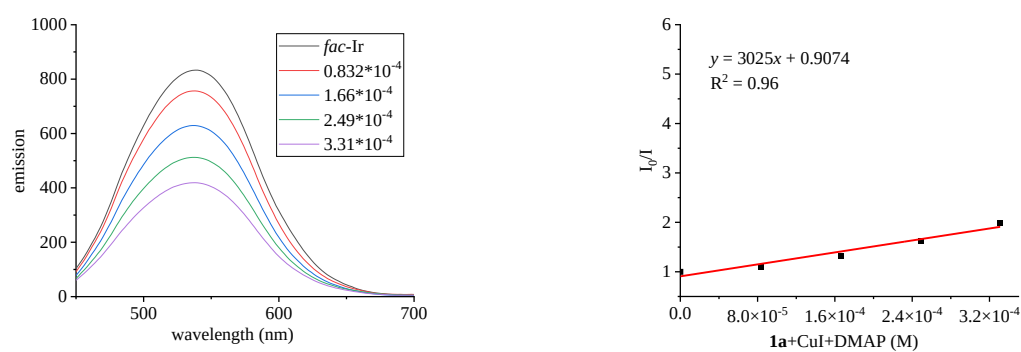


Figure S8. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) as a function of concentration of the combination of 1.0 equiv **1a**, 1.0 equiv CuI and 1.0 equiv DMAP in degassed MeCN with excitation at 380 nm (left). Quenching constant (right).

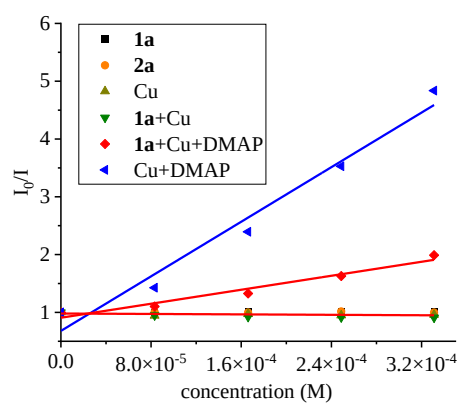
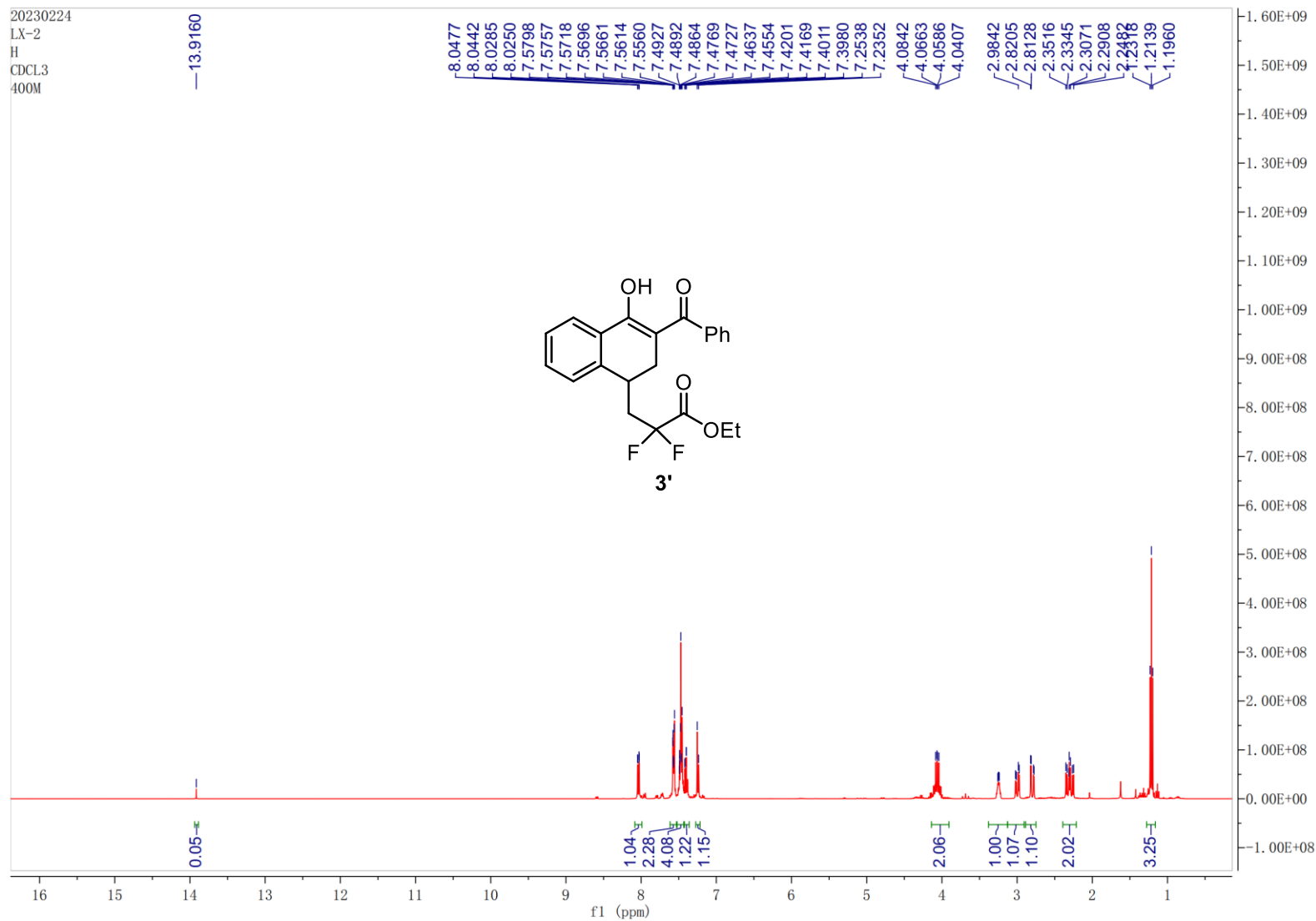


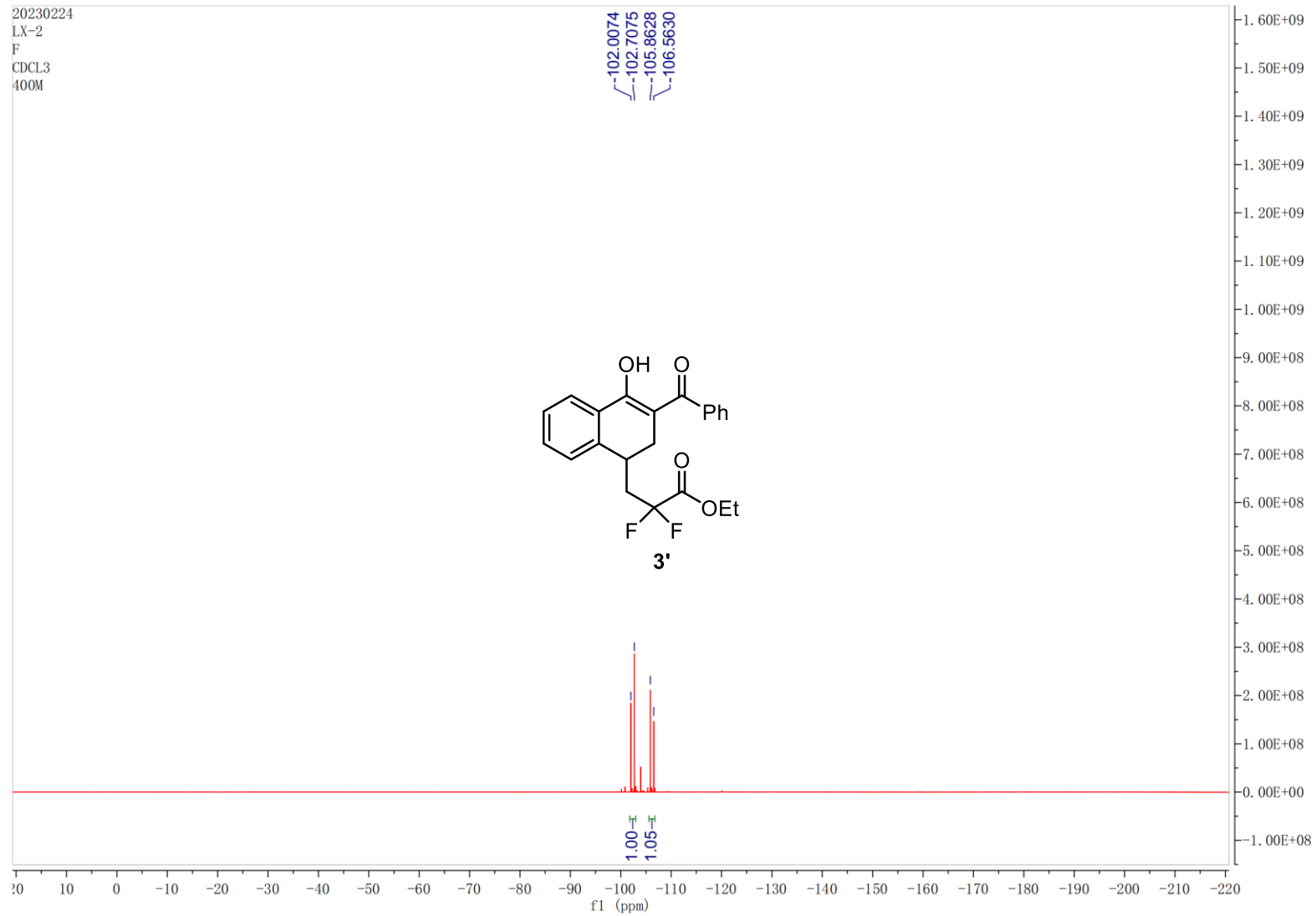
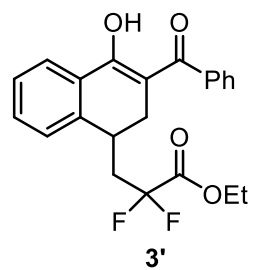
Figure S9. The luminescence spectrum of *fac*-Ir (3.33 × 10⁻⁵ M) with different compounds.

5. Copies of NMR Spectra

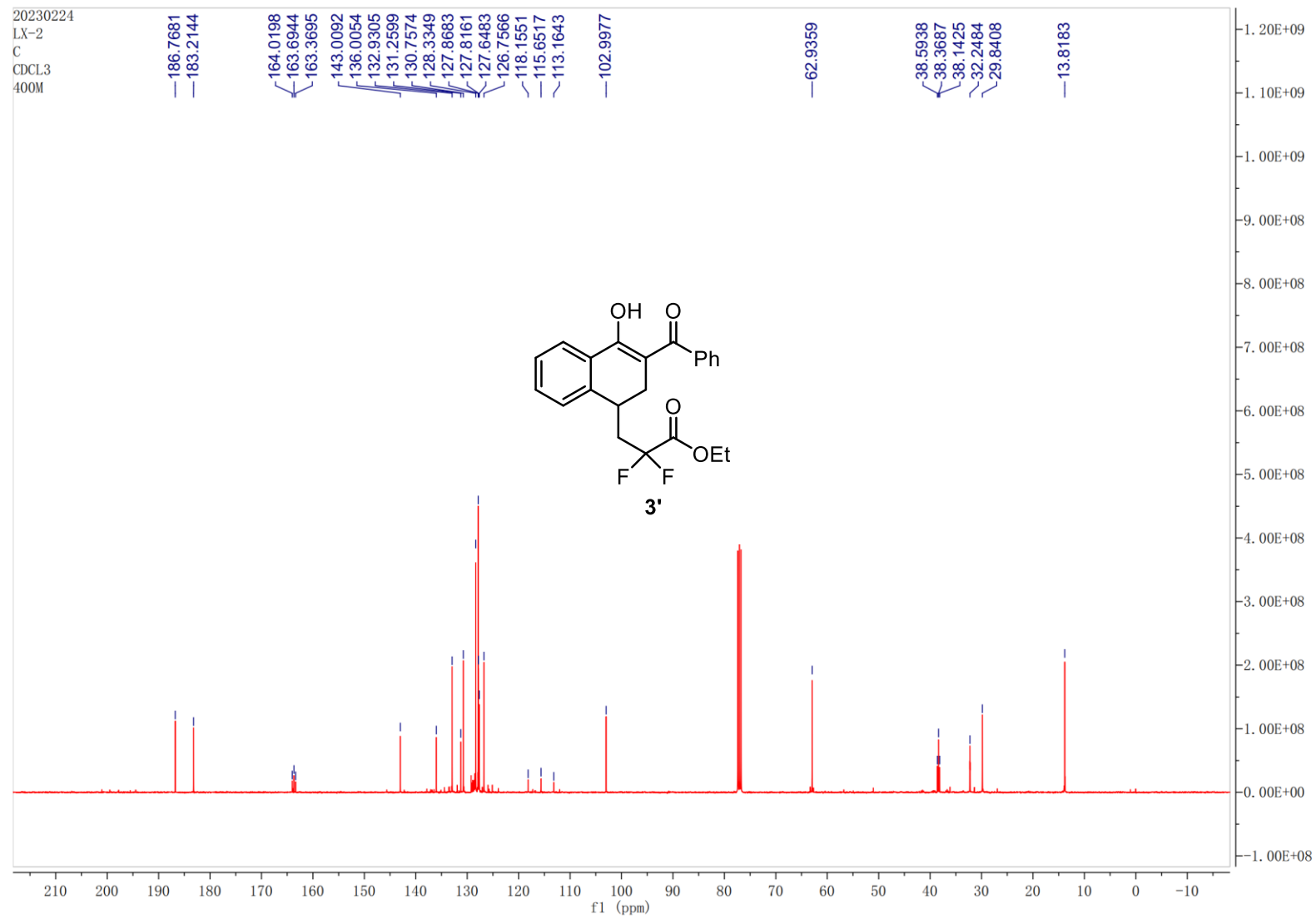
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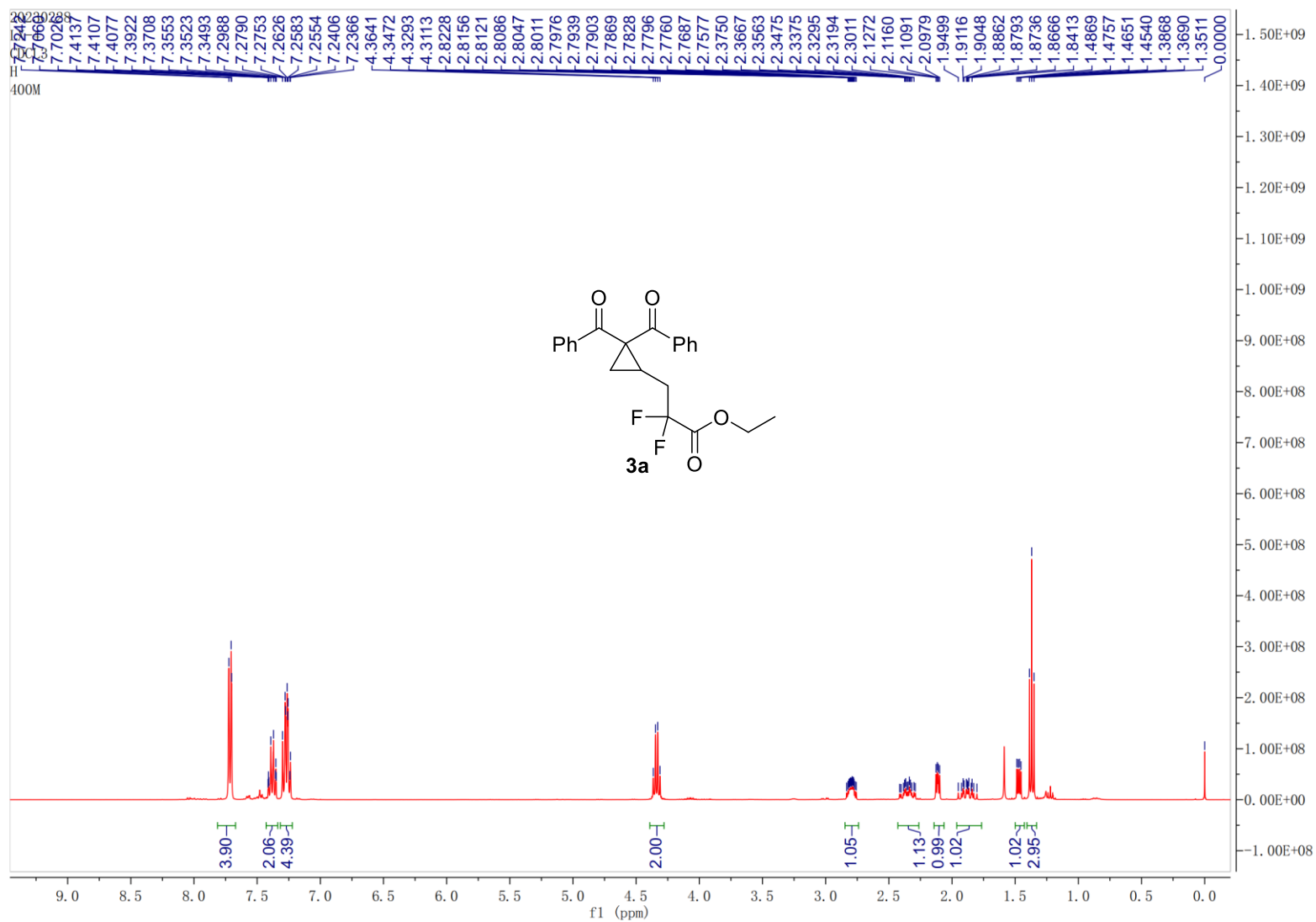


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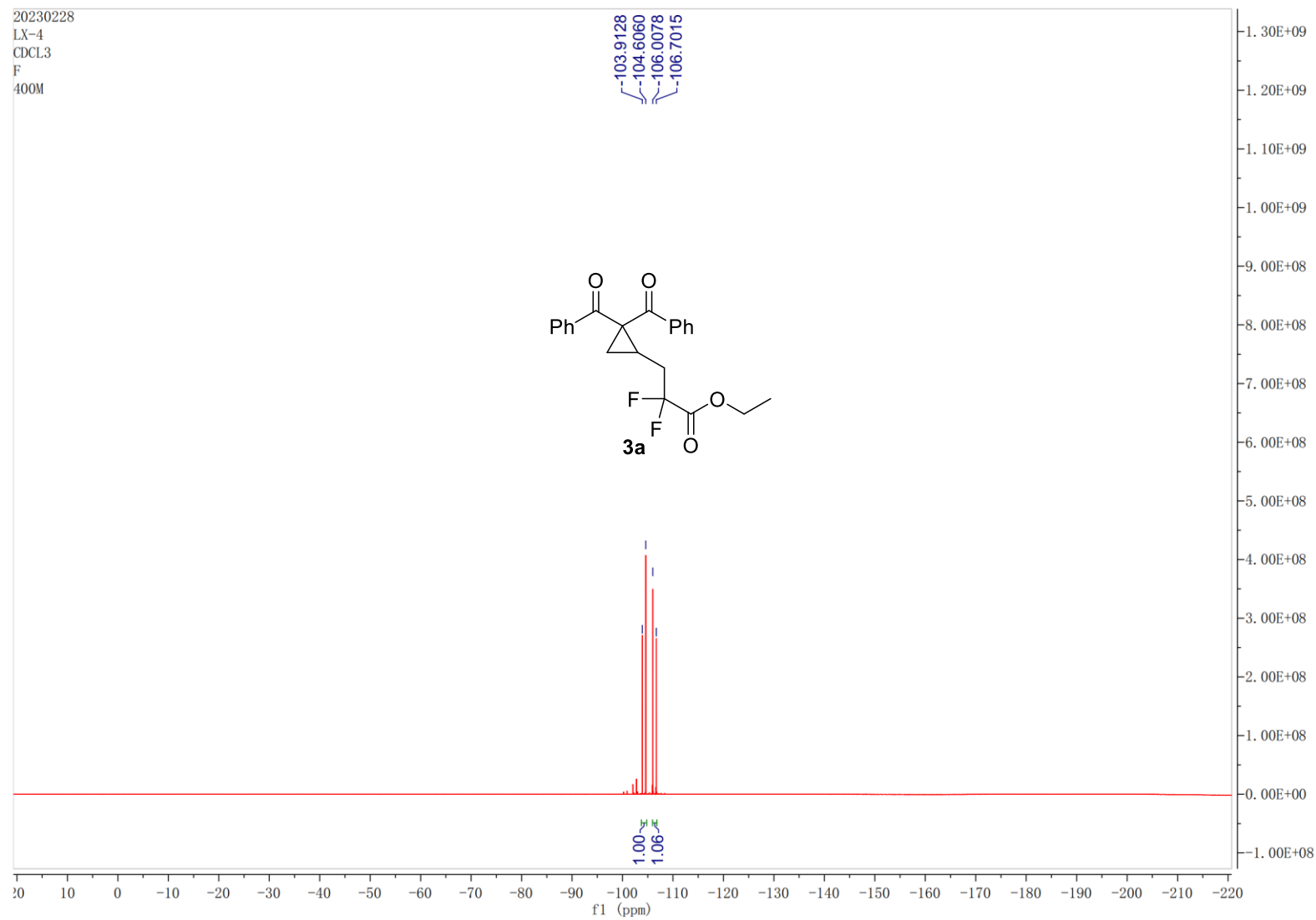
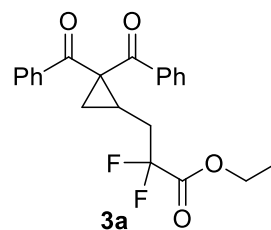


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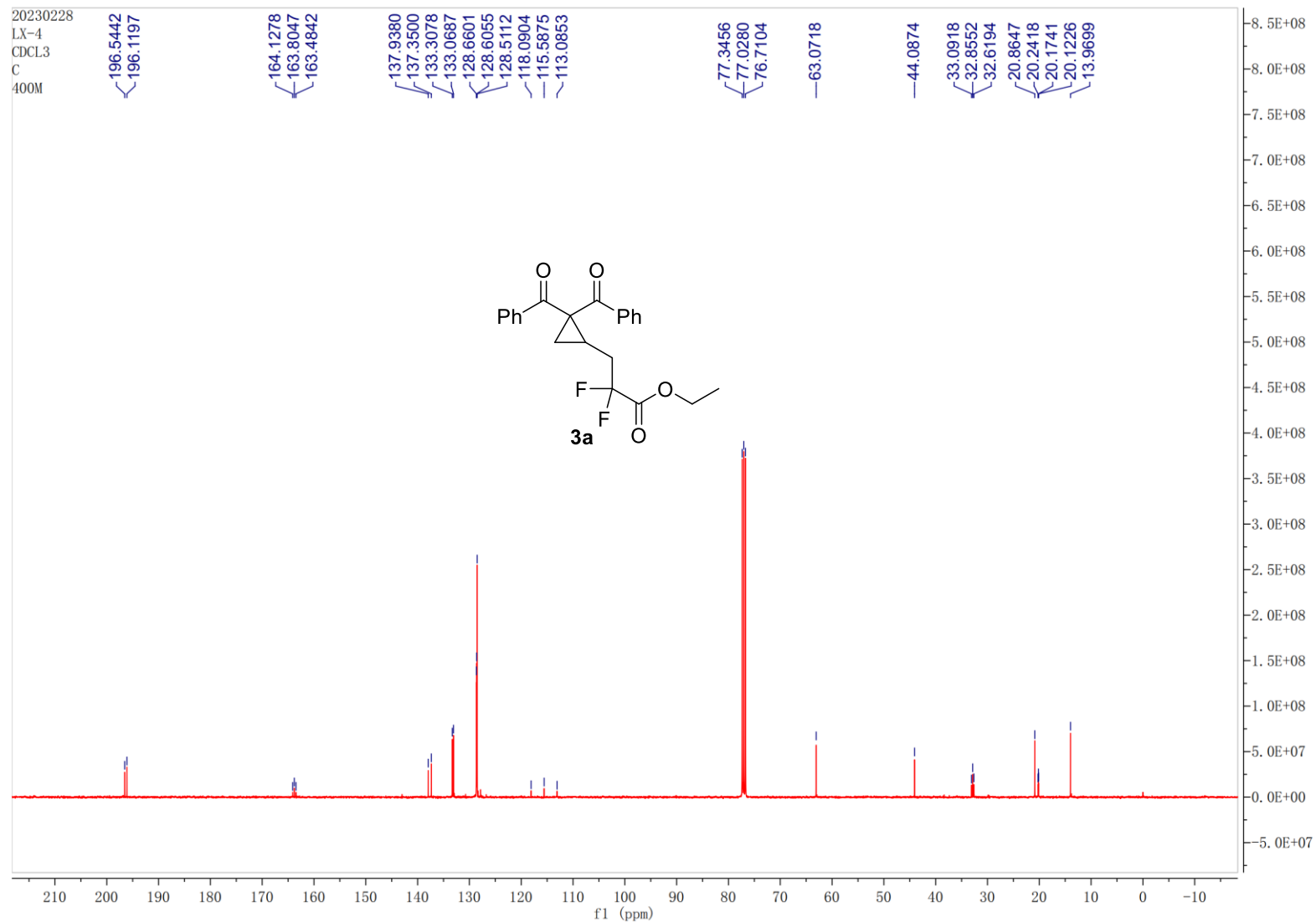


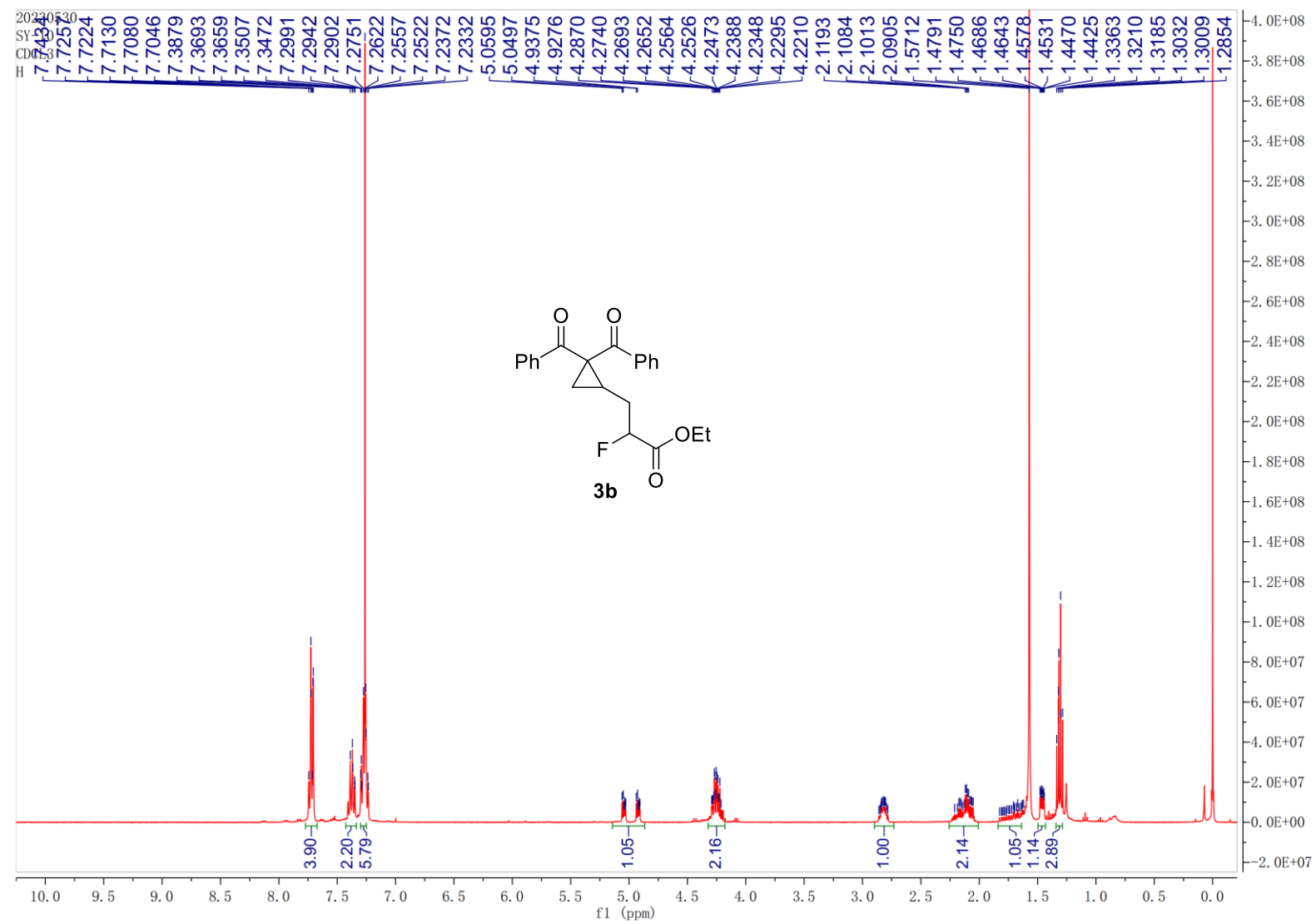


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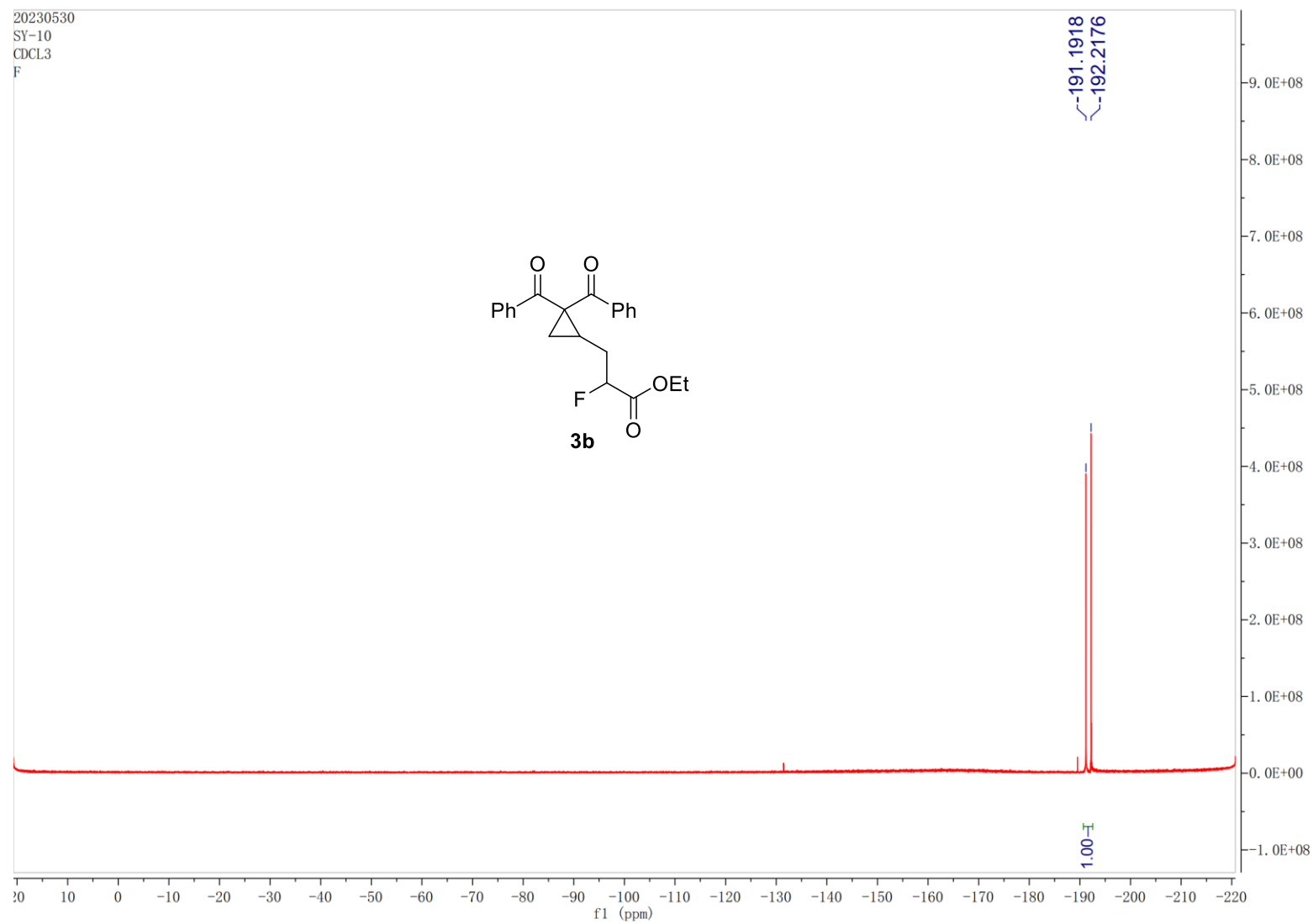
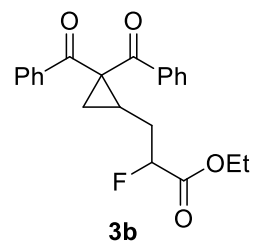


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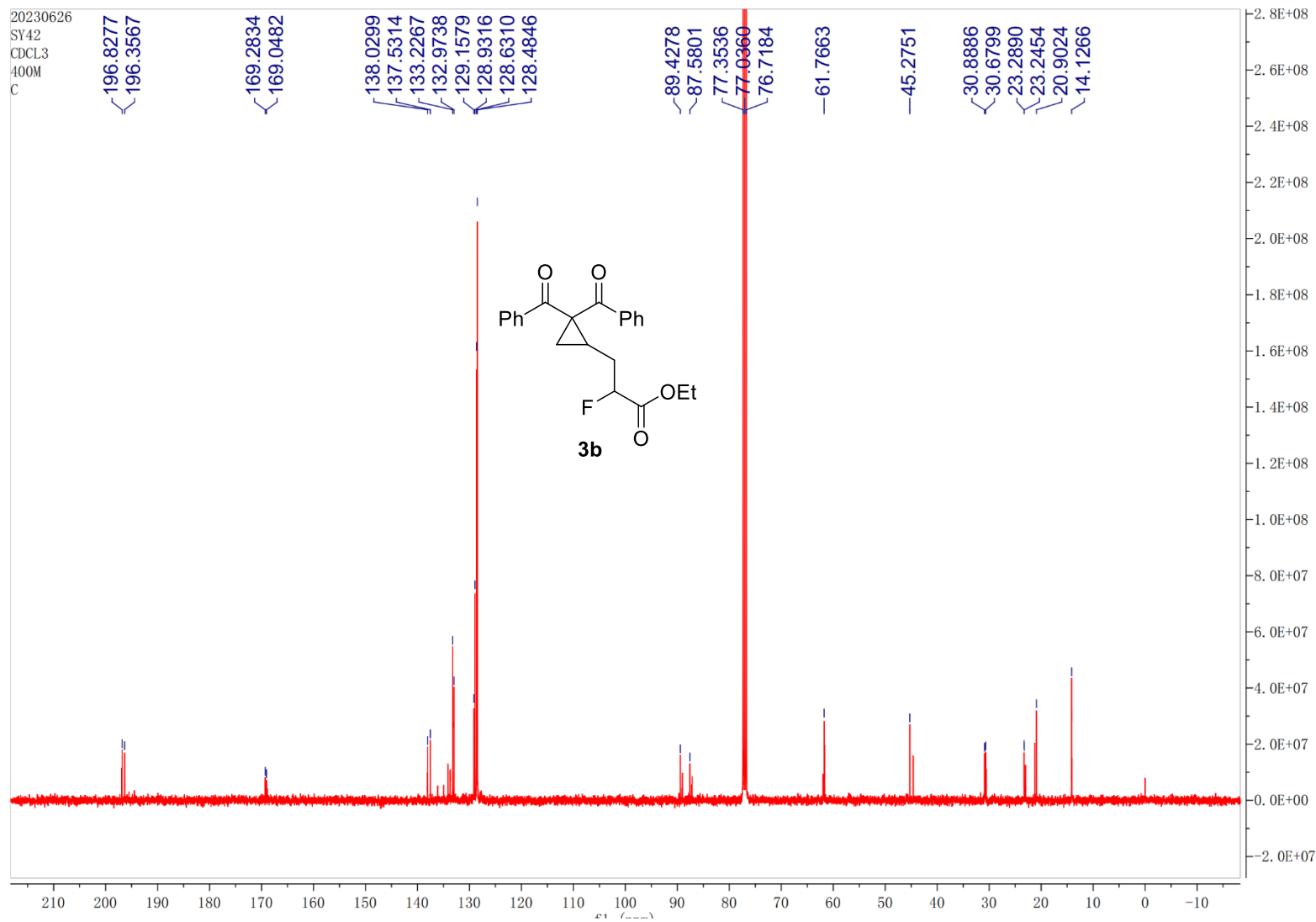


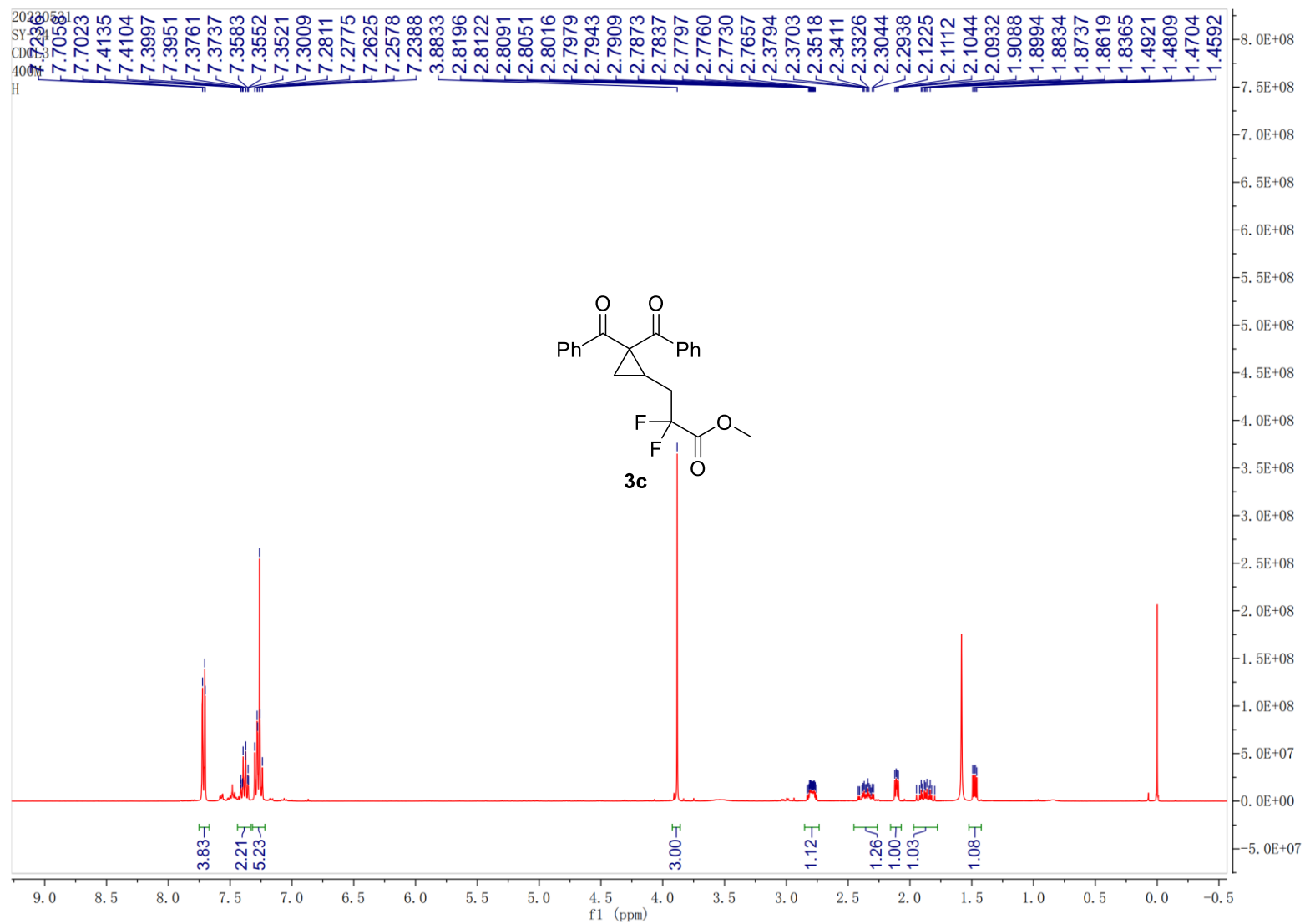


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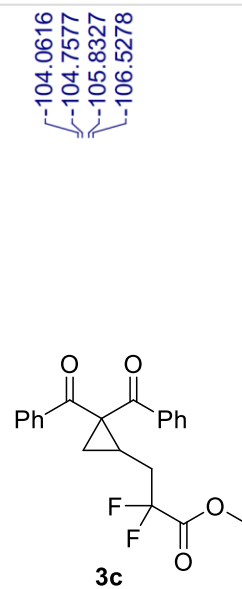


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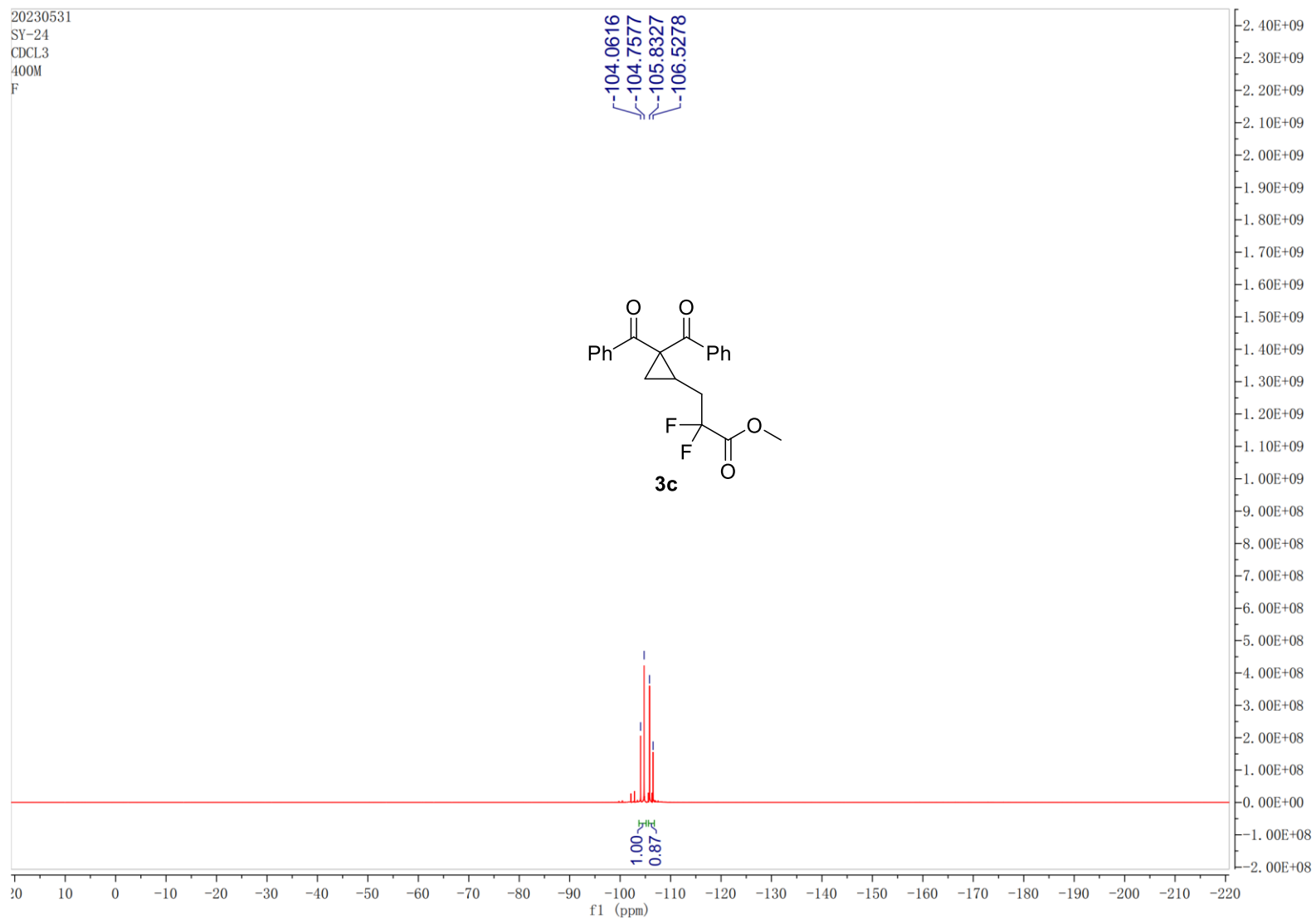




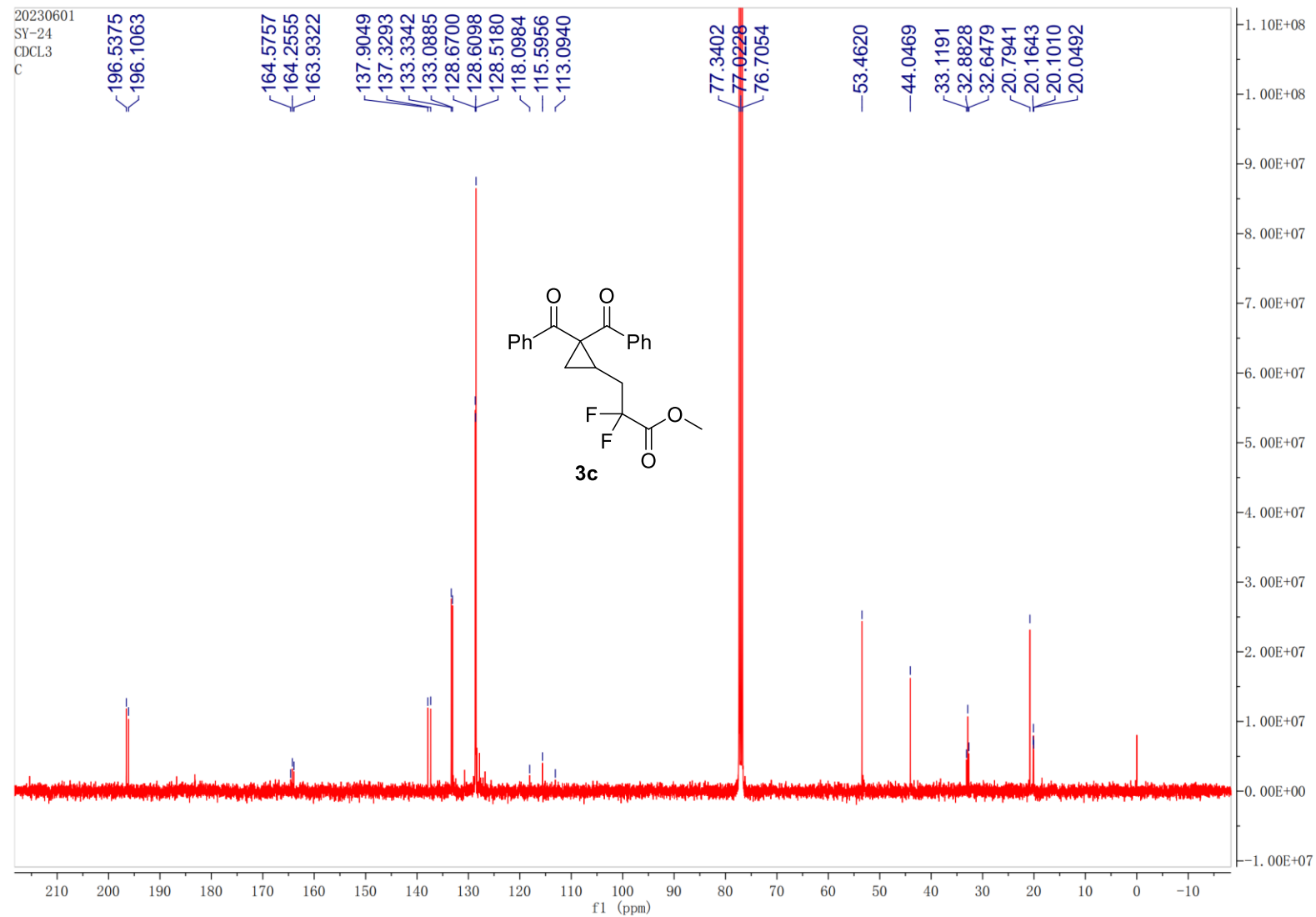
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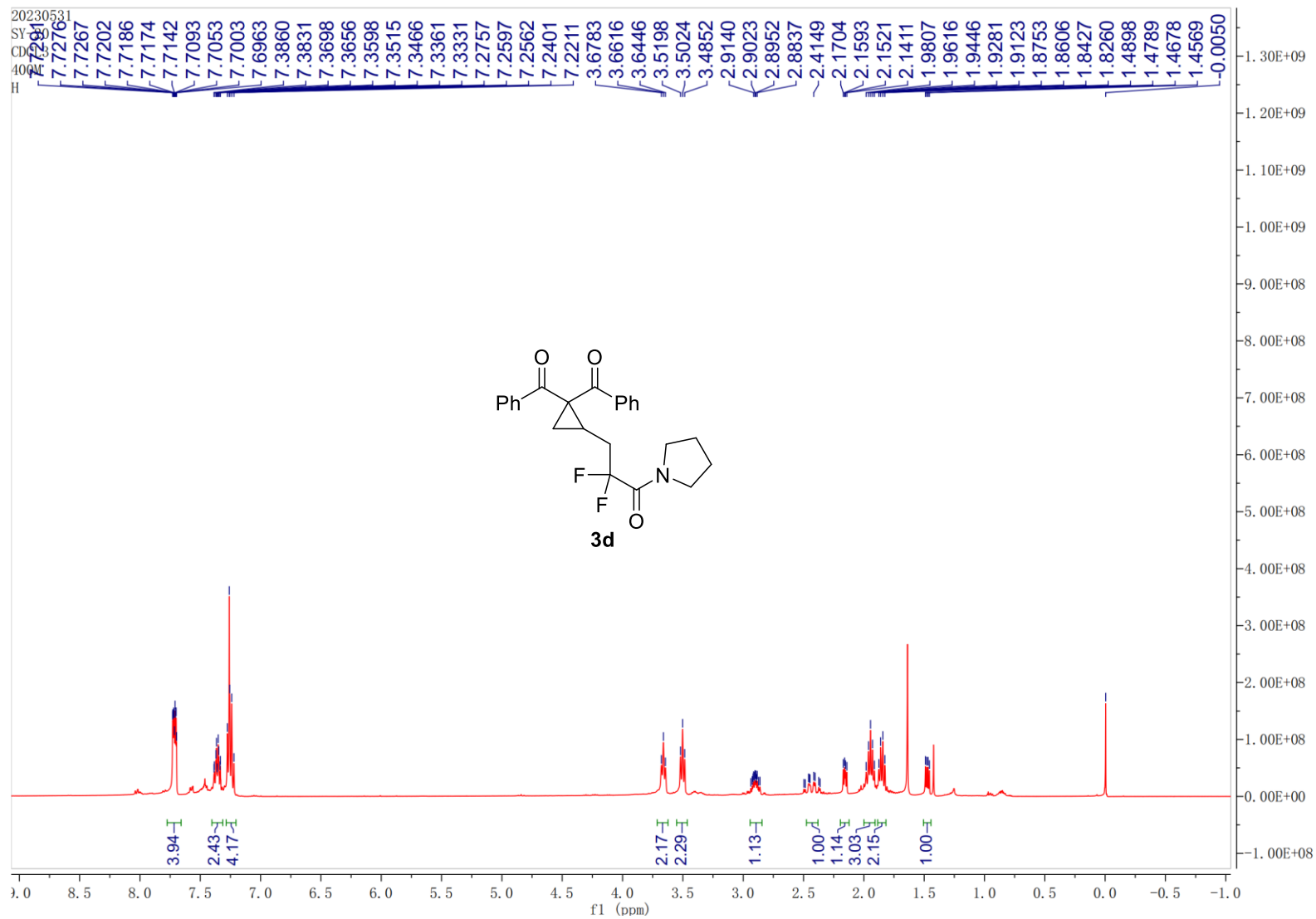


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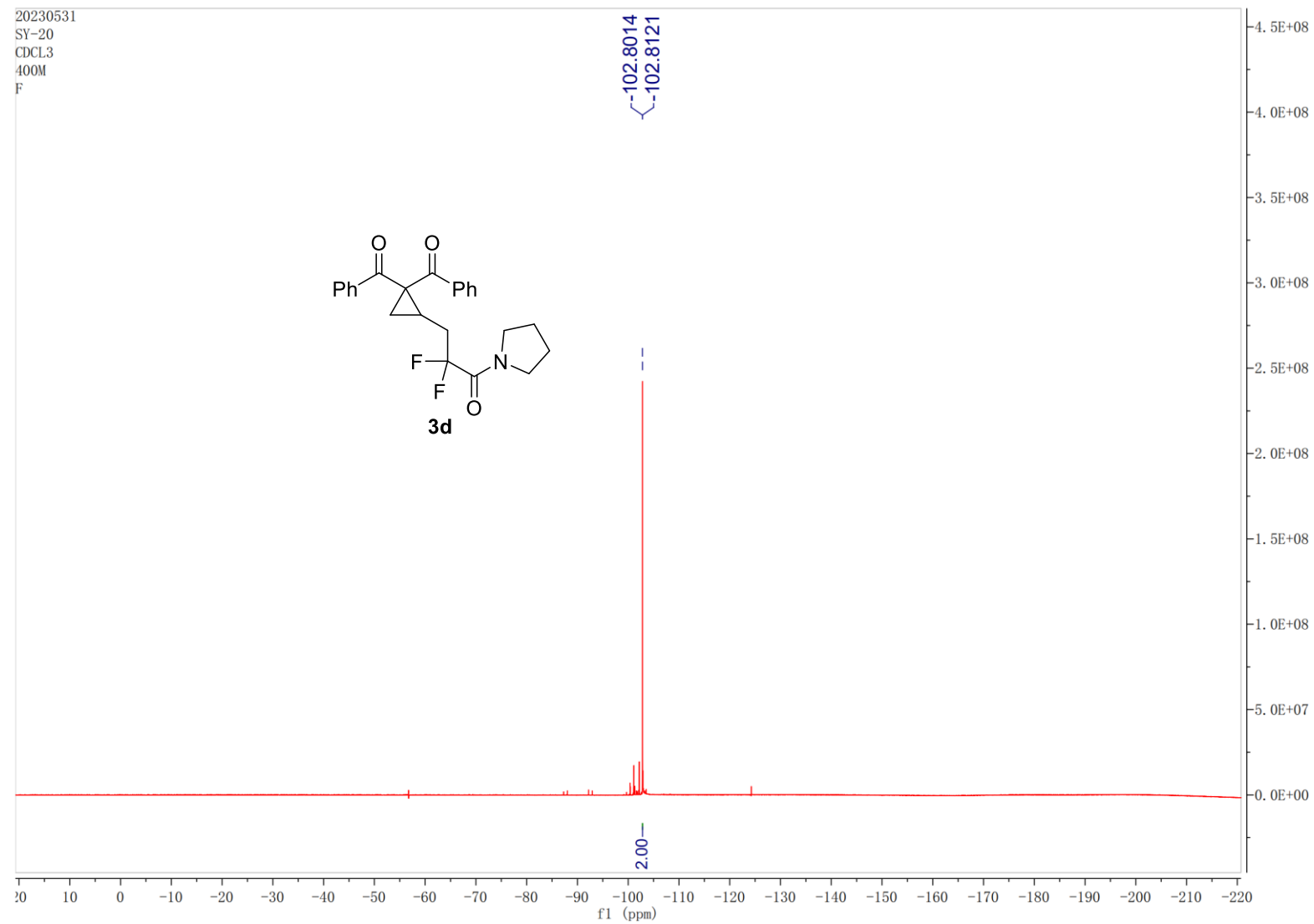
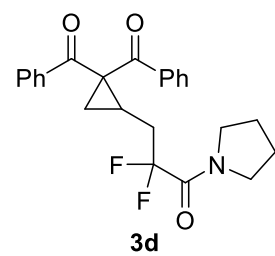


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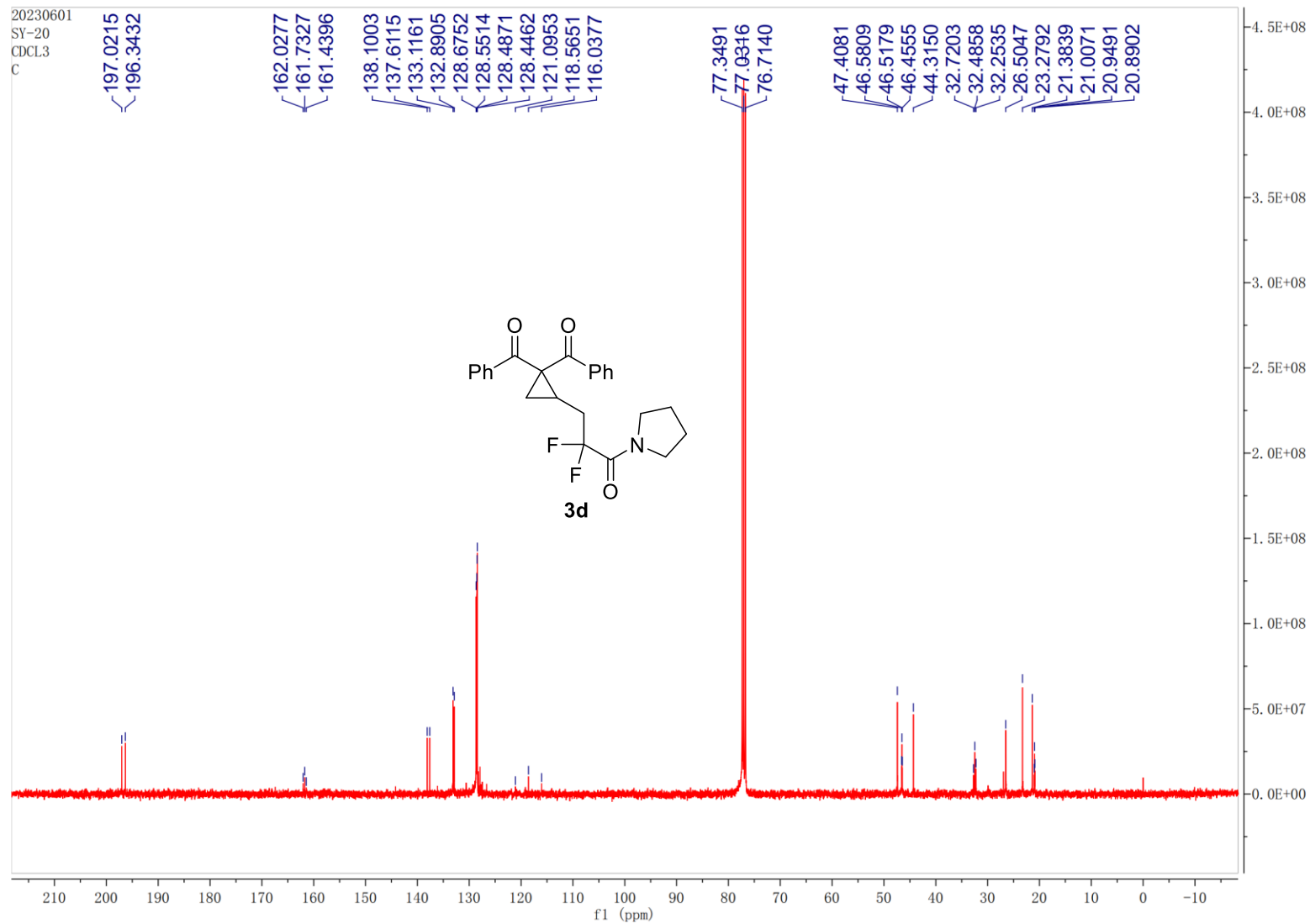


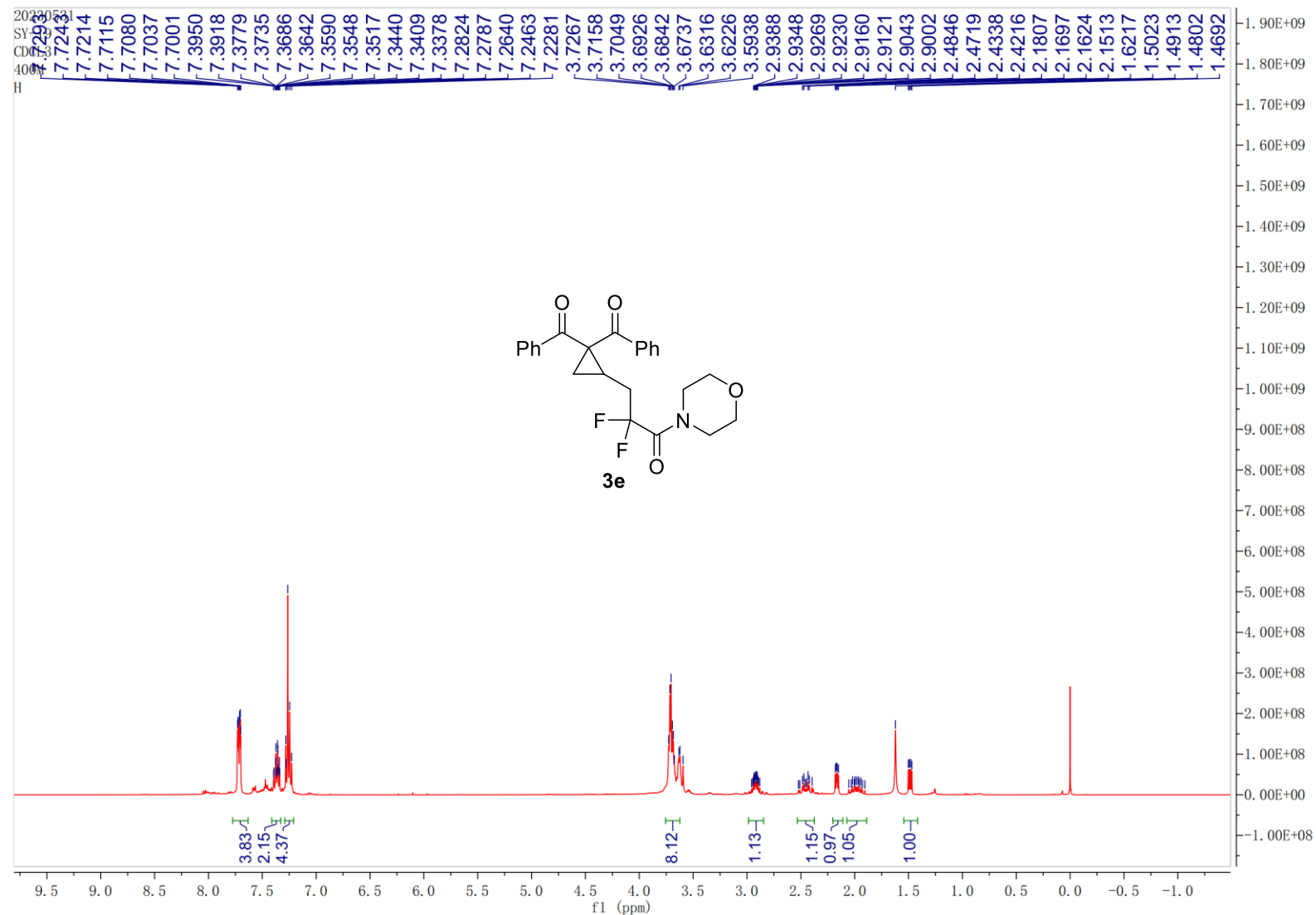


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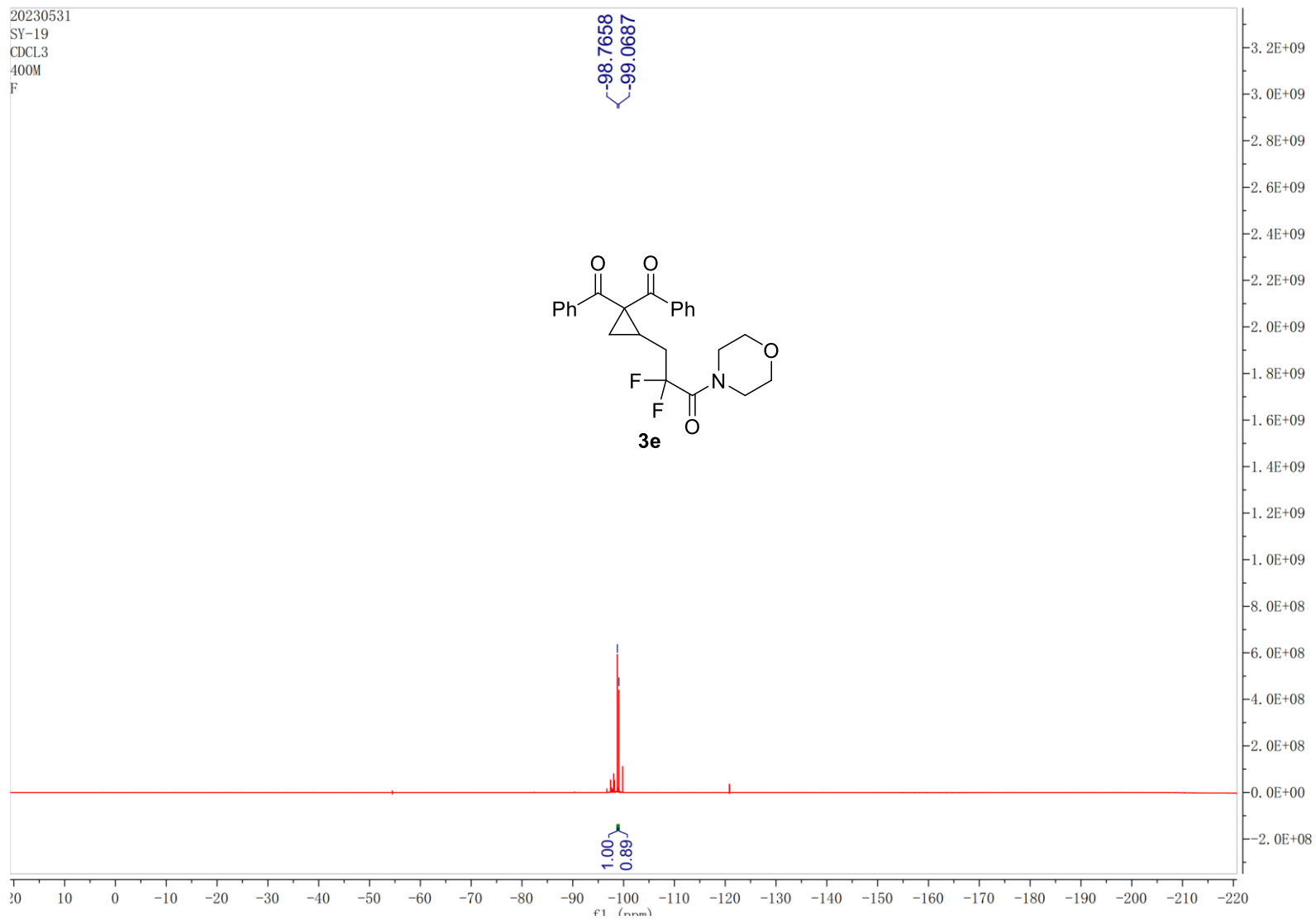
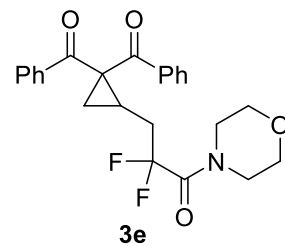


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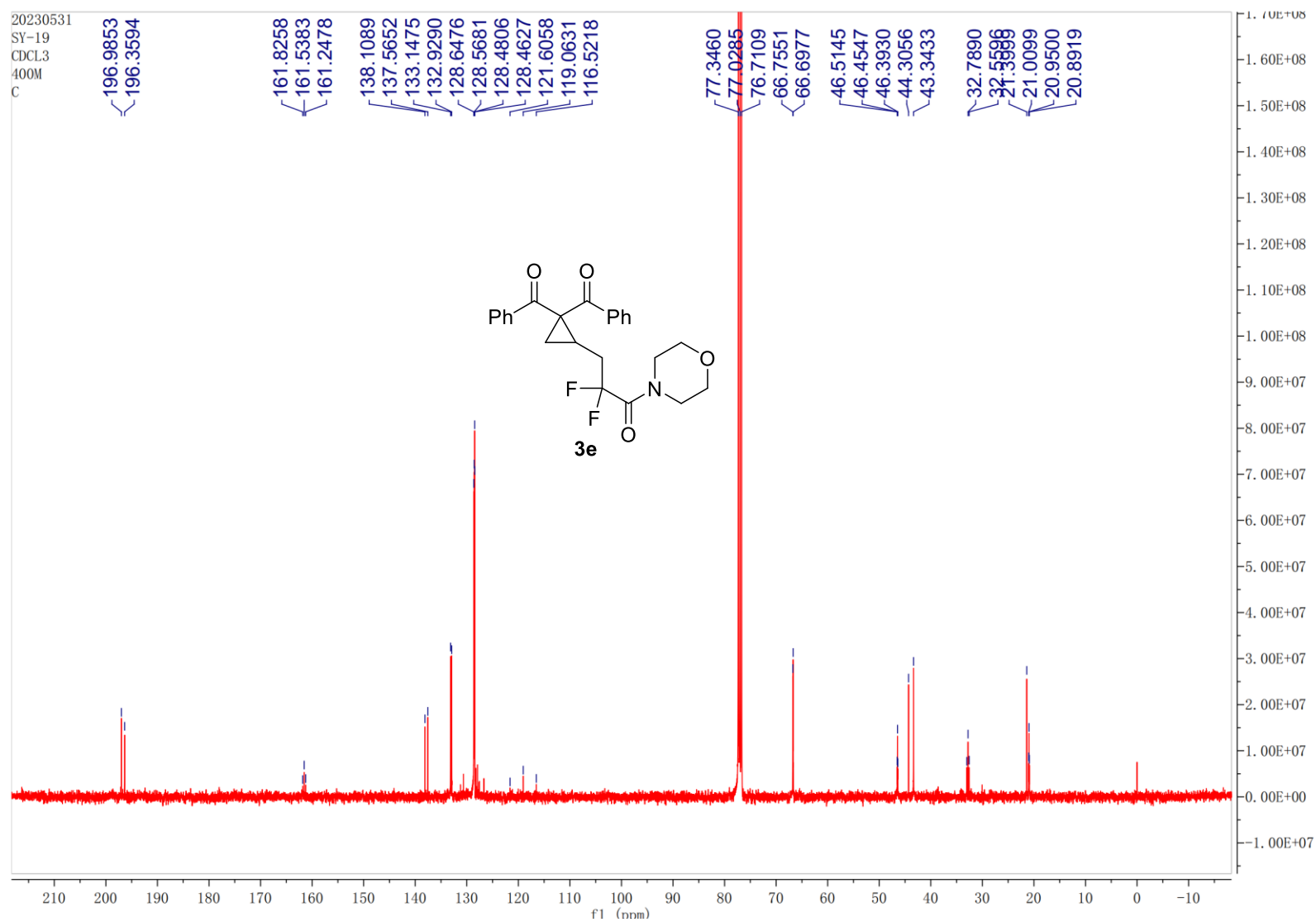


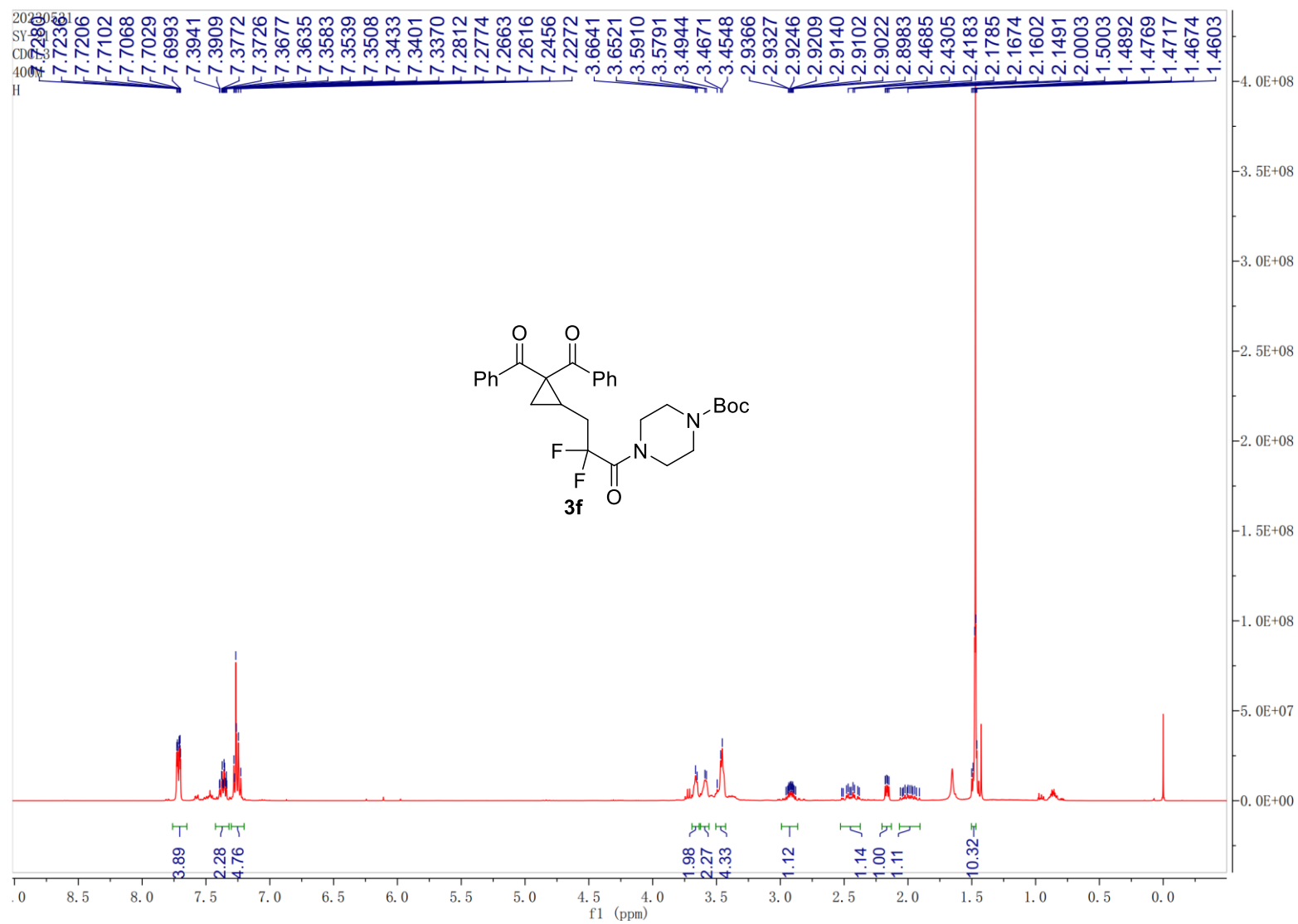


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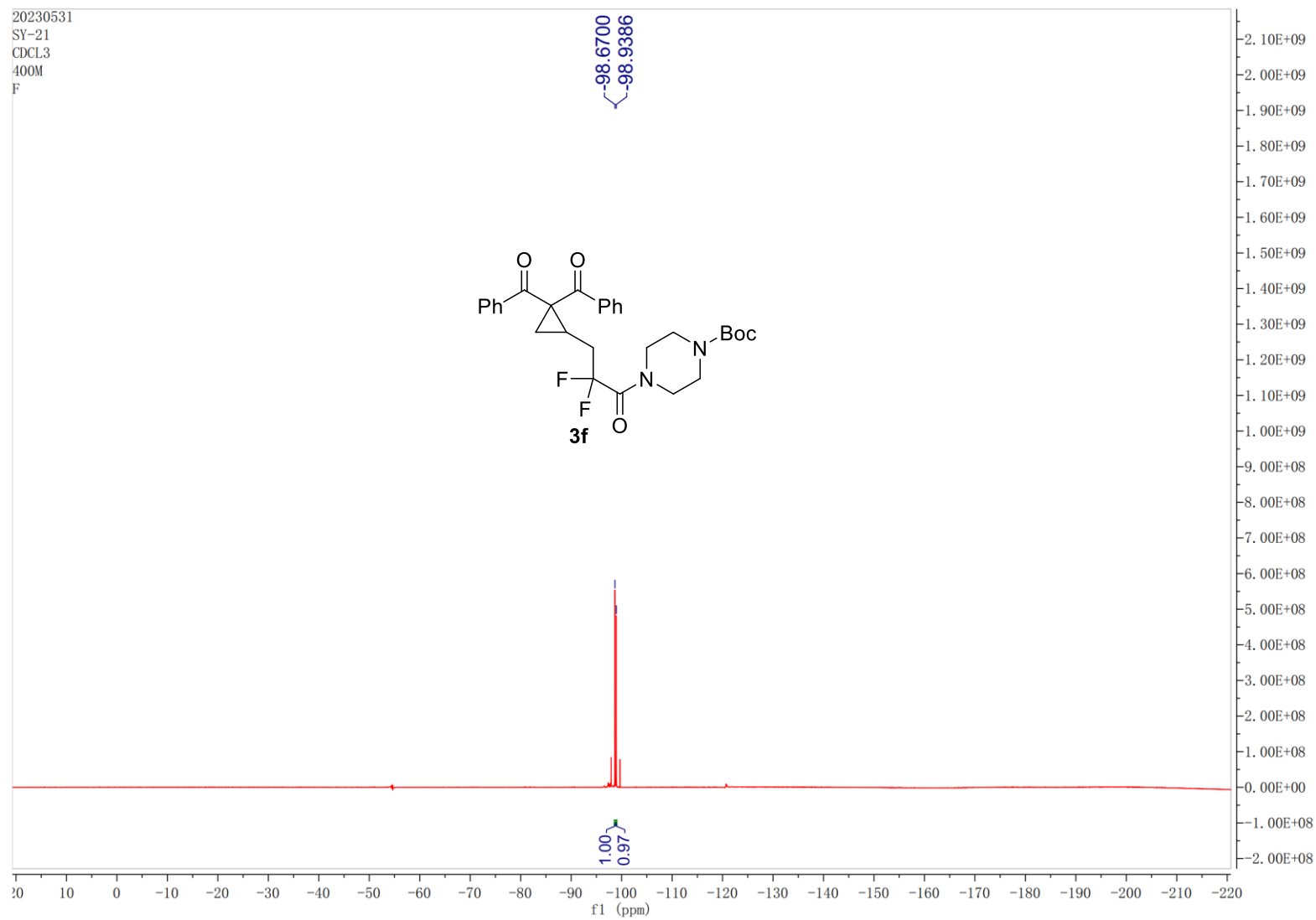
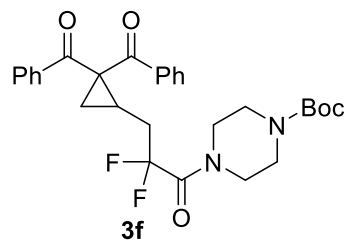


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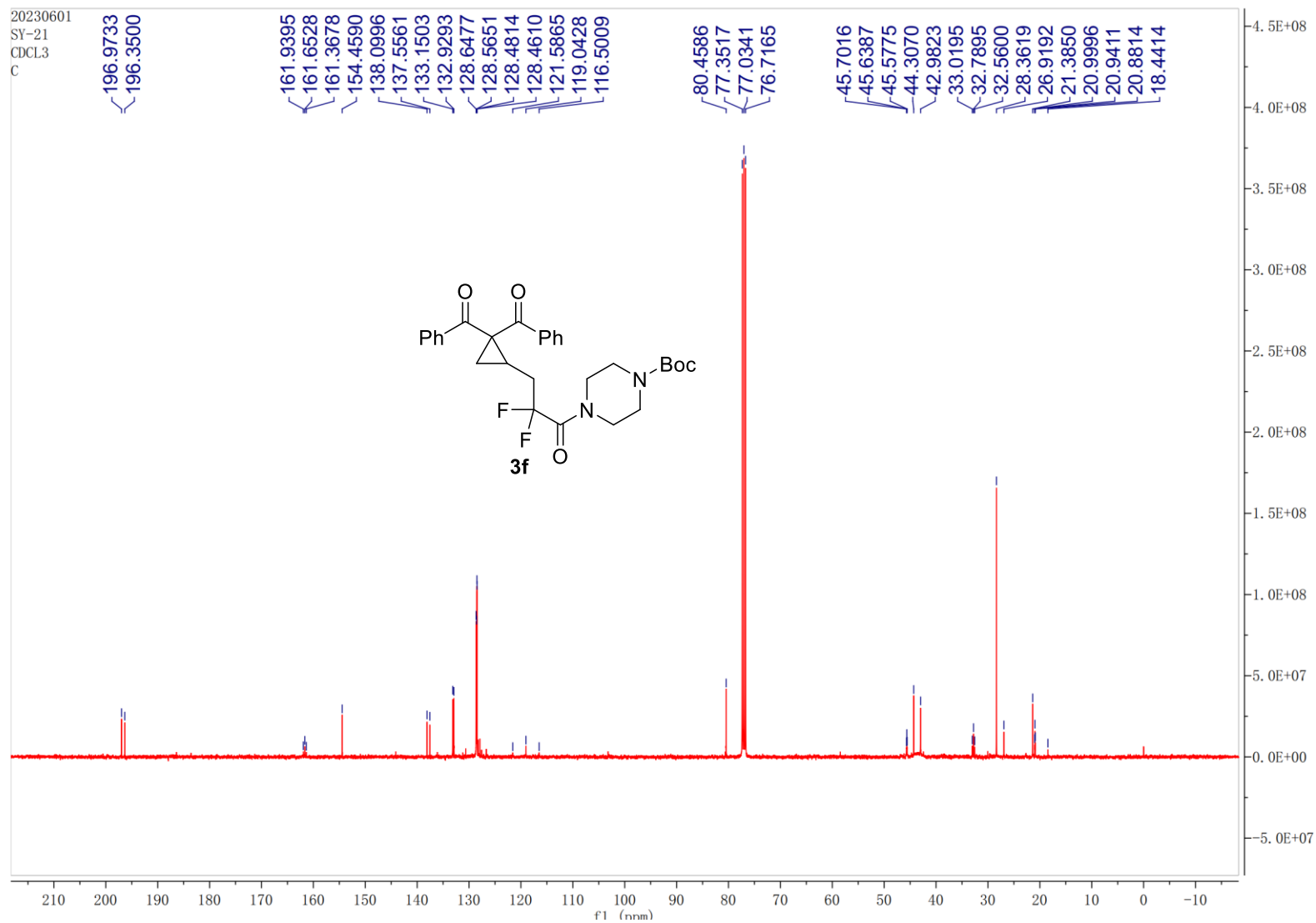




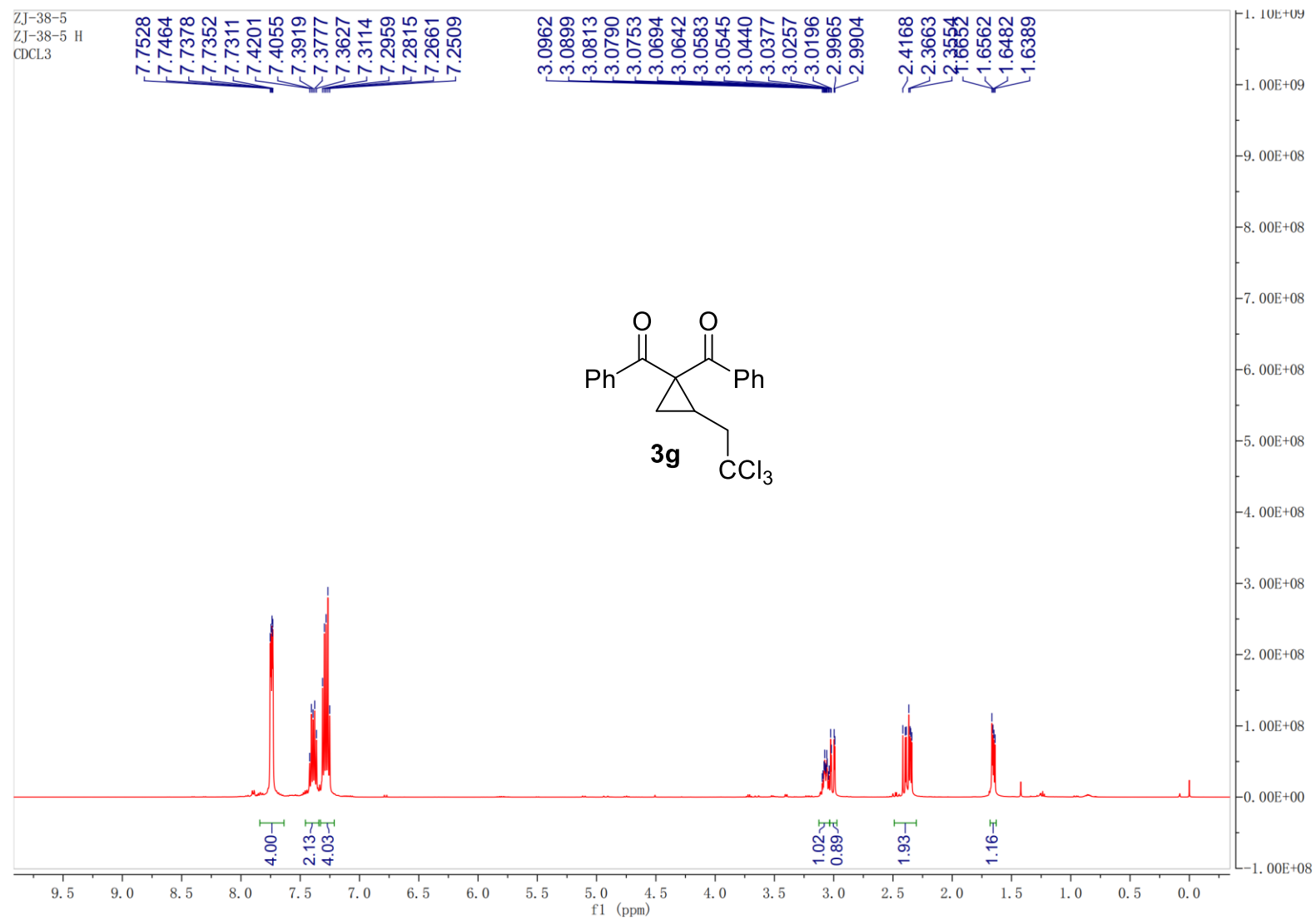
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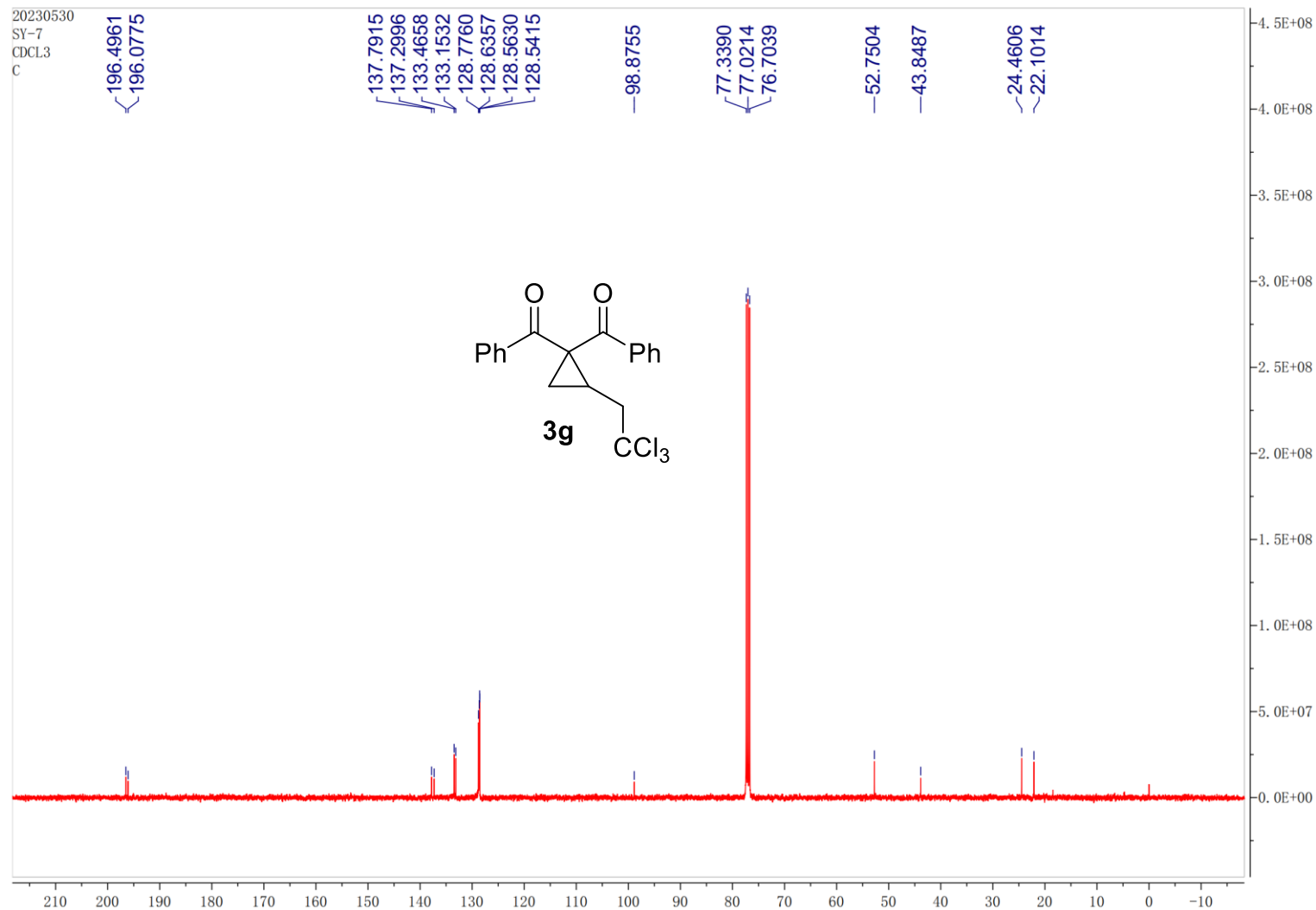
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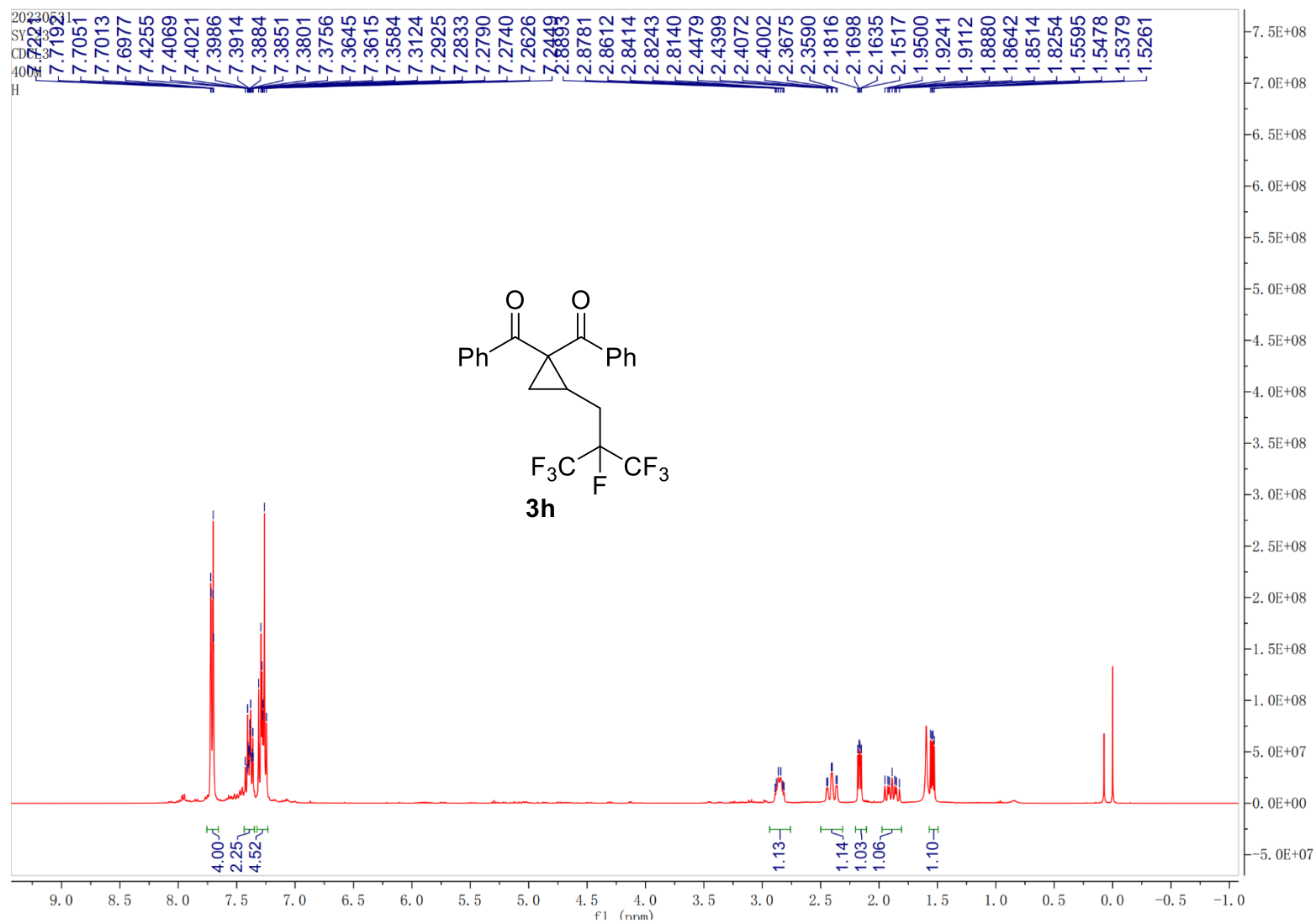


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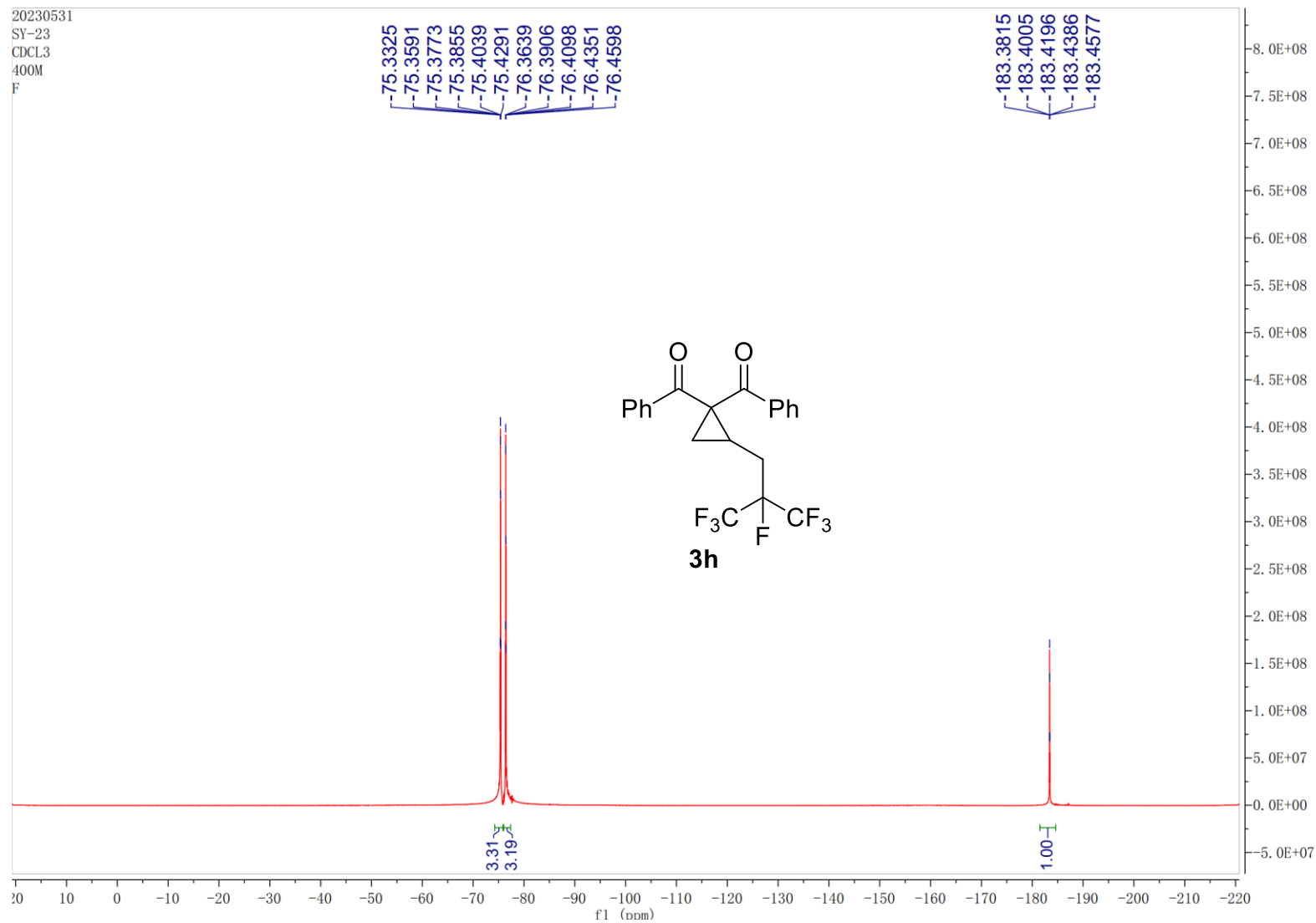


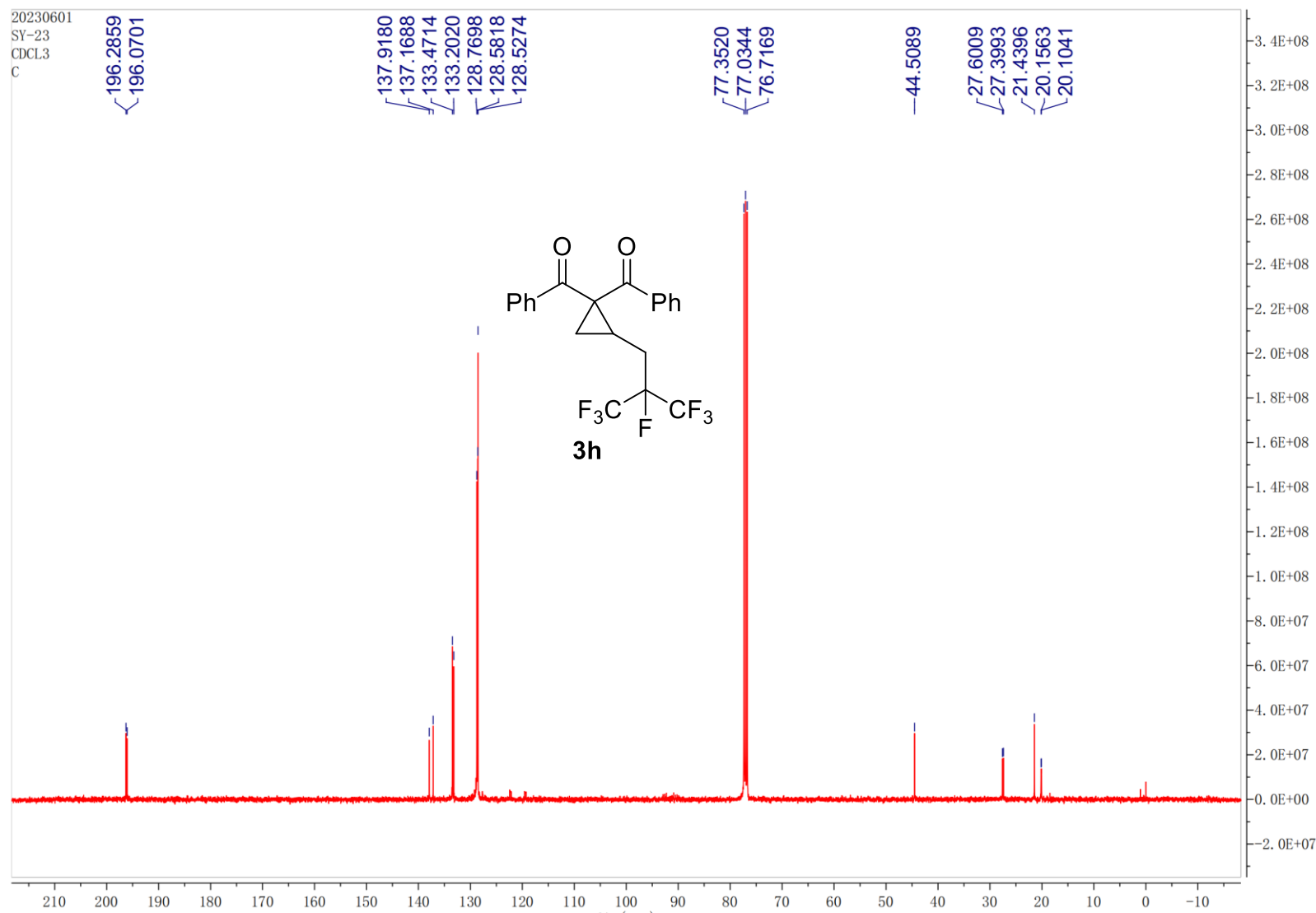
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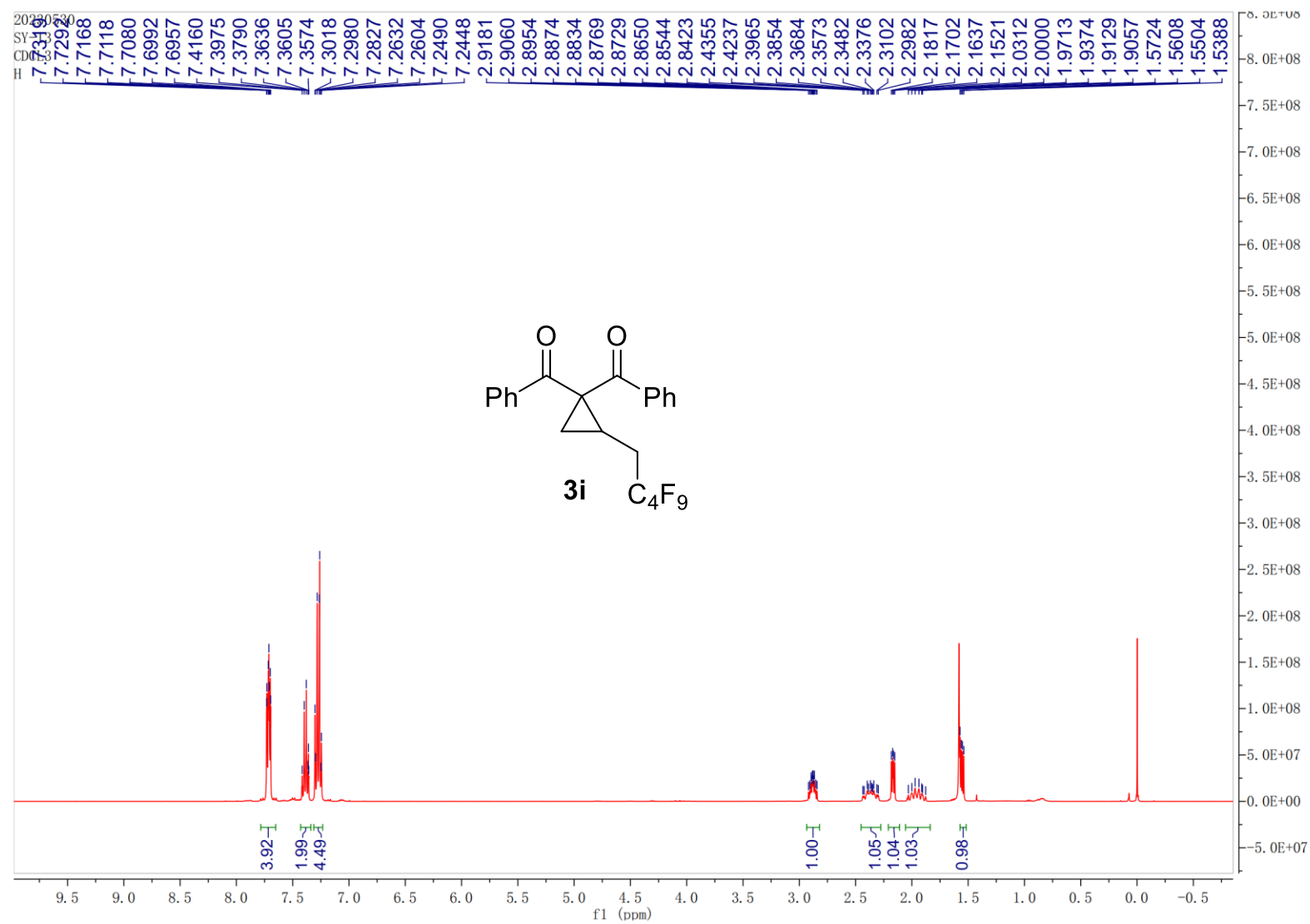




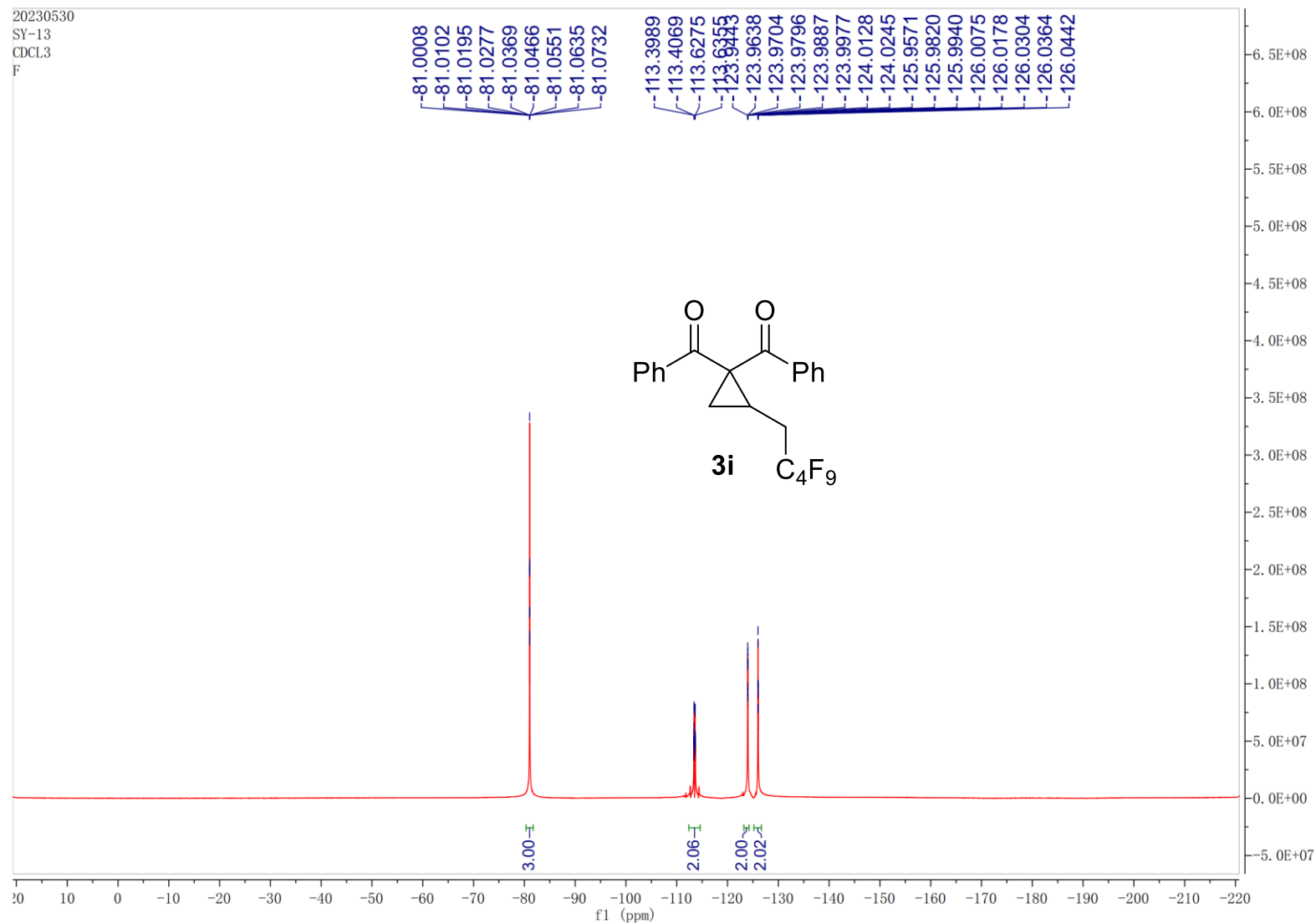
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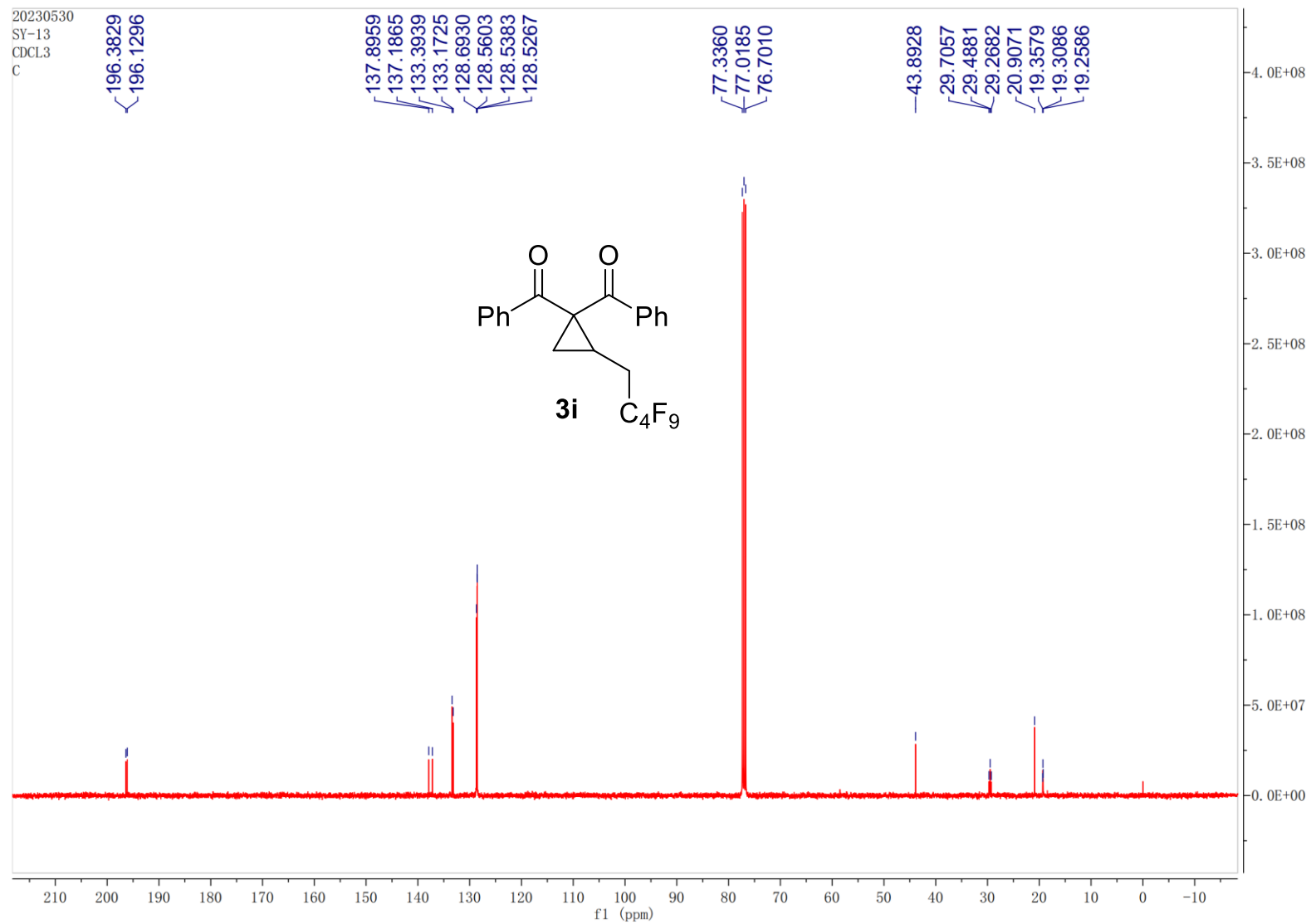


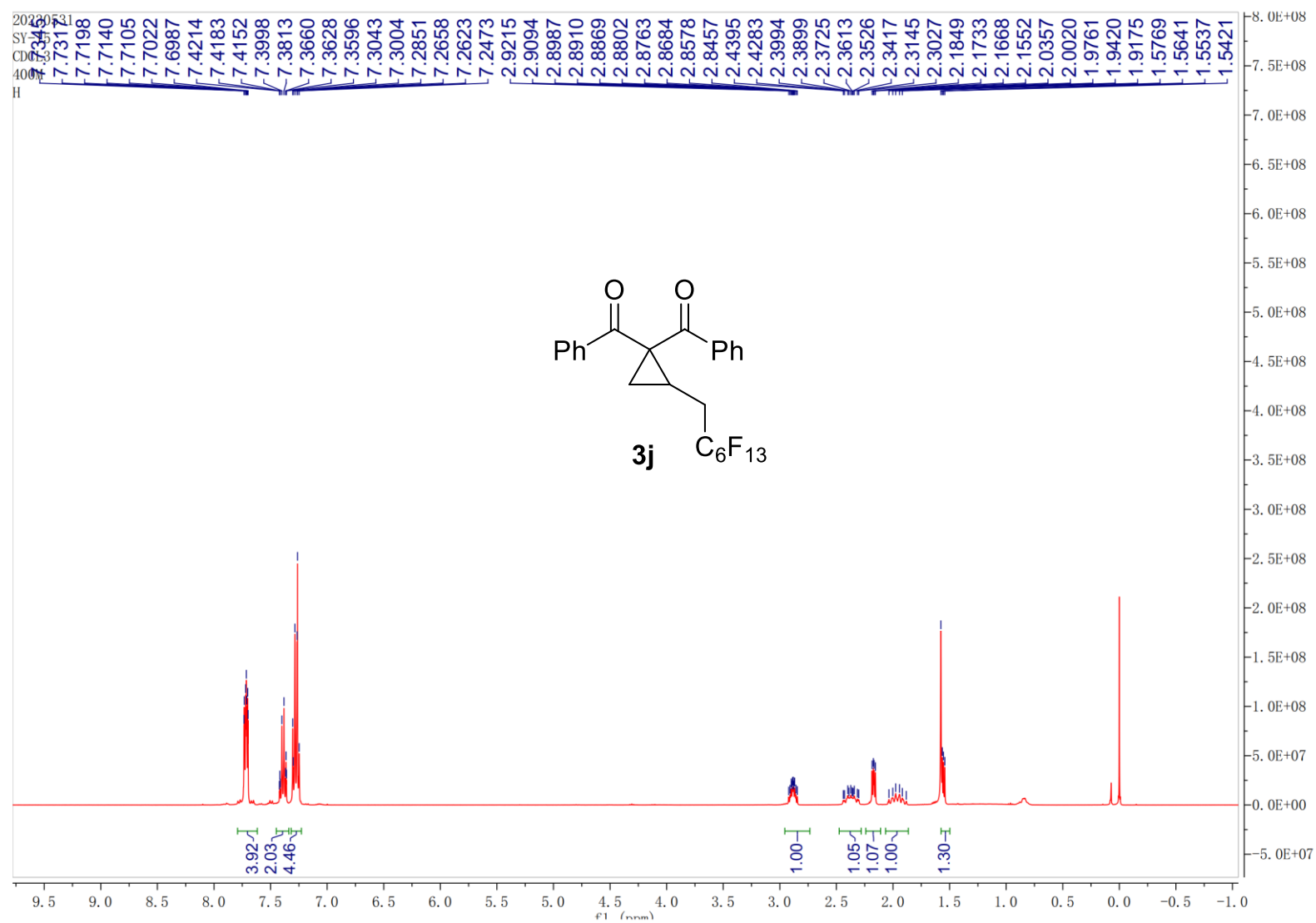


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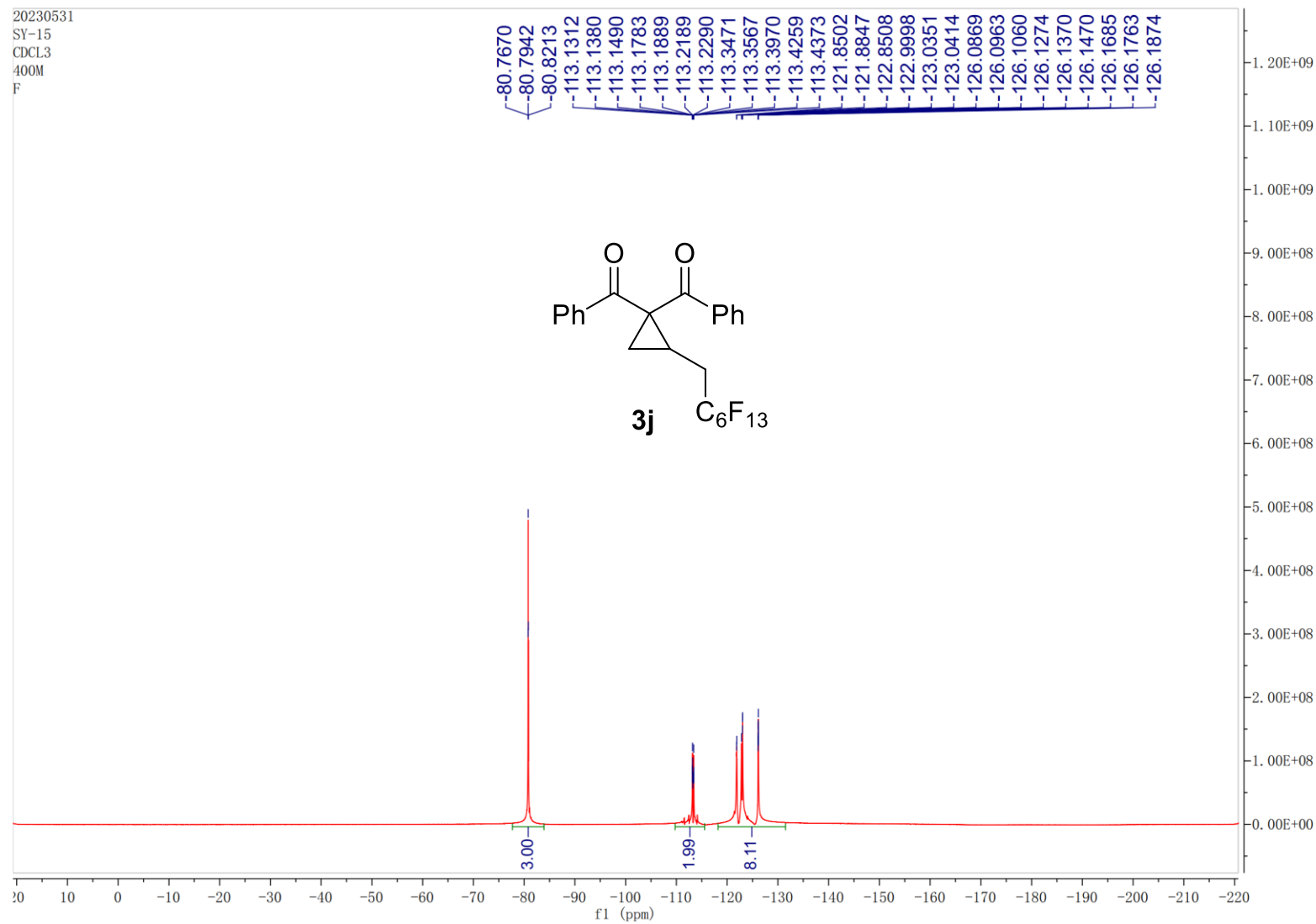


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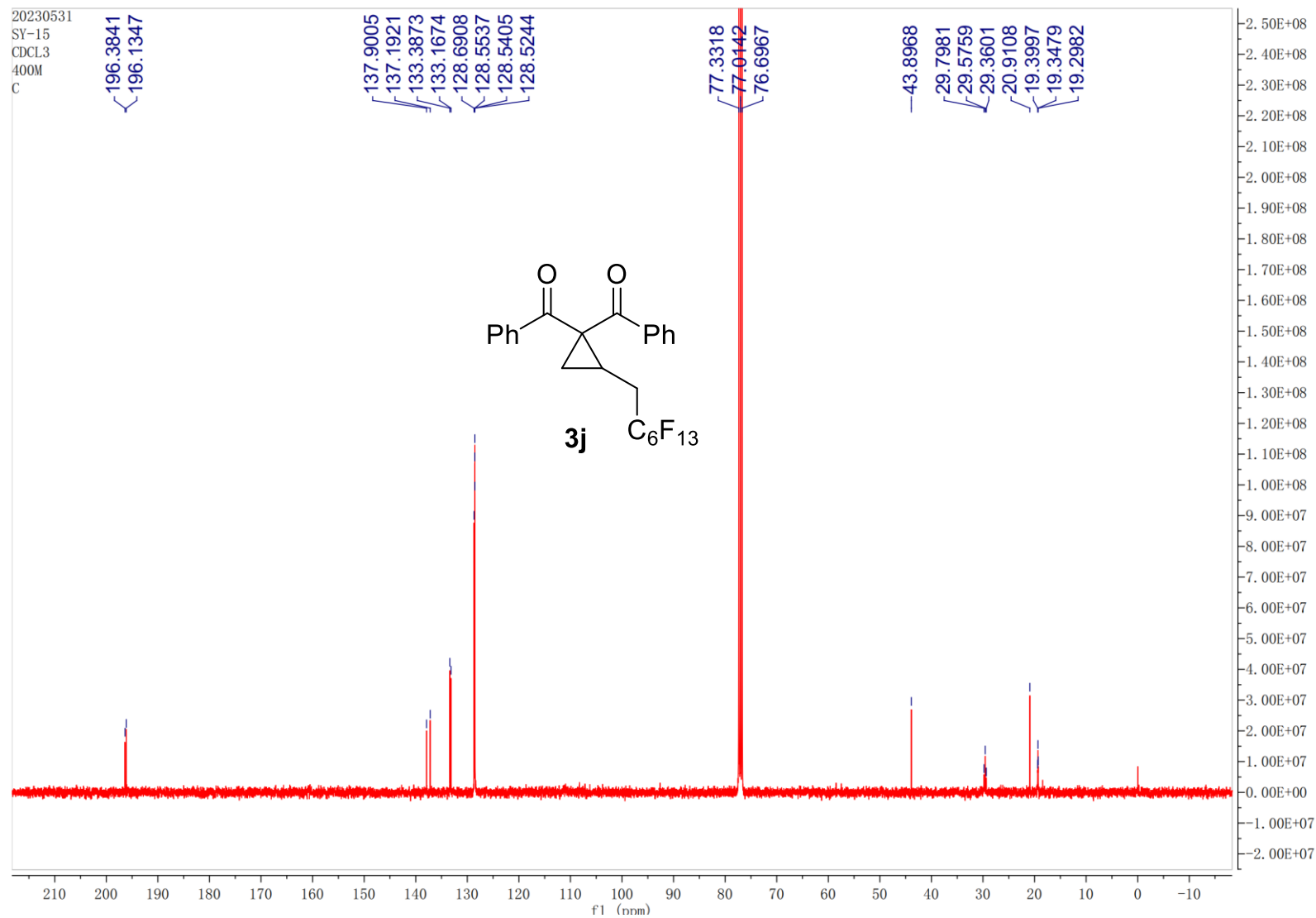


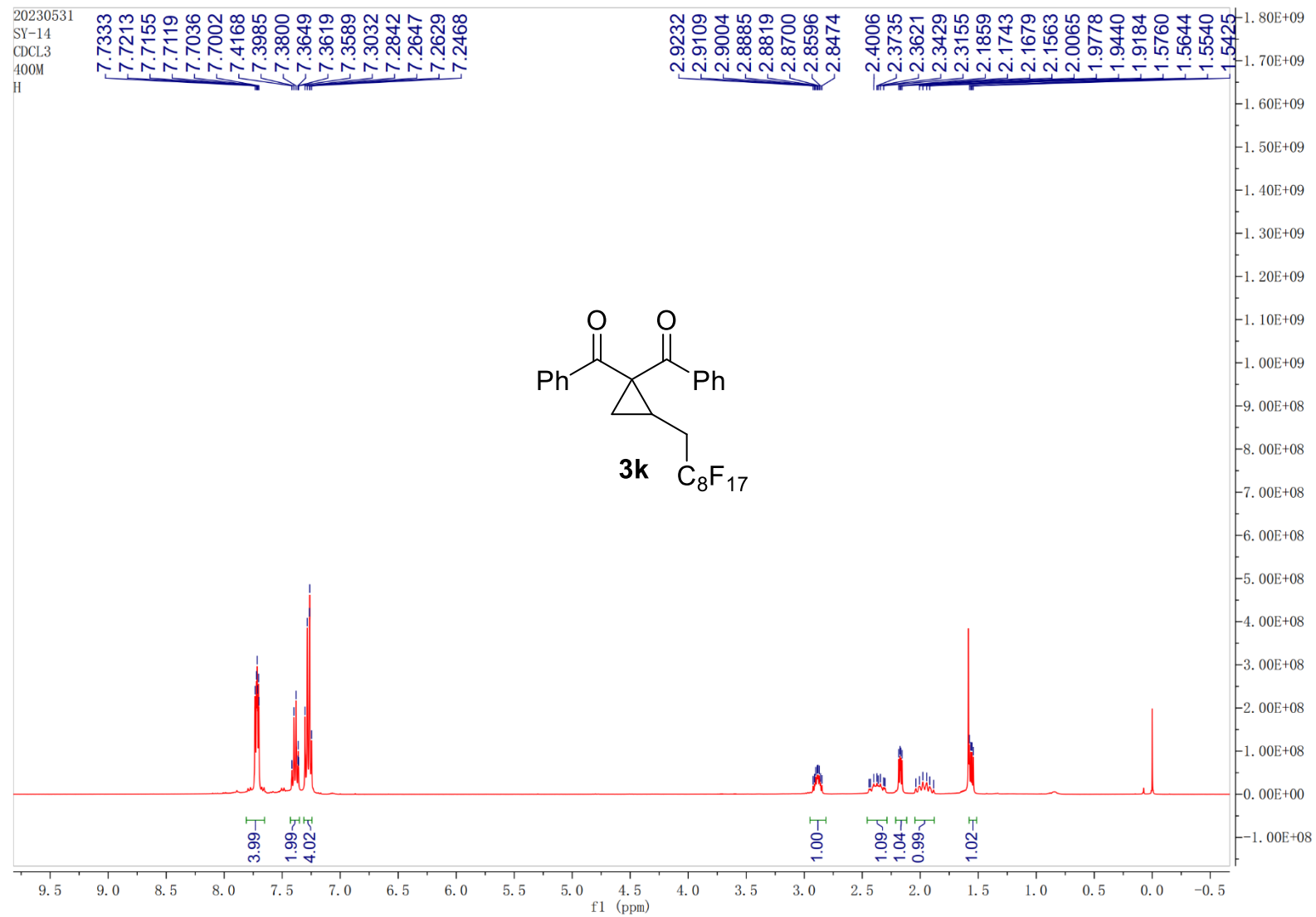


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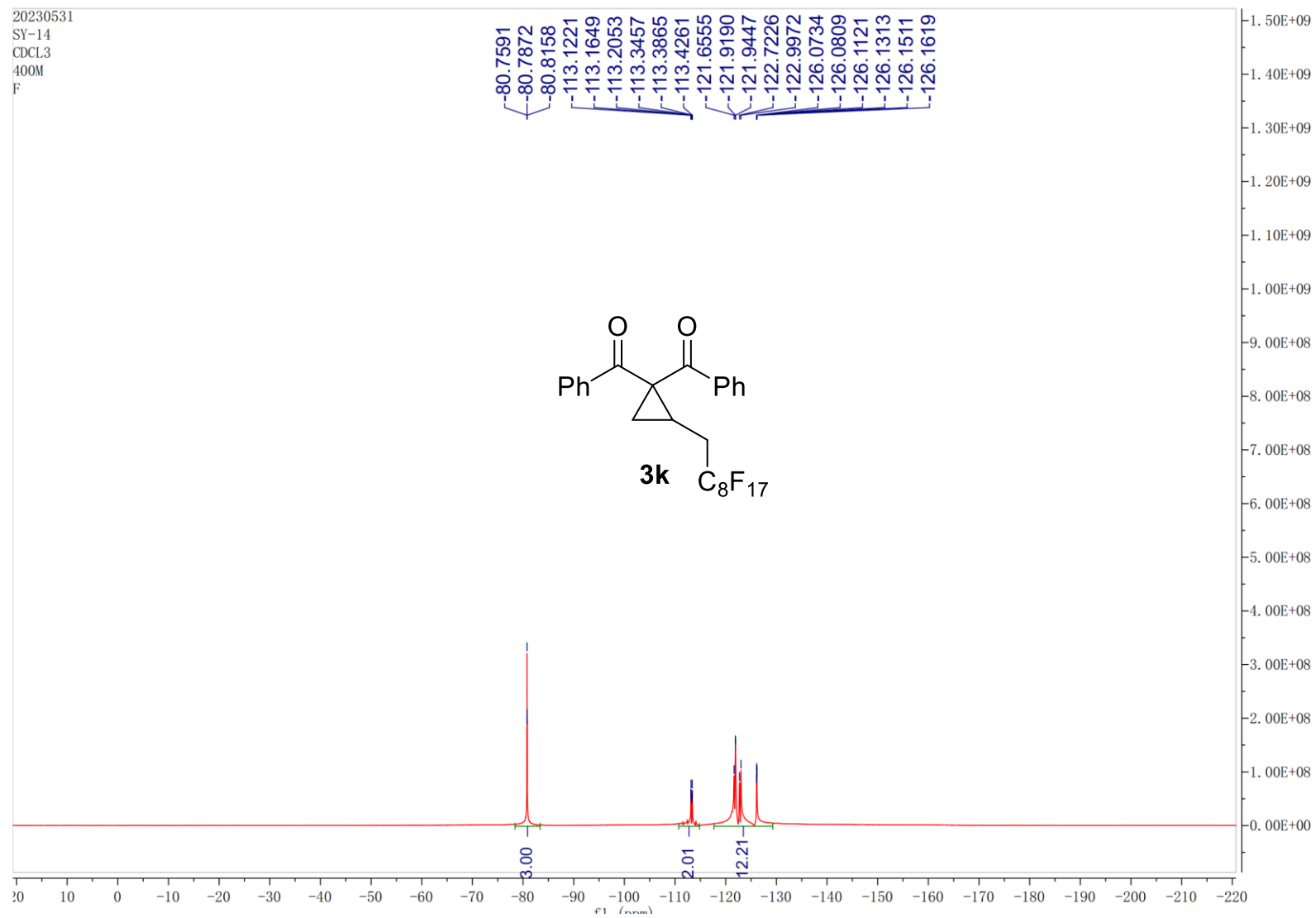


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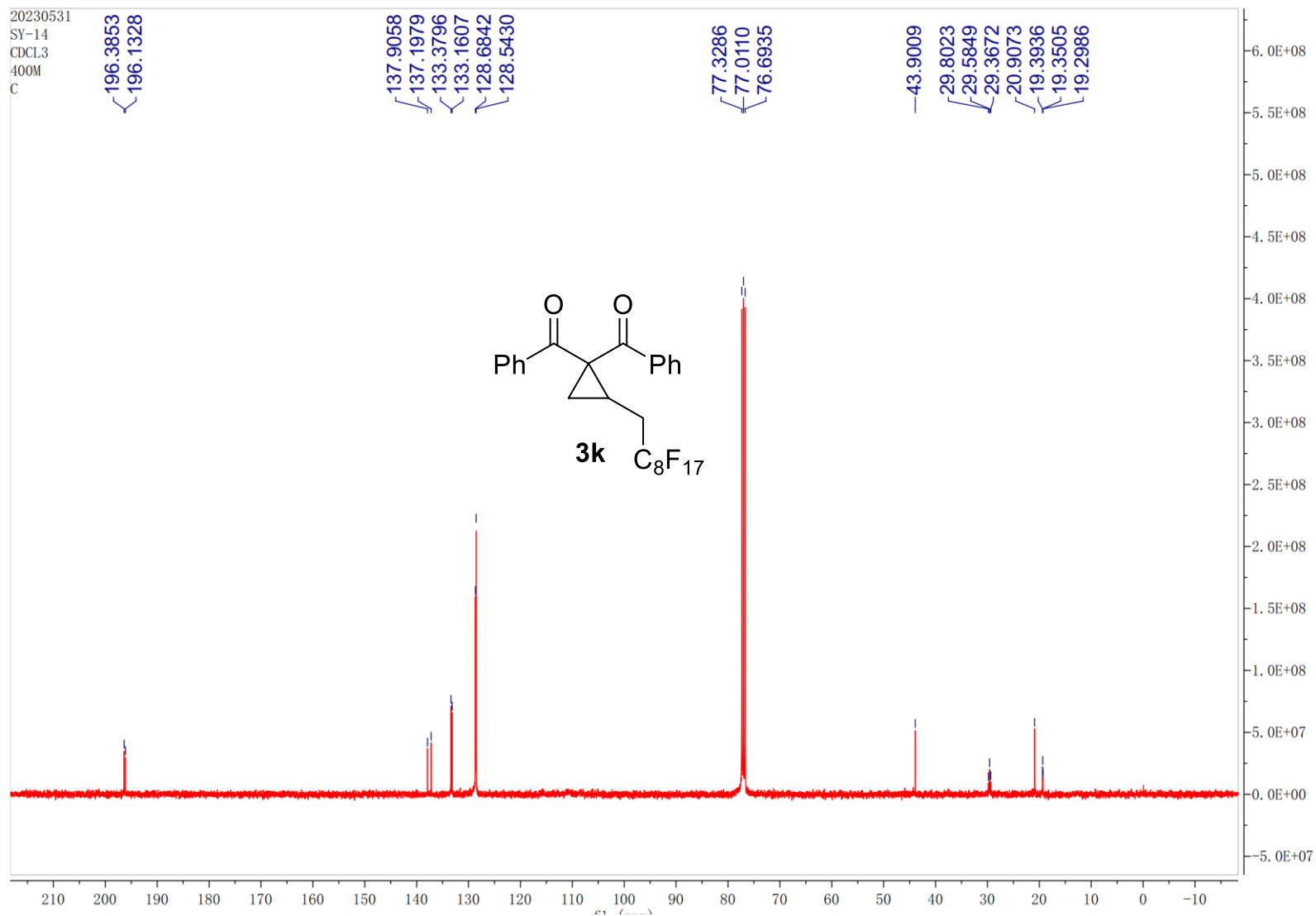


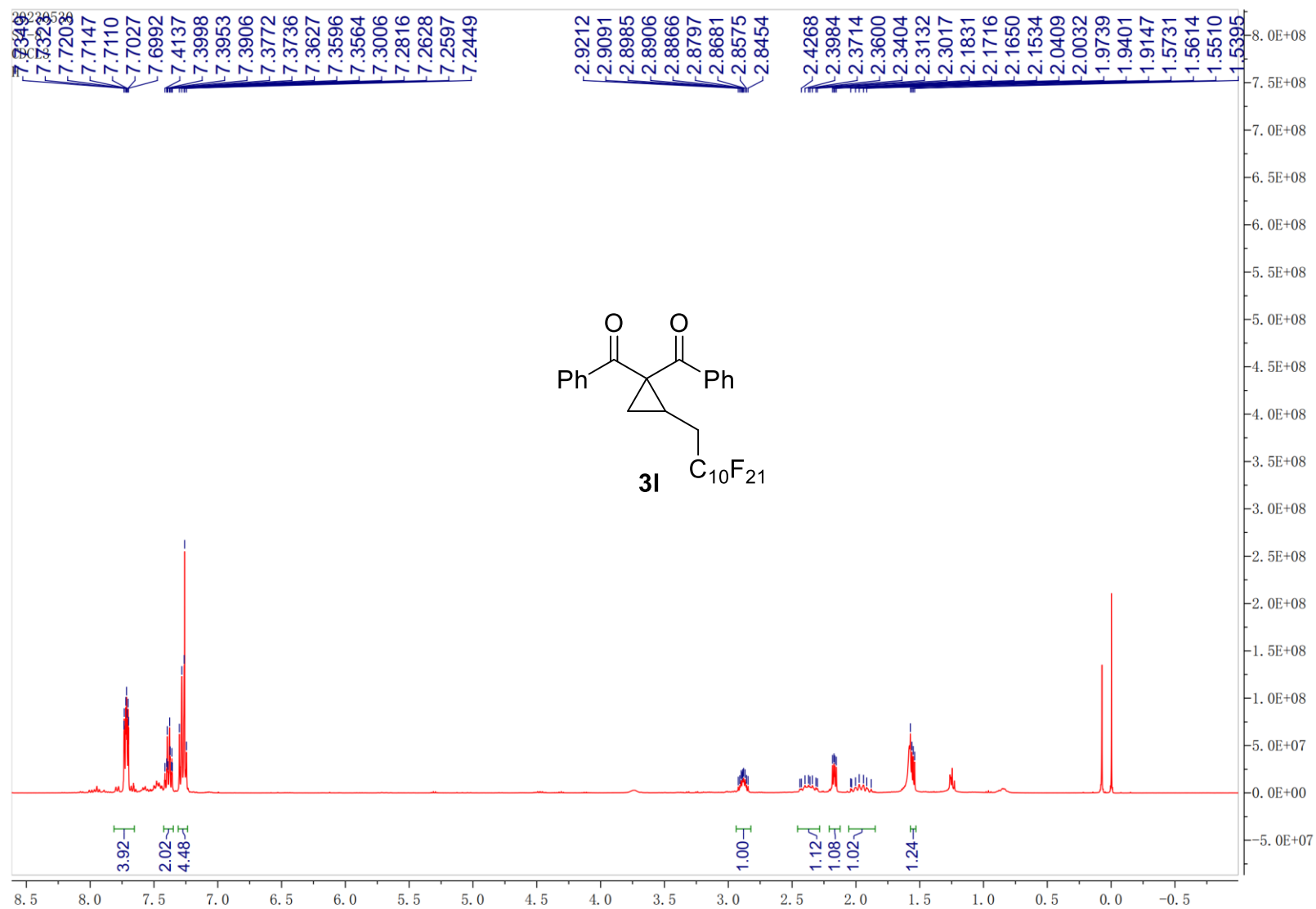


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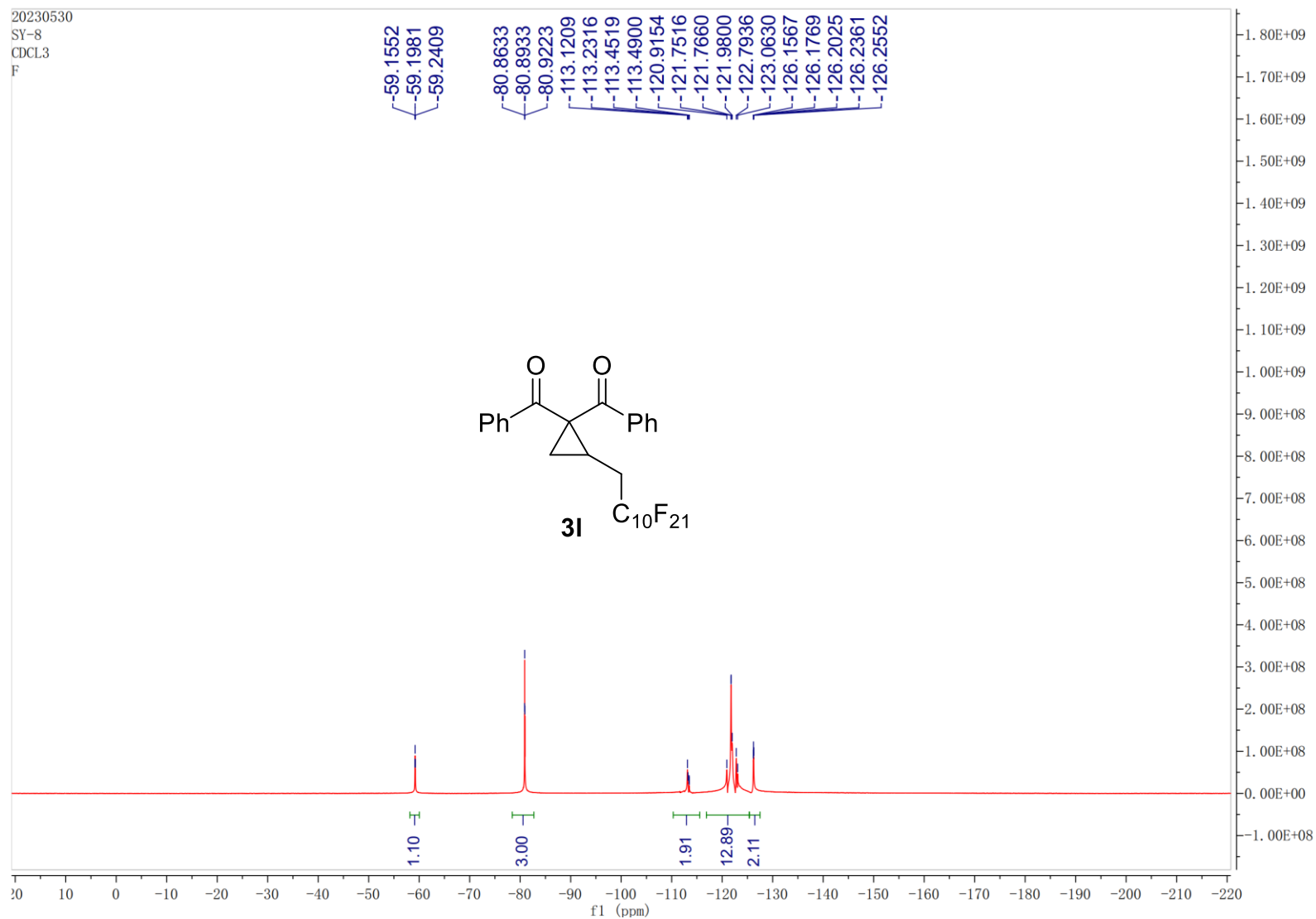
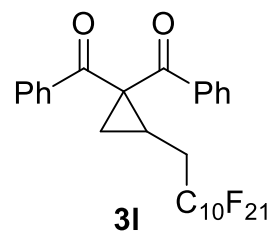
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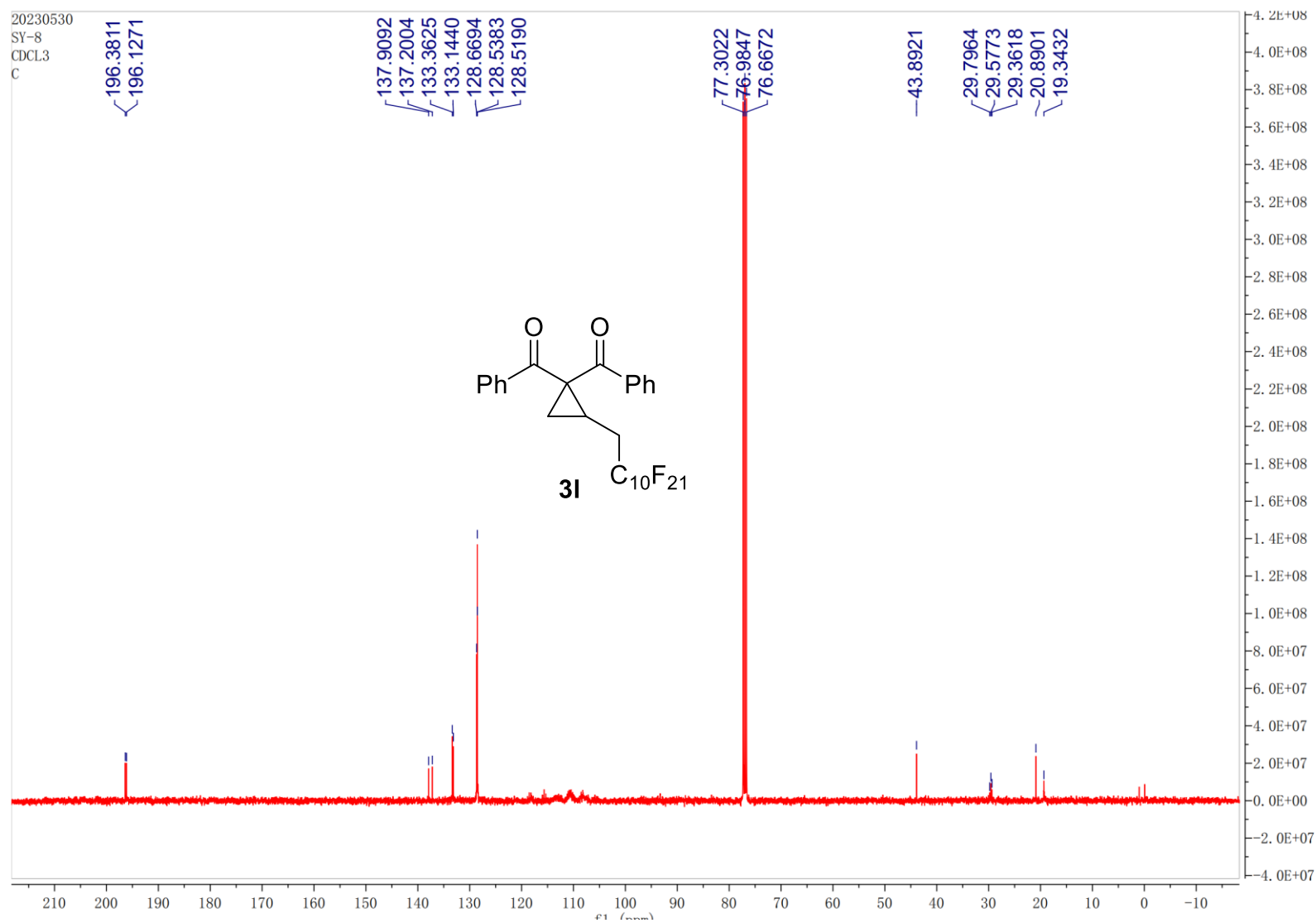


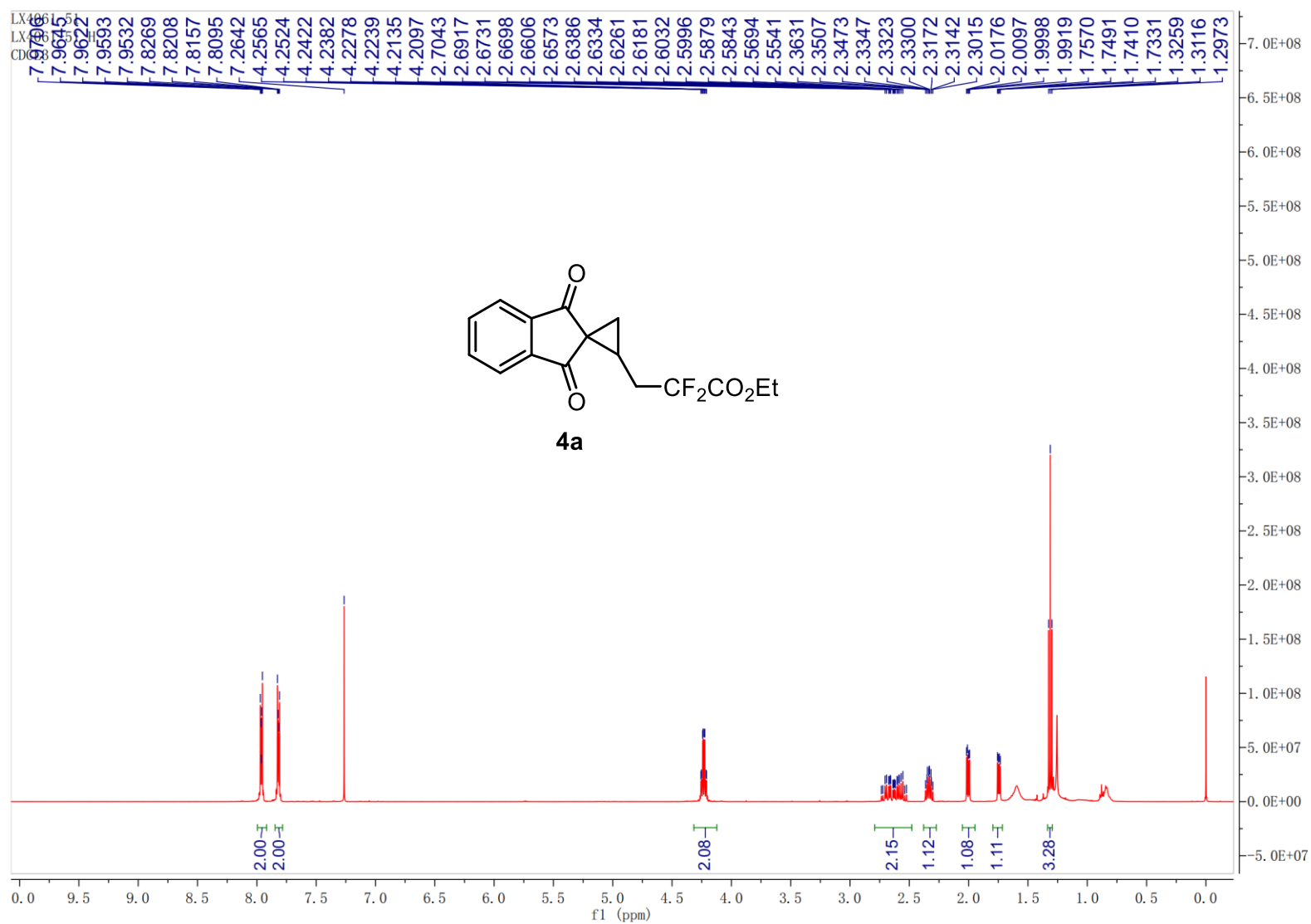
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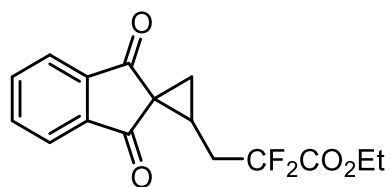


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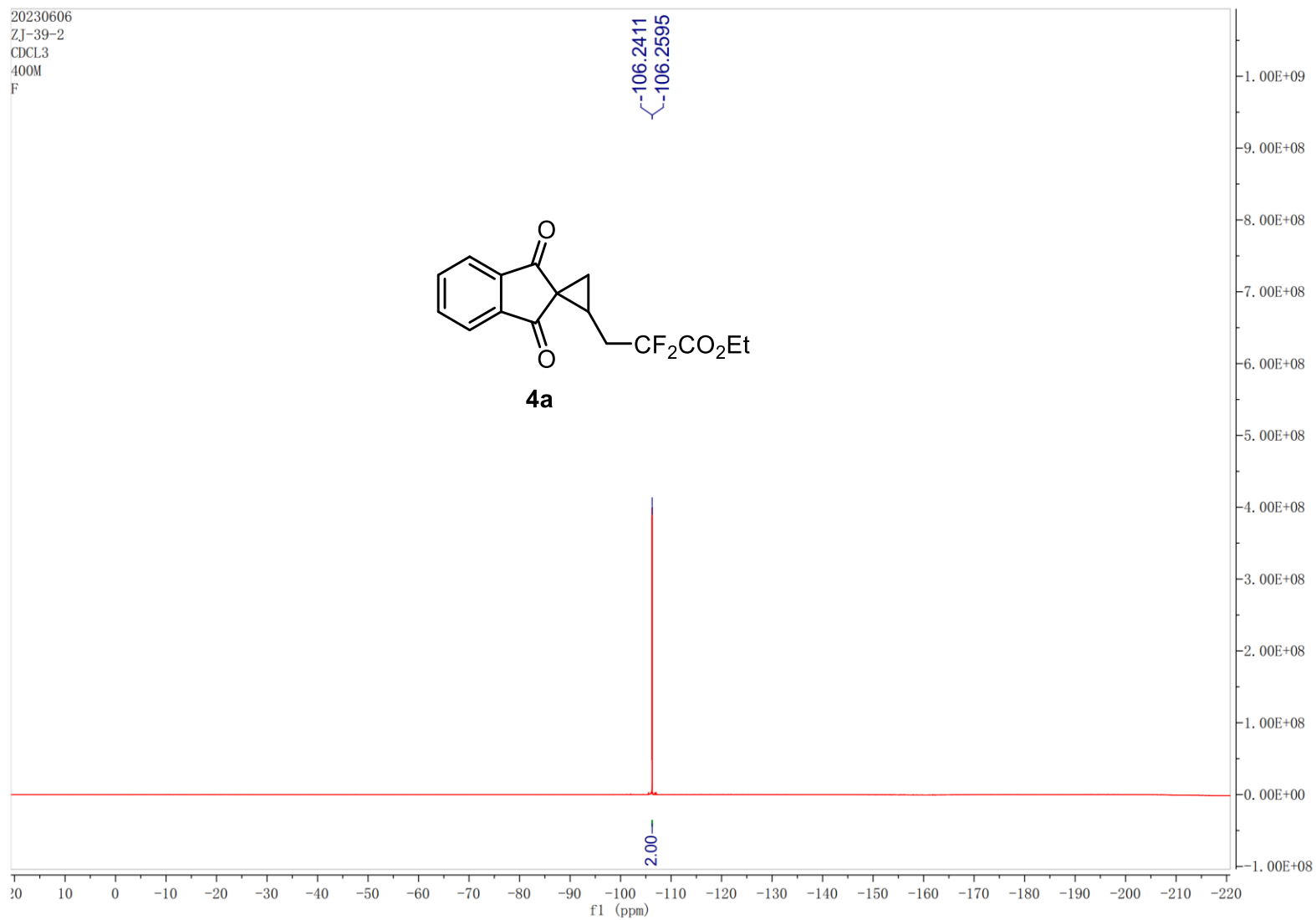


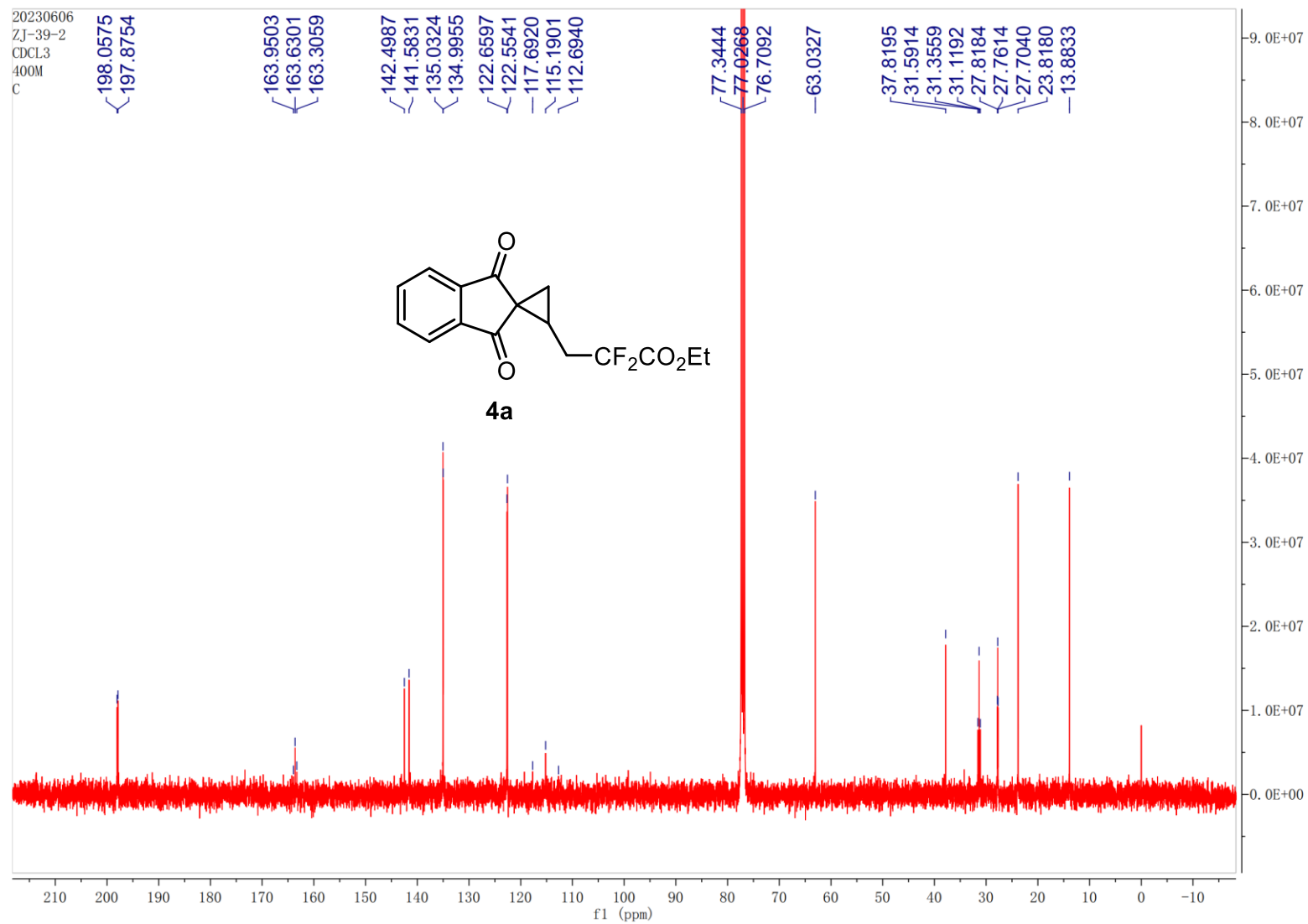


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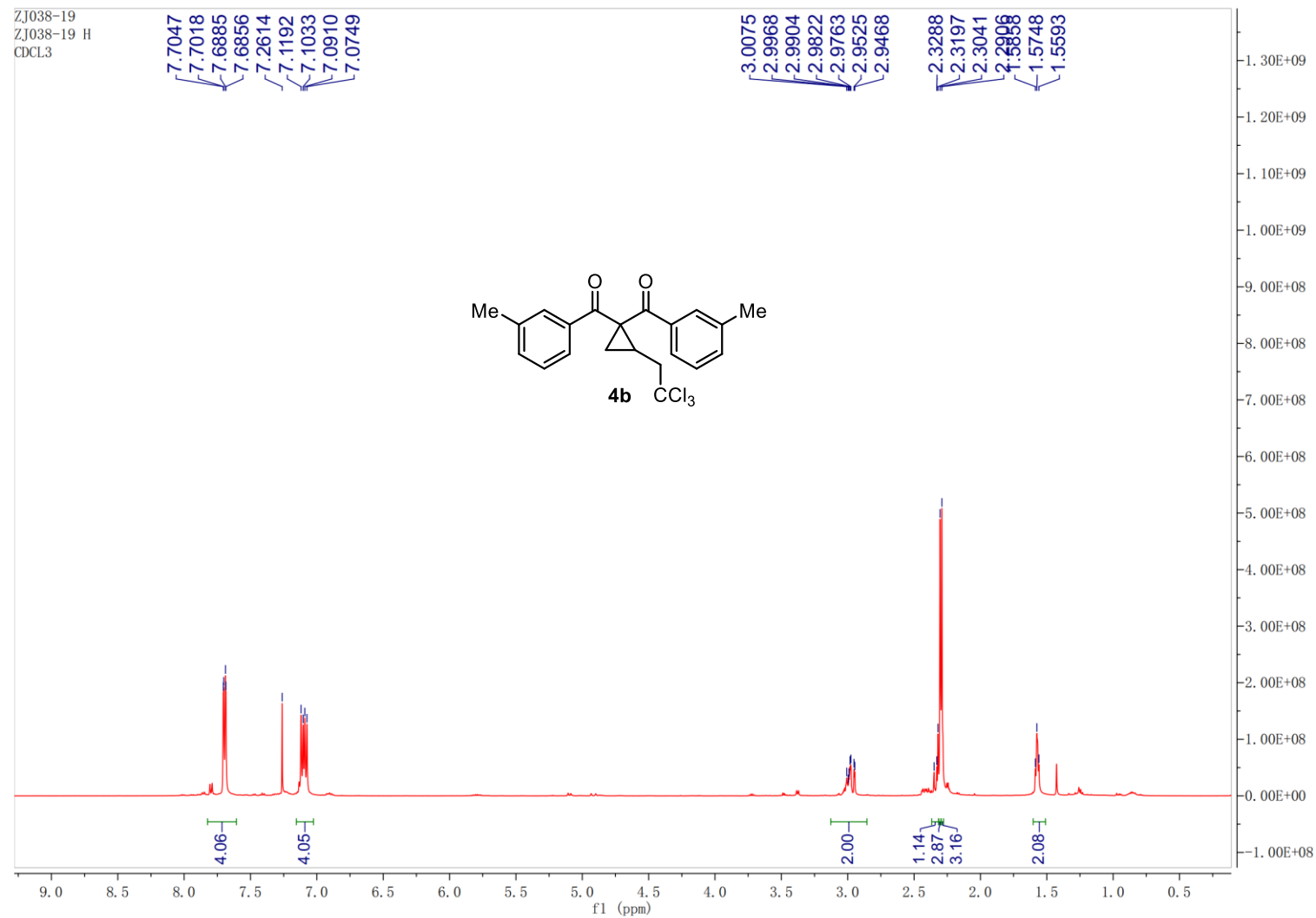


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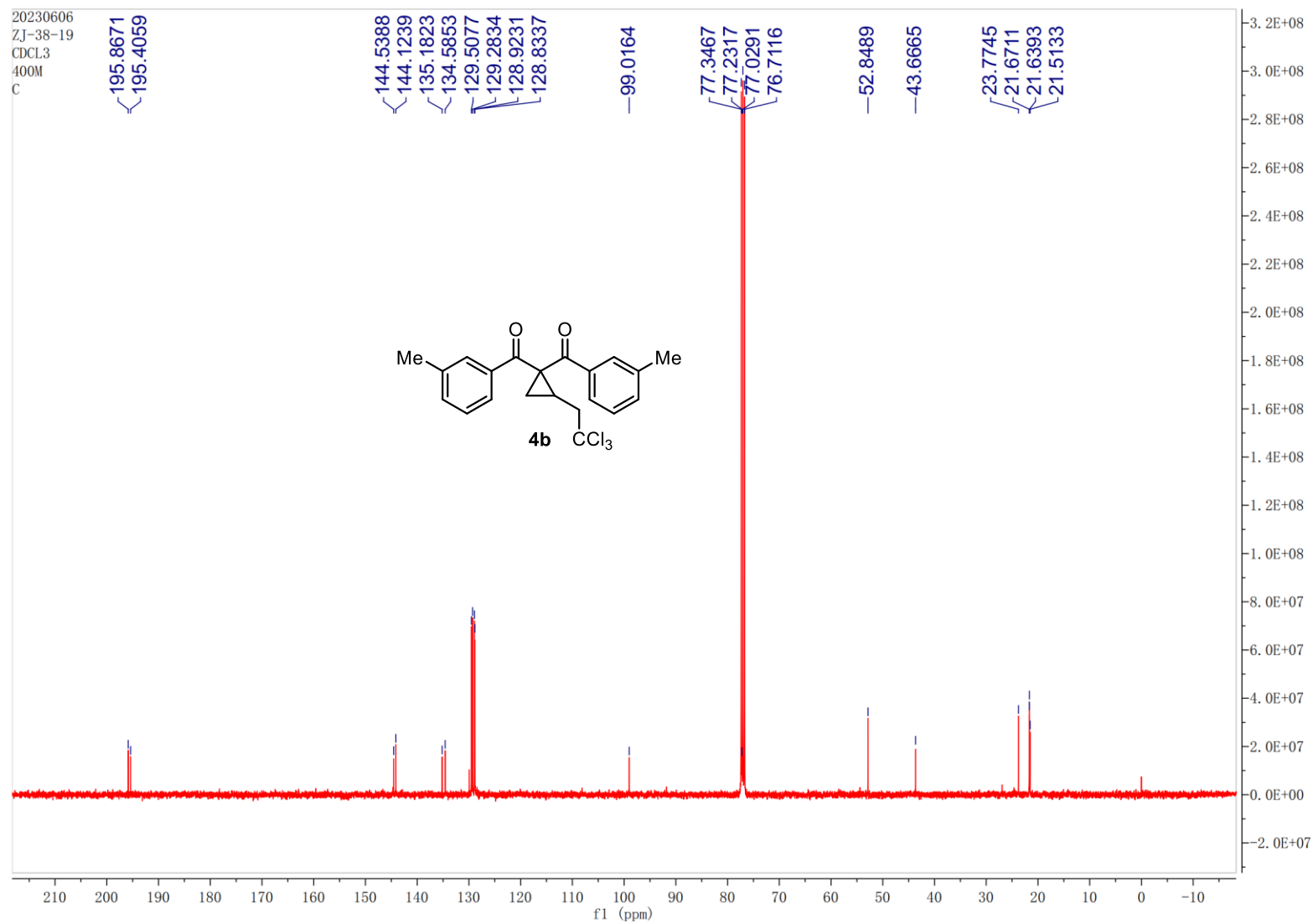


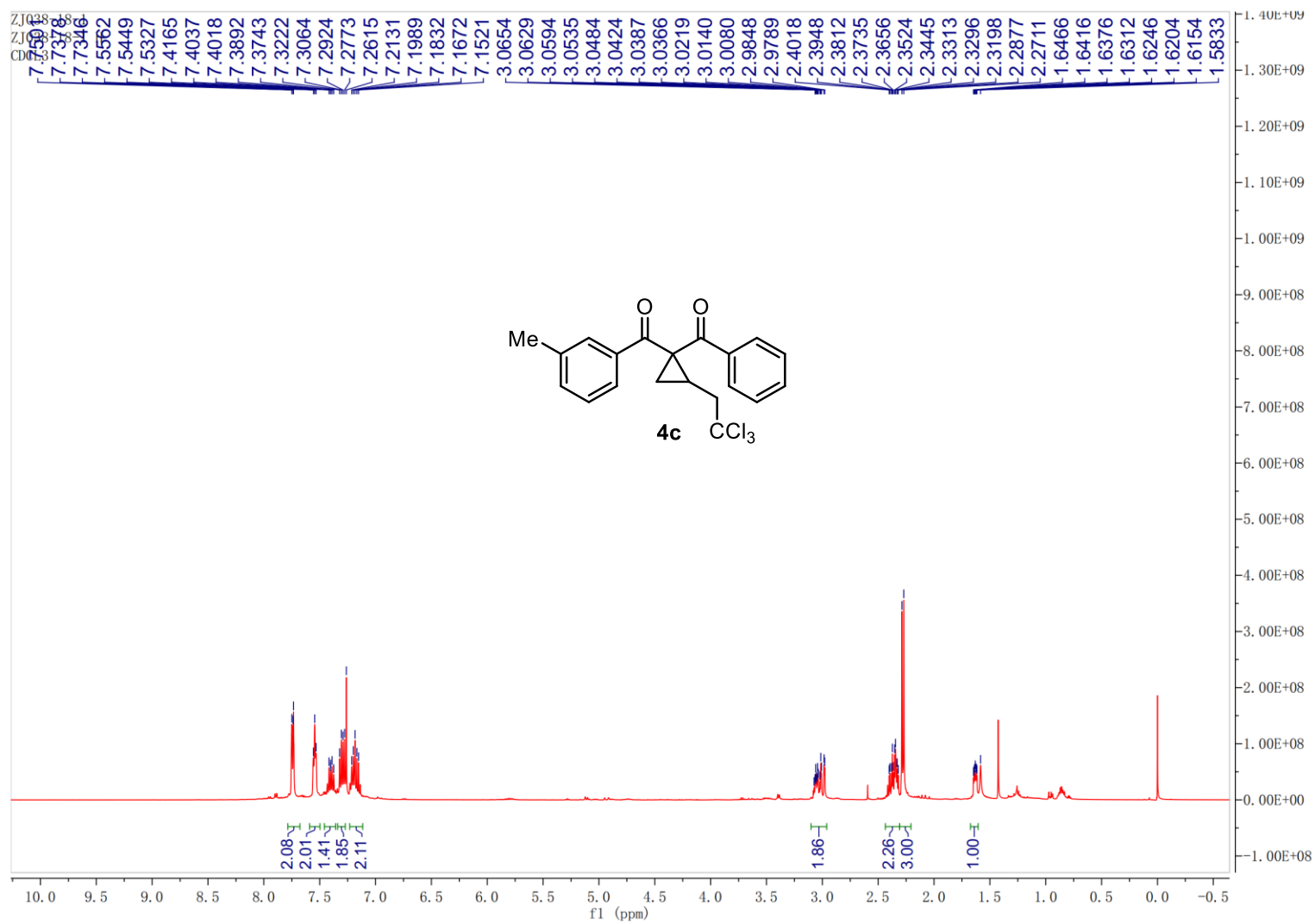


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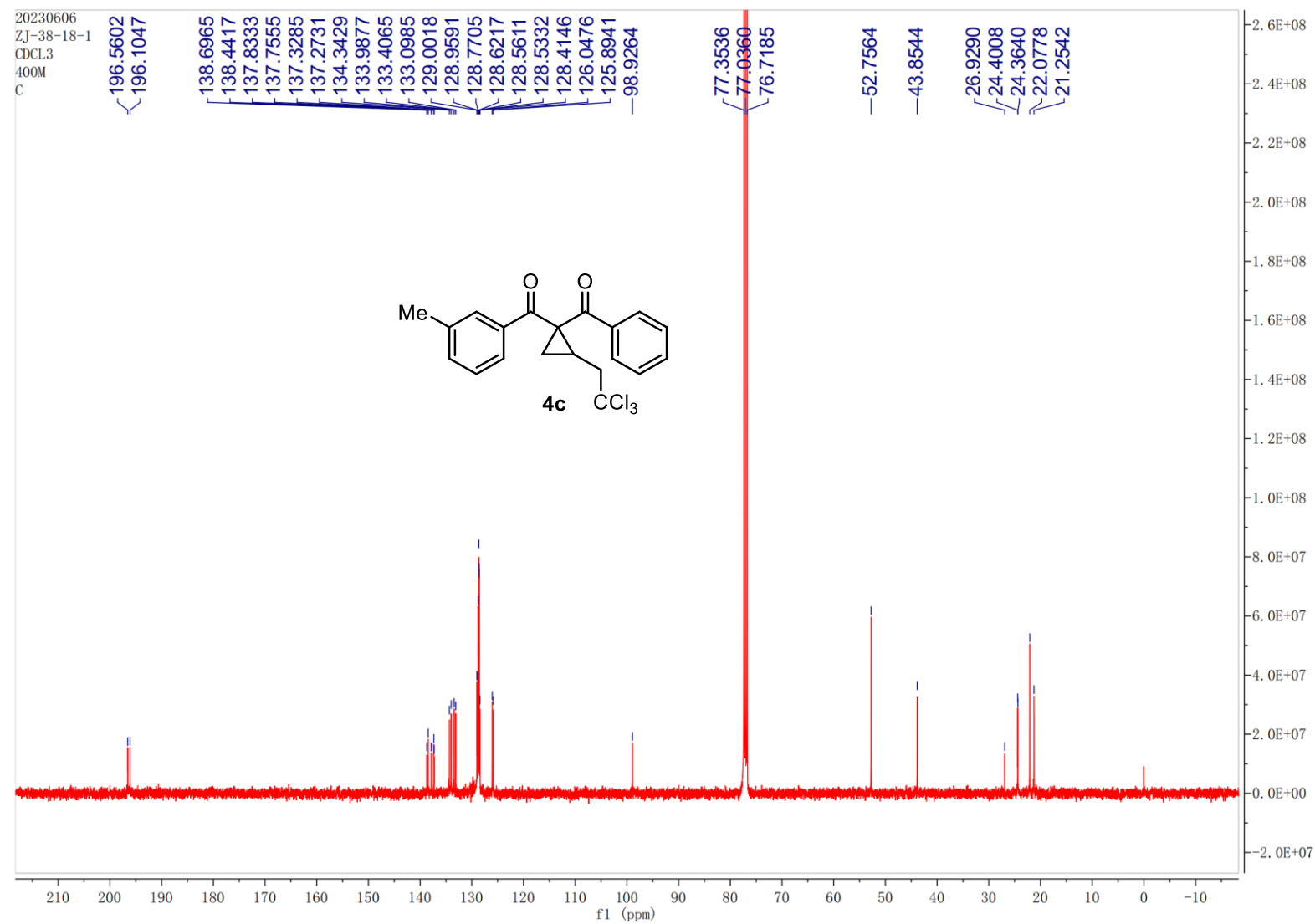


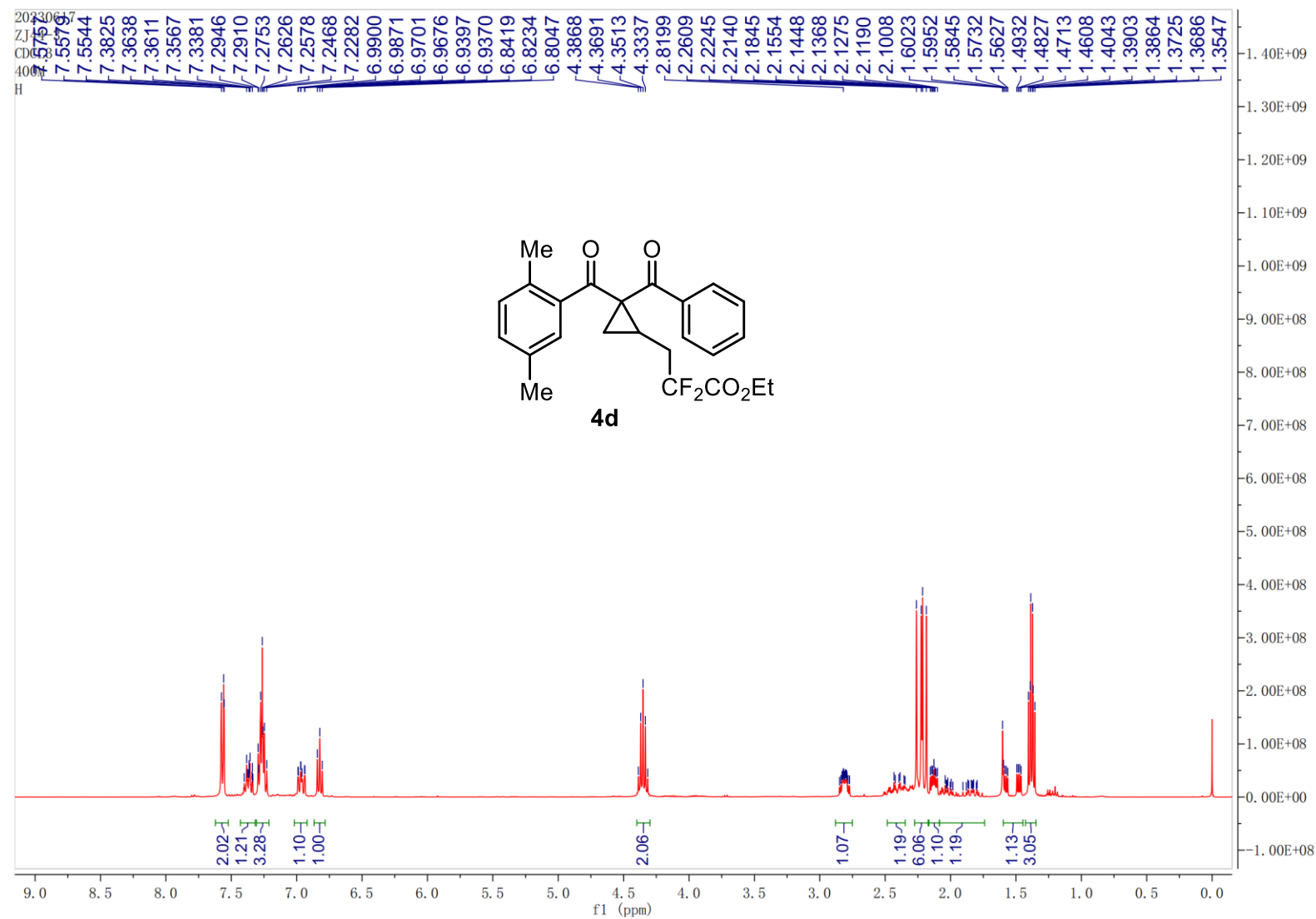
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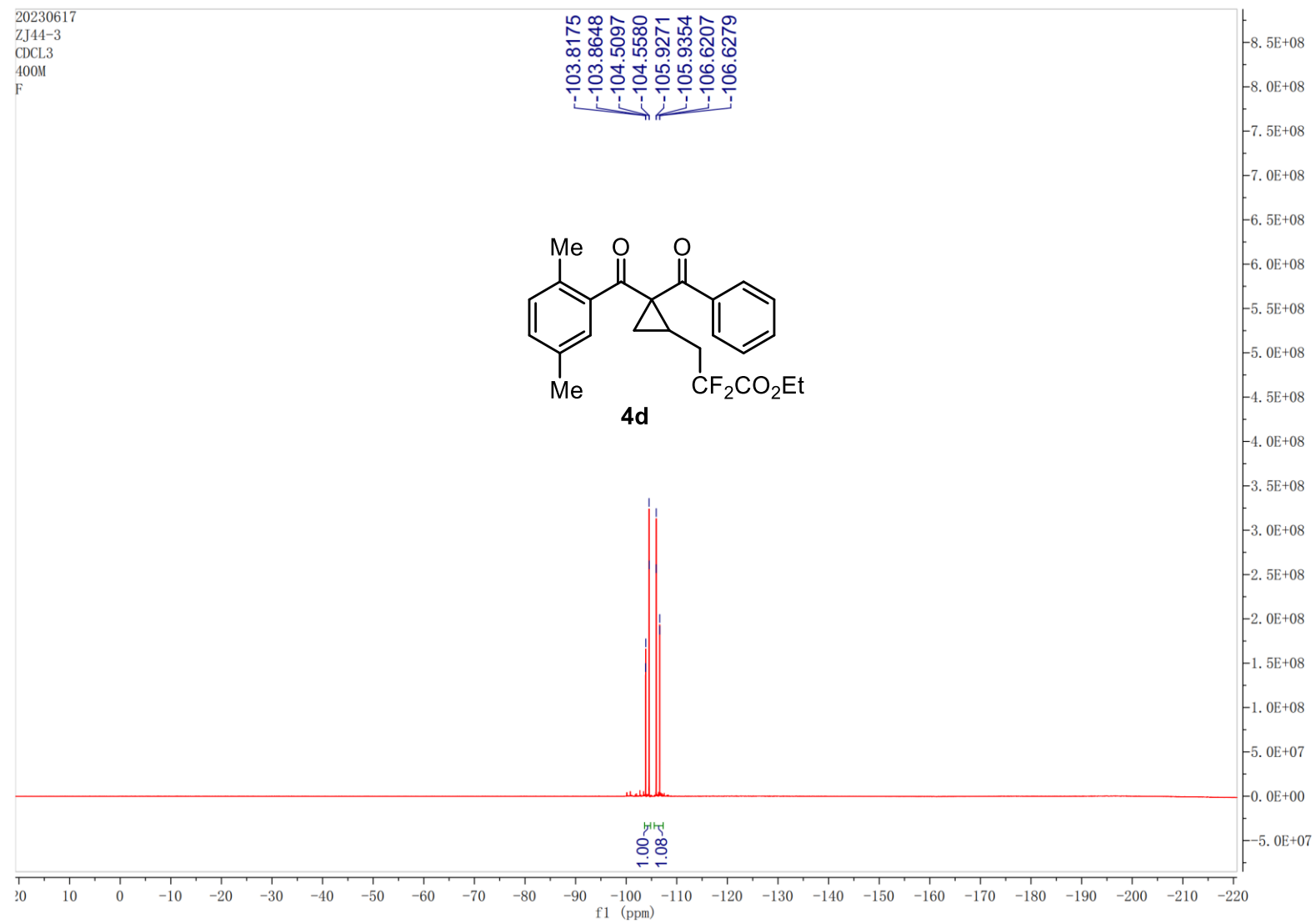
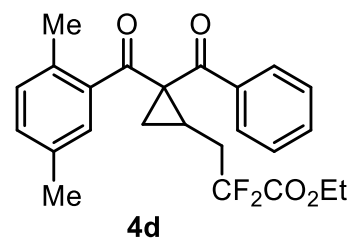


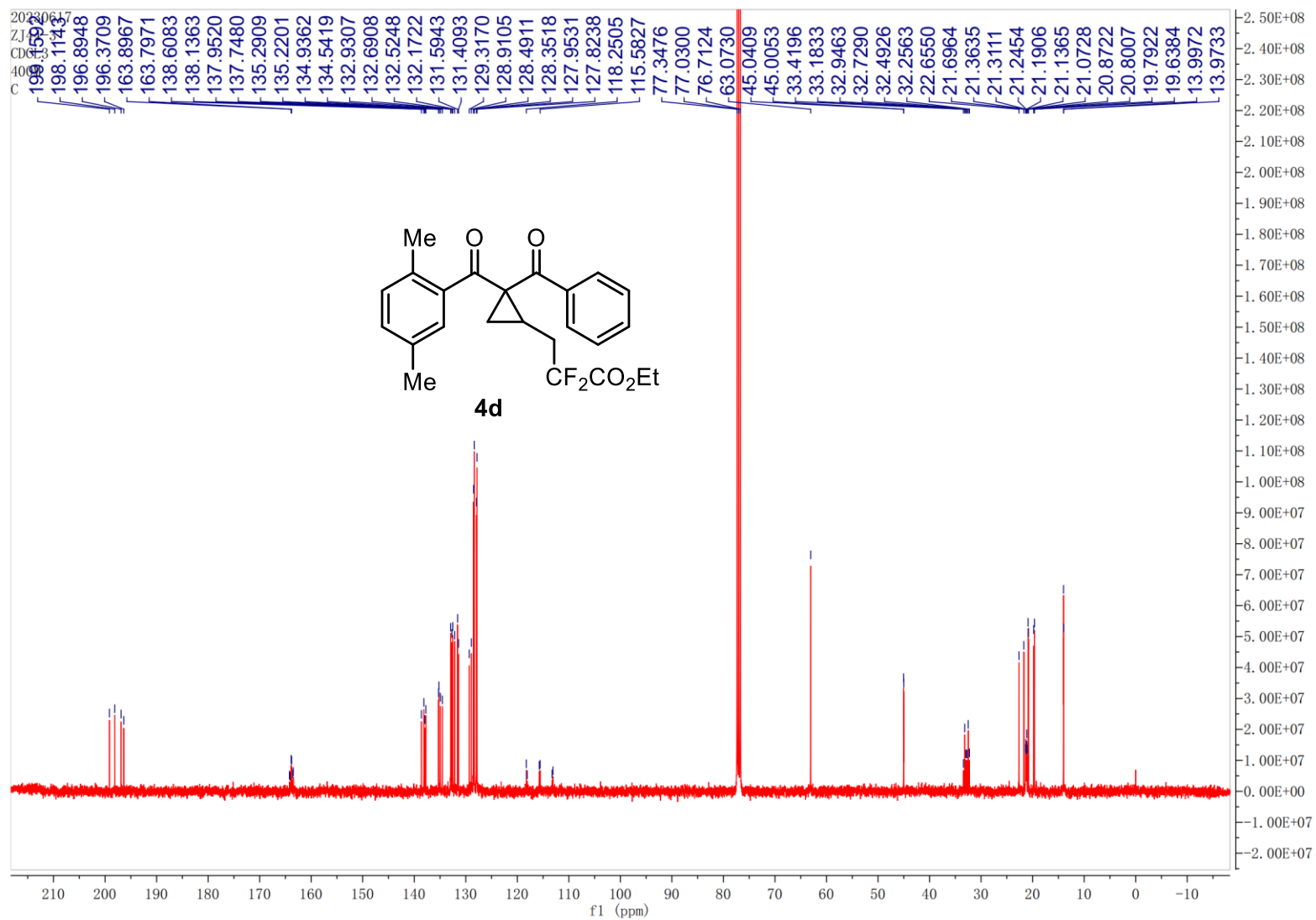
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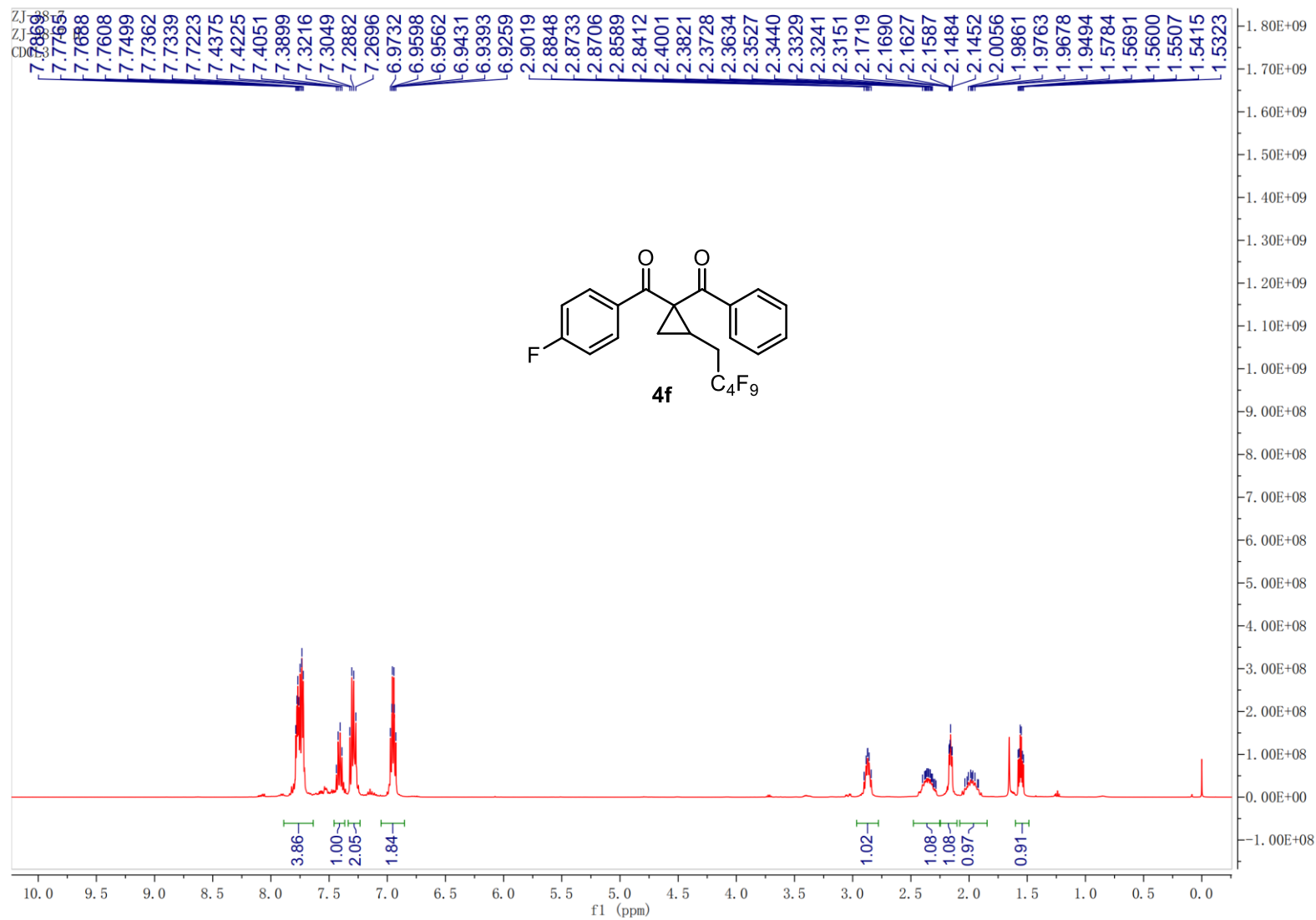




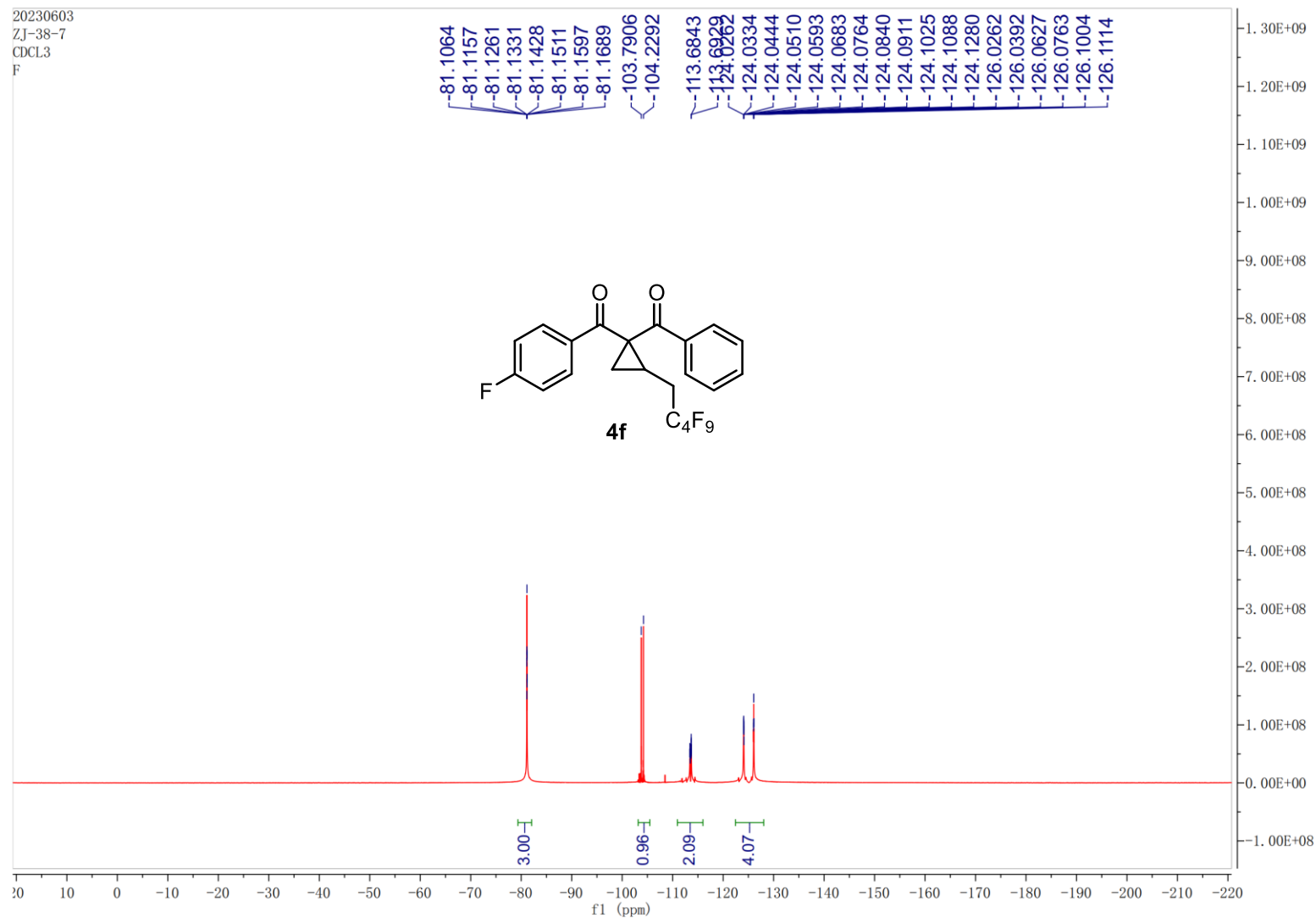
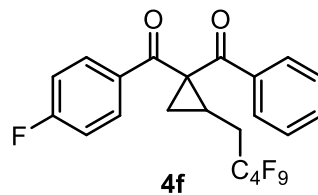
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400M
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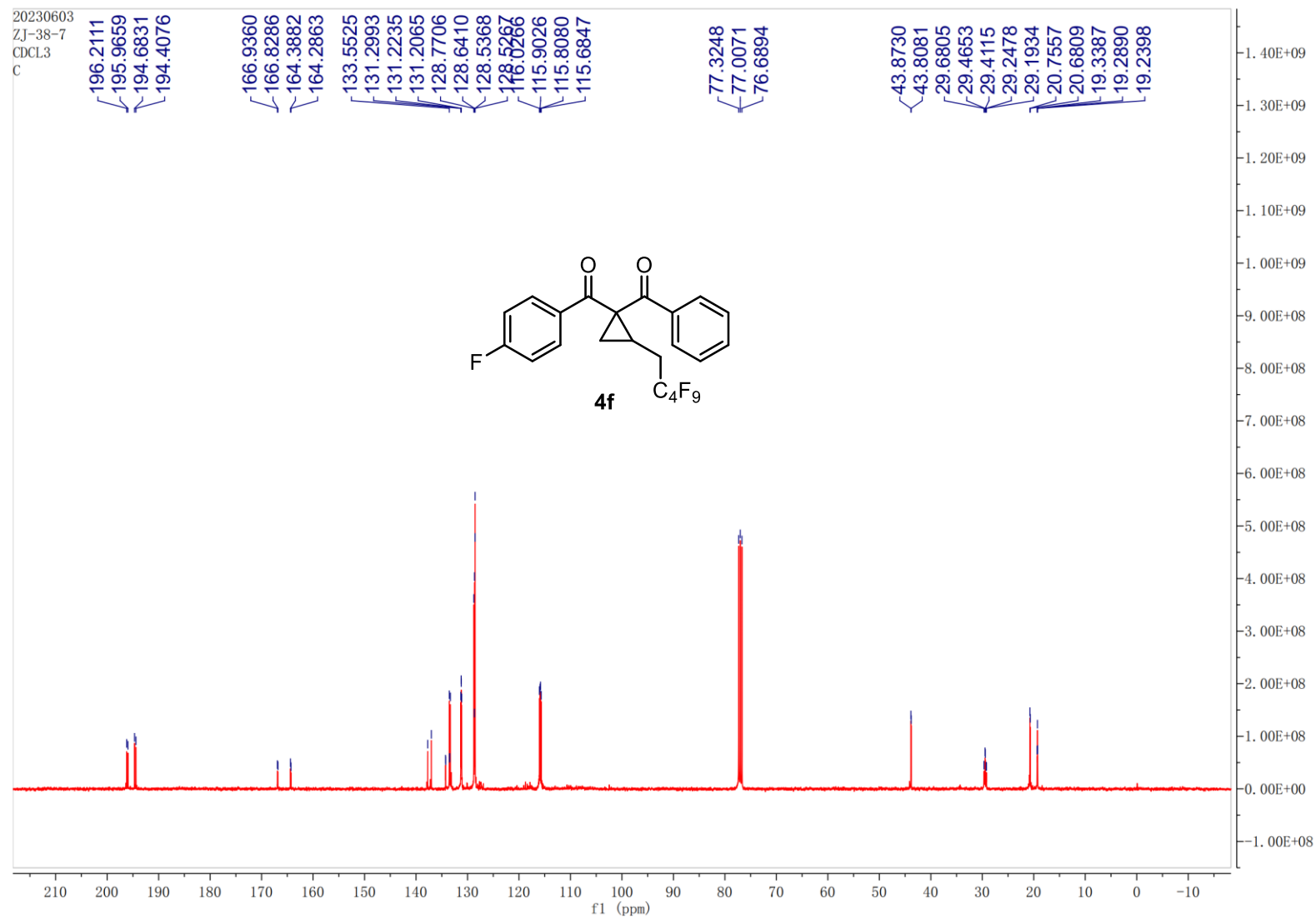


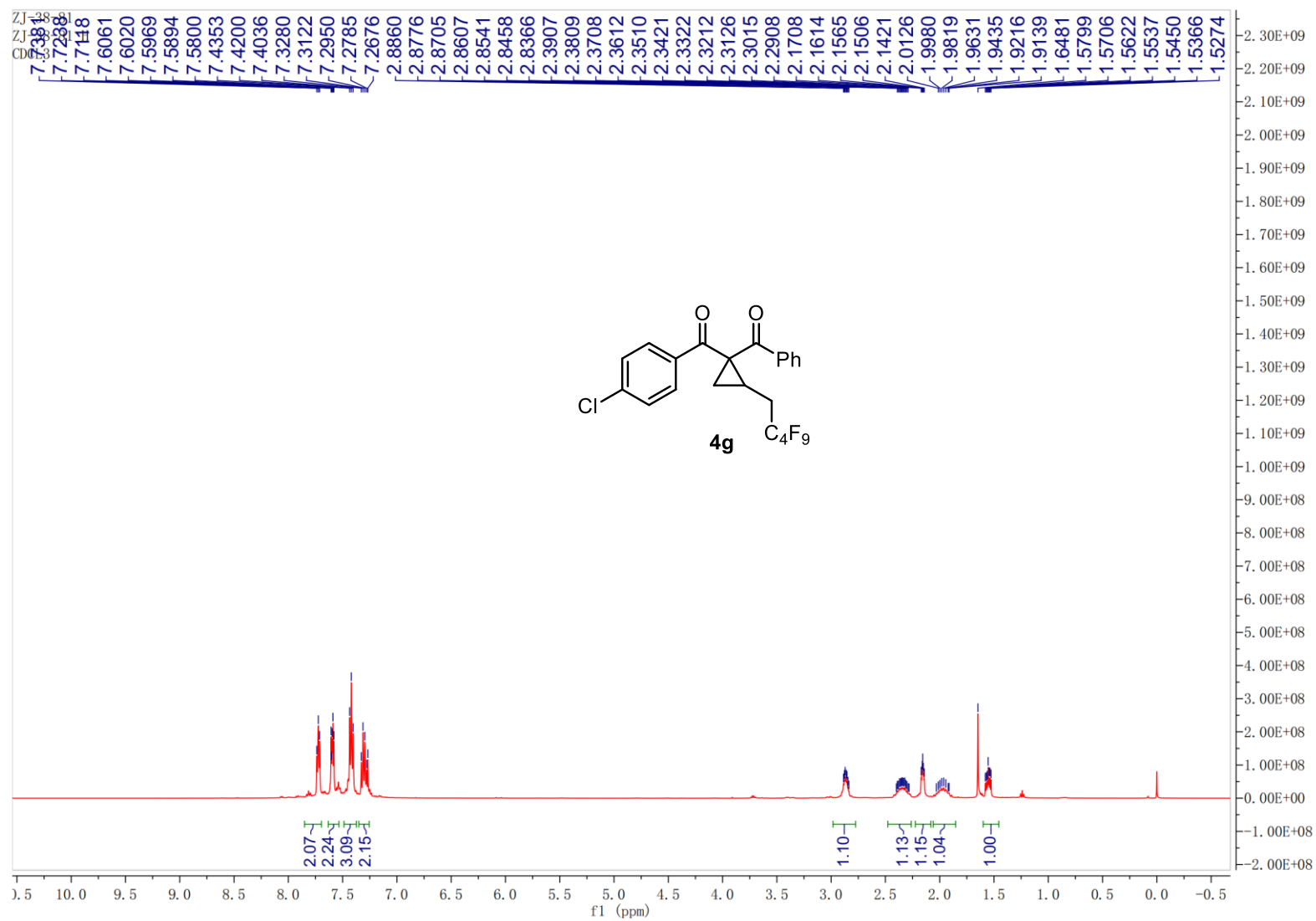


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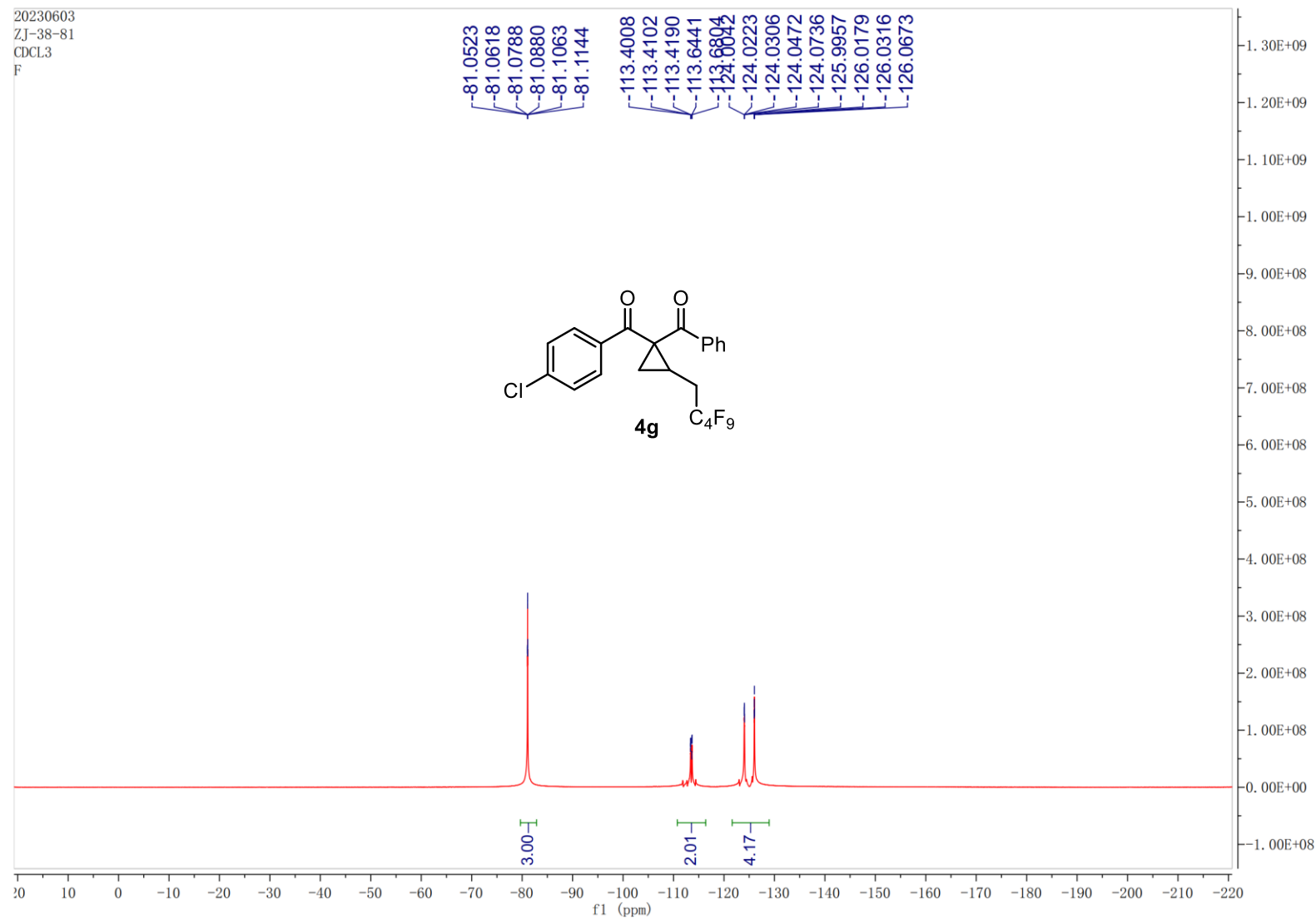


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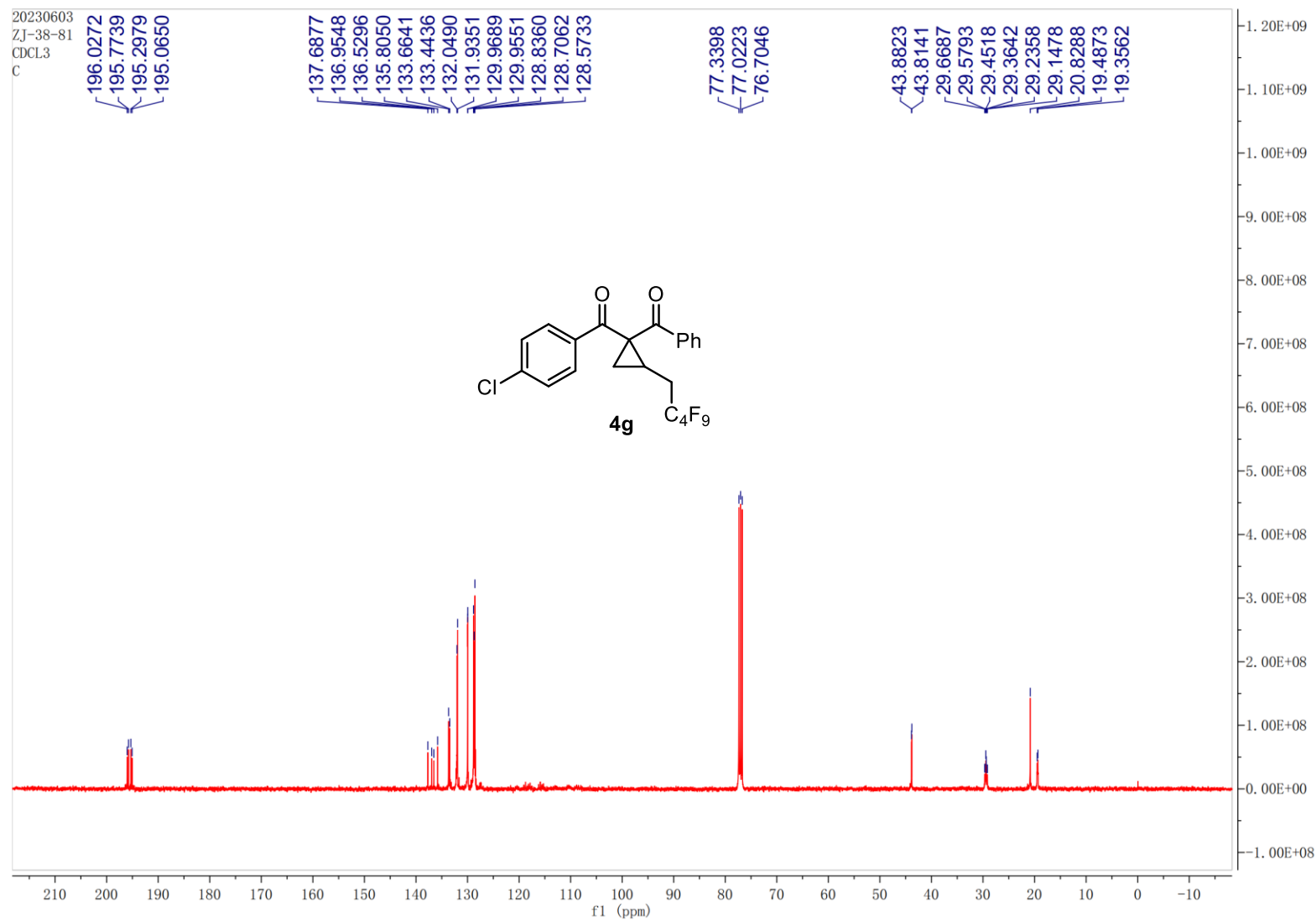


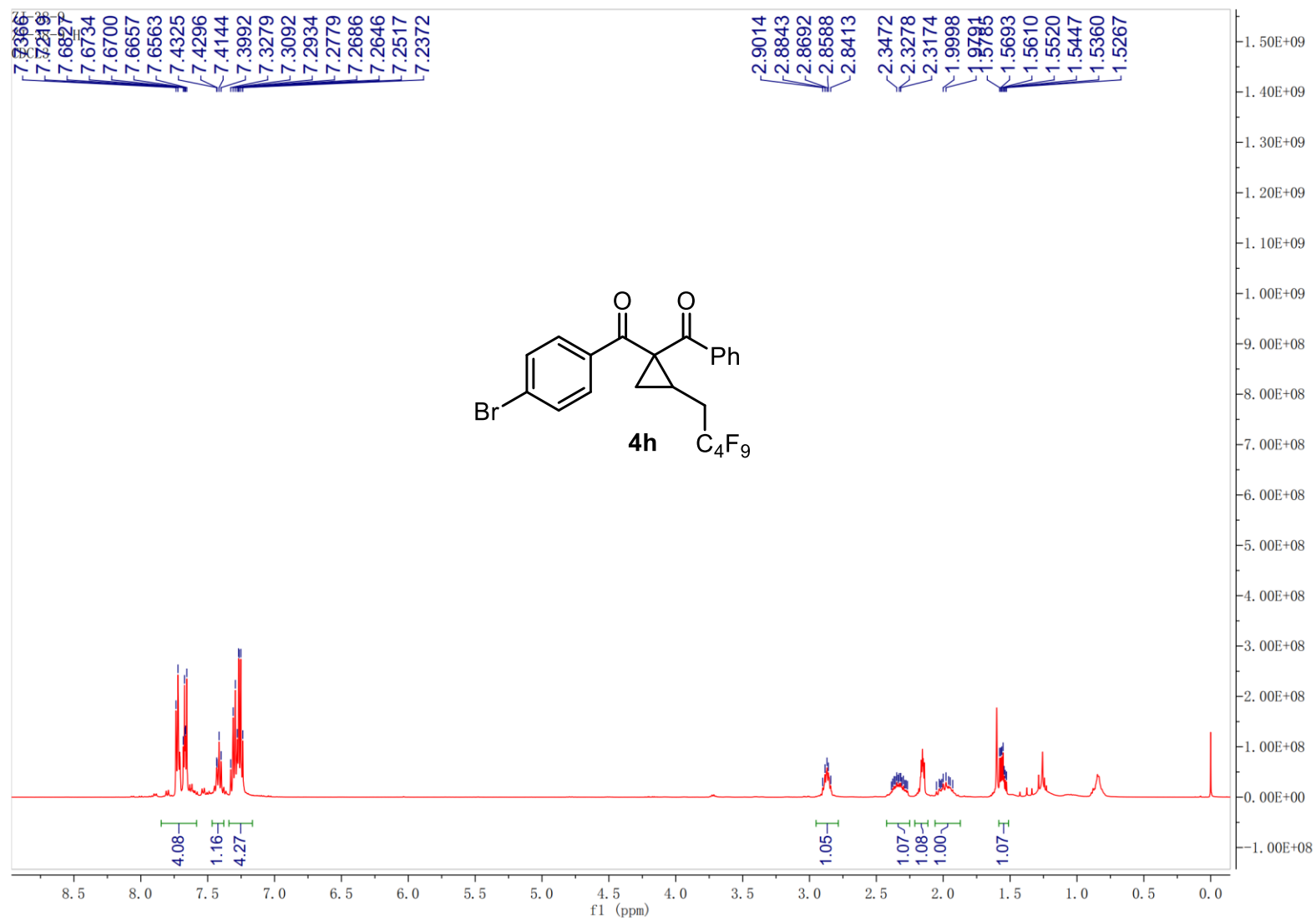


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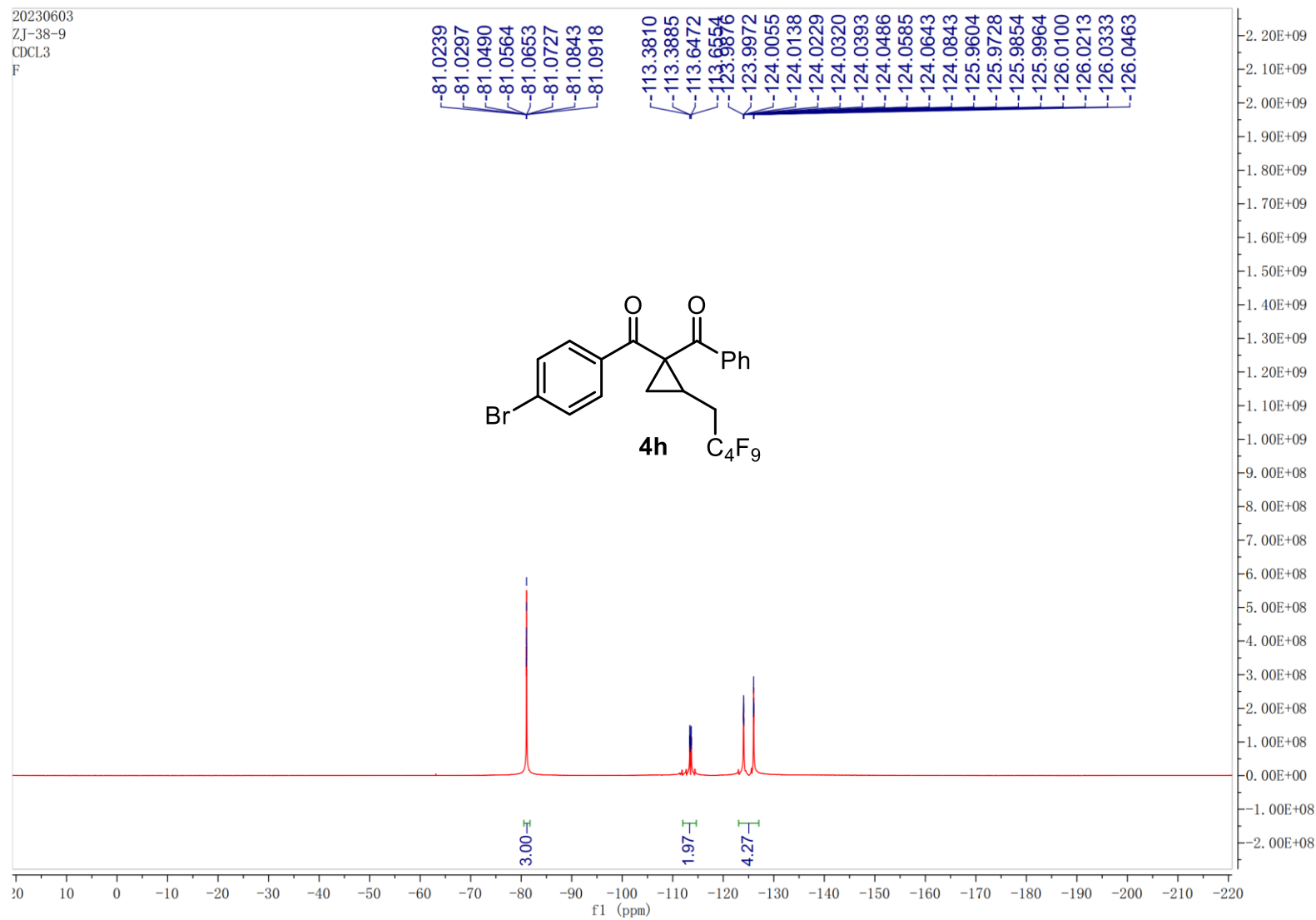


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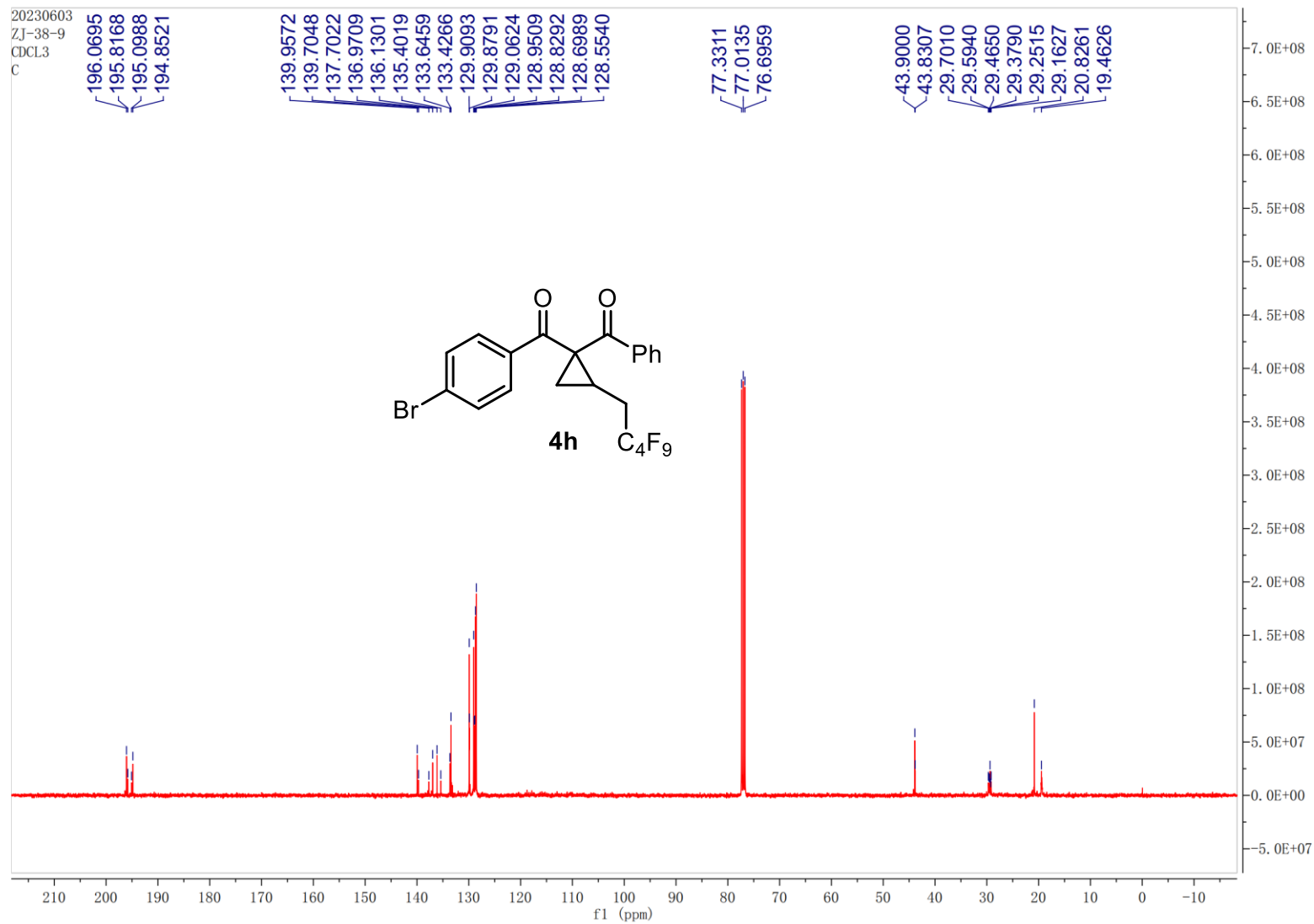


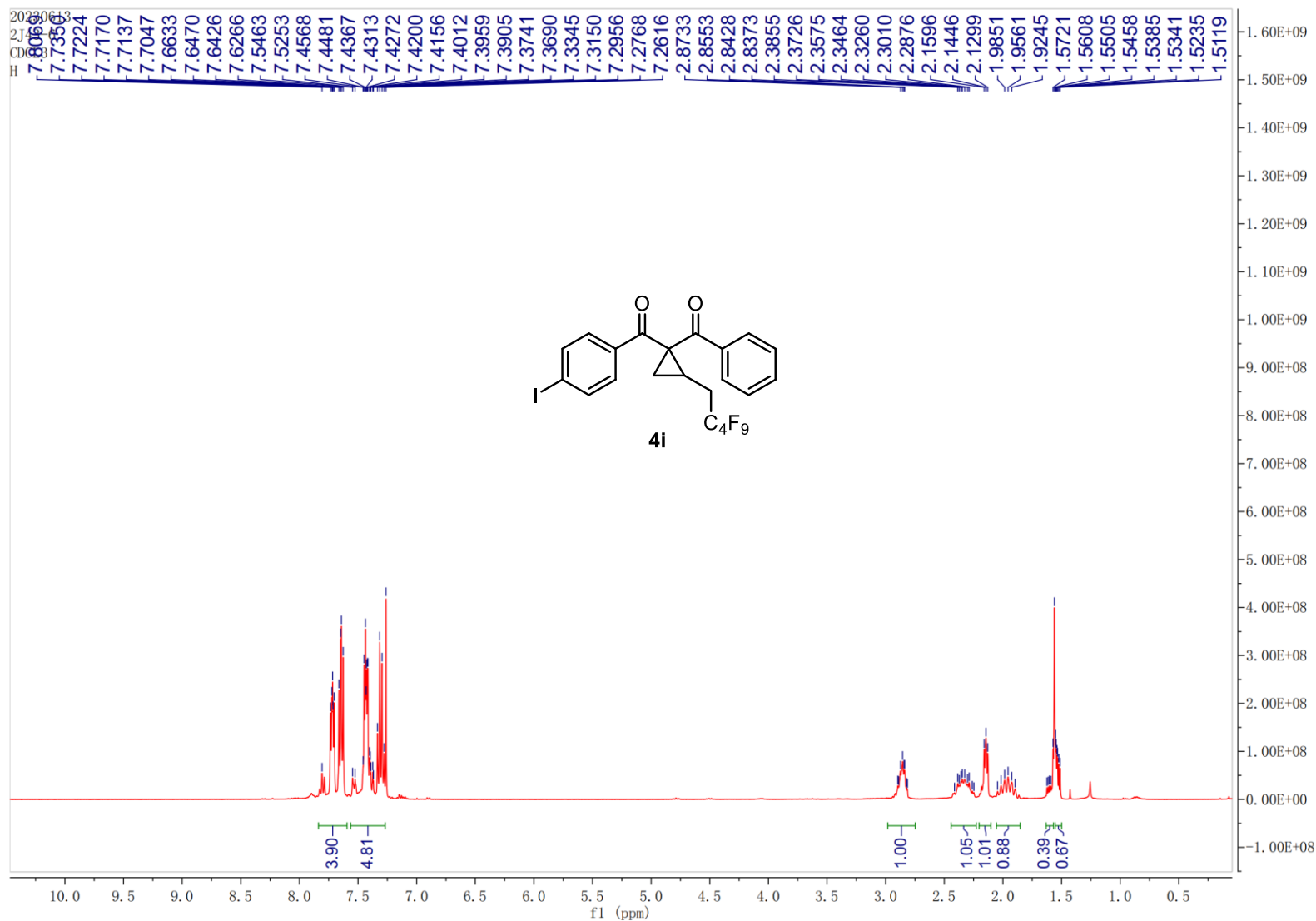


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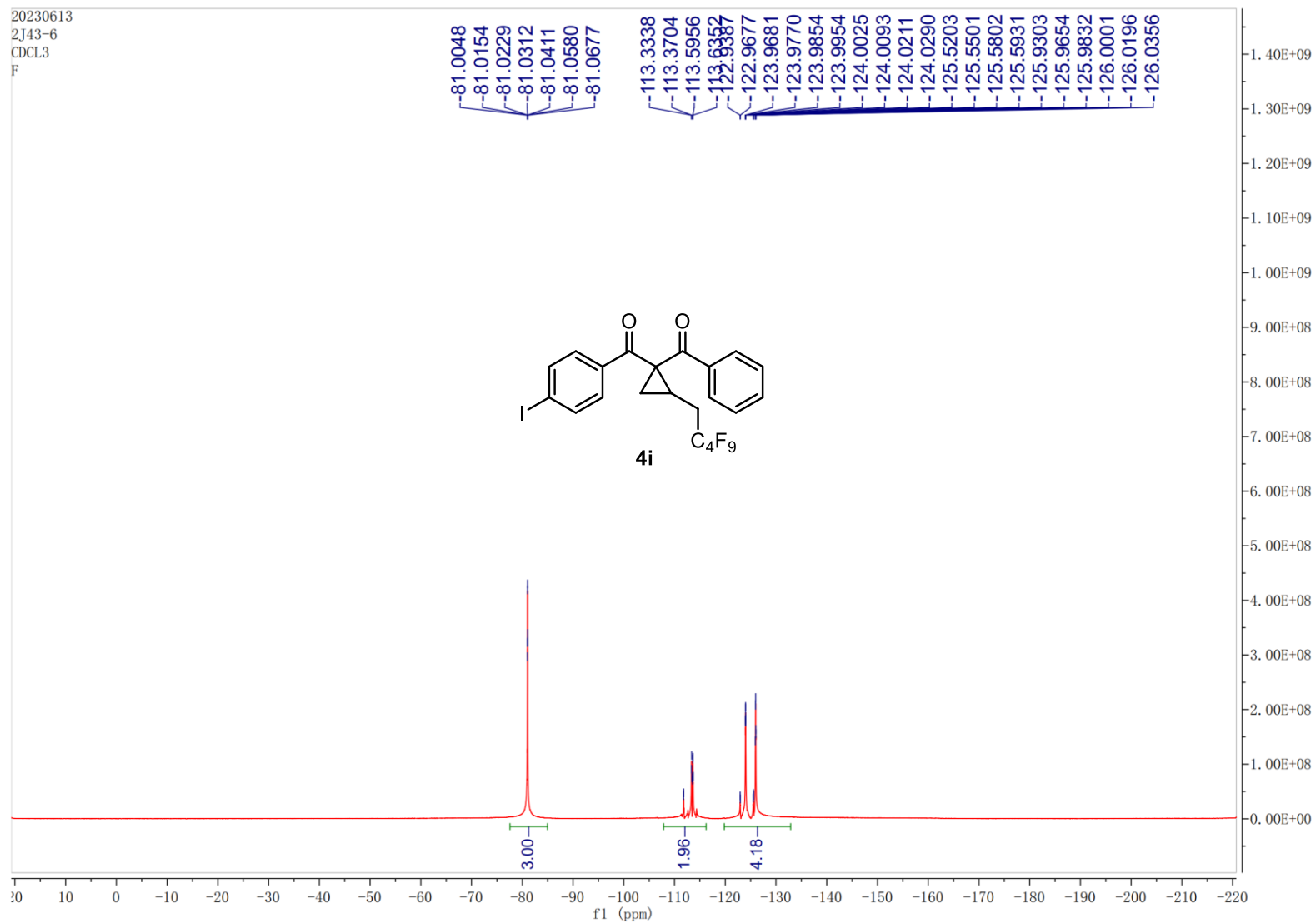


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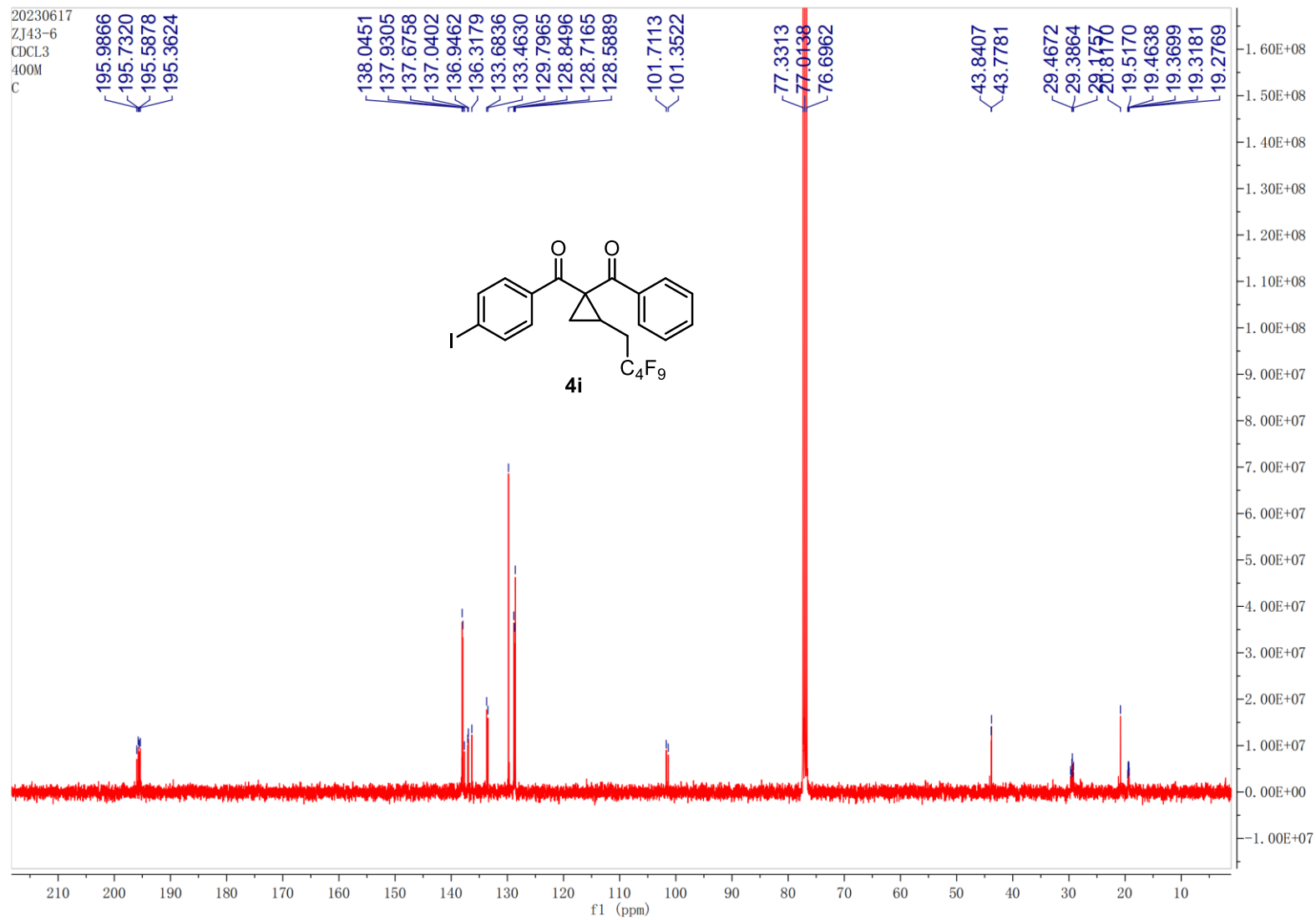


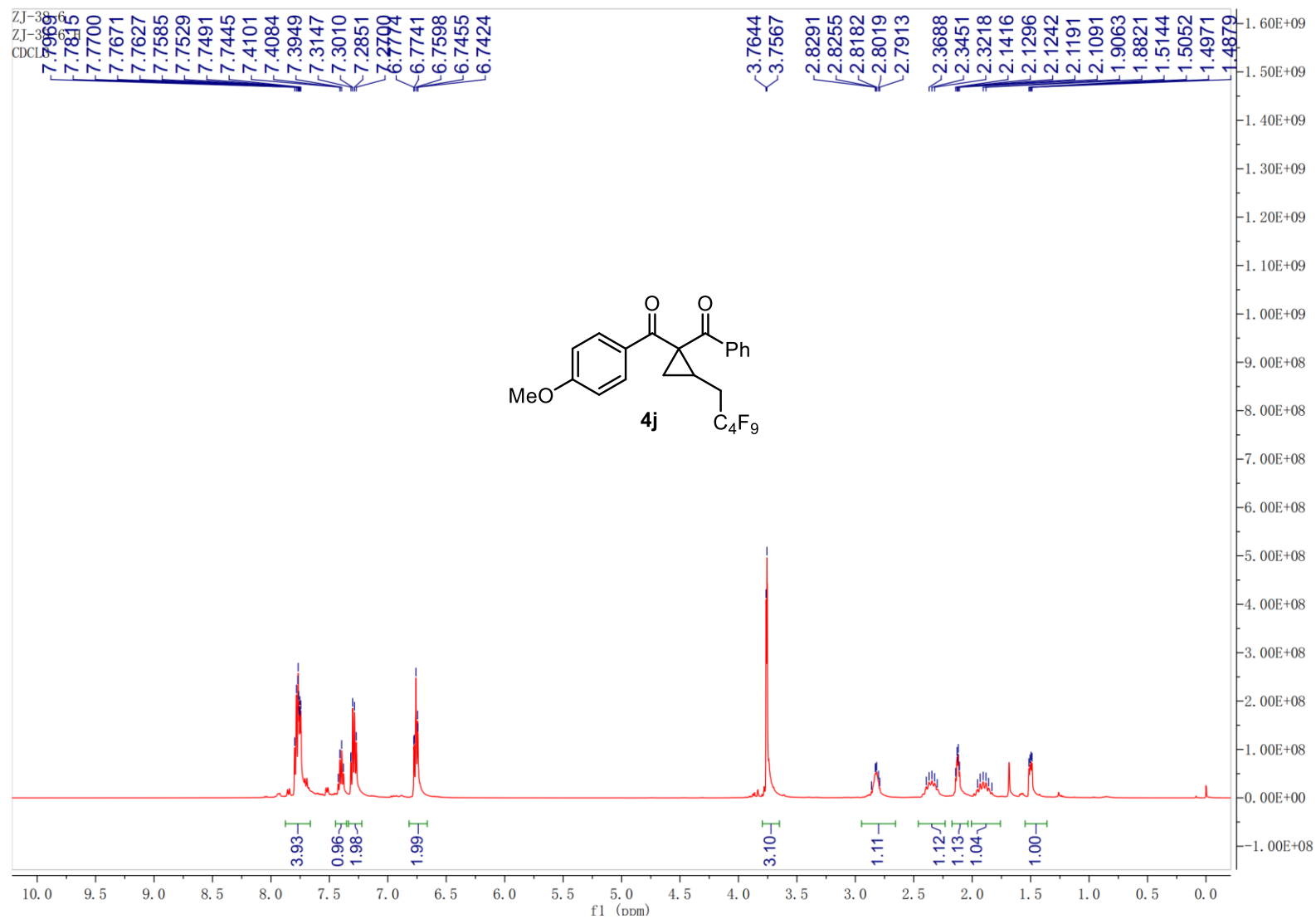


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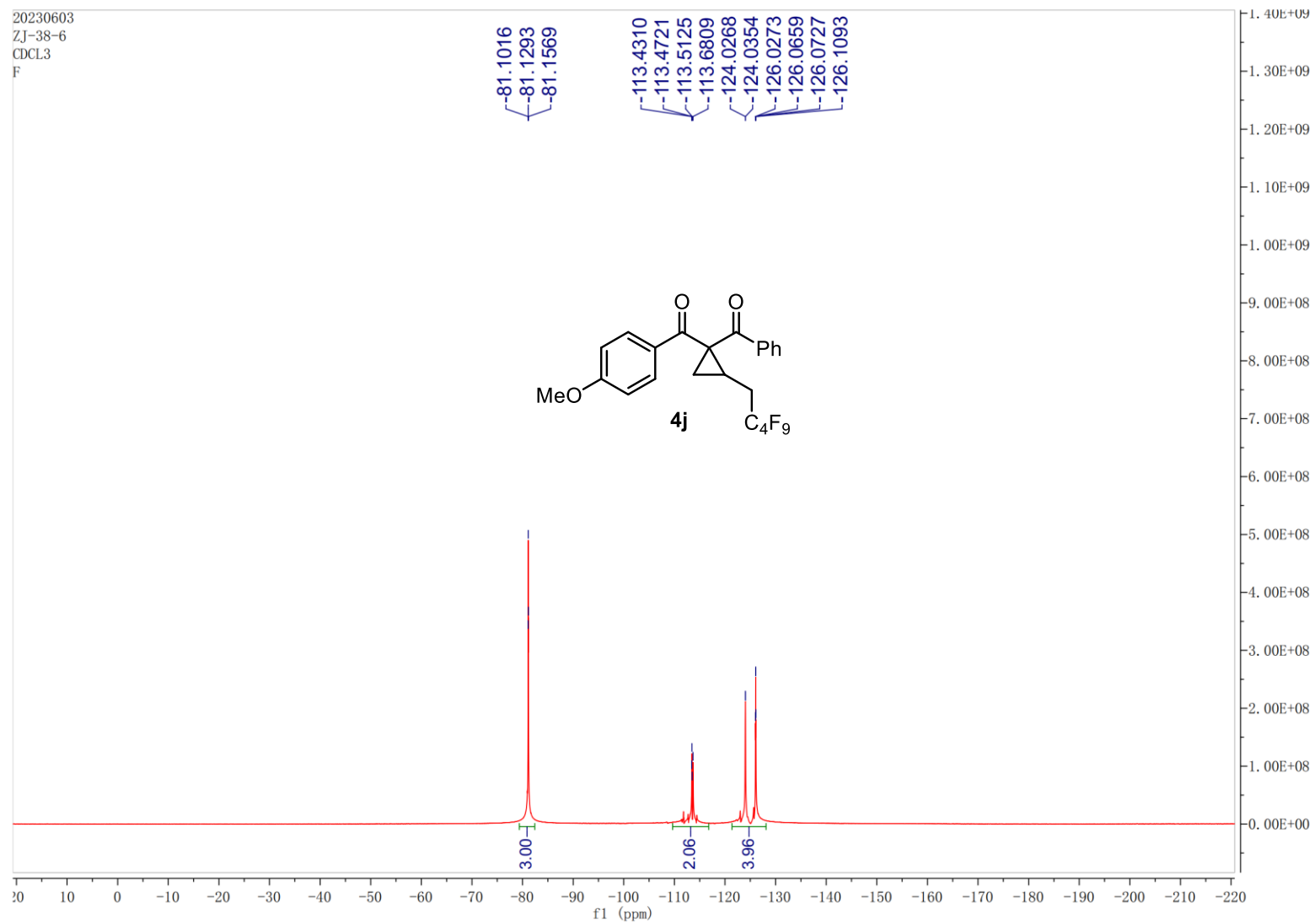


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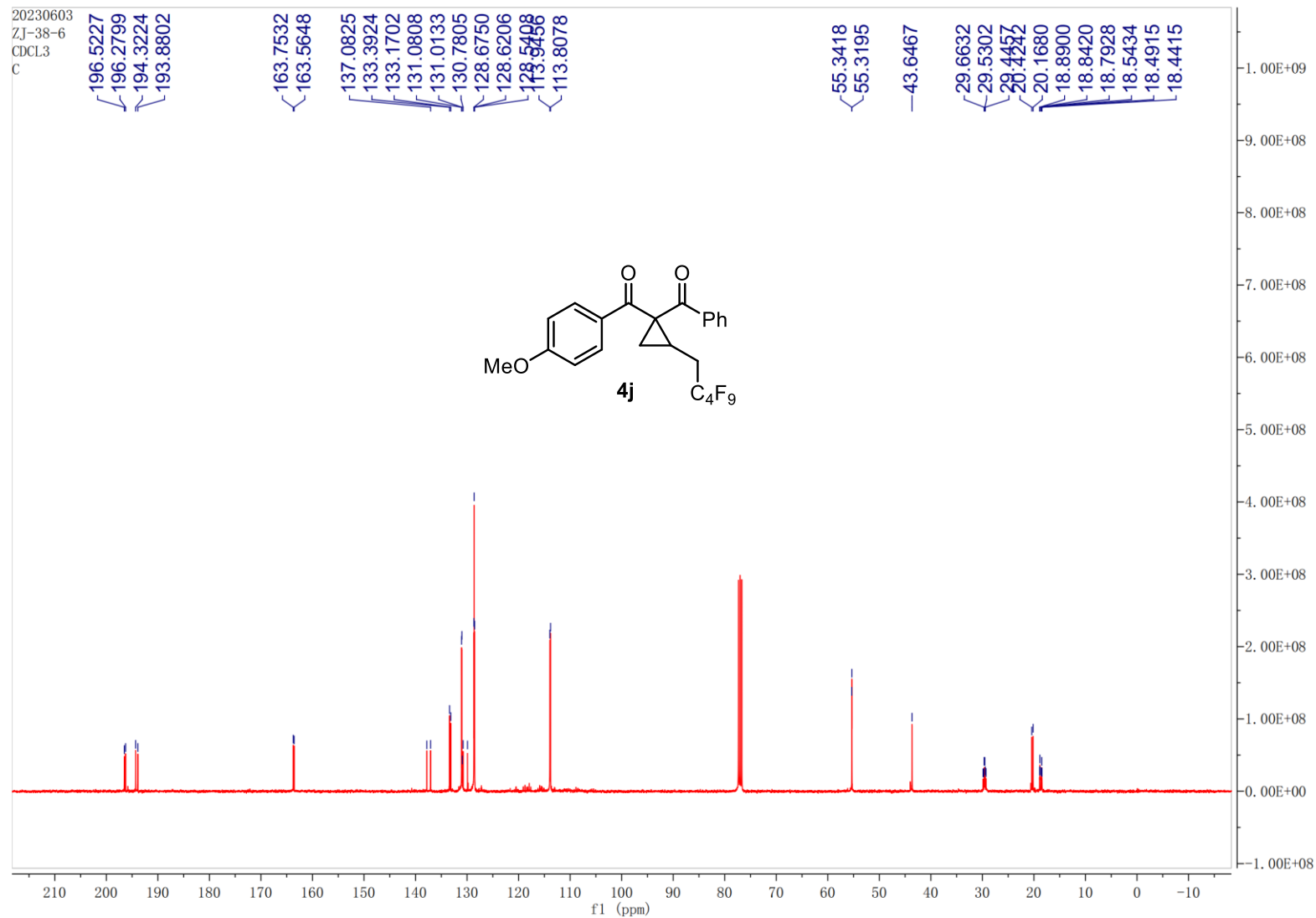


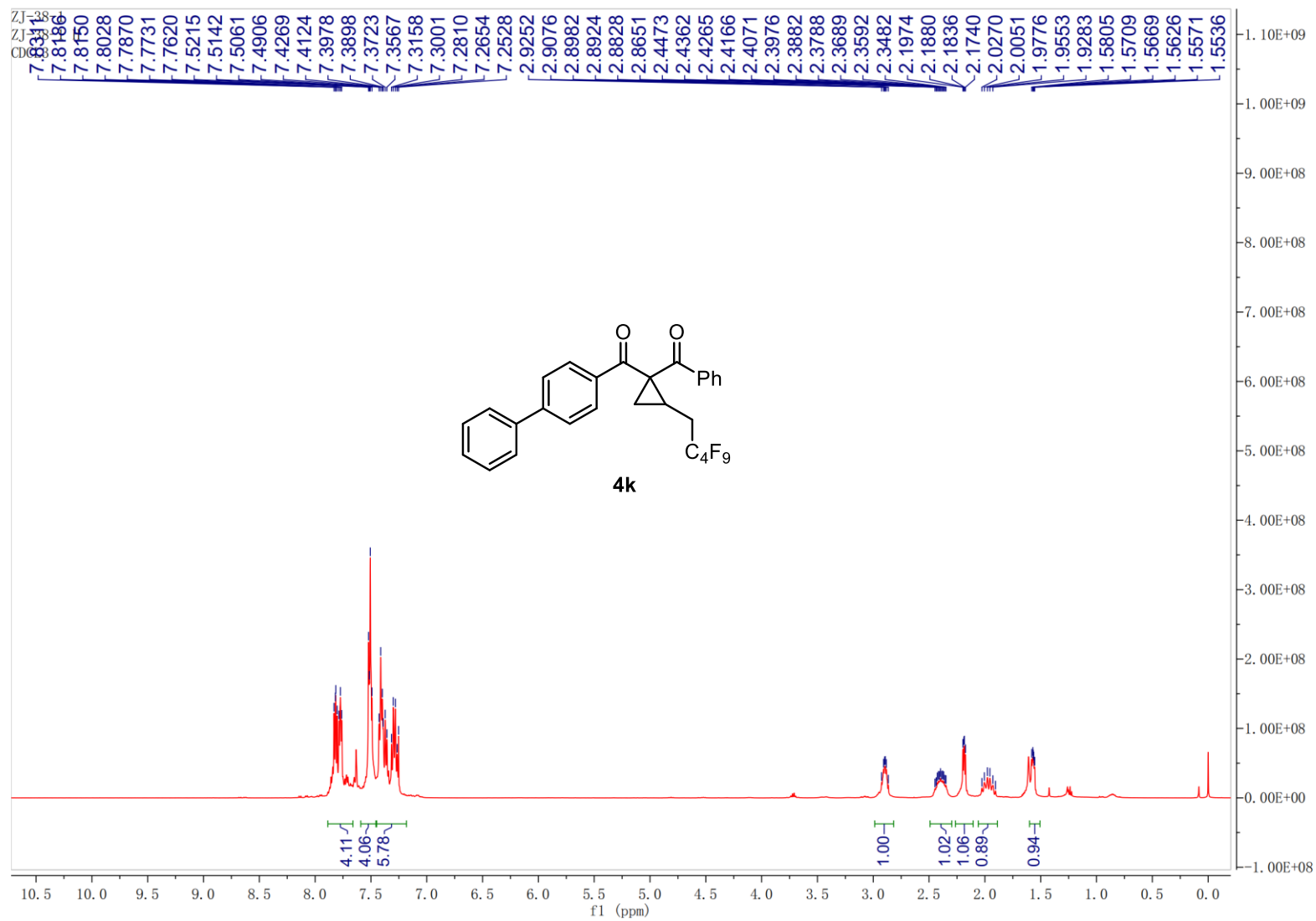


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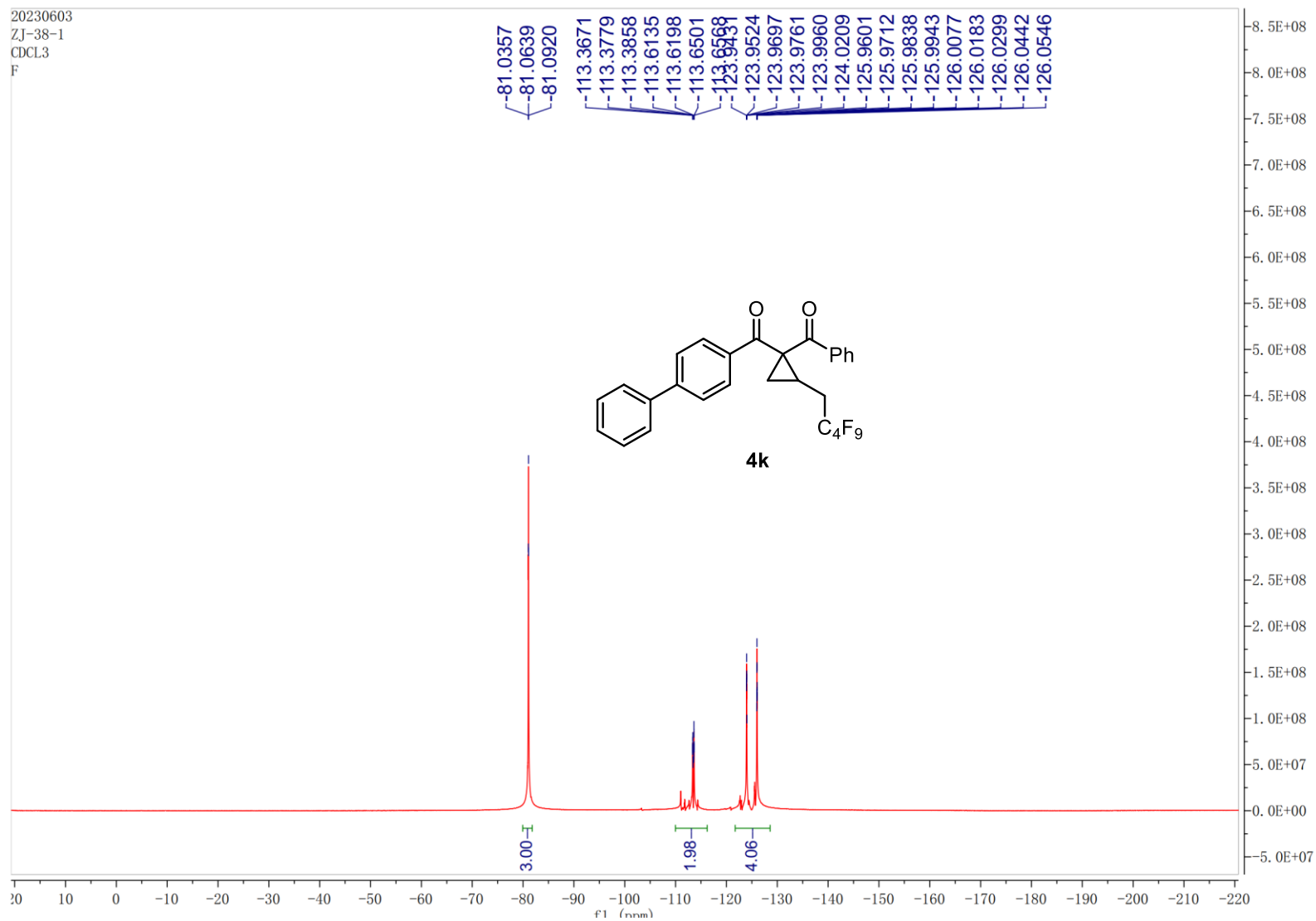


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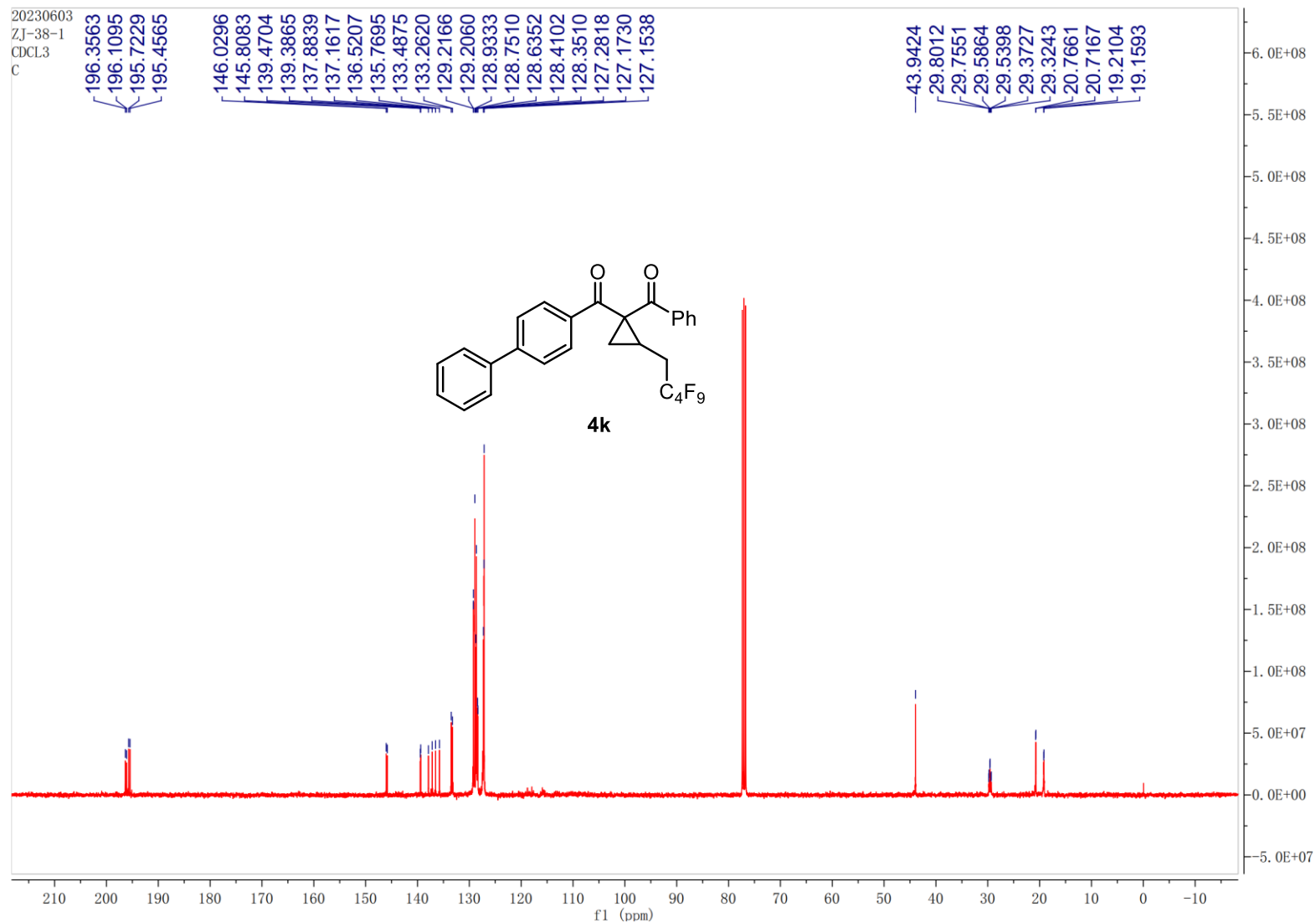


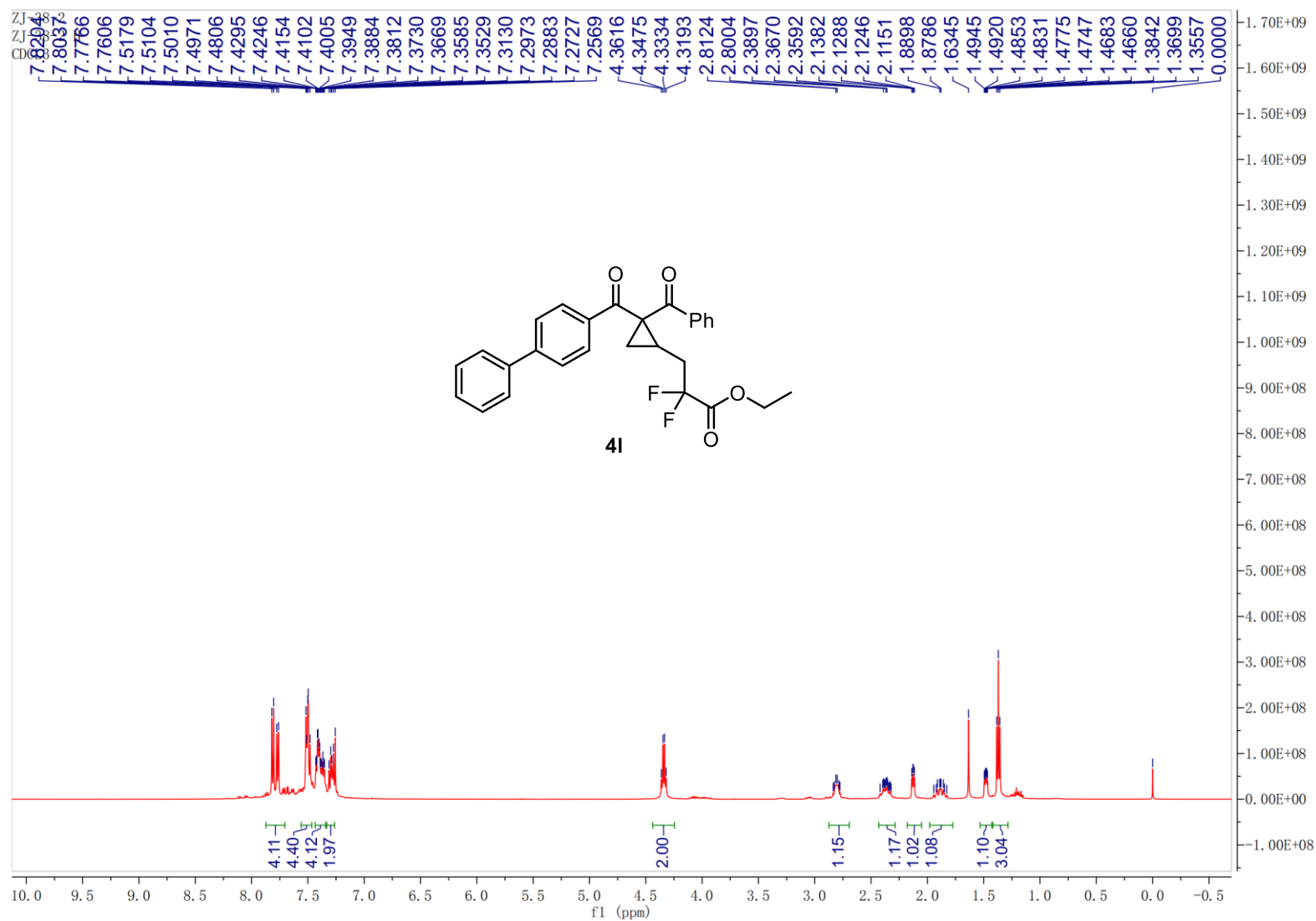


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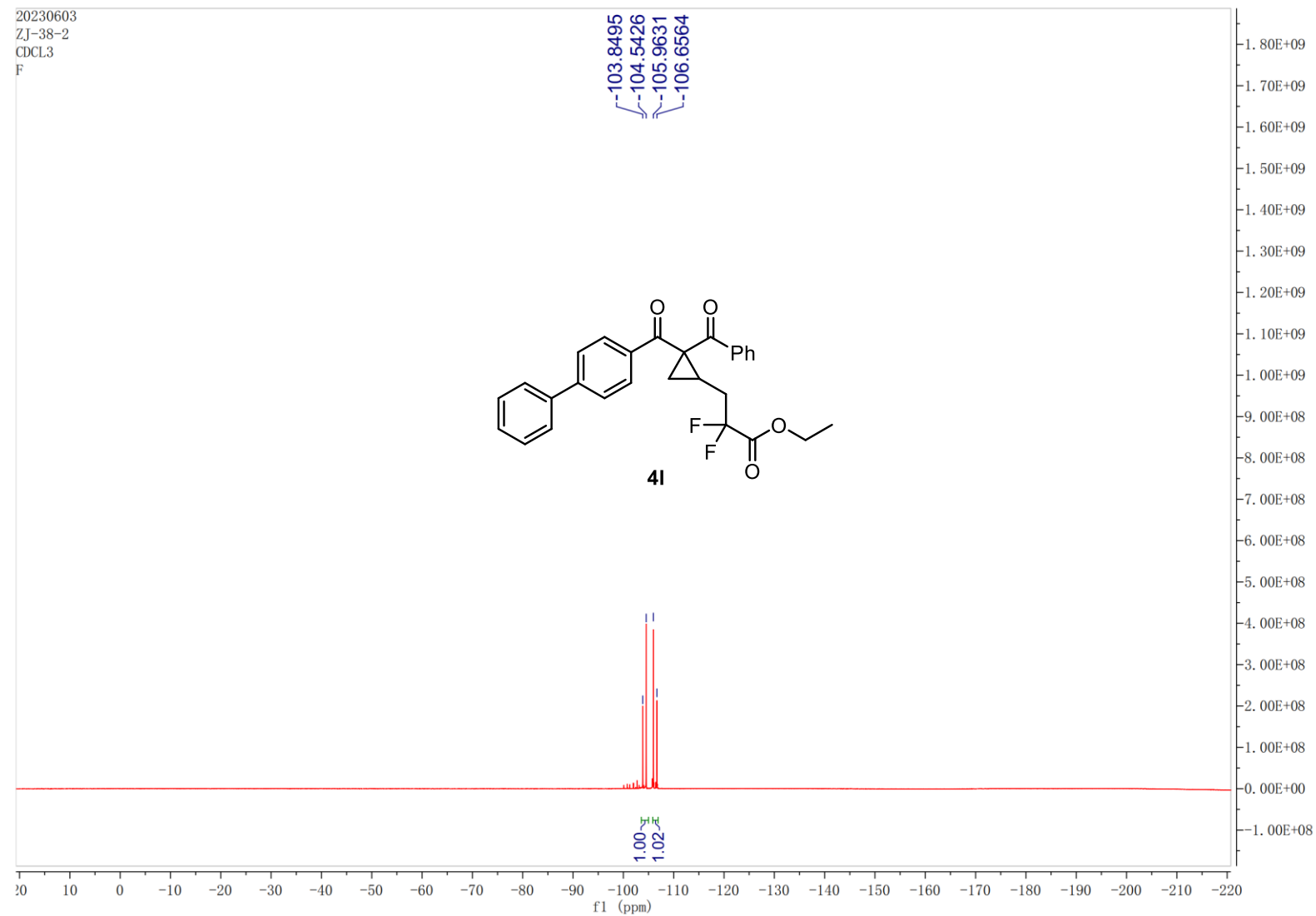


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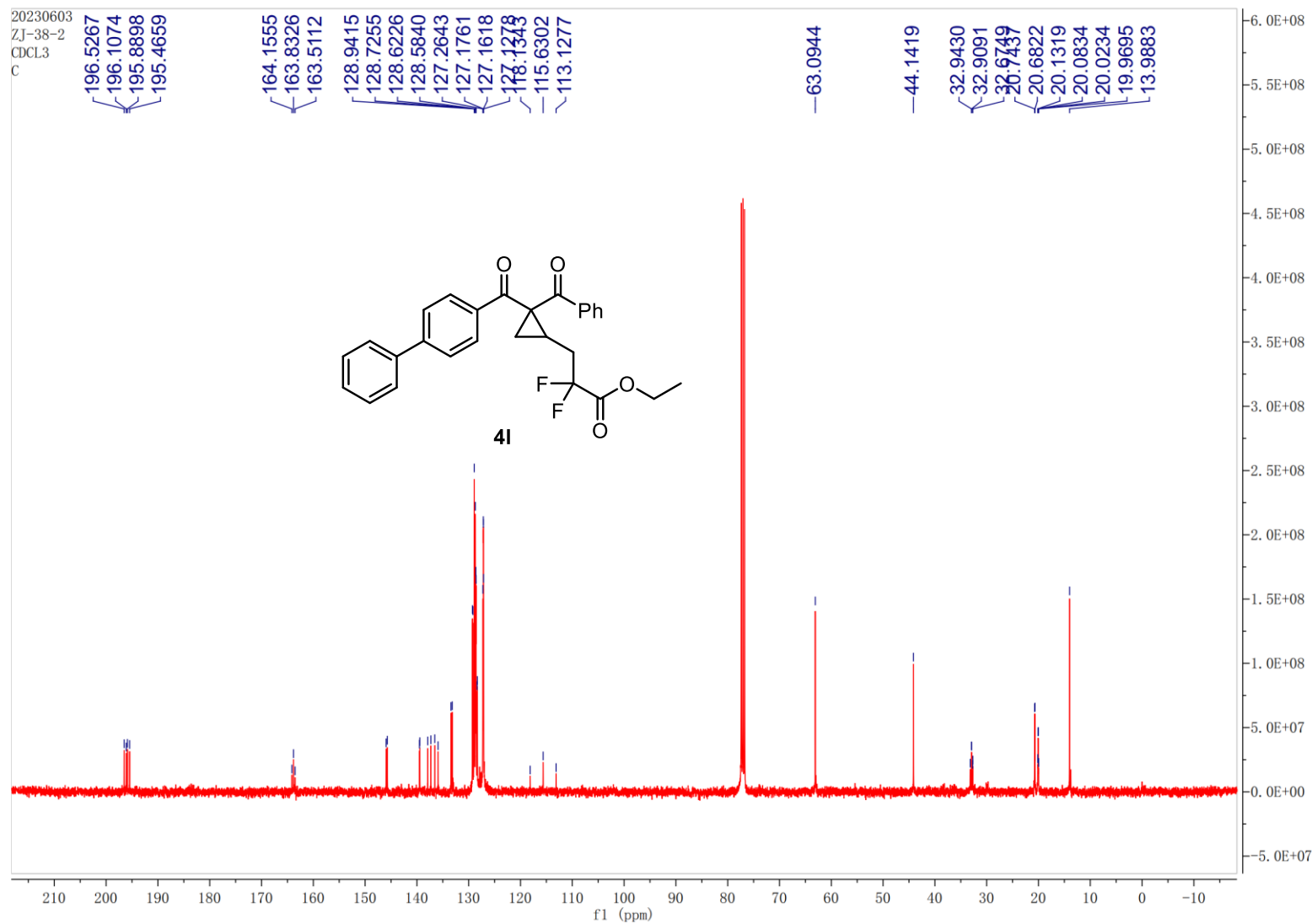


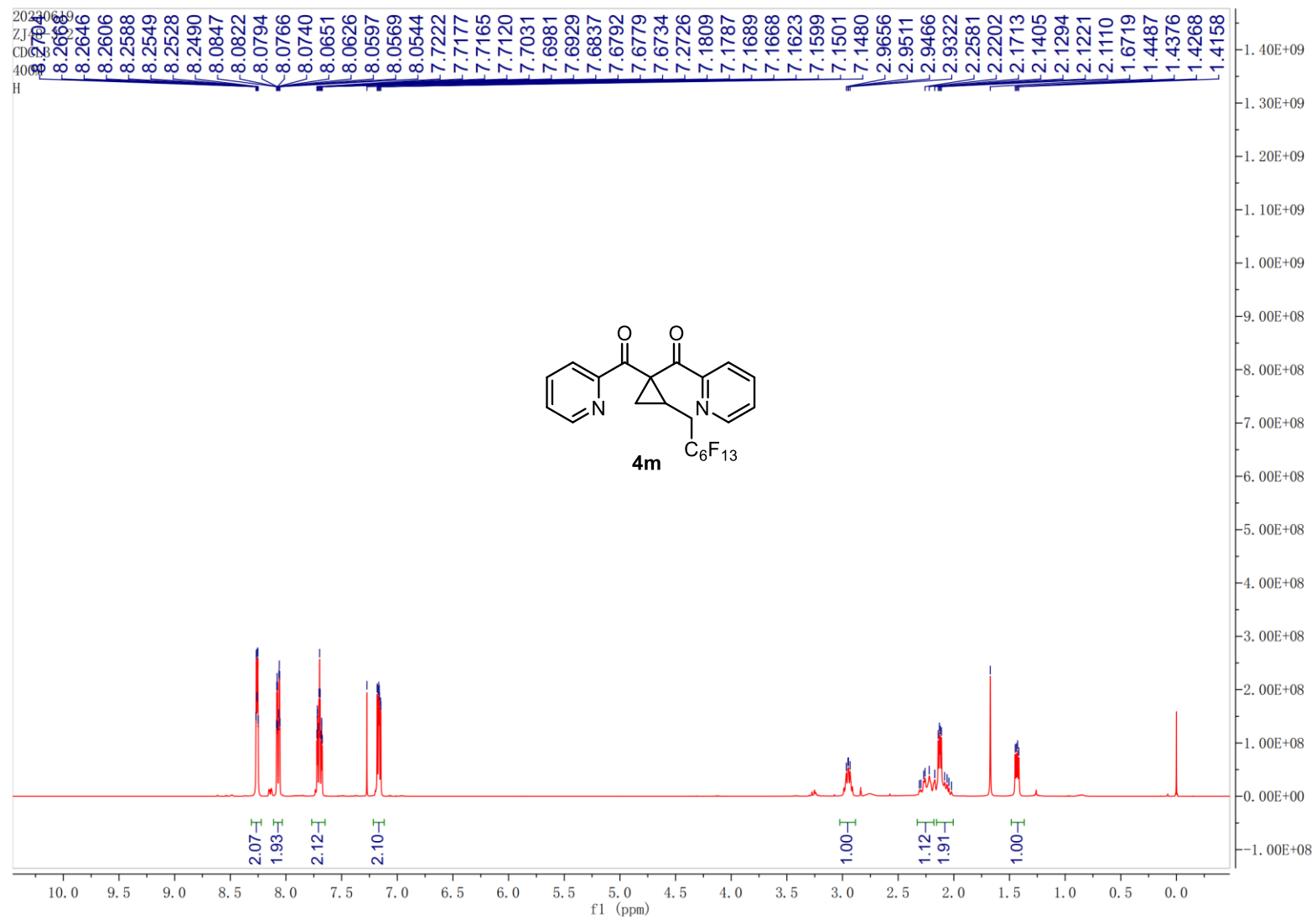


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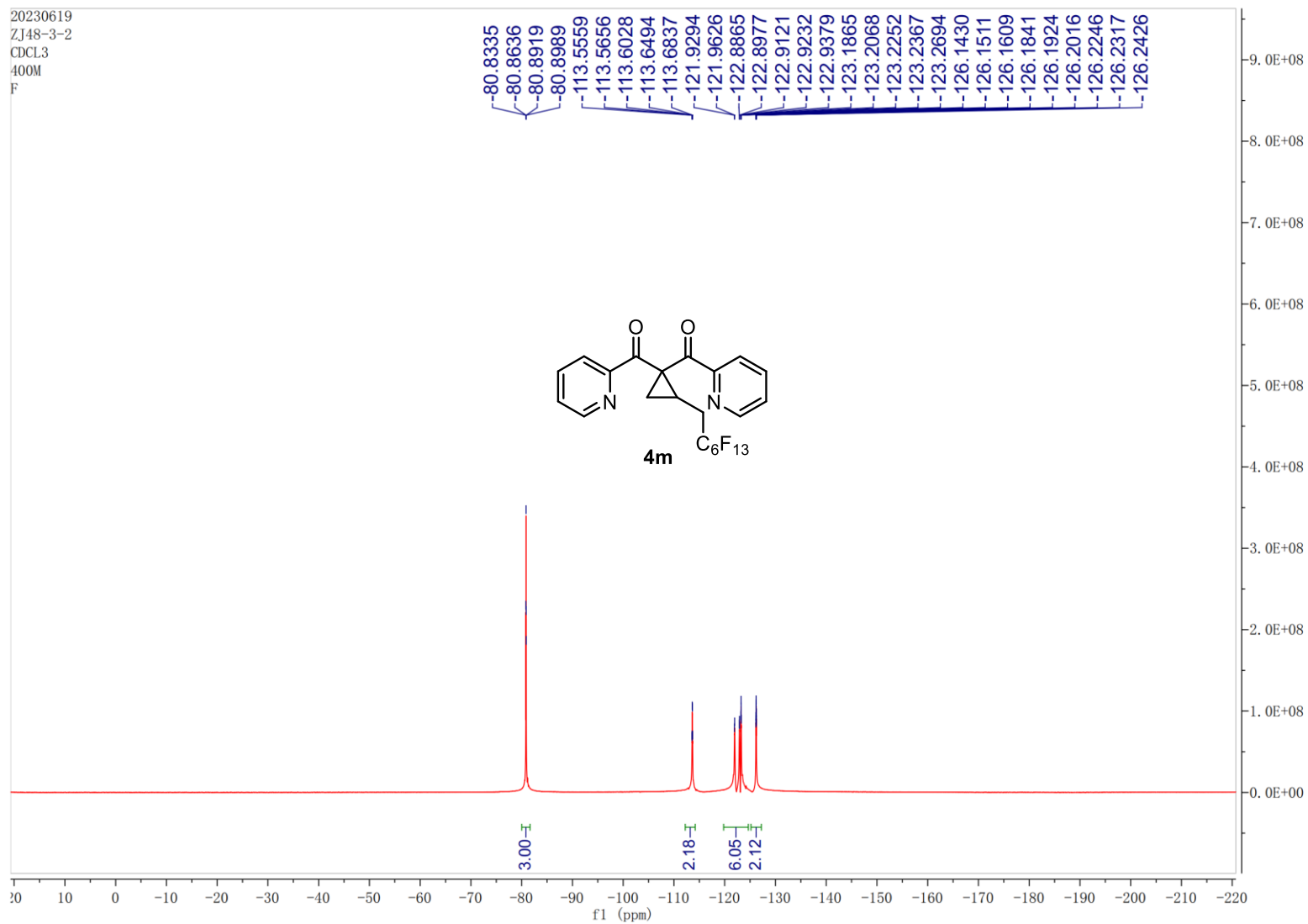


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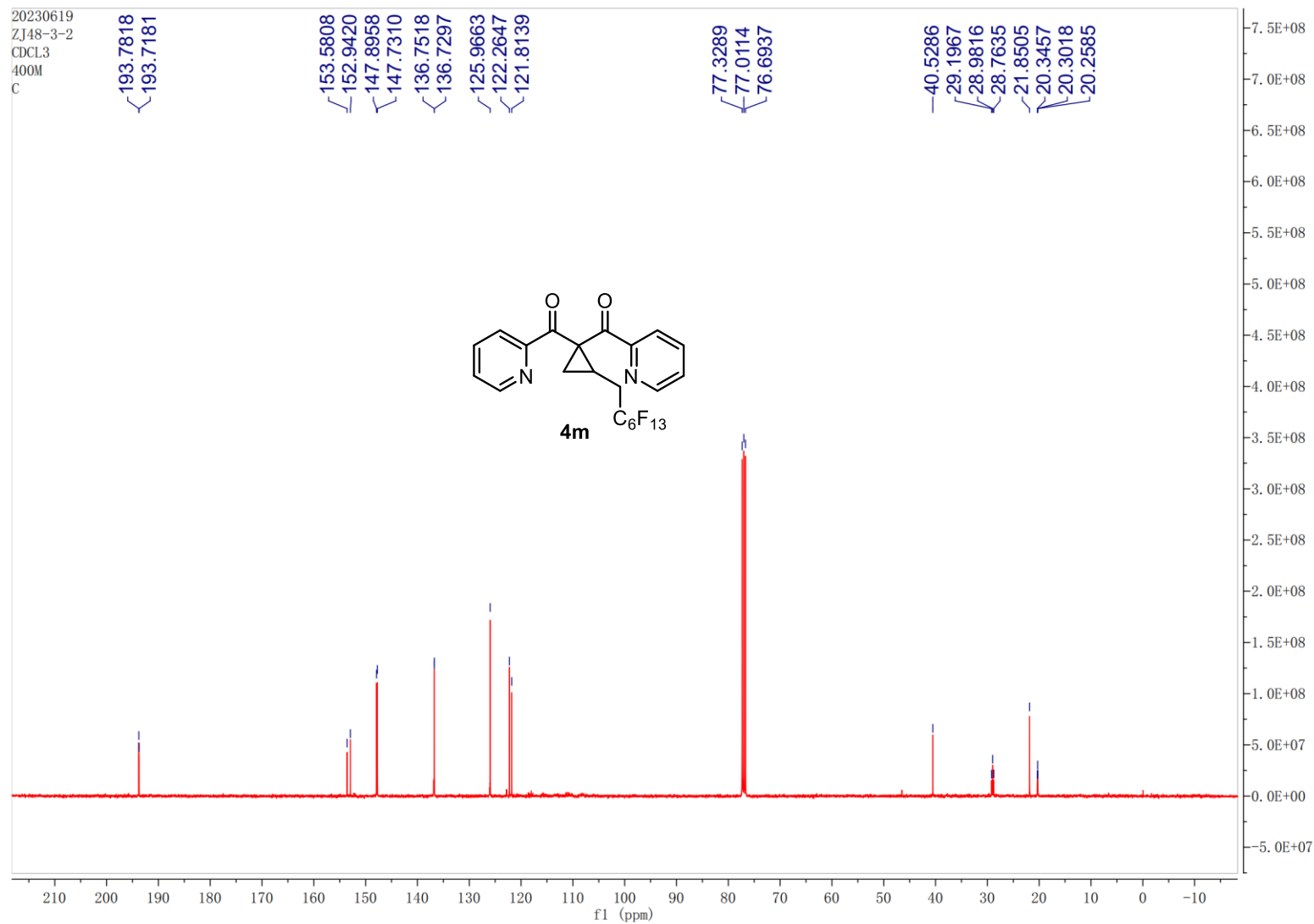


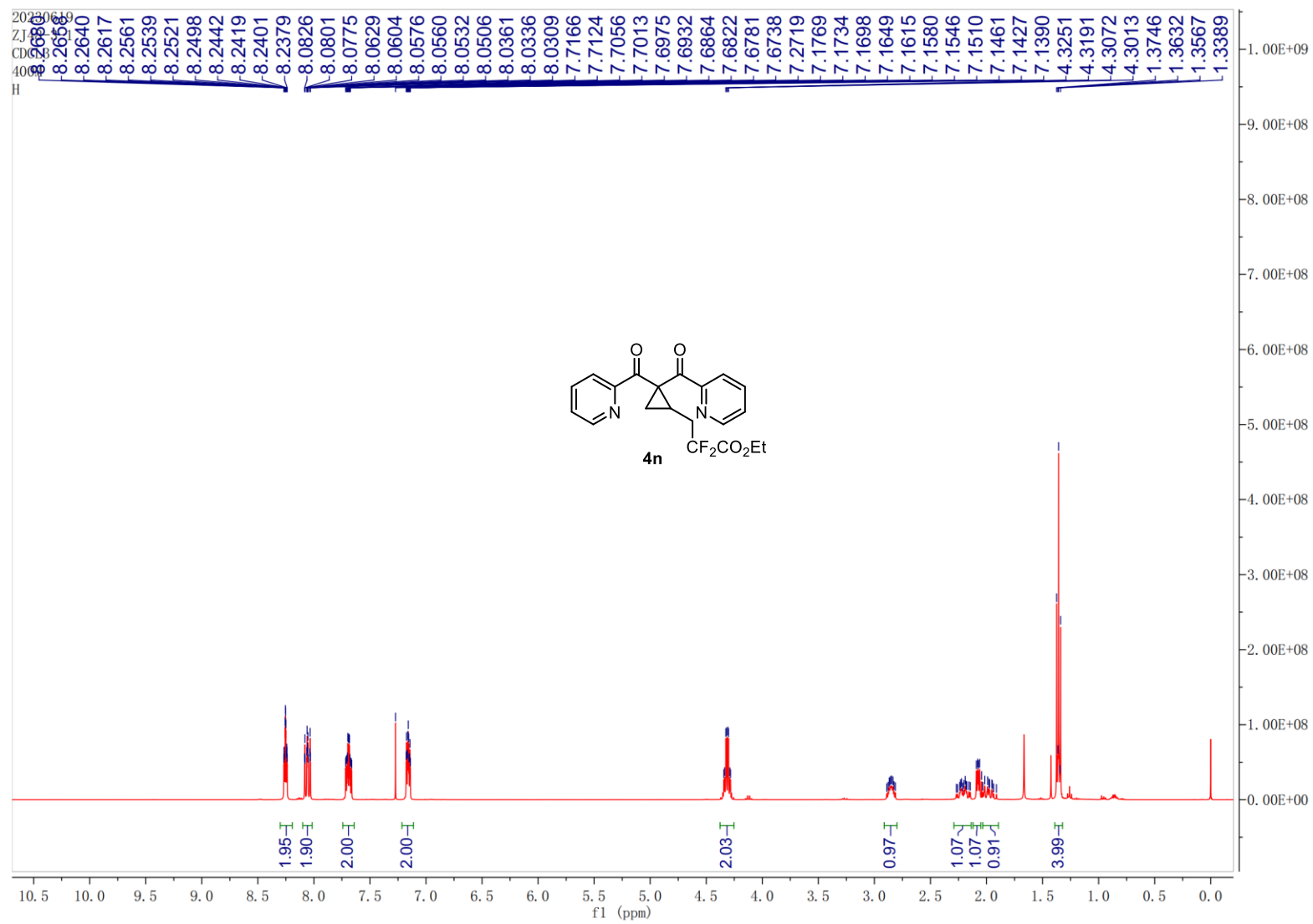


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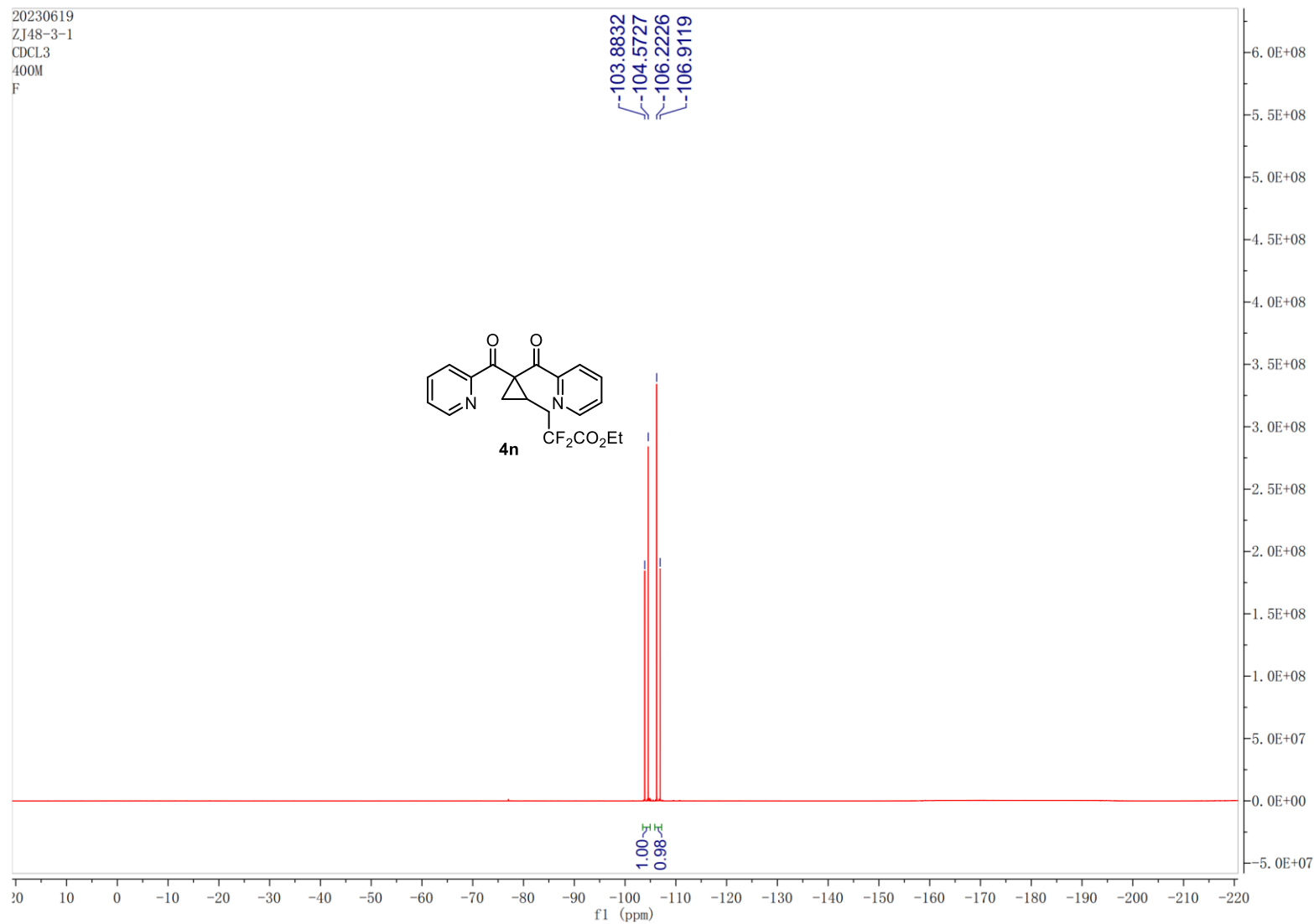
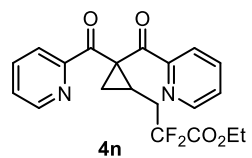


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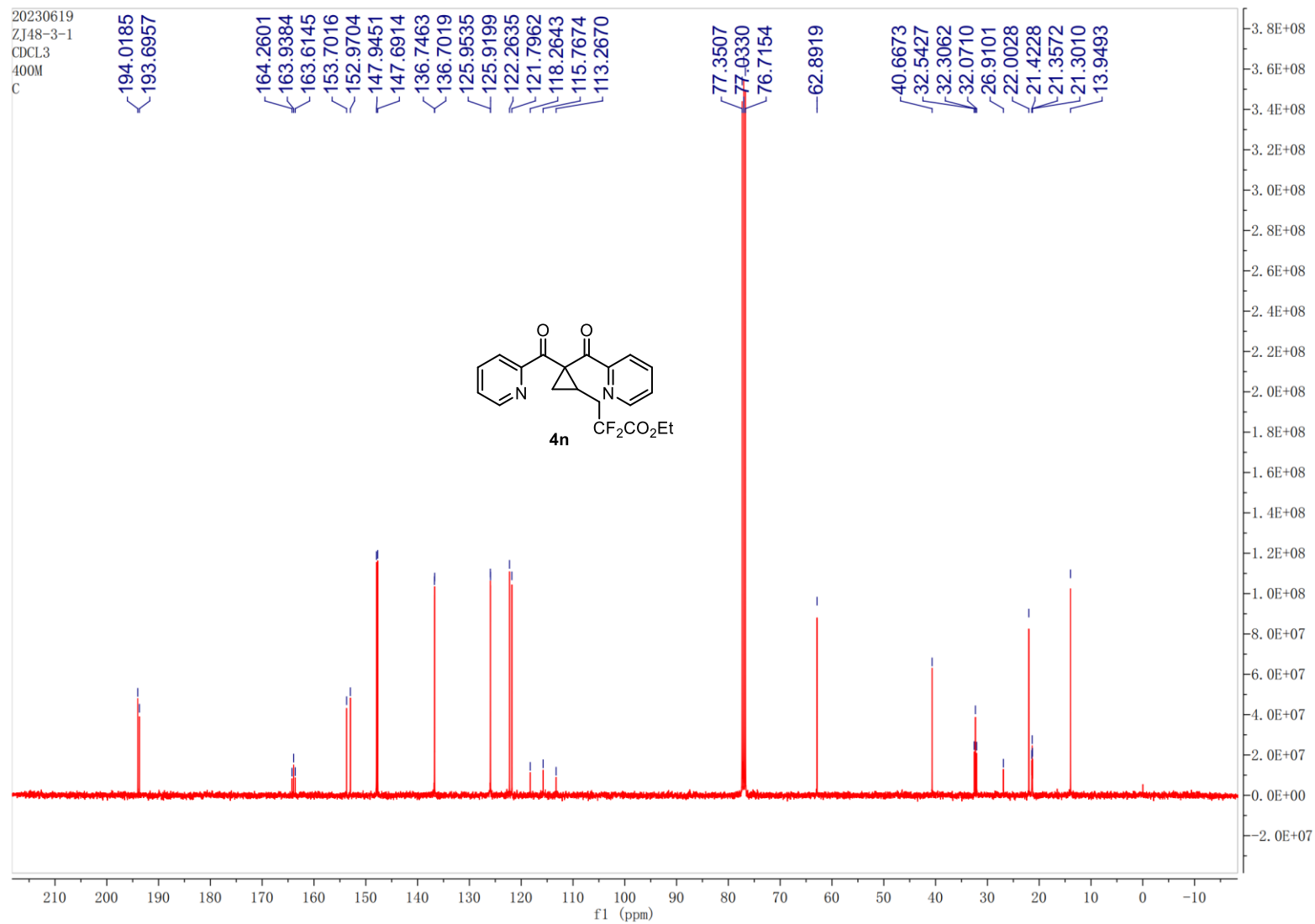


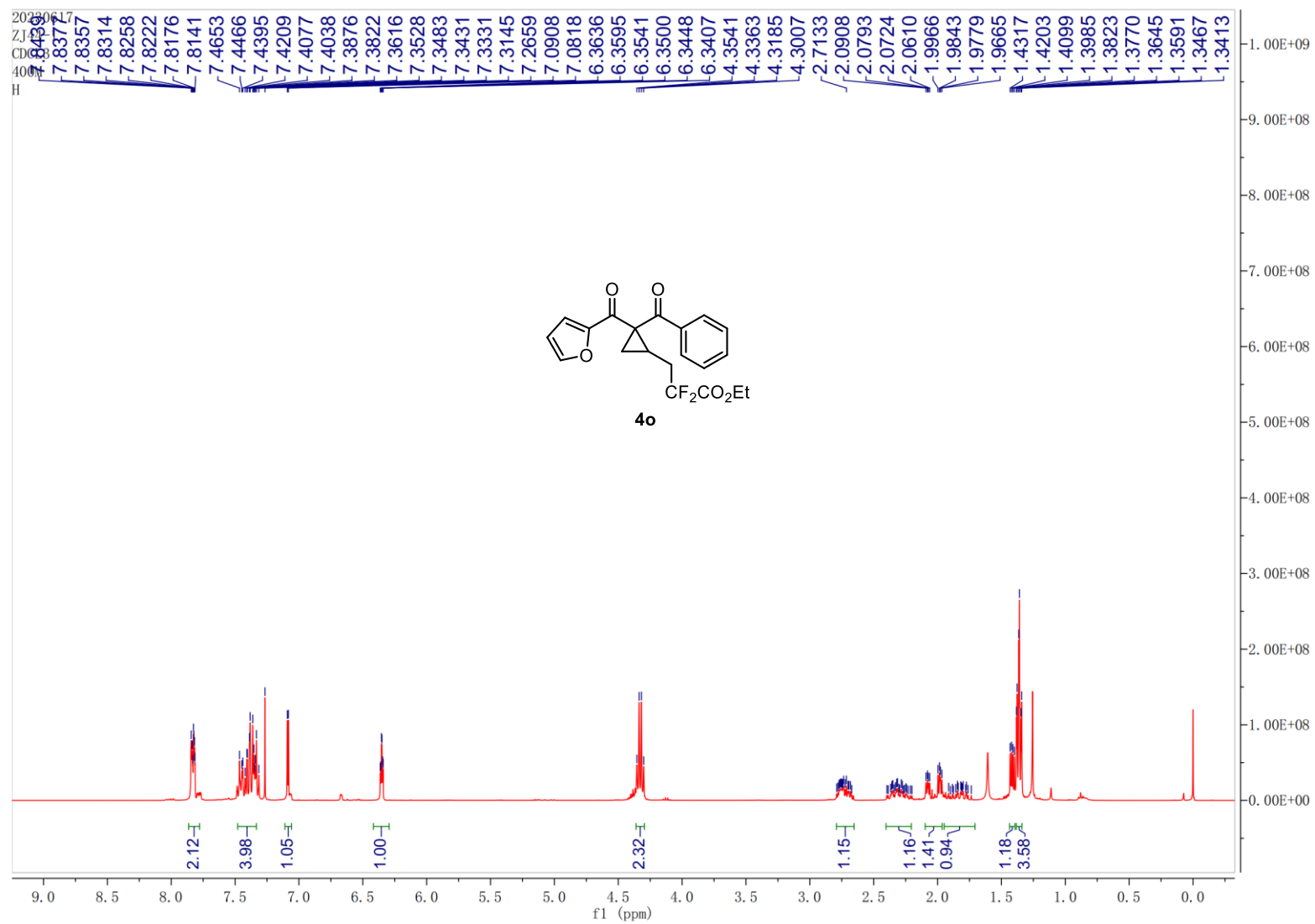


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CDCL3
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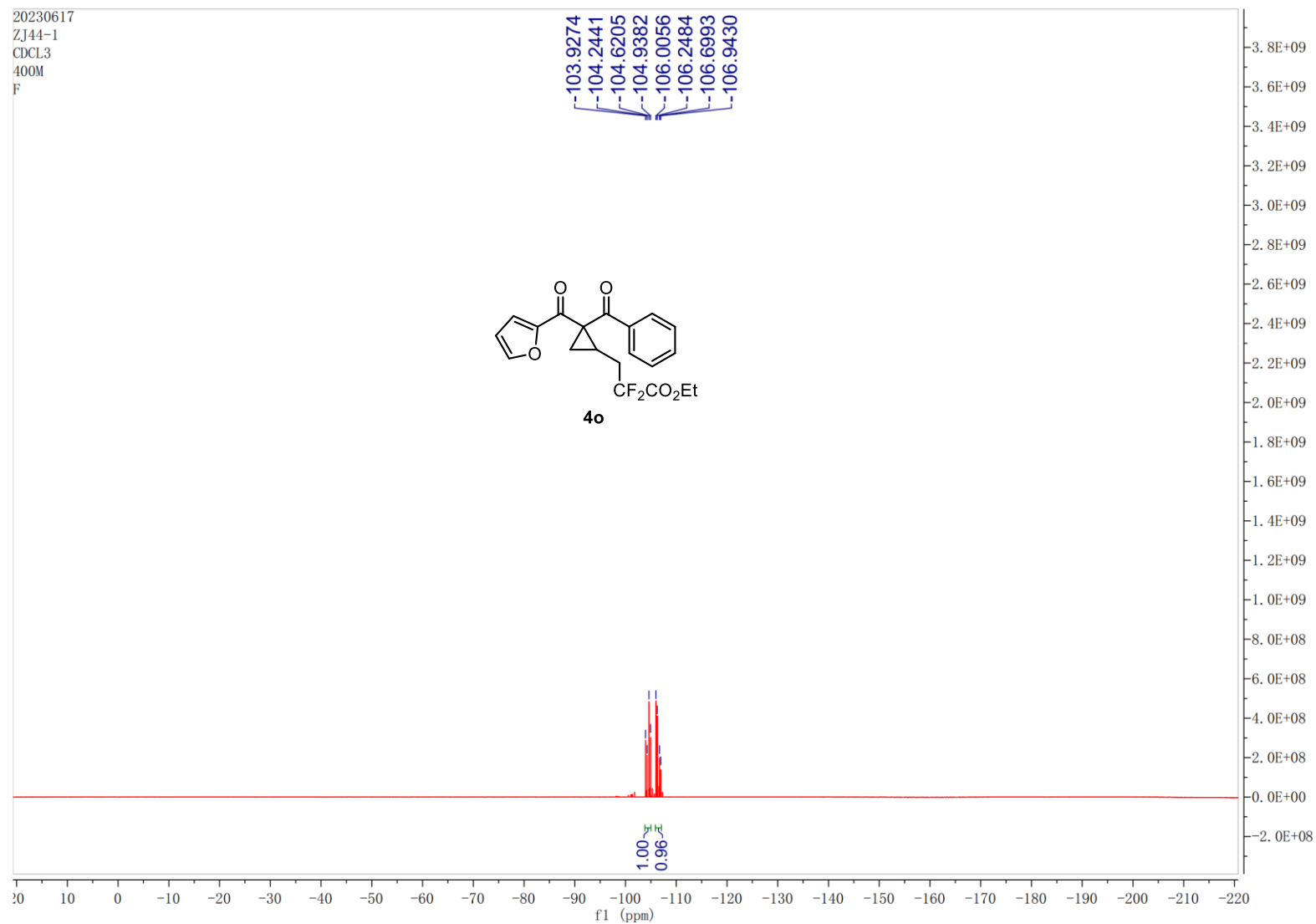
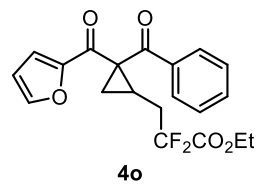


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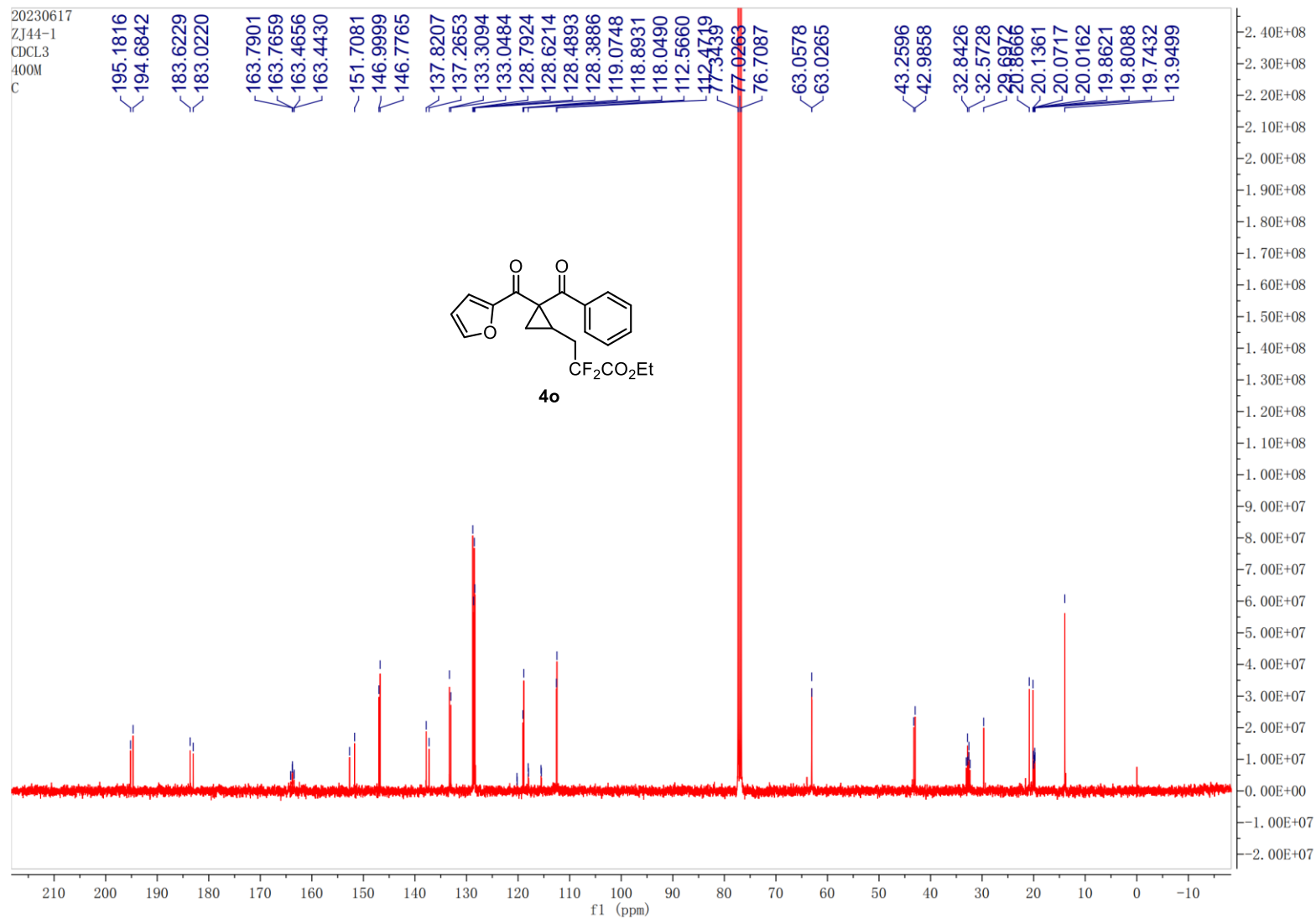
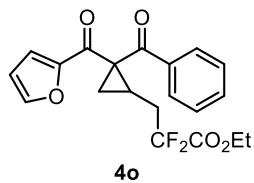


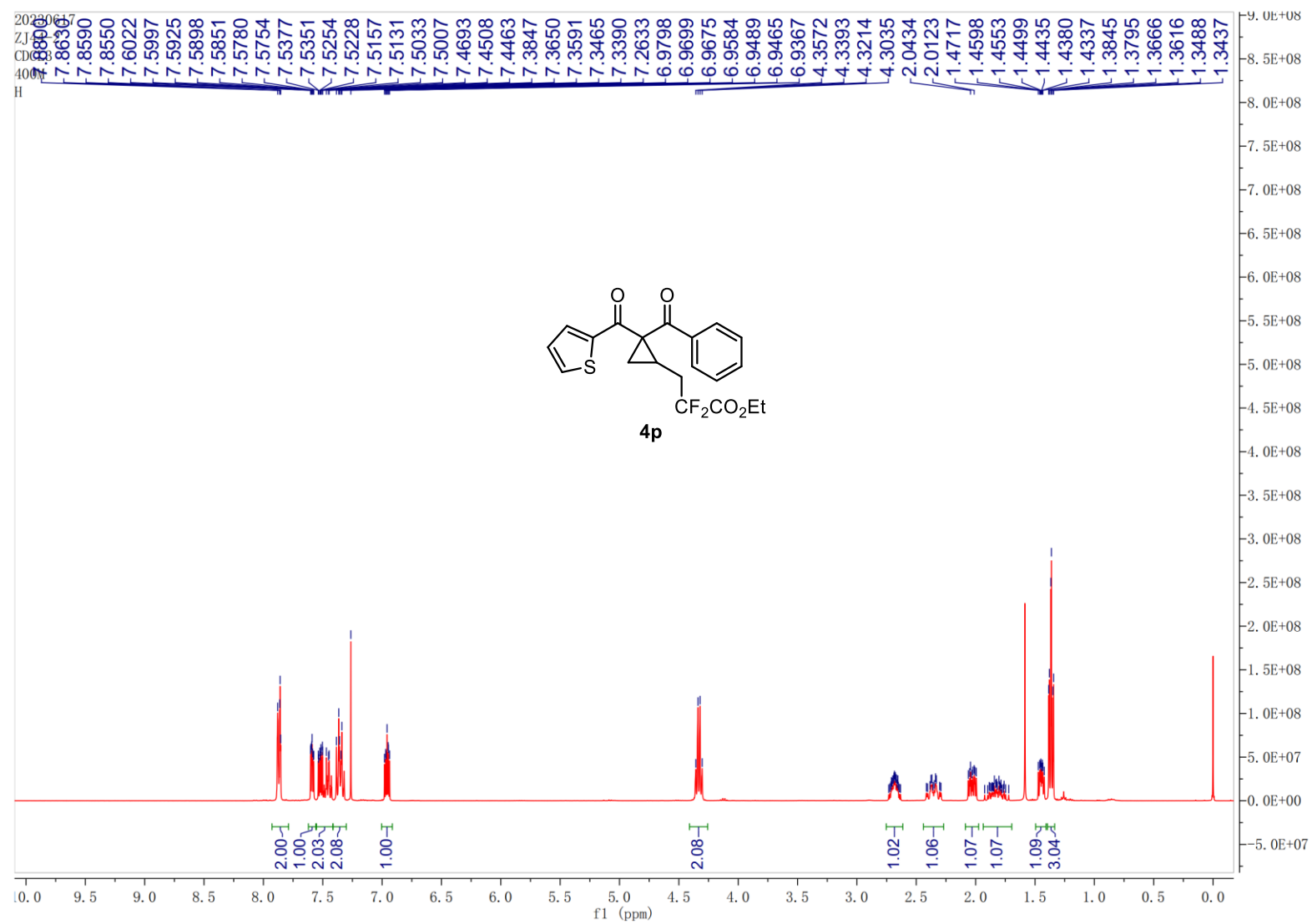


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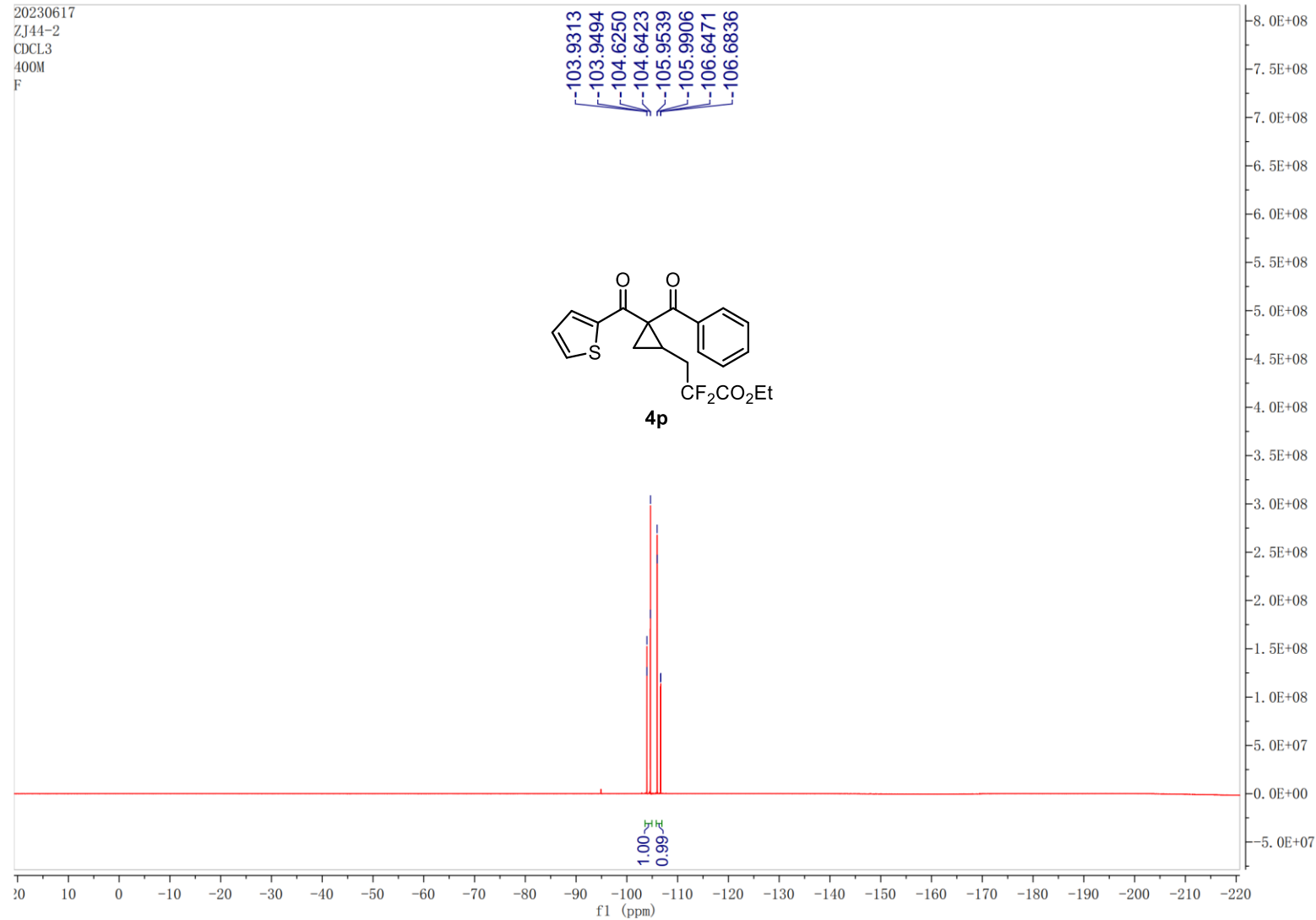
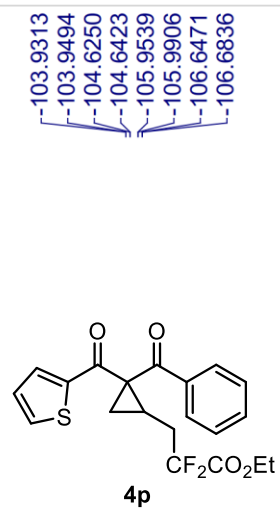


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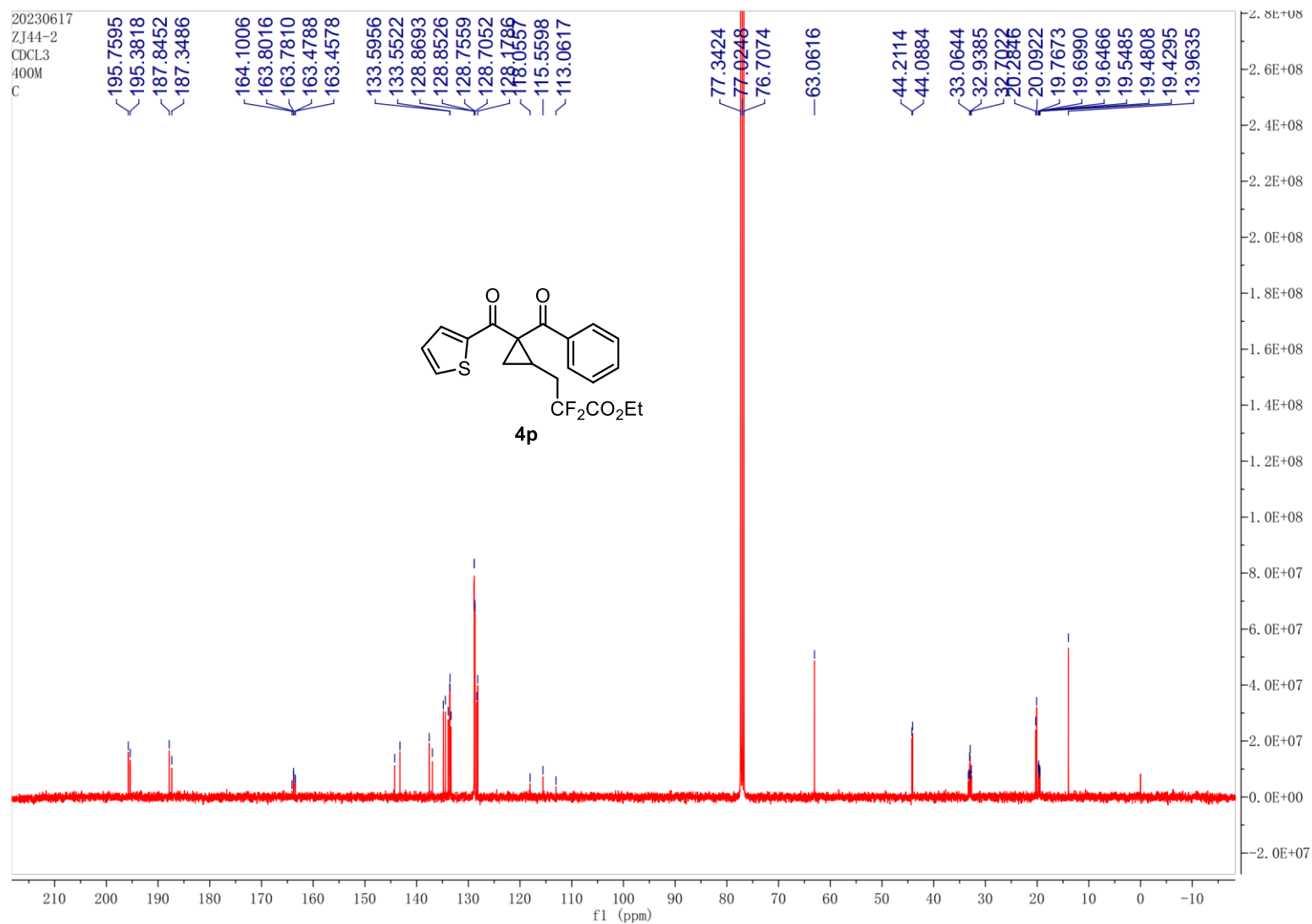




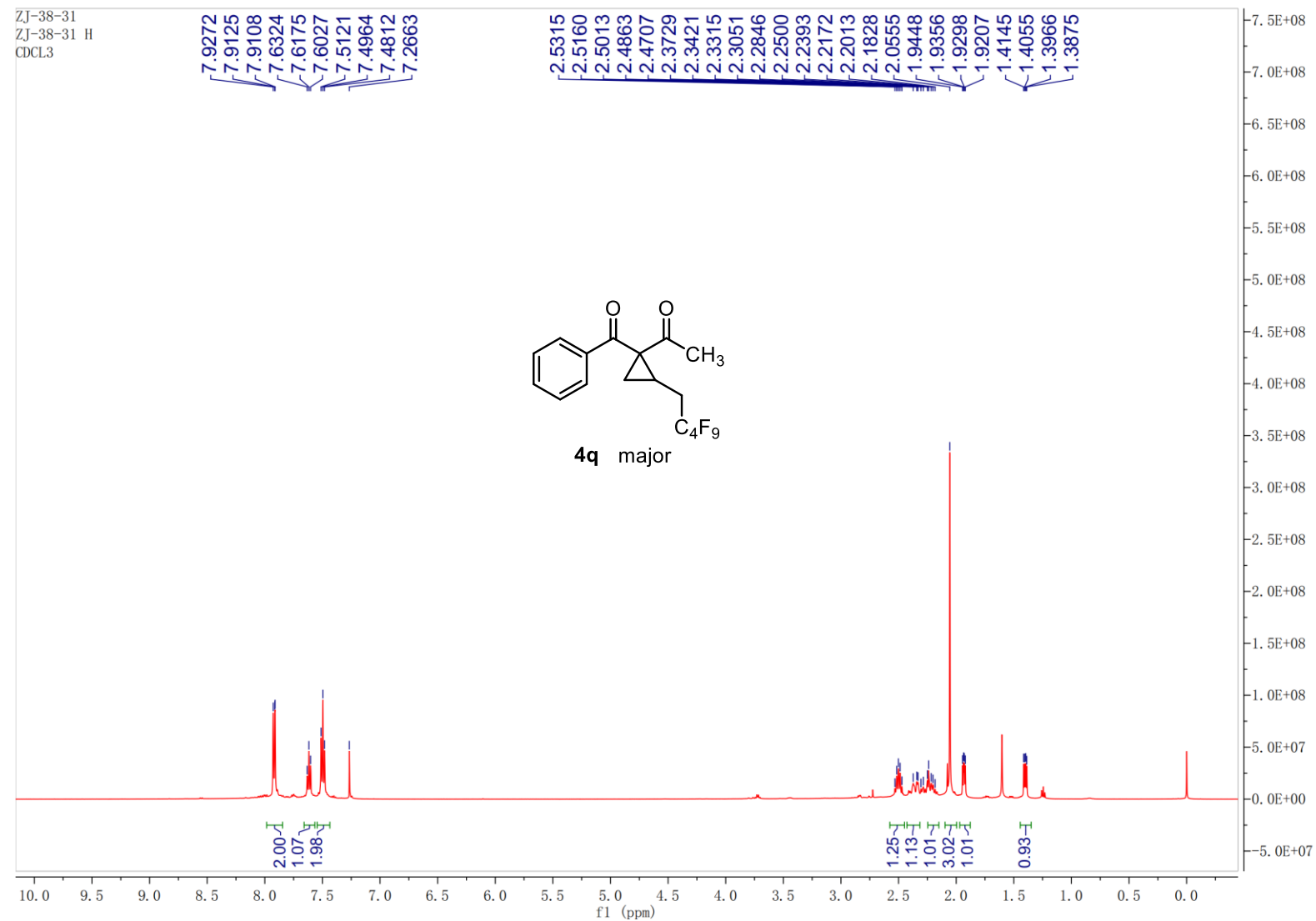
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CDCL3
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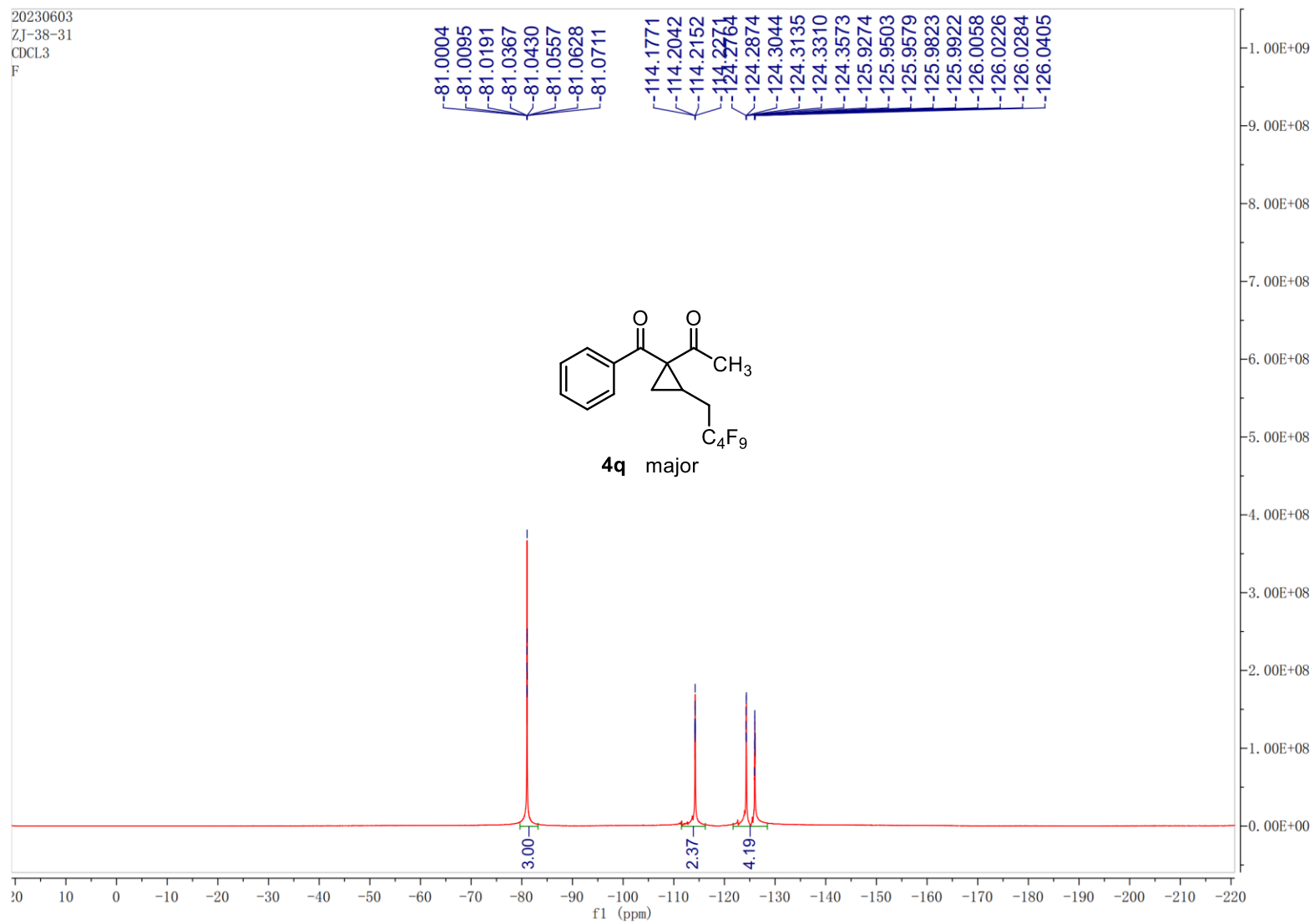
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CDCL3
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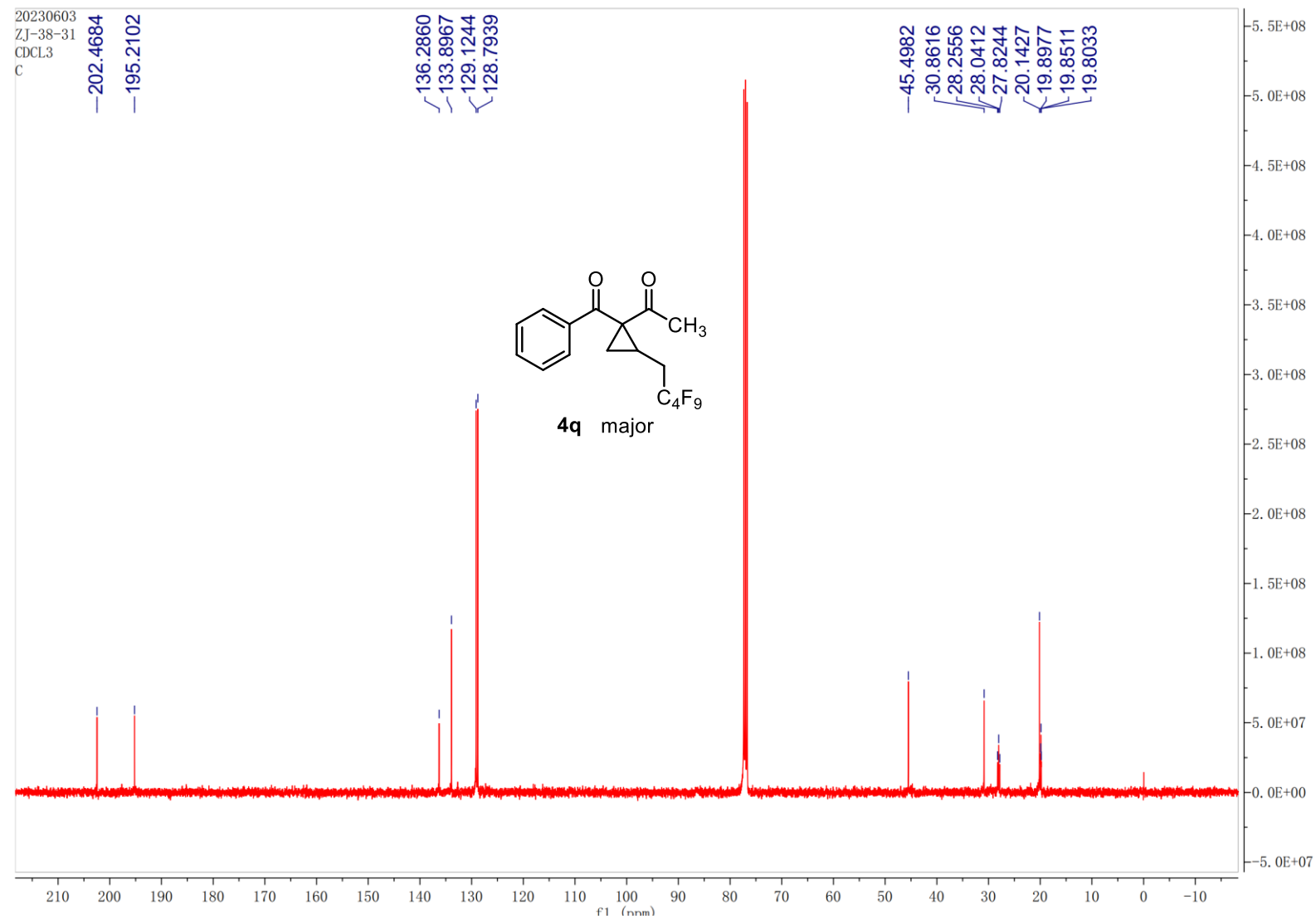


ZJ-38-31
ZJ-38-31 H
CDCL3

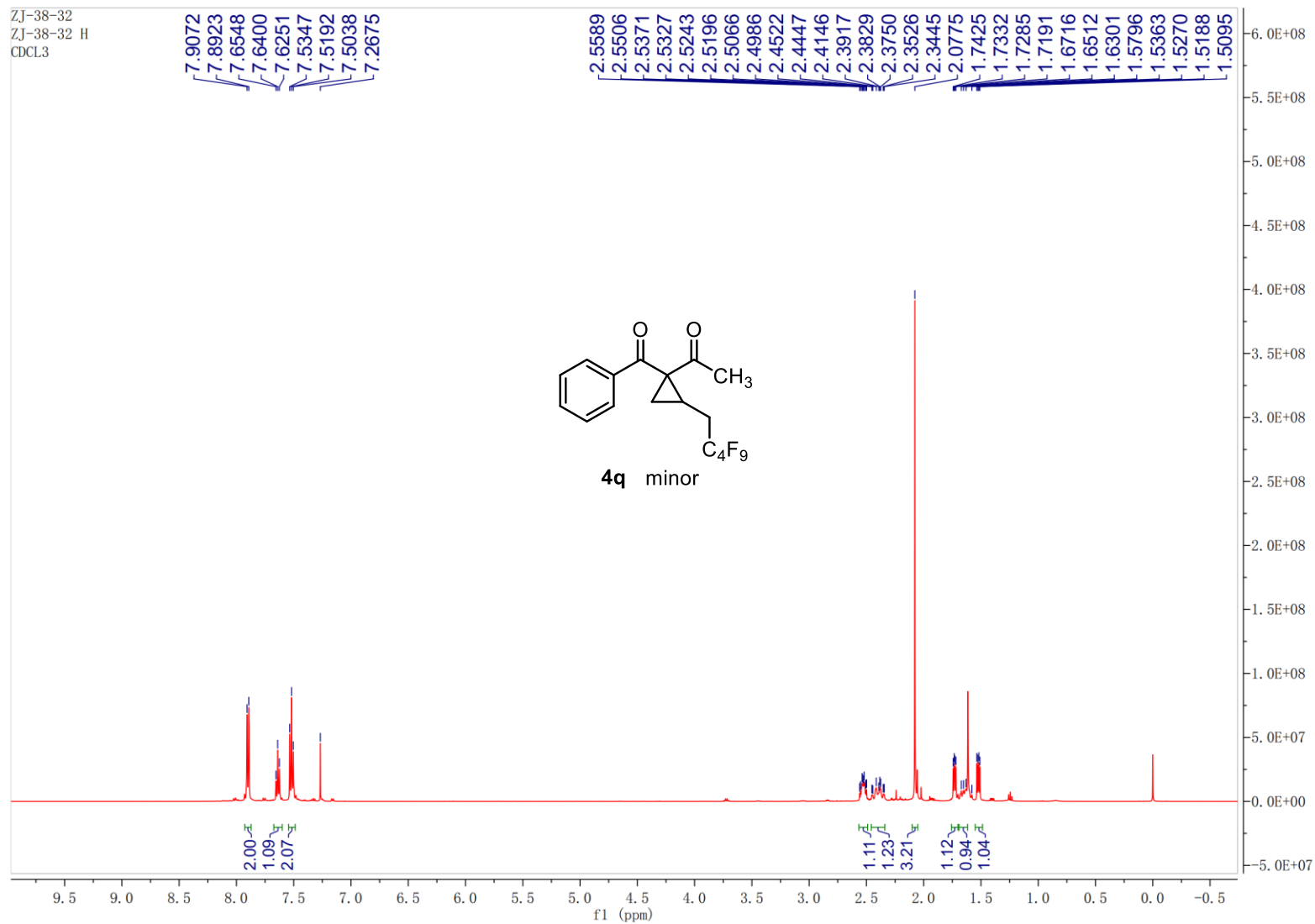


20230603
ZJ-38-31
CDCL3
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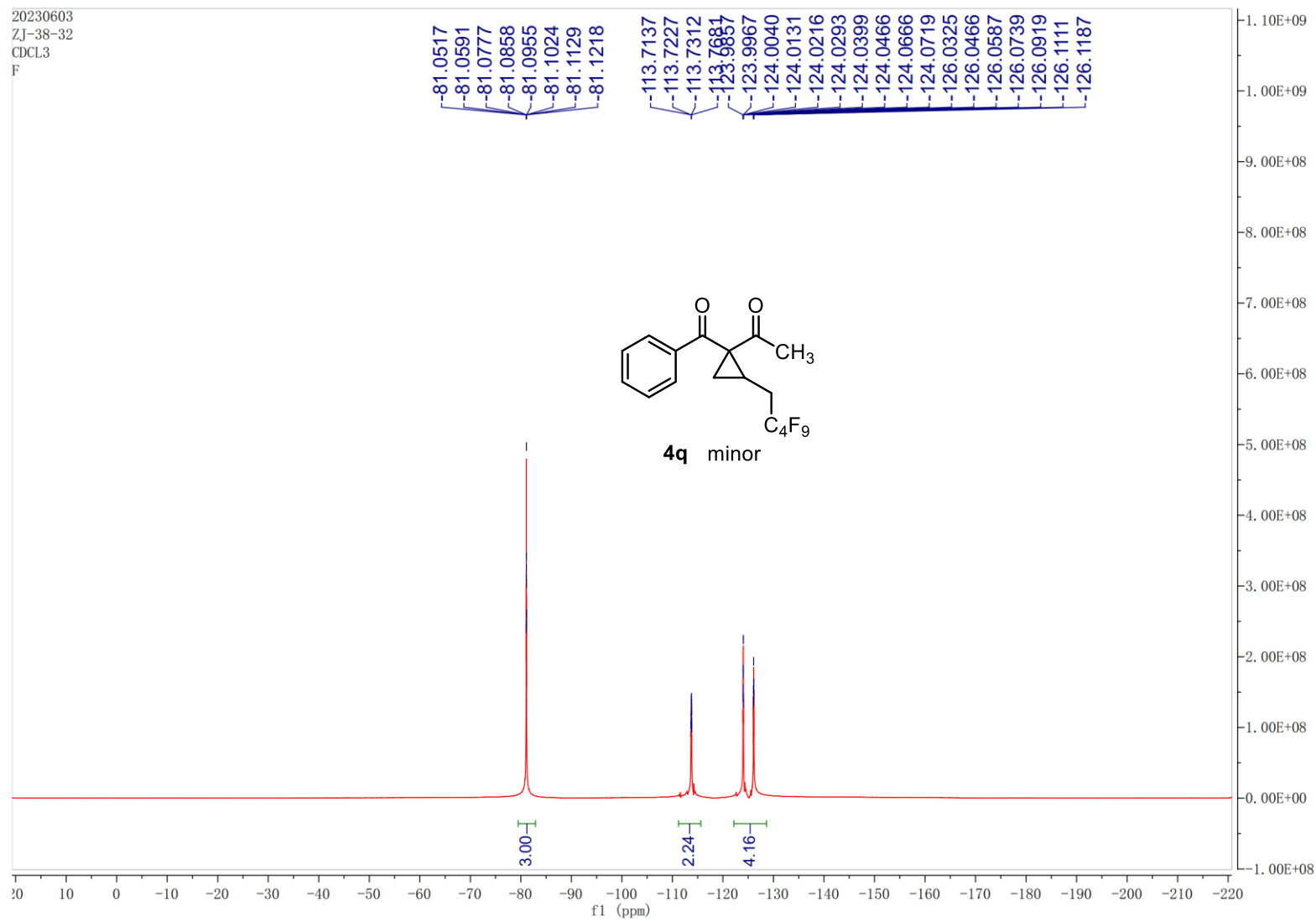




ZJ-38-32
ZJ-38-32 H
CDCL₃



20230603
ZJ-38-32
CDCL₃
F



20230603
ZJ-38-32
CDCL3
C

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—195.1030

136.9244

134.1498

129.2560

128.7965

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77.0141

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44.7338

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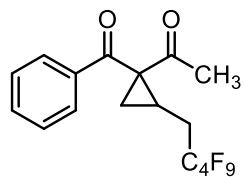
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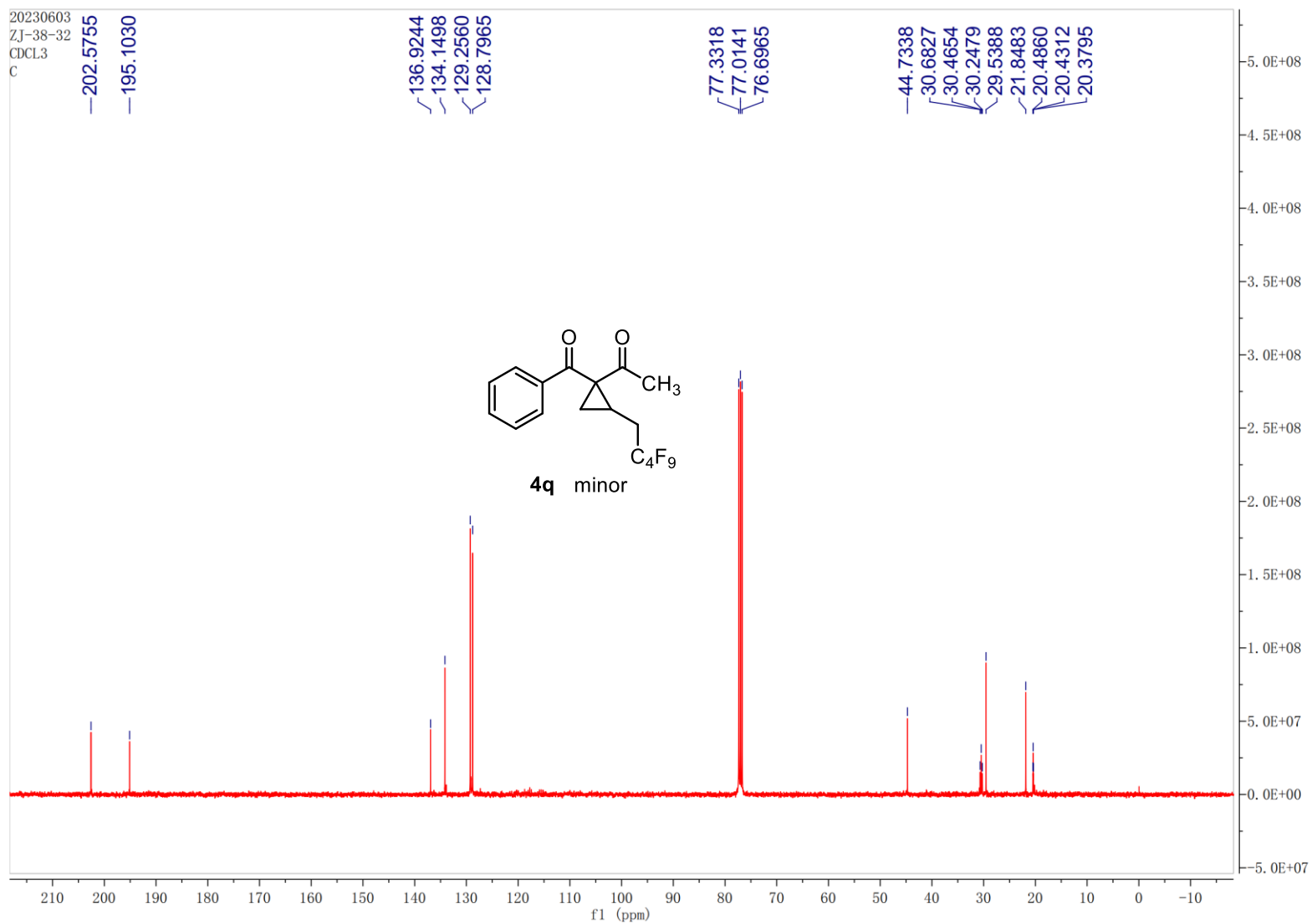
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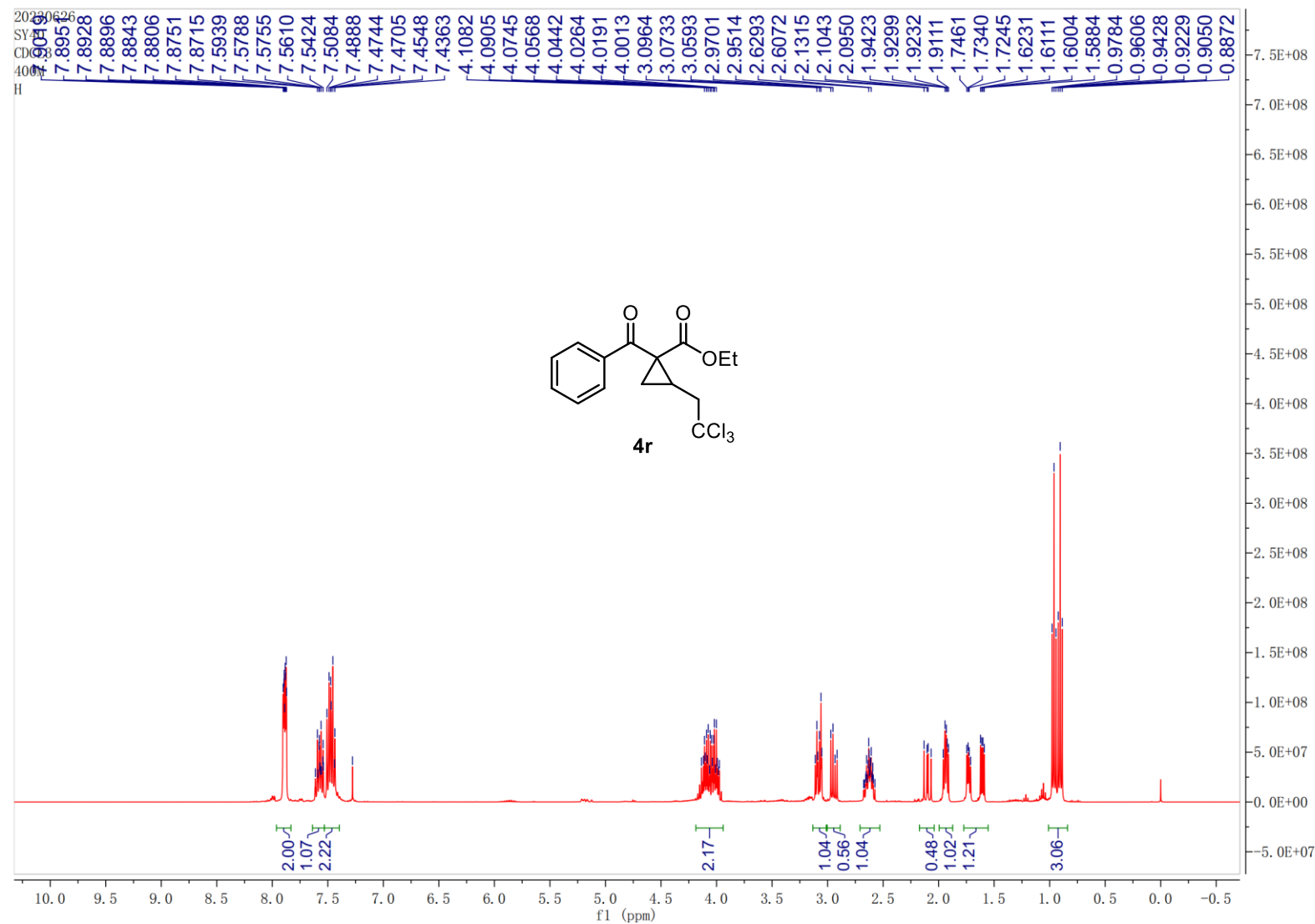
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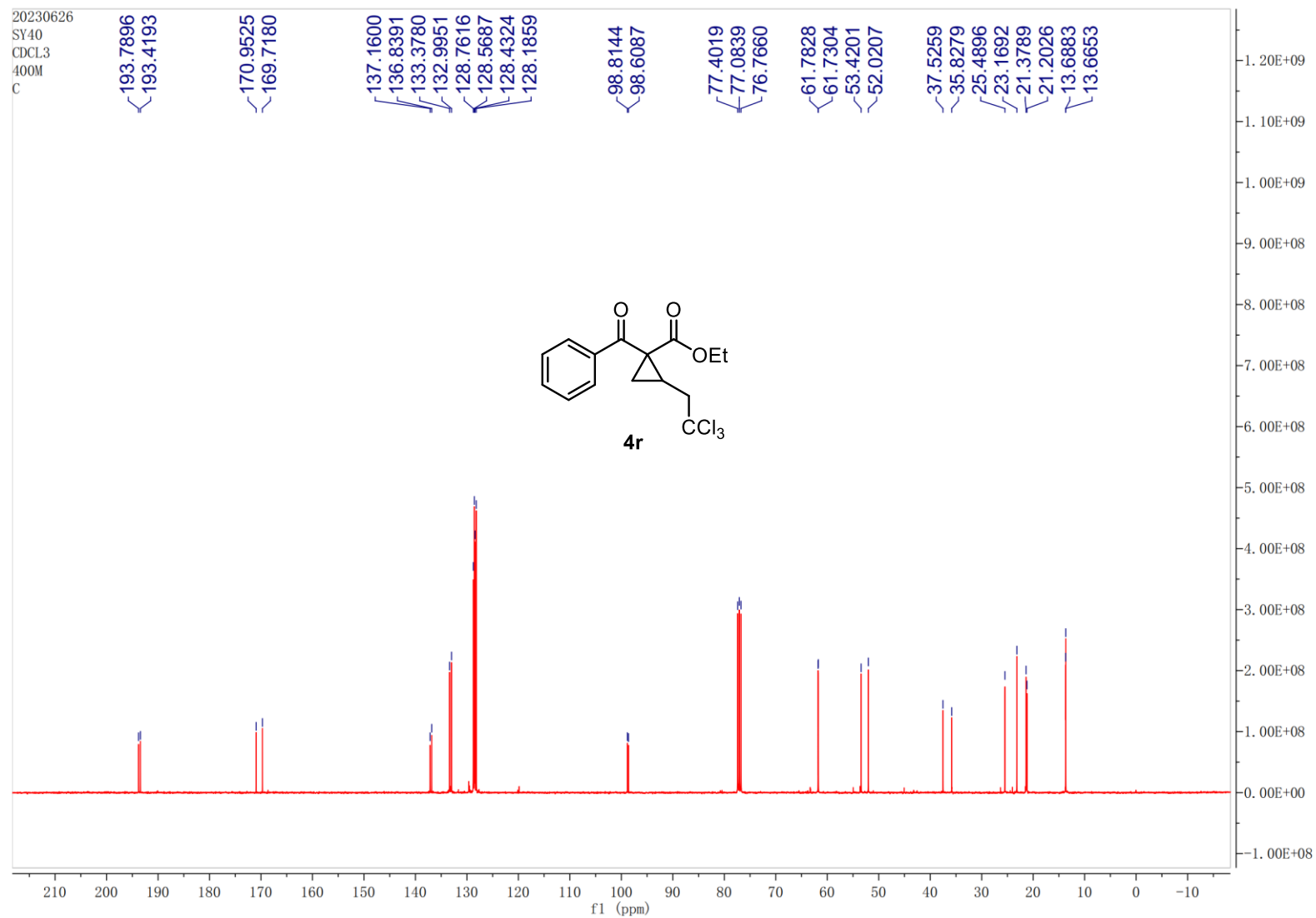


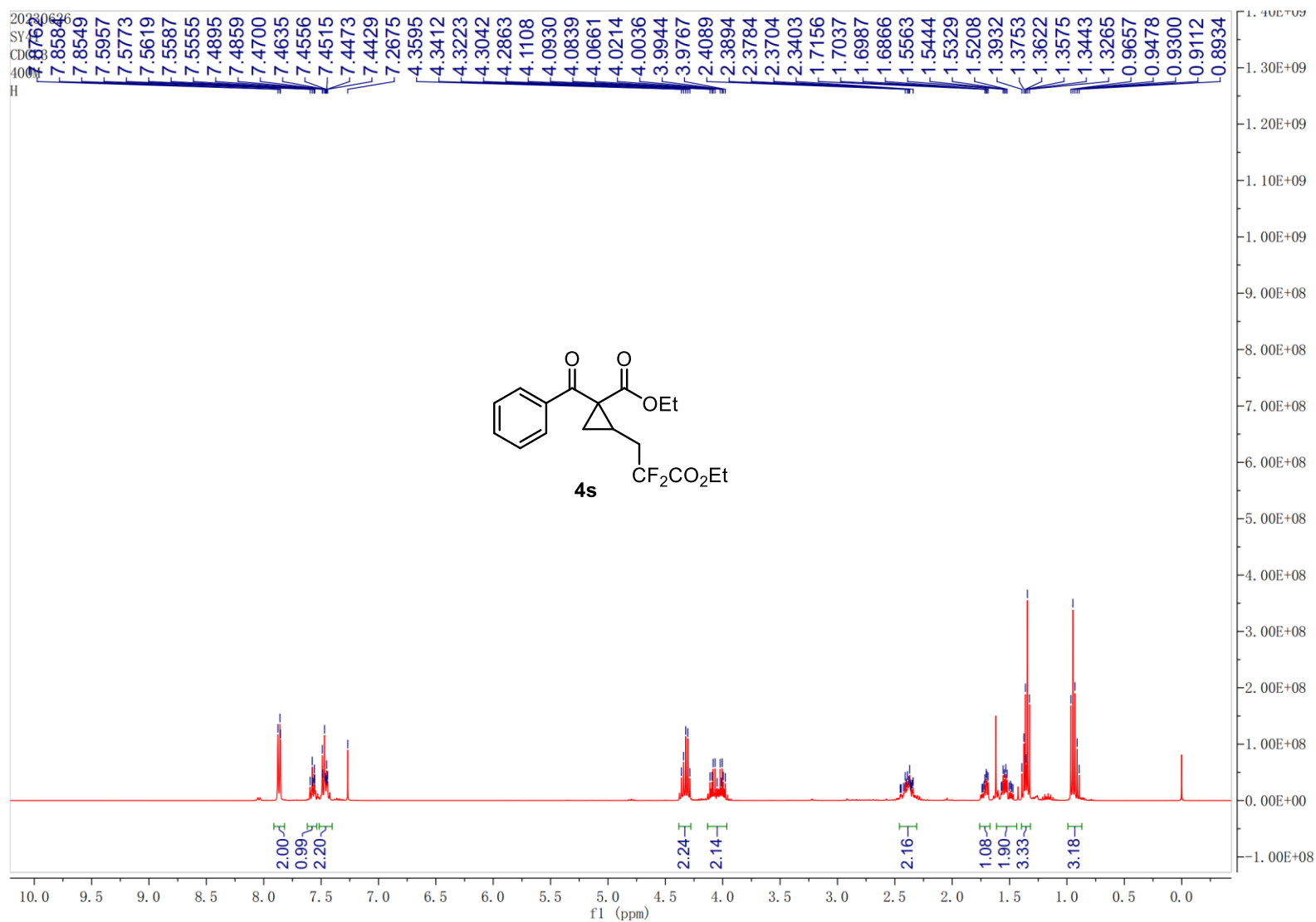
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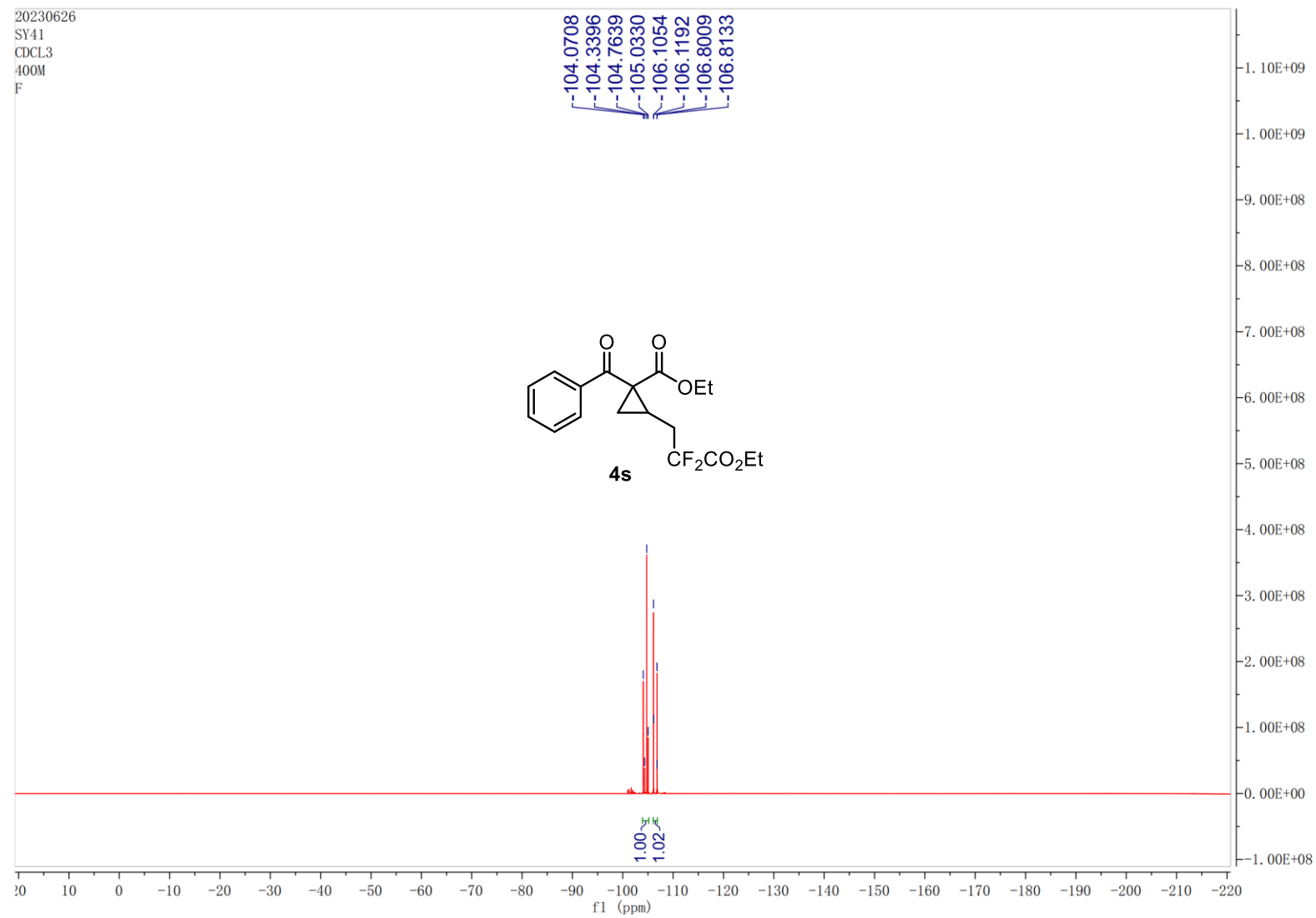
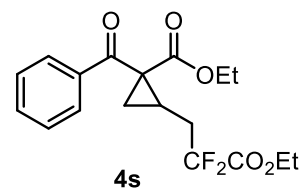


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CDCL3
400M
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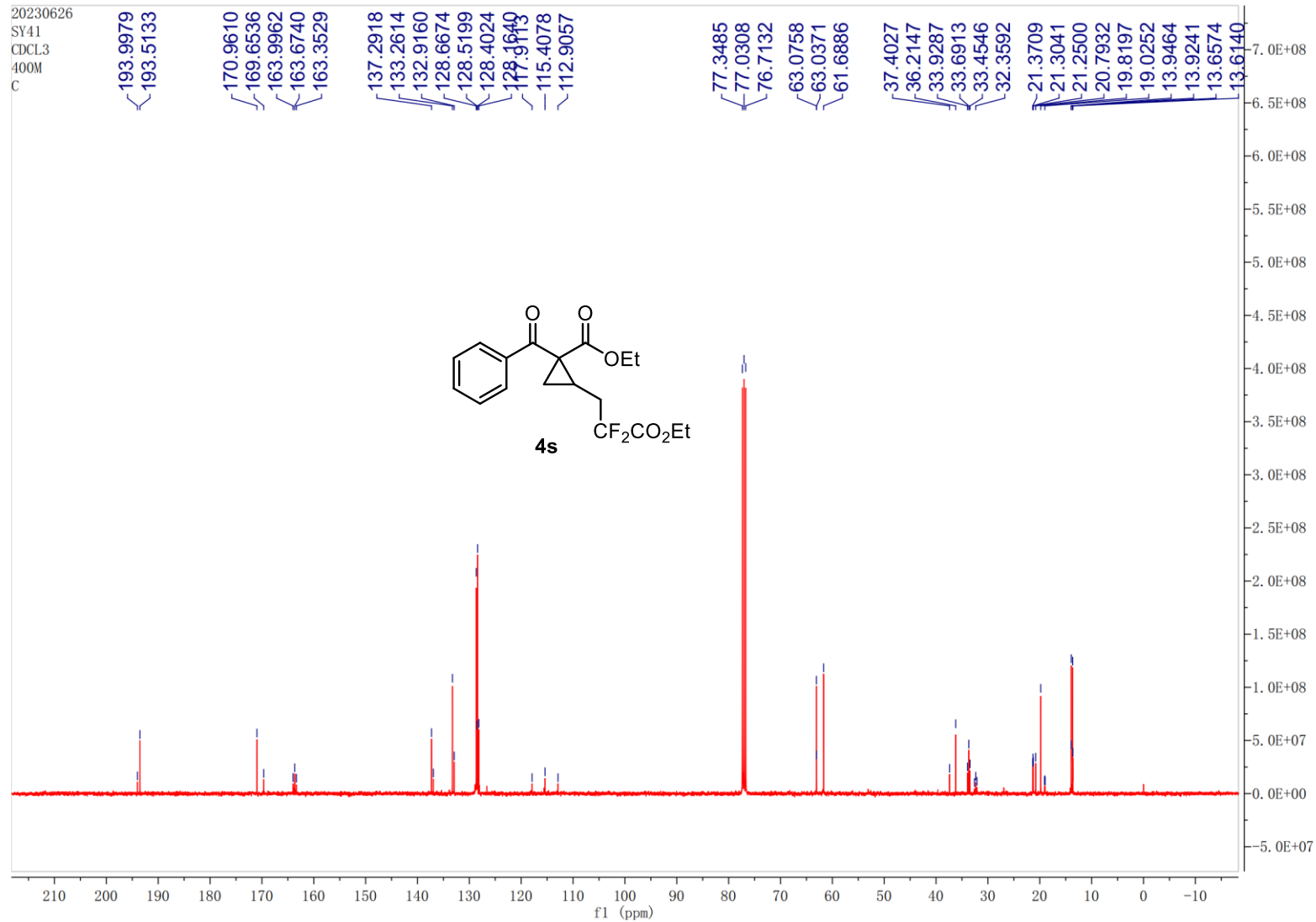


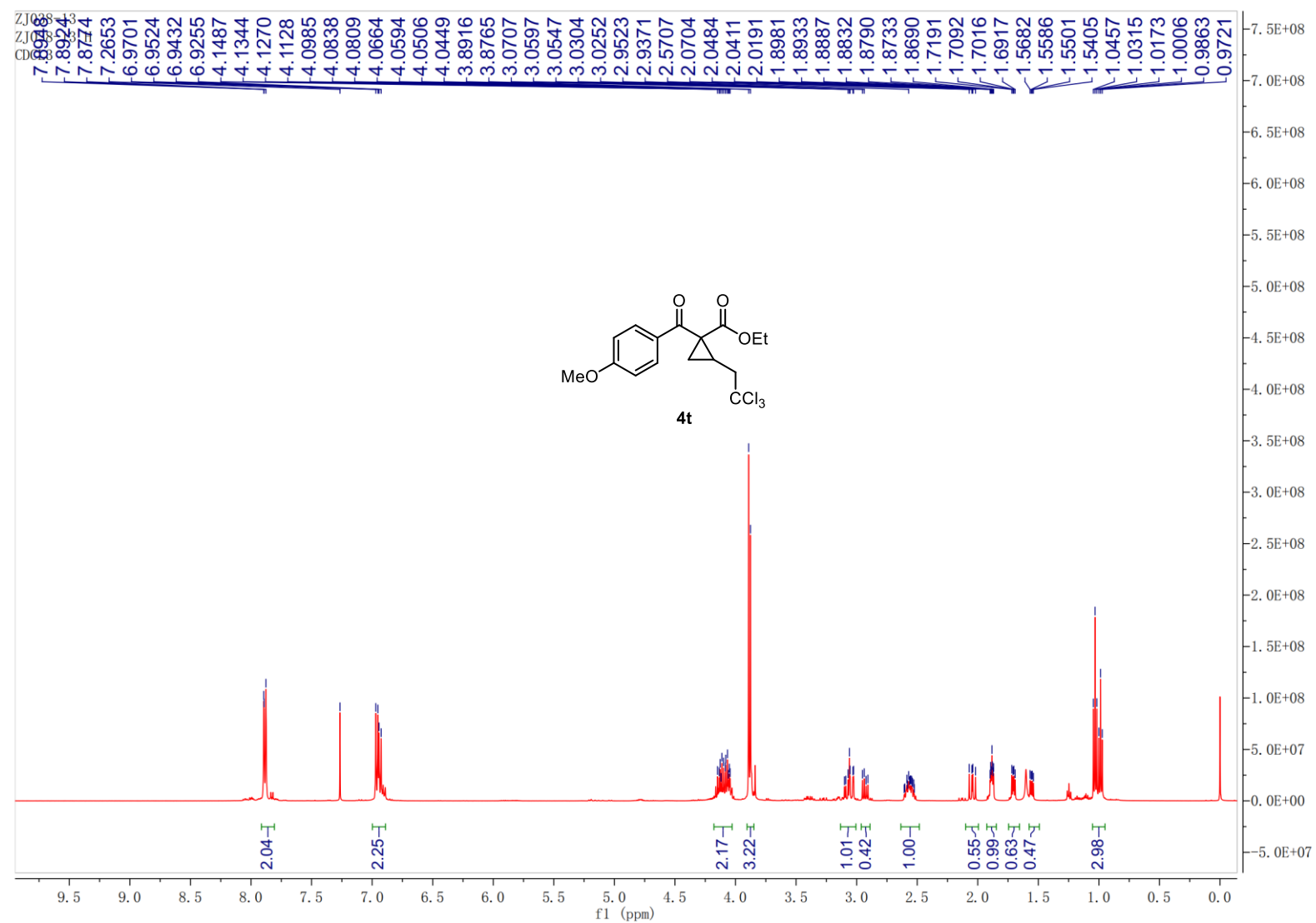


20230626
SY41
CDCL3
400M
F

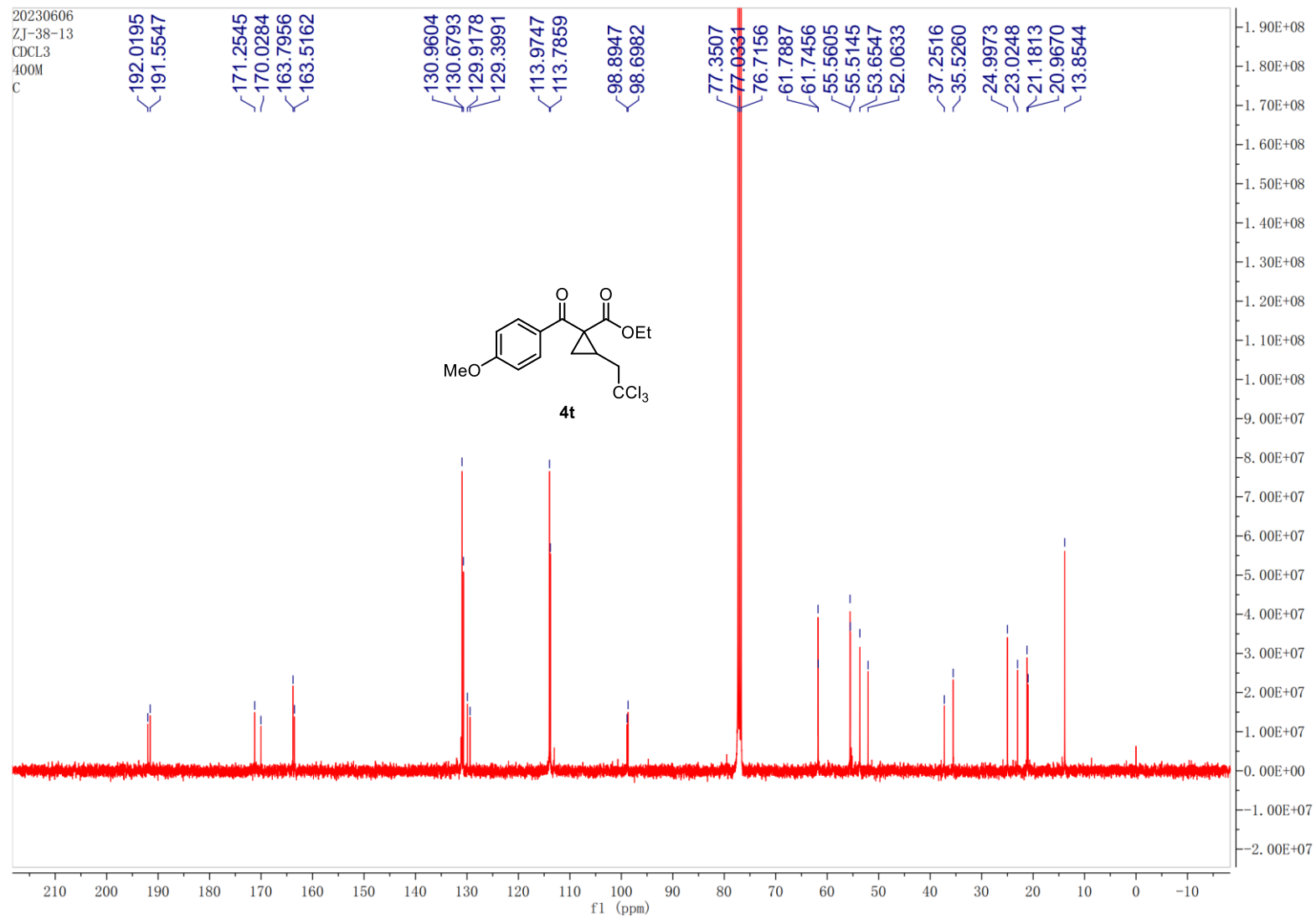


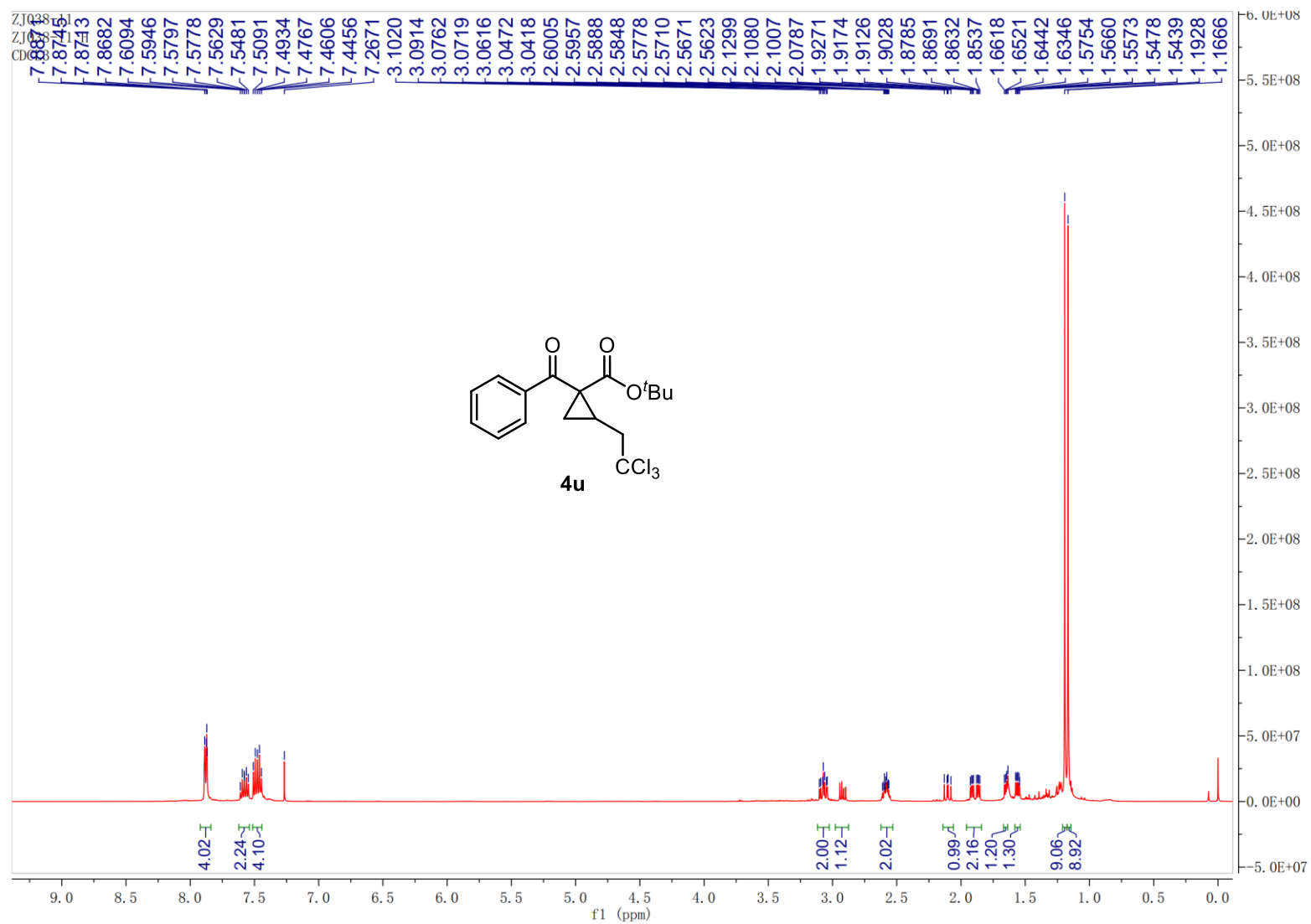
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SY41
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400M
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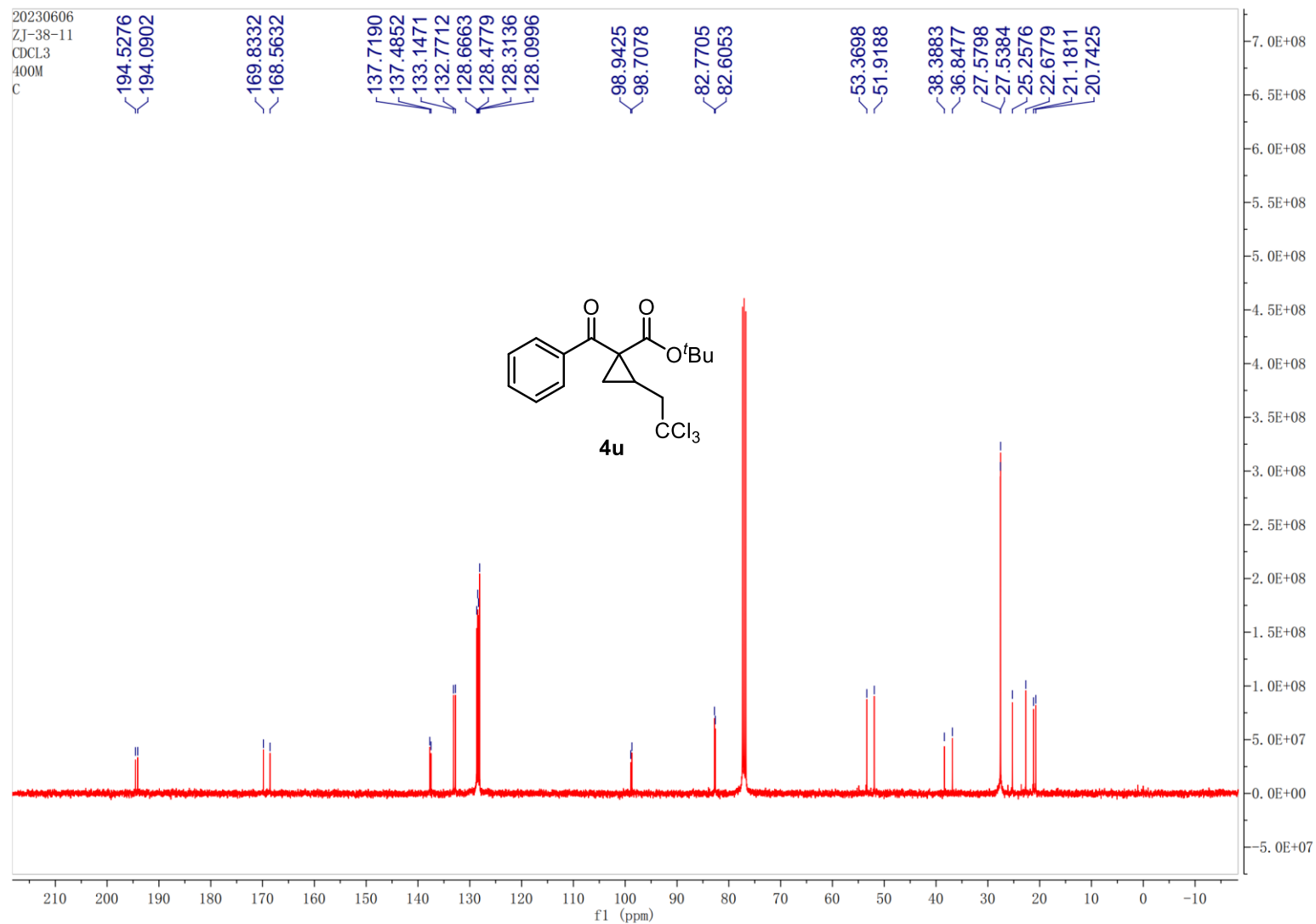


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ZJ-38-13
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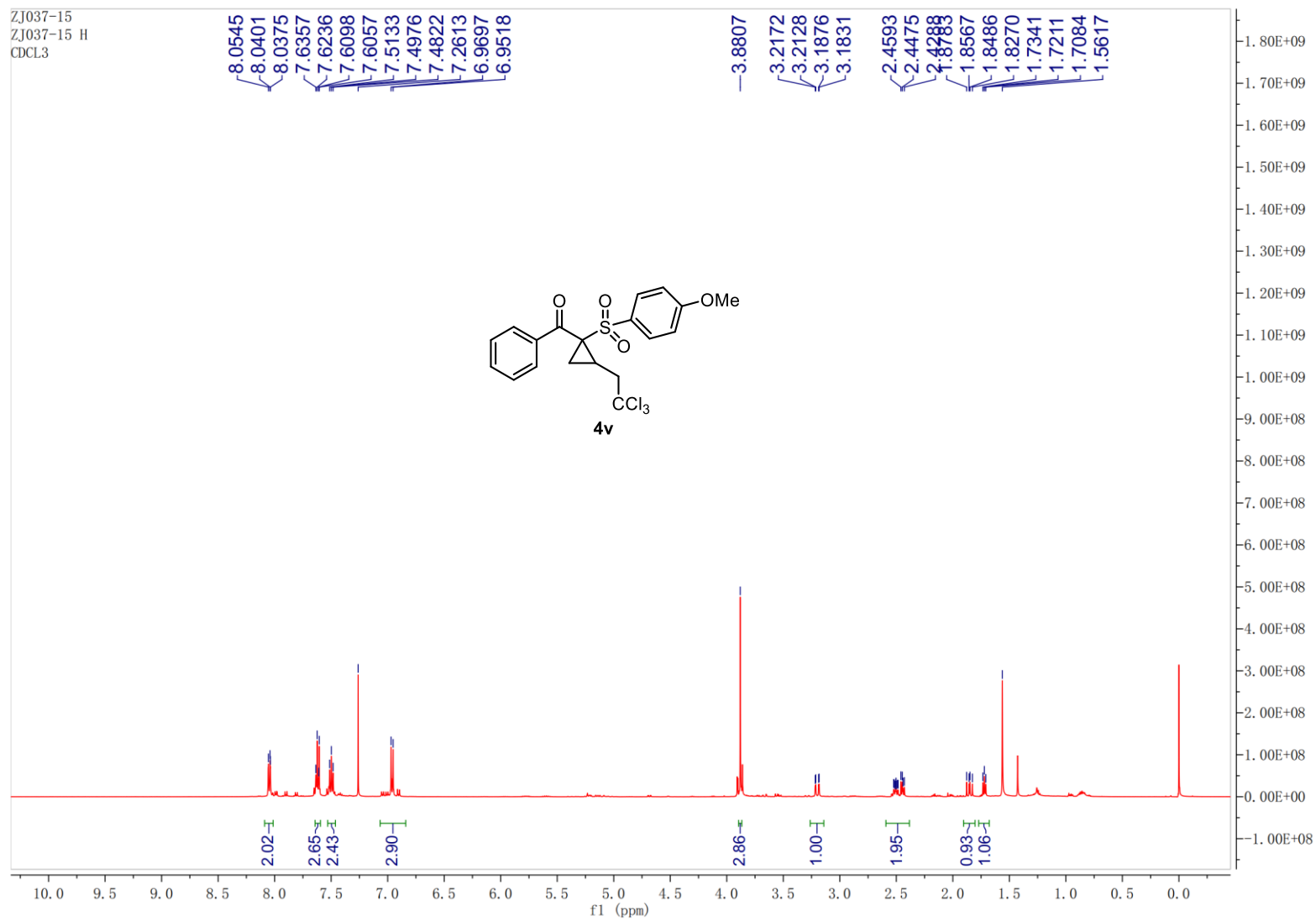




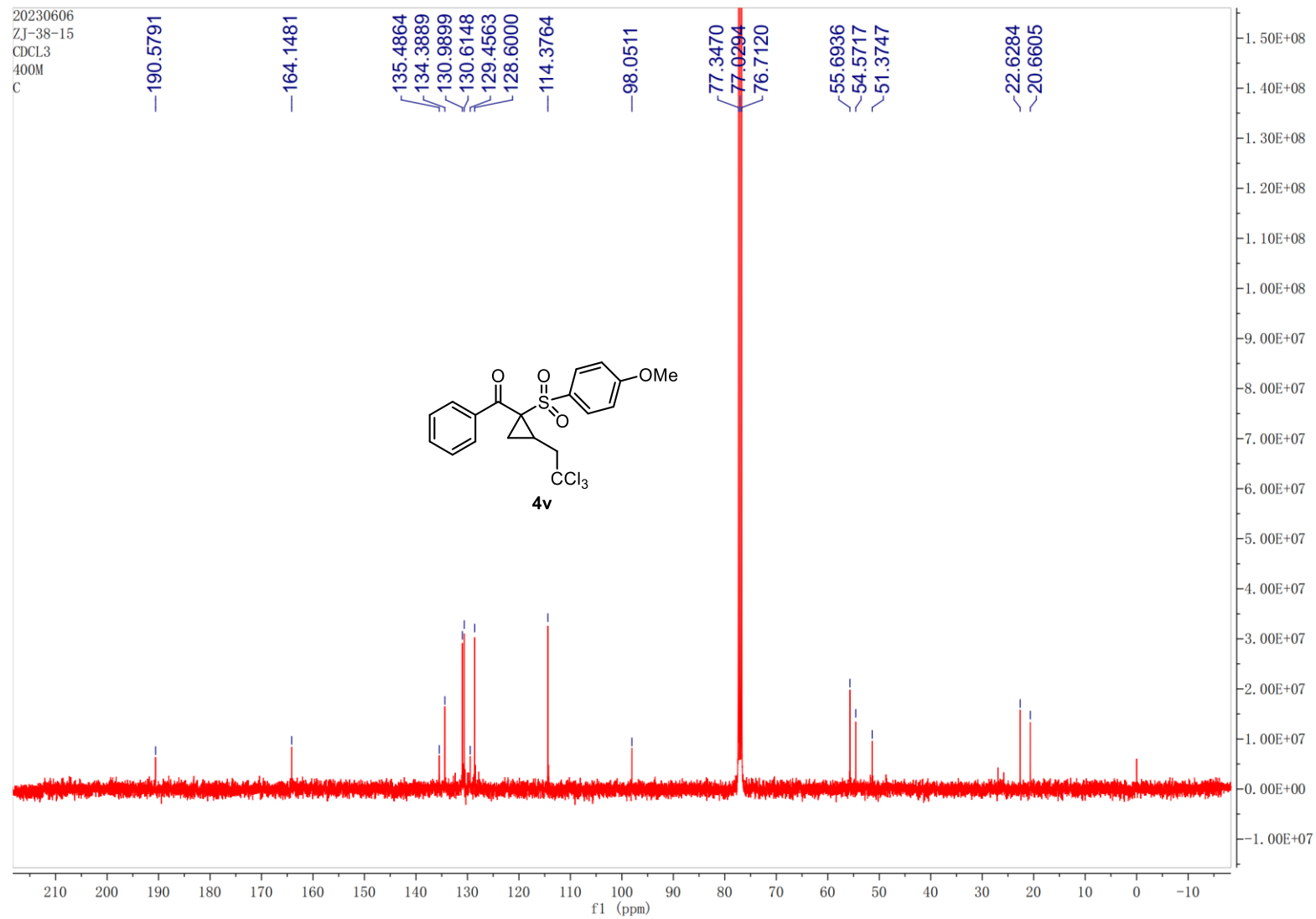
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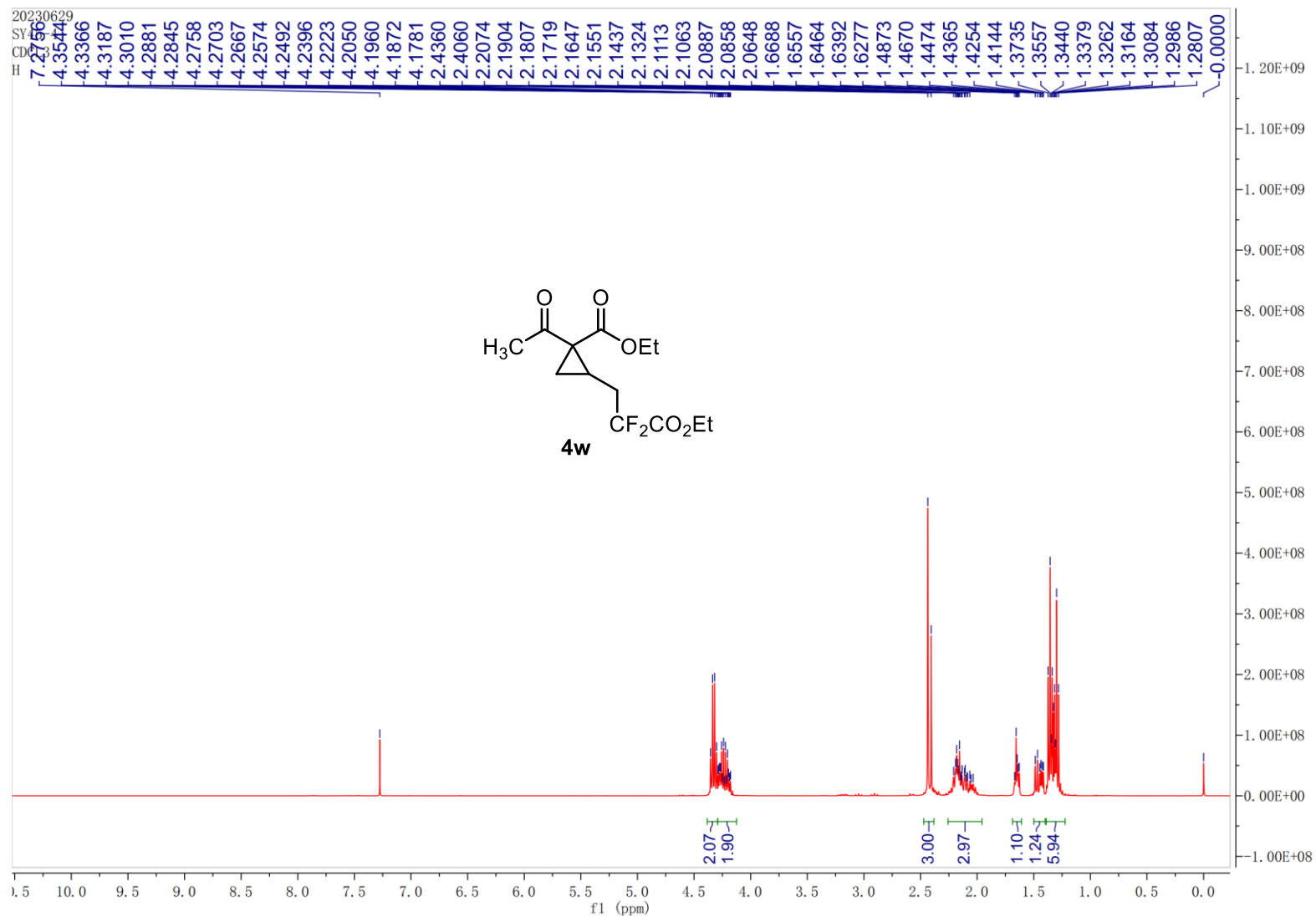


ZJ037-15
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CDCl₃

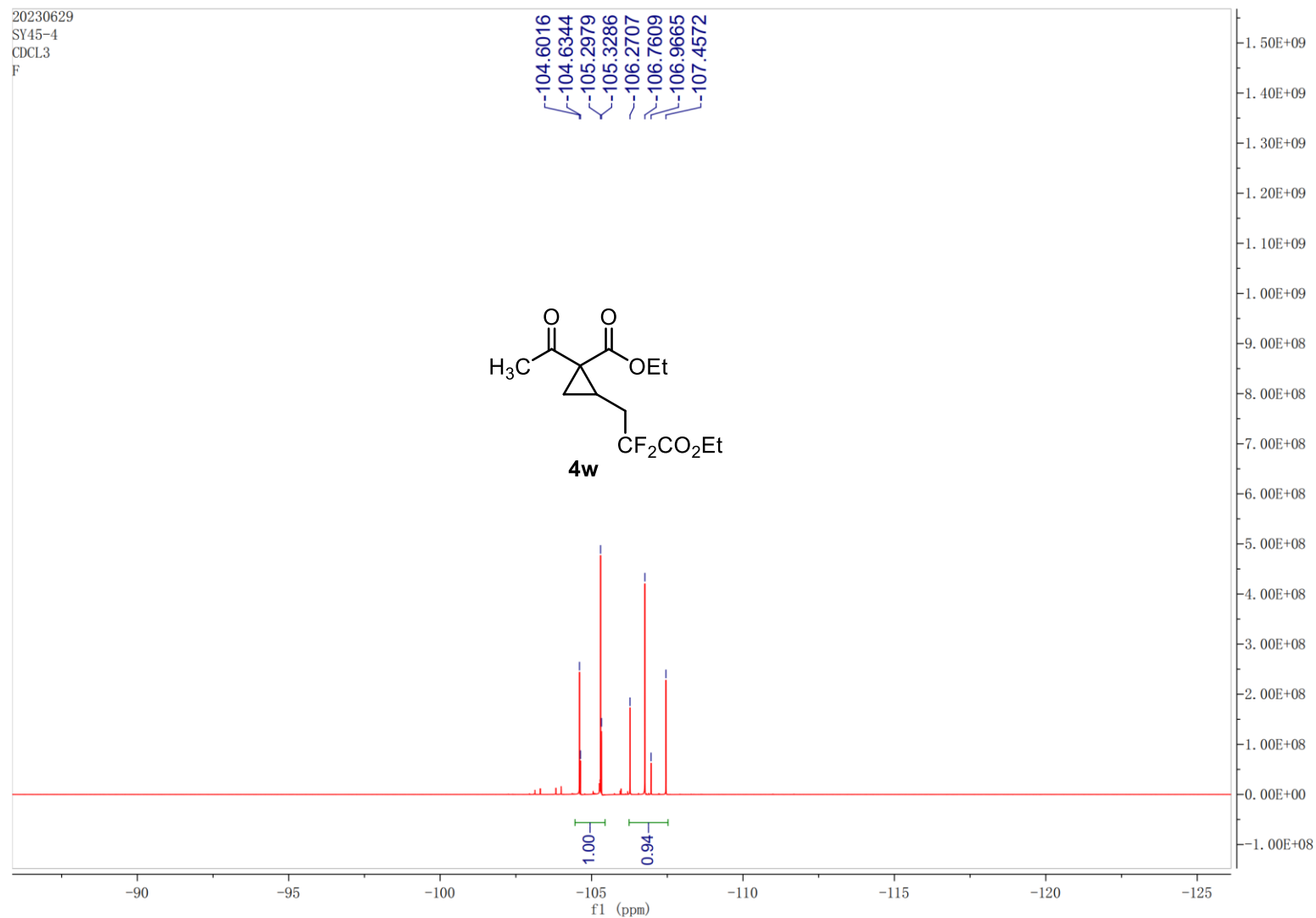
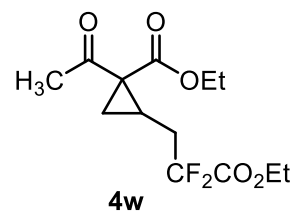


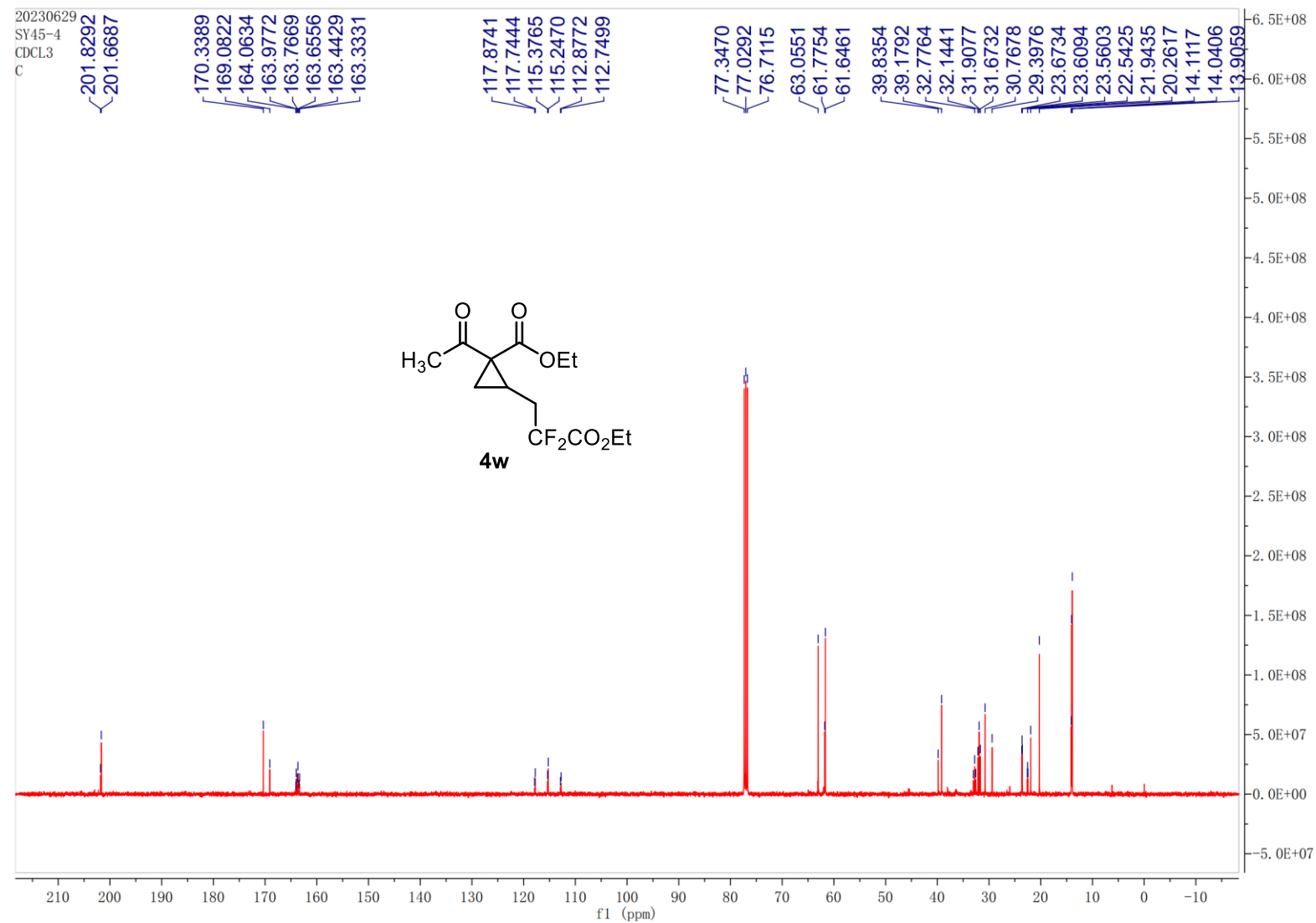
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CDCL₃
400M
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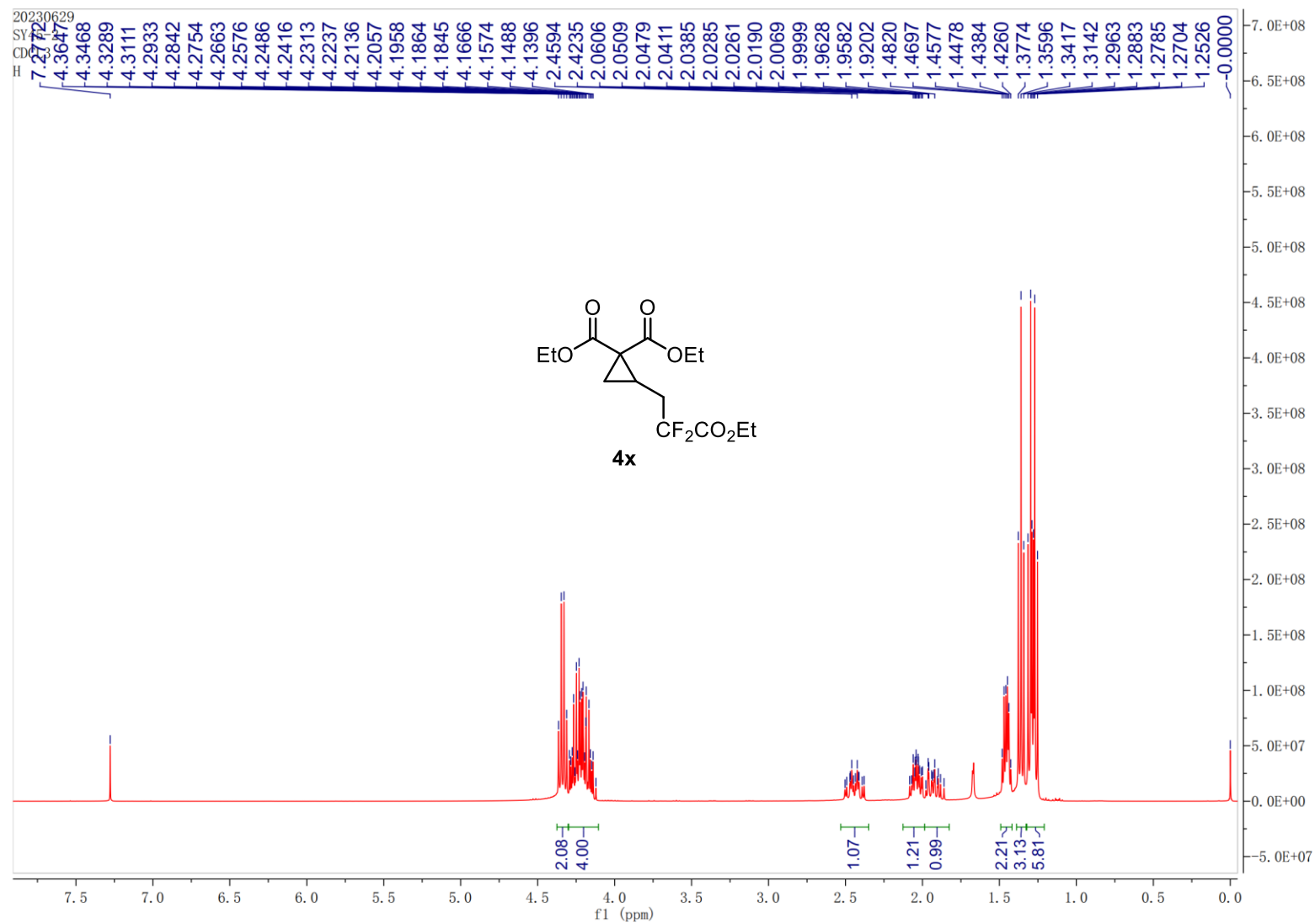




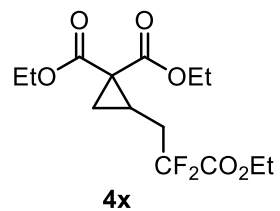
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SY45-4
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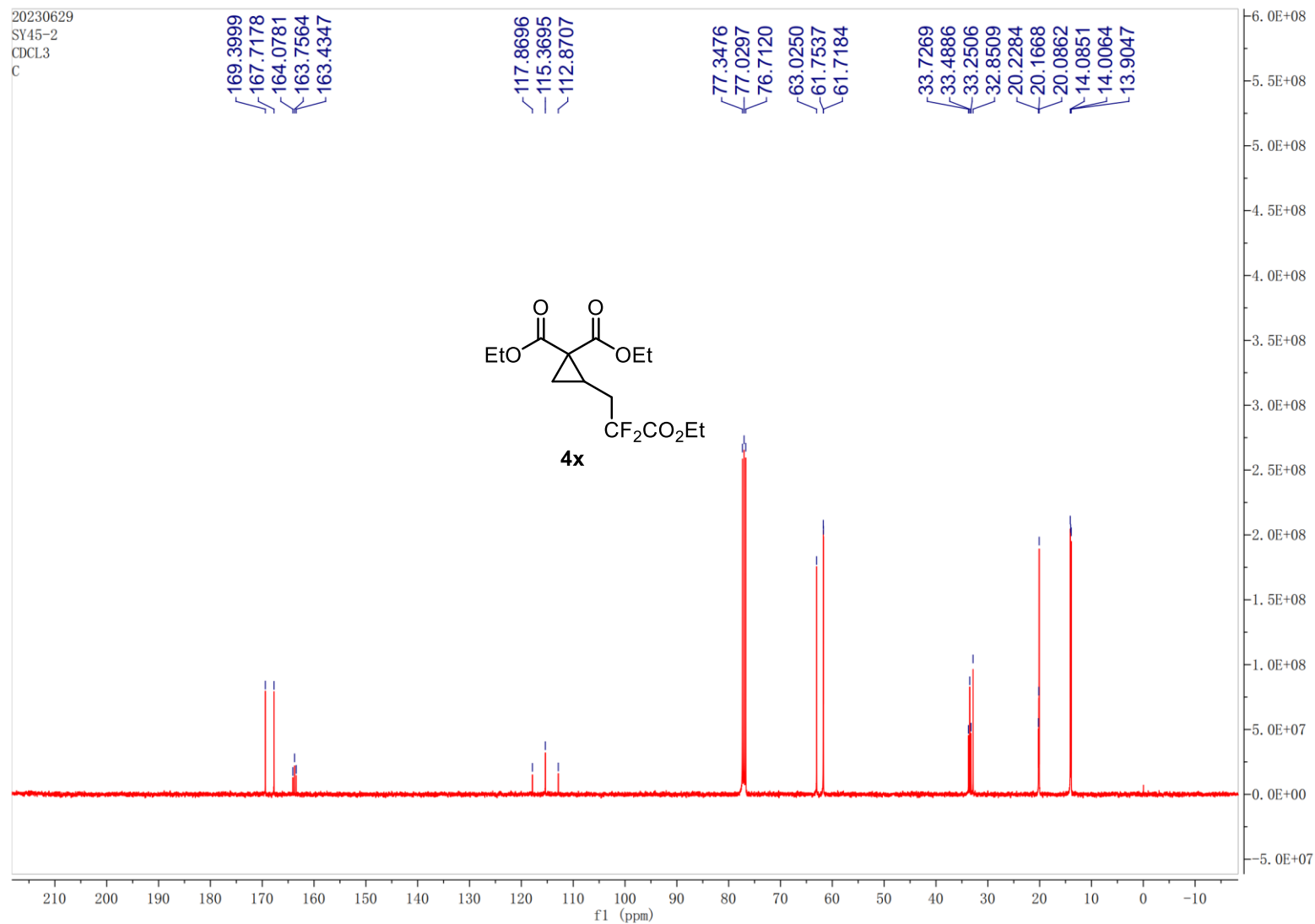
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CDCL3
F

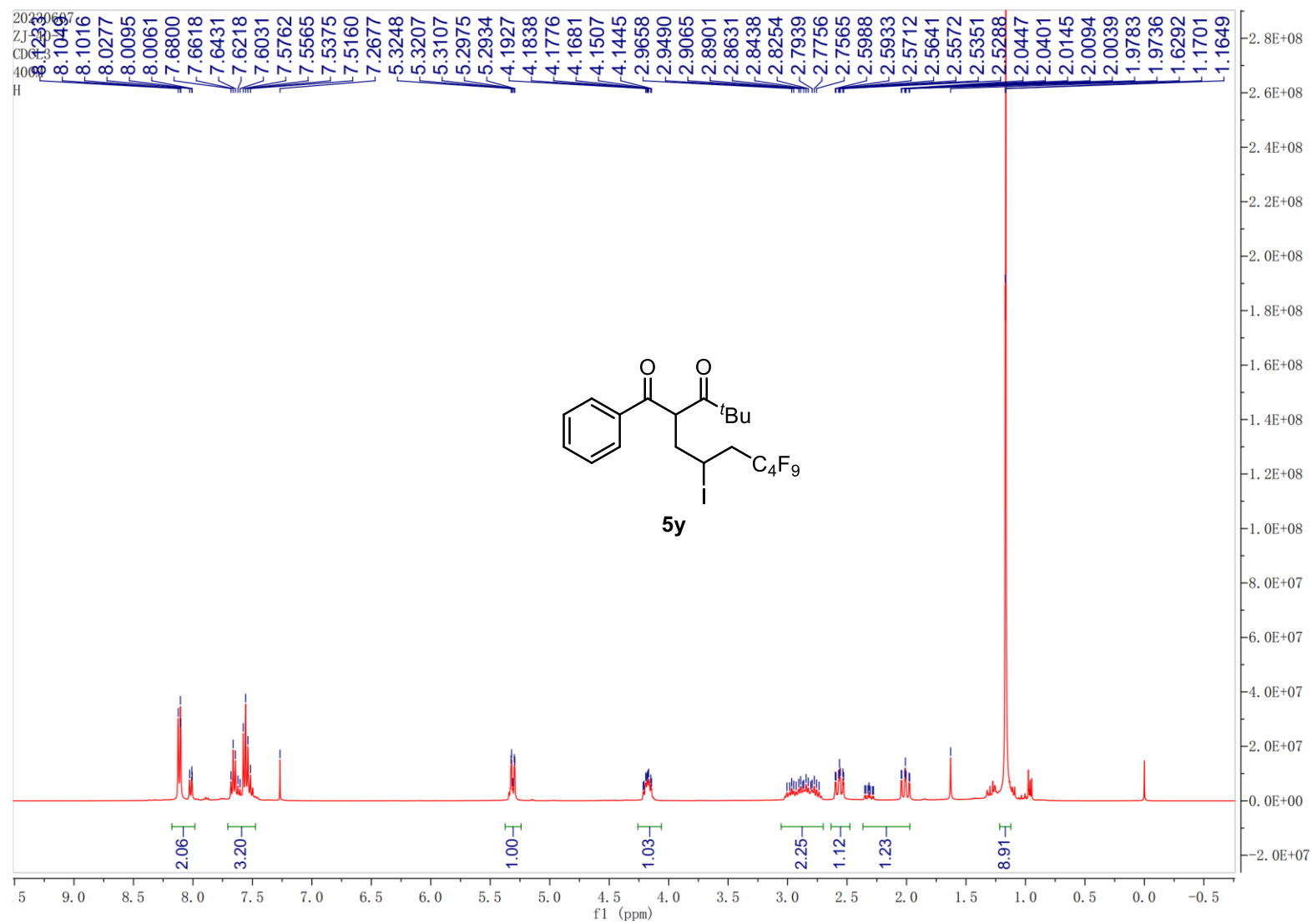


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20230629
SY45-2
CDCL3
C





20230607
ZJ-40-1
CDCL3
400M
F

