Supporting Information

Exploring the Reducing Ability of Organic dye (Acr^+-Mes) for Fluorination and Oxidation of Benzylic C(sp^3)-H Bonds under Visible Light Irradiation

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1. General Information

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded using a Bruker Avance DPX 400 MHz, 100 MHz and 564 MHz instrument and referenced to the internal solvent signals. Mass spectra were obtained using a Q-Exactive instrument or a Bruker-Solarix ESI (or MALDI)-FT spectrometer. Crude ^{19}F NMR spectra were obtained on a Bruker Avance DPX 376 MHz instrument using fluorobenzene as an internal standard. GC quantitative analysis was performed using a SHIMADZU 2010plus instrument (Helium as the carrier gas, n-tetradecane as an internal standard, SH-Rtx-5 capillary column, FID detector). ESR spectra were recorded using a Bruker E500 spectrometer at X-band, with 100Hz field modulation frequency. UV-Vis spectrum was measured on a U-3900 UV-VIS spectrophotometer. Commercially available reagents and solvents were used without further purification. All photoreactions were performed using common dry, inert atmosphere techniques. Irradiation with blue light was performed using High Power UV 1W®TaoYuan LED (λ = 450±10 nm, 300mA). Reactions were monitored by TLC, and column chromatography purifications were carried out using silica gel GF254.

2. Preparation of substrates

Preparation of Substrate (1f)[1]

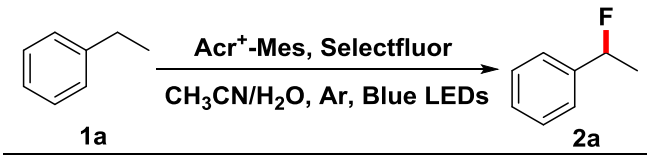
611 mg (6.6 mmol, 1.5 eq) of potassium phtalimide was added to 332 μL (4.4 mmol) of (3-chloropropyl)benzene solved in 25 mL DMF. The mixture was heated over a period of 2 h at 80 ℃ and then cooled down to room temperature. 100 mL of brine and 25 mL ethyl acetate were added, the reaction mixture was extracted three times with 25 mL ethyl acetate each. The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. Purification by column chromatography afforded the pure product as a white solid.

Preparation of Diphenylmethane Derivatives (3b, 3d, 3h ~ 3g)[2]

A mixture of phenyl boronic acid (4 mmol), potassium carbonate (10 mmol), benzyl bromide (4 mmol) in acetone-water (3:1, 40 mL) was stirred at room temperature until the reaction mixture became homogeneous. Then, the mixture was cooled in an ice bath and $PdCl_2$ (12 mg, 0.068 mmol) was added at 0 ℃ under a nitrogen atmosphere. Stirring was continued at room temperature for 15 hours. The acetone was removed under reduced pressure and the product was extracted with diethyl ether (10 mL × 3). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. Purification by column chromatography afforded the pure product.

3. Condition optimization for the benzylic fluorination reaction

Table S1. Optimization of Reaction Conditions[a]



	Amount of Selectfluor (equiv.)	Ratio for CH_3CN/H_2O	Time (h)	Yield[b] (%)
1	2.0	4:0	12	15
2	2.0	3:1	12	71
3	2.0	1:3	12	37
4	2.0	2:2	12	69
5[c]	2.0	3:1	12	20
6	1.1	3:1	12	65
7	1.5	3:1	12	69
8	3.0	3:1	12	68
9	2.0	3:1	1	82
10[d]	2.0	3:1	1	0
11[e]	2.0	3:1	1	0

[a]**1a** (0.3 mmol), Acr^+-Mes (5 mol %) and Fluorine donor (2.0 equiv.) in the solvent (4 mL) were irradiated by Blue LEDs under an argon atmosphere. [b]Determined by ^{19}H NMR spectra using C_6H_5F as an internal standard. [c]Replace Selectfluor with NFSI. [d]General conditions, but with no Acr^+-Mes or light. [e]Replace Acr^+-Mes (5 mol %) with $Ir(ppy)_3$ or $Ru(bpy)_3Cl_2$ (3 mol %).

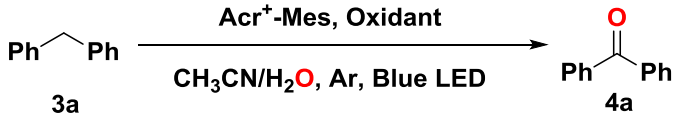
4. General procedure for the benzylic fluorination reaction

A 10 mL reaction tube equipped with magnetic stirring bar was charged with Acr^{+}-Mes ClO_4^{-} (0.015 mmol, 5 mol %), Selectfluor (0.6 mmol, 2 equiv.), 3 mL acetonitrile, 1 mL H_2O, ethylbenzene derivate (0.3 mmol, 1 equiv.). The reaction tube was sealed and the reaction mixture was degassed by bubbling with argon for 15 minutes. The mixture was stirred and irradiated with blue LEDs (λ = 450±10 nm) for 1 h (or 12 h) at room temperature. After that, the solution was diluted with H_2O (2 mL), and extracted with dichloromethane (6 mL × 3). The combined organic phase was dried (Na_2SO_4) and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the desired benzylic fluoride, which was characterized by NMR and HRMS.

Note: The identity of volatile praducts were confirmed by crude ^{19}F NMR spectra and by comparision with literaure values.[3]

5. Condition optimization for the benzylic oxidation reaction

Table S2. Optimization of Reaction Conditions[a]



	Oxidant	Ratio for CH_3CN/H_2O	Yield[b] %
1	Selectfluor	3:1	72
2	$K_2S_2O_8$	3:1	15
3	NFSI	3:1	55
4[c]	$BrCCl_3$	3:1	20
5	Selectfluor	1:1	77
6	Selectfluor	1:3	46
7	Selectfluor	4:0	36
8[d]	Selectfluor	1:1	2

[a]**1a** (0.3 mmol), Acr^+-Mes (5 mol %) and Oxidant (2.0 equiv.) in the solvent (4 mL) were irradiated by Blue LEDs for 12 hours under an argon atmosphere. [b]Determined by GC using n-tetradecane as an internal standard. [c]3.0 equiv. $BrCCl_3$, reaction time: 18 hours. [d]General conditions, but with no Acr^+-Mes or light.

6. General procedure for the benzylic oxidation reaction

A 10 mL reaction tube equipped with magnetic stirring bar was charged with Acr^{+}-Mes ClO_4^{-} (0.015 mmol, 5 mol %), Selectfluor (0.6 mmol, 2 equiv.), 2 mL acetonitrile, 2 mL H_2O, diphenylmethane derivate (0.3 mmol, 1 equiv.). The reaction tube was sealed and the reaction mixture was degassed by bubbling with argon for 15 minutes. The mixture was stirred and irradiated with blue LEDs (λ = 450±10 nm) for 12 h at room temperature. After that, the solution was diluted with H_2O (4 mL), and extracted with ethyl acetate (8 mL × 3). The combined organic phase was dried (Na_2SO_4) and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel using hexane/ethyl acetate as eluent to afford the desired diarylketone, which was characterized by NMR and HRMS.

7. Mechanism study

7.1 Procedure for the electron paramagnetic resonance (EPR) experiment

The measurement was carried out in an argon-saturated MeCN/H_2O (3:1) solution of Acr^+–Mes (3.75 mM) with or without Selectfluor (0.15 M). The sample cavity was first irradiated by a high-pressure mercury lamp for 2 min at 233 K. After the irradiation, the sample cell was immediately cooled to 123 K and the ESR spectra were recorded. At last, measuring temperature was increased to 178K or 233K, and corresponding ESR spectra were recorded.

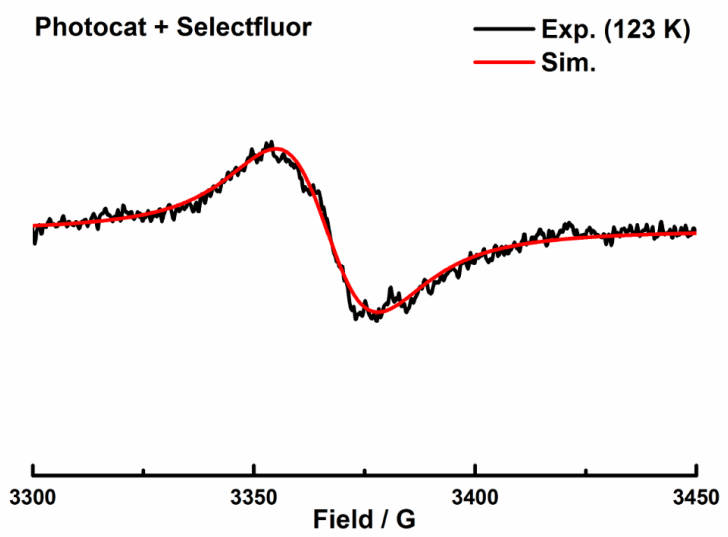


Figure S1. Black Line: EPR spectrum observed after irradiation of an argon-saturated MeCN/H_2O solution of Acr^+-Mes (3.75 mM) and Selectfluor (0.15 M) at 233 K for 2 minutes and then measured at 123 K; Red Line: the computer-simulated spectrum (g Facter: 2.00655, Line Width: 23.0239, Line Shape: 0.144237, Area: 86.31).

7.2 Procedure for the Uv-vis absorption experiment

The measurement was carried out in an argon-saturated MeCN/H_2O (3:1) solution of Acr^+–Mes (0.01 mM) with or without Selectfluor (0.4 mM). We first detected the Uv-vis absorption of Acr^+–Mes, Selectfluor and both of them in MeCN/H_2O before irradiation. Subsequently, the mixture of Acr^+–Mes and Selectfluor was irradiated by blue LEDs for 60 s, 180 s and 360 s, and corresponding Uv-vis absorption spectra were detected.

7.3 Procedure for the light-dark cycle experiment

Six 10 mL reaction tubes were equipped with magnetic stirring bars, and each tube was charged with Acr^+-Mes ClO_4^- (0.015 mmol), Selectfluor (0.6 mmol), 3 mL CH_3CN and 1 mL H_2O. The reaction tubes were sealed and the reaction mixtures were degassed by bubbling with argon for 15 minutes. Then, **1a** (0.3 mmol) was added to each tube through a micro syringe. Each mixture was stirred and irradiated with blue LEDs (λ = 450±10 nm) at room temperature.

The first one: stir with light for 5 mins;

The second one: stir with light for 5 mins, then without light for 5 mins;

The third one: stir with light for 5 mins, then without light for 5 mins, then with light for 5 mins;

The fourth one: stir with light for 5 mins, then without light for 5 mins, then with light for 5 mins, then without light for 5 mins;

The fifth one: stir with light for 5 mins, then without light for 5 mins, then with light for 5 mins, then without light for 5 mins, then with light for 5 mins;

The sixth one: stir with light for 5 mins, then without light for 5 mins; then with light for 5 mins, then without light for 5 mins, then with light for 5 mins, then without light for 5 mins.

After that, 2,6-di-tert-butyl-4-methylphenol (BHT, 0.6 mmol) was added to terminate the reaction. At last, the yield was determined by acquiring a crude ^{19}H NMR spectrum of each mixture using fluorobenzene as an internal standard.

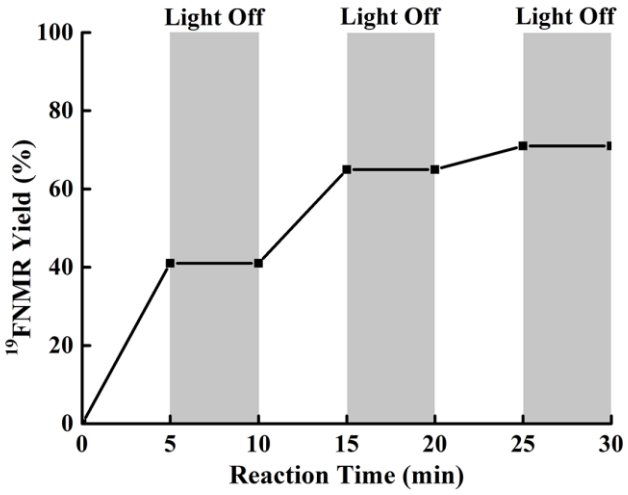


Figure S2. Time profile of fluorinated reaction with or without visible light.

7.4 Detected the benzylic fluorination reaction of **1a** in deuterated solvents

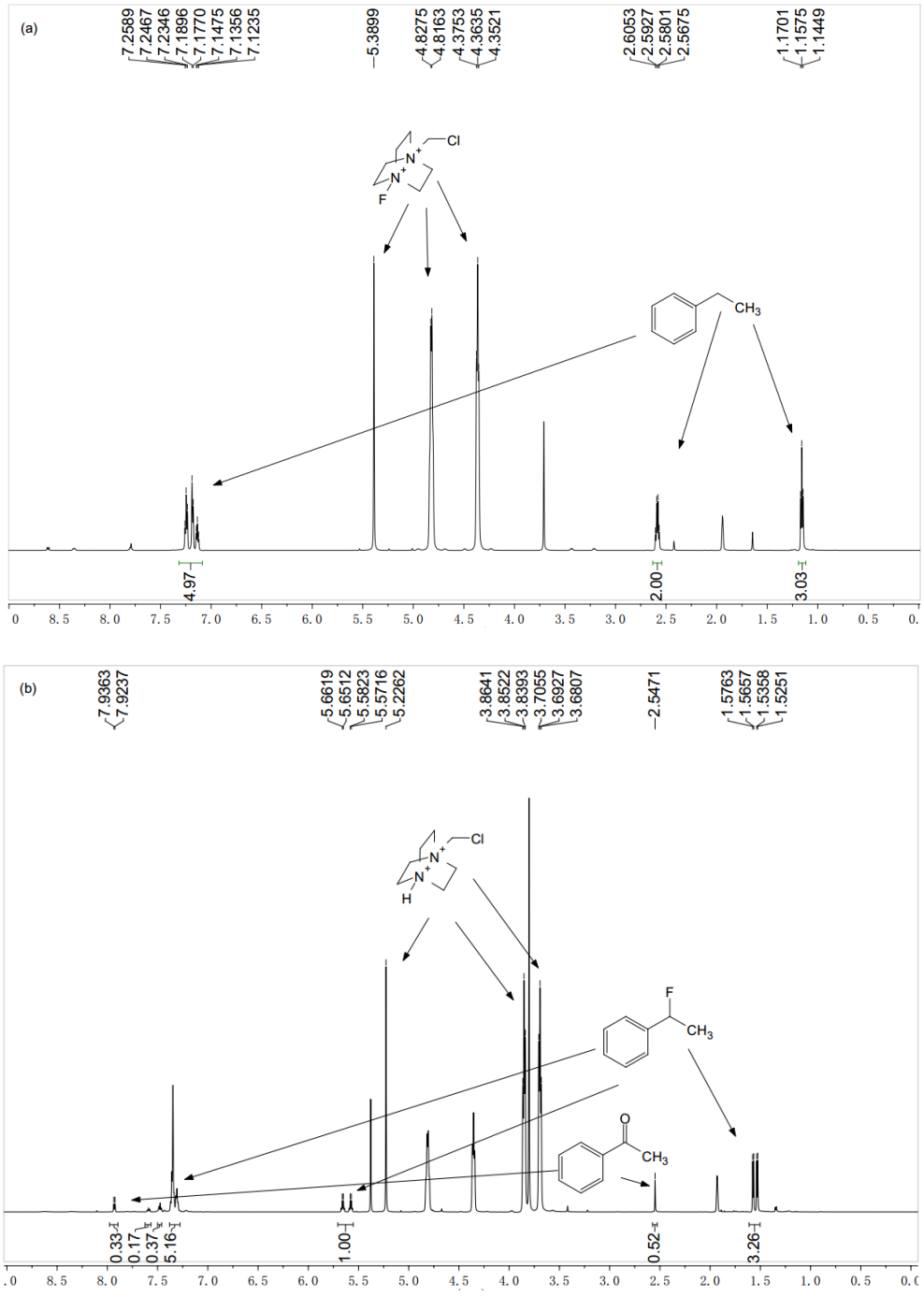


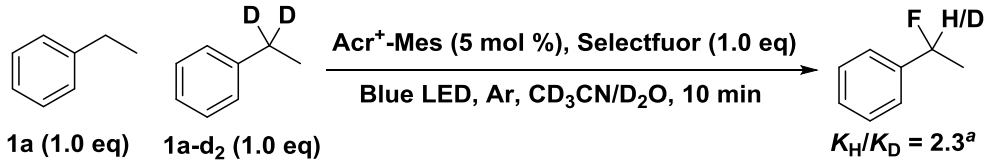
Figure S3. ^{1}H NMR of the reaction mixture. (a) before the reaction; (b) after the reaction.

7.5. Procedure for the intermolecular kinetic isotope effect experiment

A 10 mL reaction tube equipped with magnetic stirring bar was charged with Acr^{+}-Mes ClO_4^{-} (0.015 mmol), Selectfluor (0.3 mmol), 3 mL CD_3CN and 1 mL D_2O. The reaction tube was sealed and the reaction mixture was degassed by bubbling with argon for 15 minutes. Then, **1a** (0.3 mmol) and **1a-d$_2$** (0.3 mmol) were added through a micro syringe. The mixture was stirred and irradiated

with blue LEDs (λ = 450±10 nm) for 10 minutes at room temperature. After that, the product ratio of **2a** to **2a-d$_1$** was calculated by acquiring a crude ^{19}H NMR spectrum of the mixture to be 1:0.44.

Scheme S1. Intermolecular KIE experiment.



8. Characterization data of synthesized compounds

2-(3-phenylpropyl)isoindoline-1,3-dione (1f).

A white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.74 – 7.64 (m, 2H), 7.22 (dd, *J* = 17.9, 7.4 Hz, 4H), 7.14 (t, *J* = 7.1 Hz, 1H), 3.75 (t, *J* = 7.2 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.14 – 1.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 141.2, 134.0, 132.3, 128.5, 126.1, 123.3, 38.0, 33.3, 30.0.

1-benzyl-4-(*tert*-butyl)benzene (3b).

A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.16 (m, 7H), 7.11 (d, *J* = 8.1 Hz, 2H,), 3.95 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 141.4, 138.2, 129.1, 128.7, 128.6, 126.1, 125.5, 41.6, 34.5, 31.6.

1-benzyl-4-methoxybenzene (3d).

A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.18 (t, *J* = 7.6 Hz, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.7 Hz, 2H), 3.92 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 141.7, 133.4, 130.0, 129.0, 128.6, 126.1, 114.0, 55.4, 41.2.

methyl 4-benzylbenzoate (3h).

A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.11 (m, 7H), 4.03 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 146.7, 140.3, 130.0, 129.1, 128.8, 128.3, 126.5, 52.1, 42.1.

1-(*tert*-butyl)-4-(4-chlorobenzyl)benzene (3i).

A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.4 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.10 (dd, *J* = 13.8, 7.8 Hz, 4H), 3.91 (s, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 139.9, 137.7, 132.0, 130.4, 128.7, 128.6, 125.6, 40.9, 34.5, 31.5.

1-chloro-4-(4-methoxybenzyl)benzene (3j).

A colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.9 Hz, 2H), 7.08 (t, *J* = 8.0 Hz, 4H), 6.83 (d, *J* = 7.5 Hz, 2H), 3.88 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 140.3, 132.9, 132.0, 130.3, 130.0, 128.7, 114.3, 55.4, 40.6.

(1-fluoroethyl)benzene (2a).

^{19}F NMR (564 MHz, CD_3CN/D_2O) δ -165.32 (dq, *J* = 47.7, 23.7 Hz, 1F).

(fluoromethyl)benzene (2b).

^{19}F NMR (564 MHz, CD_3CN/D_2O) δ -204.85 (t, *J* = 47.8 Hz, 1F).

(2-fluoropropan-2-yl)benzene (2c).

^{19}F NMR (564 MHz, CD_3CN/D_2O) δ -135.88 (hept, *J* = 22.2 Hz, 1F).

methyl 3-fluoro-3-phenylpropanoate (2d).

A colorless oil (24.5 mg, 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 5H), 5.93 (ddd, *J* = 47.0, 9.1, 4.1 Hz, 1H), 3.74 (s, 3H), 3.12 – 2.96 (m, 1H), 2.80 (ddd, *J* = 32.5, 16.0, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.2, 138.9, 138.7, 129.0, 128.8, 125.8, 125.7, 91.6, 89.9, 52.2, 42.6, 42.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -173.16 (ddd, *J* = 46.0, 32.9, 12.9 Hz, 1F); MS (HRMALDI): m/z calcd for $C_{10}H_{11}FO_2$ $[M+Na]^+$ 205.0635, found 205.0636.

3-fluoro-3-phenylpropyl acetate (2e).

A colorless oil (31.9 mg, 54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 5H), 5.57 (ddd, *J* = 47.8, 8.7, 4.2 Hz, 1H), 4.23 (ddd, *J* = 17.4, 11.2, 5.0 Hz, 2H), 2.37 – 2.08 (m, 2H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 139.7, 139.6, 128.7, 128.6, 125.6, 125.5, 92.4, 90.7, 60.6, 60.5, 36.5, 36.2, 20.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -177.37 (ddd, *J* = 46.2, 30.2, 14.8 Hz, 1F); MS (HRESI): m/z calcd for $C_{11}H_{13}FO_2$ $[M+Na]^+$ 219.0792, found 219.0784.

2-(3-fluoro-3-phenylpropyl)isoindoline-1,3-dione (2f).

A colorless oil (61.0 mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.2, 4.6 Hz, 2H), 7.71 (dd, *J* = 8.3, 3.8 Hz, 2H), 7.42 – 7.21 (m, 5H), 5.54 (ddd, *J* = 47.8, 8.6, 4.0 Hz, 1H), 3.98 – 3.81 (m, 2H), 2.50 – 2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 139.6, 139.4, 134.1, 132.3, 128.7, 128.6, 125.7, 123.4, 93.5, 91.8, 35.8, 35.6, 34.8, 34.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -175.68 (ddd, *J* = 46.9, 30.1, 16.3 Hz, 1F); MS (HRMALDI): m/z calcd for $C_{17}H_{14}FNO_2$ $[M+Na]^+$ 306.0901, found 306.0901.

4-(1-fluoroethyl)-1,1'-biphenyl (2g).

A white solid (30.5 mg, 51%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.43 (dd, *J* = 11.6, 8.0 Hz, 4H), 7.22 (t, *J* = 7.6 Hz, 4H), 7.13 (d, *J* = 7.5 Hz, 1H), 5.36 (dq, *J* = 47.7, 6.3 Hz, 1H), 1.38 (dd, *J* = 23.4, 6.4 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 141.6, 141.3, 141.2, 141.0, 129.1, 127.6, 127.5, 126.0, 125.9, 91.4, 89.7, 23.1, 22.9; ^{19}F NMR (564 MHz, C_6D_6) δ -167.47 (dq, *J* = 46.8, 23.2 Hz, 1F); MS (HRSI): m/z calcd for $C_{14}H_{13}F$ $[M]^+$ 200.1001, found 200.1002.

4-(1-fluoroethyl)phenyl acetate (2h).

A colorless oil (35.5 mg, 65%): ^{1}H NMR (400 MHz, C_6D_6) δ 7.06 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 5.23 (dq, *J* = 47.6, 6.4 Hz, 1H), 1.74 (s, 3H), 1.28 (dd, *J* = 23.5, 6.4 Hz, 3H); ^{13}C

NMR (100 MHz, C_6D_6) δ 168.4, 151.2, 139.5, 139.3, 126.6, 126.5, 121.9, 91.1, 89.4, 23.0, 22.8, 20.5; ^{19}F NMR (564 MHz, C_6D_6) δ -166.83 (dq, *J* = 46.8, 23.3 Hz, 1F); MS (HRMALDI): m/z calcd for $C_{10}H_{11}FO_2$ $[M+Na]^+$ 205.0635, found 205.0637.

4.5 mmol scale of 1h

A 100 mL reaction tube equipped with magnetic stirring bar was charged with Acr^+-Mes ClO_4^- (0.225 mmol, 5 mol %), Selectfluor (9 mmol, 2 equiv.), 45 mL acetonitrile, 15 mL H_2O, **1h** (4.5 mmol, 1 equiv.). The reaction tube was sealed and the reaction mixture was degassed by bubbling with argon for 30 minutes. The mixture was stirred and irradiated with blue LEDs (λ = 450±10 nm) for 3 h at room temperature. After that, the solution was extracted with dichloromethane (30 mL × 4). The combined organic phase was dried (Na_2SO_4) and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel using hexane/ethyl acetate (25:1) as eluent to afford **2h** (498 mg, 61% yield).

1-chloro-4-(fluoromethyl)benzene (2i).

^{19}F NMR (564 MHz, CD_3CN/D_2O) -166.15 (dq, *J* = 47.7, 23.7 Hz, 1F).

1-(4-(1-fluoroethyl)phenyl)ethan-1-one (2j).

A colorless oil (12.5 mg, 25%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.68 (dq, *J* = 47.6, 6.5 Hz, 1H), 2.60 (s, 3H), 1.64 (dd, *J* = 24.0, 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 147.0, 146.8, 137.2, 128.7, 125.3, 125.2, 91.2, 89.5, 26.7, 23.2, 22.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ -171.30 (dq, *J* = 47.6, 23.8 Hz, 1F); MS (HRSI): m/z calcd for $C_{10}H_{11}FO$ $[M]^+$ 166.0794, found 166.0791.

benzophenone (4a).

A white solid (38.8 mg, 71%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.7 Hz, 4H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 137.8, 132.5, 130.2, 128.4; MS (HRSI): m/z calcd for $C_{13}H_{10}O$ $[M]^+$ 182.0732, found 182.0732.

(4-(*tert*-butyl)phenyl)(phenyl)methanone (4b).

A white solid (58.5 mg, 82%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 15.3, 7.8 Hz, 4H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.49 (dd, *J* = 13.1, 7.3 Hz, 4H), 1.37 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 156.3, 138.2, 135.1, 132.2, 130.3, 130.1, 128.3, 125.4, 35.3, 31.3; MS (HRSI): m/z calcd for $C_{17}H_{18}O$ $[M]^+$ 238.1358, found 238.1357.

[1,1'-biphenyl]-4-yl(phenyl)methanone (4c).

A white solid (56.5 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.51 (dd, *J* = 14.9, 7.4 Hz, 4H), 7.42 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 145.3, 140.1, 138.0, 136.5, 132.4, 130.8, 130.1, 129.1, 128.4, 128.3, 127.4, 127.1; MS (HRSI): m/z calcd for $C_{19}H_{14}O$ $[M]^+$ 258.1045, found 258.1046.

(4-methoxyphenyl)(phenyl)methanone (4d).

A colorless oil (58.5 mg, 92%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 163.3, 138.4, 132.6, 131.9, 130.2, 129.8, 128.2, 113.6, 55.5; MS (HRSI): m/z calcd for $C_{14}H_{12}O_2$ $[M]^+$ 212.0837, found 212.0838.

9*H*-xanthen-9-one (4e).

A white solid (54.7 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.9 Hz, 2H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 156.2, 134.8, 126.8, 124.0, 121.9, 118.0; MS (HRSI): m/z calcd for $C_{13}H_8O_2$ $[M]^+$ 196.0524, found 196.0526.

(4-fluorophenyl)(phenyl)methanone (4f).

A white solid (32.4 mg, 54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.8, 5.7 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 166.8, 164.3, 137.7, 134.0, 132.8, 132.7, 132.6, 130.0, 128.5, 115.7, 115.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.95; MS (HRSI): m/z calcd for $C_{13}H_9FO$ $[M]^+$ 200.0637, found 200.0646.

(4-chlorophenyl)(phenyl)methanone (4g).

A white solid (27.9 mg, 43%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.9 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 15.9, 7.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 139.1, 137.5, 136.2, 132.7, 131.6, 130.0, 128.8, 128.6; MS (HRSI): m/z calcd for $C_{13}H_9ClO$ $[M]^+$ 216.0342, found 216.0343.

methyl 4-benzoylbenzoate (4h).

A white solid (18.8 mg, 26%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 2H), 7.82 (dd, *J* = 14.6, 7.8 Hz, 4H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 166.4, 141.5, 137.1, 133.4, 133.1, 130.2, 129.9, 129.6, 128.6, 52.6; MS

(HRSI): m/z calcd for $C_{15}H_{12}O_3$ $[M]^+$ 240.0786, found 240.0786.

(4-(*tert*-butyl)phenyl)(4-chlorophenyl)methanone (4i).

A colorless solid (44.2 mg, 54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 7.6 Hz, 4H), 7.37 (dd, *J* = 23.5, 7.8 Hz, 4H), 1.26 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 156.6, 138.8, 136.4, 134.7, 131.5, 130.2, 128.7, 125.5, 35.3, 31.3; MS (HRSI): m/z calcd for $C_{17}H_{17}ClO$ $[M]^+$ 272.0968, found 272.0969.

(4-chlorophenyl)(4-methoxyphenyl)methanone (4j).

A white solid (65.9 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 163.5, 138.3, 136.7, 132.5, 131.2, 129.9, 128.6, 113.8, 55.6; MS (HRSI): m/z calcd for $C_{14}H_{11}ClO_2$ $[M]^+$ 246.0448, found 246.0449.

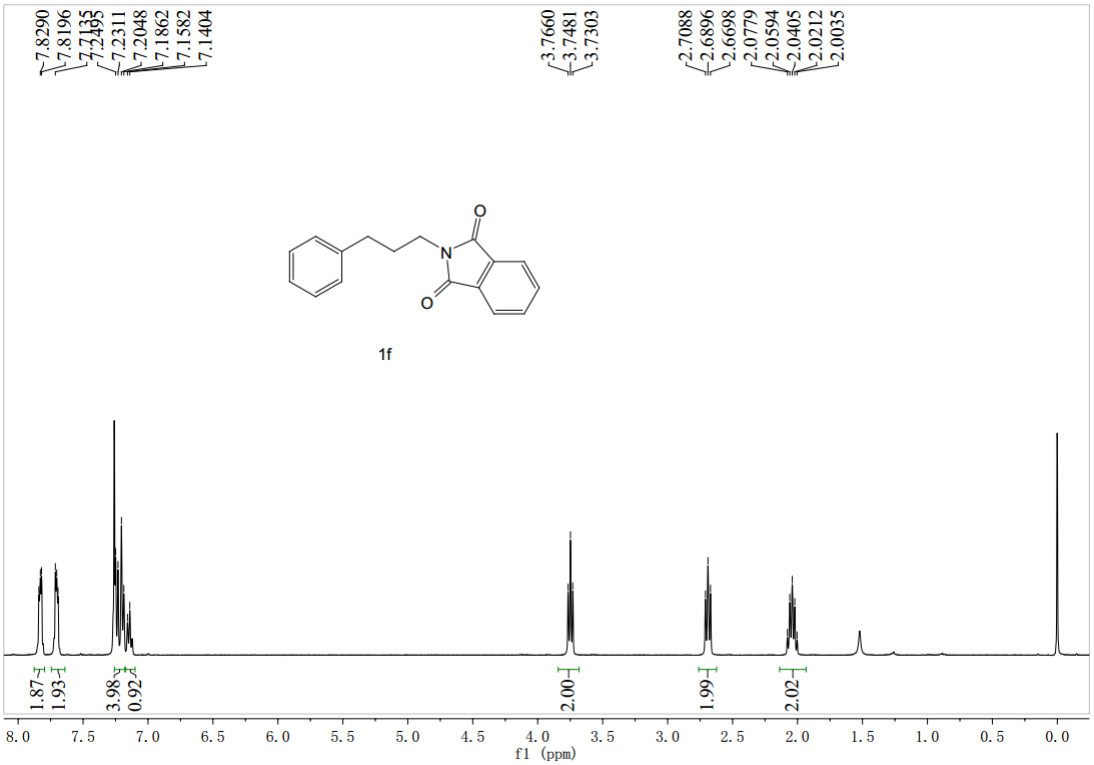
Reference:

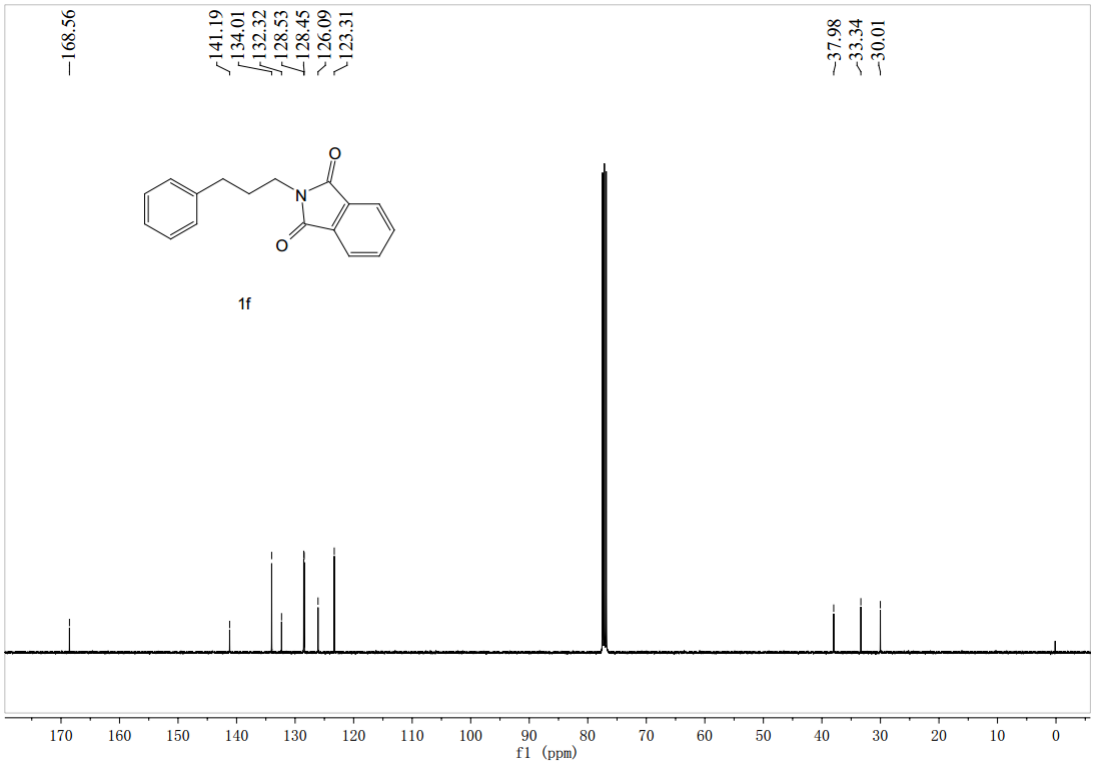
[1] Kumar, S.; Schwingenschlögl, U. *Phys. Chem. Chem. Phys.* **2016**, *18*, 19158.

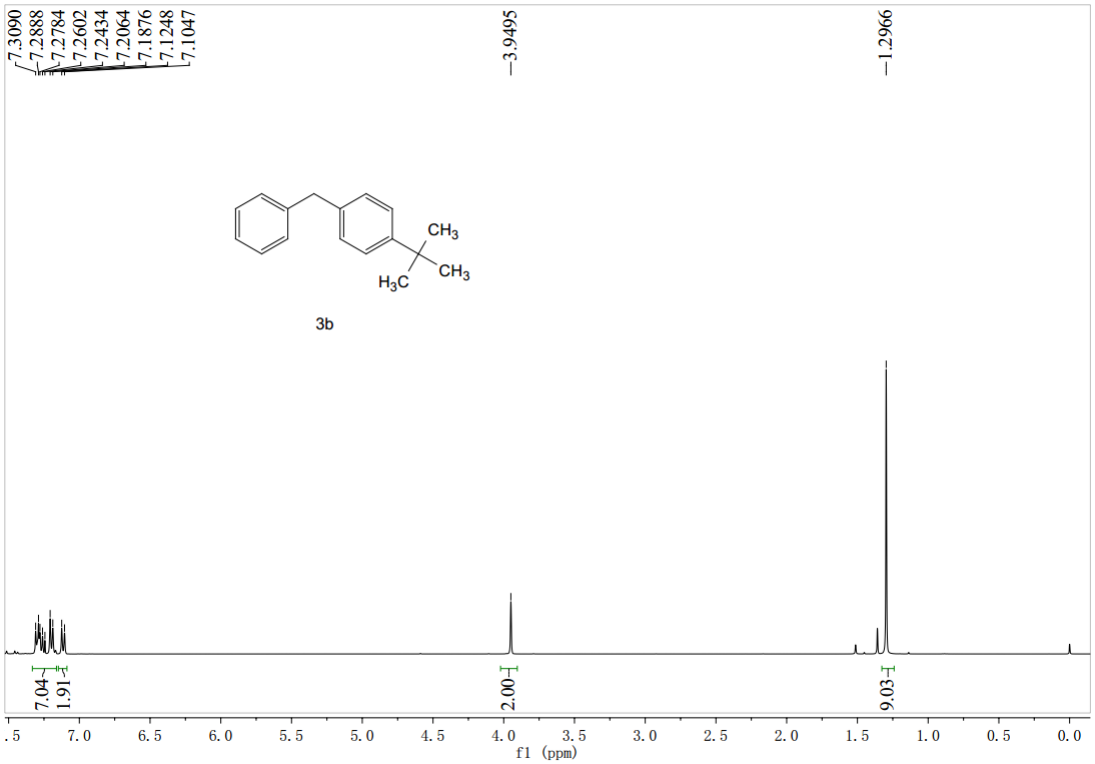
[2] Bandgar, B. P.; Bettigeri, S. V.; Phopase, J. *Tetrahedron Lett.* **2004**, *45*, 6959.

[3] Xia, J.-B.; Zhu, C.; Chen, C. *J. Am. Chem. Soc.* **2013**, *135*, 17494.

9. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra for synthesized compounds



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CH3
3b
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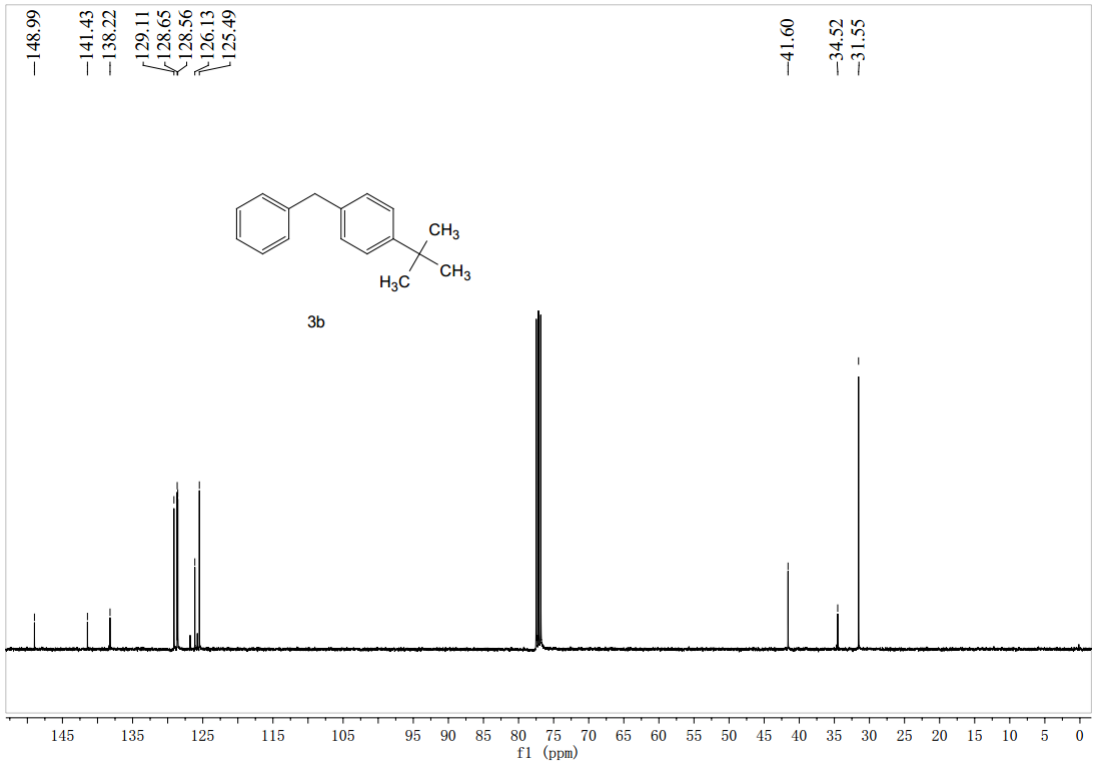
1.91
2.00
9.03
f1 (ppm)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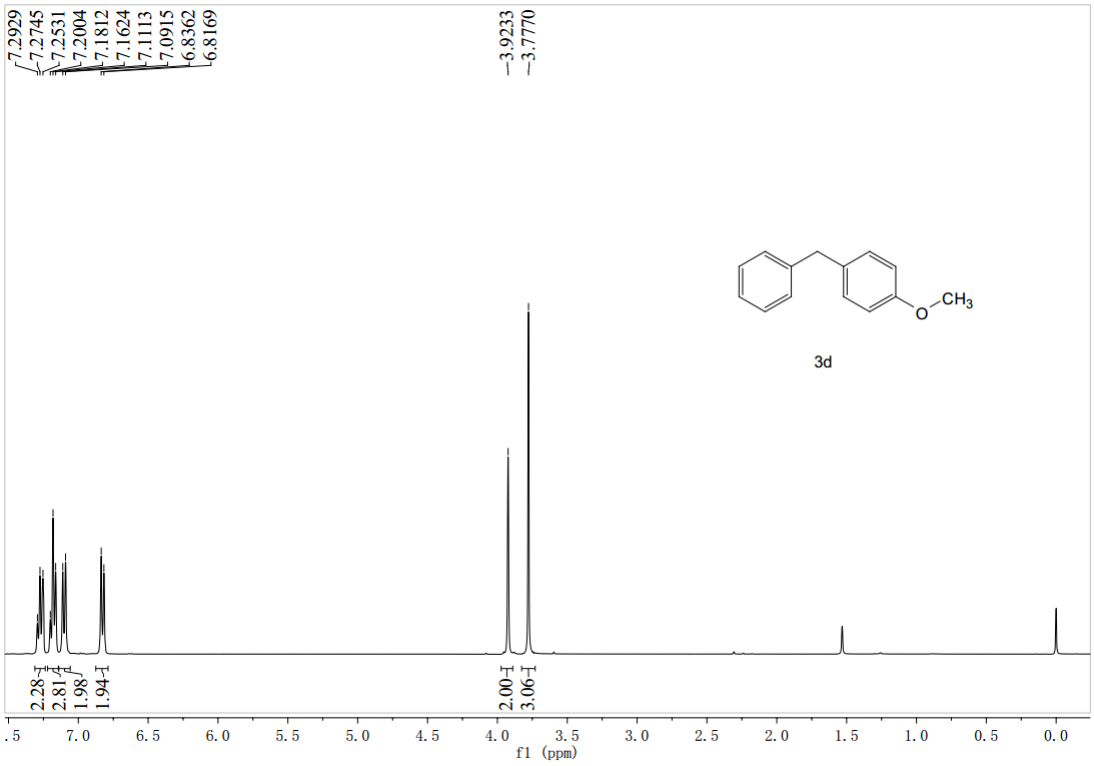
CH3
H3C
CH3
3b
f1 (ppm)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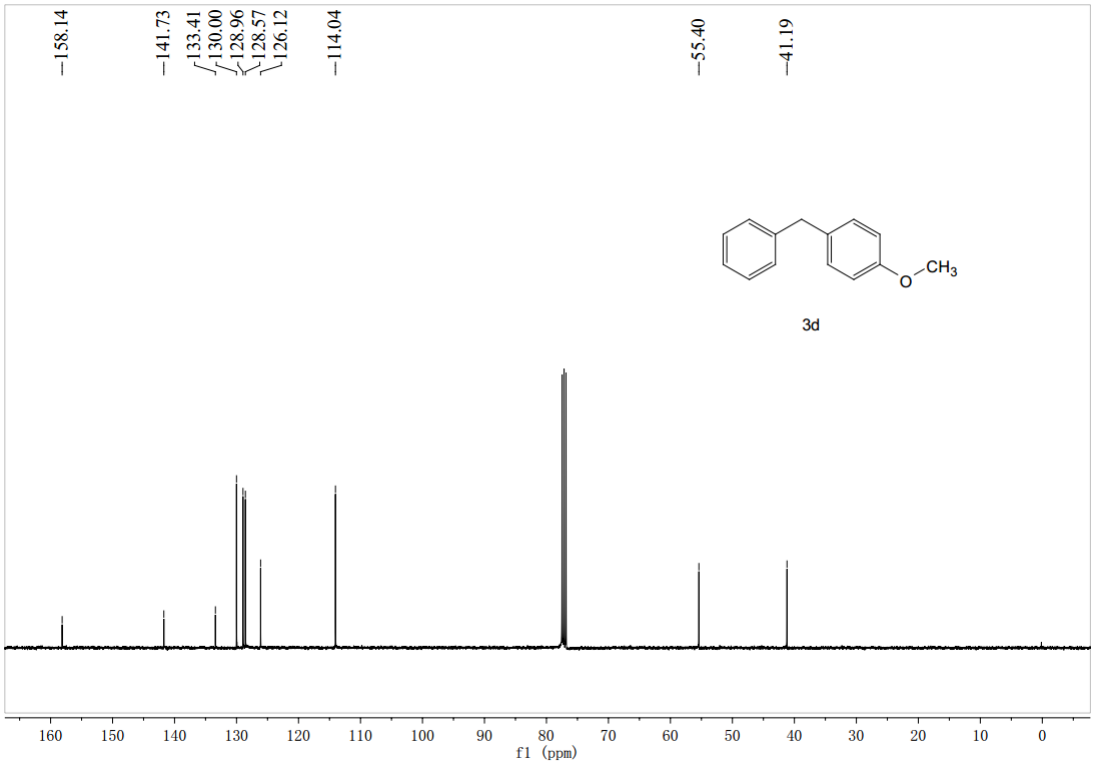
2.81
1.98
1.94
2.00
3.06
f1 (ppm)
3d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41.19
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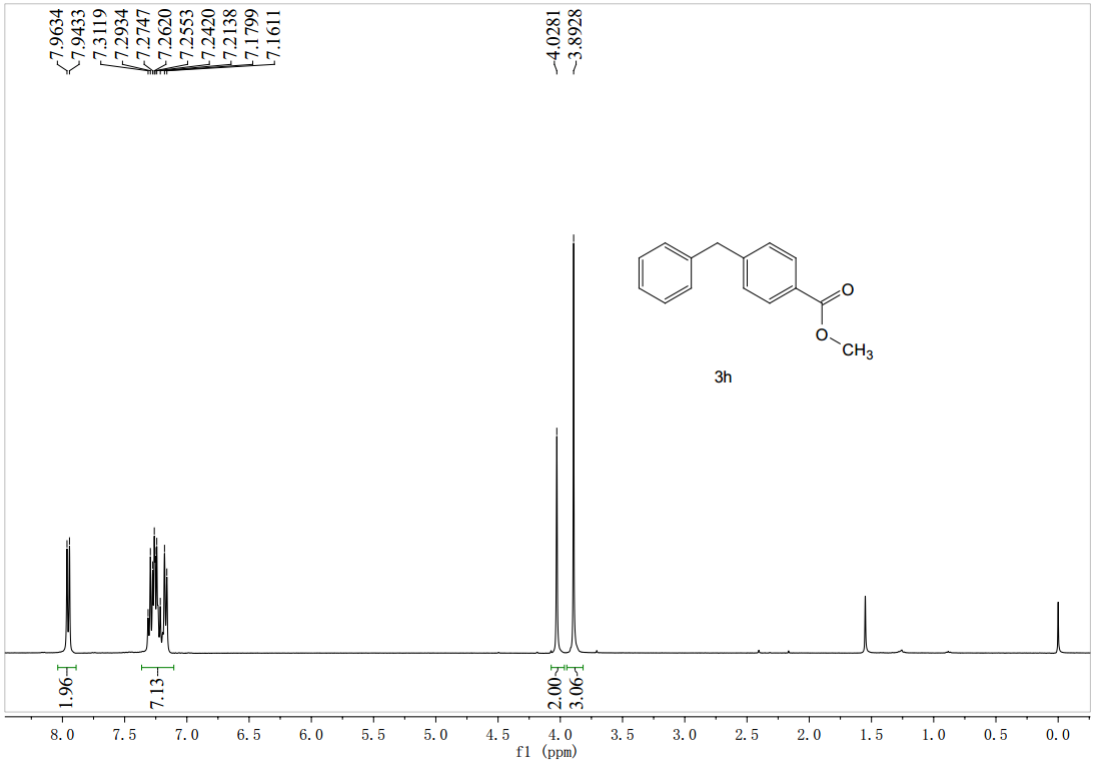
3d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7.1611
4.0281
3.8928
O
O
CH3
3h
1.96
7.13
2.00
3.06
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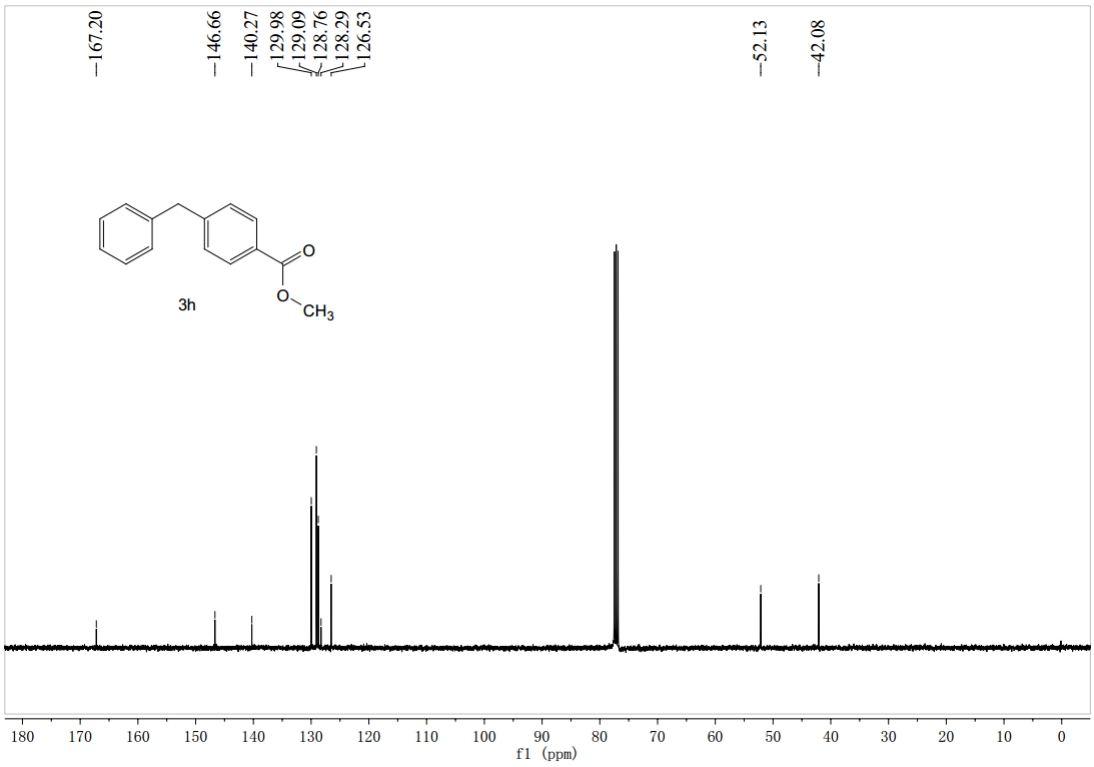
f1 (ppm)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3h
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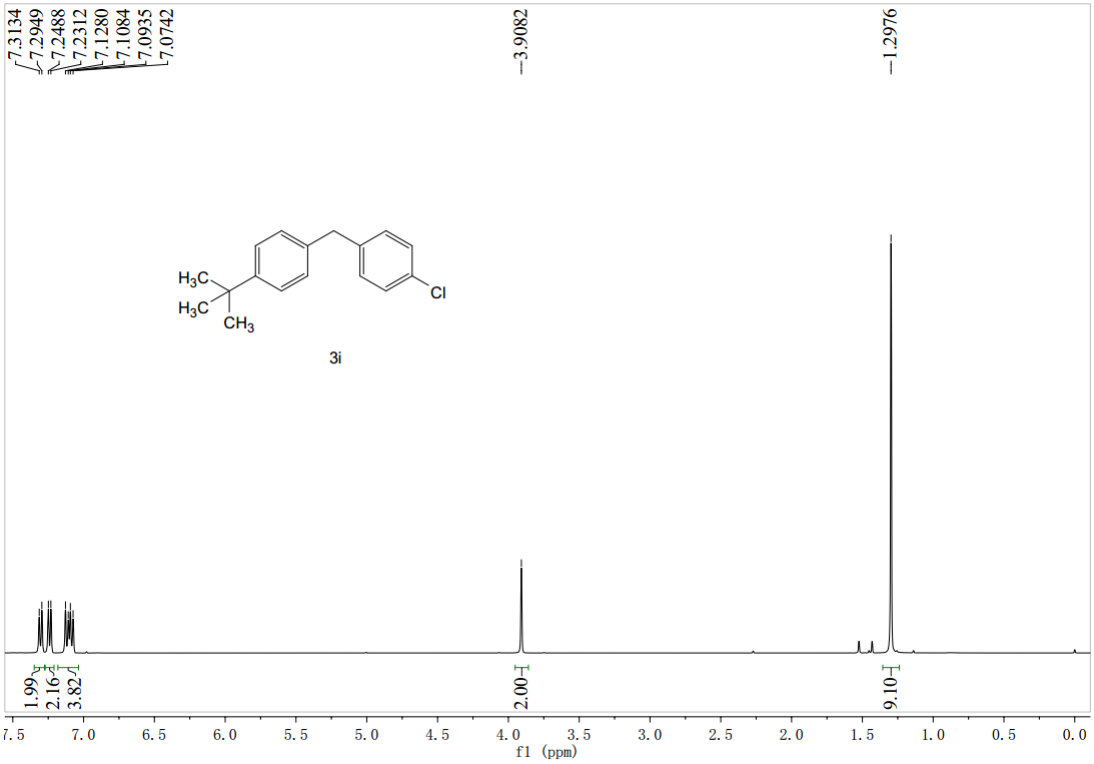
f1 (ppm)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H3C
CH3
Cl
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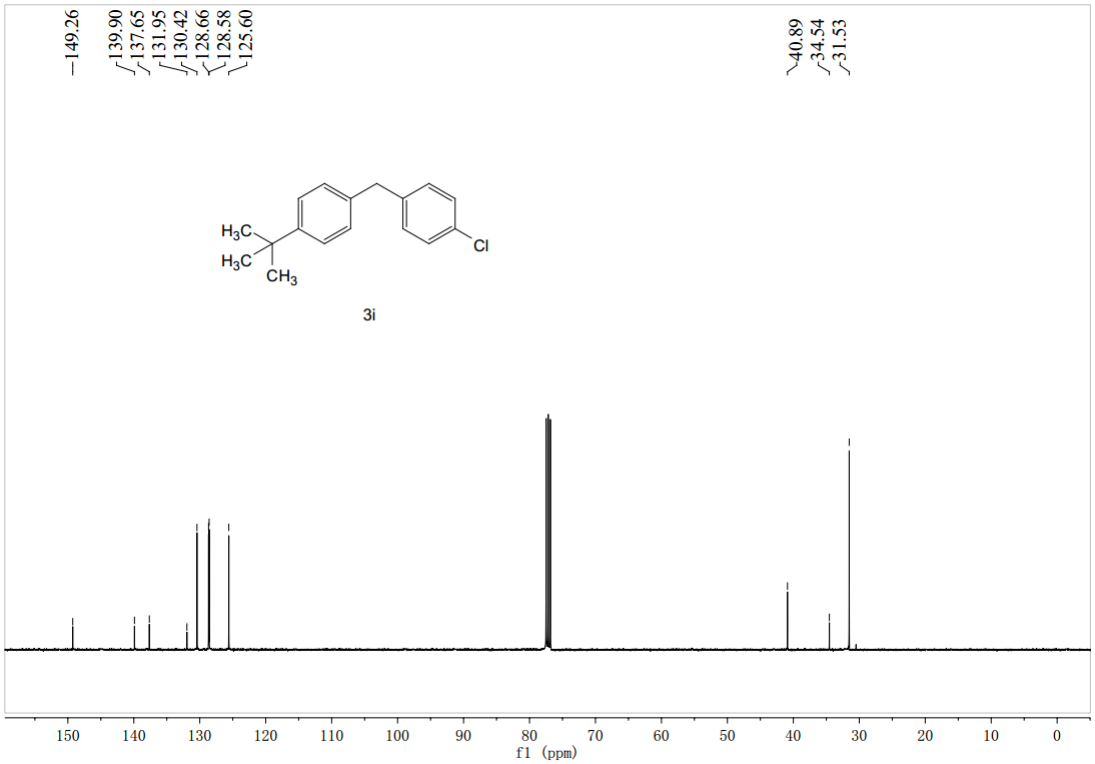
f1 (ppm)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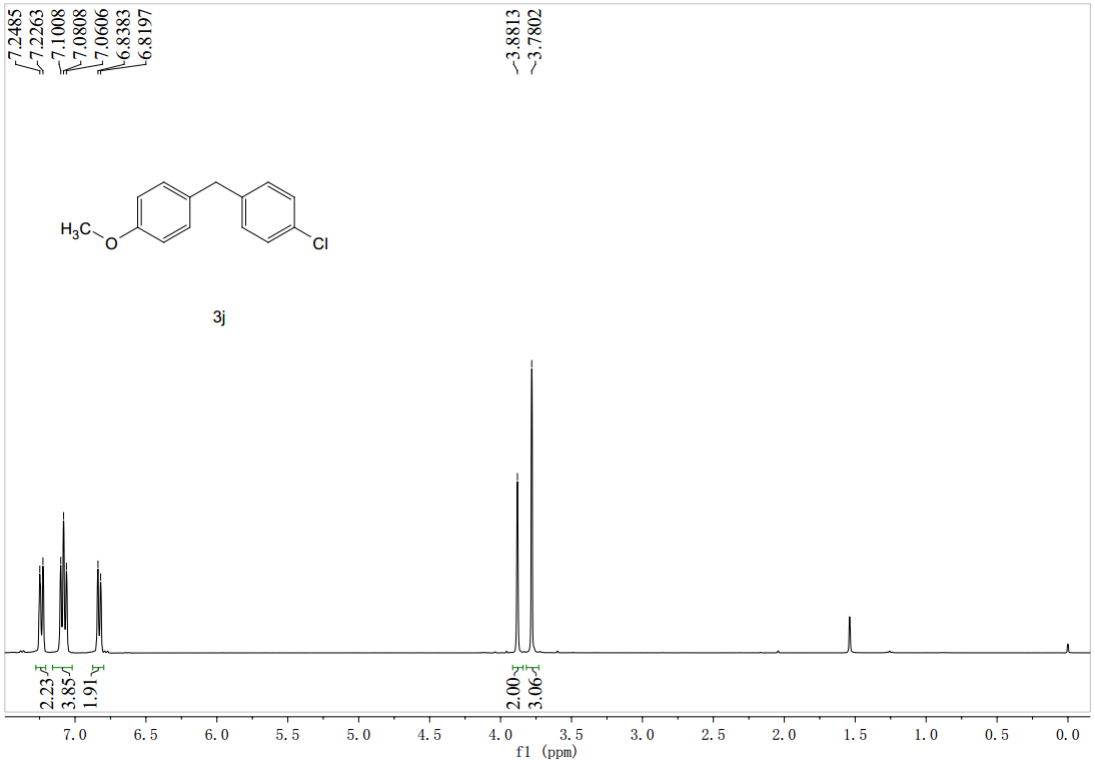
H3C
CH3
Cl
3i
f1 (ppm)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3.85
1.91
2.00
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6.5
6.0
5.5
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1.0
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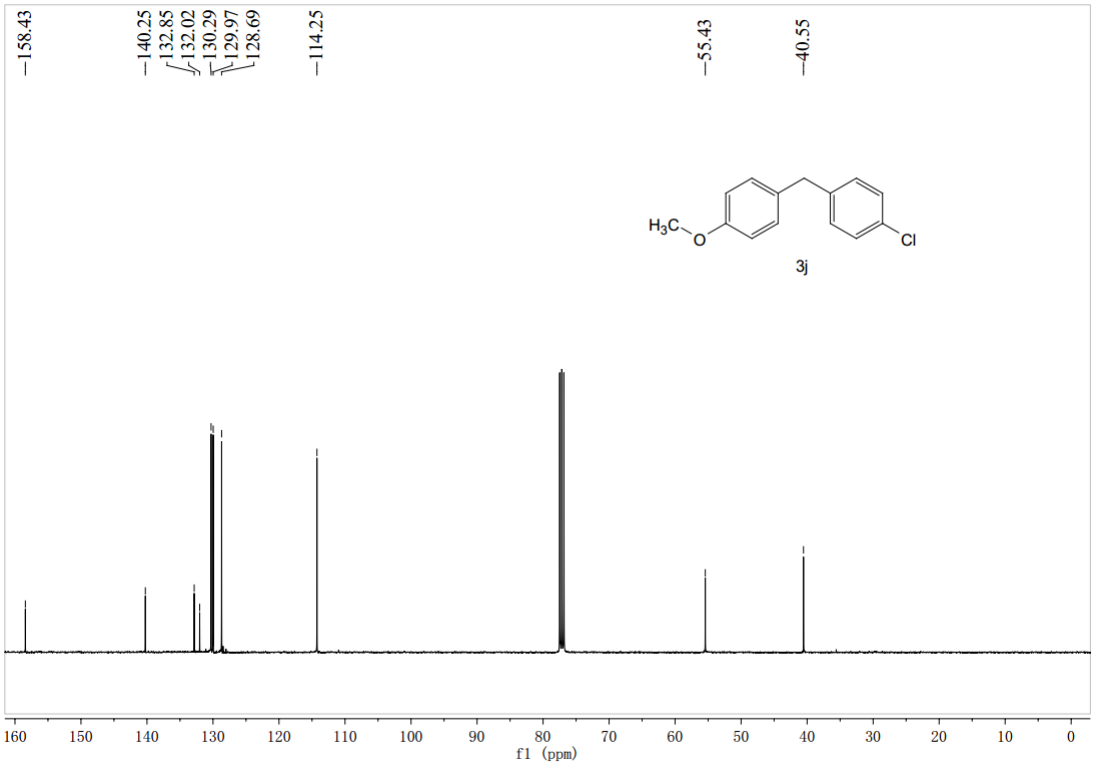
f1 (ppm)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40.55
H3C
O
Cl
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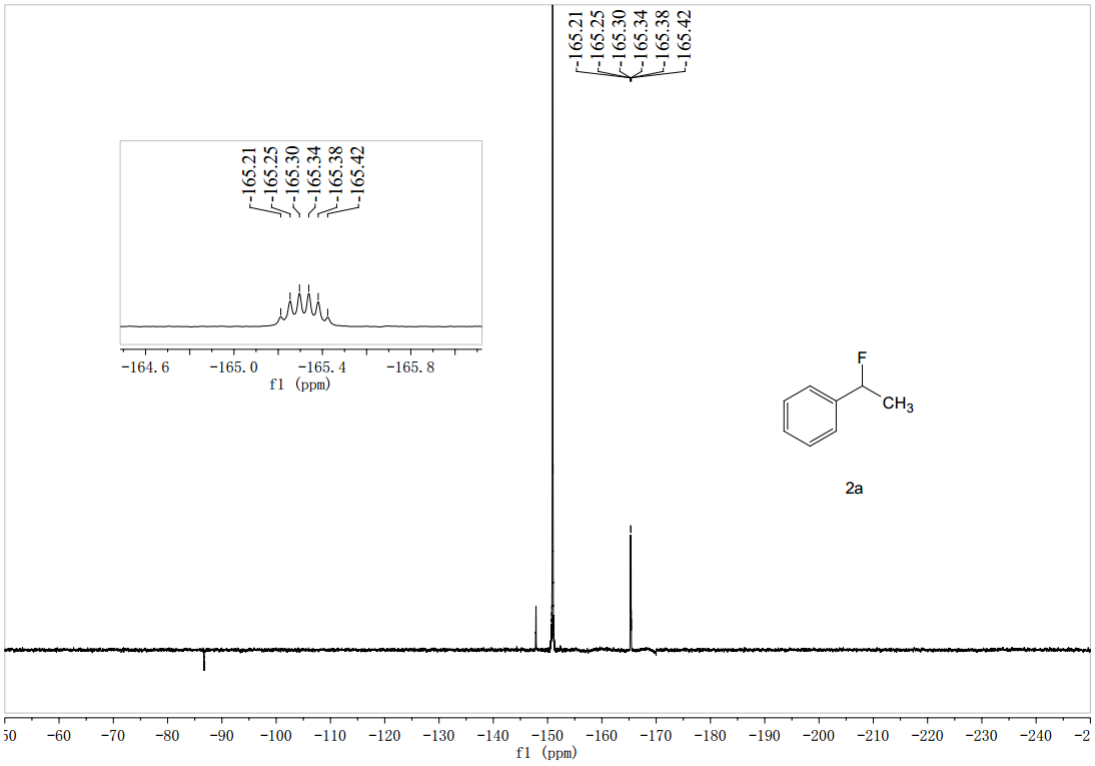
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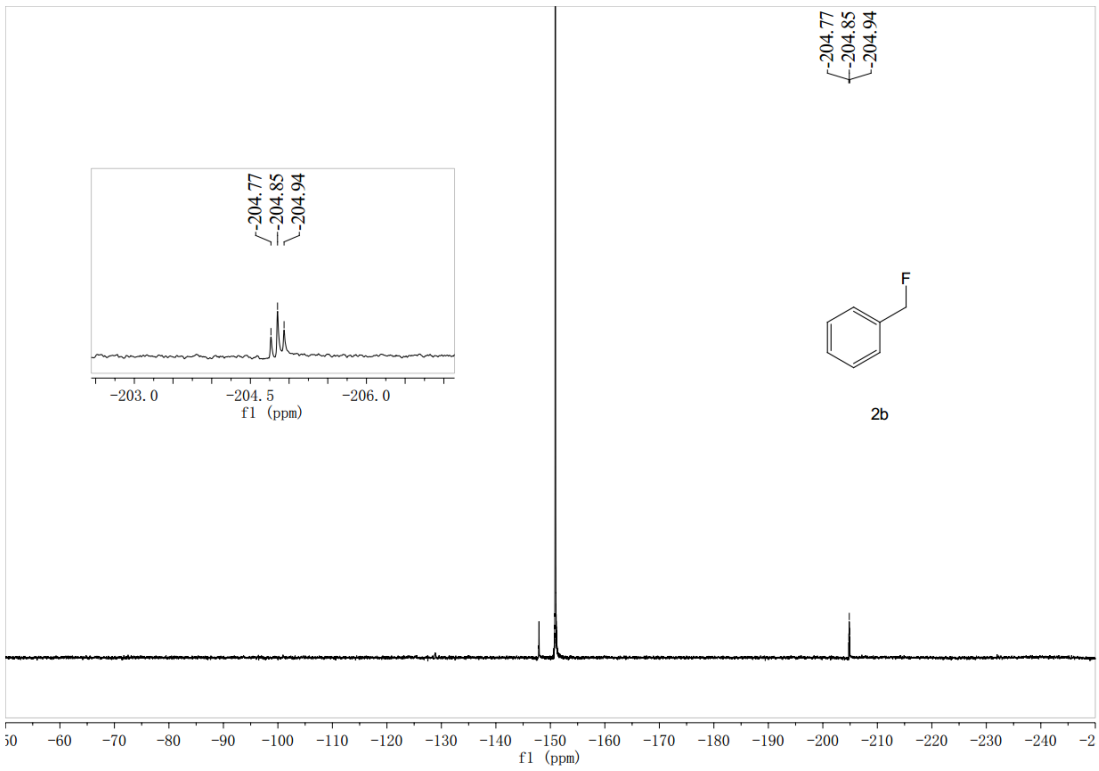
F
CH3
2a
f1 (ppm)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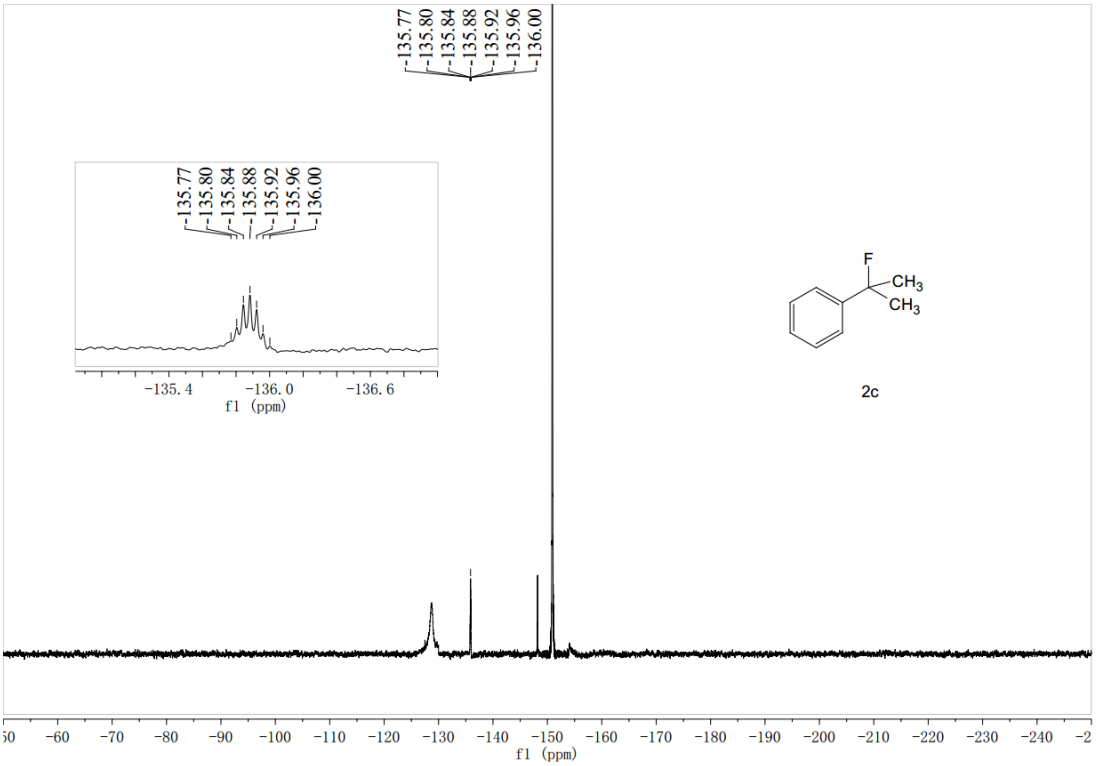
f1 (ppm)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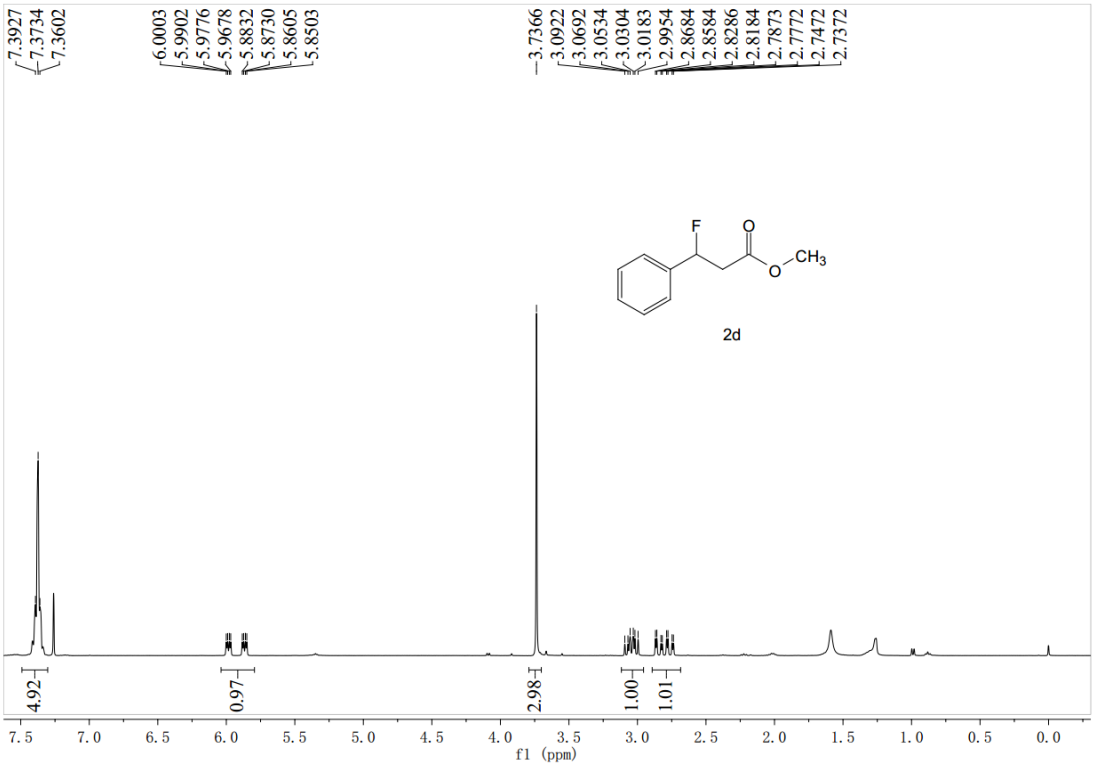
CH3
2c
f1 (ppm)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O
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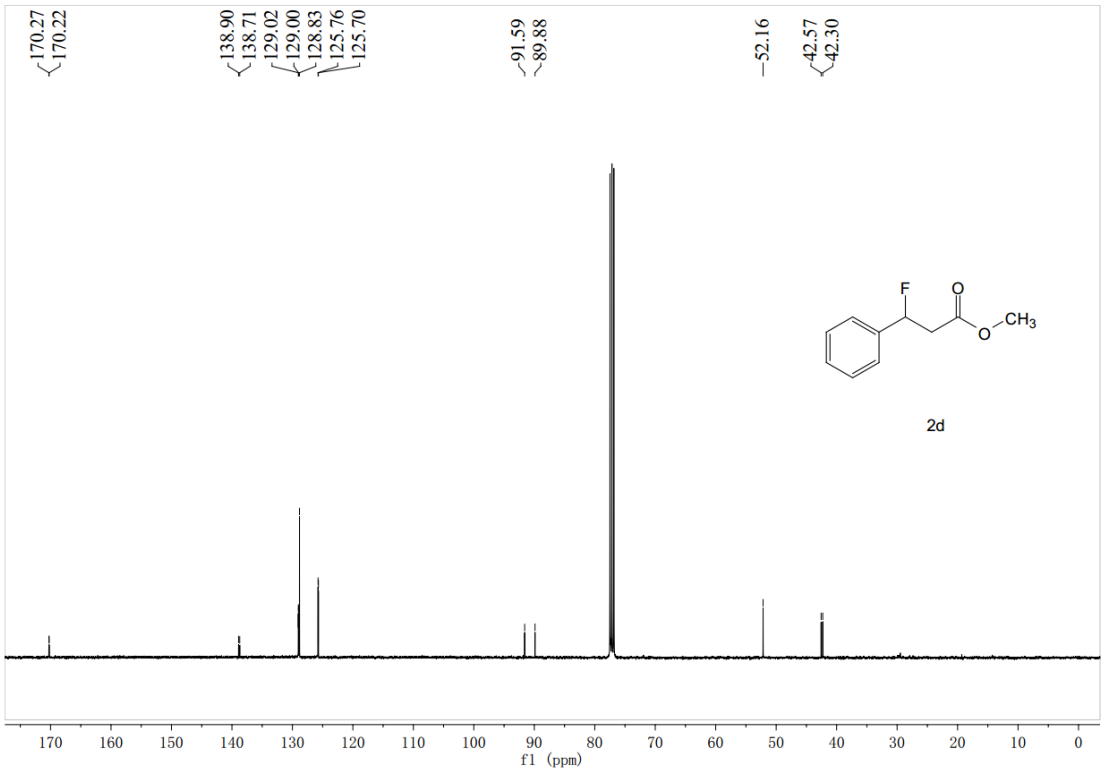
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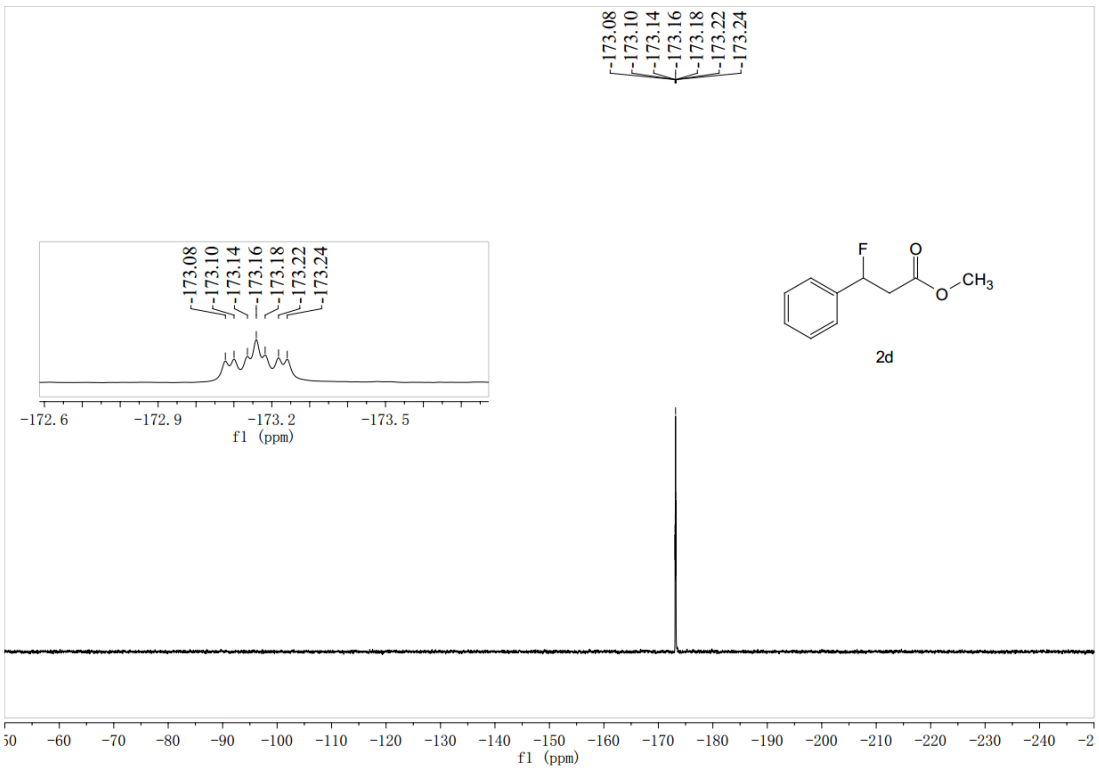
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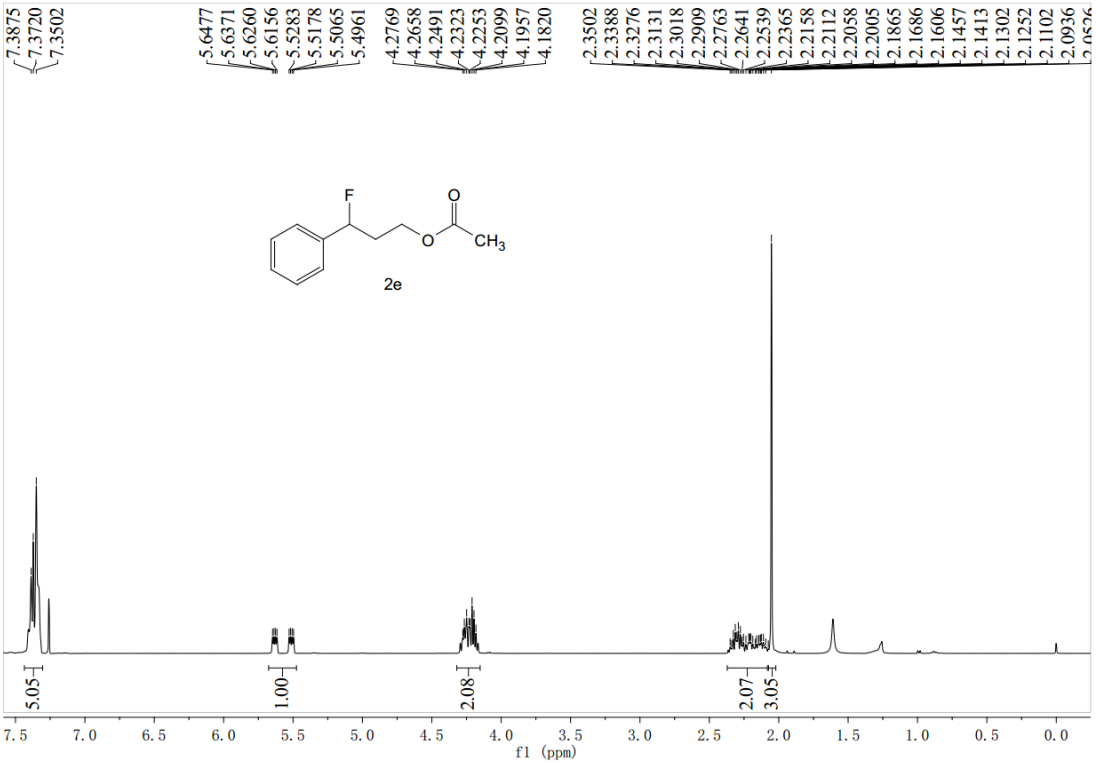
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CH3
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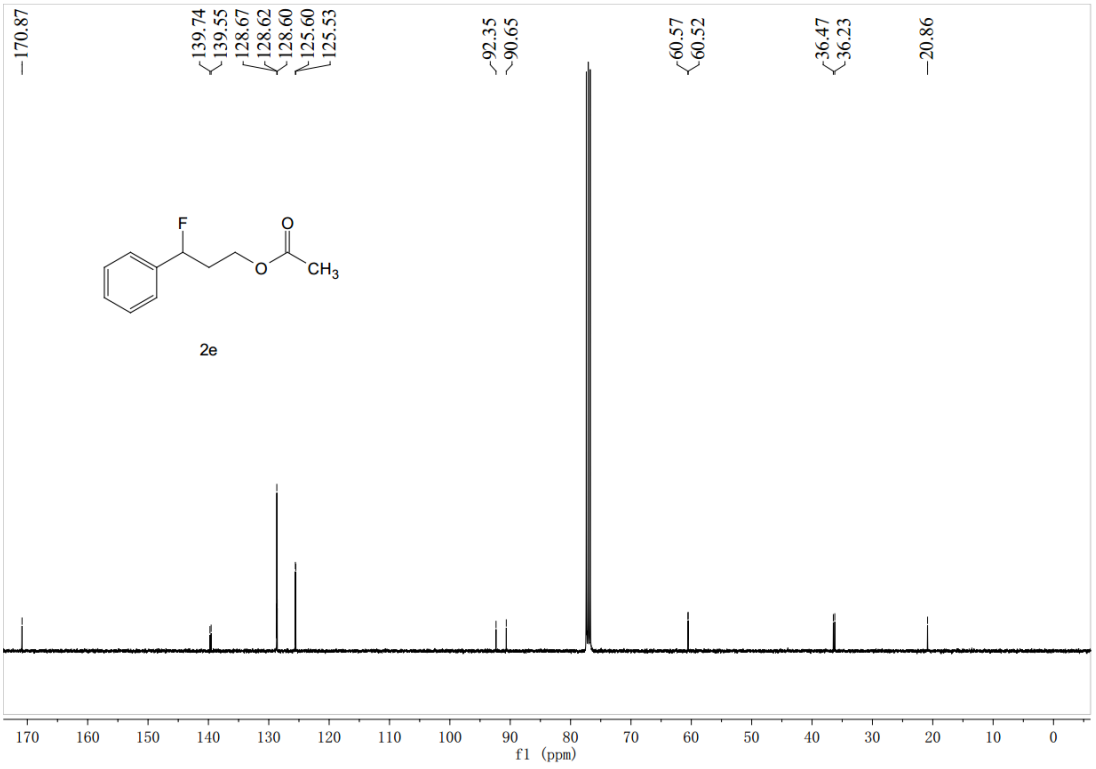
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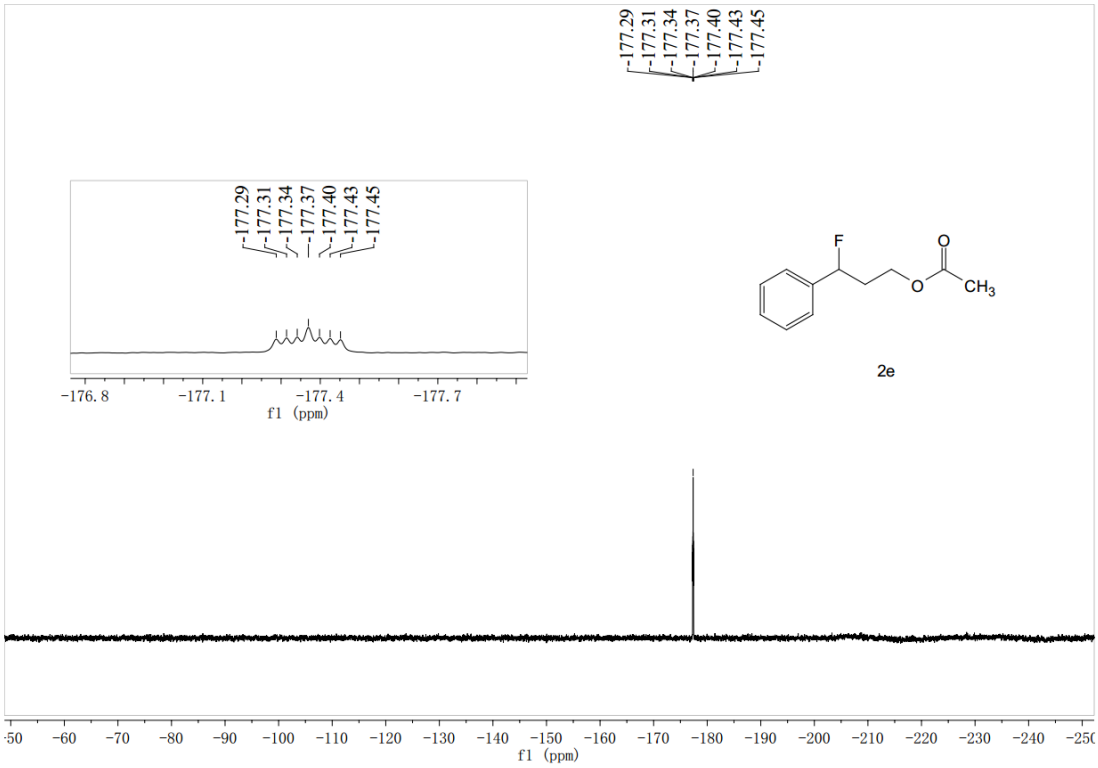
f1 (ppm)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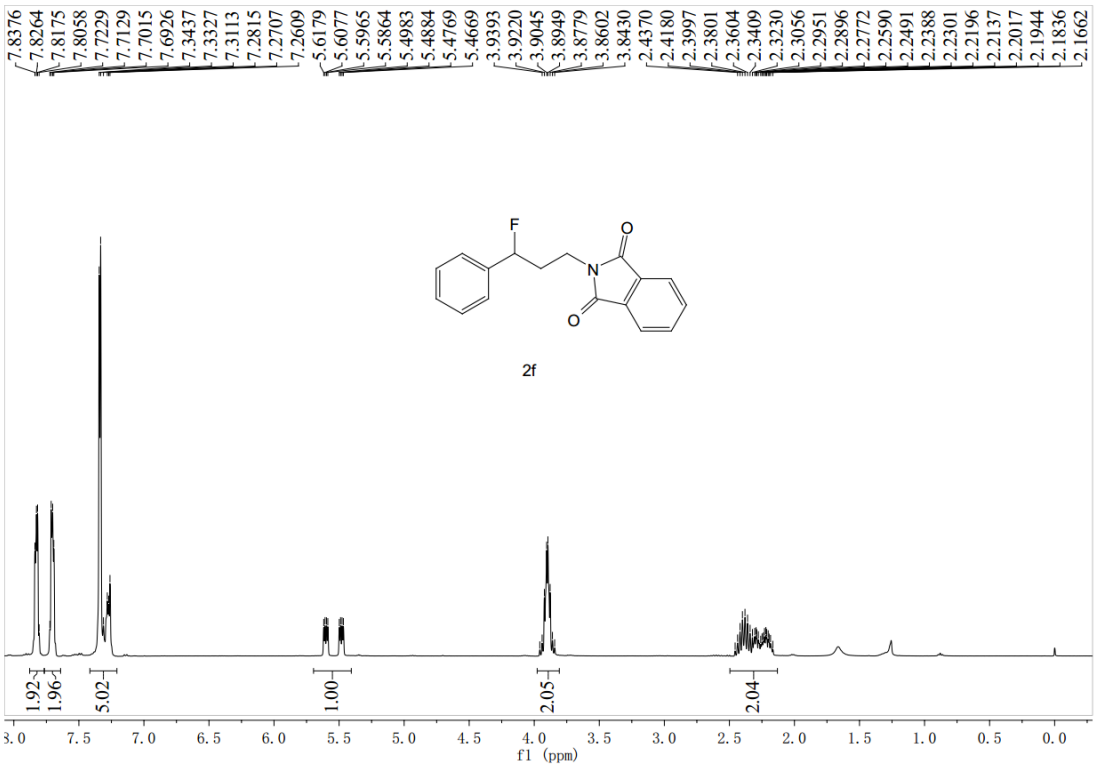
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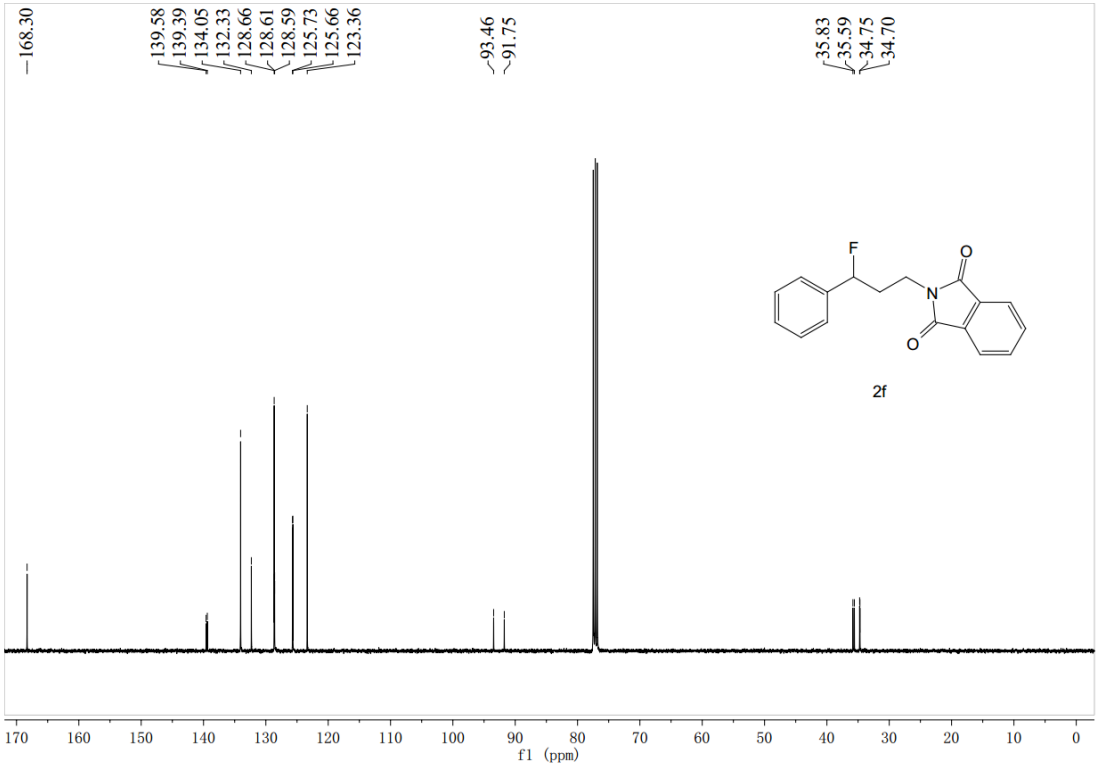
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34.70
F
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N
O
2f
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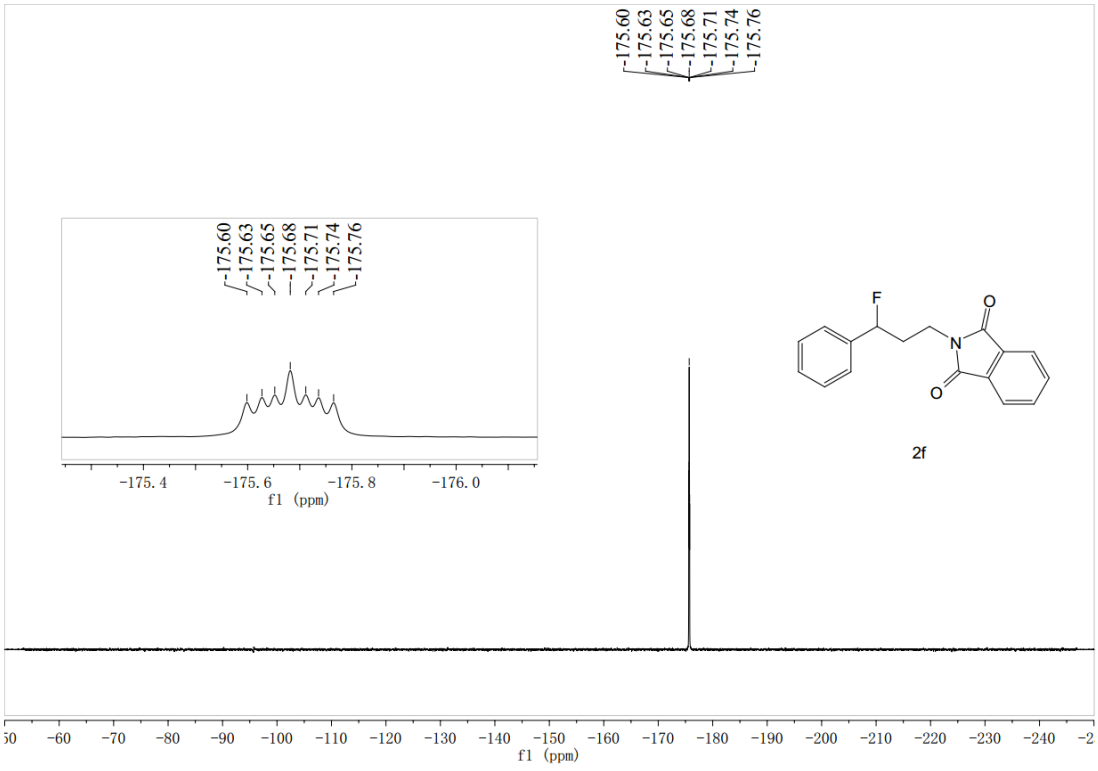
f1 (ppm)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175.74
175.76
−175.4 −175.6 −175.8 −176.0
f1 (ppm)
F
O
N
O
2f
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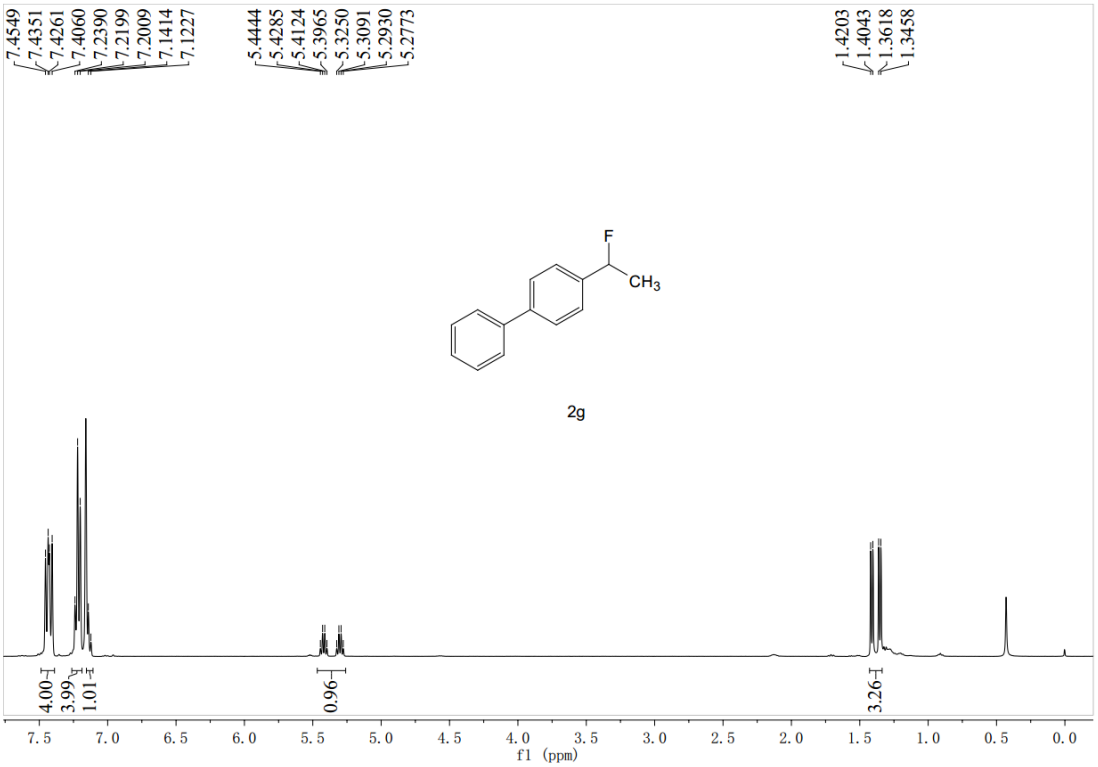
f1 (ppm)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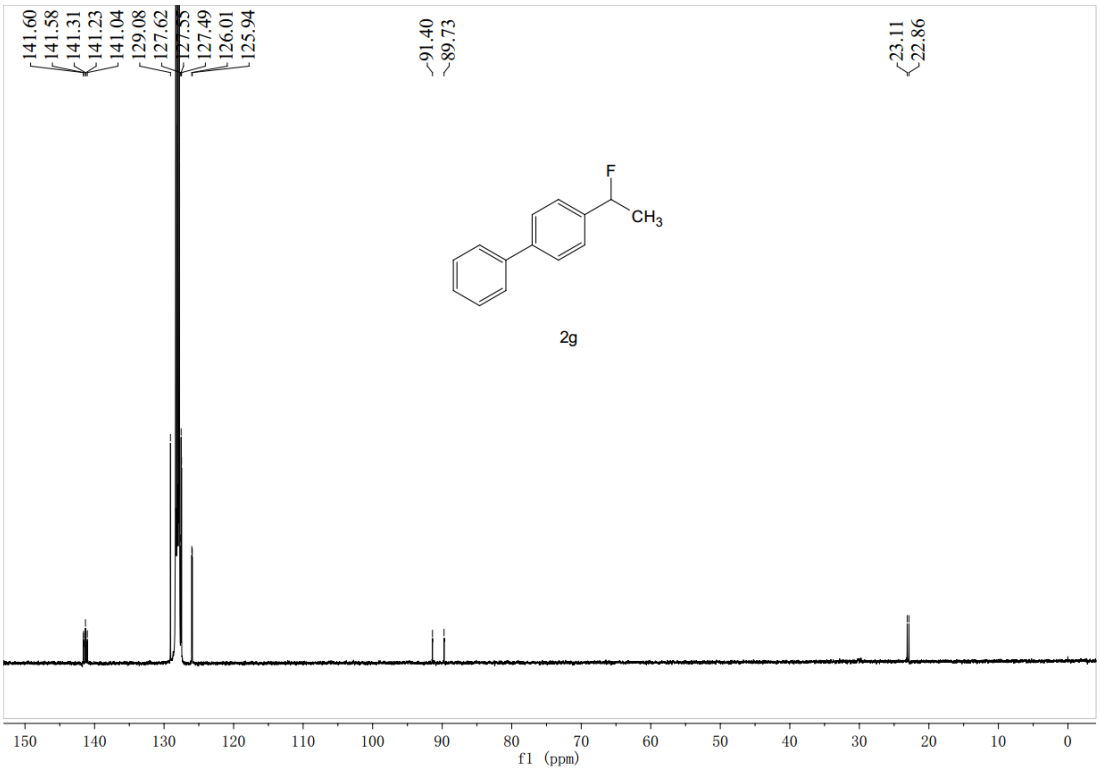
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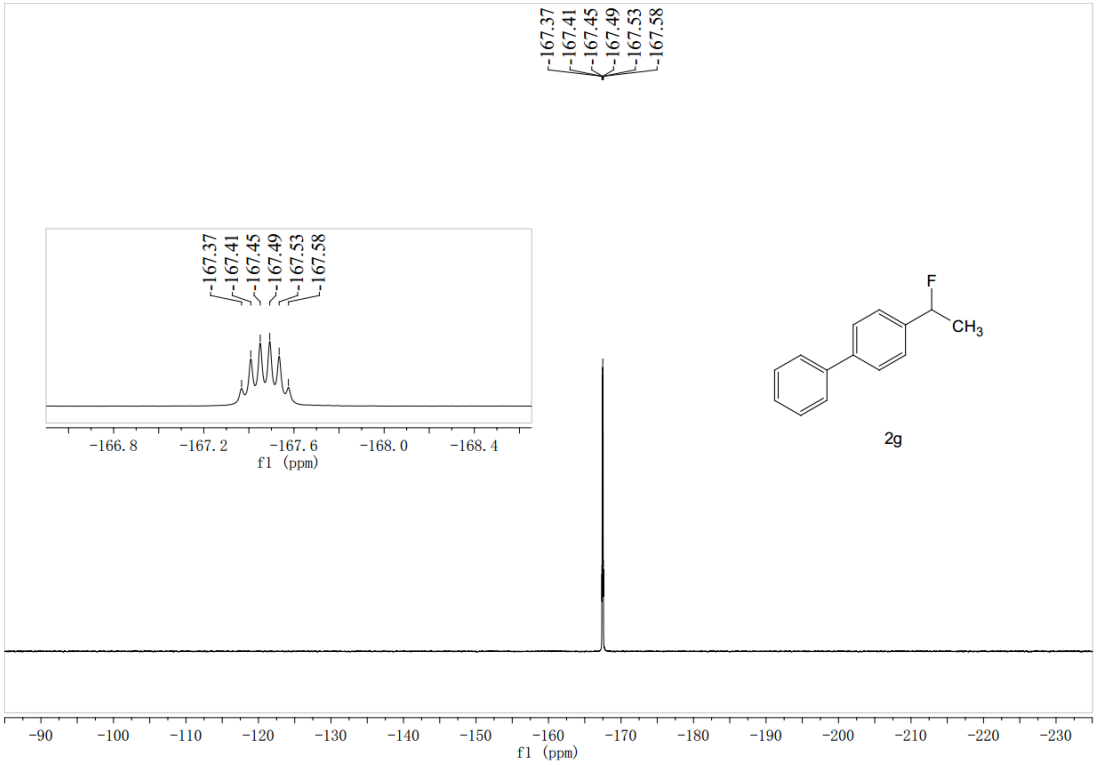
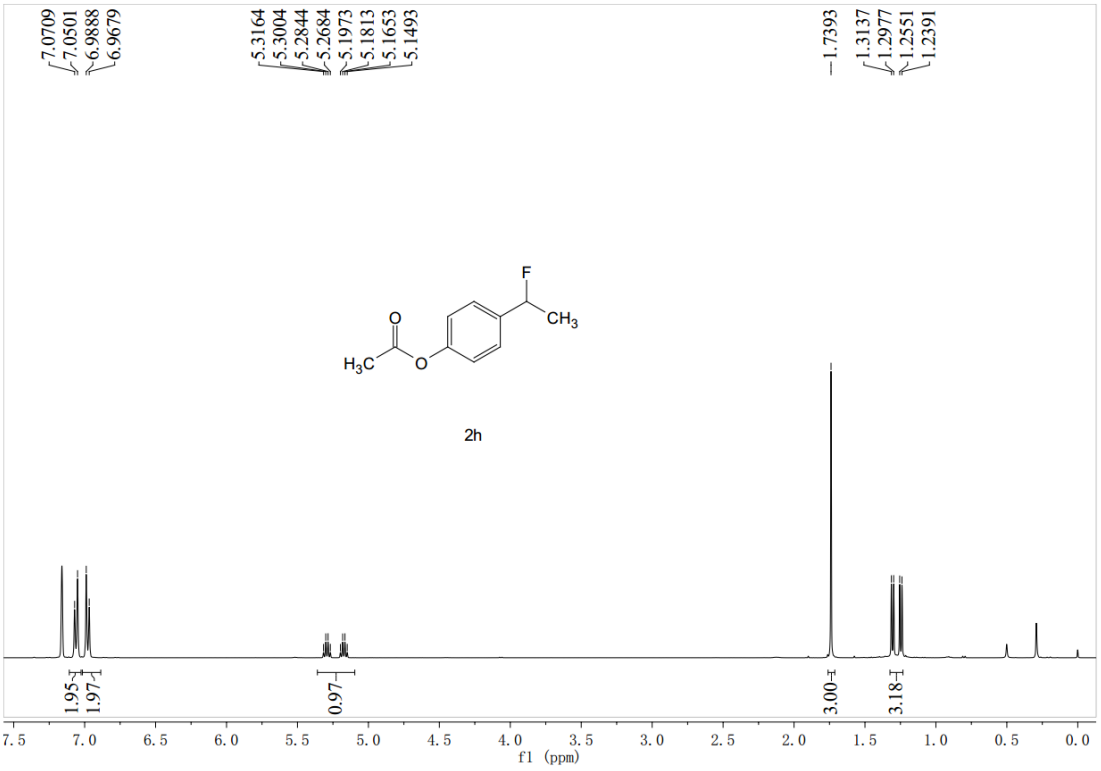
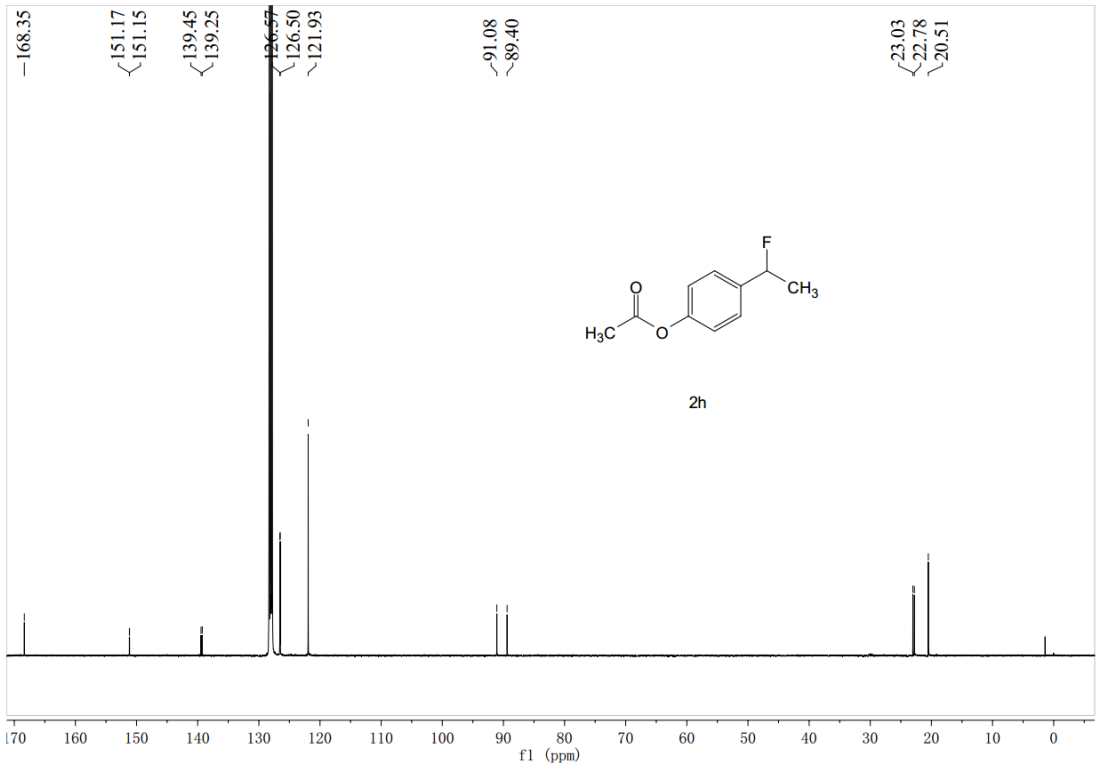
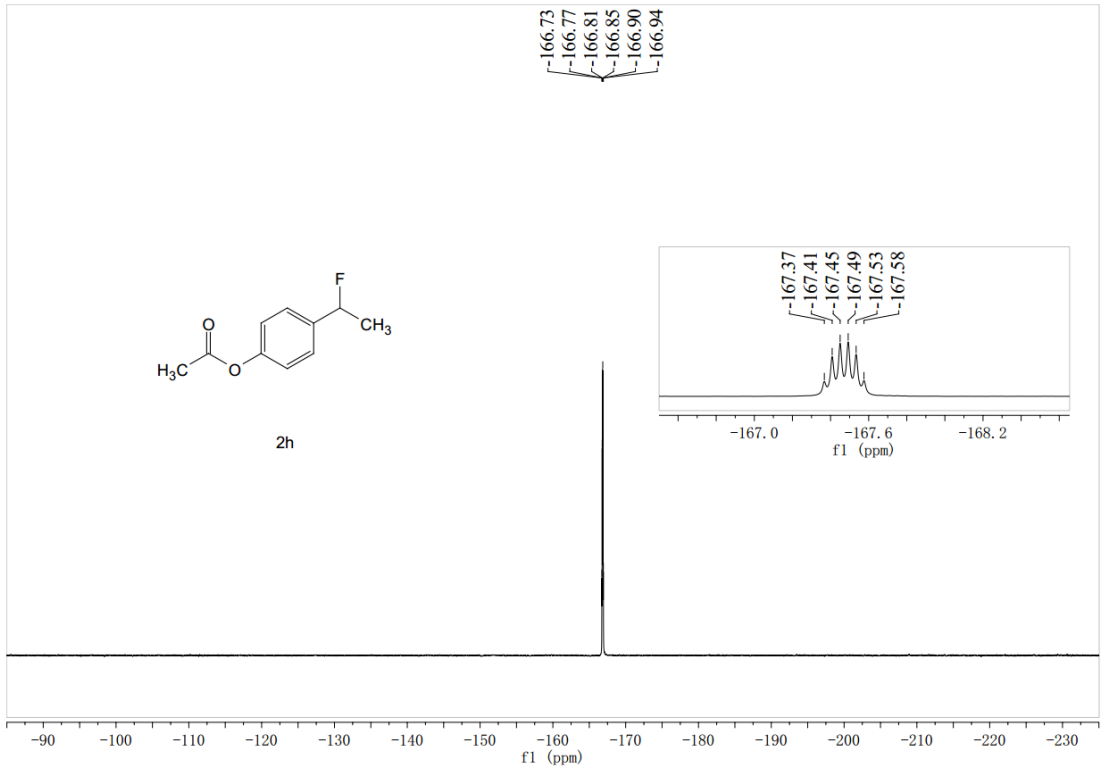
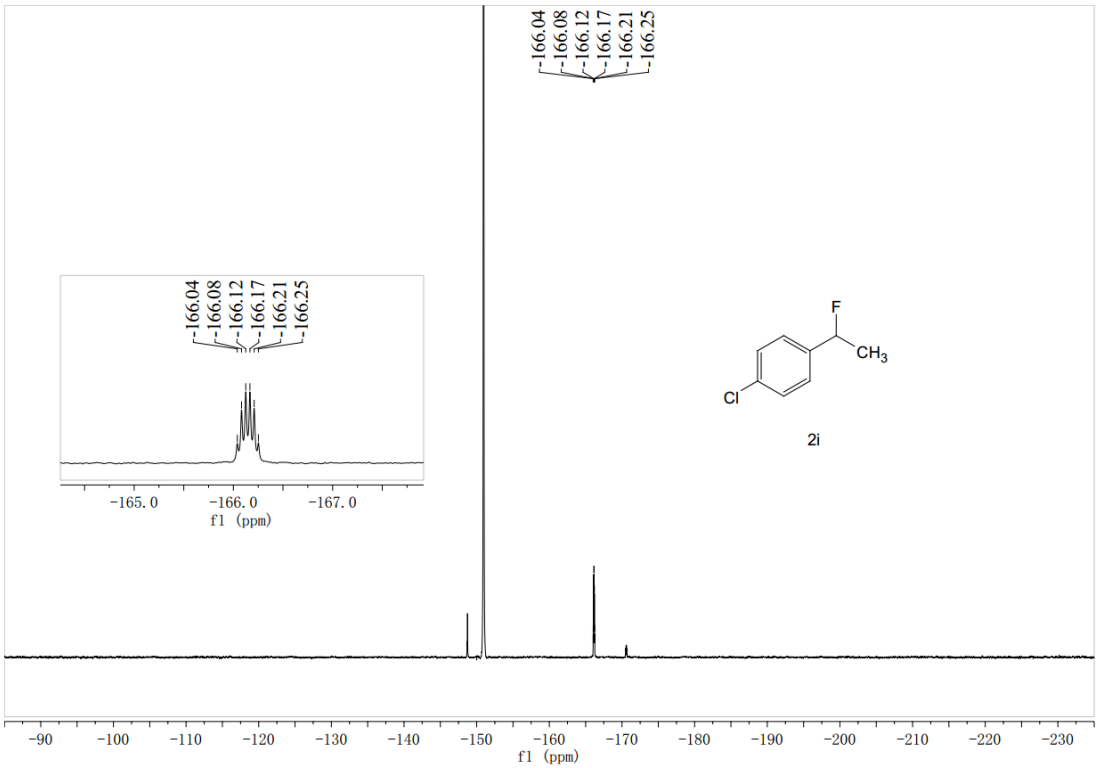
23.11
22.86
F
CH3
2g
f1 (ppm)

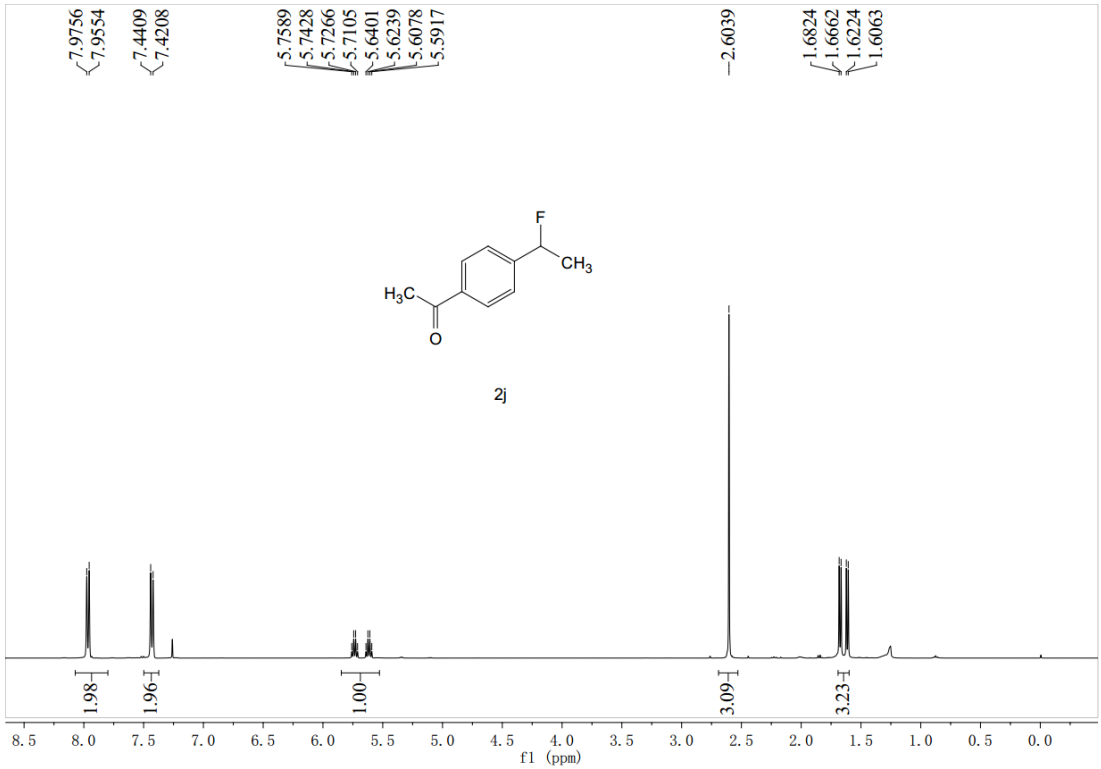

-167.37
-167.41
-167.45
-167.49
-167.53
-167.58
F
CH3
2g
-166.8
-167.2
-167.6
-168.0
-168.4
f1 (ppm)
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
f1 (ppm)

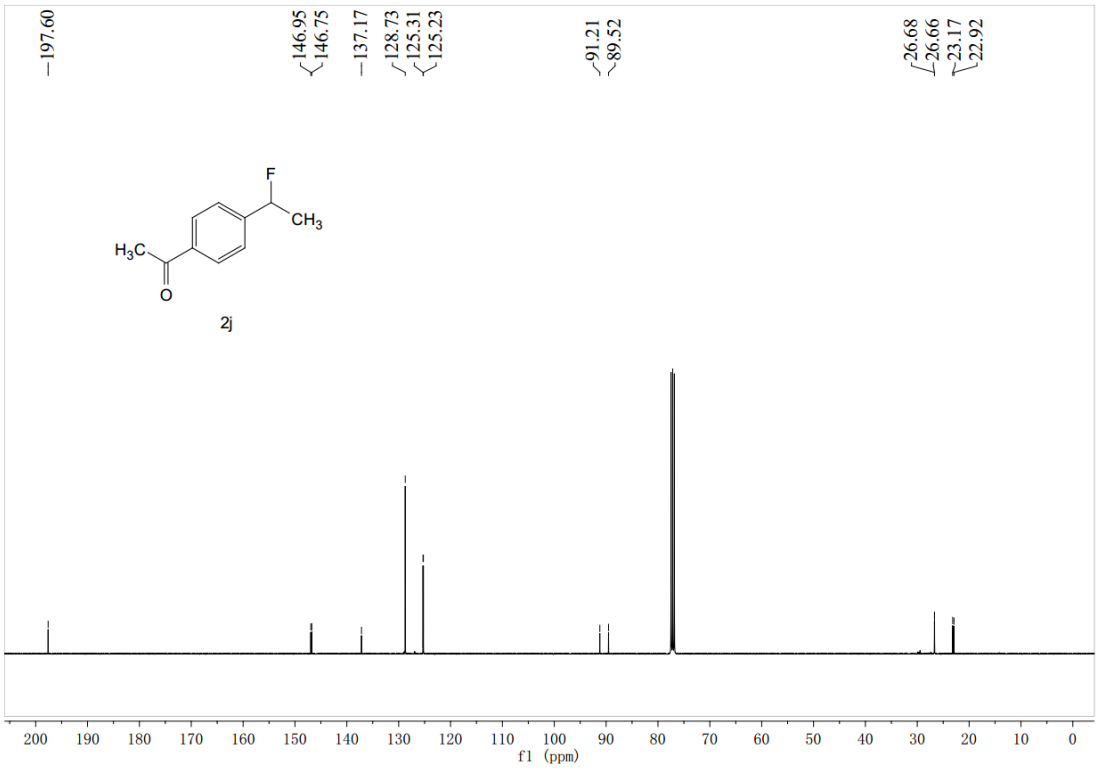

7.0709
7.0501
6.9888
6.9679
5.3164
5.3004
5.2844
5.2684
5.1973
5.1813
5.1653
5.1493
1.7393
1.3137
1.2977
1.2551
1.2391
F
CH3
O
H3C
O
2h
1.95
1.97
0.97
3.00
3.18
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

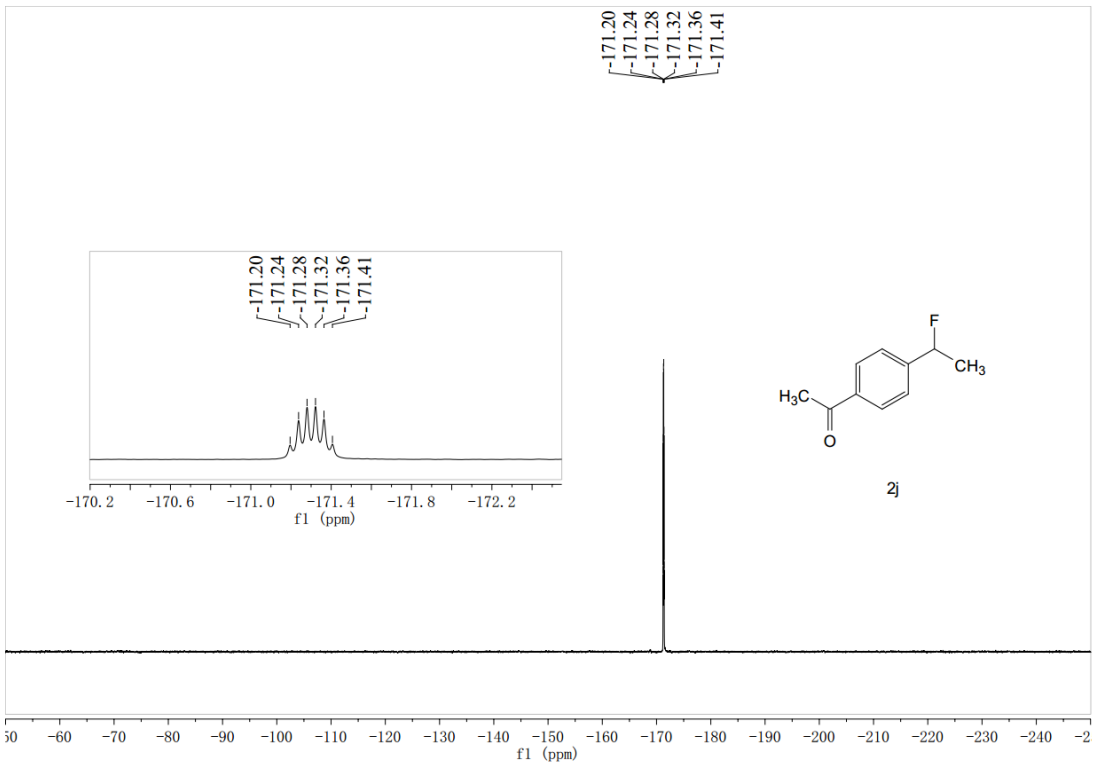

168.35
151.17
151.15
139.45
139.25
126.50
121.93
91.08
89.40
23.03
22.78
20.51
F
CH3
O
H3C
O
2h
f1 (ppm)

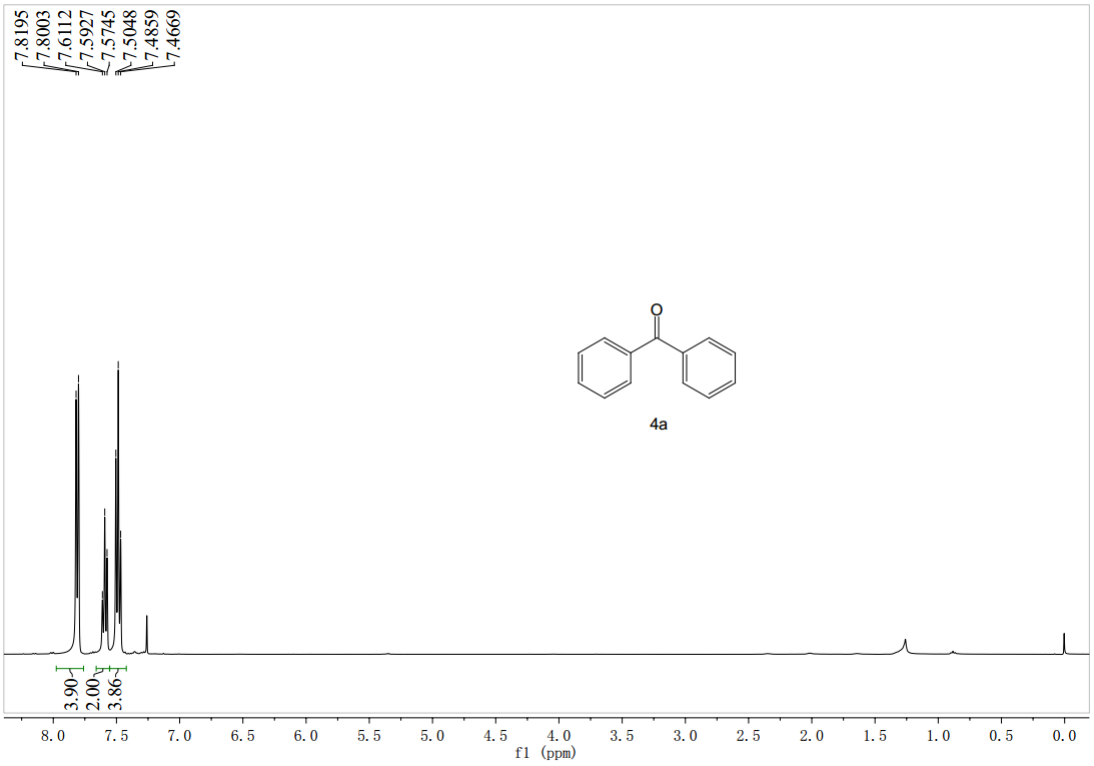

-166.73
-166.77
-166.81
-166.85
-166.90
-166.94
F
CH3
O
H3C
O
2h
-167.37
-167.41
-167.45
-167.49
-167.53
-167.58
-167.0
-167.6
-168.2
f1 (ppm)
f1 (ppm)

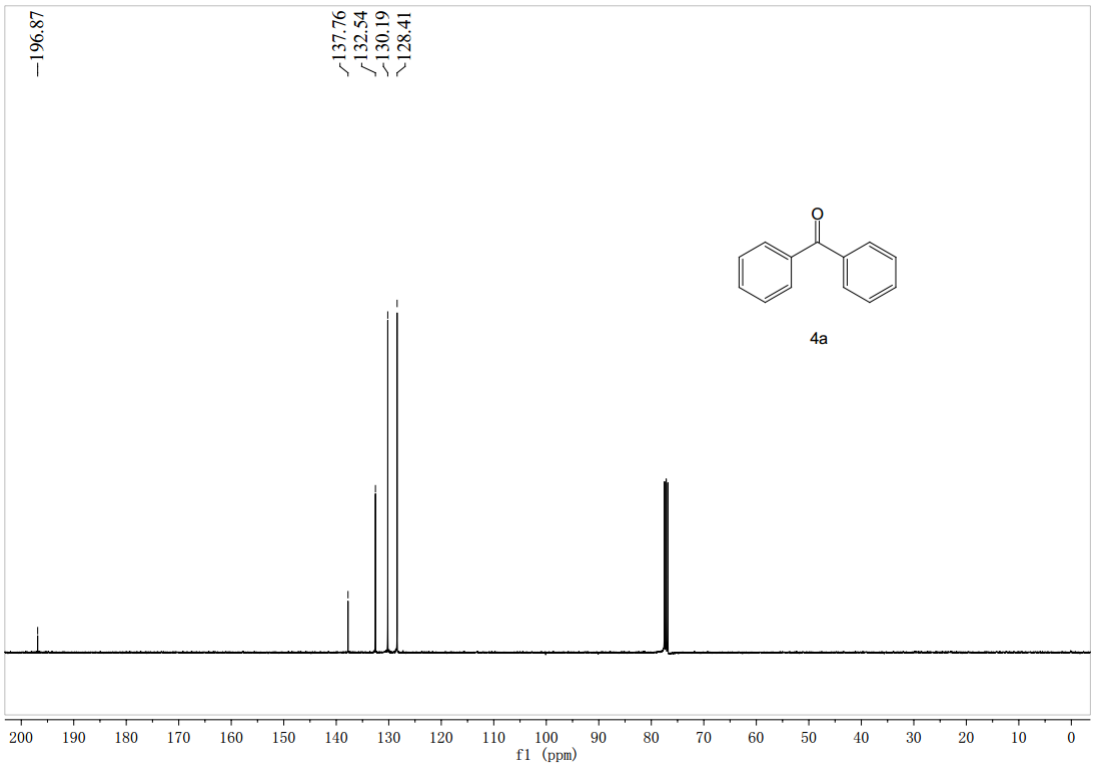

-166.04
-166.08
-166.12
-166.17
-166.21
-166.25
F
CH3
Cl
2i
f1 (ppm)

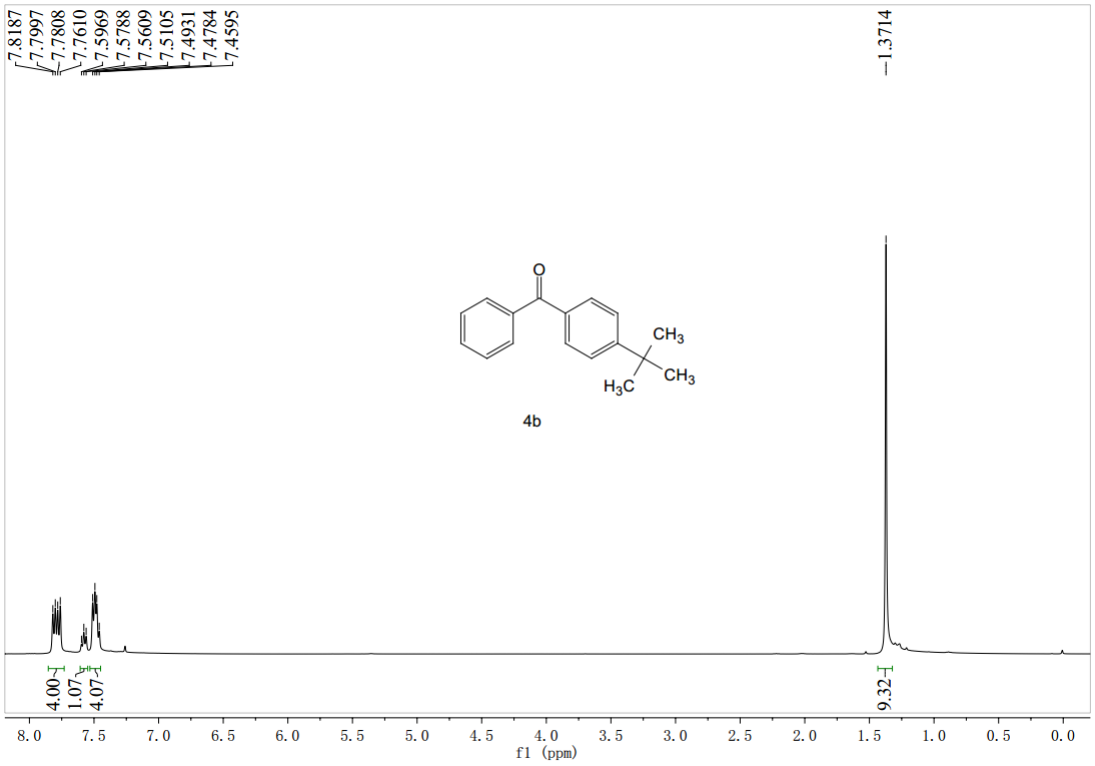

7.9756
7.9554
7.4409
7.4208
5.7589
5.7428
5.7266
5.7105
5.6401
5.6239
5.6078
5.5917
2.6039
1.6824
1.6662
1.6224
1.6063
F
CH3
H3C
O
2j
1.98
1.96
1.00
3.09
3.23
f1 (ppm)

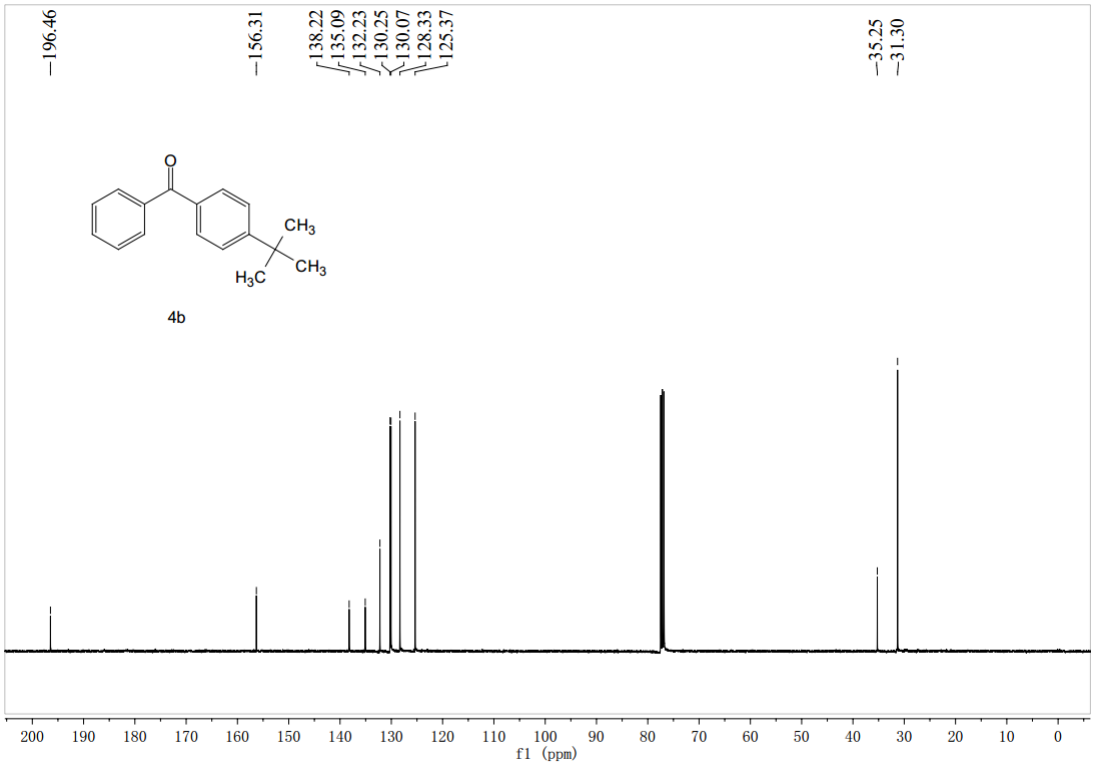

197.60
146.95
146.75
137.17
128.73
125.31
125.23
91.21
89.52
26.68
26.66
23.17
22.92
F
CH3
H3C
O
2j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

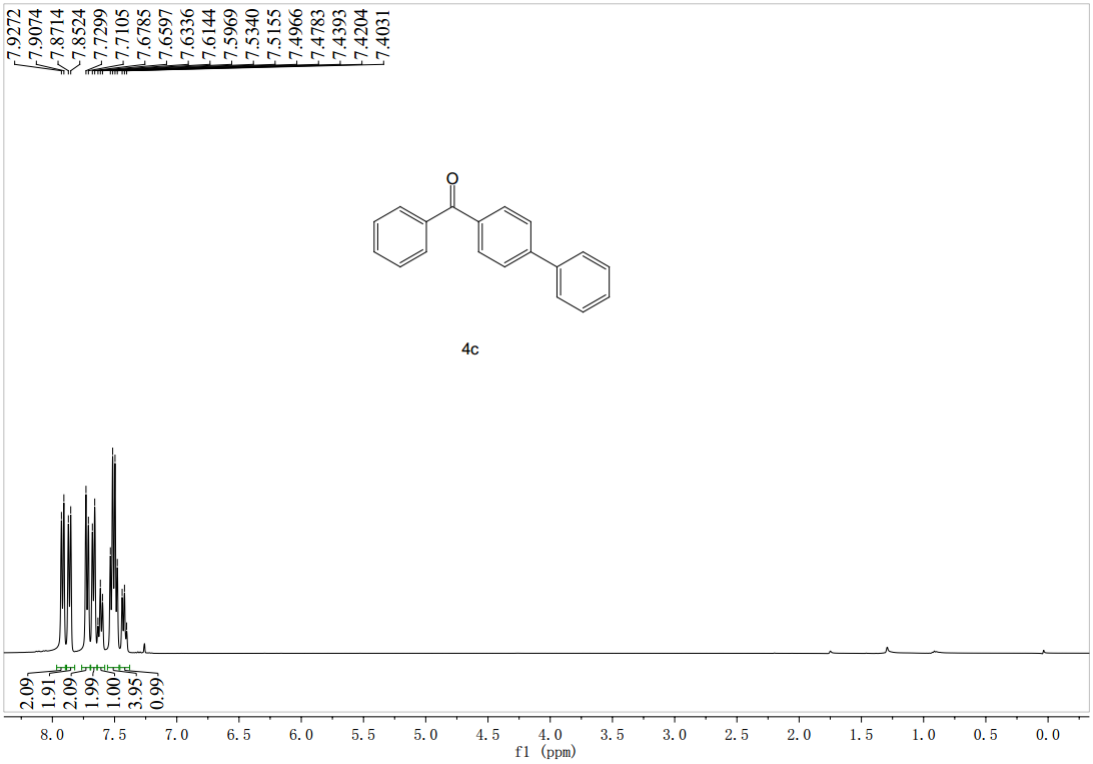

171.20
171.24
171.28
171.32
171.36
171.41
171.20
171.24
171.28
171.32
171.36
171.41
−170.2 −170.6 −171.0 −171.4 −171.8 −172.2
f1 (ppm)
F
CH3
H3C
O
2j
50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −2
f1 (ppm)

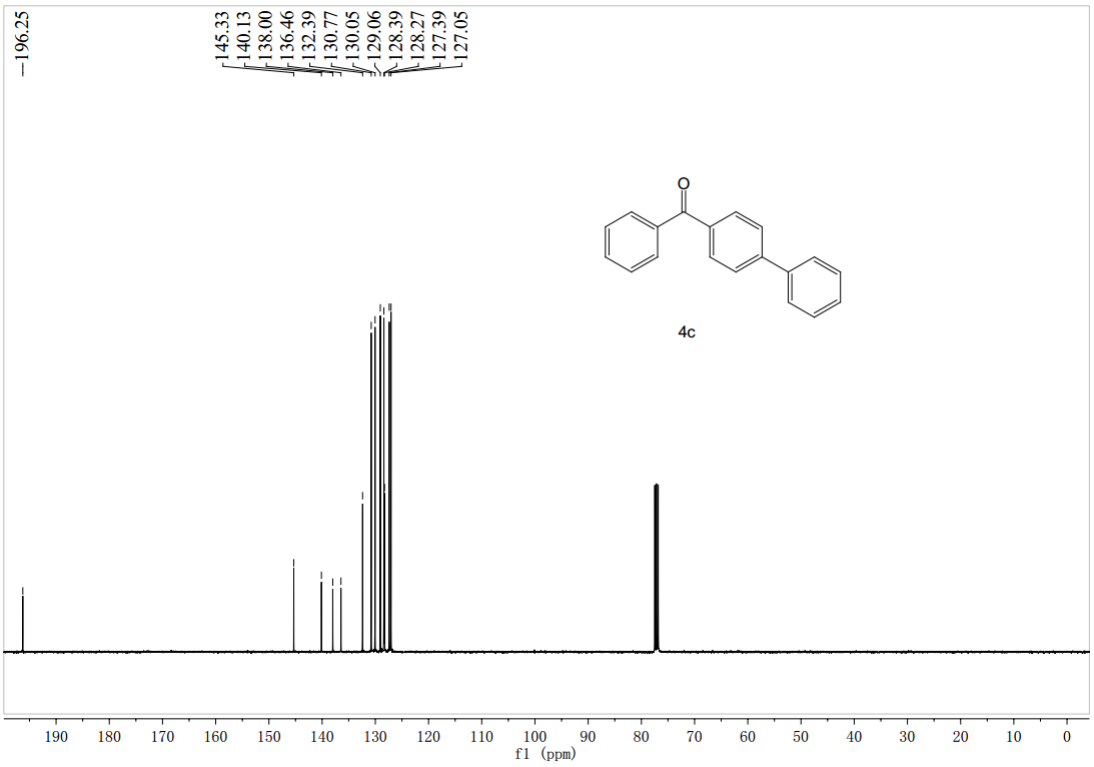

7.8195
7.8003
7.6112
7.5927
7.5745
7.5048
7.4859
7.4669
3.90
2.00
3.86
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
4a

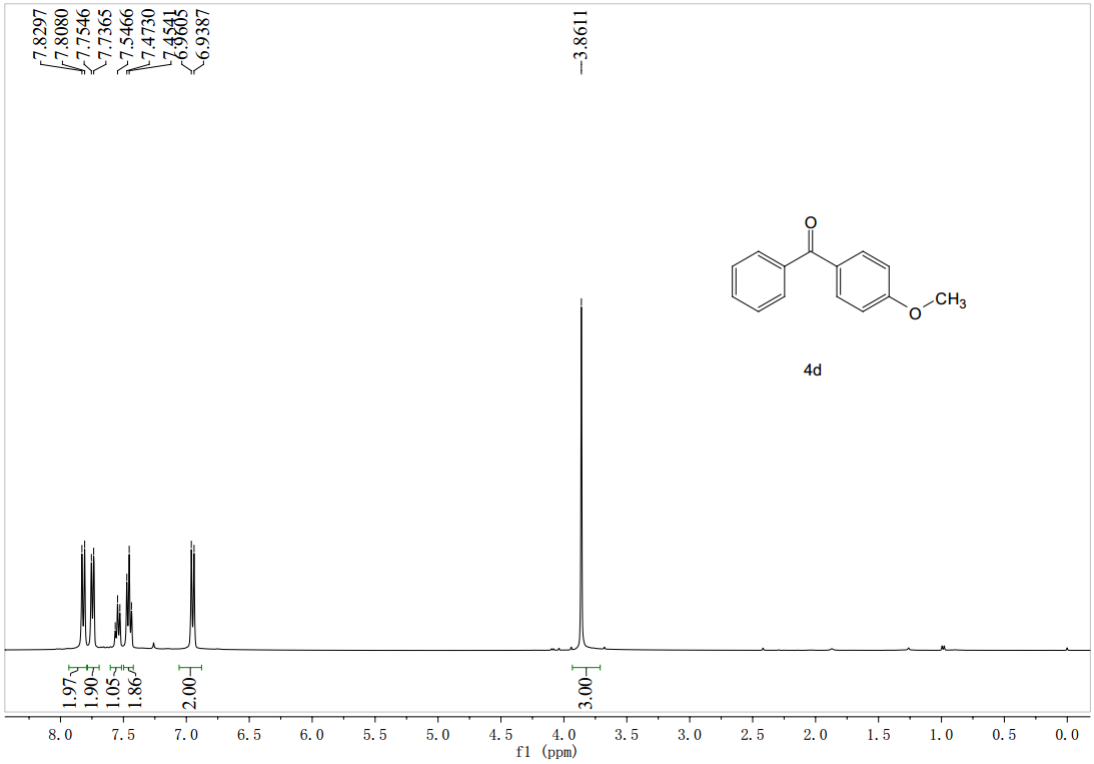

196.87
137.76
132.54
130.19
128.41
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
4a

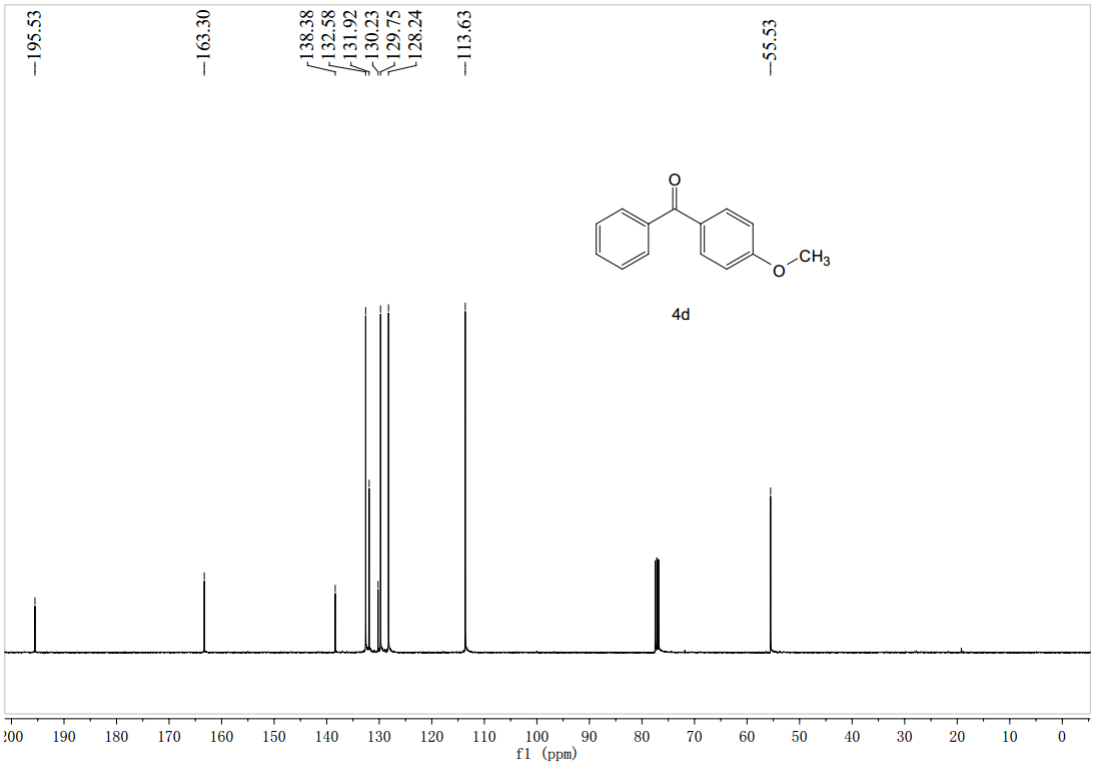

7.8187
7.7997
7.7808
7.7610
7.5969
7.5788
7.5609
7.5105
7.4931
7.4784
7.4595
1.3714
O
CH3
H3C
CH3
4b
4.00
1.07
4.07
9.32
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

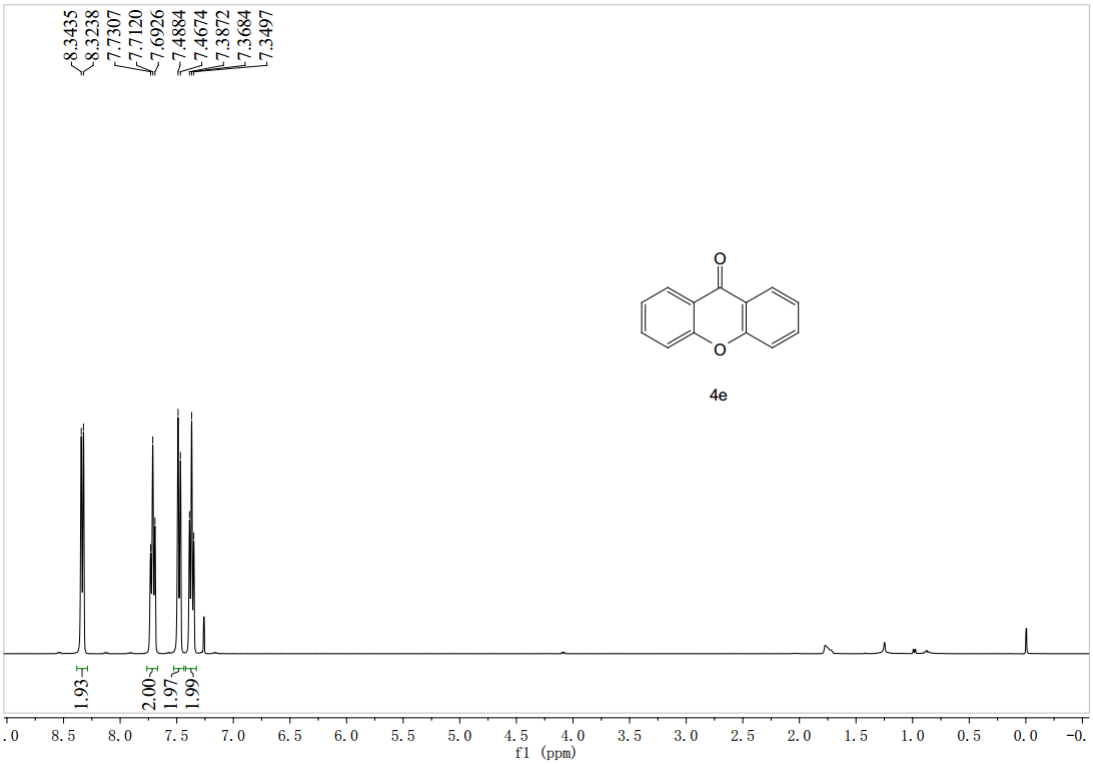

196.46
156.31
138.22
135.09
132.23
130.25
130.07
128.33
125.37
35.25
31.30
O
CH3
H3C
CH3
4b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

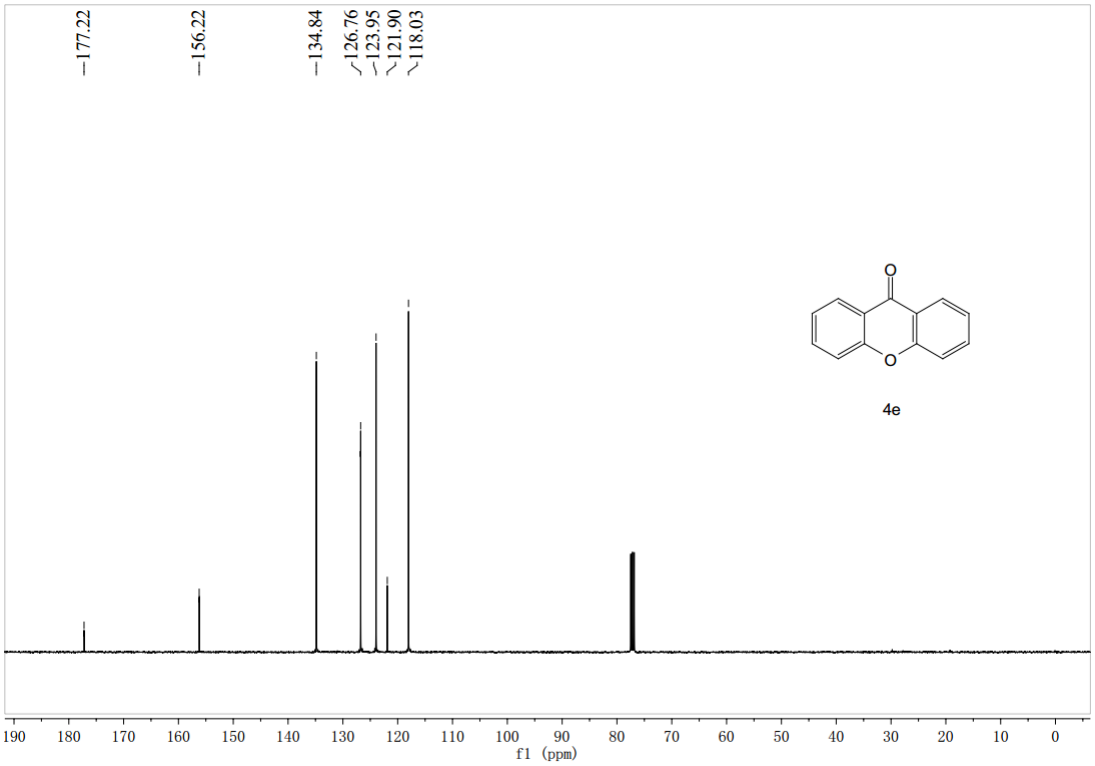

7.9272
7.9074
7.8714
7.8524
7.7299
7.7105
7.6785
7.6597
7.6336
7.6144
7.5969
7.5340
7.5155
7.4966
7.4783
7.4393
7.4204
7.4031
O
4c
2.09
1.91
2.09
1.99
1.00
3.95
0.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

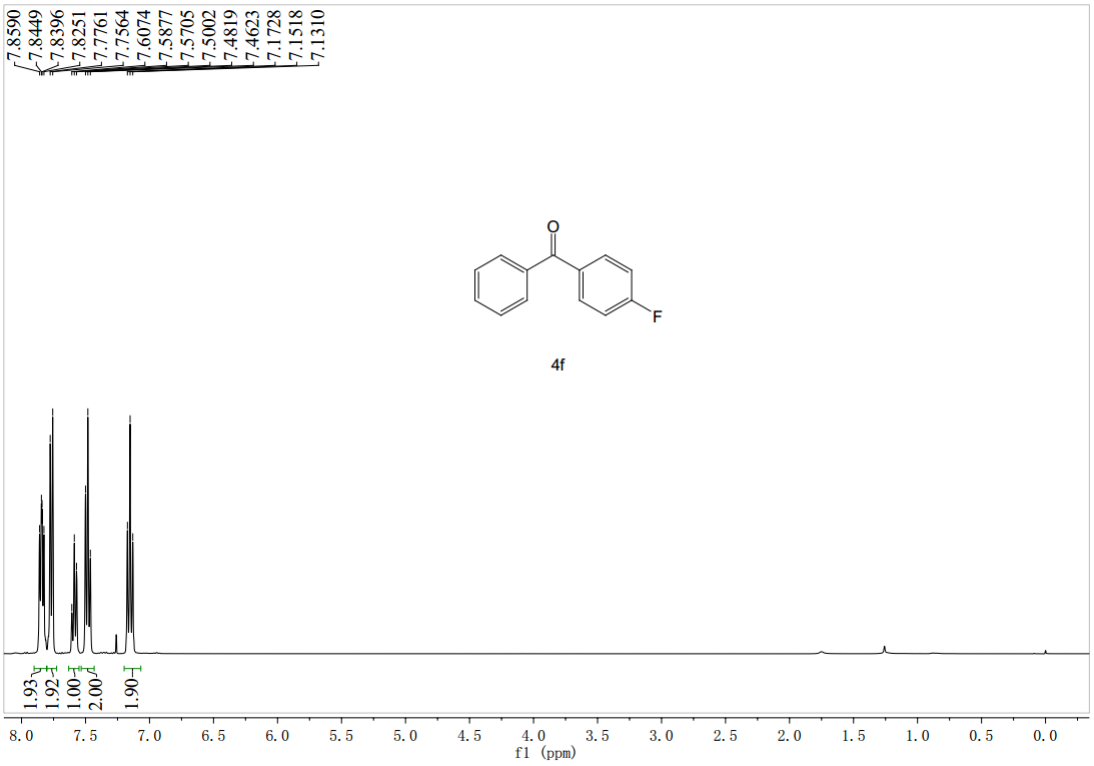

196.25
145.33
140.13
138.00
136.46
132.39
130.77
130.05
129.06
128.39
128.27
127.39
127.05
O
4c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

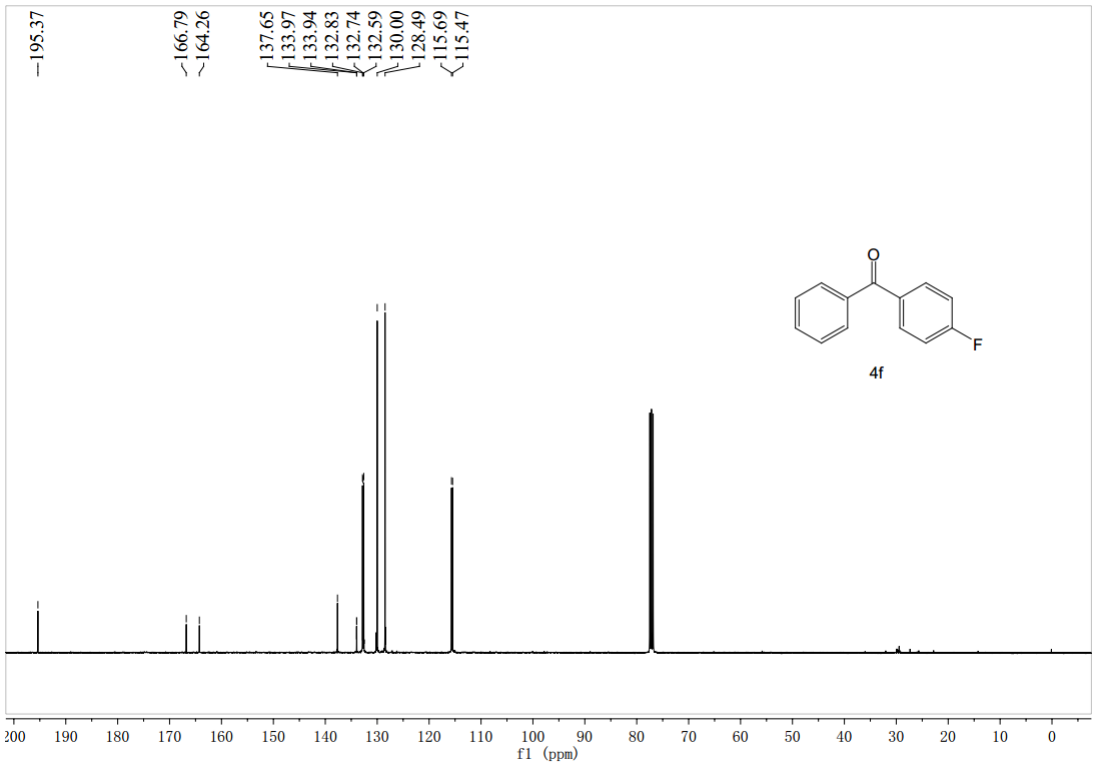

7.8297
7.8080
7.7546
7.7365
7.5466
7.4730
7.4541
6.9605
6.9387
3.8611
O
O
CH3
4d
1.97
1.90
1.05
1.86
2.00
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

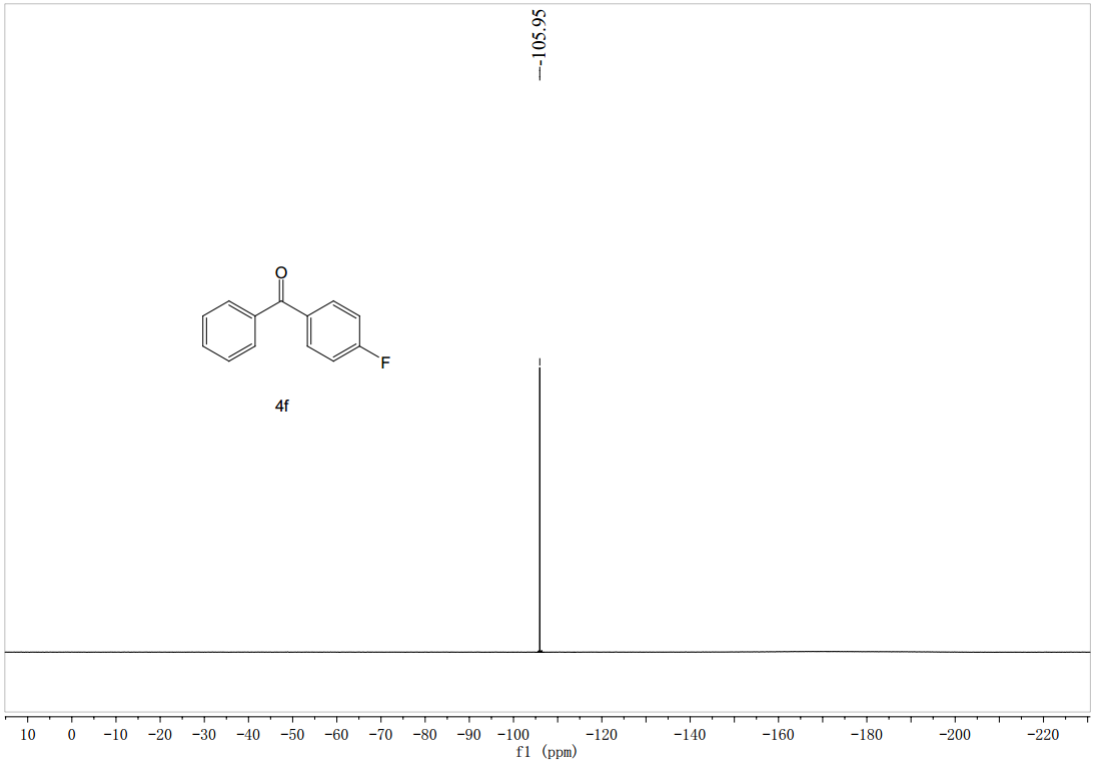

195.53
163.30
138.38
132.58
131.92
130.23
129.75
128.24
113.63
55.53
O
O
CH3
4d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

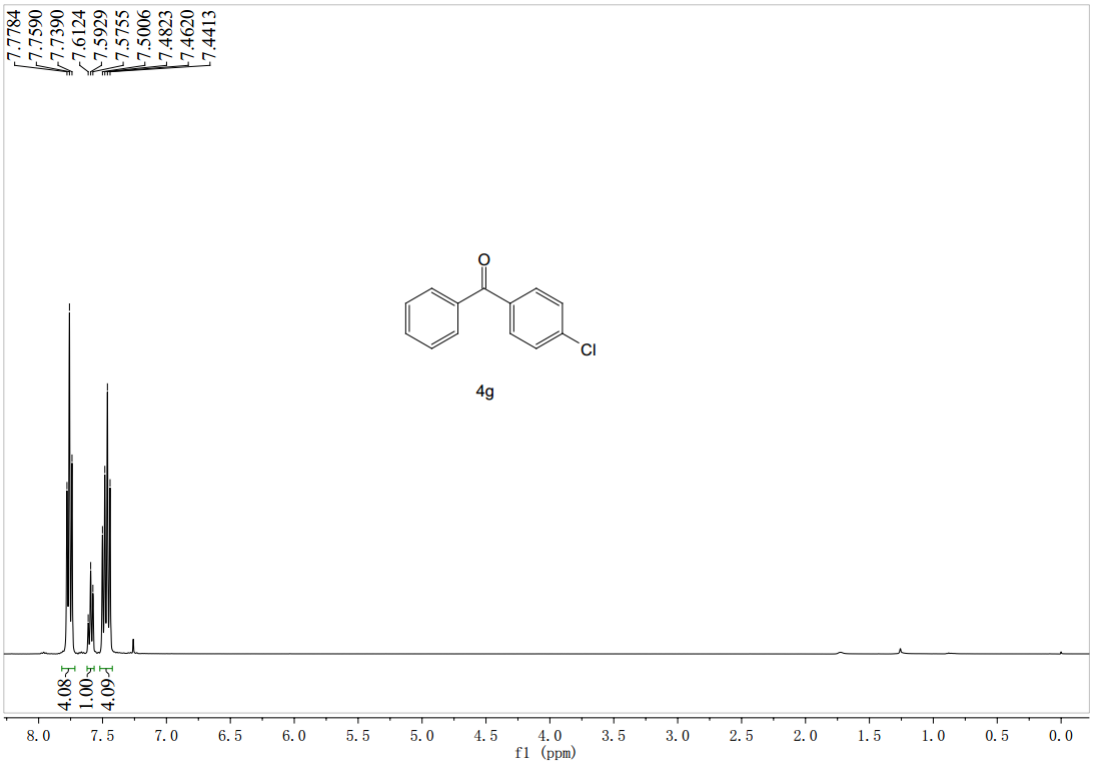

8.3435
8.3238
7.7307
7.7120
7.6926
7.4884
7.4674
7.3872
7.3684
7.3497
O
O
4e
1.93
2.00
1.97
1.99
f1 (ppm)

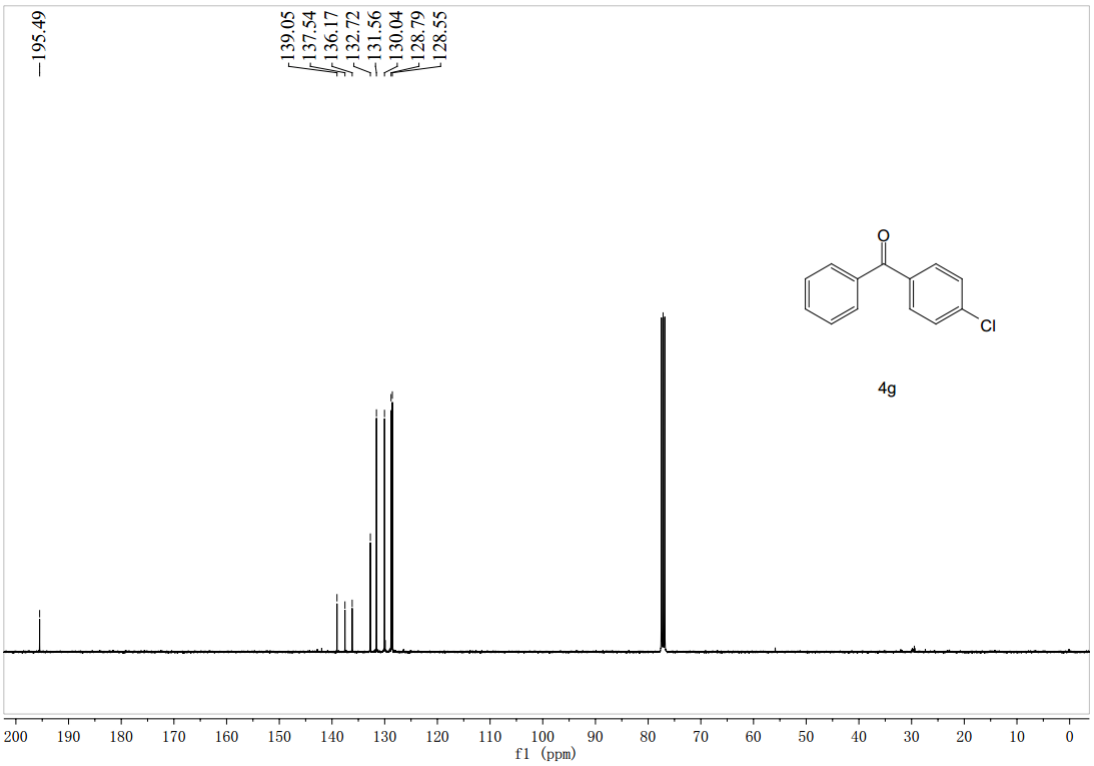

177.22
156.22
134.84
126.76
123.95
121.90
118.03
O
O
4e
f1 (ppm)

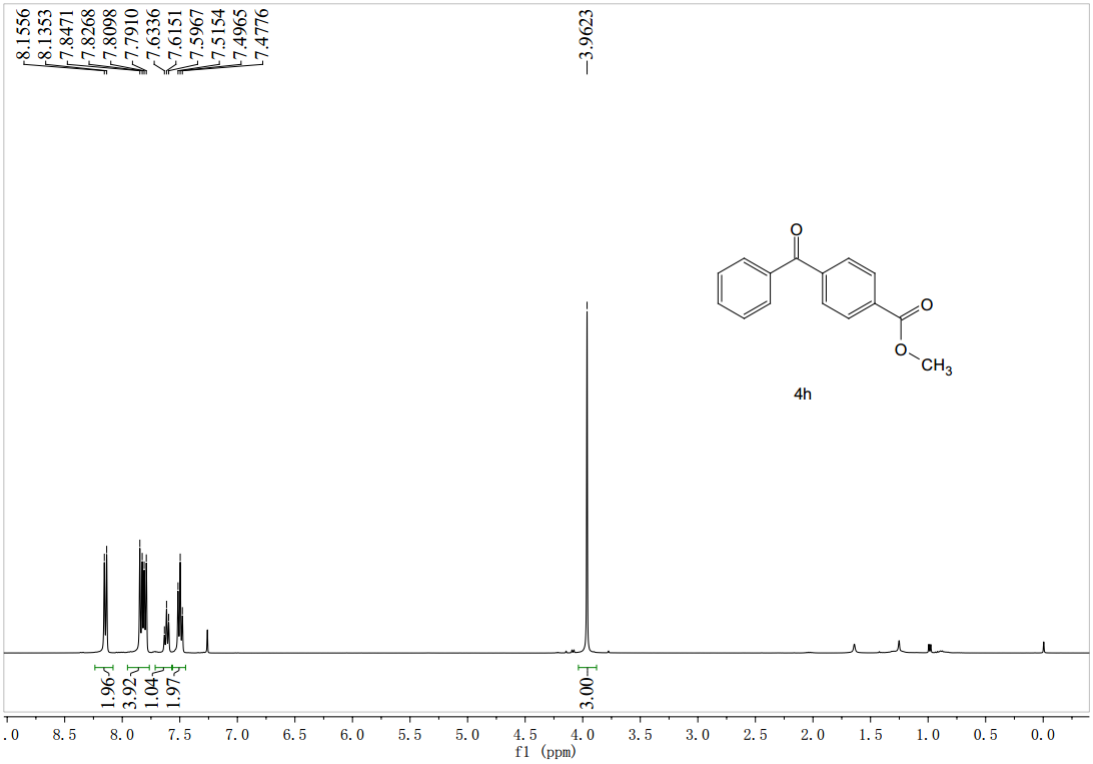

7.8590
7.8449
7.8396
7.8251
7.7761
7.7564
7.6074
7.5877
7.5705
7.5002
7.4819
7.4623
7.1728
7.1518
7.1310
O
F
4f
1.93
1.92
1.00
2.00
1.90
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.37
166.79
164.26
137.65
133.97
133.94
132.83
132.74
132.59
130.00
128.49
115.69
115.47
O
F
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-105.95
O
F
4f
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)


7.7784
7.7590
7.7390
7.6124
7.5929
7.5755
7.5006
7.4823
7.4620
7.4413
O
Cl
4g
4.08
1.00
4.09
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.49
139.05
137.54
136.17
132.72
131.56
130.04
128.79
128.55
O
Cl
4g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.1556
8.1353
7.8471
7.8268
7.8098
7.7910
7.6336
7.6151
7.5967
7.5154
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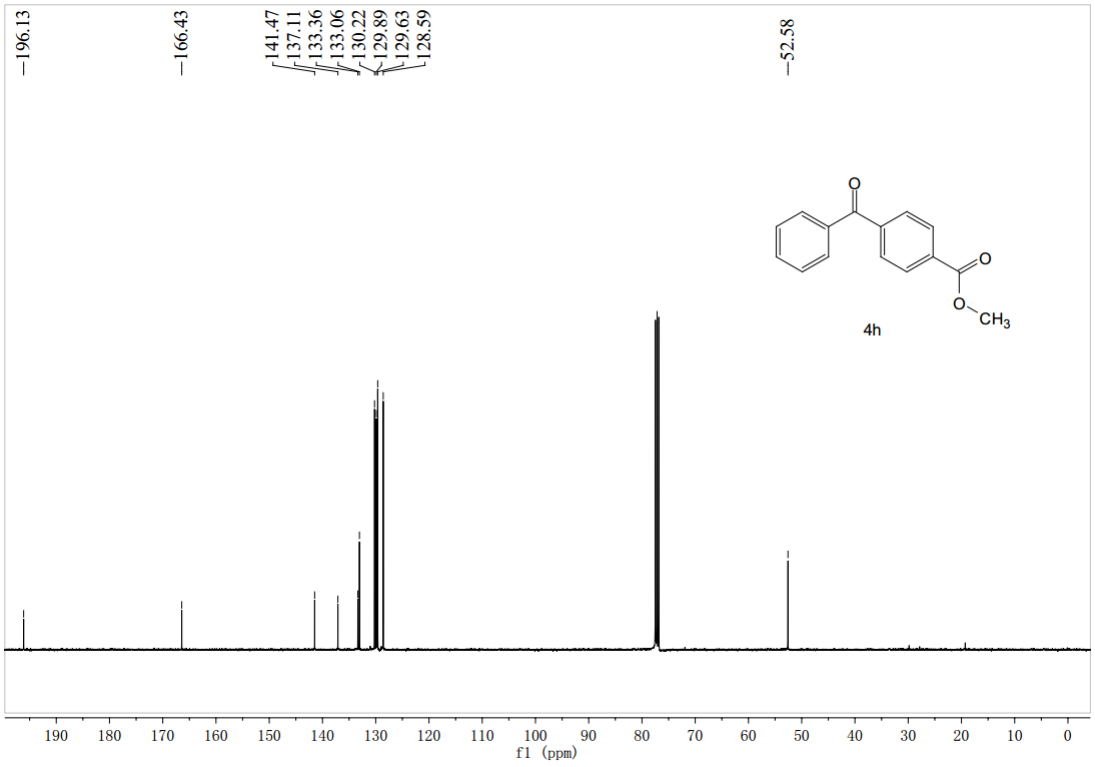
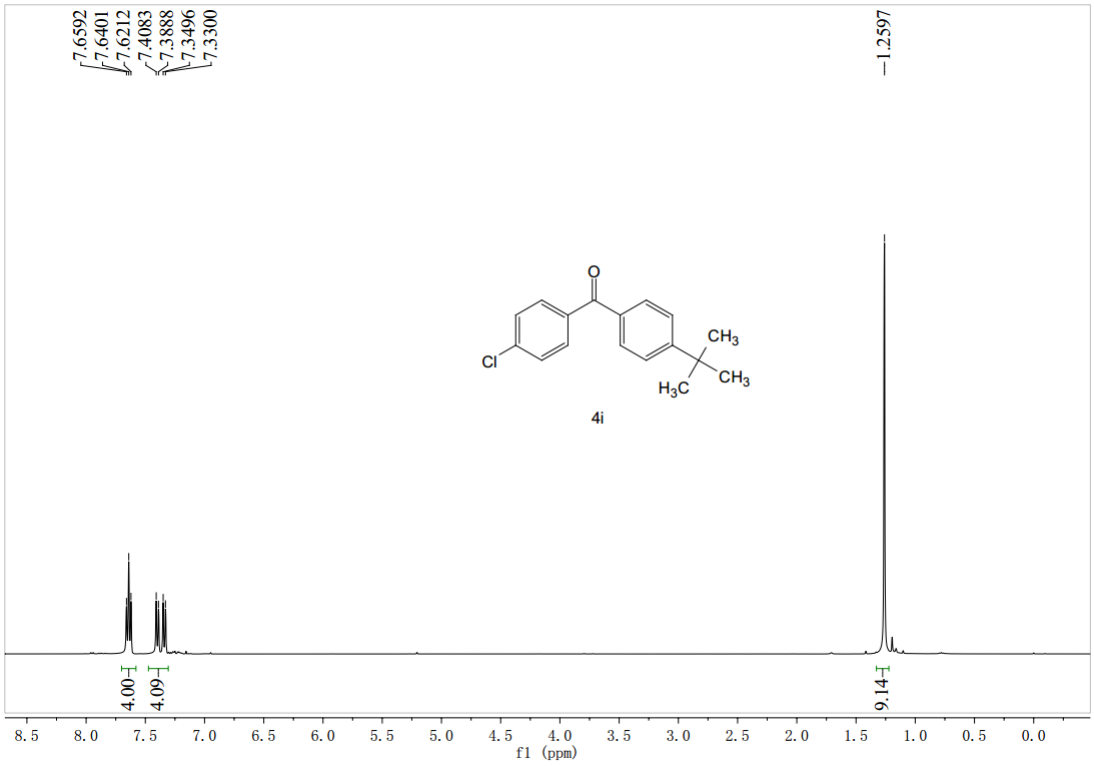
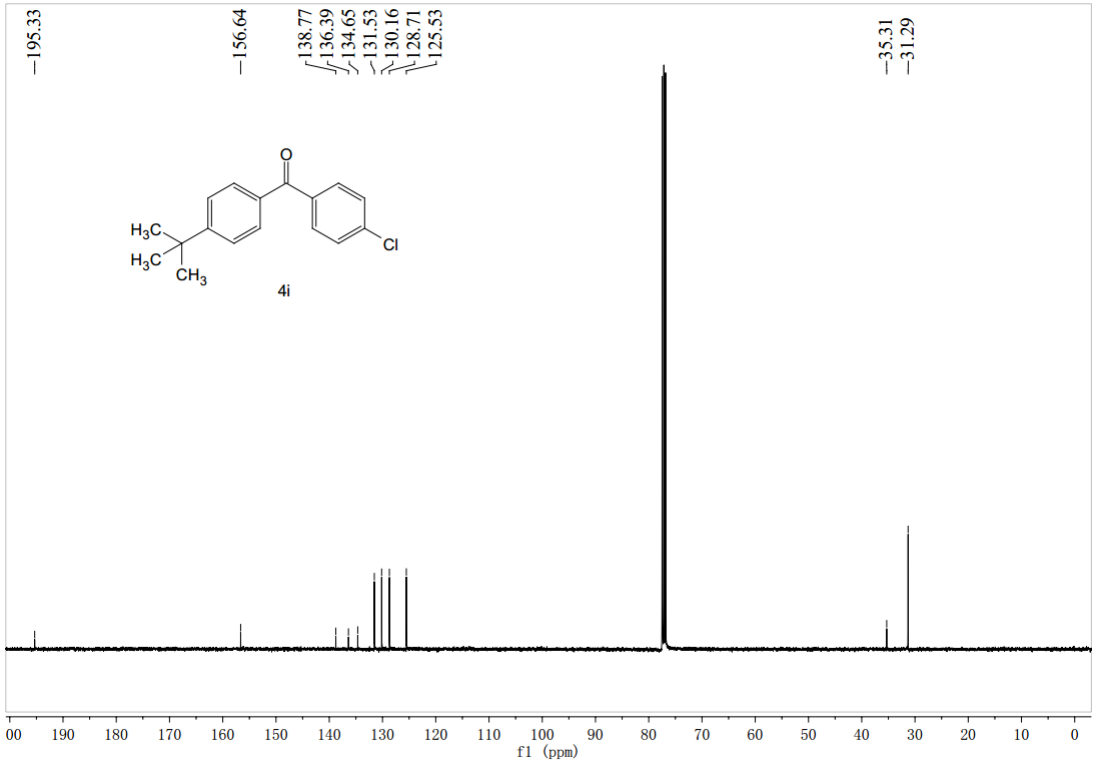
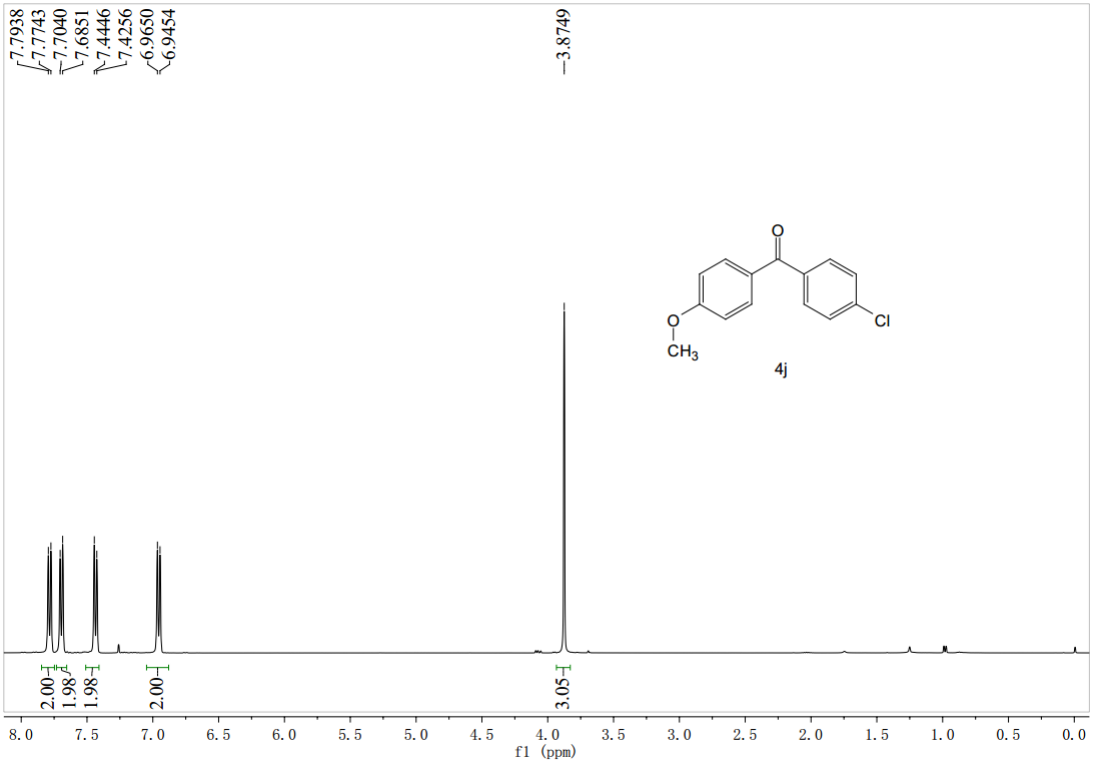
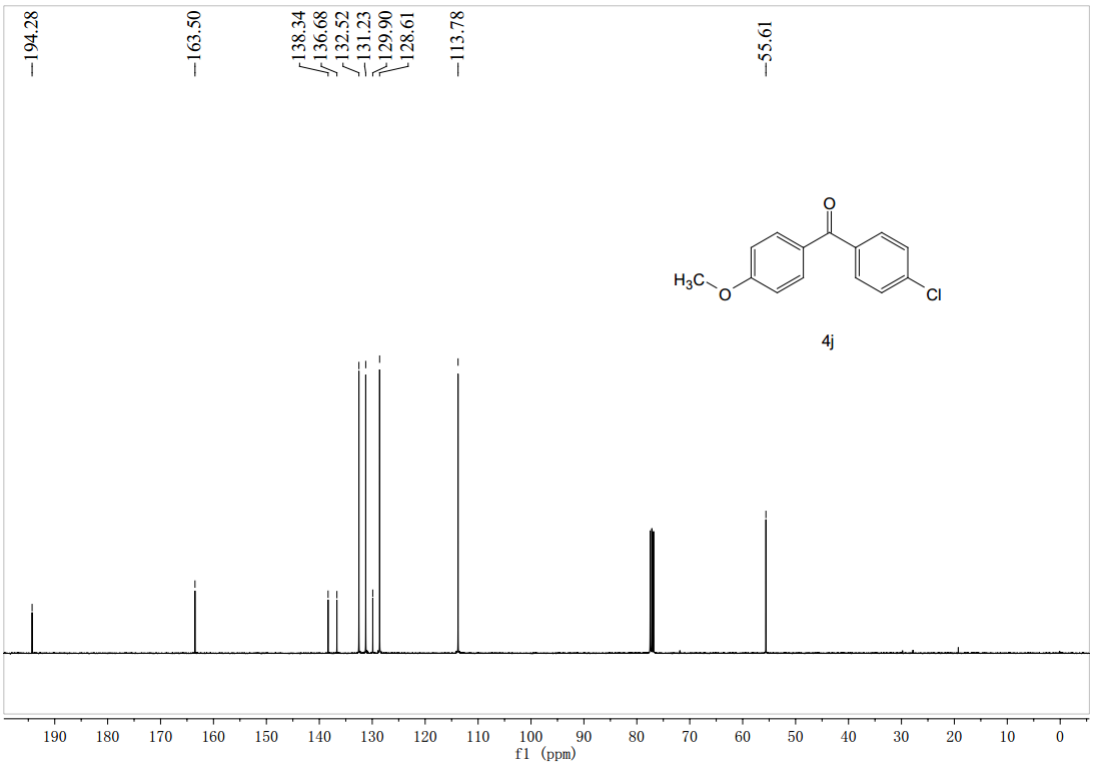
3.92
1.04
1.97
3.00
4h
f1 (ppm)


196.13
166.43
141.47
137.11
133.36
133.06
130.22
129.89
129.63
128.59
52.58
4h
f1 (ppm)


7.6592
7.6401
7.6212
7.4083
7.3888
7.3496
7.3300
1.2597
O
Cl
CH3
H3C
CH3
4i
4.00
4.09
9.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


195.33
156.64
138.77
136.39
134.65
131.53
130.16
128.71
125.53
35.31
31.29
O
H3C
H3C
CH3
Cl
4i
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.7938
7.7743
7.7040
7.6851
7.4446
7.4256
6.9650
6.9454
3.8749
O
O
CH3
Cl
4j
2.00
1.98
1.98
2.00
3.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


194.28
163.50
138.34
136.68
132.52
131.23
129.90
128.61
113.78
55.61
O
H3C
O
Cl
4j
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)