Supporting Information

Solvent-free base-controlled addition reaction of *H*-phosphonates and *H*-phosphine oxides to α-CF_3 styrenes: facile synthesis of β-CF_3-substituted phosphonates and phosphine oxides

Qianding Zeng,[a] Ying Liu,[a] Jingjing He,[a] Yupian Deng,[a] Pai Zheng,[a] Zhudi Sun,[a] and Song Cao*[a,b]

[a]*Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (ECUST), Shanghai 200237, China*

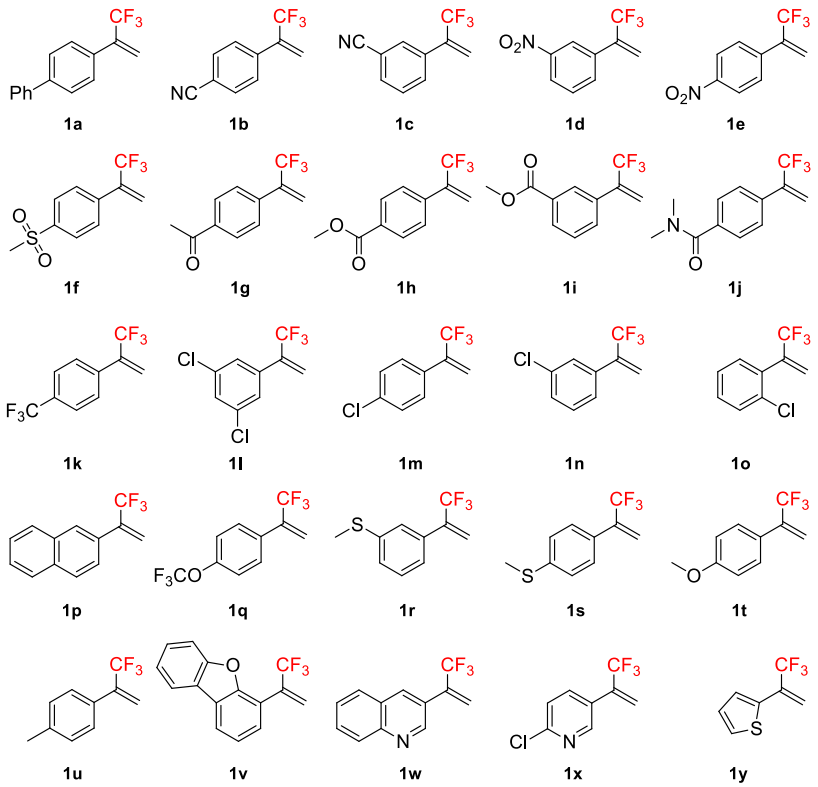
[b]*Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, 200032, China*

Contents

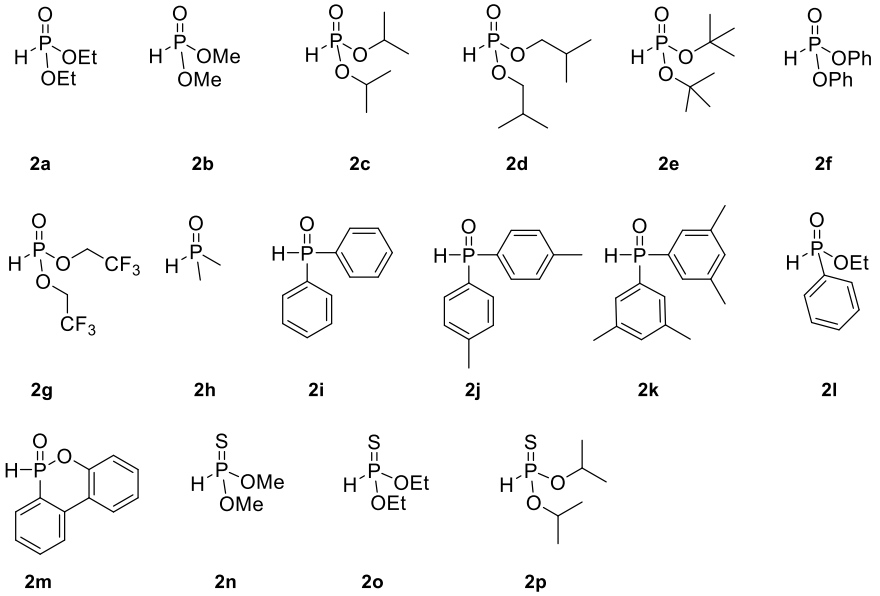
1. General information

All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Melting points were measured in an open capillary using EZ-Melt automated melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a 400 spectrometer (400 MHz) using TMS as internal standard. ^{13}C NMR spectra were obtained on a 400 spectrometer (100 MHz) or 600 spectrometer (150 MHz) using TMS as internal standard. ^{19}F NMR spectra were obtained on a 600 spectrometer (564 MHz) with CF_3COOH as an internal standard. $CDCl_3$ was used as the NMR solvents. ^{31}P NMR spectra were obtained on a 600 spectrometer (243 MHz) with H_3PO_4 as an internal standard. $CDCl_3$ was used as the NMR solvents. High resolution mass spectra (HRMS) were acquired in the EI mode using a TOF mass analyzer. The GC-MS was recorded on Agilent 5977. The LC was recorded on Shimadzu LC-20AT. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

2. *α*-(Trifluoromethyl)styrenes (1a–y), *H*-phosphonates and *H*-phosphine oxides (2a–p) used in this reaction



All α-(trifluoromethyl)styrenes are known compounds. Substrates **1a**, **1g–h**, **1m–q**, **1t–u**, **1w** were prepared according to reference.[1] Substrates **1b**, **1f**, **1j–k**, **1s**, **1x** were prepared according to reference.[2] Substrates **1c–e**, **1i** were prepared according to reference.[3] Substrates **1r**, **1y** were prepared according to reference.[4] Substrate **1l** was prepared according to reference.[5] Substrate **1v** was prepared according to reference.[6]



H-phosphinates and *H*-phosphine oxides (**2a**–**m**) were obtained from commercial suppliers.

Substrate **2n** was prepared according to reference.[7]

Substrate **2o** was prepared according to reference.[8]

Substrate **2p** was prepared according to reference.[9]

3. General Procedure for the Synthesis of Compounds 3aa–ya, 3hb–hg and 3hl–hp

To a glass tube charged with a stirring bar were added α-(trifluoromethyl)styrenes **1a**–**y** (1.0 mmol), *H*-Phosphonates **2a**–**l**, **2l**–**p** (276 mg, 2.0 mmol, 2.0 equiv) and DBN (248 mg, 2.0 mmol, 2.0 equiv) under argon atmosphere. The tube was flushed with argon three times to remove the air and then sealed with a septum. Subsequently, the reaction mixture was stirred at room temperature for 2 h (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was separated and dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resultant residue was purified by column chromatography on silica gel to afford the final compound (**3aa**–**ya**, **3hb**–**hg** and **3hl**–**hp**). Compounds **3aa-ya** and **3hb**–**hg** were purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (4/1) as an eluent. Compounds **3hl**–**hm** were purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (3/1) as an eluent. Compounds **3hn**–**hp** were purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (20/1) as an eluent.

4. General Procedure for the Synthesis of Compounds 3hh–hk

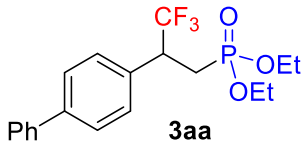
To a glass tube charged with a stirring bar were added methyl 4-(3,3,3-trifluoroprop-1-en-2-yl)-benzoate **1h** (230 mg, 1.0 mmol), *H*-Phosphine oxides **2h**–**k** (2.0 mmol, 2.0 equiv), DBN (248 mg, 2.0 mmol, 2.0 equiv) and DMF (6 mL) under argon atmosphere. The tube was flushed with argon three times to remove the air and then sealed with a septum. Subsequently, the reaction mixture was stirred at room temperature for 2 h (monitored by

TLC). After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was separated and dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resultant residue was purified by column chromatography on silica gel to afford the final compound (**3hh**–**hk**). Compounds **3hh** was purified by column chromatography on silica gel using dichloromethane/methanol (15/1) as an eluent. Compounds **3hi**–**hk** were purified by column chromatography on silica gel using *n*-hexane/ethyl acetate (3/1) as an eluent.

5. Procedure for the Synthesis of Compound 4

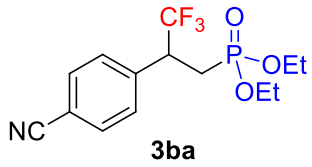
To a glass tube charged with a stirring bar were added **3aa** (1.0 mmol), TMSBr (612 mg, 4.0 mmol, 4.0 equiv) and DCM (4 mL) under argon atmosphere. The tube was flushed with argon three times to remove the air and then sealed with a septum. Subsequently, the reaction mixture was stirred at room temperature under inert atmosphere for 5 h (monitored by TLC). After the completion of reaction, the solvent was removed under vacuum and to the crude was added 6 ml solvent ($MeOH/H_2O$ = 5/1). After 1 h reaction (monitored by TLC), the solvent was removed under vacuum giving the crude phosphonic acid. and then the crude product was dissolved in anhydrous CH_3CN (4 mL). Diisopropylethylamine (387.8 mg, 3.0 mmol, 3.0 equiv) was added, followed by iodomethylpivalate (605.2 mg, 2.5 mmol, 2.5 equiv). the reaction mixture was stirred at room temperature for 12 h (monitored by TLC). After the completion of reaction, the reaction mixture was quenched with saturated aqueous solution of NH_4Cl (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic layer was separated and dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resultant residue was purified by column chromatography on silica using *n*-hexane/ethyl acetate (4/1) as eluent to gel to afford the final compound **4**.

6. Analytical data of the target compounds



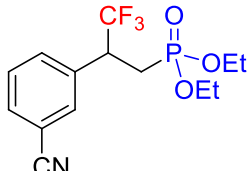
3aa

Diethyl (2-([1,1'-biphenyl]-4-yl)-3, 3,3-trifluoropropyl)phosphonate (3aa). white solid, m.p. 96.1−97.5 °C, 68% yield (262.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.55 (m, 4H), 7.47–7.40 (m, 4H), 7.39–7.33 (m, 1H), 4.01–3.87 (m, 2H), 3.85–3.73 (m, 2H), 3.69–3.58 (m, 1H), 2.51–2.35 (m, 2H), 1.16 (t, J = 8.0 Hz, 3H), 1.04 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 139.4, 131.5, 128.7, 127.8, 126.6, 126.3, 126.1, 125.3 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 60.8 (d, $J_{C–P}$ = 5.0 Hz), 60.7 (d, $J_{C–P}$ = 6.0 Hz), 43.8 (q, $J_{C–F}$ = 28.0 Hz), 25.1 (d, $J_{C–P}$ = 146.0 Hz), 15.1 (d, $J_{C–P}$ = 7.0 Hz), 15.0 (d, $J_{C–P}$ = 7.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.96 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.7 (s); HRMS (EI) calcd for $C_{19}H_{22}F_3O_3P$ $[M]^+$: 386.1259, found: 386.1263.



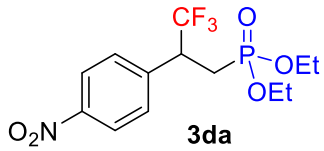
3ba

Diethyl (2-(4-cyanophenyl)-3,3,3-trifluoropropyl)phosphonate (3ba). colorless oil, 76% yield (254.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 4.03–3.90 (m, 2H), 3.88–3.77 (m, 2H), 3.76–3.67 (m, 1H), 2.50–2.27 (m, 2H), 1.19 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 132.3, 130.2, 125.8 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 118.2, 112.8, 62.1 (d, $J_{C–P}$ = 6.0 Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 45.4 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 25.9 (d, $J_{C–P}$ = 147.0 Hz), 16.2 (d, $J_{C–P}$ = 6.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.71 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.5 (s); HRMS (EI) calcd for $C_{14}H_{17}F_3NO_3P$ $[M]^+$: 335.0898, found: 335.0900.



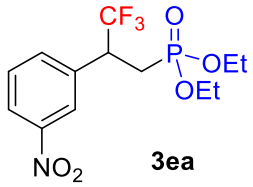
3ca

Diethyl (2-(3-cyanophenyl)-3,3,3-trifluoropropyl)phosphonate (3ca). colorless oil, 74% yield (247.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.59 (m, 3H), 7.55–7.48 (m, 1H), 4.03–3.89 (m, 2H), 3.89–3.76 (m, 2H), 3.76–3.68 (m, 1H), 2.50–2.28 (m, 2H), 1.19 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3, 133.8, 132.8, 132.2, 129.5, 125.8 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 118.2, 112.9, 62.1 (d, $J_{C–P}$ = 7.0 Hz), 61.8 (d, $J_{C–P}$ = 7.0 Hz), 45.0 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 16.2 (d, $J_{C–P}$ = 6.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.97 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.6 (s); HRMS (EI) calcd for $C_{14}H_{17}F_3NO_3P$ $[M]^+$: 335.0898, found: 335.0900.



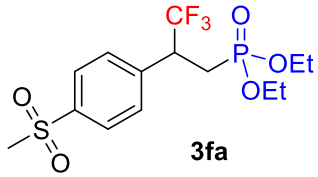
3da

Diethyl (3,3,3-trifluoro-2-(4-nitrophenyl)propyl)phosphonate (3da). colorless oil, 74% yield (262.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 12.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 4.05–3.94 (m, 2H), 3.93–3.82 (m, 2H), 3.81–3.71 (m, 1H), 2.53–2.32 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 140.7, 130.7, 125.7 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 22.0 Hz), 123.7, 62.1 (d, $J_{C–P}$ = 6.0 Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 45.1 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 25.9 (d, $J_{C–P}$ = 147.0 Hz), 16.2 (d, $J_{C–P}$ = 6.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.67 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.4 (s); HRMS (EI) calcd for $C_{13}H_{17}F_3NO_5P$ $[M]^+$: 355.0796, found: 355.0793.



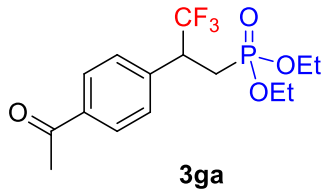
3ea

Diethyl (3,3,3-trifluoro-2-(3-nitrophenyl)propyl)phosphonate (3ea). colorless oil, 76% yield (269.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.64–7.55 (m, 1H), 4.03–3.93 (m, 2H), 3.92–3.82 (m, 2H), 3.82–3.72 (m, 1H), 2.53–2.34 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 134.6, 128.7, 124.8 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 123.2, 122.7, 61.1 (d, $J_{C–P}$ = 6.0 Hz), 60.9 (d, $J_{C–P}$ = 7.0 Hz), 44.0 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 2.0 Hz), 24.8 (d, $J_{C–P}$ = 145.0 Hz), 15.2 (d, $J_{C–P}$ = 6.0 Hz), 15.1 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.96 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.4 (s); HRMS (EI) calcd for $C_{13}H_{17}F_3NO_5P$ $[M]^+$: 355.0796, found:355.0799.



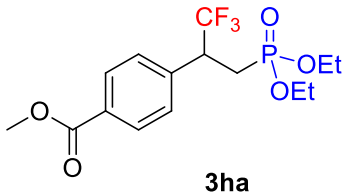
3fa

Diethyl (3,3,3-trifluoro-2-(4-(methylsulfonyl)phenyl)propyl)phosphonate (3fa). colorless oil, 67% yield (260.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 4.02–3.91 (m, 2H), 3.90–3.79 (m, 2H), 3.78–3.68 (m, 1H), 3.08 (s, 3H), 2.51–2.34 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.06 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.8, 130.4, 127.6, 125.8 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 23.0 Hz), 62.1 (d, $J_{C–P}$ = 6.0 Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 45.2 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 2.0 Hz), 44.4, 25.9 (d, $J_{C–P}$ = 147.0 Hz), 16.2 (d, $J_{C–P}$ = 7.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.62 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.8–25.3 (m); HRMS (EI) calcd for $C_{14}H_{20}F_3O_5PS$ $[M]^+$: 388.0721, found: 388.0719.



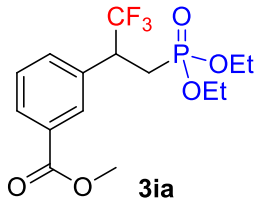
3ga

Diethyl (2-(4-acetylphenyl)-3,3,3-trifluoropropyl)phosphonate (3ga). colorless oil, 72% yield (253.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 3.94–3.81 (m, 2H), 3.80–3.69 (m, 2H), 3.66–3.56 (m, 1H), 2.54 (s, 3H), 2.42–2.26 (m, 2H), 1.09 (t, *J* = 8.0 Hz, 3H), 0.98 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 138.8, 137.3, 129.6, 128.5, 126.0 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 62.0 (d, $J_{C–P}$ = 6.0 Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 45.2 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 26.6, 25.9 (d, $J_{C–P}$ = 145.0 Hz), 16.1 (d, $J_{C–P}$ = 7.0 Hz), 16.0 (d, $J_{C–P}$ = 7.0 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.76 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.0 (s); HRMS (EI) calcd for $C_{15}H_{20}F_3O_4P$ $[M]^+$: 352.1051, found: 352.1054.



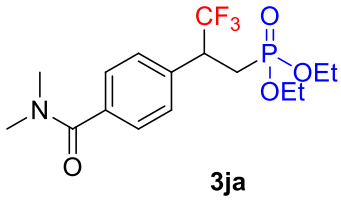
3ha

Methyl 4-(3-(diethoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3ha). colorless oil, 74% yield (272.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 4.01–3.87 (m, 5H), 3.86–3.75 (m, 2H), 3.72–3.60 (m, 1H), 2.50–2.32 (m, 2H), 1.16 (t, *J* = 8.0 Hz, 3H), 1.05 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 138.6, 130.5, 129.8, 129.4, 126.0 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 61.8 (d, $J_{C–P}$ = 8.0 Hz), 52.2, 45.2 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 26.0 (d, $J_{C–P}$ = 147.0 Hz), 16.2 (d, $J_{C–P}$ = 7.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.82 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.1 (s); HRMS (EI) calcd for $C_{15}H_{20}F_3O_5P$ $[M]^+$: 368.1000, found: 368.0998.



3ia

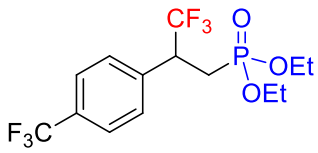
Methyl 3-(3-(diethoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3ia). colorless oil, 78% yield (287.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.00 (m, 2H), 7.56 (d, *J* = 8.0 Hz 1H), 7.46 (t, *J* = 8.0 Hz 1H),4.01–3.87 (m, 5H), 3.86–3.76 (m, 2H), 3.73–3.62 (m, 1H), 2.50–2.35 (m, 2H), 1.15 (t, *J* = 8.0 Hz, 3H), 1.05 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 134.1, 133.8, 130.6, 130.4, 129.8, 128.8, 126.1 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 61.8 (d, $J_{C–P}$ = 6.0 Hz), 52.3, 45.1 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 2.0 Hz), 25.9 (d, $J_{C–P}$ = 145.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz), 16.0 (d, $J_{C–P}$ = 5.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.98 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.5–25.9 (m); HRMS (EI) calcd for $C_{15}H_{20}F_3O_5P$ $[M]^+$: 368.1000, found: 368.0997.



3ja

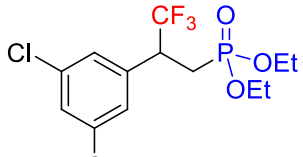
Diethyl (2-(4-(dimethylcarbamoyl)phenyl)-3,3,3-trifluoropropyl)phosphonate (3ja). colorless oil, 80% yield (304.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 4.04–3.87 (m, 2H), 3.86–3.73 (m, 2H), 3.72–3.62 (m, 1H), 3.11 (s, 3H), 2.98 (s, 3H), 2.50–2.31 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.08 (t, *J* = 8.0 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 170.8, 136.6, 135.1, 129.3, 127.4, 126.1 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 61.9 (d, $J_{C–P}$ = 4.0 Hz), 61.8 (d, $J_{C–P}$ = 4.0 Hz), 45.0 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 39.5, 35.3, 25.9

(d, J_{C-P} = 147.0 Hz), 16.2 (d, J_{C-P} = 4.0 Hz), 16.1 (d, J_{C-P} = 4.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -70.91 (d, J_{H-F} = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.6–26.1 (m); HRMS (EI) calcd for $C_{16}H_{23}F_3NO_4P$ $[M]^+$: 381.1317, found: 381.1316.



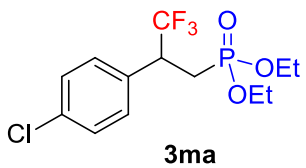
3ka

Diethyl (3,3,3-trifluoro-2-(4-(trifluoromethyl)phenyl)propyl)phosphonate (3ka). colorless oil, 74% yield (279.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 4.02–3.88 (m, 2H), 3.87–3.76 (m, 2H), 3.73–3.63 (m, 1H), 2.51–2.31 (m, 2H), 1.16 (t, *J* = 8.0 Hz, 3H), 1.03 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 131.0 (q, J_{C-F} = 32.0 Hz), 129.8, 126.2 (qd, J_{C-F} = 278.0 Hz, J_{C-P} = 22.0 Hz), 125.5 (q, J_{C-F} = 4.0 Hz), 123.9 (q, J_{C-F} = 270.0 Hz), 62.0 (d, J_{C-P} = 6.0 Hz), 61.8 (d, J_{C-P} = 7.0 Hz), 45.2 (qd, J_{C-F} = 28.0 Hz, J_{C-P} = 2.0 Hz), 26.0 (d, J_{C-P} = 147.0 Hz), 16.1 (d, J_{C-P} = 6.0 Hz), 16.0 (d, J_{C-P} = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –62.87 (s, 3F), –70.87 (d, J_{H-F} = 5.6 Hz, 3F); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.9 (s); HRMS (EI) calcd for $C_{14}H_{17}F_6O_3P$ $[M]^+$: 378.0820, found: 378.0818.



3la

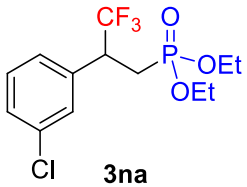
Diethyl (2-(3,5-dichlorophenyl)-3,3,3-trifluoropropyl)phosphonate (3la). colorless oil, 66% yield (249.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.25 (s, 2H), 4.04–3.93 (m, 2H), 3.92–3.84 (m, 1H), 3.83–3.75 (m, 1H), 3.74–3.64 (m, 1H), 2.46–2.23 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H), 1.12 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 135.2, 128.9, 127.9, 125.8 (qd, J_{C-F} = 279.0 Hz, J_{C-P} = 22.0 Hz), 62.1 (d, J_{C-P} = 6.0 Hz), 61.9 (d, J_{C-P} = 6.0 Hz), 44.9 (q, J_{C-F} = 28.0 Hz), 26.0 (d, J_{C-P} = 147.0 Hz), 16.2 (d, J_{C-P} = 6.0 Hz), 16.1 (d, J_{C-P} = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.84 (d, J_{H-F} = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.5 (s); HRMS (EI) calcd for $C_{13}H_{16}Cl_2F_3O_3P$ $[M]^+$: 378.0166, found: 378.0176.



3ma

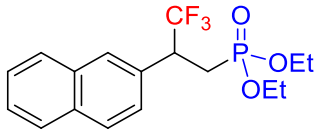
Diethyl (2-(4-chlorophenyl)-3,3,3-trifluoropropyl)phosphonate (3ma). colorless oil, 68% yield (233.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 12.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.01–3.87 (m, 2H), 3.86–3.78 (m, 1H), 3.77–3.63 (m, 2H), 2.46–2.25 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.08 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 134.7, 132.1, 130.6, 128.8, 126.1 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 61.9 (d, $J_{C–P}$ = 6.0 Hz), 61.8 (d, $J_{C–P}$ = 6.0 Hz), 44.7 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 26.0 (d, $J_{C–P}$ = 146.0 Hz), 16.2 (d, $J_{C–P}$ = 6.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –71.19 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.3 (s); HRMS (EI) calcd for $C_{13}H_{17}ClF_3O_3P$ $[M]^+$: 344.0556, found: 344.0552.



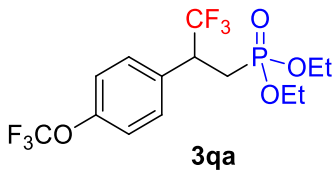
3na

Diethyl (2-(3-chlorophenyl)-3,3,3-trifluoropropyl)phosphonate (3na). colorless oil, 61% yield (209.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 3H), 7.27–7.22 (m, 1H), 4.02–3.88 (m, 2H), 3.87–3.78 (m, 1H), 3.77–3.62 (m, 2H), 2.47–2.27 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.08 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 134.5, 129.9, 129.4, 128.8, 127.6, 126.2 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 61.9 (d, $J_{C–P}$ = 7.0 Hz), 61.8 (d, $J_{C–P}$ = 7.0 Hz), 45.0 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 1.0 Hz), 26.0 (d, $J_{C–P}$ = 147.0 Hz), 16.1 (d, $J_{C–P}$ = 7.0 Hz), 16.0 (d, $J_{C–P}$ = 7.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.98 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.1 (s); HRMS (EI) calcd for $C_{13}H_{17}ClF_3O_3P$ $[M]^+$: 344.0556, found: 344.0551.



3pa

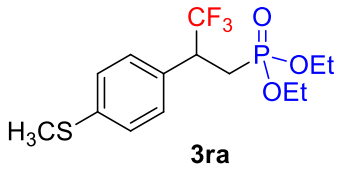
Diethyl (3,3,3-trifluoro-2-(naphthalen-2-yl)propyl)phosphonate (3pa). colorless oil, 61% yield (219.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.78 (m, 4H), 7.54–7.42 (m, 3H), 4.00–3.79 (m, 3H), 3.78–3.68 (m, 1H), 3.57–3.46 (m, 1H), 2.56–2.45 (m, 2H), 1.09 (t, *J* = 8.0 Hz, 3H), 0.89 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.2, 133.1, 131.0, 129.1, 128.4, 128.0, 127.6, 126.5, 126.4 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 23.0 Hz), 126.3, 126.1, 61.8 (d, $J_{C–P}$ = 7.0 Hz), 45.3 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 1.0 Hz), 26.2 (d, $J_{C–P}$ = 145.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz), 15.9 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.72 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.7 (s); HRMS (EI) calcd for $C_{17}H_{20}F_3O_3P$ $[M]^+$: 360.1102, found: 360.1100.



3qa

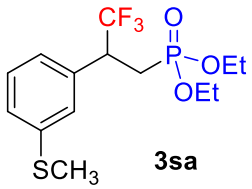
Diethyl (3,3,3-trifluoro-2-(4-(trifluoromethoxy)phenyl)propyl)phosphonate (3qa). colorless oil, 72% yield (283.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.03–3.87 (m, 2H), 3.86–3.72 (m, 2H), 3.70–3.59 (m, 1H), 2.48–2.28 (m, 2H), 1.17 (t, *J* = 8.0 Hz, 3H), 1.04 (t, *J* = 8.0 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 149.4, 132.4, 130.8, 126.1 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 23.0 Hz), 121.1, 120.4 (q, $J_{C–F}$ = 250.0 Hz), 61.9 (d, $J_{C–P}$ = 6.0 Hz), 61.8 (d, $J_{C–P}$ = 6.0 Hz), 44.7 (q, $J_{C–F}$ = 29.0 Hz), 26.2 (d, $J_{C–P}$ = 147.0 Hz), 16.1 (d, $J_{C–P}$ = 7.0 Hz), 16.0 (d, $J_{C–P}$ = 7.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –57.99 (s, 3F), –71.19 (d, $J_{H–F}$ = 11.3 Hz, 3F); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.2 (s); HRMS (EI) calcd for $C_{14}H_{17}F_6O_4P$ $[M]^+$: 394.0769, found: 394.0774.



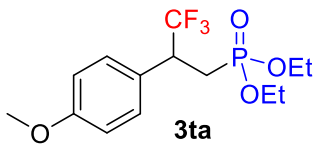
3ra

Diethyl (3,3,3-trifluoro-2-(4-(methylthio)phenyl)propyl)phosphonate (3ra). colorless oil, 60% yield (213.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.00–3.86 (m, 2H), 3.85–3.76 (m, 1H), 3.74–3.58 (m, 2H), 2.48 (s, 3H), 2.46–2.29 (m, 2H), 1.17 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 130.2, 129.6, 126.5, 126.3 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 23.0 Hz), 61.8 (d, $J_{C–P}$ = 3.0 Hz), 61.7 (d, $J_{C–P}$ = 3.0 Hz), 44.7 (q, $J_{C–F}$ = 28.0 Hz), 26.1 (d, $J_{C–P}$ = 146.0 Hz), 16.2 (d, $J_{C–P}$ = 6.0 Hz), 16.1 (d, $J_{C–P}$ = 7.0 Hz), 15.6; ^{19}F NMR (564 MHz, $CDCl_3$) δ –71.20 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.7 (s); HRMS (EI) calcd for $C_{14}H_{20}F_3O_3PS$ $[M]^+$: 356.0823, found: 356.0820.



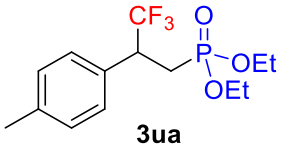
3sa

Diethyl (3,3,3-trifluoro-2-(3-(methylthio)phenyl)propyl)phosphonate (3sa). colorless oil, 64% yield (227.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.22 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 4.02–3.86 (m, 2H), 3.85–3.76 (m, 1H), 3.74–3.60 (m, 2H), 2.49 (s, 3H), 2.45–2.28 (m, 2H), 1.17 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 134.4, 129.0, 127.4, 126.6, 126.2 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 23.0 Hz), 125.9, 61.8 (d, $J_{C–P}$ = 3.0 Hz), 61.7 (d, $J_{C–P}$ = 2.0 Hz), 45.1 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 1.0 Hz), 26.1 (d, $J_{C–P}$ = 146.0 Hz), 16.2 (d, $J_{C–P}$ = 6.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz), 16.0; ^{19}F NMR (564 MHz, $CDCl_3$) δ –72.25 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.5 (s); HRMS (EI) calcd for $C_{14}H_{20}F_3O_3PS$ $[M]^+$: 356.0823, found: 356.0825.



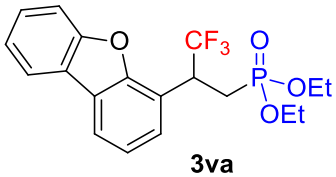
3ta

Diethyl (3,3,3-trifluoro-2-(4-methoxyphenyl)propyl)phosphonate (3ta). colorless oil, 51% yield (173.4 mg);. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 12.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 2H), 3.98–3.85 (m, 2H), 3.84–3.75 (m, 4H), 3.74–3.59 (m, 2H), 2.45–2.28 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 3H), 1.07 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 130.3, 126.4 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 23.0 Hz), 125.6, 114.0, 61.8 (d, $J_{C–P}$ = 7.0 Hz), 61.7 (d, $J_{C–P}$ = 7.0 Hz), 55.3, 44.4 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 26.2 (d, $J_{C–P}$ = 145.0 Hz), 16.2 (d, $J_{C–P}$ = 5.0 Hz), 16.1 (d, $J_{C–P}$ = 4.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –71.47 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.2–28.5 (m); HRMS (EI) calcd for $C_{14}H_{20}F_3O_4P$ $[M]^+$: 340.1051, found: 340.1048.



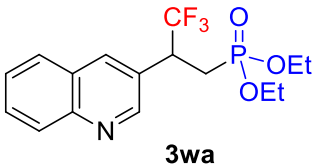
3ua

Diethyl (3,3,3-trifluoro-2-(p-tolyl)propyl)phosphonate (3ua). colorless oil, 58% yield (187.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.98–3.74 (m, 3H), 3.73–3.55 (m, 2H), 2.46–2.35 (m, 2H), 2.34 (s, 3H), 1.16 (t, *J* = 8.0 Hz, 3H), 1.06 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 130.6, 129.3, 129.1, 126.4 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 61.8 (d, $J_{C–P}$ = 7.0 Hz), 61.7 (d, $J_{C–P}$ = 7.0 Hz), 44.7 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 1.0 Hz), 26.1 (d, $J_{C–P}$ = 147.0 Hz), 21.1, 16.1 (d, $J_{C–P}$ = 6.0 Hz), 16.0 (d, $J_{C–P}$ = 7.0 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ –71.24 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.9 (s); HRMS (EI) calcd for $C_{14}H_{20}F_3O_3P$ $[M]^+$: 324.1102, found: 324.1098.



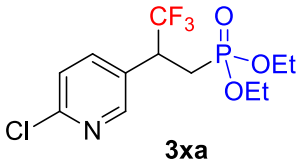
3va

Diethyl (2-(dibenzo[b,d]furan-4-yl)-3,3,3-trifluoropropyl)phosphonate (3va). colorless oil, 74% yield (296.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.90 (m, 2H), 7.64–7.56 (m, 1H), 7.52–7.42 (m, 2H), 7.40–7.31 (m, 2H), 4.56–4.36 (m, 1H), 3.90–3.62 (m, 4H), 2.88–2.68 (m, 1H), 2.62–2.48 (m, 1H), 1.00 (t, *J* = 8.0 Hz, 3H), 0.97 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 154.9, 127.5, 127.2, 126.3 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 22.0 Hz), 124.6, 124.0, 123.0, 122.9, 120.9, 120.8, 117.8, 111.9, 61.8 (d, $J_{C–P}$ = 5.0 Hz), 61.7 (d, $J_{C–P}$ = 6.0 Hz), 39.6 (q, $J_{C–F}$ = 29.0 Hz), 25.0 (d, $J_{C–P}$ = 147.0 Hz), 16.0 (d, $J_{C–P}$ = 6.0 Hz), 15.9 (d, $J_{C–P}$ = 7.0 Hz). ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.76 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.4 (s); HRMS (EI) calcd for $C_{19}H_{20}F_3O_4P$ $[M]^+$: 400.1051, found: 400.1049.



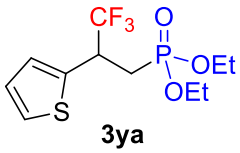
3wa

Diethyl (3,3,3-trifluoro-2-(quinolin-3-yl)propyl)phosphonate (3wa). colorless oil, 72% yield (259.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.18 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H),7.76 (t, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 4.05–3.86 (m, 3H), 3.85–3.74 (m, 1H), 3.74–3.59 (m, 1H), 2.60–2.45 (m, 2H), 1.09 (t, *J* = 8.0 Hz, 3H), 0.94 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 147.7, 136.7, 130.3, 129.1, 127.9, 127.5, 127.3, 126.7, 126.1 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 62.1 (d, $J_{C–P}$ = 6.0 Hz), 61.9 (d, $J_{C–P}$ = 6.0 Hz), 43.3 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 2.0 Hz), 26.0 (d, $J_{C–P}$ = 146.0 Hz), 16.1 (d, $J_{C–P}$ = 6.0 Hz), 16.0 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.80 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.9–25.4 (m); HRMS (EI) calcd for $C_{16}H_{19}F_3NO_3P$ $[M]^+$: 361.1055, found: 361.1057.



3xa

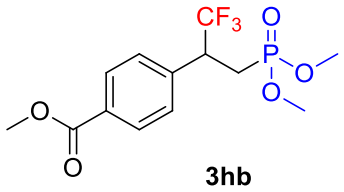
Diethyl (2-(6-chloropyridin-3-yl)-3,3,3-trifluoropropyl)phosphonate (3xa). colorless oil, 75% yield (258.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.67 (dd, *J* = 4.0, 8.0 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 4.03–3.93 (m, 2H), 3.92–3.85 (m, 1H), 3.84–3.72 (m, 2H), 2.49–2.25 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H), 1.12 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 150.5, 139.0, 128.5, 125.7 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 124.2, 62.2 (d, $J_{C–P}$ = 6.0 Hz), 62.0 (d, $J_{C–P}$ = 6.0 Hz), 42.6 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 2.0 Hz) 25.7 (d, $J_{C–P}$ = 148.0 Hz), 16.2 (d, $J_{C–P}$ = 7.0 Hz), 16.1 (d, $J_{C–P}$ = 7.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –71.09 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.3 (s); HRMS (EI) calcd for $C_{12}H_{16}ClF_3NO_3P$ $[M]^+$: 345.0508, found: 345.0505.



3ya

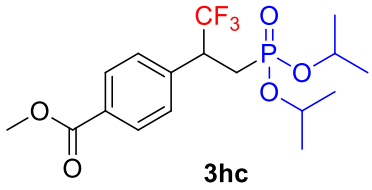
Diethyl (3,3,3-trifluoro-2-(thiophen-2-yl)propyl)phosphonate (3ya). colorless oil, 70% yield (221.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 4.0 Hz, 1H), 7.11 (d, *J* = 4.0 Hz, 1H), 7.03–6.97 (m, 1H), 4.15–4.03 (m, 1H), 4.01–3.83 (m, 3H), 3.78–3.69 (m, 1H), 2.51–2.26 (m, 2H), 1.20 (t, *J* = 8.0 Hz, 3H), 1.13 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4, 128.3, 126.8, 126.1, 125.6 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 62.0 (d, $J_{C–P}$ = 4.0 Hz), 61.9 (d, $J_{C–P}$ = 4.0 Hz), 40.7 (qd, $J_{C–F}$ = 30.0 Hz, $J_{C–P}$ = 2.0 Hz), 27.6 (d, $J_{C–P}$ = 146.0 Hz), 16.2 (d,

J_{C-P} = 2.0 Hz), 16.1 (d, J_{C-P} = 1.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.67 (d, J_{H-F} = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 25.9 (s); HRMS (EI) calcd for $C_{11}H_{16}F_3NO_3PS$ $[M]^+$: 316.0510, found: 316.0507.



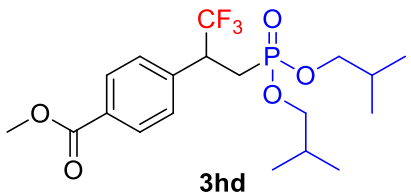
3hb

Methyl 4-(3-(dimethoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hb). colorless oil, 78% yield (265.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.87–3.74 (m, 1H), 3.57 (d, *J* = 12.0 Hz, 3H), 3.36 (d, *J* = 12.0 Hz, 3H), 2.54–2.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 138.5, 130.6, 129.9, 129.3, 125.9 (qd, J_{C-F} = 278.0 Hz, J_{C-P} = 22.0 Hz), 52.4 (d, J_{C-P} = 7.0 Hz), 52.3 (d, J_{C-P} = 6.0 Hz), 52.2, 45.1 (qd, J_{C-F} = 29.0 Hz, J_{C-P} = 2.0 Hz), 25.3 (d, J_{C-P} = 147.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.80 (d, J_{H-F} = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.0 (s); HRMS (EI) calcd for $C_{13}H_{16}F_3O_5P$ $[M]^+$: 340.0687, found: 340.0685.



3hc

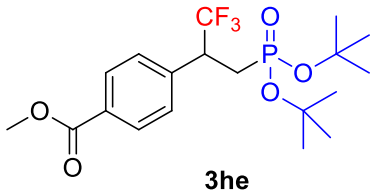
Methyl 4-(3-(diisopropoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hc). colorless oil, 71% yield (281.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 4.63–4.52 (m, 1H), 4.52–4.41 (m, 1H), 3.92 (s, 3H), 3.86–3.72 (m, 1H), 2.45–2.39 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 6H), 1.12 (d, *J* = 4.0 Hz, 3H), 1.00 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 138.8, 130.3, 129.7, 129.5, 126.1 (qd, J_{C-F} = 278.0 Hz, J_{C-P} = 22.0 Hz), 70.8 (d, J_{C-P} = 7.0 Hz), 70.7 (d, J_{C-P} = 6.0 Hz), 52.2, 45.4 (qd, J_{C-F} = 28.0 Hz, J_{C-P} = 2.0 Hz), 27.1 (d, J_{C-P} = 147.0 Hz), 23.9 (d, J_{C-P} = 3.0 Hz), 23.8 (d, J_{C-P} = 4.0 Hz), 23.7 (d, J_{C-P} = 4.0 Hz), 23.5 (d, J_{C-P} = 5.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.80 (d, J_{H-F} = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 23.8 (s); HRMS (EI) calcd for $C_{17}H_{24}F_3O_5P$ $[M]^+$: 396.1313, found: 396.1310.



3hd

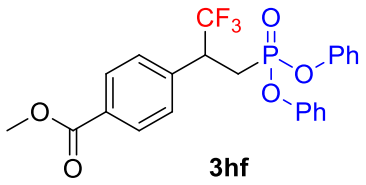
Methyl 4-(3-(diisobutoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hd). white solid, m.p. 79.8−82.8 °C, 76% yield (322.2 mg);. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 3.93 (s, 3H), 3.88–3.76 (m, 1H), 3.71–3.64 (m, 1H), 3.63–3.49 (m, 2H), 3.41–3.31 (m, 1H), 2.56–2.28 (m, 2H), 1.79–1.69 (m, 1H), 1.68–1.56 (m, 1H), 0.83 (d, *J* = 4.0 Hz, 3H), 0.82 (d, *J* = 4.0 Hz, 3H) , 0.76 (d, *J* = 8.0 Hz,

6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 138.6, 130.5, 129.9, 129.3, 126.0 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 22.0 Hz), 71.9 (d, $J_{C–P}$ = 7.0 Hz), 70.7 (d, $J_{C–P}$ = 7.0 Hz), 52.2, 45.2 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 29.1 (d, $J_{C–P}$ = 7.0 Hz), 28.9 (d, $J_{C–P}$ = 7.0 Hz), 25.8 (d, $J_{C–P}$ = 147.0 Hz), 18.5, 18.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.81 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 26.0 (s); HRMS (EI) calcd for $C_{19}H_{28}F_3O_5P$ $[M]^+$: 424.1626, found: 424.1623.



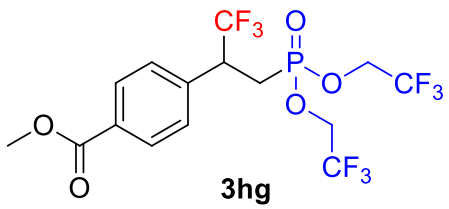
3he

Methyl 4-(3-(di-*tert*-butoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3he). white solid, m.p. 82.3−84.1 °C, 79% yield (335.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.92 (s, 3H), 3.81–3.66 (m, 1H), 2.39–2.25 (m, 2H), 1.35 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 139.3, 130.2, 129.7, 129.6, 126.3 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 22.0 Hz), 82.8 (d, $J_{C–P}$ = 6.0 Hz), 82.7 (d, $J_{C–P}$ = 5.0 Hz), 52.2, 46.1 (qd, $J_{C–F}$ = 28.0 Hz, $J_{C–P}$ = 2.0 Hz), 30.2 (d, $J_{C–P}$ = 4.0 Hz), 30.1 (d, $J_{C–P}$ = 3.0 Hz), 29.6 (d, $J_{C–P}$ = 150.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.86 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 17.8–16.4 (m); HRMS (EI) calcd for $C_{19}H_{28}F_3O_5P$ $[M]^+$: 424.1626, found: 424.1628.



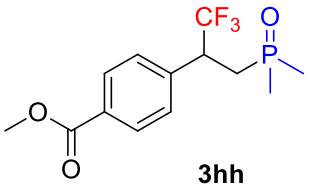
3hf

Methyl 4-(3-(diphenoxyphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hf). white solid, m.p. 153.4−155.6 °C, 52% yield (241.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 12.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.29–7.24 (m, 2H), 7.23–7.06 (m, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 4.10–3.96 (m, 1H), 3.92 (s, 3H), 2.85–2.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 149.9 (d, $J_{C–P}$ = 9.0 Hz), 149.7 (d, $J_{C–P}$ = 9.0 Hz), 137.9, 130.8, 130.1, 129.9, 129.7, 129.4, 125.9 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 125.4 (d, $J_{C–P}$ = 14.0 Hz), 120.2 (d, $J_{C–P}$ = 4.0 Hz), 120.1 (d, $J_{C–P}$ = 4.0 Hz), 52.3, 45.2 (qd, $J_{C–F}$ = 29.0 Hz, $J_{C–P}$ = 2.0 Hz), 26.4 (d, $J_{C–P}$ = 148.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.60 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.4–19.0 (m); HRMS (EI) calcd for $C_{23}H_{20}F_3O_5P$ $[M]^+$: 464.1000, found: 464.0996.



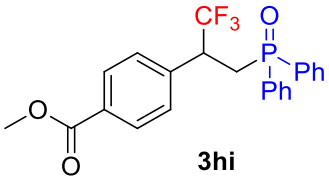
3hg

Methyl 4-(3-(bis(2,2,2-trifluoroethoxy)phosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hg). colorless oil, 46% yield (219.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 12.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.28–4.19 (m, 2H), 4.16–4.05 (m, 1H), 3.94 (s, 3H), 3.88–3.77 (m, 1H), 3.69–3.56 (m, 1H), 2.72–2.55 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 137.2, 131.1, 130.2, 129.2, 125.6 (qd, J_{C-F} = 276.0, J_{C-P} = 24.0 Hz), 122.3 (qd, J_{C-F} = 276.0 Hz, J_{C-P} = 7.5 Hz), 122.2 (qd, J_{C-F} = 276.0 Hz, J_{C-P} = 7.5 Hz), 62.0 (qd, J_{C-F} = 37.5 Hz, J_{C-P} = 7.5 Hz), 61.9 (qd, J_{C-F} = 37.5 Hz, J_{C-P} = 6.0 Hz), 52.3, 44.8 (q, J_{C-F} = 28.5 Hz), 26.4 (d, J_{C-P} = 150.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.90 (d, *J* = 11.3 Hz, 3F), –75.31 (t, J_{H-F} = 5.6 Hz, 3F) , –75.42 (t, J_{H-F} = 5.6 Hz, 3F); ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.1–29.6 (m); HRMS (EI) calcd for $C_{15}H_{14}F_9O_5P$ $[M]^+$: 476.0435, found: 476.0433.



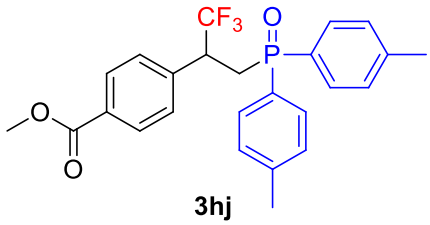
3hh

Methyl 4-(3-(dimethylphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hh). white solid, m.p. 141.5−143.2 °C, 75% yield (231.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 4.12–3.98 (m, 1H), 3.93 (s, 3H), 2.57–2.47 (m, 1H), 2.32–2.19 (m, 1H), 1.50 (d, *J* = 12.0 Hz, 3H), 0.92 (d, *J* = 12.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 137.7, 129.8, 129.2, 128.4, 125.2 (qd, J_{C-F} = 279.0 Hz, J_{C-P} = 16.0 Hz), 51.3, 43.0 (q, J_{C-F} = 29.0 Hz), 30.4 (d, J_{C-P} = 68.0 Hz), 17.0 (d, J_{C-P} = 70.0 Hz), 16.1 (d, J_{C-P} = 69.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.38 (d, J_{H-F} = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 38.9 (s); HRMS (EI) calcd for $C_{13}H_{16}F_3O_3P$ $[M]^+$: 308.0789, found: 308.0787.



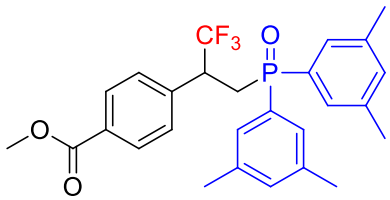
3hi

Methyl 4-(3-(diphenylphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hi). white solid, m.p. 156.8−158.4 °C, 84% yield (362.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.67 (m, 4H), 7.57–7.45 (m, 3H), 7.42–7.33 (m, 2H), 7.32–7.27 (m, 1H), 7.24–7.12 (m, 4H), 4.16–4.02 (m, 1H), 3.89 (s, 3H), 3.07–2.94 (m, 1H), 2.93–2.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 137.9, 132.2, 131.4, 130.6 (d, J_{C-P} = 9.0 Hz), 130.4 (d, J_{C-P} = 9.0 Hz), 130.1, 129.5, 129.4, 128.9 (d, J_{C-P} = 11.0 Hz), 128.2 (d, J_{C-P} = 12.0 Hz), 126.3 (qd, J_{C-F} = 278.0 Hz, J_{C-P} = 16.0 Hz), 52.1, 44.2 (q, J_{C-F} = 28.0 Hz), 29.9 (d, J_{C-P} = 72.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.22 (d, J_{H-F} = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.4 (s); HRMS (EI) calcd for $C_{23}H_{20}F_3O_3P$ $[M]^+$: 432.1102, found: 432.1103.



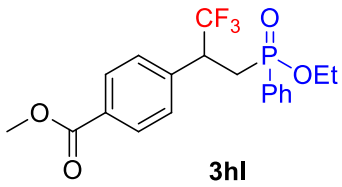
3hj

Methyl 4-(3-(di-*p*-tolylphosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hj). white solid, m.p. 166.3−168.6 °C, 81% yield (372.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 12.0 Hz, 2H), 7.63–7.54 (m, 2H), 7.29–7.25 (m, 2H), 7.24–7.14 (m, 4H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.12–3.98 (m, 1H), 3.90 (s, 3H), 3.00–2.88 (m, 1H), 2.86–2.70 (m, 1H), 2.38 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 142.7, 142.0, 138.1, 130.7 (d, $J_{C–P}$ = 8.0 Hz), 130.5 (d, $J_{C–P}$ = 9.0 Hz), 129.9, 129.6 (d, $J_{C–P}$ = 12.0 Hz), 129.5, 128.9 (d, $J_{C–P}$ = 11.0 Hz), 126.4 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 15.0 Hz), 52.1, 44.3 (q, $J_{C–F}$ = 28.0 Hz), 30.2 (d, $J_{C–P}$ = 70.0 Hz), 21.5, 21.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.23 (d, $J_{H–F}$ = 5.6 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.9 (s); HRMS (EI) calcd for $C_{25}H_{24}F_3O_3P$ $[M]^+$: 460.1415, found: 460.1412.



3hk

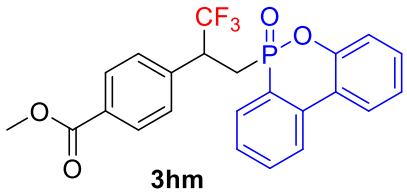
Methyl 4-(3-(bis(3,5-dimethylphenyl)phosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hk). white solid, m.p. 205.9−207.8 °C, 82% yield (400.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 12.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.14 (s, 1H), 6.92 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.13–4.00 (m, 1H), 3.90 (s, 3H), 2.99–2.88 (m, 1H), 2.85–2.74 (m, 1H), 2.33 (s, 6H), 2.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 138.6 (d, $J_{C–P}$ = 12.0 Hz), 138.1, 137.9 (d, $J_{C–P}$ = 13.0 Hz), 133.9, 133.0, 129.9, 129.4, 129.2, 128.2 (d, $J_{C–P}$ = 10.0 Hz), 127.9 (d, $J_{C–P}$ = 9.0 Hz), 126.4 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 16.0 Hz), 52.1, 44.2 (q, $J_{C–F}$ = 28.0 Hz), 29.9 (d, $J_{C–P}$ = 71.0 Hz), 21.3, 20.9; ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.18 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.9 (s); HRMS (EI) calcd for $C_{27}H_{28}F_3O_3P$ $[M]^+$: 488.1728, found: 488.1732.



3hl

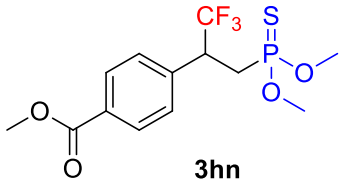
Methyl 4-(3-(ethoxy(phenyl)phosphoryl)-1,1,1-trifluoropropan-2-yl)benzoate (3hl). white solid, m.p. 88.6−90.1 °C, 77% yield (308.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.70–7.61 (m, 1H), 7.58–7.51 (m, 0.5H), 7.50–7.40 (m, 2.0H), 7.39–7.32 (m, 1.5H), 7.24–7.18 (m, 1.0H),

7.16 (d, J = 8.0 Hz, 1H), 4.04–3.58 (m, 6H), 2.73–2.40 (m, 2H), 1.24 (t, J = 8.0 Hz, 1.5H), 0.94 (t, J = 8.0 Hz, 1.5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.6, 166.5, 138.7, 137.6, 132.7, 132.2, 131.4 (d, $J_{C–P}$ = 4.5 Hz), 131.3 (d, $J_{C–P}$ = 4.5 Hz), 130.3, 130.2, 129.7, 129.6, 129.5, 129.4, 128.8 (d, $J_{C–P}$ = 12.0 Hz), 128.4 (d, $J_{C–P}$ = 13.5 Hz), 126.1 (qd, $J_{C–F}$ = 277.5 Hz, $J_{C–P}$ = 19.5 Hz), 126.0 (qd, $J_{C–F}$ = 277.5 Hz, $J_{C–P}$ = 19.5 Hz), 60.9 (d, $J_{C–P}$ = 6.0 Hz), 60.7 (d, $J_{C–P}$ = 6.0 Hz), 52.2, 52.1, 44.8 (q, $J_{C–F}$ = 28.5 Hz), 44.4 (q, $J_{C–F}$ = 28.5 Hz), 30.0 (d, $J_{C–P}$ = 102.0 Hz), 29.5 (d, $J_{C–P}$ = 103.5 Hz), 16.4 (d, $J_{C–P}$ = 4.5 Hz), 16.0 (d, $J_{C–P}$ = 6.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.60 (d, $J_{H–F}$ = 5.6 Hz, 1.5F), –70.80 (d, $J_{H–F}$ = 5.6 Hz, 1.6F); ^{31}P NMR (243 MHz, $CDCl_3$) δ 39.4 (s); HRMS (EI) calcd for $C_{19}H_{20}F_3O_4P$ $[M]^+$: 400.1051, found: 400.1054.



3hm

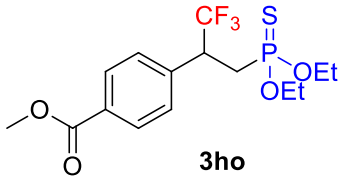
Methyl-4-(1,1,1-trifluoro-3-(6-oxido-6*H*-dibenzo[c,e][1,2]oxaphosphinin-6-yl)propan-2-yl)benzoate (3hm). white solid, m.p. 158.4−160.6 °C, 68% yield (303.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.92–7.81 (m, 3H), 7.80–7.76 (m, 0.4H), 7.70–7.58 (m, 1.0H), 7.49–7.42 (m, 0.6H), 7.39–7.15 (m, 5.0H), 7.08 (d, J = 8.0 Hz, 0.4H), 6.46 (d, J = 8.0 Hz, 0.6H), 4.07–4.02 (m, 0.6H), 3.98 (s, 1.8H), 3.94 (s, 1.2H), 3.91–3.75 (m, 0.4H), 2.82–2.53 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 165.3, 147.8 (d, $J_{C–P}$ = 9.0 Hz), 147.4 (d, $J_{C–P}$ = 7.5 Hz), 137.0, 136.5, 134.7 (d, $J_{C–P}$ = 6.0 Hz), 134.6 (d, $J_{C–P}$ = 6.0 Hz), 132.7, 132.5, 129.9, 129.6, 129.5, 129.4, 129.2 (d, $J_{C–P}$ = 6.0 Hz), 129.1 (d, $J_{C–P}$ = 4.5 Hz), 128.9, 128.8, 128.4, 128.3, 127.6 (d, $J_{C–P}$ = 13.5 Hz), 127.4 (d, $J_{C–P}$ = 13.5 Hz), 125.0 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 19.5 Hz), 124.8 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 19.5 Hz), 124.0, 123.9, 123.8, 123.7, 123.0, 122.7 (d, $J_{C–P}$ = 10.5 Hz), 122.6 (d, $J_{C–P}$ = 10.5 Hz), 122.1, 121.9, 120.7 (d, $J_{C–P}$ = 12.0 Hz), 120.6 (d, $J_{C–P}$ = 10.5 Hz), 119.3 (d, $J_{C–P}$ = 6.0 Hz), 119.2 (d, $J_{C–P}$ = 6.0 Hz), 51.3, 51.2, 43.6 (q, $J_{C–F}$ = 28.5 Hz), 43.2 (qd, $J_{C–F}$ = 28.5 Hz, $J_{C–P}$ = 3.0 Hz), 28.0 (d, $J_{C–P}$ = 48.75 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.47 (d, $J_{H–F}$ = 5.6 Hz, 1.8F), –70.79 (d, $J_{H–F}$ = 5.6 Hz, 1.2F); ^{31}P NMR (243 MHz, $CDCl_3$) δ 33.5 (s, 0.4P), 32.7 (s, 0.6P); HRMS (EI) calcd for $C_{23}H_{18}F_3O_4P$ $[M]^+$: 446.0895, found: 446.0892.



3hn

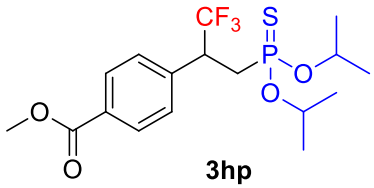
Methyl 4-(3-(dimethoxyphosphorothioyl)-1,1,1-trifluoropropan-2-yl)benzoate (3hn). white solid, m.p. 78.3−81.1 °C, 78% yield (277.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 4.03–3.93 (m, 1H), 3.92, (s, 3H), 3.58 (d, J = 12.0 Hz, 3H), 3.20 (d, J = 12.0 Hz, 3H), 2.72–2.53 (m, 2H); ^{13}C

NMR (100 MHz, $CDCl_3$) δ 166.6, 138.4, 130.5, 129.8, 129.6, 126.1 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 24.0 Hz), 53.1 (d, $J_{C–P}$ = 6.0 Hz), 52.7 (d, $J_{C–P}$ = 7.0 Hz), 52.3, 45.8 (q, $J_{C–F}$ = 28.0 Hz), 33.4 (d, $J_{C–P}$ = 118.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.27 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 98.5–97.9 (m); HRMS (EI) calcd for $C_{13}H_{16}F_3O_4PS$ $[M]^+$: 356.0459, found: 356.0461.



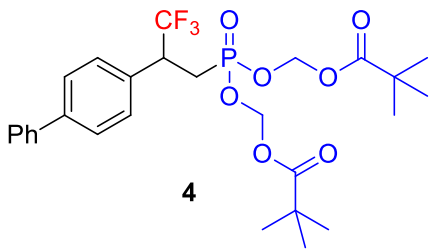
3ho

Methyl 4-(3-(diethoxyphosphorothioyl)-1,1,1-trifluoropropan-2-yl)benzoate (3ho). white solid, m.p. 82.1−83.7 °C, 74% yield (284.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.04–3.93 (m, 3H), 3.92, (s, 3H), 3.78–3.68 (m, 1H), 3.56–3.45 (m, 1H), 2.72–2.48 (m, 2H), 1.19 (t, *J* = 8.0 Hz, 3H), 0.92 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 138.6, 130.4, 129.7, 126.1 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 25.0 Hz), 62.6 (d, $J_{C–P}$ = 6.0 Hz), 52.3, 45.8 (q, $J_{C–F}$ = 28.0 Hz), 34.0 (d, $J_{C–P}$ = 119.0 Hz), 16.0 (d, $J_{C–P}$ = 8.0 Hz), 15.8 (d, $J_{C–P}$ = 7.0 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.28 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 93.6–93.0 (m); HRMS (EI) calcd for $C_{15}H_{20}F_3O_4PS$ $[M]^+$: 384.0772, found: 384.0775.



3hp

Methyl 4-(3-(diisopropoxyphosphorothioyl)-1,1,1-trifluoropropan-2-yl)benzoate (3hp). white solid, m.p. 83.7−85.4 °C, 75% yield (309.0 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 4.77–4.69 (m, 1H), 4.57–4.48 (m, 1H), 4.01–3.93 (m, 1H), 3.92, (s, 3H), 2.67–2.59 (m, 1H), 2.47–2.40 (m, 1H), 1.20 (d, *J* = 4.0 Hz, 3H), 1.15 (d, *J* = 6.0 Hz, 6H), 0.77 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 138.8, 130.3, 129.8, 129.7, 126.3 (qd, $J_{C–F}$ = 279.0 Hz, $J_{C–P}$ = 22.5 Hz), 72.0 (d, $J_{C–P}$ = 6.0 Hz), 71.4 (d, $J_{C–P}$ = 7.5 Hz), 52.3, 46.0 (q, $J_{C–F}$ = 28.5 Hz), 35.3 (d, $J_{C–P}$ = 118.5 Hz), 23.8 (d, $J_{C–P}$ = 4.5 Hz), 23.7 (d, $J_{C–P}$ = 3.0 Hz), 23.5 (d, $J_{C–P}$ = 4.5 Hz), 22.9 (d, $J_{C–P}$ = 7.5 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.31 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 89.7–89.2 (m); HRMS (EI) calcd for $C_{17}H_{24}F_3O_4PS$ $[M]^+$: 412.1085, found: 412.1084.



4

(((2-([1,1'-biphenyl]-4-yl)-3,3,3-trifluoropropyl)phosphoryl)bis(oxy))bis(methylene)bis(2,2-dimethylpropanoate) (4). White solid, m.p. 92.8−94.1 °C, 56% yield (312.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.57 (m, 4H), 7.48–7.40 (m, 4H), 7.39–7.33 (m, 1H), 5.98–5.48 (m, 2H), 5.30 (dd, *J* = 12.0 Hz, *J* = 8.0 Hz, 1H), 5.08 (dd, *J* = 12.0 Hz, *J* = 4.0 Hz, 1H), 3.88–3.75 (m, 1H), 2.62–2.45 (m, 2H), 1.22 (s, 9H), 0.96 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 141.8, 140.2, 131.8, 129.6, 128.9, 127.7, 127.5, 127.1, 126.1 (qd, $J_{C–F}$ = 278.0 Hz, $J_{C–P}$ = 23.0 Hz), 81.5 (d, $J_{C–P}$ = 6.0 Hz), 81.3 (d, $J_{C–P}$ = 6.0 Hz), 44.6 (q, $J_{C–F}$ = 28.0 Hz), 38.7 (d, $J_{C–P}$ = 5.0 Hz), 27.2 (d, $J_{C–P}$ = 148.0 Hz), 26.8, 26.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ –70.93 (d, $J_{H–F}$ = 11.3 Hz); ^{31}P NMR (243 MHz, $CDCl_3$) δ 27.7–26.8 (m); HRMS (EI) calcd for $C_{27}H_{34}F_3O_7P$ $[M]^+$: 558.1994, found: 558.1996.

7. Reference

(1) Y.-Q. Guo, Y.-P. Cao, H.-J. Song, Y.-X. Liu and Q.-M. Wang, *Chem. Commun.*, 2021, **57**, 9768–9771.

(2) J.-J. Zhang, J.-D. Yang and J.-P. Chen, *Nat. Commun.*, 2021, **12**, 2835.

(3) Y. Li, B. Zhao, K. Dai, D.-H. Tu, Wang, B.; Y.-Y. Wang, Z.-T. Liu, Z.-W. Liu and J. Lu, *Tetrahedron*, 2016, **72**, 5684–5690.

(4) Y.-F. Chen,; N.-N. Ni, D.-P. Cheng and X.-L. Xu, *Tetrahedron Lett.*, 2020, **61**, 152425.

(5) W.-J. Yue, C. S. Day and R. Martin, *J. Am. Chem. Soc.*, 2021, **143**, 6395–6400.

(6) F.-L. Chen, X.-F. Xu, Y.-L. He, G.-P. Huang and S.-L. Zhu, *Angew. Chem., Int. Ed.*, 2020, **59**, 5398–5402.

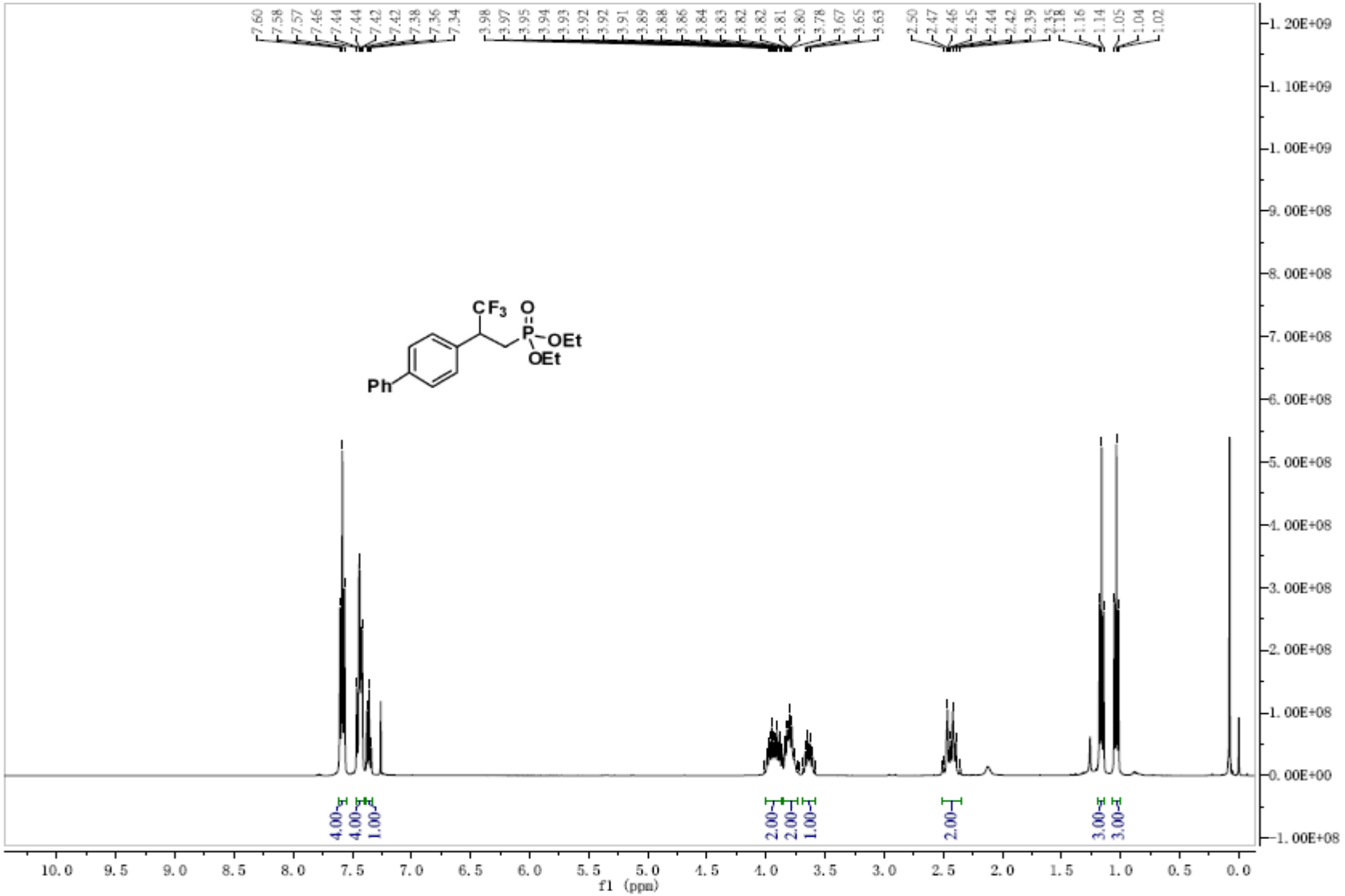
(7) P. Tongcharoensirikul, A. I. Suarez, T. Voelker and C. M. Thompson, *J. Org. Chem.*, 2004, **69**, 2322–2326.

(8) C. M. Jessop, A. F. Parsons, A. Routledge, J. Derek and D. J. Irvine, *Eur. J. Org. Chem.*, 2006, **2006**, 1547–1554.

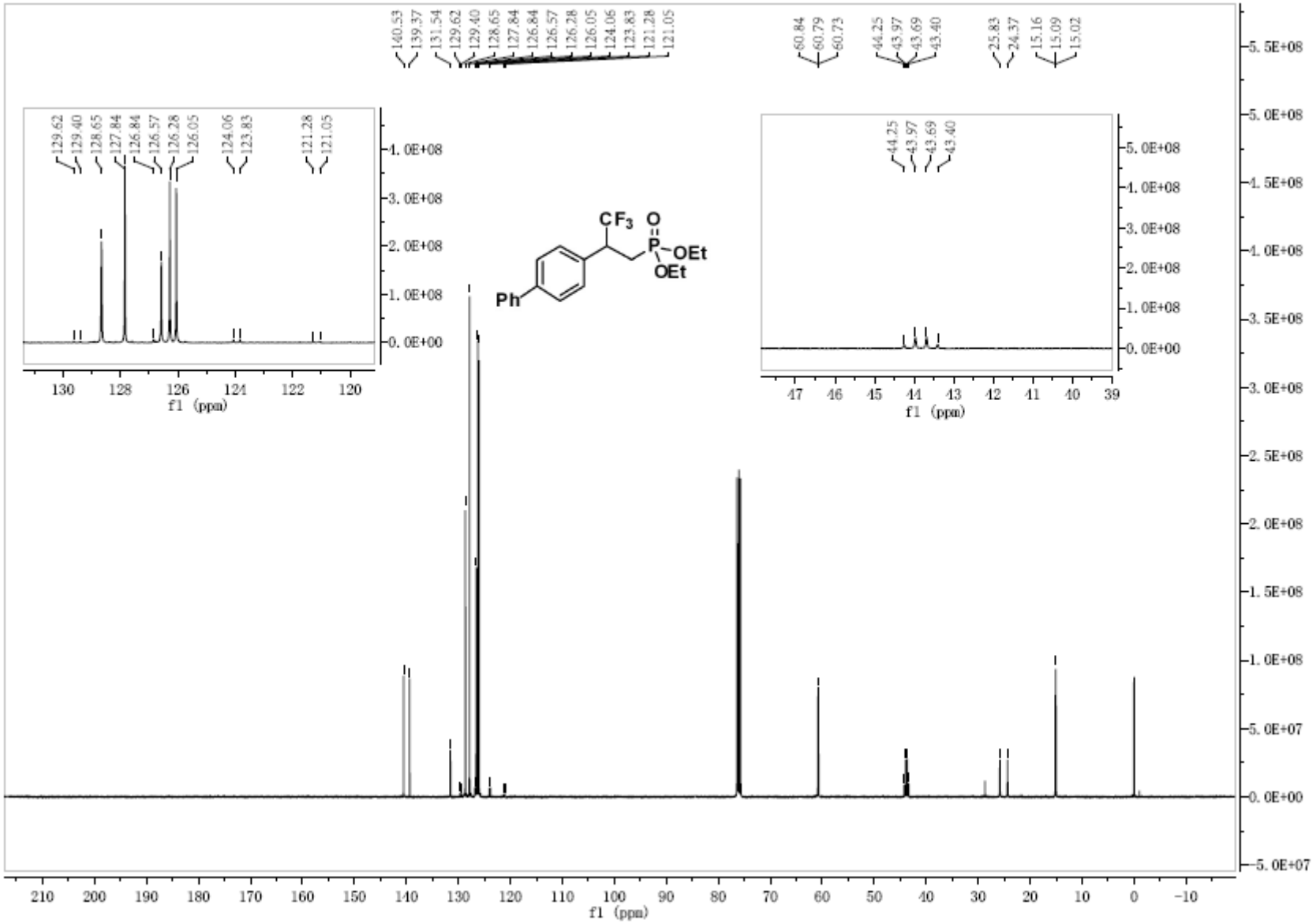
(9) A. Hałuszczuk, N. Babul, L. Nierzwicki and W. Przychodzeń, *Eur. J. Org. Chem.* 2019, **2019**, 4411– 4416.

8. ^{1}H, ^{13}C, ^{19}F, ^{31}P NMR and HRMS (EI) spectra of the target compounds

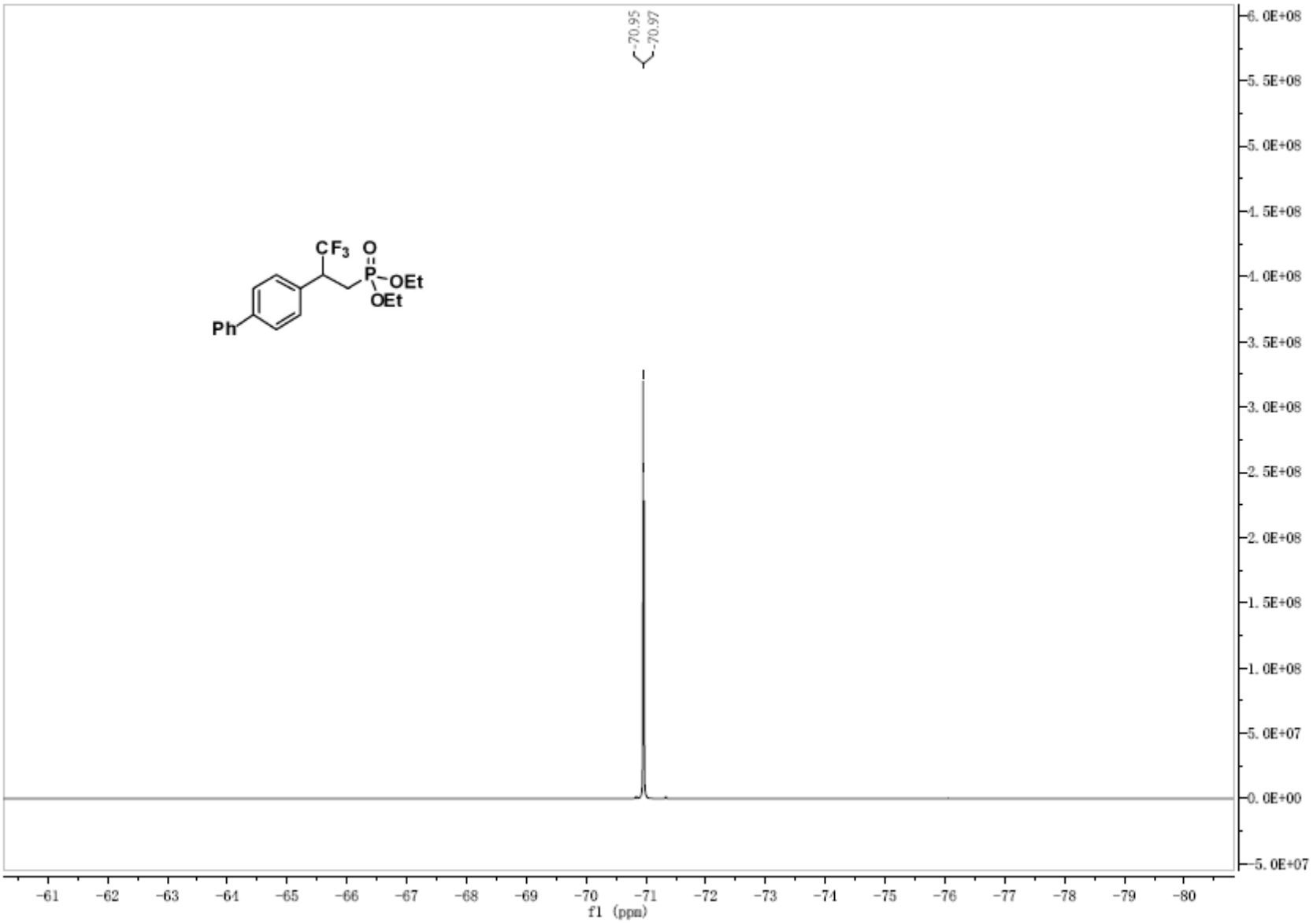
^{1}H NMR spectrum of 3aa



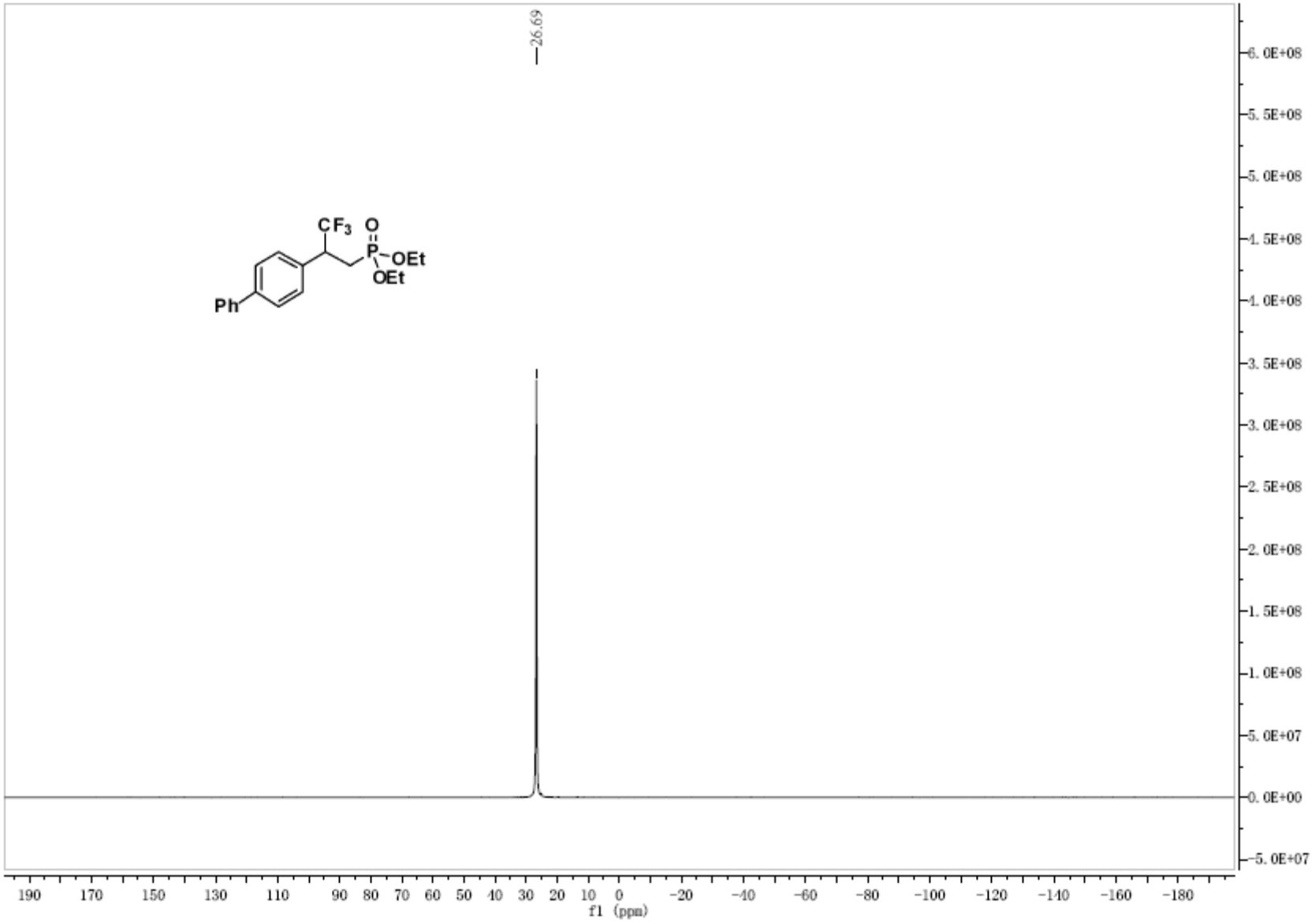
^{13}C NMR spectrum of 3aa



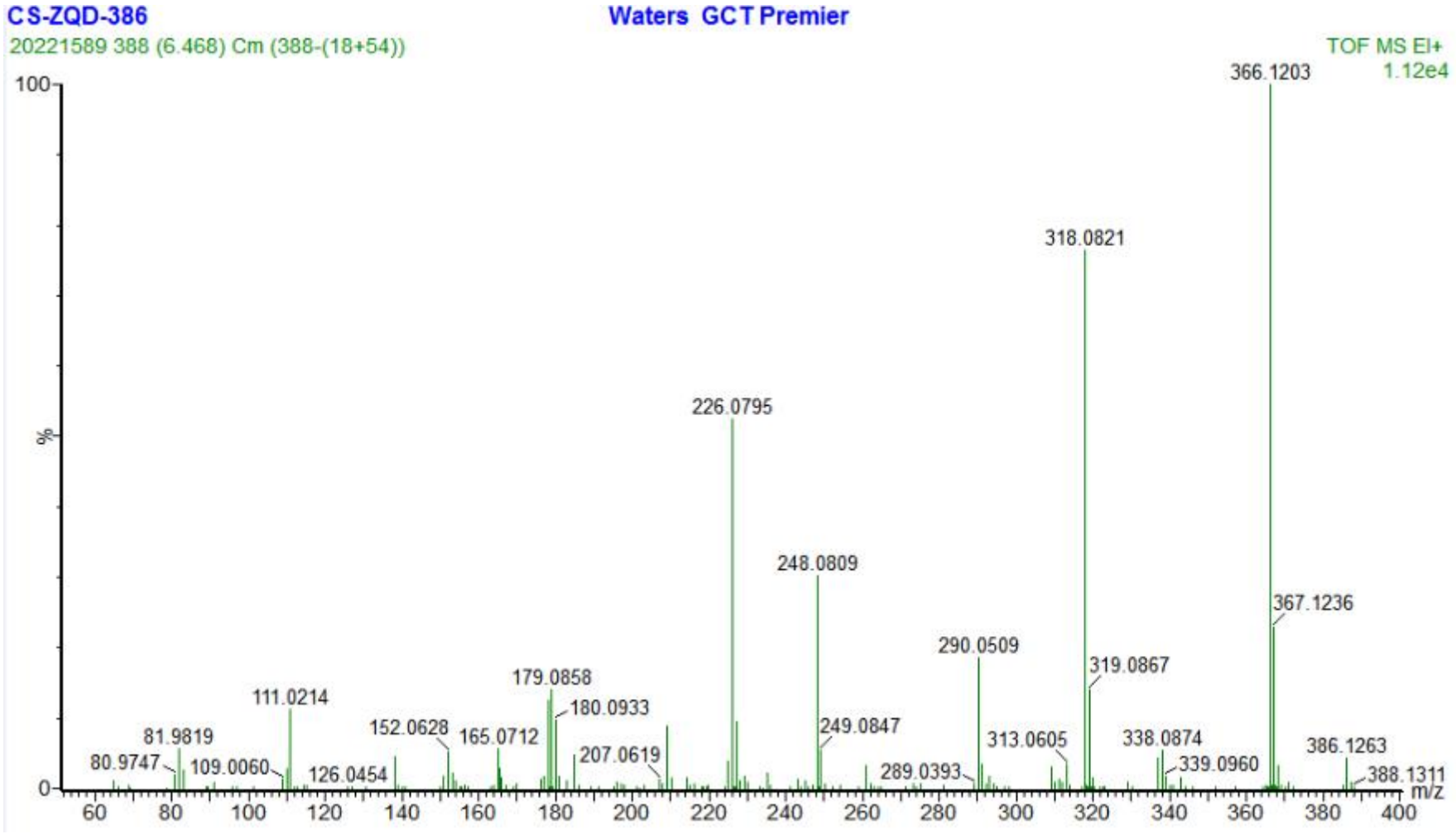
^{19}F NMR spectrum of 3aa



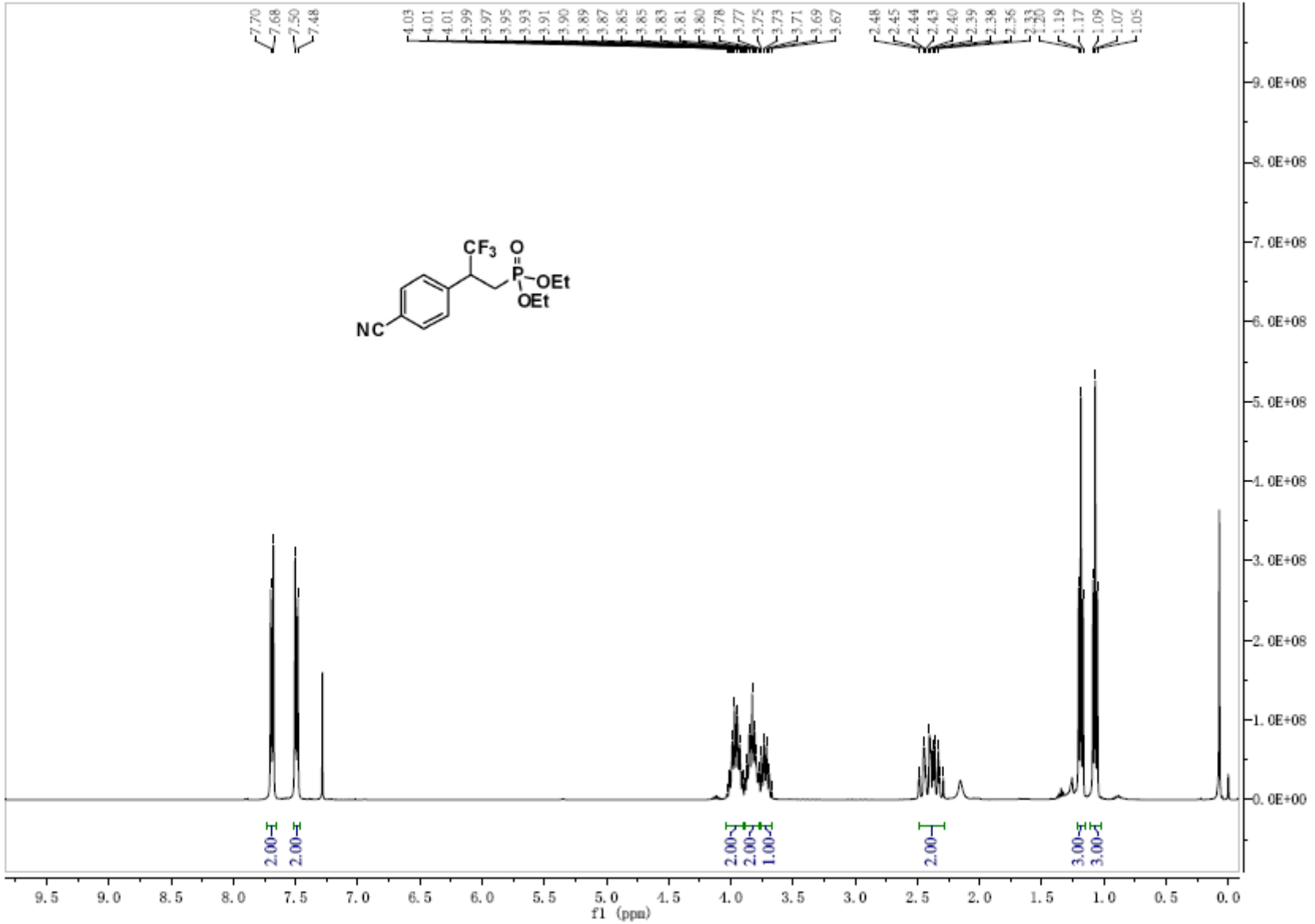
^{31}P NMR spectrum of 3aa



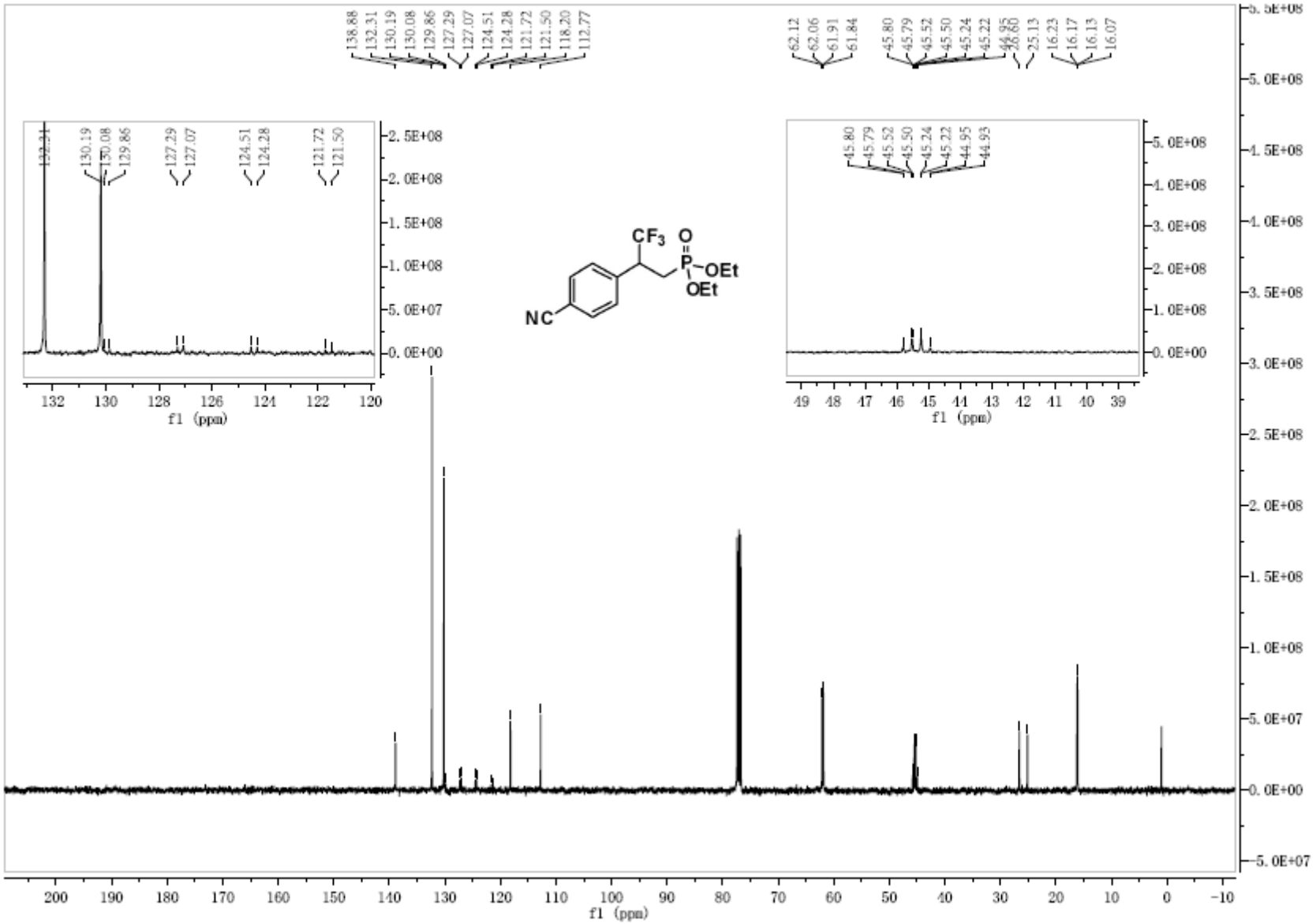
HRMS (EI) spectrum of 3aa



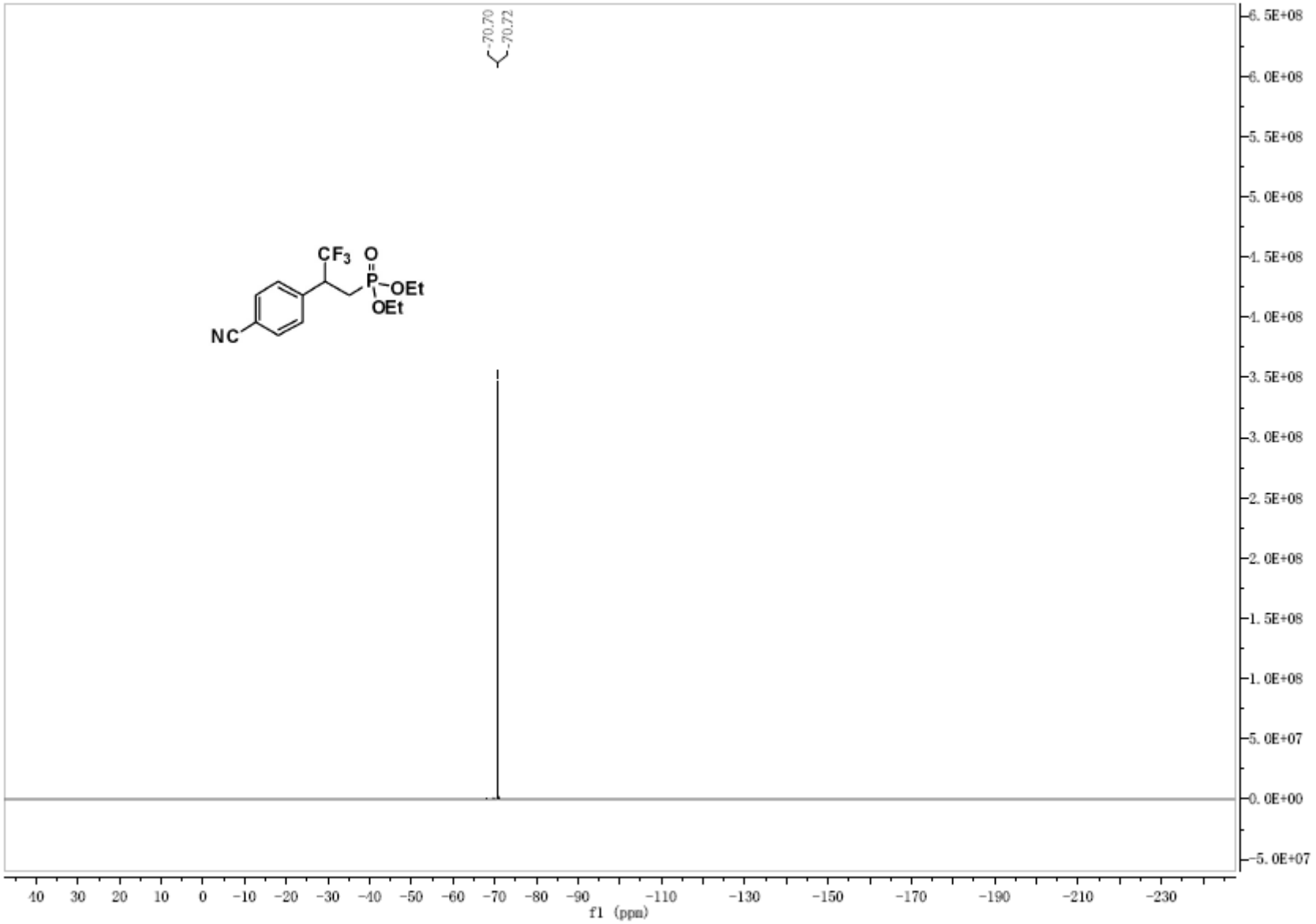
[1]H NMR spectrum of 3ba



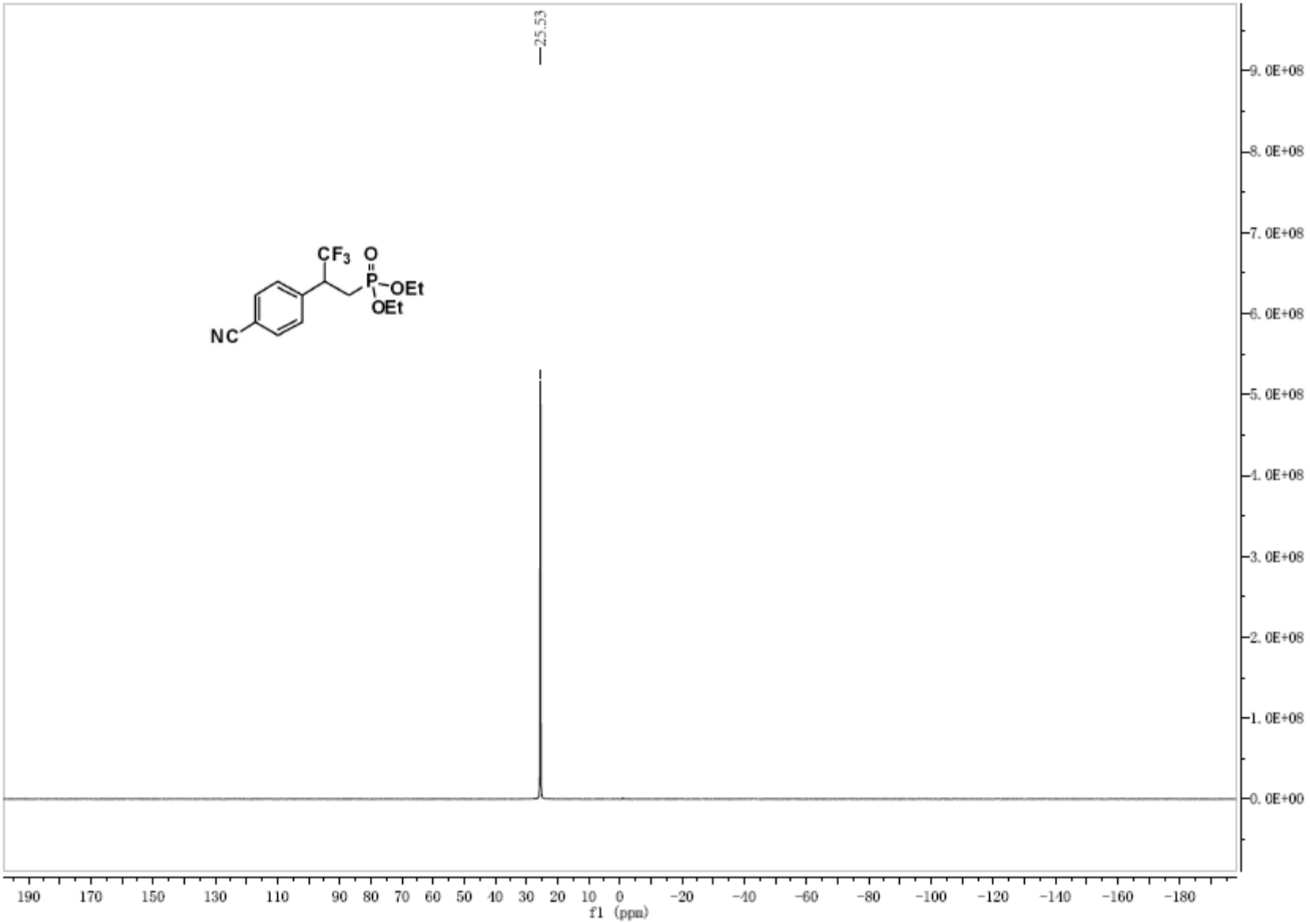
^{13}C NMR spectrum of 3ba



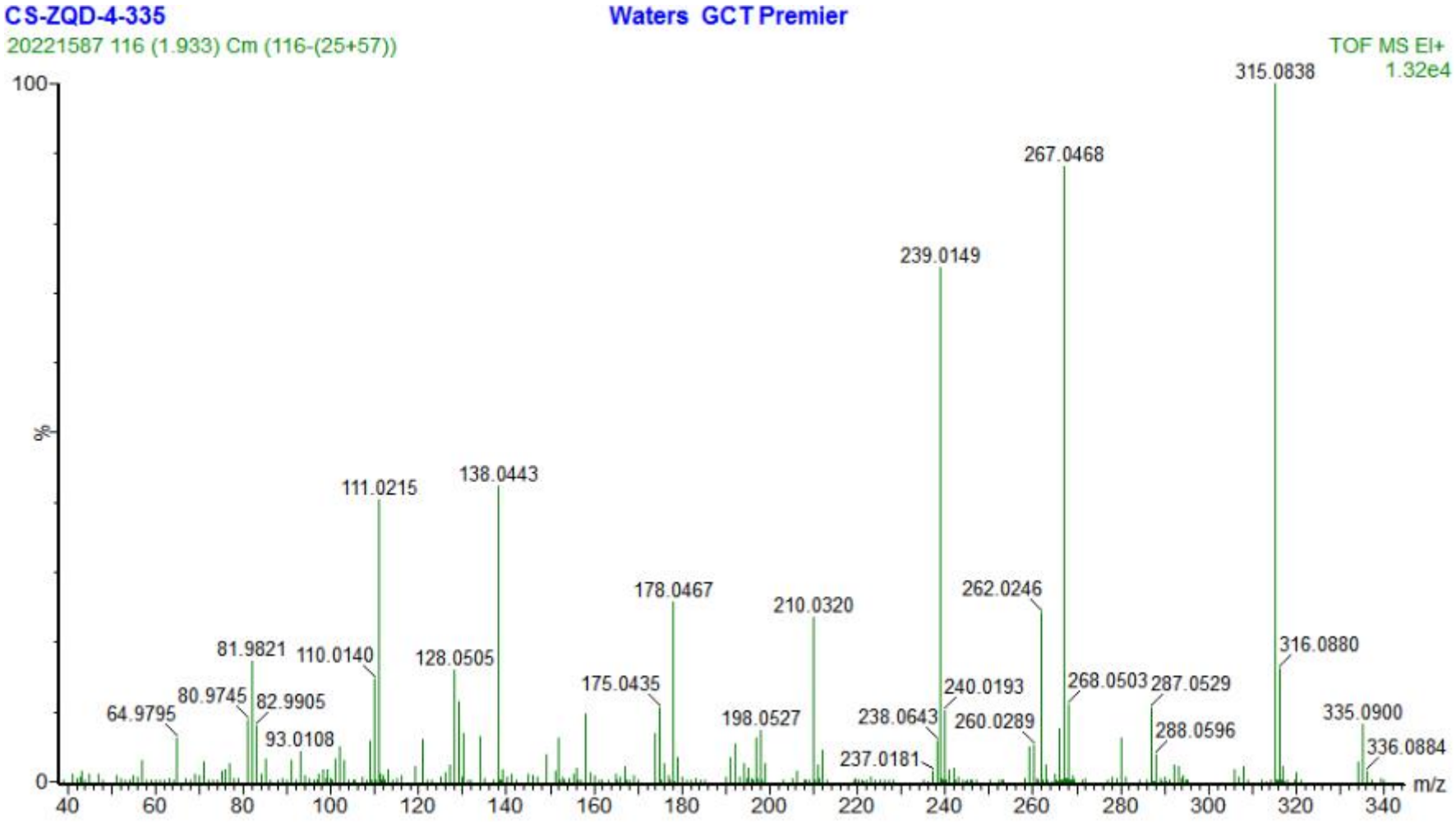
^{19}F NMR spectrum of 3ba



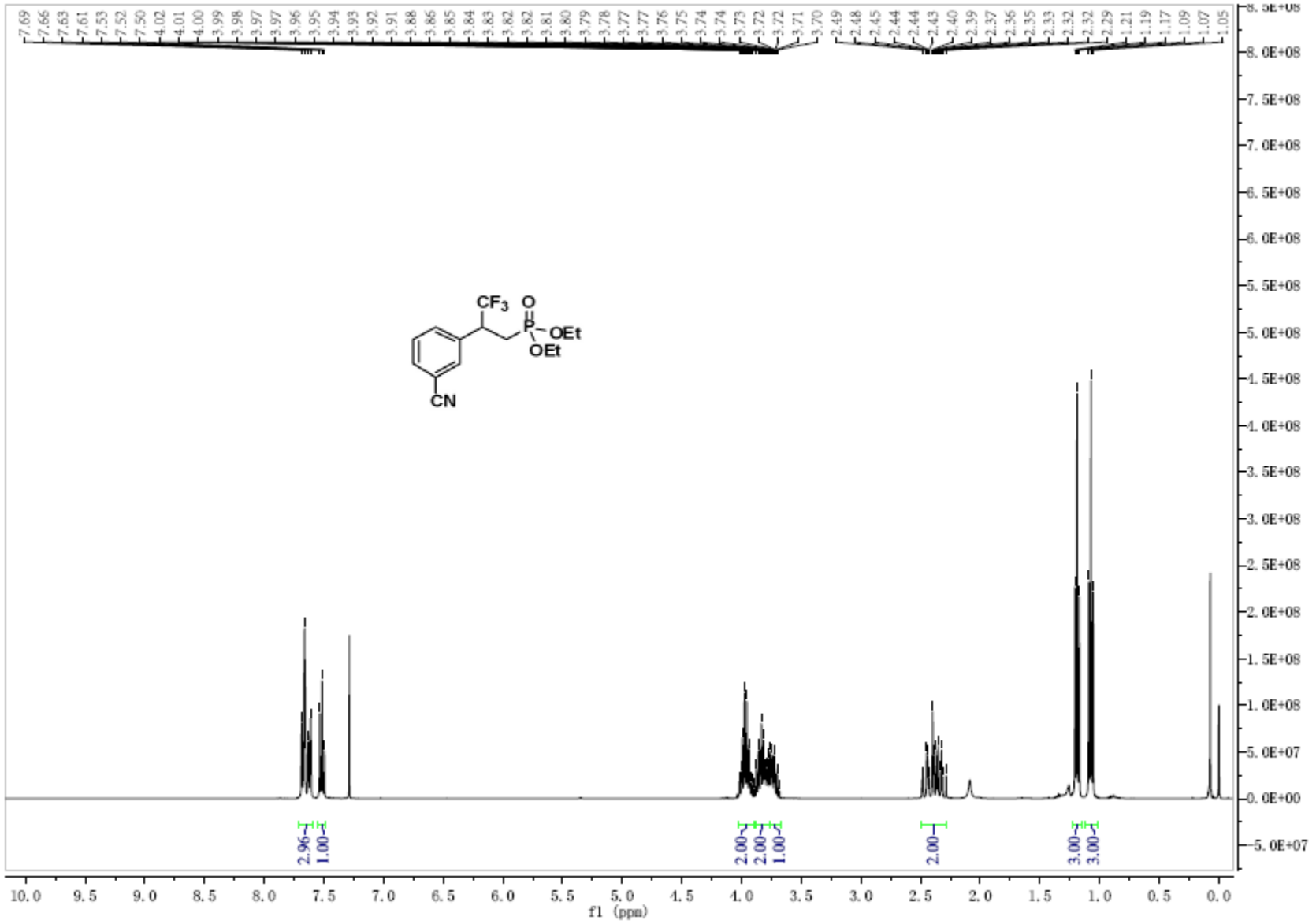
^{31}P NMR spectrum of 3ba



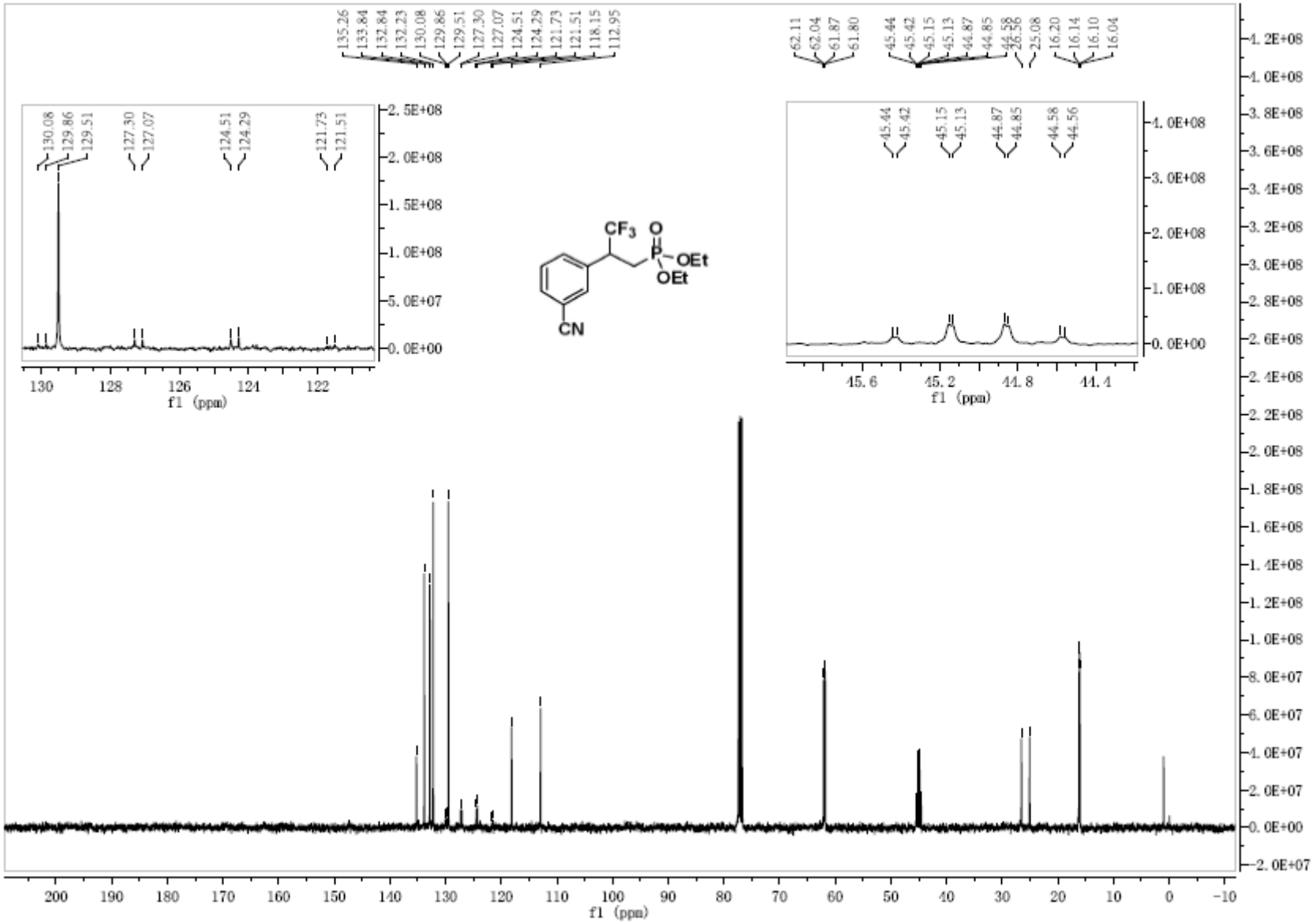
HRMS (EI) spectrum of 3ba



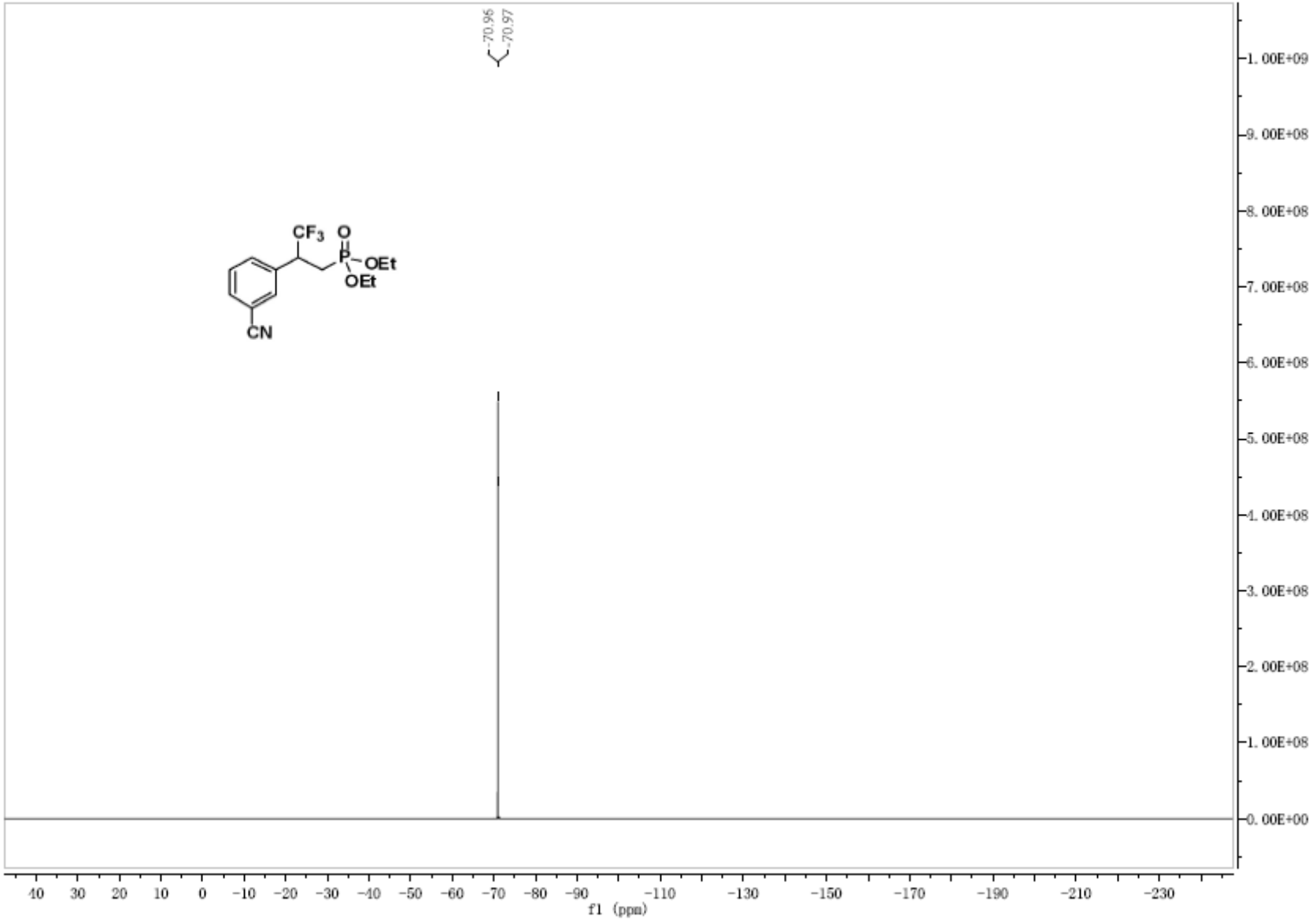
^{1}H NMR spectrum of 3ca



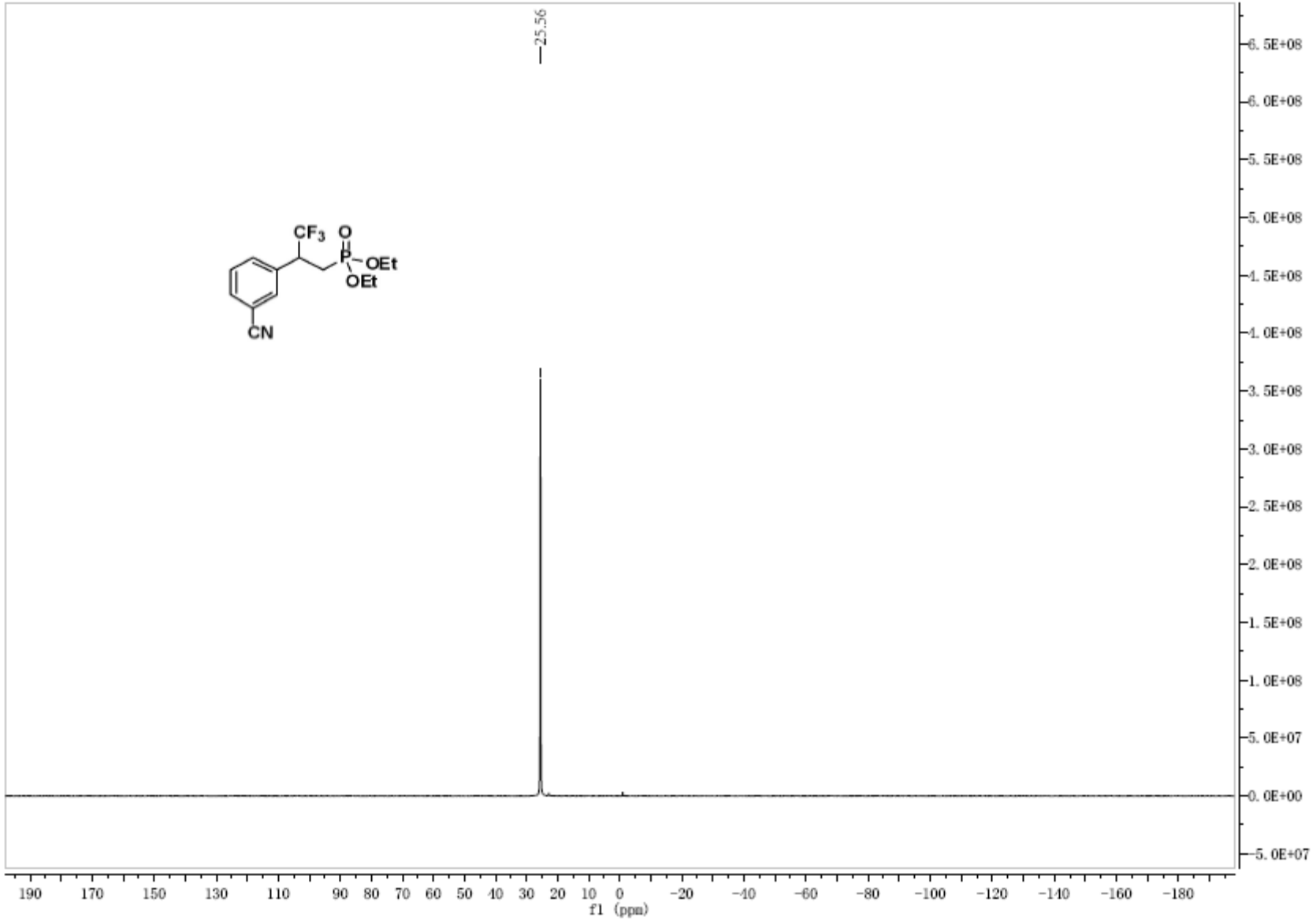
^{13}C NMR spectrum of 3ca



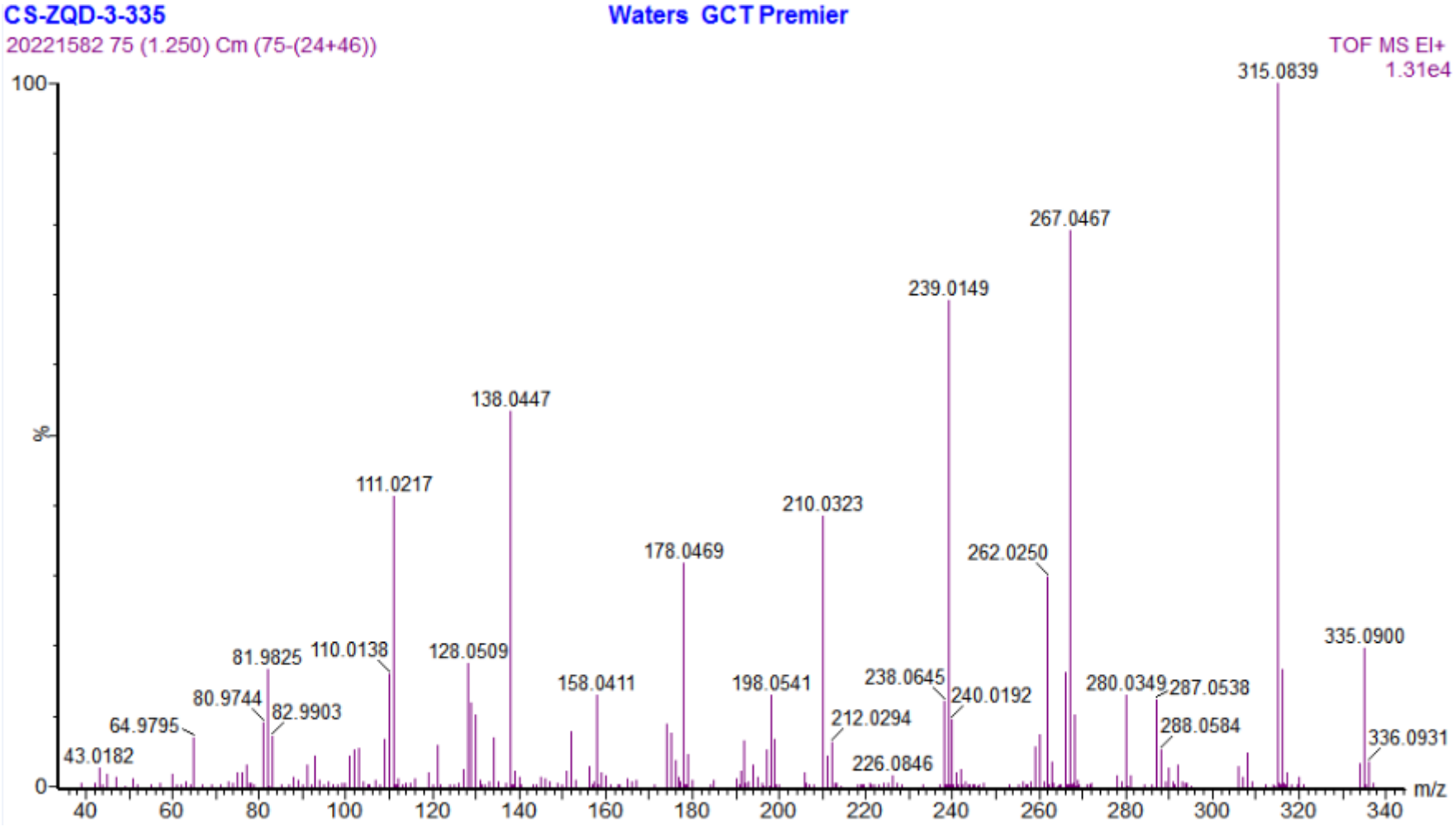
^{19}F NMR spectrum of 3ca



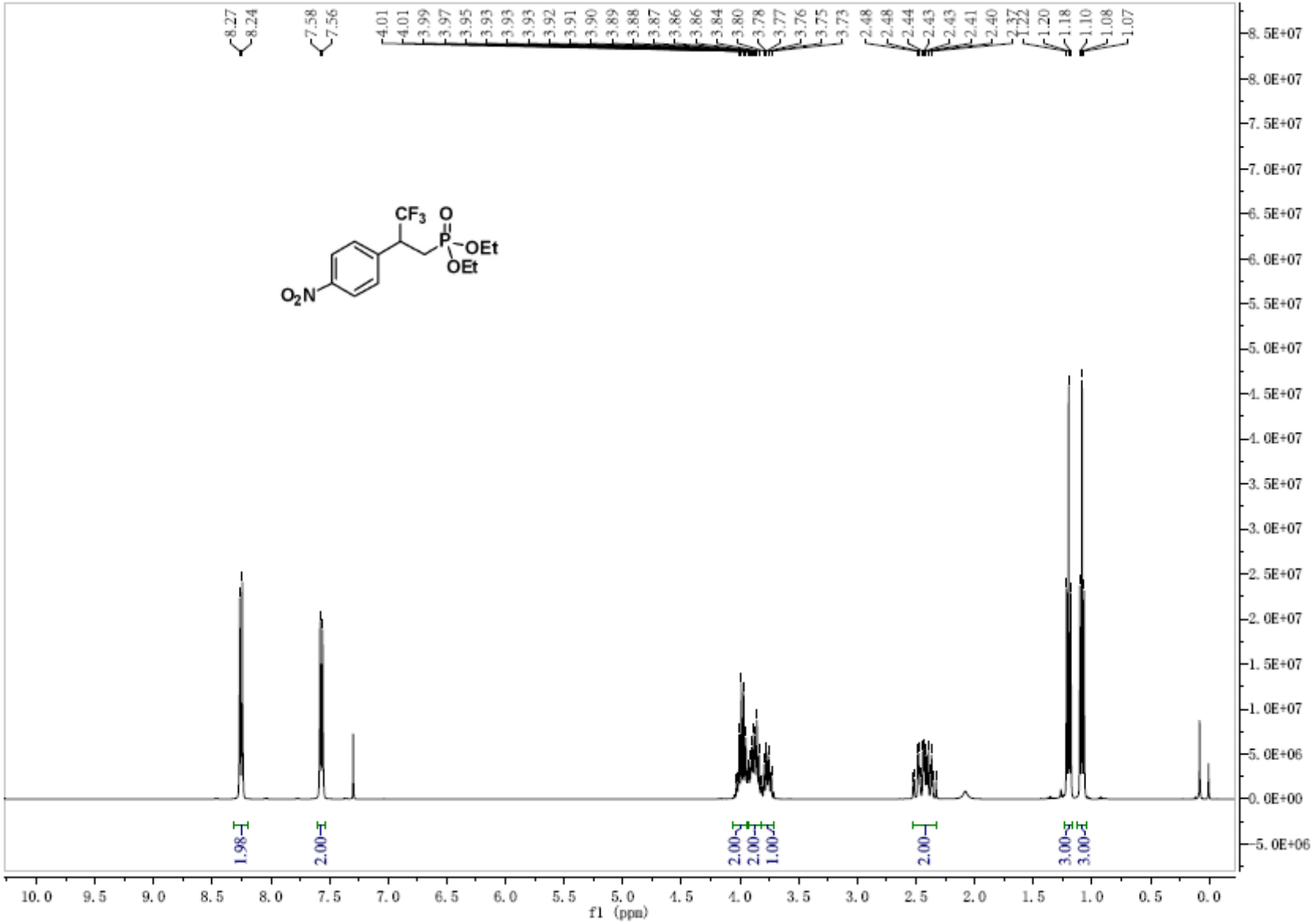
^{31}P NMR spectrum of 3ca



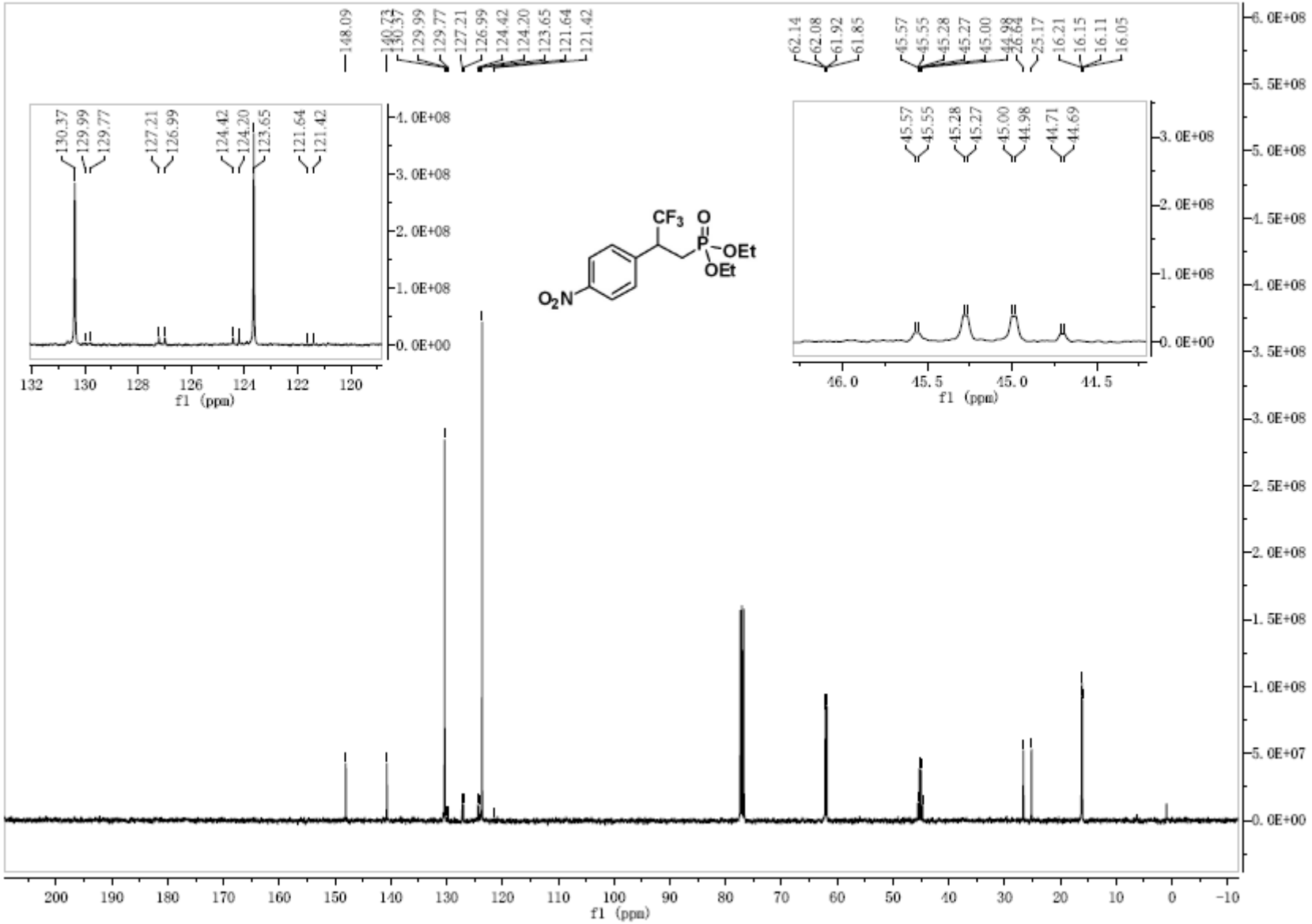
HRMS (EI) spectrum of 3ca



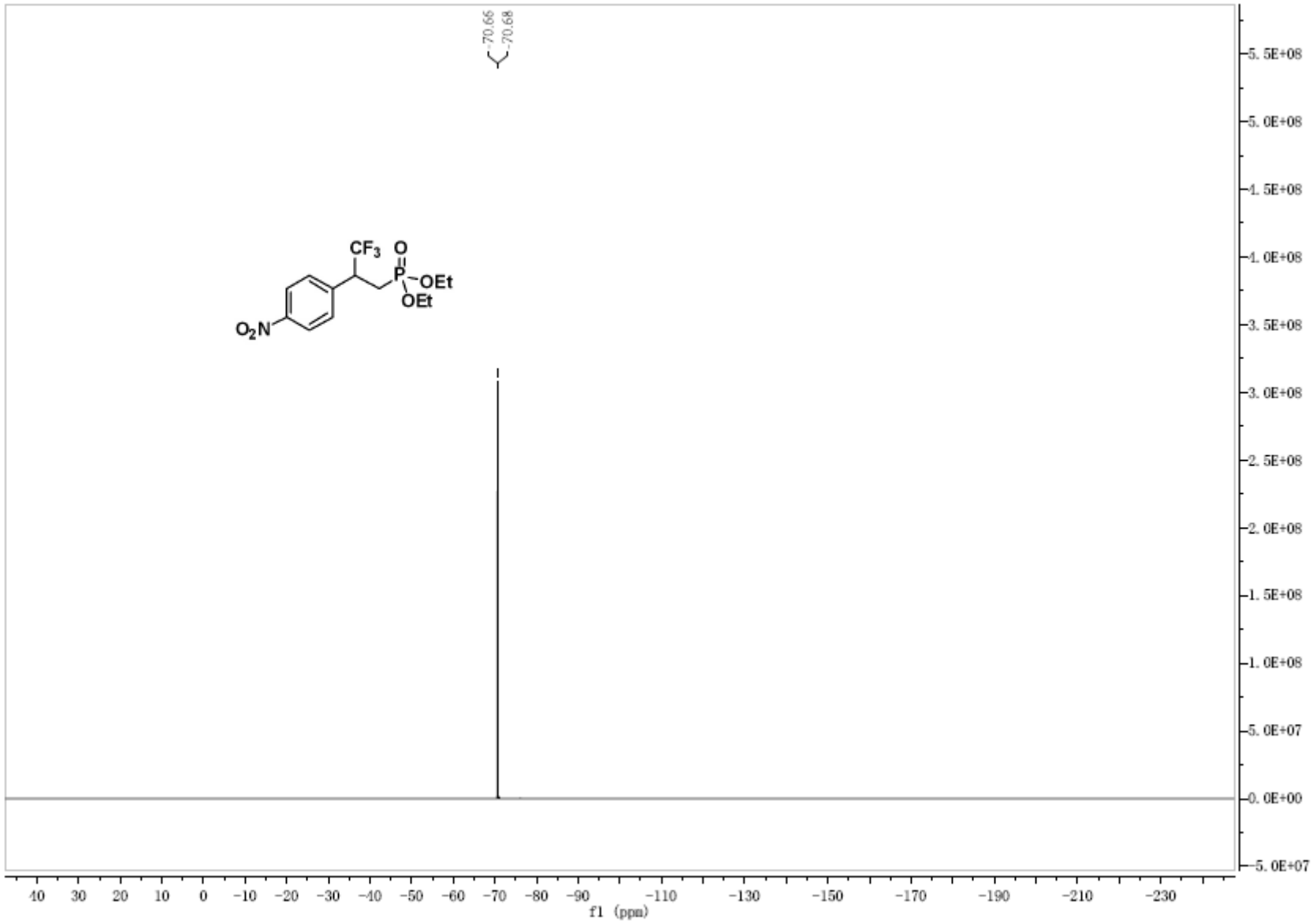
^{1}H NMR spectrum of 3da



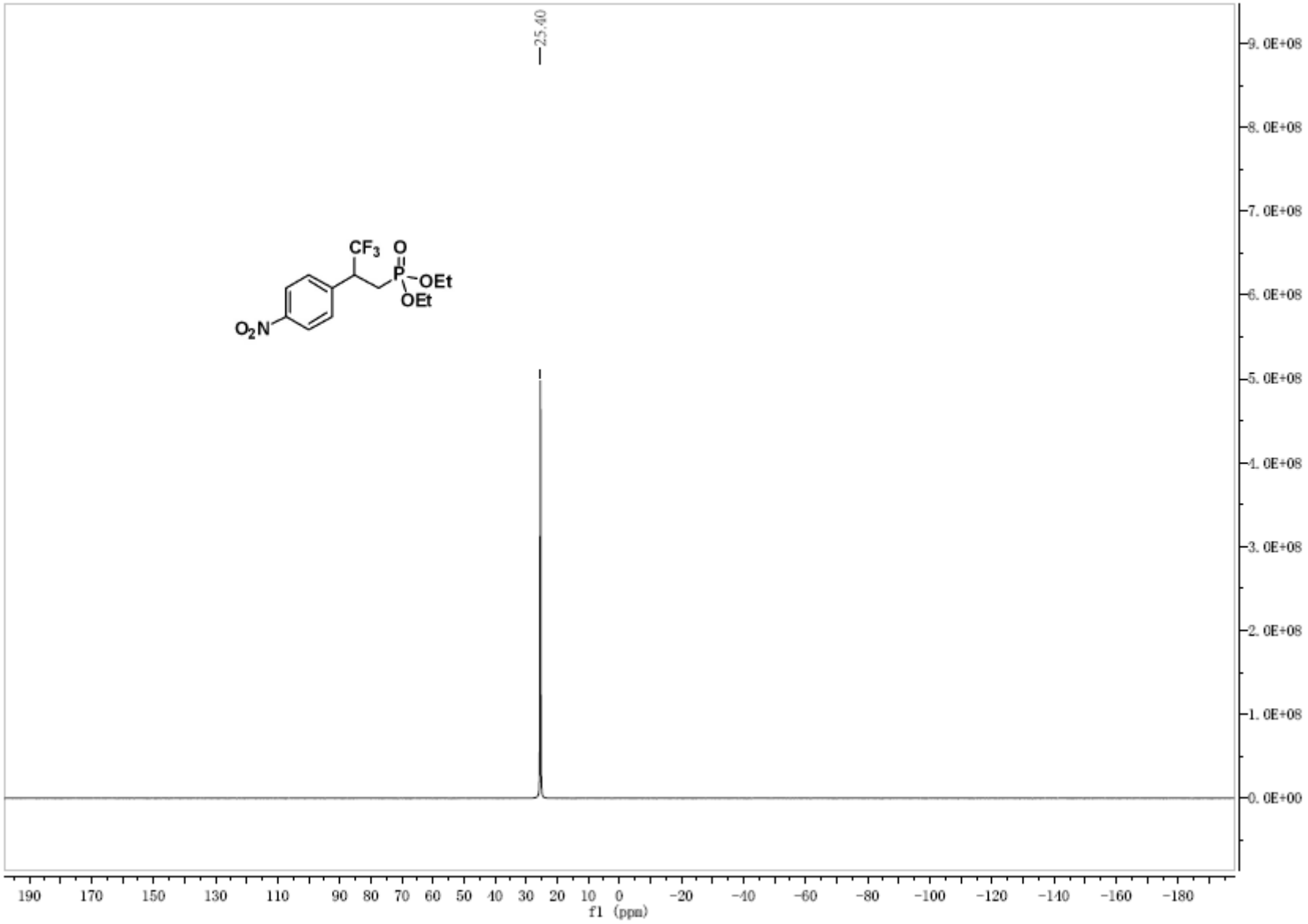
^{13}C NMR spectrum of 3da



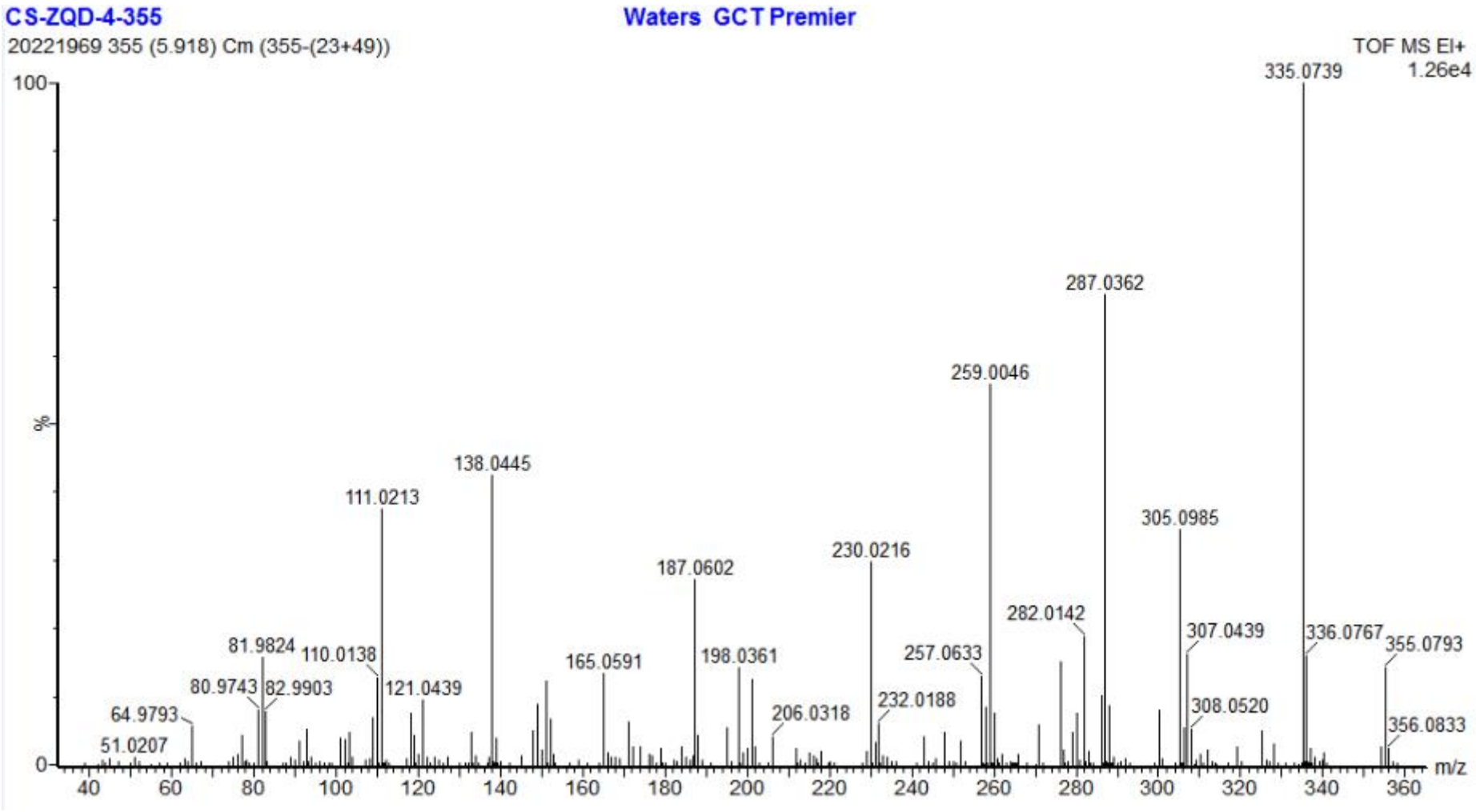
^{19}F NMR spectrum of 3da



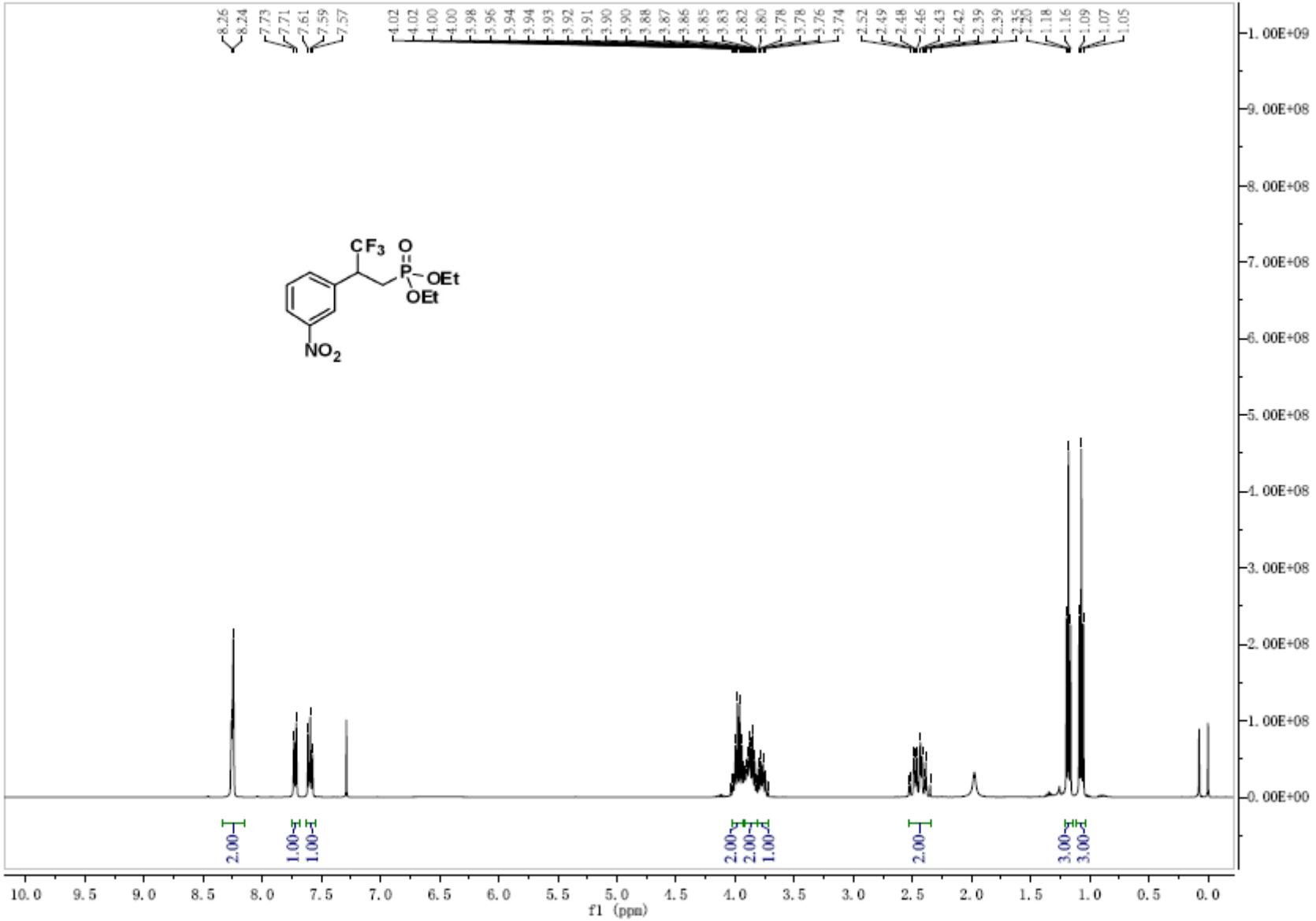
^{31}P NMR spectrum of 3da



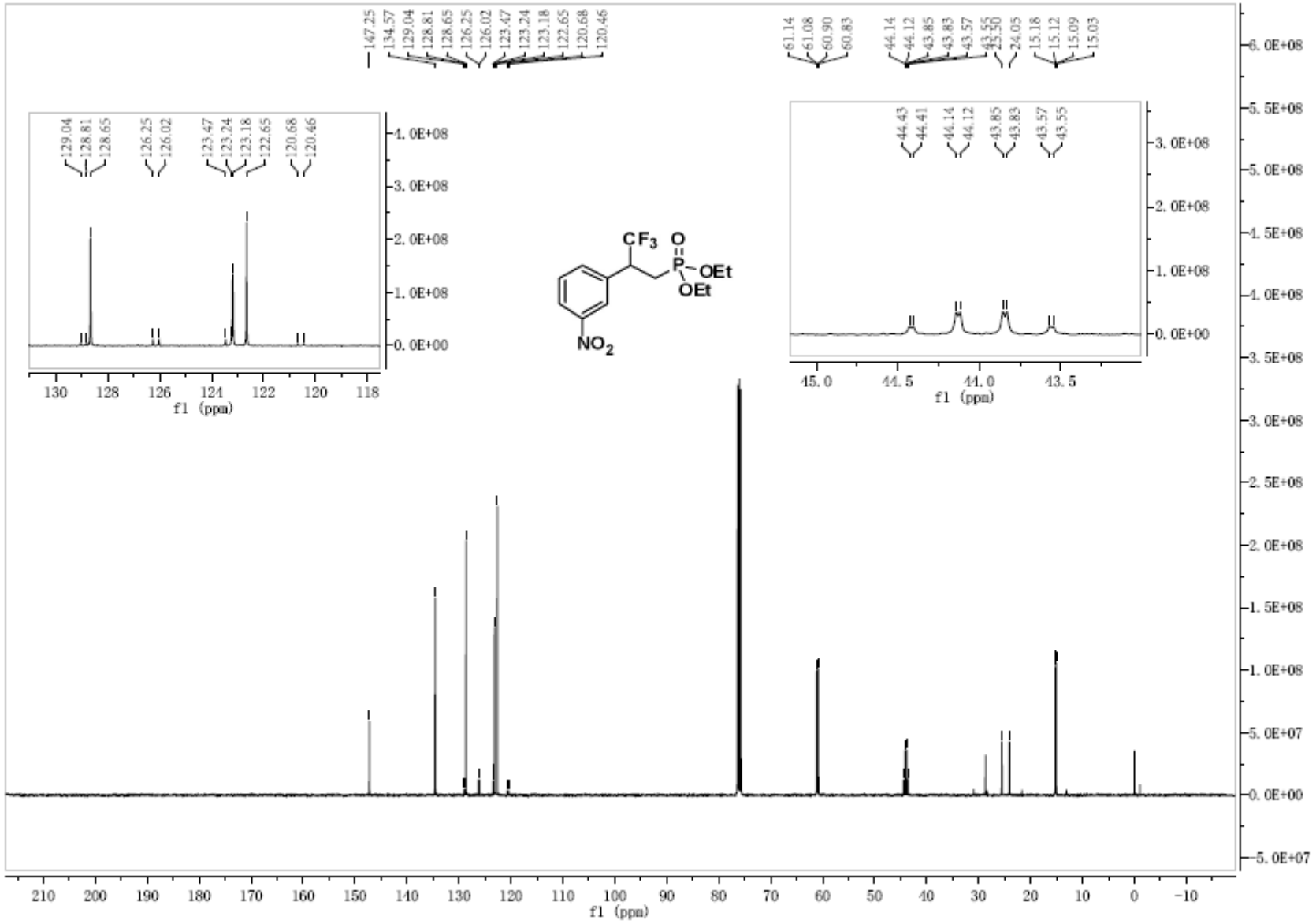
HRMS (EI) spectrum of 3da



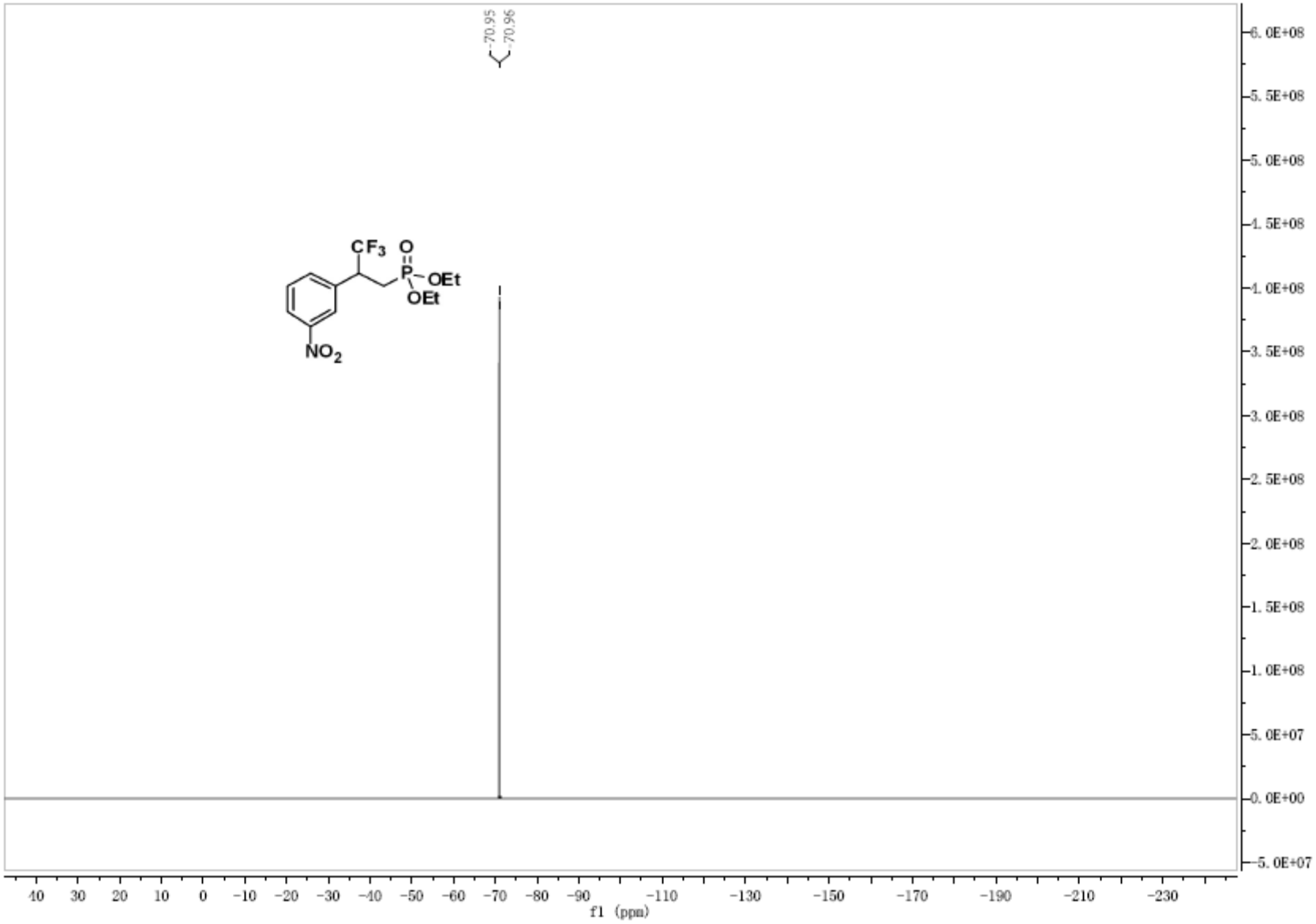
^{1}H NMR spectrum of 3ea



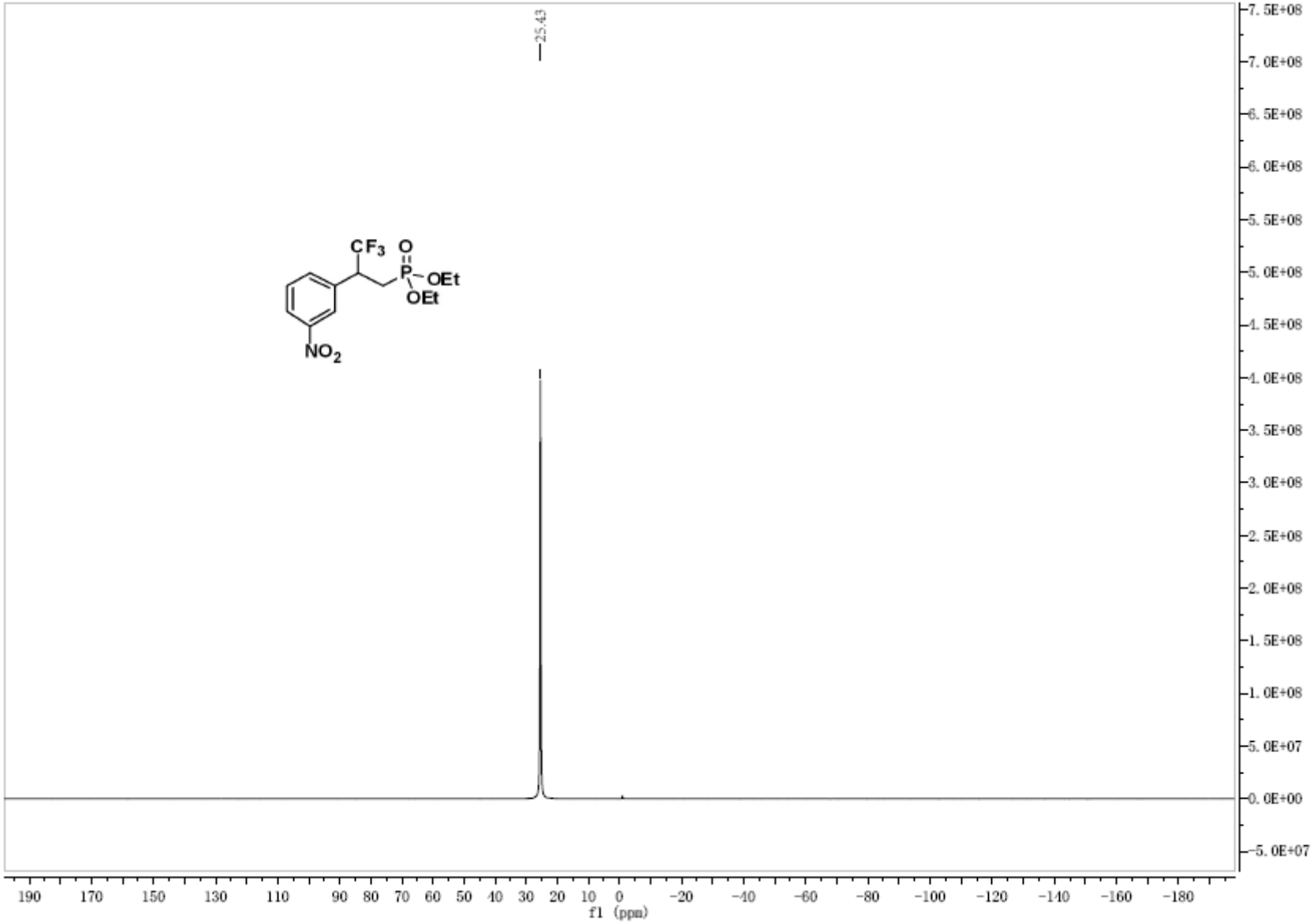
^{13}C NMR spectrum of 3ea



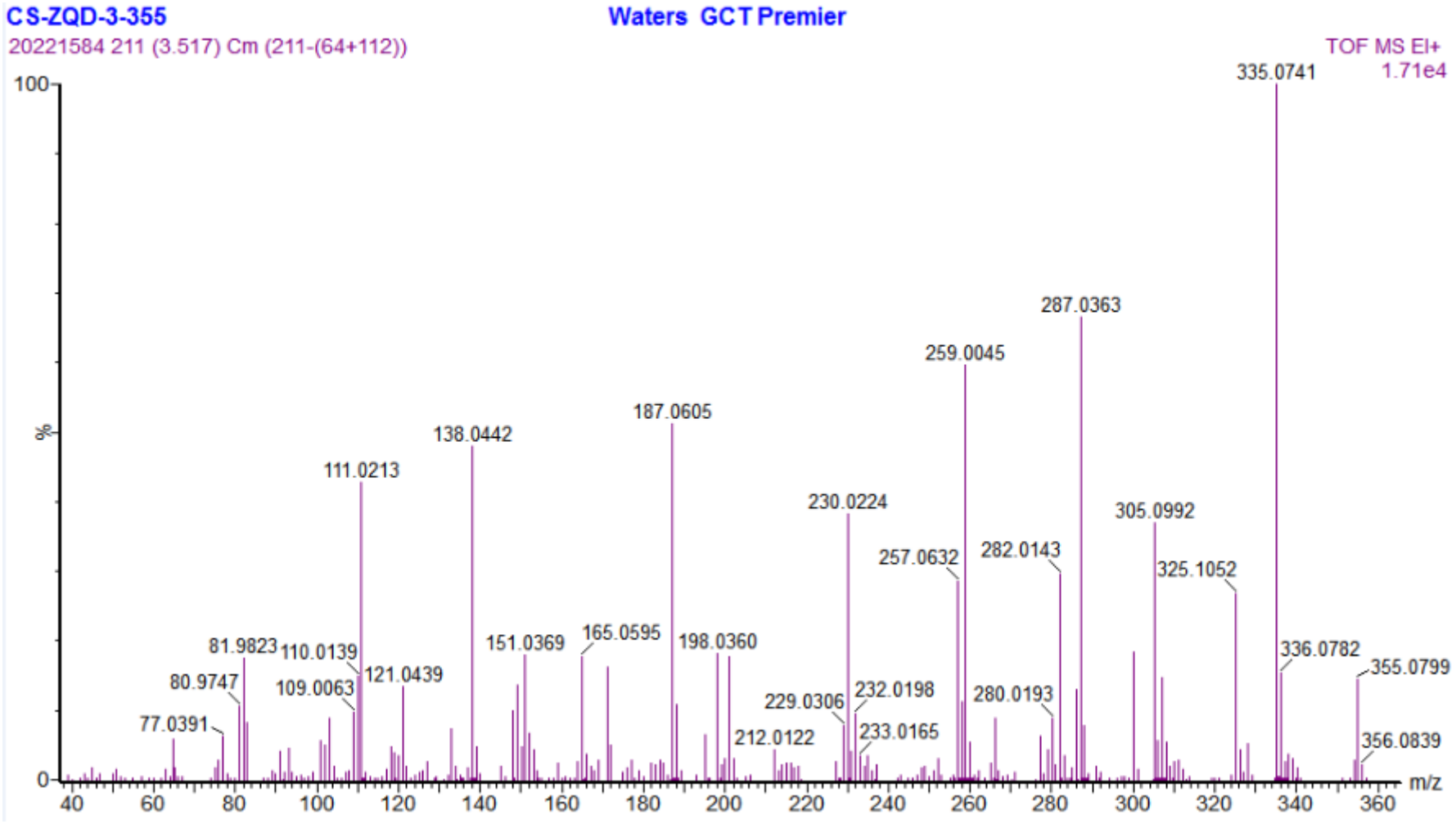
^{19}F NMR spectrum of 3ea



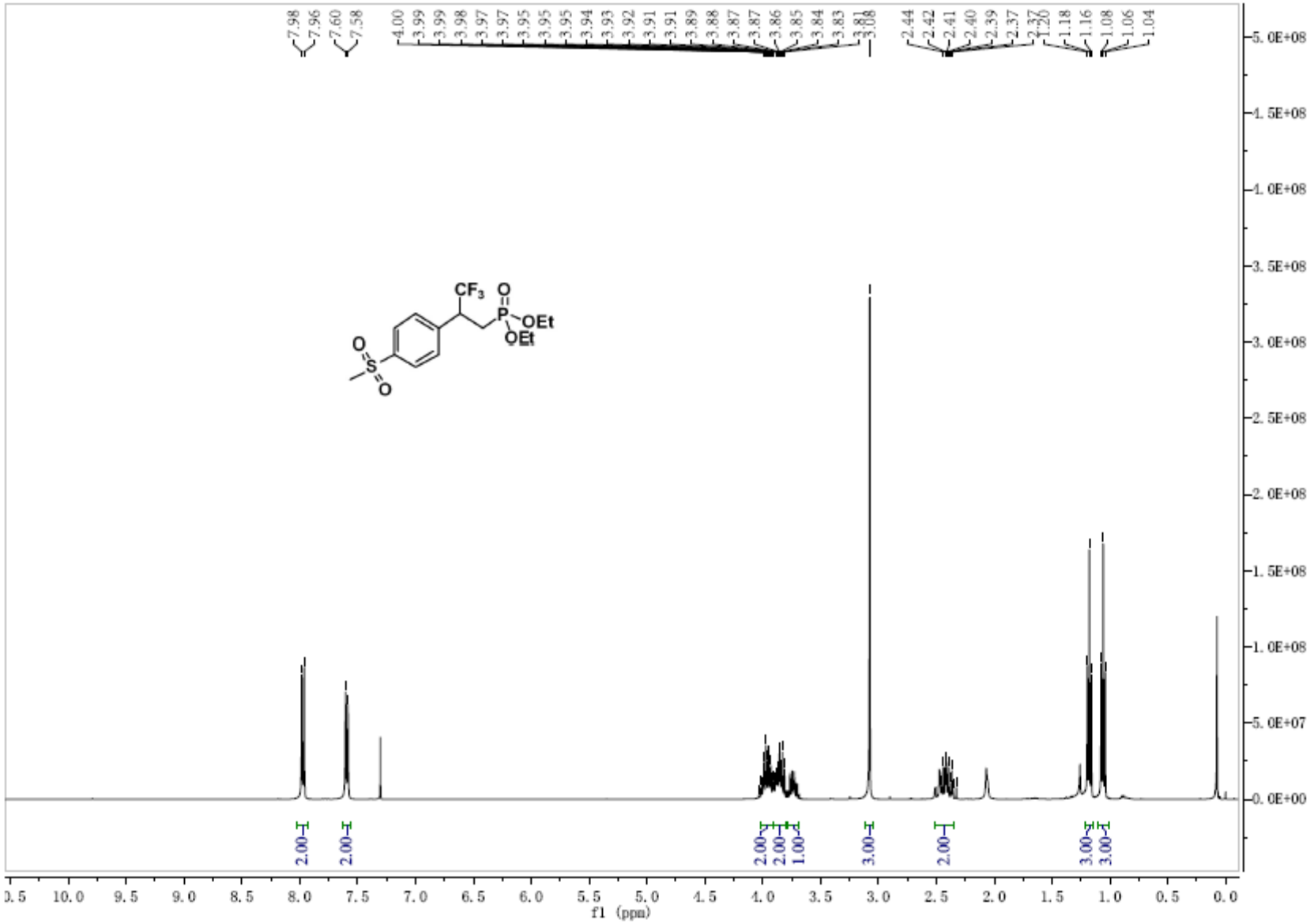
^{31}P NMR spectrum of 3ea



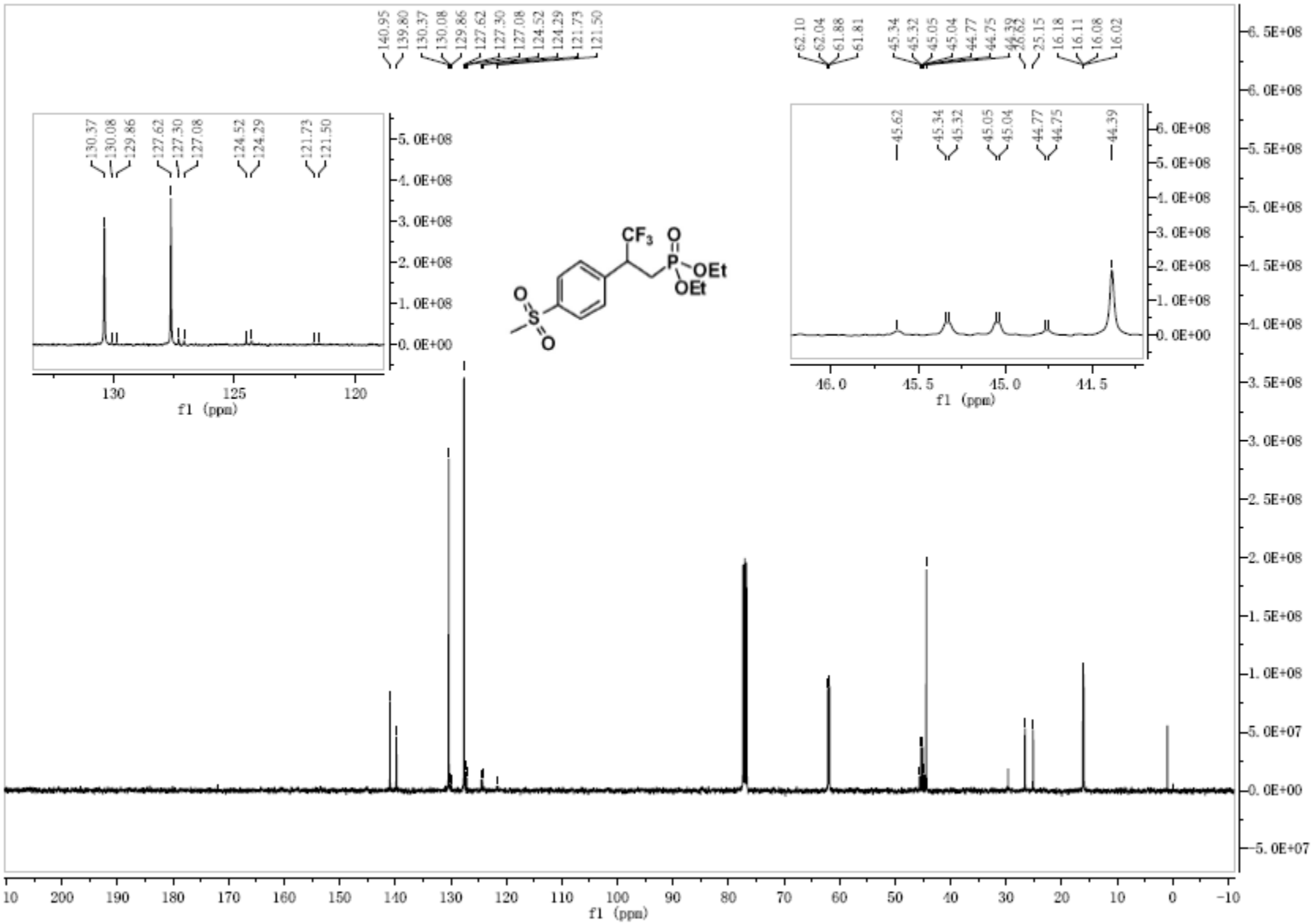
HRMS (EI) spectrum of 3ea



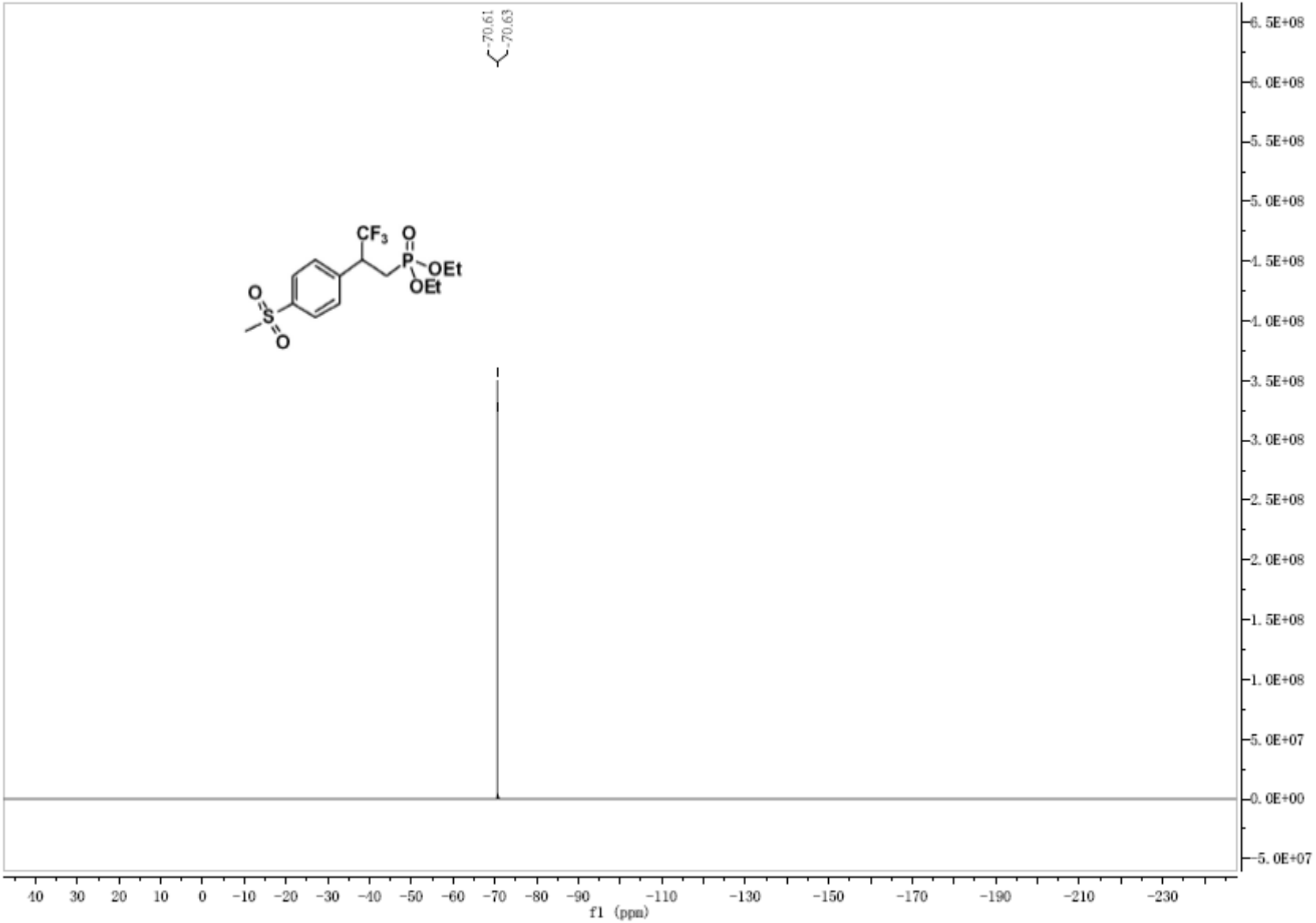
^{1}H NMR spectrum of 3fa



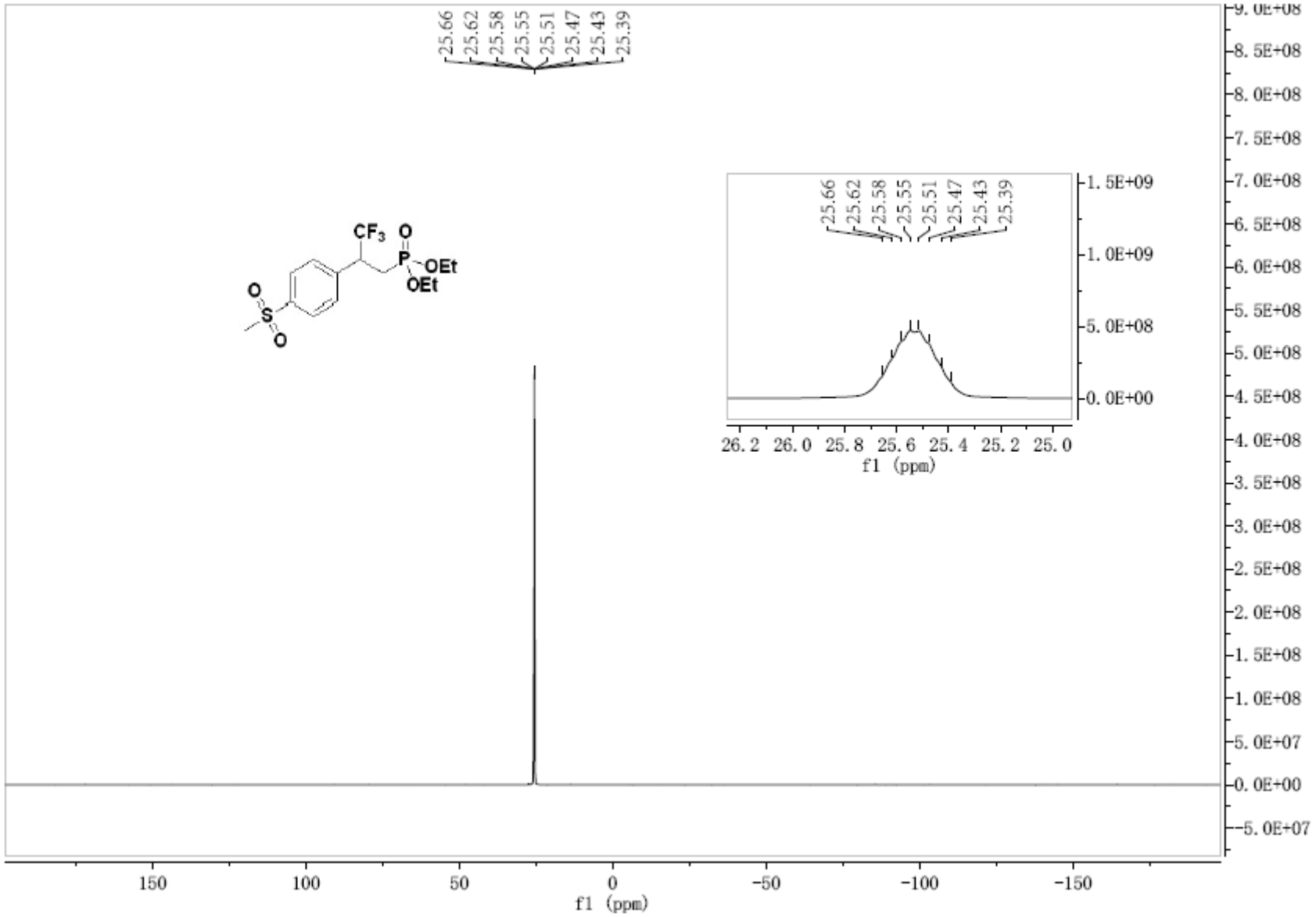
^{13}C NMR spectrum of 3fa



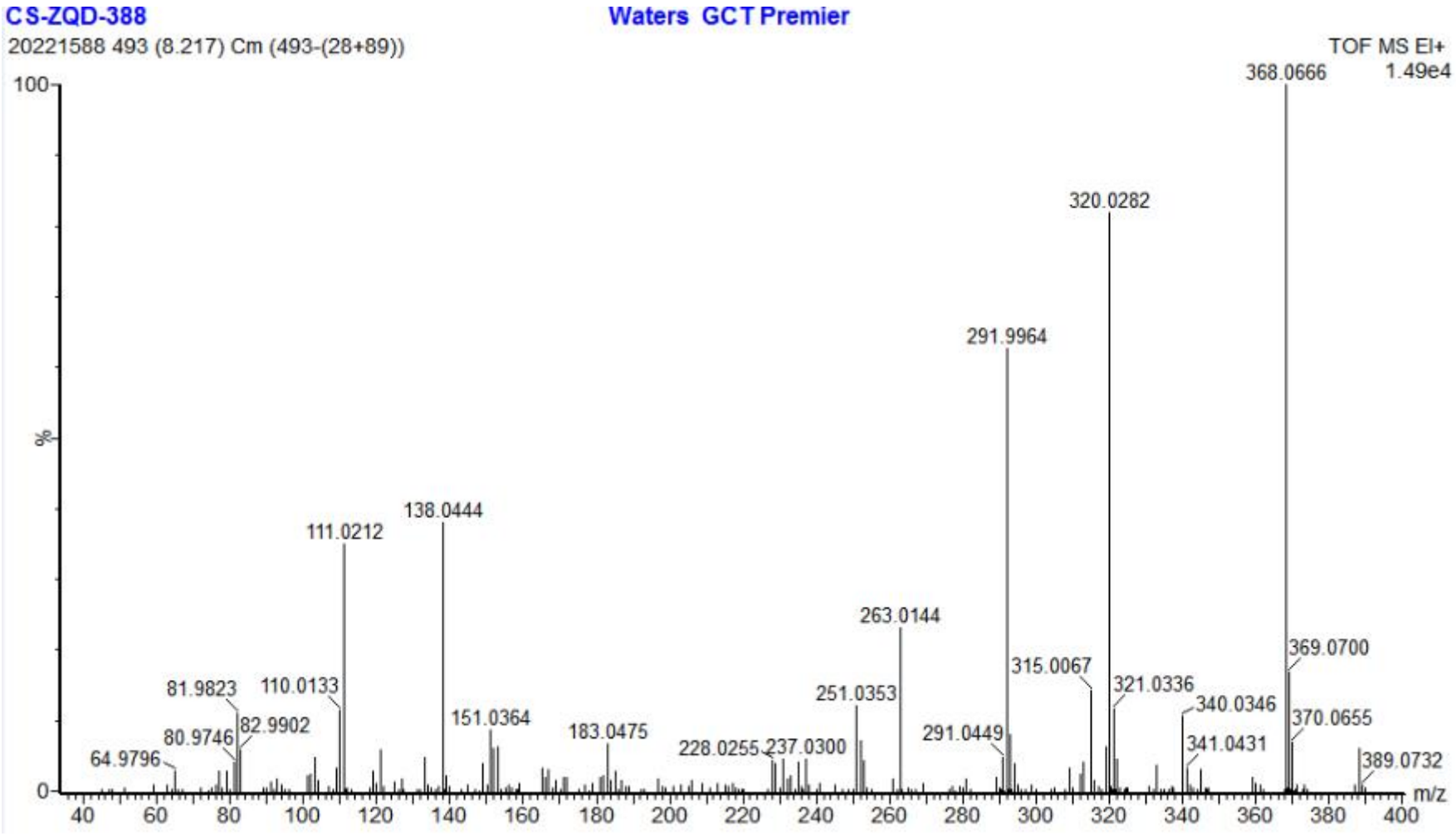
^{19}F NMR spectrum of 3fa



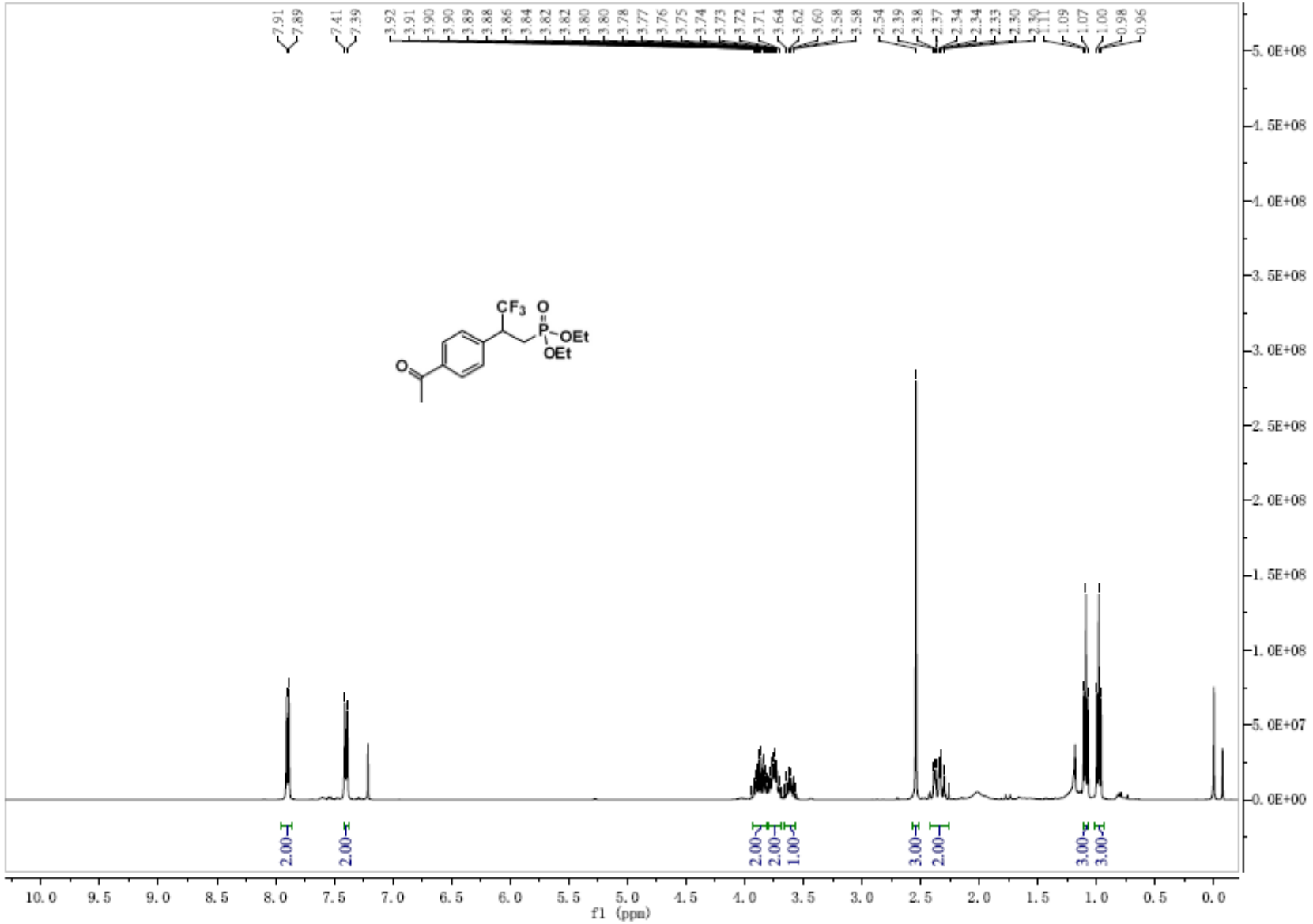
^{31}P NMR spectrum of 3fa



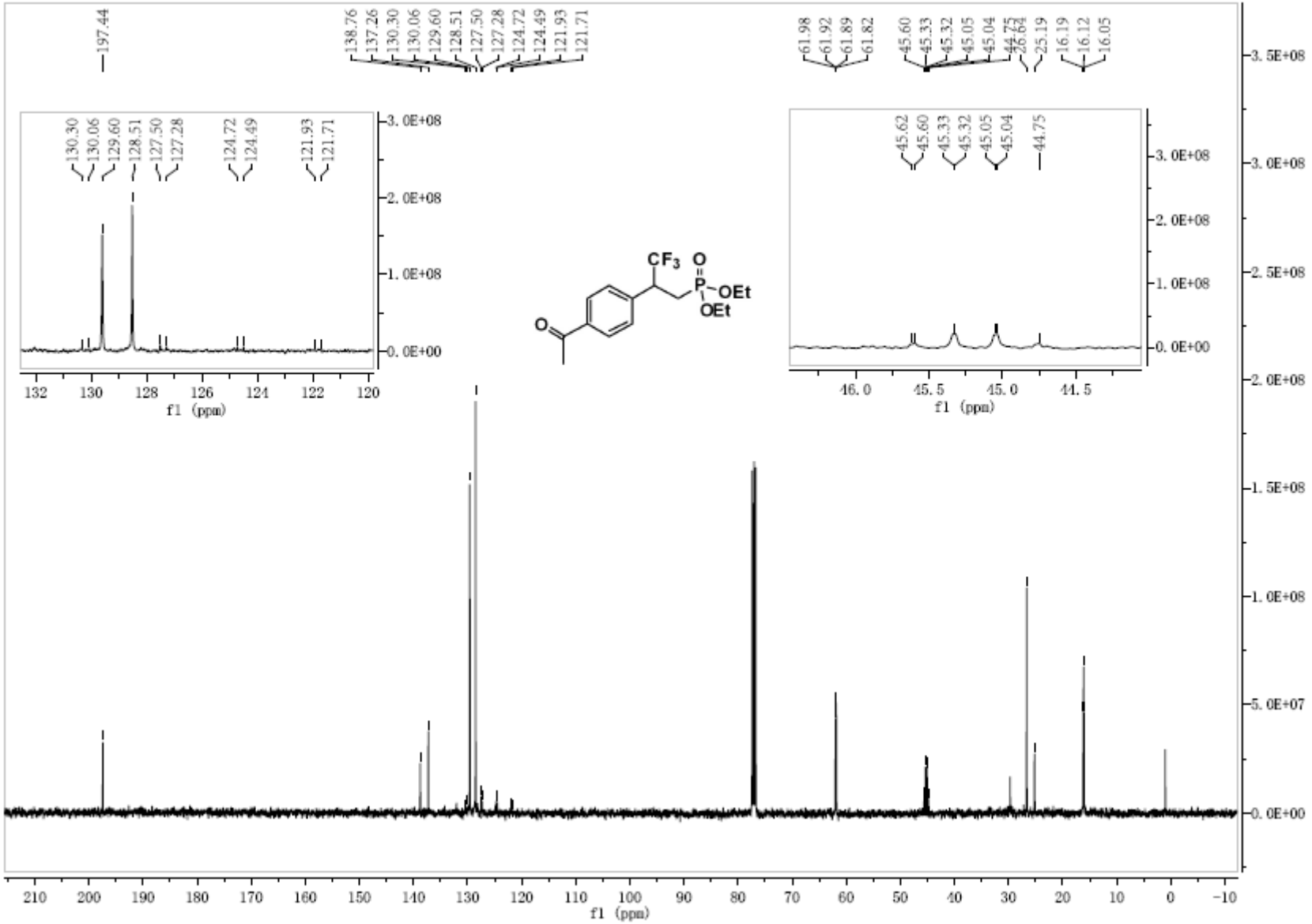
HRMS (EI) spectrum of 3fa



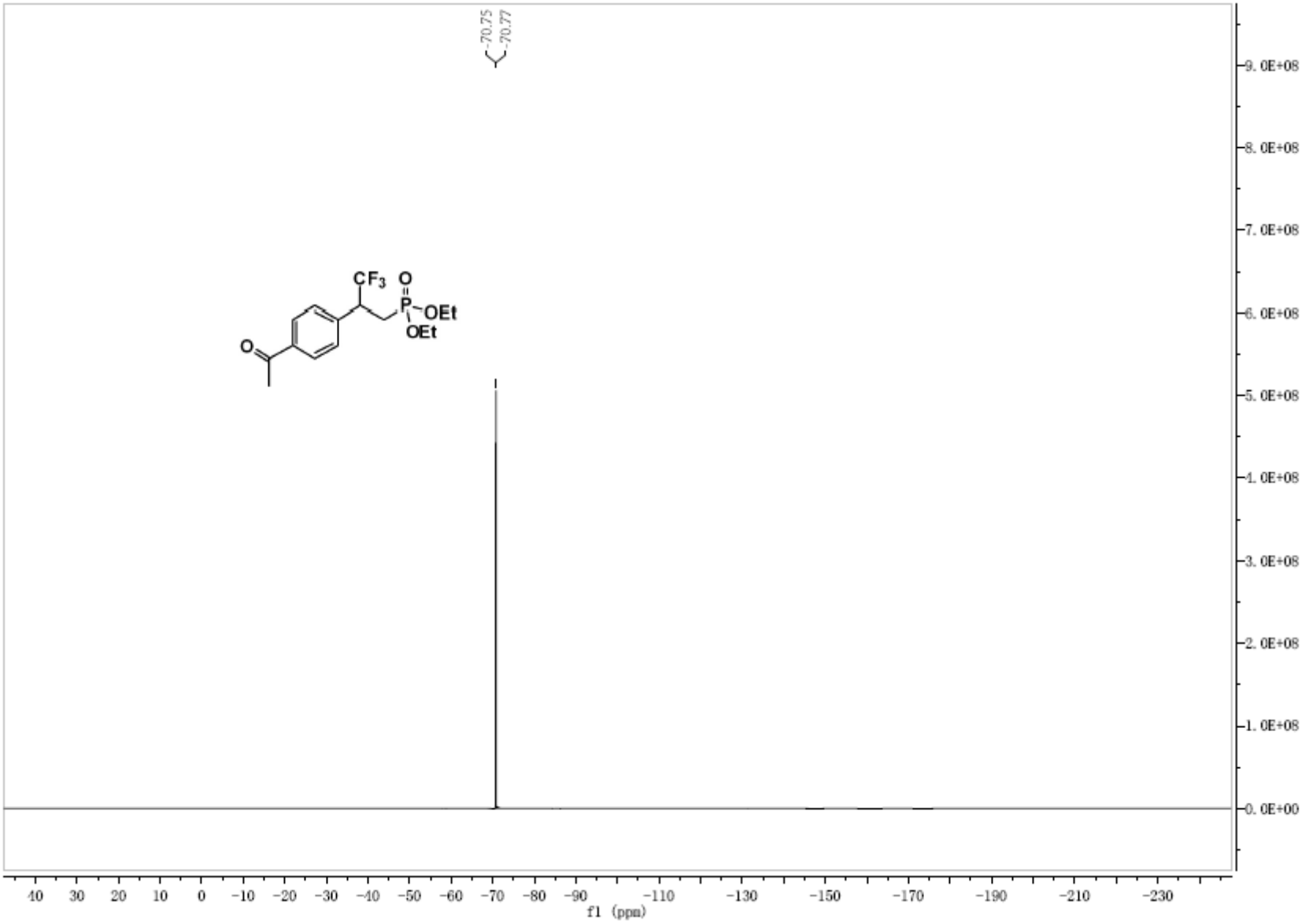
^{1}H NMR spectrum of 3ga



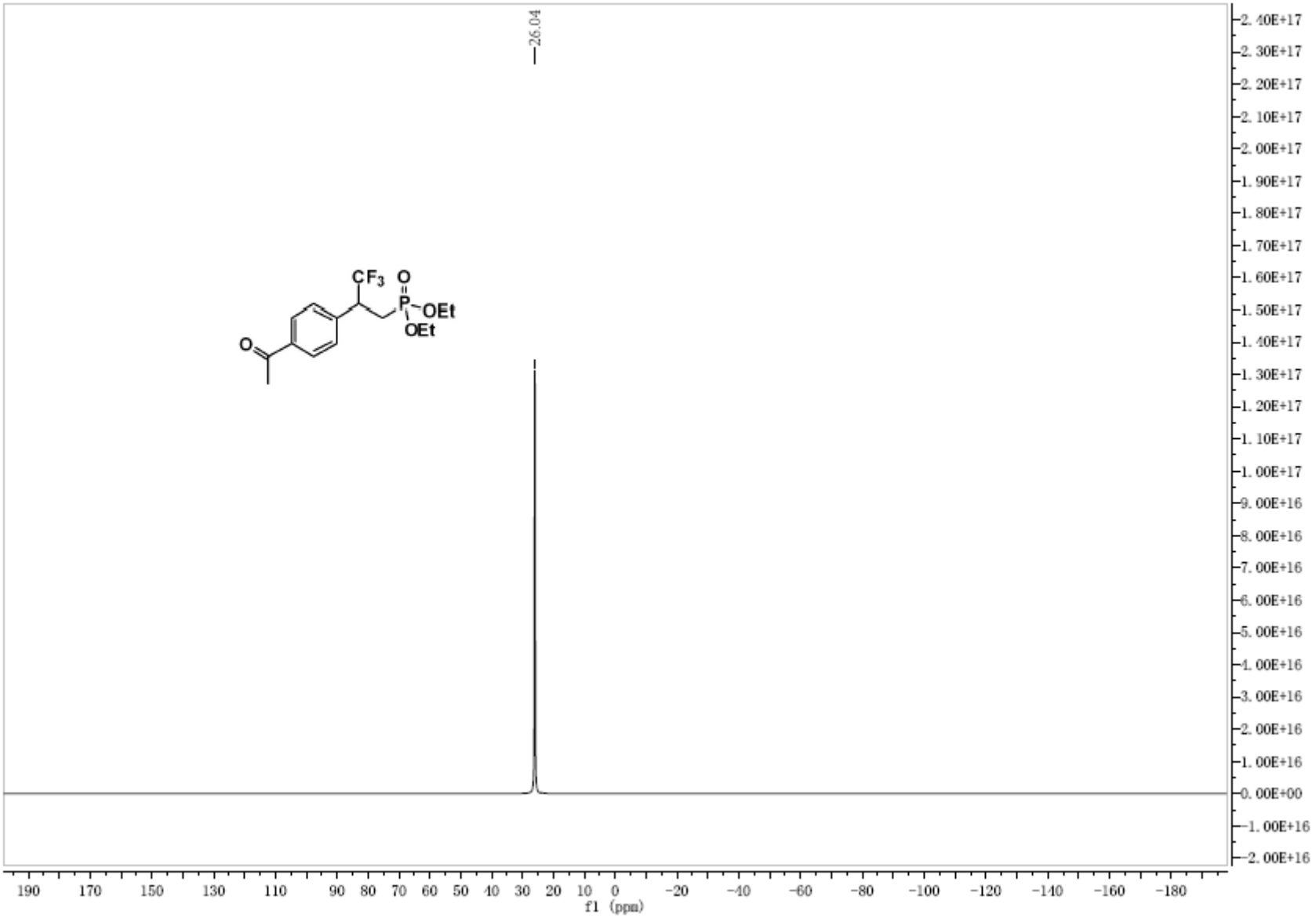
^{13}C NMR spectrum of 3ga



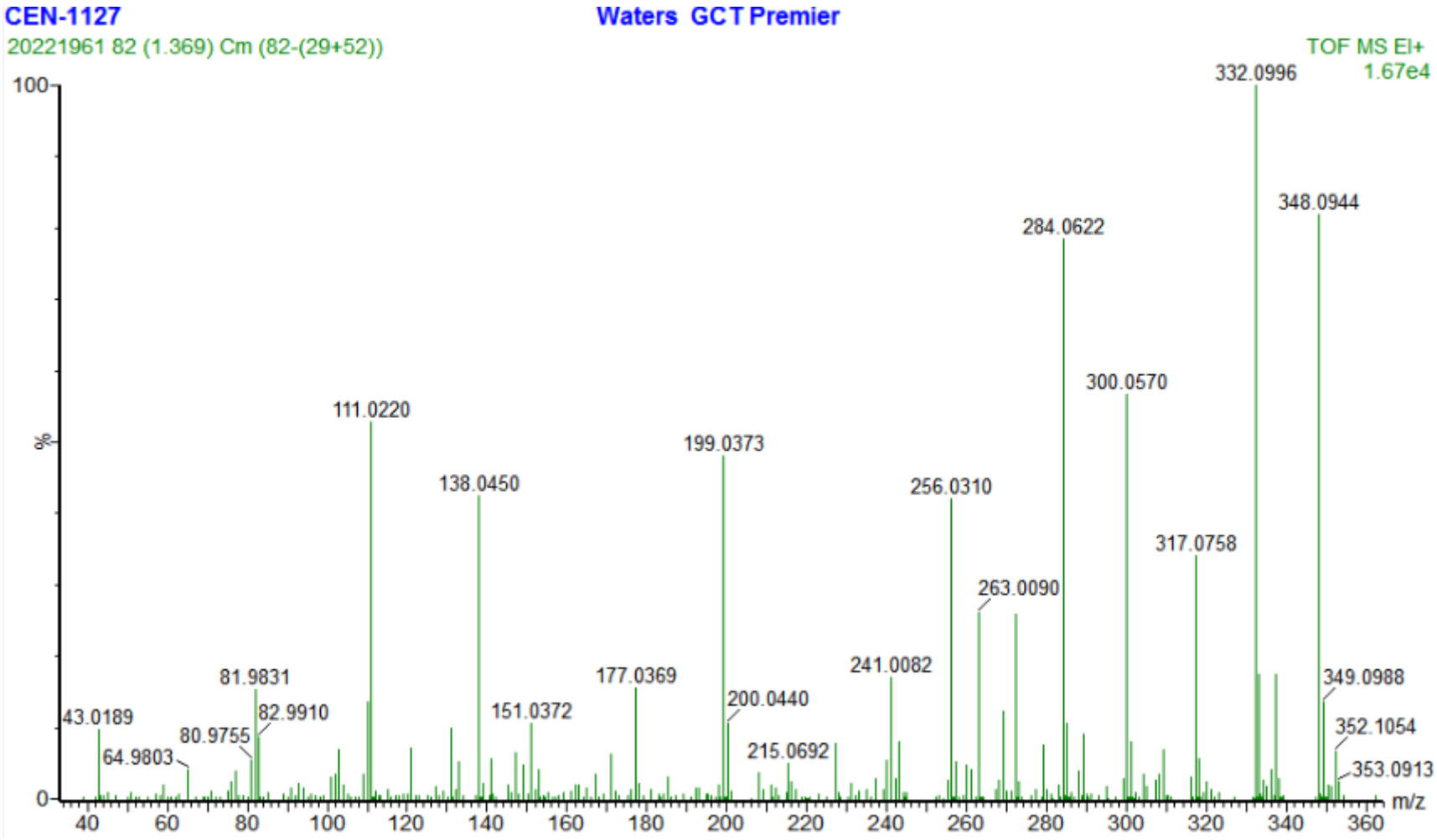
^{19}F NMR spectrum of 3ga



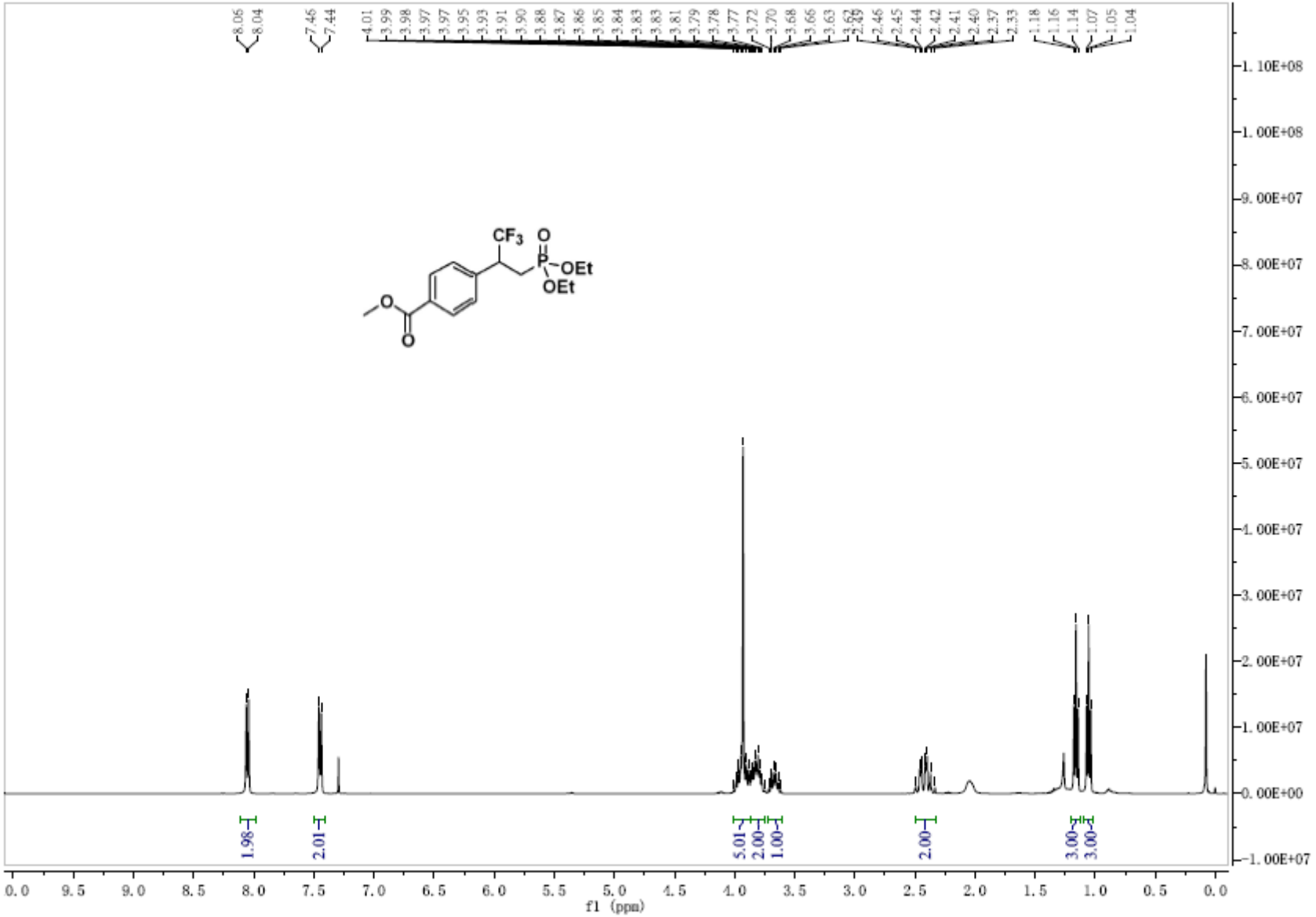
^{31}P NMR spectrum of 3ga



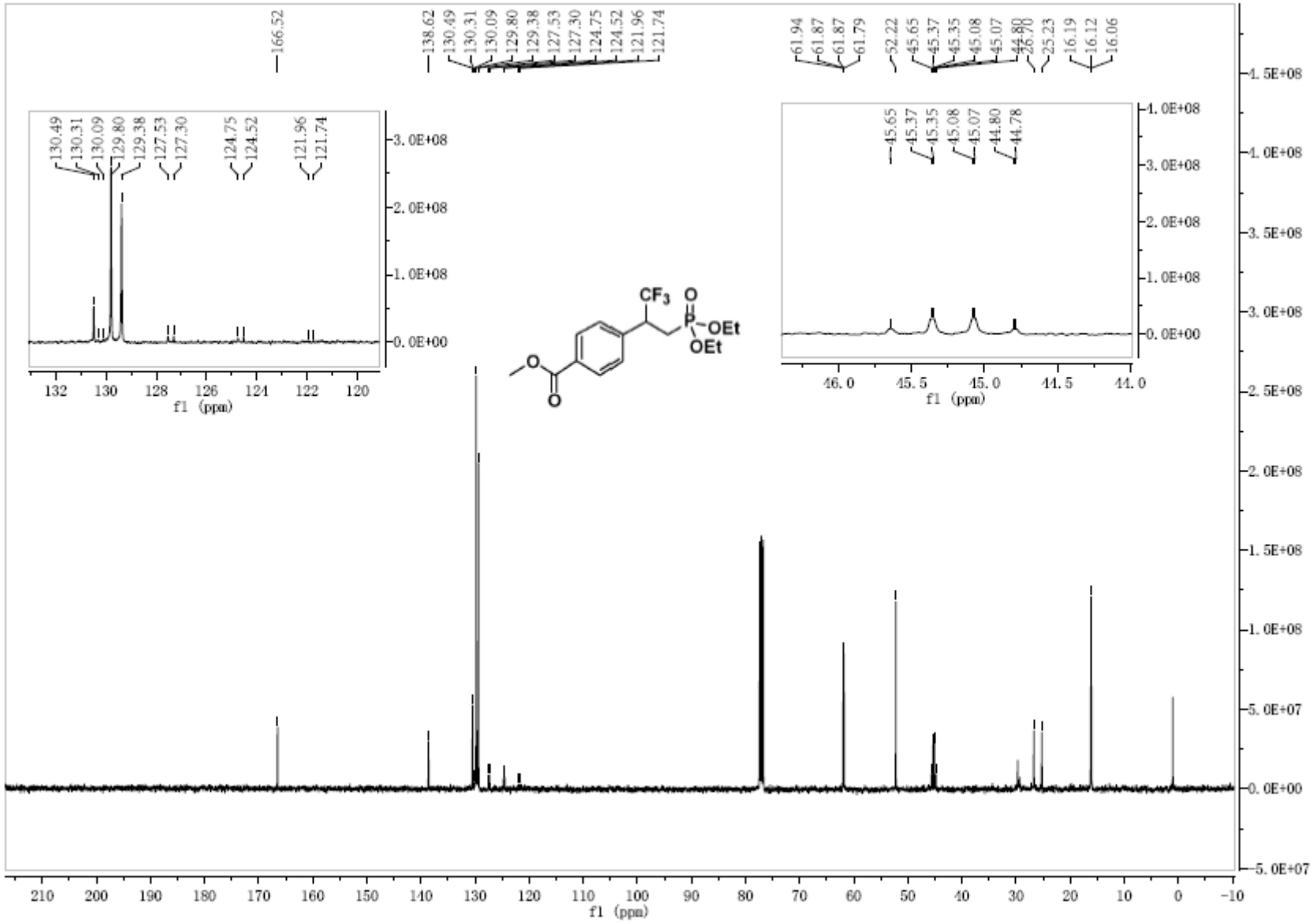
HRMS (EI) spectrum of 3ga



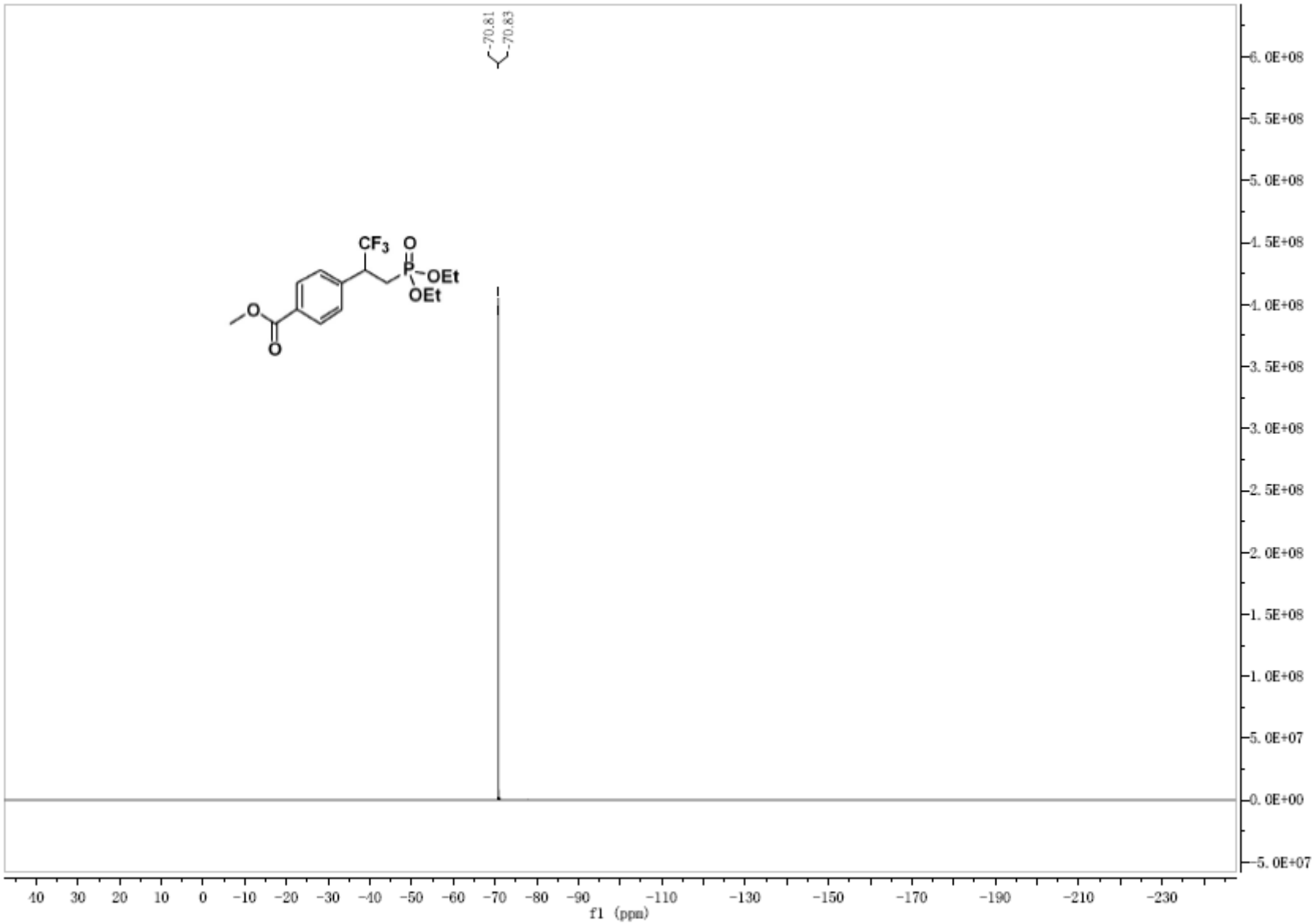
^{1}H NMR spectrum of 3ha



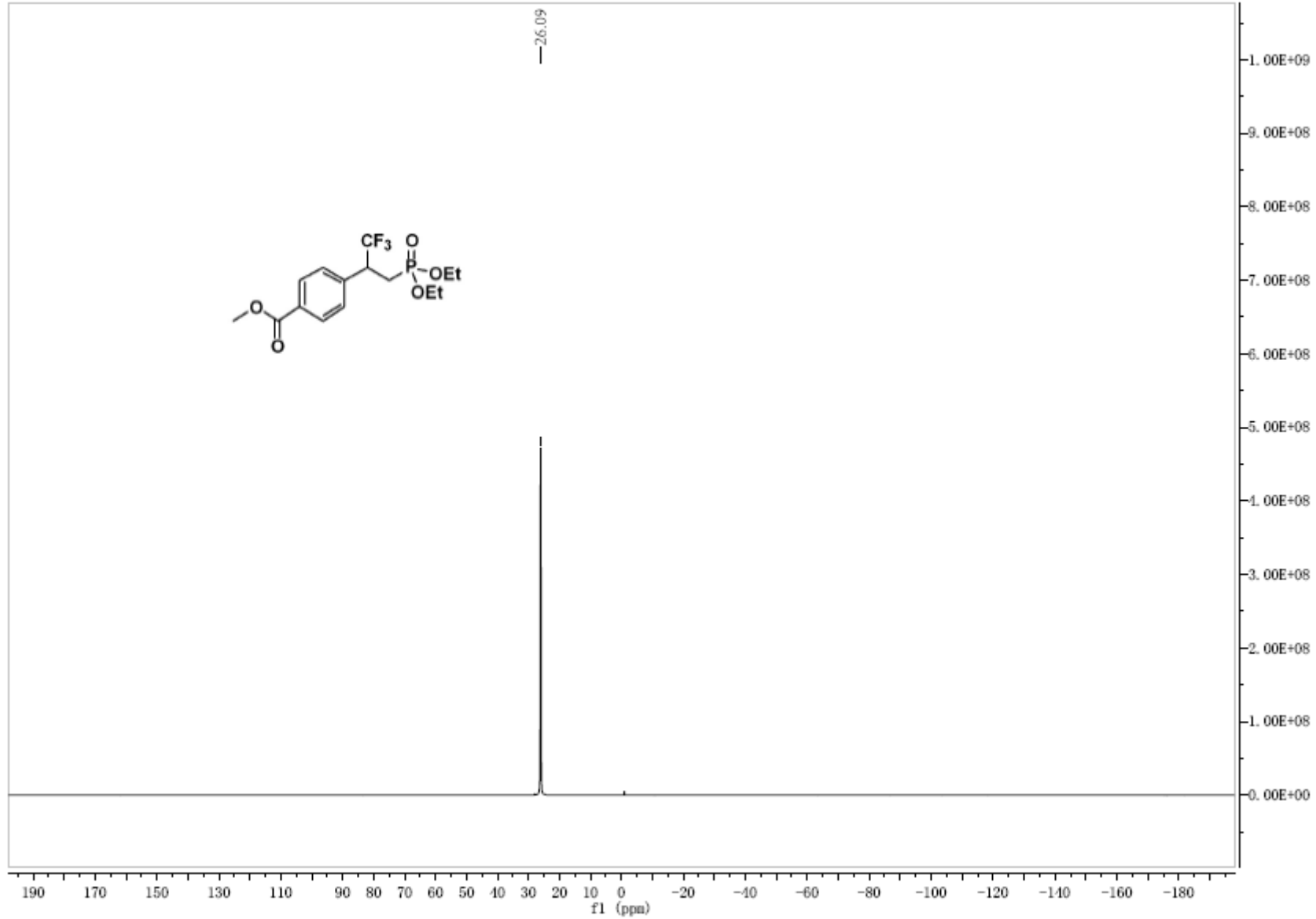
^{13}C NMR spectrum of 3ha



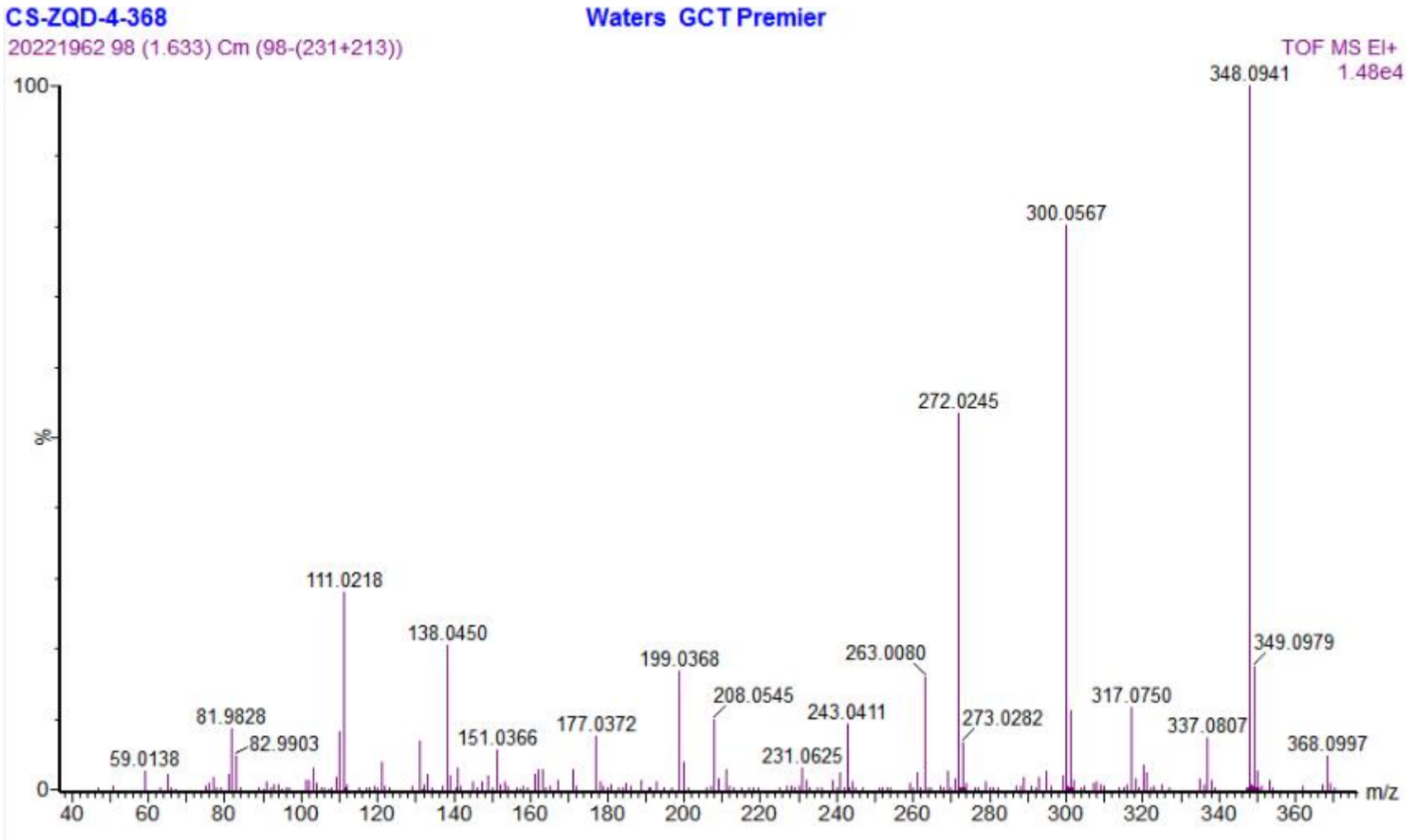
^{19}F NMR spectrum of 3ha



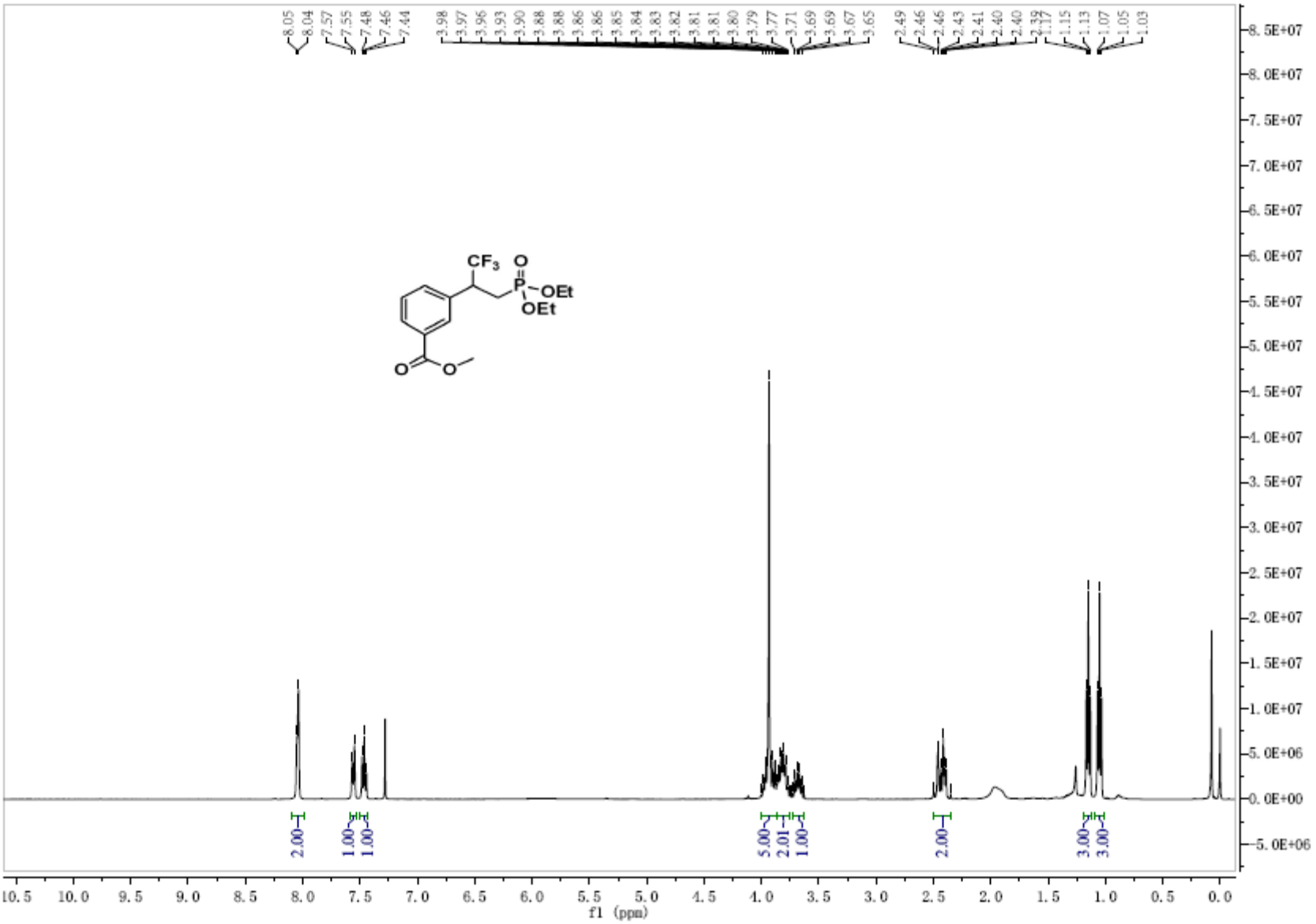
^{31}P NMR spectrum of 3ha



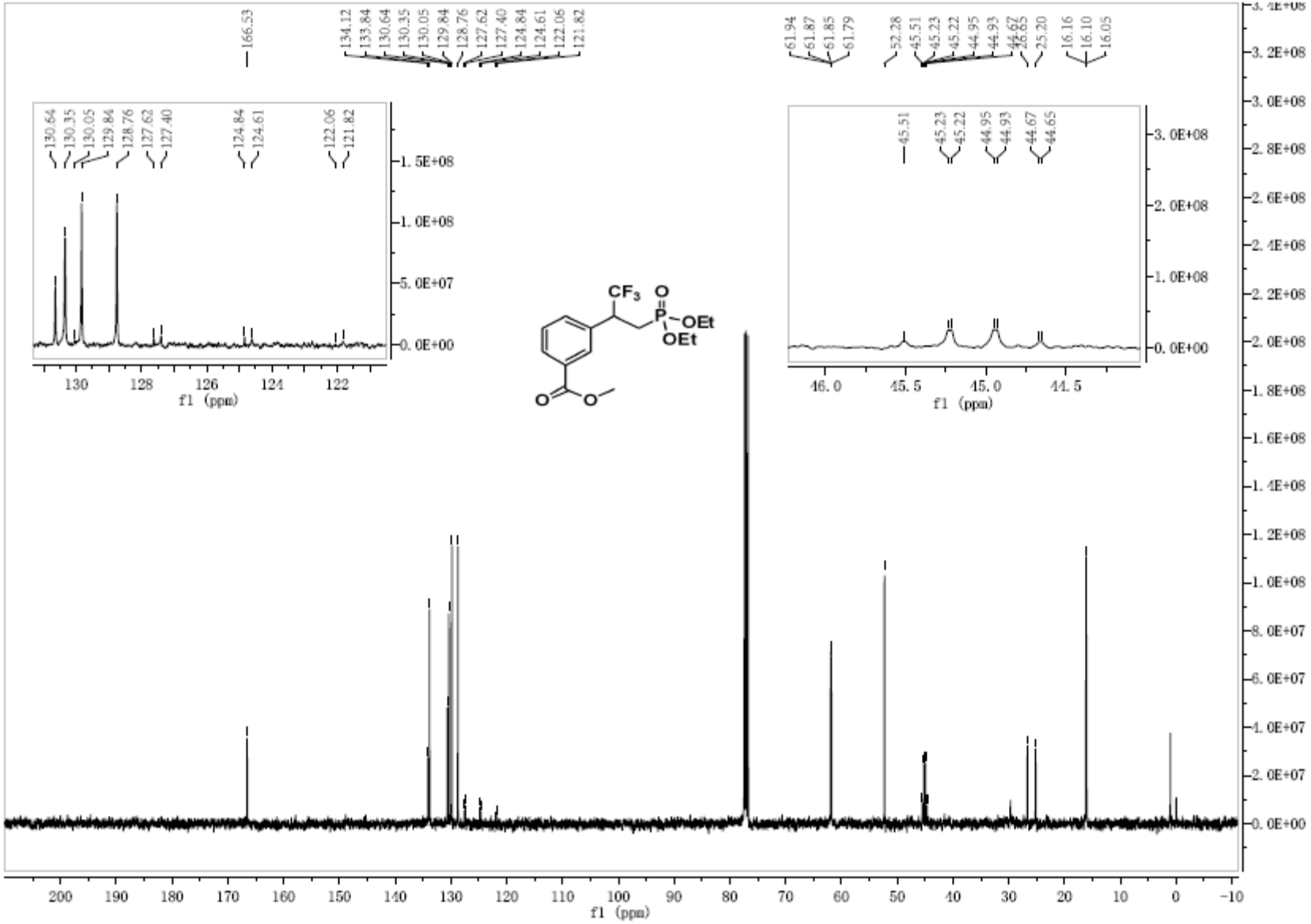
HRMS (EI) spectrum of 3ha



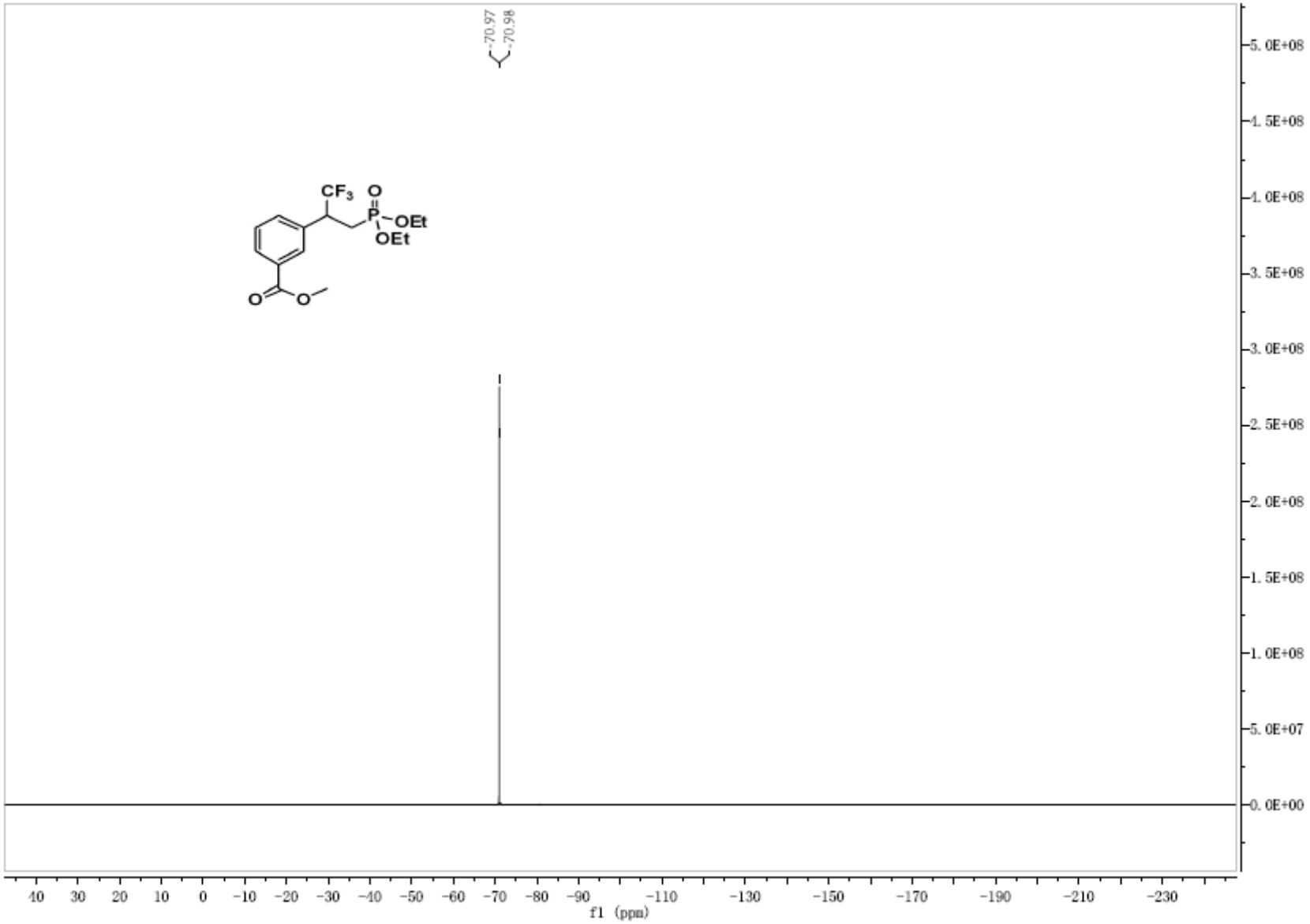
^{1}H NMR spectrum of 3ia



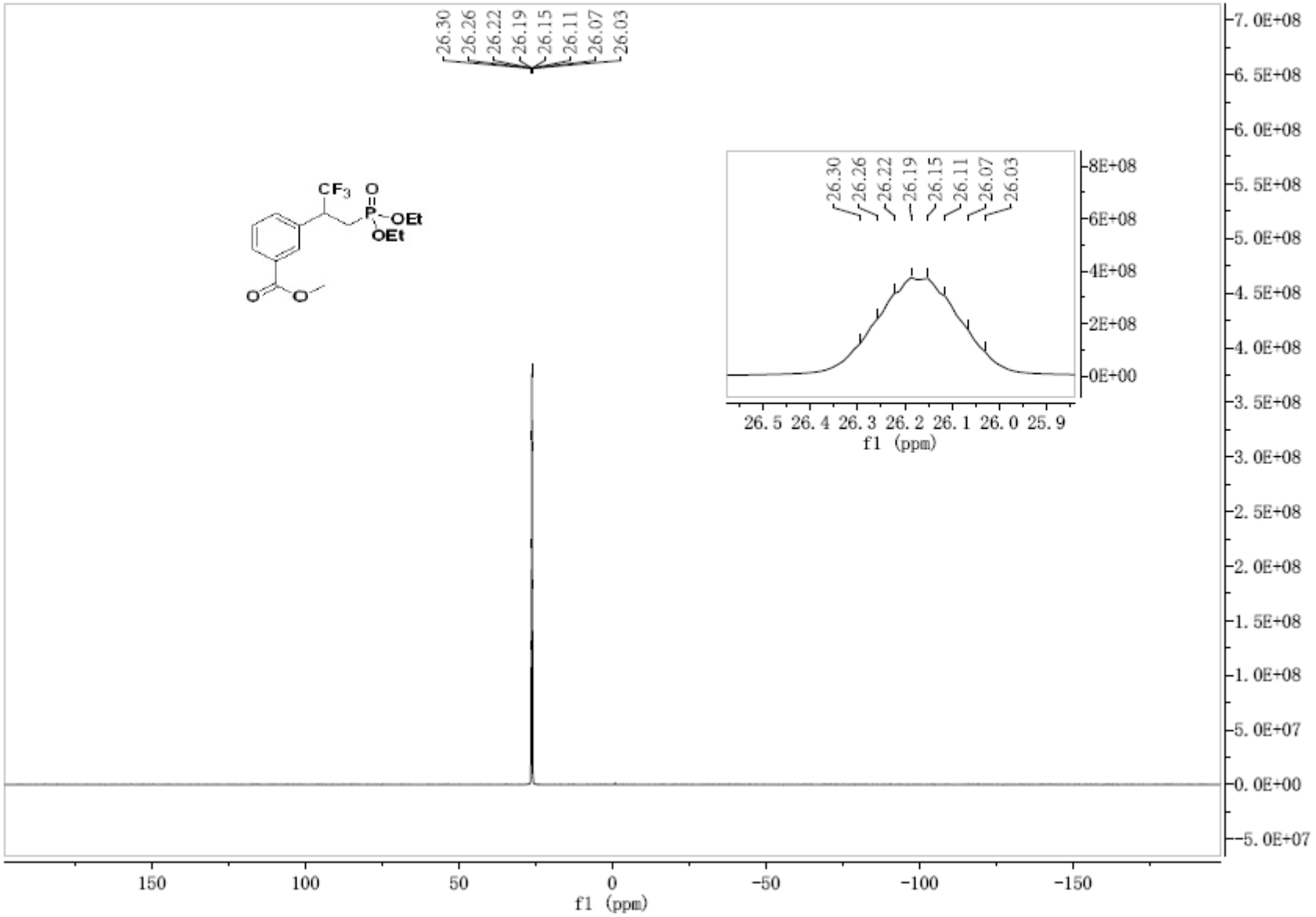
^{13}C NMR spectrum of 3ia



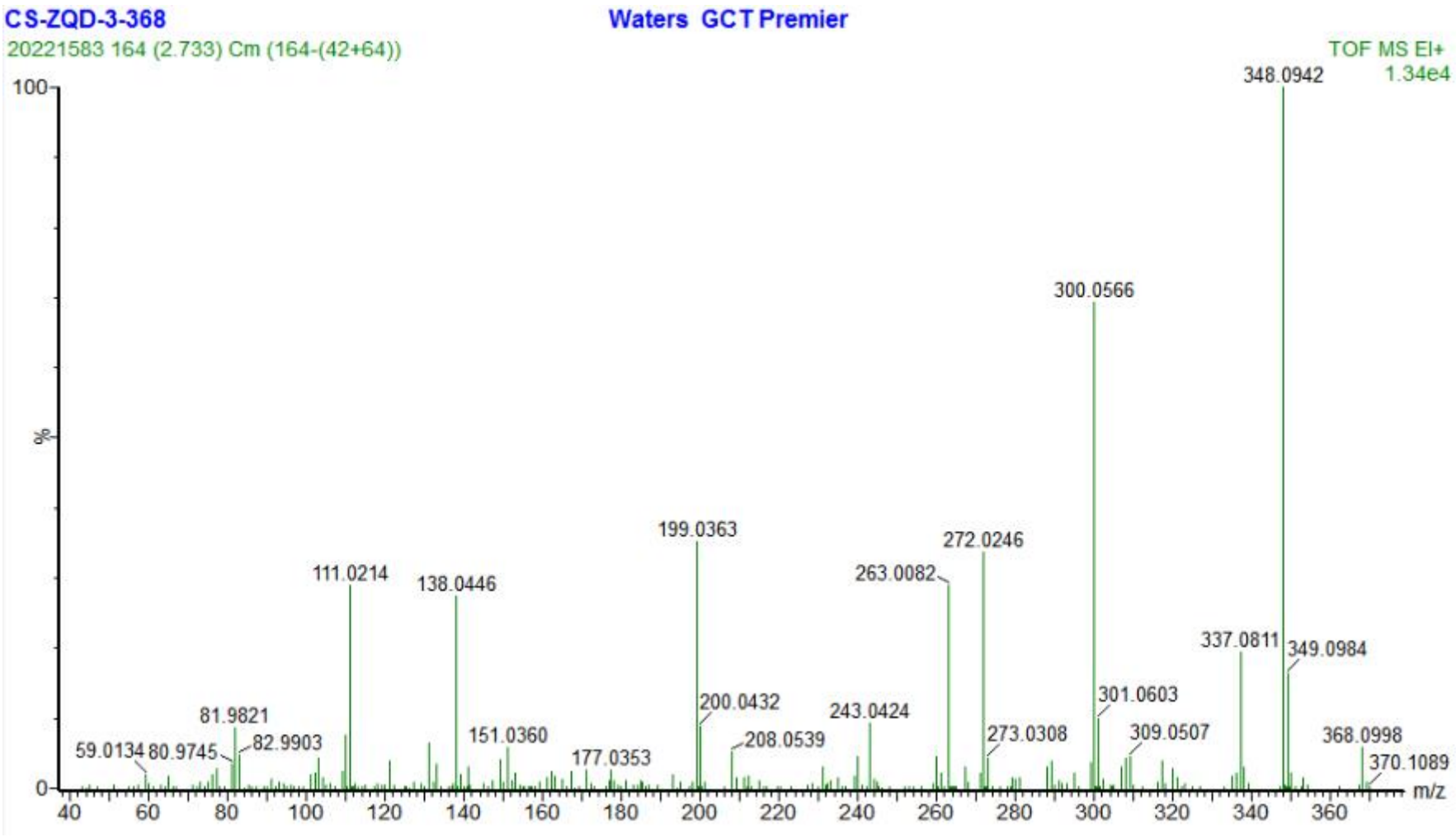
^{19}F NMR spectrum of 3ia



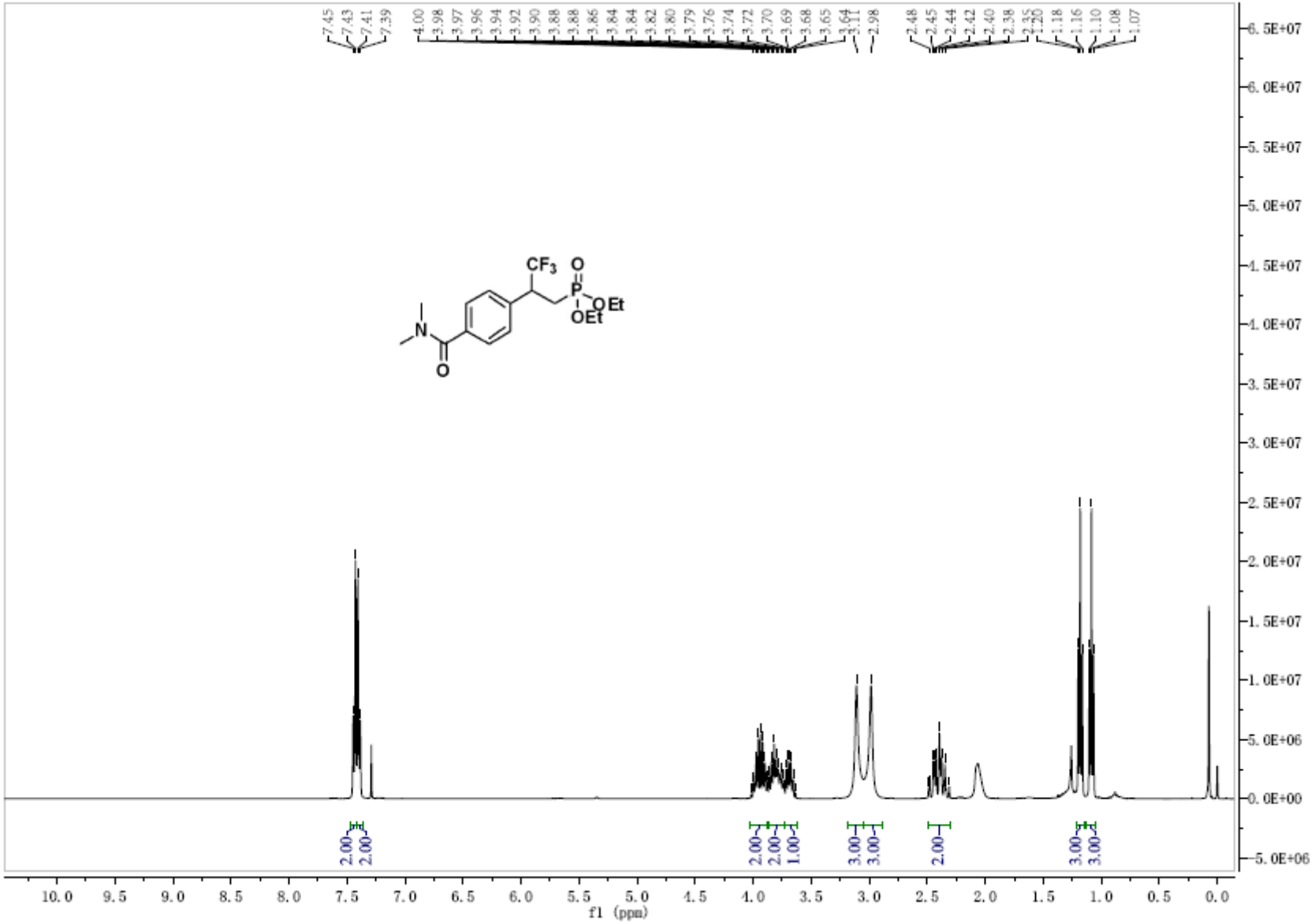
^{31}P NMR spectrum of 3ia



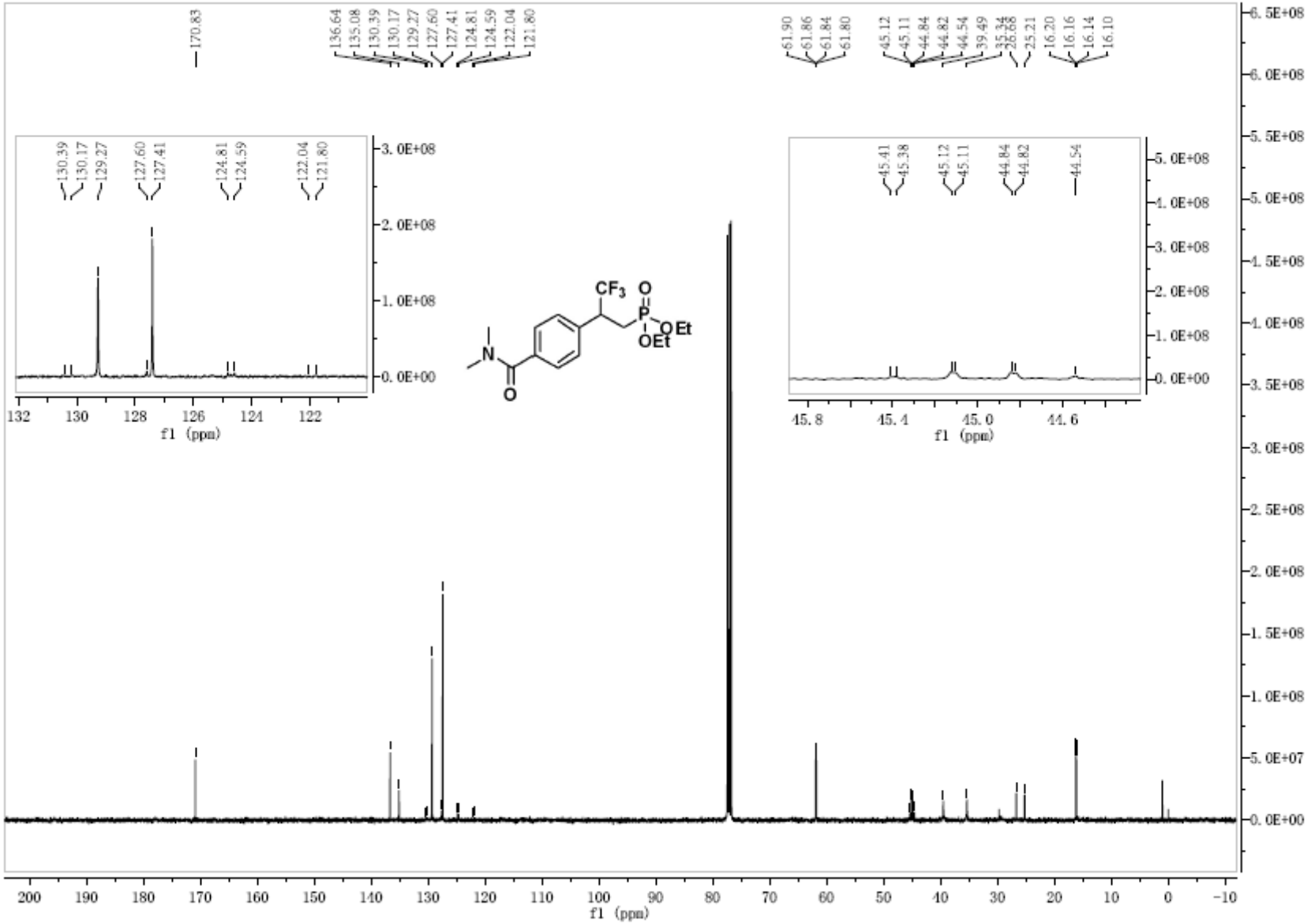
HRMS (EI) spectrum of 3ia



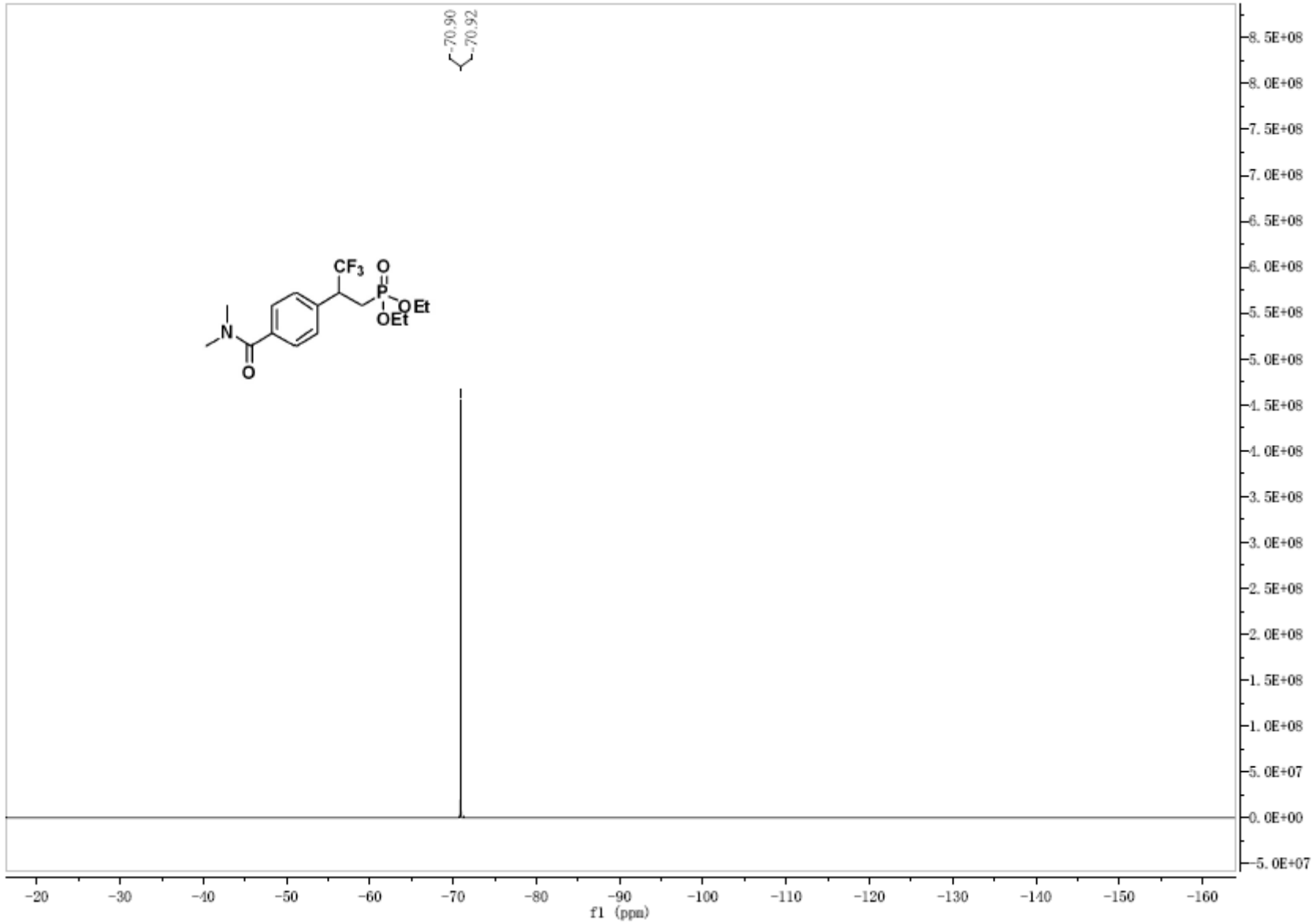
^{1}H NMR spectrum of 3ja



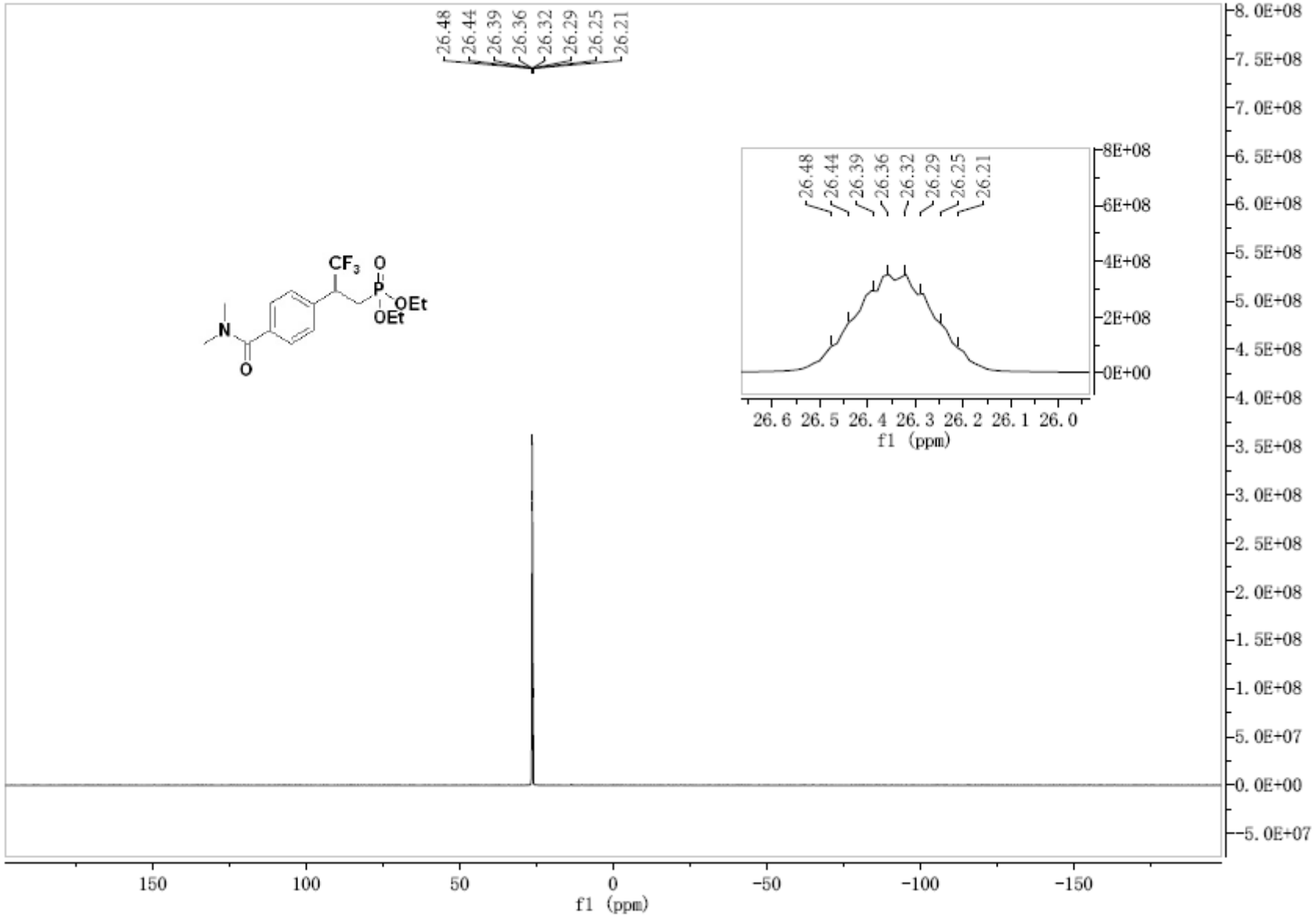
^{13}C NMR spectrum of 3ja



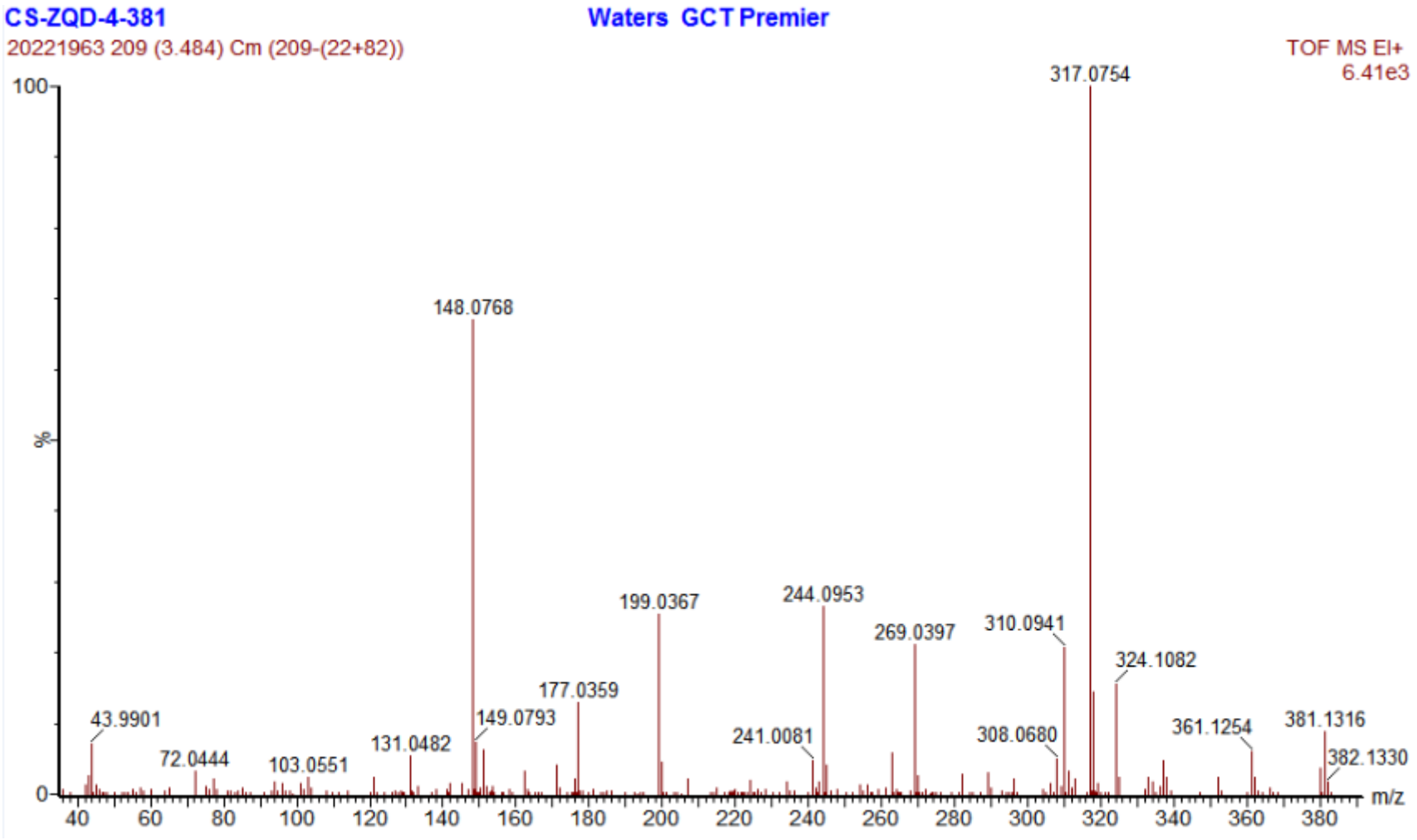
^{19}F NMR spectrum of 3ja



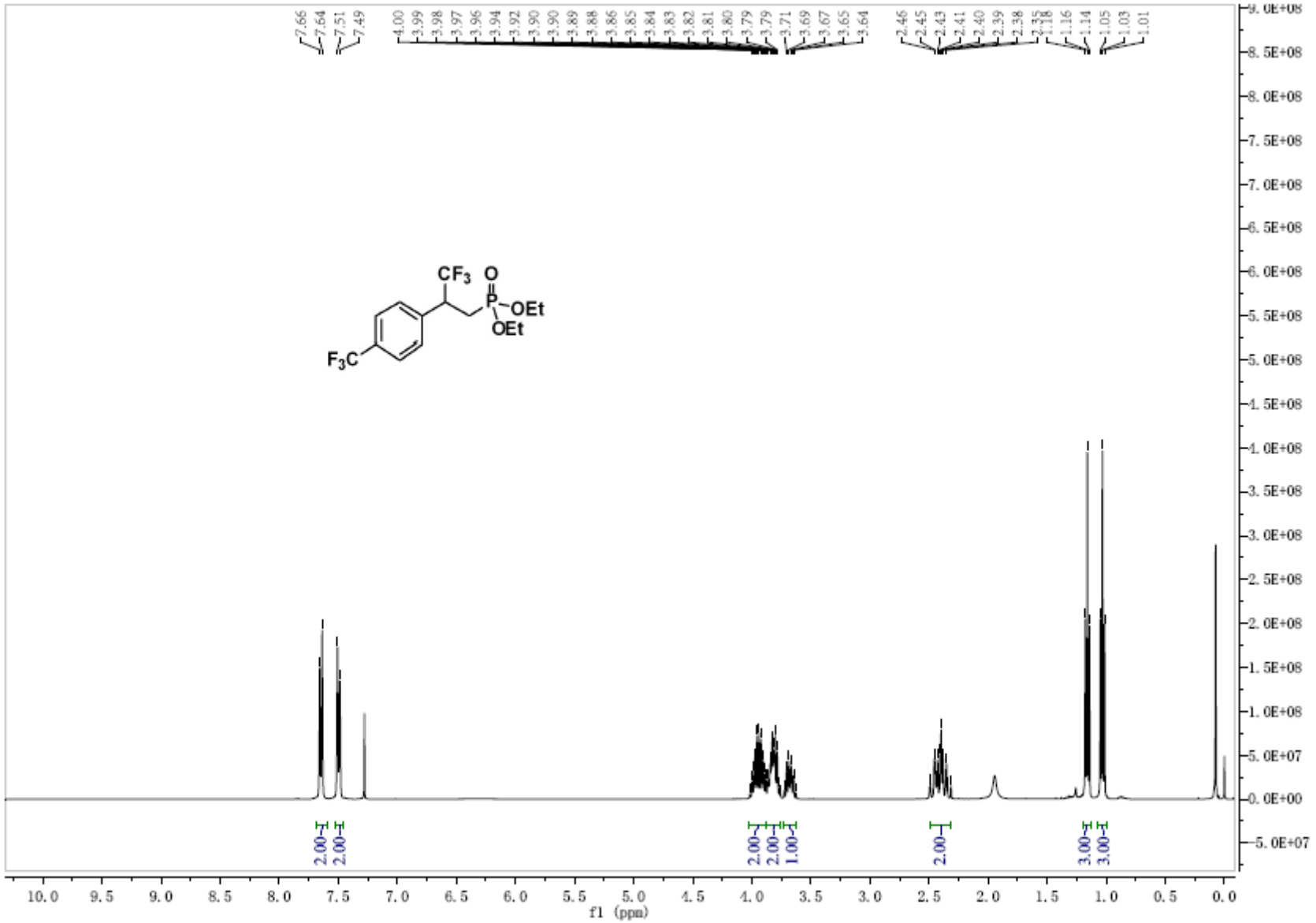
^{31}P NMR spectrum of 3ja



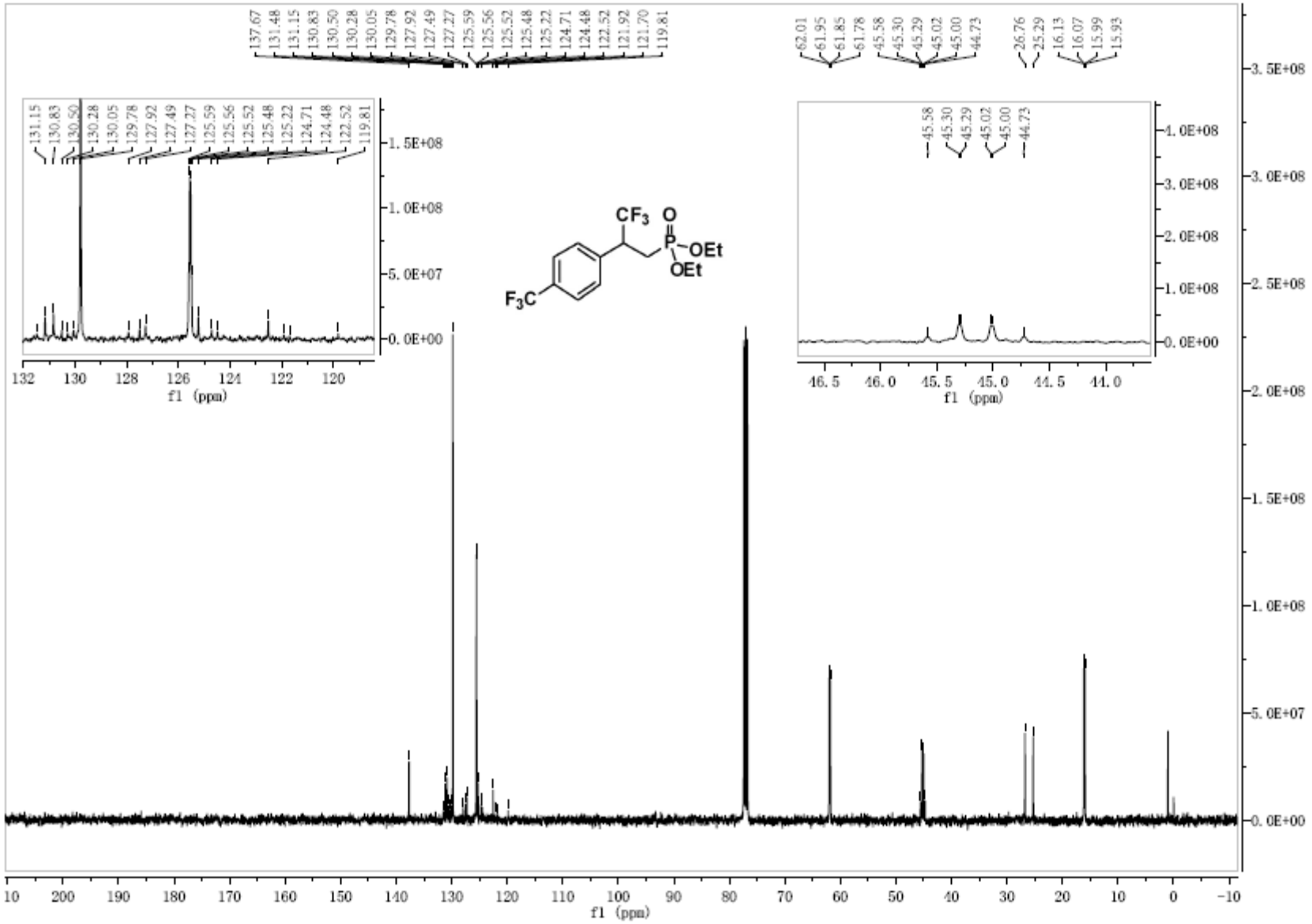
HRMS (EI) spectrum of 3ja



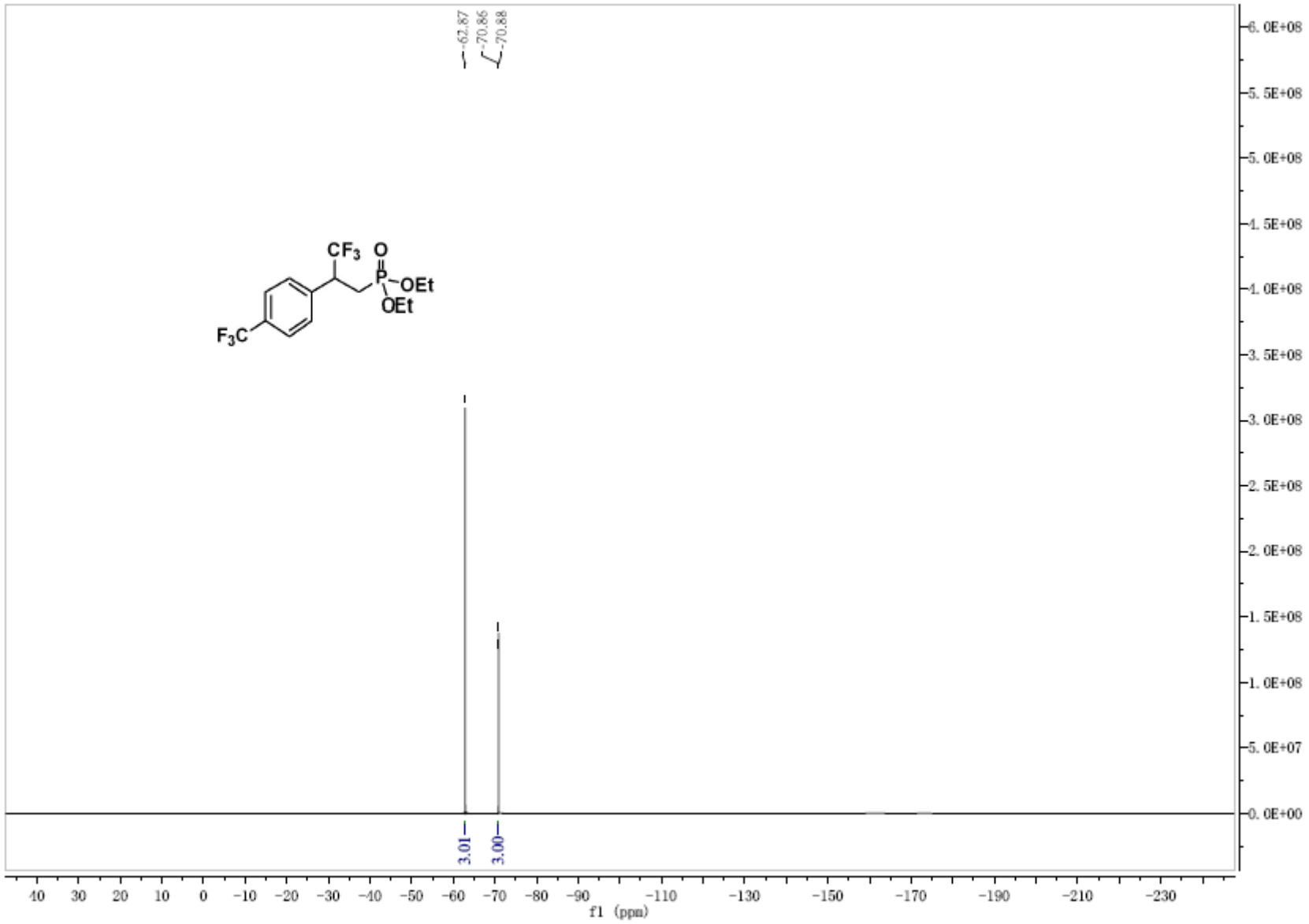
^{1}H NMR spectrum of 3ka



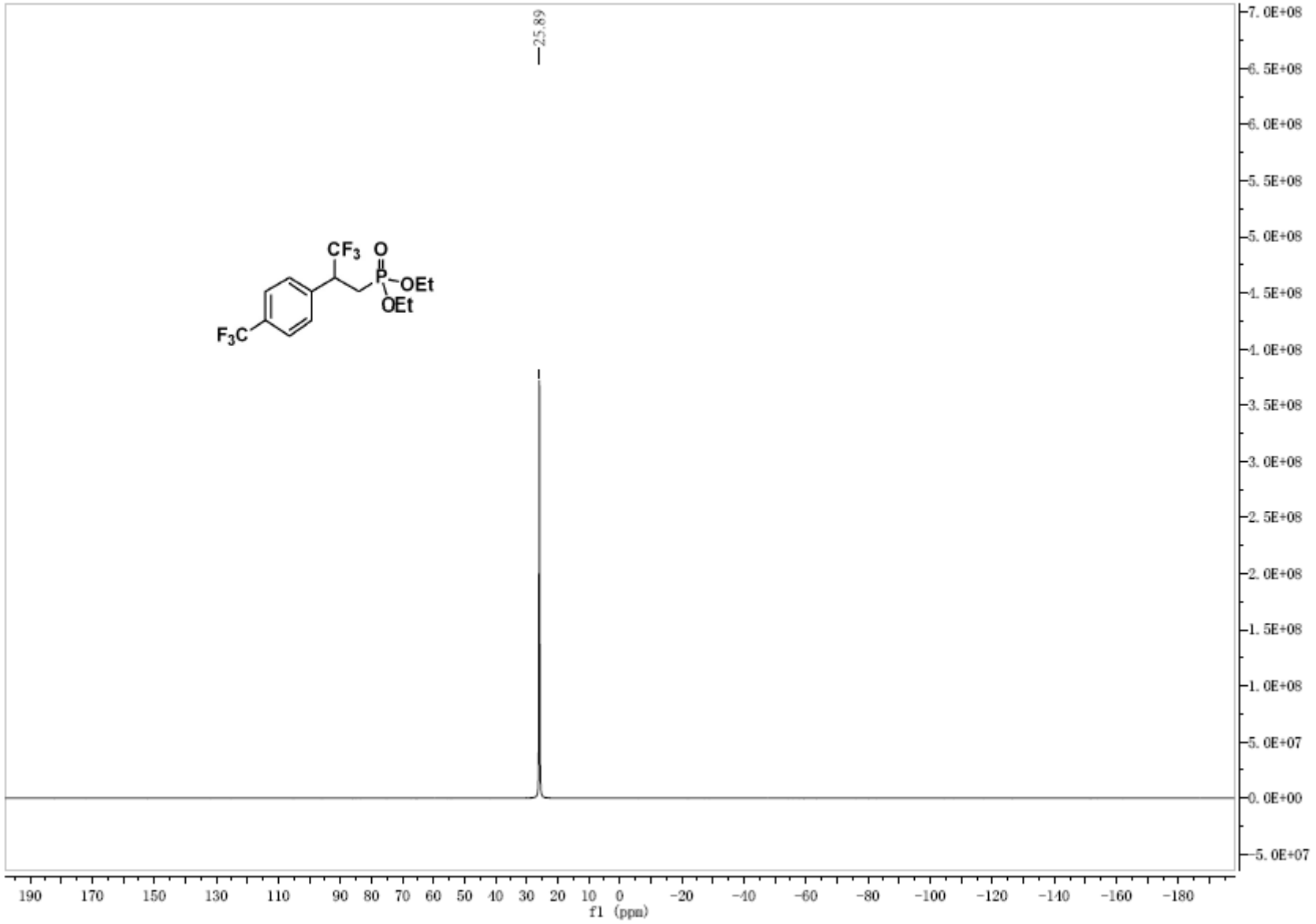
^{13}C NMR spectrum of 3ka



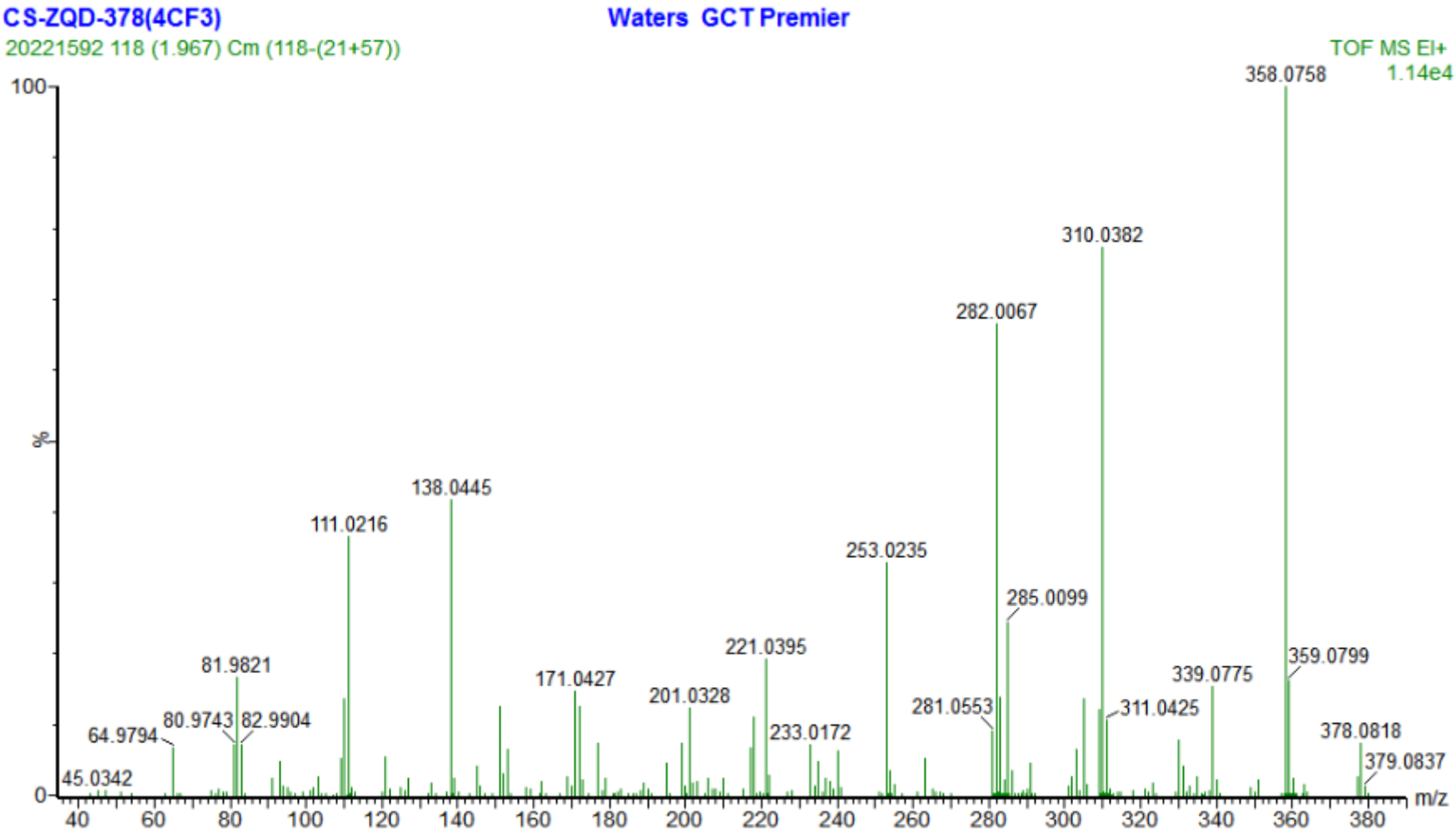
^{19}F NMR spectrum of 3ka



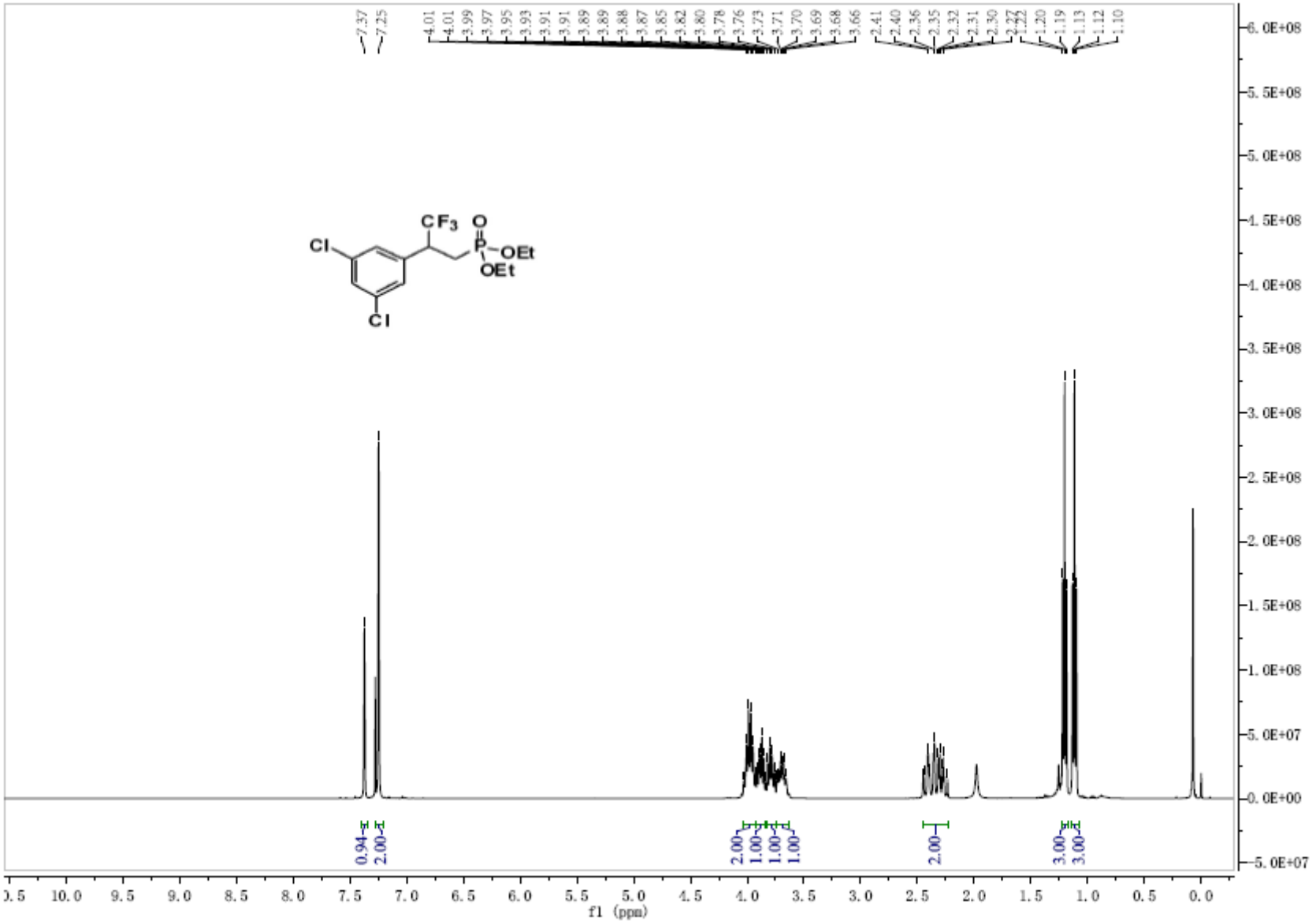
^{31}P NMR spectrum of 3ka



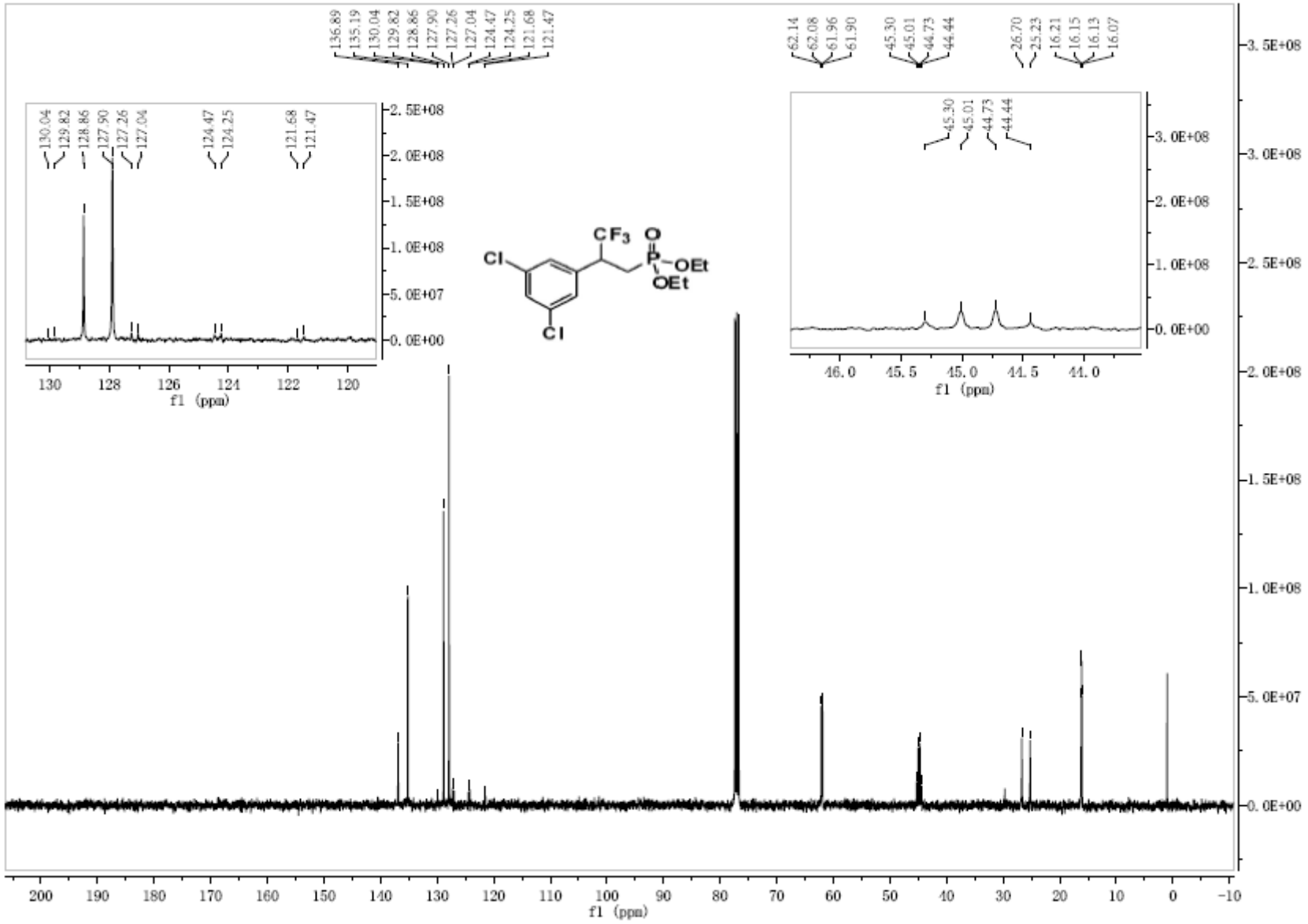
HRMS (EI) spectrum of 3ka



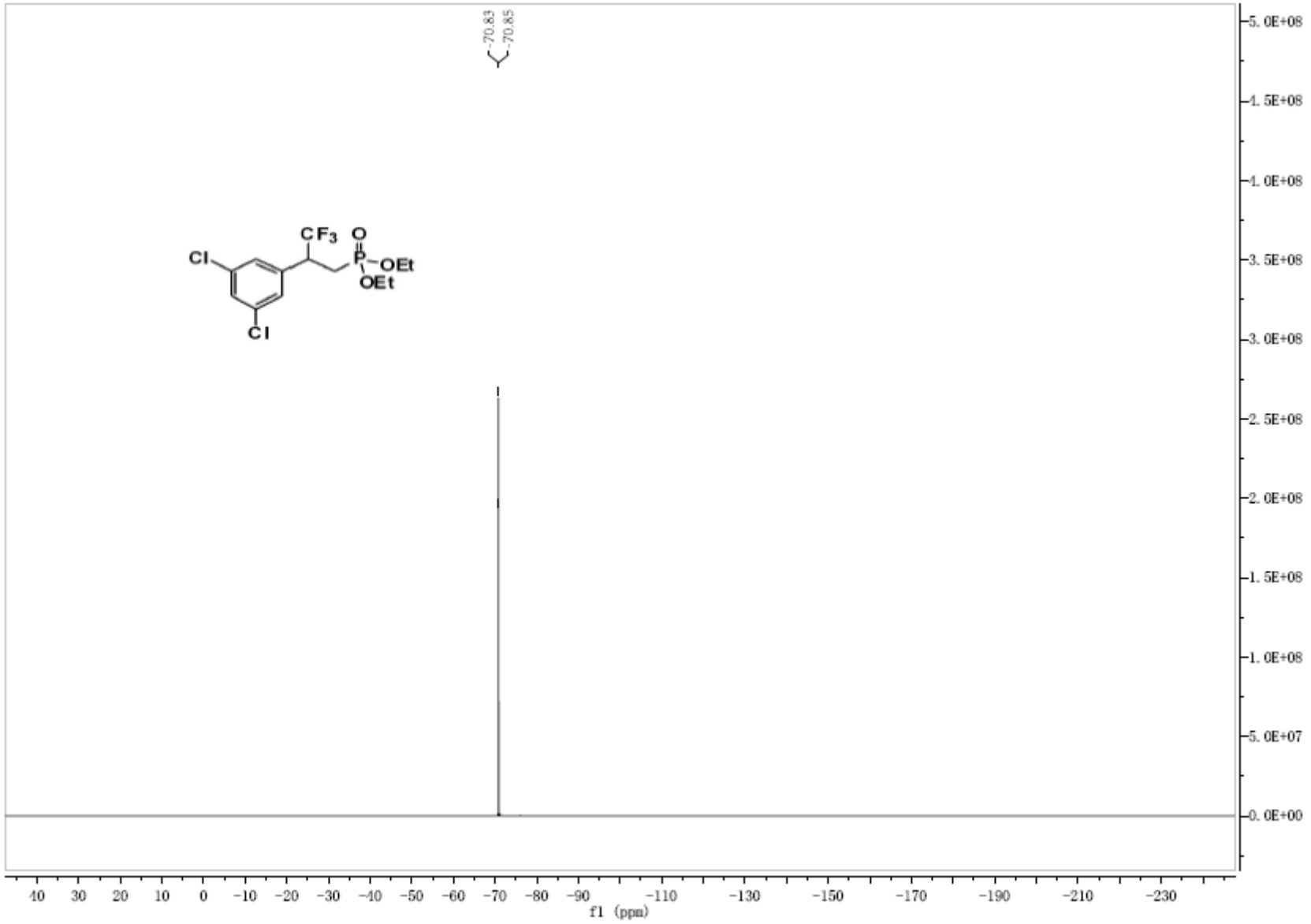
^{1}H NMR spectrum of 3la



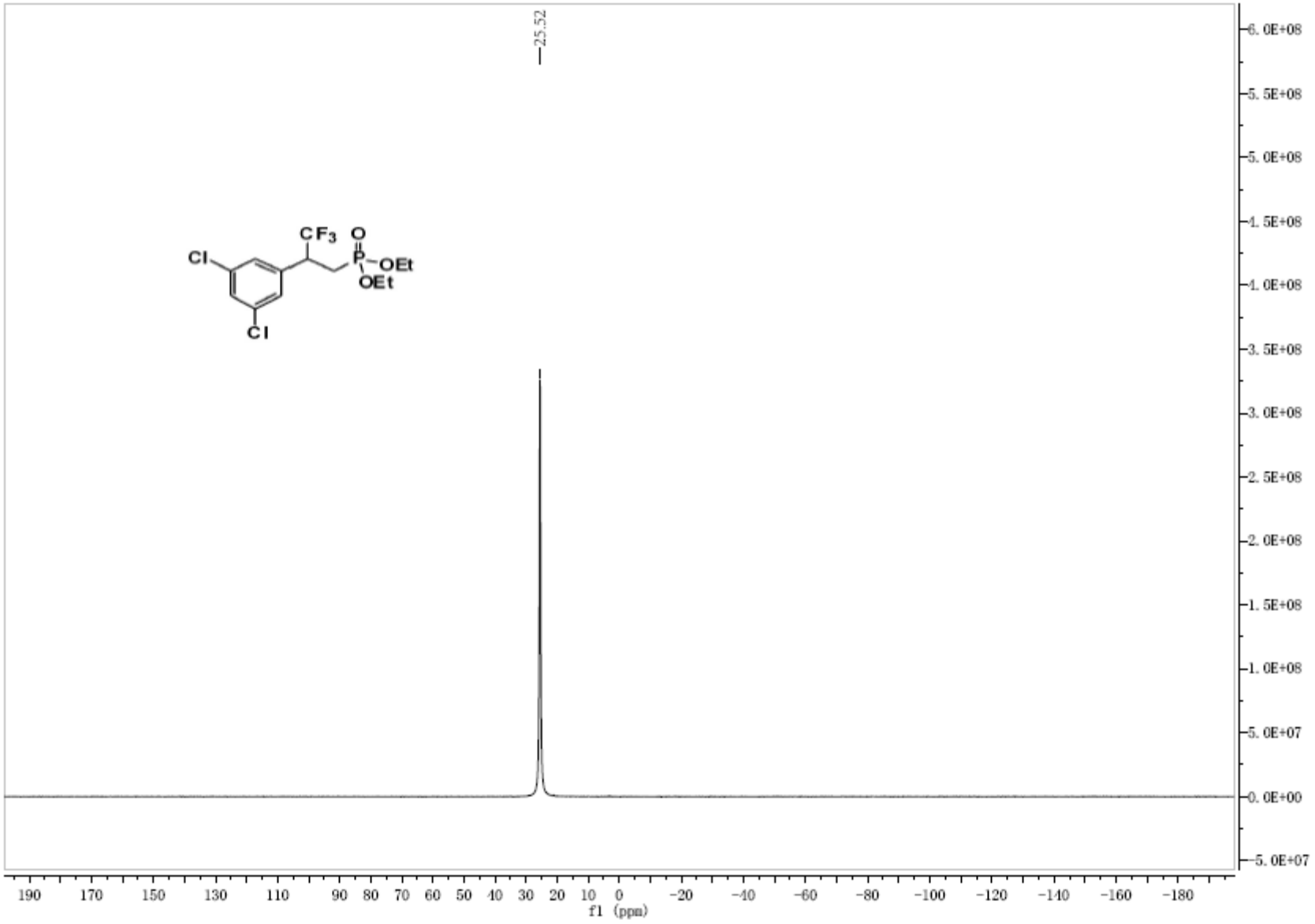
^{13}C NMR spectrum of 3la



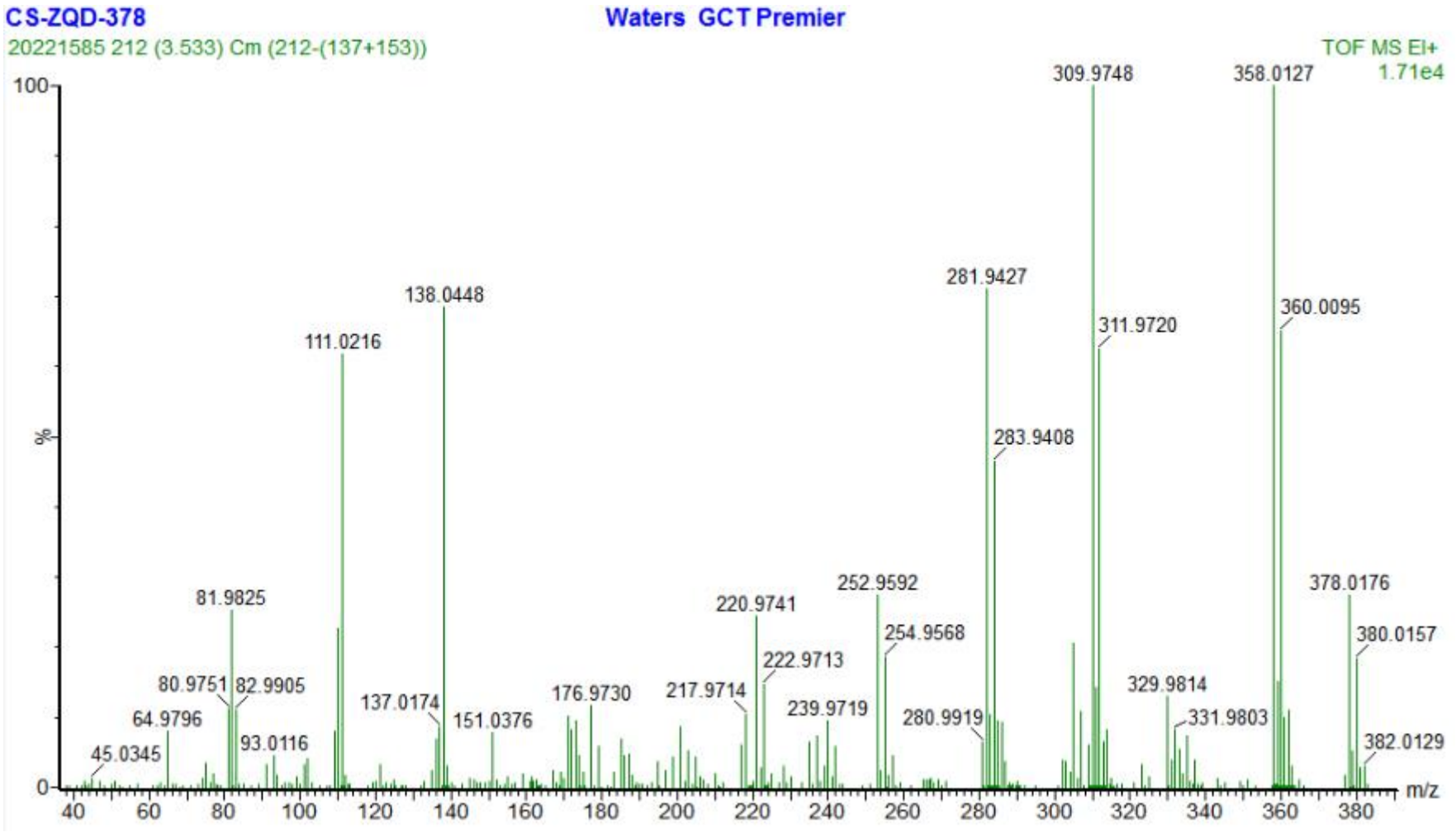
^{19}F NMR spectrum of 3la



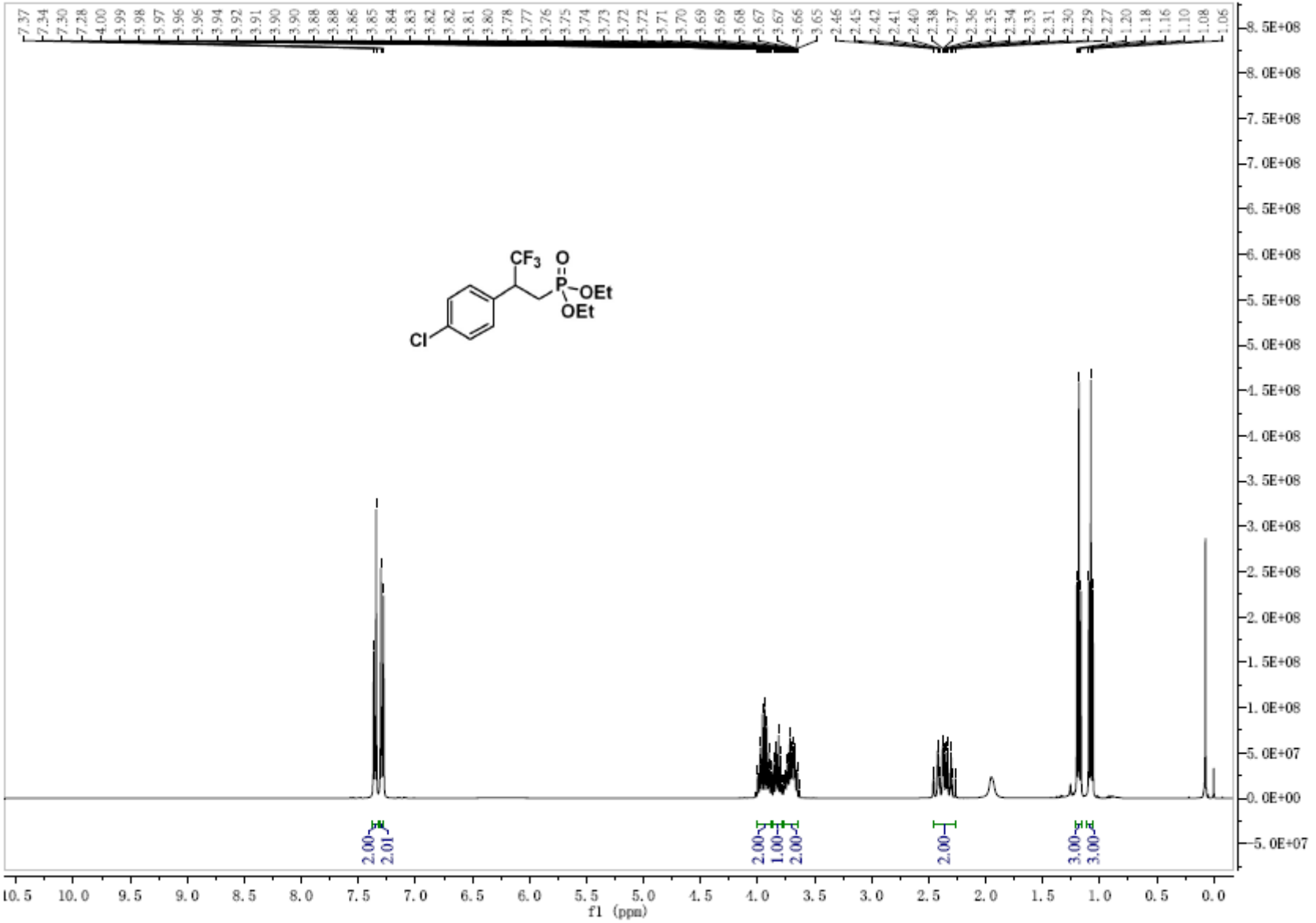
^{31}P NMR spectrum of 3la



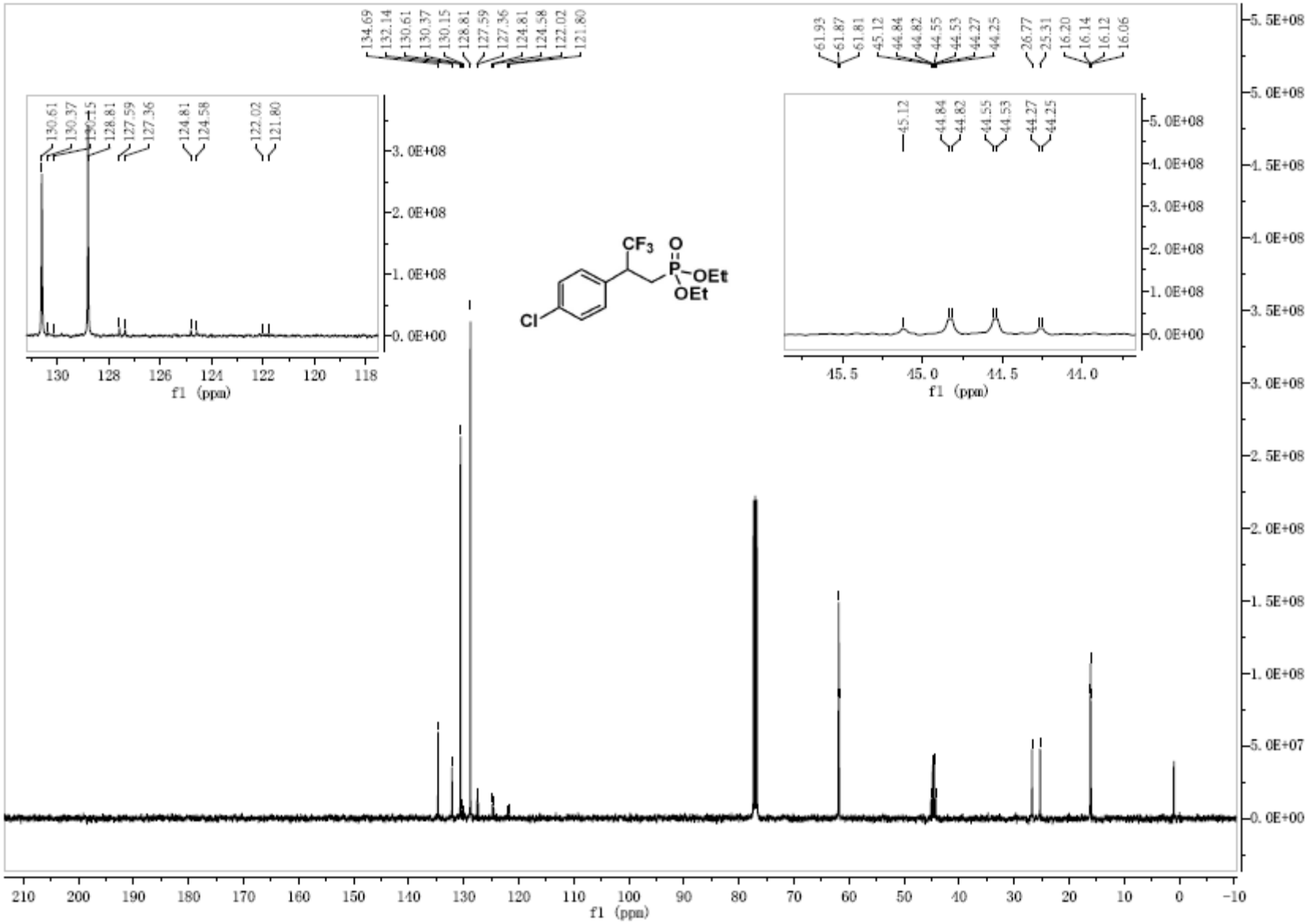
HRMS (EI) spectrum of 3la



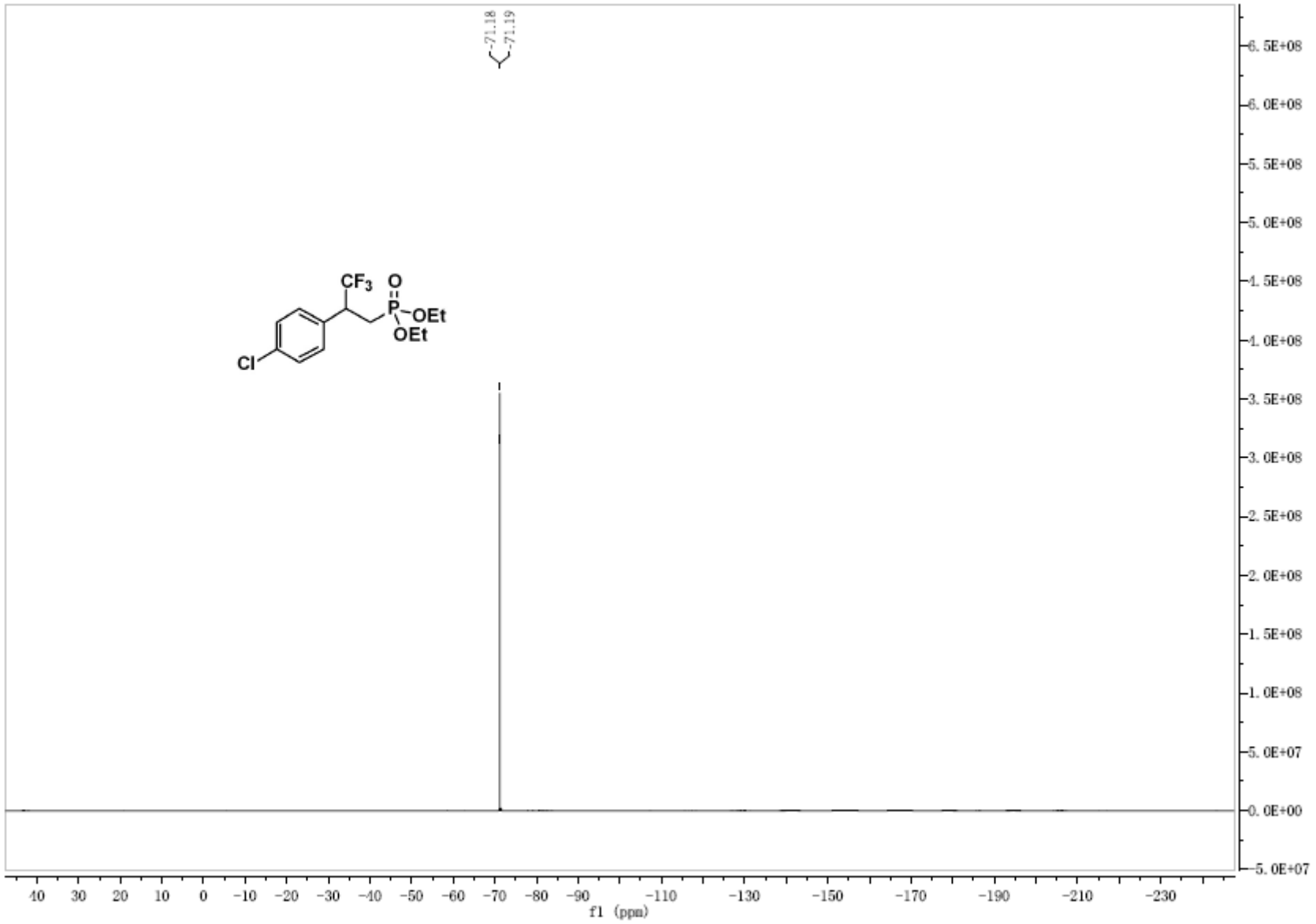
^{1}H NMR spectrum of 3ma



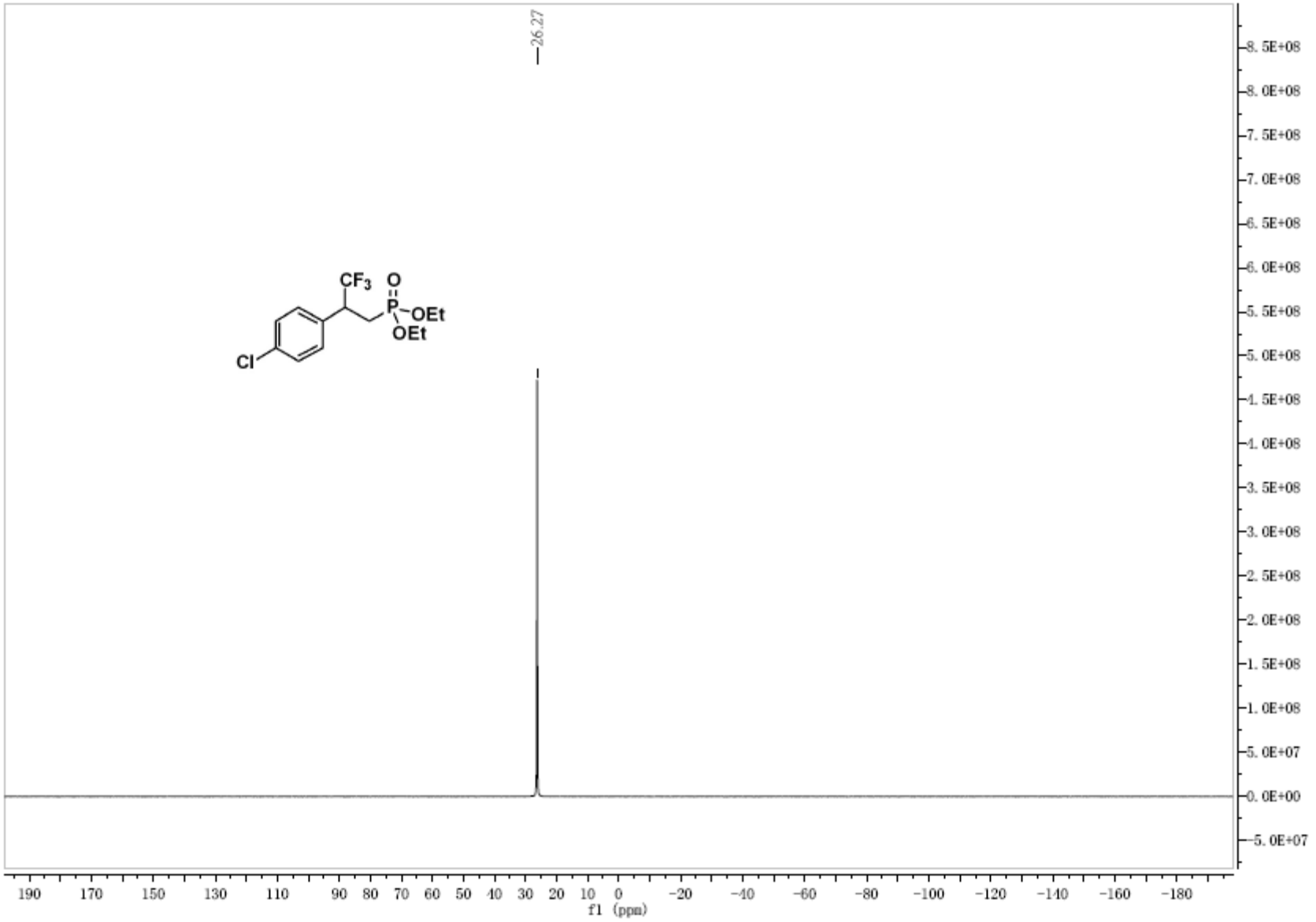
^{13}C NMR spectrum of 3ma



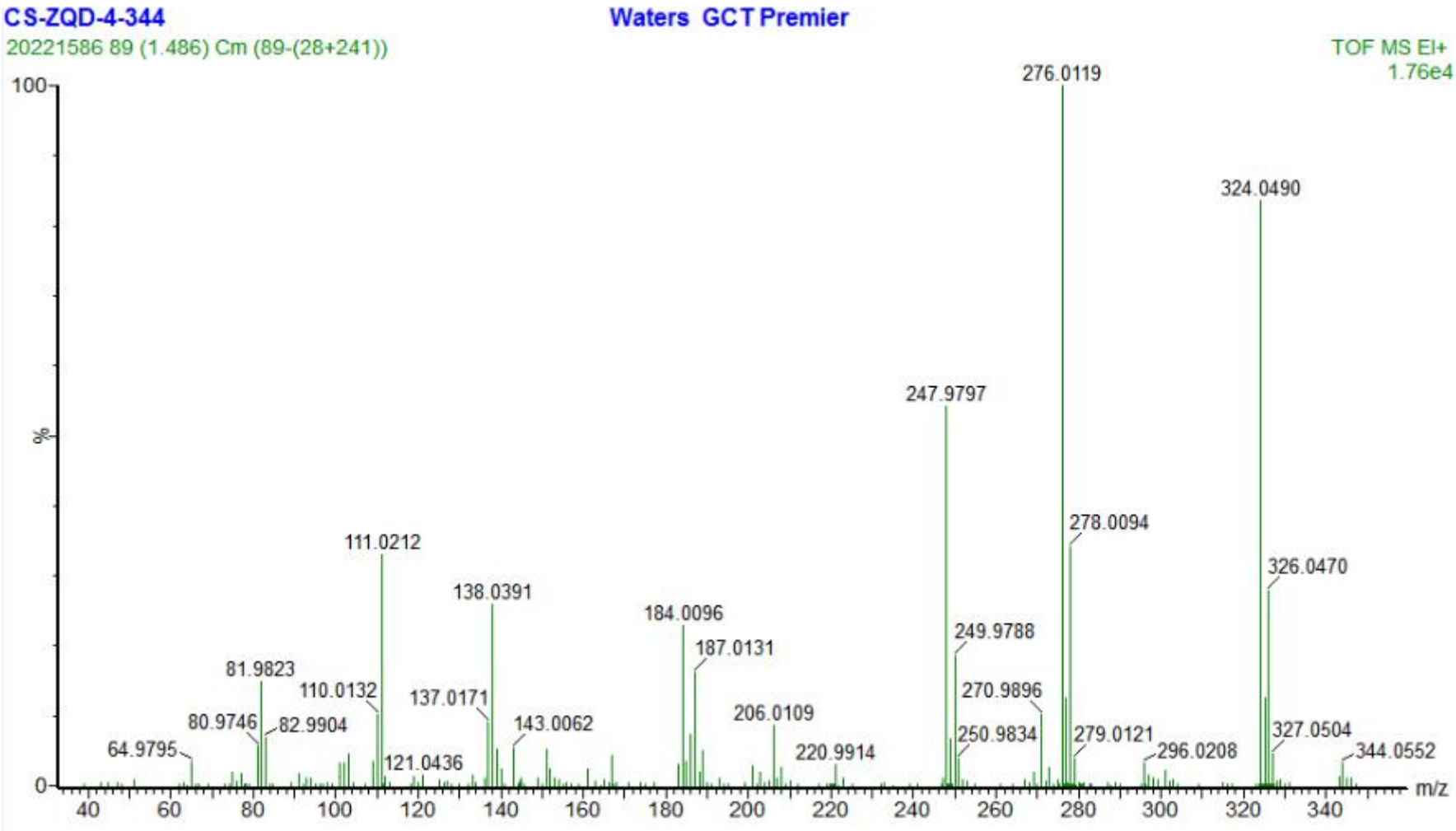
^{19}F NMR spectrum of 3ma



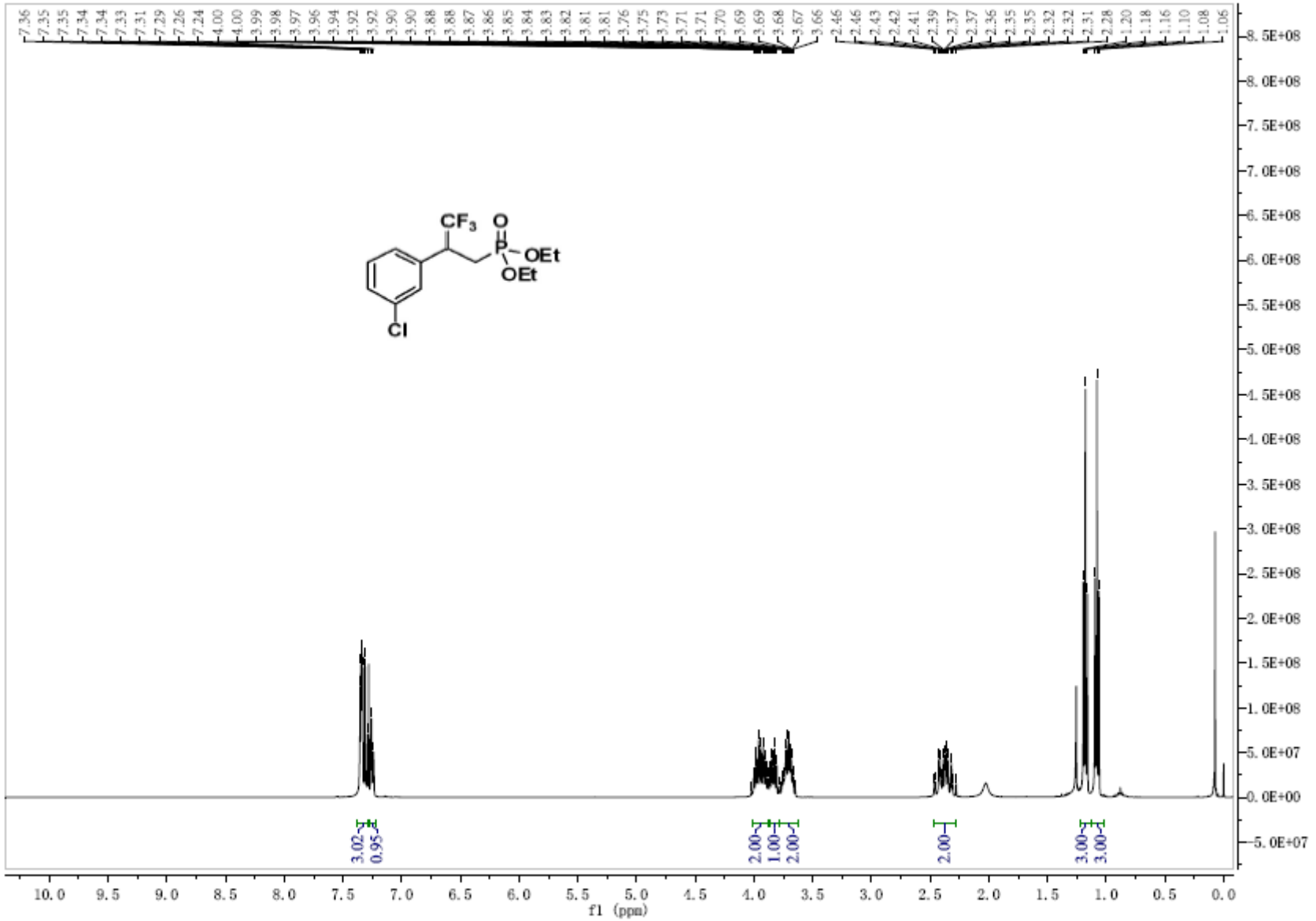
^{31}P NMR spectrum of 3ma



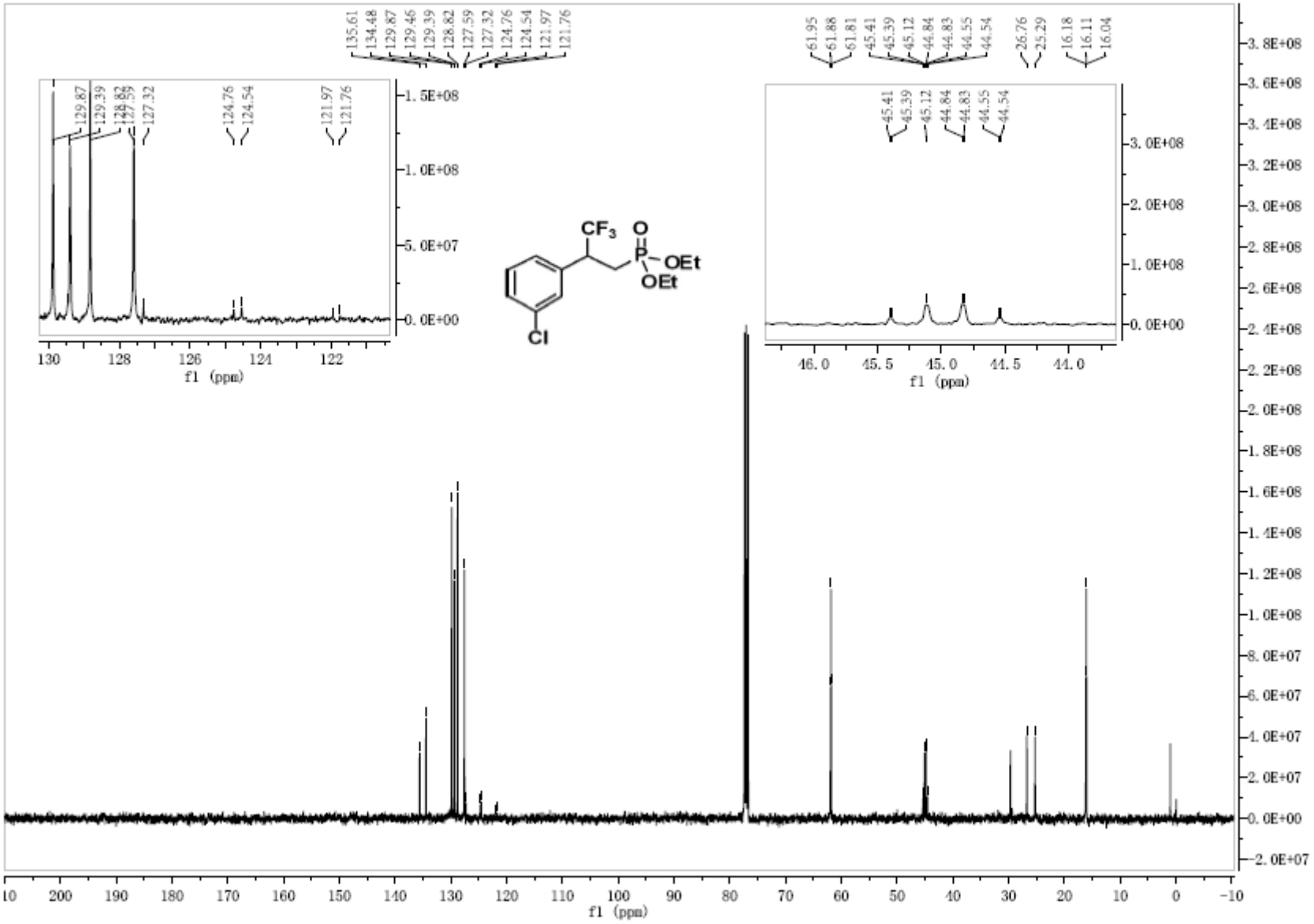
HRMS (EI) spectrum of 3ma



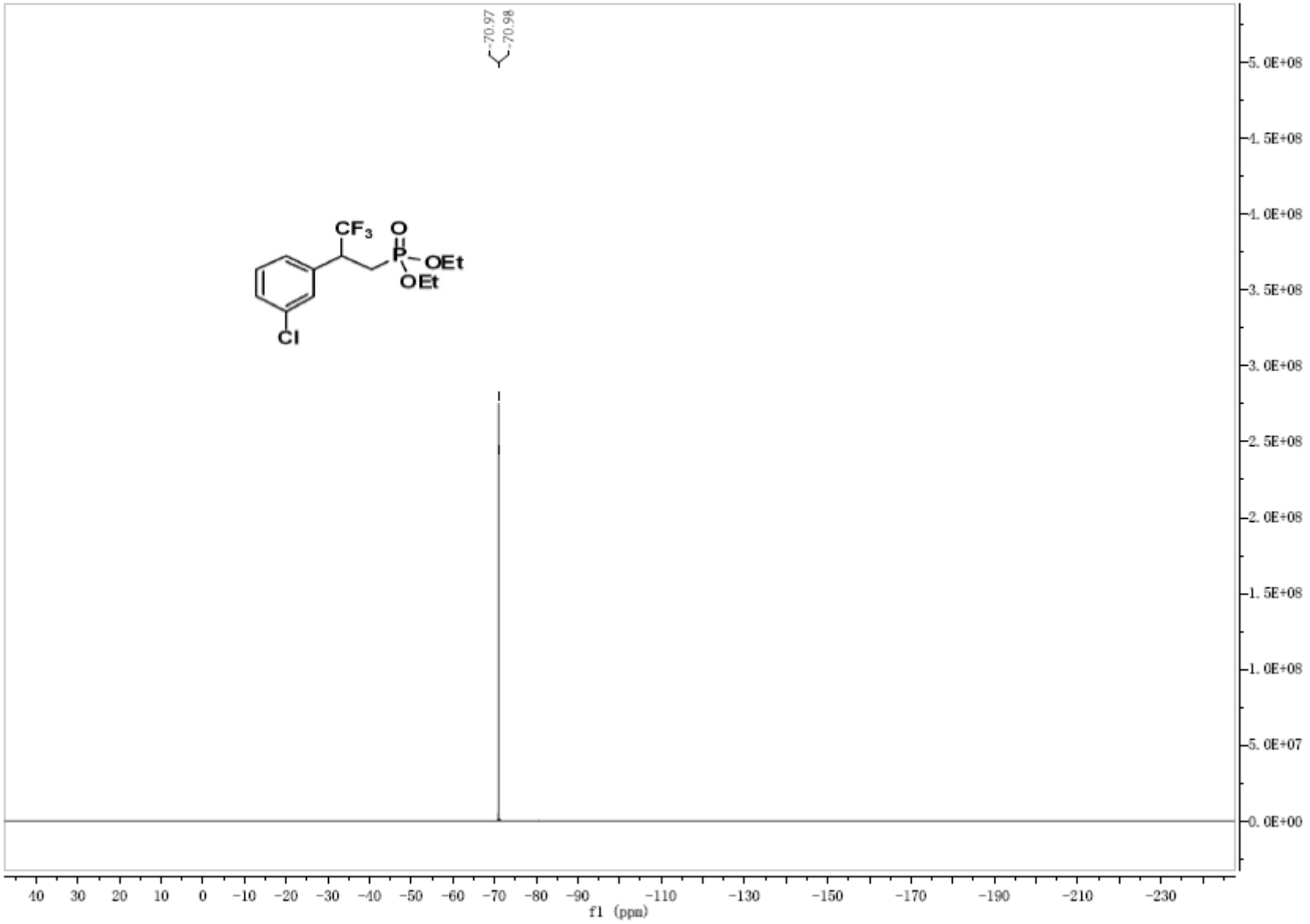
^{1}H NMR spectrum of 3na



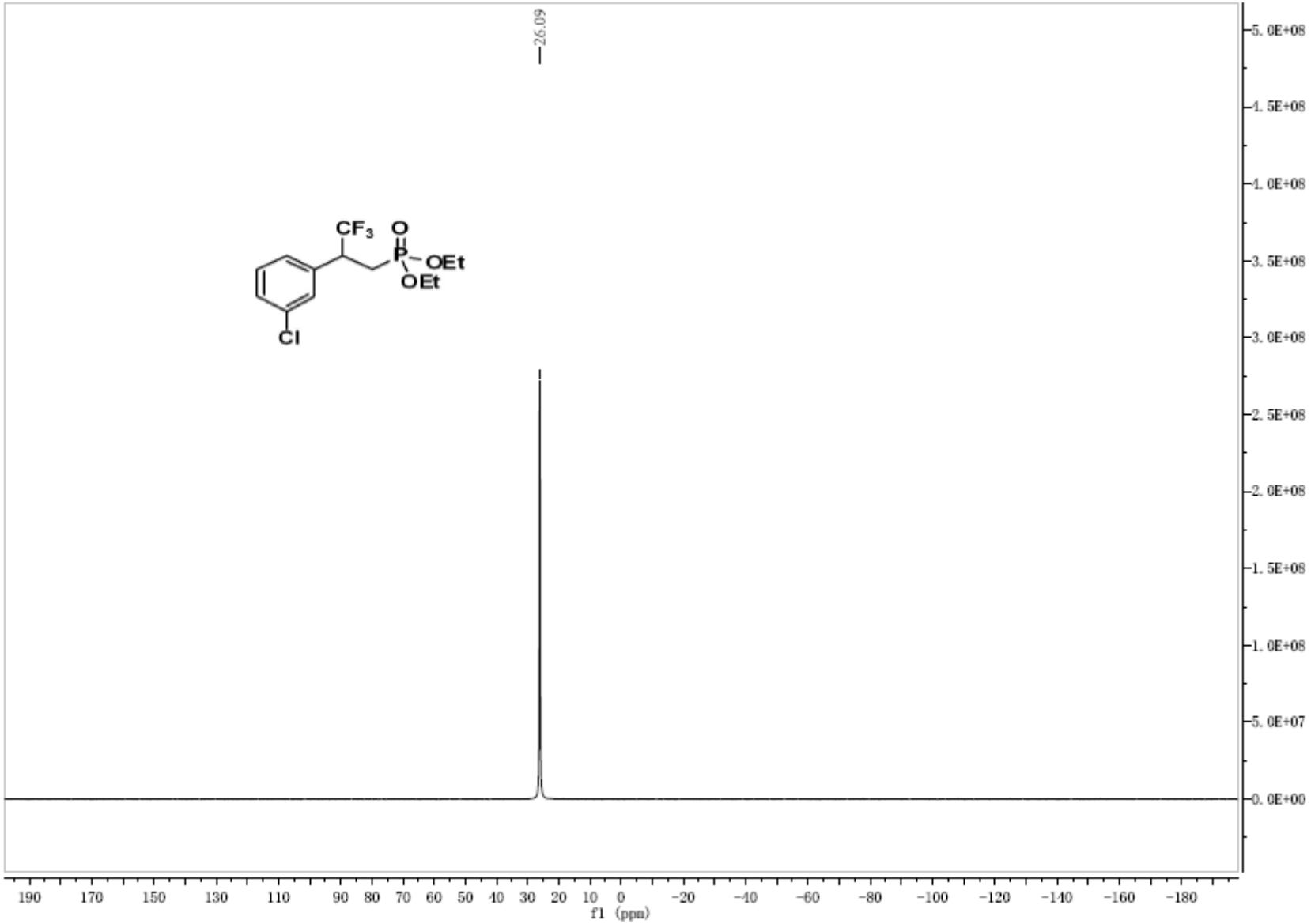
^{13}C NMR spectrum of 3na



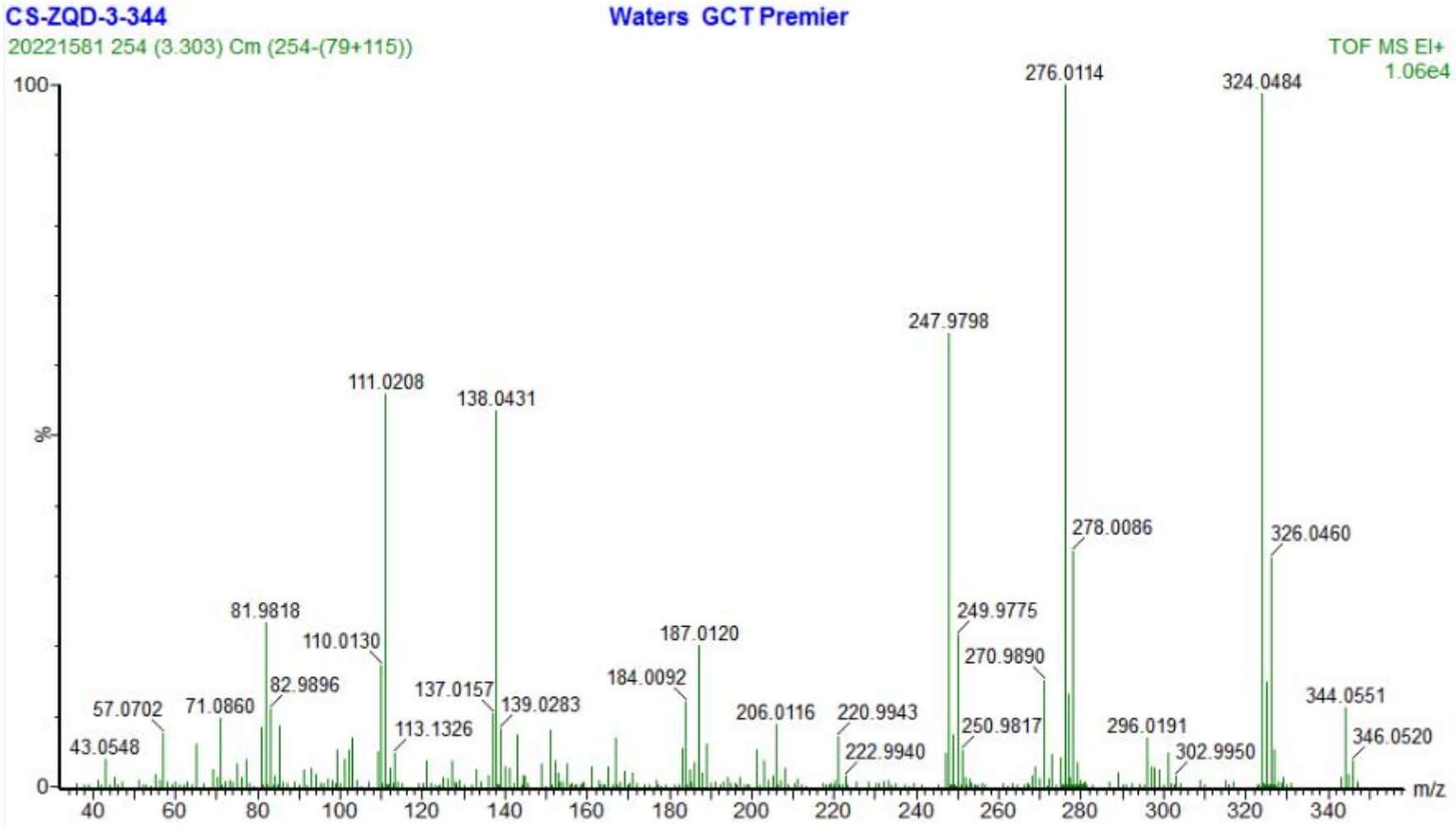
^{19}F NMR spectrum of 3na



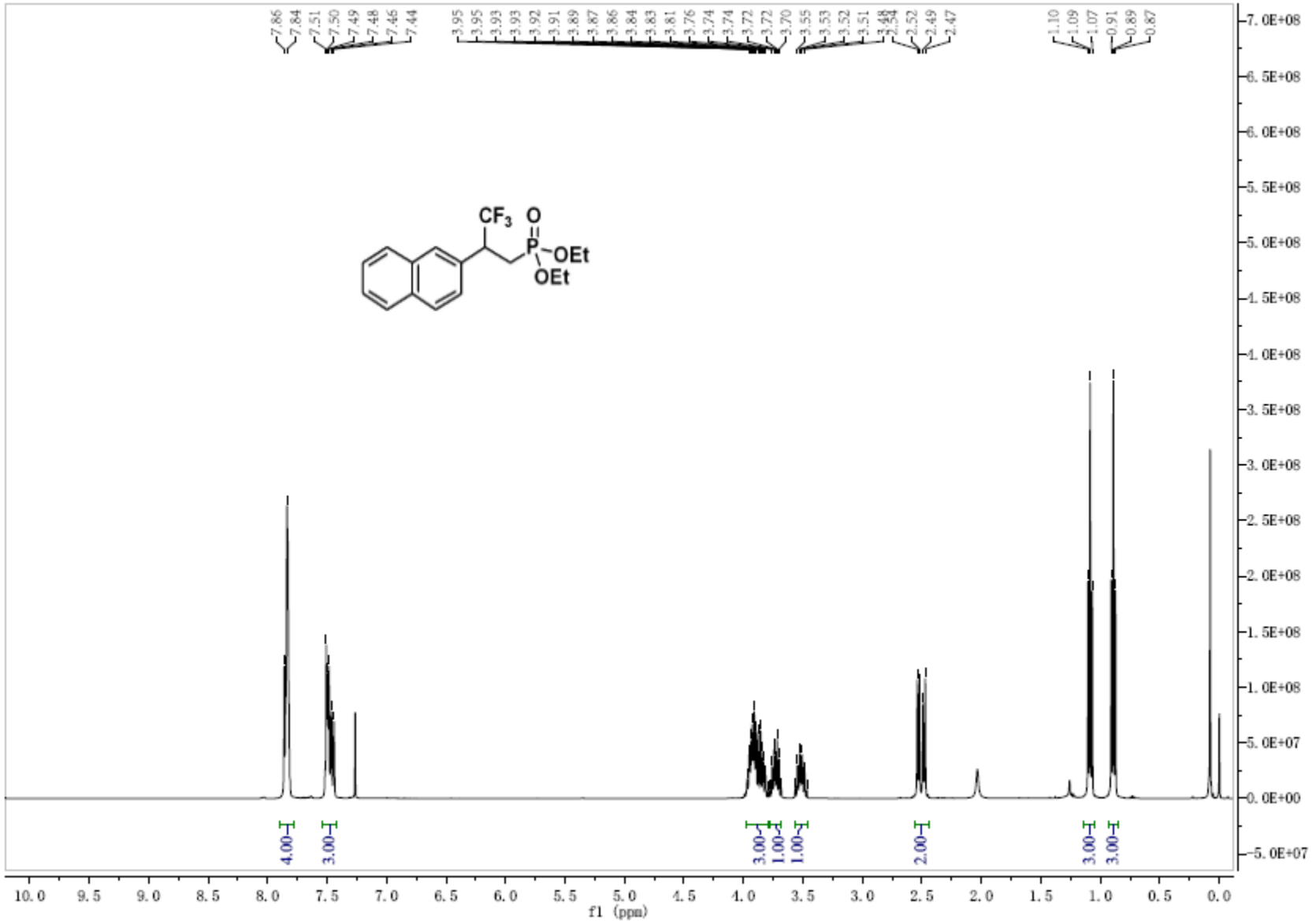
^{31}P NMR spectrum of 3na



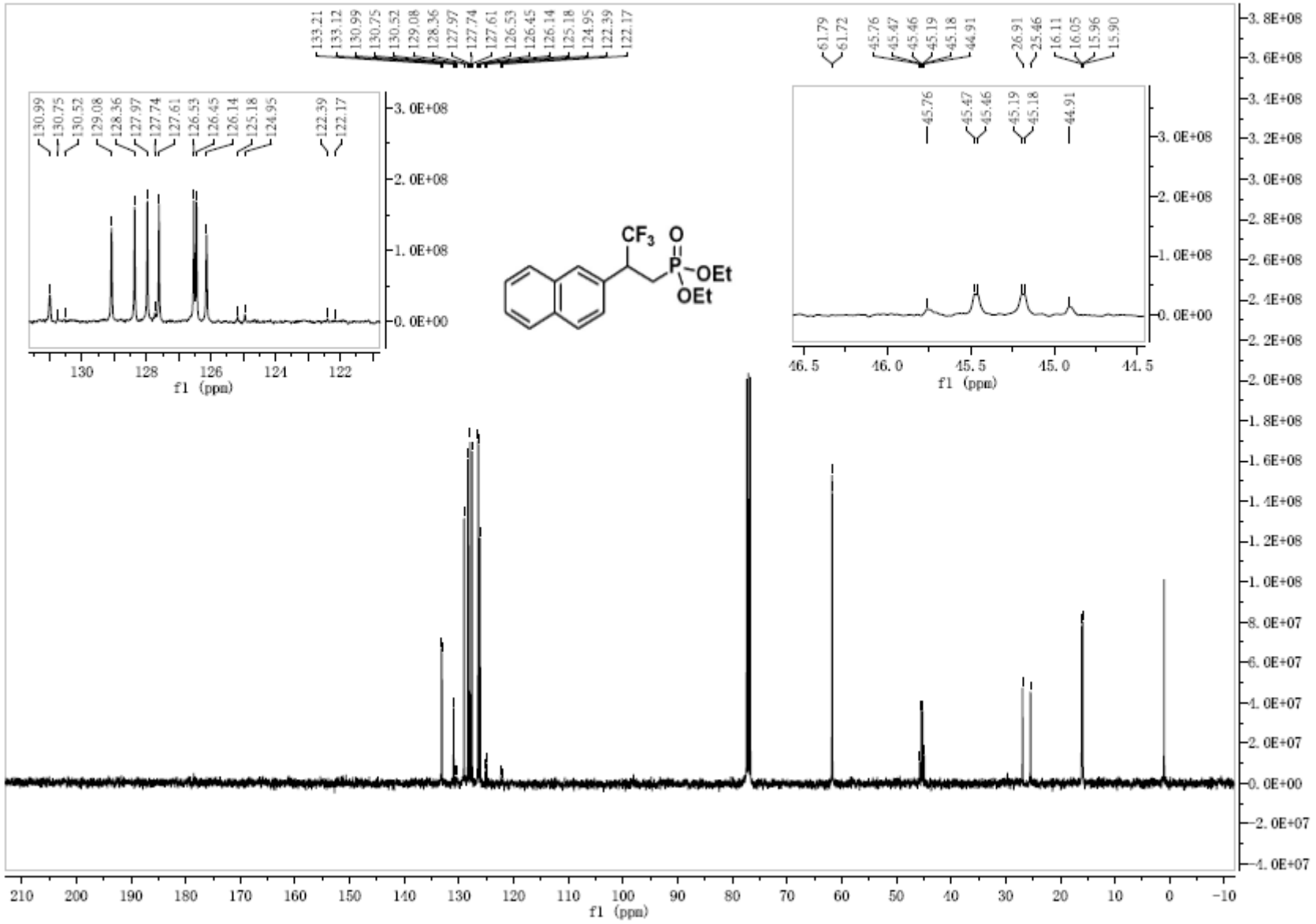
HRMS (EI) spectrum of 3na



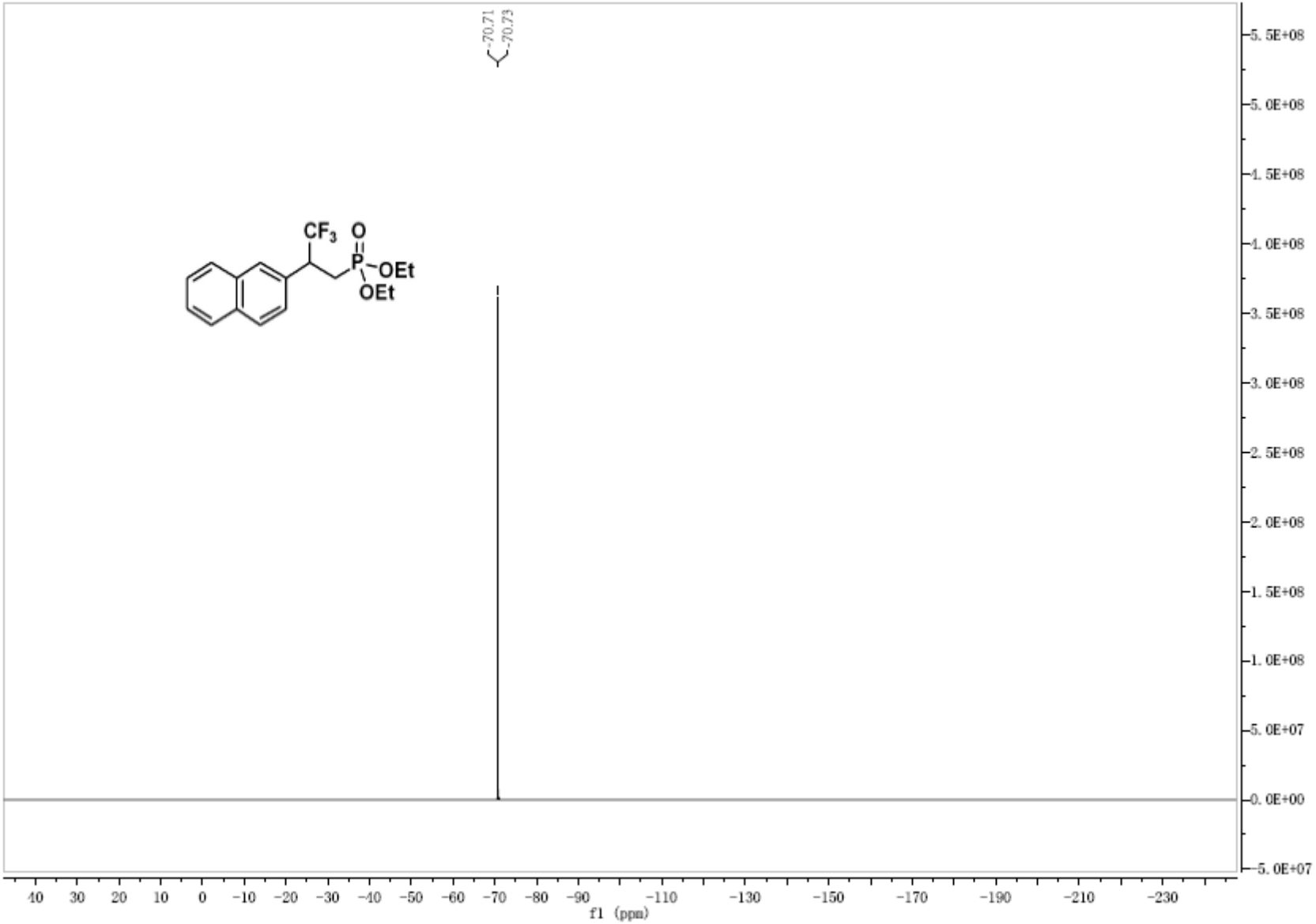
^{1}H NMR spectrum of 3pa



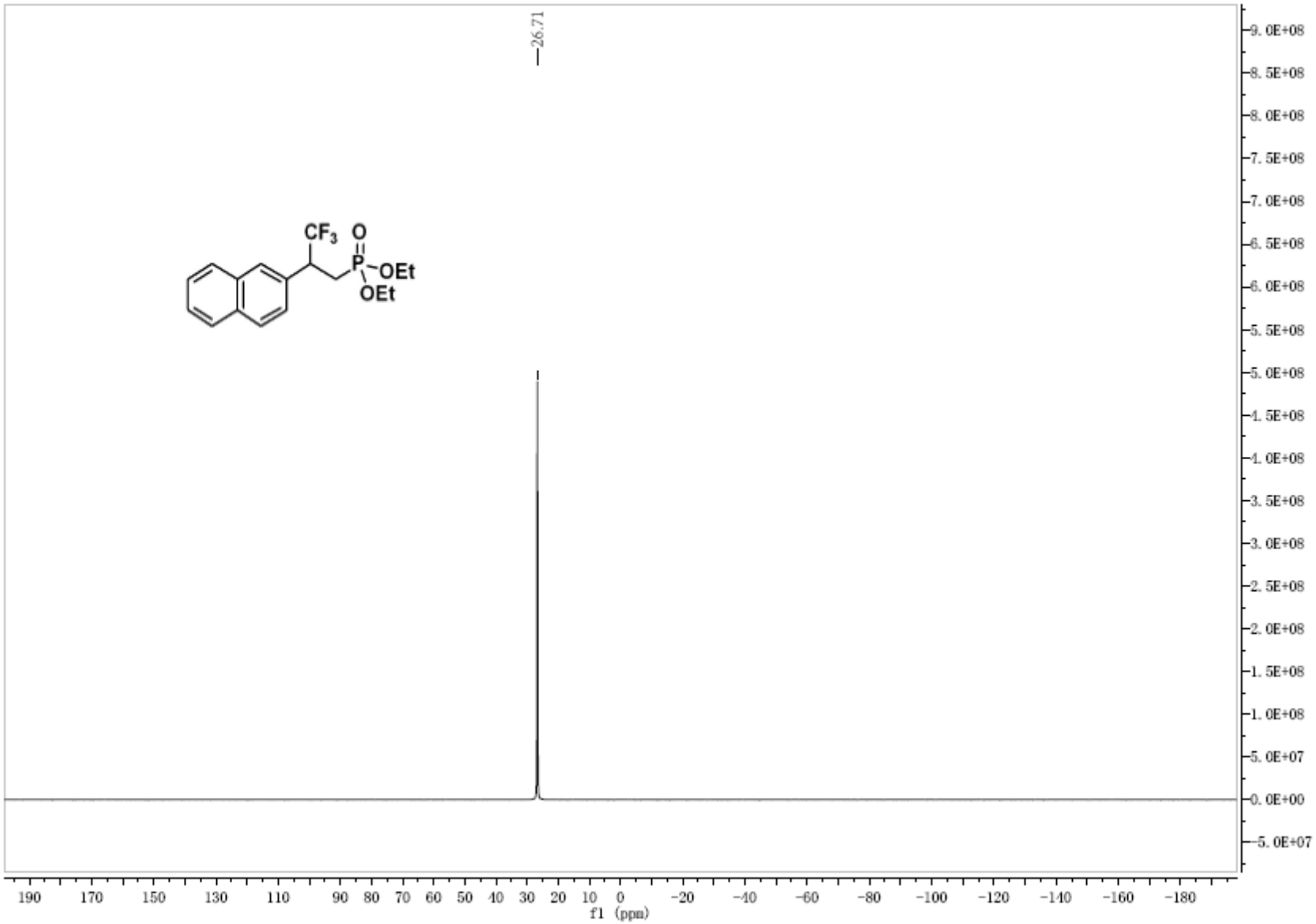
^{13}C NMR spectrum of 3pa



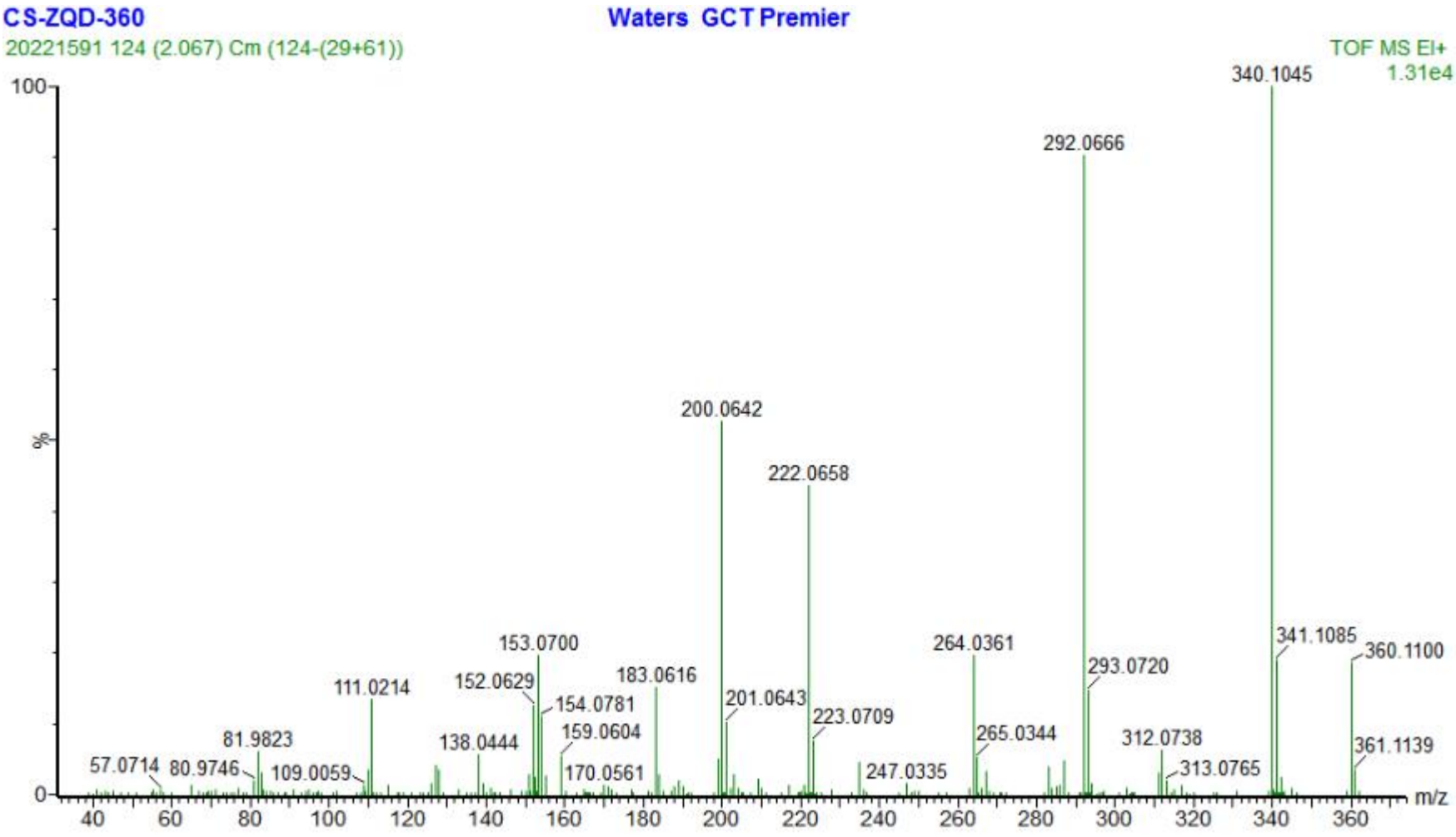
^{19}F NMR spectrum of 3pa



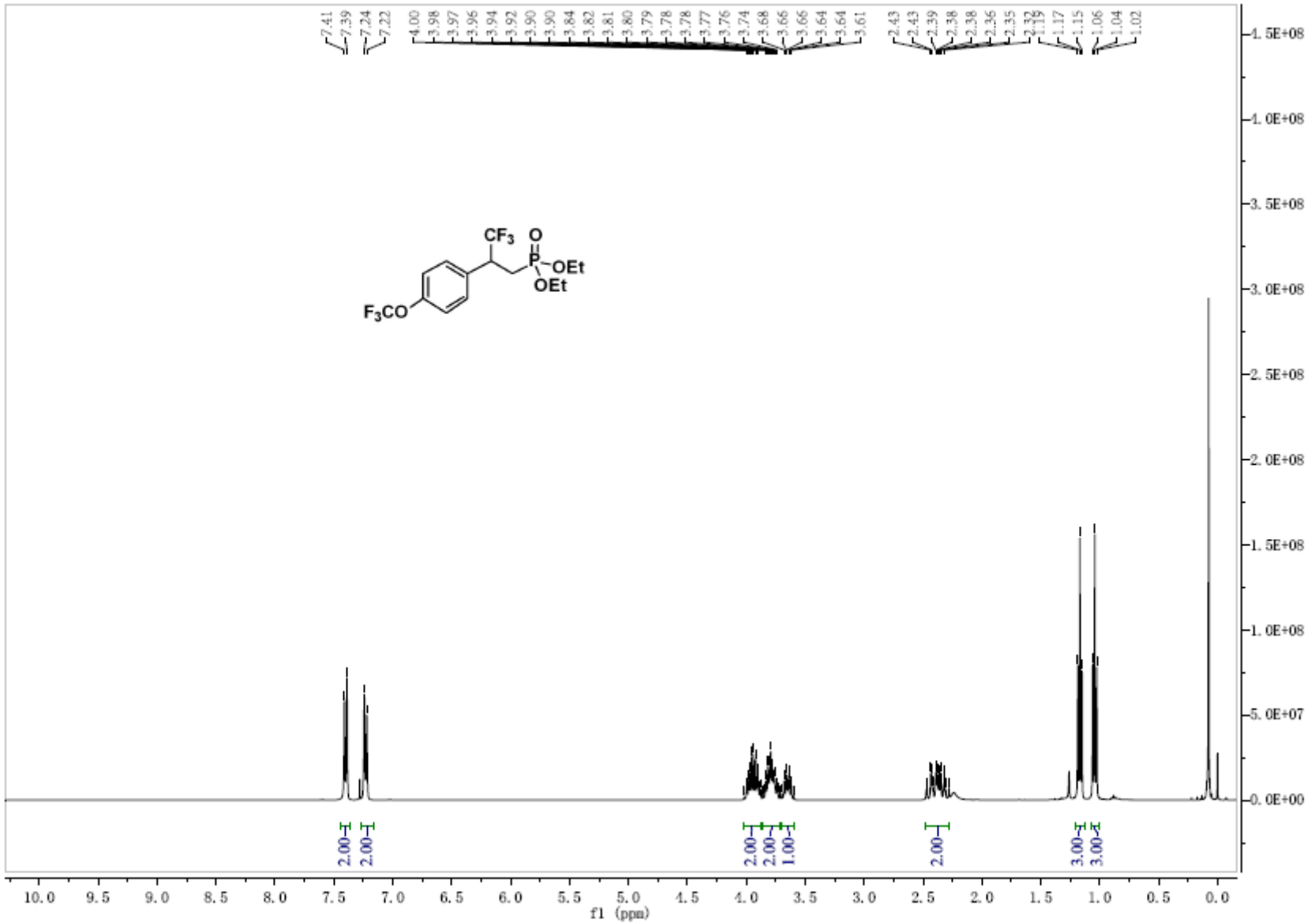
^{31}P NMR spectrum of 3pa



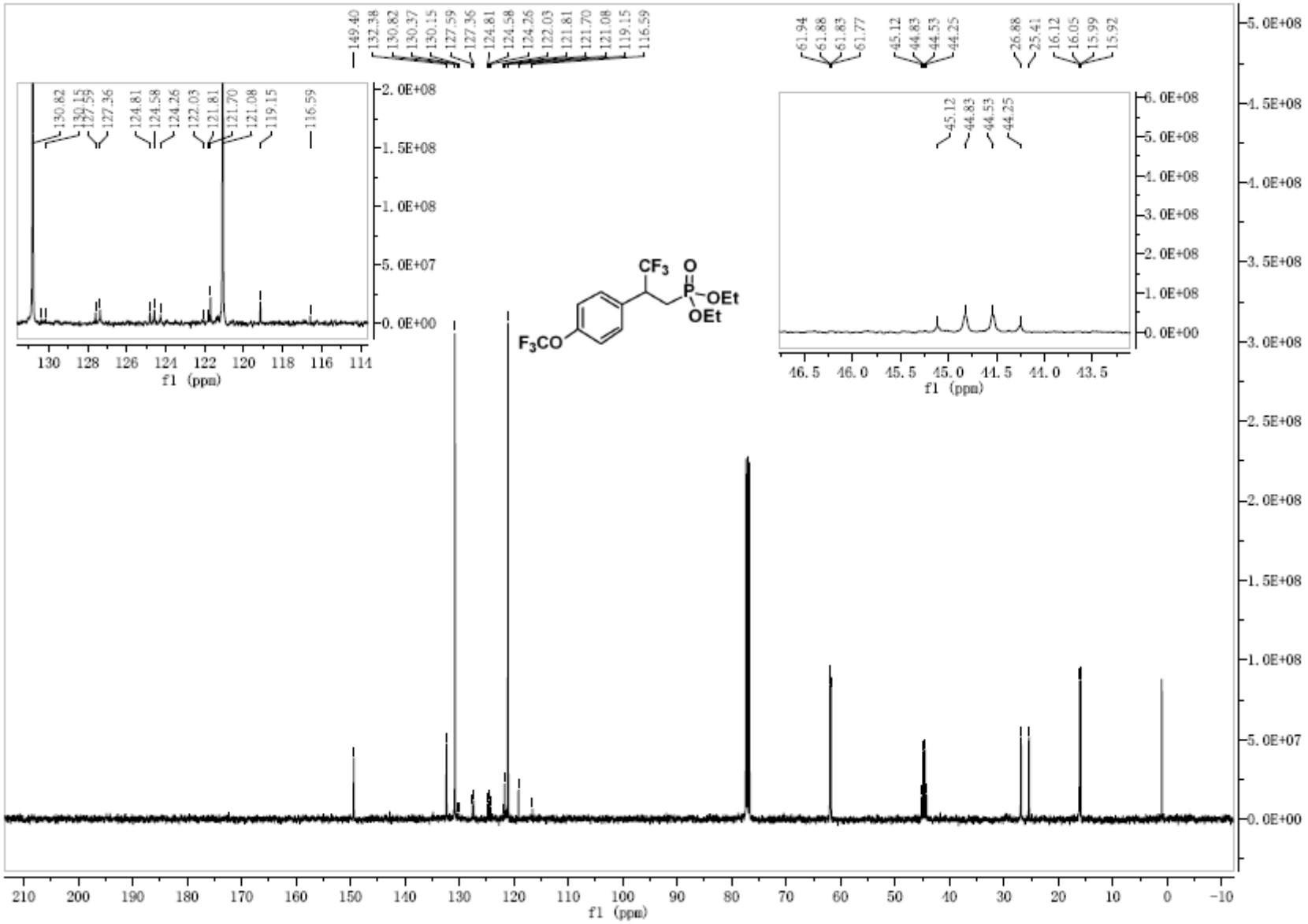
HRMS (EI) spectrum of 3pa



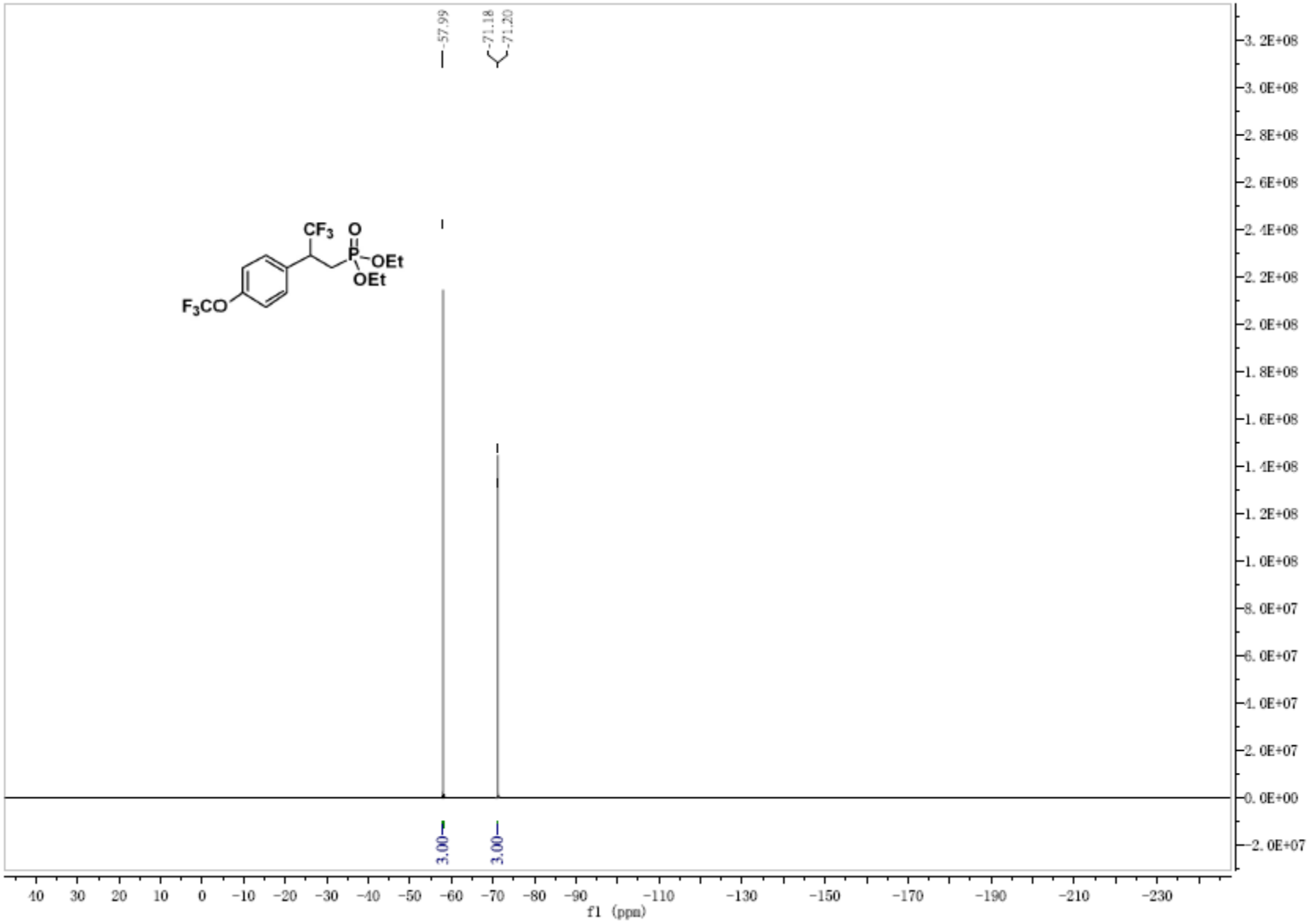
^{1}H NMR spectrum of 3qa



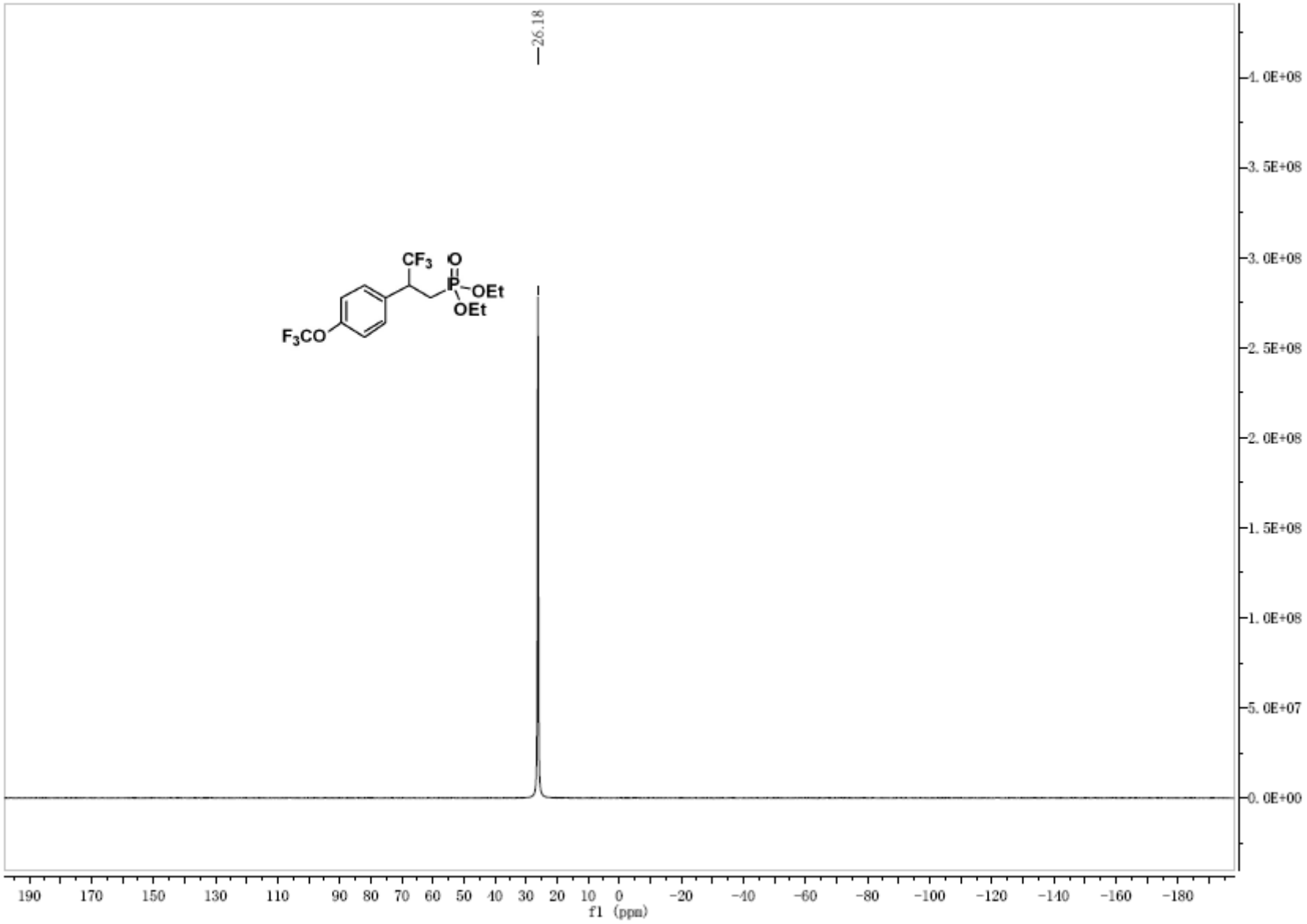
^{13}C NMR spectrum of 3qa



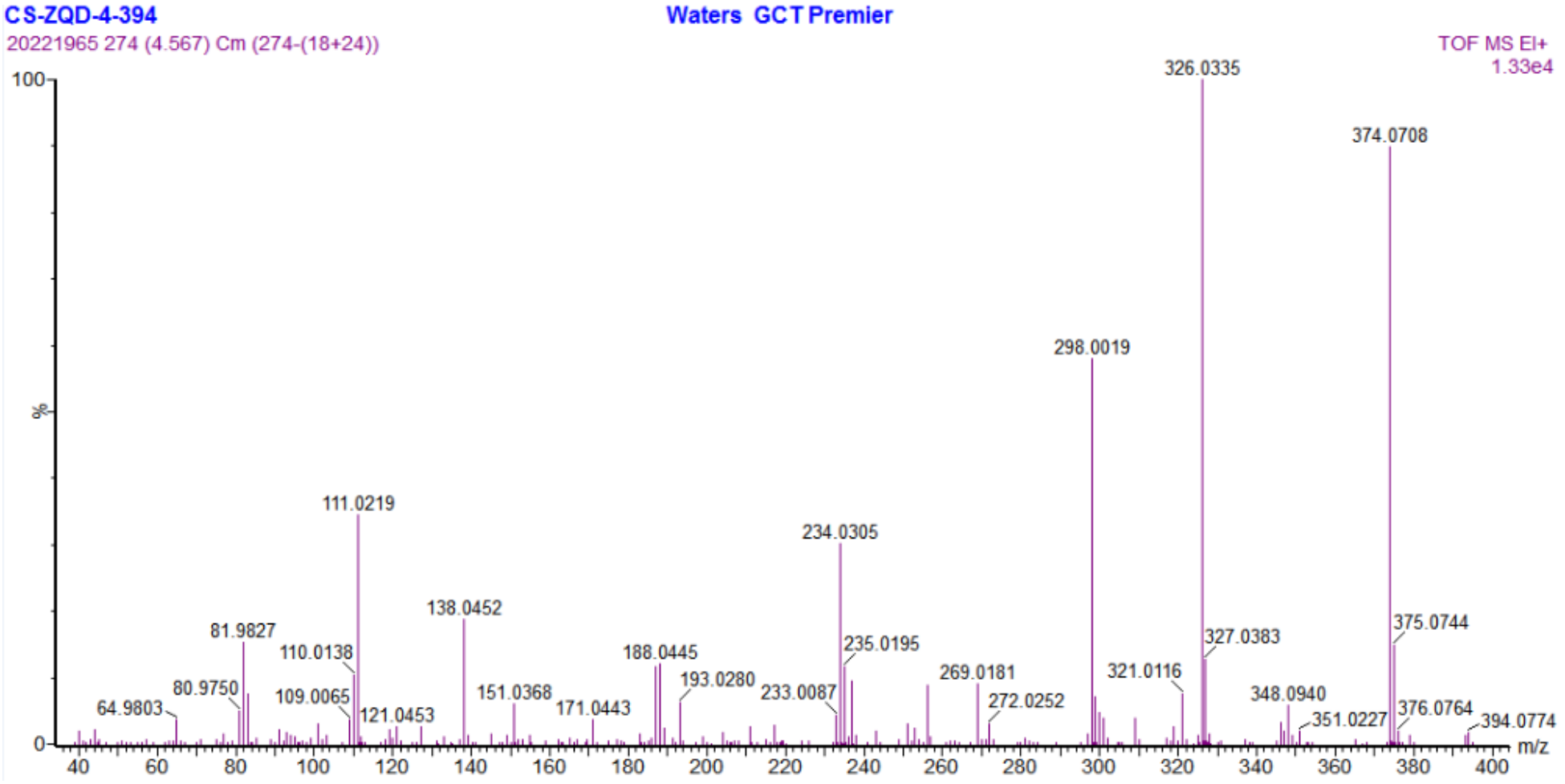
^{19}F NMR spectrum of 3qa



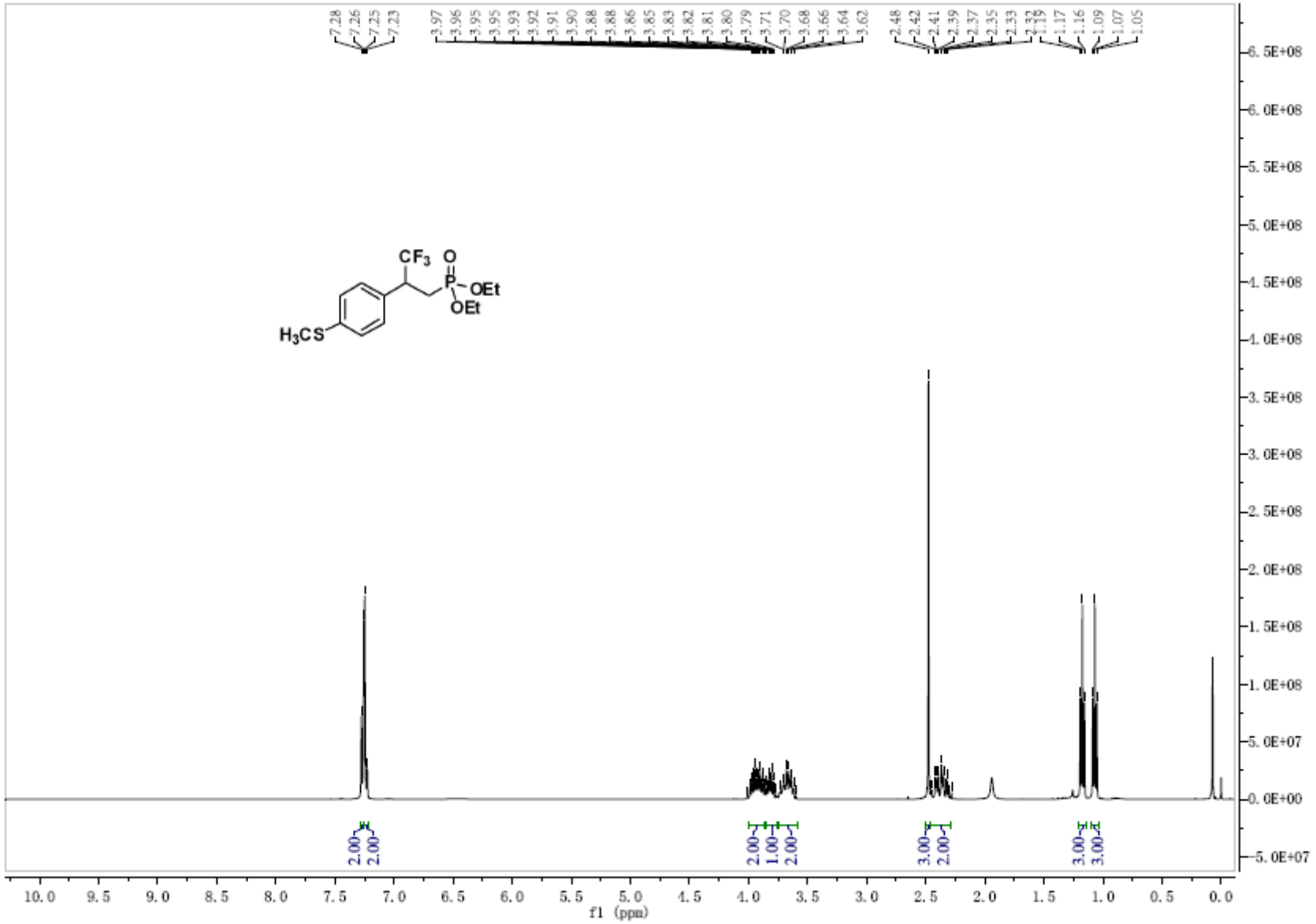
^{31}P NMR spectrum of 3qa



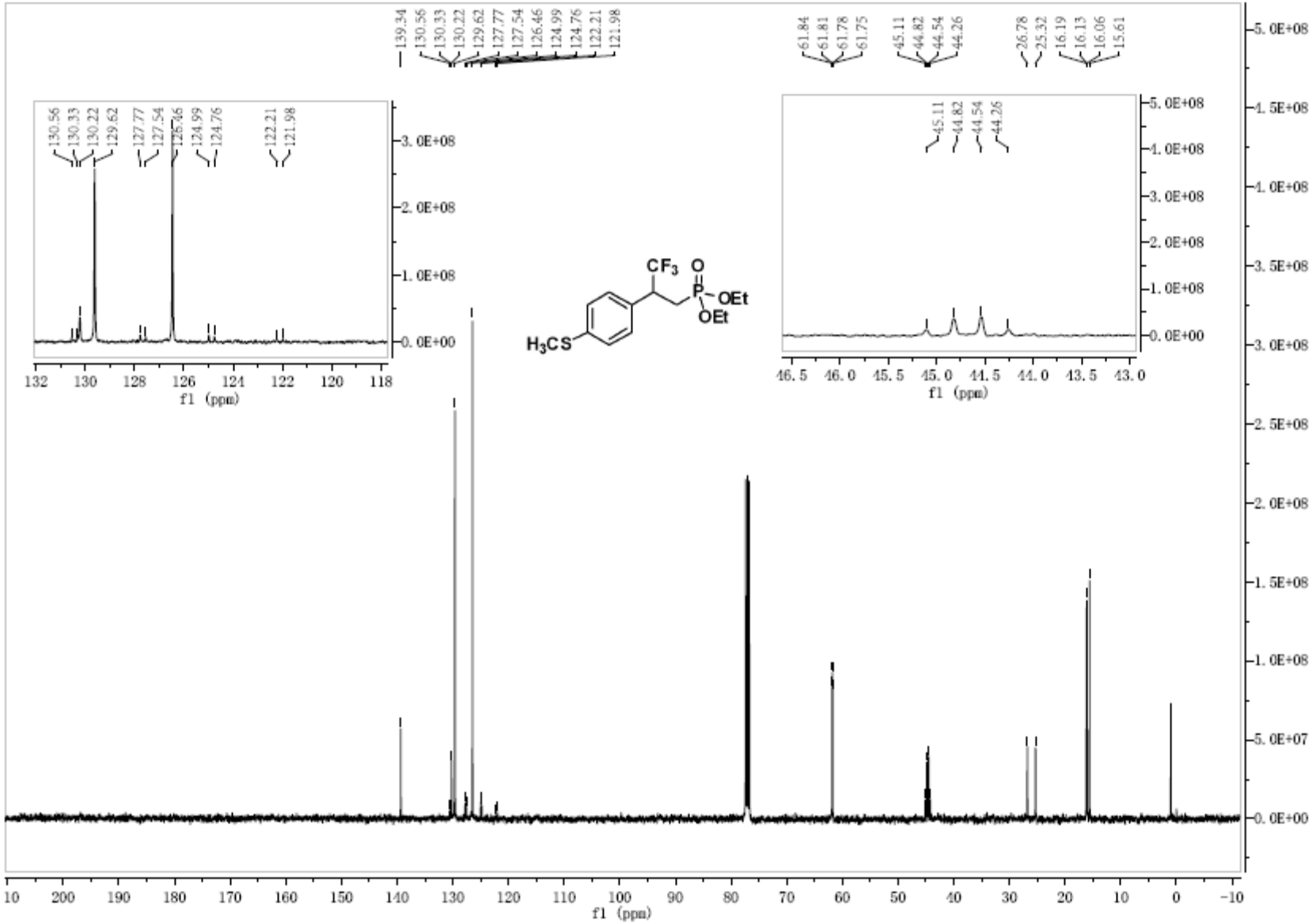
HRMS (EI) spectrum of 3qa



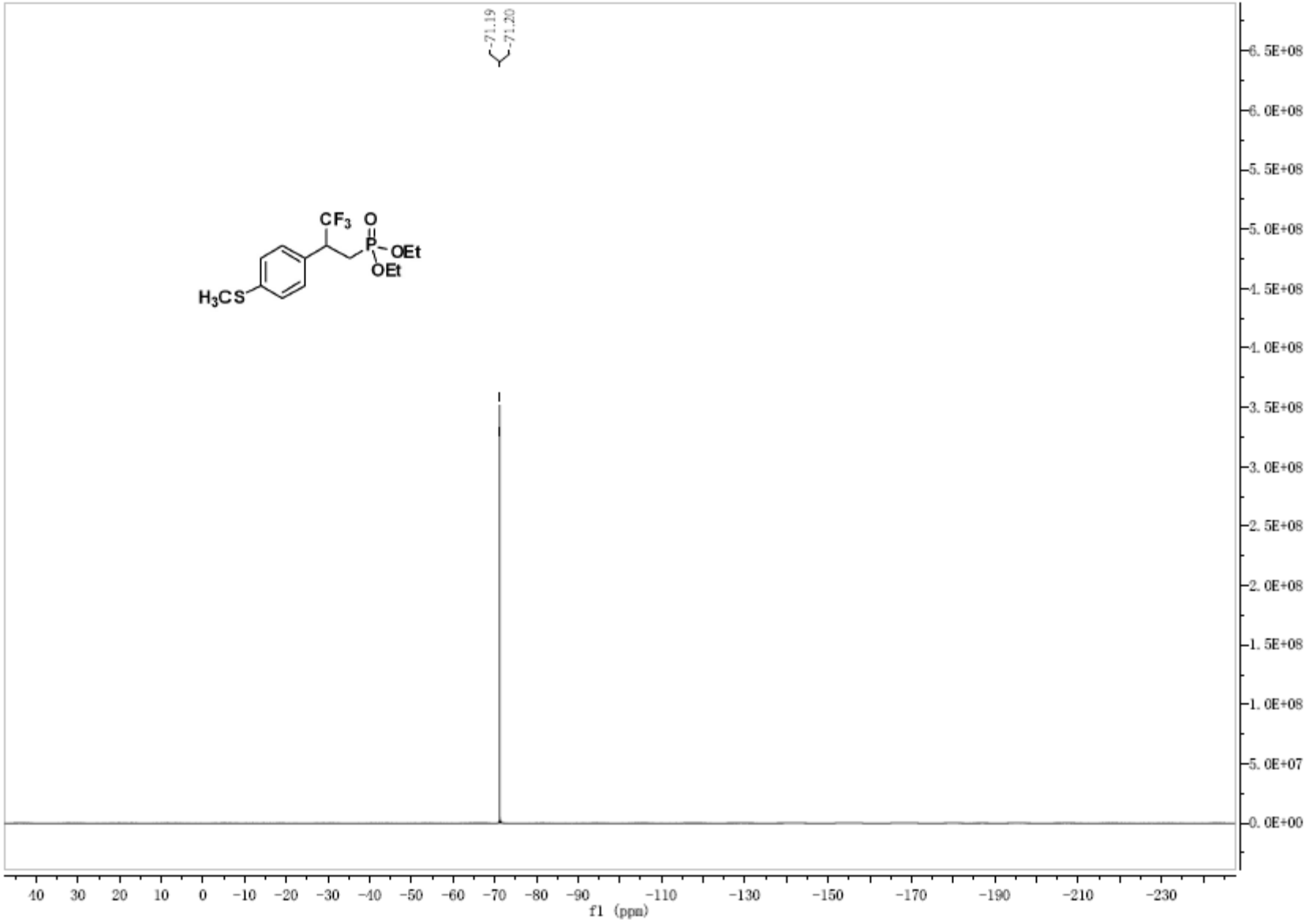
^{1}H NMR spectrum of 3ra



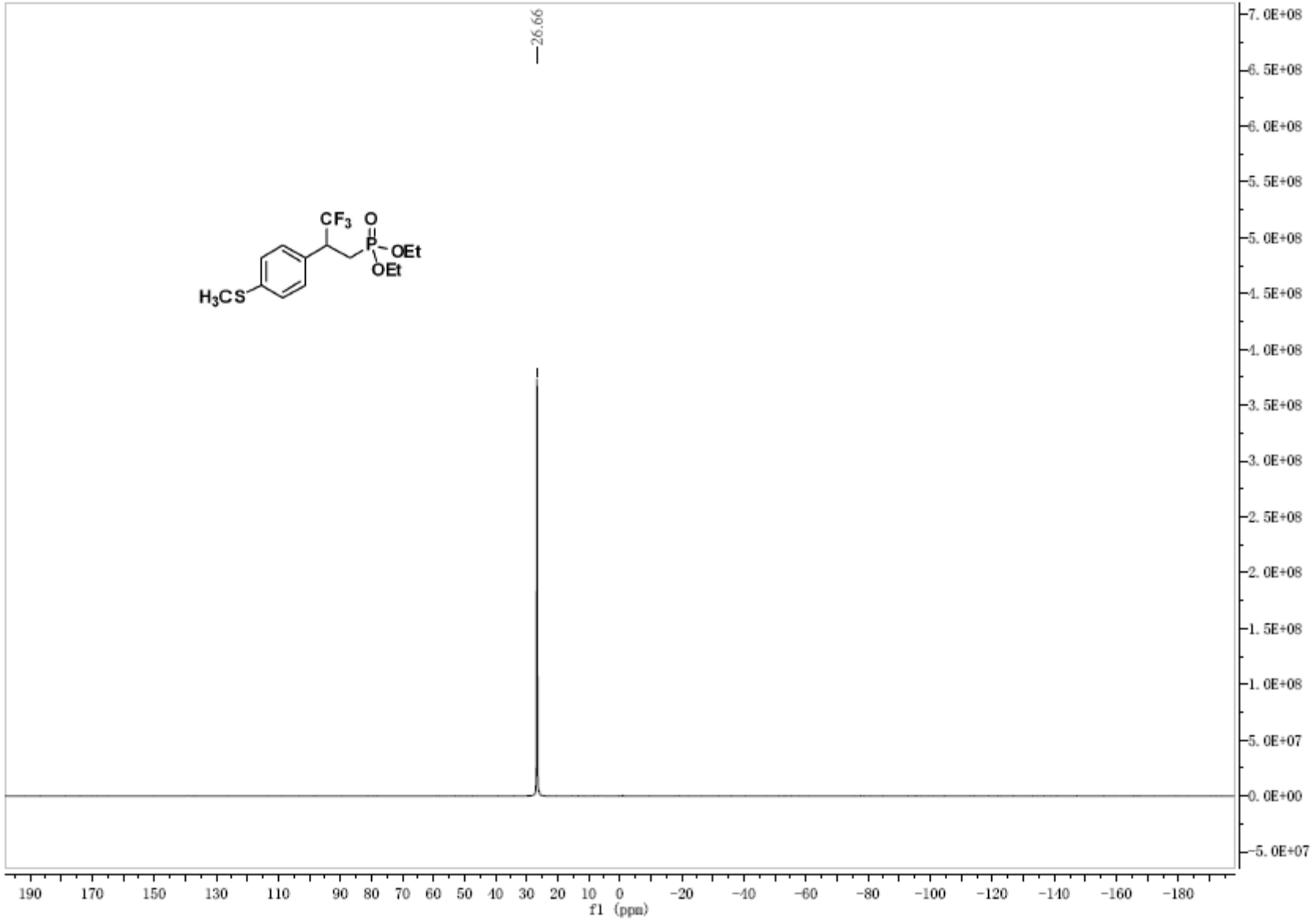
^{13}C NMR spectrum of 3ra



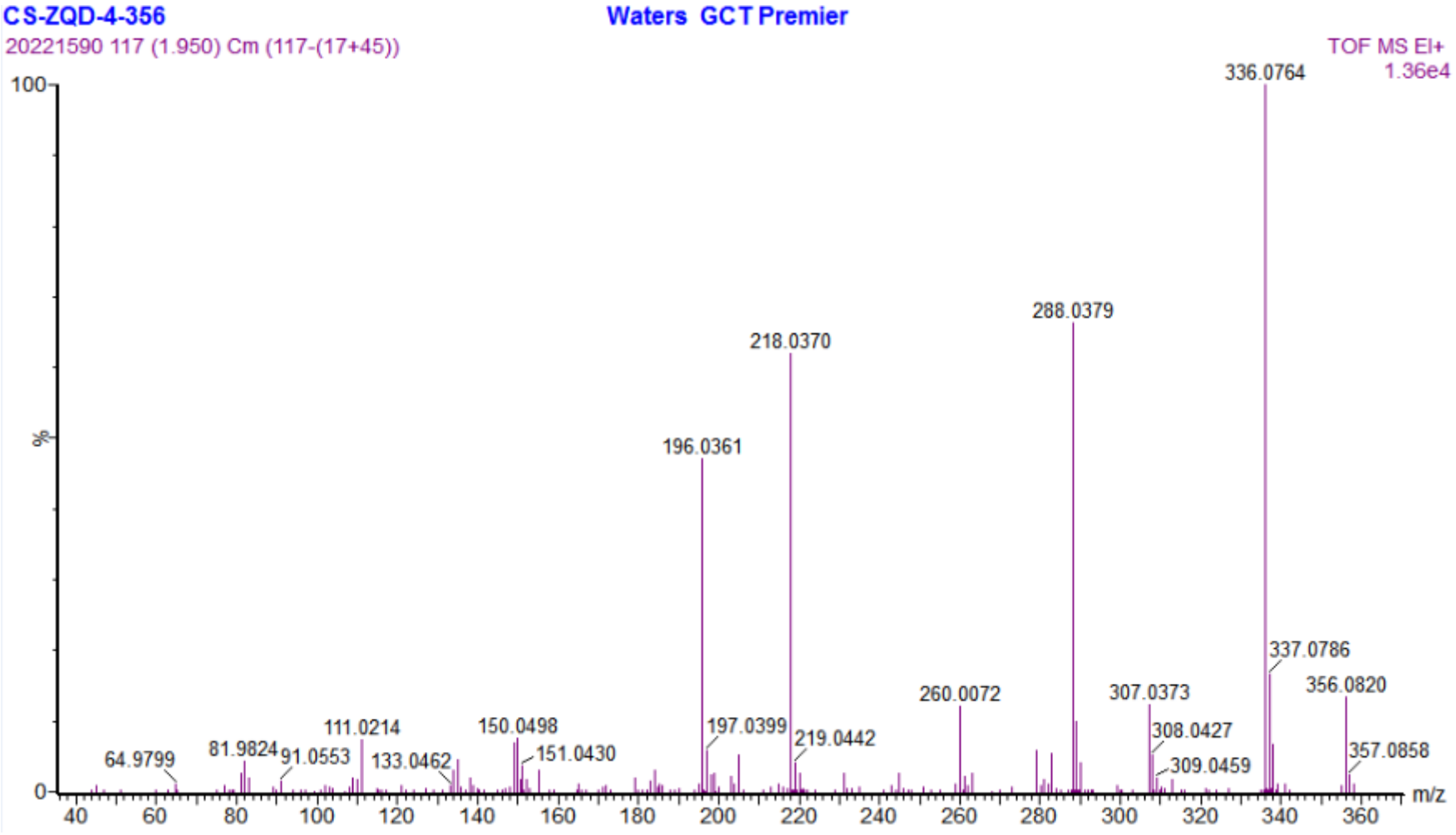
^{19}F NMR spectrum of 3ra



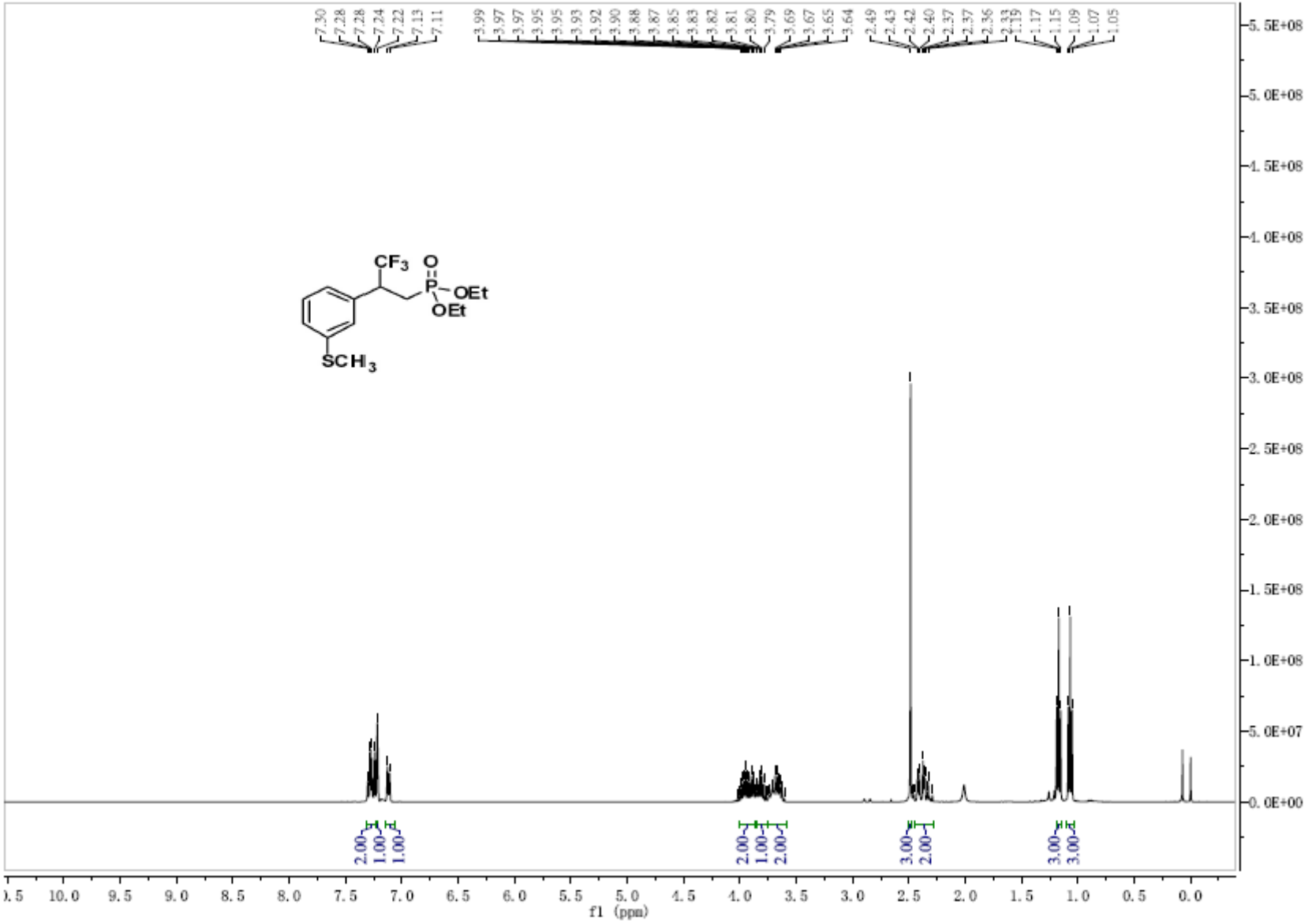
^{31}P NMR spectrum of 3ra



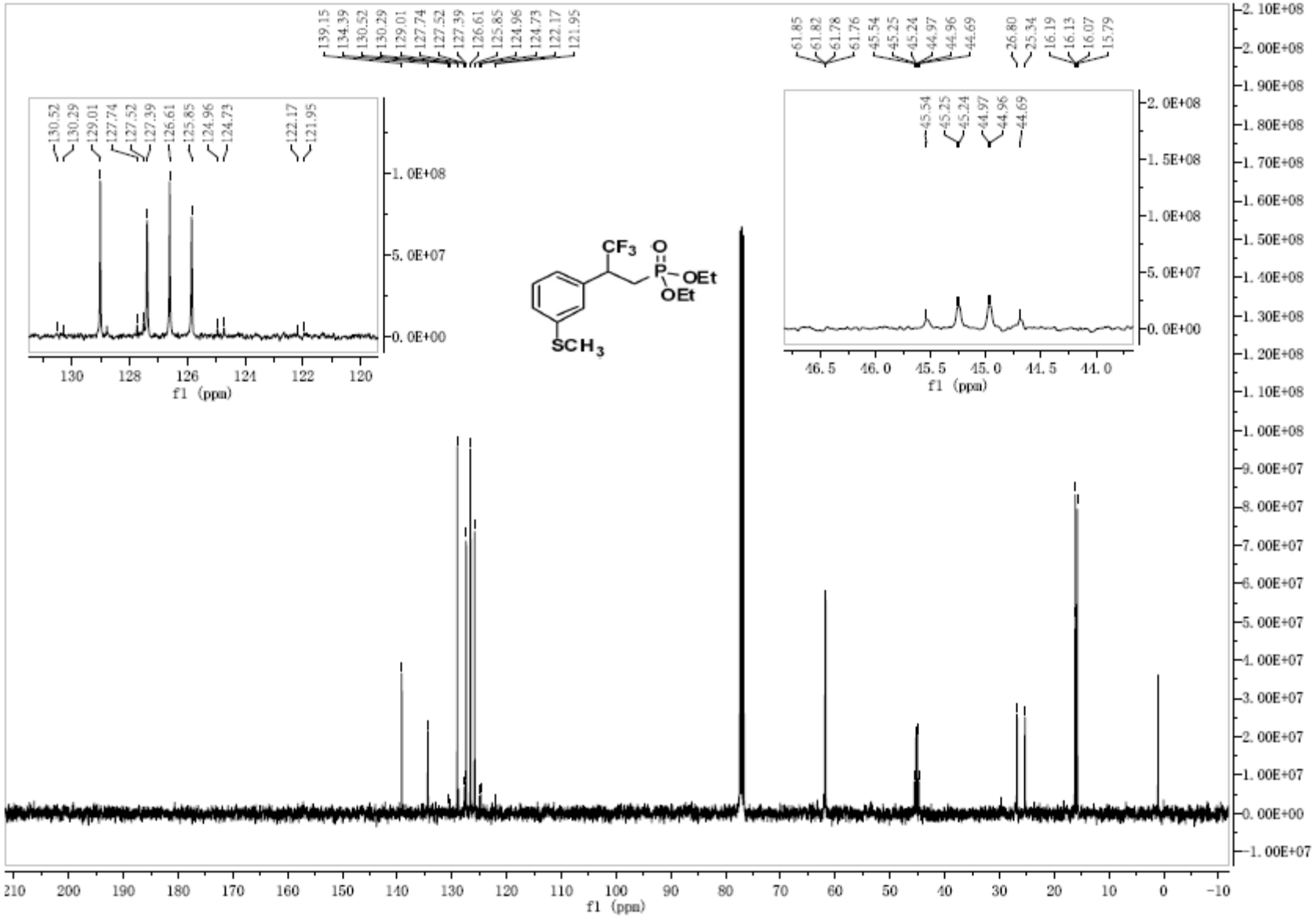
HRMS (EI) spectrum of 3ra



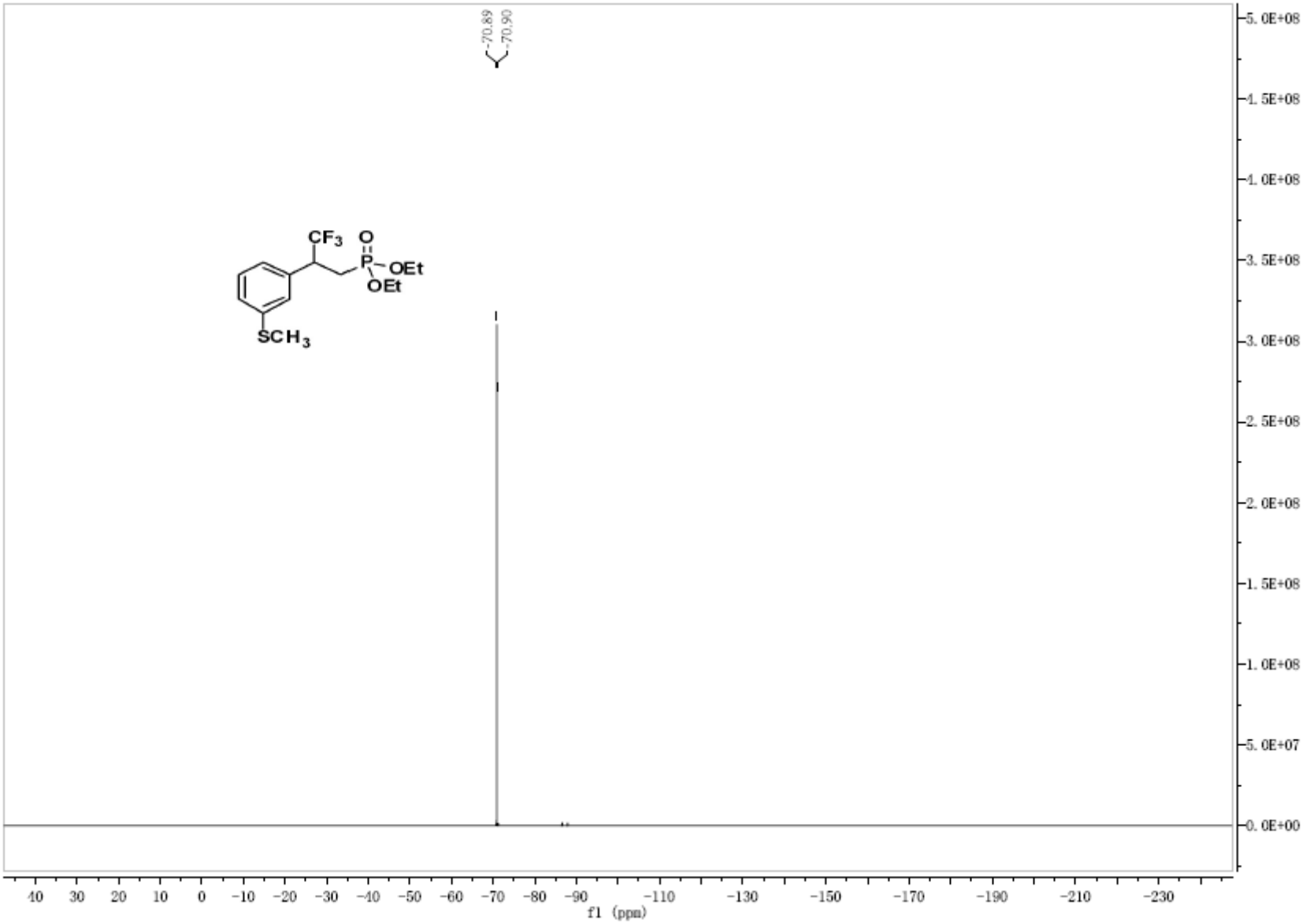
^{1}H NMR spectrum of 3sa



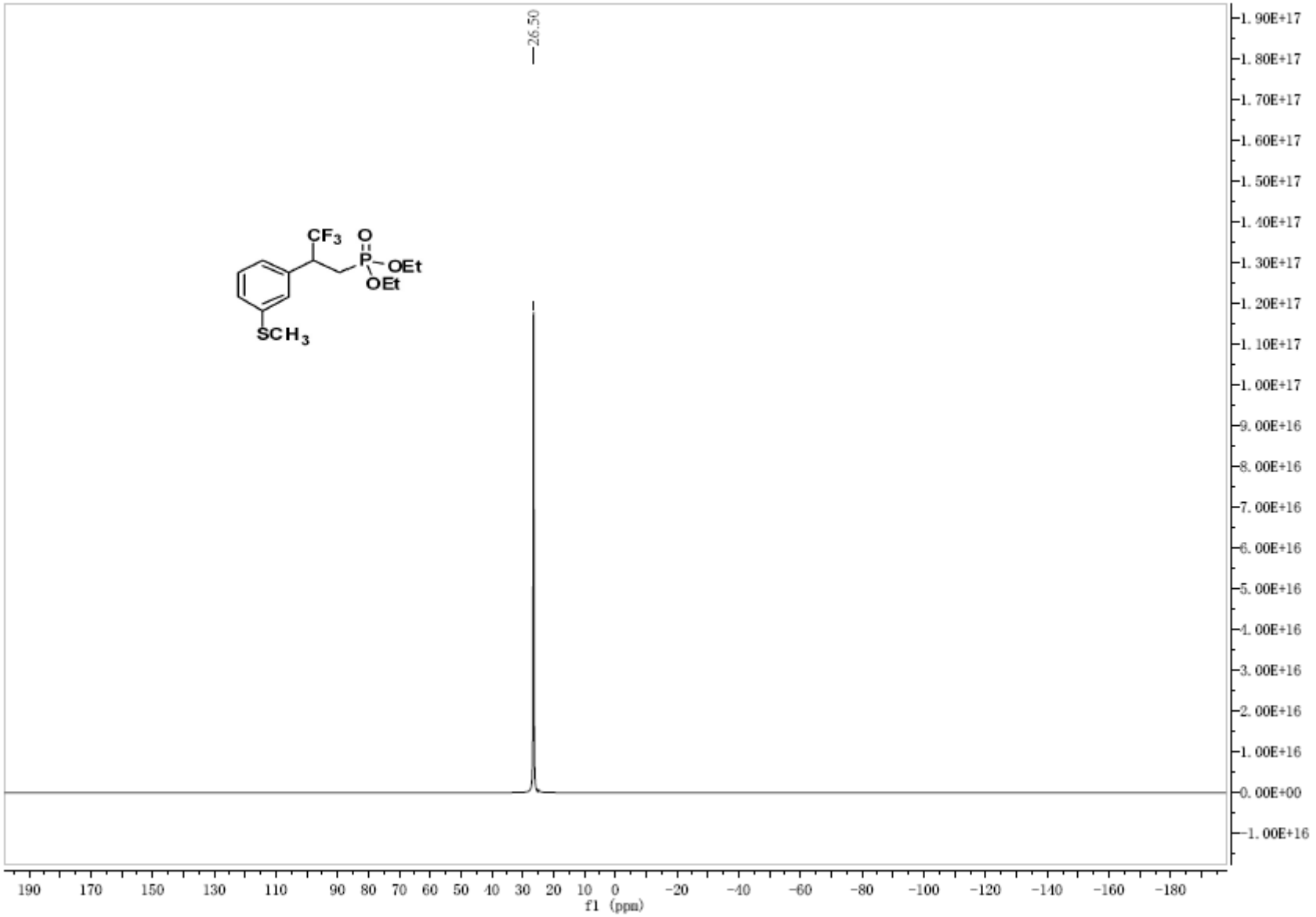
^{13}C NMR spectrum of 3sa



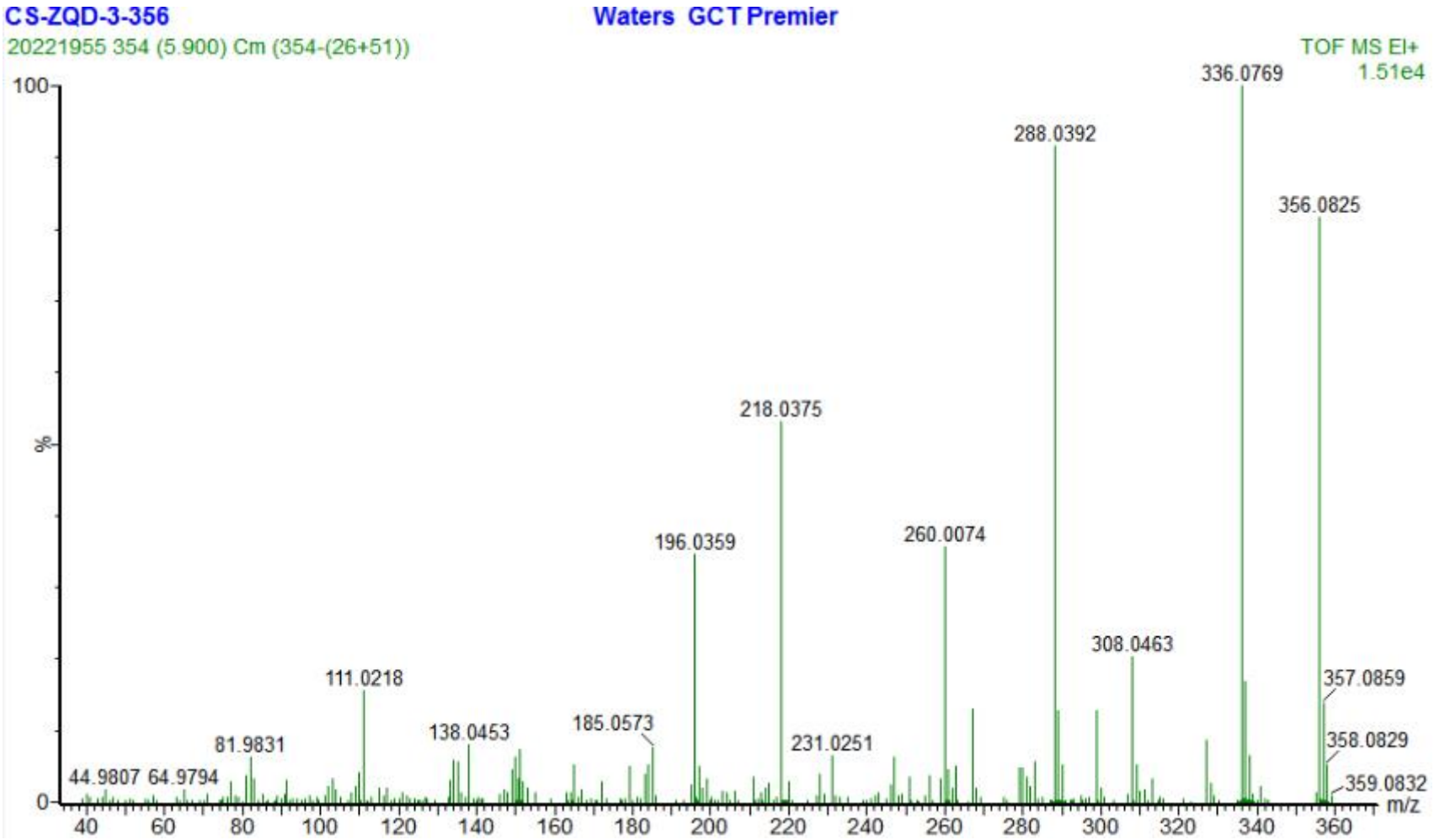
^{19}F NMR spectrum of 3sa



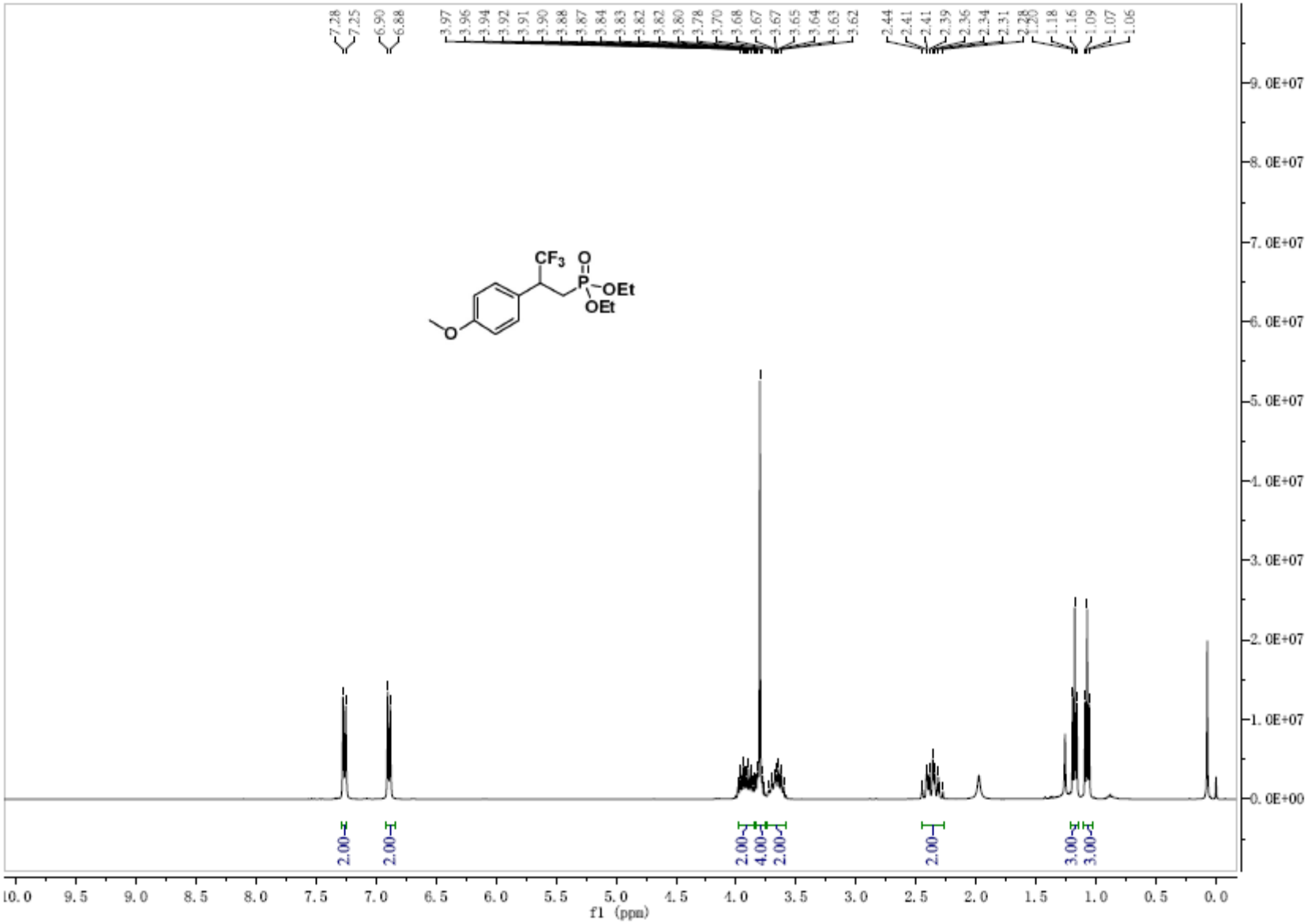
^{31}P NMR spectrum of 3sa



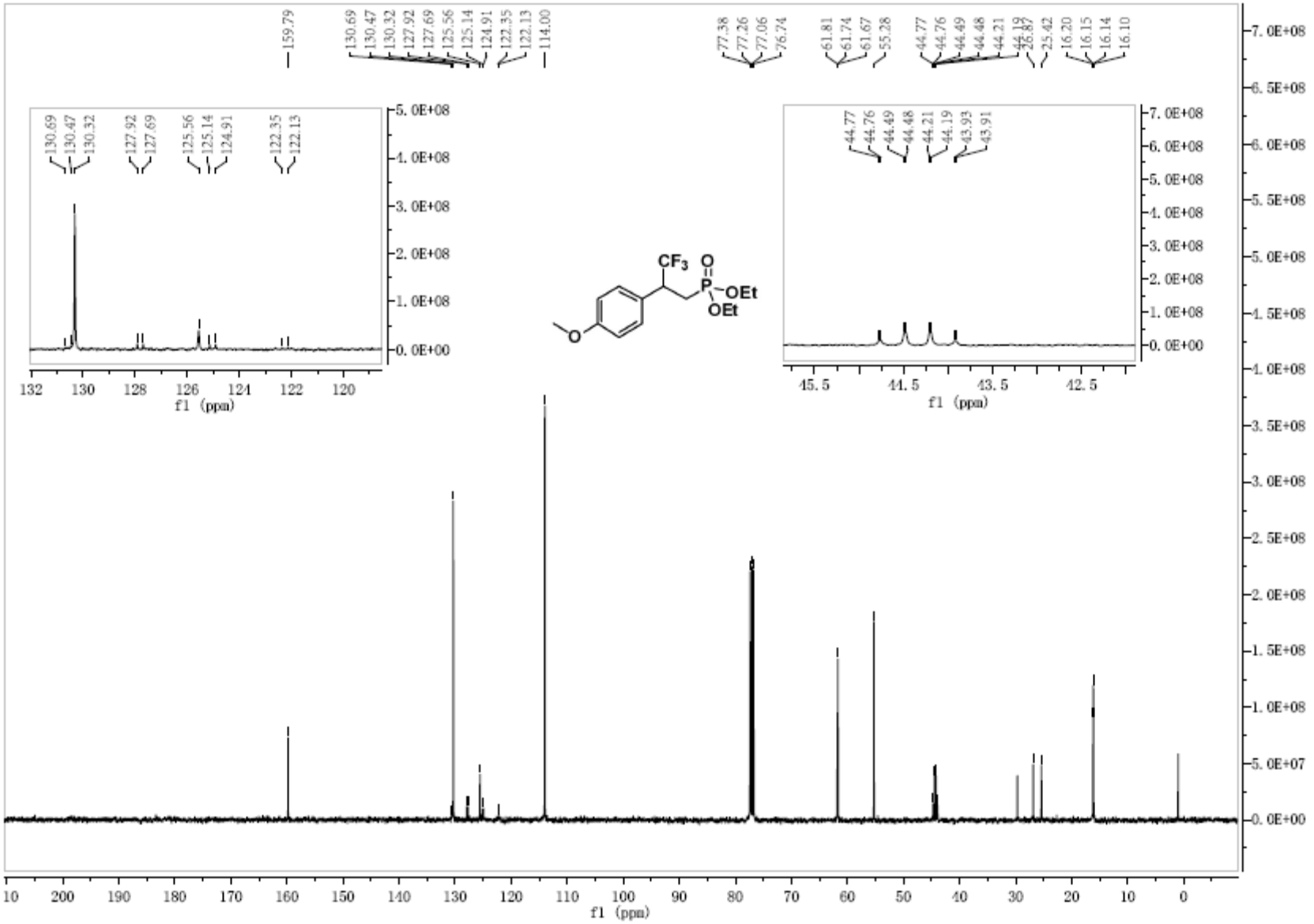
HRMS (EI) spectrum of 3sa



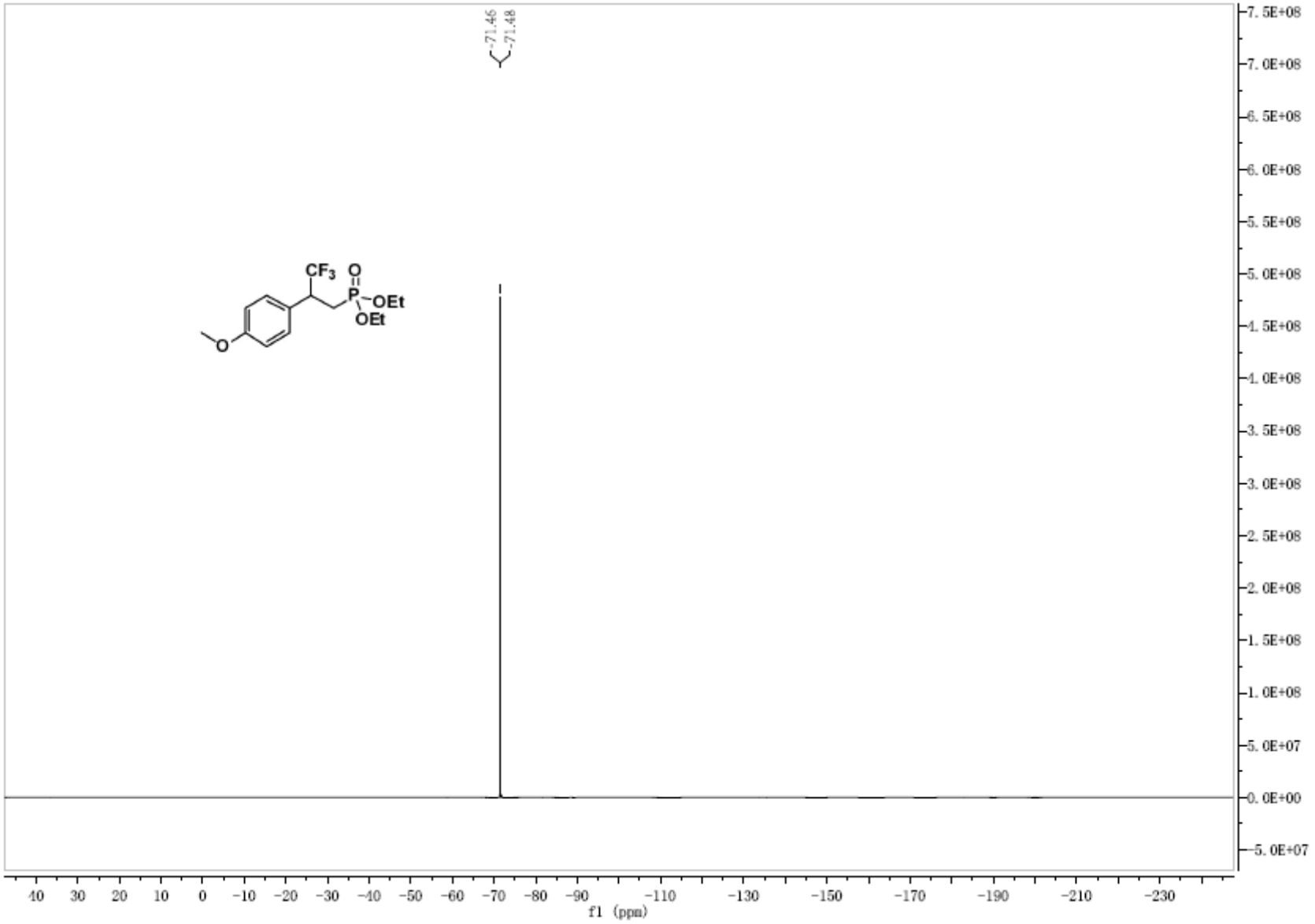
^{1}H NMR spectrum of 3ta



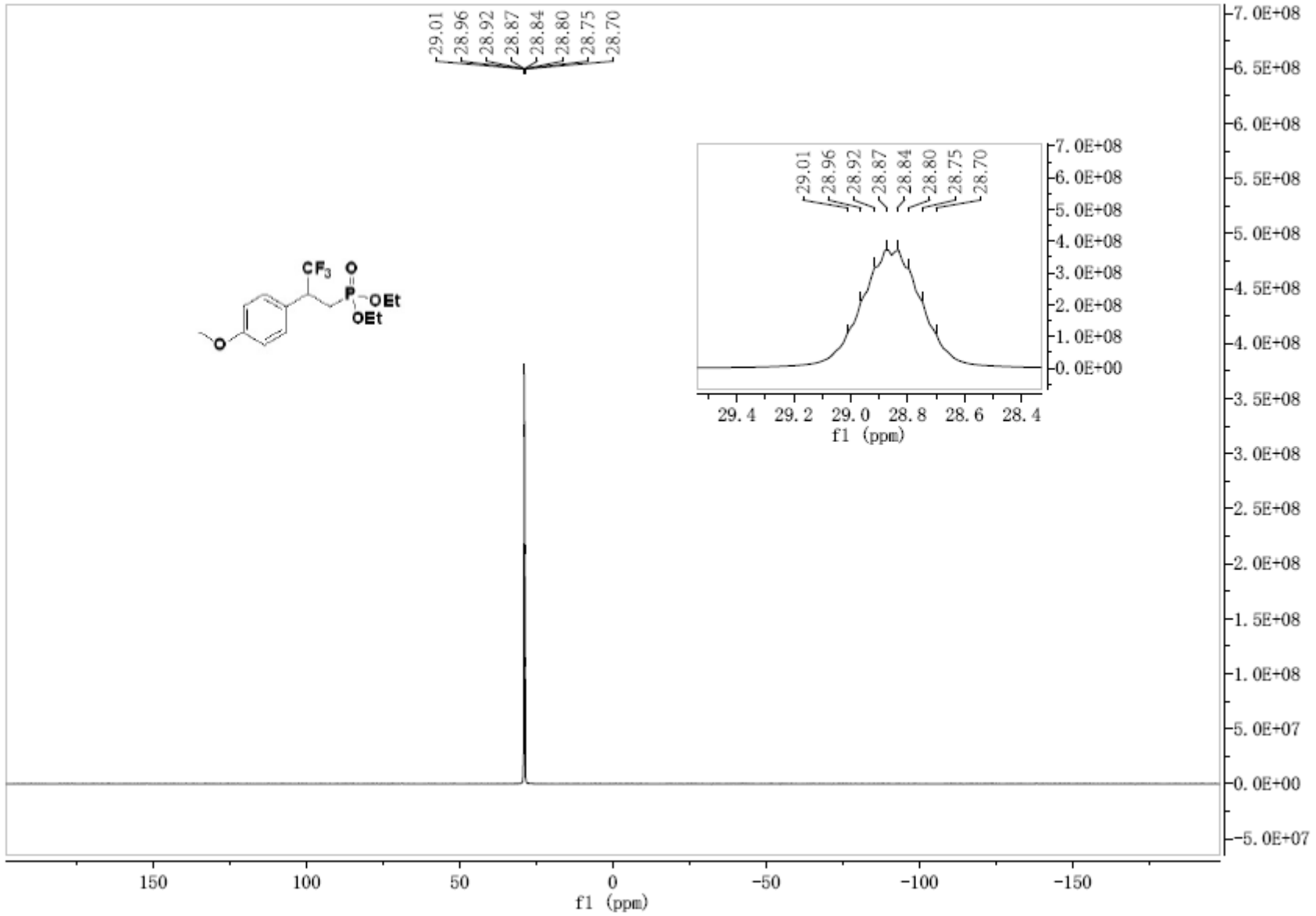
^{13}C NMR spectrum of 3ta



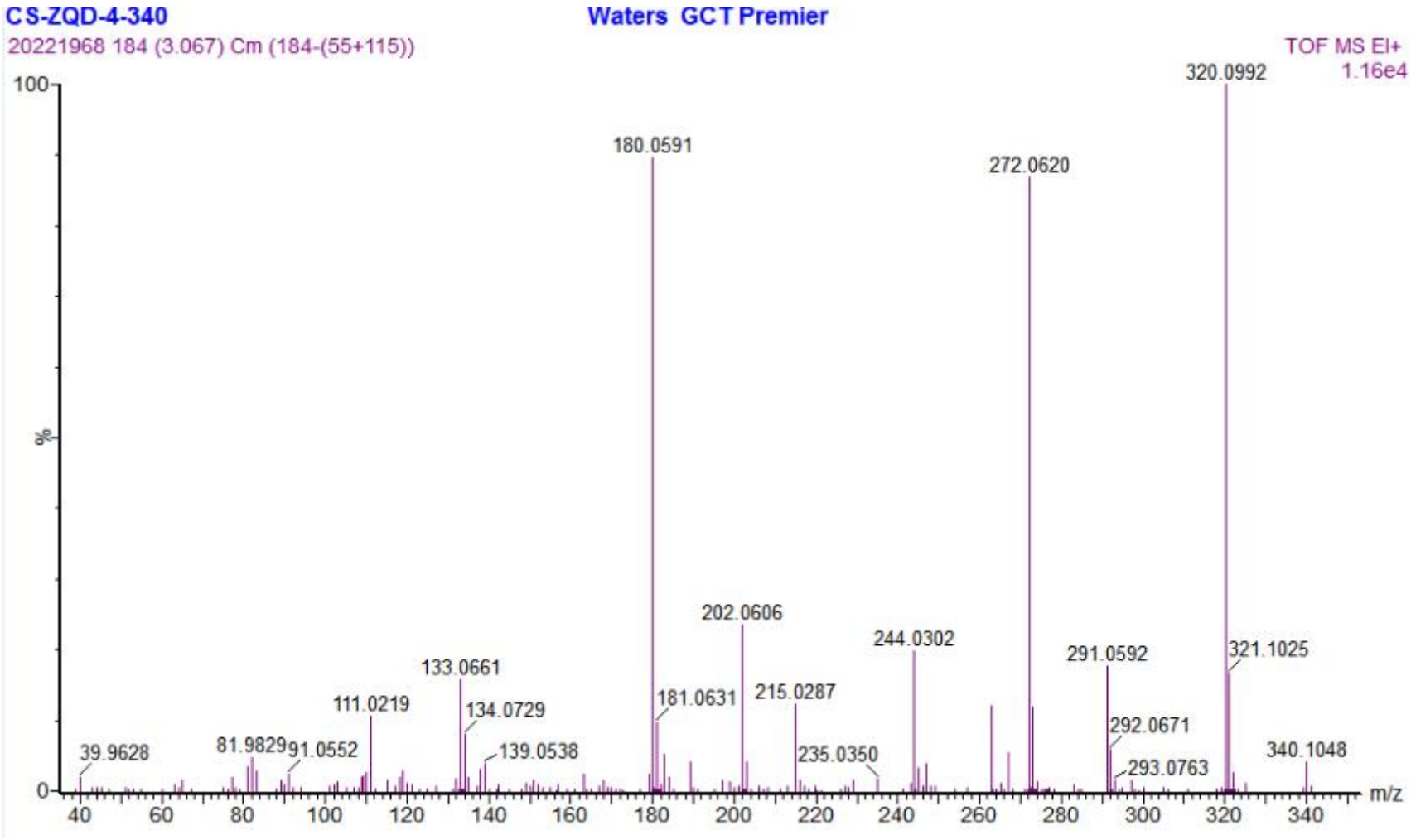
^{19}F NMR spectrum of 3ta



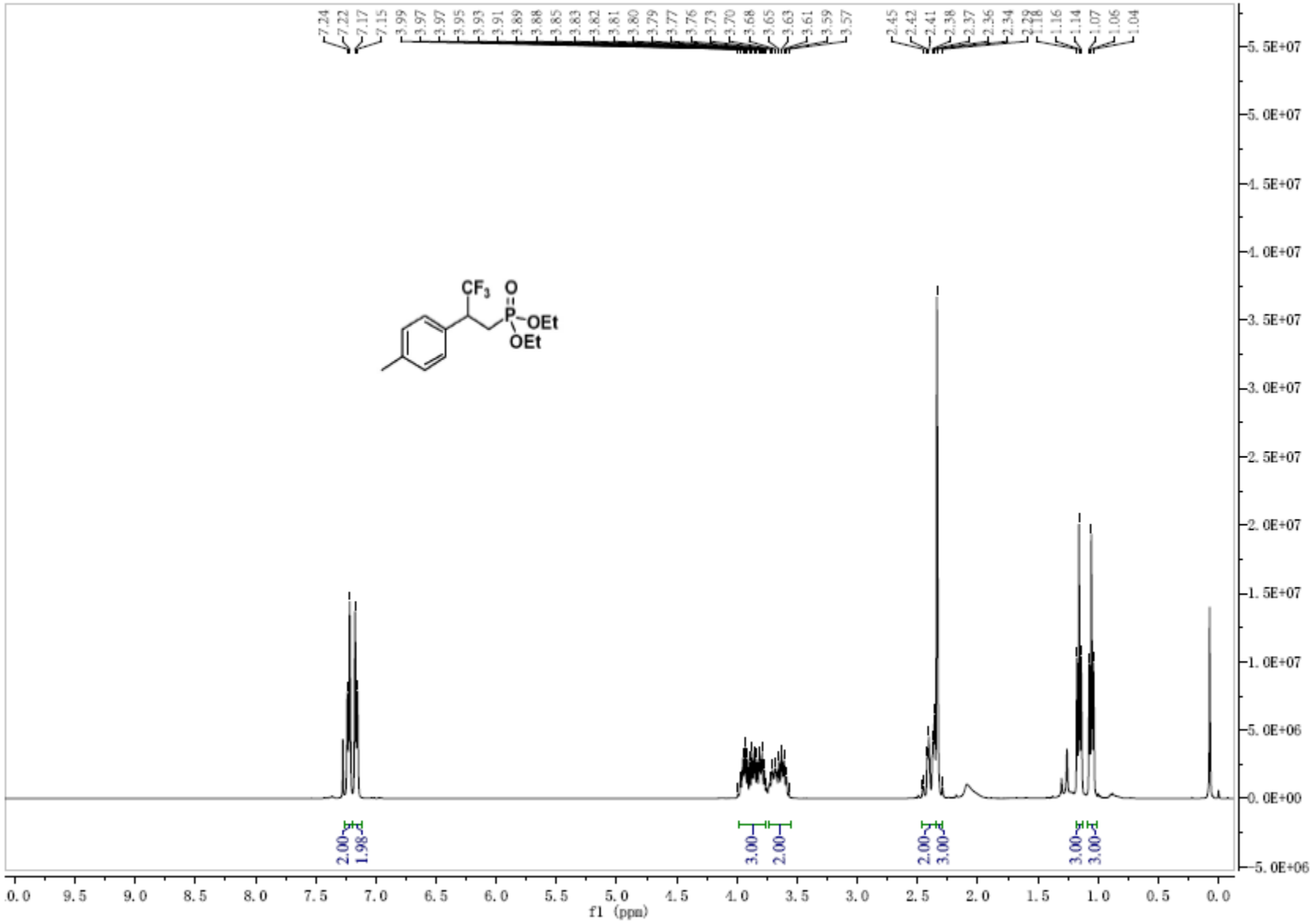
^{31}P NMR spectrum of 3ta



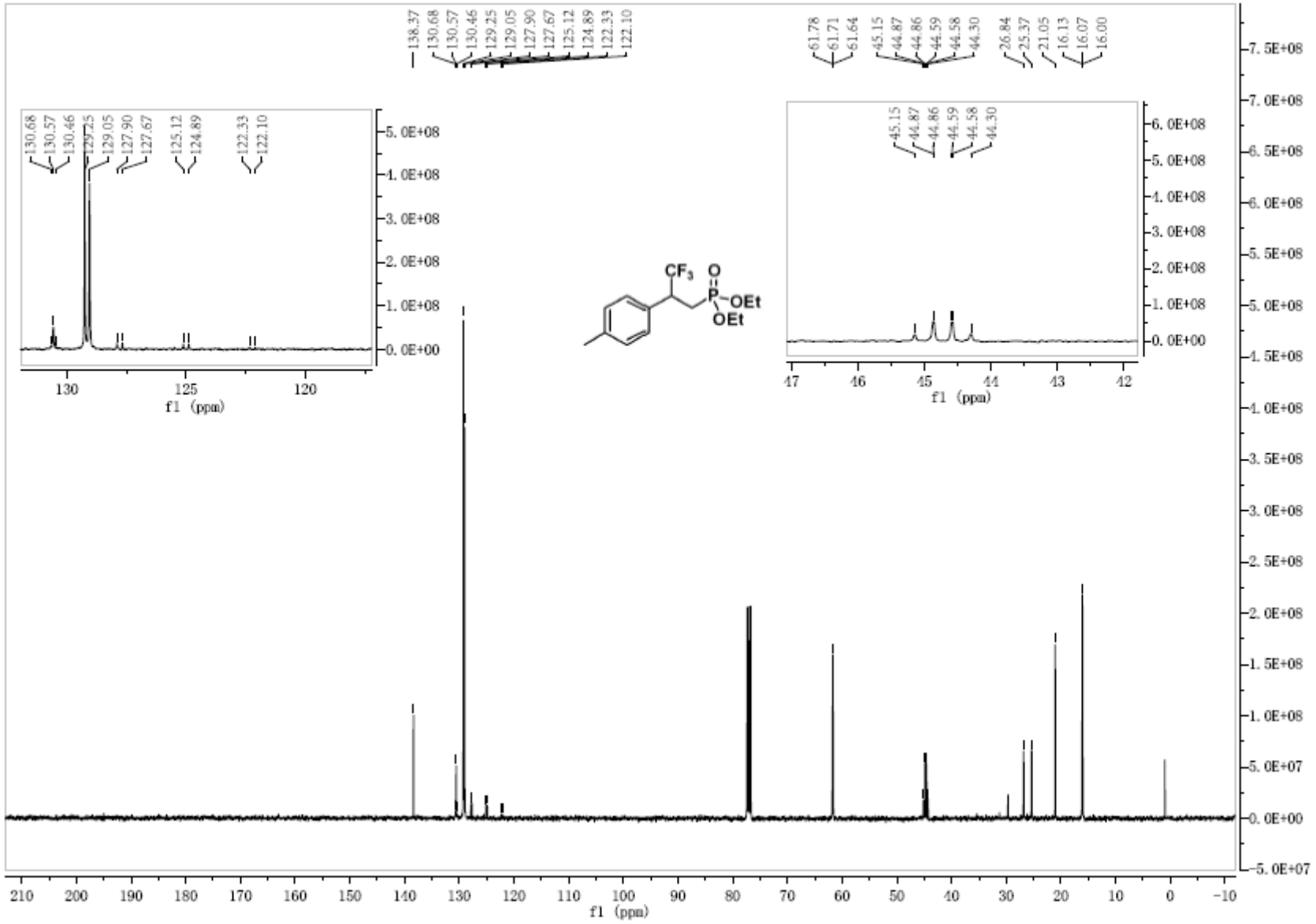
HRMS (EI) spectrum of 3ta



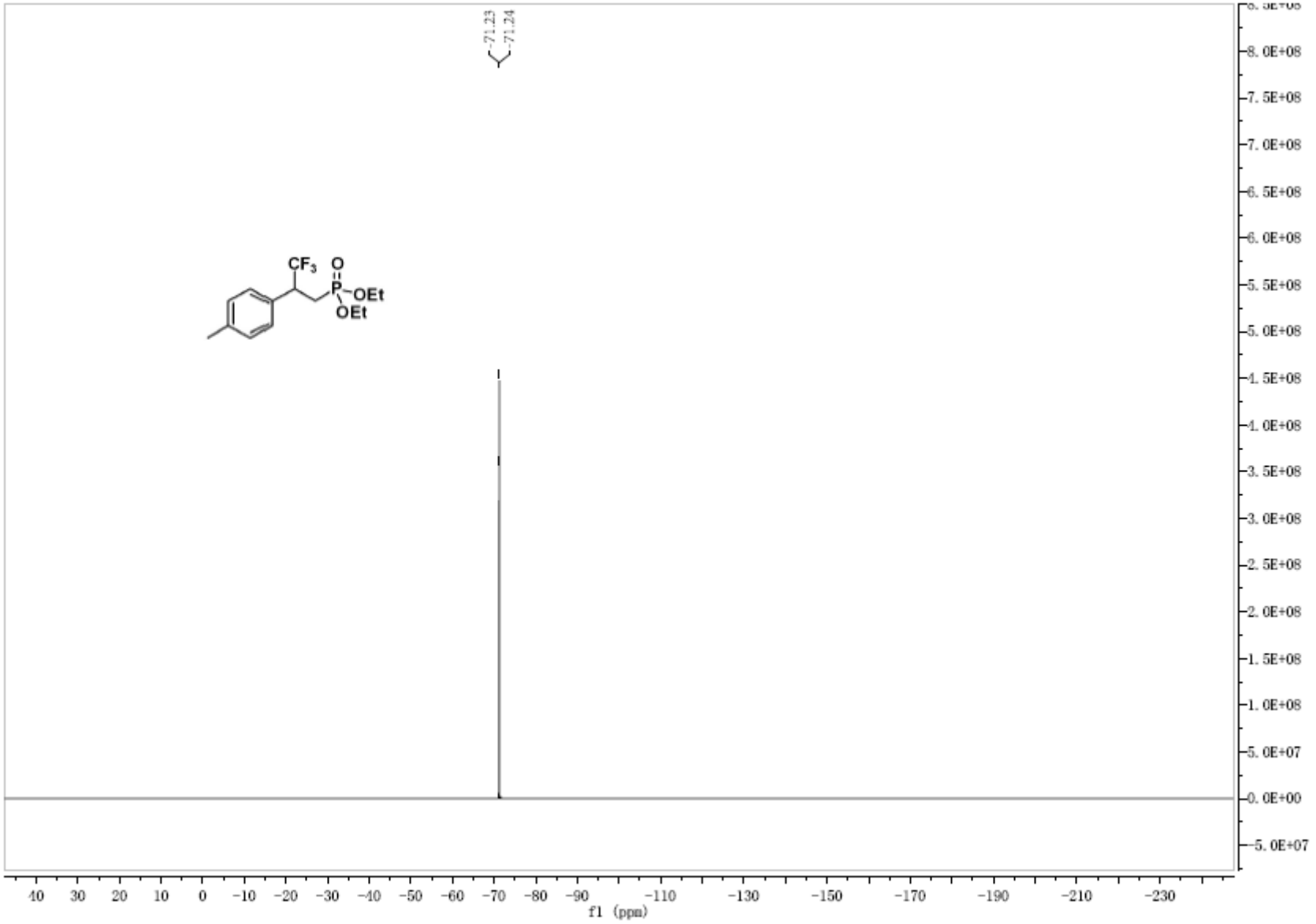
^{1}H NMR spectrum of 3ua



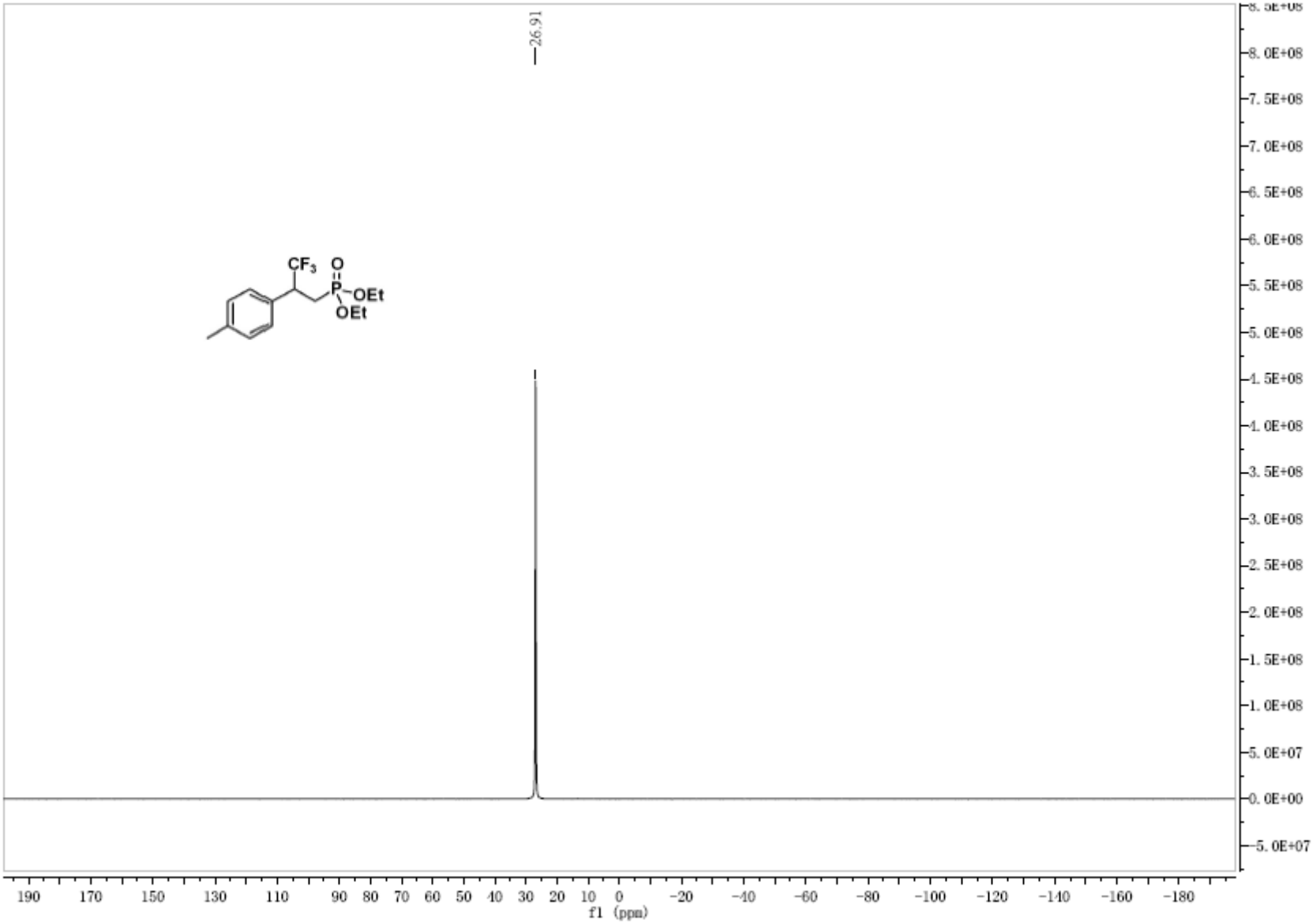
^{13}C NMR spectrum of 3ua



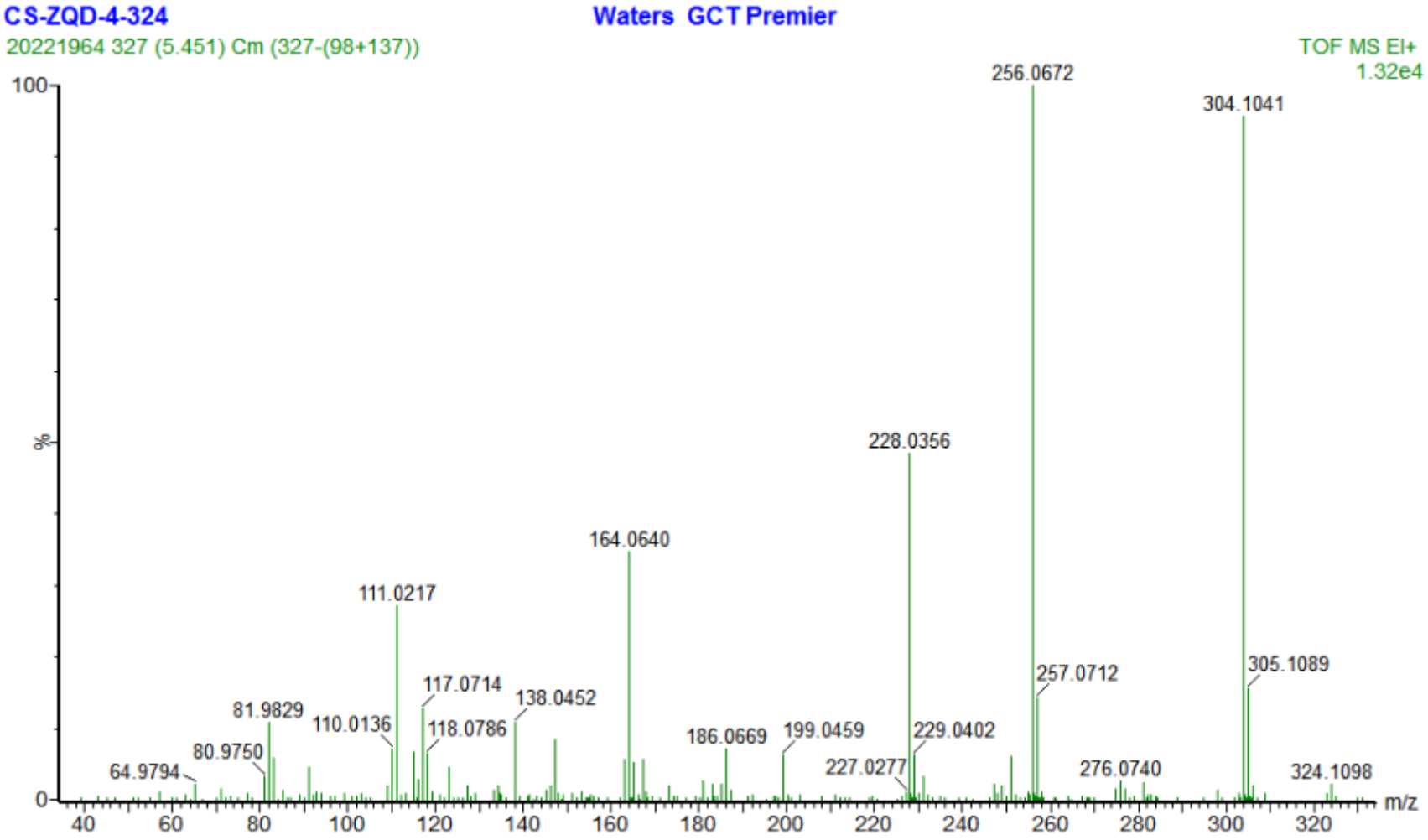
^{19}F NMR spectrum of 3ua



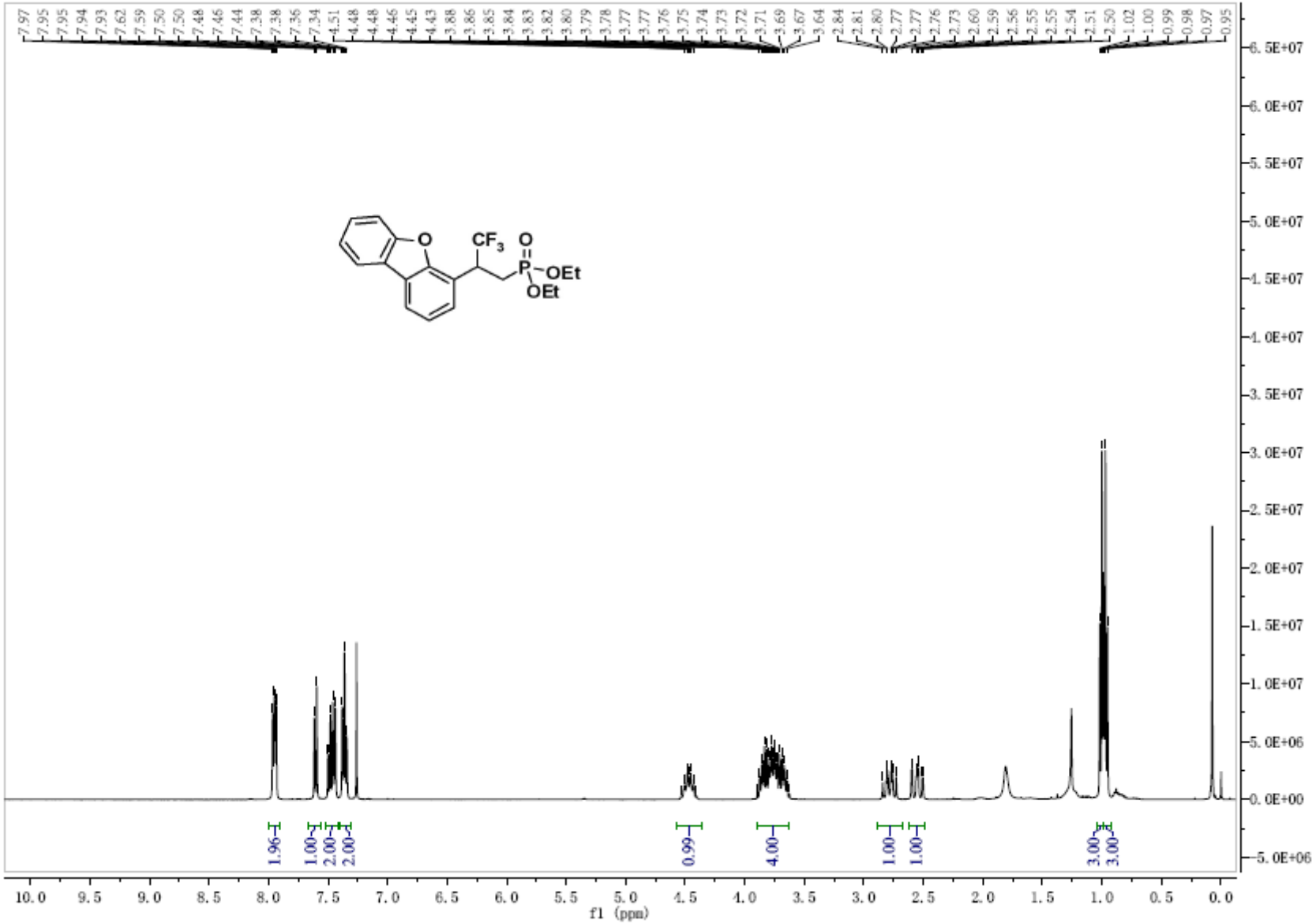
^{31}P NMR spectrum of 3ua



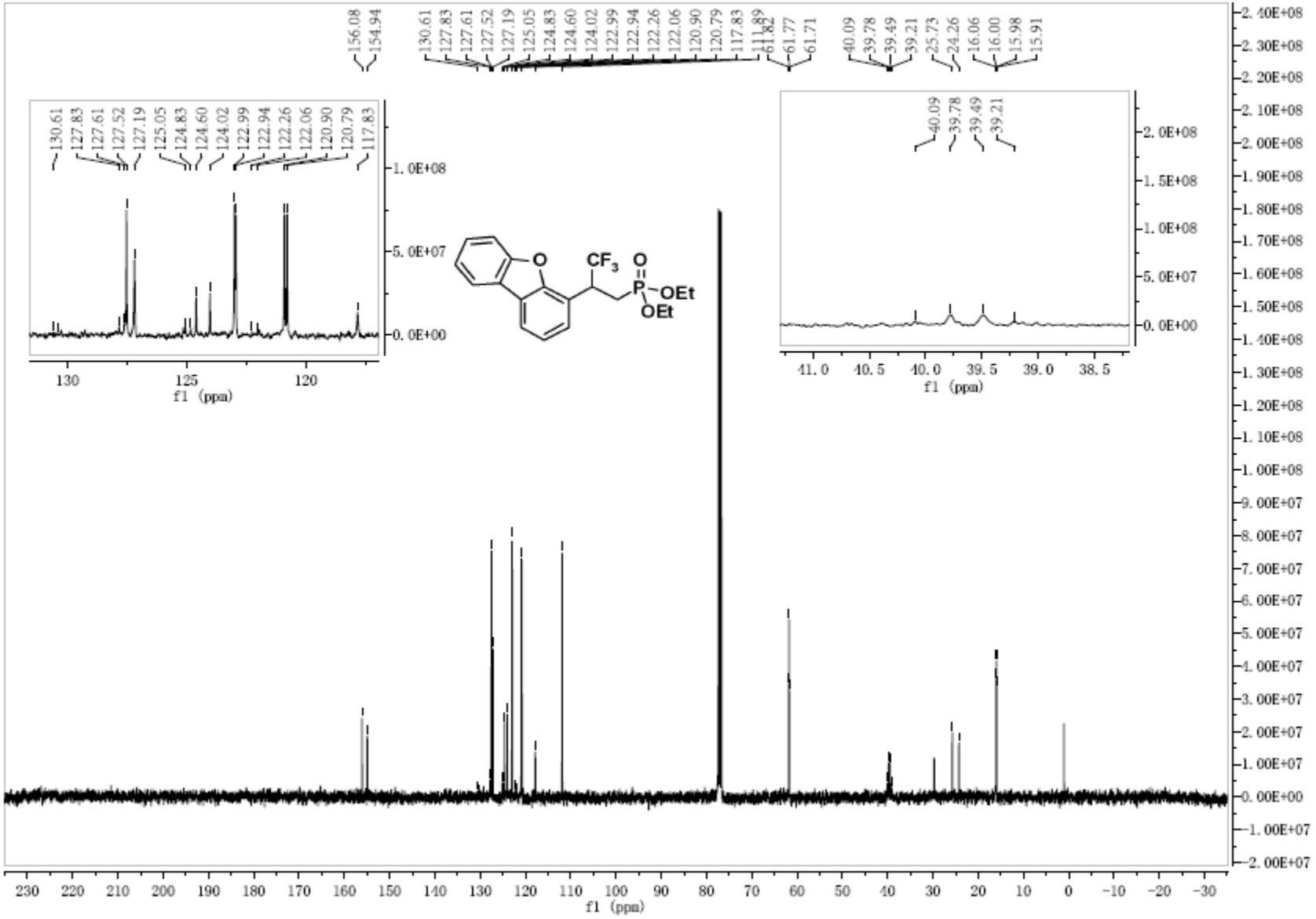
HRMS (EI) spectrum of 3ua



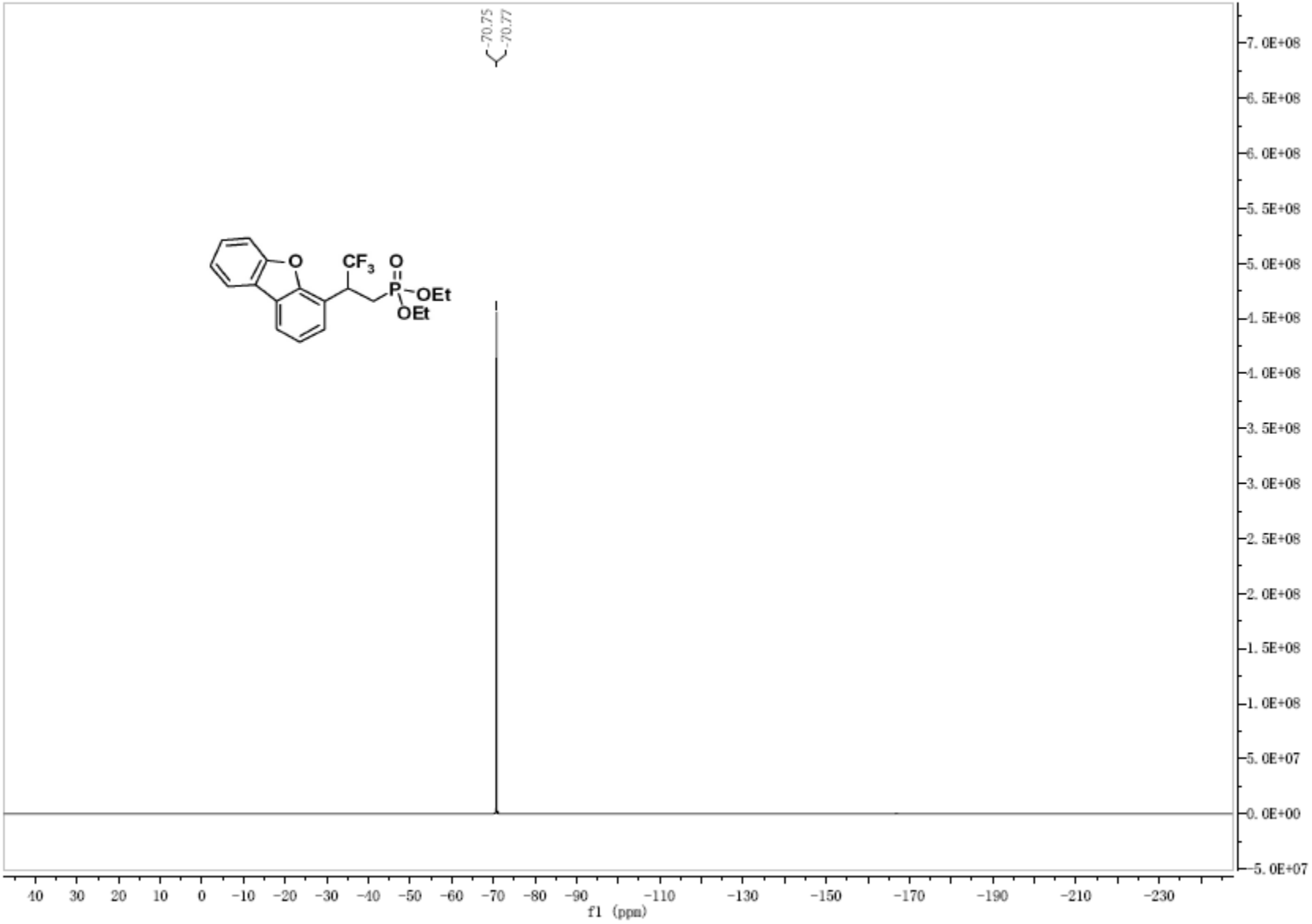
^{1}H NMR spectrum of 3va



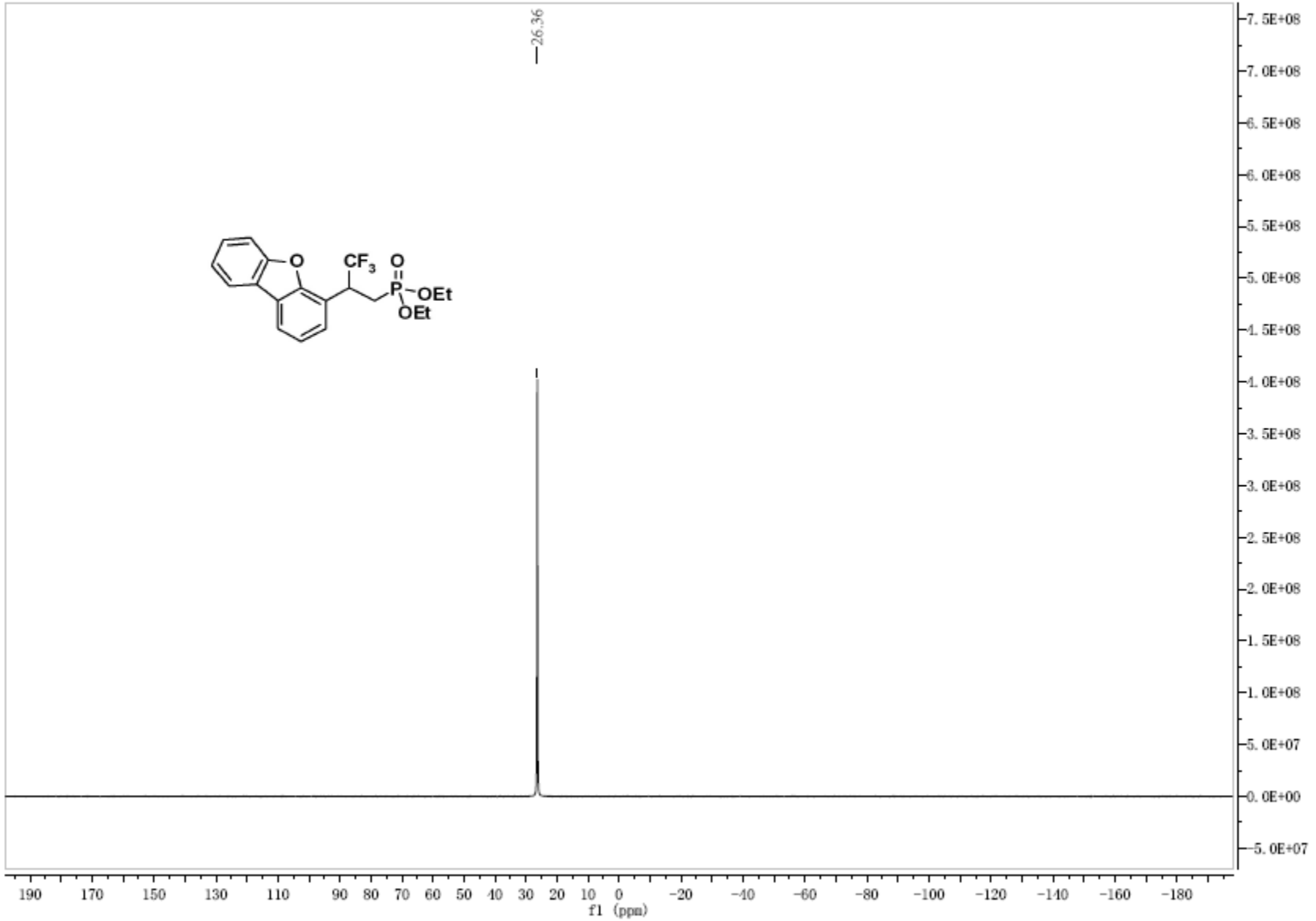
^{13}C NMR spectrum of 3va



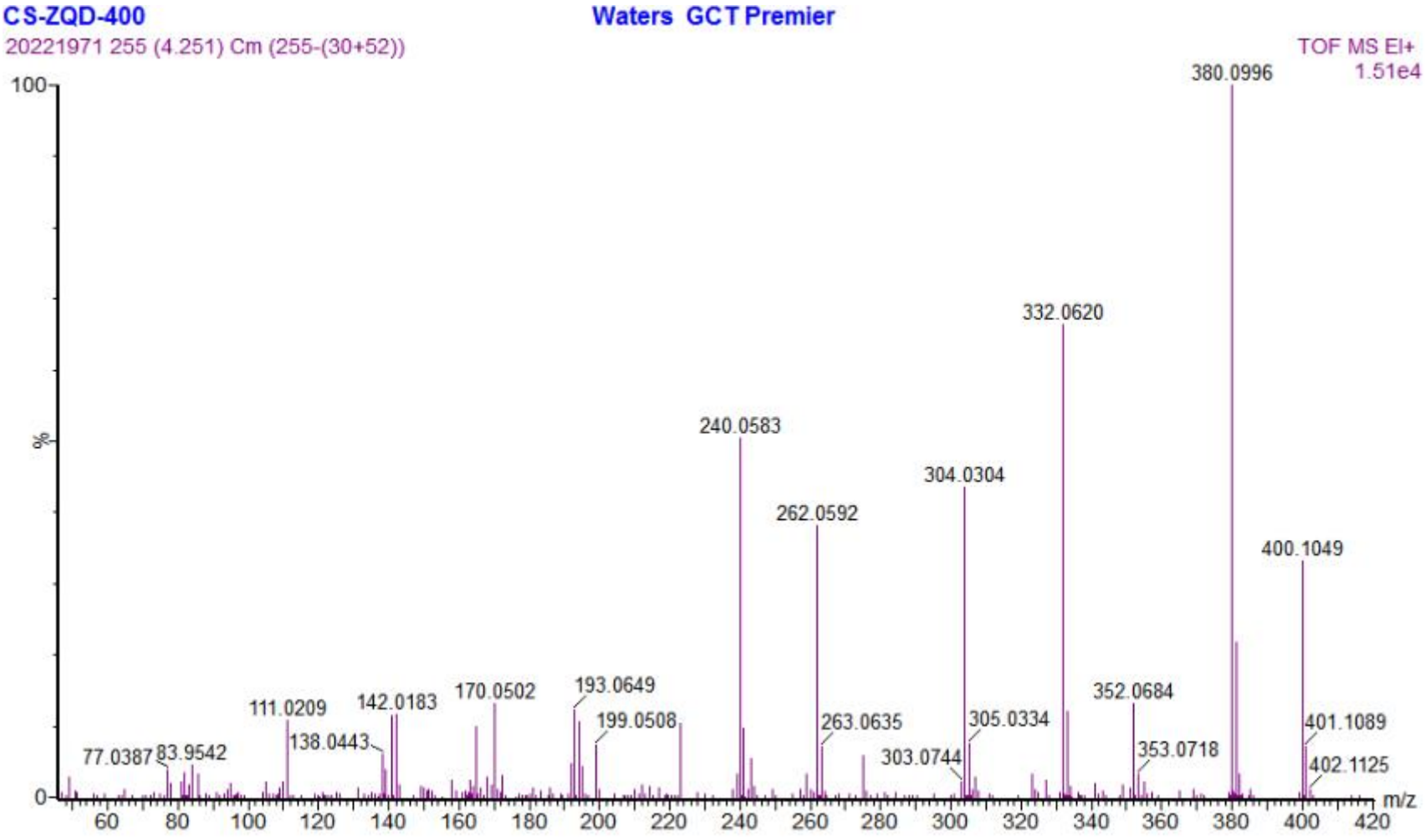
^{19}F NMR spectrum of 3va



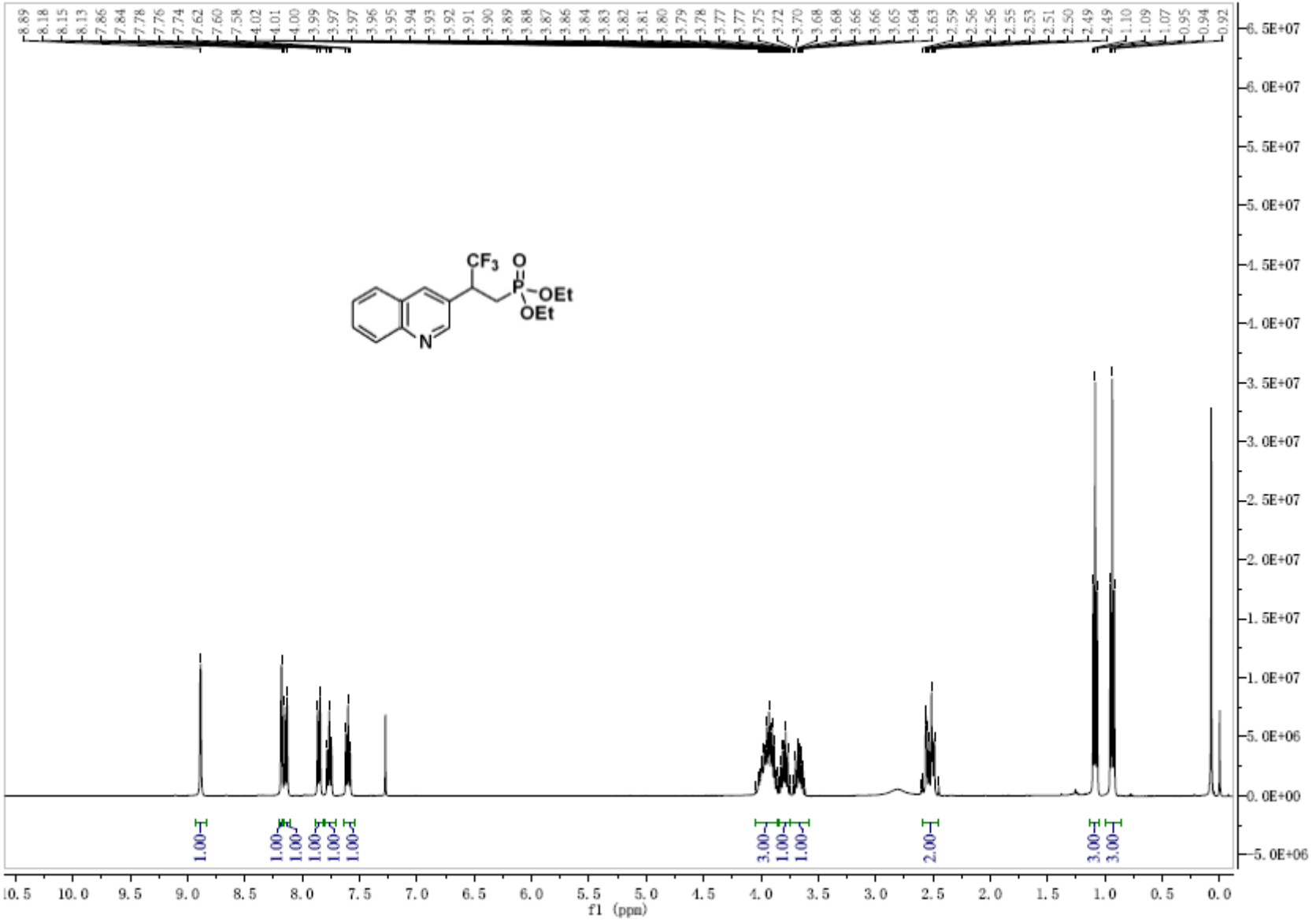
^{31}P NMR spectrum of 3va



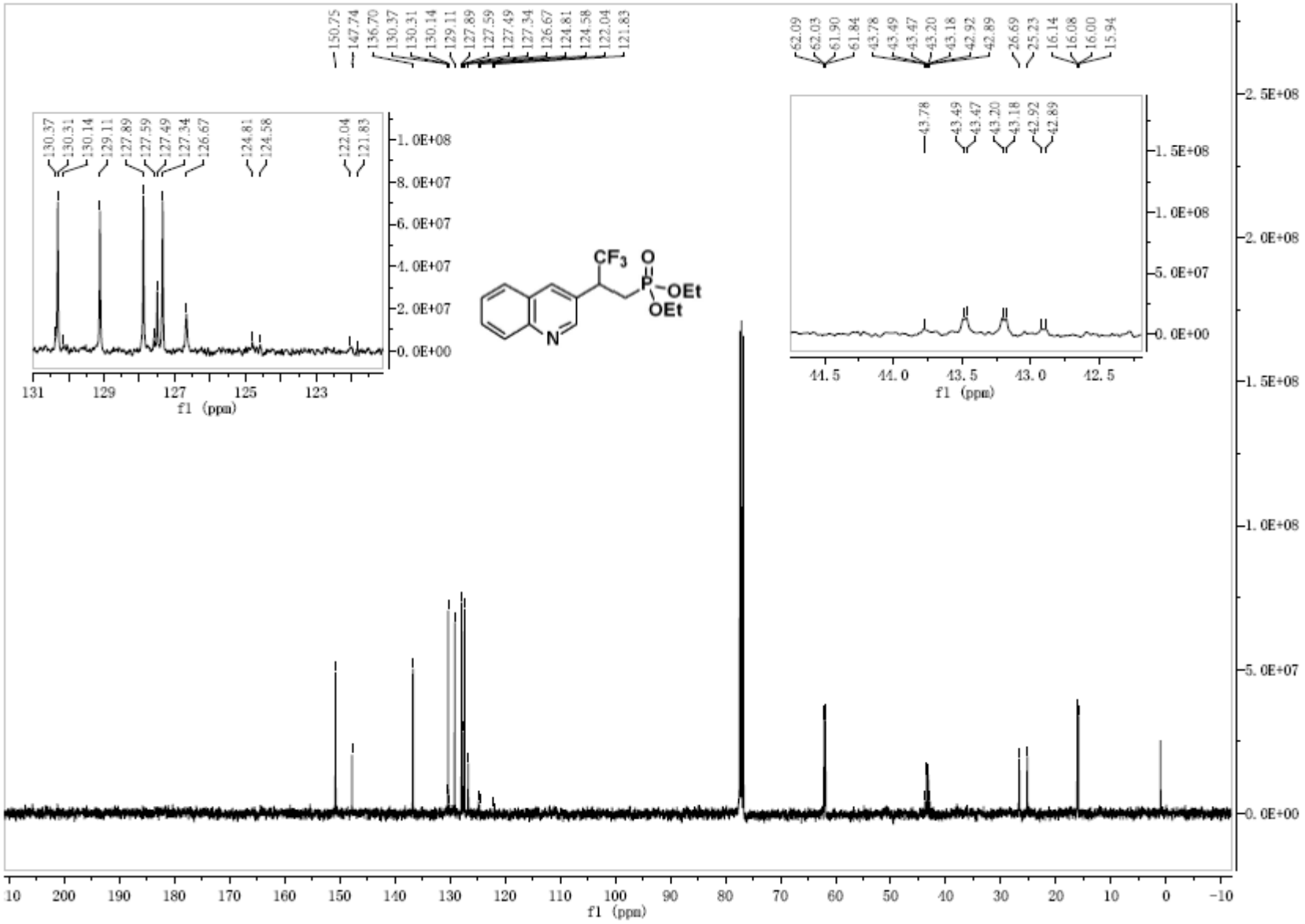
HRMS (EI) spectrum of 3va



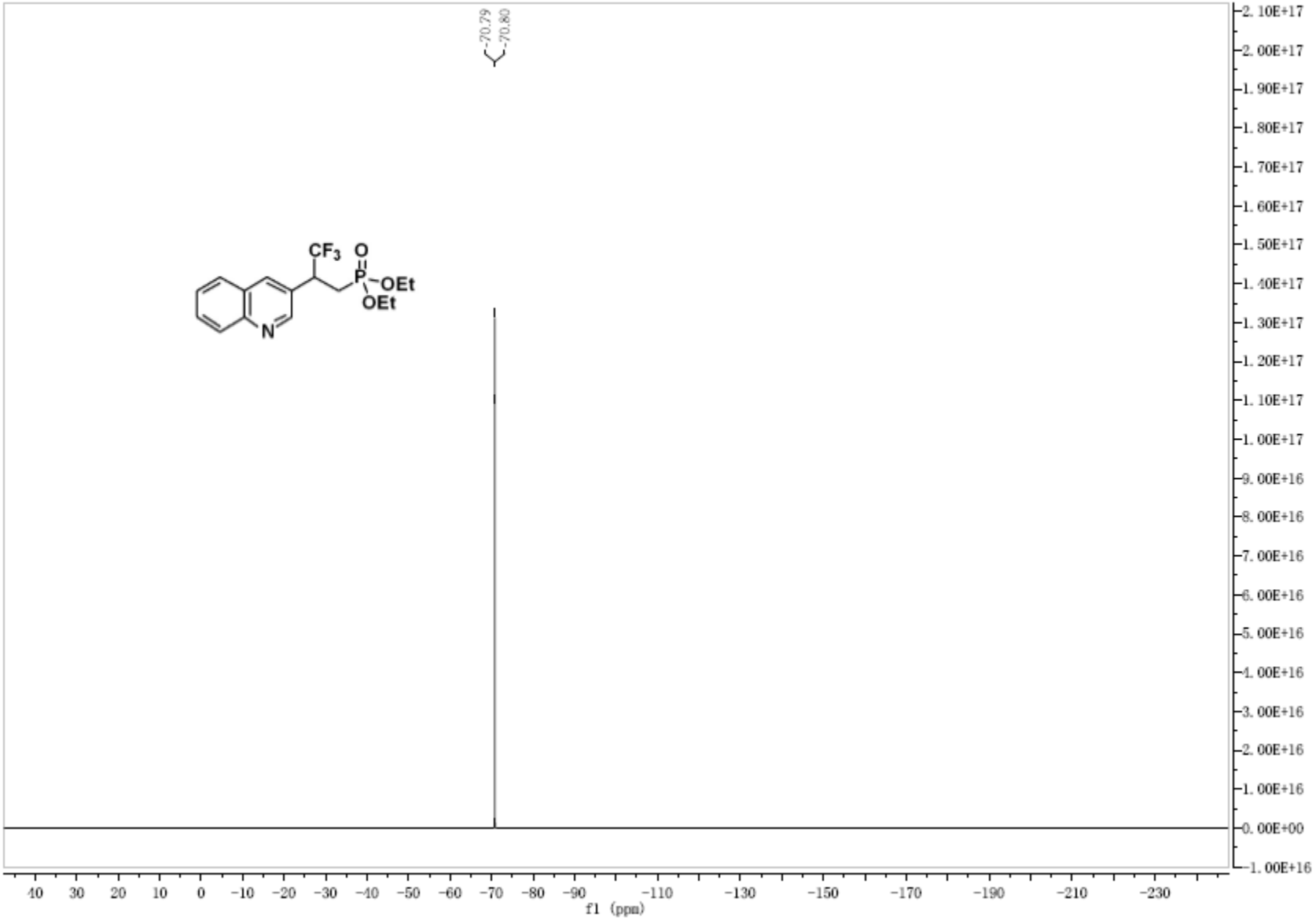
^{1}H NMR spectrum of 3wa



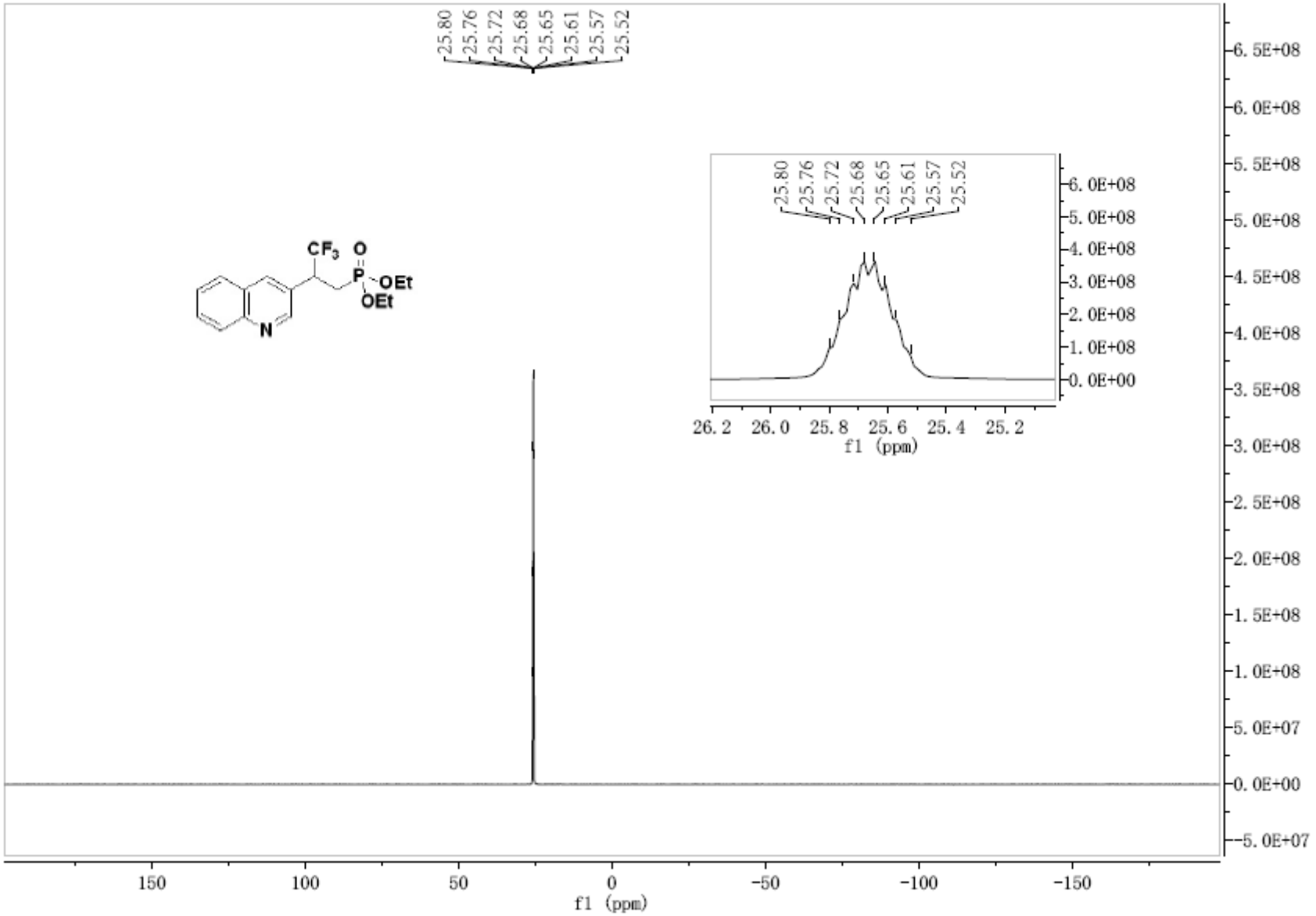
^{13}C NMR spectrum of 3wa



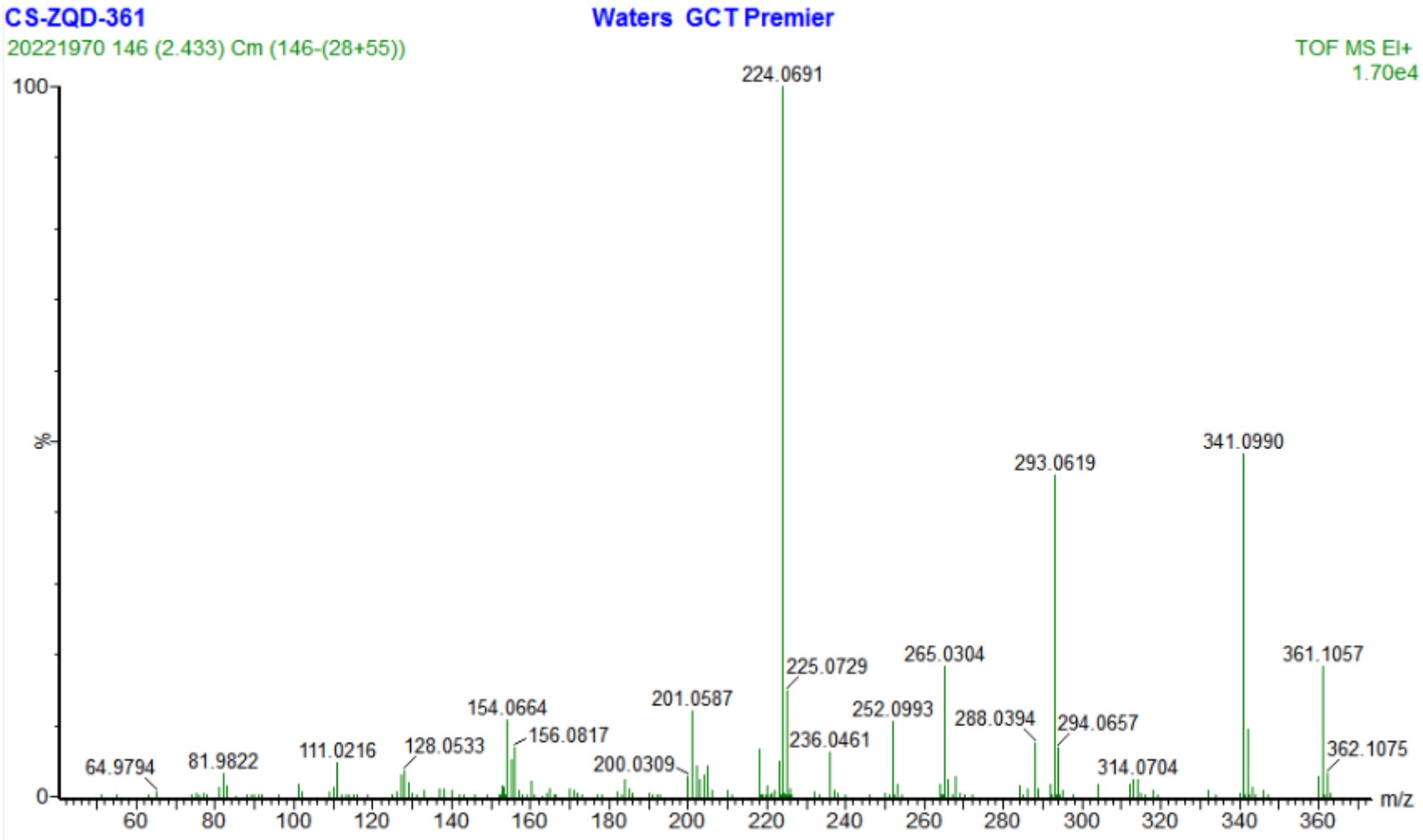
^{19}F NMR spectrum of 3wa



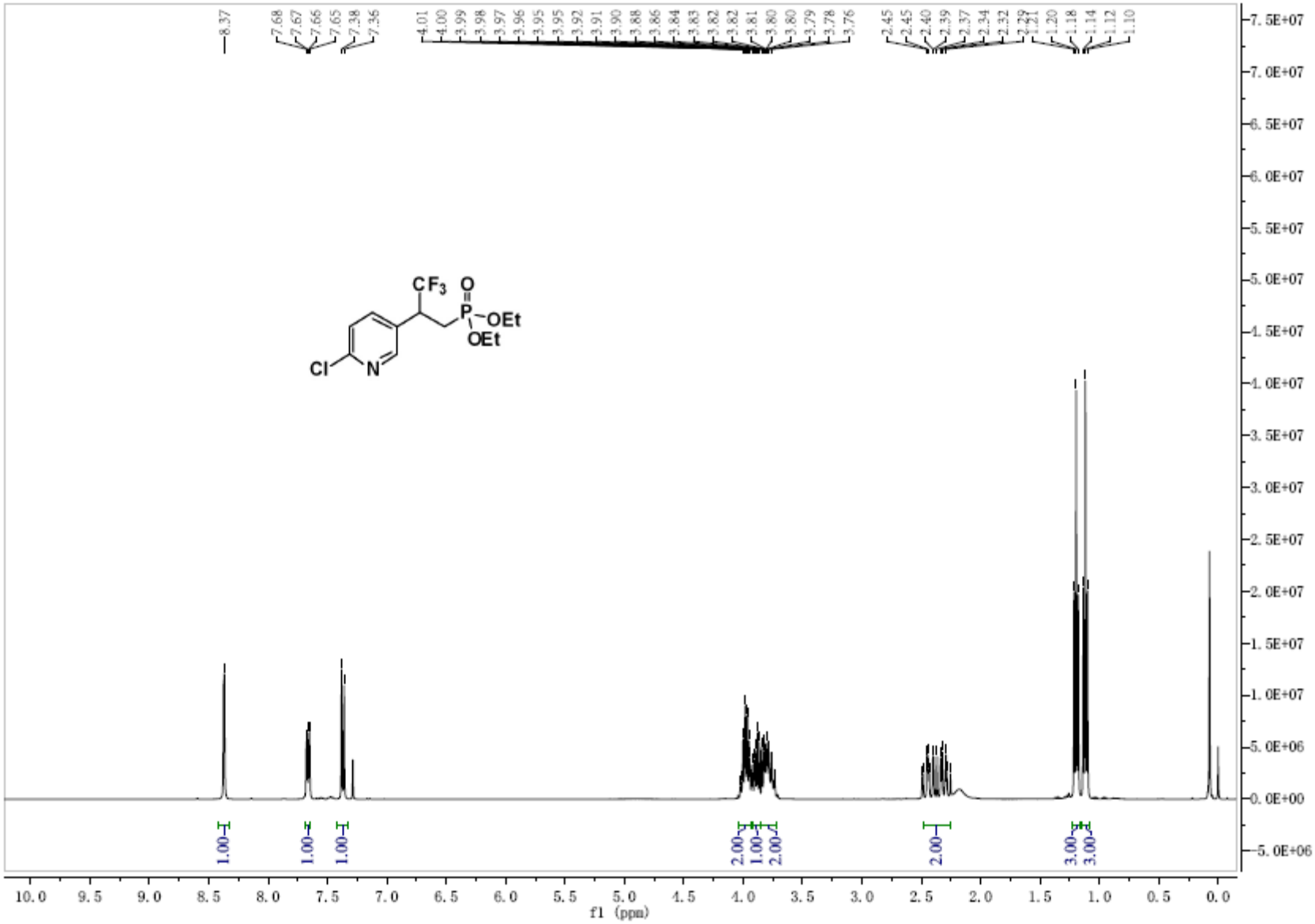
^{31}P NMR spectrum of 3wa



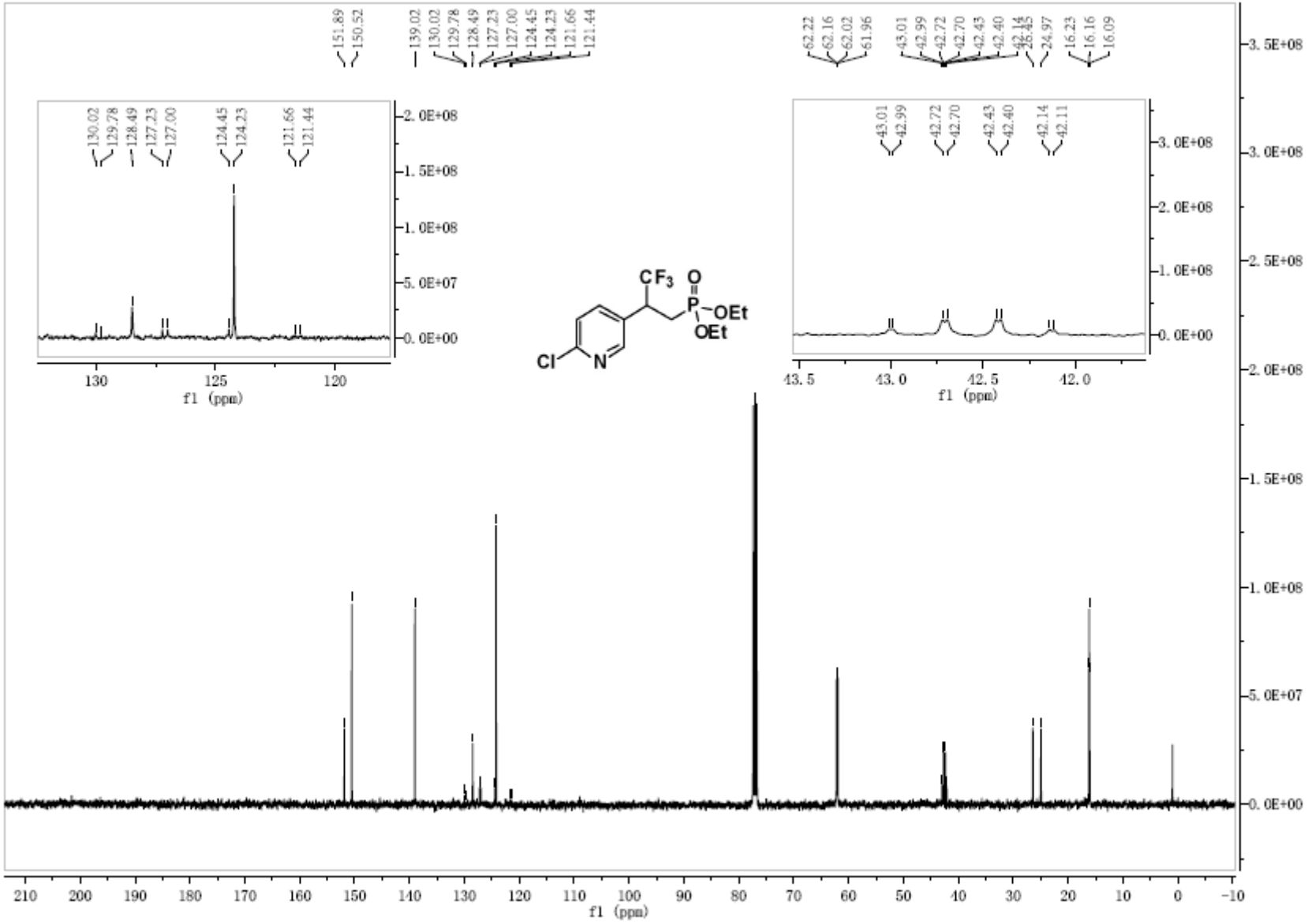
HRMS (EI) spectrum of 3wa



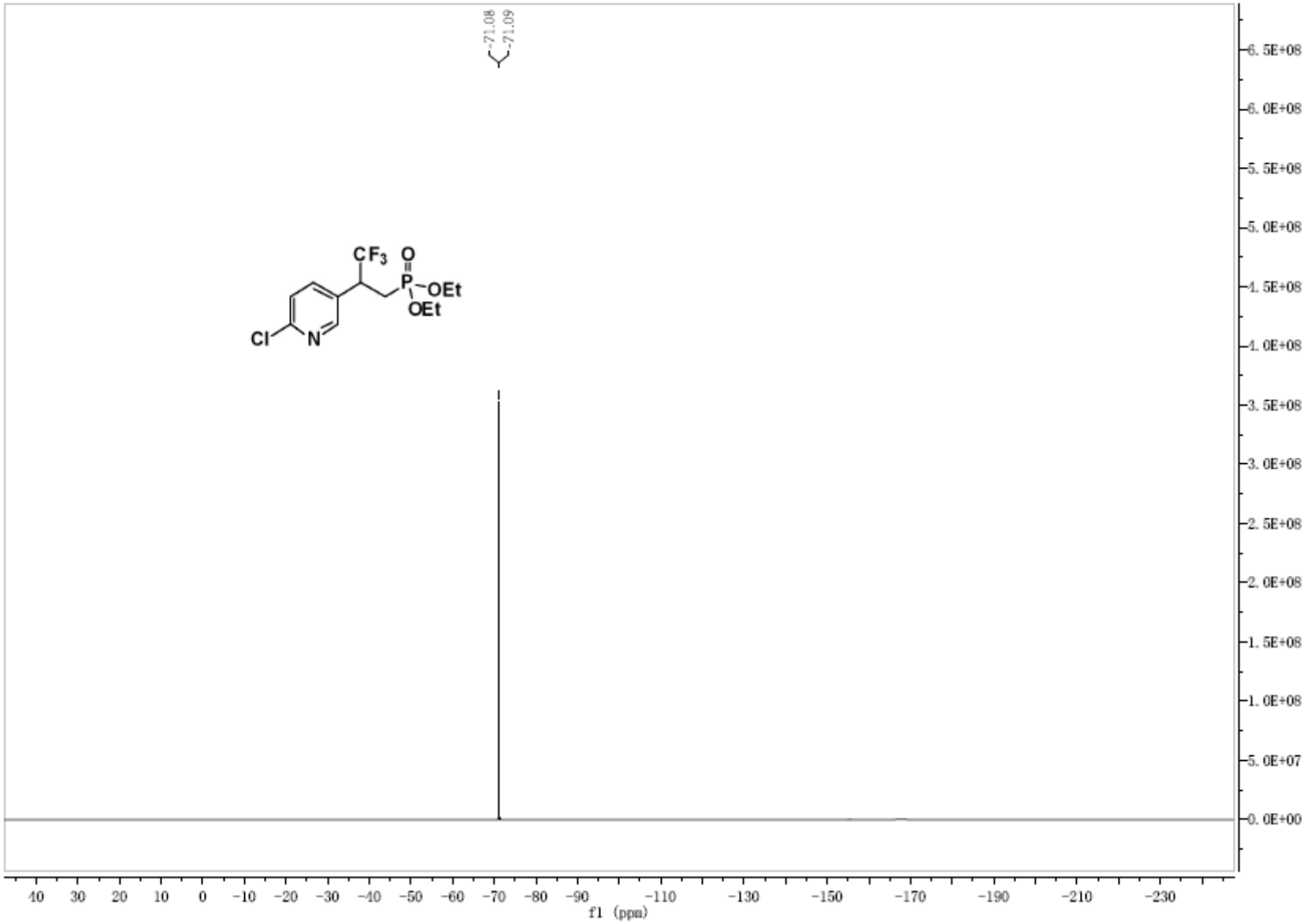
[1]H NMR spectrum of 3xa



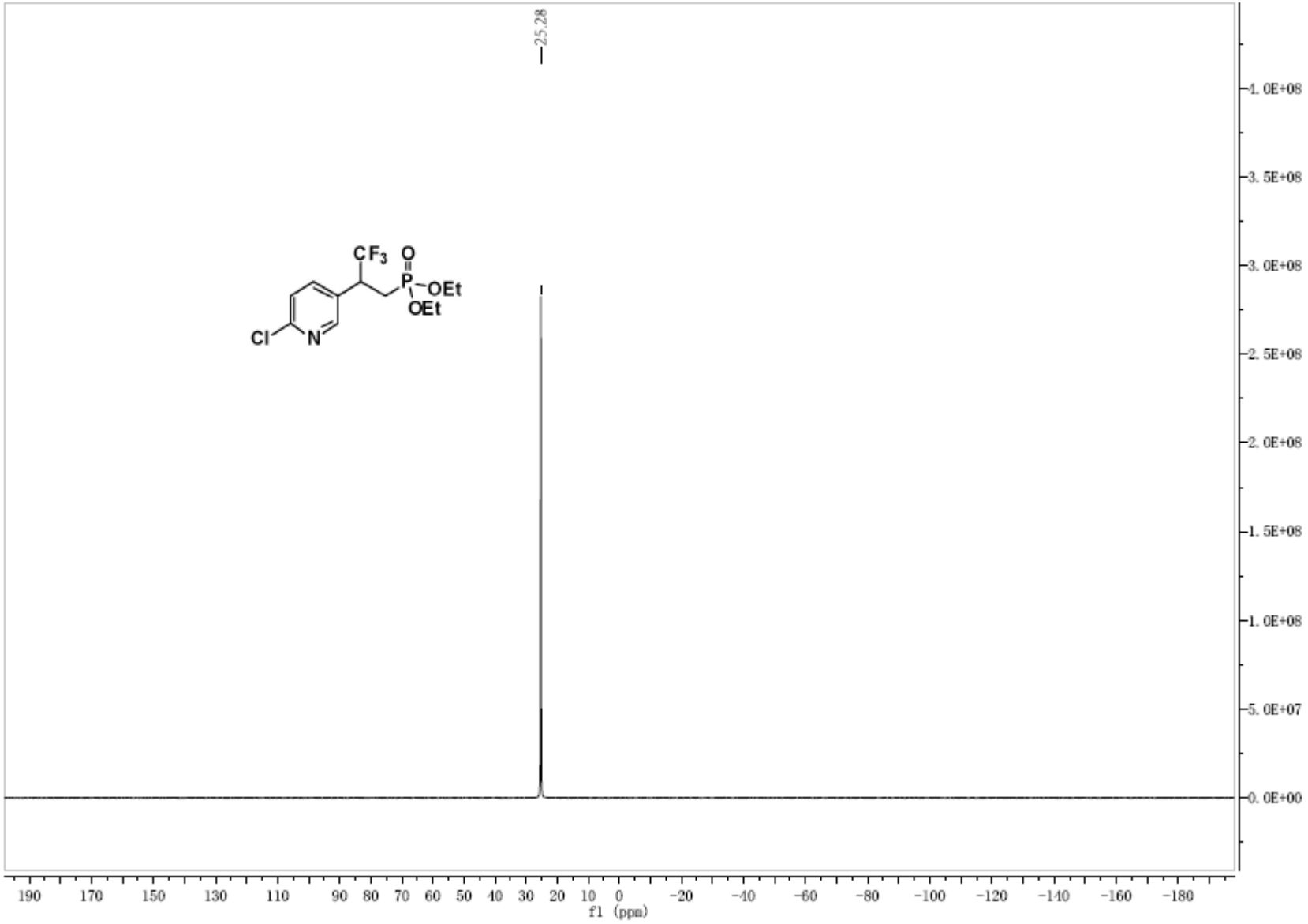
^{13}C NMR spectrum of 3xa



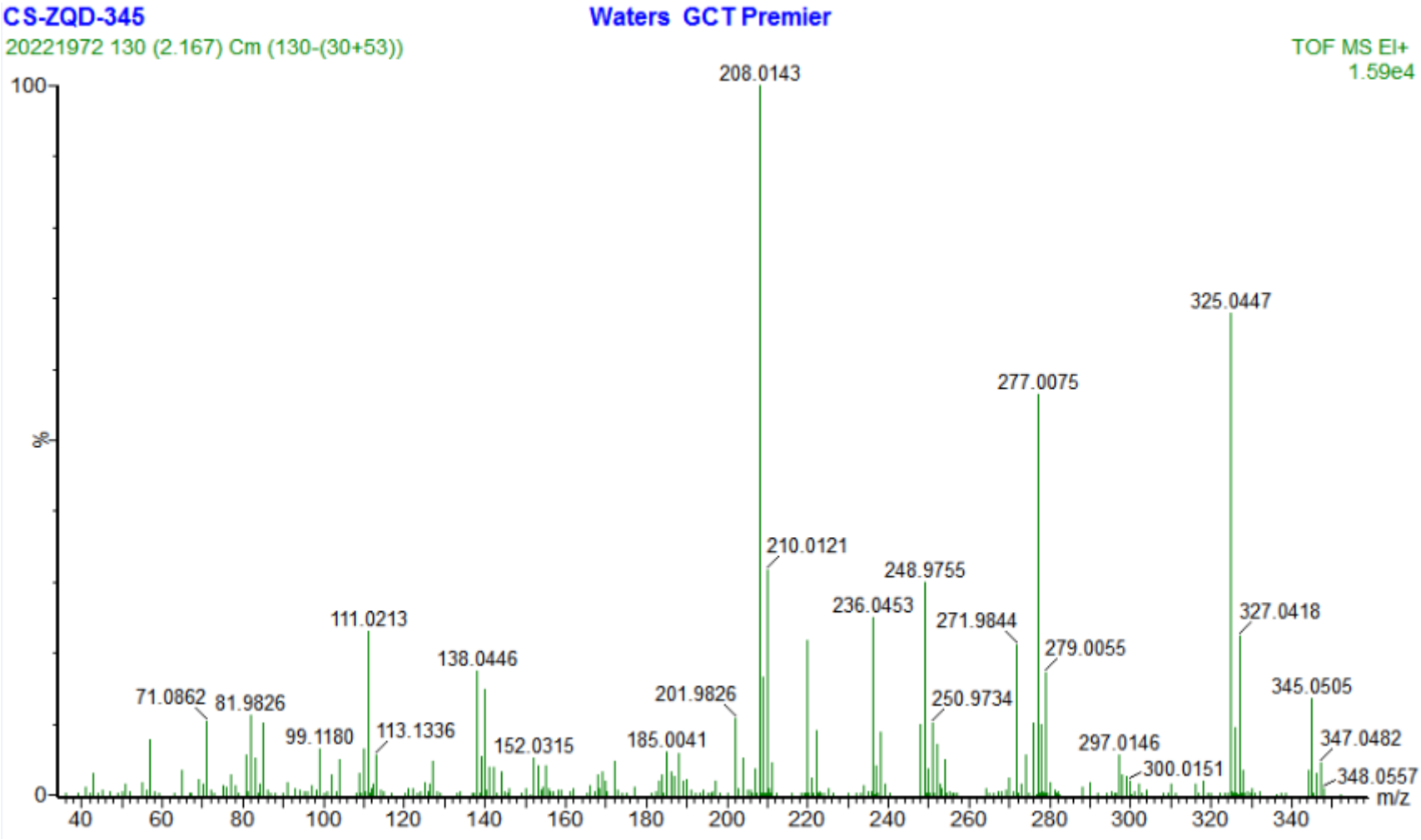
^{19}F NMR spectrum of 3xa



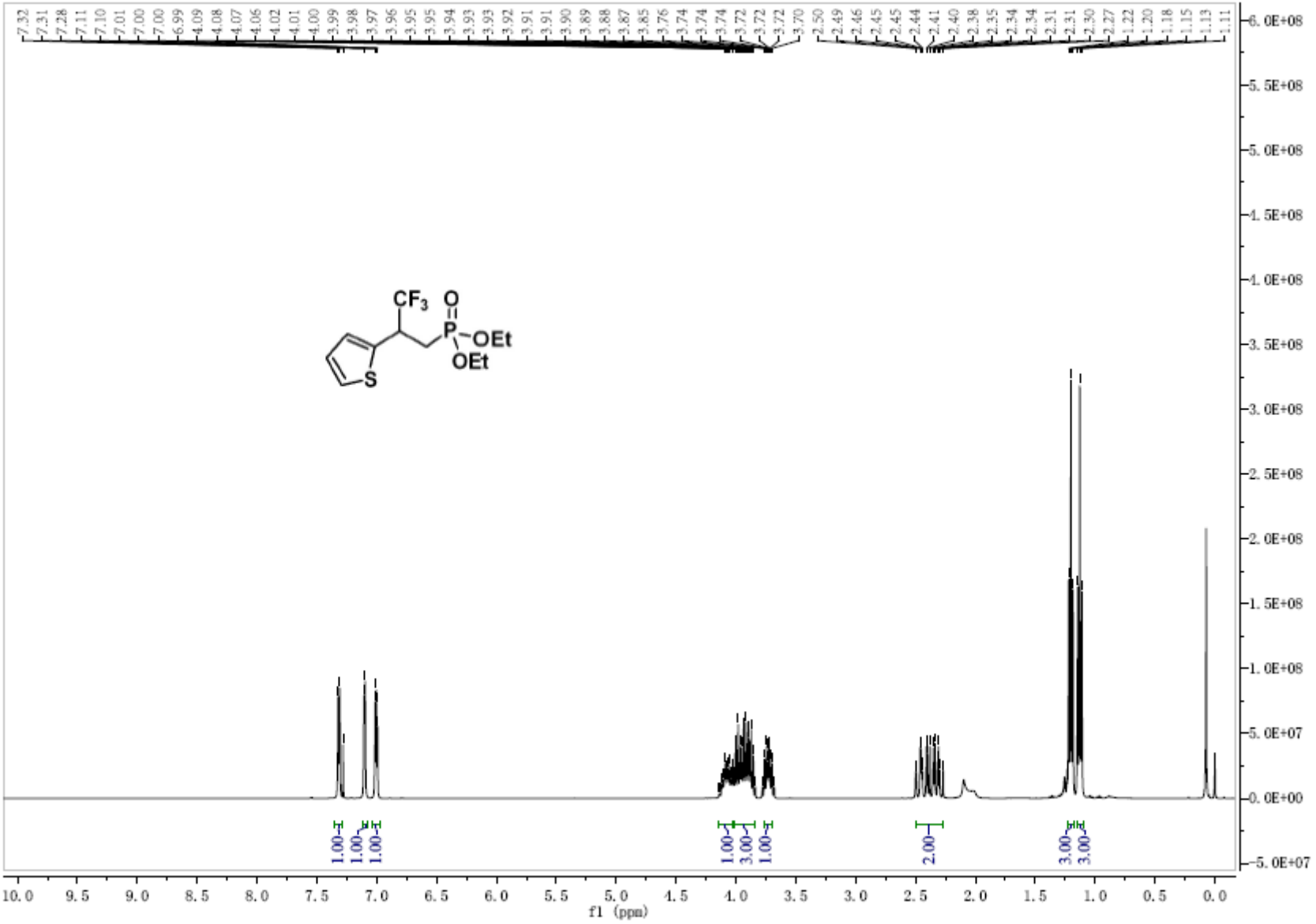
^{31}P NMR spectrum of 3xa



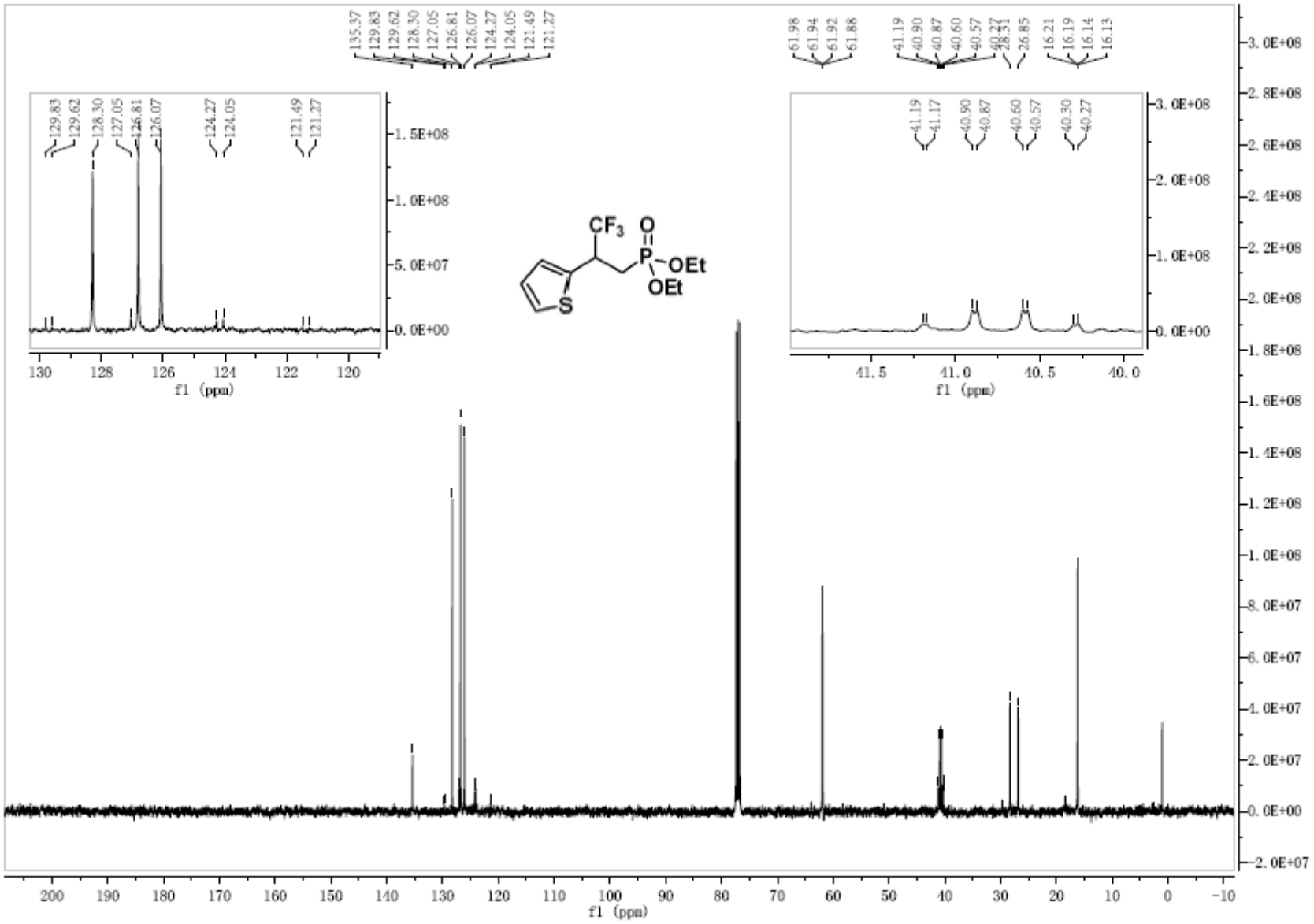
HRMS (EI) spectrum of 3xa



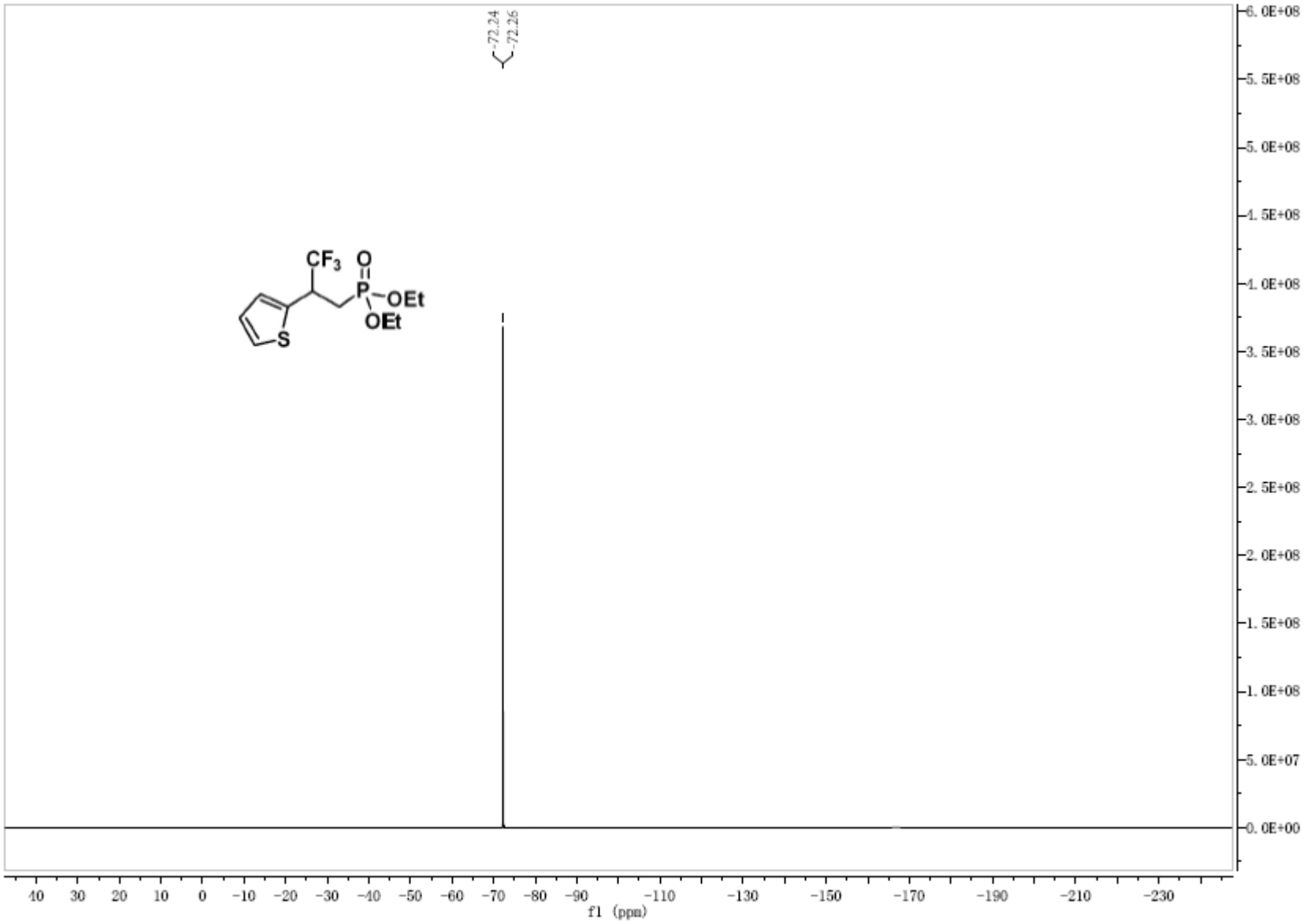
^{1}H NMR spectrum of 3ya



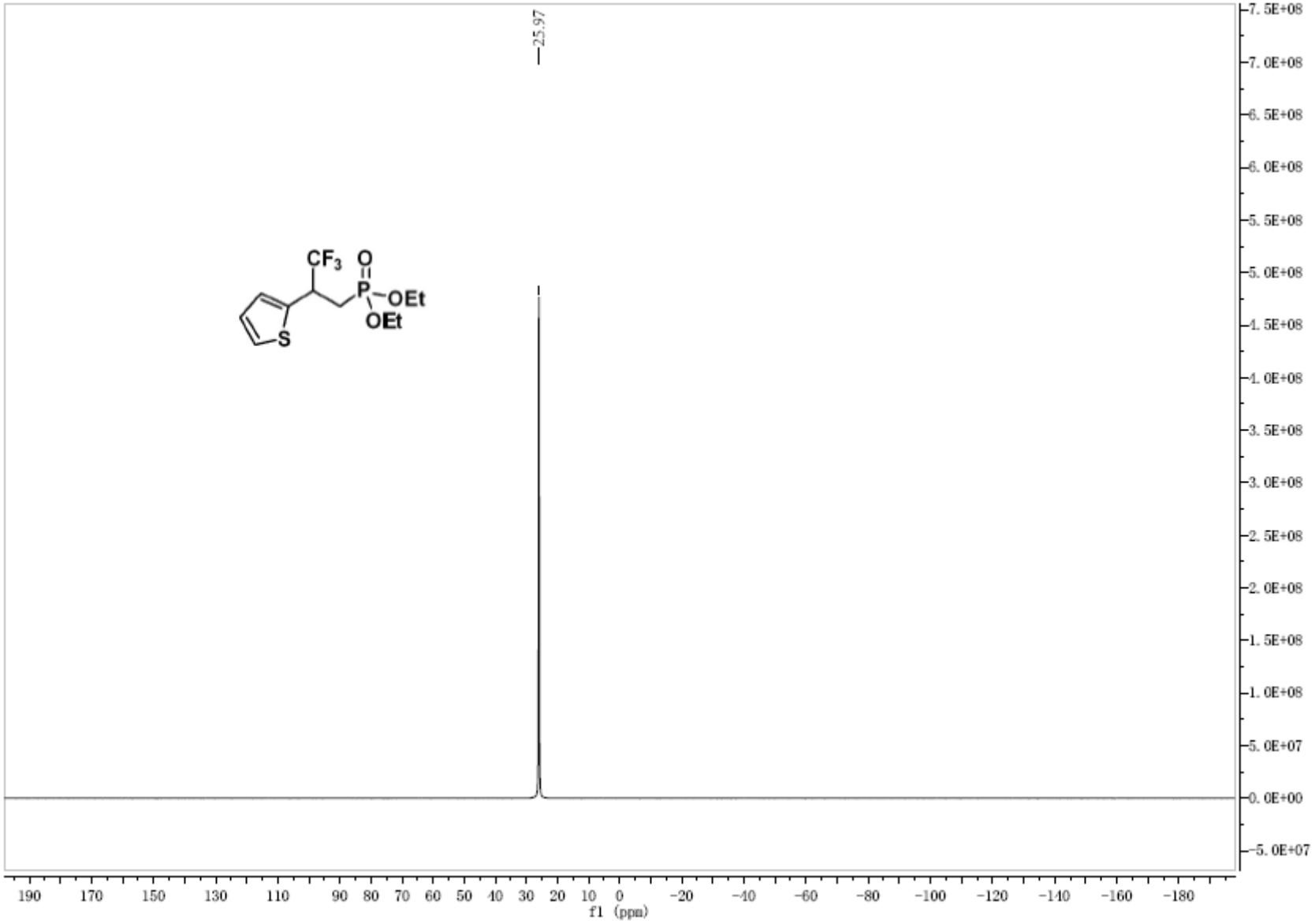
^{13}C NMR spectrum of 3ya



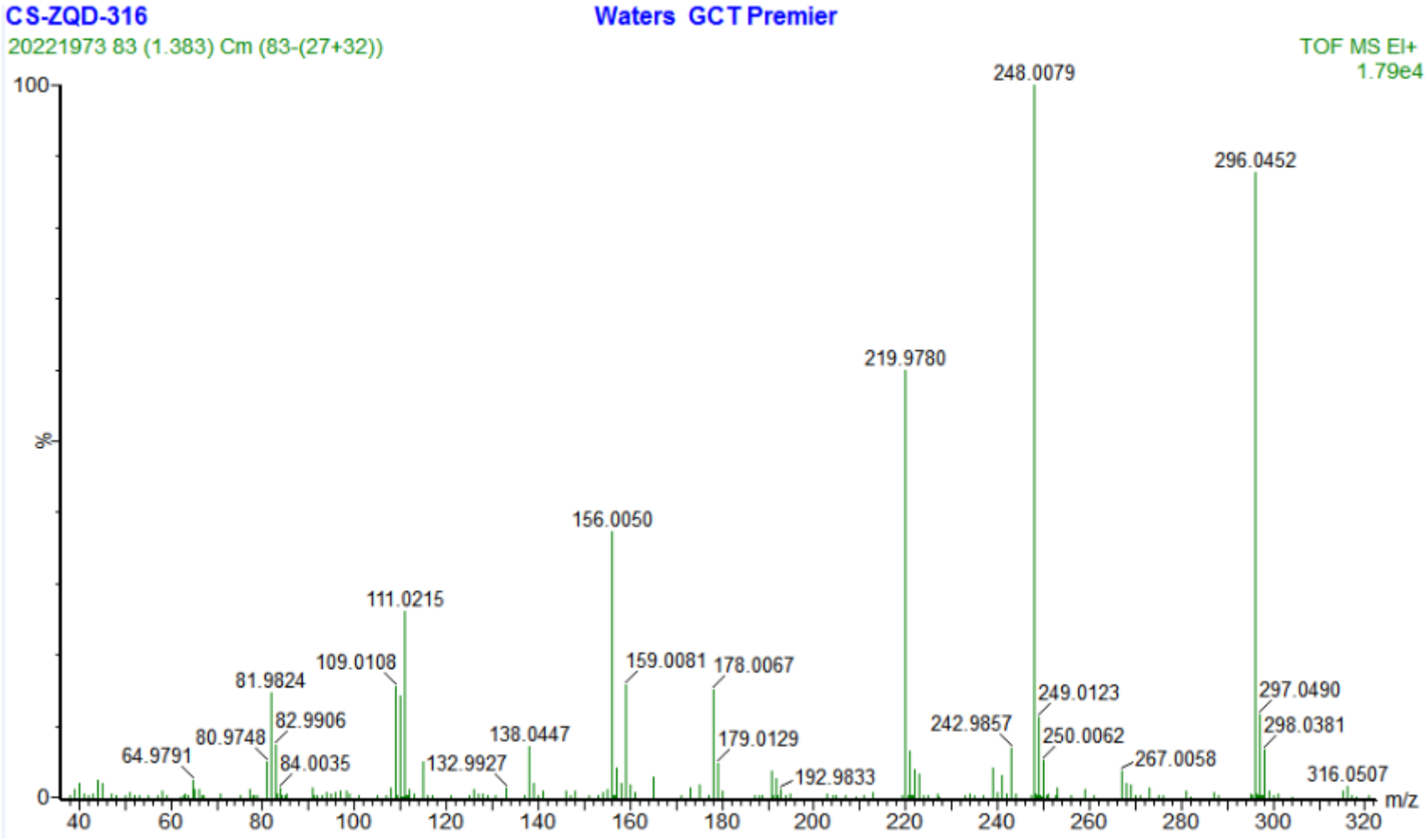
^{19}F NMR spectrum of 3ya



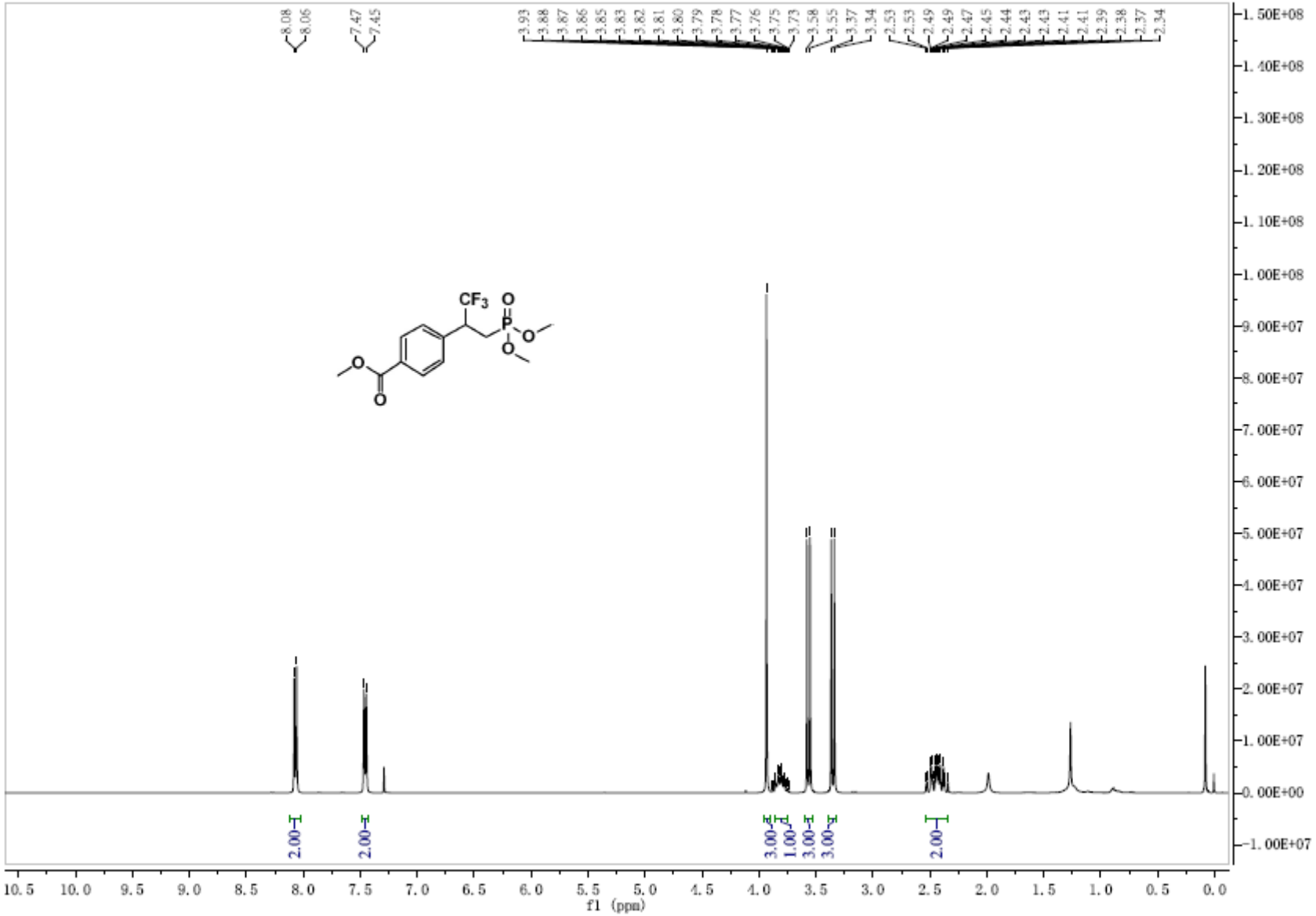
^{31}P NMR spectrum of 3ya



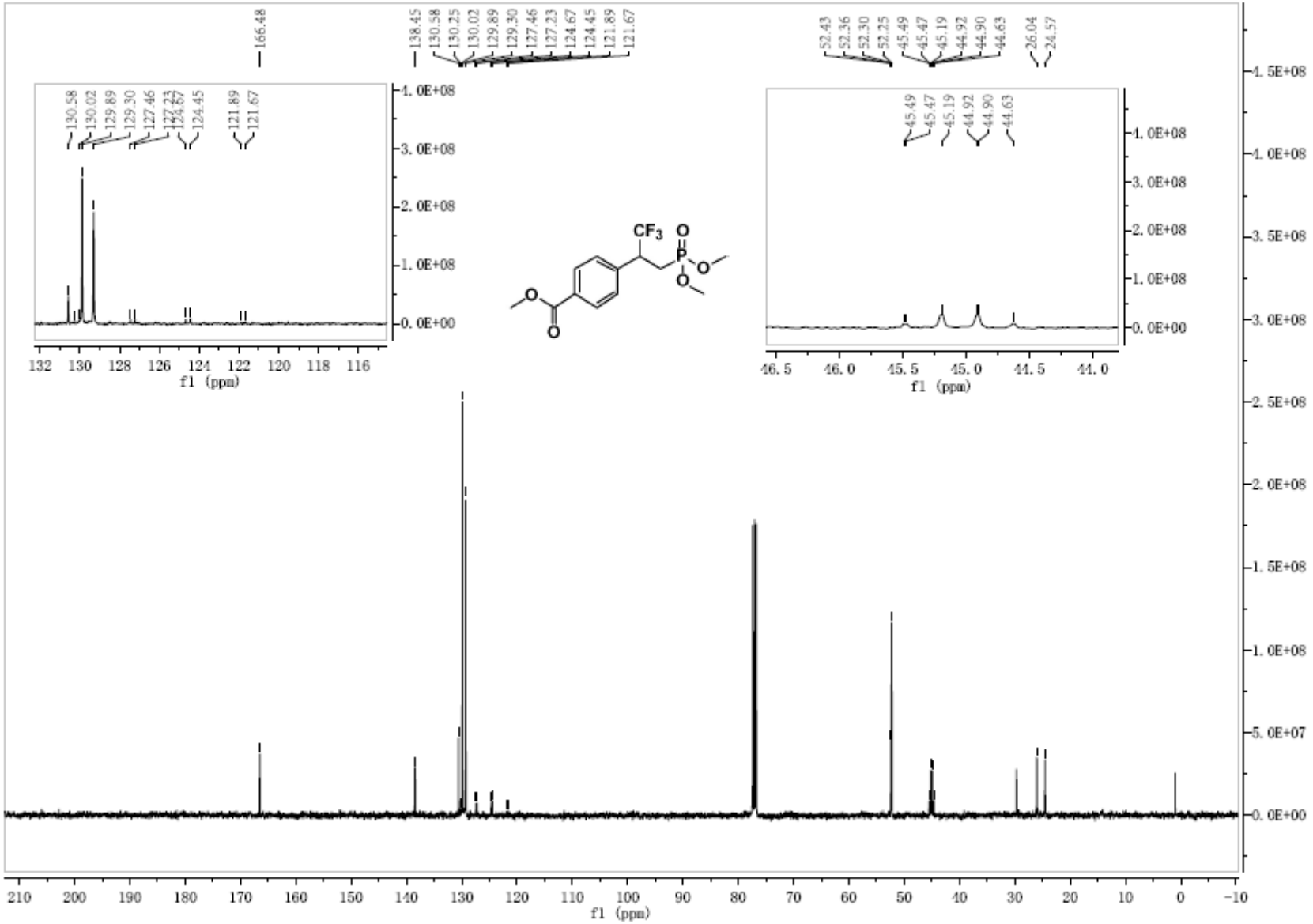
HRMS (EI) spectrum of 3ya



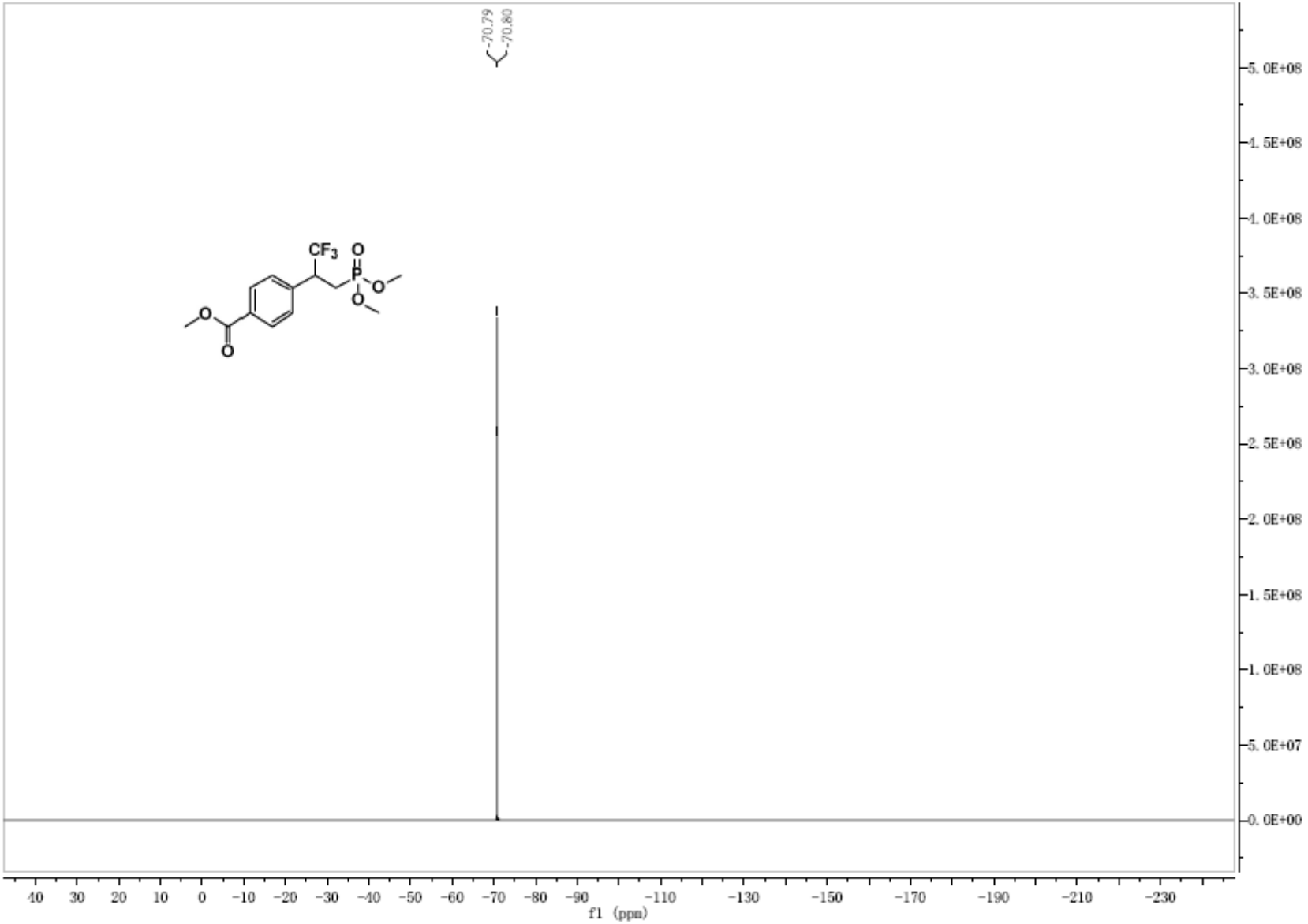
^{1}H NMR spectrum of 3hb



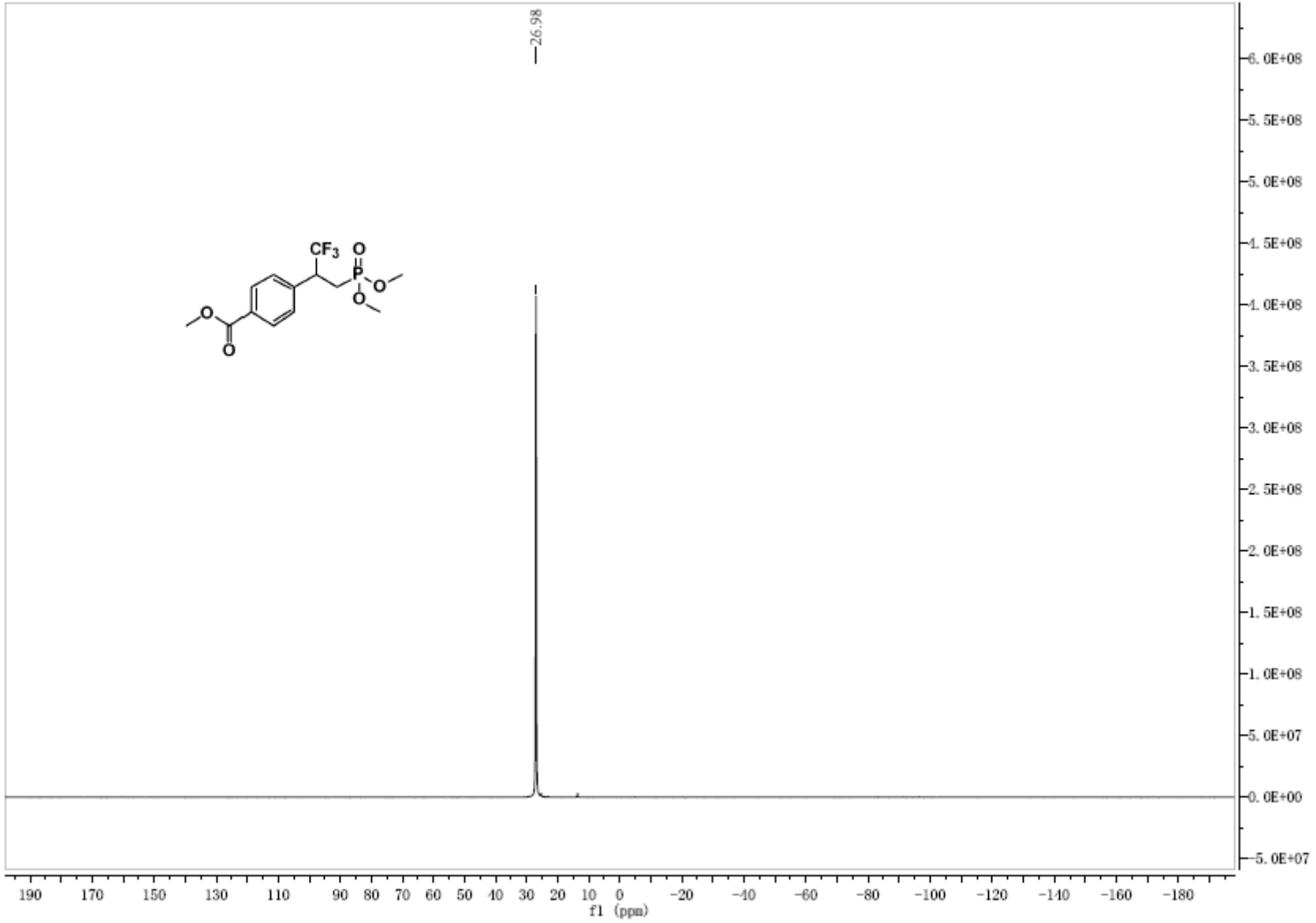
^{13}C NMR spectrum of 3hb



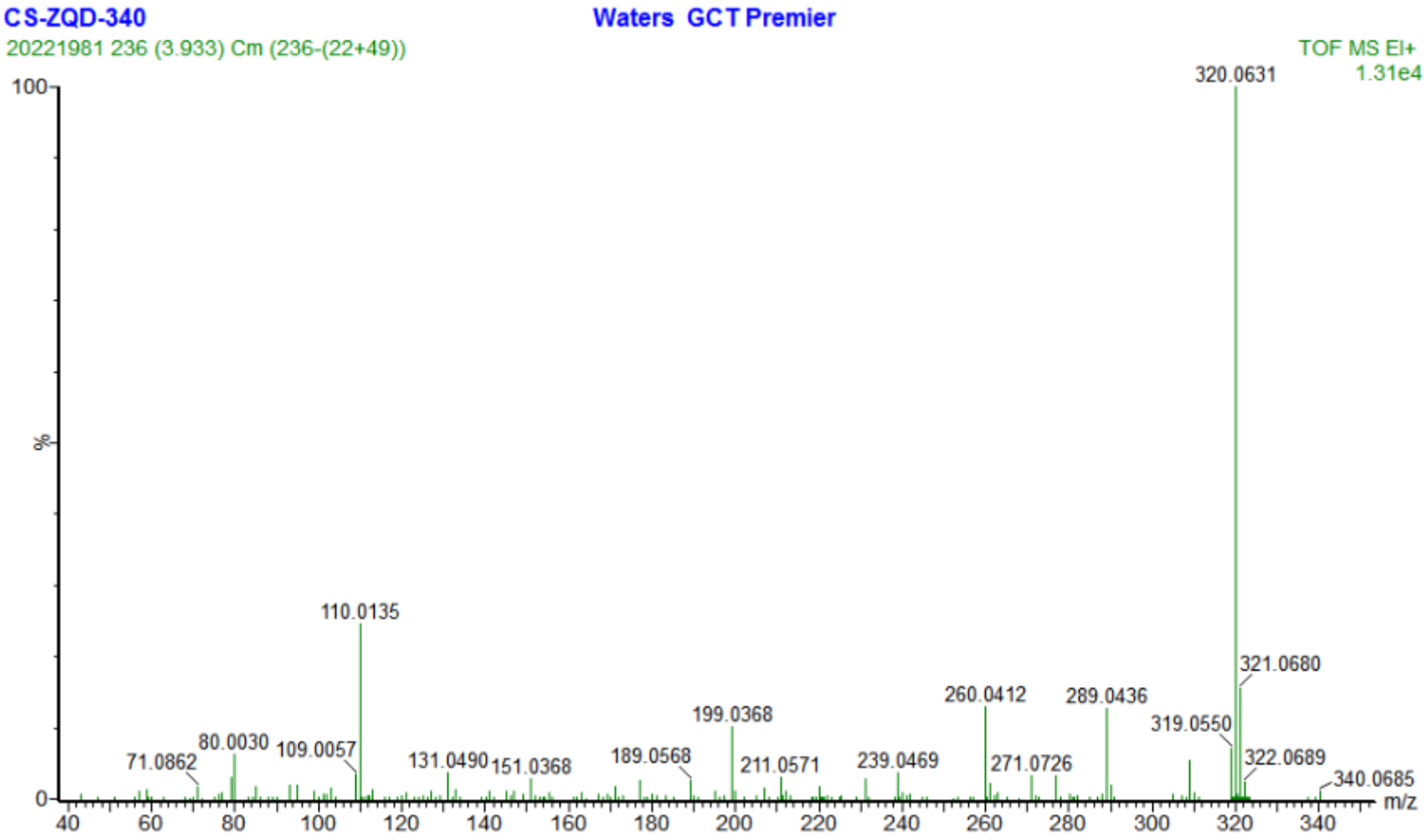
^{19}F NMR spectrum of 3hb



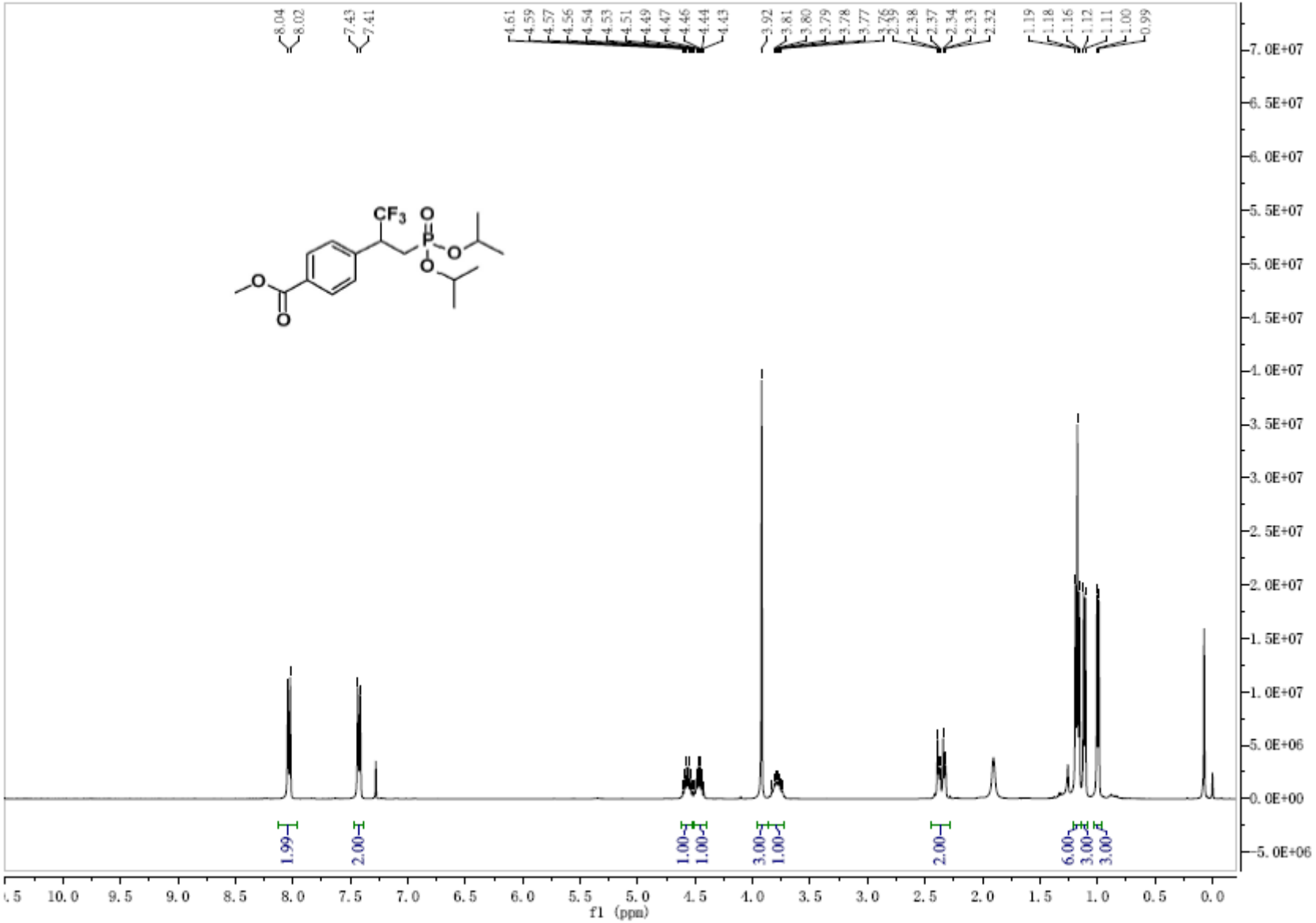
^{31}P NMR spectrum of 3hb



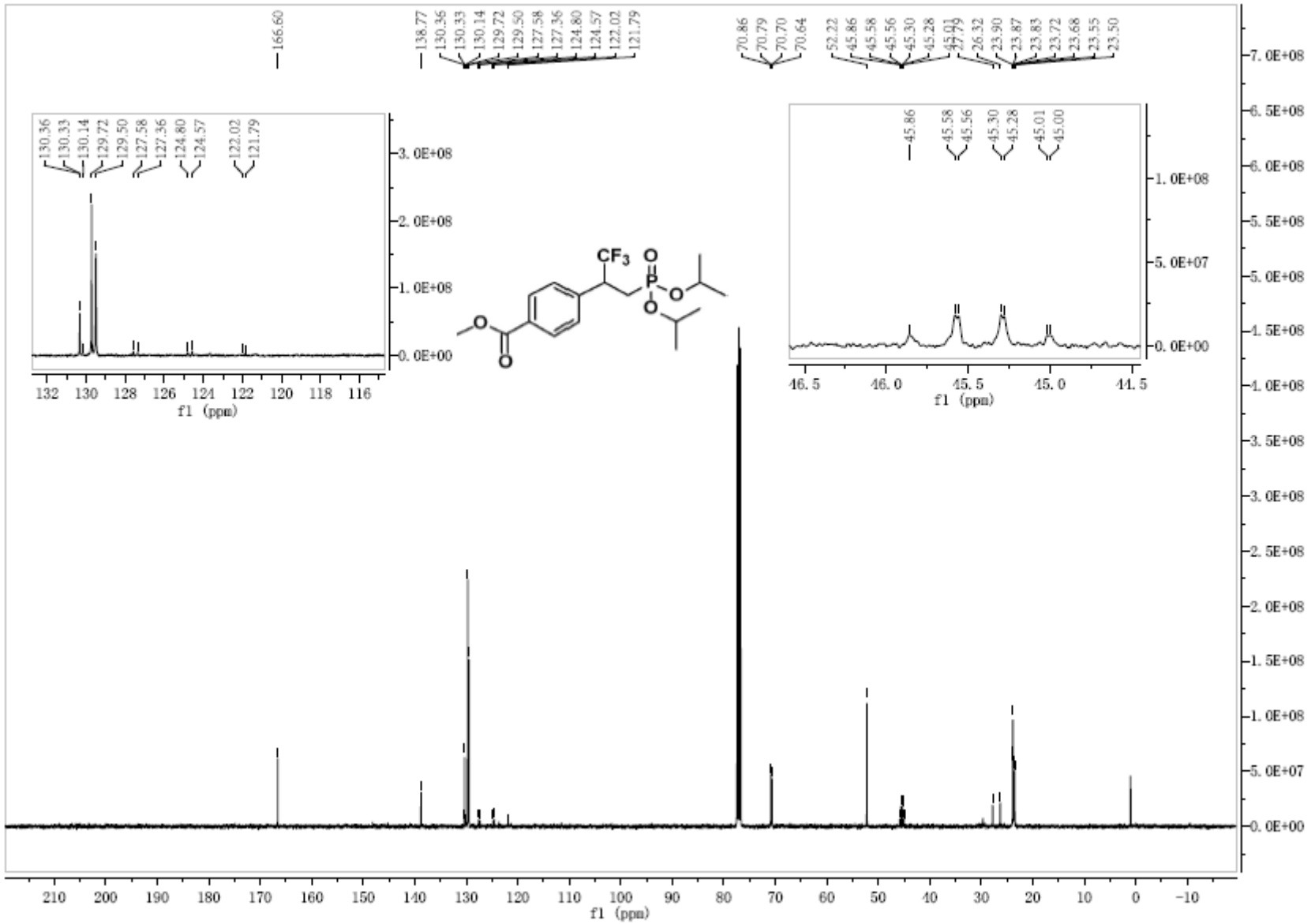
HRMS (EI) spectrum of 3hb



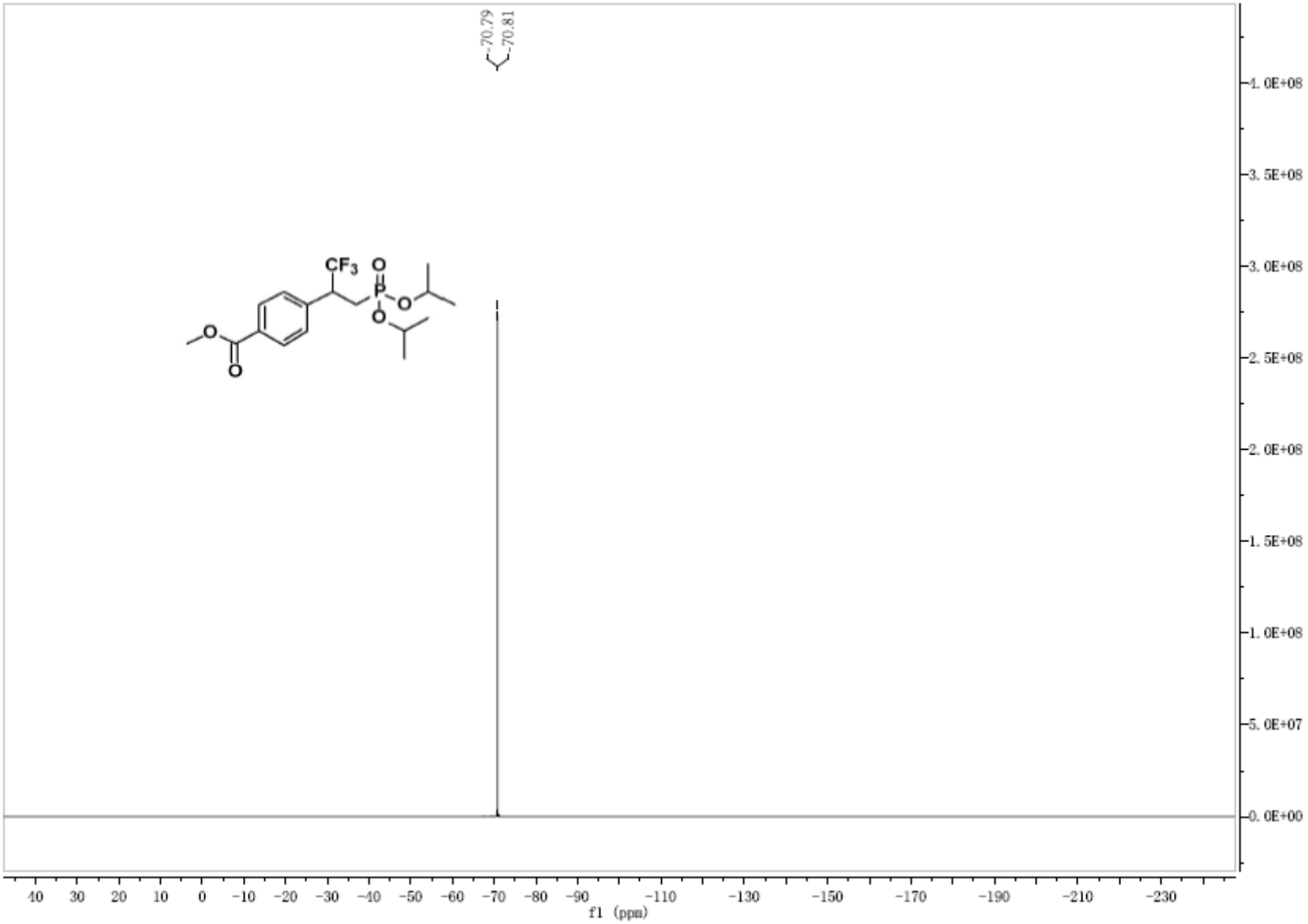
^{1}H NMR spectrum of 3hc



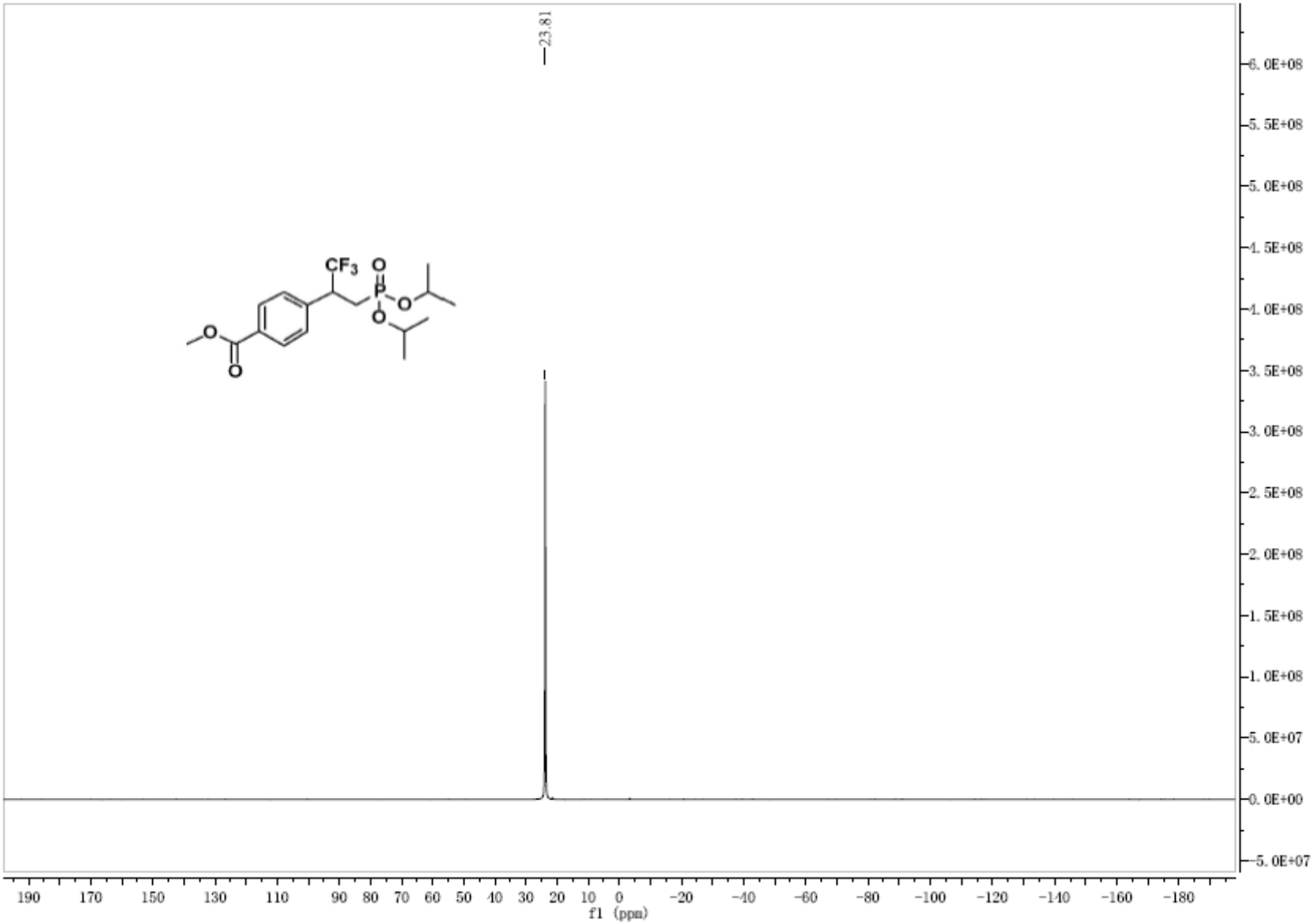
^{13}C NMR spectrum of 3hc



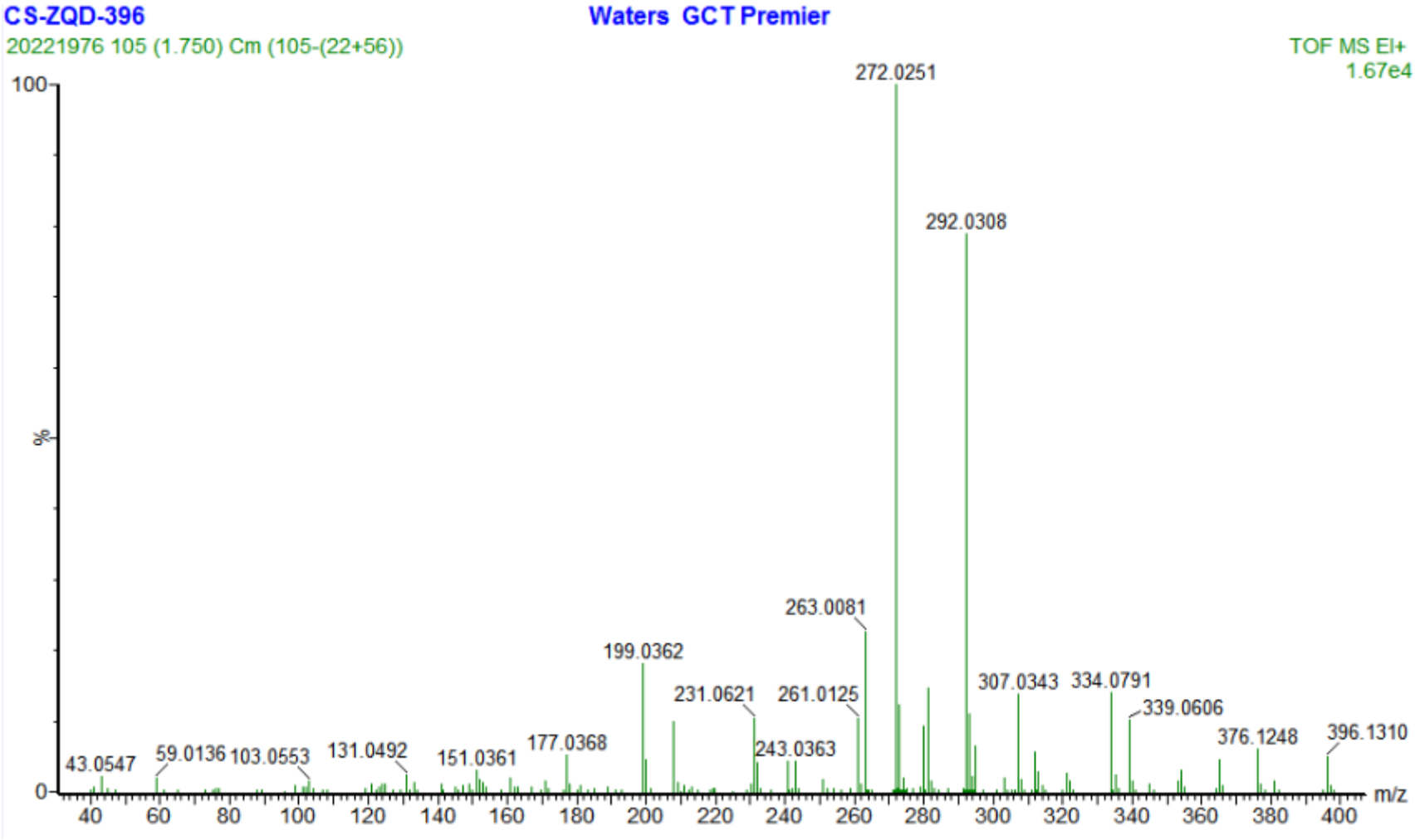
^{19}F NMR spectrum of 3hc



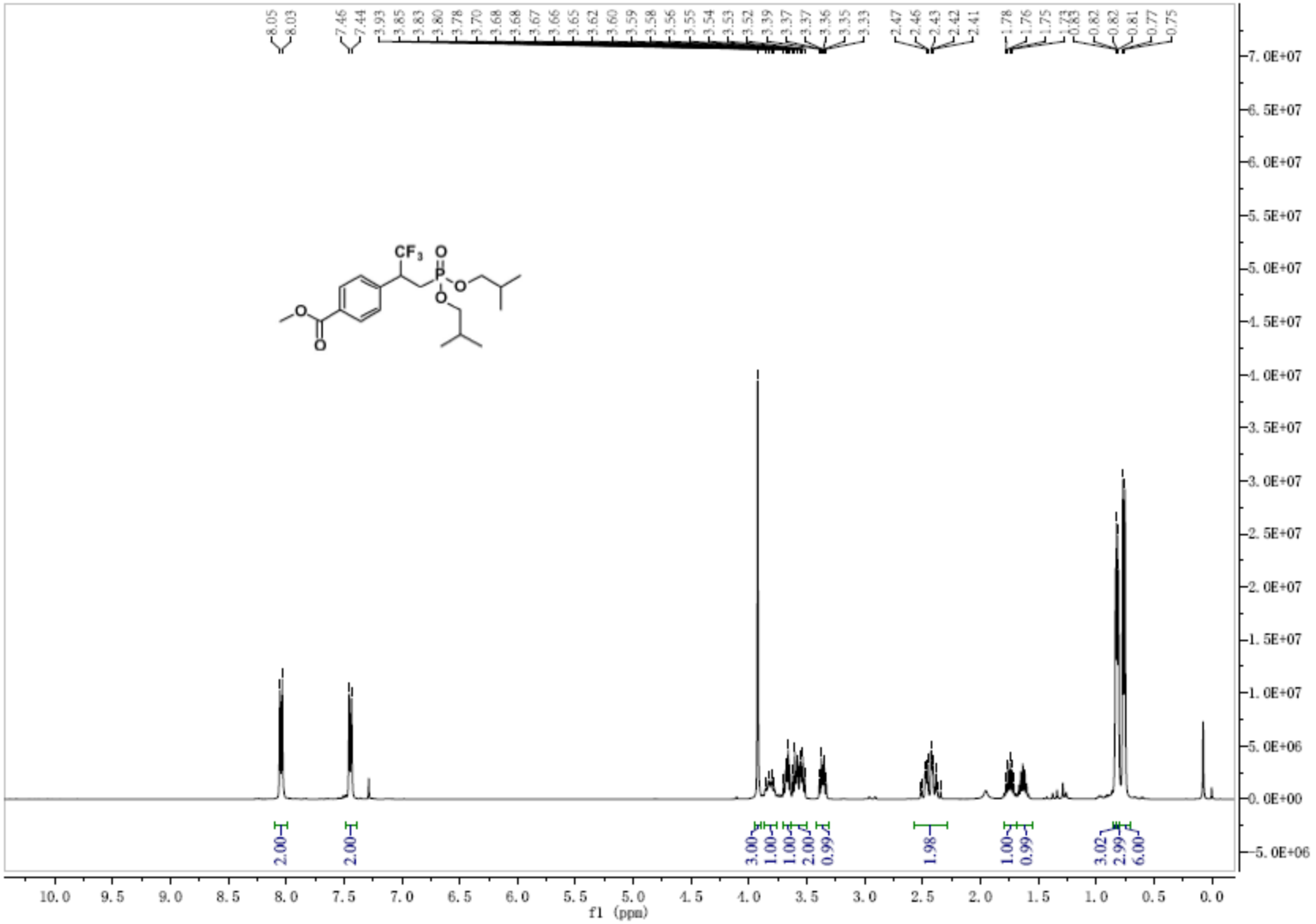
^{31}P NMR spectrum of 3hc



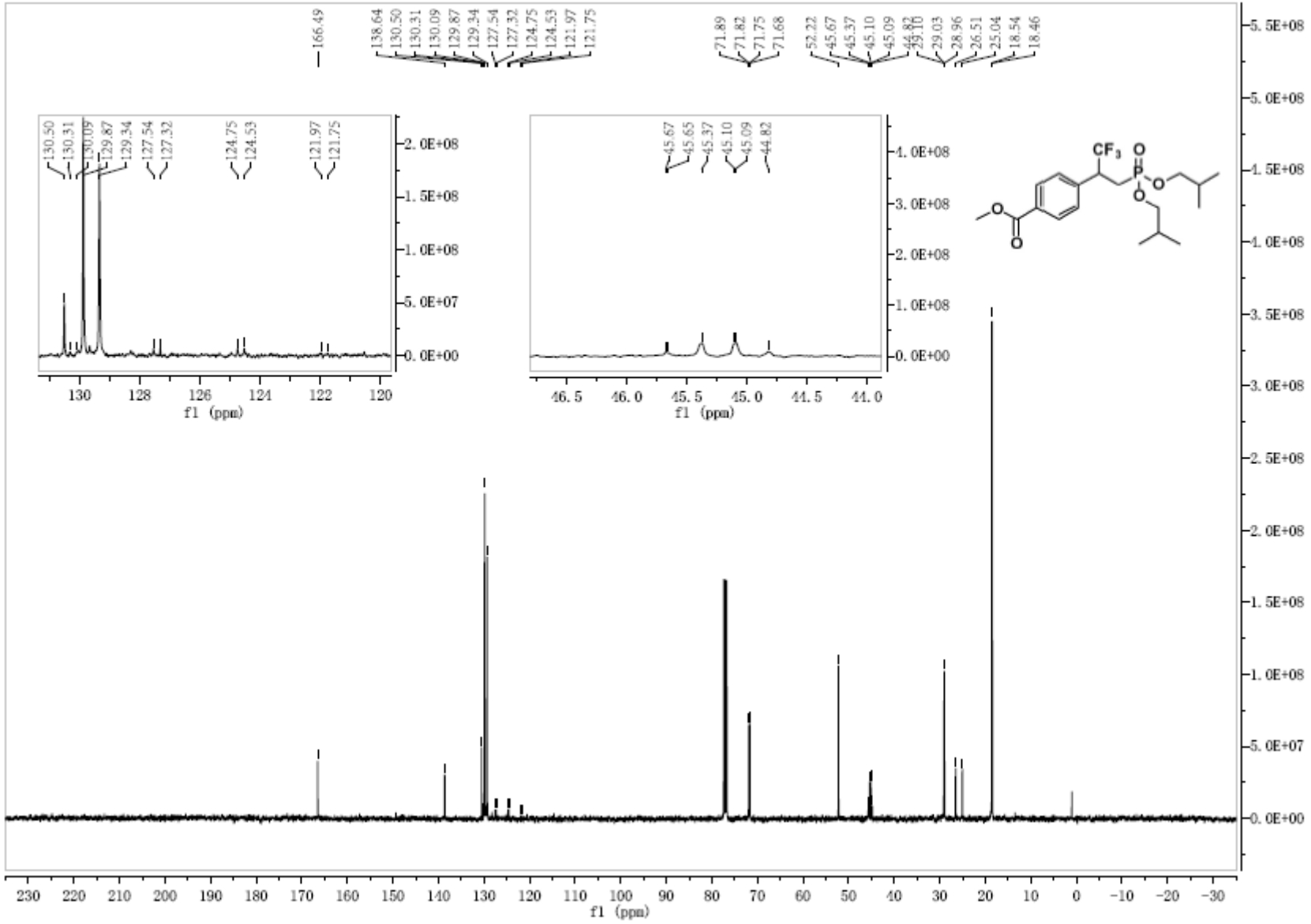
HRMS (EI) spectrum of 3hc



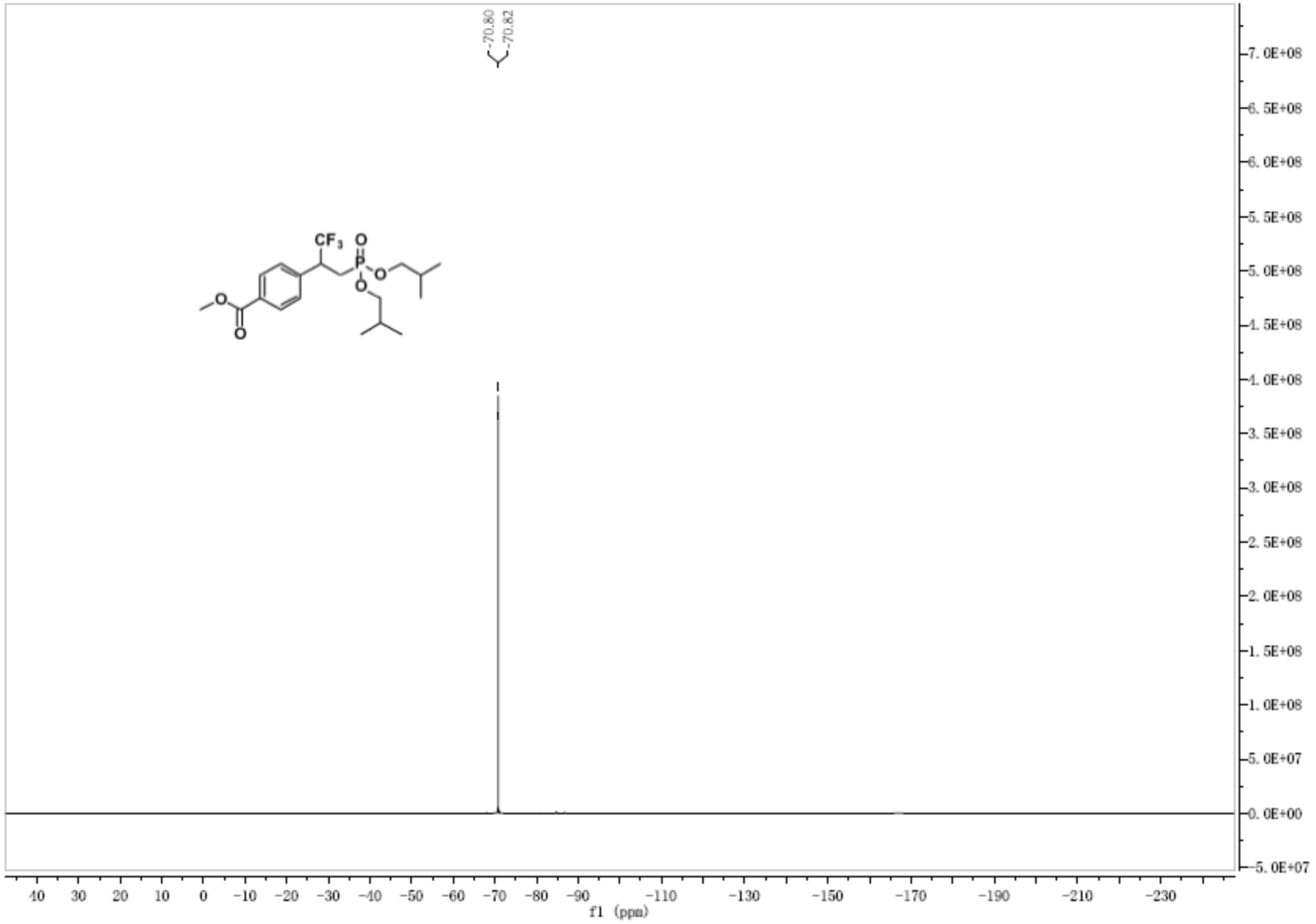
^{1}H NMR spectrum of 3hd



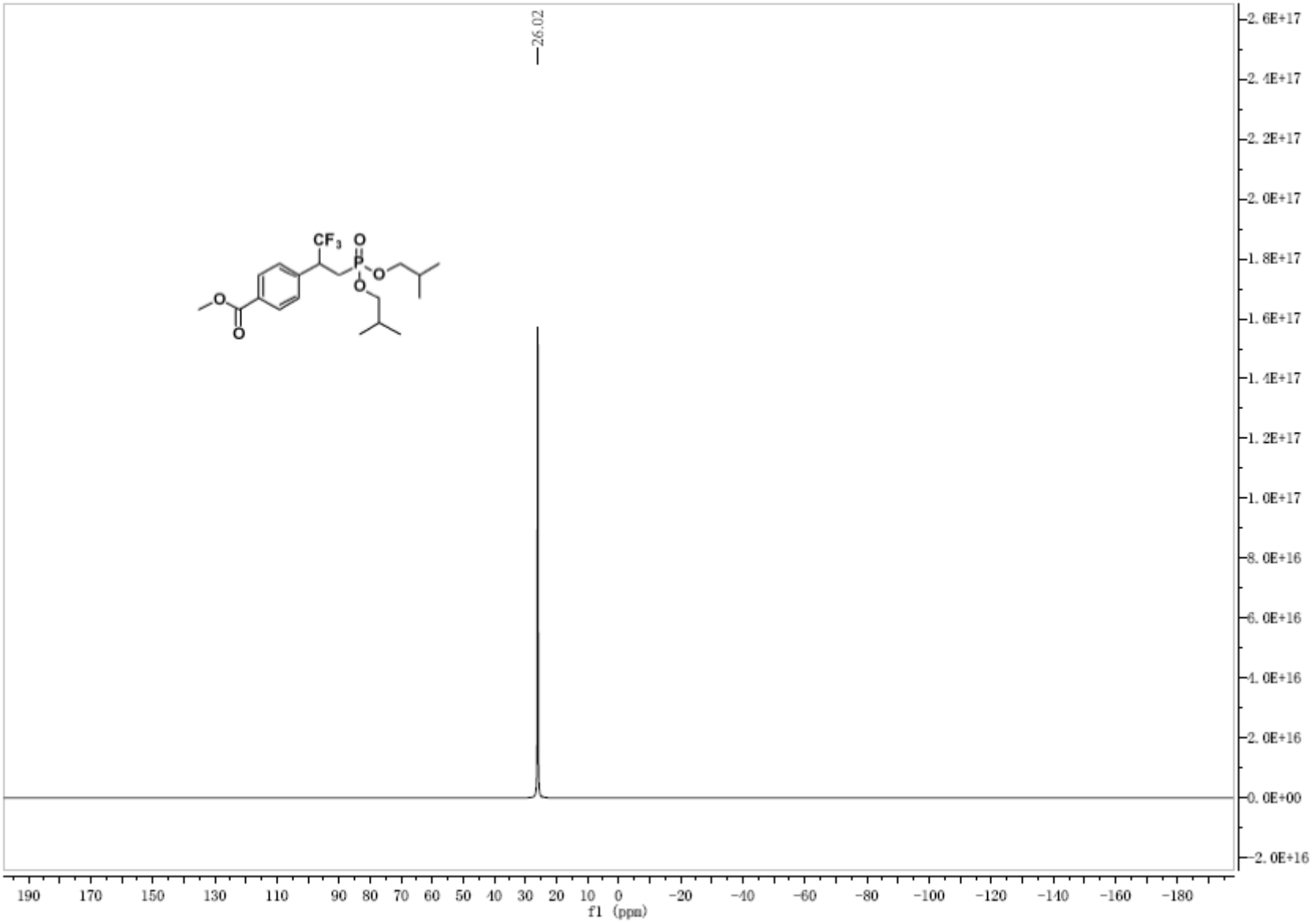
^{13}C NMR spectrum of 3hd



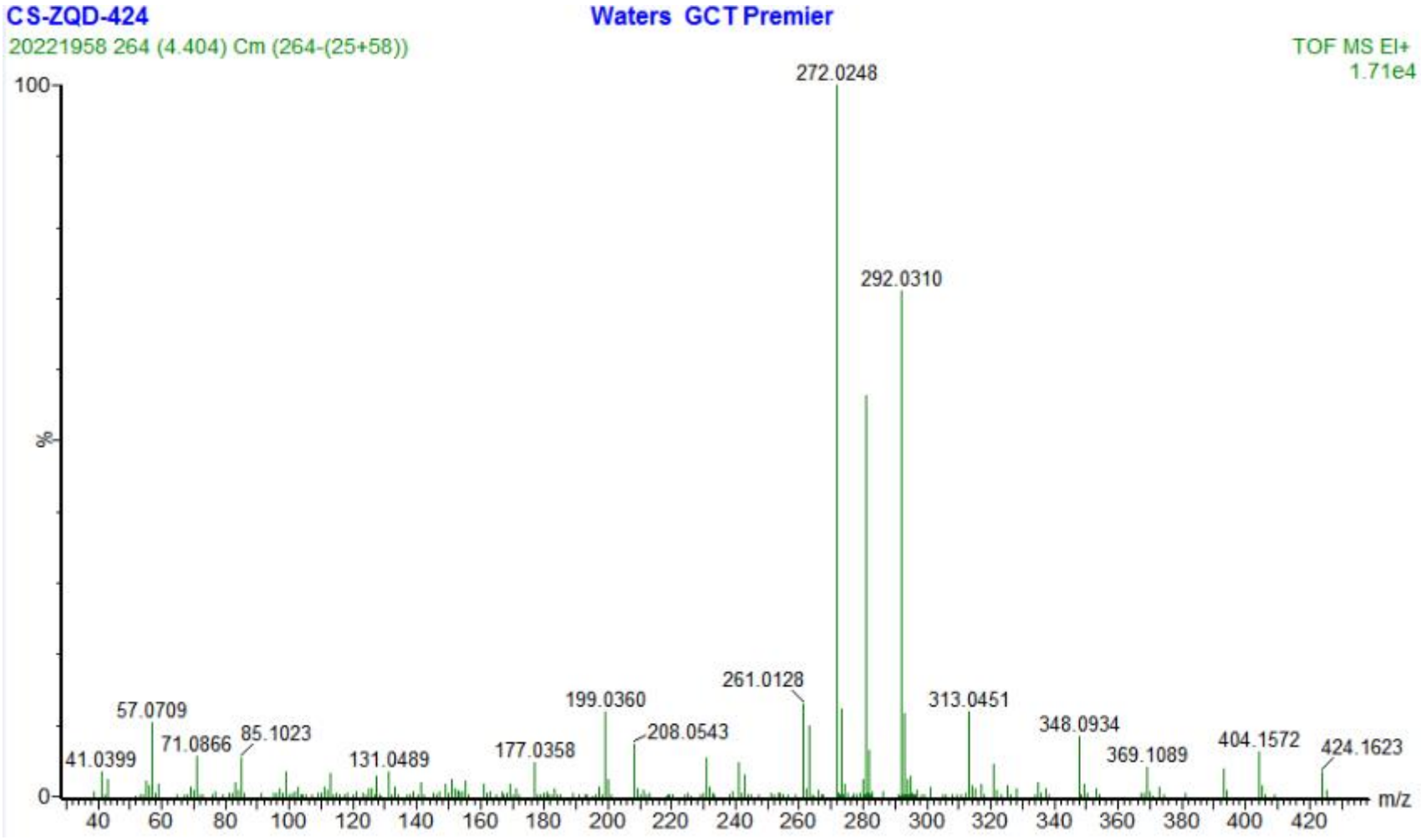
^{19}F NMR spectrum of 3hd



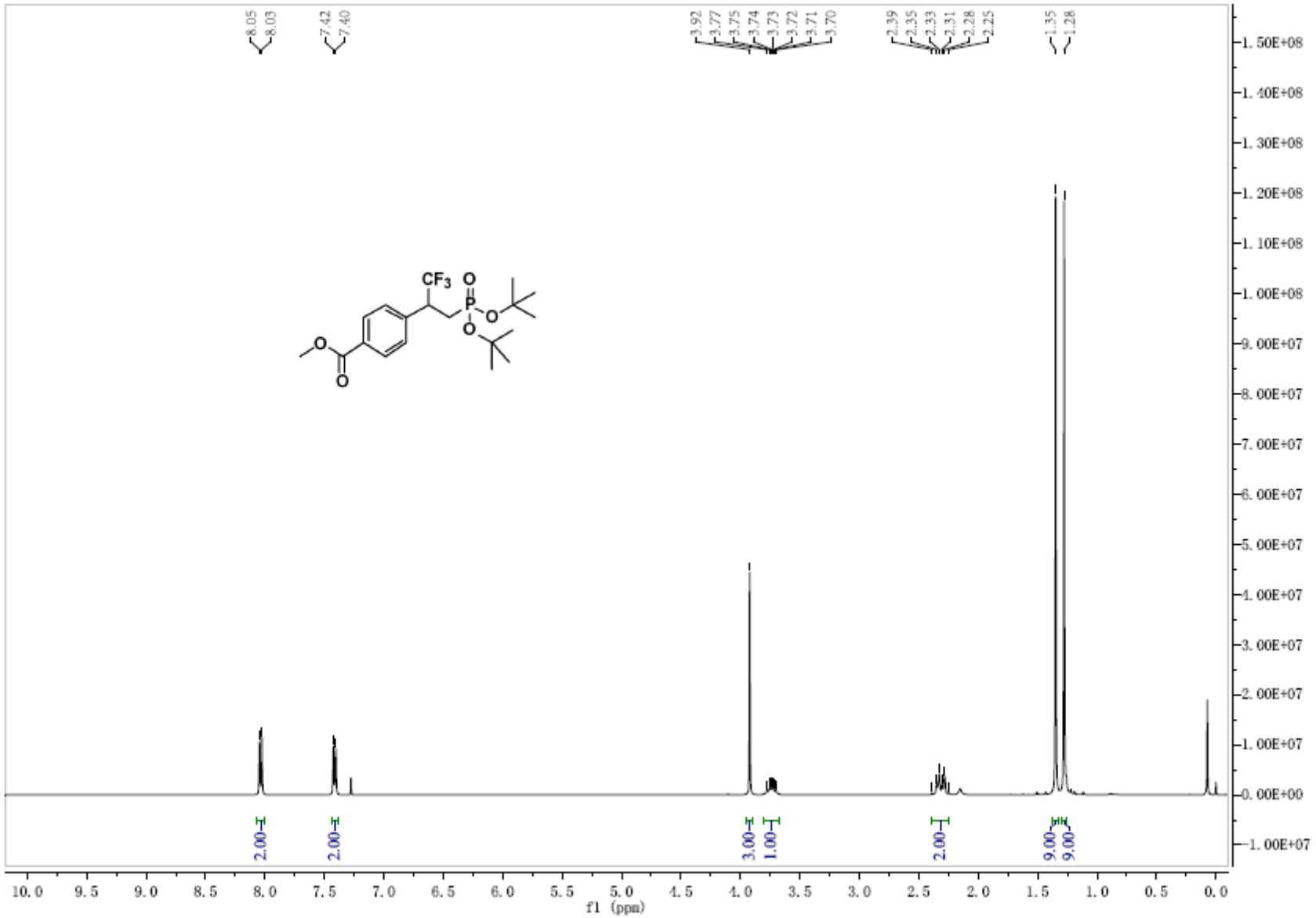
^{31}P NMR spectrum of 3hd



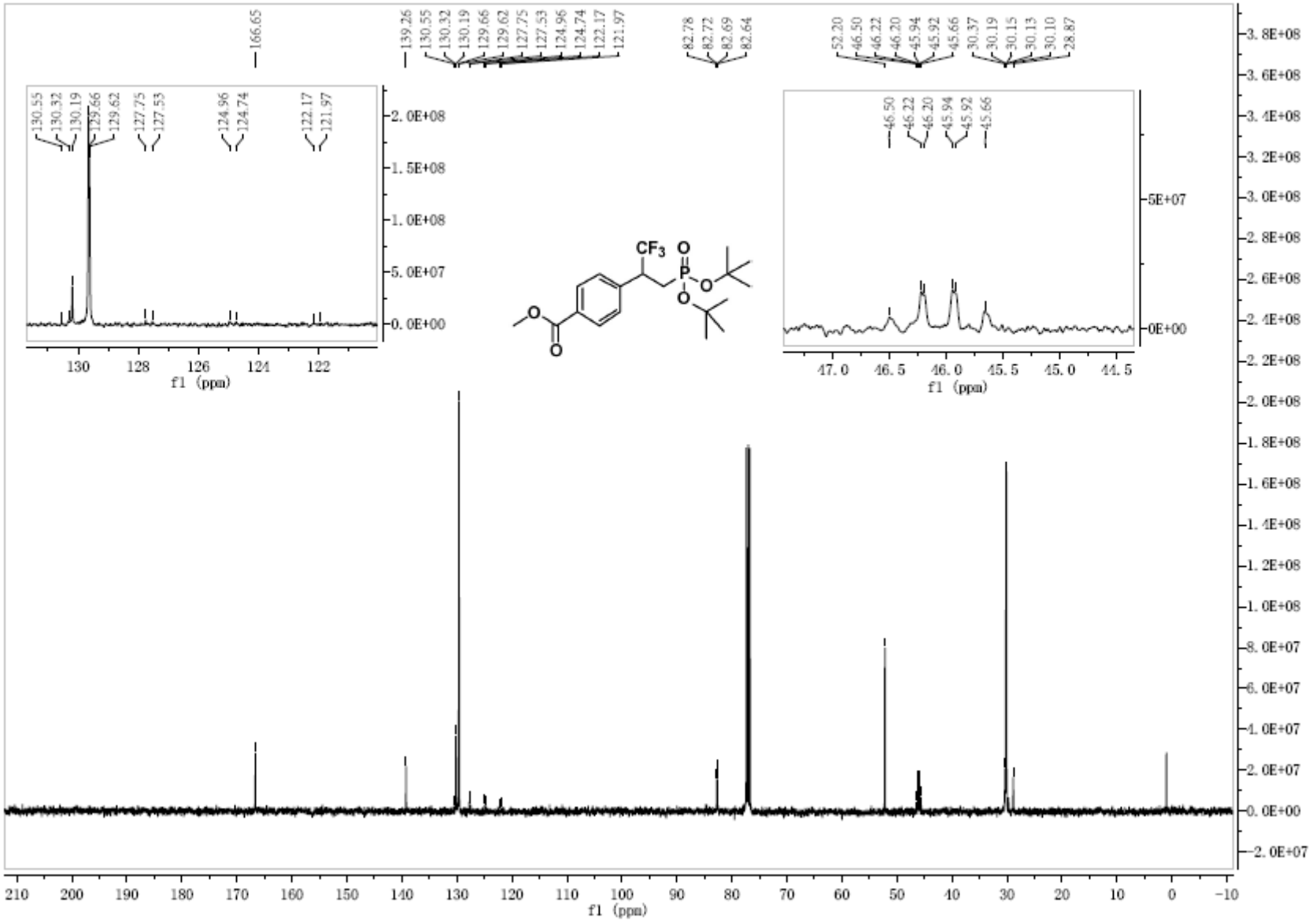
HRMS (EI) spectrum of 3hd



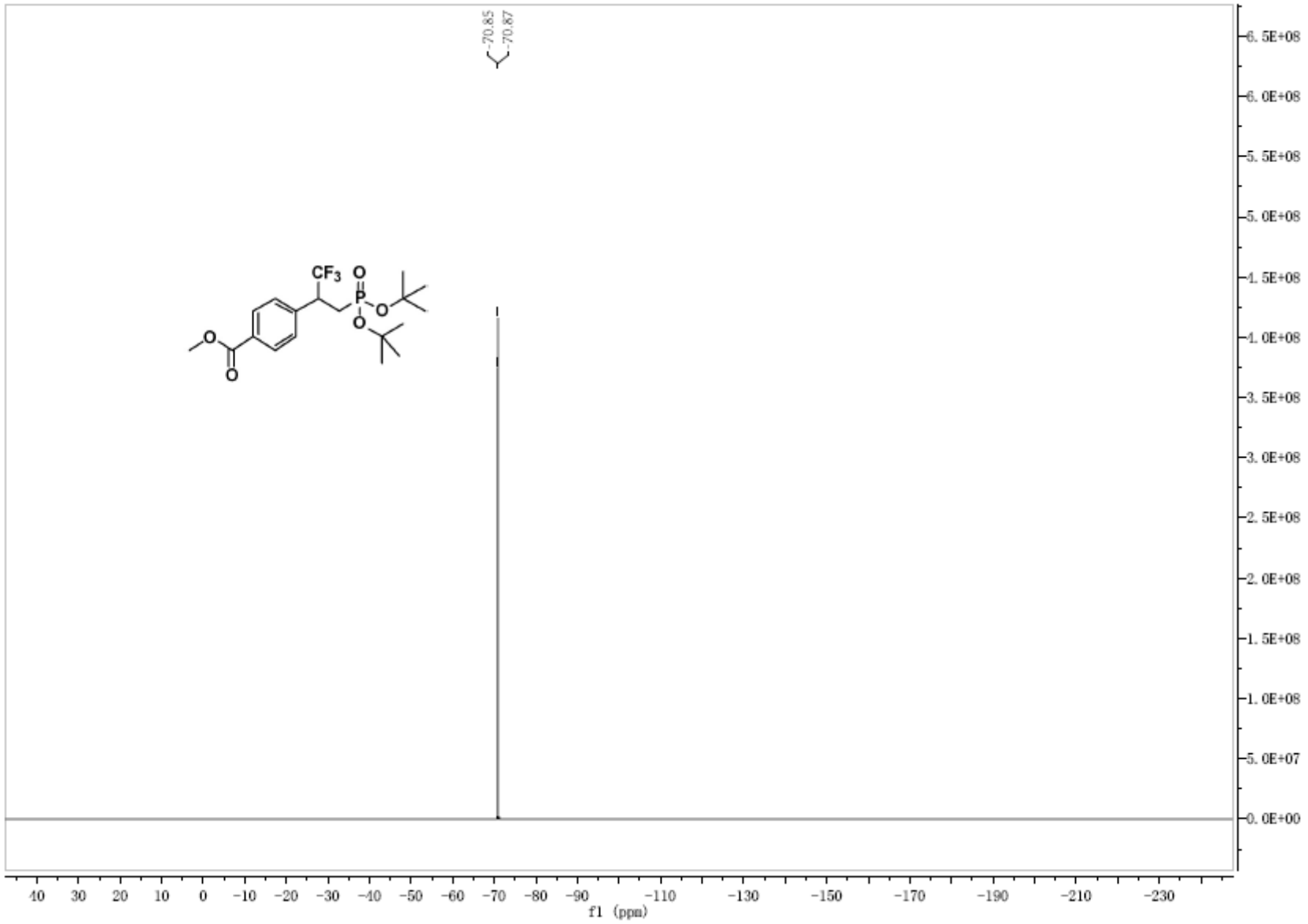
^{1}H NMR spectrum of 3he



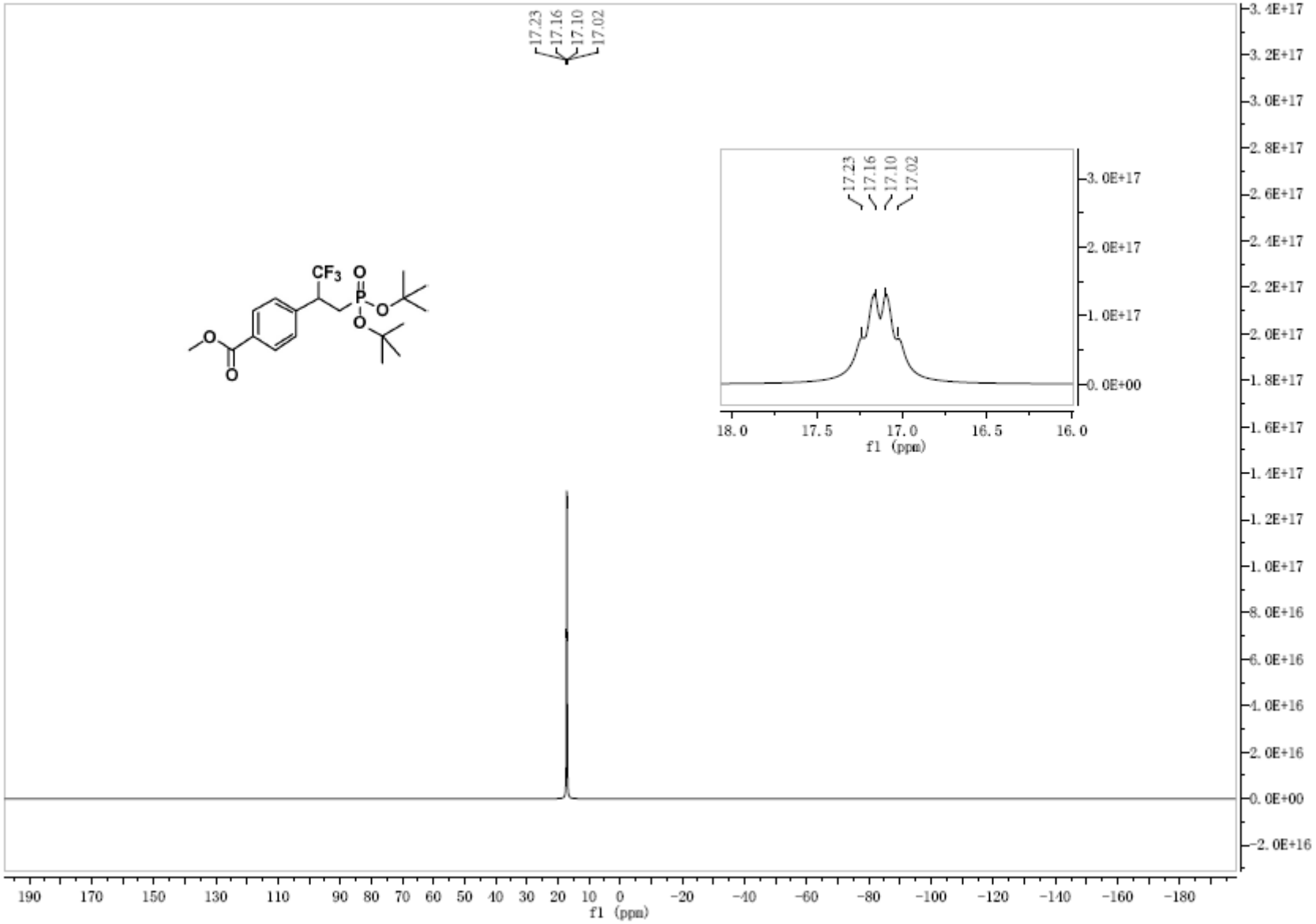
^{13}C NMR spectrum of 3he



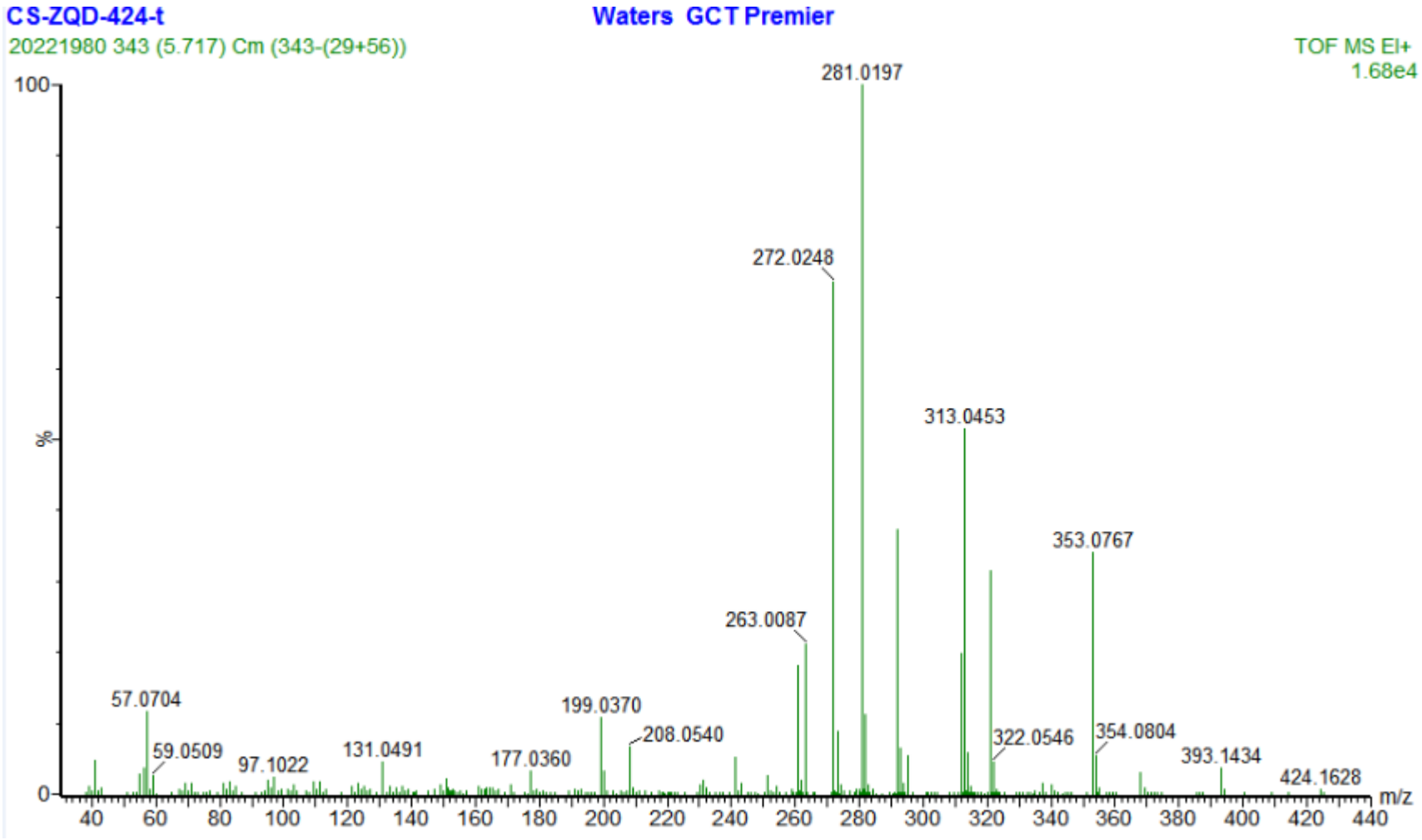
^{19}F NMR spectrum of 3he



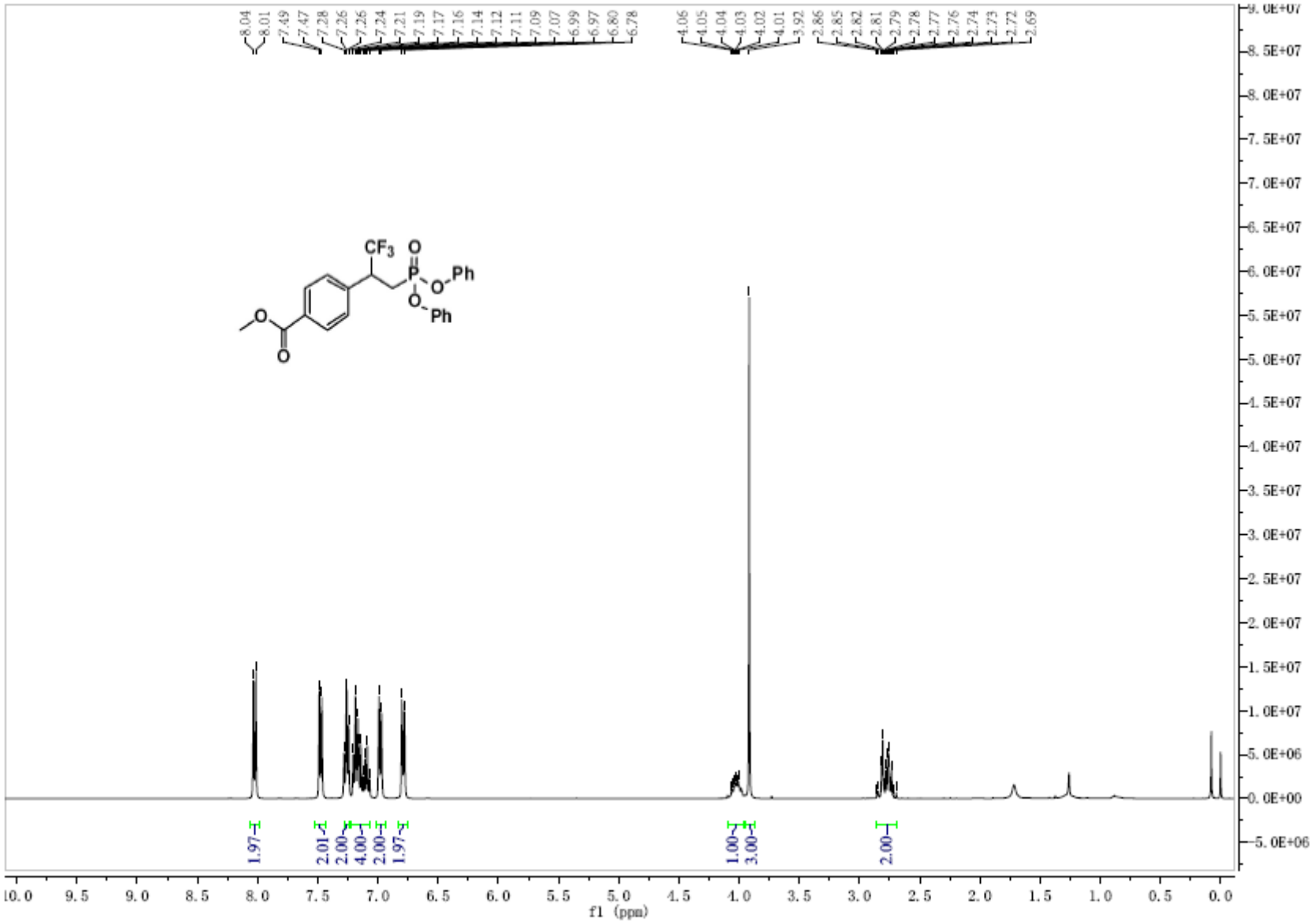
^{31}P NMR spectrum of 3he



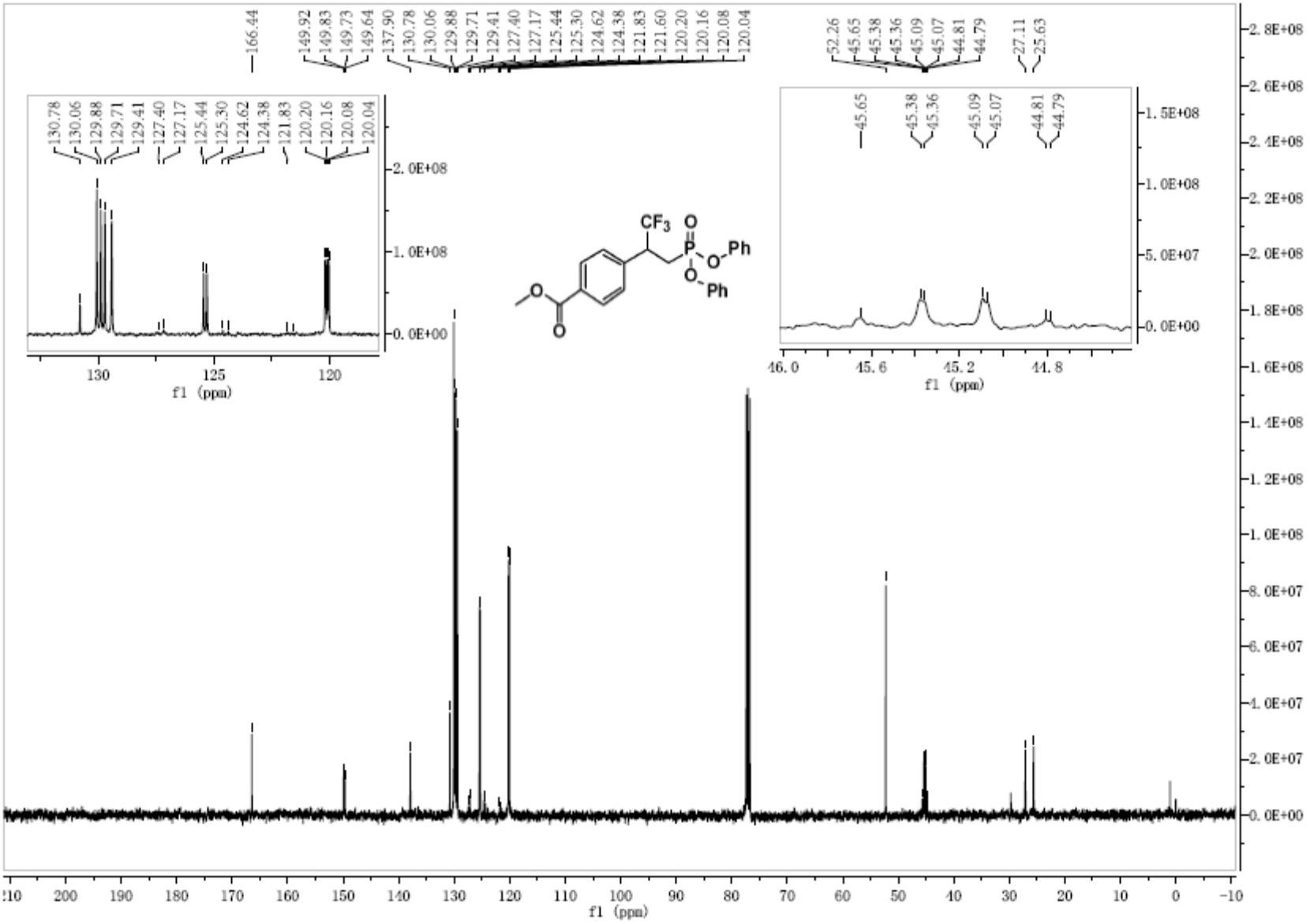
HRMS (EI) spectrum of 3he



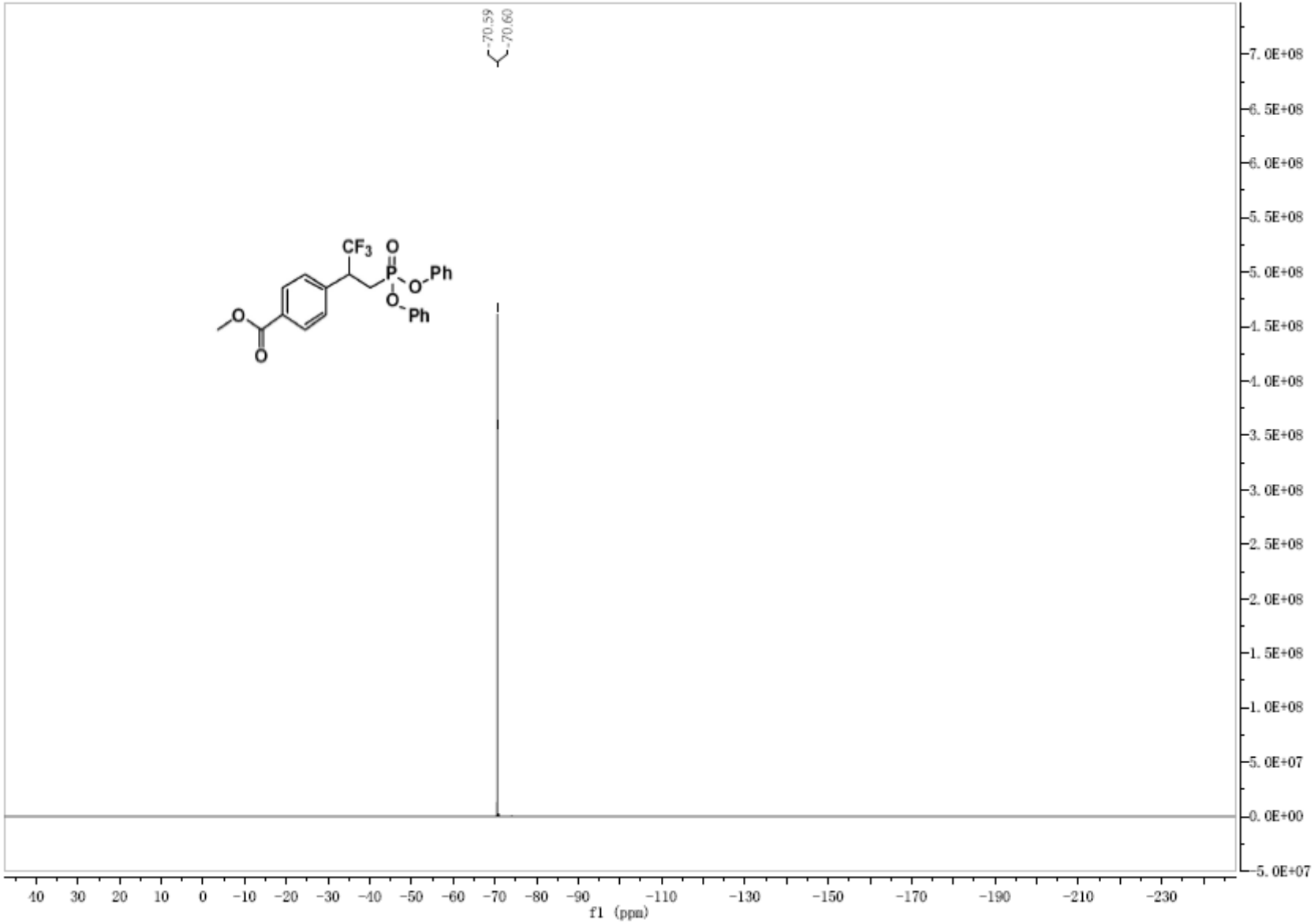
^{1}H NMR spectrum of 3hf



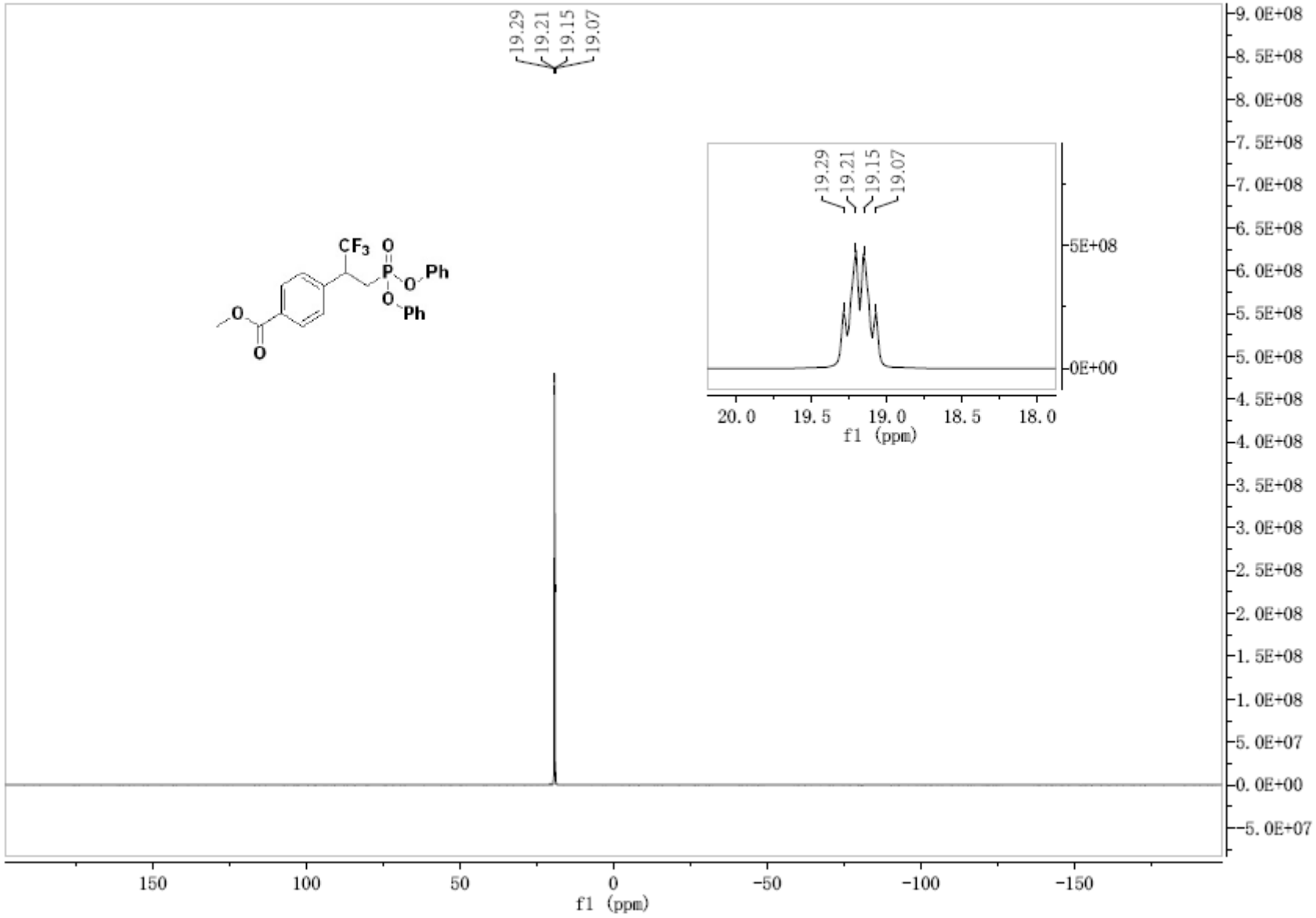
^{13}C NMR spectrum of 3hf



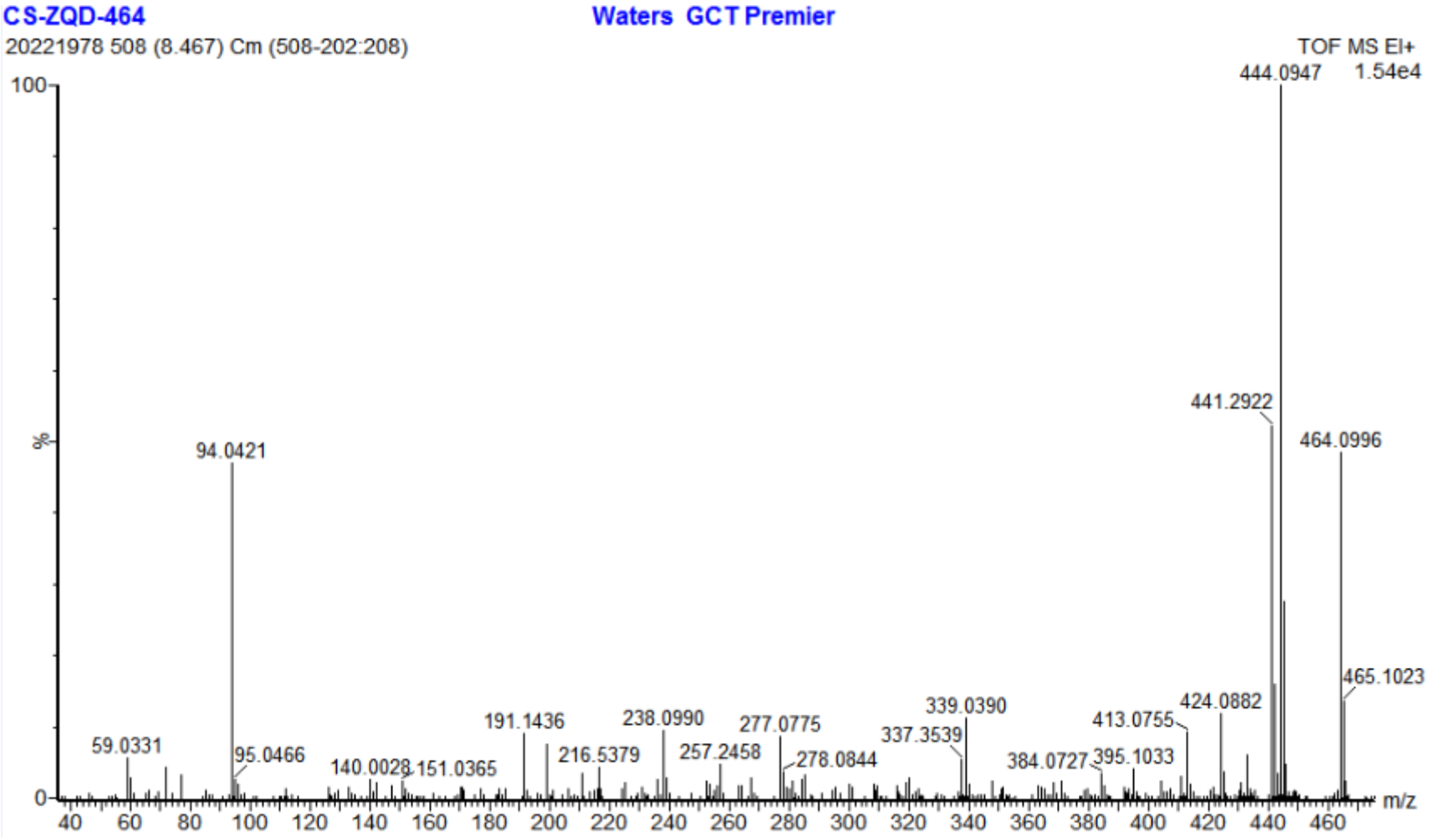
^{19}F NMR spectrum of 3hf



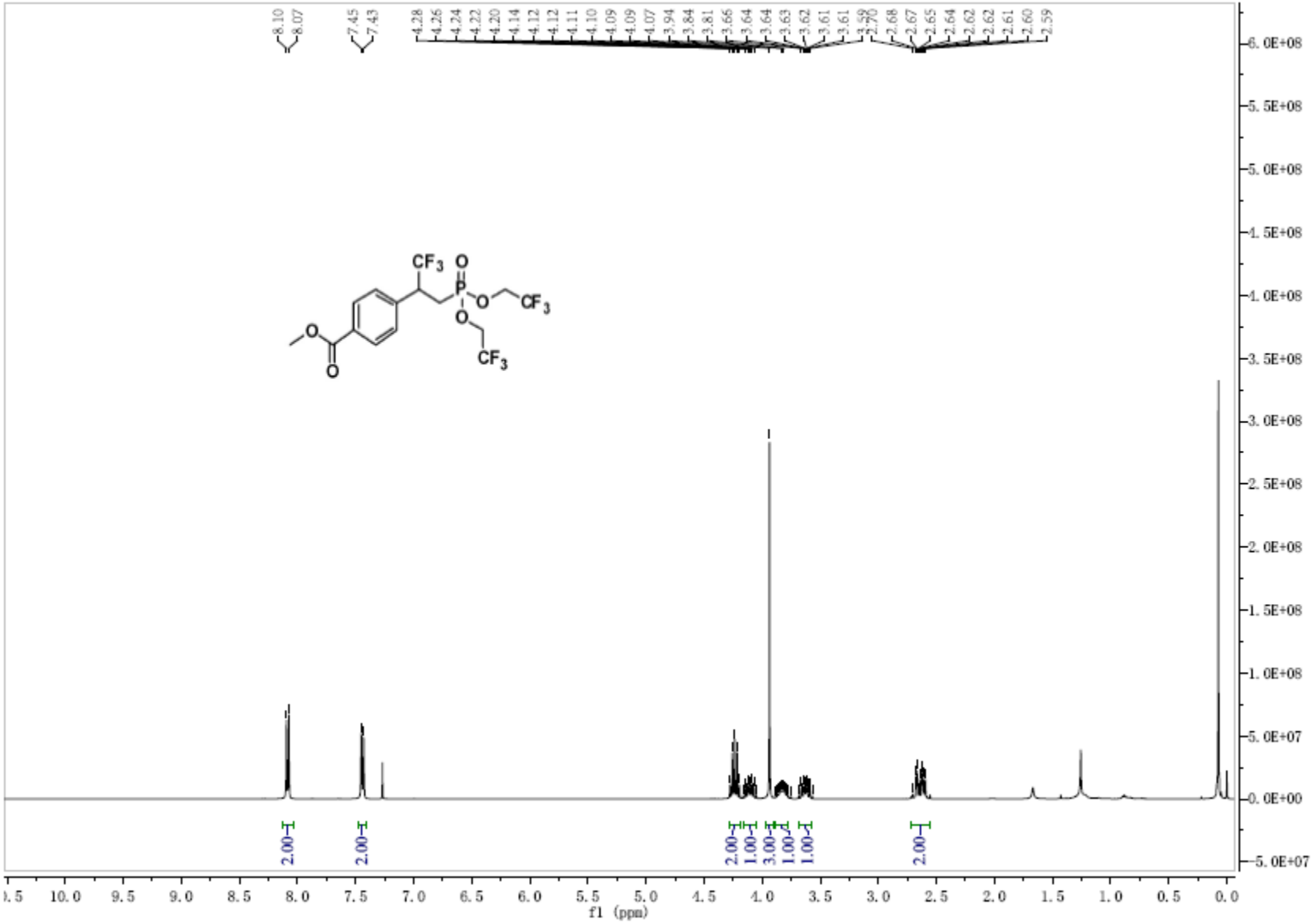
^{31}P NMR spectrum of 3hf



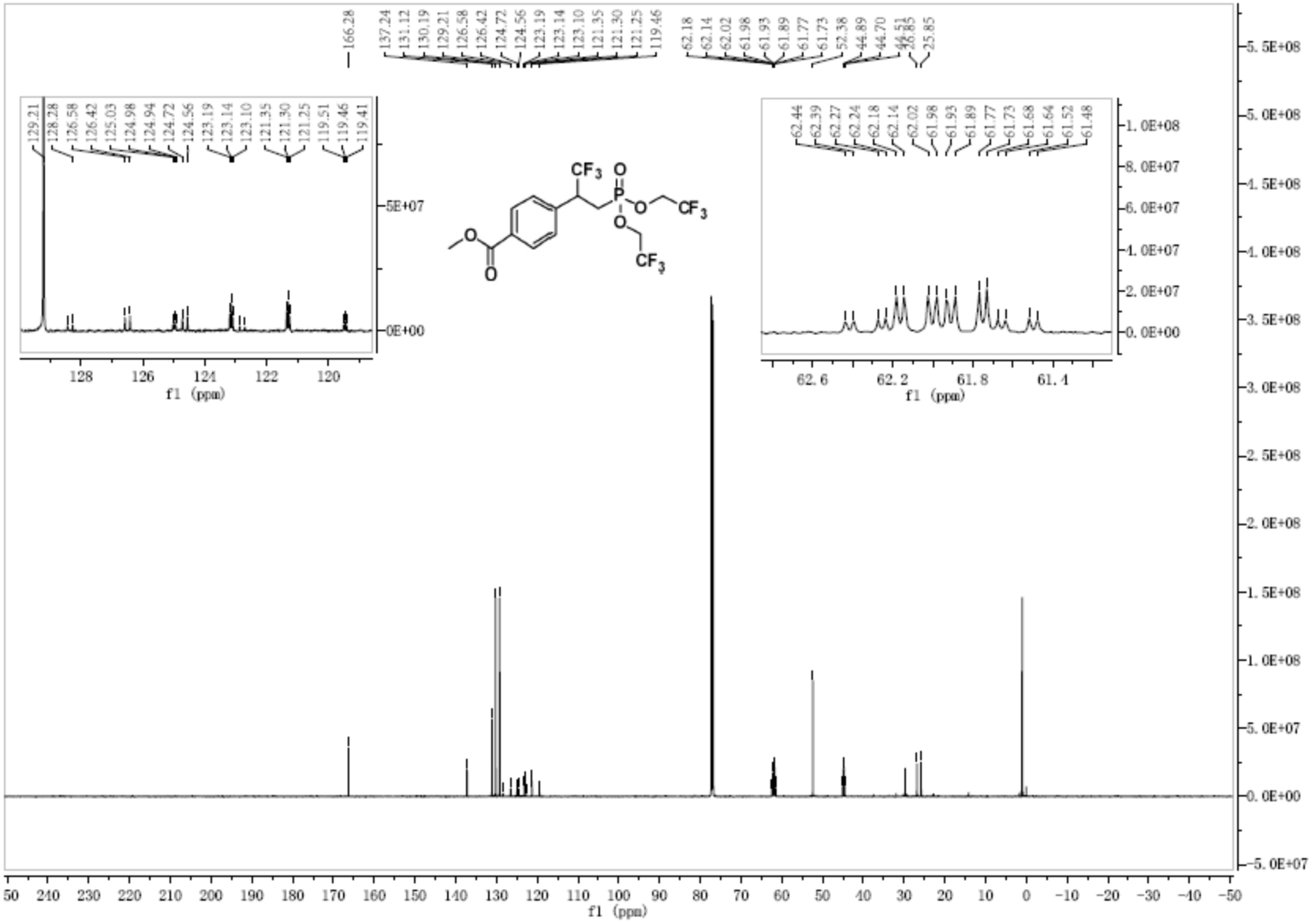
HRMS (EI) spectrum of 3hf



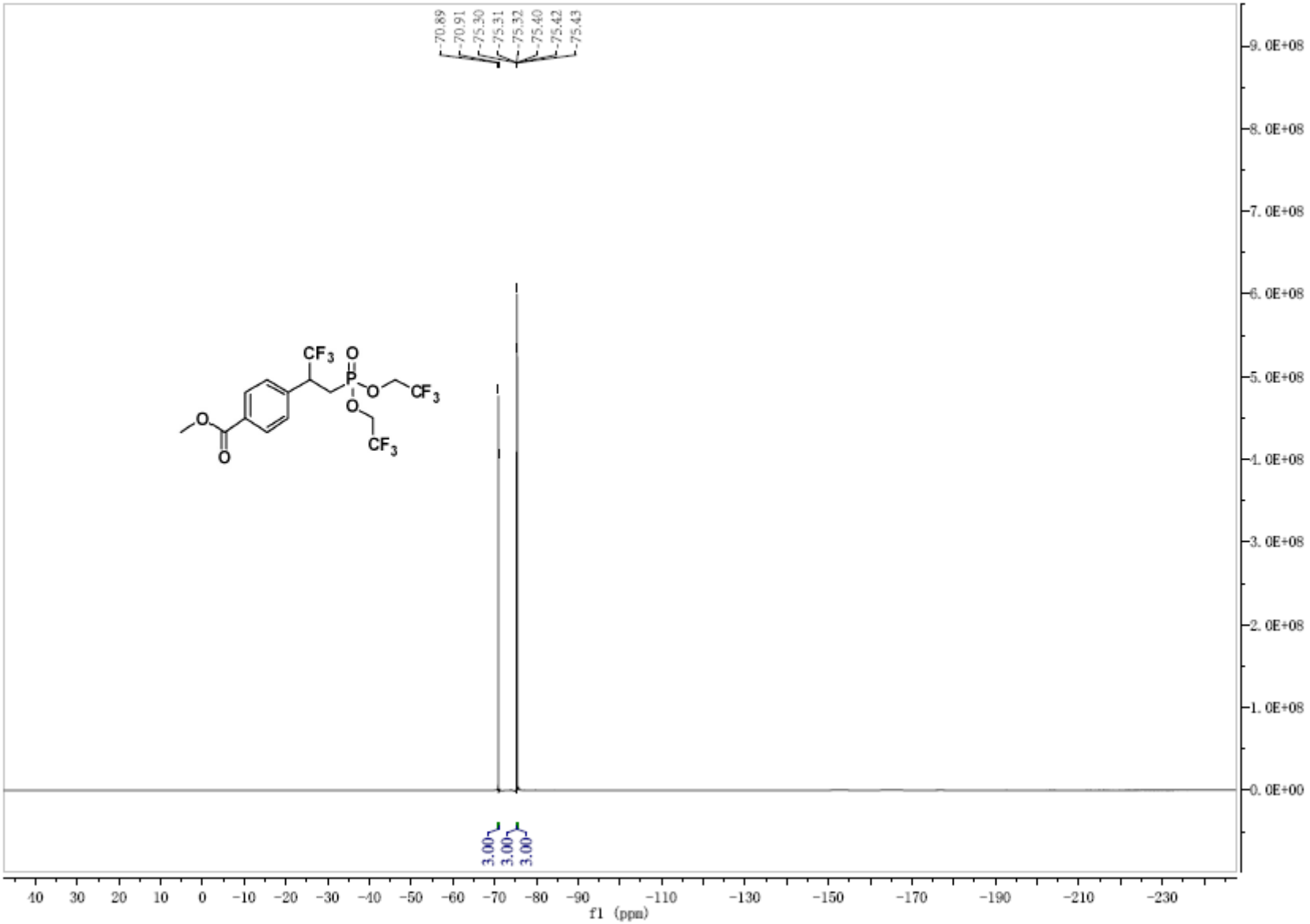
^{1}H NMR spectrum of 3hg



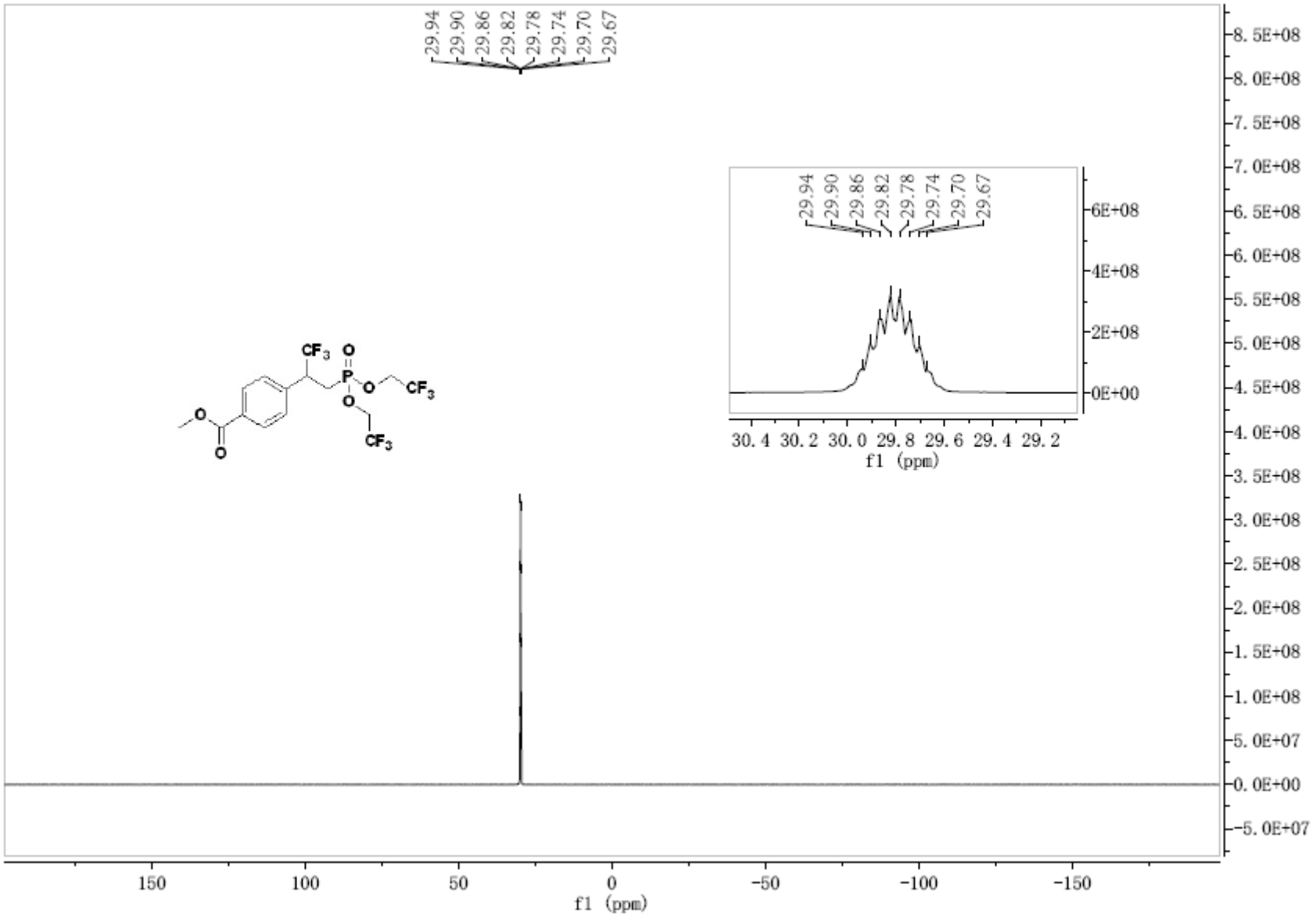
^{13}C NMR spectrum of 3hg



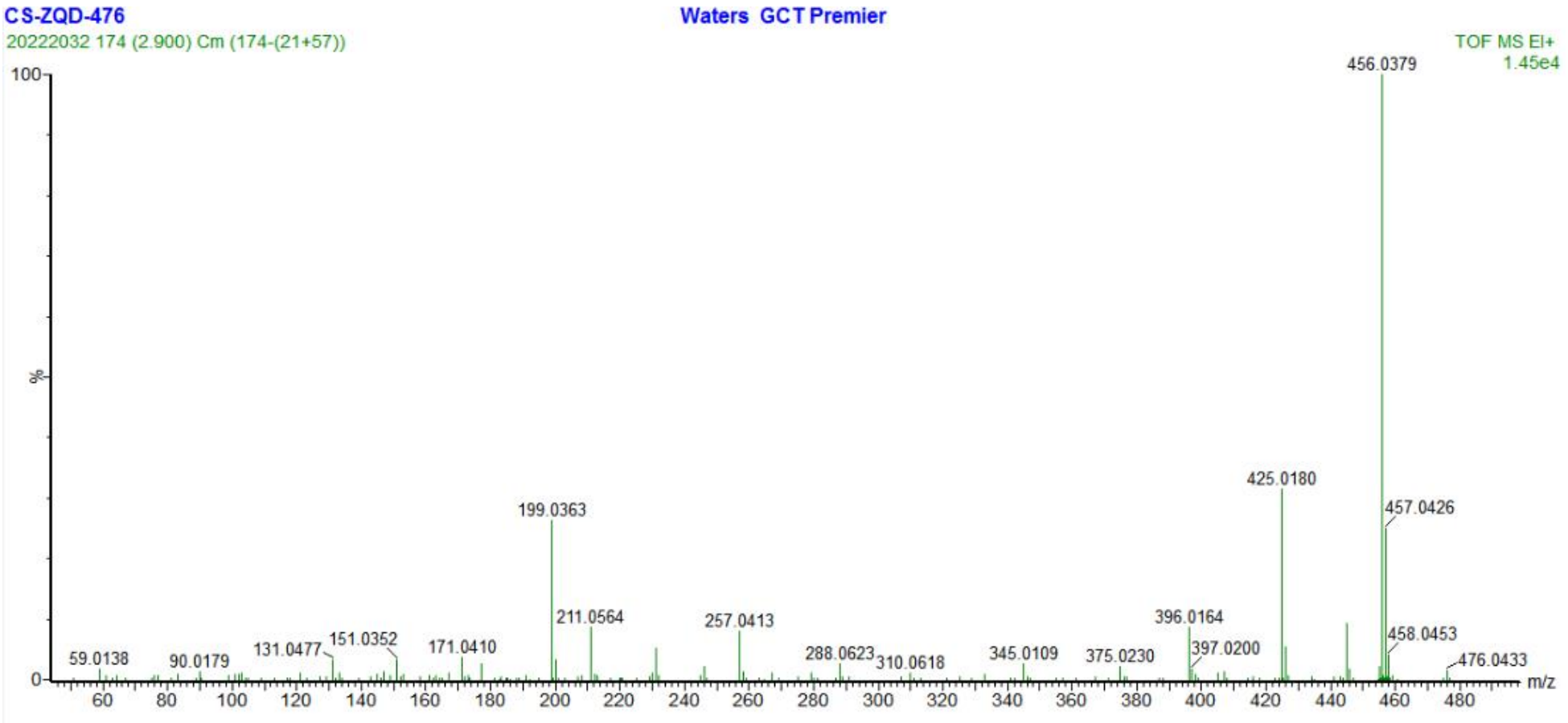
^{19}F NMR spectrum of 3hg



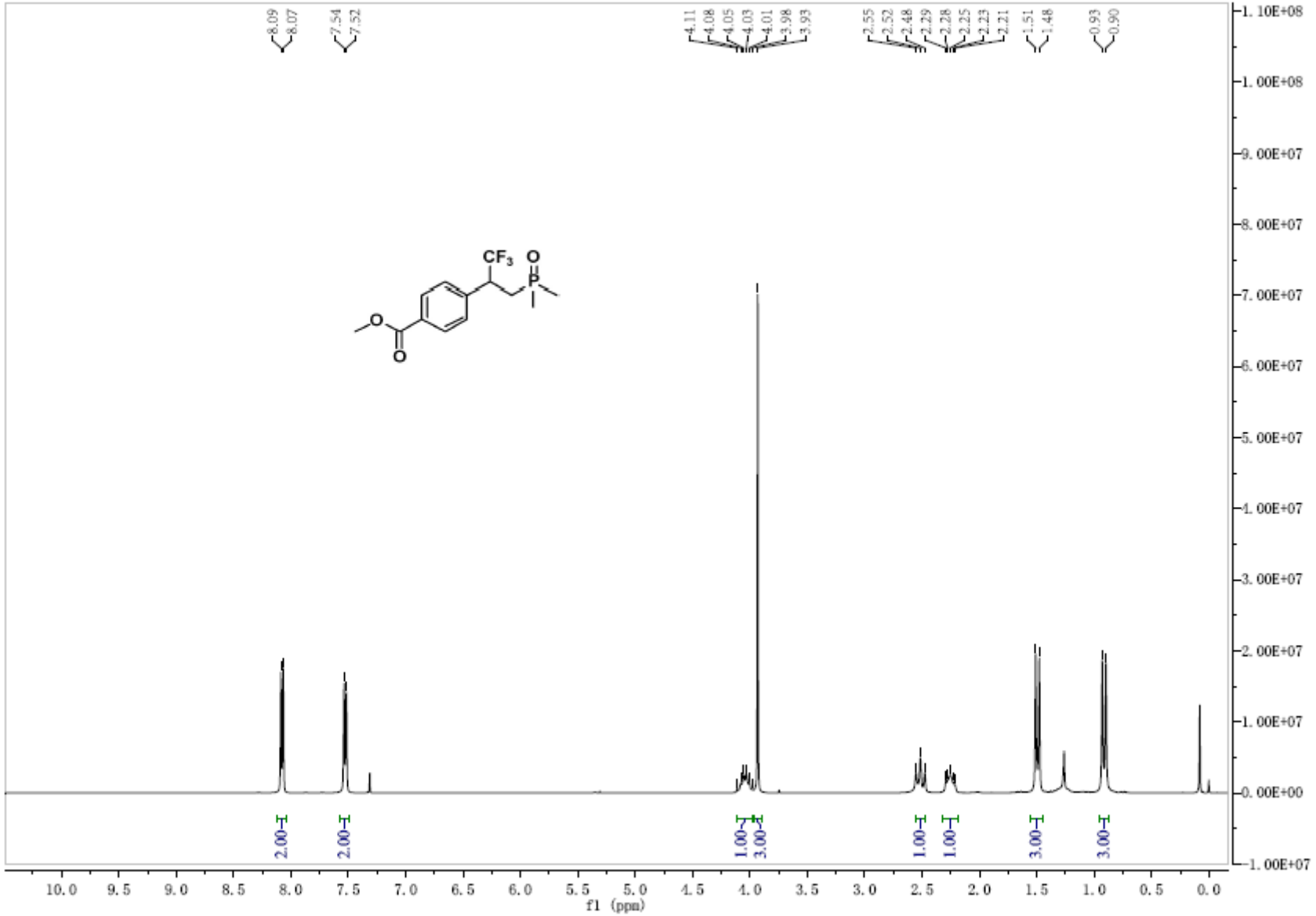
^{31}P NMR spectrum of 3hg



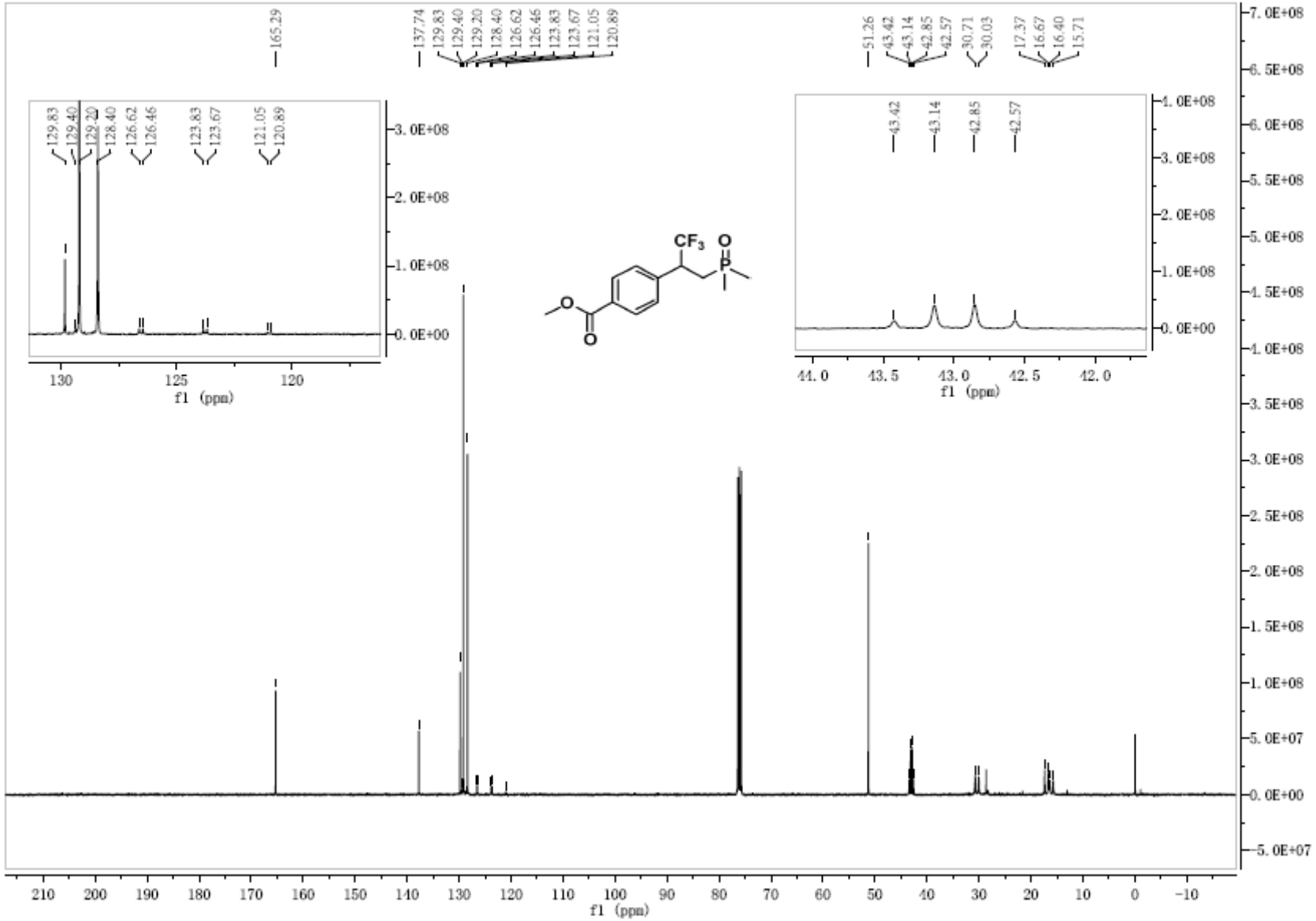
HRMS (EI) spectrum of 3hg



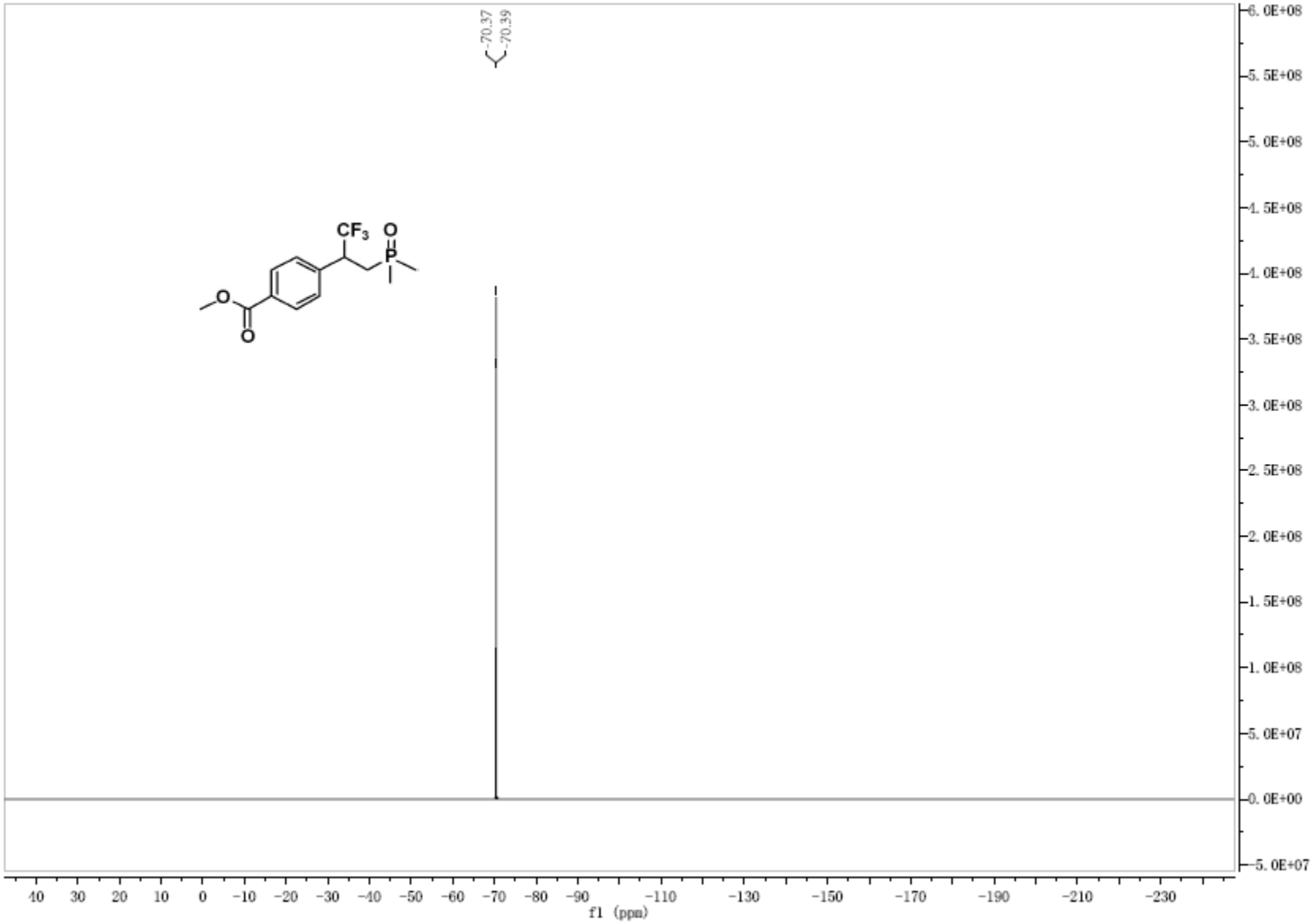
^{1}H NMR spectrum of 3hh



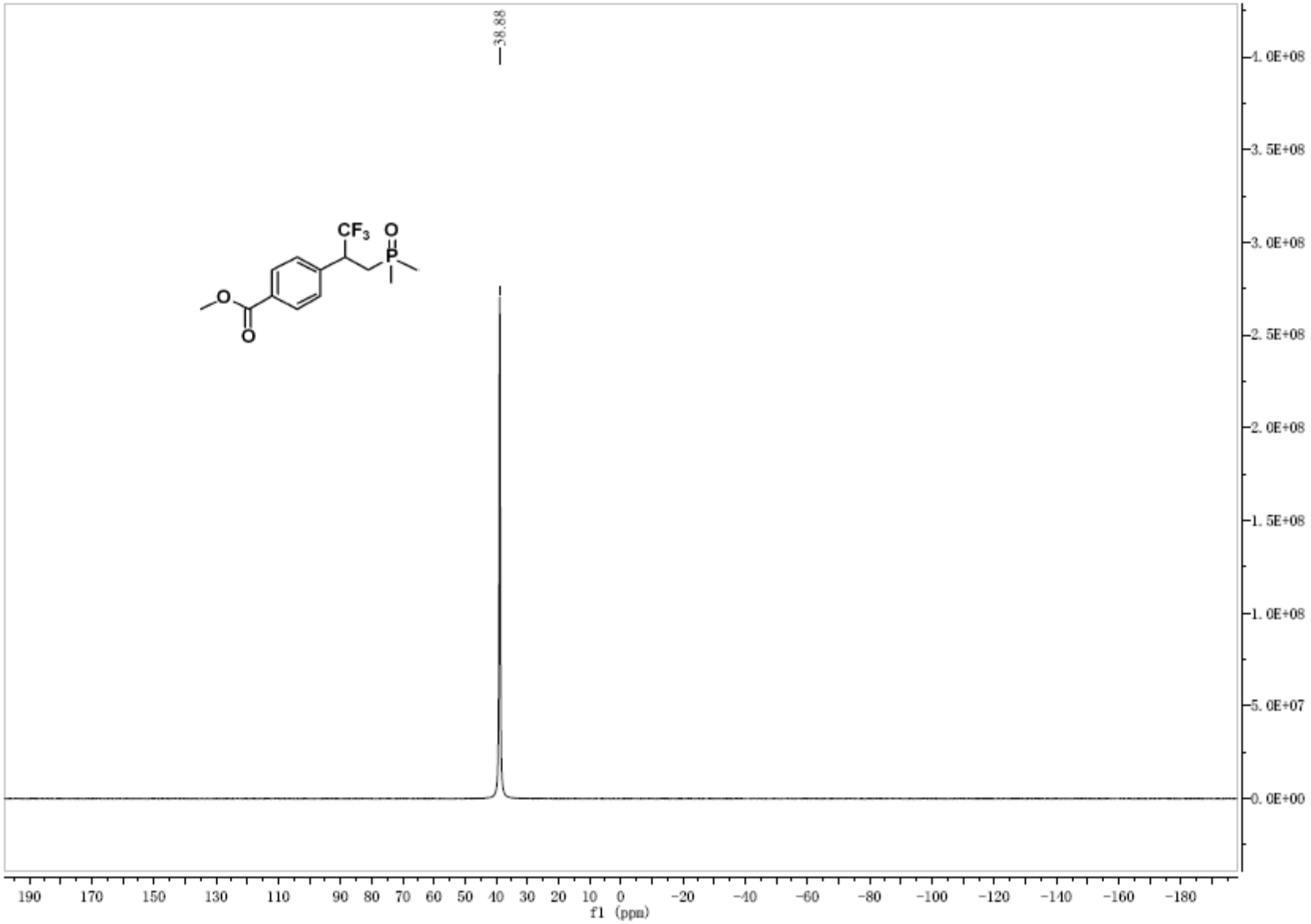
^{13}C NMR spectrum of 3hh



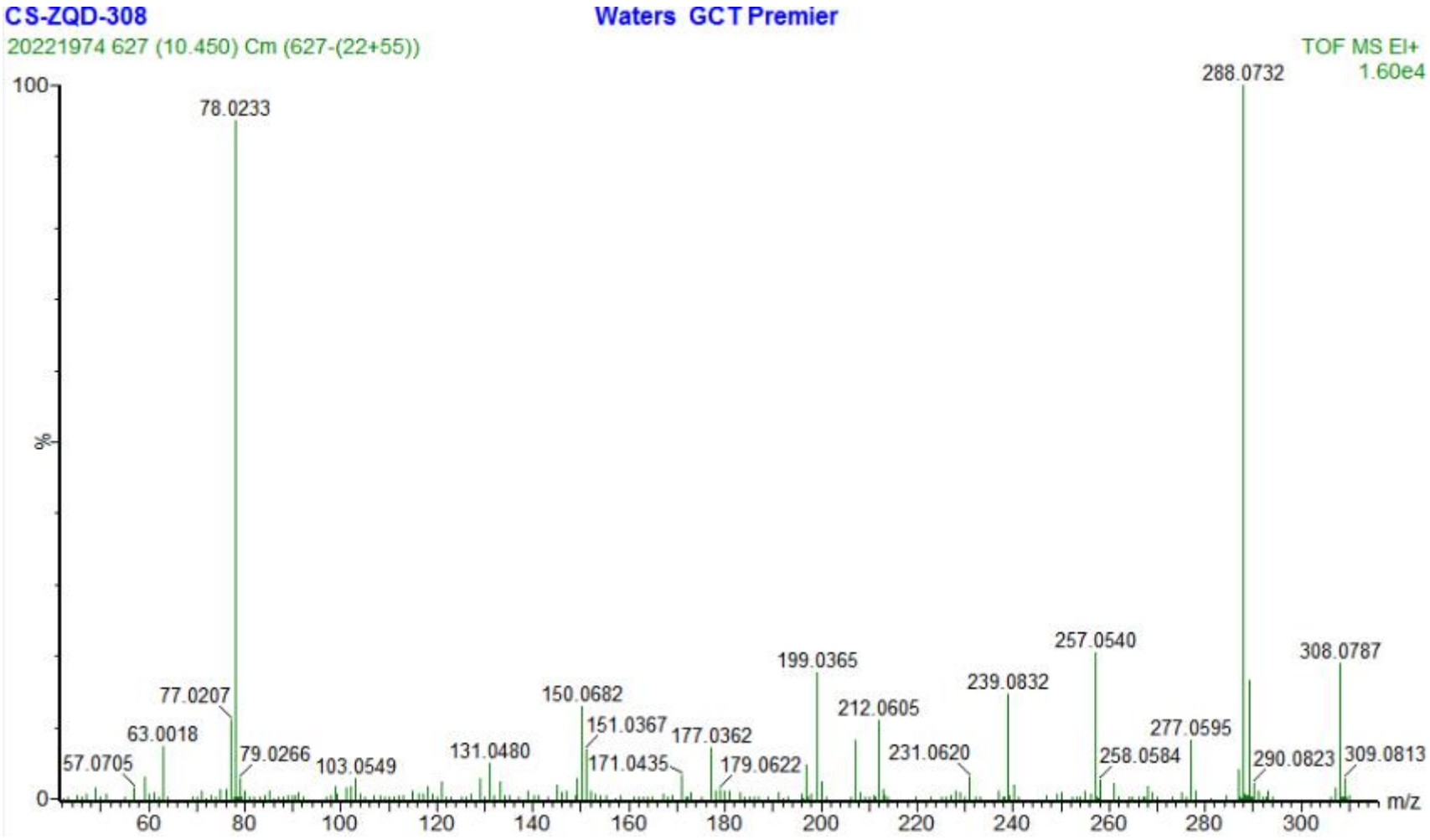
^{19}F NMR spectrum of 3hh



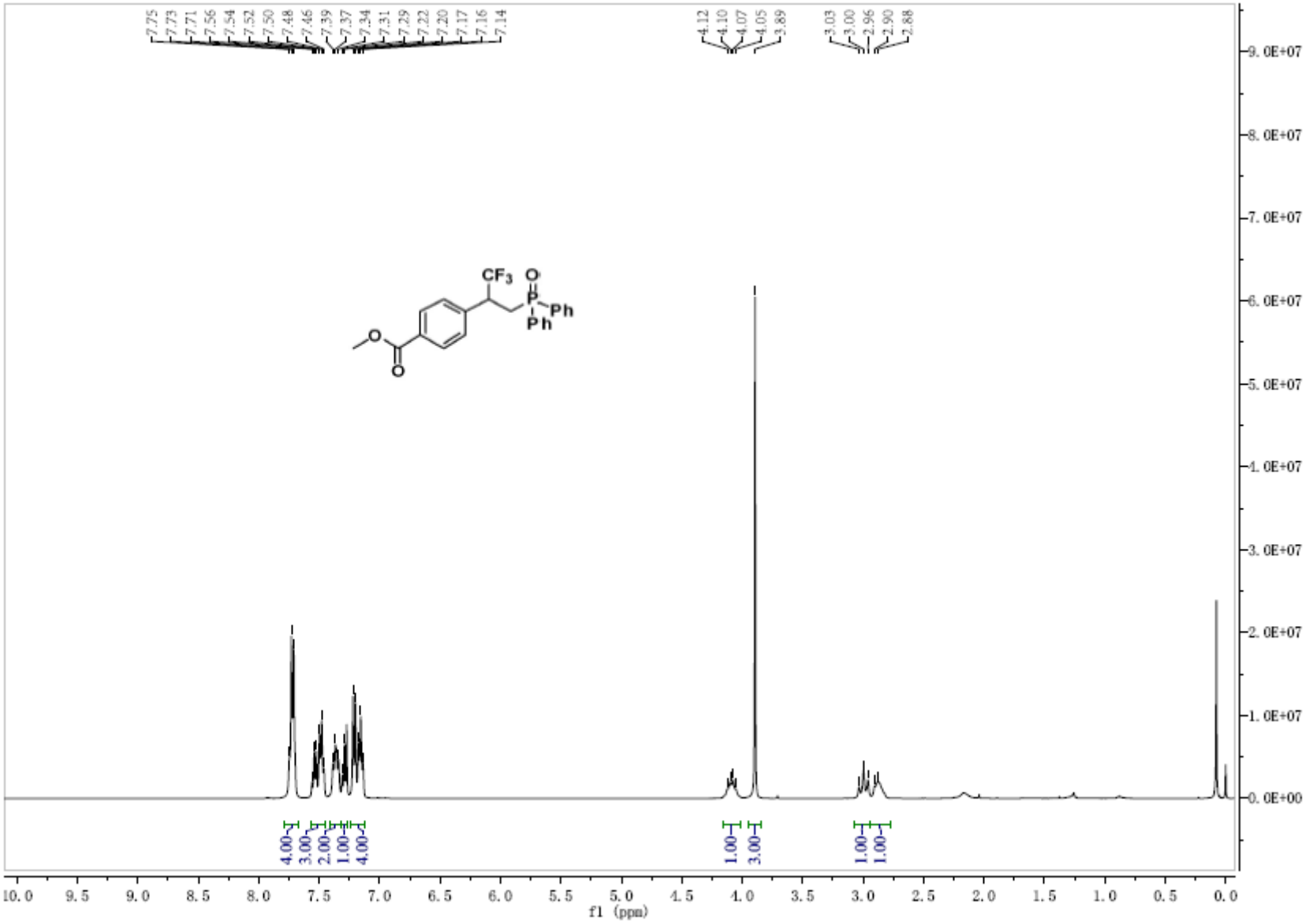
^{31}P NMR spectrum of 3hh



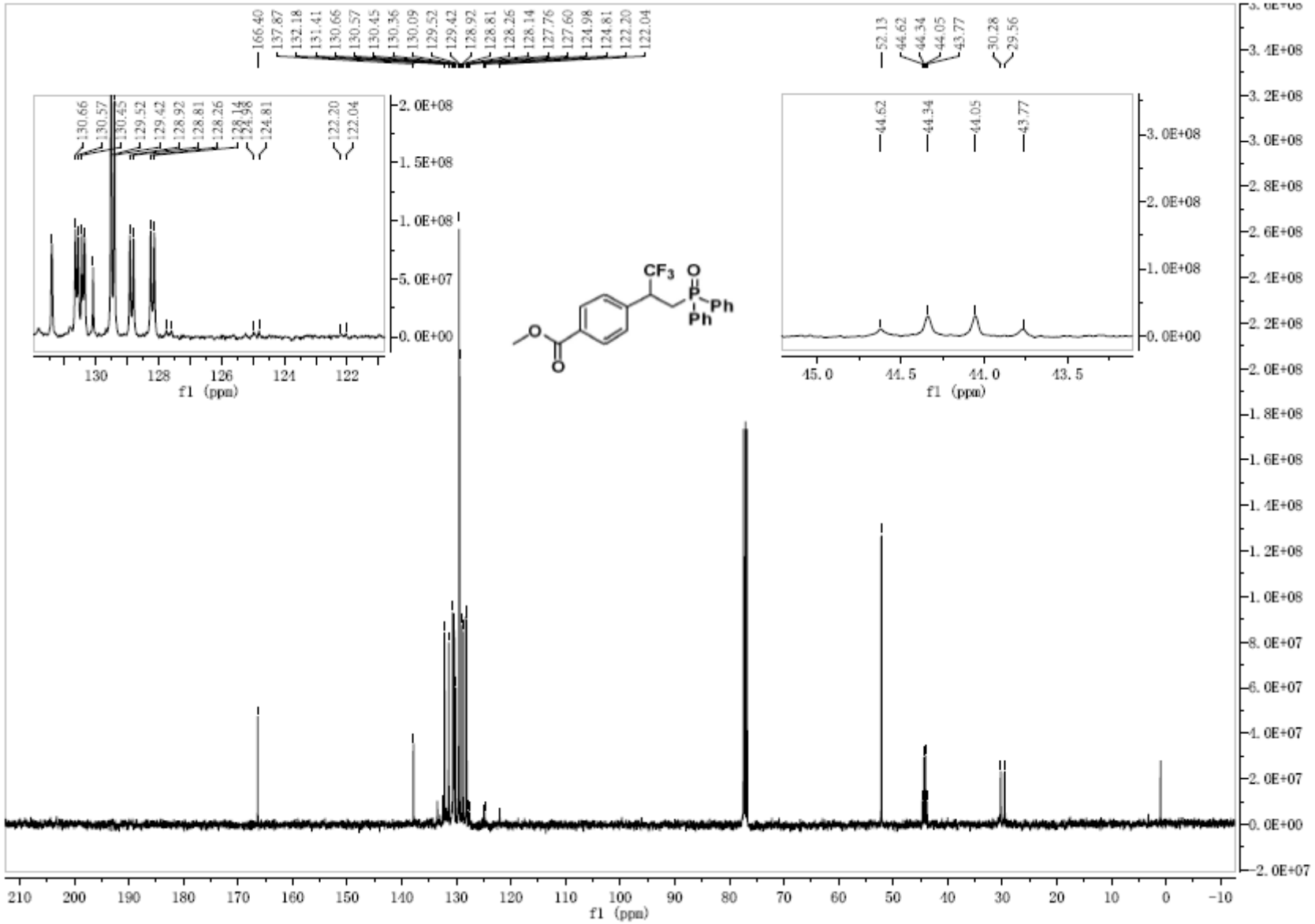
HRMS (EI) spectrum of 3hh



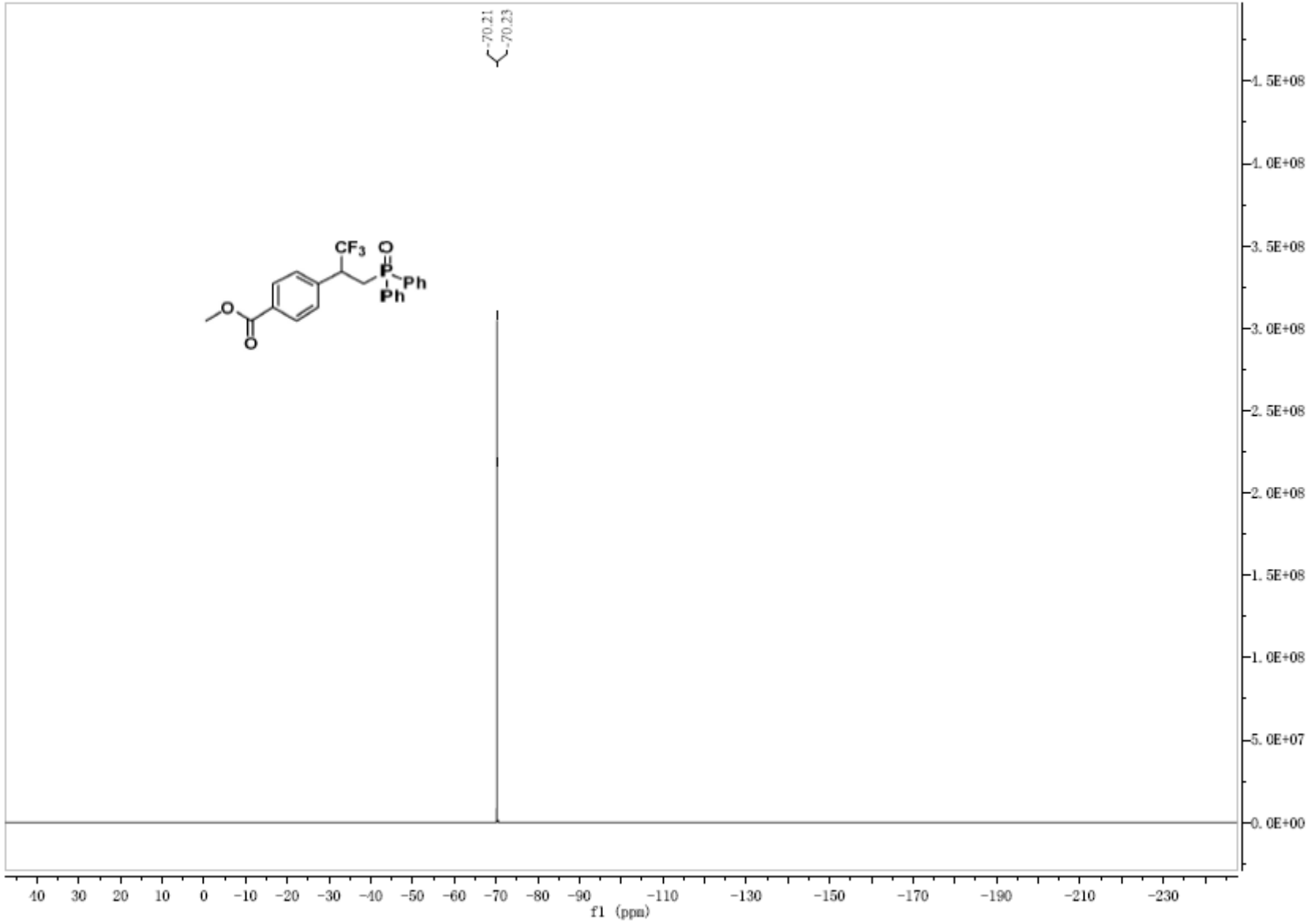
^{1}H NMR spectrum of 3hi



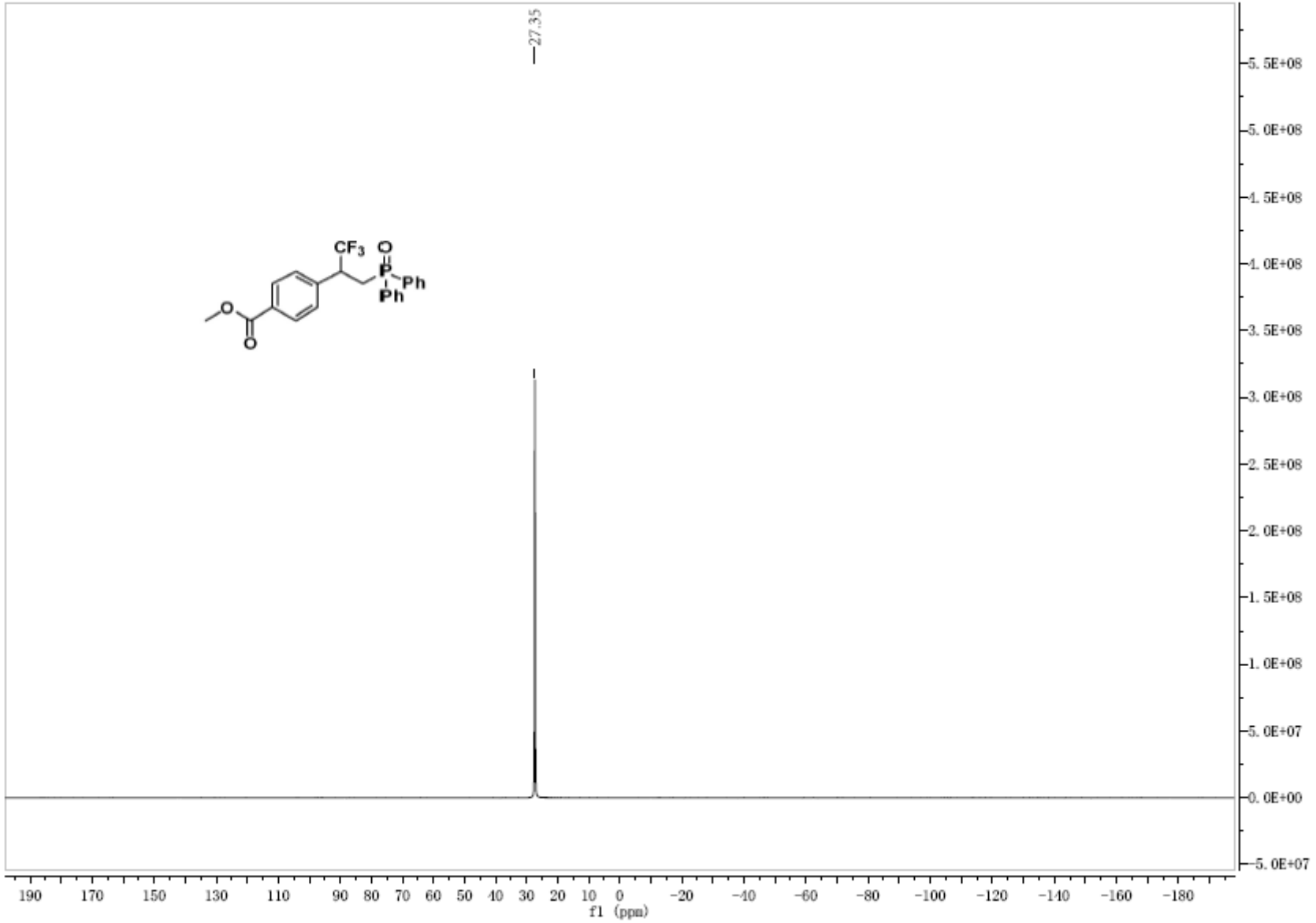
^{13}C NMR spectrum of 3hi



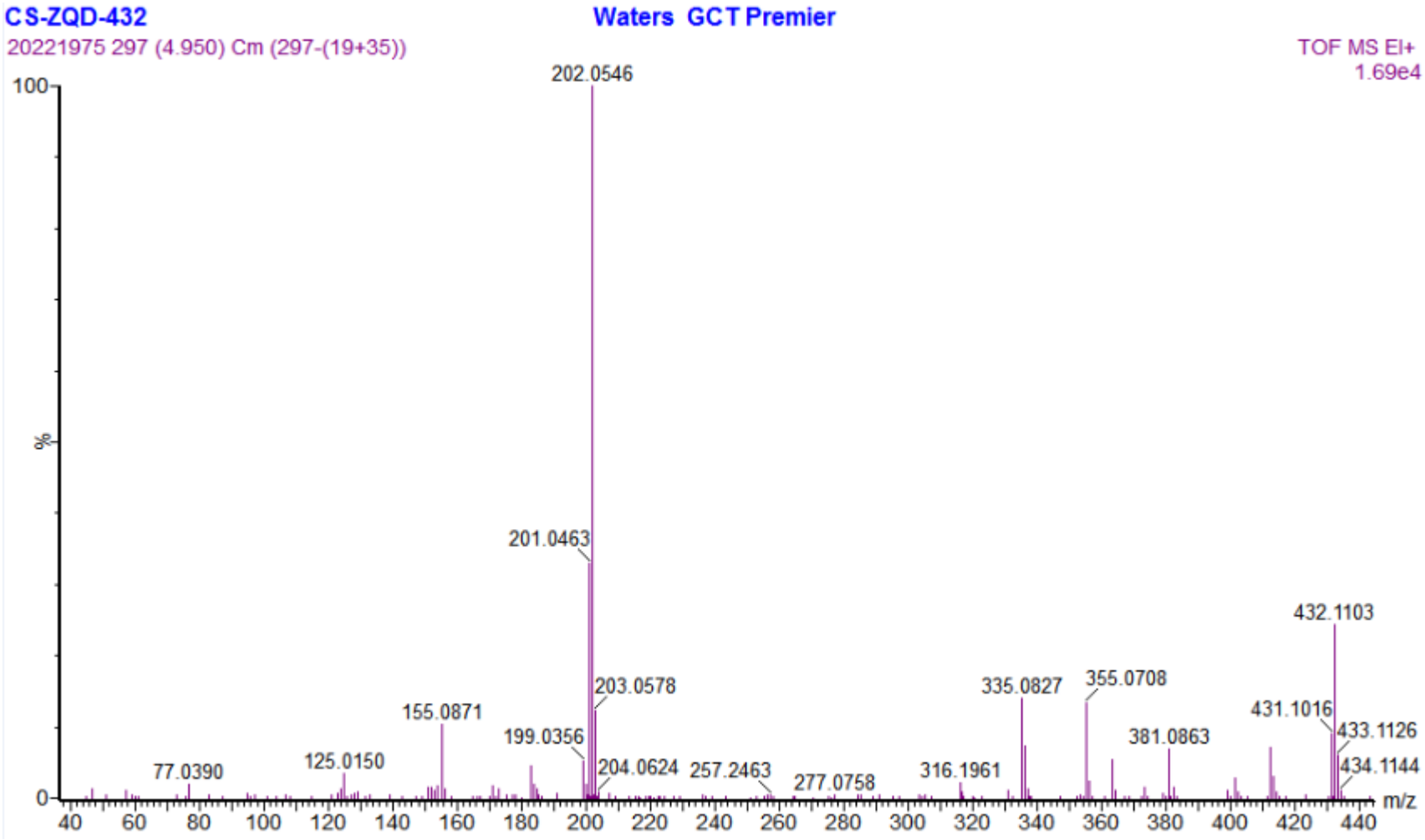
^{19}F NMR spectrum of 3hi



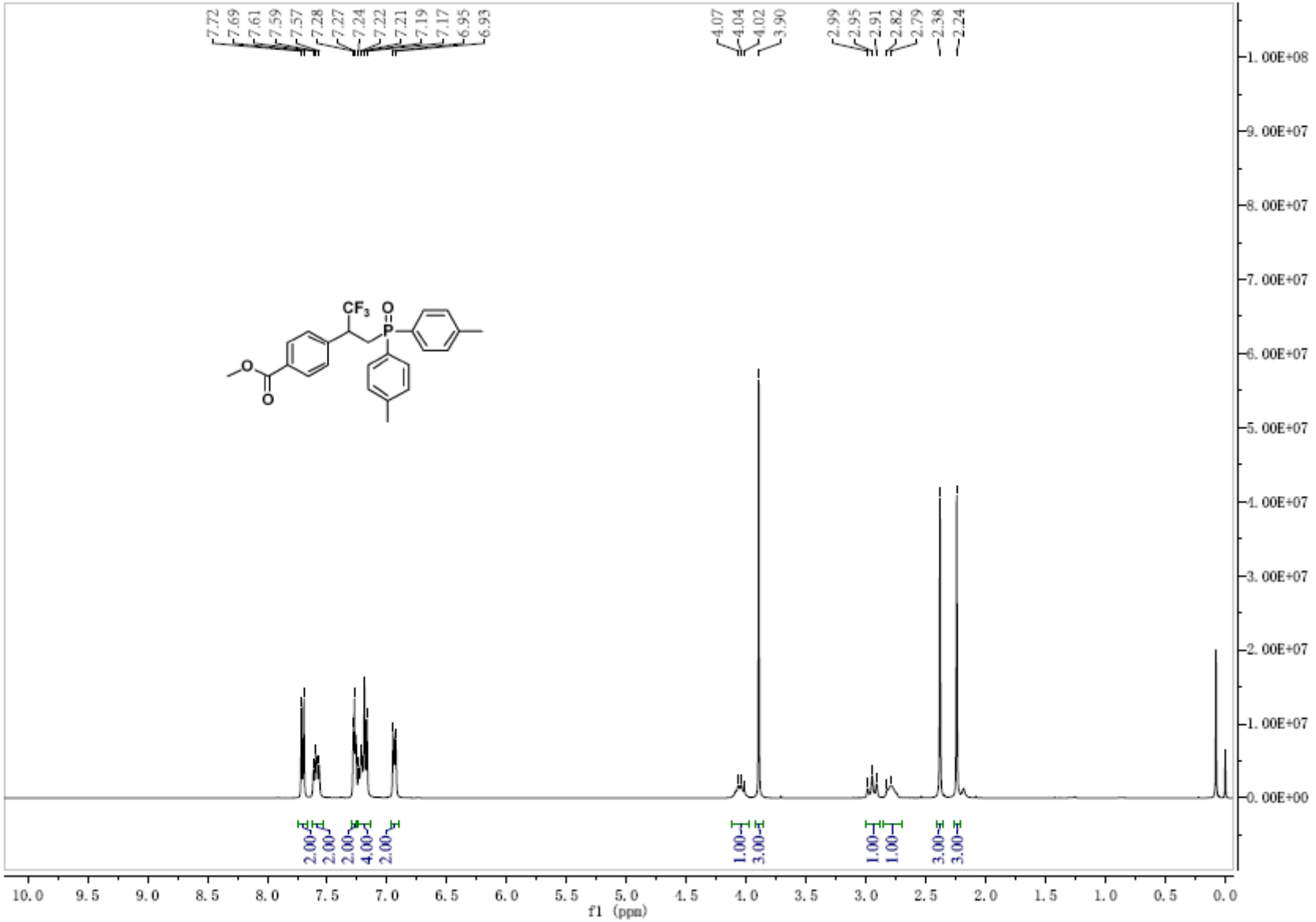
^{31}P NMR spectrum of 3hi



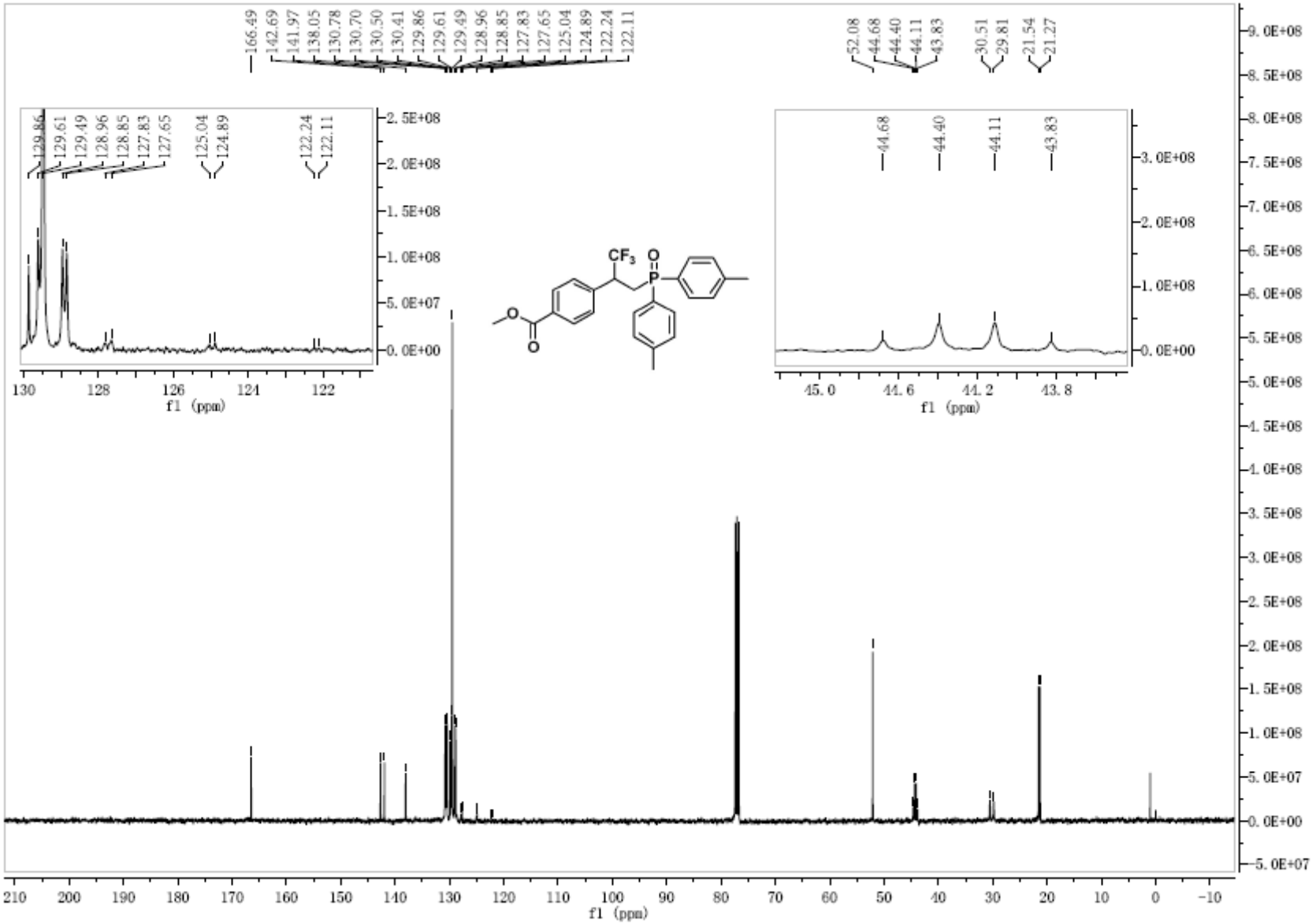
HRMS (EI) spectrum of 3hi



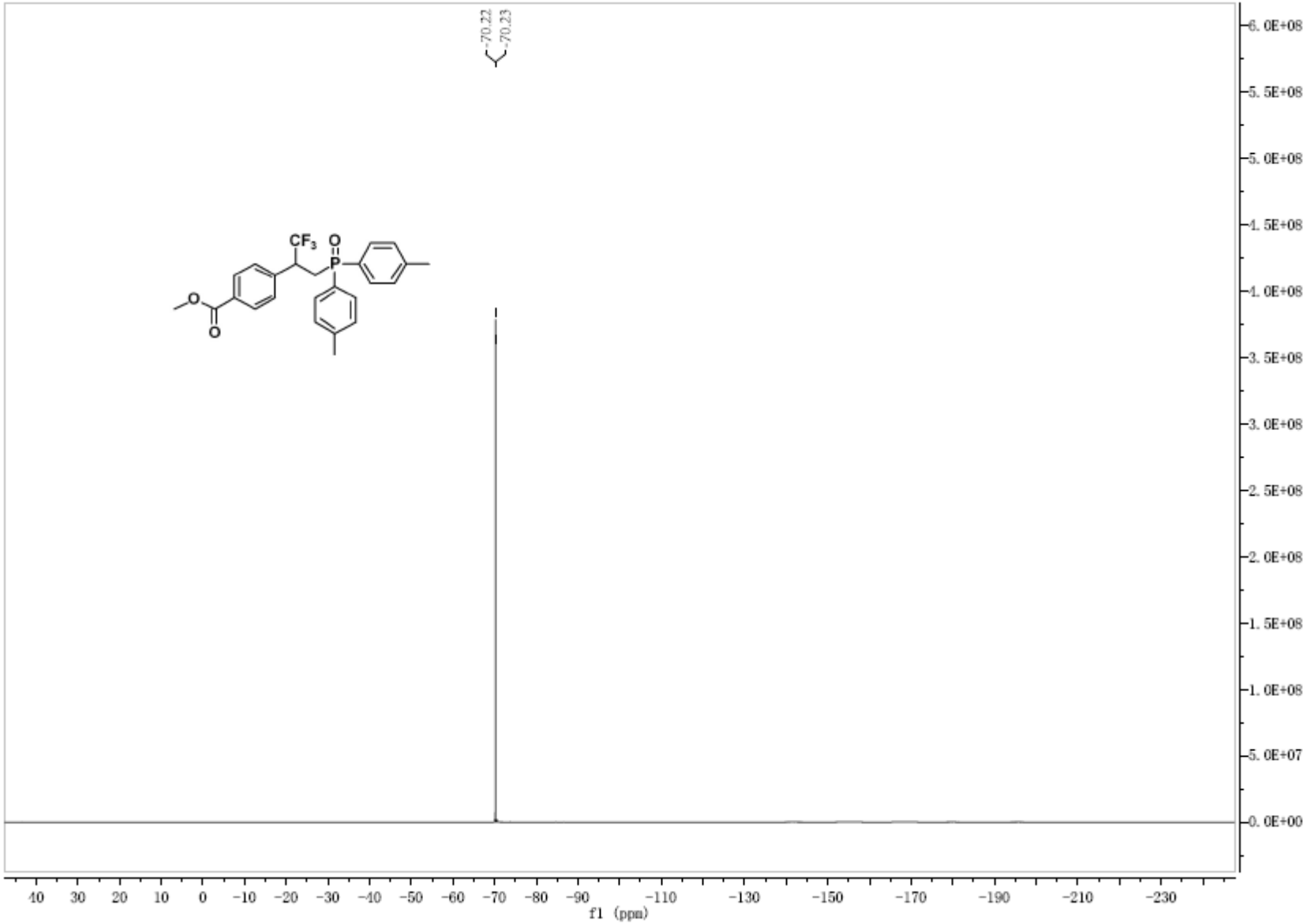
^{1}H NMR spectrum of 3hj



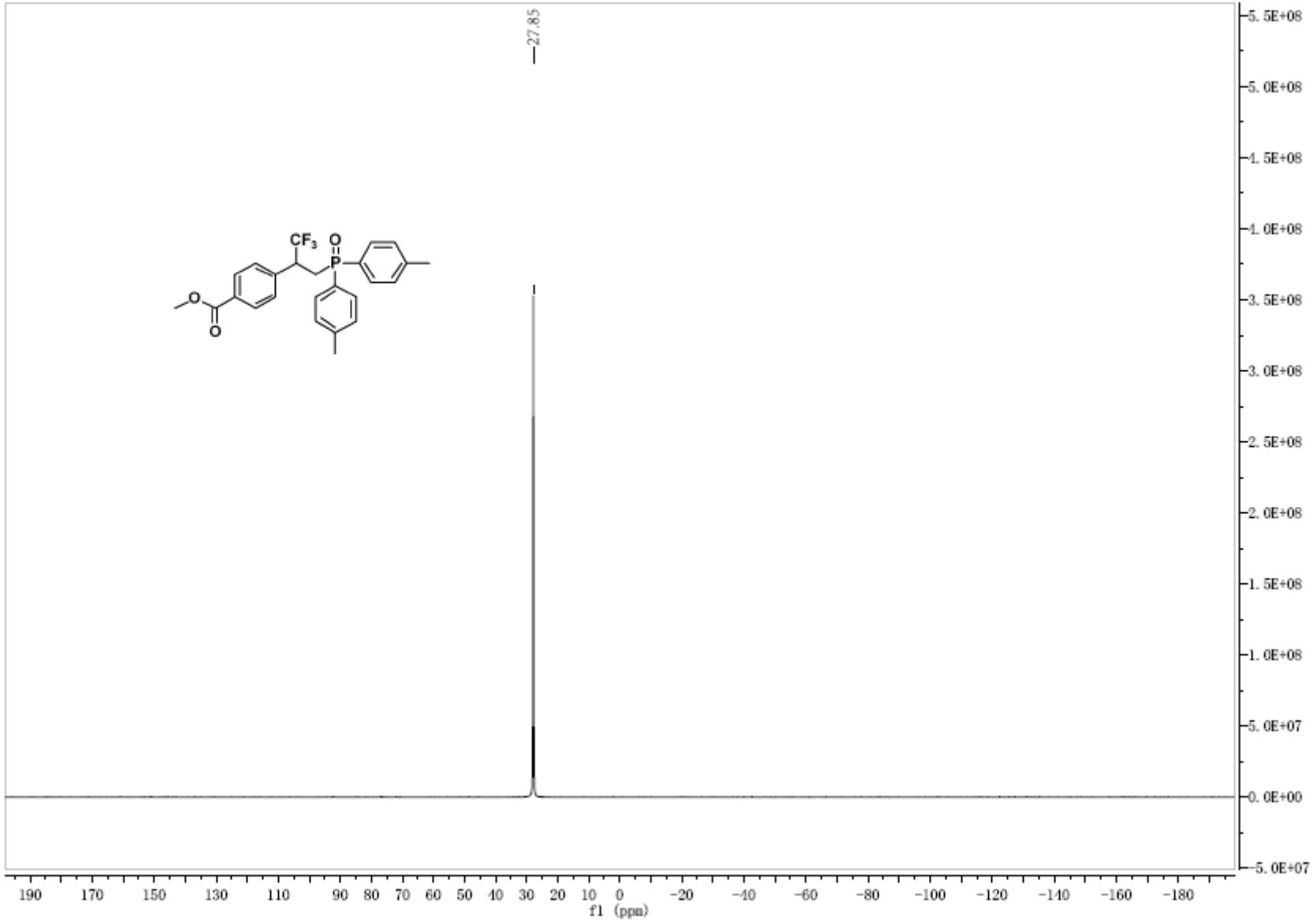
^{13}C NMR spectrum of 3hj



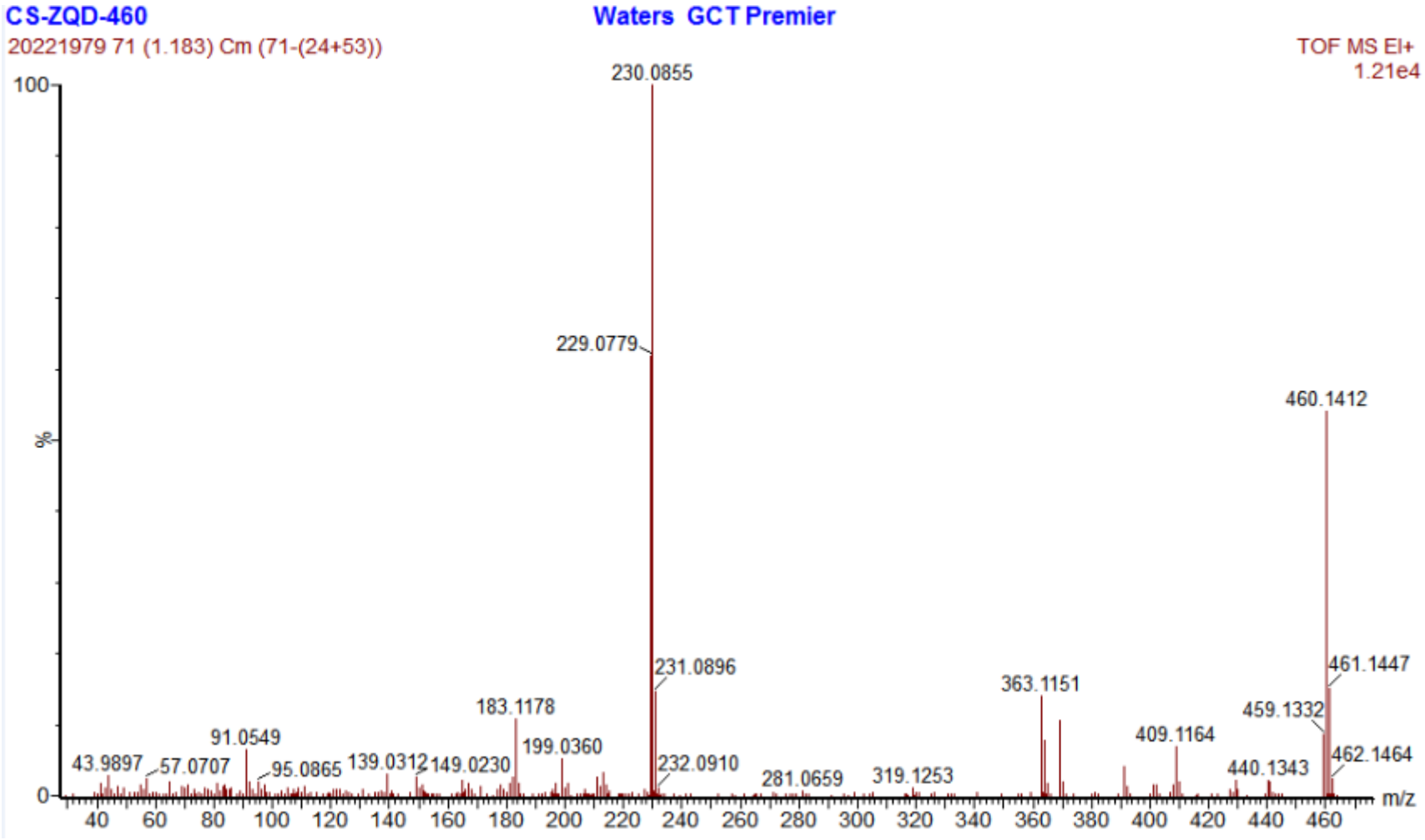
^{19}F NMR spectrum of 3hj



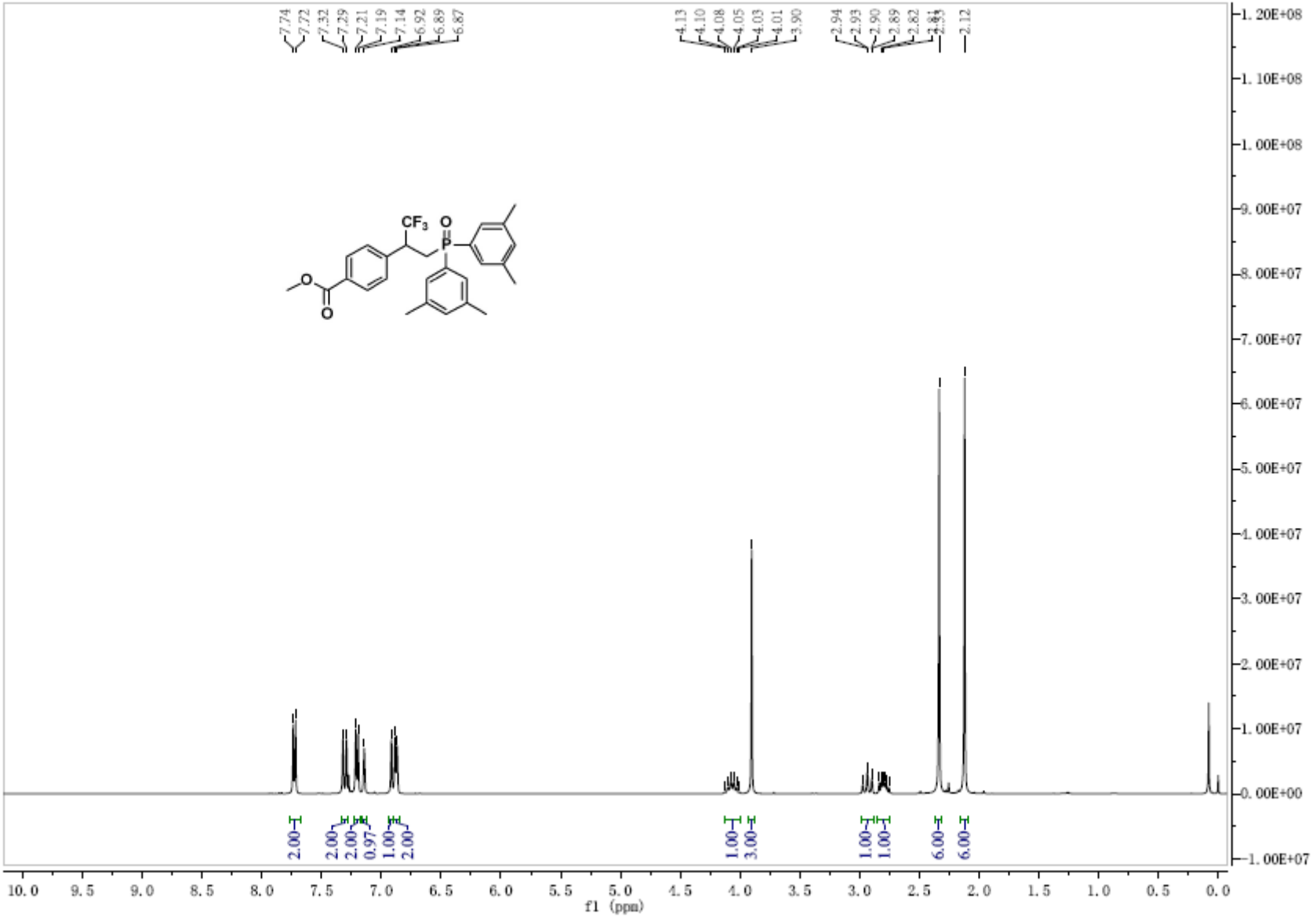
^{31}P NMR spectrum of 3hj



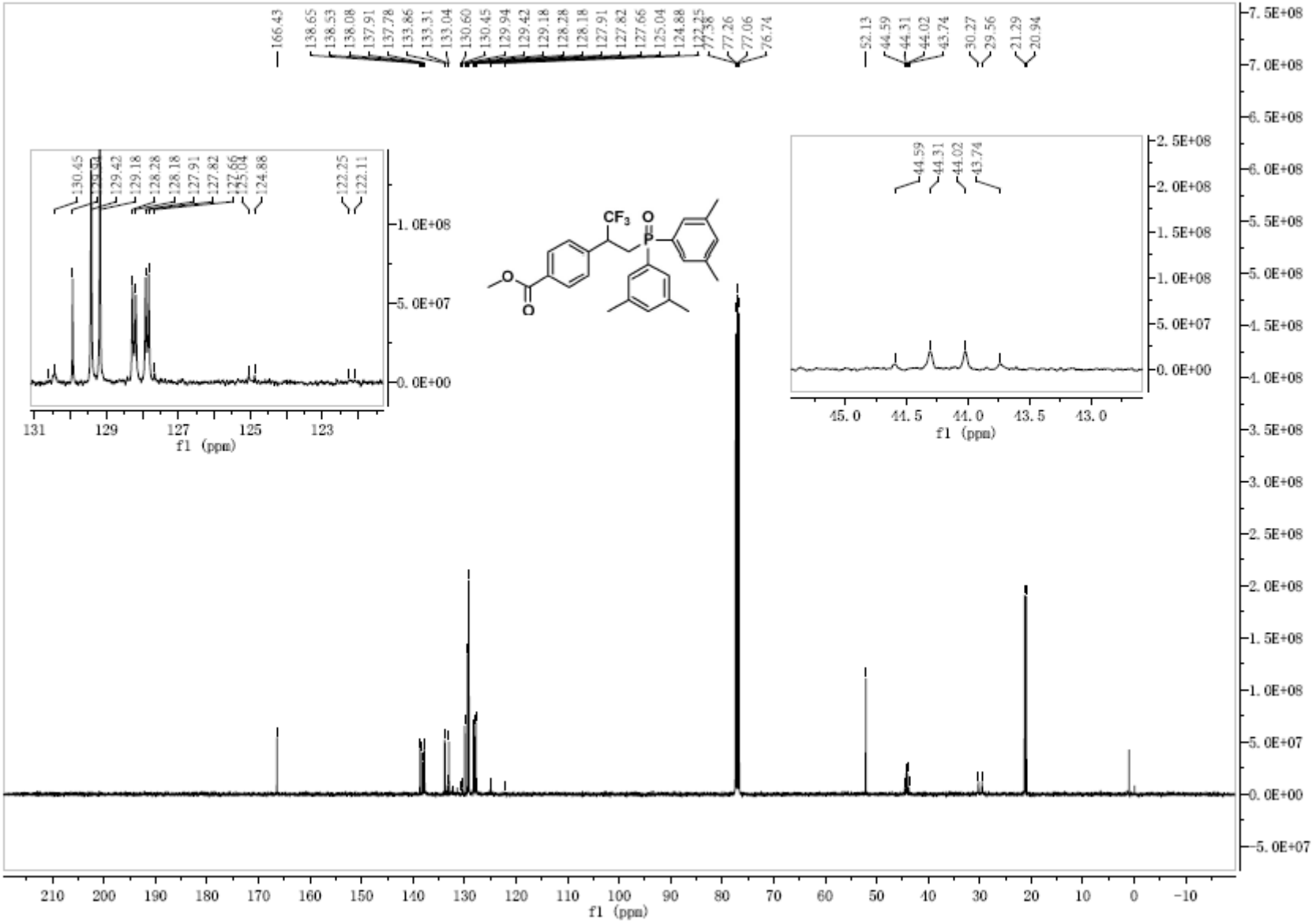
HRMS (EI) spectrum of 3hj



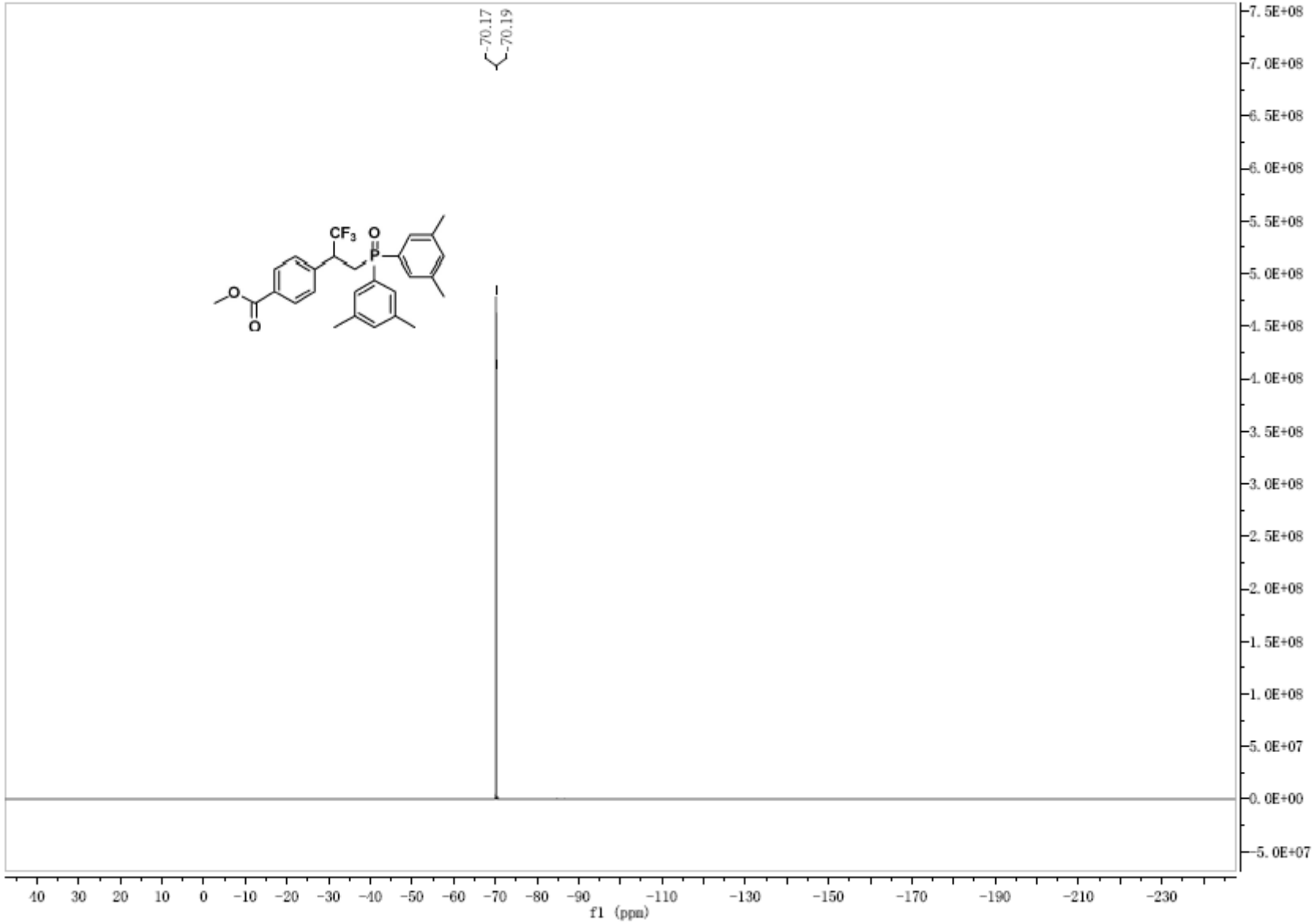
^{1}H NMR spectrum of 3hk



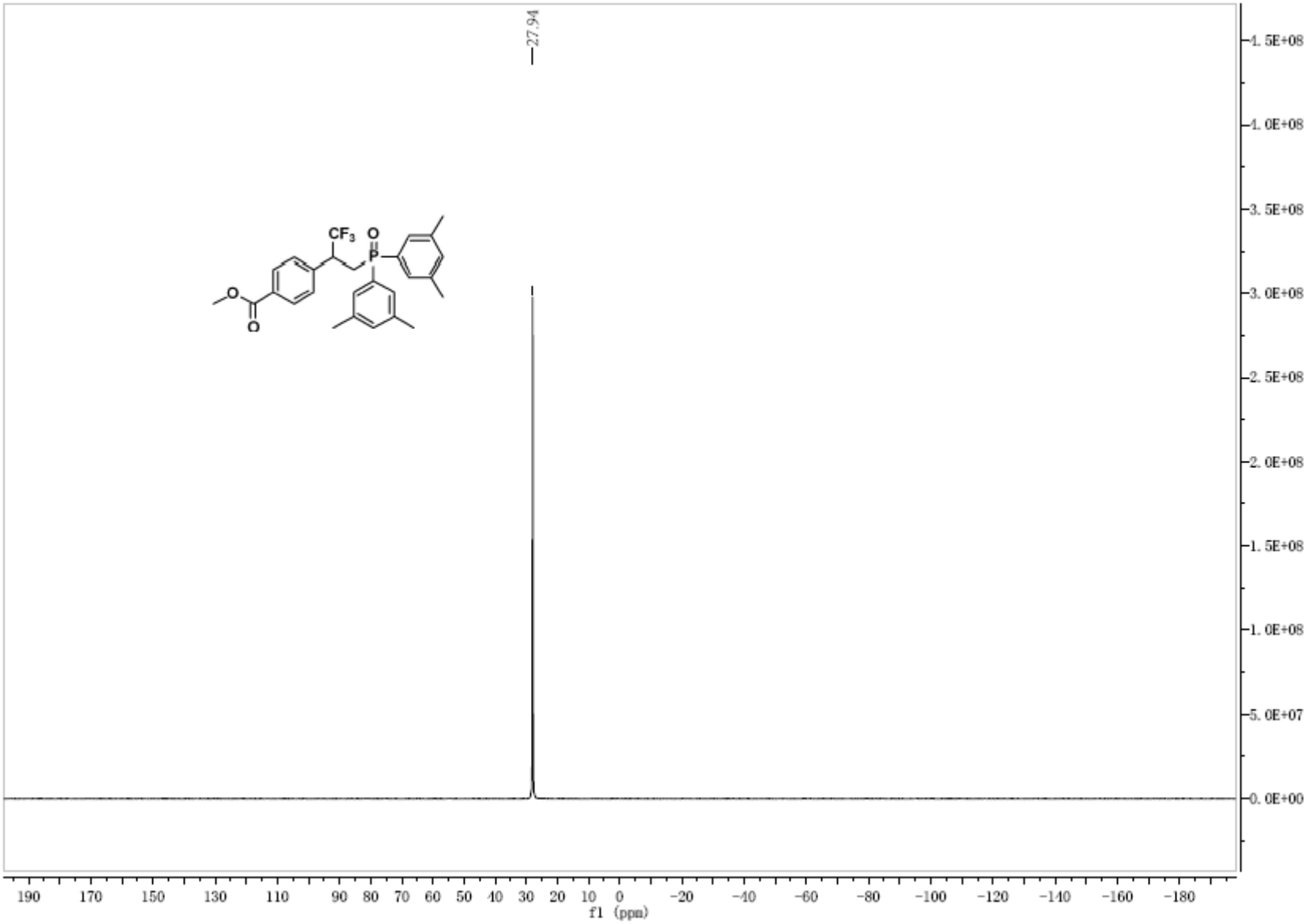
^{13}C NMR spectrum of 3hk



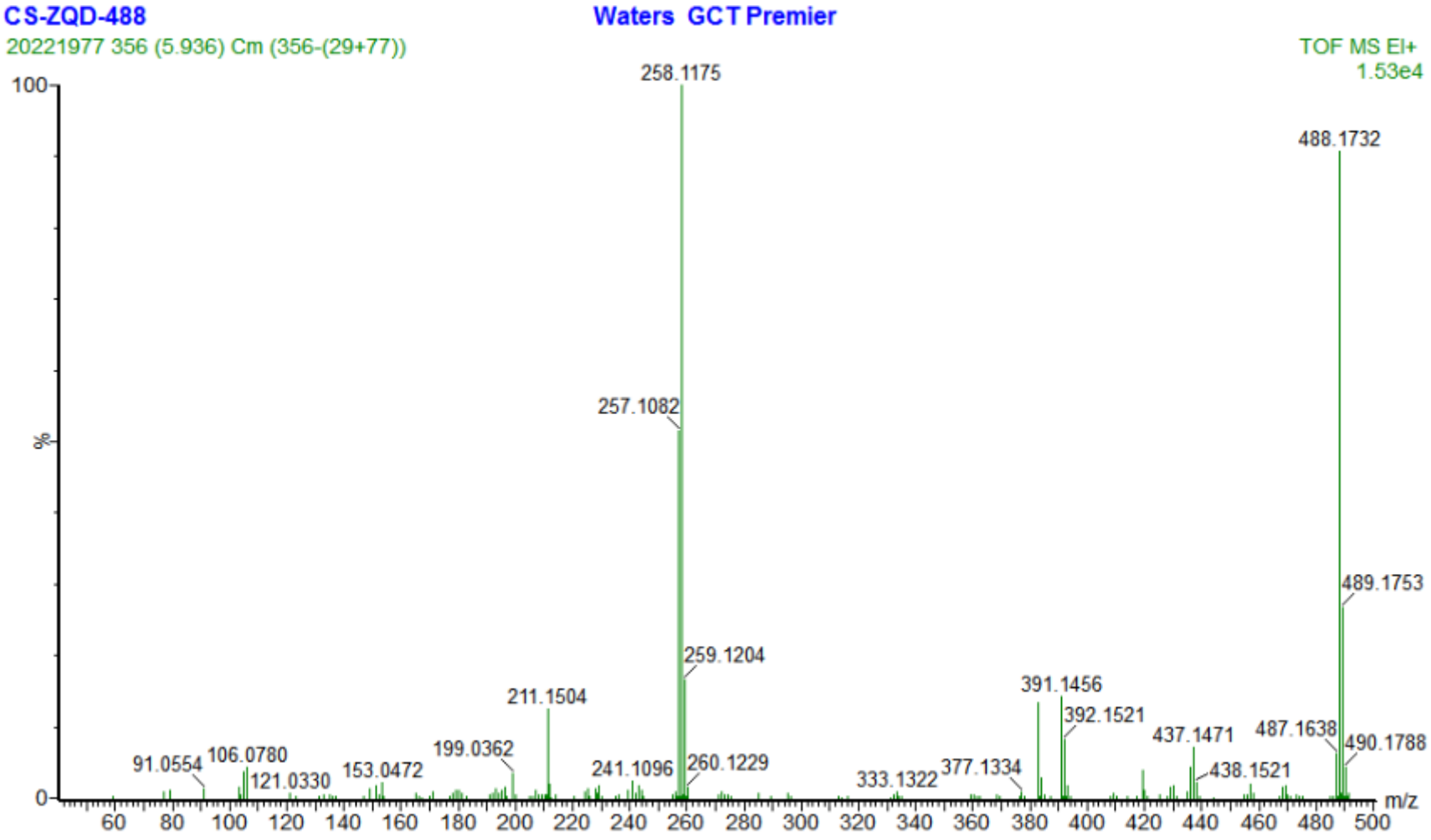
^{19}F NMR spectrum of 3hk



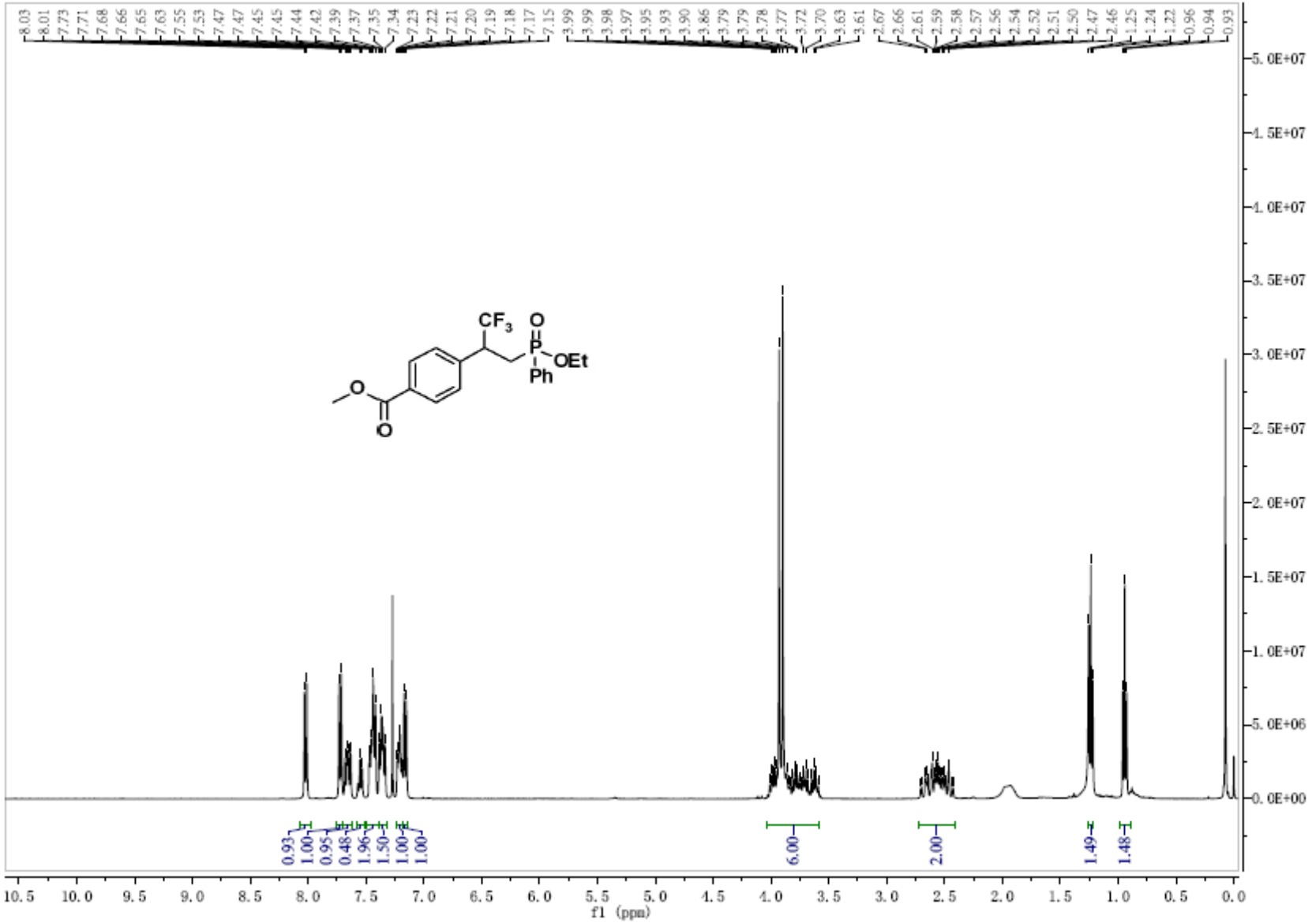
^{31}P NMR spectrum of 3hk



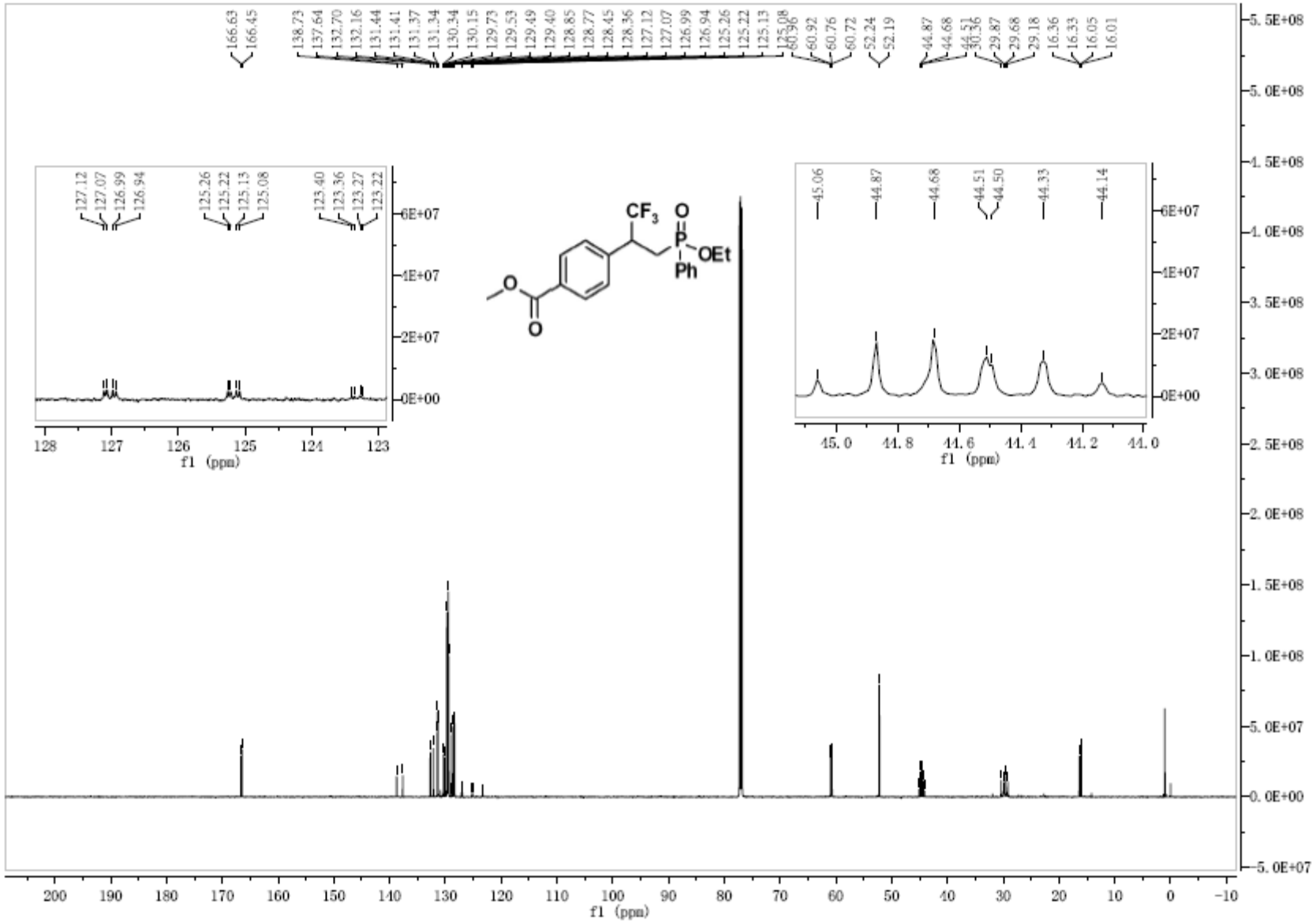
HRMS (EI) spectrum of 3hk



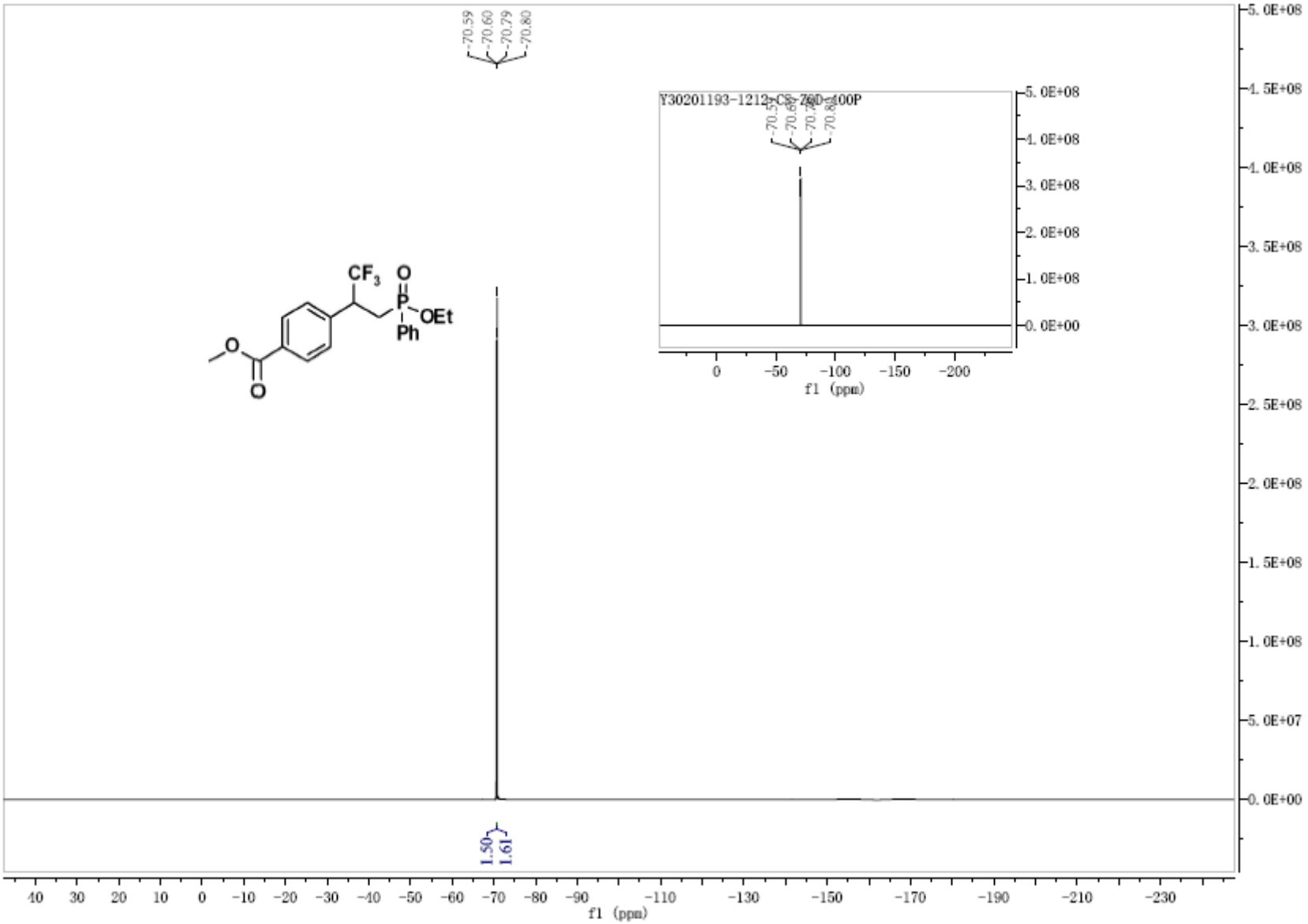
^{1}H NMR spectrum of 3hl



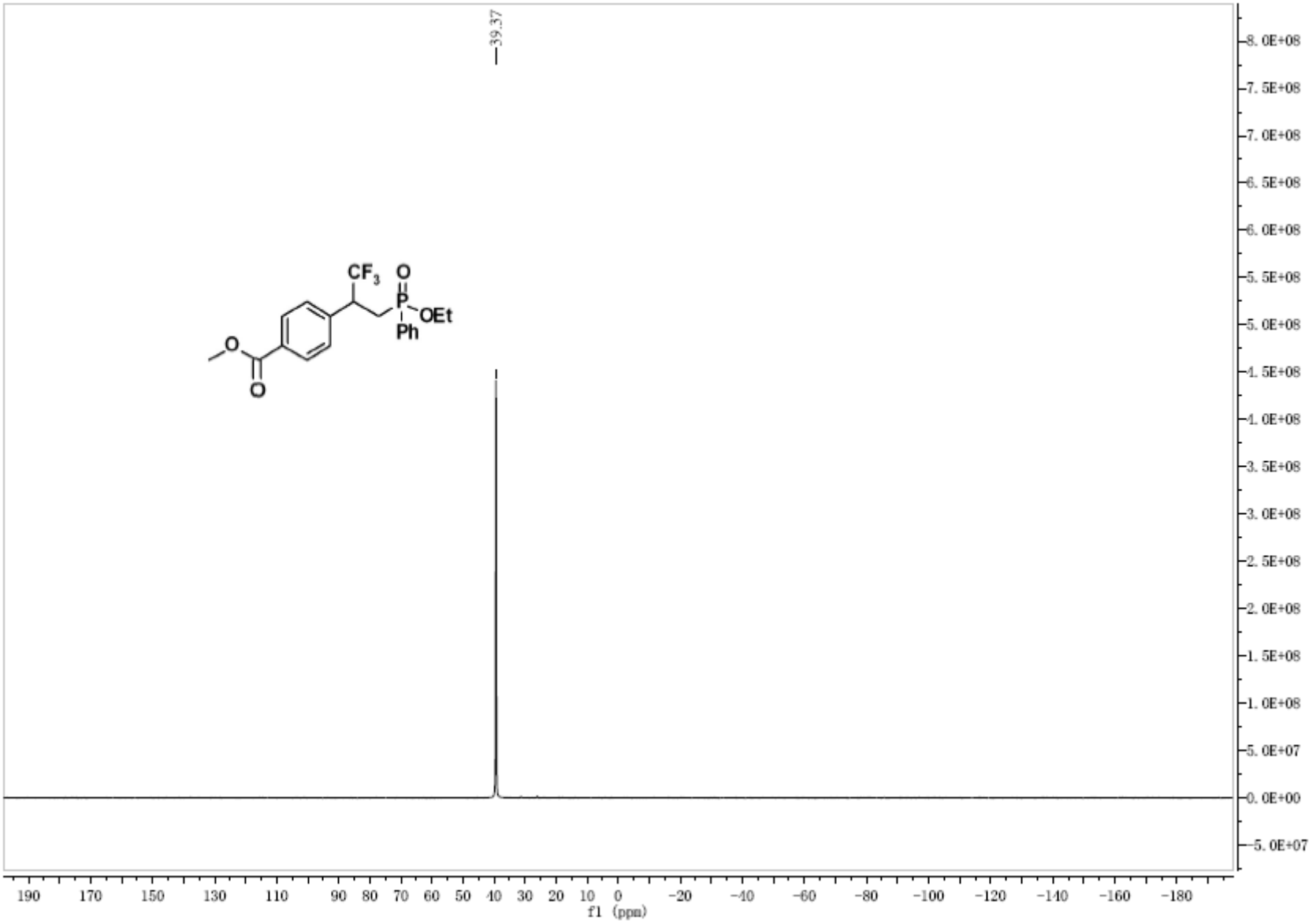
^{13}C NMR spectrum of 3hl



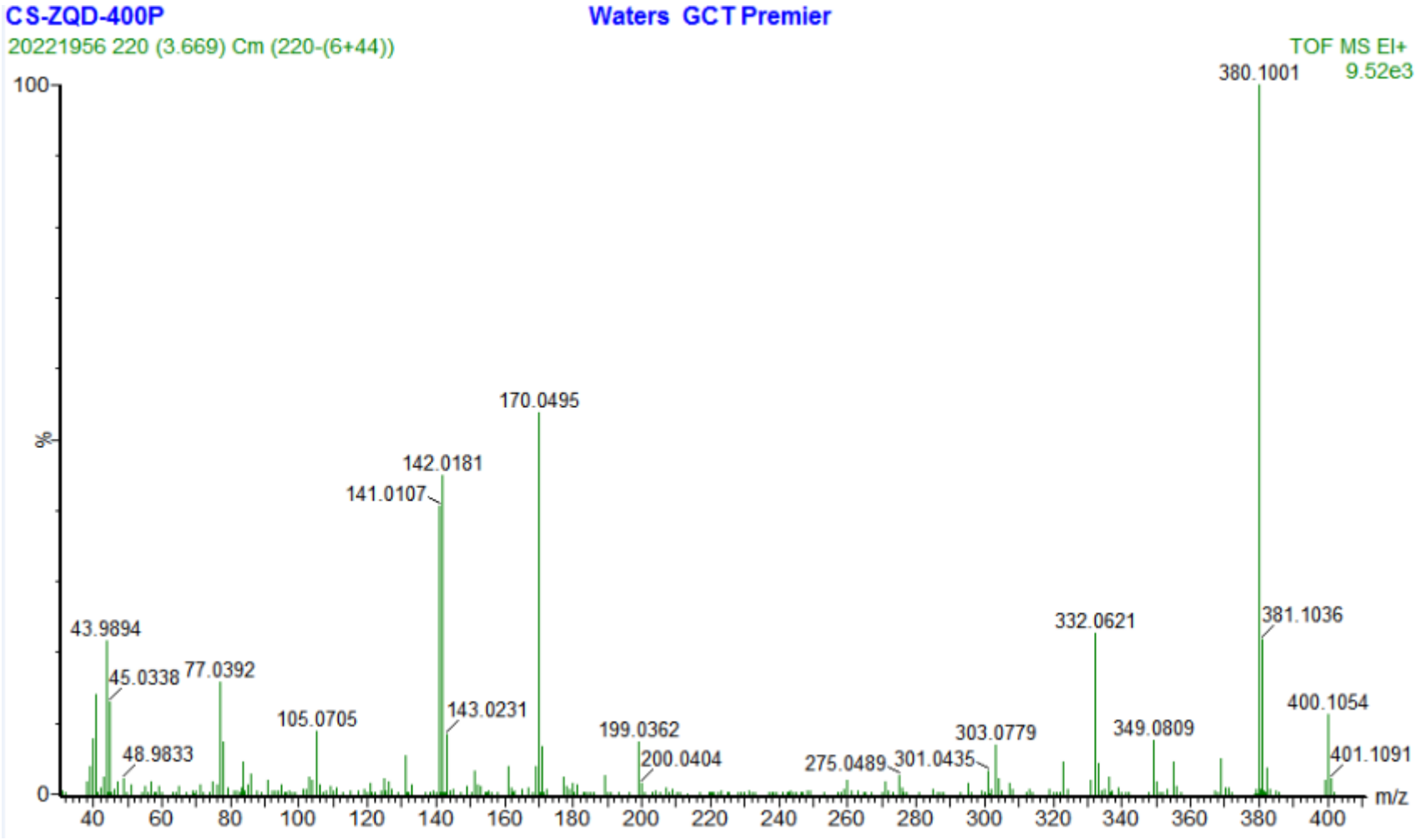
^{19}F NMR spectrum of 3hl



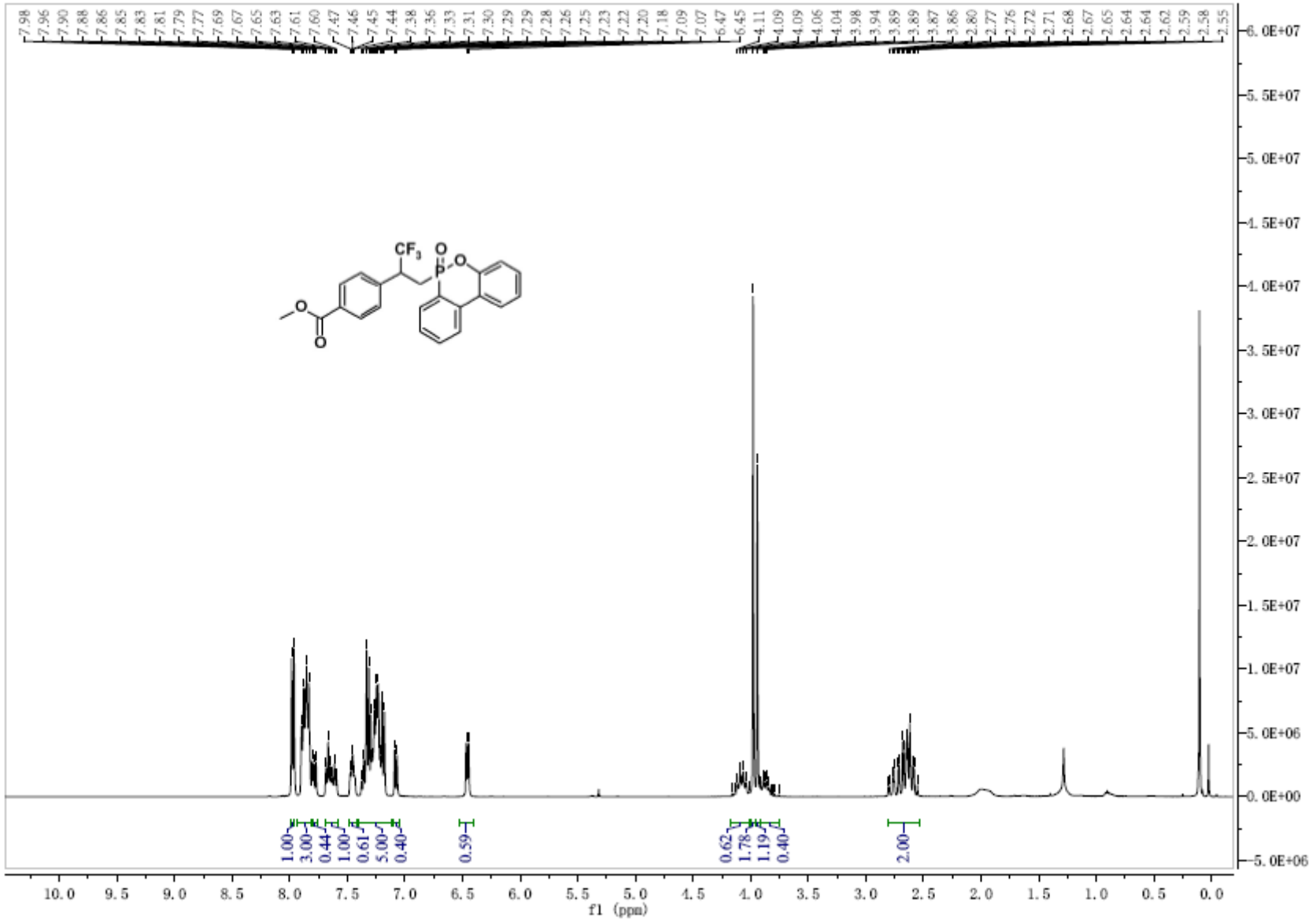
^{31}P NMR spectrum of 3hl



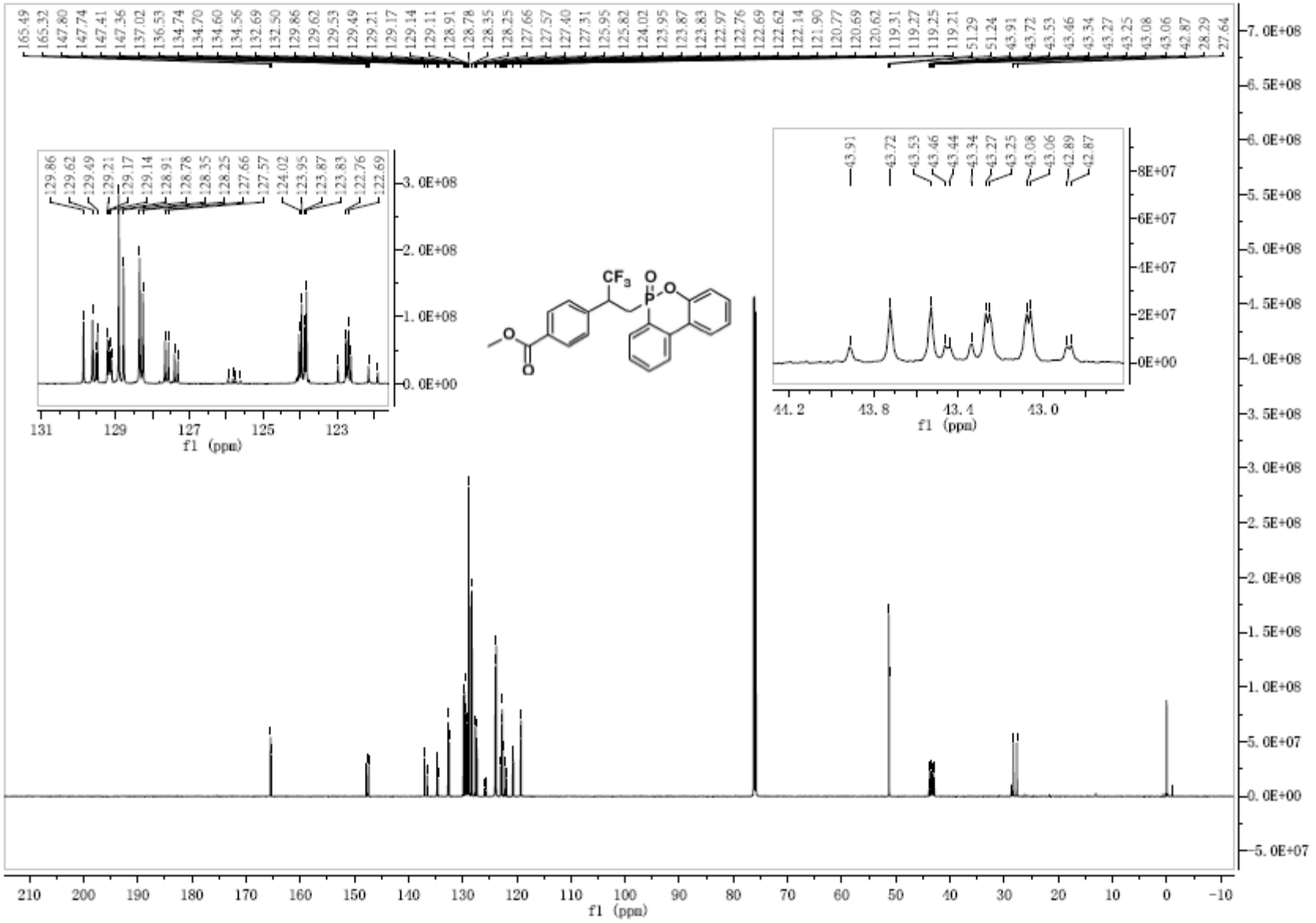
HRMS (EI) spectrum of 3hl



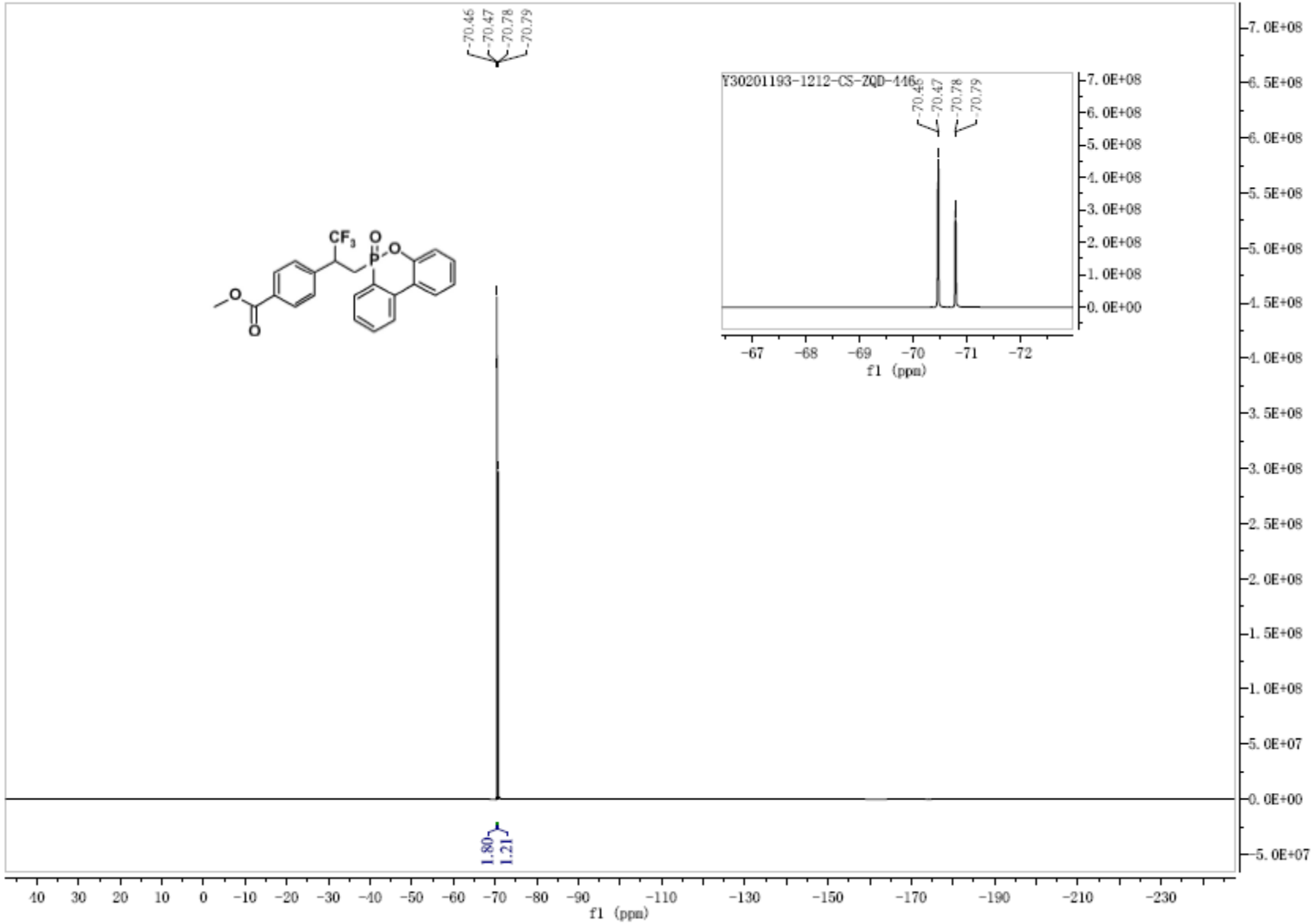
^{1}H NMR spectrum of 3hm



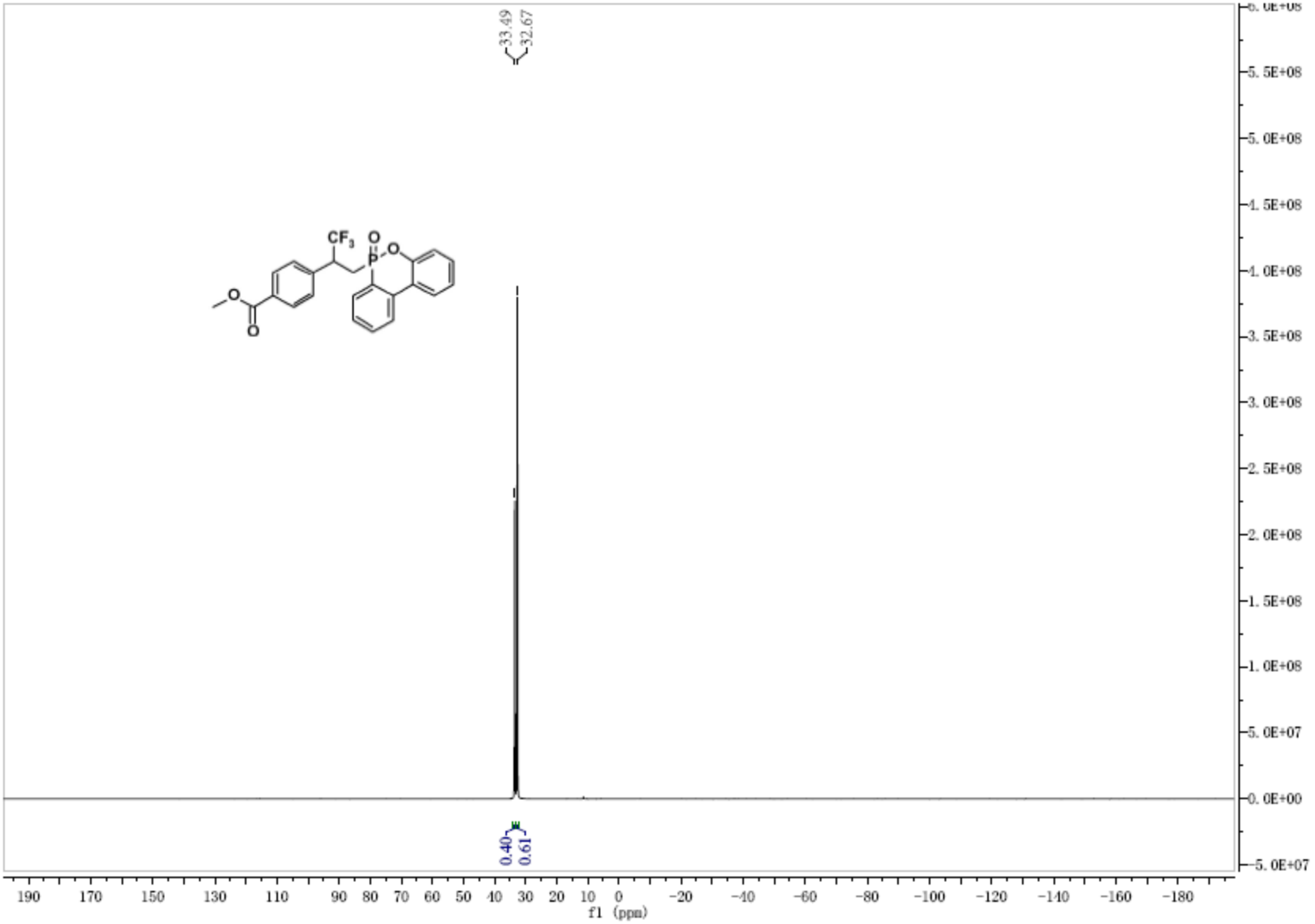
^{13}C NMR spectrum of 3hm



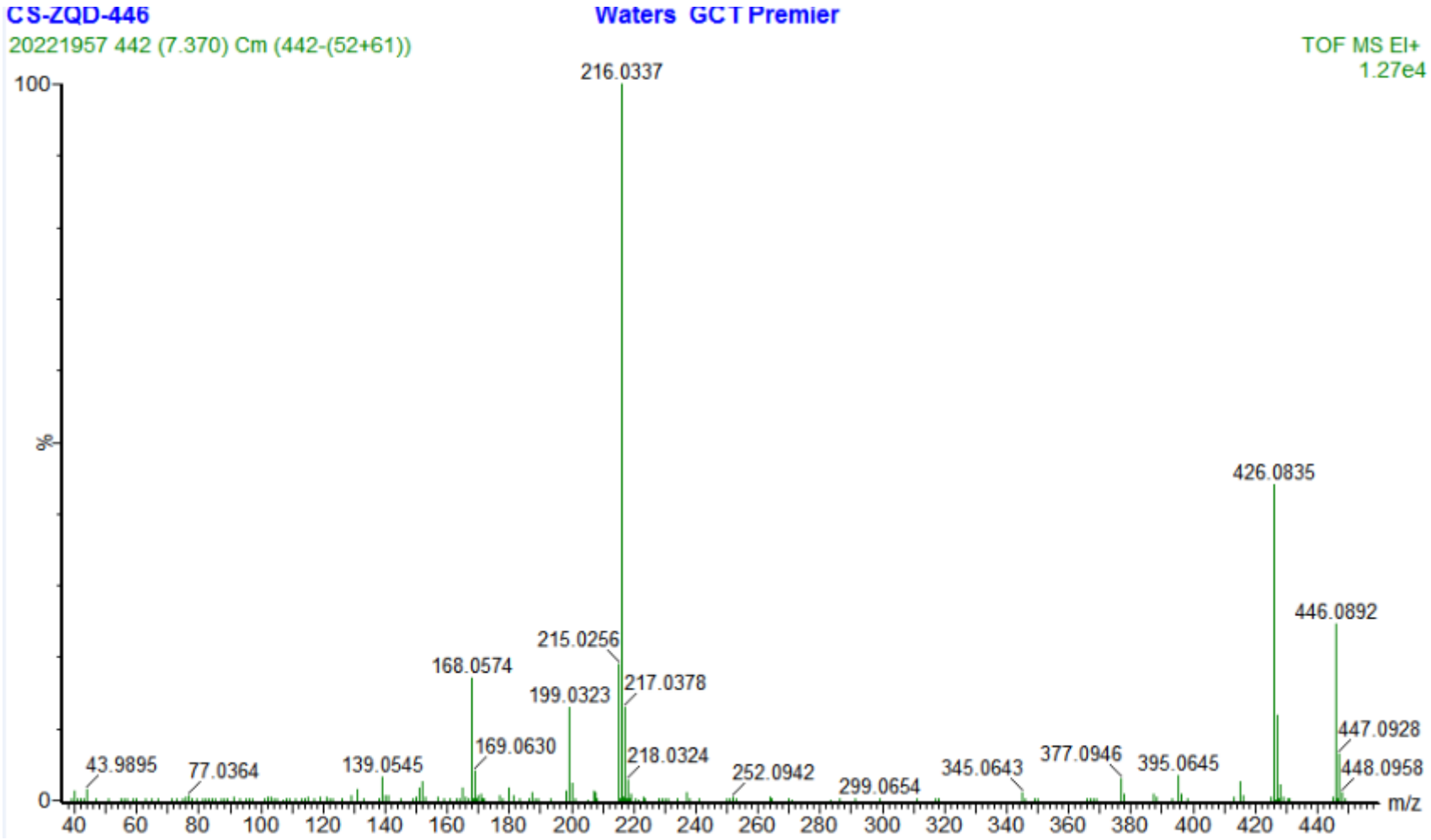
^{19}F NMR spectrum of 3hm



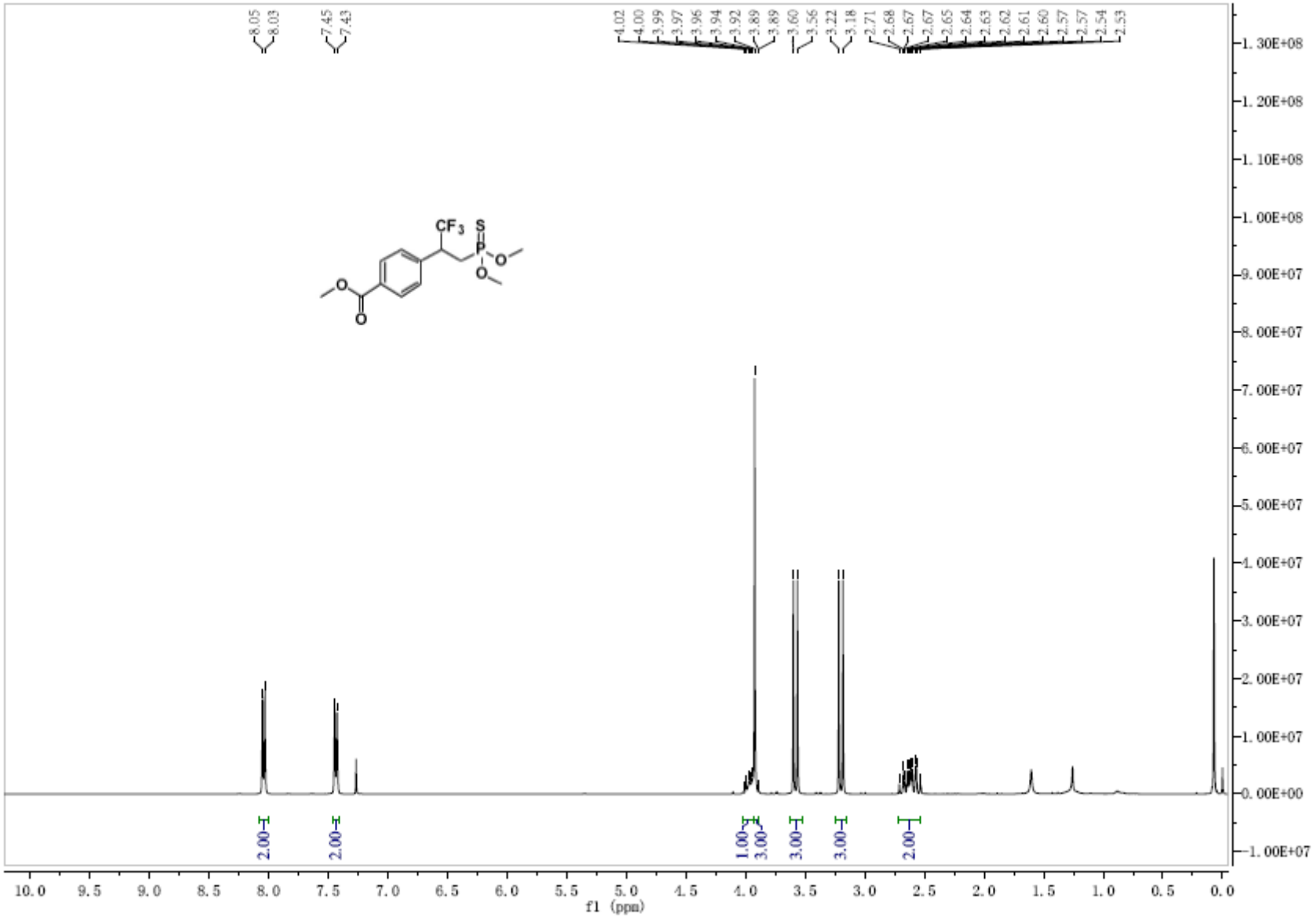
^{31}P NMR spectrum of 3hm



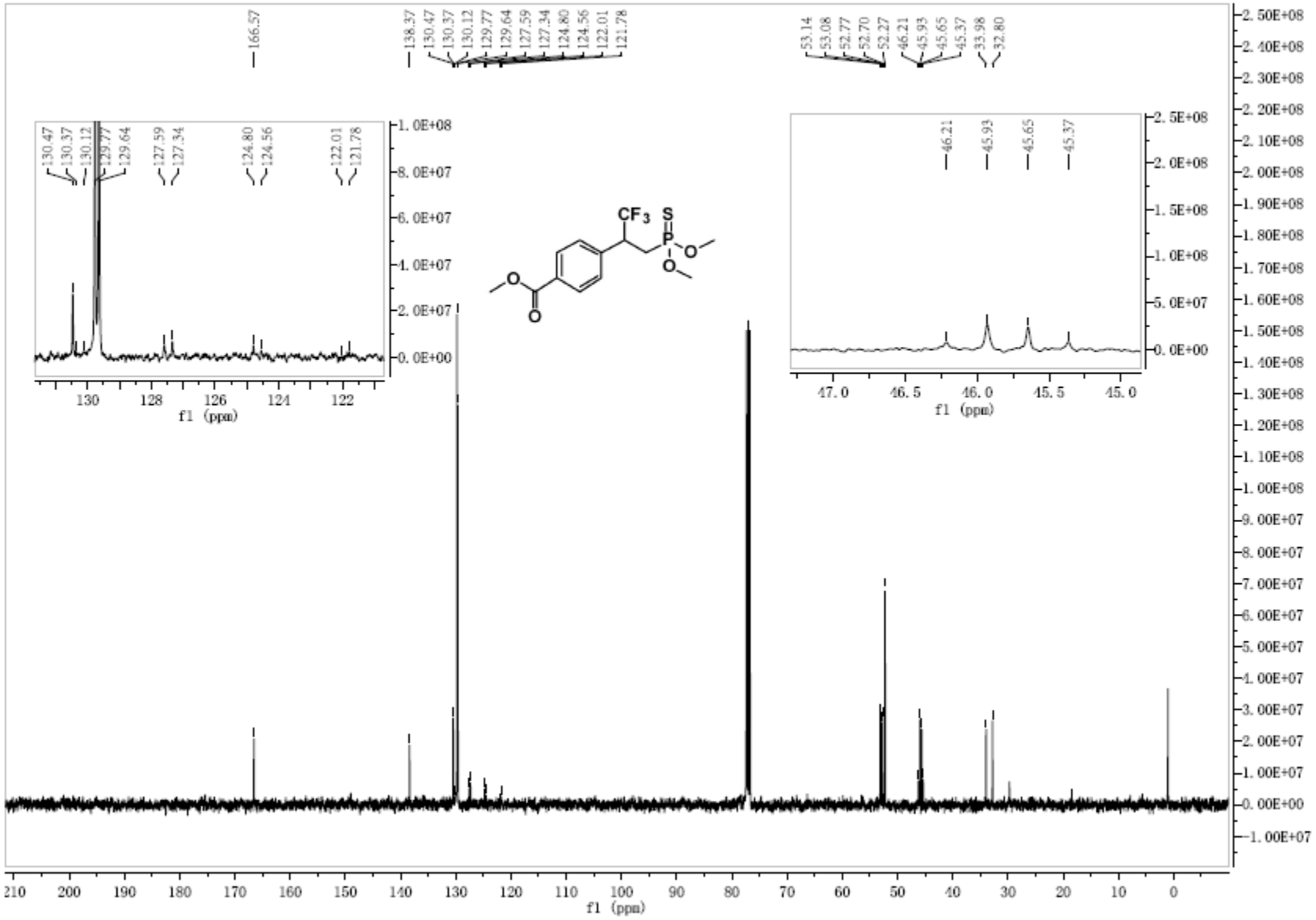
HRMS (EI) spectrum of 3hm



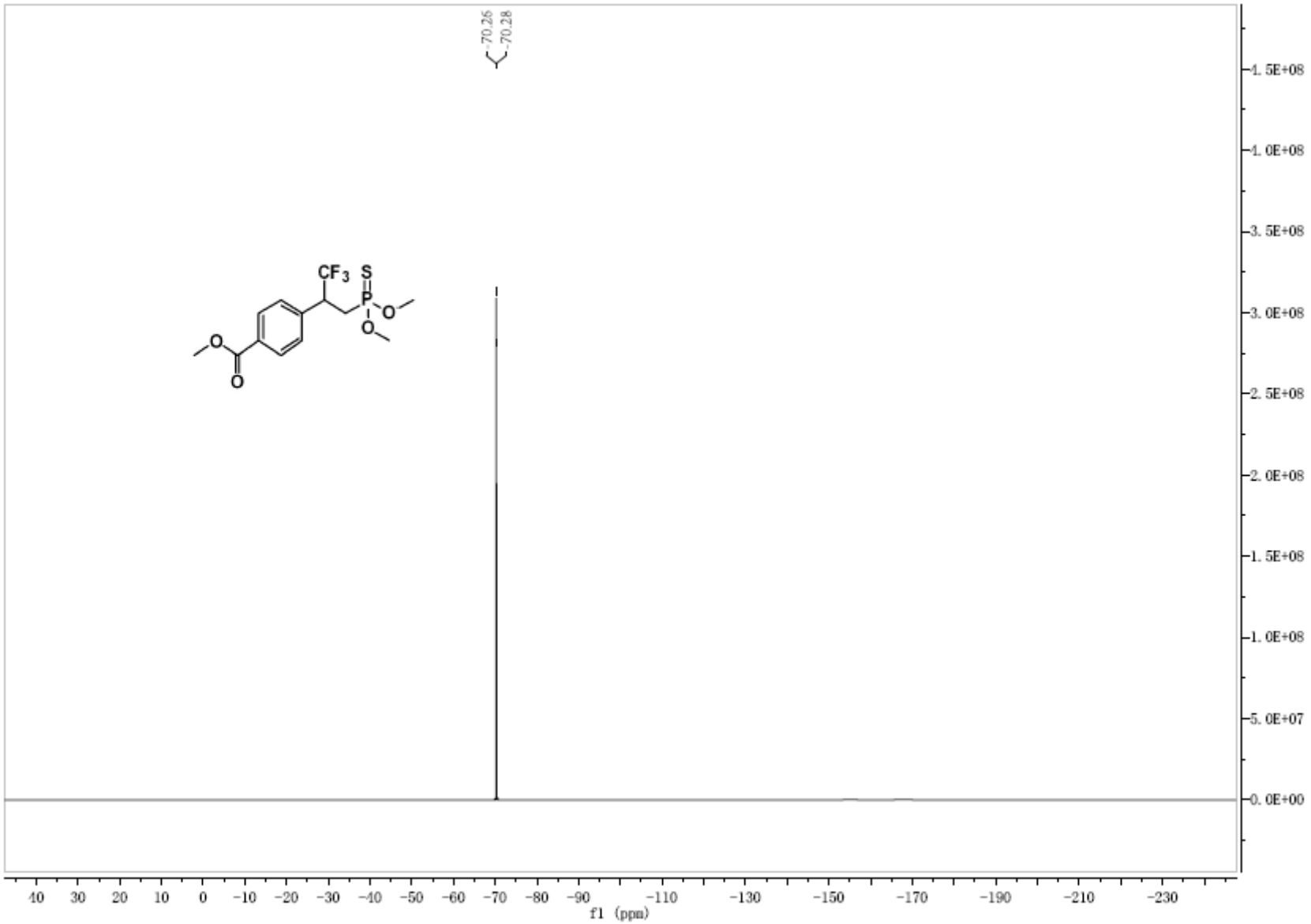
^{1}H NMR spectrum of 3hn



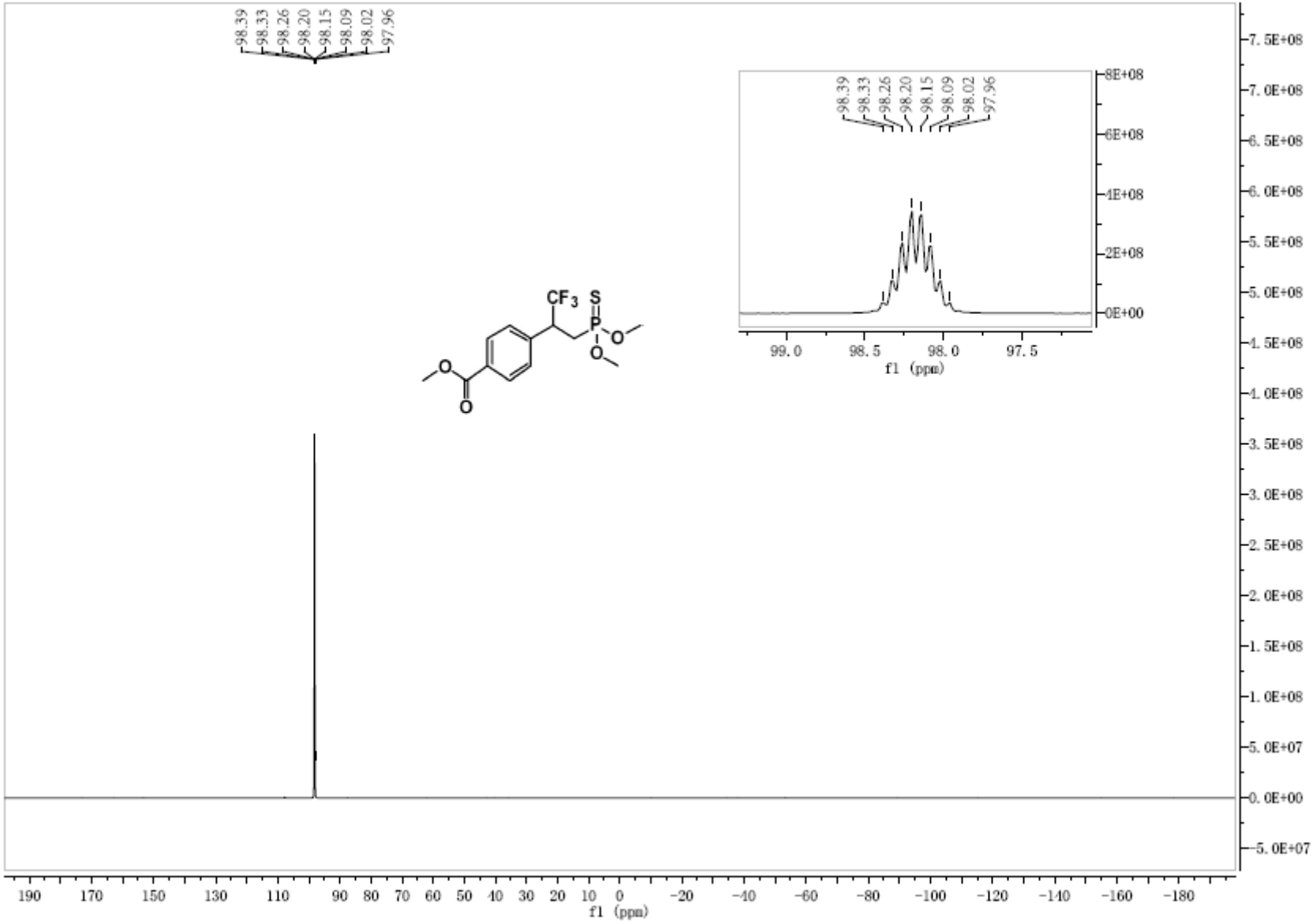
^{13}C NMR spectrum of 3hn



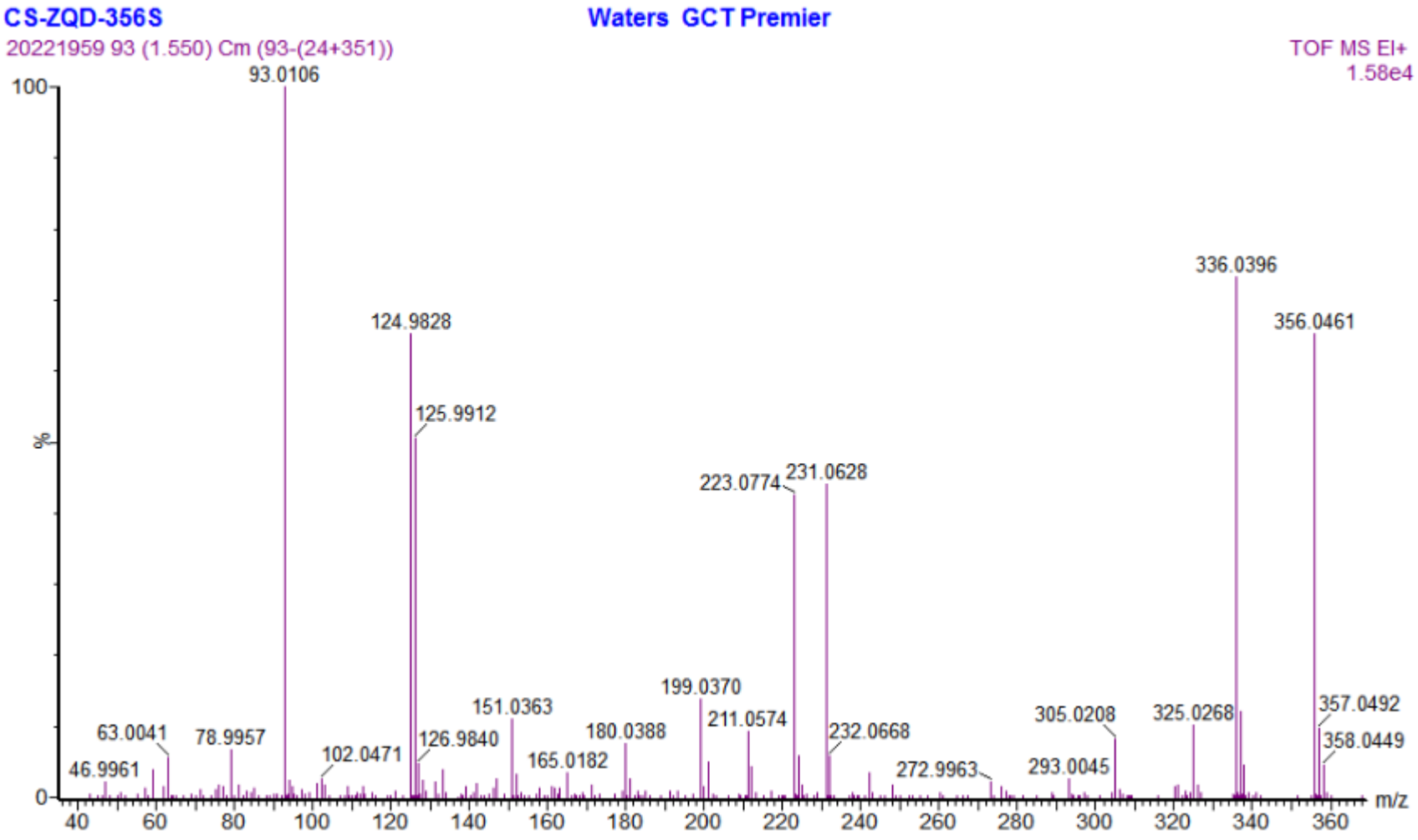
^{19}F NMR spectrum of 3hn



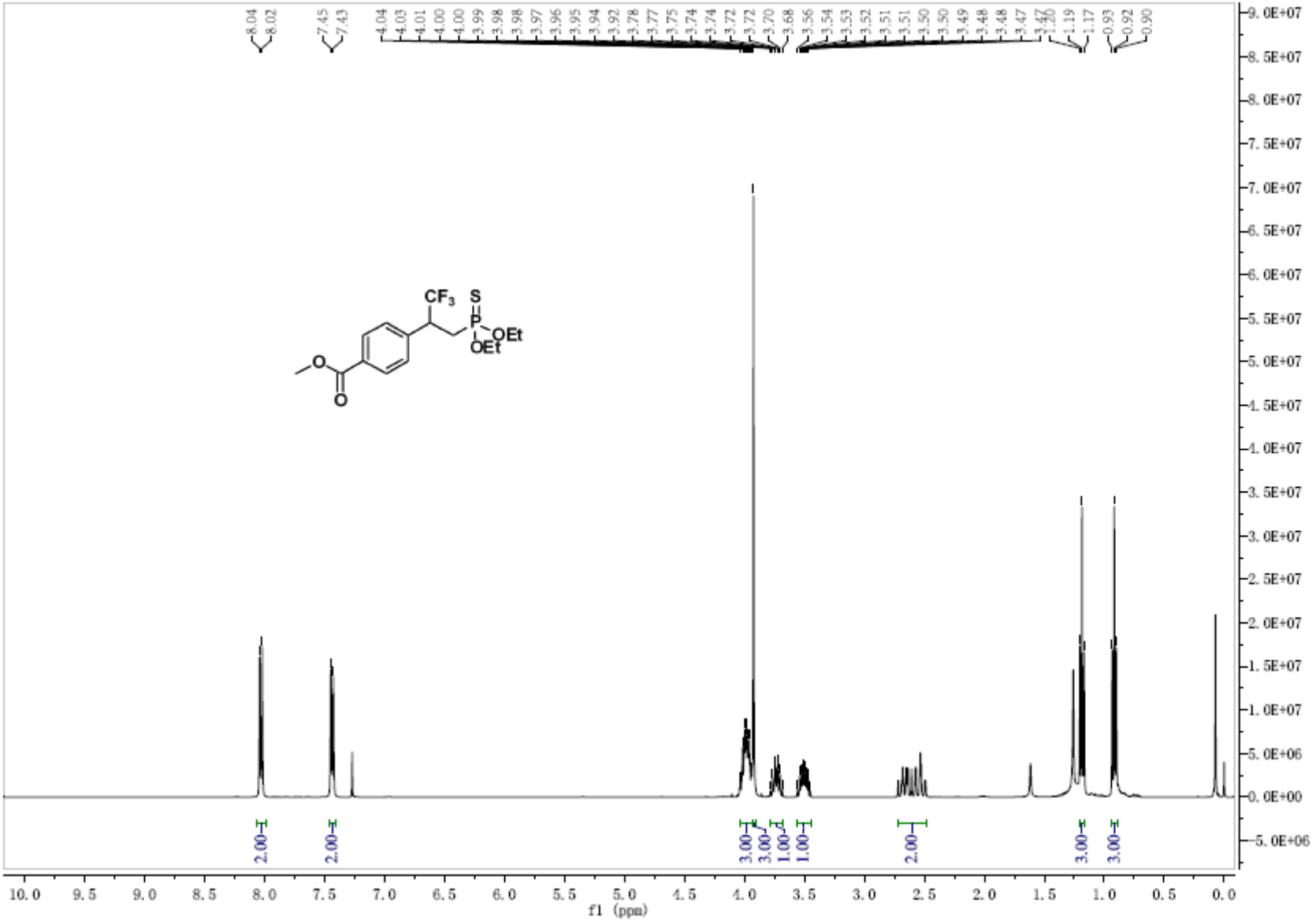
^{31}P NMR spectrum of 3hn



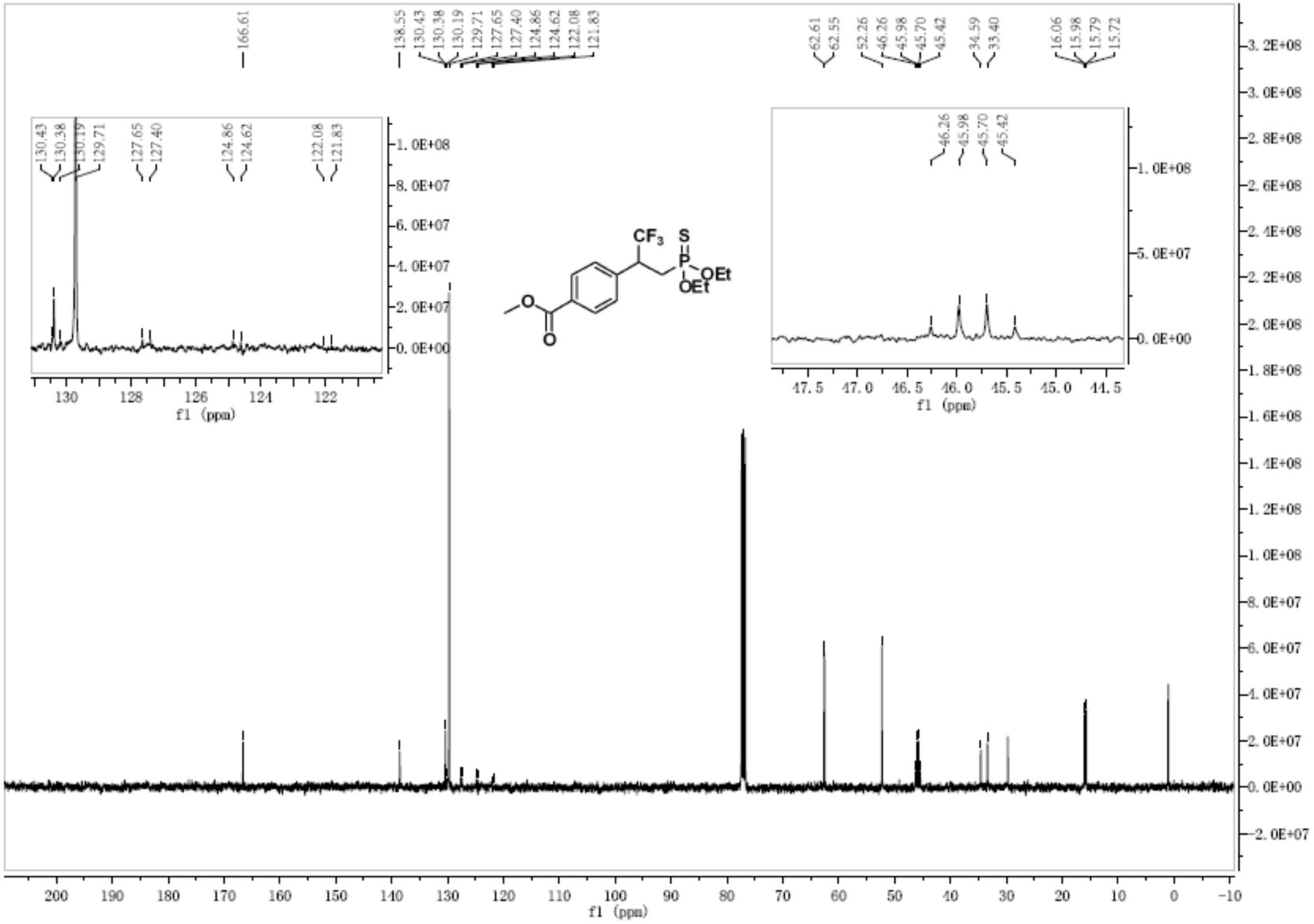
HRMS (EI) spectrum of 3hn



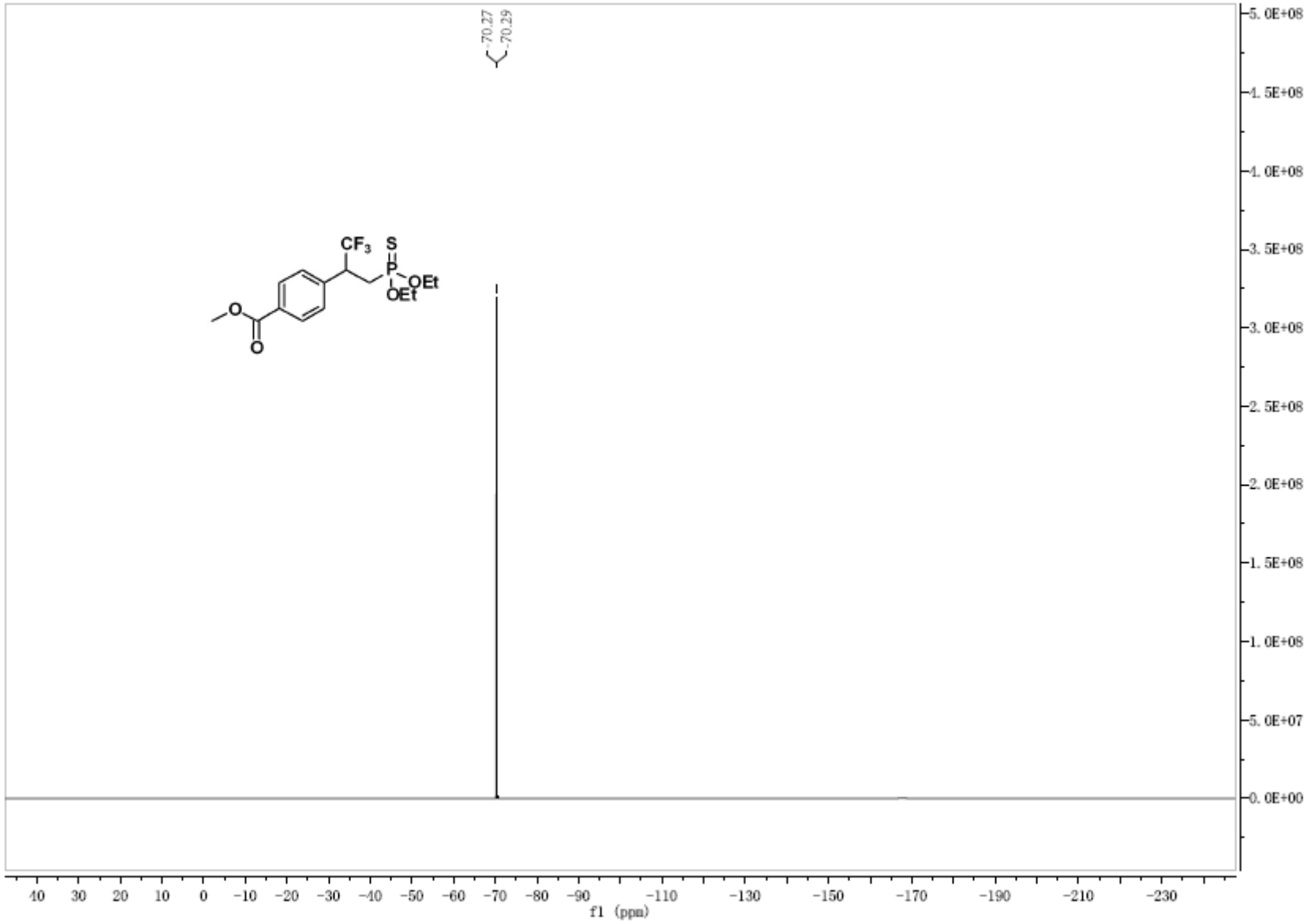
^{1}H NMR spectrum of 3ho



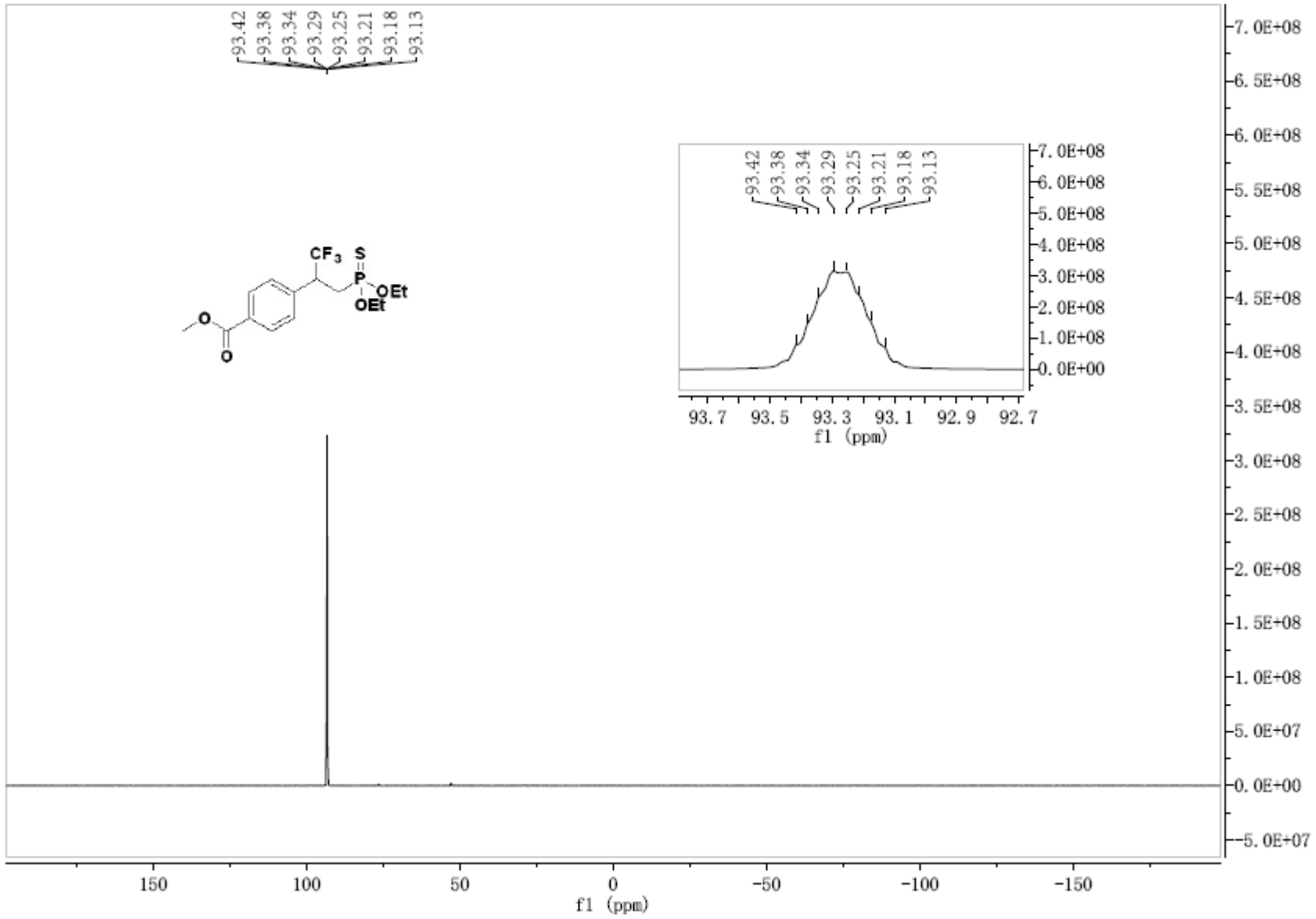
^{13}C NMR spectrum of 3ho



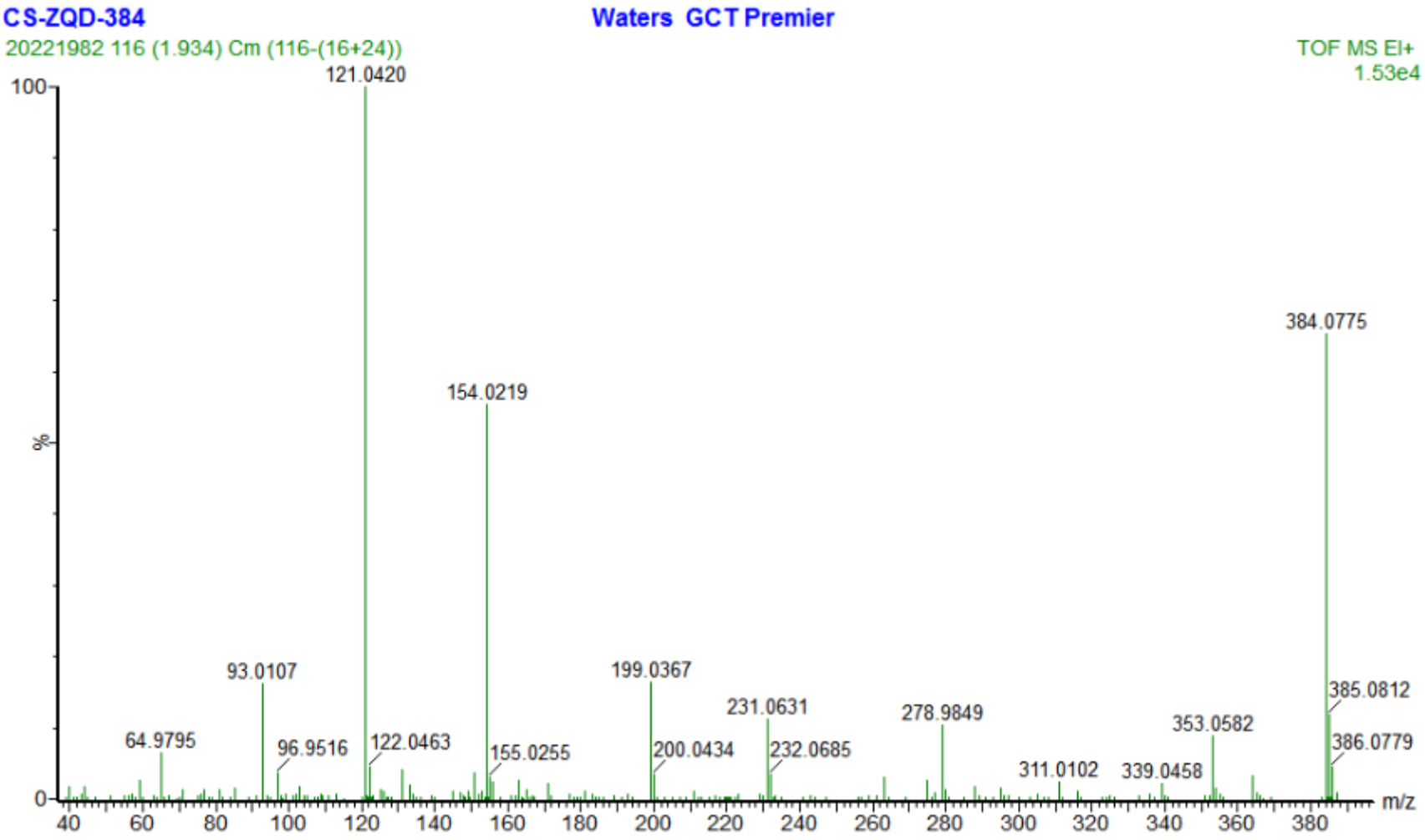
^{19}F NMR spectrum of 3ho



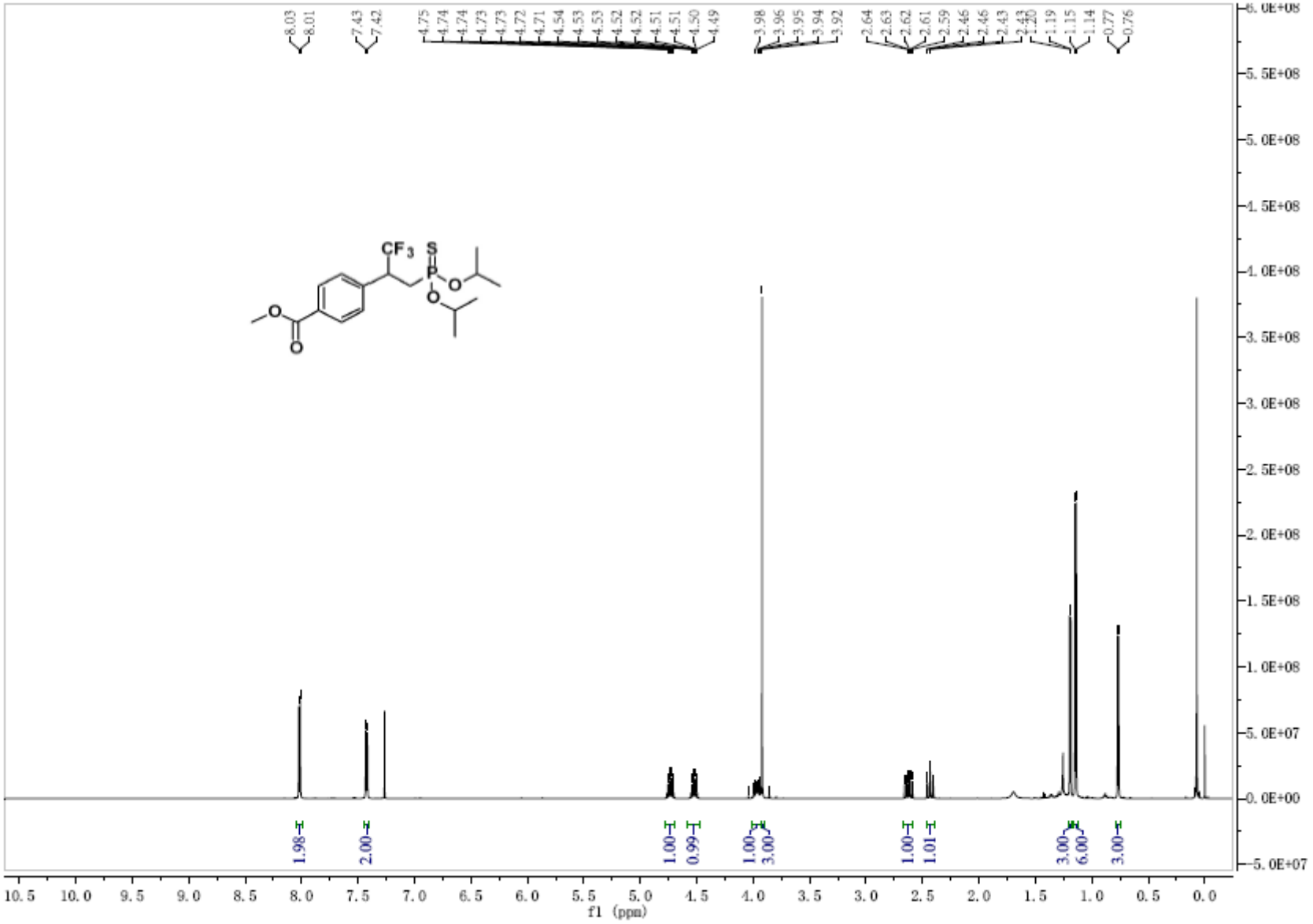
^{31}P NMR spectrum of 3ho



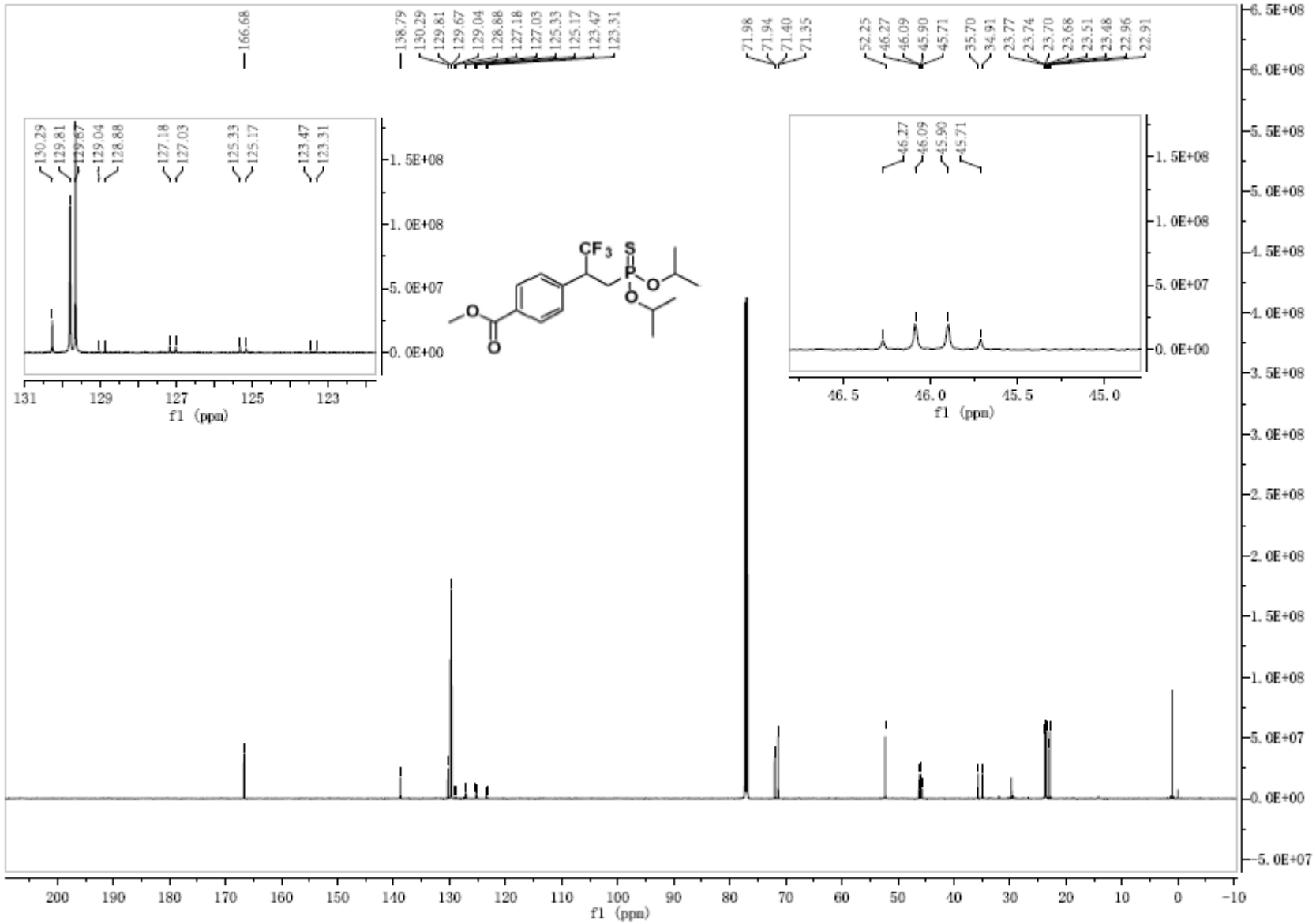
HRMS (EI) spectrum of 3ho



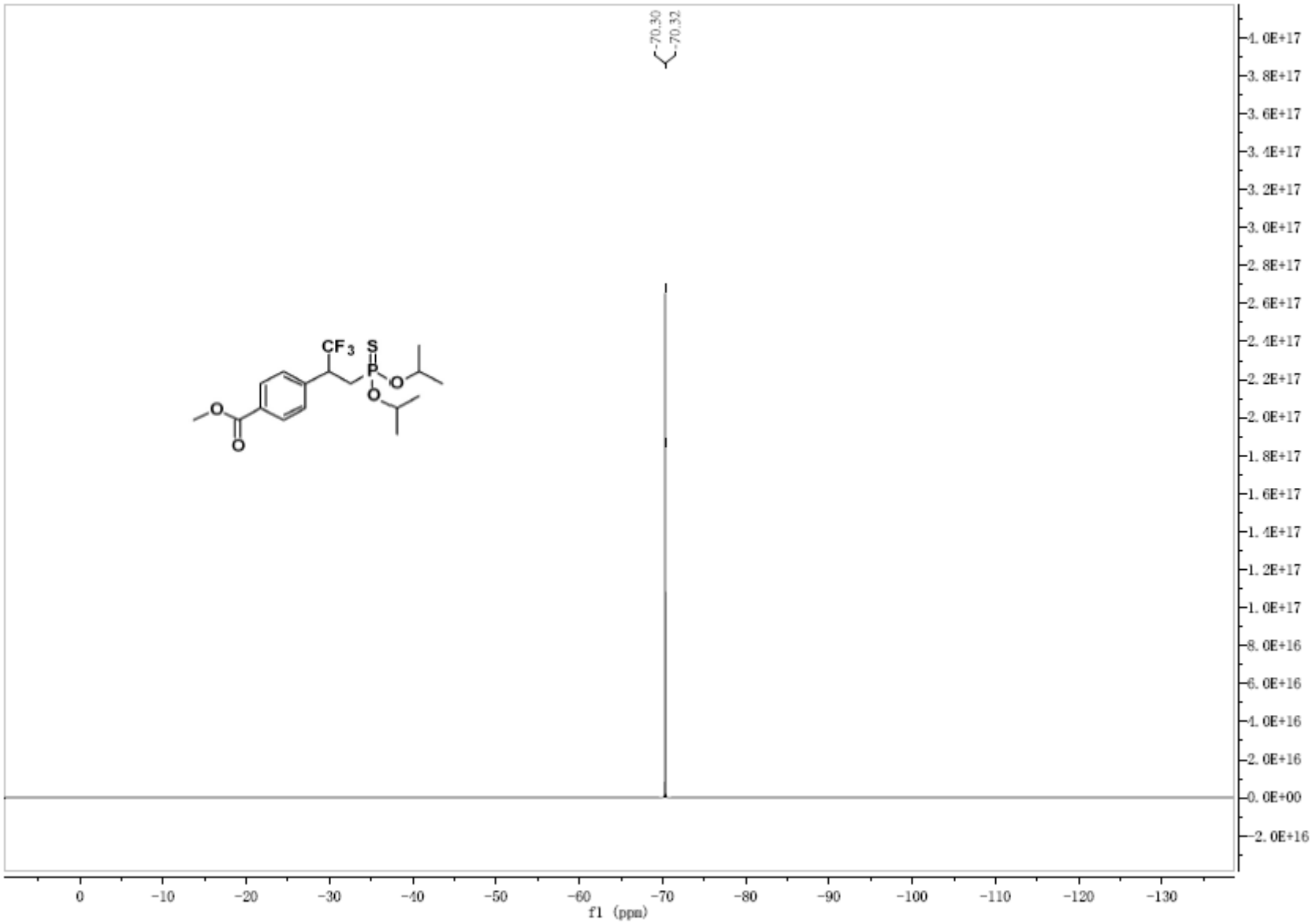
^{1}H NMR spectrum of 3hp



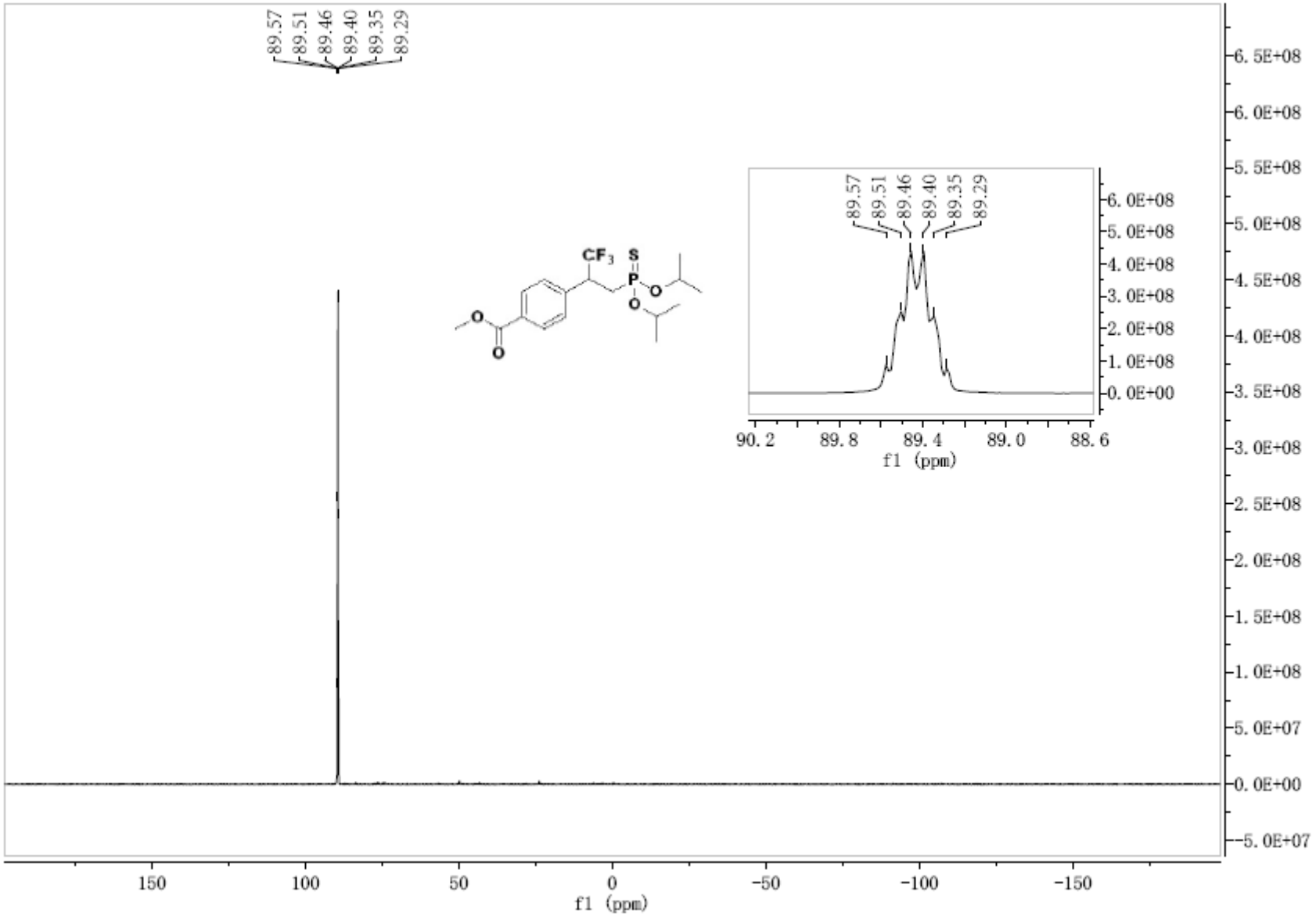
^{13}C NMR spectrum of 3hp



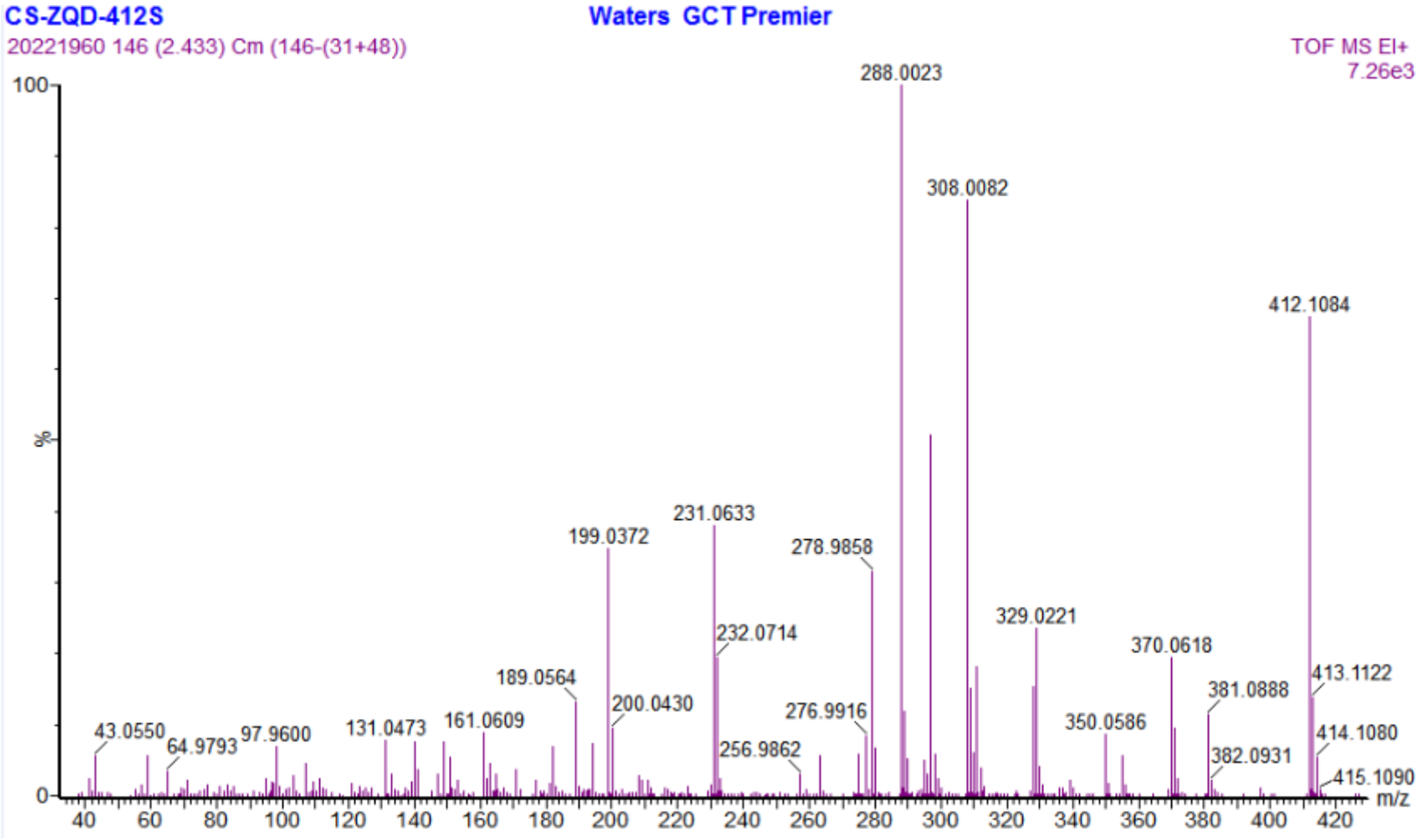
^{19}F NMR spectrum of 3hp



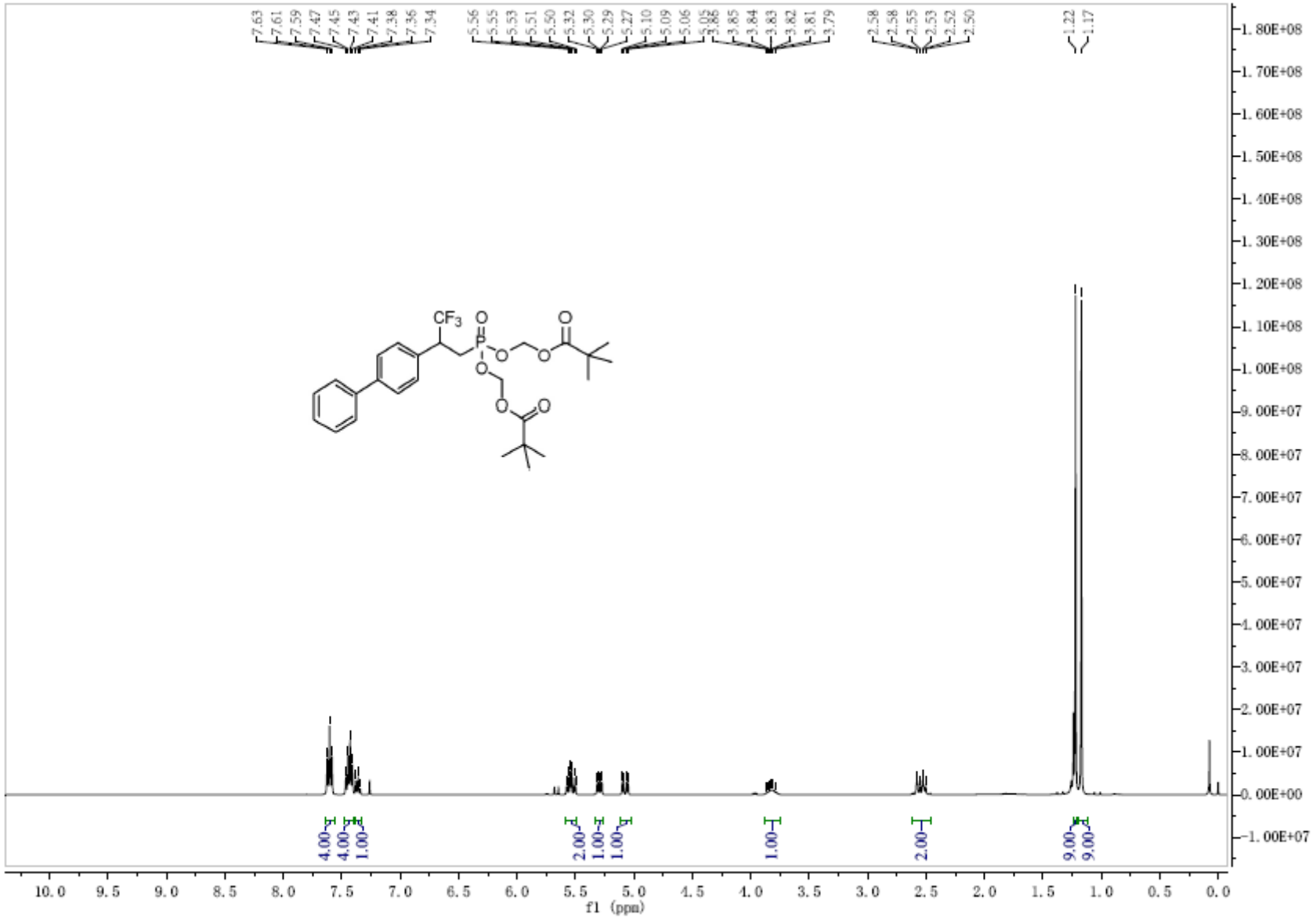
^{31}P NMR spectrum of 3hp



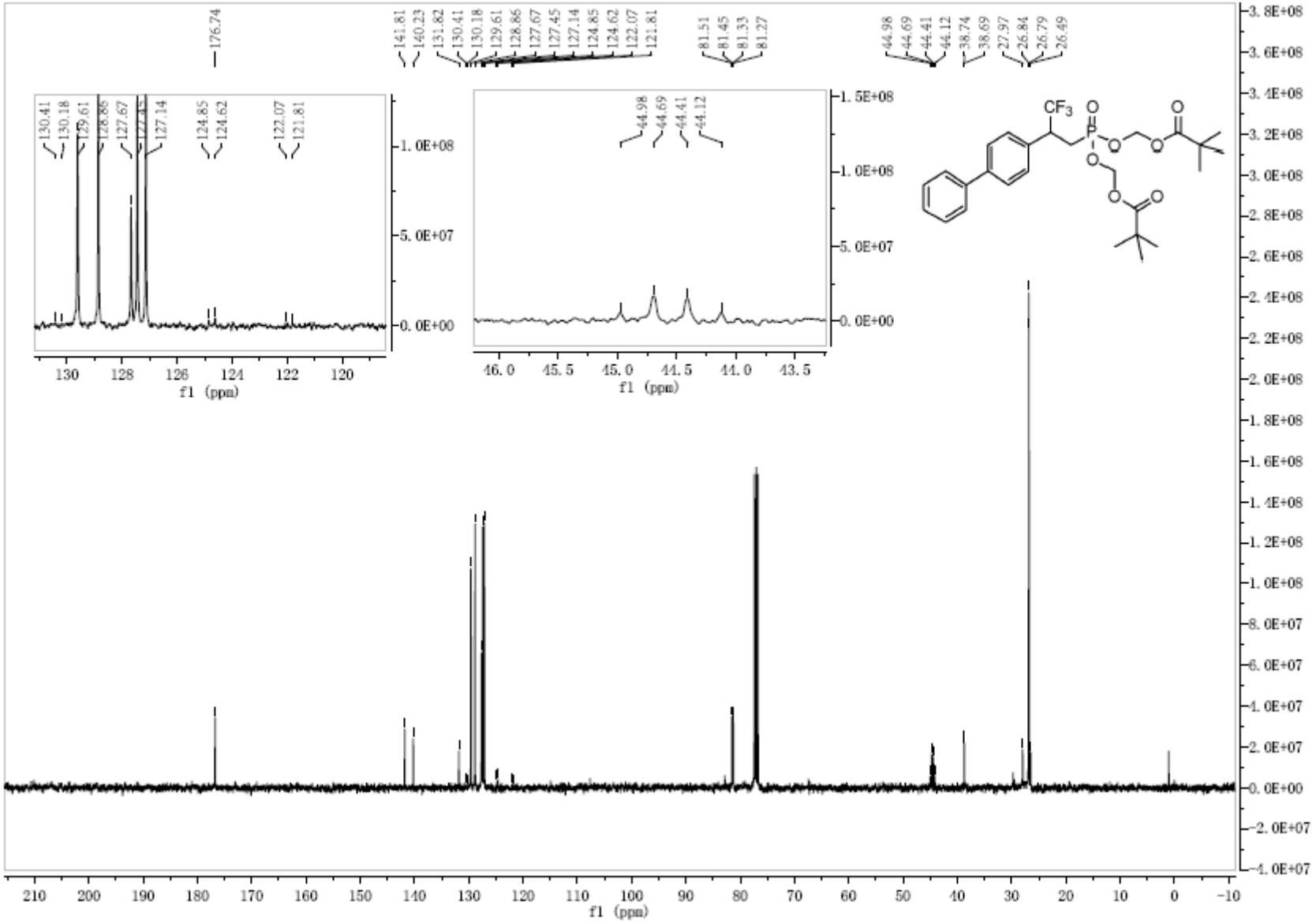
HRMS (EI) spectrum of 3hp



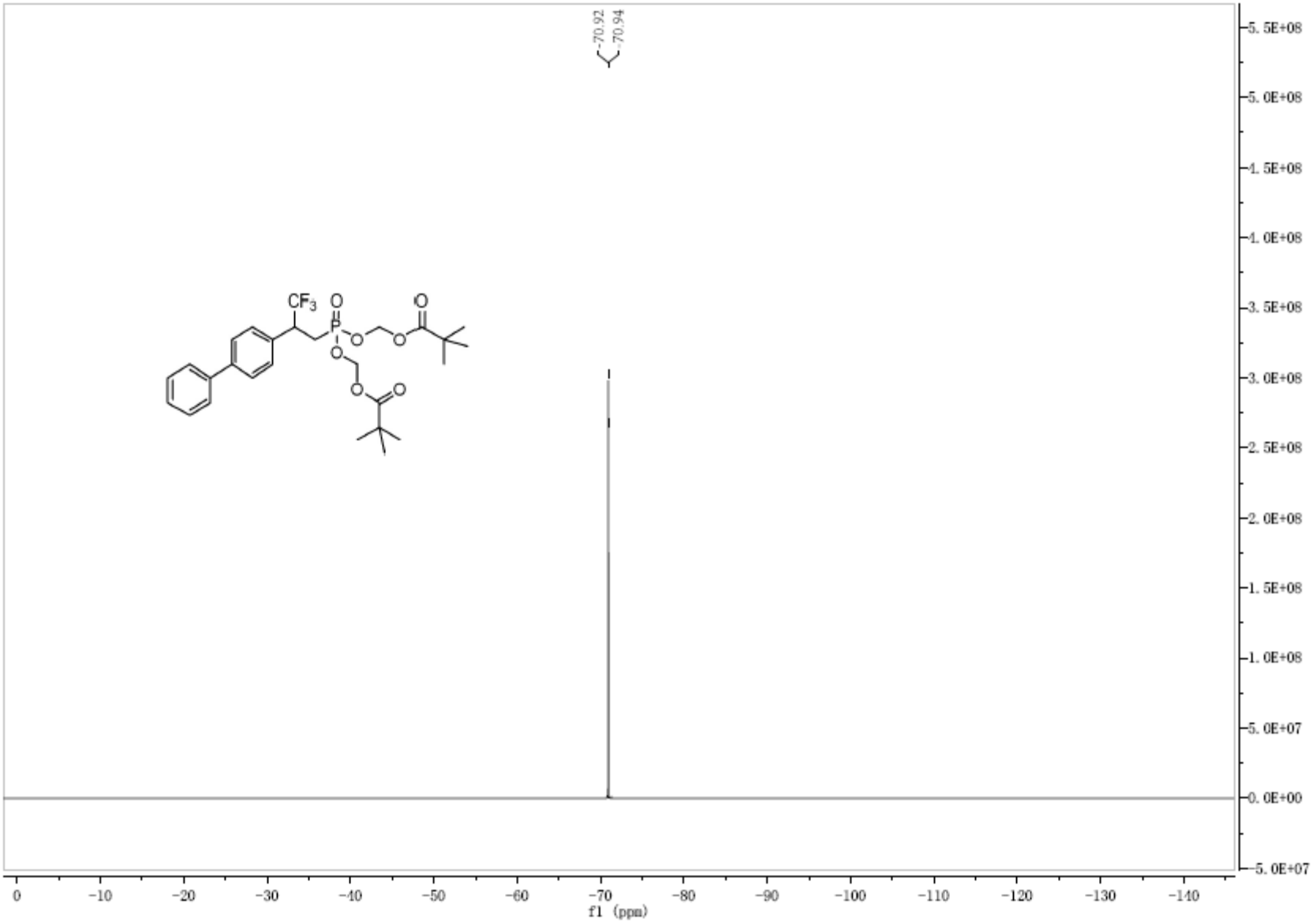
^{1}H NMR spectrum of compound 4



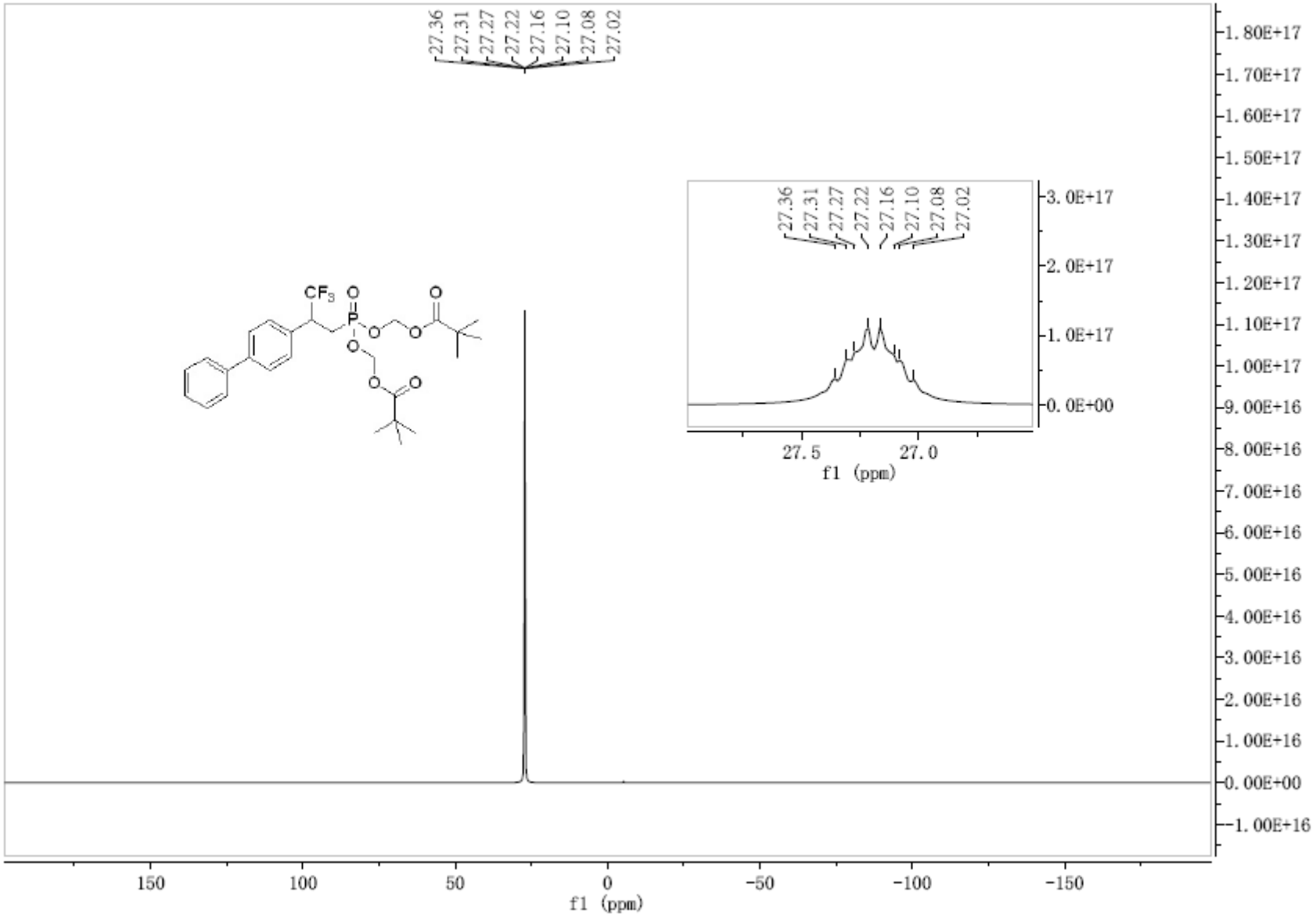
^{13}C NMR spectrum of compound 4



^{19}F NMR spectrum of compound 4



^{31}P NMR spectrum of compound 4



HRMS (EI) spectrum of compound 4