Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Magnesium Salt Promoted Tandem Nucleophilic Addition-Oppenauer Oxidation of Aldehydes with Organozinc Reagents **

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Table of Contents:

General Experimental Section:

Analytic methods. All the reactions were carried out under argon or nitrogen atmosphere. ^{1}H NMR (400 MHz), and ^{13}C NMR (100 MHz) were recorded on Bruker AV400 NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) with TMS as an internal standard. Column chromatography was performed on silica gel 300 - 400 mesh. Analytical thin layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm). GC-MS experiments were performed with an Agilent 6890N GC system equipped with a 5973N mass-selective detector.

Compound characterization: Tabulated ^{1}H and ^{13}C NMR data and copies of ^{1}H and ^{13}C spectra are given for all ketone products. For new compounds, **3j**, **9b~9e, 9g**, HRMS data is provided. The other compounds have previously been reported in the literature. Spectral data obtained herein were in agreement with literature data.

General Procedure A1: Preparation of polyfunctional arylzinc reagents by using magnesium in the presence of LiCl and $ZnCl_2$.

A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with magnesium turnings (0.17g, 7 mmol). $ZnCl_2$ (0.54g, 4 mmol), and LiCl (0.21g, 5 mmol) was added and the magnesium was activated with *i*Bu_2AlH (0.4 mL, 0.04 mmol). After 5 min of stirring the aryl bromide (5.0 mmol) was added dropwise at room temperature and was stirred for 3 h.

General Procedure A2: preparation of functionalized organozinc reagents by Mg/I exchange reaction

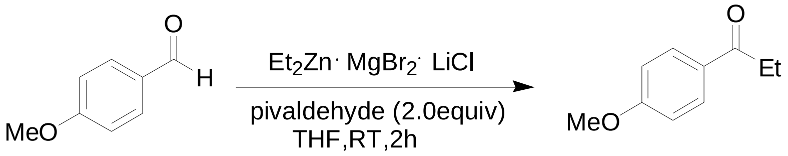
Preparation of the reagent *i*PrMgCl·LiCl: Magnesium turnings (0.17g, 7.0 mmol) and anhydrous LiCl (0.21g, 5.0 mmol) were placed in an Ar-flushed flask, and THF (5 mL) was added. A solution of *i*PrCl(5.0 mmol) in THF (5 mL) was slowly added at room temperature. The reaction started within a few minutes. After the addition, the reaction mixture was stirred for 12 h at room temperature.

A dry and argon-flushed 10-mL flask equipped with a magnetic stirrer and a septum was charged with *i*PrMgCl·LiCl (5 mmol). The reaction mixture was cooled to -40 ^{o}C, and aryl halide (5.0 mmol) was added in one portion. The reaction temperature was increased to -10 ^{o}C, and the I/Mg exchange was complete after 15 min (checked by GC analysis of reaction aliquots, the conversion was more than 98%). $ZnCl_2$ (4 mmol) was then added and the reaction mixture was stirred for additional 0.5h .

General Procedure B: Reaction of Organozinc Reagents with aldehydes:

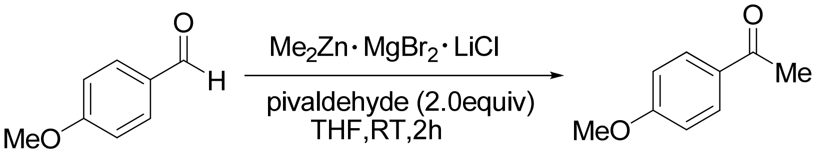
Diorganozinc (4.0 mmol) or organozinc reagent prepared above was added slowly to a solution of substrate aldehyde (2.0 mmol) and pivaldehyde (0.34g, 4.0 mmol) in 10 ml THF at RT. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. All products were characterized by ^1H NMR, and ^{13}C NMR.

3a: Ethyl 4-methoxyphenyl ketone[1]



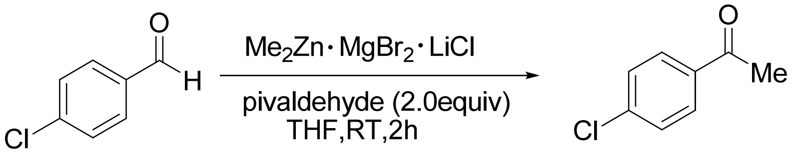
Diethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-methoxybenzaldehyde (0.27 g, 2 mmol), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. Ethyl 4-methoxyphenyl ketone **3a** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.28 g, 84% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.21 (t, J = 7.2 Hz, 3H), 2.94 (q, J = 7.2 Hz, 2H), 3.87 (s, 3H), 6.93 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 8.4, 31.4, 55.4, 113.6, 130.0, 130.2, 163.3, 199.5.

3b: Methyl 4-methoxyphenyl ketone [1,2]



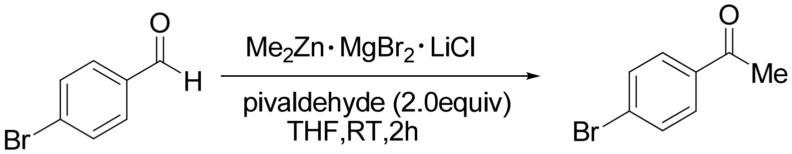
Dimethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-methoxybenzaldehyde (0.27 g, 2 mmol), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. Mthyl 4-methoxyphenyl ketone **3b** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. White solid (0.22 g, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.56 (s, 3H), 3.88 (s, 3H), 6.94 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 26.3, 55.4, 113.7, 130.3, 130.6, 163.5, 196.7.

3c: Methyl 4-chlorophenyl ketone[2]



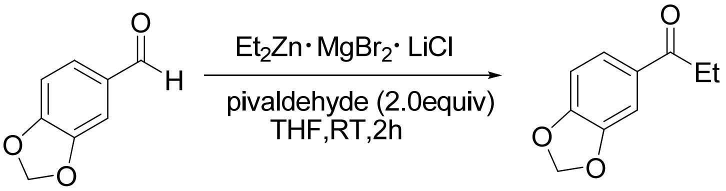
Dimethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-chlorobenzaldehyde (0.28 g, 2 mmol), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. Mthyl 4-chlorophenyl ketone **3c** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. White solid (0.24 g, 77% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.59 (s, 3H), 7.44 (d, J = 8.5 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 26.5, 128.9, 129.7, 135.4, 139.5, 196.8.

3d: Methyl 4-bromophenyl ketone [2]



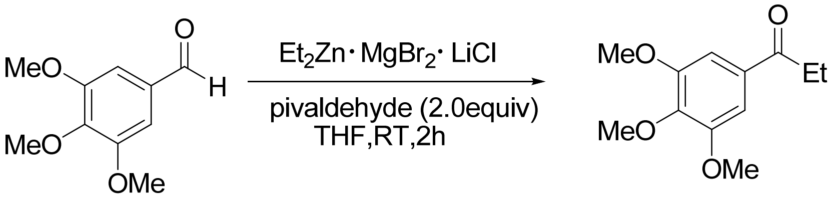
Dimethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-bromobenzaldehyde (0.37 g, 2 mmol), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. Mthyl 4-bromophenyl ketone **3d** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. White solid (0.29 g, 74% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.59 (s, 3H), 7.61 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 26.5, 128.3, 129.8, 131.8, 135.8, 196.9.

3e: 1-Benzo[1,3]dioxol-5-yl-propan-1-one [3]



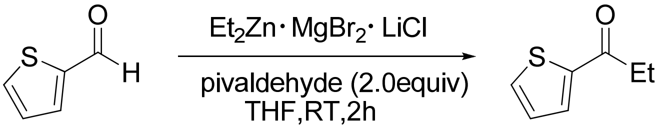
Diethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), piperonal (2.0 mmol, 0.30 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 1-(4-Methoxyphenyl)propan-1-one **3e** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0. 28g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.22 (dd, J = 17.5, 10.3 Hz, 3H), 2.92 (dd, J = 14.4, 7.2 Hz, 2H), 6.05 (d, J = 16.7 Hz, 2H), 6.84 (d, J = 8.1 Hz, 1H), 7.44 (s, 1H), 7.56 (d, J = 6.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 8.4, 31.4, 101.7, 107.7, 107.8, 124.0, 131.7, 148.0, 151.4, 198.8.

3f: 1-(3,4,5-Trimethoxy-phenyl)-propan-1-one [1]



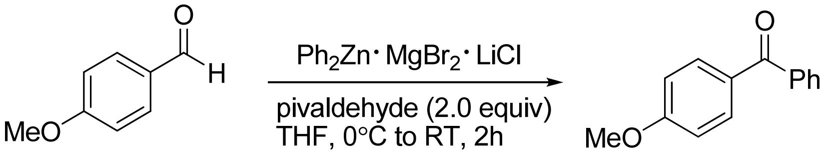
Diethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 3,4,5-trimethoxybenzaldehyde (2.0 mmol, 0.39 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 1-(3,4,5-trimethoxyphenyl)propan-1-one **3f** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.35g, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm):1.34-1.13 (m, 3H), 2.98 (d, J = 7.1 Hz, 2H), 3.92 (s, 9H), 7.25 (d, J = 11.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 8.4, 31.5, 56.3, 60.8, 105.6, 132.3, 142.4, 153.1, 199.6.

3g: 1-Thiophen-2-yl-propan-1-one [4]



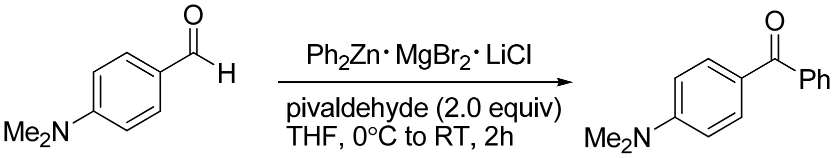
Diethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 3,4,5-trimethoxybenzaldehyde (2.0 mmol, 0.39 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 1-Thiophen-2-yl-propan-1-one **3g** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 1-(4-Methoxyphenyl)propan-1-one was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.17g, 63% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.22 (dd, J = 7.3, 4.8 Hz, 3H), 2.93 (dt, J = 7.3, 6.1 Hz, 2H), 7.11 (t, J = 4.3 Hz, 1H), 7.60 (d, J = 4.9 Hz, 1H), 7.72-7.68 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 8.5, 32.5, 127.9, 131.5, 133.1, 144.1, 193.8.

3h: 4-methoxybenzophenone [5]



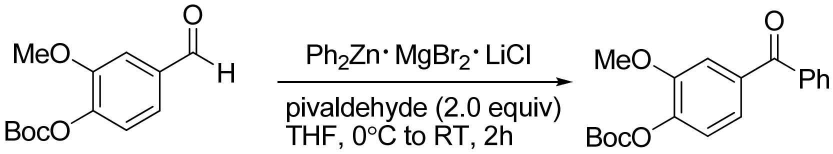
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-methoxybenzaldehyde (2.0 mmol, 0.27 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 4-Methoxyphenone **3h** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.35g, 82% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.89 (s, 3H), 6.96 (d, J = 8.0 Hz, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 55.5, 113.5, 128.1,129.7, 130.1, 131.8, 132.5, 138.2, 163.2, 195.5.

3i: 4-Dimethylaminobenzophenone[6]



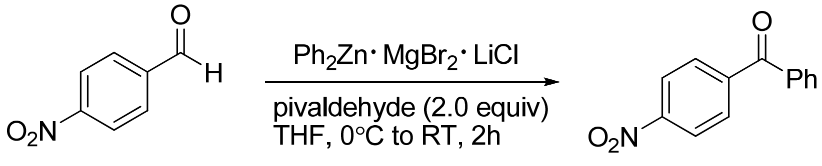
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-dimethylaminobenzaldehyde (2.0 mmol, 0.30 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone 4-dimethylaminobenzophenone **3i** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.31 g, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.08 (s, 6H), 6.69 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 7.3 Hz, 2H), 7.53 (s, 1H), 7.73 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 39.9, 110.4, 139.2, 127.4, 129.3, 127.9, 131.0, 132.6, 153.2, 190.2.

3j: 3-methoxy-4-(tert-butyl) benzophenone



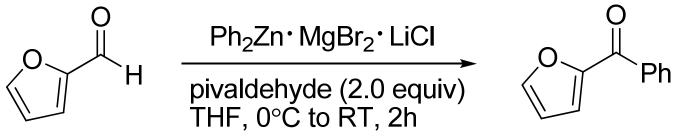
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), tert-butyl 4-formyl-2-methoxyphenyl carbonate (2.0 mmol, 0.52 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **3j** The ketone was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.40 g, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.57 (s, 9H), 3.92 (s, 3H), 7.22 (s, 1H), 7.34 (d, J = 7.1 Hz, 1H), 7.50 (d, J = 10.5 Hz, 3H), 7.59 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 29.6, 56.1, 83.9, 113.5, 122.0, 123.7, 128.2, 129.9, 132.4, 136.0, 137.5, 143.6, 151.1, 151.6, 152.2, 195.5. HRMS-ESI: calcd for $C_{19}H_{20}NaO_5$ $[M + Na]^+$: 351.1208. Found: 351.1209.

3k: 4-Nitrobenzophenone [7]



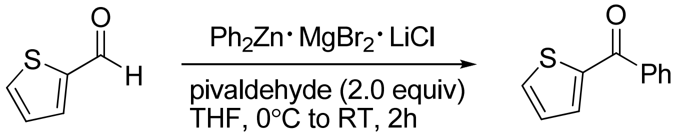
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 4-nitrobenzaldehyde (2.0 mmol, 030 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **3k** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent, 0.33 g, 72% yield. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (t, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.2 Hz, 2H), 7.94 (dt, *J* = 8.8, 2.0 Hz, 2H), 8.34 (dt, *J* = 8.8, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 123.5, 128.6, 130.0, 130.6, 133.4, 136.2, 142.8, 149.8, 194.7.

3l: furan-2-yl(phenyl)methanone[7]



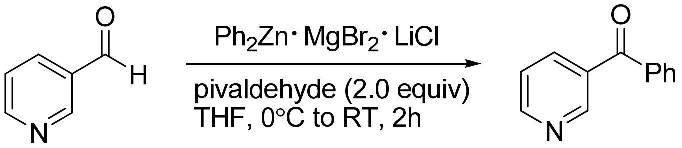
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), furfural (2.0 mmol, 0.19 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **3l** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. Oil, 0.19 g, 54% yield. ^1H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 6.60 (q, *J* = 2.0 Hz, 1H), 7.24 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.60 (tt, *J* = 7.2, 0.8 Hz, 1H), 7.715-7.717(m, 1H), 7.94-7.99(dd, *J* = 7.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 112.1, 120.5, 128.3, 129.2, 132.5, 137.2, 147.0, 152.2, 182.5.

3m: phenyl(thiophen-3-yl)methanone [5]



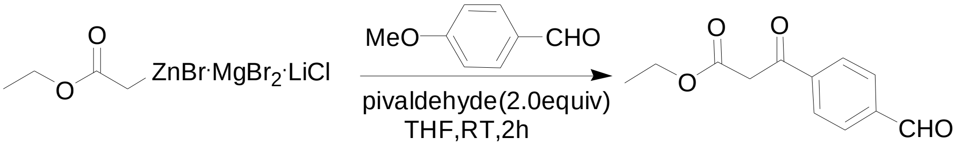
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 2-thiophenaldehyde (2.0 mmol, 0.22 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **3m** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. Oil, 0.28 g, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.39 (dd, J = 4.8, 3.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.58 (dt, J = 7.6, 2.4 Hz, 1H), 7.61 (dd, J = 4.8, 0.8 Hz, 1H), 7.85 (dt, J = 8.0, 1.6 Hz, 2H), 7.94 (dd, J = 3.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 126.1, 128.3, 128.5, 128.6, 129.3, 132.2, 132.3, 133.9, 138.5, 141.2, 189.9.

3n: phenyl(pyridin-3-yl)methanone[8]



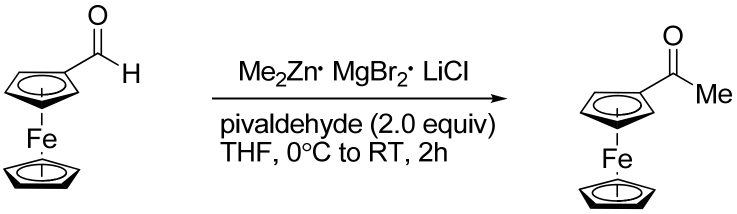
Diphenylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), 3-pyridinecarboxaldehyde (2.0 mmol, 0.21 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **3n** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.27 g, 74% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.47 (dd, J = 7.3, 5.3 Hz, 1H), 7.52 (t, J = 7.4 Hz, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.82 (d, J = 7.7 Hz, 2H), 8.17-8.11 (m, 1H), 8.82 (d, J = 4.8 Hz, 1H), 9.00 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm):120.2, 123.4, 128.6, 129.5, 130.0, 136.6, 137.2, 150.8, 152.6, 194.8.

3o: 3-(4-Methoxy-phenyl)-3-oxo-propionic acid ethyl ester [9]



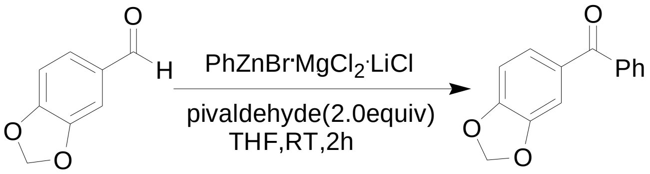
Anhydrous LiCl (0.21g, 5 mmol) was placed in an Ar-flushed flask and dried for 20 min at 150–170°C under high vacuum (1 mbar). Zinc powder (0.46g, 7 mmol) was added under Ar and the heterogeneous mixture of Zn and LiCl was dried again for 10–20 min at 150–170°C under high vacuum (1 mbar). The reaction flask was evacuated and refilled with argon three times. THF (5 mL) was added and the Zn was activated with $BrCH_2CH_2Br$ (5 mol%) and Me_3SiCl (1 mol%). Ethyl-2-bromoacetate (0.84g, 5 mmol), $MgBr_2$(0.74g, 4mmol), 4-methoxybenzaldehyde (2.0 mmol, 0.27 g), pivaldehyde (0.30g, 4.0 mmol,) were then added neat at room temperature. After the reaction mixture was stirred at room temperature for 2 hours. the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.34 g, 76% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 1.25 (dd, J = 7.8, 6.3 Hz, 3H), 3.88 (s, 3H), 3.94 (s, 2H), 4.21 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 8.5 Hz, 2H), 7.93 (d, J = 8.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 14.1, 45.8, 55.5, 61.4, 113.9, 129.1, 130.9, 163.9, 167.9, 190.9.

3p: Acetylferrocene [10]



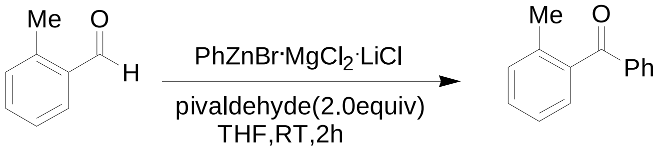
Dimethylzinc (4.0 ml, 4.0 mmol, 1.0 M in toluene) was added slowly to a THF solution (10 ml) containing $MgBr_2$ (0.74g, 4.0 mmol), ferrocenecarboxaldehyde (2.0 mmol, 0.19 g), pivaldehyde (0.34g, 4mmol) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone acetylferrocene **3p** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.33 g, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.39 (s, 3H), 4.16 (s, 1H), 4.21(s, 4H), 4.50 (s, 2H), 4.77 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 27.4, 67.9, 69.6, 69.8, 72.3, 202.0.

6a: benzo[d][1,3]dioxol-5-yl(phenyl)methanone[5]



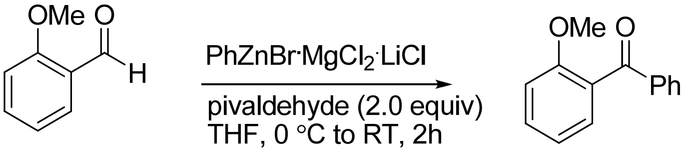
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing piperonal (2.0 mmol, 0.30 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.36g, 79% yield of **6a** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.07 (s, 2H), 6.85 (dt, J = 8.4, 0.8 Hz, 1H), 7.30-7.40 (m, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 101.9, 107.9, 109.7, 126.6, 127.7, 128.7, 129.6, 138.0, 147.6, 151.4, 195.1.

6b: 2-Methylbenzaldehyde [5]



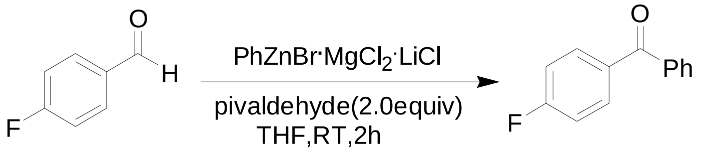
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 2-methylbenzaldehyde (2.0 mmol, 0.24 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.33 g, 84% yield of **6b** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* (ppm): 2.33 (s, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 19.9, 125.1, 128.4, 128.4, 130.1, 130.2, 130.9, 133.0, 136.7, 137.7, 138.6, 198.6.

6c: 2-Methoxybenzaldehyde [8]



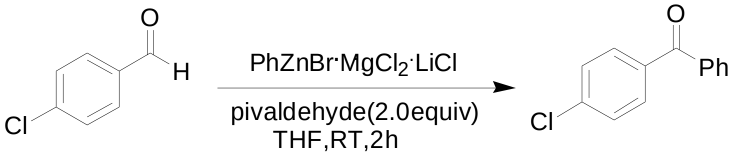
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 2-methoybenzaldehyde (2.0 mmol, 0.27 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.32 g, 76% yield of **6c** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (600 MHz, $CDCl_3$) *δ* (ppm): 3.76 (s, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 6.6 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1), 7.81 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 55.6, 111.4, 120.5, 128.2, 128.9, 129.6, 129.8, 131.8, 132.9, 137.7, 157.6, 196.6.

6d: 4-Fluorobenzophenone[5]



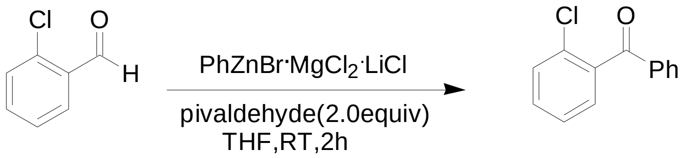
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-fluorobenzaldehyde (2.0 mmol, 0.25 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.32g, 80% yield of 4-Fluorobenzophenone **6d** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.16 (t, J = 8.4 Hz, 2H), 7.49 (t, J = 8.0 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.77 (ttd, J = 6.8, 1.6, 0.4 Hz, 2H), 7.82-7.87 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -106.4. ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 115.4 (d, J = 21.7 Hz), 128.3, 129.8, 132.4, 132.6 (d, J = 9.1 Hz), 133.7 (d, J = 3.0 Hz), 137.4, 165.3 (d, J = 252.6 Hz), 195.1.

6e: 4-Chlorobenzophenone [11]



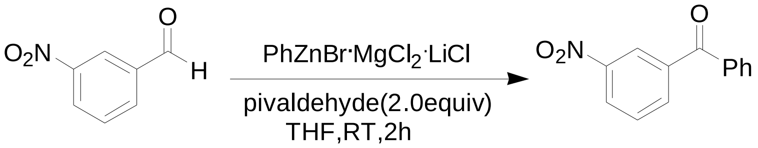
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-chlorobenzaldehyde (2.0 mmol, 0.28 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.35 g, 81% yield of 4-chlorobenzophenone **6e** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44-7.53 (m, 4H), 7.61 (tt, J = 7.6, 2.0 Hz, 1H), 7.75-7.80 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 128.3, 128.6, 129.9, 131.4, 132.6, 135.8, 137.1, 138.8, 195.5.

6f: 2-Chlorobenzophenone [7]



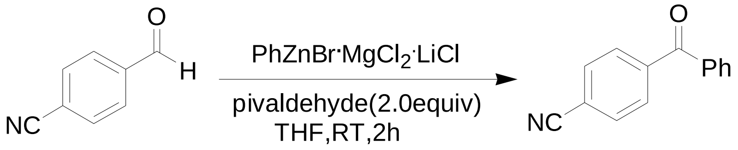
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 2-chlorobenzaldehyde (2.0 mmol, 0.28 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0. 32g, 75% yield of 2-chlorobenzophenone **6f** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.40 (m, 2H), 7.45-7.50 (m, 4H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 126.7, 128.6, 129.1, 130.1, 131.1, 133.7, 136.5, 138.6, 195.2.

6g: 3-Nitrobenzophenone[7]



According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 3-nitrobenzaldehyde (2.0 mmol, 0.30 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.35 g, 77% yield of 3-nitrobenzophenone **6g** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm): 7.54 (t, *J* = 7.2 Hz, 2H), 7.67 (tt, *J* = 7.6, 2.0 Hz, 2H), 7.71(t, *J* = 8.0 Hz, 1H), 7.79-7.83 (m, 1H), 8.15 (ddd, *J* = 7.6, 1.6, 1.2 Hz, 1H), 8.45 (ddd, *J* = 8.4, 2.4, 1.2 Hz, 1H), 8.63 (td, *J* = 2.0, 0.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 124.7, 126.7, 128.7, 129.6, 129.9, 133.3, 135.4, 136.2, 139.0, 148.0, 194.1.

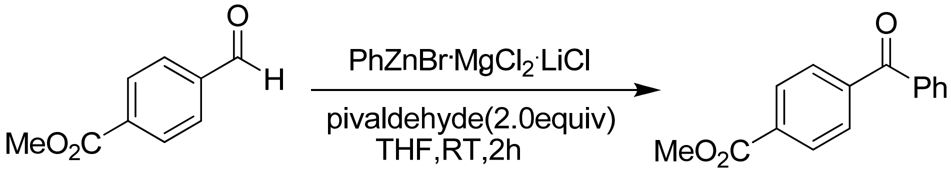
6h: 4-Cyanobenzophenone[8]



According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-cyanobenzaldehyde (2.0 mmol, 0.26 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous

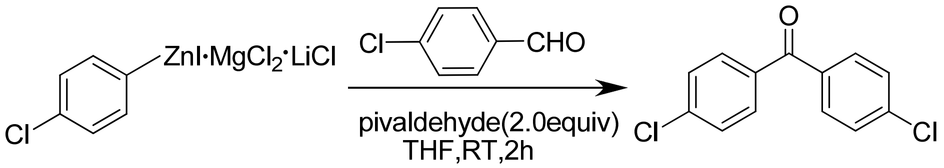
NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.31 g, 75% yield of 4-cyanobenzophenone **6h** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.52 (t, *J* = 7.6 Hz, 2H), 7.65 (tt, *J* = 7.6, 1.6 Hz, 1H), 7.77-7.83 (m, 4H), 7.89 (dt, *J* = 8.8, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 115.6, 118.0, 128.6, 130.1, 130.2, 132.0, 133.3, 136.33, 141.3, 195.0.

6i: Methyl-4-acetylbenzoate[11]



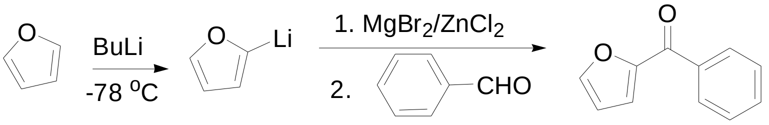
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing methyl 4-formylbenzoate (2.0 mmol, 0.33 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.33 g, 70% yield of methyl-4-acetylbenzoate **6i** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^1H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.97 (d, *J* = 0.6 Hz, 3H), 7.50 (s, 2H), 7.62 (s, 1H), 7.83 (dd, *J* = 22.6, 5.6 Hz, 4H), 8.15 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 52.4, 128.4, 129.4, 129.7, 130.0, 132.9, 133.2, 136.9, 141.3, 166.3, 196.0.

6j: 4,4'-Dichlorobenzophenone [12]



According to general procedure B: The 4-chlorophenylzinciodide prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-chlorobenzoate (2.0 mmol, 0.28 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.36 g, 71% yield of 4,4'-Dichlorobenzophenone **6j** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.47 (d, *J* = 8.0 Hz, 4H), 7.73 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 128.7, 131.2, 135.5, 139.1, 194.1.

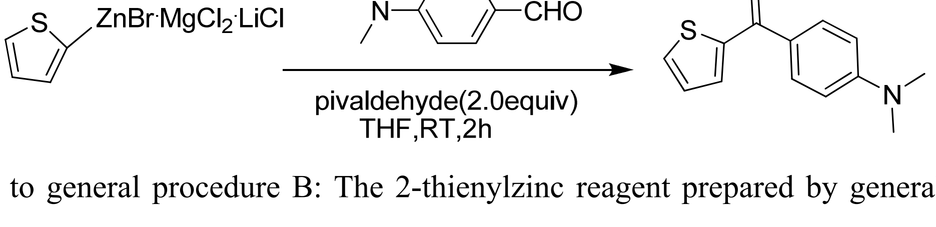
6k: 2-benzoylfuran [11]



To a to a dry, three-necked 100 mL round-bottomed flask equipped with an argon inlet, an addition funnel was placed a magnetic stirring bar and the air in the reaction system was then changed to argon. Furan (0.27g, 0.29 mL, 4.0 mmol) in 5 ml of THF was added and the reaction system was cooled to -78 °C. *n*-BuLi in hexane (2.5 M, 1.6 mL, 4.0 mmol) was then added and the reaction temperature was raise to -40 °C gradually. MgBr$_2$ and ZnCl$_2$ in THF prepared according to general procedure A was then added and the reaction mixture was stirred until the reaction temperature reached room temperature.

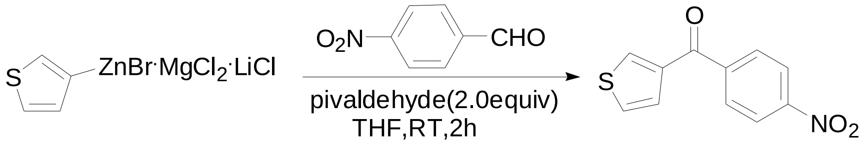
The above prepared methoxyl 2-furanyl methylzincate was added slowly to a THF solution (10 ml) containing benzaldehyde (2.0 mmol, 0.21g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH$_4$Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The pure product **6k** was obtained as a yellowish liquid (0.24 g, 68%) after purification on silica gel (10:1~5:1 petroleum ether: EtOAc). IR (KBr) *ν* (cm^{-1}): 2924, 2852, 1647, 1599, 1561, 1463, 1390, 1297, 1226, 1178, 1148, 1080, 1020, 956; ^{1}H NMR (400 MHz, CDCl$_3$) *δ* (ppm): 6.60 (q, *J* = 2.0 Hz, 1H), 7.24 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.60 (tt, *J* = 7.2, 0.8 Hz, 1H), 7.715-7.717(m, 1H), 7.96 (dd, *J* = 7.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 112.2, 120.5, 128.3, 129.2, 132.5, 137.2, 147.0, 152.2, 182.5.

6l: (4-Dimethylamino-phenyl)-thiophen-2-yl-methanone [13]



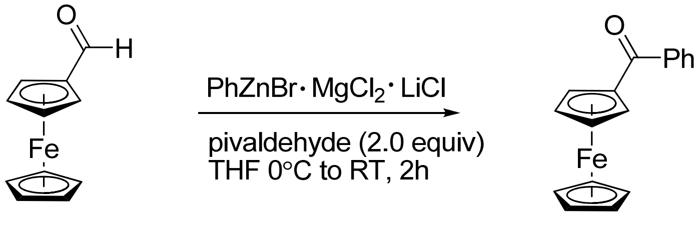
According to general procedure B: The 2-thienylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-dimethylamino benzaldehyde (2.0 mmol, 0.30 g) and pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **6l** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.29 g, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.08 (d, J = 1.7 Hz, 6H), 6.71 (dd, J = 8.9, 1.8 Hz, 2H), 7.26 (m, 1H), 7.63 (m, 2H), 7.90 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 40.6, 111.5, 120.9, 127.7, 131.1, 132.0, 132.5, 133.2, 144.5, 186.4.

6m: 3-(4-nitrobenzoyl) thiophene [7]



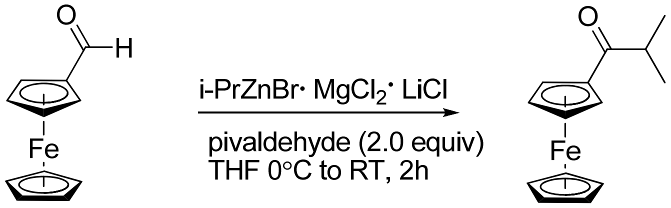
According to general procedure B: The 3-thienylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-nitrobenzaldehyde (2.0 mmol, 0.21 g) and pivaldehyde (0.30g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.26 g, 56% yield of 3-(4'-Nitrobenzoyl) thiophene **6m** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21 (dd, J = 4.8, 4.0 Hz, 1H), 7.62 (dd, J = 3.6, 1.2 Hz, 1H), 7.83 (dd, J = 5.2, 1.2 Hz, 1H), 8.00 (dt, J = 8.0, 2.4 Hz, 2H), 8.37 (dt, J = 8.8, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 123.7, 128.4, 129.8, 129.9, 135.4, 135.6, 142.6, 143.3, 149.8, 186.2.

6n: Benzoylferrocene [10]



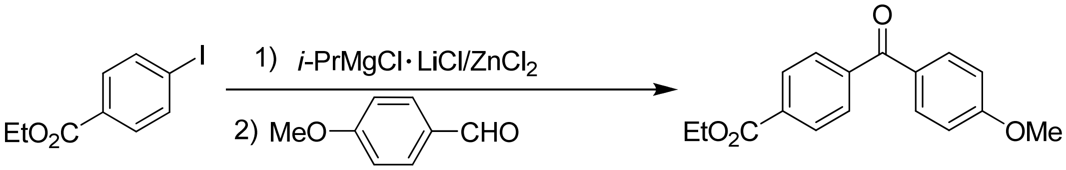
According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing ferrocenecarboxaldehyde (2.0 mmol, 0.19 g) and pivaldehyde (0.30g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.52 g, 82% yield of benzoylferrocene **6n** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.19 (s, 4H), 4.57 (s, 2H), 4.89 (s, 2H), 7.30 (s, 1H), 7.45 (s, 2H), 7.53 (s, 1H), 7.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 70.2, 71.5, 72.5, 78.2, 128.0, 128.2, 131.4, 139.8, 199.1.

6o: *i*-Butyrylferrocene [10]



According to general procedure B: The phenylzinc reagent prepared by general procedure A1 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing ferrocenecarboxaldehyde (2.0 mmol, 0.19 g) and pivaldehyde (0.30g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 0.42 g, 74% yield of *i*-butyrylferrocene **6o** was obtained after column chromatography on silica gel using petroleum/ethyl acetate as an eluent. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.19 (s, 4H), 4.57 (s, 2H), 4.89 (s, 2H), 7.30 (s, 1H), 7.45 (s, 2H), 7.53 (s, 1H), 7.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 70.2, 71.5, 72.5, 78.2, 128.0, 128.2, 131.4, 139.8, 199.1.

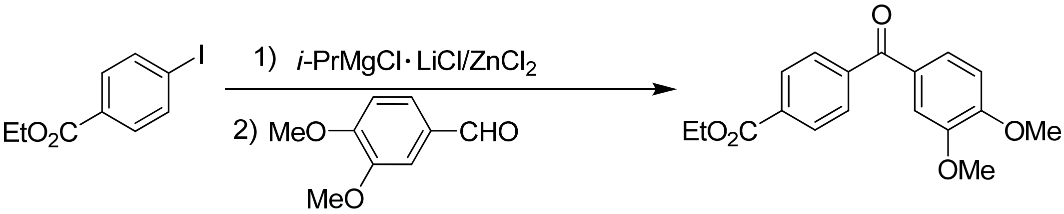
9a: 4-(4-Methoxy-benzoyl)-benzoic acid ethyl ester [14]



According to general procedure B: The (4-(ethoxycarbonyl)phenyl)zinc iodide prepared from ethyl 4-iodobenzoate by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-methoxybenzaldehyde (2.0 mmol, 0.27 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9a** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.40 g, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.26 (t, J = 7.1 Hz, 3H), 3.90 (s, 3H), 4.43 (q, J = 7.1 Hz, 2H), 6.97 (d, J =

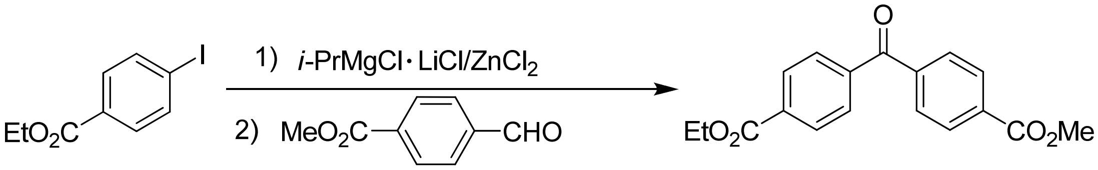
8.7 Hz, 2H), 7.80 (dd, *J* = 14.1, 8.4 Hz, 4H), 8.14 (d, *J* = 8.1 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 14.3, 55.5, 61.3, 113.7, 129.3, 129.6, 132.6, 133.1, 142.1, 163.6, 165.9, 194.8.

9b: 4-(3,4-Dimethoxy-benzoyl)-benzoic acid ethyl ester



According to general procedure B: The (4-(ethoxycarbonyl)phenyl)zinc iodide prepared from ethyl 4-iodobenzoate by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 3,4-dimethoxybenzaldehyde (2.0 mmol, 0.33 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9b** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.42 g, 74% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 1.43 (t, *J* = 7.1 Hz, 3H), 3.96 (d, *J* = 13.8 Hz, 6H), 4.43 (q, *J* = 7.1 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 7.36-7.33 (m, 1H), 7.50 (d, *J* = 1.7 Hz, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 8.15 (d, *J* = 8.2 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 14.3, 56.1, 61.3, 109.8, 111.9, 125.6, 129.3, 129.6, 133.1, 142.0, 149.1, 153.4, 165.9, 194.8. HRMS-ESI: calcd for $C_{18}H_{18}NaO_5$ $[M + Na]^+$: 337.1052. Found: 337.1050.

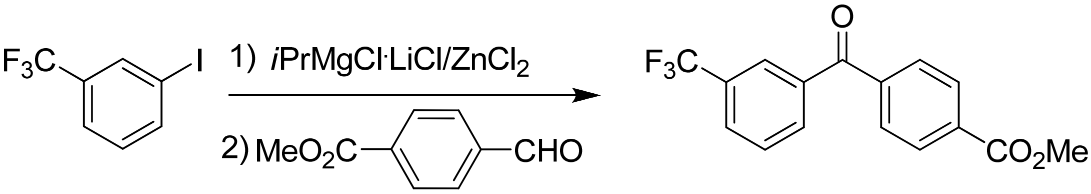
9c: Carbonyl-4-ethyl-(4'-methyl-carbonyl)–benzophenone



According to general procedure B: The (4-(ethoxycarbonyl)phenyl)zinc iodide prepared from ethyl 4-iodobenzoate by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing methyl 4-acetylbenzoate (2.0 mmol, 0.36 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9c** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.47 g, 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ

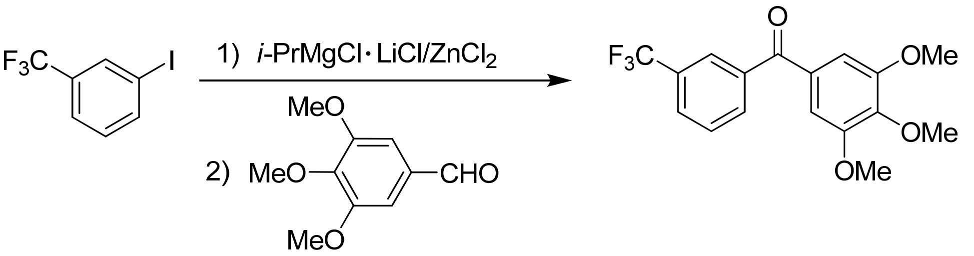
(ppm): 4.07 (s, 3H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 8.07 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 2H),8.19 (d, *J* = 8.3 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 14.3, 52.5, 61.5, 129.5, 129.6, 129.7, 129.8, 133.9, 134.0, 140.4, 140.6, 165.9, 166.1, 195.3. HRMS-ESI: calcd for $C_{18}H_{16}NaO_5$ [M + Na]$^+$: 335.0895. Found: 335.0892.

9d: 4-(3-Trifluoromethyl-benzoyl)-benzoic acid methyl ester



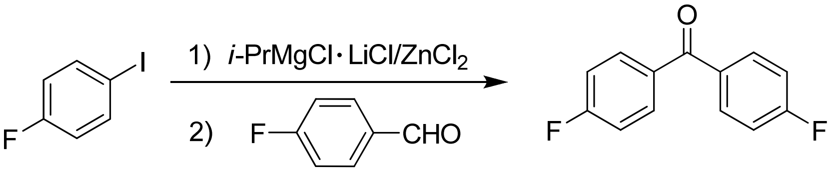
According to general procedure B: The 3-trifluoromethylphenylzinc iodide prepared from 1-iodo-3-(trifluoromethyl)benzene by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing Methyl 4-acetylbenzoate (2.0 mmol, 0.36 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9d** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.49 g, 80% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.07 (s, 3H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 8.07 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 2H), 8.19 (d, *J* = 8.3 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -63.2. ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 74.7, 123.5 (q, *J* = 271.1 Hz, CF_3), 126.7 (q, *J* = 3.5 Hz), 129.1, 129.3 (q, *J* = 3.0 Hz), 129.6, 129.7, 131.2 (q, *J* = 32.6 Hz), 133.1, 134.2, 137.6, 140.2, 165.6, 194.5. HRMS-ESI: calcd for $C_{16}H_{11}F_3NaO_3$ [M + Na]$^+$: 331.0558. Found: 331.0554.

9e: (3-(trifluoromethyl)phenyl)(3,4,5-trimethoxyphenyl)methanone



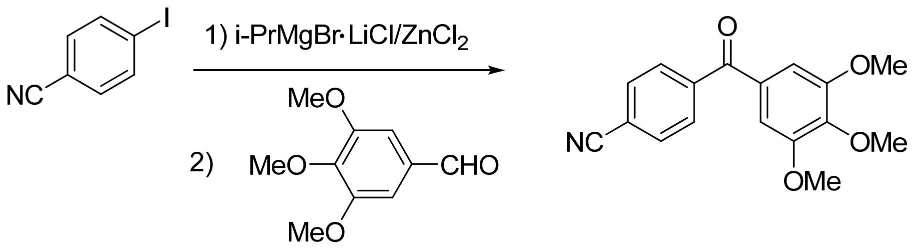
According to general procedure B: The 3-trifluoromethylphenylzinc iodide prepared from 1-iodo-3-(trifluoromethyl)benzene by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 3,4,5-trimethoxybenzaldehyde (2.0 mmol, 0.39 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9e** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.57 g, 84% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.88 (s, 6H), 3.96 (s, 3H), 7.05 (s, 2H), 7.64 (t, J = 7.8 Hz, 2H), 7.85 (d, J = 7.8 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 8.06 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -63.1. ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 56.3, 61.0, 107.8, 123.6 (q, J = 270.6 Hz, CF_3), 126.7 (q, J = 3.6 Hz), 128.6 (q, J = 3.8 Hz), 128.9, 130.8 (q, J = 33.0 Hz), 131.6, 132.9, 138.5, 142.6, 153.0, 194.1. HRMS-ESI: calcd for $C_{17}H_{15}F_3NaO_4$ $[M + Na]^+$: 363.0820. Found: 363.0814.

9f: bis(4-fluorophenyl)methanone [15]



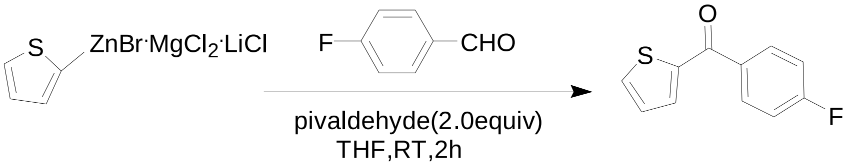
According to general procedure B: The 4-fluorophenylzinc iodide prepared from 4-fluoroiodobenzene by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 4-fluorobenzaldehyde (2.0 mmol, 0.39 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9f** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.34 g, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.17 (t, J = 8.6 Hz, 4H), 7.79-7.84 (m, 4H). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -106.0. ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 115 (d, J = 21 Hz), 132.4 (d, J = 9.0 Hz), 133.7 (q, J = 3.0 Hz), 165.3 (d, J = 252 Hz), 193.8.

9g: 4-(3,4,5-trimethoxybenzoyl)benzonitrile



According to general procedure B: The 4-cyanophenylzinc iodide prepared from 4-iodobenzonitrile by general procedure A2 (about 4.0 mmol) was added slowly to a THF solution (10 ml) containing 3,4,5-trimethoxybenzaldehyde (2.0 mmol, 0.39 g), pivaldehyde (0.34g, 4.0 mmol, 0.43 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (10 mL). 10 mL of ethyl acetate was then added and the organic phase was separated, washed with 10 mL of water and then with 10 ml of brine. The water phase was extracted with ethyl acetate (2×10 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. The ketone **9g** was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 0.43 g, 72% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 3.86 (s, 6H), 3.95 (s, 3H), 7.01 (s, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 8.4 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 56.4, 61.0, 107.8, 115.5, 117.9, 130.0, 131.2, 132.1, 141.6, 142.9, 153.1, 194.0. HRMS-ESI: calcd for $C_{17}H_{15}NNaO_4$ $[M + Na]^+$: 320.0899. Found: 320.0897.

10: (4-Fluoro-phenyl)-thiophen-2-yl-methanone[16]



According to general procedure B: The 2-thienylzinc reagent prepared by general procedure A1 from 2-bromothiophene (4.89g, 30 mmol), magnesium turnings (0.9 g, 37 mmol). $ZnCl_2$ (4.1g, 30 mmol), and LiCl (1.3g, 30 mmol) was added slowly to a THF solution (100 ml) containing 4-fluorobenzaldehyde (20 mmol, 2.5 g), pivaldehyde (3.0g, 40 mmol, 4.3 ml) under ice-water bath. After the reaction mixture was stirred at room temperature for 2 hours, the reaction mixture was quenched by aqueous NH_4Cl (100 mL). 100 mL of ethyl acetate was then added and the organic phase was separated, washed with 100 mL of water and then with 100 ml of brine. The water phase was extracted with ethyl acetate (2×100 mL). The organic phase was combined, dried (Na_2SO_4) and concentrated under reduced pressure. 2-(4'-4-fluorobenzoyl) thiophene was obtained by column chromatography on silica gel using petroleum/ethyl acetate as an eluent. 3.2 g, 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.18 (dd, J = 10.3, 6.7 Hz, 3H), 7.63 (d, J = 2.9 Hz, 1H), 7.73 (d, J = 4.1 Hz, 1H), 7.91 (dd, J = 8.5, 5.5 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -106.6. ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 115.5 (d, J = 21 Hz), 127.9, 131.6 (d, J = 9.0 Hz), 134.2, 134.6, 143.3, 165.7 (d, J = 252.3 Hz), 186.6.

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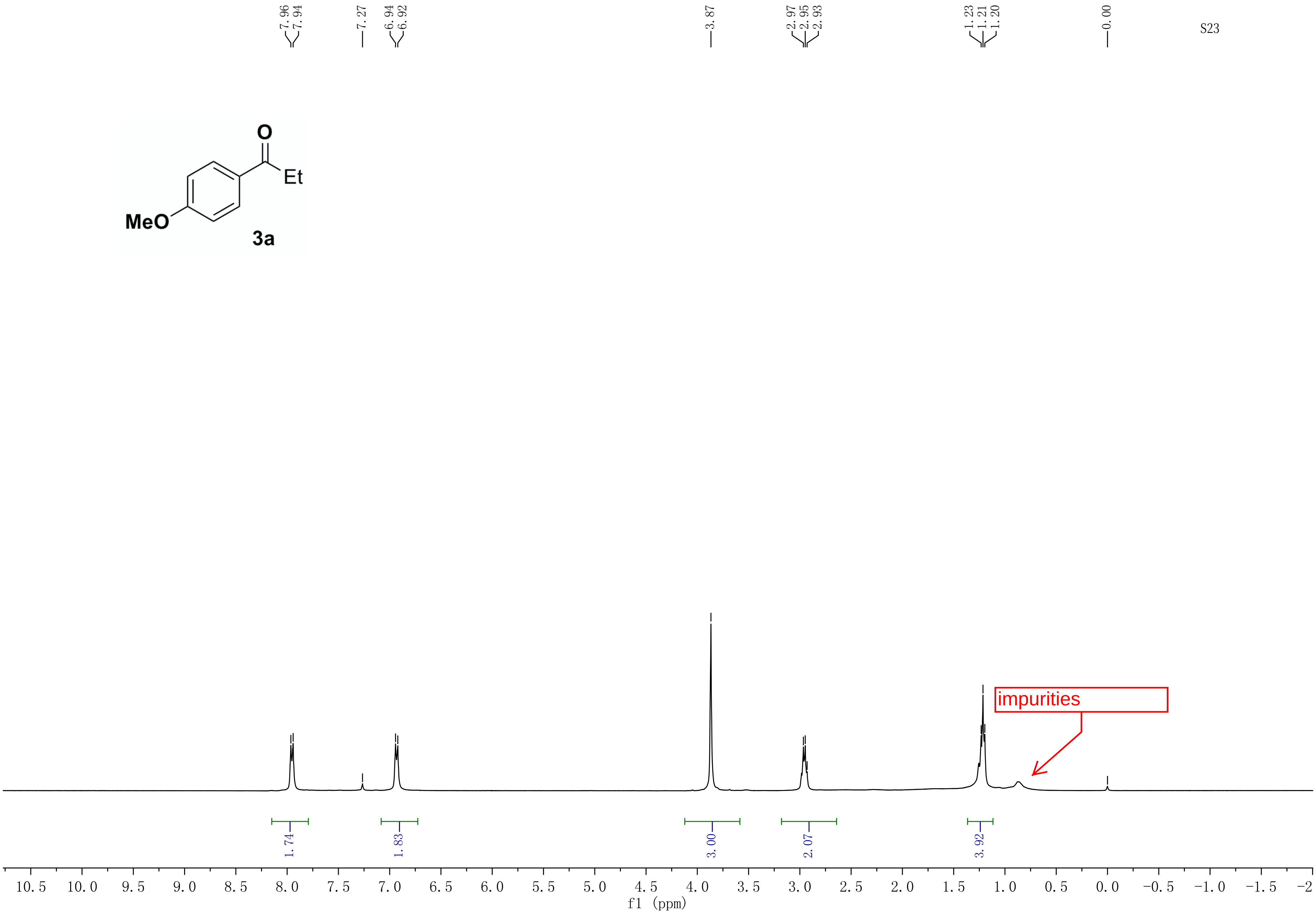
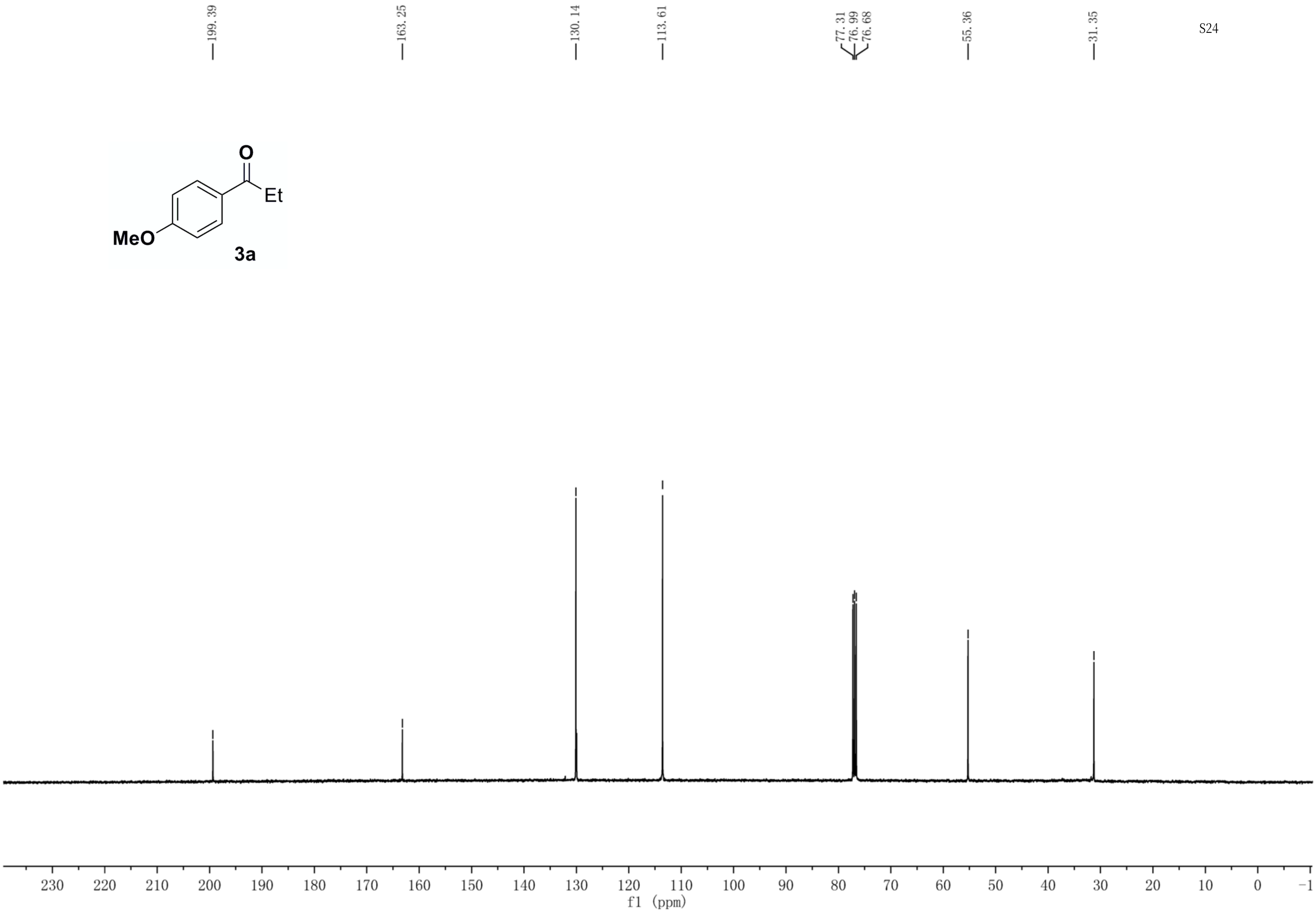
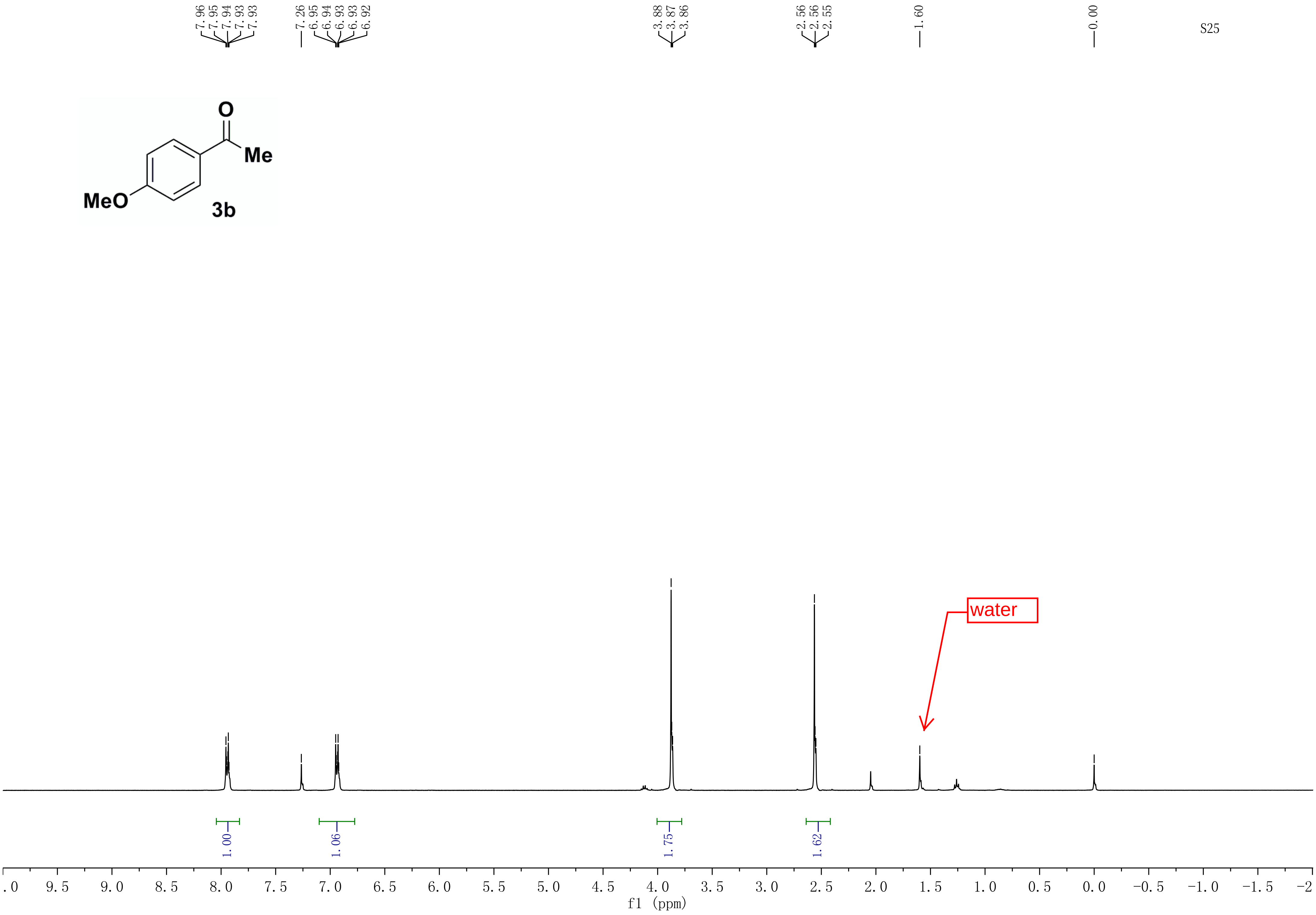

3a
O
Et
MeO
7.96
7.94
7.27
6.94
6.92
3.87
2.97
2.95
2.93
1.23
1.21
1.20
0.00
impurities
1.74
1.83
3.00
2.07
3.92
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2
f1 (ppm)


199.39
163.25
130.14
113.61
77.31
76.99
76.68
55.36
31.35
O
Et
MeO
3a
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



3b

7.96
7.95
7.94
7.93
7.93
7.26
6.95
6.94
6.93
6.93
6.92
3.88
3.87
3.86
2.56
2.56
2.55
1.60
0.00
O
Me
MeO
water
1.00
1.06
1.75
1.62
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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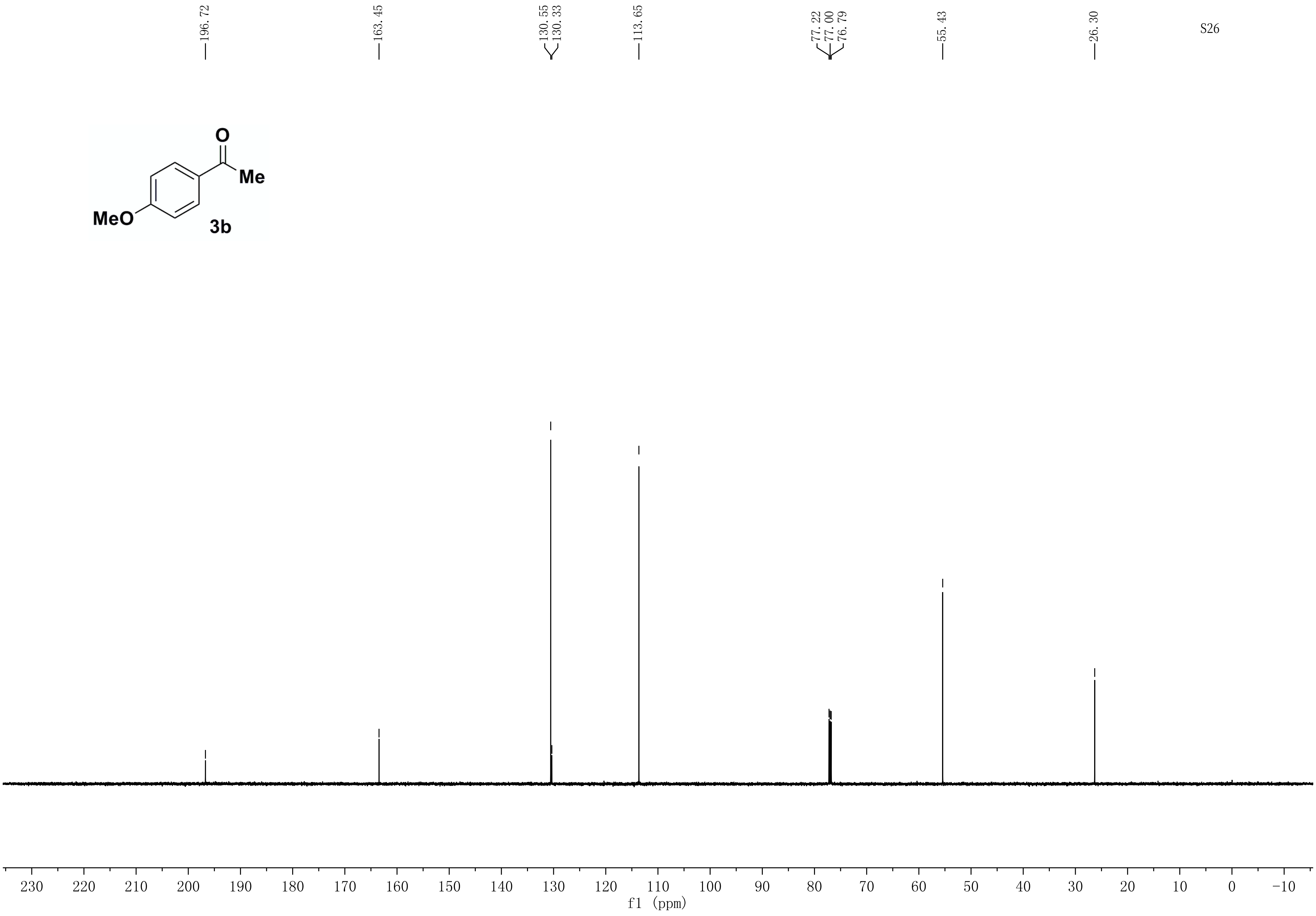
-1.0
-1.5
-2
f1 (ppm)


196.72
163.45
130.55
130.33
113.65
77.22
77.00
76.79
55.43
26.30
O
Me
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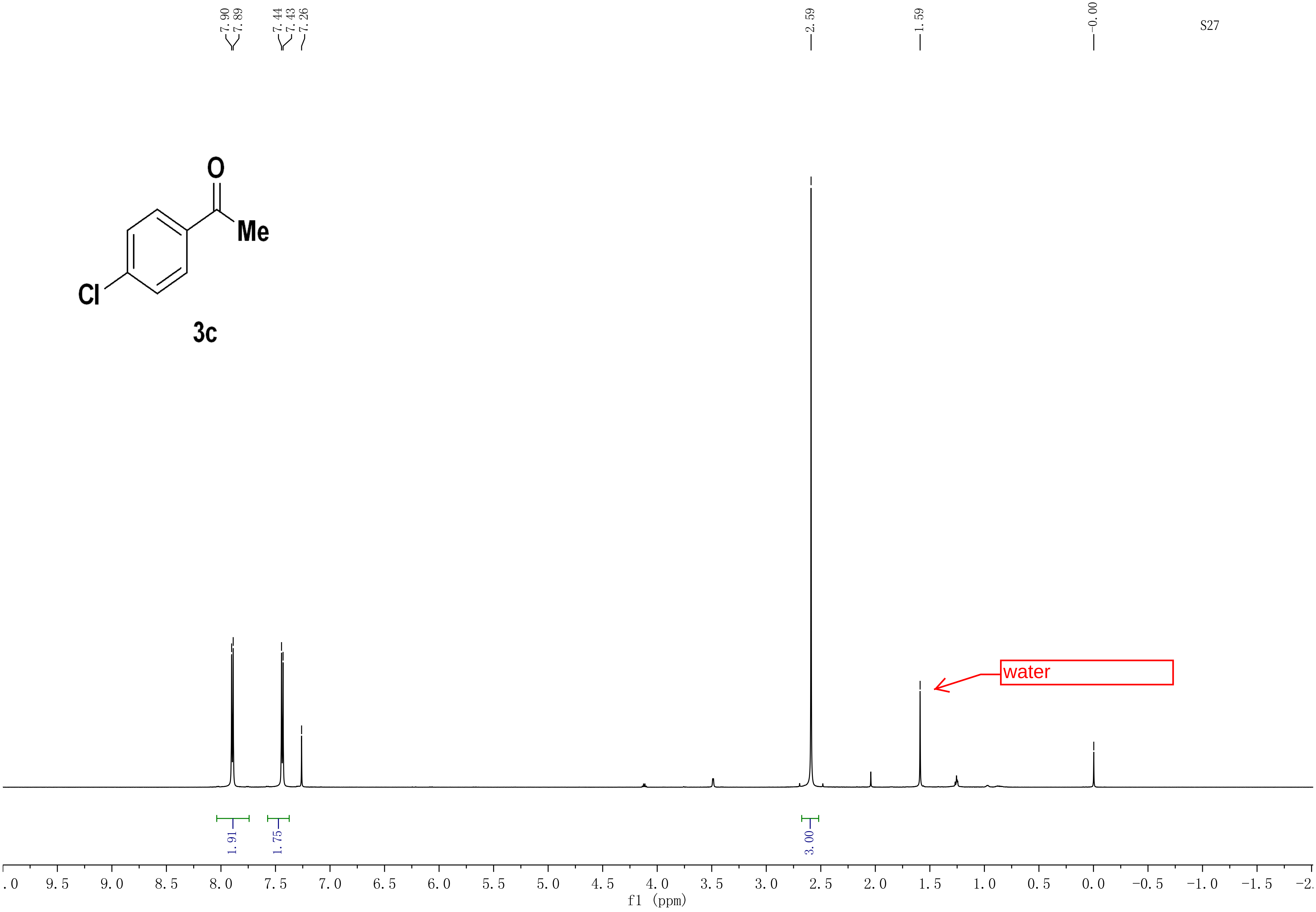
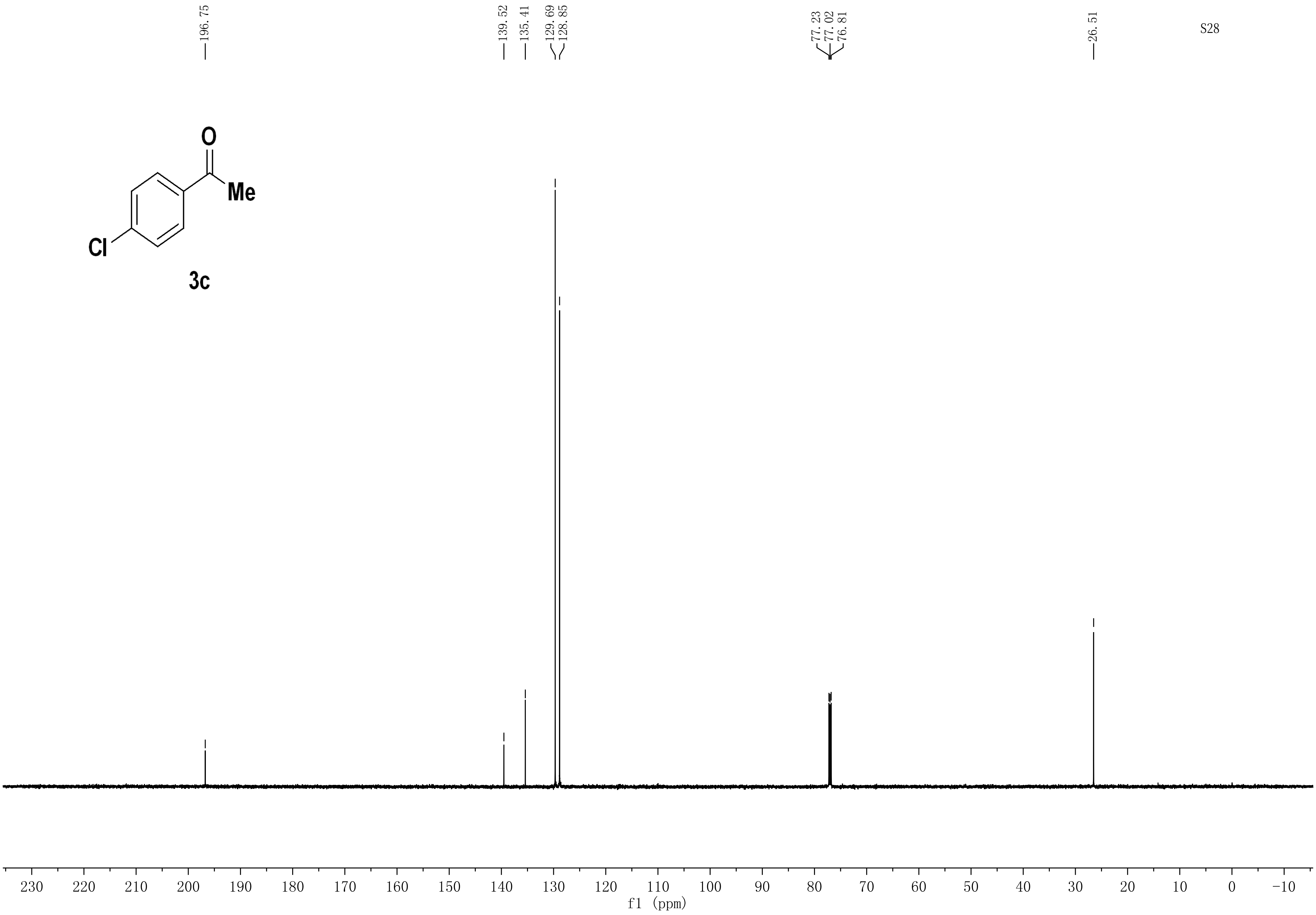
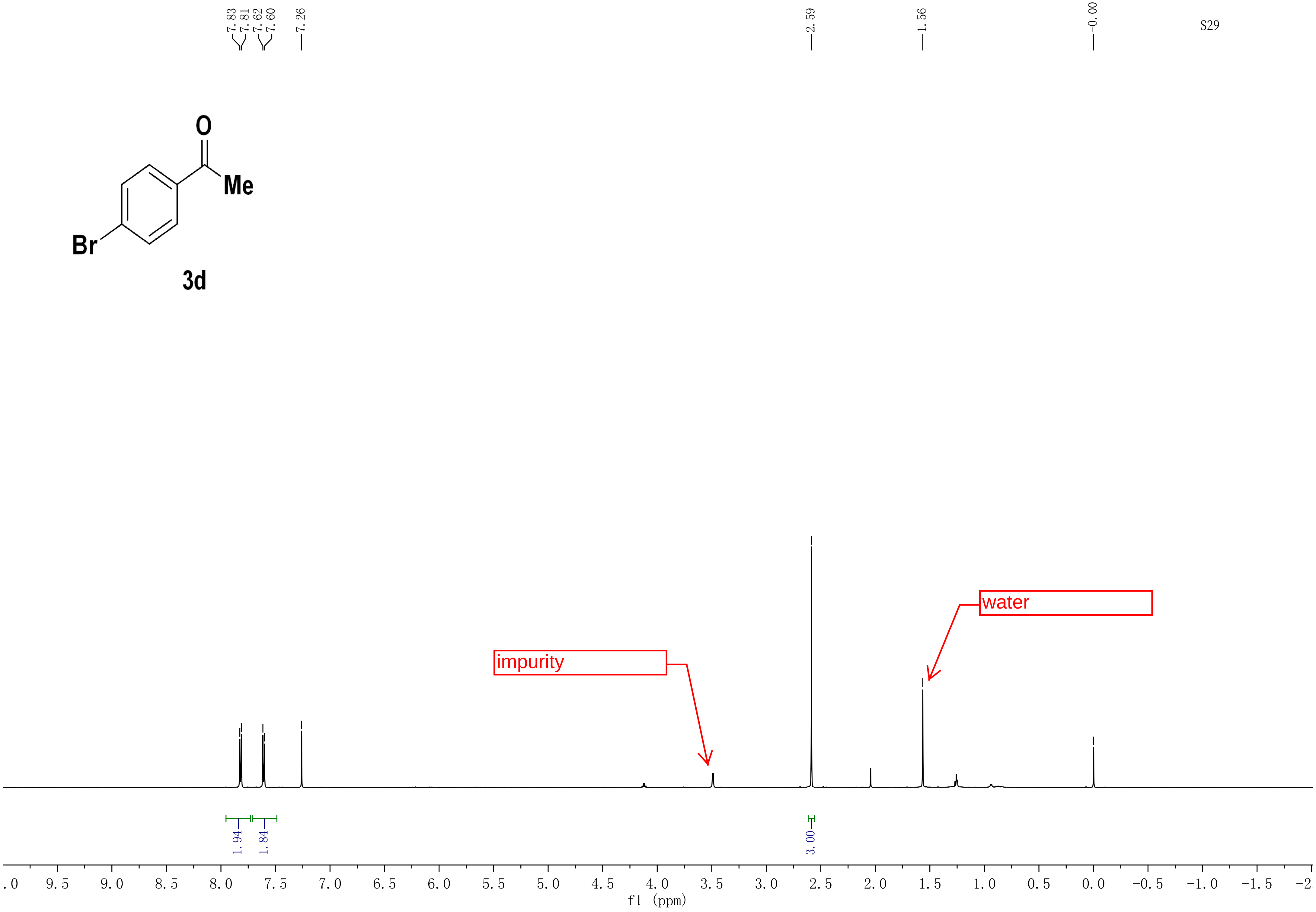
3b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



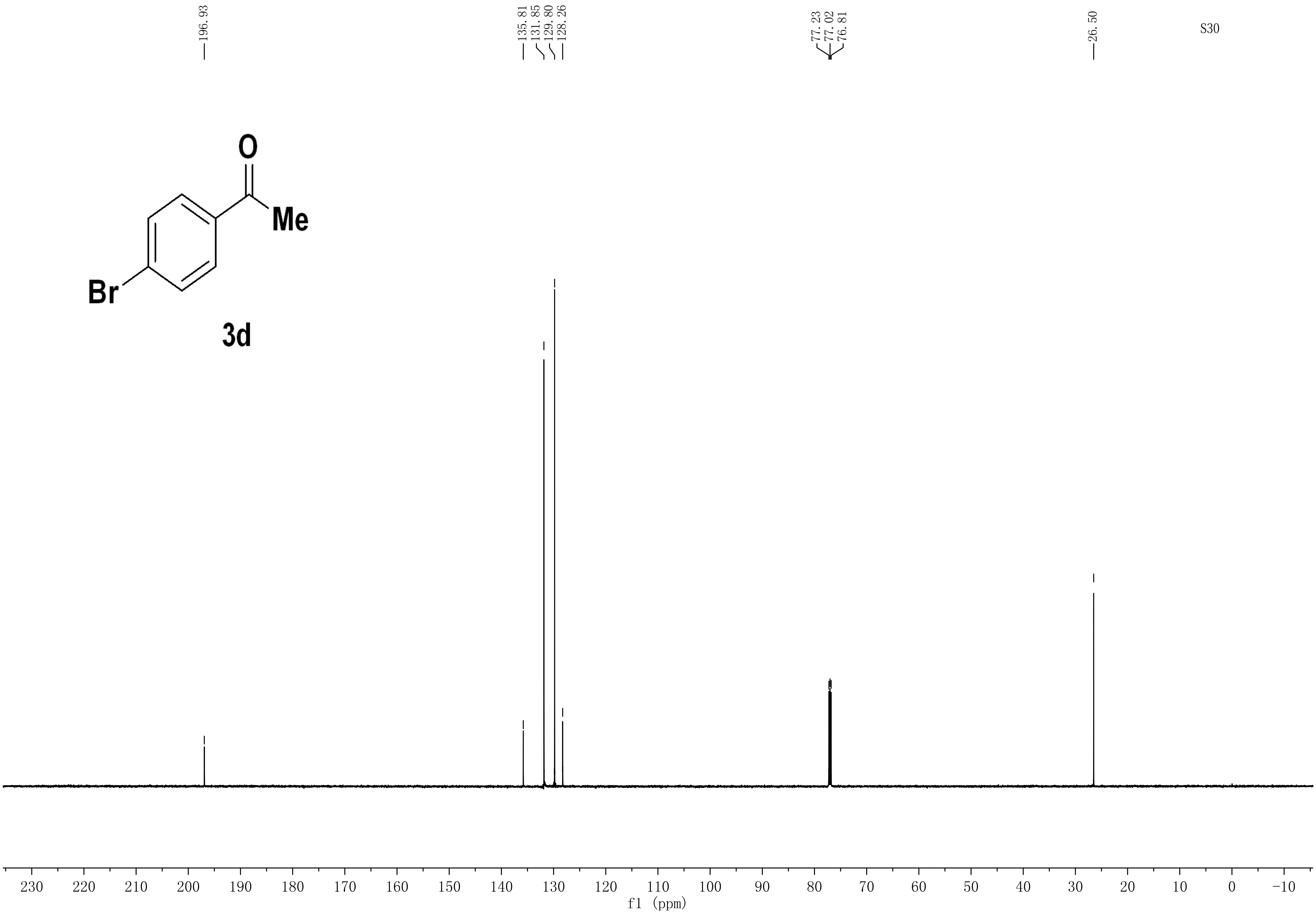
3c

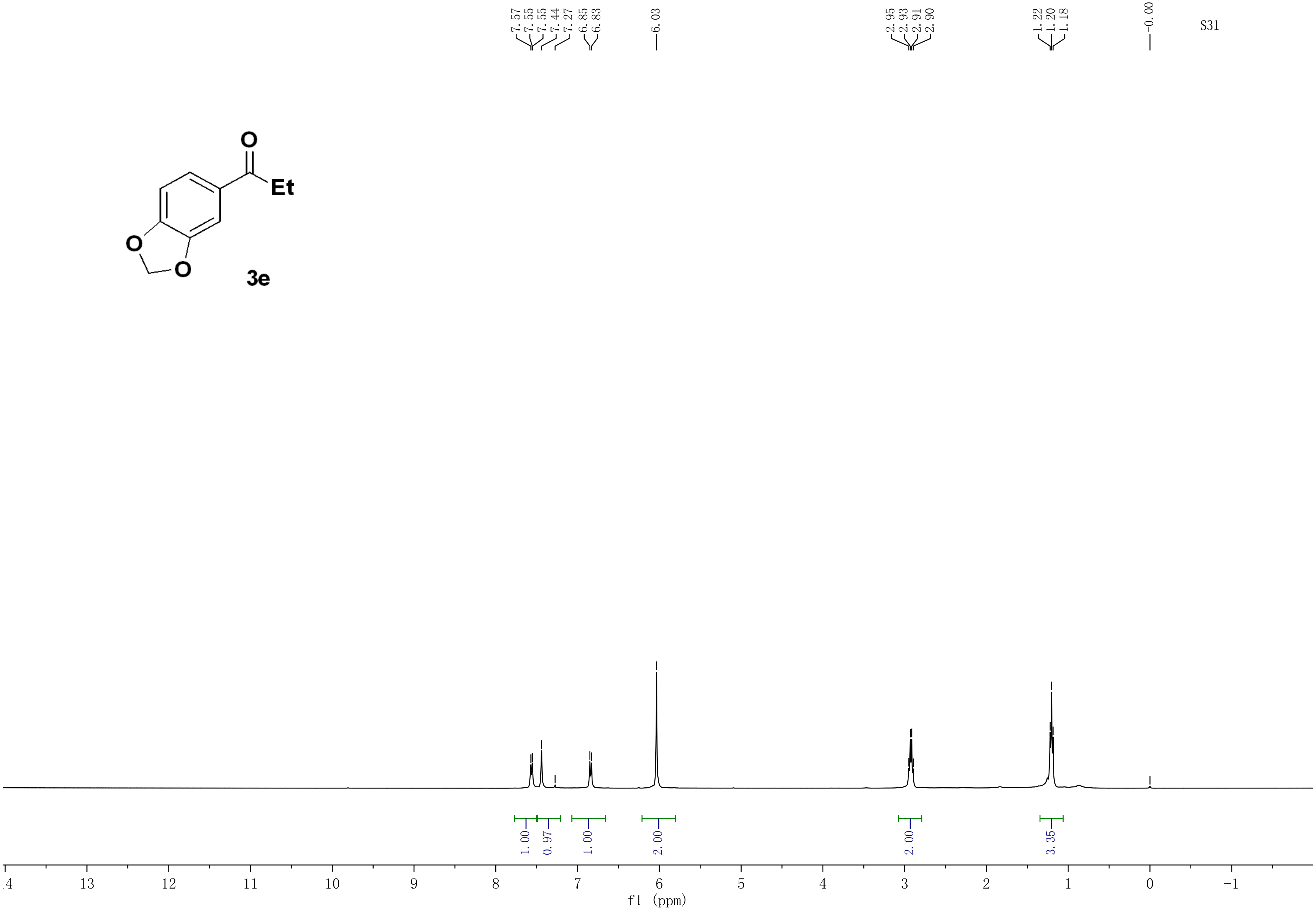
7.90
7.89
7.44
7.43
7.26
2.59
1.59
-0.00
O
Me
Cl
water
1.91
1.75
3.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.
f1 (ppm)


196.75
139.52
135.41
129.69
128.85
77.23
77.02
76.81
26.51
O
Me
Cl
3c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.83
7.81
7.62
7.60
7.26
2.59
1.56
-0.00
O
Me
Br
impurity
water
1.94
1.84
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)

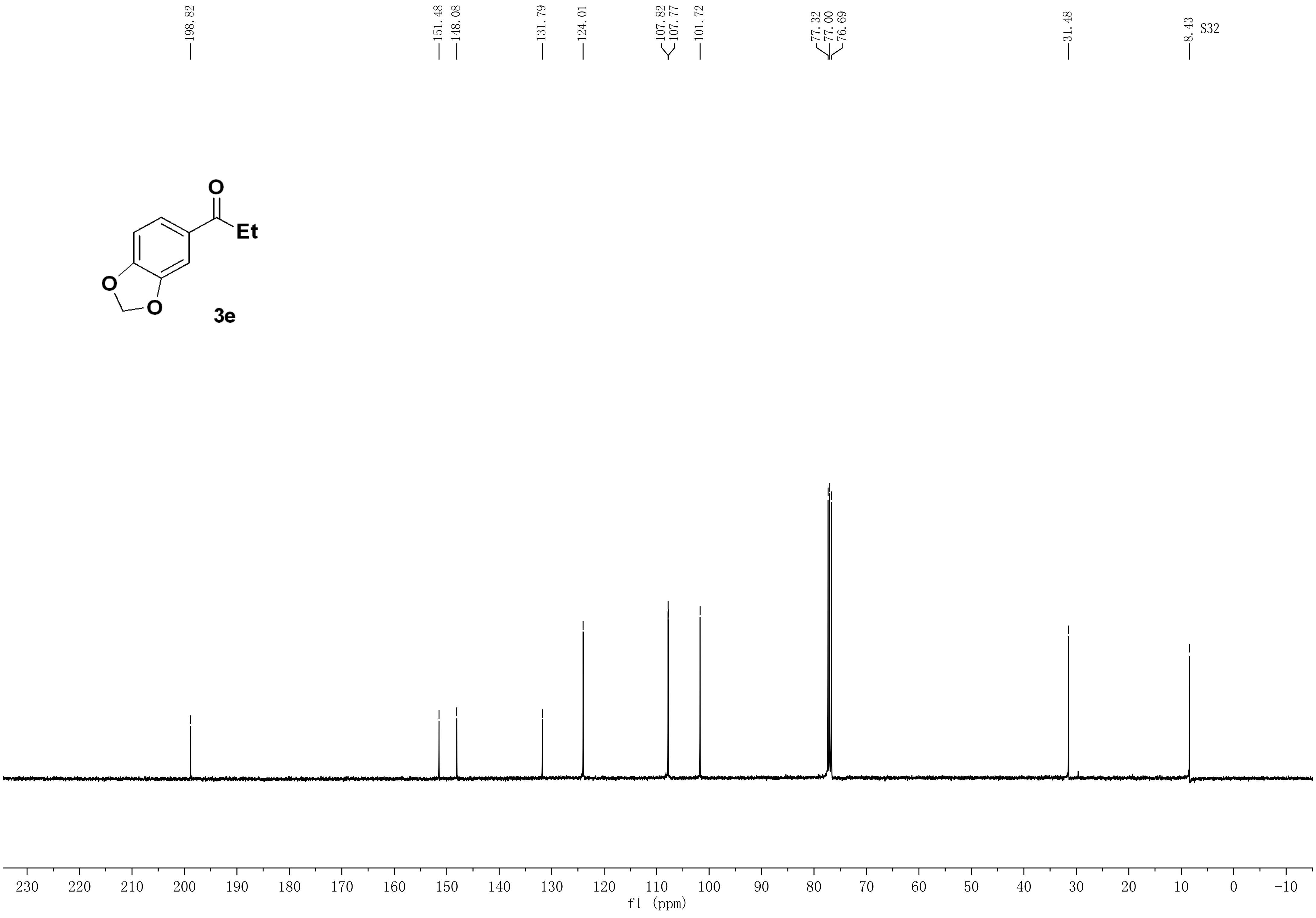
3d


196.93
135.81
131.85
129.80
128.26
77.23
77.02
76.81
26.50
O
Me
Br
3d
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

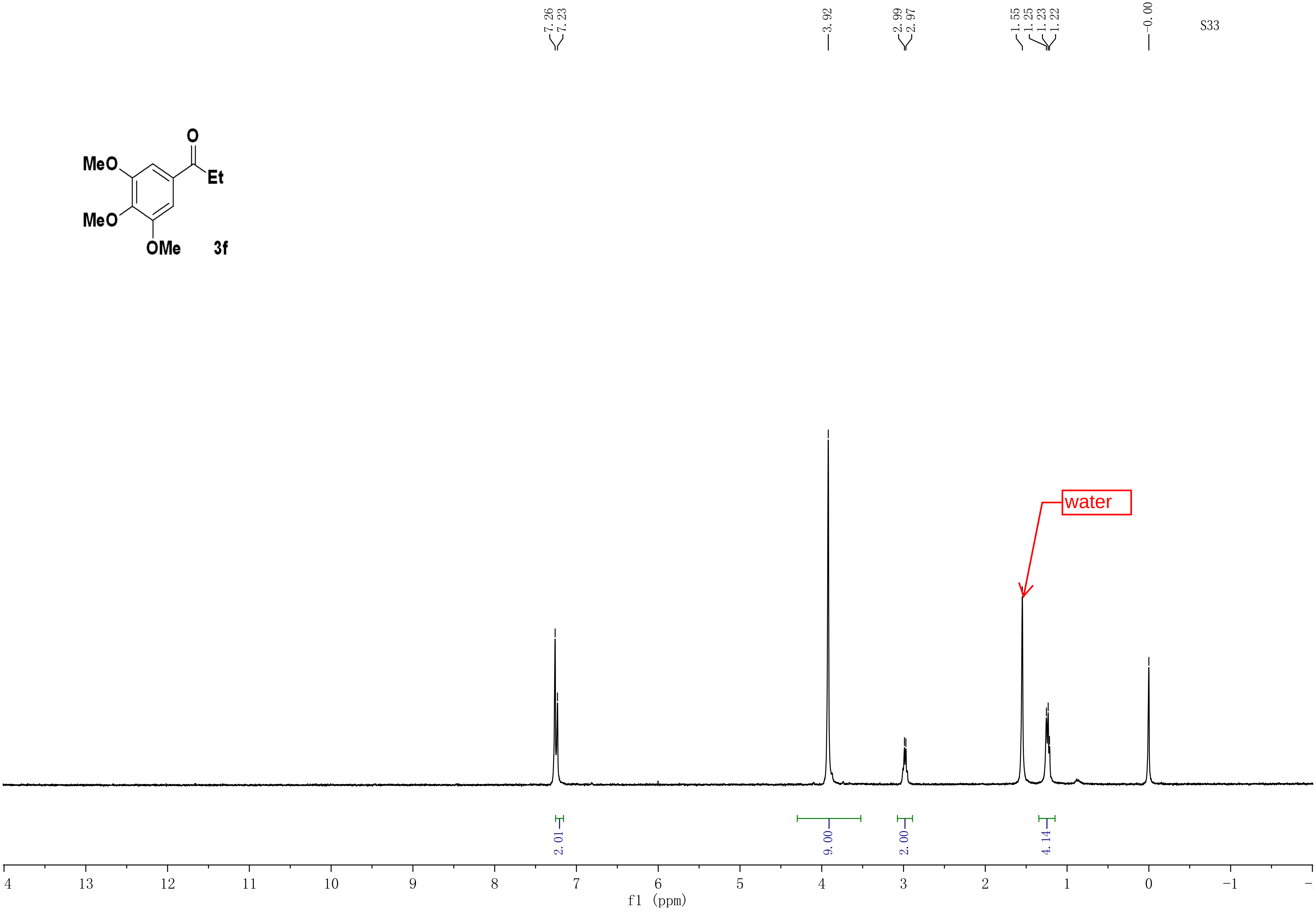


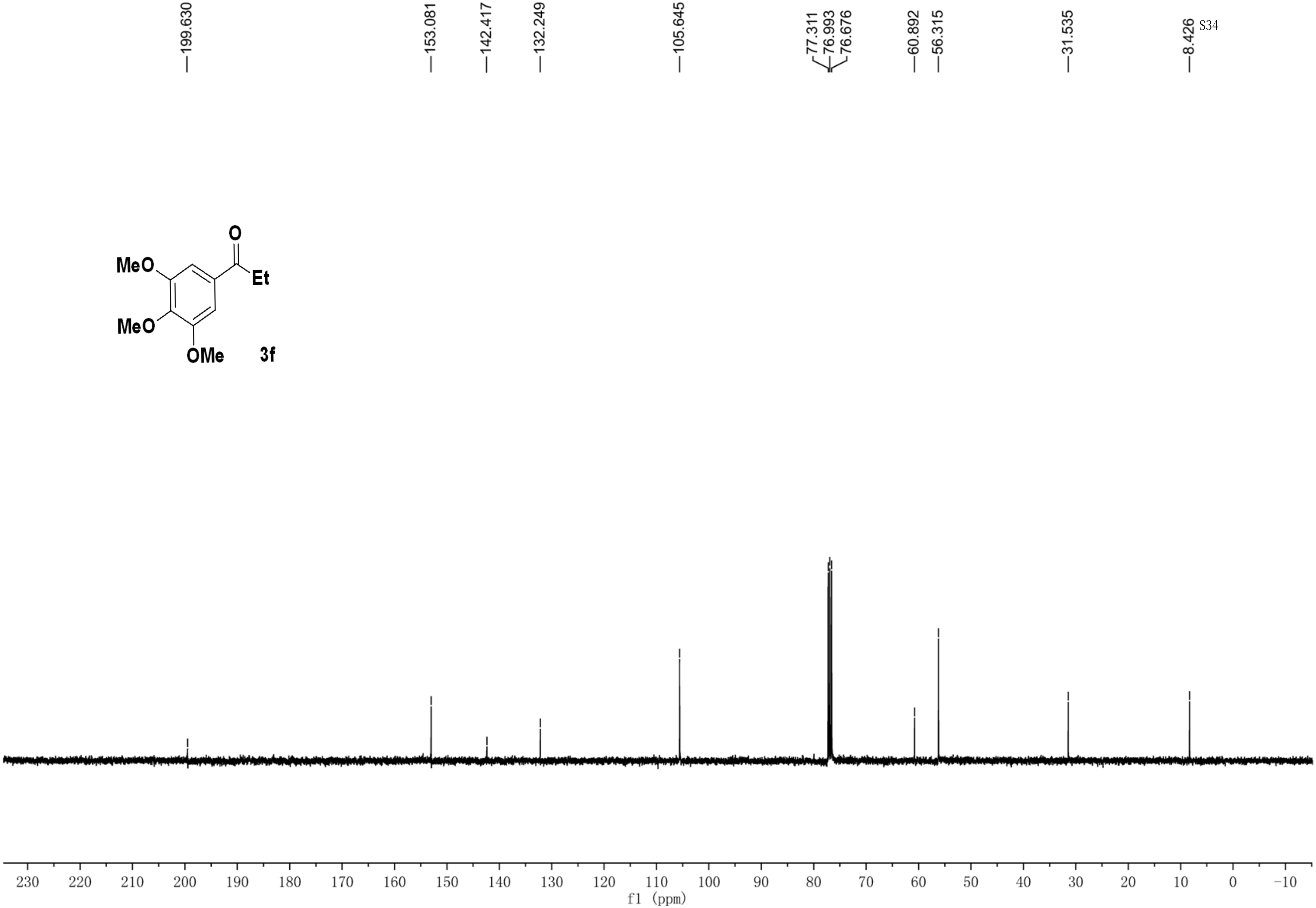
3e

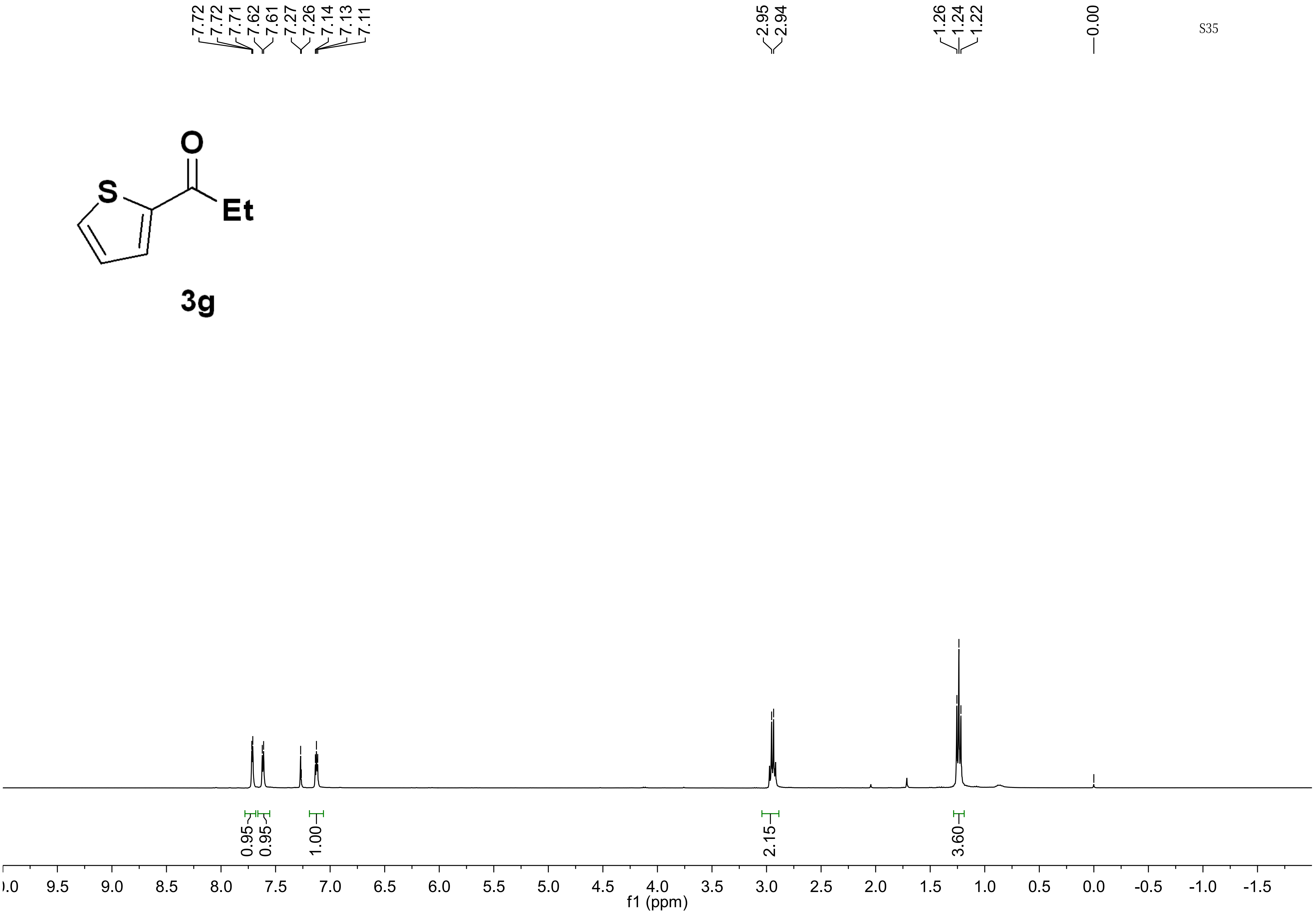
7.57
7.55
7.55
7.44
7.27
6.85
6.83
6.03
2.95
2.93
2.91
2.90
1.22
1.20
1.18
-0.00
O
Et
O
O
1.00
0.97
1.00
2.00
2.00
3.35
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

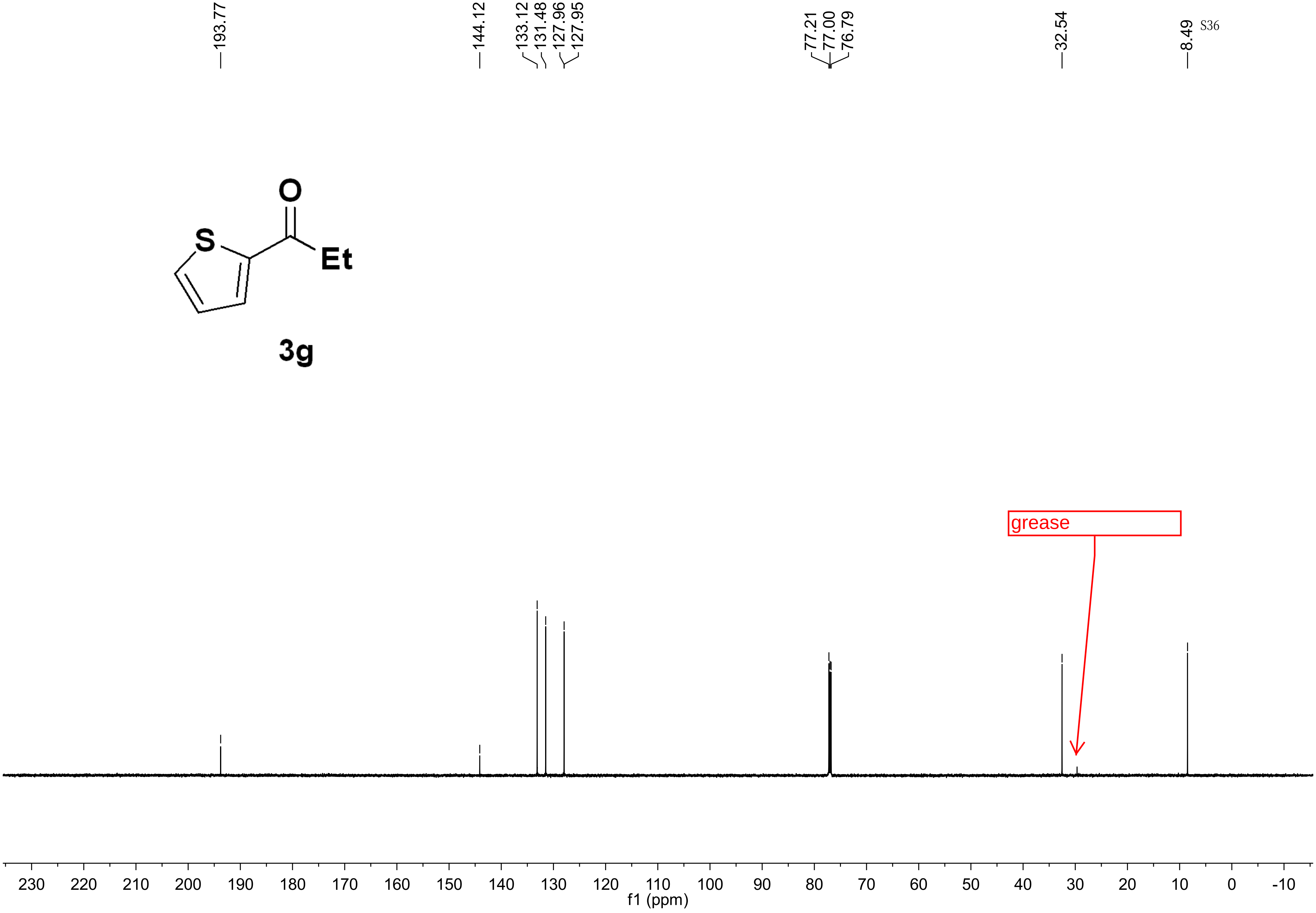

198.82
151.48
148.08
131.79
124.01
107.82
107.77
101.72
77.32
77.00
76.69
31.48
8.43
O
Et
O
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

3e

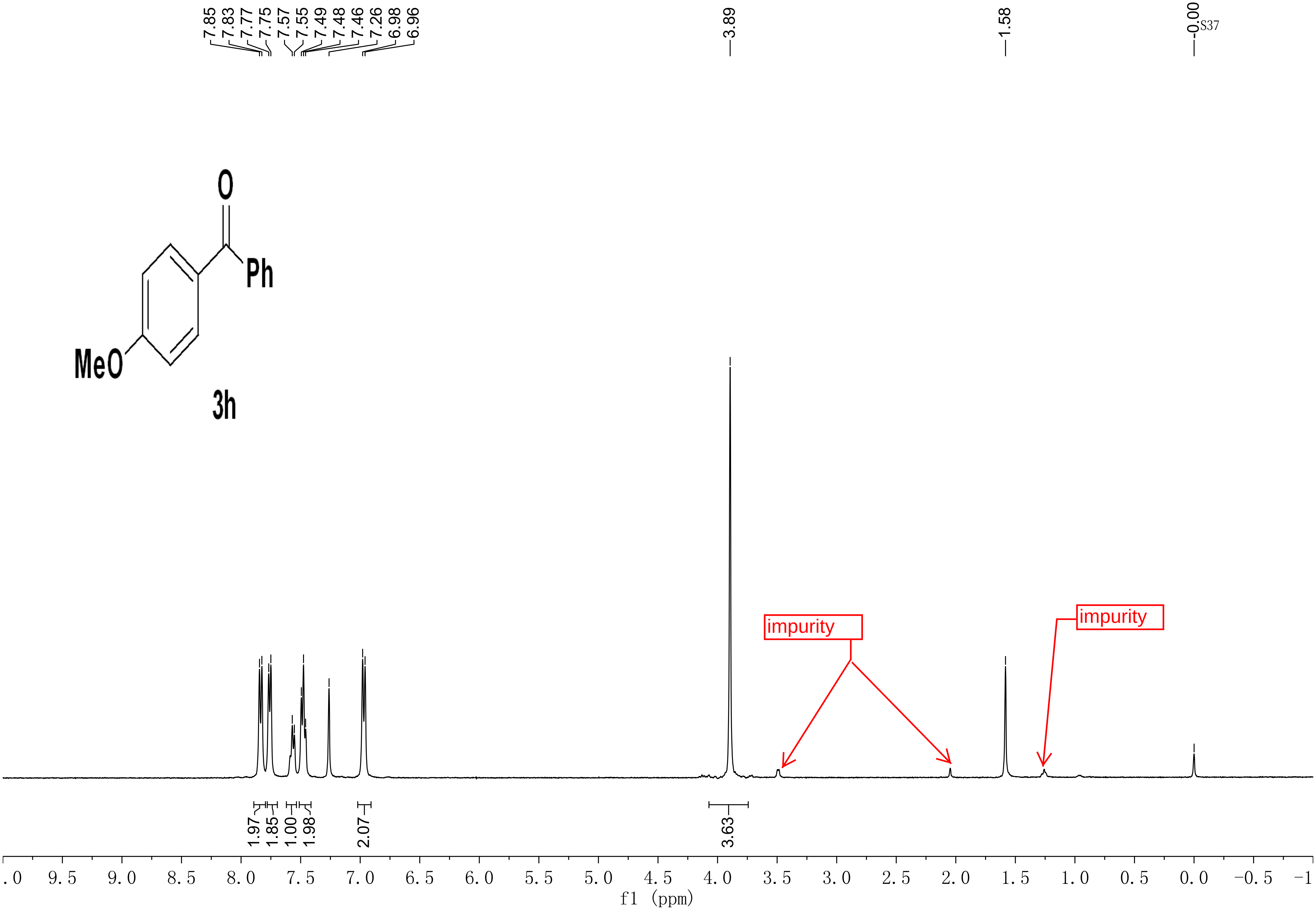

7.26
7.23
3.92
2.99
2.97
1.55
1.25
1.23
1.22
-0.00
O
MeO
Et
MeO
OMe
3f
water
2.01
9.00
2.00
4.14
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

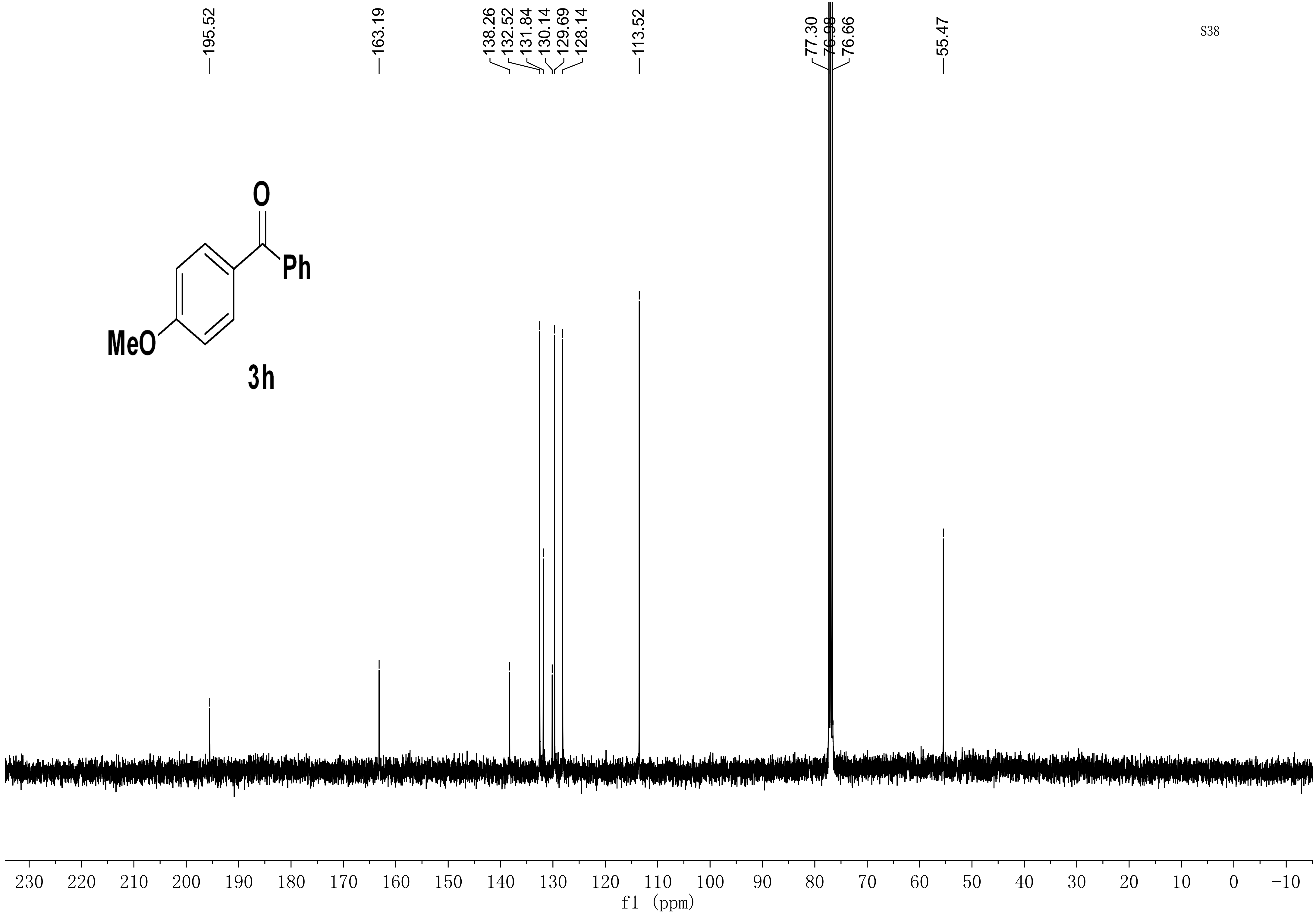

199.630
153.081
142.417
132.249
105.645
77.311
76.993
76.676
60.892
56.315
31.535
8.426
O
MeO
Et
MeO
OMe
3f
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

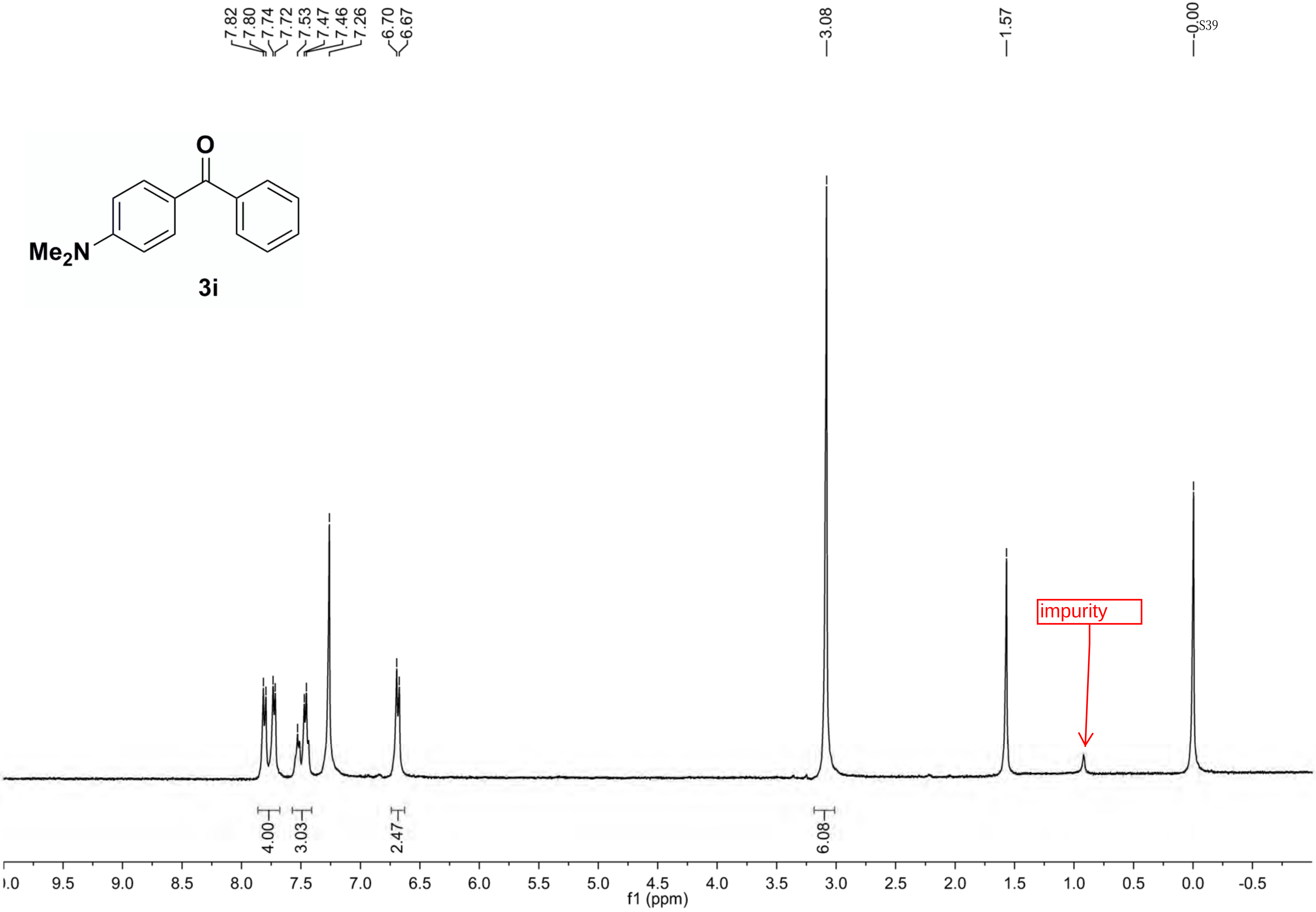

7.72
7.72
7.71
7.62
7.61
7.27
7.26
7.14
7.13
7.11
2.95
2.94
1.26
1.24
1.22
0.00
O
S
Et
3g
0.95
0.95
1.00
2.15
3.60
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

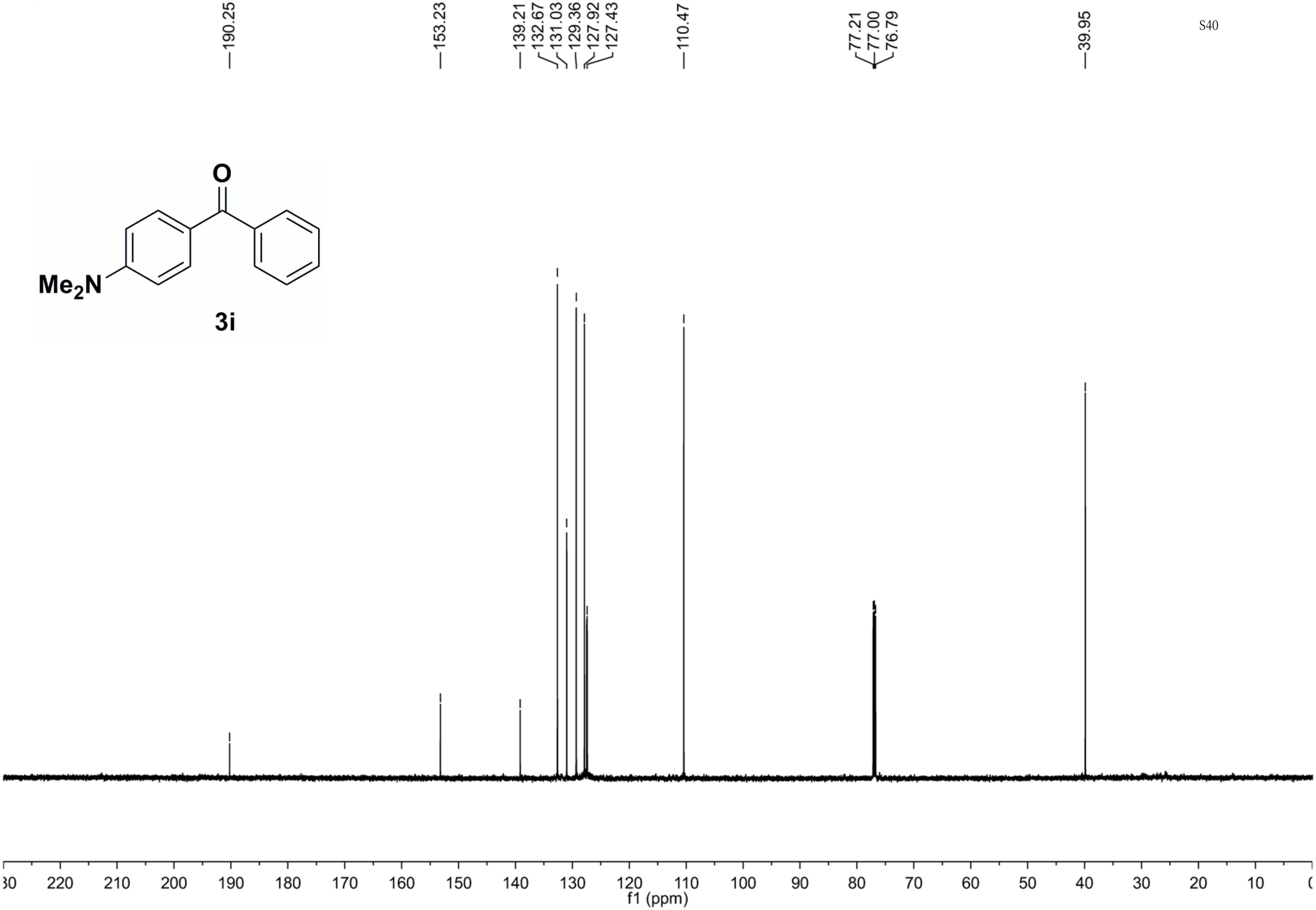

193.77
144.12
133.12
131.48
127.96
127.95
77.21
77.00
76.79
32.54
8.49
O
S
Et
grease
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3g

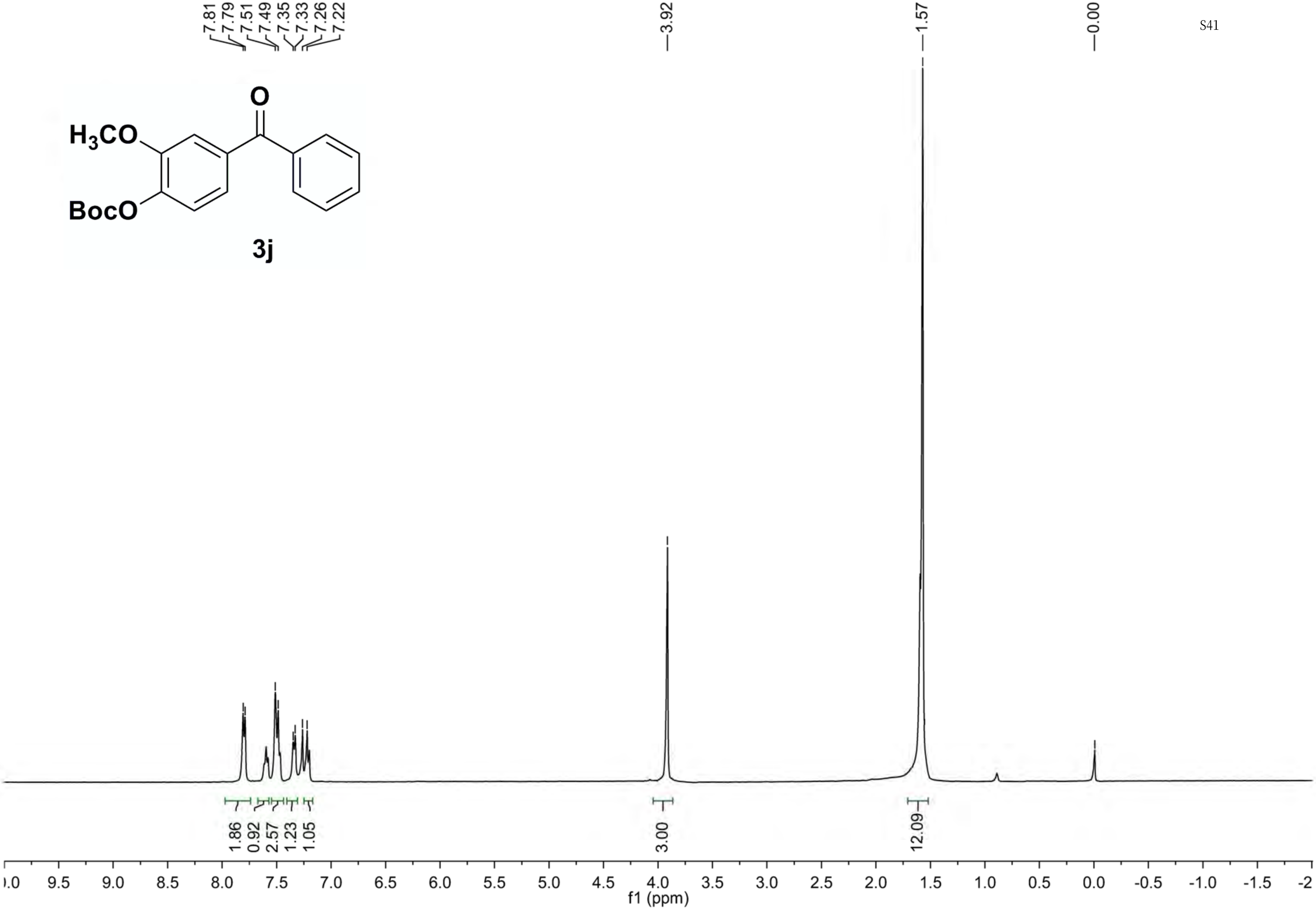

7.85
7.83
7.77
7.75
7.57
7.55
7.49
7.48
7.46
7.26
6.98
6.96
3.89
1.58
-0.00
O
Ph
MeO
3h
impurity
impurity
1.97
1.85
1.00
1.98
2.07
3.63
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


195.52
163.19
138.26
132.52
131.84
130.14
129.69
128.14
113.52
77.30
76.98
76.66
55.47
O
Ph
MeO
3h
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

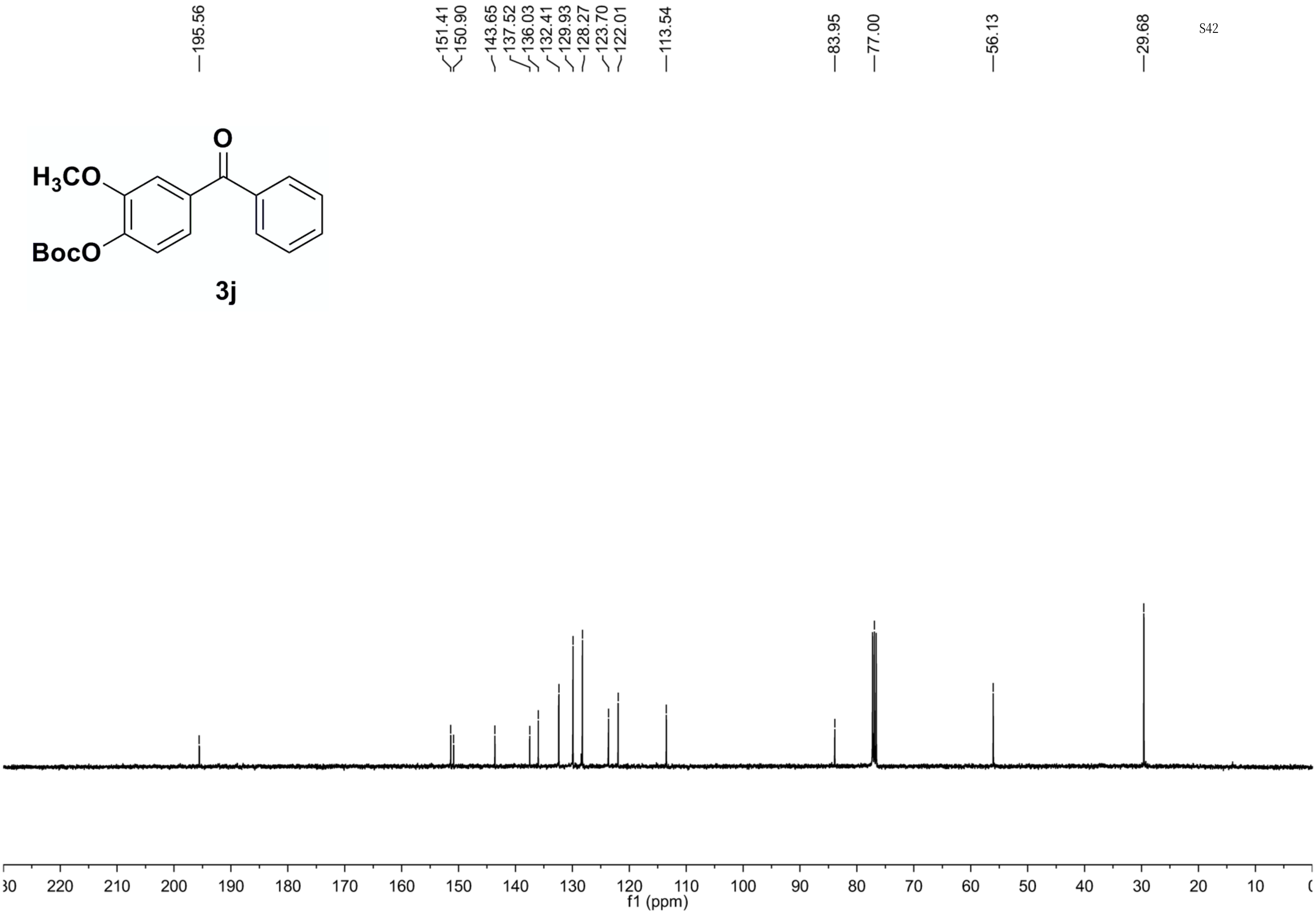

7.82
7.80
7.74
7.72
7.53
7.47
7.46
7.26
6.70
6.67
3.08
1.57
-0.00
O
Me2N
3i
impurity
4.00
3.03
2.47
6.08
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

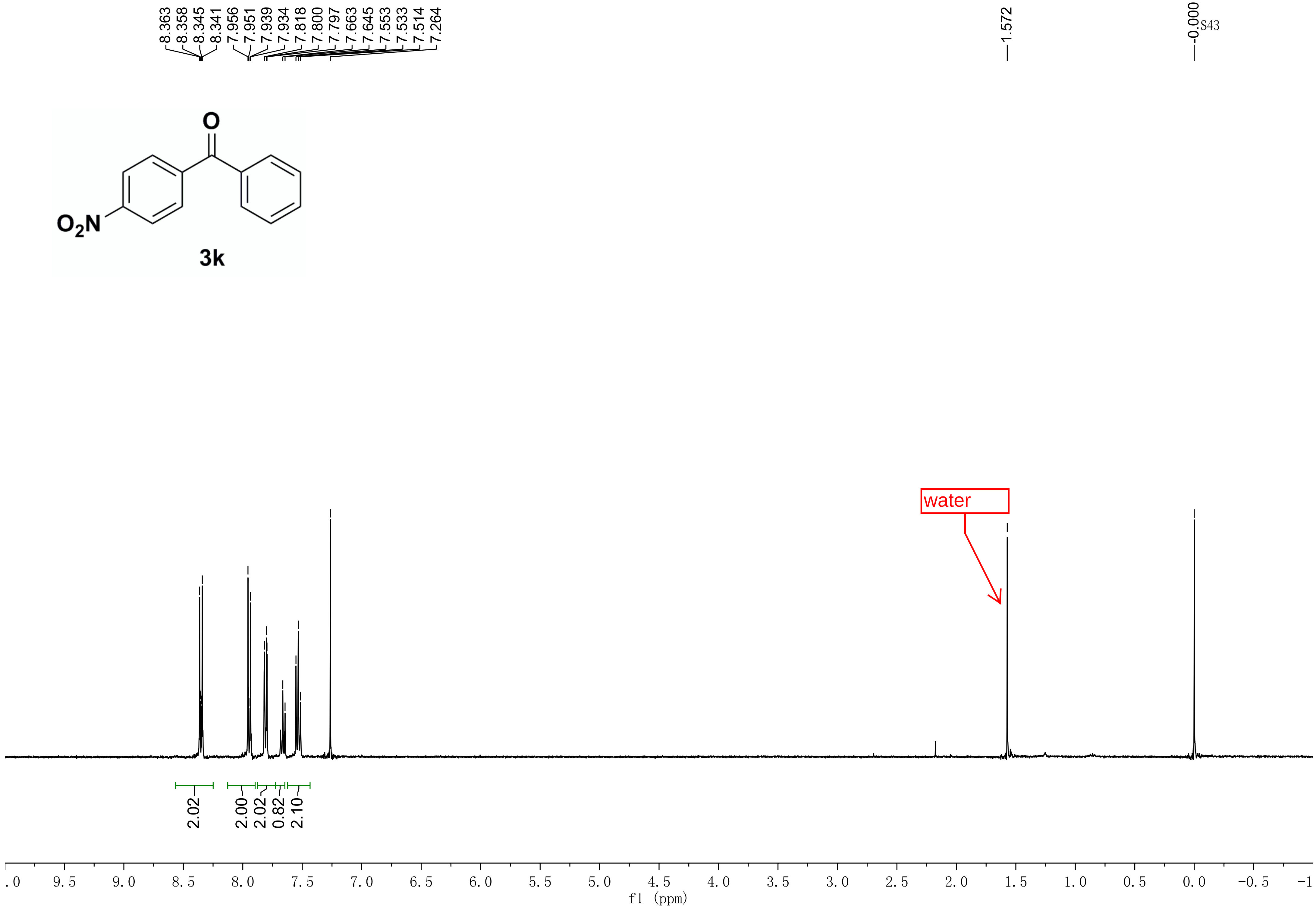

190.25
153.23
139.21
132.67
131.03
129.36
127.92
127.43
110.47
77.21
77.00
76.79
39.95
O
Me_2N
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

3i

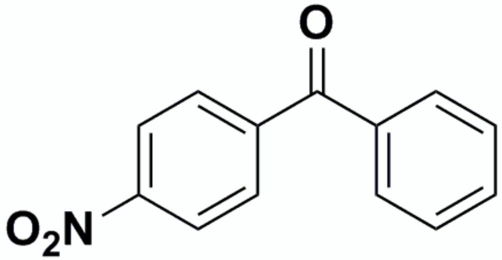

7.81
7.79
7.51
7.49
7.35
7.33
7.26
7.22
3.92
1.57
0.00
O
H3CO
BocO
1.86
0.92
2.57
1.23
1.05
3.00
12.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

3j

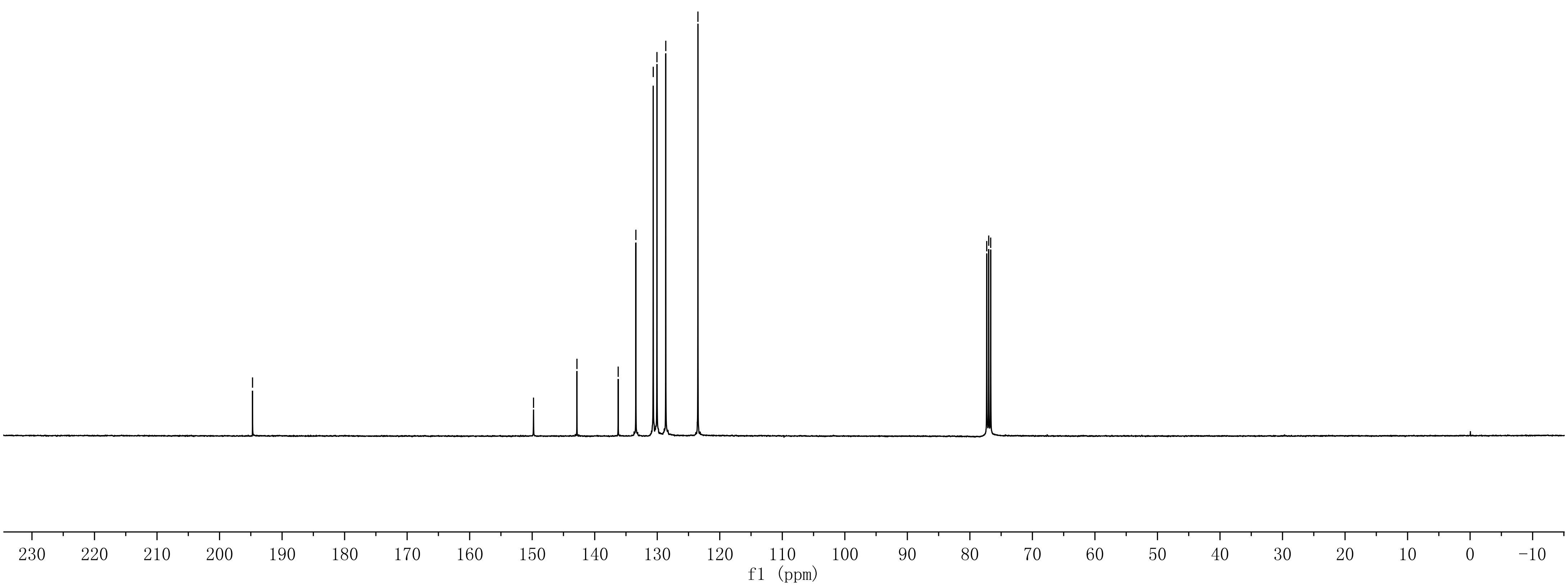

195.56
151.41
150.90
143.65
137.52
136.03
132.41
129.93
128.27
123.70
122.01
113.54
83.95
77.00
56.13
29.68
O
H3CO
BocO
3j
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

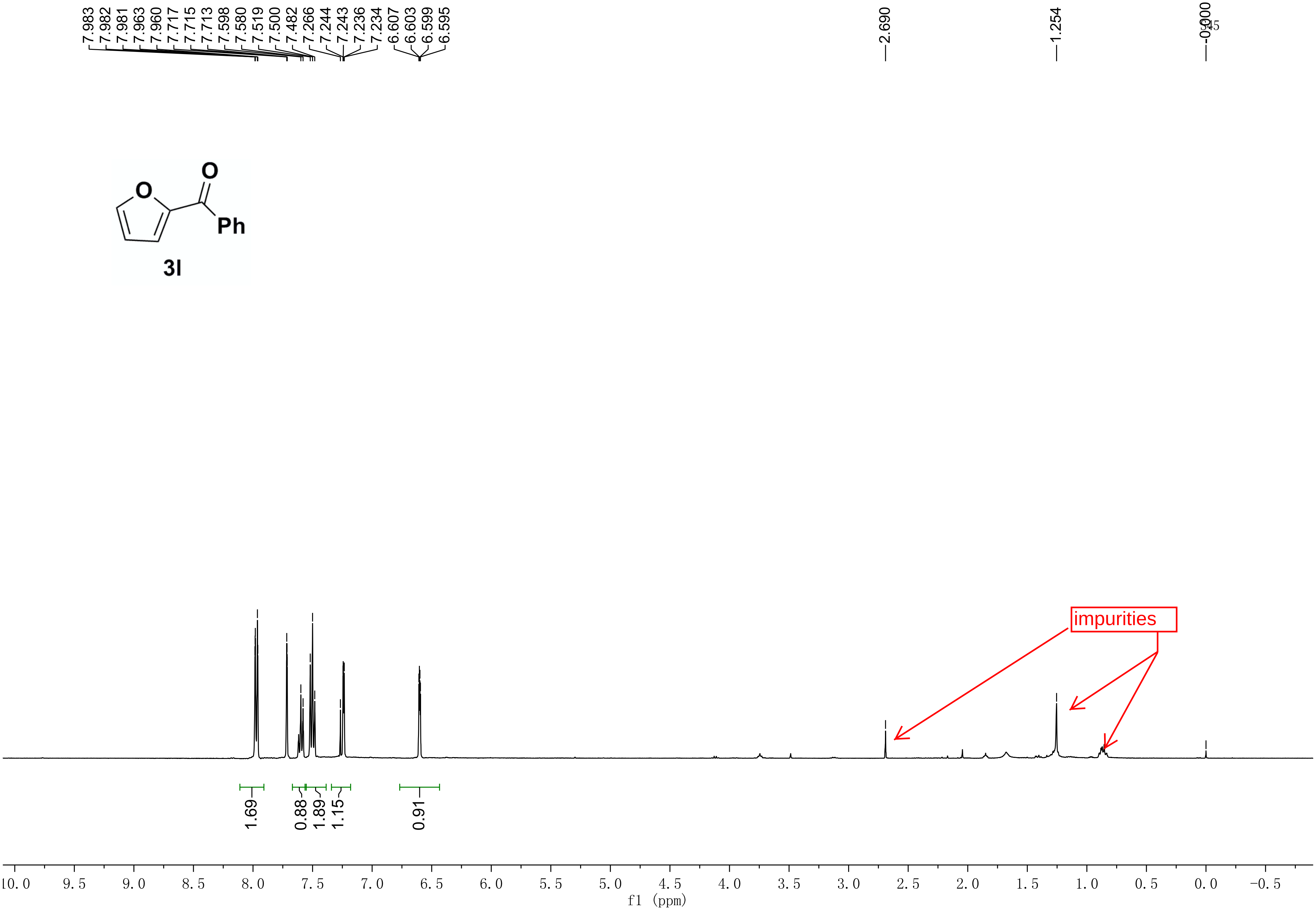

8.363
8.358
8.345
8.341
7.956
7.951
7.939
7.934
7.818
7.800
7.797
7.663
7.645
7.553
7.533
7.514
7.264
1.572
-0.000
O
O_2N
water
2.02
2.00
2.02
0.82
2.10
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

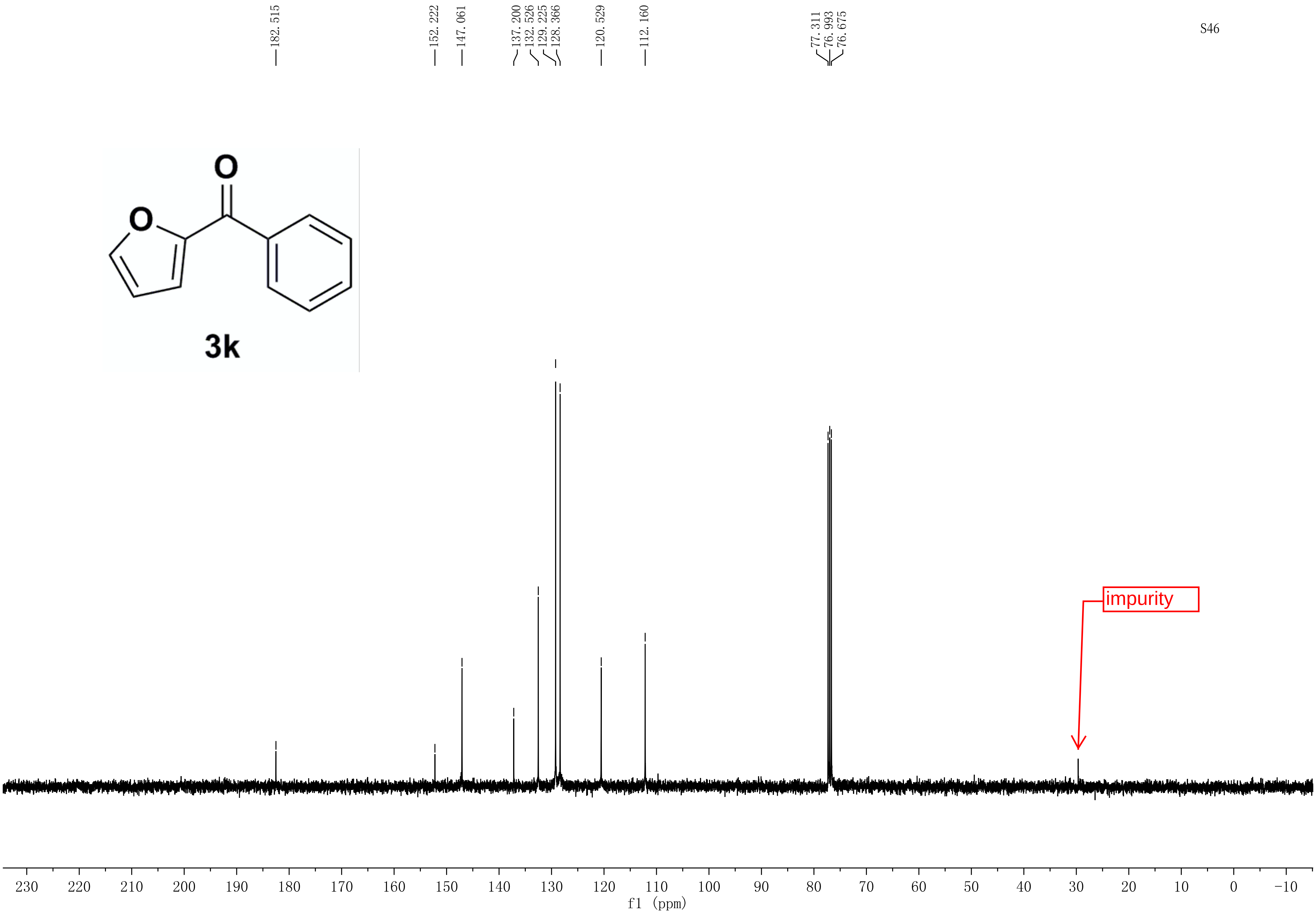
3k

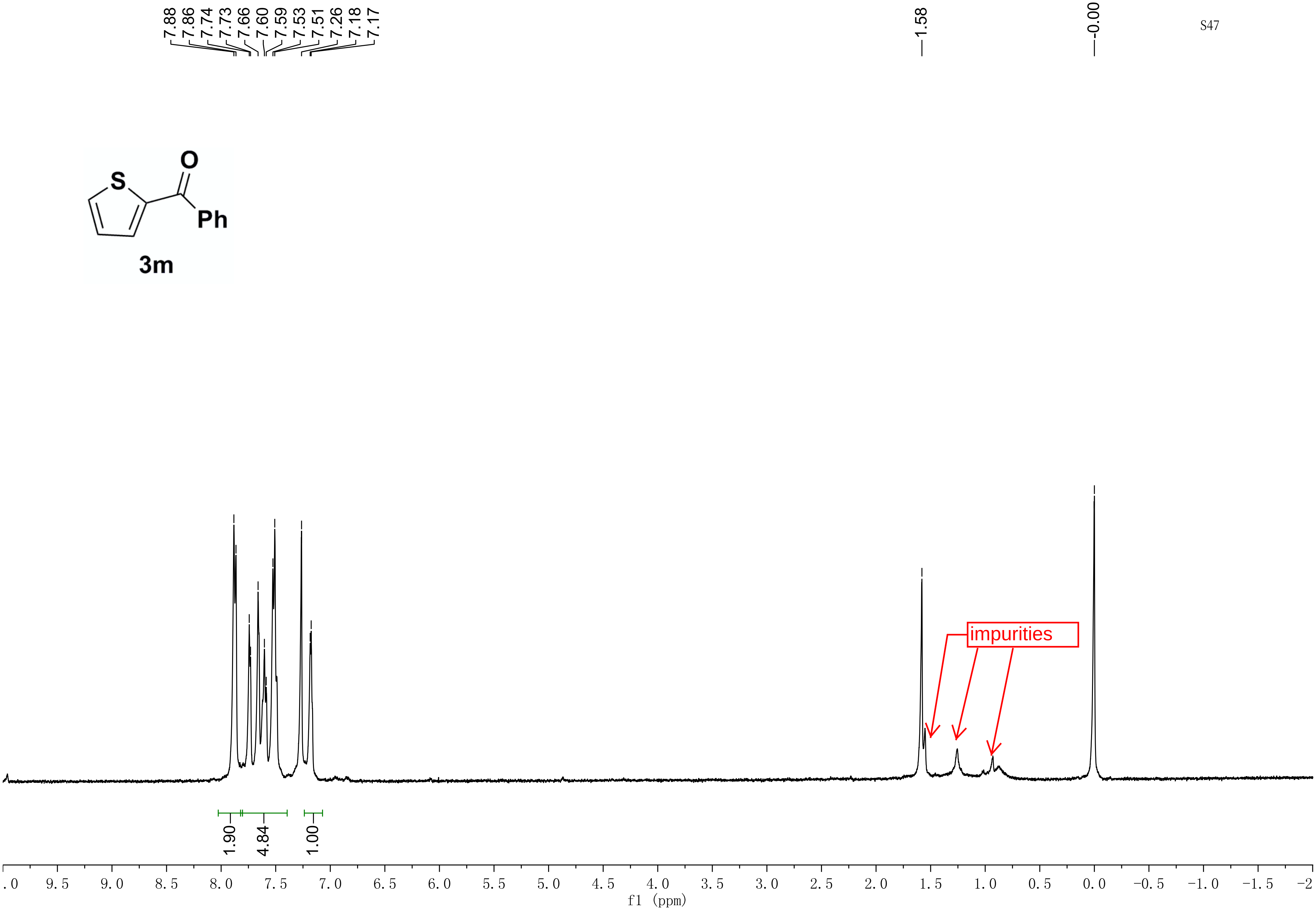


3k


194.724
149.787
142.843
136.246
133.419
130.642
130.046
128.637
123.493
77.307
76.989
76.672
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

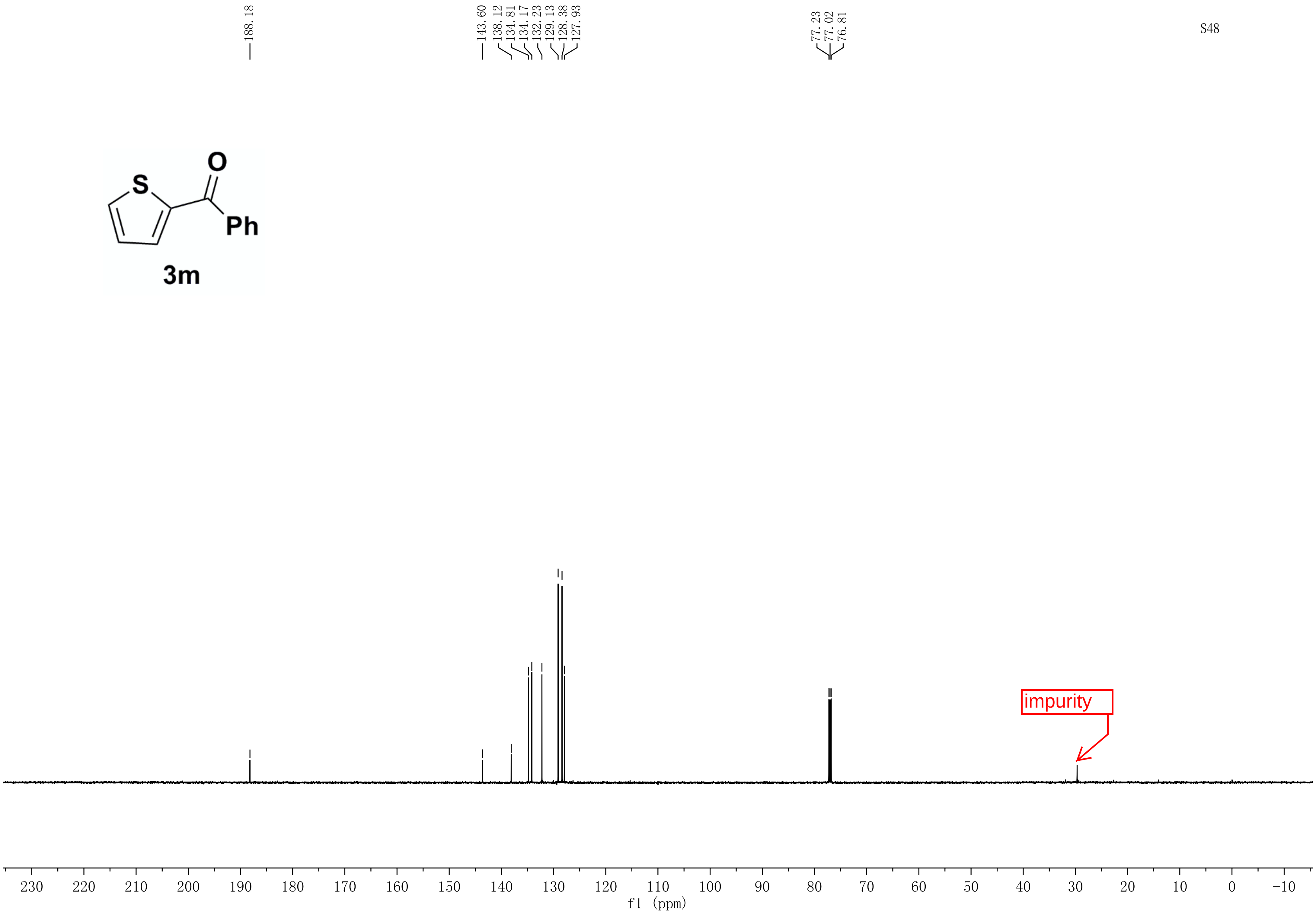

7.983
7.982
7.981
7.963
7.960
7.717
7.715
7.713
7.598
7.580
7.519
7.500
7.482
7.266
7.244
7.243
7.236
7.234
6.607
6.603
6.599
6.595
2.690
1.254
-0.000
O
O
Ph
3l
impurities
1.69
0.88
1.89
1.15
0.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


3k
182.515
152.222
147.061
137.200
132.526
129.225
128.366
120.529
112.160
77.311
76.993
76.675
impurity
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



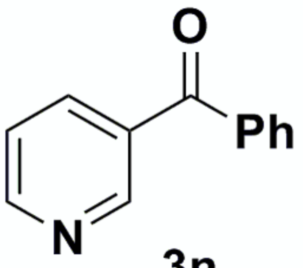
3m

7.88
7.86
7.74
7.73
7.66
7.60
7.59
7.53
7.51
7.26
7.18
7.17
1.58
-0.00
S
O
Ph
impurities
1.90
4.84
1.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2
f1 (ppm)

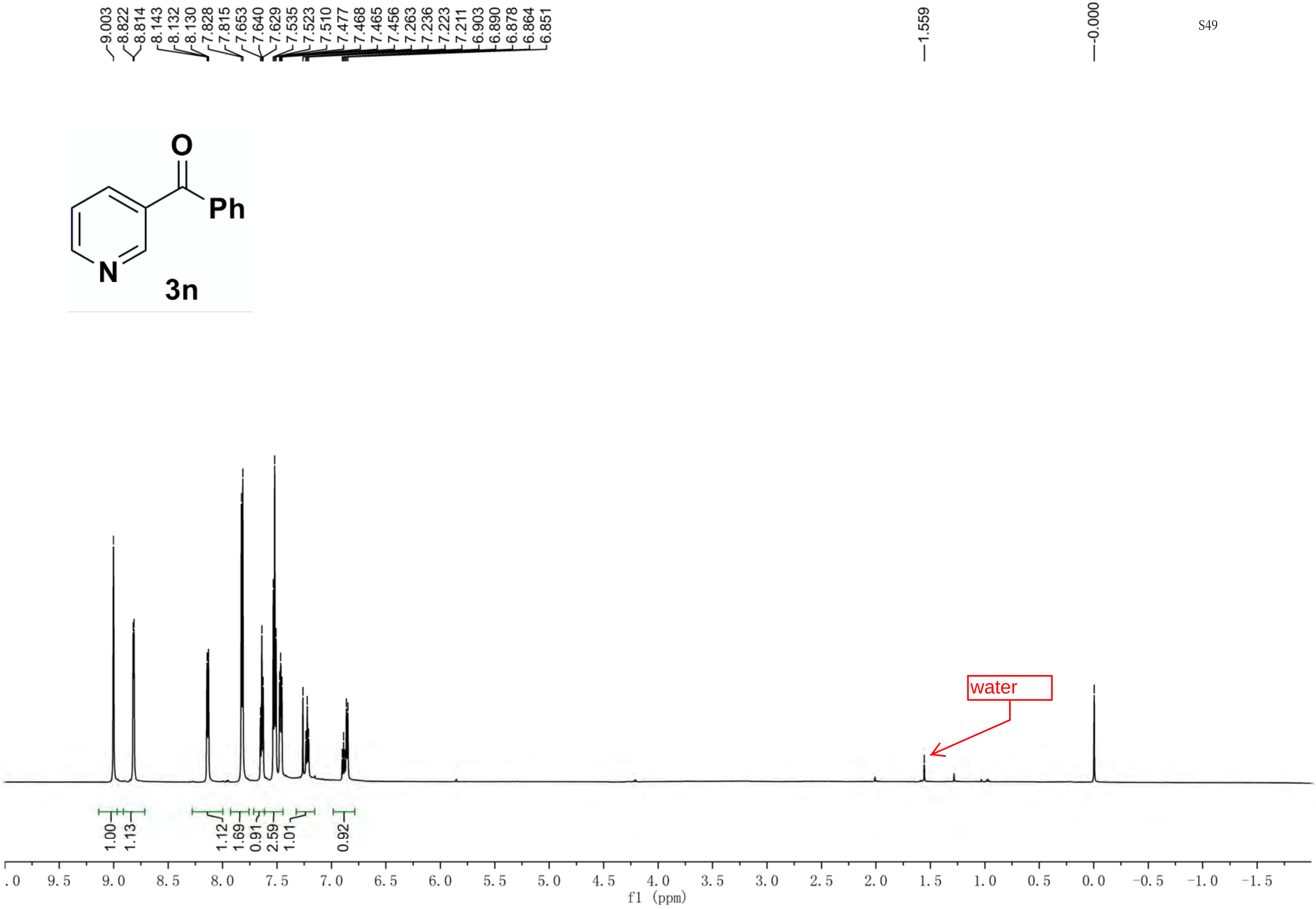


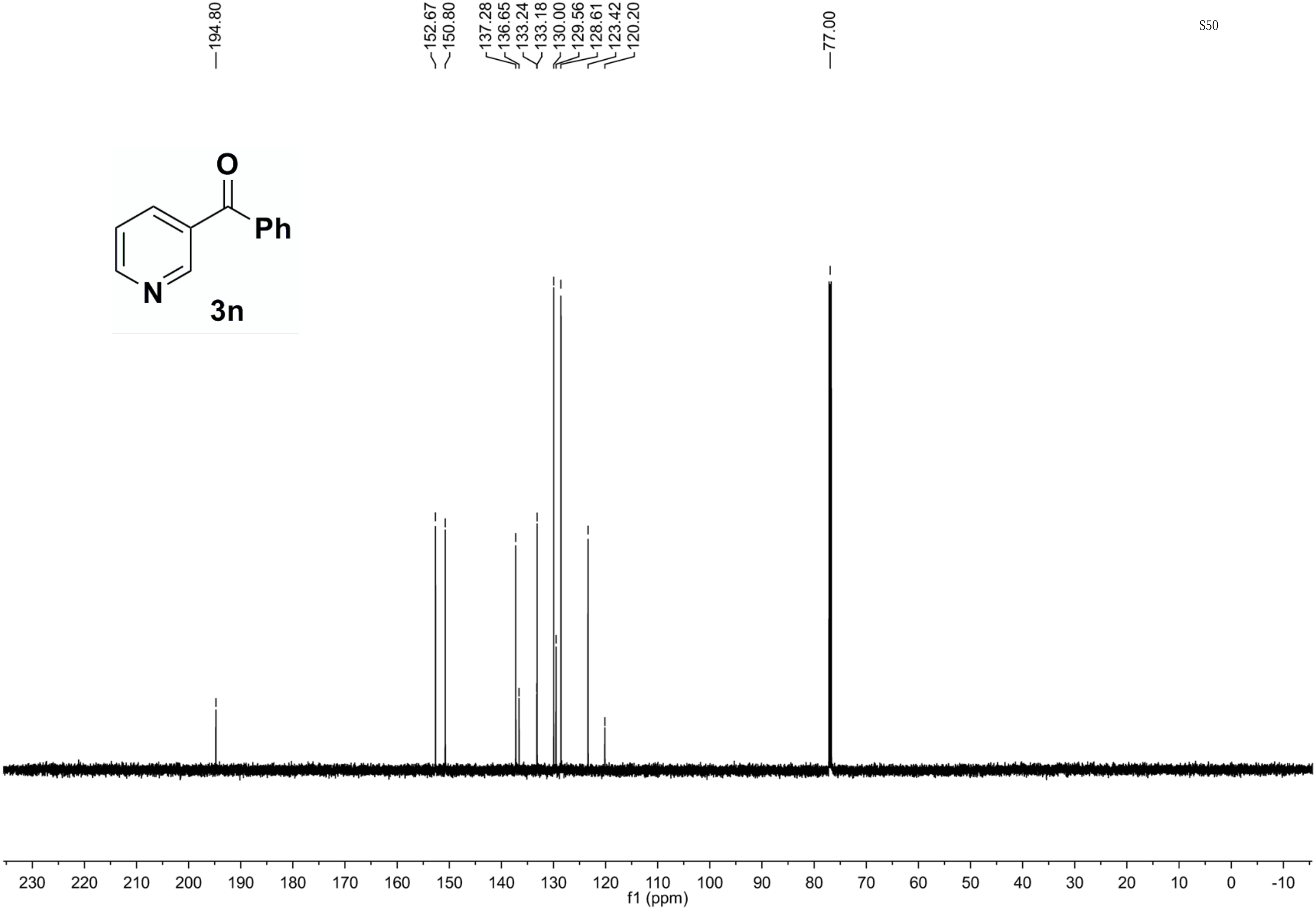
3m

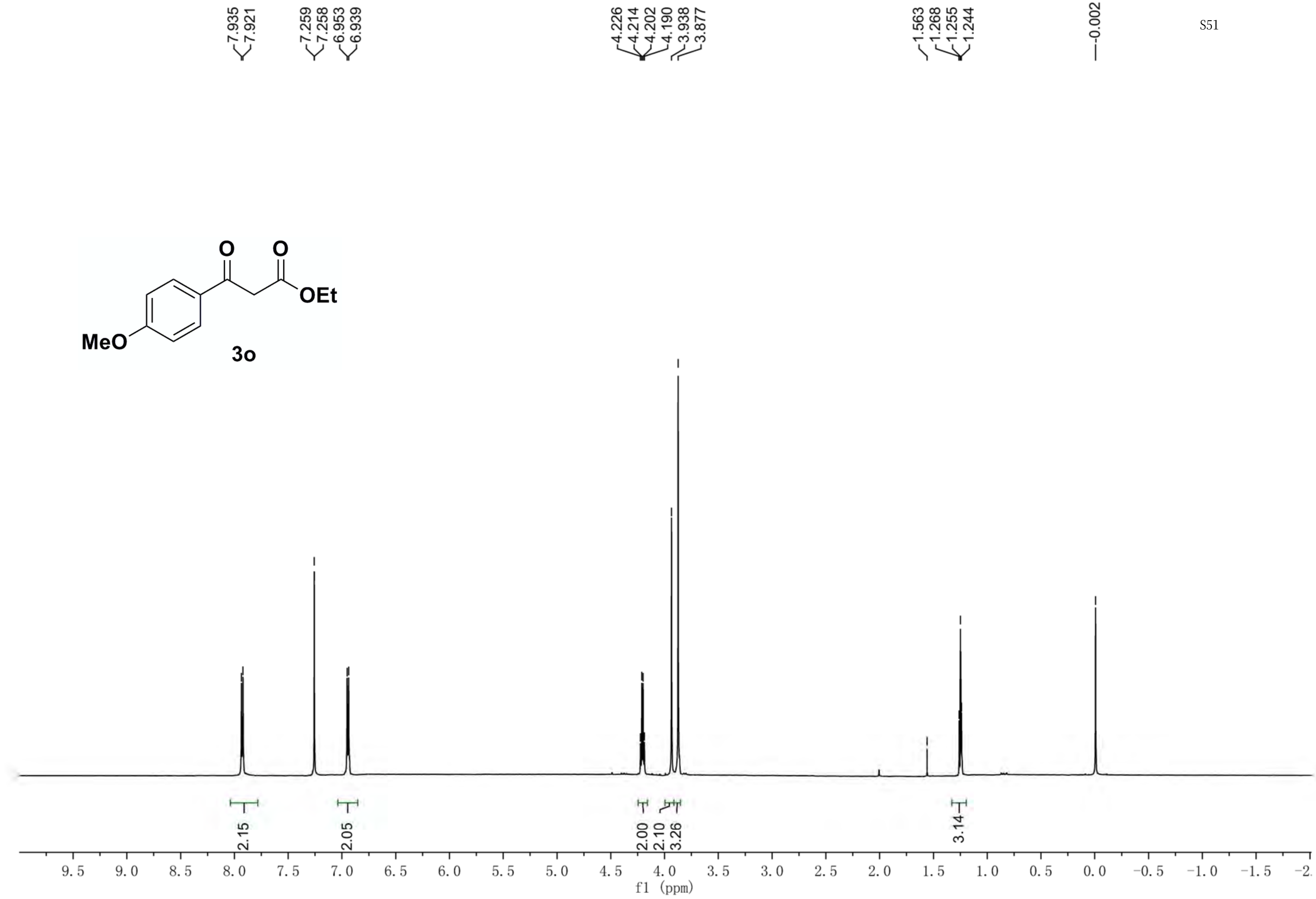
188.18
143.60
138.12
134.81
134.17
132.23
129.13
128.38
127.93
77.23
77.02
76.81
S
O
Ph
impurity
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

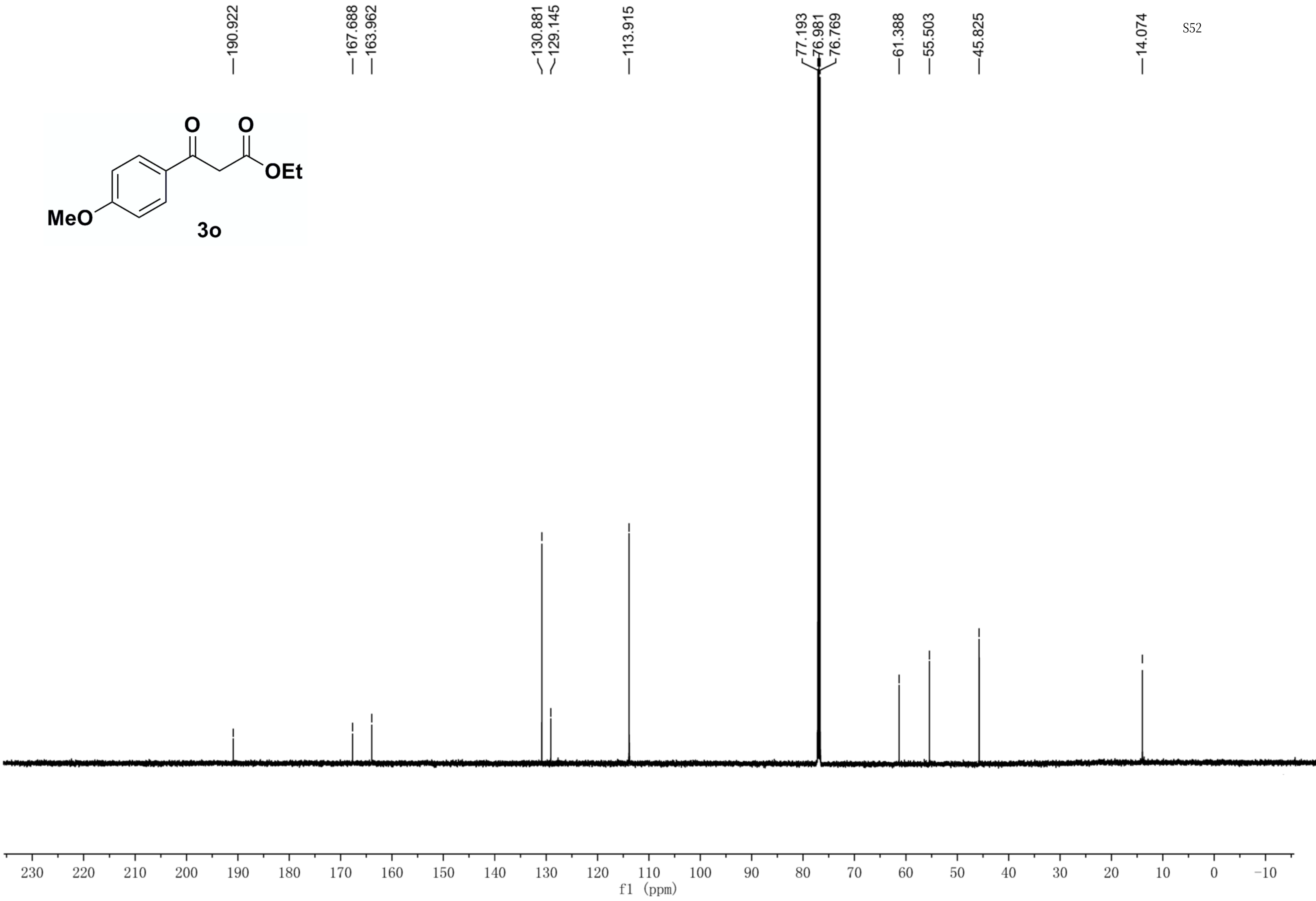

O
Ph
N

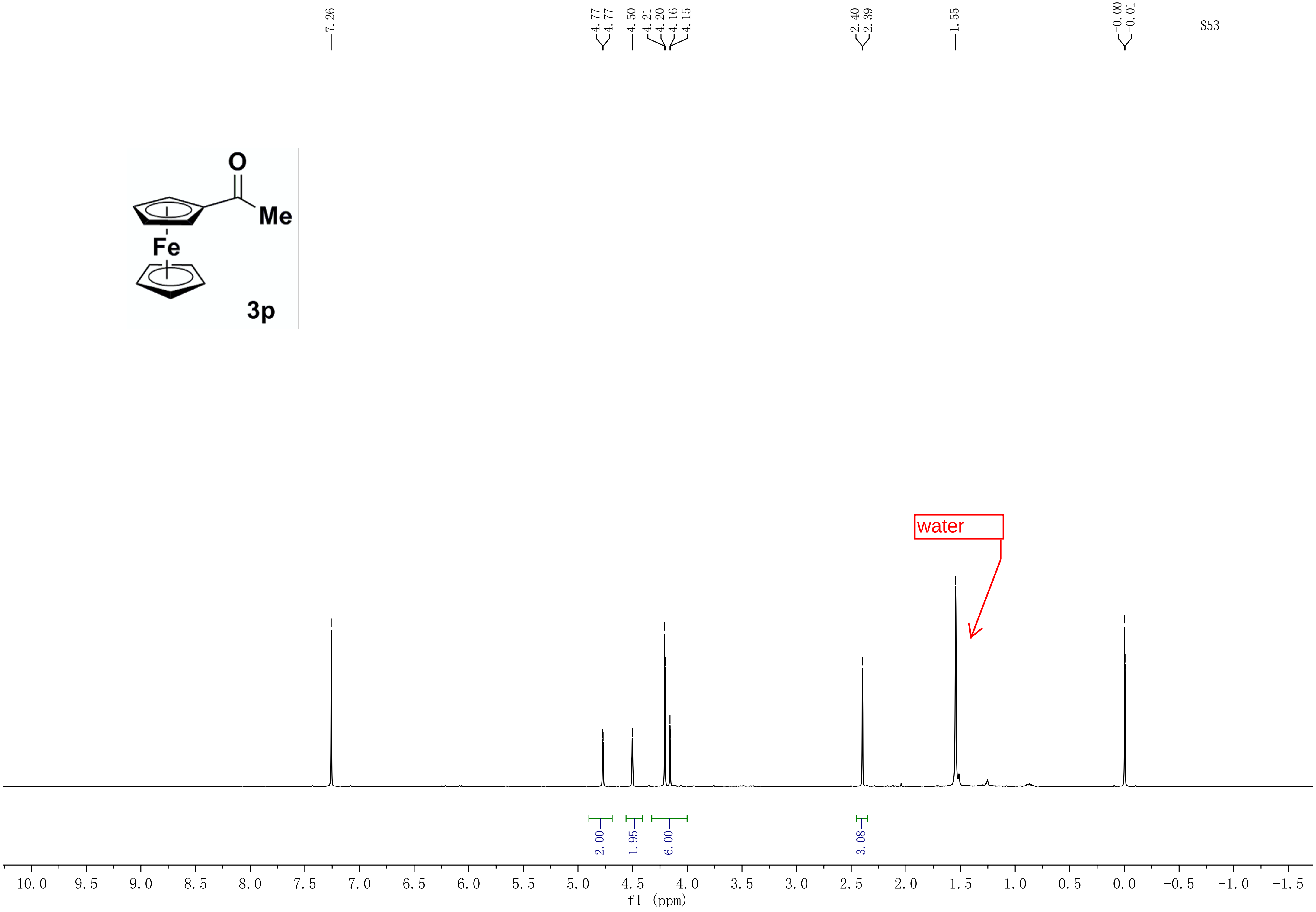
3n


9.003
8.822
8.814
8.143
8.132
8.130
7.828
7.815
7.653
7.640
7.629
7.535
7.523
7.510
7.477
7.468
7.465
7.456
7.263
7.236
7.223
7.211
6.903
6.890
6.878
6.864
6.851
1.559
-0.000
water
1.00
1.13
1.12
1.69
0.91
2.59
1.01
0.92
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

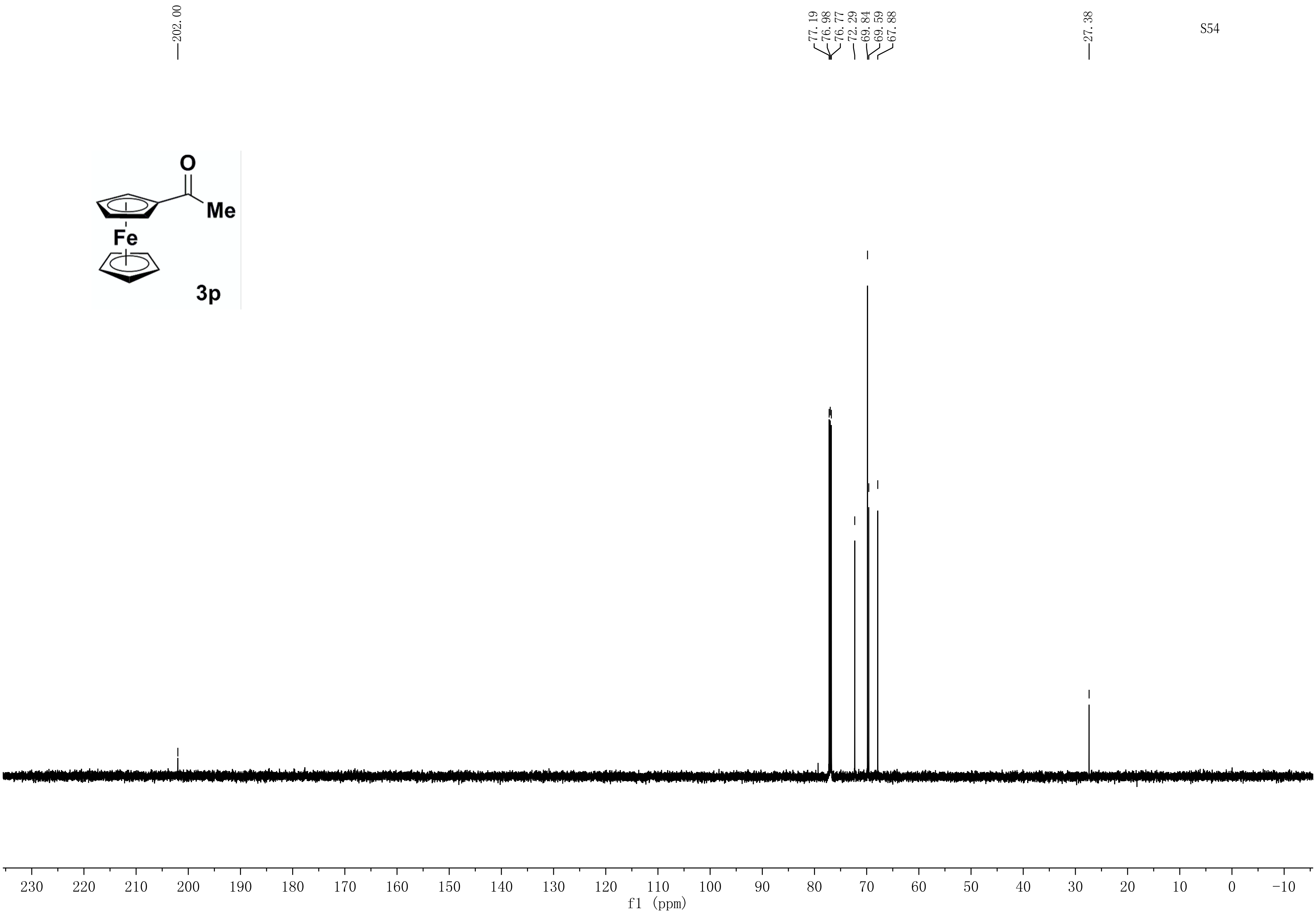

194.80
152.67
150.80
137.28
136.65
133.24
133.18
130.00
129.56
128.61
123.42
120.20
77.00
O
Ph
N
3n
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

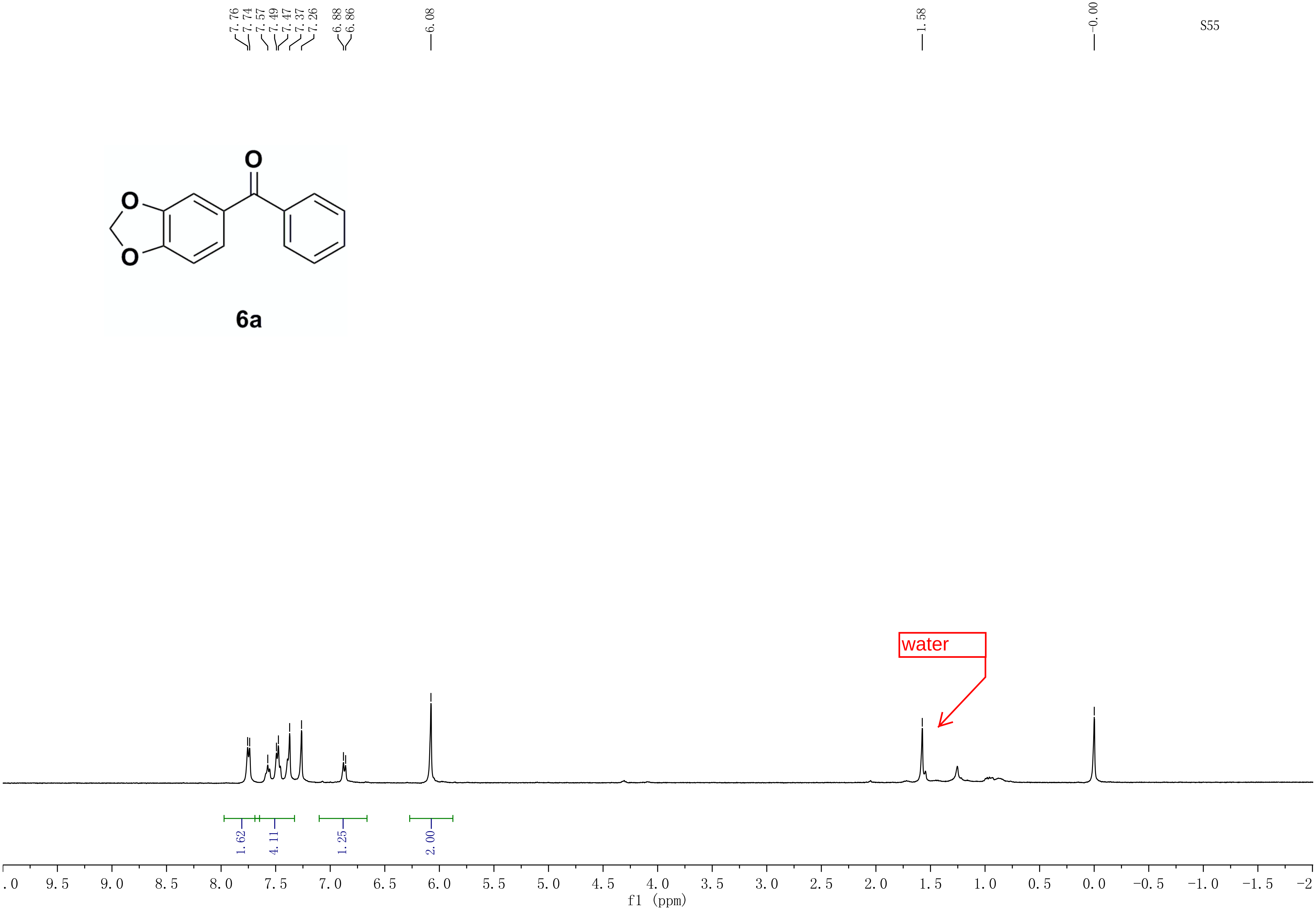

7.935
7.921
7.259
7.258
6.953
6.939
4.226
4.214
4.202
4.190
3.938
3.877
1.563
1.268
1.255
1.244
-0.002
O
O
OEt
MeO
3o
2.15
2.05
2.00
2.10
3.26
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.
f1 (ppm)


190.922
167.688
163.962
130.881
129.145
113.915
77.193
76.981
76.769
61.388
55.503
45.825
14.074
O
O
OEt
MeO
3o
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

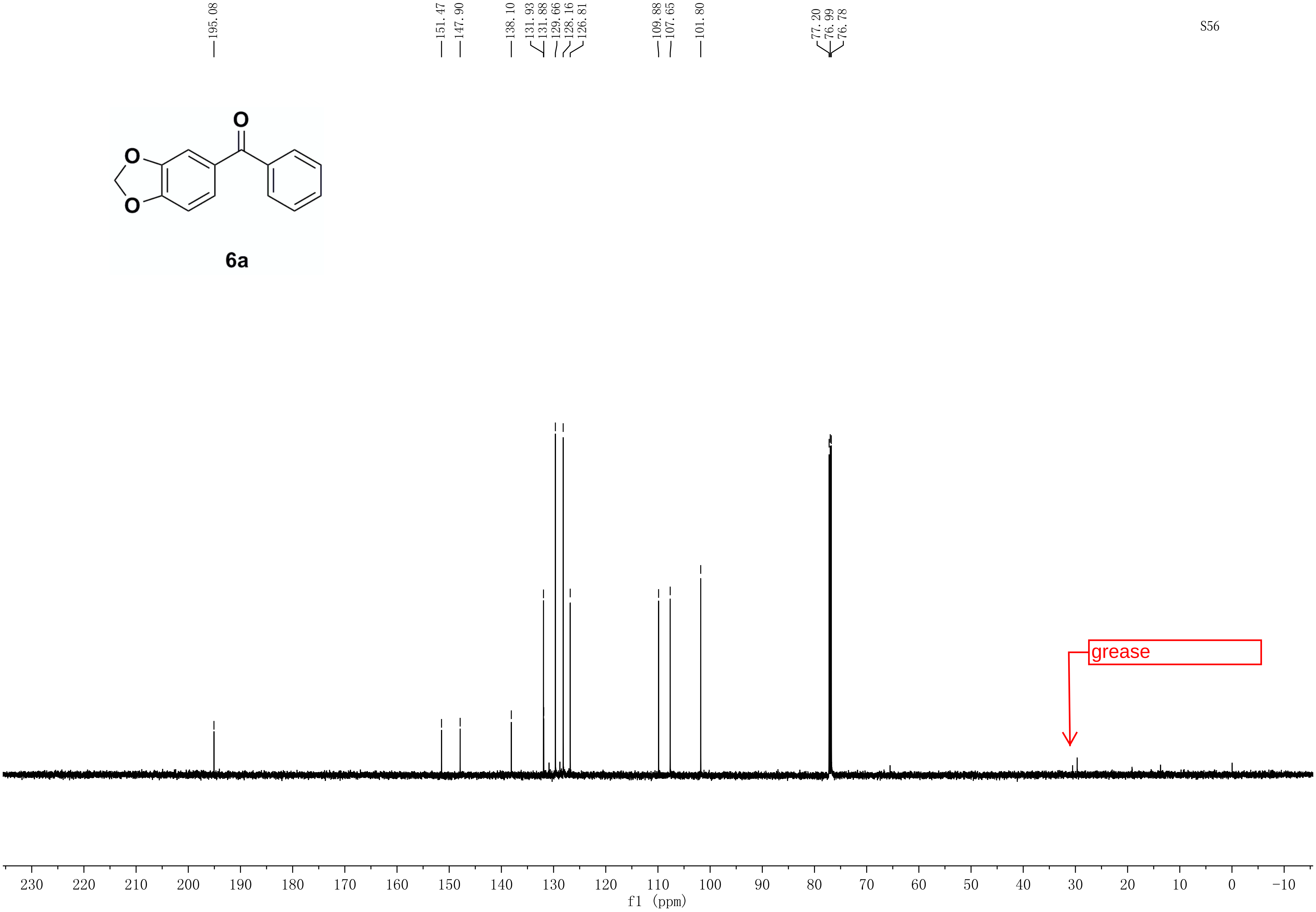

7.26
4.77
4.77
4.50
4.21
4.20
4.16
4.15
2.40
2.39
1.55
-0.00
-0.01
O
Me
Fe
water
2.00
1.95
6.00
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

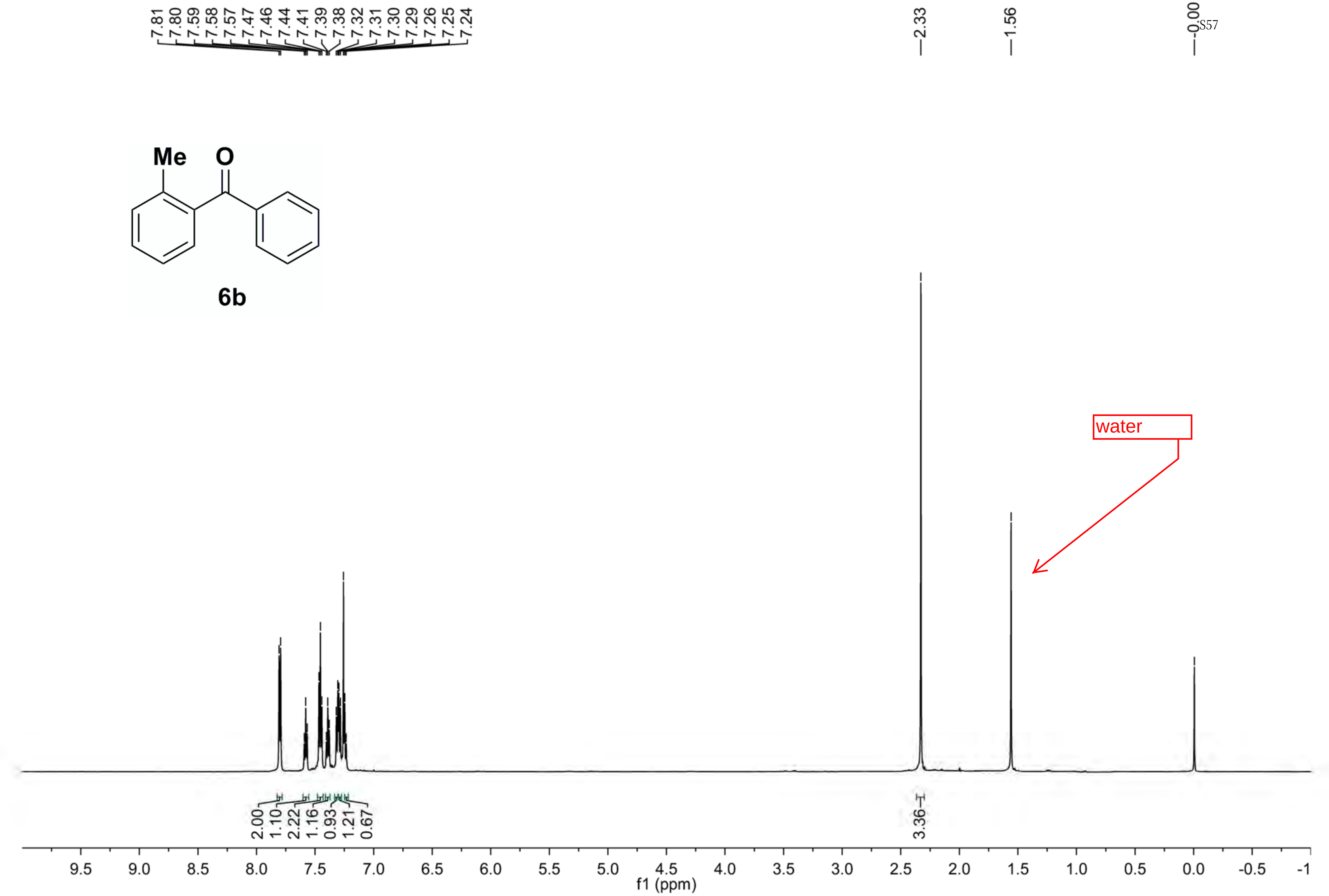
3p


202.00
77.19
76.98
76.77
72.29
69.84
69.59
67.88
27.38
O
Me
Fe
3p
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.76
7.74
7.57
7.49
7.47
7.37
7.26
6.88
6.86
6.08
1.58
-0.00
O
O
O
water
1.62
4.11
1.25
2.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

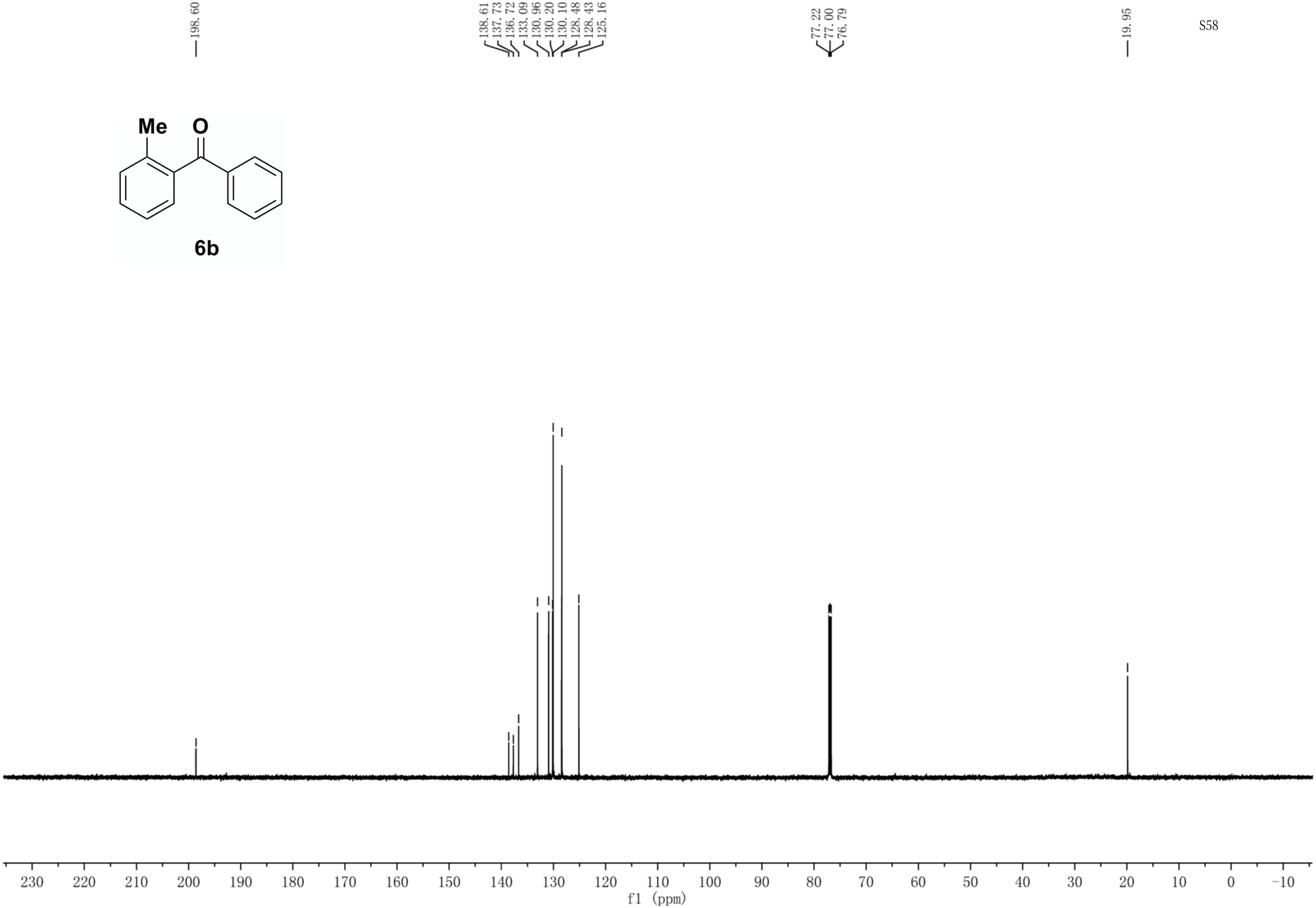
6a


195.08
151.47
147.90
138.10
131.93
131.88
129.66
128.16
126.81
109.88
107.65
101.80
77.20
76.99
76.78
6a
grease
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

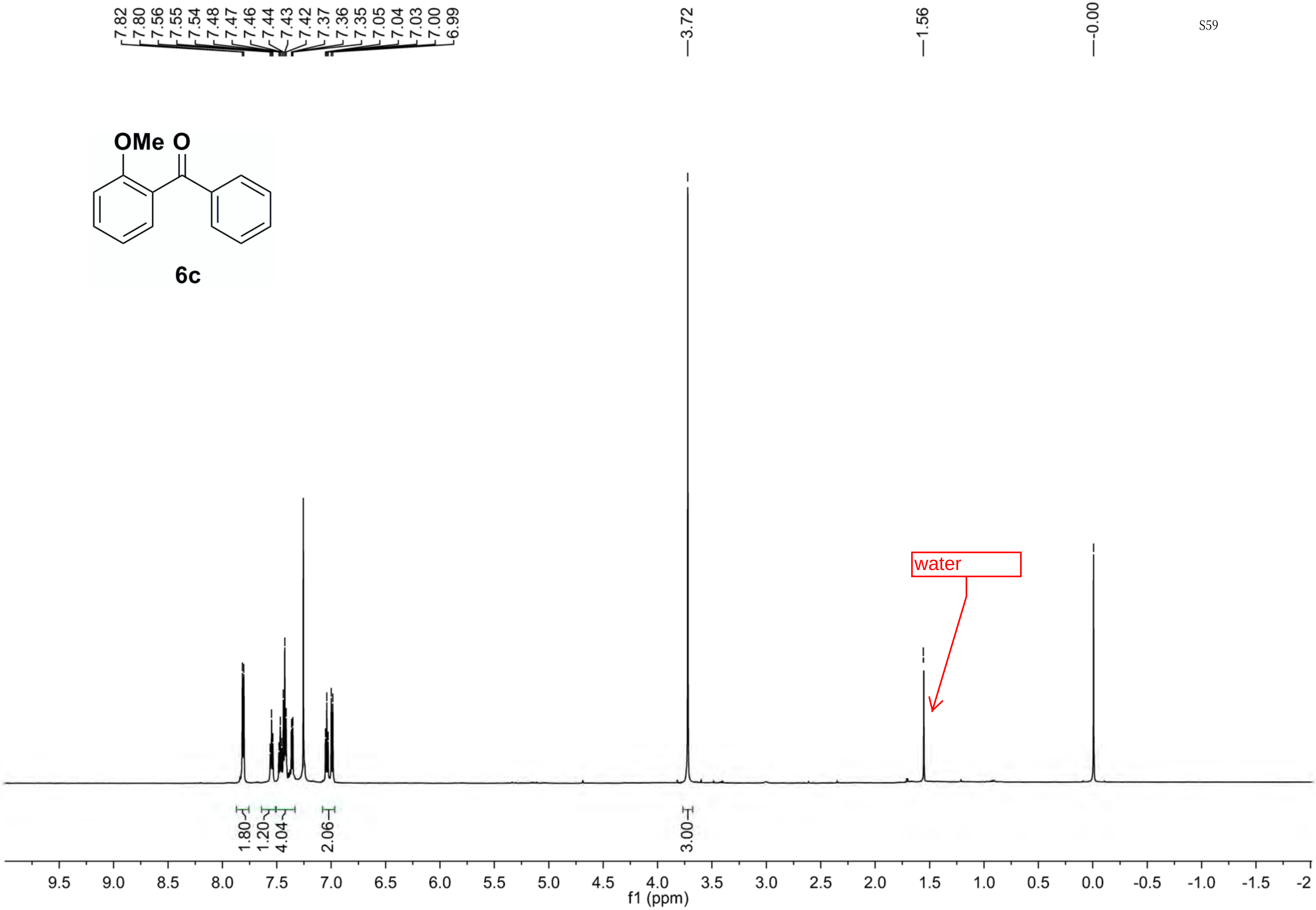


6b

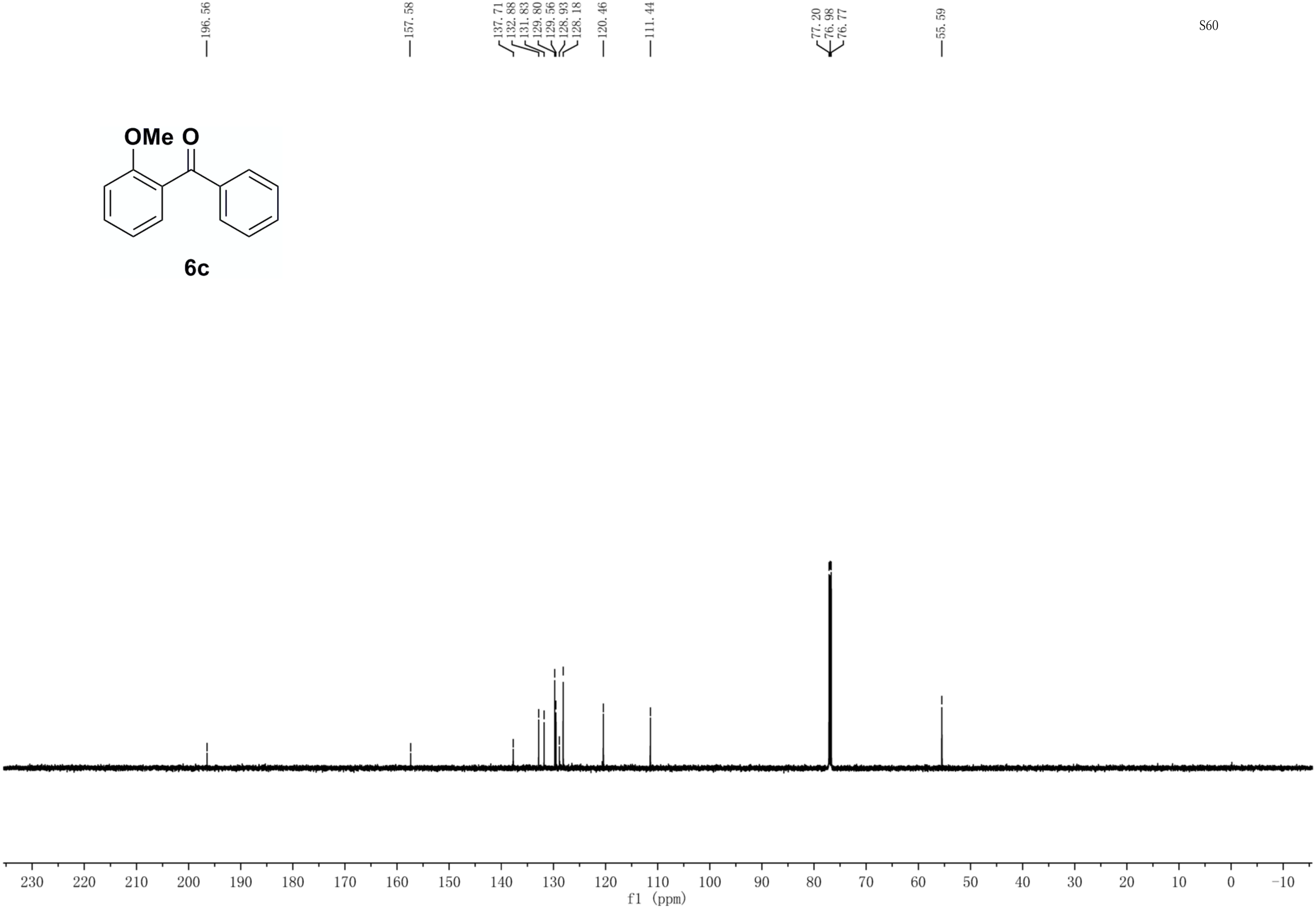
7.81
7.80
7.59
7.58
7.57
7.47
7.46
7.44
7.41
7.39
7.38
7.32
7.31
7.30
7.29
7.26
7.25
7.24
2.33
1.56
0.00
Me
O
water
2.00
1.10
2.22
1.16
0.93
1.21
0.67
3.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

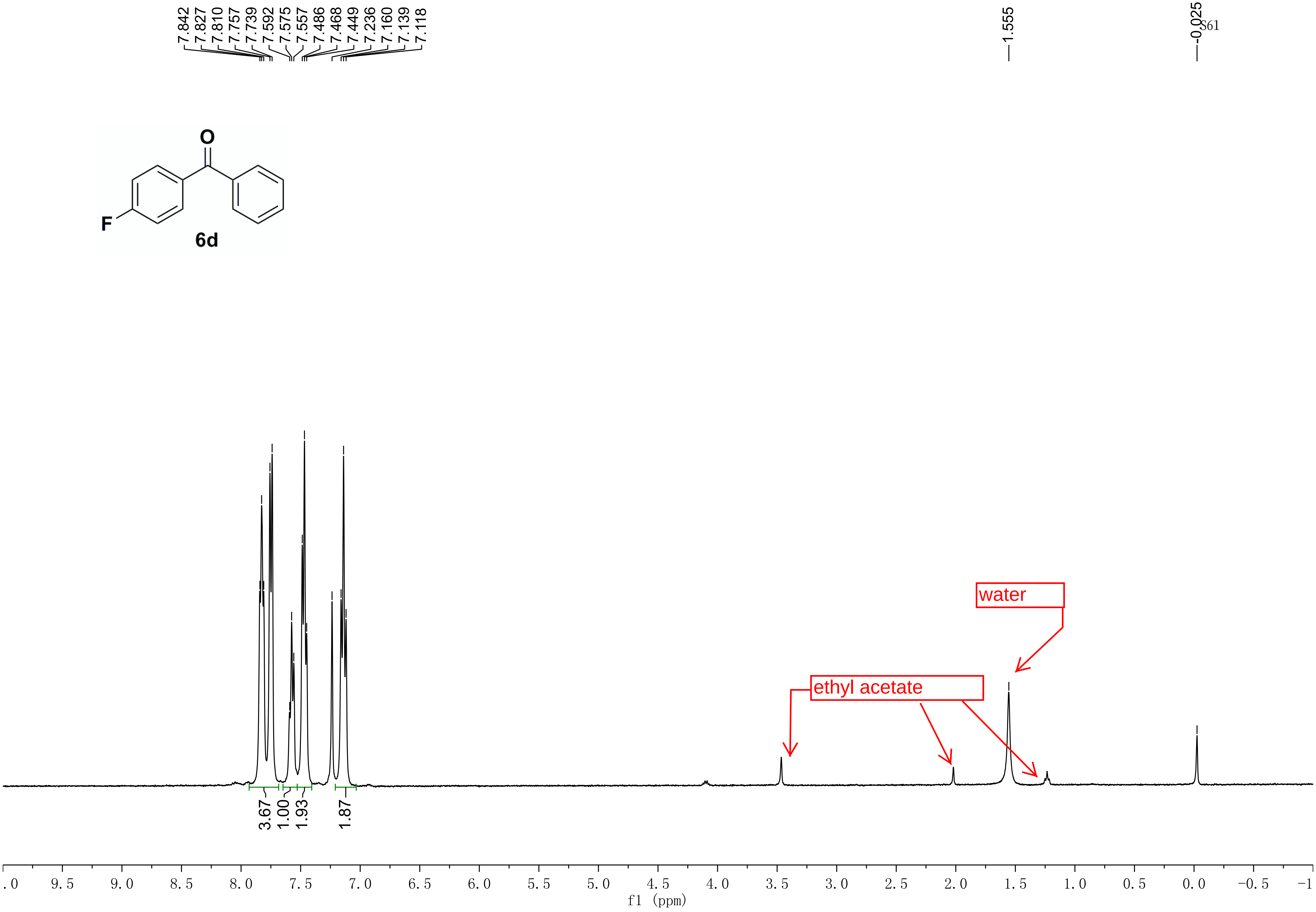

198.60
138.61
137.73
136.72
133.09
130.96
130.20
130.10
128.48
128.43
125.16
77.22
77.00
76.79
19.95
Me
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

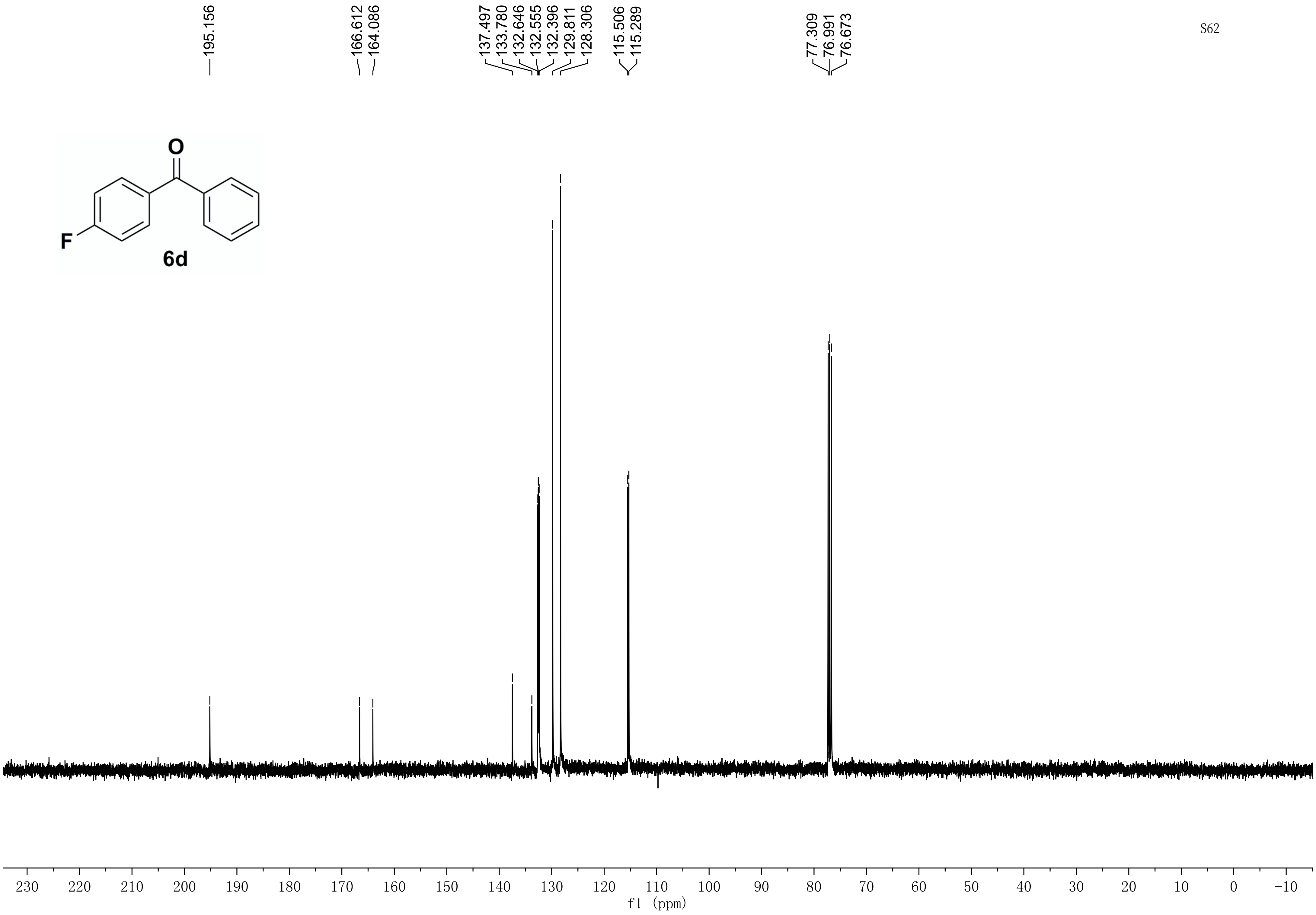
6b

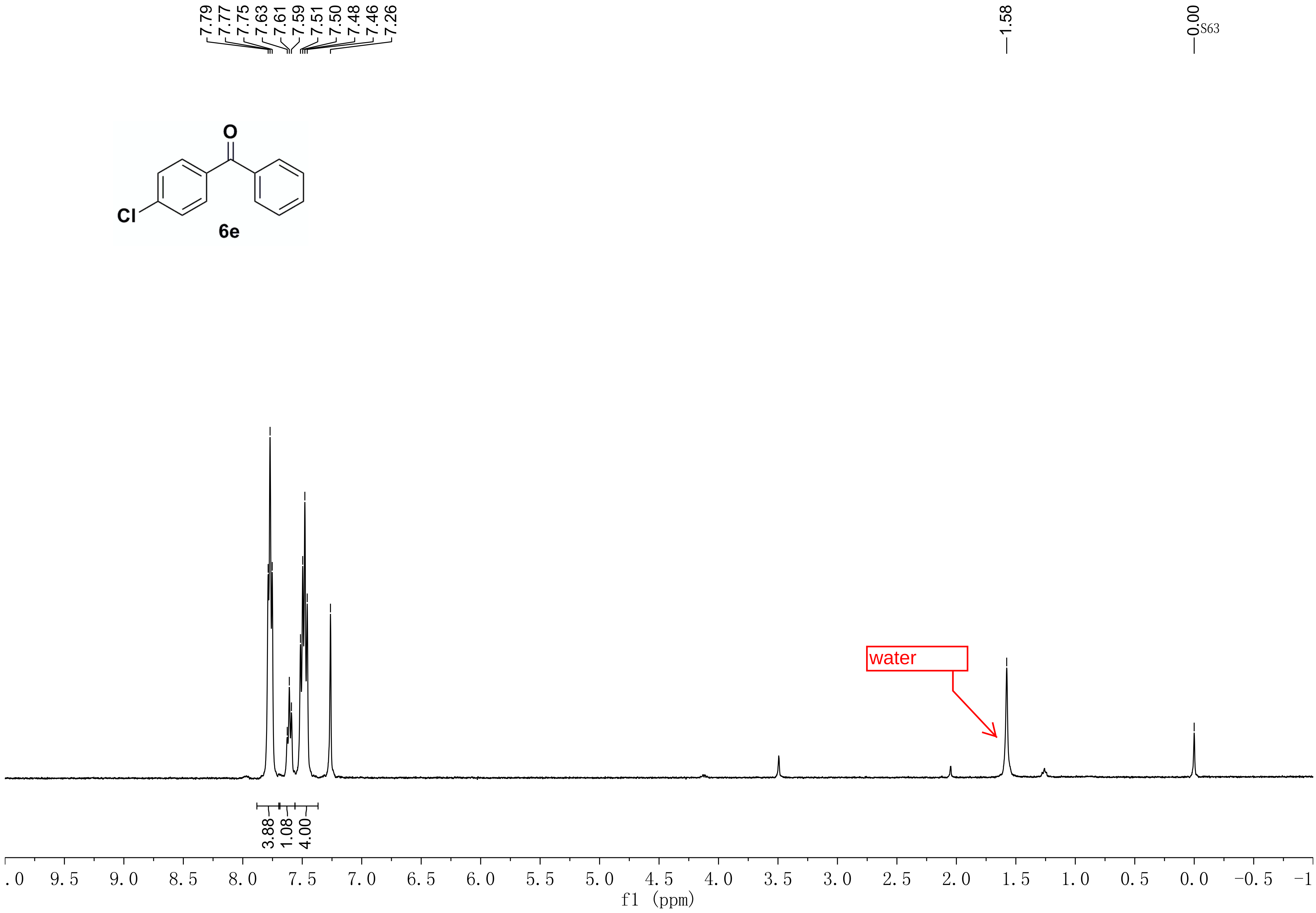

7.82
7.80
7.56
7.55
7.54
7.48
7.47
7.46
7.44
7.43
7.42
7.37
7.36
7.35
7.05
7.04
7.03
7.00
6.99
3.72
1.56
-0.00
OMe
O
water
1.80
1.20
4.04
2.06
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

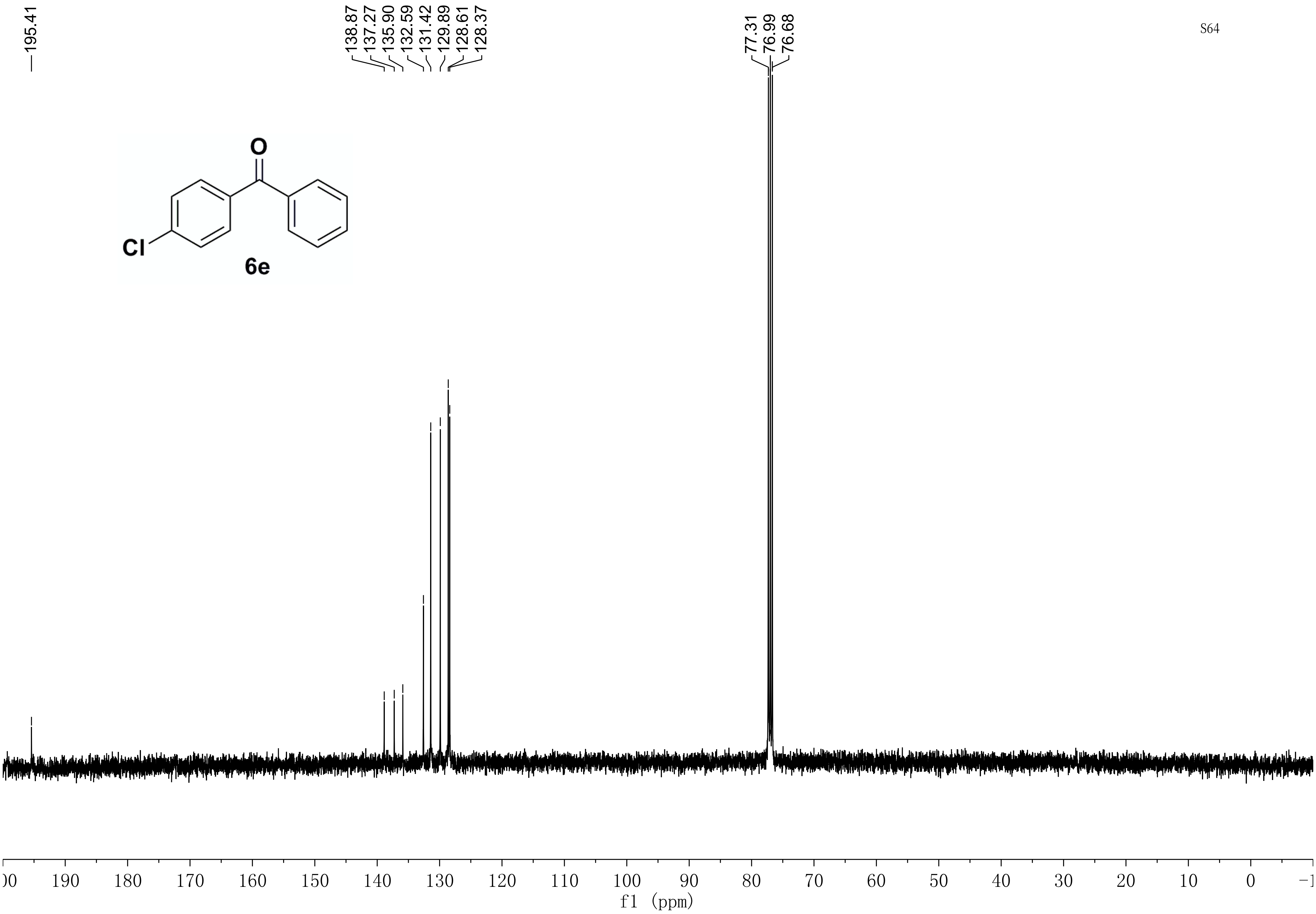
6c

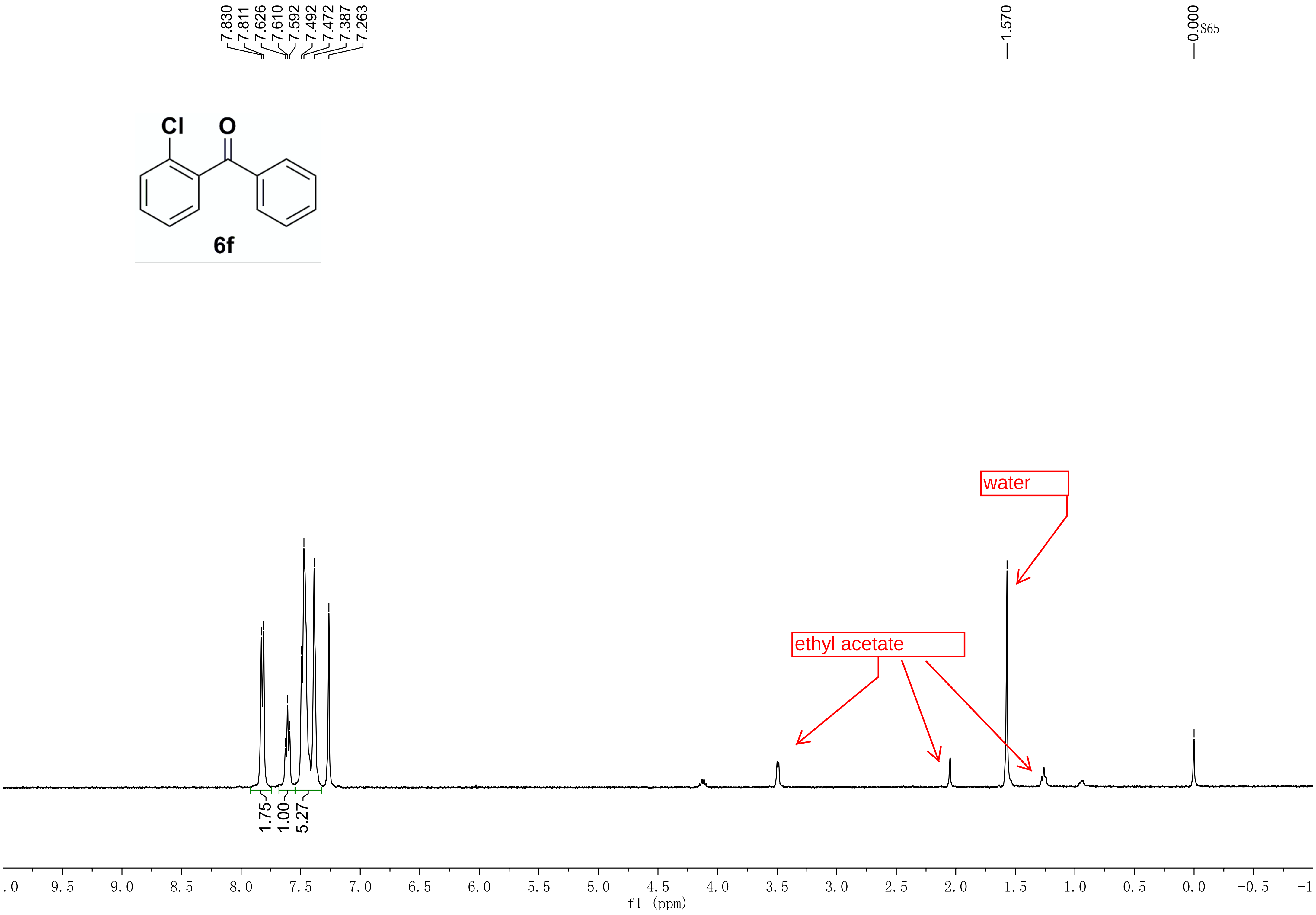

196.56
157.58
137.71
132.88
131.83
129.80
129.56
128.93
128.18
120.46
111.44
77.20
76.98
76.77
55.59
OMe O
6c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.842
7.827
7.810
7.757
7.739
7.592
7.575
7.557
7.486
7.468
7.449
7.236
7.160
7.139
7.118
1.555
-0.025
O
F
6d
water
ethyl acetate
3.67
1.00
1.93
1.87
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


6d
O
F
195.156
166.612
164.086
137.497
133.780
132.646
132.555
132.396
129.811
128.306
115.506
115.289
77.309
76.991
76.673
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

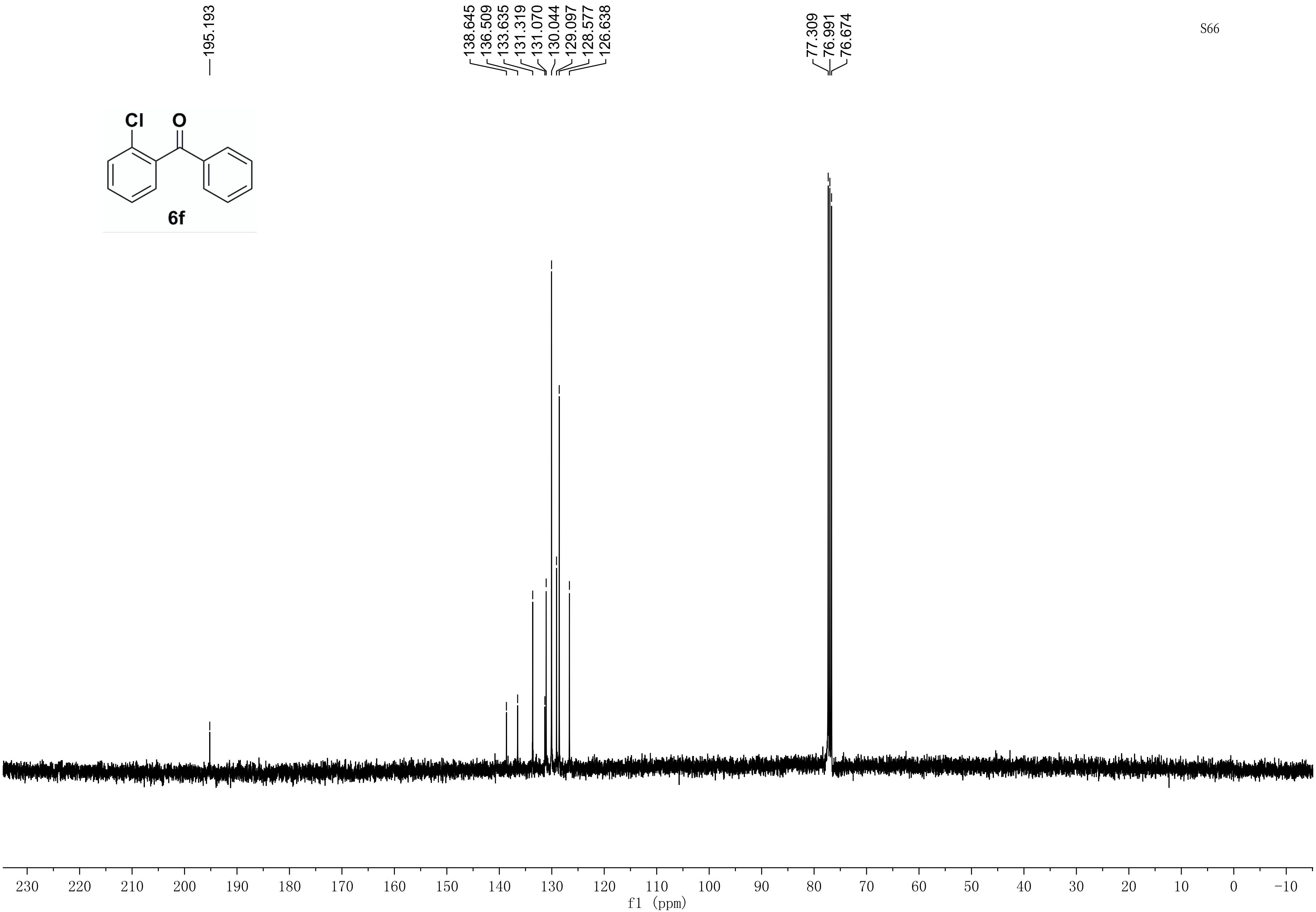

7.79
7.77
7.75
7.63
7.61
7.59
7.51
7.50
7.48
7.46
7.26
1.58
0.00
O
Cl
6e
water
3.88
1.08
4.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

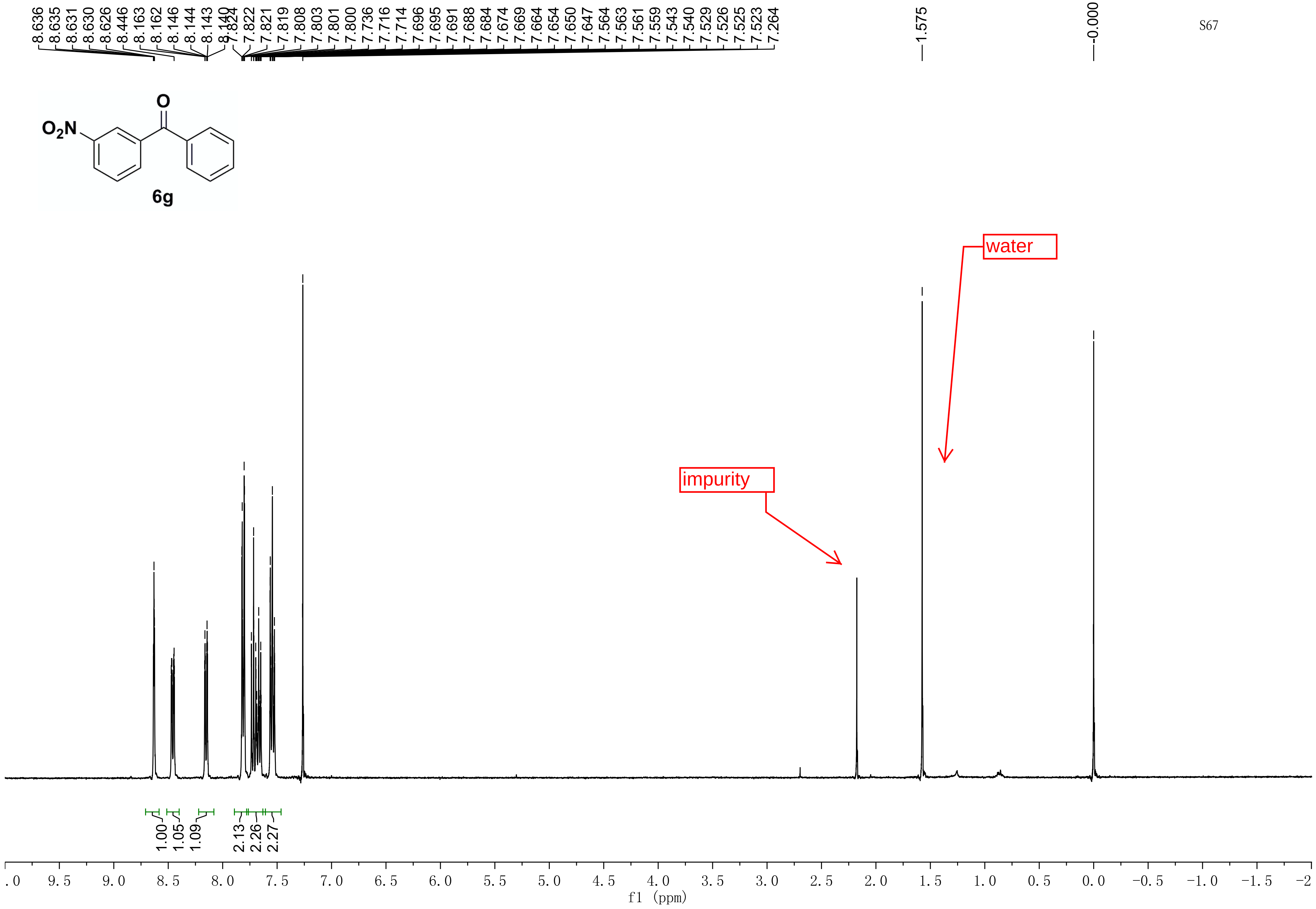

195.41
138.87
137.27
135.90
132.59
131.42
129.89
128.61
128.37
77.31
76.99
76.68
O
Cl
6e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

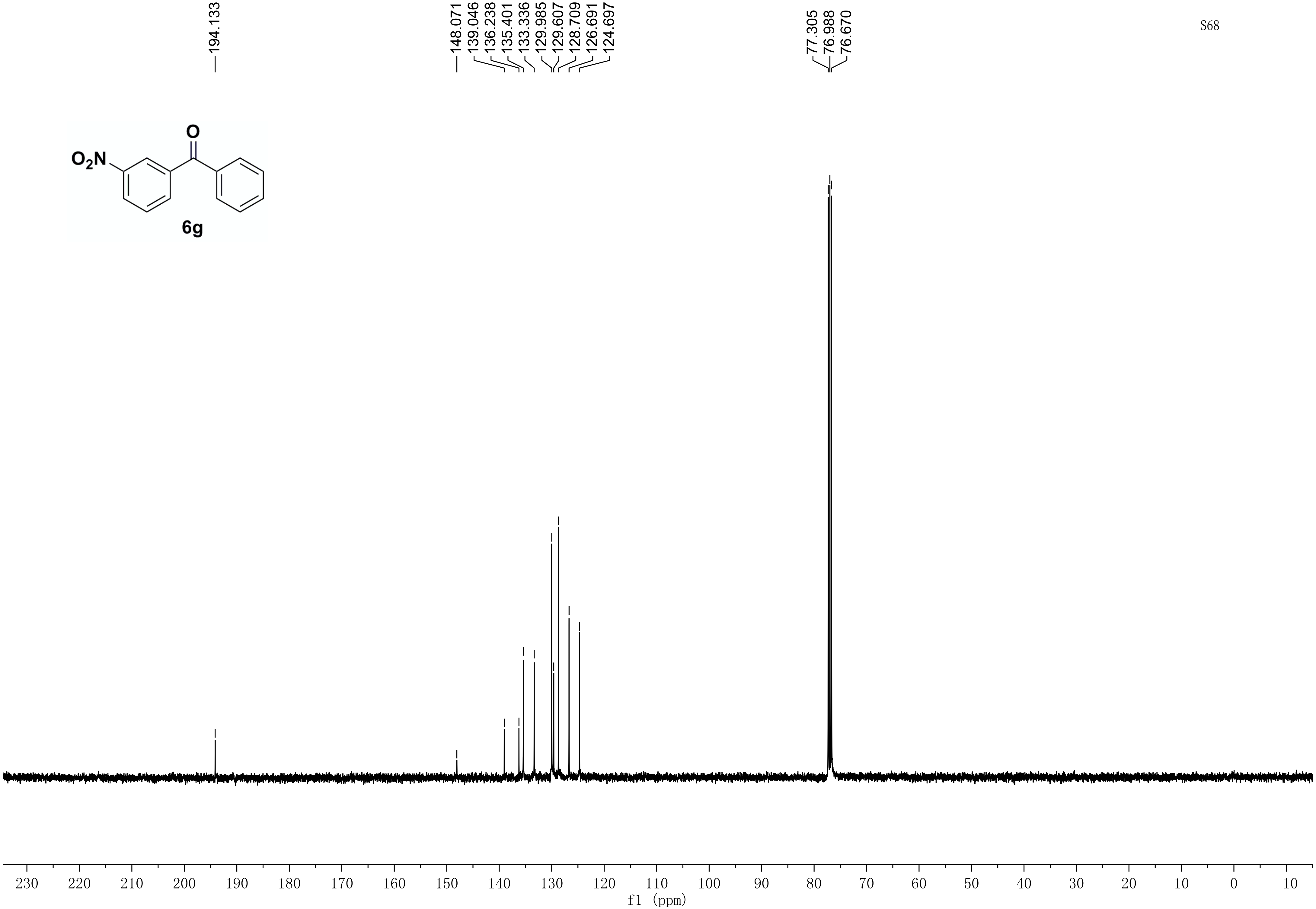


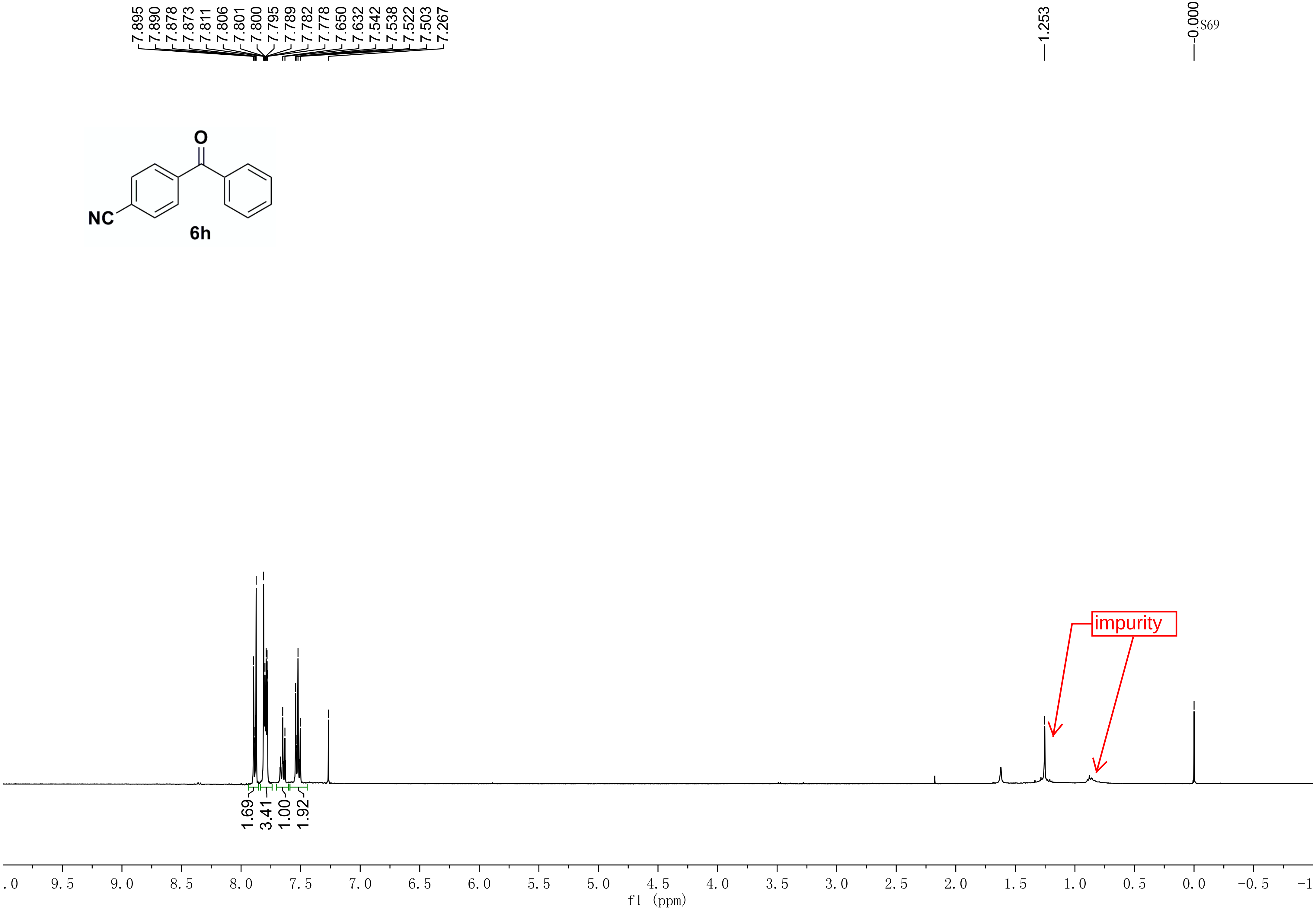
6f

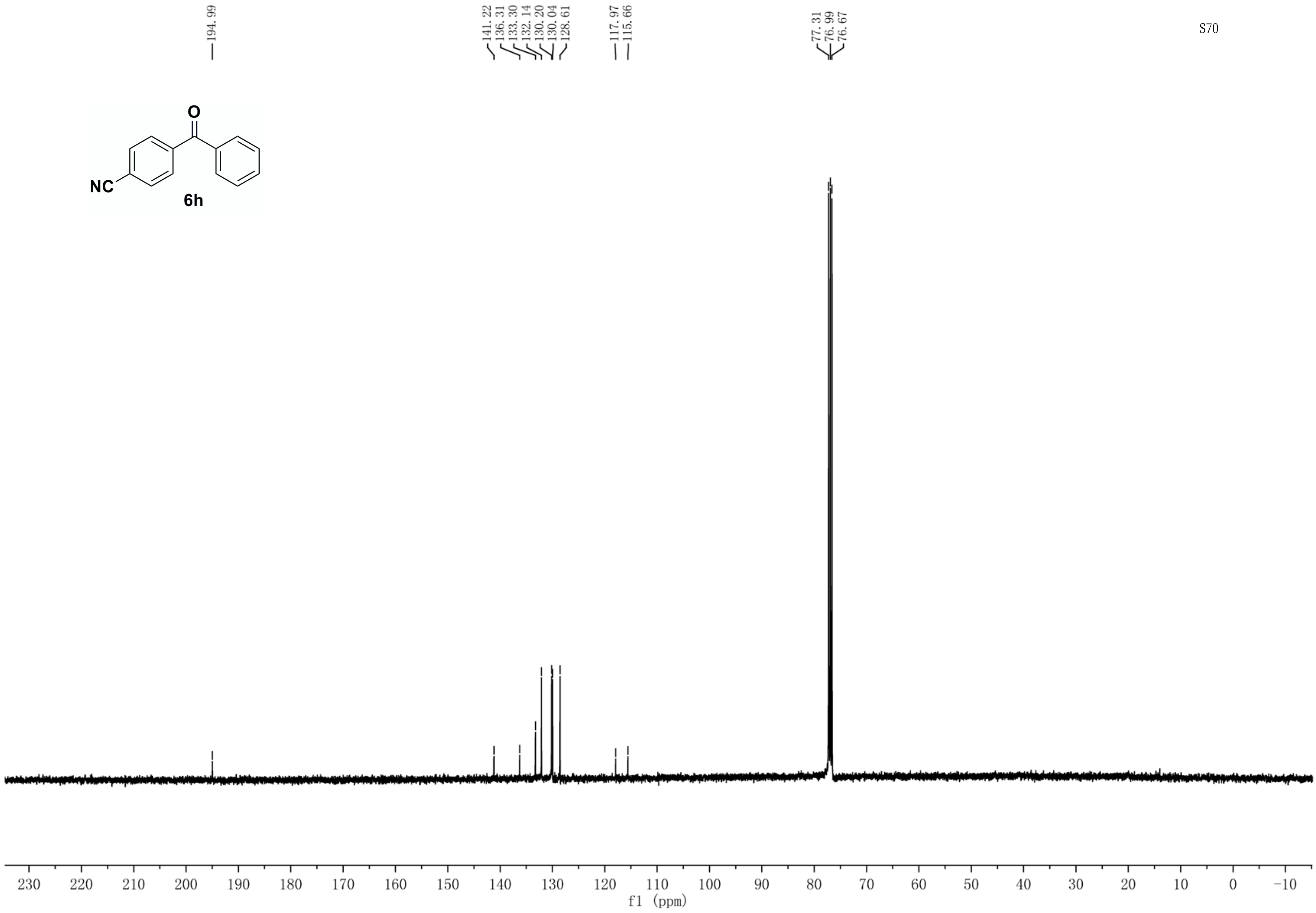
7.830
7.811
7.626
7.610
7.592
7.492
7.472
7.387
7.263
1.570
0.000
Cl
O
water
ethyl acetate
1.75
1.00
5.27
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

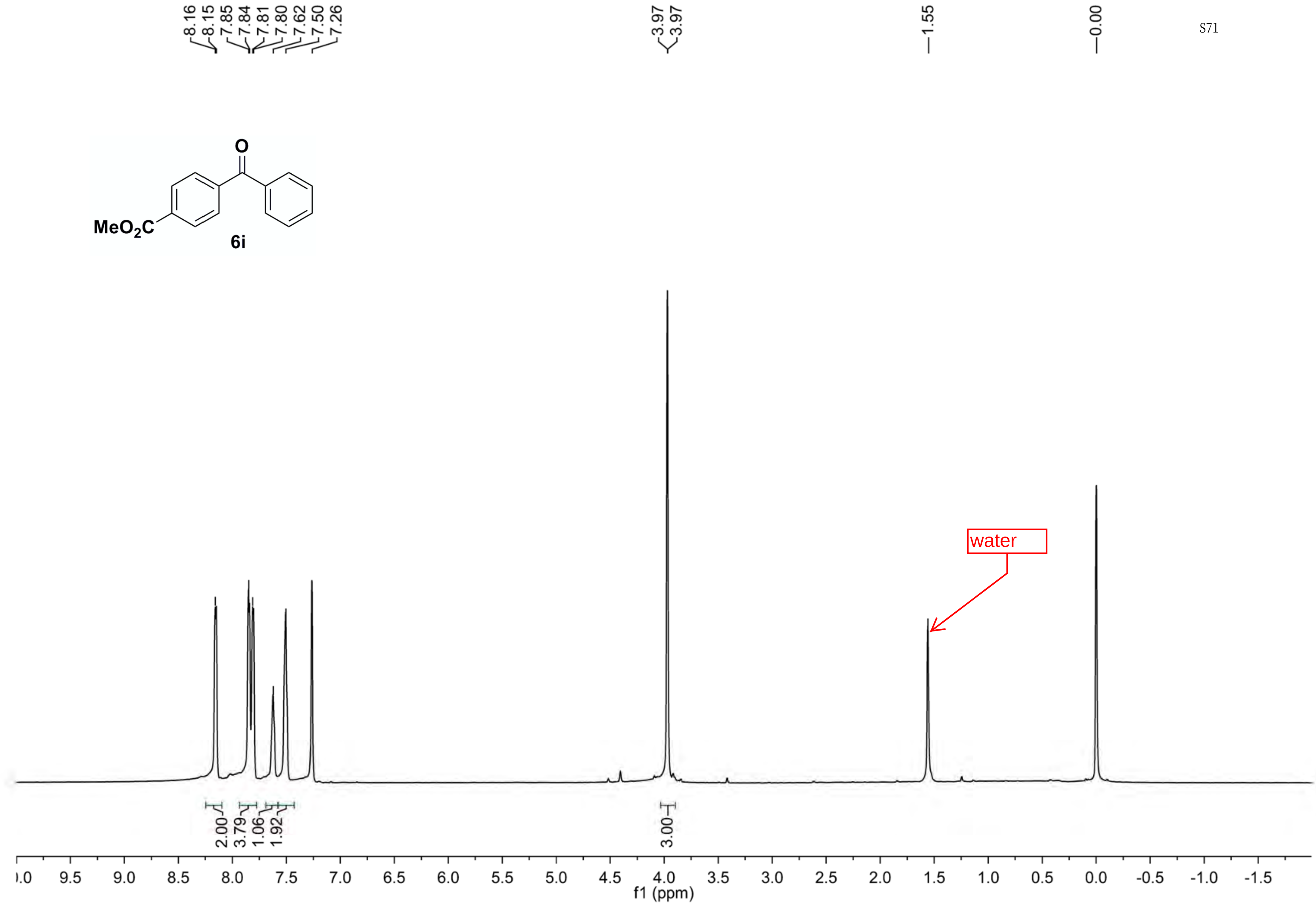

195.193
138.645
136.509
133.635
131.319
131.070
130.044
129.097
128.577
126.638
77.309
76.991
76.674
Cl
O
6f
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

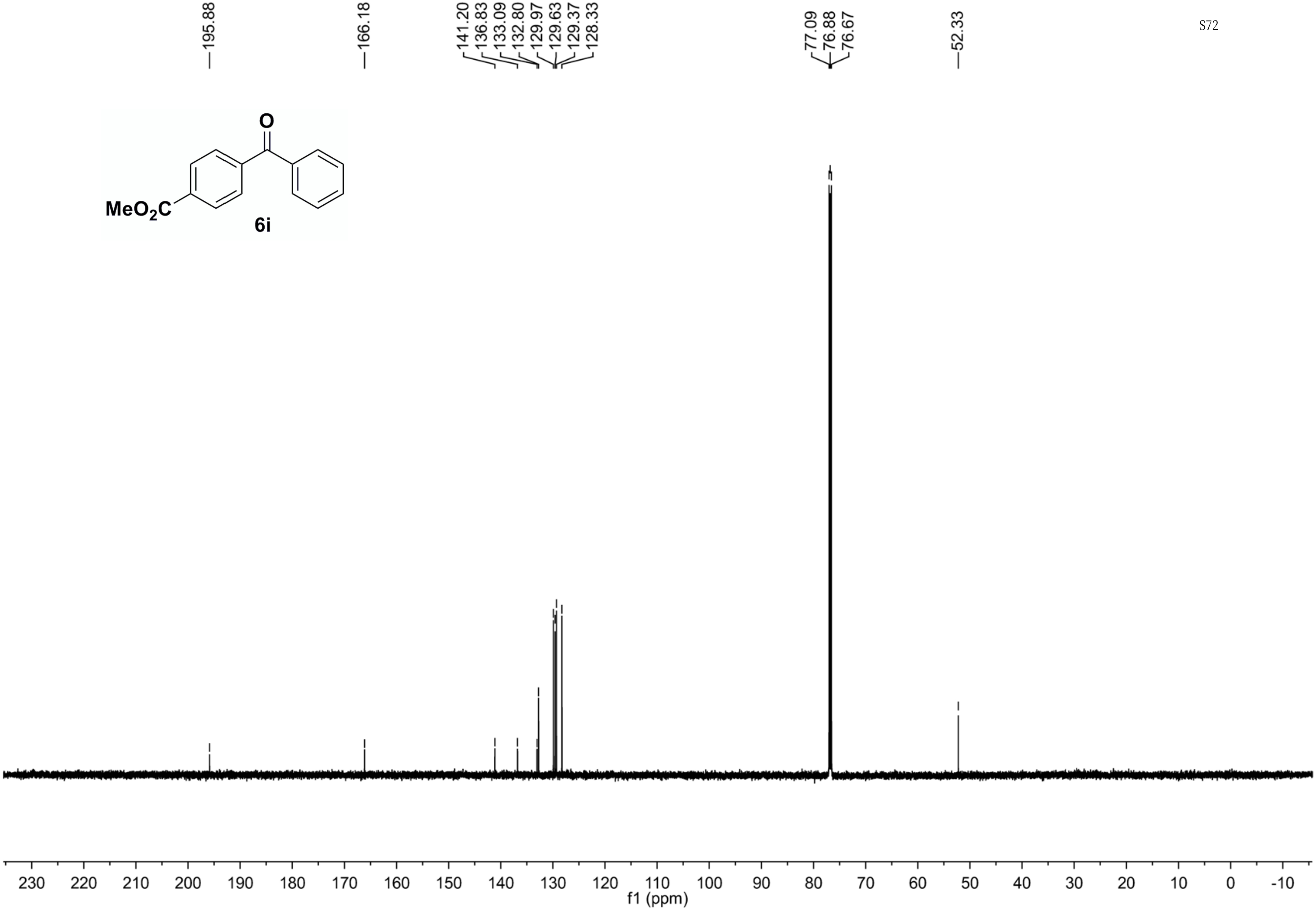

8.636
8.635
8.631
8.630
8.626
8.446
8.163
8.162
8.146
8.144
8.143
8.140
7.824
7.822
7.821
7.819
7.808
7.803
7.801
7.800
7.736
7.716
7.714
7.696
7.695
7.691
7.688
7.684
7.674
7.669
7.664
7.654
7.650
7.647
7.564
7.563
7.561
7.559
7.543
7.540
7.529
7.526
7.525
7.523
7.264
1.575
-0.000
O
O2N
6g
water
impurity
1.00
1.05
1.09
2.13
2.26
2.27
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

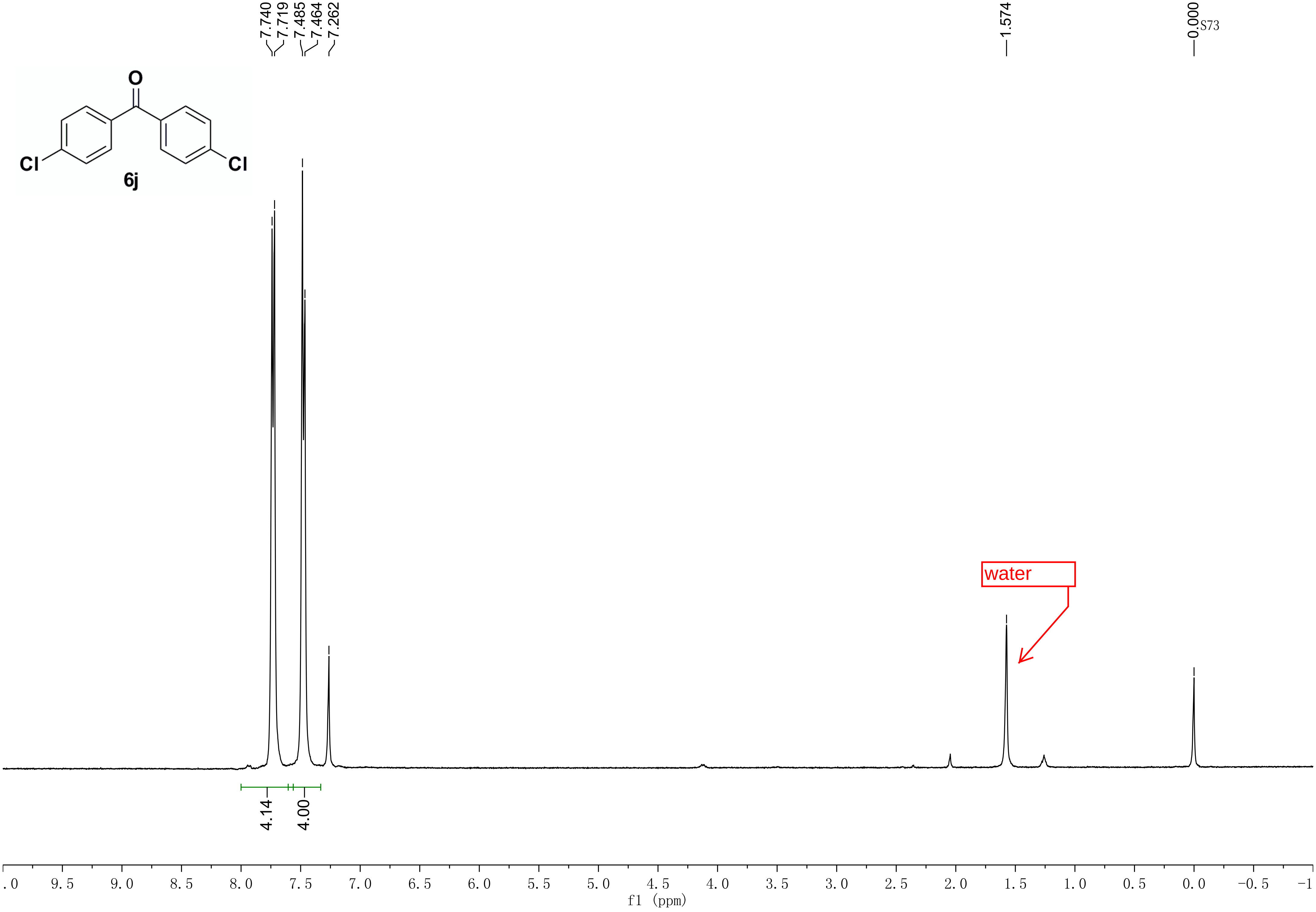

194.133
148.071
139.046
136.238
135.401
133.336
129.985
129.607
128.709
126.691
124.697
77.305
76.988
76.670
O
O_2N
6g
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

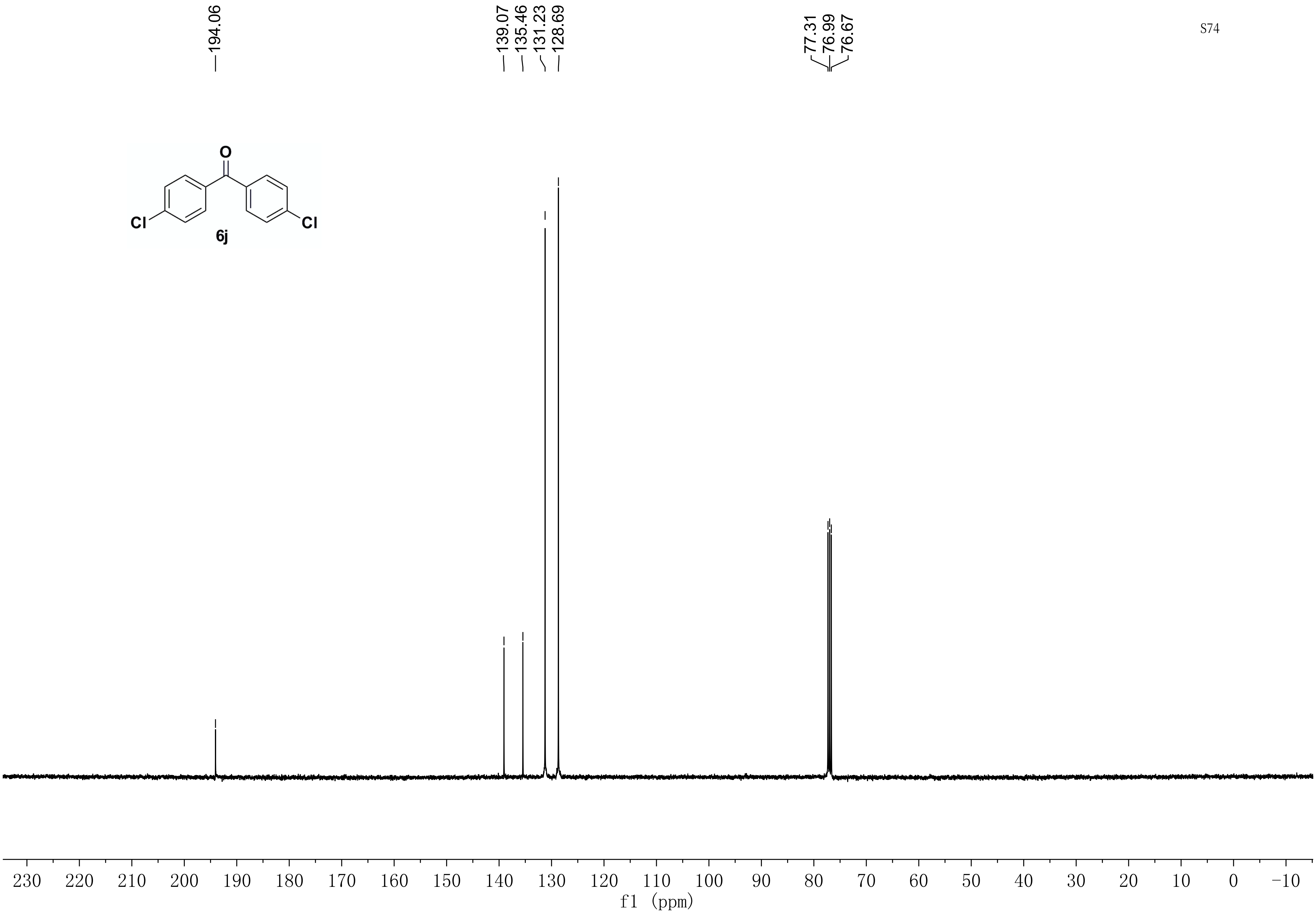

6h
O
NC
7.895
7.890
7.878
7.873
7.811
7.806
7.801
7.800
7.795
7.789
7.782
7.778
7.650
7.632
7.542
7.538
7.522
7.503
7.267
1.253
-0.000
impurity
1.69
3.41
1.00
1.92
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

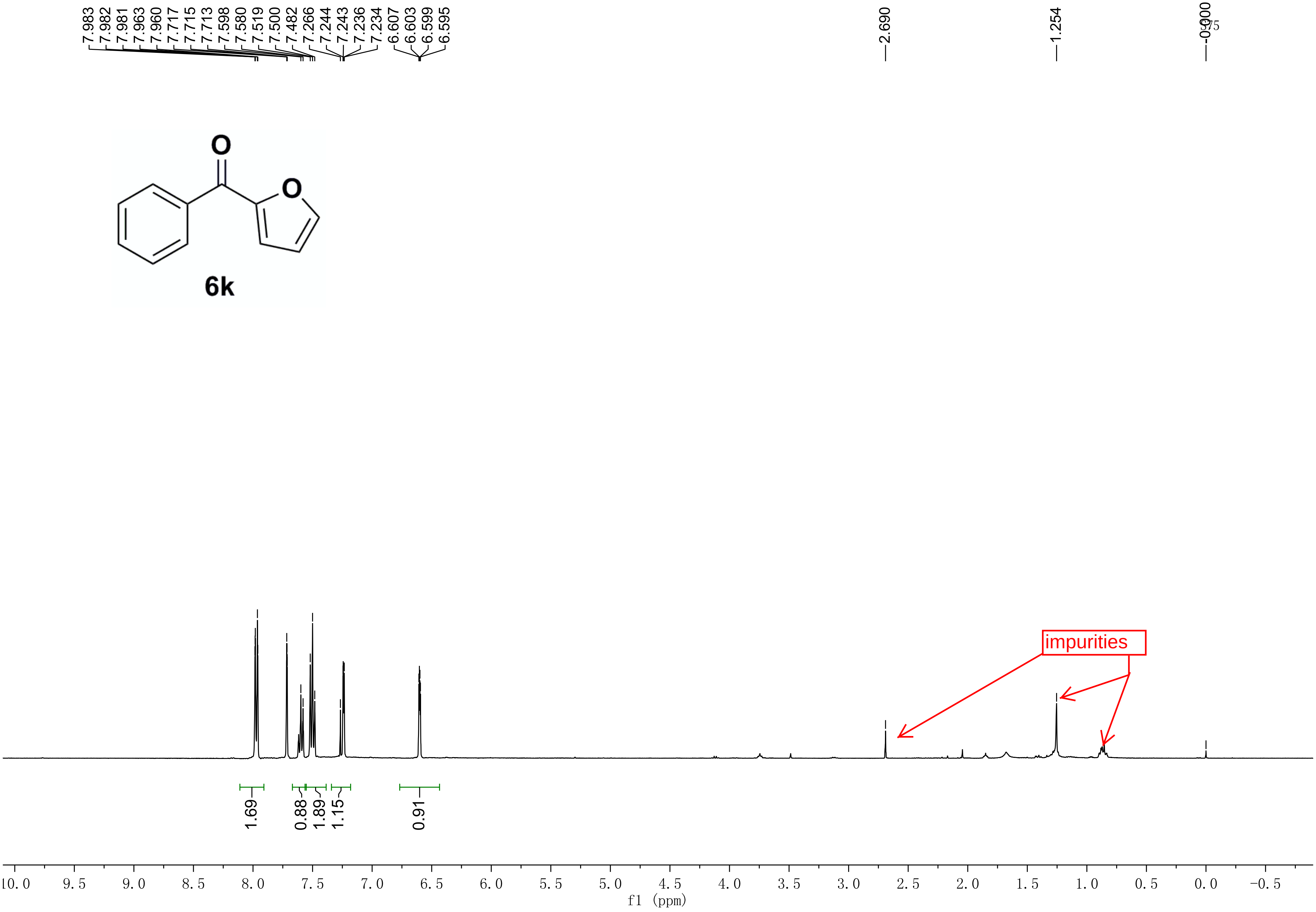

194.99
141.22
136.31
133.30
132.14
130.20
130.04
128.61
117.97
115.66
77.31
76.99
76.67
O
NC
6h
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.16
8.15
7.85
7.84
7.81
7.80
7.62
7.50
7.26
3.97
3.97
1.55
0.00
O
MeO2C
6i
water
2.00
3.79
1.06
1.92
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

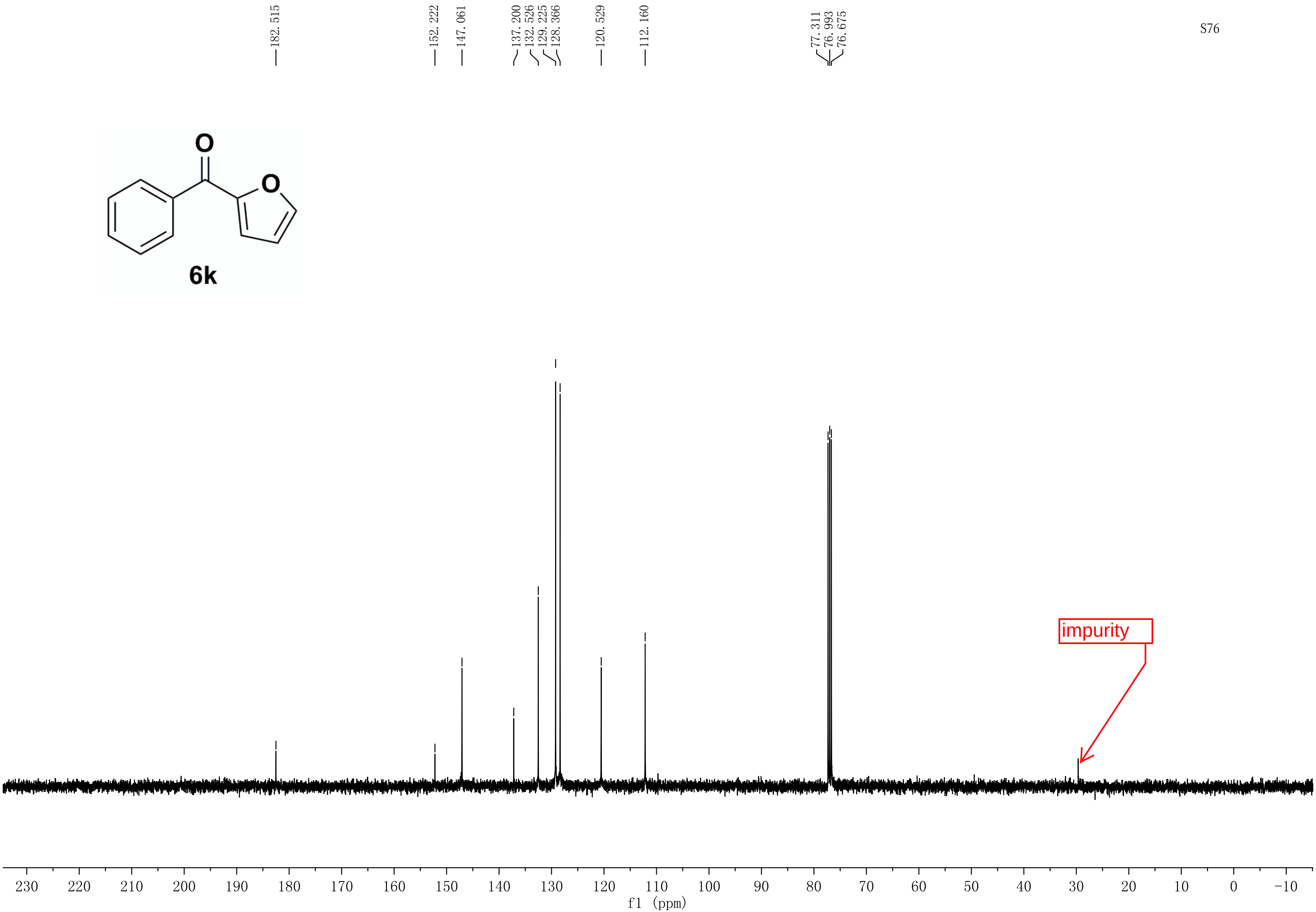

195.88
166.18
141.20
136.83
133.09
132.80
129.97
129.63
129.37
128.33
77.09
76.88
76.67
52.33
O
MeO2C
6i
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

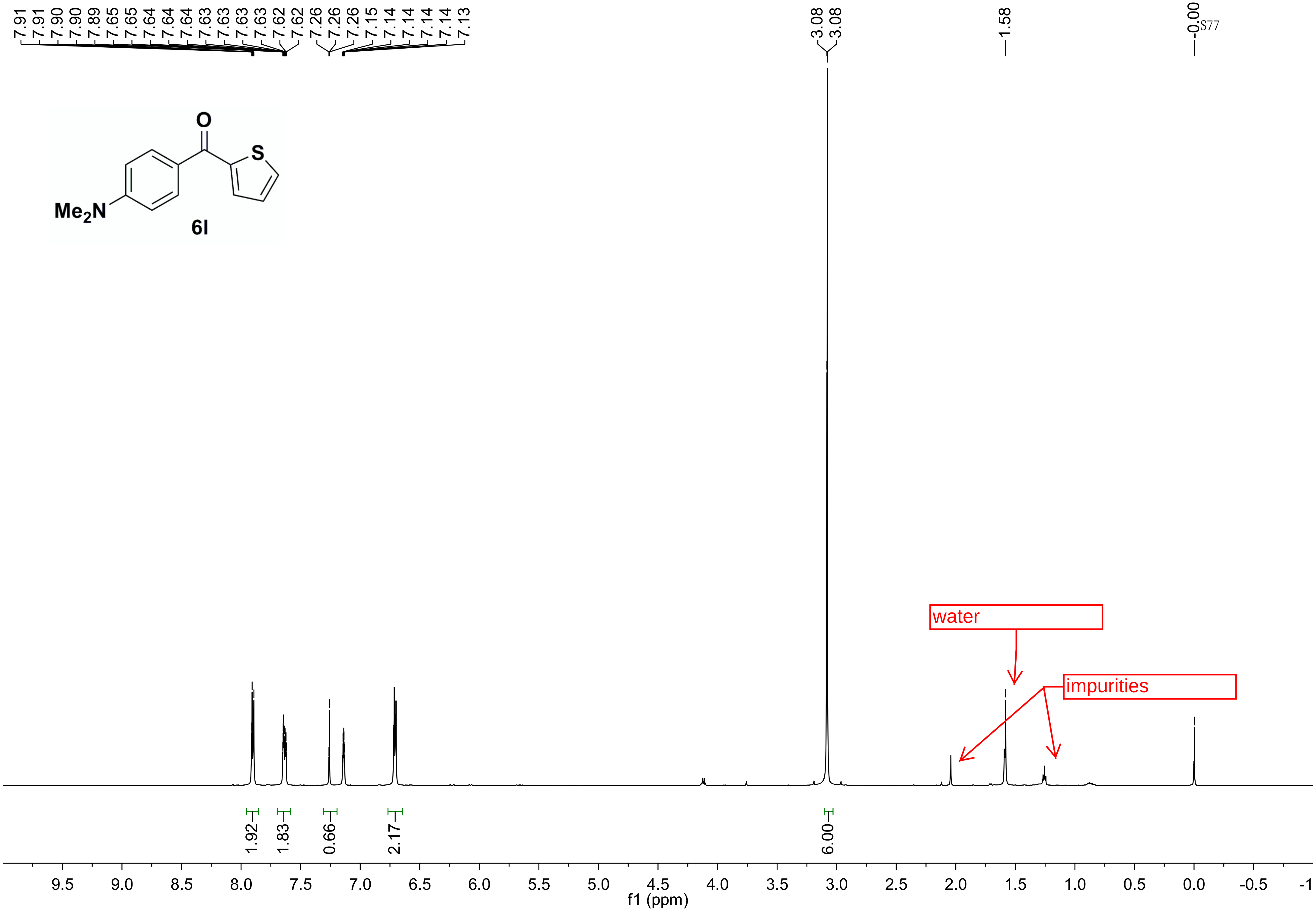

7.740
7.719
7.485
7.464
7.262
1.574
0.000
O
Cl
Cl
6j
water
4.14
4.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

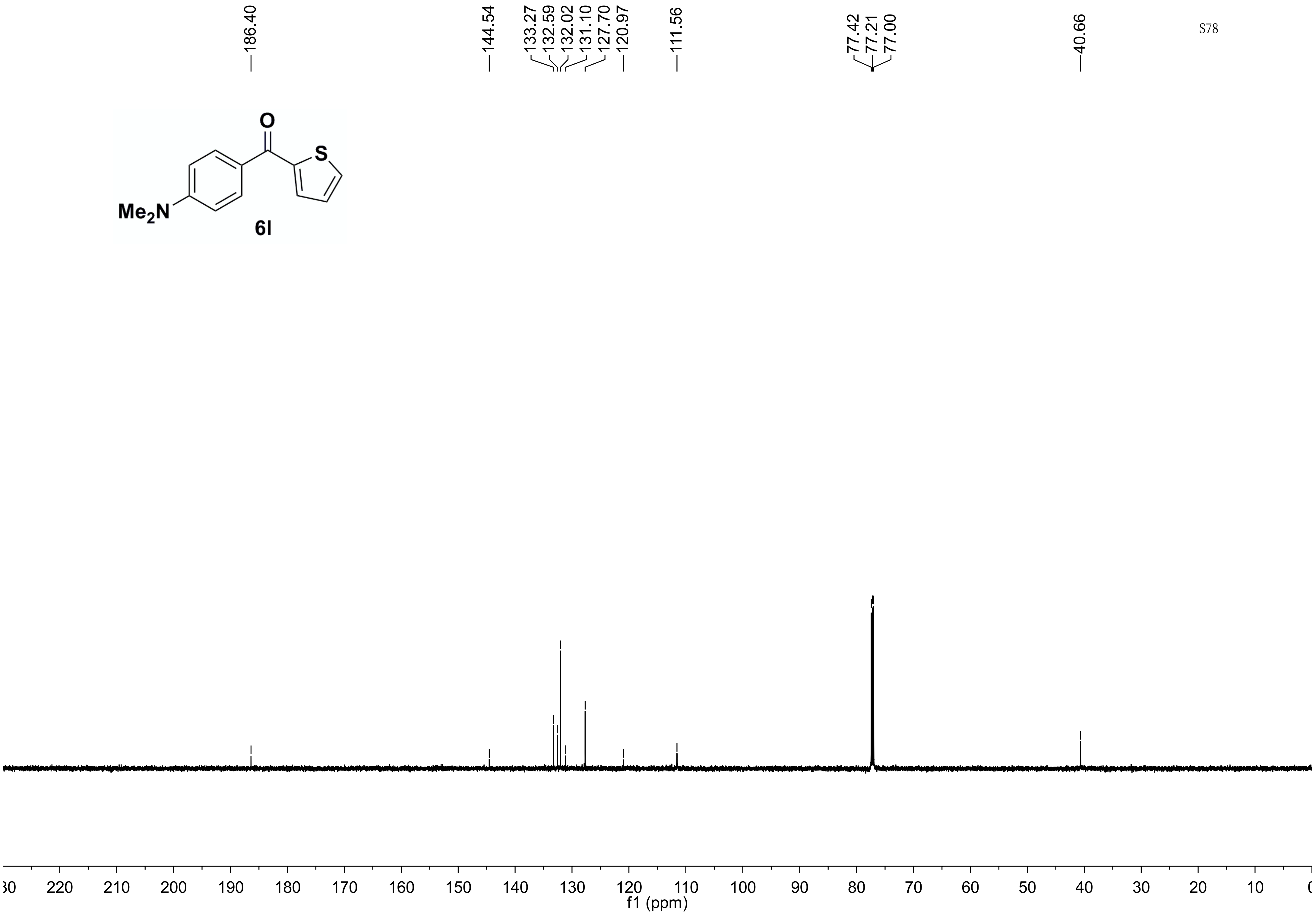

194.06
139.07
135.46
131.23
128.69
77.31
76.99
76.67
O
Cl
Cl
6j
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.983
7.982
7.981
7.963
7.960
7.717
7.715
7.713
7.598
7.580
7.519
7.500
7.482
7.266
7.244
7.243
7.236
7.234
6.607
6.603
6.599
6.595
2.690
1.254
0.000
O
O
6k
impurities
1.69
0.88
1.89
1.15
0.91
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

6k


182.515
152.222
147.061
137.200
132.526
129.225
128.366
120.529
112.160
77.311
76.993
76.675
impurity
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

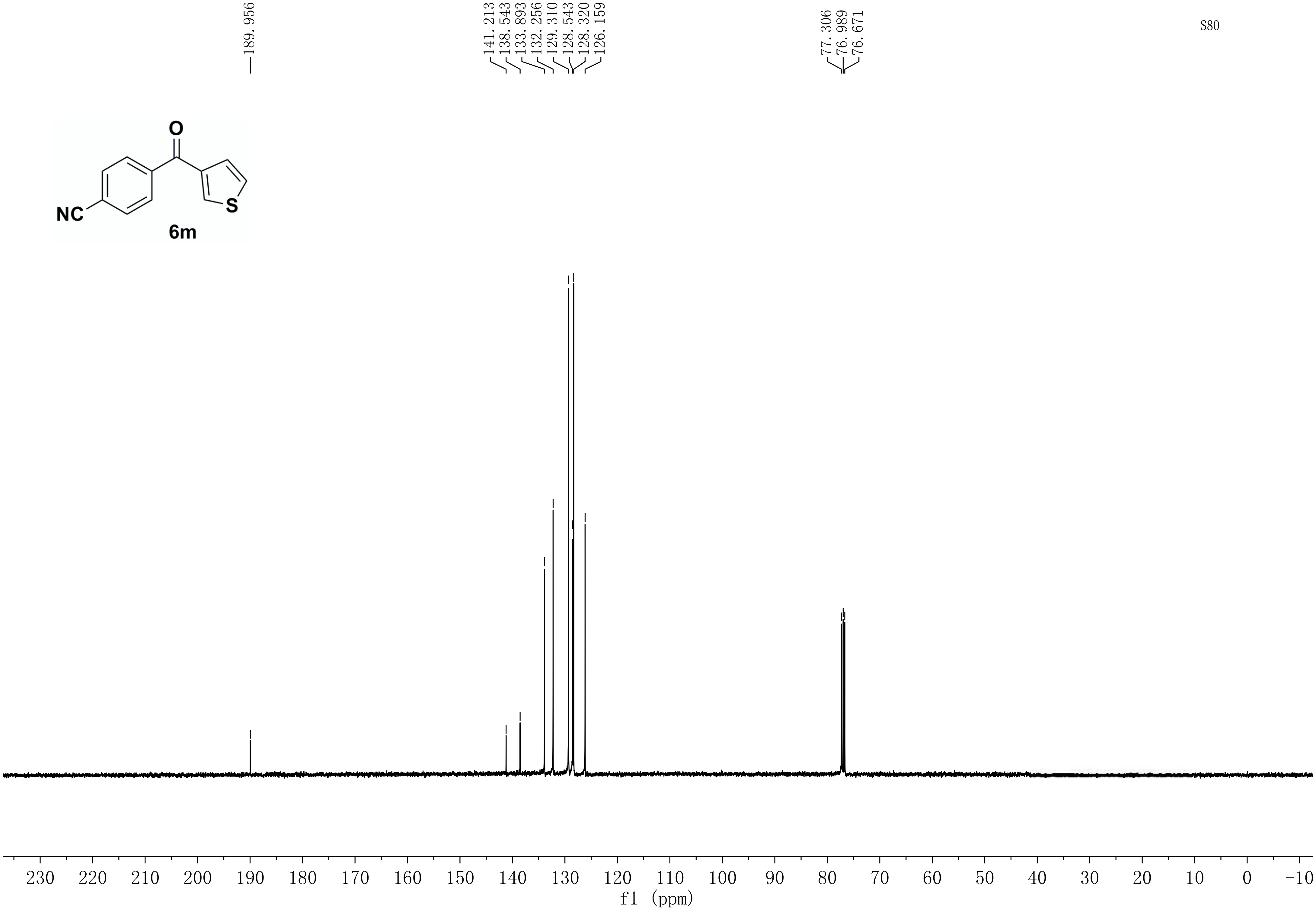

7.91
7.91
7.90
7.90
7.89
7.65
7.65
7.64
7.64
7.64
7.63
7.63
7.63
7.63
7.62
7.62
7.26
7.26
7.26
7.15
7.14
7.14
7.14
7.14
7.13
3.08
3.08
1.58
-0.00
O
S
Me2N
6l
water
impurities
1.92
1.83
0.66
2.17
6.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

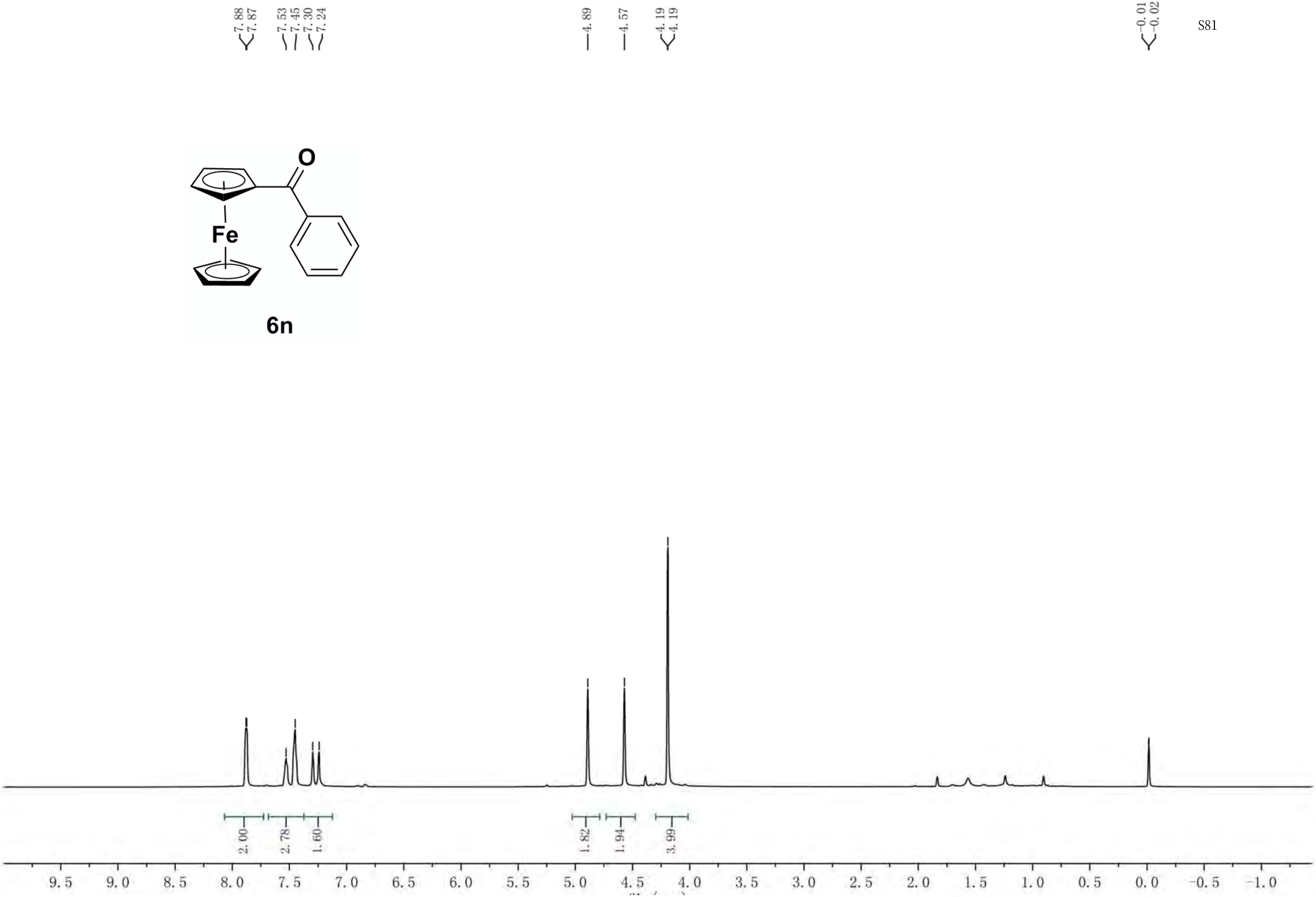


6l

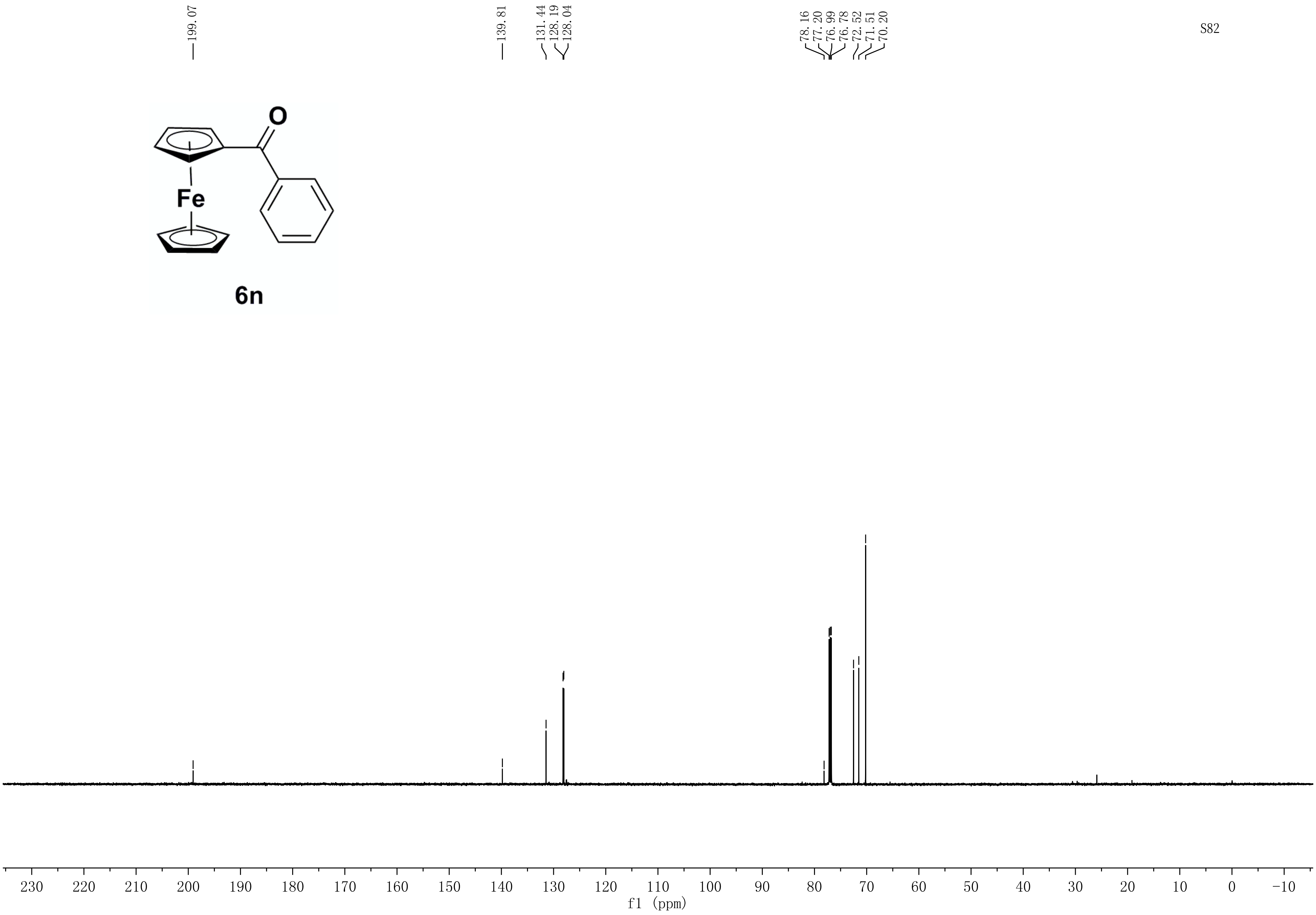
186.40
144.54
133.27
132.59
132.02
131.10
127.70
120.97
111.56
77.42
77.21
77.00
40.66
O
S
Me2N
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.26
4.78
4.78
4.77
4.50
4.49
4.49
3.49
3.48
3.06
3.05
3.04
3.03
3.02
1.56
1.21
1.20
-0.00
O
NC
S
6m
water
2.00
2.10
3.93
1.44
3.92
7.63
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

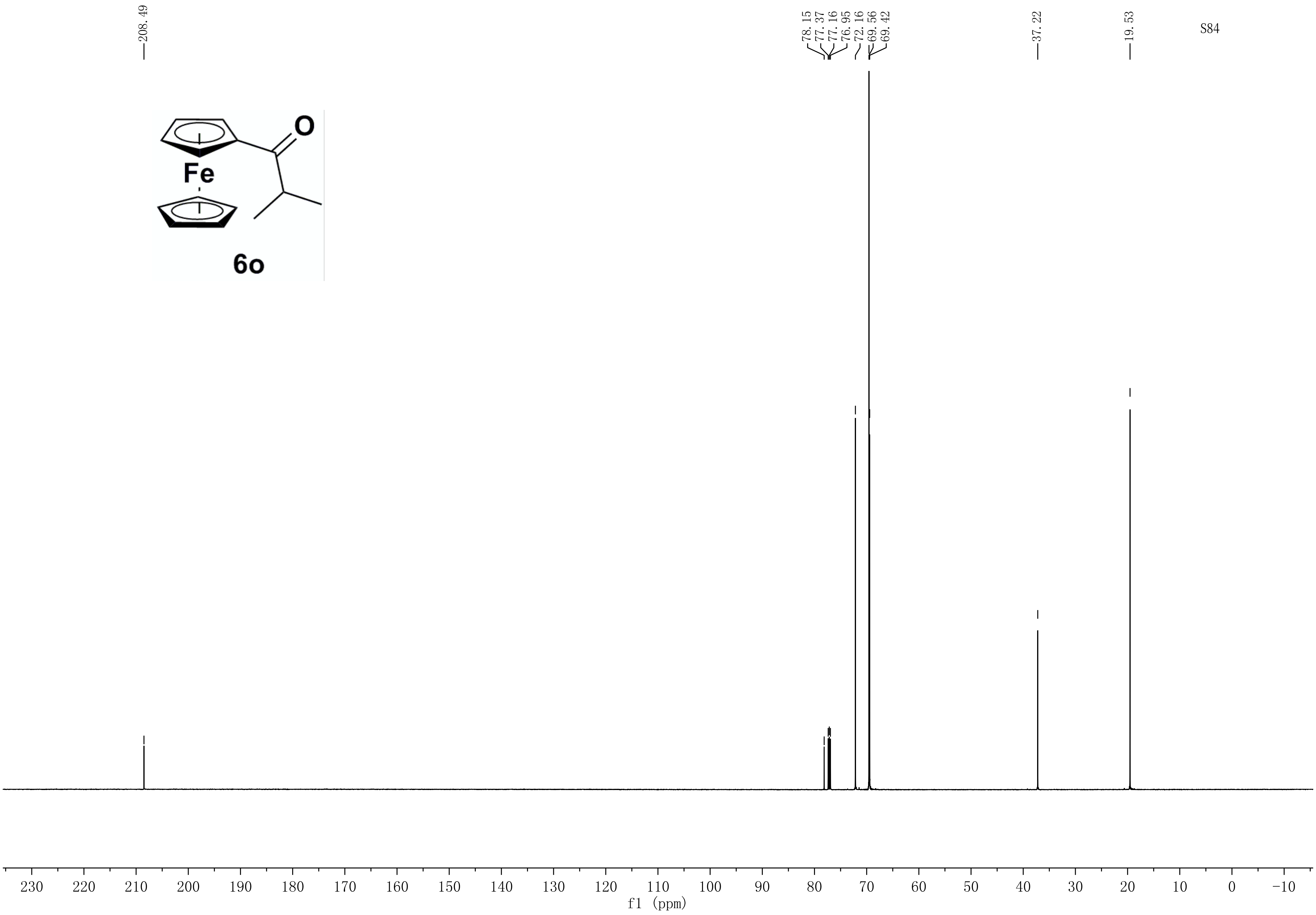

189.956
141.213
138.543
133.893
132.256
129.310
128.543
128.320
126.159
77.306
76.989
76.671
O
NC
S
6m
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

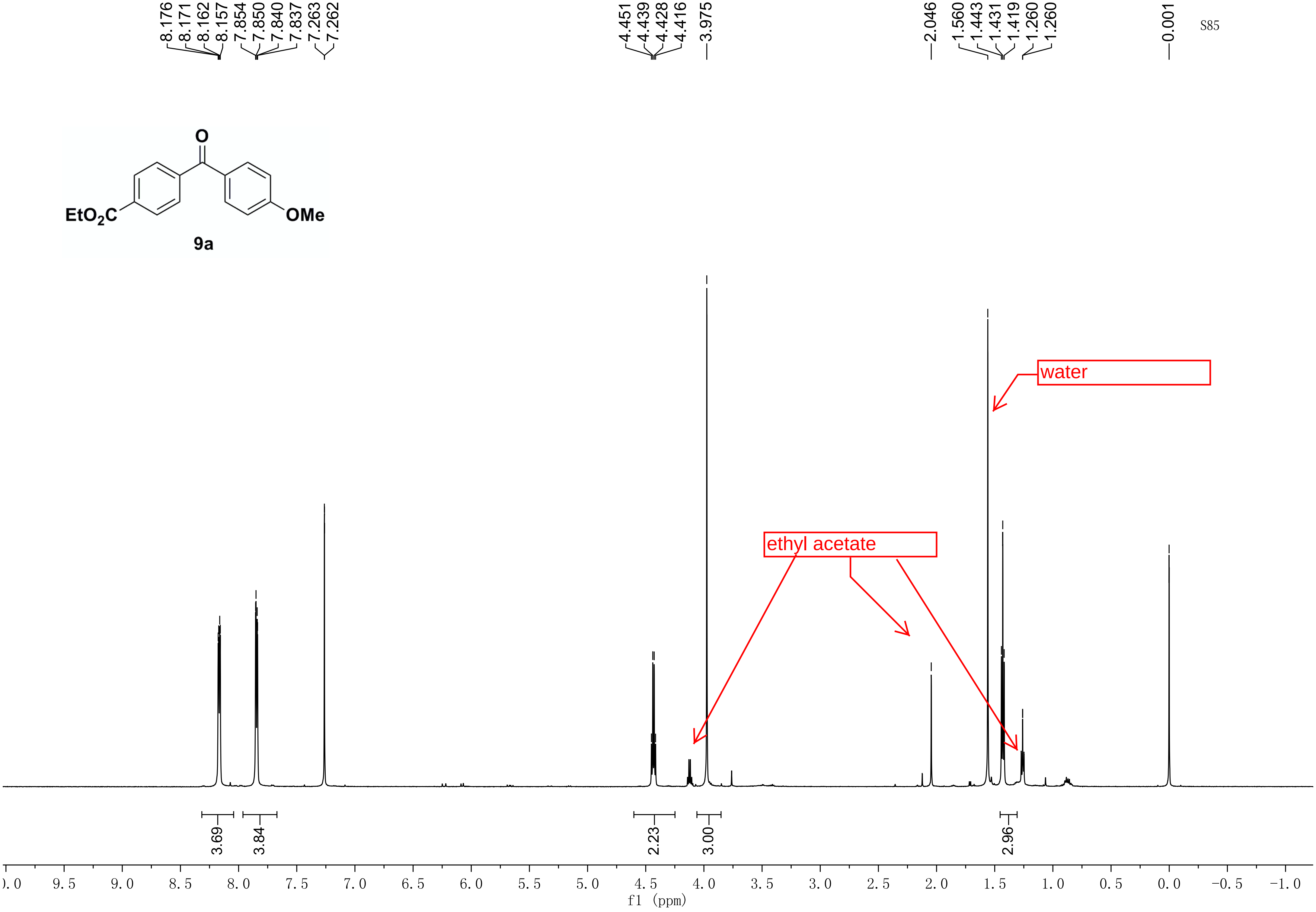

7.88
7.87
7.53
7.45
7.30
7.24
4.89
4.57
4.19
4.19
0.01
-0.02
O
Fe
2.00
2.78
1.60
1.82
1.94
3.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0

6n

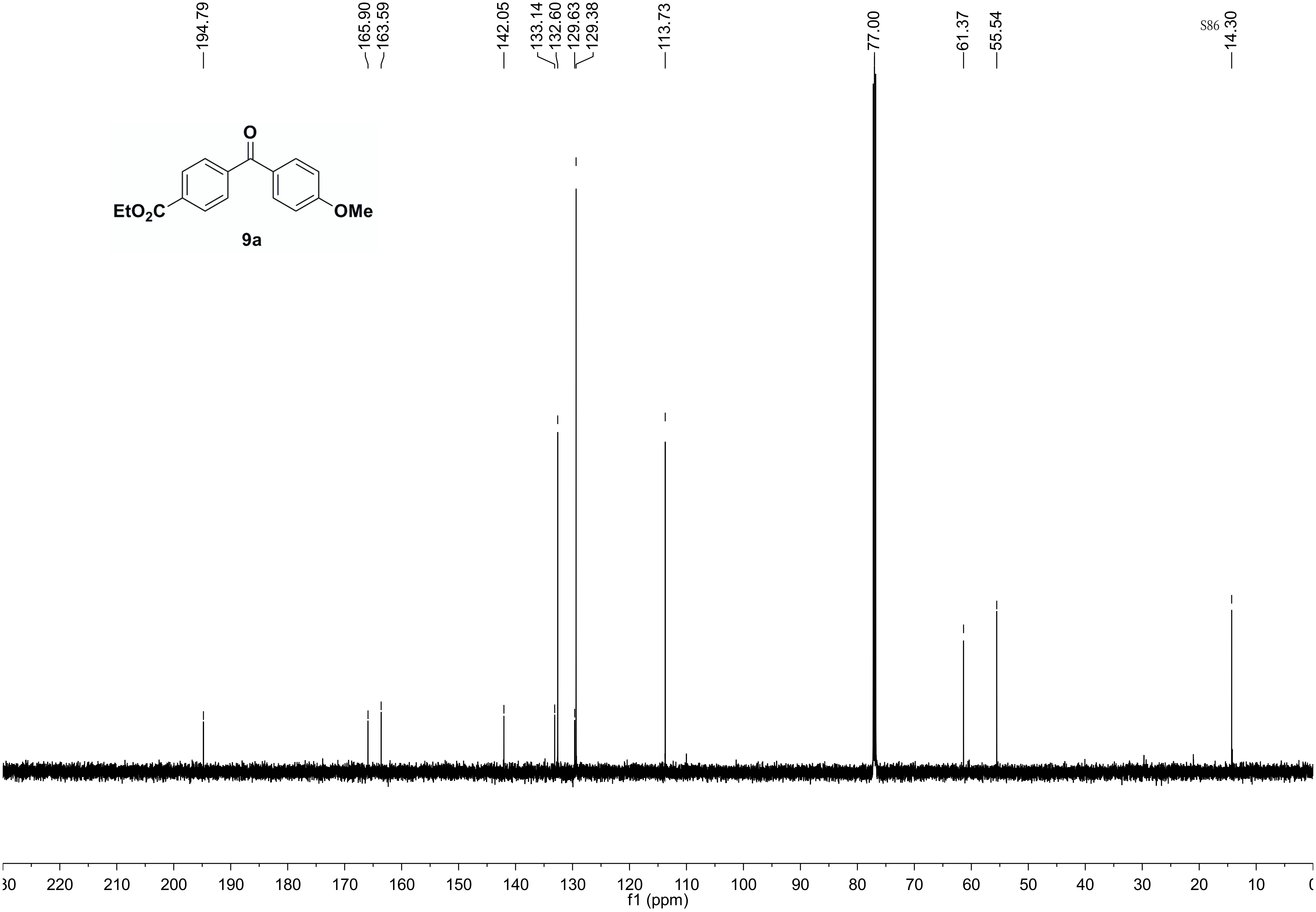

199.07
139.81
131.44
128.19
128.04
78.16
77.20
76.99
76.78
72.52
71.51
70.20
O
Fe
6n
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

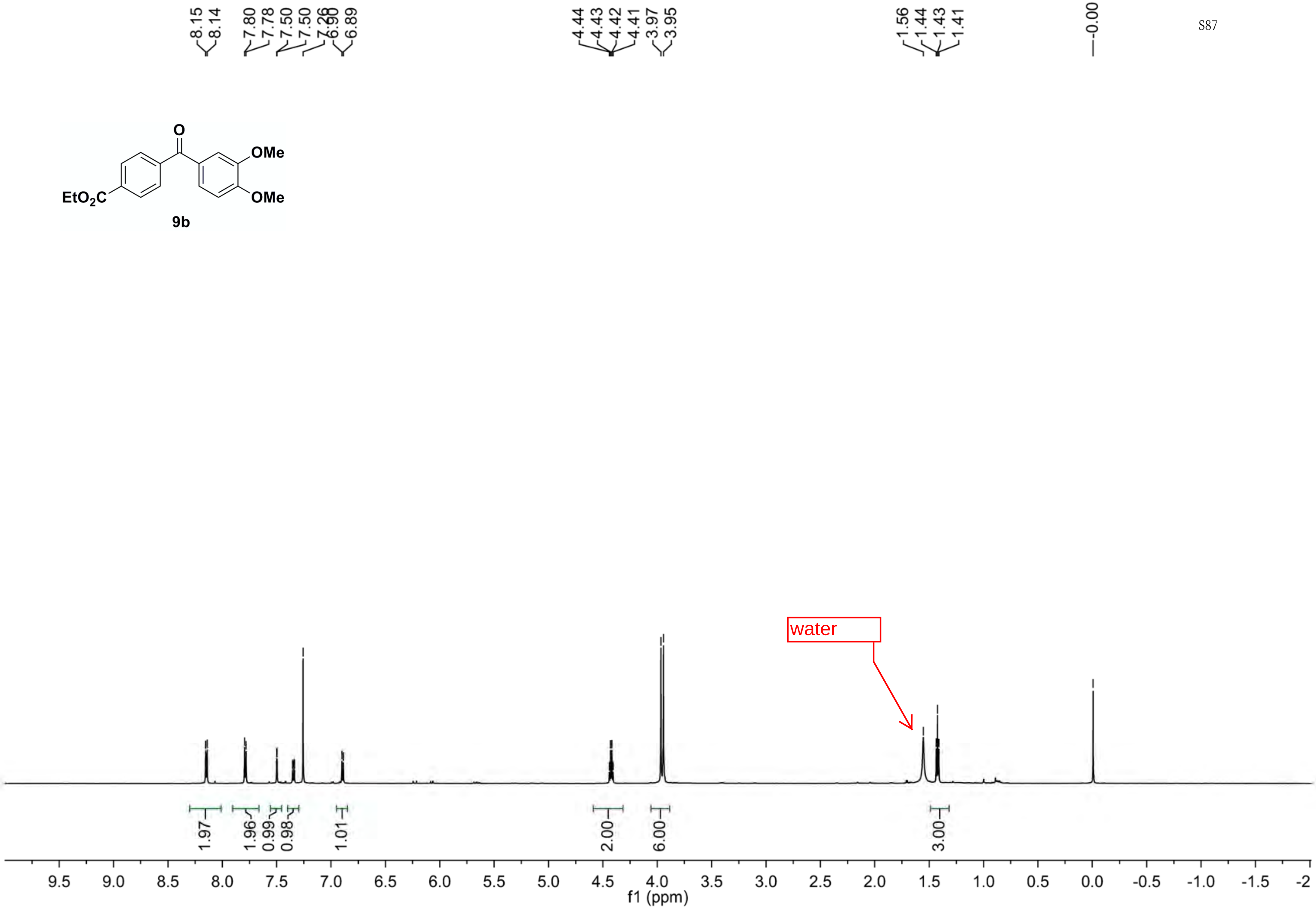

7.26
4.78
4.78
4.77
4.50
4.49
4.49
3.49
3.48
3.06
3.05
3.04
3.03
3.02
1.56
1.21
1.20
-0.00
O
Fe
6o
water
2.00
2.10
4.10
1.17
6.85
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

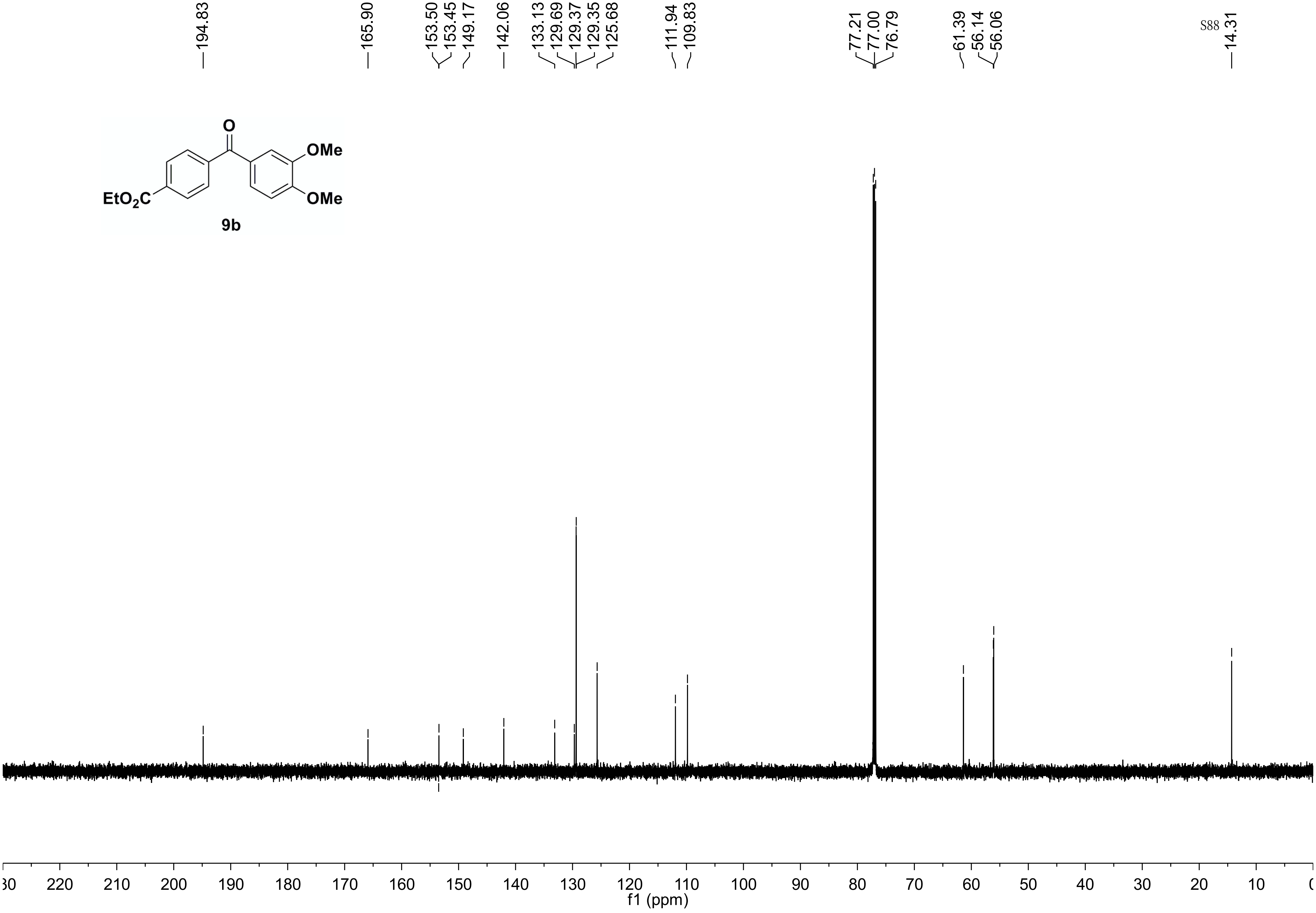

208.49
78.15
77.37
77.16
76.95
72.16
69.56
69.42
37.22
19.53
O
Fe
6o
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

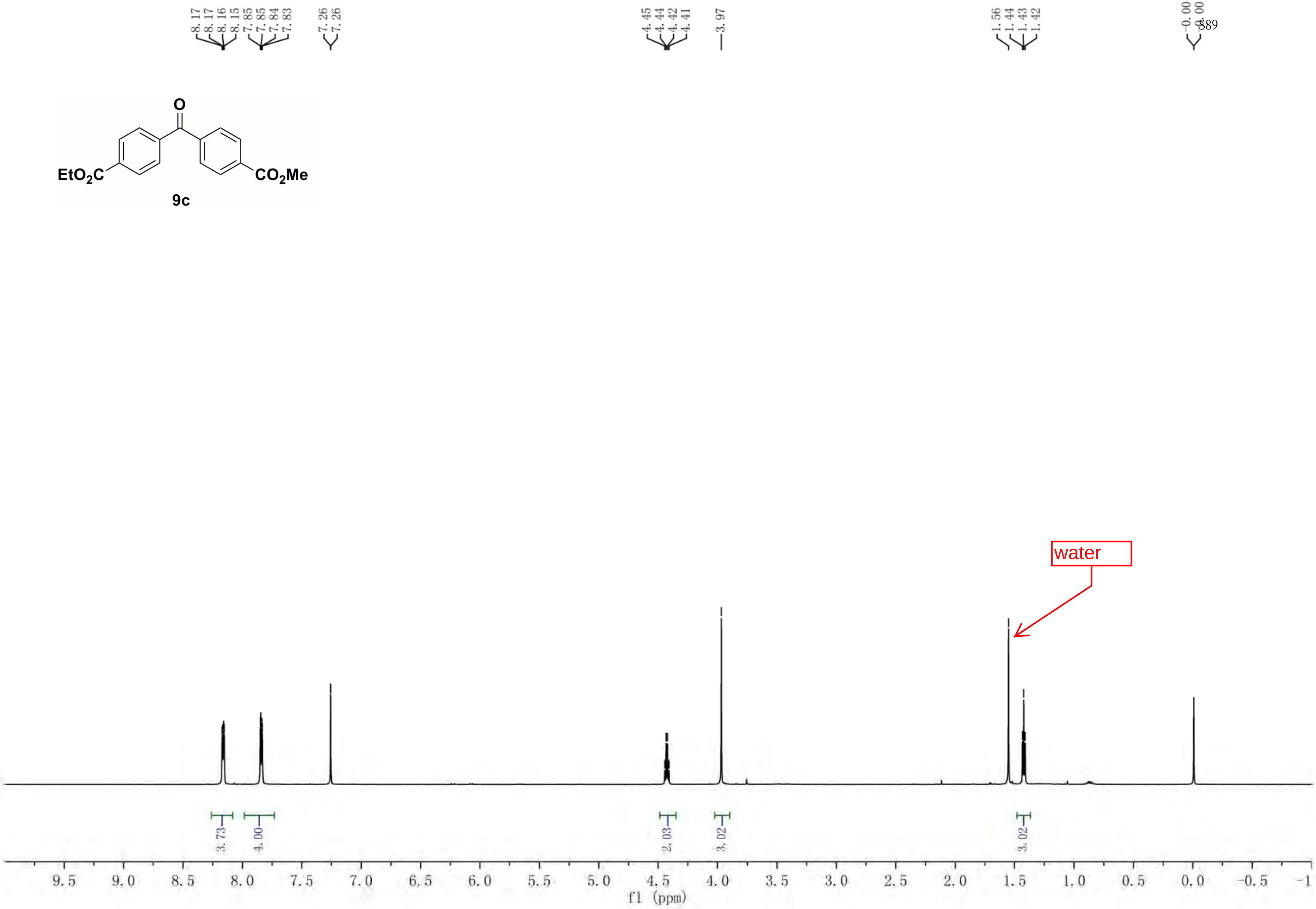

8.176
8.171
8.162
8.157
7.854
7.850
7.840
7.837
7.263
7.262
4.451
4.439
4.428
4.416
3.975
2.046
1.560
1.443
1.431
1.419
1.260
1.260
0.001
O
EtO2C
OMe
water
ethyl acetate
3.69
3.84
2.23
3.00
2.96
).0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

9a

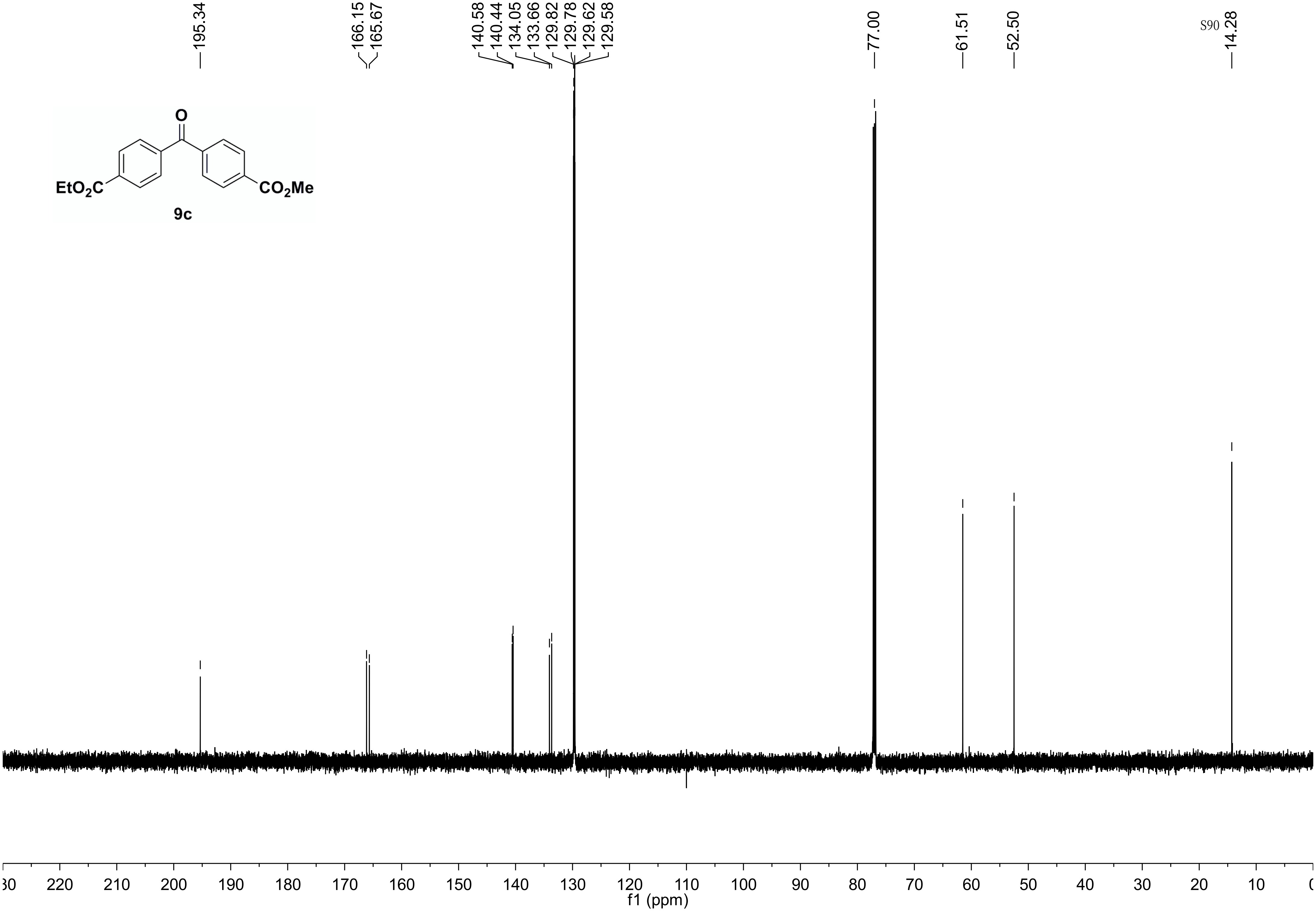

194.79
165.90
163.59
142.05
133.14
132.60
129.63
129.38
113.73
77.00
61.37
55.54
14.30
O
EtO2C
OMe
9a
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

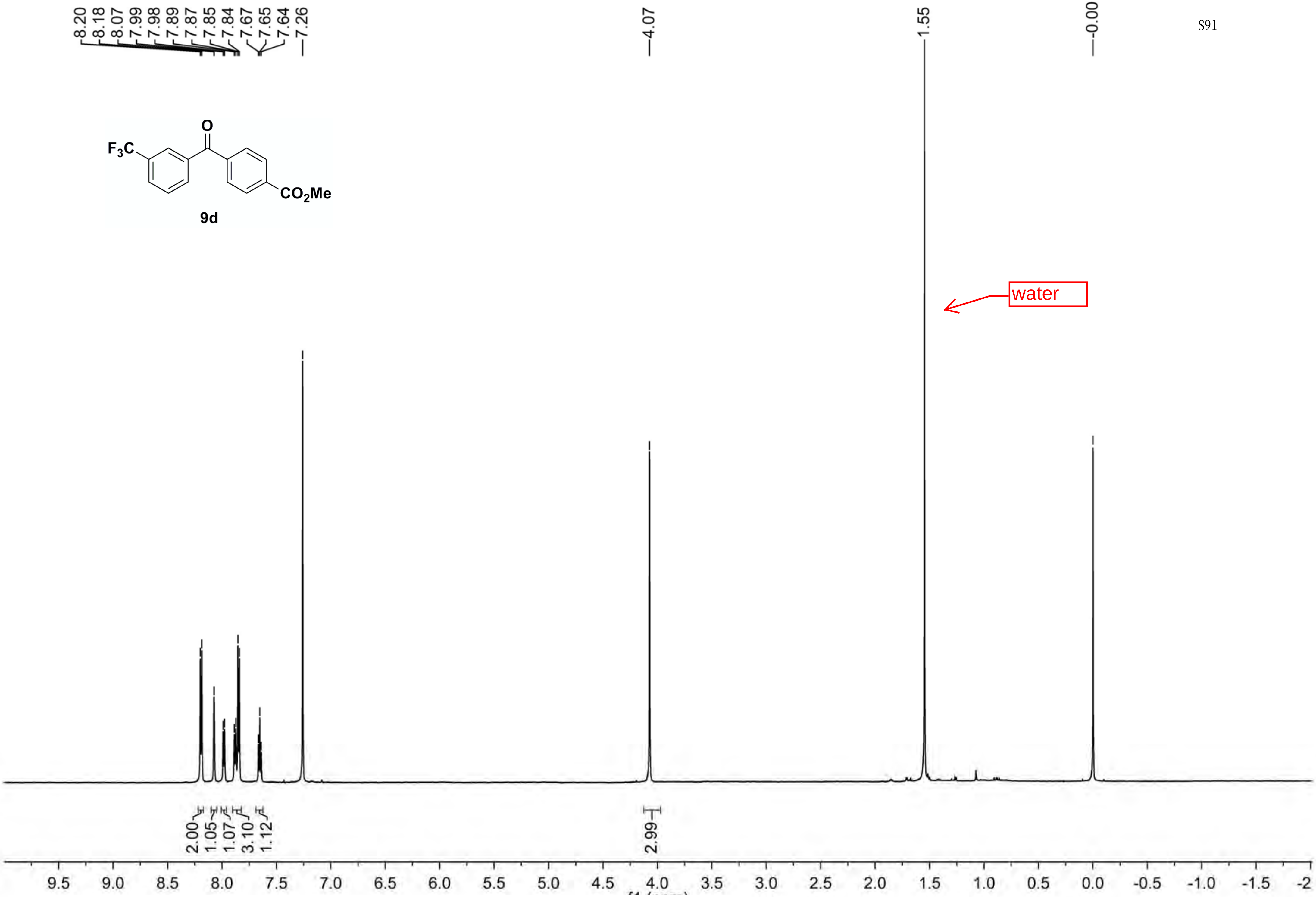

8.15
8.14
7.80
7.78
7.50
7.50
7.26
6.90
6.89
4.44
4.43
4.42
4.41
3.97
3.95
1.56
1.44
1.43
1.41
-0.00
O
OMe
OMe
EtO2C
9b
water
1.97
1.96
0.99
0.98
1.01
2.00
6.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

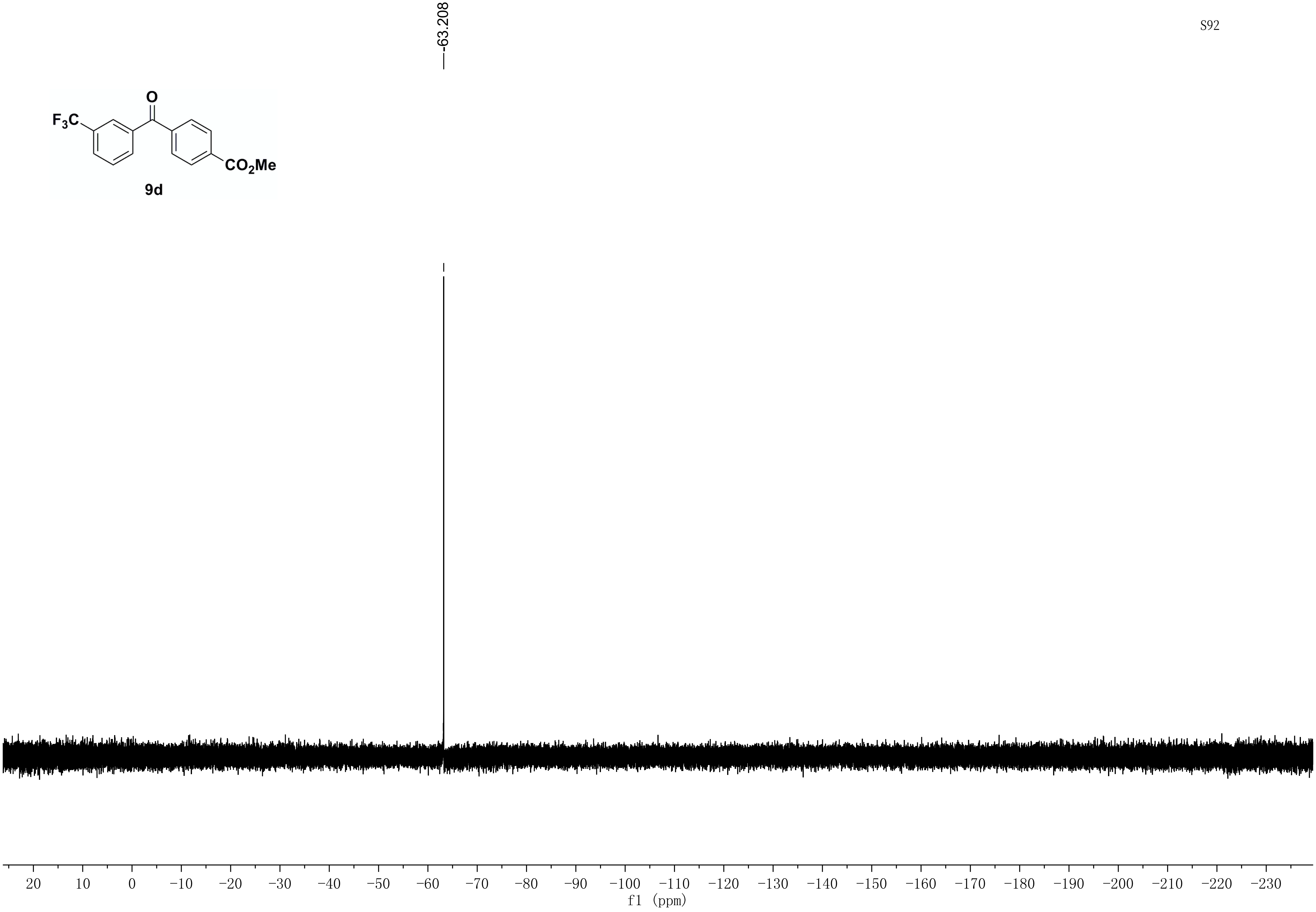

194.83
165.90
153.50
153.45
149.17
142.06
133.13
129.69
129.37
129.35
125.68
111.94
109.83
77.21
77.00
76.79
61.39
56.14
56.06
14.31
O
OMe
OMe
EtO2C
9b
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

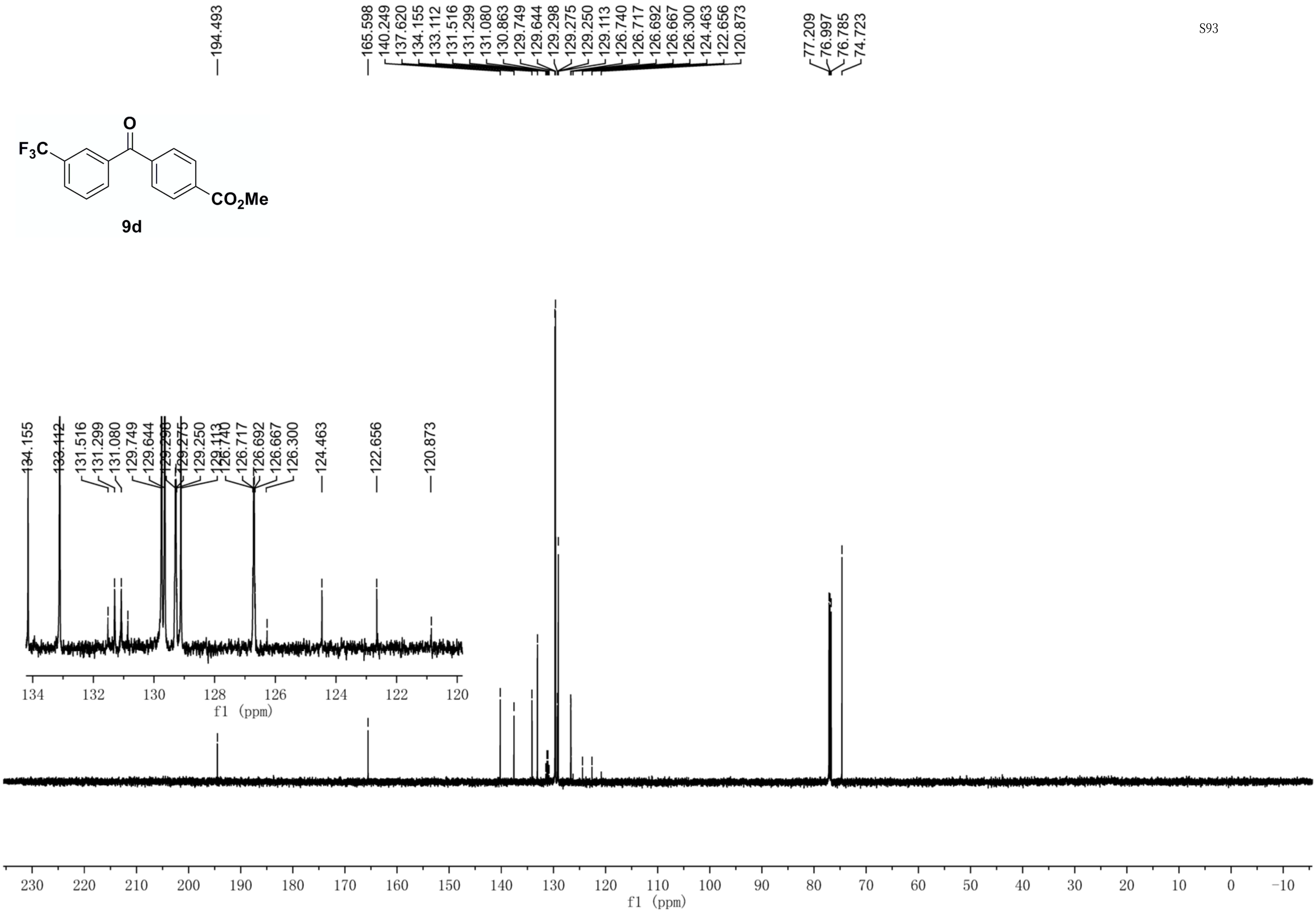

8.17
8.17
8.16
8.15
7.85
7.85
7.84
7.83
7.26
7.26
4.45
4.44
4.42
4.41
3.97
1.56
1.44
1.43
1.42
-0.00
0.00
O
EtO2C
CO2Me
water
3.73
4.00
2.03
3.02
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

9c


195.34
166.15
165.67
140.58
140.44
134.05
133.66
129.82
129.78
129.62
129.58
77.00
61.51
52.50
14.28
O
EtO$_2$C
CO$_2$Me
9c
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

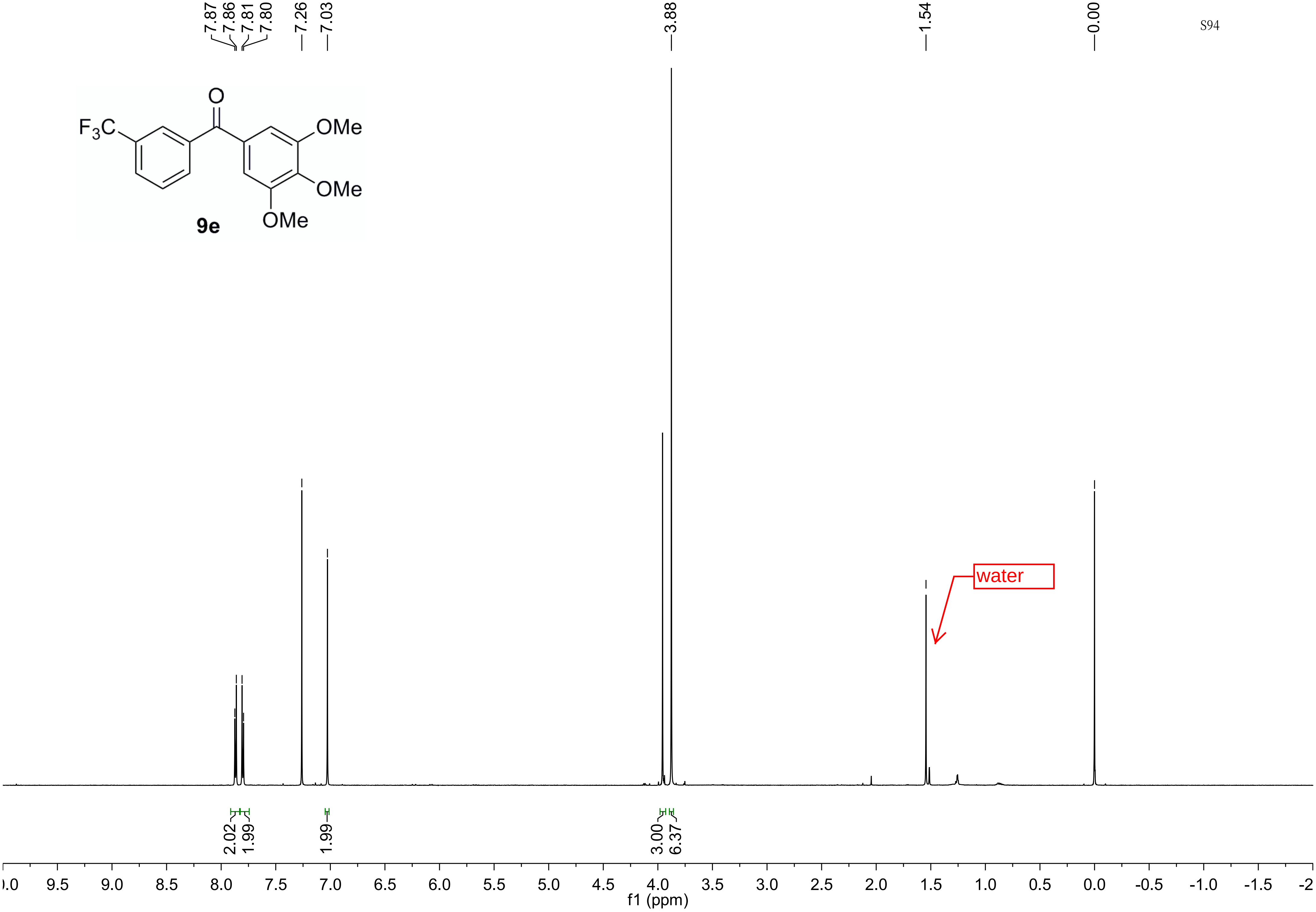

8.20
8.18
8.07
7.99
7.98
7.89
7.87
7.85
7.84
7.67
7.65
7.64
7.26
4.07
1.55
-0.00
O
F_3C
CO_2Me
9d
water
2.00
1.05
1.07
3.10
1.12
2.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2

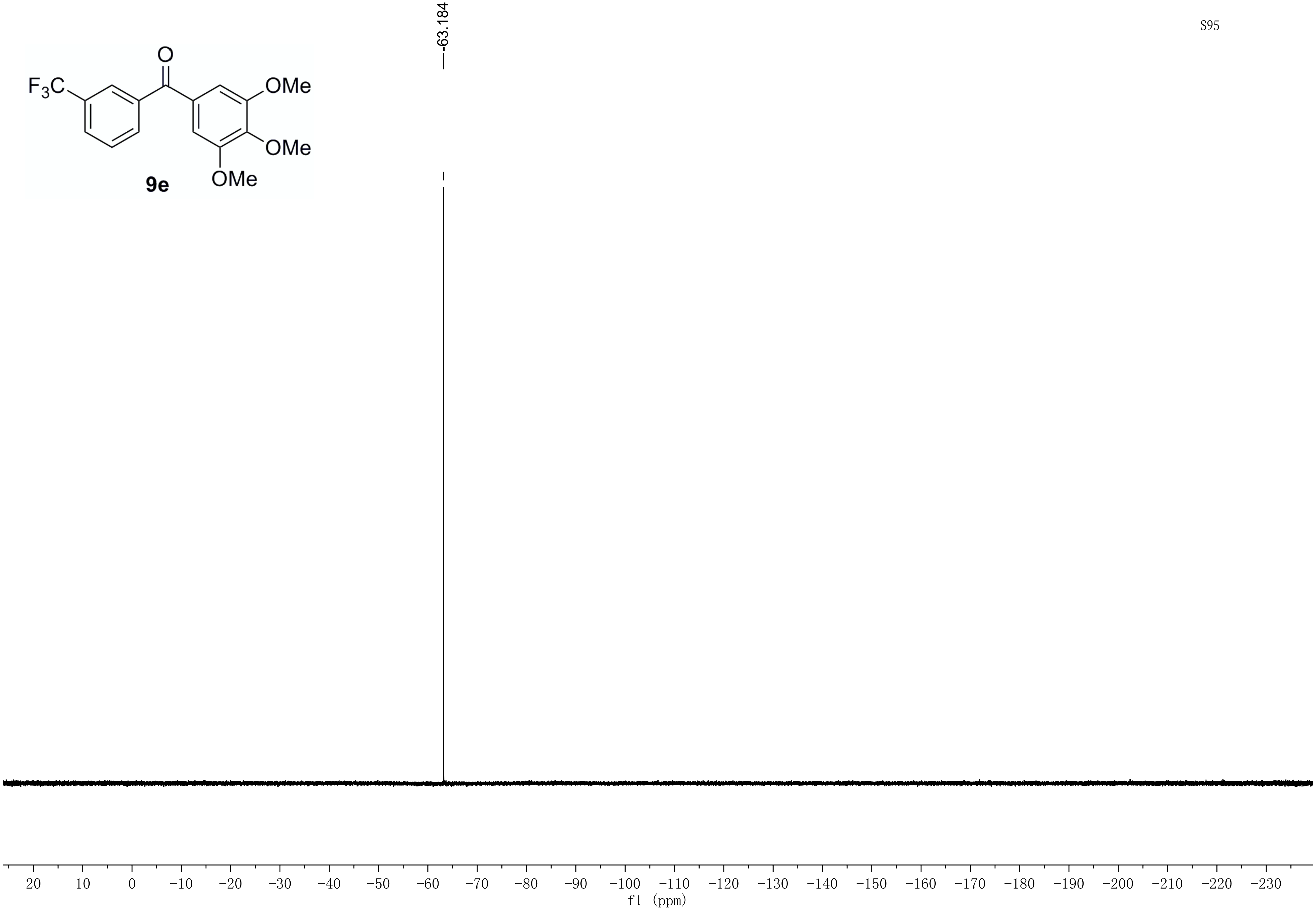

-63.208
F3C
O
CO2Me
9d
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
−230
f1 (ppm)

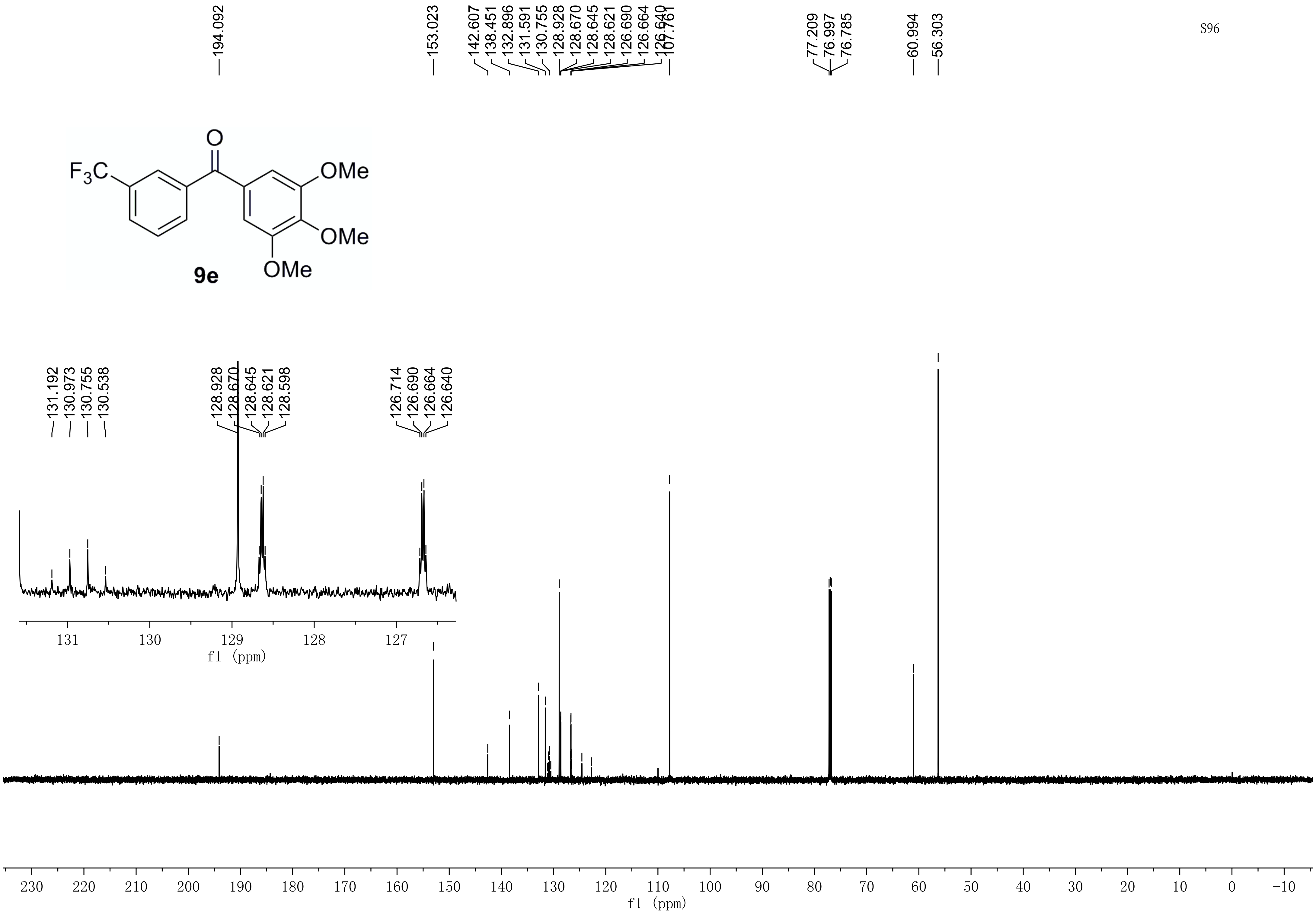


9d

F3C
O
CO2Me
194.493
165.598
140.249
137.620
134.155
133.112
131.516
131.299
131.080
130.863
129.749
129.644
129.298
129.275
129.250
129.113
126.740
126.717
126.692
126.667
126.300
124.463
122.656
120.873
77.209
76.997
76.785
74.723
134 132 130 128 126 124 122 120
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

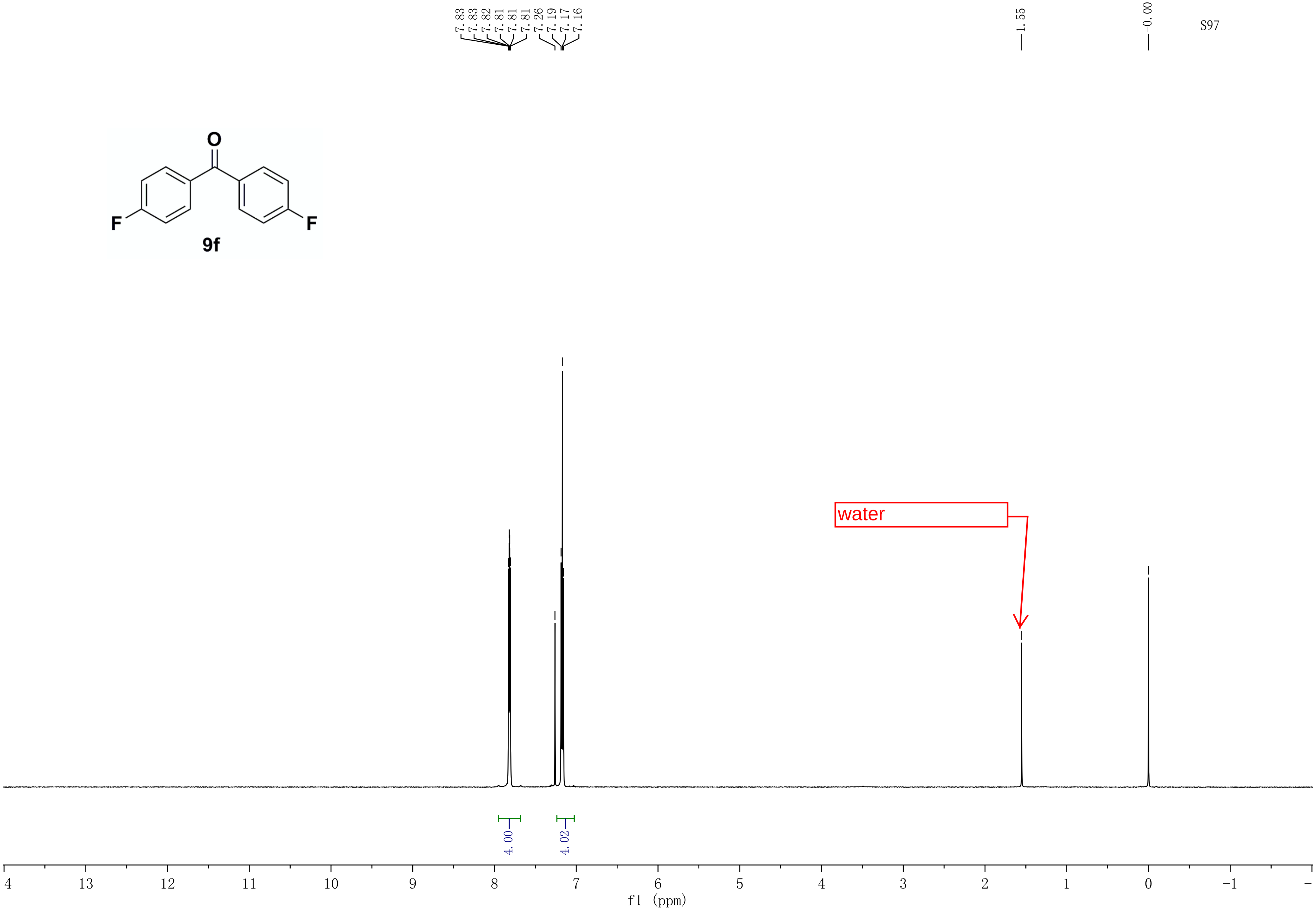

7.87
7.86
7.81
7.80
7.26
7.03
3.88
1.54
0.00
F3C
O
OMe
OMe
OMe
9e
water
2.02
1.99
1.99
3.00
6.37
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)


-63.184
O
F$_3$C
OMe
OMe
OMe
9e
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
−230
f1 (ppm)

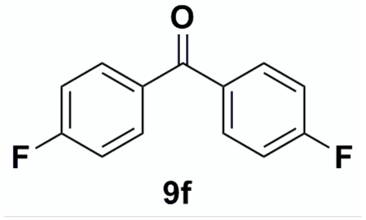


9e

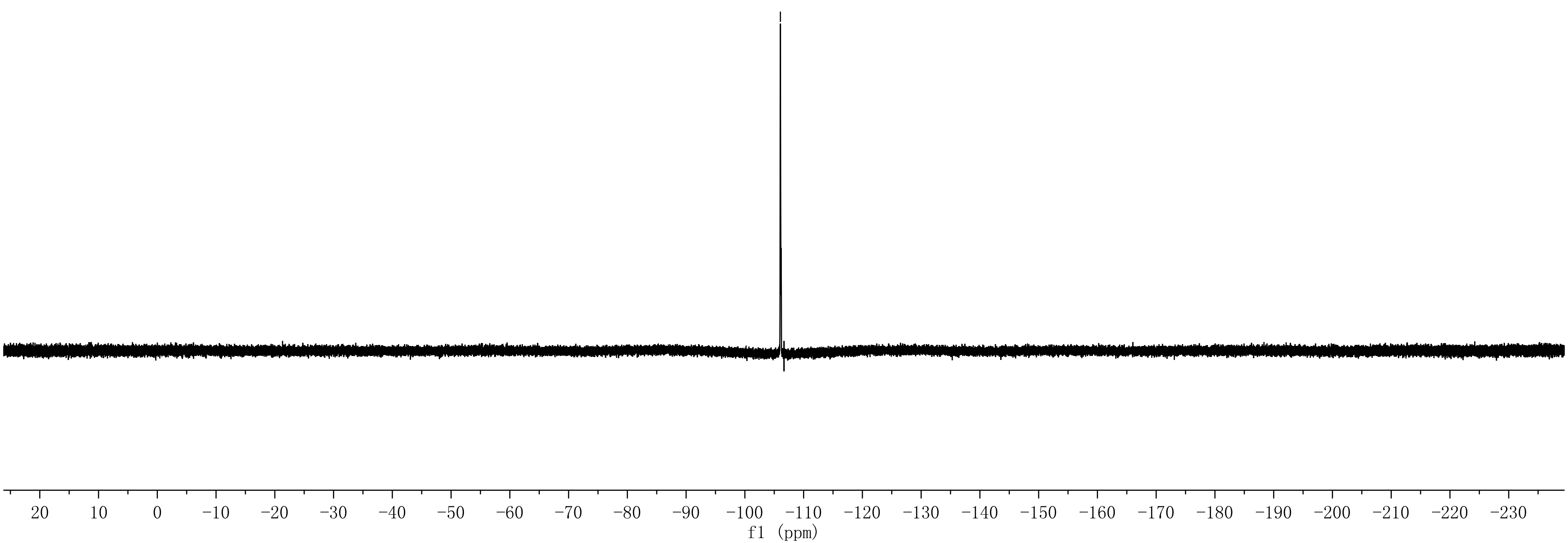
194.092
153.023
142.607
138.451
132.896
131.591
130.755
128.928
128.670
128.645
128.621
126.690
126.664
126.640
107.761
77.209
76.997
76.785
60.994
56.303
F3C
O
OMe
OMe
OMe
131.192
130.973
130.755
130.538
128.928
128.670
128.645
128.621
128.598
126.714
126.690
126.664
126.640
131
130
129
128
127
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

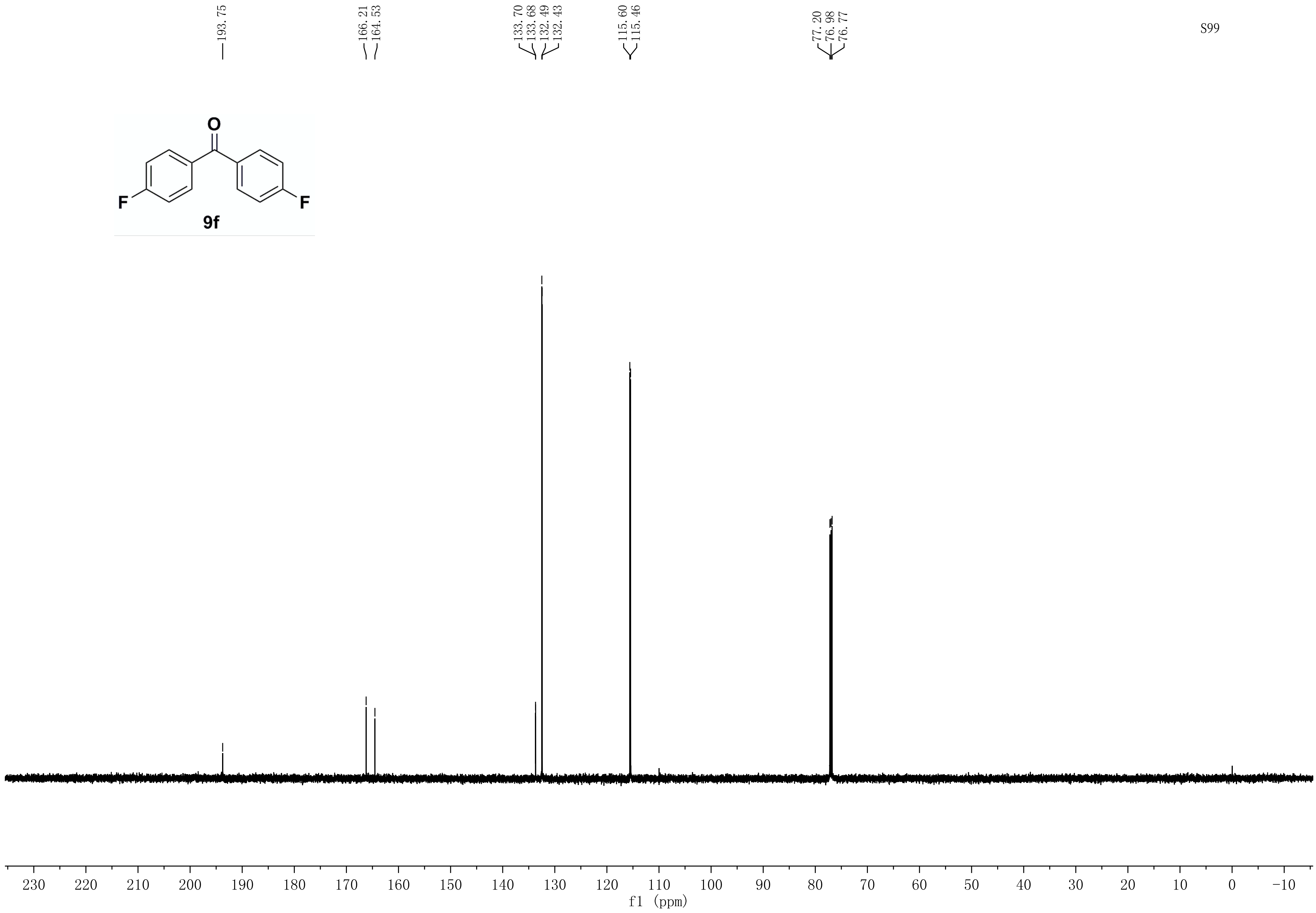


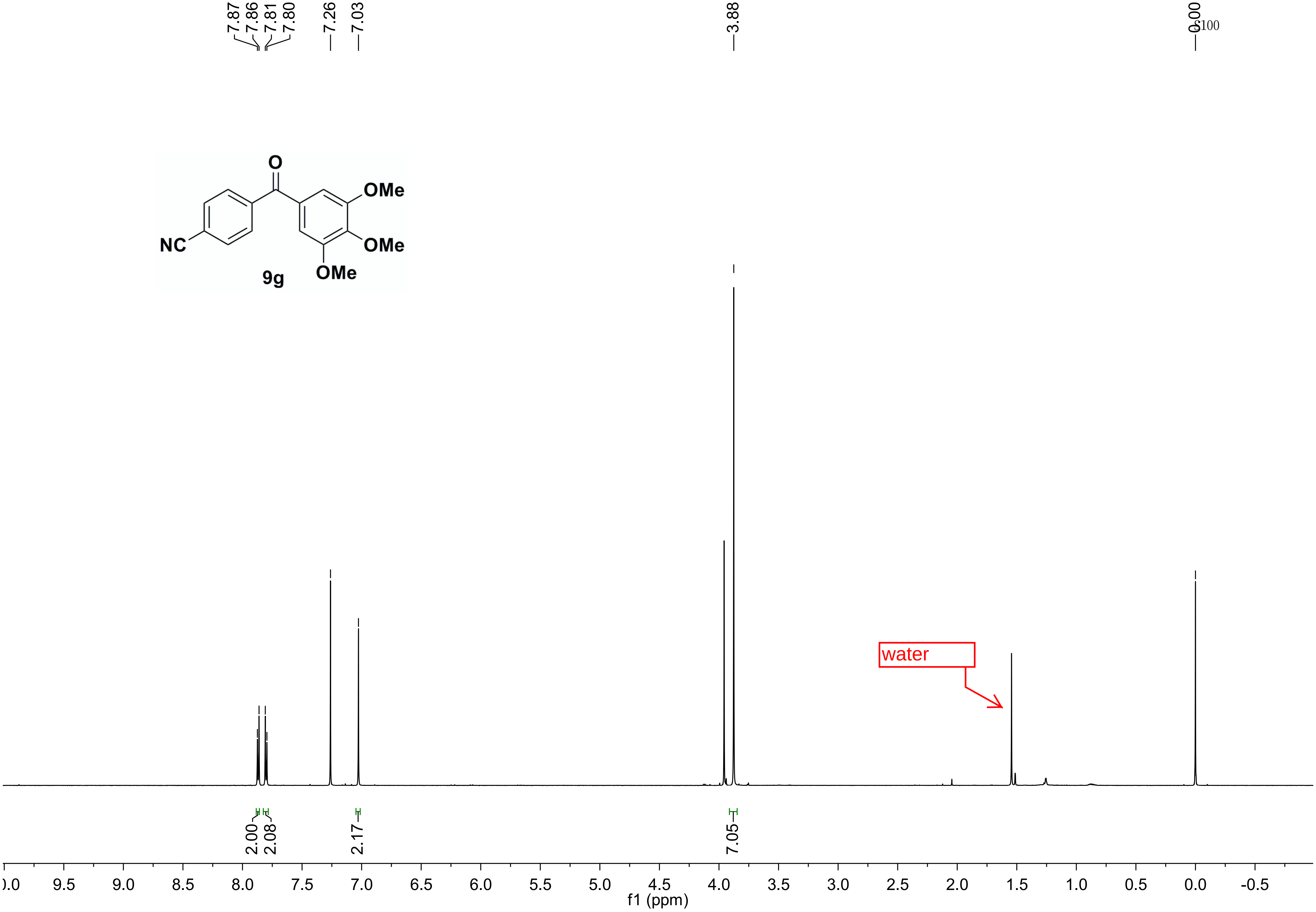
9f
7.83
7.83
7.82
7.81
7.81
7.81
7.26
7.19
7.17
7.16
1.55
−0.00
water
4.00
4.02
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−
f1 (ppm)

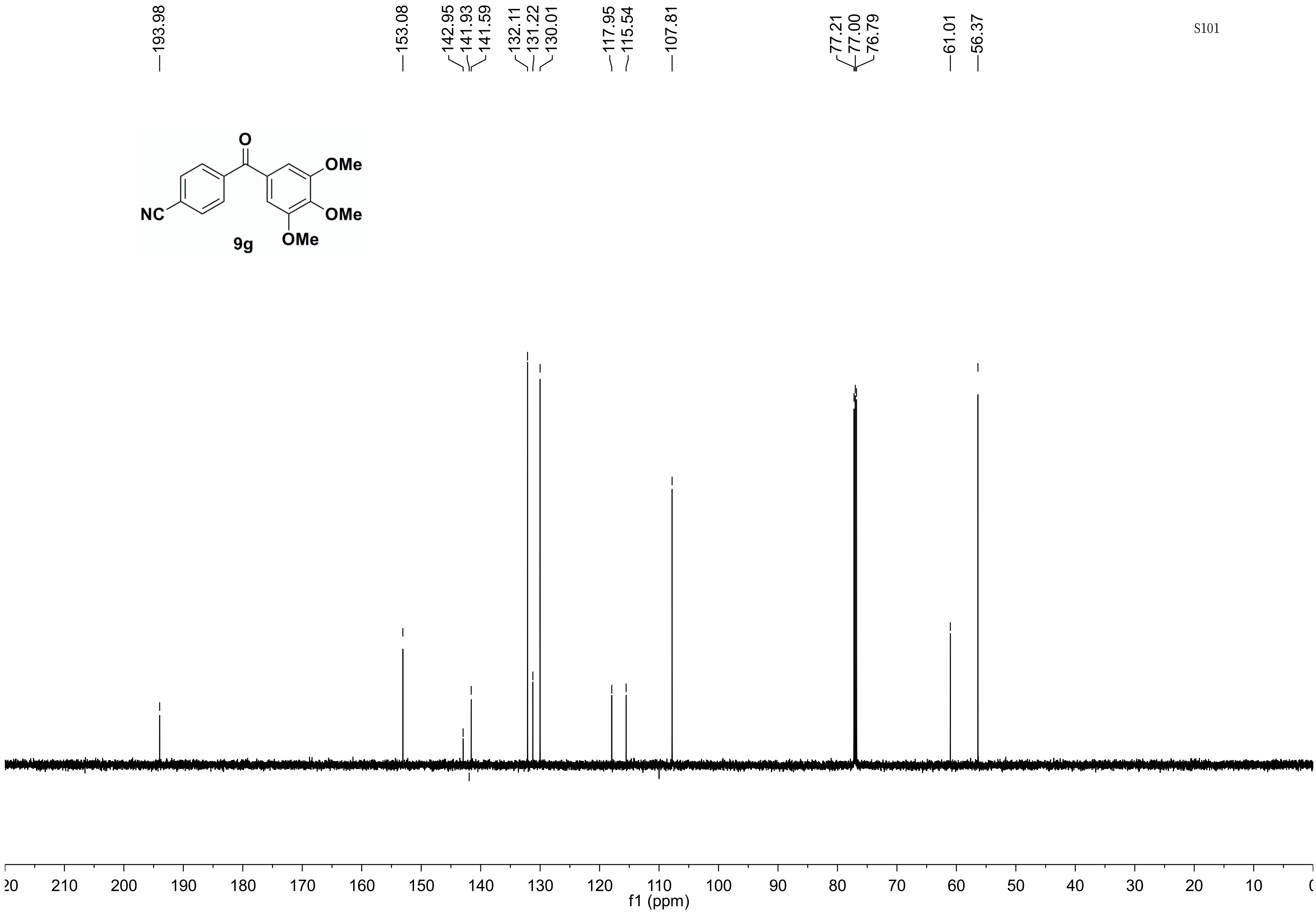


9f


-106.043
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
−230
f1 (ppm)

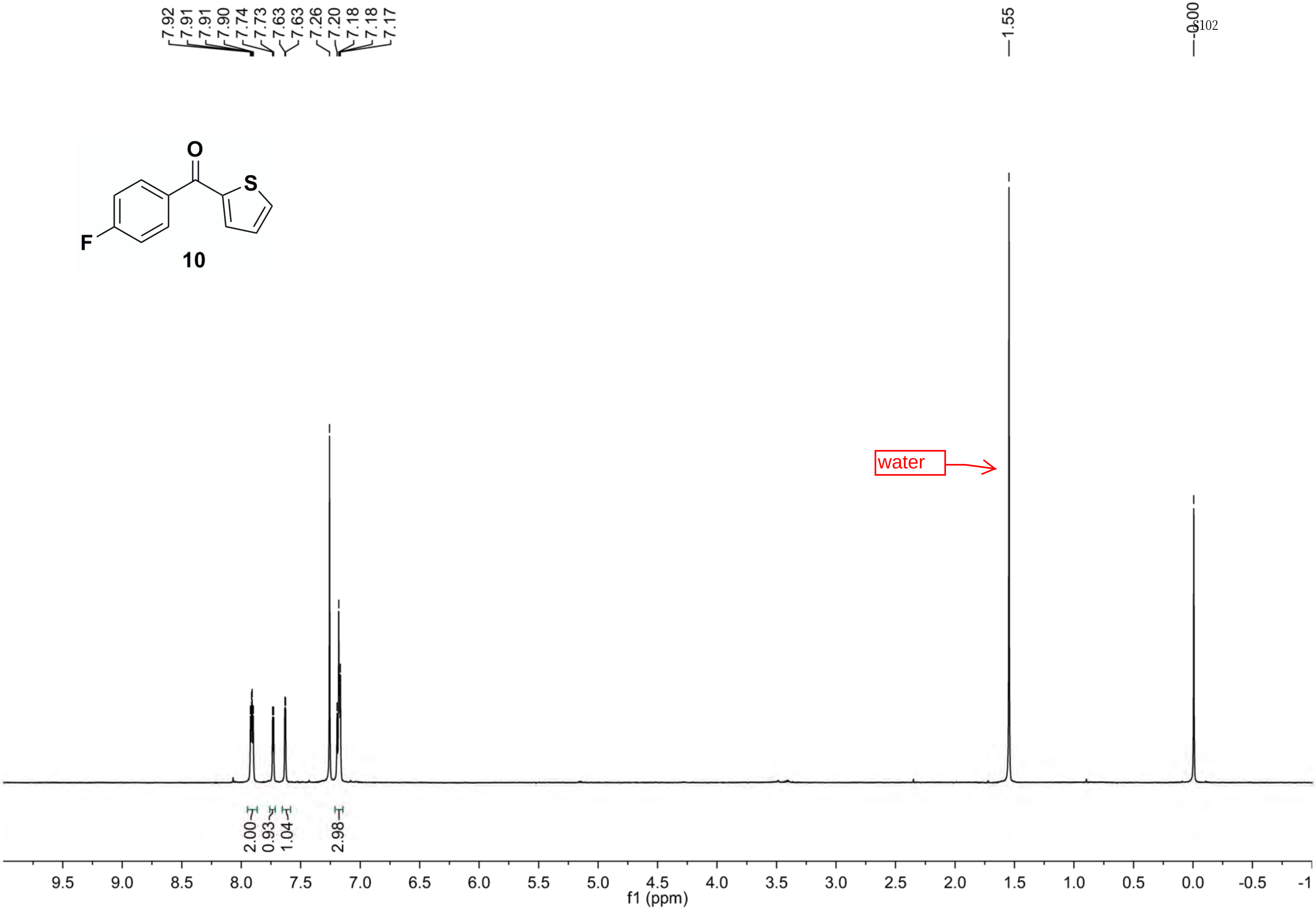

193.75
166.21
164.53
133.70
133.68
132.49
132.43
115.60
115.46
77.20
76.98
76.77
O
F
F
9f
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.87
7.86
7.81
7.80
7.26
7.03
3.88
0.00
O
OMe
OMe
OMe
NC
9g
water
2.00
2.08
2.17
7.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

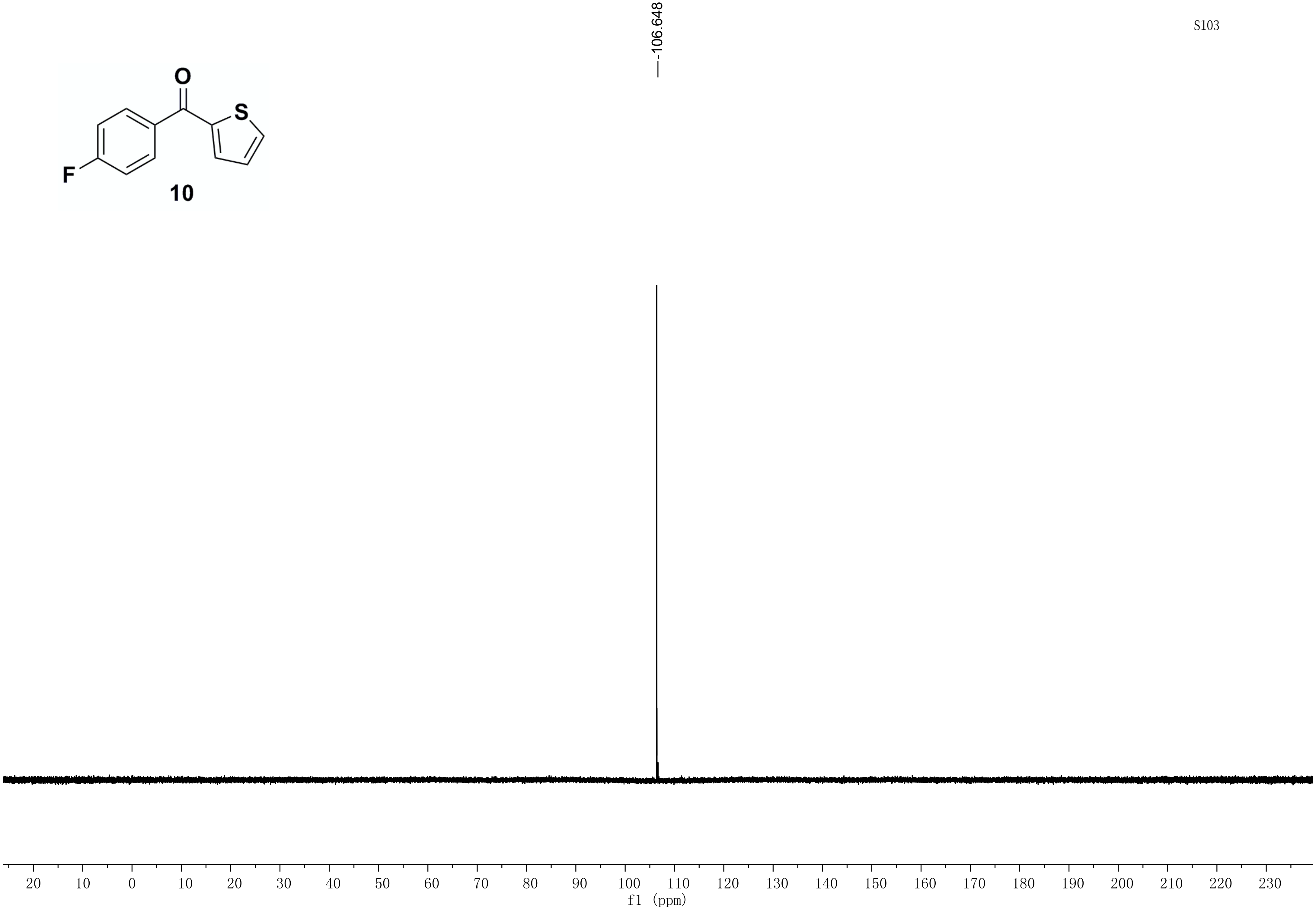


9g

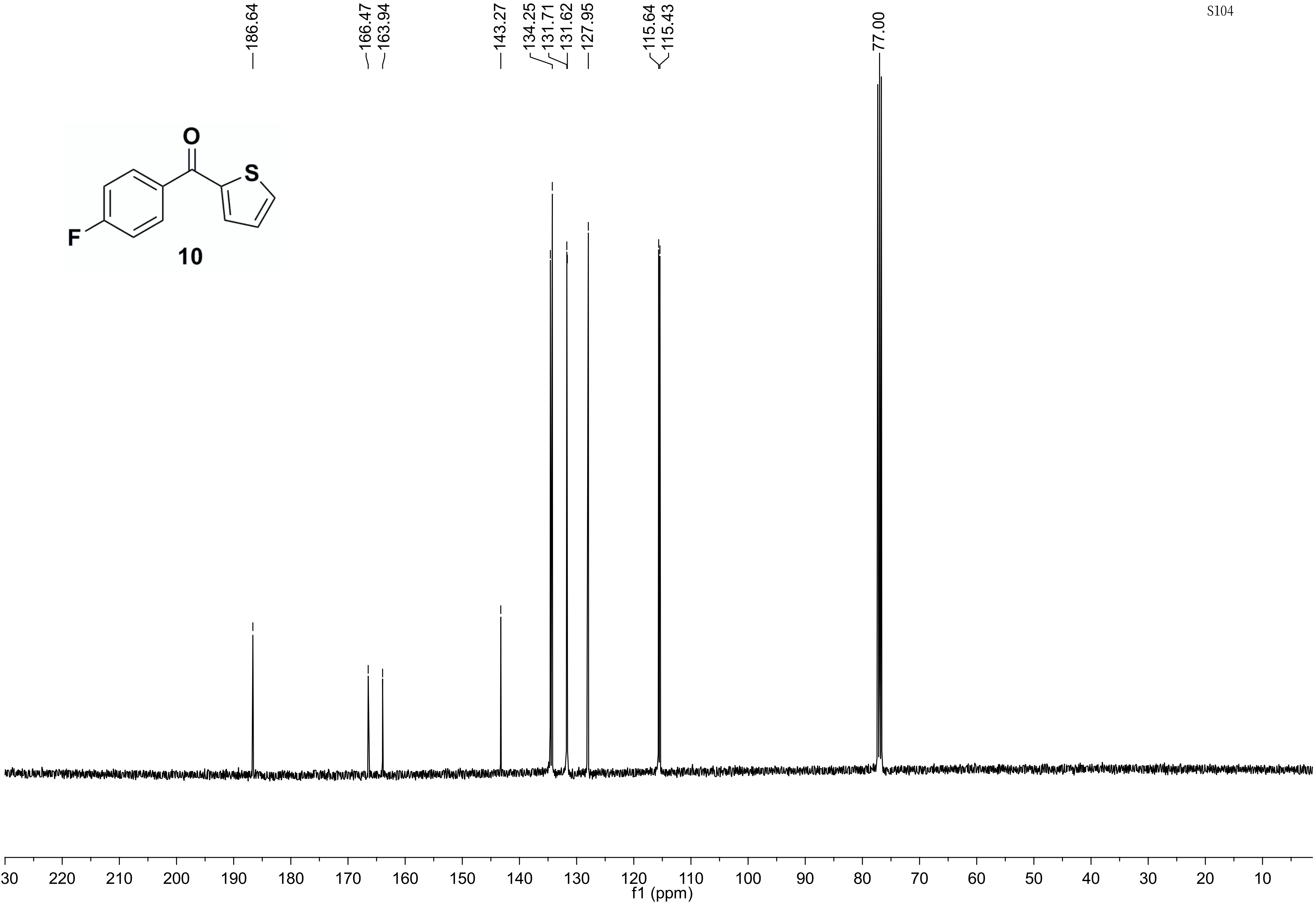
193.98
153.08
142.95
141.93
141.59
132.11
131.22
130.01
117.95
115.54
107.81
77.21
77.00
76.79
61.01
56.37
O
OMe
OMe
OMe
NC
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.92
7.91
7.91
7.90
7.74
7.73
7.63
7.63
7.26
7.20
7.18
7.18
7.17
1.55
0.00
O
S
F
water
2.00
0.93
1.04
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

10


-106.648
O
S
F
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
−230
f1 (ppm)

10


186.64
166.47
163.94
143.27
134.25
131.71
131.62
127.95
115.64
115.43
77.00
O
S
F
10
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)