Supporting Information

Wavelength-Regulated Stereodivergent Synthesis of (*Z*)- and (*E*)-1,4-Enediones from Phosphonium Ylides

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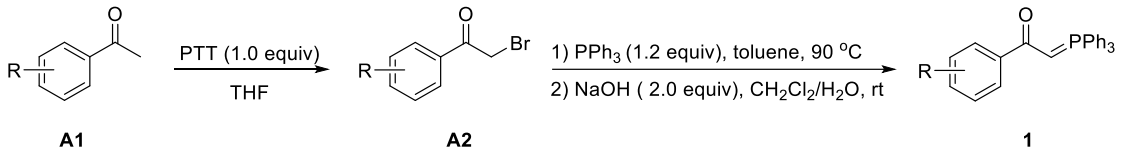
1. General Information

The phosphorus ylides used were prepared according to the reported literature.[1] CH_3CN, EtOAc and DCE were extra dry solvent purchased from chemical energy. If no special indicated, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out in open air. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated; chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^1H spectrum as 0.00 ppm or $CHCl_3$ resonance in $CDCl_3$ as 7.26 ppm, $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm, and DMSO-d_6 resonance in the ^1H spectrum as 2.50 ppm and ^{13}C spectrum as 39.52 ppm. Coupling constants are reported in Hz with multiplicities denoted as br (broad), s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). HRMS were performed on Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. The UV-vis spectra were recorded using a HITACHI F-4500 Fluorescence Spectrometer. Electron paramagnetic resonance (EPR) spectra were recorded on a Bruker EMXplus-9.5/12 spectrometer.

2. General Procedure for Preparation of 1.



Following a literature procedure:[1a] to a solution of **A1** (20.0 mmol, 1.0 equiv.) in THF (50 mL) was added PTT (trimethyl phenylammonium perbromide, 7.50 g, 20 mmol, 1.0 equiv.). The resulting mixture was stirred at room temperature for 4.0 h. Then, filter the reaction mixture, concentrate the filtrate and dissolve it with dichloromethane, wash with distilled water (3×60 mL), saturated brine (3×60 mL), dry with anhydrous magnesium sulfate, concentrate under reduced pressure, and pass through silica gel flash column chromatography to give the product **A2**.

Next, stabilized phosphonium ylides were prepared according to known procedures.[1b,1c] A mixture of **A2** (10.0 mmol, 1.0 equiv) and triphenylphospine (10.0 mmol, 1.0 equiv.) was stirred at room temperature in toluene for 12 h under Ar atmosphere. Upon completion of the reaction, the white solid was collected by vacuum filtration and the filter cake was washed with toluene. The phosphonium salt was added to a one liter separatory funnel and dissolved in CH_2Cl_2 and 1M NaOH was added and shaken vigorously with adequate venting. The layers were separated and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated to yield the target compound **1** as solid.

3. General Procedure for Synthesis of 2 and 3 from Phosphorus Ylides (Procedure A)

To a Schlenk tube containing a stirring bar was added methylene blue ([MB], 0.02 mmol, 10 mol%) and phosphorous ylide **1** (0.20 mmol, 1.0 equiv). Then, 4.0 mL EtOAc or DCE was added to the reaction tube via syringe in air condition. The reaction mixture was stirred for 12 h at Wattecs Parallel Light Reactor (Blue (445 nm–450 nm) or Green LED (515 nm–520 nm) Light source, 10 W every position) at ambient temperature (the temperature range from 28 ^{o}C to 32 ^{o}C). A coolant circulating pump is equipped with the Parallel Light Reactor to keep the temperature constant. Finally, the solvent was removed in vacuum and the residue was purified by rapid column chromatography on silica gel to afford the compound **2** or **3.**

Wattecs Parallel Light Reactor equipped with a coolant circulating pump (Blue or Green LED Light source, 10 W every position)

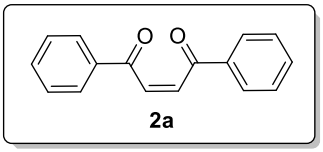
4. General Procedure for the synthesis of alkene from Phosphonium Salts (Procedure B)

To a Schlenk tube equipped with a rubber septum and magnetic stir bar was charged base (Sodium hydride (60% stabilized in mineral oil) or t-BuOLi) (2 equiv) and Phosphonium salt (0.2 mmol, 1 equiv). 4.0 mL EtOAc or DCE was then added to the reaction tube via syringe. Then, left the solution stirred for about 30 minutes. Subsequently, methylene blue (10 mol%) was added. A small needle was inserted through the septum to maintain oxygen level inside the vial. The reaction mixture was stirred under blue

or Green LED irradiation for 12 h at ambient temperature (the temperature range from 28 ^{o}C to 32 ^{o}C). A coolant circulating pump is equipped with the Parallel Light Reactor to keep the temperature constant. Finally, the solvent was removed in vacuum and the residue was purified by rapid column chromatography on silica gel to afford the corresponding alkenes**.**

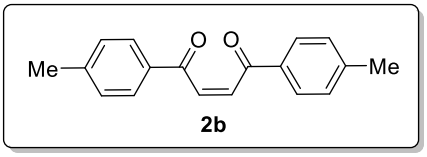
5. Characterization Data for Products

(Z)-1,4-diphenylbut-2-ene-1,4-dione **2a**[2]



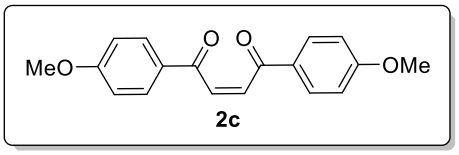
According to the general procedure A, **2a** (white solid, 21.9 mg, mp: 125–127 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 4H), 7.56 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 7.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4 (2C), 136.1 (2C), 135.6 (2C), 133.5 (2C), 128.7 (4C), 128.6 (4C); MS: *m/z*: $[M]^+$, 236.0.

(Z)-1,4-di-tolylbut-2-ene-1,4-dione **2b**[3]



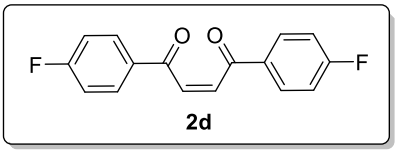
According to the general procedure A, **2b** (white solid, 25.4 mg, mp: 93–95 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 96% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.81 (d, *J* = 8.0 Hz, 4H), 7.36 (s, 2H), 7.32 (d, *J* = 8.0 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.9 (2C),144.1 (2C), 135.9 (2C), 133.4 (2C), 129.4 (4C), 128.5 (4C), 21.2 (2C); MS: *m/z*: $[M]^+$, 264.0.

(Z)-1,4-bis(4-methoxyphenyl)but-2-ene-1,4-dione **2c**[3]



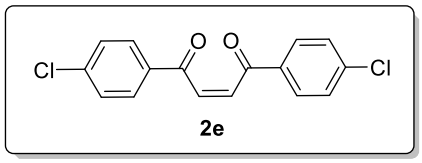
According to the general procedure A, **2c** (white solid, 28.2 mg, mp: 114–116 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 5:1) in 95% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.89 (d, *J* = 7.2 Hz, 4H), 7.31 (s, 2H), 7.04 (d, *J* = 7.2 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.8 (2C), 163.4 (2C), 135.5 (2C), 130.7 (4C), 128.9 (2C), 114.1 (2C), 55.6 (2C); MS: *m/z*: $[M]^+$, 296.0.

(Z)-1,4-bis(4-fluorophenyl)but-2-ene-1,4-dione **2d**[4]



According to the general procedure A, **2d** (white solid, 25.9 mg, mp: 117–119 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.94 (m, 4H), 7.16–7.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7 (2C), 166.0 (d, $^{1}J_{C\text{-}F}$ = 254.4 Hz, 2C), 135.4 (2C), 132.5 (2C), 131.3 (d, $^{3}J_{C\text{-}F}$ = 9.3 Hz, 4C), 115.9 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz, 4C); ^{19}F NMR (376 MHz, $CDCl_3$): δ -103.854; MS: *m/z*: $[M]^+$, 272.0.

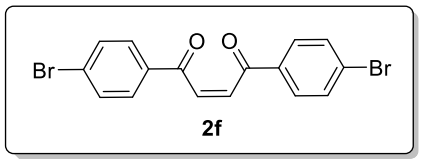
(Z)-1,4-bis(4-chlorophenyl)but-2-ene-1,4-dione **2e**[4]



2e

According to the general procedure A, **2e** (white solid, 27.2 mg, mp: 100–102 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 4H), 7.44 (d, *J* = 8.4 Hz, 4H), 7.13 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0 (2C), 140.2 (2C), 135.5 (2C), 134.4 (2C), 130.0 (4C), 129.2 (4C); MS: *m/z*: $[M]^+$, 303.9.

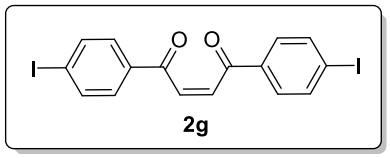
(*Z*)-1,4-bis(4-bromophenyl)but-2-ene-1,4-dione **2f**[5]



2f

According to the general procedure A, **2f** (white solid, 36.4 mg, mp: 180–182 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 9:1) in 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 4H), 7.60 (d, *J* = 8.4 Hz, 4H), 7.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.3 (2C), 135.5 (2C), 134.7 (2C), 132.1 (4C), 130.0 (4C), 129.0 (2C); MS: *m/z*: $[M]^+$, 391.9.

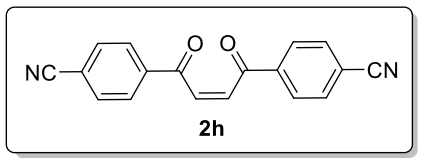
(Z)-1,4-bis(4-iodophenyl)but-2-ene-1,4-dione **2g**



2g

According to the general procedure A, **2g** (white solid, 34.7 mg, mp: 140–142 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 6:1) in 71% yield. The structure of **2g** was unambiguously confirmed by X-ray crystallography (see figure S1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, *J* = 8.4 Hz, 4H), 7.66 (d, *J* = 8.4 Hz, 4H), 7.39 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.9 (2C), 137.9 (4C), 136.0 (2C), 135.0 (2C), 130.0 (4C), 102.4 (2C); MS: *m/z*: $[M]^+$, 487.8.

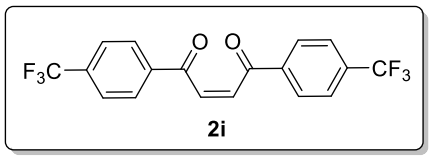
(Z)-1,4-bis(4-cyanophenyl)but-2-ene-1,4-dione **2h**



2h

According to the general procedure A, **2h** (white solid, 24.7 mg, mp: 175–177 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 2:1) in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 4H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7 (2C), 138.7 (2C), 135.8 (2C), 132.7 (4C), 128.9 (4C), 117.7 (2C), 117.0 (2C); HRMS (ESI): calculated for $[M+H]^+$ ($C_{18}H_{11}N_2O_2^+$) requires *m/z*: 287.0815, found *m/z*: 287.0821.

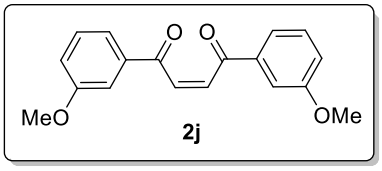
(Z)-1,4-bis(4-(trifluoromethyl)phenyl)but-2-ene-1,4-dione **2i**[6]



2i

According to the general procedure A, **2i** (white solid, 35.4 mg, mp: 175–177 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 95% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.08 (d, *J* = 8.0 Hz, 4H), 7.85 (d, *J* = 8.0 Hz, 4H), 7.50 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 191.9 (2C), 138.7 (2C), 136.5 (2C), 133.0 (q, $^{2}J_{C\text{-}F}$ = 31.7 Hz, 2C), 125.9 (4C), 125.9 (4C), 123.7 (q, $^{1}J_{C\text{-}F}$ = 271.1 Hz, 2C); ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -61.74; MS: *m/z*: $[M]^+$, 372.0.

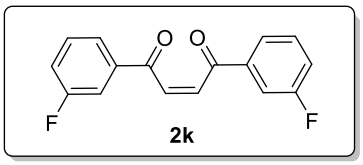
(Z)-1,4-bis(3-methoxyphenyl)but-2-ene-1,4-dione **2j**[3]



2j

According to the general procedure A, **2j** (white solid, 27.4 mg, mp: 63–65 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 99% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.52 (d, *J* = 7.6 Hz, 2H), 7.46–7.40 (m, 6H), 7.23–7.21 (m, 2H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 192.1 (2C), 159.5 (2C), 137.2 (2C), 136.2 (2C), 130.1 (2C), 121.1 (2C), 119.8 (2C), 112.5 (2C), 55.3 (2C); MS: *m/z*: $[M]^+$, 296.0.

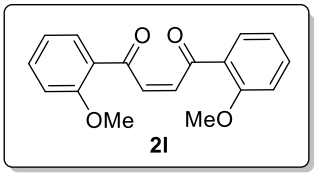
(Z)-1,4-bis(3-fluorophenyl)but-2-ene-1,4-dione **2k**[3]



2k

According to the general procedure A, **2k** (white solid, 27.0 mg, mp: 85–87 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 99% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.71–7.68 (m, 2H), 7.61–7.45 (m, 6H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 191.4 (2C), 162.3 (d, $^{1}J_{C\text{-}F}$ = 244.1 Hz, 2C), 137.9 (2C), 136.2 (2C), 131.2 (d, $^{3}J_{C\text{-}F}$ = 7.5 Hz, 2C), 124.7 (2C), 120.7 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz, 2C), 114.7 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz, 2C); ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -111.93; MS: *m/z*: $[M]^+$, 272.0.

(Z)-1,4-bis(2-methoxyphenyl)but-2-ene-1,4-dione **2l**

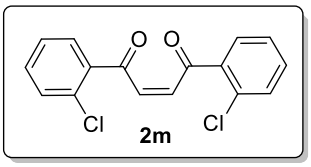


2l

According to the general procedure A, **2l** (white solid, 29.0 mg, mp: 70–72 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 6:1) in 98% yield.^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.57–7.52 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.03–6.95 (m, 4H), 3.83 (s, 6H); ^{13}C NMR (400 MHz, DMSO-*d*$_6$) δ 192.6 (2C), 158.7 (2C), 136.2 (2C), 134.3 (2C), 130.1 (2C), 126.6 (2C), 120.5 (2C), 112.6

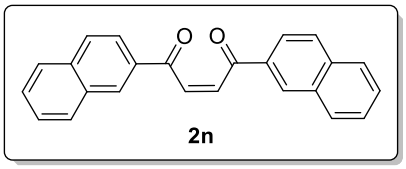
(2C), 55.8 (2C); HRMS (ESI): calculated for $[M+H]^+$ ($C_{18}H_{17}O_4^+$) requires *m/z*: 297.1121, found *m/z*: 297.1125.

(Z)-1,4-bis(2-chlorophenyl)but-2-ene-1,4-dione **2m**[7]



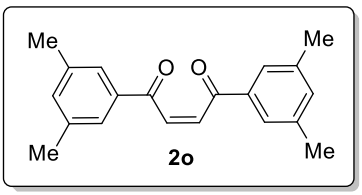
According to the general procedure A, **2m** (white solid, 30.2 mg, mp: 85–87 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 99% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.57–7.51 (m, 4H), 7.46–7.42 (m, 2H), 7.18 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 192.6 (2C), 137.0 (2C), 135.8 (2C), 133.4 (2C), 131.2 (2C), 131.0 (2C), 130.7 (2C), 127.3 (2C); MS: *m/z*: $[M]^+$, 303.9.

(Z)-1,4-di(naphthalen-2-yl)but-2-ene-1,4-dione **2n**



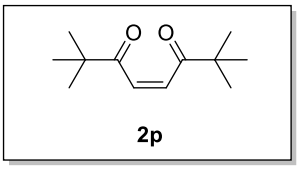
According to the general procedure A, **2n** (white solid, 32.3 mg, mp: 198–199 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 4:1) in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 2H), 8.01–7.99 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.87 (t, *J* = 8.0 Hz, 4H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4 (2C), 135.8 (2C), 135.7 (2C), 133.6 (2C), 132.5 (2C), 130.7 (2C), 129.6 (2C), 128.7 (2C), 128.7 (2C), 127.8 (2C), 126.8 (2C), 123.9 (2C); HRMS (ESI): calculated for $[M+H]^+$ ($C_{24}H_{17}O_2^+$) requires *m/z* :337.1223, found *m/z*: 337.1224.

(Z)-1,4-bis(3,5-dimethylphenyl)but-2-ene-1,4-dione **2o**



According to the general procedure A, **2o** (white solid, 28.1 mg, mp: 107–109 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 4H), 7.18 (s, 2H), 7.10 (s, 2H), 2.33 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8 (2C), 138.3 (4C), 136.3 (2C), 135.7 (2C), 135.1 (2C), 126.4 (4C), 21.1 (4C); HRMS (ESI): calculated for $[M+H]^+$ ($C_{20}H_{21}O_2^+$) requires *m/z* 293.1536, found *m/z*: 293.1540.

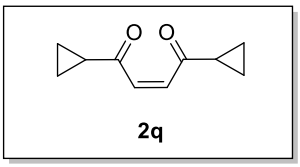
(Z)-2,2,7,7-tetramethyloct-4-ene-3,6-dione **2p**[8]



According to the general procedure A, **2p** (colorless liquid, 16.1 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 2H), 1.19

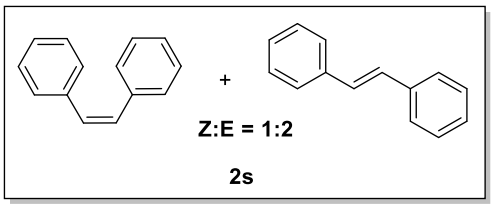
(s, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2 (2C), 134.4 (2C), 43.5 (2C), 26.2 (6C); MS: *m/z*: $[M]^+$, 197.0.

(Z)-1,4-dicyclopropylbut-2-ene-1,4-dione **2q**



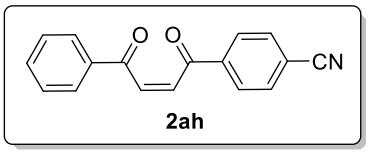
According to the general procedure A, **2q** (Oily liquid, 13.6 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (s, 2H), 2.08–2.02 (m, 2H), 1.18–1.14 (m, 4H), 1.02–0.97 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6 (2C), 135.4 (2C), 21.4 (2C), 11.9 (4C); HRMS (ESI): calculated for $[M+H]^+$ ($C_{10}H_{13}O_2^+$) requires *m/z*: 165.0910, found *m/z*: 165.0911.

(Z)-1,2-diphenylethene and (E)-1,2-diphenylethene **2s**[9]



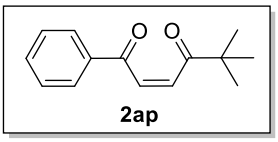
According to the general procedure B, NaH was selected as the base, **2s** (a mixture of (*Z*)-1,2-diphenylethene and (*E*)-1,2-diphenylethene, 14.4 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 200:1) in 80% yield, *Z:E* = 1:2. (Z)-**2s**: ^{1}H NMR (400 MHz, CDCl3) δ 7.25-7.17 (m, 10H), 6.59 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (2C), 130.2 (2C), 128.9 (4C), 128.2 (4C), 127.1 (2C); (E)-**2s**: ^{1}H NMR (400 MHz, CDCl3) δ 7.56 (d, *J* = 7.6 Hz, 4H), 7.40 (t, *J* = 7.6 Hz, 4H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.15 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3 (2C), 128.7 (2C), 128.7 (4C), 127.6 (2C), 126.5 (4C). MS: *m/z*: $[M]^+$, 180.2.

(Z)-4-(4-oxo-4-phenylbut-2-enoyl)benzonitrile **2ah**



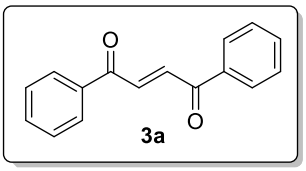
According to the general procedure A, **1a** (0.1 mmol) and **1h** (0.1 mmol) were added to the reaction tube in a ratio of 1:1. **2ah** (white solid, 16.7 mg, mp: 90–92 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 64% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.56–7.52 (m, 3H), 7.41 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 192.5, 191.7, 138.9, 136.9, 135.6 (2C), 133.8, 132.9 (2C), 128.9 (2C), 128.8 (2C), 128.5 (2C), 118.0, 115.4; HRMS (ESI): calculated for $[M+H]^+$ ($C_{17}H_{12}NO_2^+$) requires *m/z*: 262.0863, found *m/z*: 262.0865.

(Z)-5,5-dimethyl-1-phenylhex-2-ene-1,4-dione **2ap**[10]



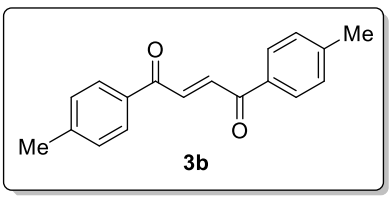
According to the general procedure A, **1a** (0.1 mmol) and **1p** (0.1 mmol) were added to the reaction tube in a ratio of 1:1. **2ap** (yellow 1iquid, 11.5 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.90 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 6.89–6.81 (m, 2H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 205.9, 137.8, 135.9, 133.4, 132.2, 128.6 (2C), 128.4 (2C), 43.3, 26.0 (3C); MS: *m/z*: $[M]^+$, 216.0

(E)-1,4-diphenylbut-2-ene-1,4-dione **3a**[11]



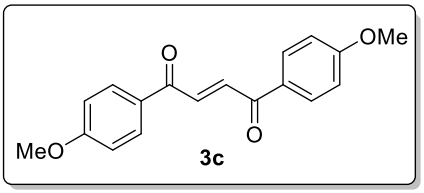
According to the general procedure A, **3a** (yellow solid, 22.4 mg, mp: 109–111 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 95% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.08 (d, *J* = 7.6 Hz, 4H), 7.92 (s, 2H), 7.72 (t, *J* = 6.8 Hz, 2H), 7.60 (t, *J* = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 190.0 (2C), 136.4 (2C), 135.3 (2C), 134.0 (2C), 129.0 (4C), 128.8 (4C); MS: *m/z*: $[M]^+$, 236.0.

(E)-1,4-di-p-tolylbut-2-ene-1,4-dione **3b**[12]



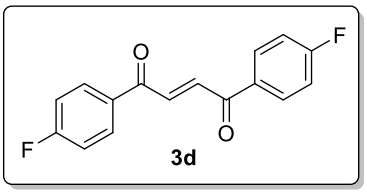
According to the general procedure A, **3b** (yellow solid, 24.1 mg, mp: 147–149 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.97 (d, *J* = 7.6 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 2.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4 (2C), 144.9 (2C), 134.9 (2C), 134.5 (2C), 129.6 (4C), 129.0 (4C), 21.7 (2C); MS: *m/z*: $[M]^+$, 264.0.

(E)-1,4-bis(4-methoxyphenyl)but-2-ene-1,4-dione **3c**[11]



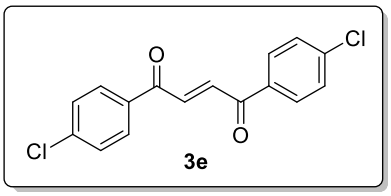
According to the general procedure A, **3c** (yellow solid, 25.5 mg, mp: 147–149 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 86% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.08 (d, *J* = 8.8 Hz, 4H), 7.91 (s, 2H), 7.11 (d, *J* = 8.8 Hz, 4H), 3.87 (s, 6H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 187.9 (2C), 163.8 (2C), 134.8 (2C), 131.3 (4C), 129.5 (2C), 114.3 (4C), 55.7 (2C). MS: *m/z*: $[M]^+$, 296.0.

(E)-1,4-bis(4-fluorophenyl)but-2-ene-1,4-dione **3d**[12]



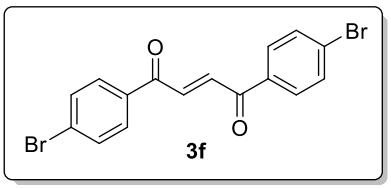
According to the general procedure A, **3d** (yellow solid, 26.4 mg, mp: 117–119 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 97% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.19–8.15 (m, 4H), 7.91 (s, 2H), 7.41 (t, *J* = 8.8 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 188.5 (2C), 165.5 (d, $^{1}J_{C\text{-}F}$ = 251.8 Hz, 2C), 135.2 (2C), 133.1 (2C), 132.0 (d, $^{3}J_{C\text{-}F}$ = 9.6 Hz, 4C), 116.1 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz, 4C); ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -104.43; MS: *m/z*: $[M]^+$, 272.0.

(E)-1,4-bis(4-chlorophenyl)but-2-ene-1,4-dione **3e**[12]



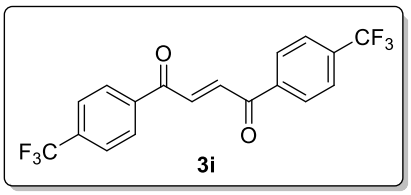
According to the general procedure A, **3e** (yellow solid, 29.0 mg, mp: 170–172 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 95% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.09 (d, *J* = 8.4 Hz, 4H), 7.89 (s, 2H), 7.65 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 189.0 (2C), 139.0 (2C), 135.3 (2C), 135.0 (2C), 130.8 (4C), 129.2 (4C); MS: *m/z*: $[M]^+$, 303.9.

(E)-1,4-bis(4-bromophenyl)but-2-ene-1,4-dione **3f**[11]



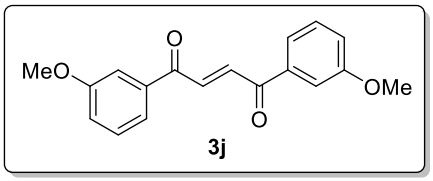
According to the general procedure A, **3f** (yellow solid, 35.3 mg, mp: 270–272 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.93 (d, *J* = 8.8 Hz, 4H), 7.68 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.6 (2C), 135.5 (2C), 134.9 (2C), 132.3 (4C), 130.3 (4C), 129.4 (2C); MS: *m/z*: $[M]^+$, 391.9.

(E)-1,4-bis(4-(trifluoromethyl)phenyl)but-2-ene-1,4-dione **3i**[3]



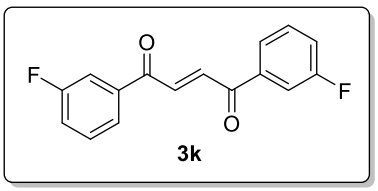
According to the general procedure A with a shorten reaction time of 1.5 h, **3i** (yellow solid, 35.5 mg, mp: 190–192 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 95% yield. ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.27 (d, *J* = 8.0 Hz, 4H), 7.96 (d, *J* = 7.6 Hz, 4H), 7.93 (s, 2H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 189.6 (2C), 139.5 (2C), 135.7 (2C), 133.1 (q, $^{2}J_{C\text{-}F}$ = 31.8 Hz, 2C), 129.7 (4C), 125.9 (q, $^{3}J_{C\text{-}F}$ = 3.3 Hz, 4C), 123.7 (q, $^{1}J_{C\text{-}F}$ = 271.2 Hz, 2C); ^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -61.65; MS: *m/z*: $[M]^+$, 372.0.

(E)-1,4-bis(3-methoxyphenyl)but-2-ene-1,4-dione **3j**[11]



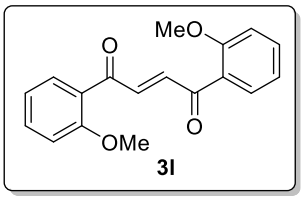
According to the general procedure A, **3j** (yellow solid, 28.7 mg, mp: 66–68 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.57–7.56 (m, 2H), 7.43 (t, *J* = 8.0 Hz, 2H), 7.19–7.16 (m, 2H), 3.88 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6 (2C), 160.1 (2C), 138.3 (2C), 135.2 (2C), 129.8 (2C), 121.6 (2C), 120.6 (2C), 112.8 (2C), 55.5 (2C); MS: *m/z*: $[M]^+$, 296.0.

(E)-1,4-bis(3-fluorophenyl)but-2-ene-1,4-dione **3k**[11]



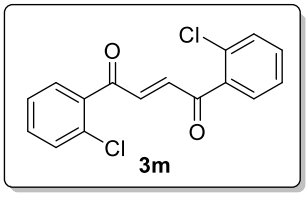
According to the general procedure A, **3k** (yellow solid, 25.9 mg, mp: 75–77 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 95% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.93 (d, *J* = 7. 6 Hz, 2H), 7.90 (s, 2H), 7.85 (d, *J* = 9.6 Hz, 2H), 7.67–7.61 (m, 2H). 7.59–7.56 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 188.9 (2C), 162.3 (d, $^{1}J_{C\text{-}F}$ = 244.3 Hz, 2C), 138.5 (d, $^{3}J_{C\text{-}F}$ = 6.0 Hz, 2C), 135.4 (2C), 131.3 (d, $^{3}J_{C\text{-}F}$ = 7.8 Hz), 125.2 (2C), 120.9 (d, $^{2}J_{C\text{-}F}$ = 21.3 Hz, 2C), 115.2 (d, $^{2}J_{C\text{-}F}$ = 22.4 Hz); ^{19}F NMR (376 MHz, DMSO-d_6): δ -111.74. MS: *m/z*: $[M]^+$, 272.0.

(E)-1,4-bis(2-methoxyphenyl)but-2-ene-1,4-dione **3l**[13]



According to the general procedure A, **3l** (yellow solid, 28.4 mg, mp: 100–102 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 8:1) in 96% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.62–7.57 (m, 4H), 7.45 (s, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 191.8 (2C), 158.4 (2C), 137.4 (2C), 134.3 (2C), 130.0 (2C), 127.3 (2C), 120.7 (2C), 112.6 (2C), 55.9 (2C); MS: *m/z*: $[M]^+$, 296.0.

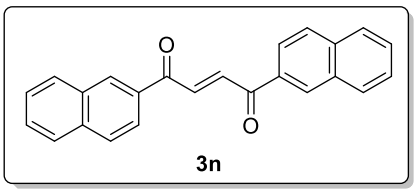
(E)-1,4-bis(2-chlorophenyl)but-2-ene-1,4-dione **3m**[12]



According to the general procedure A, **3m** (yellow solid, 30.2 mg, mp: 75–77 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 99% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.66–7.59 (m, 6H), 7.53–7.48 (m, 2H), 7.18 (s, 2H); ^{13}C NMR (100 MHz,

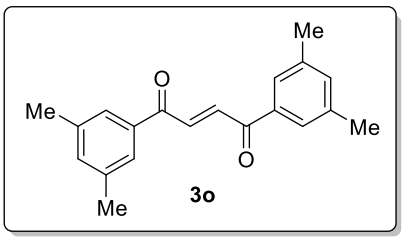
DMSO-d_6) δ 192.5 (2C), 138.3 (2C), 136.8 (2C), 133.1 (2C), 130.4 (2C), 130.4 (2C), 130.1 (2C), 127.6 (2C). MS: *m/z*: $[M]^+$, 303.9.

(E)-1,4-di(naphthalen-2-yl)but-2-ene-1,4-dione **3n**[4]



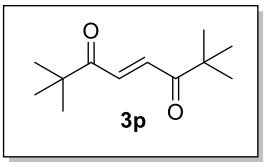
According to the general procedure A, **3n** (yellow solid, 32.0 mg, mp: 190–191 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 4:1) in 95% yield. The structure of **3n** was unambiguously confirmed by X-ray crystallography. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.02–7.92 (m, 6H), 7.68–7.60 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 192.4 (2C), 136.3 (2C), 135.2 (2C), 133.3 (2C), 132.1 (2C), 130.8 (2C), 129.6 (2C), 128.9 (2C), 128.6 (2C), 127.7 (2C), 127.0 (2C), 123.5 (2C). MS: *m/z*: $[M]^+$, 336.0.

(E)-1,4-bis(3,5-dimethylphenyl)but-2-ene-1,4-dione **3o**



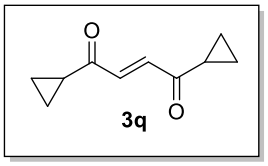
According to the general procedure A, **3o** (yellow solid, 28.9 mg, mp: 170–172 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 99% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.88 (s, 2H), 7.67 (s, 4H), 7.34 (s, 2H), 2.36 (s, 12H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.0 (2C), 138.5 (4C), 136.6 (2C), 135.4 (2C), 135.3 (2C), 126.5 (4C), 20.7 (4C). HRMS (ESI): calculated for $[M+H]^+$ ($C_{20}H_{21}O_2^+$) requires *m/z*: 293.1536, found *m/z*: 293.1541.

(E)-2,2,7,7-tetramethyloct-4-ene-3,6-dione **3p**[8]



According to the general procedure A, **3p** (yellow solid, 17.7 mg, mp: 95–96 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 10:1) in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 1.20 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7 (2C), 133.1 (2C), 43.7 (2C), 25.8 (6C); MS: *m/z*: $[M]^+$, 197.0.

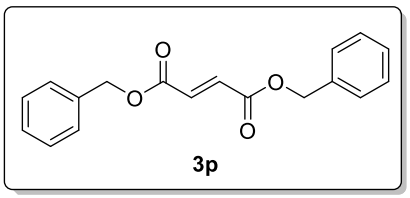
(E)-1,4-dicyclopropylbut-2-ene-1,4-dione **3q**



According to the general procedure A, **3q** (yellow solid, 14.6 mg, mp: 82–83 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 2H), 2.26 –

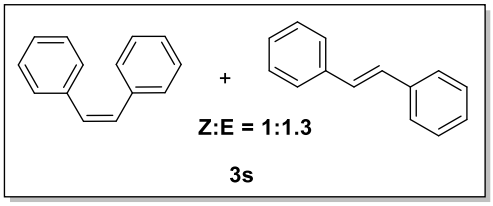
2.22 (m, 2H), 2.20–1.17(m, 4H), 1.07–1.04(m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4 (2C), 136.1 (2C), 20.4 (2C), 12.2 (4C). HRMS (ESI): calculated for $[M+H]^+$ ($C_{10}H_{13}O_2^+$) requires *m/z* 165.0910, found *m/z*: 165.0913.

dibenzyl fumarate **3r**[14]



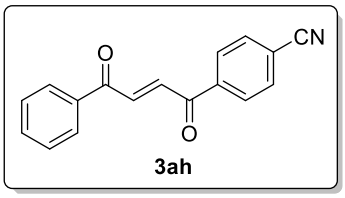
According to the general procedure A, **3r** (yellow solid, 27.3 mg, mp: 62–64 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 20:1) in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (br, 10H), 6.92 (s, 2H), 5.24 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (2C), 135.2 (2C), 133.7 (2C), 128.6 (4C), 128.5 (2C), 128.3 (4C), 67.1 (2C); MS: *m/z*: $[M]^+$, 296.0.

(Z)-1,2-diphenylethene and (E)-1,2-diphenylethene **3s**[9]



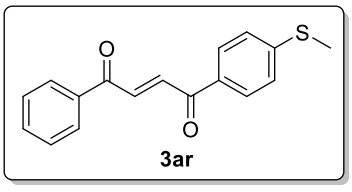
According to the general procedure B, *t*-BuOLi was selected as the base, **3s** (a mixture of (*Z*)-1,2-diphenylethene and (*E*)-1,2-diphenylethene, 13.3 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 200:1) in 74% yield, *Z:E* = 1:1.3. The spectrum of corresponding (Z)-1,2-diphenylethene and (E)-1,2-diphenylethene see (Z)-**2s** and (E)-**2s**.

(E)-4-(4-oxo-4-phenylbut-2-enoyl)benzonitrile **3ah**



Following the general procedure A, **1a** (0.1 mmol) and **1h** (0.1 mmol) were added to the reaction tube in ratio of 1:1. **3ah** (yellow solid, 12.3 mg, mp: 76–78 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 47% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, *J* = 8.4 Hz, 2H), 8.07 (t, *J* = 8.4 Hz, 4H), 7.94 (d, *J* = 15.6 Hz, 1H), 7.87 (d, *J* = 15.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 189.8, 189.5, 139.6, 136.2 (2C), 134.7, 134.0, 132.9 (2C), 129.4 (2C), 129.0 (2C), 128.8 (2C), 118.0, 115.6; HRMS (ESI): calculated for $[M+H]^+$ ($C_{17}H_{12}NO_2^+$) requires *m/z*: 262.0863, found *m/z*: 262.0866.

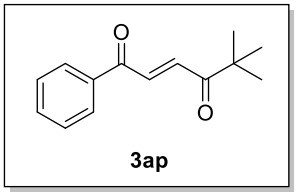
(E)-1-(4-(methylthio)phenyl)-4-phenylbut-2-ene-1,4-dione **3at**



Following the general procedure A, **1a** (0.1 mmol) and **1t** (0.1 mmol) were added to the reaction tube in a ratio of 1:1. **3at** (yellow solid, 22.5

mg, mp: 120–122 °C) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 15:1) in 80% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08 (d, J = 7.2 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H), 7.92 (s, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 190.0, 188.6, 146.9, 136.4, 135.3, 135.0, 134.0, 132.6, 129.3 (2C), 129.0 (2C), 128.8 (2C), 125.1 (2C), 13.9; HRMS (ESI): calculated for $[M+H]^+$ ($C_{17}H_{15}O_2S^+$) requires *m/z*: 283.0787, found *m/z*: 283.0793.

(E)-5,5-dimethyl-1-phenylhex-2-ene-1,4-dione **3ap**[2]



Following the general procedure A, **1a** (0.1 mmol) and **1p** (0.1 mmol) were added to the reaction tube in a ratio of 1:1. **3ap** (yellow liquid, 13.6 mg) was obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 50:1) in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 15.2 Hz, 1H), 7.64– 7.49 (m, 4H), 1.24 (s, 9H). ^{13}C NMR (10 MHz, $CDCl_3$) δ 204.3 (s), 189.9 (s), 137.0 (s), 134.3 (s), 134.0 (s), 133.7 (s), 128.8 (2C), 128.8 (2C), 43.7 (s), 25.8 (3C). MS: *m/z*: $[M]^+$, 216.0.

5. X-ray Crystallography

5.1 Compounds 2g

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **2g** in methanol in a loosely caped vial.

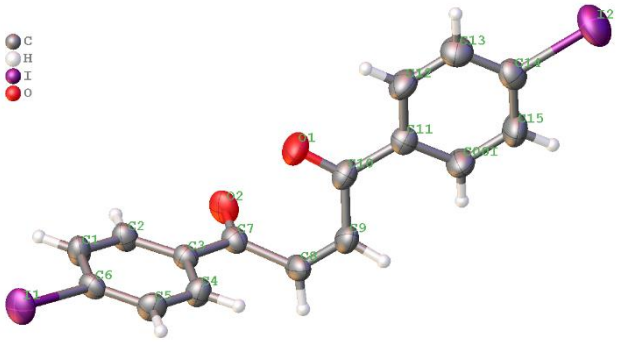


Figure S1. Crystal structure of compound **2g**.

Summary of Data CCDC: 2097346

Compound Name: **2g**

Formula: $C_{16}H_{10}I_2O_2$

Crystal System: monoclinic

Space Group: $P2_1/c$

Unit Cell Parameters: a 14.4263(17) b 5.4210(6) c 20.143(2)

5.2 Compounds 3n

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of **3n** in DCM in a loosely caped vial.

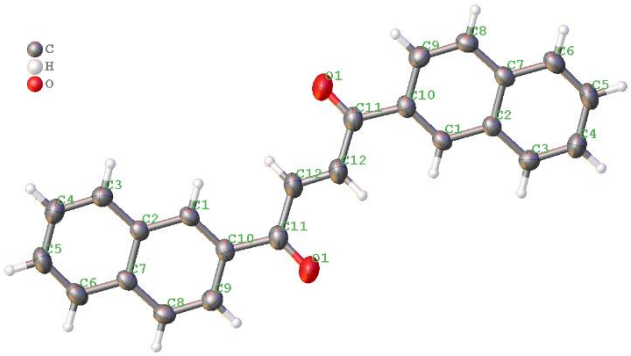


Figure S2. Crystal structure of compound **3n**.

Summary of Data CCDC: 2097344

Compound Name: **3n**

Formula: $C_{24}H_{16}O_2$

Crystal System: monoclinic

Space Group: $P2_1/c$

Unit Cell Parameters: a 7.9088(11) b 5.8824(8) c 18.453(2)

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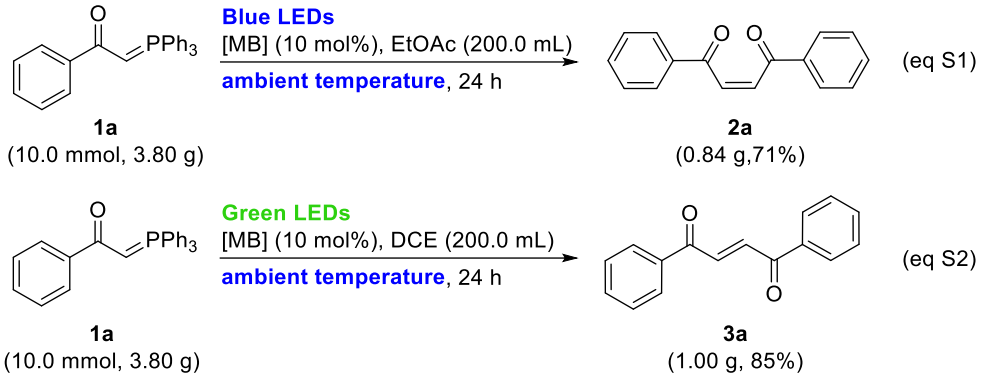
6. Gram-scale Reaction

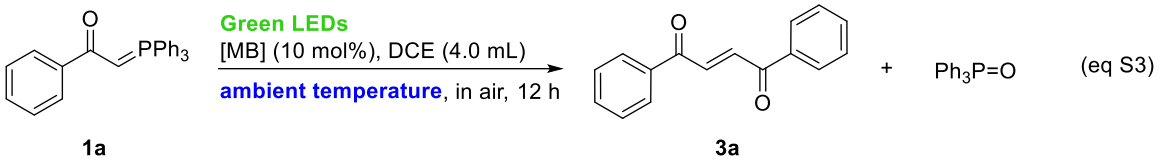


Scheme S1. Gram-scale reactions.

Gram-scale reaction was conducted under standard conditions with 24 hours irradiation: 10.0 mmol of **1a** (3.80 g) and 10 mol% [MB] in 200 mL of EtOAc or DCE, blue LEDs strip or green LEDs strip, at ambient temperature, affording the product **2a** (0.84 g) and **3a** in 71% and 85% isolated yield, respectively (Scheme S1).

7. Mechanistic Studies

7.1 Monitoring the ^{31}P NMR During the Reaction



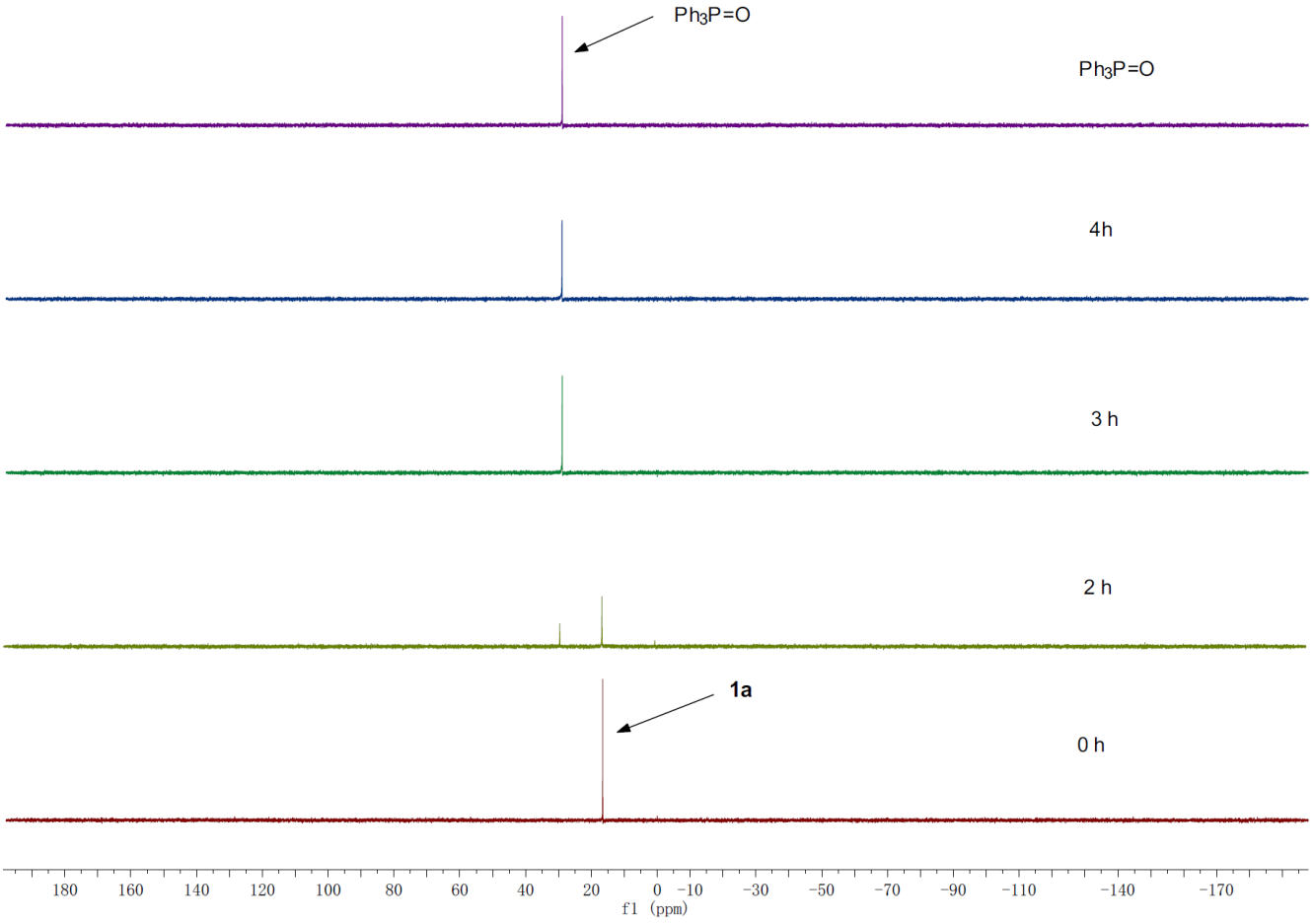
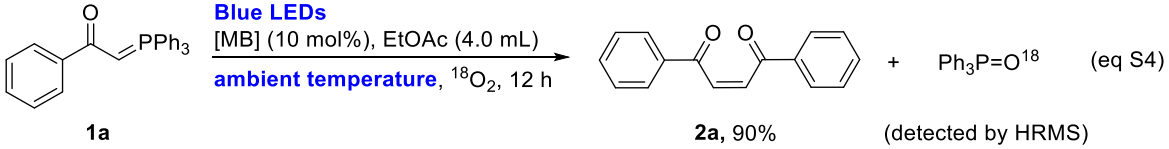


Figure S3. Monitoring of the ^{13}P NMR during the reaction.

7.2 $^{18}O_2$ Labeling Experiments



To a Schlenk tube containing a stirring bar was added [MB] (0.02 mmol, 10 mol%) and **1a** (0.20 mmol, 1.0 equiv). Then, the reaction tube was equipped with a rubber stopper and pumped to a negative pressure. Subsequently, the same amount of $^{18}O_2$ as the volume of the reaction tube was injected via a

needle tube. Finally, 4.0 mL of EtOAc were added to the reaction tube via syringe. The reaction mixture was stirred on Wattecs Parallel Light Reactor for 12 hours. It should be noted that under this kind of operation, part of the O_2 will inevitably enter the reaction tube, resulting in the formation of part of Ph_3PO. 90% yield of **2a** was determined via crude ^1H NMR. $Ph_3P{=}O^{18}$was isolated and determined by HRMS. HRMS (ESI): calculated for $[M+H]^+$ ($Ph_3P{=}O^{18}H^+$) requires *m/z* 281.0976, found *m/z*: 281.0979; calculated for $[M+Na]^+$ ($Ph_3P{=}O^{18}Na^+$) requires *m/z*: 303.0796, found *m/z*: 303.0800 (see figure S4).

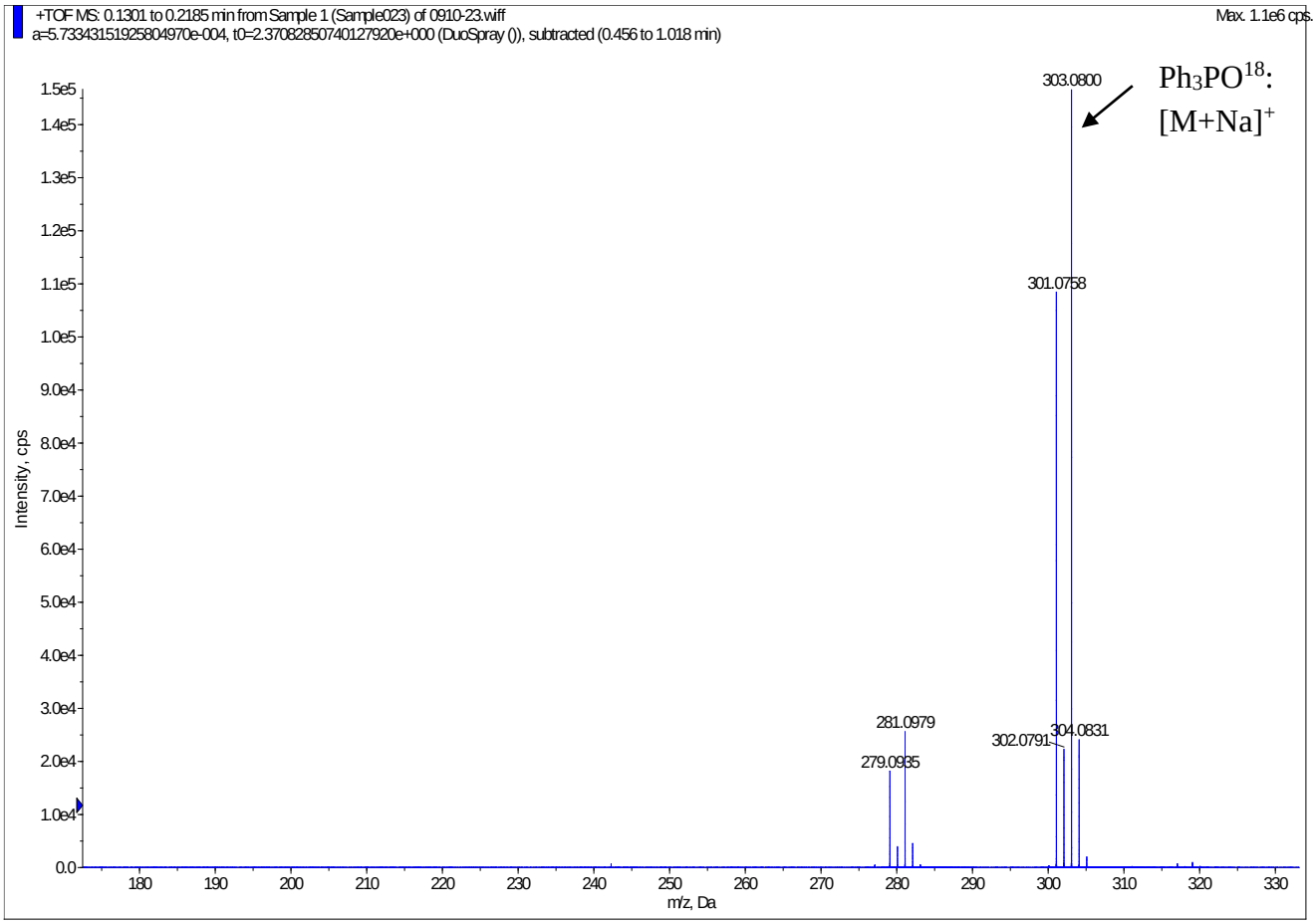
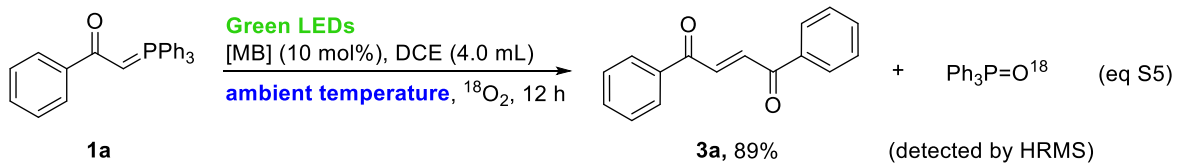


Figure S4. HRMS (ESI-TOF) spectrum of $Ph_3P{=}O^{18}$ in reaction of eq S4.



Following the same procedure as above with 4.0 mL DCE instead, the reaction mixture was stirred on Wattecs Parallel Light Reactor for 12 hours. 89% yield of **3a** was determined via crude ^1H NMR. Ph_3PO^{18} was isolated and determined by HRMS. HRMS (ESI): calculated for $[M+H]^+$ ($Ph_3P{=}O^{18}H^+$)

requires *m/z*: 281.0976, found *m/z*: 281.0979; calculated for $[M+Na]^+$ ($Ph_3P=O^{18}Na^+$) requires *m/z* :303.0796, found *m/z*: 303.0798 (see figure S5).

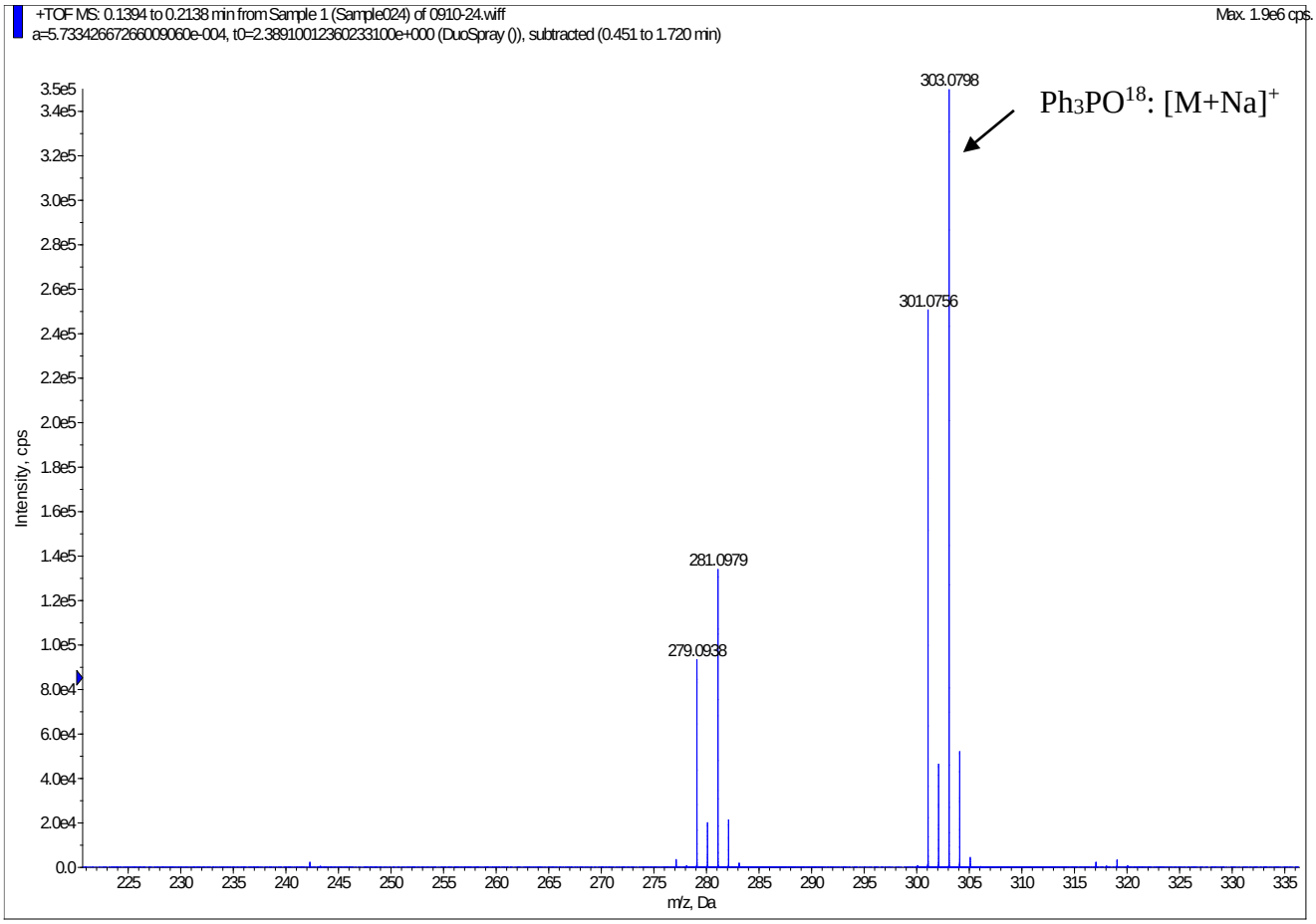


Figure S5. HRMS (ESI-TOF) spectrum of $Ph_3P=O^{18}$ in reaction of eq S5.

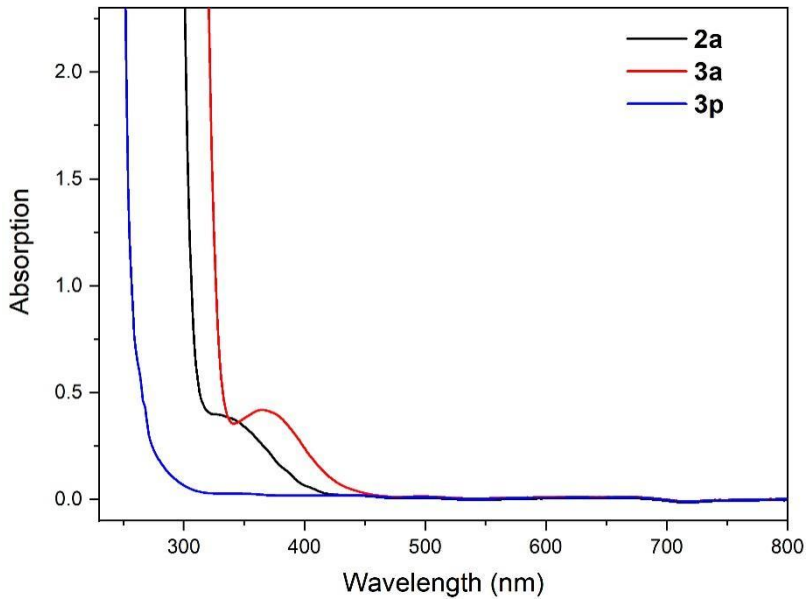


Figure S6. UV-vis spectrum of **2a**, **3a**, **3p** in EtOAc.

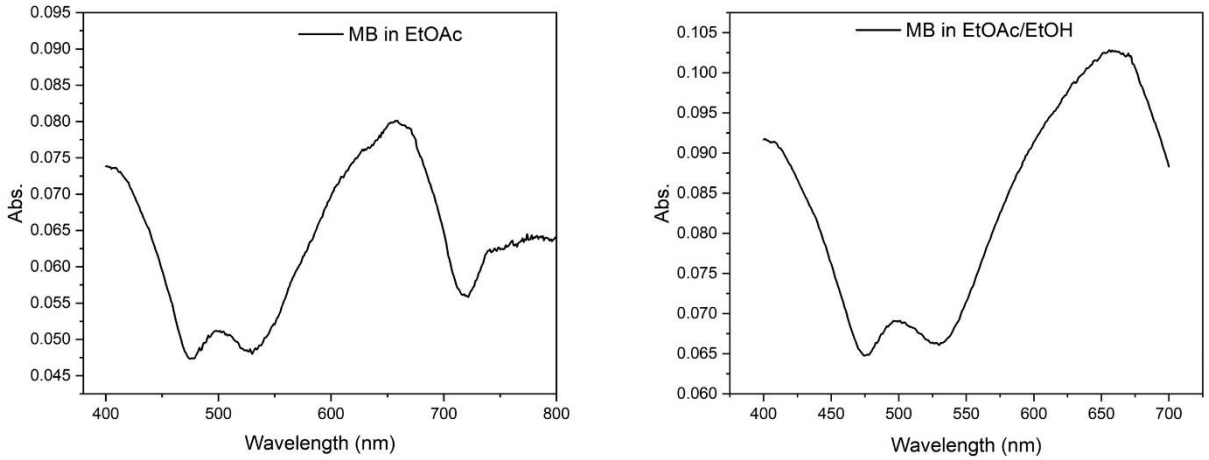
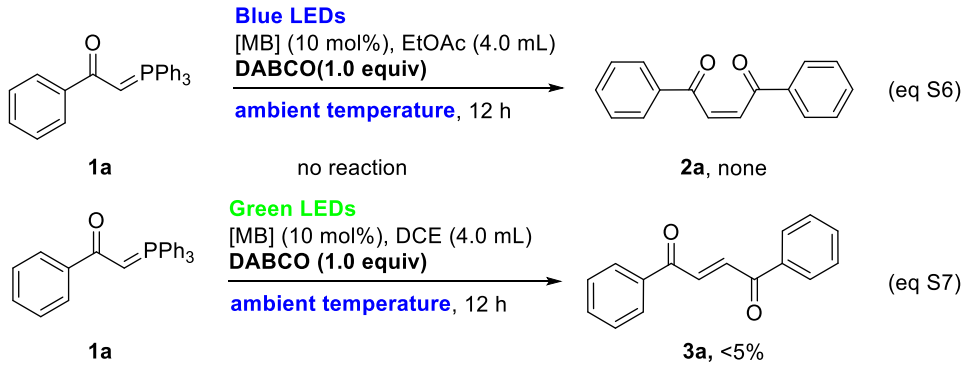


Figure S7. UV-vis spectra of methylene blue in EtOAc and EtOAc/EtOH.

7.3 $^1O_2$ Detection Experiments

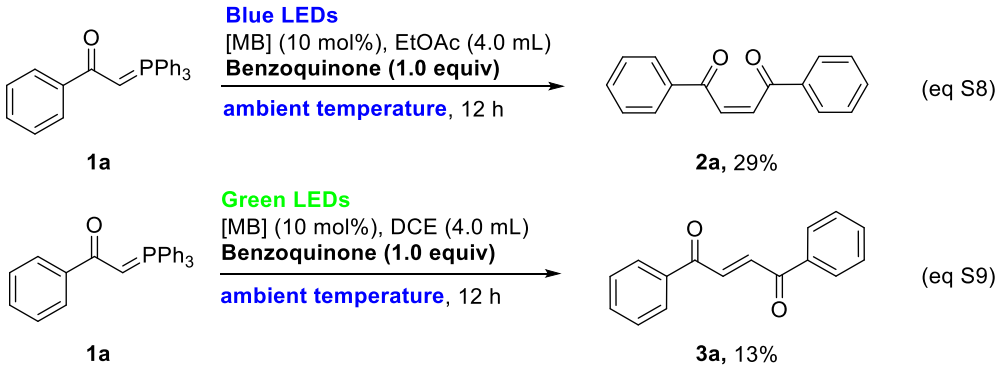


Scheme S2. $^1O_2$ detection experiments.

To a Schlenk tube containing a stirring bar was added [MB] (0.02 mmol, 10 mol%), **1a** (0.20 mmol, 1.0 equiv) and DABCO (0.2 mmol, 1.0 equiv). Then, 4.0 mL of EtOAc or DCE were added to the reaction tube. The reaction mixture was stirred under blue LED (conditions A) or green LED (conditions B) irradiation for 12 hours. These reactions were completely suppressed and no **2a** or trace of **3a** was formed (Scheme S2).

The addition of 1,4-diazabicyclo(2.2.2) octane (DABCO) completely suppressed the reactions, suggesting that $^1O_2$ is involved in the reaction.

7.4 $O_2^{\bullet-}$ Detection Experiments



Scheme S3. $O_2^{\bullet-}$ detection experiments.

To a Schlenk tube containing a stirring bar was added [MB] (0.02 mmol, 10 mol%), **1a** (0.20 mmol, 1.0 equiv) and benzoquinone (0.2 mmol, 1.0 equiv). Then, 4.0 mL of EtOAc or DCE were added to the reaction tube. The reaction mixture was stirred under blue LED (conditions A) or green LED (conditions B) irradiation for 12 hours. The yields of **2a** and **3a** were finally determined as 29% and 13%, respectively, via crude ^1H NMR analysis (eq S8).

Adding benzoquinone to the reactions sharply decreased the yields, suggesting that $O_2^{\bullet-}$ is involved in the reaction.

7.5 EPR Experiments

EPR spectra were obtained using a Bruker EMXplus-9.5/12 spectrometer. A series of experiments were conducted to investigate the active species in the reaction. A common operation of the EPR experiments is taking the solution of the reaction into a small quartz tube, and then analyzed by EPR.

7.5.1 DMPO as Spin Trapping Reagent

a. A Schlenk tube containing a stirring bar, **1a** (0.20 mmol, 1.0 equiv), [MB] (0.02 mmol, 10 mol%), and 4.0 mL of EtOAc was stirred for 15 minutes in air under darkness. The corresponding EPR spectrum of the reaction is showed in figure S8a.

b. A Schlenk tube containing a stirring bar, **1a** (0.20 mmol, 1.0 equiv), [MB] (0.02 mmol, 10 mol%), and 4.0 mL of EtOAc was stirred for 15 minutes under blue LEDs irradiation in air. The corresponding EPR spectrum of the reaction is showed in figure S8b.

c. A Schlenk tube containing a stirring bar, **1a** (0.20 mmol, 1.0 equiv), [MB] (0.02 mmol, 10 mol%), DMPO (5,5-Dimethyl-1-pyrroline N-oxide, 0.1 mmol, 50 mol%), and 4.0 mL of EtOAc was stirred for 15 minutes in air under darkness. The corresponding EPR spectrum of the reaction is showed in figure S8c.

d. A Schlenk tube containing a stirring bar, **1a** (0.20 mmol, 1.0 equiv), [MB] (0.02 mmol, 10 mol%), DMPO (5,5-Dimethyl-1-pyrroline N-oxide, 0.1 mmol, 50 mol%), and 4.0 mL of EtOAc was stirred for 15 minutes under blue LEDs irradiation in air. The corresponding EPR spectrum of the reaction is showed in figure S8c.

Notably, a strong EPR signal is generated in the conditions, suggesting that a radical is generated (g = 2.0057, hyperfine splitting constants a^N = 15.89 G, a^H = 26.26 G). These signals were assigned as a spin trapped adducts of DMPO-•C after simulation (see figure S8c).[15]

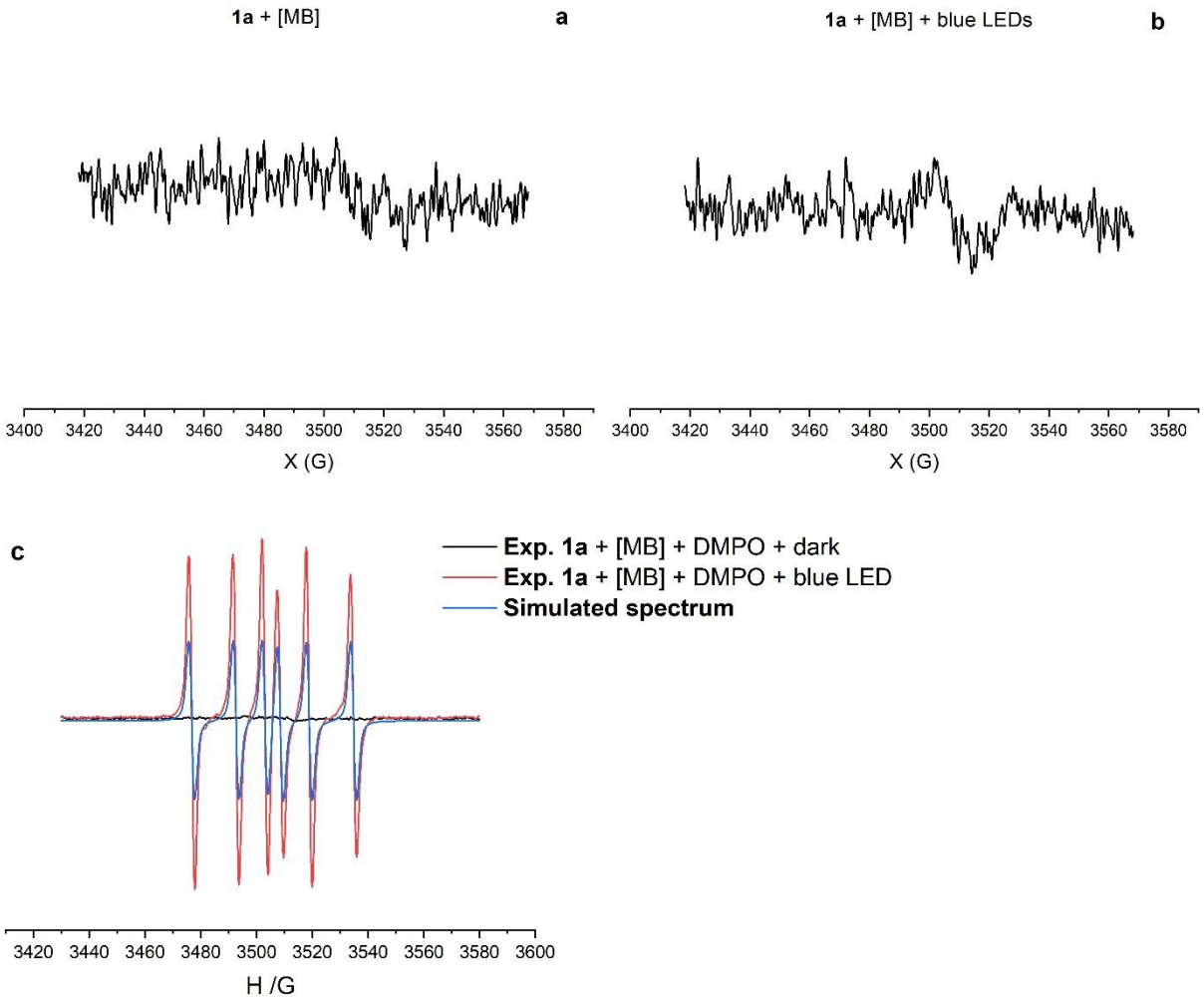


Figure S8. Electron paramagnetic resonance (EPR) spectra.

7.5.2 PBN as Spin Trapping Reagent

a. A Schlenk tube containing a stirring bar, **1a** (0.20 mmol, 1.0 equiv), [MB] (0.02 mmol, 10 mol%), PBN (*N*-tert-butyl-α-phenylnitrone, 0.1 mmol, 50 mol%), and 4.0 mL of EtOAc was stirred for 15 minutes in air under darkness.

b. A Schlenk tube containing a stirring bar, **1a** (0.20 mmol, 1.0 equiv), [MB] (0.02 mmol, 10 mol%), PBN (*N*-tert-butyl-α-phenylnitrone, 0.1 mmol, 50 mol%), and 4.0 mL of EtOAc was stirred for 15 minutes under blue LEDs irradiation in air.

Notably, a clear EPR signal was generated in the conditions, suggesting that a radical is generated (g = 2.0059, hyperfine splitting constants a^N = 14.62 G, a^H = 2.68 G). These signals were assigned as a spin trapped adducts of PBN-•C after simulation (see figure S9).[12]

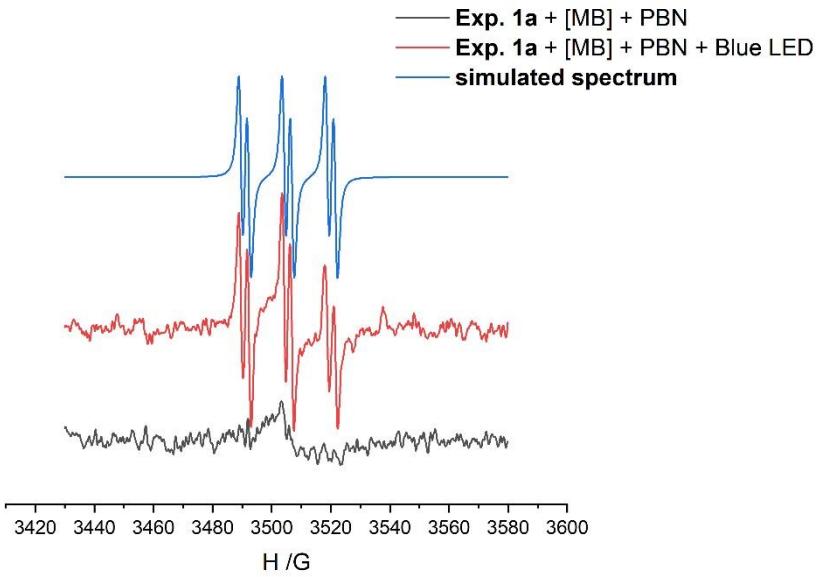
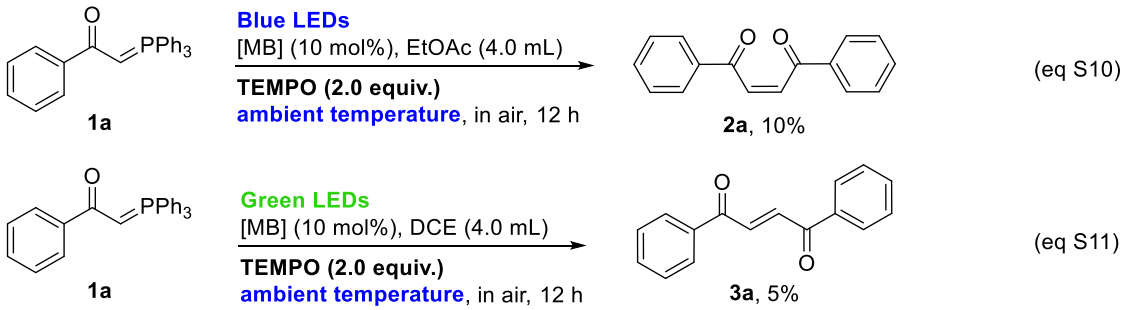


Figure S9. (a)→(b), Electron paramagnetic resonance (EPR) spectra obtained by experiments; (c) simulated spectrum.

7.6 radical capture experiments



Scheme S4. Radical-capture experiments.

Following the general procedure A, 2.0 equivalent of TEMPO was separately added to the model reactions (conditions A and B). These reactions were stirred on Wattecs Parallel Light Reactor for 12 h. Then, the LEDs was turned off and the reaction mixture under green LED irradiation was taken for mass spectrometry analysis (using CH_3CN solvent, ESI method). Afterwards, compounds **2a** and **3a** were determined as 10% and 5% yields via crude ^1H NMR analysis, respectively (eq S10, S11). As a comparison, the reaction mixture of model reaction with green LED irradiation was also taken for mass spectrometry analysis. After carefully analysis the spectra, none of TEMPO adduct was detected.

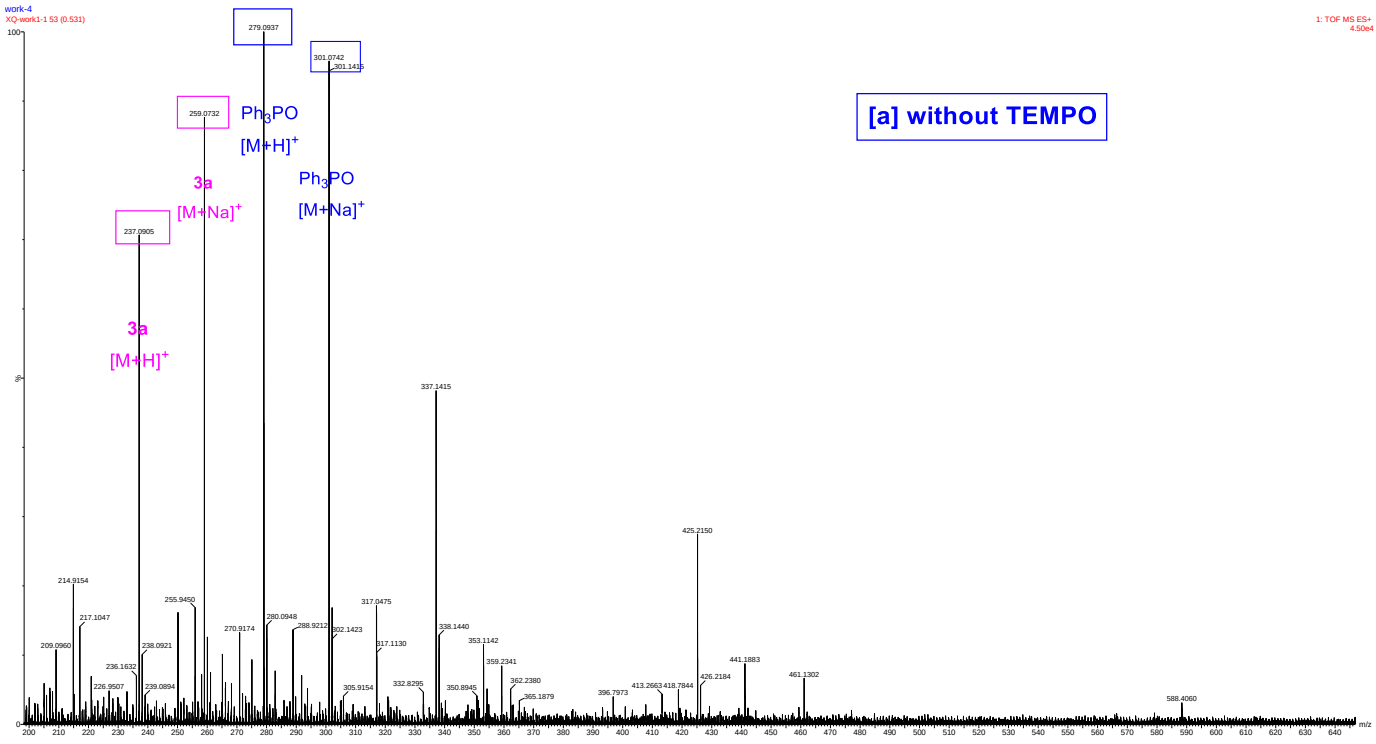


Figure S9. Analysis of mass spectrum of the model reaction mixture without TEMPO scavenger.

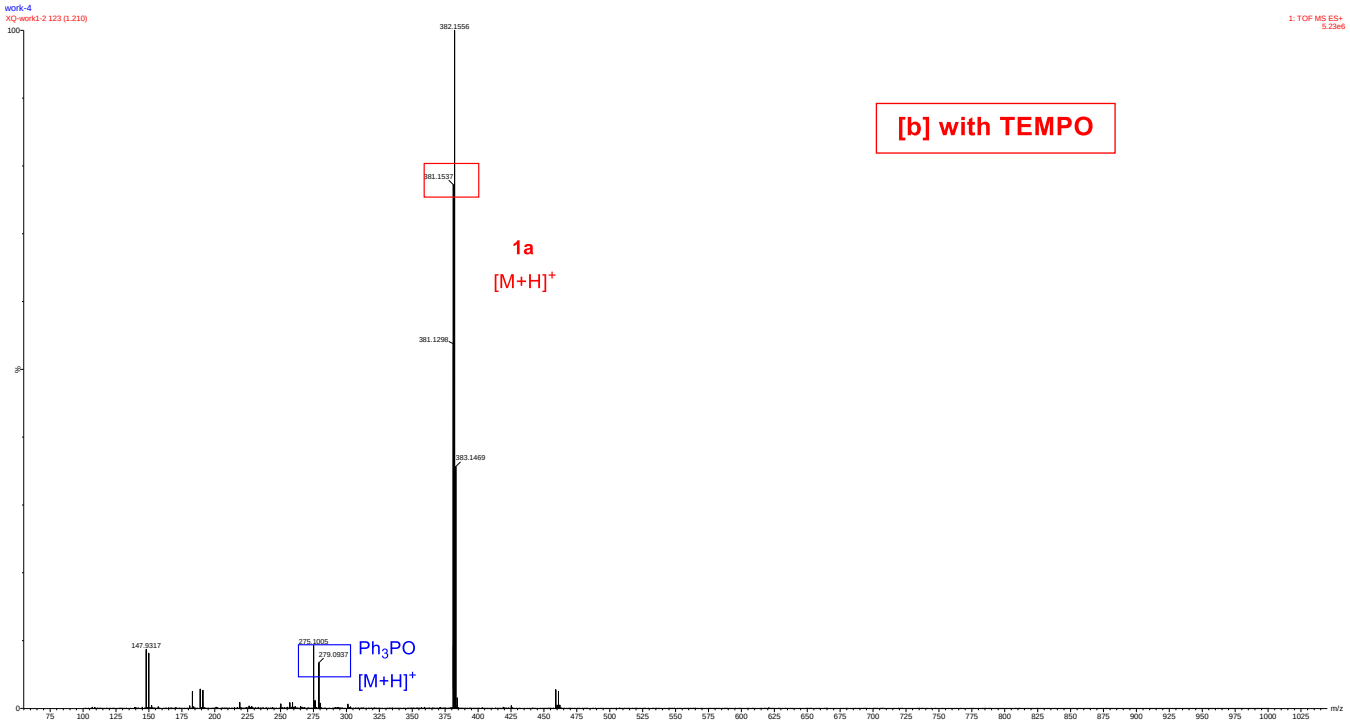
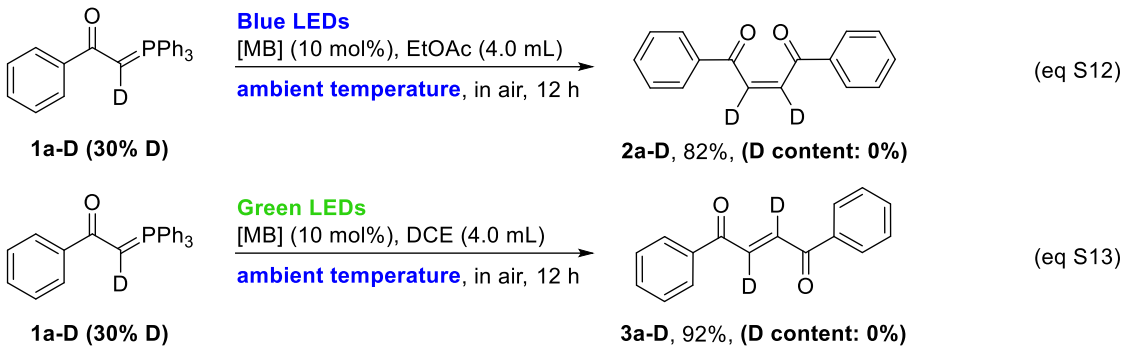


Figure S10. Analysis of mass spectrum of the reaction mixture with TEMPO scavenger.

7.7 Deuterium experiments.

7.7.1 Deuterium experiments employing 1a-D as substrate



Scheme S5. Deuterium experiments using **1a-D** as substrate.

1a-D was prepared via reported procedure. In our work, the D-content of **1a-D** was determined as 30% (see Figure S11 and S12 below). Following the general procedure As, **1a-D** was employed as the substrate under conditions A and B. After the reaction was finished, the corresponding alkenes were isolated and analysized via ^{1}H NMR. From ^{1}H NMR analysis, the obtained alkene products do not contain any deuterium.

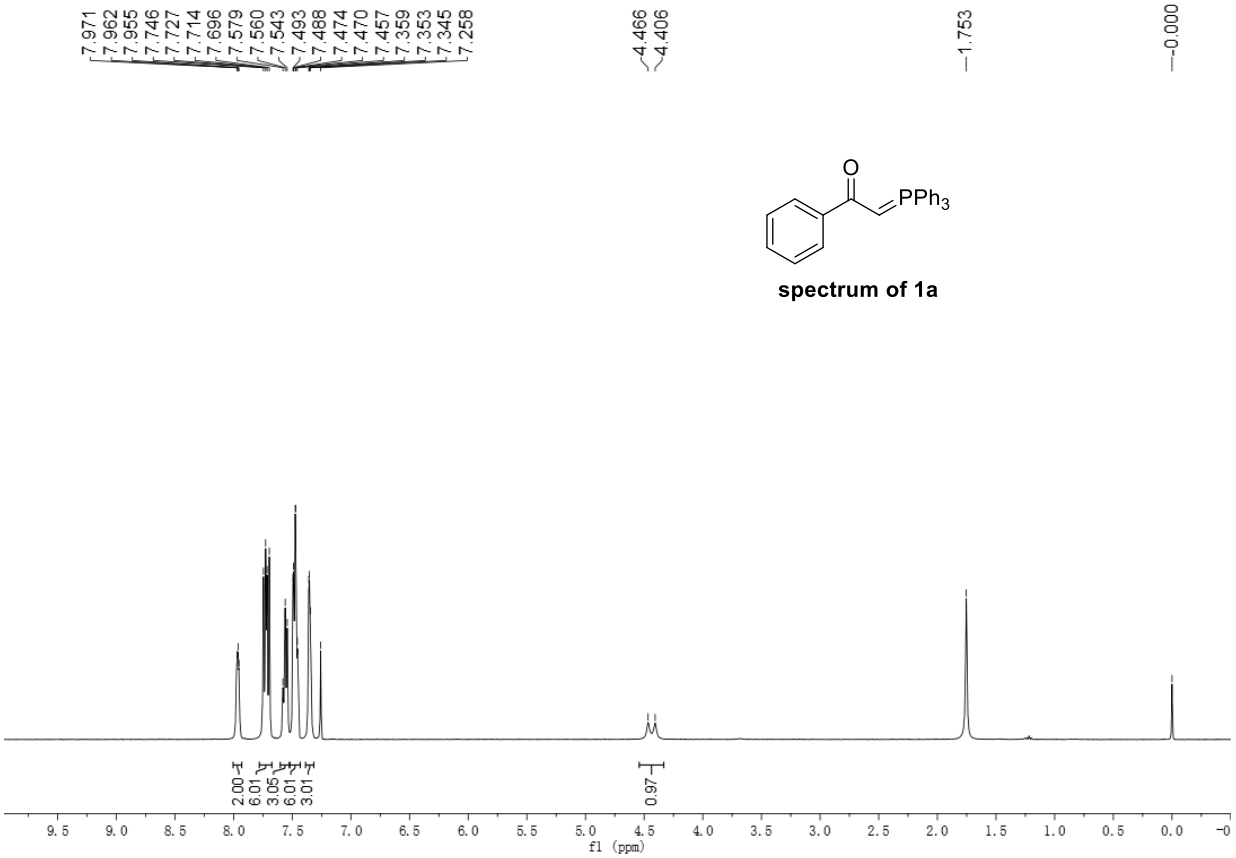


Figure S11. Spectrum of **1a**.

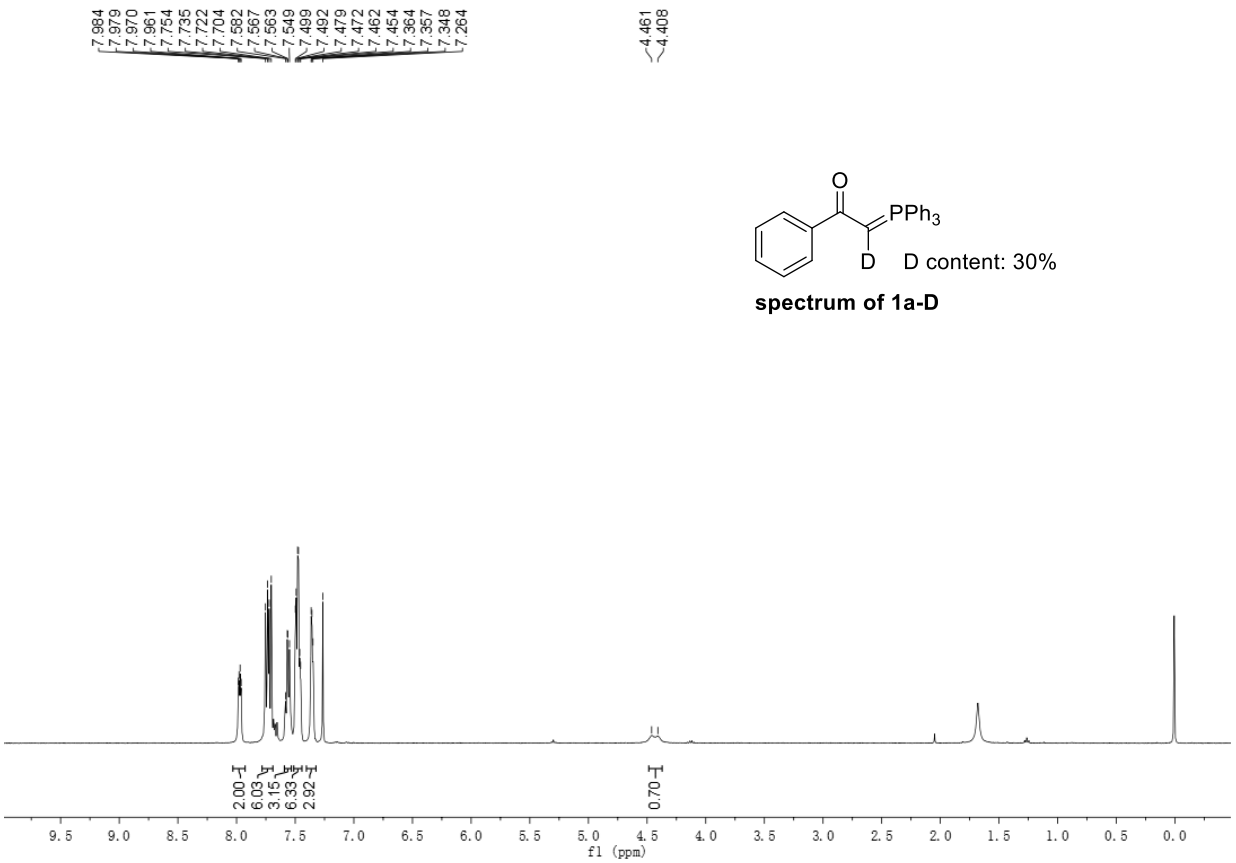


Figure S12. Spectrum of **1a**-D.

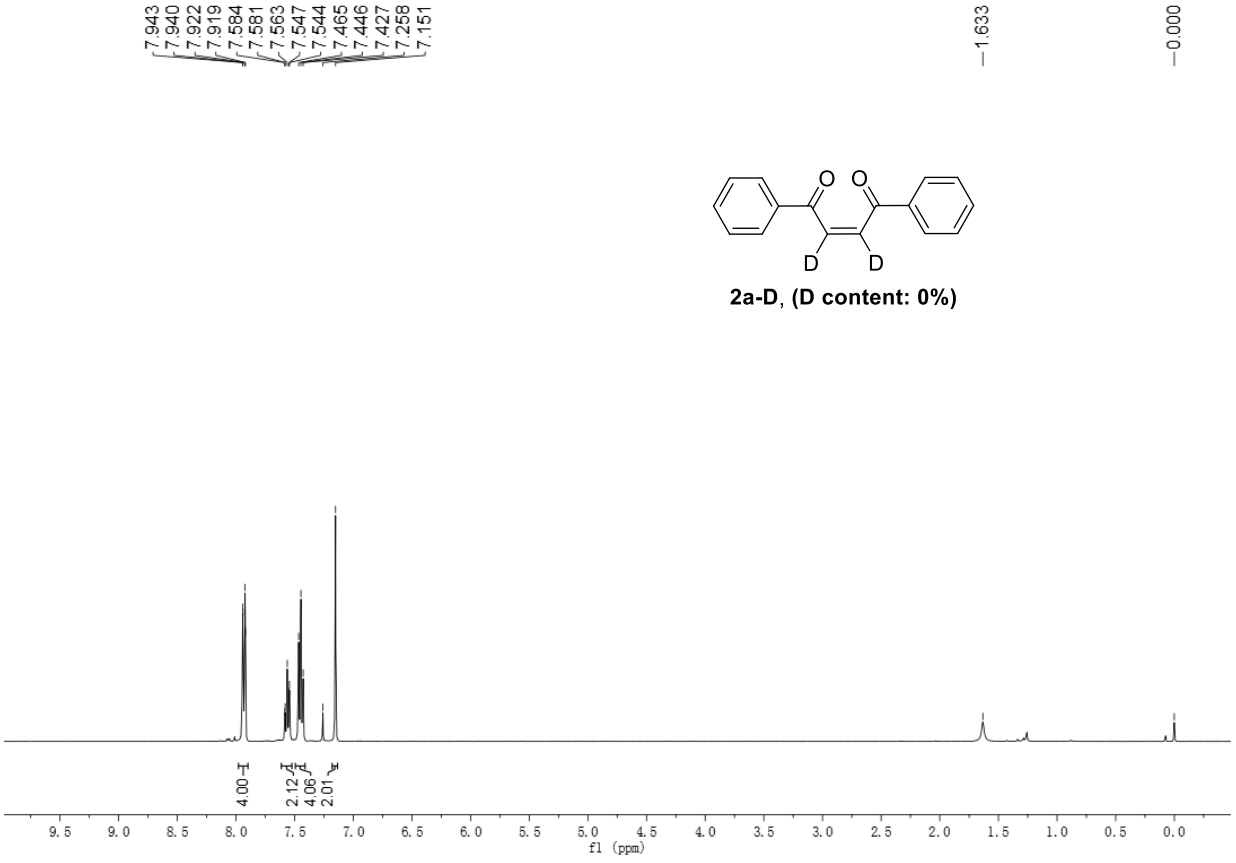


Figure S13. Spectrum of **2a-D**.

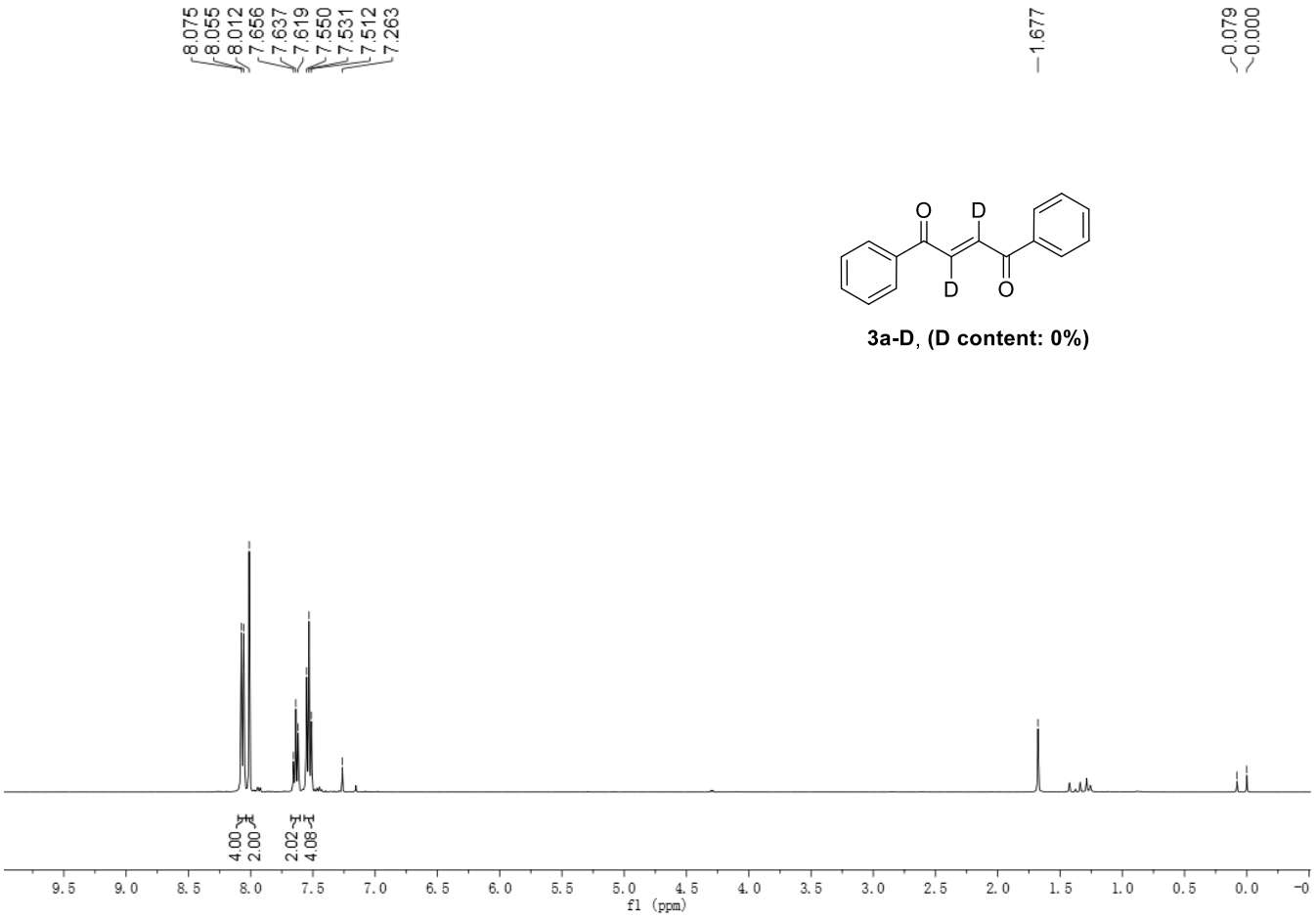
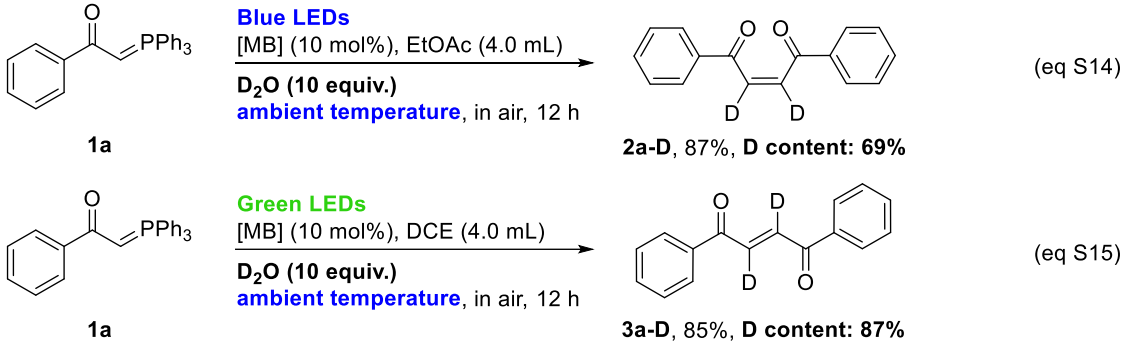


Figure S14. Spectrum of **3a-D**.

7.7.2 Deuterium experiments by adding equivalent of D_2O.



Scheme S6. Deuterium experiments by adding equivalent D_2O.

Following the general procedure A, 10.0 equivalent of D_2O was separately added to the model reactions (conditions A and B). After the reactions were finished, the corresponding **2a-D** and **3a-D** were isolated and analyzed via ^1H NMR (figure S15, S16). From ^1H NMR analysis, a large amount of deuterium has been incorporated into the olefin molecules. Based on above experiments, we hence postulate that the hydrogen in phosphorus ylides undergoes a fast proton exchange with the medium in the process.

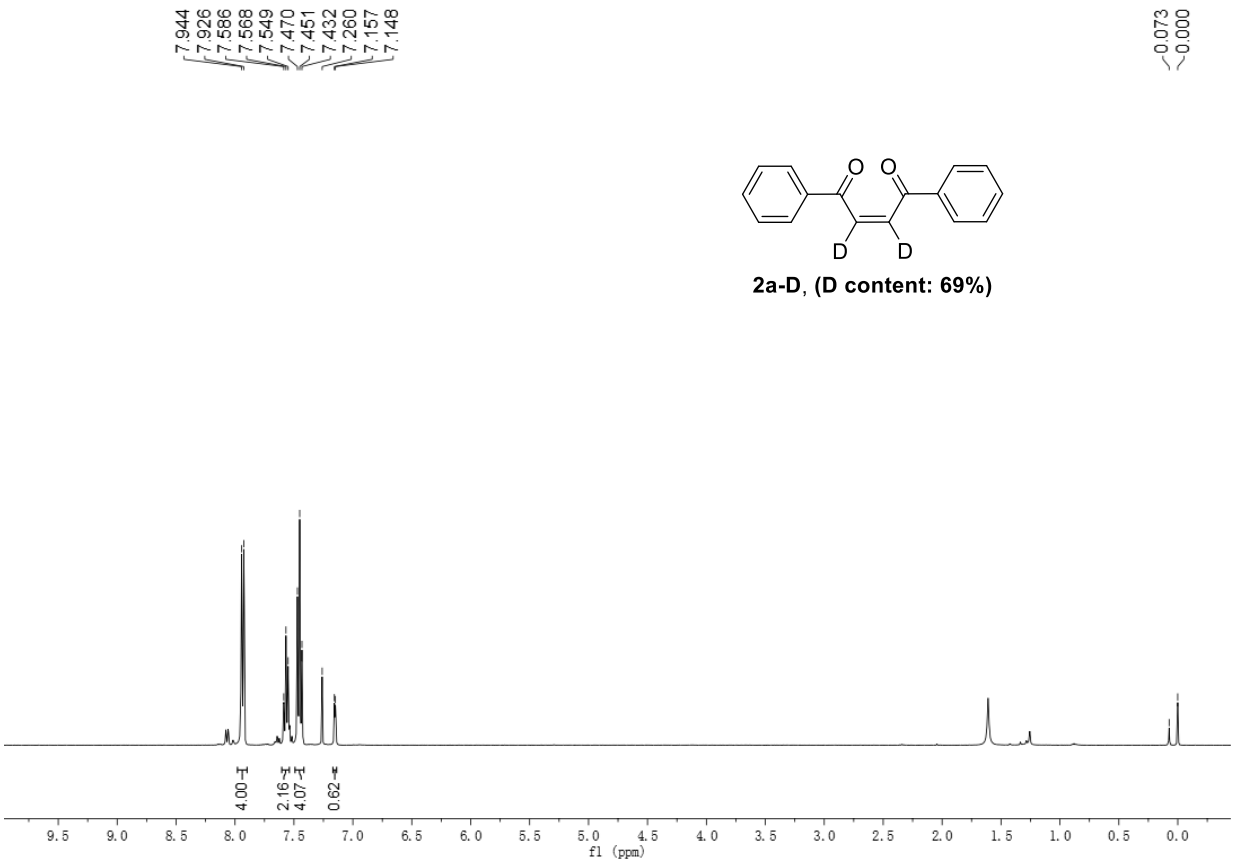


Figure S15. Spectrum of **2a-D.**

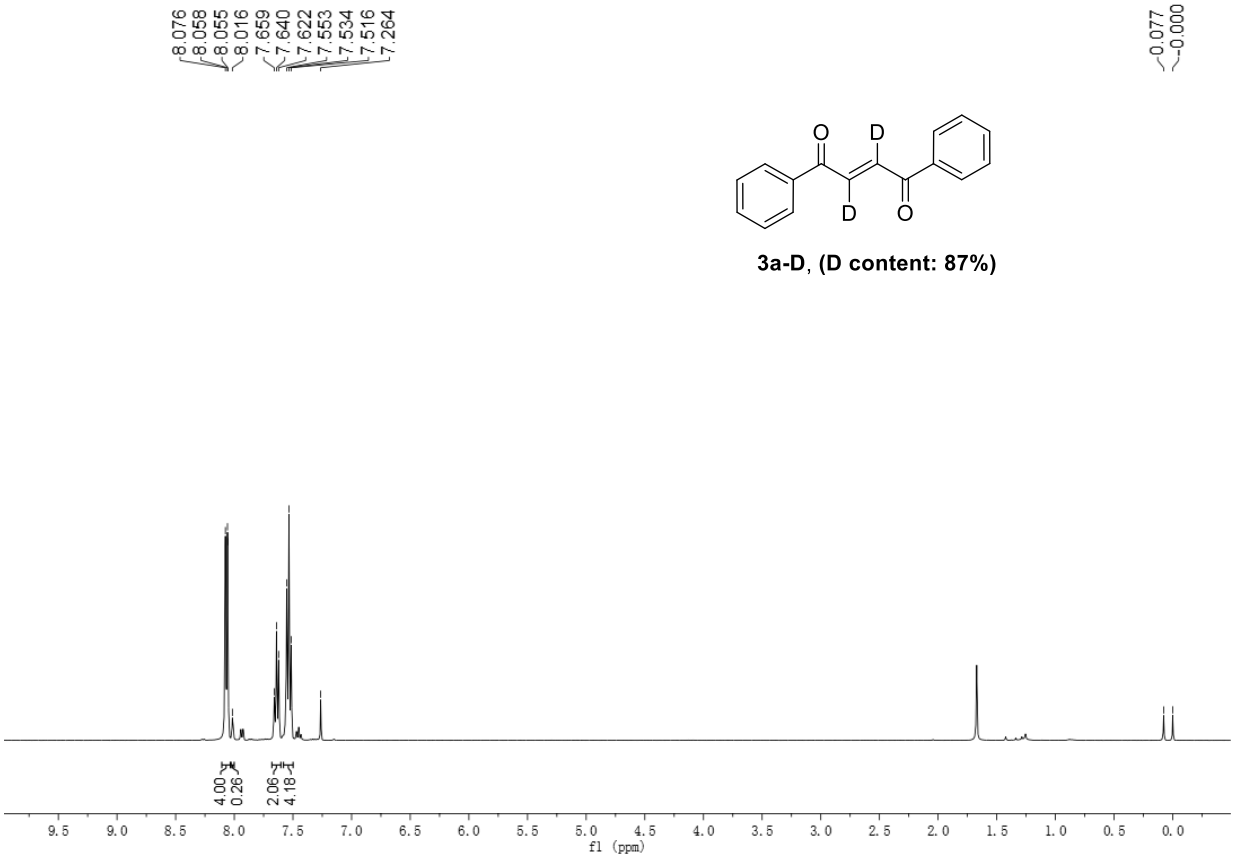
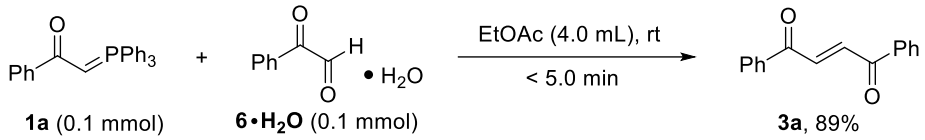


Figure S16. Spectrum of **3a-D.**

7.8 determination the involvement of intermediate 6.



Scheme S7. determination the involvement of intermediate **6**.

To a Schlenk tube containing a stirring bar, **1a** (0.1 mmol) and **6•H_2O** (0.1 mmol) was added EtOAc (4.0 mL) at room temperature. This reaction was stirred for 5 minutes. Then, TLC analysis showed that the starting materials were completely consumed and **3a** was formed as an only new point. Crude ^{1}H NMR analysis using $Cl_2CHCHCl_2$ as internal standard revealed the formation of **3a** in 89% yield.

8. References

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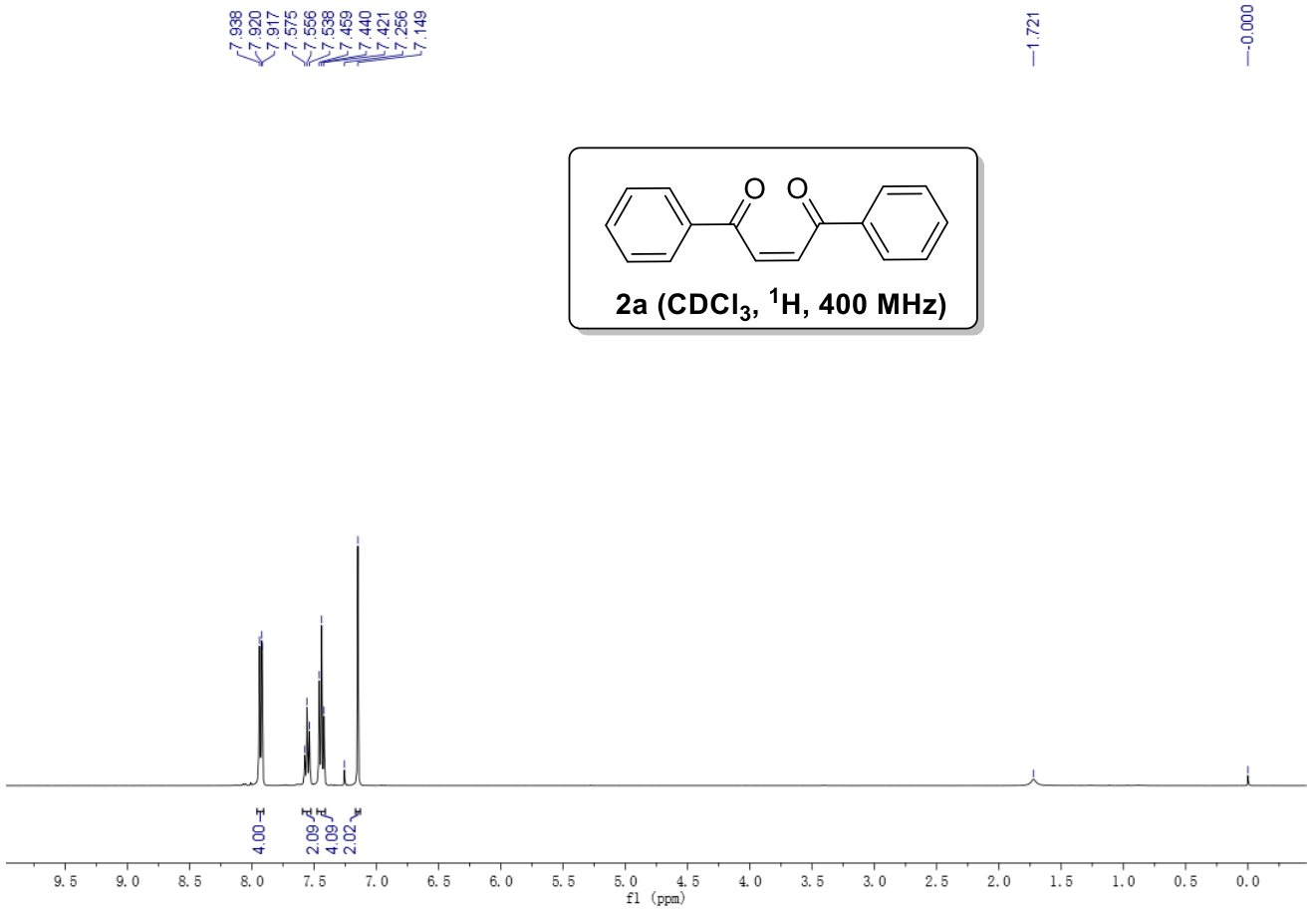
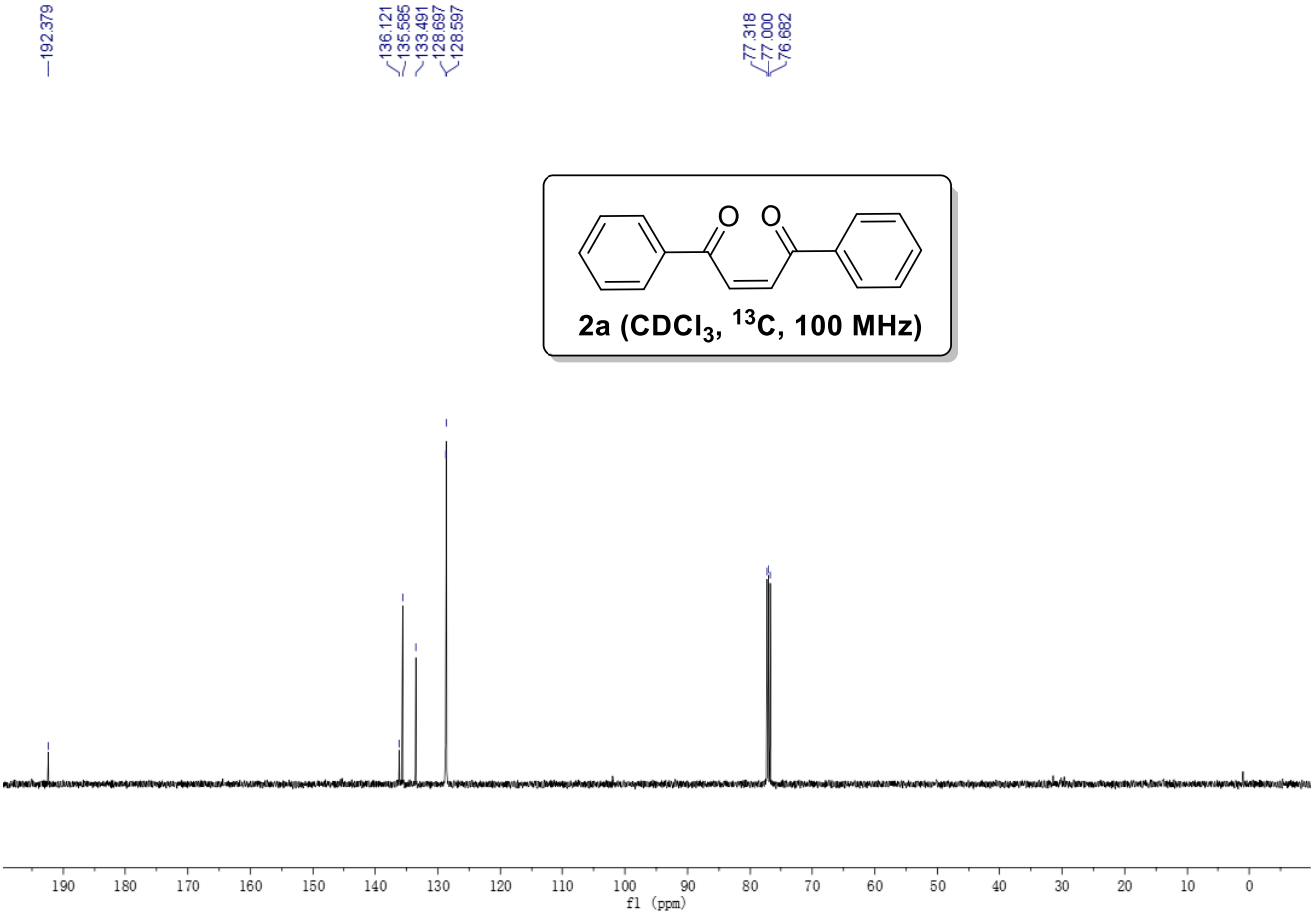
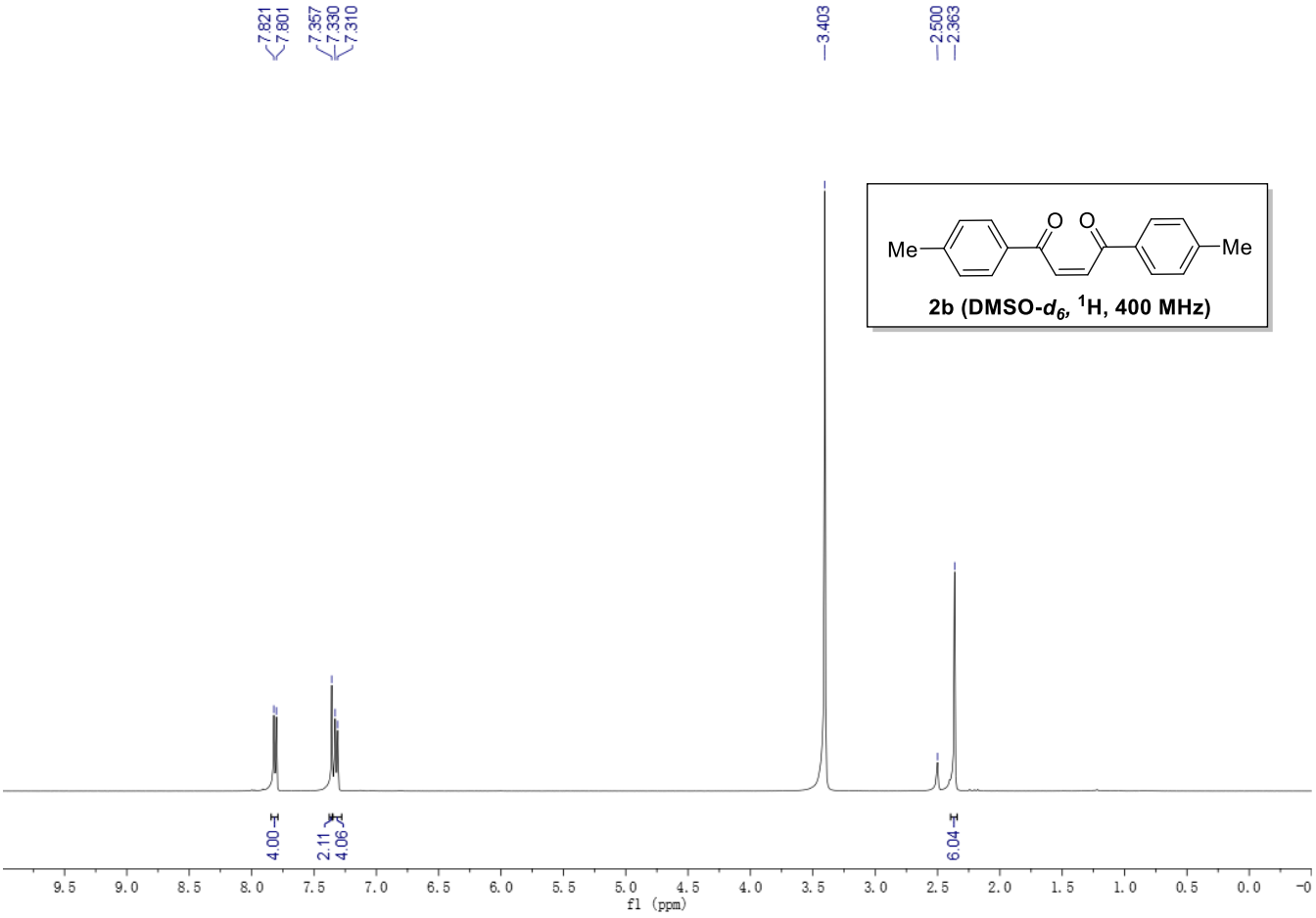
9. Spectrum



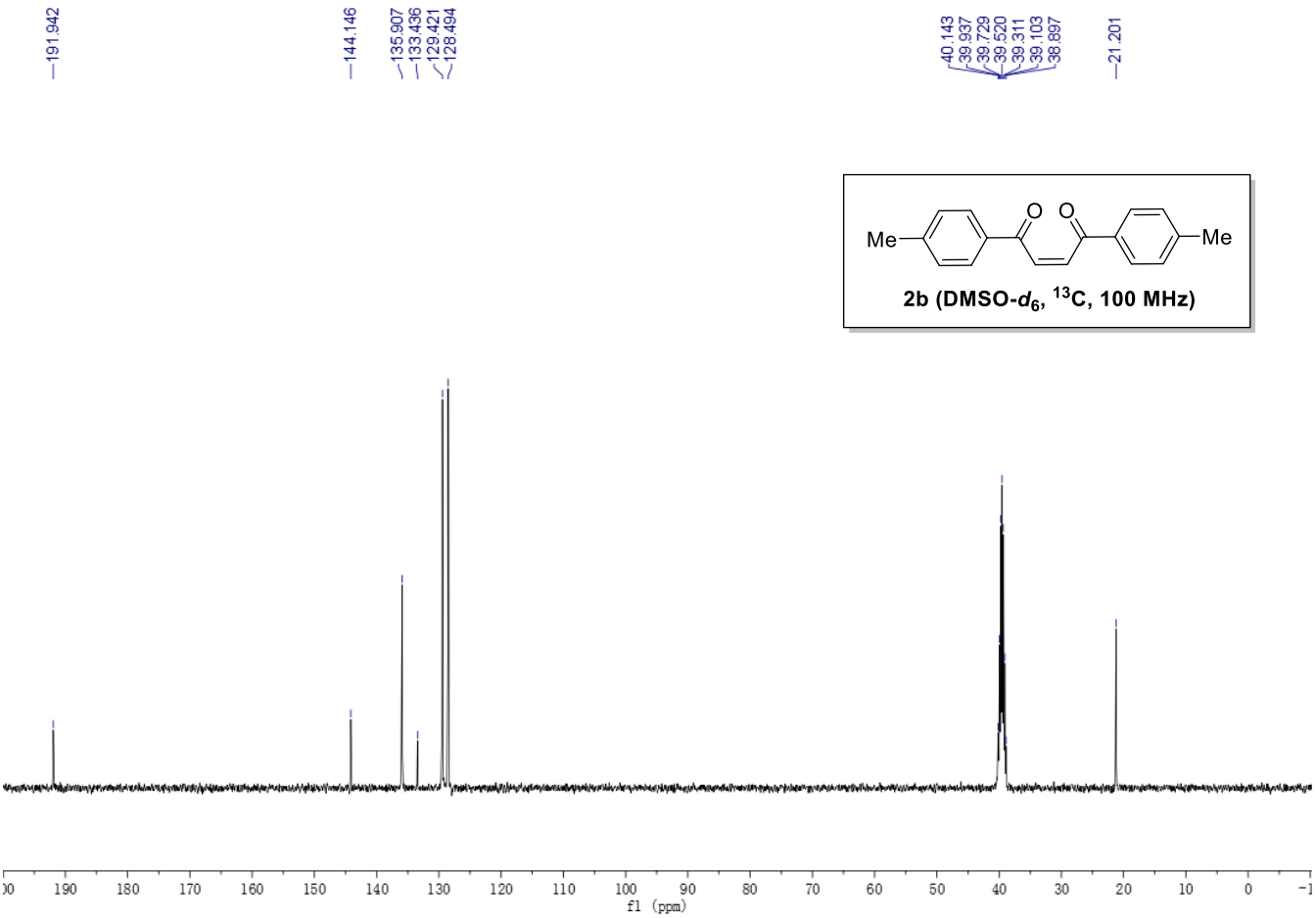
2a ($CDCl_3$, ^1H, 400 MHz)



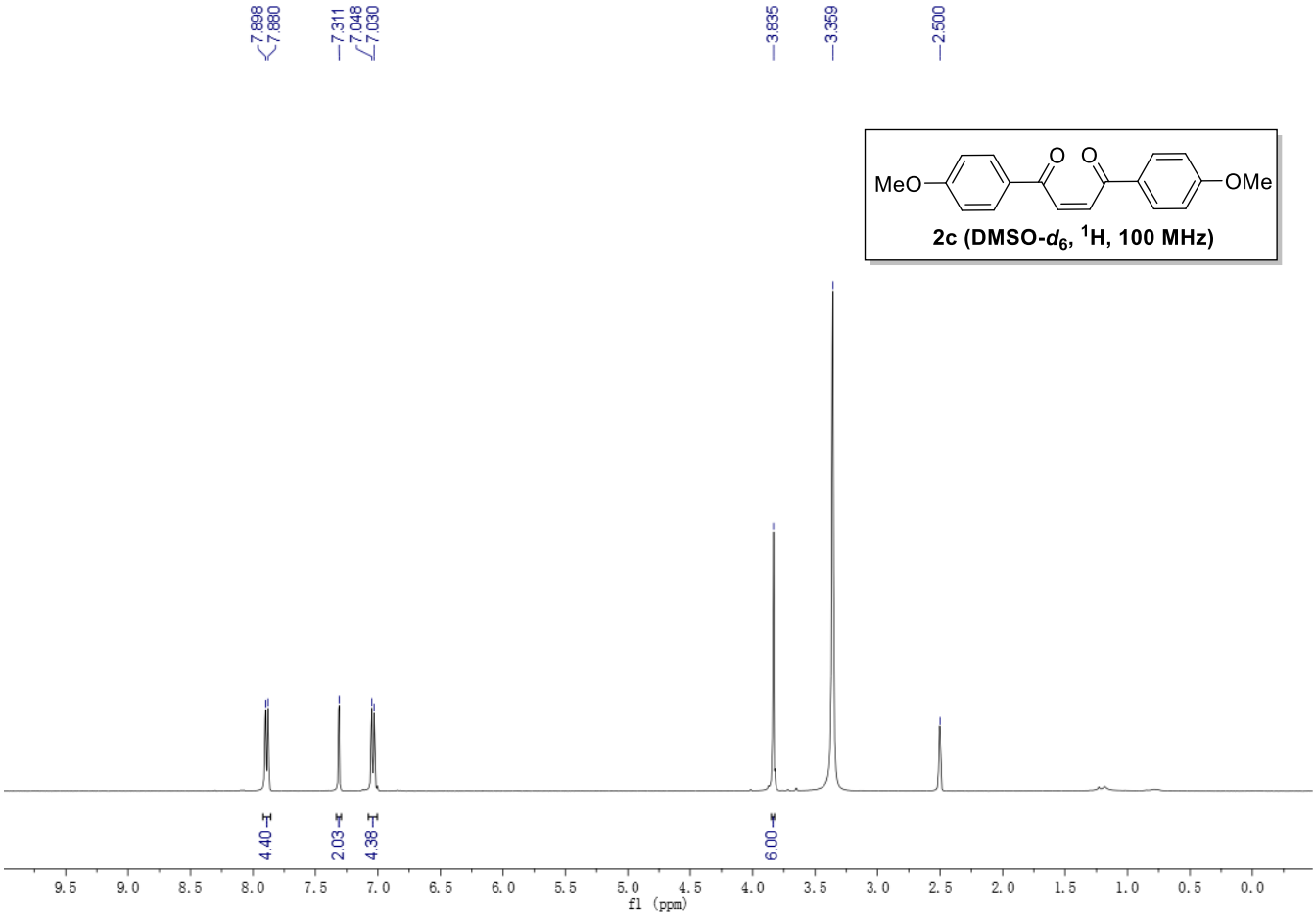
2a ($CDCl_3$, ^{13}C, 100 MHz)

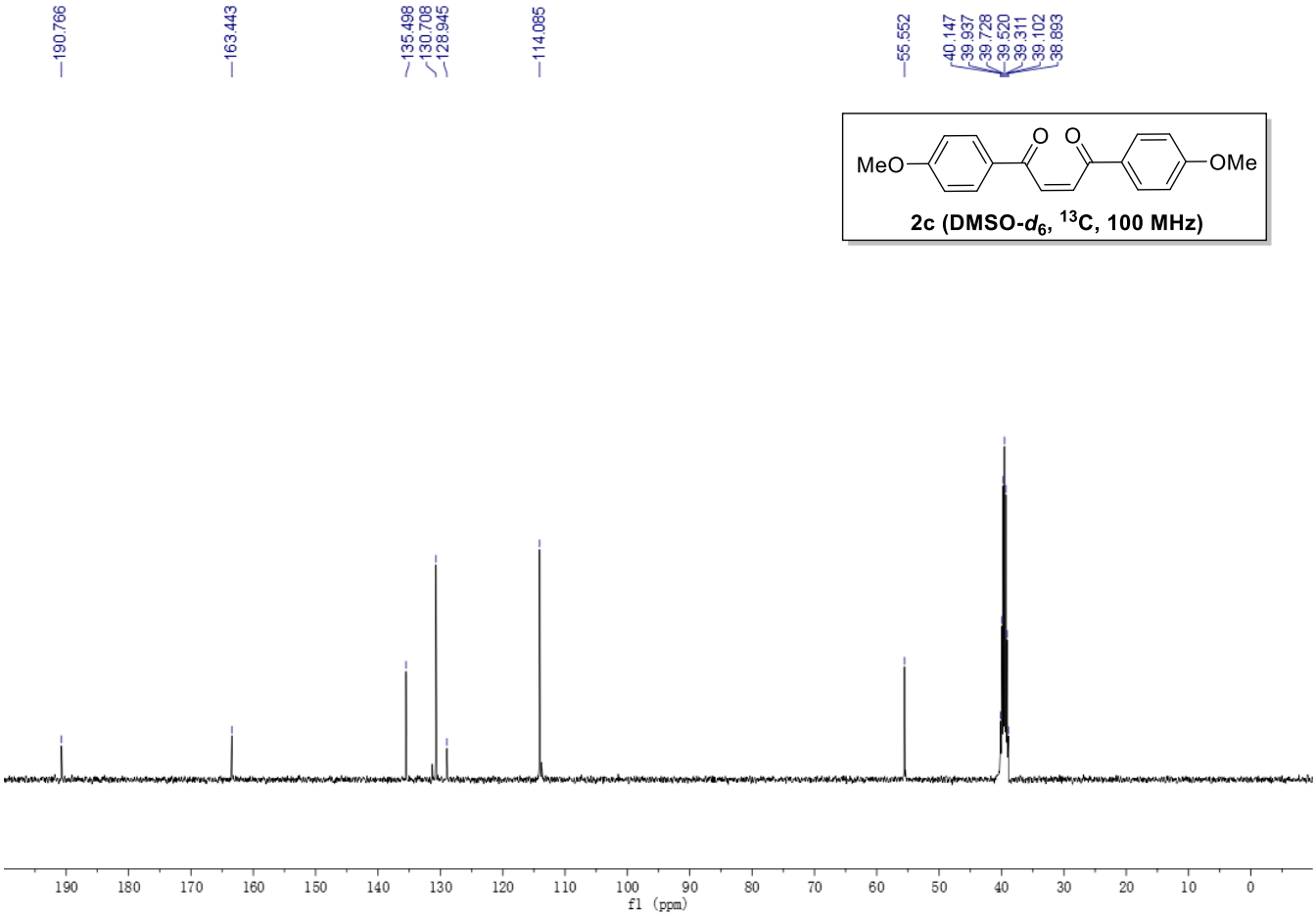


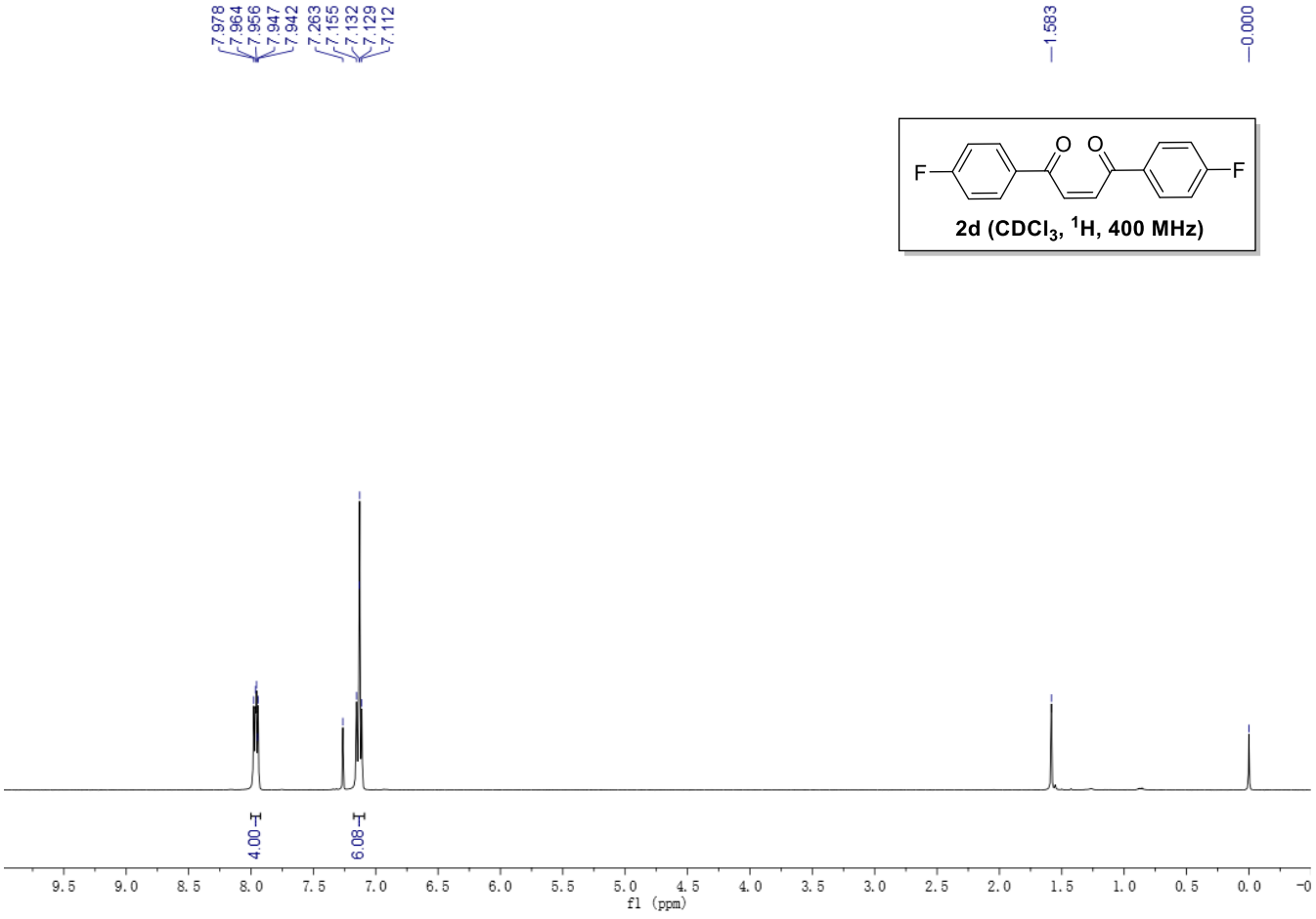
2b (DMSO-d_6, ^{1}H, 400 MHz)



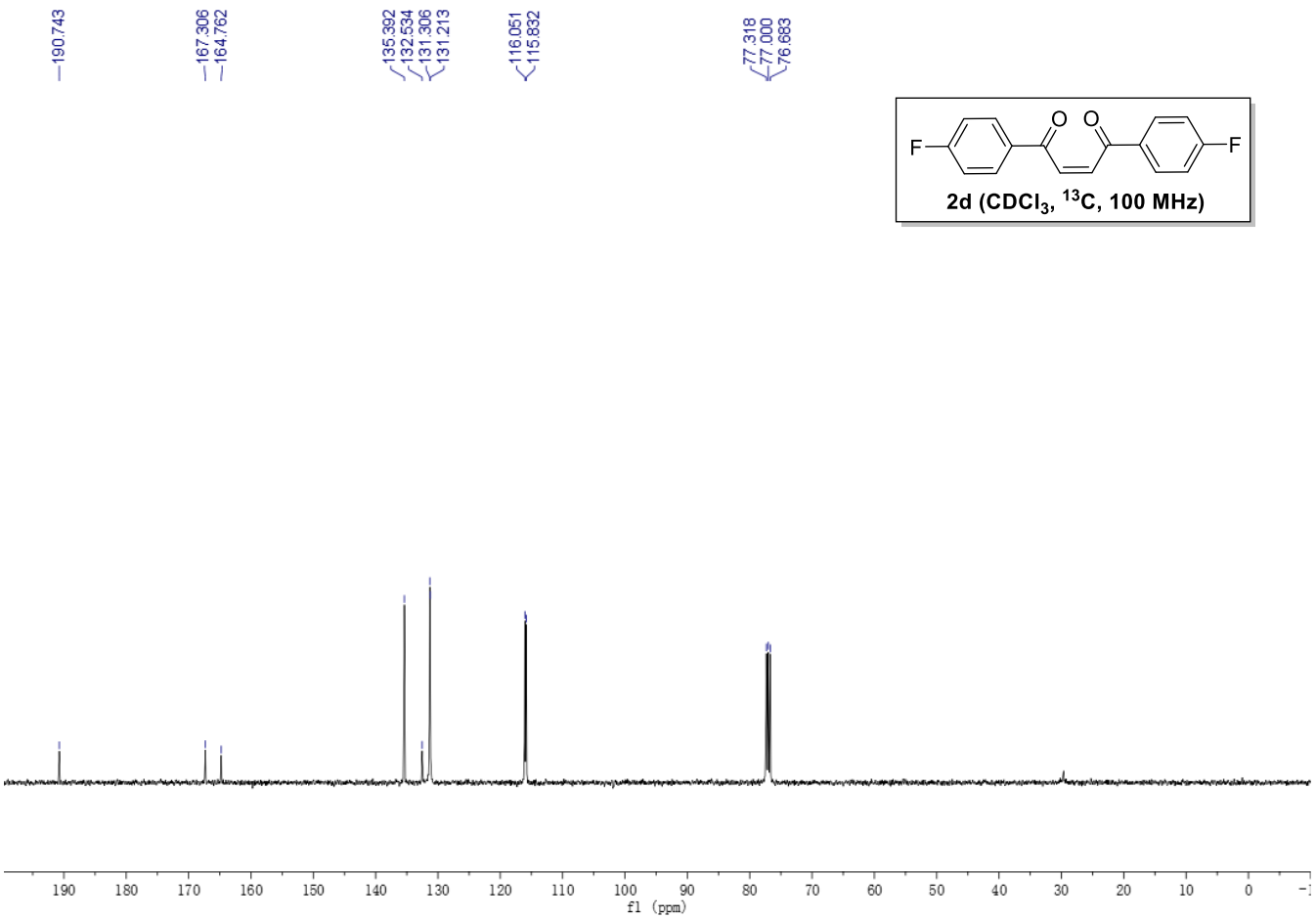
2b (DMSO-d_6, ^{13}C, 100 MHz)


7.898
7.880
7.311
7.048
7.030
3.835
3.359
2.500
MeO
OMe
2c (DMSO-d_6, ^{1}H, 100 MHz)
4.40
2.03
4.38
6.00
f1 (ppm)


190.766
163.443
135.498
130.708
128.945
114.085
55.552
40.147
39.937
39.728
39.520
39.311
39.102
38.893
MeO
OMe
2c (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

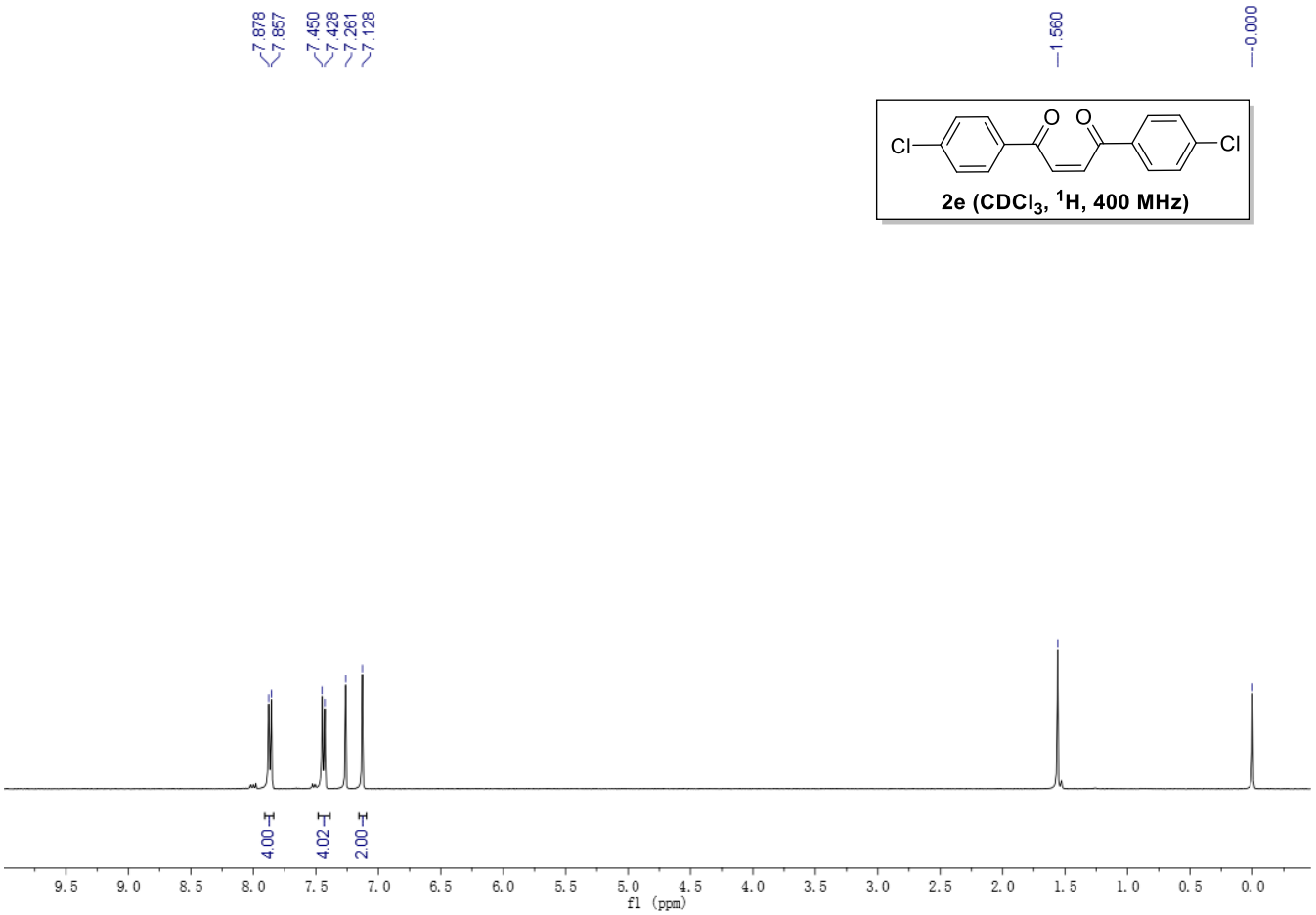


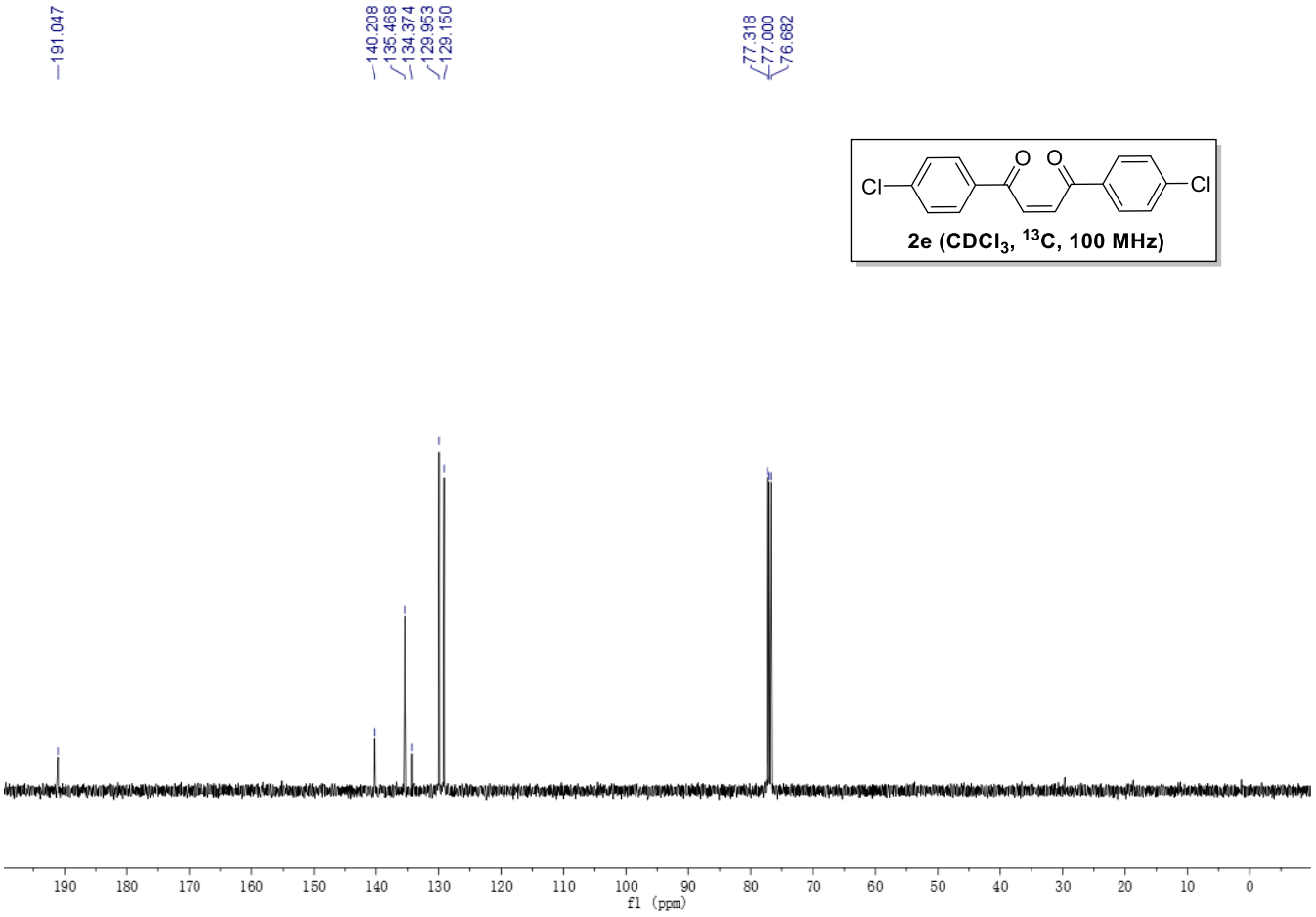
2d ($CDCl_3$, ^1H, 400 MHz)

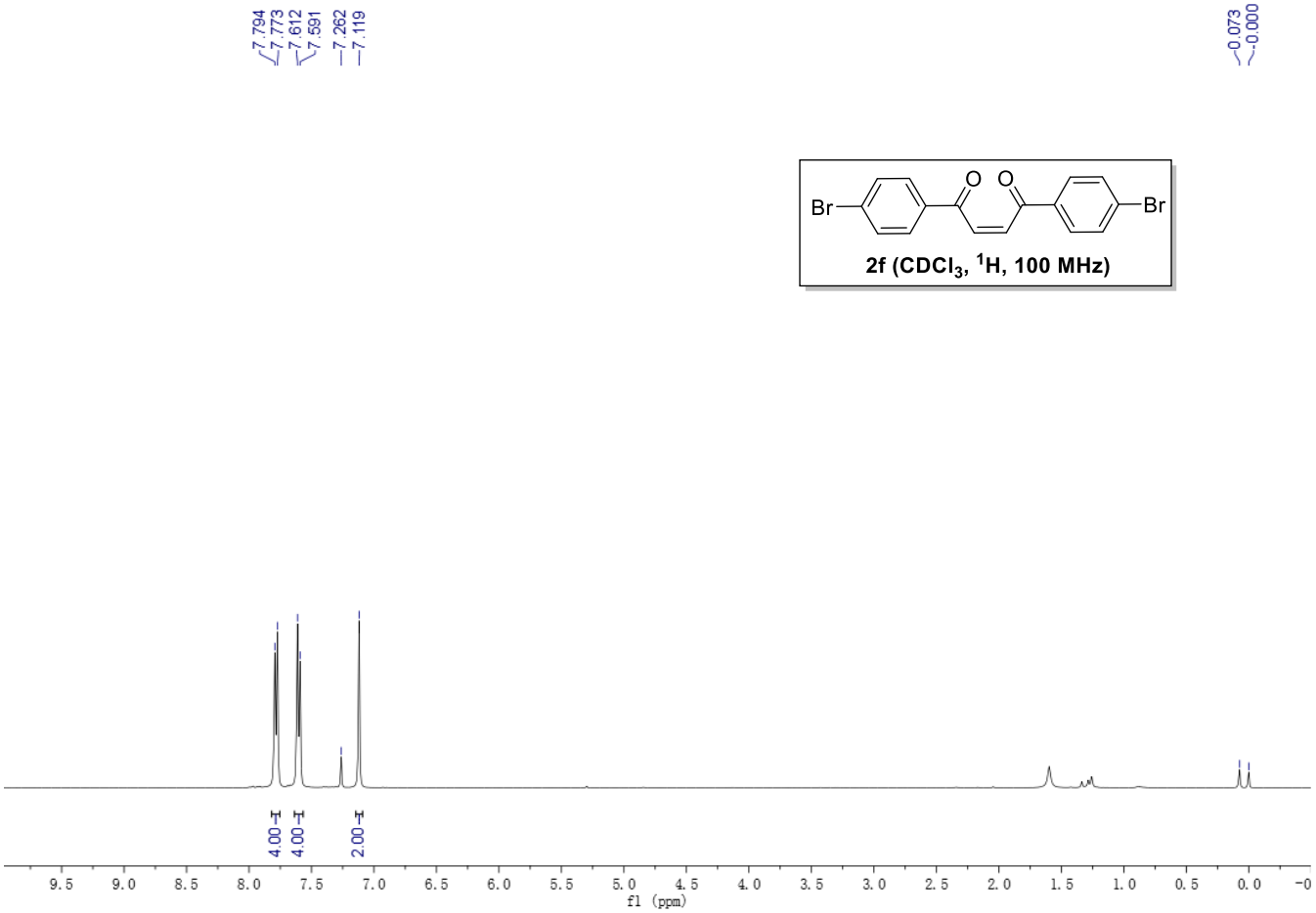


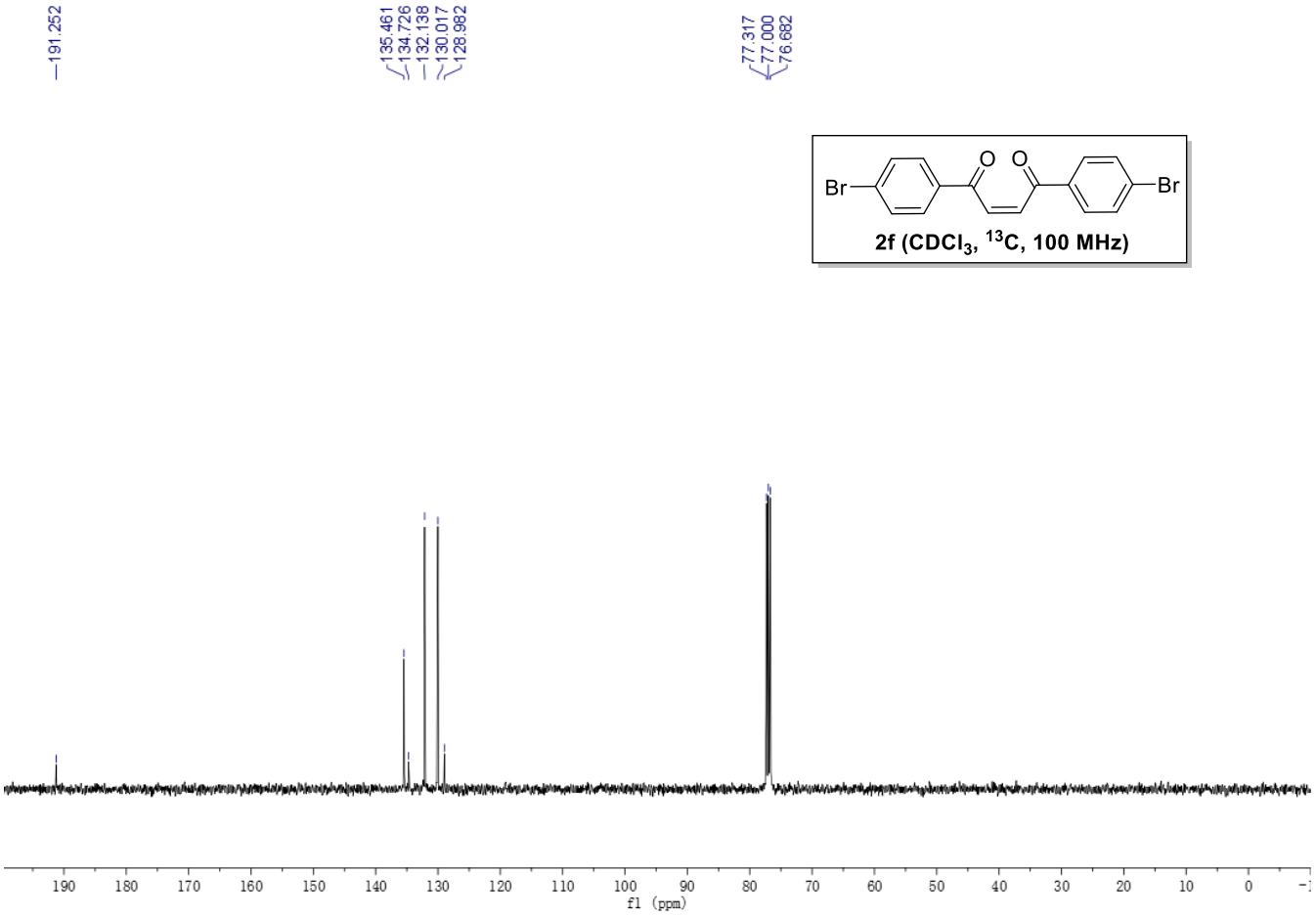
2d ($CDCl_3$, ^{13}C, 100 MHz)

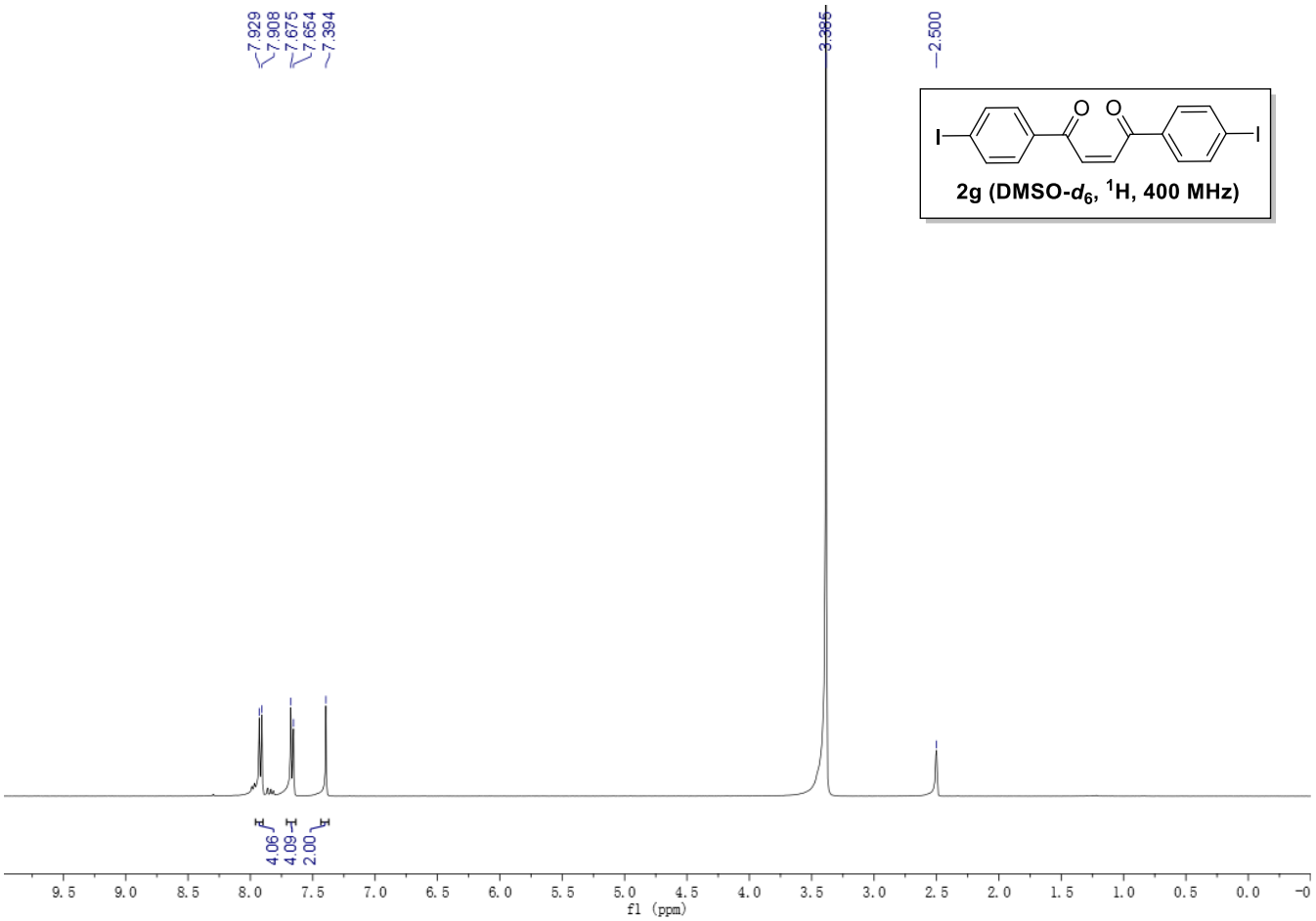

-103.854
F
O
O
F
2d (CDCl3, 19F, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

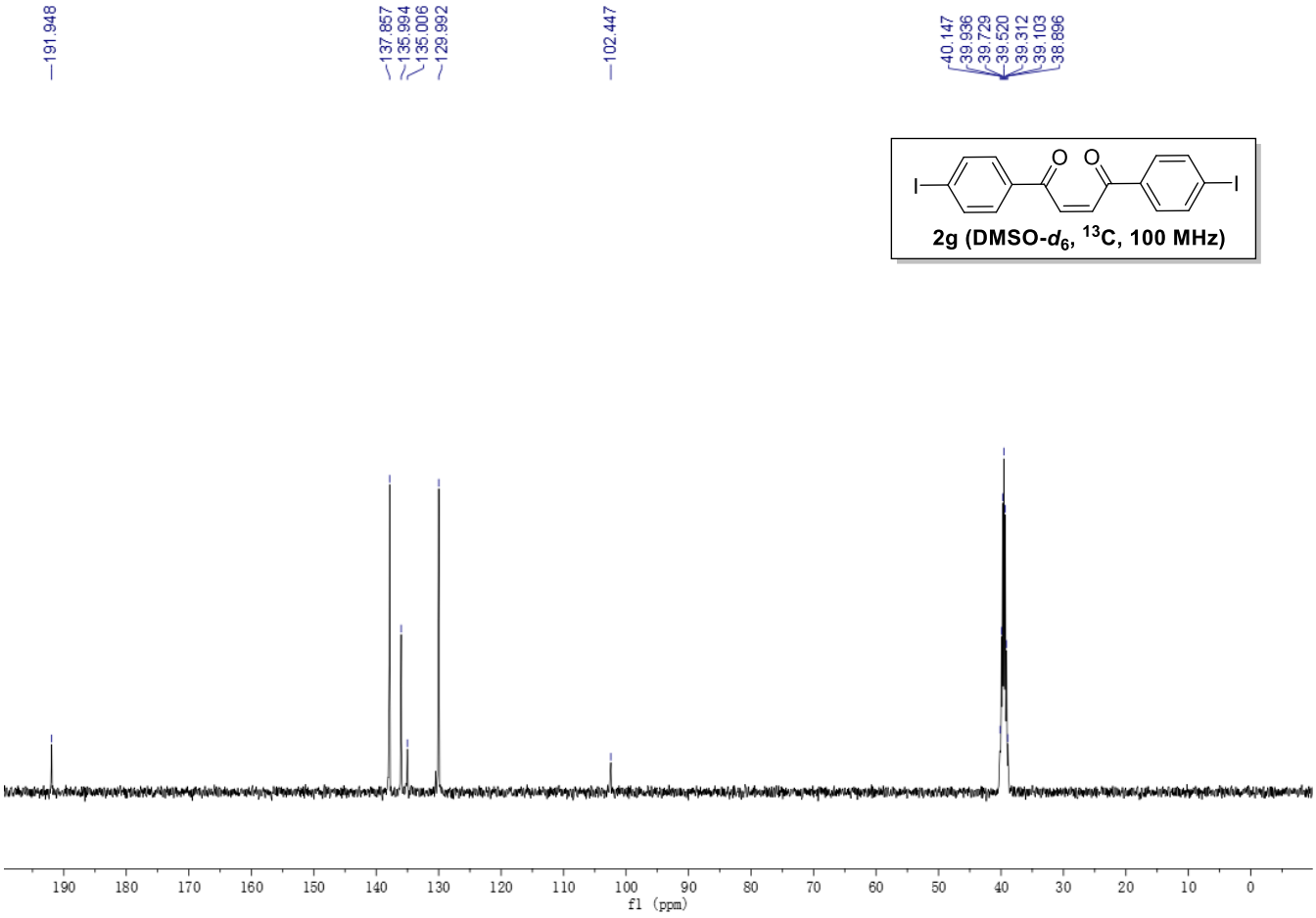

7.878
7.857
7.450
7.428
7.261
7.128
1.560
0.000
Cl
O
O
Cl
2e (CDCl3, 1H, 400 MHz)
4.00
4.02
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


191.047
140.208
135.468
134.374
129.953
129.150
77.318
77.000
76.682
Cl
O
O
Cl
2e (CDCl3, 13C, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

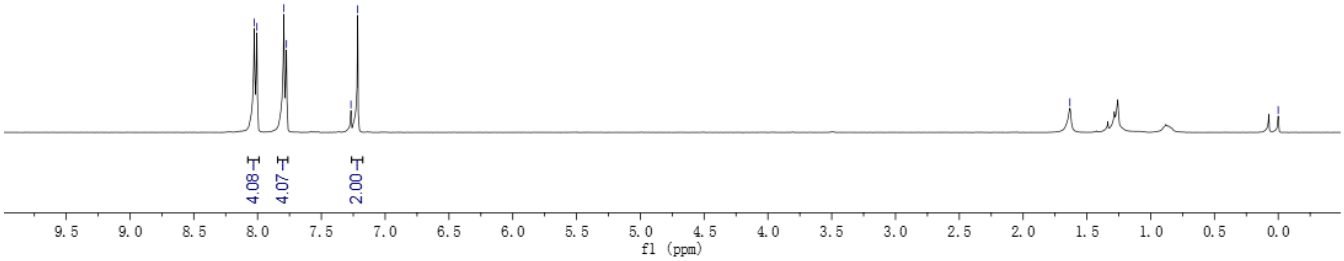

7.794
7.773
7.612
7.591
7.262
7.119
0.073
0.000
Br
O
O
Br
2f (CDCl3, 1H, 100 MHz)
4.00
4.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

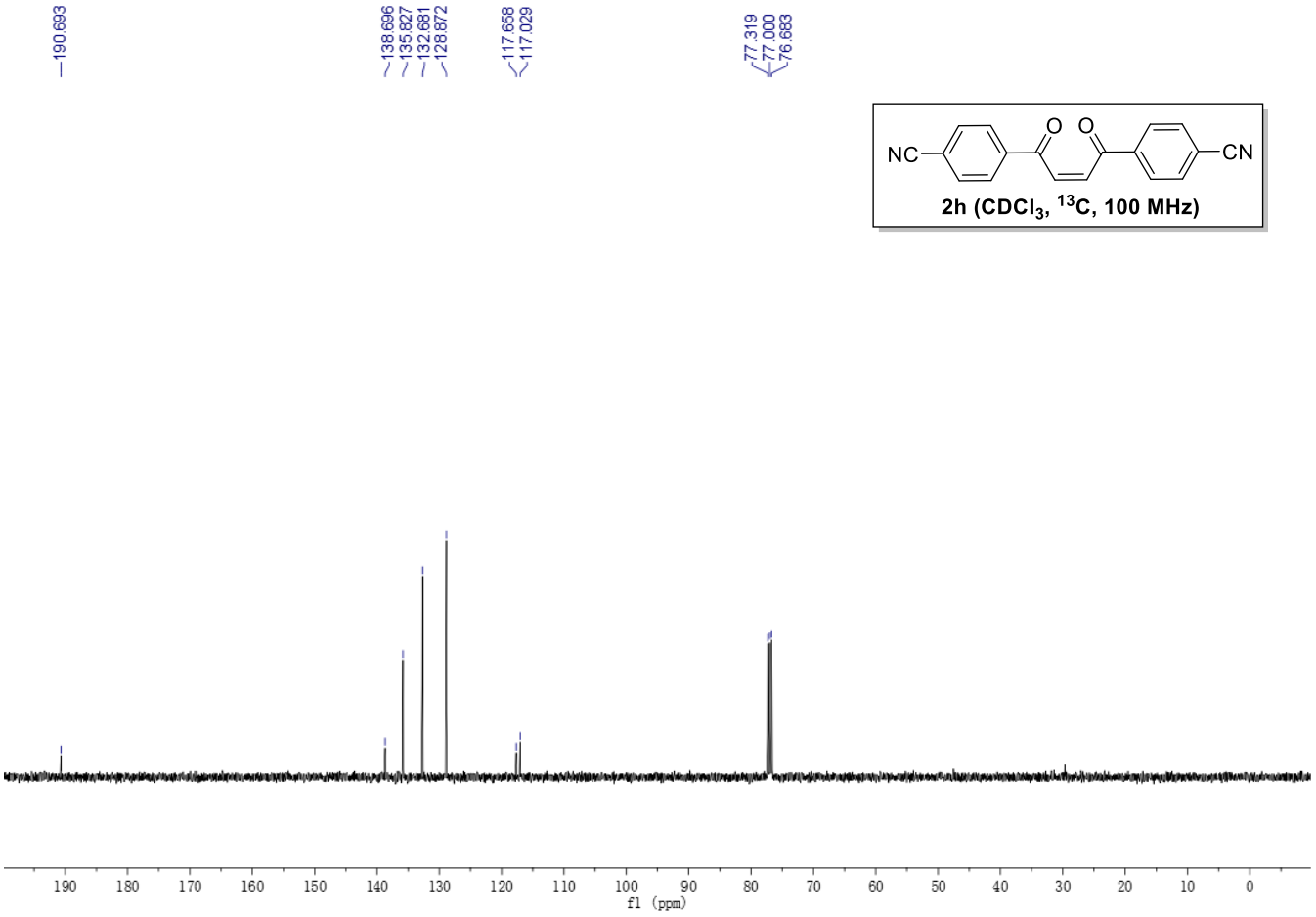

191.252
135.461
134.726
132.138
130.017
128.982
77.317
77.000
76.682
Br
O
O
Br
2f (CDCl3, 13C, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

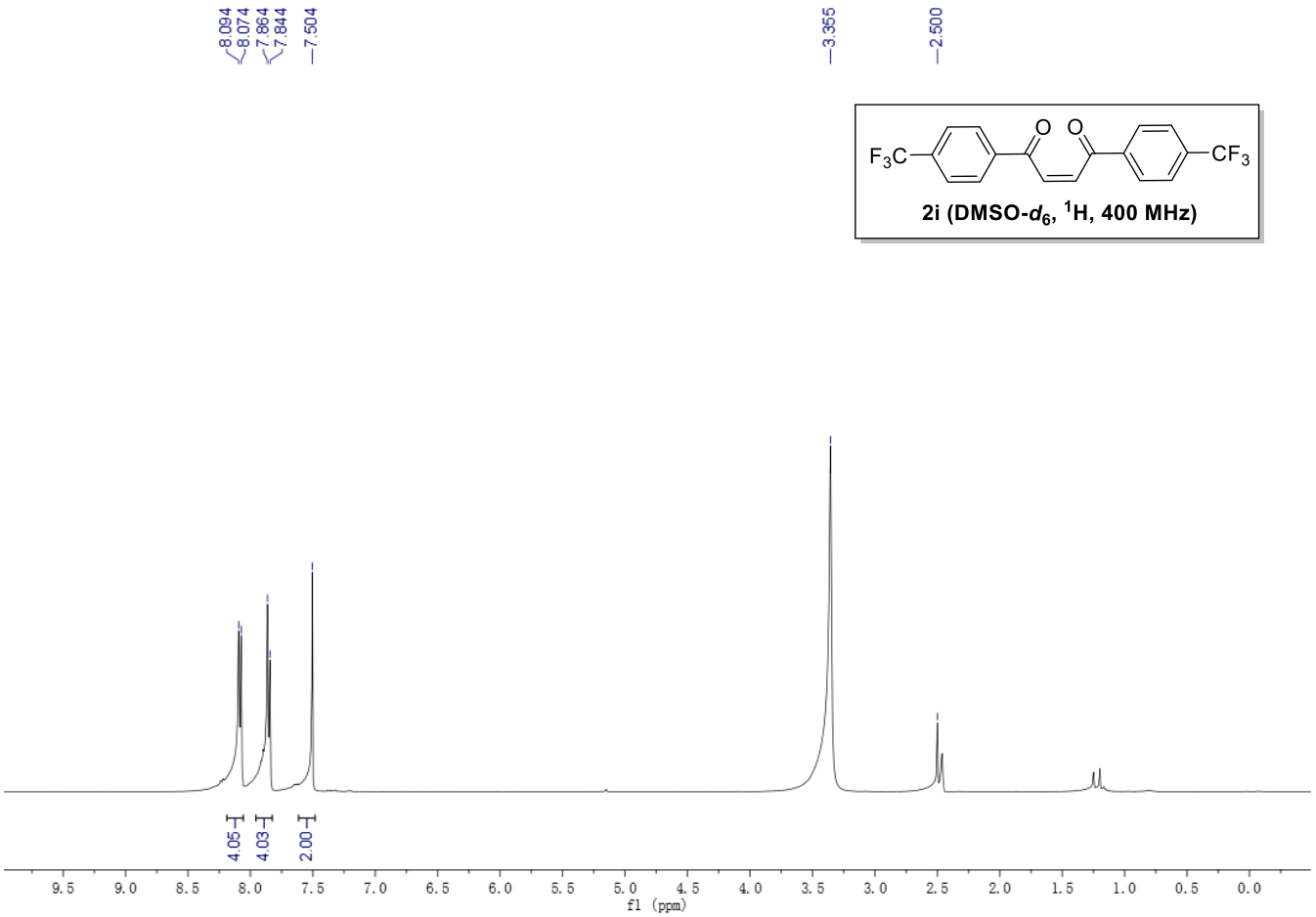

7.929
7.908
7.675
7.654
7.394
3.385
2.500
I
O
O
I
2g (DMSO-d6, 1H, 400 MHz)
4.06
4.09
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

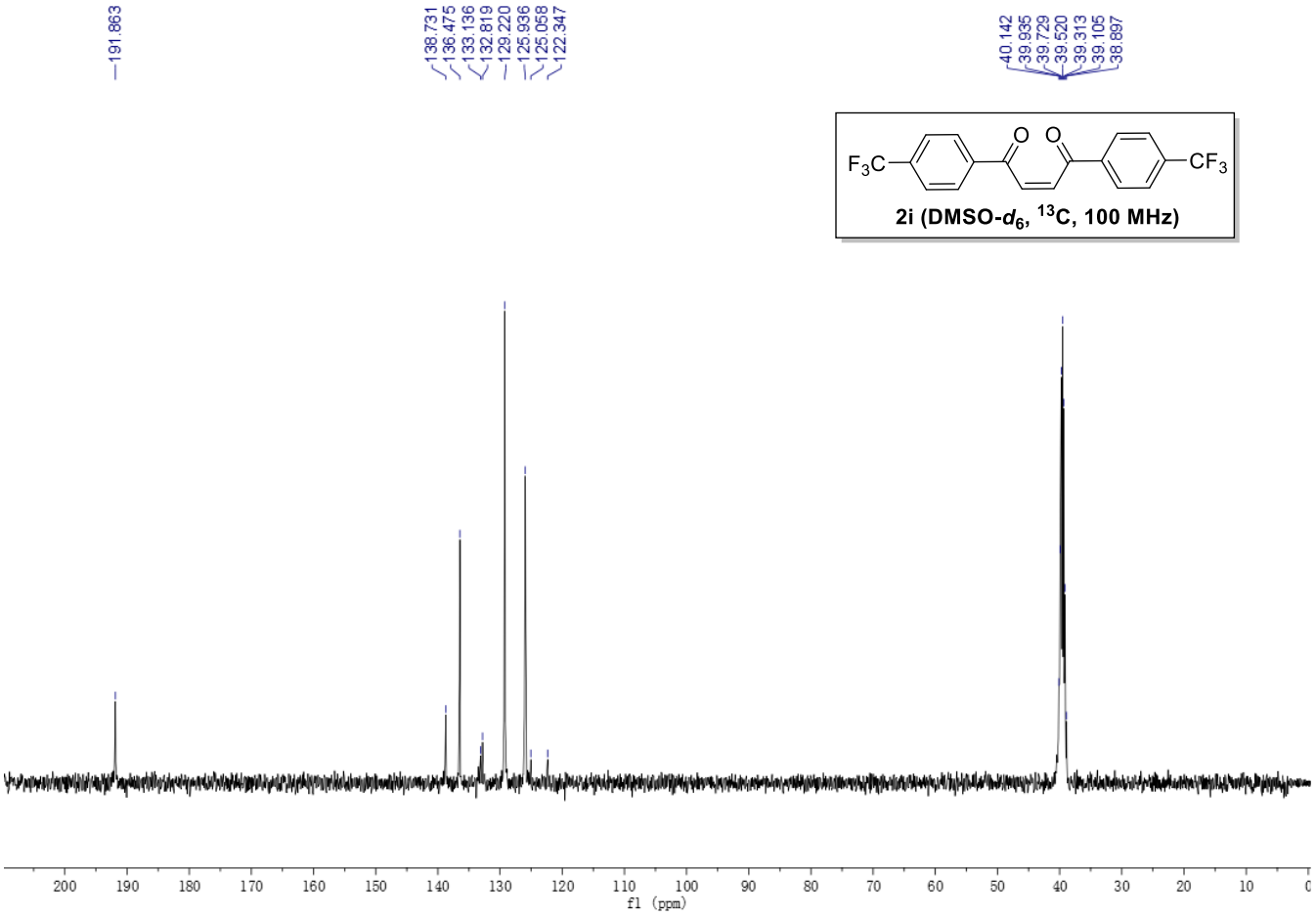

191.948
137.857
135.994
135.006
129.992
102.447
40.147
39.936
39.729
39.520
39.312
39.103
38.896
O
O
I
I
2g (DMSO-d_6, ^{13}C, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

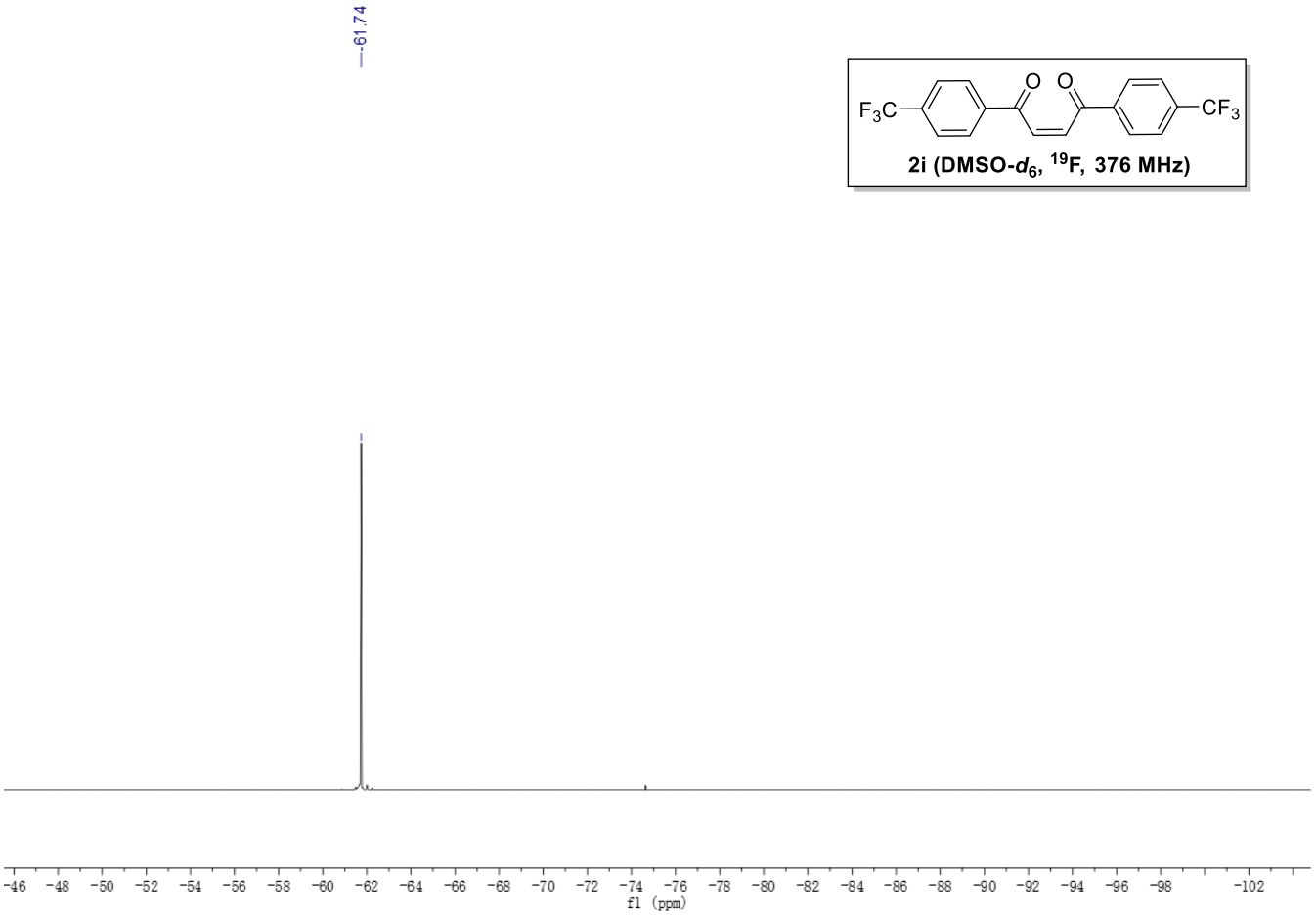

8.026
8.005
7.794
7.774
7.268
7.215
1.633
0.000
O
O
NC
CN
2h ($CDCl_3$, ^{1}H, 400 MHz)

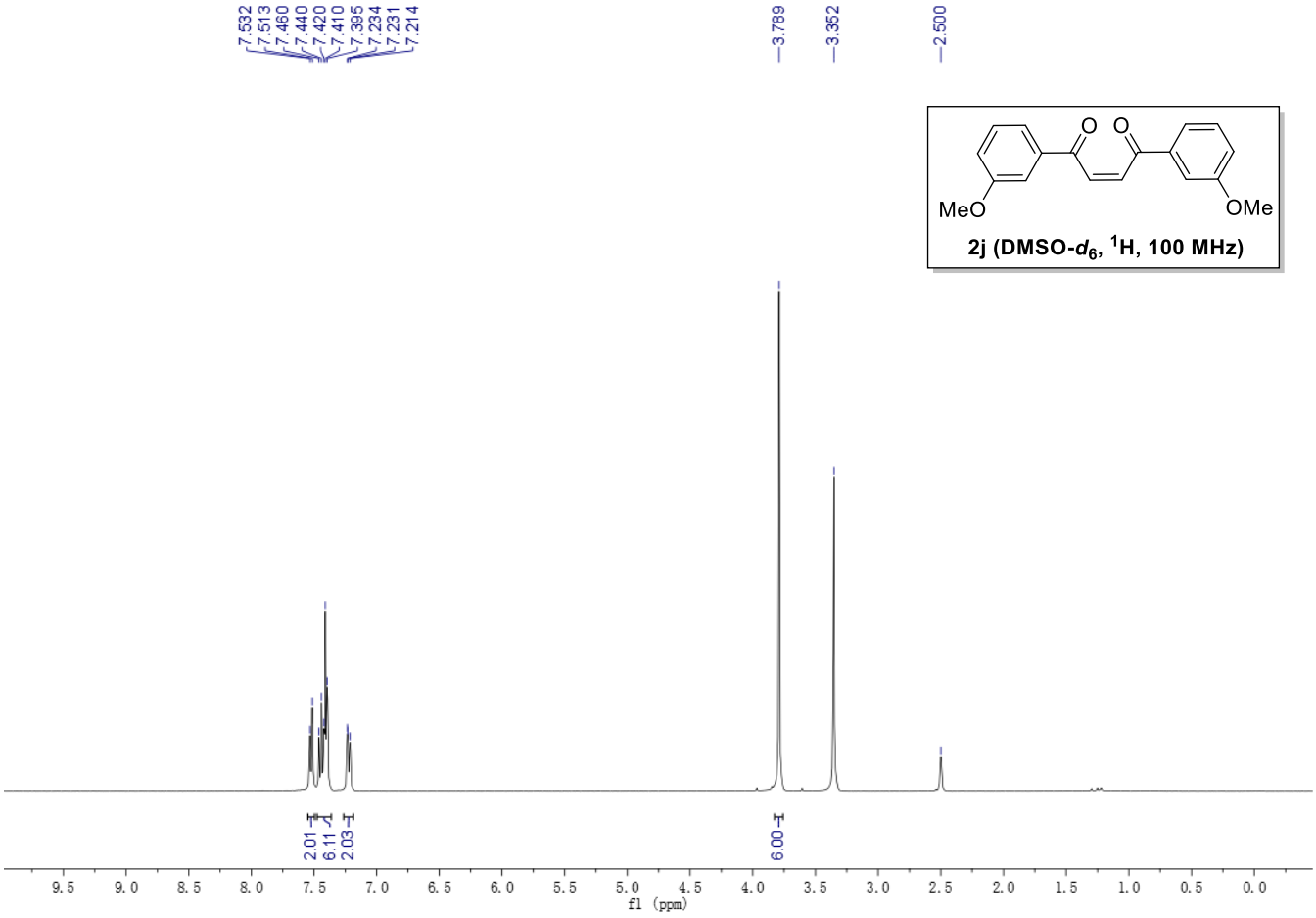

4.08
4.07
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

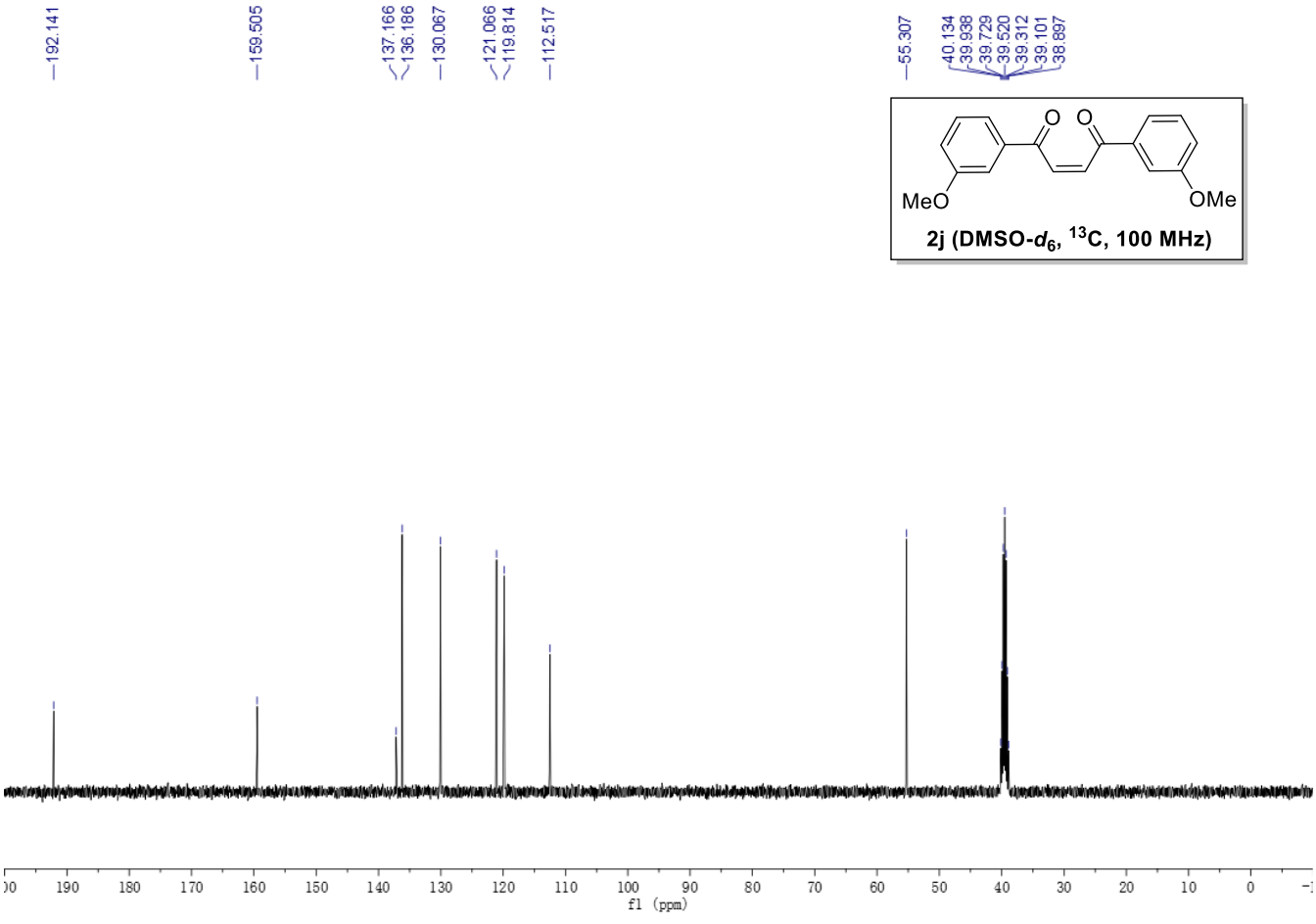

190.693
138.696
135.827
132.681
128.872
117.658
117.029
77.319
77.000
76.683
NC
O
O
CN
2h (CDCl3, 13C, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

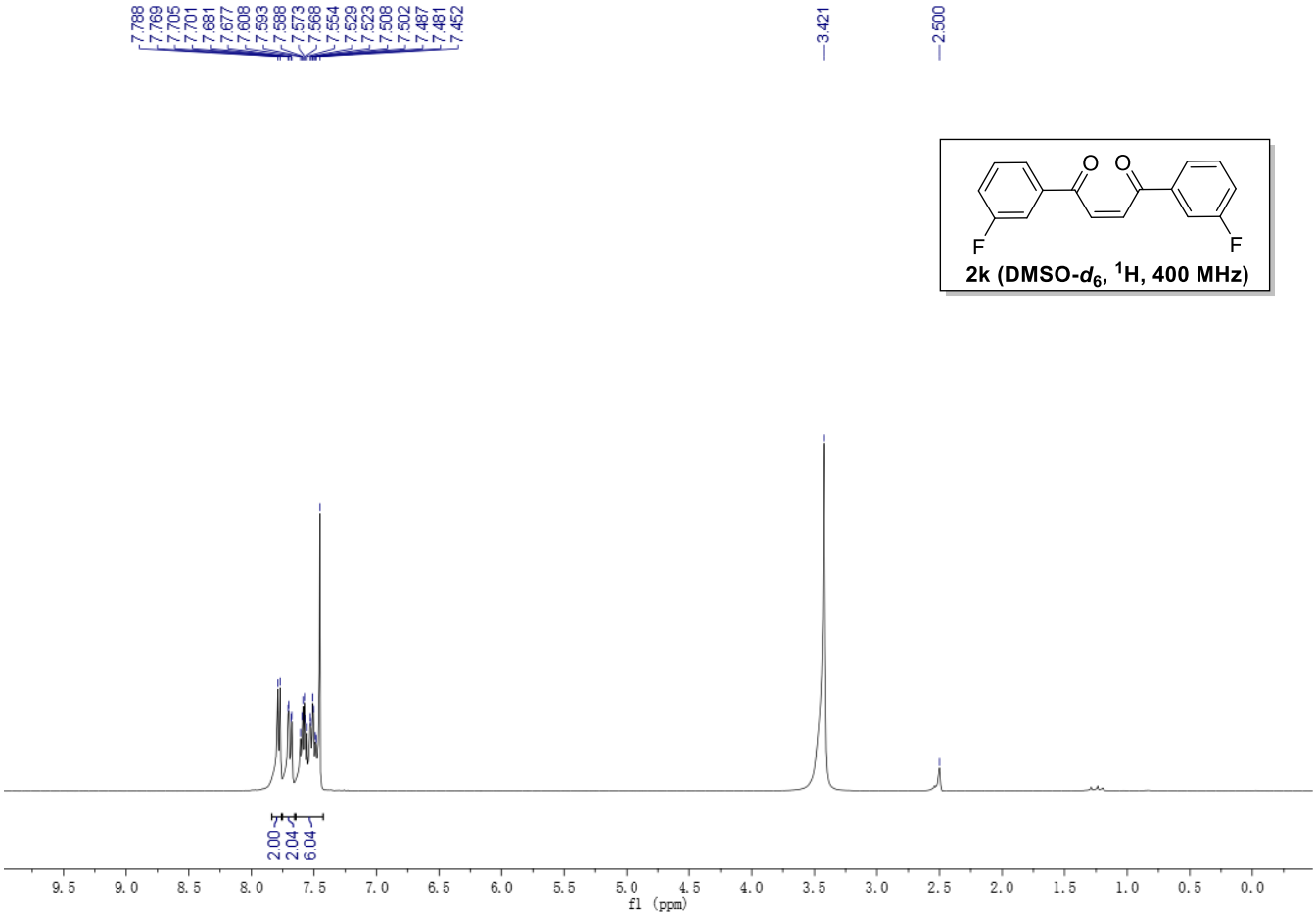

8.094
8.074
7.864
7.844
7.504
3.355
2.500
F3C
O
O
CF3
2i (DMSO-d6, 1H, 400 MHz)
4.05
4.03
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


191.863
138.731
136.475
133.136
132.819
129.220
125.936
125.058
122.347
40.142
39.935
39.729
39.520
39.313
39.105
38.897
F3C
O
O
CF3
2i (DMSO-d6, 13C, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

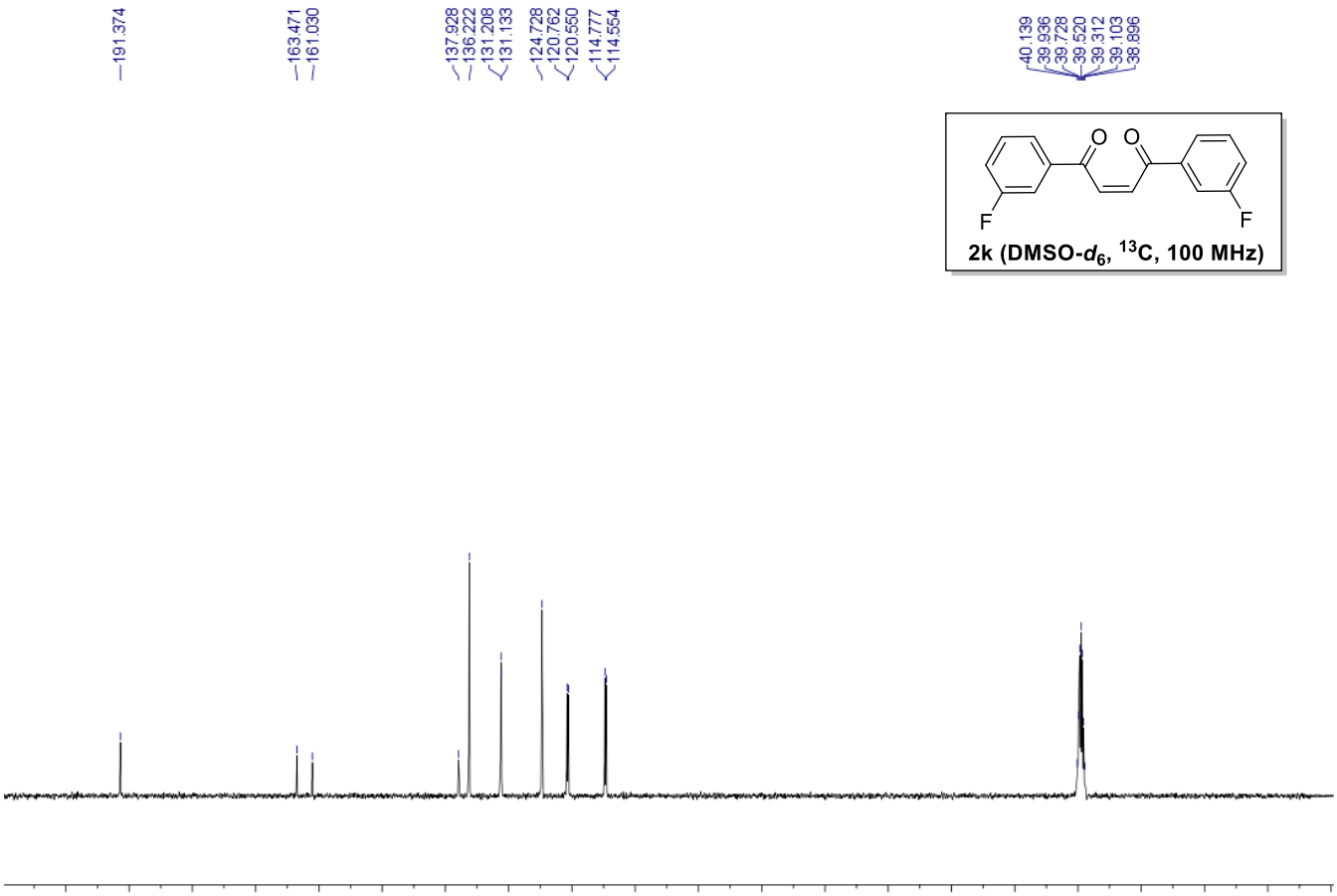

61.74
F3C
O
O
CF3
2i (DMSO-d6, 19F, 376 MHz)
-46 -48 -50 -52 -54 -56 -58 -60 -62 -64 -66 -68 -70 -72 -74 -76 -78 -80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -102
f1 (ppm)


7.532
7.513
7.460
7.440
7.420
7.410
7.395
7.234
7.231
7.214
3.789
3.352
2.500
O
O
MeO
OMe
2j (DMSO-d_6, ^{1}H, 100 MHz)
2.01
6.11
2.03
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
f1 (ppm)

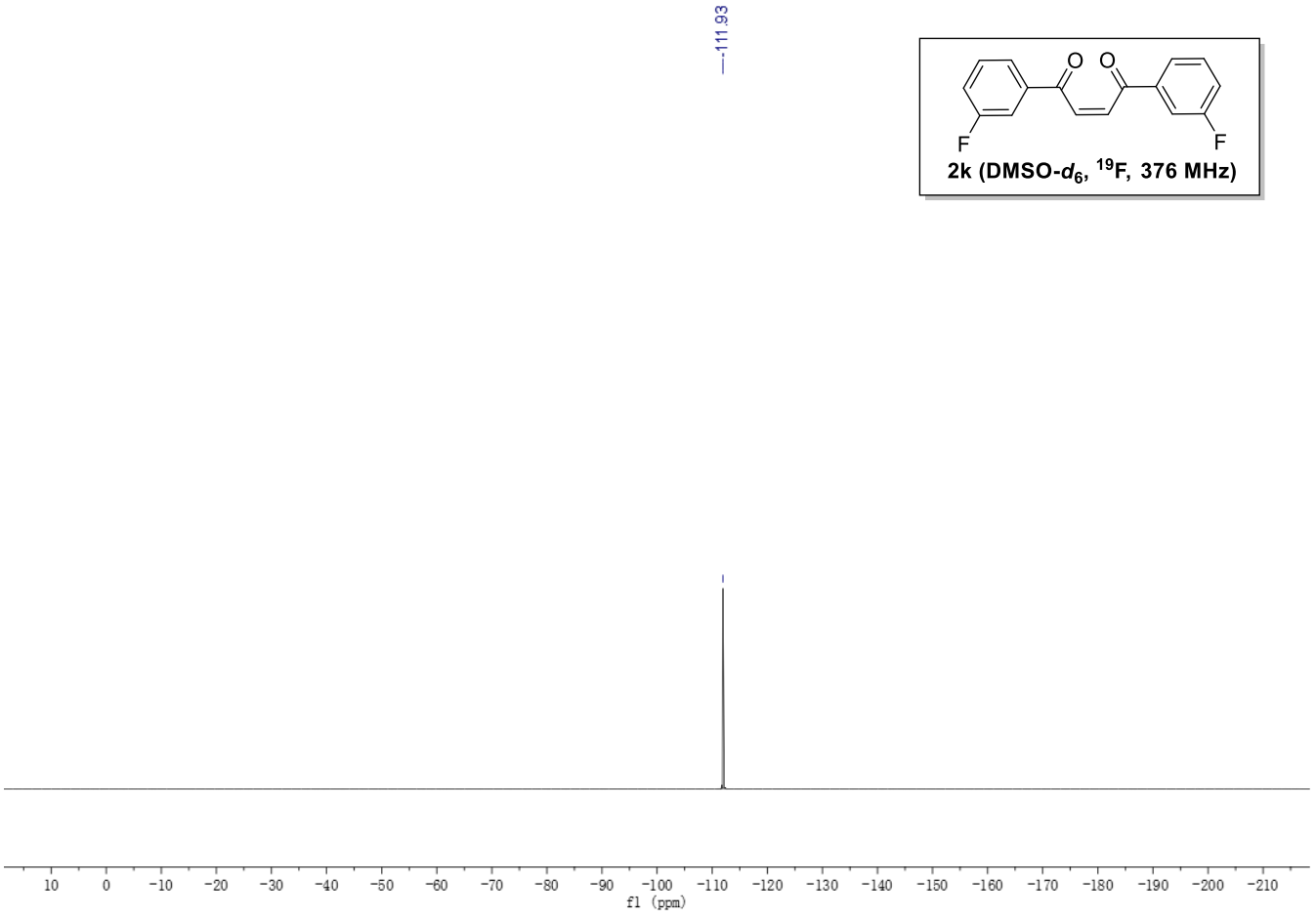

192.141
159.505
137.166
136.186
130.067
121.066
119.814
112.517
55.307
40.134
39.938
39.729
39.520
39.312
39.101
38.897
O
O
MeO
OMe
2j (DMSO-d_6, ^{13}C, 100 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

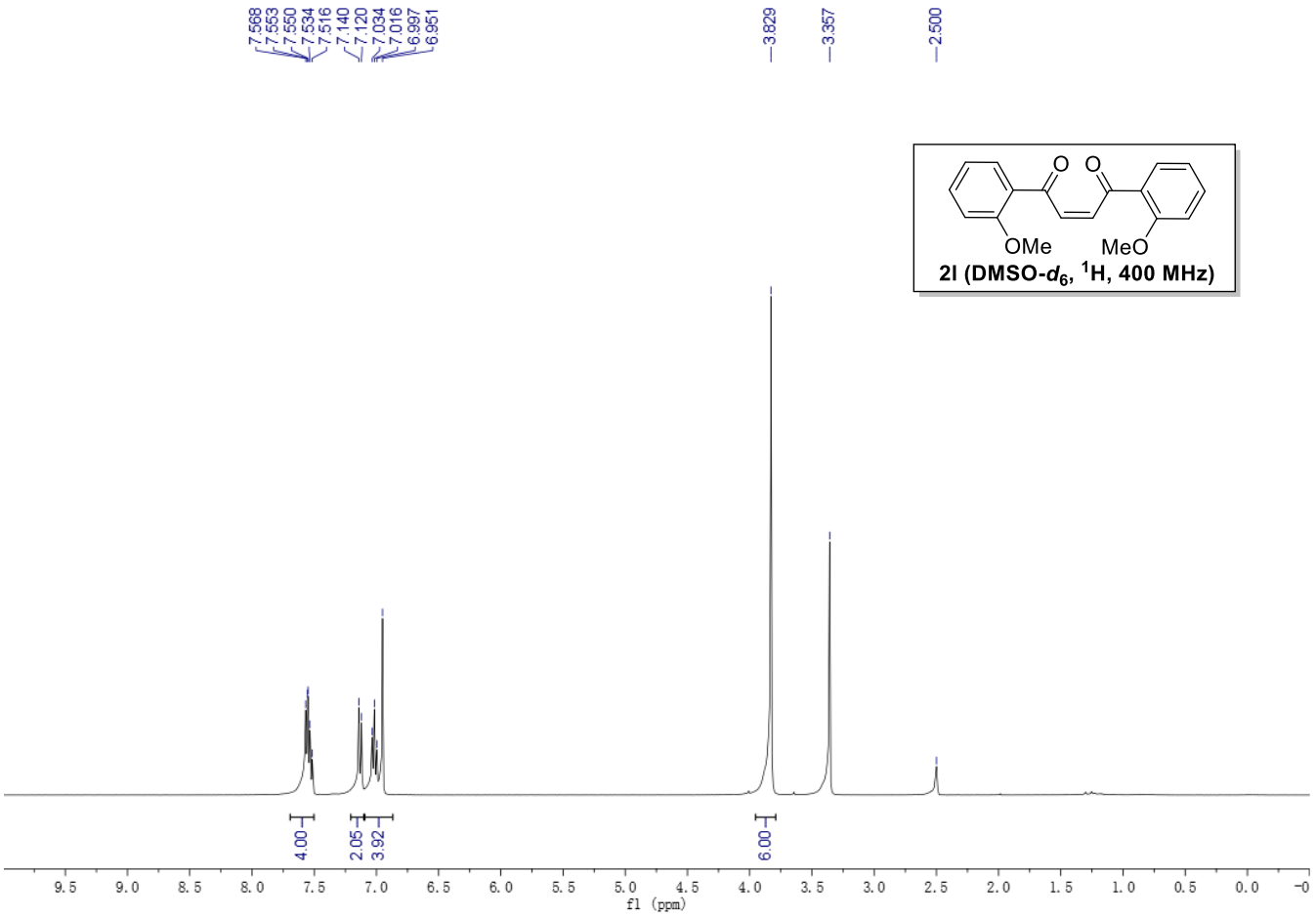


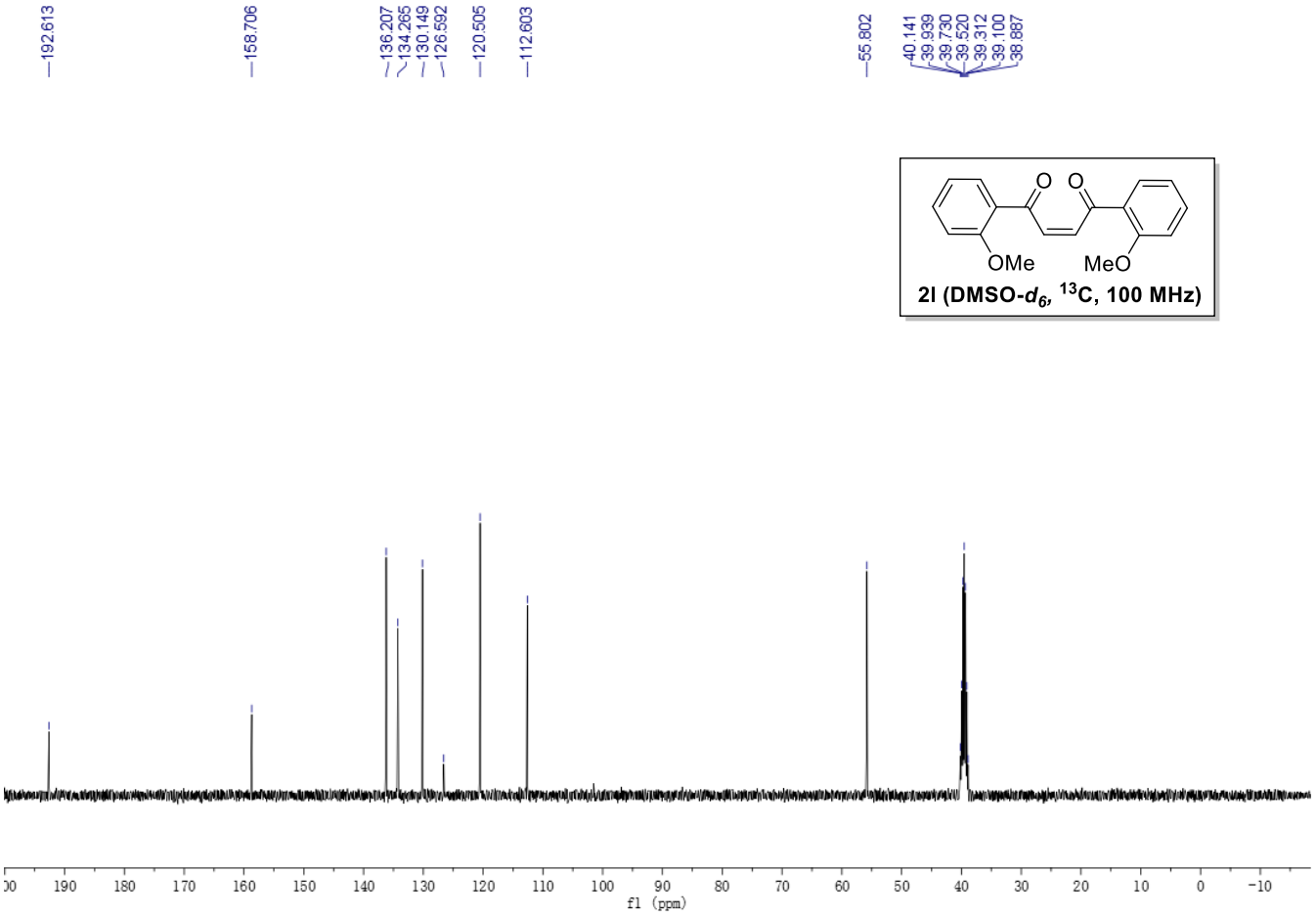
2k (DMSO-d_6, ^{1}H, 400 MHz)

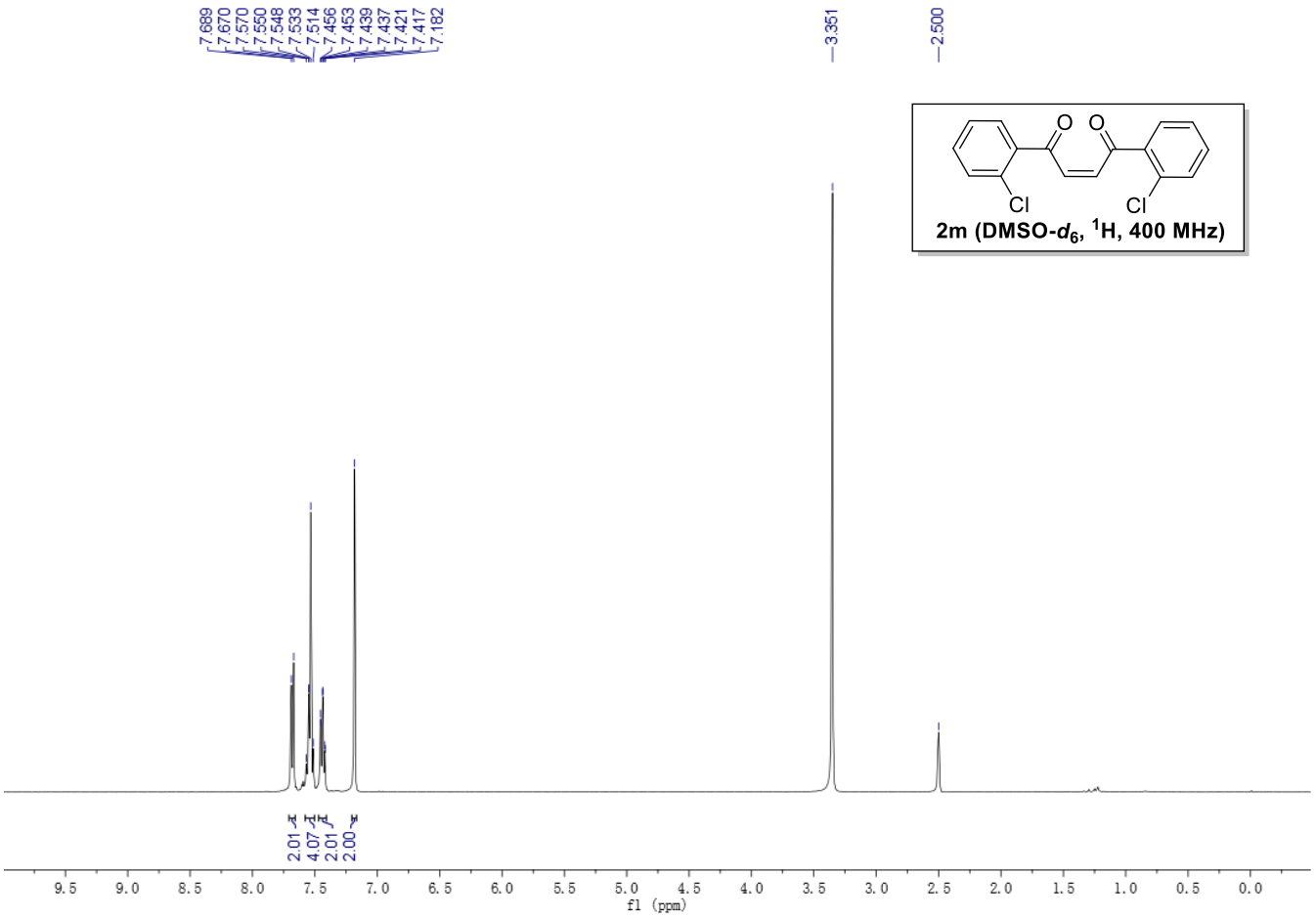


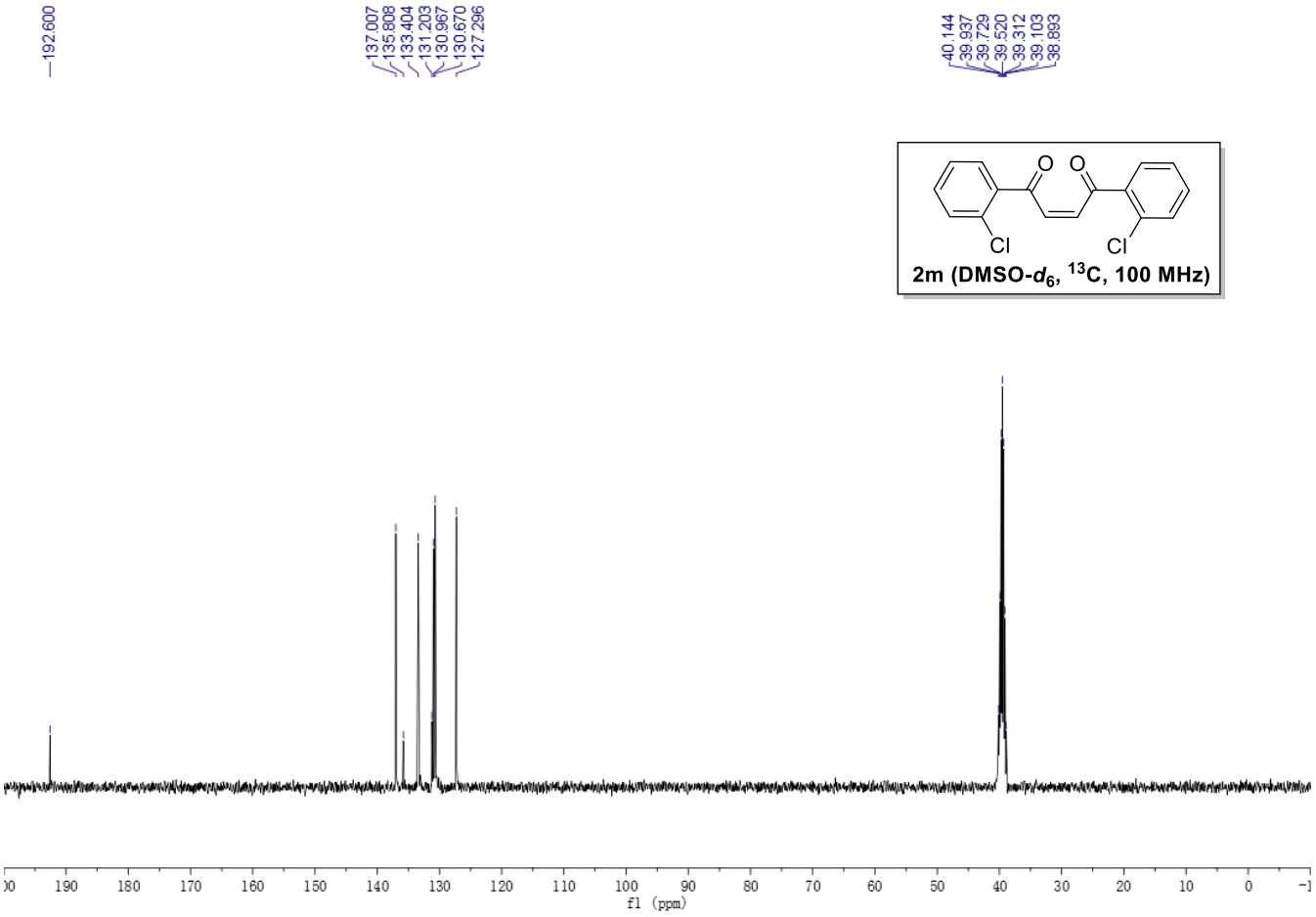
2k (DMSO-d_6, ^{13}C, 100 MHz)

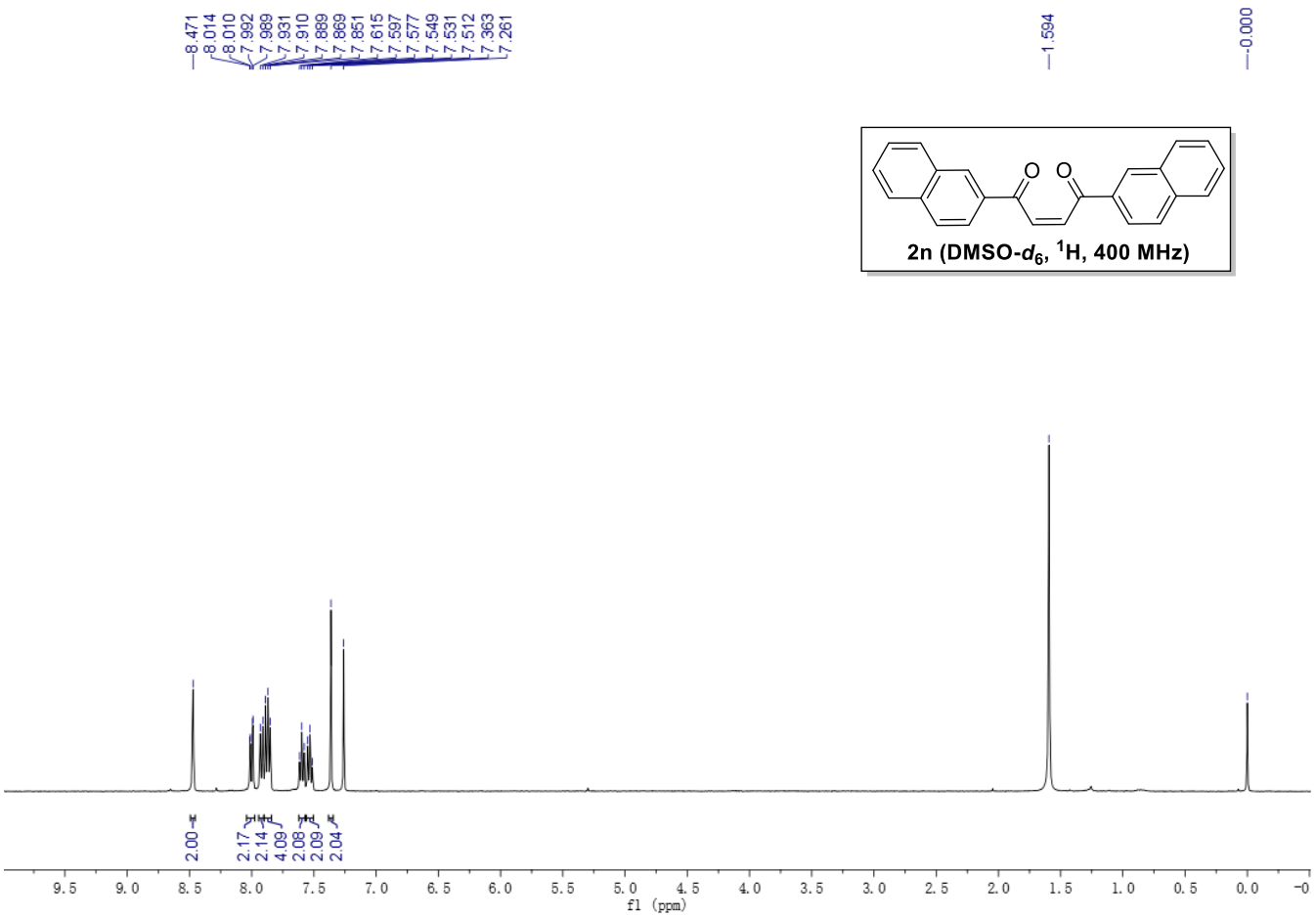

-111.93
F
F
2k (DMSO-d_6, ^{19}F, 376 MHz)
f1 (ppm)

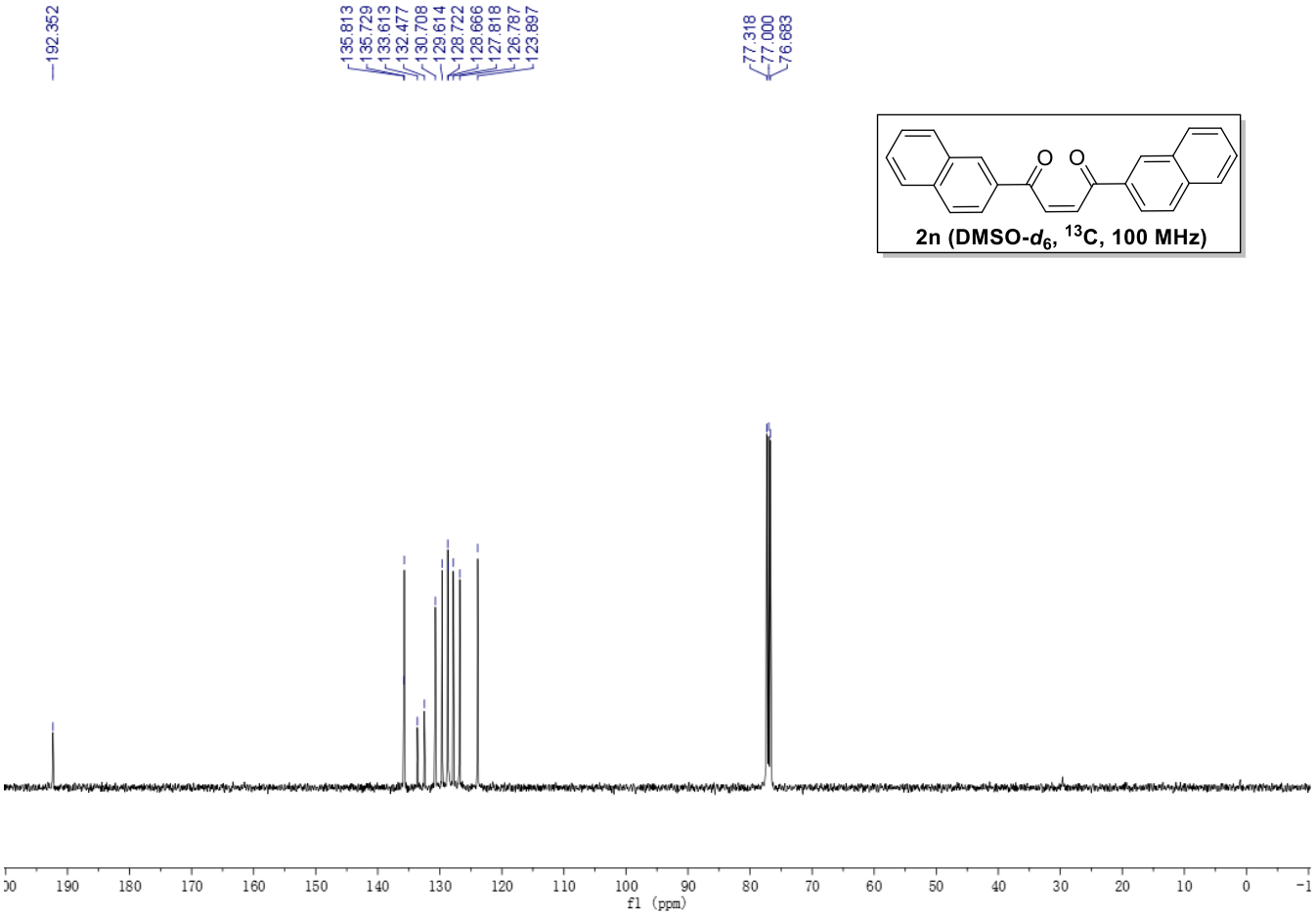

7.568
7.553
7.550
7.534
7.516
7.140
7.120
7.034
7.016
6.997
6.951
3.829
3.357
2.500
OMe
MeO
2l (DMSO-d_6, ^{1}H, 400 MHz)
4.00
2.05
3.92
6.00
f1 (ppm)

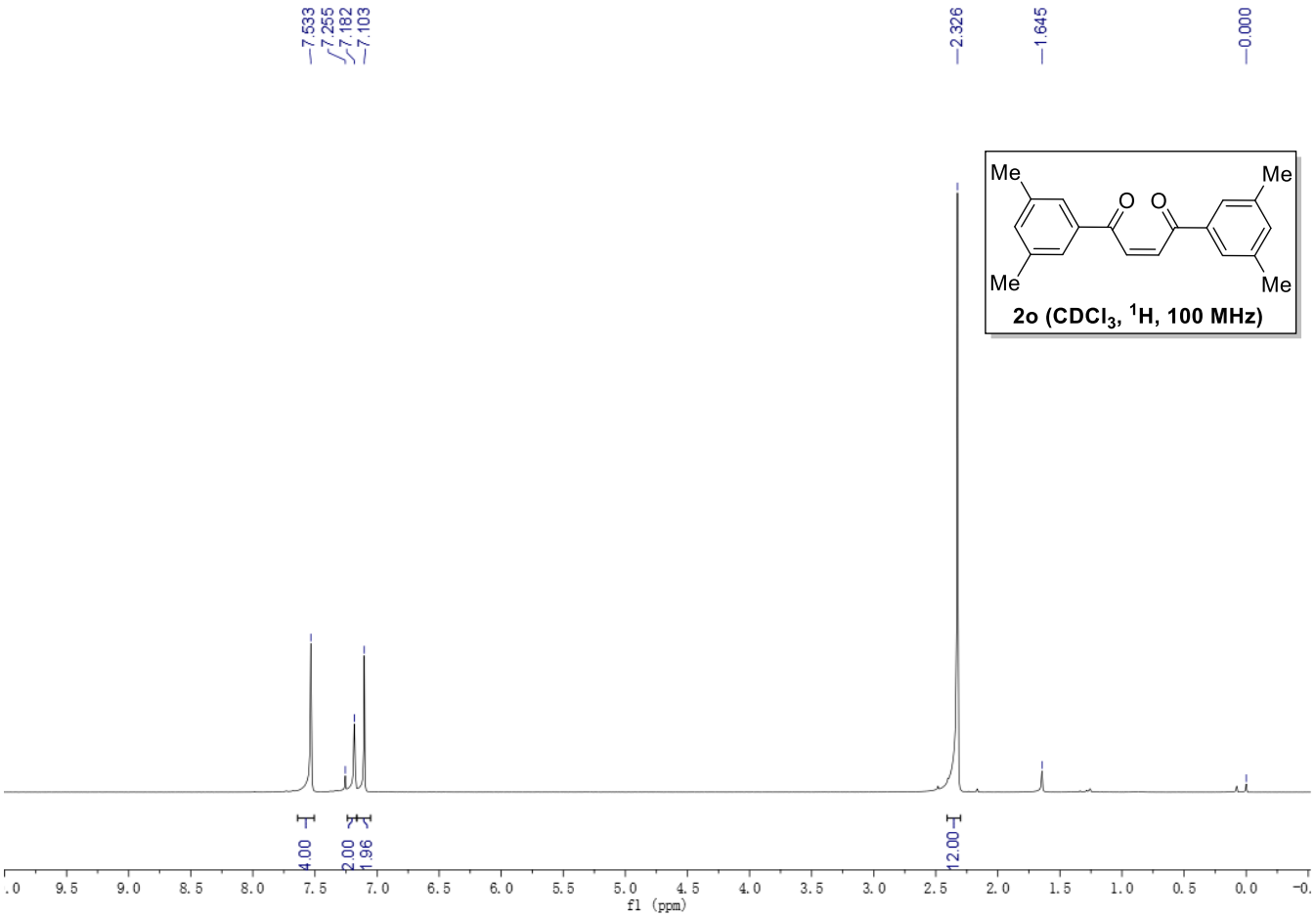

192.613
158.706
136.207
134.265
130.149
126.592
120.505
112.603
55.802
40.141
39.939
39.730
39.520
39.312
39.100
38.887
O
O
OMe
MeO
2l (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

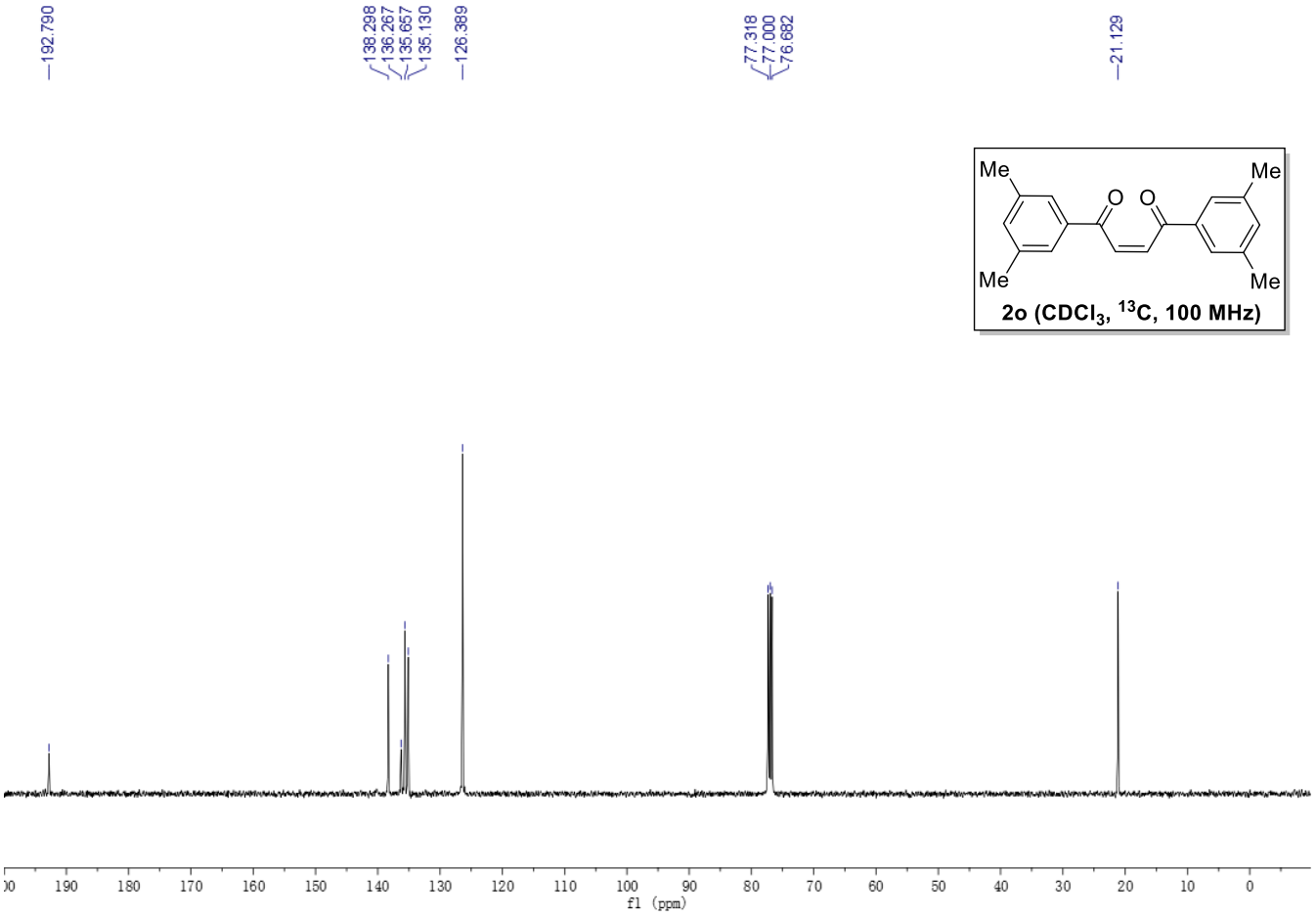

7.689
7.670
7.570
7.550
7.548
7.533
7.514
7.456
7.453
7.439
7.437
7.421
7.417
7.182
3.351
2.500
O
O
Cl
Cl
2m (DMSO-d_6, ^{1}H, 400 MHz)
2.01
4.07
2.01
2.00
f1 (ppm)

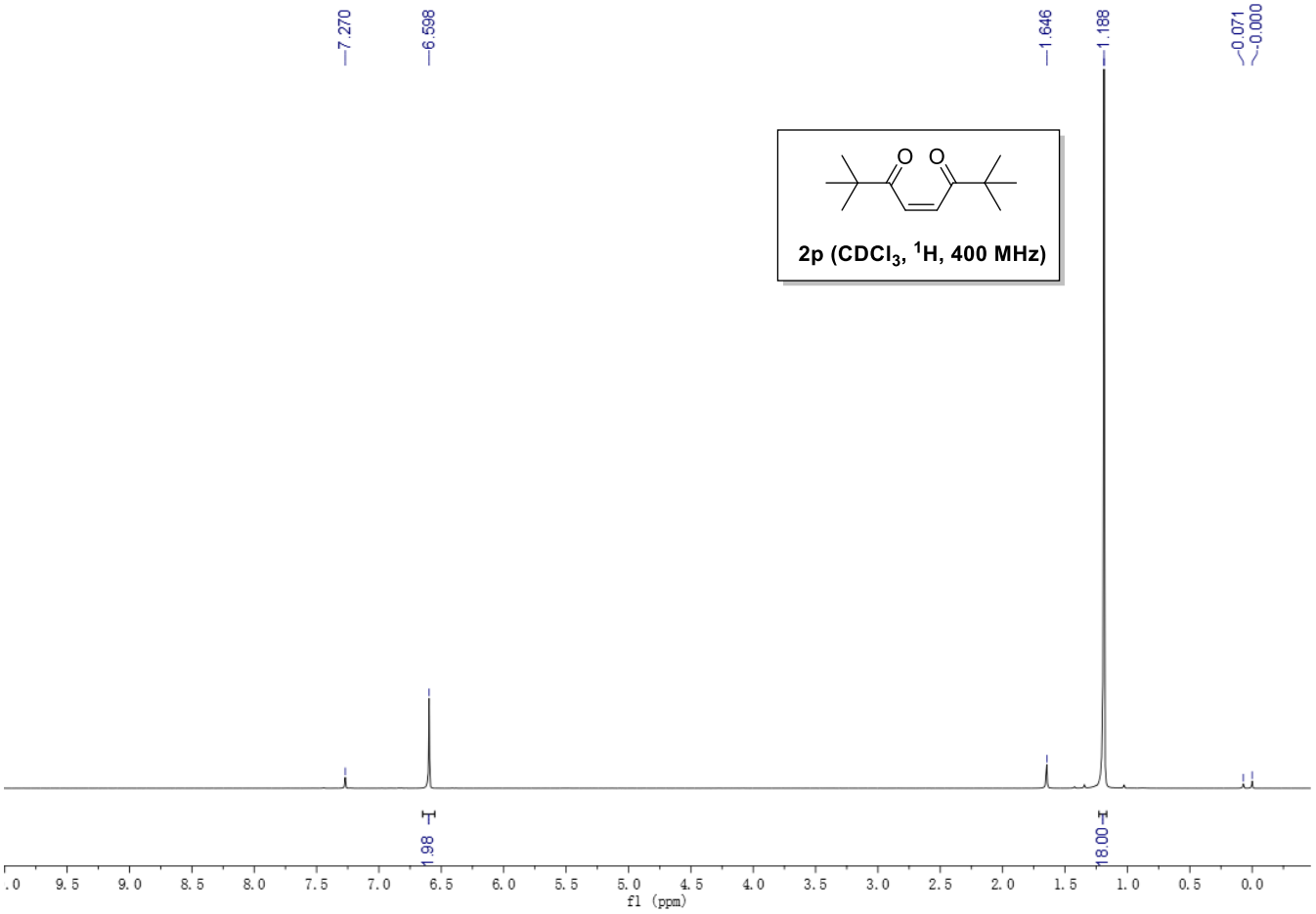

192.600
137.007
135.808
133.404
131.203
130.967
130.670
127.296
40.144
39.937
39.729
39.520
39.312
39.103
38.893
O
O
Cl
Cl
2m (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

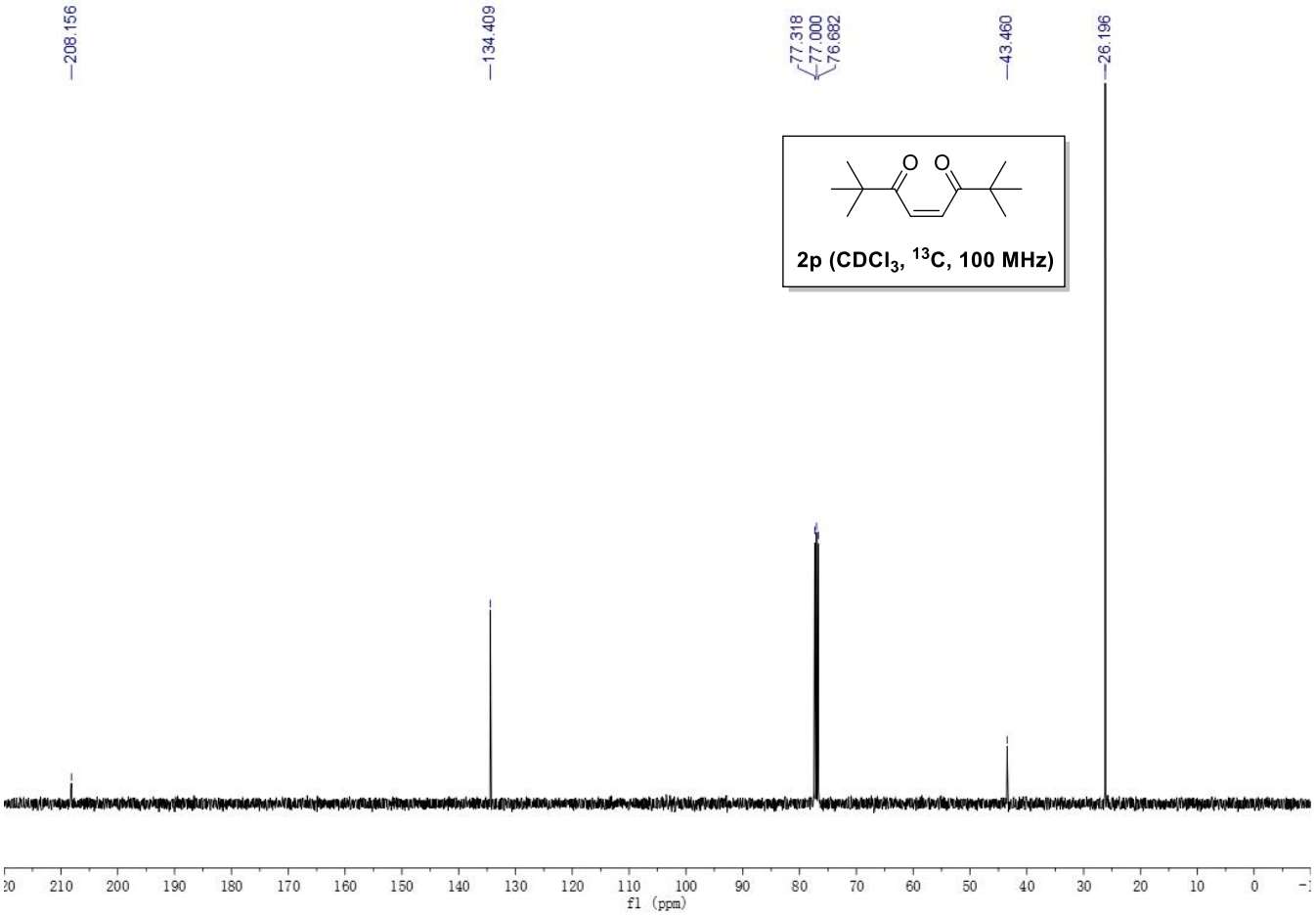

8.471
8.014
8.010
7.992
7.989
7.931
7.910
7.889
7.869
7.851
7.615
7.597
7.577
7.549
7.531
7.512
7.363
7.261
1.594
0.000
O
O
2n (DMSO-d_6, ^{1}H, 400 MHz)
2.00
2.17
2.14
4.09
2.08
2.09
2.04
f1 (ppm)

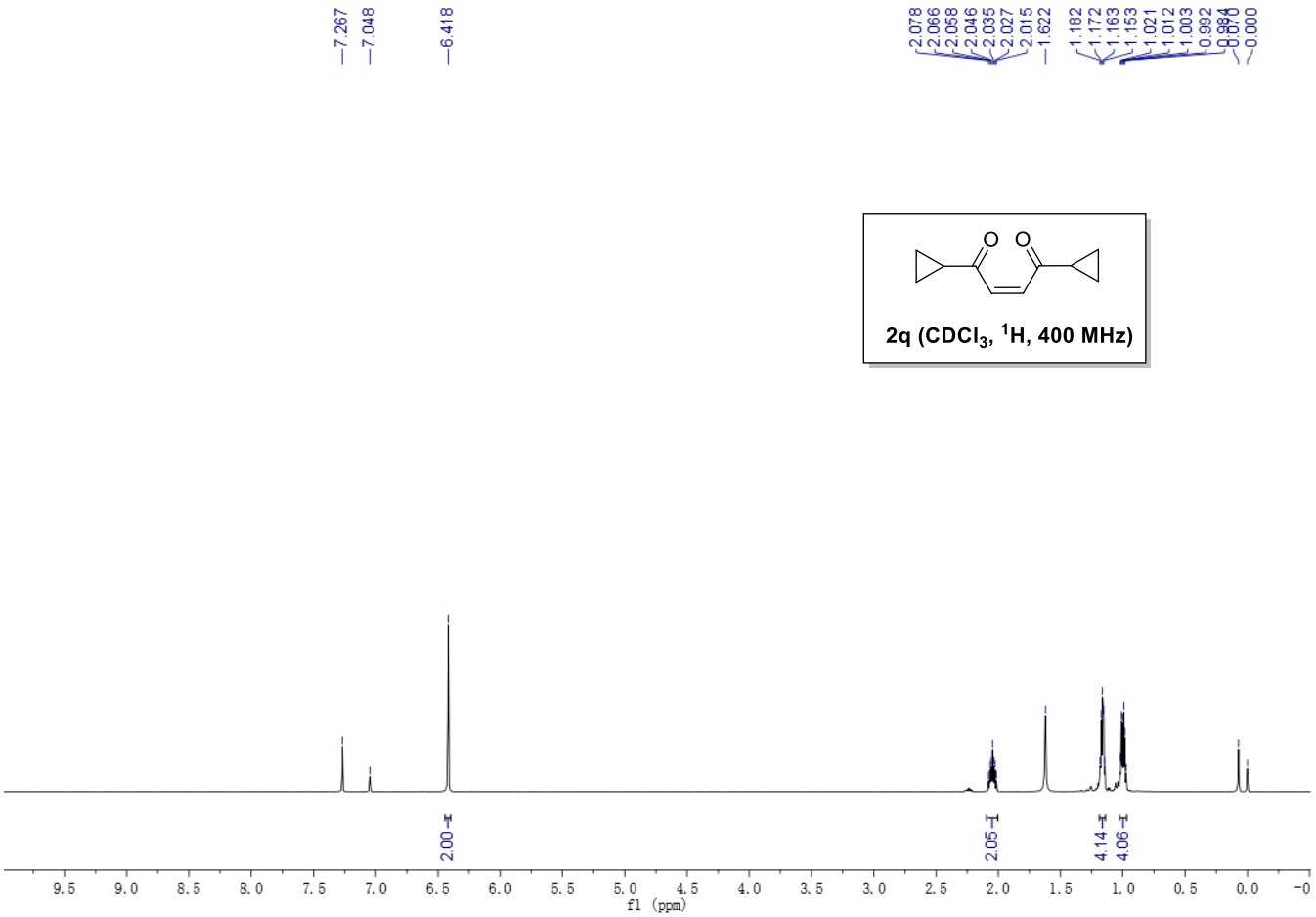

192.352
135.813
135.729
133.613
132.477
130.708
129.614
128.722
128.666
127.818
126.787
123.897
77.318
77.000
76.683
2n (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

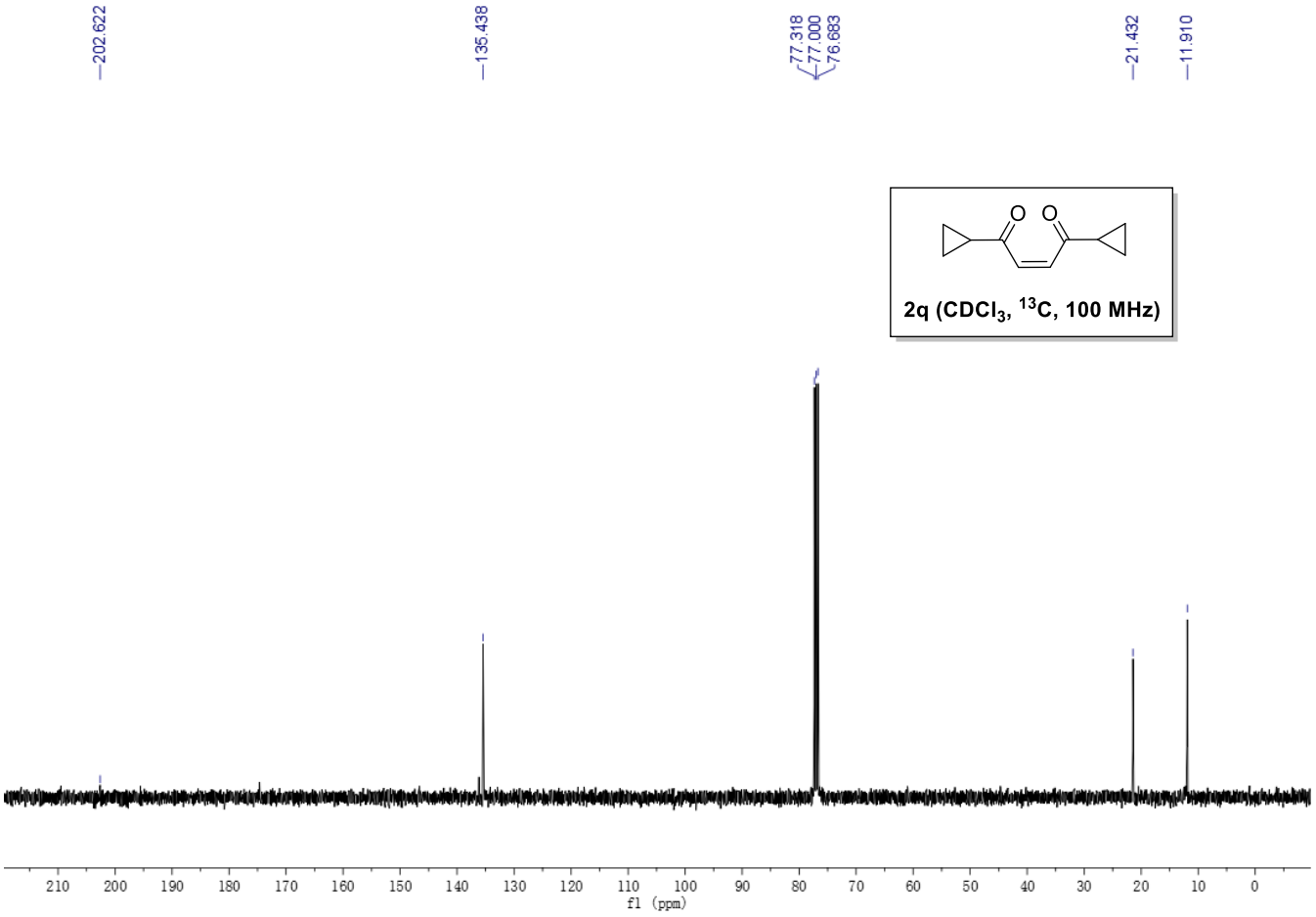

7.533
7.255
7.182
7.103
2.326
1.645
0.000
Me
Me
Me
Me
2o ($CDCl_3$, ^{1}H, 100 MHz)
4.00
2.00
1.96
12.00
f1 (ppm)

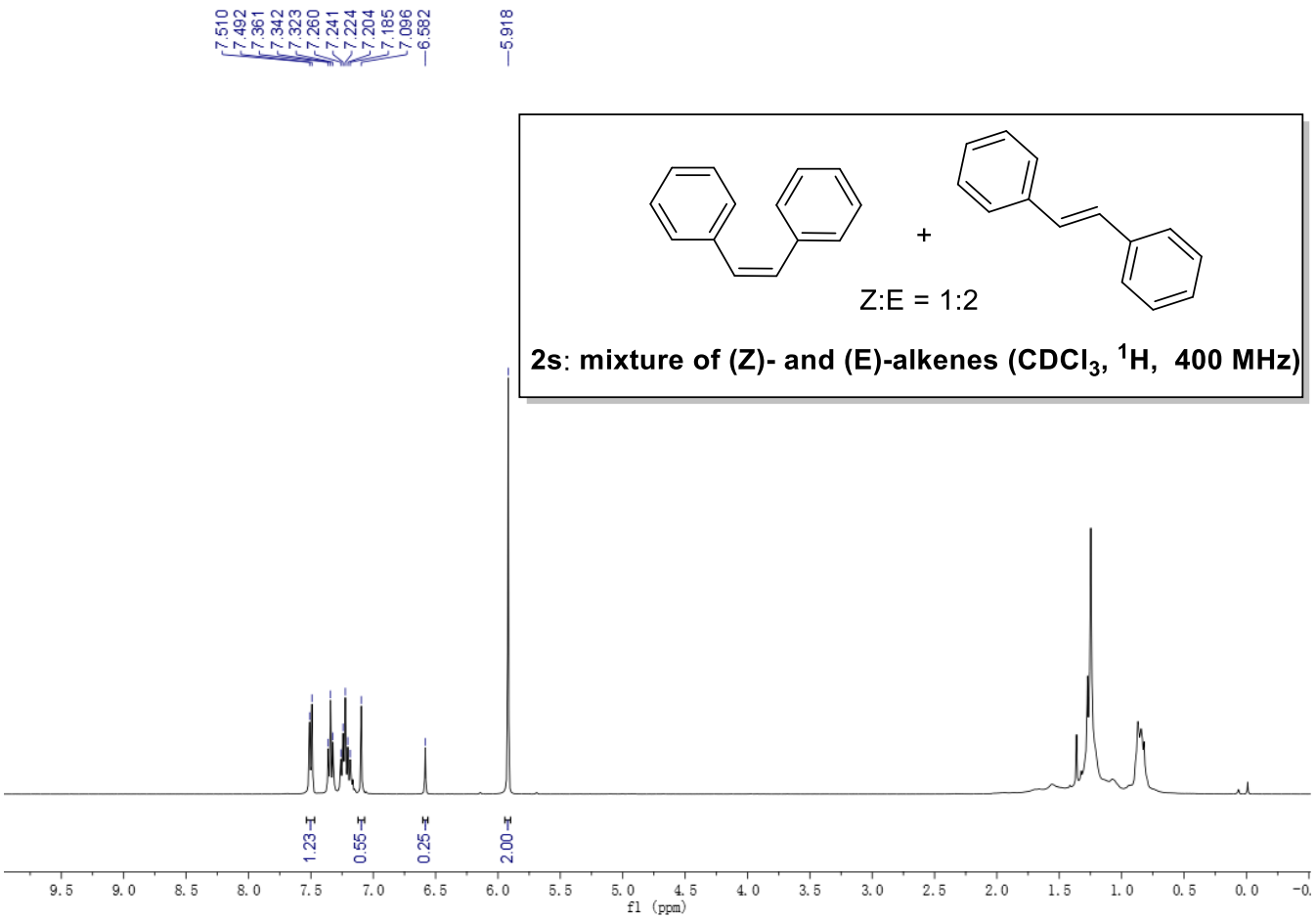

192.790
138.298
136.267
135.657
135.130
126.389
77.318
77.000
76.682
21.129
Me
Me
Me
Me
O
O
2o (CDCl3, 13C, 100 MHz)
f1 (ppm)

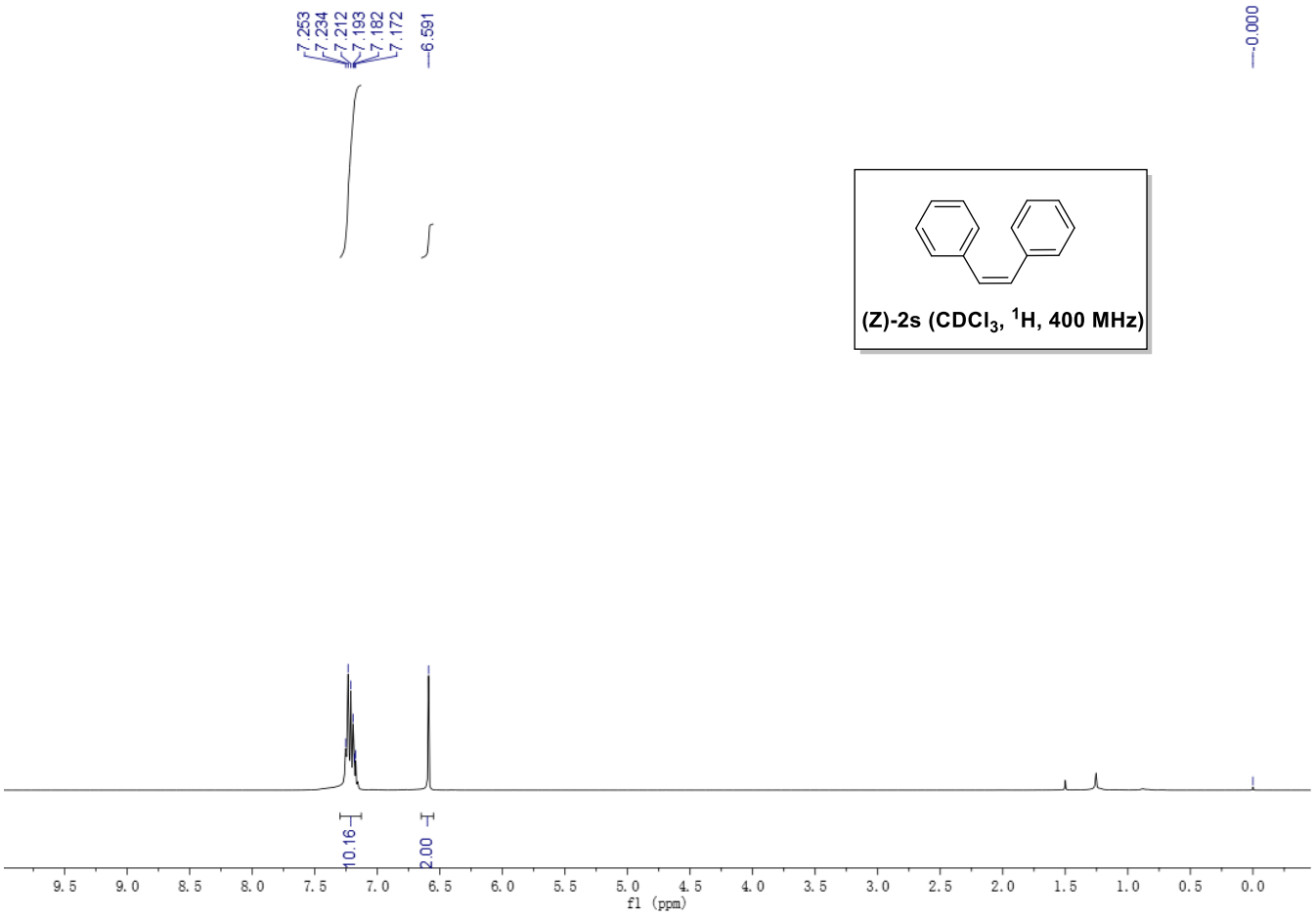

7.270
6.598
1.646
1.188
0.071
0.000
O
O
2p (CDCl3, 1H, 400 MHz)
1.98
18.00
f1 (ppm)


208.156
134.409
77.318
77.000
76.682
43.460
26.196
O
O
2p (CDCl3, 13C, 100 MHz)
f1 (ppm)

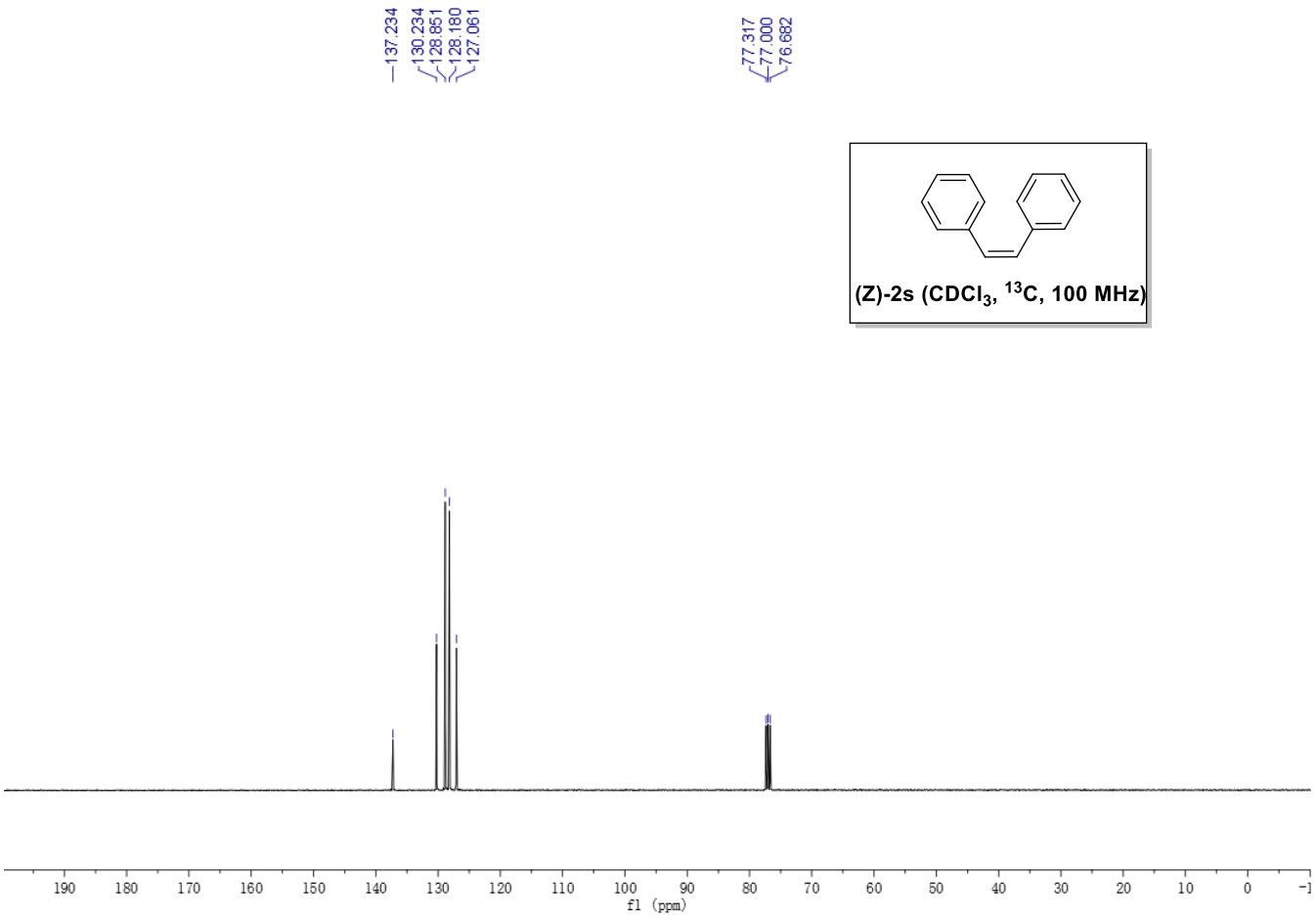

7.267
7.048
6.418
2.078
2.066
2.058
2.046
2.035
2.027
2.015
1.622
1.182
1.172
1.163
1.153
1.021
1.012
1.003
0.992
0.000
O
O
2q (CDCl3, 1H, 400 MHz)
2.00
2.05
4.14
4.06
f1 (ppm)


202.622
135.438
77.318
77.000
76.683
21.432
11.910
O
O
2q (CDCl3, 13C, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

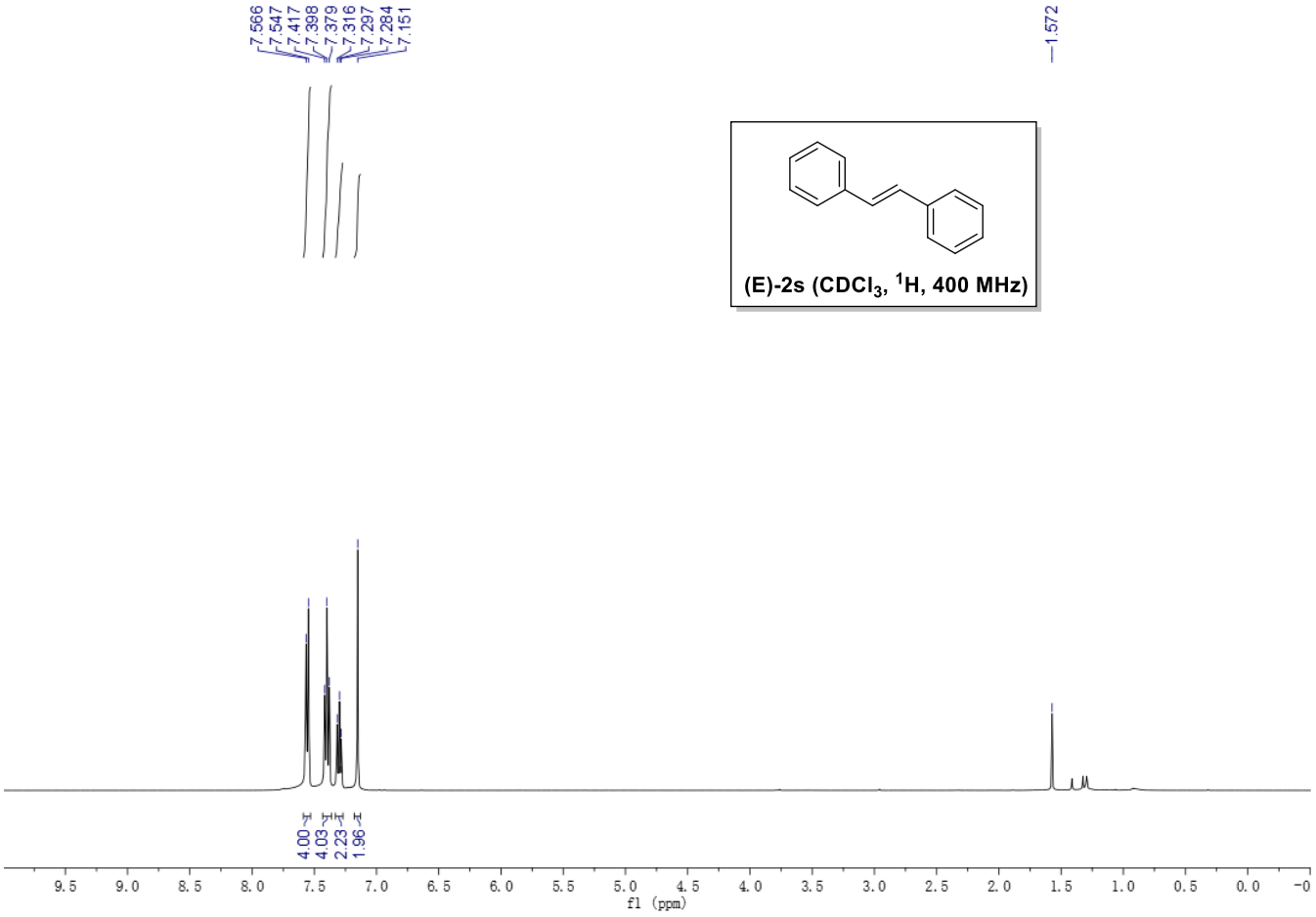

7.510
7.492
7.361
7.342
7.323
7.260
7.241
7.224
7.204
7.185
7.096
6.582
5.918
+
Z:E = 1:2
2s: mixture of (Z)- and (E)-alkenes (CDCl3, 1H, 400 MHz)
1.23
0.55
0.25
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



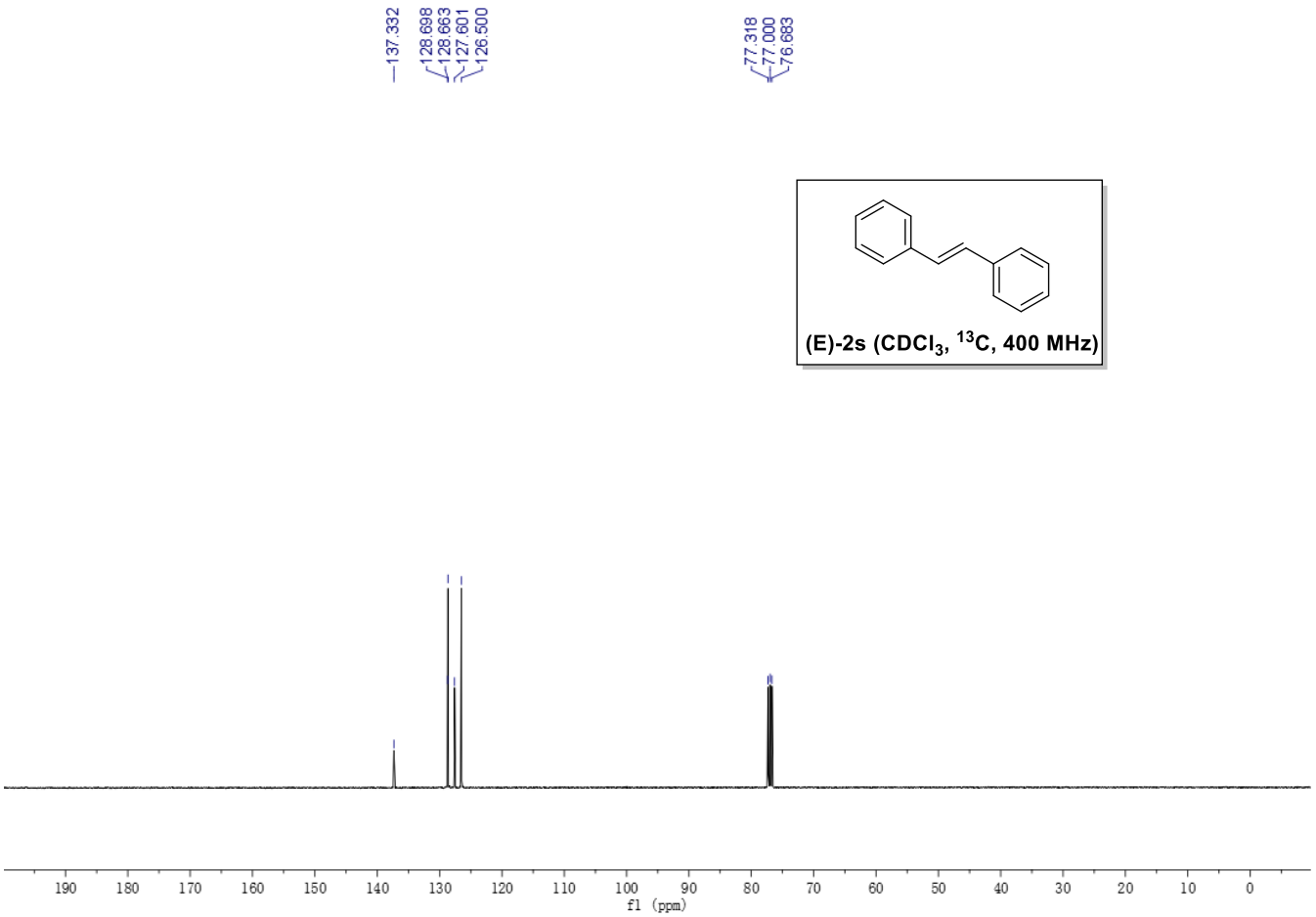
(Z)-2s ($CDCl_3$, ^1H, 400 MHz)



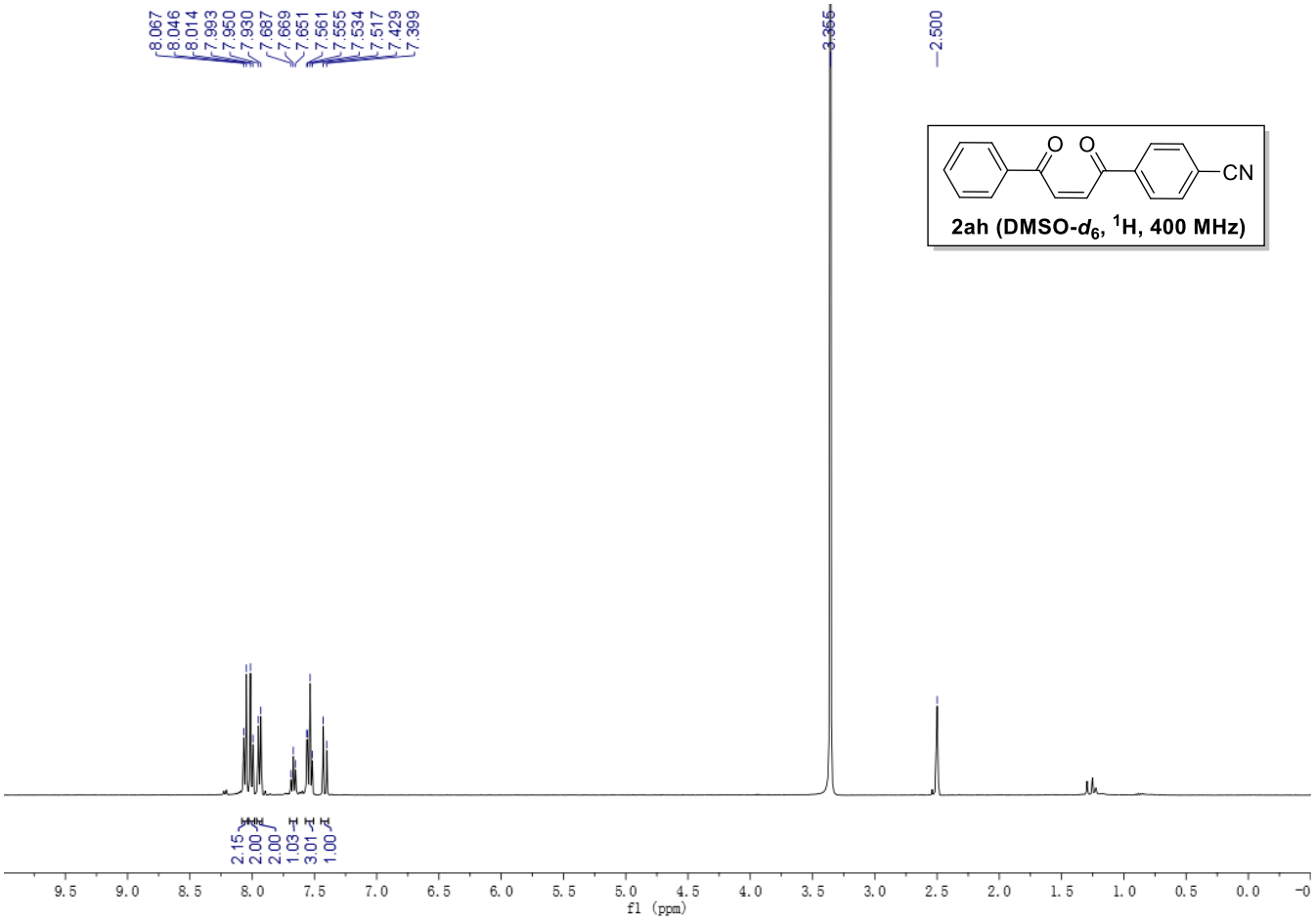
(Z)-2s ($CDCl_3$, ^{13}C, 100 MHz)

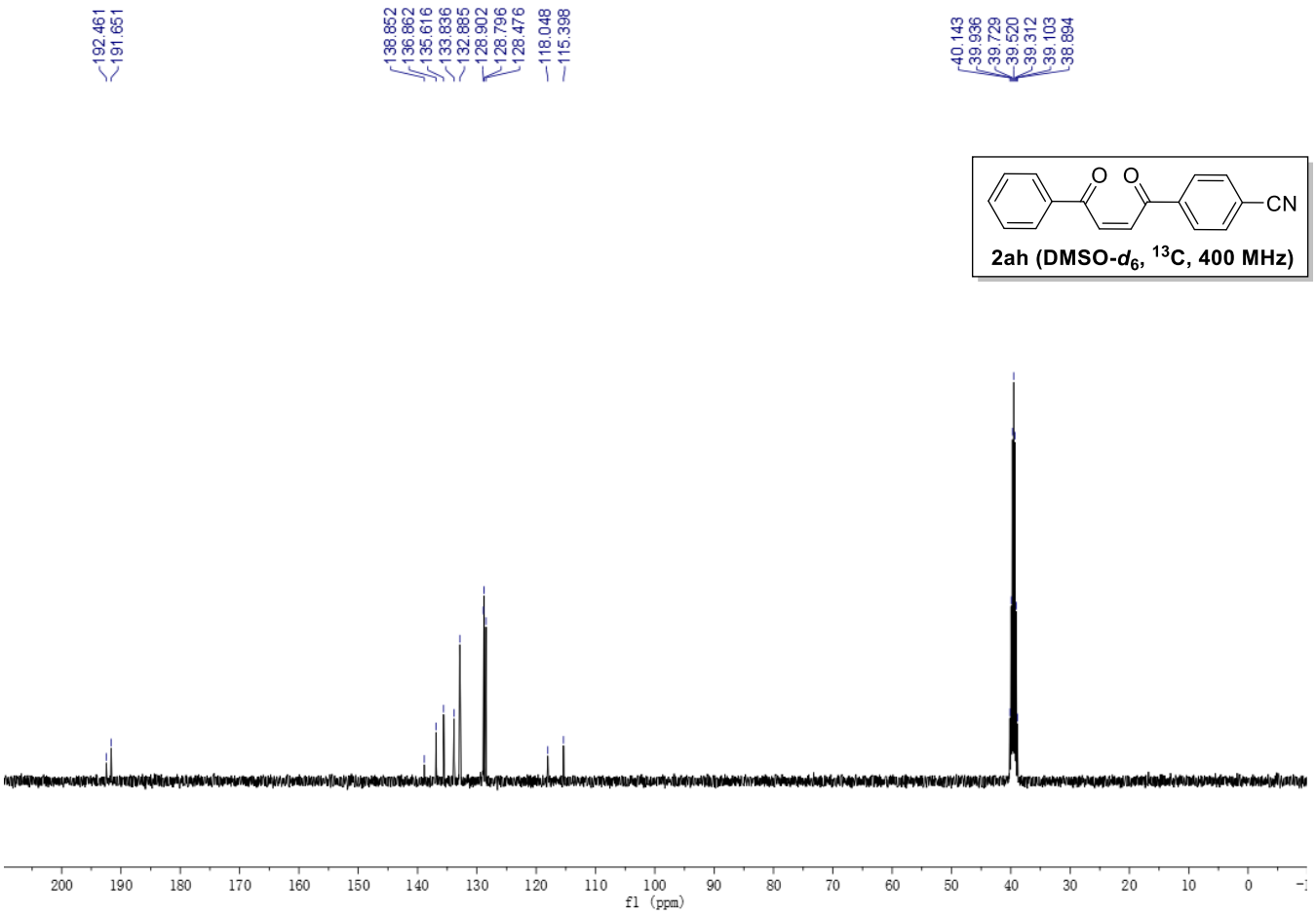


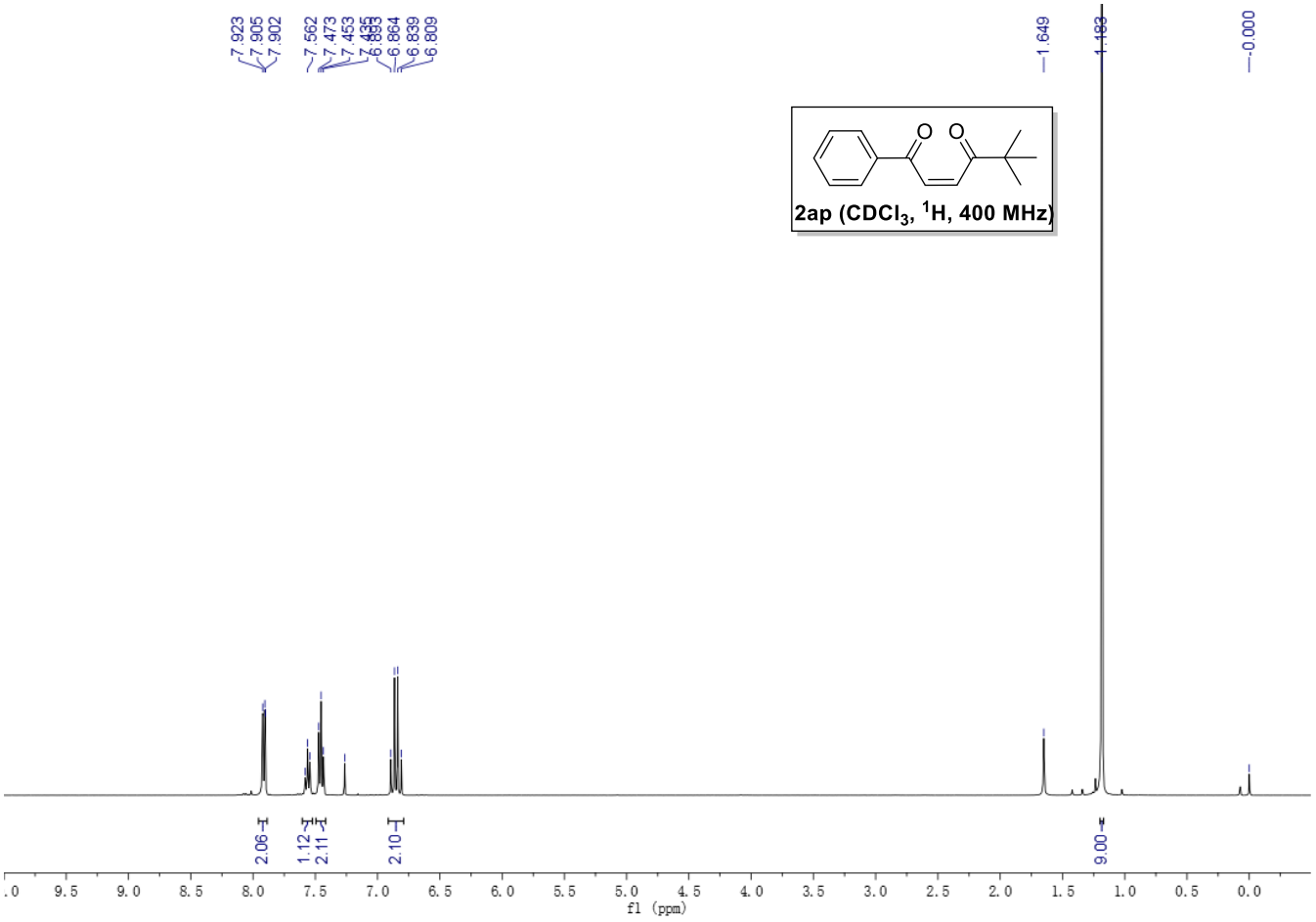
(E)-2s ($CDCl_3$, ^1H, 400 MHz)



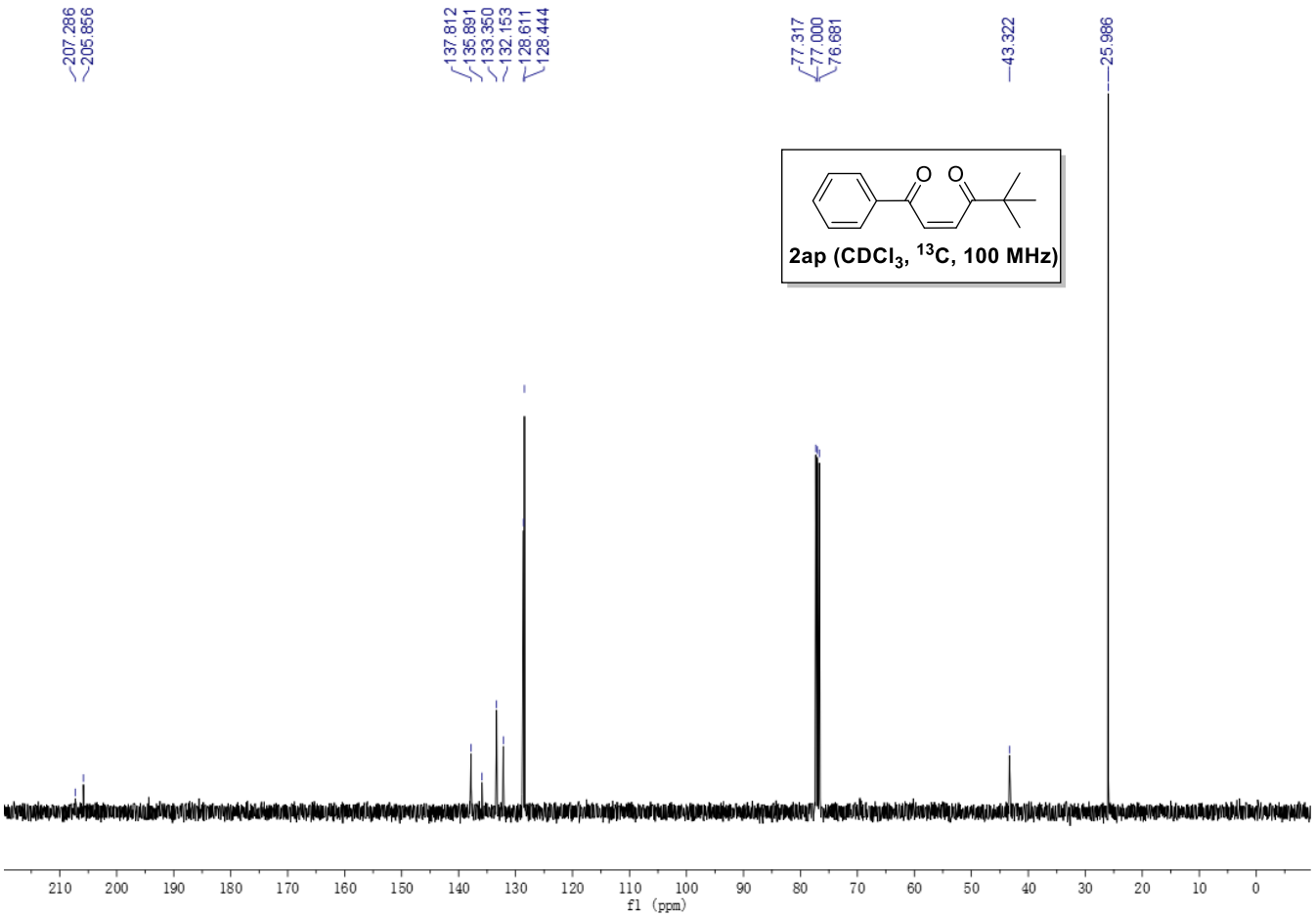
(E)-2s ($CDCl_3$, ^{13}C, 400 MHz)


8.067
8.046
8.014
7.993
7.950
7.930
7.687
7.669
7.651
7.561
7.555
7.534
7.517
7.429
7.399
3.365
2.500
O
O
CN
2ah (DMSO-d_6, ^{1}H, 400 MHz)
2.15
2.00
2.00
1.03
3.01
1.00
f1 (ppm)

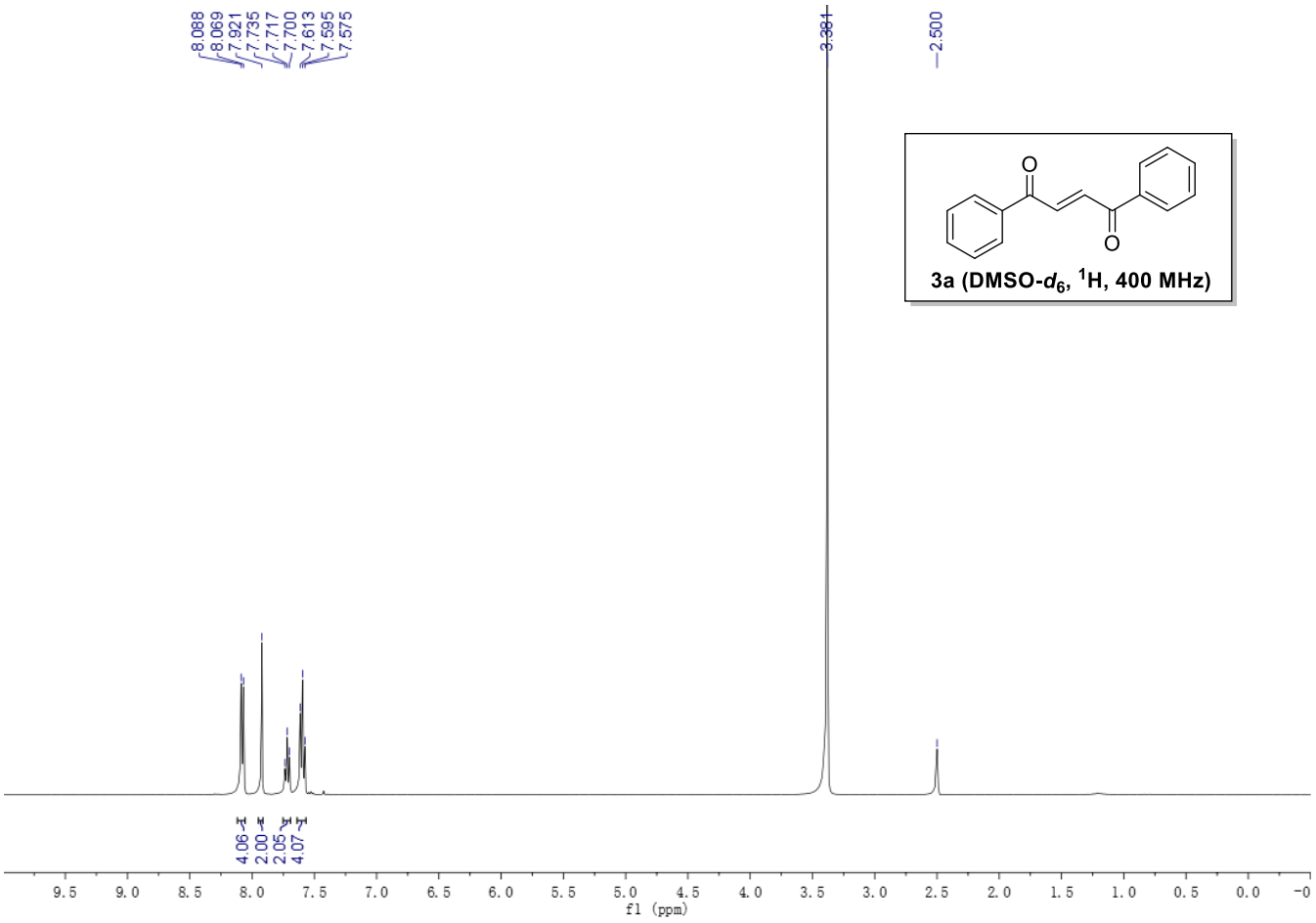

192.461
191.651
138.852
136.862
135.616
133.836
132.885
128.902
128.796
128.476
118.048
115.398
40.143
39.936
39.729
39.520
39.312
39.103
38.894
O
O
CN
2ah (DMSO-d_6, ^{13}C, 400 MHz)
f1 (ppm)



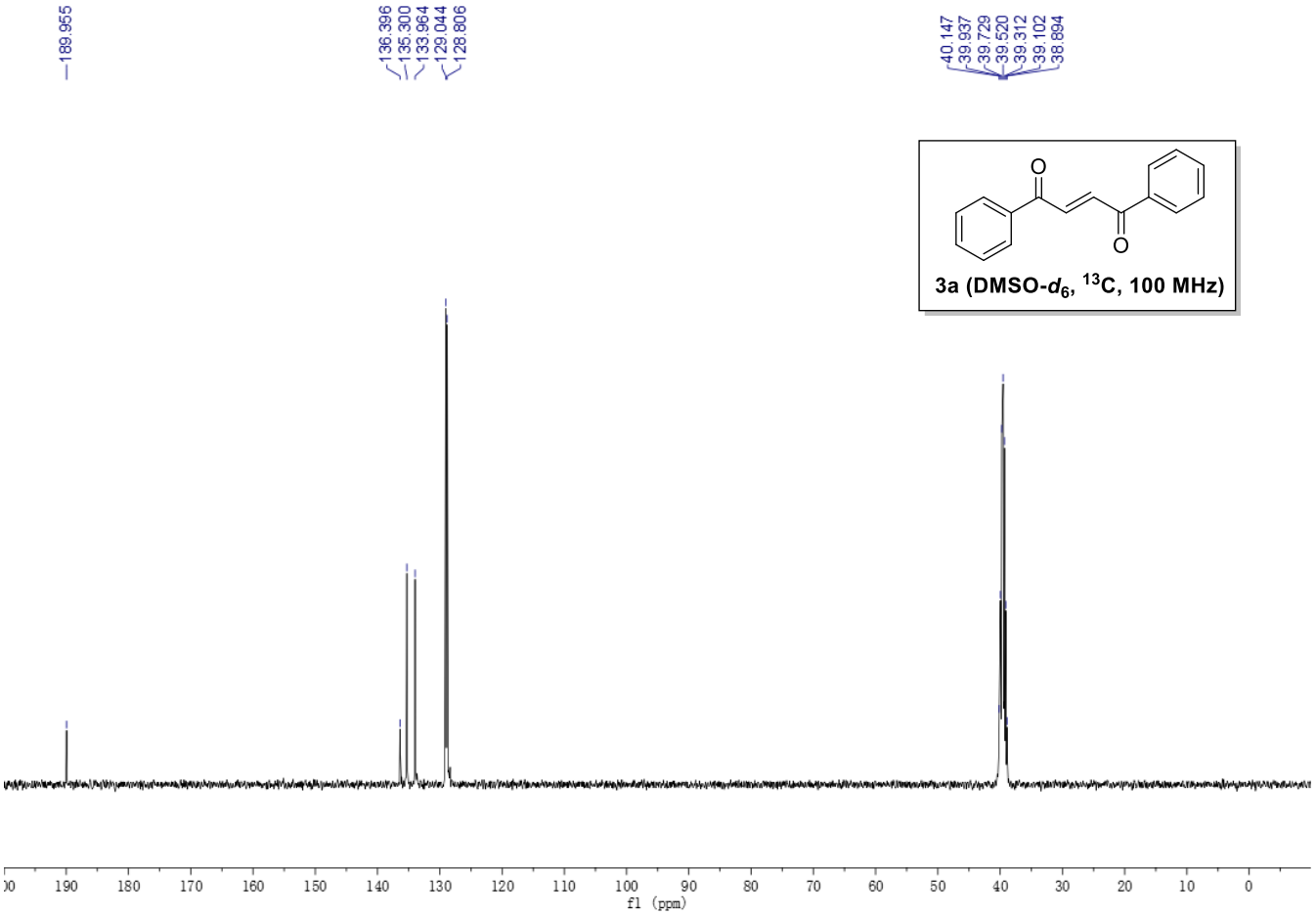
2ap ($CDCl_3$, ^1H, 400 MHz)



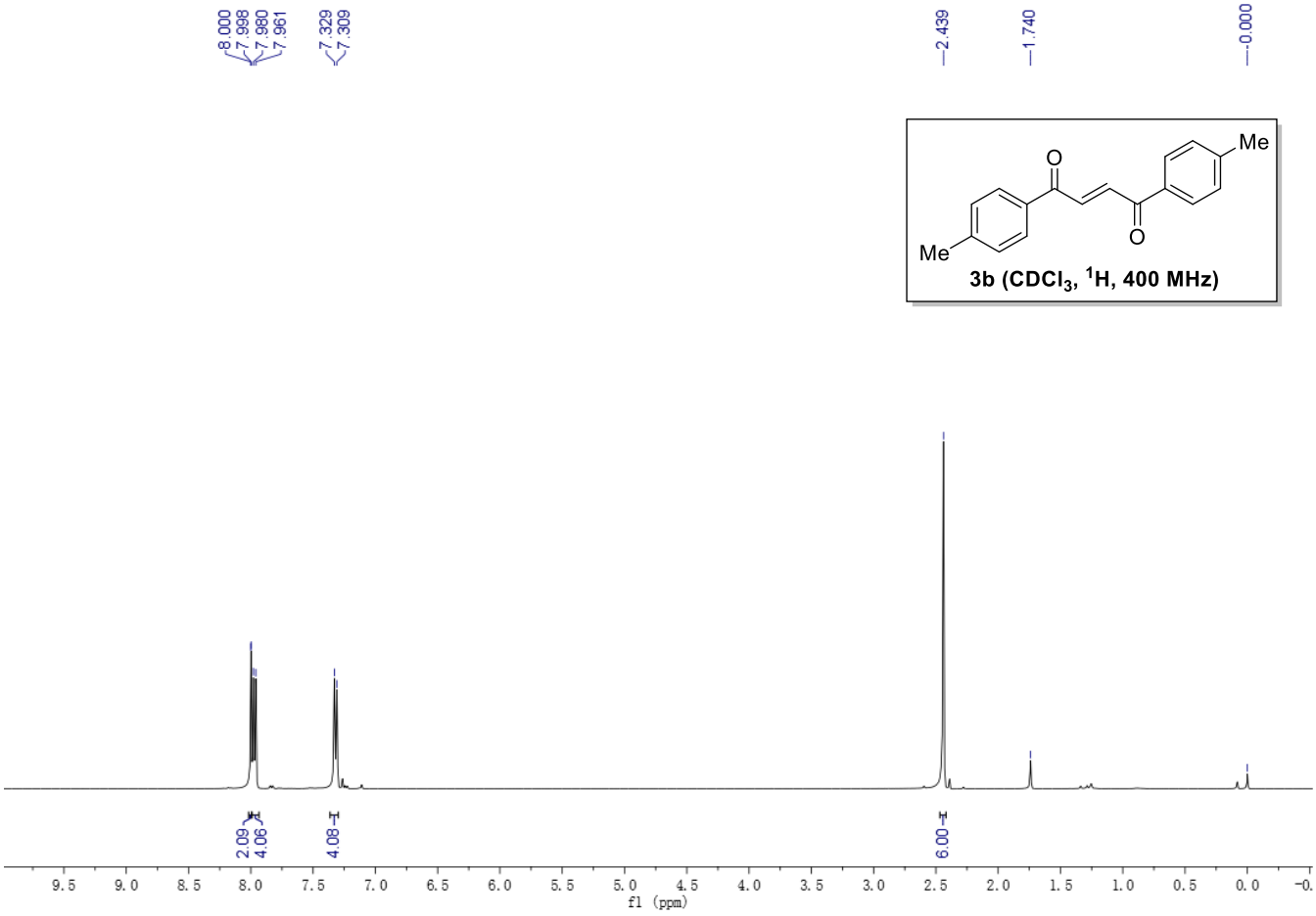
2ap ($CDCl_3$, ^{13}C, 100 MHz)

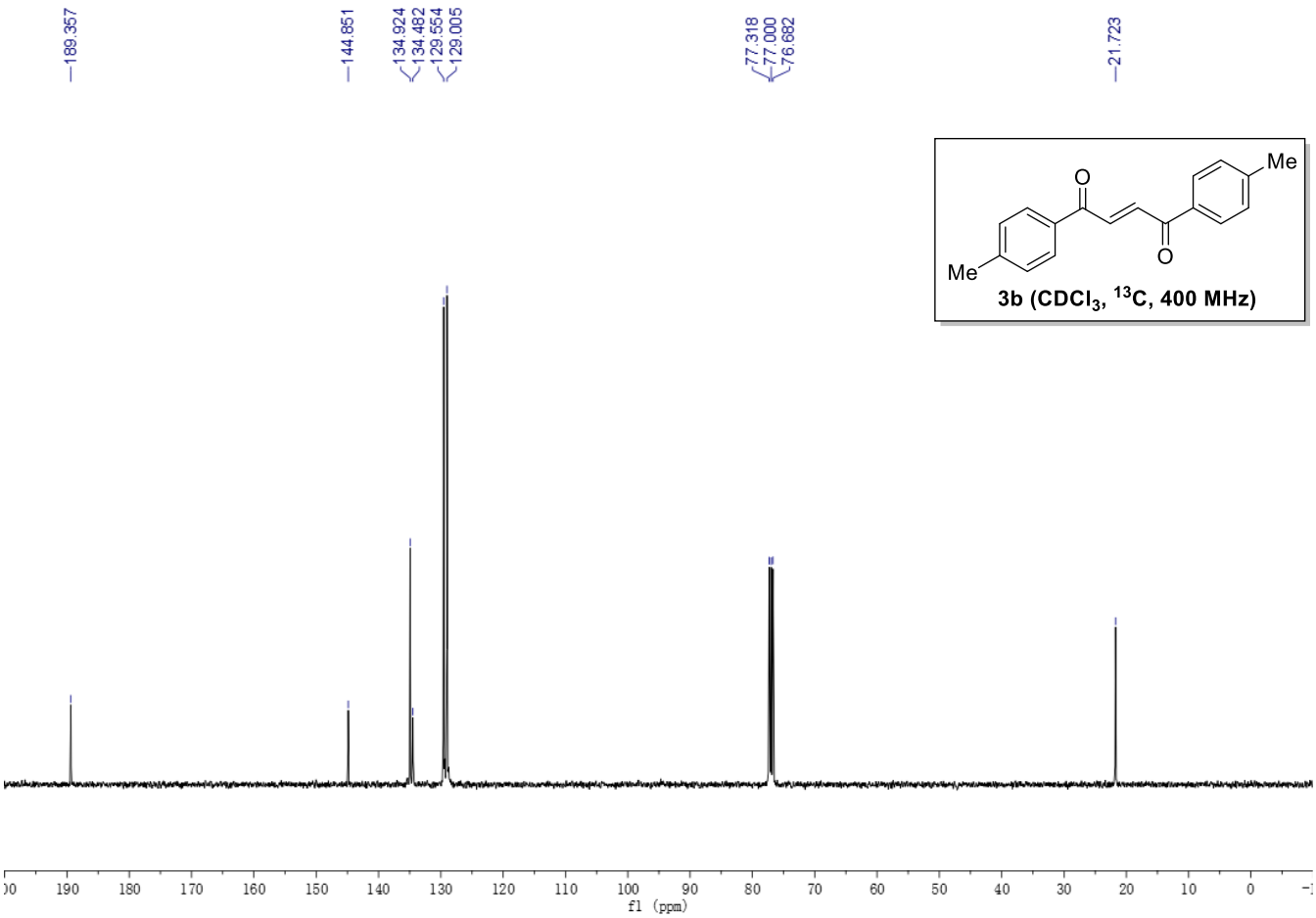


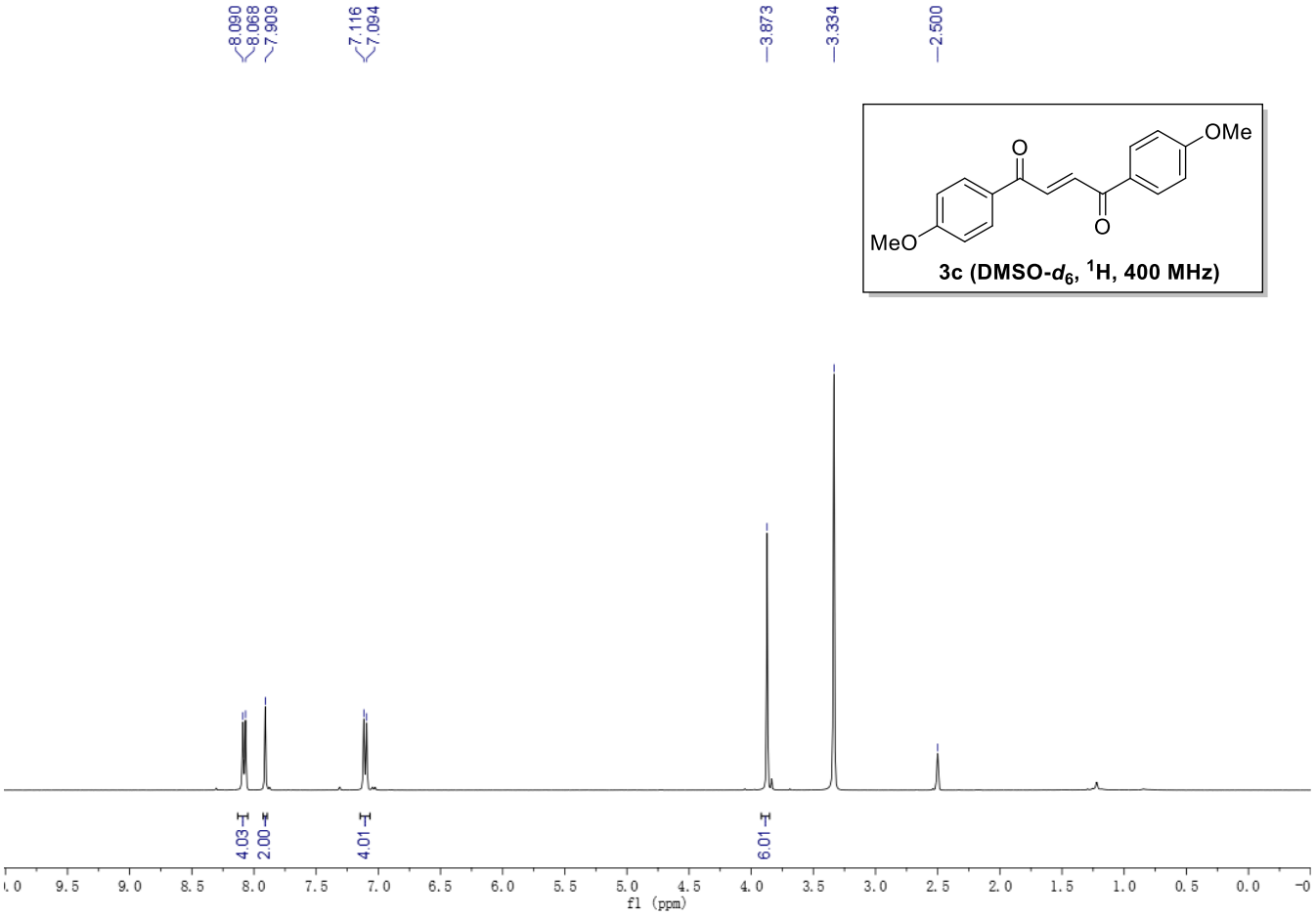
3a (DMSO-d_6, ^{1}H, 400 MHz)

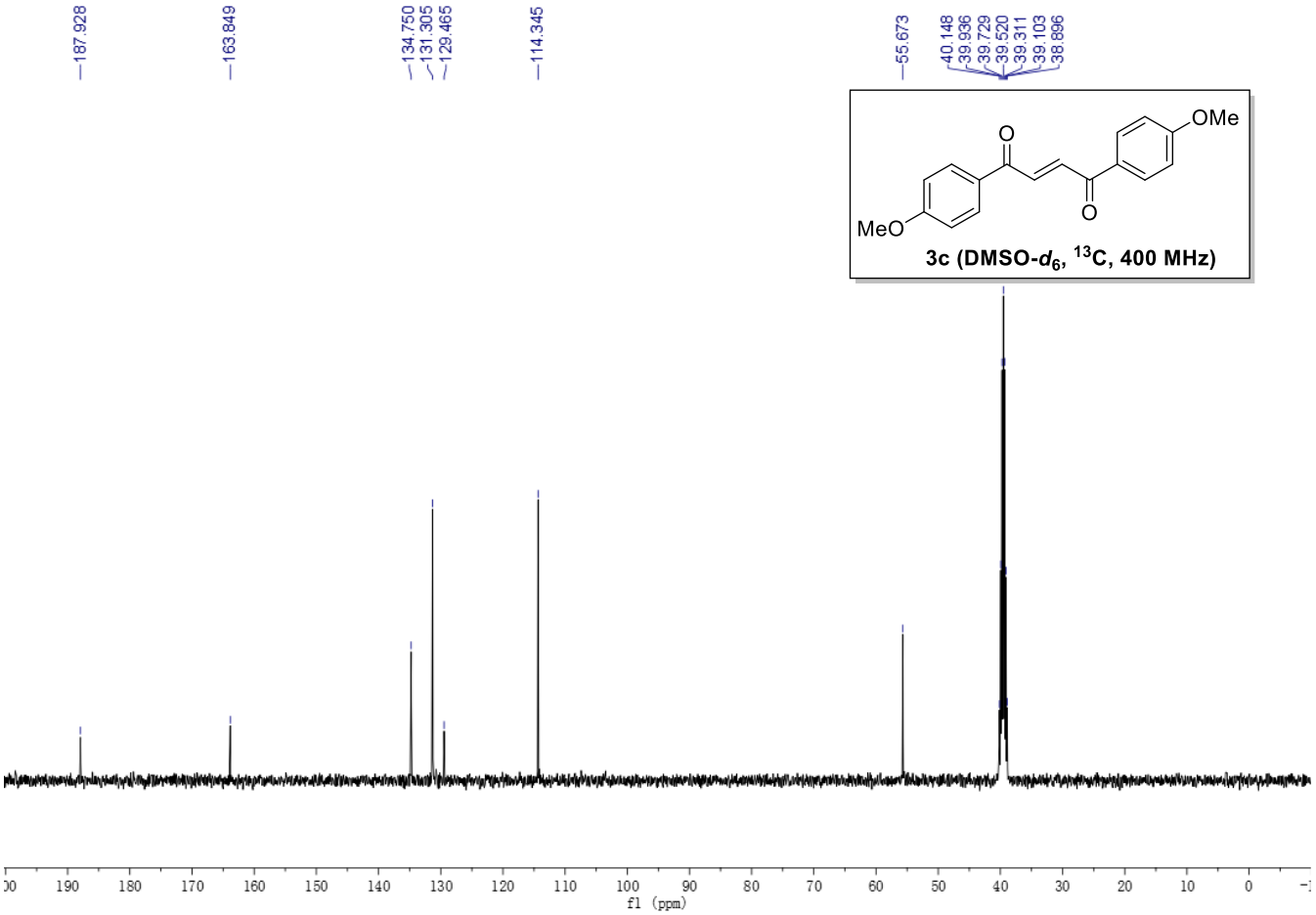


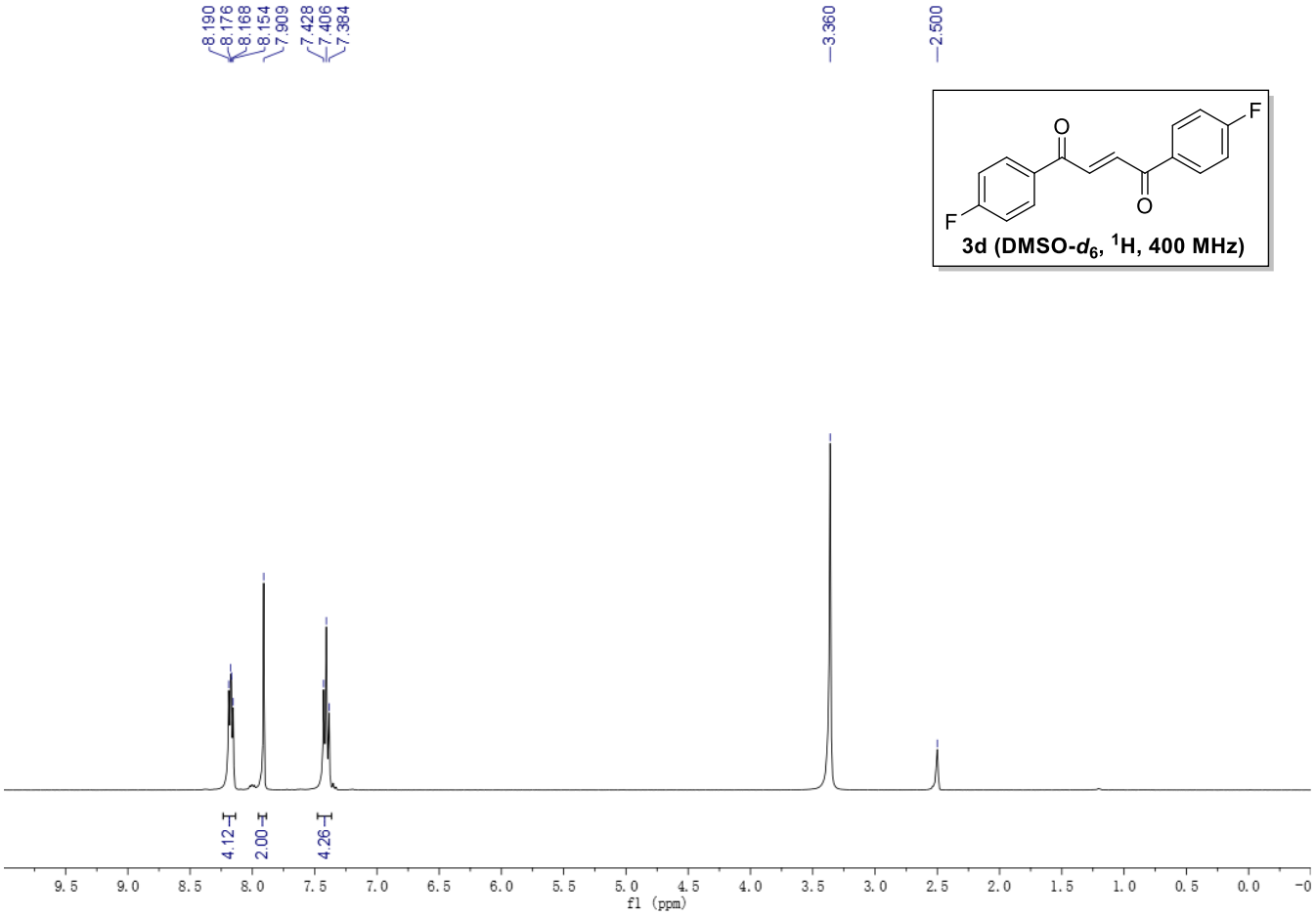
3a (DMSO-d_6, ^{13}C, 100 MHz)

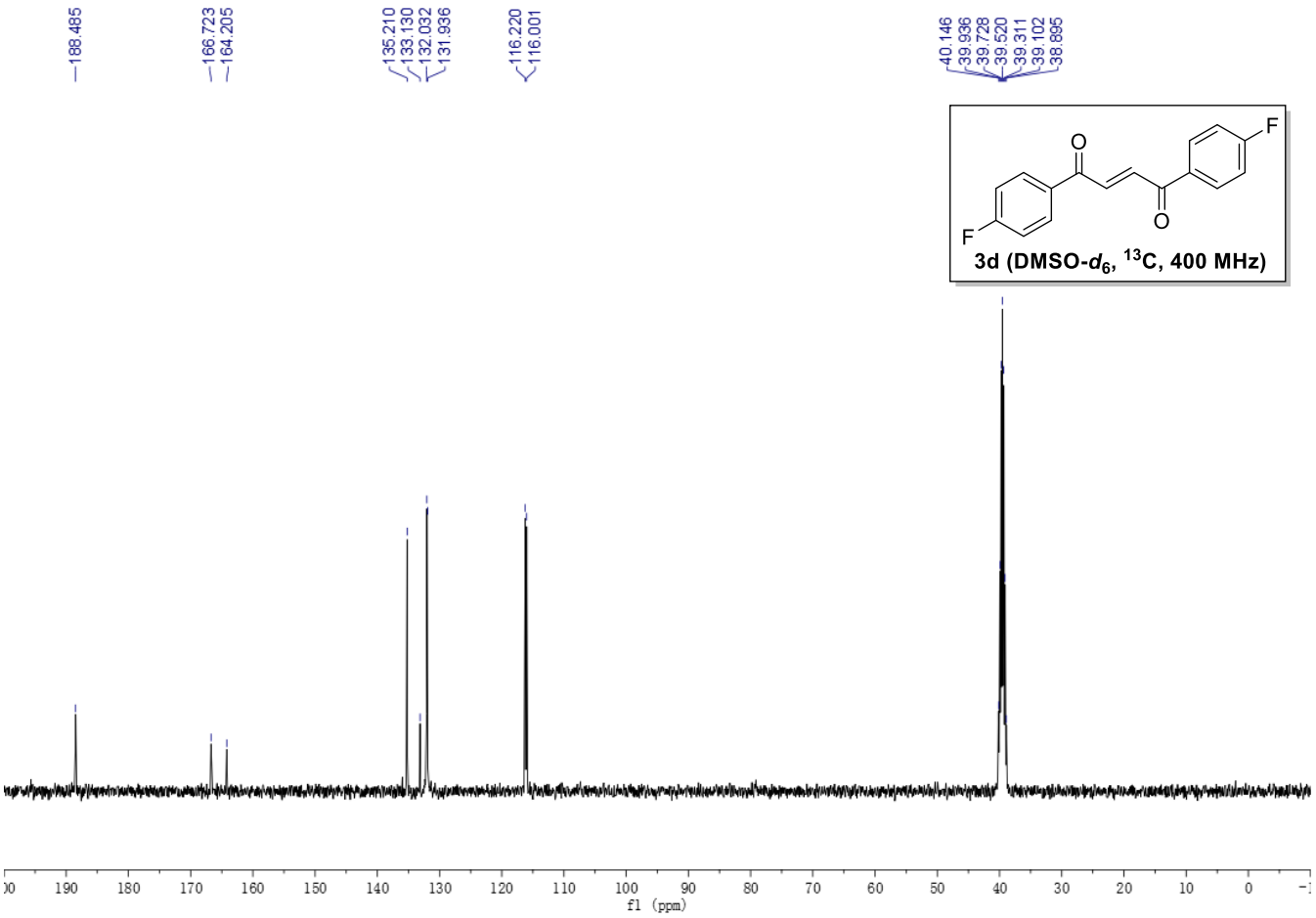

8.000
7.998
7.980
7.961
7.329
7.309
2.439
1.740
0.000
Me
O
O
Me
3b (CDCl3, 1H, 400 MHz)
2.09
4.06
4.08
6.00
f1 (ppm)

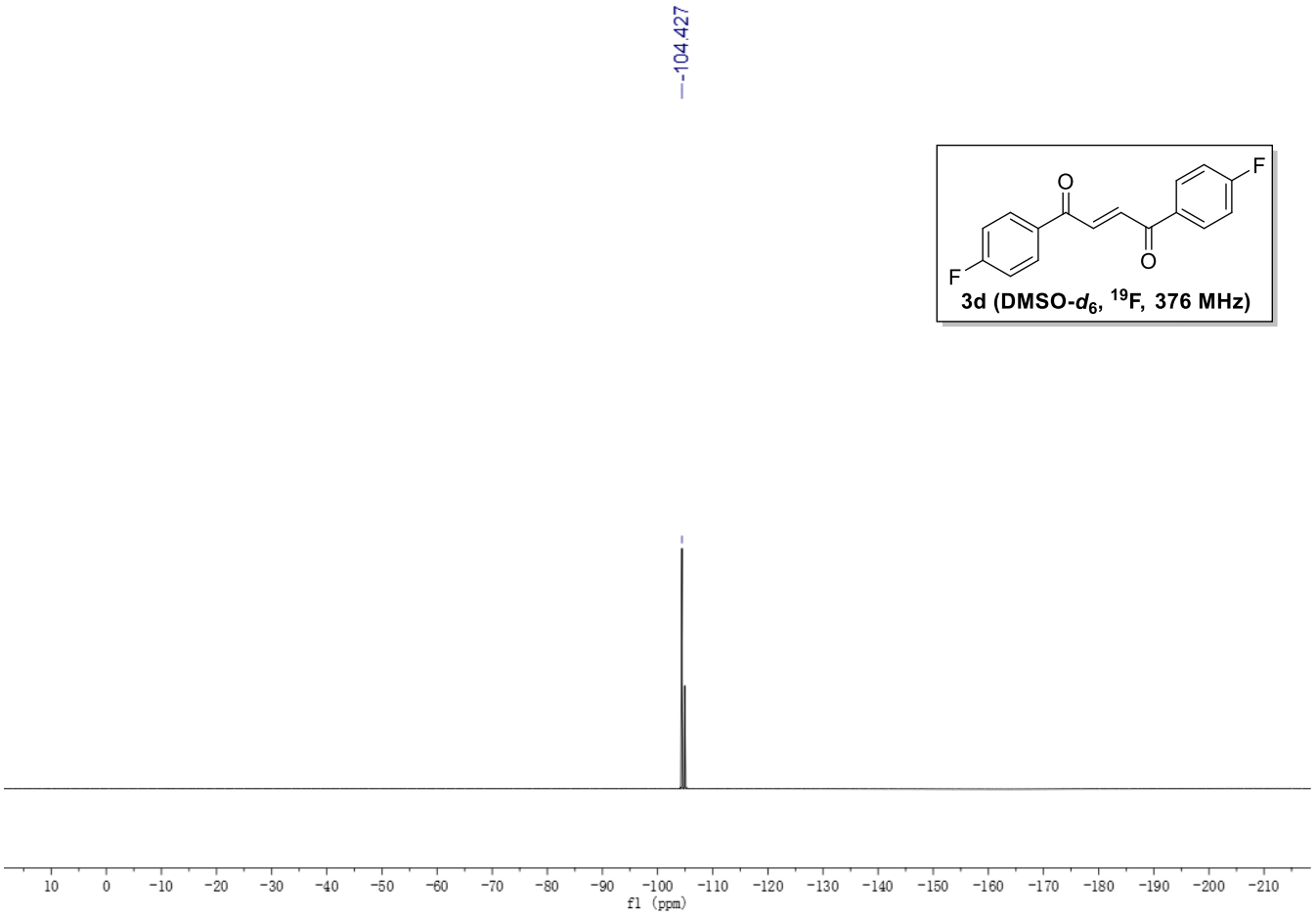

189.357
144.851
134.924
134.482
129.554
129.005
77.318
77.000
76.682
21.723
Me
O
O
Me
3b (CDCl3, 13C, 400 MHz)
f1 (ppm)

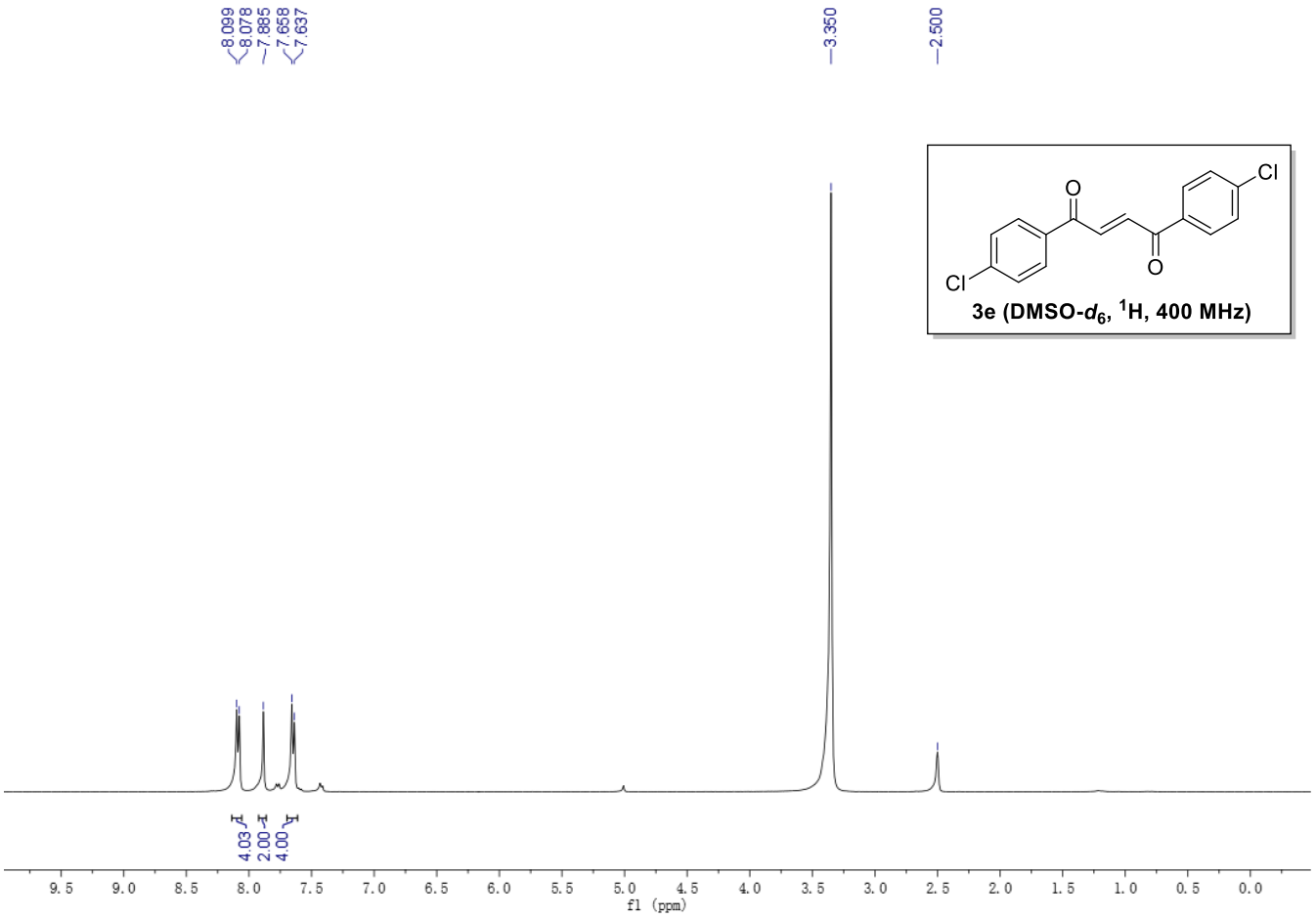

8.090
8.068
7.909
7.116
7.094
3.873
3.334
2.500
OMe
O
O
MeO
3c (DMSO-d_6, ^{1}H, 400 MHz)
4.03
2.00
4.01
6.01
f1 (ppm)

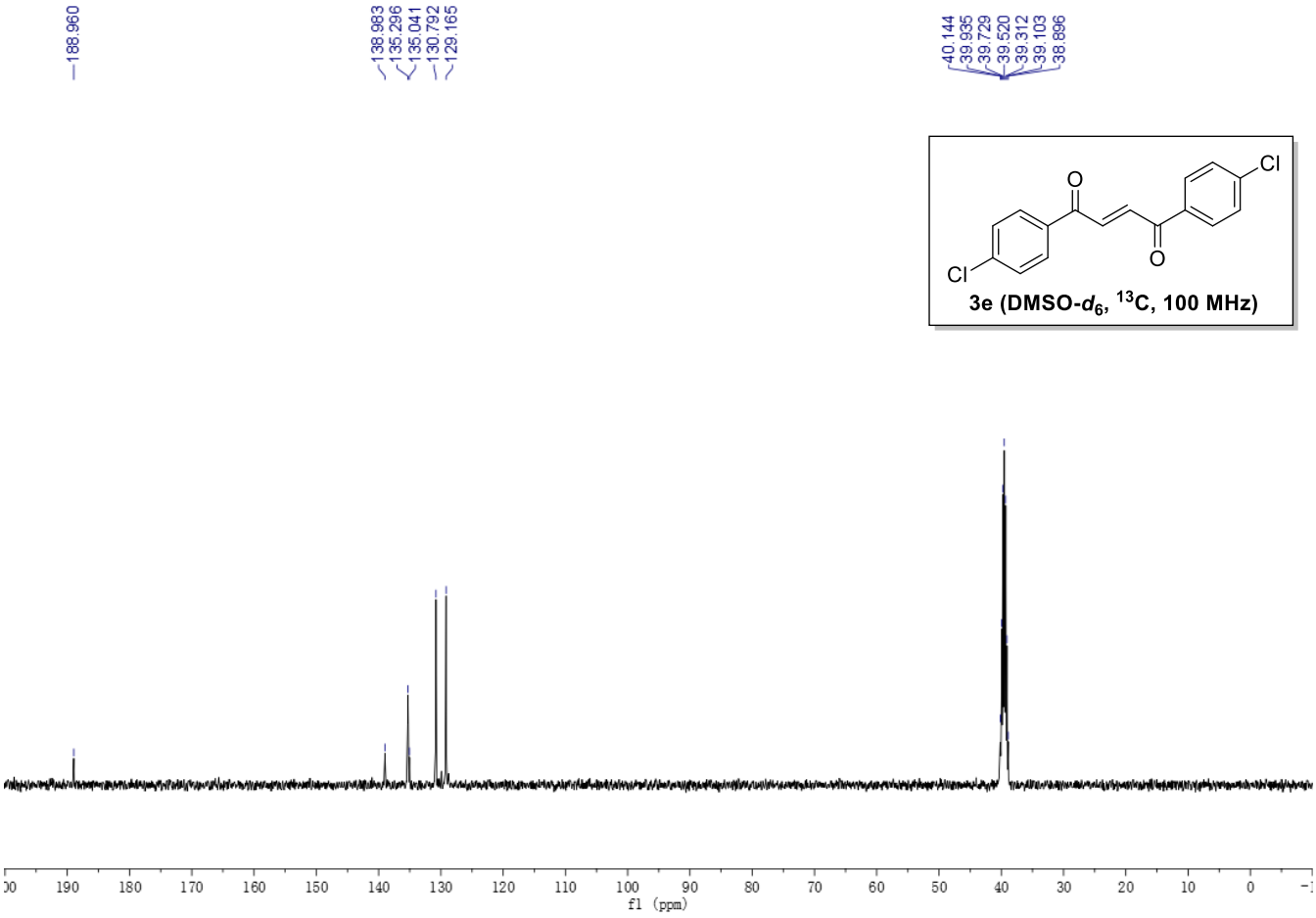

187.928
163.849
134.750
131.305
129.465
114.345
55.673
40.148
39.936
39.729
39.520
39.311
39.103
38.896
OMe
O
O
MeO
3c (DMSO-d_6, ^{13}C, 400 MHz)
f1 (ppm)

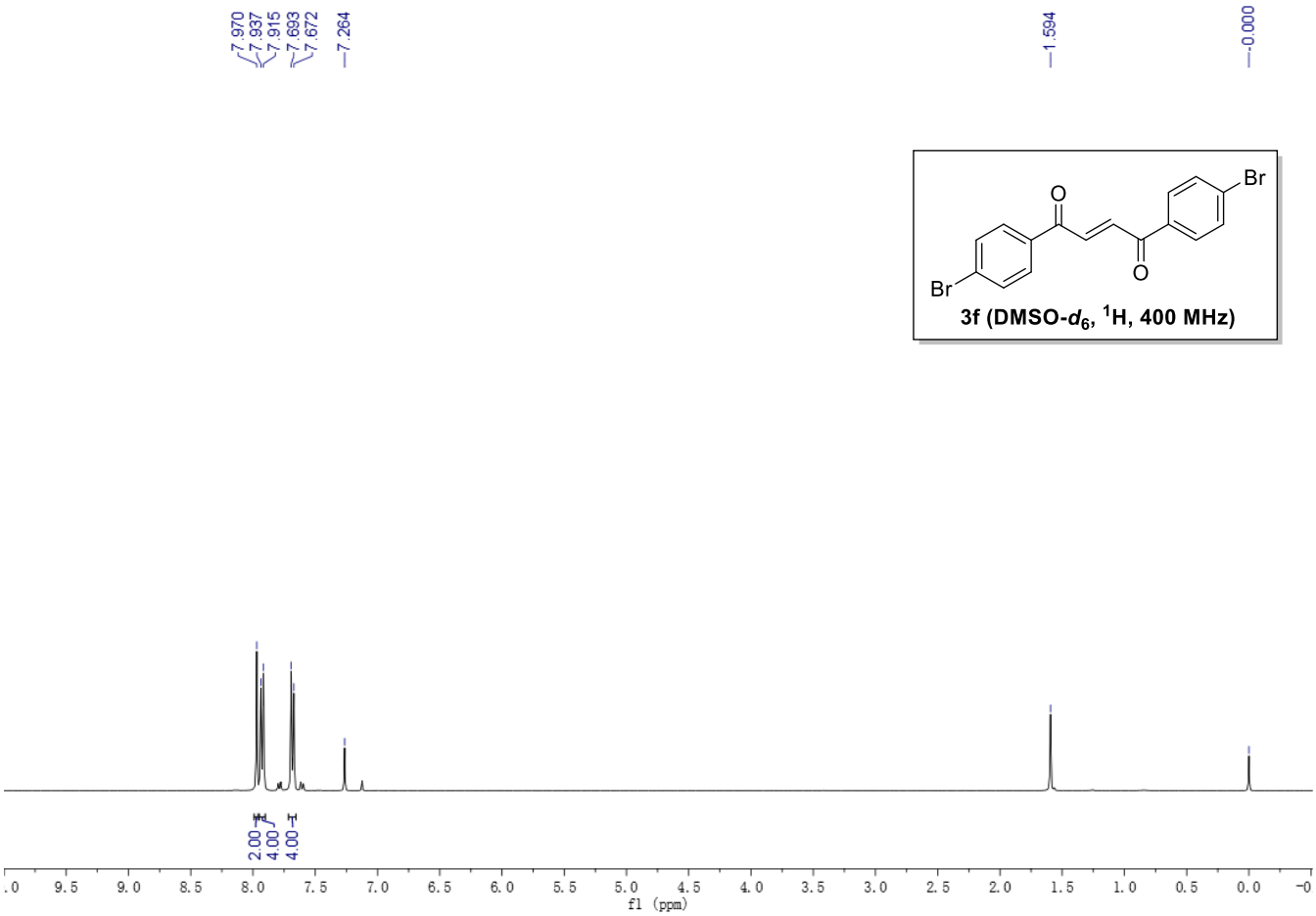

8.190
8.176
8.168
8.154
7.909
7.428
7.406
7.384
3.360
2.500
F
O
O
F
3d (DMSO-d_6, ^{1}H, 400 MHz)
4.12
2.00
4.26
f1 (ppm)

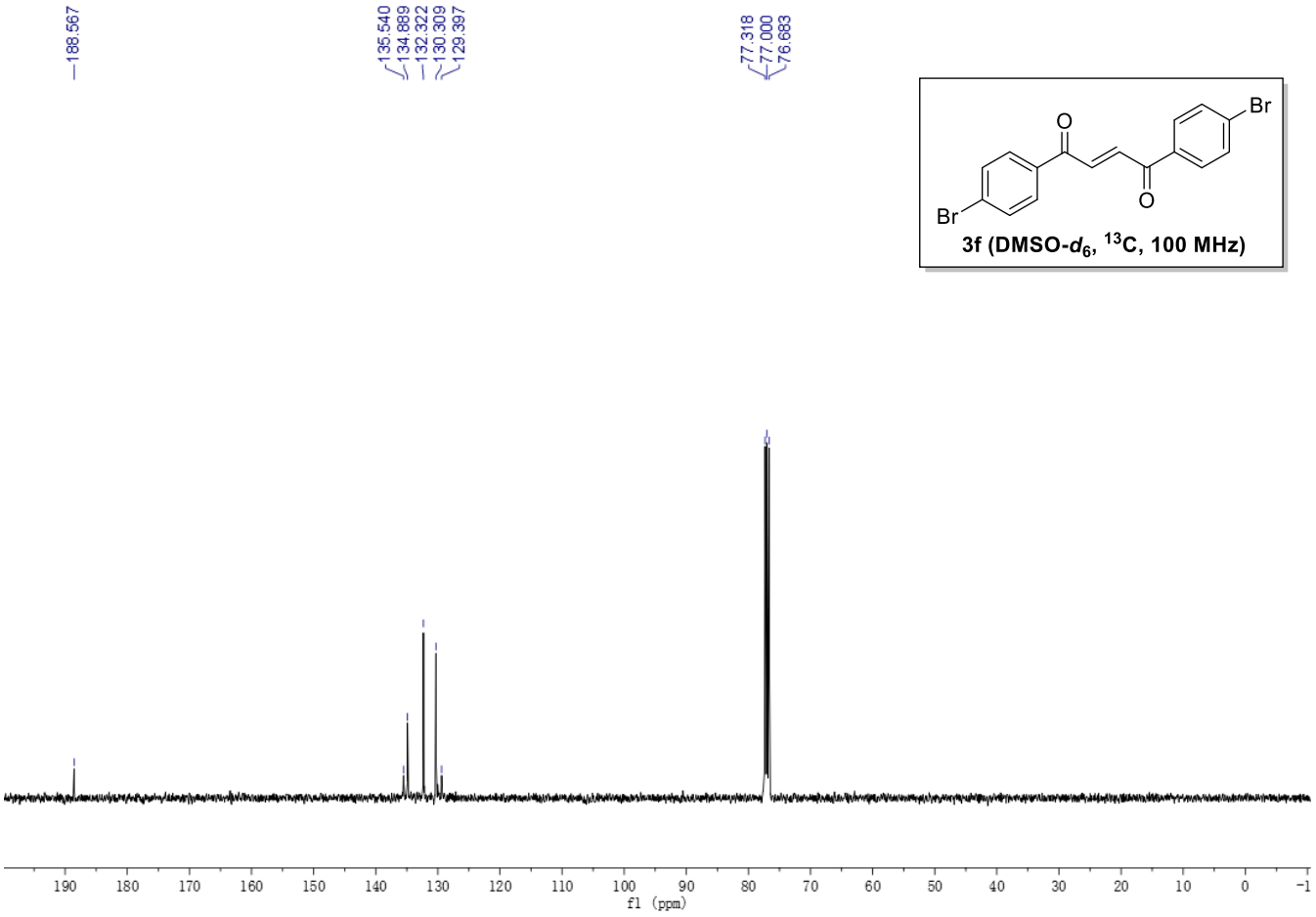

188.485
166.723
164.205
135.210
133.130
132.032
131.936
116.220
116.001
40.146
39.936
39.728
39.520
39.311
39.102
38.895
F
O
O
F
3d (DMSO-d_6, ^{13}C, 400 MHz)
f1 (ppm)

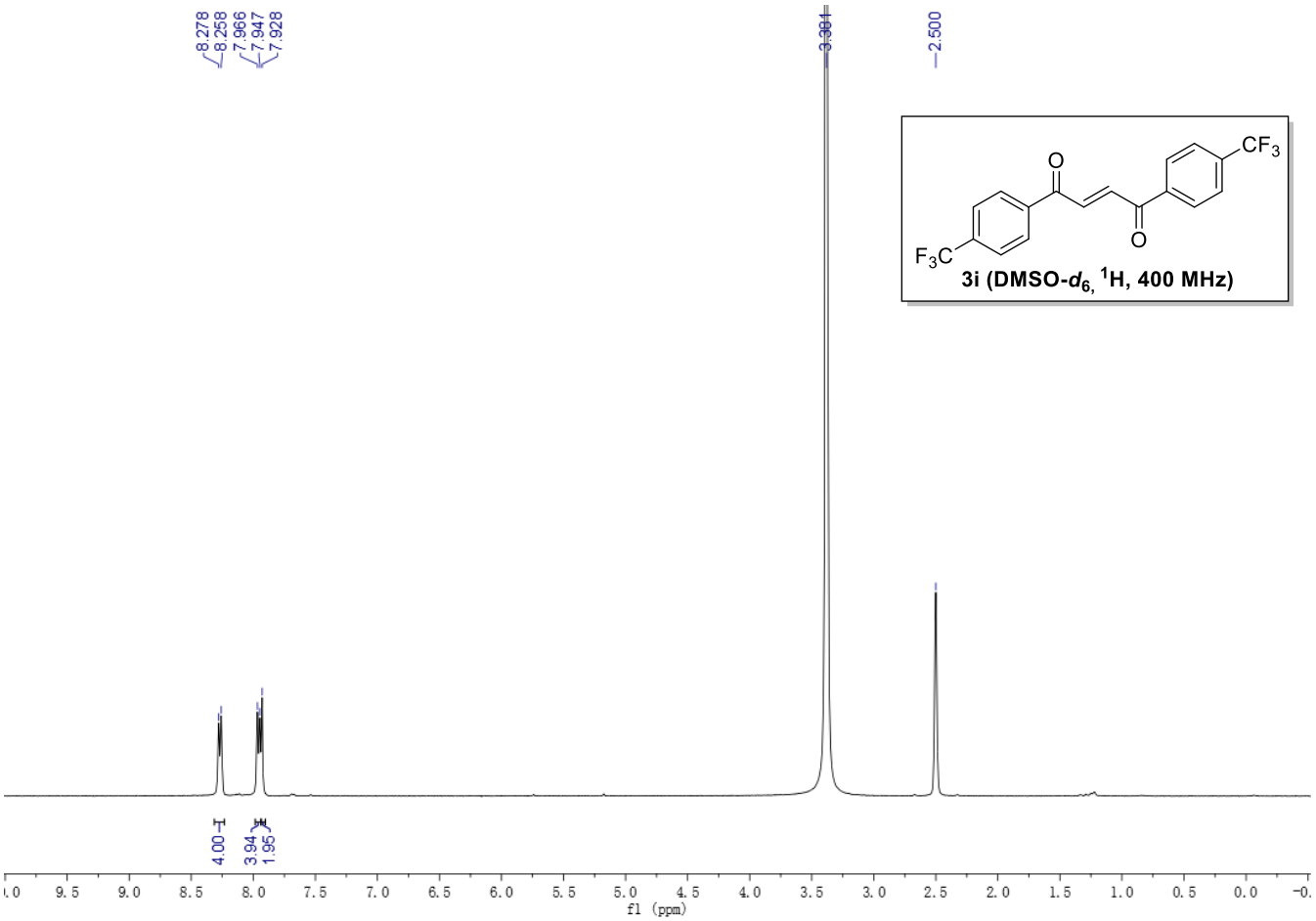

-104.427
F
O
O
F
3d (DMSO-d_6, ^{19}F, 376 MHz)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

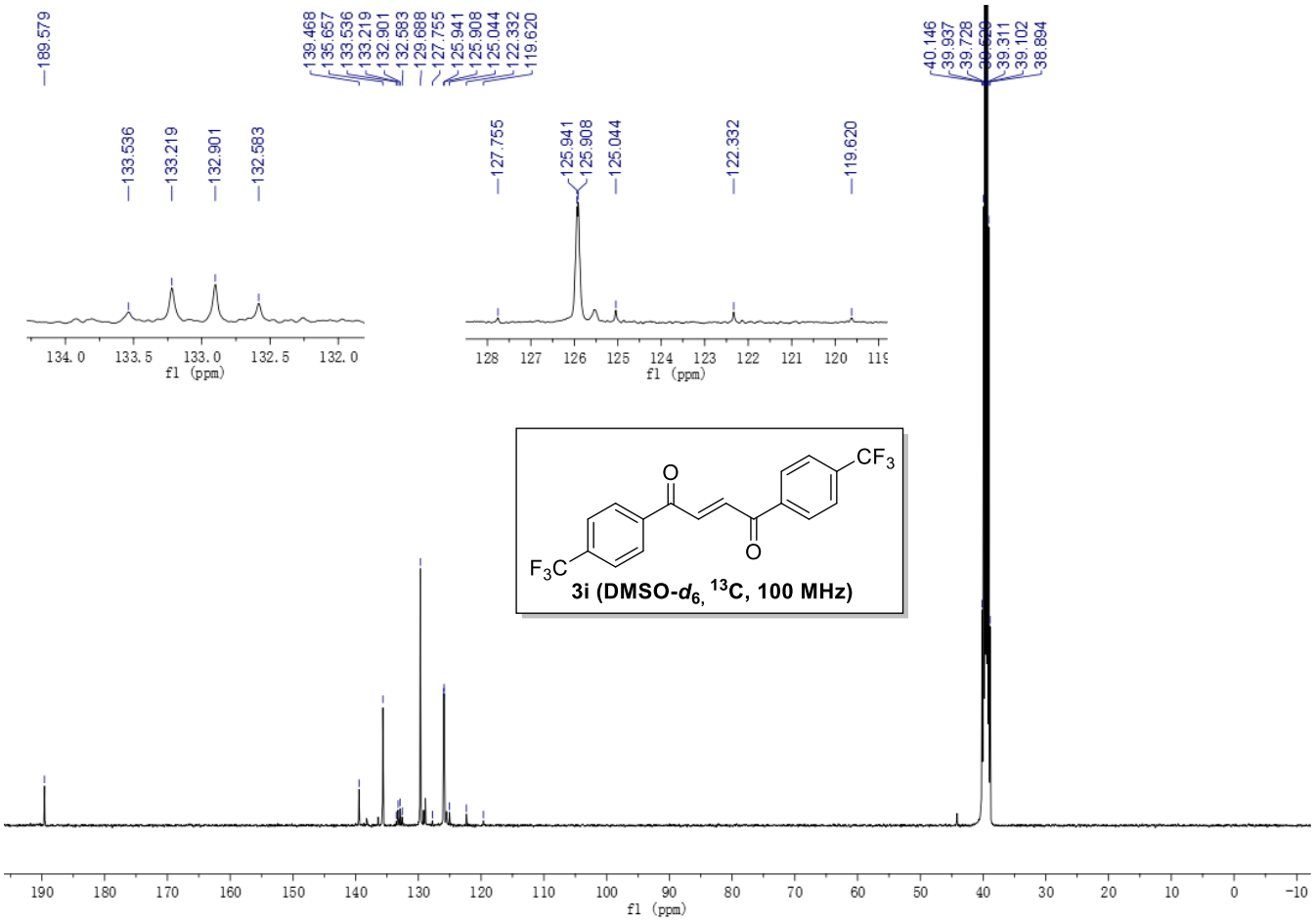

8.099
8.078
7.885
7.658
7.637
3.350
2.500
Cl
O
O
Cl
3e (DMSO-d_6, ^{1}H, 400 MHz)
4.03
2.00
4.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


188.960
138.983
135.296
135.041
130.792
129.165
40.144
39.935
39.729
39.520
39.312
39.103
38.896
Cl
O
O
Cl
3e (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

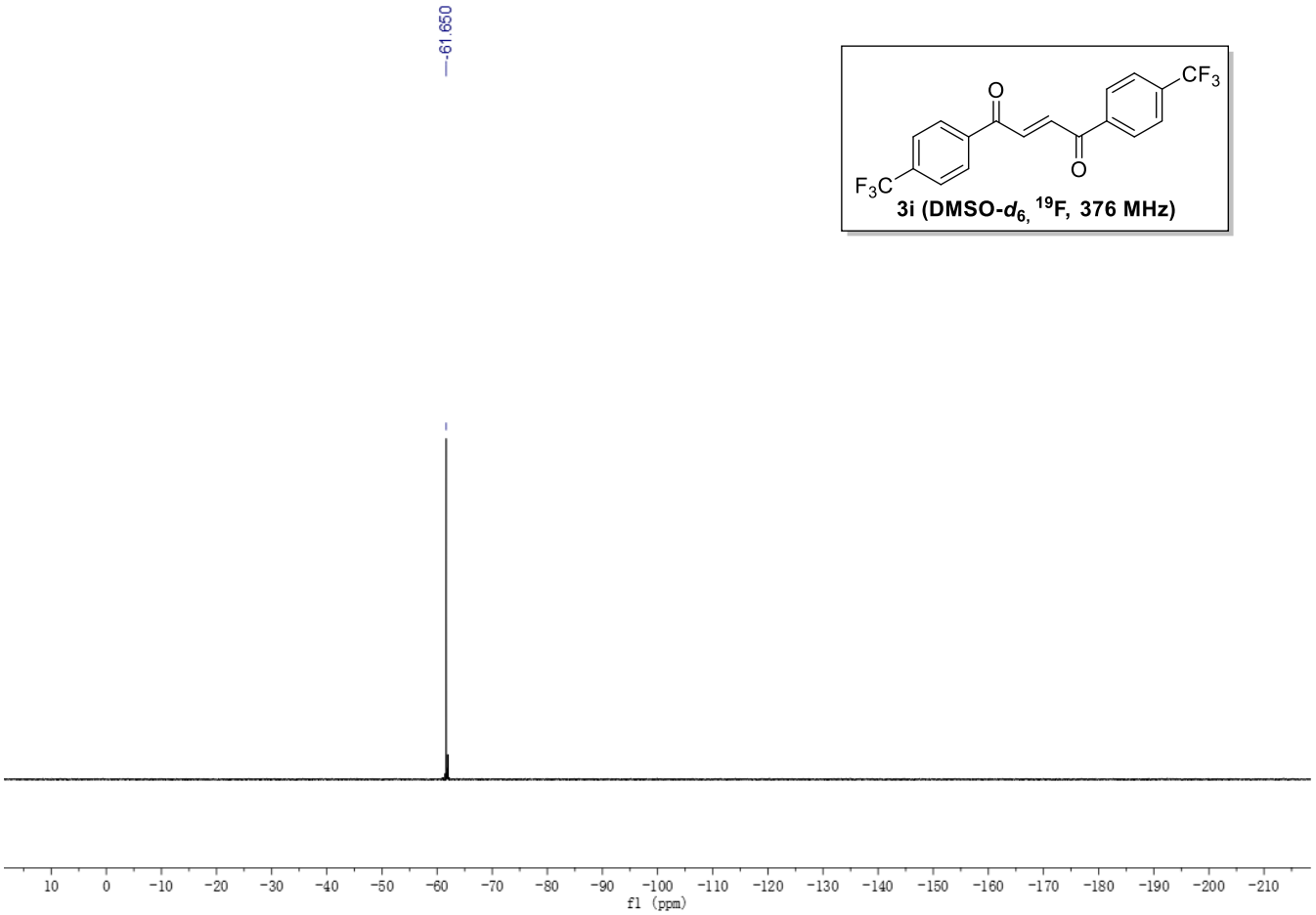

7.970
7.937
7.915
7.693
7.672
7.264
1.594
0.000
Br
O
O
Br
3f (DMSO-d_6, ^{1}H, 400 MHz)
2.00
4.00
4.00
f1 (ppm)


188.567
135.540
134.889
132.322
130.309
129.397
77.318
77.000
76.683
Br
O
O
Br
3f (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

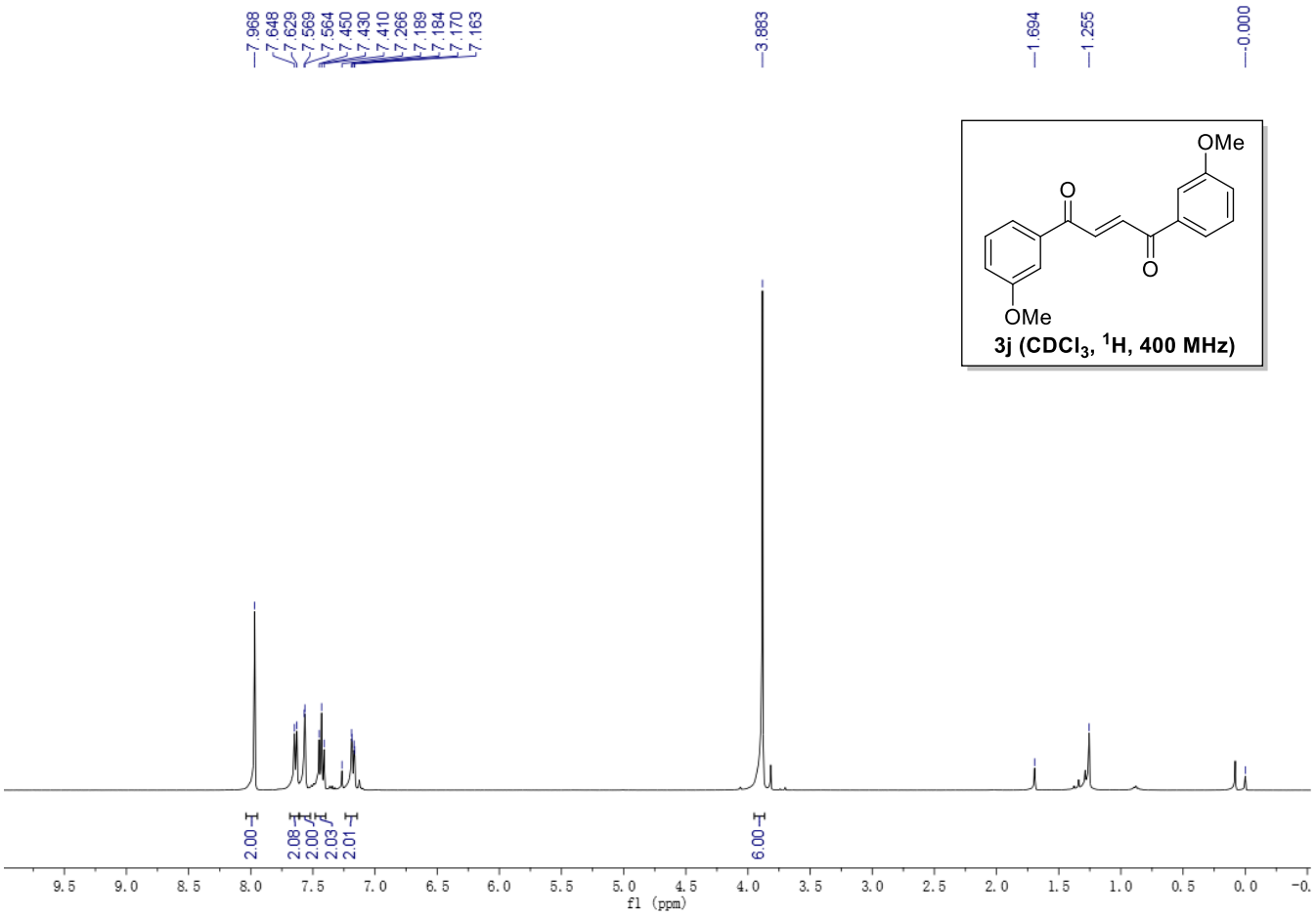

8.278
8.258
7.966
7.947
7.928
3.391
2.500
4.00
3.94
1.95
CF_3
O
O
F_3C
3i (DMSO-d_6, ^{1}H, 400 MHz)
f1 (ppm)



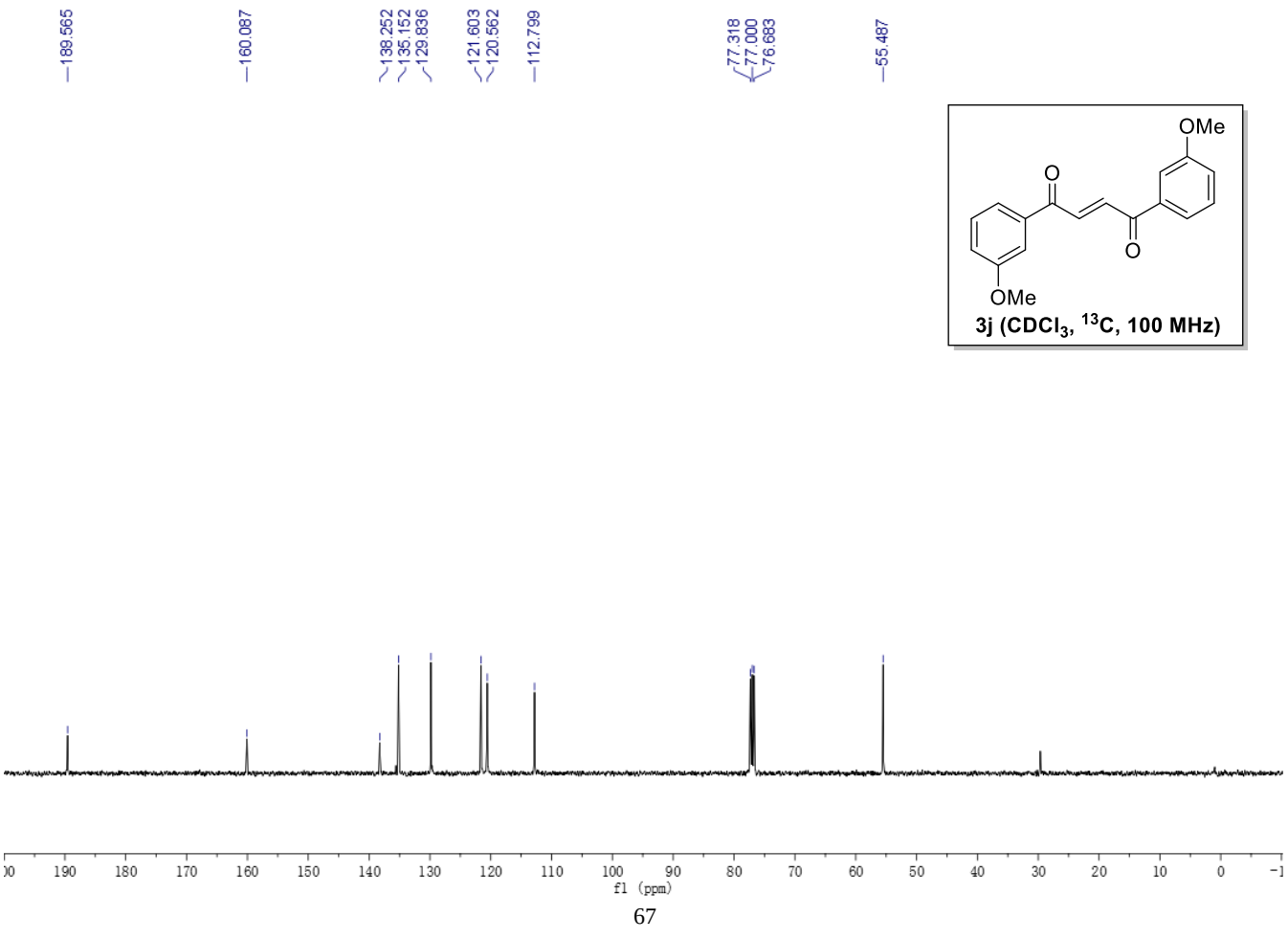
3i (DMSO-d_6, ^{13}C, 100 MHz)



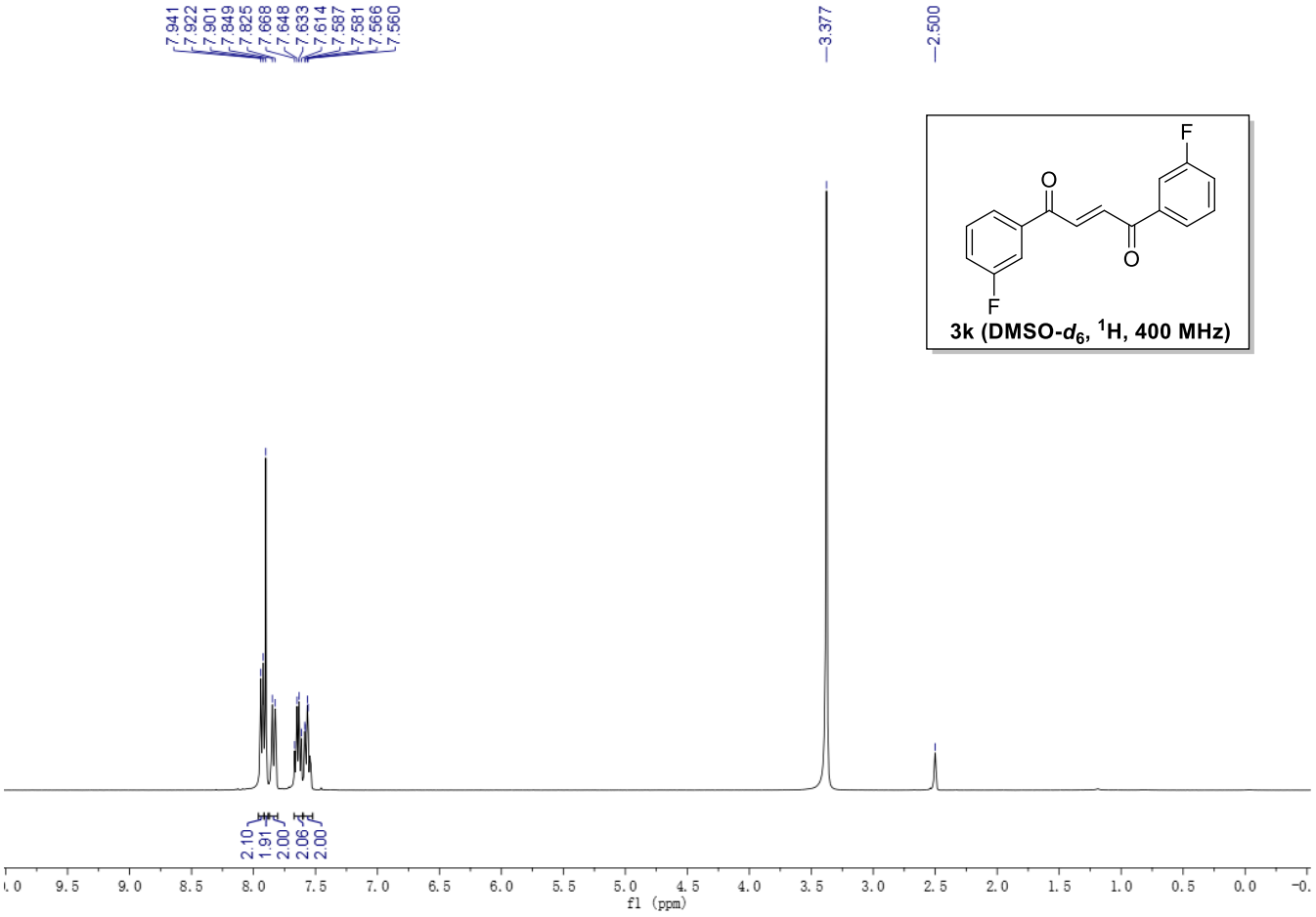
3i (DMSO-d_6, ^{19}F, 376 MHz)



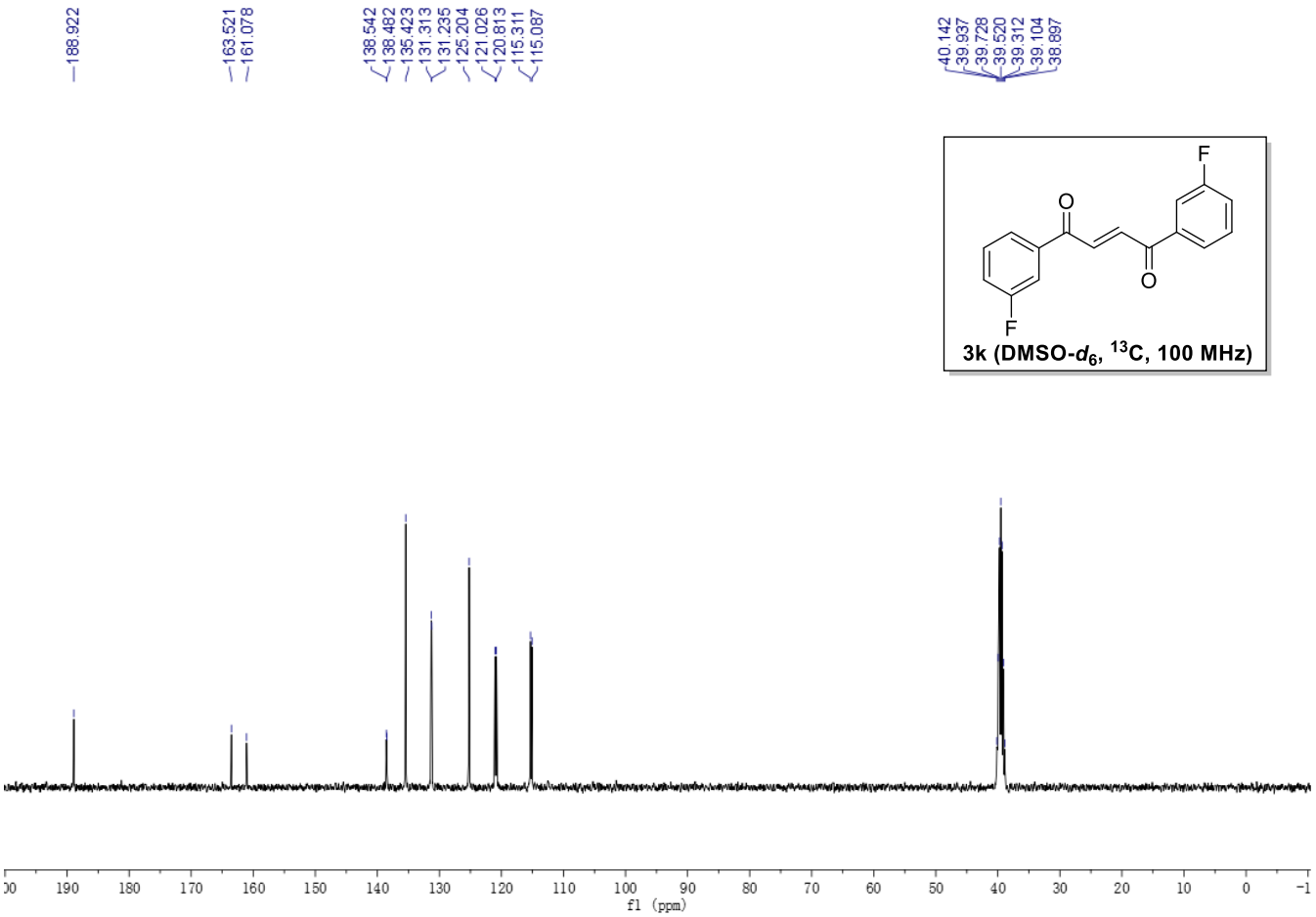
3j ($CDCl_3$, ^1H, 400 MHz)



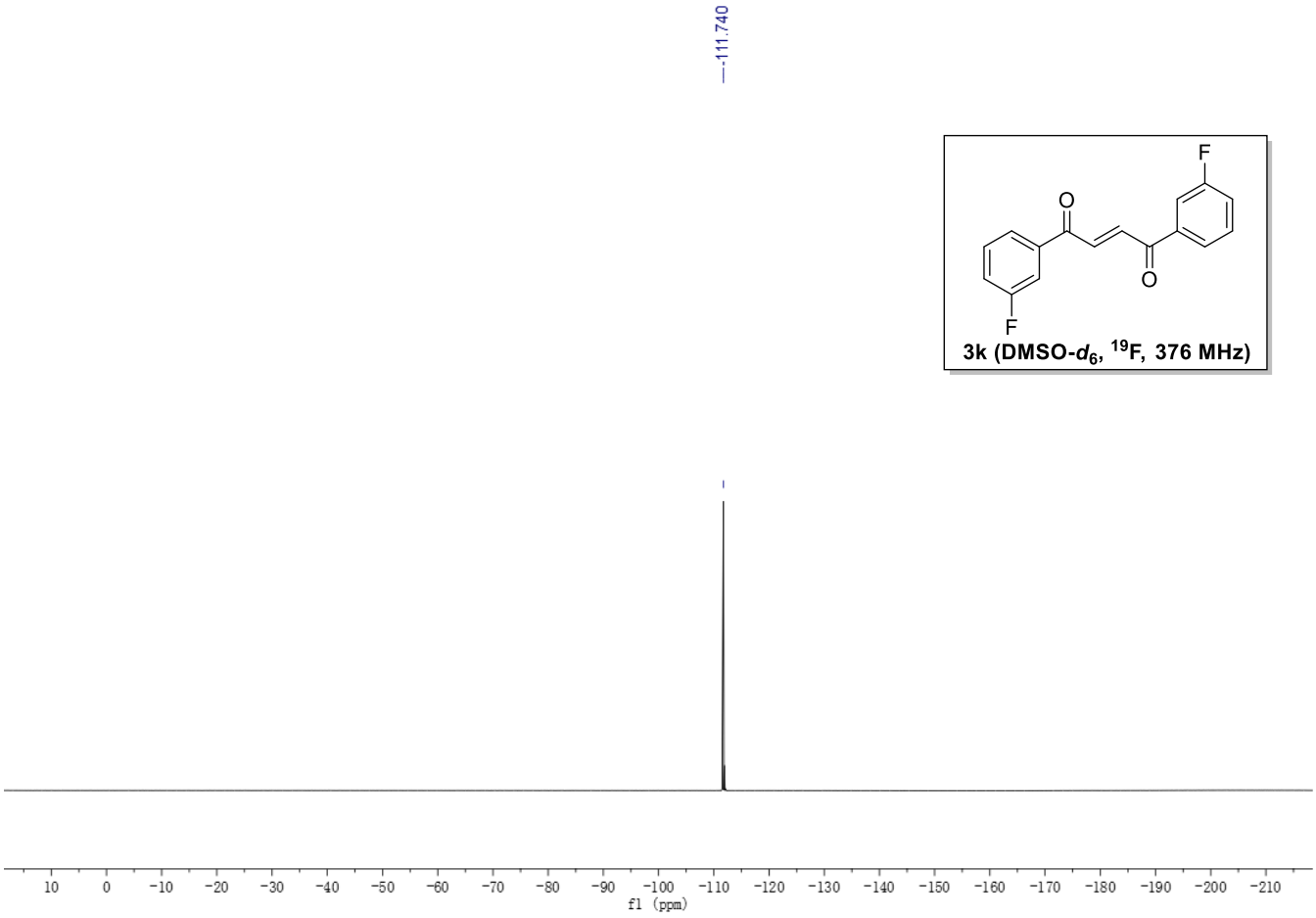
3j ($CDCl_3$, ^{13}C, 100 MHz)



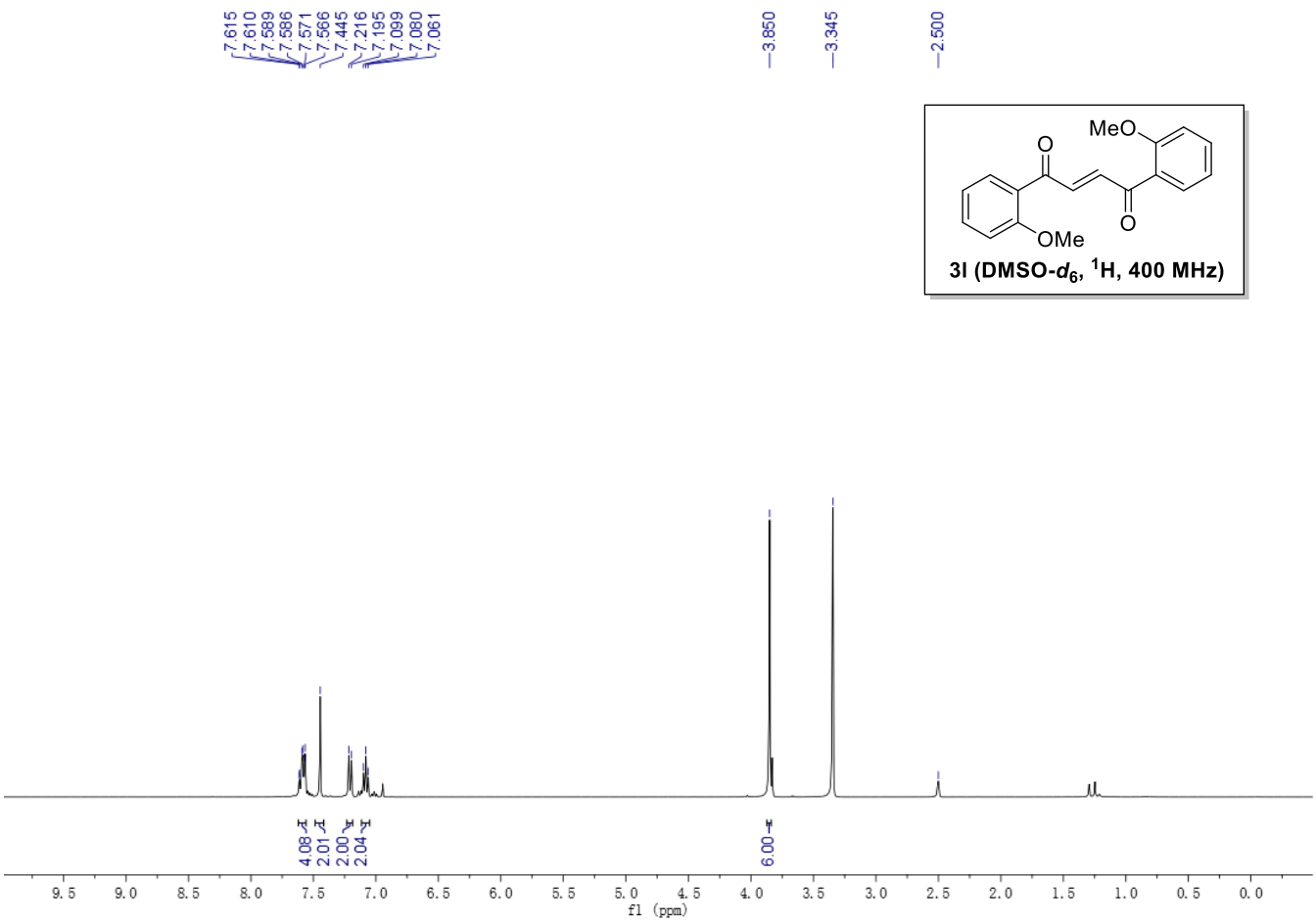
3k (DMSO-d_6, ^{1}H, 400 MHz)



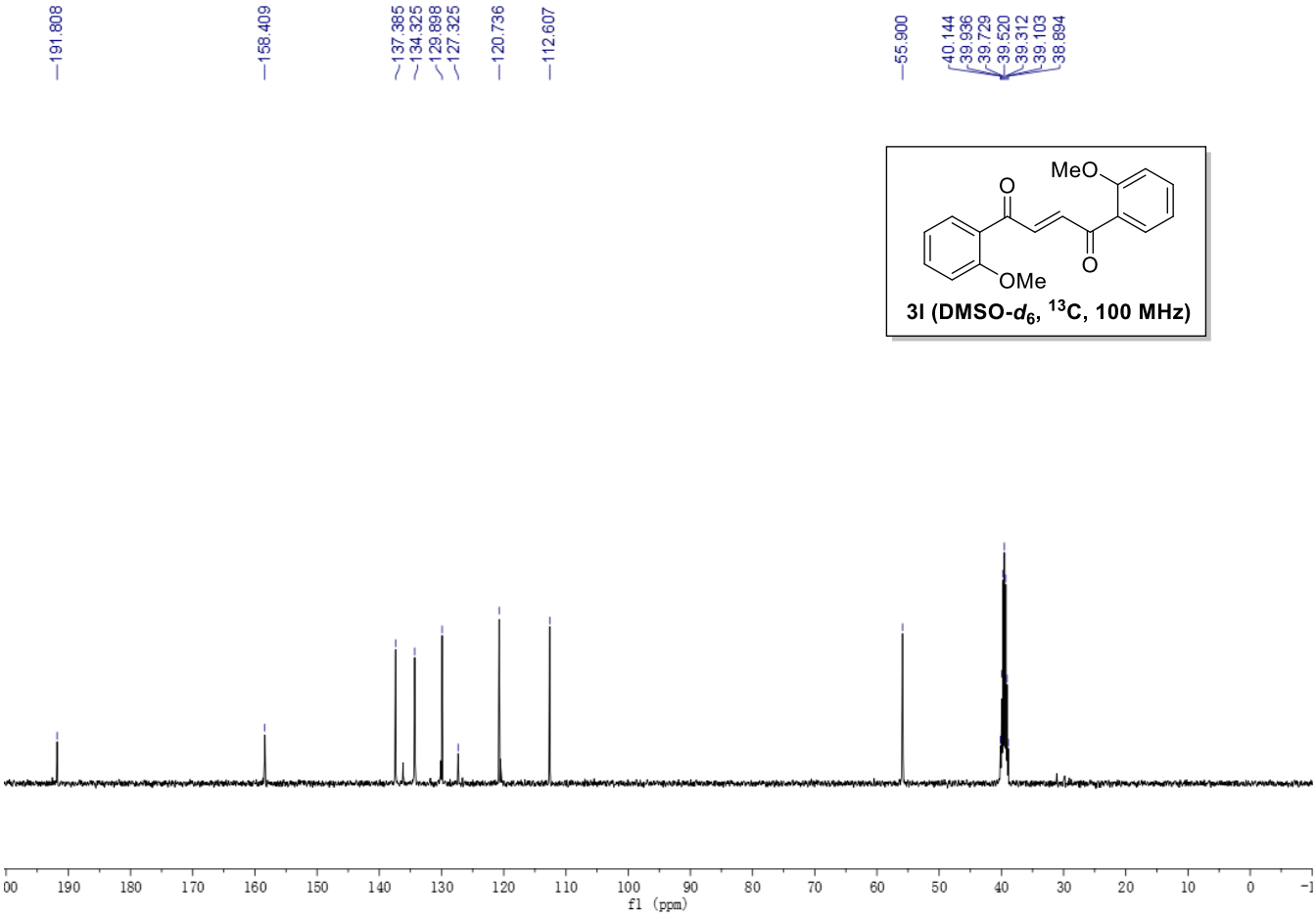
3k (DMSO-d_6, ^{13}C, 100 MHz)

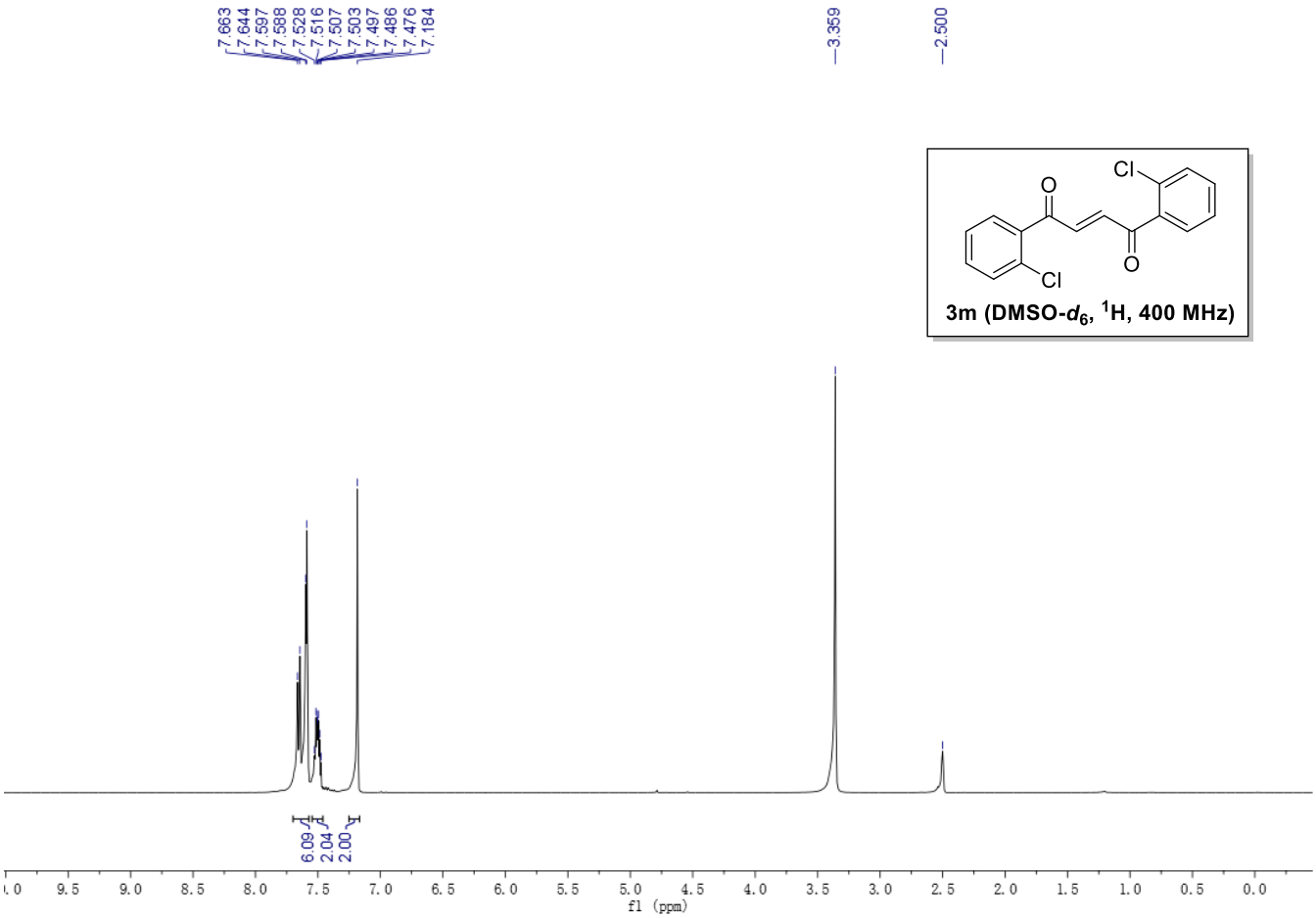


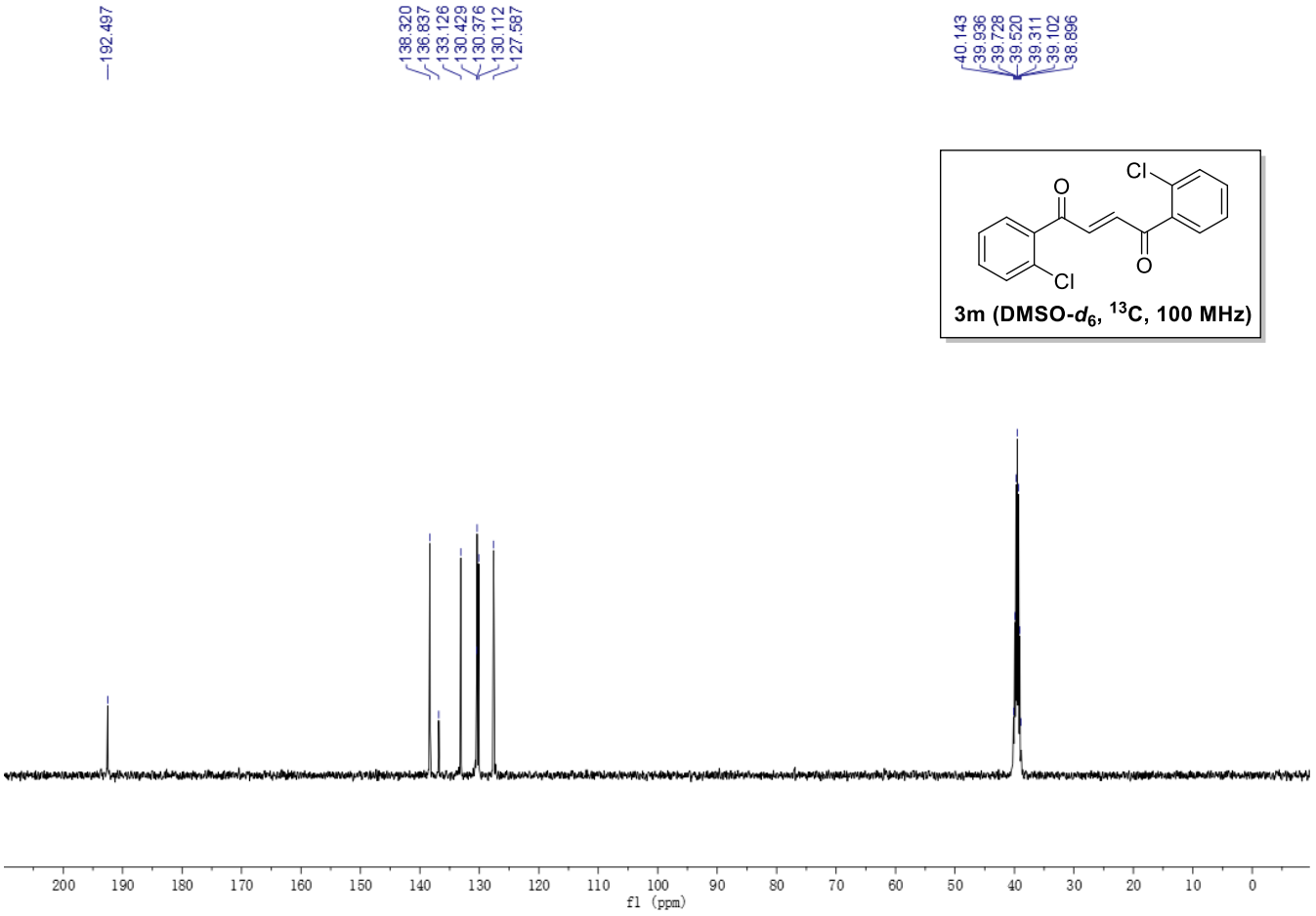
3k (DMSO-d_6, ^{19}F, 376 MHz)

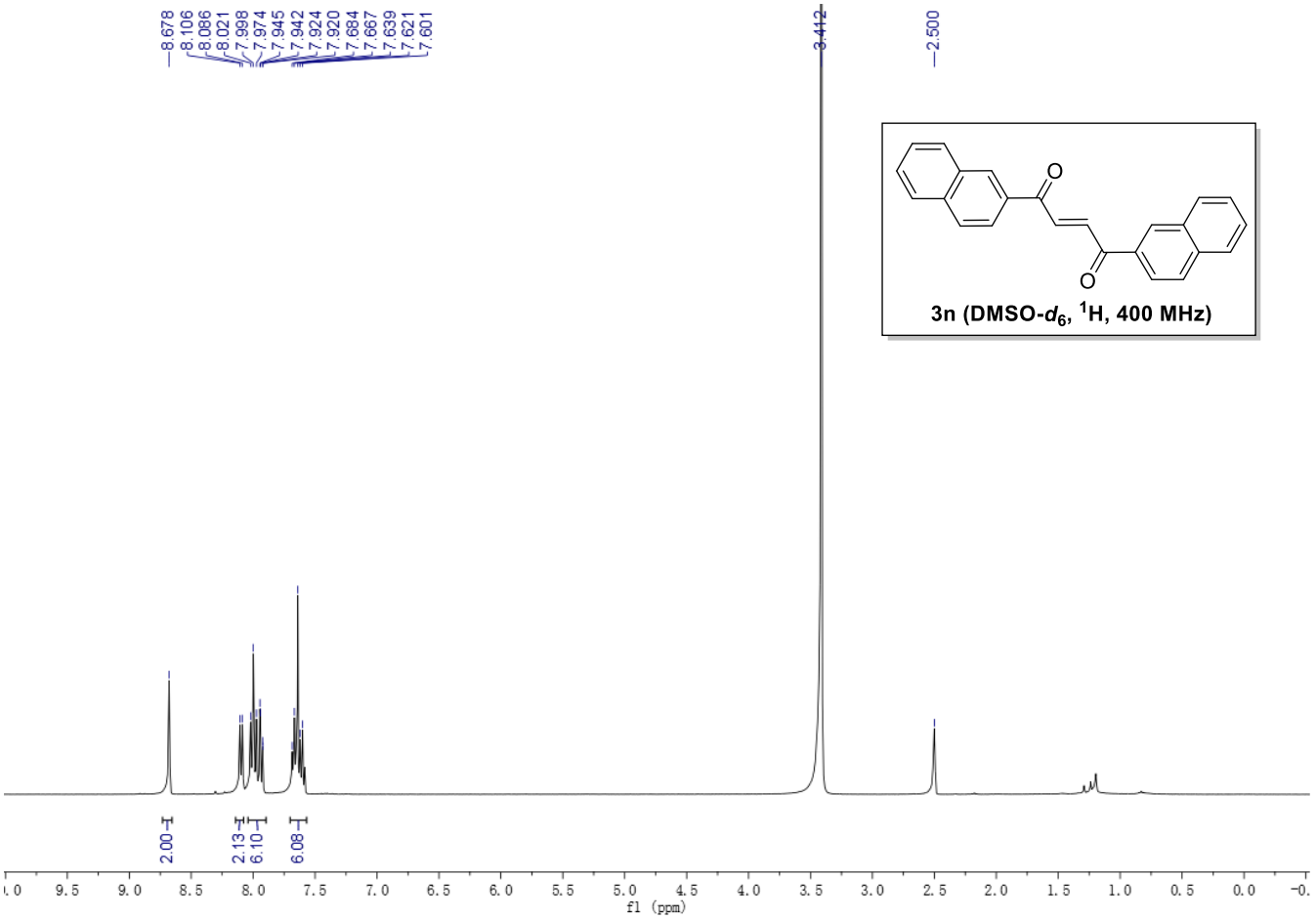


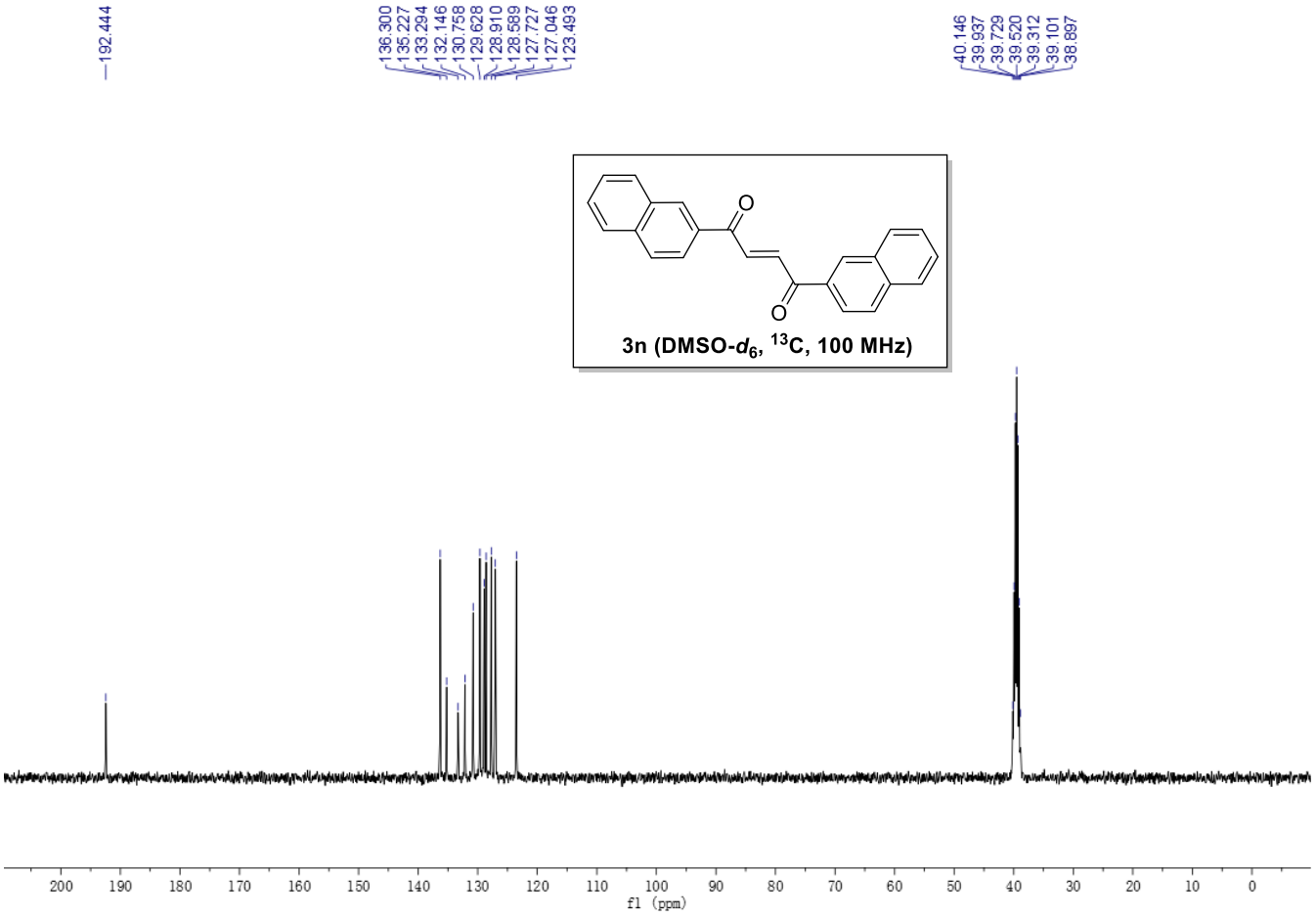
3l (DMSO-d_6, ^{1}H, 400 MHz)

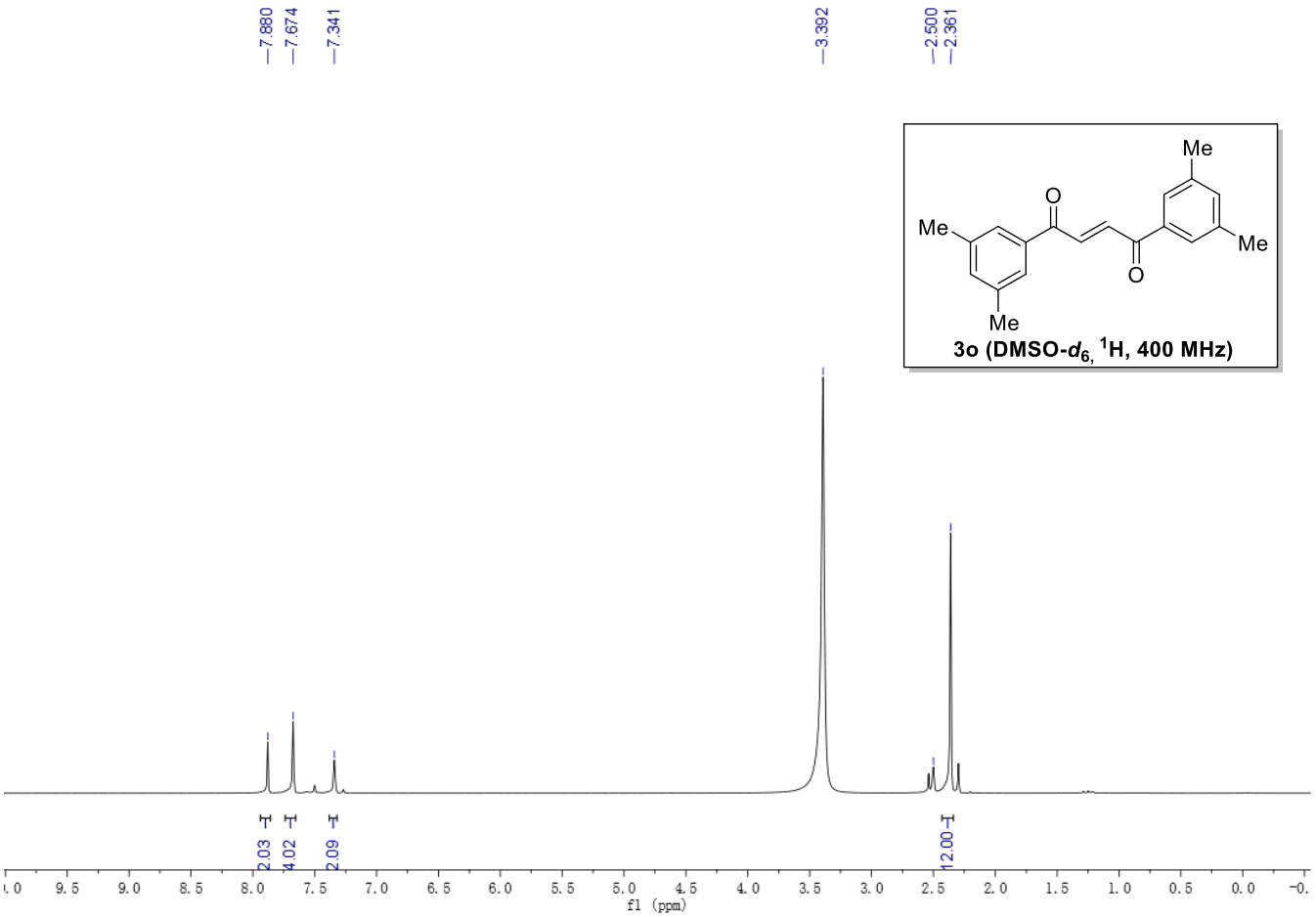

191.808
158.409
137.385
134.325
129.898
127.325
120.736
112.607
55.900
40.144
39.936
39.729
39.520
39.312
39.103
38.894
MeO
O
O
OMe
3l (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

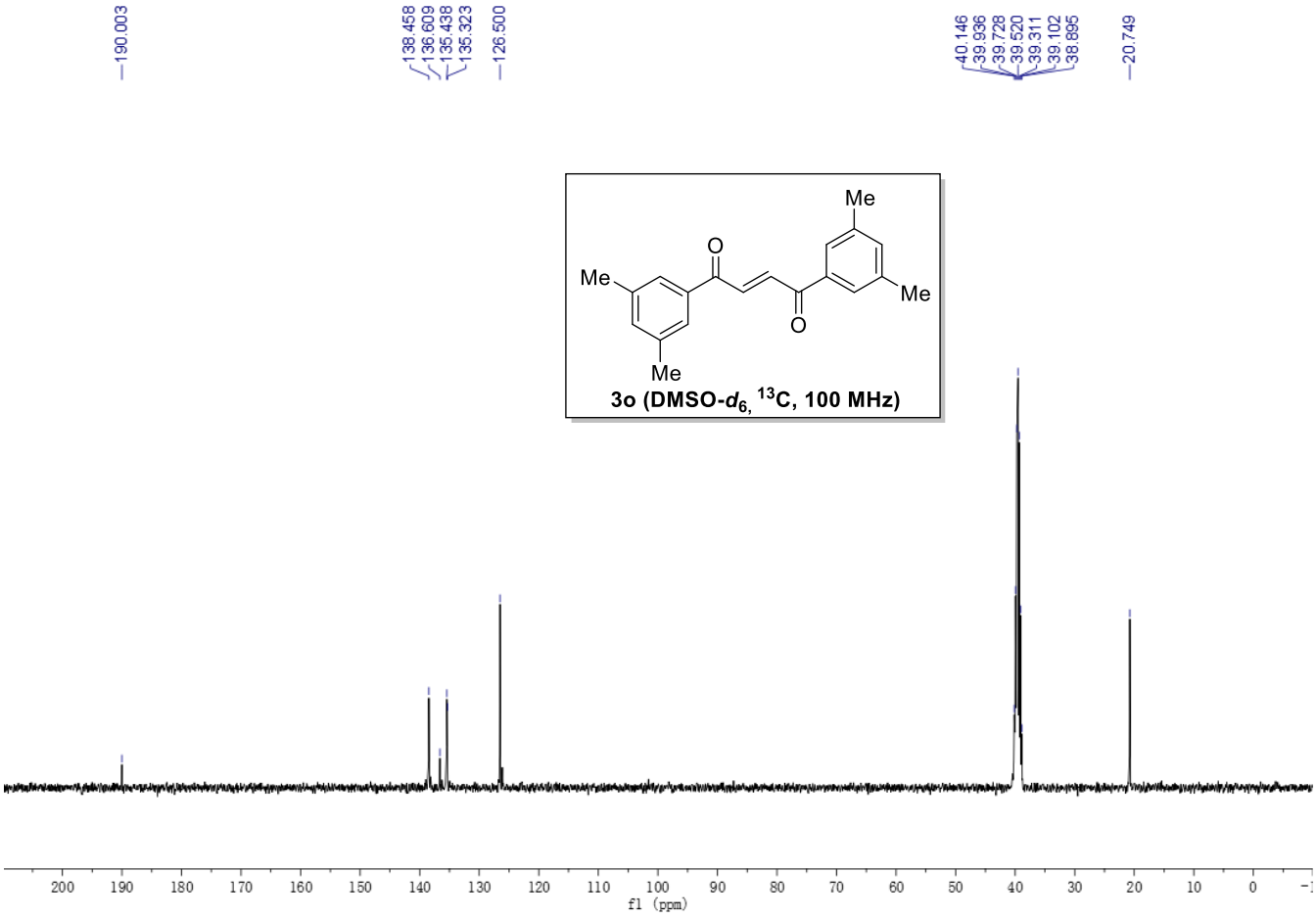

7.663
7.644
7.597
7.588
7.528
7.516
7.507
7.503
7.497
7.486
7.476
7.184
3.359
2.500
Cl
O
O
Cl
3m (DMSO-d_6, ^{1}H, 400 MHz)
6.09
2.04
2.00
f1 (ppm)

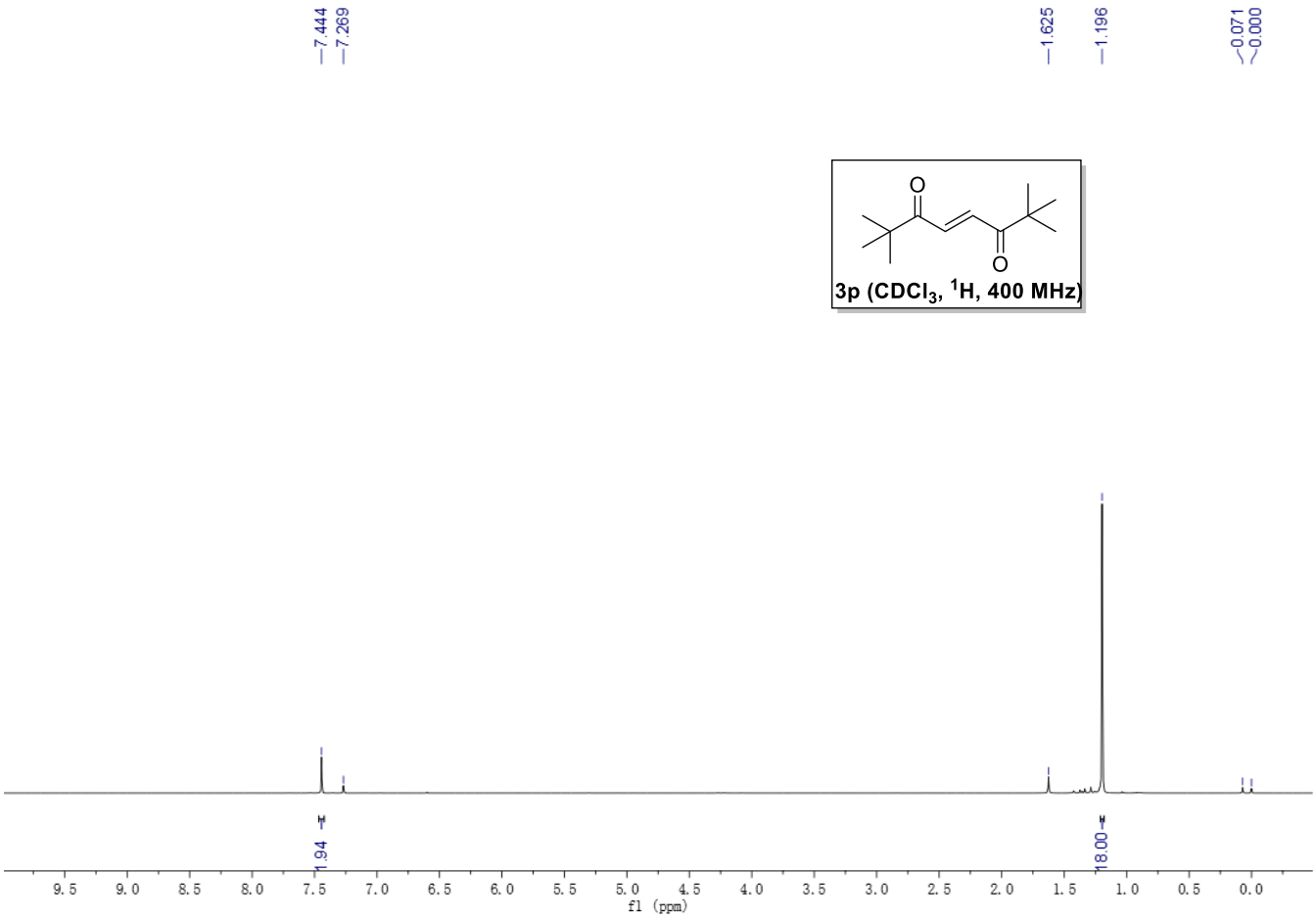

192.497
138.320
136.837
133.126
130.429
130.376
130.112
127.587
40.143
39.936
39.728
39.520
39.311
39.102
38.896
Cl
O
O
Cl
3m (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

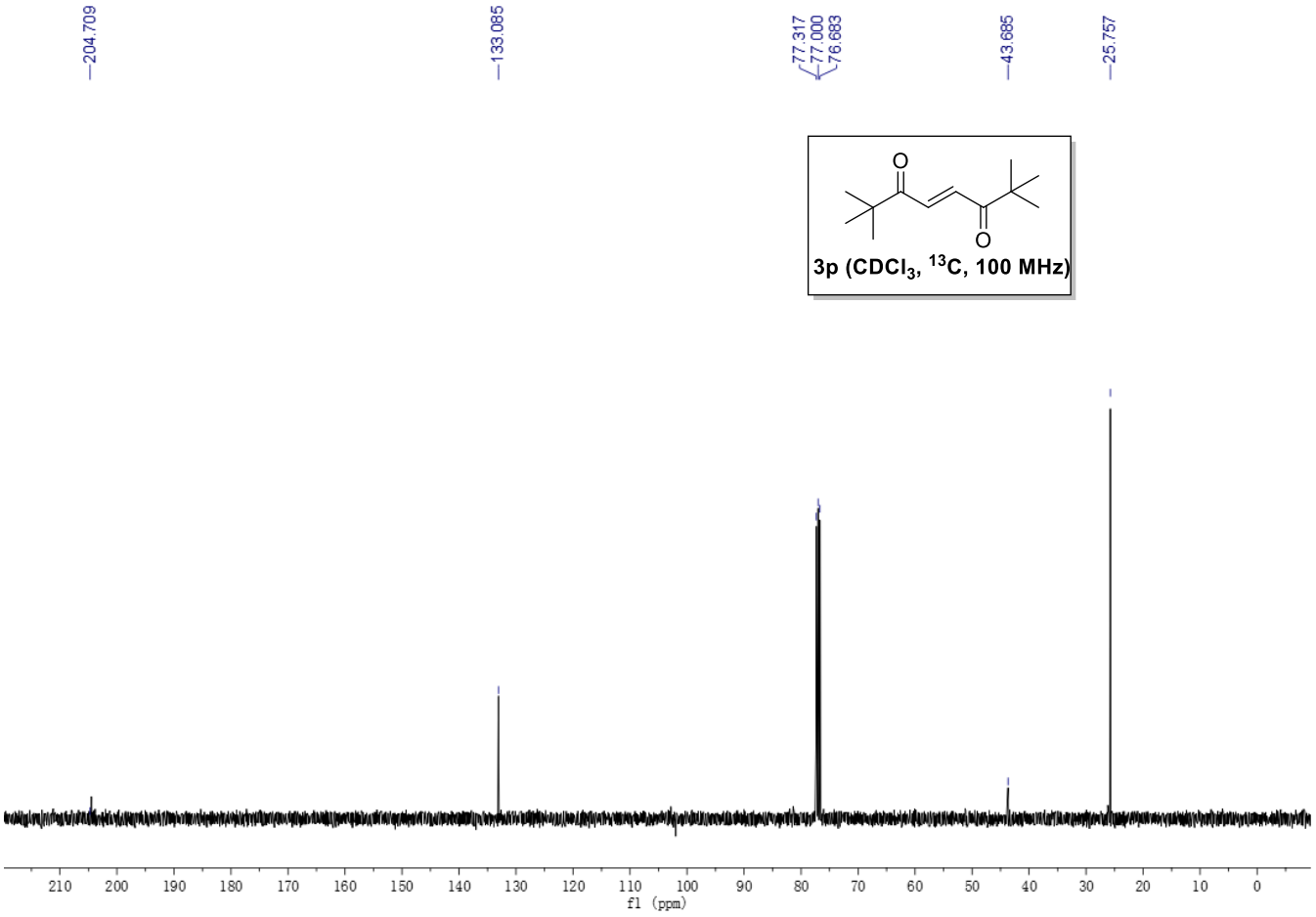

8.678
8.106
8.086
8.021
7.998
7.974
7.945
7.942
7.924
7.920
7.684
7.667
7.639
7.621
7.601
3.412
2.500
O
O
3n (DMSO-d_6, ^{1}H, 400 MHz)
2.00
2.13
6.10
6.08
f1 (ppm)

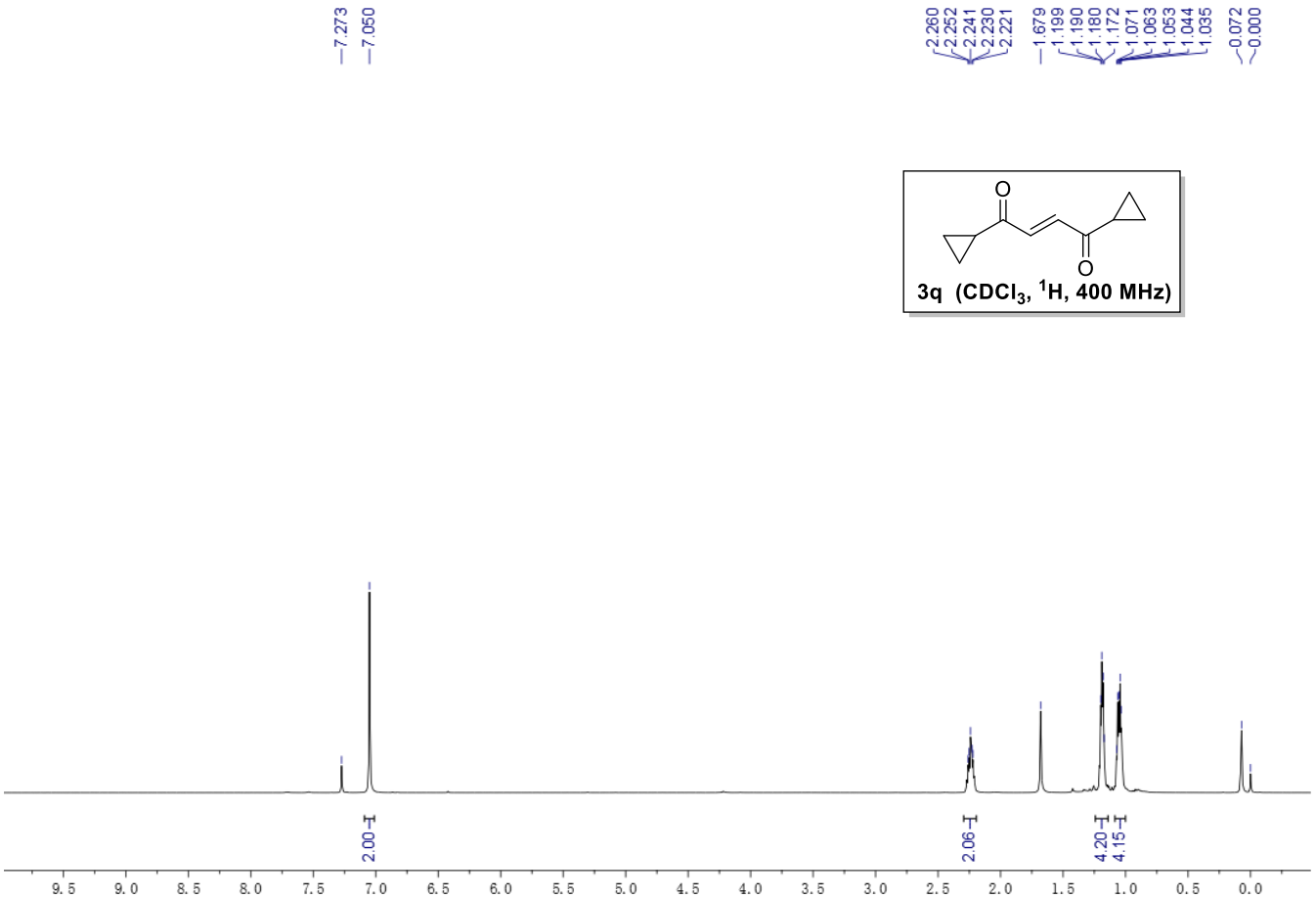

192.444
136.300
135.227
133.294
132.146
130.758
129.628
128.910
128.589
127.727
127.046
123.493
40.146
39.937
39.729
39.520
39.312
39.101
38.897
O
O
3n (DMSO-d_6, ^{13}C, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

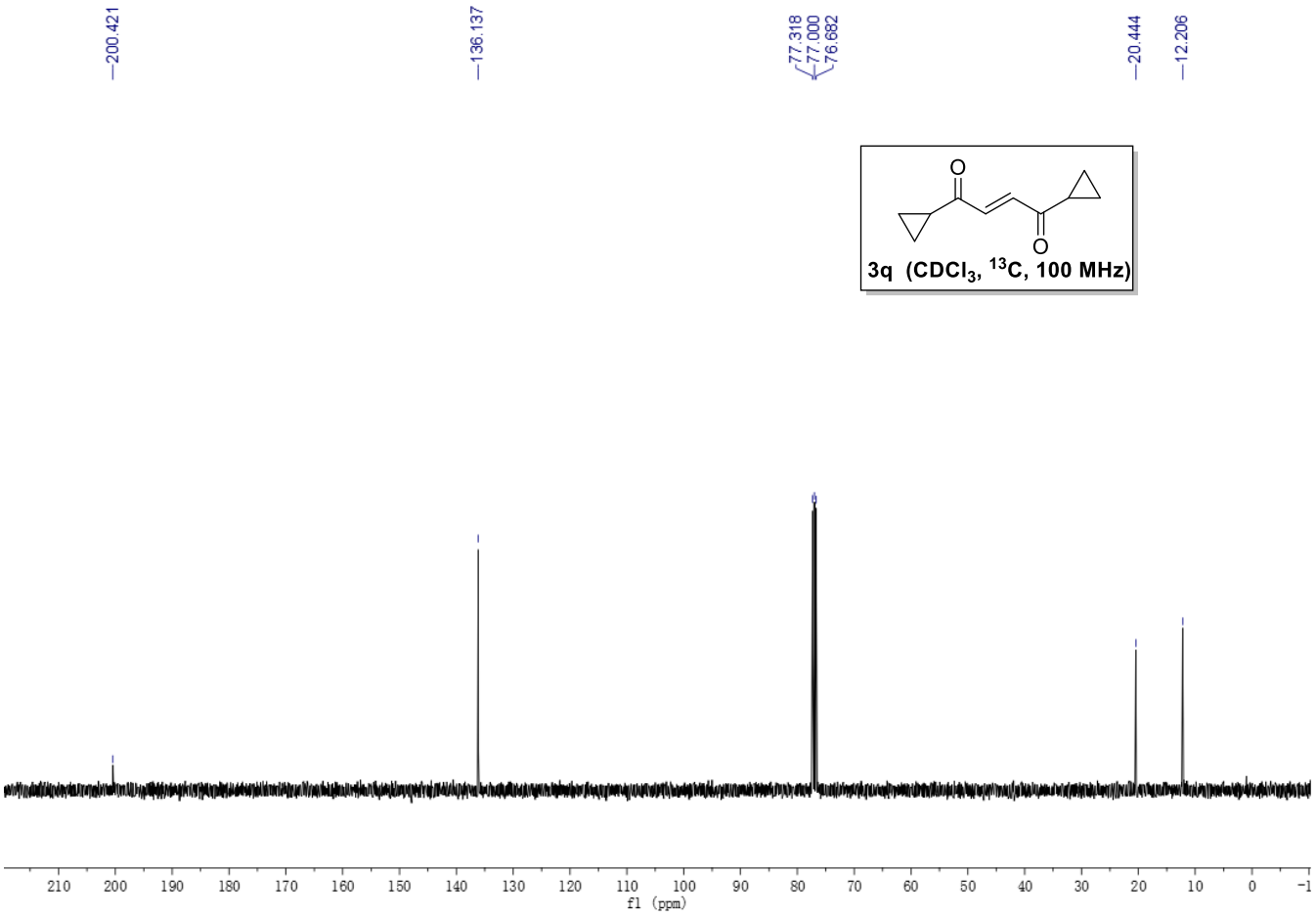

7.880
7.674
7.341
3.392
2.500
2.361
Me
Me
Me
Me
O
O
3o (DMSO-d_6, ^{1}H, 400 MHz)
2.03
4.02
2.09
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

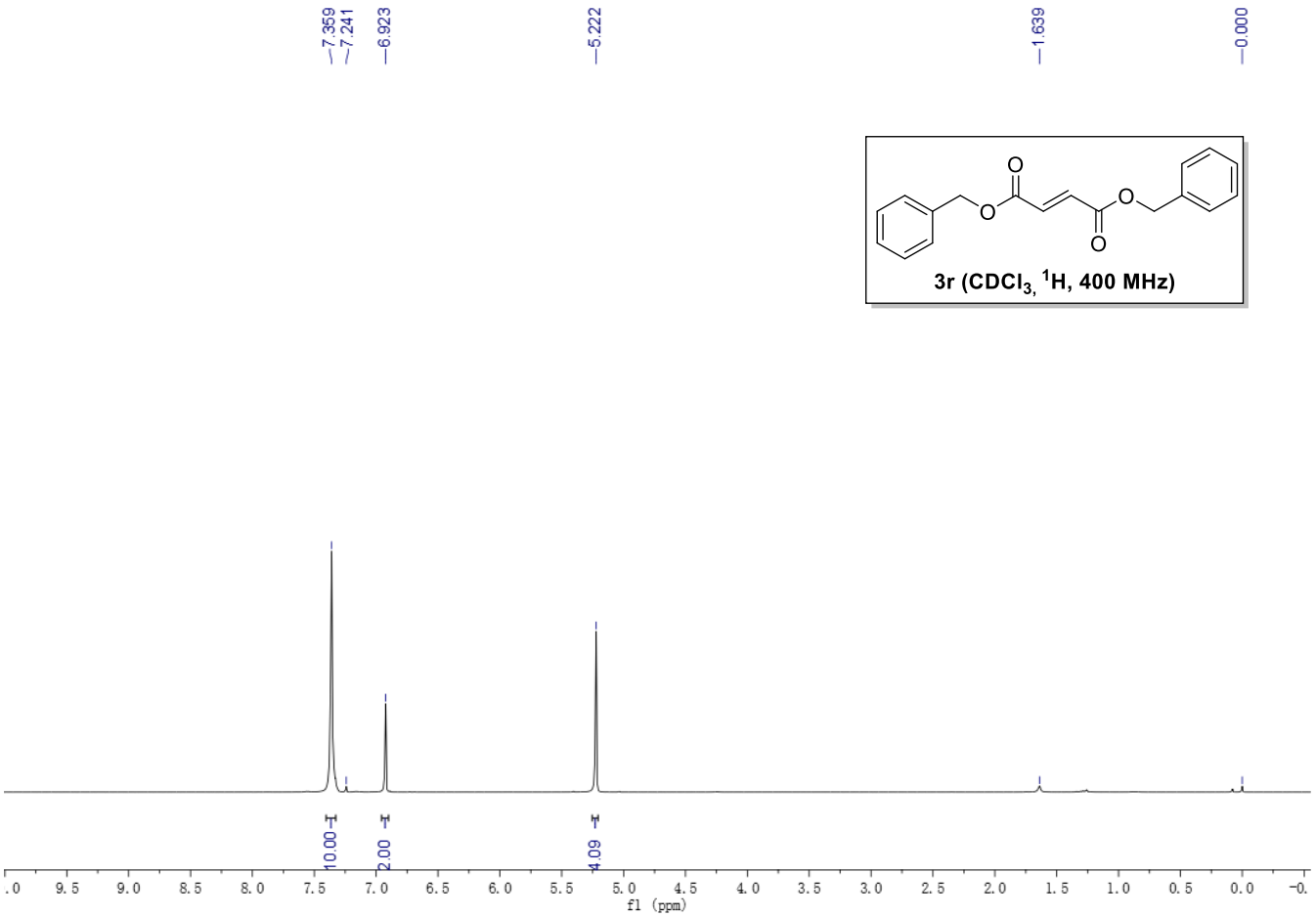

190.003
138.458
136.609
135.438
135.323
126.500
40.146
39.936
39.728
39.520
39.311
39.102
38.895
20.749
Me
Me
Me
O
O
3o (DMSO-d_6, ^{13}C, 100 MHz)
f1 (ppm)

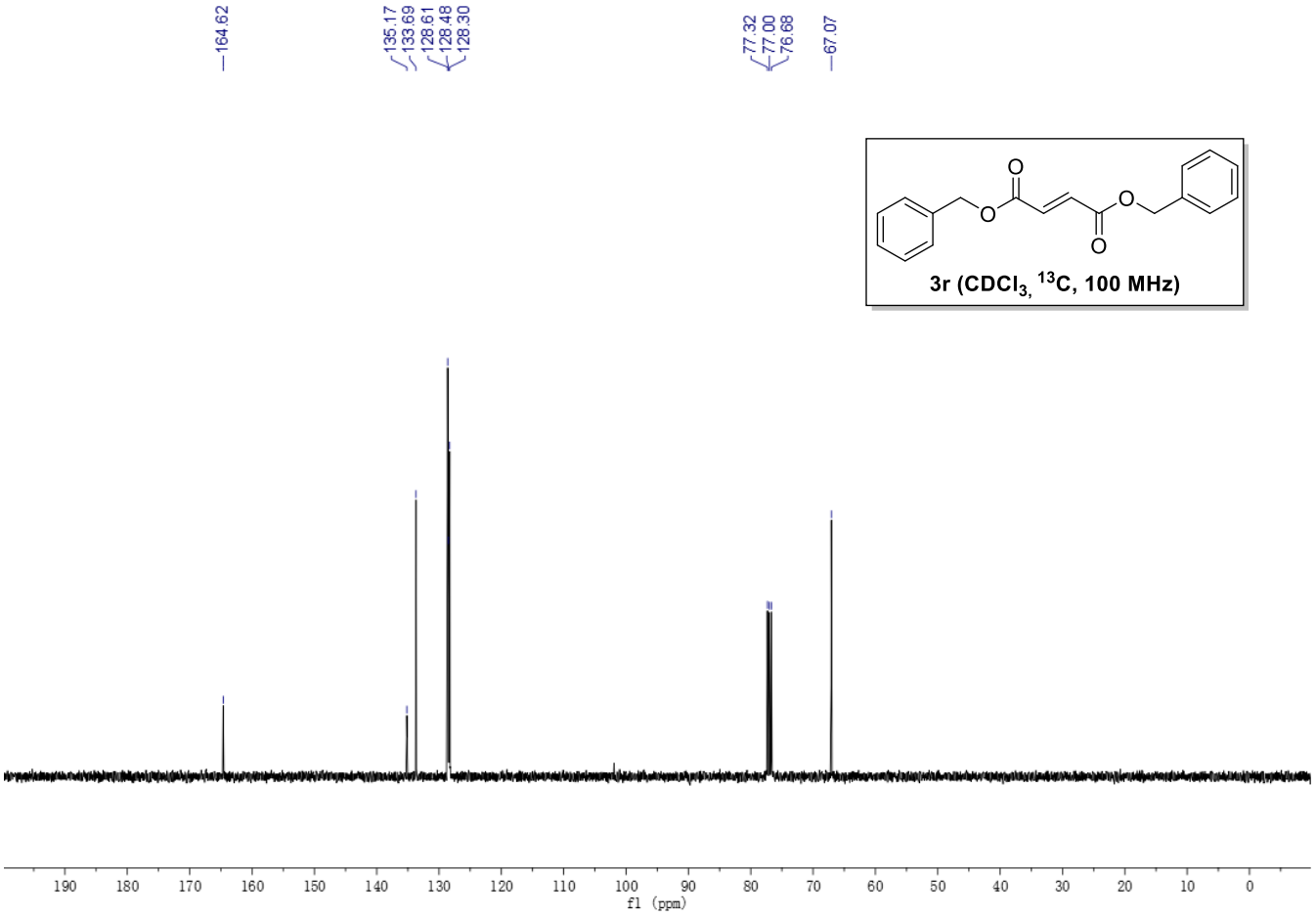

7.444
7.269
1.625
1.196
0.071
0.000
O
O
3p ($CDCl_3$, ^{1}H, 400 MHz)
1.94
18.00
f1 (ppm)

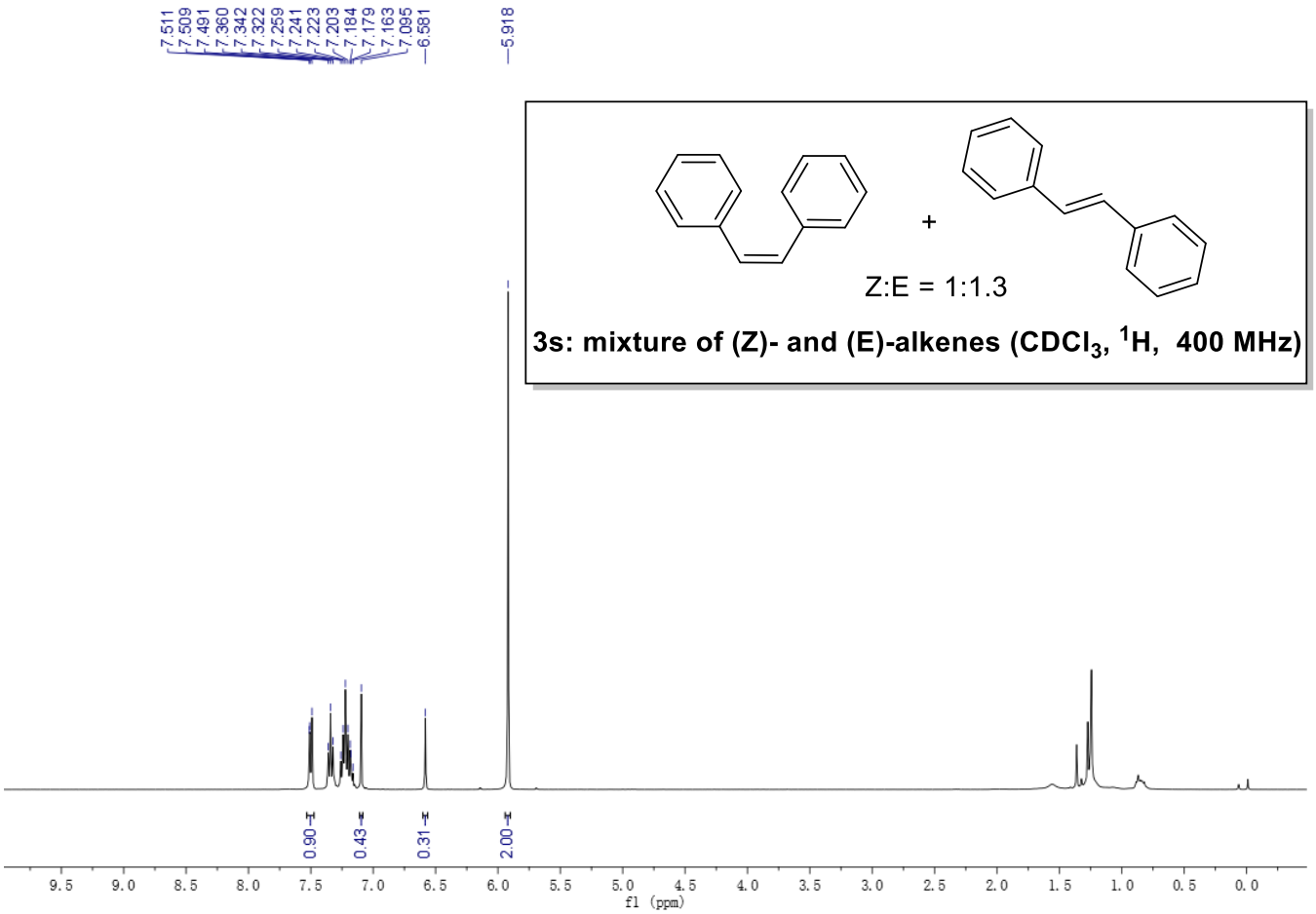

204.709
133.085
77.317
77.000
76.683
43.685
25.757
3p (CDCl3, 13C, 100 MHz)
f1 (ppm)

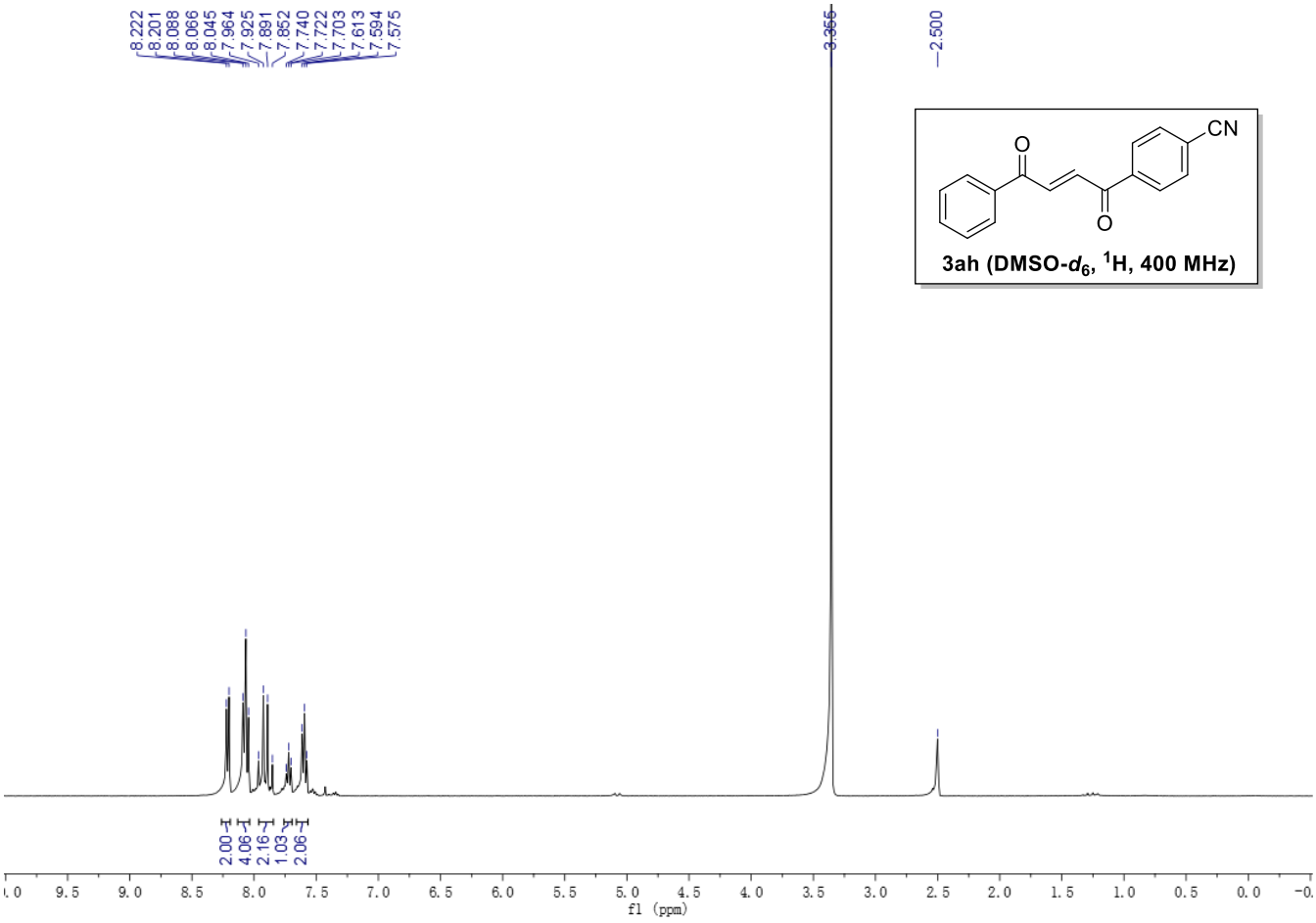

7.273
7.050
2.260
2.252
2.241
2.230
2.221
1.679
1.199
1.190
1.180
1.172
1.071
1.063
1.053
1.044
1.035
0.072
0.000
3q (CDCl3, 1H, 400 MHz)
2.00
2.06
4.20
4.15
f1 (ppm)


200.421
136.137
77.318
77.000
76.682
20.444
12.206
3q (CDCl3, 13C, 100 MHz)
f1 (ppm)

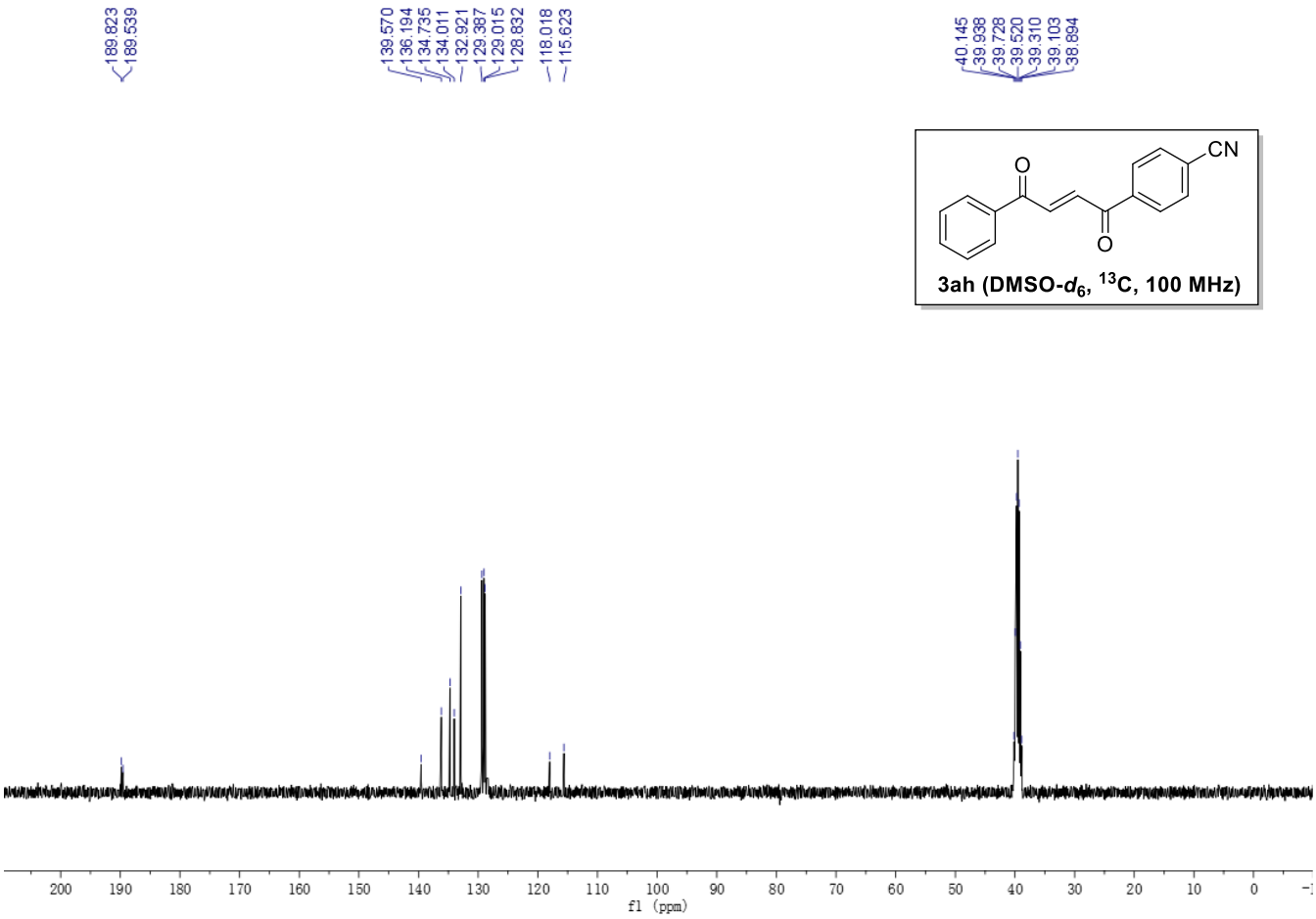

7.359
7.241
6.923
5.222
1.639
0.000
3r (CDCl3, 1H, 400 MHz)
10.00
2.00
4.09
f1 (ppm)


164.62
135.17
133.69
128.61
128.48
128.30
77.32
77.00
76.68
67.07
3r (CDCl3, 13C, 100 MHz)
f1 (ppm)

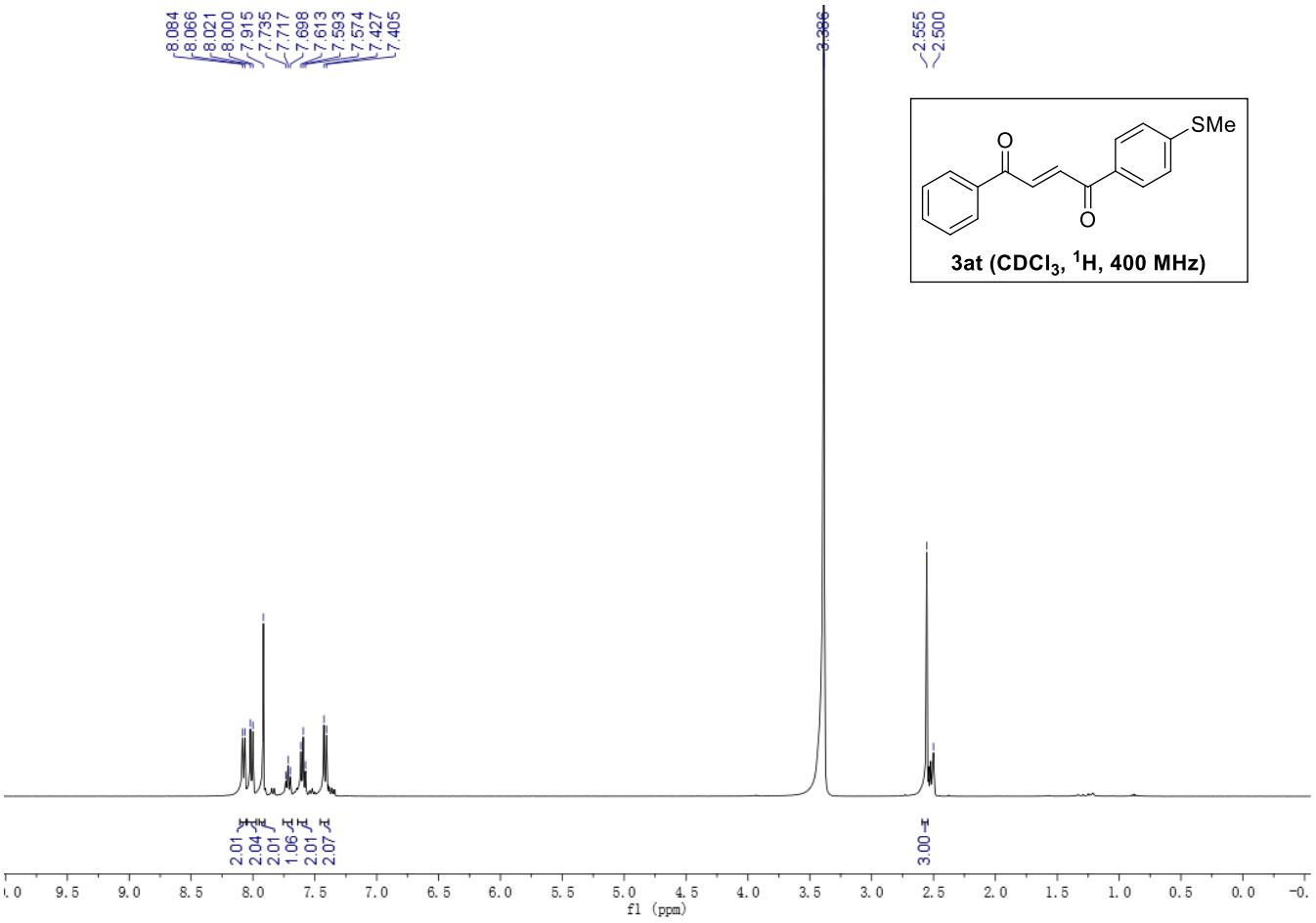

7.511
7.509
7.491
7.360
7.342
7.322
7.259
7.241
7.223
7.203
7.184
7.179
7.163
7.095
6.581
5.918
Z:E = 1:1.3
3s: mixture of (Z)- and (E)-alkenes (CDCl3, 1H, 400 MHz)
0.90
0.43
0.31
2.00
f1 (ppm)



3ah (DMSO-d_6, ^{1}H, 400 MHz)

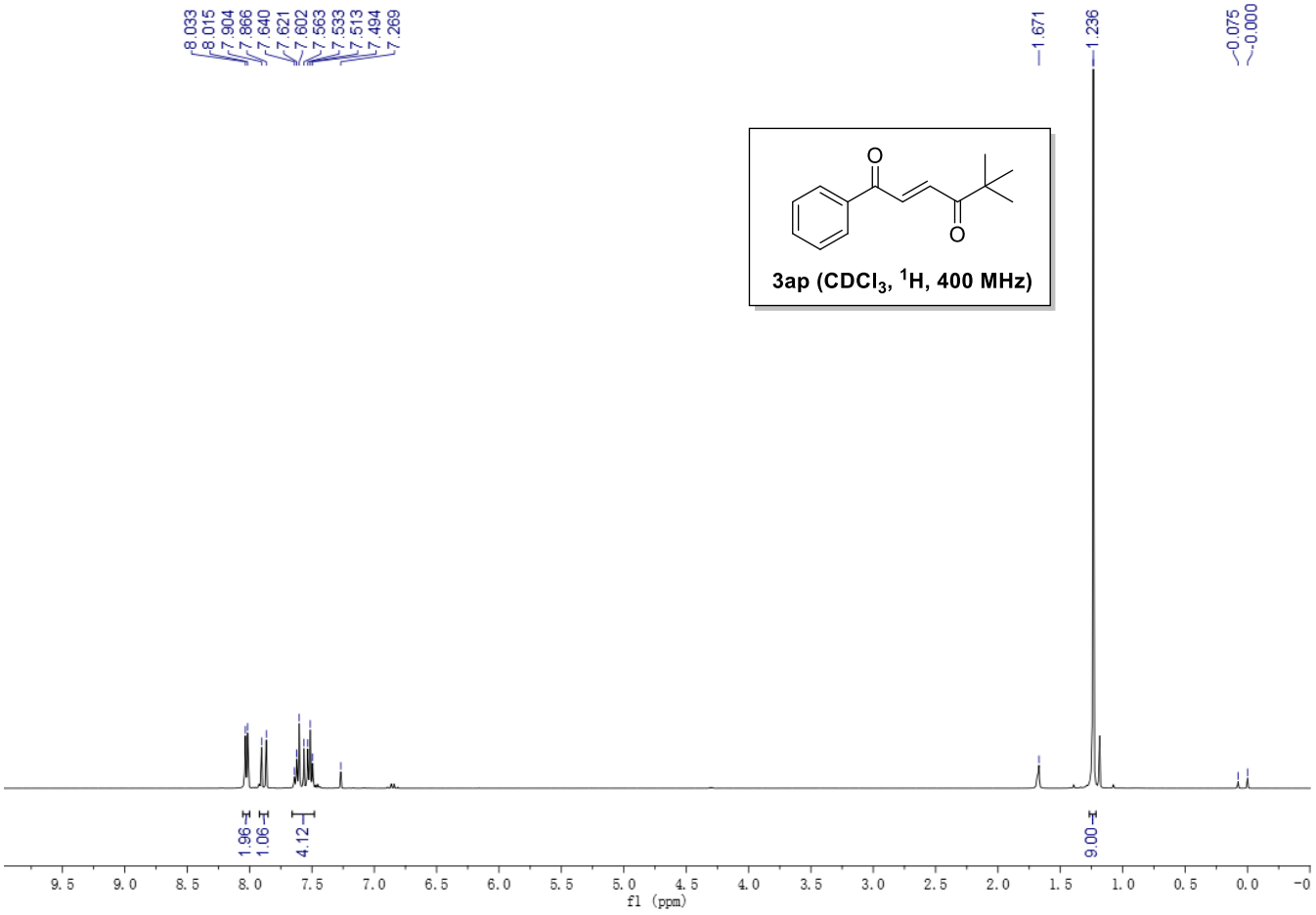


3ah (DMSO-d_6, ^{13}C, 100 MHz)

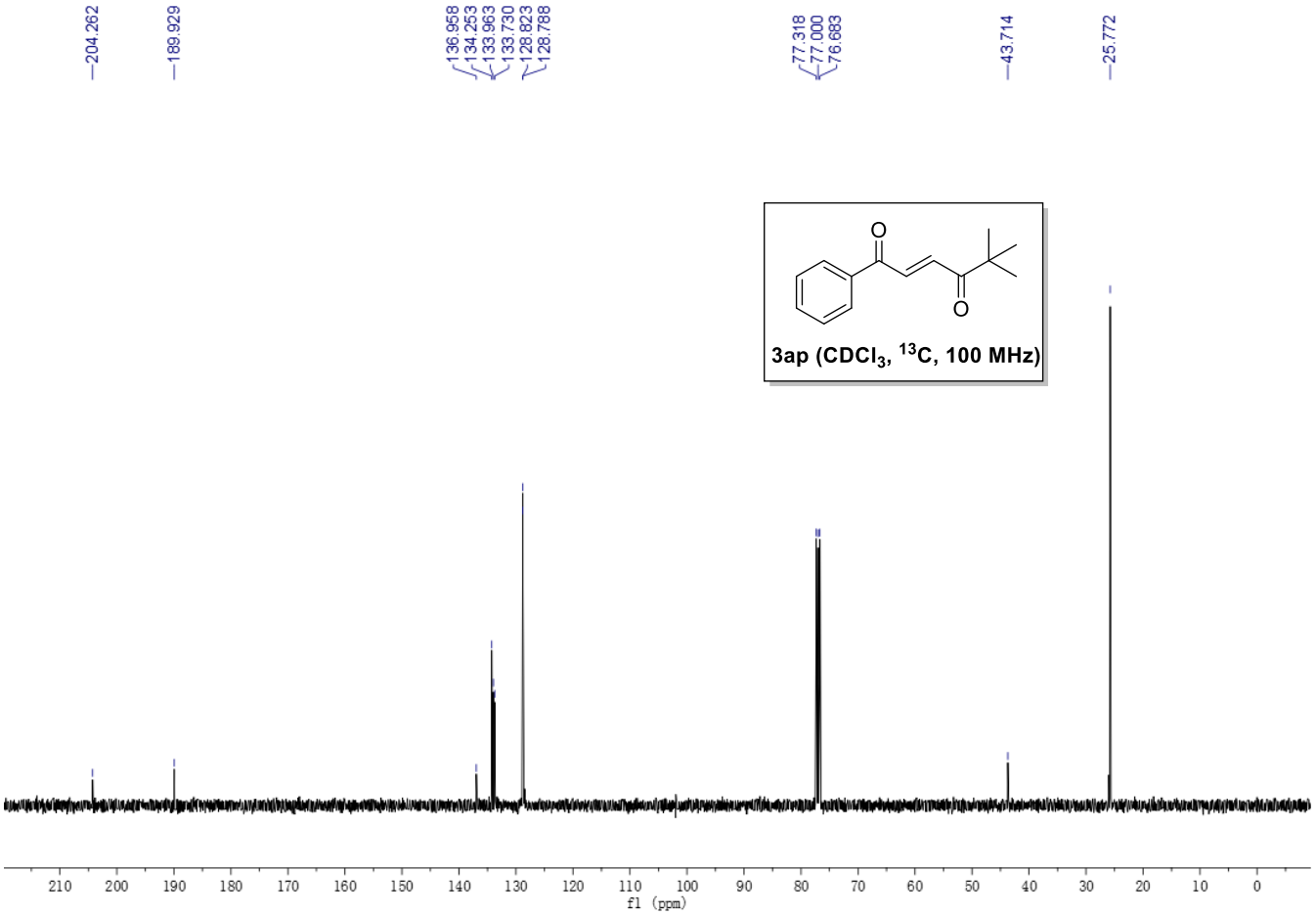


3at ($CDCl_3$, ^1H, 400 MHz)

3at ($CDCl_3$, ^{13}C, 100 MHz)



3ap ($CDCl_3$, ^1H, 400 MHz)



3ap ($CDCl_3$, ^{13}C, 100 MHz)