*Supporting Information*

# Electrochemical Halogenation/Semi-pinacol Rearrangement of Allylic Alcohols Using Inorganic Halide Salt: An Eco-friendly Route to Synthesis of β-halocarbonyls

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## 1. General information

**Reagents:** All commercial materials were used as received from Energy Chemical or Adamas-beta, Alfa Aesar, TCI and Acros unless otherwise noted. $MgCl_2$ (99%, Energy), $MgBr_2 \cdot 6H_2O$ (98+%, Alfa Aesar) were used in the electrochemical reactions.

**Reactions:** All reactions were carried out in undivided electrochemical cells (30 mL) using pre-dried glassware, if not noted otherwise. The electrochemical cells were fitted with a threaded Teflon cap with electrical feed-throughs. Electrocatalysis was conducted using an DC-power supplier HY3005ET in constant current mode, CV studies were performed using a CHI660E workstation.

**Chromatography:** Thin layer chromatography (TLC) was carried out on silica gel 60 F254 pre-coated glass plates. Visualization was detected by irradiation with UV light (254 nm), or by treatment with a solution of phosphomolybdic acid in ethanol followed by heating. Flash chromatography was carried out on 200 – 300 mesh silica gel, eluting with a mixture of petroleum ether (b.p. 60 – 90 °C) and ethyl acetate.

**NMR Spectroscope:** $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker AVANCE III HD 400 or 500 spectrometer, operating at 400 (or 500) MHz and 100 (or 125) MHz respectively. Chemical shifts (δ) were given in parts per million (ppm), and referenced relative to residual solvent $CHCl_3$ (7.26 ppm) in $CDCl_3$, or tetramethylsilane (0.00 ppm) as an internal standard for $^{1}H$ NMR spectra and deuterated solvent $CDCl_3$ (77.0 ppm) for $^{13}C$ NMR spectra. Coupling constants (*J*) were reported in hertz (Hz). The following abbreviations are used to indicate the multiplicity of the signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and associated combinations, e.g. dd = doublet of doublets.

**Mass Spectrometry:** High-resolution mass spectra (HRMS) were obtained on a Waters ACQUITYTM UPLC & Q-TOF MS Premier using the electrospray ionization (ESI) technique.

**X-Ray**: X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer.

**Preparation of substrates:** The allylic alcohols and alkenyl bromides were prepared

according to the related references.[1-7]

## 2. Cyclic voltammetry studies

**General information:** Cyclic voltammetry (CV) experiments were conducted in a 30 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter, BASi), a saturated calomel electrode as reference electrode, and a platinum wire counter electrode. The solution of interest was sparged with nitrogen for 3-5 minutes before data collection. The diagrams were made using OriginLab 8.0.

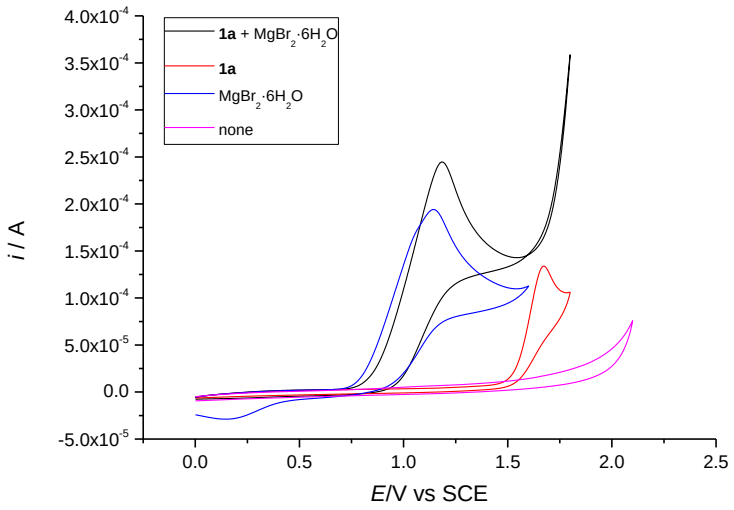



**Fig. S1.** Cyclic voltammogram of **1a**, $MgBr_2 \bullet 6H_2O$, and their mixture in MeCN/MeOH. Conditions: $LiClO_4$ (1 mmol) in MeCN/MeOH (6/3 mL), and with (a) none, (b) **1a** (0.04mmol), (c) $MgBr_2 \bullet 6H_2O$ (0.08 mmol) and (d) $MgBr_2 \bullet 6H_2O$ (0.08 mmol) and **1a** (0.04mmol). **Scan rate: 50 mV/s.**

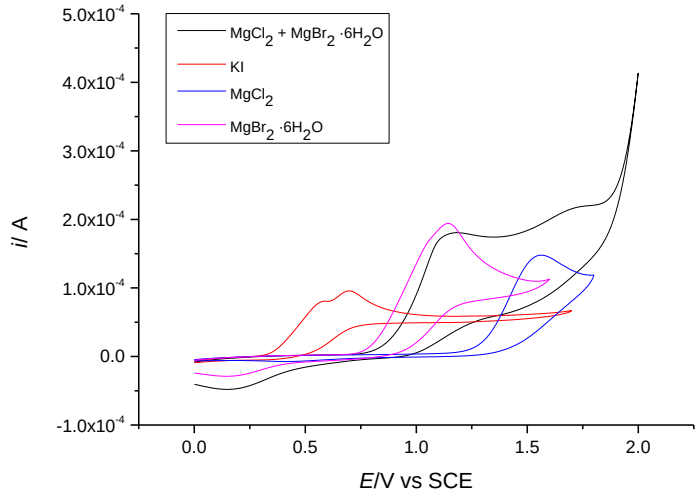



**Fig. S2.** Cyclic voltammogram of halide salt and their mixture in MeCN/MeOH. Conditions: $LiClO_4$ (1 mmol) in MeCN/MeOH (6/3 mL), and with (a) $MgBr_2 \bullet 6H_2O$ (0.08 mmol), (b) $MgCl_2$ (0.08 mmol), (c) KI (0.16 mmol) and (d) $MgBr_2 \bullet 6H_2O$ (0.08 mmol) and $MgCl_2$ (0.08 mmol). **Scan rate: 50 mV/s.**

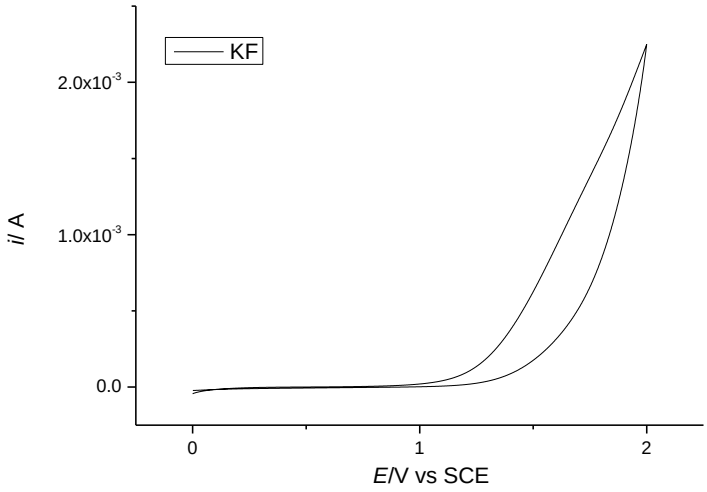
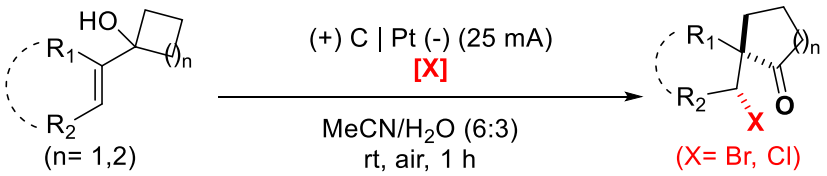
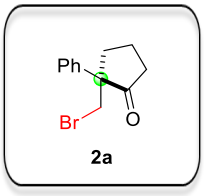



**Fig. S3.** Cyclic voltammogram of halide salt and their mixture in MeCN/MeOH. Conditions: $LiClO_4$ (1 mmol) in MeCN/MeOH (6/3 mL), KF (0.16 mmol). **Scan rate: 50 mV/s.**

## 3. General procedure for electrochemical semi-pinacol rearrangement




**General procedure:** To an oven-dried, undivided electrochemical cell equipped with a magnetic stir bar, a carbon anode (10.0 mm * 10.0 mm), and a Pt plate cathode (10.0 mm * 10.0 mm) were added $MgCl_2$ or $MgBr_2 \cdot 6H_2O$ (4.0 equiv., 1.6 mmol), allylic alcohol (1.0 equiv., 0.4 mmol) and followed by the addition of 6 mL MeCN and 3 mL $H_2O$. The mixture was stirred for 5 min. The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h, electricity = 2.3 F. Ethyl acetate (10 mL) and water (10 mL) was added, the aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.



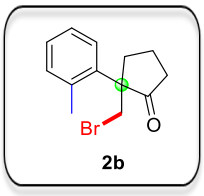
**2a**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2a** as colorless oil in 81% yield (82.5 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.38 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 3.77 (d, *J* = 10.3 Hz, 1H), 3.57 (d, *J* = 10.3 Hz, 1H), 2.71 – 2.65 (m, 1H), 2.53 – 2.19 (m, 3H), 2.07 – 1.93 (m, 1H), 1.86 – 1.66 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.1, 136.9, 128.9, 127.9, 126.8, 57.8, 39.1, 37.6, 32.8, 18.3.

**HRMS** (ESI) *m/z* calculated for $C_{12}H_{14}BrO^+$ [M+H$^+$] 255.0202, found 255.0218.



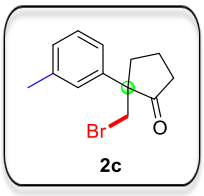
**2b**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2b** as pale yellow oil in 83% yield (88.8 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 2H), 7.15 – 7.06 (m, 2H), 3.85 (m, 2H), 2.68 – 2.52 (m, 2H), 2.52 – 2.38 (m, 4H), 2.36 – 2.27 (m, 1H), 2.04 – 1.94 (m, 1H), 1.82 – 1.71 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 217.7, 137.3, 136.1, 133.3, 127.8, 127.6, 126.2, 58.5, 37.9, 36.3, 34.2, 21.8, 18.8.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}BrO$ [M+H$^+$] 267.0379, found 267.0382.



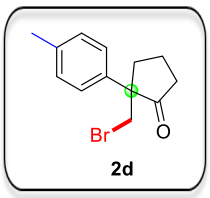
**2c**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2c** as colorless oil in 72% yield (52.3 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 1H), 7.15 – 7.07 (m, 1H), 3.76 (d, *J* = 10.3 Hz, 1H), 3.56 (d, *J* = 10.3 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.50 – 2.30 (m, 2H), 2.35 (s, 3H), 2.31 – 2.21 (m, 1H), 2.06 – 1.94 (m, 1H), 1.86 – 1.69 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.3, 138.6, 136.8, 128.8, 128.7, 127.5, 123.8, 57.8, 39.1, 37.6, 32.8, 21.6, 18.3.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}BrO$ [M+H$^+$] 267.0379, found 267.0381.



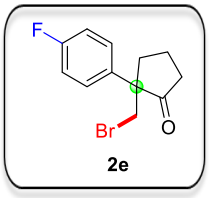
**2d**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2d** as colorless oil in 92% yield (98.2 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.18 – 7.16 (m, 2H), 3.76 (d, *J* = 10.3 Hz, 1H), 3.55 (d, *J* = 10.3 Hz, 1H), 2.69 – 2.63 (m, 1H), 2.51 – 2.16 (m, 6H), 2.07 – 1.93 (m, 1H), 1.89 – 1.68 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.4, 137.8, 133.7, 129.7, 126.7, 57.6, 39.3, 37.6, 32.7, 21.0, 18.3.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}BrO$ [M+H$^+$] 267.0379, found 267.0391.



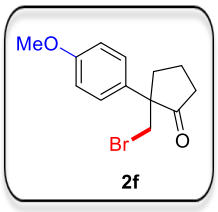
**2e**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2e** as white solid in 79% yield (85.7 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 2H), 7.07 – 7.02 (m, 2H), 3.71 (d, *J* = 10.3 Hz, 1H), 3.53 (d, *J* = 10.4 Hz, 1H), 2.67 – 2.62 (m, 1H), 2.47 – 2.22 (m, 3H), 2.05 – 1.98 (m, 1H), 1.83 – 1.68 (m, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 216.0, 162.3 (d, *J* = 248.3 Hz), 132.5 (d, *J* = 3.2 Hz), 128.7 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.4 Hz), 57.1, 39.3 (d, *J* = 1.6 Hz), 37.6, 33.0, 18.3.

**HRMS** (ESI) *m/z* calculated for $C_{12}H_{12}BrFNaO$ [M+Na$^+$] 292.9948, found 292.9956.



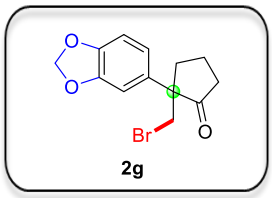
**2f**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2f** as pale yellow oil in 98% yield (111.0 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 6.92 – 6.83 (m, 2H), 3.80 (s, 3H), 3.75 (d, *J* = 10.3 Hz, 1H), 3.52 (d, *J* = 10.3 Hz, 1H), 2.67 – 2.61 (m, 1H), 2.48 – 2.17 (m, 3H), 2.04 – 1.95 (m, 1H), 1.85 – 1.67 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.4, 159.2, 128.4, 128.1, 114.3, 57.2, 55.2, 39.4, 37.6, 32.7, 18.3.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}BrO_2$ [M+H$^+$] 285.0308, found 285.0320.



**2g**

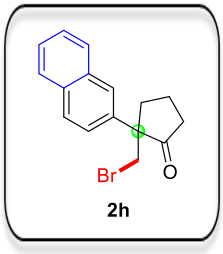
Purification of the crude product by flash column chromatography afforded the

semi-pinacol rearrangement product **2g** as white solid in 92% yield (109.3 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.91 (d, *J* = 2.0 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 5.94 (d, *J* = 1.1 Hz, 2H), 3.70 (d, *J* = 10.3 Hz, 1H), 3.50 (d, *J* = 10.3 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.46 – 2.15 (m, 3H), 2.02 – 1.94 (m, 1H), 1.88 – 1.65 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 215.9, 148.2, 147.2, 130.3, 120.4, 108.4, 107.3, 101.3, 57.4, 39.3, 37.5, 33.0, 18.2.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{14}BrO_3$ [M+H$^+$] 299.0100, found 299.0106.



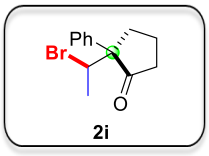
**2h**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2h** as white solid in 93% yield (113.2 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.76 (m, 4H), 7.56 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.53 – 7.48 (m, 2H), 3.85 (d, *J* = 10.3 Hz, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 2.85 – 2.79 (m, 1H), 2.61 – 2.24 (m, 3H), 2.09 – 2.01 (m, 1H), 1.89 – 1.76 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.2, 134.1, 133.2, 132.6, 128.8, 128.1, 127.4, 126.5, 126.4, 126.3, 124.2, 58.0, 39.0, 37.7, 32.8, 18.4.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{16}BrO$ [M+H$^+$] 305.0359, found 305.0351.



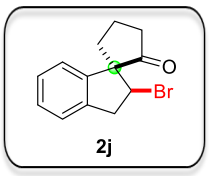
**2i**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2i** as white solid in 79% yield (84.2 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 4.78 (q, *J* = 6.9 Hz, 1H), 2.75 – 2.66 (m, 1H), 2.63 – 2.57 (m, 1H), 2.31 – 2.21 (m, 2H), 2.11 – 2.01 (m, 1H), 1.86 – 1.68 (m, 1H), 1.35 (d, *J* = 6.9 Hz, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 216.1, 134.8, 129.0, 127.9, 127.4, 61.8, 54.9, 37.5, 27.7, 21.5, 18.6.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}BrO$ [M+H$^+$] 267.0379, found 267.0388.



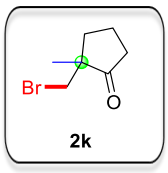

**2j**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2j** as white solid in 45% yield (47.8 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.13 (m, 3H), 7.13 – 7.03 (m, 1H), 4.36 (dd, *J* = 10.2, 7.7 Hz, 1H), 3.66 (dd, *J* = 15.3, 10.2 Hz, 1H), 3.31 (dd, *J* = 15.3, 7.7 Hz, 1H), 2.56 – 2.41 (m, 2H), 2.41 – 2.23 (m, 3H), 2.21 – 2.00 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 215.6, 143.8, 141.8, 128.0, 127.3, 124.5, 122.2, 63.5, 54.0, 41.2, 38.6, 34.7, 20.2.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{14}BrO$ [M+H$^+$] 265.0223, found 265.0215.



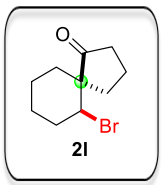

**2k**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2k** as colorless oil in 66% yield (50.4 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.48 (d, *J* = 10.1 Hz, 1H), 3.31 (d, *J* = 10.1 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.29 – 2.16 (m, 2H), 2.04 – 1.92 (m, 1H), 1.92 – 1.77 (m, 2H), 1.13 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 219.5, 49.7, 39.0, 38.0, 34.7, 21.7, 18.5.

**HRMS** (ESI) *m/z* calculated for $C_7H_{12}BrO$ [M+H$^+$] 191.0066, found 191.0072.



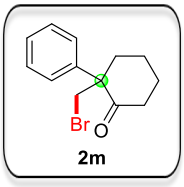

**2l**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2l** as pale yellow oil in 55% yield (51.0 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.99 (dd, *J* = 12.0, 4.8 Hz, 1H), 2.70 (qd, *J* = 12.8, 4.1 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.38 – 2.18 (m, 2H), 2.18 – 2.06 (m, 1H), 2.04 – 1.94 (m, 2H), 1.92 – 1.75 (m, 2H), 1.74 – 1.62 (m, 2H), 1.54 – 1.39 (m, 1H), 1.39 – 1.19 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 218.2, 58.4, 52.2, 39.6, 37.9, 34.6, 33.4, 27.1, 20.4, 18.7.

**HRMS** (ESI) *m/z* calculated for $C_{10}H_{16}BrO$ [M+H$^+$] 233.0359, found 233.0368.



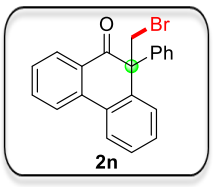
**2m**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2m** as pale yellow oil in 42% yield (34 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.14 (m, 2H), 3.80 (d, *J* = 10.5 Hz, 1H), 3.50 (d, *J* = 10.5 Hz, 1H), 2.90 – 2.84 (m, 1H), 2.38 – 2.22 (m, 2H), 2.04 – 1.89 (m, 2H), 1.86 – 1.63 (m, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.8, 137.7, 129.1, 127.8, 127.0, 57.2, 42.9, 40.0, 33.9, 27.7, 21.4.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}BrO$ [M+H$^+$] 267.0379, found 267.0385.



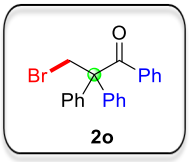
**2n**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2n** as white solid in 81% yield (116.7 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.5, 1.9 Hz, 1H), 8.07 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 7.42 (dd, *J* = 7.3, 1.9 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.24 – 7.15 (m, 3H), 7.14 – 7.04 (m, 2H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.02 (d, *J* = 10.1 Hz, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 196.6, 140.0, 137.8, 136.8, 134.7, 131.3, 129.1, 129.1, 128.8, 128.7, 128.3, 128.2, 128.2, 128.0, 127.2, 124.2, 123.0, 60.5, 36.2.

**HRMS** (ESI) *m/z* calculated for $C_{21}H_{16}BrO$ [M+H$^+$] 363.0379, found 363.0386.



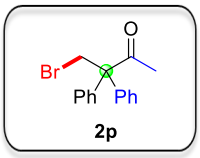
**2o**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2o** as white solid in 79% yield (116.1 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 2H), 7.50 – 7.44 (m, 4H), 7.41 – 7.30 (m, 7H), 7.23 – 7.19 (m, 2H), 4.32 (s, 2H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 198.9, 139.3, 136.9, 132.0, 129.9, 129.6, 128.5, 127.9, 127.8, 65.0, 42.1.

**HRMS** (ESI) *m/z* calculated for $C_{21}H_{18}BrO$ [M+H$^+$] 365.0536, found 365.0533.



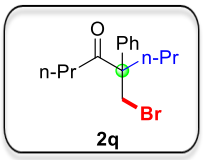
**2p**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2p** as white solid in 74% yield (90 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.30 (m, 10H), 4.21 (s, 2H), 2.13 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 206.0, 138.8, 129.4, 128.4, 127.8, 66.6, 40.2, 27.5.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{16}BrO$ [M+H$^+$] 303.0379, found 303.0385.



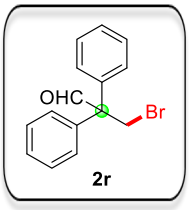
**2q**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2q** as pale yellow oil in 56% yield (66.8 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.20 (dd, *J* = 7.5, 1.8 Hz, 2H), 4.03 (d, *J* = 10.9 Hz, 1H), 3.86 (dd, *J* = 10.9, 1.1 Hz, 1H), 2.34 – 2.27 (m, 1H), 2.23 – 2.11 (m, 2H), 2.12 – 2.03 (m, 1H), 1.52 – 1.42 (m, 2H), 1.34 – 1.15 (m, 1H), 1.13 – 0.94 (m, 4H), 0.73 (t, *J* = 7.4 Hz, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 210.2, 139.7, 128.8, 127.5, 126.5, 59.4, 39.8, 38.9, 33.9, 17.3, 16.9, 14.5, 13.5.

**HRMS** (ESI) *m/z* calculated for $C_{15}H_{22}BrO$ [M+H$^+$] 297.0849, found 297.0856.



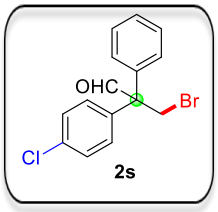
**2r**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2r** as white solid in 73% yield (89.1 mg).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.44 – 7.31 (m, 6H), 7.25 – 7.22 (m, 4H), 4.17 (s, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.2, 137.5, 129.1, 128.8, 128.0, 63.9, 36.2.

**HRMS** (ESI) *m/z* calculated for $C_{15}H_{14}BrO$ [M+H$^+$] 289.0223, found 289.0226.



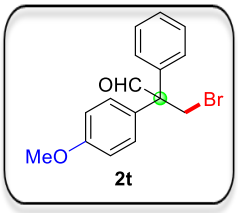
**2s**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2s** as pale yellow oil in 58% yield (74.5 mg).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.48 – 7.31 (m, 5H), 7.25 – 7.13 (m, 4H), 4.21 – 4.06 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.8, 137.0, 136.1, 134.2, 130.5, 129.0, 129.0, 128.3, 63.5, 35.9.

**HRMS** (ESI) *m/z* calculated for $C_{15}H_{13}BrClO$ [M+H$^+$] 322.9833, found 322.9851.



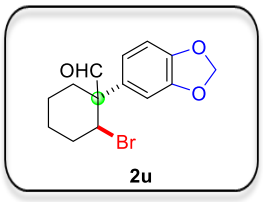
**2t**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2t** as pale yellow oil in 76% yield (96.9 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.43 – 7.31 (m, 3H), 7.25 – 7.20 (m, 2H), 7.17 – 7.11 (m, 2H), 6.95 – 6.86 (m, 2H), 4.16 – 4.12 (m, 2H), 3.81 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 196.2, 159.2, 137.8, 130.3, 129.1, 128.7, 128.0, 114.2, 63.2, 55.2, 36.5.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{16}BrO_2$ [M+H$^+$] 319.0328, found 319.0331.



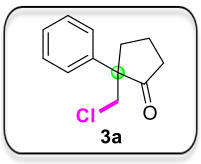
**2u**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2u** as white solid in 52% yield (64.9 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 6.84 – 6.82 (m, 2H), 6.76 (dd, *J* = 8.1, 2.0 Hz, 1H), 5.98 (q, *J* = 1.4 Hz, 2H), 5.00 (dd, *J* = 6.7, 3.3 Hz, 1H), 2.35 – 2.28 (m, 1H), 2.20 – 1.93 (m, 3H), 1.89 – 1.78 (m, 1H), 1.70 – 1.61 (m, 1H), 1.54 – 1.41 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 199.0, 148.6, 147.0, 130.6, 121.1, 108.7, 107.7, 101.4, 57.4, 55.4, 31.9, 28.5, 22.9, 21.2.

**HRMS** (ESI) *m/z* calculated for $C_{14}H_{16}BrO_3$ [M+H$^+$] 311.0277, found 311.0290.



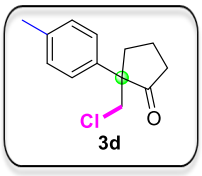
**3a**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3a** as colorless oil in 64% yield (53.5 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 4H), 7.33 – 7.27 (m, 1H), 3.91 (d, *J* = 11.1 Hz, 1H), 3.67 (d, *J* = 11.1 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.52 – 2.44 (m, 1H), 2.42 – 2.33 (m, 1H), 2.31 – 2.22 (m, 1H), 2.08 – 1.96 (m, 1H), 1.86 – 1.70 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.5, 136.8, 128.9, 127.9, 126.8, 58.4, 49.7, 37.7, 31.6, 18.4.

**HRMS** (ESI) *m/z* calculated for $C_{12}H_{13}ClNaO$ [M+Na$^+$] 231.0547, found 231.0553.



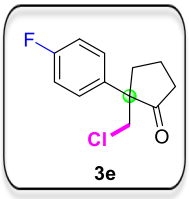
3d

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3d** as colorless oil in 75% yield (66.9 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 3.89 (d, *J* = 11.1 Hz, 1H), 3.64 (d, *J* = 11.1 Hz, 1H), 2.65 – 2.61 (m, 1H), 2.49 – 2.43 (m, 1H), 2.40 – 2.30 (m, 4H), 2.29 – 2.21 (m, 1H), 2.04 – 1.97 (m, 1H), 1.84 – 1.71 (m, 1H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 216.6, 137.7, 133.6, 129.6, 126.7, 58.2, 49.8, 37.6, 31.5, 20.9, 18.4.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}ClO$ [M+H$^+$] 223.0884, found 223.0883.



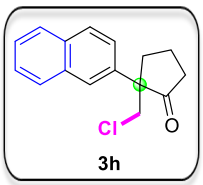
3e

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3e** as pale yellow solid in 61% yield (60 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 2H), 7.11 – 6.95 (m, 2H), 3.85 (d, *J* = 11.1 Hz, 1H), 3.63 (d, *J* = 11.1 Hz, 1H), 7.44 – 7.31 (m, 1H), 2.52 – 2.22 (m, 3H), 2.09 – 1.95 (m, 1H), 1.83 – 1.71 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.4, 162.3 (d, *J* = 248.7 Hz), 132.4 (d, *J* = 3.2 Hz), 128.8 (d, *J* = 8.1 Hz), 115.8 (d, *J* = 21.4 Hz), 57.8, 49.9 (d, *J* = 1.5 Hz), 37.7, 31.8, 18.4.

**HRMS** (ESI) *m/z* calculated for $C_{12}H_{13}ClFO$ [M+H$^+$] 227.0633, found 227.0636.



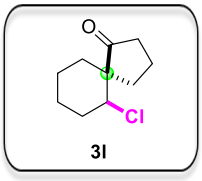
3h

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3h** as white solid in 64% yield (66.7 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.81 (m, 4H), 7.55 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.53 – 7.44 (m, 2H), 3.99 (d, *J* = 11.1 Hz, 1H), 3.78 (d, *J* = 11.2 Hz, 1H), 2.82 – 2.76 (m, 1H), 2.60 – 2.52 (m, 1H), 2.47 – 2.24 (m, 2H), 2.10 – 2.02 (m, 1H), 1.92 – 1.73 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 216.5, 134.0, 133.2, 132.6, 128.8, 128.1, 127.4, 126.5, 126.4, 126.3, 124.2, 58.7, 49.6, 37.8, 31.7, 18.5.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{16}ClO$ [M+H$^+$] 259.0884, found 259.0880.



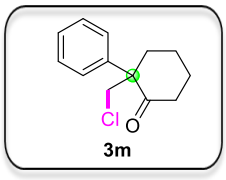
**3l**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3l** as colorless oil in 48% yield (35.9 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 3.85 (dd, *J* = 11.6, 4.7 Hz, 1H), 2.62 – 2.42 (m, 2H), 2.42 – 2.18 (m, 2H), 2.07 – 1.92 (m, 3H), 1.92 – 1.75 (m, 2H), 1.75 – 1.54 (m, 2H), 1.54 – 1.38 (m, 1H), 1.38 – 1.19 (m, 2H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 218.3, 64.7, 52.2, 39.9, 36.8, 34.2, 32.3, 25.8, 20.4, 18.7.

**HRMS** (ESI) *m/z* calculated for $C_{10}H_{16}ClO$ [M+H$^+$] 187.0884, found 187.0887.



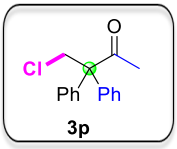
**3m**

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3m** as colorless oil in 40% yield (35.6 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.34 – 7.27 (m, 1H), 7.25 – 7.18 (m, 2H), 3.90 (d, *J* = 11.2 Hz, 1H), 3.61 (d, *J* = 11.2 Hz, 1H), 2.90 – 2.85 (m, 1H), 2.40 – 2.20 (m, 2H), 2.01 – 1.90 (m, 2H), 1.86 – 1.61 (m, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 211.0, 137.5, 129.0, 127.7, 127.0, 57.9, 52.7, 40.0, 32.7, 27.6, 21.2.

**HRMS** (ESI) *m/z* calculated for $C_{13}H_{16}ClO$ [M+H$^+$] 223.0884, found 223.0890.



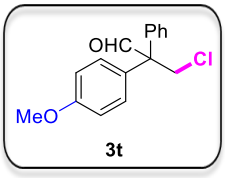

3p

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3p** as white solid in 58% yield (59.6 mg).

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.31 (m, 10H), 4.36 (s, 2H), 2.14 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 206.3, 138.5, 129.4, 128.4, 127.7, 67.2, 50.2, 27.5.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{16}ClO$ [M+H$^+$] 259.0884, found 259.0885.




3t

Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **3t** as colorless oil in 40% yield (35.6 mg).

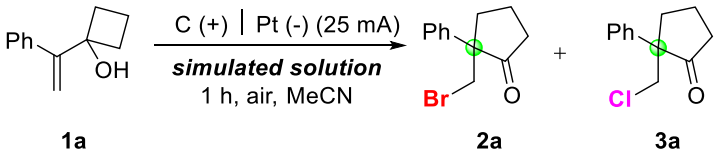
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 7.41 – 7.38 (m, 2H), 7.37 – 7.31 (m, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.11 (m, 2H), 6.96 – 6.89 (m, 2H), 4.29 (s, 2H), 3.81 (s, 3H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 196.5, 159.2, 137.5, 130.3, 129.1, 128.9, 128.8, 128.0, 114.2, 63.9, 55.2, 47.3.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{15}ClNaO_2$ [M+Na$^+$] 297.0653, found 297.0642.

## 4. Preparation of simulated solutions and applications

Simulated solution ***A*** (Bittern after making salt with seawater), ***B*** (Dead sea water), ***C*** (Industrial effluent (producing $Na_2CO_3$)), ***D*** (sea water) were prepared according to relative literature[8-11] by adding calculated inorganic salt (NaCl, $MgCl_2$, $MgSO_4$, $CaSO_4$, $K_2SO_4$, $CaCO_3$, $MgBr_2$, et al) into water.




1a 2a 3a

| entry | scale of **1a** (mmol) | simulated solution (Br :Cl) | calculation standard | total yield | Ratio (**2a**: **3a**) |
|---|---|---|---|---|---|
| 1 | 0.055 | ***A*** (1: 128) | Br, 4 equiv. | 98% | 5.1:1 |
| 2 | 0.11 | ***A*** (1: 128) | Br, 2 equiv. | 85% | 4:1 |
| 3 | 0.4 | ***B*** (1: 97) | Cl, 4 equiv. | 54% | 1:20 |
| 4 | 0.07875 | ***B*** (1: 97) | Br, 2 equiv. | 96% | 3:1 |
| 5 | 0.4 | ***C*** (0:100) | Cl, 4 equiv. | 36% | 0:100 |
| 6 | 0.21 | ***D*** (1:651) | Cl, 8 equiv. | 62% | 1:27 |

Components of simulated solution:

***A*** (Bittern after making salt with seawater, g/L): Br 5~7, $MgSO_4$ 13.51, $MgCl_2$ 452.18, NaCl 2.18, KCl 2.47.

***B*** (Dead sea water, g/L): $Cl^-$ (181.4), $Br^-$ (4.2), $SO_4^{2-}$ (0.4), $HCO_3^-$ (0.2), $Ca^{2+}$ (14.1), $Na^+$ (32.5), $K^+$ (6.2), $Mg^{2+}$ (35.2).

***C*** (Industrial effluent (producing $Na_2CO_3$), g/L): $Cl^-$ 99-115, $OH^-$ 1-2.7, $SO_4^{2-}$ 0.1-1.2, $Ca^{2+}$ 39-45, $Na^+$ 18-25, $NH_3$ 0.01-0.03, Suspended solids 11-70, CaO 0.7-9.0, $CaCO_3$ 3.8-11, $CaSO_4$ 1.7-7.1, Others By difference, pH 11-12.)

***D*** (Seawater, mg/L): $Na^+$ 11061.28, $Mg^{2+}$ 1330.23, $K^+$ 410.17, $Ca^{2+}$ 423.54, $Cl^-$ 19891.90, $Br^-$ 68.88, $F^-$ 4.73, $SO_4^{2-}$ 929.31.

For simulated solution ***A*** (Bittern after making salt with seawater), the concentration of bromine was 6 g/L (75 mmol/L). 3 mL simulated solution ***A*** (containing 0.225 mmol Br) was added into undivided electrochemical cells (30 mL), followed by the addition of allyl alcohol **1a** (calculation basis, 1 equiv., 0.055 mmol or 0.11 mmol) which is dissolved in acetonitrile (6 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. Ethyl acetate (10 mL) and water (10 mL) was added, the aqueous layer was separated and extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed with brine and dried over sodium sulfate. Following concentration in vacuo and column chromatography, NMR yields and ratio of **2a**/**3a** were obtained by dissolving the crude residue in $CDCl_3$ using $CH_2Br_2$ as the internal standard.

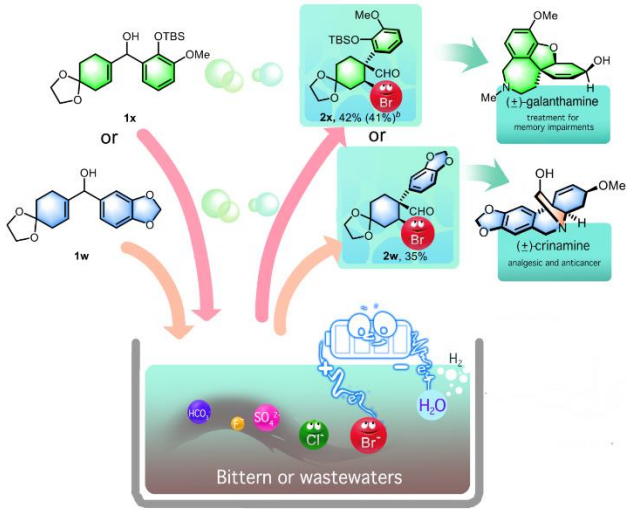
For simulated solution ***B*** (Dead sea water), the concentration of bromine and chlorine was 4.2 g/L (52.5 mmol/L) and 181.4 g/L (5.11 mol/L), respectively. When calculation standard was amount of substance of Cl, 315 μL simulated solution ***B*** (containing 1.6 mmol Cl, 4 equiv.), allyl alcohol **1a** (0.4 mmol, 1 equiv.) which is

dissolved in MeCN (6 mL) and additional water (2.685 mL to ensure that the total volume is 9 mL) were added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields and ratio of **2a**/**3a** were obtained by dissolving the crude residue in $CDCl_3$ using $CH_2Br_2$ as the internal standard. When calculation standard was amount of substance of Br, 3 mL simulated solution ***B*** (containing 0.1575 mmol Br, 2 equiv.) and allyl alcohol **1a** (0.07875 mmol) which is dissolved in MeCN (6 mL) were added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields and ratio of **2a**/**3a** were obtained by dissolving the crude residue in $CDCl_3$ using $CH_2Br_2$ as the internal standard.

For simulated solution ***C*** (Industrial effluent (producing $Na_2CO_3$)), the concentration of chlorine was 116 g/L (3.2676 mol/L). When calculation standard was amount of substance of Cl, 490 μL simulated solution ***C*** (containing 1.6 mmol Cl, 4 equiv.), allyl alcohol **1a** (0.4 mmol, 1 equiv.) which is dissolved in MeCN (6 mL) and additional water (2.51 mL to ensure that the total volume is 9 mL) was added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields of **3a** were obtained by dissolving the crude residue in $CDCl_3$ using $CH_2Br_2$ as the internal standard.

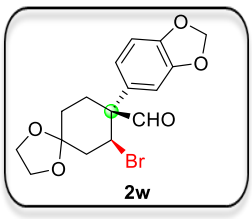
For simulated solution ***D*** (sea water), the concentration of chlorine was 19.891 g/L (560.34 mol/L). When calculation standard was amount of substance of Cl, 3 mL simulated solution ***D*** (containing 1.681 mmol Cl, 8 equiv.), allyl alcohol **1a** (0.21 mmol, 1 equiv.) which is dissolved in MeCN (6 mL) was added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. After extraction, concentration and column chromatography, NMR yields and ratio of **2a**/**3a** were obtained by dissolving the crude residue in $CDCl_3$ using $CH_2Br_2$ as the internal standard.

## 5. Using wastewaters to synthesize bioactive natural products




Allyl alcohol **1w** or **1x** (0.055 mmol) which is dissolved in MeCN (6 mL) and 3 mL simulated solution ***A*** (containing 0.225 mmol Br) were added into undivided electrochemical cells (30 mL). The electrolysis was controlled at a constant current 3 mA and was terminated after 2.5 h. After extraction and concentration, the crude residue was purified by column chromatography and product **2w** and **2x** were isolated in 35% and 42% yield respectively. No aldehyde containing chlorine was detected in NMR spectra.

When allyl alcohol **1x** (0.02375 mmol) was added into water (9 mL) directly, following by the addition of $MgBr_2 \cdot 6H_2O$ (0.095 mmol), **2x** was obtained in 41% isolated yield under the electrochemical reaction condition. Br-concentration of water is consistant with Br-concentration of produced water from shale gas extraction (Br: 1.7 g/L ).[12]

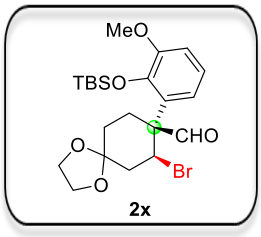


Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2w** as colorless oil in 35% yield (7.3 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 6.82 – 6.74 (m, 2H), 6.64 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.02 – 5.93 (m, 2H), 4.72 (dd, *J* = 12.5, 4.2 Hz, 1H), 4.03 – 3.87 (m, 4H), 2.53 – 2.47 (m, 1H), 2.36 – 2.30 (m, 1H), 2.23 (t, *J* = 13.0 Hz, 1H), 1.90 – 1.77 (m, 2H), 1.74 – 1.63 (m, 1H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.2, 148.4, 147.1, 132.2, 120.4, 108.5, 108.0, 107.0, 101.3, 64.7, 64.4, 56.6, 51.0, 43.7, 32.2, 31.8.

**HRMS** (ESI) *m/z* calculated for $C_{16}H_{18}BrO_5$ [M+H$^+$] 369.0332, found 369.0341.



**2x**

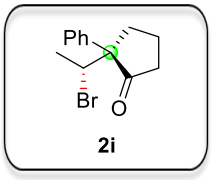
Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2x** as pale yellow solid in 42% yield (11.2 mg).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 1.9 Hz, 1H), 7.03 – 6.90 (m, 2H), 6.89 – 6.75 (m, 1H), 4.79 (t, *J* = 8.6 Hz, 1H), 4.05 – 3.83 (m, 4H), 3.78 (s, 3H), 2.67 – 2.48 (m, 2H), 2.48 – 2.30 (m, 2H), 1.73 – 1.47 (m, 3H), 0.94 (s, 9H), 0.24 (s, 3H), 0.20 (s, 3H).

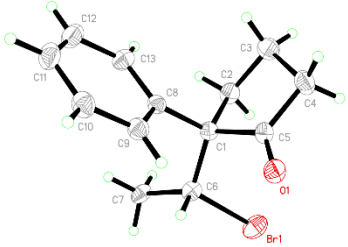
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 202.8, 149.2, 142.8, 130.9, 120.9, 118.6, 110.4, 108.6, 64.6, 64.3, 54.3, 53.4, 49.9, 42.4, 31.5, 30.9, 26.7, 19.7, -2.0, -2.3.

**HRMS** (ESI) *m/z* calculated for $C_{22}H_{34}BrO_5Si$ [M+H$^+$] 485.1353, found 485.1362.

## 6. X-ray structure of compound 2i



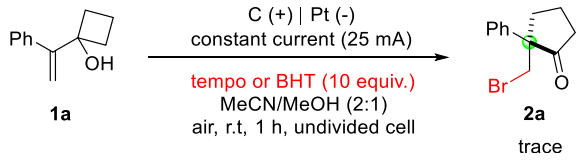
**2i**



A colorless block shaped crystal of **2i** ($C_{13}H_{15}BrO$) was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 173(2) K, on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochrmator Cu-Kα radiation (λ = 1.54178 Å). The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers **CCDC 1904039** for **2i**. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

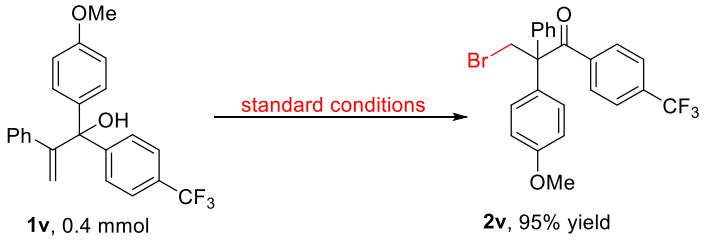
## 7. Preliminary mechanistic studies

### a) Radical trapping experiments



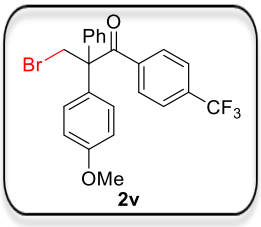

To an oven-dried, undivided electrochemical cell equipped with a magnetic stir bar, a carbon anode (10.0 mm * 10.0 mm), and a Pt plate cathode (10.0 mm * 10.0 mm) were added $MgBr_2 \cdot 6H_2O$ (4.0 equiv., 1.6 mmol), allylic alcohol (1.0 equiv., 0.4 mmol), radical scavenger (tempo or BHT, 10 equiv.) and followed by the addition of 6 mL MeCN and 3 mL MeOH. The mixture was stirred for 5 min. The electrolysis was controlled at a constant current 25 mA and was terminated after 1 h. Trace **2a** was detected by thin layer chromatography.

### b) The study on the migration process




Allyl alcohol **1v** was tested under the standard condition, and **2v** was obtained in 95% isolated yield. To further confirm the structure of **2v**, N-Bromosuccinimide (0.8

equiv.) and allyl alcohol (**1v**) were reacted in MeCN/MeOH (2:1) for 1 hour, and NMR $^{1}H$ and $^{13}C$ spectrum of product were consistent with that of product obtained from electrochemical semi-pinacol rearrangement.




Purification of the crude product by flash column chromatography afforded the semi-pinacol rearrangement product **2v** as colorless oil in 95% yield (176 mg).

**$^{1}H$ NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.29 (m, 7H), 6.93 – 6.85 (m, 2H), 4.25 – 4.20 (m, 2H), 3.81 (s, 3H).

**$^{13}C$ NMR** (101 MHz, $CDCl_3$) δ 198.2, 159.0, 139.9, 138.9, 133.1 (d, *J* = 32.7 Hz), 130.7, 130.2, 130.1, 129.5, 128.5, 128.0, 124.9 (q, *J* = 3.7 Hz), 122.1, 114.0, 64.5, 55.2, 41.9.

**HRMS** (ESI) *m/z* calculated for $C_{23}H_{19}BrF_3O_2$ [M+H$^+$] 463.0515, found 463.0523.

## 8. Reference

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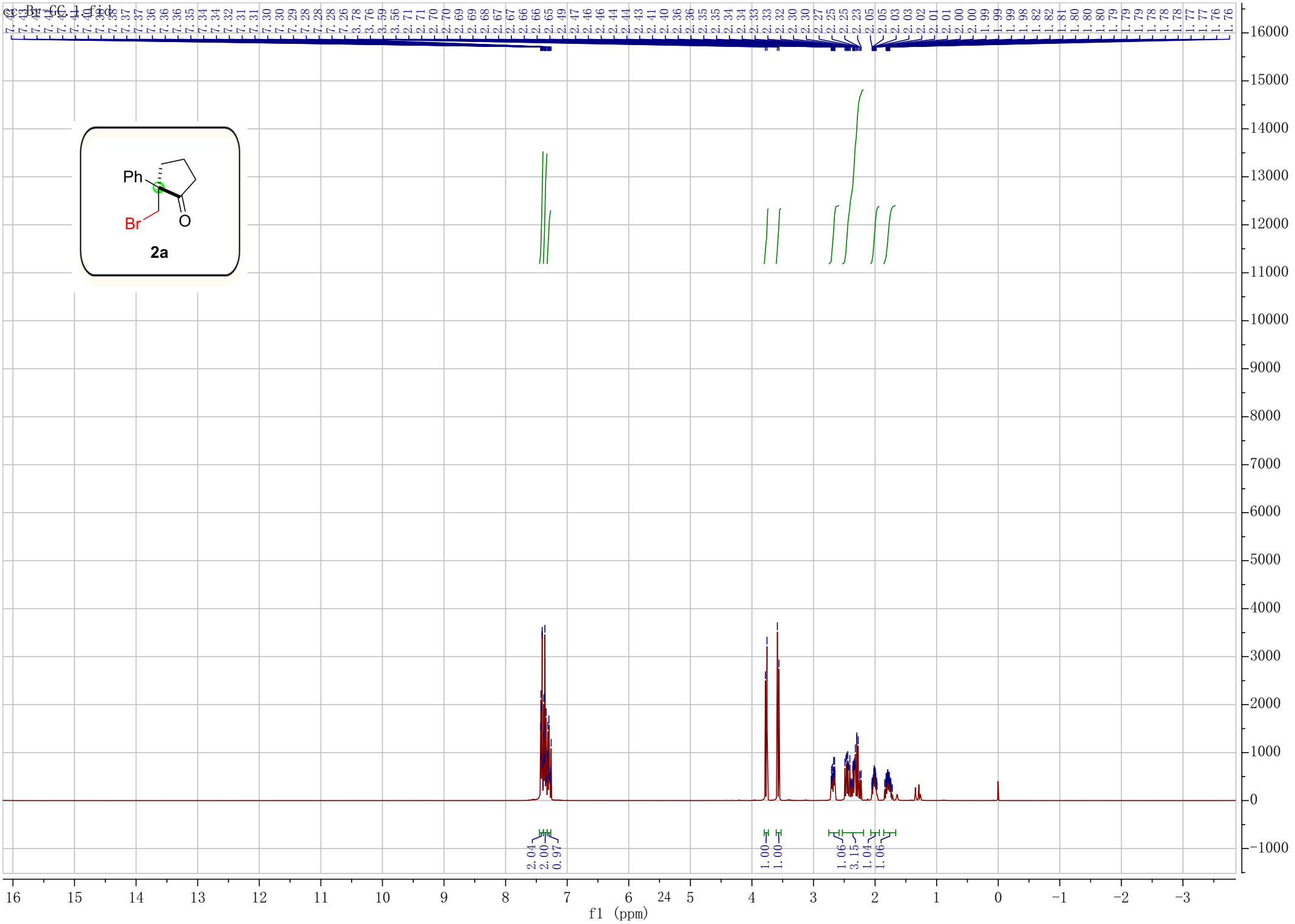
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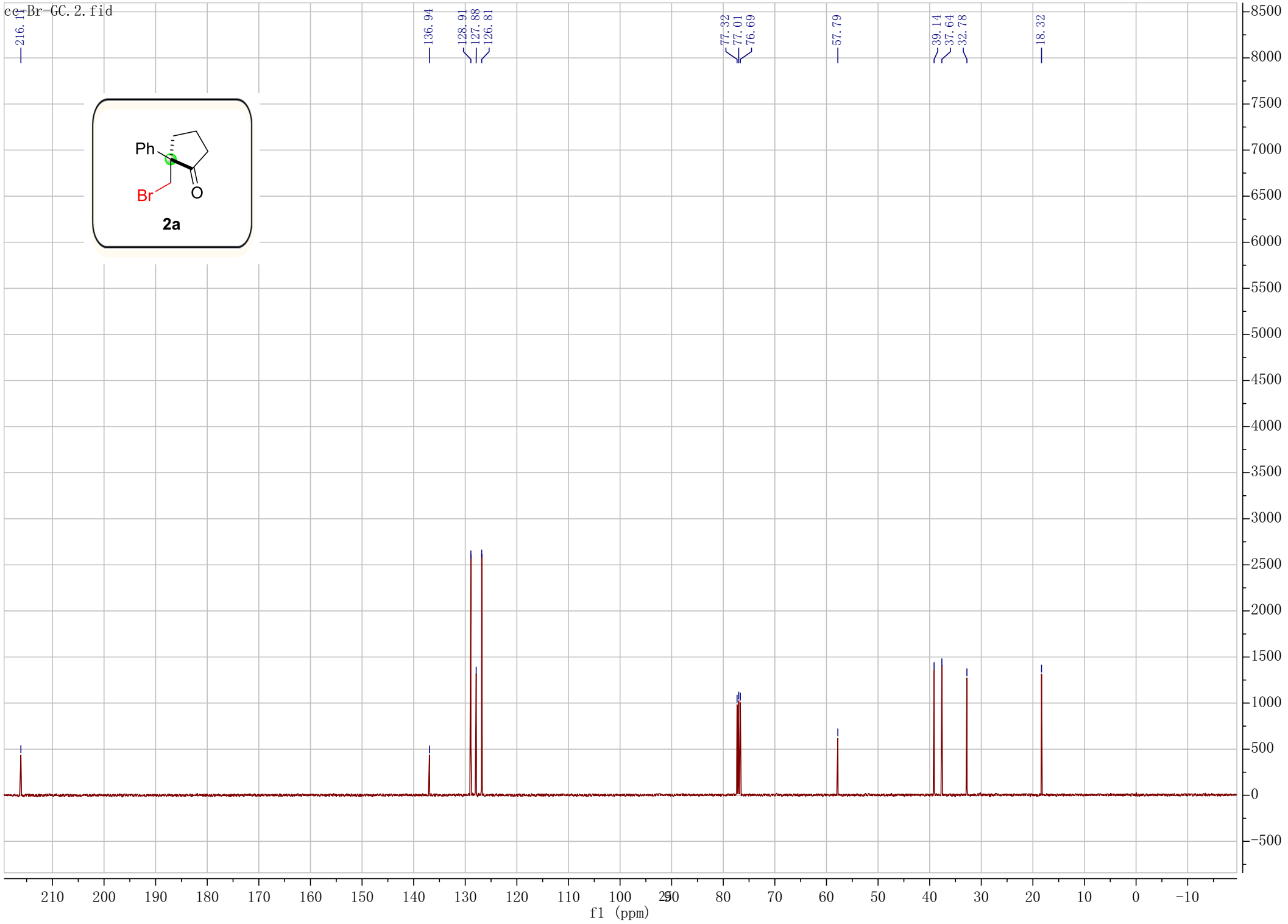
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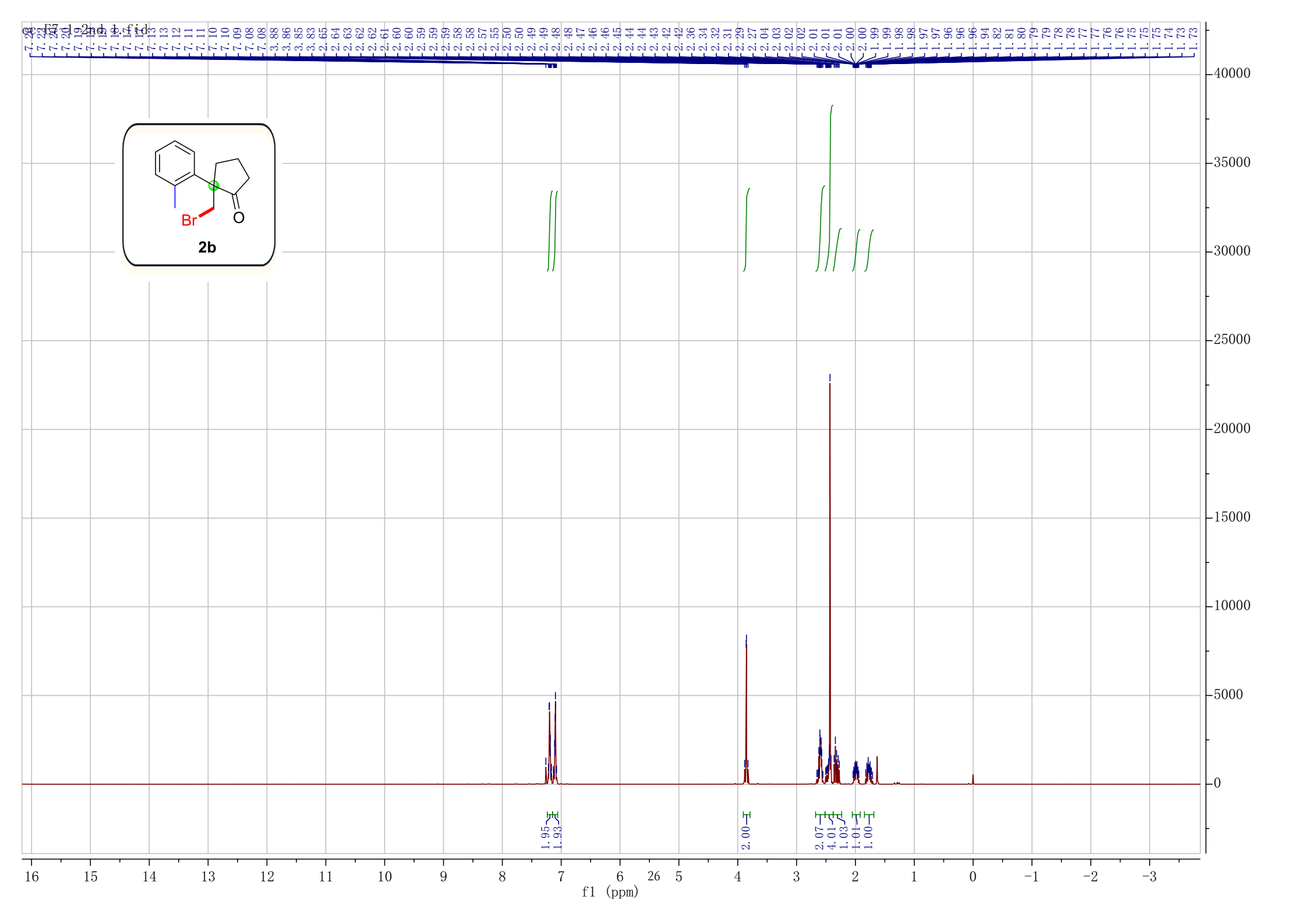
Br
O
2a
f1 (ppm)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O
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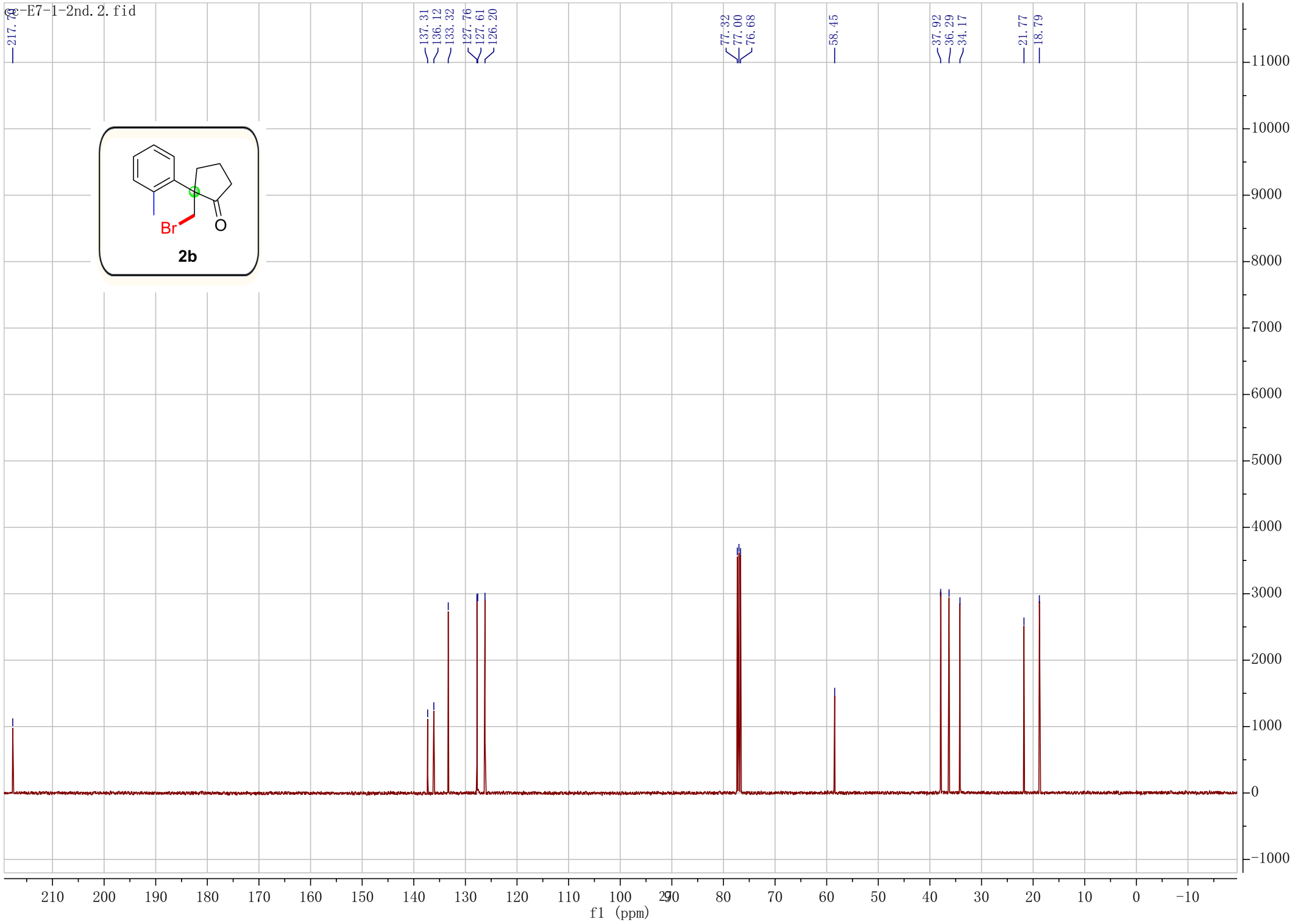
f1 (ppm)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O
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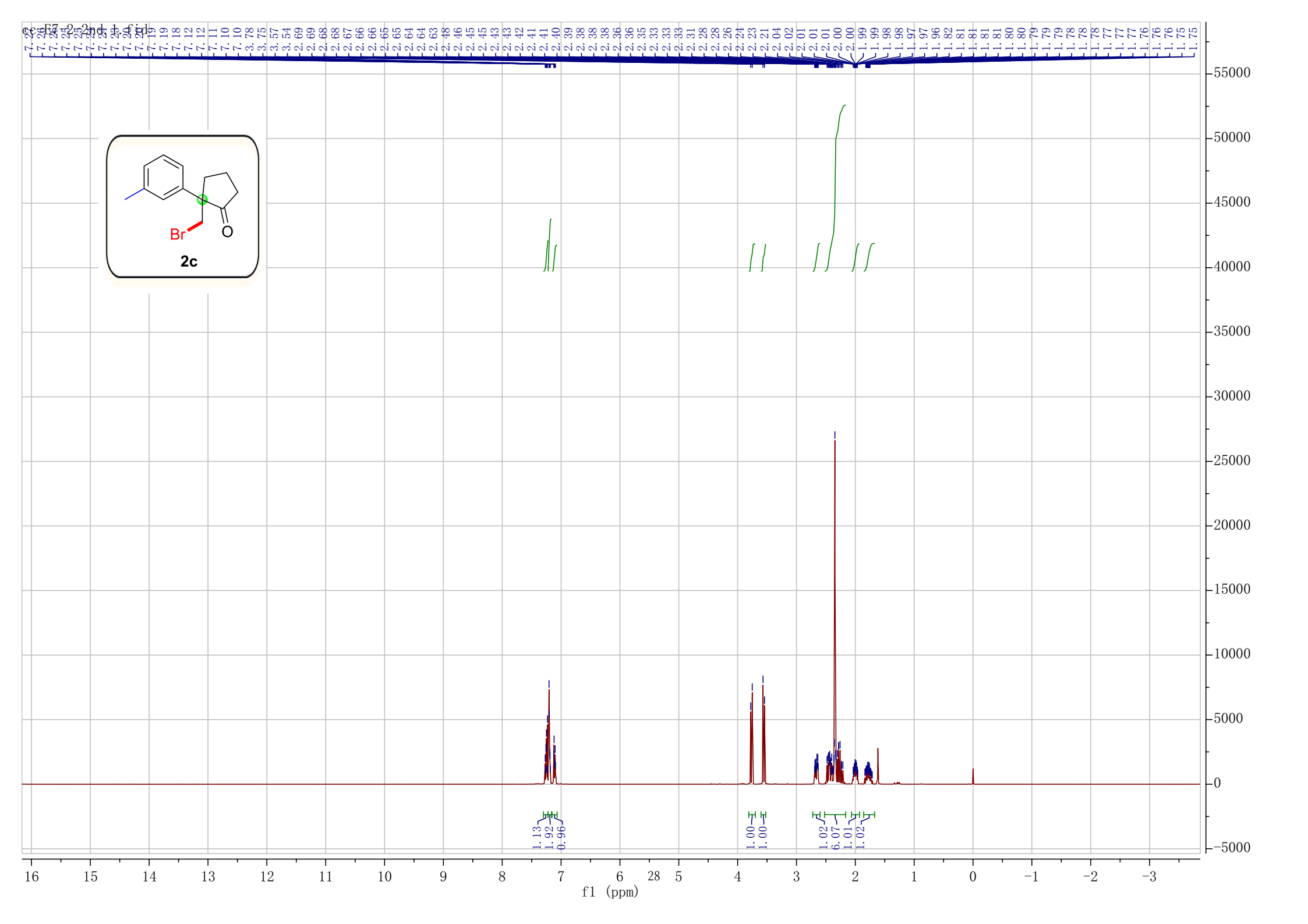
f1 (ppm)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f1 (ppm)

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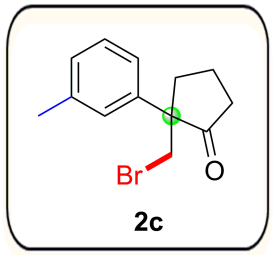


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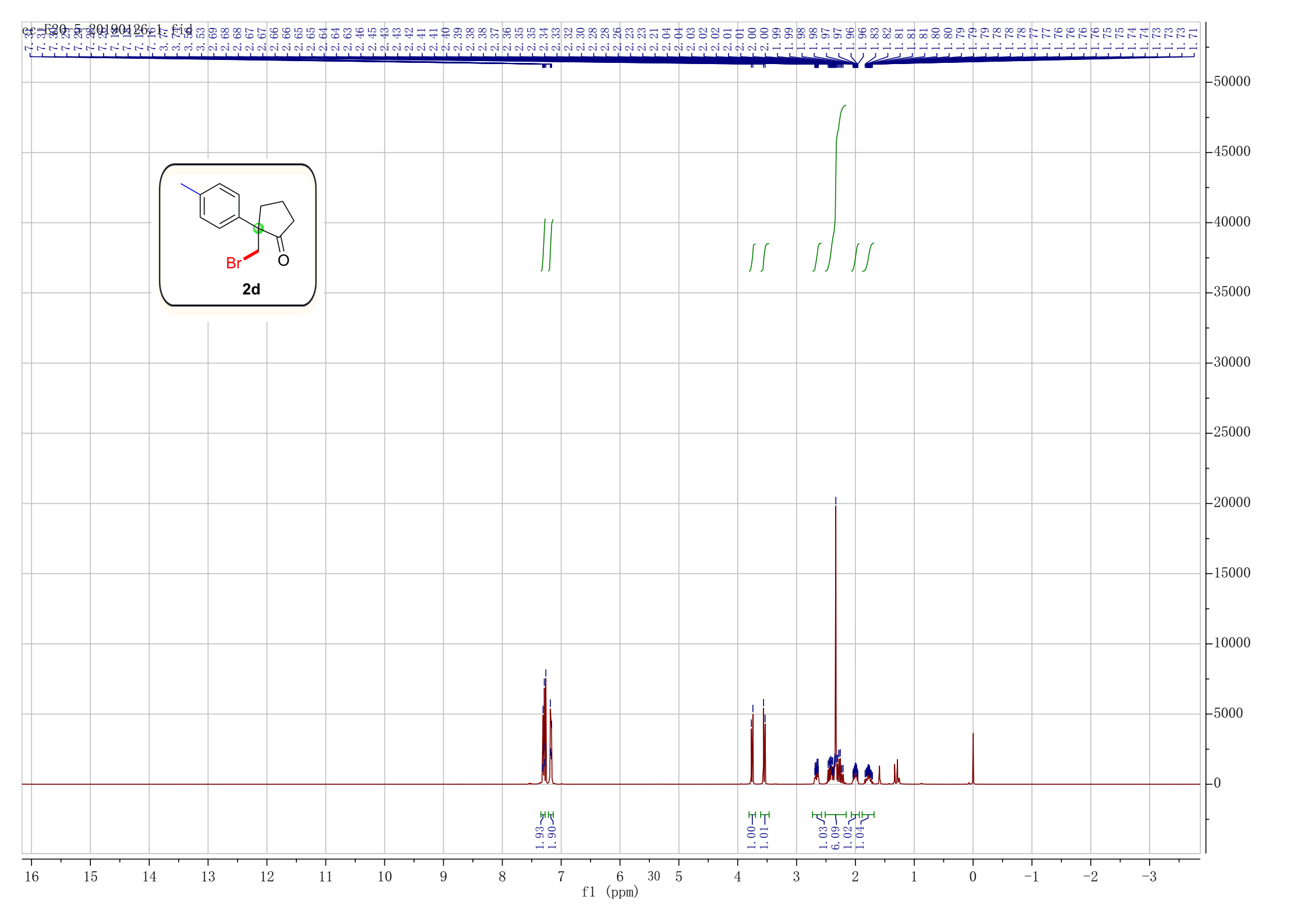
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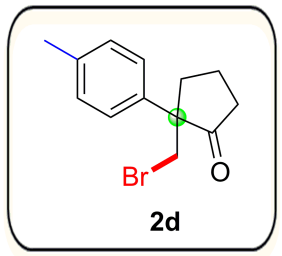


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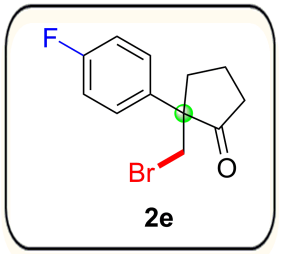


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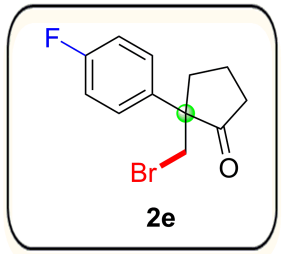


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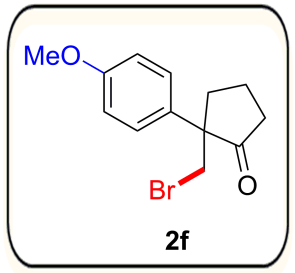


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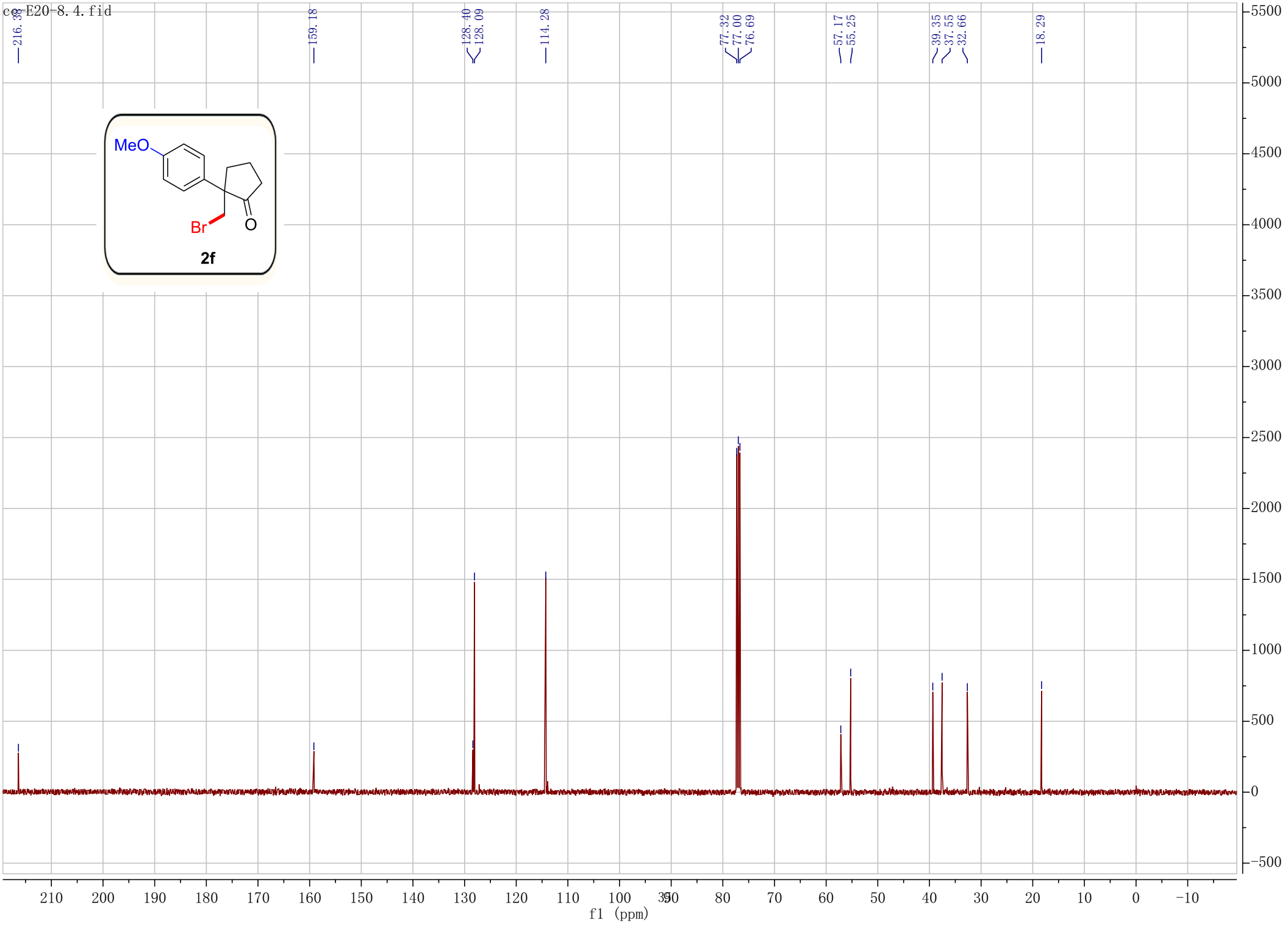
f1 (ppm)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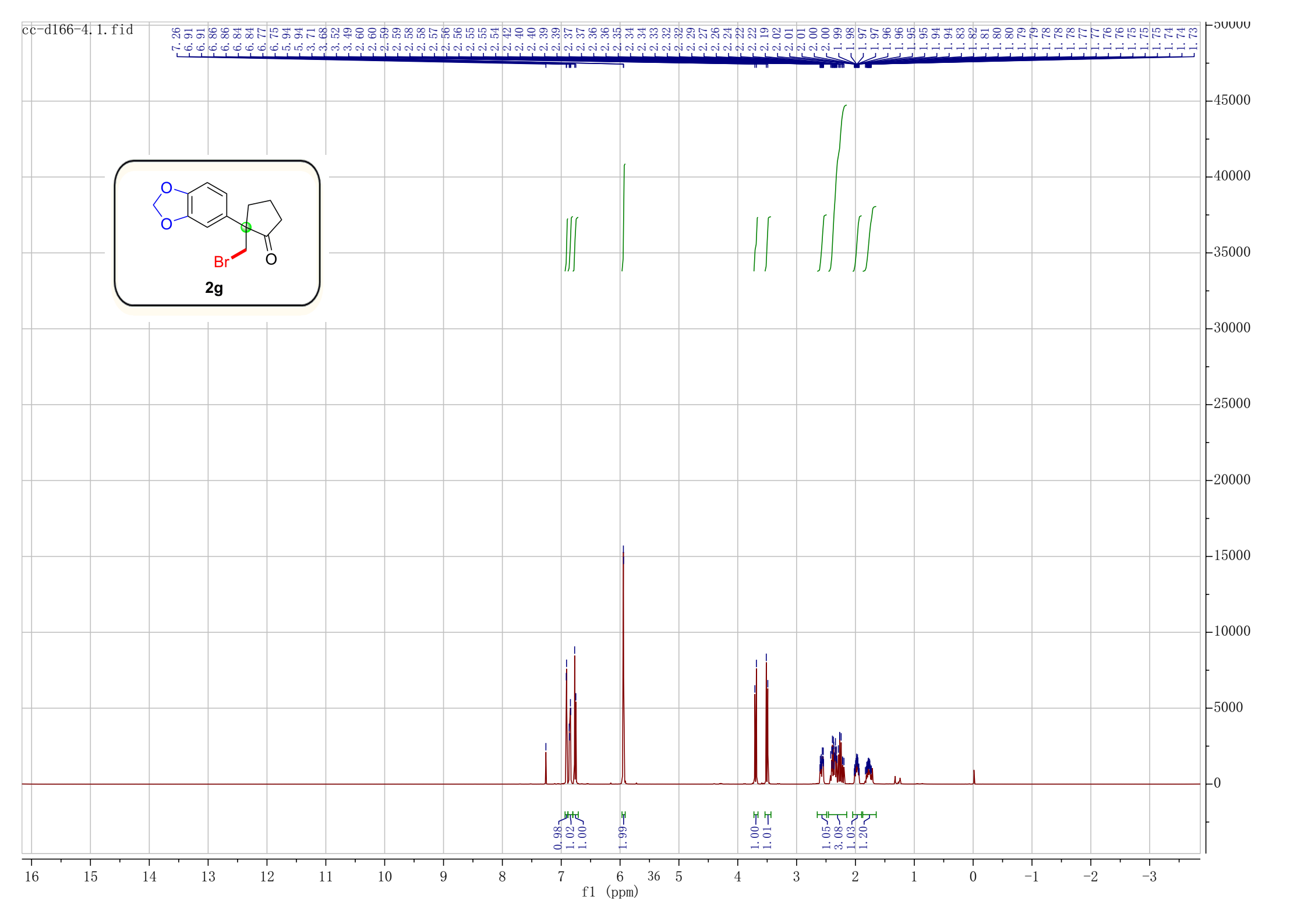
f1 (ppm)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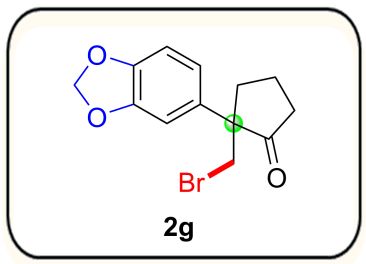


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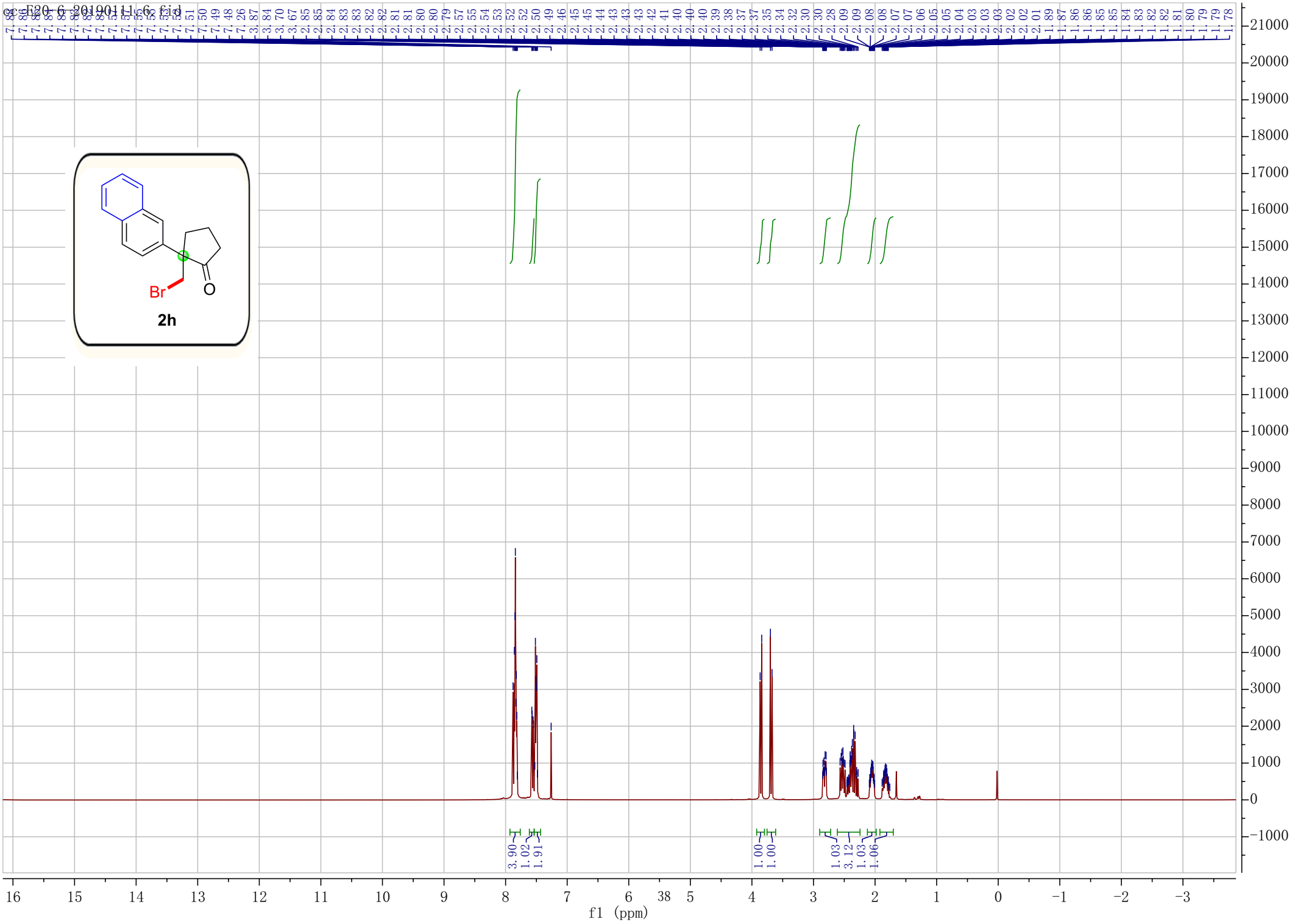
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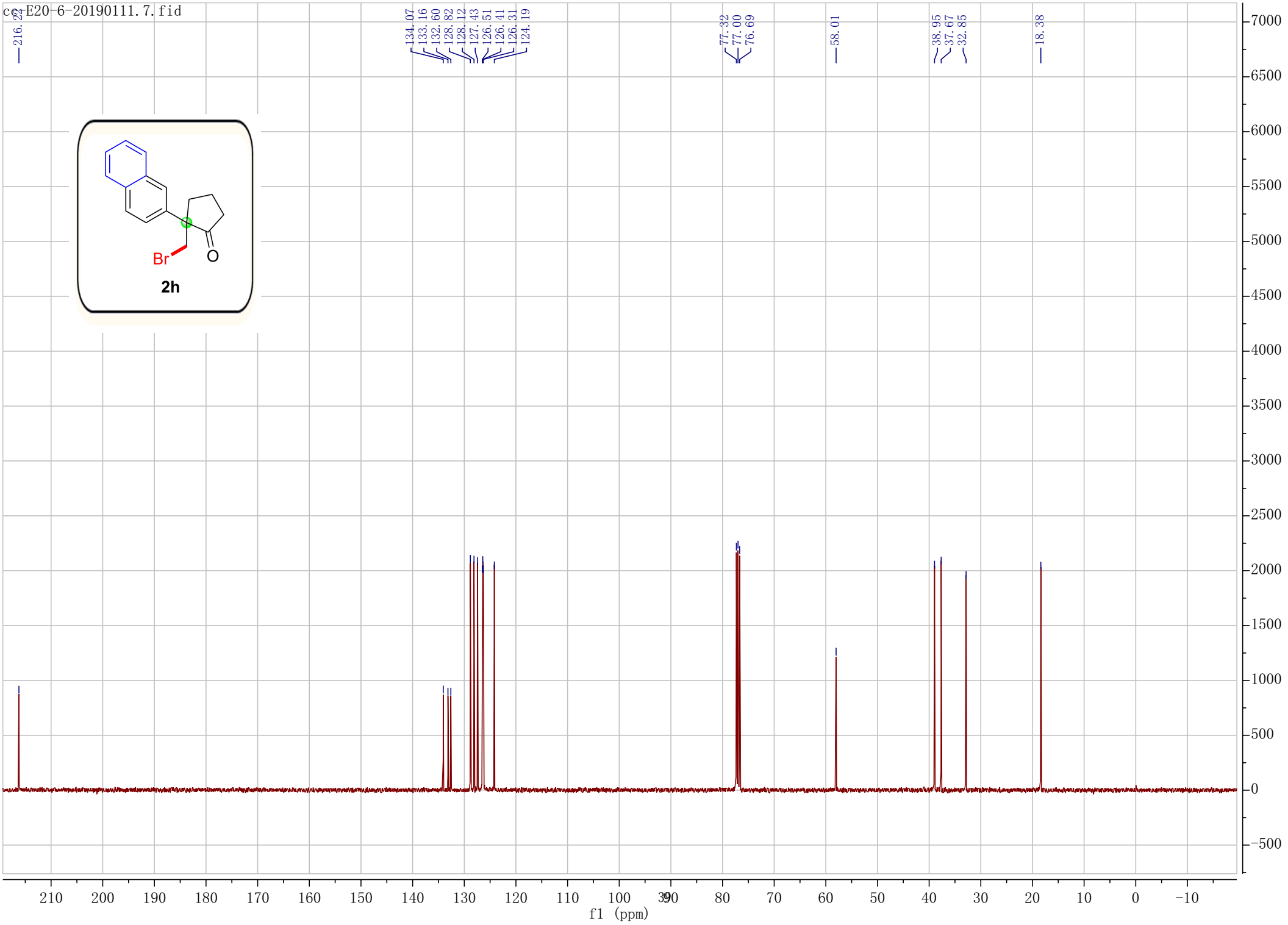
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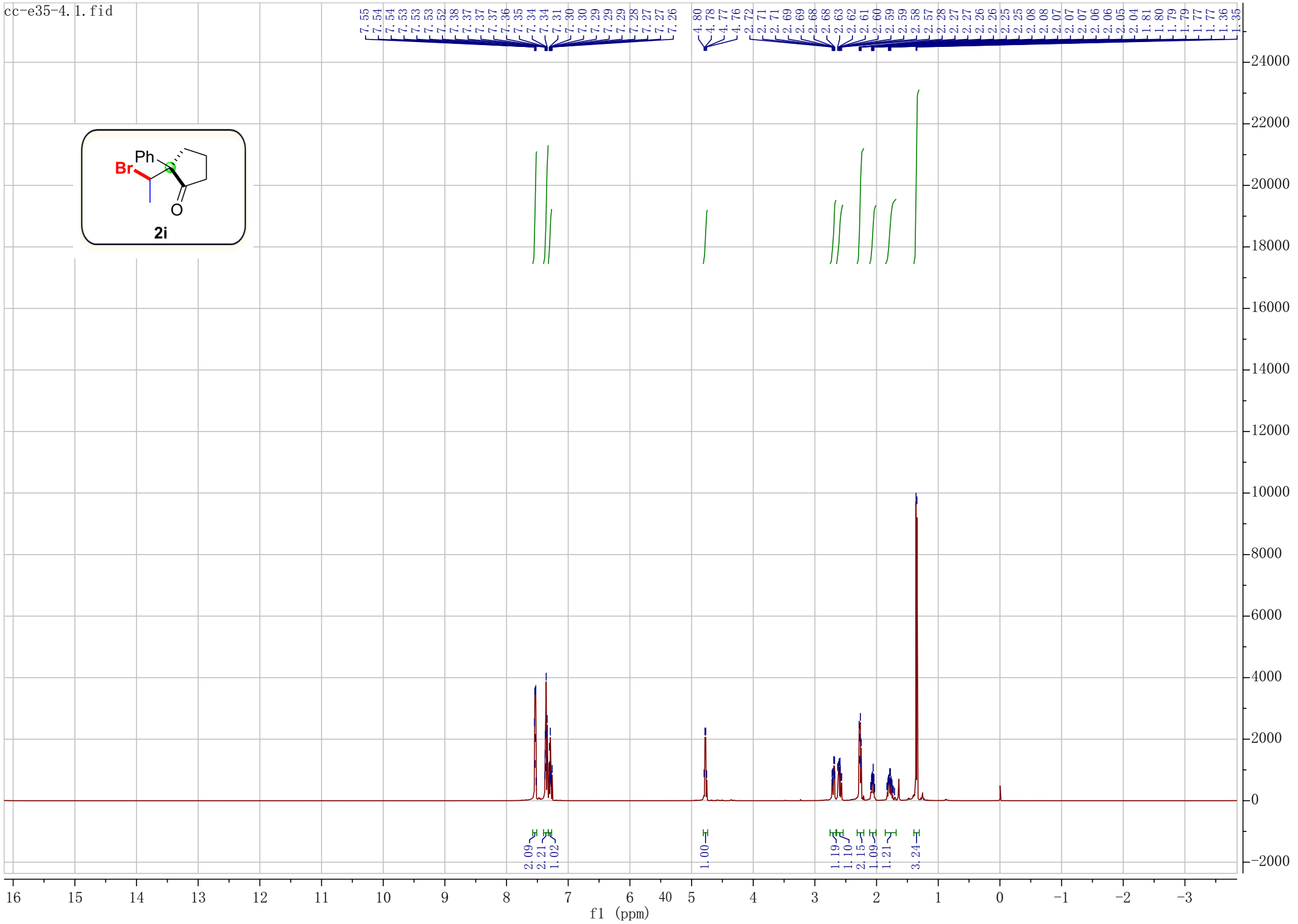
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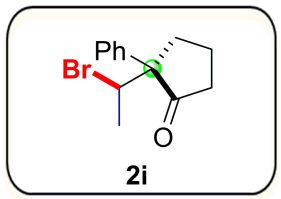


2i

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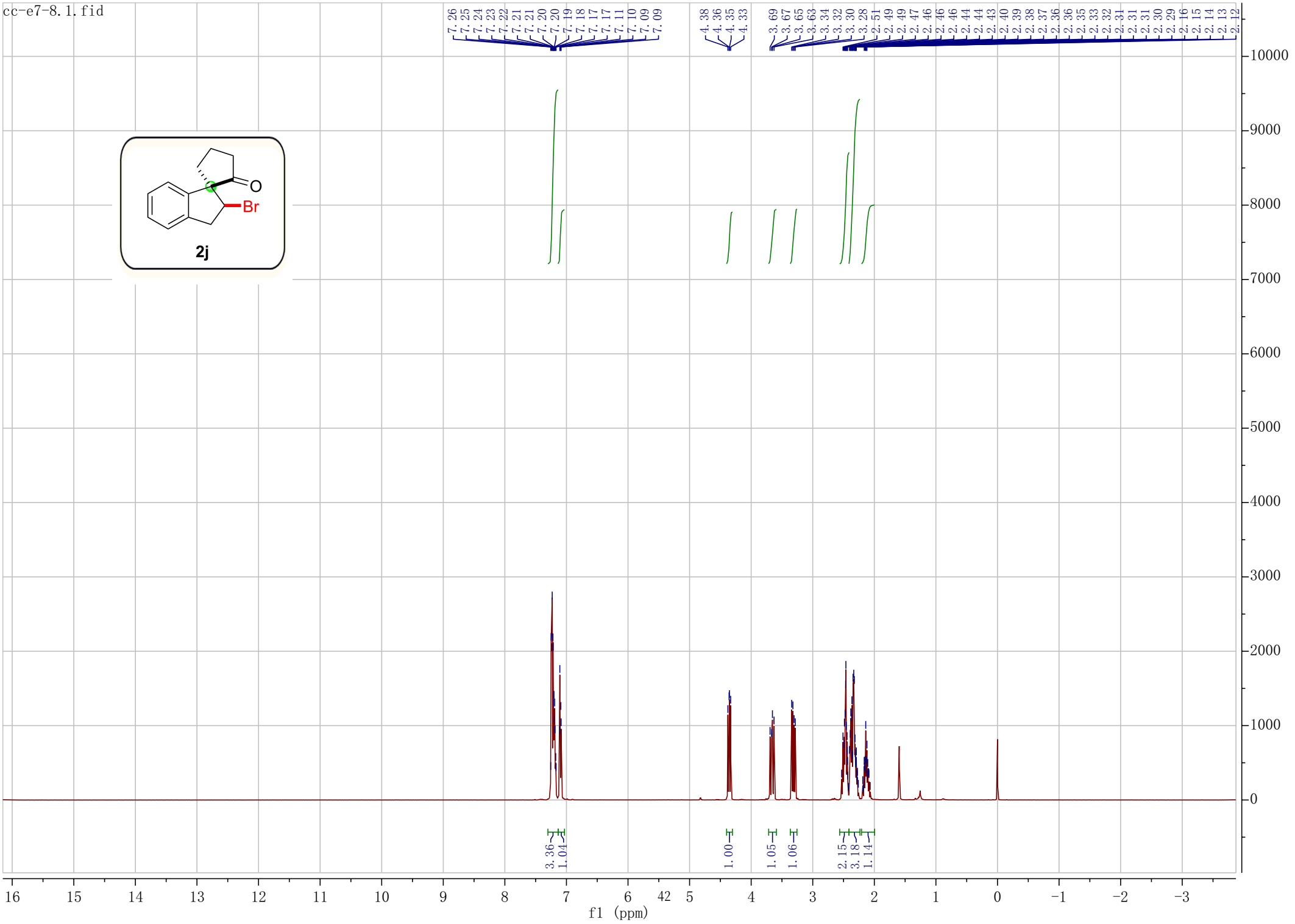
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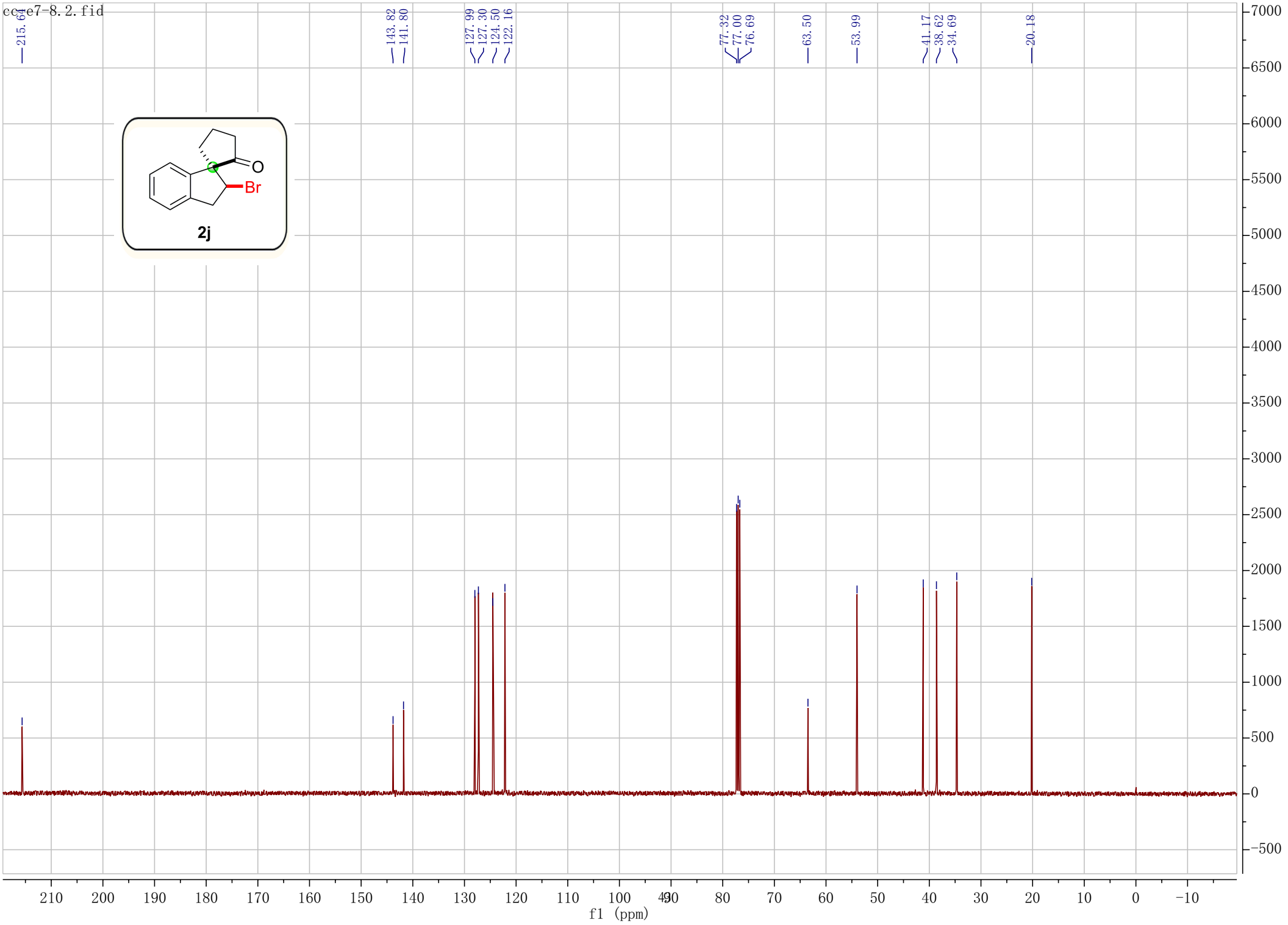
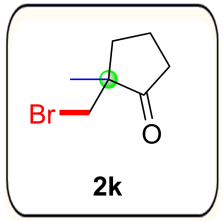
7.26 7.25 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.11 7.10 7.09 7.09
4.38 4.36 4.35 4.33
3.69 3.67 3.65 3.63 3.34 3.32 3.30 3.28 2.51 2.49 2.49 2.47 2.46 2.46 2.46 2.44 2.44 2.43 2.40 2.39 2.38 2.37 2.36 2.36 2.35 2.33 2.32 2.31 2.31 2.31 2.30 2.29 2.16 2.15 2.14 2.13 2.12
O
Br
2j
3.36
1.04
1.00
1.05
1.06
2.15
3.18
1.14
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
16 15 14 13 12 11 10 9 8 7 6 42 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

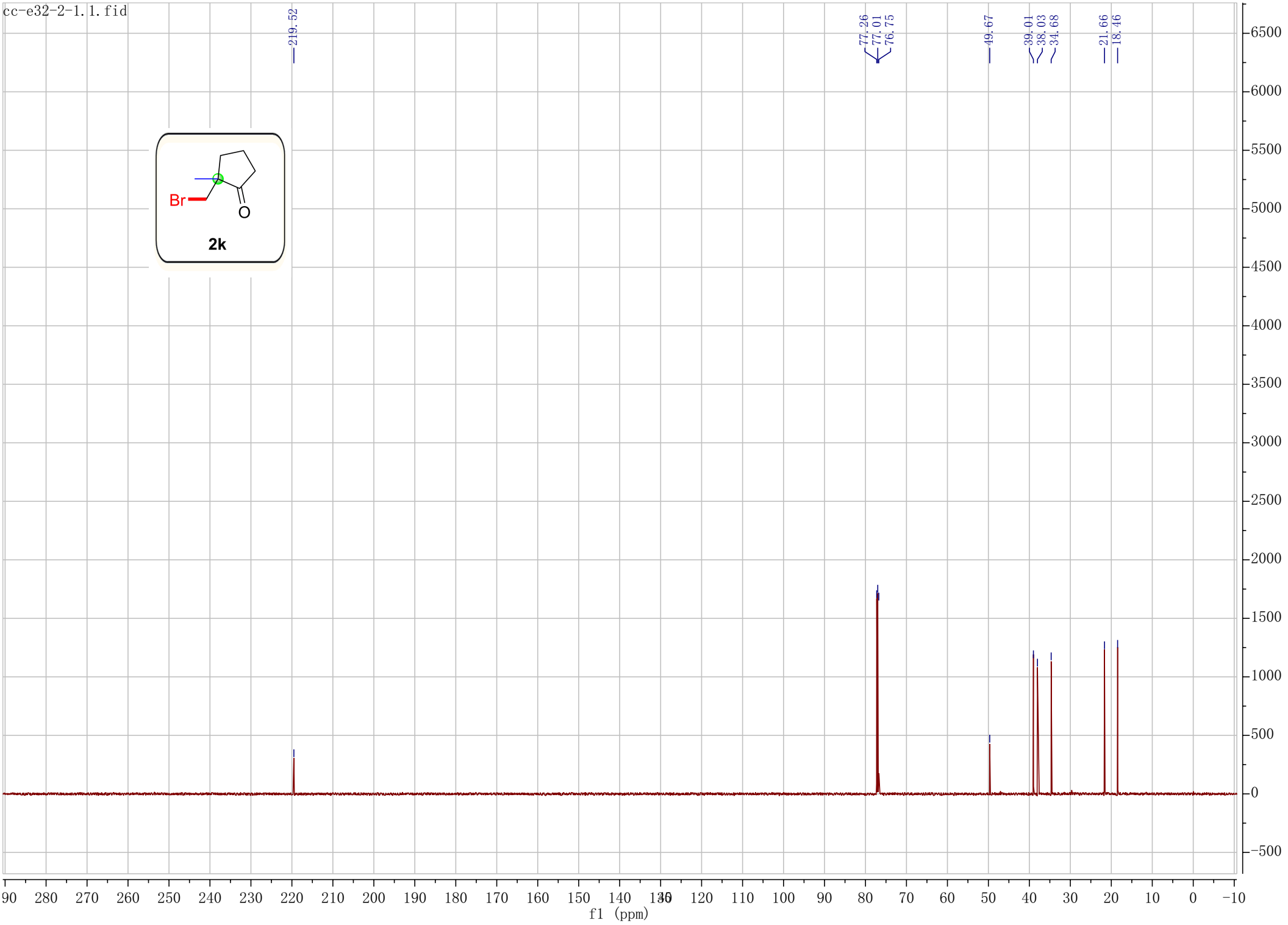

cc-e7-8.2.fid
215.60
143.82
141.80
127.99
127.30
124.50
122.16
77.32
77.00
76.69
63.50
53.99
41.17
38.62
34.69
20.18
O
Br
2j
f1 (ppm)

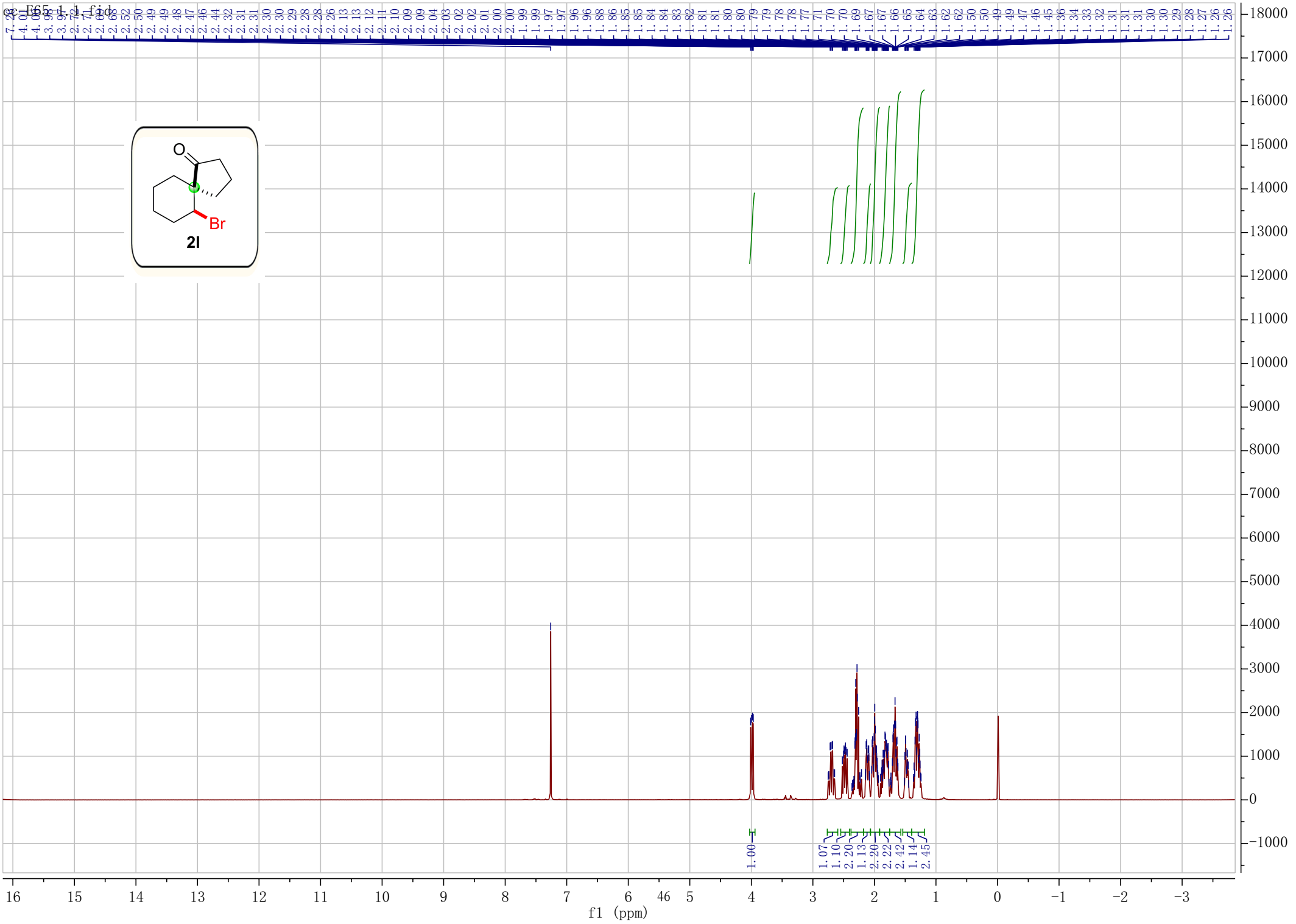
cc-e32-2-2.fid



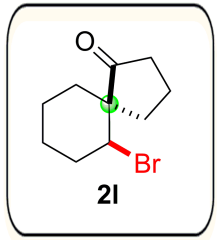

2k

f1 (ppm)


cc-e32-2-1.1.fid
219.52
77.26
77.01
76.75
49.67
39.01
38.03
34.68
21.66
18.46
Br
O
2k
f1 (ppm)


cc-E65-1.fid
O
Br
2l
1.00
1.07
1.10
2.20
1.13
2.20
2.22
2.42
1.14
2.45
f1 (ppm)

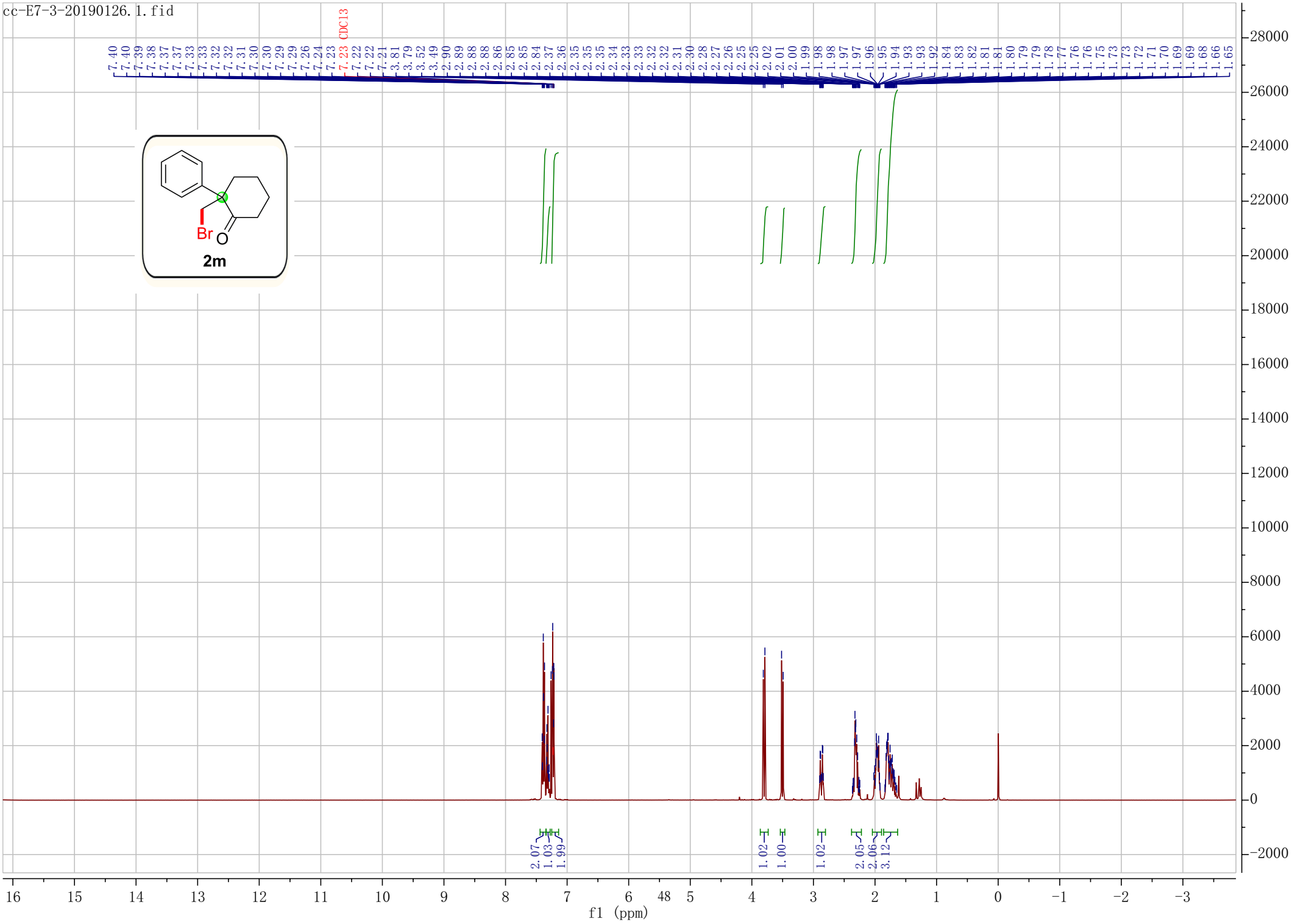
ec-E65-1.2.fid



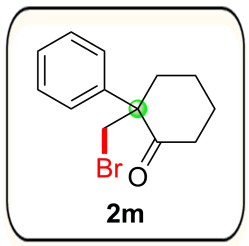

2l

218.22
77.32
77.00
76.69
58.37
52.20
39.58
37.95
34.62
33.42
27.12
20.44
18.68

f1 (ppm)


cc-E7-3-20190126.1.fid
CDCl3
Br
O
2m
f1 (ppm)

cc-E7-3-20190126.2.fid

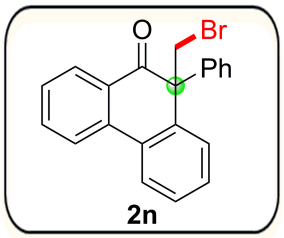



2m

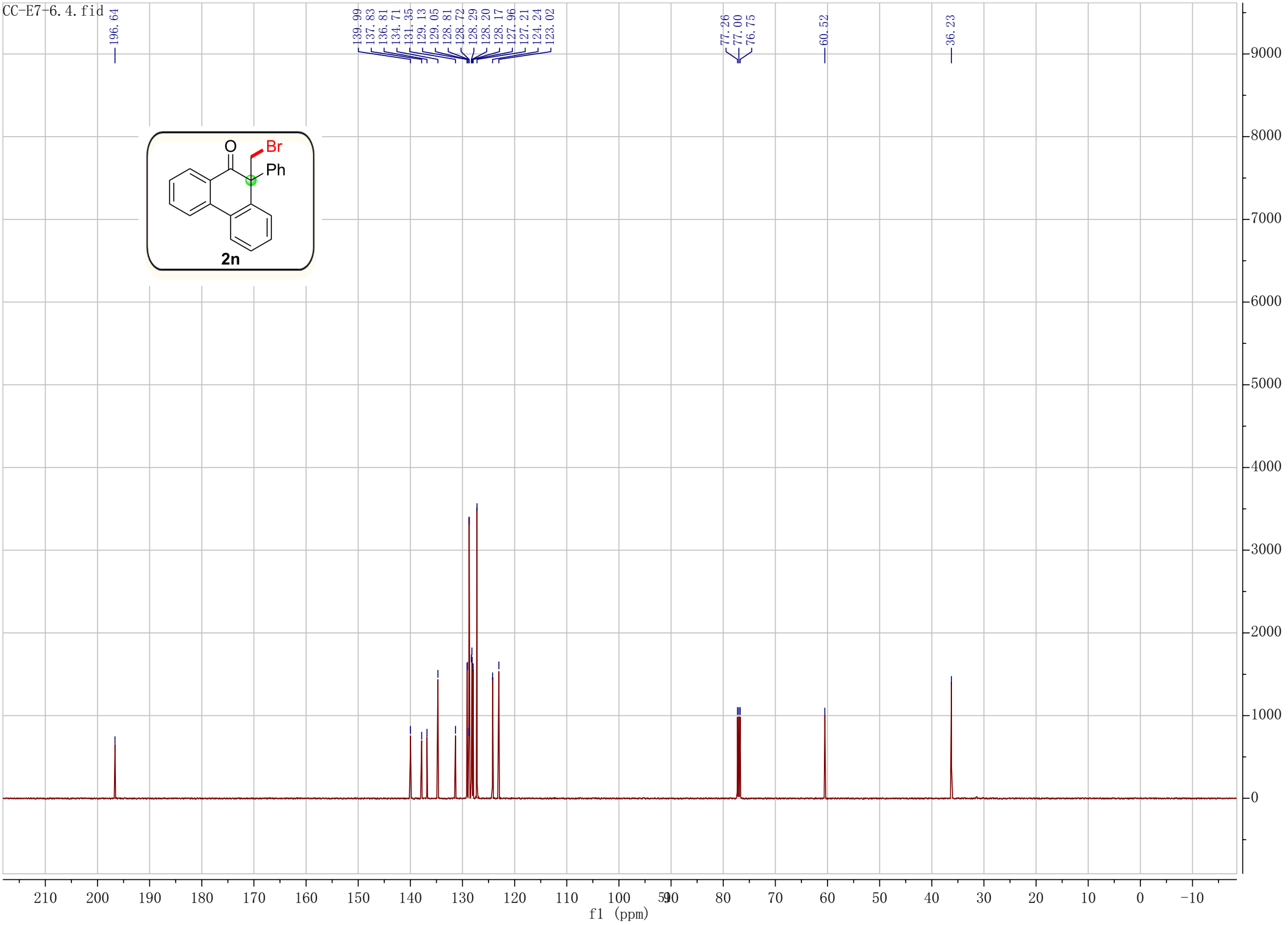
210.85
137.72
129.06
127.76
127.00
77.32
77.00
76.69
57.18
42.86
40.04
33.90
27.69
21.40

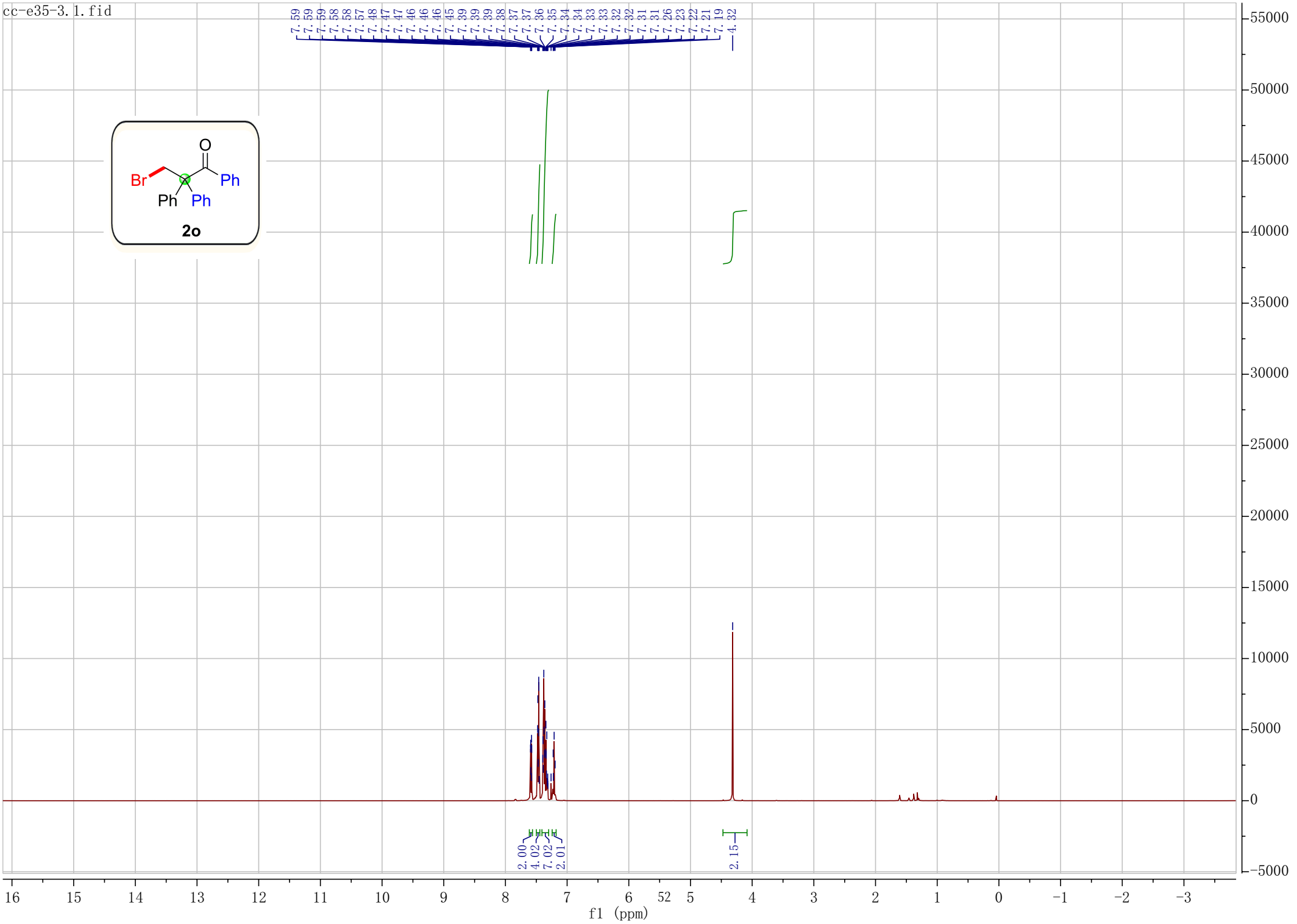
f1 (ppm)

CC-E7-6-3.fid



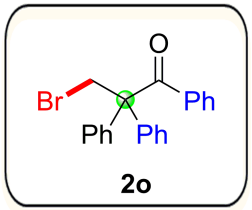

f1 (ppm)


CC-E7-6.4.fid
196.64
139.99
137.83
136.81
134.71
131.35
129.13
129.05
128.81
128.72
128.29
128.20
128.17
127.96
127.21
124.24
123.02
77.26
77.00
76.75
60.52
36.23
O
Br
Ph
2n
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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)


cc-e35-3.1.fid
7.59 7.59 7.59 7.58 7.58 7.57 7.48 7.47 7.47 7.46 7.46 7.46 7.45 7.39 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.26 7.23 7.22 7.21 7.19 4.32
O
Br
Ph
Ph
Ph
2o
2.00
4.02
7.02
2.01
2.15
f1 (ppm)

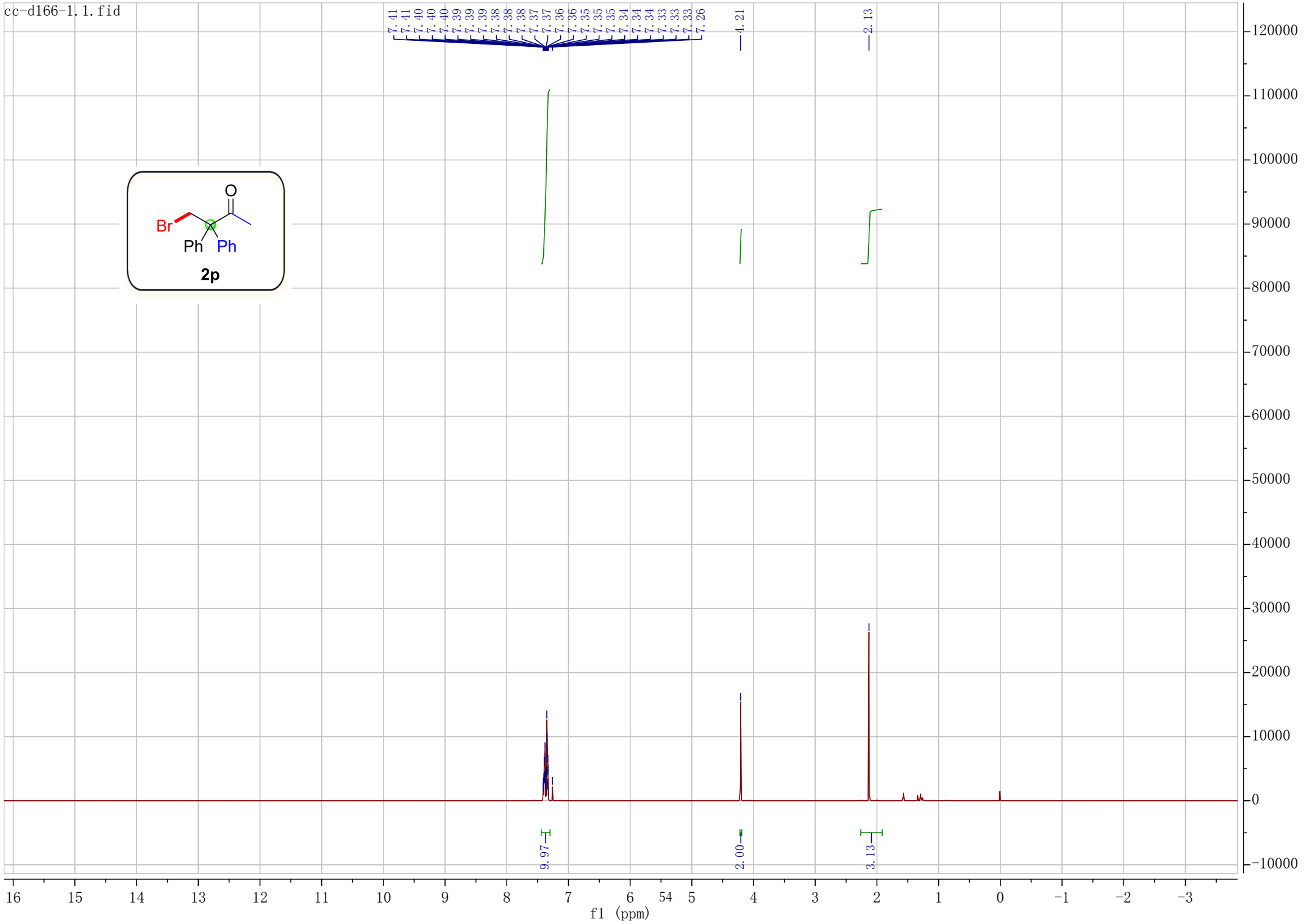
cc-e35-3.2.fid

198.92
139.29
136.87
132.03
129.95
129.59
128.47
127.93
127.78
77.40
77.14
76.89
64.99
42.13



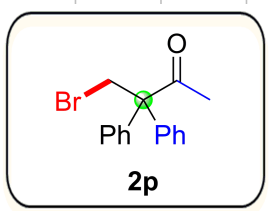

**2o**

f1 (ppm)


cc-d166-1.1.fid
7.41
7.41
7.40
7.40
7.40
7.39
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.33
7.26
4.21
2.13
Br
O
Ph
Ph
2p
9.97
2.00
3.13
f1 (ppm)

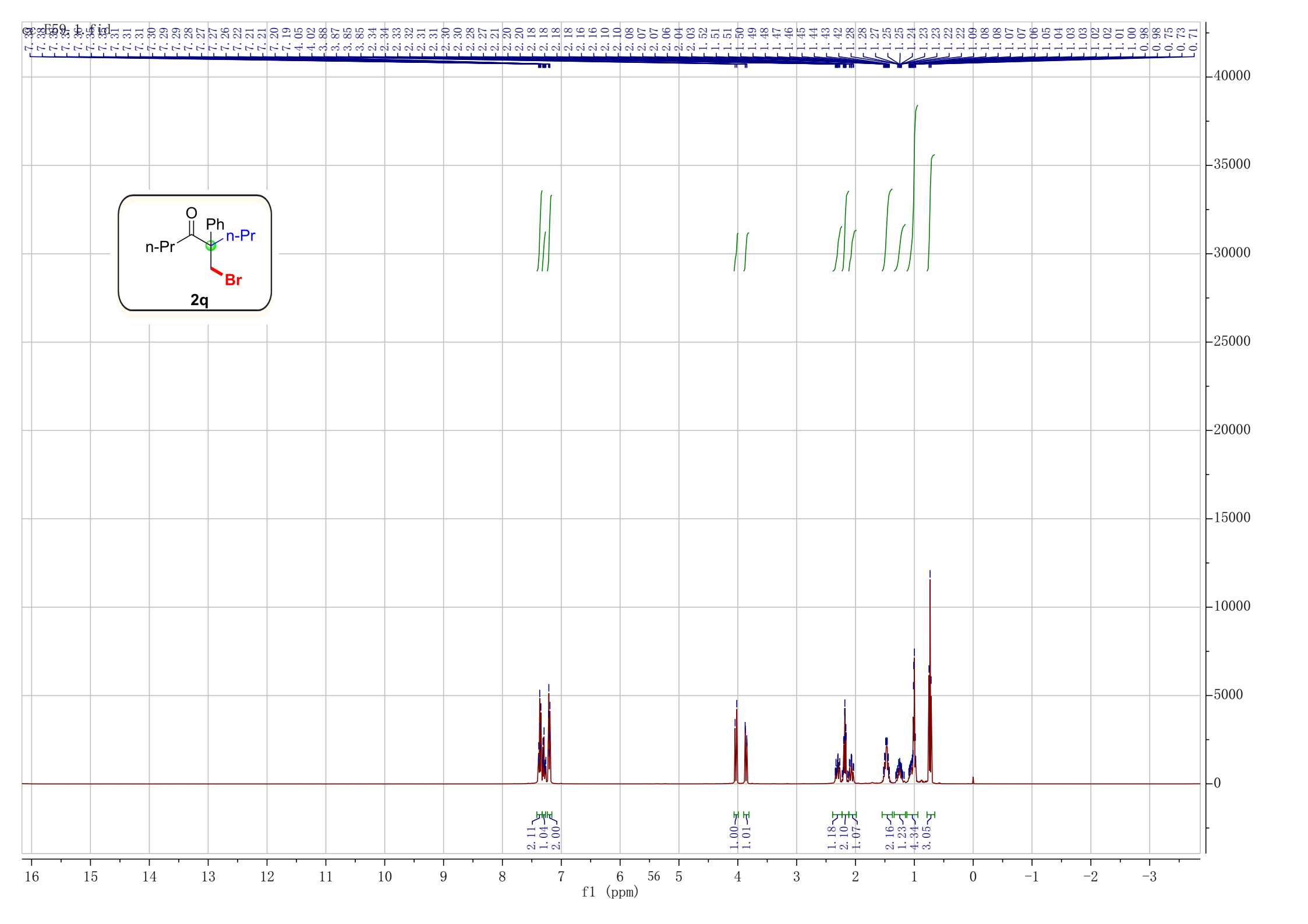
cc-d166-1.2.fid

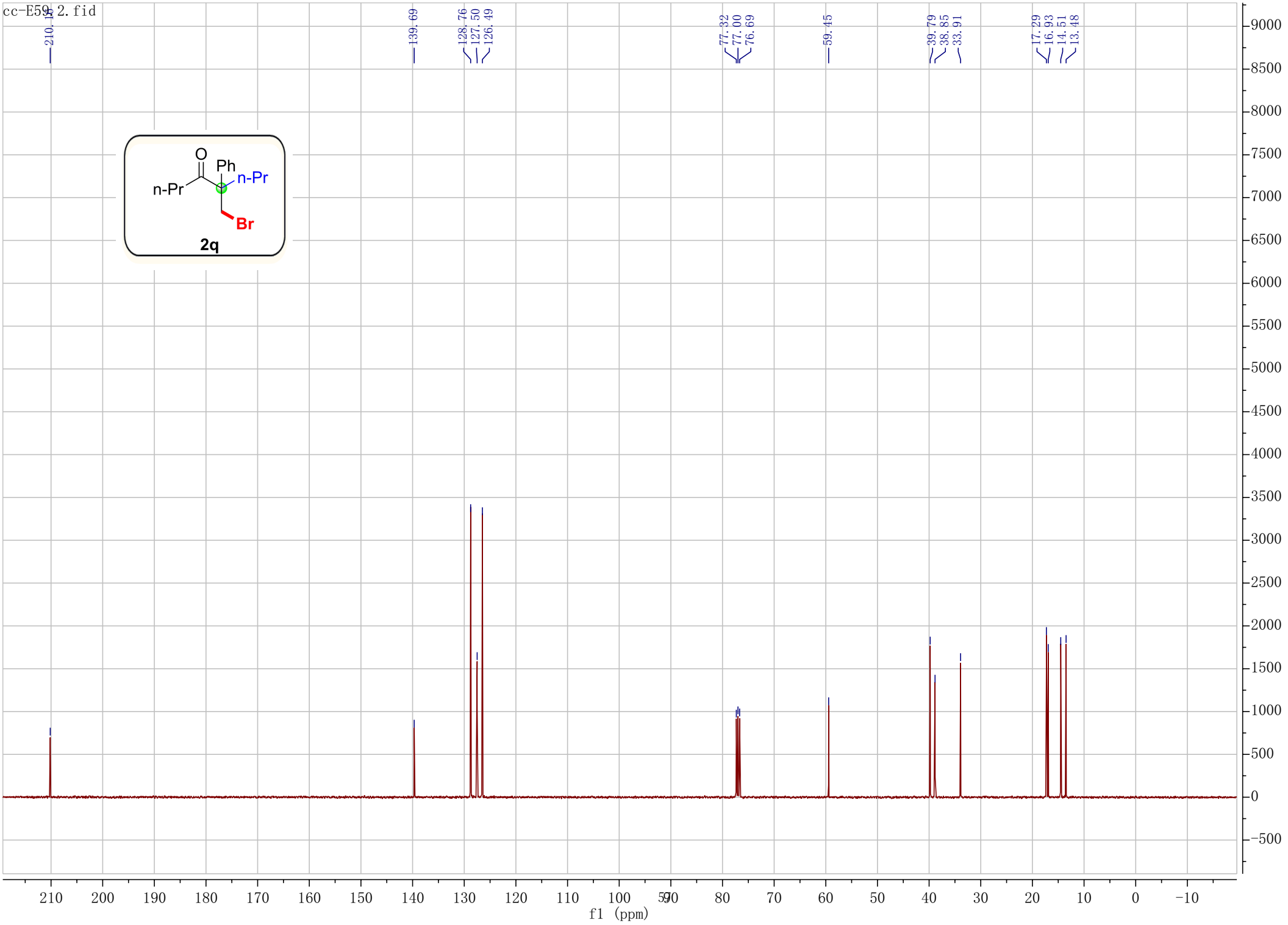
205.94
138.79
129.43
128.38
127.77
77.26
77.01
76.75
66.65
40.15
27.52

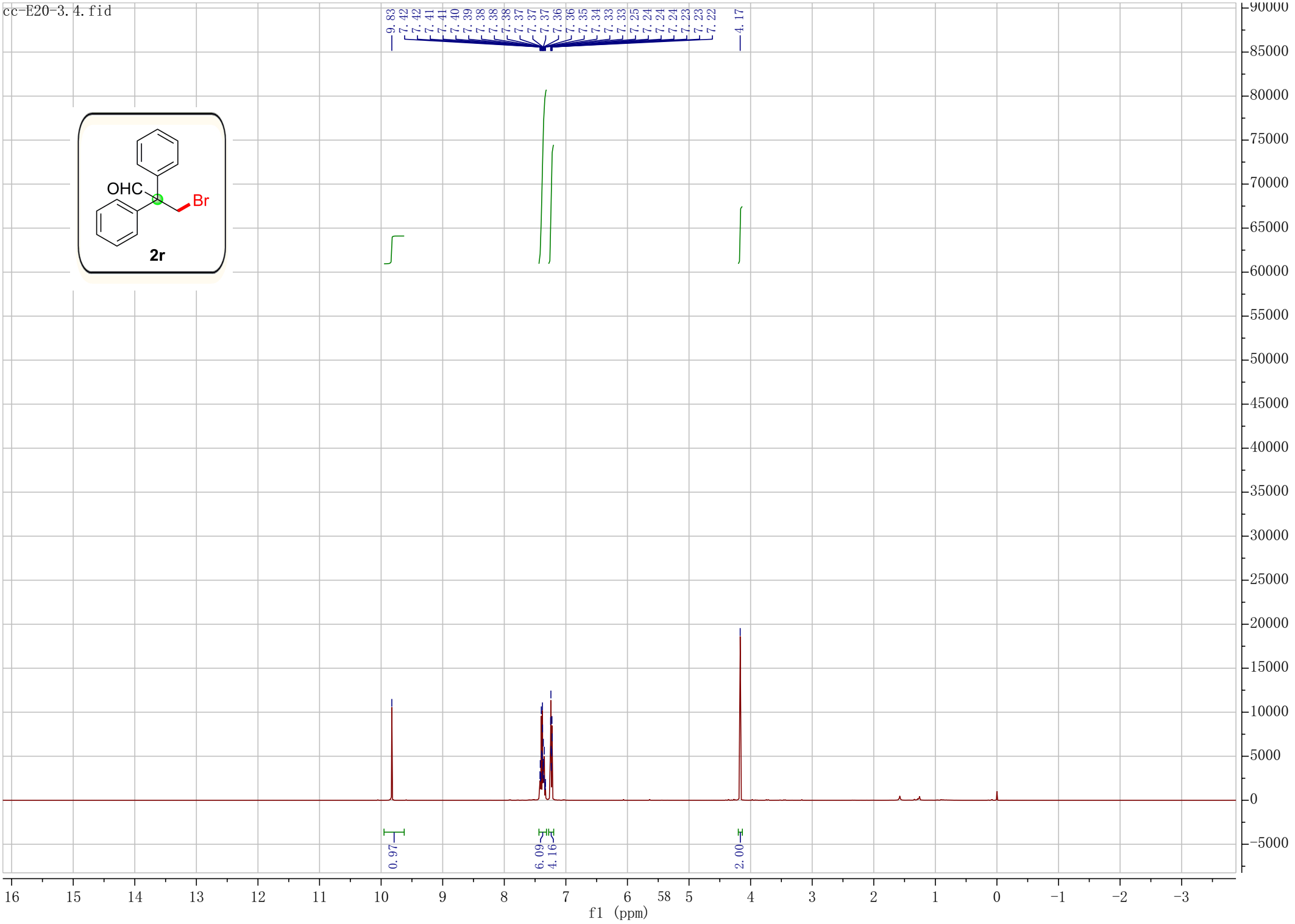


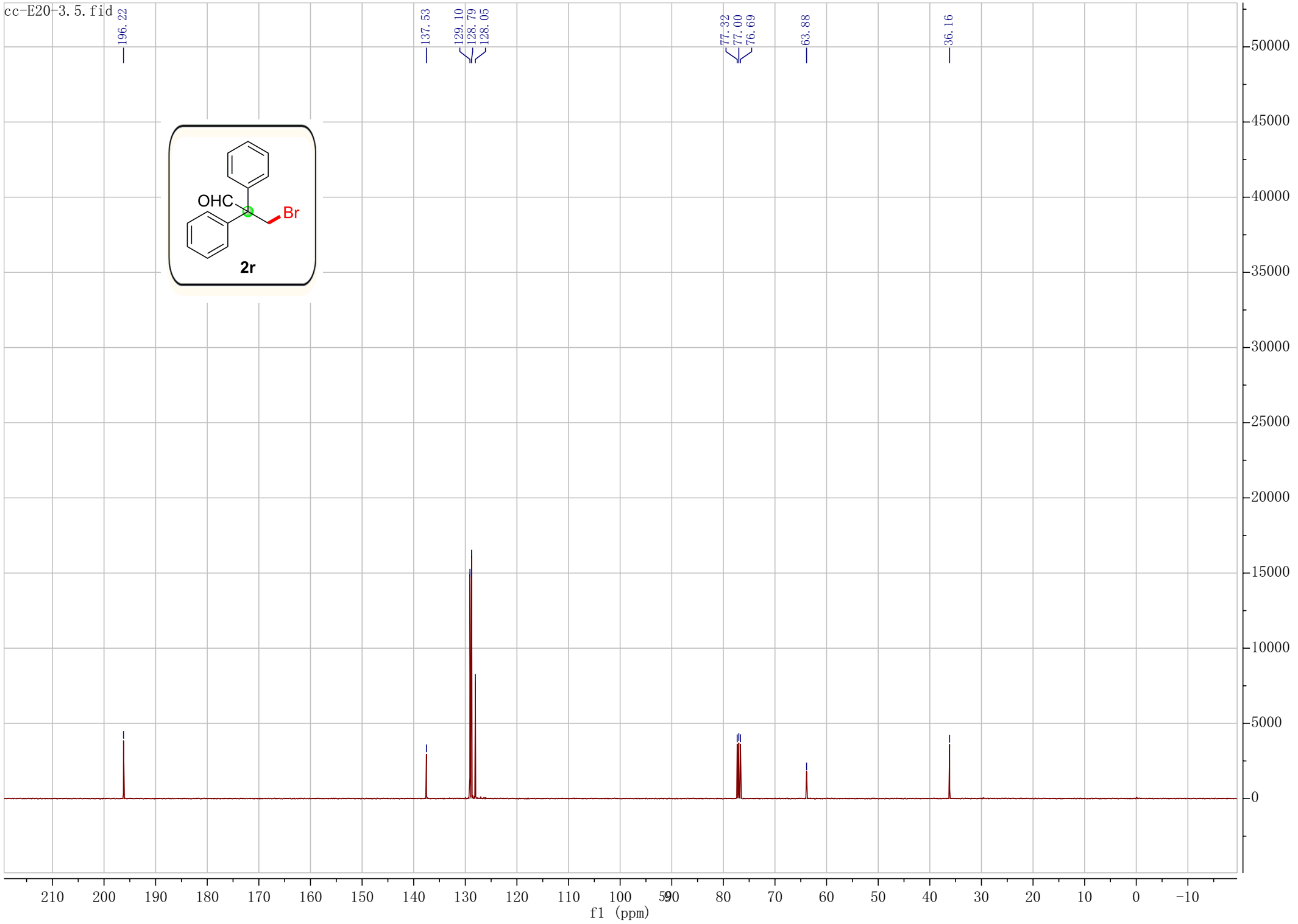

**2p**

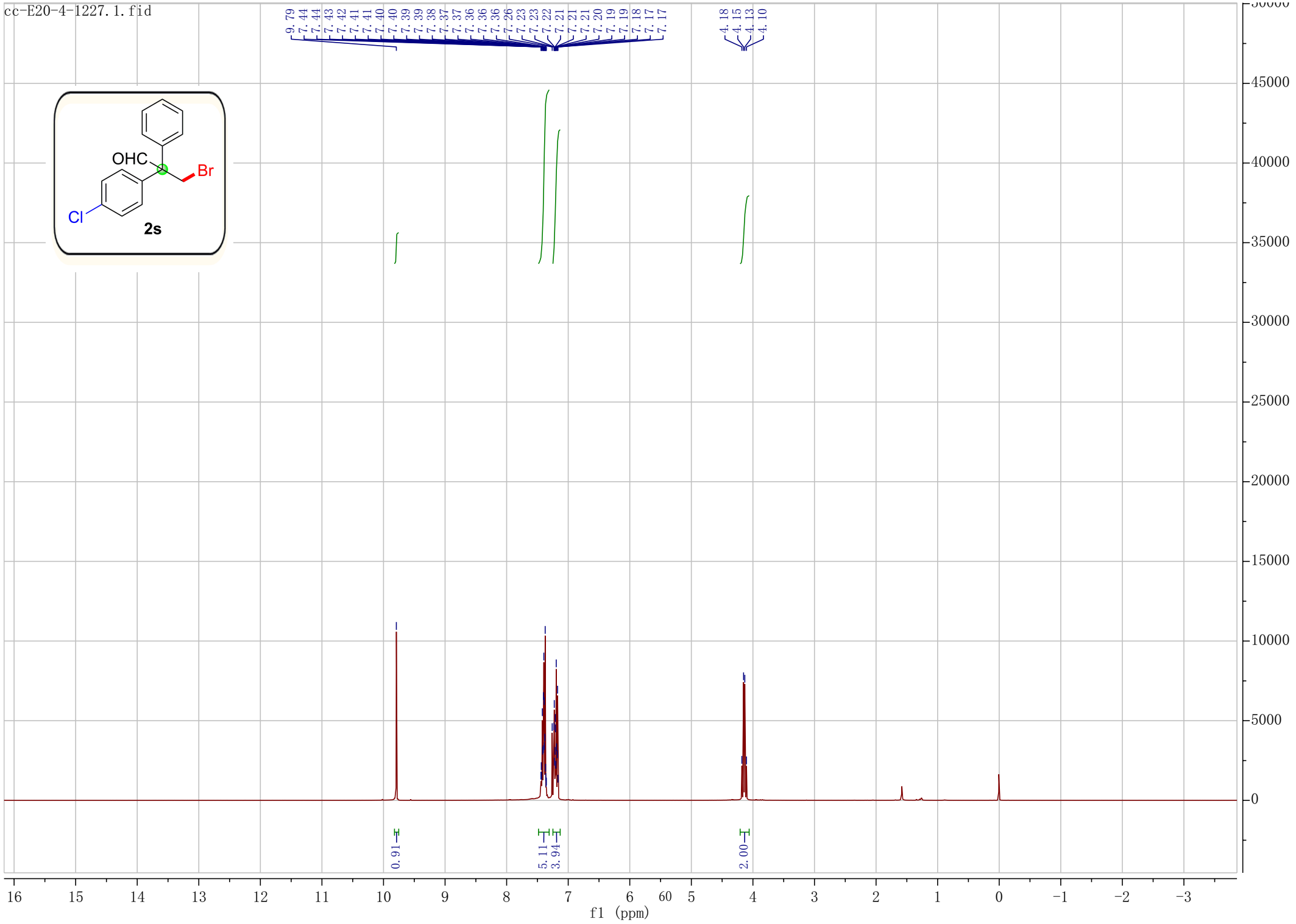
f1 (ppm)

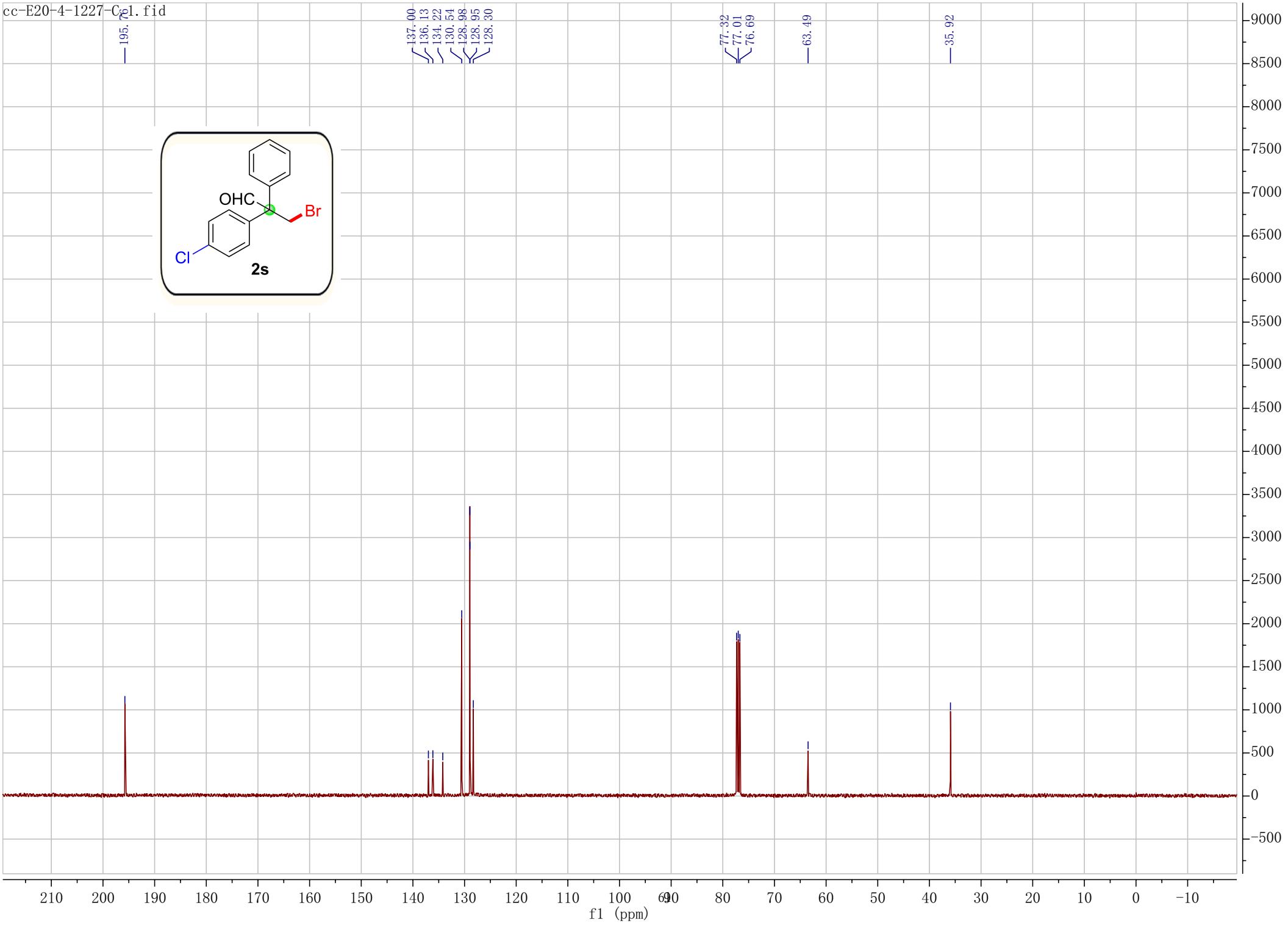

cc-E59-1.fid
O
Ph
n-Pr
n-Pr
Br
2q
f1 (ppm)


cc-E59-2.fid
210.18
139.69
128.76
127.50
126.49
77.32
77.00
76.69
59.45
39.79
38.85
33.91
17.29
16.93
14.51
13.48
O
Ph
n-Pr
n-Pr
Br
2q
f1 (ppm)

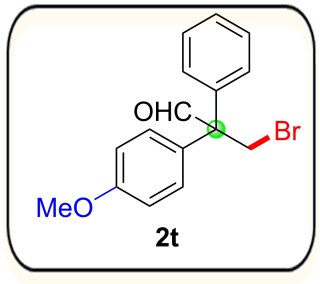

cc-E20-3.4.fid
9.83
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.33
7.25
7.24
7.24
7.24
7.23
7.22
4.17
OHC
Br
2r
0.97
6.09
4.16
2.00
f1 (ppm)


cc-E20-3.5.fid
196.22
137.53
129.10
128.79
128.05
77.32
77.00
76.69
63.88
36.16
OHC
Br
2r
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
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)


cc-E20-4-1227.1.fid
9.79
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.36
7.36
7.26
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
4.18
4.15
4.13
4.10
OHC
Br
Cl
2s
0.91
5.11
3.94
2.00
f1 (ppm)


cc-E20-4-1227-Cal.fid
195.76
137.00
136.13
134.22
130.54
128.98
128.95
128.30
77.32
77.01
76.69
63.49
35.92
OHC
Br
Cl
2s
f1 (ppm)

cc-E7-9.1.fid

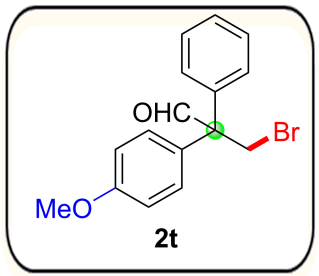



**2t**

f1 (ppm)

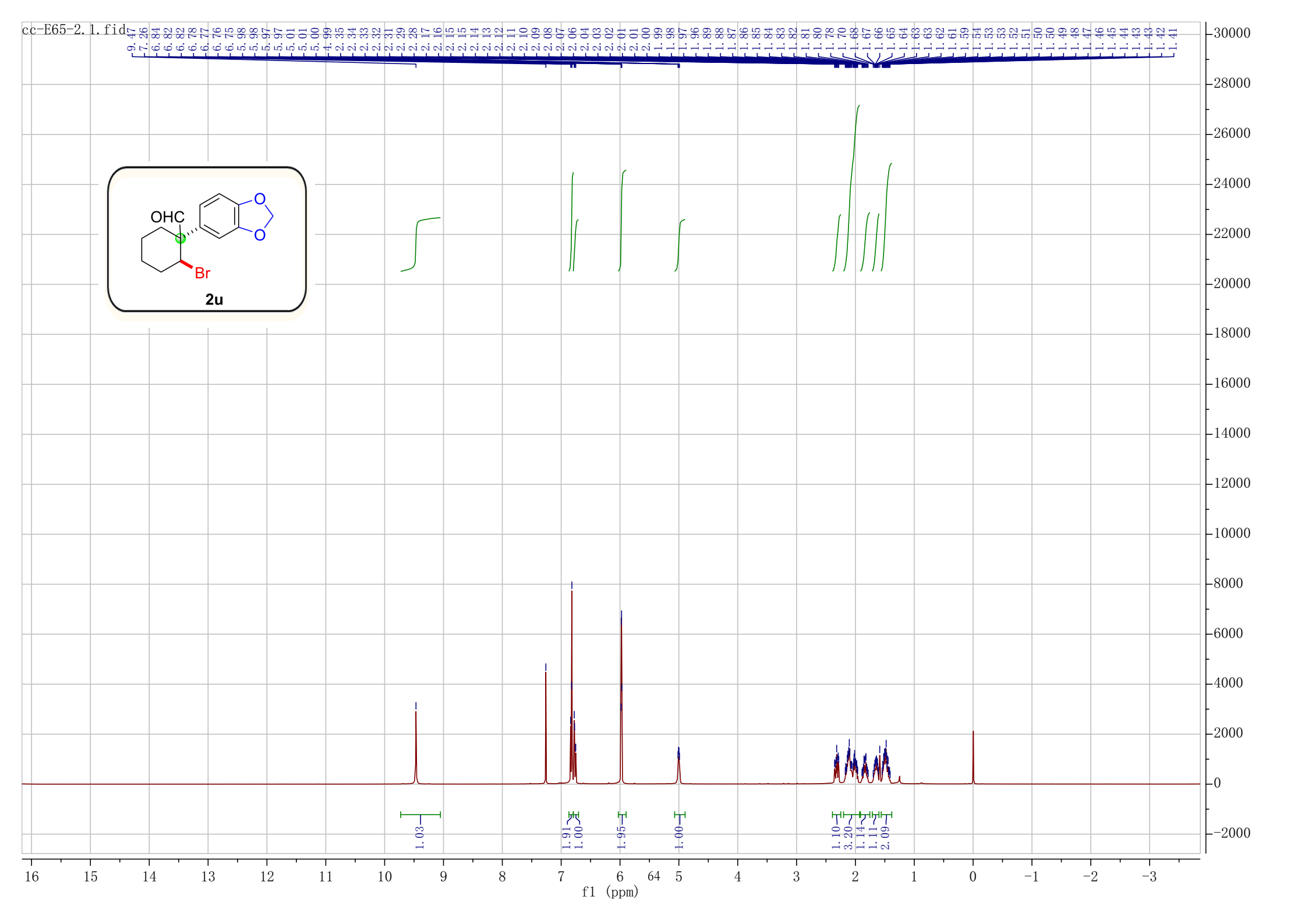
cc-E7-9.2.fid

196.15
159.21
137.79
130.27
129.05
128.73
127.98
114.19
77.26
77.00
76.75
63.24
55.25
36.49



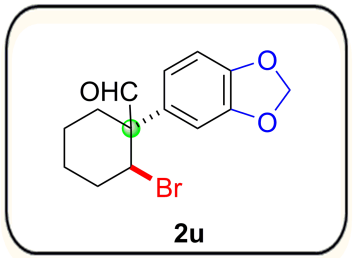

**2t**

f1 (ppm)


cc-E65-2.1.fid
OHC
Br
2u
f1 (ppm)

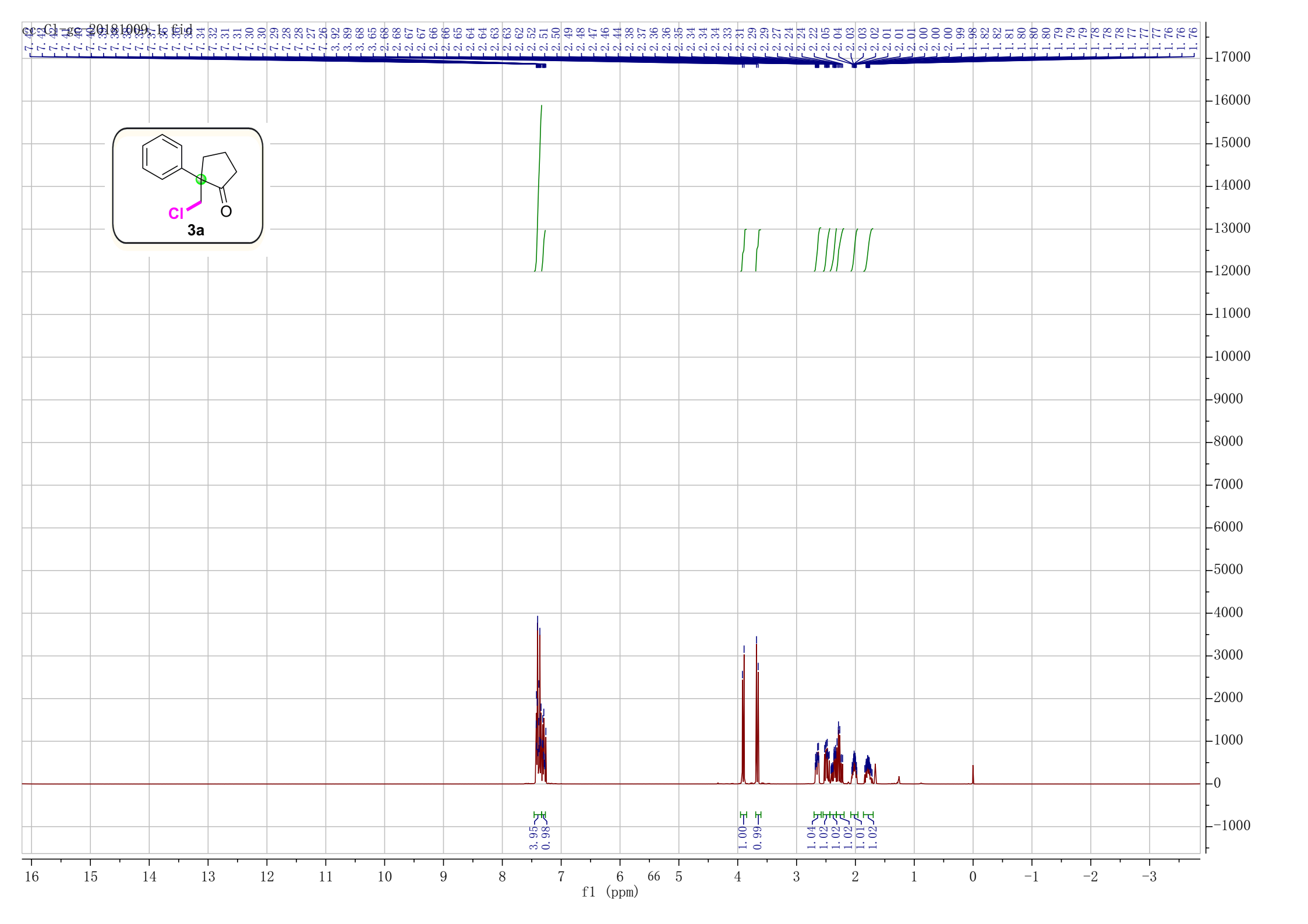
cc-E65-2-20190126.3.fid

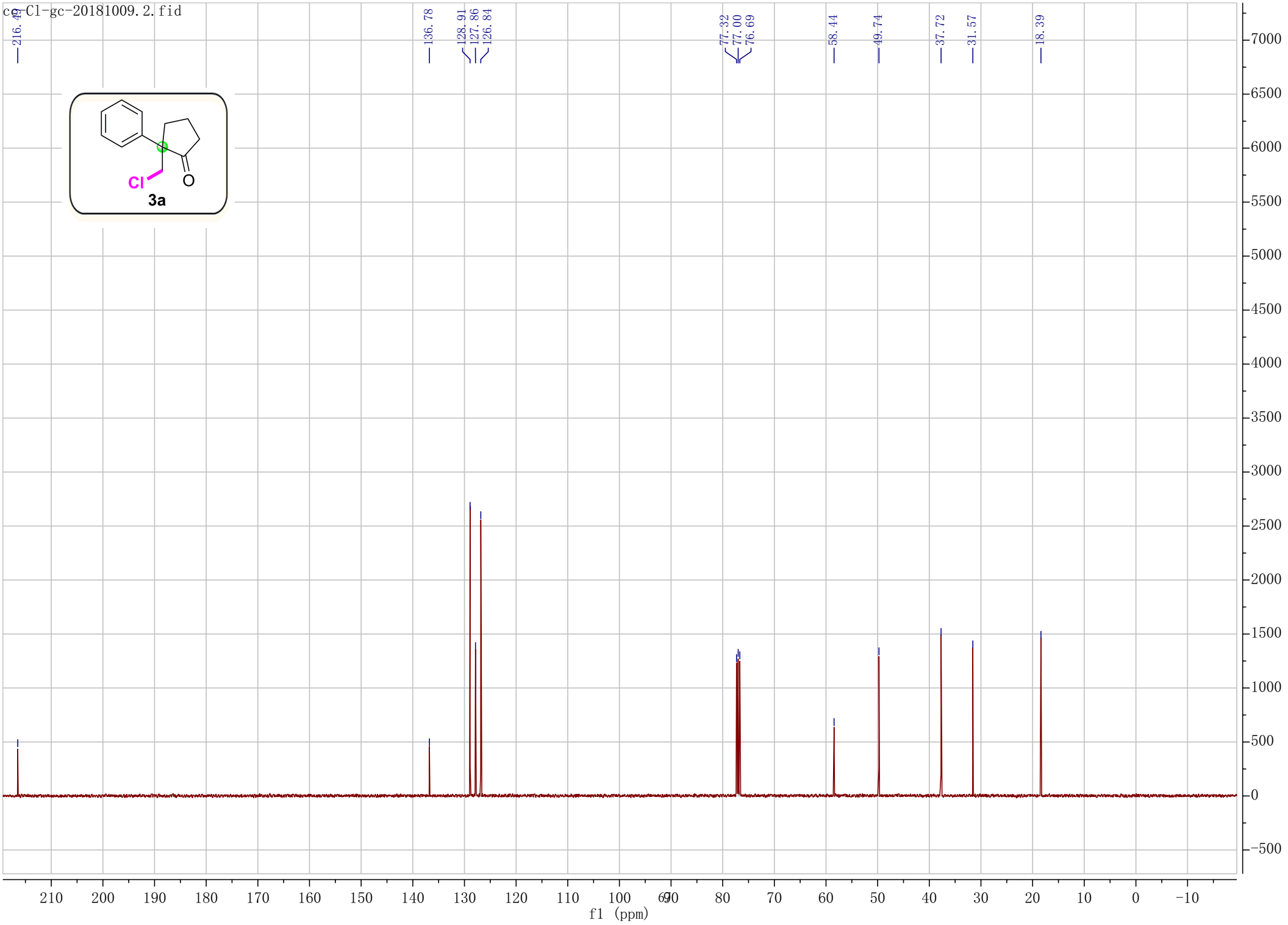
198.99
148.64
147.02
130.55
121.12
108.74
107.74
101.39
77.32
77.00
76.69
57.41
55.44
31.93
28.51
22.94
21.16

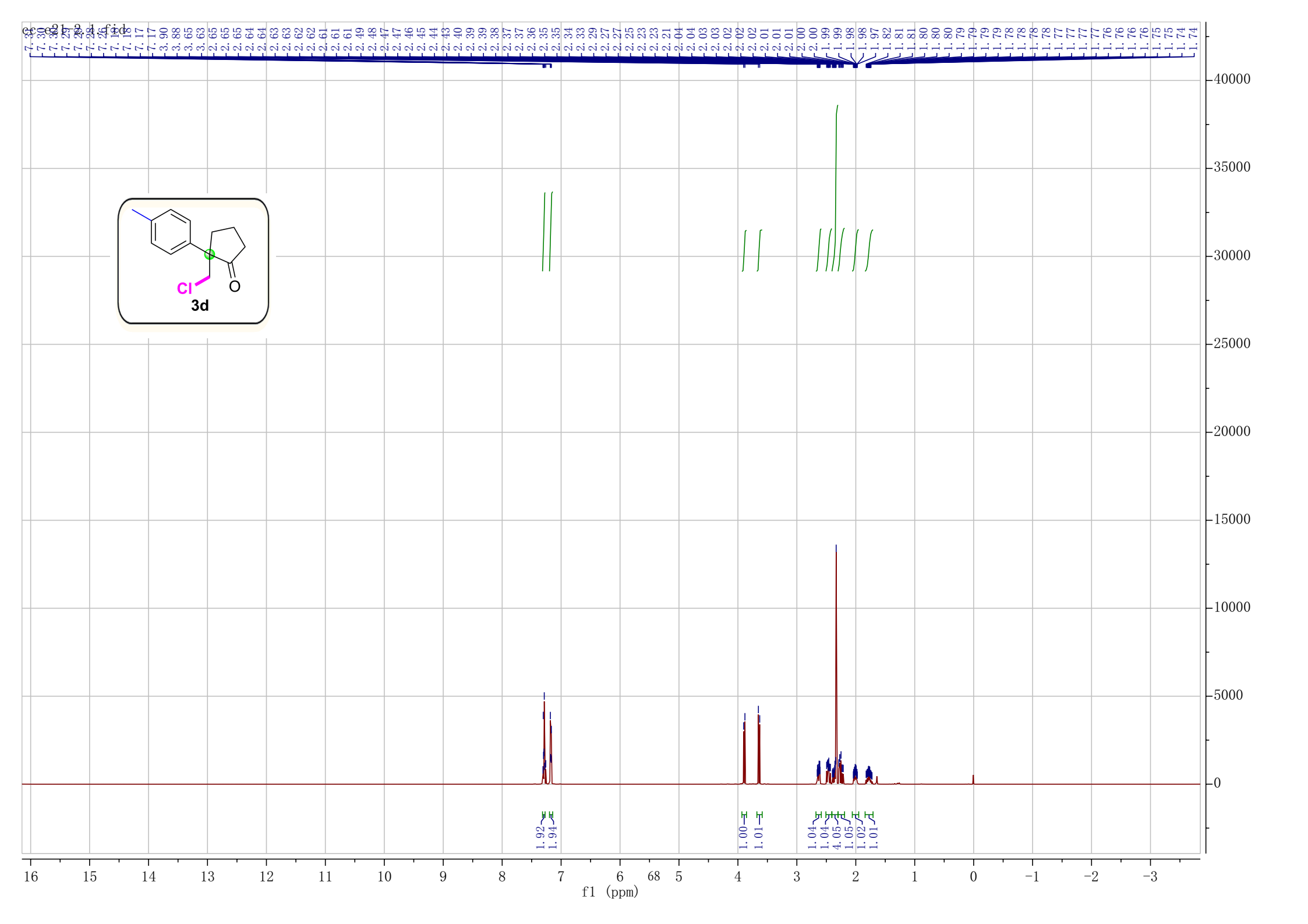



2u

f1 (ppm)

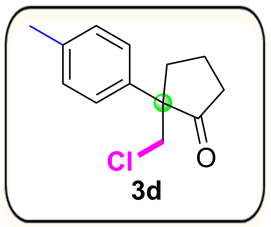

cc-Cl-gc-20181009-1.fid
Cl
O
3a
f1 (ppm)


cg-Cl-gc-20181009.2.fid
216.49
136.78
128.91
127.86
126.84
77.32
77.00
76.69
58.44
49.74
37.72
31.57
18.39
Cl
O
3a
f1 (ppm)


cc-221-2.fid
Cl
O
3d
f1 (ppm)

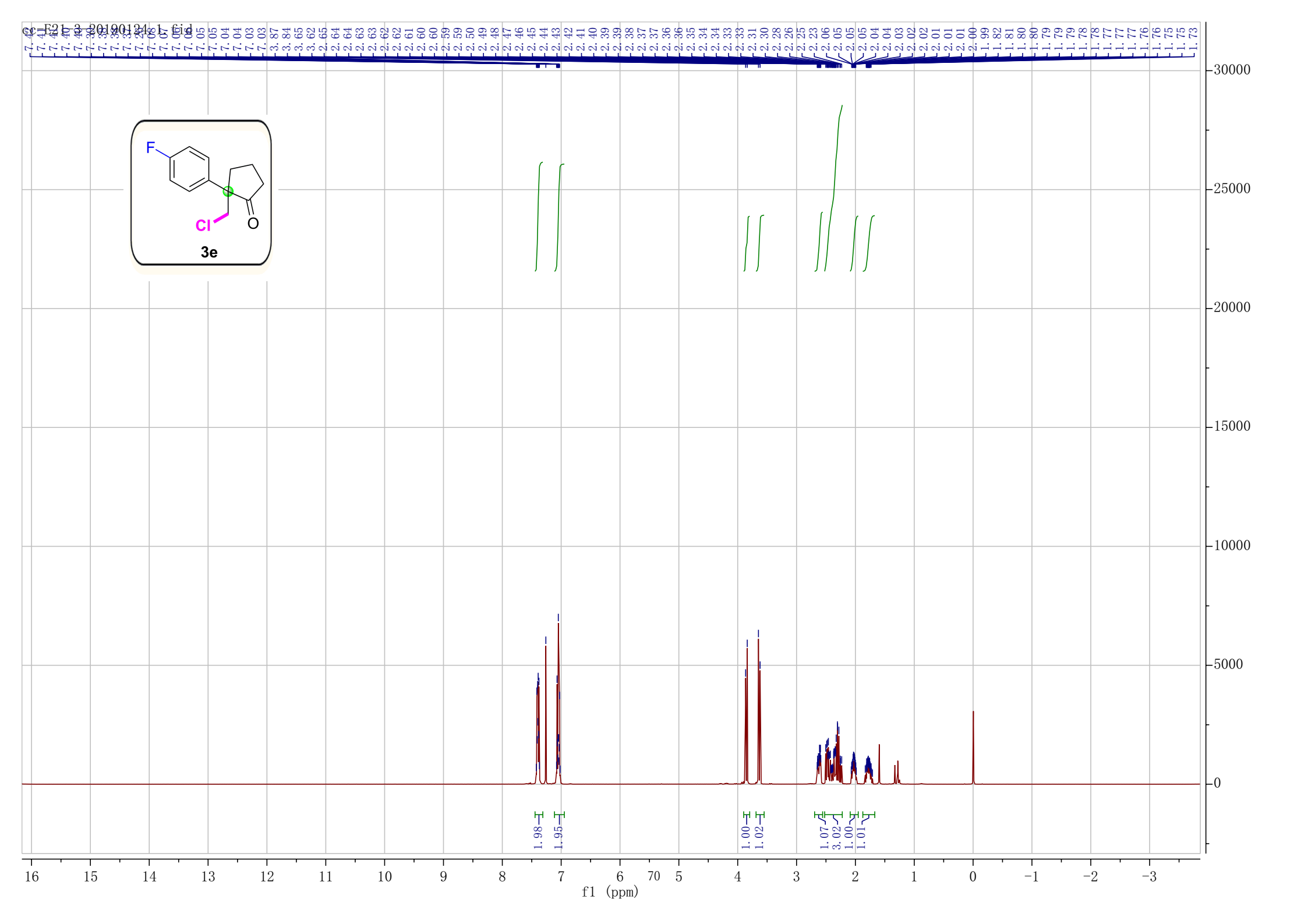
cc-e21-2.2.fid

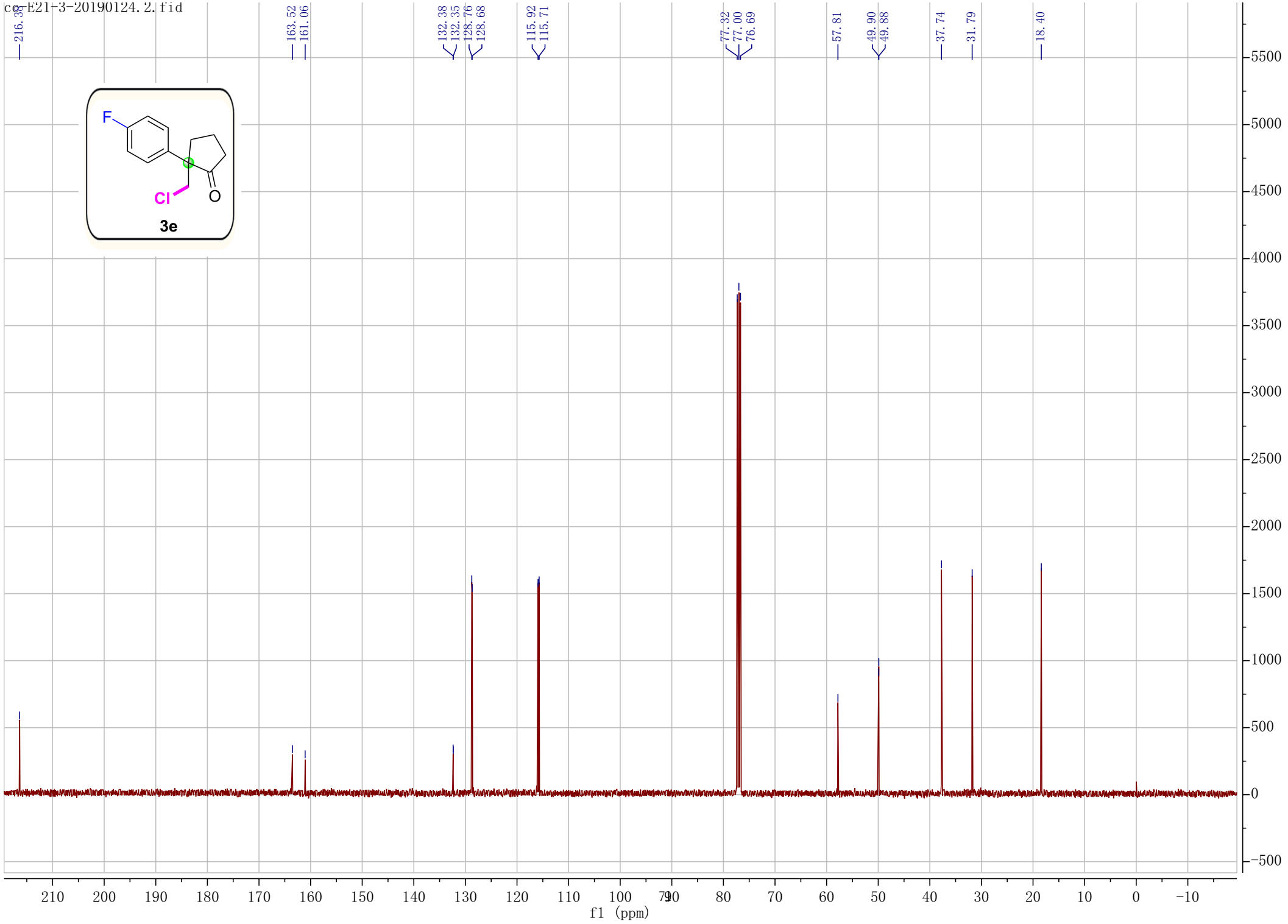
216.58
137.72
133.63
129.65
126.74
77.26
77.00
76.75
58.16
49.76
37.65
31.48
20.92
18.36

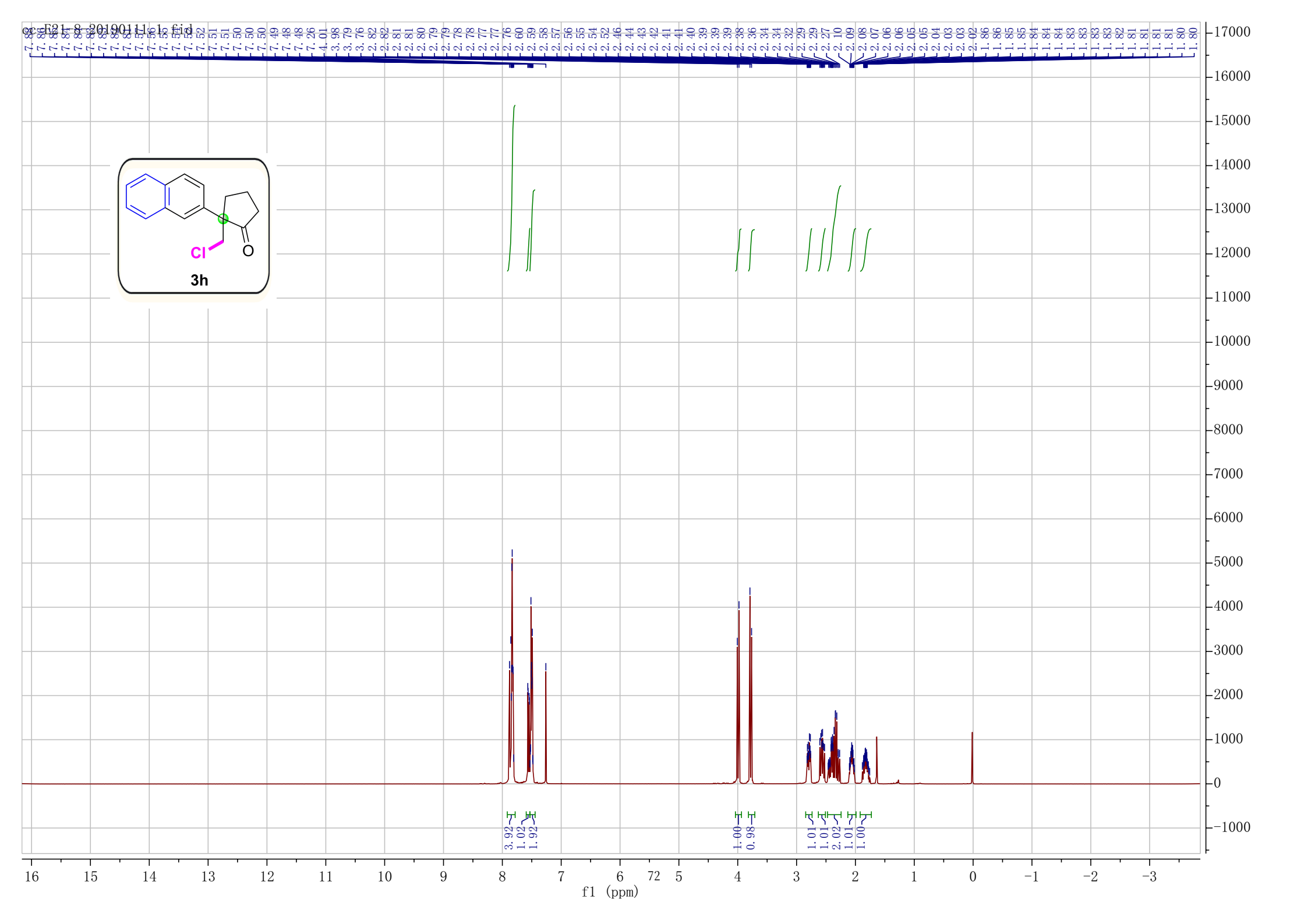


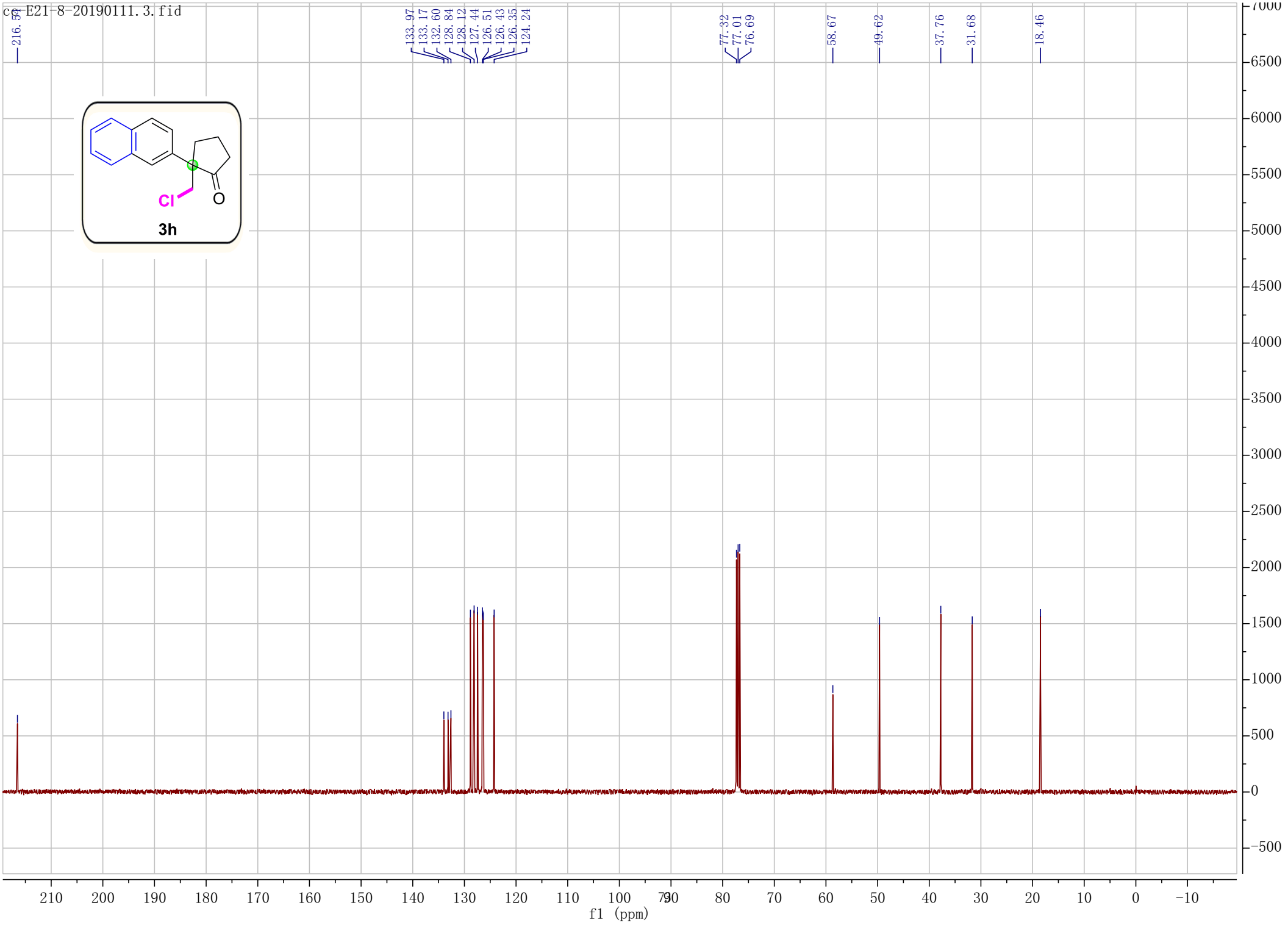

3d

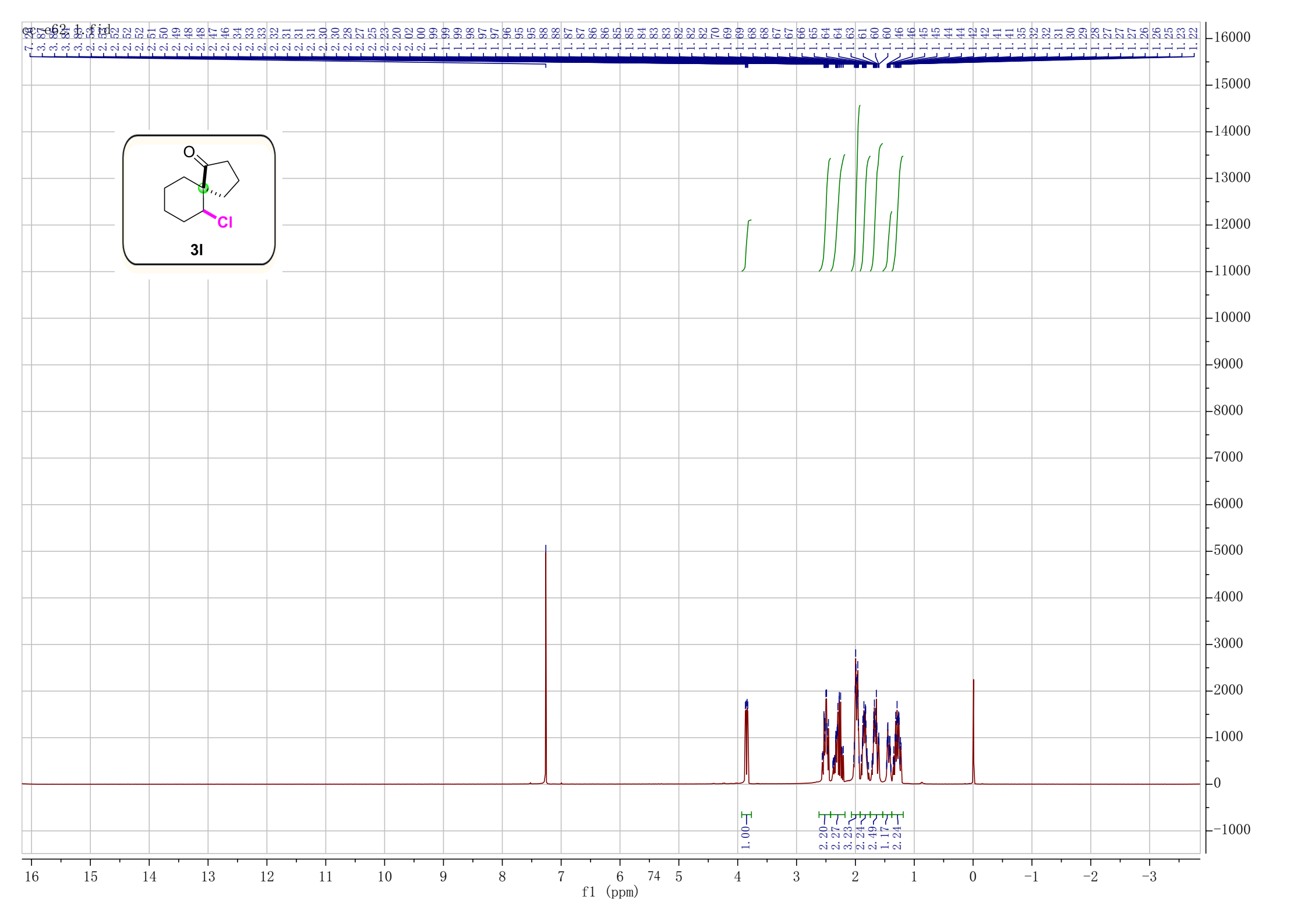
f1 (ppm)

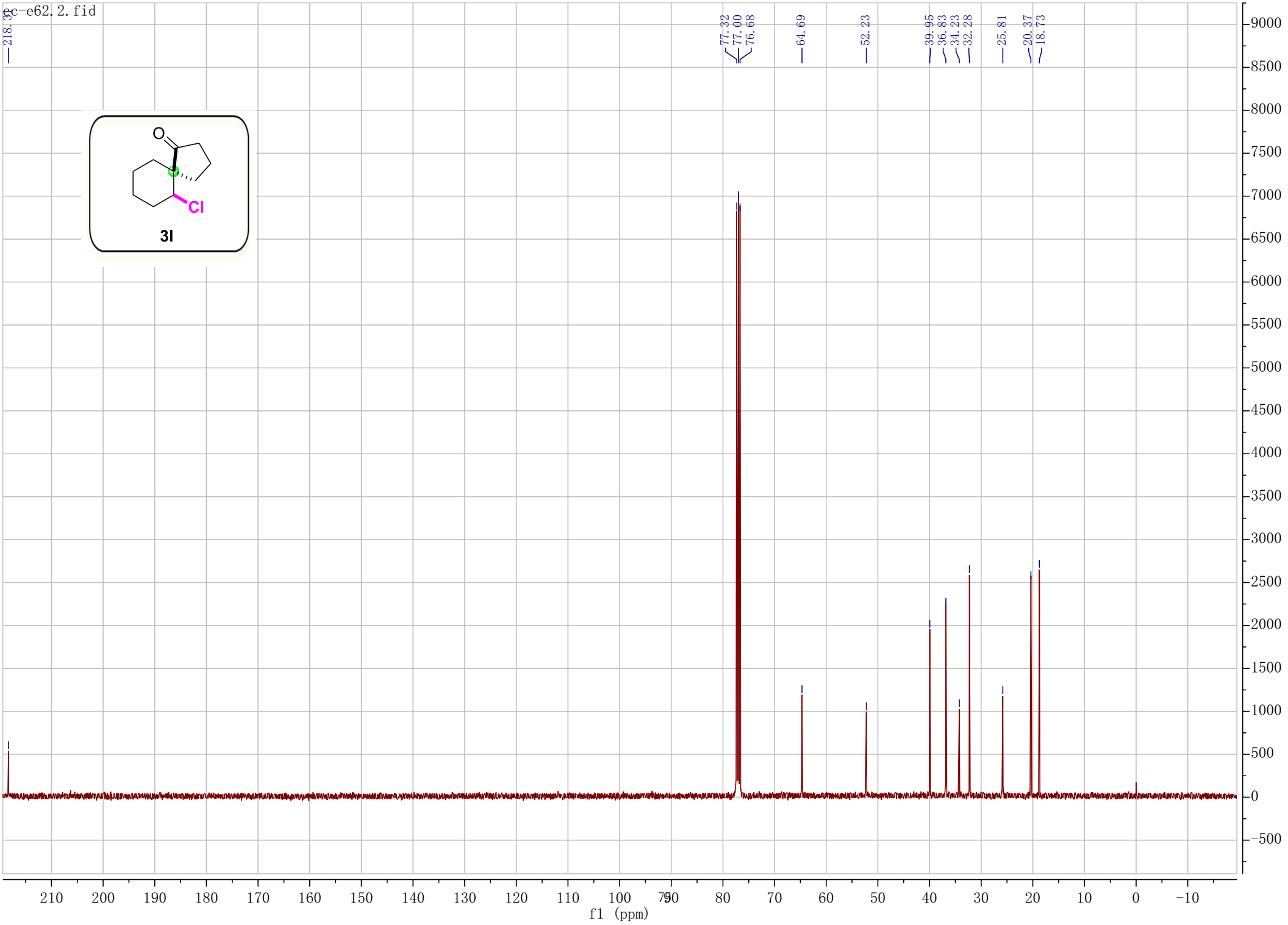

cc-F2L-3-20190124-1.fid
F
Cl
O
3e
1.98
1.95
1.00
1.02
1.07
3.02
1.00
1.01
f1 (ppm)


cg-E21-3-20190124.2.fid
216.38
163.52
161.06
132.38
132.35
128.76
128.68
115.92
115.71
77.32
77.00
76.69
57.81
49.90
49.88
37.74
31.79
18.40
F
Cl
O
3e
f1 (ppm)

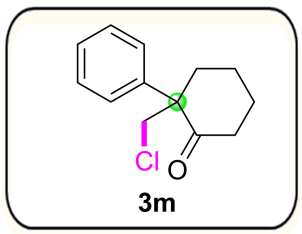

cc-F21-8-20190111-1.fid
Cl
O
3h
f1 (ppm)


cg-E21-8-20190111.3.fid
216.58
133.97
133.17
132.60
128.84
128.12
127.44
126.51
126.43
126.35
124.24
77.32
77.01
76.69
58.67
49.62
37.76
31.68
18.46
Cl
O
3h
f1 (ppm)


cc-e62-1.fid
O
Cl
3l
f1 (ppm)


cc-e62.2.fid
218.36
77.32
77.00
76.68
64.69
52.23
39.95
36.83
34.23
32.28
25.81
20.37
18.73
O
Cl
3l
f1 (ppm)

cc-F21-6-1223-1.fid

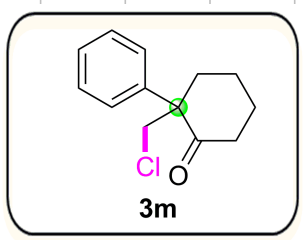



3m

f1 (ppm)

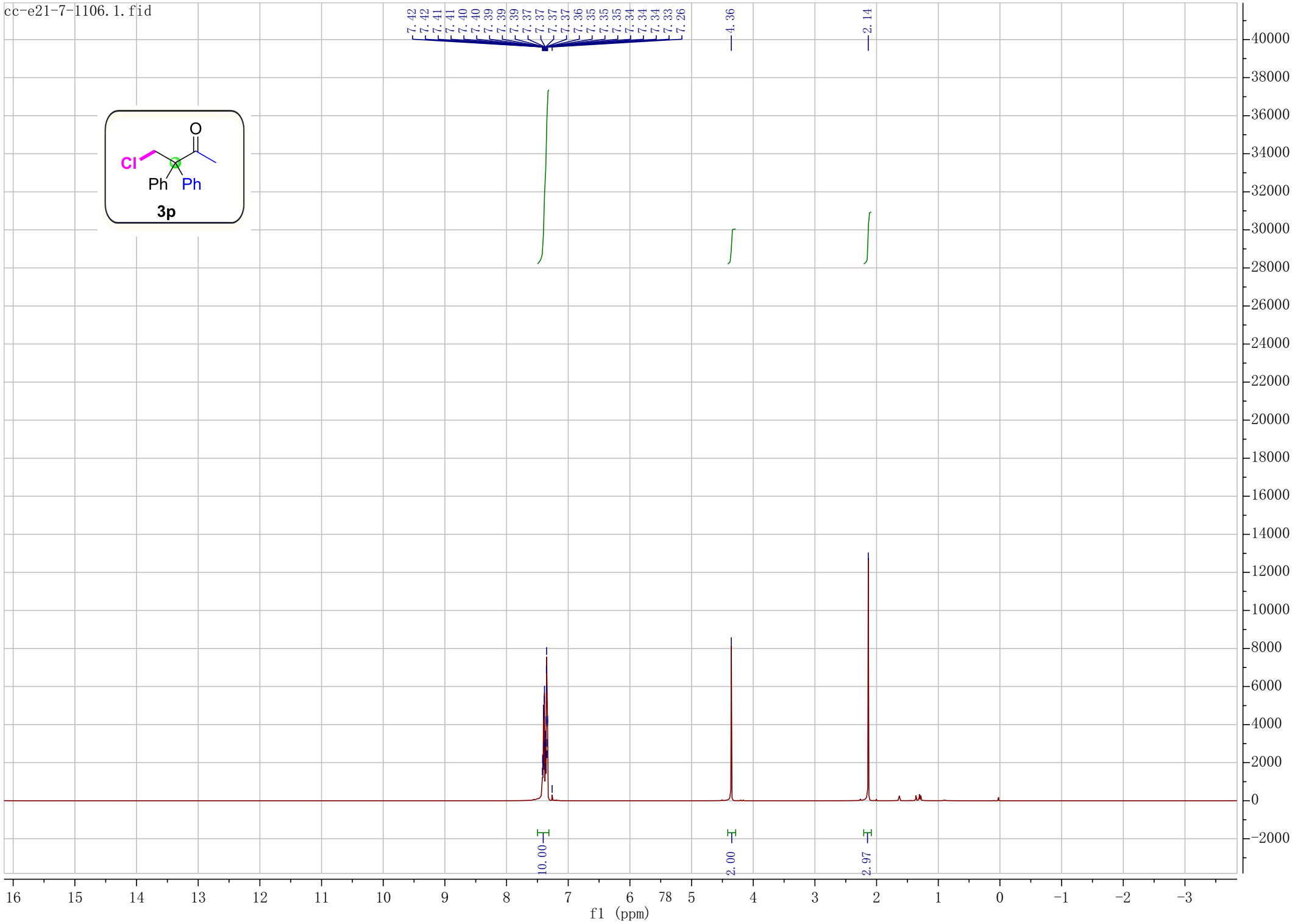
cc-E21-6-1223.2.fid

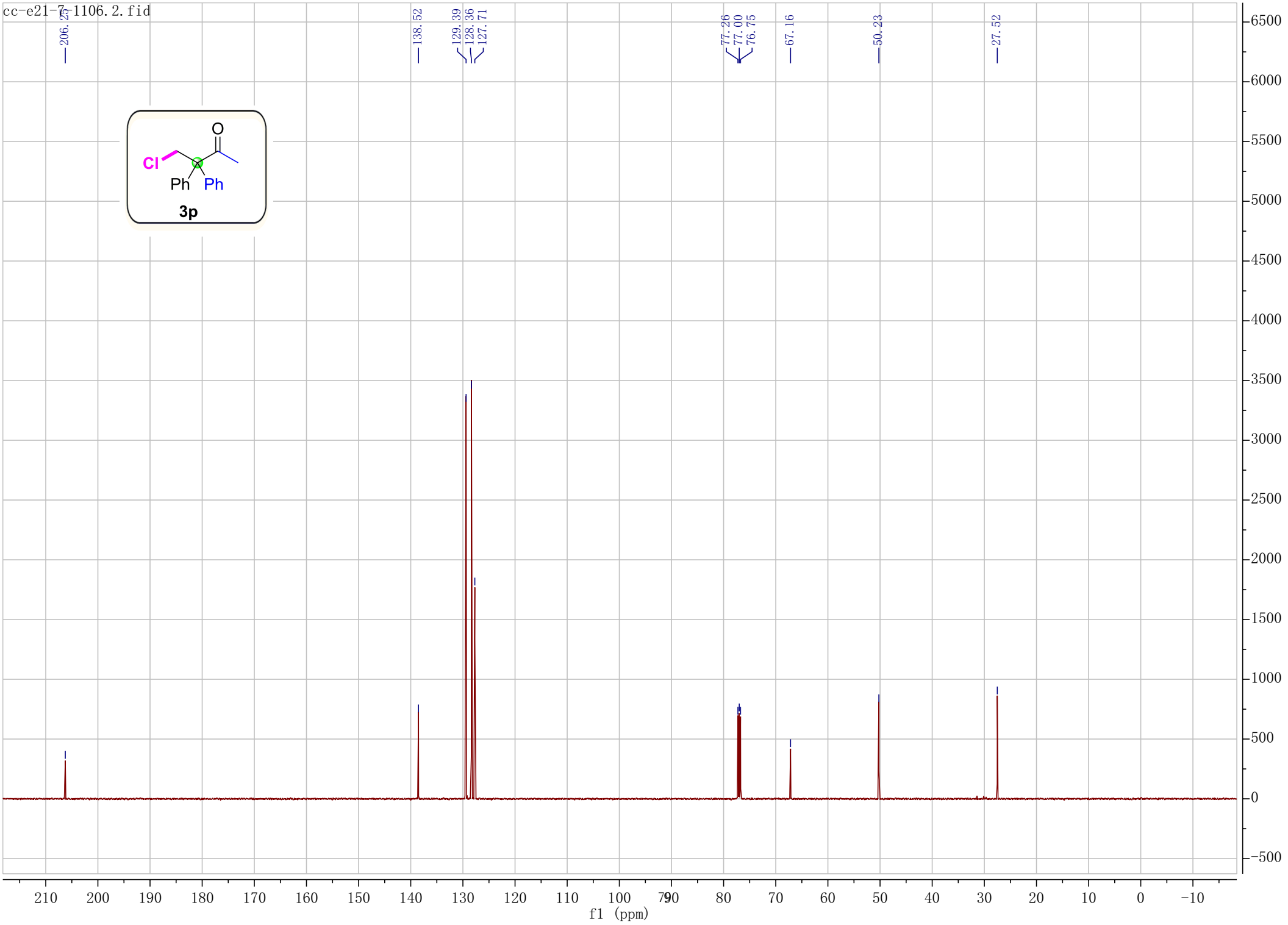
211.08
137.51
129.01
127.69
127.04
77.32
77.00
76.69
57.89
52.72
39.97
32.70
27.65
21.18

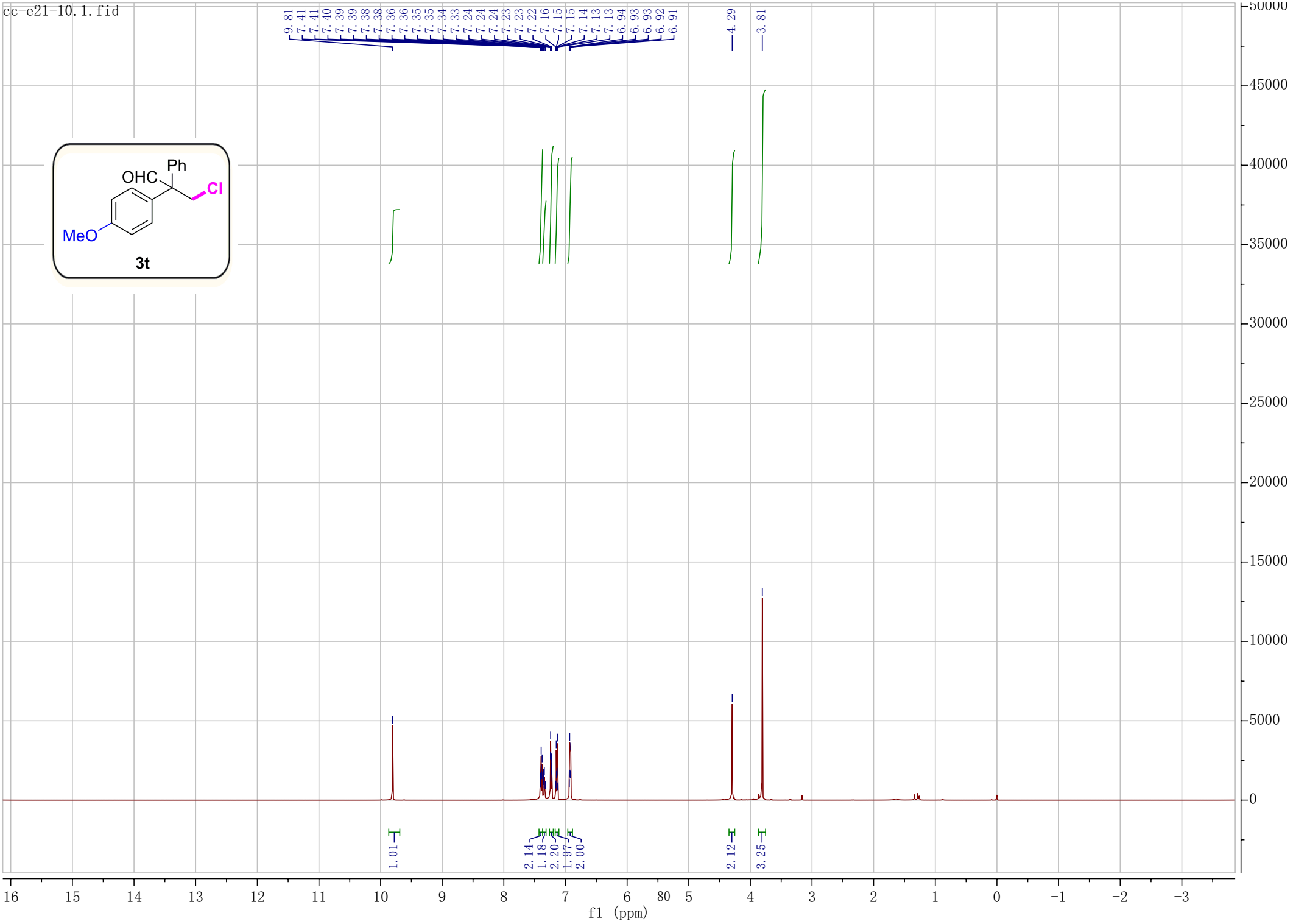



3m

f1 (ppm)

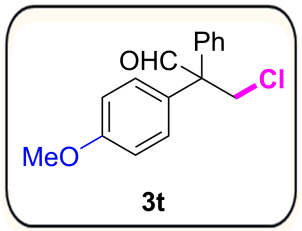

cc-e21-7-1106.1.fid
7.42
7.42
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.37
7.37
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.26
4.36
2.14
Cl
O
Ph
Ph
3p
10.00
2.00
2.97
f1 (ppm)


cc-e21-7-1106.2.fid
206.29
138.52
129.39
128.36
127.71
77.26
77.00
76.75
67.16
50.23
27.52
Cl
O
Ph
Ph
3p
f1 (ppm)


cc-e21-10.1.fid
9.81
7.41
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.36
7.36
7.35
7.35
7.34
7.33
7.24
7.24
7.24
7.23
7.23
7.22
7.16
7.15
7.15
7.14
7.13
6.94
6.93
6.93
6.92
6.91
4.29
3.81
OHC
Ph
Cl
MeO
3t
1.01
2.14
1.18
2.20
1.97
2.00
2.12
3.25
f1 (ppm)

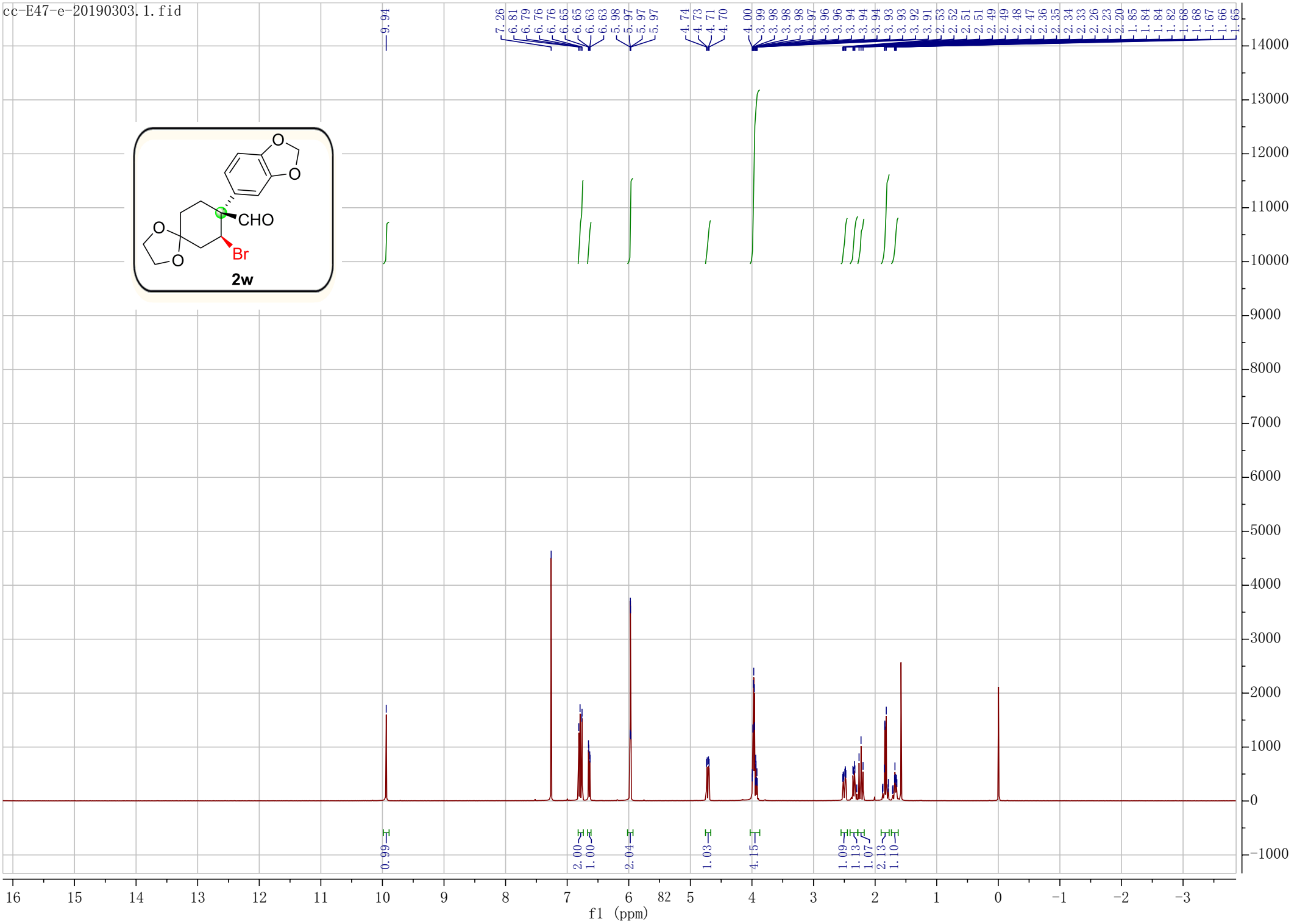
cc-e21-10.2.fid

196.42
159.21
137.47
130.28
129.07
128.85
128.76
127.96
114.23
77.26
77.00
76.75
63.95
55.23
47.34



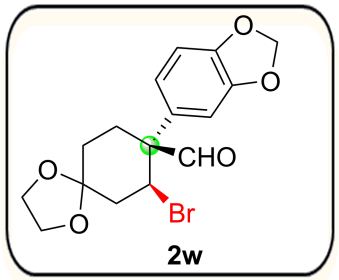

**3t**

f1 (ppm)


cc-E47-e-20190303.1.fid
9.94
7.26
6.81
6.79
6.76
6.76
6.65
6.65
6.63
6.63
5.98
5.97
5.97
5.97
4.74
4.73
4.71
4.70
4.00
3.99
3.98
3.98
3.98
3.97
3.96
3.96
3.94
3.94
3.94
3.94
3.93
3.93
3.92
3.91
2.53
2.52
2.51
2.51
2.49
2.49
2.48
2.47
2.36
2.35
2.34
2.33
2.26
2.23
2.20
1.85
1.84
1.84
1.82
1.68
1.68
1.67
1.66
1.65
O
O
CHO
O
O
Br
2w
0.99
2.00
1.00
2.04
1.03
4.15
1.09
1.13
1.07
2.13
1.10
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
16
15
14
13
12
11
10
9
8
7
6
82
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

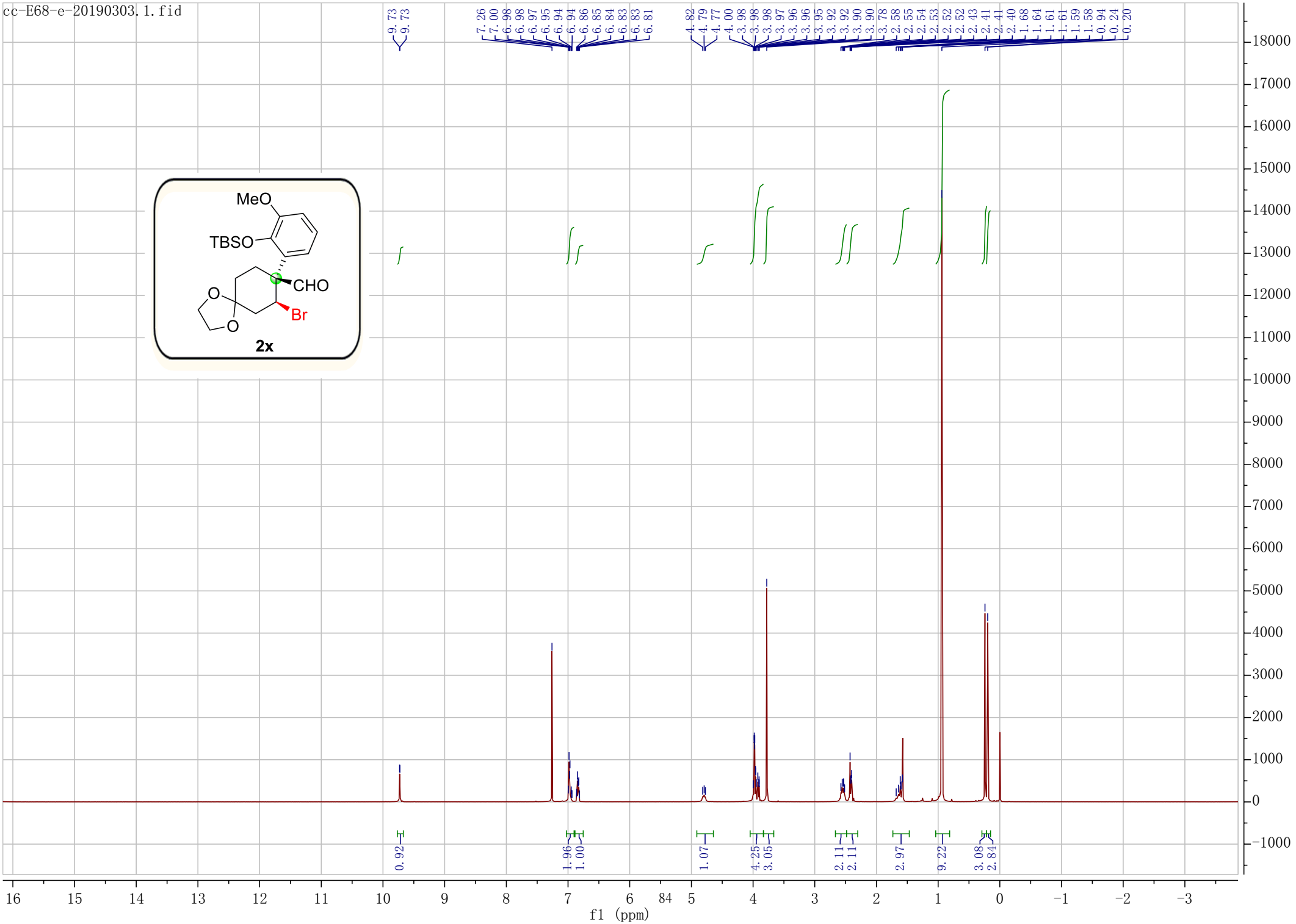
cc-E47-e-20190303.2.fid

202.11
148.38
147.05
132.22
120.37
108.51
108.03
107.05
101.33
77.32
77.00
76.69
64.66
64.45
56.59
50.98
43.70
32.19
31.84

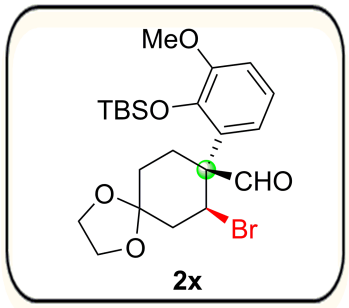



2w

f1 (ppm)


cc-E68-e-20190303.1.fid
MeO
TBSO
CHO
Br
O
O
2x
f1 (ppm)

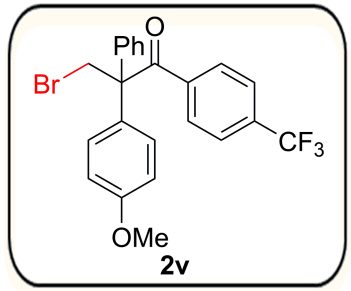
cc-E68-e-20190303.2.fid



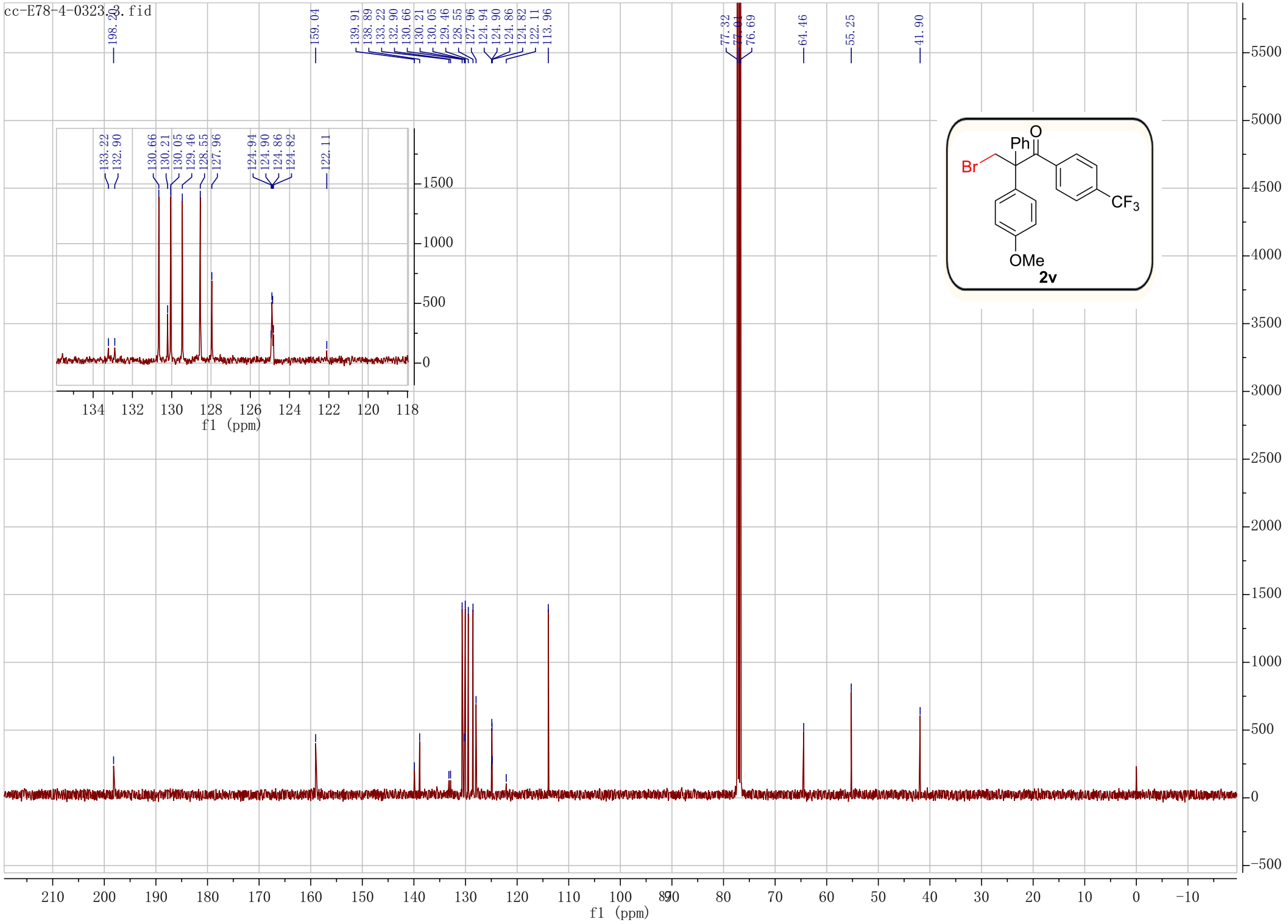

202.70
149.24
142.84
130.95
120.94
118.64
110.42
108.65
77.32
77.01
76.69
64.56
64.32
54.29
53.44
49.85
42.44
31.45
30.90
26.72
19.72
-1.97
-2.30

f1 (ppm)

cc-E78-4-0323.2.fid




f1 (ppm)


cc-E78-4-0323.3.fid
198.20
159.04
139.91
138.89
133.22
132.90
130.66
130.21
130.05
129.46
128.55
127.96
124.94
124.90
124.86
124.82
122.11
113.96
77.32
77.01
76.69
64.46
55.25
41.90
f1 (ppm)
Ph
O
Br
CF3
OMe
2v