Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Transition-metal-free radical relay cyclization of vinyl azides with 1,4-dihydropyridines involving a 1,5-hydrogen-atom transfer: an access to α-tetralone scaffolds

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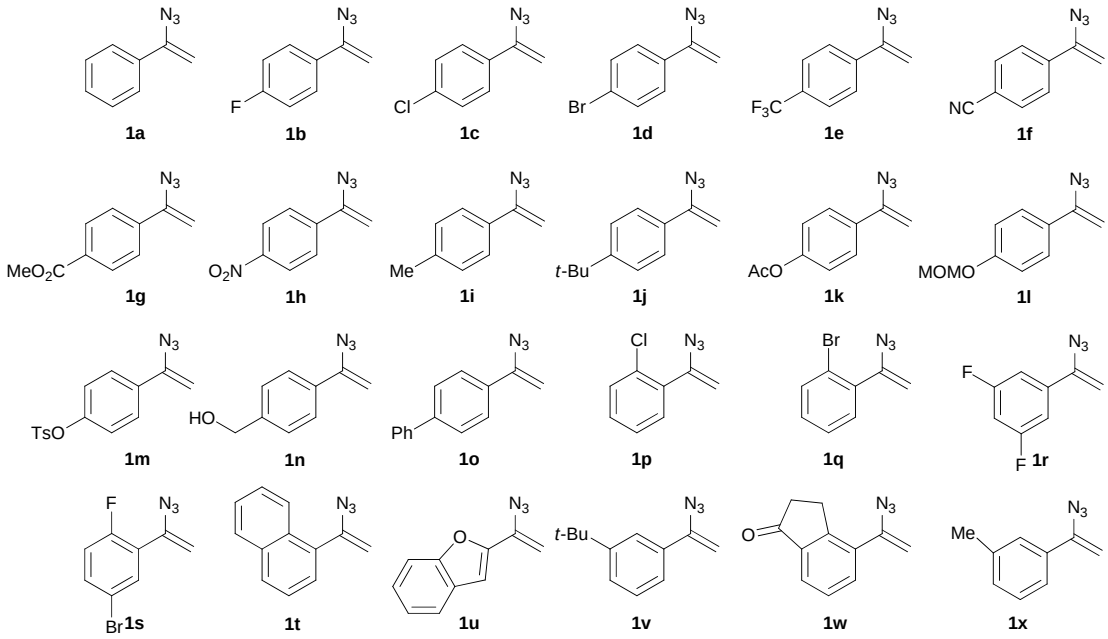
1. General information

All reactions were carried out in oven-dried sealed tubes with magnetic stirring. Unless otherwise noted, all the experiments were performed under argon atmosphere. Solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Commercially available chemicals were obtained from commercial suppliers and used as received without further purification unless otherwise stated. Anhydrous tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were purchased from Energy Chemical and stored under argon. All reactions were monitored by Thin-layer chromatography (TLC) with Huanghai GF254 silica gel coated plates. TLC plates were visualized by exposure to ultraviolet light, and/or staining with the solvent of 2,4-dinitrophenylhydrazine. Purification of reaction products were carried out by flash chromatography using silica gel (Qingdao Haiyang Co. Ltd, 200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on an Agilent DD2 400-MR or Brucker AV-400 spectrometer at ambient temperature. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for $CDCl_3$). The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.00 ppm). Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), quarter (q), triplet (t) and broad (br). High-resolution mass spectra (HRMS) were performed on a Thermo Q Exactive Plus mass instrument (ESI). Melting points (°C) are uncorrected and were recorded on a SGW X-4 apparatus.

No attempts were made to optimize yields for substrate synthesis.

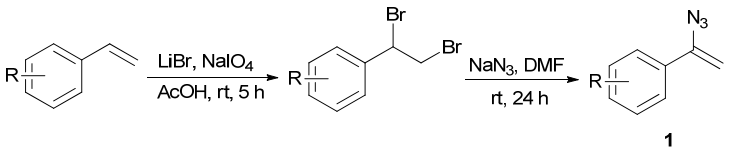
2. Preparation of substrates

2.1 Preparation of α-aryl vinyl azides



The vinyl azides **1a**–**1d**, **1m**, and **1o** were synthesized following the reported procedures from corresponding stryenes.[1] The vinyl azides **1e**–**1l**, **1n**, and **1p**–**1s** were prepared according to the literature method from corresponding terminal alkynes.[2] Among them, vinyl azides (**1l**, **1m**, **1r**, **1s**, and **1w**) were new compounds and their spectra data are shown in this supporting information.

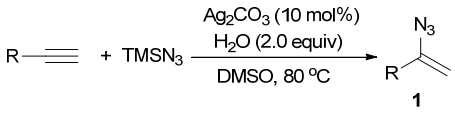
General procedure A[1]



To a stirred mixture of substituted styrene (5.0 mmol, 1.0 equiv) and LiBr (12 mmol, 2.2 equiv) in AcOH (8 mL) was added $NaIO_4$ (2.6 mmol, 0.5 equiv) portion wise during 15 min. The reaction mixture was stirred at room temperature for 5 h, and diluted with water. The resultant mixture was extracted with CH_2Cl_2 (30 mL × 3). The organic layers were washed with saturated aq. $NaHCO_3$, Na_2SO_3, and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give dibromide. To a stirred solution of dibromide in dry DMF (20 mL) was added NaN_3 (15.0 mmol, 3.0 equiv). The mixture was stirred for 24 h at room temperature, then diluted with water and extracted with EtOAc (30 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent under reduced

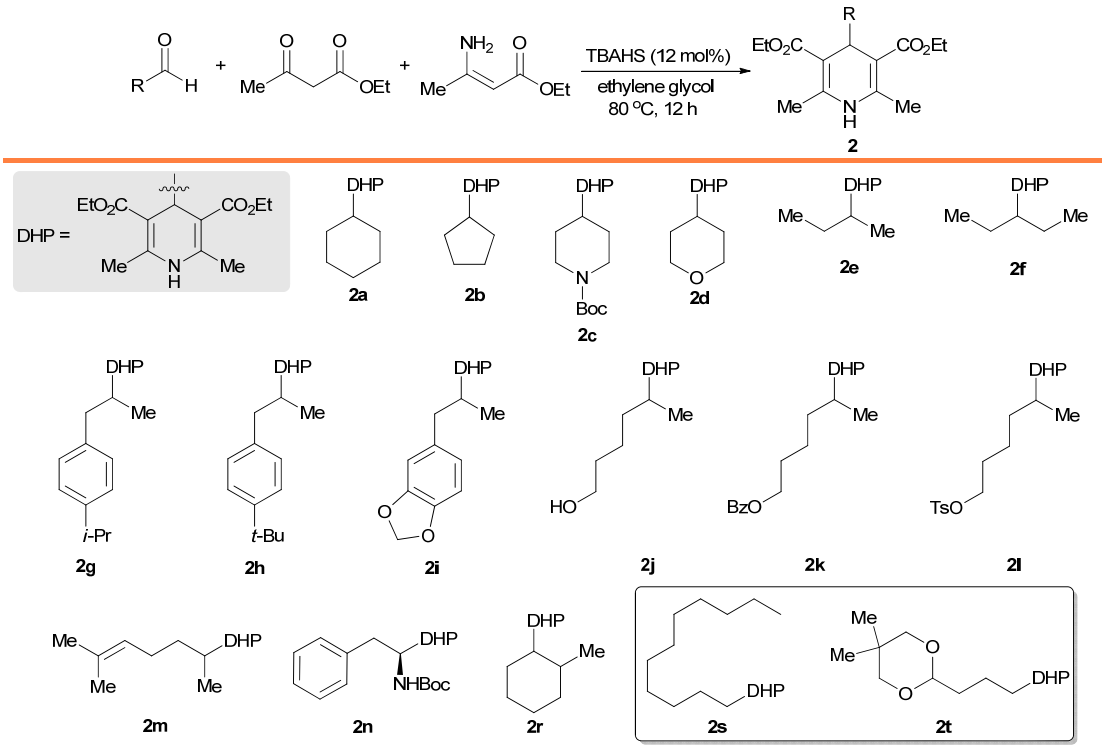
pressure, the crude residue was purified by flash column chromatography on silica gel using the appropriate gradient of petroleum ether and EtOAc to afford the desired vinyl azide **1**.

General procedure B[2]



According to the reported literature, vinyl azides **1** were conveniently synthesized under slightly modified reaction conditions. To a stirred solution of terminal alkyne (3.0 mmol, 1.0 equiv), $TMSN_3$ (6.0 mmol, 2.0 equiv) and H_2O (6.0 mmol, 2.0 equiv) in diemthyl sulfoxide (DMSO) (12 mL) at 80 °C, Ag_2CO_3 (10 mol%) was added. The mixture was then stirred for 2.5–3.0 h (TLC tracking detection). The resulting mixture was cooled to room temperature, diluted with H_2O, and extracted with EtOAc three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product with flash column chromatography on silica gel (petroleum ether/ EtOAc) afforded the desired vinyl azide **1**.

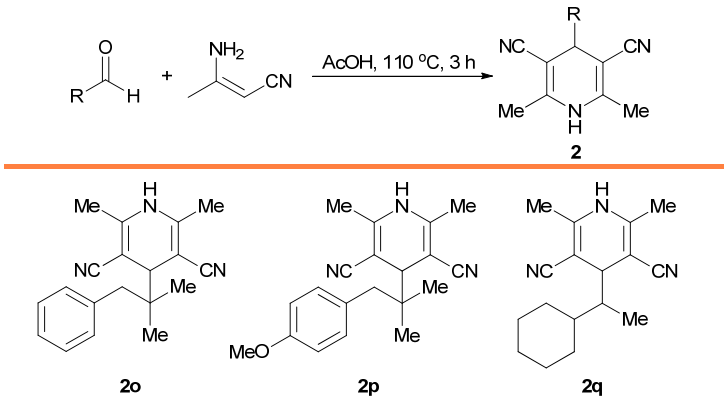
2.2 General procedure for the synthesis of 4-alkyl Hantzsch esters[3]



To a stirred mixture of aldehyde (5.0 mmol, 1.0 equiv), ethyl 3-aminocrotonate (5.0 mmol, 1.0 equiv), and ethyl acetoacetate (5.0 mmol, 1.0 equiv) in ethylene glycol (2.0 mL) was added Bu_4NHSO_4 (12 mol%) in one portion. The reaction mixture was

warmed to 80 °C and stirred for 12 h. After consumption of the aldehyde, the reaction mixture was cooled to room temperature and diluted with brine. The resulting mixture was extracted with EtOAc three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc) to give the desired 4-alkyl Hantzsch ester **2**.

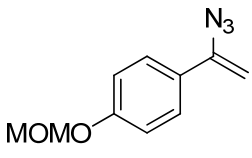
2.3 General procedure for the synthesis of 4- alkyl Meyer nitriles[4]



To an oven-dried two-neck flask (50 mL) equipped with a magnetic stir bar, 3-aminocrotononitrile (5.0 mmol, 2.0 equiv), the aldehyde (2.5 mmol, 1.0 equiv), and AcOH (5 mL) were added. The reaction mixture was heated at 110 ºC with stirring for 3 h, and then cooled to room temperature. The resulting mixture was diluted with water and extracted with EtOAc for three times. The combined organic layers were neutralized with saturated aq. $NaHCO_3$, washed with brine, dried over anhydrous Na_2SO_4, and filtered. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (petroleum ether/ EtOAc) to give the desired 4-alkyl Meyer nitrile **2**.

2.4 The spectra data of new substrates

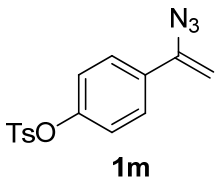
1-(1-Azidovinyl)-4-(methoxymethoxy)benzene (**1l**)



1l

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 5.33 (d, *J* = 2.4 Hz, 1H), 5.19 (s, 2H), 4.88 (d, *J* = 2.4 Hz, 1H), 3.48 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.89, 144.55, 127.99, 126.87, 115.94, 96.50, 94.23, 56.02.

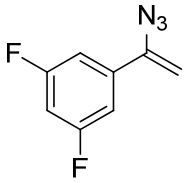
4-(1-Azidovinyl)phenyl 4-methylbenzenesulfonate (**1m**)



1m

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 5.41 (d, *J* = 2.6 Hz, 1H), 4.96 (d, *J* = 2.7 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 150.03, 145.47, 143.88, 133.12, 132.27, 129.78, 128.49, 126.83, 122.34, 98.46, 21.69.

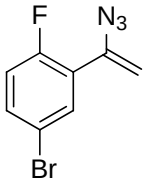
1-(1-Azidovinyl)-3,5-difluorobenzene (**1r**)



1r

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.01 (m, 2H), 6.79 (tt, *J* = 8.7, 2.3 Hz, 1H), 5.49 (d, *J* = 2.9 Hz, 1H), 5.04 (d, *J* = 2.8 Hz, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 162.97 (dd, *J* = 248.2, 12.8 Hz), 143.11 (t, *J* = 3.2 Hz), 137.49 (t, *J* = 1.9 Hz), 108.56 (dd, *J* = 19.2, 7.6 Hz), 104.35 (t, *J* = 25.4 Hz), 99.44.

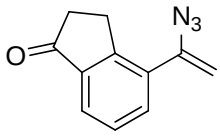
2-(1-Azidovinyl)-4-bromo-1-fluorobenzene (**1s**)



1s

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 6.8, 2.6 Hz, 1H), 7.43 – 7.39 (m, 1H), 6.99 (dd, *J* = 10.7, 8.7 Hz, 1H), 5.52 (d, *J* = 2.3 Hz, 1H), 5.23 – 5.22 (m, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 159.06 (d, *J* = 252.5 Hz), 138.41 (d, *J* = 3.6 Hz), 133.13 (d, *J* = 8.8 Hz), 131.82 (d, *J* = 2.6 Hz), 124.13 (d, *J* = 12.5 Hz), 117.93 (d, *J* = 24.4 Hz), 116.67 (d, *J* = 3.4 Hz), 104.27 (d, *J* = 10.3 Hz).

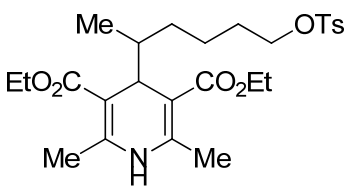
4-(1-Azidovinyl)-2,3-dihydro-1H-inden-1-one (**1w**)



1w

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.68 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 5.23 (d, *J* = 2.2 Hz, 1H), 5.18 (d, *J* = 2.2 Hz, 1H), 3.28 – 3.25 (m, 2H), 2.73 – 2.70 (m, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 206.51, 152.49, 143.66, 137.77, 133.48, 133.46, 127.67, 124.40, 102.17, 36.11, 26.00.

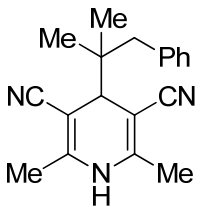
Diethyl 2,6-dimethyl-4-(6-(tosyloxy)hexan-2-yl)-1,4-dihydropyridine-3,5-Dicarboxylate (**2l**)



2l

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.68 (s, 1H), 4.21 – 4.09 (m, 4H), 3.99 – 3.95 (m, 3H), 2.44 (s, 3H), 2.27 (s, 6H), 1.61 – 1.52 (m, 2H), 1.37 – 1.19 (m, 10H), 0.95 – 0.88 (m, 1H), 0.67 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.73, 168.37, 144.73, 144.64, 144.60, 133.15, 129.78, 127.81, 101.93, 101.07, 70.84, 59.57, 40.82, 37.73, 31.88, 29.16, 23.39, 21.60, 19.39, 19.35, 15.04, 14.38, 14.36.

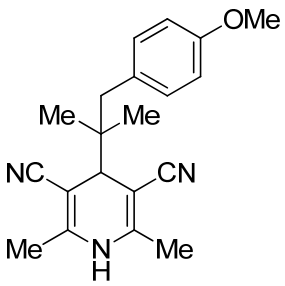
2,6-Dimethyl-4-(2-methyl-1-phenylpropan-2-yl)-1,4-dihydropyridine-3,5-dicarbonitril e (**2o**)



2o

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.19 (m, 3H), 7.12 (d, *J* = 6.9 Hz, 2H), 6.53 (s, 1H), 3.08 (s, 1H), 2.58 (s, 2H), 2.23 (s, 6H), 0.86 (s, 6H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 148.92, 137.67, 130.80, 127.75, 126.09, 120.50, 81.21, 46.90, 44.57, 43.43, 22.80, 18.59.

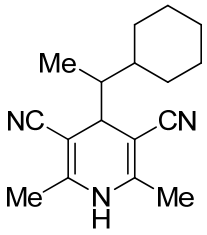
4-(1-(4-Methoxyphenyl)-2-methylpropan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-d icarbonitrile (**2p**)



2p

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.03 (d, *J* = 8.6 Hz, 1H), 6.94 (s, 1H), 6.80 (d, *J* = 8.6 Hz, 1H), 3.79 (s, 2H), 3.04 (s, 1H), 2.52 (s, 1H), 2.21 (s, 3H), 0.83 (s, 3H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 157.94, 148.98, 131.67, 129.63, 120.56, 113.17, 81.08, 55.18, 46.68, 44.58, 42.48, 22.73, 18.52.

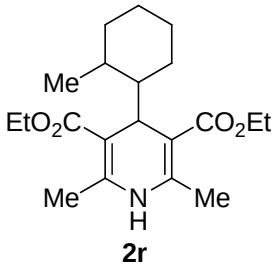
4-(1-Cyclohexylethyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarbonitrile (**2q**)



2q

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.46 (s, 1H), 2.11 (s, 3H), 2.10 (s, 3H), 1.90 – 1.62 (m, 5H), 1.55 – 1.12 (m, 5H), 1.02 – 0.96 (m, 1H), 0.92 – 0.81 (m, 4H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 148.43, 147.32, 119.91, 119.29, 84.44, 80.68, 46.19, 38.39, 37.14, 31.52, 30.29, 26.34, 26.31, 26.22, 18.35, 18.28, 12.04.

Diethyl 2,6-dimethyl-4-(2-methylcyclohexyl)-1,4-dihydropyridine-3,5-dicarboxylate (**2r**)

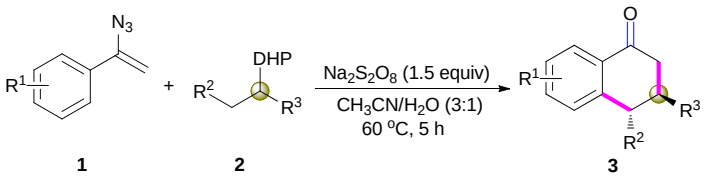


2r

dr = 1:1; **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 5.94 (s, 1H), 5.57 (s, 1H), 4.32 (s, 1H), 4.24 – 4.08 (m, 8H), 3.94 (d, *J* = 9.5 Hz, 1H), 2.33 – 2.22 (m, 12H), 1.75 – 0.84 (m, 38H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.41, 168.96, 168.48, 168.07, 145.42, 144.15, 143.97, 143.16, 104.06, 102.43, 102.29 , 100.82 , 59.71 , 59.65 , 59.56 , 59.51 , 53.77 , 46.99 , 36.42, 34.97, 34.07, 33.86, 32.48, 28.48, 27.24, 26.46, 26.26, 25.55, 22.43, 20.86, 20.52, 19.49, 19.47, 19.28, 19.11, 14.36, 14.32, 14.26, 14.24, 11.79.

3. General procedure for the synthesis of α-tetralones 3 *via* remote

C(sp^3)–H functionalization

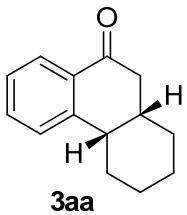


To an oven-dried Schlenk tube (15 mL) equipped with a magnetic stir bar, vinyl azide **1** (0.80 mmol, 1.0 equiv), 4-alkyl Hantzsch ester **2** (0.96 mmol, 1.2 equiv), $Na_2S_2O_8$ (285.7 mg, 1.2 mmol, 1.5 equiv), and CH_3CN/H_2O (8 mL, v/v = 3:1) were added. The reaction vessel was evacuated and backfilled with argon for 3 times. The reaction mixture was stirred at 60 °C for 5 h (TLC tracking detection). After the reaction was finished, the reaction mixture was diluted with brine (5 mL). The resulting mixture was extracted with EtOAc (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel using the appropriate gradient of petroleum ether and EtOAc to afford the desired product **3**.

Note: substrates (**2s**–**2t**) derived from primary aldehydes are incompetent in this reaction.

4. Characterization data of the products

2,3,4,4a,10,10a-Hexahydrophenanthren-9(1H)-one (**3aa**)[5]



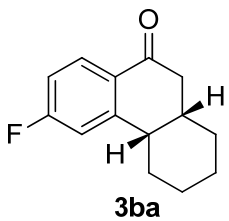
3aa

Following the general procedure, **1a** and **2a** were used. Title compound **3aa** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (114.1 mg, 71%), dr = 11.1:1, signal of major isomer was reported here. R_f = 0.72 (eluent: petroleum ether/EtOAc = 8:1). The characterization data is consistent with the reported data in the literature.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.02 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 – 7.27 (m, 2H), 2.96 – 2.85 (m, 1H), 2.88 (dd, *J* = 16.8, 12.3 Hz, 1H), 2.55 – 2.49 (m, 1H), 2.46 (dd, *J* = 16.8, 4.2 Hz, 1H), 1.79 – 1.44 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.14, 148.62, 133.64, 131.47, 128.36, 127.01, 126.40, 40.45, 39.71, 33.62, 30.00, 29.91, 25.18, 20.75.

6-Fluoro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ba**)



3ba

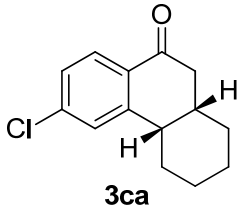
Following the general procedure, **1b** and **2a** were used. Title compound **3ba** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (103.2 mg, 59%), dr = 8.5:1, signal of major isomer was reported here. R_f = 0.61 (eluent: petroleum ether/EtOAc = 8:1). m.p. 54.7-56.1 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.5, 6.1 Hz, 1H), 7.99 – 6.94 (m, 1H), 2.96 – 2.93 (m, 1H), 2.84 (dd, *J* = 16.5, 11.6 Hz, 1H), 2.53 – 2.44 (m, 2H), 1.76 – 1.44 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.44, 166.00 (d, *J* = 255.2 Hz), 130.16 (d, *J* = 9.7 Hz), 128.21 (d, *J* = 2.4 Hz), 114.53 (d, *J* = 21.2 Hz), 114.07 (d, *J* = 22.0 Hz), 40.53, 39.69, 33.76, 29.79, 29.63, 24.85, 20.88.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}FO^+$ 219.1180; Found 219.1187.

6-Chloro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ca**)



3ca

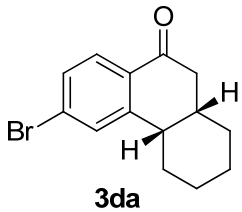
Following the general procedure, **1c** and **2a** were used. Title compound **3ca** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (137.3 mg, 73%), dr = 10.8:1, signal of major isomer was reported here. R_f = 0.64 (eluent: petroleum ether/EtOAc = 8:1). m.p. 64.3-65.5 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.25 (m, 2H), 2.94 – 2.91 (m, 1H), 2.85 (dd, *J* = 16.5, 11.5 Hz, 1H), 2.53 – 2.44 (m, 2H), 1.83 – 1.46 (m, 8H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.77, 150.08, 139.91, 130.06, 128.82, 128.27, 126.98, 40.41, 39.72, 33.70, 29.88, 29.74, 24.99, 20.83.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}ClO^+$ 235.08842; Found 235.08792.

6-Bromo-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3da**)



3da

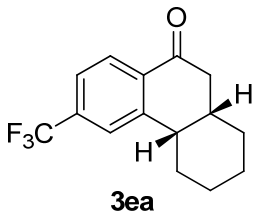
Following the general procedure, **1d** and **2a** were used. Title compound **3da** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (138.0 mg, 62%), dr = 9.3:1, signal of major isomer was reported here. R_f = 0.66 (eluent: petroleum ether/EtOAc = 8:1). m.p. 84.6-86.9 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.43 (dd, *J* = 8.3, 1.9 Hz, 1H), 2.94 – 2.90 (m, 1H), 2.85 (dd, *J* =16.5, 11.5 Hz, 1H), 2.53 – 2.44 (m, 2H), 1.83 – 1.45 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.06, 150.22, 131.29, 130.31, 129.87, 128.82, 128.77, 40.29, 39.61, 33.56, 29.83, 29.71, 24.98, 20.71.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}BrO^+$ 279.0379; Found 279.0377.

6-(Trifluoromethyl)-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ea**)



3ea

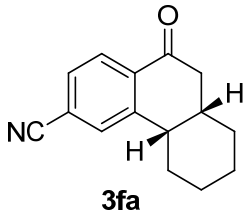
Following the general procedure, **1e** and **2a** were used. Title compound **3ea** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (142.4 mg, 66%), dr = 8.8:1, signal of major isomer was reported here. R_f = 0.66 (eluent: petroleum ether/EtOAc = 8:1). m.p. 103.7-104.9 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.1 Hz, 1H), 7.55 (s, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 3.03 – 3.00 (m, 1H), 2.94 – 2.87 (m, 1H), 2.57 – 2.49 (m, 2H), 1.83 – 1.46 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.0, 149.03, 134.76 (q, *J* = 32.3 Hz), 133.89, 127.79, 125.53 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 274.2 Hz), 123.18 (q, *J* = 3.6 Hz), 40.45, 39.65, 33.40, 29.92, 29.75, 25.03, 20.62.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}F_3O^+$ 269.11478; Found 269.11404.

10-Oxo-4b,5,6,7,8,8a,9,10-octahydrophenanthrene-3-carbonitrile (**3fa**)



3fa

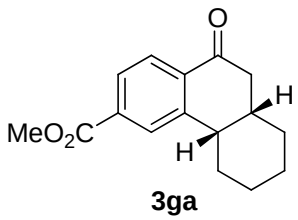
Following the general procedure, **1f** and **2a** were used. Title compound **3fa** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). White solid (129.9 mg, 72%), dr = 8.8:1, signal of major isomer was reported here. R_f = 0.68 (eluent: petroleum ether/EtOAc = 8:1). m.p. 95.5-96.7 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.61 (s, 1H), 7.57 (dd, *J* = 8.1, 1.4 Hz, 1H), 3.02 – 2.98 (m, 1H), 2.89 (dd, *J* = 18.0, 13.1 Hz, 1H), 2.55 – 2.51 (m, 2H), 1.88 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.55, 148.89, 134.22, 132.54, 129.65, 127.72, 118.09, 116.64, 39.99, 39.67, 33.22, 29.80, 29.52, 24.77, 20.61.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}NO^+$ 226.12264; Found 226.12239.

Methyl 10-oxo-4b,5,6,7,8,8a,9,10-octahydrophenanthrene-3-carboxylate (**3ga**)



3ga

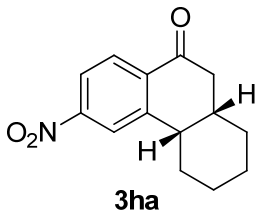
Following the general procedure, **1g** and **2a** were used. Title compound **3ga** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). White solid (132.5 mg, 64%), dr = 10.6:1, signal of major isomer was reported here. R_f = 0.47 (eluent: petroleum ether/EtOAc = 8:1). m.p. 96.8-98.3 ^{o}C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.97 (s, 1H), 7.91 (dd, *J* = 8.1, 1.5 Hz, 1H), 3.93 (s, 3H), 3.03 – 2.99 (m, 1H), 2.93 – 2.86 (m, 1H), 2.55 – 2.48 (m, 2H), 1.84 – 1.45 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.46, 166.30, 148.37, 134.42, 134.16, 129.86, 127.16, 127.13, 52.33, 40.31, 39.76, 33.44, 29.84, 29.73, 24.99, 20.67.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}O_3^+$ 259.13287; Found 259.13214.

6-Nitro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ha**)



3ha

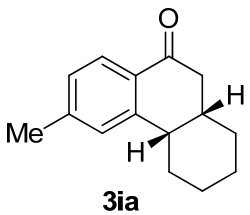
Following the general procedure, **1h** and **2a** were used. Title compound **3ha** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (106.0 mg, 54%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.51 (eluent: petroleum ether/EtOAc = 8:1). m.p. 133.8-134.9 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.16 (s, 1H), 8.10 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.12 – 3.07 (m, 1H), 2.92 (dd, *J* = 18.0, 13.0 Hz, 1H), 2.59 – 2.54 (m, 2H), 1.89 – 1.48 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.40, 150.65, 149.79, 135.60, 128.71, 123.70, 121.21, 40.45, 39.81, 33.42, 29.83, 29.54, 24.80, 20.70.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}NO_3^+$ 246.11247; Found 246.11171.

6-Methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ia**)



3ia

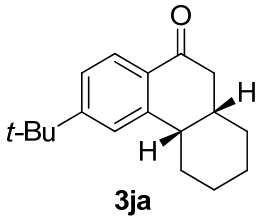
Following the general procedure, **1i** and **2a** were used. Title compound **3ia** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (109.8 mg, 64%), dr = 18.6:1, signal of major isomer was reported here. R_f = 0.63 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.07 (s, 1H), 2.90 – 2.81 (m, 2H), 2.51 – 2.37 (m, 2H), 2.37 (s, 3H), 1.77 – 1.40 (m, 8H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.7, 148.73, 144.36, 129.28, 128.76, 127.46, 127.17, 40.54, 39.66, 33.77, 30.03, 29.98, 25.27, 21.71, 20.78.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O^+$ 215.1430; Found 215.1433.

6-(tert-Butyl)-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ja**)



3ja

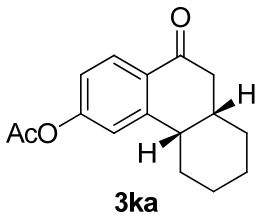
Following the general procedure, **1j** and **2a** were used. Title compound **3ja** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (125.3 mg, 61%), dr = 13.9:1, signal of major isomer was reported here. R_f = 0.66 (eluent: petroleum ether/EtOAc = 8:1). m.p. 54.5-55.6 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.33 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.26 (s, 1H), 2.93 – 2.83 (m, 2H), 2.55 – 2.49 (m, 1H), 2.42 (dd, *J* = 17.0, 4.3 Hz, 1H), 1.80 – 1.44 (m, 8H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.98, 157.34, 148.69, 129.11, 126.90, 125.03, 123.84, 40.96, 39.44, 35.13, 33.67, 31.06, 30.20, 30.11, 25.45, 20.61.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{25}O^+$ 257.1900; Found 257.1894.

10-Oxo-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl acetate (**3ka**)



3ka

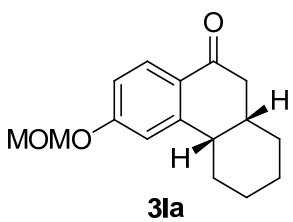
Following the general procedure, **1k** and **2a** were used. Title compound **3ka** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). White solid (135.8 mg, 66%), dr = 20:1, signal of major isomer was reported here. R_f = 0.32 (eluent: petroleum ether/EtOAc = 8:1). m.p. 100.4-101.7 °C.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.6 Hz, 1H), 7.03 – 7.01 (m, 2H), 2.97 – 2.82 (m, 1H), 2.85 (dd, *J* = 16.7, 11.8 Hz, 1H), 2.55 – 2.45 (m, 2H), 2.31 (s, 3H), 1.78 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.82, 168.82, 154.60, 150.28, 129.30, 128.98, 120.94, 119.93, 40.43, 39.73, 33.67, 29.78, 29.65, 24.87, 21.11, 20.85.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{19}O_3^+$ 259.1329; Found 259.1328.

6-Methoxy-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3la**)



3la

Following the general procedure, **1l** and **2a** were used. Title compound **3la** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (30 : 1). Colorless oil (106.3 mg, 58%), dr = 12.5:1, signal of major isomer was reported here. R_f = 0.47 (eluent: petroleum

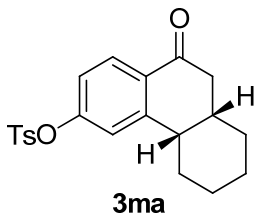
ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.7 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 5.24 – 5.20 (m, 2H), 3.48 (s, 3H), 2.92 – 2.80 (m, 2H), 2.52 – 2.47 (m, 1H), 2.41 (dd, *J* = 16.9, 4.1 Hz, 1H), 1.79 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.89, 161.45, 133.90, 129.44, 126.02, 114.63, 114.41, 94.00, 56.26, 40.88, 39.48, 33.77, 29.96, 29.91, 25.22, 20.78.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}O_3^+$ 261.1485; Found 261.1494.

10-Oxo-4b,5,6,7,8,8a,9,10-octahydrophenanthren-3-yl-4-methylbenzenesulfonate (**3ma**)



3ma

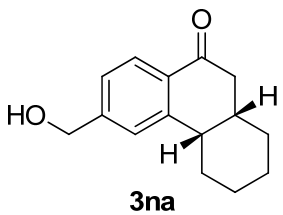
Following the general procedure, **1m** and **2a** were used. Title compound **3ma** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1). White solid (213.0 mg, 72%), dr > 20:1. R_f = 0.26 (eluent: petroleum ether/EtOAc = 8:1). m.p. 135.4-137.2 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 2.1 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.3 Hz, 1H), 2.92 – 2.88 (m, 1H), 2.81 (dd, *J* = 18.4, 13.6 Hz, 1H), 2.52 – 2.43 (m, 5H), 1.67 – 1.43 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.69, 153.22, 150.45, 145.64, 132.10, 130.23, 129.82, 129.14, 128.42, 121.95, 120.34, 40.24, 39.83, 33.64, 29.74, 29.55, 24.74, 21.68, 20.92.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_4S^+$ 371.13116; Found 371.13058.

6-(Hydroxymethyl)-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3na**)



3na

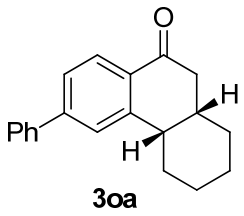
Following the general procedure, **1n** and **2a** were used. Title compound **3na** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (7:1). Colorless oil (125.3 mg, 68%), dr = 8.3:1, signal of major isomer was reported here. R_f = 0.23 (eluent: petroleum ether/EtOAc = 4:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.26 (m, 2H), 4.74 (s, 2H), 2.96 – 2.91 (m, 1H), 2.86 (dd, *J* = 16.5, 12.1 Hz, 1H), 2.53 – 2.42 (m, 2H), 2.06 (s, 1H), 1.81 – 1.47 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.17, 146.98, 146.94, 130.59, 127.35, 126.20, 124.59, 64.57, 40.54, 39.59, 33.56, 29.94, 29.87, 25.19, 20.64.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O_2^+$ 231.1380; Found 231.1375.

6-Phenyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3oa**)



3oa

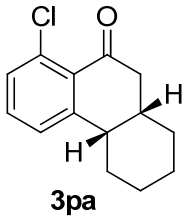
Following the general procedure, **1o** and **2a** were used. Title compound **3oa** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (143.4 mg, 65%), dr > 20:1. R_f = 0.58 (eluent: petroleum ether/EtOAc = 8:1). m.p.114.7-115.5 ^oC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.62 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.53 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.40 (t, *J* = 7.3 Hz, 1H), 3.04 – 3.00 (m, 1H), 2.91 (dd, *J* = 16.9, 12.5 Hz, 1H), 2.60 – 2.54 (m, 1H), 2.49 (dd, *J* = 17.0, 4.3 Hz, 1H), 1.86 – 1.44 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.84, 146.26, 140.10, 130.35, 128.85, 128.13, 127.71, 127.24, 126.95, 125.34, 40.74, 39.69, 33.69, 30.10, 29.96, 25.27, 20.76.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}O^+$ 277.15869; Found 277.15826.

8-Chloro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3pa**)



3pa

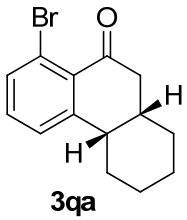
Following the general procedure, **1p** and **2a** were used. Title compound **3pa** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (97.7 mg, 52%), dr = 5:1, signal of major isomer was reported here. R_f = 0.61 (eluent: petroleum ether/EtOAc = 8:1). m.p. 61.6-62.8 ^oC.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.28 (m, 2H), 7.17 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.94 – 2.88 (m, 2H), 2.54 – 2.46 (m, 2H), 1.84 – 1.40 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.43, 151.54, 133.98, 132.87, 130.13, 127.36, 123.82, 41.81, 40.54, 32.63, 30.29, 29.73, 25.44, 20.08.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}ClO^+$ 235.0884; Found 235.0887.

8-Bromo-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3qa**)



3qa

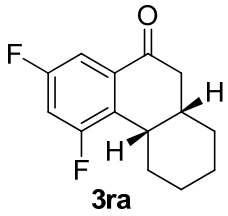
Following the general procedure, **1q** and **2a** were used. Title compound **3qa** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (129.7 mg, 58%), dr = 2.9:1, signal of major isomer was reported here. R_f = 0.66 (eluent: petroleum ether/EtOAc = 8:1). m.p. 51.8-52.9 ^oC.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (dd, *J* = 7.0, 2.0 Hz, 1H), 7.30 – 7.22 (m, 2H), 2.97 – 2.89 (m, 2H), 2.56 – 2.36 (m, 2H), 1.86 – 1.22 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.54, 151.70, 133.76, 133.05, 128.08, 124.50, 121.64, 41.95, 40.15, 32.50, 30.32, 29.73, 25.44, 20.03.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}BrO$ 279.03790; Found 279.03735.

5,7-Difluoro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ra**)



3ra

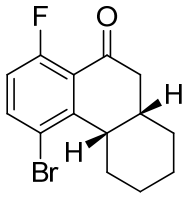
Following the general procedure, **1r** and **2a** were used. Title compound **3ra** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (153.0 mg, 81%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.69 (eluent: petroleum ether/EtOAc = 8:1). m.p. 103.6-104.6 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.52 (m, 1H), 7.01 – 6.96 (m, 1H), 3.15 – 3.11 (m, 1H), 2.99 – 2.91 (m, 1H), 2.51 – 2.40 (m, 2H), 1.90 – 1.42 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.00 (dd, *J* = 2.9, 2.0 Hz,), 161.00 (dd, *J* = 249.7, 12.1 Hz), 160.41 (dd, *J* = 250.7, 10.7 Hz), 133.95 (dd, *J* = 7.3, 4.9 Hz), 132.24 (dd, *J* = 16.7, 3.6 Hz), 109.07 (dd, *J* = 21.9, 3.7 Hz), 108.64 (t, *J* = 26.0 Hz), 38.34, 33.87, 32.60, 30.54, 27.54, 25.74, 19.71.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}F_2O^+$ 237.10855; Found 237.10800.

5-Bromo-8-fluoro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3sa**)



3sa

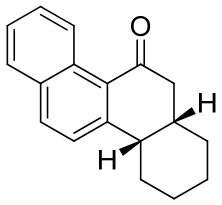
Following the general procedure, **1s** and **2a** were used. Title compound **3sa** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (189.2 mg, 80%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.61 (eluent: petroleum ether/EtOAc = 8:1). m.p. 106.9-107.9 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 8.8, 4.8 Hz, 1H), 6.90 (dd, *J* = 10.6, 8.9 Hz, 1H), 3.21 – 3.14 (m, 1H), 2.97 (dd, *J* = 17.1, 14.0 Hz, 1H), 2.53 – 2.41 (m, 2H), 2.01 – 1.98 (m, 1H), 1.86 – 1.83 (m, 1H), 1.67 – 1.25 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.54 (d, *J* = 1.2 Hz), 161.51 (d, *J* = 266.8 Hz), 149.41, 138.52 (d, *J* = 10.1 Hz), 122.04 (d, *J* = 4.8 Hz), 118.21 (d, *J* = 3.9 Hz), 116.54 (d, *J* = 23.6 Hz), 41.70 (d, *J* = 1.9 Hz), 39.00, 32.12, 30.03, 26.22, 25.72, 19.44.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{15}BrFO^+$ 297.0285; Found 297.0291.

6a,7,8,9,10,10a-Hexahydrochrysen-5(6H)-one (**3ta**)



3ta

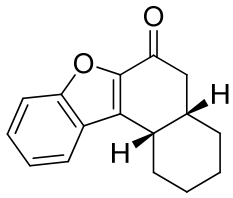
Following the general procedure, **1t** and **2a** were used. Title compound **3ta** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (118.4 mg, 57%), dr > 20:1. R_f = 0.71 (eluent: petroleum ether/EtOAc = 8:1). m.p. 71.9-73.8 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.43 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 3.10 – 2.98 (m, 2H), 2.68 – 2.61 (m, 1H), 2.56 (dd, *J* = 16.5, 4.7 Hz, 1H), 1.91 – 1.79 (m, 2H), 1.74 – 1.68 (m, 2H), 1.66 – 1.59 (m, 2H), 1.56 – 1.46 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 201.27, 151.22, 134.45, 132.73, 131.26, 128.72, 128.16, 126.81, 126.71, 126.18, 125.80, 42.66, 41.09, 33.10, 30.03, 30.00, 25.84, 20.25.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O^+$ 251.1430; Found 251.1432.

1,3,4,4a,5,11c-Hexahydronaphtho[2,1-b]benzofuran-6(2H)-one (**3ua**)



3ua

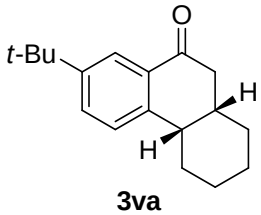
Following the general procedure, **1u** and **2a** were used. Title compound **3ua** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (50:1). Light yellow solid (102.0 mg, 53%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.53 (eluent: petroleum ether/EtOAc = 8:1). m.p. 94.3-95.1 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 7.9 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.33 – 7.29 (m, 1H), 3.24 – 3.19 (m, 1H), 2.91 (dd, *J* = 16.8, 12.1 Hz, 1H), 2.67 – 2.60 (m, 1H), 2.48 (dd, *J* = 16.9, 4.2 Hz, 1H), 2.05 – 2.00 (m, 1H), 1.75 – 1.47 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.80, 156.09, 147.01, 138.61, 128.89, 125.81, 123.53, 121.87, 112.95, 40.36, 35.82, 34.46, 29.87, 28.33, 24.84, 21.28.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}O_2^+$ 241.1223; Found 241.1218.

7-(tert-Butyl)-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3va**)



3va

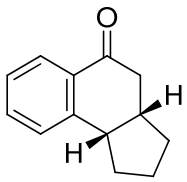
Following the general procedure, **1v** and **2a** were used. Title compound **3va** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (127.0 mg, 62%), dr = 16.7:1, signal of major isomer was reported here. R_f = 0.72 (eluent: petroleum ether/EtOAc = 8:1). m.p. 95.3-96.9 ^{o}C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 2.95 – 2.83 (m, 2H), 2.54 – 2.43 (m, 2H), 1.79 – 1.45 (m, 8H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.45, 149.41, 145.76, 131.12, 131.09, 128.14, 123.47, 40.05, 39.99, 34.60, 33.84, 31.23, 30.00, 29.97, 25.15, 20.95.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{25}O^+$ 257.1900; Found 257.1887.

2,3,3a,4-Tetrahydro-1H-cyclopenta[a]naphthalen-5(9bH)-one (**3ab**)[5]



3ab

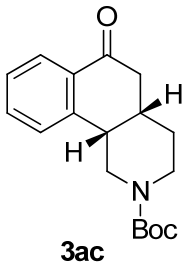
Following the general procedure, **1a** and **2b** were used. Title compound **3ab** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (96.2 mg, 65%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.69 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.48 (td, *J* = 7.7, 1.4 Hz, 1H), 7.29 – 7.25 (m, 2H), 3.28 – 3.23 (m, 1H), 2.77 – 2.71 (m, 1H), 2.64 – 2.53 (m, 2H), 2.23 – 2.17 (m, 1H), 2.00 – 1.93 (m, 1H), 1.88 – 1.74 (m, 3H), 1.54 – 1.48 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.85, 146.21, 133.60, 131.50, 129.10, 126.52, 126.24, 42.74, 40.73, 38.49, 33.08, 31.30, 23.64.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}O^+$ 187.1117; Found 187.1119.

tert-Butyl- 6-oxo-1,4,4a,5,6,10b-hexahydrobenzo[h]isoquinoline-2(3H)-carboxylate (**3ac**)



3ac

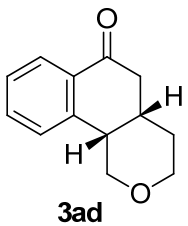
Following the general procedure, **1a** and **2c** were used. Title compound **3ac** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (25:1). Colorless oil (136.0 mg, 56%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.55 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 3.79 – 3.62 (m, 3H), 3.35 – 3.29 (m, 1H), 3.17 – 3.13 (m, 1H), 2.89 (dd, *J* = 18.0, 11.6 Hz, 1H), 2.66 – 2.58 (m, 2H), 1.83 – 1.75 (m, 1H), 1.59 – 1.53 (m, 1H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.38, 154.62, 143.34, 133.84, 132.08, 128.65, 127.16, 79.74, 41.07, 39.99, 39.60, 39.03, 32.69, 28.36, 28.29.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{23}NNaO_3^+$ 324.1570; Found 324.1553.

3,4,4a,5-Tetrahydro-1H-benzo[h]isochromen-6(10bH)-one (**3ad**)



3ad

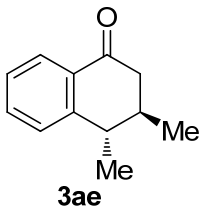
Following the general procedure, **1a** and **2d** were used. Title compound **3ad** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1). Colorless oil (95.3 mg, 59%), dr > 20:1. R_f = 0.55 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.8 Hz, 1H), 7.54 (td, *J* = 7.6, 1.3 Hz, 1H), 7.37 – 7.32 (m, 2H), 3.88 – 3.71 (m, 4H), 3.27 – 3.23 (m, 1H), 3.01 (dd, *J* = 16.9, 12.1 Hz, 1H), 2.75 – 2.67 (m, 1H), 2.59 (dd, *J* = 17.0, 4.6 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.58 – 1.52 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.75, 142.93, 133.92, 132.19, 128.76, 127.30, 127.25, 68.46, 63.48, 39.38, 38.96, 30.99, 29.42.

HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{15}O_2^+$ 203.1067; Found 203.1057.

3,4-Dimethyl-3,4-dihydronaphthalen-1(2H)-one (**3ae**)[5]



3ae

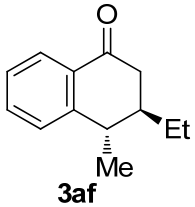
Following the general procedure, **1a** and **2e** were used. Title compound **3ae** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (109.0 mg, 78%), dr = 5.5:1, signal of major isomer was reported here. R_f = 0.61 (eluent: petroleum ether/EtOAc = 8:1). The characterization data is consistent with the reported data in the literature.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.51 (td, *J* = 7.8, 1.4 Hz, 1H), 7.34 – 7.27 (m, 2H), 2.86 (dd, *J* = 17.0, 4.5 Hz, 1H), 2.81 – 2.76 (m, 1H), 2.40 (dd, *J* = 17.0, 6.9 Hz, 1H), 2.19 – 2.11 (m, 1H), 1.40 (d, *J* = 7.1 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.12, 147.62, 133.78, 131.45, 128.28, 126.72, 126.35, 43.34, 39.89, 35.37, 20.52, 20.24.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}O^+$ 175.1117; Found 175.1122.

3-Ethyl-4-methyl-3,4-dihydronaphthalen-1(2H)-one (**3af**)



3af

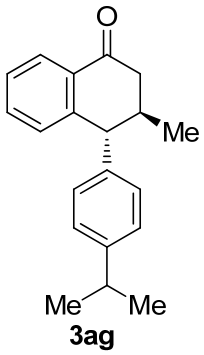
Following the general procedure, **1a** and **2f** were used. Title compound **3af** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (116.3 mg, 77%), dr = 10.3:1, signal of major isomer was reported here. R_f = 0.68 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.30 – 7.26 (m, 2H), 2.99 – 2.89 (m, 2H), 2.51 (dd, *J* = 17.1, 5.0 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.49 – 1.34 (m, 5H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.23, 147.76, 133.82, 131.43, 128.82, 126.70, 126.40, 41.83, 39.70, 37.63, 26.53, 21.78, 11.52.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{17}O^+$ 189.12739; Found 189.12703.

4-(4-Isopropylphenyl)-3-methyl-3,4-dihydronaphthalen-1(2H)-one (**3ag**)



3ag

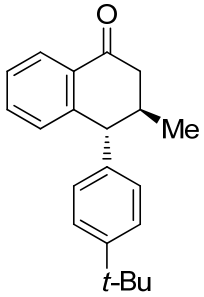
Following the general procedure, **1a** and **2g** were used. Title compound **3ag** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (153.8 mg, 69%), dr > 20:1. R_f = 0.65 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.84 (d, *J* = 8.2 Hz, 1H), 2.95 – 2.88 (m, 1H), 2.82 (d, *J* = 12.8 Hz, 1H), 2.52 – 2.45 (m, 2H), 1.26 (d, *J* = 6.9 Hz, 6H), 0.98 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.24, 147.33, 146.56, 140.36, 133.58, 132.43, 130.00, 128.96, 126.65, 126.60, 126.51, 53.03, 45.70, 37.39, 33.66, 24.01, 23.96, 20.35.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{23}O^+$ 279.17434; Found 279.17380.

4-(4-(tert-Butyl)phenyl)-3-methyl-3,4-dihydronaphthalen-1(2H)-one (**3ah**)



3ah

Following the general procedure, **1a** and **2h** were used. Title compound **3ah** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (183.5 mg, 78%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.66 (eluent: petroleum ether/EtOAc = 8:1). m.p. 76.3-77.6 ^{o}C.

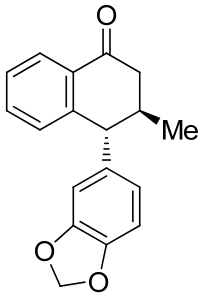
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 1H), 3.85 (d, *J* = 8.3 Hz, 1H), 2.82 (d, *J* = 12.9 Hz, 1H), 2.49 – 2.42 (m, 2H), 1.33 (s, 9H), 0.99 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.25, 149.58, 146.48, 139.95, 133.59, 132.41, 130.01, 128.66, 126.64, 126.50, 125.43, 52.87, 45.62, 37.34, 34.43, 31.36, 20.36.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O^+$ 293.1900; Found 293.1906.

4-(Benzo[d][1,3]dioxol-5-yl)-3-methyl-3,4-dihydronaphthalen-1(2H)-one (**3ai**)

Following the general procedure, **1a** and **2i** were used. Title compound **3ai** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (50:1). Colorless oil (168.0 mg, 75%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.53 (eluent: petroleum ether/EtOAc = 8:1).



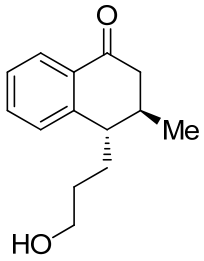
3ai

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 6.55 (s, 1H), 5.96 (s, 2H), 3.77 (d, *J* = 8.7 Hz, 1H), 2.82 (d, *J* = 13.0 Hz, 1H), 2.49 – 2.40 (m, 2H), 0.98 (d, *J* = 5.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.97, 147.99, 146.50, 146.40, 136.86, 133.59, 132.33, 129.77, 126.74, 126.57, 122.65, 108.88, 108.13, 101.00, 53.22, 45.98, 37.43, 20.21.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{17}O_3^+$ 281.1172; Found 281.1166.

4-(3-Hydroxypropyl)-3-methyl-3,4-dihydronaphthalen-1(2H)-one (**3aj**)



3aj

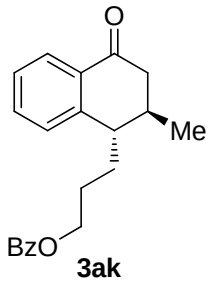
Following the general procedure, **1a** and **2j** were used. Title compound **3aj** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1). Colorless oil (114.6 mg, 66%), dr = 17.5:1, signal of major isomer was reported here. R_f = 0.47 (eluent: petroleum ether/EtOAc = 2:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.47 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 (td, *J* = 7.6, 0.8 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 3.65 (t, *J* = 6.2 Hz, 2H), 2.89 (dd, *J* = 18.3, 5.8 Hz, 1H), 2.71 – 2.67 (m, 1H), 2.42 – 2.37 (m, 2H), 1.89 – 1.57 (m, 4H), 1.02 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.92, 146.14, 133.60, 131.40, 129.58, 126.92, 126.63, 62.65, 45.19, 41.48, 32.04, 32.01, 30.45, 20.24.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}O_2^+$ 219.1380; Found 291.1378.

3-(2-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)propyl benzoate (**3ak**)



3ak

Following the general procedure, **1a** and **2k** were used. Title compound **3ak** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (40:1). Colorless oil (182.5 mg, 71%), dr = 10.7:1, signal of major isomer was reported here. R_f = 0.34 (eluent: petroleum ether/EtOAc = 8:1).

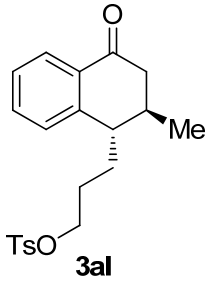
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.8 Hz, 3H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 4.35 (t, *J* = 4.8 Hz, 2H), 2.92 (dd, *J* = 18.3, 5.6

Hz, 1H), 2.78 – 2.74 (m, 1H), 2.44 (d, *J* = 14.8 Hz, 2H), 2.00 – 1.77 (m, 4H), 1.05 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.70, 166.54, 145.74, 133.71, 132.95, 131.43, 130.13, 129.48, 129.46, 128.35, 127.04, 126.78, 64.72, 44.96, 41.52, 32.01, 31.98, 26.56, 20.24.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_3^+$ 323.1642; Found 323.1649.

3-(2-Methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)propyl 4-methylbenzenesulfonae (**3al**)



3al

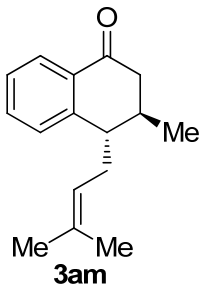
Following the general procedure, **1a** and **2l** were used. Title compound **3al** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1). Colorless oil (219.2 mg, 74%), dr = 10.0:1, signal of major isomer was reported here. R_f = 0.51 (eluent: petroleum ether/EtOAc = 4:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.16 (d, *J* = 8.1 Hz, 1H), 4.04 (t, *J* = 5.3 Hz, 2H), 2.81 (dd, *J* = 17.6, 5.0 Hz, 1H), 2.65 – 2.61 (m, 1H), 2.43 (s, 3H), 2.38 (dd, *J* = 17.6, 3.7 Hz, 1H), 2.33 – 2.27 (m, 1H), 1.82 – 1.62 (m, 4H), 1.00 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.35, 145.31, 144.80, 133.65, 133.07, 131.44, 129.82, 129.44, 127.81, 127.07, 126.86, 70.25, 44.77, 41.38, 32.02, 31.53, 26.78, 21.58, 20.18.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_4S^+$ 373.1468; Found 373.1473.

3-Methyl-4-(3-methylbut-2-en-1-yl)-3,4-dihydronaphthalen-1(2H)-one (**3am**)



3am

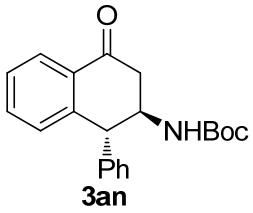
Following the general procedure, **1a** and **2m** were used. Title compound **3am** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (86.2 mg, 47%), dr > 20:1. R_f = 0.68 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 5.17 (t, *J* = 7.2 Hz, 1H), 2.91 (dd, *J* = 18.1, 5.7 Hz, 1H), 2.73 – 2.69 (m, 1H), 2.49 – 2.33 (m, 4H), 1.71 (s, 3H), 1.52 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.11, 146.14, 133.71, 133.60, 131.41, 129.65, 126.70, 126.49, 121.87, 45.69, 41.47, 34.59, 31.32, 25.80, 20.32, 17.77.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}O^+$ 229.1587; Found 229.1595.

tert-Butyl(4-oxo-1-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)carbamate (**3an**)[6]



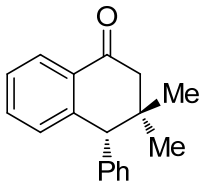
3an

Following the general procedure, **1a** and **2n** were used. Title compound **3an** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). White solid (148.3 mg, 55%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.46 (eluent: petroleum ether/EtOAc = 4:1). m.p 197.1-199.1 ^{o}C. The characterization data is consistent with the reported data in the literature.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.24 (m, 3H), 7.13 – 7.08 (m, 3H),, 4.74 (s, 1H), 4.48 – 4.41 (m, 2H), 2.91 (dd, *J* = 17.3, 3.9 Hz, 1H), 2.68 (dd, *J* = 17.2, 5.8 Hz, 1H), 1.38 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.96, 154.89, 142.63, 140.79, 134.50, 132.38, 130.78, 128.84, 128.68, 127.64, 127.17, 126.90, 79.84, 53.40, 50.63, 41.09, 28.26.

3-Methyl-4-phenyl-3,4-dihydronaphthalen-1(2H)-one (**3ao**)[7]



3ao

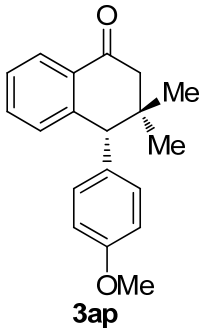
Following the general procedure, **1a** and **2o** were used. Title compound **3ao** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). White solid (152.5 mg, 76%). R_f = 0.68 (eluent: petroleum ether/EtOAc = 8:1). m.p. 96.1-97.8 ^{o}C. The characterization data is consistent with the reported data in the literature.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H), 7.36 – 7.24 (m, 4H), 7.08 – 7.03 (m, 3H), 4.04 (s, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 2.42 (d, *J* = 16.8 Hz, 1H), 1.11 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.53, 145.34, 140.61, 133.93, 132.09, 130.42, 130.15, 128.02, 126.81, 126.73, 126.40, 57.00, 49.53, 36.78, 29.36, 26.38.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O^+$ 251.1430; Found 251.1424.

4-(4-Methoxyphenyl)-3,3-dimethyl-3,4-dihydronaphthalen-1(2H)-one (**3ap**)



3ap

Following the general procedure, **1a** and **2p** were used. Title compound **3ap** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (164.0 mg, 73%). R_f = 0.50 (eluent: petroleum ether/EtOAc = 8:1).

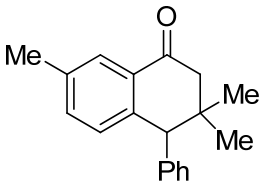
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.7 Hz,

1H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.99 (s, 1H), 3.78 (s, 3H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.41 (d, *J* = 16.8 Hz, 1H), 1.08 (s, 3H), 0.87 (s, 3H).

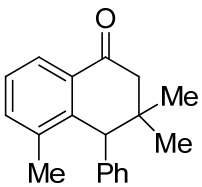
^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.62, 158.30, 145.68, 133.91, 132.66, 132.03, 131.08, 130.37, 126.71, 126.36, 113.36, 56.18, 55.17, 49.60, 36.85, 29.27, 26.25.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O_2^+$ 281.1536; Found 381.1529.

3,3,7-Trimethyl-4-phenyl-3,4-dihydronaphthalen-1(2H)-one (**3xo**) *and 3,3,5-trimethyl-4-phenyl-3,4-dihydronaphthalen-1(2H)-one* (**3xo'**)



3xo



3xo'

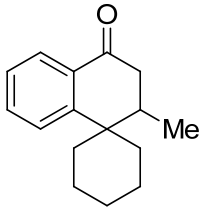
Following the general procedure, **1x** and **2o** were used. An inseparable mixture of regioisomers **3xo** and **3xo'** in a ratio of 1:1 was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (165.0 mg, 78%). R_f = 0.69 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.2 Hz, 1H), 7.91 (s, 1H), 7.33 – 7.19 (m, 9H), 7.04 – 6.95 (m, 5H), 4.00 (s, 1H), 3.97 (s, 1H), 2.70 (dd, *J* = 17.1, 13.3 Hz, 2H), 2.40 (d, *J* = 17.8 Hz, 4H), 2.25 (dd, *J* = 17.4, 1.2 Hz, 1H), 2.09 (s, 3H), 1.13 (s, 3H), 1.09 (s, 3H), 0.88 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.21, 198.88, 142.54, 140.83, 139.20, 137.36, 136.54, 136.19, 134.95, 132.10, 130.35, 130.14, 130.03, 128.01, 127.98, 126.66, 126.66, 126.55, 126.52, 124.55, 56.66, 53.82, 49.64, 46.67, 36.83, 35.71, 29.36, 29.09, 29.07, 26.34, 20.94, 19.45.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O^+$ 265.1587; Found 265.1594.

2'-Methyl-2'H-spiro[cyclohexane-1,1'-naphthalen]-4'(3'H)-one (**3aq**)



3aq

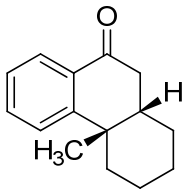
Following the general procedure, **1a** and **2q** were used. Title compound **3aq** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (88.6 mg, 49%). R_f = 0.69 (eluent: petroleum ether/EtOAc = 8:1).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.54 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.00 (dd, *J* = 17.8, 5.3 Hz, 1H), 2.82 – 2.75 (m, 1H), 2.42 (dd, *J* = 17.8, 2.2 Hz, 1H), 2.07 – 1.97 (m, 2H), 1.88 – 1.70 (m, 3H), 1.66 – 1.59 (m, 3H), 1.42 – 1.34 (m, 2H), 0.88 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.50, 150.77, 134.08, 131.42, 126.92, 126.03, 125.65, 41.85, 40.15, 39.10, 32.29, 29.74, 25.80, 22.35, 20.77, 15.33.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{21}O^+$ 229.1587; Found 229.1599.

4a-Methyl-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (**3ar**)[8]



3ar

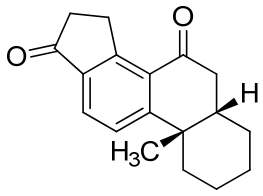
Following the general procedure, **1a** and **2r** were used. Title compound **3ar** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (60:1). Colorless oil (125.6 mg, 73%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.71 (eluent: petroleum ether/EtOAc = 8:1). The characterization data is consistent with the reported data in the literature.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.36 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.31 – 7.27 (m, 1H), 3.06 (dd, *J* = 17.5, 5.1 Hz, 1H), 2.45 (dd, *J* = 17.5, 3.4 Hz, 1H), 2.41 – 2.35 (m, 1H), 2.04 – 1.98 (m, 1H), 1.64 – 1.16 (m, 7H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.29, 149.15, 134.13, 131.72, 127.40, 126.08, 126.05, 42.82, 41.71, 38.25, 37.58, 31.66, 29.30, 25.85, 22.24.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}O^+$ 215.1430; Found 215.1440.

10-Methyl-3,4,5,6,15,16-hexahydro-1H-cyclopenta[a]phenanthrene-7,17(2H,10H)-dione (**3wr**)



3wr

Following the general procedure, **1w** and **2r** were used. Title compound **3wr** was isolated by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1). White solid (147.5 mg, 69%), a single diastereoisomer was detected by ^{1}H and ^{13}C NMR. R_f = 0.29 (eluent: petroleum ether/EtOAc = 8:1). m.p. 122.3-123.4 ^{o}C.

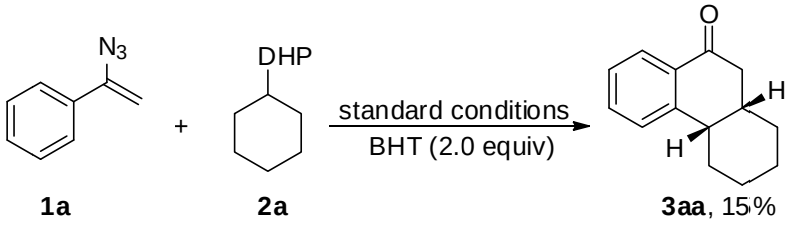
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 3.55 – 3.52 (m, 2H), 3.09 (dd, *J* = 17.4, 5.1 Hz, 1H), 2.70 – 2.67 (m, 2H), 2.51 – 2.39 (m, 2H), 2.08 – 1.02 (m, 1H), 1.67 – 1.49 (m, 4H), 1.44 – 1.32 (m, 1H), 1.38 (s, 3H), 1.29 – 1.09 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.54, 198.84, 157.74, 136.39, 128.34, 126.06, 42.55, 42.46, 39.43, 38.06, 36.41, 31.55, 29.29, 28.33, 25.66, 22.31.

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}O_2^+$ 269.1536; Found 269.1546.

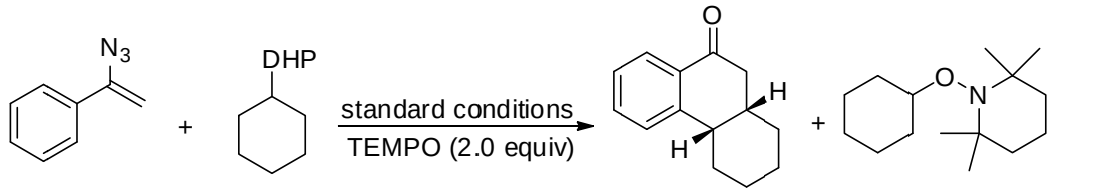
5. Control Experiments

5.1 Radical inhibition experiments



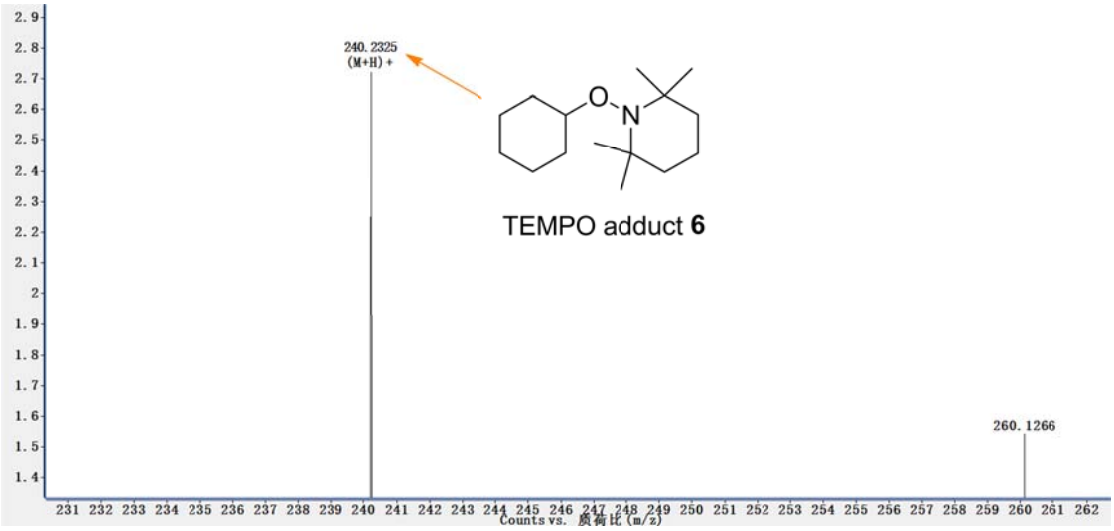
1a **2a** **3aa**, 15%

Followed the general procedure, to a mixture of vinyl azide **1a** (72.6 mg, 0.5 mmol, 1.0 equiv), 4-cyclohexyl Hantzsch ester **2a** (201.3 mg, 0.6 mmol, 1.2 equiv), and $Na_2S_2O_8$ (178.6 mg, 0.75 mmol, 1.5 equiv) in CH_3CN/H_2O (5 mL, v/v = 3/1) was added BHT (220.3 mg, 1.0 mmol, 2.0 equiv). The reaction mixture was then stirred at 60 °C for 5 h. Product **3a** was obtained as a colorless oil (14.8 mg, 15%).

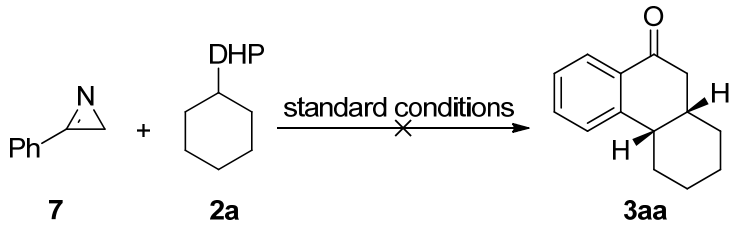


1a **2a** **3aa**, 0% **6**, detected by HRMS
caclld: 240.2322
found: 240.2325

Followed the general procedure, to a mixture of vinyl azide **1a** (72.6 mg, 0.5 mmol, 1.0 equiv), 4-cyclohexyl Hantzsch ester **2a** (201.3 mg, 0.6 mmol, 1.2 equiv), and $Na_2S_2O_8$ (178.6 mg, 0.75 mmol, 1.5 equiv) in CH_3CN/H_2O (5 mL, v/v = 3/1) was added TEMPO (156.3 mg, 1.0 mmol, 2.0 equiv). The reaction mixture was then stirred at 60 °C for 5 h. The cyclohexyl-captured TEMPO **6** was detected by HRMS analysis, whereas the desired product **3a** was not observed.

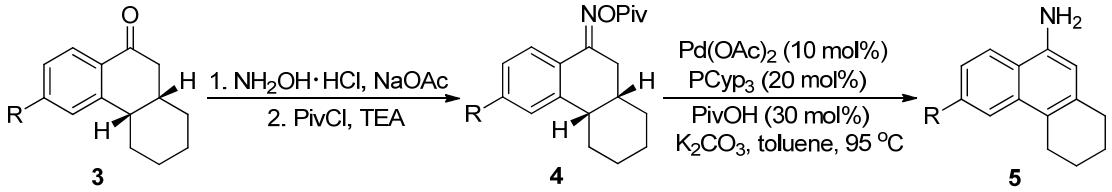


5.2 Reaction of 2*H*-azirine 7 with 2a under standard conditions



Followed the general procedure, 2*H*-azirine **7** was used as starting material instead of vinyl azide **1a**. A mixture of **7** (58.6 mg, 0.5 mmol, 1.0 equiv), 4-cyclohexyl Hantzsch ester **2a** (201.3 mg, 0.6 mmol, 1.2 equiv), and $Na_2S_2O_8$ (178.6 mg, 0.75 mmol, 1.5 equiv) in CH_3CN/H_2O (5 mL, v/v = 3/1) was stirred at 60 ^oC for 5 h. The desired product **3a** was not observed by TLC and HRMS analyses.

6. Chemical transformations of the fused ketones 3aa, 3ga, and 3la



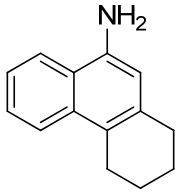
To a solution of ketone **3** (1.0 mmol, 1.0 equiv) in MeOH (3.0 mL) was added hydroxylamine hydrochloride (1.2 mmol, 1.2 equiv) and sodium acetate (2.4 mmol, 2.4 equiv). The reaction mixture was heated at reflux for 4 h. After removal of solvent under reduced pressure, saturated $NaHCO_3$ was added and the mixture was extracted with EtOAc (10 mL × 3). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was used for next step without further purification.

To a stirred solution of above oxime (1.0 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) at 0 ^oC was added triethylamine (0.42 mL, 3.0 mmol, 3.0 equiv). Then, pivaloyl chloride (0.225 mL, 2.0 mmol, 2.0 equiv) was added dropwise. At the end of addition, the reaction mixture was warmed to room temperature and stirred for further 6 h. The resultant mixture was diluted with CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel using ethyl acetate/petroleum ether = 1/8 as eluent to afford the product **4**.

An oven-dried Schlenk tube (15 mL) with a magnetic stir bar was charged with 1-tetralone pivaloyl oxime **4** (0.5 mmol, 1.0 equiv) and toluene (5 mL). Then to the tube, $Pd(OAc)_2$ (11.2 mg, 10 mol%), tricyclopentylphosphine (24.2 μL, 20 mol%),

PivOH (15.3 mg, 30 mol%) and K_2CO_3 (276.4 mg, 2.0 mmol, 4.0 equiv) were added under argon atmosphere. The reaction vessel was evacuated and backfilled with argon for 3 times. The mixture was stirred for 8 h at 95 °C (TLC tracking detection). After that, the resultant mixture was cooled to room temperature and filtered. The filtrate was concentrated under reduced pressure. Purification of the crude residue by flash column chromatography on silica gel using ethyl acetate/petroleum ether as eluent yielded the desired product **5**.

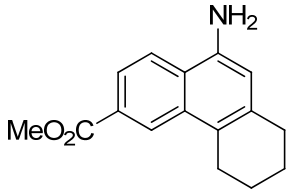
1,2,3,4-Tetrahydrophenanthren-9-amine (**5aa**)



5aa

Brown solid, 78.2 mg, 79% yield (purified by silica gel chromatography using PE/EA = 20:1). R_f = 0.33 (eluent: petroleum ether/EtOAc = 8:1). m.p. 64.9-66.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.41 (m, 1H), 6.55 (s, 1H), 3.98 (s, 2H), 3.03 (t, *J* = 6.2 Hz, 2H), 2.83 (t, *J* = 6.0 Hz, 2H), 1.98 – 1.93 (m, 2H), 1.88 – 1.82 (m, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 139.53, 134.72, 133.21, 125.77, 123.81, 123.41, 123.06, 122.65, 121.14, 111.84, 30.48, 25.20, 23.49, 23.03; **HRMS** (ESI) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}N^+$ 198.1277, found 198.1291.

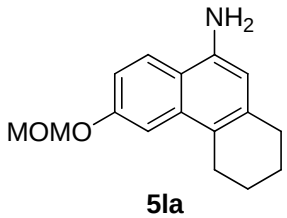
Methyl 10-amino-5,6,7,8-tetrahydrophenanthrene-3-carboxylate (**5ga**)



5ga

Brown solid, 96.0 mg, 75% yield (purified by silica gel chromatography using PE/EA = 15:1). R_f = 0.39 (eluent: petroleum ether/EtOAc = 4:1). m.p. 128.4-129.7 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.71 (d, *J* = 1.2 Hz, 1H), 7.99 (dd, *J* = 8.7, 1.6 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 6.63 (s, 1H), 4.01 (s, 2H), 3.98 (s, 3H), 3.08 (t, *J* = 6.3 Hz, 2H), 2.81 (t, *J* = 6.0 Hz, 2H), 1.97 – 1.91 (m, 2H), 1.87 – 1.81 (m, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 167.61, 139.46, 135.75, 132.51, 126.92, 126.49, 125.16, 124.24, 123.23, 121.50, 114.19, 52.16, 30.41, 25.18, 23.27, 22.88; **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}NO_2^+$ 256.1332; Found 256.1341.

6-(Methoxymethoxy)-1,2,3,4-tetrahydrophenanthren-9-amine (**5la**)



5la

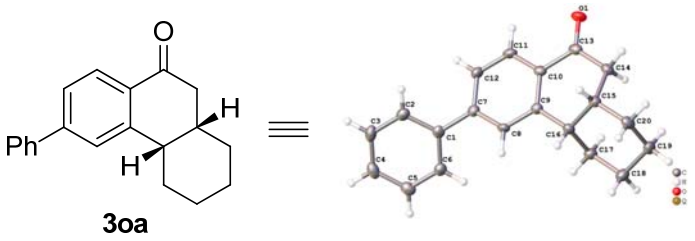
Brown solid, 88.1 mg, 68% yield (purified by silica gel chromatography using PE/EA = 15:1). R_f = 0.26 (eluent: petroleum ether/EtOAc = 8:1). m.p. 116.4-117.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 (d, *J* = 9.1 Hz, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 9.1, 2.5 Hz, 1H), 6.43 (s, 1H), 5.30 (s, 2H), 3.93 (brs, 2H), 3.53 (s, 3H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.79 (t, *J* = 6.1 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.85 – 1.79 (m, 2H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.23, 139.59, 135.60, 134.59, 122.83, 121.88, 119.01, 115.76, 110.40, 107.05,

94.66, 56.05, 30.55, 25.35, 23.50, 23.05; **HRMS** (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{20}NO_2^+$ 258.1489; Found 258.1497.

7. Single crystal structure and crystallographic data

7.1 Single crystal structure and crystallographic data of 3oa

A single crystal of **3oa** was obtained by evaporative diffusion in dichloromethane with pentane as the anti-solvent at room temperature. The structure was shown at 50% ellipsoid contour present probability level. This crystal structure has been deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2018584.



3oa

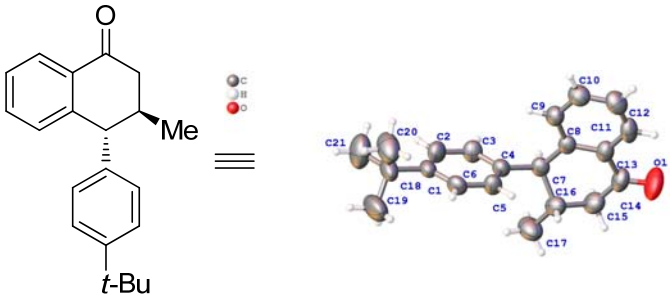
Table S1. Crystal data and structure refinement for 3oa.

Identification code	**3oa**
Empirical formula	$C_{20}H_{20}O$
Formula weight	276.36
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.4699(8)
b/Å	7.4654(6)
c/Å	17.2634(12)
α/°	90
β/°	96.445(6)
γ/°	90
Volume/Å^3	1468.88(19)
Z	4
ρ_{calc}g/cm^3	1.250
μ/mm^{-1}	0.075
F(000)	592.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.75 to 49.982
Index ranges	$-13 \le h \le 11$, $-7 \le k \le 8$, $-20 \le l \le 18$
Reflections collected	6549
Independent reflections	2583 [R_{int} = 0.0288, R_{sigma} = 0.0385]

Data/restraints/parameters	2583/0/190
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0470, wR_2 = 0.1043
Final R indexes [all data]	R_1 = 0.0592, wR_2 = 0.1118
Largest diff. peak/hole / e $Å^{-3}$	0.20/-0.22

7.2 Single crystal structure and crystallographic data of 3ah

A single crystal of **3ah** was obtained by evaporative diffusion in dichloromethane with pentane as the anti-solvent at room temperature. The structure was shown at 50% ellipsoid contour present probability level. This crystal structure has been deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2018583.



3ah

Table S2. Crystal data and structure refinement for 3ah.

Identification code	**3ah**
Empirical formula	$C_{21}H_{24}O$
Formula weight	292.40
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.0580(13)
b/Å	10.9276(12)
c/Å	16.1095(18)
α/°	88.164(9)
β/°	78.300(10)
γ/°	88.386(10)
Volume/$Å^3$	1732.5(4)
Z	4
$\rho_{calc}g/cm^3$	1.121
μ/mm^{-1}	0.067
F(000)	632.0
Crystal size/mm^3	0.14 × 0.13 × 0.12
Radiation	Mo Kα (λ = 0.71073)

2Θ range for data collection/°	4.136 to 49.996
Index ranges	$-8 \leq h \leq 11$, $-11 \leq k \leq 12$, $-19 \leq l \leq 18$
Reflections collected	12269
Independent reflections	6089 [R_{int} = 0.0225, R_{sigma} = 0.0396]
Data/restraints/parameters	6089/14/405
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0859, wR_2 = 0.2449
Final R indexes [all data]	R_1 = 0.1170, wR_2 = 0.2746
Largest diff. peak/hole / e $Å^{-3}$	0.56/-0.51

8. References

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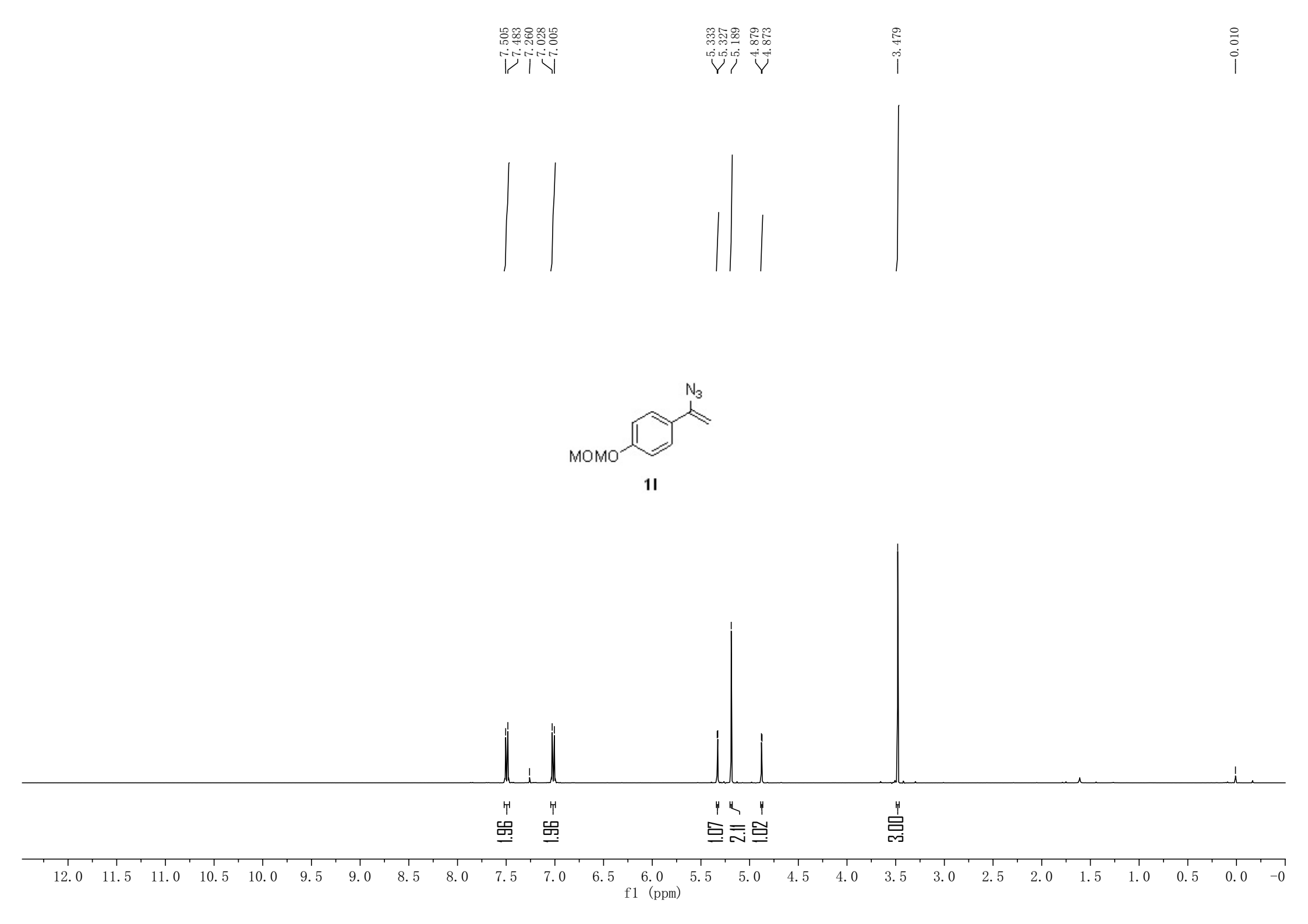
7. Shu, W.; Nevado C. Visible-Light-Mediated Remote Aliphatic C–H Functionalizations through a 1,5-Hydrogen Transfer Cascade. *Angew. Chem. Int. Ed.* **2017**, *56*, 1881 –1884.
8. Spanevello, R. A.; González-sierra, M.; Mcchesney, J. D. Stereoselective Synthesis of 4a-Methyloctahydrophenanthrenes: A Novel Approach. III. C-9 and C-10 Substituted Series. *Syn. Commun.* **1993**, *23*, 2463–2480.

9. The ^{1}H NMR and ^{13}C NMR spectra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4.873
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N3
MOMO
1l
1.96
1.96
1.07
2.11
1.02
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
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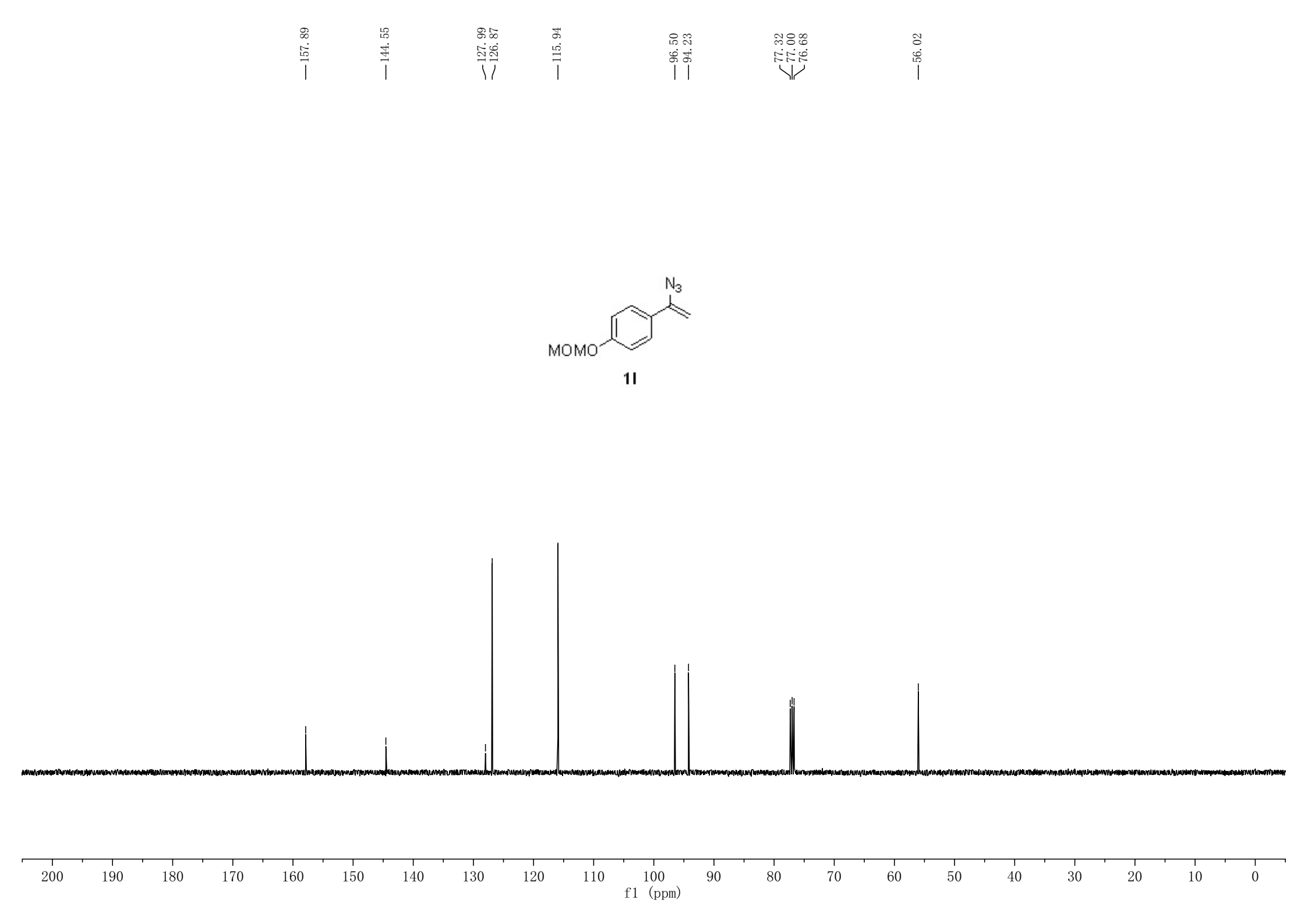
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126.87
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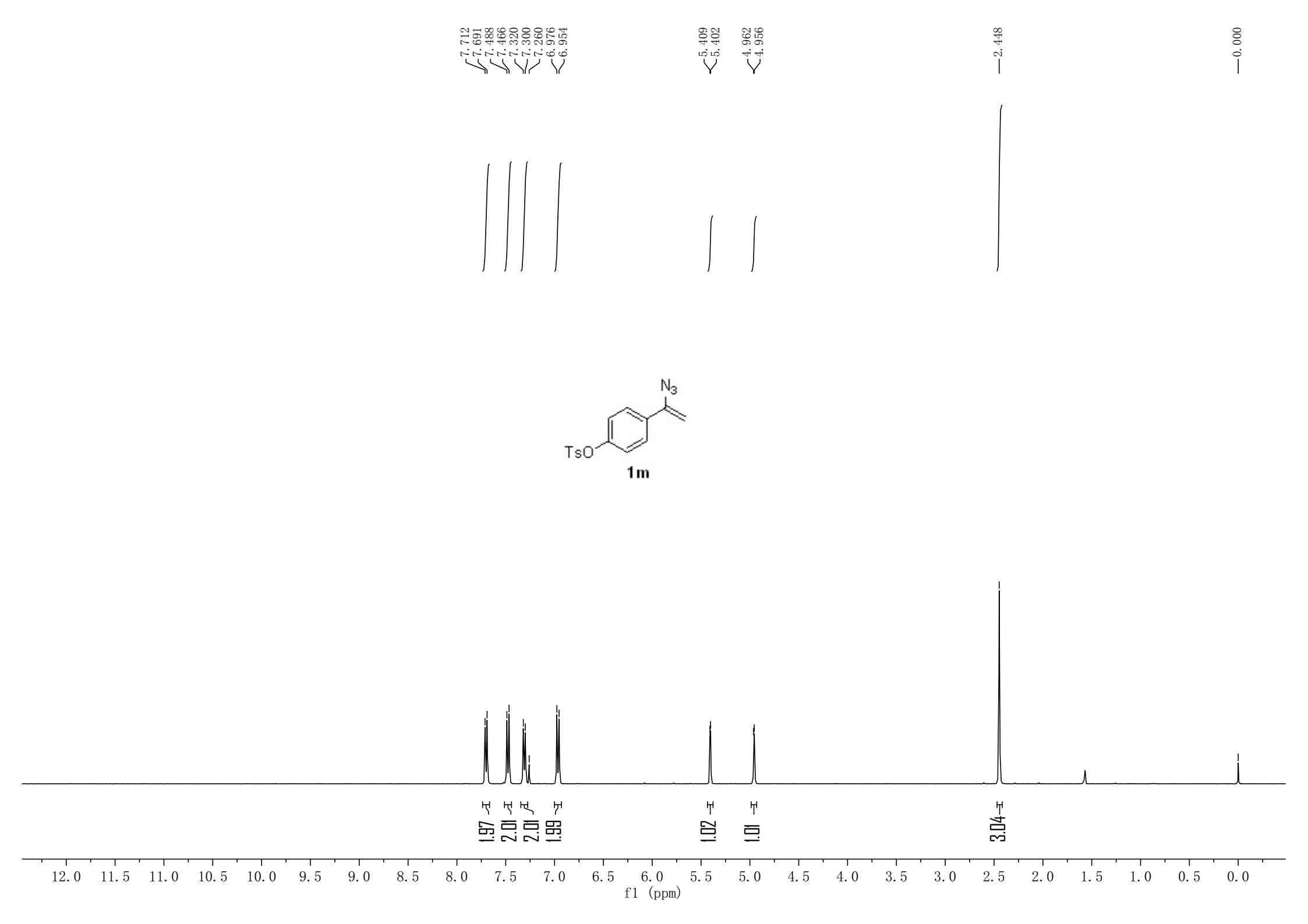
96.50
94.23
77.32
77.00
76.68
56.02
N3
MOMO
1l
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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4.956
2.448
0.000
N3
TsO
1m
1.97
2.01
2.01
1.99
1.02
1.01
3.04
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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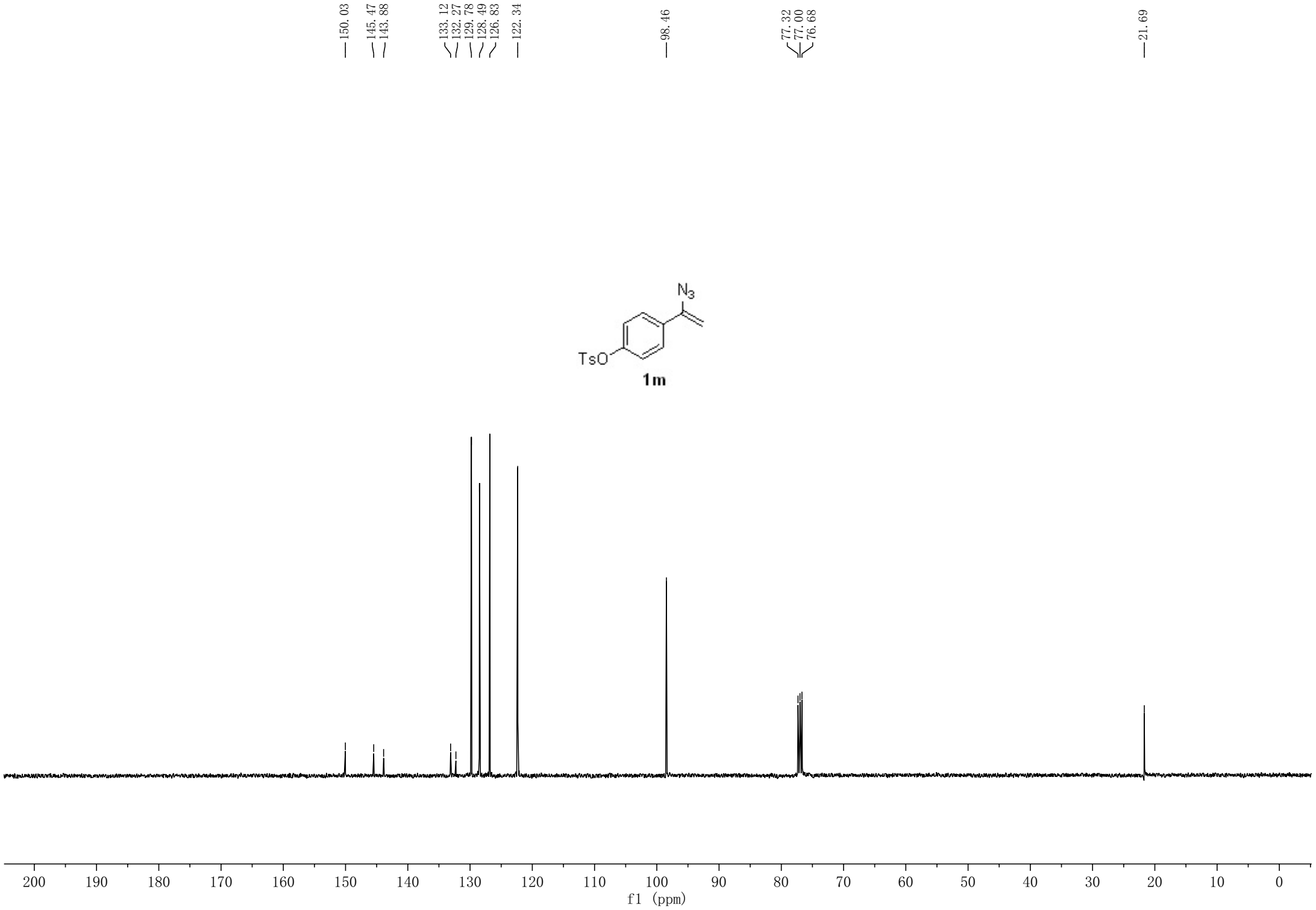
f1 (ppm)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143.88
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132.27
129.78
128.49
126.83
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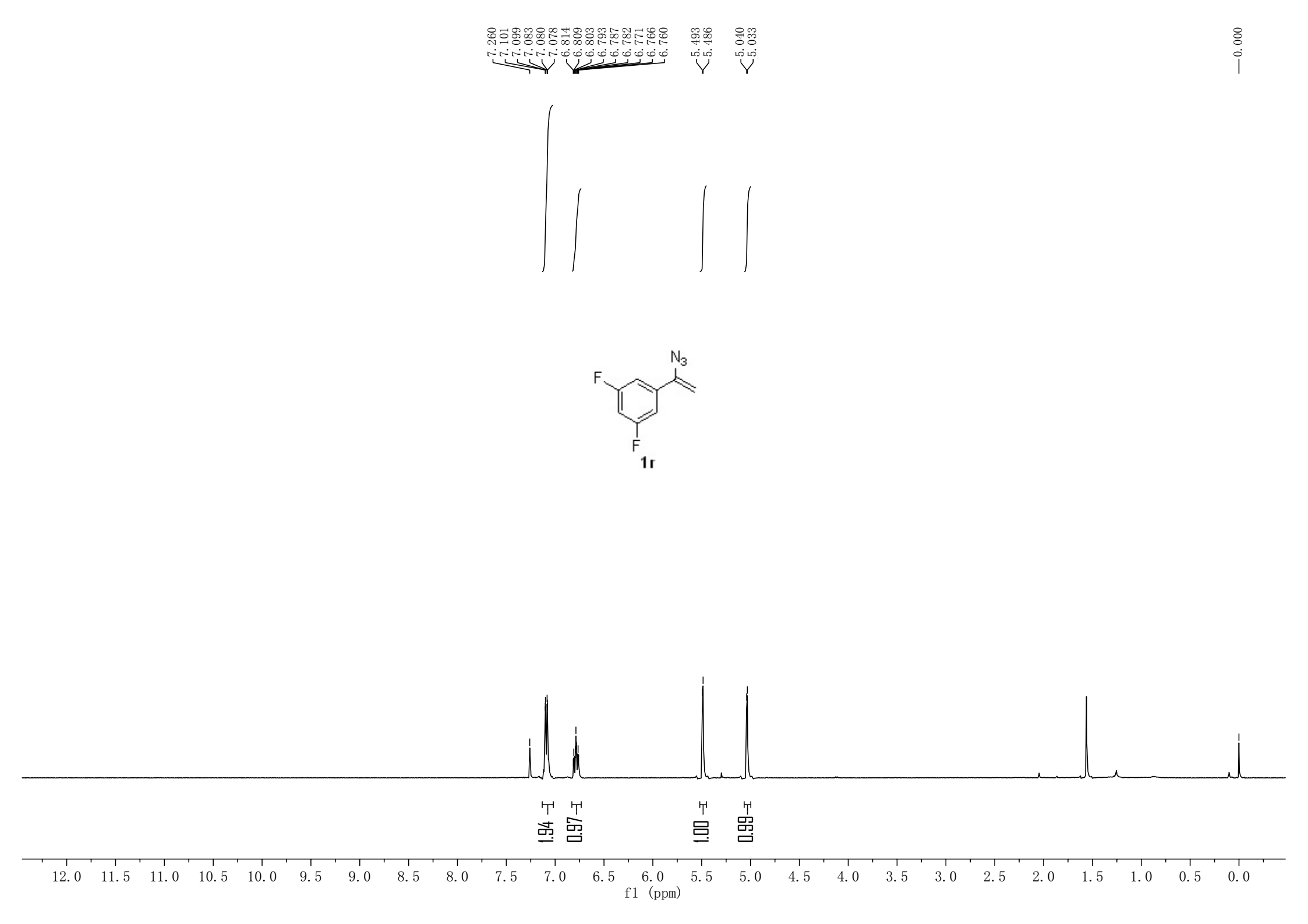
98.46
77.32
77.00
76.68
21.69
N3
TsO
1m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.771
6.766
6.760
5.493
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5.040
5.033
0.000
N3
F
F
1r
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0.97
1.00
0.99
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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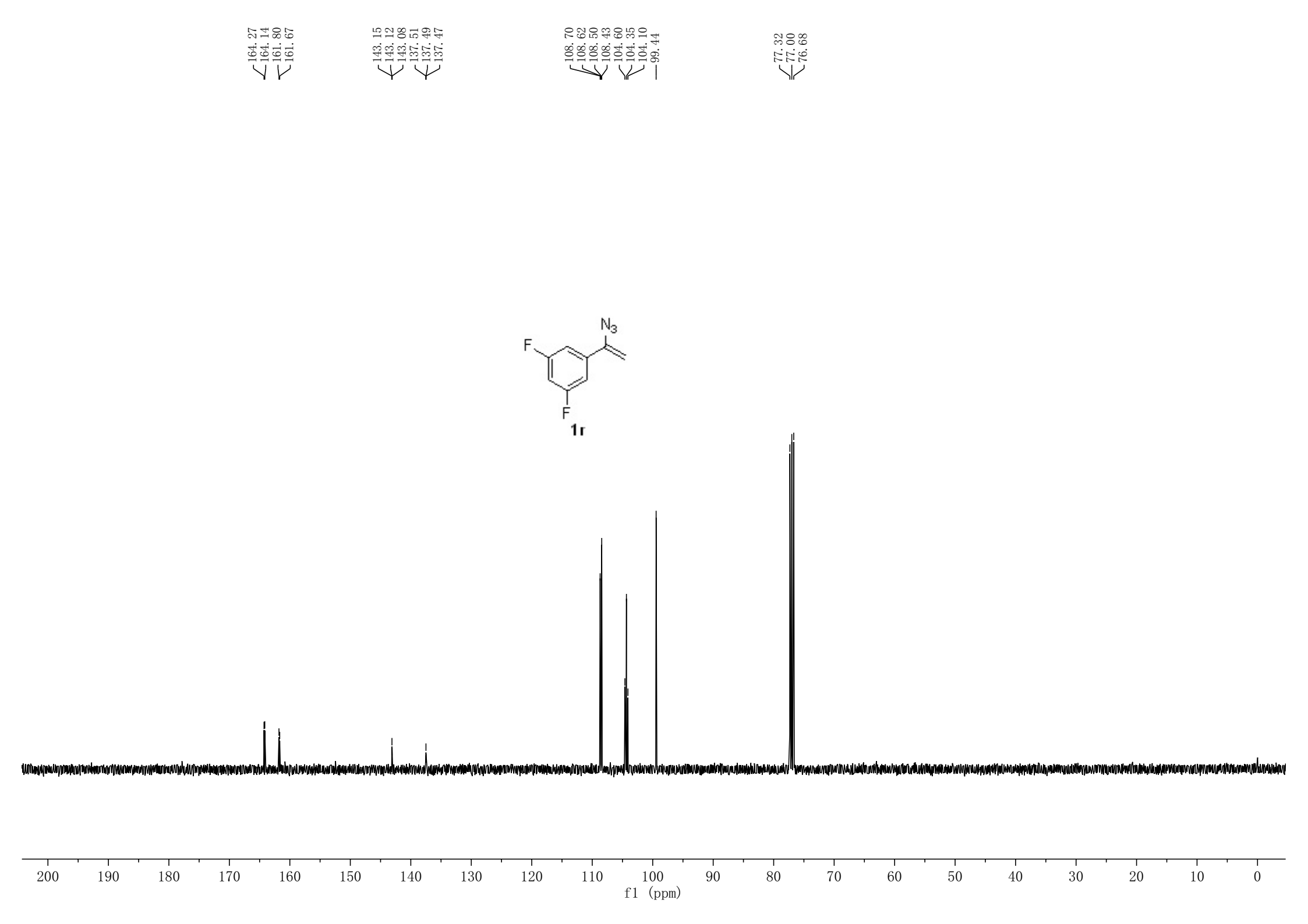
f1 (ppm)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108.43
104.60
104.35
104.10
99.44
77.32
77.00
76.68
N3
F
F
1r
200
190
180
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30
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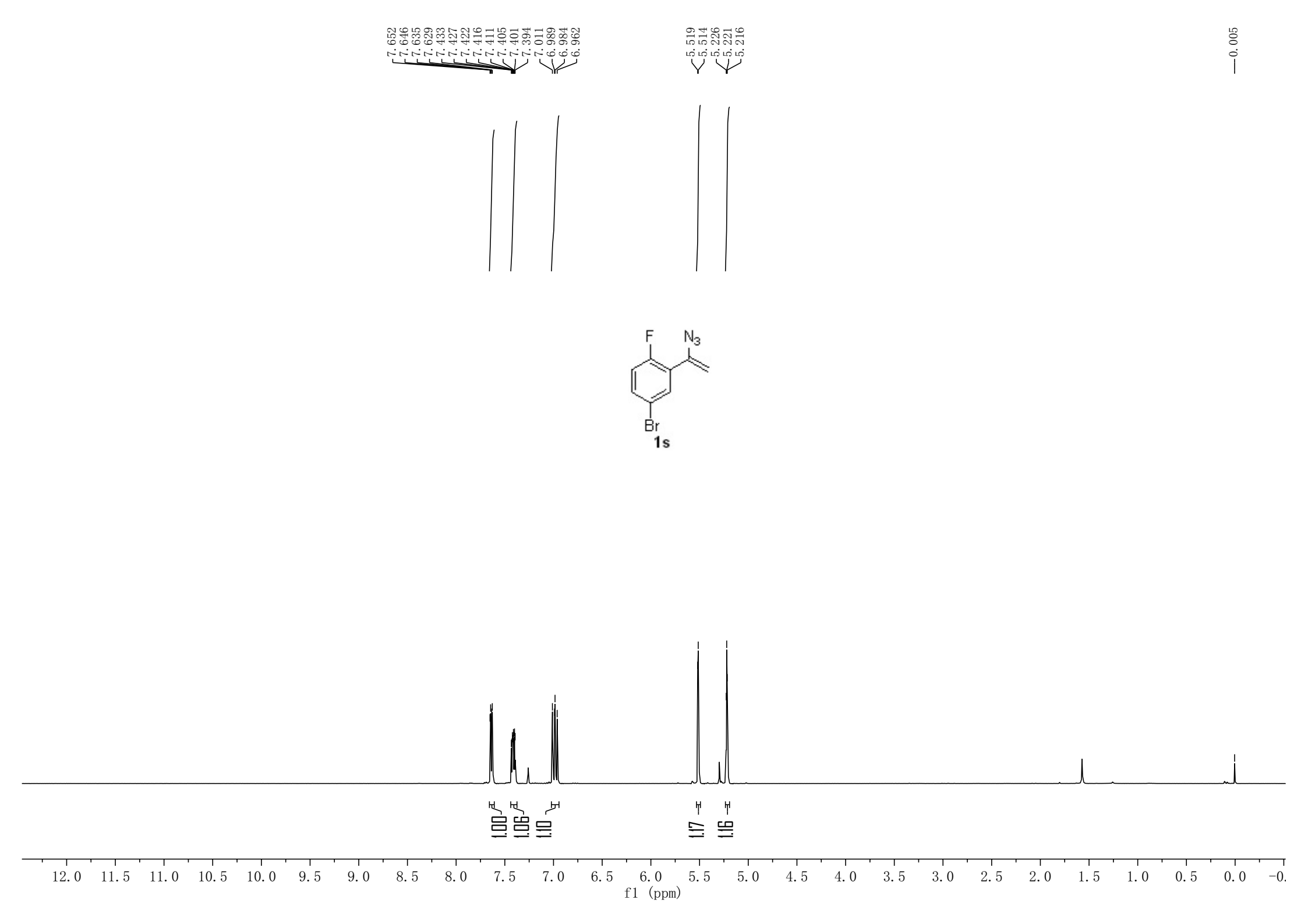
f1 (ppm)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7.405
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7.011
6.989
6.984
6.962
5.519
5.514
5.226
5.221
5.216
0.005
F
N3
Br
1s
1.00
1.06
1.10
1.17
1.16
12.0
11.5
11.0
10.5
10.0
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9.0
8.5
8.0
7.5
7.0
6.5
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5.0
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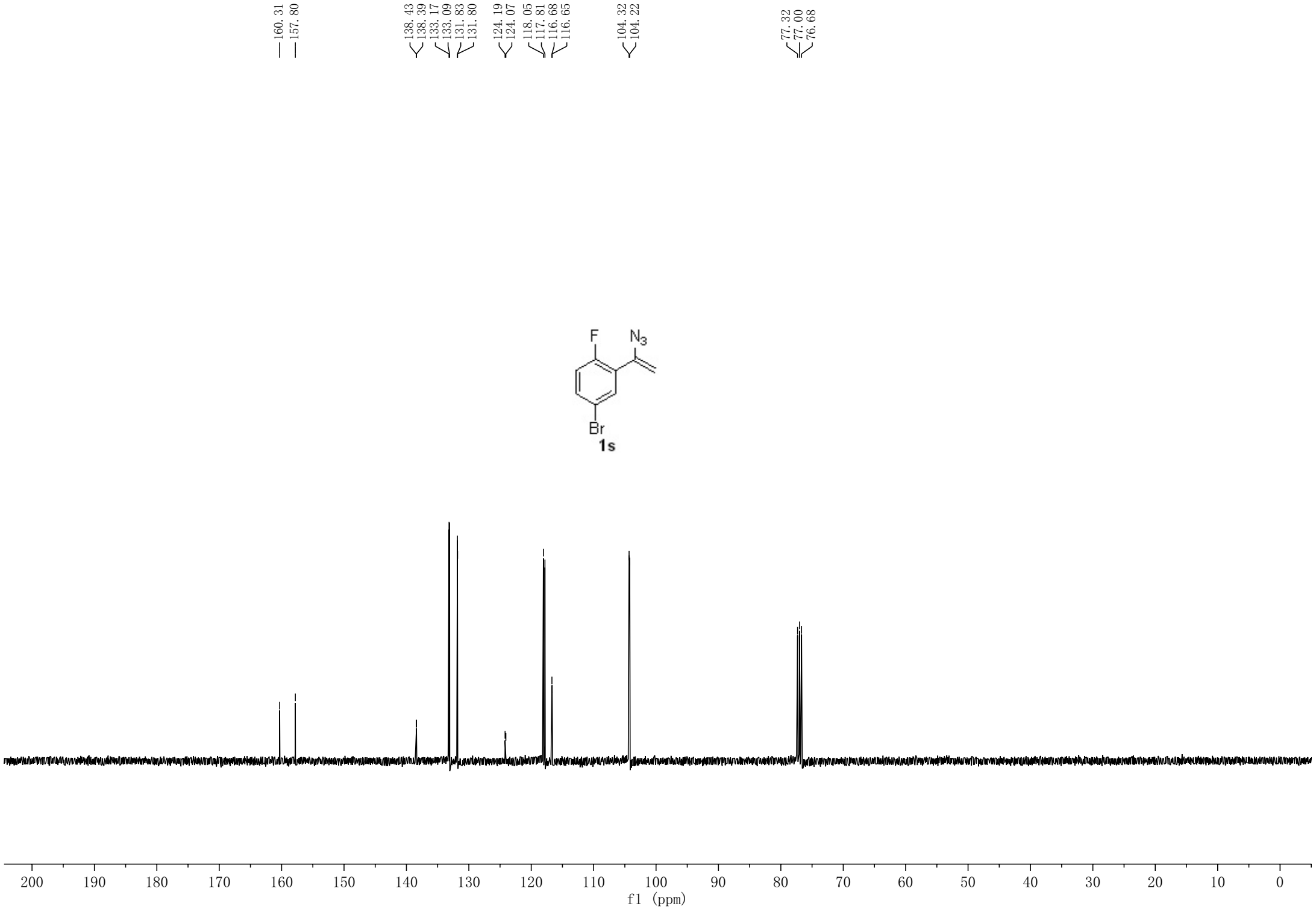
f1 (ppm)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133.09
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116.68
116.65
104.32
104.22
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77.00
76.68
F
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Br
1s
200
190
180
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120
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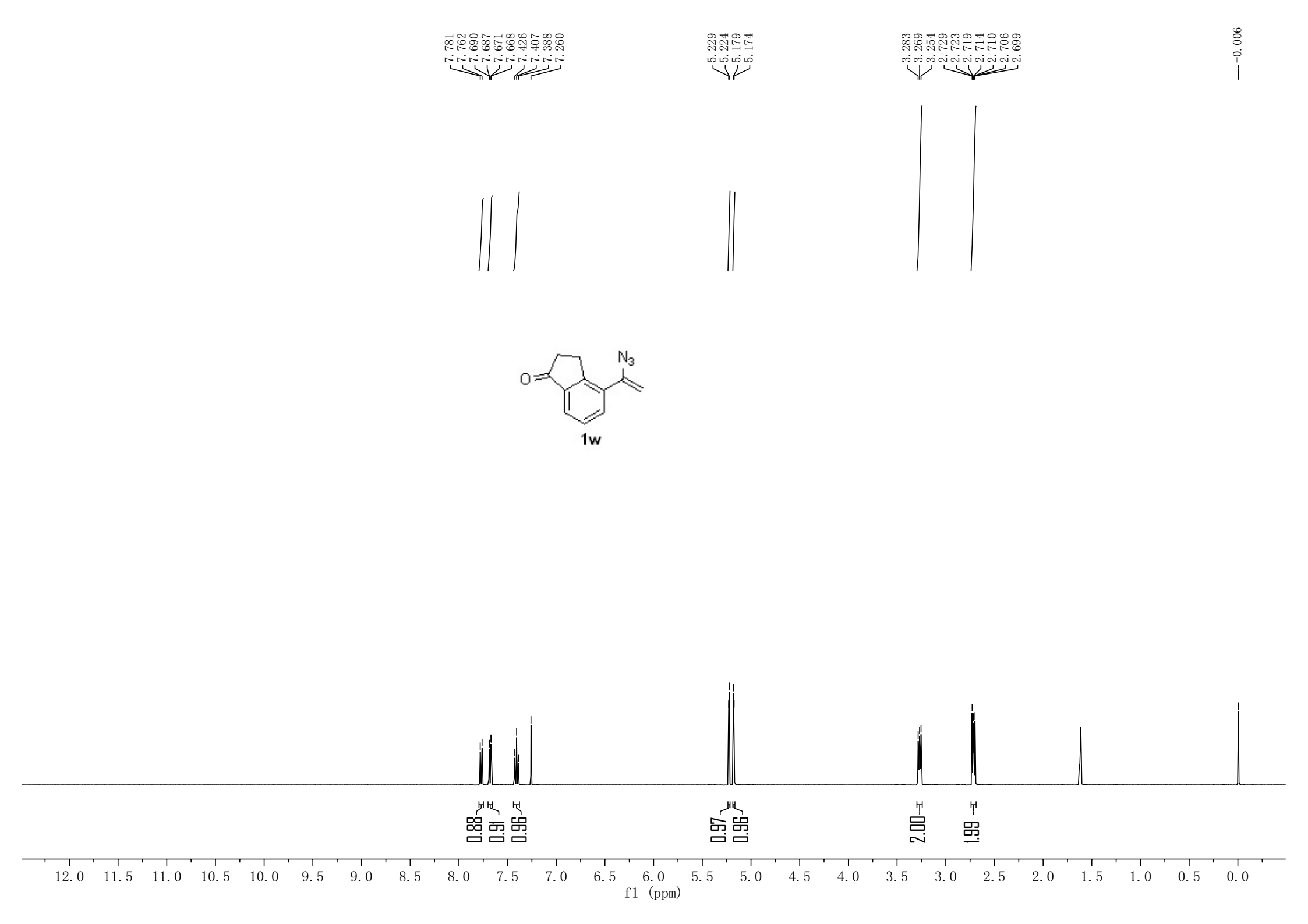
f1 (ppm)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2.706
2.699
-0.006
O
N3
1w
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0.91
0.96
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0.96
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1.99
12.0
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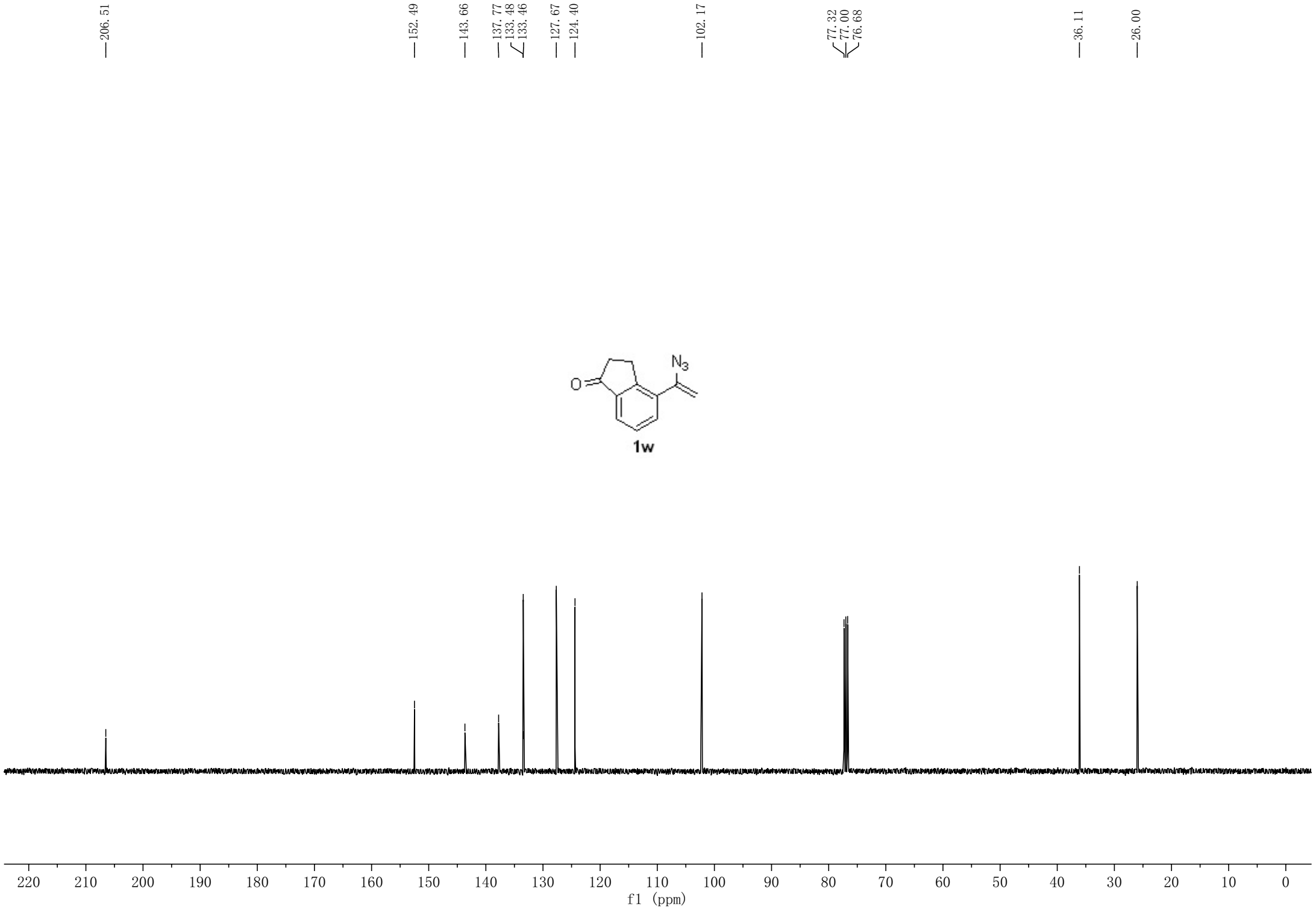
f1 (ppm)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200
190
180
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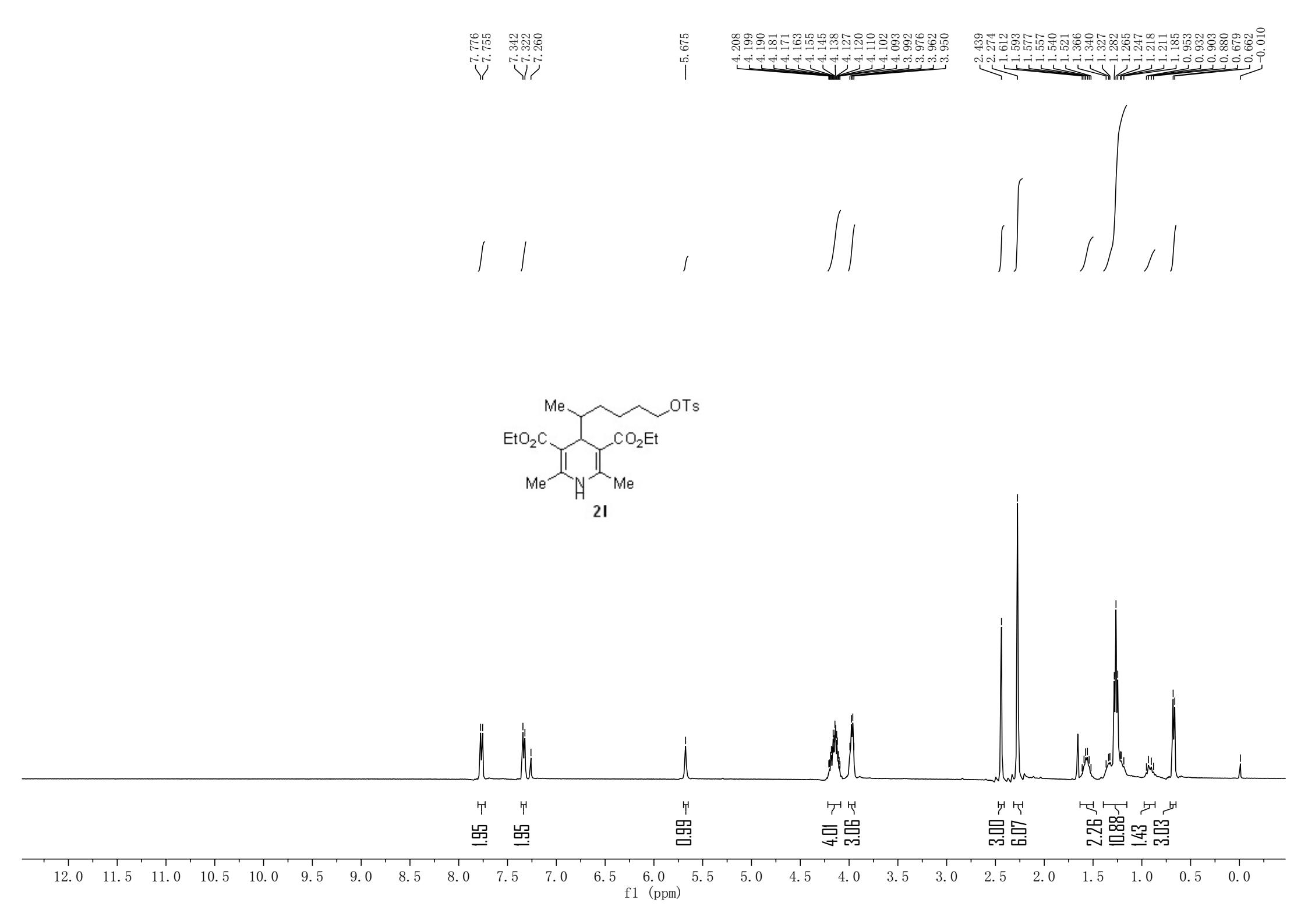
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Me
OTs
EtO2C
CO2Et
Me
N
H
Me
21
1.95
1.95
0.99
4.01
3.06
3.00
6.07
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10.88
1.43
3.03
12.0
11.5
11.0
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9.0
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6.5
6.0
5.5
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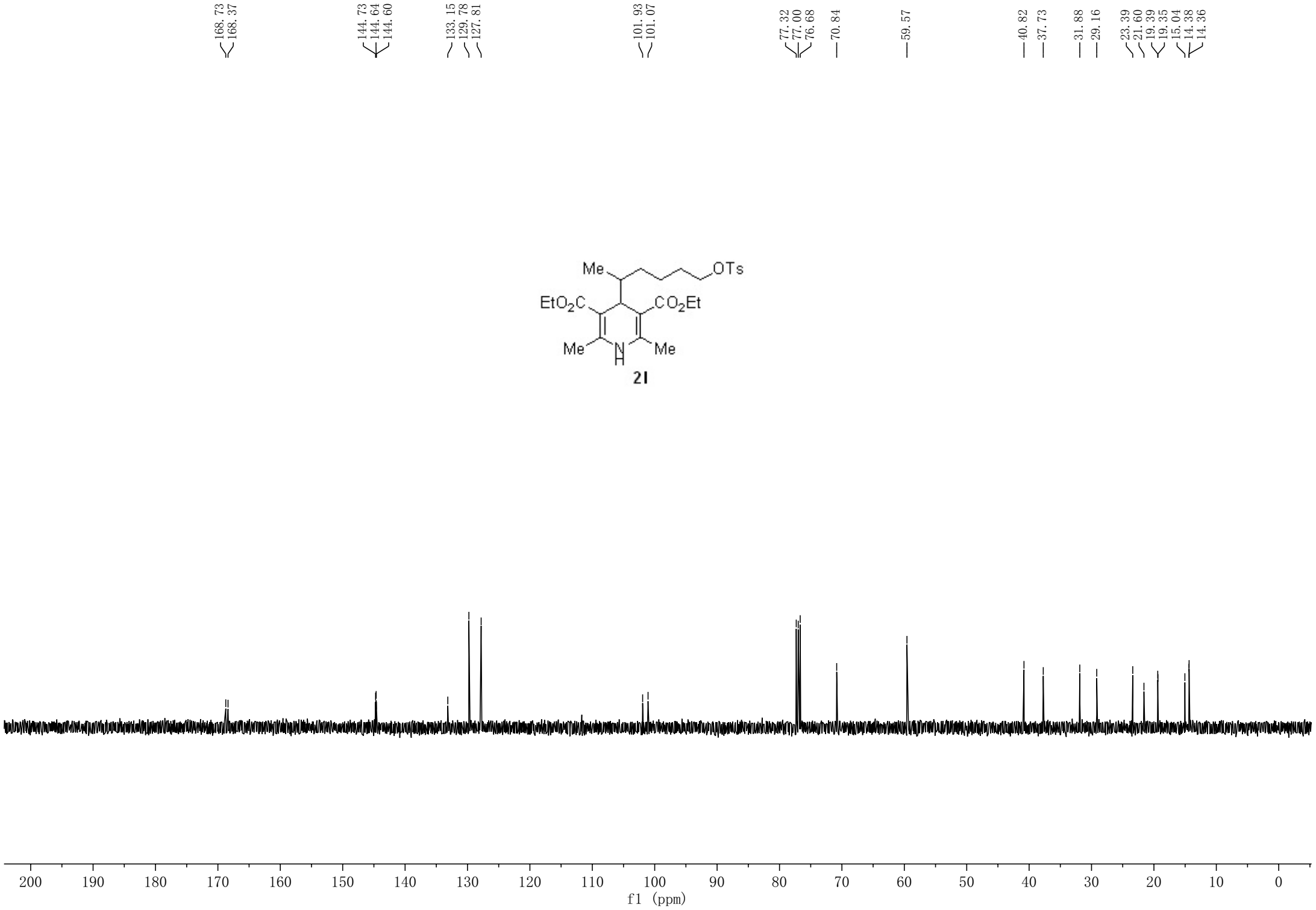
f1 (ppm)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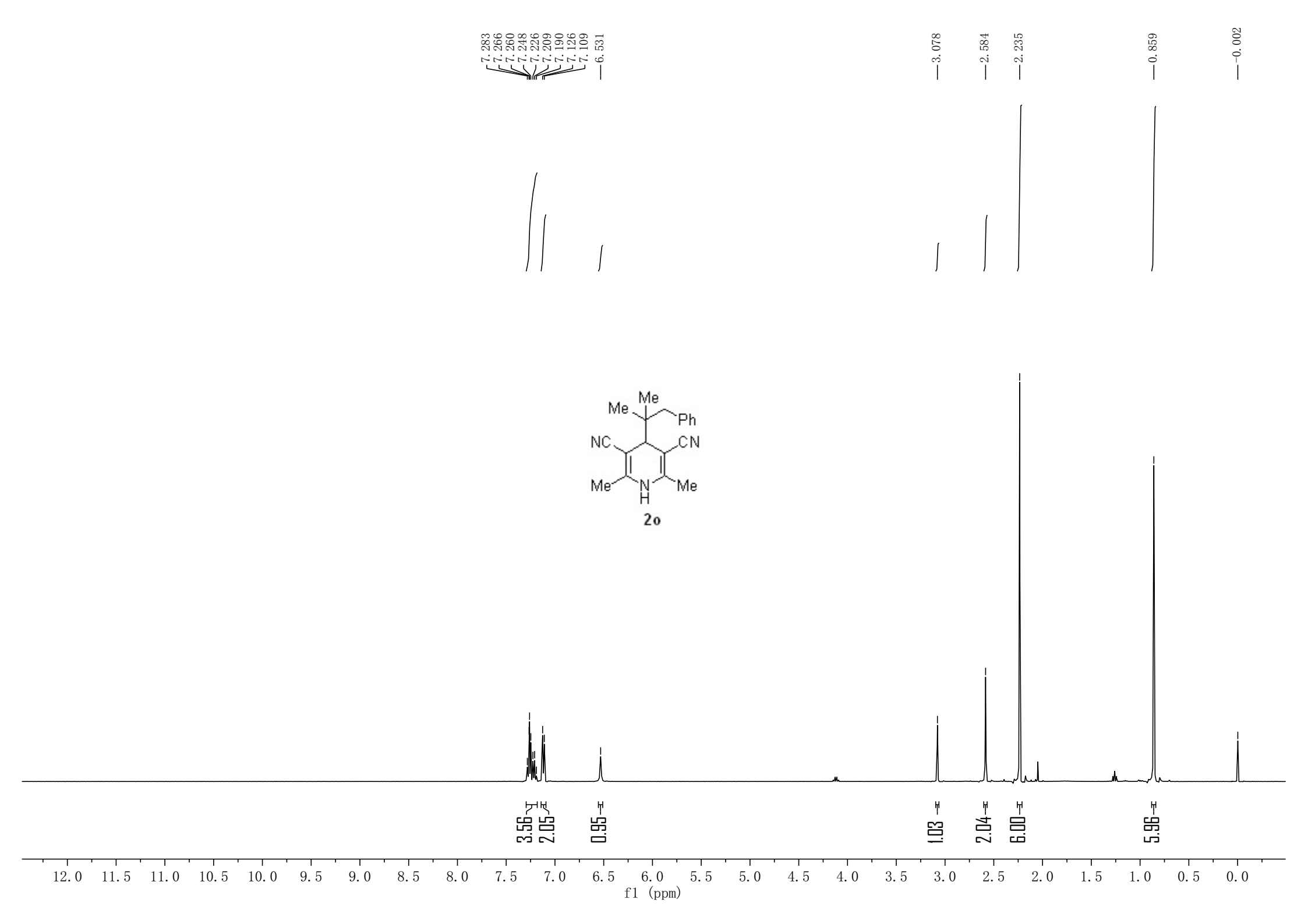
77.00
76.68
70.84
59.57
40.82
37.73
31.88
29.16
23.39
21.60
19.39
19.35
15.04
14.38
14.36
Me
OTs
EtO2C
CO2Et
Me
N
H
Me
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

2l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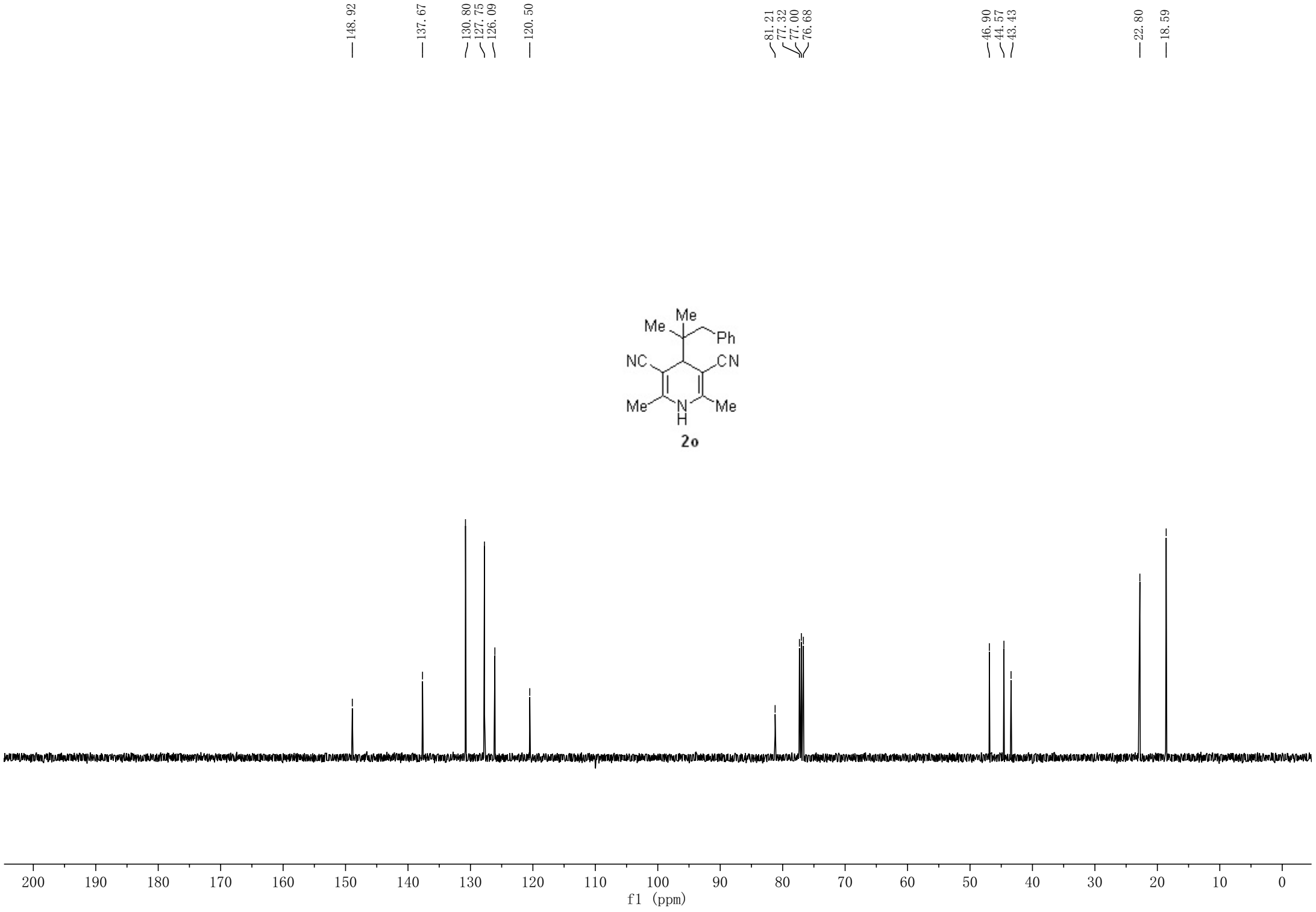
7.260
7.248
7.226
7.209
7.190
7.126
7.109
6.531
3.078
2.584
2.235
0.859
-0.002
Me
Me
Ph
NC
CN
Me
N
H
Me
2o
3.56
2.05
0.95
1.03
2.04
6.00
5.96
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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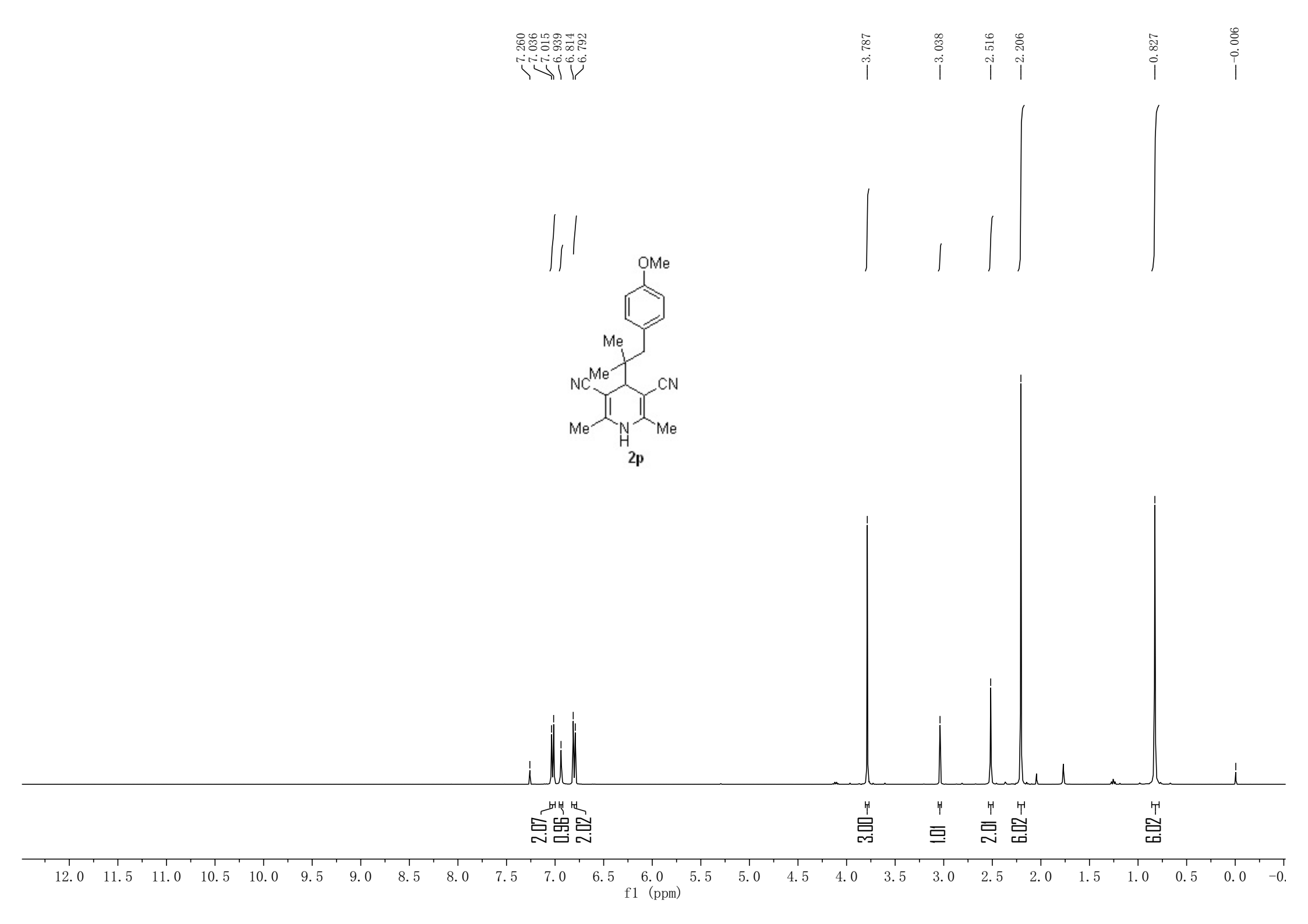
137.67
130.80
127.75
126.09
120.50
81.21
77.32
77.00
76.68
46.90
44.57
43.43
22.80
18.59
Me
Me
Ph
NC
CN
Me
N
H
Me
2o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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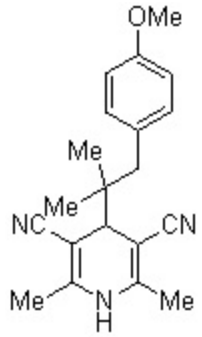
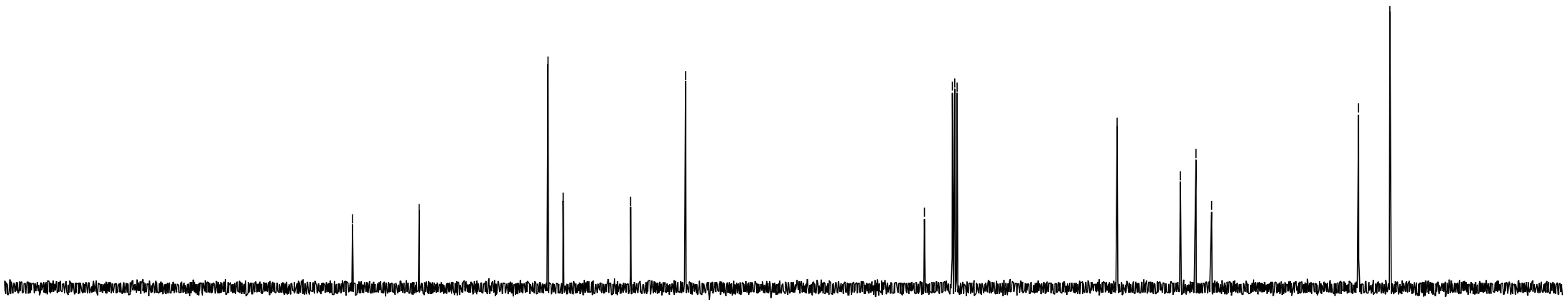
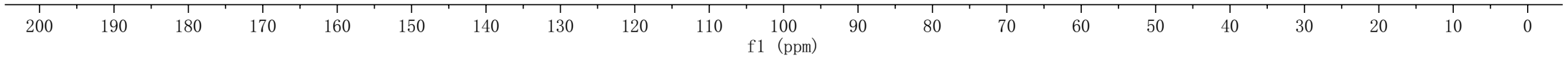
7.036
7.015
6.939
6.814
6.792
3.787
3.038
2.516
2.206
0.827
-0.006
OMe
Me
Me
NC
CN
Me
N
H
Me
2p
2.07
0.96
2.02
3.00
1.01
2.01
6.02
6.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

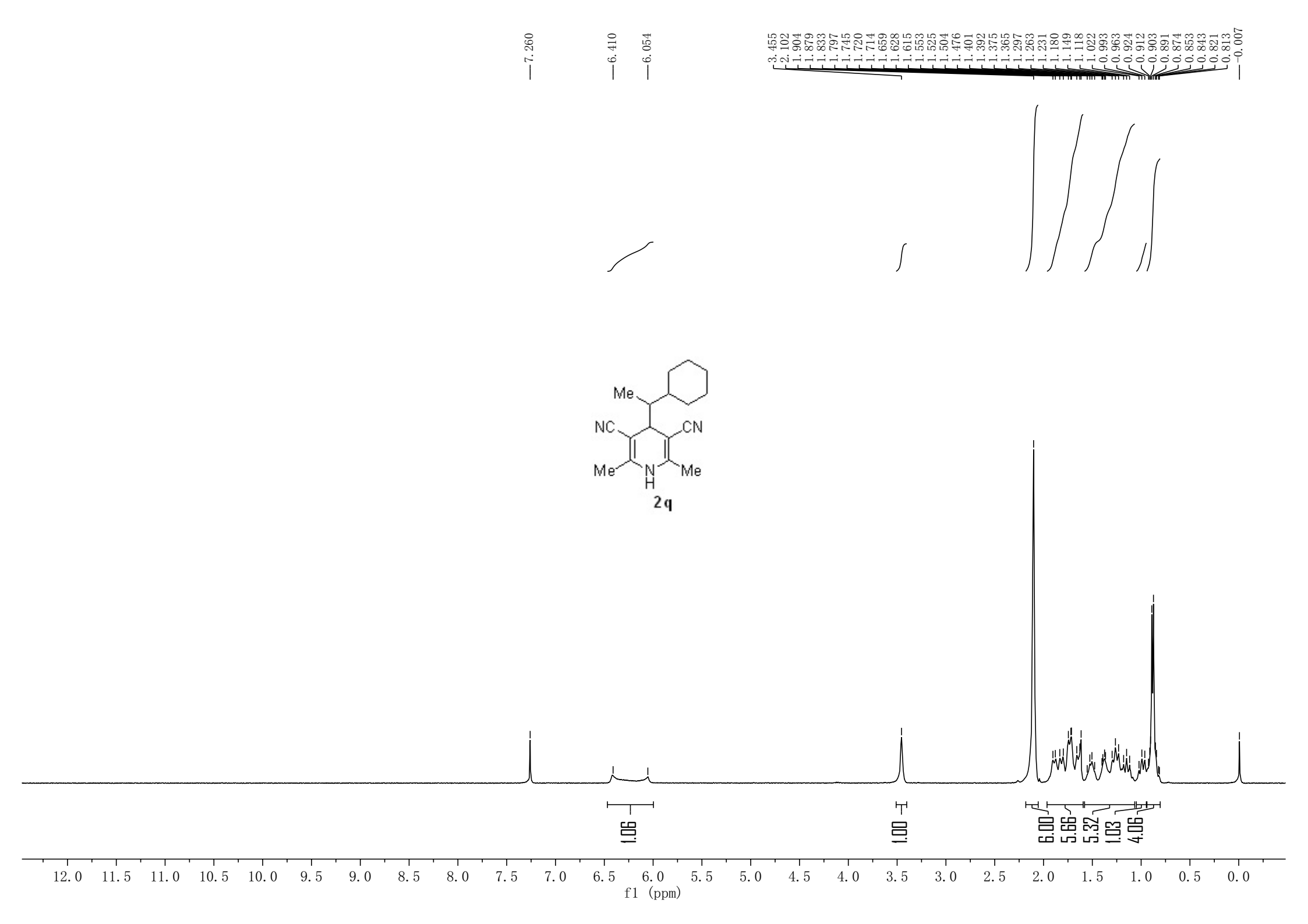
157.94
148.98
131.67
129.63
120.56
113.17
81.08
77.32
77.00
76.68
55.18
46.68
44.58
42.48
22.73
18.52



2p



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1.904
1.879
1.833
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1.745
1.720
1.714
1.659
1.628
1.615
1.553
1.525
1.504
1.476
1.401
1.392
1.375
1.365
1.297
1.263
1.231
1.180
1.149
1.118
1.022
0.993
0.963
0.924
0.912
0.903
0.891
0.874
0.853
0.843
0.821
0.813
-0.007
Me
NC
CN
Me
N
H
Me
2q
1.06
1.00
6.00
5.66
5.32
1.03
4.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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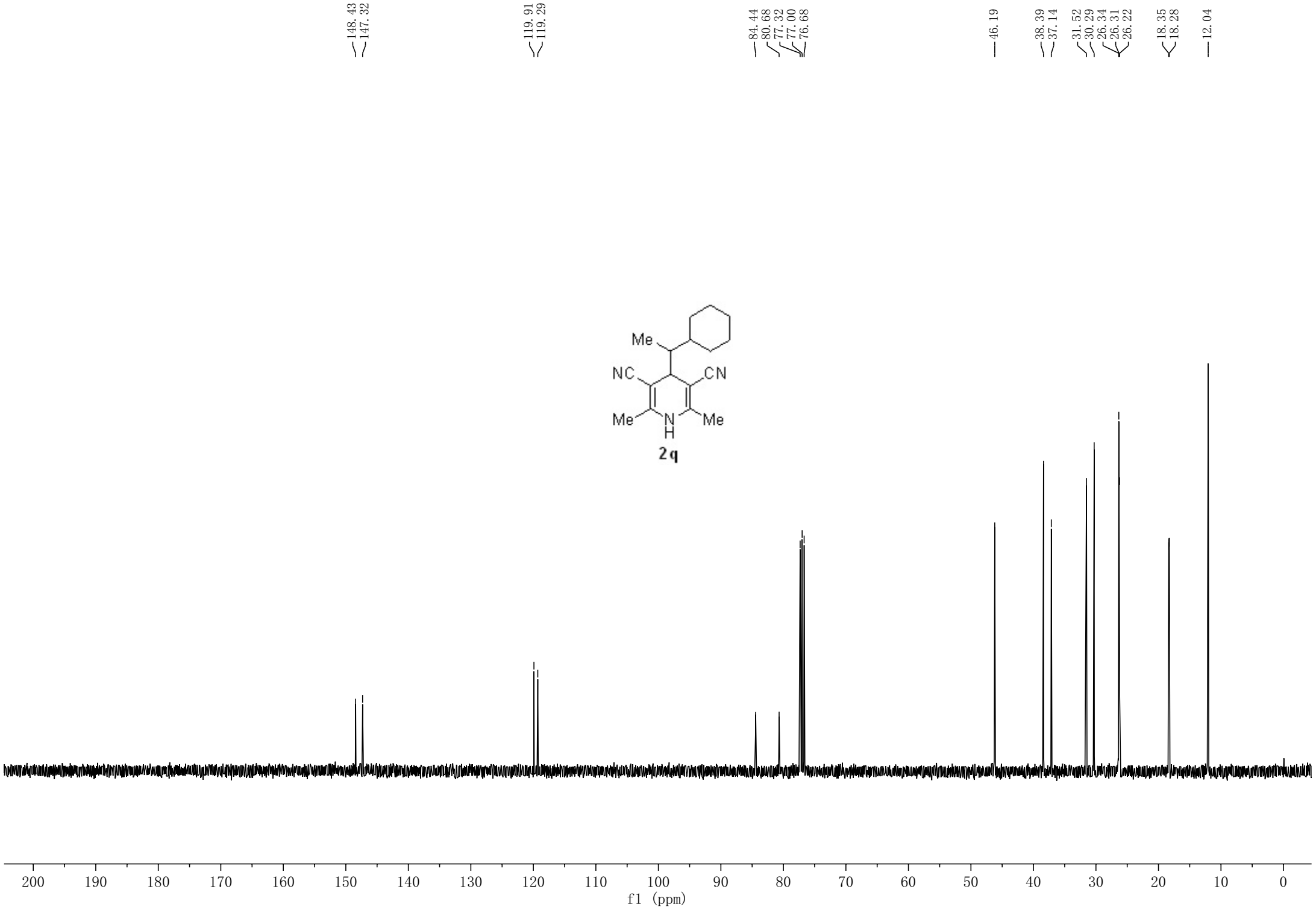
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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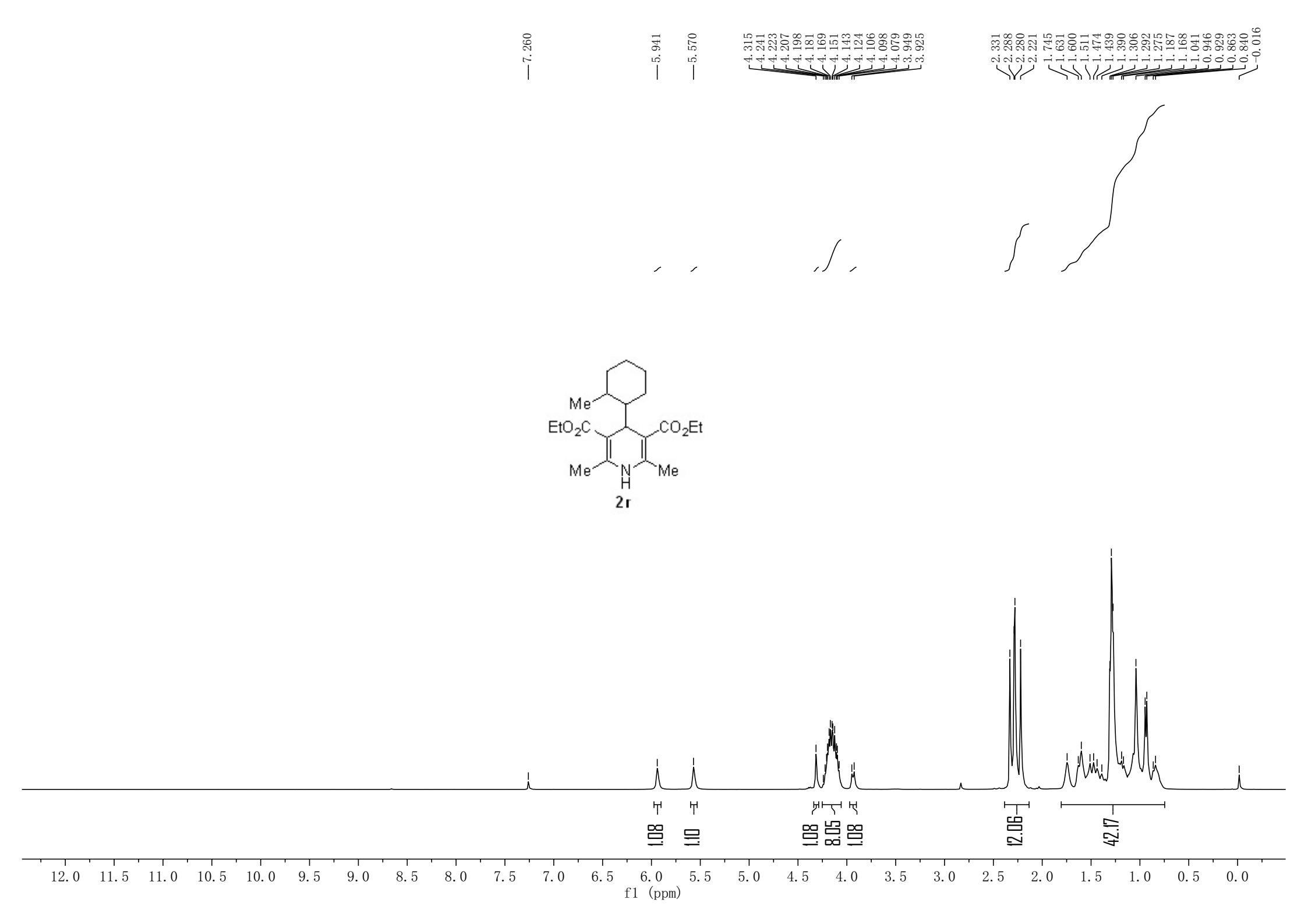
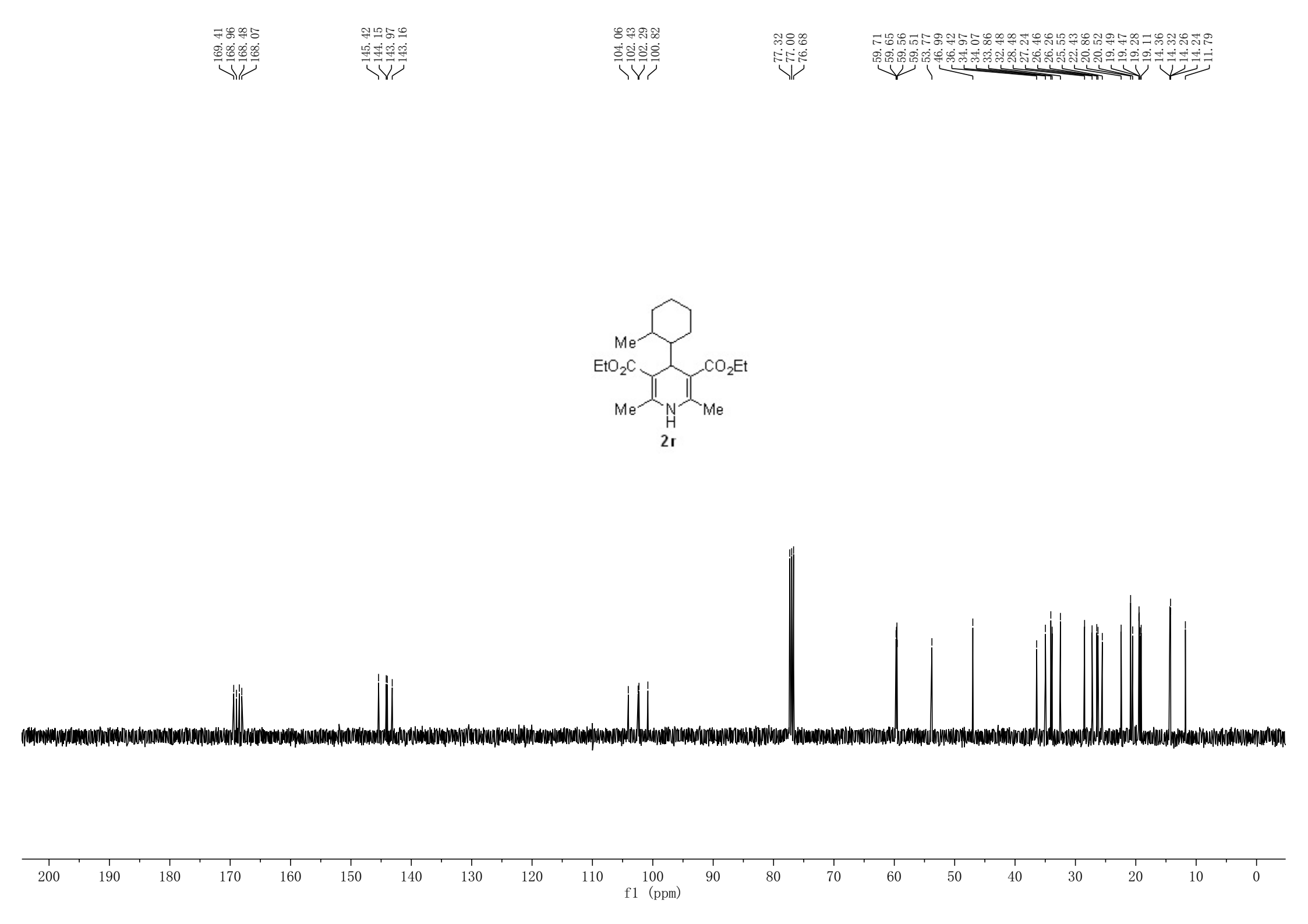
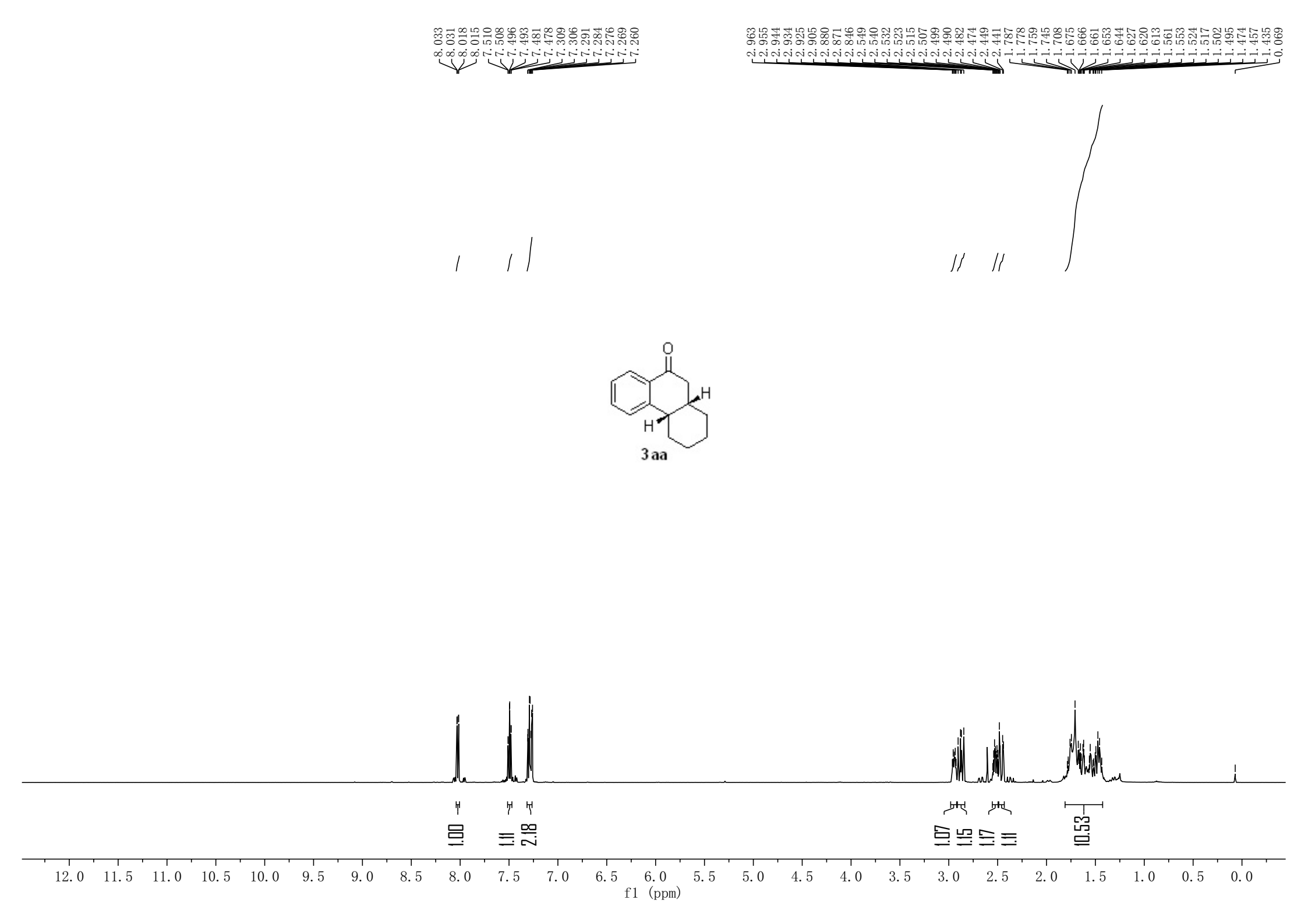
119.29
84.44
80.68
77.32
77.00
76.68
46.19
38.39
37.14
31.52
30.29
26.34
26.31
26.22
18.35
18.28
12.04
Me
NC
CN
Me
N
H
Me
2q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
5.941
5.570
4.315
4.241
4.223
4.207
4.198
4.181
4.169
4.151
4.143
4.124
4.106
4.098
4.079
3.949
3.925
2.331
2.288
2.280
2.221
1.745
1.631
1.600
1.511
1.474
1.439
1.390
1.306
1.292
1.275
1.187
1.168
1.041
0.946
0.929
0.863
0.840
-0.016
Me
EtO2C
CO2Et
Me
N
H
Me
2r
1.08
1.10
1.08
8.05
1.08
12.06
42.17
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


169.41
168.96
168.48
168.07
145.42
144.15
143.97
143.16
104.06
102.43
102.29
100.82
77.32
77.00
76.68
59.71
59.65
59.56
59.51
53.77
46.99
36.42
34.97
34.07
33.86
32.48
28.48
27.24
26.46
26.26
25.55
22.43
20.86
20.52
19.49
19.47
19.28
19.11
14.36
14.32
14.26
14.24
11.79
Me
EtO2C
CO2Et
Me
N
H
Me
2r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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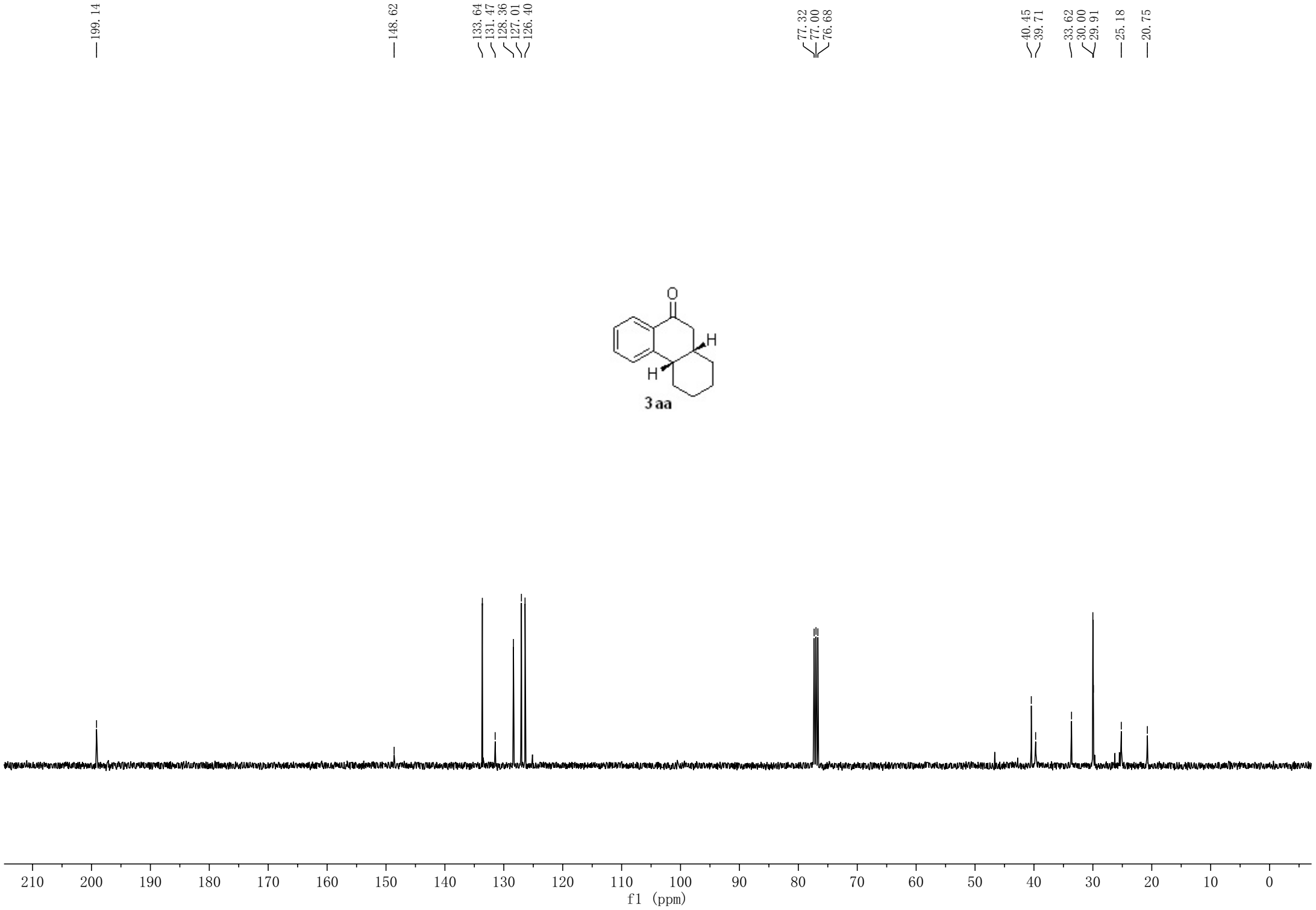
8.031
8.018
8.015
7.510
7.508
7.496
7.493
7.481
7.478
7.309
7.306
7.291
7.284
7.276
7.269
7.260
2.963
2.955
2.944
2.934
2.925
2.905
2.880
2.871
2.846
2.549
2.540
2.532
2.523
2.515
2.507
2.499
2.490
2.482
2.474
2.449
2.441
1.787
1.778
1.759
1.745
1.708
1.675
1.666
1.661
1.653
1.644
1.627
1.620
1.613
1.561
1.553
1.524
1.517
1.502
1.495
1.474
1.457
1.435
0.069
O
H
H
3aa
1.00
1.11
2.18
1.07
1.15
1.17
1.11
10.53
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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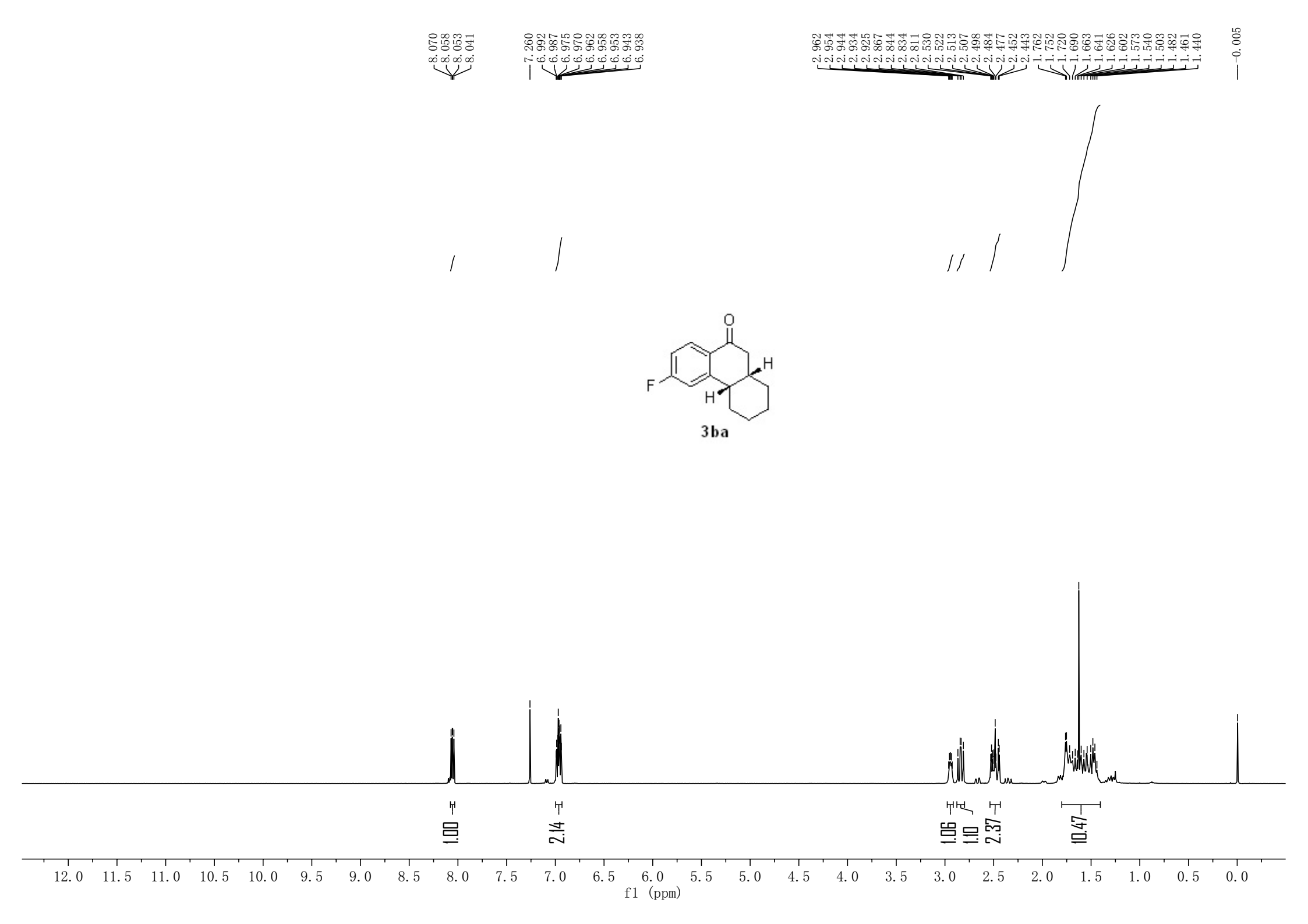
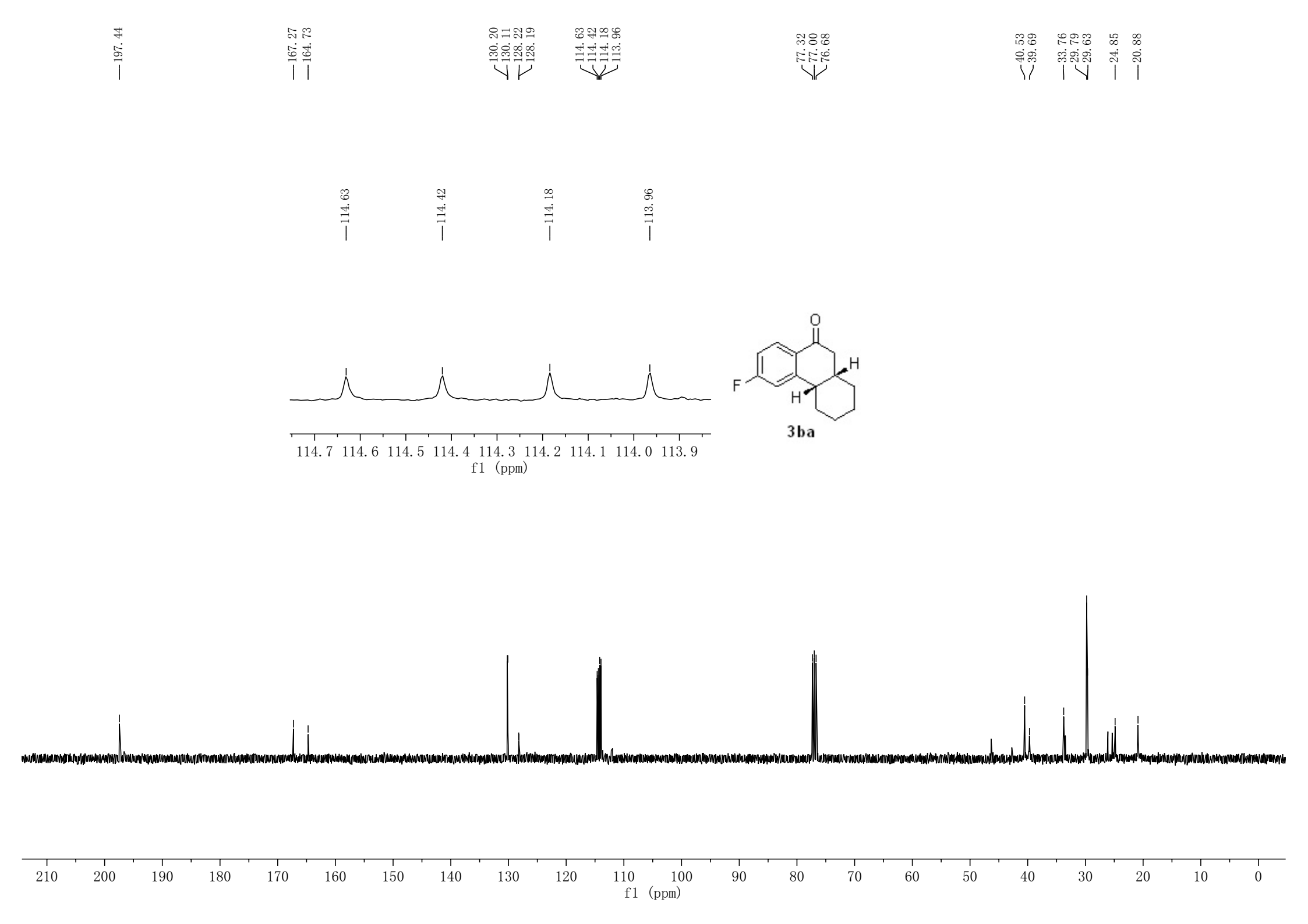
133.64
131.47
128.36
127.01
126.40
77.32
77.00
76.68
40.45
39.71
33.62
30.00
29.91
25.18
20.75
O
H
H
3aa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.070
8.058
8.053
8.041
7.260
6.992
6.987
6.975
6.970
6.962
6.958
6.953
6.943
6.938
2.962
2.954
2.944
2.934
2.925
2.867
2.844
2.834
2.811
2.530
2.522
2.513
2.507
2.498
2.484
2.477
2.452
2.443
1.762
1.752
1.720
1.690
1.663
1.641
1.626
1.602
1.573
1.540
1.503
1.482
1.461
1.440
-0.005
O
F
H
H
3ba
1.00
2.14
1.06
1.10
2.37
10.47
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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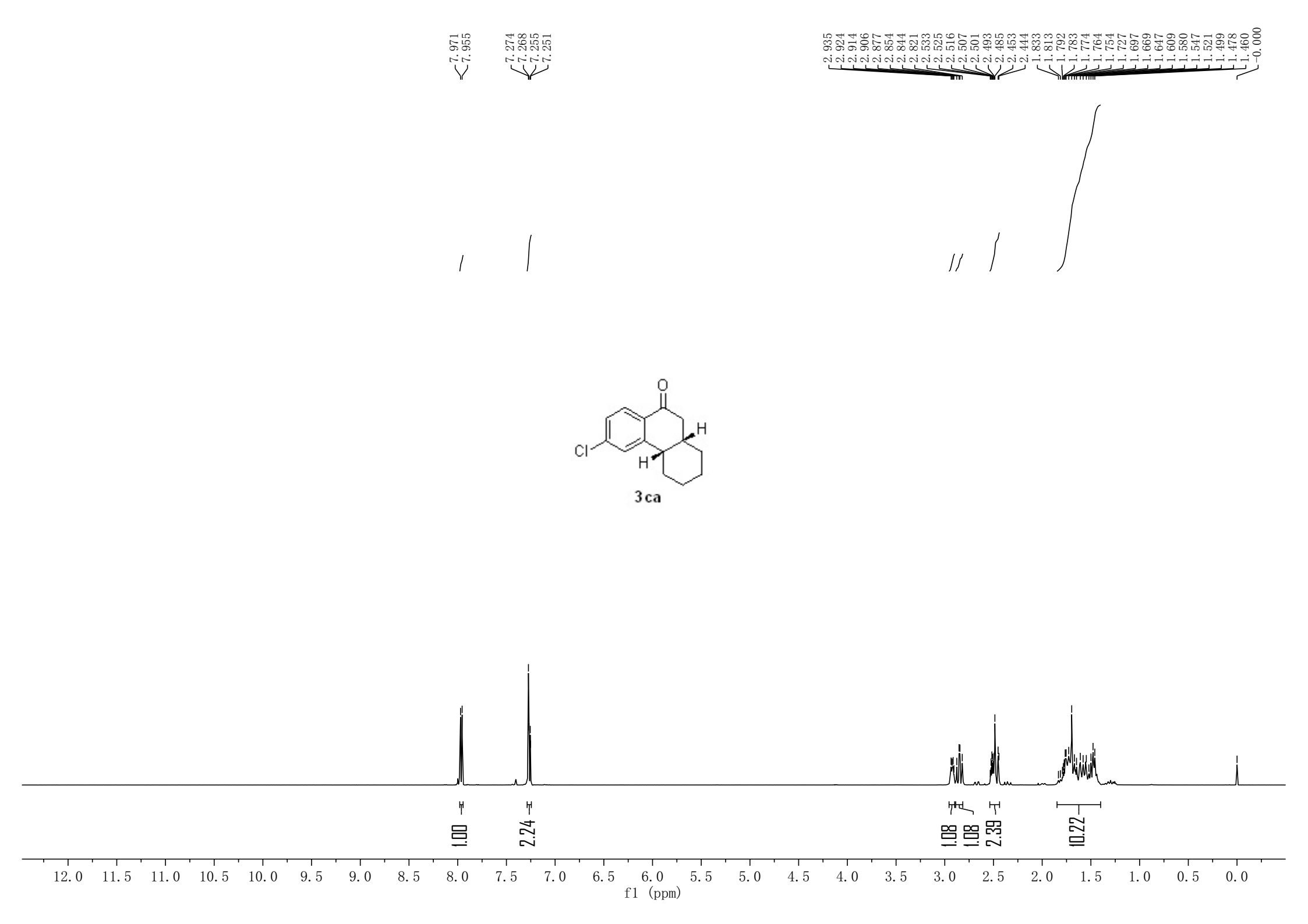
130.11
128.22
128.19
114.63
114.42
114.18
113.96
77.32
77.00
76.68
40.53
39.69
33.76
29.79
29.63
24.85
20.88
114.63
114.42
114.18
113.96
114.7 114.6 114.5 114.4 114.3 114.2 114.1 114.0 113.9
f1 (ppm)
O
H
F
H
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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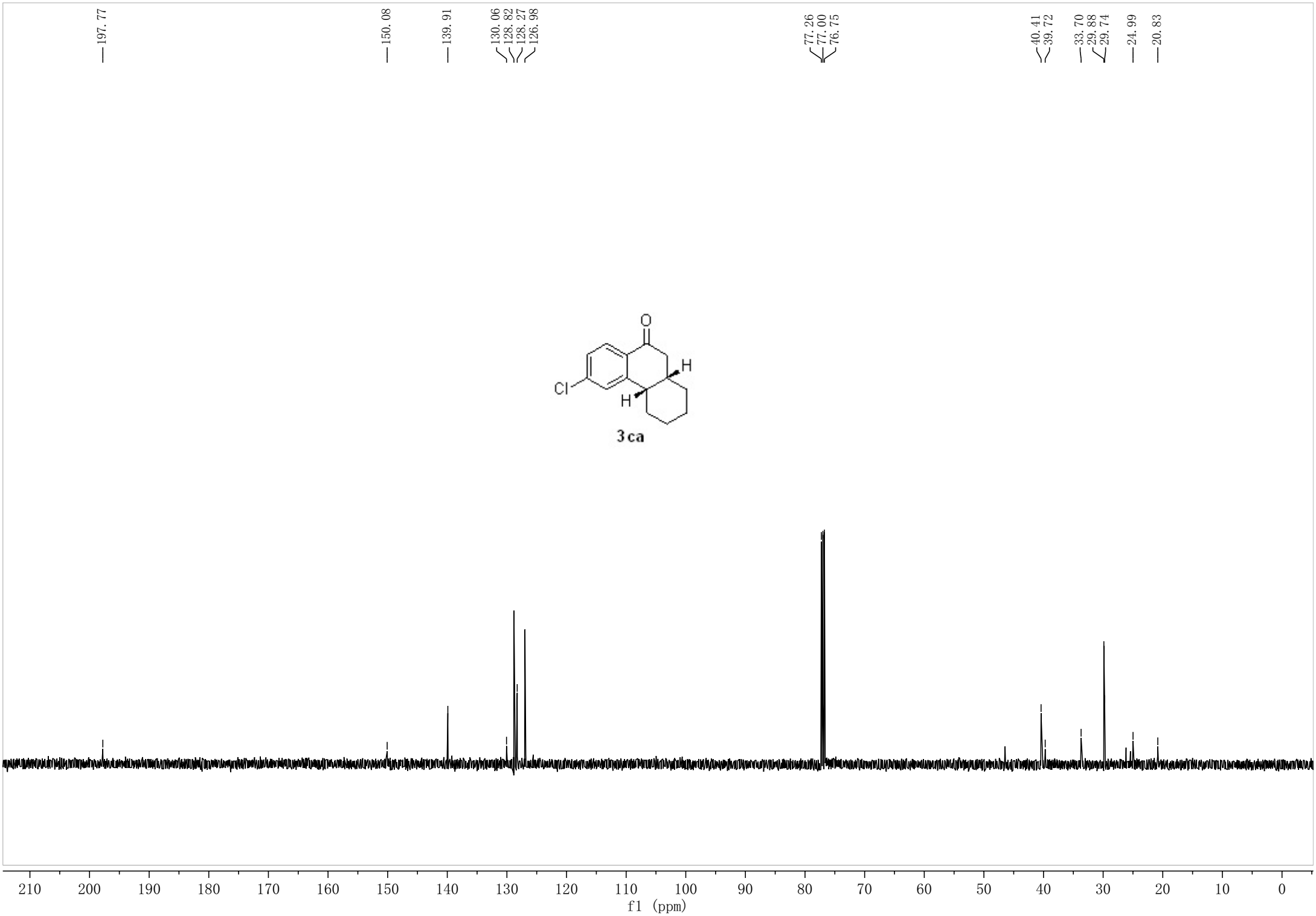
2.924
2.914
2.906
2.877
2.854
2.844
2.821
2.533
2.525
2.516
2.507
2.501
2.493
2.485
2.453
2.444
1.833
1.813
1.792
1.783
1.774
1.764
1.754
1.727
1.697
1.669
1.647
1.609
1.580
1.547
1.521
1.499
1.478
1.460
-0.000
O
Cl
H
H
3ca
1.00
2.24
1.08
1.08
2.39
10.22
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130.06
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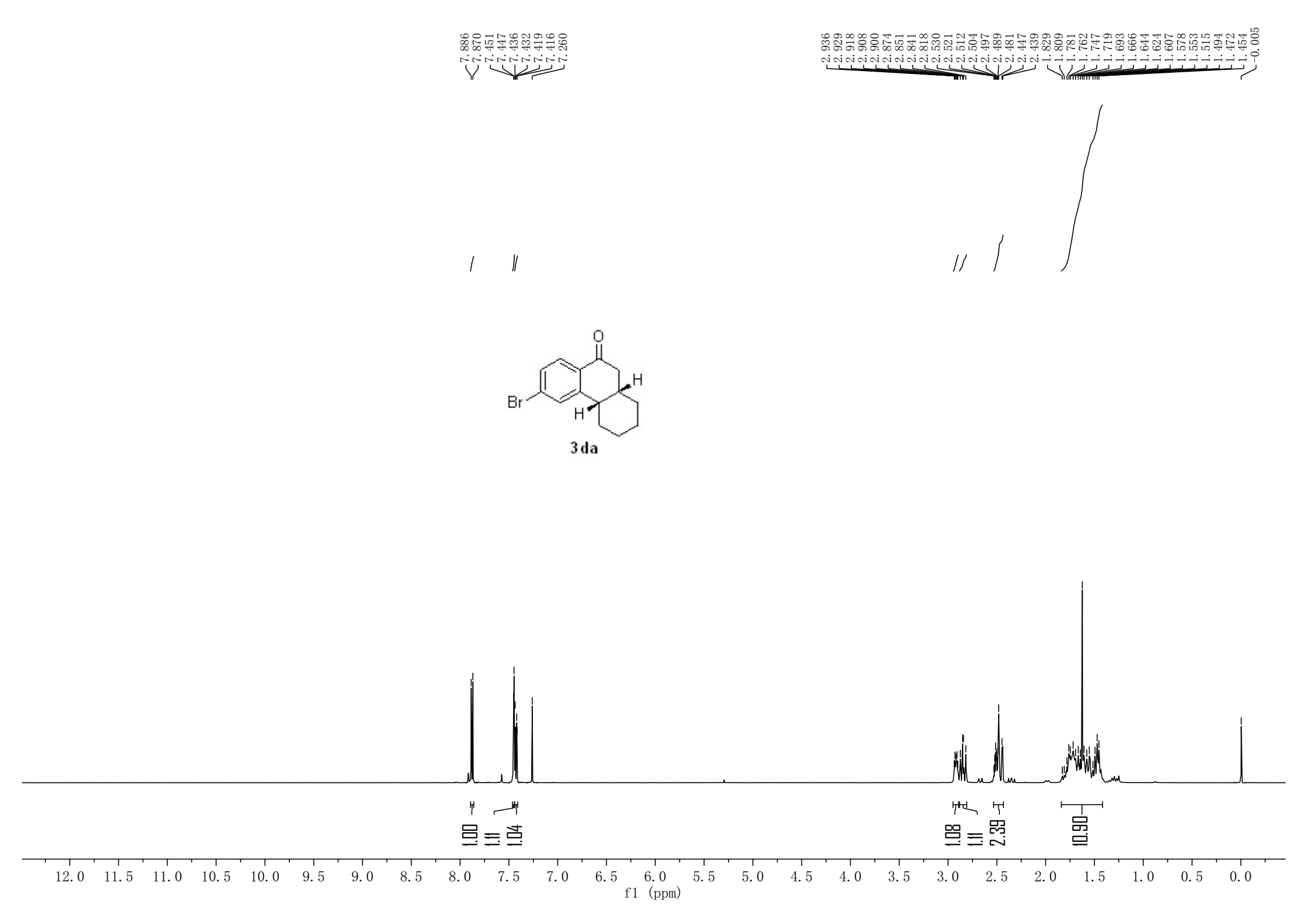
128.27
126.98
77.26
77.00
76.75
40.41
39.72
33.70
29.88
29.74
24.99
20.83
O
Cl
H
H
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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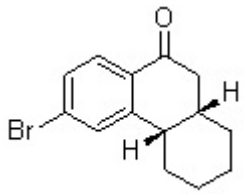
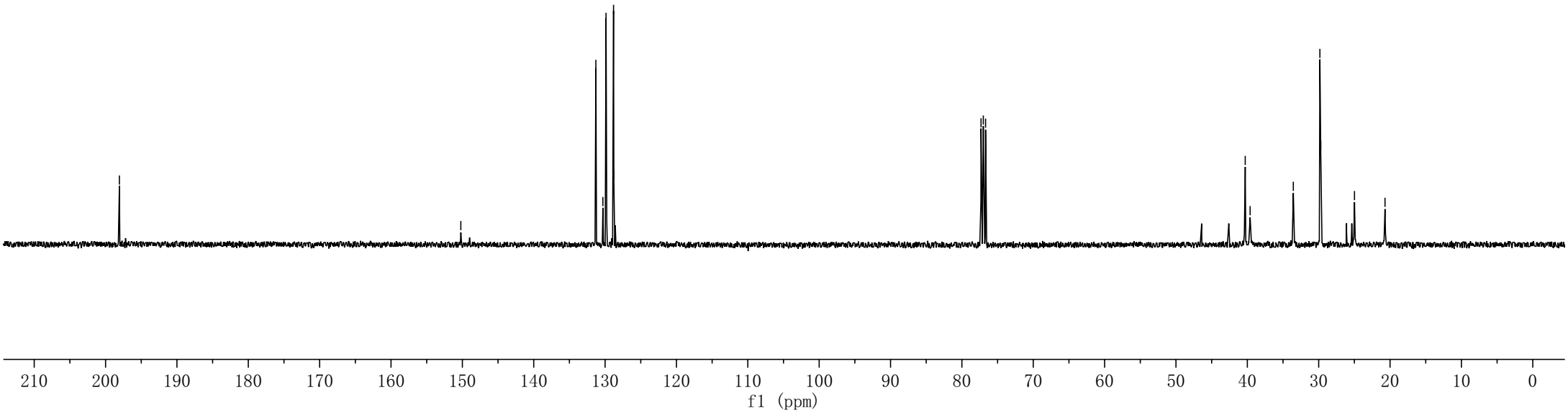
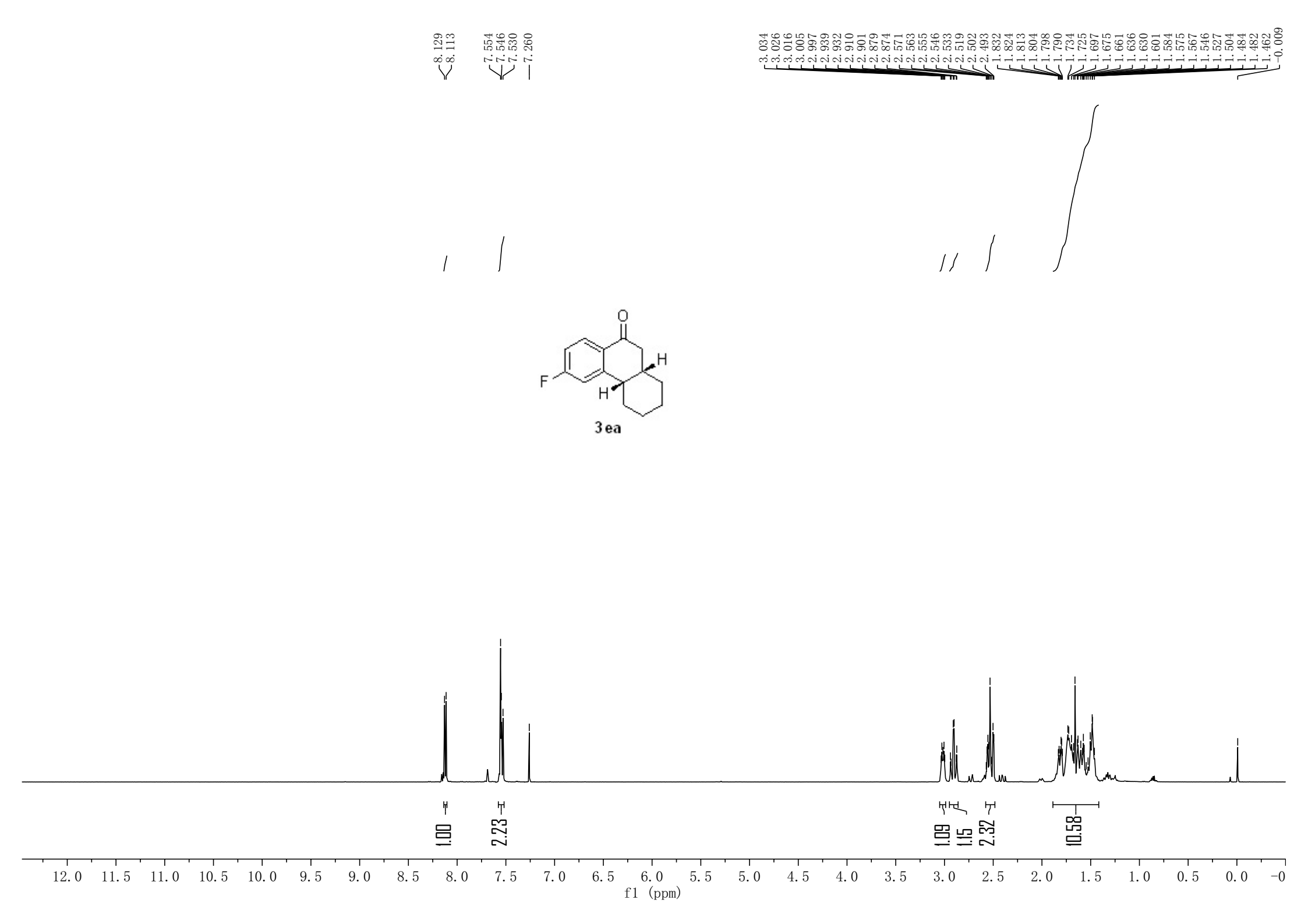
7.416
7.260
2.936
2.929
2.918
2.908
2.900
2.874
2.851
2.841
2.818
2.530
2.521
2.512
2.504
2.497
2.489
2.481
2.447
2.439
1.829
1.809
1.781
1.762
1.747
1.719
1.693
1.666
1.644
1.624
1.607
1.578
1.553
1.515
1.494
1.472
1.454
-0.005
O
Br
H
H
3da
1.00
1.11
1.04
1.08
1.11
2.39
10.90
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.06
150.22
131.29
130.31
129.87
128.82
128.77
77.32
77.00
76.68
40.29
39.61
33.56
29.83
29.71
24.98
20.71



3da

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7.530
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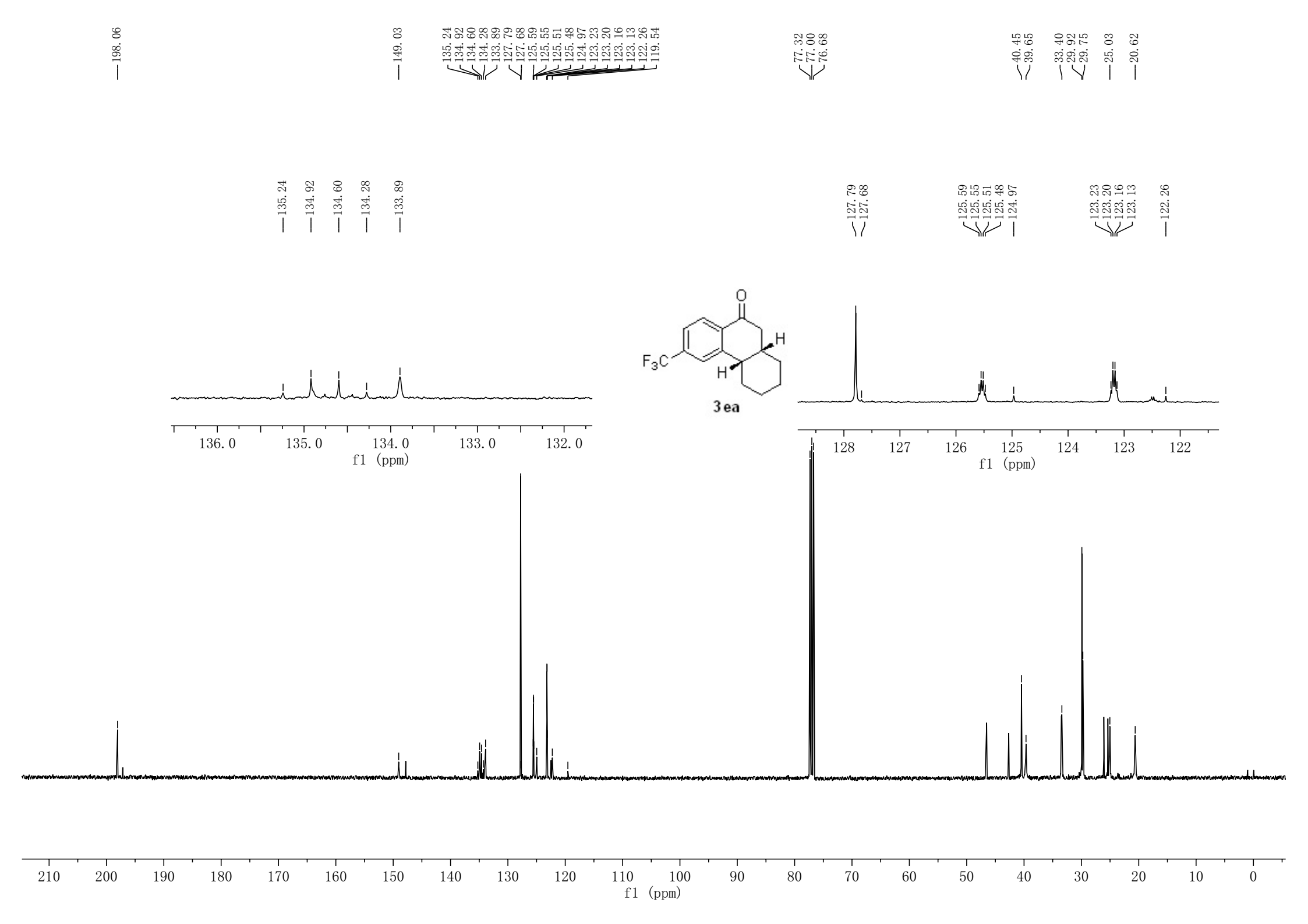
3.026
3.016
3.005
2.997
2.939
2.932
2.910
2.901
2.879
2.874
2.571
2.563
2.555
2.546
2.533
2.519
2.502
2.493
1.832
1.824
1.813
1.804
1.798
1.790
1.734
1.725
1.697
1.675
1.661
1.636
1.630
1.601
1.584
1.575
1.567
1.546
1.527
1.504
1.484
1.482
1.462
-0.009
O
F
H
H
3ea
1.00
2.23
1.09
1.15
2.32
10.58
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


198.06
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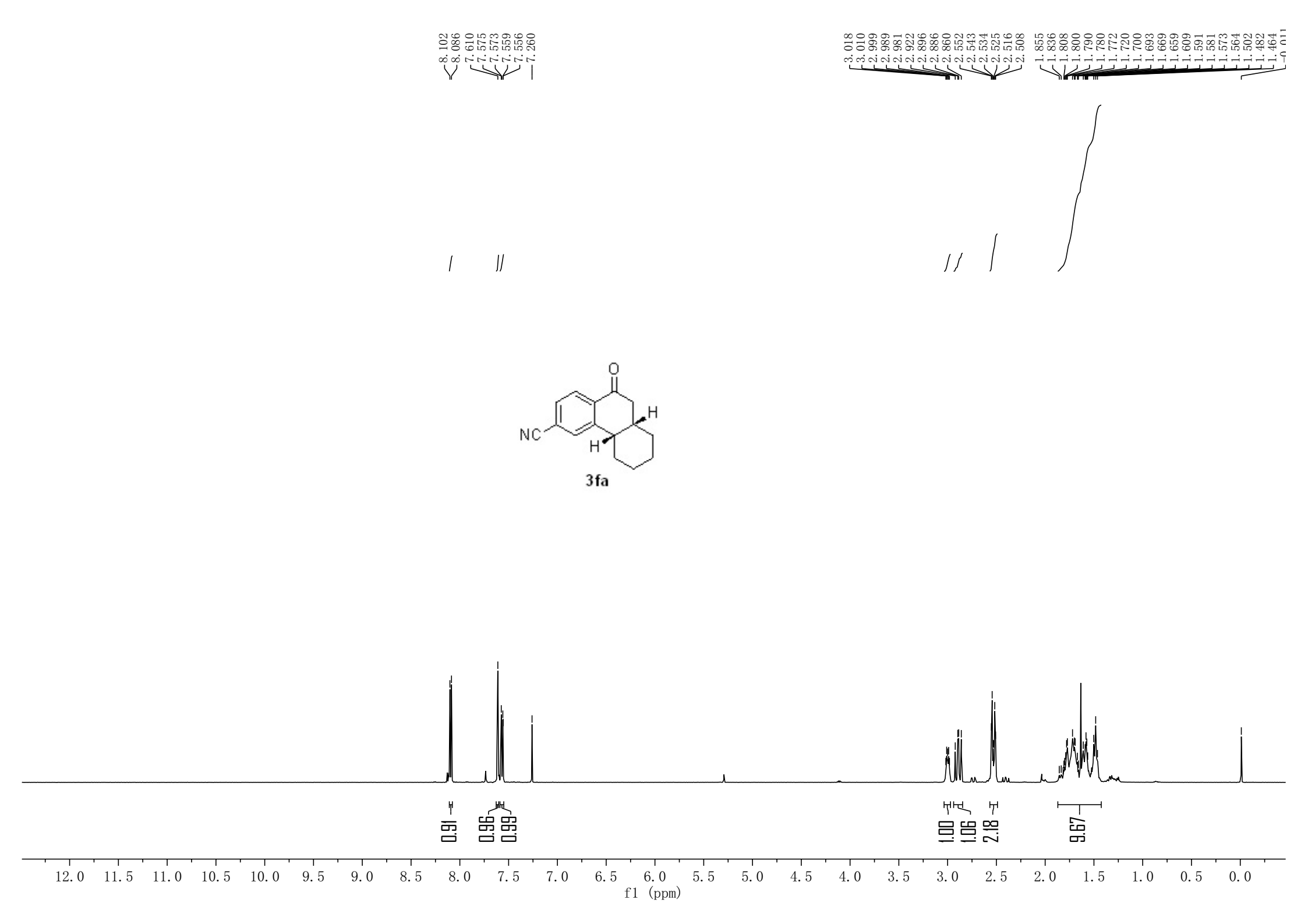
134.92
134.60
134.28
133.89
127.79
127.68
125.59
125.55
125.51
125.48
124.97
123.23
123.20
123.16
123.13
122.26
119.54
77.32
77.00
76.68
40.45
39.65
33.40
29.92
29.75
25.03
20.62
O
H
H
F3C
3ea
f1 (ppm)
f1 (ppm)
f1 (ppm)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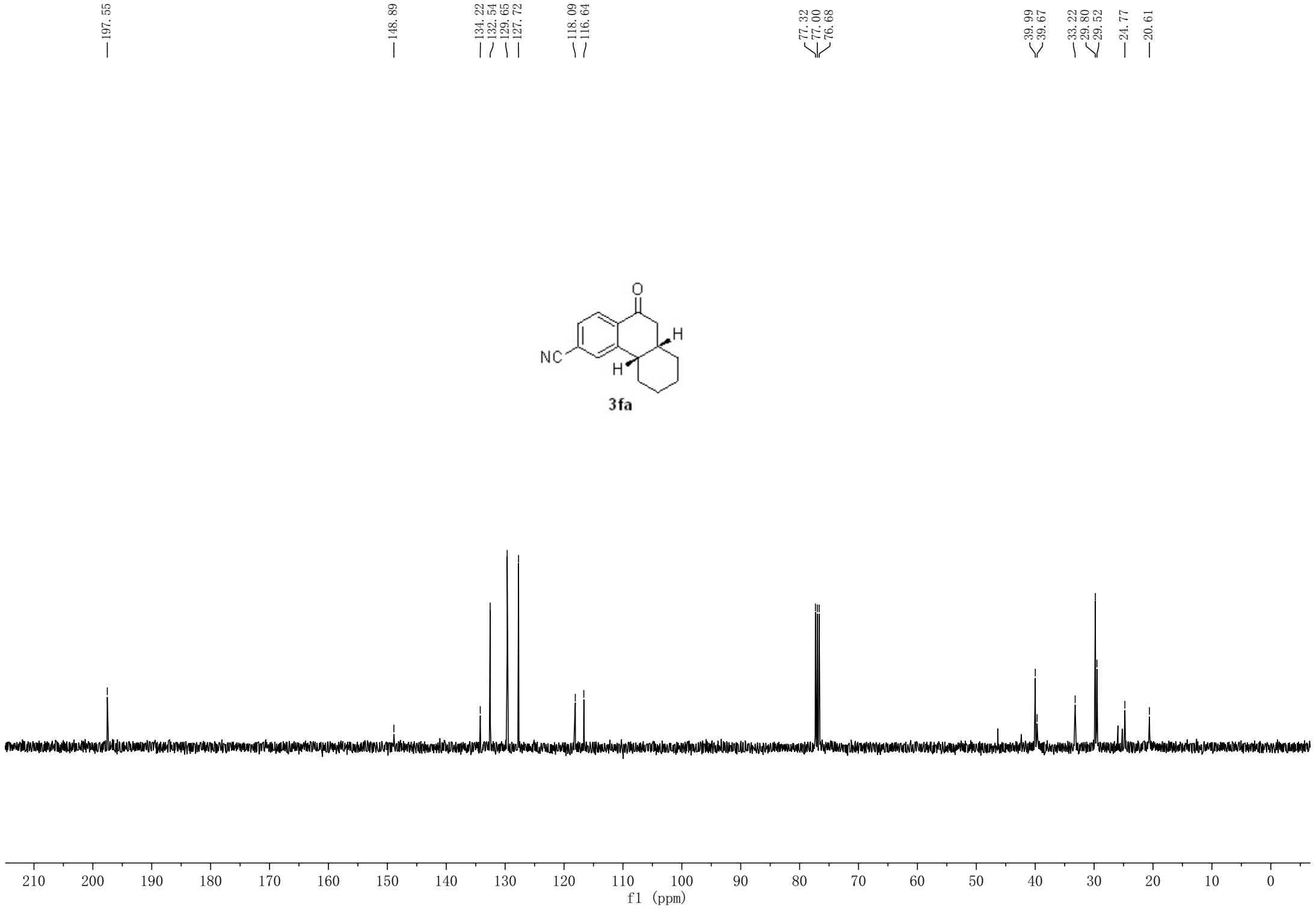
8.086
7.610
7.575
7.573
7.559
7.556
7.260
3.018
3.010
2.999
2.989
2.981
2.922
2.896
2.886
2.860
2.552
2.543
2.534
2.525
2.516
2.508
1.855
1.836
1.808
1.800
1.790
1.780
1.772
1.720
1.700
1.693
1.669
1.659
1.609
1.591
1.581
1.573
1.564
1.502
1.482
1.464
O
NC
H
H
3fa
0.91
0.96
0.99
1.00
1.06
2.18
9.67
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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148.89
134.22
132.54
129.65
127.72
118.09
116.64
77.32
77.00
76.68
39.99
39.67
33.22
29.80
29.52
24.77
20.61
O
NC
H
H
3fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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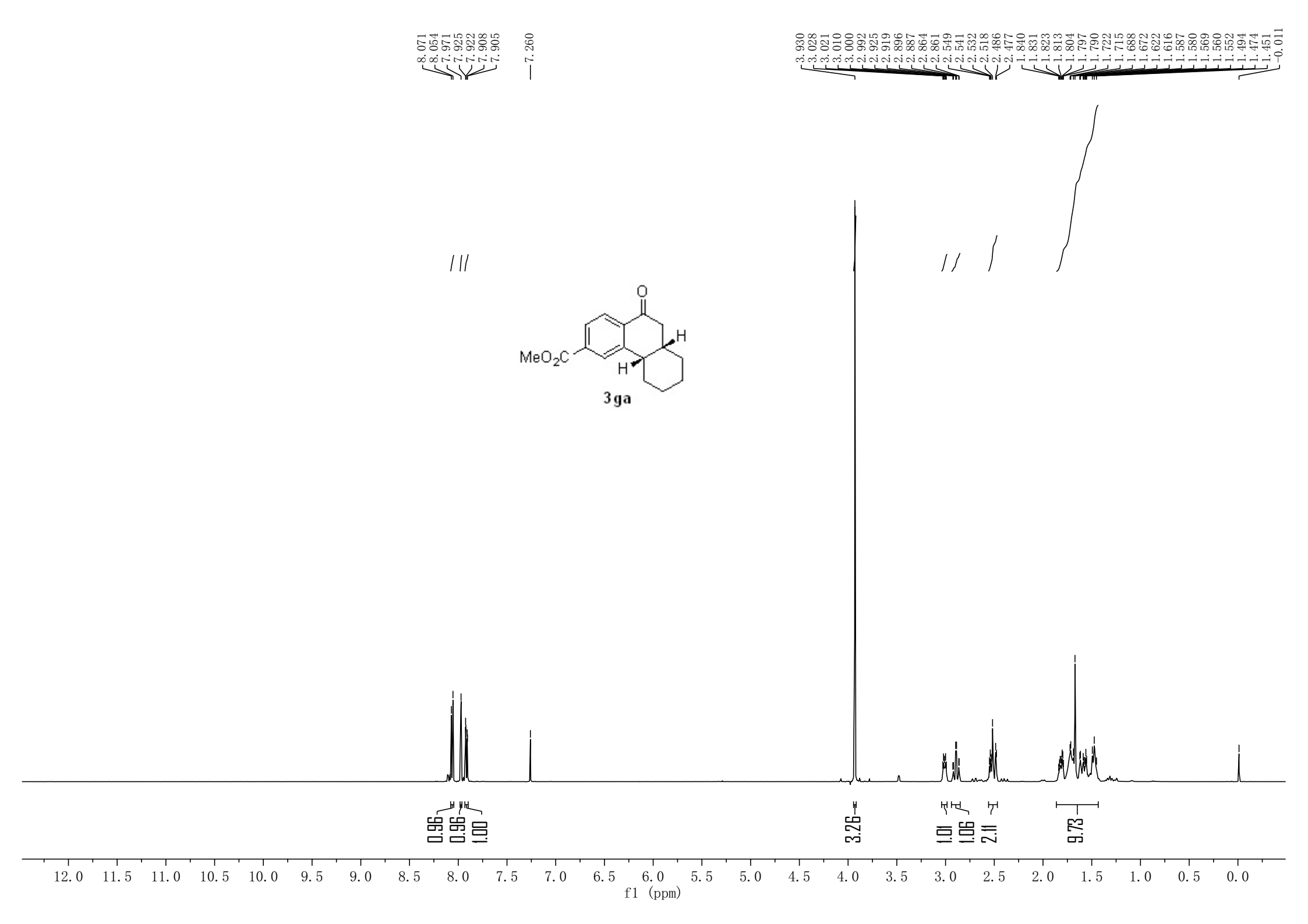
f1 (ppm)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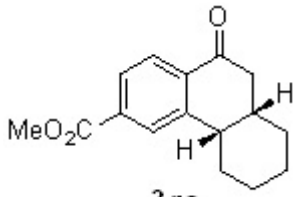
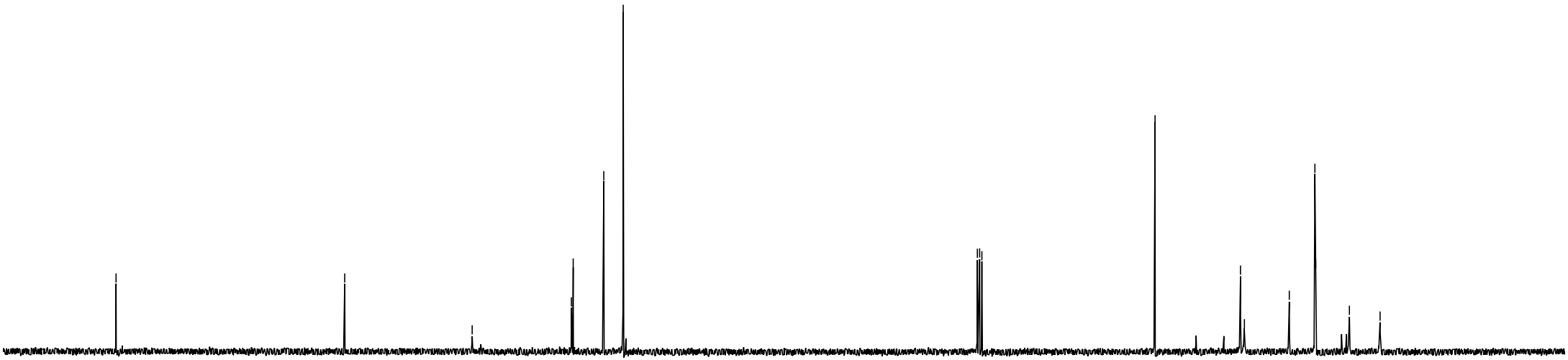
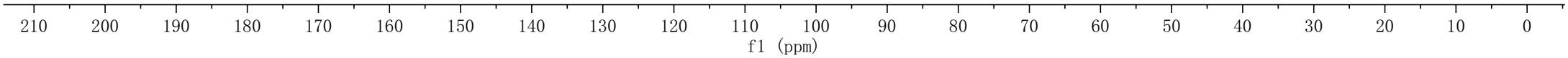
8.054
7.971
7.925
7.922
7.908
7.905
7.260
3.930
3.028
3.021
3.010
3.000
2.992
2.925
2.919
2.896
2.887
2.864
2.861
2.549
2.541
2.532
2.518
2.486
2.477
1.840
1.831
1.823
1.813
1.804
1.797
1.790
1.722
1.715
1.688
1.672
1.622
1.616
1.587
1.580
1.569
1.560
1.552
1.494
1.474
1.451
-0.011
O
MeO2C
H
H
3ga
0.96
0.96
1.00
3.26
1.01
1.06
2.11
9.73
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

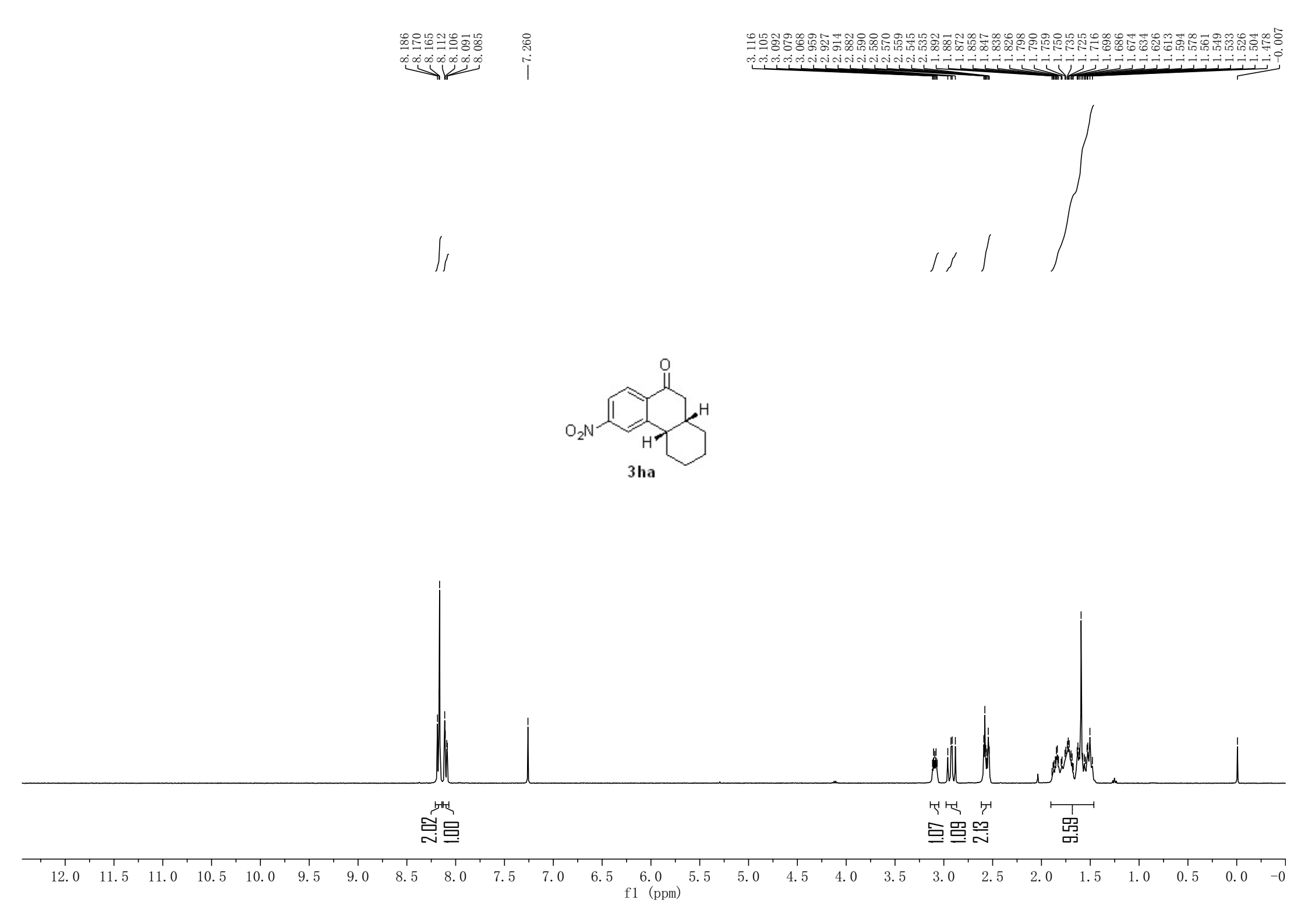
198.46
166.30
148.37
134.42
134.16
129.86
127.16
127.13
77.32
77.00
76.68
52.33
40.31
39.76
33.44
29.84
29.73
24.99
20.67



3ga



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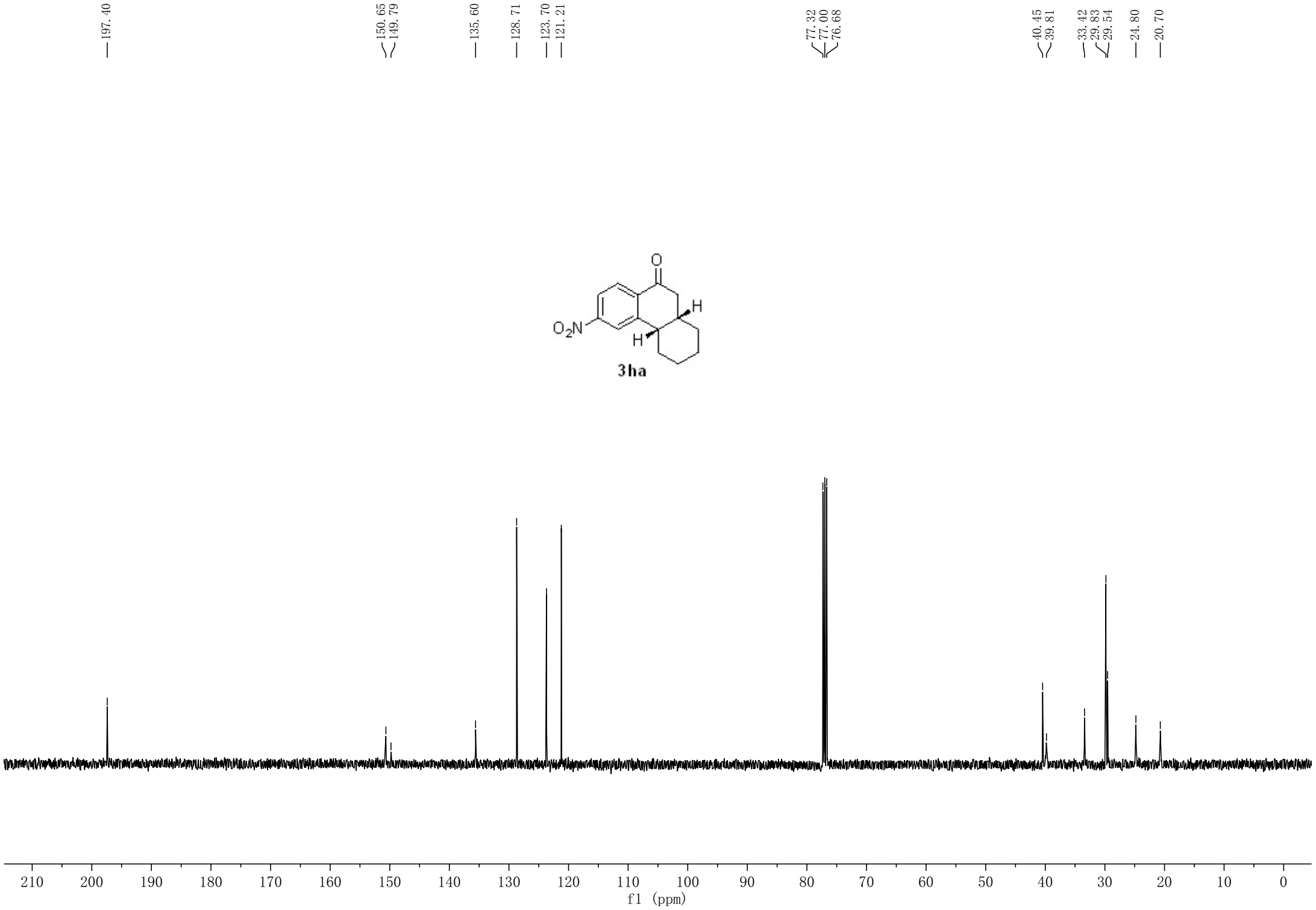
8.170
8.165
8.112
8.106
8.091
8.085
7.260
3.116
3.105
3.092
3.079
3.068
2.959
2.927
2.914
2.882
2.590
2.580
2.570
2.559
2.545
2.535
1.892
1.881
1.872
1.858
1.847
1.838
1.826
1.798
1.790
1.759
1.750
1.735
1.725
1.716
1.698
1.686
1.674
1.634
1.626
1.613
1.594
1.578
1.561
1.549
1.533
1.526
1.504
1.478
-0.007
O
H
H
O2N
3ha
2.02
1.00
1.07
1.09
2.13
9.59
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)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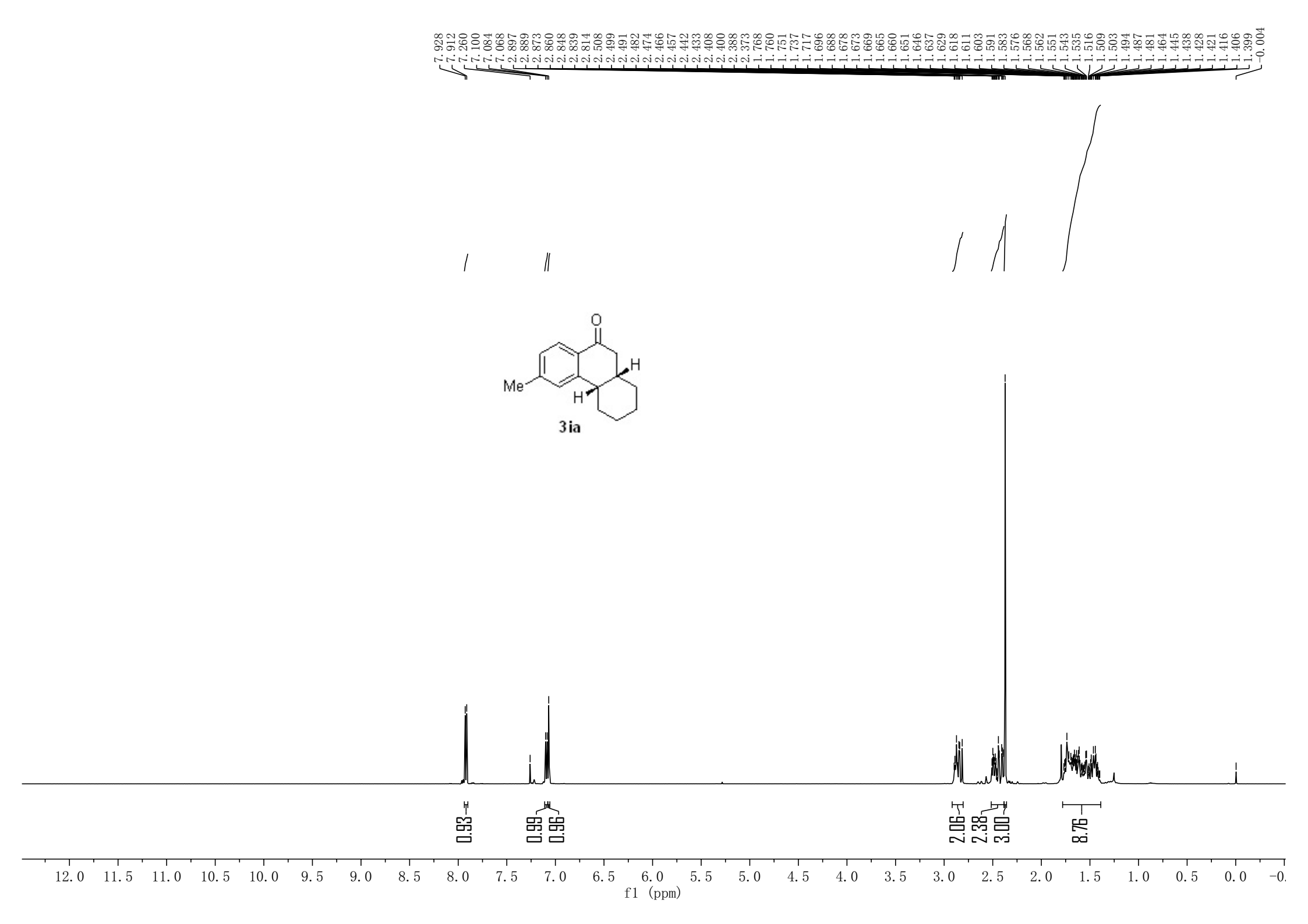
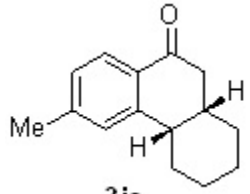
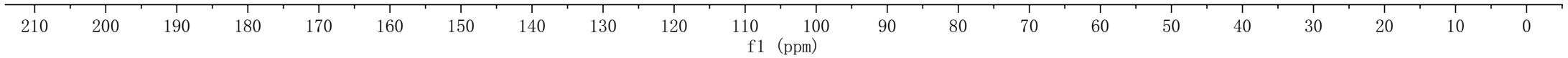
150.65
149.79
135.60
128.71
123.70
121.21
77.32
77.00
76.68
40.45
39.81
33.42
29.83
29.54
24.80
20.70
O
H
H
O2N
3ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

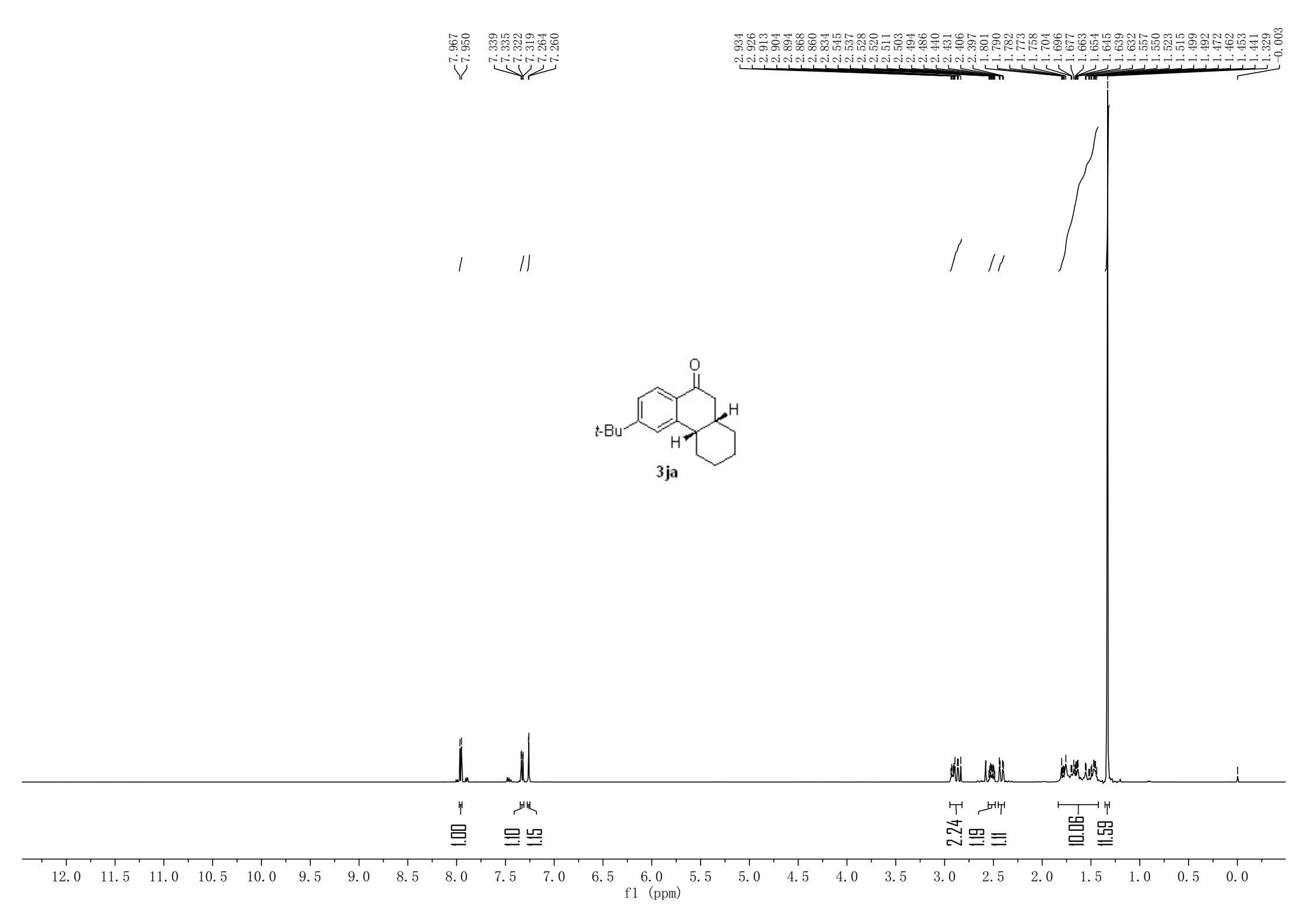

7.928
7.912
7.260
7.100
7.084
7.068
2.897
2.889
2.873
2.860
2.848
2.839
2.814
2.508
2.499
2.491
2.482
2.474
2.466
2.457
2.442
2.433
2.408
2.400
2.388
2.373
1.768
1.760
1.751
1.737
1.717
1.696
1.688
1.678
1.673
1.669
1.665
1.660
1.651
1.646
1.637
1.629
1.618
1.611
1.603
1.591
1.583
1.576
1.568
1.562
1.551
1.543
1.535
1.516
1.509
1.503
1.494
1.487
1.481
1.464
1.445
1.438
1.428
1.421
1.416
1.406
1.399
-0.004
O
Me
H
H
3ia
0.93
0.99
0.96
2.06
2.38
3.00
8.76
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.69
148.73
144.36
129.28
128.76
127.46
127.17
77.26
77.00
76.75
40.54
39.66
33.77
30.03
29.98
25.27
21.71
20.78



3ia

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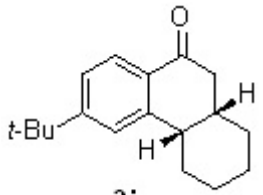
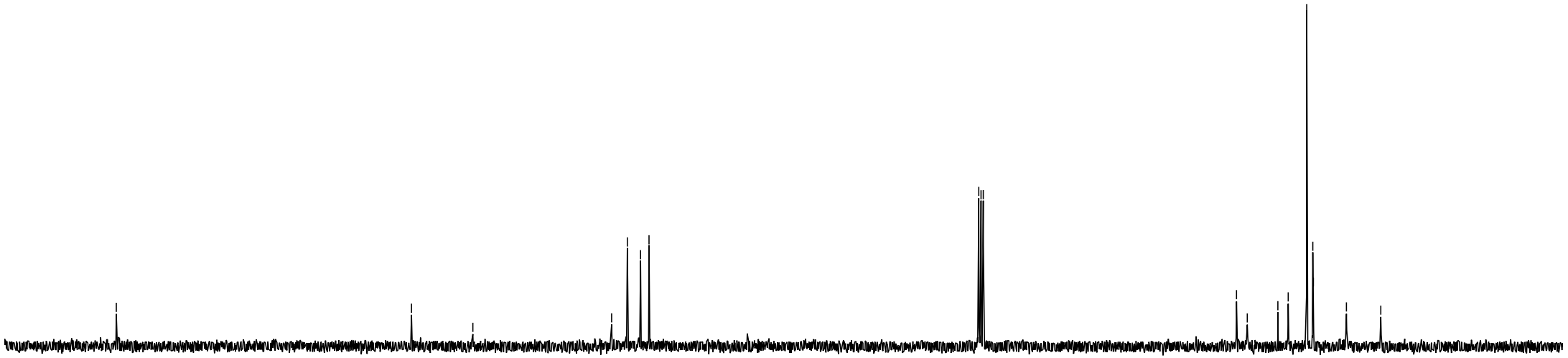
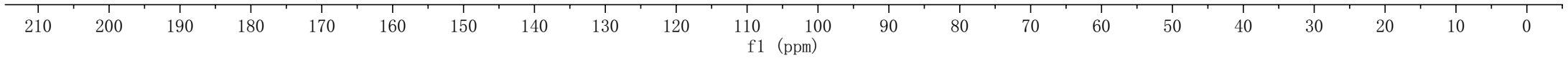
7.322
7.319
7.264
7.260
2.934
2.926
2.913
2.904
2.894
2.868
2.860
2.834
2.545
2.537
2.528
2.520
2.511
2.503
2.494
2.486
2.440
2.431
2.406
2.397
1.801
1.790
1.782
1.773
1.758
1.704
1.696
1.677
1.663
1.654
1.645
1.639
1.632
1.557
1.550
1.523
1.515
1.499
1.492
1.472
1.462
1.453
1.441
1.329
-0.003
O
t-Bu
H
H
3ja
1.00
1.10
1.15
2.24
1.19
1.11
10.06
11.59
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

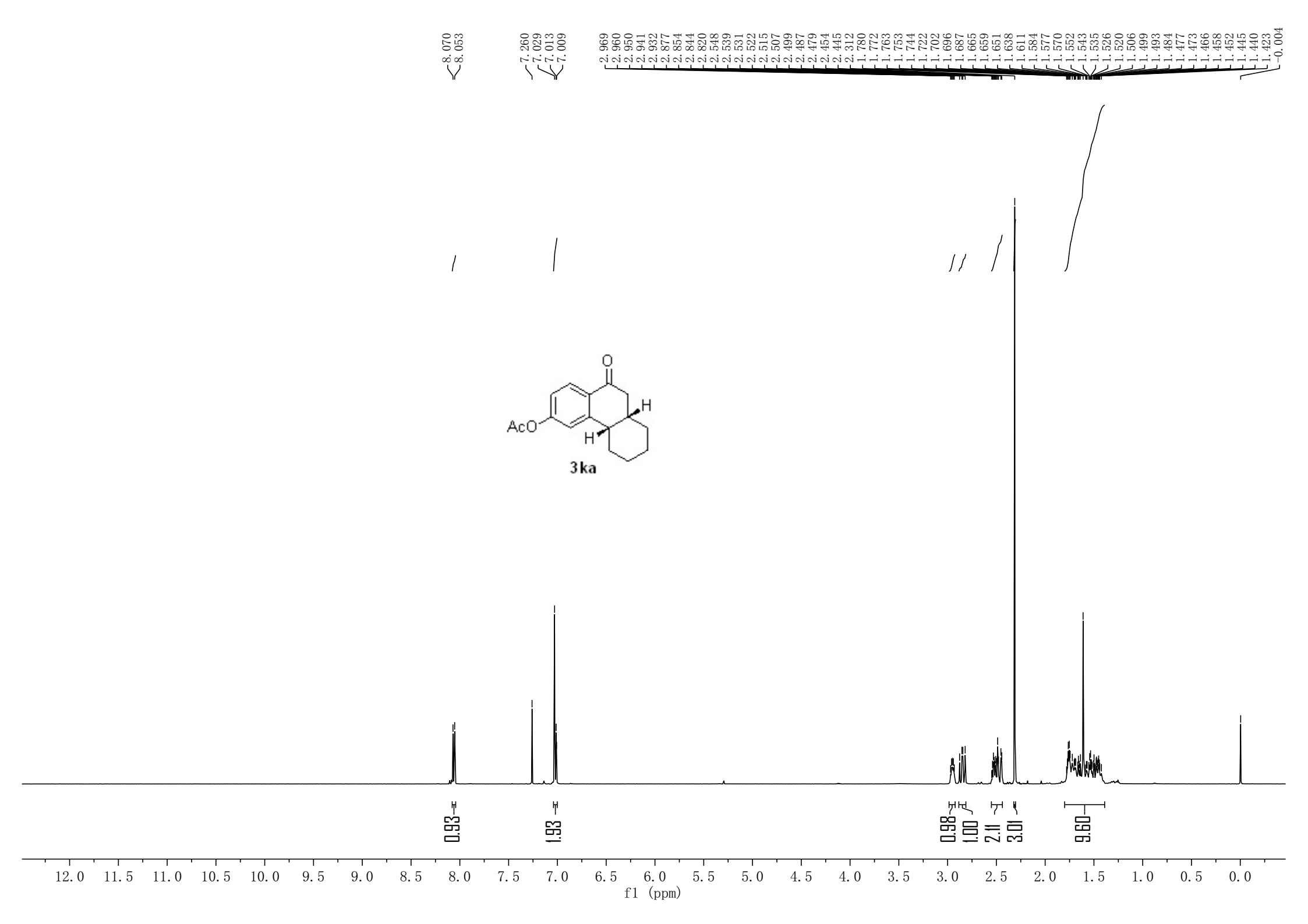
198.98
157.34
148.69
129.11
126.90
125.03
123.84
77.32
77.00
76.68
40.96
39.44
35.13
33.67
31.06
30.20
30.11
25.45
20.61

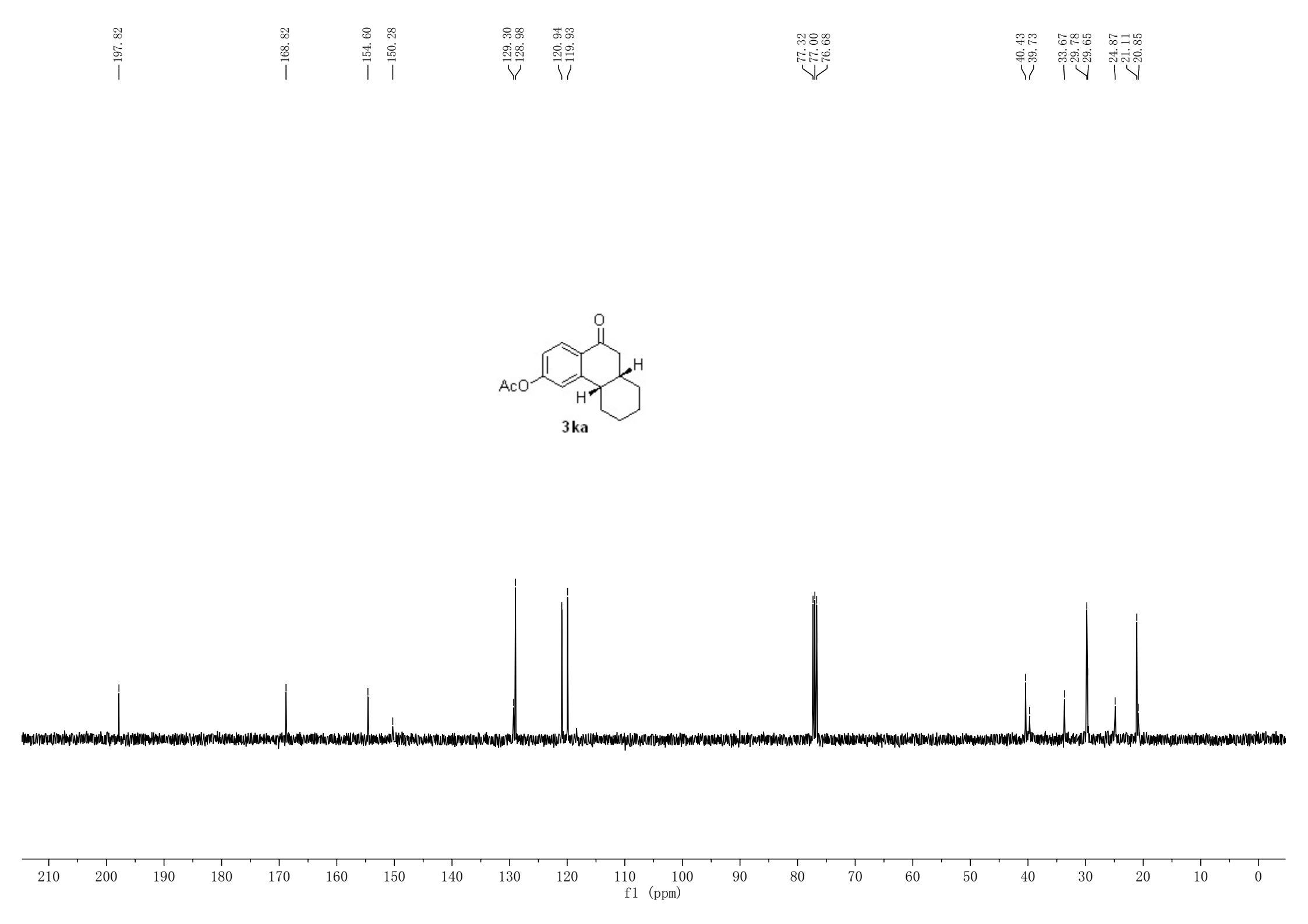


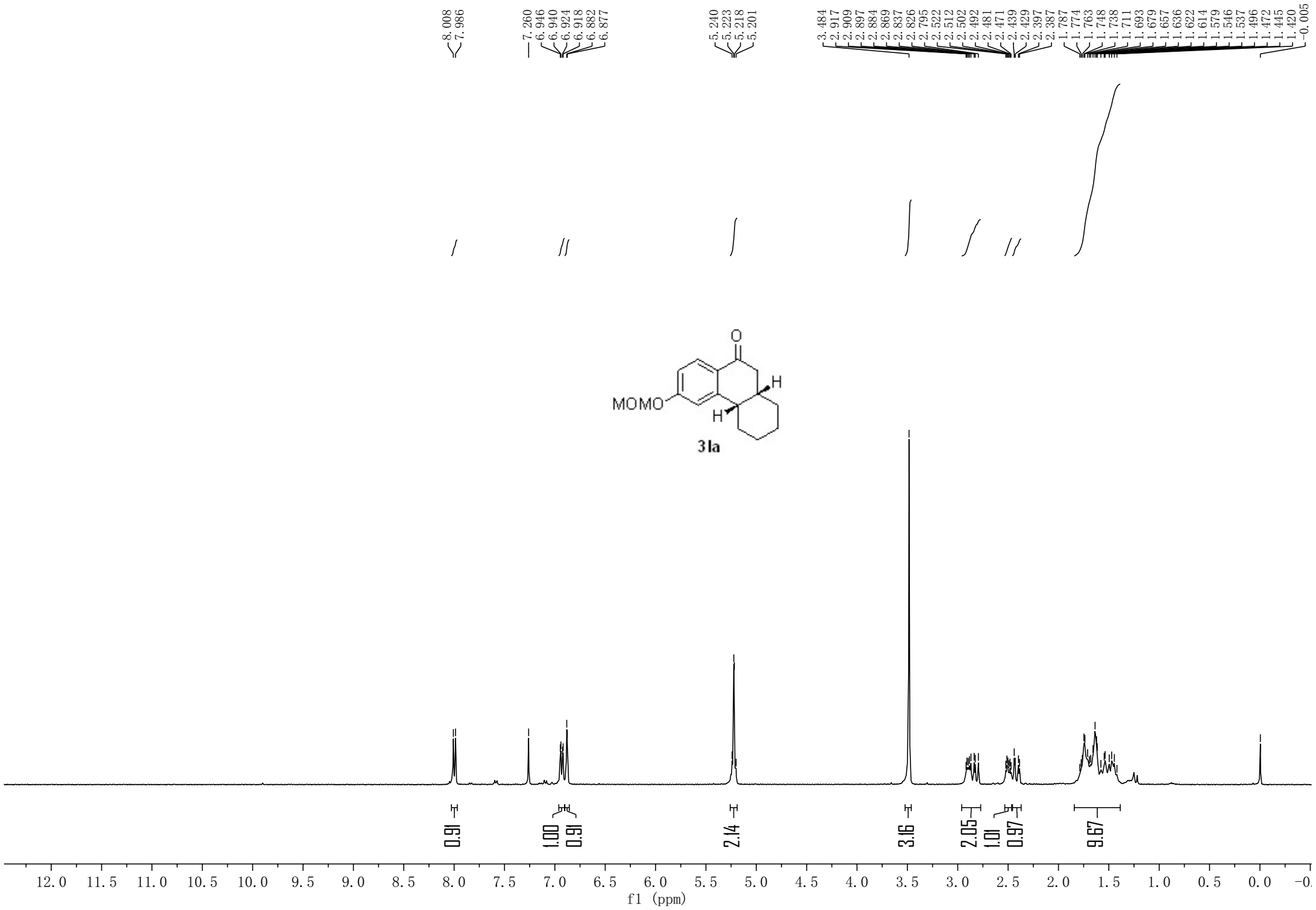
3ja






8.070
8.053
7.260
7.029
7.013
7.009
2.969
2.960
2.950
2.941
2.932
2.877
2.854
2.844
2.820
2.548
2.539
2.531
2.522
2.515
2.507
2.499
2.487
2.479
2.454
2.445
2.312
1.780
1.772
1.763
1.753
1.744
1.722
1.702
1.696
1.687
1.665
1.659
1.651
1.638
1.611
1.584
1.577
1.570
1.552
1.543
1.535
1.526
1.520
1.506
1.499
1.493
1.484
1.477
1.473
1.466
1.458
1.452
1.445
1.440
1.423
-0.004
O
AcO
H
H
3ka
0.93
1.93
0.98
1.00
2.11
3.01
9.60
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.82
168.82
154.60
150.28
129.30
128.98
120.94
119.93
77.32
77.00
76.68
40.43
39.73
33.67
29.78
29.65
24.87
21.11
20.85
O
AcO
H
H
3ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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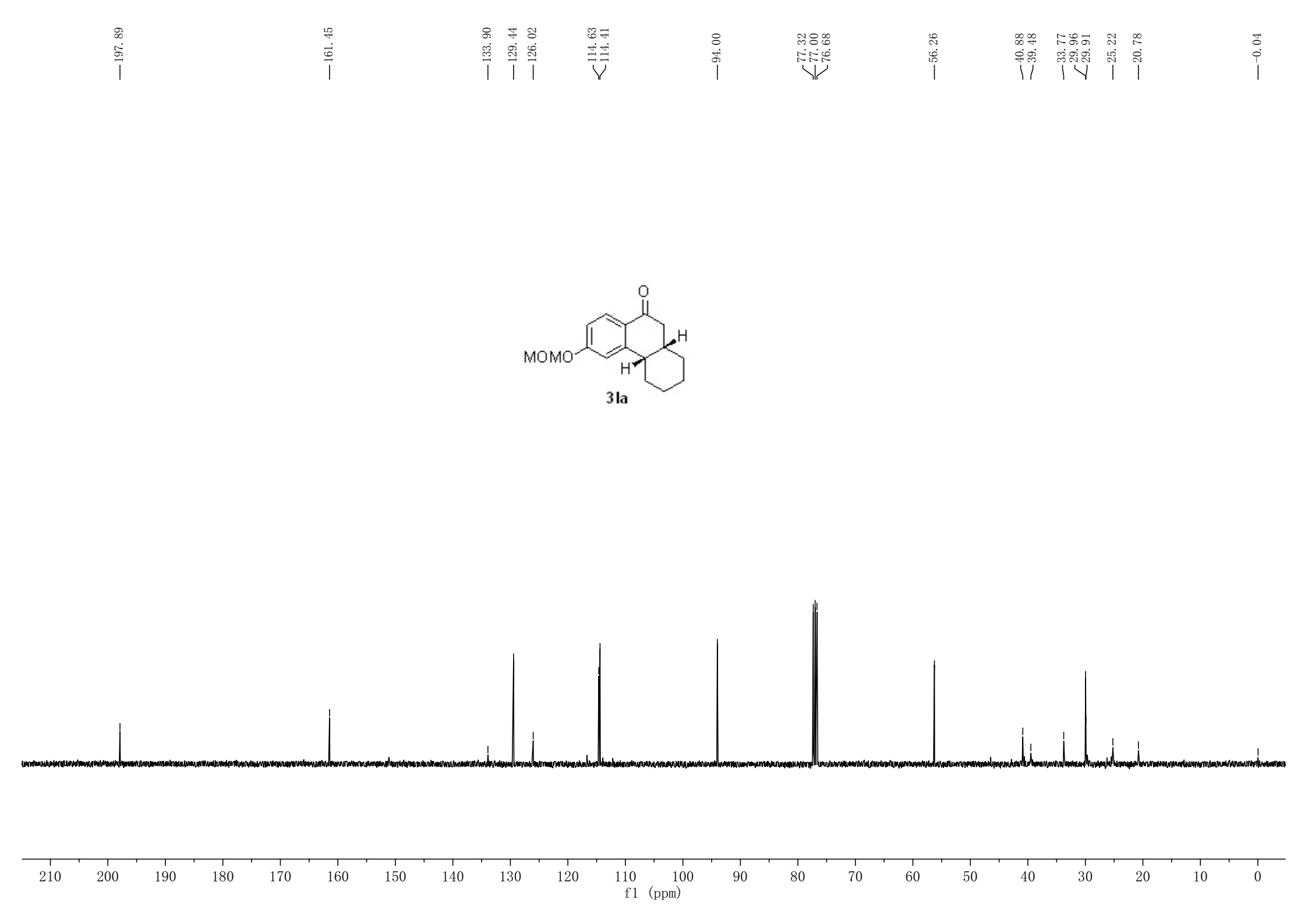
7.986
7.260
6.946
6.940
6.924
6.918
6.882
6.877
5.240
5.223
5.218
5.201
3.484
2.917
2.909
2.897
2.884
2.869
2.837
2.826
2.795
2.522
2.512
2.502
2.492
2.481
2.471
2.439
2.429
2.397
2.387
1.787
1.774
1.763
1.748
1.738
1.711
1.693
1.679
1.657
1.636
1.622
1.614
1.579
1.546
1.537
1.496
1.472
1.445
1.420
-0.005
O
MOMO
H
H
3la
0.91
1.00
0.91
2.14
3.16
2.05
1.01
0.97
9.67
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.89
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133.90
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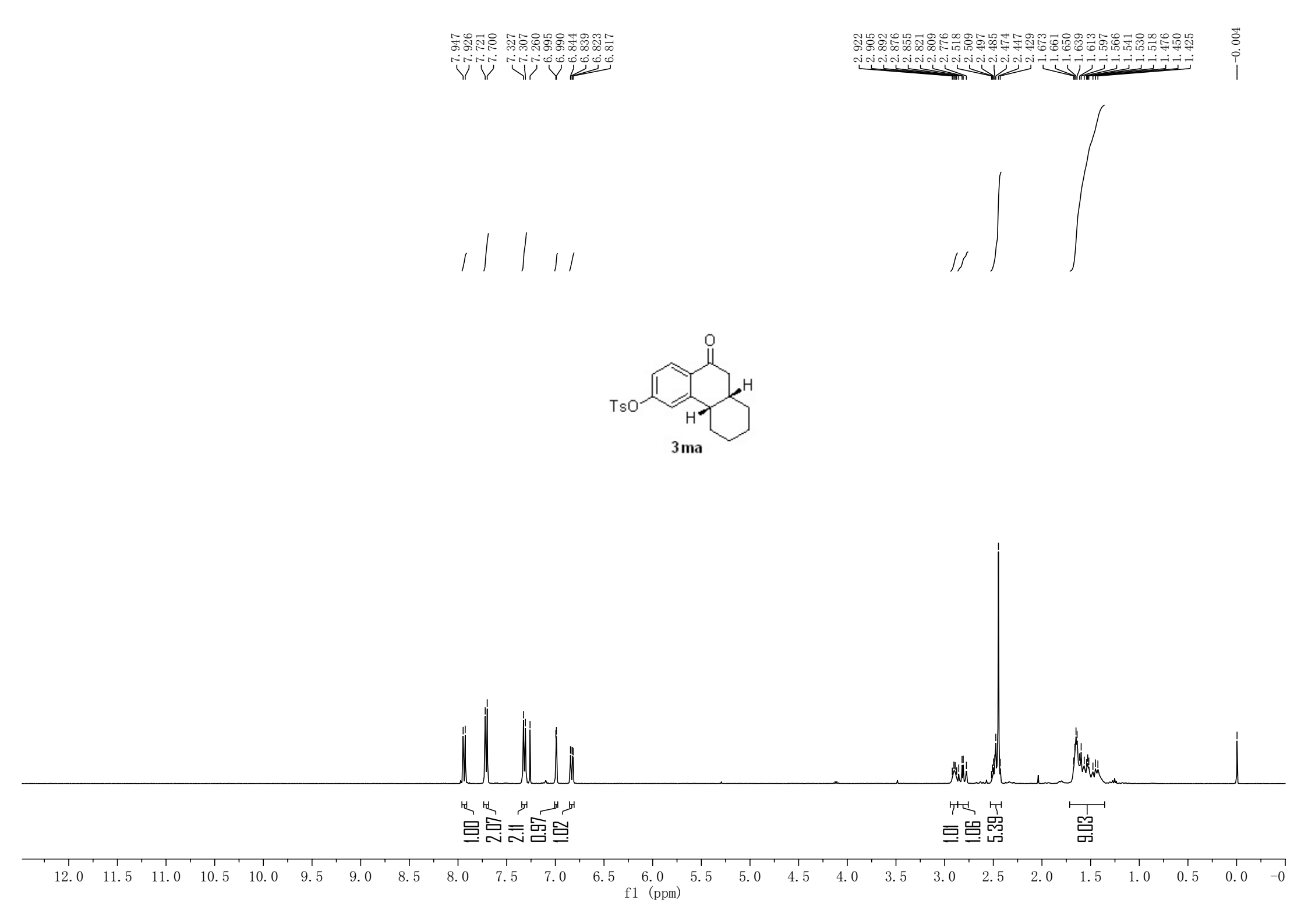
114.63
114.41
94.00
77.32
77.00
76.68
56.26
40.88
39.48
33.77
29.96
29.91
25.22
20.78
-0.04
O
MOMO
H
H
3la
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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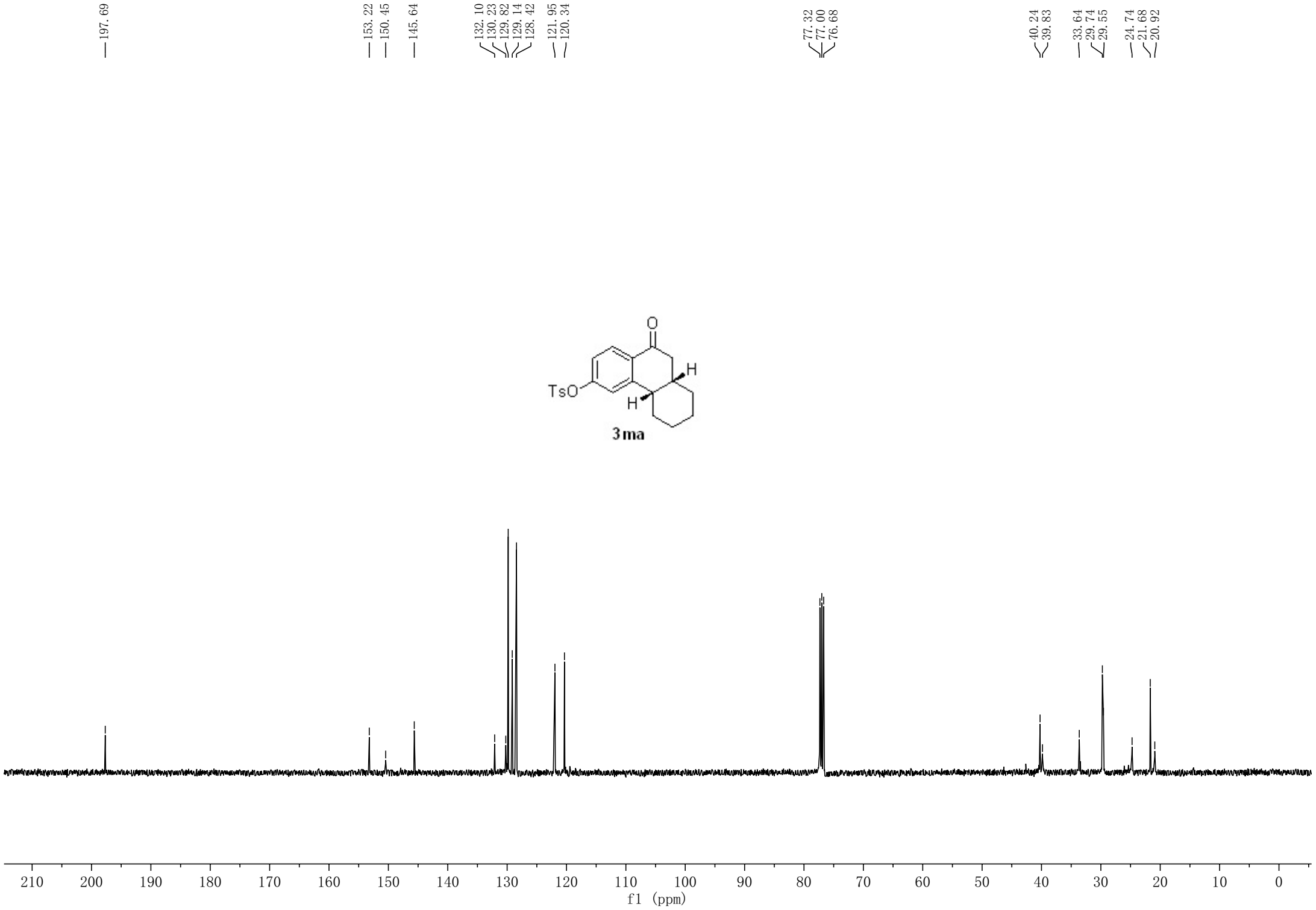
7.721
7.700
7.327
7.307
7.260
6.995
6.990
6.844
6.839
6.823
6.817
2.922
2.905
2.892
2.876
2.855
2.821
2.809
2.776
2.518
2.509
2.497
2.485
2.474
2.447
2.429
1.673
1.661
1.650
1.639
1.613
1.597
1.566
1.541
1.530
1.518
1.476
1.450
1.425
-0.004
O
TsO
H
H
3ma
1.00
2.07
2.11
0.97
1.02
1.01
1.06
5.39
9.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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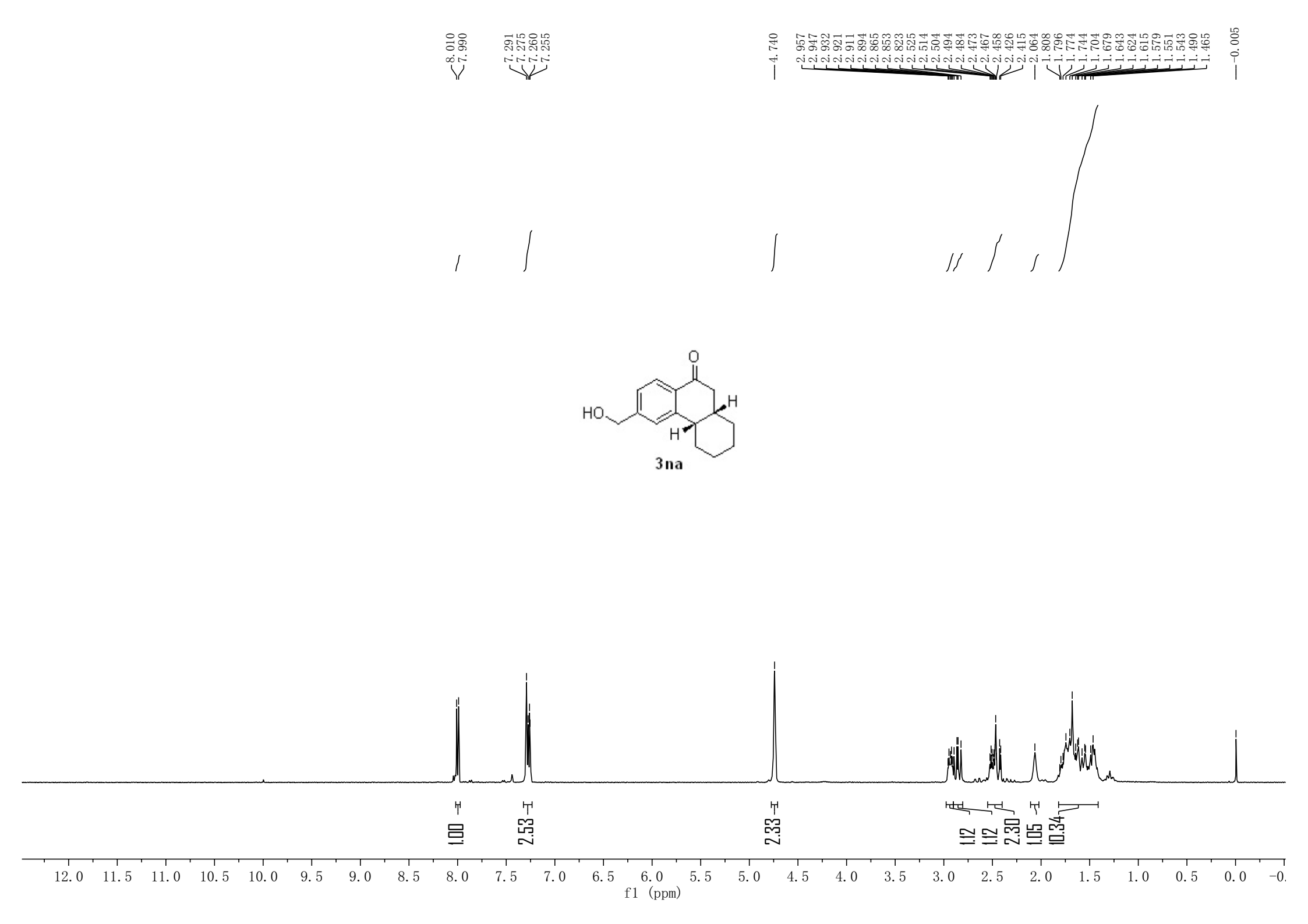
150.45
145.64
132.10
130.23
129.82
129.14
128.42
121.95
120.34
77.32
77.00
76.68
40.24
39.83
33.64
29.74
29.55
24.74
21.68
20.92
O
TsO
H
H
3ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.275
7.260
7.255
4.740
2.957
2.947
2.932
2.921
2.911
2.894
2.865
2.853
2.823
2.525
2.514
2.504
2.494
2.484
2.473
2.467
2.458
2.426
2.415
2.064
1.808
1.796
1.774
1.744
1.704
1.679
1.643
1.624
1.615
1.579
1.551
1.543
1.490
1.465
-0.005
HO
O
H
H
3na
1.00
2.53
2.33
1.12
1.12
2.30
1.05
10.34
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

199.17

146.98
146.94

130.59
127.35
126.20
124.59

77.32
77.00
76.68

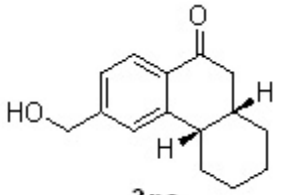
64.57

40.54
39.59

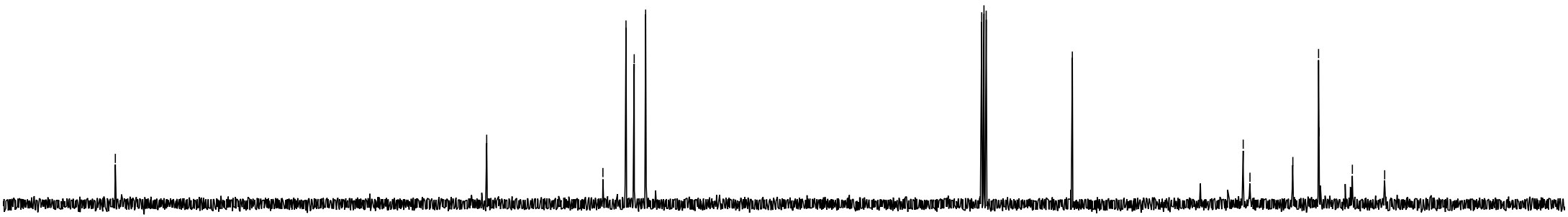
33.56
29.94
29.87

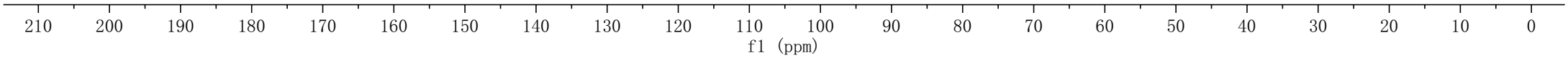
25.19

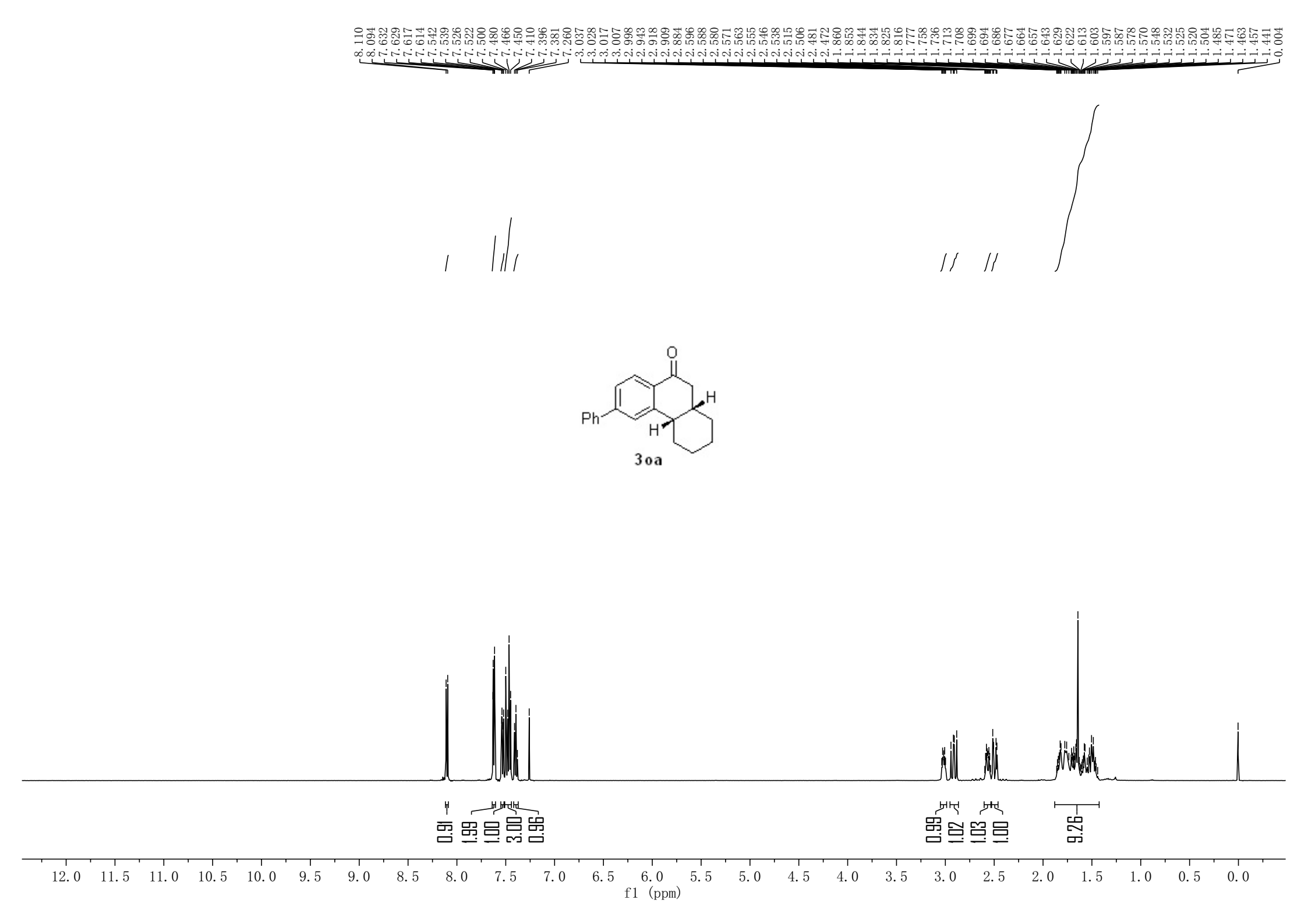
20.64



3na



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Ph
H
H
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3.00
0.96
0.99
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1.03
1.00
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11.0
10.5
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9.0
8.5
8.0
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6.5
6.0
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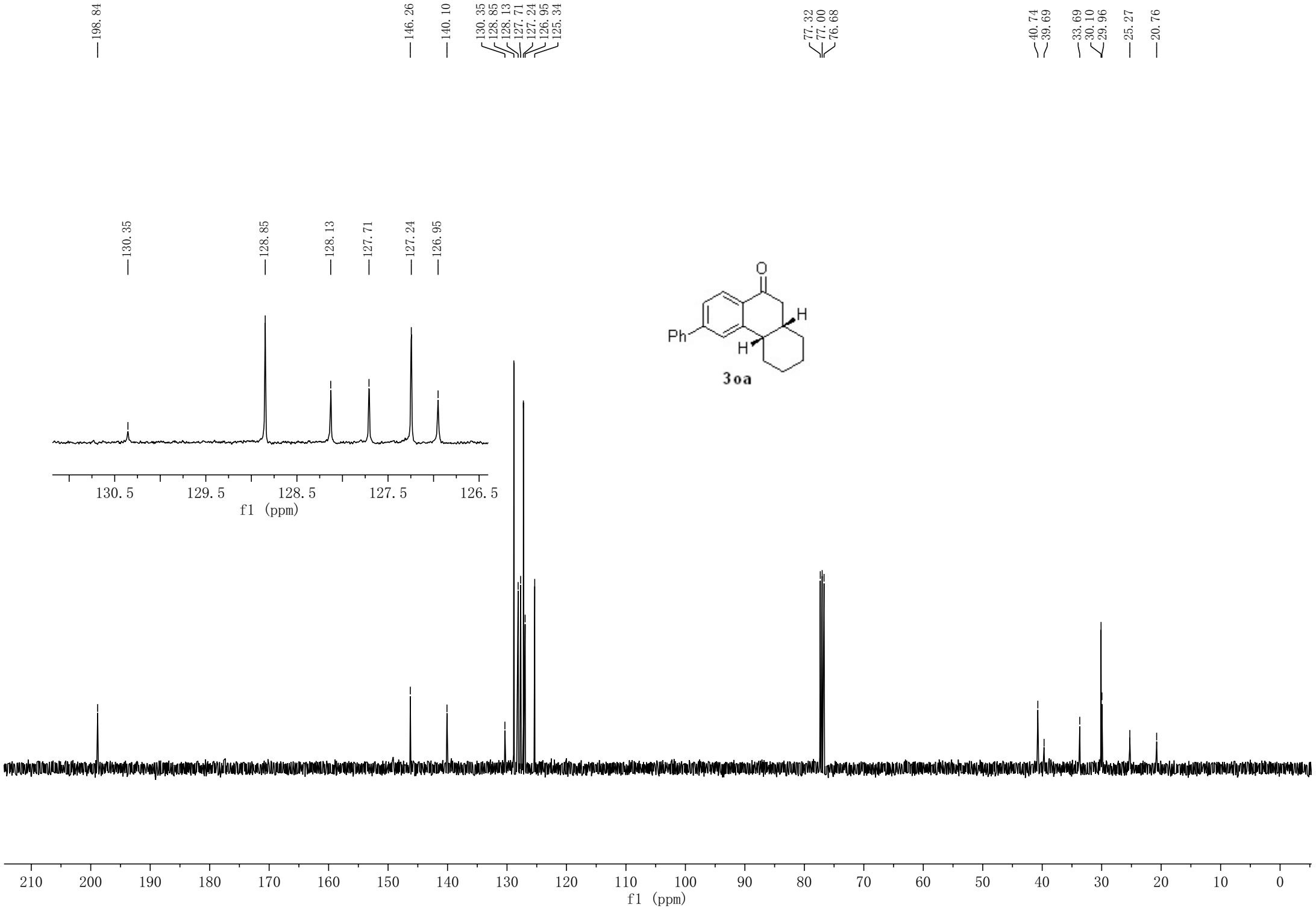
f1 (ppm)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130.5
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126.5
f1 (ppm)
O
H
Ph
H
3oa
210
200
190
180
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50
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10
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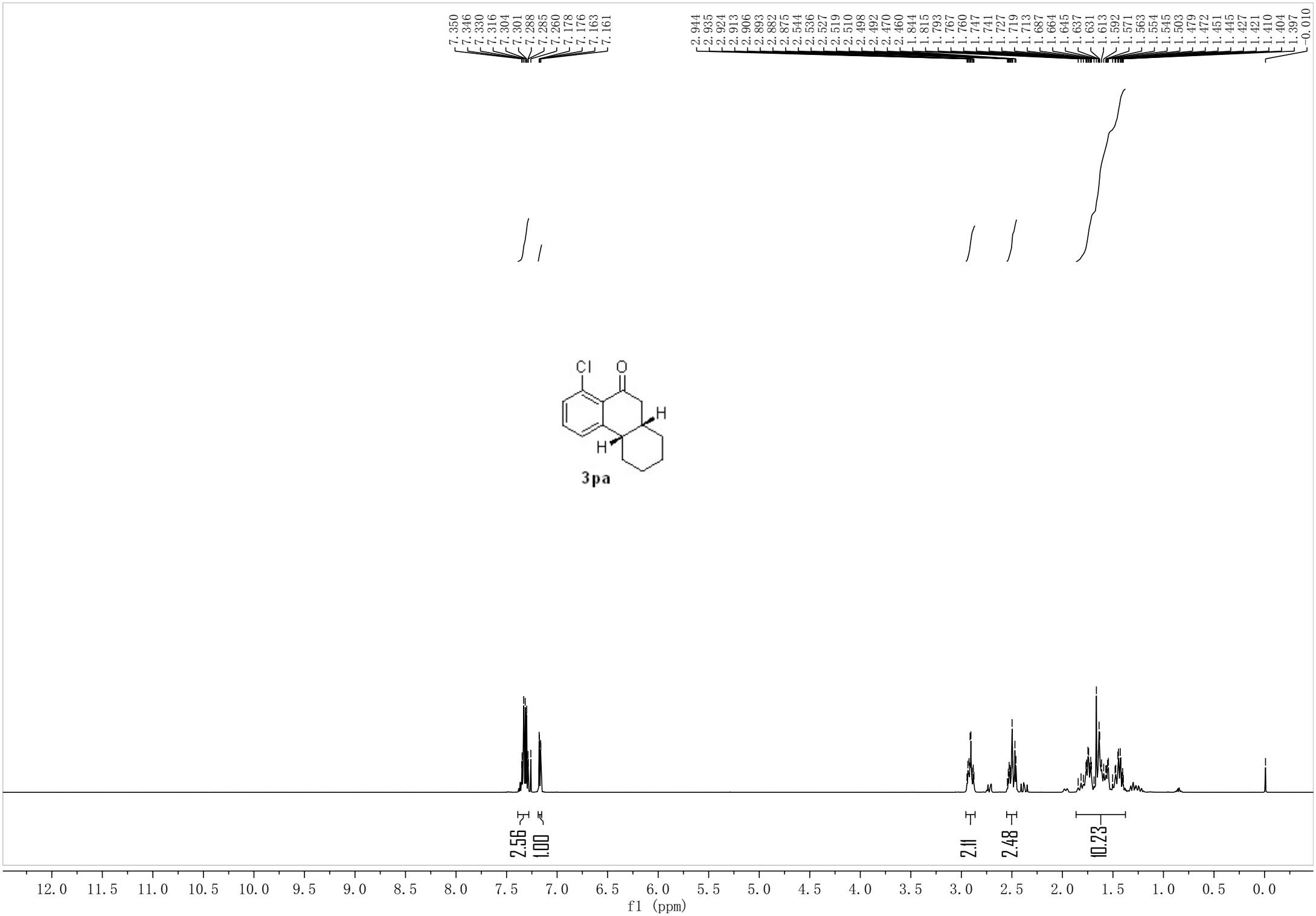
f1 (ppm)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2.536
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2.519
2.510
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2.492
2.470
2.460
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1.793
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1.727
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1.645
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1.563
1.554
1.545
1.503
1.479
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1.445
1.427
1.421
1.410
1.404
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O
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H
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11.0
10.5
10.0
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6.0
5.5
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2.5
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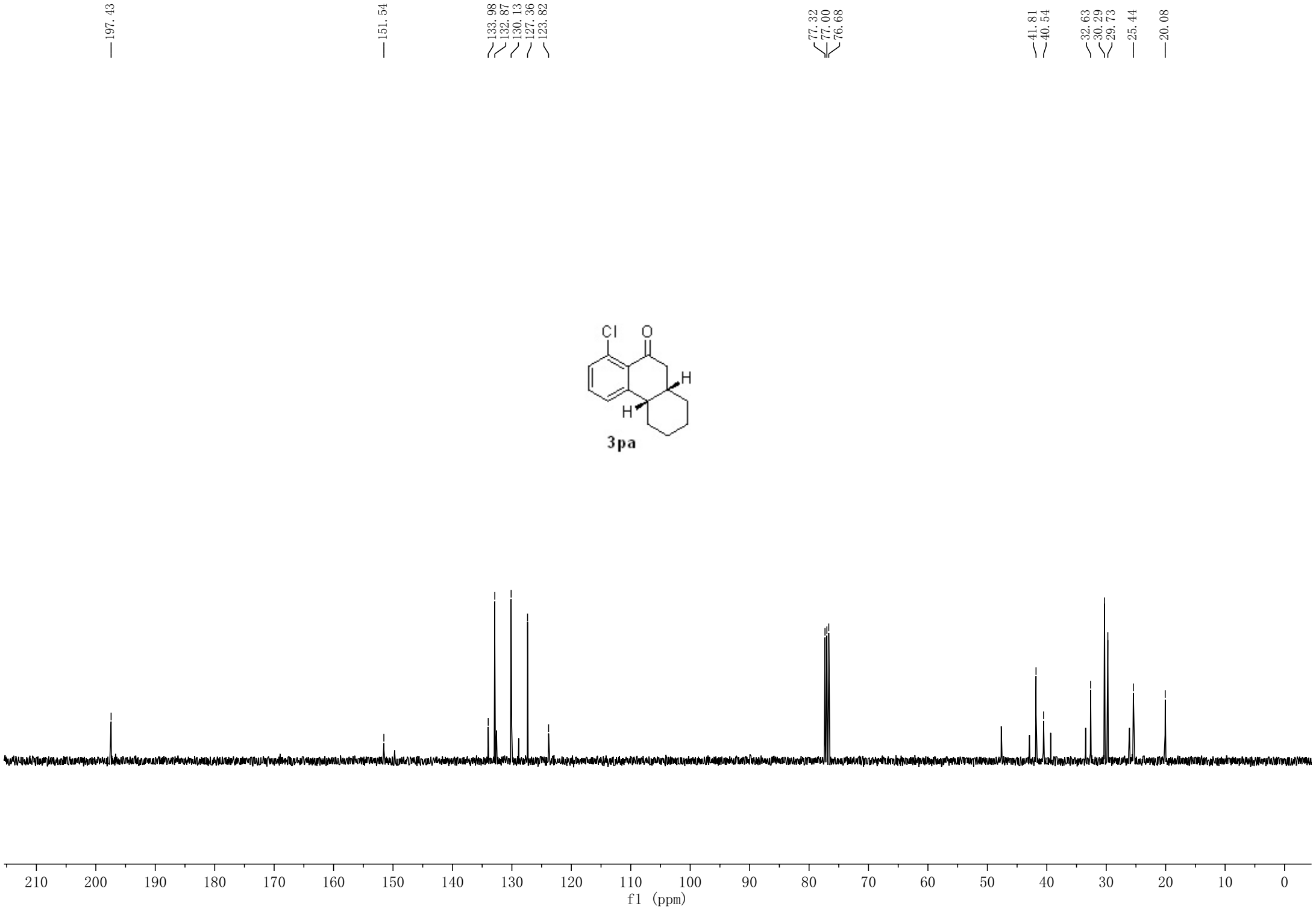
0.0
f1 (ppm)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77.00
76.68
41.81
40.54
32.63
30.29
29.73
25.44
20.08
Cl
O
H
H
3pa
210
200
190
180
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130
120
110
100
90
80
70
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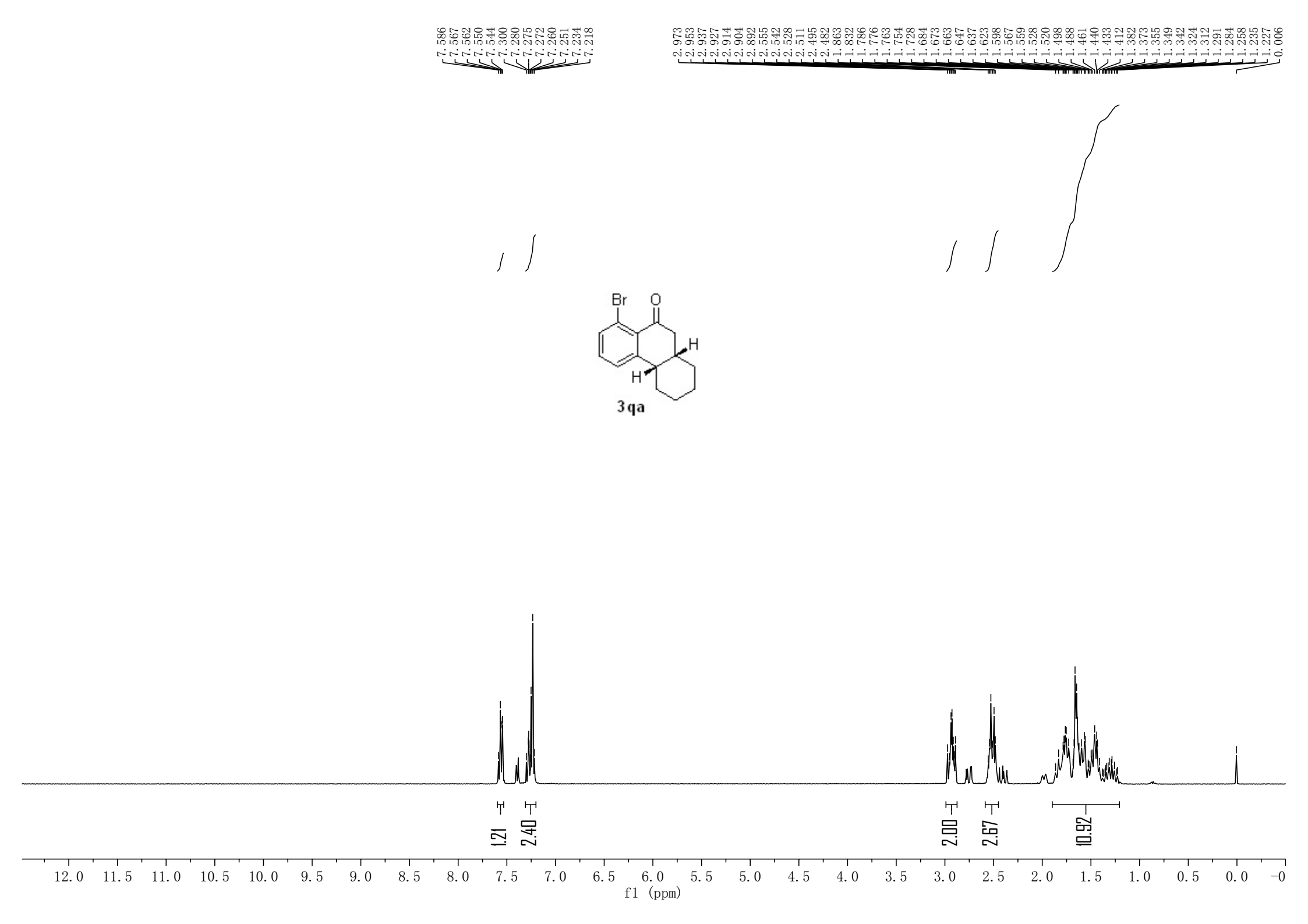
50
40
30
20
10
0
f1 (ppm)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7.260
7.251
7.234
7.218
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2.953
2.937
2.927
2.914
2.904
2.892
2.555
2.542
2.528
2.511
2.495
2.482
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1.832
1.786
1.776
1.763
1.754
1.728
1.684
1.673
1.663
1.647
1.637
1.623
1.598
1.567
1.559
1.528
1.520
1.498
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1.461
1.440
1.433
1.412
1.382
1.373
1.355
1.349
1.342
1.324
1.312
1.291
1.284
1.258
1.235
1.227
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O
H
H
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2.00
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5.0
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2.0
1.5
1.0
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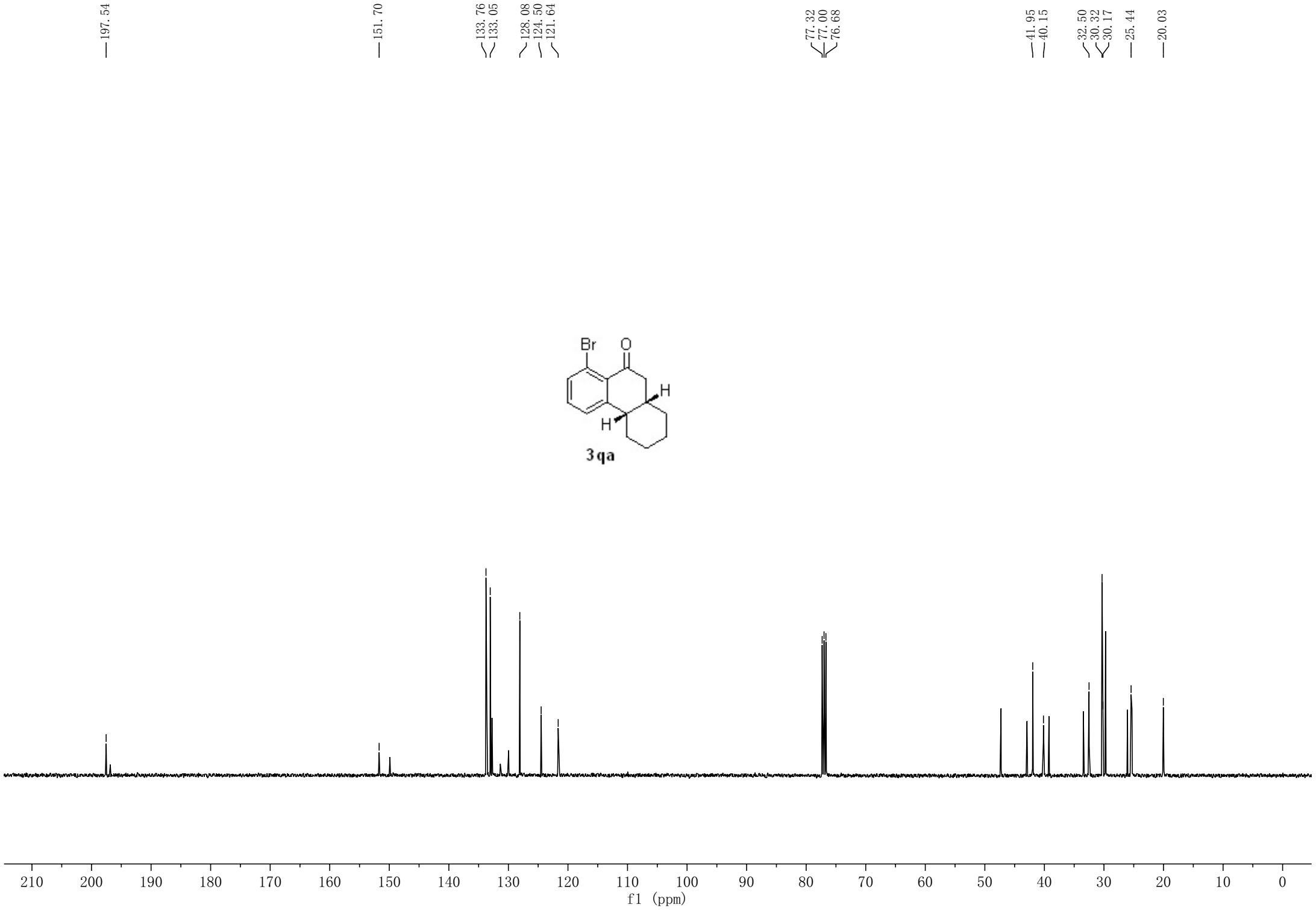
f1 (ppm)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30.32
30.17
25.44
20.03
Br
O
H
H
3qa
210
200
190
180
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150
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130
120
110
100
90
80
70
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50
40
30
20
10
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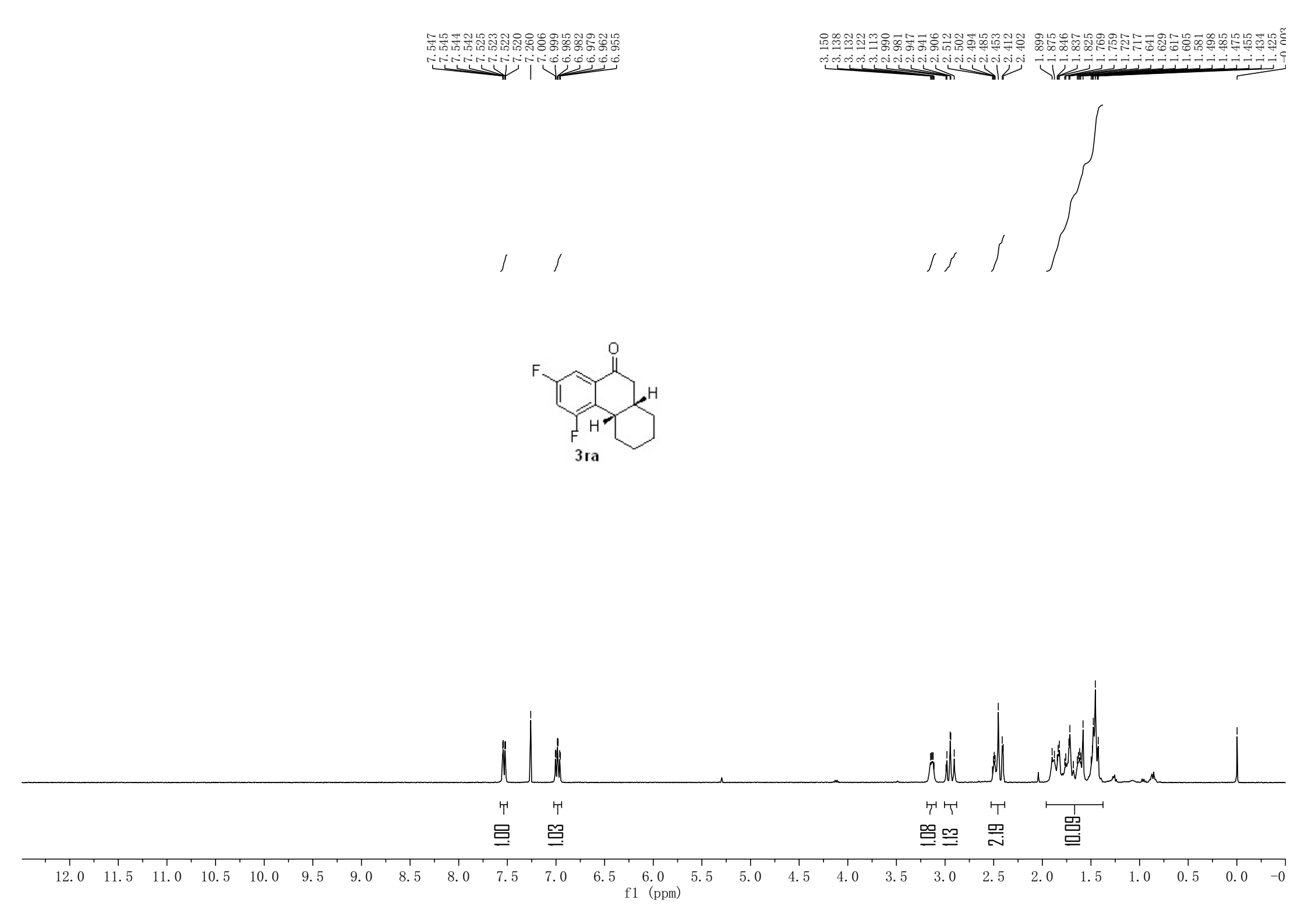
f1 (ppm)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7.520
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6.979
6.962
6.955
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3.132
3.122
3.113
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2.981
2.947
2.941
2.906
2.512
2.502
2.494
2.485
2.453
2.412
2.402
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1.875
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1.825
1.769
1.759
1.727
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1.617
1.605
1.581
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1.485
1.475
1.455
1.434
1.425
O
F
H
H
F
3ra
1.00
1.03
1.08
1.13
2.19
10.09
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11.5
11.0
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10.0
9.5
9.0
8.5
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7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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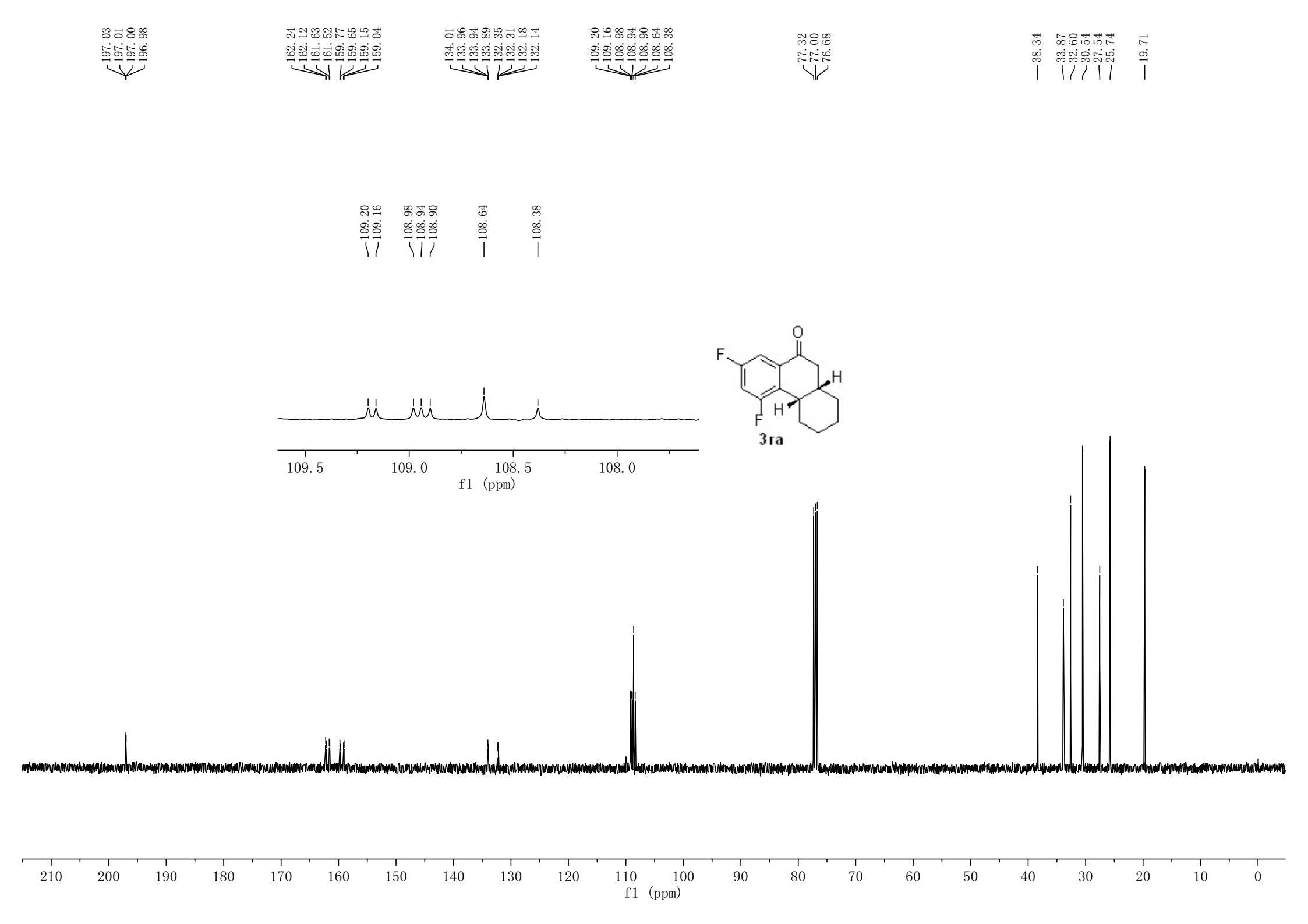
f1 (ppm)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133.94
133.89
132.35
132.31
132.18
132.14
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109.16
108.98
108.94
108.90
108.64
108.38
77.32
77.00
76.68
38.34
33.87
32.60
30.54
27.54
25.74
19.71
109.20
109.16
108.98
108.94
108.90
108.64
108.38
109.5
109.0
108.5
108.0
f1 (ppm)
O
F
H
H
F
3ra
210
200
190
180
170
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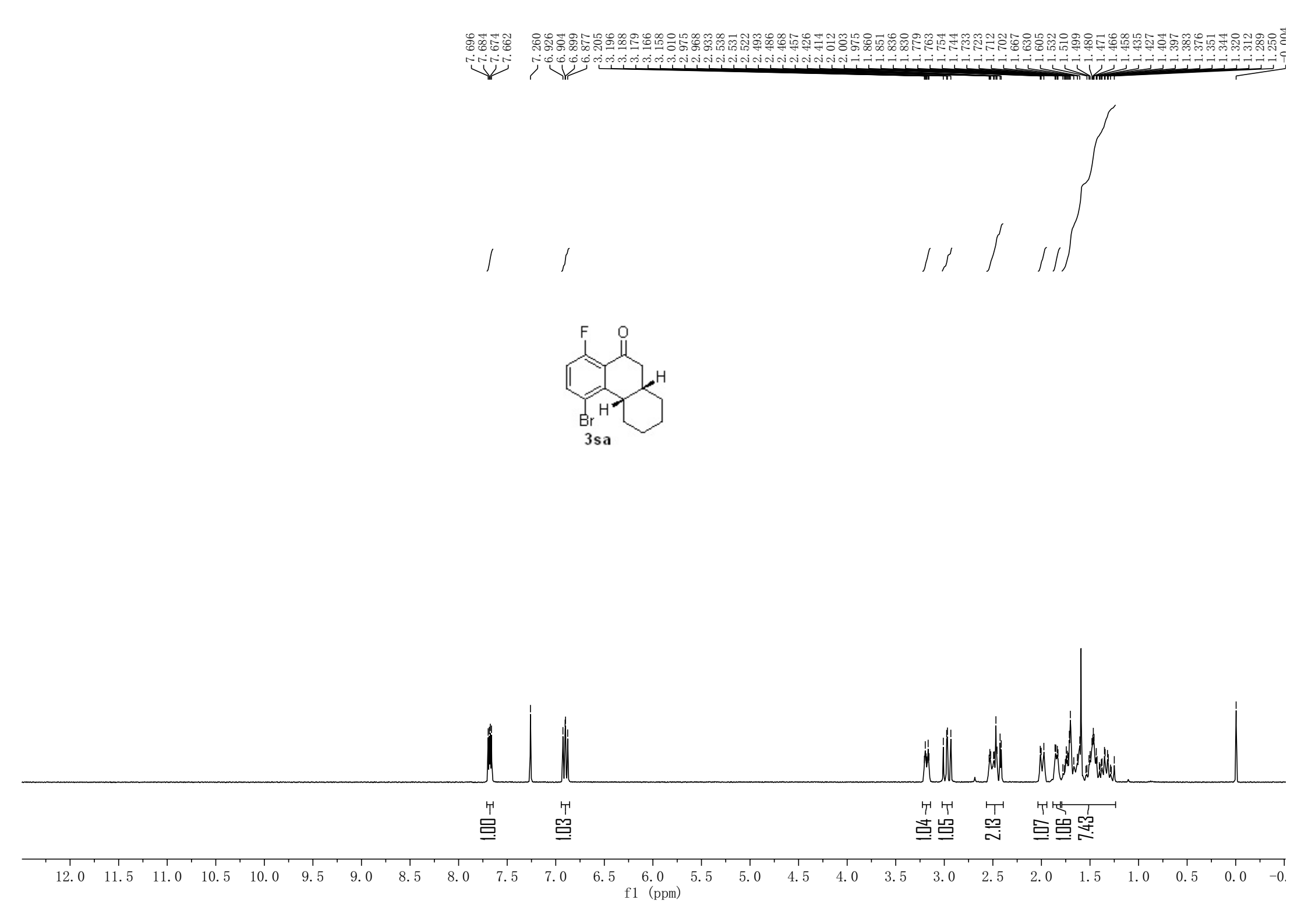
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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1.312
1.289
1.250
F
O
H
H
Br
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1.04
1.05
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1.07
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6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

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196.53
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138.47
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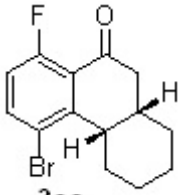

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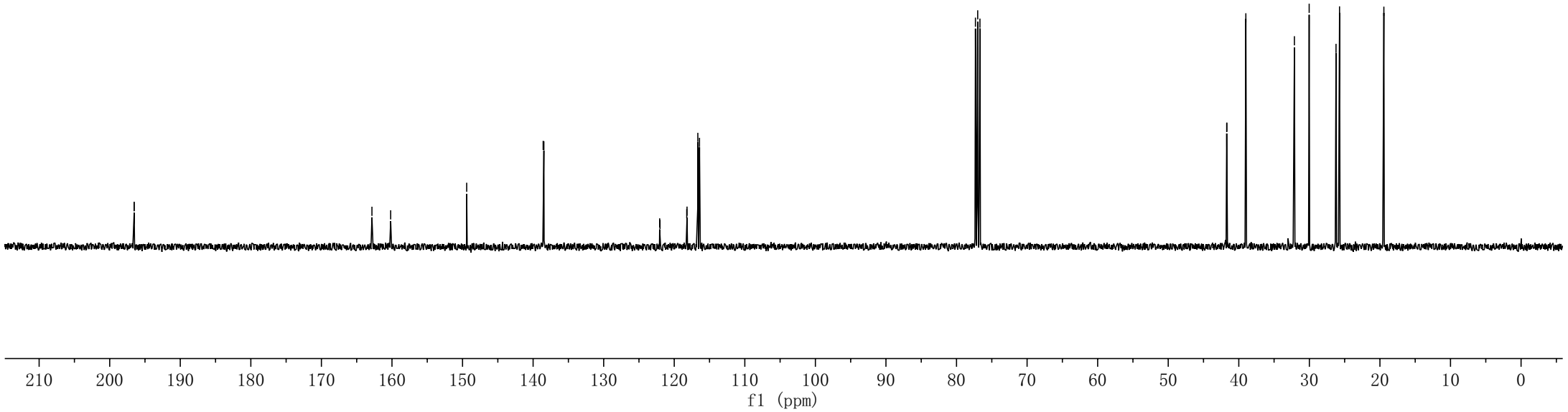

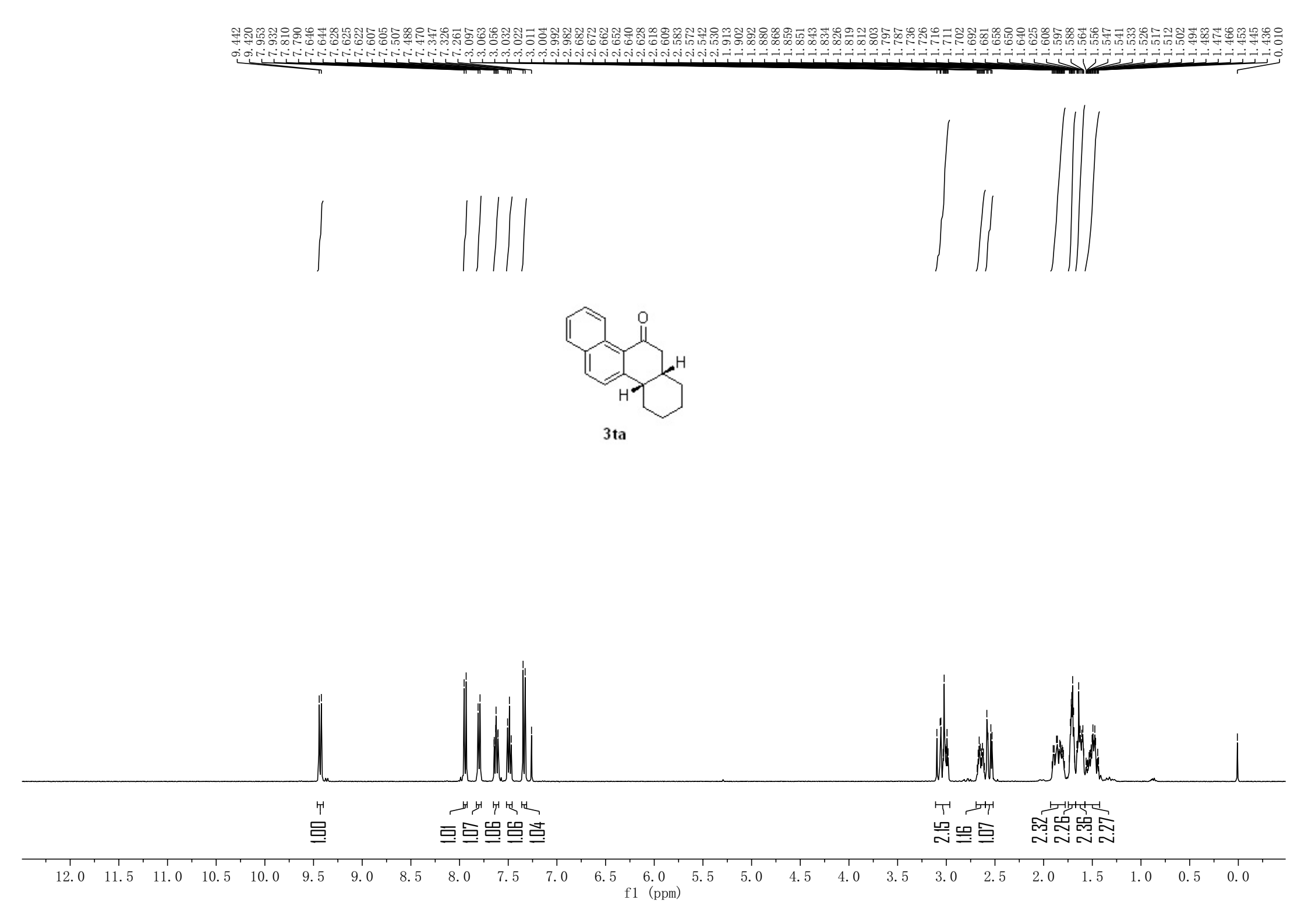
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7.605
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7.488
7.470
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7.326
7.261
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3.063
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3.032
3.022
3.011
3.004
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2.618
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H
H
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1.01
1.07
1.06
1.06
1.04
2.15
1.16
1.07
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2.36
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7.0
6.5
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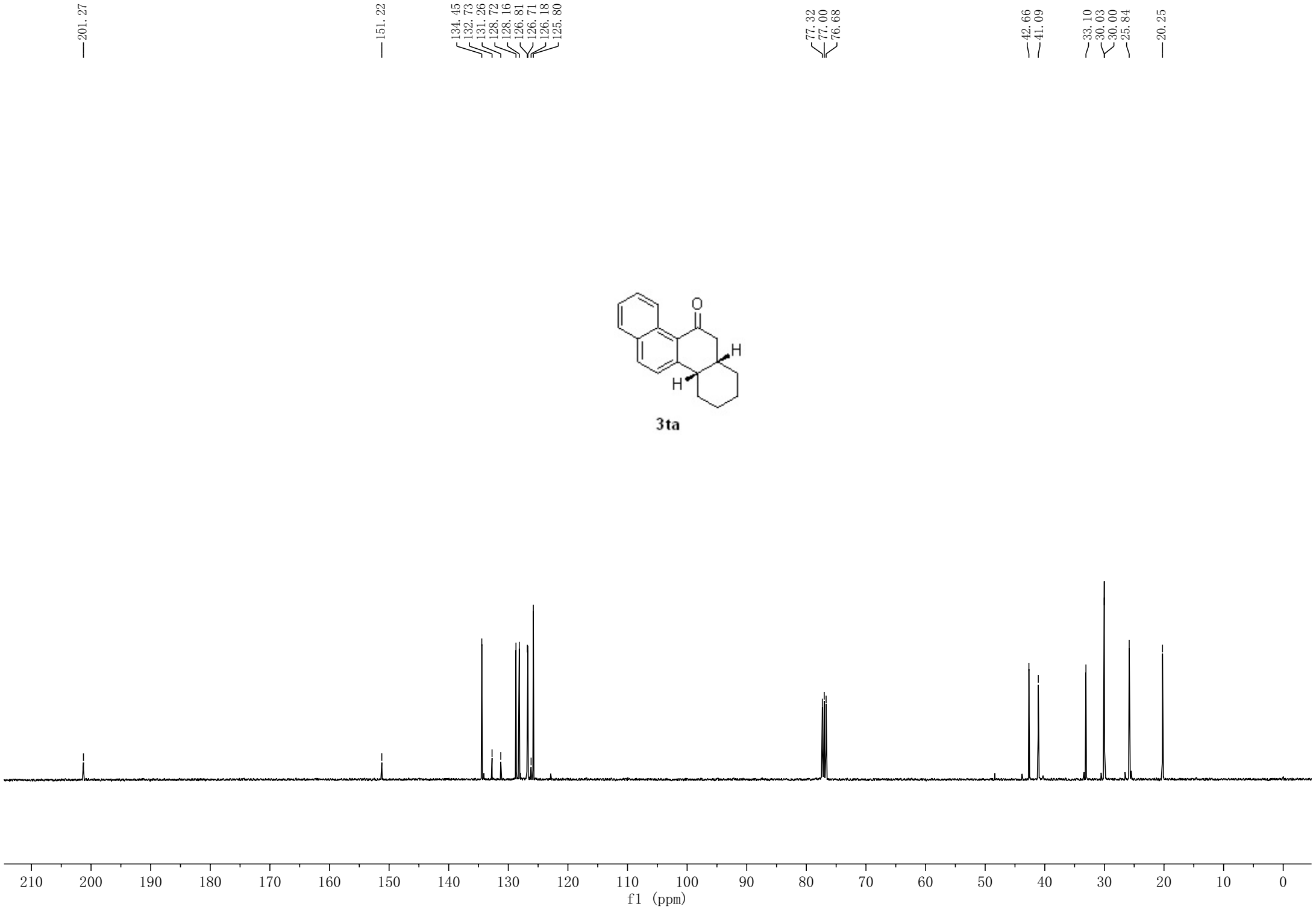
f1 (ppm)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77.00
76.68
42.66
41.09
33.10
30.03
30.00
25.84
20.25
O
H
H
3ta
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200
190
180
170
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130
120
110
100
90
80
70
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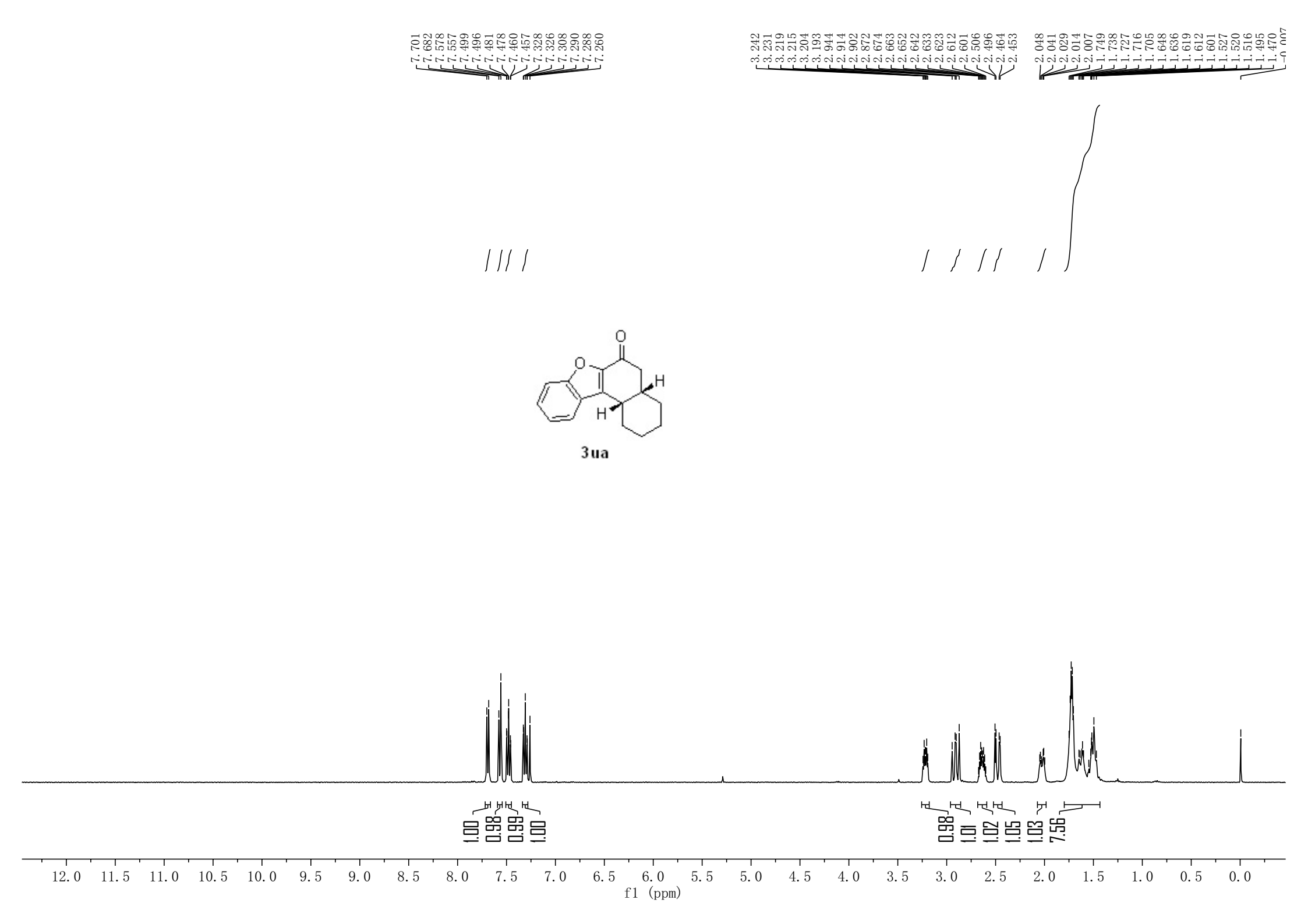
50
40
30
20
10
0
f1 (ppm)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H
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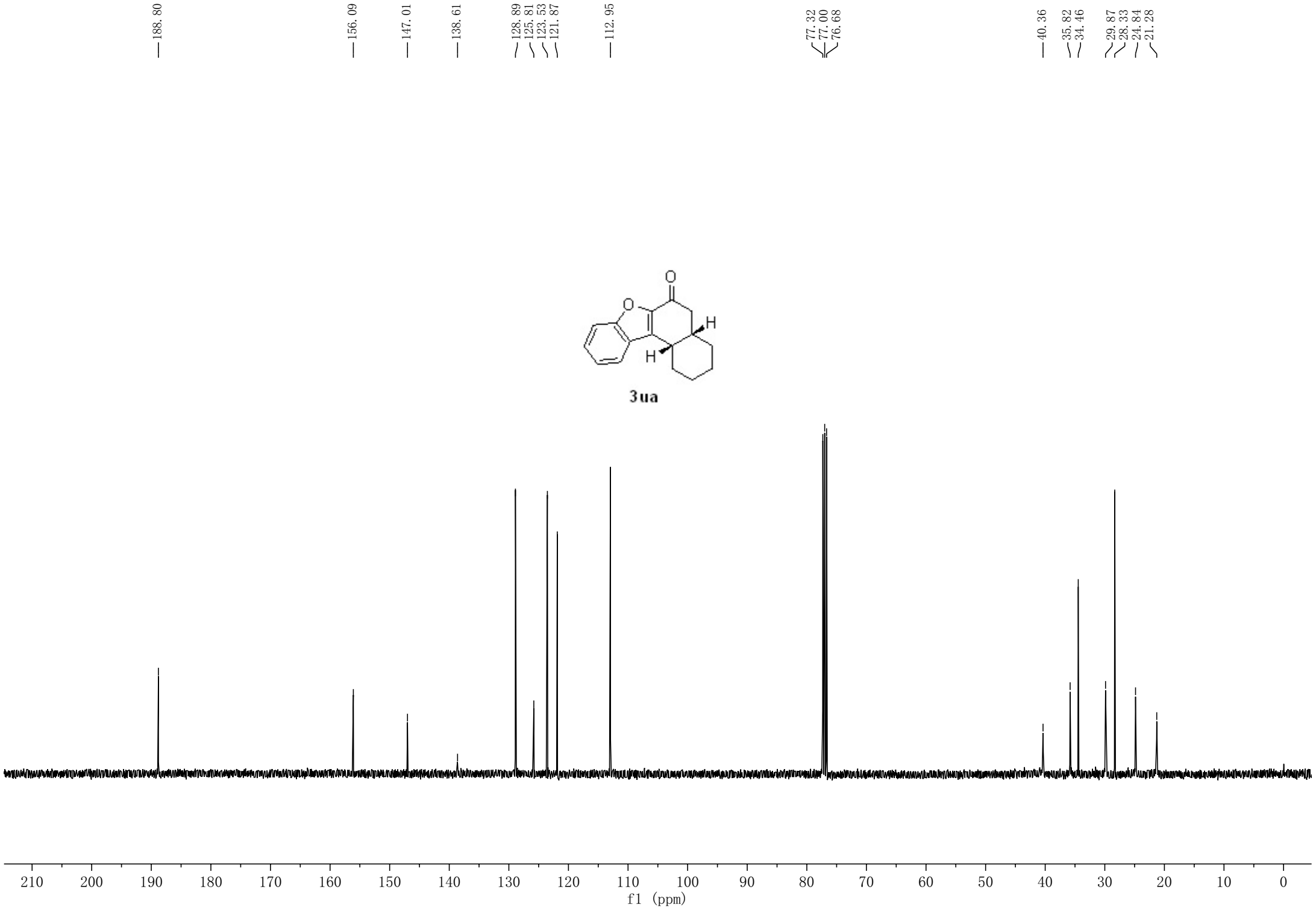
f1 (ppm)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121.87
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77.00
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35.82
34.46
29.87
28.33
24.84
21.28
O
O
H
H
3ua
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200
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180
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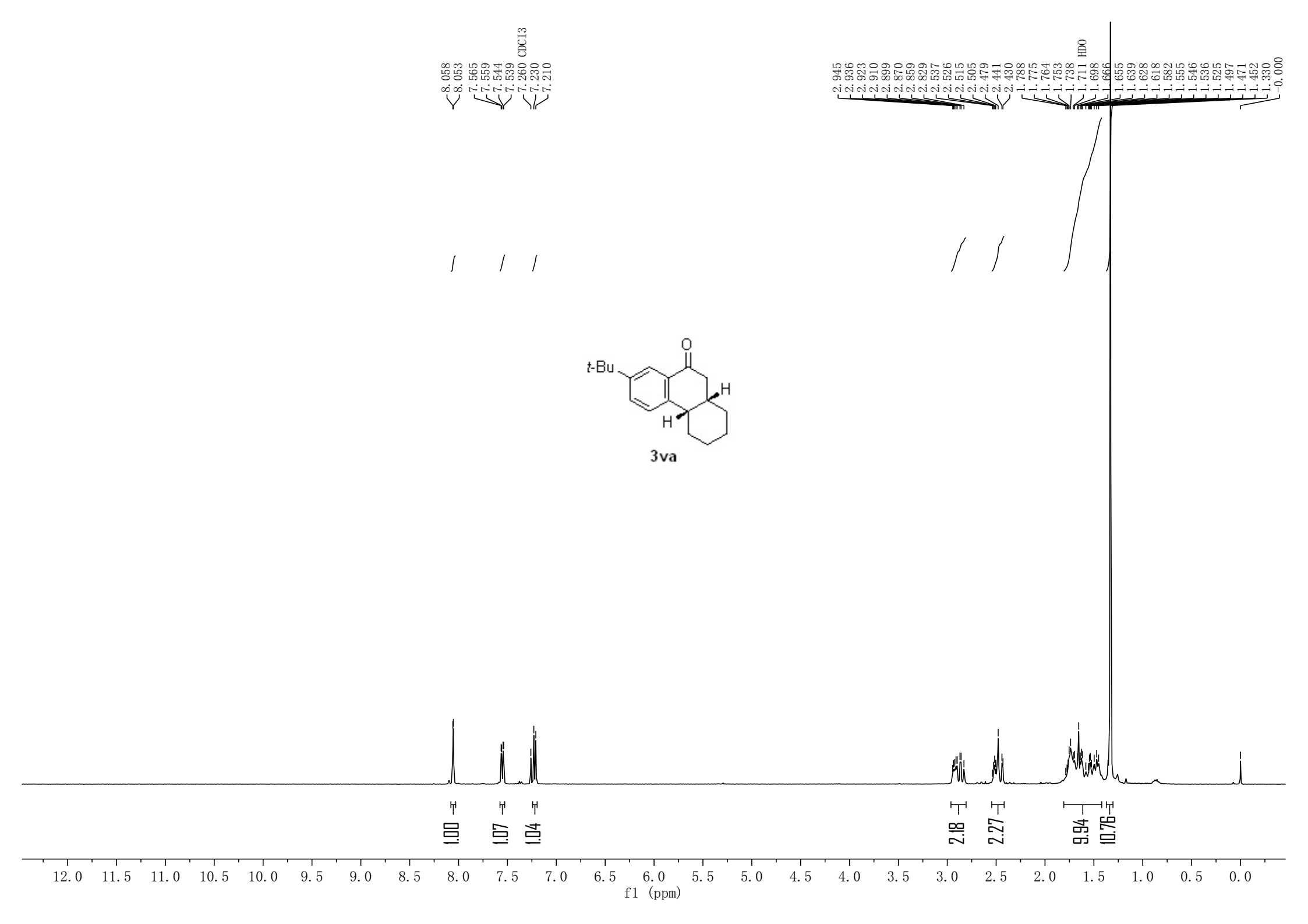
f1 (ppm)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2.430
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1.753
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3.0
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2.0
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1.0
0.5
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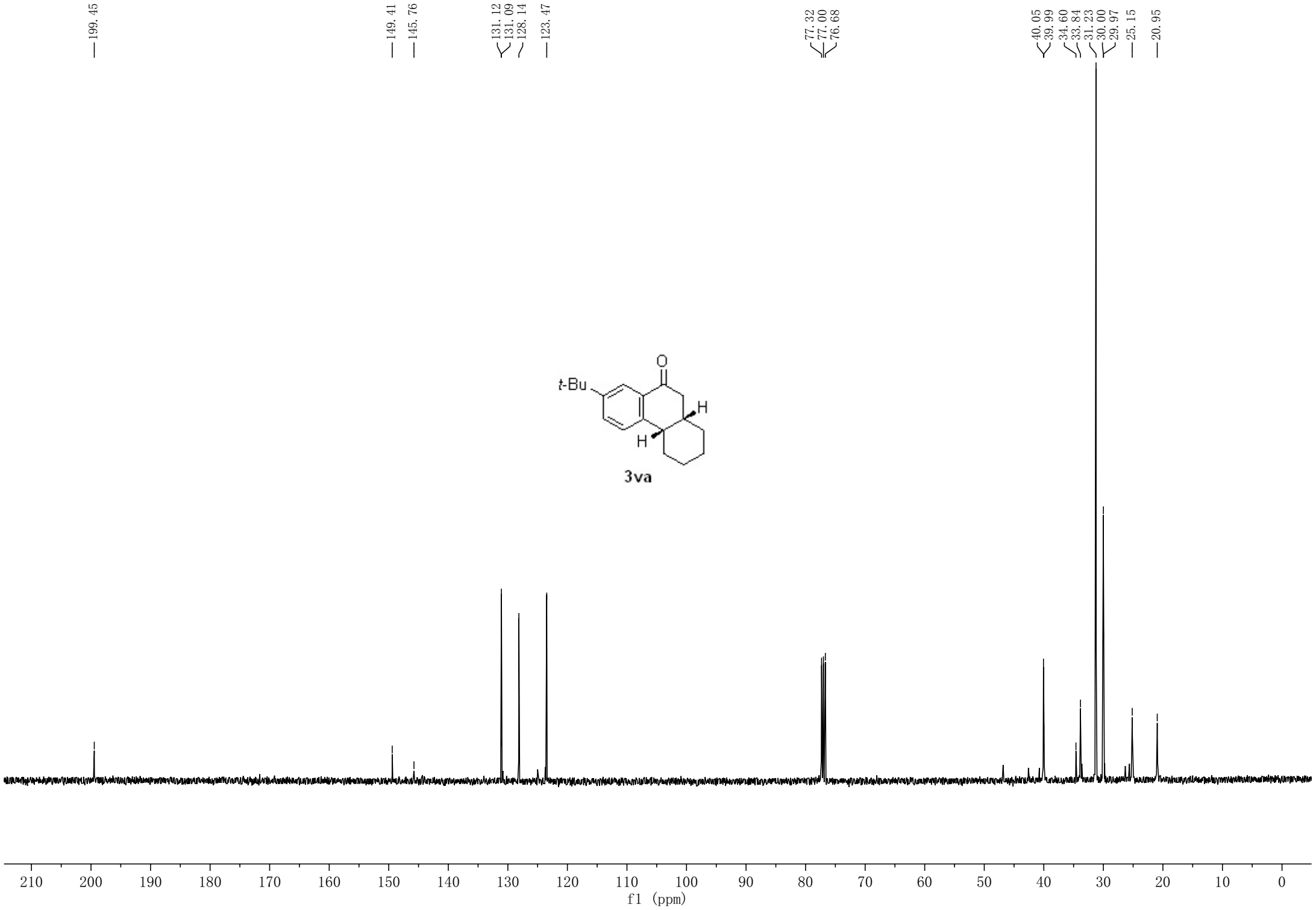
f1 (ppm)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34.60
33.84
31.23
30.00
29.97
25.15
20.95
O
t-Bu
H
H
3va
210
200
190
180
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50
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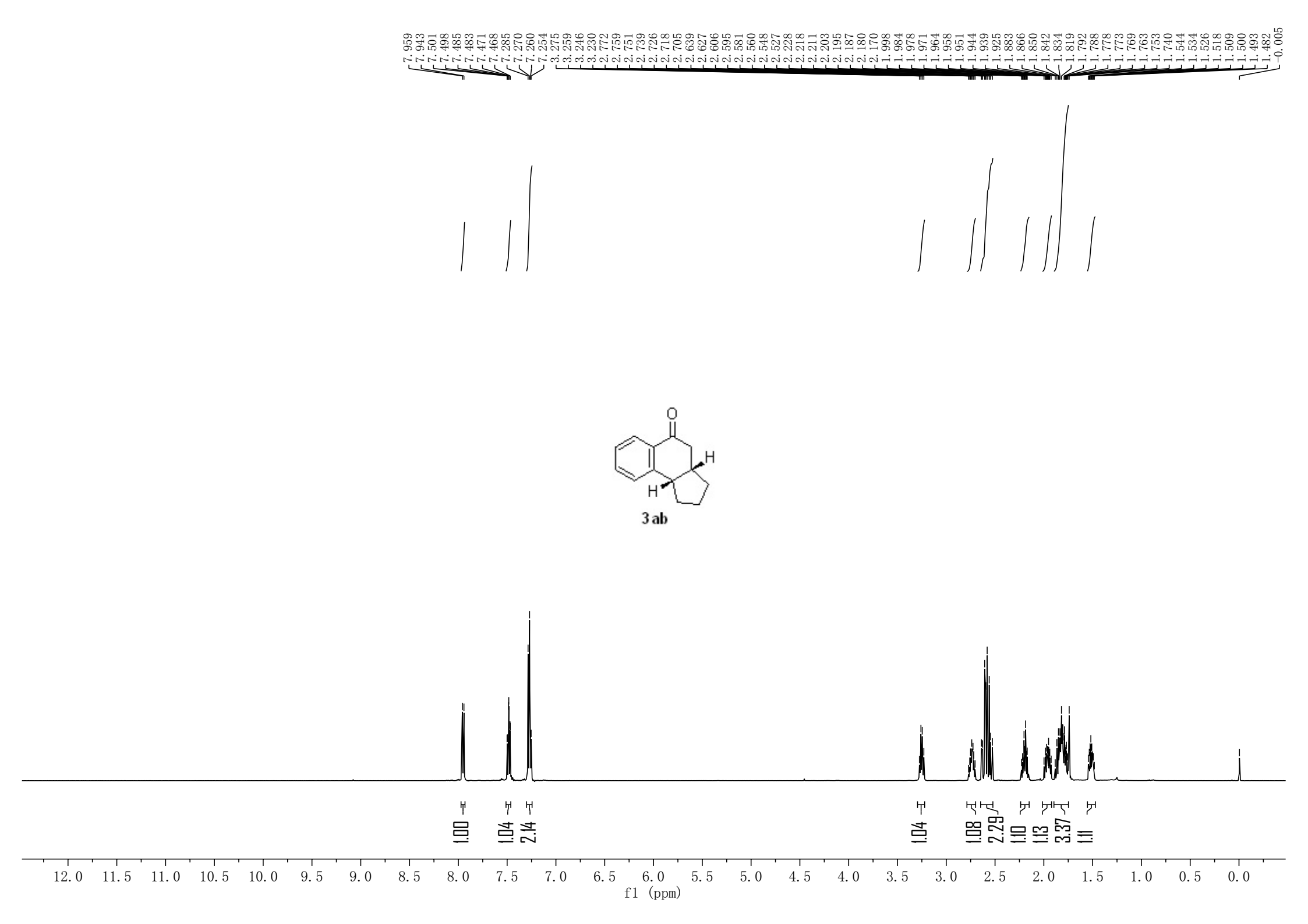
f1 (ppm)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7.254
3.275
3.259
3.246
3.230
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2.751
2.739
2.726
2.718
2.705
2.639
2.627
2.606
2.595
2.581
2.560
2.548
2.527
2.228
2.218
2.211
2.203
2.195
2.187
2.180
2.170
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1.971
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1.951
1.944
1.939
1.925
1.883
1.866
1.850
1.842
1.834
1.819
1.792
1.788
1.778
1.773
1.769
1.763
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1.740
1.544
1.534
1.526
1.518
1.509
1.500
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1.482
-0.005
O
H
H
3ab
1.00
1.04
2.14
1.04
1.08
2.29
1.10
1.13
3.37
1.11
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11.5
11.0
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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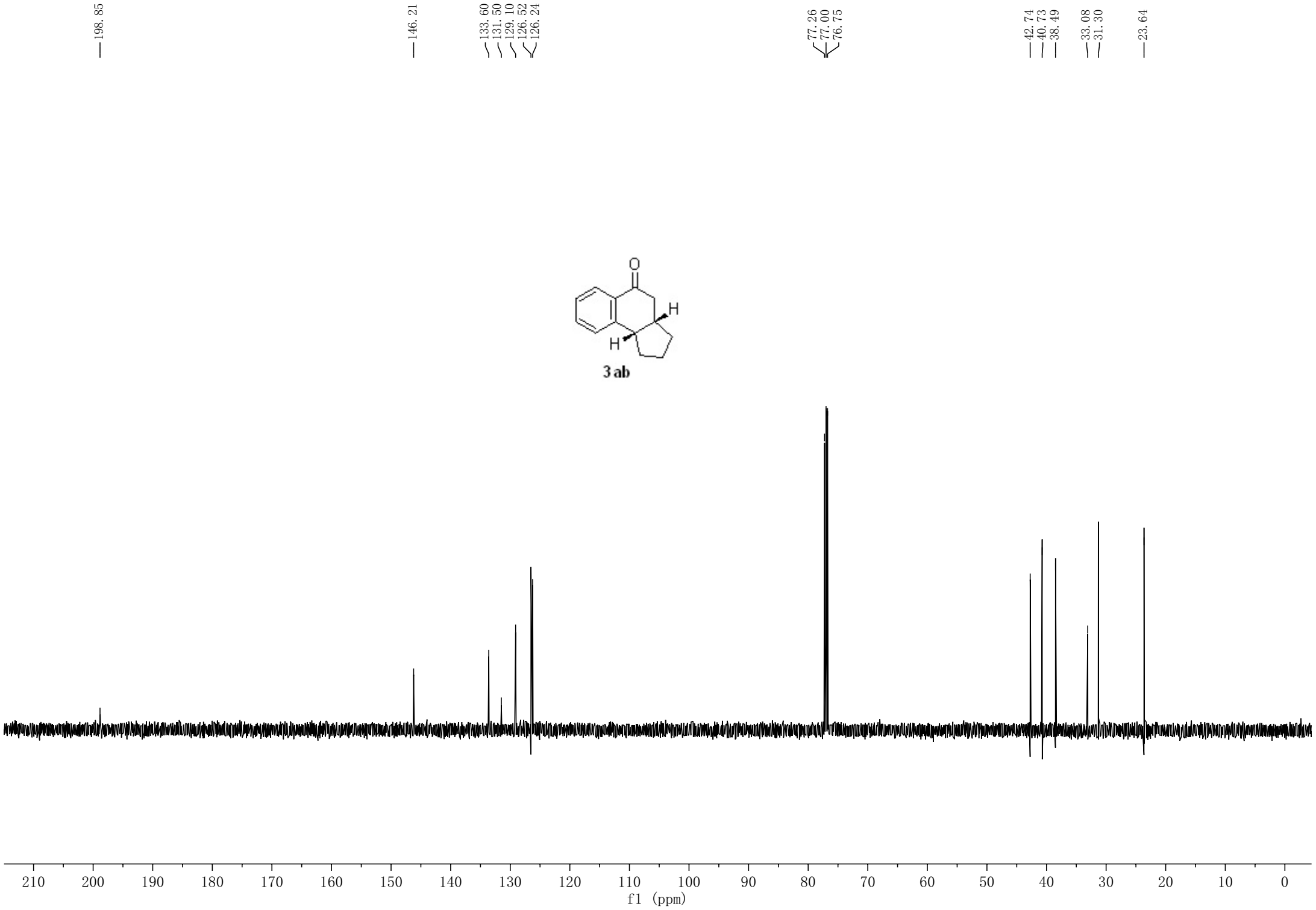
f1 (ppm)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38.49
33.08
31.30
23.64
O
H
H
3ab
210
200
190
180
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130
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110
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90
80
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50
40
30
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10
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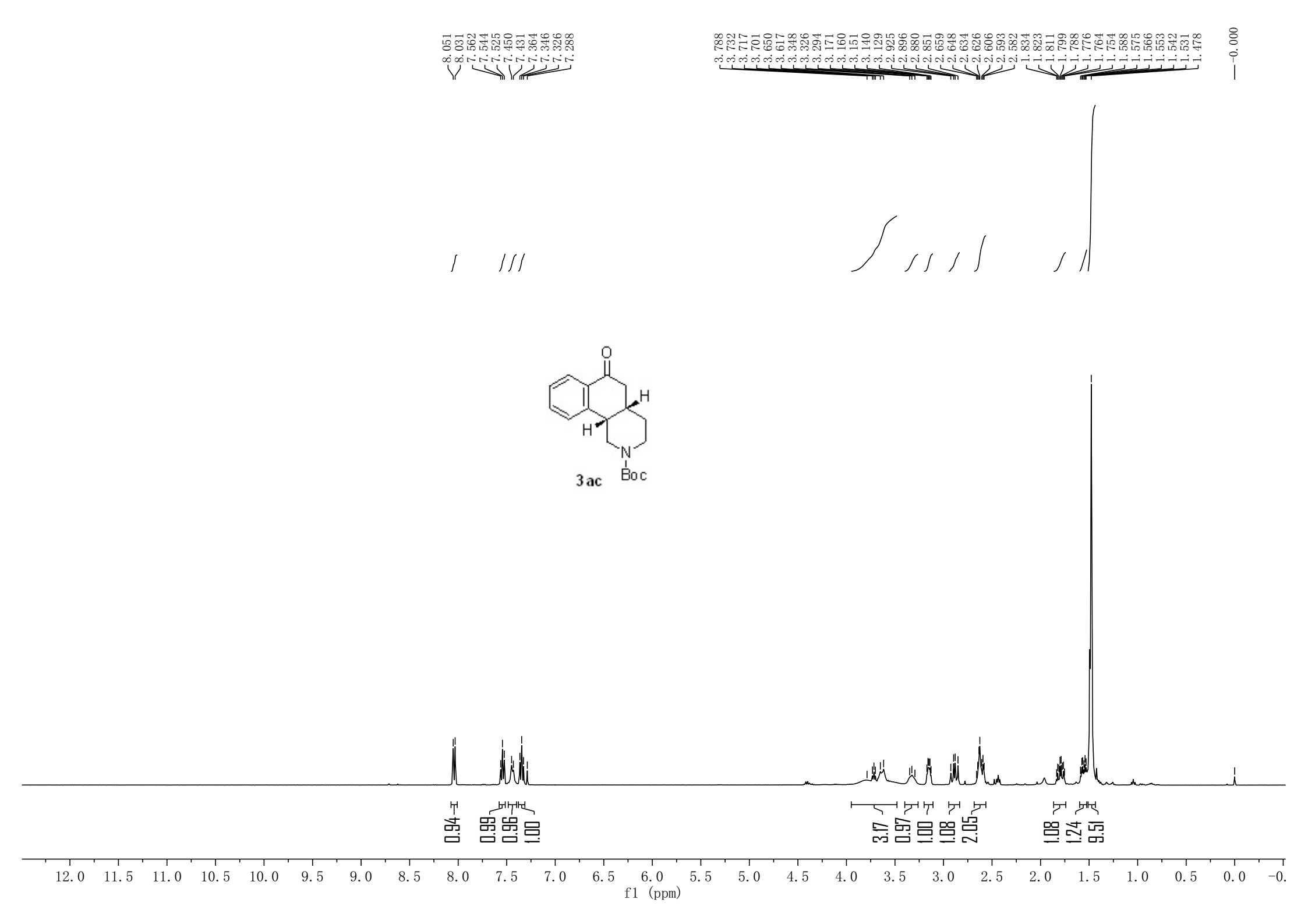
f1 (ppm)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3.732
3.717
3.701
3.650
3.617
3.348
3.326
3.294
3.171
3.160
3.151
3.140
3.129
2.925
2.896
2.880
2.851
2.659
2.648
2.634
2.626
2.606
2.593
2.582
1.834
1.823
1.811
1.799
1.788
1.776
1.764
1.754
1.588
1.575
1.566
1.553
1.542
1.531
1.478
-0.000
O
H
H
N
Boc
3ac
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0.99
0.96
1.00
3.17
0.97
1.00
1.08
2.05
1.08
1.24
9.51
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11.5
11.0
10.5
10.0
9.5
9.0
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6.5
6.0
5.5
5.0
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2.5
2.0
1.5
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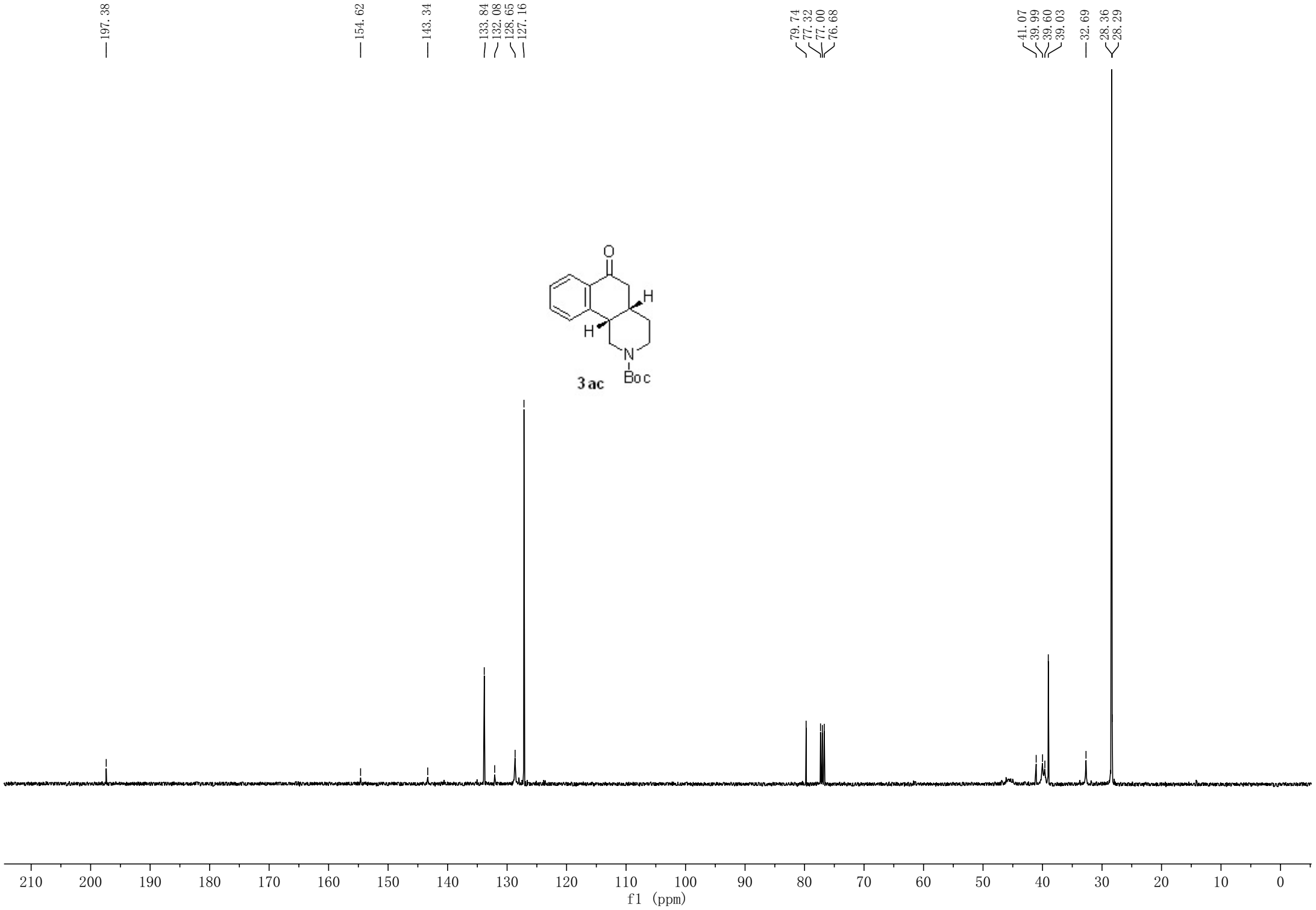
0.5
0.0
-0.
f1 (ppm)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77.00
76.68
41.07
39.99
39.60
39.03
32.69
28.36
28.29
O
H
H
N
Boc
3ac
210
200
190
180
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50
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30
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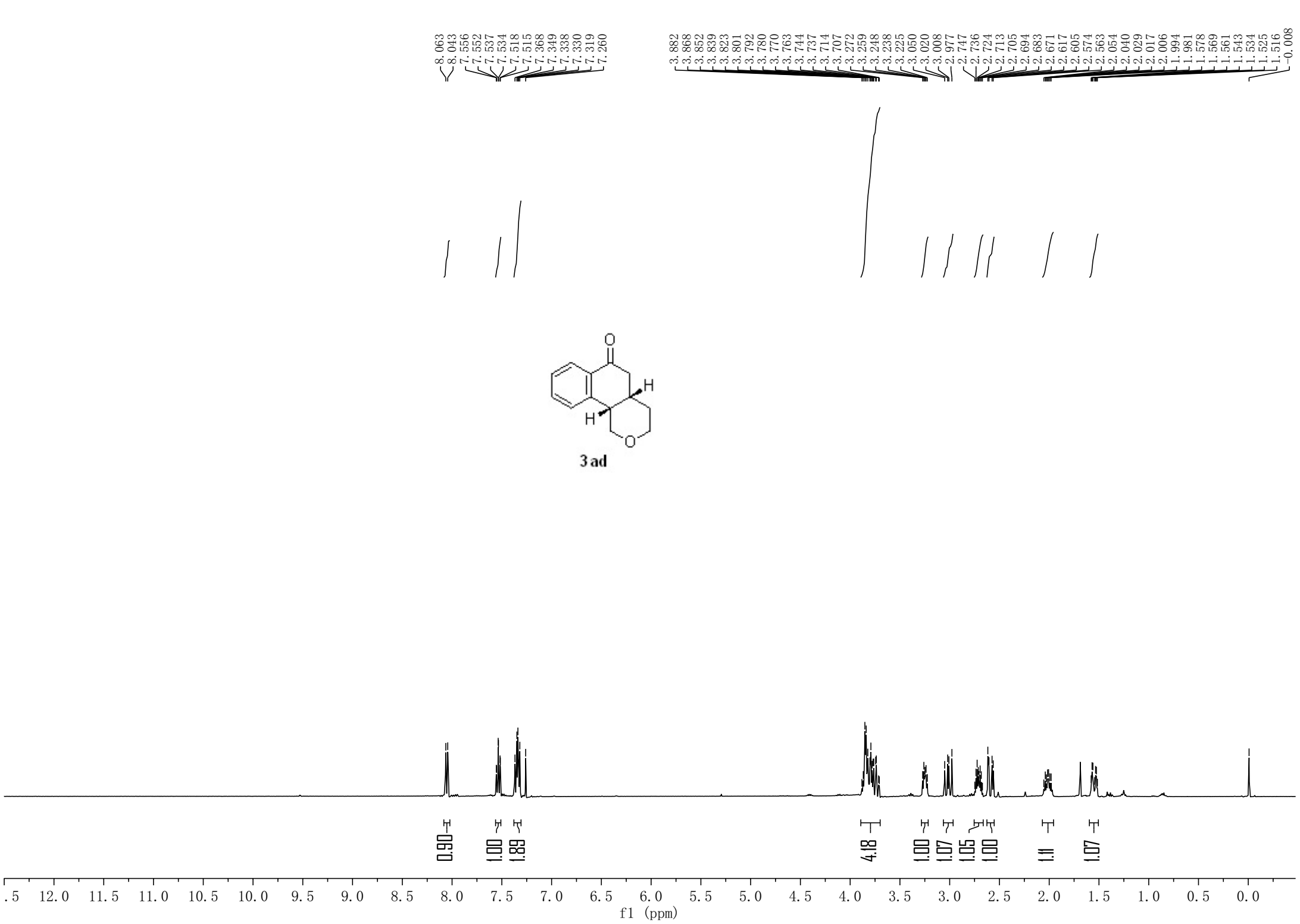
f1 (ppm)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7.534
7.518
7.515
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7.349
7.338
7.330
7.319
7.260
3.882
3.868
3.852
3.839
3.823
3.801
3.792
3.780
3.770
3.763
3.744
3.737
3.714
3.707
3.272
3.259
3.248
3.238
3.225
3.050
3.020
3.008
2.977
2.747
2.736
2.724
2.713
2.705
2.694
2.683
2.671
2.617
2.605
2.574
2.563
2.054
2.040
2.029
2.017
2.006
1.994
1.981
1.578
1.569
1.561
1.543
1.534
1.525
1.516
-0.008
O
H
H
O
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1.89
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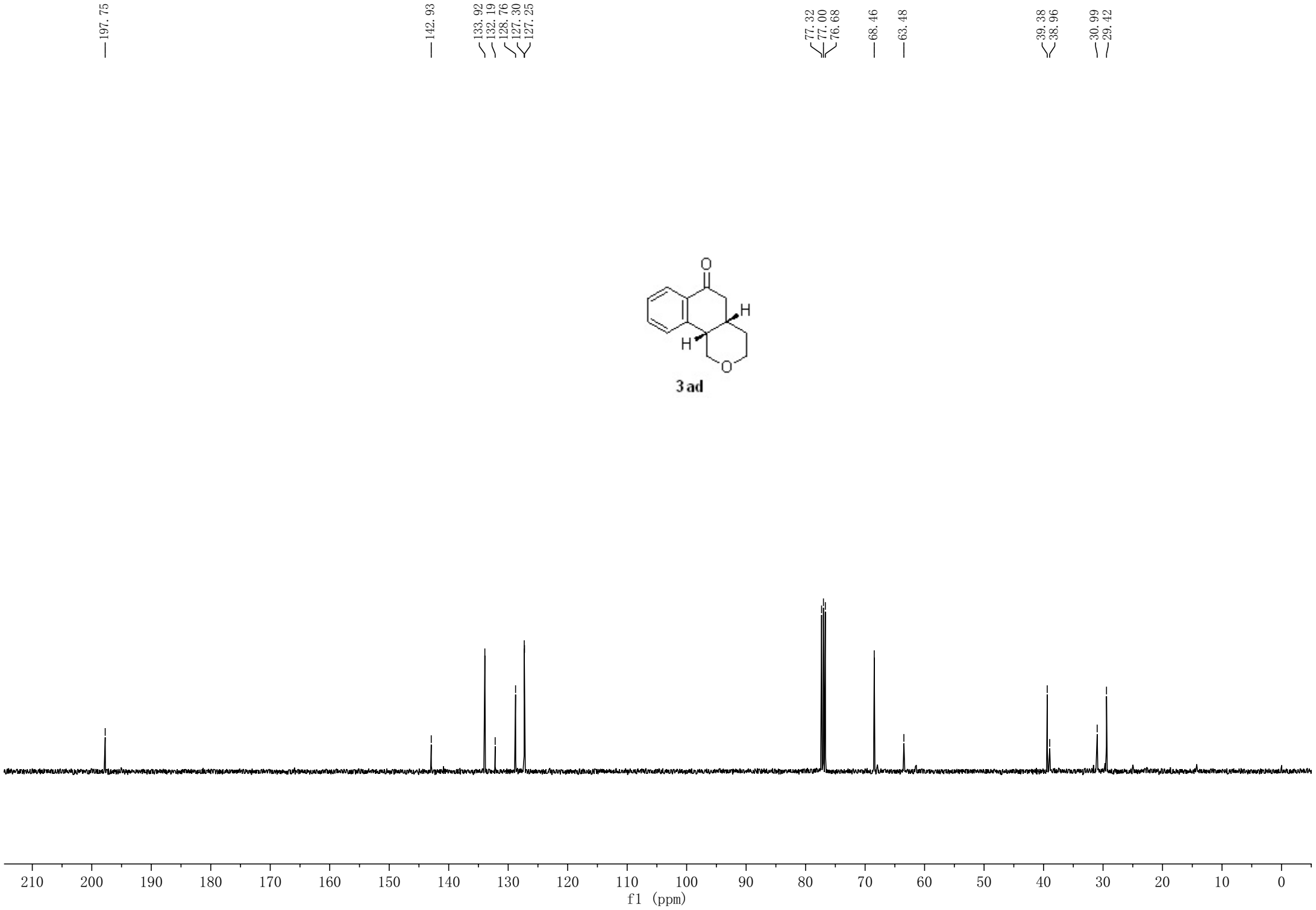
1.00
1.07
1.05
1.00
1.11
1.07
f1 (ppm)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68.46
63.48
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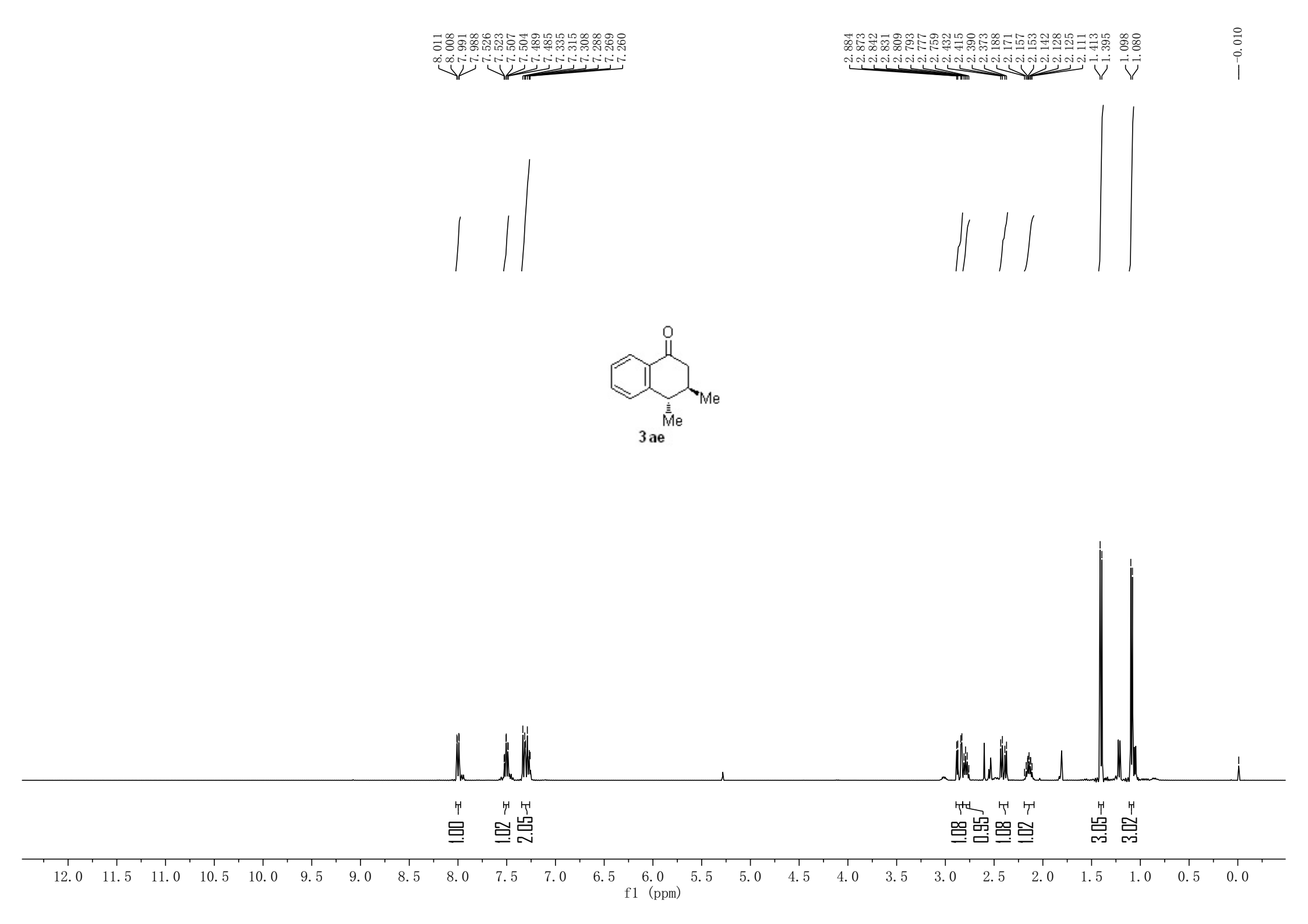
38.96
30.99
29.42
O
H
H
O
3ad
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.485
7.335
7.315
7.308
7.288
7.269
7.260
2.884
2.873
2.842
2.831
2.809
2.793
2.777
2.759
2.432
2.415
2.390
2.373
2.188
2.171
2.157
2.153
2.142
2.128
2.125
2.111
1.413
1.395
1.098
1.080
-0.010
O
Me
Me
3ae
1.00
1.02
2.05
1.08
0.95
1.08
1.02
3.05
3.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.12
147.62
133.78
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128.28
126.72
126.35
77.32
77.00
76.68
43.34
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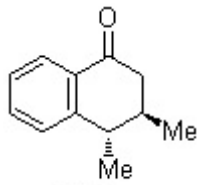
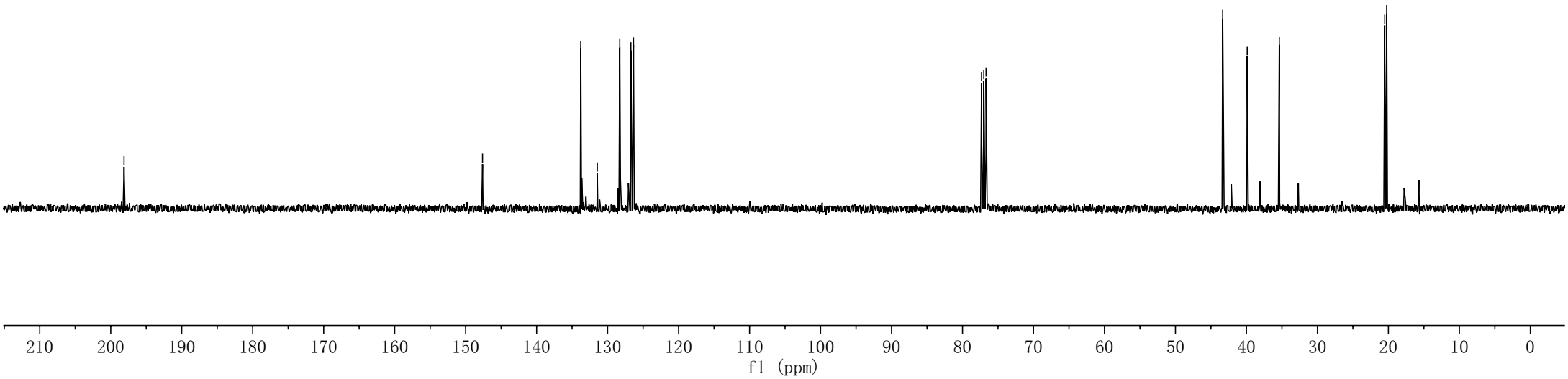
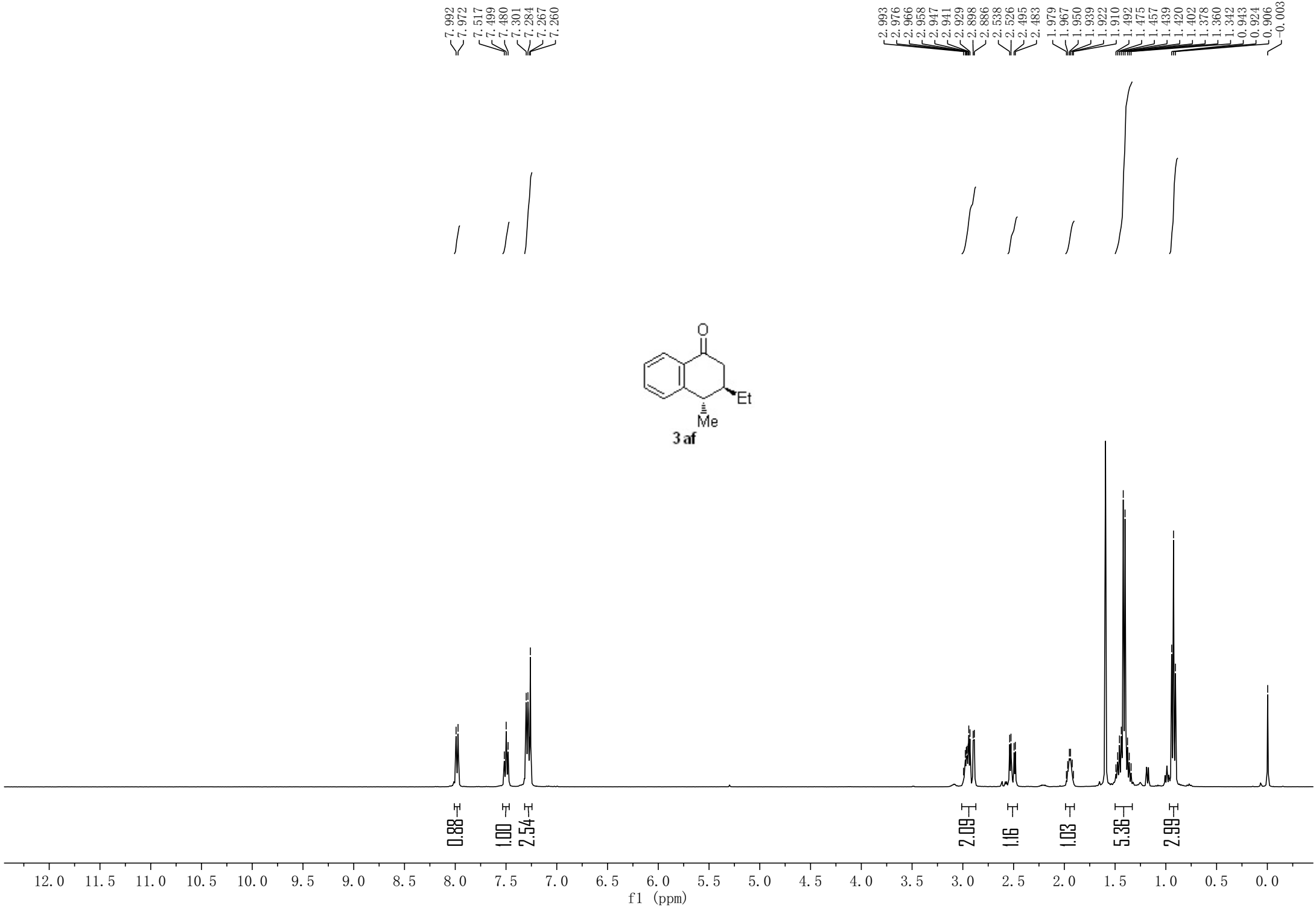
35.37
20.52
20.24



3ae

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7.267
7.260
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2.966
2.958
2.947
2.941
2.929
2.898
2.886
2.538
2.526
2.495
2.483
1.979
1.967
1.950
1.939
1.922
1.910
1.492
1.475
1.457
1.439
1.420
1.402
1.378
1.360
1.342
0.943
0.924
0.906
-0.003
O
Et
Me
3af
0.88
1.00
2.54
2.09
1.16
1.03
5.36
2.99
12.0
11.5
11.0
10.5
10.0
9.5
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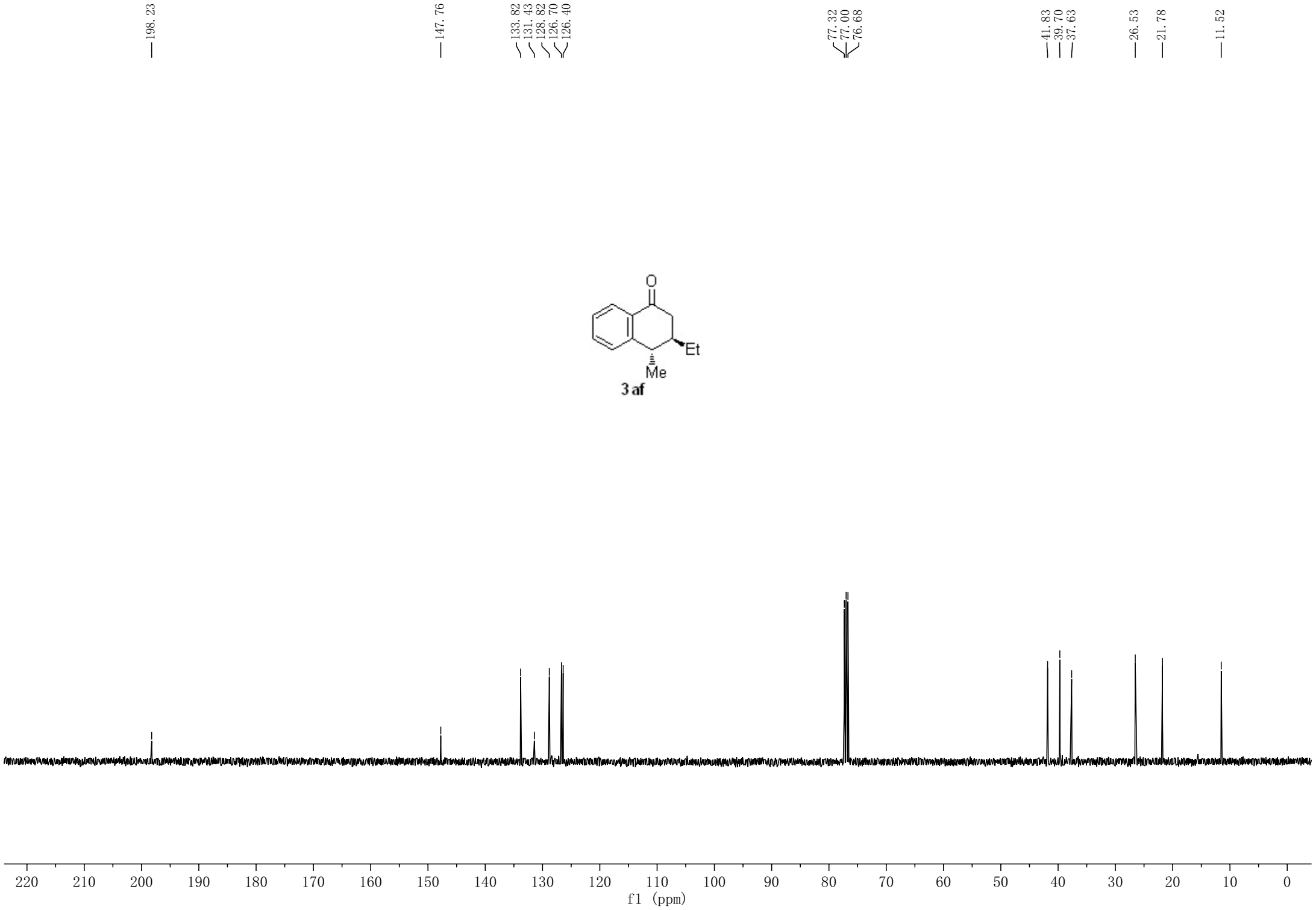
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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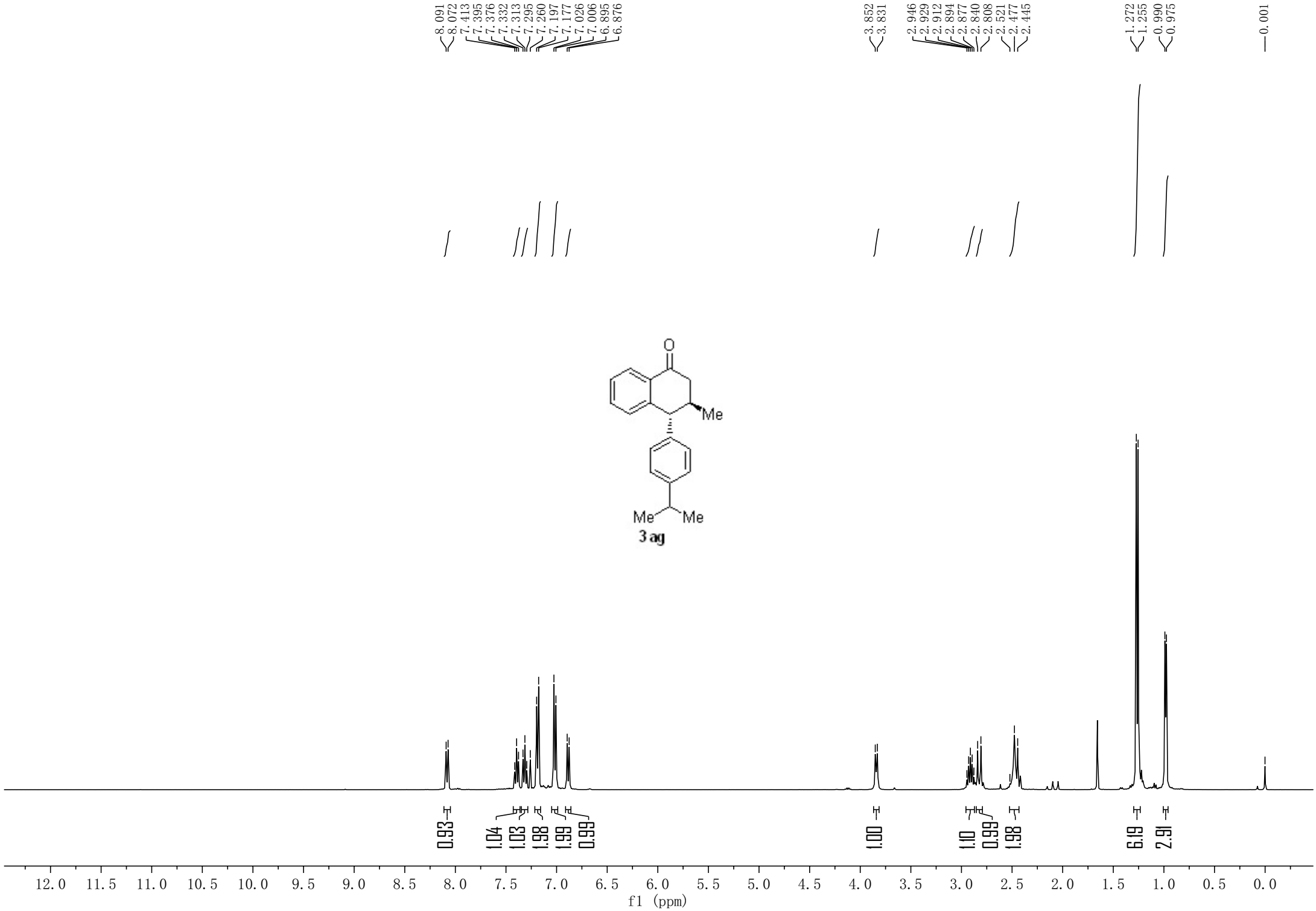
77.32
77.00
76.68
41.83
39.70
37.63
26.53
21.78
11.52
O
Et
Me
3af
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.295
7.260
7.197
7.177
7.026
7.006
6.895
6.876
3.852
3.831
2.946
2.929
2.912
2.894
2.877
2.840
2.808
2.521
2.477
2.445
1.272
1.255
0.990
0.975
0.001
O
Me
Me
Me
3ag
0.93
1.04
1.03
1.98
1.99
0.99
1.00
1.10
0.99
1.98
6.19
2.91
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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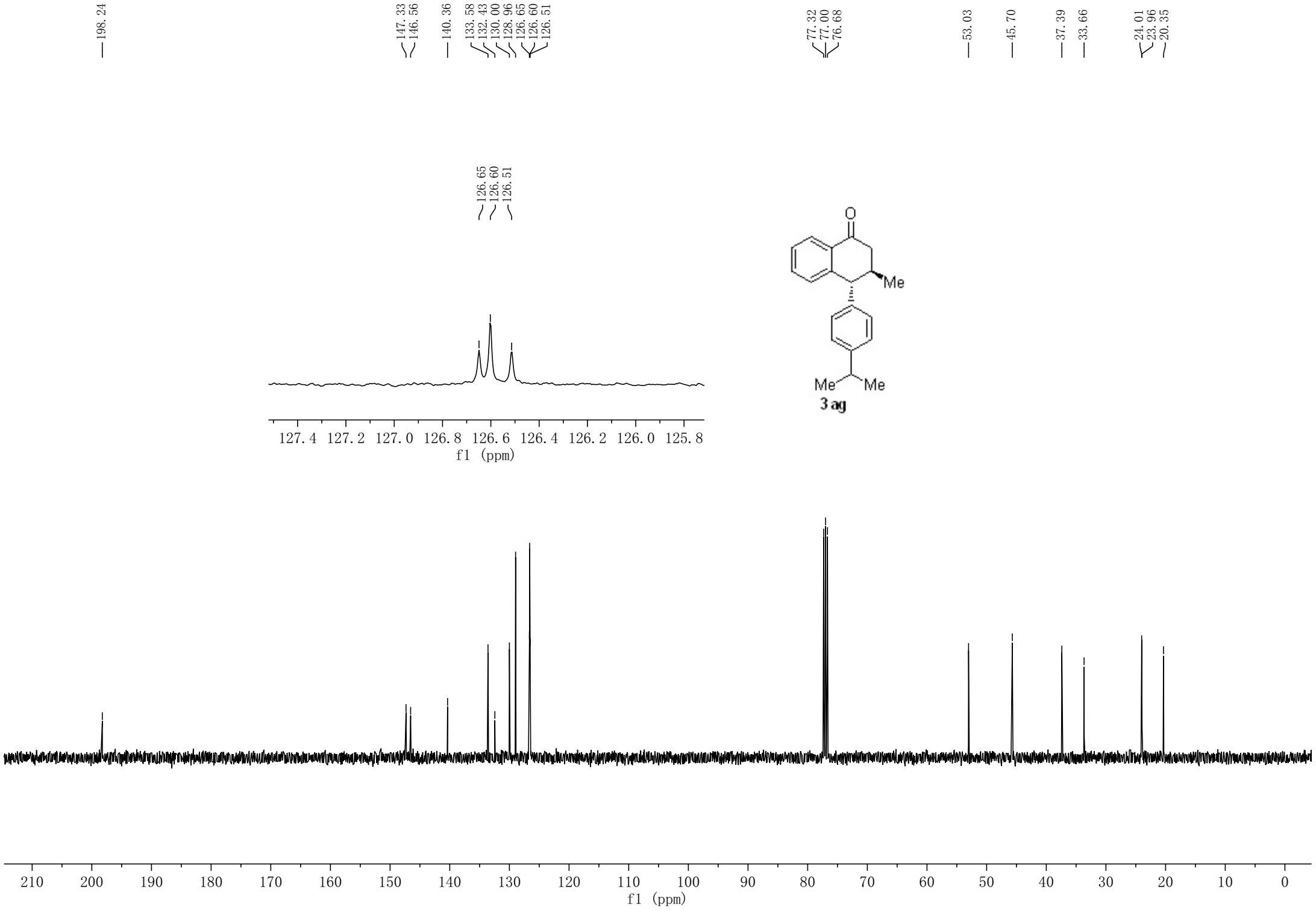
0.0
f1 (ppm)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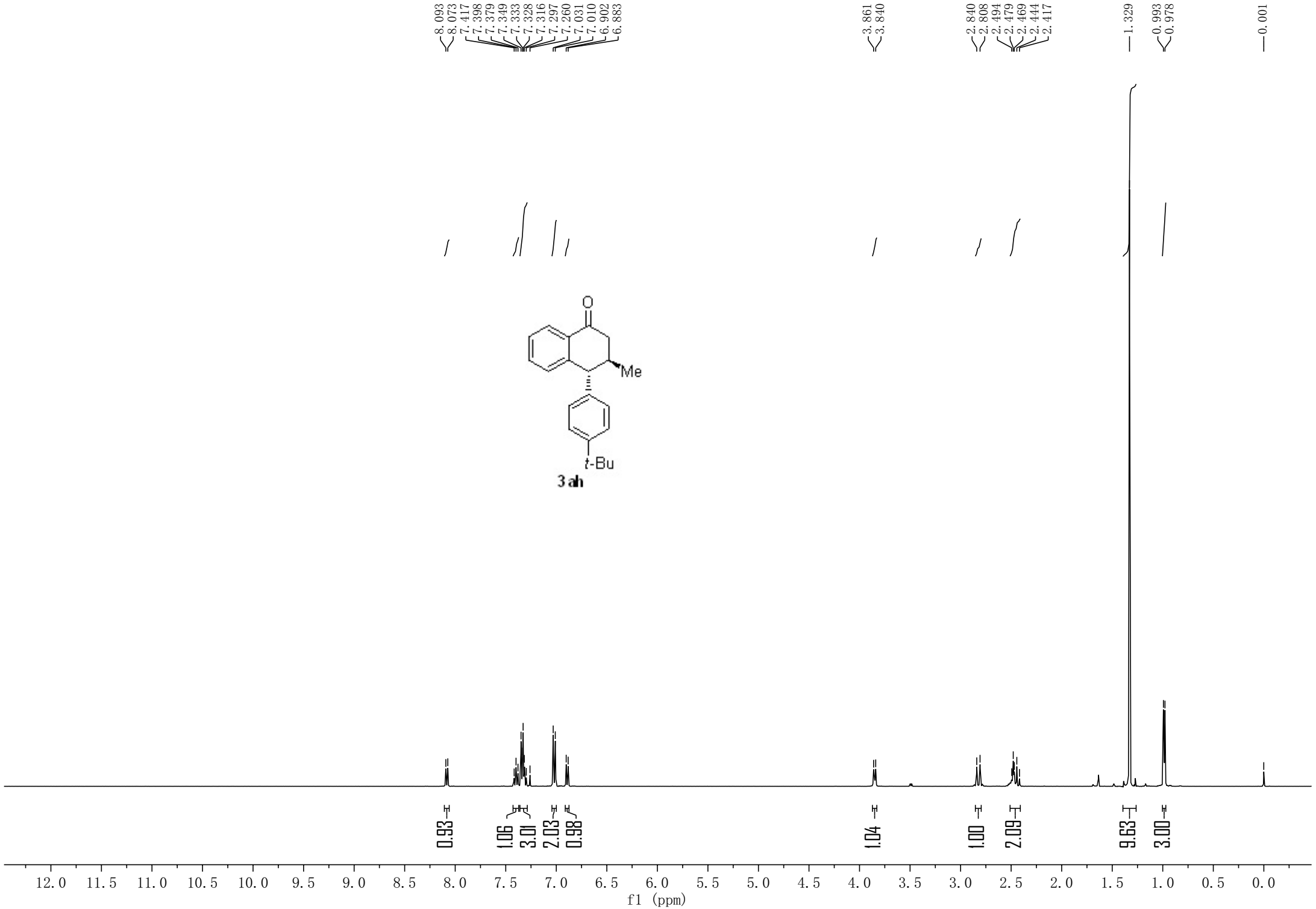
126.60
126.51
77.32
77.00
76.68
53.03
45.70
37.39
33.66
24.01
23.96
20.35
126.65
126.60
126.51
127.4 127.2 127.0 126.8 126.6 126.4 126.2 126.0 125.8
f1 (ppm)
O
Me
Me
Me
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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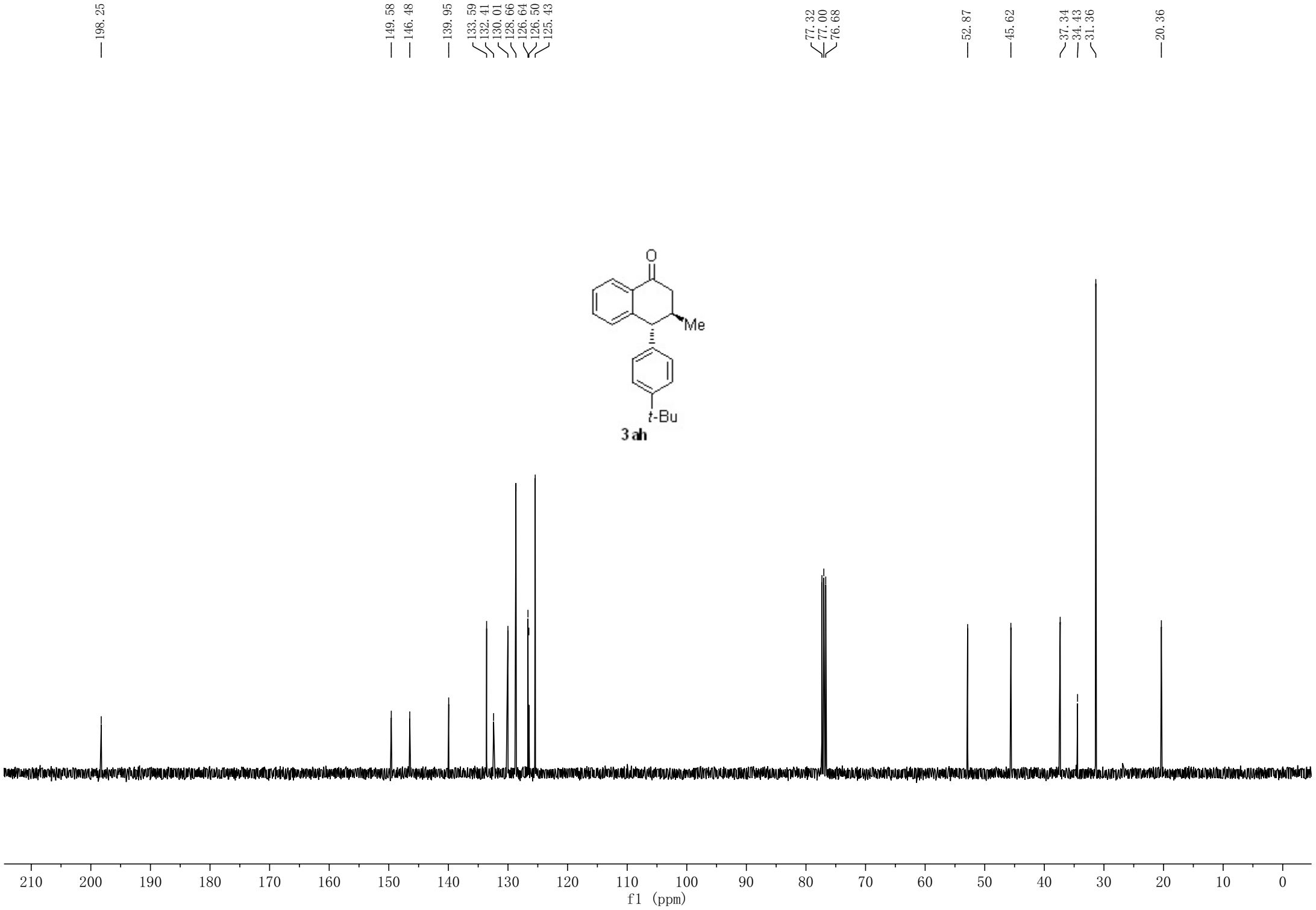
7.328
7.316
7.297
7.260
7.031
7.010
6.902
6.883
3.861
3.840
2.840
2.808
2.494
2.479
2.469
2.444
2.417
1.329
0.993
0.978
0.001
O
Me
t-Bu
3ah
0.93
1.06
3.01
2.03
0.98
1.04
1.00
2.09
9.63
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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77.00
76.68
52.87
45.62
37.34
34.43
31.36
20.36
O
Me
t-Bu
3ah
210
200
190
180
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160
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130
120
110
100
90
80
70
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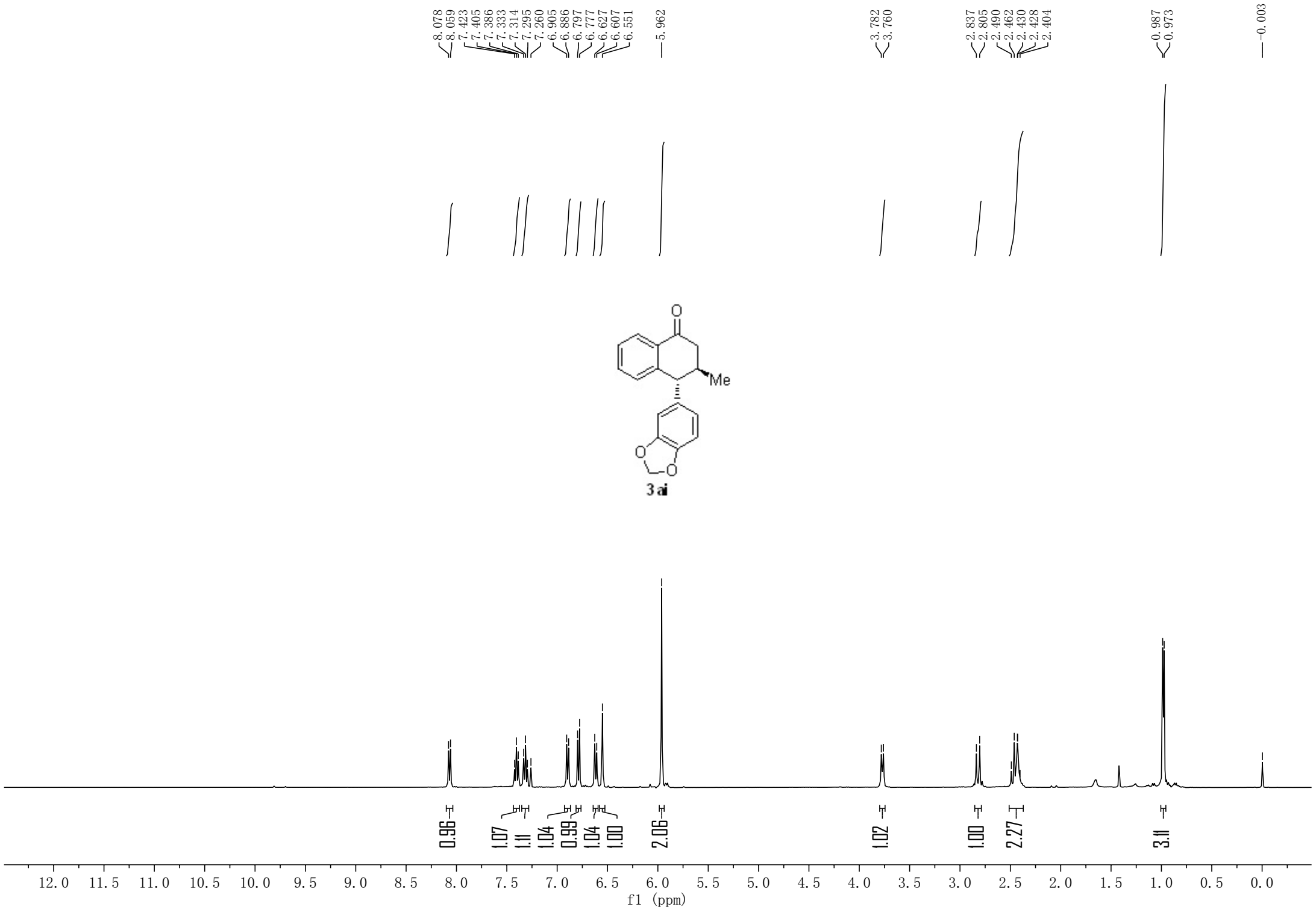
50
40
30
20
10
0
f1 (ppm)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7.260
6.905
6.886
6.797
6.777
6.627
6.607
6.551
5.962
3.782
3.760
2.837
2.805
2.490
2.462
2.430
2.428
2.404
0.987
0.973
-0.003
O
Me
O
O
3ai
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1.11
1.04
0.99
1.04
1.00
2.06
1.02
1.00
2.27
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11.5
11.0
10.5
10.0
9.5
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6.5
6.0
5.5
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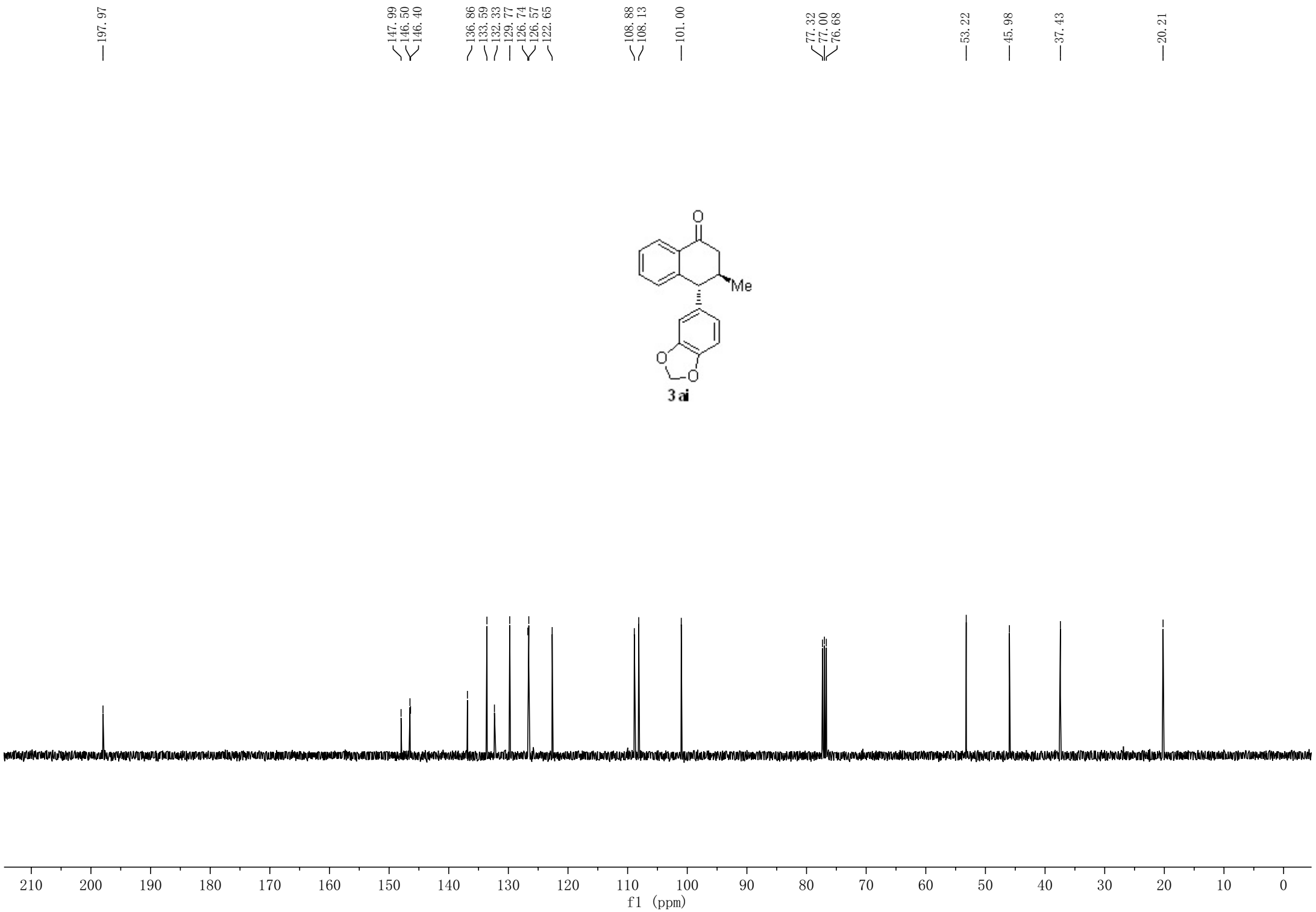
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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108.13
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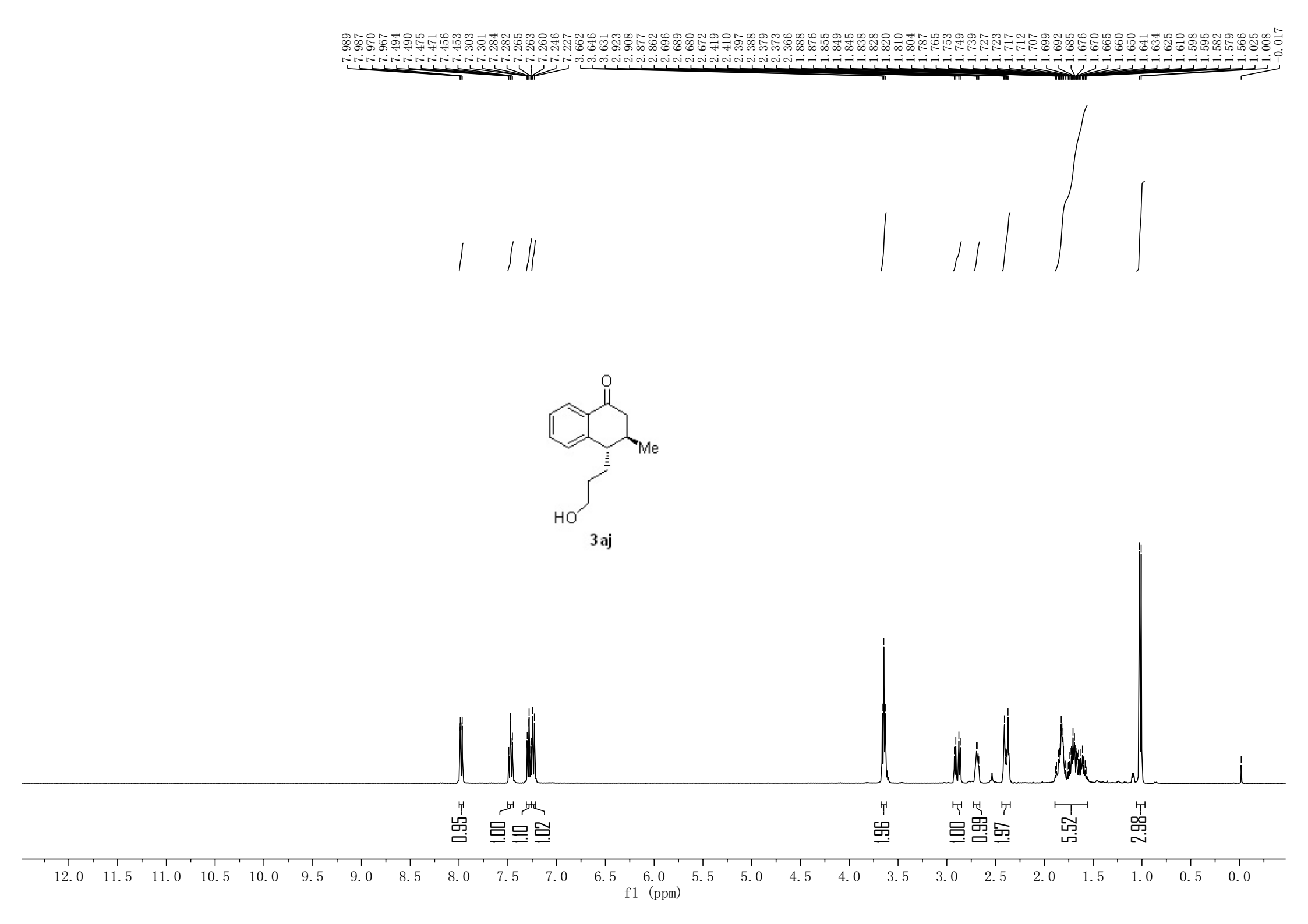
77.00
76.68
53.22
45.98
37.43
20.21
O
Me
O
O
3ai
f1 (ppm)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7.282
7.265
7.263
7.260
7.246
7.227
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3.646
3.631
2.923
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2.366
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1.845
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1.820
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1.787
1.765
1.753
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1.727
1.723
1.717
1.712
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1.699
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1.665
1.660
1.650
1.641
1.634
1.625
1.610
1.598
1.595
1.582
1.579
1.566
1.025
1.008
-0.017
O
Me
HO
3aj
0.95
1.00
1.10
1.02
1.96
1.00
0.99
1.97
5.52
2.98
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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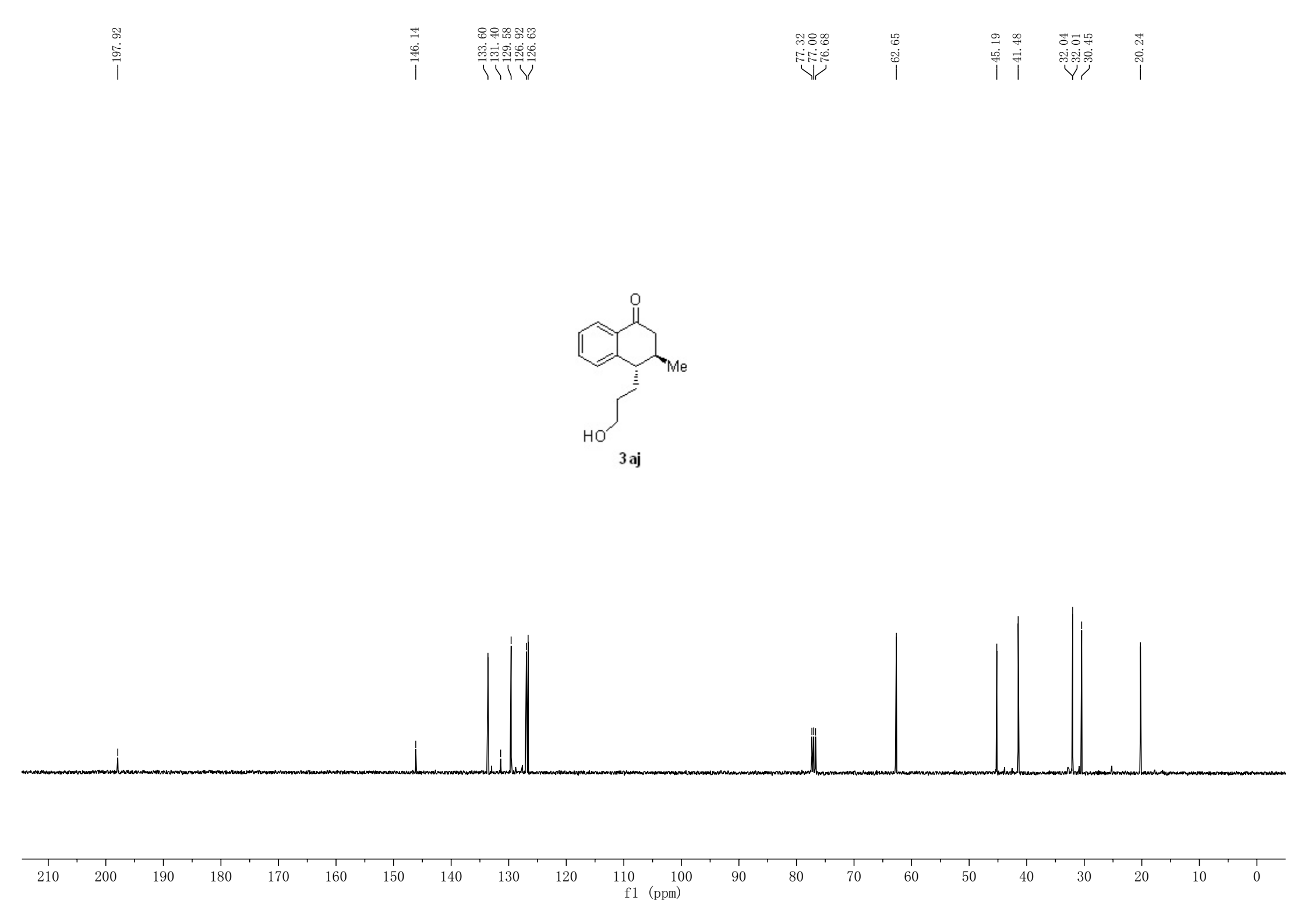
1.0
0.5
0.0
f1 (ppm)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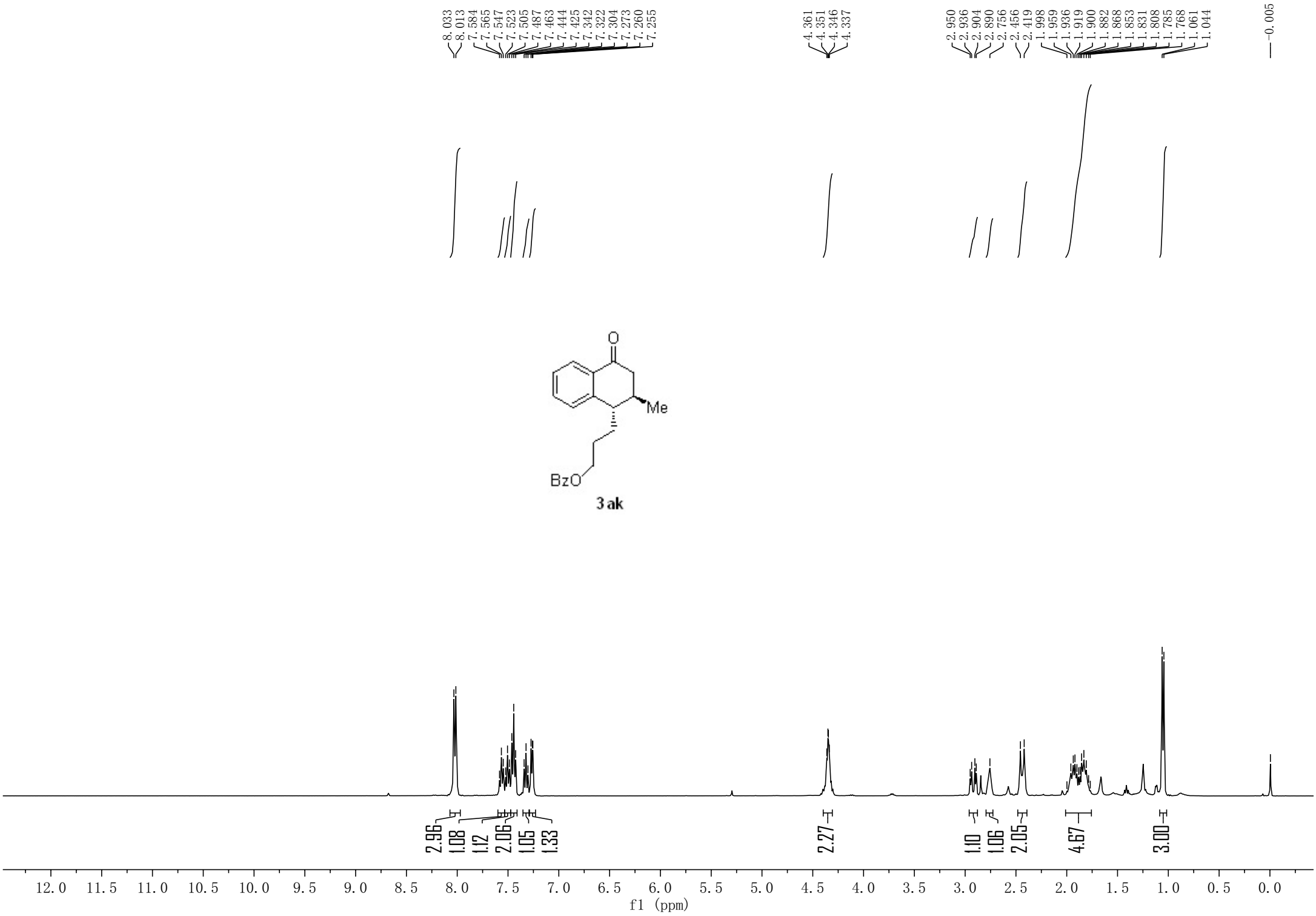
76.68
62.65
45.19
41.48
32.04
32.01
30.45
20.24
O
Me
HO
3aj
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.487
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7.444
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7.342
7.322
7.304
7.273
7.260
7.255
4.361
4.351
4.346
4.337
2.950
2.936
2.904
2.890
2.756
2.456
2.419
1.998
1.959
1.936
1.919
1.900
1.882
1.868
1.853
1.831
1.808
1.785
1.768
1.061
1.044
-0.005
O
Me
BzO
3ak
2.96
1.08
1.12
2.06
1.05
1.33
2.27
1.10
1.06
2.05
4.67
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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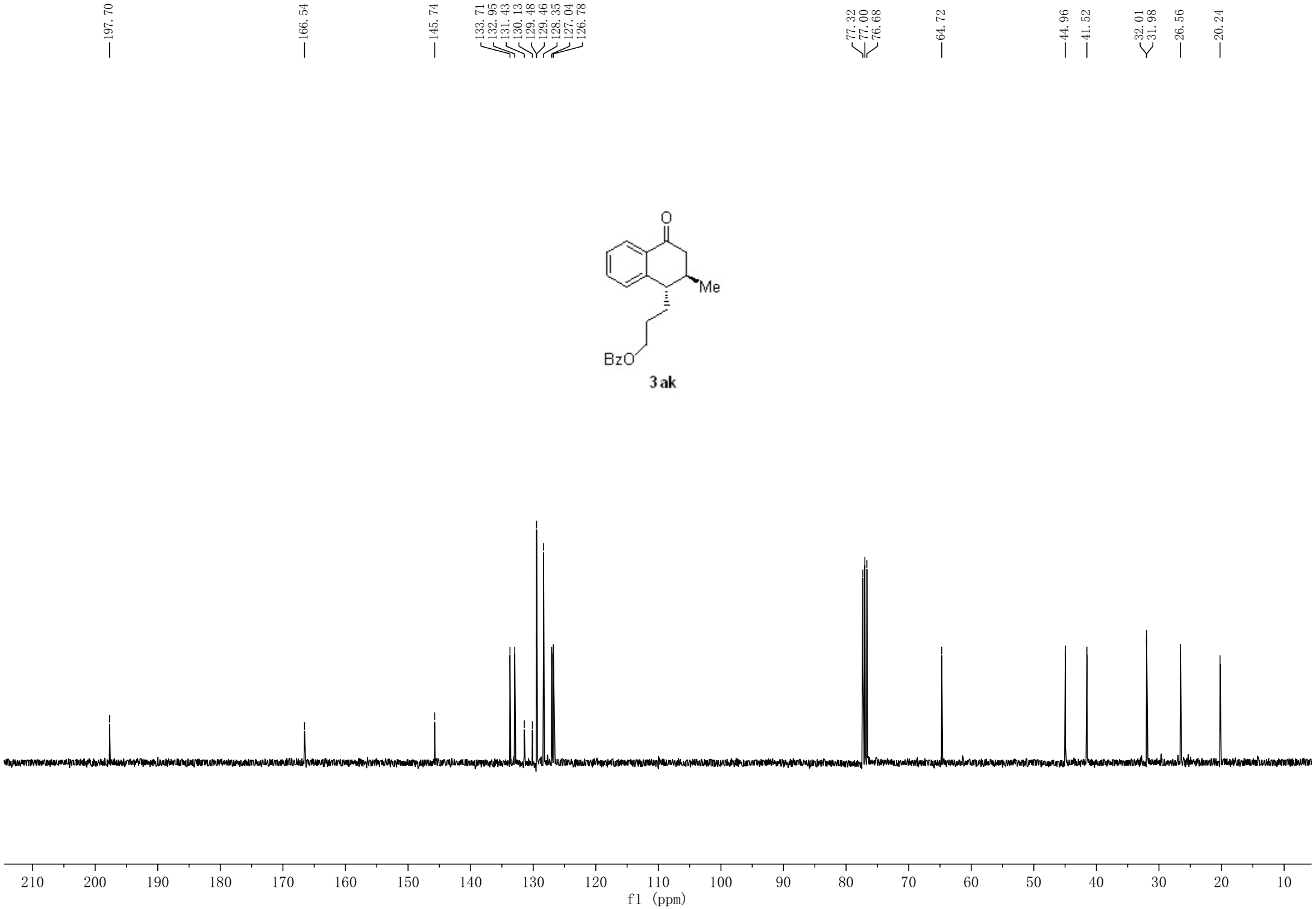
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.95
131.43
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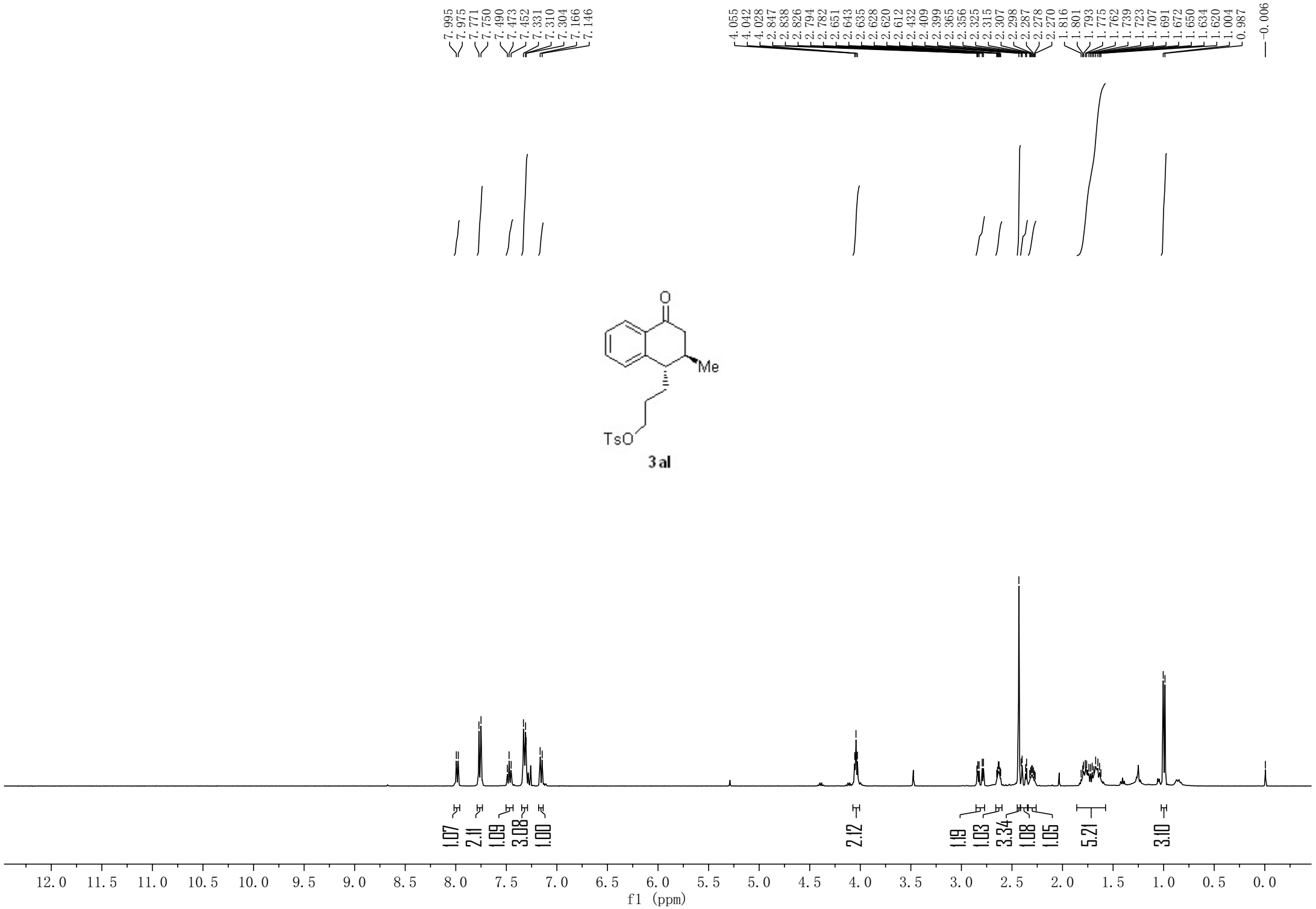
129.48
129.46
128.35
127.04
126.78
77.32
77.00
76.68
64.72
44.96
41.52
32.01
31.98
26.56
20.24
O
Me
BzO
3ak
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.146
4.055
4.042
4.028
2.847
2.838
2.826
2.794
2.782
2.651
2.643
2.635
2.628
2.620
2.612
2.432
2.409
2.399
2.365
2.356
2.325
2.315
2.307
2.298
2.287
2.278
2.270
1.816
1.801
1.793
1.775
1.762
1.739
1.723
1.707
1.691
1.672
1.650
1.634
1.620
1.004
0.987
-0.006
O
Me
TsO
3al
1.07
2.11
1.09
3.08
1.00
2.12
1.19
1.03
3.34
1.08
1.05
5.21
3.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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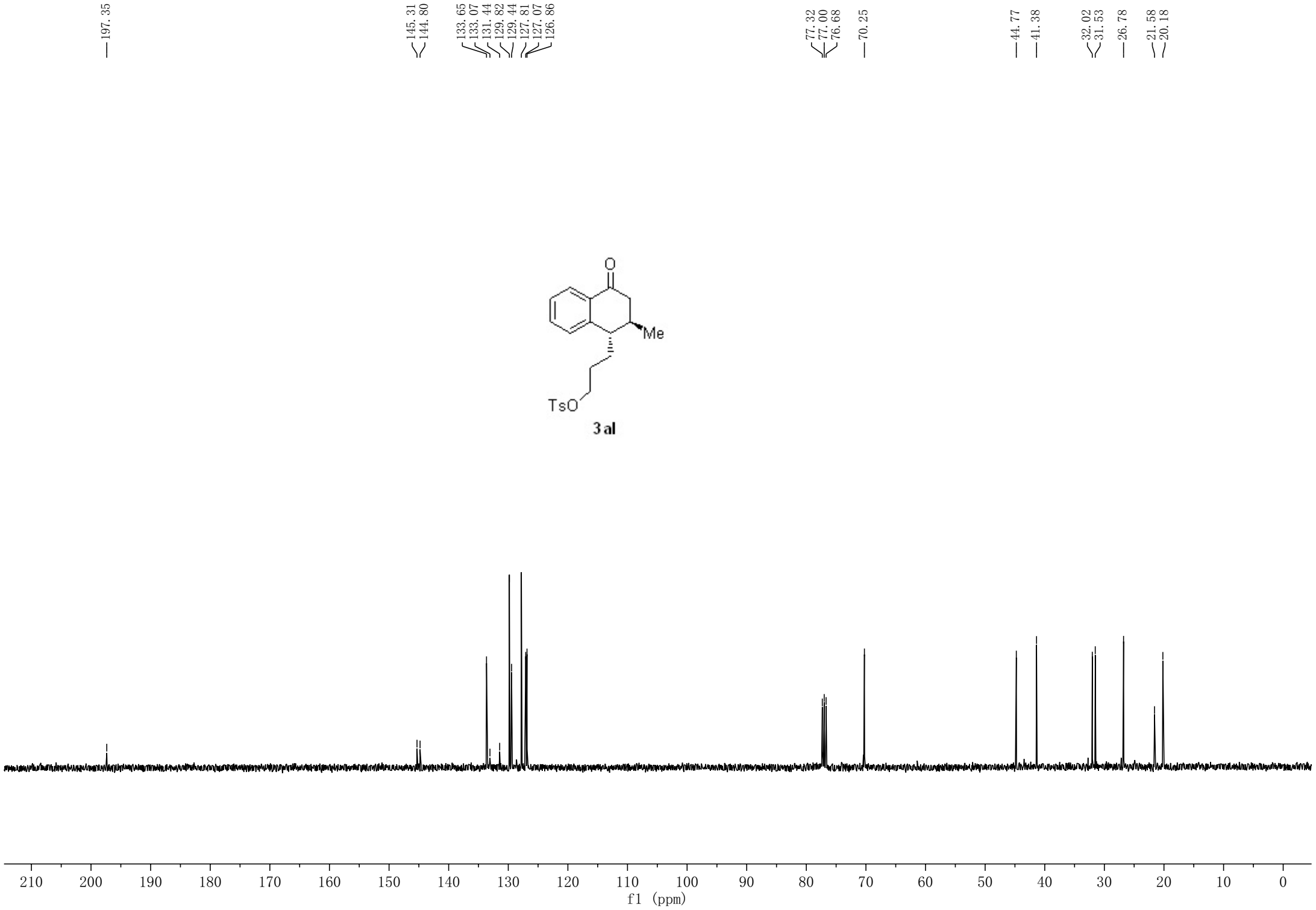
0.0
f1 (ppm)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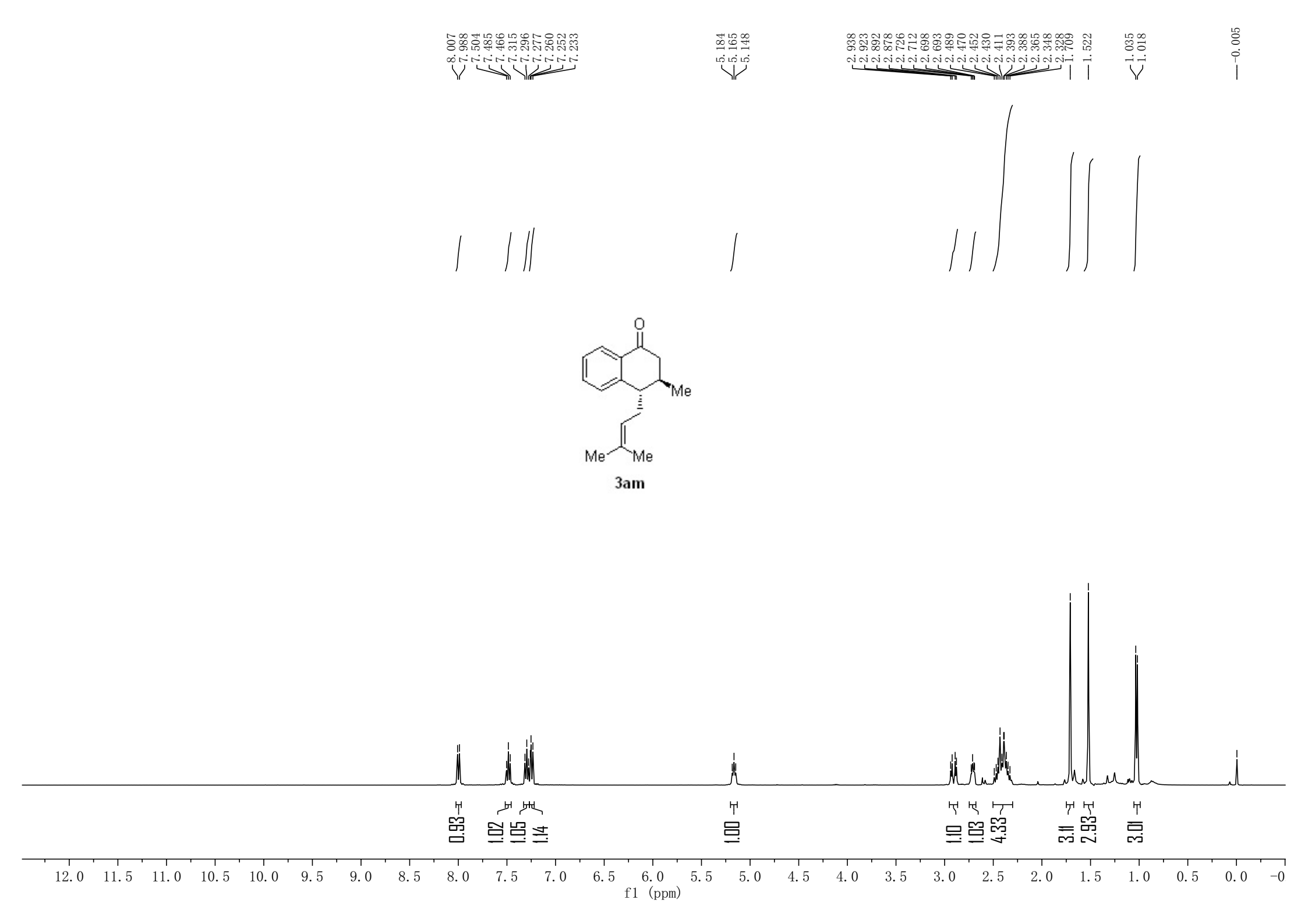
131.44
129.82
129.44
127.81
127.07
126.86
77.32
77.00
76.68
70.25
44.77
41.38
32.02
31.53
26.78
21.58
20.18
O
Me
TsO
3al
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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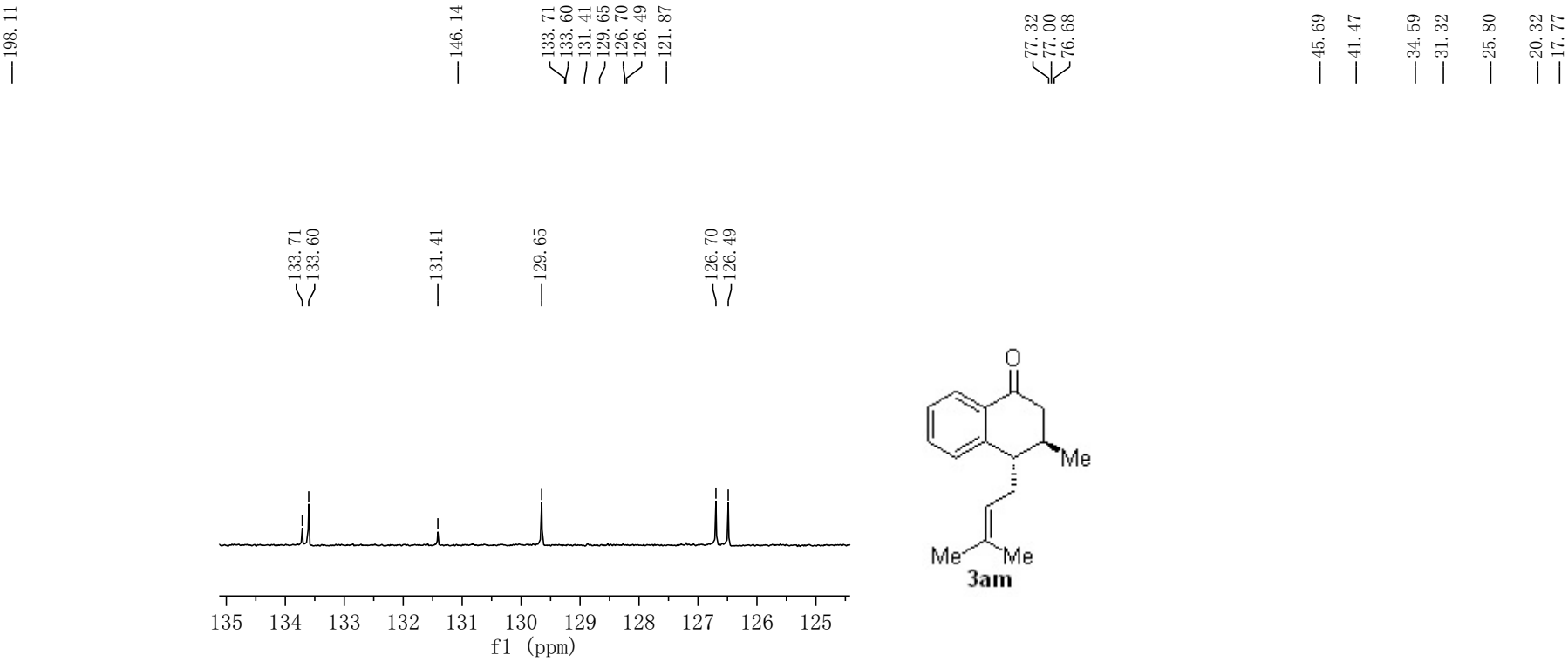
7.296
7.277
7.260
7.252
7.233
5.184
5.165
5.148
2.938
2.923
2.892
2.878
2.726
2.712
2.698
2.693
2.489
2.470
2.452
2.430
2.411
2.393
2.388
2.365
2.348
2.328
1.709
1.522
1.035
1.018
-0.005
O
Me
Me
Me
3am
0.93
1.02
1.05
1.14
1.00
1.10
1.03
4.33
3.11
2.93
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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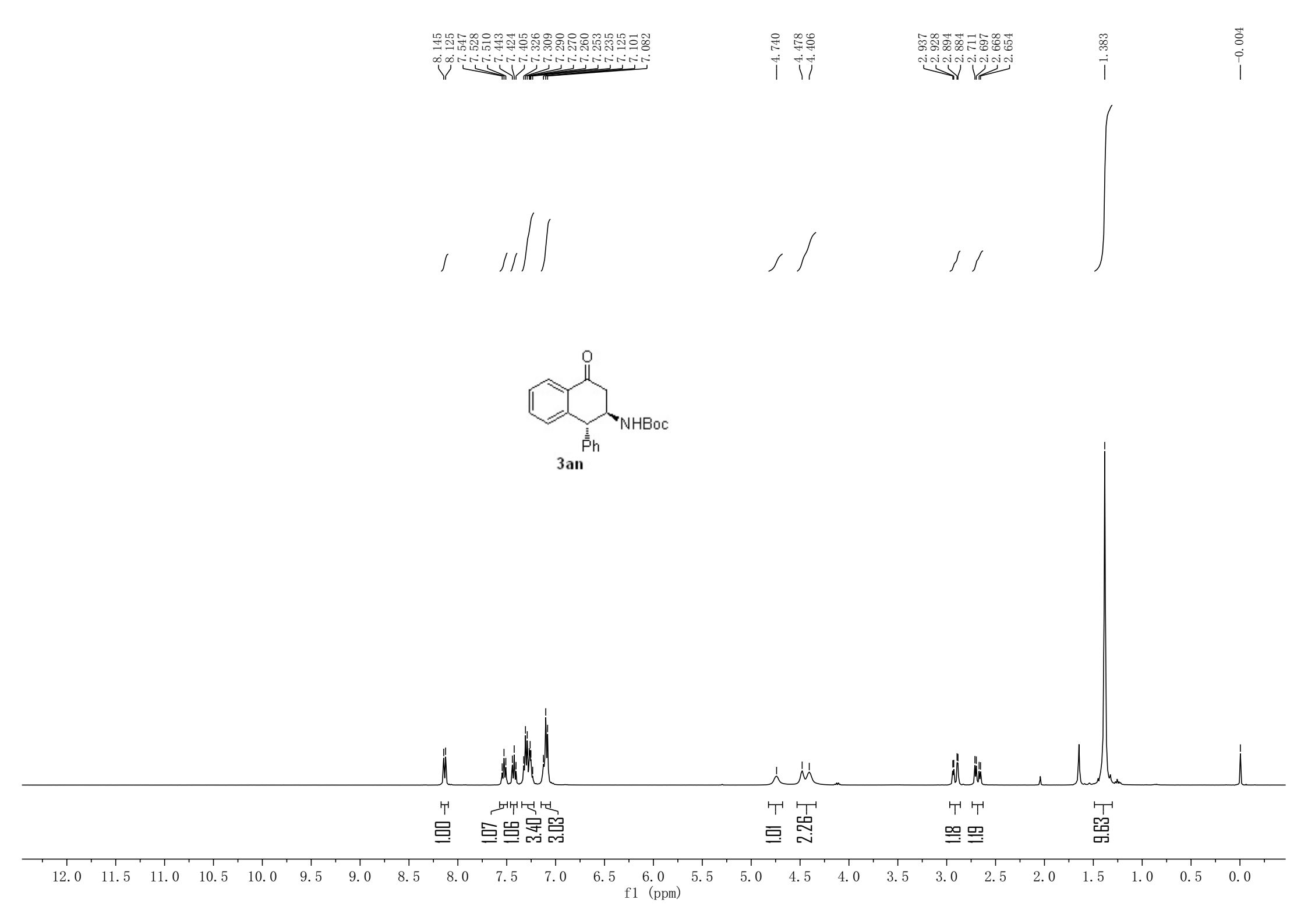
129.65
126.70
126.49
121.87
77.32
77.00
76.68
45.69
41.47
34.59
31.32
25.80
20.32
17.77
133.71
133.60
131.41
129.65
126.70
126.49
135 134 133 132 131 130 129 128 127 126 125
f1 (ppm)
O
Me
Me
Me
3am
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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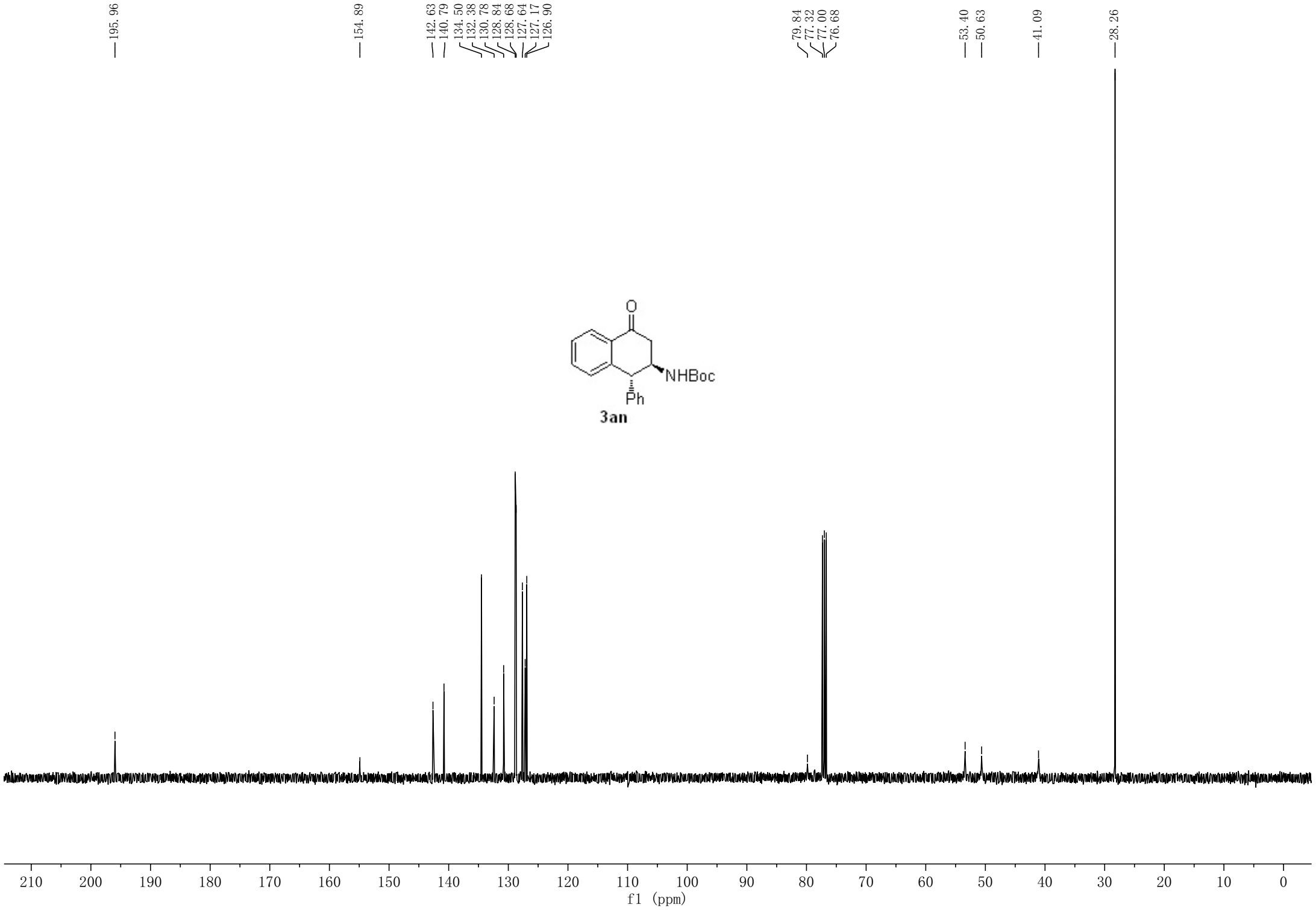
8.125
7.547
7.528
7.510
7.443
7.424
7.405
7.326
7.309
7.290
7.270
7.260
7.253
7.235
7.125
7.101
7.082
4.740
4.478
4.406
2.937
2.928
2.894
2.884
2.711
2.697
2.668
2.654
1.383
0.004
O
NHBoc
Ph
3an
1.00
1.07
1.06
3.40
3.03
1.01
2.26
1.18
1.19
9.63
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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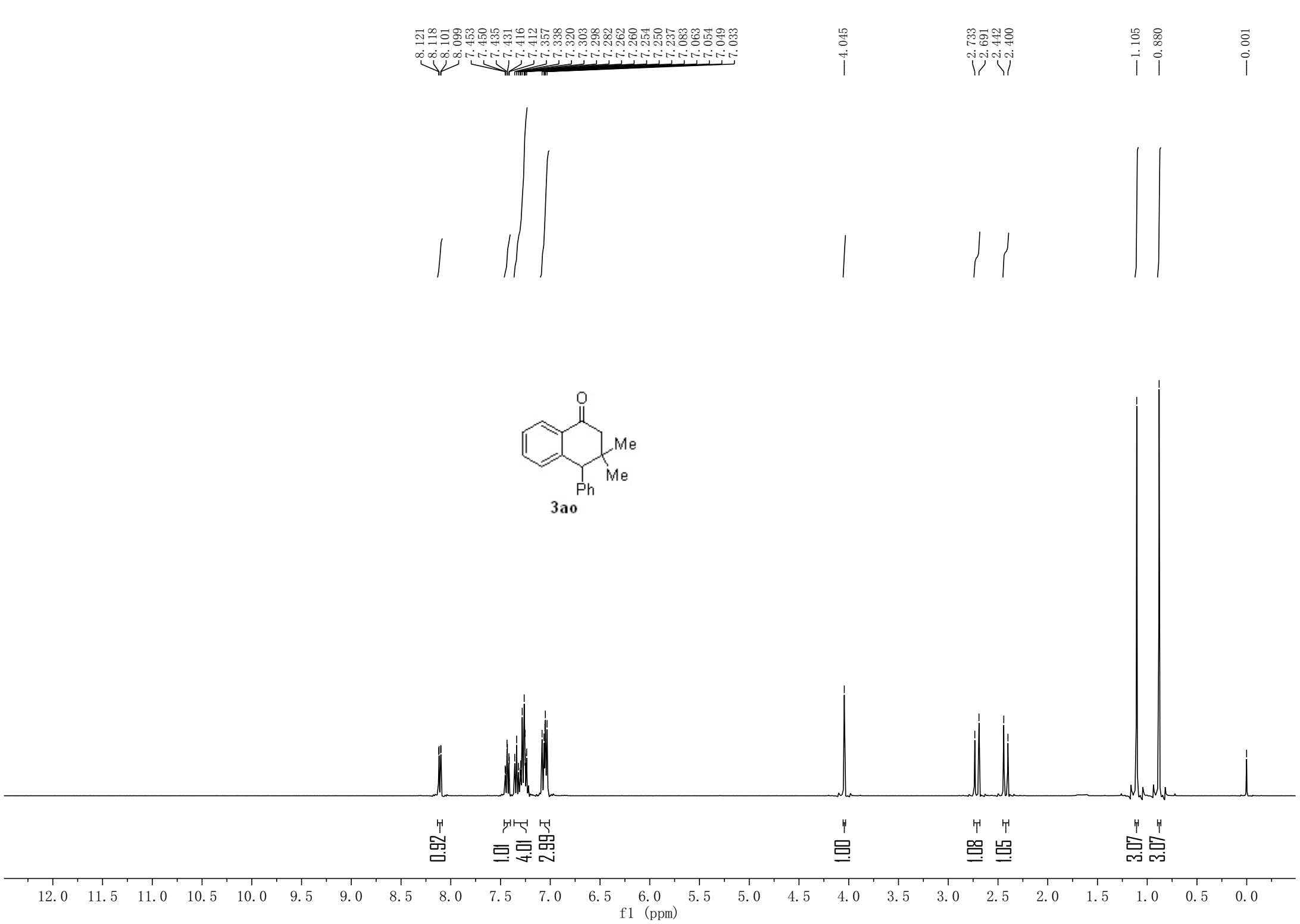
154.89
142.63
140.79
134.50
132.38
130.78
128.84
128.68
127.64
127.17
126.90
79.84
77.32
77.00
76.68
53.40
50.63
41.09
28.26
O
NHBoc
Ph
3an
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.118
8.101
8.099
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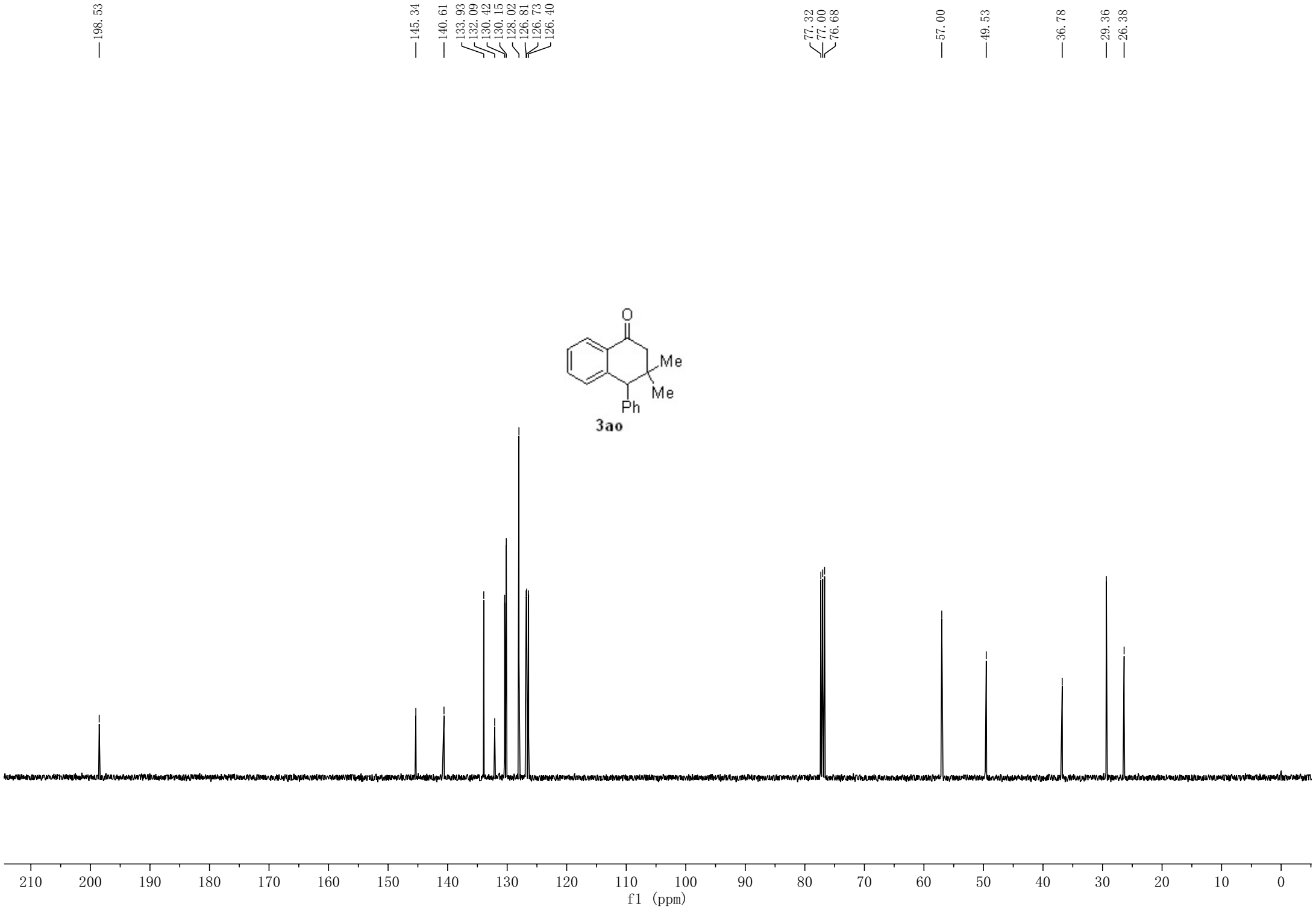
7.450
7.435
7.431
7.416
7.412
7.357
7.338
7.320
7.303
7.298
7.282
7.262
7.260
7.254
7.250
7.237
7.083
7.063
7.054
7.049
7.033
4.045
2.733
2.691
2.442
2.400
1.105
0.880
0.001
O
Me
Me
Ph
3ao
0.92
1.01
4.01
2.99
1.00
1.08
1.05
3.07
3.07
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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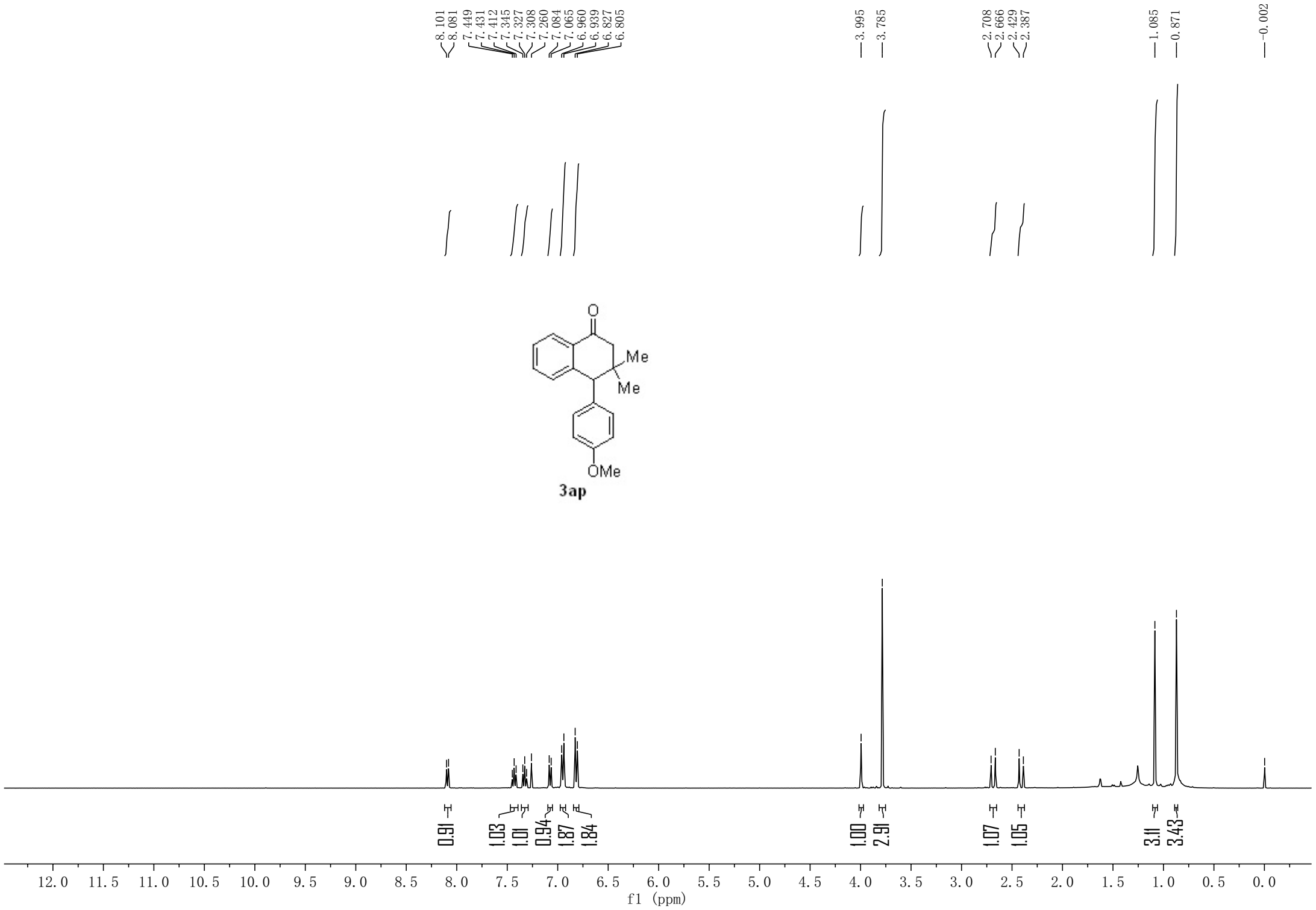
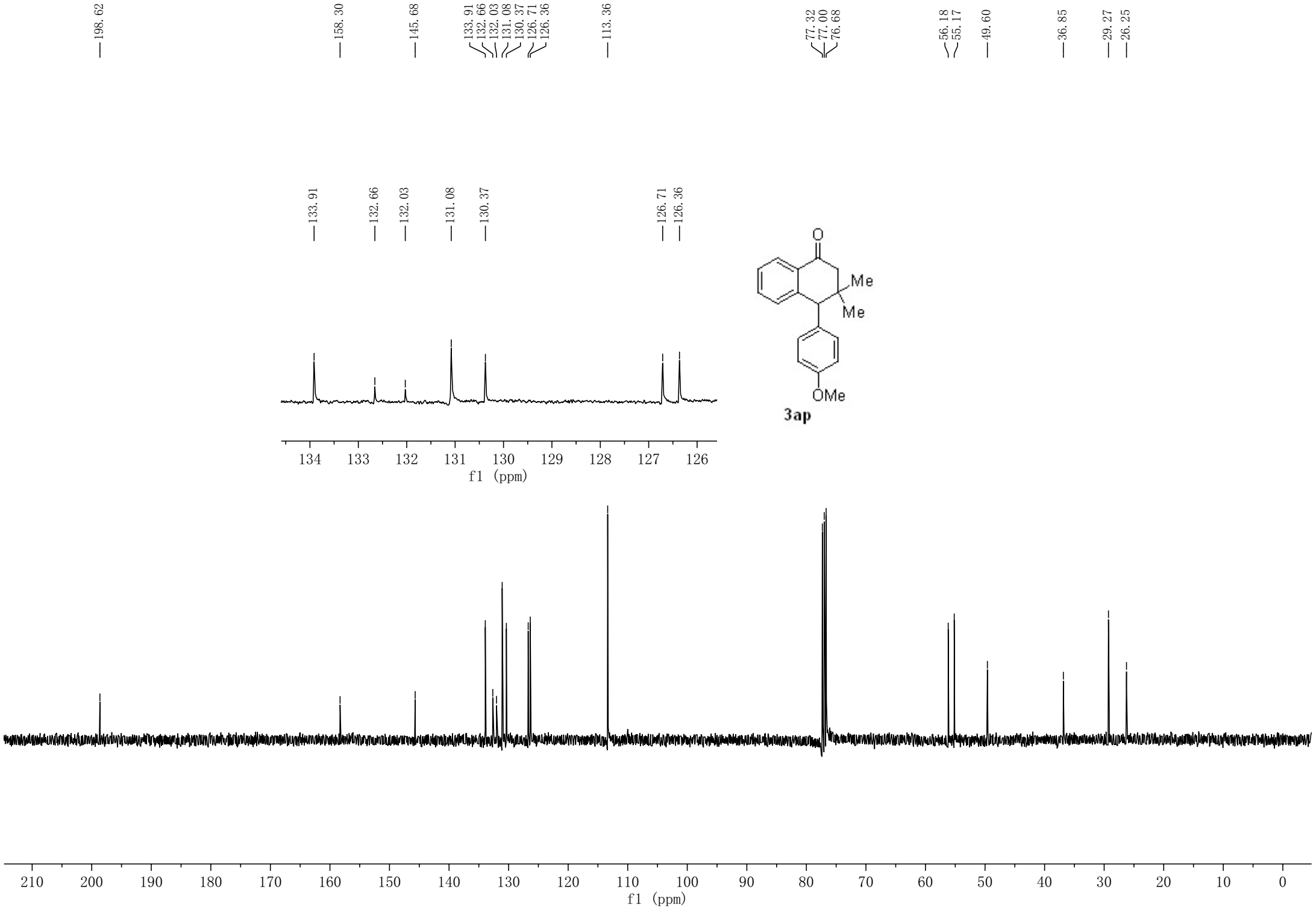
140.61
133.93
132.09
130.42
130.15
128.02
126.81
126.73
126.40
77.32
77.00
76.68
57.00
49.53
36.78
29.36
26.38
O
Me
Me
Ph
3ao
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.101
8.081
7.449
7.431
7.412
7.345
7.327
7.308
7.260
7.084
7.065
6.960
6.939
6.827
6.805
3.995
3.785
2.708
2.666
2.429
2.387
1.085
0.871
0.002
O
Me
Me
OMe
3ap
0.91
1.03
1.01
0.94
1.87
1.84
1.00
2.91
1.07
1.05
3.11
3.43
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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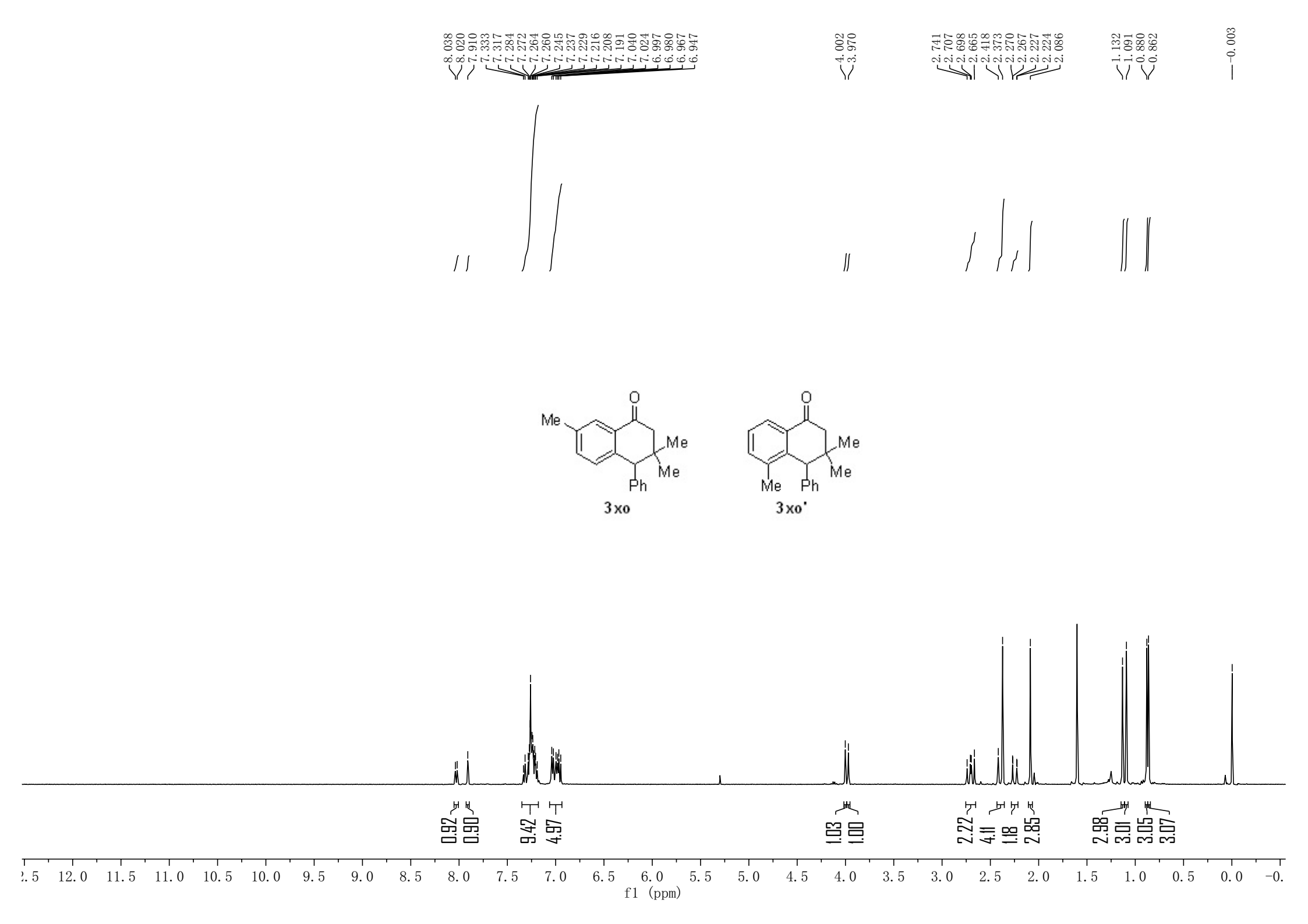
131.08
130.37
126.71
126.36
113.36
77.32
77.00
76.68
56.18
55.17
49.60
36.85
29.27
26.25
O
Me
Me
OMe
3ap
f1 (ppm)
f1 (ppm)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7.317
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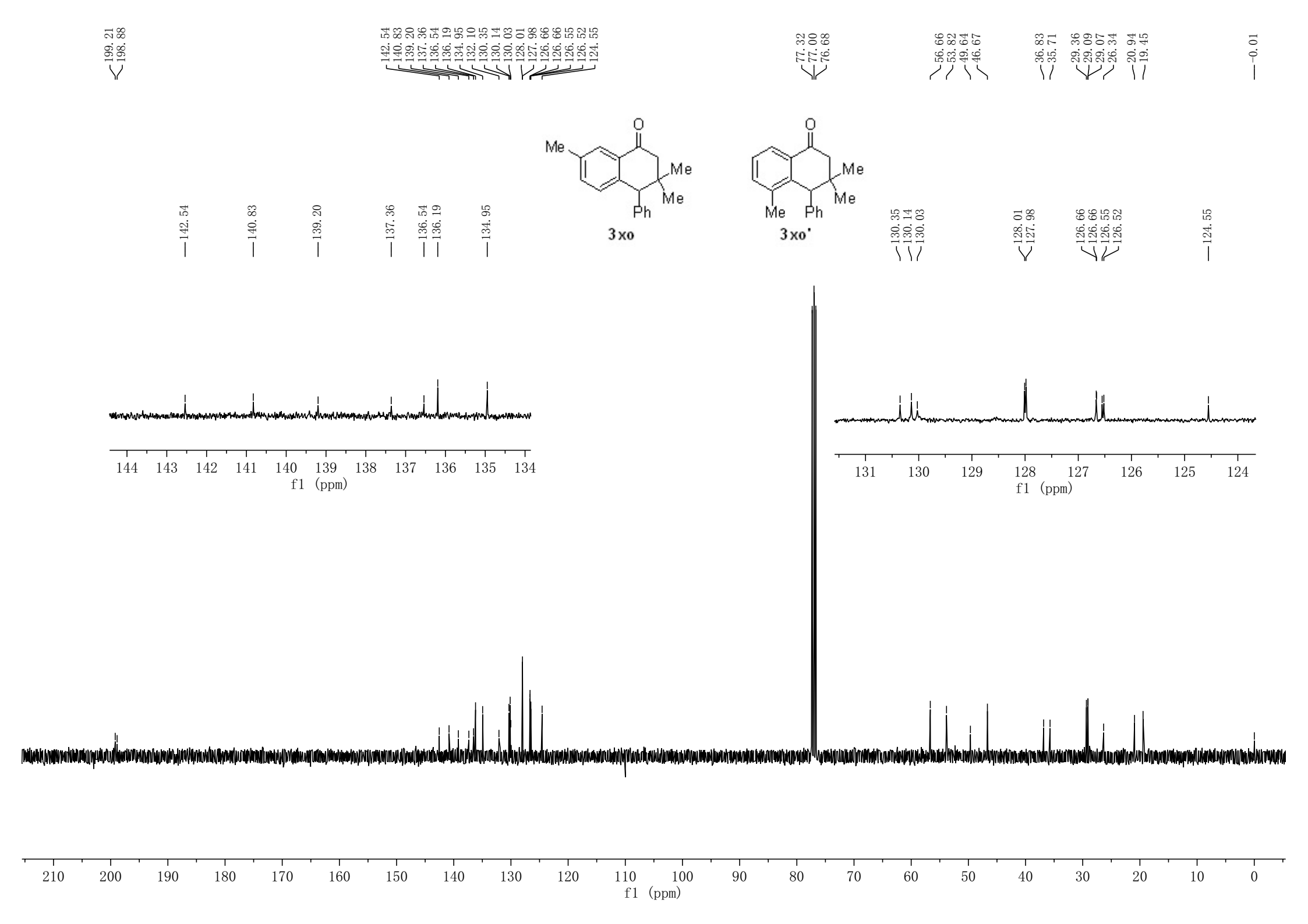
7.272
7.264
7.260
7.245
7.237
7.229
7.216
7.208
7.191
7.040
7.024
6.997
6.980
6.967
6.947
4.002
3.970
2.741
2.707
2.698
2.665
2.418
2.373
2.270
2.267
2.227
2.224
2.086
1.132
1.091
0.880
0.862
-0.003
Me
Me
Me
Ph
3xo
Me
Me
Me
Ph
3xo'
0.92
0.90
9.42
4.97
1.03
1.00
2.22
4.11
1.18
2.85
2.98
3.01
3.05
3.07
f1 (ppm)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198.88
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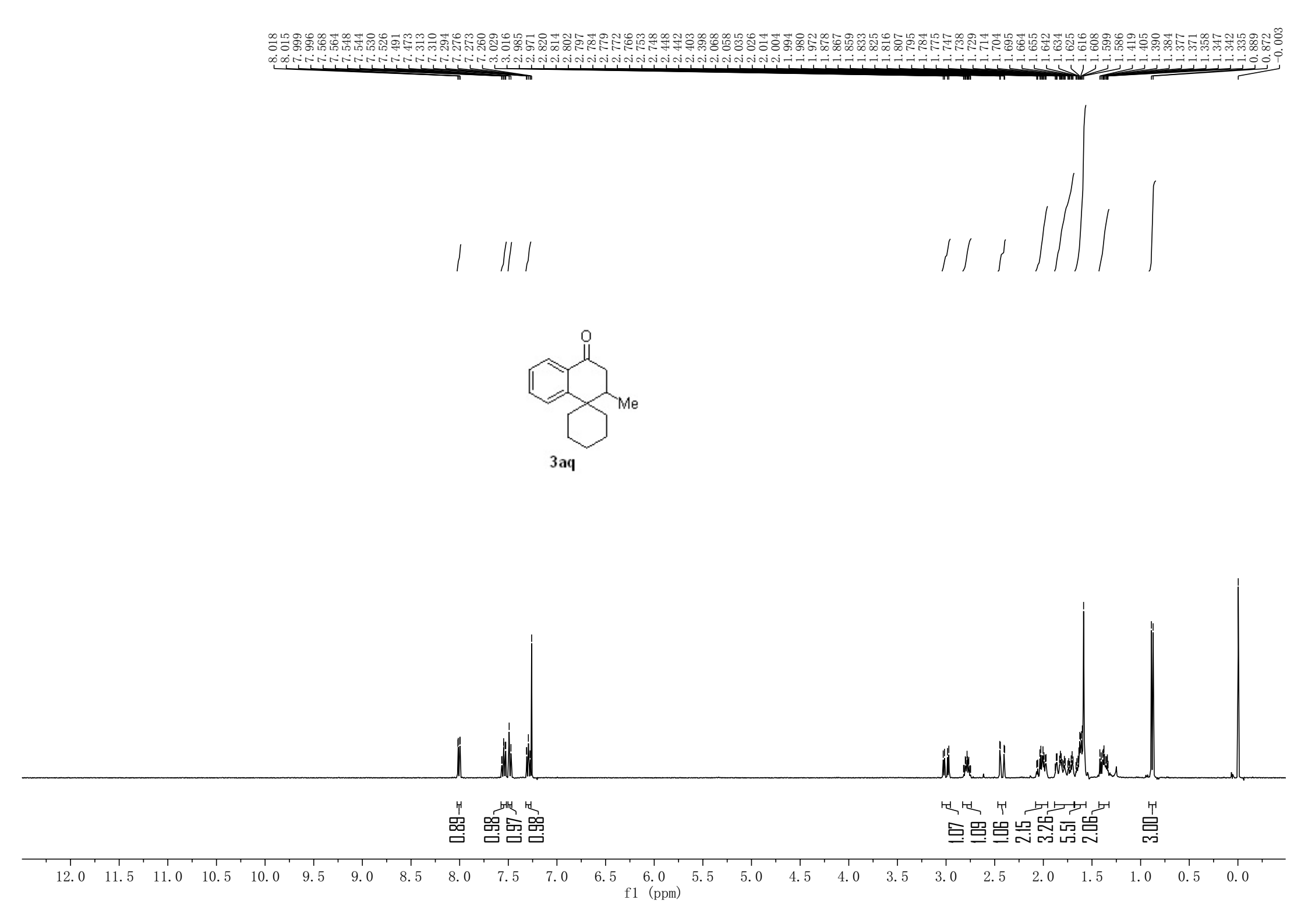
140.83
139.20
137.36
136.54
136.19
134.95
132.10
130.35
130.14
130.03
128.01
127.98
126.66
126.66
126.55
126.52
124.55
77.32
77.00
76.68
56.66
53.82
49.64
46.67
36.83
35.71
29.36
29.09
29.07
26.34
20.94
19.45
-0.01
Me
Me
Me
Ph
O
3xo
Me
Me
Me
Ph
O
3xo'
f1 (ppm)
f1 (ppm)
f1 (ppm)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7.526
7.491
7.473
7.313
7.310
7.294
7.276
7.273
7.260
3.029
3.016
2.985
2.971
2.820
2.814
2.802
2.797
2.784
2.779
2.772
2.766
2.753
2.748
2.448
2.442
2.403
2.398
2.068
2.058
2.035
2.026
2.014
2.004
1.994
1.980
1.972
1.878
1.867
1.859
1.833
1.825
1.816
1.807
1.795
1.784
1.775
1.747
1.738
1.729
1.714
1.704
1.695
1.664
1.655
1.642
1.634
1.625
1.616
1.608
1.599
1.586
1.419
1.405
1.390
1.384
1.377
1.371
1.358
1.347
1.342
1.335
0.889
0.872
-0.003
O
Me
3aq
0.89
0.98
0.97
0.98
1.07
1.09
1.06
2.15
3.26
5.51
2.06
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

198.50
150.77
134.08
131.42
126.92
126.03
125.65
77.32
77.00
76.68
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32.29
29.74
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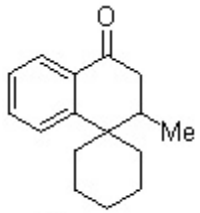
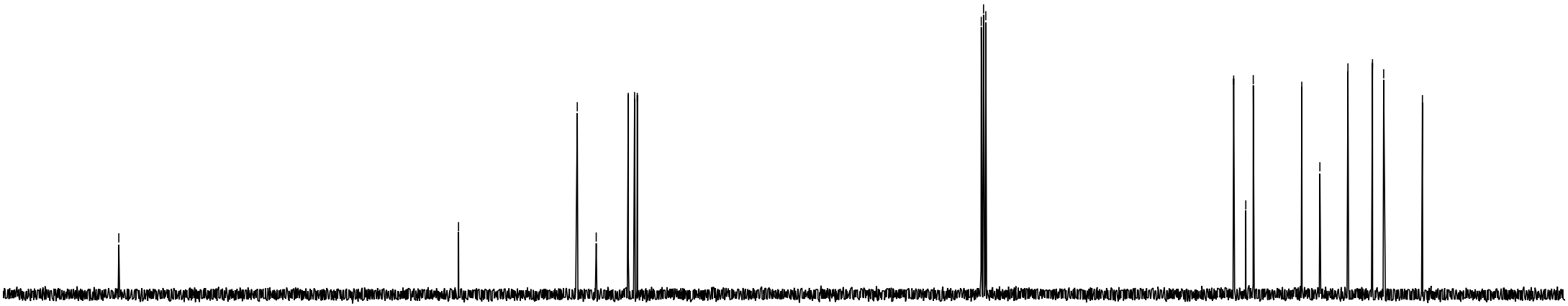
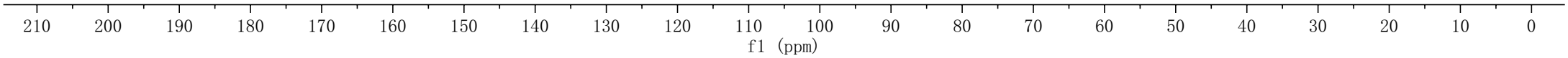
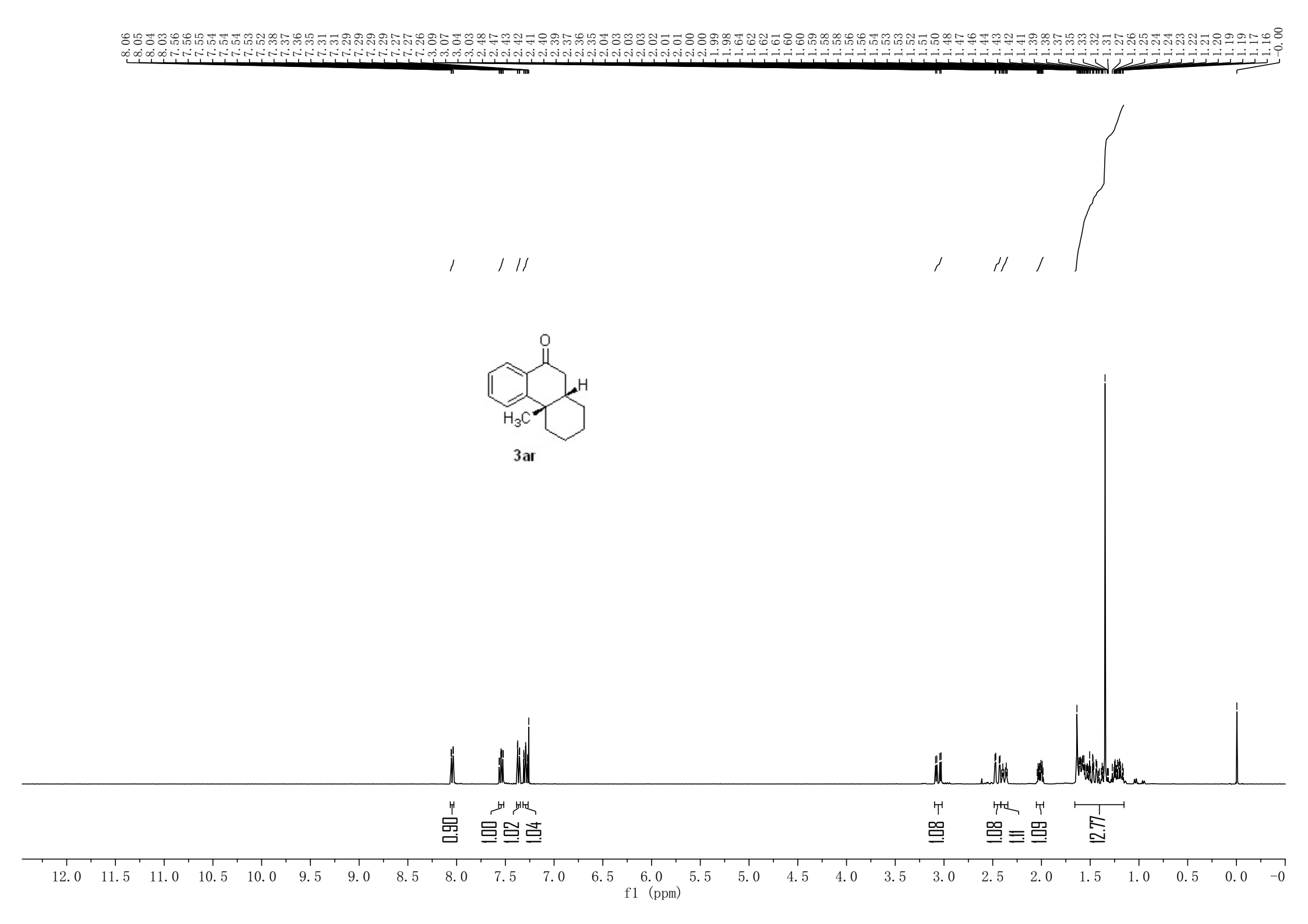
22.35
20.77
15.33



3aq



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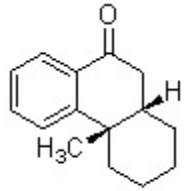
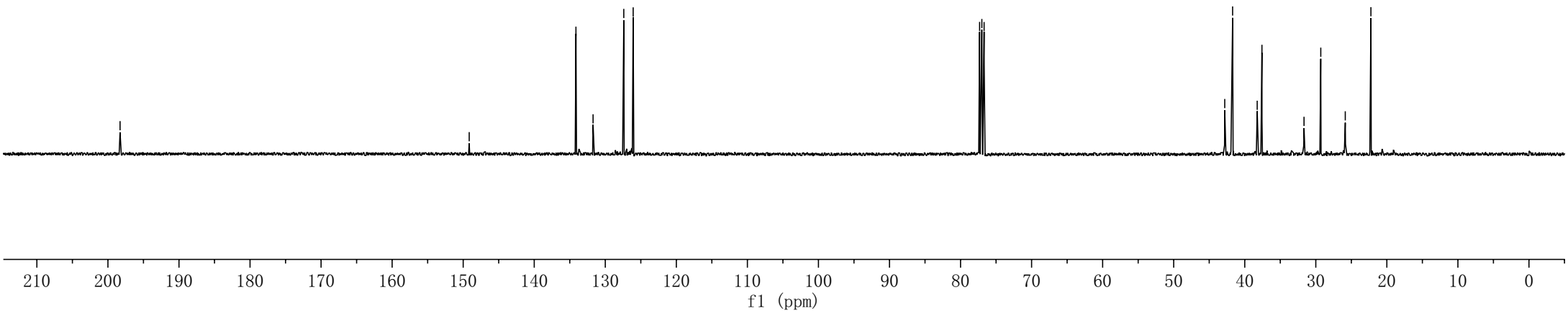
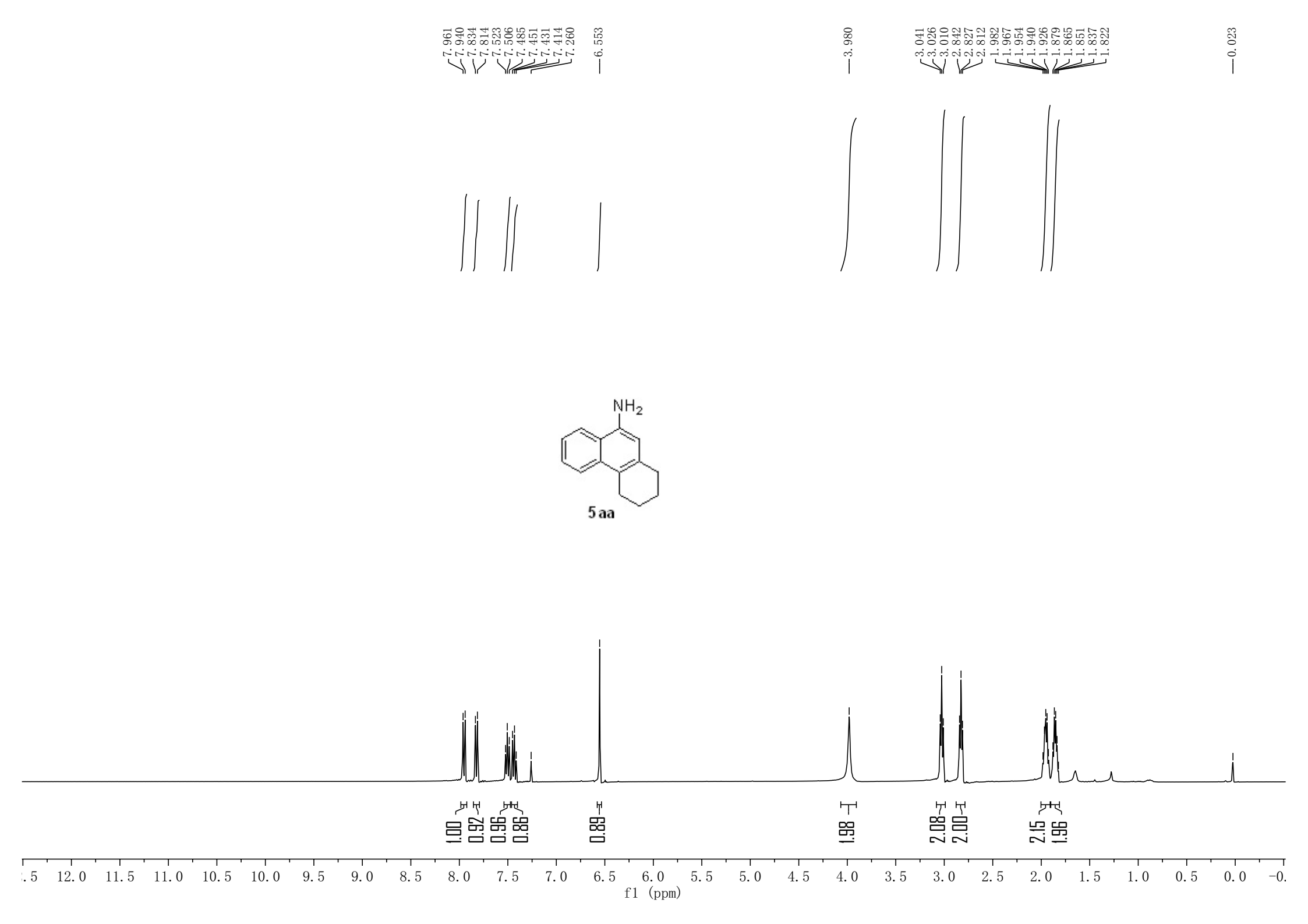
O
H
H3C
3ar
0.90
1.00
1.02
1.04
1.08
1.08
1.11
1.09
12.77
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

198.29
149.15
134.13
131.72
127.40
126.08
126.05
77.32
77.00
76.68
42.82
41.71
38.25
37.58
31.66
29.30
25.85
22.24



3ar

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7.834
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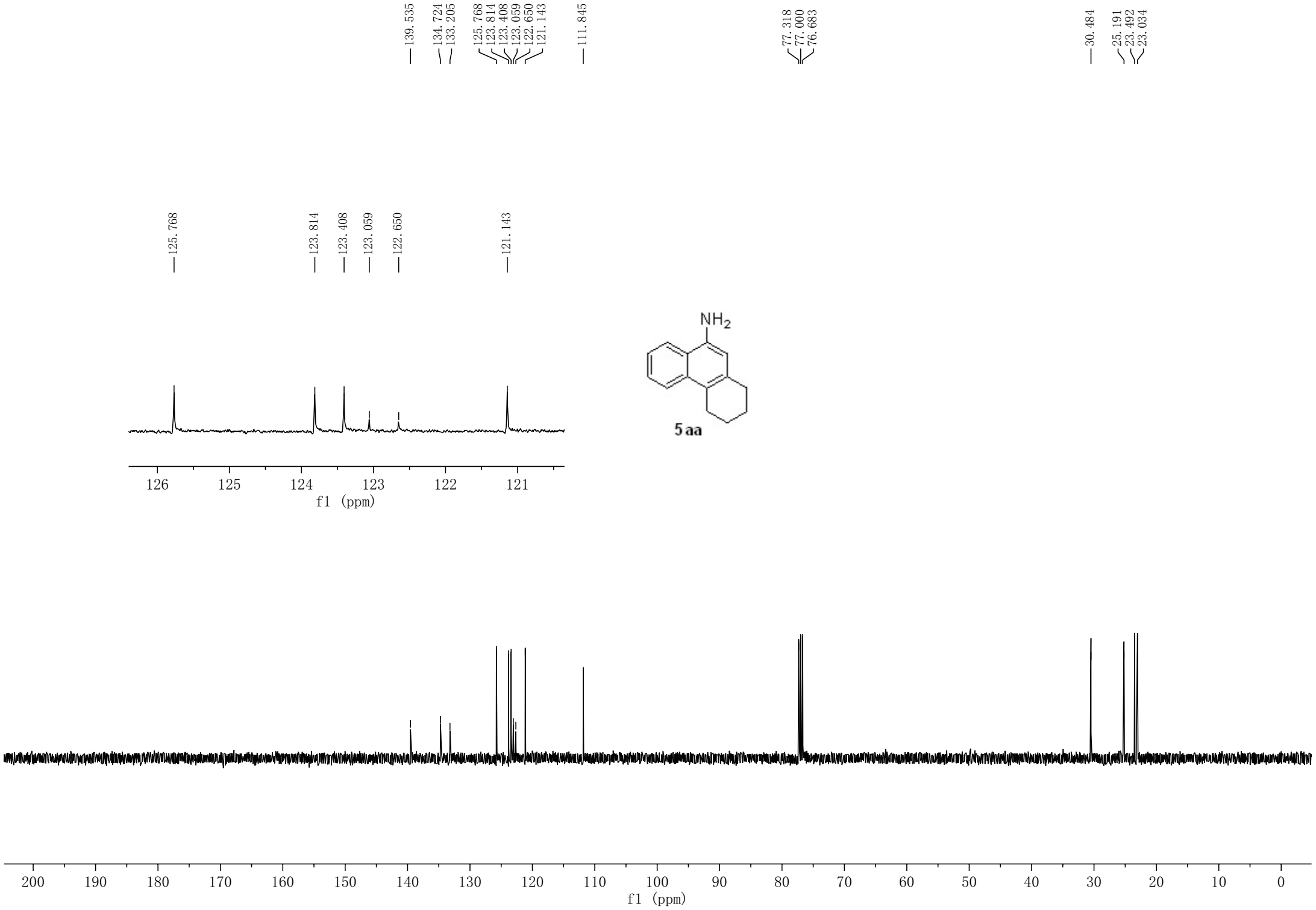
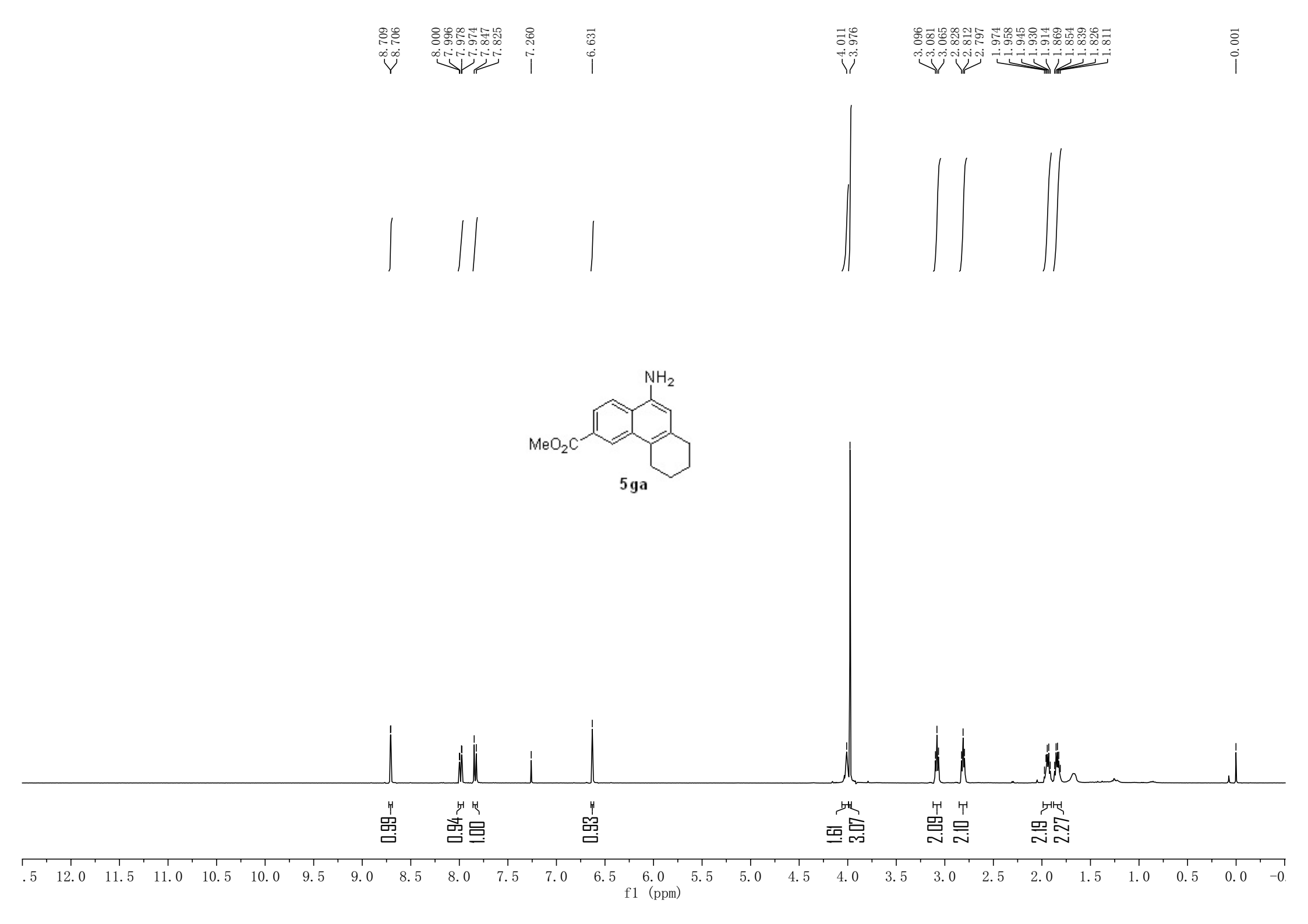
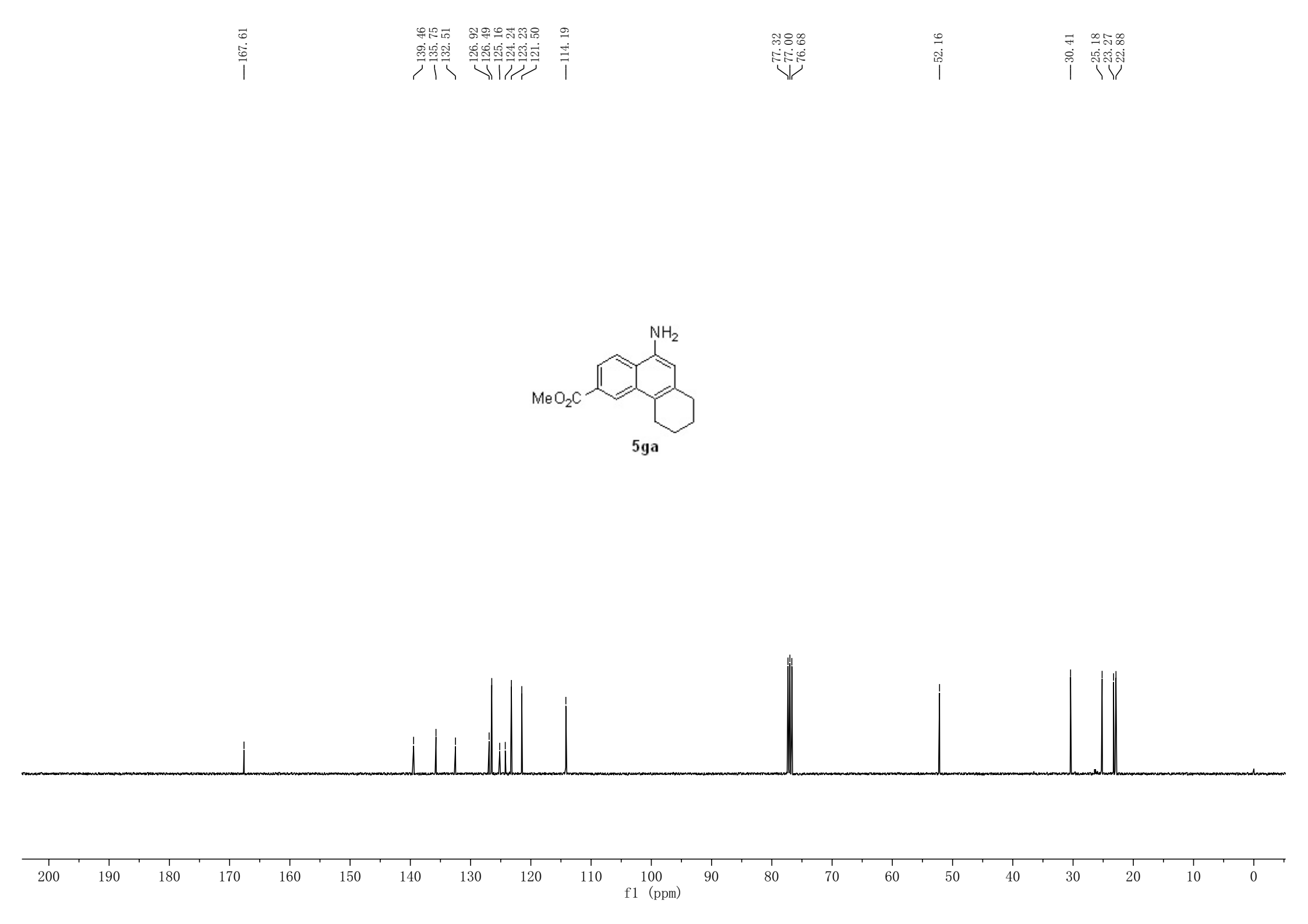
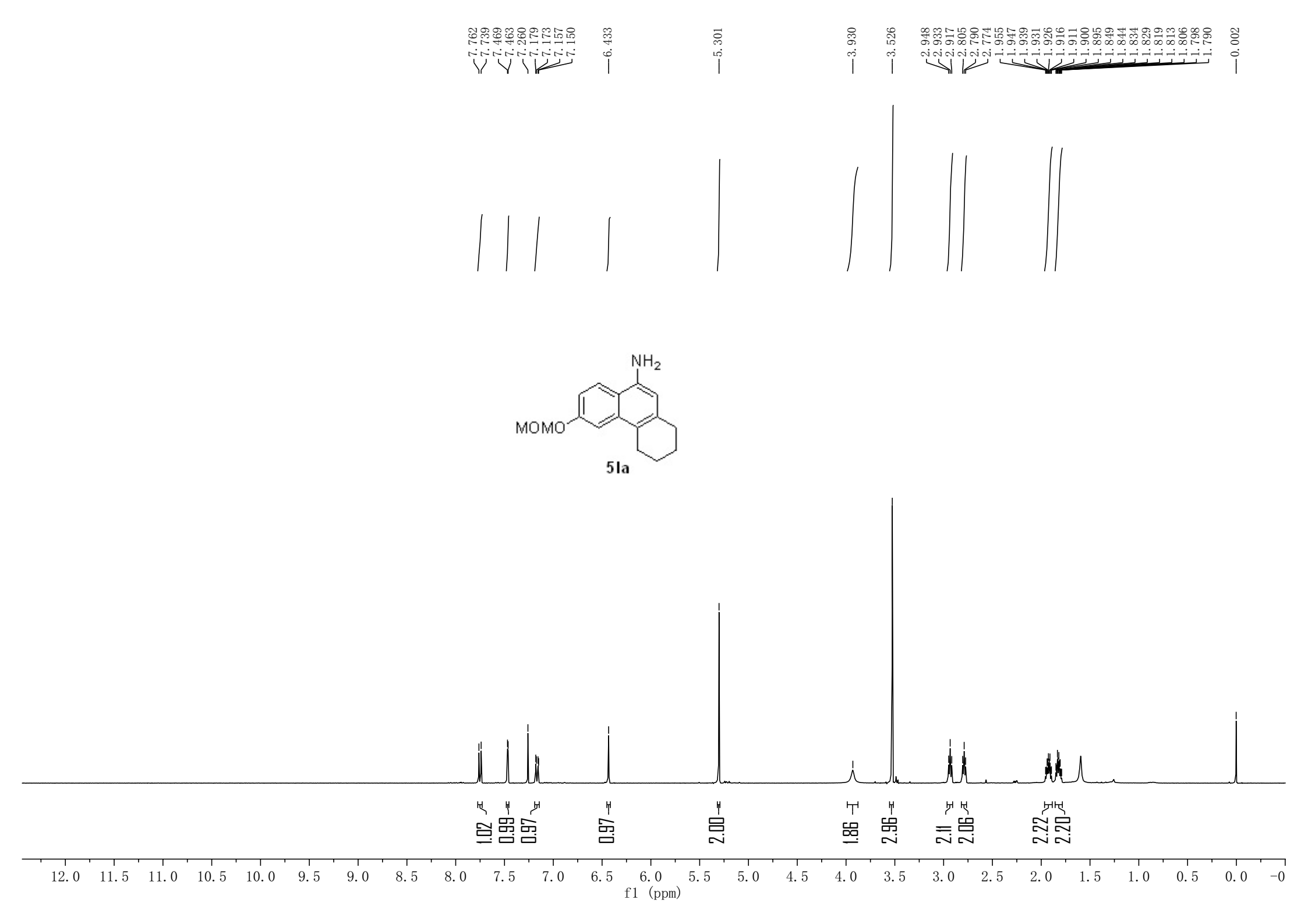
7.506
7.485
7.451
7.431
7.414
7.260
6.553
3.980
3.041
3.026
3.010
2.842
2.827
2.812
1.982
1.967
1.954
1.940
1.926
1.879
1.865
1.851
1.837
1.822
0.023
NH2
5aa
1.00
0.92
0.96
0.86
0.89
1.98
2.08
2.00
2.15
1.96
f1 (ppm)


139.535
134.724
133.205
125.768
123.814
123.408
123.059
122.650
121.143
111.845
77.318
77.000
76.683
30.484
25.191
23.492
23.034
125.768
123.814
123.408
123.059
122.650
121.143
126
125
124
123
122
121
f1 (ppm)
NH2
5aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.709
8.706
8.000
7.996
7.978
7.974
7.847
7.825
7.260
6.631
4.011
3.976
3.096
3.081
3.065
2.828
2.812
2.797
1.974
1.958
1.945
1.930
1.914
1.869
1.854
1.839
1.826
1.811
0.001
NH2
MeO2C
5ga
0.99
0.94
1.00
0.93
1.61
3.07
2.09
2.10
2.19
2.27
f1 (ppm)


167.61
139.46
135.75
132.51
126.92
126.49
125.16
124.24
123.23
121.50
114.19
77.32
77.00
76.68
52.16
30.41
25.18
23.27
22.88
NH2
MeO2C
5ga
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.762
7.739
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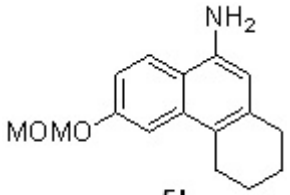
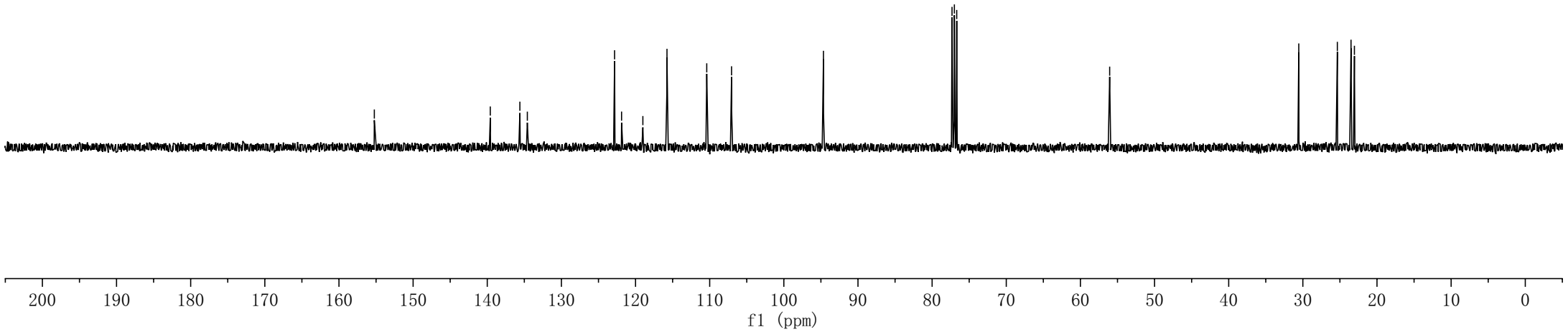
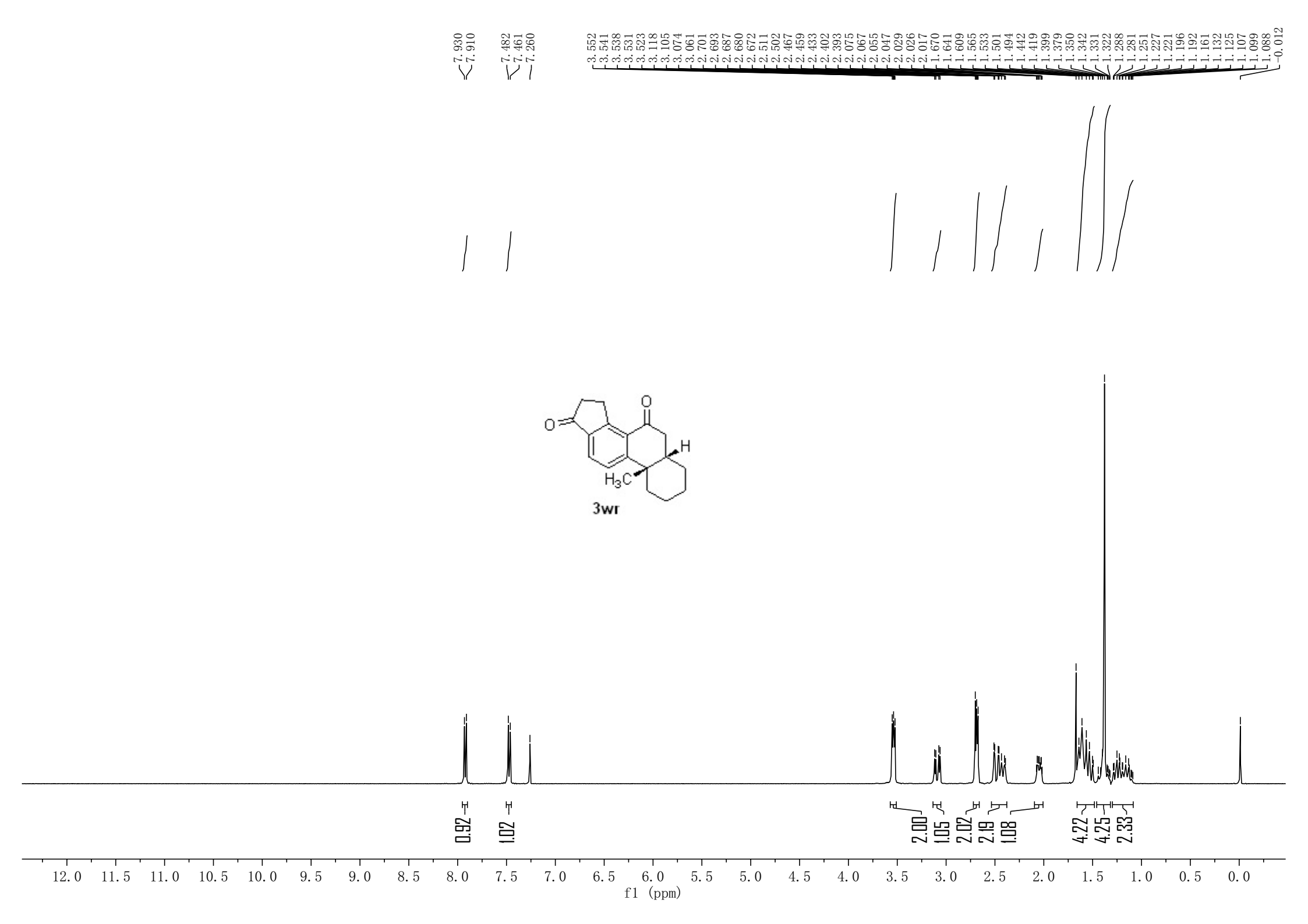
7.463
7.260
7.179
7.173
7.157
7.150
6.433
5.301
3.930
3.526
2.948
2.933
2.917
2.805
2.790
2.774
1.955
1.947
1.939
1.931
1.926
1.916
1.911
1.900
1.895
1.849
1.844
1.834
1.829
1.819
1.813
1.806
1.798
1.790
0.002
NH2
MOMO
5la
1.02
0.99
0.97
0.97
2.00
1.86
2.96
2.11
2.06
2.22
2.20
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

155.23
139.59
135.60
134.59
122.83
121.88
119.01
115.76
110.40
107.05
94.66
77.32
77.00
76.68
56.05
30.55
25.35
23.50
23.05



5la

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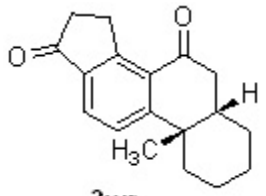
7.910
7.482
7.461
7.260
3.552
3.541
3.538
3.531
3.523
3.118
3.105
3.074
3.061
2.701
2.693
2.687
2.680
2.672
2.511
2.502
2.467
2.459
2.433
2.402
2.393
2.075
2.067
2.055
2.047
2.029
2.026
2.017
1.670
1.641
1.609
1.565
1.533
1.501
1.494
1.442
1.419
1.399
1.379
1.350
1.342
1.331
1.322
1.288
1.281
1.251
1.227
1.221
1.196
1.192
1.161
1.132
1.125
1.107
1.099
1.088
-0.012
O
O
H
H3C
3wr
0.92
1.02
2.00
1.05
2.02
2.19
1.08
4.22
4.25
2.33
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

206.54
198.84
157.74
157.13
136.39
129.19
128.34
126.06
77.32
77.00
76.68
42.55
42.46
39.43
38.06
36.41
31.55
29.29
28.33
25.66
22.31



3wr