Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Catalyzed Dearomative 1,4-Carboxylate Rearrangement of 2-Carbonateindoles

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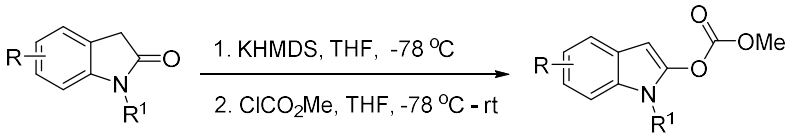
General information

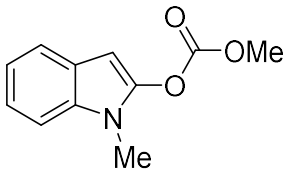
All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F_{254} indicator. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz, 400 MHz spectrometer in $CDCl_3$. ^{13}C NMR were recorded on Bruker 75 MHz or 100 MHz spectrometer in $CDCl_3$. ^{19}F NMR were recorded on Bruker 282 MHz or 377 MHz spectrometer in $CDCl_3$. Data for ^{1}H NMR spectra were reported relative to tetramethylsilane (TMS) as an internal standard (0 ppm), and were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets and m = multiplet. Data for ^{13}C NMR spectra were reported relative to $CDCl_3$ as an internal standard (77.16 ppm), and were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 QTOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus without correction.

Preparation of substrates

The diazo was prepared according to the literature procedures[1]. The N-substituted indolin-2-ones were prepared according to the literature procedures[2]. 2-carbonateindoles were prepared according to the general procedure:



A solution of N-substituted indolin-2-one (1.0 eq) in THF was added slowly to a solution of KHMDS (1.0 mol/L in THF, 1.2 eq) at -78 °C under argon atmosphere. The solution was stirred at -78 °C for 30 min, then transferred via a syringe to a solution of methyl carbonochloridate (1.2 eq) in THF at -78 °C under argon atmosphere. The solution was allowed to worm to rt, then poured into 1 M HCl, and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 40:1 to 20:1).



methyl (1-methyl-1H-indol-2-yl) carbonate(1a)

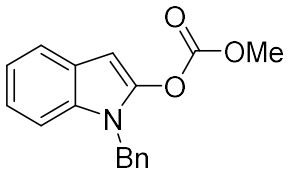
Prepared via general procedure from 1-methylindolin-2-one (2.94 g, 20 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1 to 10:1) and obtained as a pale yellow oil (1.07 g, yield: 26%).

R_f = 0.5 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.19 (dd, J_1 = 8.2 Hz, J_2 = 6.8 Hz, 1H), 7.12 (dd, J_1 = 7.8 Hz, J_2 = 6.8 Hz, 1H) 6.29 (s, 1H), 3.95 (s, 3H), 3.61 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 142.8, 132.6, 125.9, 121.4, 120.7, 120.2, 109.0, 87.2, 56.1, 28.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}NO_3$ 206.0812; Found 206.0808.



1-benzyl-1H-indol-2-yl methyl carbonate(1b)

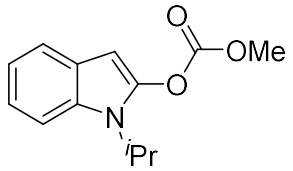
Prepared via general procedure from 1-benzylindolin-2-one (466 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1 to 10:1) and obtained as a pale yellow oil (140 mg, yield: 25%).

R_f = 0.5 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.54 (m, 1H), 7.28-7.26 (m, 1H), 7.25-7.20 (m, 2H), 7.20-7.16 (m, 1H), 7.15-7.08 (m, 4H), 6.38 (s, 1H), 5.22 (s, 2H), 3.85 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 142.8, 137.0, 132.1, 128.8, 127.6, 126.7, 126.2, 121.7, 120.8, 120.5, 109.6, 87.8, 56.0, 45.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}NO_3$ 282.1125; Found 282.1124.



1-isopropyl-1H-indol-2-yl methyl carbonate(1c)

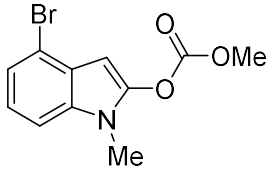
Prepared via general procedure from 1-isopropylindolin-2-one (350 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1 to 10:1) and obtained as a pale yellow oil (149 mg, 32%).

R_f = 0.45 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.15 (dd, J_1 = 7.1 Hz, J_2 = 8.0 Hz, 1H), 7.09 (dd, J_1 = 7.6 Hz, J_2 = 7.1 Hz, 1H) 6.28 (s, 1H), 4.69-4.58 (m, 1H), 3.91 (s, 3H), 1.58-1.51 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 142.6, 130.9, 126.4, 121.0, 120.8, 119.8, 110.4, 88.0, 56.0, 46.5, 21.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_3$ 234.1125; Found 234.1123.



4-bromo-1-methyl-1H-indol-2-yl methyl carbonate(1d)

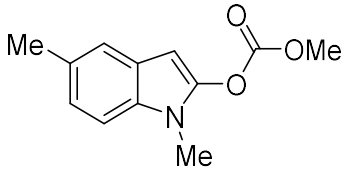
Prepared via general procedure from 4-bromo-1-methylindolin-2-one (350 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 30:1) and obtained as a white solid (192 mg, yield: 34%), mp: 105-107 °C.

R_f = 0.6 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 1H), 7.15-7.13 (m, 1H), 7.07-6.98 (m, 1H), 6.36 (s, 1H), 3.95 (s, 3H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 143.1, 132.8, 126.7, 123.2, 122.2, 114.5, 108.2, 87.9, 56.2, 28.7.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}BrNO_3$ 283.9917; Found 283.9908.



1,5-dimethyl-1H-indol-2-yl methyl carbonate(1e)

Prepared via general procedure from 1,5-dimethylindolin-2-one (322 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate =

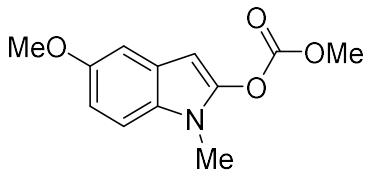
40:1 to 20:1) and obtained as a white solid (127 mg, yield: 29%), mp: 81-83 °C.

R_f = 0.55 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 7.12 (d, *J* = 8.3 Hz, 1H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.20 (s, 1H), 3.93 (s, 3H), 3.56 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 142.9, 130.9, 129.4, 126.1, 122.9, 120.5, 108.7, 86.8, 56.0, 28.3, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_3$ 220.0968; Found 220.0968.



5-methoxy-1-methyl-1H-indol-2-yl methyl carbonate(1f)

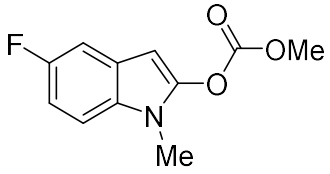
Prepared via general procedure from 5-methoxy-1-methylindolin-2-one (354 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 30:1) and obtained as a white solid (178 mg, yield: 38%), mp: 83-85 °C.

R_f = 0.55 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.8 Hz, 1H), 7.03 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.22 (s, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.55 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 152.5, 143.1, 127.7, 126.3, 111.2, 109.8, 103.0, 87.2, 56.0, 55.9, 28.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_4$ 236.0917; Found 236.0917.



5-fluoro-1-methyl-1H-indol-2-yl methyl carbonate(1g)

Prepared via general procedure from 5-fluoro-1-methylindolin-2-one (370 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) and obtained as a white solid (107 mg, yield: 24%), mp: 71-73 °C.

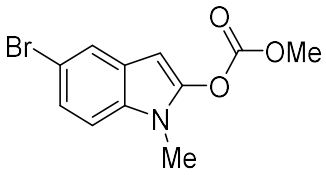
R_f = 0.5 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J_1 = 9.3 Hz, J_2 = 2.4 Hz, 1H), 7.07-7.04 (m, 1H), 6.85 (td, J_1 = 9.3 Hz, J_2 = 2.4 Hz, 1H), 6.19 (s, 1H), 3.88 (s, 3H), 3.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3 (d, *J* = 232.7 Hz), 152.3, 129.1, 126.3 (d, *J* = 10.6 Hz), 109.7, 109.6 (d, *J* = 34.7 Hz), 105.8 (d, *J* = 23.9 Hz), 87.6 (d, *J* = 4.5 Hz), 56.2, 28.5.

^{19}F NMR (377 MHz, $CDCl_3$) δ -123.96.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}FO_3$ 224.0717; Found 224.0713.



5-bromo-1-methyl-1H-indol-2-yl methyl carbonate(1h)

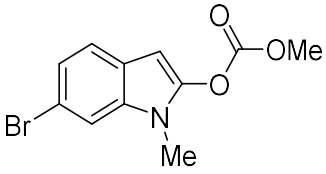
Prepared via general procedure from 5-bromo-1-methylindolin-2-one (350 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 30:1) and obtained as a white solid (147 mg, yield: 26%), mp: 85-87 °C.

R_f = 0.55 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.26 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 8.6 Hz, 1H), 6.25 (s, 1H), 3.95 (s, 3H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 143.5, 131.2, 127.6, 124.2, 123.1, 113.4, 110.6, 86.9, 56.2, 28.5.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}BrNO_3$ 283.9917; Found 283.9914.



6-bromo-1-methyl-1H-indol-2-yl methyl carbonate(1i)

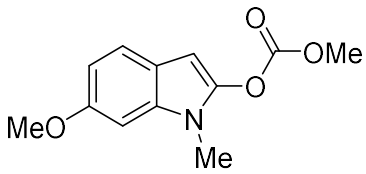
Prepared via general procedure from 6-bromo-1-methylindolin-2-one (350 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 30:1) and obtained as a white solid (170 mg, yield: 30%), mp: 99-101 °C.

R_f = 0.55 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (m, 2H), 7.24-7.17 (m, 1H), 6.28 (s, 1H), 3.96 (s, 3H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 143.1, 133.4, 124.8, 123.5, 122.0, 114.7, 112.1, 87.5, 56.2, 28.5.

HRMS (ESI) m/z: Calcd for $C_{11}H_{11}BrNO_3$ $[M+H]^+$: 283.9917; Found 283.9914.



6-methoxy-1-methyl-1H-indol-2-yl methyl carbonate(1j)

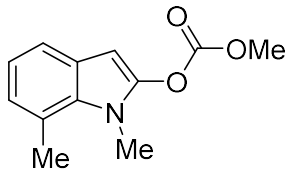
Prepared via general procedure from 6-methoxy-1-methylindolin-2-one (354 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) and obtained as a yellow oil (80 mg, yield: 17%).

R_f = 0.6 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.73 (s, 1H), 6.20 (s, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 152.7, 141.9, 133.4, 121.5, 119.9, 109.6, 93.3, 87.1, 56.1, 55.9, 28.4.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_4$ 236.0917; Found 236.0916.



1,7-dimethyl-1H-indol-2-yl methyl carbonate(1k)

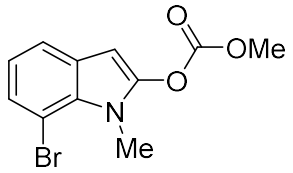
Prepared via general procedure from 1,7-dimethylindolin-2-one (322 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 30:1) and obtained as a white solid (118 mg, yield: 27%), mp: 75-77 °C.

R_f = 0.6 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7 Hz, 1H), 6.93-6.84 (m, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.17 (s, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 2.63 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 142.7, 131.5, 126.6, 124.4, 120.9, 120.2, 118.8, 87.8, 56.0, 31.1, 19.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_3$ 220.0968; Found 220.0969.



7-bromo-1-methyl-1H-indol-2-yl methyl carbonate(1l)

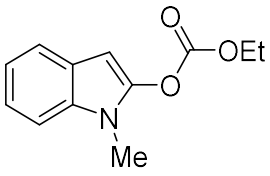
Prepared via general procedure from 7-bromo-1-methylindolin-2-one (350 mg, 2.0 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 40:1 to 20:1) and obtained as a white solid (232 mg, yield: 41%), mp: 72-74 °C.

R_f = 0.55 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 6.29 (s, 1H), 3.96 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 143.5, 129.4, 129.0, 126.7, 121.2, 120.1, 103.6, 88.2, 56.2, 31.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{11}BrNO_3$ 283.9917; Found 283.9914.



ethyl (1-methyl-1H-indol-2-yl) carbonate(1m)

Prepared via following procedure: To a solution of 1-methylindolin-2-one (294 mg, 2.0 mmol) and triethylamine (242 mg, 2.4 mmol) in THF was added ethyl carbonochloridate (260 mg, 2.4 mmol) slowly at 0 oC and stirred for 30 min. Then the reaction was quenched with water, extracted with EtOAc, dried over Na2SO4, filtered and concentrated. The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 15:1) and obtained as a pale

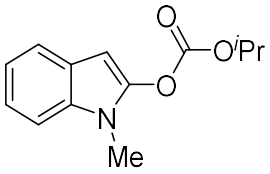
yellow oil (175 mg, yield: 40%).

R_f = 0.55 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.20-7.10 (m, 2H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.22 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 142.9, 132.6, 126.0, 121.3, 120.7, 120.2, 109.0, 87.3, 65.7, 28.3, 14.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{14}NO_3$ 220.0968; Found 220.0968.



isopropyl (1-methyl-1H-indol-2-yl) carbonate(1n)

Prepared via following procedure: To a solution of 1-methylindolin-2-one (294 mg, 2.0 mmol) and triethylamine (242 mg, 2.4 mmol) in THF was added isopropyl carbonochloridate (294 mg, 2.4 mmol) slowly at 0 oC and stirred for 30 min. Then the reaction was quenched with water, extracted with EtOAc, dried over Na2SO4, filtered and concentrated. The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 30:1) and obtained as a white solid (284 mg, yield: 61%), mp: 72-74 °C.

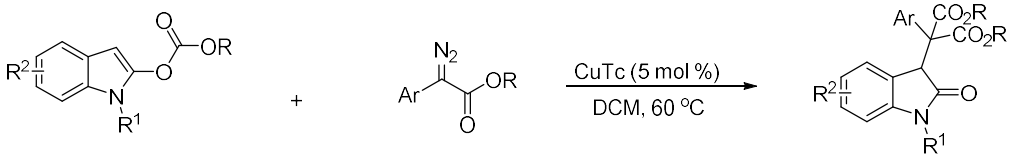
R_f = 0.6 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 1H), 7.19 (dd, J_1 = 7.9 Hz, J_2 = 1.0 Hz, 1H), 7.11 (dd, J_1 = 7.8 Hz, J_2 = 1.0 Hz, 1H) 6.29 (s, 1H), 5.10-4.93 (m, 1H), 3.61 (s, 3H), 1.41-1.40 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 151.3, 143.0, 132.6, 126.0, 121.3, 120.7, 120.2, 109.0, 87.3, 74.2, 28.3, 21.7.

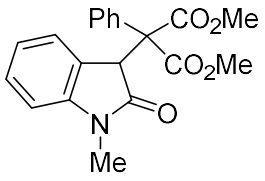
HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{15}NO_3Na$ 256.0944; Found 256.0937.

General procedure for scheme 2 and scheme 3



1 **2** **3**

To a dry tube equipped with a magnetic stirrer and an oil bath, were added **1** (0.2 mmol), **2** (0.36 mmol), CuTc (1.9 mg, 0.01 mmol) and anhydrous DCM (4 mL). The reaction solution was stirred at 60 °C for 6 hours under argon atmosphere in a heating block. Then the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography to afford the desired product **3**.



dimethyl 2-(1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3aa)

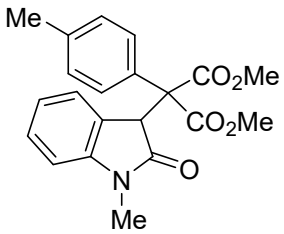
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a pale yellow solid (54 mg, yield: 77%), mp: 163-165 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.14 (m, 6H), 7.11 (d, *J* = 7.7 Hz, 1H), 6.86 (t, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 4.67 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 170.4, 168.7, 144.4, 133.6, 128.8, 128.4, 127.9, 127.7, 126.6, 125.2, 122.2, 107.8, 65.9, 53.4, 53.2, 51.4, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}NO_5$ 354.1336; Found 354.1340.



dimethyl 2-(1-methyl-2-oxoindolin-3-yl)-2-(p-tolyl)malonate(3ab)

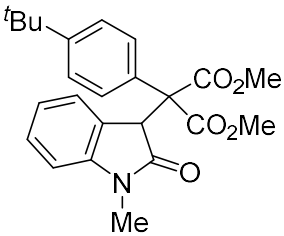
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-(*p*-tolyl)acetate (68.4 mg, 0.36 mmol).The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a red oil (59 mg, yield: 81%).

R_f = 0.2 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.07 (m, 4H), 6.99 (s, 1H), 6.97 (s, 1H), 6.85 (t, *J* = 7.6Hz, 1H), 6.60 (d, *J* = 7.6Hz, 1H), 4.65 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.10 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 170.5, 168.8, 144.4, 137.7, 130.7, 128.6, 128.4, 128.4, 126.5, 125.2, 122.1, 107.8, 65.6, 53.3, 53.1, 51.3, 26.2, 21.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_5$ 368.1492; Found 368.1495.



dimethyl 2-(4-(tert-butyl)phenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3ac)

Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-(4-(*tert*-butyl)phenyl)-2-diazoacetate (83.5 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a yellow solid

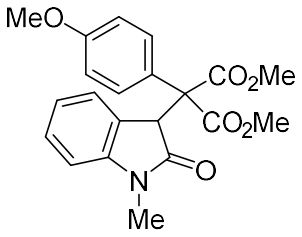
(59.5 mg, yield: 74%), mp: 145-147 °C.

R_f = 0.3 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23-7.09 (m, 5H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 4.63 (s, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.09 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 170.4, 168.8, 150.8, 144.5, 130.6, 128.3, 126.3, 125.2, 124.6, 122.1, 107.7, 65.6, 53.3, 53.0, 51.2, 34.4, 31.2, 26.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}NO_5$ 410.1962; Found 410.1965.



dimethyl 2-(4-methoxyphenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3ad)

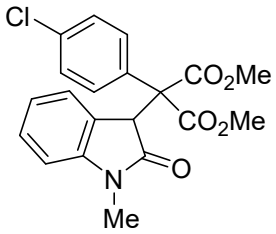
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-(4-methoxyphenyl)acetate (74.2 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) and obtained as a red solid (53.4 mg, yield: 69%), mp: 147-149 °C.

R_f = 0.25 (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.10 (m, 4H), 6.87 (t, *J* = 7.7 Hz, 1H), 6.72-6.67 (m, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 4.64 (s, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 3.09 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 170.5, 168.9, 159.0, 144.4, 130.0, 128.4, 126.5, 125.7, 125.3, 122.2, 113.0, 107.8, 65.3, 55.2, 53.4, 53.1, 51.5, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_6$ 384.1442; Found 384.1449.



dimethyl 2-(4-chlorophenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3ae)

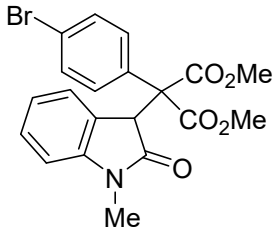
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-(4-chlorophenyl)-2-diazoacetate (75.6 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a white solid (58.7 mg, yield: 74%), mp: 141-143 °C.

R_f = 0.35 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 7.7Hz, 1H), 7.17-7.04 (m, 5H), 6.89 (t, *J* = 7.7Hz, 1H), 6.60 (d, *J* = 7.7Hz, 1H), 4.68 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.07 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 170.0, 168.4, 144.3, 133.9, 132.0, 130.2, 128.7, 127.7, 126.5, 124.8, 122.4, 108.0, 65.4, 53.6, 53.3, 51.3, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}ClNO_5$ 388.0946; Found 388.0951.



dimethyl 2-(4-bromophenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3af)

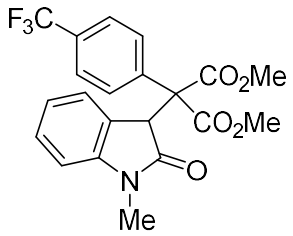
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-(4-bromophenyl)-2-diazoacetate (91.5 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a white solid (63 mg, yield: 73%), mp: 140-142 °C.

R_f = 0.2 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.24 (m, 3H), 7.15 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 2.5 Hz, 1H), 7.02 (t, *J* = 2.5 Hz, 1H), 6.89 (t, t, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 4.67 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 169.9, 168.3, 144.3, 132.6, 130.7, 130.5, 128.7, 126.5, 124.7, 122.4, 122.2, 108.0, 65.4, 53.6, 53.3, 51.2, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}BrNO_5$ 432.0441; Found 432.0440.



dimethyl 2-(1-methyl-2-oxoindolin-3-yl)-2-(4-(trifluoromethyl)phenyl)malonate(3ag)

Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (87.9 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a white solid (50 mg, yield: 59%), mp: 146-148 °C.

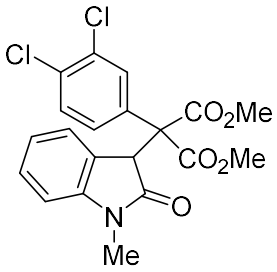
R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.37 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.29-7.26 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.58 (t, *J* = 7.8 Hz, 1H), 4.73 (s, 1H), 3.88 (s, 6H), 3.07 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 169.8, 168.2, 144.2, 137.5, 130.4 (d, *J* = 32.4 Hz), 129.4, 128.8, 126.5, 123.9 (d, *J* = 270.4 Hz), 124.5, 124.4 (q, *J* = 3.8 Hz), 122.5, 108.0, 65.8, 53.7, 53.4, 51.2, 25.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ -120.76.

HRMS (ESI) m/z: Calcd for $C_{21}H_{19}F_3NO_5$ $[M+H]^+$: 422.1210; Found 422.1213.



dimethyl 2-(3,4-dichlorophenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3ah)

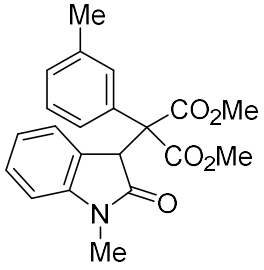
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-(3,4-dichlorophenyl)acetate (88.2 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a pale yellow solid (61.5 mg, yield: 72%), mp: 129-131 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H), 7.22-7.15 (m, 2H), 6.96-6.90 (m, 2H), 6.65-6.60 (m, 1H), 4.67 (s, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.09 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 169.5, 168.0, 144.2, 133.6, 132.2, 131.8, 130.9, 129.3, 128.9, 128.3, 126.5, 124.5, 122.6, 108.2, 65.2, 53.7, 53.5, 51.2, 26.2.

HRMS (ESI) m/z: Calcd for $C_{20}H_{18}Cl_2NO_5$ $[M+H]^+$: 422.0557; Found 422.0557.



dimethyl 2-(1-methyl-2-oxoindolin-3-yl)-2-(m-tolyl)malonate(3ai)

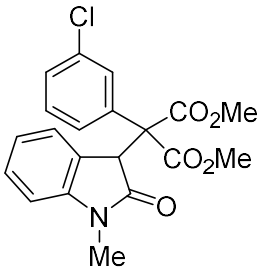
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-(*m*-tolyl)acetate (68.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a yellow solid (56.5 mg, yield: 78%), mp: 131-133 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.10 (m, 2H), 7.08-7.02 (m, 2H), 7.00-6.93 (m, 2H), 6.85 (t, J = 7.7 Hz, 1H), 6.60 (d, J = 7.7 Hz, 1H), 4.65 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.09 (s, 3H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 170.4, 168.7, 144.4, 137.3, 133.5, 129.4, 128.7, 128.4, 127.5, 126.5, 125.8, 125.2, 122.1, 107.7, 65.9, 53.4, 53.1, 51.3, 26.1, 21.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_5$ 368.1492; Found 368.1491.



dimethyl 2-(3-chlorophenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3aj)

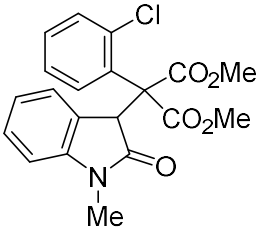
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-(3-chlorophenyl)-2-diazoacetate (75.6 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as an orange solid (59.5 mg, yield: 76%), mp: 99-101 °C.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.17 (m, 1H), 7.13 (s, 1H), 7.10-7.02 (m, 2H), 7.01-6.95 (m, 1H), 6.93-6.87 (m, 1H), 6.82 (t, *J* = 7.7 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 4.58 (s, 1H), 3.79 (s, 6H), 3.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 169.8, 168.2, 144.3, 135.4, 133.6, 129.0, 128.7, 128.7, 128.1, 127.1, 126.6, 124.7, 122.4, 107.9, 65.6, 53.6, 53.3, 51.3, 26.2.

HRMS (ESI) m/z: Calcd for $C_{20}H_{19}NO_5$ $[M+H]^+$: 388.0946; Found 388.0947.



dimethyl 2-(2-chlorophenyl)-2-(1-methyl-2-oxoindolin-3-yl)malonate(3ak)

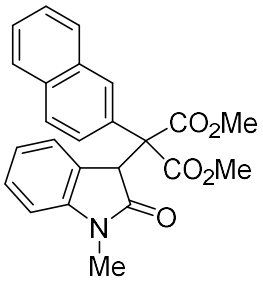
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-(2-chlorophenyl)-2-diazoacetate (75.6 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a yellow oil (38.9 mg, yield: 50%).

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.45 (m, 1H), 7.28-7.15 (m, 5H), 6.89 (t, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 4.90 (s, 1H), 3.72 (s, 3H), 3.45 (s, 3H), 3.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 169.6, 168.7, 144.5, 134.4, 133.3, 130.6, 129.4, 128.6, 126.9, 126.6, 125.7, 122.2, 107.6, 66.6, 53.6, 53.0, 48.5, 26.3.

HRMS (ESI) m/z: Calcd for $C_{20}H_{19}ClNO_5$ $[M+H]^+$: 388.0946; Found 388.09.



dimethyl 2-(1-methyl-2-oxoindolin-3-yl)-2-(naphthalen-2-yl)malonate(3al)

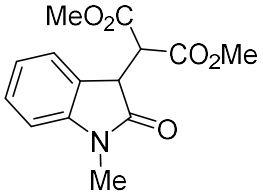
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazo-2-(naphthalen-2-yl)acetate (81.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a white solid (74.5 mg, yield: 92%), mp: 154-156 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.60 (m, 3H), 7.58-7.52 (m, 1H), 7.37-7.30 (m, 2H), 7.21-7.16 (m, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.01-6.95 (m, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 6.45-6.43 (m, 1H), 4.69 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 2.99 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 170.3, 168.8, 144.4, 132.6, 132.6, 131.2, 128.5, 128.4, 128.2, 127.4, 127.1, 126.5, 126.5, 126.4, 126.2, 125.1, 122.2, 107.9, 66.0, 53.5, 53.2, 51.2, 26.2.

HRMS (ESI) m/z: Calcd for $C_{24}H_{22}NO_5$ $[M+H]^+$: 404.1492; Found 404.1496.



dimethyl 2-(1-methyl-2-oxoindolin-3-yl)malonate(3am)

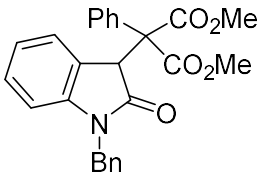
Prepared via general procedure from **1a** (41 mg, 0.2 mmol) and methyl 2-diazoacetate (80 mg, 0.8 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a brown oil (38.1 mg, yield: 66%).

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 7.6 Hz, 1H), 4.20 (d, *J* = 4.3 Hz, 1H), 4.04 (d, *J* = 4.3 Hz, 1H), 3.80 (s, 3H), 3.59 (s, 3H), 3.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 168.4, 167.5, 144.7, 128.8, 125.5, 124.6, 122.7, 108.2, 53.0, 52.8, 52.2, 44.7, 26.5.

HRMS (ESI) m/z: Calcd for $C_{14}H_{16}NO_5$ $[M+H]^+$: 278.1023; Found 278.1022.



dimethyl 2-(1-benzyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ba)

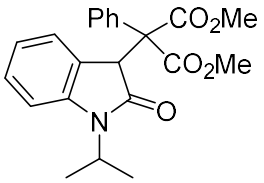
Prepared via general procedure from **1b** (56.2 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a orange oil (60 mg, yield: 68%).

R_f = 0.3 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 6H), 7.17-7.10 (m, 5H), 7.04-6.98 (m, 1H), 6.87-6.80 (m, 1H), 6.53-6.47 (m, 1H), 4.86 (d, *J* = 15.7 Hz, 1H), 4.81 (s, 1H), 4.74 (d, *J* = 15.7 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 170.4, 168.7, 143.6, 135.6, 133.6, 128.9, 128.7, 128.3, 127.9, 127.8, 127.6, 127.5, 126.6, 125.1, 122.2, 108.8, 65.8, 53.5, 53.2, 51.5, 43.9.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{24}NO_5$ 430.1649; Found 430.1650.



dimethyl 2-(1-isopropyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ca)

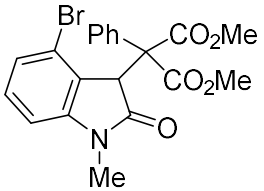
Prepared via general procedure from **1c** (46.6 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as an orange solid (56.4 mg, yield: 75%), mp: 165-167 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.25 (m, 1H), 7.19-7.12 (m, 5H), 7.11-7.05 (m, 1H), 6.89-6.80 (m, 1H), 6.76-6.70 (m, 1H), 4.67 (s, 1H), 4.55 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 1.38 (d, *J* = 7.0 Hz, 3H), 1.32 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.3, 170.5, 168.7, 143.0, 133.5, 129.0, 128.1, 127.9, 127.6, 126.9, 125.6, 121.6, 109.4, 65.9, 53.4, 53.1, 51.2, 43.7, 19.2, 18.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}NO_5$ 382.1649; Found 382.1650.



dimethyl 2-(4-bromo-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3da)

Prepared via general procedure from **1d** (56.6 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography

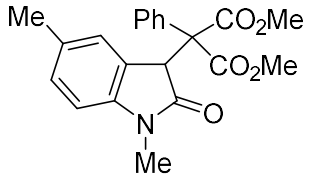
(eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) and obtained as a yellow solid (73 mg, yield: 85%), mp: 111-113 °C.

R_f = 0.3 (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 1H), 7.25-7.23 (m, 1H), 7.20-7.13 (m, 3H), 7.06-7.01 (m, 2H), 6.61-6.53 (m, 1H), 4.83 (s, 1H), 3.90 (s, 3H), 3.82 (s, 3H), 2.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 169.1, 168.8, 147.0, 133.8, 130.1, 129.3, 128.0, 127.5, 126.9, 125.2, 120.7, 106.7, 66.4, 53.6, 53.2, 52.8, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}BrNO_5$ 432.0441; Found 432.0439.



dimethyl 2-(1,5-dimethyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ea)

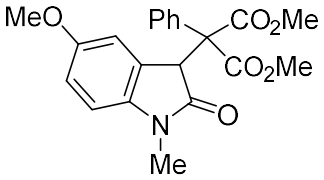
Prepared via general procedure from **1e** (43.8 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a yellow solid (60.5 mg, yield: 83%), mp: 117-119 °C.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.14 (s, 5H), 6.96 (s, 1H), 6.92 (d, J = 9.0 Hz, 1H), 6.47 (d, J = 9.0 Hz, 1H), 4.63 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.06 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 170.4, 168.7, 142.0, 133.7, 131.6, 128.8, 128.6, 127.9, 127.6, 127.3, 125.1, 107.4, 65.9, 53.4, 53.1, 51.4, 26.2, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_5$ 368.1492; Found 368.1495.



dimethyl 2-(5-methoxy-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3fa)

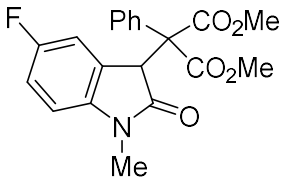
Prepared via general procedure from **1f** (47 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a red oil (55.4 mg, yield: 72%).

R_f = 0.2 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.14 (s, 5H), 6.79 (s, 1H), 6.65 (d, J = 8.4 Hz, 1H), 6.47 (d, J = 8.4 Hz, 1H), 4.63 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.66 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 170.4, 168.7, 155.4, 138.1, 133.6, 128.8, 127.9, 127.7, 126.4, 114.2, 112.7, 107.9, 65.9, 55.8, 53.5, 53.1, 51.9, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_6$ 384.1442; Found384.1441.



dimethyl 2-(5-fluoro-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ga)

Prepared via general procedure from **1g** (44.6 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a pale yellow solid (59.7 mg, yield: 80%), mp: 142-144 ºC.

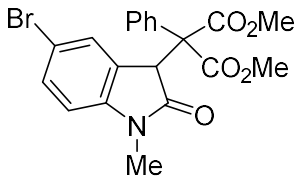
R_f = 0.2 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.11 (m, 5H), 7.06-6.99 (m, 1H), 6.85-6.77 (m, 1H), 6.50-6.44 (m, 1H), 4.65 (s, 1H), 3.88 (s, 6H), 3.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 170.4, 168.5, 158.8 (d, J = 237.5 Hz), 140.4 (d, J = 1.7 Hz), 133.2, 128.6, 128.1, 127.8, 126.7 (d, J = 9.0 Hz), 115.0 (d, J = 26.0 Hz), 114.6 (d, J = 23.5Hz), 108.0 (d, J = 8.3 Hz), 65.8, 53.6, 53.3, 52.0, 26.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.8.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}FNO_5$ 372.1242; Found 372.1242.



dimethyl 2-(5-bromo-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ha)

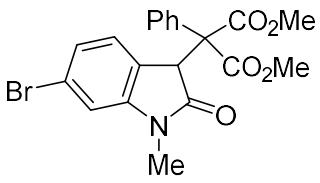
Prepared via general procedure from **1h** (56.6 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) and obtained as a pale yellow solid (71 mg, yield: 83%), mp: 153-155 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.27 (m, 1H), 7.26-7.21 (m, 1H), 7.20-7.10 (m, 5H), 6.45-6.42 (m, 1H), 4.63 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 170.2, 168.4, 143.4, 133.1, 131.2, 129.8, 128.6, 128.1, 127.8, 127.1, 114.9, 109.0, 65.8, 53.6, 53.2, 51.7, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}BrNO_5$ 432.0441; Found 432.0443.



dimethyl 2-(6-bromo-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ia)

Prepared via general procedure from **1i** (56.6 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography

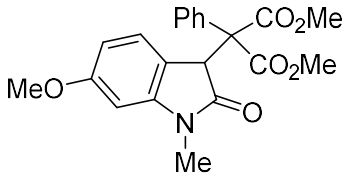
(eluent: petroleum ether/ethyl acetate = 10:1 to 3:1) and obtained as a red solid (63.6 mg, yield: 74%), mp: 174-176 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 3:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.08 (m, 5H), 7.04-6.92 (m, 2H), 6.72 (s, 1H), 4.59 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 170.3, 168.5, 145.7, 133.3, 128.6, 128.2, 128.0, 127.9, 125.0, 124.1, 122.1, 111.3, 65.8, 53.6, 53.2, 51.4, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}BrNO_5$ 432.0441; Found 432.0442.



dimethyl 2-(6-methoxy-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ja)

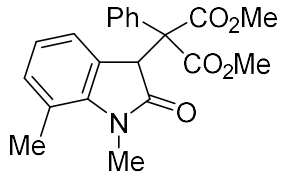
Prepared via general procedure from **1j** (47 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a red solid (51.3 mg, yield: 67%), mp: 163-165 ºC.

R_f = 0.35 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.15 (m, 5H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 8.4 Hz, 1H), 6.17 (s, 1H), 4.61 (s, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.72 (s, 3H), 3.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 170.4, 168.8, 160.3, 145.7, 133.7, 128.7, 127.9, 127.7, 127.3, 116.9, 105.9, 95.7, 66.0, 55.4, 53.4, 53.1, 50.9, 26.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}BrNO_6$ 384.1442; Found 384.1441.



dimethyl 2-(1,7-dimethyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ka)

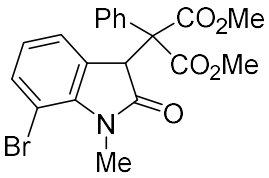
Prepared via general procedure from **1k** (43.8 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as an orange solid (58.6 mg, yield: 79%), mp: 142-144 ºC.

R_f = 0.3 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.15 (m, 5H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 4.62 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.37 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 170.4, 168.7, 142.2, 133.6, 132.2, 128.8, 127.9, 127.6, 125.6, 124.3, 122.0, 119.2, 66.2, 53.4, 53.1, 50.9, 29.7, 19.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}NO_5$ 368.1492; Found 368.1492.



dimethyl 2-(7-bromo-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3la)

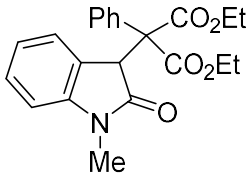
Prepared via general procedure from **1l** (56.6 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as an orange solid (63 mg, yield: 73%), mp: 124-126 ºC.

R_f = 0.4 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.10 (m, 4H), 7.09-7.05 (m, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 7.7 Hz, 1H), 4.57 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 170.2, 168.5, 141.7, 134.1, 133.2, 128.7, 128.2, 127.8, 125.5, 123.2, 102.0, 66.2, 53.5, 53.2, 51.2, 30.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}BrNO_5$ 432.0441; Found 432.0442.



diethyl 2-(1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3mn)

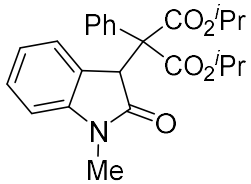
Prepared via general procedure from **1m** (43.8 mg, 0.2 mmol) and ethyl 2-diazo-2-phenylacetate (68.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a yellow solid (58.4 mg, yield: 76%), mp: 125-127 ºC.

R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 3H), 7.17-7.09 (m, 4H), 6.90-6.81 (m, 1H), 6.62-6.52 (m, 1H), 4.69 (s, 1H), 4.42-4.27 (m, 4H), 3.08 (s, 3H), 1.29-1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 169.9, 168.1, 144.4, 133.8, 128.8, 128.4, 127.8, 127.6, 126.6, 125.4, 122.2, 107.7, 65.9, 62.5, 62.1, 51.2, 26.1, 14.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{24}NO_5$ 382.1649; Found 382.1649.



diisopropyl 2-(1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3no)

Prepared via general procedure from **1n** (46.6 mg, 0.2 mmol) and isopropyl 2-diazo-2-phenylacetate (74.5 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a pale yellow oil (43 mg, yield: 53%).

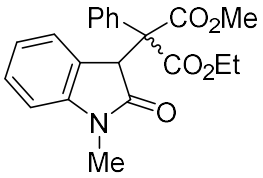
R_f = 0.35 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.27 (m, 1H), 7.24-7.18 (m, 2H), 7.17-7.08 (m, 4H), 6.90-6.82 (m, 1H), 6.59-6.52 (m, 1H), 5.29-5.20 (m, 1H), 5.20-5.12 (m, 1H), 4.68 (s, 1H), 3.07 (s, 3H), 1.28-1.25 (m, 6H), 1.25-1.21 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 169.3, 167.5, 144.4, 134.1, 128.9, 128.3, 127.6, 127.4, 126.7, 125.5, 122.1, 107.6, 70.2, 69.9, 65.8, 51.0, 26.1, 21.6, 21.5, 21.5.

$CDCl_3$

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{28}NO_5$ 410.1962; Found 410.1964.



1-ethyl 3-methyl 2-(1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(3ma)

Prepared via general procedure from **1m** (43.8 mg, 0.2 mmol) and methyl 2-diazo-2-phenylacetate (63.4 mg, 0.36 mmol). The desired product was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 10:1 to 5:1) and obtained as a white solid (60.2 mg, yield: 80%), mp: 115-117 °C.

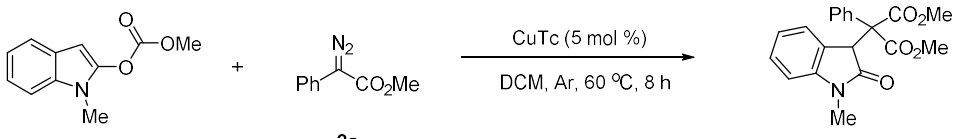
R_f = 0.25 (petroleum ether/ethyl acetate = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.22 (m, 4H), 7.22-7.17 (m, 3H), 7.16-7.11 (m, 7H), 6.90-6.83 (m, 2H), 6.63-6.58 (m, 1H), 6.58-6.53 (m, 1H), 4.68 (s, 2H), 4.45-4.22 (m, 4H), 3.86 (s, 6H), 3.10 (s, 3H), 3.08 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H).

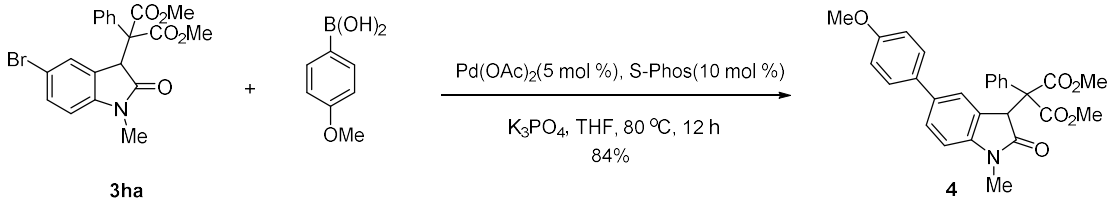
^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 169.8, 144.4, 133.6, 128.8, 128.8, 128.4, 128.4, 128.0, 127.8, 127.7, 127.6, 126.8, 126.4, 125.2, 122.2, 122.2, 107.7, 107.7, 66.0, 62.6, 62.2, 53.4, 53.1, 51.5, 51.1, 26.2, 26.2, 14.0, 13.9.

HRMS (ESI) m/z: Calcd for $C_{21}H_{22}NO_5$ $[M+H]^+$: 368.1492; Found 368.1494.

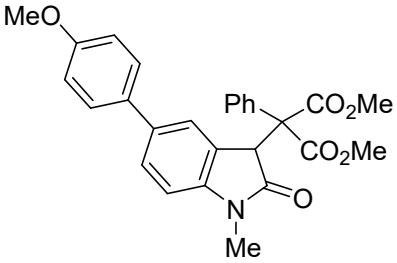
Further elaboration for Scheme 4



To a dry bottom equipped with a magnetic stirrer, an oil bath and a condensator, were added **1a** (4 mmol), **2a** (7.2 mmol), CuTc (38 mg, 0.2 mmol) and anhydrous DCM (80 mL). The reaction solution was stirred at 60 °C for 6 hours under argon atmosphere in a heating block. Then the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography (Petroleum ether/EtOAc = 20:1 to 5:1) to afford **3a** (1.03 g, 73% yield).



To a dry tube equipped with a magnetic stirrer and an oil bath, were added **3ha** (65 mg, 0.15 mmol), (4-methoxyphenyl)boronic acid (68 mg, 0.45 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), Sphos (6.2 mg, 0.015 mmol), K_3PO_4 (95.5 mg, 0.45 mmol) and anhydrous THF (3 mL). The reaction solution was stirred at 80 °C for 6 hours under argon atmosphere in a heating block. Then the reaction mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography (Petroleum ether/EtOAc = 10:1 to 3:1) to afford the desired product **4** as a pink solid (57.8 mg, 84% yield, mp: 167-169 °C).



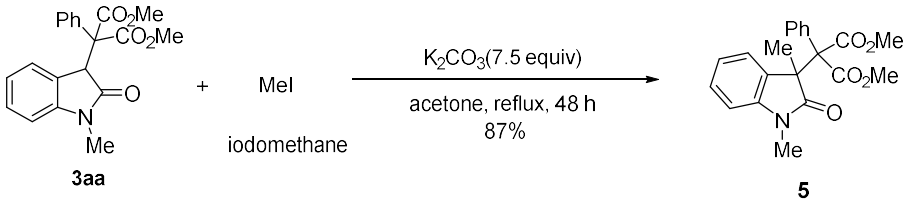
dimethyl 2-(5-(4-methoxyphenyl)-1-methyl-2-oxoindolin-3-yl)-2-phenylmalonate(4)

Rf = 0.45 (petroleum ether/ethyl acetate = 2:1)

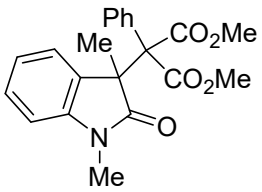
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 1H), 7.33-7.32 (m, 1H), 7.31-7.28 (m, 1H), 7.28-7.25 (m, 1H), 7.24-7.20 (m, 2H), 7.19-7.16 (m, 3H), 6.95-6.91 (m, 2H), 6.65-6.59 (m, 1H), 4.69 (s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 168.7, 158.9, 143.3, 135.0, 133.7, 133.6, 128.8, 128.0, 127.8, 127.7, 126.7, 125.7, 125.1, 114.2, 107.9, 66.0, 55.4, 53.5, 53.2, 51.8, 26.3.

HRMS (ESI) m/z: Calcd for $C_{27}H_{26}NO_6$ $[M+H]^+$: 460.1755; Found 460.1752.



To a solution of 3aa (53 mg, 0.15 mmol) in acetone (4 mL) was added K_2CO_3 (0.16 g, 1.13 mmol). The mixture was stirred at rt for 30 min. The mixture was treated with iodomethane (0.17 g, 1.2 mmol) and heated at reflux for 24 hours. Then additional iodomethane (0.17 g, 1.2 mmol) was added and stirred for further 24 hours. After cooling to rt, the mixture was concentrated under vacuum. The residue was purified by silica gel column chromatography (Petroleum ether/EtOAc = 20:1 to 5:1) to afford the desired product **5** as a white solid (48 mg, 87% yield, mp: 131-133 °C).



dimethyl 2-(1,3-dimethyl-2-oxoindolin-3-yl)-2-phenylmalonate

Rf = 0.45 (petroleum ether/ethyl acetate = 2:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.31 (m, 1H), 7.22-6.96 (m, 6H), 6.90-6.83 (m, 1H), 6.54-6.39 (m, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.06 (s, 3H), 1.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 169.4, 169.1, 142.8, 134.0, 132.2, 129.3, 127.9, 127.6, 126.7, 126.1, 122.1, 107.6, 67.6, 52.8, 52.7, 26.1, 21.4.

HRMS (ESI) m/z: Calcd for $C_{28}H_{28}NO_6$ $[M+H]^+$: 368.1492; Found 368.1494.

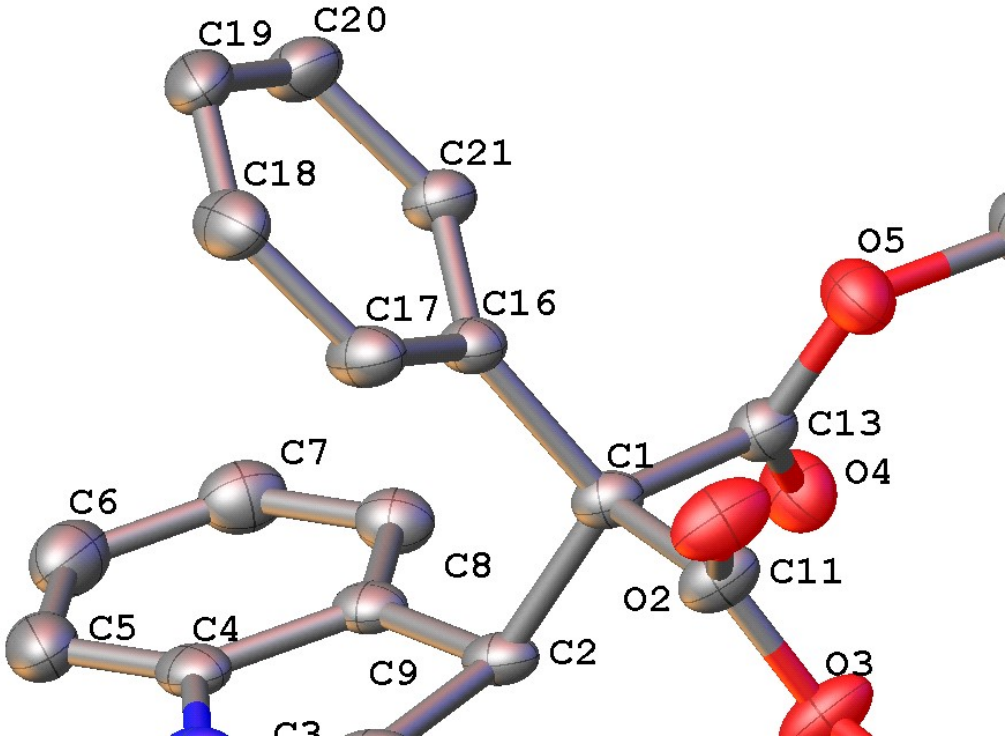
X-ray crystallographic data

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2213330 (**3ma**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/. The measurements were taken in a Bruker D8 Venture diffractometer. The data were integrated by Bruker D8 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL (2018/3).

X-ray crystallographic data for 3ma

Method of crystallization: A solution of **3ma** in ethyl acetate and petroleum ether was evaporated the solvent slowly at room temperature.

Crystal data and structure for 3ma (thermal ellipsoids are shown at the 50% level**)**



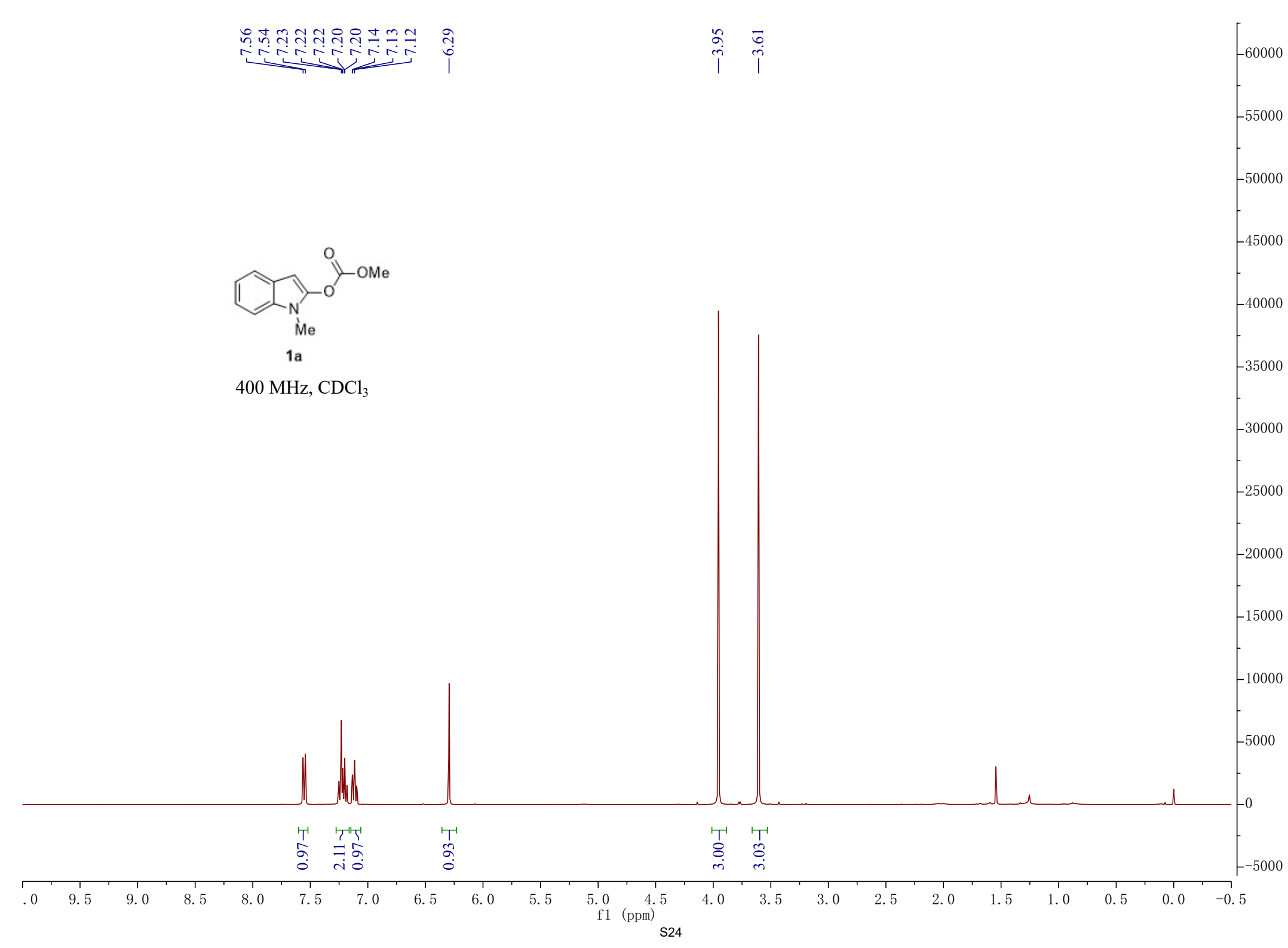
Identification code	220113sjt_0m	
Empirical formula	C21 H21 N O5	
Formula weight	367.39	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	= 103.416(6)°
Unit cell dimensions	a = 13.2122(2) Å	= 99.690(6)°
	b = 9.2500(2) Å	= 99.558(6)°
	c = 15.7120(3) Å	
Volume	1879.53(6) Å^3	
Z	4	
Density (calculated)	1.298 Mg/m^3	
Absorption coefficient	0.487 mm^{-1}	
F(000)	776	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
Theta range for data collection	2.973 to 54.960°.	
Index ranges	-16<=h<=16, -11<=k<=11, -19<=l<=16	
Reflections collected	18555	
Independent reflections	3527 [R(int) = 0.0407]	
Completeness to theta = 53.594°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.5810	
Refinement method	Full-matrix least-squares on F^2	

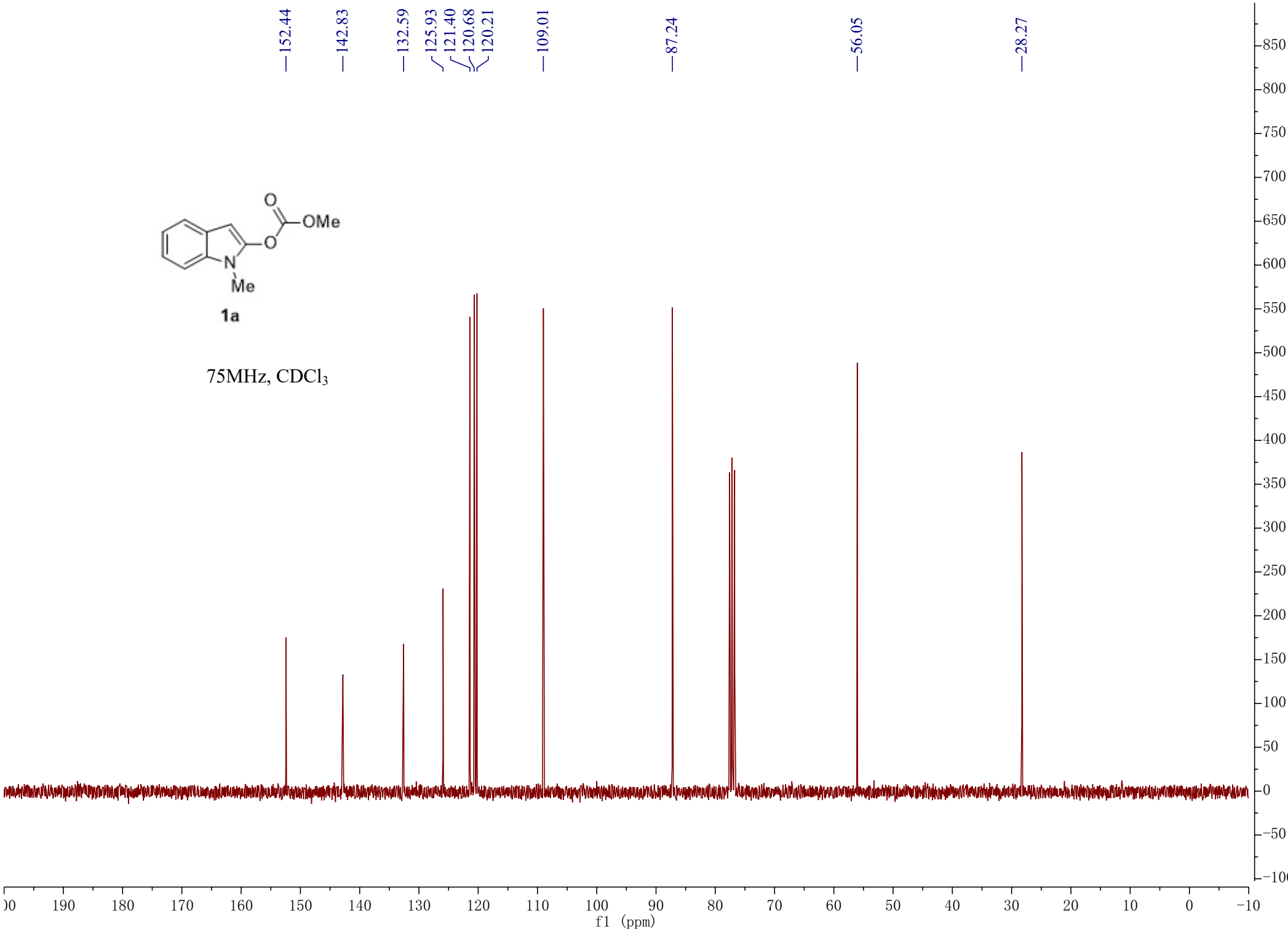
Data / restraints / parameters	3527 / 0 / 247
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1560
R indices (all data)	R1 = 0.0605, wR2 = 0.1619
Extinction coefficient	n/a

References

1. (a) H. Keipour, A. Jalba, L. Delage-Laurin and T. Ollevier, Copper-Catalyzed Carbenoid Insertion Reactions of α-Diazoesters and α-Diazoketones into Si-H and S-H Bonds. *J. Org. Chem*. 2017, **82**, 3000–3010. (b) C. T. Maier and C. G. Fu, Catalytic Enantioselective O-H Insertion Reactions. *J. Am. Chem. Soc*. 2006, **128**, 4594. (c) Z. Xue, Y. Li and S. Luo, Chiral Primary Amine-Catalyzed Divergent Coupling of α-Substituted Acrylaldehydes with α-Diazoesters. *ACS Catal*. 2020, **10**, 10989-10998. (d) M. Rubina, W. E. Woodward and M. Rubin, Remarkable Stereoelectronic Control in the Lewis Base Assisted [2,3]-Rearrangement of Cyclopropenylmethyl Phosphinites. *Org. Lett*. 2007, **9**, 5501-5504. (e) L. M. H. Davies, T. Hansen and R. M. Churchill, Catalytic Asymmetric C-H Activation of Alkanes and Tetrahydrofuran. *J. Am. Chem. Soc*. 2000, **122**, 3063-3070. (f) P. Zhang, J. Zeng, P. Pan, X.-j. Zhang and M. Yan, Palladium-Catalyzed Migratory Insertion of Carbenes and C-C Cleavage of Cycloalkanecarboxamides. *Org. Lett*. 2022, **24**, 536-541.

2. (a) R. Le Goff, M. Sanselme, M. A. Lawson, A. Daïch and S. Comesse, Highly Stereoselective Domino Oxa-Michael/Aza-Michael/Cyclization: Synthesis of Bicyclic Lactams and Spiroox-indole Skeleton. *Eur. J. Org. Chem*. 2015, **33**, 7244-7248. (b) D.-Z. Chen, W.-J. Xiao and J.-R. Chen, Synthesis of spiropyrazoline oxindoles by a formal [4 + 1] annulation reaction between 3-bromooxindoles and in situ-derived 1,2-diaza-1,3-dienes. *Org. Chem. Front*. 2017, **4**, 1289-1293.


7.56
7.54
7.23
7.22
7.22
7.20
7.20
7.14
7.13
7.12
6.29
3.95
3.61
O
OMe
O
N
Me
1a
400 MHz, CDCl3
0.97
2.11
0.97
0.93
3.00
3.03
f1 (ppm)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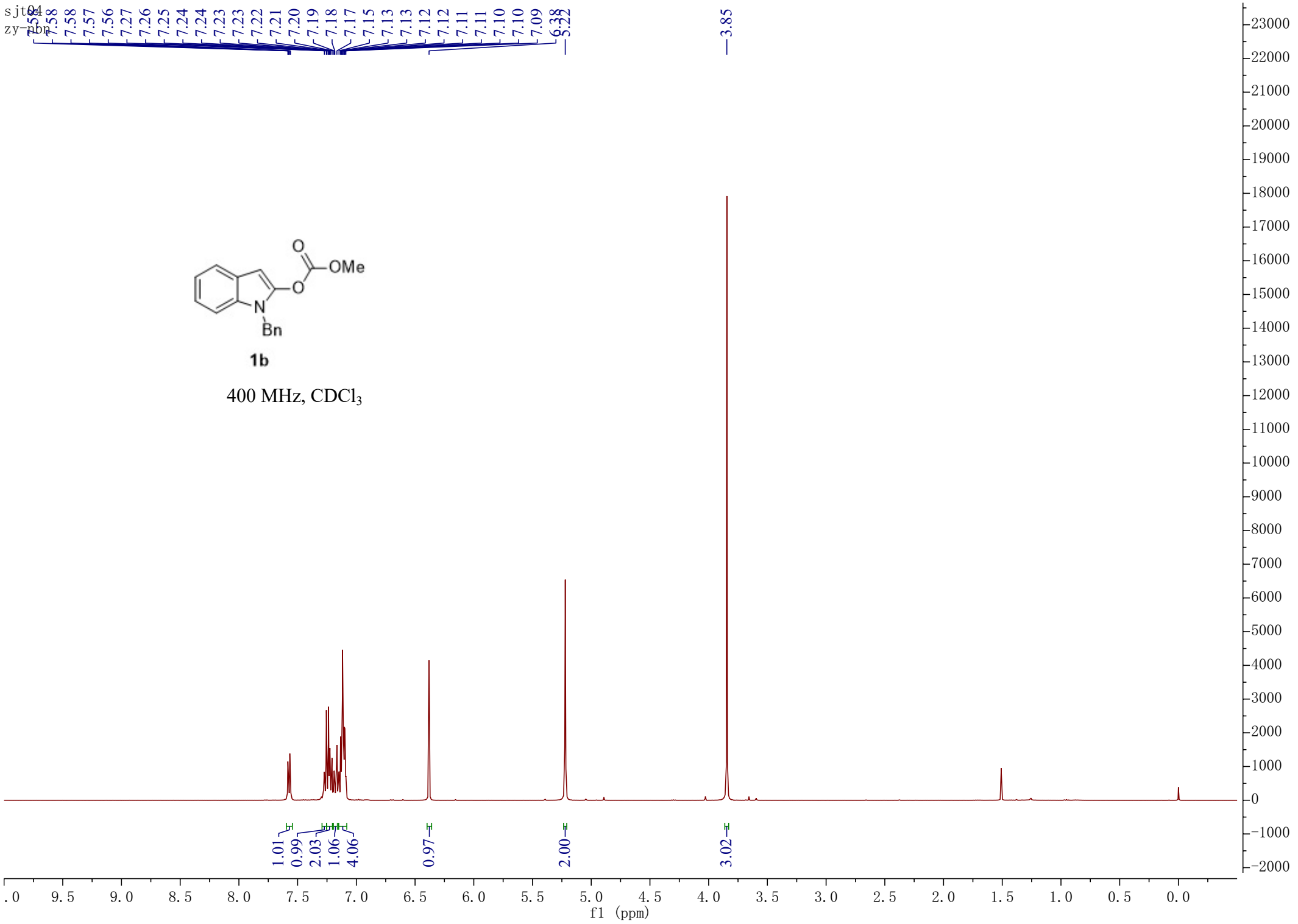
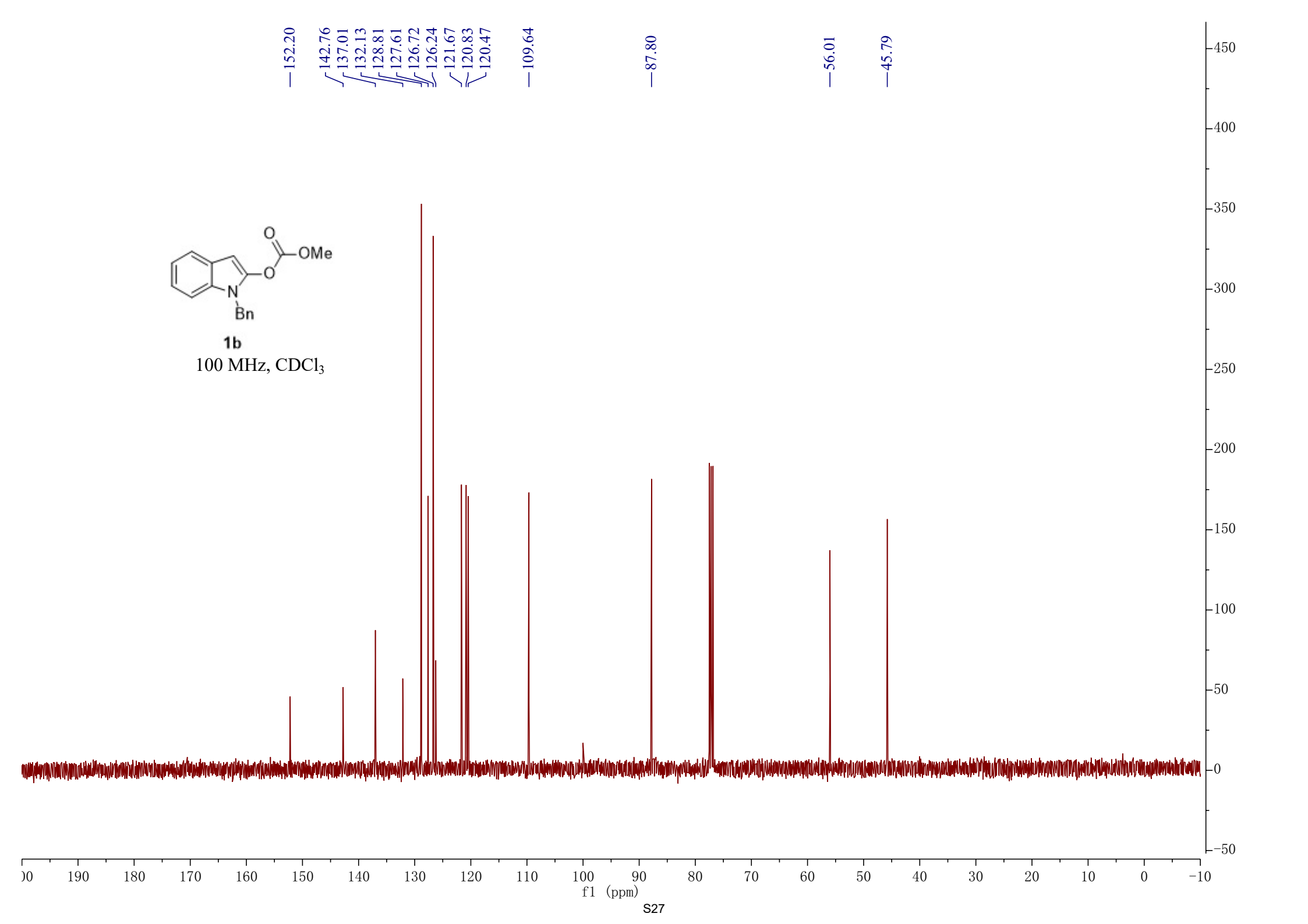
142.83
132.59
125.93
121.40
120.68
120.21
109.01
87.24
56.05
28.27
O
OMe
O
N
Me
1a
75MHz, CDCl3
f1 (ppm)


sjt04
zy-nbn
7.58
7.58
7.57
7.56
7.27
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.15
7.13
7.13
7.12
7.12
7.11
7.11
7.10
7.10
7.09
6.38
5.22
3.85
O
OMe
O
N
Bn
1b
400 MHz, CDCl3
1.01
0.99
2.03
1.06
4.06
0.97
2.00
3.02
f1 (ppm)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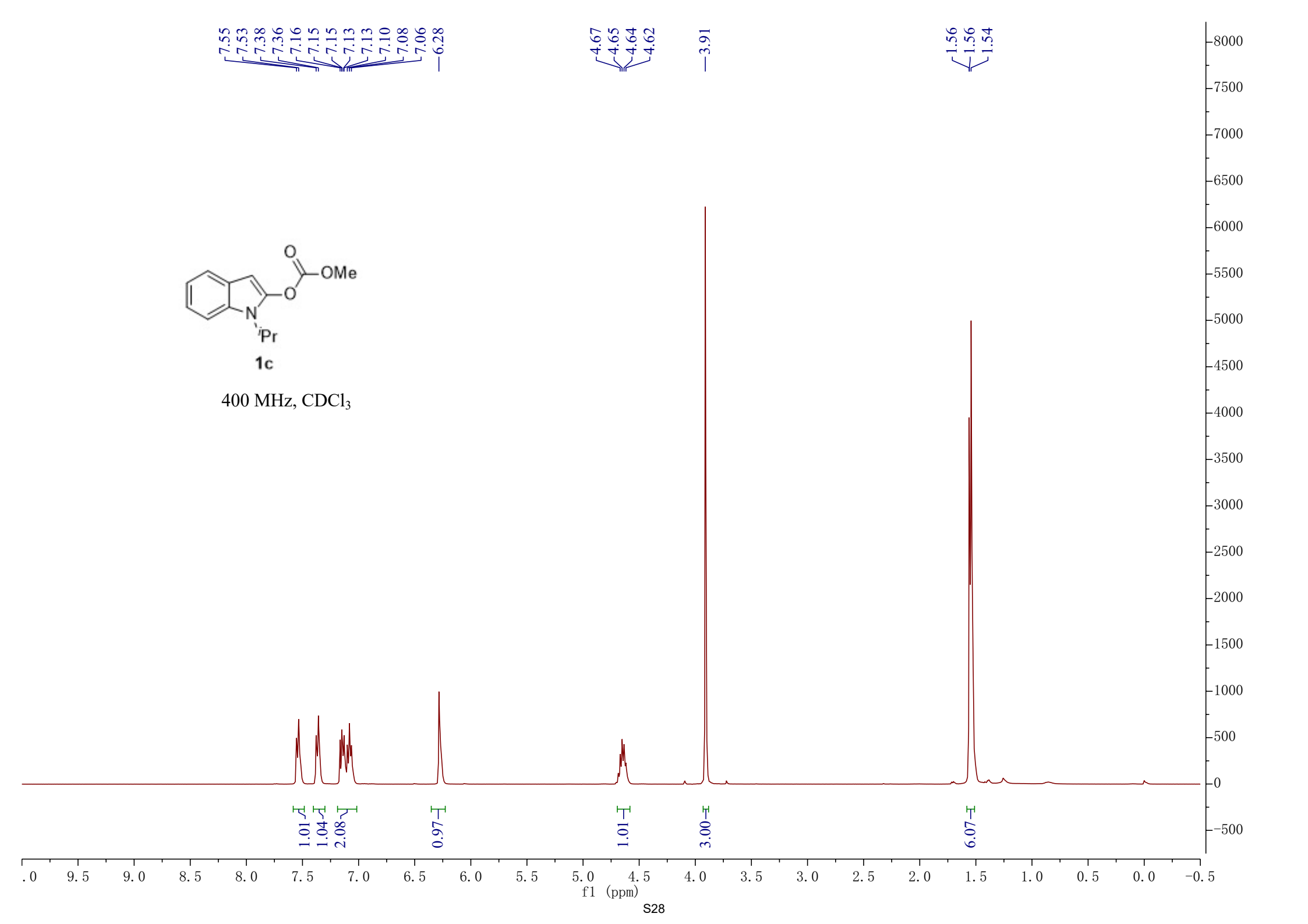
142.76
137.01
132.13
128.81
127.61
126.72
126.24
121.67
120.83
120.47
109.64
87.80
56.01
45.79
O
OMe
O
N
Bn
1b
100 MHz, CDCl3
f1 (ppm)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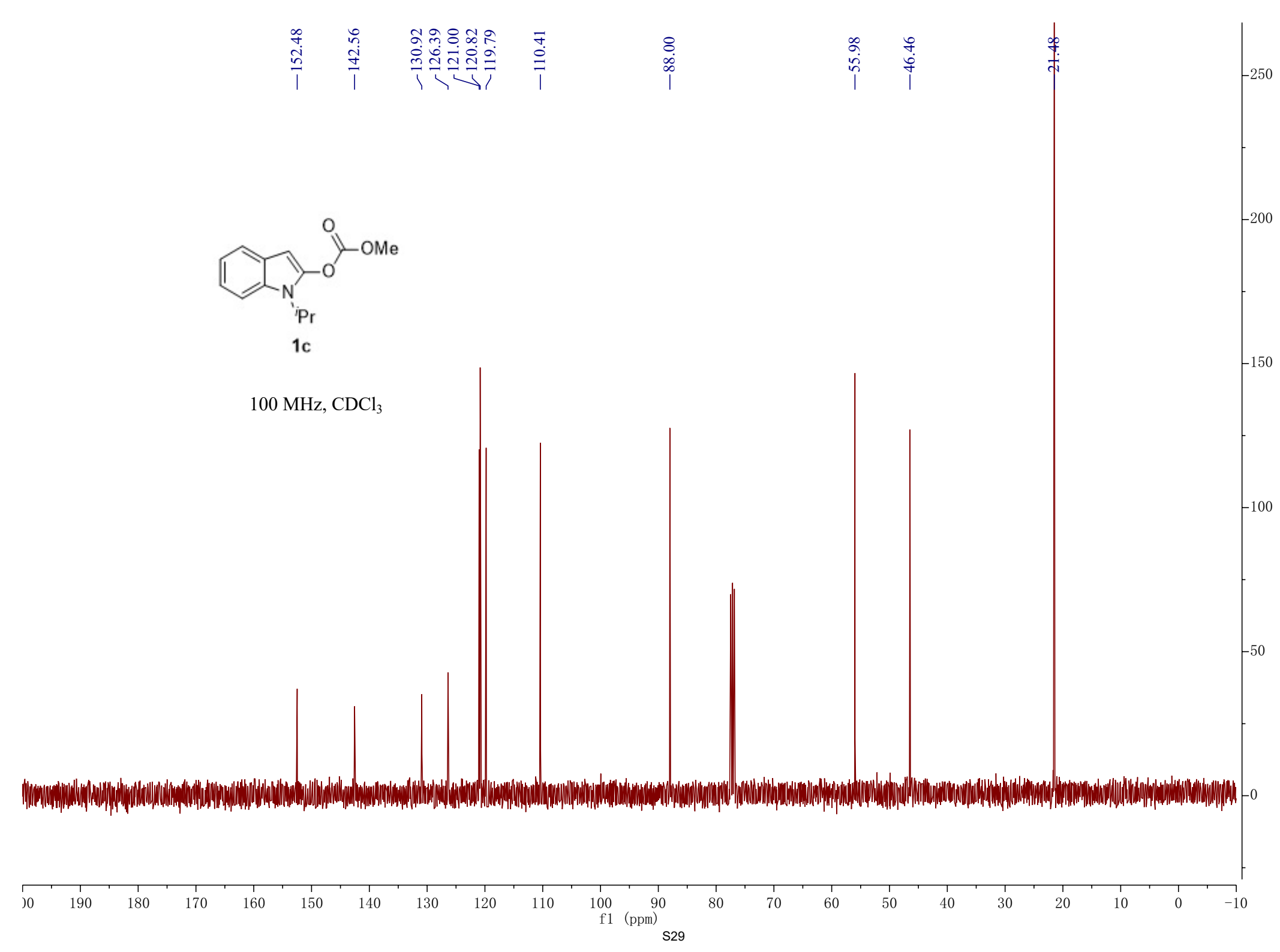
7.53
7.38
7.36
7.16
7.15
7.15
7.13
7.13
7.10
7.08
7.06
6.28
4.67
4.65
4.64
4.62
3.91
1.56
1.56
1.54
O
OMe
O
N
iPr
1c
400 MHz, CDCl3
1.01
1.04
2.08
0.97
1.01
3.00
6.07
f1 (ppm)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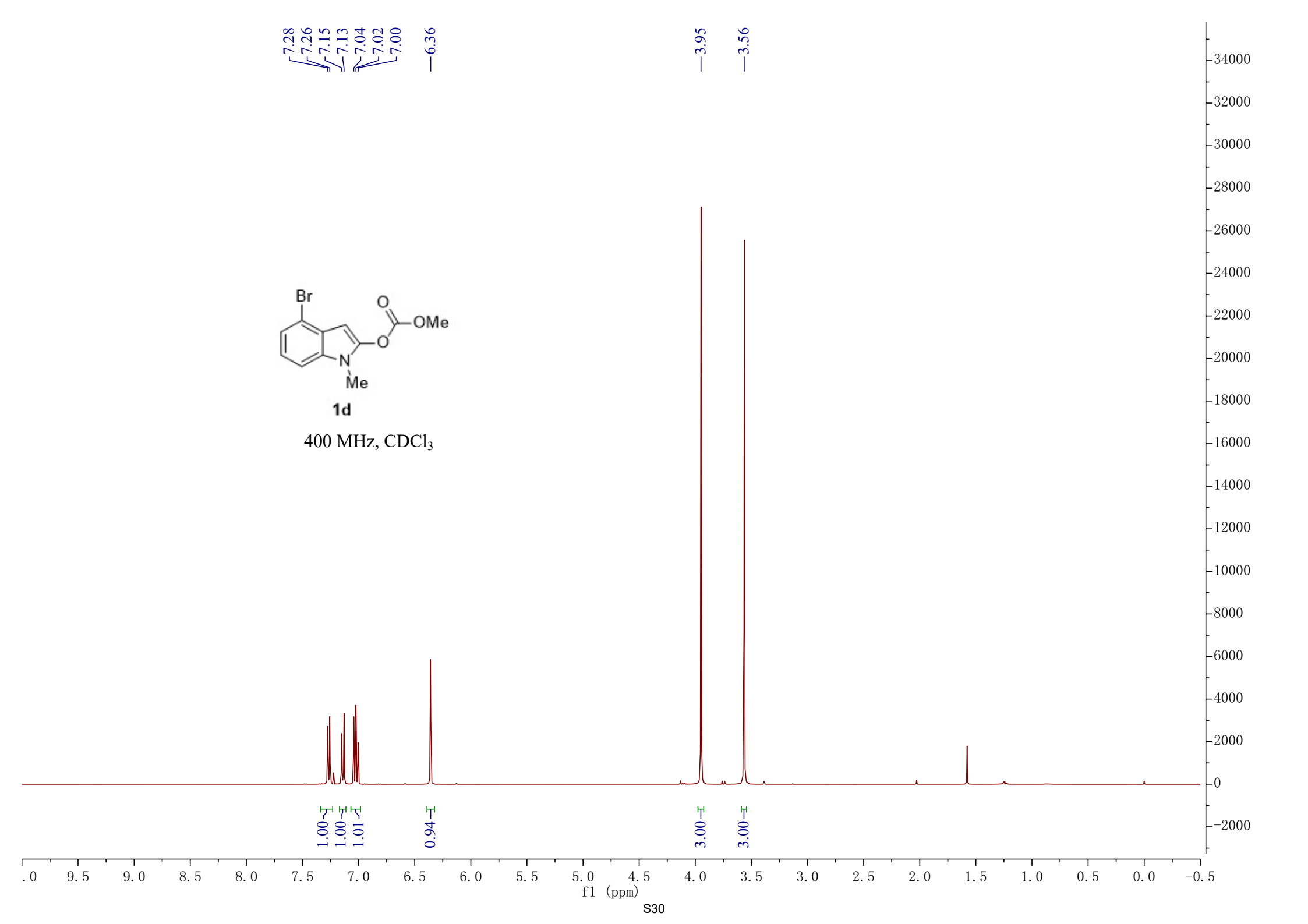
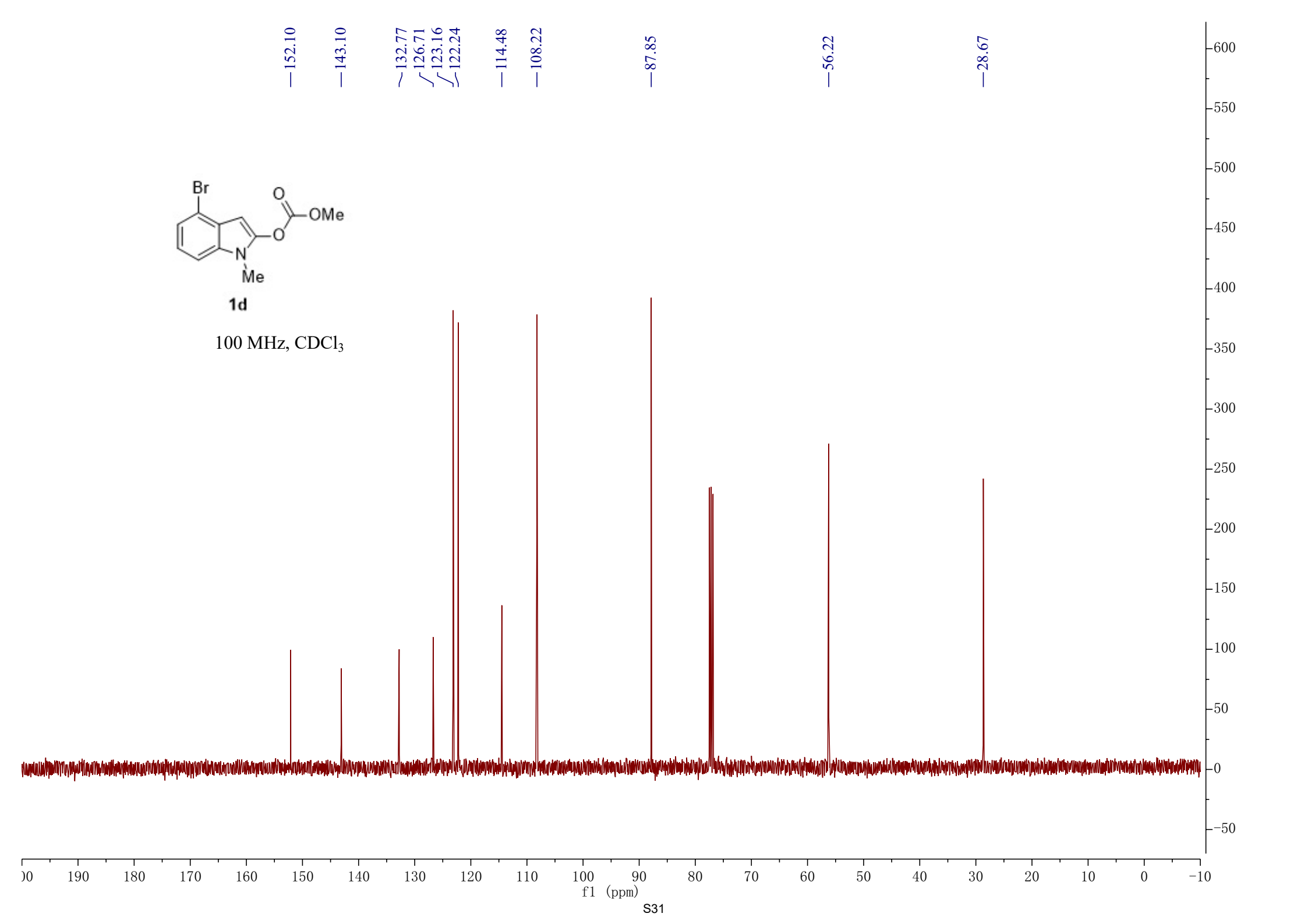
142.56
130.92
126.39
121.00
120.82
119.79
110.41
88.00
55.98
46.46
21.48
O
OMe
O
N
iPr
1c
100 MHz, CDCl3
250
200
150
100
50
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.28
7.26
7.15
7.13
7.04
7.02
7.00
6.36
3.95
3.56
Br
O
OMe
O
N
Me
1d
400 MHz, CDCl3
1.00
1.00
1.01
0.94
3.00
3.00
f1 (ppm)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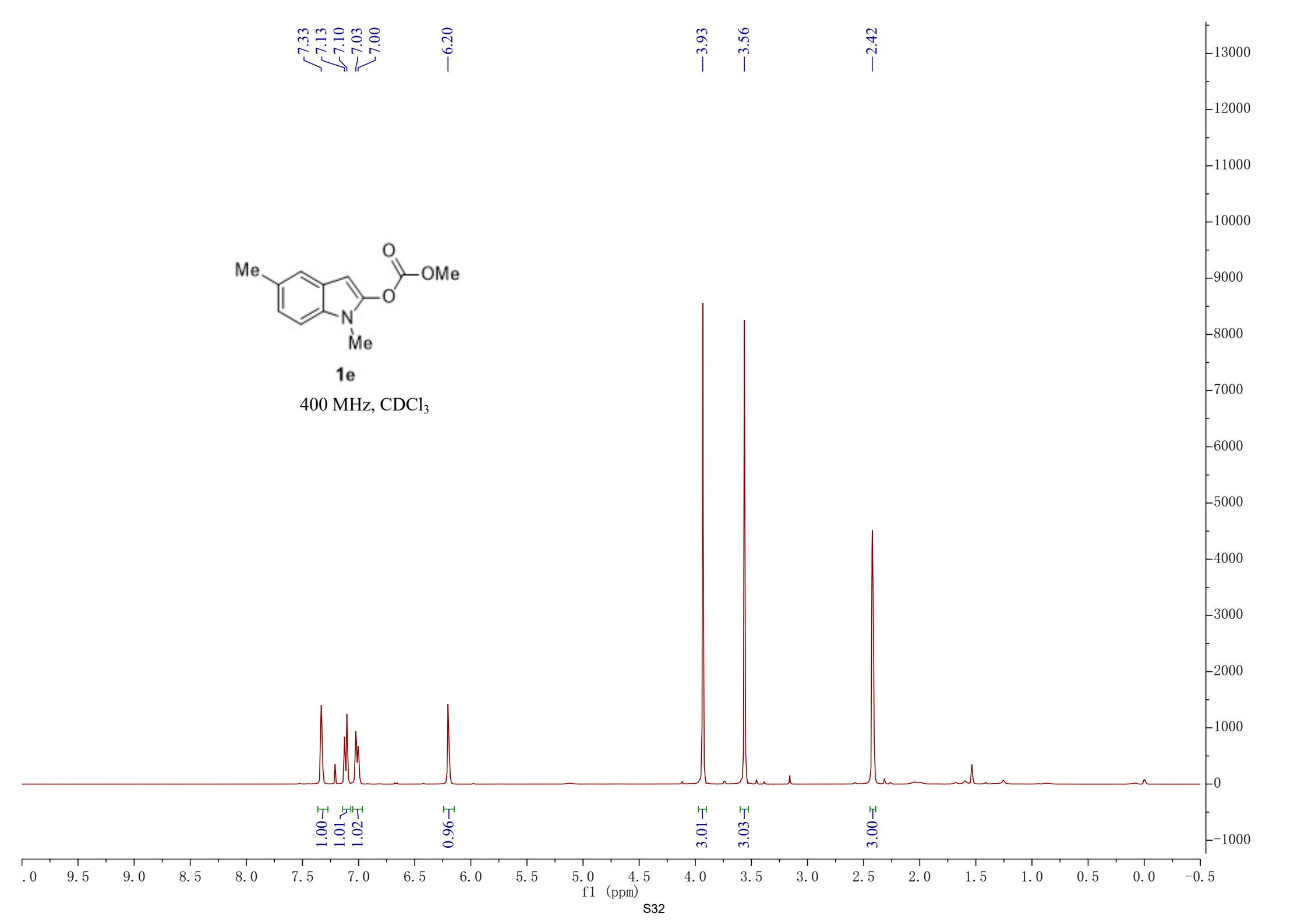
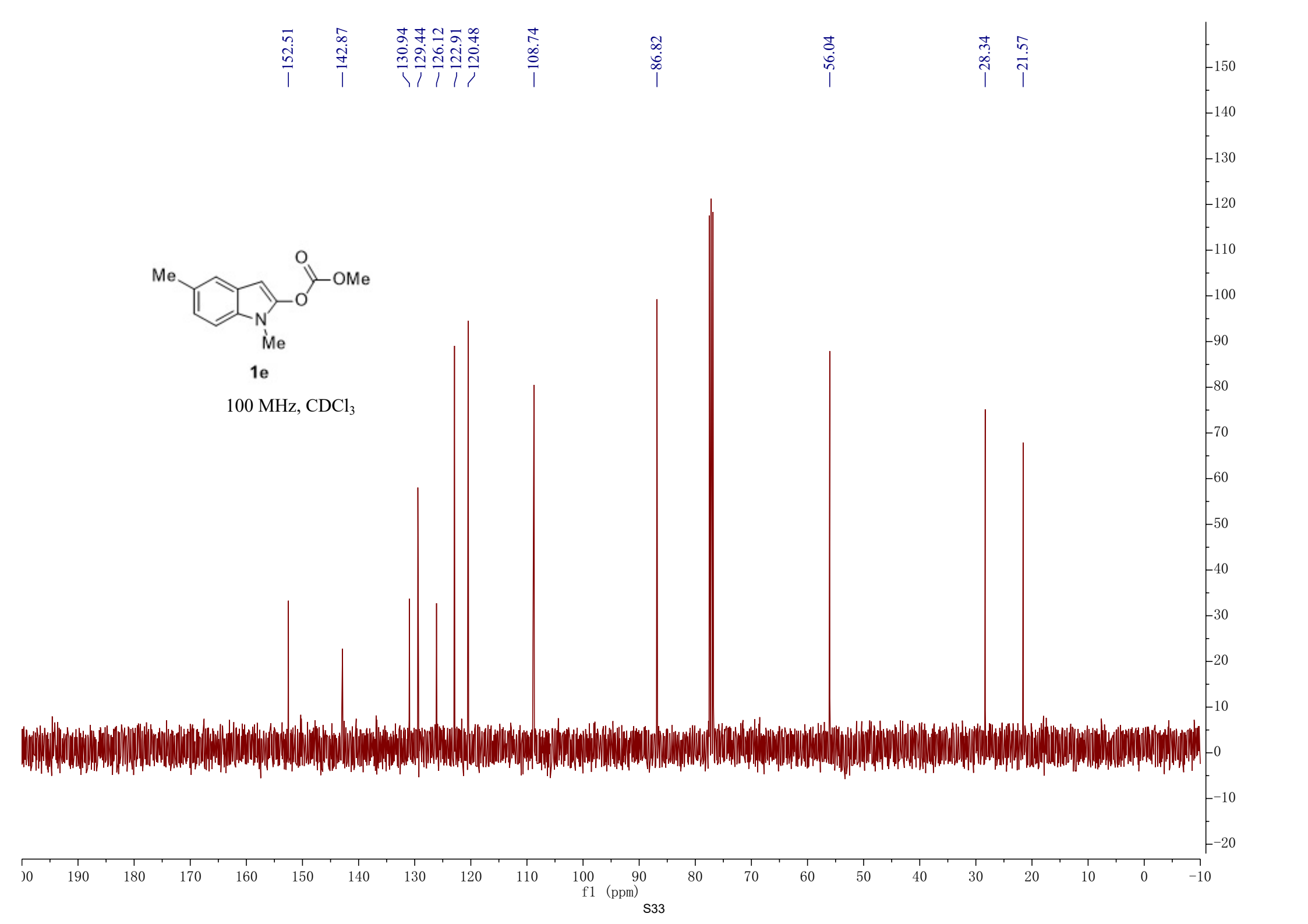
143.10
132.77
126.71
123.16
122.24
114.48
108.22
87.85
56.22
28.67
Br
O
OMe
O
N
Me
1d
100 MHz, CDCl3
600
550
500
450
400
350
300
250
200
150
100
50
0
−50
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.33
7.13
7.10
7.03
7.00
6.20
3.93
3.56
2.42
Me
O
OMe
O
N
Me
1e
400 MHz, CDCl3
1.00
1.01
1.02
0.96
3.01
3.03
3.00
f1 (ppm)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129.44
126.12
122.91
120.48
108.74
86.82
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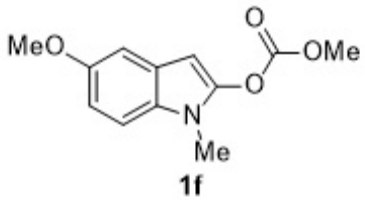
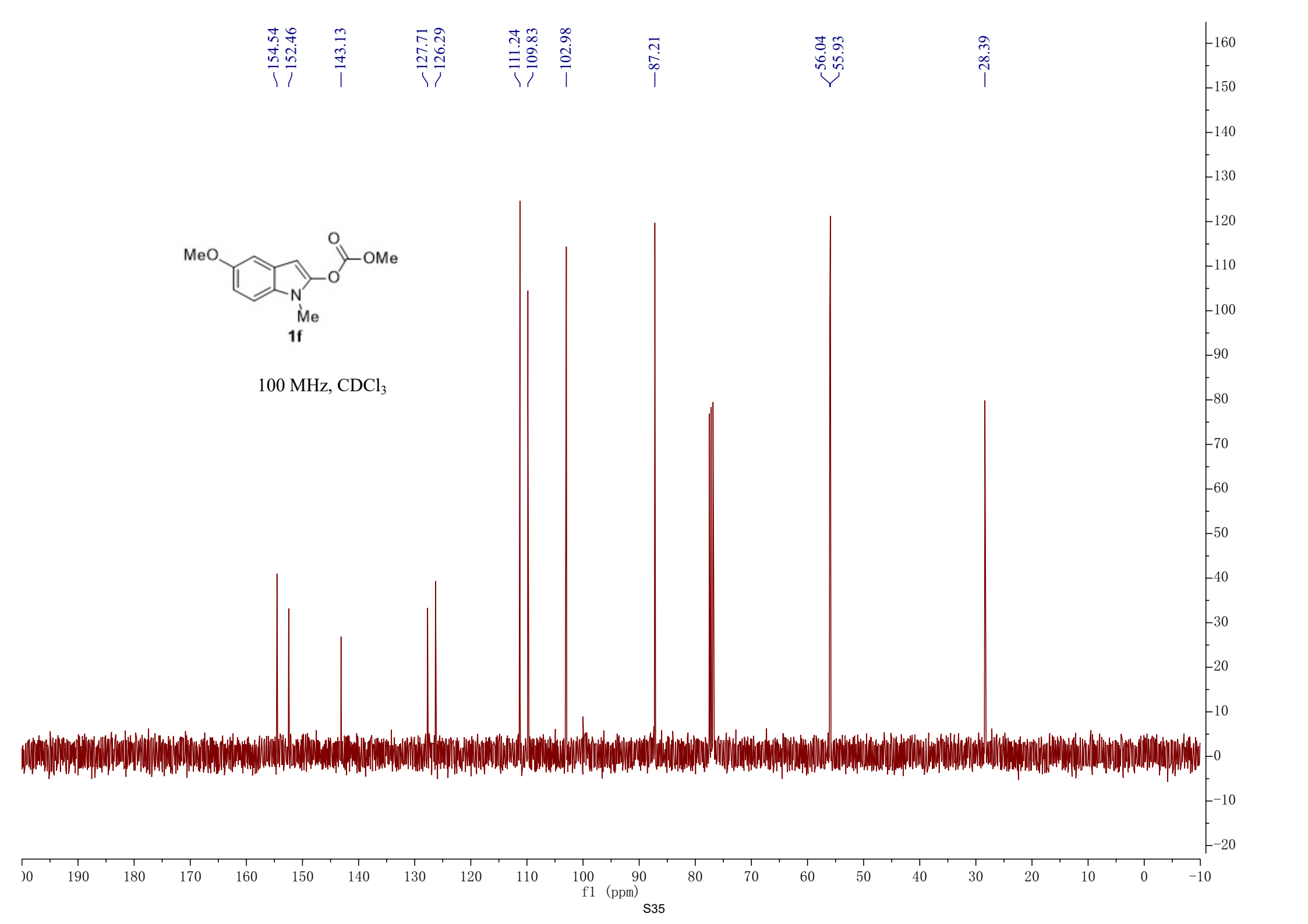
28.34
21.57
Me
O
OMe
O
N
Me
1e
100 MHz, CDCl3
f1 (ppm)



1f

400 MHz, $CDCl_3$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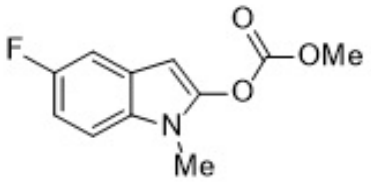
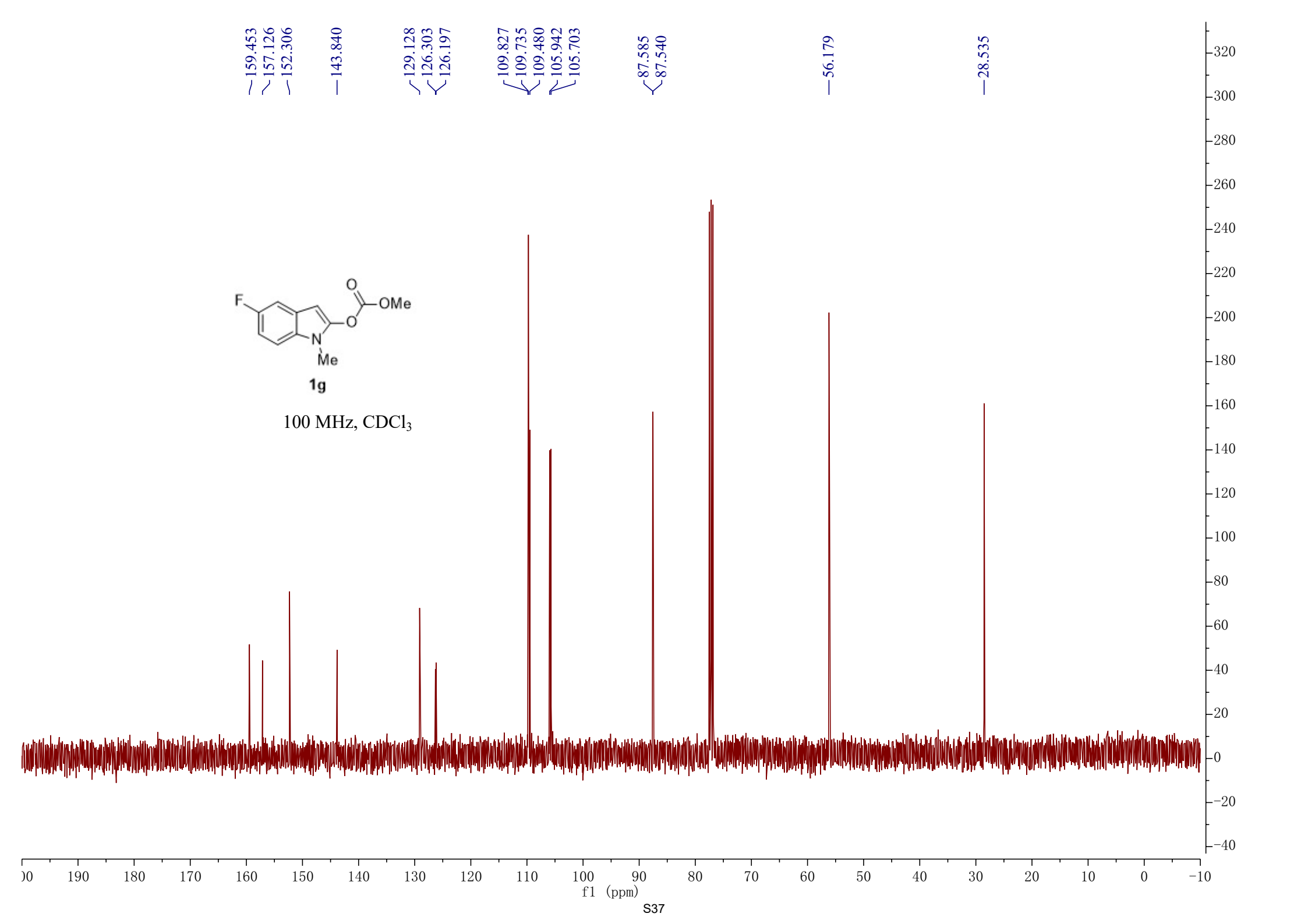
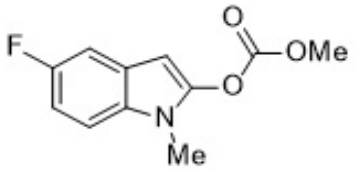
152.46
143.13
127.71
126.29
111.24
109.83
102.98
87.21
56.04
55.93
28.39
MeO
OMe
O
O
N
Me
1f
100 MHz, CDCl3
f1 (ppm)



1g

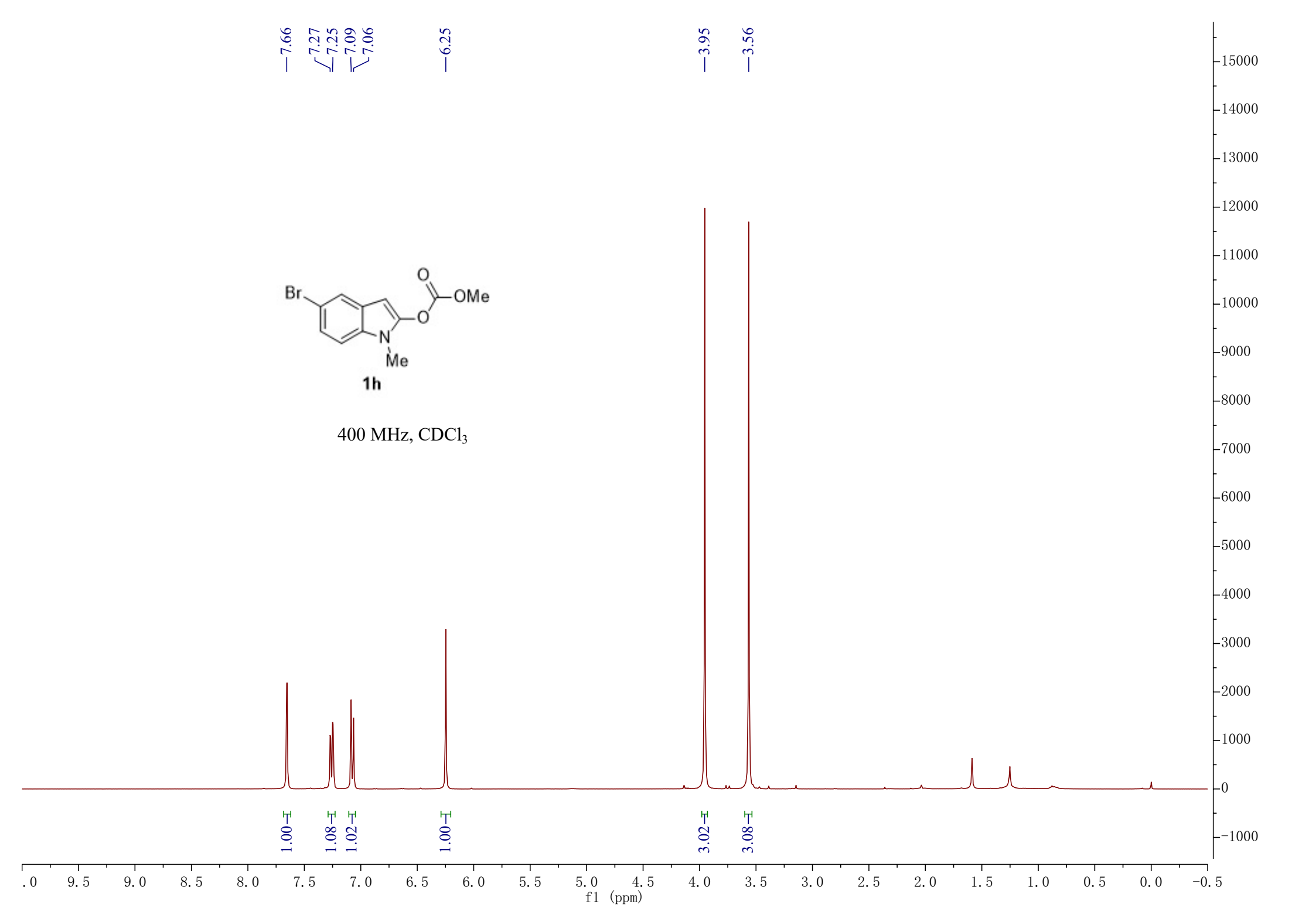
400 MHz, $CDCl_3$

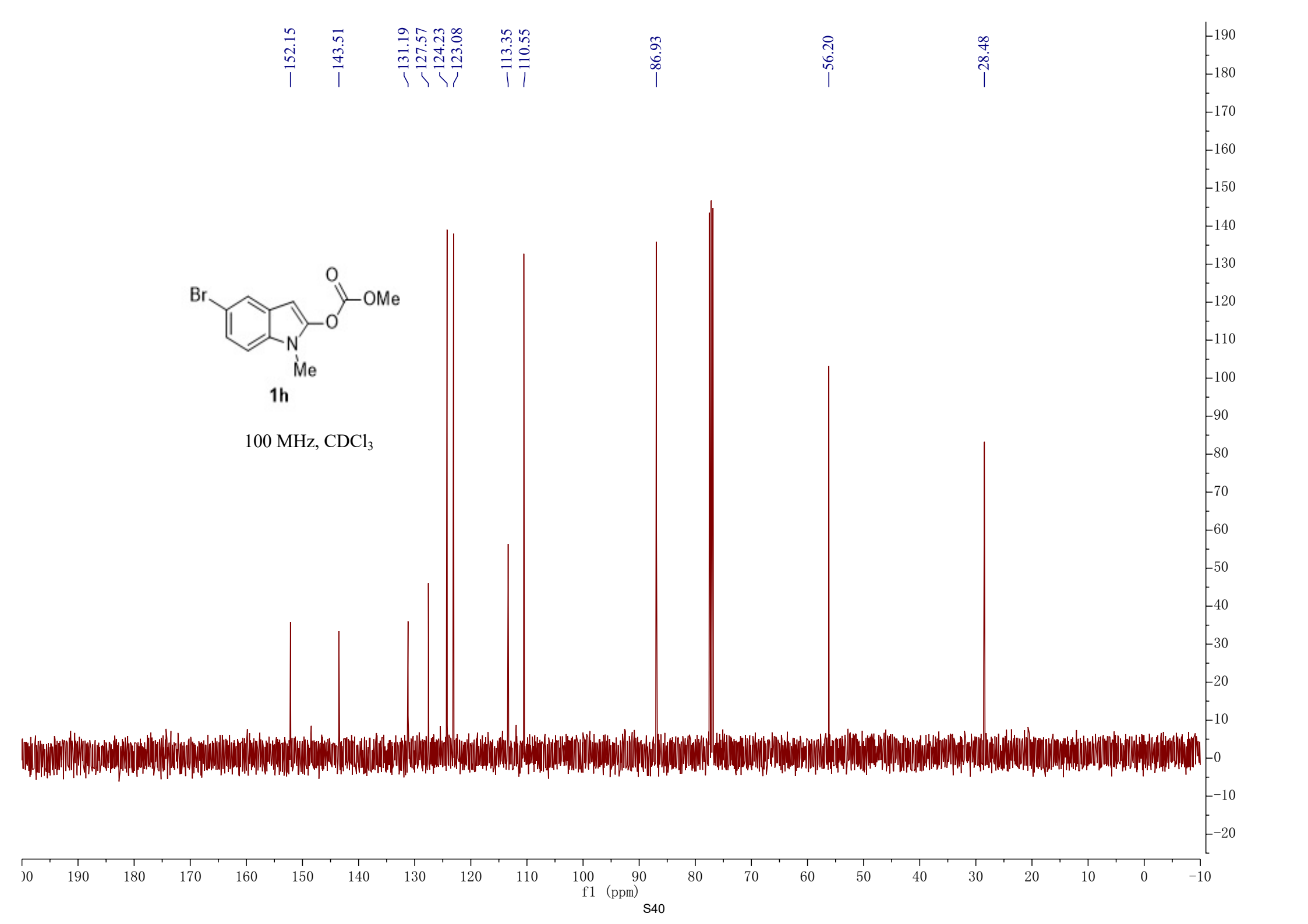

159.453
157.126
152.306
143.840
129.128
126.303
126.197
109.827
109.735
109.480
105.942
105.703
87.585
87.540
56.179
28.535
F
O
OMe
O
N
Me
1g
100 MHz, CDCl3
f1 (ppm)



1g

377 MHz, $CDCl_3$


7.66
7.27
7.25
7.09
7.06
6.25
3.95
3.56
Br
O
OMe
O
N
Me
1h
400 MHz, CDCl3
1.00
1.08
1.02
1.00
3.02
3.08
f1 (ppm)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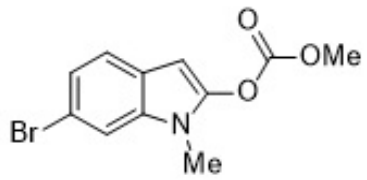
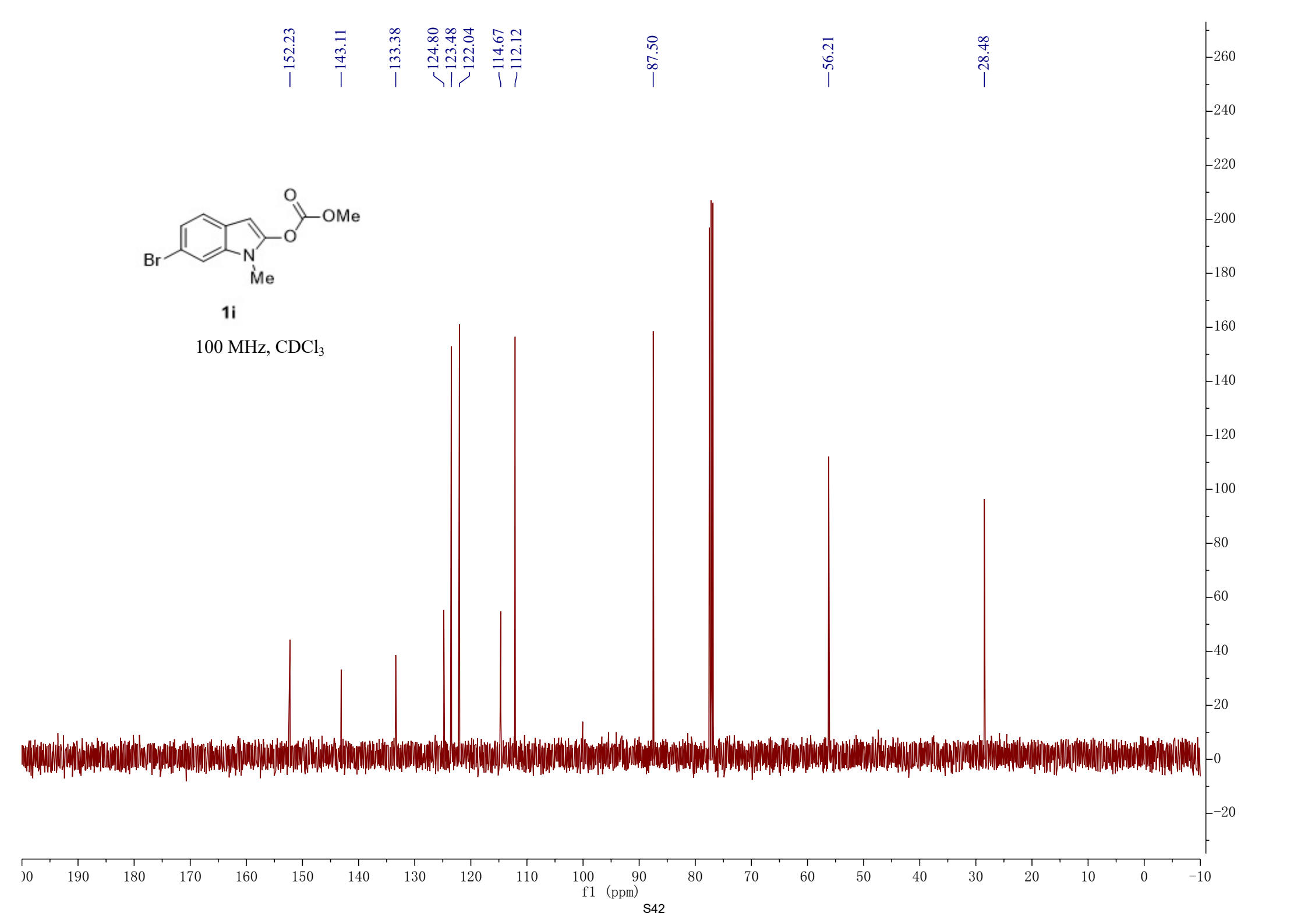
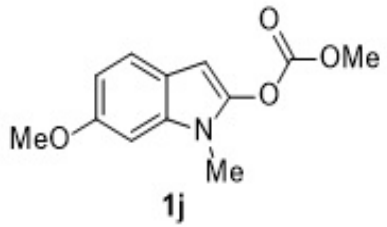
131.19
127.57
124.23
123.08
113.35
110.55
86.93
56.20
28.48
Br
O
OMe
O
N
Me
1h
100 MHz, CDCl3
f1 (ppm)



1i

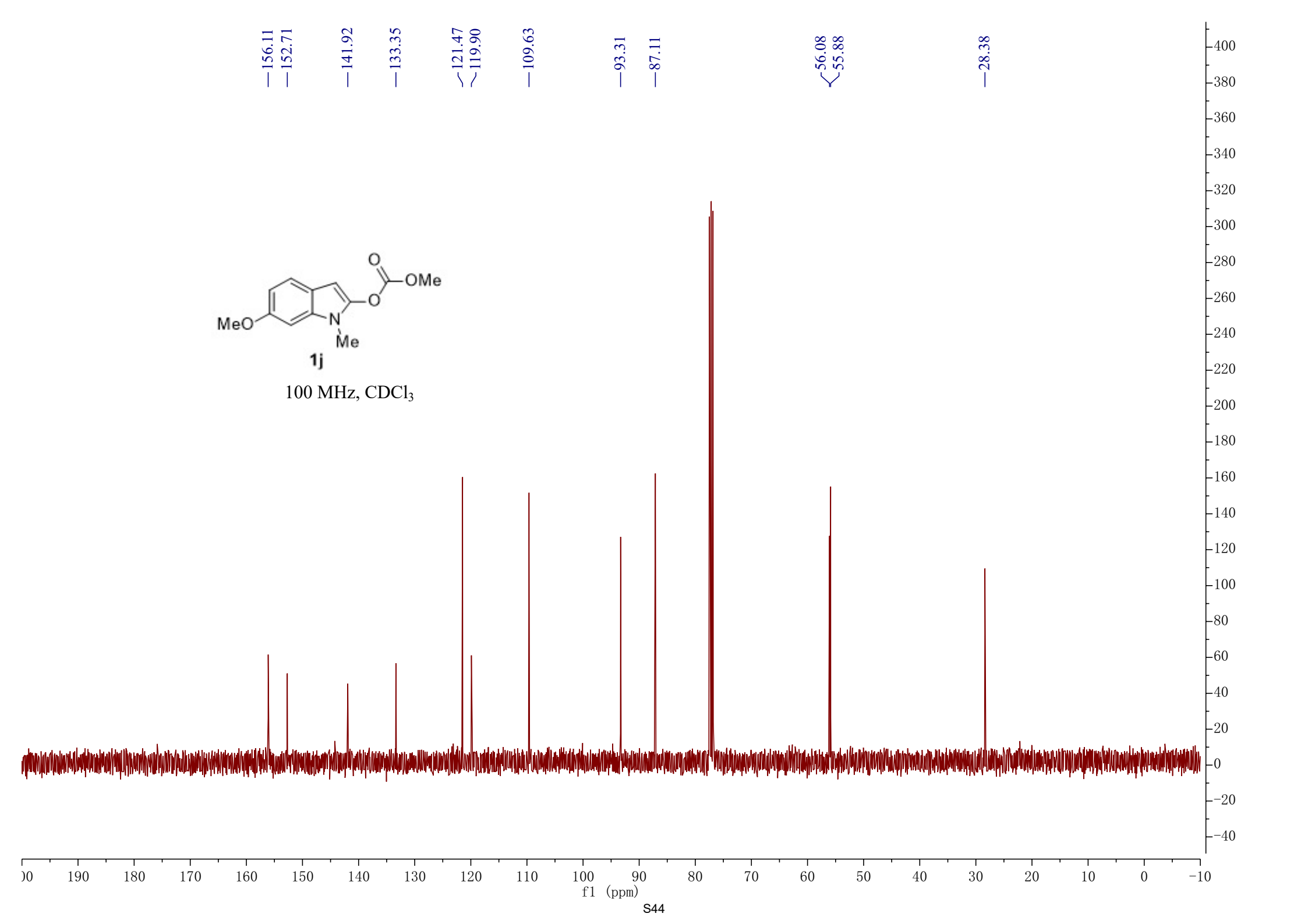
400 MHz, $CDCl_3$

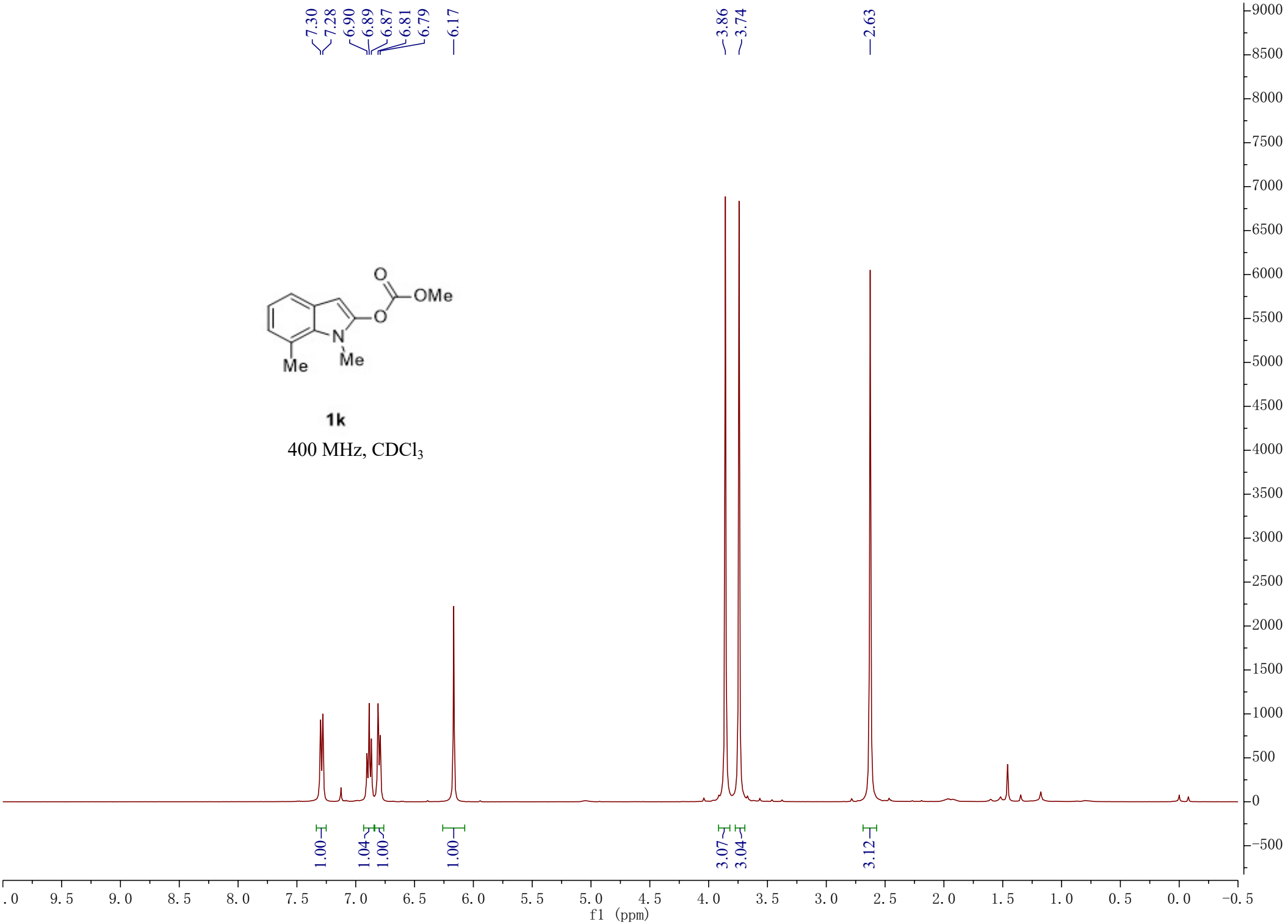

152.23
143.11
133.38
124.80
123.48
122.04
114.67
112.12
87.50
56.21
28.48
O
OMe
O
Br
N
Me
1i
100 MHz, CDCl3
f1 (ppm)



1j

300 MHz, $CDCl_3$


156.11
152.71
141.92
133.35
121.47
119.90
109.63
93.31
87.11
56.08
55.88
28.38
MeO
N
Me
O
OMe
O
1j
100 MHz, CDCl3
f1 (ppm)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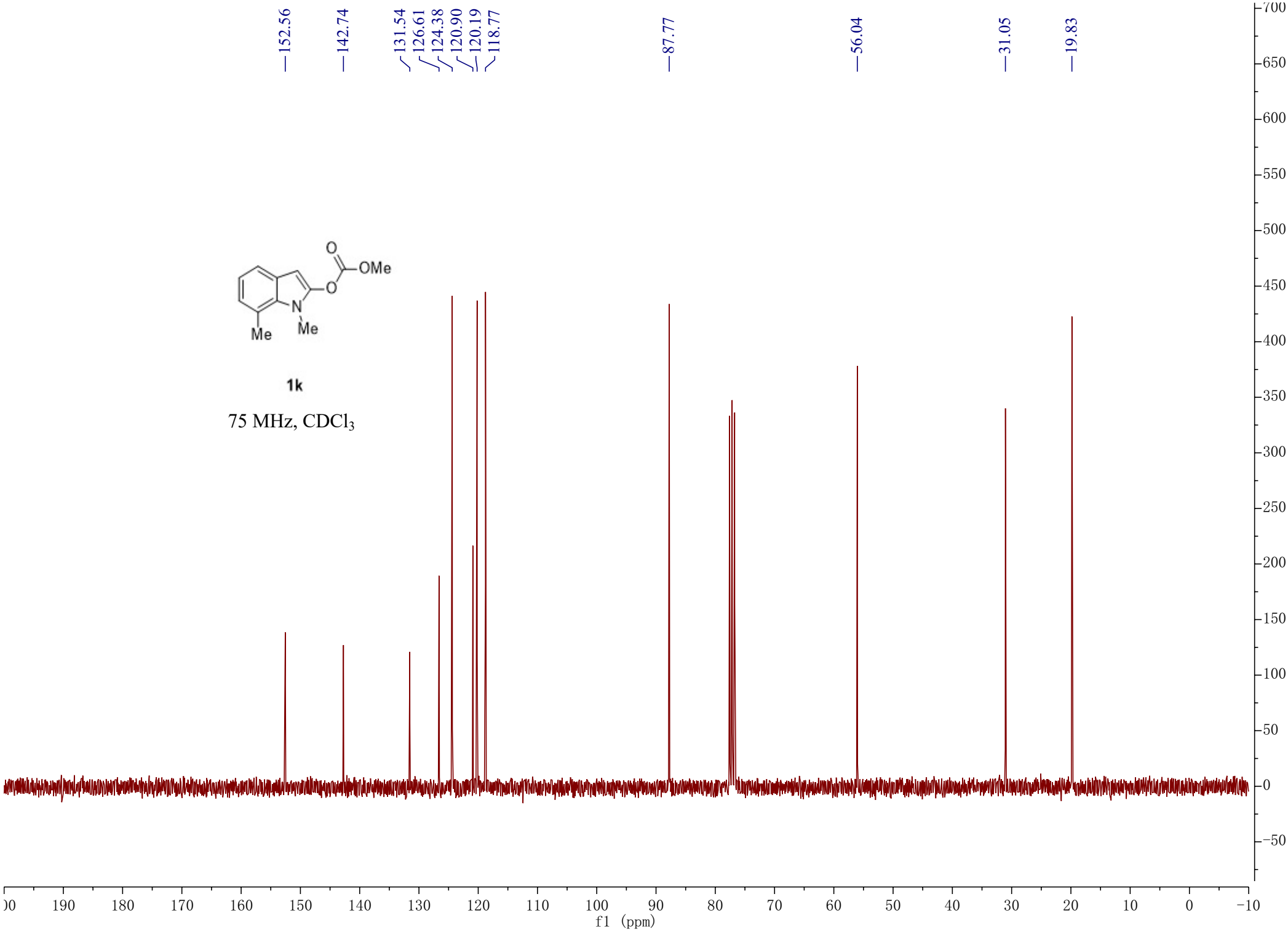
7.28
6.90
6.89
6.87
6.81
6.79
6.17
3.86
3.74
2.63
O
OMe
O
N
Me
Me
1k
400 MHz, CDCl3
1.00
1.04
1.00
1.00
3.07
3.04
3.12
f1 (ppm)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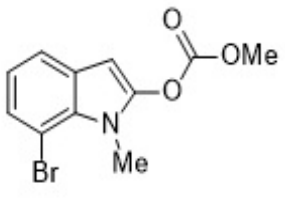
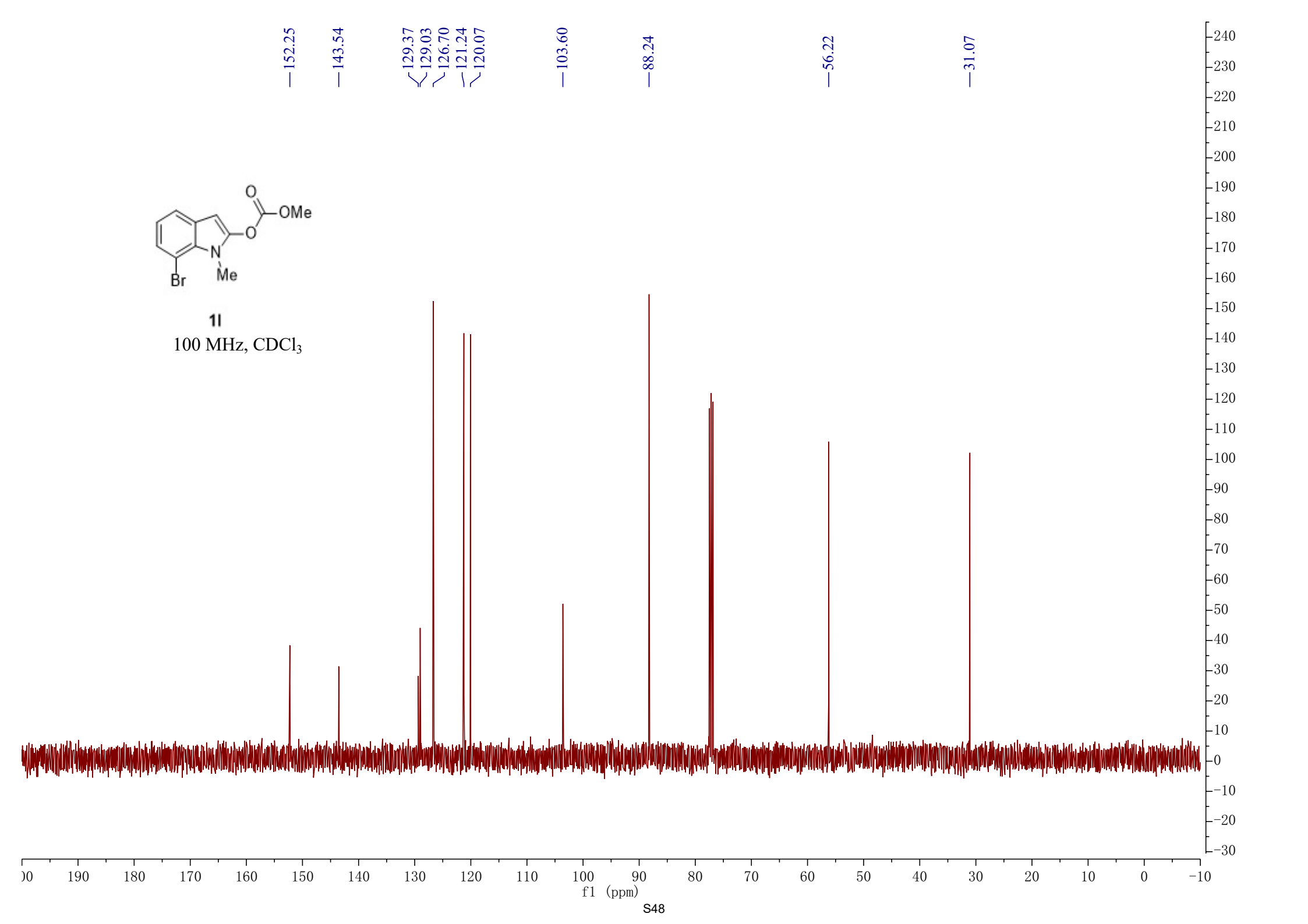
142.74
131.54
126.61
124.38
120.90
120.19
118.77
87.77
56.04
31.05
19.83
O
OMe
O
N
Me
Me
1k
75 MHz, CDCl3
f1 (ppm)

sjt04
zy-7br



1l

400 MHz, $CDCl_3$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143.54
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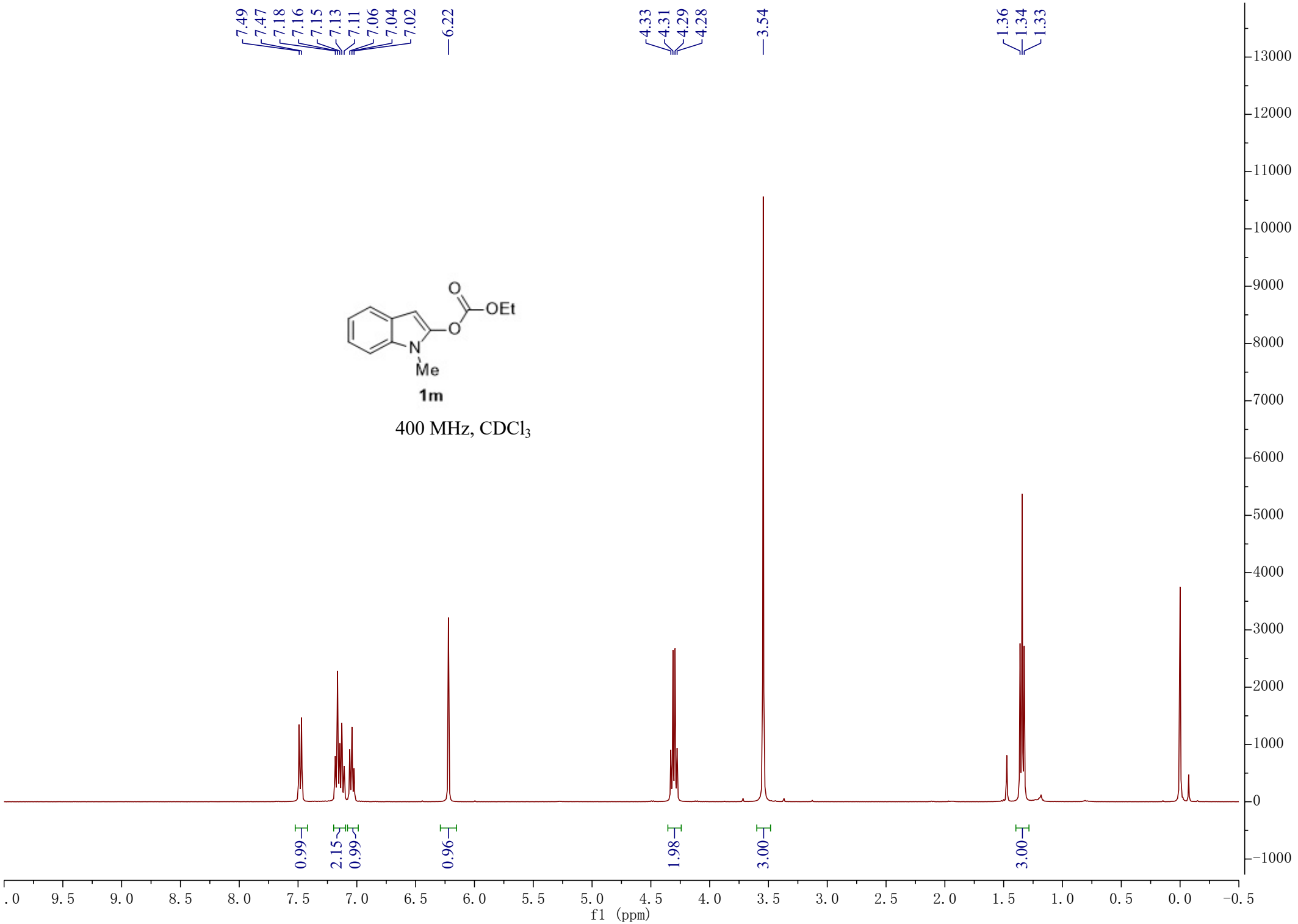
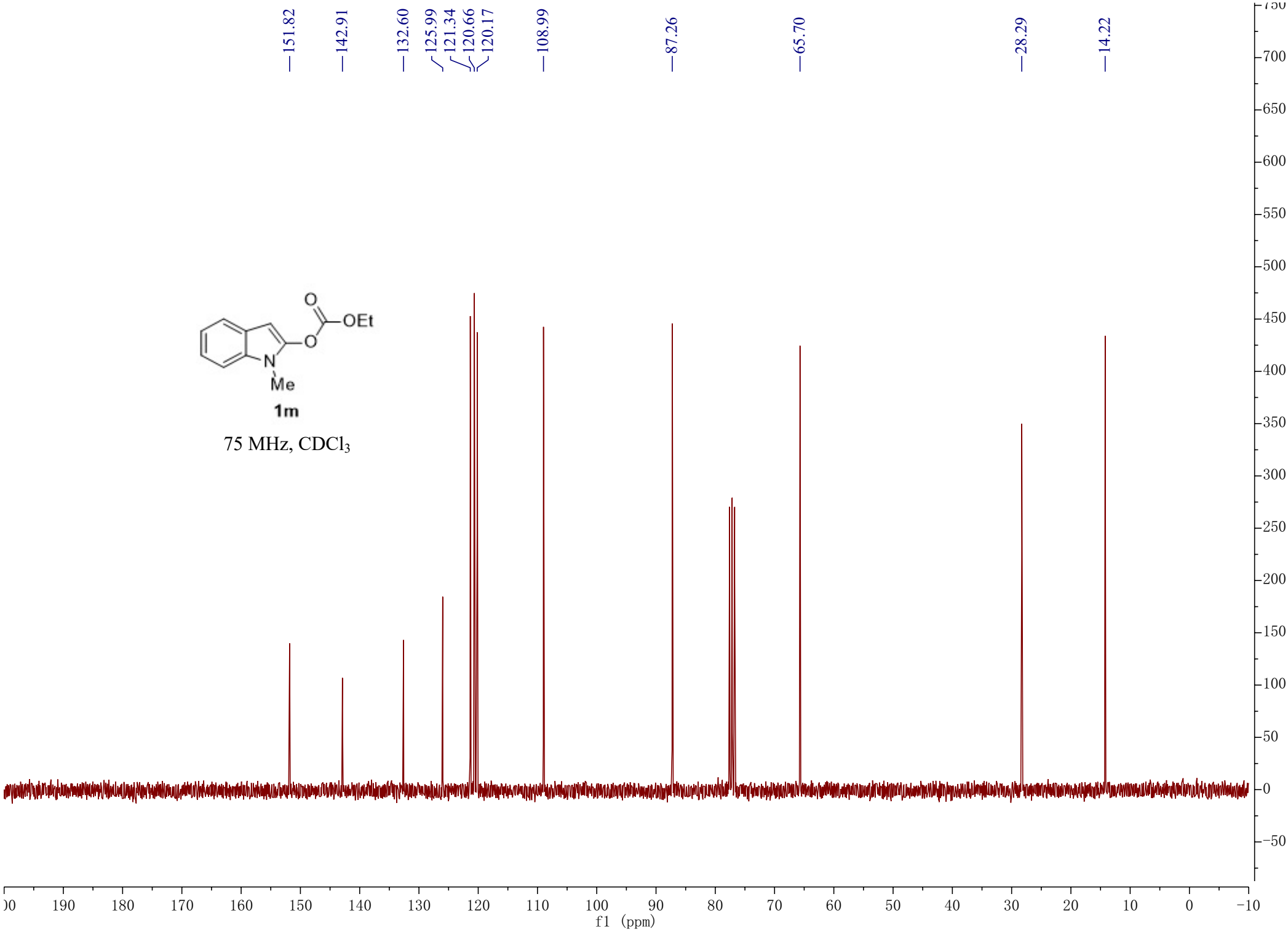
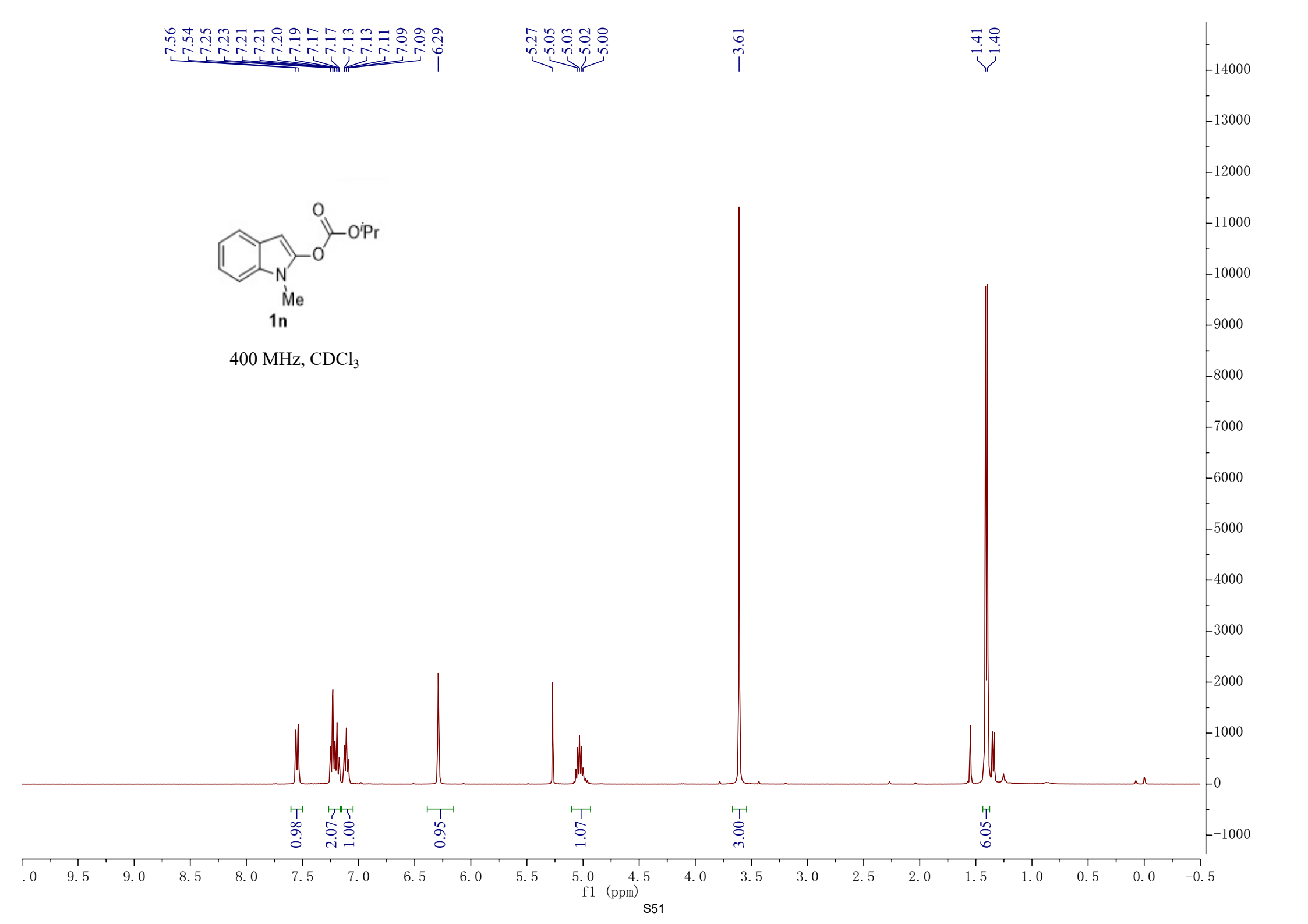
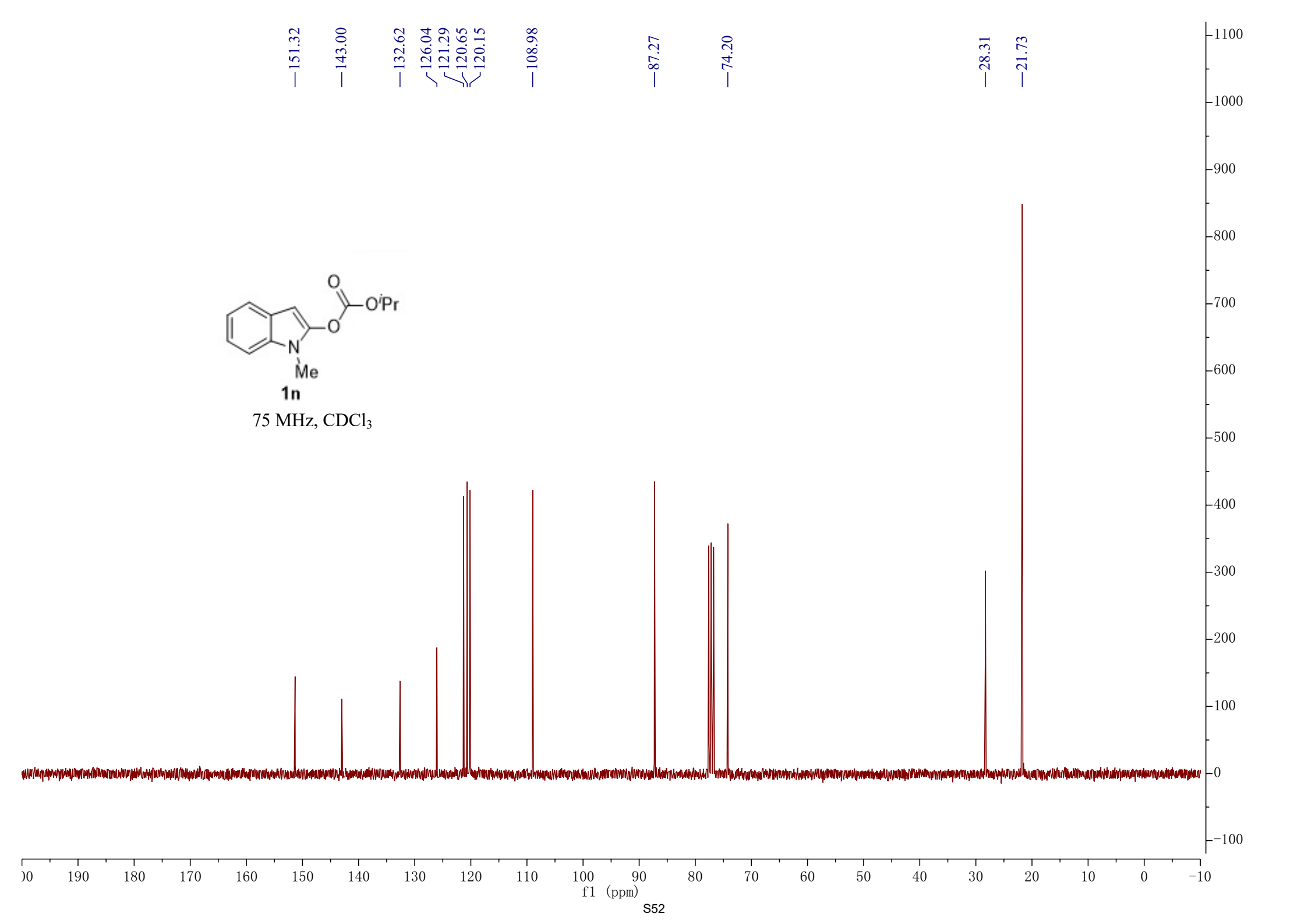
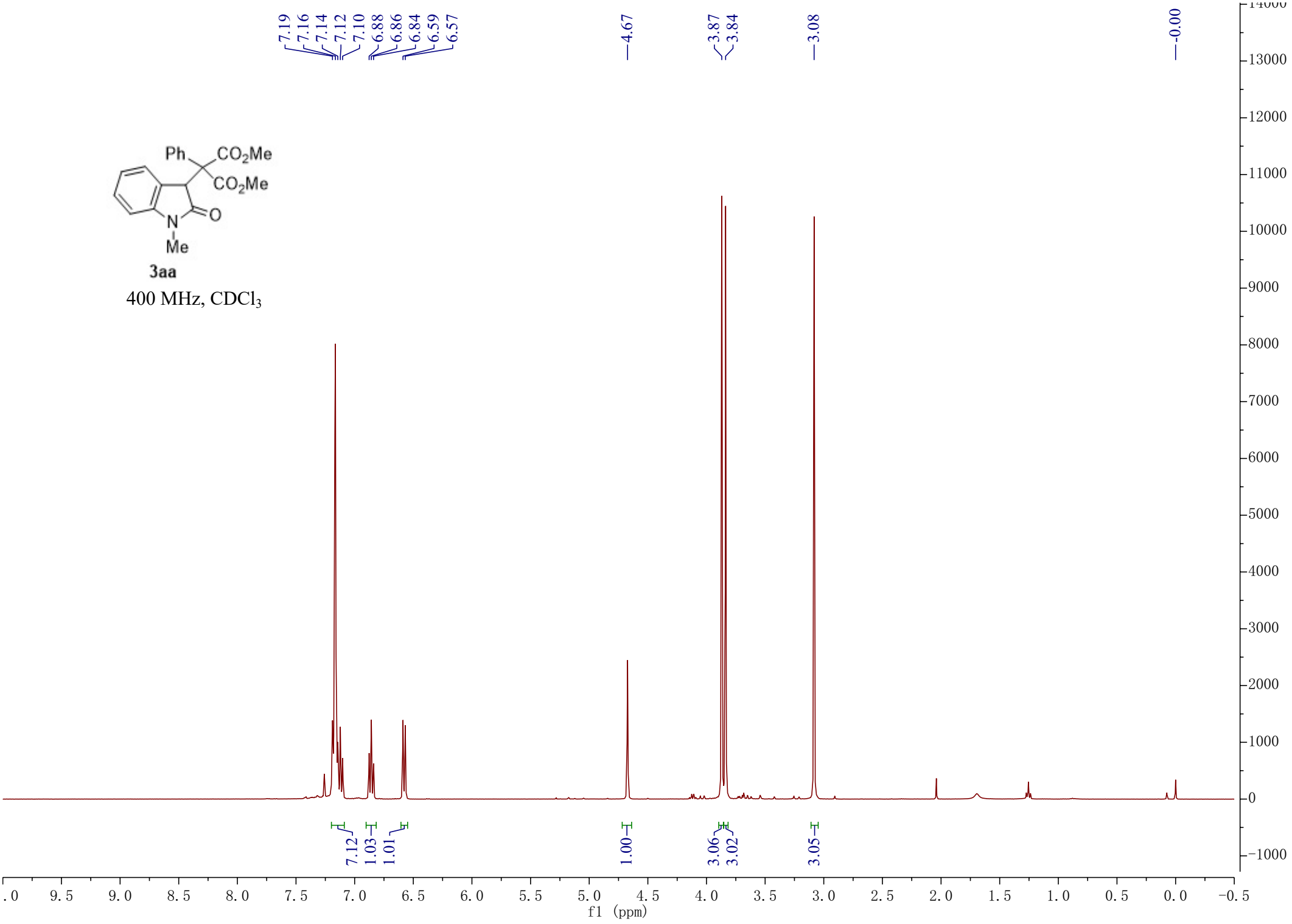
126.70
121.24
120.07
103.60
88.24
56.22
31.07
OMe
O
O
N
Me
Br
1l
100 MHz, CDCl3
f1 (ppm)

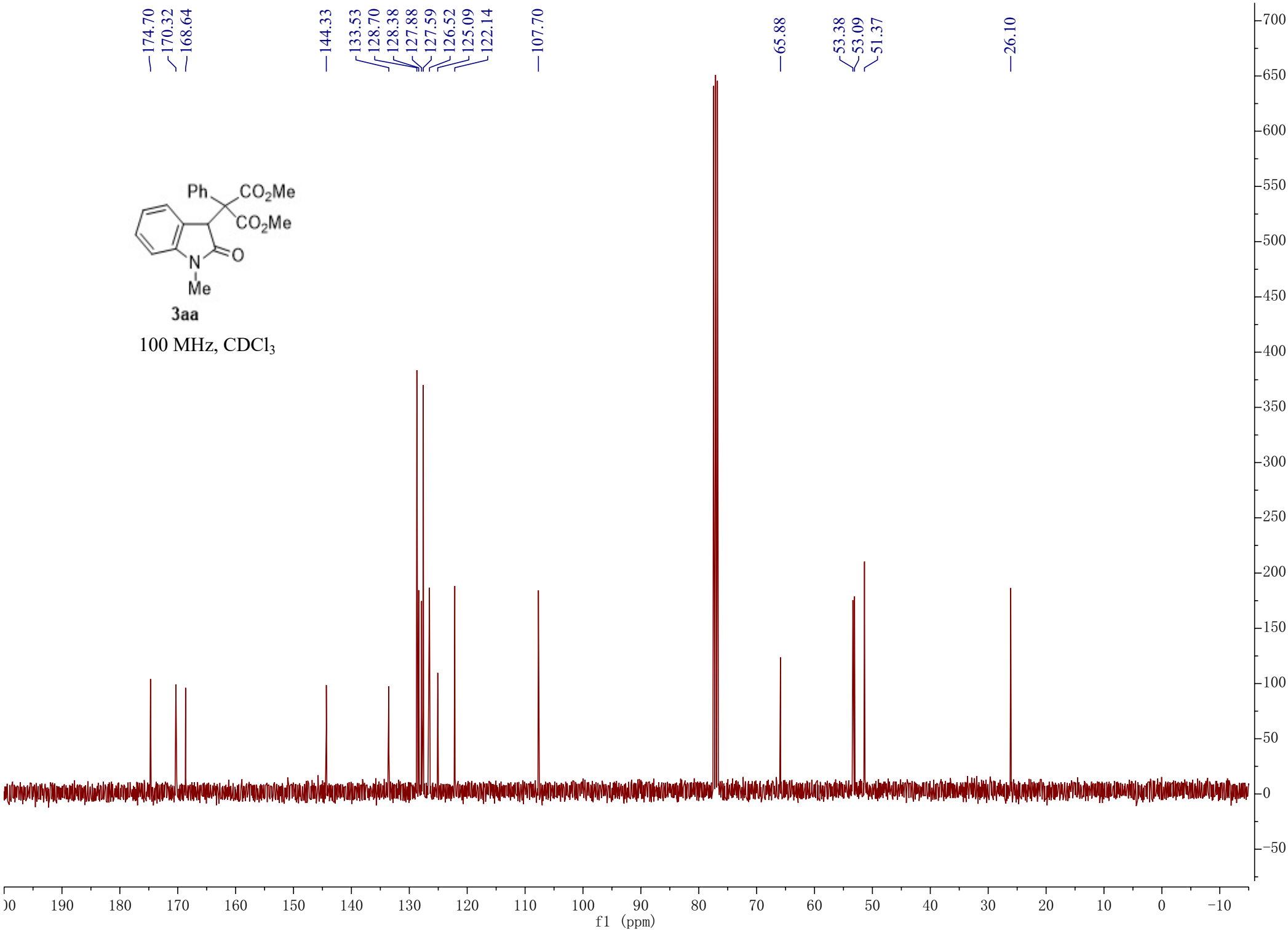

7.49
7.47
7.18
7.16
7.15
7.13
7.11
7.06
7.04
7.02
6.22
4.33
4.31
4.29
4.28
3.54
1.36
1.34
1.33
O
OEt
O
N
Me
1m
400 MHz, CDCl3
0.99
2.15
0.99
0.96
1.98
3.00
3.00
f1 (ppm)

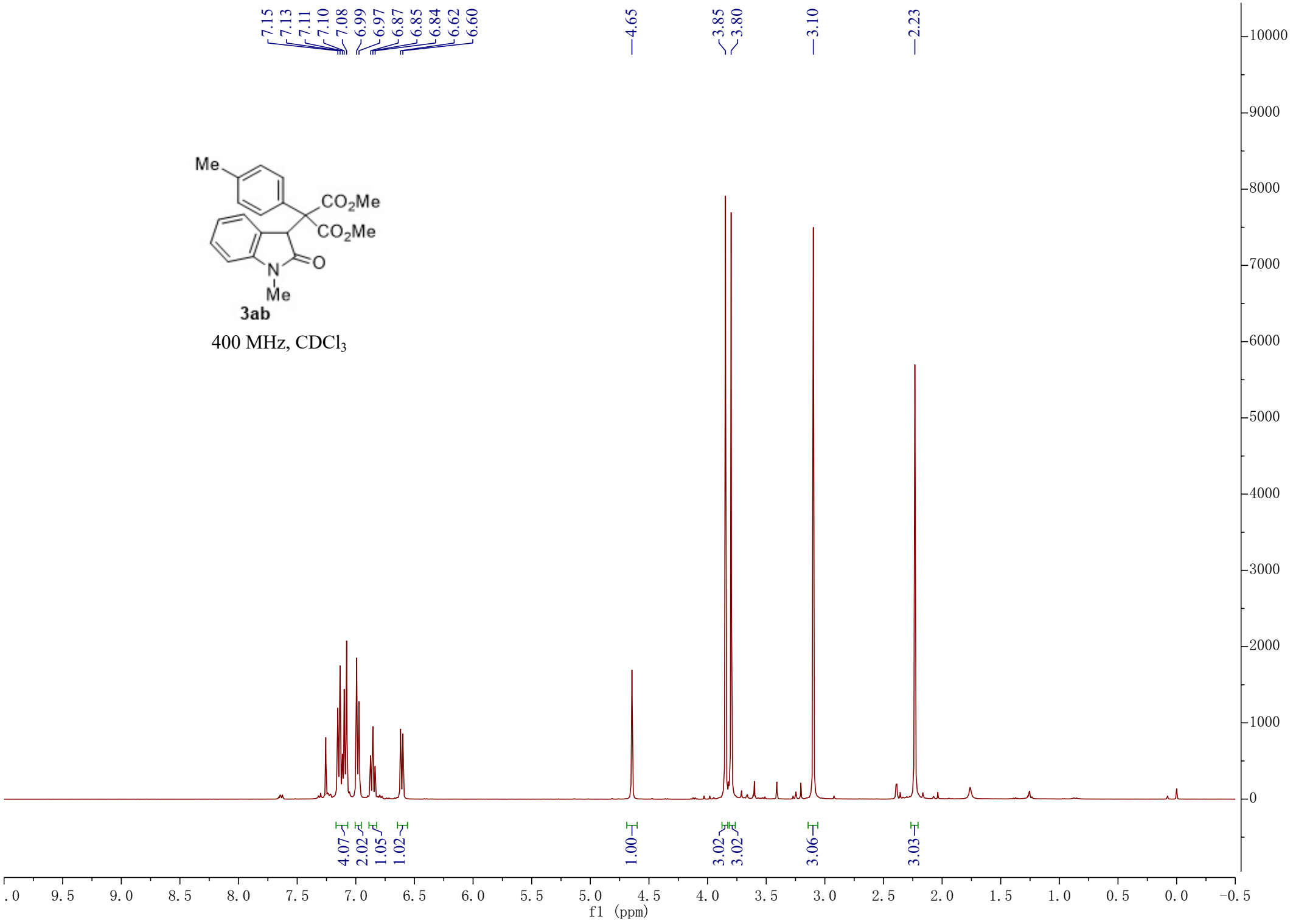

151.82
142.91
132.60
125.99
121.34
120.66
120.17
108.99
87.26
65.70
28.29
14.22
O
OEt
O
N
Me
1m
75 MHz, CDCl3
f1 (ppm)

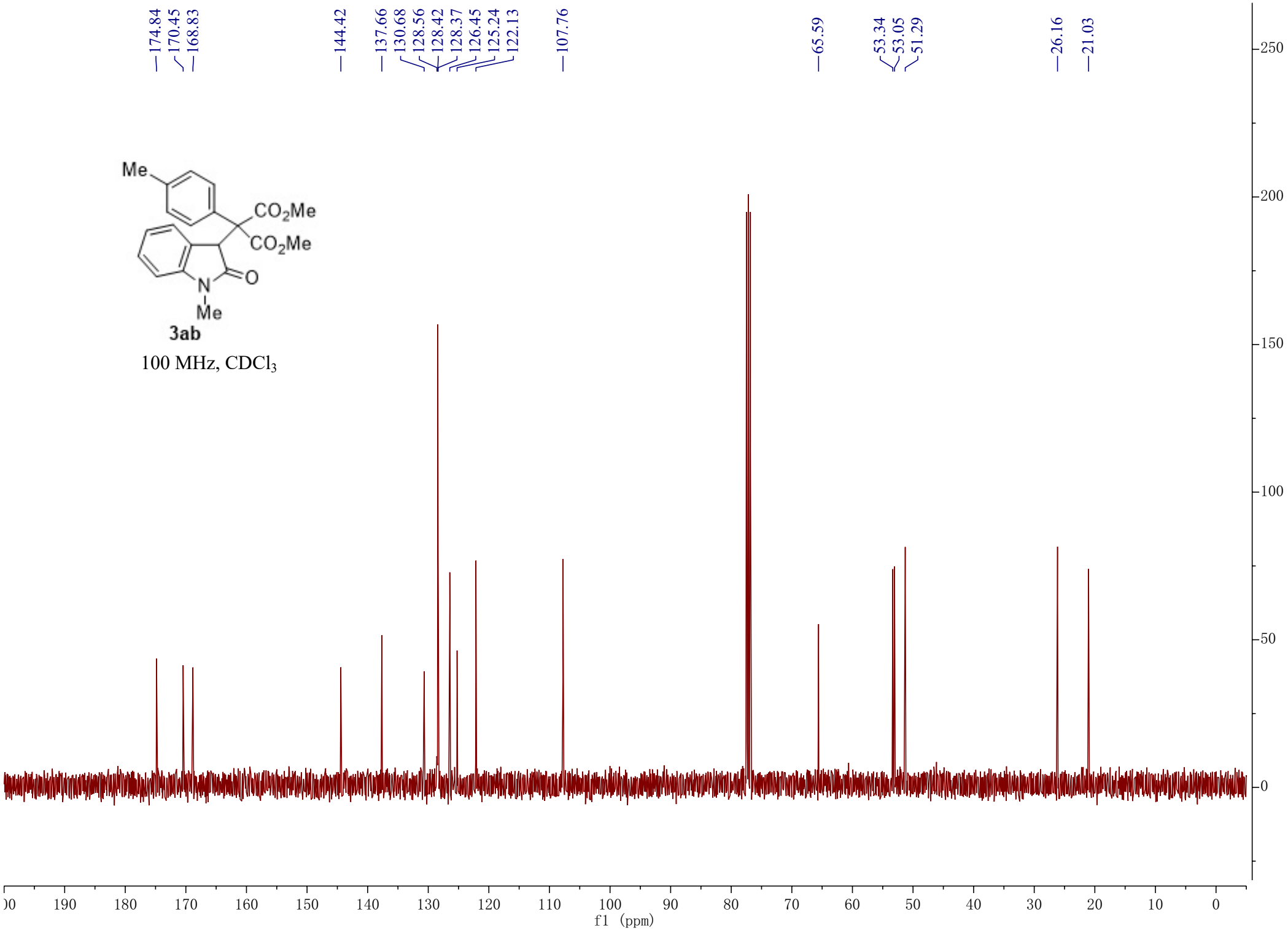

7.56
7.54
7.25
7.23
7.21
7.21
7.20
7.19
7.17
7.17
7.13
7.13
7.11
7.09
7.09
6.29
5.27
5.05
5.03
5.02
5.00
3.61
1.41
1.40
O
O
O
iPr
N
Me
1n
400 MHz, CDCl3
0.98
2.07
1.00
0.95
1.07
3.00
6.05
f1 (ppm)

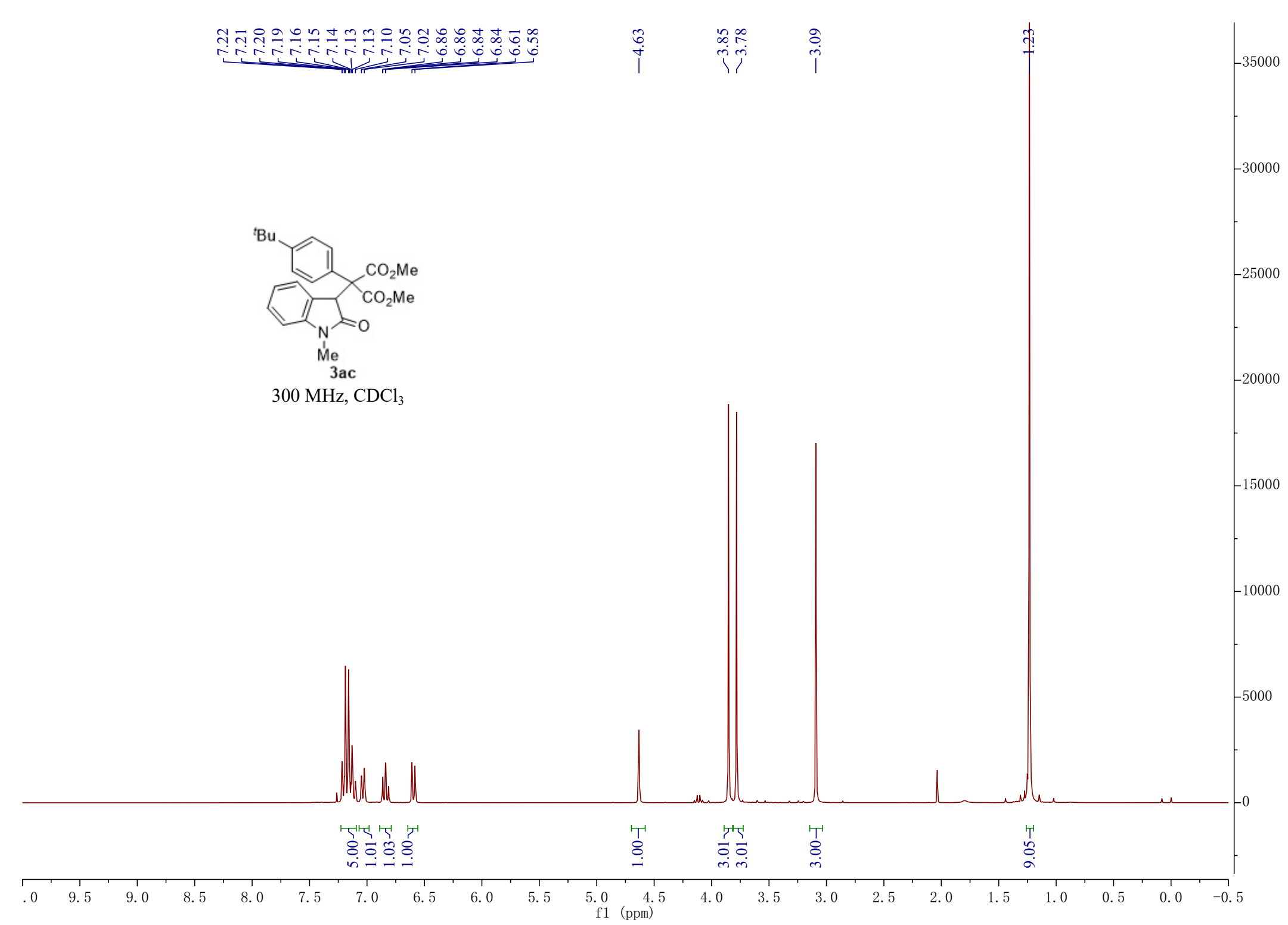

151.32
143.00
132.62
126.04
121.29
120.65
120.15
108.98
87.27
74.20
28.31
21.73
O
O
O^{i}Pr
N
Me
1n
75 MHz, CDCl$_3$
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

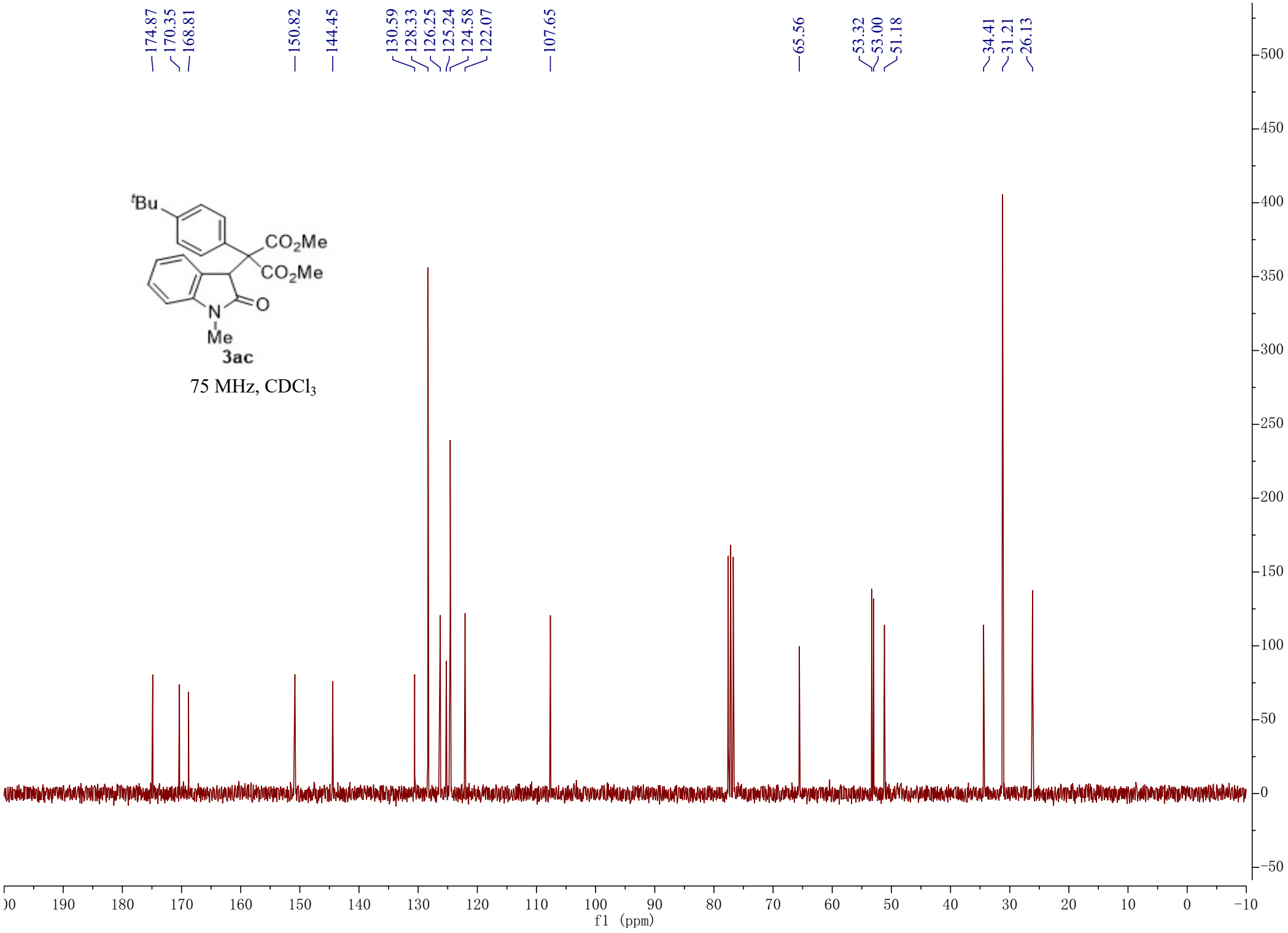

7.19
7.16
7.14
7.12
7.10
6.88
6.86
6.84
6.59
6.57
4.67
3.87
3.84
3.08
-0.00
Ph
CO2Me
CO2Me
O
N
Me
3aa
400 MHz, CDCl3
7.12
1.03
1.01
1.00
3.06
3.02
3.05
f1 (ppm)

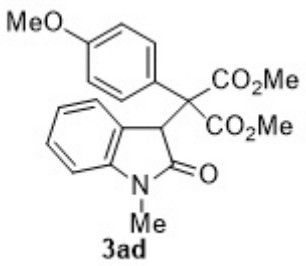

174.70
170.32
168.64
144.33
133.53
128.70
128.38
127.88
127.59
126.52
125.09
122.14
107.70
65.88
53.38
53.09
51.37
26.10
Ph
CO2Me
CO2Me
O
N
Me
3aa
100 MHz, CDCl3
f1 (ppm)


7.15
7.13
7.11
7.10
7.08
6.99
6.97
6.87
6.85
6.84
6.62
6.60
4.65
3.85
3.80
3.10
2.23
Me
CO2Me
CO2Me
O
N
Me
3ab
400 MHz, CDCl3
4.07
2.02
1.05
1.02
1.00
3.02
3.02
3.06
3.03
f1 (ppm)


174.84
170.45
168.83
144.42
137.66
130.68
128.56
128.42
128.37
126.45
125.24
122.13
107.76
65.59
53.34
53.05
51.29
26.16
21.03
Me
CO2Me
CO2Me
O
N
Me
3ab
100 MHz, CDCl3
250
200
150
100
50
0
f1 (ppm)

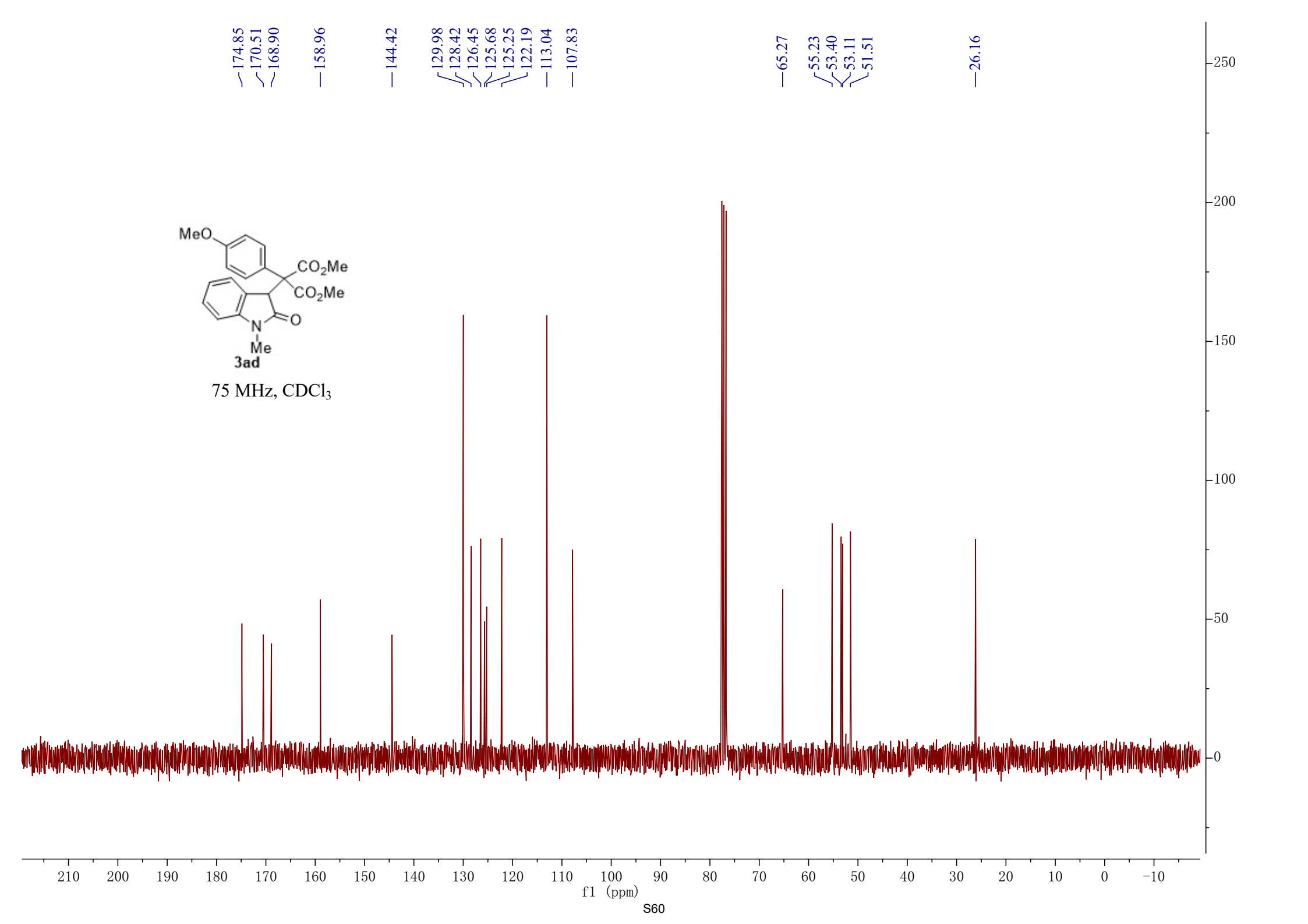

7.22
7.21
7.20
7.19
7.16
7.15
7.14
7.13
7.13
7.10
7.05
7.02
6.86
6.86
6.84
6.84
6.61
6.58
4.63
3.85
3.78
3.09
1.23
tBu
CO2Me
CO2Me
O
N
Me
3ac
300 MHz, CDCl3
5.00
1.01
1.03
1.00
1.00
3.01
3.01
3.00
9.05
f1 (ppm)

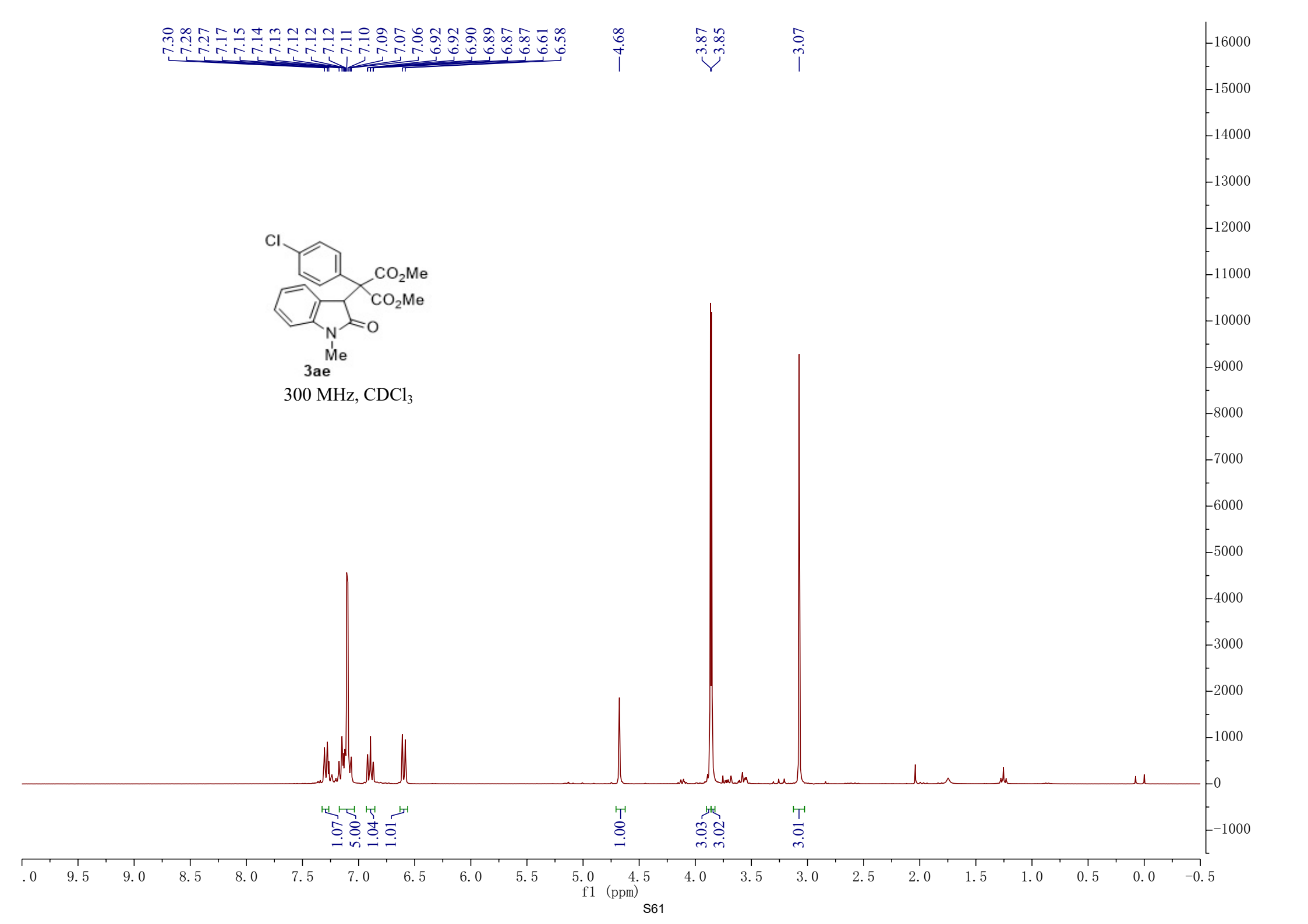

174.87
170.35
168.81
150.82
144.45
130.59
128.33
126.25
125.24
124.58
122.07
107.65
65.56
53.32
53.00
51.18
34.41
31.21
26.13
tBu
CO2Me
CO2Me
O
N
Me
3ac
75 MHz, CDCl3
f1 (ppm)

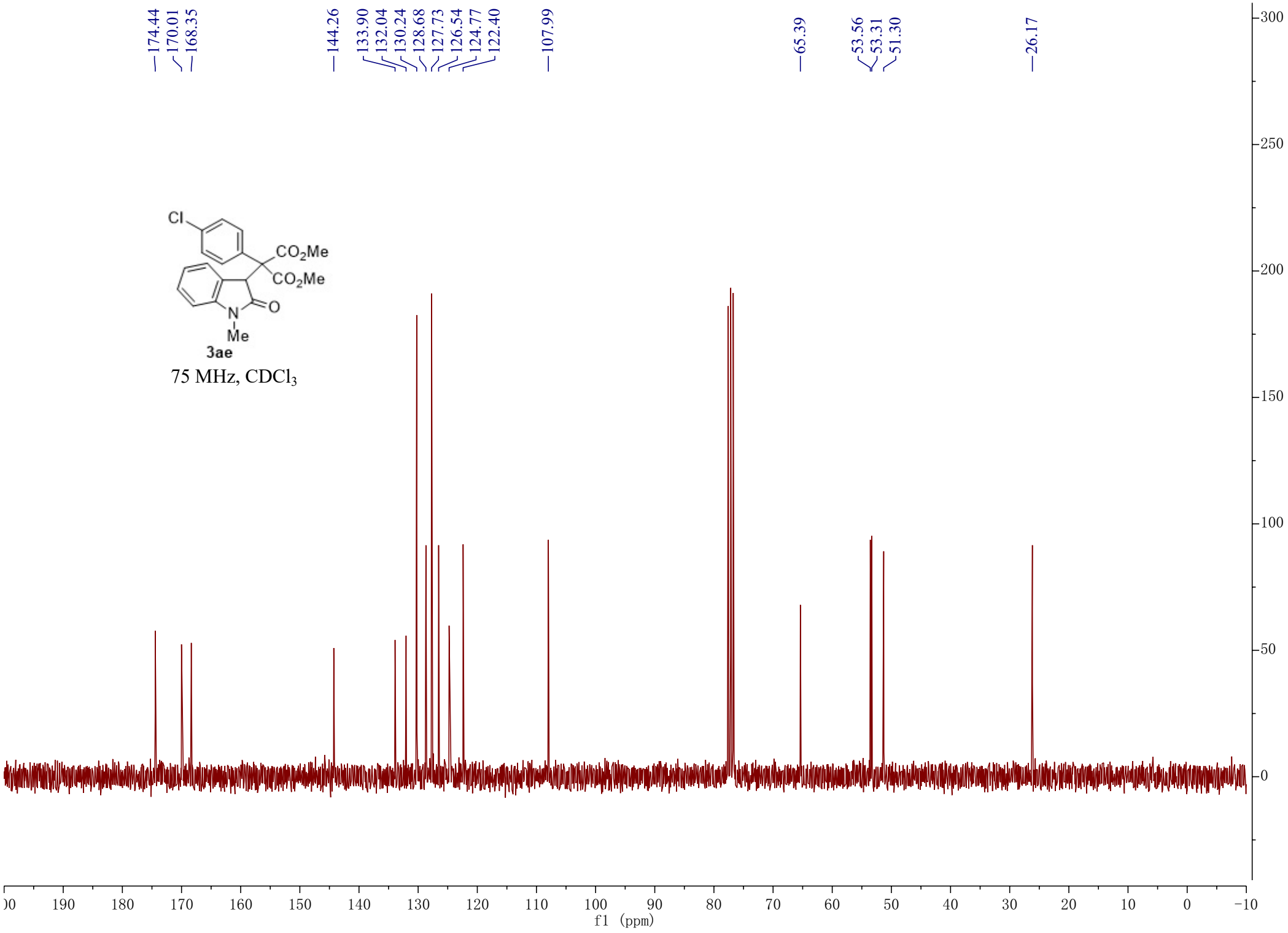


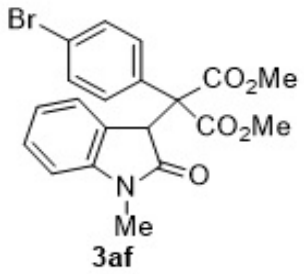
3ad

400 MHz, $CDCl_3$


174.85
170.51
168.90
158.96
144.42
129.98
128.42
126.45
125.68
125.25
122.19
113.04
107.83
65.27
55.23
53.40
53.11
51.51
26.16
MeO
CO2Me
CO2Me
N
O
Me
3ad
75 MHz, CDCl3
250
200
150
100
50
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

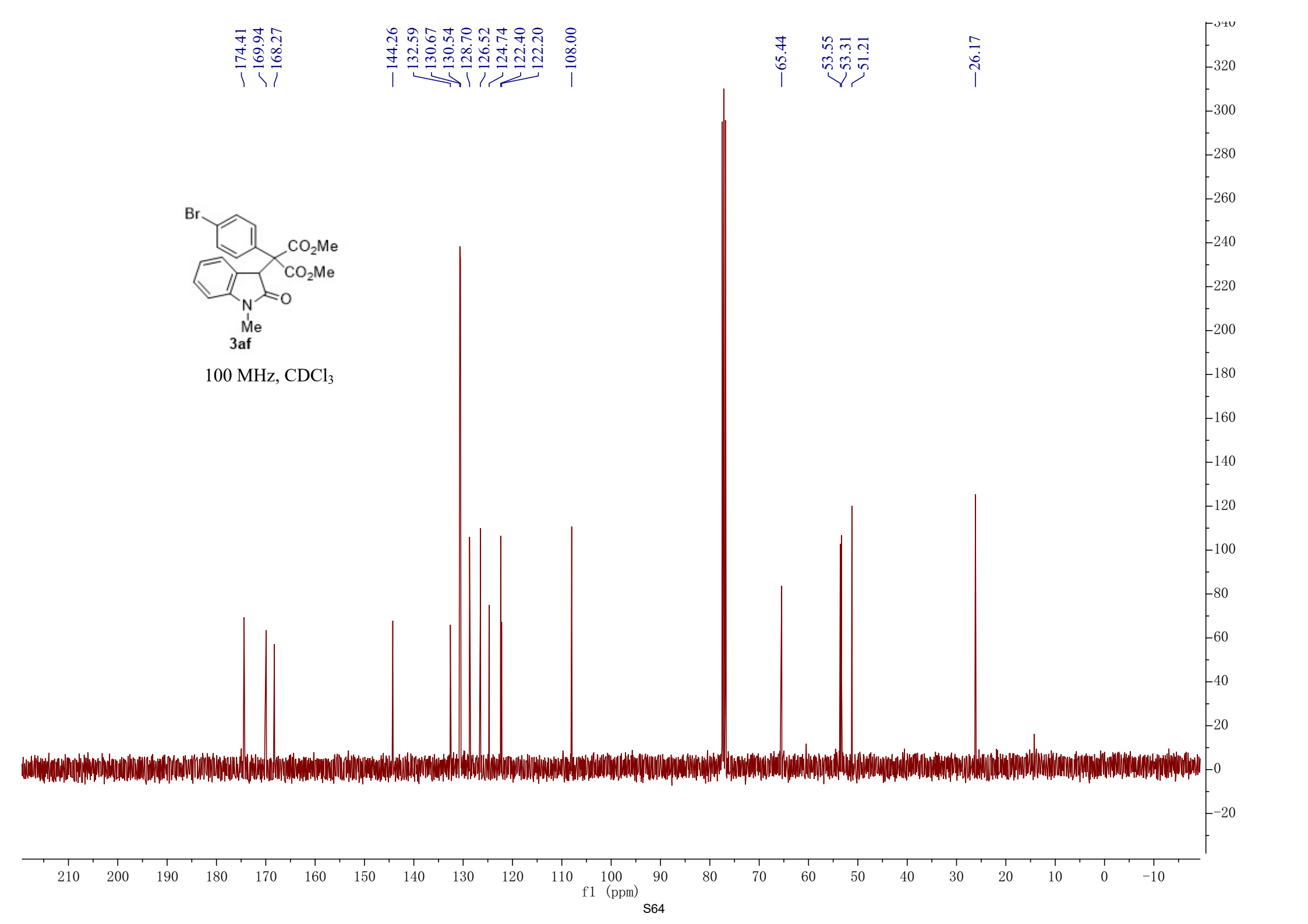

7.30
7.28
7.27
7.17
7.15
7.14
7.13
7.12
7.12
7.12
7.11
7.10
7.09
7.07
7.06
6.92
6.92
6.90
6.89
6.87
6.87
6.61
6.58
4.68
3.87
3.85
3.07
Cl
CO2Me
CO2Me
O
N
Me
3ae
300 MHz, CDCl3
1.07
5.00
1.04
1.01
1.00
3.03
3.02
3.01
f1 (ppm)

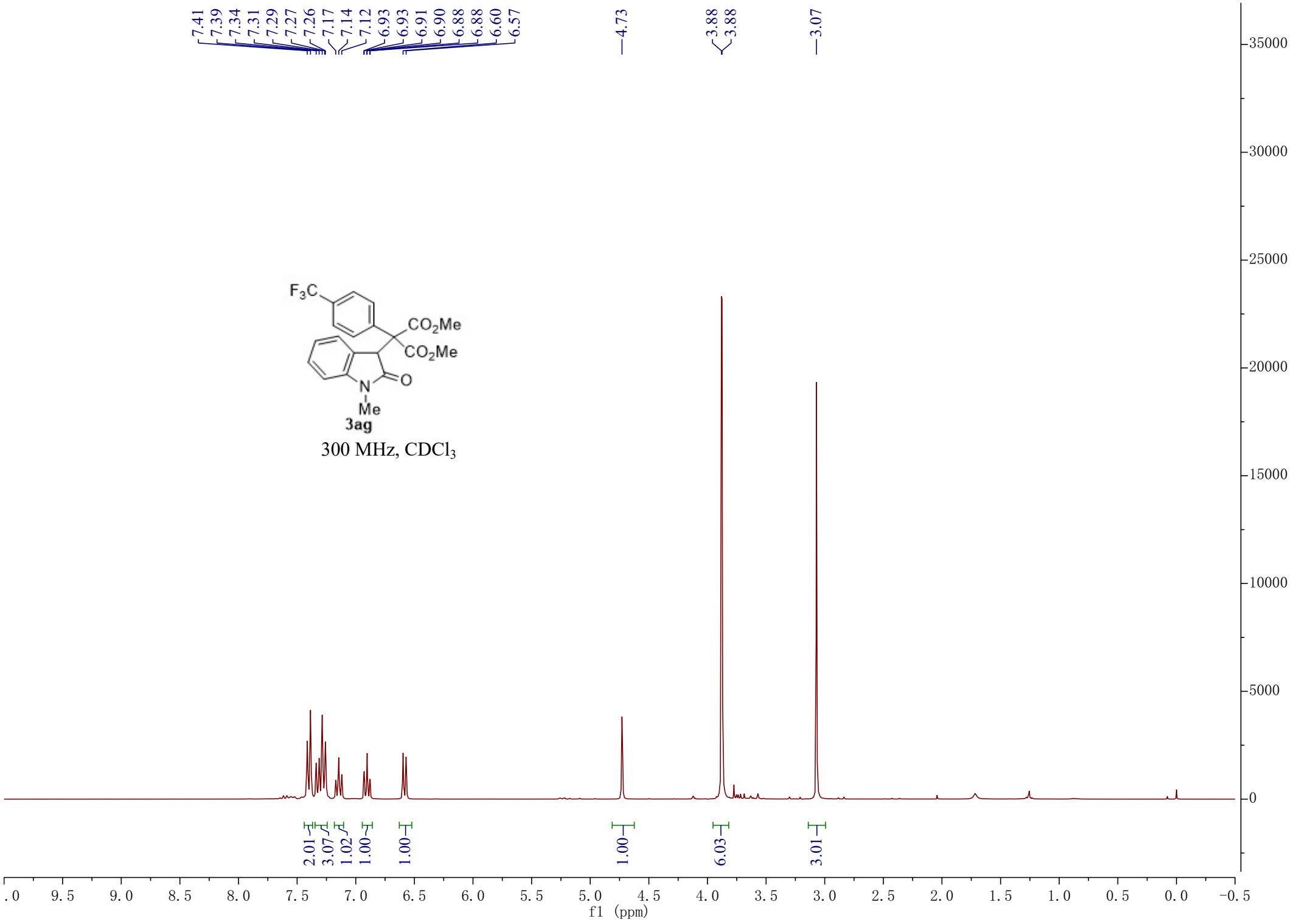

174.44
170.01
168.35
144.26
133.90
132.04
130.24
128.68
127.73
126.54
124.77
122.40
107.99
65.39
53.56
53.31
51.30
26.17
Cl
CO2Me
CO2Me
O
N
Me
3ae
75 MHz, CDCl3
300
250
200
150
100
50
0
f1 (ppm)

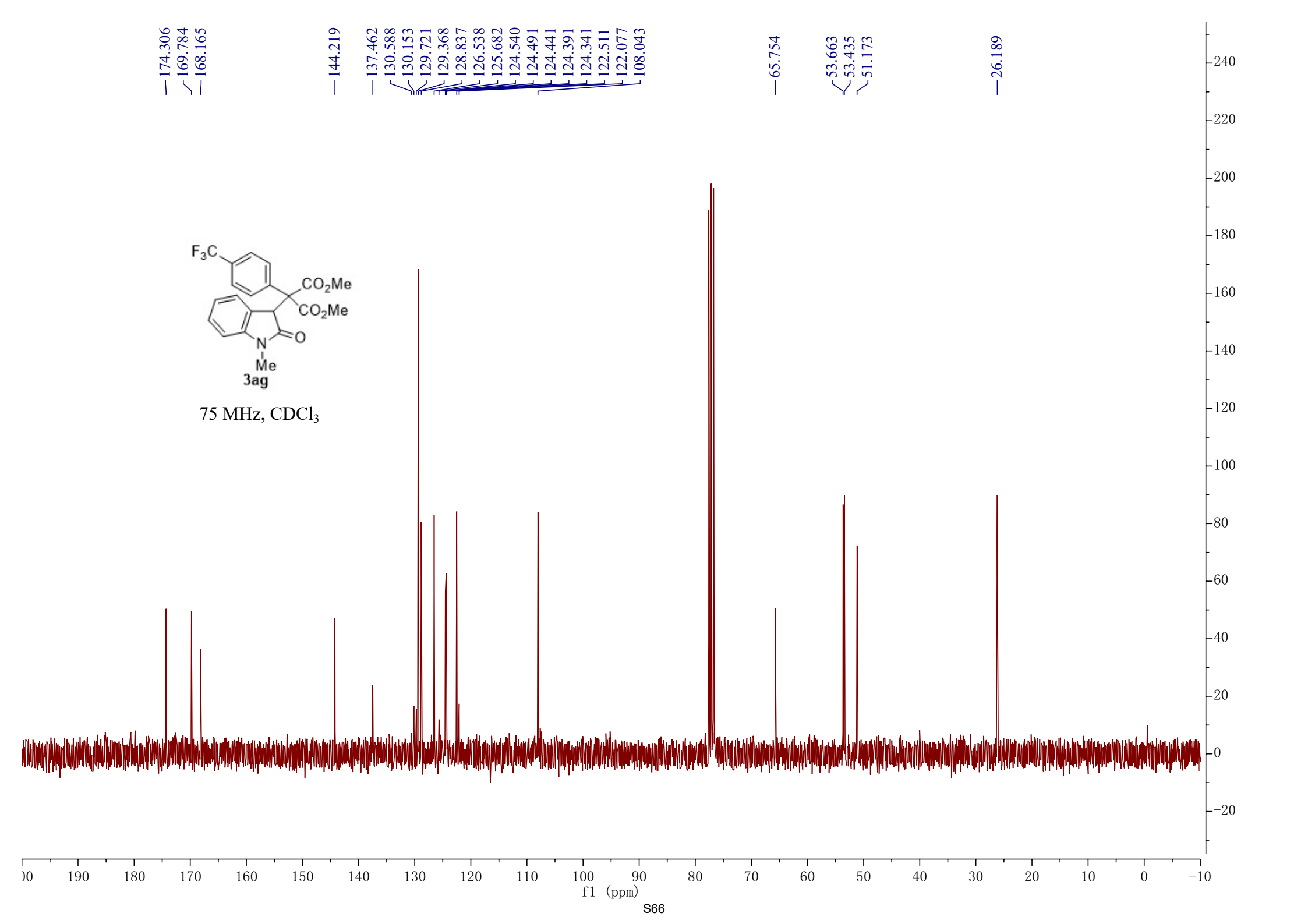


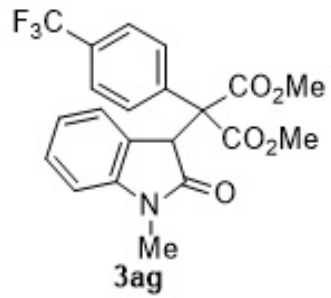
3af

400 MHz, $CDCl_3$


174.41
169.94
168.27
144.26
132.59
130.67
130.54
128.70
126.52
124.74
122.40
122.20
108.00
65.44
53.55
53.31
51.21
26.17
Br
CO2Me
CO2Me
O
N
Me
3af
100 MHz, CDCl3
f1 (ppm)

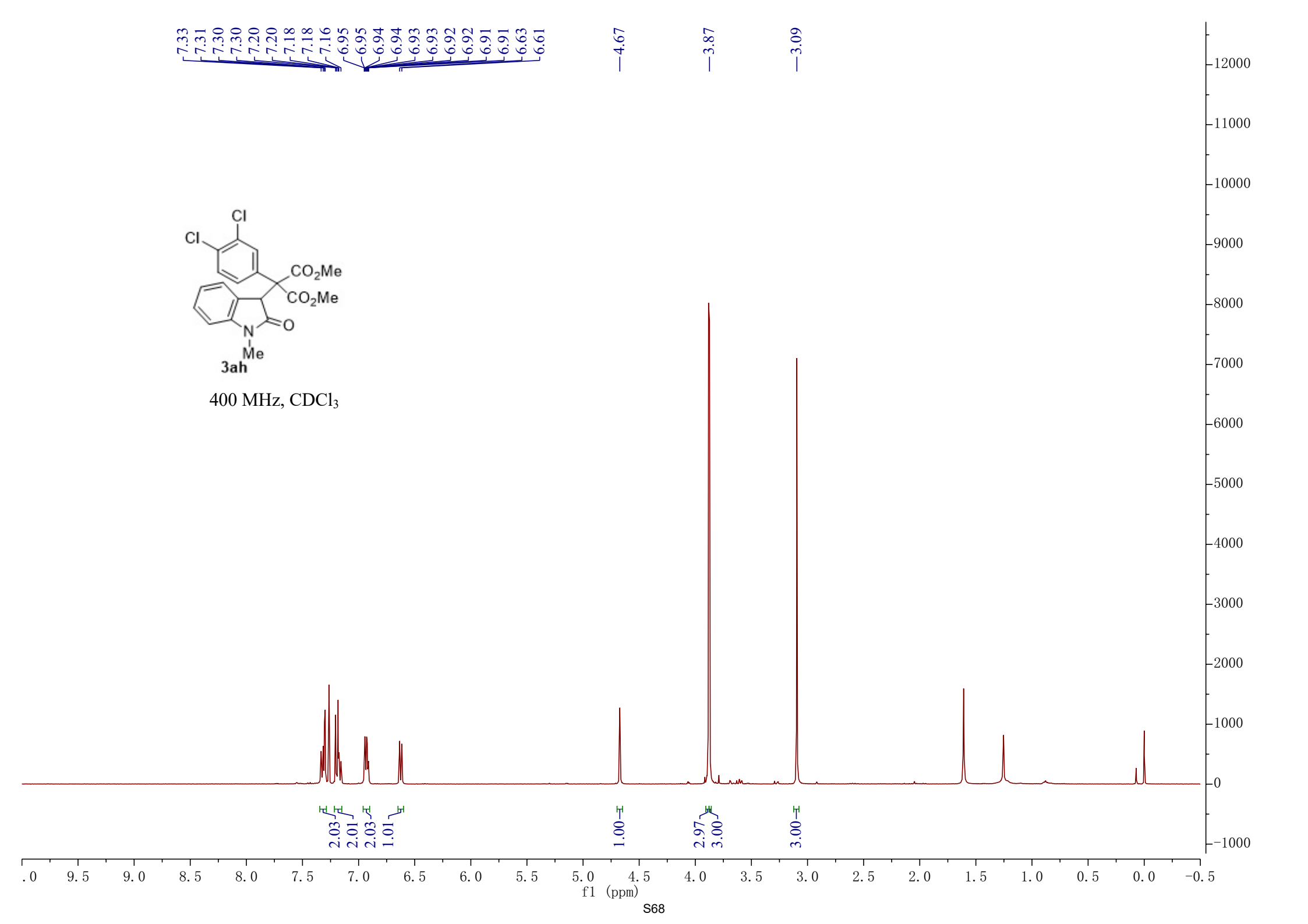

7.41
7.39
7.34
7.31
7.29
7.27
7.26
7.17
7.14
7.12
6.93
6.93
6.91
6.90
6.88
6.88
6.60
6.57
4.73
3.88
3.88
3.07
F3C
CO2Me
CO2Me
N
O
Me
3ag
300 MHz, CDCl3
35000
30000
25000
20000
15000
10000
5000
0
2.01
3.07
1.02
1.00
1.00
1.00
6.03
3.01
f1 (ppm)

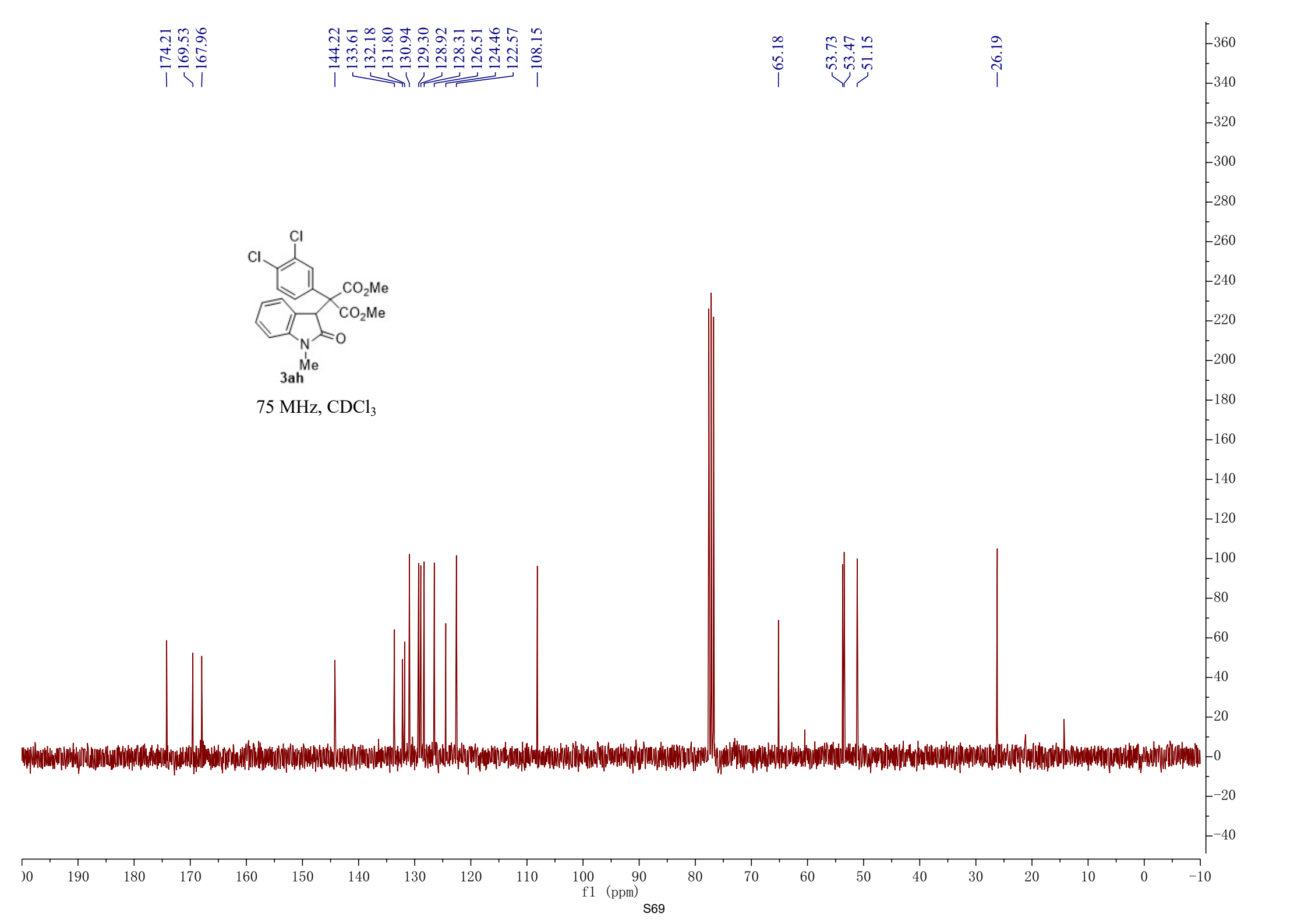

174.306
169.784
168.165
144.219
137.462
130.588
130.153
129.721
129.368
128.837
126.538
125.682
124.540
124.491
124.441
124.391
124.341
122.511
122.077
108.043
65.754
53.663
53.435
51.173
26.189
F3C
CO2Me
CO2Me
O
N
Me
3ag
75 MHz, CDCl3
f1 (ppm)

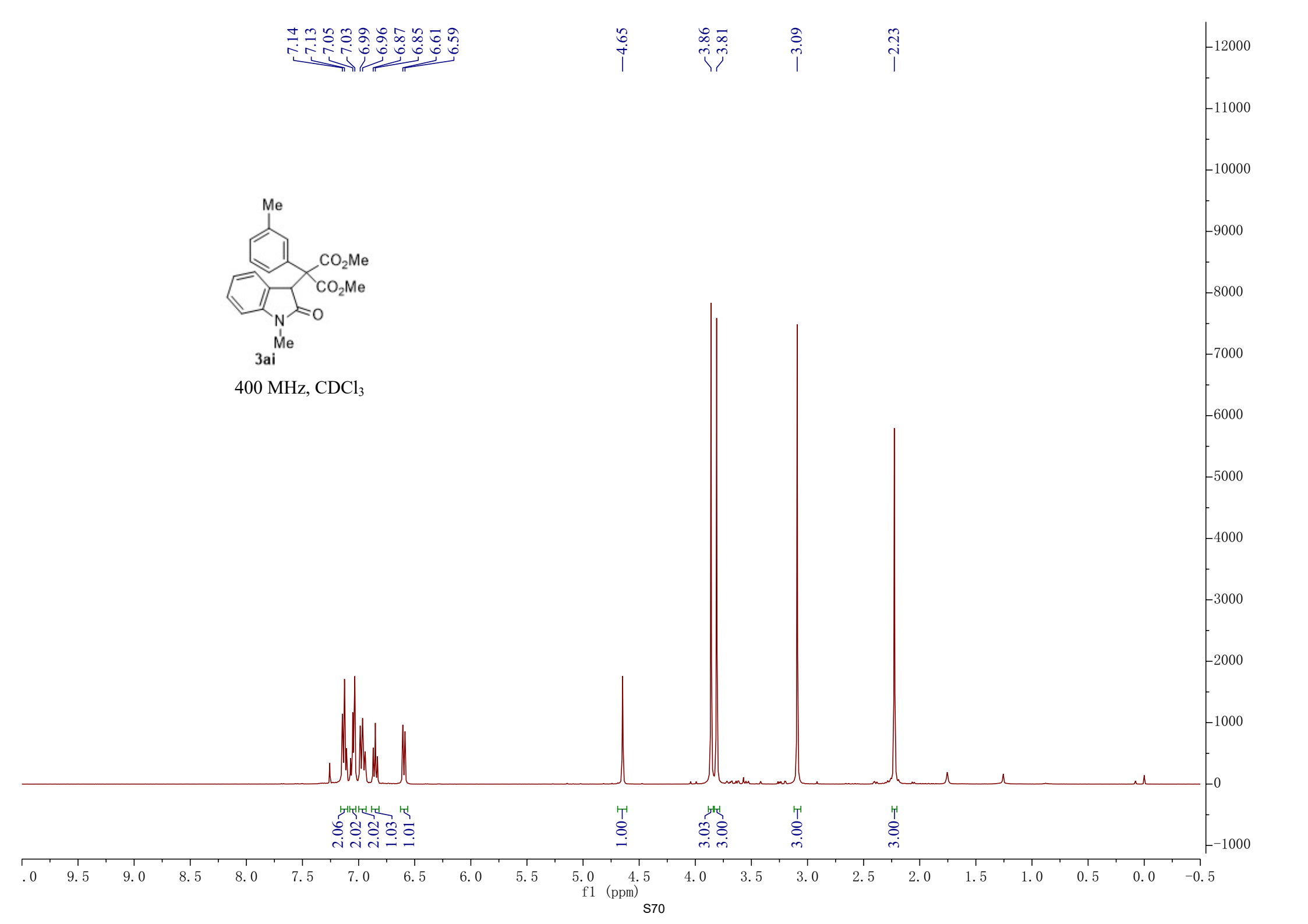


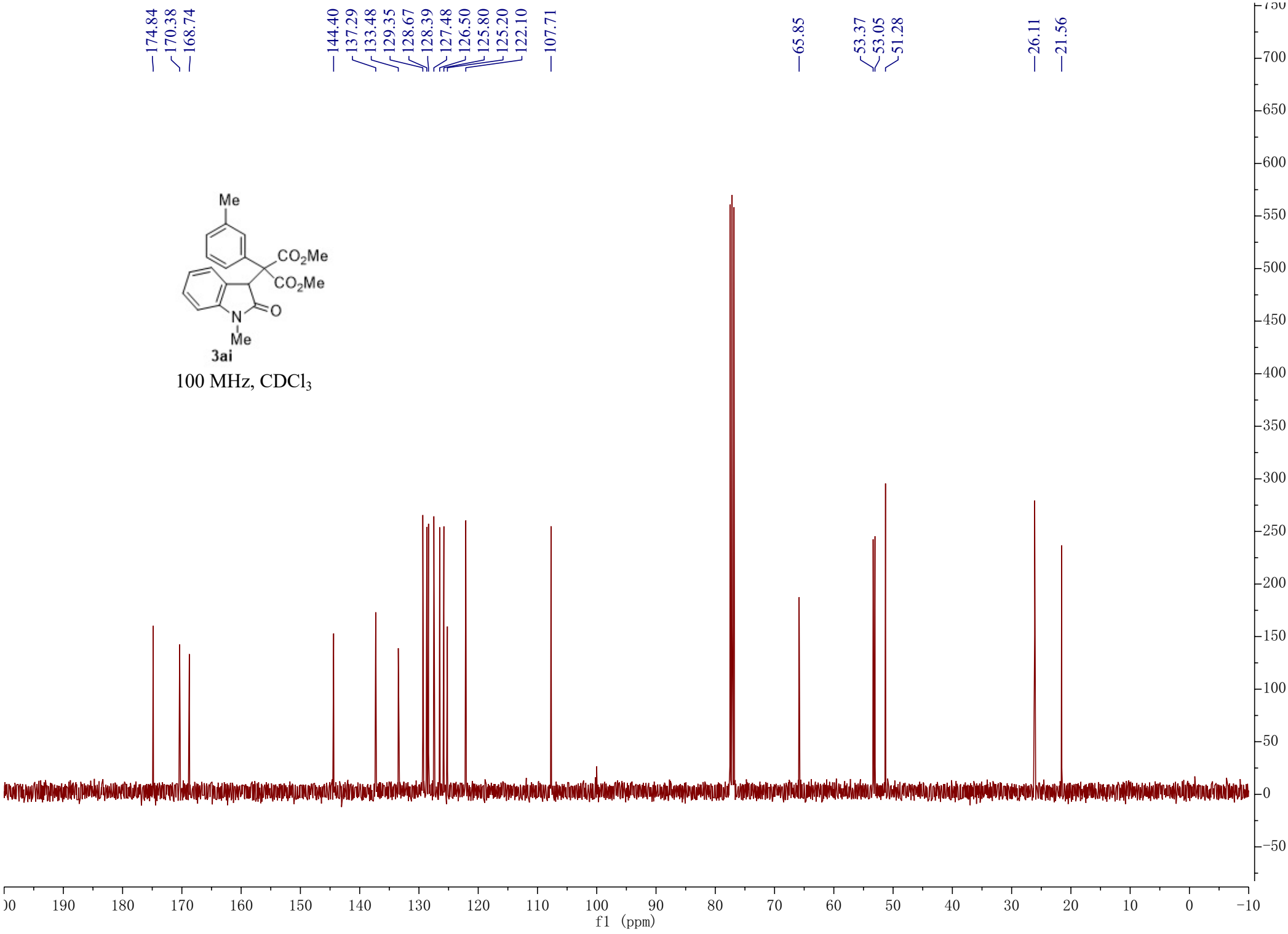
3ag

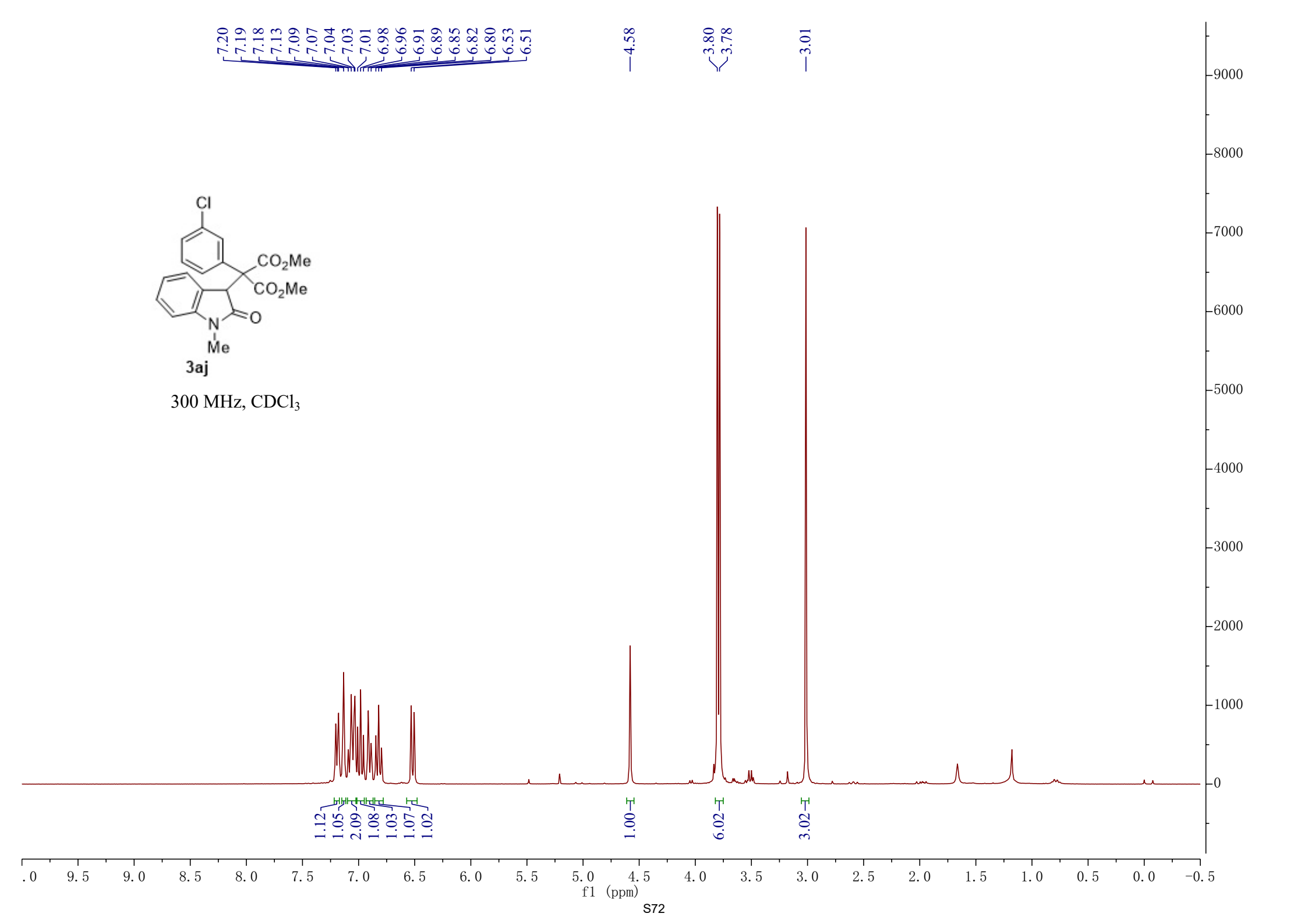
282 MHz, $CDCl_3$

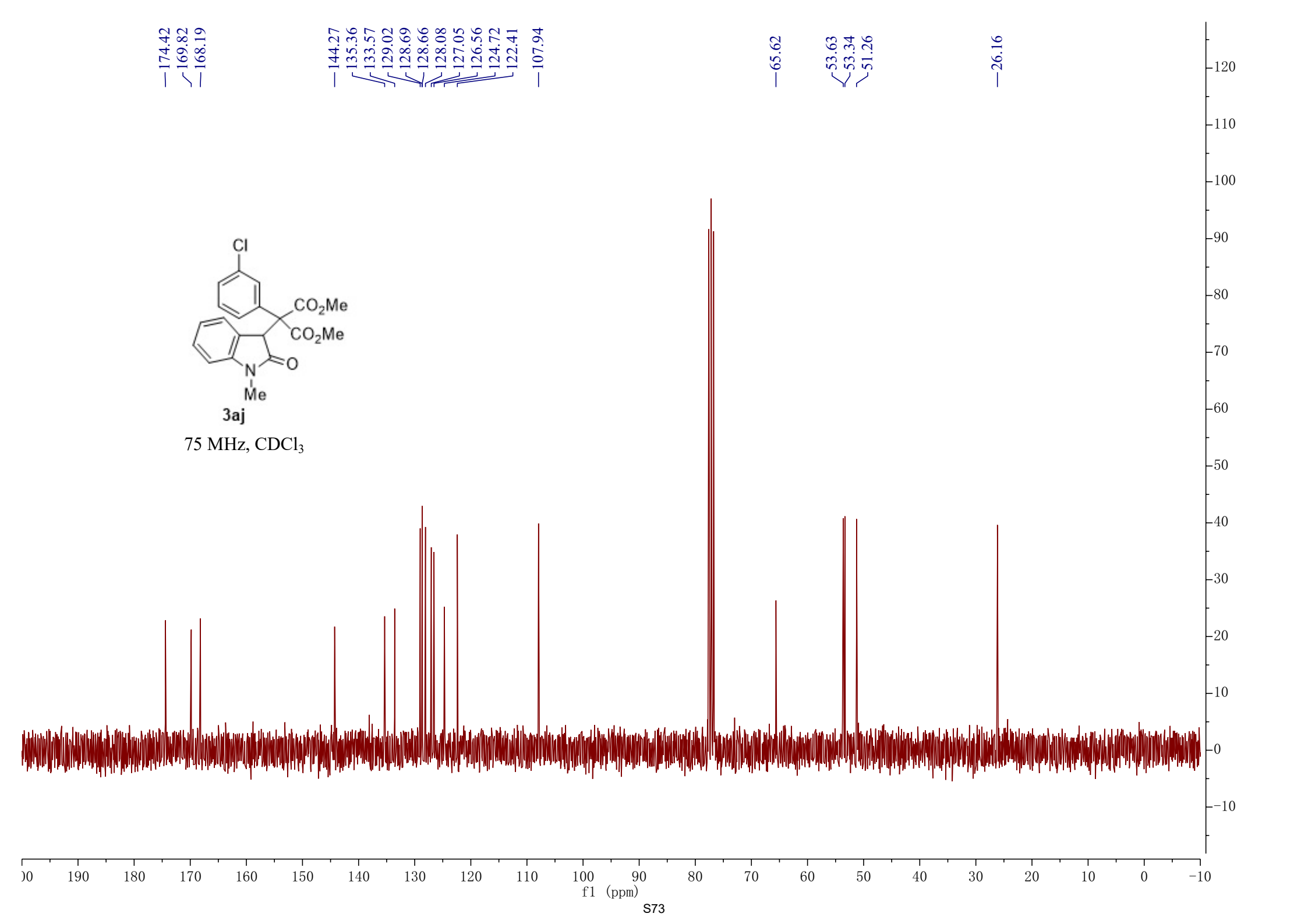

7.33
7.31
7.30
7.30
7.20
7.20
7.18
7.18
7.16
6.95
6.95
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.91
6.63
6.61
4.67
3.87
3.09
Cl
Cl
CO2Me
CO2Me
O
N
Me
3ah
400 MHz, CDCl3
2.03
2.01
2.03
1.01
1.00
2.97
3.00
3.00
f1 (ppm)

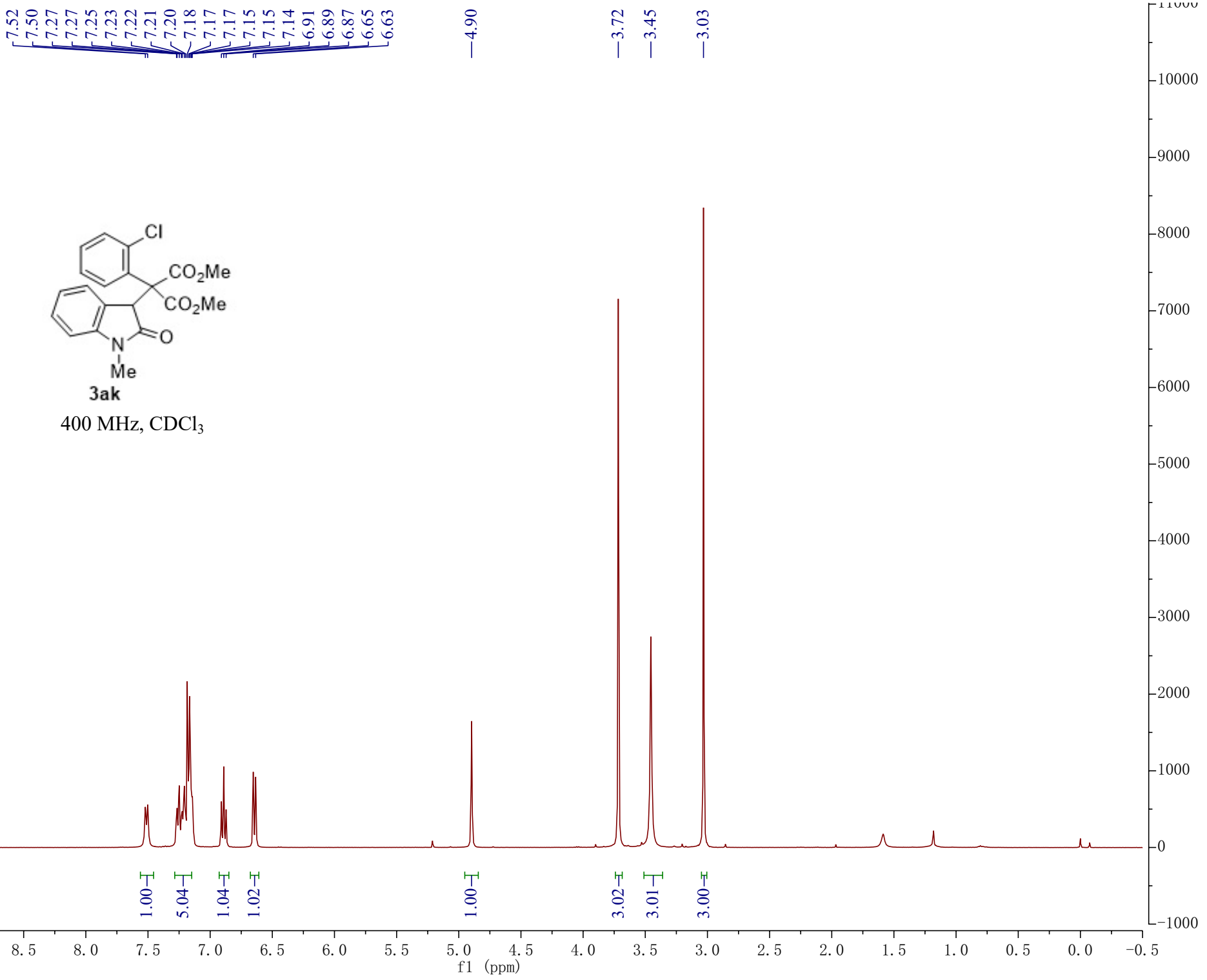

174.21
169.53
167.96
144.22
133.61
132.18
131.80
130.94
129.30
128.92
128.31
126.51
124.46
122.57
108.15
65.18
53.73
53.47
51.15
26.19
Cl
Cl
CO2Me
CO2Me
N
Me
O
3ah
75 MHz, CDCl3
f1 (ppm)

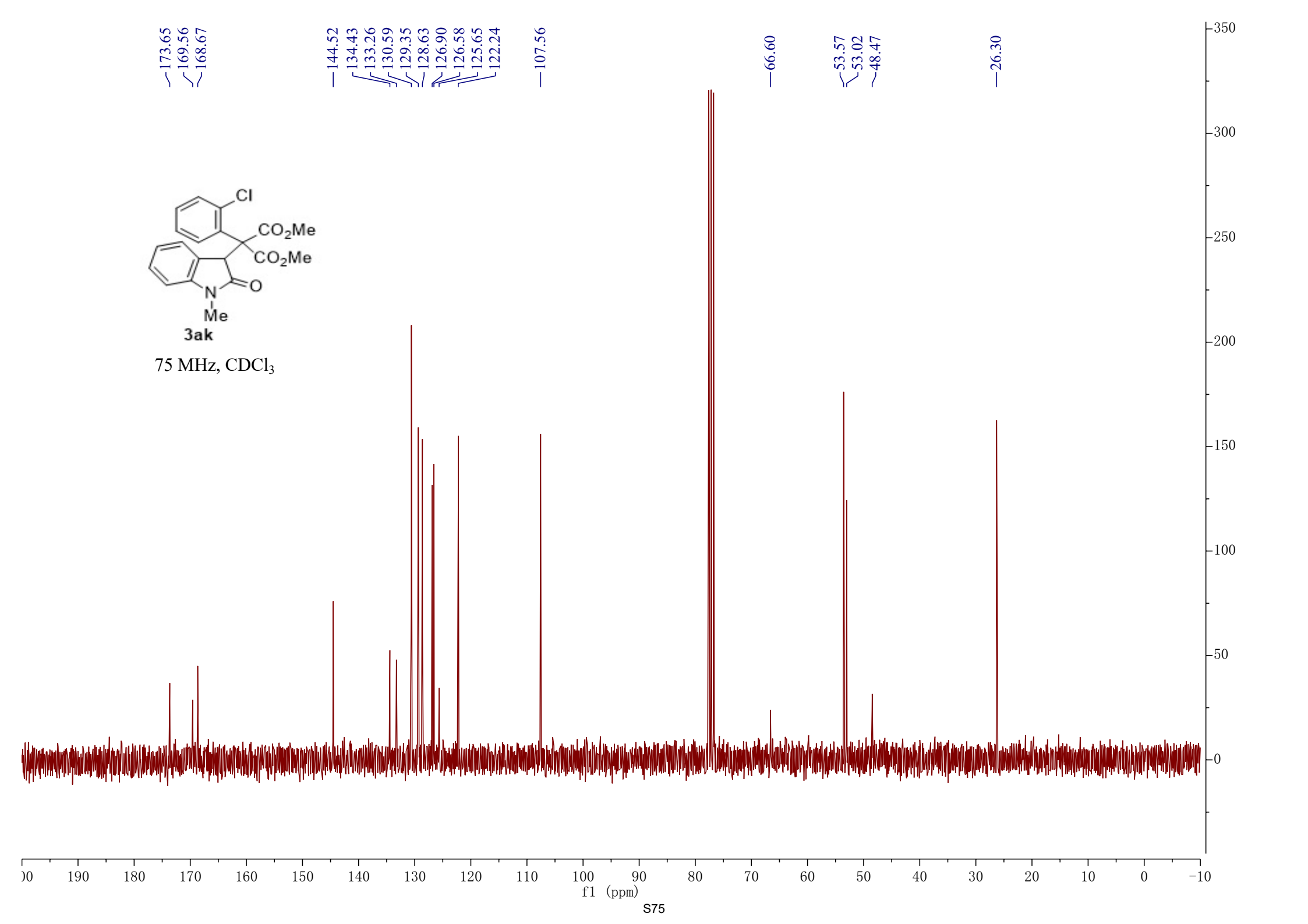

7.14
7.13
7.05
7.03
6.99
6.96
6.87
6.85
6.61
6.59
4.65
3.86
3.81
3.09
2.23
Me
CO2Me
CO2Me
O
N
Me
3ai
400 MHz, CDCl3
2.06
2.02
2.02
1.03
1.01
1.00
3.03
3.00
3.00
3.00
f1 (ppm)

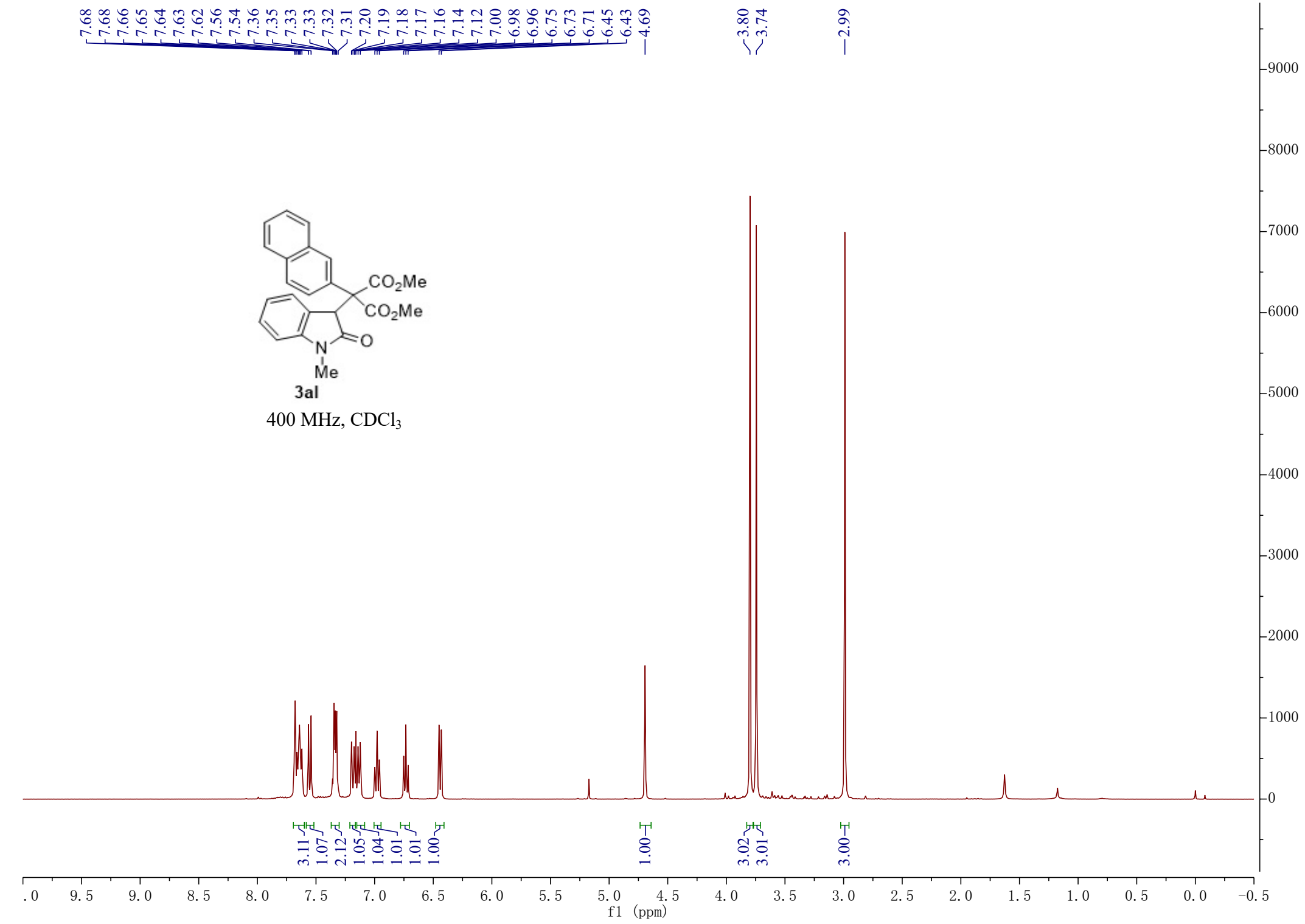

174.84
170.38
168.74
144.40
137.29
133.48
129.35
128.67
128.39
127.48
126.50
125.80
125.20
122.10
107.71
65.85
53.37
53.05
51.28
26.11
21.56
Me
CO2Me
CO2Me
O
N
Me
3ai
100 MHz, CDCl3
f1 (ppm)

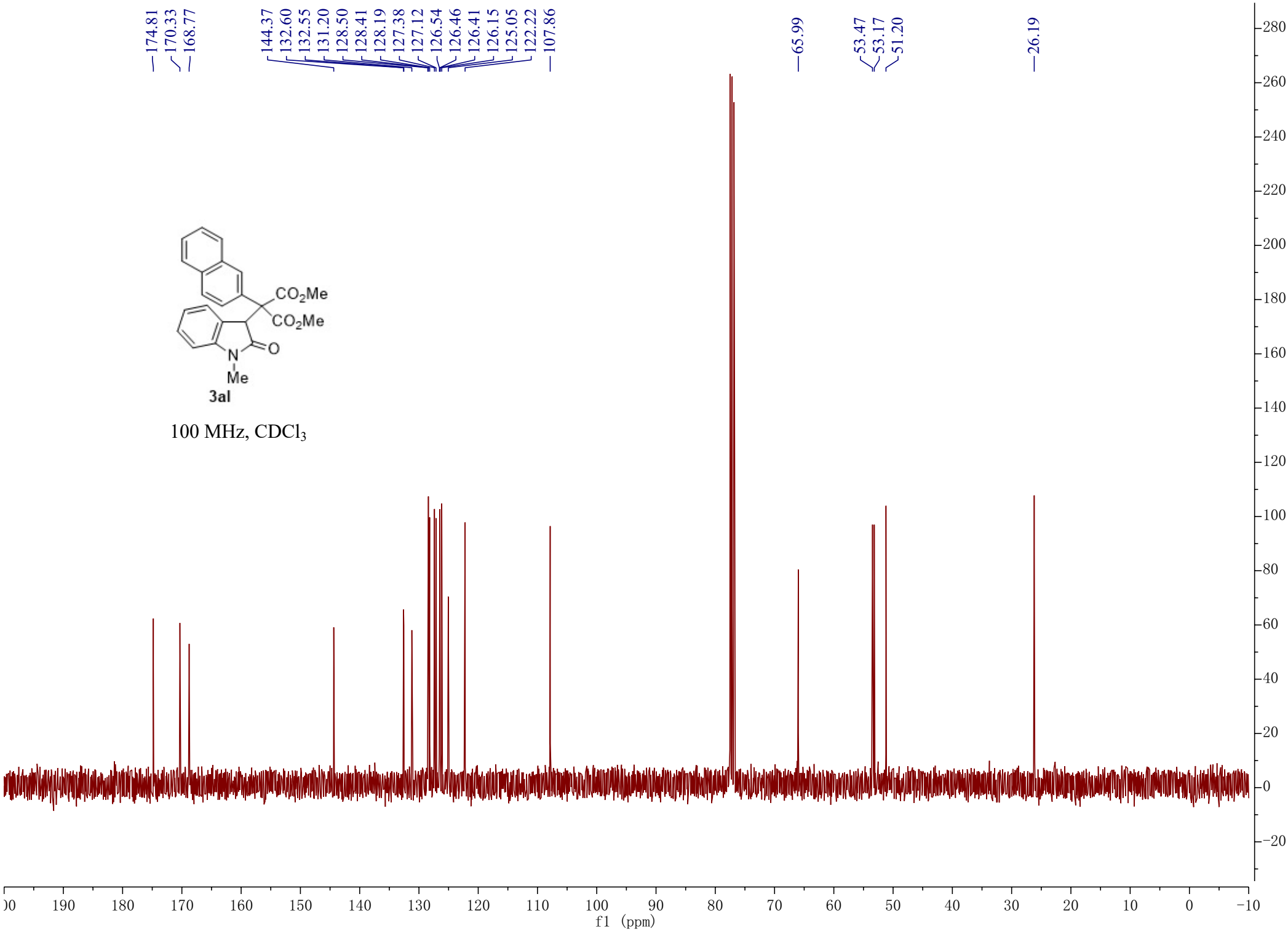

7.20
7.19
7.18
7.13
7.09
7.07
7.04
7.03
7.01
6.98
6.96
6.91
6.89
6.85
6.82
6.80
6.53
6.51
4.58
3.80
3.78
3.01
Cl
CO2Me
CO2Me
O
N
Me
3aj
300 MHz, CDCl3
1.12
1.05
2.09
1.08
1.03
1.07
1.02
1.00
6.02
3.02
f1 (ppm)

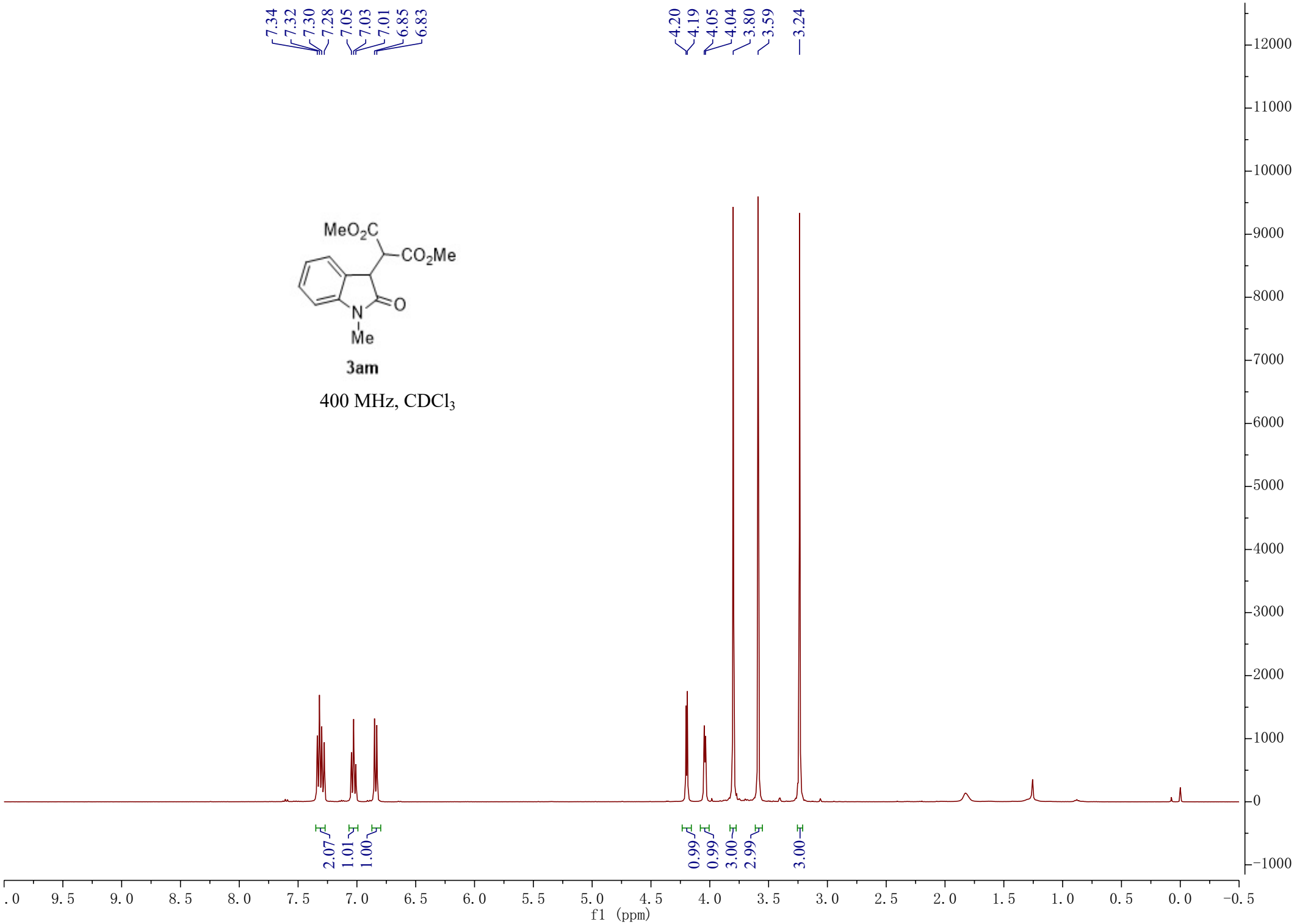

174.42
169.82
168.19
144.27
135.36
133.57
129.02
128.69
128.66
128.08
127.05
126.56
124.72
122.41
107.94
65.62
53.63
53.34
51.26
26.16
Cl
CO2Me
CO2Me
O
N
Me
3aj
75 MHz, CDCl3
f1 (ppm)

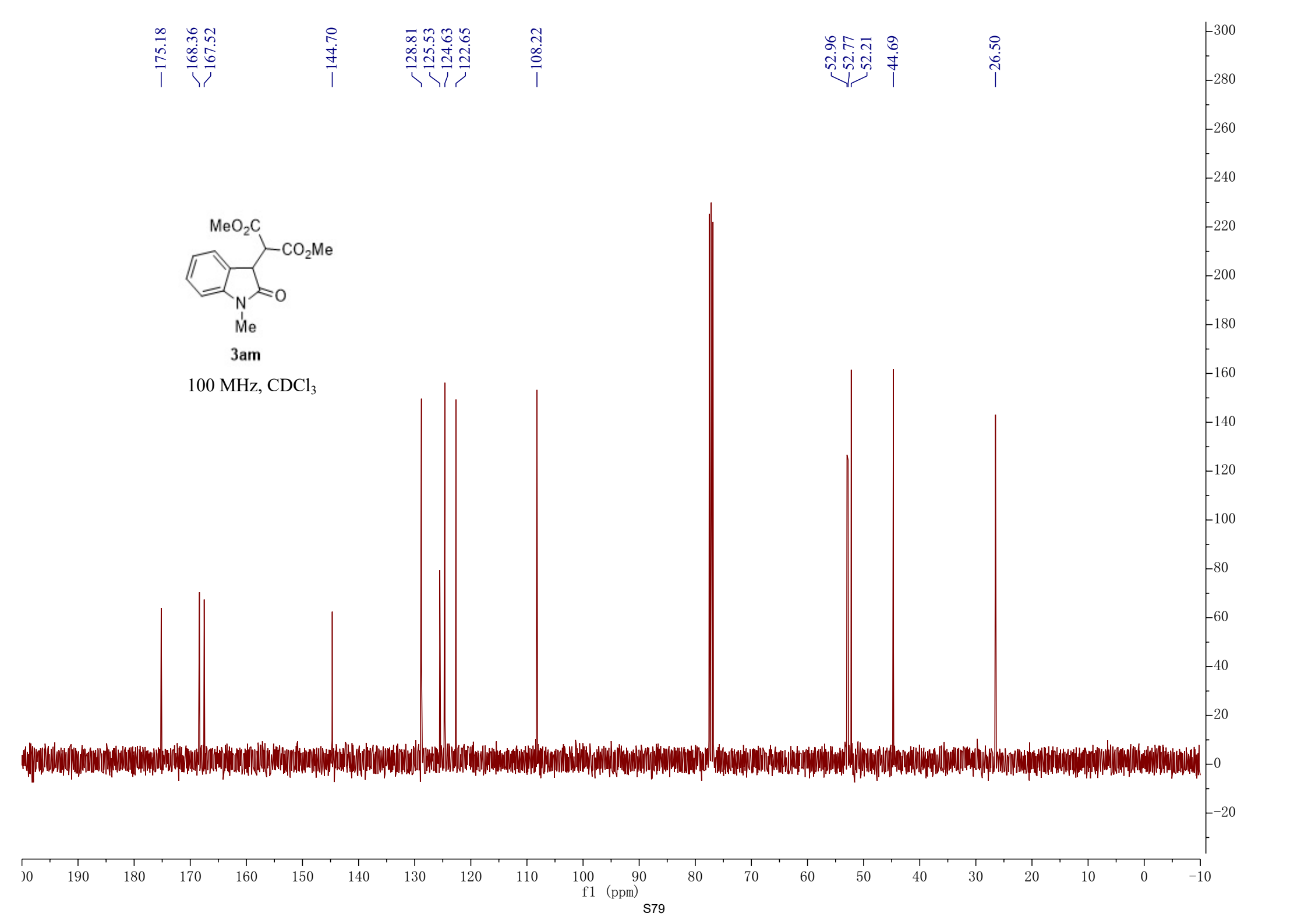

7.52
7.50
7.27
7.27
7.25
7.23
7.22
7.21
7.20
7.18
7.17
7.17
7.15
7.15
7.14
6.91
6.89
6.87
6.65
6.63
4.90
3.72
3.45
3.03
Cl
CO2Me
CO2Me
O
N
Me
3ak
400 MHz, CDCl3
1.00
5.04
1.04
1.02
1.00
3.02
3.01
3.00
f1 (ppm)

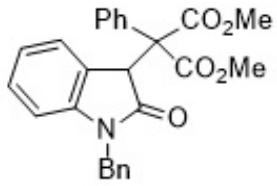

173.65
169.56
168.67
144.52
134.43
133.26
130.59
129.35
128.63
126.90
126.58
125.65
122.24
107.56
66.60
53.57
53.02
48.47
26.30
Cl
CO2Me
CO2Me
O
N
Me
3ak
75 MHz, CDCl3
f1 (ppm)


7.68
7.68
7.66
7.65
7.64
7.63
7.62
7.56
7.54
7.36
7.35
7.33
7.33
7.32
7.31
7.20
7.19
7.18
7.17
7.16
7.14
7.12
7.00
6.98
6.96
6.75
6.73
6.71
6.45
6.43
4.69
3.80
3.74
2.99
CO2Me
CO2Me
O
N
Me
3al
400 MHz, CDCl3
3.11
1.07
2.12
1.05
1.04
1.01
1.01
1.00
1.00
3.02
3.01
3.00
f1 (ppm)


174.81
170.33
168.77
144.37
132.60
132.55
131.20
128.50
128.41
128.19
127.38
127.12
126.54
126.46
126.41
126.15
125.05
122.22
107.86
65.99
53.47
53.17
51.20
26.19
CO2Me
CO2Me
N
O
Me
3al
100 MHz, CDCl3
f1 (ppm)

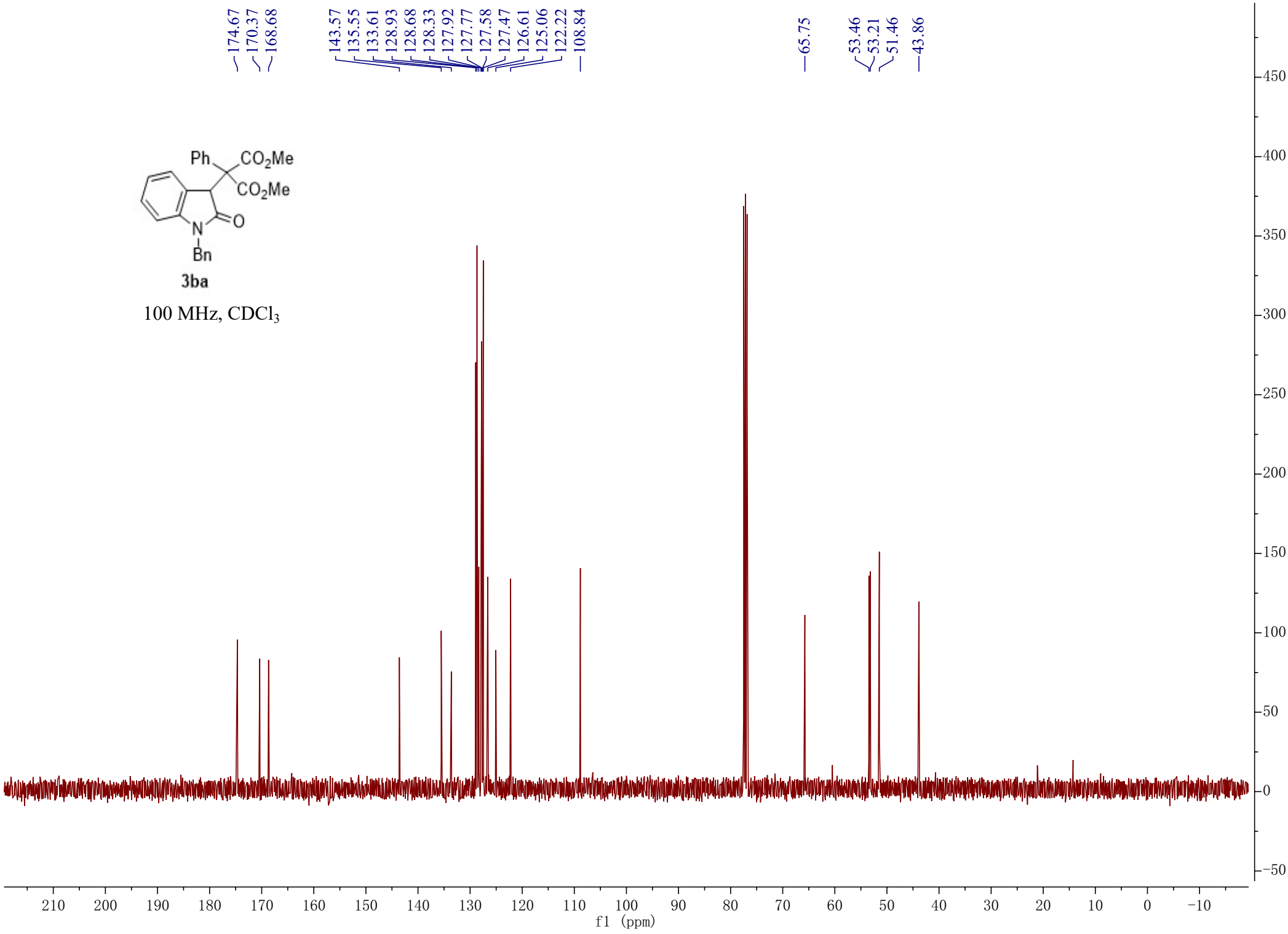

7.34
7.32
7.30
7.28
7.05
7.03
7.01
6.85
6.83
4.20
4.19
4.05
4.04
3.80
3.59
3.24
MeO2C
CO2Me
O
N
Me
3am
400 MHz, CDCl3
2.07
1.01
1.00
0.99
0.99
3.00
2.99
3.00
f1 (ppm)

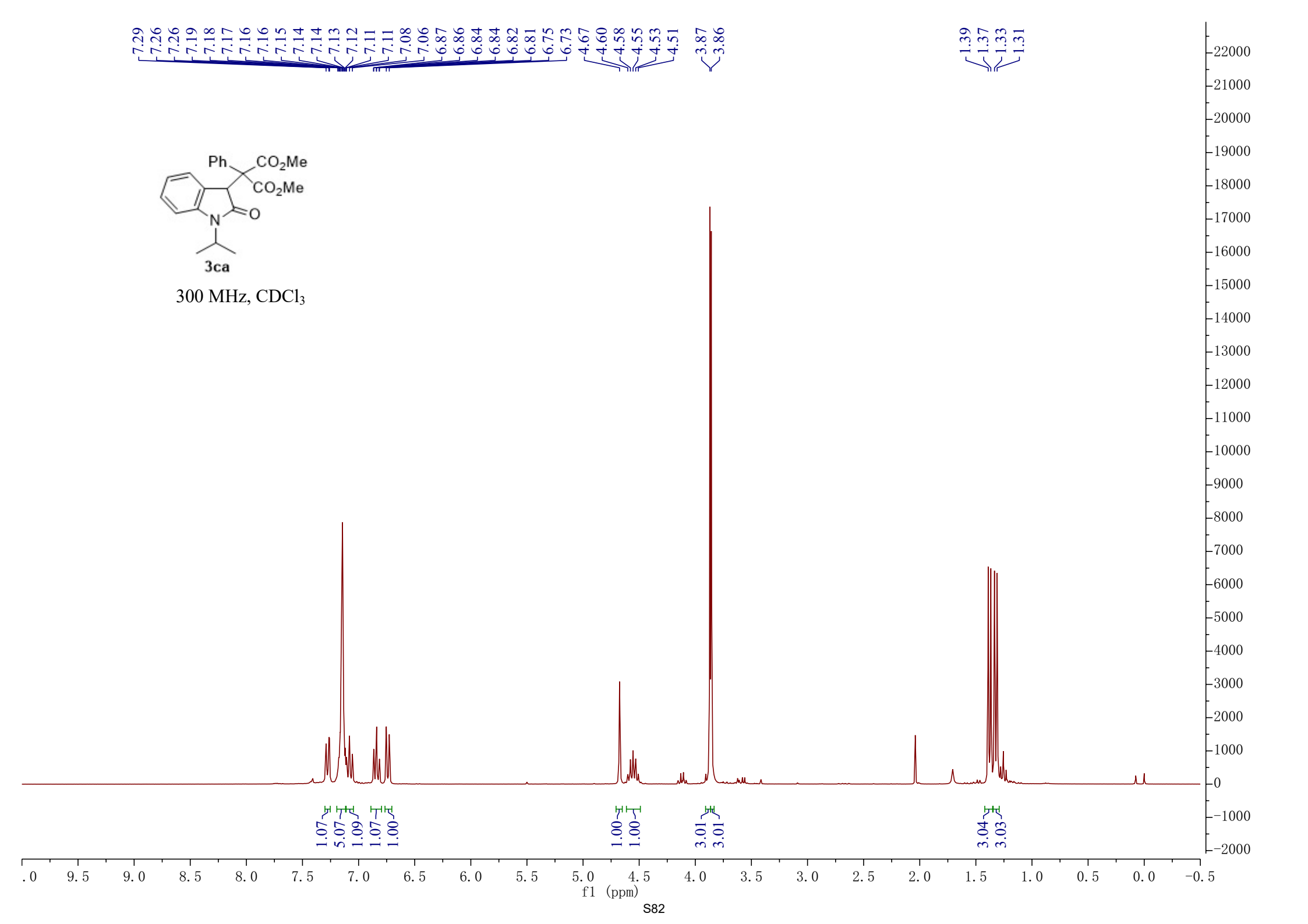

175.18
168.36
167.52
144.70
128.81
125.53
124.63
122.65
108.22
52.96
52.77
52.21
44.69
26.50
MeO2C
CO2Me
O
N
Me
3am
100 MHz, CDCl3
f1 (ppm)

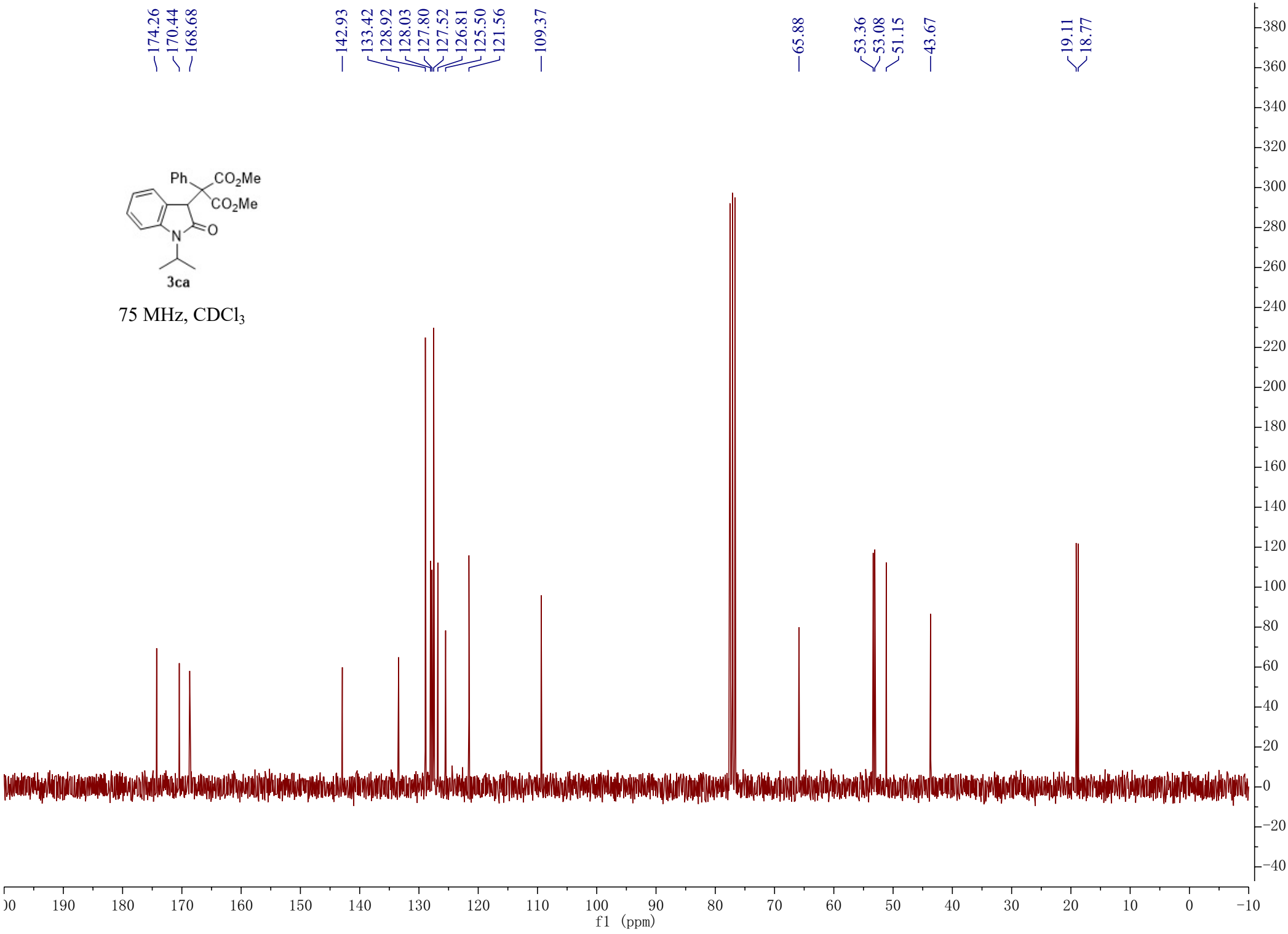


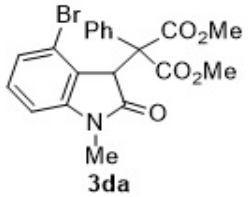
3ba

400 MHz, $CDCl_3$


174.67
170.37
168.68
143.57
135.55
133.61
128.93
128.68
128.33
127.92
127.77
127.58
127.47
126.61
125.06
122.22
108.84
65.75
53.46
53.21
51.46
43.86
Ph
CO2Me
CO2Me
O
N
Bn
3ba
100 MHz, CDCl3
450
400
350
300
250
200
150
100
50
0
−50
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

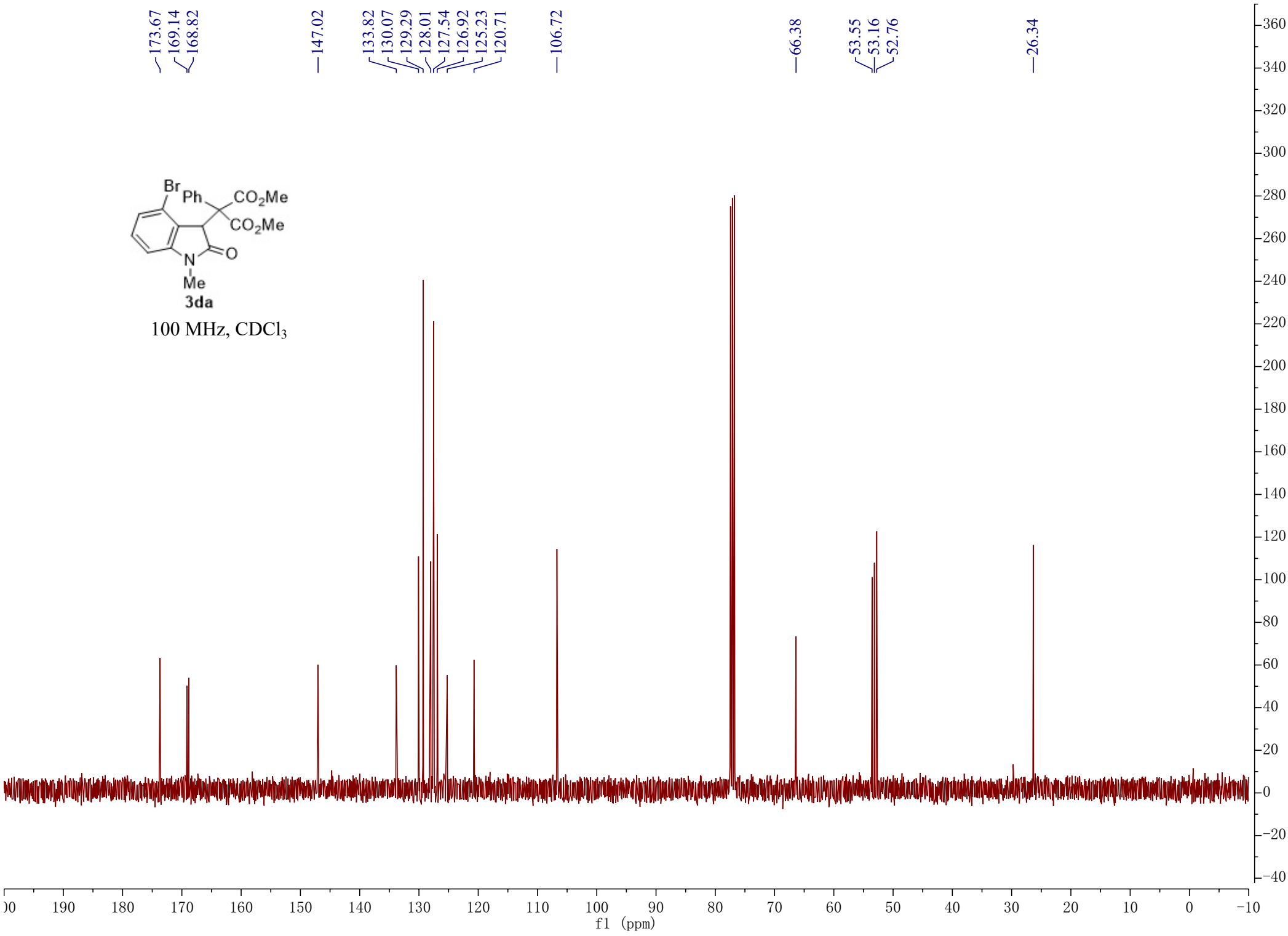

7.29
7.26
7.26
7.19
7.18
7.17
7.16
7.16
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.08
7.06
6.87
6.86
6.84
6.84
6.82
6.81
6.75
6.73
4.67
4.60
4.58
4.55
4.53
4.51
3.87
3.86
1.39
1.37
1.33
1.31
Ph
CO2Me
CO2Me
N
O
3ca
300 MHz, CDCl3
1.07
5.07
1.09
1.07
1.00
1.00
1.00
3.01
3.01
3.04
3.03
f1 (ppm)

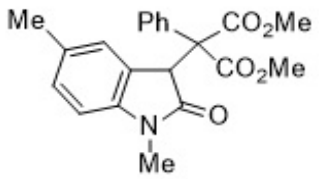

174.26
170.44
168.68
142.93
133.42
128.92
128.03
127.80
127.52
126.81
125.50
121.56
109.37
65.88
53.36
53.08
51.15
43.67
19.11
18.77
Ph
CO2Me
CO2Me
O
N
3ca
75 MHz, CDCl3
f1 (ppm)



3da

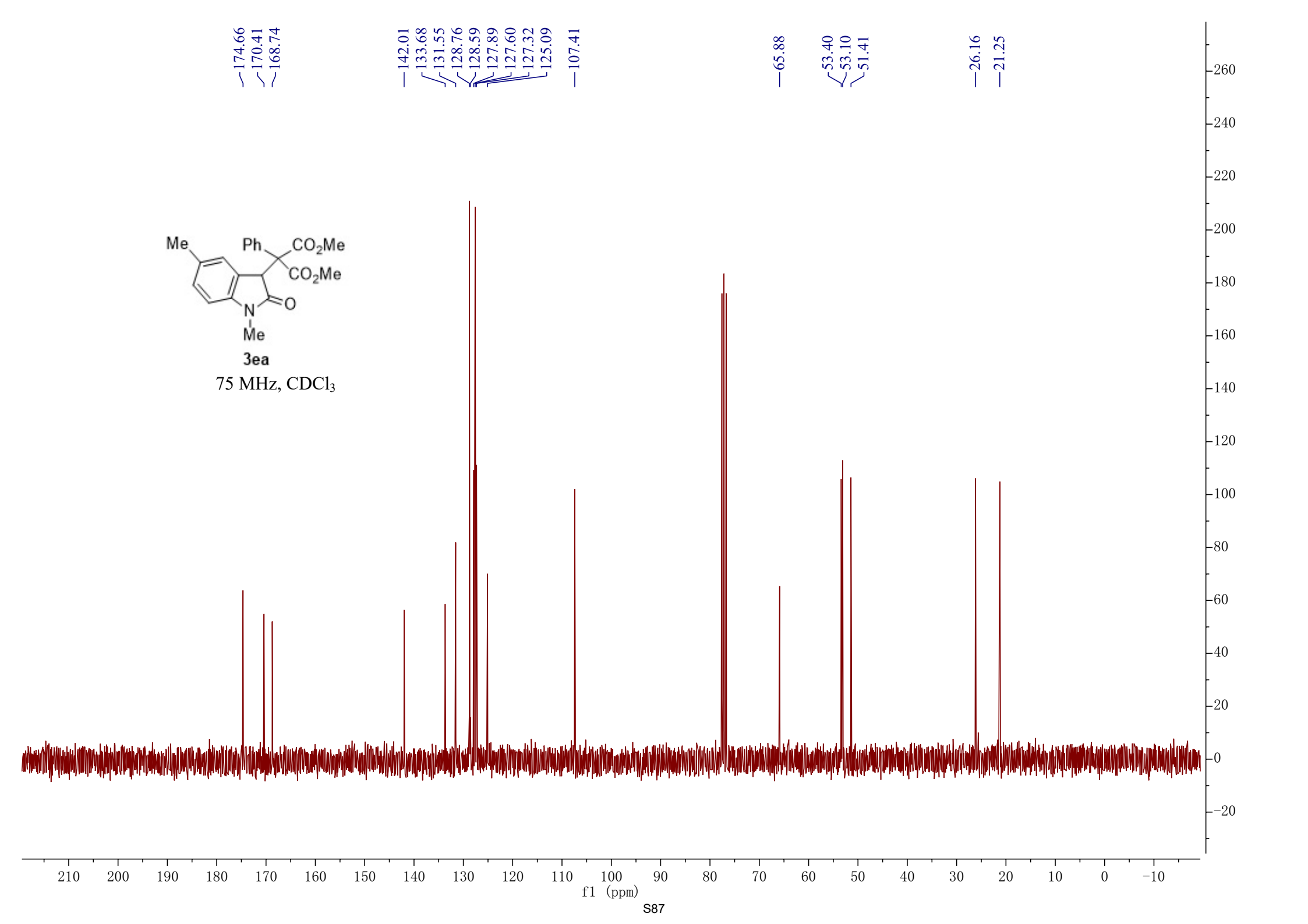
400 MHz, $CDCl_3$

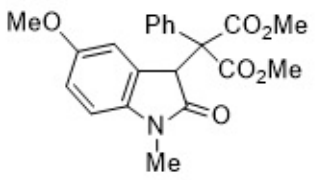

173.67
169.14
168.82
147.02
133.82
130.07
129.29
128.01
127.54
126.92
125.23
120.71
106.72
66.38
53.55
53.16
52.76
26.34
Br
Ph
CO2Me
CO2Me
O
N
Me
3da
100 MHz, CDCl3
f1 (ppm)



3ea

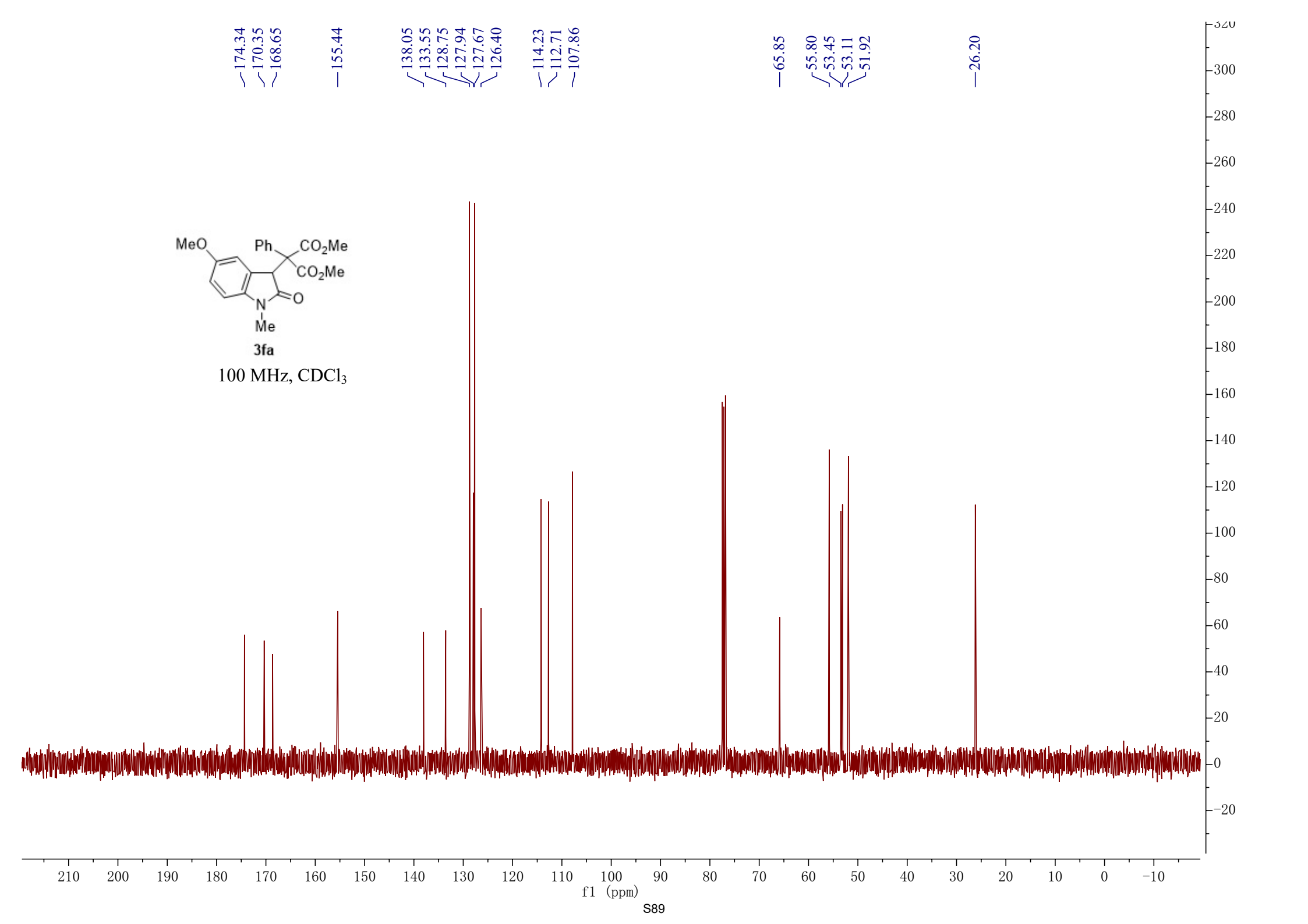
300 MHz, $CDCl_3$

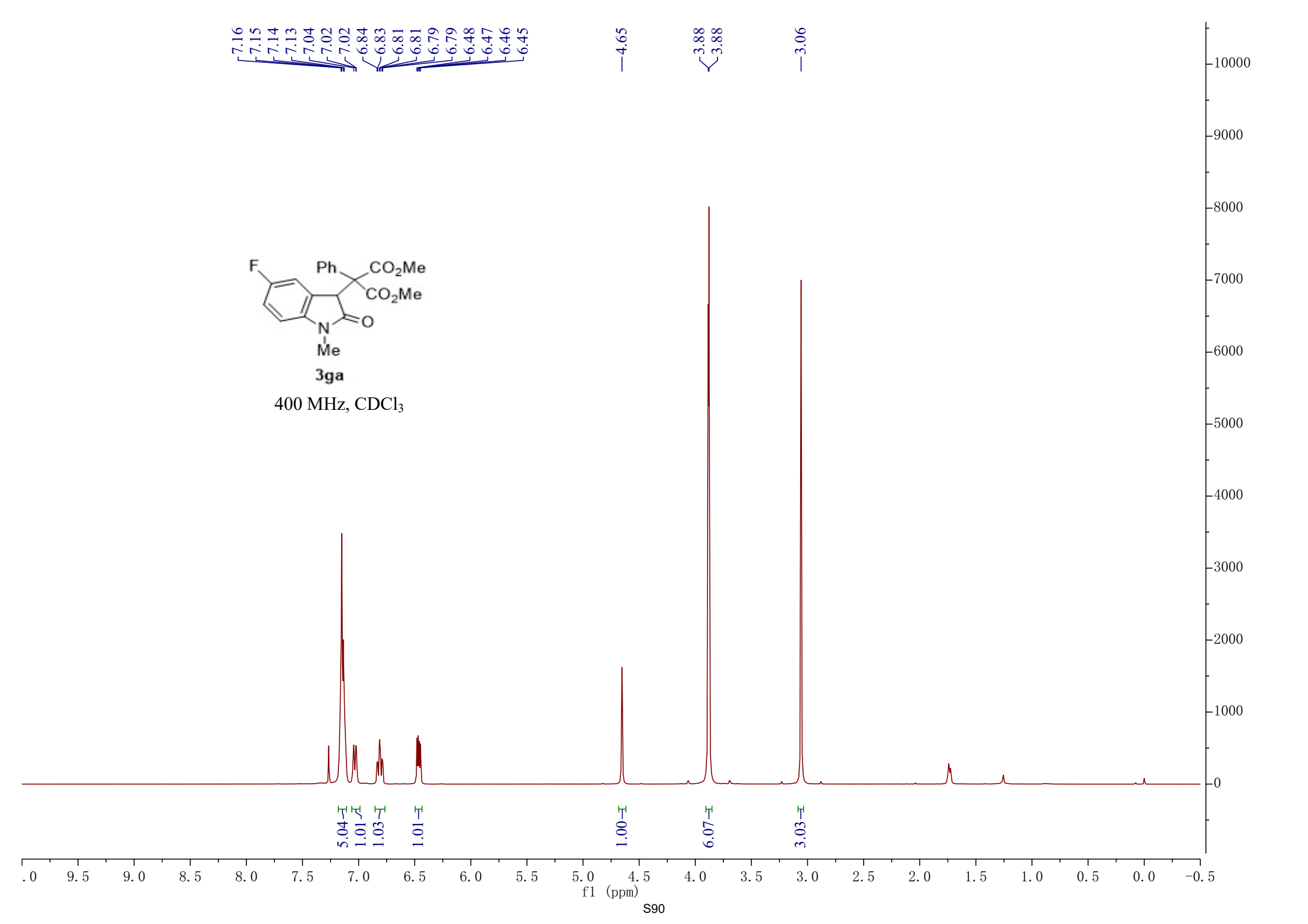

174.66
170.41
168.74
142.01
133.68
131.55
128.76
128.59
127.89
127.60
127.32
125.09
107.41
65.88
53.40
53.10
51.41
26.16
21.25
Me
Ph
CO2Me
CO2Me
N
O
Me
3ea
75 MHz, CDCl3
f1 (ppm)

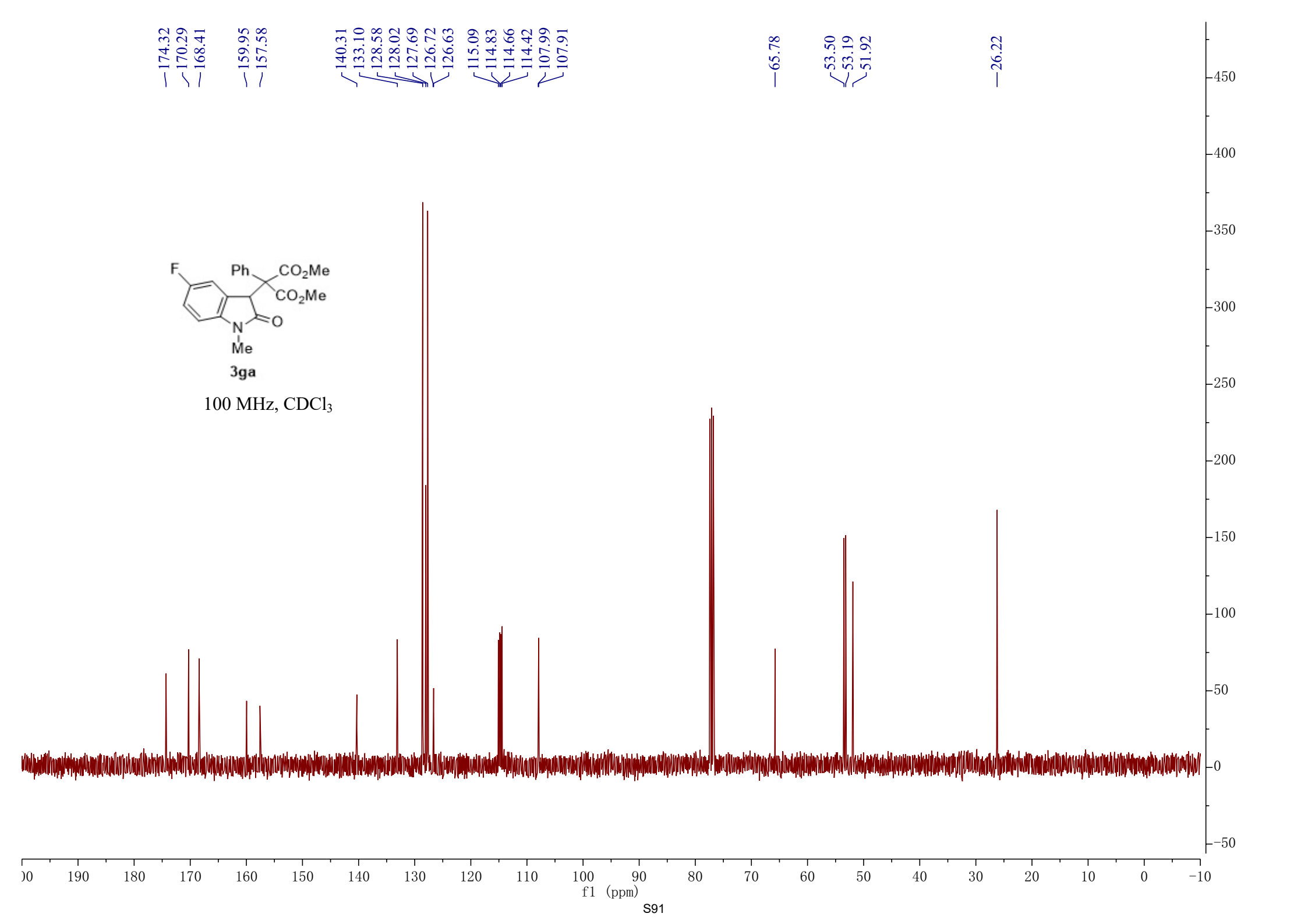


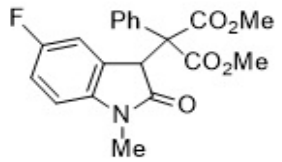
3fa

400 MHz, $CDCl_3$


174.34
170.35
168.65
155.44
138.05
133.55
128.75
127.94
127.67
126.40
114.23
112.71
107.86
65.85
55.80
53.45
53.11
51.92
26.20
MeO
Ph
CO2Me
CO2Me
O
N
Me
3fa
100 MHz, CDCl3
f1 (ppm)

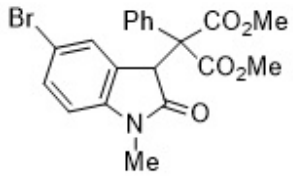

7.16
7.15
7.14
7.13
7.04
7.02
7.02
6.84
6.83
6.81
6.81
6.79
6.79
6.48
6.47
6.46
6.45
4.65
3.88
3.88
3.06
F
Ph
CO2Me
CO2Me
O
N
Me
3ga
400 MHz, CDCl3
5.04
1.01
1.03
1.01
1.00
6.07
3.03
f1 (ppm)


174.32
170.29
168.41
159.95
157.58
140.31
133.10
128.58
128.02
127.69
126.72
126.63
115.09
114.83
114.66
114.42
107.99
107.91
65.78
53.50
53.19
51.92
26.22
F
Ph
CO2Me
CO2Me
N
Me
O
3ga
100 MHz, CDCl3
f1 (ppm)



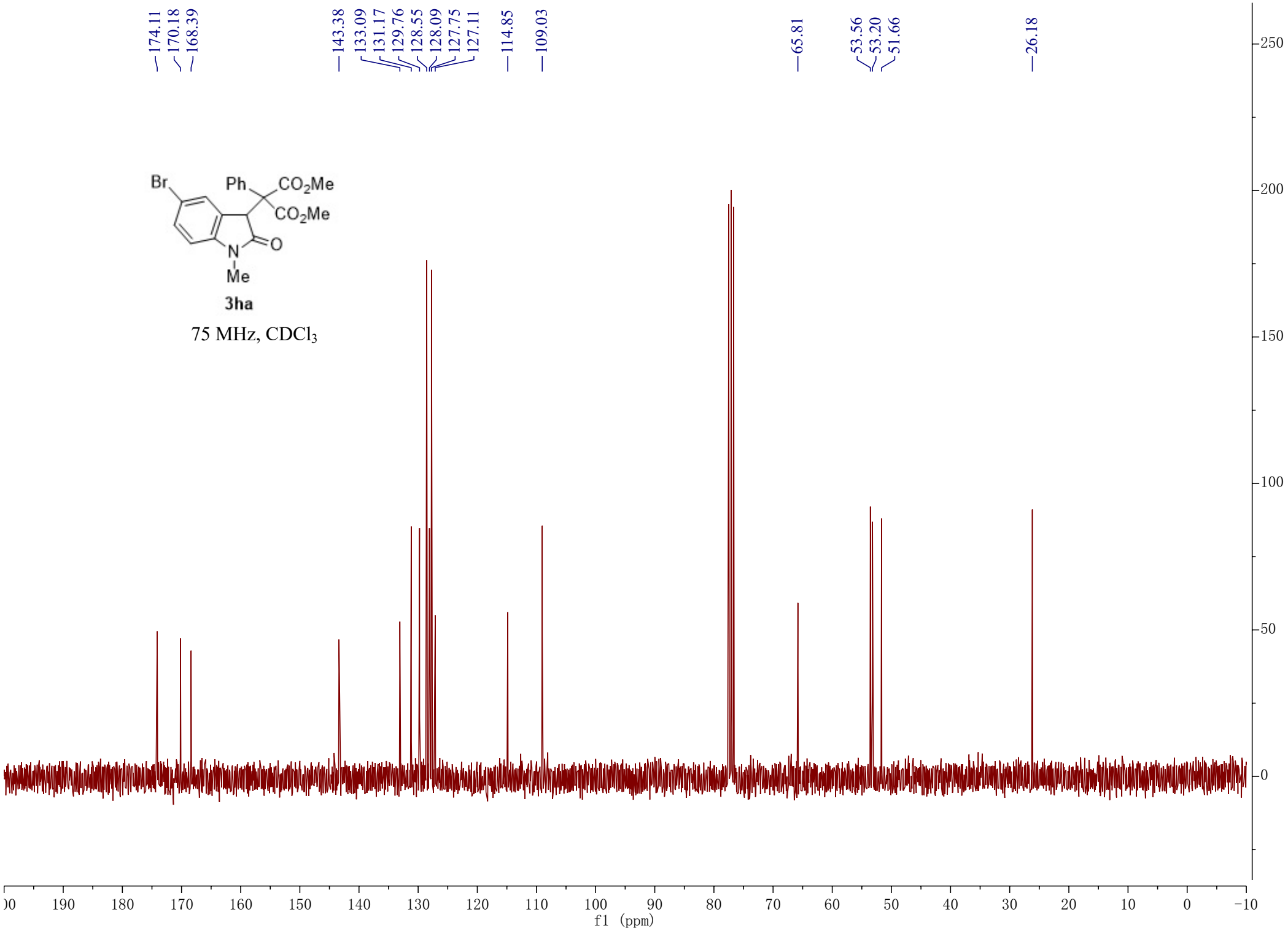
3ga

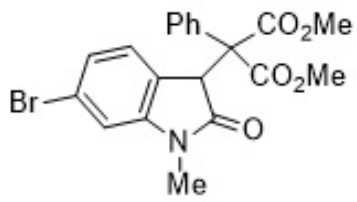
282 MHz, $CDCl_3$



3ha

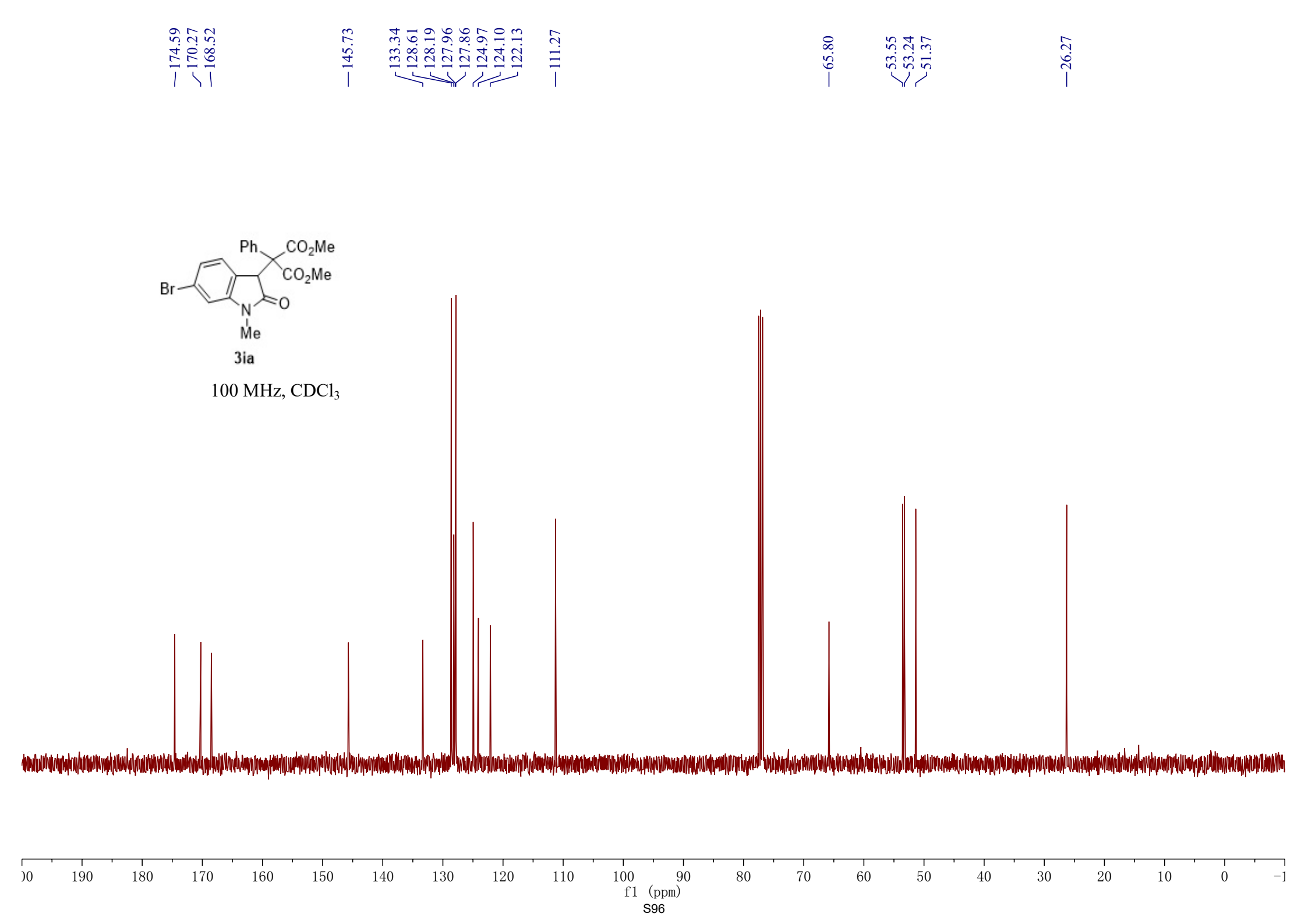
300 MHz, $CDCl_3$

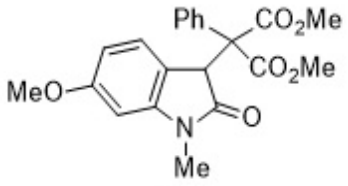

174.11
170.18
168.39
143.38
133.09
131.17
129.76
128.55
128.09
127.75
127.11
114.85
109.03
65.81
53.56
53.20
51.66
26.18
Br
Ph
CO2Me
CO2Me
O
N
Me
3ha
75 MHz, CDCl3
250
200
150
100
50
0
f1 (ppm)



3ia

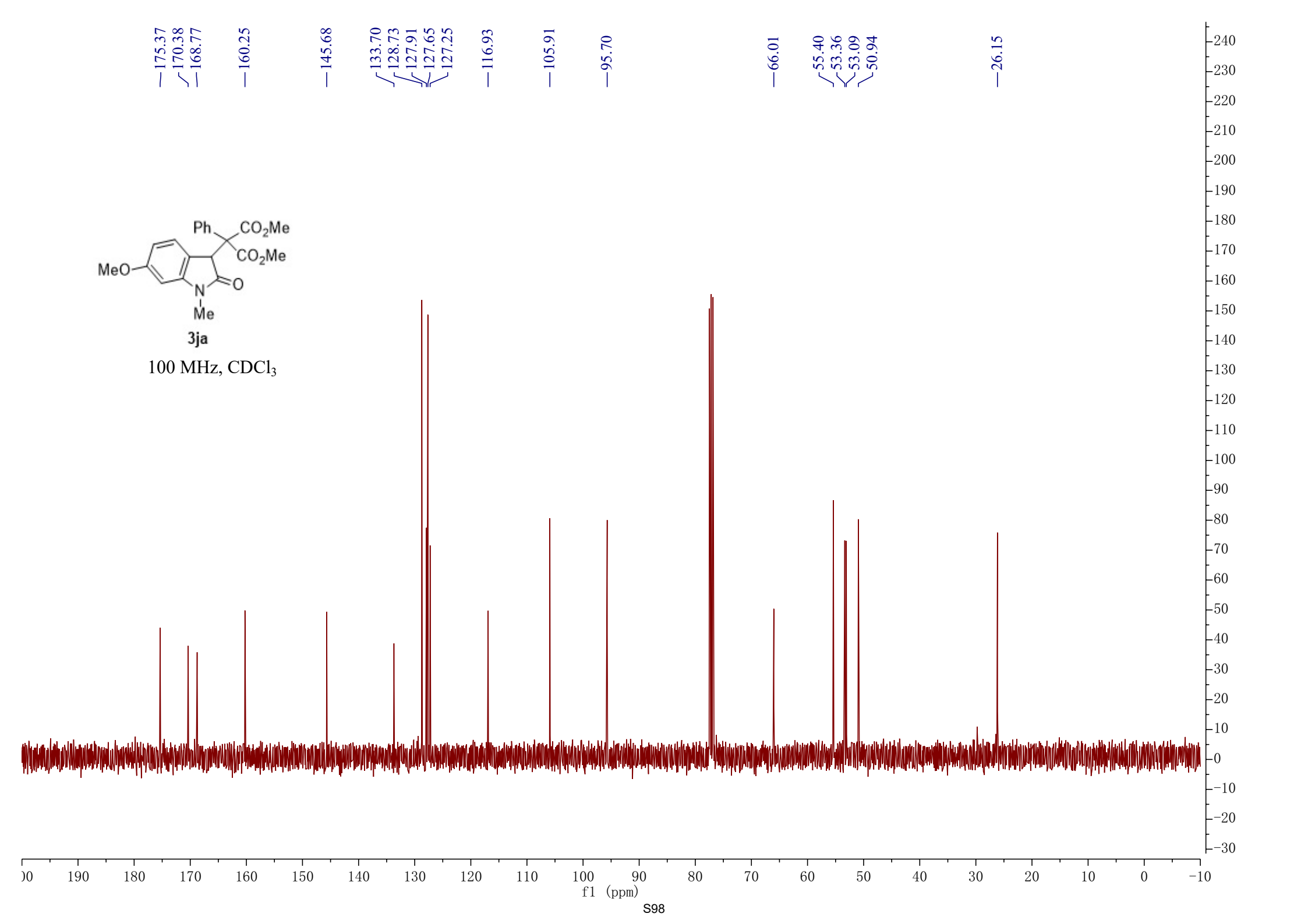
400 MHz, $CDCl_3$

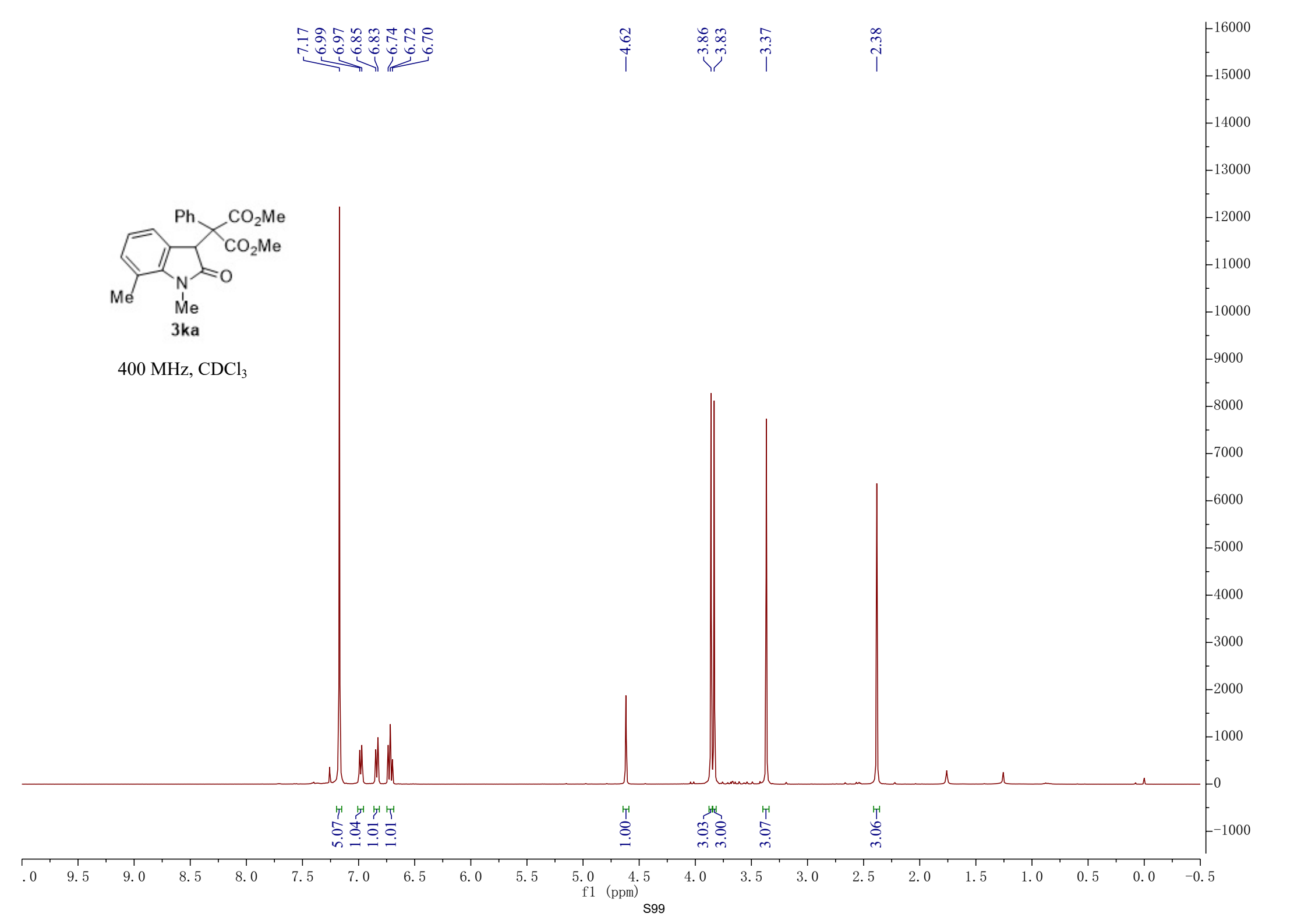

174.59
170.27
168.52
145.73
133.34
128.61
128.19
127.96
127.86
124.97
124.10
122.13
111.27
65.80
53.55
53.24
51.37
26.27
Ph
CO2Me
CO2Me
Br
N
O
Me
3ia
100 MHz, CDCl3
f1 (ppm)

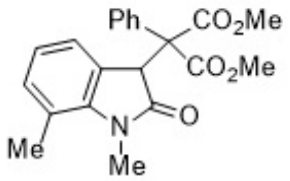


3ja

400 MHz, $CDCl_3$


175.37
170.38
168.77
160.25
145.68
133.70
128.73
127.91
127.65
127.25
116.93
105.91
95.70
66.01
55.40
53.36
53.09
50.94
26.15
Ph
CO2Me
CO2Me
MeO
O
N
Me
3ja
100 MHz, CDCl3
f1 (ppm)


7.17
6.99
6.97
6.85
6.83
6.74
6.72
6.70
4.62
3.86
3.83
3.37
2.38
Ph
CO2Me
CO2Me
O
N
Me
Me
3ka
400 MHz, CDCl3
5.07
1.04
1.01
1.01
1.00
3.03
3.00
3.07
3.06
f1 (ppm)

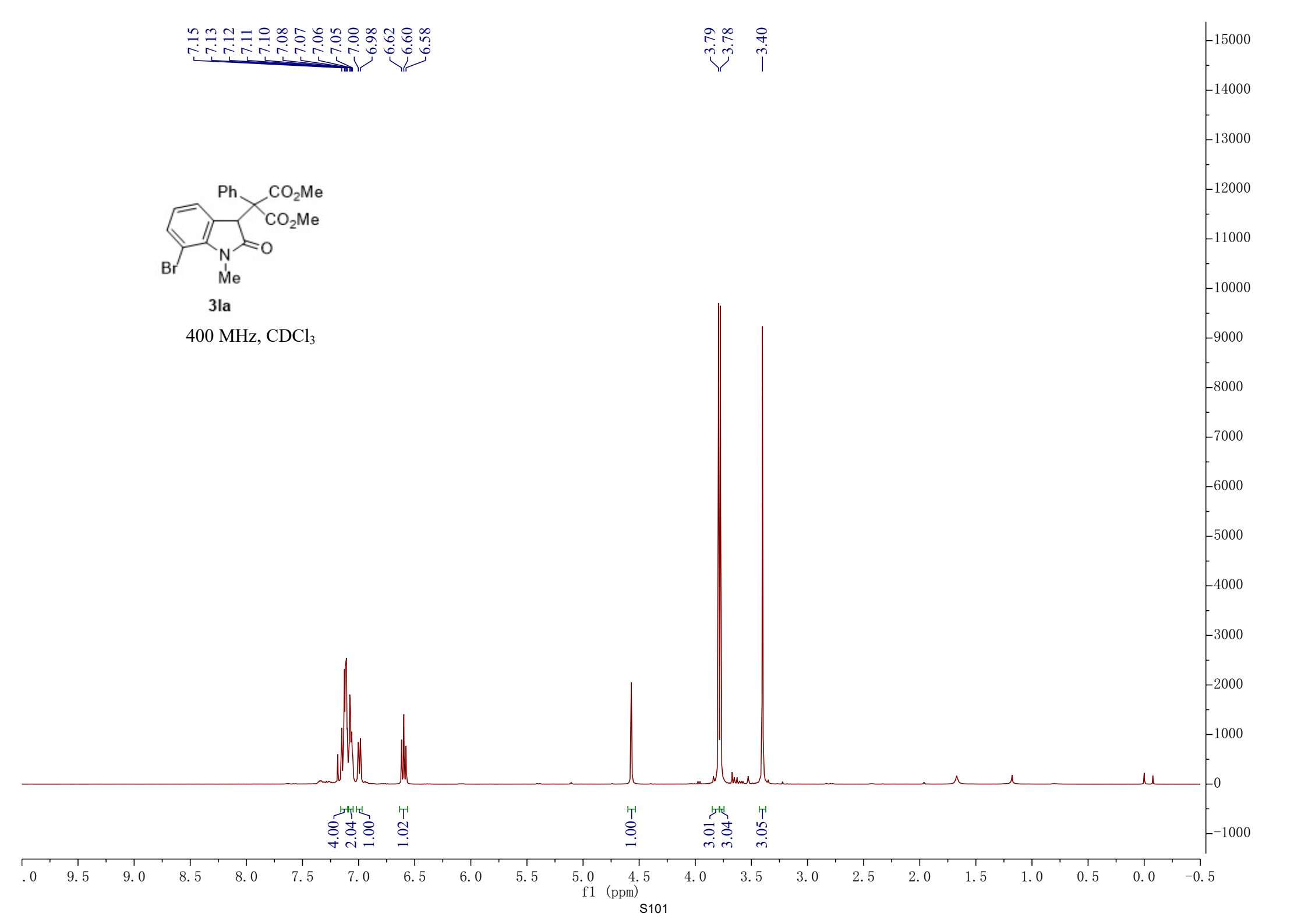


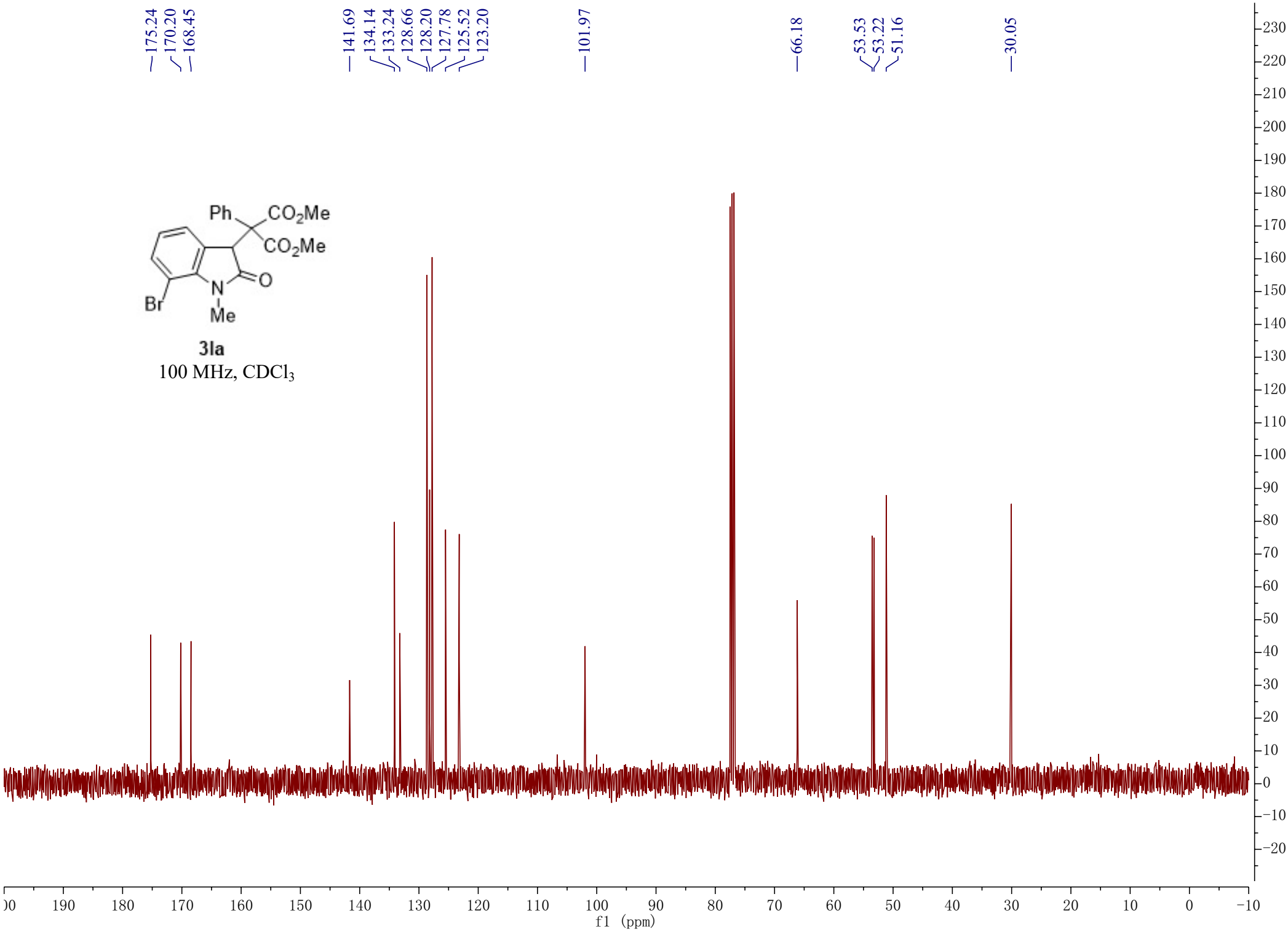
3ka

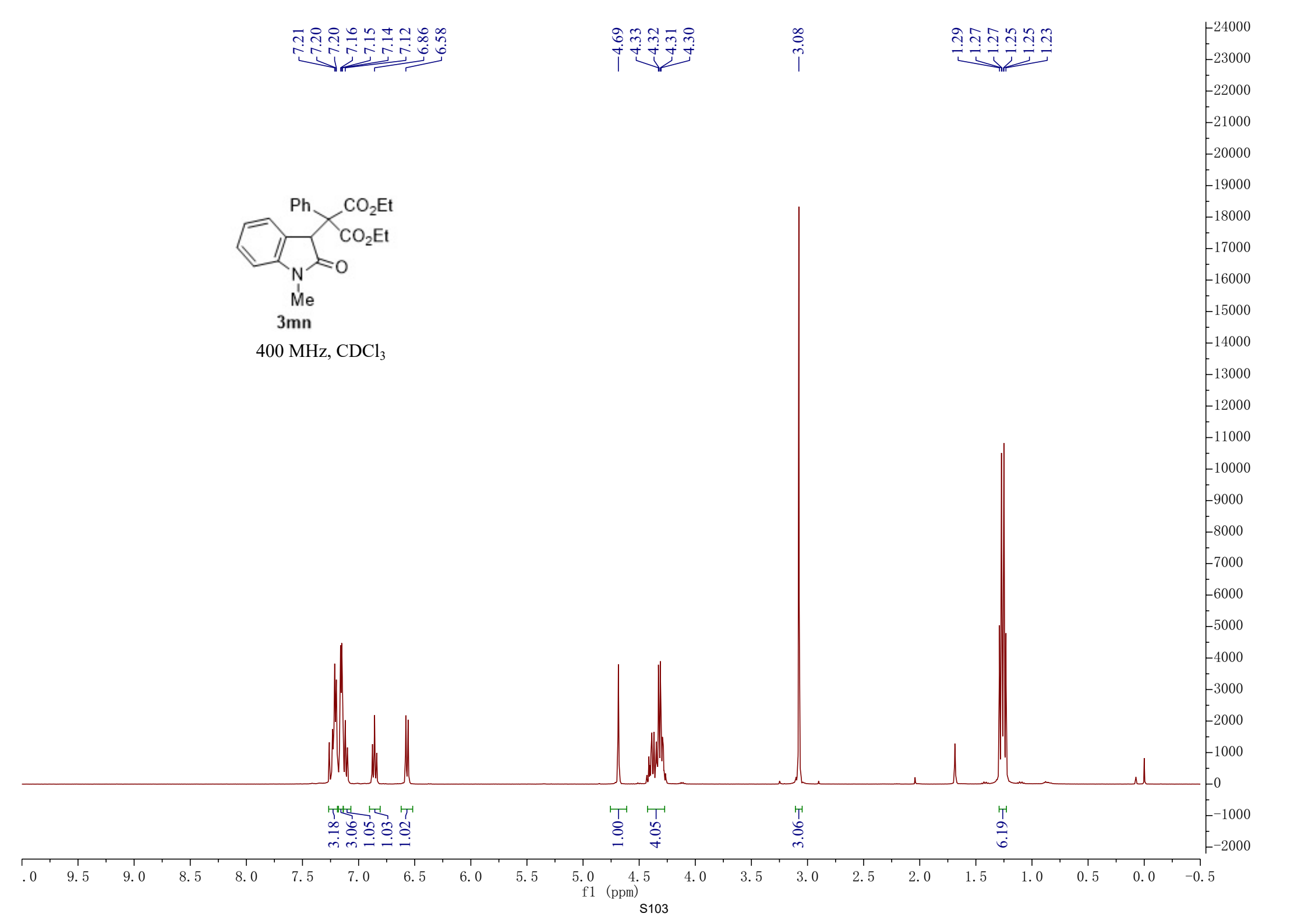
100 MHz, $CDCl_3$

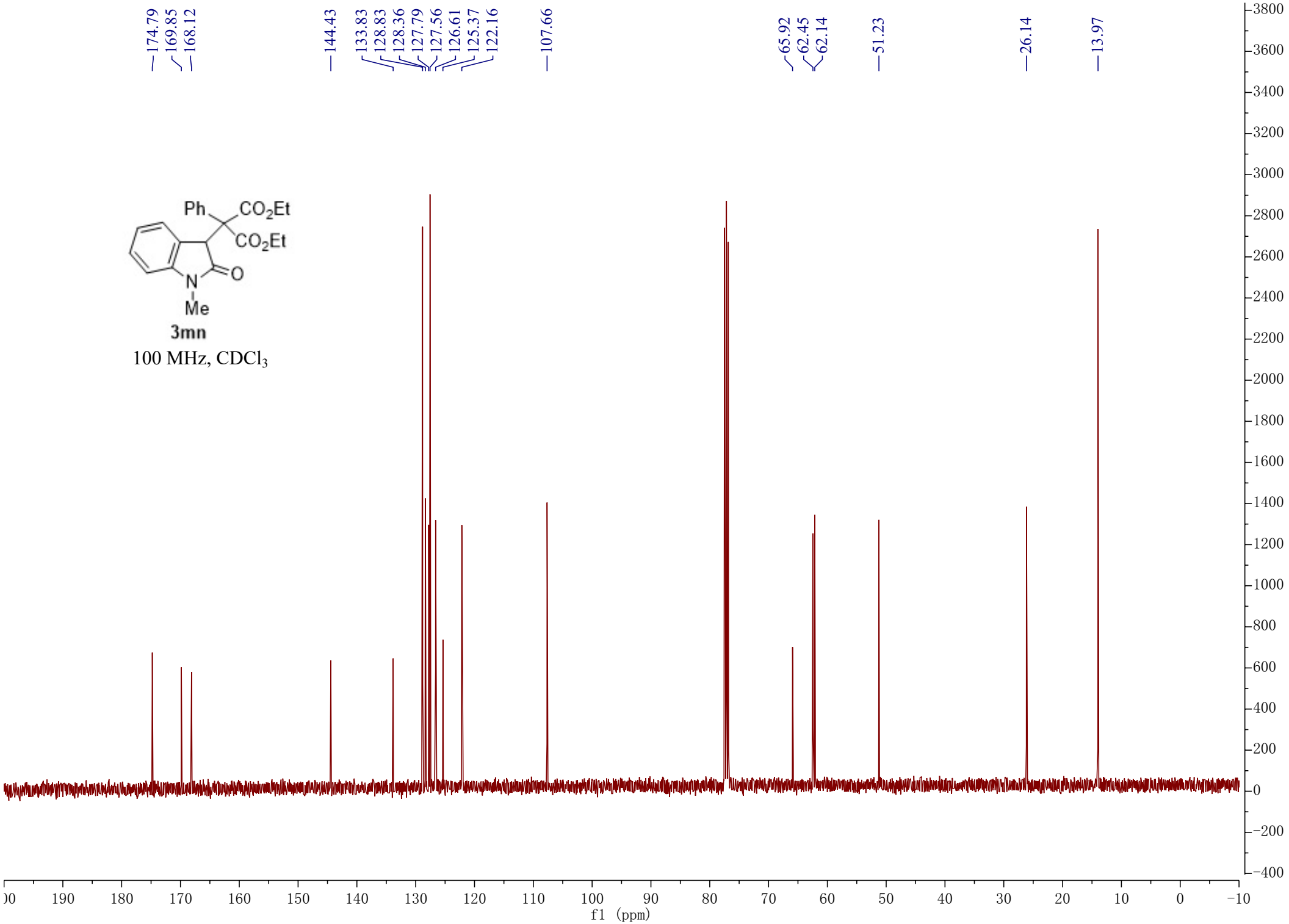
175.52
170.35
168.73
142.23
133.63
132.20
128.82
127.89
127.55
125.63
124.28
121.95
119.16
66.17
53.37
53.07
50.85
29.68
19.09

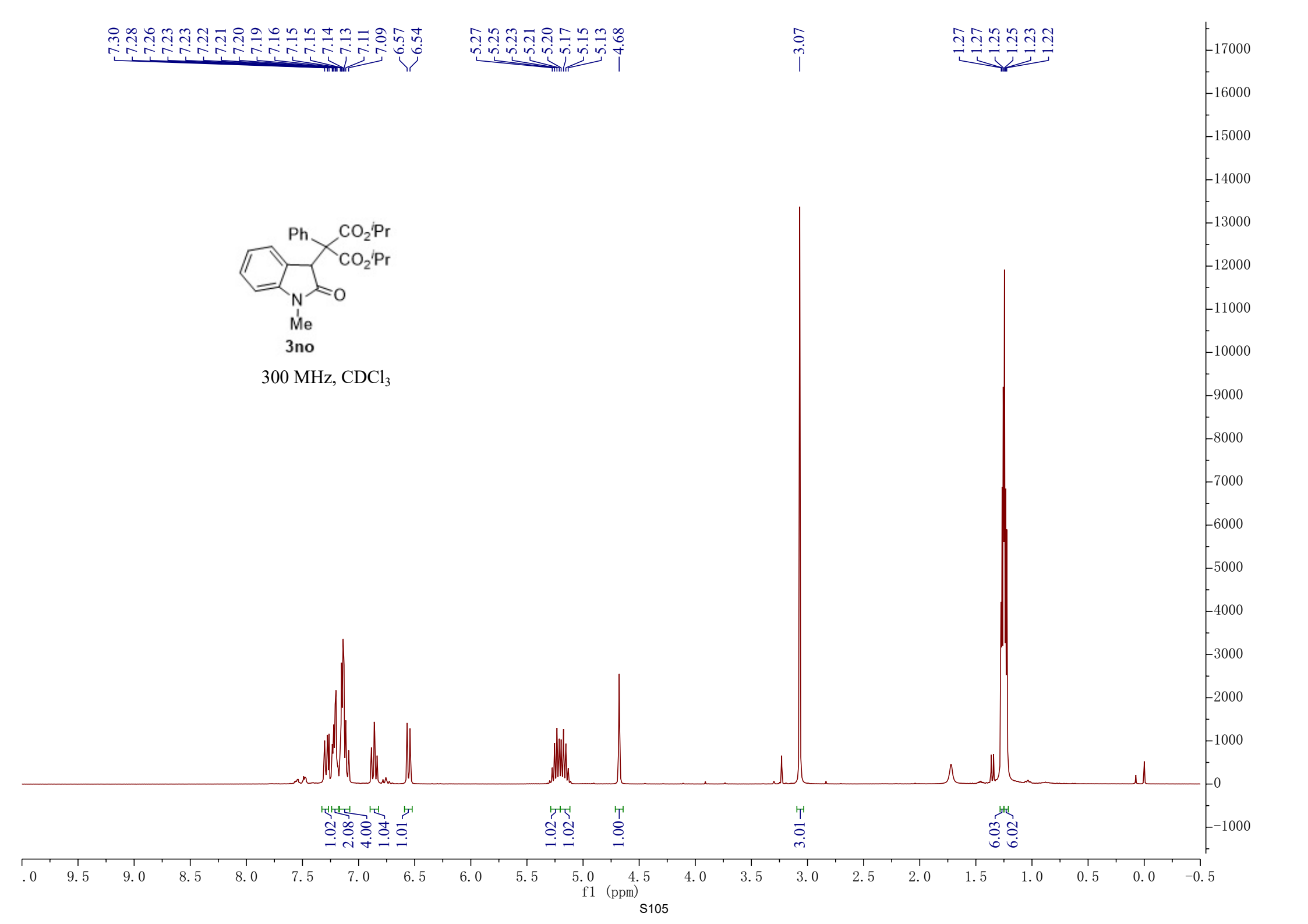
f1 (ppm)

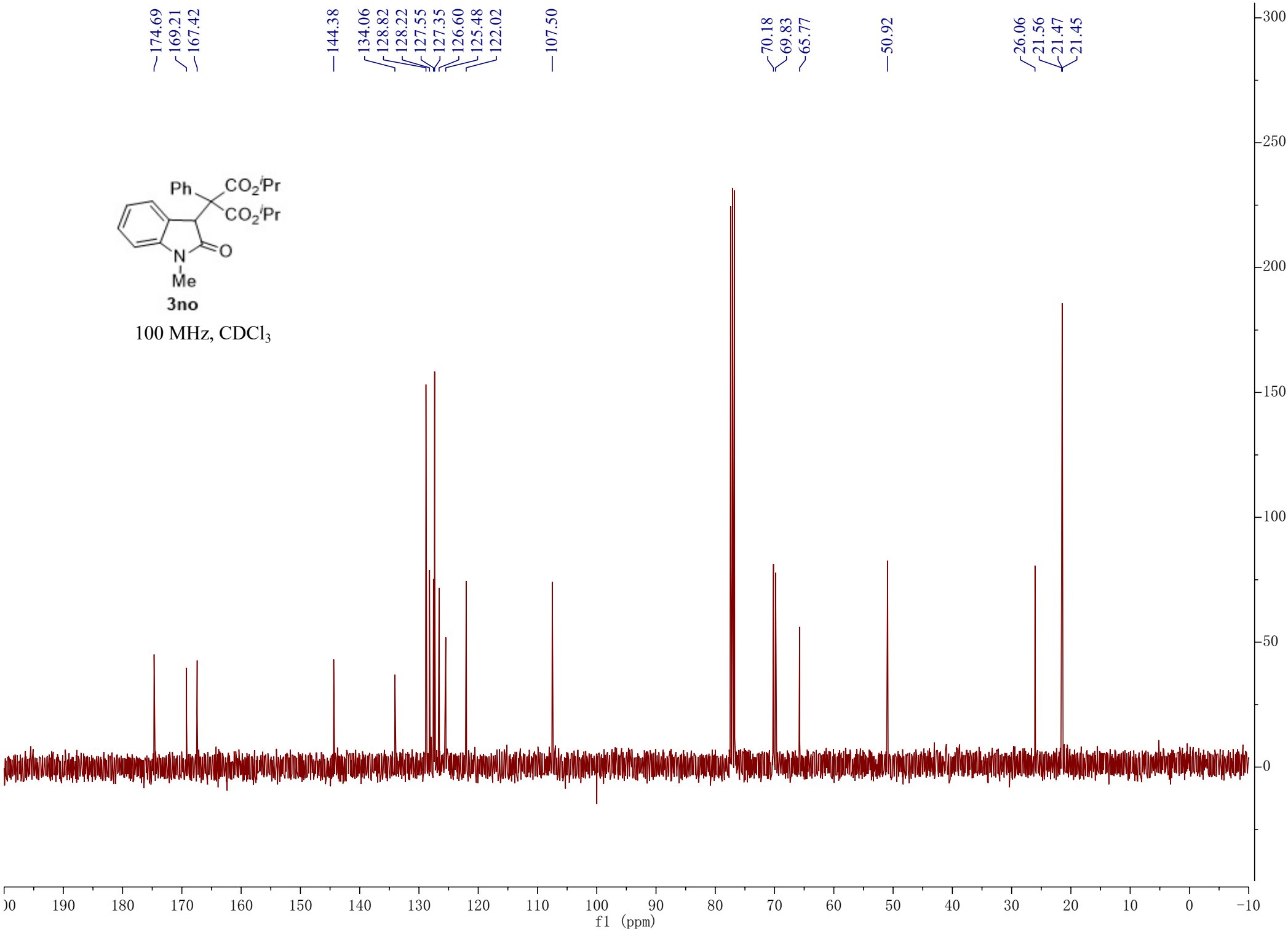

7.15
7.13
7.12
7.11
7.10
7.08
7.07
7.06
7.05
7.00
6.98
6.62
6.60
6.58
3.79
3.78
3.40
Ph
CO2Me
CO2Me
O
N
Me
Br
3la
400 MHz, CDCl3
4.00
2.04
1.00
1.02
1.00
3.01
3.04
3.05
f1 (ppm)

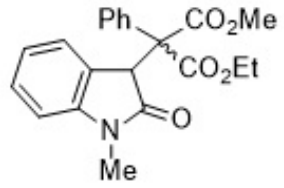

175.24
170.20
168.45
141.69
134.14
133.24
128.66
128.20
127.78
125.52
123.20
101.97
66.18
53.53
53.22
51.16
30.05
Ph
CO2Me
CO2Me
O
N
Me
Br
3la
100 MHz, CDCl3
f1 (ppm)


7.21
7.20
7.20
7.16
7.15
7.14
7.12
6.86
6.58
4.69
4.33
4.32
4.31
4.30
3.08
1.29
1.27
1.27
1.25
1.25
1.23
Ph
CO2Et
CO2Et
O
N
Me
3mn
400 MHz, CDCl3
3.18
3.06
1.05
1.03
1.02
1.00
4.05
3.06
6.19
f1 (ppm)


174.79
169.85
168.12
144.43
133.83
128.83
128.36
127.79
127.56
126.61
125.37
122.16
107.66
65.92
62.45
62.14
51.23
26.14
13.97
Ph
CO2Et
CO2Et
O
N
Me
3mn
100 MHz, CDCl3
f1 (ppm)

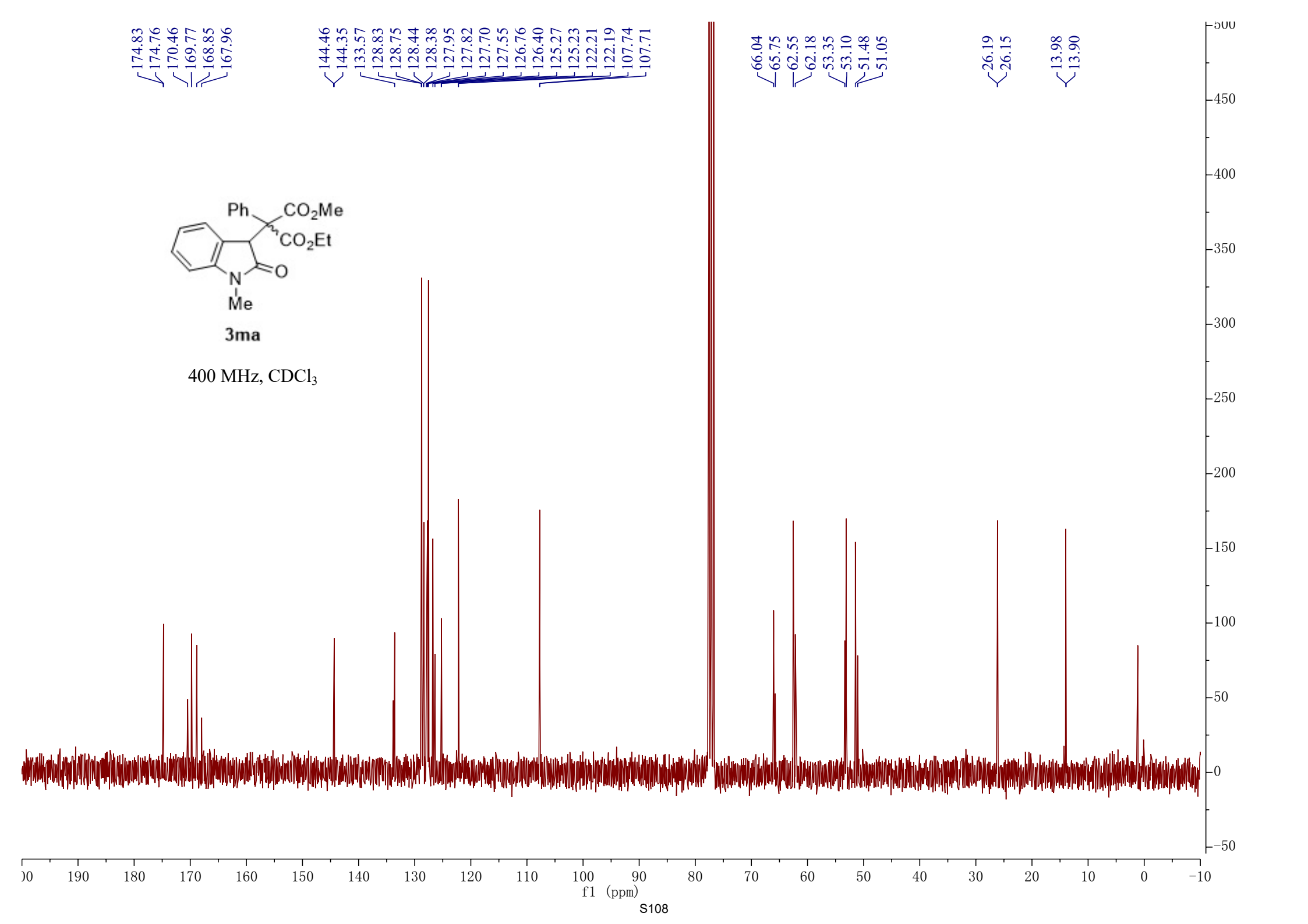

7.30
7.28
7.26
7.23
7.23
7.22
7.21
7.20
7.19
7.16
7.15
7.15
7.14
7.13
7.11
7.09
6.57
6.54
5.27
5.25
5.23
5.21
5.20
5.17
5.15
5.13
4.68
3.07
1.27
1.27
1.25
1.25
1.23
1.22
Ph
CO2iPr
CO2iPr
N
O
Me
3no
300 MHz, CDCl3
1.02
2.08
4.00
1.04
1.01
1.02
1.02
1.00
3.01
6.03
6.02
f1 (ppm)

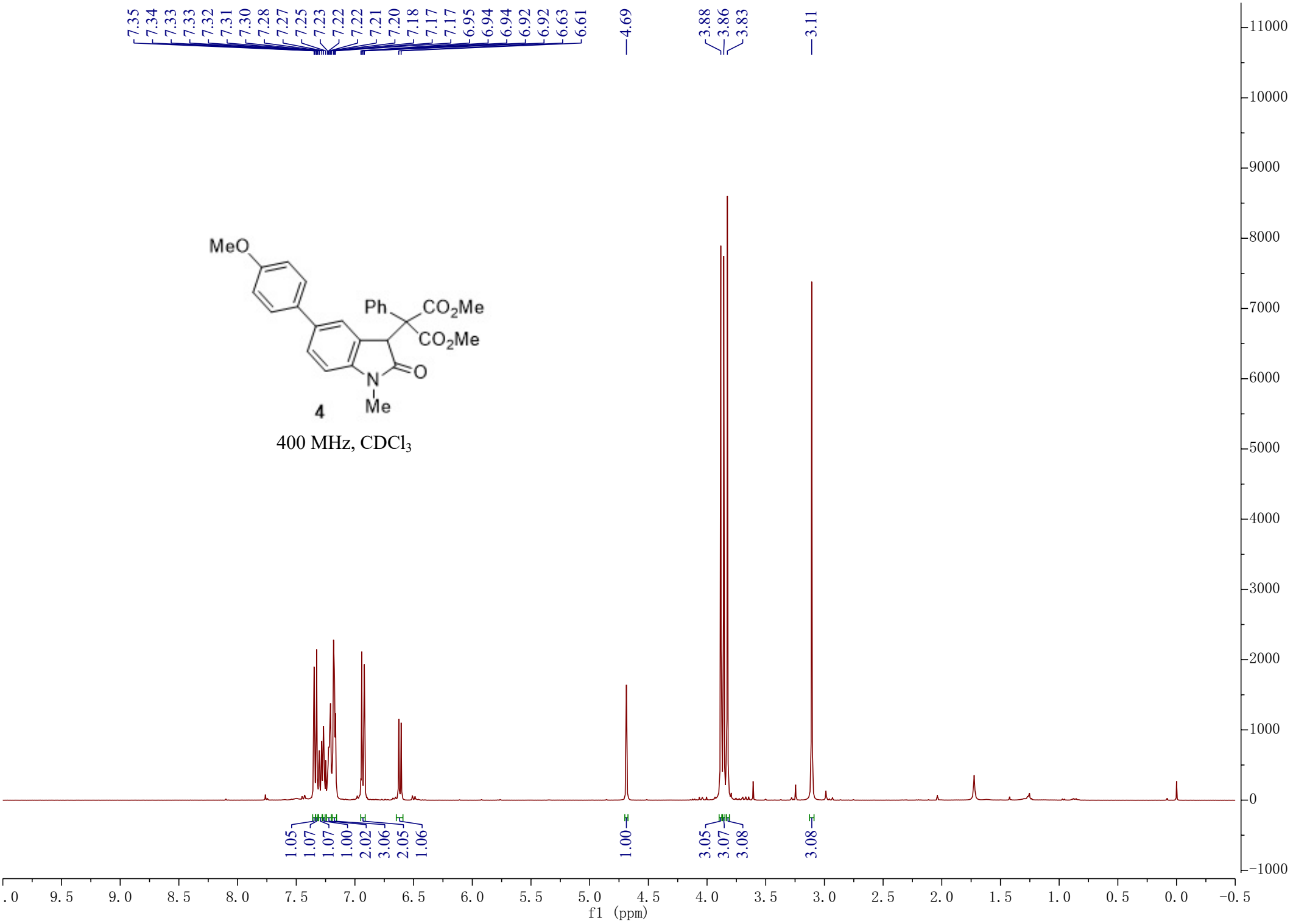

174.69
169.21
167.42
144.38
134.06
128.82
128.22
127.55
127.35
126.60
125.48
122.02
107.50
70.18
69.83
65.77
50.92
26.06
21.56
21.47
21.45
Ph
CO2iPr
CO2iPr
N
Me
O
3no
100 MHz, CDCl3
300
250
200
150
100
50
0
f1 (ppm)

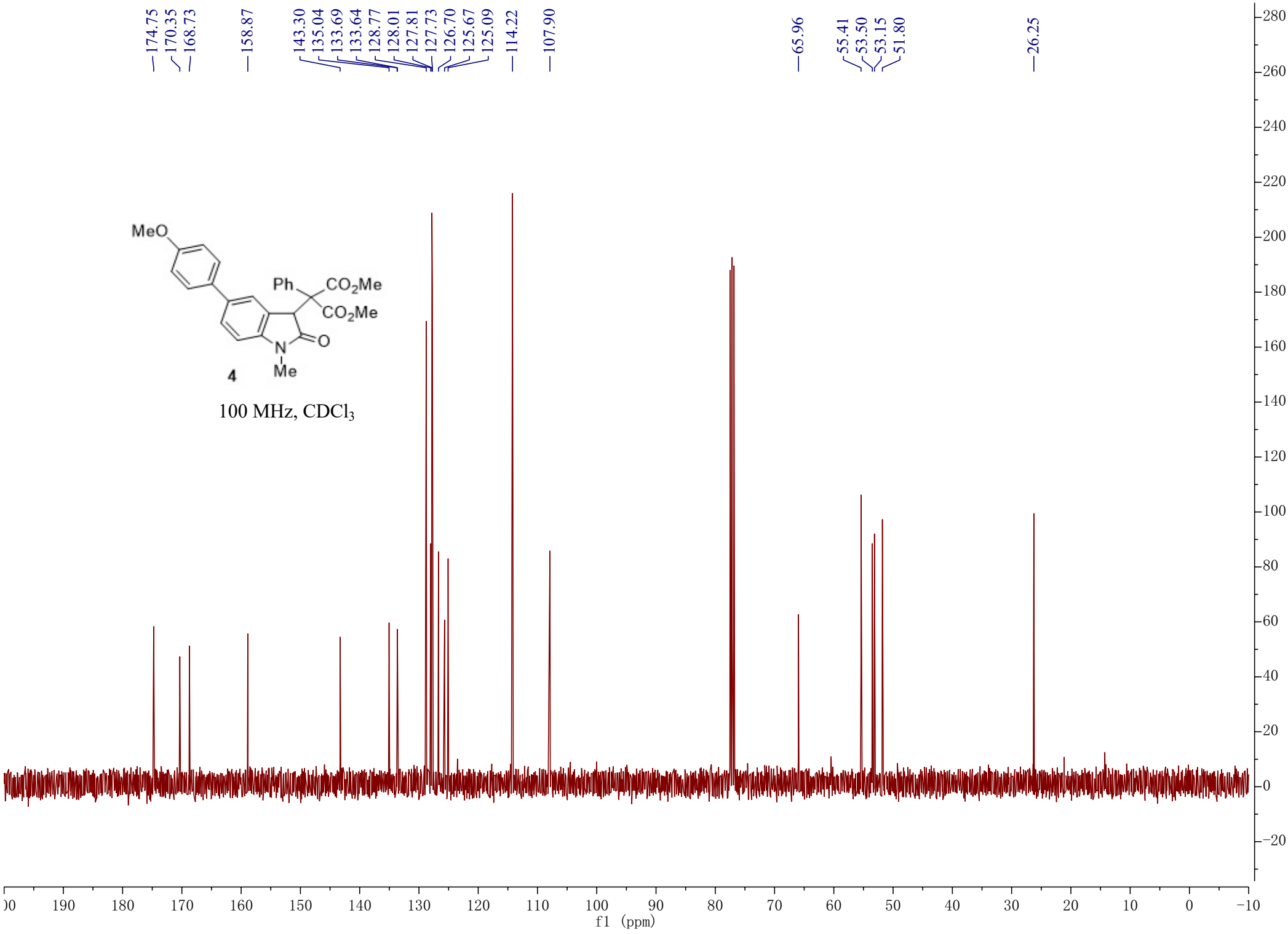


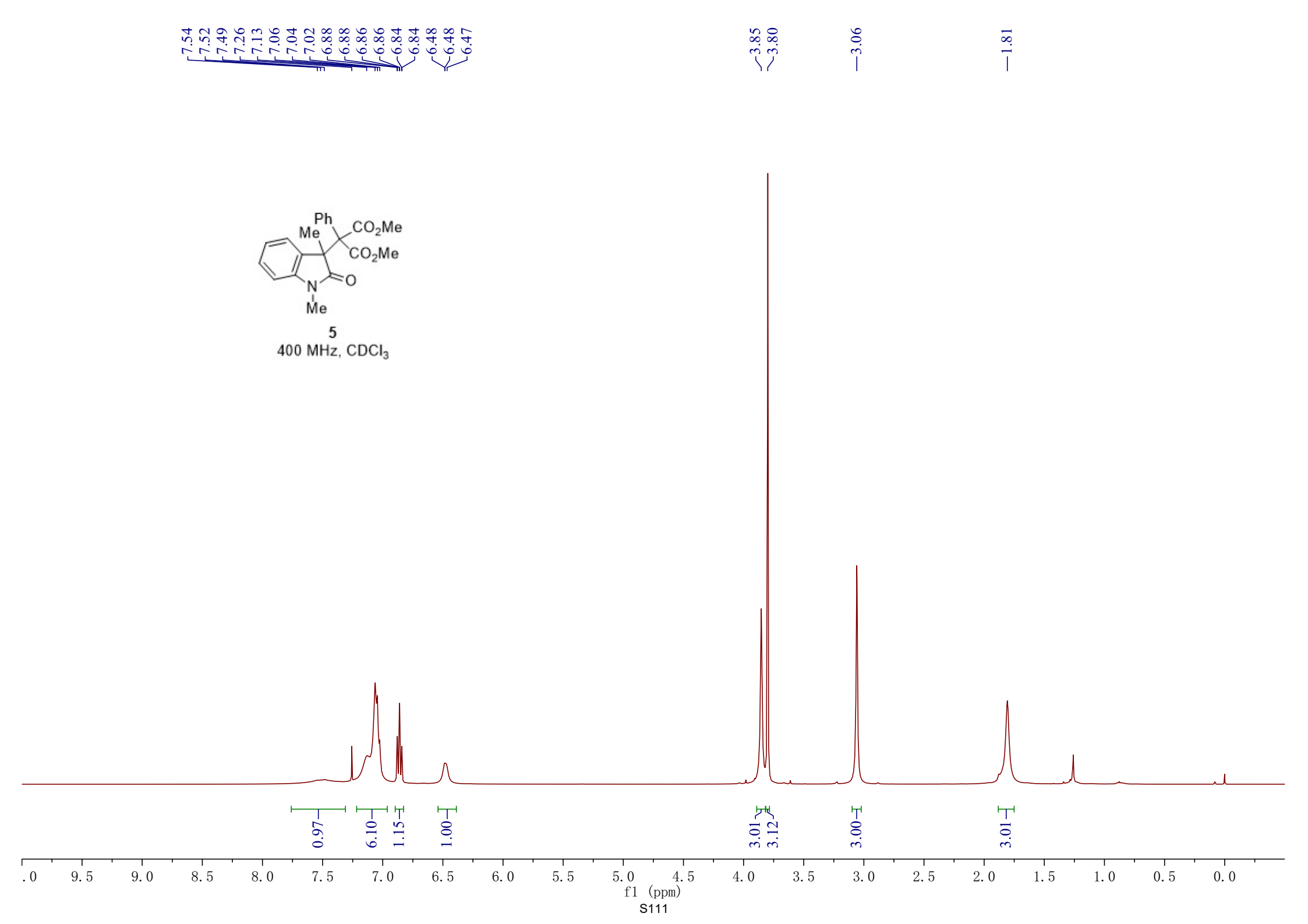
3ma

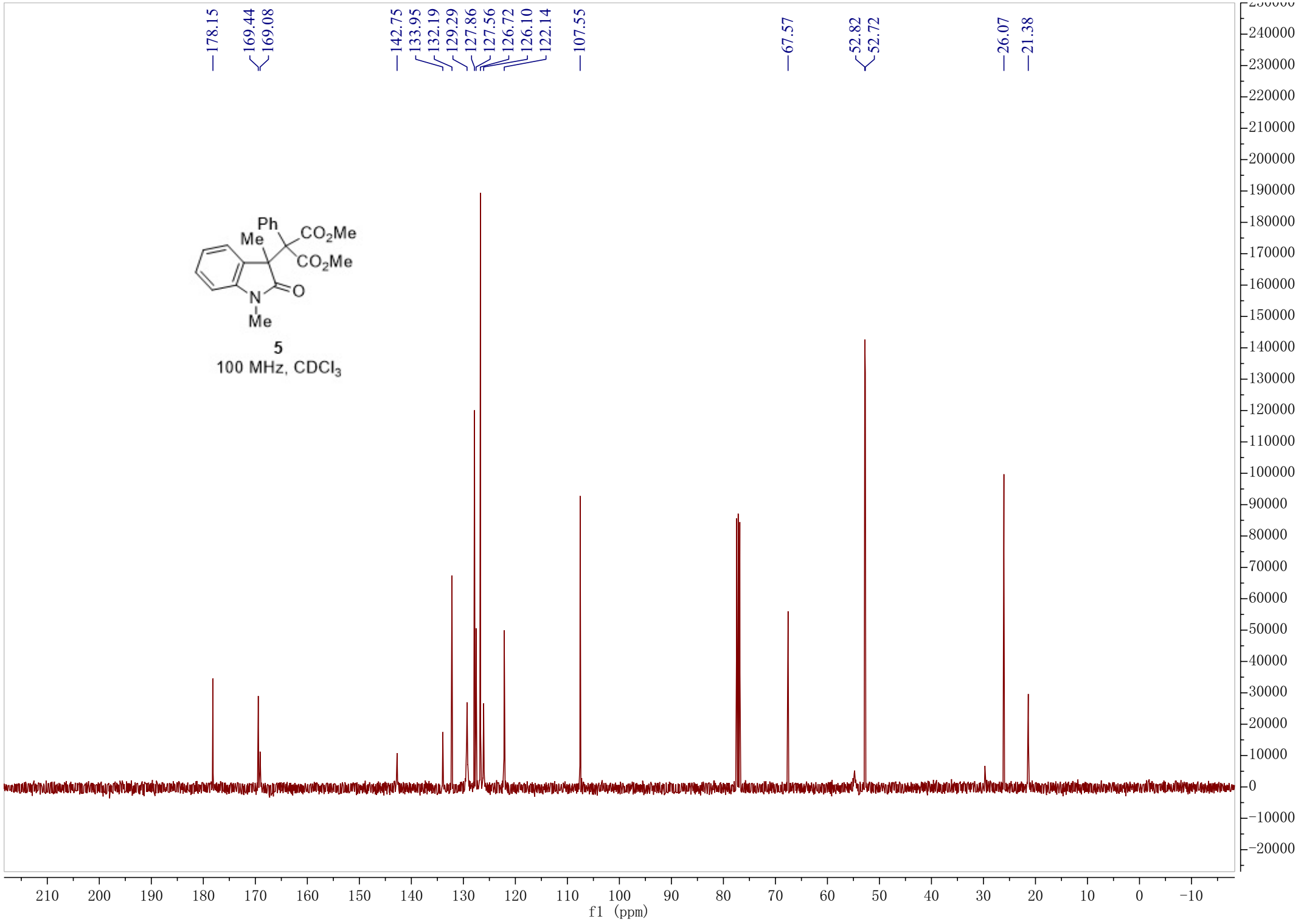
400 MHz, $CDCl_3$

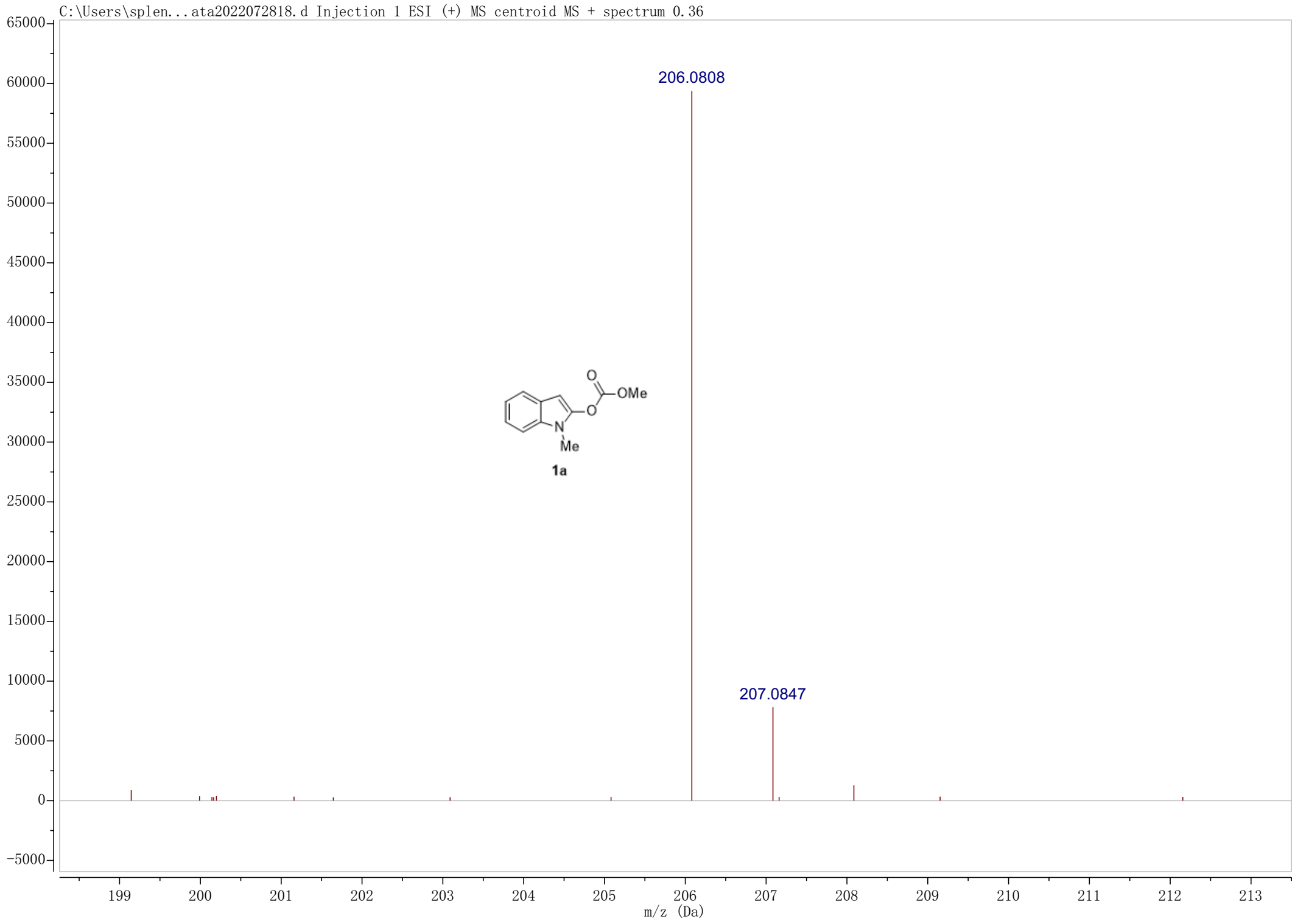

174.83
174.76
170.46
169.77
168.85
167.96
144.46
144.35
133.57
128.83
128.75
128.44
128.38
127.95
127.82
127.70
127.55
126.76
126.40
125.27
125.23
122.21
122.19
107.74
107.71
66.04
65.75
62.55
62.18
53.35
53.10
51.48
51.05
26.19
26.15
13.98
13.90
Ph
CO2Me
CO2Et
O
N
Me
3ma
400 MHz, CDCl3
f1 (ppm)

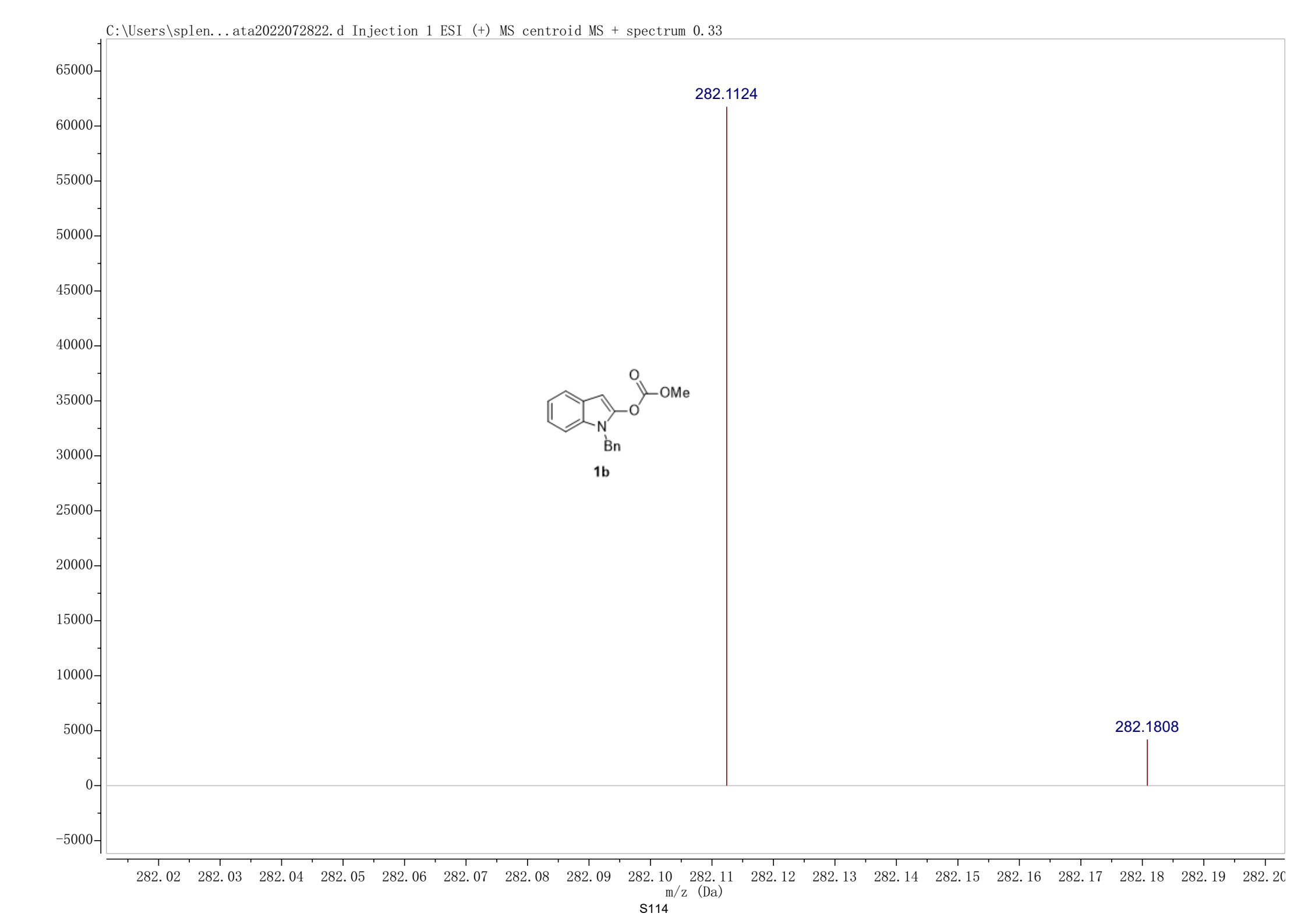

7.35
7.34
7.33
7.33
7.32
7.31
7.30
7.28
7.27
7.25
7.23
7.22
7.22
7.21
7.20
7.18
7.17
7.17
6.95
6.94
6.94
6.92
6.92
6.63
6.61
4.69
3.88
3.86
3.83
3.11
MeO
Ph
CO2Me
CO2Me
O
N
Me
4
400 MHz, CDCl3
1.05
1.07
1.07
1.00
2.02
3.06
2.05
1.06
1.00
3.05
3.07
3.08
3.08
f1 (ppm)


174.75
170.35
168.73
158.87
143.30
135.04
133.69
133.64
128.77
128.01
127.81
127.73
126.70
125.67
125.09
114.22
107.90
65.96
55.41
53.50
53.15
51.80
26.25
MeO
Ph
CO2Me
CO2Me
O
N
Me
4
100 MHz, CDCl3
f1 (ppm)

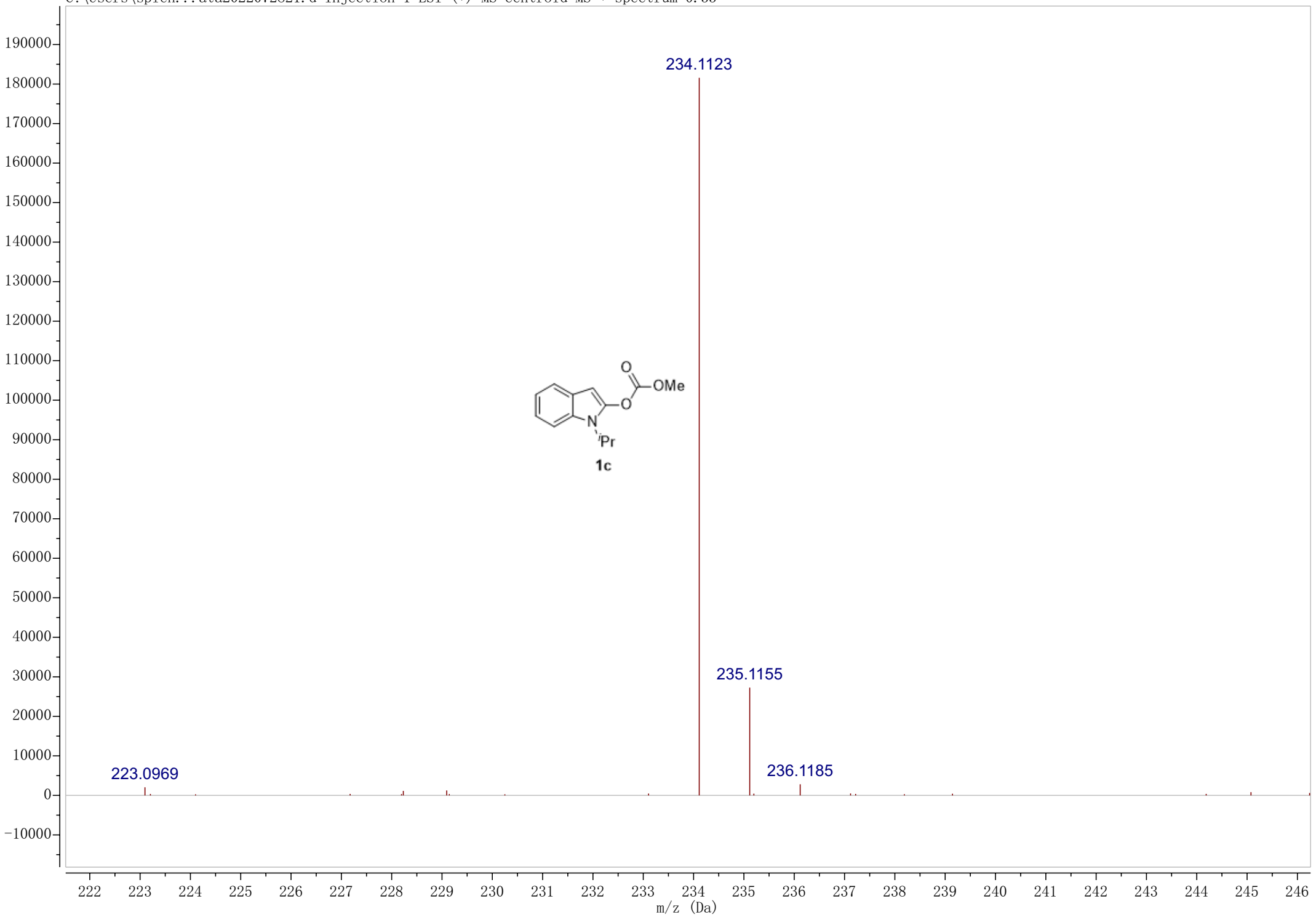

7.54
7.52
7.49
7.26
7.13
7.06
7.04
7.02
6.88
6.88
6.86
6.86
6.84
6.84
6.48
6.48
6.47
3.85
3.80
3.06
1.81
Ph
Me
CO2Me
CO2Me
O
N
Me
5
400 MHz, CDCl3
0.97
6.10
1.15
1.00
3.01
3.12
3.00
3.01
f1 (ppm)

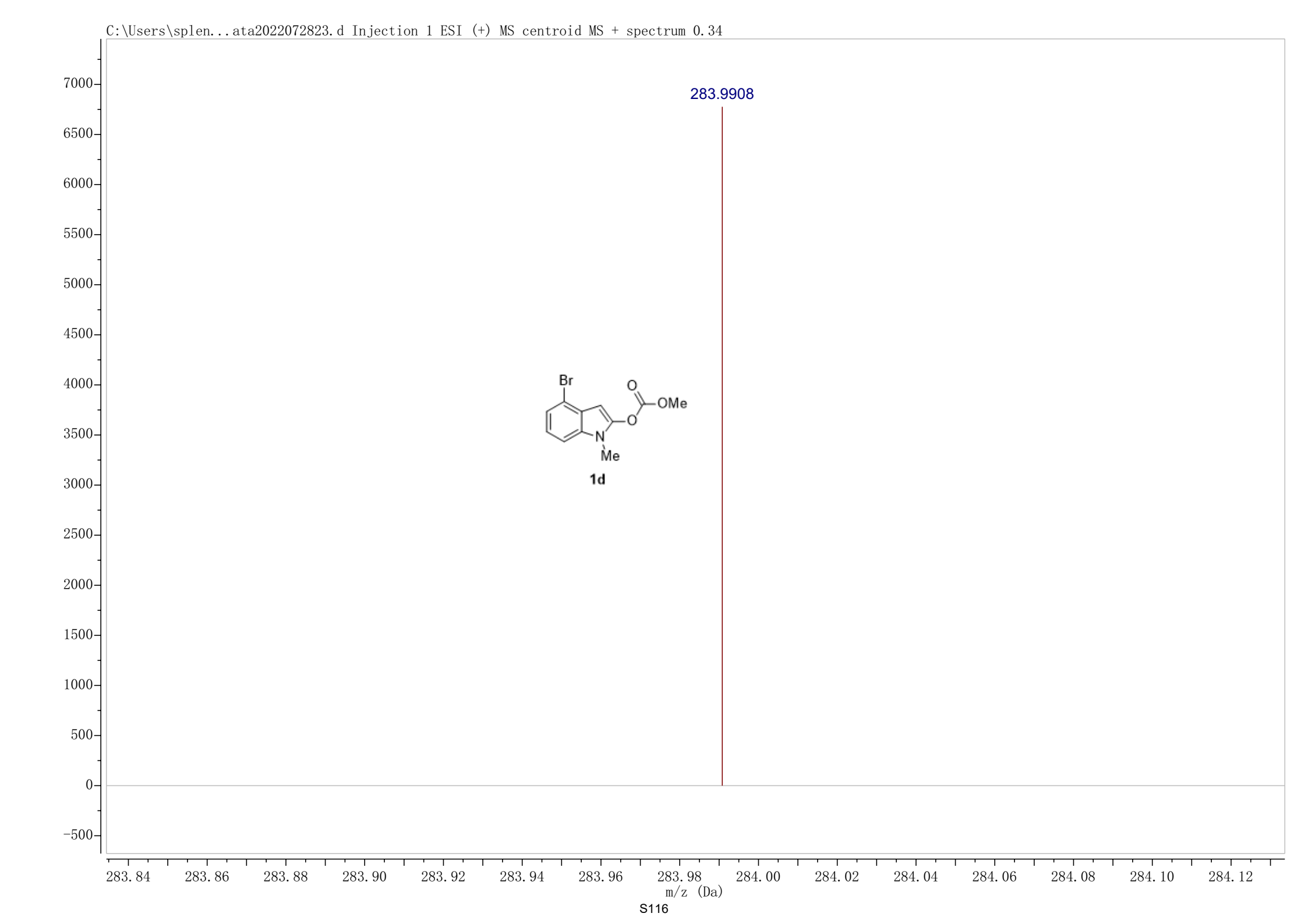

178.15
169.44
169.08
142.75
133.95
132.19
129.29
127.86
127.56
126.72
126.10
122.14
107.55
67.57
52.82
52.72
26.07
21.38
Ph
Me
CO2Me
CO2Me
N
O
Me
5
100 MHz, CDCl3
f1 (ppm)

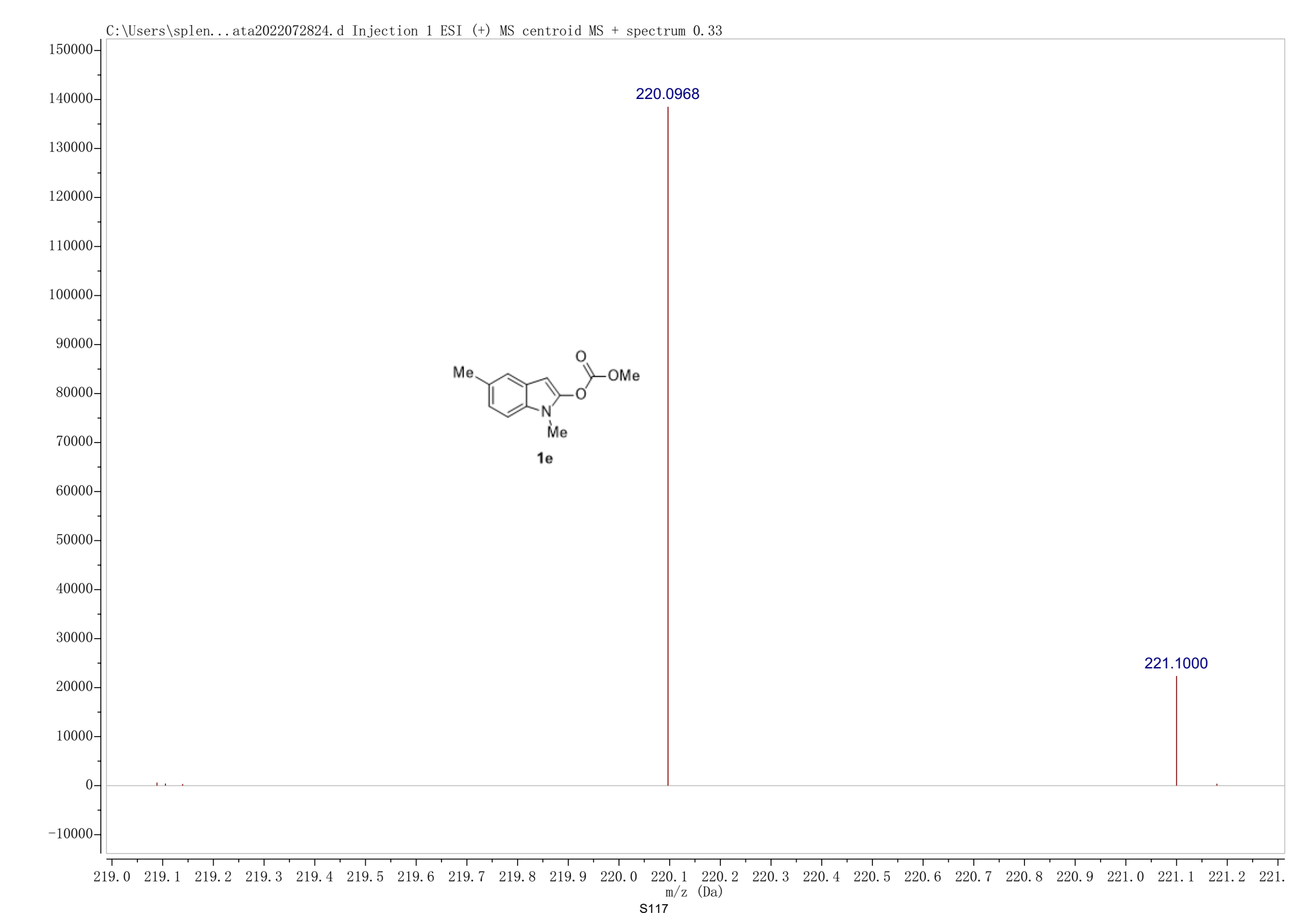

C:\Users\splen...ata2022072818.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
206.0808
207.0847
OMe
O
O
N
Me
1a
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
m/z (Da)

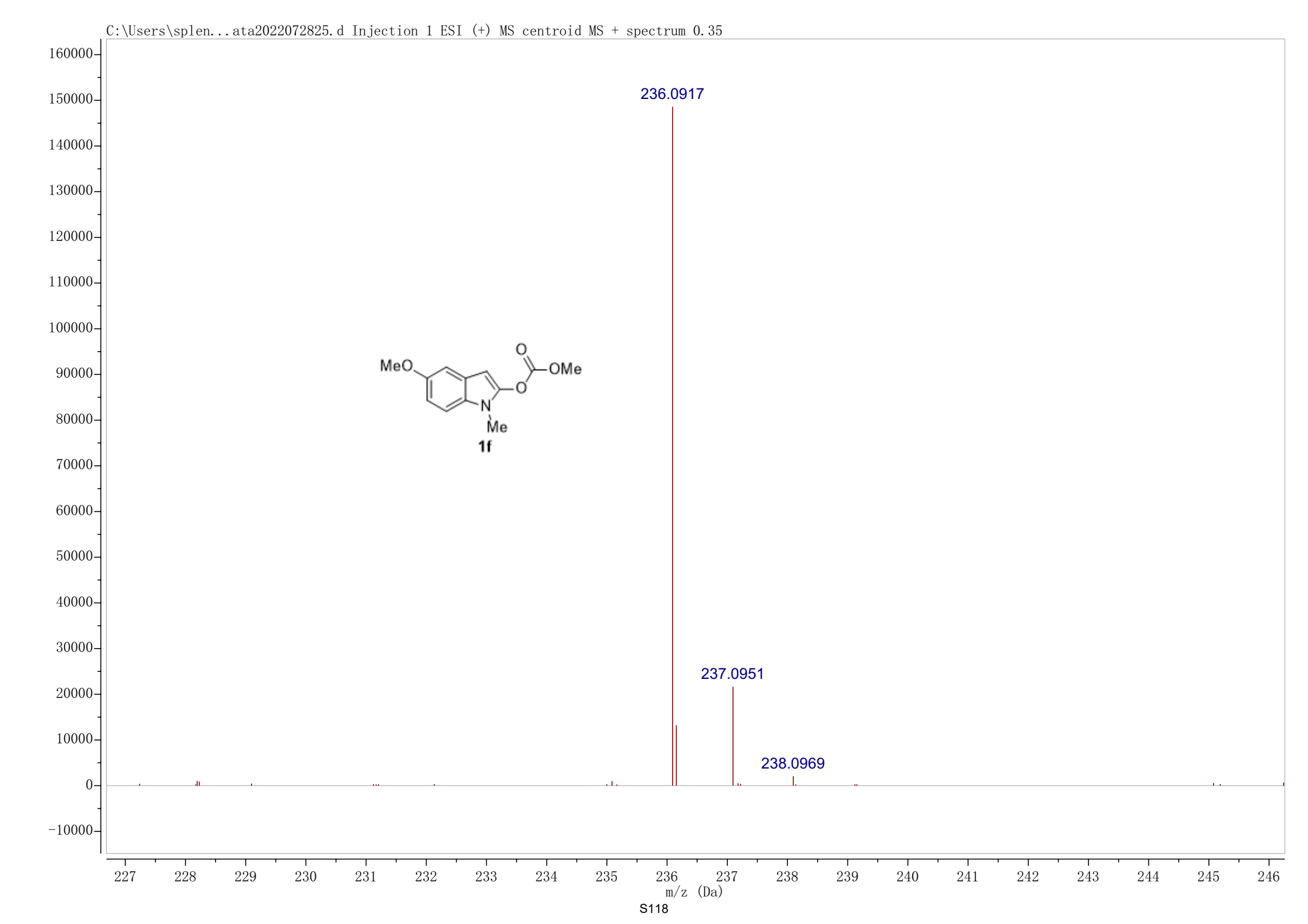

C:\Users\splen...ata2022072822.d Injection 1 ESI (+) MS centroid MS + spectrum 0.33
282.1124
282.1808
O
OMe
O
N
Bn
1b
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
282.02
282.03
282.04
282.05
282.06
282.07
282.08
282.09
282.10
282.11
282.12
282.13
282.14
282.15
282.16
282.17
282.18
282.19
282.20
m/z (Da)

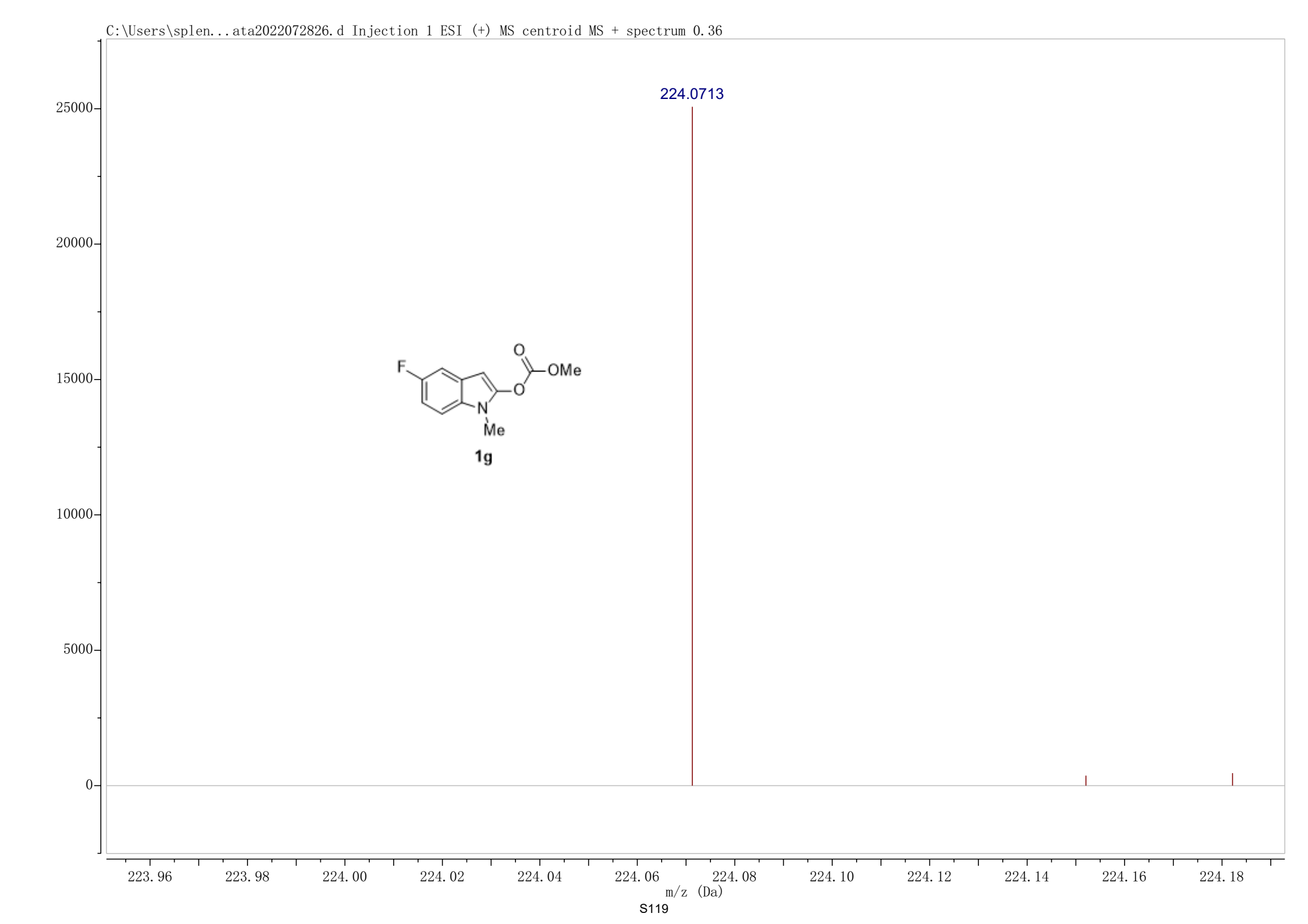
C:\Users\splen...ata2022072821.d Injection 1 ESI (+) MS centroid MS + spectrum 0.33

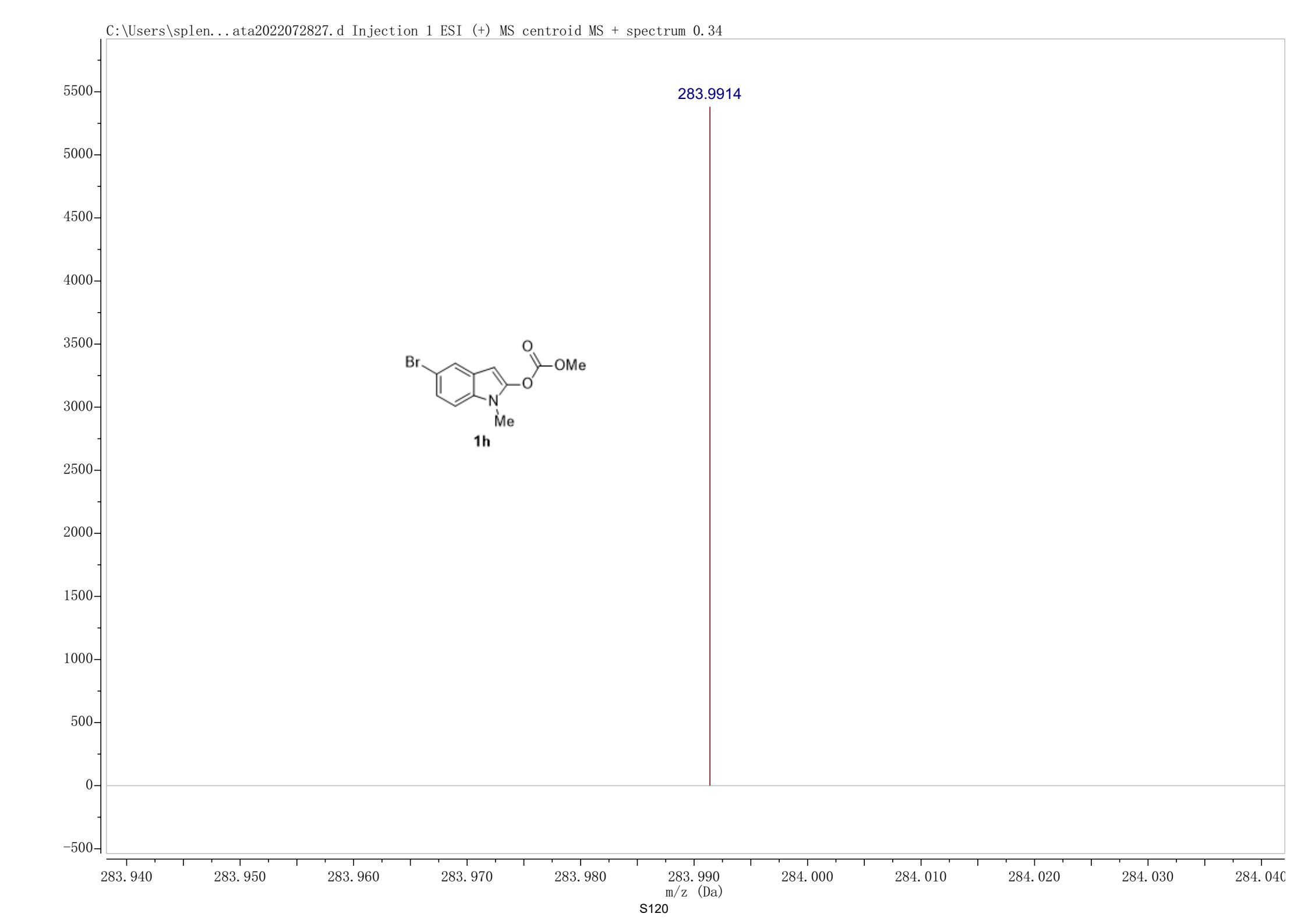


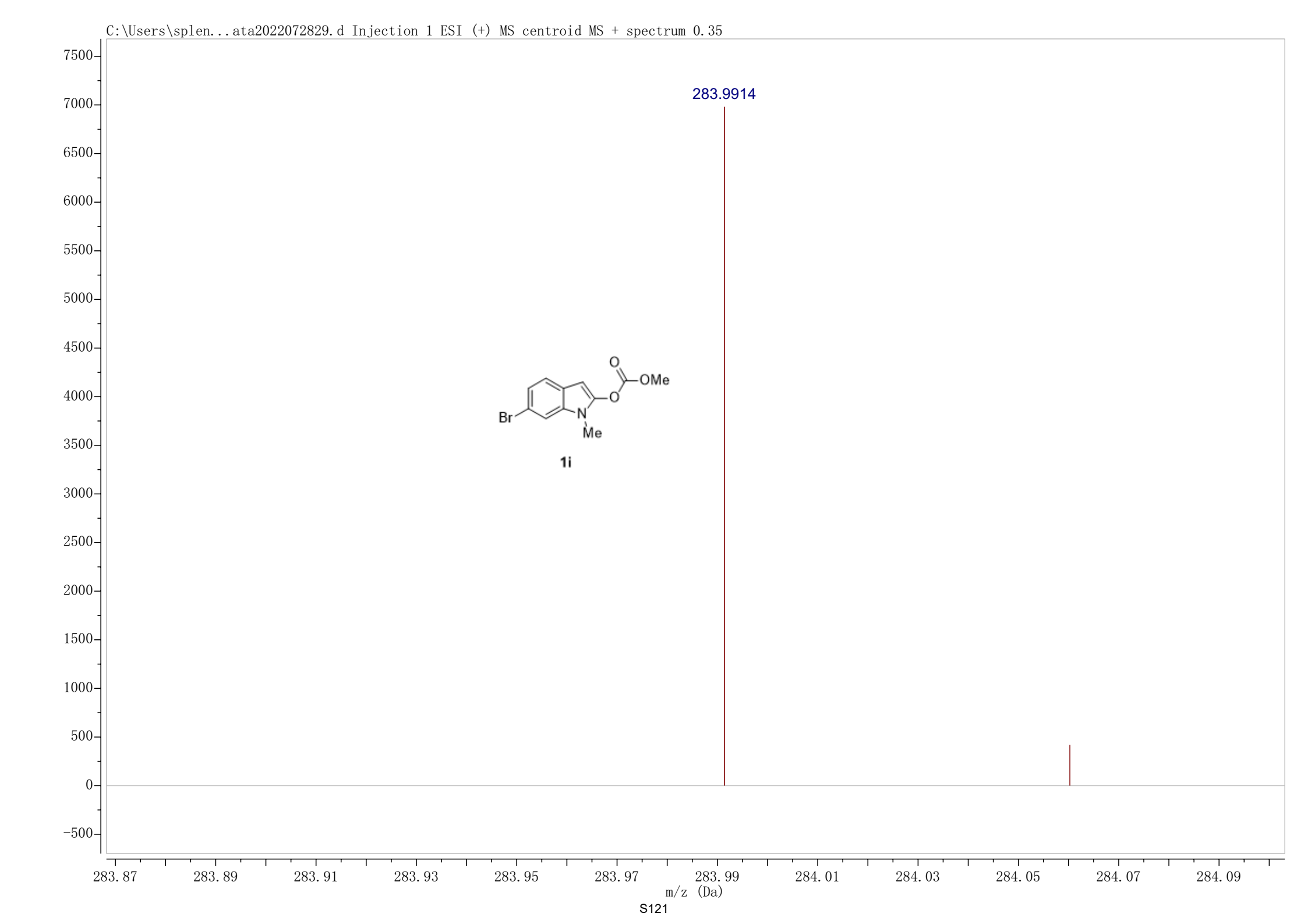

C:\Users\splen...ata2022072823.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
283.9908
Br
O
OMe
O
N
Me
1d
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
283.84
283.86
283.88
283.90
283.92
283.94
283.96
283.98
284.00
284.02
284.04
284.06
284.08
284.10
284.12
m/z (Da)

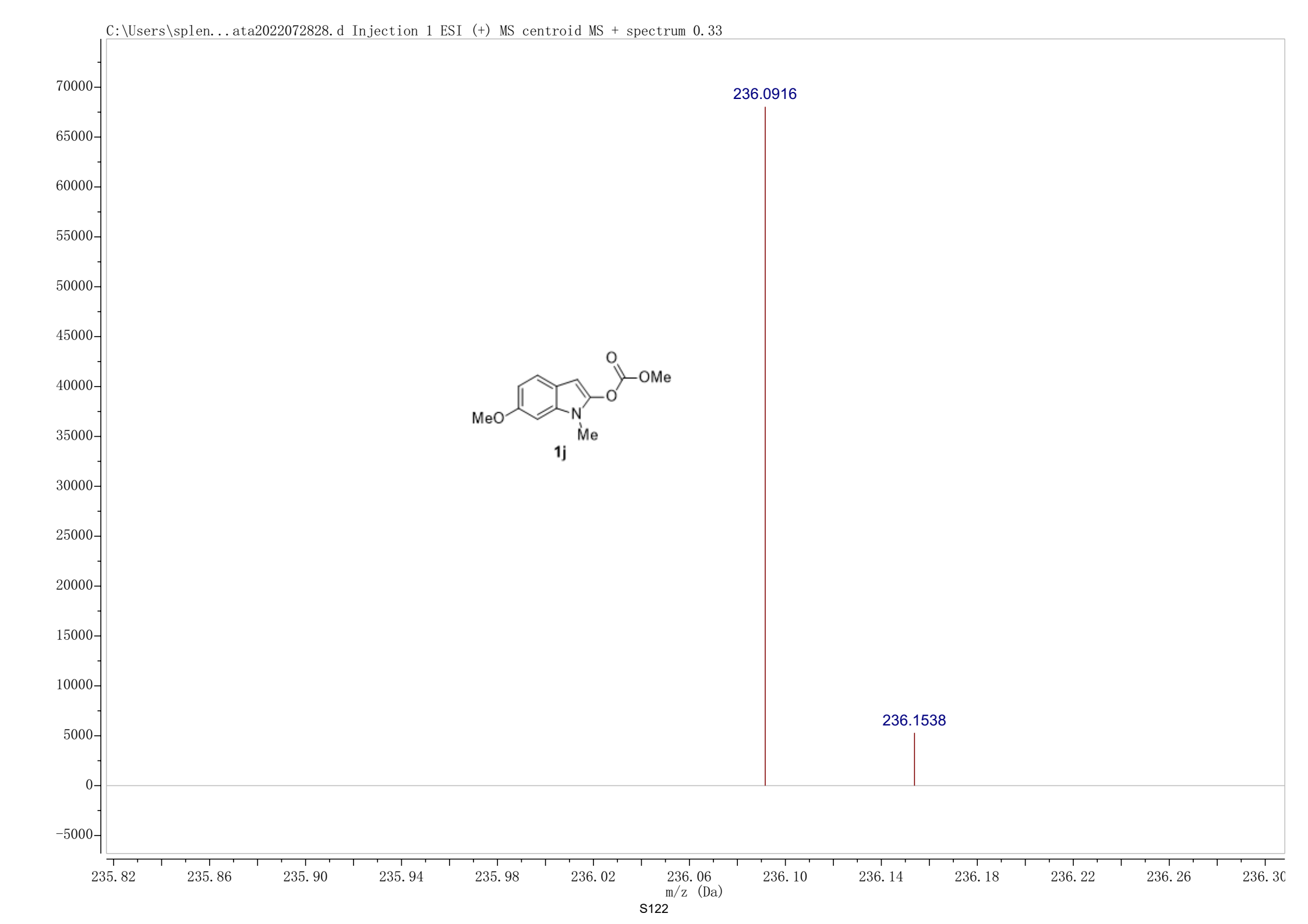

C:\Users\splen...ata2022072824.d Injection 1 ESI (+) MS centroid MS + spectrum 0.33
220.0968
221.1000
Me
O
OMe
O
N
Me
1e
m/z (Da)

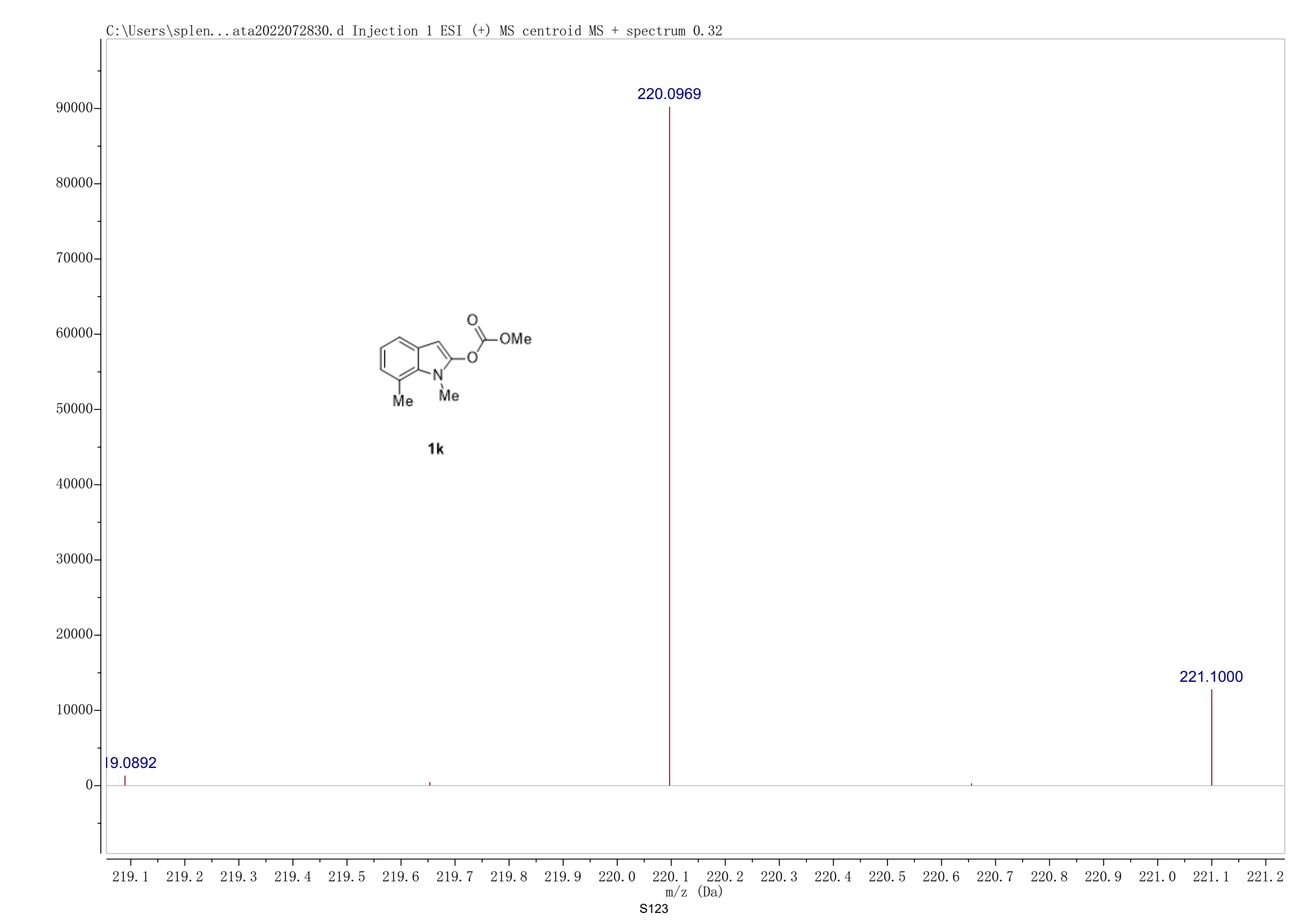

C:\Users\splen...ata2022072825.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
236.0917
237.0951
238.0969
MeO
O
OMe
O
N
Me
1f
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
m/z (Da)


C:\Users\splen...ata2022072826.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
224.0713
25000
20000
15000
10000
5000
0
F
O
OMe
O
N
Me
1g
223.96
223.98
224.00
224.02
224.04
224.06
224.08
224.10
224.12
224.14
224.16
224.18
m/z (Da)

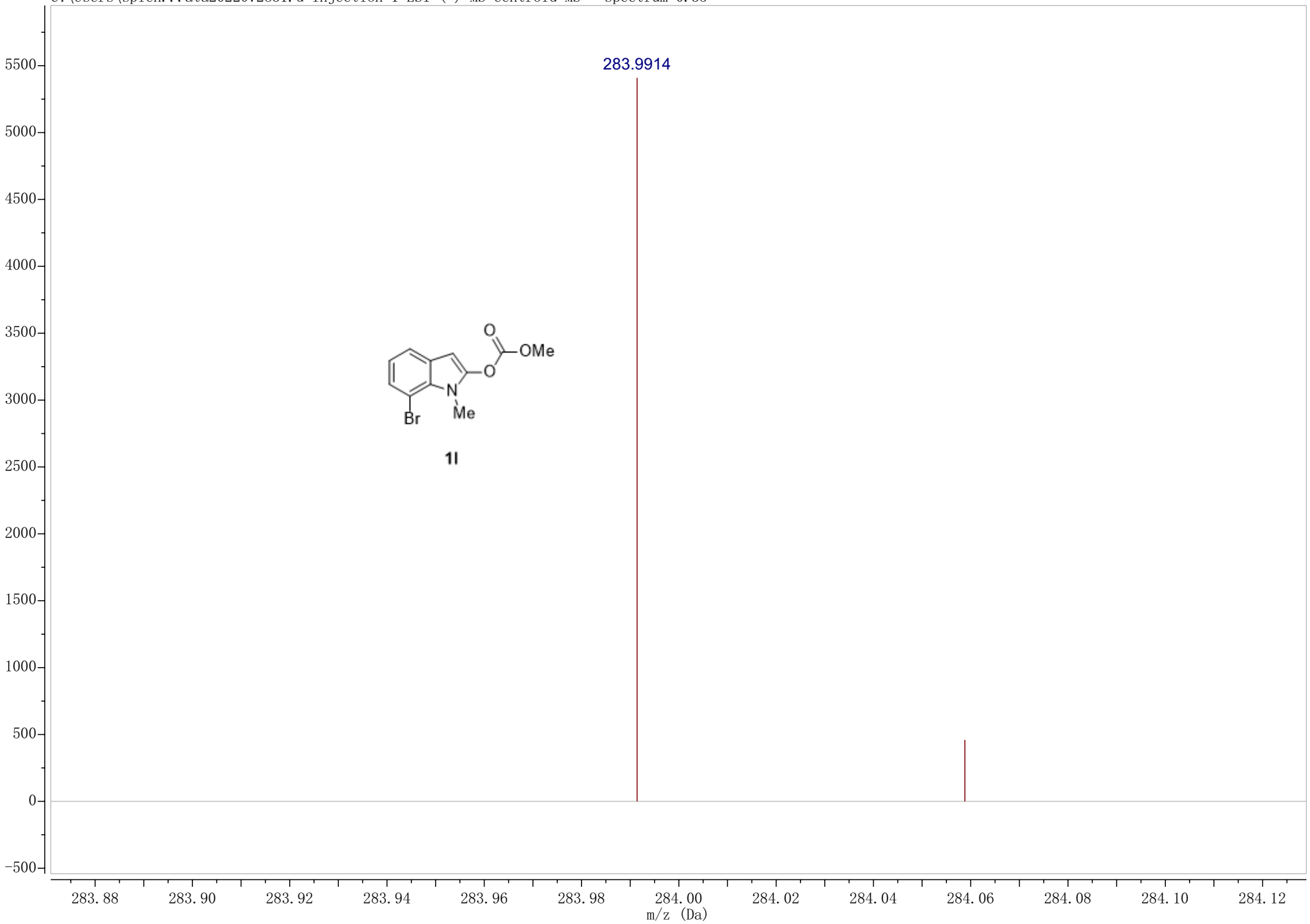

C:\Users\splen...ata2022072827.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
283.9914
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Br
O
OMe
O
N
Me
1h
283.940
283.950
283.960
283.970
283.980
283.990
284.000
284.010
284.020
284.030
284.040
m/z (Da)


C:\Users\splen...ata2022072829.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
283.9914
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
Br
N
Me
O
O
OMe
1i
283.87
283.89
283.91
283.93
283.95
283.97
283.99
284.01
284.03
284.05
284.07
284.09
m/z (Da)

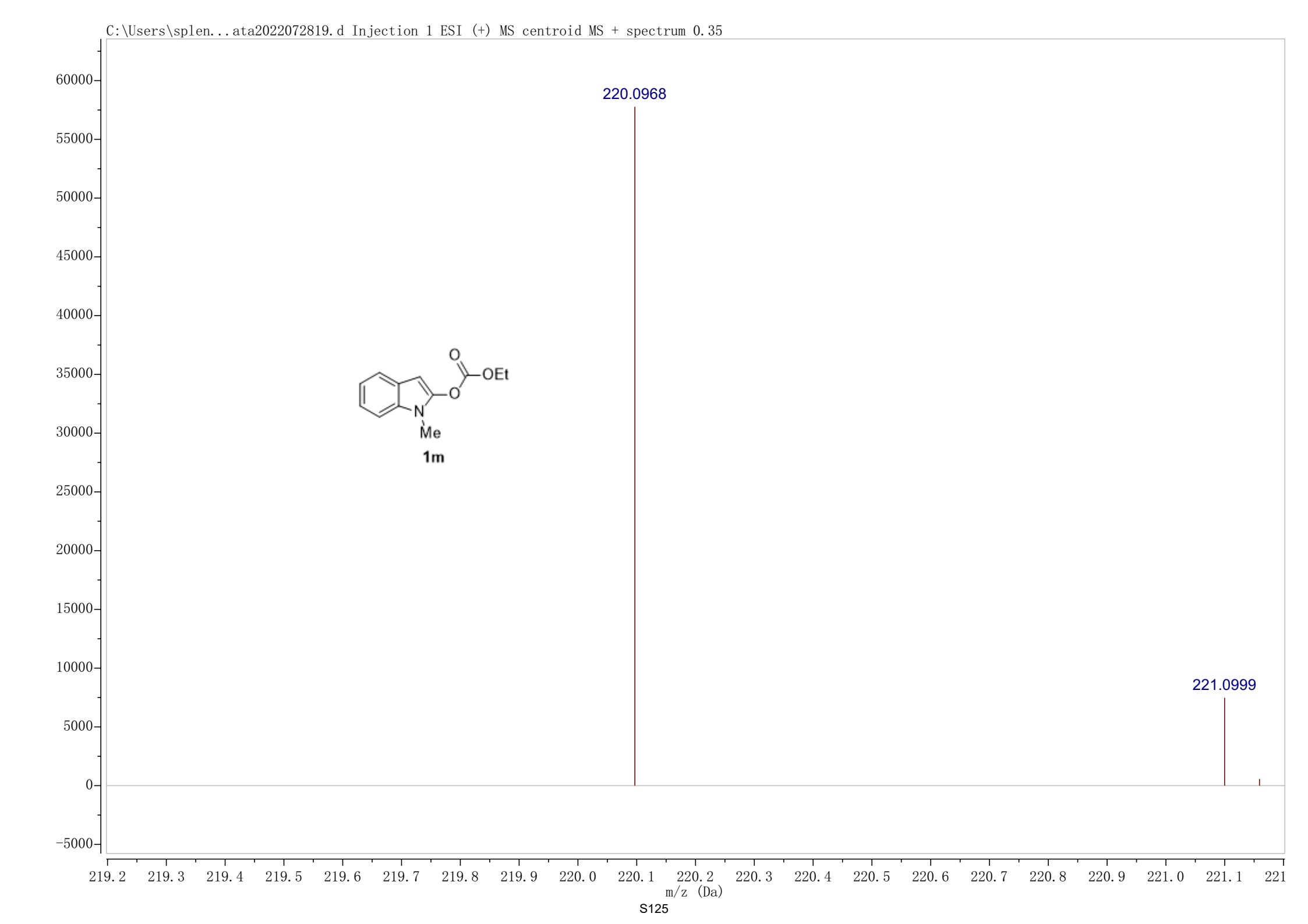

C:\Users\splen...ata2022072828.d Injection 1 ESI (+) MS centroid MS + spectrum 0.33
236.0916
236.1538
MeO
N
Me
O
OMe
1j
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
235.82
235.86
235.90
235.94
235.98
236.02
236.06
236.10
236.14
236.18
236.22
236.26
236.30
m/z (Da)

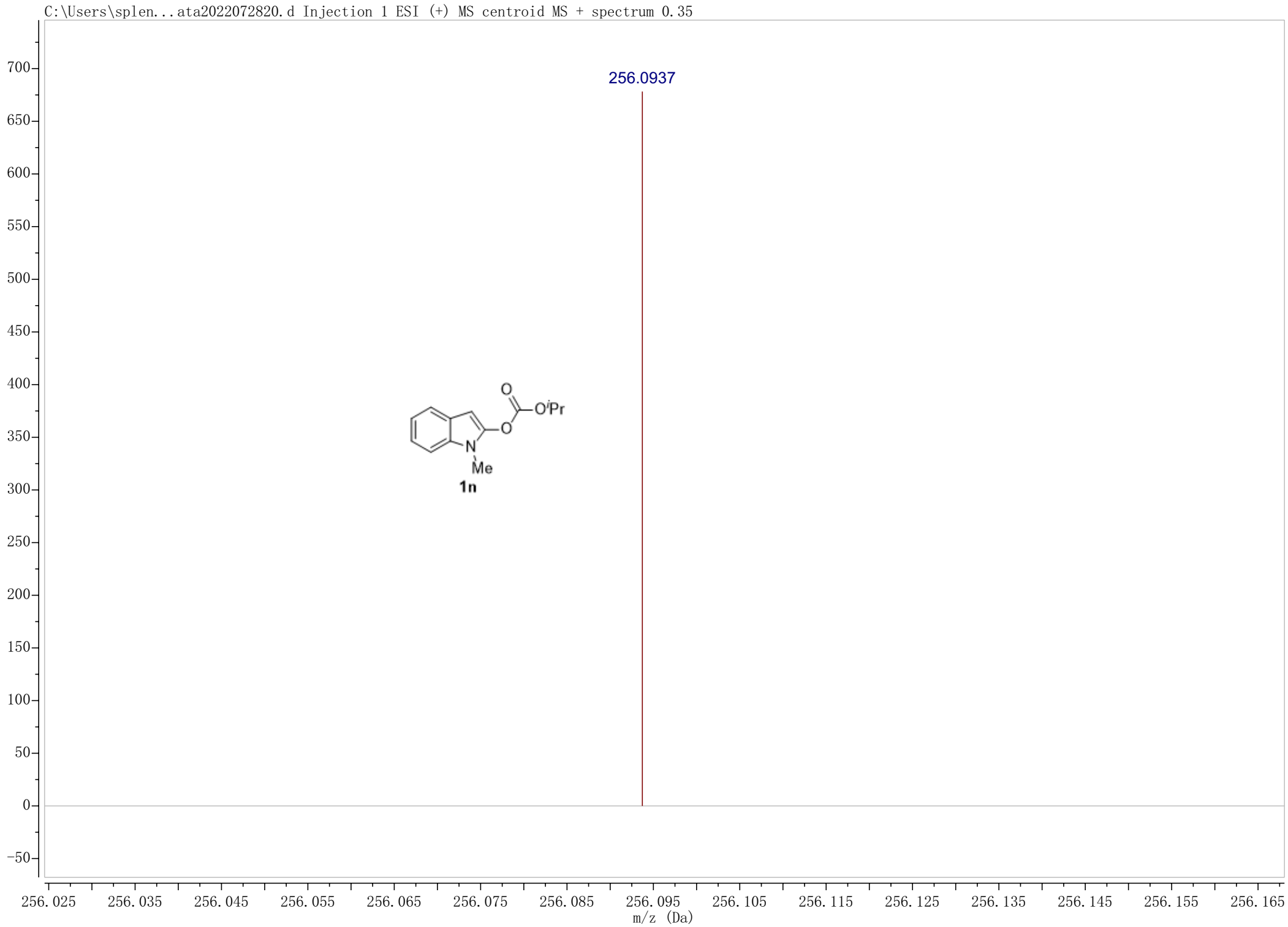

C:\Users\splen...ata2022072830.d Injection 1 ESI (+) MS centroid MS + spectrum 0.32
220.0969
221.1000
19.0892
O
OMe
O
N
Me
Me
1k
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
219.1
219.2
219.3
219.4
219.5
219.6
219.7
219.8
219.9
220.0
220.1
220.2
220.3
220.4
220.5
220.6
220.7
220.8
220.9
221.0
221.1
221.2
m/z (Da)

C:\Users\splen...ata2022072831.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35

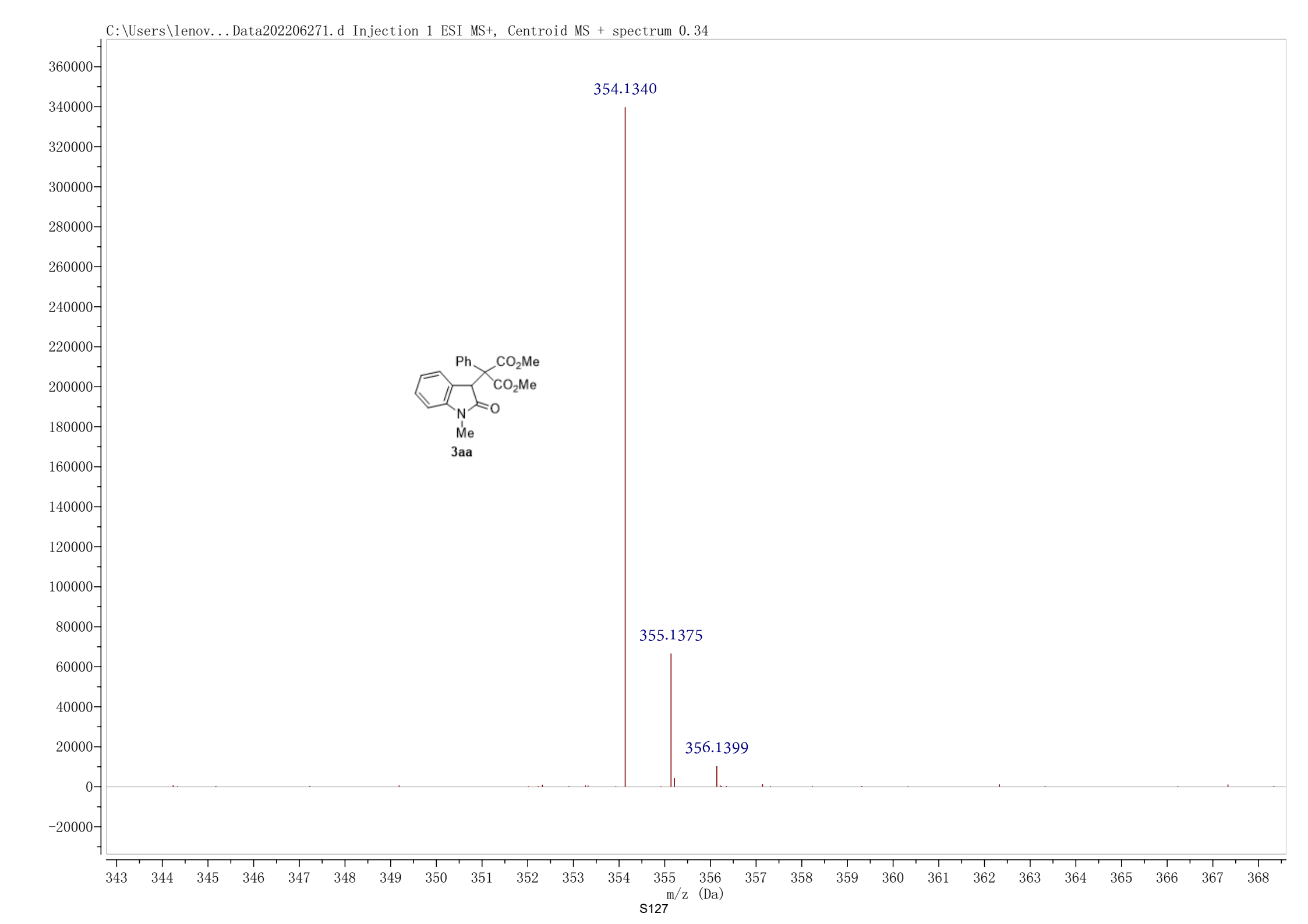


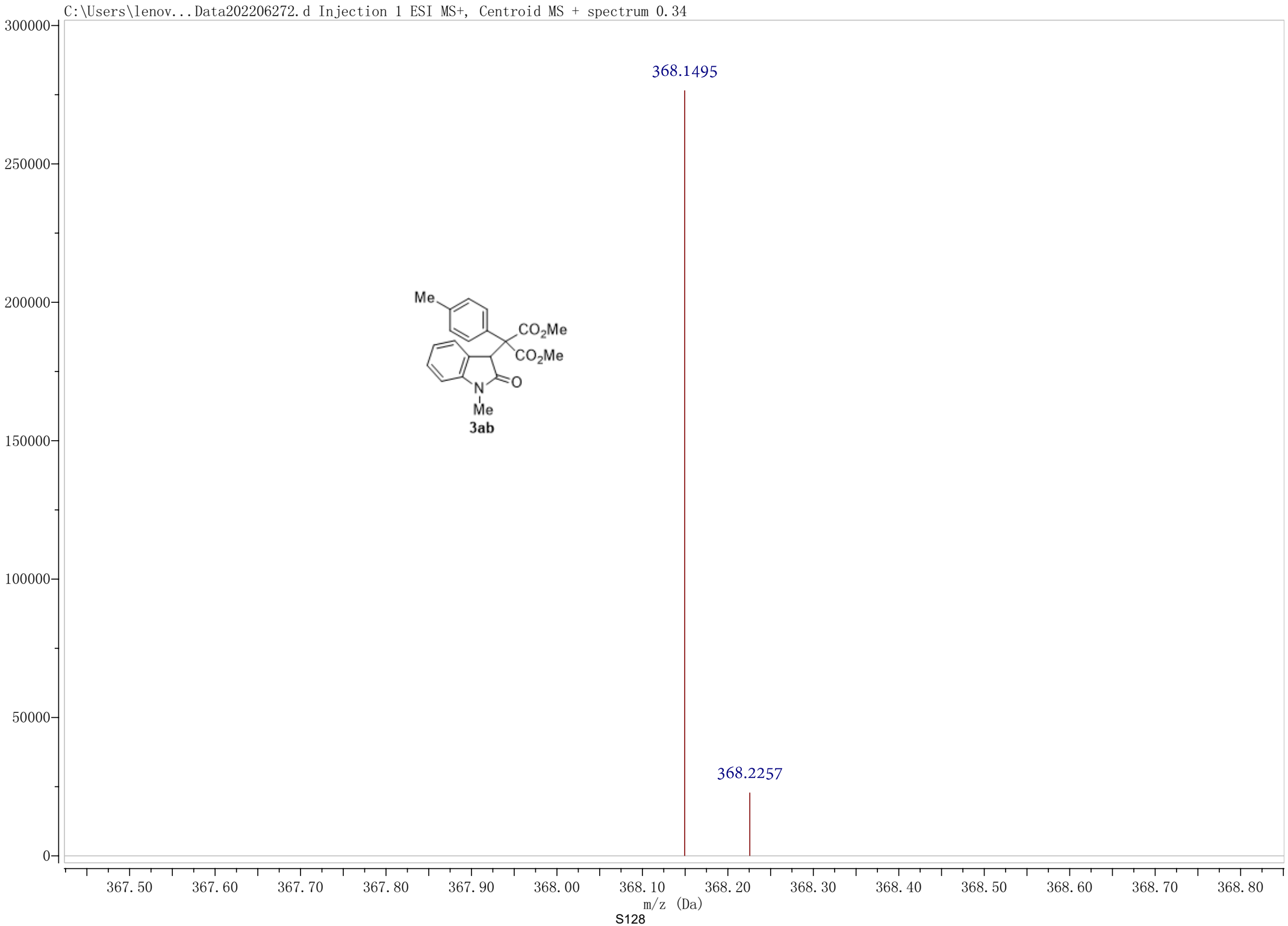
1l

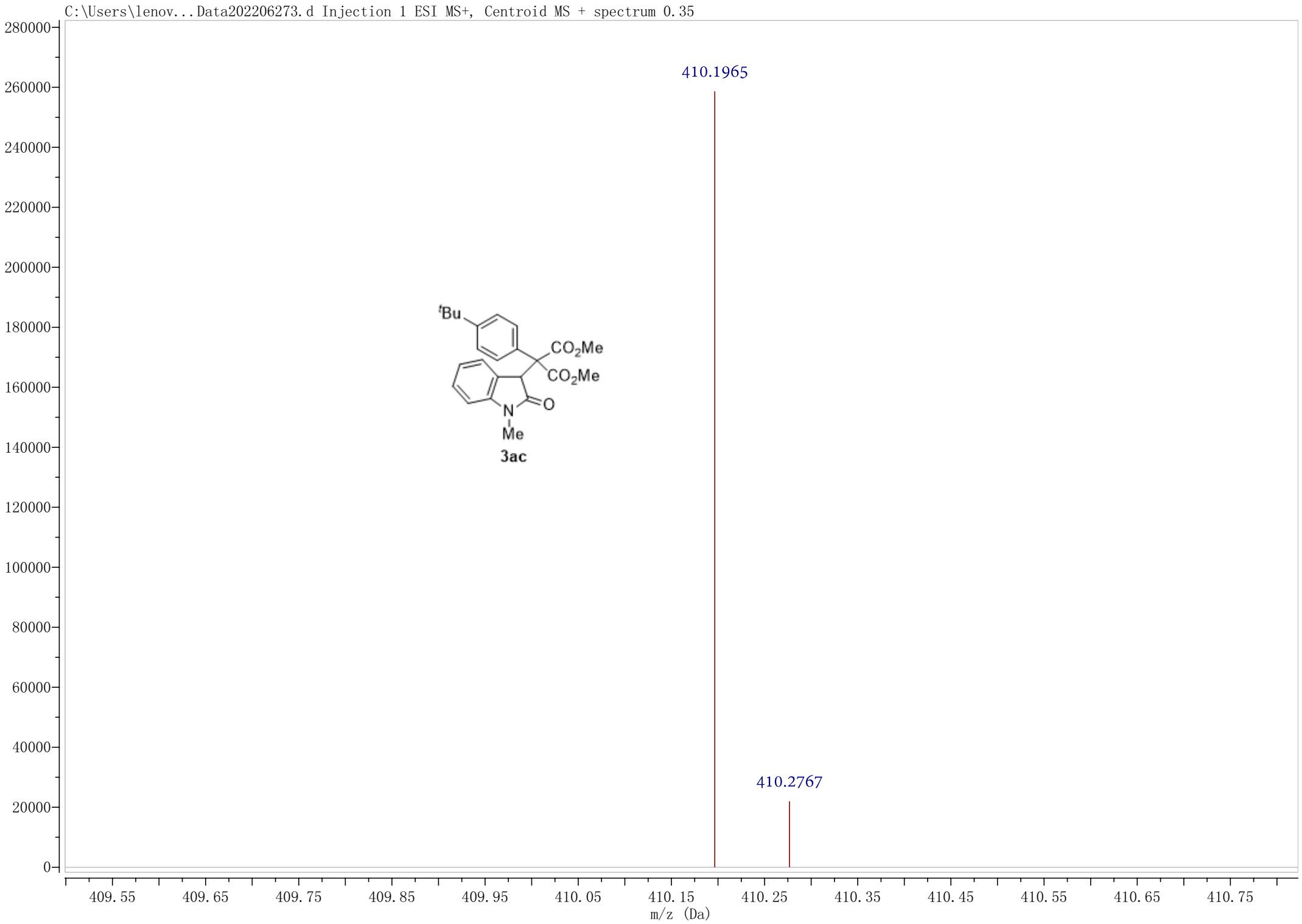

C:\Users\splen...ata2022072819.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
220.0968
221.0999
O
OEt
O
N
Me
1m
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
219.2
219.3
219.4
219.5
219.6
219.7
219.8
219.9
220.0
220.1
220.2
220.3
220.4
220.5
220.6
220.7
220.8
220.9
221.0
221.1
221
m/z (Da)

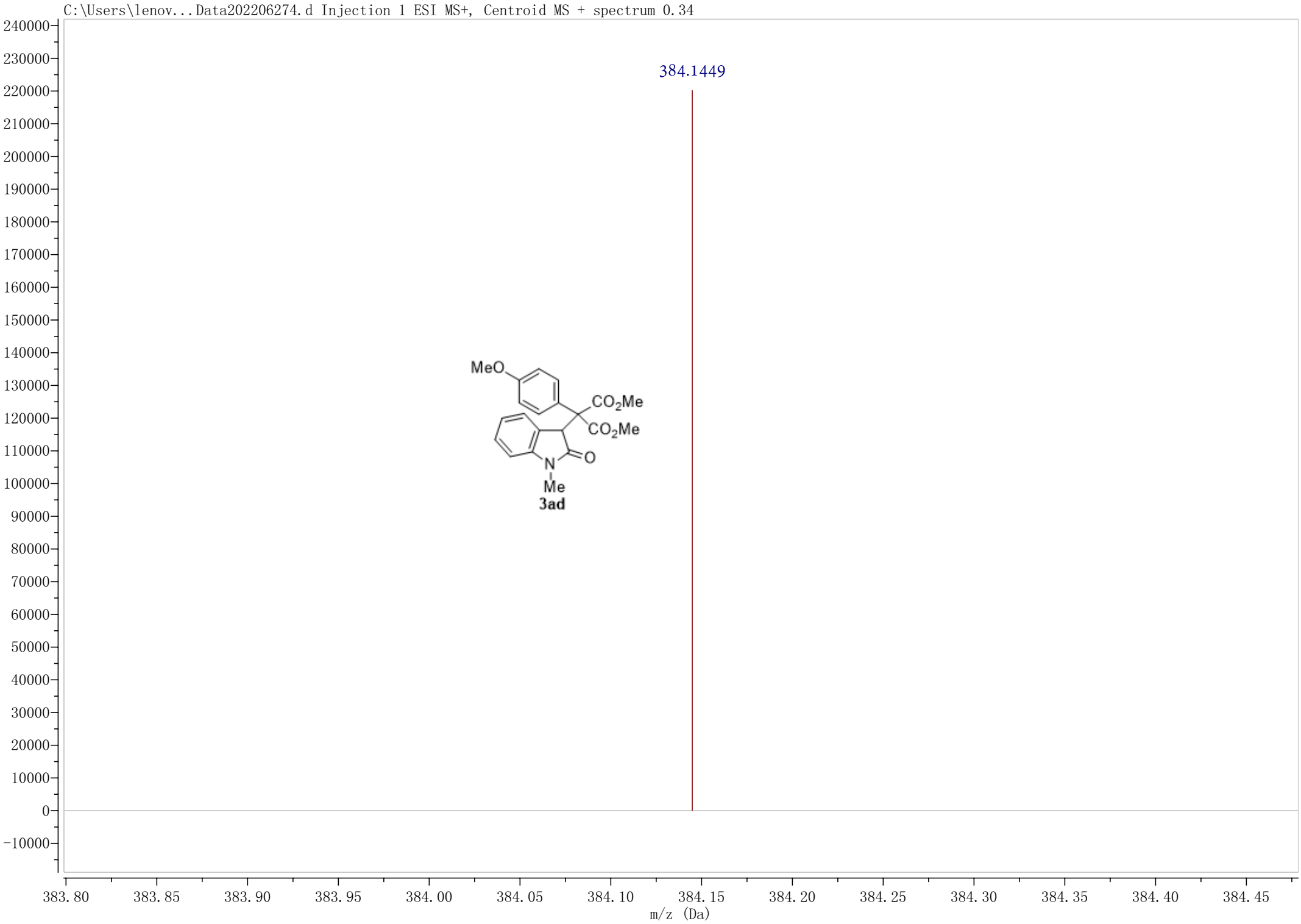

C:\Users\splen...ata2022072820.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
256.0937
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
O
O
O
iPr
N
Me
1n
256.025
256.035
256.045
256.055
256.065
256.075
256.085
256.095
256.105
256.115
256.125
256.135
256.145
256.155
256.165
m/z (Da)

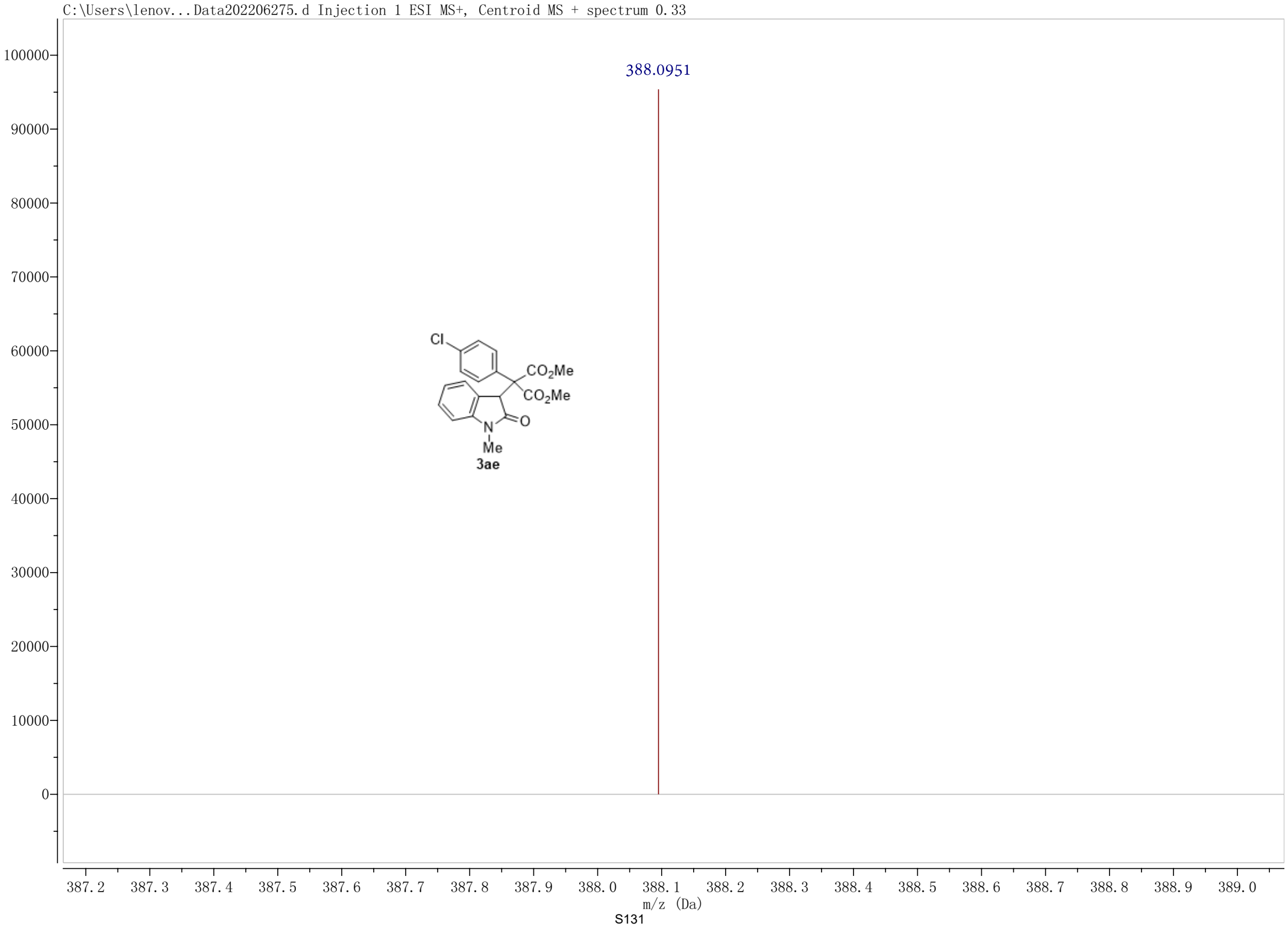
C:\Users\lenov...Data202206271.d Injection 1 ESI MS+, Centroid MS + spectrum 0.34

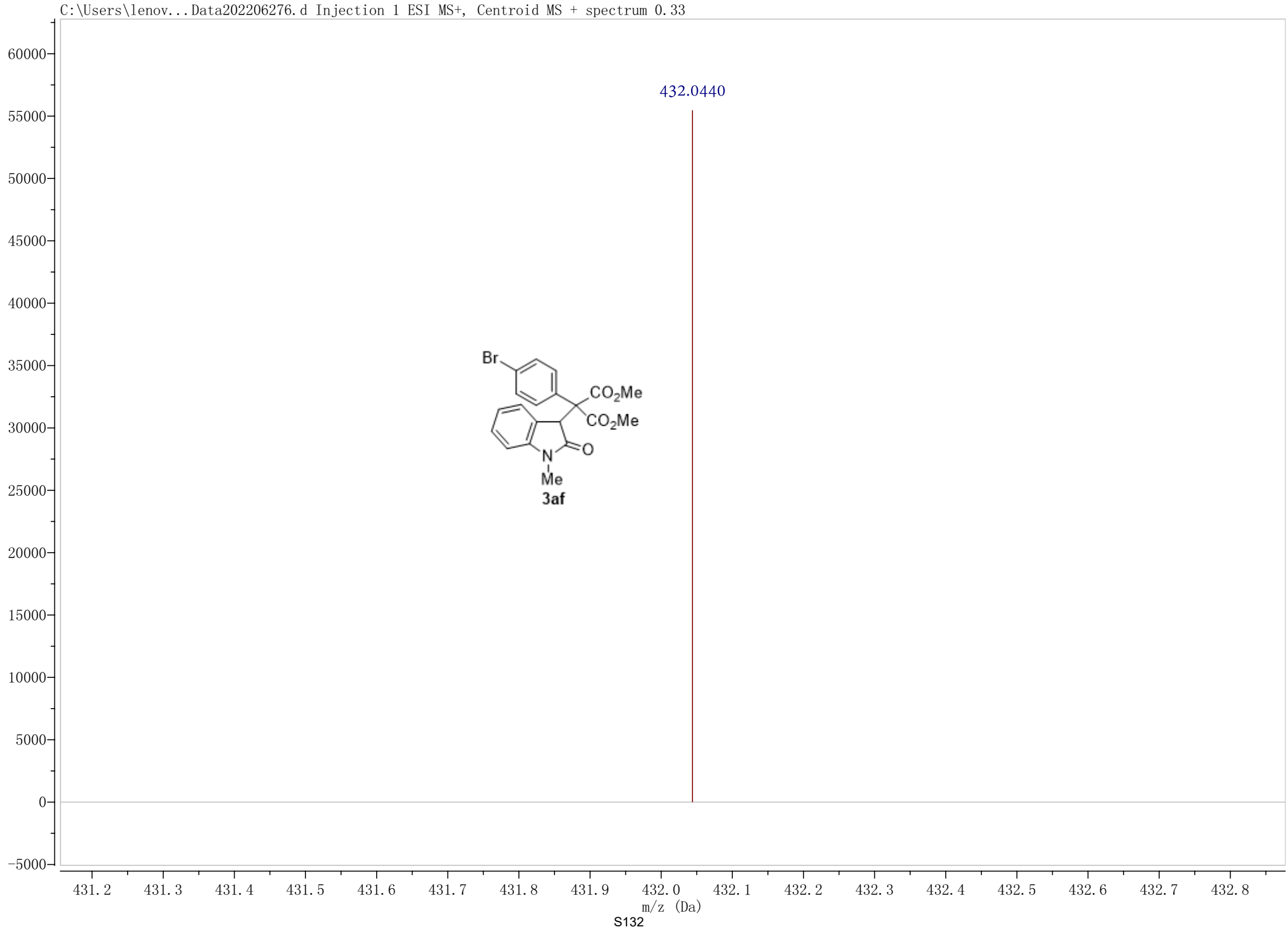


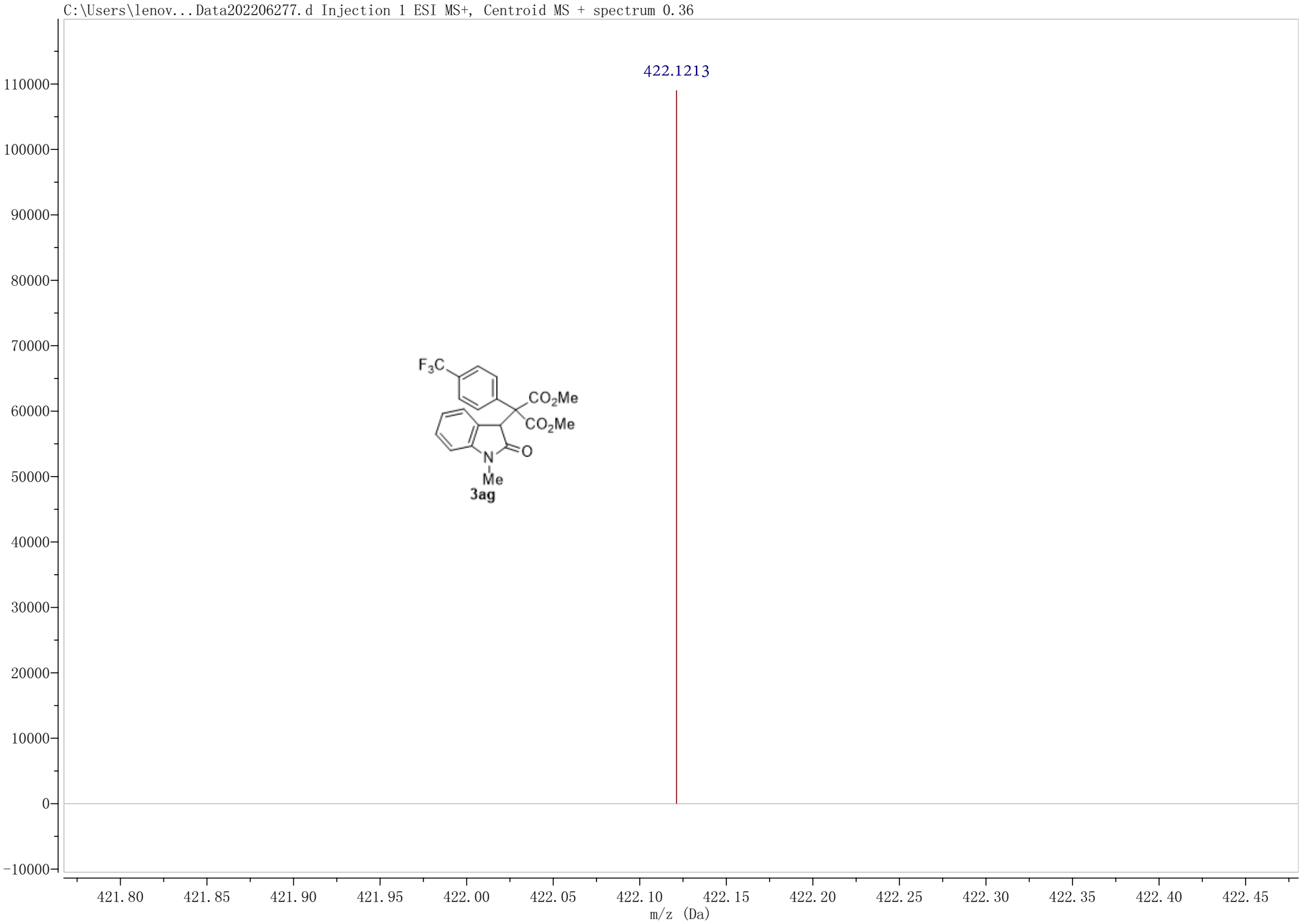

C:\Users\lenov...Data202206272.d Injection 1 ESI MS+, Centroid MS + spectrum 0.34
368.1495
368.2257
Me
CO2Me
CO2Me
O
N
Me
3ab
300000
250000
200000
150000
100000
50000
0
367.50
367.60
367.70
367.80
367.90
368.00
368.10
368.20
368.30
368.40
368.50
368.60
368.70
368.80
m/z (Da)

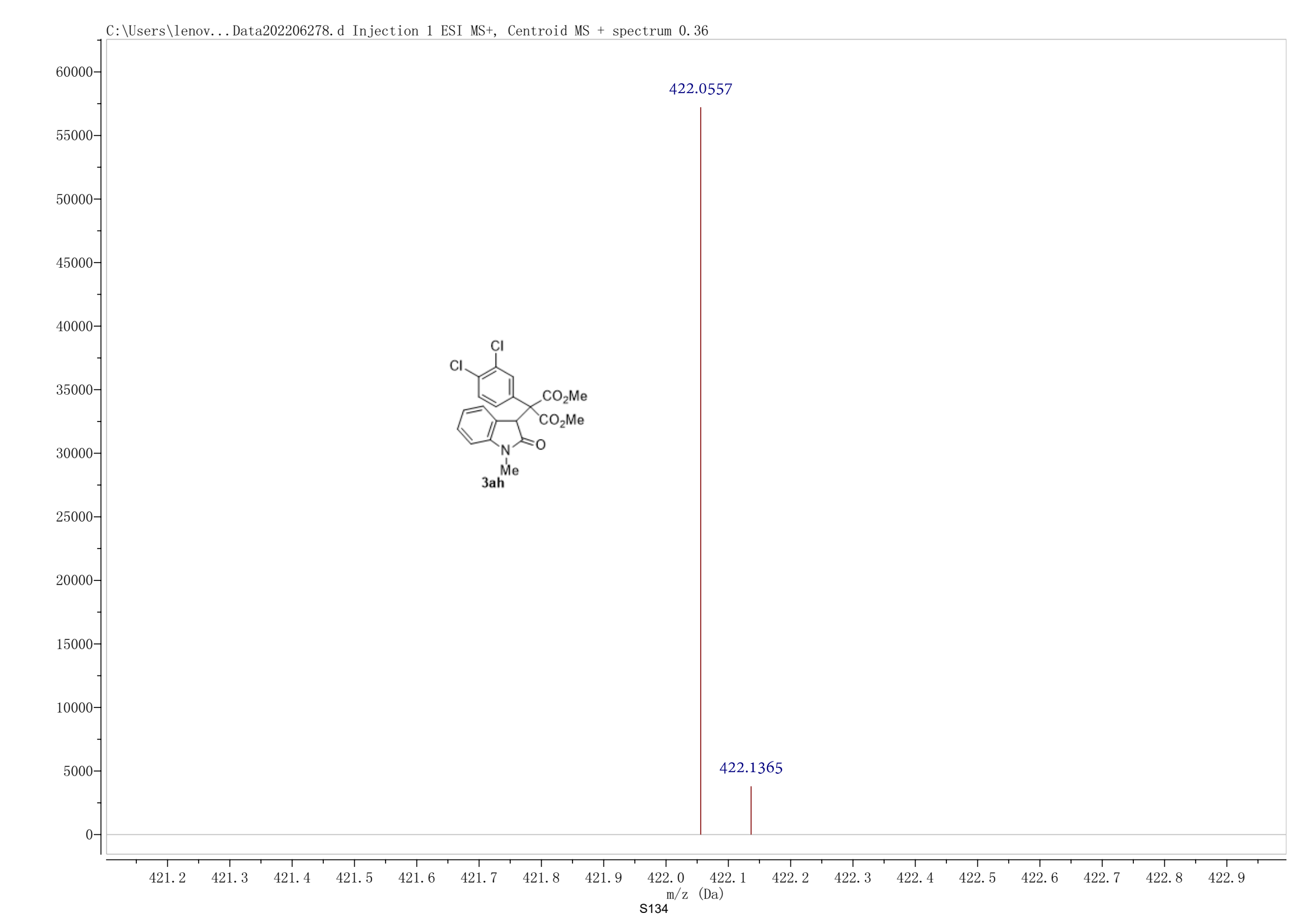

C:\Users\lenov...Data202206273.d Injection 1 ESI MS+, Centroid MS + spectrum 0.35
410.1965
410.2767
tBu
CO2Me
CO2Me
N
O
Me
3ac
m/z (Da)

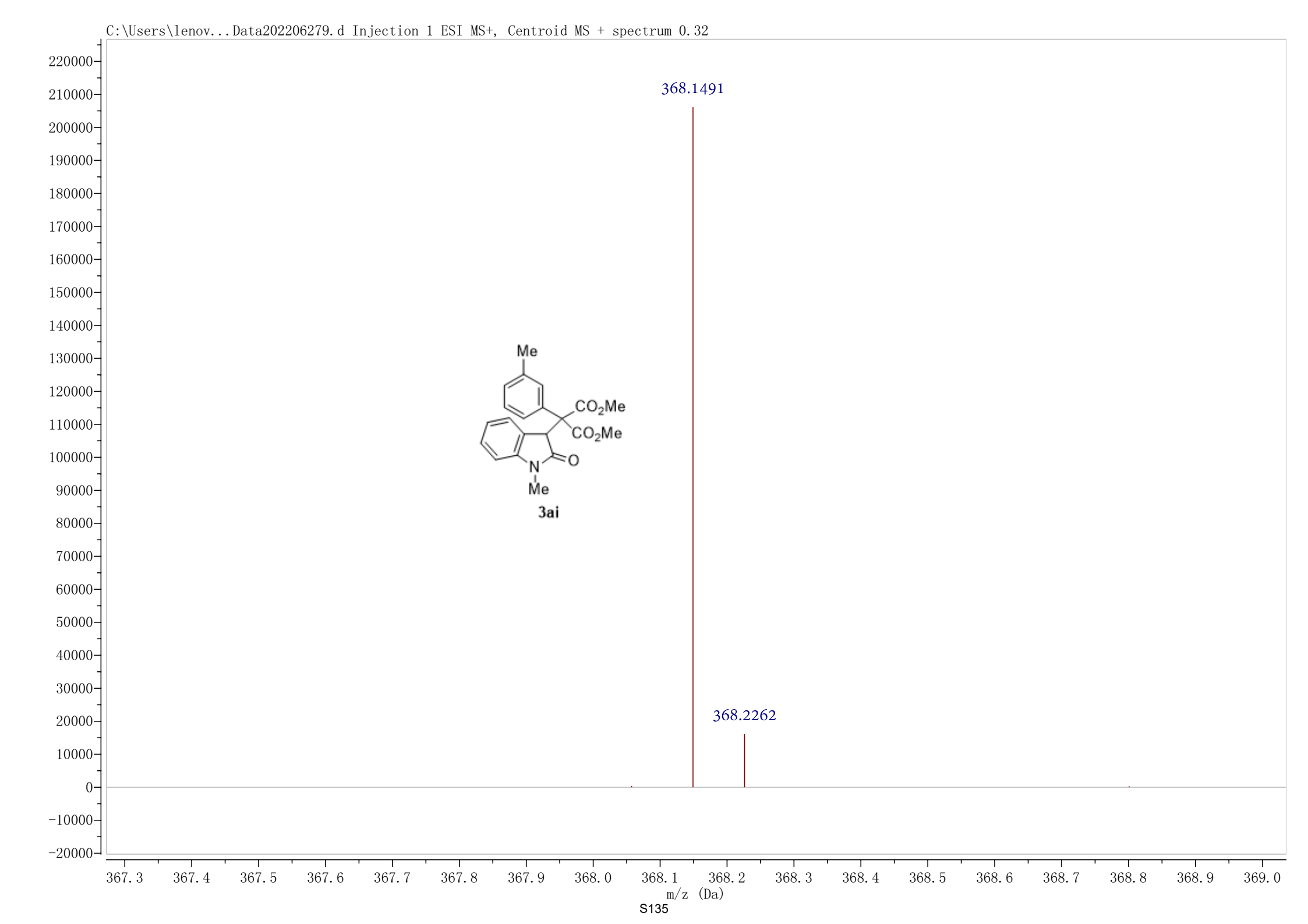

C:\Users\lenov...Data202206274.d Injection 1 ESI MS+, Centroid MS + spectrum 0.34
384.1449
MeO
CO2Me
CO2Me
O
N
Me
3ad
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
383.80
383.85
383.90
383.95
384.00
384.05
384.10
384.15
384.20
384.25
384.30
384.35
384.40
384.45
m/z (Da)

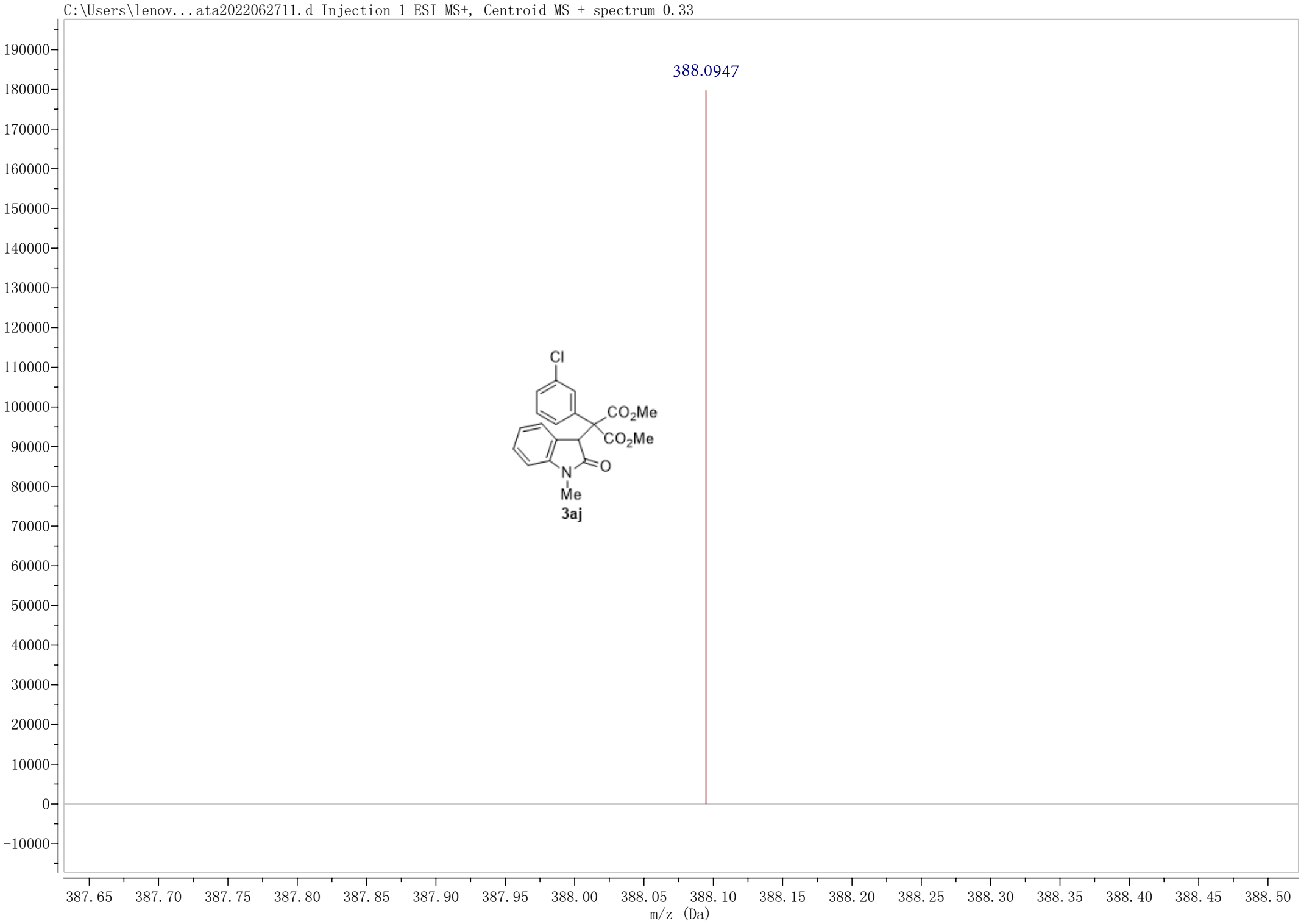

C:\Users\lenov...Data202206275.d Injection 1 ESI MS+, Centroid MS + spectrum 0.33
388.0951
Cl
CO2Me
CO2Me
O
N
Me
3ae
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
387.2
387.3
387.4
387.5
387.6
387.7
387.8
387.9
388.0
388.1
388.2
388.3
388.4
388.5
388.6
388.7
388.8
388.9
389.0
m/z (Da)

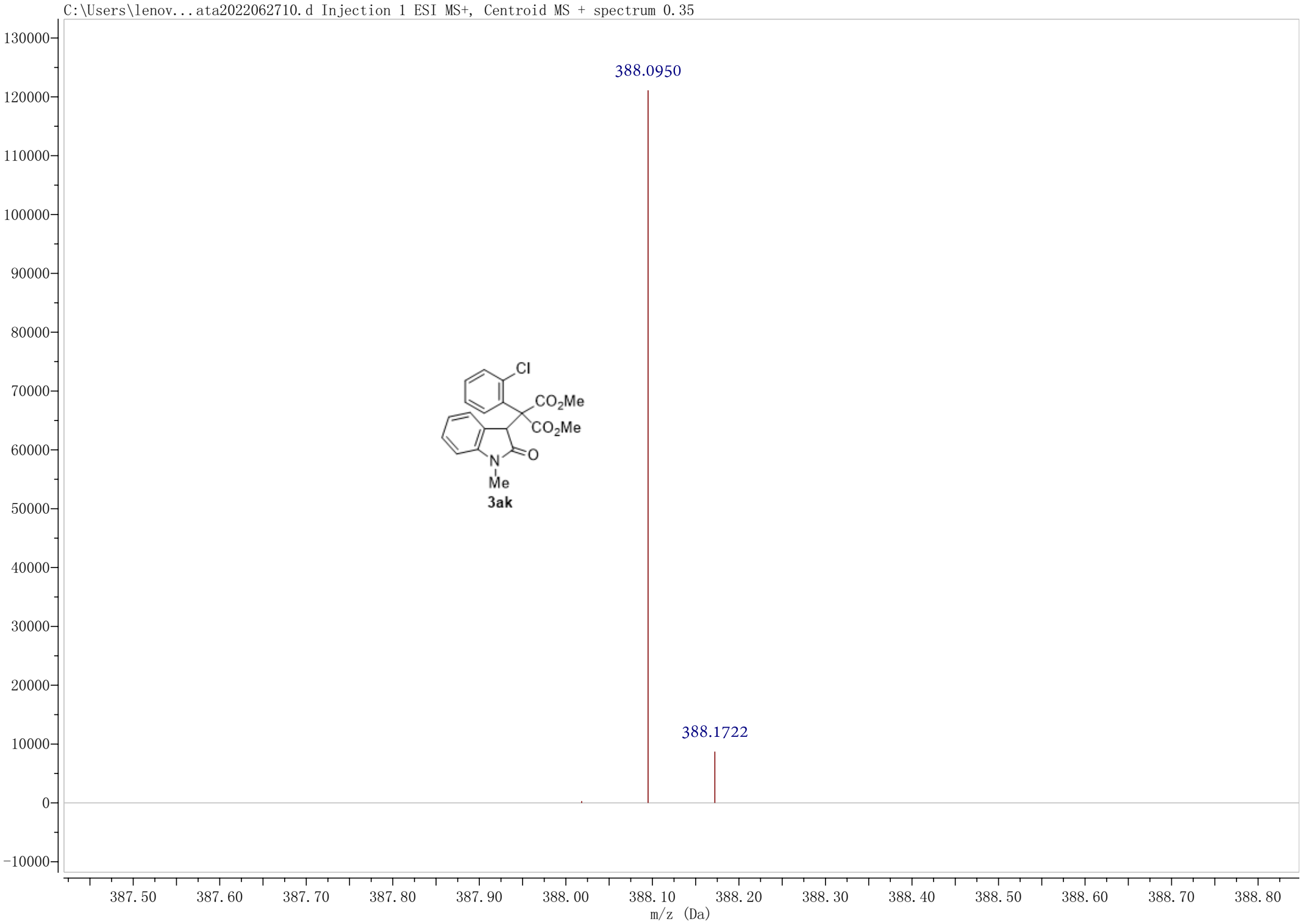

C:\Users\lenov...Data202206276.d Injection 1 ESI MS+, Centroid MS + spectrum 0.33
432.0440
Br
CO2Me
CO2Me
O
N
Me
3af
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
431.2
431.3
431.4
431.5
431.6
431.7
431.8
431.9
432.0
432.1
432.2
432.3
432.4
432.5
432.6
432.7
432.8
m/z (Da)

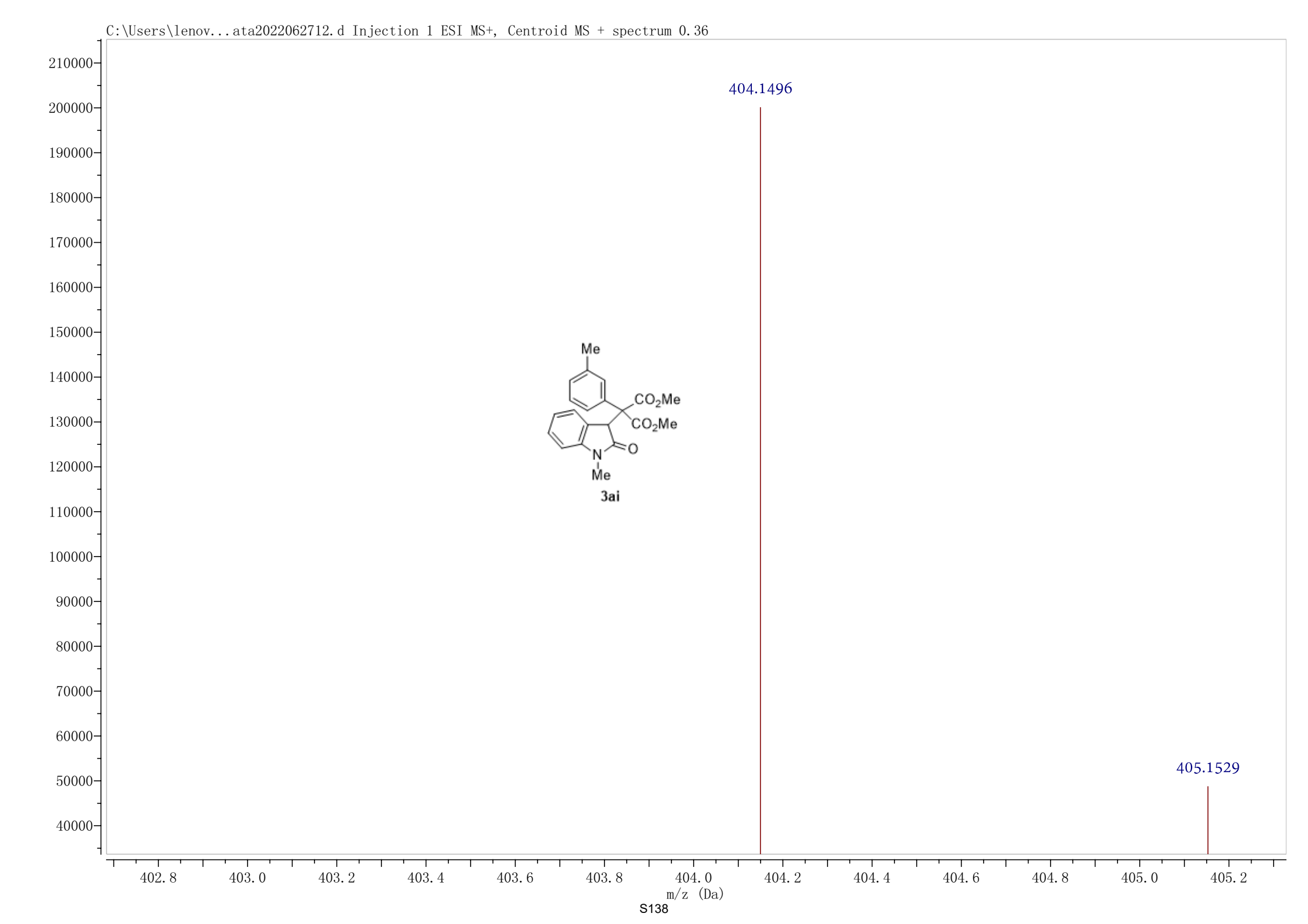

C:\Users\lenov...Data202206277.d Injection 1 ESI MS+, Centroid MS + spectrum 0.36
422.1213
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
421.80
421.85
421.90
421.95
422.00
422.05
422.10
422.15
422.20
422.25
422.30
422.35
422.40
422.45
m/z (Da)
F3C
CO2Me
CO2Me
O
N
Me
3ag

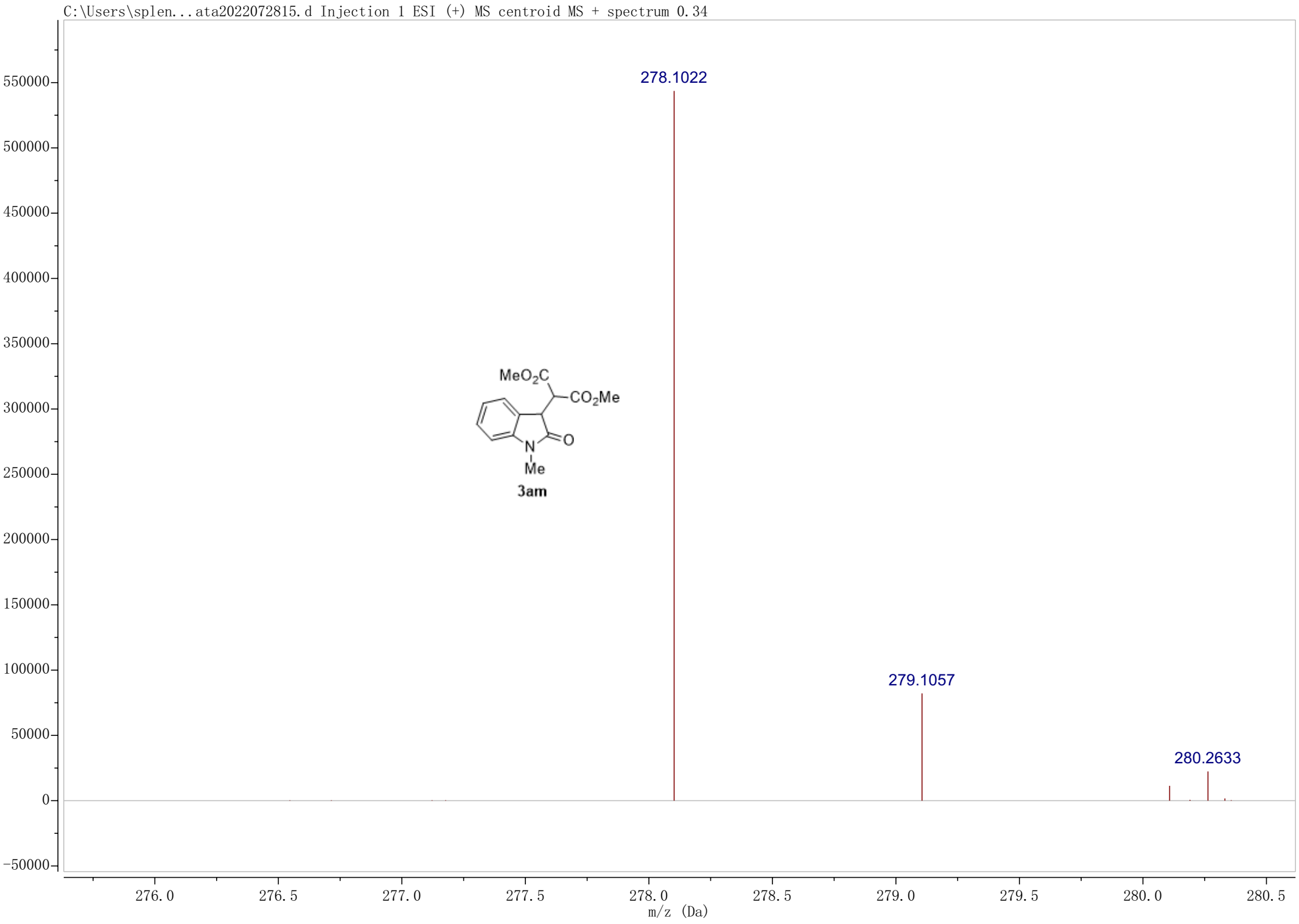

C:\Users\lenov...Data202206278.d Injection 1 ESI MS+, Centroid MS + spectrum 0.36
422.0557
422.1365
Cl
Cl
CO2Me
CO2Me
N
Me
O
3ah
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
421.2
421.3
421.4
421.5
421.6
421.7
421.8
421.9
422.0
422.1
422.2
422.3
422.4
422.5
422.6
422.7
422.8
422.9
m/z (Da)

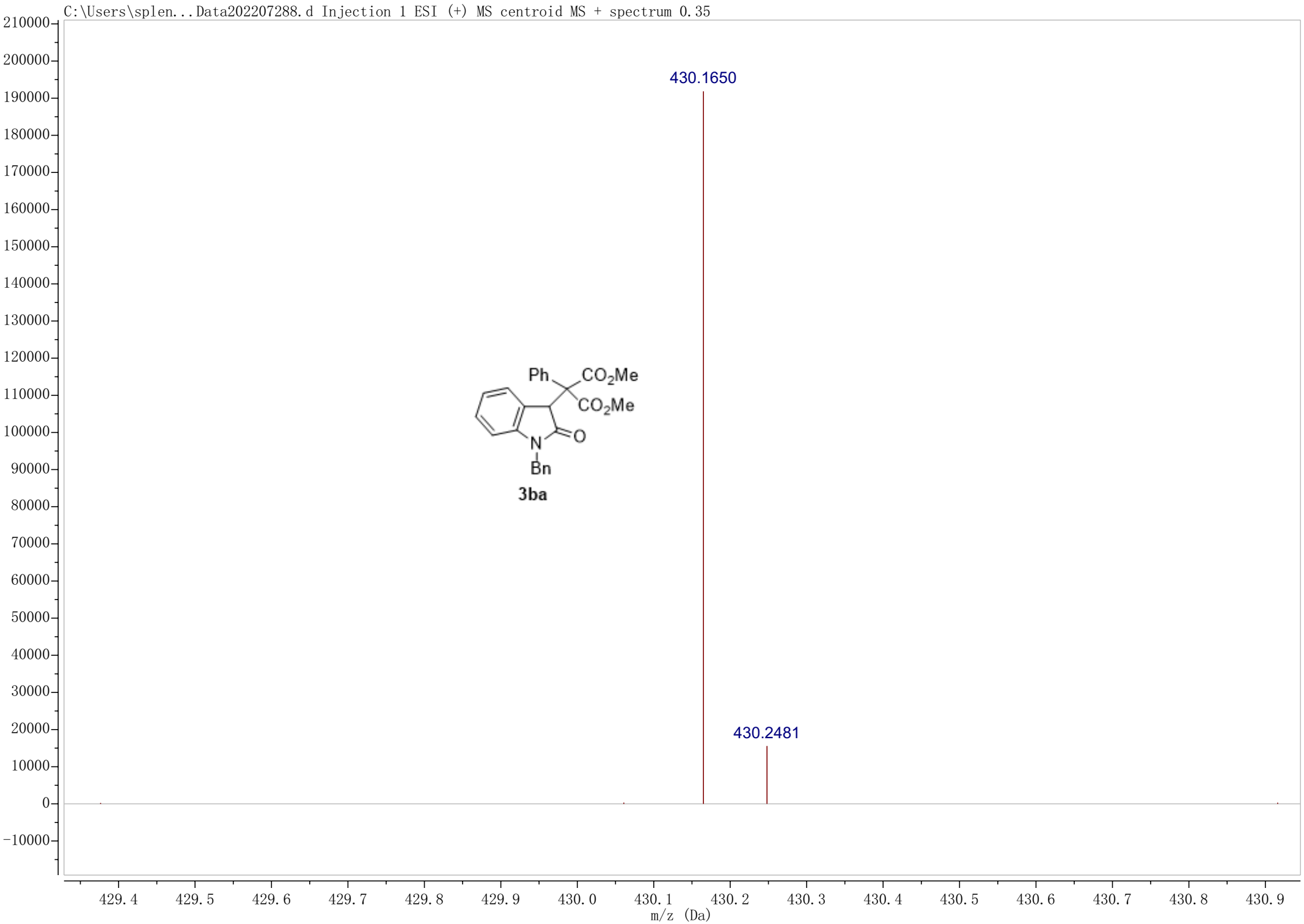

C:\Users\lenov...Data202206279.d Injection 1 ESI MS+, Centroid MS + spectrum 0.32
368.1491
368.2262
Me
CO2Me
CO2Me
O
N
Me
3ai
m/z (Da)

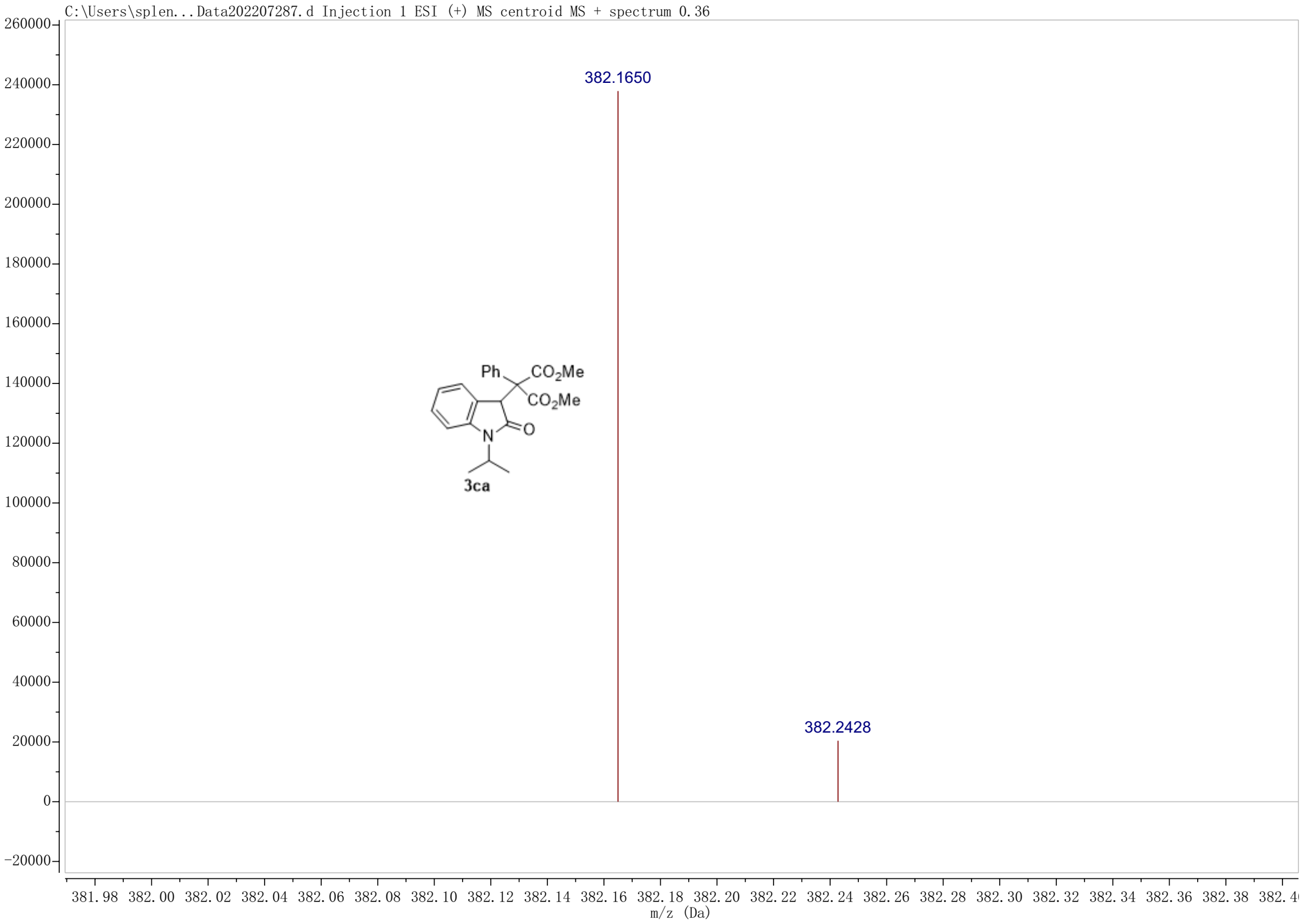

C:\Users\lenov...ata2022062711.d Injection 1 ESI MS+, Centroid MS + spectrum 0.33
388.0947
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
Cl
CO2Me
CO2Me
O
N
Me
3aj
387.65
387.70
387.75
387.80
387.85
387.90
387.95
388.00
388.05
388.10
388.15
388.20
388.25
388.30
388.35
388.40
388.45
388.50
m/z (Da)

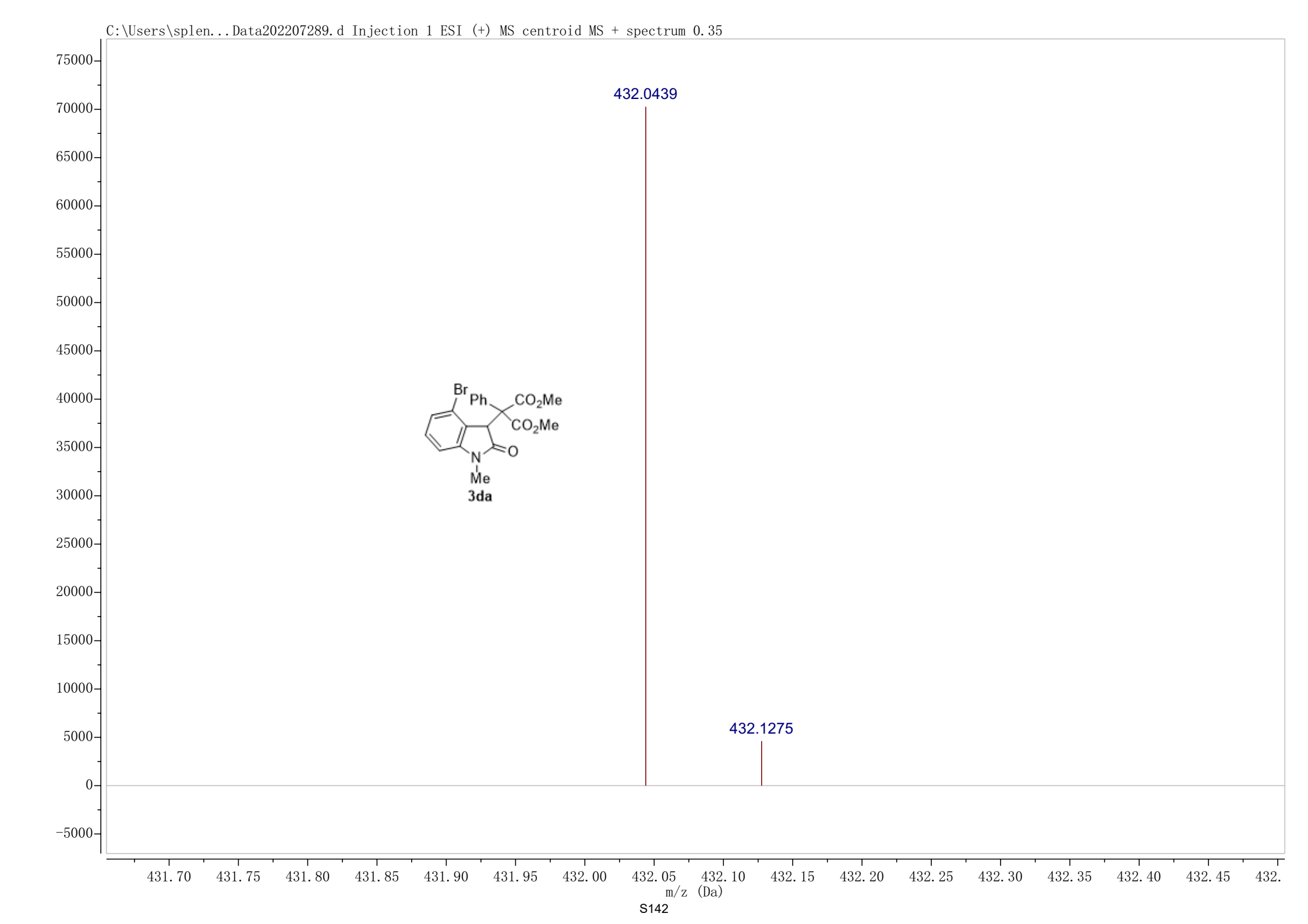

C:\Users\lenov...ata2022062710.d Injection 1 ESI MS+, Centroid MS + spectrum 0.35
388.0950
388.1722
Cl
CO2Me
CO2Me
O
N
Me
3ak
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
387.50
387.60
387.70
387.80
387.90
388.00
388.10
388.20
388.30
388.40
388.50
388.60
388.70
388.80
m/z (Da)

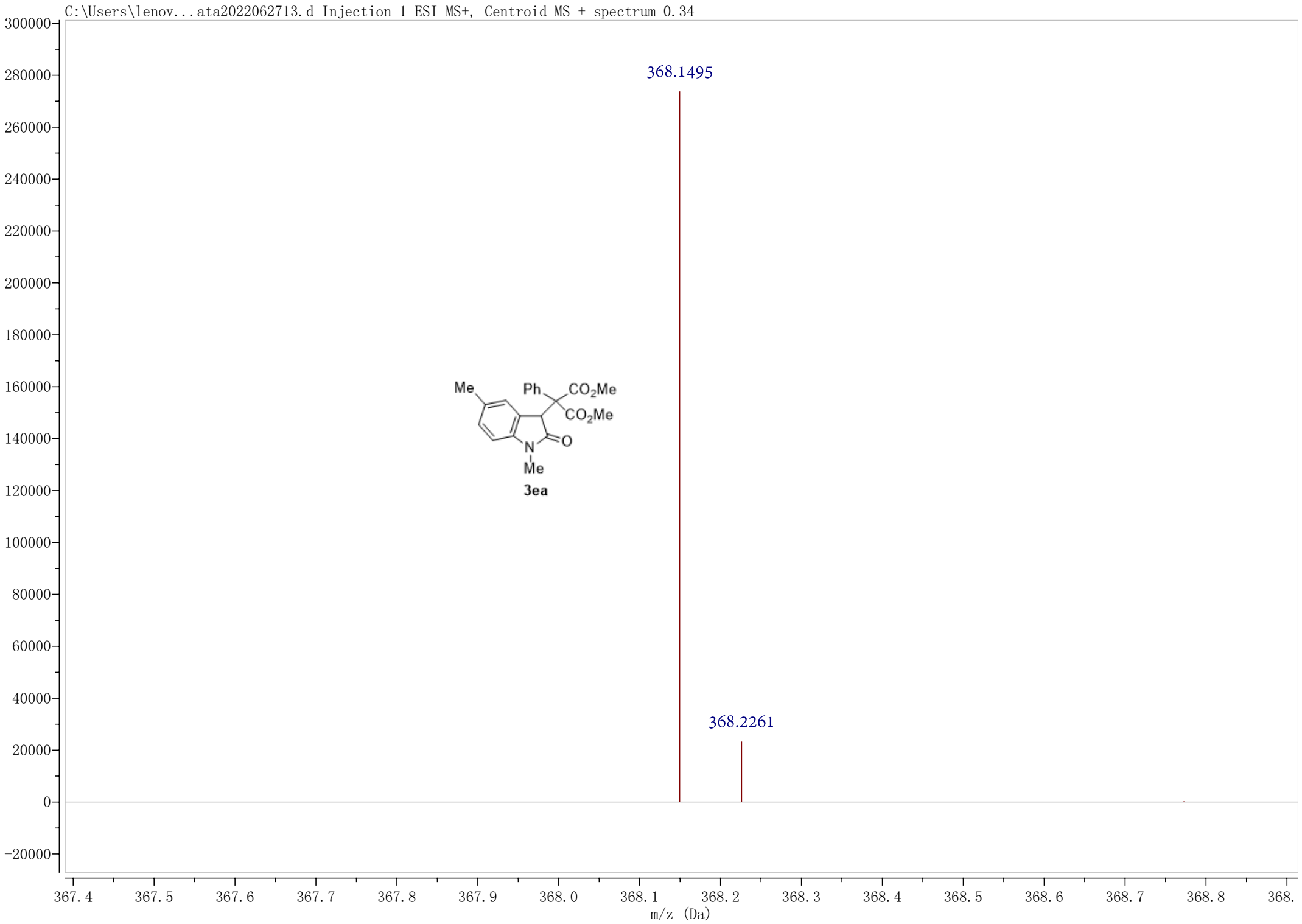

C:\Users\lenov...ata2022062712.d Injection 1 ESI MS+, Centroid MS + spectrum 0.36
404.1496
405.1529
Me
CO2Me
CO2Me
O
N
Me
3ai
m/z (Da)

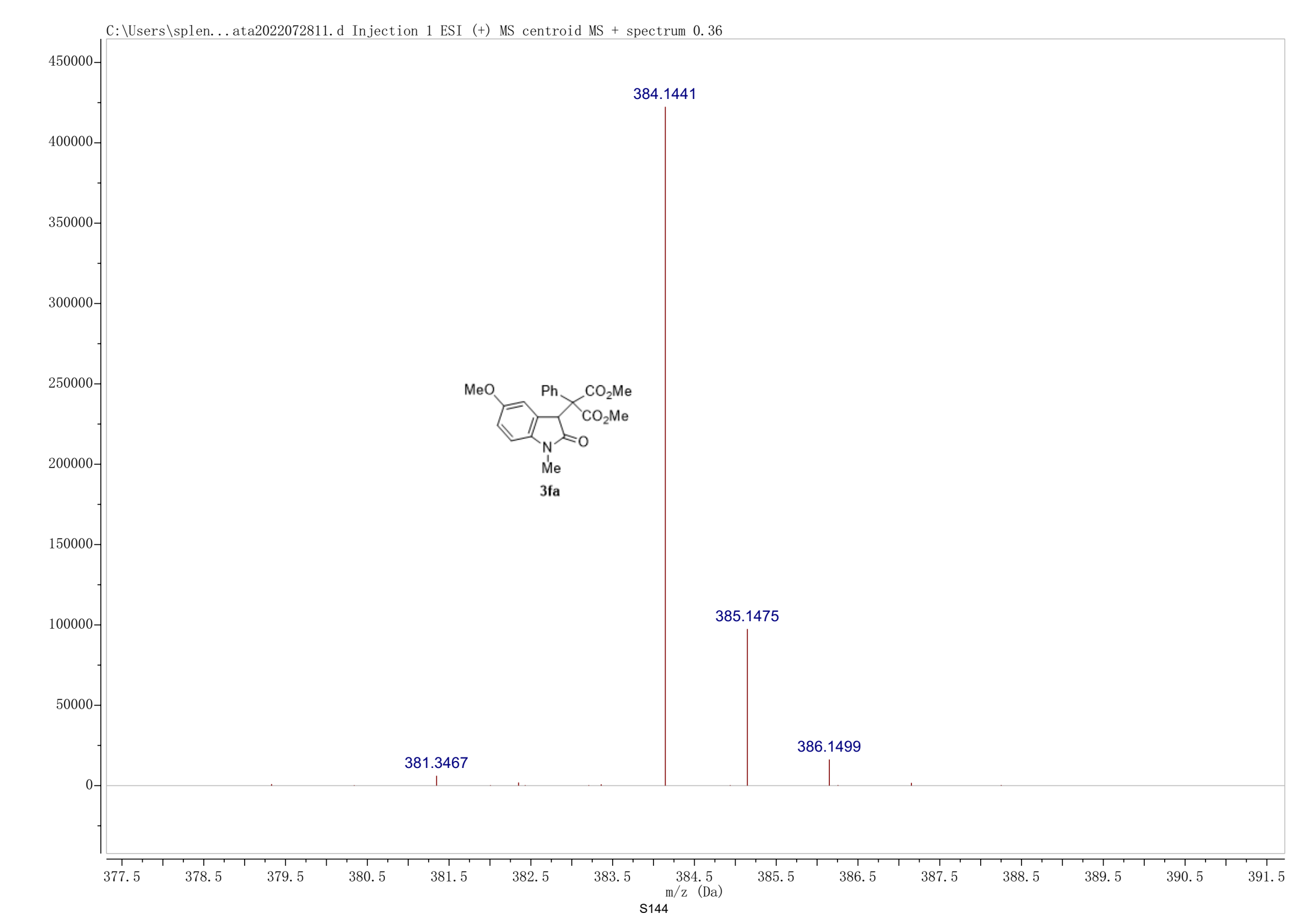

C:\Users\splen...ata2022072815.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
278.1022
279.1057
280.2633
MeO2C
CO2Me
O
N
Me
3am
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
276.0
276.5
277.0
277.5
278.0
278.5
279.0
279.5
280.0
280.5
m/z (Da)


C:\Users\splen...Data202207288.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
430.1650
430.2481
Ph
CO2Me
CO2Me
O
N
Bn
3ba
m/z (Da)

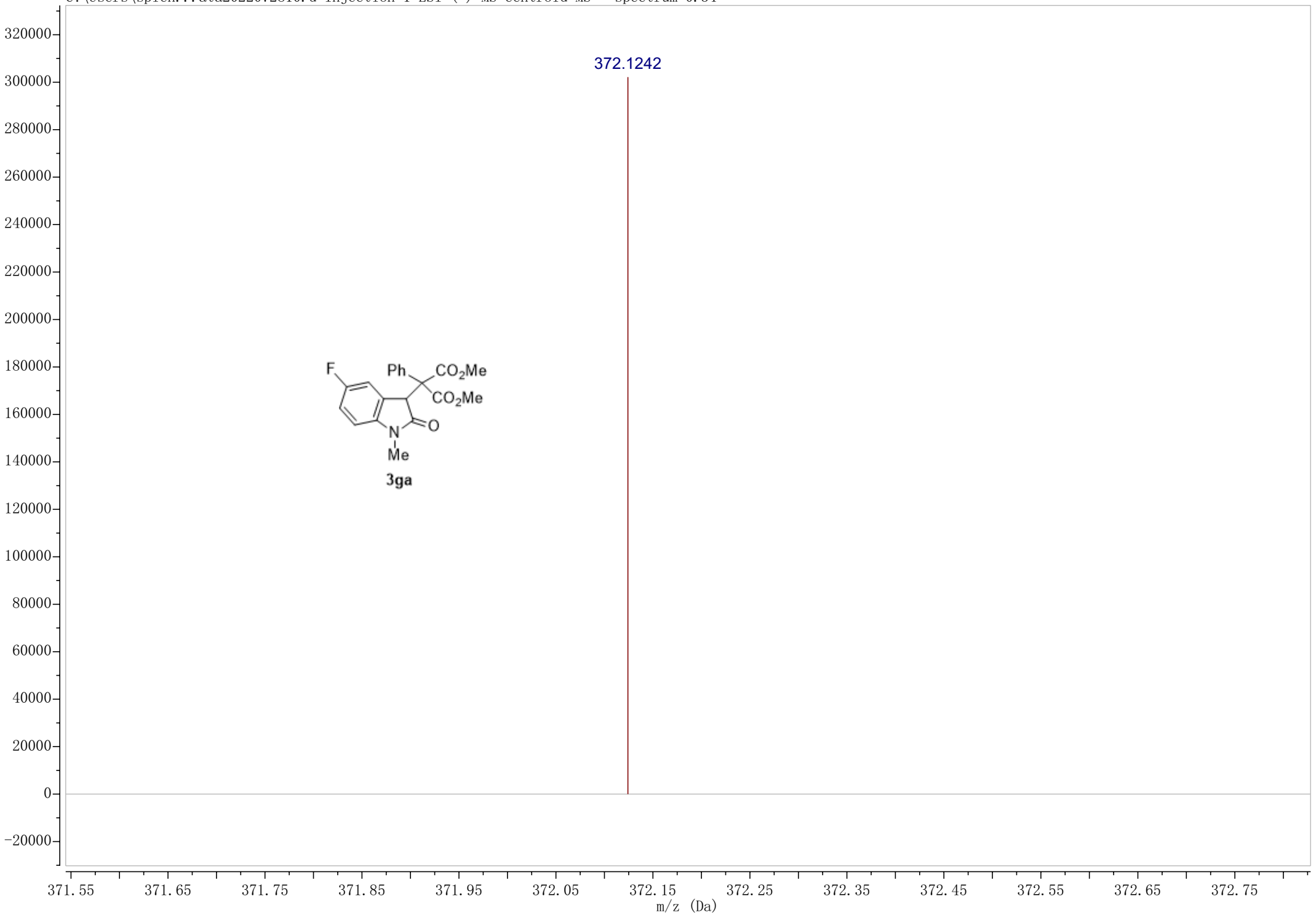

C:\Users\splen...Data202207287.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
382.1650
382.2428
Ph
CO2Me
CO2Me
N
O
3ca
m/z (Da)

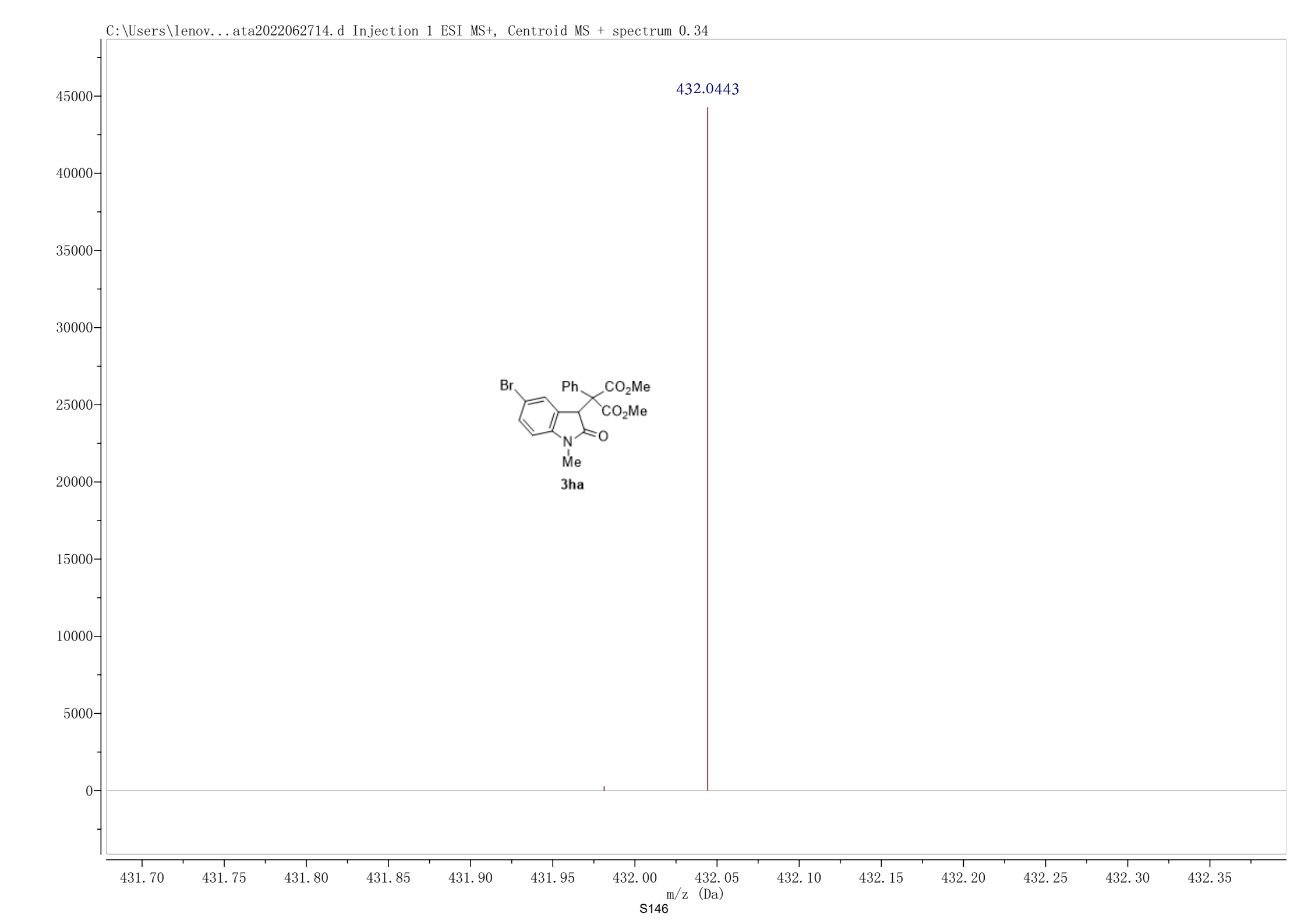

C:\Users\splen...Data202207289.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
432.0439
432.1275
Br
Ph
CO2Me
CO2Me
O
N
Me
3da
431.70
431.75
431.80
431.85
431.90
431.95
432.00
432.05
432.10
432.15
432.20
432.25
432.30
432.35
432.40
432.45
432.
m/z (Da)

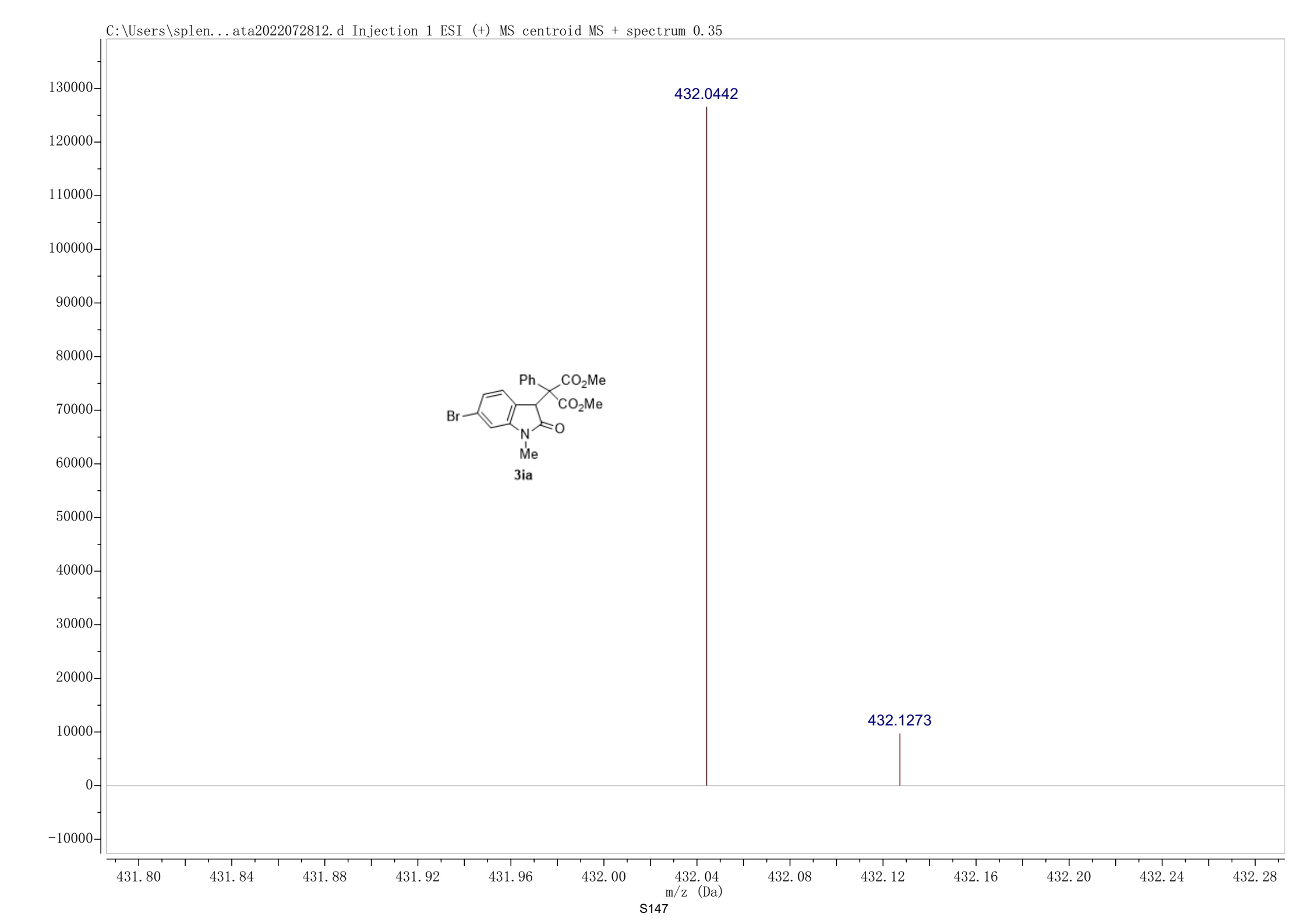

C:\Users\lenov...ata2022062713.d Injection 1 ESI MS+, Centroid MS + spectrum 0.34
368.1495
368.2261
Me
Ph
CO2Me
CO2Me
O
N
Me
3ea
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
367.4
367.5
367.6
367.7
367.8
367.9
368.0
368.1
368.2
368.3
368.4
368.5
368.6
368.7
368.8
368.
m/z (Da)


C:\Users\splen...ata2022072811.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
384.1441
385.1475
386.1499
381.3467
MeO
Ph
CO2Me
CO2Me
O
N
Me
3fa
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
377.5
378.5
379.5
380.5
381.5
382.5
383.5
384.5
385.5
386.5
387.5
388.5
389.5
390.5
391.5
m/z (Da)

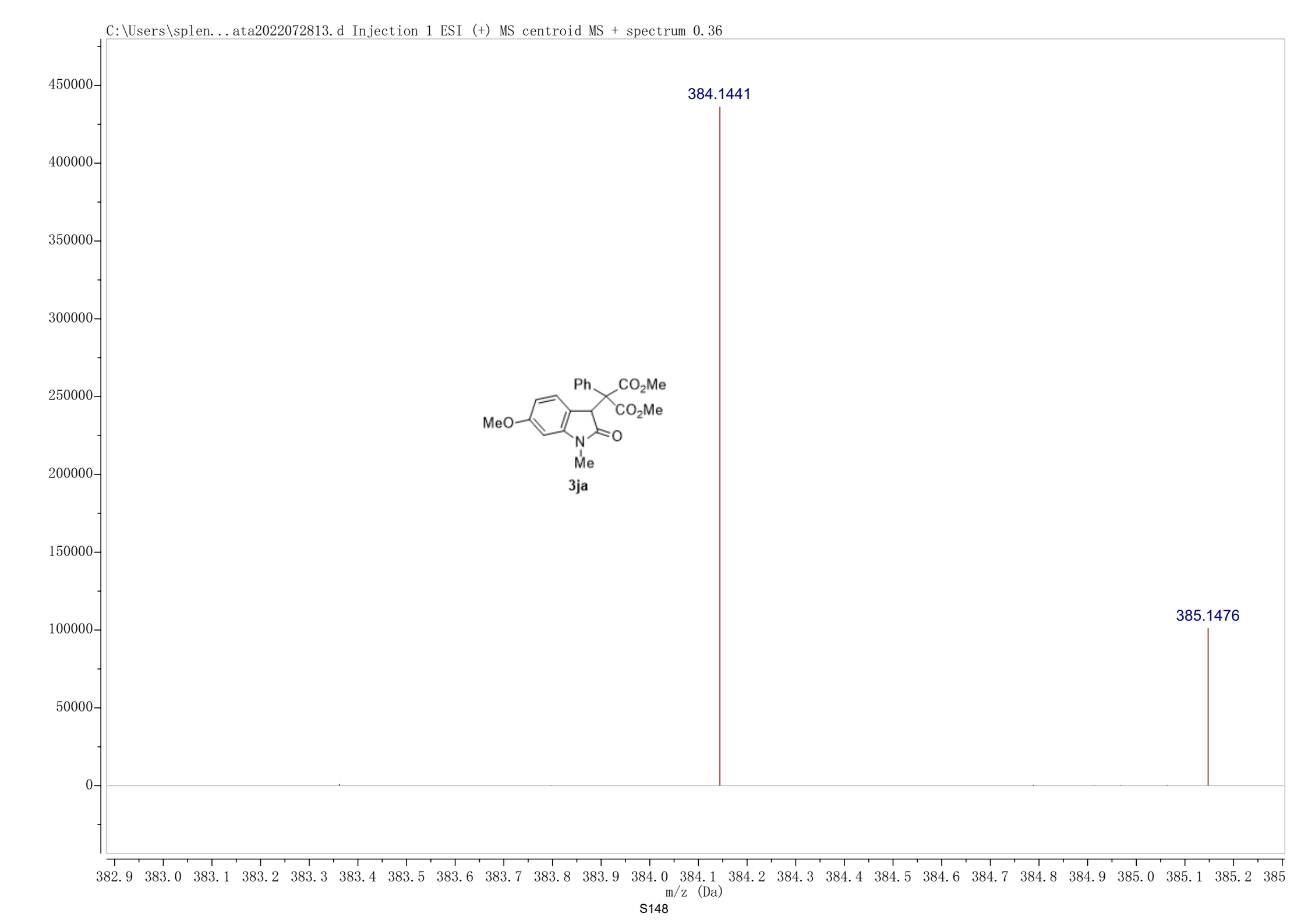
C:\Users\splen...ata2022072810.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34



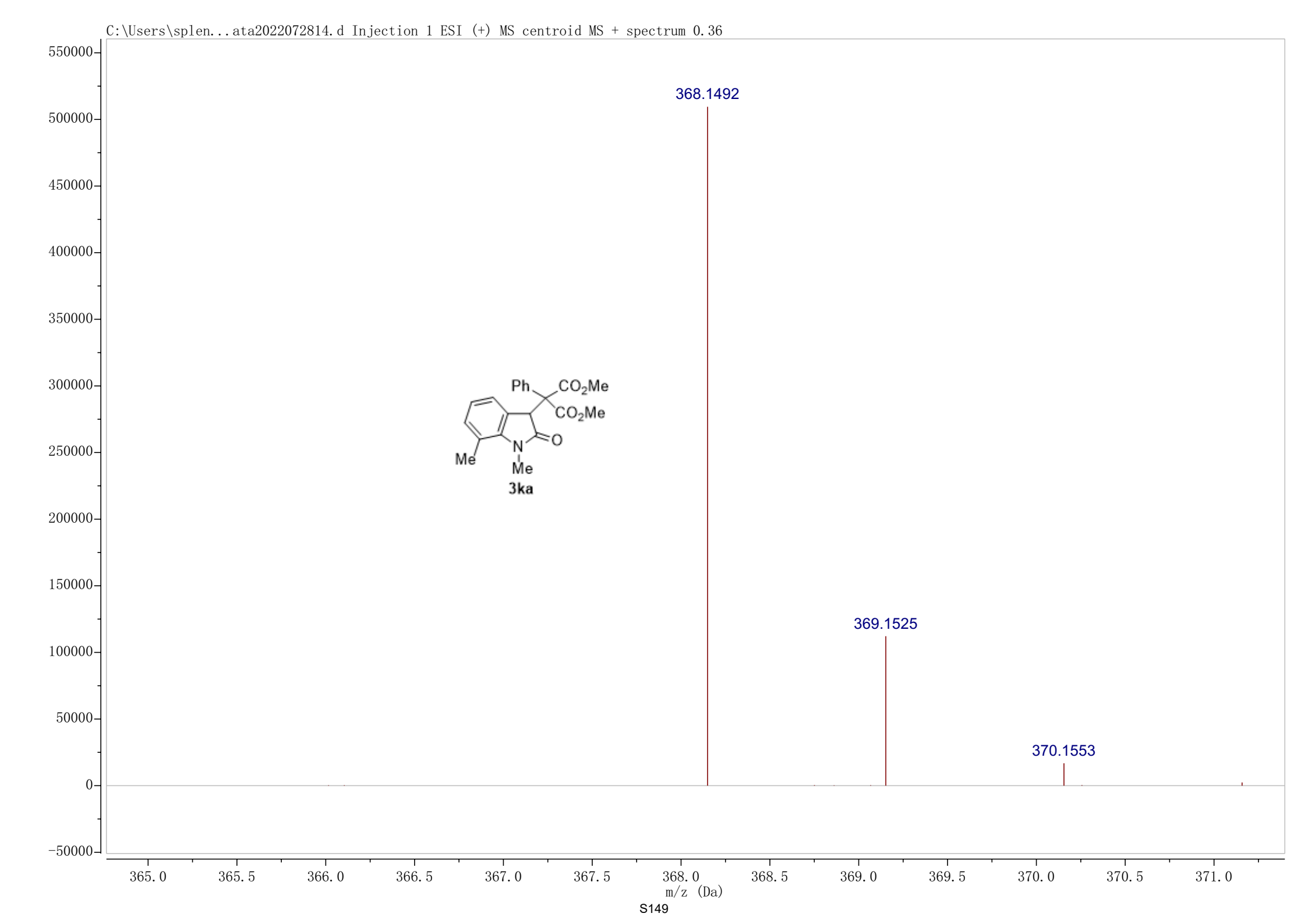

C:\Users\lenov...ata2022062714.d Injection 1 ESI MS+, Centroid MS + spectrum 0.34
432.0443
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
Br
Ph
CO2Me
CO2Me
O
N
Me
3ha
431.70
431.75
431.80
431.85
431.90
431.95
432.00
432.05
432.10
432.15
432.20
432.25
432.30
432.35
m/z (Da)

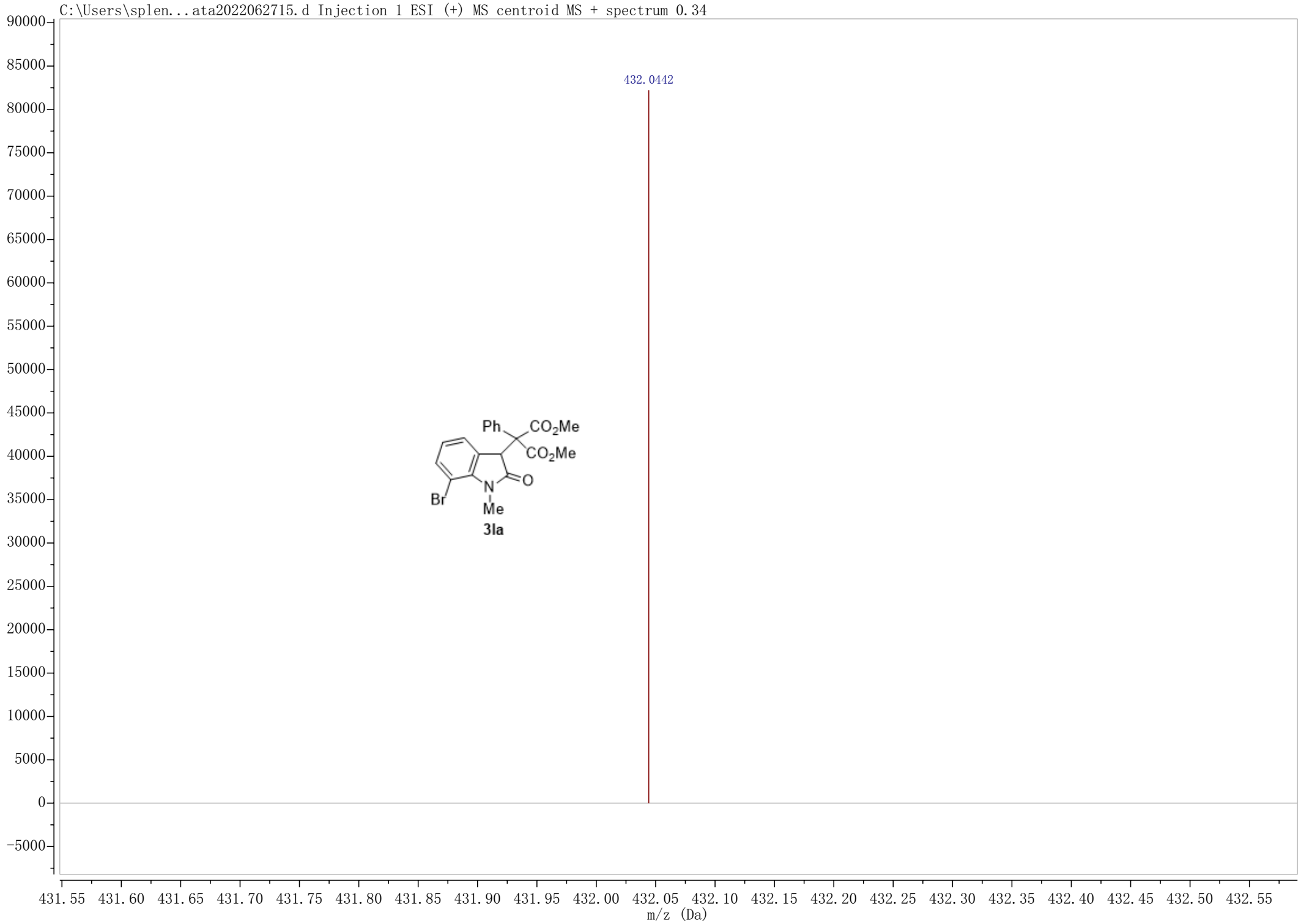

C:\Users\splen...ata2022072812.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
432.0442
432.1273
Ph
CO2Me
CO2Me
Br
O
N
Me
3ia
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
431.80
431.84
431.88
431.92
431.96
432.00
432.04
432.08
432.12
432.16
432.20
432.24
432.28
m/z (Da)

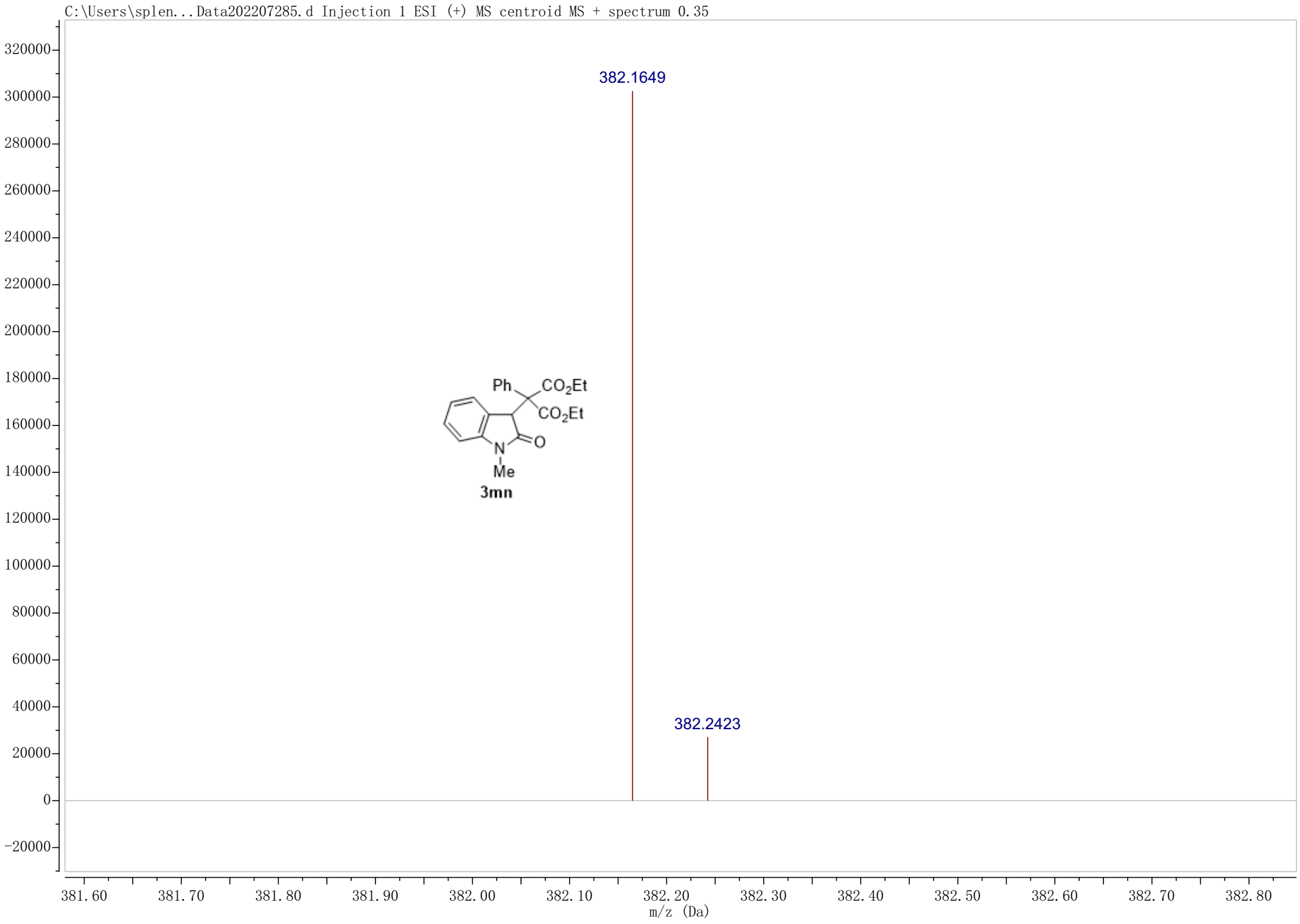
C:\Users\splen...ata2022072813.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36

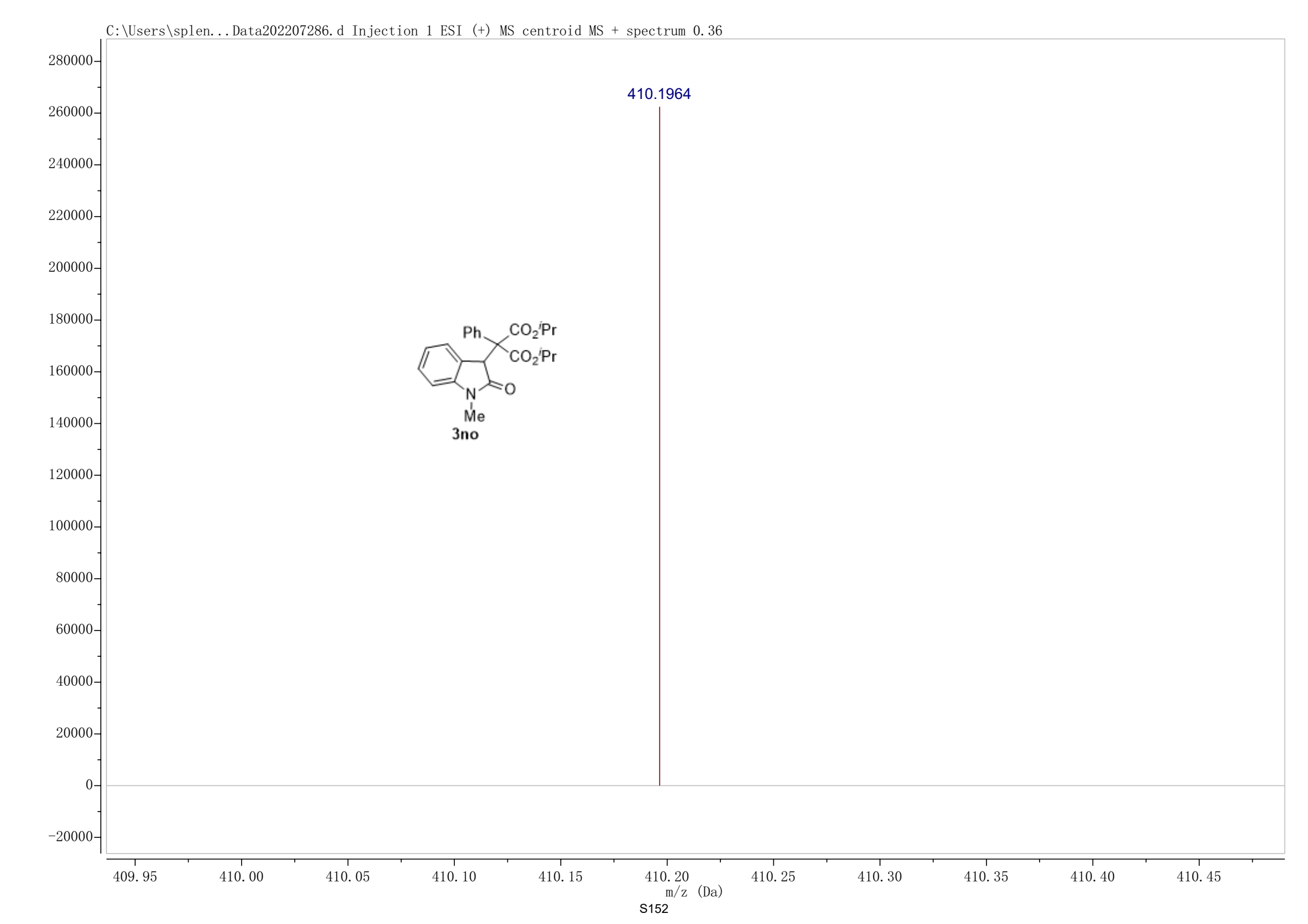


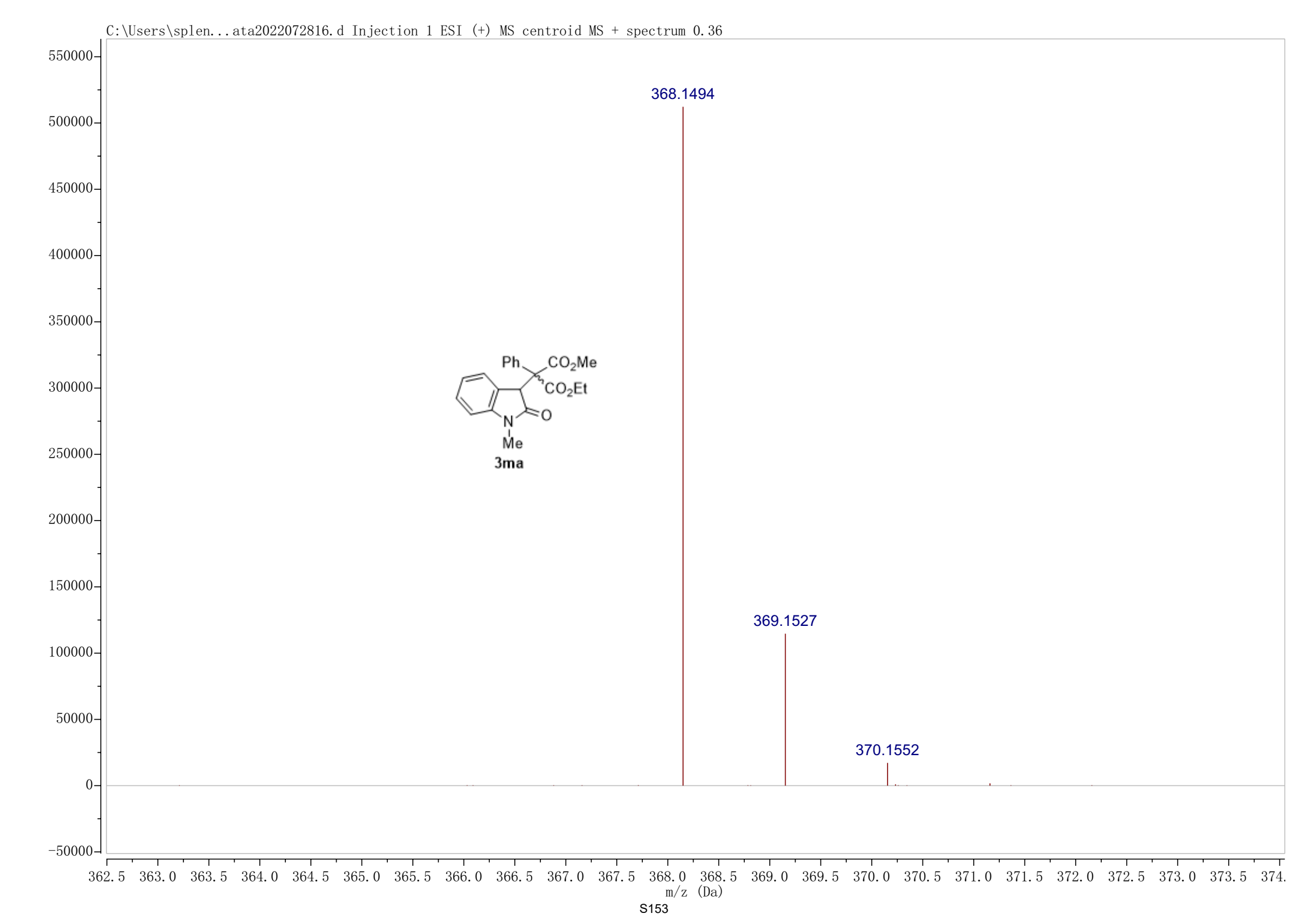
C:\Users\splen...ata2022072814.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36

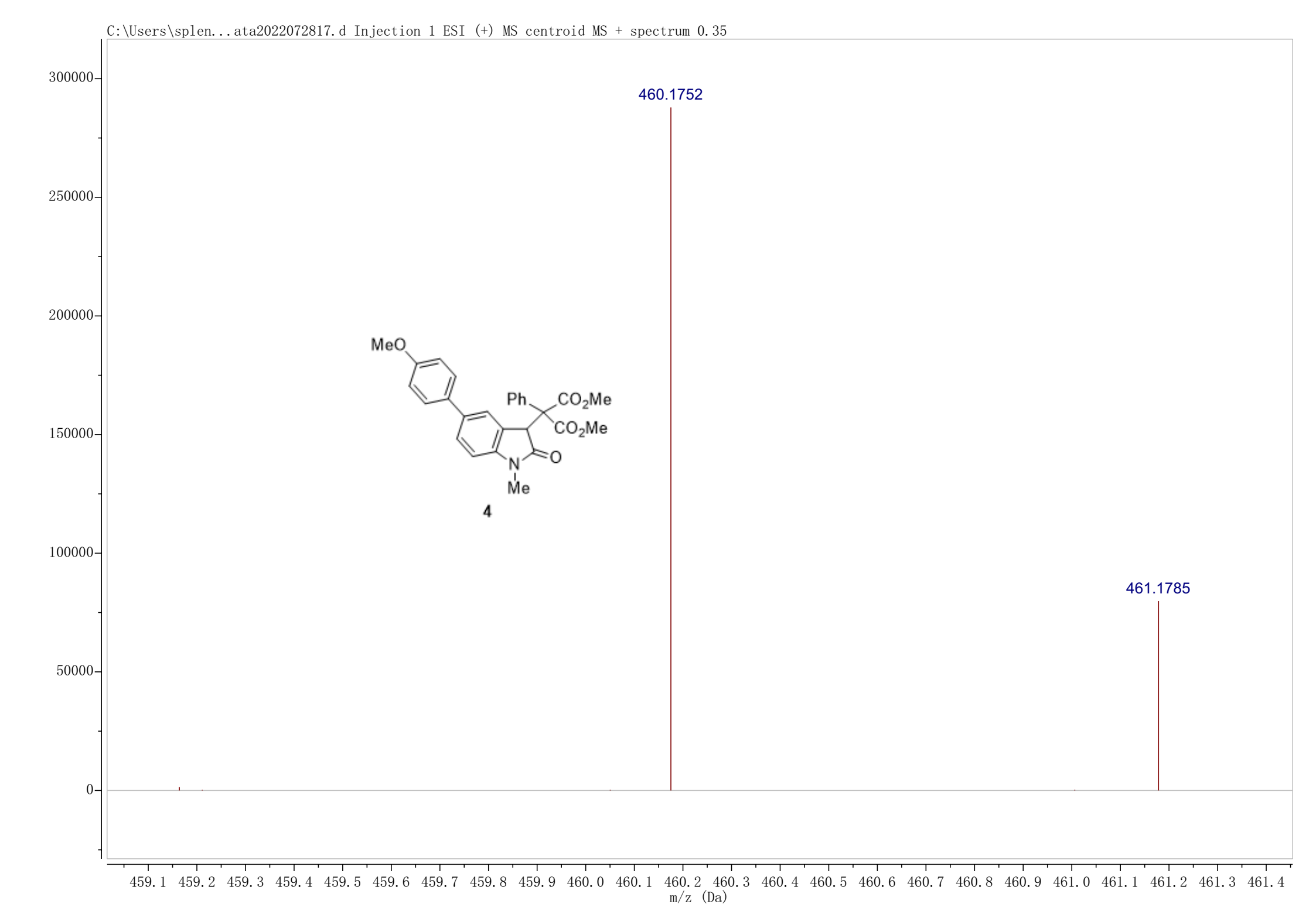


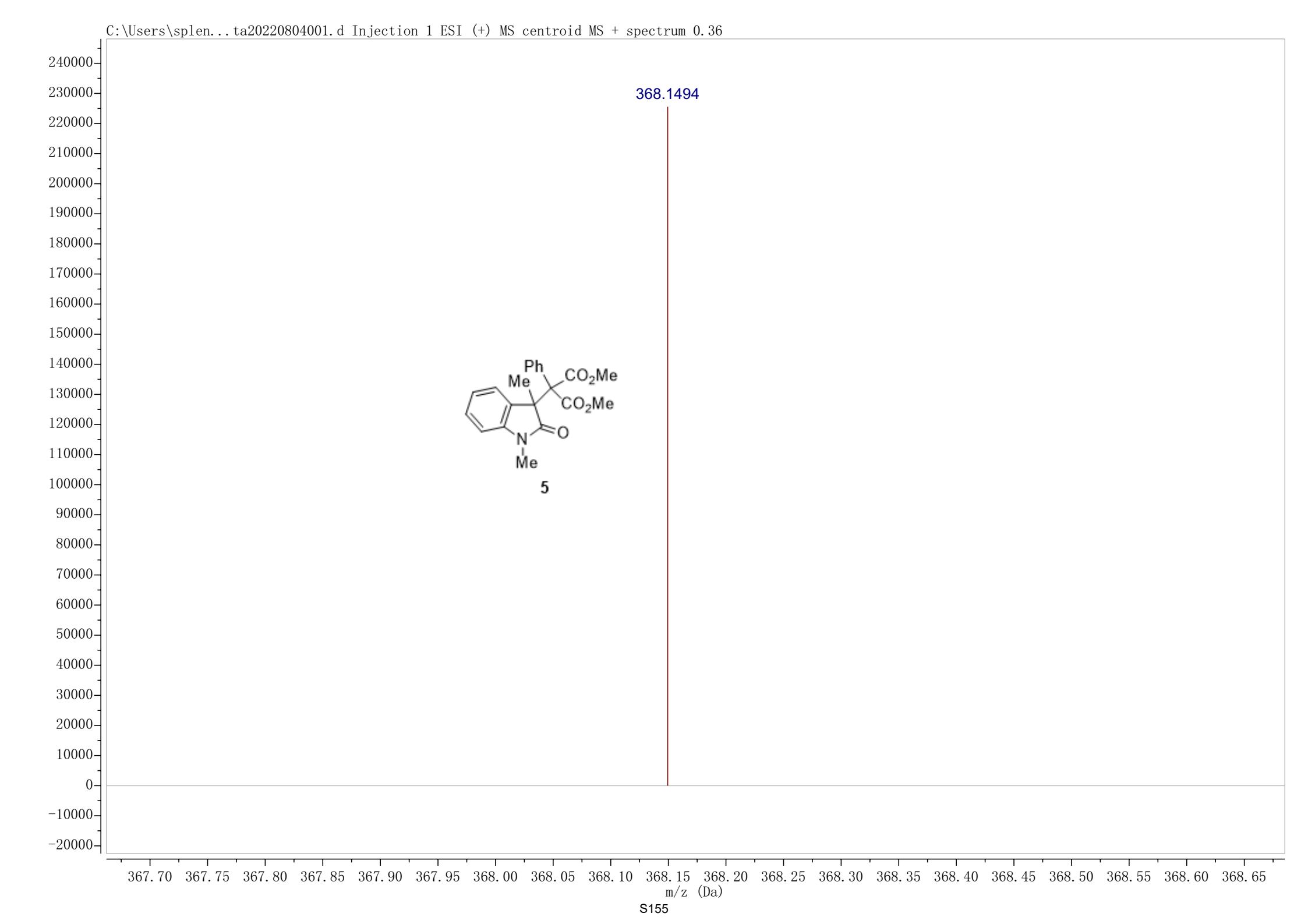

C:\Users\splen...ata2022062715.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
432.0442
Ph
CO2Me
CO2Me
O
N
Me
Br
3la
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
431.55
431.60
431.65
431.70
431.75
431.80
431.85
431.90
431.95
432.00
432.05
432.10
432.15
432.20
432.25
432.30
432.35
432.40
432.45
432.50
432.55
m/z (Da)


C:\Users\splen...Data202207285.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
382.1649
382.2423
Ph
CO2Et
CO2Et
O
N
Me
3mn
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
381.60
381.70
381.80
381.90
382.00
382.10
382.20
382.30
382.40
382.50
382.60
382.70
382.80
m/z (Da)


C:\Users\splen...Data202207286.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
410.1964
Ph
CO2iPr
CO2iPr
N
O
Me
3no
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
409.95
410.00
410.05
410.10
410.15
410.20
410.25
410.30
410.35
410.40
410.45
m/z (Da)


C:\Users\splen...ata2022072816.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
368.1494
369.1527
370.1552
Ph
CO2Me
CO2Et
O
N
Me
3ma
m/z (Da)


C:\Users\splen...ata2022072817.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
460.1752
461.1785
MeO
Ph
CO2Me
CO2Me
O
N
Me
4
300000
250000
200000
150000
100000
50000
0
459.1 459.2 459.3 459.4 459.5 459.6 459.7 459.8 459.9 460.0 460.1 460.2 460.3 460.4 460.5 460.6 460.7 460.8 460.9 461.0 461.1 461.2 461.3 461.4
m/z (Da)


C:\Users\splen...ta20220804001.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
368.1494
Ph
Me
CO2Me
CO2Me
O
N
Me
5
240000
230000
220000
210000
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
-20000
367.70 367.75 367.80 367.85 367.90 367.95 368.00 368.05 368.10 368.15 368.20 368.25 368.30 368.35 368.40 368.45 368.50 368.55 368.60 368.65
m/z (Da)