Supporting Information

Catalytic Transformations of 2-Pyridones by Rhodium-Mediated Carbene Transfer

Jiahui Su, Qiongya Li, Ying Shao and Jiangtao Sun*

Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, P. R. China

E-mail: jtsun@cczu.edu.cn

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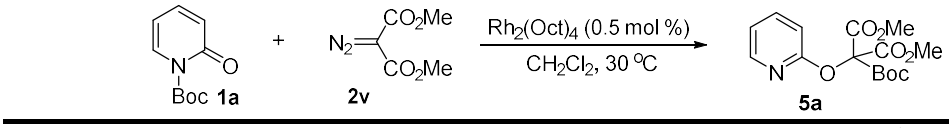
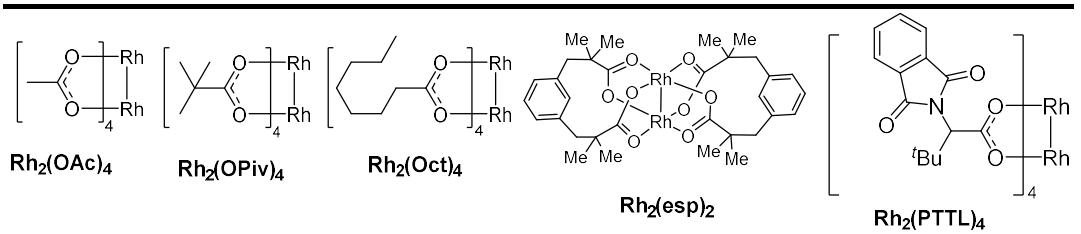
General information

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 $CDCl_3$ or CD_3SOCD_3. ^{13}C NMR were recorded on Bruker 75 MHz or 101 MHz spectrometer in $CDCl_3$ or CD_3SOCD_3. ^{19}F NMR were recorded on Bruker 282 MHz or 376 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, td = triplet of doublets, dt = doublets of triplet 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 Q-TOF or Agilent 6230A TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus without correction. Enantiomeric excesses (ee) values were determined by chiral HPLC analysis on Daicel Chiralpak IA, IE or OD-H column. Optical rotations were determined on a Rudolph Autopol IV polarimeter and reported as follows: $[\alpha]_D^T$ (c: g/100 mL, solvent).

Optimization of the reaction conditions for 5a[a]





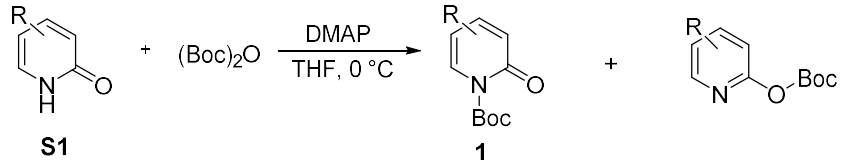
Entry	Catalyst	Solvent	**5a** (%)[b]
1	$Rh_2(PTTL)_4$	CH_2Cl_2	52
2	$Rh_2(OAc)_4$	CH_2Cl_2	<5
3	$Rh_2(esp)_2$	CH_2Cl_2	44
4	$Rh_2(Oct)_4$	CH_2Cl_2	64
5	$Rh_2(OPiv)_4$	CH_2Cl_2	50
6[c]	$Rh_2(Oct)_4$	CH_2Cl_2	26
7[d]	$Rh_2(Oct)_4$	CH_2Cl_2	72
8[d]	$Rh_2(Oct)_4$	Et_2O	41
9[d]	$Rh_2(Oct)_4$	PhMe	<5

[a]Reaction conditions: A solution of **1a** (0.1 mmol), **2v** (0.2 mmol) and catalyst (0.5 mol %) in solvent (2 mL) was stirred at 30 °C for 12 h under argon atmosphere. [b]Isolated yield. [c]0.1 mmol **2v** was used. [d]0.3 mmol **2v** was used.

Preparation of substrates

The diazo compounds **2** were known compounds and prepared according to literature procedures.[1] Compounds **1** were prepared according to the literature procedures.[2]

General procedure for synthesis of substrates 1

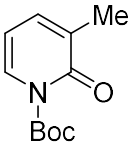


To a solution of pyridin-2(1H)-one (10 mmol) and DMAP (1-5 mol %) in THF (30 ml) was added dropwise $(Boc)_2O$ (15 mmol) at 0 °C. Then the reaction mixture was stirred at 0 °C for 15-30 min, the reaction mixture was poured into water and then the product was extracted with EtOAc (30 mL*3), the combined layers were dried over Na_2SO_4, and concentrated in vacuo.

It should be noted that the amount of O-Boc product is 10-20% in 30 min. After 1 hour, the amount of O-Boc product is about 50%. After 10 hours or longer, only O-Boc product exists in the reaction mixture.

The residue was purified by column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1:5-1:3) to **1**. **1b**, **1d-1f**, **1h**, **1j-1o**, and **1q** were new compounds.

tert-butyl 3-methyl-2-oxopyridine-1(2H)-carboxylate (1b)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:4) to afford as white solid (1.42 g, 68%), mp: 47-49 ℃.

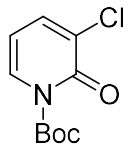
R_f (Petroleum ether/EtOAc = 5:1) = 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.45 (d, *J* = 7.3 Hz, 1H), 7.14 (d, *J* = 6.5 Hz, 1H), 6.06 (t, *J* = 6.9 Hz, 1H), 2.12 (s, 3H), 1.63 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 161.5, 151.2, 136.8, 132.1, 130.8, 105.5, 85.9, 27.7, 17.1.

HRMS (ESI): calculated for $C_{11}H_{15}NO_3Na$ $[M+Na]^+$: 232.0944; Found: 232.0942.

tert-butyl 3-chloro-2-oxopyridine-1(2H)-carboxylate (1d)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (1.58 g, 69%), mp: 98-100 ℃.

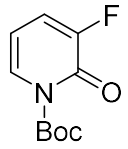
R_f (Petroleum ether/EtOAc = 5:1) = 0.2

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.56 (dd, *J* = 7.2, 1.9 Hz, 1H), 7.50 (dd, *J* = 7.2, 1.9 Hz, 1H), 6.15 (t, *J* = 7.2 Hz, 1H), 1.63 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 157.0, 150.4 138.0, 132.1, 128.3, 105.1, 87.2, 27.7.

HRMS (ESI): calculated for $C_{10}H_{12}ClNO_3Na$ $[M+Na]^+$: 252.0398; Found: 252.0395.

tert-butyl 3-fluoro-2-oxopyridine-1(2H)-carboxylate (1e)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (1.19 g, 56%), mp: 63-65 ℃.

R_f (Petroleum ether/EtOAc = 5:1) = 0.3

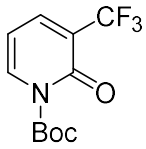
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.45 (dt, *J* = 7.4, 1.7 Hz, 1H), 7.08-7.00 (m, 1H), 6.09 (td, *J* = 7.4, 4.4 Hz, 1H), 1.63 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 155.0 (d, $^2J_{C\text{-}F}$ = 27.3 Hz), 152.9 (d, $^1J_{C\text{-}F}$ = 254.5 Hz), 149.8, 128.6 (d, $^4J_{C\text{-}F}$ = 6.1 Hz), 119.7 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 103.54 (d, $^3J_{C\text{-}F}$ = 6.1 Hz), 87.1, 27.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) δ -128.5 (1F).

HRMS (ESI): calculated for $C_{10}H_{12}FNO_3Na$ $[M+Na]^+$: 236.0693; Found: 236.0690.

tert-butyl 2-oxo-3-(trifluoromethyl)pyridine-1(2H)-carboxylate (1f)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:4) to afford as white solid (0.89 g, 34%), mp: 60-62 ℃.

R_f (Petroleum ether/EtOAc = 5:1) = 0.4

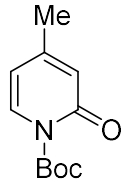
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 6.8 Hz, 1H), 6.25 (t, *J* = 7.1 Hz, 1H), 1.63 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 156.5, 150.02, 139.9 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 137.5, 123.0 (q, $^2J_{C\text{-}F}$ = 30.8 Hz), 122.2 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 103.9, 87.6, 27.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) δ -66.0 (3F).

HRMS (ESI): calculated for $C_{11}H_{12}F_3NO_3Na$ $[M+Na]^+$: 286.0661; Found: 286.0662.

tert-butyl 4-methyl-2-oxopyridine-1(2H)-carboxylate (1h)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (1.13 g, 54%), mp: 35-37 ℃.

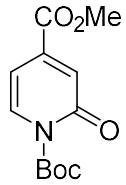
R_f (Petroleum ether/EtOAc = 3:1) = 0.2

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.50 (d, *J* = 7.5 Hz, 1H), 6.29 (s, 1H), 5.97 (dd, *J* = 7.5, 1.8 Hz, 1H), 2.15 (s, 3H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 161.0, 151.8, 150.6, 132.1, 121.2, 108.6, 85.9, 27.7, 21.2.

HRMS (ESI): calculated for $C_{11}H_{15}NO_3Na$ $[M+Na]^+$: 232.0944; Found: 232.0941.

1-(tert-butyl) 4-methyl 2-oxopyridine-1,4(2H)-dicarboxylate (1j)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (1.13 g, 45%), mp: 53-55 ℃.

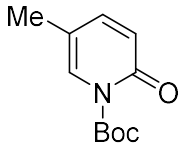
R_f (Petroleum ether/EtOAc = 5:1) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.66 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 6.59 (dd, *J* = 7.6, 1.8 Hz, 1H), 3.92 (s, 3H), 1.63 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 164.5, 160.6, 150.2, 140.6, 133.7, 125.8, 104.0, 86.9, 53.0, 27.7.

HRMS (ESI): calculated for $C_{12}H_{15}NO_5Na$ $[M+Na]^+$: 276.0842; Found: 276.0842.

tert-butyl 5-methyl-2-oxopyridine-1(2H)-carboxylate (1k)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as yellow solid (0.79 g, 38%), mp: 68-70 ℃.

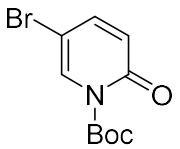
R_f (Petroleum ether/EtOAc = 3:1) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.36-7.32 (m, 1H), 7.13 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.45 (d, *J* = 9.5 Hz, 1H), 2.06 (s, 3H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 160.5, 150.9, 143.0, 129.9, 123.0, 114.5, 85.9, 27.7, 17.2.

HRMS (ESI): calculated for $C_{11}H_{15}NO_3Na$ $[M+Na]^+$: 232.0944; Found: 232.0942.

tert-butyl 5-bromo-2-oxopyridine-1(2H)-carboxylate (1l)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (0.68 g, 25%), mp: 85-87 ℃.

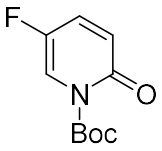
R_f (Petroleum ether/EtOAc = 5:1) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.76 (s, 1H), 7.27 (dd, *J* = 9.8, 1.7 Hz, 1H), 6.45 (d, *J* = 9.8 Hz, 1H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 159.3, 149.6, 143.0, 132.9, 124.8, 98.6, 87.1, 27.7.

HRMS (ESI): calculated for $C_{10}H_{12}BrNO_3Na$ $[M+Na]^+$: 295.9893; Found: 295.9896.

tert-butyl 5-fluoro-2-oxopyridine-1(2H)-carboxylate (1m)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as colorless oil (0.83 g, 39%).

R_f (Petroleum ether/EtOAc = 5:1) = 0.2

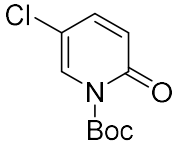
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.63-7.55 (m, 1H), 7.28-7.20 (m, 1H), 6.51 (dd, *J* = 10.1, 5.3 Hz, 1H), 1.62 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 159.3, 149.7, 146.7 (d, $^1J_{C\text{-}F}$ = 231.8 Hz), 132.9 (d, $^2J_{C\text{-}F}$ = 26.2 Hz), 124.8 (d, $^3J_{C\text{-}F}$ = 6.8 Hz), 118.1 (d, $^2J_{C\text{-}F}$ = 40.5 Hz), 86.7, 27.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -148.1 (1F).

HRMS (ESI): calculated for $C_{10}H_{12}FNO_3Na$ $[M+Na]^+$: 236.0693; Found: 236.0693.

tert-butyl 5-chloro-2-oxopyridine-1(2H)-carboxylate (1n)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (0.48 g, 21%), mp: 50-52 ℃.

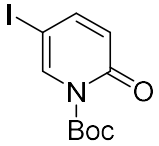
R_f (Petroleum ether/EtOAc = 5:1) = 0.2

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.67 (d, *J* = 2.9 Hz, 1H), 7.20 (dd, *J* = 9.9, 2.9 Hz, 1H), 6.49 (d, *J* = 9.9 Hz, 1H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 159.3, 149.6, 141.0, 130.5, 124.6, 112.8, 87.0, 27.7.

HRMS (ESI): calculated for $C_{10}H_{12}ClNO_3Na$ $[M+Na]^+$: 252.0398; Found: 252.0402.

tert-butyl 5-iodo-2-oxopyridine-1(2H)-carboxylate (1o)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:3) to afford as white solid (1.86 g, 58%), mp: 70-72 ℃.

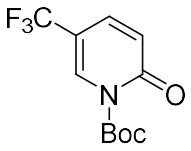
R_f (Petroleum ether/EtOAc = 5:1) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.85-7.79 (m, 1H), 7.37-7.31 (m, 1H), 6.34 (d, *J* = 9.7 Hz, 1H), 1.62 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 159.2, 149.6, 147.1, 137.9, 125.2, 87.1, 65.1, 27.8.

HRMS (ESI): calculated for $C_{10}H_{12}INO_3Na$ $[M+Na]^+$: 343.9754; Found: 343.9759.

tert-butyl 2-oxo-5-(trifluoromethyl)pyridine-1(2H)-carboxylate (1q)



The title compound was prepared via general procedure, purified by flash chromatography on silica gel (EtOAc/Petroleum ether = 1:5-1:4) to afford as white solid (1.58 g, 60%), mp: 25-27 ℃.

R_f (Petroleum ether/EtOAc = 5:1) = 0.4

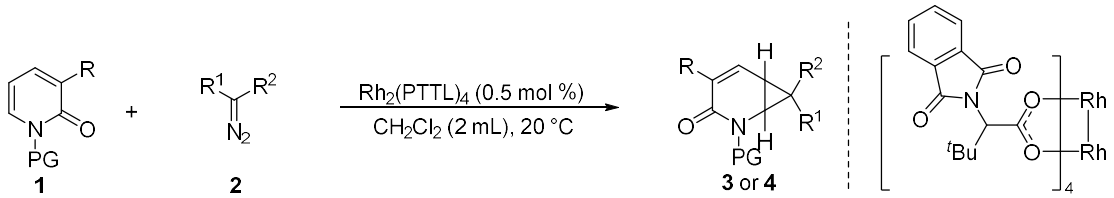
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.03 (s, 1H), 7.37 (d, *J* = 9.8 Hz, 1H), 6.61 (d, *J* = 9.8 Hz, 1H), 1.64 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 159.6, 149.8, 135.0 (q, $^4J_{C\text{-}F}$ = 2.3 Hz), 133.5 (q, $^3J_{C\text{-}F}$ = 6.0 Hz), 124.4, 122.9 (q, $^1J_{C\text{-}F}$ = 268.5 Hz), 109.9 (q, $^2J_{C\text{-}F}$ = 34.5 Hz), 87.7, 27.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -63.5 (3F).

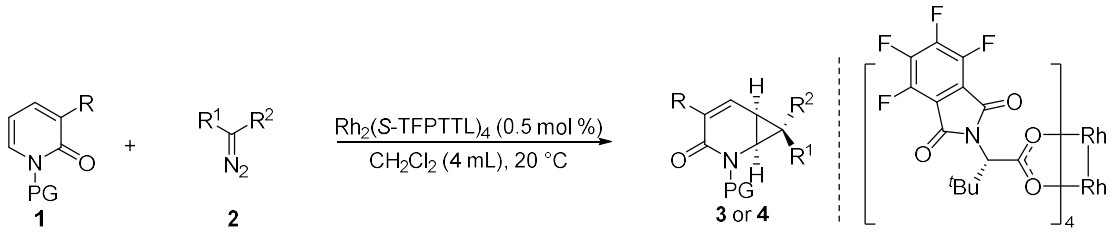
HRMS (ESI): calculated for $C_{11}H_{12}F_3NO_3Na$ $[M+Na]^+$: 286.0661; Found: 286.0662.

General procedure for synthesis of racemic product 3 or 4



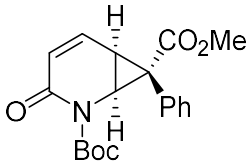
To a dry tube was added $Rh_2(PTTL)_4$ (1.2 mg, 0.001 mmol, 0.5 mol%), **1** (0.20 mmol, 1.0 equiv) and anhydrous DCM (2 mL), and then **2** (0.40 mmol, 2.0 equiv) dissolved in anhydrous DCM (2 mL) was added via a syringe pump over 15 min under an argon atmosphere. The reaction mixture was stirred at 20 ℃ in a heating block for 15 min. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/Petroleum ether = 1:5-1:1) to give desired racemic product.

General procedure for synthesis of Chiral product 3 or 4 and analytical data



To a dry tube was added Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%), **1** (0.20 mmol, 1.0 equiv) and anhydrous DCM (2 mL), and then **2** (0.40 mmol, 2.0 equiv) dissolved in anhydrous DCM (2 mL) was added via a syringe pump over 15 min under an argon atmosphere. The reaction mixture was stirred at 20 ℃ in a heating block for 15 min. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/Petroleum ether = 1:5-1:1) to give desired chiral product.

2-(tert-butyl) 7-methyl (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3a)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (65.0 mg, 95%), mp: 103-105 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.3

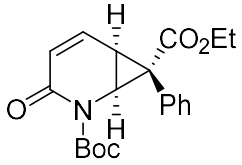
HPLC analysis: 92% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 14.42 min (major) and 17.90 min (minor). $[\alpha]_D^{20}$: -415.3 (c = 0.50, CH_2Cl_2; 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.31-7.25 (m, 3H), 7.10-7.04 (m, 2H), 6.77 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 4.41 (d, *J* = 8.9 Hz, 1H), 3.65 (s, 3H), 2.94 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.61 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 172.6, 160.1, 152.2, 137.9, 133.2, 129.1, 128.5, 128.2, 127.0, 84.1, 53.1, 46.1, 35.4, 28.0, 26.3.

HRMS (ESI): calculated for $C_{19}H_{21}NO_5Na$ $[M+Na]^+$: 366.1312; Found: 366.1314.

2-(tert-butyl) 7-ethyl (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3b)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and ethyl 2-diazo-2-phenylacetate (76.0 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (66.4 mg, 93%), mp: 110-112 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.35

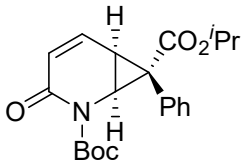
HPLC analysis: 90% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 12.32 min (major) and 14.18 min (minor). $[\alpha]_D^{20}$: -383.2 (c = 0.50, CH_2Cl_2; 90% ee).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.24 (m, 3H), 7.11-7.04 (m, 2H), 6.78 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 4.41 (d, *J* = 8.8 Hz, 1H), 4.20-4.05 (m, 2H), 2.93 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.61 (s, 9H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 172.0, 160.2, 152.0, 138.0, 133.1, 129.3, 128.4, 128.1, 127.0, 84.0, 61.9, 45.9, 35.5, 28.0, 26.1, 14.1.

HRMS (ESI): calculated for $C_{20}H_{23}NO_5Na$ $[M+Na]^+$: 380.1468; Found: 380.1469.

2-(tert-butyl) 7-isopropyl (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3c)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and isopropyl 2-diazo-2-phenylacetate (81.6 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (18.6 mg, 25%), mp: 109-111 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.35

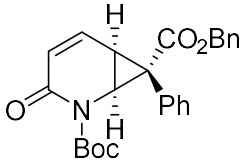
HPLC analysis: 81% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 19.38 min (minor) and 21.15 min (major). $[\alpha]_D^{20}$: -260.7 (c = 0.50, CH_2Cl_2; 81% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.28-7.23 (m, 3H), 7.08-7.03 (m, 2H), 6.78 (ddd, *J* = 9.8, 5.2, 0.6 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 5.04-4.92 (m, 1H), 4.39 (dd, *J* = 8.9, 0.6 Hz, 1H), 2.91 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.61 (s, 9H), 1.15 (d, *J* = 6.2 Hz, 3H), 1.13 (d, *J* = 6.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 171.5, 160.4, 151.7, 138.2, 133.1, 129.5, 128.4, 128.1, 127.0, 84.0, 69.5, 45.8, 35.8, 28.1, 26.0, 21.7.

HRMS (ESI): calculated for $C_{21}H_{25}NO_5Na$ $[M+Na]^+$: 394.1625; Found: 394.1622.

7-benzyl 2-(tert-butyl) (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3d)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and benzyl 2-diazo-2-phenylacetate (100.8 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (56.2 mg, 67%), mp: 46-48 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.35

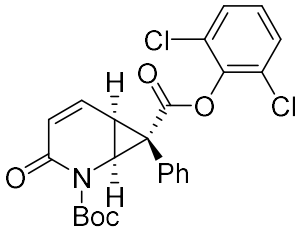
HPLC analysis: 86% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 95/5, flow rate =1.0 mL/min, λ = 225 nm, t_R = 16.46 min (minor) and 19.60 min (major). $[\alpha]_D^{20}$: -425.8 (c = 0.50, CH_2Cl_2; 86% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.32-7.25 (m, 6H), 7.17-7.12 (m, 2H), 7.11-7.05 (m, 2H), 6.76 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.63 (d, *J* = 9.8, 1H), 5.13 (dd, *J* = 20.9, 12.7 Hz, 2H), 4.43 (d, *J* = 8.9 Hz, 1H), 2.94 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.55 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 171.8, 160.2, 151.9, 137.9, 135.7, 133.1, 129.1, 128.52, 128.48, 128.2, 128.1, 127.4, 127.1, 84.1, 67.2, 46.0, 35.6, 28.0, 26.3.

HRMS (ESI): calculated for $C_{25}H_{25}NO_5Na$ $[M+Na]^+$: 442.1625; Found: 442.1625.

2-(tert-butyl) 7-(2,6-dichlorophenyl) (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3e)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and 2,6-dichlorophenyl 2-diazo-2-phenylacetate (122.8 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (65.2 mg, 69%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

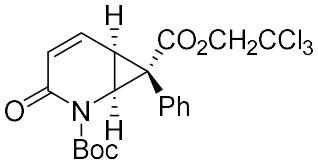
HPLC analysis: 79% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 97/3, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 22.27 min (minor) and 24.69 min (major). $[\alpha]_D^{20}$: -164.1 (c = 0.50, CH_2Cl_2; 79% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.37-7.27 (m, 6H), 7.25-7.22 (m, 1H), 7.08 (t, *J* = 8.1 Hz, 1H), 6.84 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 4.67 (d, *J* = 8.9 Hz, 1H), 3.11 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.64 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 169.1, 160.1, 151.5, 144.0, 137.3, 133.4, 128.7, 128.64, 128.60, 128.3, 127.6, 127.4, 84.4, 46.7, 35.2, 28.1, 27.4.

HRMS (ESI): calculated for $C_{24}H_{21}Cl_2NO_5Na$ $[M+Na]^+$: 496.0689; Found: 496.0683.

2-(tert-butyl) 7-(2,2,2-trichloroethyl) (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3f)



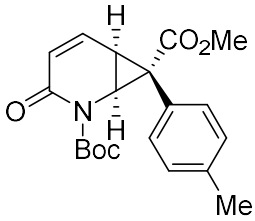
Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and 2,2,2-trichloroethyl 2-diazo-2-phenylacetate (117.2 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 ℃. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (84.7 mg, 92%), mp: 103-105 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

HPLC analysis: 73% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 98/2, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 12.54 min (minor) and 13.27 min (major). $[\alpha]_D^{20}$: -232.3 (c = 0.50, CH_2Cl_2; 73% ee).

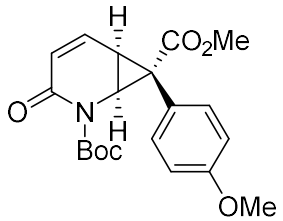
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.30-7.25 (m, 3H), 7.13-7.07 (m, 2H), 6.81 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.68 (d, *J* = 9.8 Hz, 1H), 4.70 (dd, *J* = 23.4, 11.9 Hz, 2H), 4.56 (d, *J* = 8.9 Hz, 1H), 3.03 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.61 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 170.6, 159.9, 152.0, 137.3, 133.2, 128.54, 128.47, 128.2, 127.5, 94.6, 84.3, 74.7, 46.2, 35.4, 28.0, 26.7.
HRMS (ESI): calculated for $C_{20}H_{20}Cl_3NO_5Na$ $[M+Na]^+$: 482.0299; Found: 482.0300.

2-(tert-butyl) 7-methyl (1S,6S,7R)-3-oxo-7-(p-tolyl)-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3g)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-(p-tolyl)acetate (76.0 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (61.5 mg, 86%).
R_f (Petroleum ether/EtOAc = 3:1) = 0.4
HPLC analysis: 94% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 10.92 min (minor) and 12.52 min (major). $[\alpha]_D^{20}$: -384.9 (c = 0.50, CH_2Cl_2; 94% ee).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.08 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.75 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.62 (dd, *J* = 9.8, 1.1 Hz, 1H), 4.39 (d, *J* = 8.8 Hz, 1H), 3.65 (s, 3H), 2.91 (dd, *J* = 8.8, 5.2 Hz, 1H), 2.29 (s, 3H), 1.60 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.8, 160.2, 152.2, 138.01, 137.97, 133.0, 129.3, 127.0, 125.9, 84.0, 53.1, 46.1, 35.0, 28.0, 26.4, 21.3.
HRMS (ESI): calculated for $C_{20}H_{23}NO_5Na$ $[M+Na]^+$: 380.1468; Found: 380.1464.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(4-methoxyphenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3h)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-(4-methoxyphenyl)acetate (82.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 °C. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (70.1 mg, 94%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.35

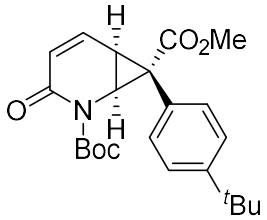
HPLC analysis: 92% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 16.30 min (minor) and 18.96 min (major). $[\alpha]_D^{20}$: -341.7 (c = 0.50, CH_2Cl_2; 92% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.02-6.95 (m, 2H), 6.82-6.72 (m, 3H), 5.64 (d, *J* = 9.8 Hz, 1H), 4.38 (dd, *J* = 8.9, 0.8 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 2.90 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.60 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 172.9, 160.2, 159.2, 152.1, 138.0, 134.3, 127.1, 120.7, 114.0, 84.0, 55.1, 53.1, 46.1, 34.7, 28.0, 26.5.

HRMS (ESI): calculated for $C_{20}H_{23}NO_6Na$ $[M+Na]^+$: 396.1418; Found: 396.1412.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(4-(tert-butyl)phenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3i)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-(4-(tert-butyl)phenyl)-2-diazoacetate (92.8 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (72.8 mg, 91%), mp: 127-129 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

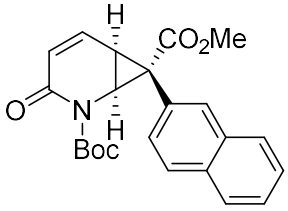
HPLC analysis: 94% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 8.52 min (minor) and 9.59 min (major). $[\alpha]_D^{20}$: -392.0 (c = 0.50, CH_2Cl_2; 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.27 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.75 (ddd, *J* = 9.8, 5.2, 0.9 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 4.39 (dd, *J* = 8.9, 0.9 Hz, 1H), 3.64 (s, 3H), 2.90 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.61 (s, 9H), 1.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.8, 160.3, 151.9, 150.9, 137.9, 132.6, 127.0, 125.9, 125.5, 84.0, 53.1, 46.1, 34.9, 34.6, 31.3, 28.0, 26.3.

HRMS (ESI): calculated for $C_{23}H_{29}NO_5Na$ $[M+Na]^+$: 422.1938; Found: 422.1939.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(naphthalen-2-yl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3j)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and

methyl 2-diazo-2-(naphthalen-2-yl)acetate (90.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (71.6 mg, 91%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

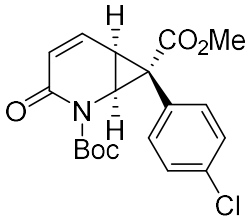
HPLC analysis: 86% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 9.61 min (minor) and 11.04 min (major). $[\alpha]_D^{20}$: -359.5 (c = 0.50, CH_2Cl_2; 86% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.81-7.72 (m, 2H), 7.71-7.65 (m, 1H), 7.56 (s, 1H), 7.49-7.40 (m, 2H), 7.15 (d, *J* = 8.2 Hz, 1H), 6.80 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.56 (d, *J* = 9.8 Hz, 1H), 4.48 (d, *J* = 8.8 Hz, 1H), 3.62 (s, 3H), 2.98 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.65 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.7, 160.0, 152.4, 137.8, 133.2, 133.0, 132.9, 130.1, 128.3, 127.9, 127.7, 127.1, 126.61, 126.58, 126.2, 84.2, 53.2, 46.2, 35.5, 28.1, 26.6.

HRMS (ESI): calculated for $C_{23}H_{23}NO_5Na$ $[M+Na]^+$: 416.1468; Found: 416.1470.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(4-chlorophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3k)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-(4-chlorophenyl)-2-diazoacetate (126.4 mg, 0.6 mmol, 3.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (71.0 mg, 94%), mp: 93-95 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

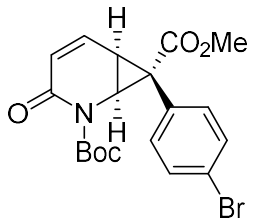
HPLC analysis: 76% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 20.16 min (minor) and 22.53 min (major). $[\alpha]_D^{20}$: -247.5 (c = 0.50, CH_2Cl_2; 76% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.77 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.66 (d, *J* = 9.8 Hz, 1H), 4.40 (d, *J* = 8.8 Hz, 1H), 3.65 (s, 3H), 2.93 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.1, 159.9, 152.2, 137.7, 134.5, 134.3, 128.9, 127.8, 127.3, 84.4, 53.2, 46.0, 34.7, 28.0, 26.3.

HRMS (ESI): calculated for $C_{19}H_{20}ClNO_5Na$ $[M+Na]^+$: 400.0922; Found: 400.0928.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(4-bromophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3l)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-(4-bromophenyl)-2-diazoacetate (102.0 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (76.9 mg, 91%), mp: 113-114 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.3

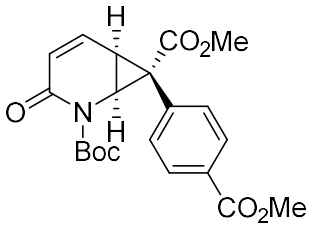
HPLC analysis: 78% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 17.52 min (minor) and 19.43 min (major). $[\alpha]_D^{20}$: -344.1 (c = 0.50, CH_2Cl_2; 78% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.41 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.76 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.66 (d, *J* = 9.8 Hz, 1H), 4.40 (d, *J* = 8.8 Hz, 1H), 3.65 (s, 3H), 2.93 (dd, *J* = 8.8, 5.2 Hz, 1H), 1.60 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 172.0, 159.9, 152.2, 137.7, 134.8, 131.8, 128.3, 127.3, 122.6, 84.4, 53.2, 46.0, 34.8, 28, 26.3.

HRMS (ESI): calculated for $C_{19}H_{20}BrNO_5Na$ $[M+Na]^+$: 444.0417; Found: 444.0418.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(4-(methoxycarbonyl)phenyl)-3-oxo-2-azabicyclo[4.1.0] hept-4-ene-2,7-dicarboxylate (3m)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 4-(1-diazo-2-methoxy-2-oxoethyl)benzoate (93.6 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (69.0 mg, 86%), mp: 76-78 ℃.

R_f (Petroleum ether/EtOAc = 2:1) = 0.4

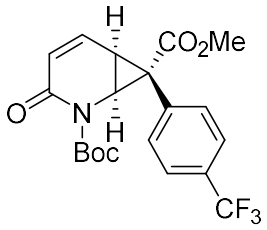
HPLC analysis: 94% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.48 min (major) and 12.84 min (minor). $[\alpha]_D^{20}$: -362.4 (c = 0.50, CH_2Cl_2; 94% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.5 Hz, 2H), 6.79 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.63 (d, *J* = 9.8 Hz, 1H), 4.44 (d, *J* = 8.9 Hz, 1H), 3.89 (s, 3H), 3.65 (s, 3H), 2.97 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.61 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 171.8, 166.6, 159.7, 152.3, 137.6, 134.4, 133.2, 129.9, 129.7, 127.2, 84.4, 53.2, 52.2, 46.0, 35.2, 28.0, 26.3.

HRMS (ESI): calculated for $C_{21}H_{23}NO_7Na$ $[M+Na]^+$: 424.1367; Found: 424.1368.

2-(tert-butyl) 7-methyl (1S,6S,7R)-3-oxo-7-(4-(trifluoromethyl)phenyl)-2-azabicyclo[4.1.0] hept-4-ene-2,7-dicarboxylate (3n)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate (97.6 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (57.5 mg, 70%), mp: 102-104 ℃.

R_f (Petroleum ether/EtOAc = 1:1) = 0.4

HPLC analysis: 83% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 7.98 min (minor) and 8.70 min (major). $[\alpha]_D^{20}$: -286.9 (c = 0.50, CH_2Cl_2; 83% ee).

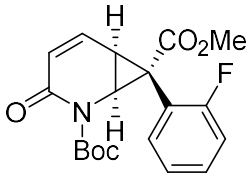
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.79 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.66 (d, *J* = 9.8 Hz, 1H), 4.44 (d, *J* = 8.9 Hz, 1H), 3.66 (s, 3H), 2.98 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.61 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 171.7, 159.7, 152.2, 137.6, 133.53, 133.49, 130.3 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 127.3, 125.5 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 272.3 Hz), 84.5, 53.3, 46.0, 35.0, 28.0, 26.2.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -62.66 (3F).

HRMS (ESI): calculated for $C_{20}H_{20}F_3NO_5Na$ $[M+Na]^+$: 434.1186; Found: 434.1185.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(2-fluorophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3o)



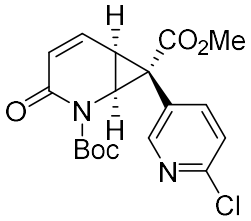
Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-(2-fluorophenyl)acetate (77.6 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (50.6 mg, 70%), mp: 109-111 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

HPLC analysis: 95% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.66 min (minor) and 13.59 min (major). $[\alpha]_D^{20}$: -286.9 (c = 0.50, CH_2Cl_2; 95% ee).

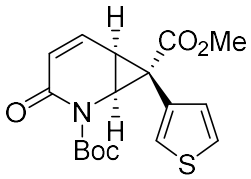
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.34-7.27 (m, 1H), 7.20-6.95 (m, 3H), 6.85-6.76 (m, 1H), 5.60 (d, *J* = 9.8 Hz, 1H), 4.50 (s, 1H), 3.66 (s, 3H), 2.98 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.61 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 171.7, 160.0, 152.1, 137.7, 133.7, 130.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 126.4, 124.4, 117.1(d, $J_{C\text{-}F}$ = 15.0 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.0 Hz), 84.2, 53.2, 45.4, 29.7, 28.0, 26.8.
^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -112.80 (1F).
HRMS (ESI): calculated for $C_{19}H_{20}FNO_5Na$ $[M+Na]^+$: 384.1218; Found: 384.1221.

2-(tert-butyl) 7-methyl (1S,6S,7R)-7-(6-chloropyridin-3-yl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3p)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-(6-chloropyridin-3-yl)-2-diazoacetate (84.8 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (34.1 mg, 45%), mp: 106-108 ℃.
R_f (Petroleum ether/EtOAc = 3:1) = 0.1
HPLC analysis: 95% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 10.79 min (minor) and 13.01 min (major). $[\alpha]_D^{20}$: -359.4 (c = 0.50, CH_2Cl_2; 95% ee).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.07 (d, *J* = 2.5 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.74 (d, *J* = 9.8 Hz, 1H), 4.42 (d, *J* = 8.9 Hz, 1H), 3.68 (s, 3H), 3.02 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.60 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 171.2, 159.4, 154.2, 152.2, 151.2, 143.1, 137.1, 127.9, 124.6, 124.4, 84.9, 53.4, 45.9, 32.2, 28.0, 26.1.
HRMS (ESI): calculated for $C_{18}H_{19}ClN_2O_5Na$ $[M+Na]^+$: 401.0875; Found: 401.0873.

2-(tert-butyl) 7-methyl (1S,6S,7R)-3-oxo-7-(thiophen-3-yl)-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3q)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-(thiophen-3-yl)acetate (72.8 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as yellow oil (62.2 mg, 89%).
R_f (Petroleum ether/EtOAc = 3:1) = 0.2

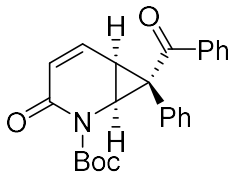
HPLC analysis: 96% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 10.15 min (minor) and 11.28 min (major). $[\alpha]_D^{20}$: -341.9 (c = 0.50, CH_2Cl_2; 96% ee).

^{1}H NMR (400 MHz, CD_3SOCD_3): δ (ppm) δ 7.45 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.17-7.10 (m, 1H), 6.95 (dd, *J* = 9.8, 5.3 Hz, 1H), 6.81 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.59 (d, *J* = 9.8 Hz, 1H), 4.23 (d, *J* = 8.8 Hz, 1H), 3.59 (s, 3H), 2.93 (dd, *J* = 8.8, 5.3 Hz, 1H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, CD_3SOCD_3): δ (ppm) δ 171.7, 159.3, 151.3, 139.6, 130.6, 129.3, 128.4, 125.72, 125.69, 83.1, 52.8, 45.8, 30.1, 27.5, 26.5.

HRMS (ESI): calculated for $C_{17}H_{19}NO_5SNa$ $[M+Na]^+$: 372.0876; Found: 372.0877.

tert-butyl (1S,6S,7R)-7-benzoyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2-carboxylate (3r)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and 2-diazo-1,2-diphenylethan-1-one (88.8 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 ℃. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (24.1 mg, 31%).

R_f (Petroleum ether/EtOAc = 2:1) = 0.5

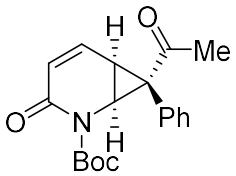
HPLC analysis: 79% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 10.76 min (minor) and 11.90 min (major). $[\alpha]_D^{20}$: -328.6 (c = 0.50, CH_2Cl_2; 79% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.51-7.44 (m, 2H), 7.37-7.29 (m, 1H), 7.24-7.16 (m, 5H), 7.15-7.09 (m, 2H), 6.80 (ddd, *J* = 9.8, 5.3, 0.8 Hz, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 4.45 (dd, *J* = 8.8, 0.8 Hz, 1H), 3.25 (dd, *J* = 8.8, 5.3 Hz, 1H), 1.59 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 199.6, 160.6, 151.9, 138.7, 138.2, 133.4, 131.6, 130.9, 128.8, 128.6, 128.3, 127.8, 127.0, 84.2, 48.6, 42.4, 28.1, 27.8.

HRMS (ESI): calculated for $C_{24}H_{23}NO_4Na$ $[M+Na]^+$: 412.1519; Found: 412.1512.

tert-butyl (1S,6S,7R)-7-acetyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2-carboxylate (3s)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and 1-diazo-1-phenylpropan-2-one (96.0 mg, 0.6 mmol, 3.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (41.3 mg, 63%),

mp: 115-117 ℃.

R_f (Petroleum ether/EtOAc = 1:1) = 0.5

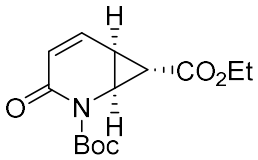
HPLC analysis: 94% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.44 min (minor) and 12.20 min (major). $[\alpha]_D^{20}$: -444.5 (c = 0.50, CH_2Cl_2; 94% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.39-7.30 (m, 3H), 7.22-6.99 (m, 2H), 6.76 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.63 (d, *J* = 9.8 Hz, 1H), 4.24 (d, *J* = 8.6 Hz, 1H), 3.01 (dd, *J* = 8.6, 5.2 Hz, 1H), 2.02 (s, 3H), 1.61 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 205.9, 160.3, 152.1, 138.7, 133.2, 130.9, 129.1, 128.5, 126.9, 84.1, 48.4, 42.9, 30.2, 28.3, 28.0.

HRMS (ESI): calculated for $C_{19}H_{22}NO_4$ $[M+H]^+$: 328.1543; Found: 328.1537.

2-(tert-butyl) 7-ethyl (1S,6S,7S)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (3t)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and ethyl 2-diazoacetate (68.4 mg, 0.6 mmol, 3.0 equiv) according to the general procedure in the presence of Rh_2(*S*-PTTL)$_4$ (1.2 mg, 0.001 mmol, 0.5 mol%) at 30 ℃. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (13.8 mg, 25%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.2

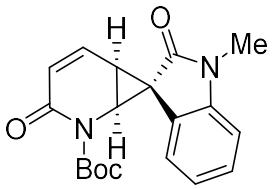
HPLC analysis: 29% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 19.02 min (minor) and 21.96 min (major). $[\alpha]_D^{20}$: -92.3 (c = 0.50, CH_2Cl_2; 29% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 6.57 (dd, *J* = 9.7, 5.1 Hz, 1H), 6.05 (d, *J* = 9.7 Hz, 1H), 4.14-4.04 (m, 2H), 3.95 (t, *J* = 7.4 Hz, 1H), 2.38-2.28 (m, 1H), 2.14 (dd, *J* = 10.2, 6.6 Hz, 1H), 1.55 (s, 9H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 166.9, 161.2, 152.1, 134.1, 127.8, 83.4, 60.7, 38.8, 28.0, 19.5, 19.1, 14.2.

HRMS (ESI): calculated for $C_{14}H_{19}NO_5Na$ $[M+Na]^+$: 304.1155; Found: 304.1151.

tert-butyl (1S,6S,7R)-1'-methyl-2',3-dioxo-2-azaspiro[bicyclo[4.1.0]heptane-7,3'-indolin]-4-ene-2-carboxylate (3u)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (39.0 mg, 0.2 mmol, 1.0 equiv) and 3-diazo-1-methylindolin-2-one (64.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (59.8 mg, 88%), mp: 118-120 ℃.

R_f (Petroleum ether/EtOAc = 1:1) = 0.4

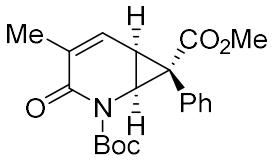
HPLC analysis: 96% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 25.27 min (minor) and 35.84 min (major). $[\alpha]_D^{20}$: -549.3 (c = 0.50, CH_2Cl_2; 96% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.35-7.28 (m, 1H), 7.0-6.93 (m, 2H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.73 (dd, *J* = 9.7, 5.0 Hz, 1H), 6.27 (d, *J* = 9.7 Hz, 1H), 4.23 (d, *J* = 8.4 Hz, 1H), 3.31 (s, 3H), 3.02 (dd, *J* = 8.4, 5.0 Hz, 1H), 1.18 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 173.7, 161.2, 150.2, 144.5, 136.1, 128.2, 127.7, 122.9, 122.4, 121.3, 108.4, 83.6, 47.4, 31.5, 28.5, 27.5, 26.7.

HRMS (ESI): calculated for $C_{19}H_{20}N_2O_4Na$ $[M+Na]^+$: 363.1315; Found: 363.1315.

2-(tert-butyl) 7-methyl (1S,6S,7R)-4-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (4a)



Prepared from tert-butyl 3-methyl-2-oxopyridine-1(2H)-carboxylate (41.8 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (67.2 mg, 94%), mp: 115-117 ℃.

R_f (Petroleum ether/EtOAc = 4:1) = 0.4

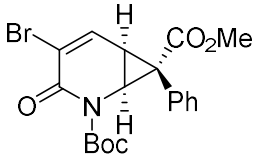
HPLC analysis: 97% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 7.00 min (major) and 8.70 min (minor). $[\alpha]_D^{20}$: -369.3 (c = 0.50, CH_2Cl_2; 97% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.29-7.23 (m, 3H), 7.10-7.04 (m, 2H), 6.56 (d, *J* = 5.4 Hz, 1H), 4.42 (d, *J* = 8.9 Hz, 1H), 3.64 (s, 3H), 2.87 (dd, *J* = 8.9, 5.4 Hz, 1H), 1.60 (s, 9H), 1.58 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.9, 161.3, 152.7, 133.8, 133.4, 132.9, 129.4, 128.3, 128.0, 83.9, 53.0, 46.3, 34.6, 28.0, 26.3, 17.0.

HRMS (ESI): calculated for $C_{20}H_{23}NO_5Na$ $[M+Na]^+$: 380.1468; Found: 380.1458.

2-(tert-butyl) 7-methyl (1S,6S,7R)-4-bromo-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (4b)



Prepared from tert-butyl 3-bromo-2-oxopyridine-1(2H)-carboxylate (54.8 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (76.2 mg, 90%), mp: 94-96 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

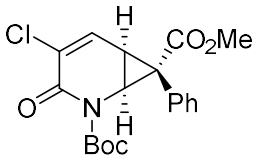
HPLC analysis: 96% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.79 min (major) and 15.47 min (minor). $[\alpha]_D^{20}$: -209.9 (c = 0.50, CH_2Cl_2; 96% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.34-7.28 (m, 3H), 7.24 (dd, *J* = 5.8, 0.8 Hz, 1H), 7.11-7.04 (m, 2H), 4.47 (dd, *J* = 9.0, 0.8 Hz, 1H), 3.65 (s, 3H), 2.93 (dd, *J* = 9.0, 5.8 Hz, 1H), 1.59 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.2, 155.3, 152.3, 139.2, 133.3, 128.7, 128.5, 128.5, 121.1, 84.9, 53.3, 46.1, 35.3, 28.0, 27.7.

HRMS (ESI): calculated for $C_{19}H_{20}BrNO_5Na$ $[M+Na]^+$: 444.0417; Found: 444.0409.

2-(tert-butyl) 7-methyl (1S,6S,7R)-4-chloro-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (4c)



Prepared from tert-butyl 3-chloro-2-oxopyridine-1(2H)-carboxylate (45.9 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (53.5 mg, 71%), mp: 126-128 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.3

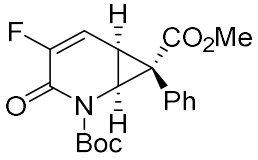
HPLC analysis: 95% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 10.39 min (major) and 14.15 min (minor). $[\alpha]_D^{20}$: -226.1 (c = 0.50, CH_2Cl_2; 95% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.33-7.27 (m, 3H), 7.11-7.05 (m, 2H), 6.97 (d, *J* = 5.7 Hz, 1H), 4.46 (d, *J* = 9.0 Hz, 1H), 3.66 (s, 3H), 2.97 (dd, *J* = 9.0, 5.7 Hz, 1H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.2, 155.6, 152.2, 134.5, 133.2, 129.8, 128.7, 128.5, 128.5, 84.9, 53.3, 45.8, 35.3, 28.0, 26.4.

HRMS (ESI): calculated for $C_{19}H_{20}ClNO_5Na$ $[M+Na]^+$: 400.0922; Found: 400.0918.

2-(tert-butyl) 7-methyl (1S,6S,7R)-4-fluoro-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (4d)



Prepared from tert-butyl 3-fluoro-2-oxopyridine-1(2H)-carboxylate (42.6 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (68.6 mg, 95%), mp: 106-108 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

HPLC analysis: 78% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.17 min (major) and 14.73 min (minor). $[\alpha]_D^{20}$: -278.7 (c = 0.50, CH_2Cl_2; 78% ee).

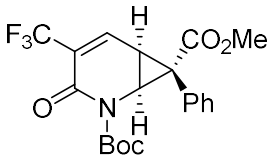
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.33-7.28 (m, 3H), 7.12-7.06 (m, 2H), 6.36-6.30 (m, 1H), 4.39 (d, *J* = 9.2 Hz, 1H), 3.64 (s, 3H), 2.95-2.88 (m, 1H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.4, 154.7 (d, $^2J_{C\text{-}F}$ = 31.3 Hz), 151.6 (d, $^4J_{C\text{-}F}$ = 1.0 Hz), 149.9 (d, $^1J_{C\text{-}F}$ = 255.5 Hz), 133.2, 128.7, 128.6, 128.5, 113.4 (d, $^2J_{C\text{-}F}$ = 20.2 Hz), 85.0, 53.2, 44.9, 34.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 27.9, 23.6 (d, $^3J_{C\text{-}F}$ = 9.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) δ -125.34 (1F).

HRMS (ESI): calculated for $C_{19}H_{20}FNO_5Na$ $[M+Na]^+$: 384.1218; Found: 384.1218.

2-(tert-butyl) 7-methyl (1S,6S,7R)-3-oxo-7-phenyl-4-(trifluoromethyl)-2-azabicyclo[4.1.0] hept-4-ene-2,7-dicarboxylate (4e)



Prepared from tert-butyl 2-oxo-3-(trifluoromethyl)pyridine-1(2H)-carboxylate (52.6 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 °C. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (67.5 mg, 82%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.2

HPLC analysis: 96% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 7.93 min (major) and 15.15 min (minor). $[\alpha]_D^{20}$: -353.7 (c = 0.50, CH_2Cl_2; 96% ee).

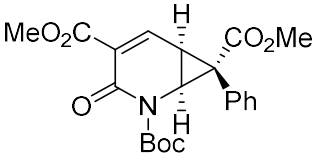
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.37 (d, *J* = 5.7 Hz, 1H), 7.33-7.27 (m, 3H), 7.08-6.99 (m, 2H), 4.49 (d, *J* = 8.6 Hz, 1H), 3.68 (s, 3H), 3.10-3.01 (m, 1H), 1.60 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 171.9, 155.3, 152.2, 141.2 (q, $^3J_{C\text{-}F}$ = 5.3 Hz), 133.1, 128.8, 128.7, 127.8, 127.1 (q, $^2J_{C\text{-}F}$ = 30.0 Hz), 120.7 (q, $^1J_{C\text{-}F}$ = 271.5 Hz), 85.1, 53.4, 45.9, 36.9, 27.9, 24.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -65.78 (3F).

HRMS (ESI): calculated for $C_{20}H_{20}F_3NO_5Na$ $[M+Na]^+$: 434.1186; Found: 434.1185.

2-(tert-butyl) 4,7-dimethyl (1S,6S,7R)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,4,7-tricarboxylate (4f)



Prepared from 1-(tert-butyl) 3-methyl 2-oxopyridine-1,3(2H)-dicarboxylate (50.6 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 °C. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as

white solid (61.8 mg, 77%), mp: 124-126 ℃.

R_f (Petroleum ether/EtOAc = 1:1) = 0.6

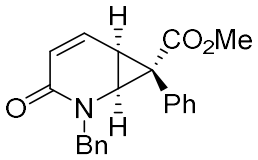
HPLC analysis: 91% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.89 min (major) and 13.20 min (minor). $[\alpha]_D^{20}$: -327.1 (c = 0.50, CH_2Cl_2; 91% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.51 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.31-7.25 (m, 3H), 7.11-7.02 (m, 2H), 4.46 (dd, *J* = 8.6, 0.9 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.04 (dd, *J* = 8.6, 5.8 Hz, 1H), 1.59 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 172.0, 163.8, 156.6, 152.6, 144.6, 133.2, 129.9, 128.6, 128.6, 128.2, 84.6, 53.3, 52.5, 46.2, 37.3, 28.0, 25.7.

HRMS (ESI): calculated for $C_{21}H_{23}NO_7Na$ $[M+Na]^+$: 424.1367; Found: 424.1368.

methyl (1S,6S,7R)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (4g)



Prepared from 1-benzylpyridin-2(1H)-one (37.0 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 ℃. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (47.3 mg, 71%), mp: 170-172 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.4

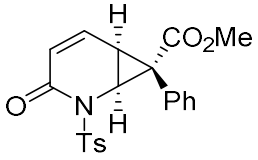
HPLC analysis: 78% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 17.46 min (minor) and 20.76 min (major). $[\alpha]_D^{20}$: -318.9 (c = 0.50, CH_2Cl_2; 78% ee).

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) δ 7.38-7.23 (m, 8H), 7.00-6.93 (m, 2H), 6.64 (dd, *J* = 9.8, 5.3 Hz, 1H), 5.69 (d, *J* = 9.8 Hz, 1H), 5.52 (d, *J* = 14.7 Hz, 1H), 4.16 (d, *J* = 14.7 Hz, 1H), 3.88 (d, *J* = 8.9 Hz, 1H), 3.61 (s, 3H), 2.87 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 173.4, 161.4, 136.3, 136.2, 133.2, 129.5, 128.9, 128.4, 128.3, 128.1, 127.9, 126.4, 53.1, 50.5, 48.7, 33.8, 28.1.

HRMS (ESI): calculated for $C_{21}H_{20}NO_3$ $[M+H]^+$: 334.1438; Found: 334.1439.

methyl (1S,6S,7R)-3-oxo-7-phenyl-2-tosyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (4h)



Prepared from 1-tosylpyridin-2(1H)-one (49.6 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%) at 30 ℃. Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (51.6 mg, 65%), mp: 128-130 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.3

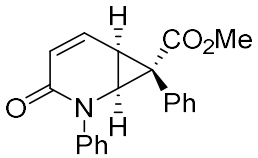
HPLC analysis: 91% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 10.29 min (minor) and 11.39 min (major). $[\alpha]_D^{20}$: -340.3 (c = 0.50, CH_2Cl_2; 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.35-7.20 (m, 7H), 6.80 (dd, *J* = 9.8, 5.3 Hz, 1H), 5.51 (d, *J* = 9.8 Hz, 1H), 4.81 (d, *J* = 9.0 Hz, 1H), 3.69 (s, 3H), 3.00 (dd, *J* = 9.0, 5.3 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.5, 159.5, 145.4, 139.9, 135.6, 133.7, 129.5, 129.0, 128.5, 128.40, 128.36, 125.6, 53.4, 46.7, 35.3, 26.9, 21.8.

HRMS (ESI): calculated for $C_{21}H_{20}NO_5S$ $[M+H]^+$: 398.1057; Found: 398.1062.

methyl (1S,6S,7R)-3-oxo-2,7-diphenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (4i)



Prepared from 1-phenylpyridin-2(1H)-one (34.2 mg, 0.2 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (70.4 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (55.7 mg, 87%), mp: 118-120 ℃.

R_f (Petroleum ether/EtOAc = 1:1) = 0.5

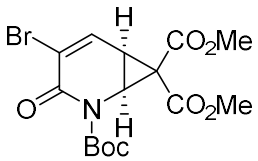
HPLC analysis: 84% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 60/40, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 6.47 min (major) and 11.46 min (minor). $[\alpha]_D^{20}$: -339.1 (c = 0.50, CH_2Cl_2; 84% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.31-7.24 (m, 4H), 7.17-7.09 (m, 2H), 6.72 (dd, *J* = 9.8, 5.3 Hz, 1H), 5.77 (d, *J* = 9.8 Hz, 1H), 4.28 (d, *J* = 8.9 Hz, 1H), 3.66 (s, 3H), 3.05 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 173.3, 160.8, 141.4, 136.5, 133.3, 129.4, 129.1, 128.5, 128.2, 127.4, 126.4, 124.8, 53.3, 50.5, 34.4, 28.0.

HRMS (ESI): calculated for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1281; Found: 320.1282.

2-(tert-butyl) 7,7-dimethyl (1S,6S)-4-bromo-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-2,7,7-tricarboxylate (4j)



Prepared from tert-butyl 3-bromo-2-oxopyridine-1(2H)-carboxylate (54.8 mg, 0.2 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (63.2 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as colorless oil (71.2 mg, 88%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.3

HPLC analysis: 59% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH =

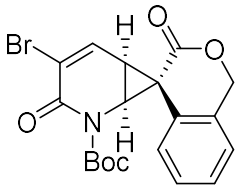
95/5, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 16.13 min (minor) and 17.43 min (major). $[\alpha]_D^{20}$: -80.1 (c = 0.50, CH_2Cl_2; 59% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.23 (d, *J* = 5.5 Hz, 1H), 4.28 (d, *J* = 9.0Hz, 1H), 3.81 (s, 3H), 3.71 (s, 3H), 2.80 (dd, *J* = 9.0, 5.5 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 167.9, 163.4, 155.2, 150.9, 137.4, 121.4, 84.7, 53.5, 53.2, 44.9, 34.9, 27.8, 26.4.

HRMS (ESI): calculated for $C_{15}H_{18}BrNO_7Na$ $[M+Na]^+$: 426.0159; Found: 426.0156.

tert-butyl (1S,6S,7R)-4-bromo-3,3'-dioxo-2-azaspiro[bicyclo[4.1.0]heptane-7,4'-isochroman]-4-ene-2-carboxylate (4k)



Prepared from tert-butyl 3-bromo-2-oxopyridine-1(2H)-carboxylate (54.8 mg, 0.2 mmol, 1.0 equiv) and 4-diazoisochroman-3-one (69.6 mg, 0.4 mmol, 2.0 equiv) according to the general procedure in the presence of Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-1:1) and obtained as white solid (42.0 mg, 0.1 mmol, 50%), mp: 125-127 ℃.

R_f (Petroleum ether/EtOAc = 3:1) = 0.5

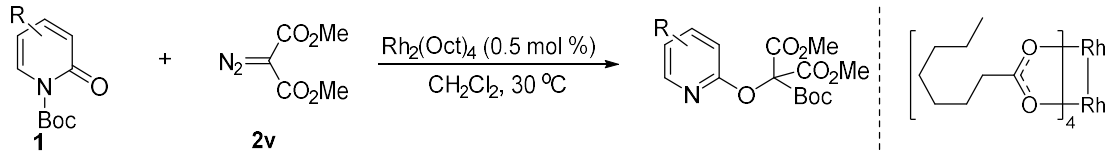
HPLC analysis: 70% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 15.07 min (minor) and 16.54 min (major). $[\alpha]_D^{20}$: -247.6 (c = 0.50, CH_2Cl_2; 70% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.51 (d, *J* = 5.8 Hz, 1H), 7.35-7.25 (m, 4H), 5.71 (d, *J* = 13.2 Hz, 1H), 5.17 (d, *J* = 13.2 Hz, 1H), 4.28 (d, *J* = 8.9 Hz, 1H), 3.32 (dd, *J* = 8.9, 5.8 Hz, 1H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 170.7, 155.8, 152.1, 139.1, 135.7, 128.7, 128.2, 127.3, 126.5, 125.7, 122.0, 85.2, 69.6, 46.0, 30.9, 27.7, 24.9.

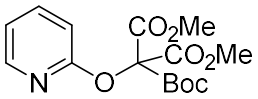
HRMS (ESI): calculated for $C_{19}H_{18}BrNO_5Na$ $[M+Na]^+$: 442.0261; Found: 442.0259.

General procedure for Scheme 5



To a dry tube was added $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%), **1** (0.1 mmol, 1.0 equiv) and **2v** (0.3 mmol, 3.0 equiv), and then anhydrous DCM (2 mL) was added in one portion. The tube was evacuated and backfilled with Argon for 3 times. The reaction mixture was stirred at 30 ℃ in a heating block for 12 h. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/petroleum ether = 1:5-1:3) to give desired product.

1-tert-butyl 1,1-dimethyl (pyridin-2-yloxy)methanetricarboxylate (5a)



Prepared from tert-butyl 2-oxopyridine-1(2H)-carboxylate (19.5 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as white solid (23.5 mg, 72%), mp: 72-74 ℃.

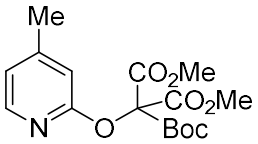
R_f (Petroleum ether/EtOAc = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.01 (d, *J* = 3.8 Hz, 1H), 7.69-7.62 (m, 1H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.93 (dd, *J* = 7.2, 5.0 Hz, 1H), 3.83 (s, 6H), 1.44 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 164.3, 162.0, 160.7, 145.5, 139.2, 118.2, 111.0, 84.2, 83.3, 53.5, 27.6.

HRMS (ESI): calculated for $C_{15}H_{20}NO_7$ $[M+H]^+$: 326.1234; Found: 326.1236.

1-tert-butyl 1,1-dimethyl ((4-methylpyridin-2-yl)oxy)methanetricarboxylate (5b)



Prepared from tert-butyl 4-methyl-2-oxopyridine-1(2H)-carboxylate (20.9 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as light yellow oil (30.8 mg, 91%).

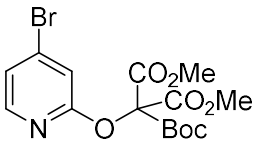
R_f (Petroleum ether/EtOAc = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.86 (d, *J* = 5.2 Hz, 1H), 6.81 (s, 1H), 6.75 (d, *J* = 5.2 Hz, 1H), 3.82 (s, 6H), 2.32 (s, 3H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 164.4, 162.1, 161.0, 150.7, 145.0, 119.7, 111.0, 84.2, 83.2, 53.5, 27.6, 21.0.

HRMS (ESI): calculated for $C_{16}H_{22}NO_7$ $[M+H]^+$: 340.1391; Found: 340.1395.

1-tert-butyl 1,1-dimethyl ((4-bromopyridin-2-yl)oxy)methanetricarboxylate (5c)



Prepared from tert-butyl 4-bromo-2-oxopyridine-1(2H)-carboxylate (27.4 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as light yellow oil (32.3 mg, 80%).

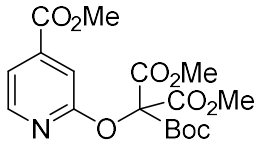
R_f (Petroleum ether/EtOAc = 3:1) = 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.85 (d, *J* = 5.4 Hz, 1H), 7.20 (s, 1H), 7.10 (dd, *J* = 5.4, 1.6 Hz, 1H), 3.83 (s, 6H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 163.9, 161.6, 161.3, 146.1, 134.4, 121.8, 114.4, 84.6, 83.5, 53.6, 27.6.

HRMS (ESI): calculated for $C_{15}H_{19}BrNO_7$ $[M+H]^+$: 404.0339; Found: 404.0345.

1-tert-butyl 1,1-dimethyl ((4-(methoxycarbonyl)pyridin-2-yl)oxy)methanetricarboxylate (5d)



Prepared from 1-(tert-butyl) 4-methyl 2-oxopyridine-1,4(2H)-dicarboxylate (25.3 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as light yellow oil (18.8 mg, 49%).

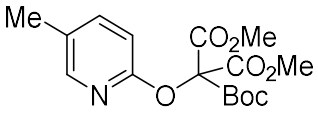
R_f (Petroleum ether/EtOAc = 3:1) = 0.3

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.14 (d, *J* = 5.2 Hz, 1H), 7.58 (s, 1H), 7.50 (d, *J* = 5.2 Hz, 1H), 3.95 (s, 3H), 3.84 (s, 6H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 165.1, 164.1, 161.7, 161.5, 146.3, 140.8, 117.5, 111.4, 84.6, 83.6, 53.6, 52.8, 27.6.

HRMS (ESI): calculated for $C_{17}H_{22}NO_9$ $[M+H]^+$: 384.1289; Found: 384.1294.

1-tert-butyl 1,1-dimethyl ((5-methylpyridin-2-yl)oxy)methanetricarboxylate (5e)



Prepared from tert-butyl 5-methyl-2-oxopyridine-1(2H)-carboxylate (20.9 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as light yellow oil (28.5 mg, 84%).

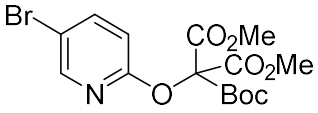
R_f (Petroleum ether/EtOAc = 3:1) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.80 (s, 1H), 7.47 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 3.83 (s, 6H), 2.23 (s, 3H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 164.5, 162.1, 158.9, 145.0, 140.1, 127.3, 110.2, 84.2, 83.2, 53.5, 27.6, 17.5.

HRMS (ESI): calculated for $C_{16}H_{22}NO_7$ $[M+H]^+$: 340.1391 Found: 340.1393.

1-tert-butyl 1,1-dimethyl ((5-bromopyridin-2-yl)oxy)methanetricarboxylate (5f)



Prepared from tert-butyl 4-bromo-2-oxopyridine-1(2H)-carboxylate (27.4 mg, 0.1 mmol, 1.0 equiv)

and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as white solid (29.1 mg, 72%), mp: 75-77 ℃.

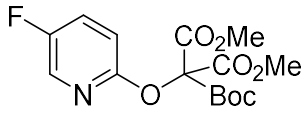
R_f (Petroleum ether/EtOAc = 3:1) = 0.6

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.05 (d, *J* = 2.3 Hz, 1H), 7.75 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 3.84 (s, 6H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 164.0, 161.6, 159.6, 146.2, 141.8, 113.4, 112.7, 84.6, 83.6, 53.6, 27.6.

HRMS (ESI): calculated for $C_{15}H_{19}BrNO_7$ $[M+H]^+$: 404.0339 Found: 404.0340.

1-tert-butyl 1,1-dimethyl ((5-fluoropyridin-2-yl)oxy)methanetricarboxylate (5g)



Prepared from tert-butyl 5-fluoro-2-oxopyridine-1(2H)-carboxylate (21.3 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as colorless oil (20.6 mg, 60%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.6

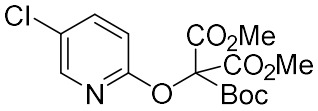
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.84 (d, *J* = 2.8 Hz, 1H), 7.46-7.39 (m, 1H), 6.97 (dd, *J* = 9.0, 3.4 Hz, 1H), 3.84 (s, 6H), 1.45 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 164.2, 161.8, 156.7 (d, ^4J = 1.3 Hz), 156.0 (d, ^1J = 246.0 Hz), 132.2 (d, ^2J = 27.0 Hz), 127.0 (d, ^2J = 21.0 Hz), 111.78 (d, ^3J = 5.3 Hz), 84.5, 83.6, 53.6, 27.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -136.87 (1F).

HRMS (ESI): calculated for $C_{15}H_{19}FNO_7$ $[M+H]^+$: 344.1140 Found: 344.1144.

1-tert-butyl 1,1-dimethyl ((5-chloropyridin-2-yl)oxy)methanetricarboxylate (5h)



Prepared from tert-butyl tert-butyl 5-chloro-2-oxopyridine-1(2H)-carboxylate (23.0 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of $Rh_2(Oct)_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as white solid (23.3 mg, 65%), mp: 71-73 ℃.

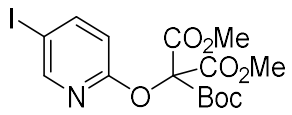
R_f (Petroleum ether/EtOAc = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.95 (d, *J* = 2.2 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 1H), 3.84 (s, 6H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 164.1, 161.7, 159.2, 143.9, 139.2, 125.7, 112.1, 84.6, 83.6, 53.6, 27.6.

HRMS (ESI): calculated for $C_{15}H_{19}ClNO_7$ $[M+H]^+$: 360.0845 Found: 360.0849.

1-tert-butyl 1,1-dimethyl ((5-iodopyridin-2-yl)oxy)methanetricarboxylate (5i)



Prepared from tert-butyl 5-iodo-2-oxopyridine-1(2H)-carboxylate (32.1 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of Rh_2(S-TFPTTL)$_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as white solid (29.3 mg, 65%), mp: 77-79 ℃.

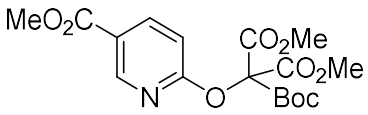
R_f (Petroleum ether/EtOAc = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.19 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 3.84 (s, 6H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 164.0, 161.6, 160.3, 151.3, 147.2, 113.4, 84.6, 84.0, 83.5, 53.7, 27.6.

HRMS (ESI): calculated for $C_{15}H_{19}INO_7$ $[M+H]^+$: 452.0201 Found: 452.0207.

1-tert-butyl 1,1-dimethyl ((5-(methoxycarbonyl)pyridin-2-yl)oxy)methanetricarboxylate (5j)



Prepared from 1-(tert-butyl) 4-methyl 2-oxopyridine-1,4(2H)-dicarboxylate (25.3 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of Rh_2(Oct)$_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as light yellow oil (29.5 mg, 77%).

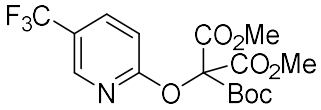
R_f (Petroleum ether/EtOAc = 3:1) = 0.4

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.68 (d, *J* = 2.1 Hz, 1H), 8.27 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.04 (d, *J* = 8.6 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 6H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 165.5, 163.8, 163.5, 161.5, 148.3, 140.4, 121.2, 110.8, 84.7, 83.7, 53.7, 52.2, 27.6.

HRMS (ESI): calculated for $C_{17}H_{22}NO_9$ $[M+H]^+$: 384.1289 Found: 384.1294.

1-tert-butyl 1,1-dimethyl ((5-(trifluoromethyl)pyridin-2-yl)oxy)methanetricarboxylate (5k)



Prepared from tert-butyl 2-oxo-5-(trifluoromethyl)pyridine-1(2H)-carboxylate (26.3 mg, 0.1 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (47.4 mg, 0.3 mmol, 3.0 equiv) according to the general procedure in the presence of Rh_2(Oct)$_4$ (0.4 mg, 0.0005 mmol, 0.5 mol%). Purified by silica gel column chromatography (petroleum ether/EtOAc = 5:1-3:1) and obtained as colorless oil (18.1 mg, 46%).

R_f (Petroleum ether/EtOAc = 3:1) = 0.5

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.85 (s, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 3.86 (s, 6H), 1.54 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 165.4, 156.5, 151.4, 145.9 (q, $^3J_{C-F}$ = 3.8 Hz), 134.3 (q, $^3J_{C-F}$ = 3.0 Hz), 127.0 (q, $^2J_{C-F}$ = 33.0 Hz), 123.1 (q, $^1J_{C-F}$ = 270.8 Hz), 122.2, 84.64, 84.56, 53.8, 27.5.

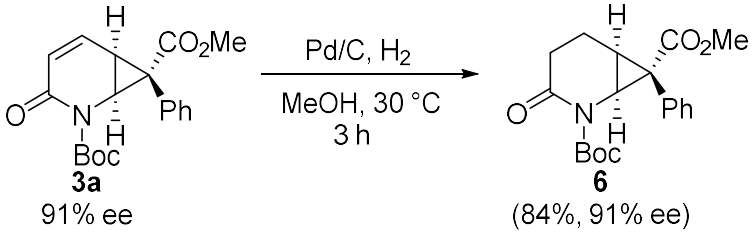
^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -62.58 (3F).

HRMS (ESI): calculated for $C_{16}H_{19}F_3NO_7$ $[M+H]^+$: 394.1108 Found: 394.1110.

Application and Elaboration for Scheme 6

Scheme 6-a

To a dry tube was added Rh_2(S-TFPTTL)$_4$ (27.6 mg, 0.018 mmol, 0.5 mol%), **1a** (702 mg, 3.60 mmol, 1.0 equiv) and anhydrous DCM (60 mL), and then **2a** (1.27g, 7.20 mmol, 2.0 equiv) dissolved in anhydrous DCM (10 mL) was added via a syringe pump over 15 min under an argon atmosphere. The reaction mixture was stirred at 20 ℃ in a heating block for 15 min. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/Petroleum ether = 1:5-1:1) to give desired **3a** (1.15g, 93%, 91% ee).



To a 50-mL flask containing a magnetic stirring bar, wet 10% Pd/C (34 mg, 0.24 mmol, 0.1 equiv.), **3a** (343 mg, 1.0 mmol, 1.0 equiv) and 15 mL of MeOH were added. The heterogeneous mixture was degassed and refilled with H_2 for three times. The mixture was stirred at 30 °C under H_2 balloon stirred for 3 h. After the hydrogenolysis was completed (monitored by TLC), the reaction mixture was filtered through a pad of Celite to remove Pd/C, the solid was washed with MeOH. The combined filtrate was concentrated under vacuum, and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 5:1 to 2:1) to give **6** as colorless oil (290.0 mg, 84%).

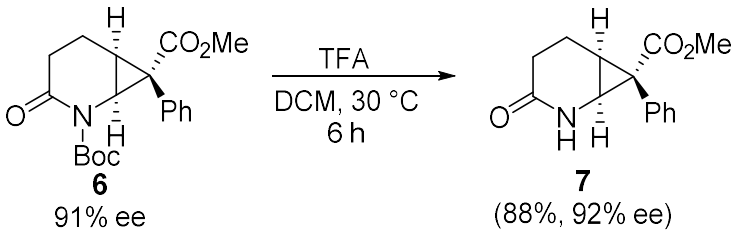
R_f (Petroleum ether/EtOAc = 3:1) = 0.3

HPLC analysis: 91% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 6.48 min (minor) and 7.22 min (major). $[\alpha]_D^{20}$: -121.9 (c = 0.50, CH_2Cl_2; 91% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.38-7.30 (m, 3H), 7.26-7.18 (m, 2H), 3.92 (d, *J* = 9.1 Hz, 1H), 3.60 (s, 3H), 2.55 (dd, *J* = 15.9, 8.6 Hz, 1H), 2.48-2.35 (m, 1H), 2.33-2.21 (m, 1H), 2.04 (dt, *J* = 15.9, 4.2 Hz, 1H), 1.71-1.63 (m, 1H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.7, 171.1, 152.7, 132.0, 131.2, 128.9, 128.1, 83.8, 52.8, 44.1, 38.6, 33.6, 28.0, 24.9, 18.0.

HRMS (ESI): calculated for $C_{19}H_{23}NO_5Na$ $[M+Na]^+$: 368.1468; Found: 368.1468.



In a round-bottom flask, **6** (275 mg, 0.80 mmol, 1.0 equiv) was dissolved in DCM (15 mL). Then TFA (273 mg, 2.4 mmol, 3.0 equiv) were added, and the solution was stirred at room temperature for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1-1:2) to give **7** as white solid (172.6 mg, 88%), mp: 128-130 ℃.

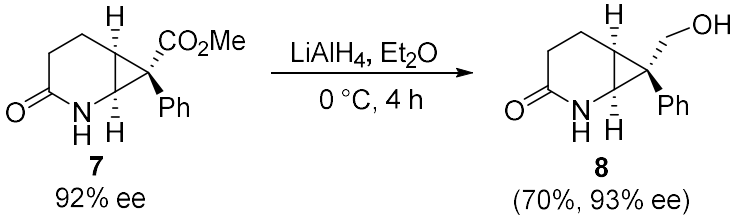
R_f (Petroleum ether/EtOAc = 1:2) = 0.2

HPLC analysis: 92% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 9.83 min (minor) and 11.08 min (major). $[\alpha]_D^{20}$: -41.7 (c = 0.50, CH_2Cl_2; 92% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 8.00 (s, 1H), 7.39-7.29 (m, 3H), 7.26-7.15 (m, 2H), 3.55 (s, 4H), 2.49-2.39 (m, 1H), 2.35-2.23 (m, 1H), 2.21-2.08 (m, 1H), 1.82-1.70 (m, 1H), 1.8-1.46 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 173.5, 172.8, 132.4, 131.4, 128.8, 127.8, 52.7, 40.8, 38.6, 28.9, 23.5, 17.9.

HRMS (ESI): calculated for $C_{14}H_{15}NO_3Na$ $[M+Na]^+$: 268.0944; Found: 268.0939.



A solution of **7** (80 mg, 0.33 mmol, 1.0 equiv) in Et_2O (10 mL) was stirred and cooled to 0 ℃, then $LiAlH_4$ (50.7 mg, 1.34 mmol, 4.0 equiv) was added in portions. The reaction mixture was stirred at 0 ℃ for 4 h. Water was added to quench the excess $LiAlH_4$. The mixture was extracted with Et_2O (5 mL), dried over anhydrous Na_2SO_4 and filtered; the filtrate was concentrated to give crude product. The residue was purified by silica gel chromatography column (MeOH/CH_2Cl_2 = 1:10) to obtain **8** as white solid (50.2 mg, 70%), mp: 184-186 ℃.

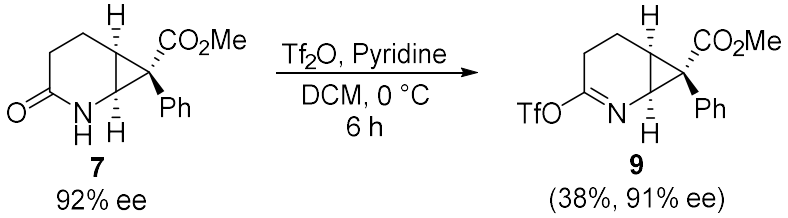
R_f (MeOH/CH_2Cl_2 = 1:10) = 0.5

HPLC analysis: 93% ee; determined by HPLC: Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.77 min (minor) and 12.58 min (major). $[\alpha]_D^{20}$: -72.5 (c = 0.50, CH_2Cl_2; 93% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.36-7.23 (m, 3H), 7.23-7.12 (m, 2H), 6.87 (s, 1H), 3.62 (d, *J* = 11.4 Hz, 1H), 3.29 (d, *J* = 11.4 Hz, 1H), 2.95 (d, *J* = 8.5 Hz, 1H), 2.32 (s, 1H), 2.24-1.96 (m, 2H), 1.76-1.48 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 174.3, 135.1, 131.9, 128.9, 127.2, 70.1, 39.4, 35.6, 29.7, 18.6, 17.7.

HRMS (ESI): calculated for $C_{13}H_{15}NO_2Na$ $[M+Na]^+$: 240.0995; Found: 240.0989.



To a flamed-dried round equipped with a stir bar, **7** (75.6 mg, 0.31 mmol, 1.0 equiv) in DCM (8 mL) was added. The reaction mixture was cooled at 0 °C. Then, Tf_2O (134 mg, 0.48 mmol, 1.5 equiv) and pyridine (37.3 mg, 0.47 mmol, 1.5 equiv) was slowly added to the reaction mixture which was then stirred at the same temperature for 6 h. The reaction was diluted with DCM and washed with satd. $NaHCO_3$. The combined organic extracts were dried over Na_2SO_4 and concentrated to give a crude product. The residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 3:1-2:1) to obtain **9** as white solid (43.9 mg, 38%), mp: 78-80 °C.

R_f (Petroleum ether/EtOAc = 2:1) = 0.5

HPLC analysis: 91% ee; determined by HPLC: Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 6.93 min (major) and 10.57 min (minor). $[\alpha]_D^{20}$: -65.7 (c = 0.50, CH_2Cl_2; 91% ee).

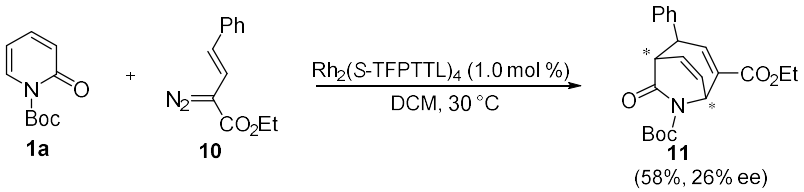
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.45-7.35 (m, 5H), 4.09 (d, *J* = 9.4 Hz, 1H), 3.62 (s, 3H), 2.61-2.52 (m, 1H), 2.45-2.30 (m, 2H), 2.11-1.98 (m, 1H), 1.82-1.72 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) δ 171.8, 169.5, 131.6, 130.2, 129.4, 128.7, 119.4 (q, ^1J = 323.2 Hz), 53.2, 46.0, 37.5, 32.0, 23.8, 18.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) δ -71.40 (3F).

HRMS (ESI): calculated for $C_{15}H_{14}F_3NO_5SNa$ $[M+Na]^+$: 400.0437; Found: 400.0430.

Scheme 6-b



To a dry tube was added Rh_2(*S*-TFPTTL)$_4$ (3.0 mg, 0.002 mmol, 1.0 mol%), **1a** (39.0 mg, 0.2 mmol, 1 equiv) and anhydrous DCM (2 mL), and then **10** (64.8 mg, 0.3 mmol, 1.5 equiv) dissolved in anhydrous DCM (2 mL) was added via a syringe pump 15 min under an argon atmosphere. The reaction mixture was stirred at 30 °C in a heating block for 15 min. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/Petroleum ether = 1:5-1:2) to give desired **11** as white solid (44.8 mg, 58%, 26% ee), mp: 81-83 °C. [Note: The racemic sample was prepared via general procedure by using $Rh_2(PTTL)_4$.]

R_f (Petroleum ether/ EtOAc = 3:1) = 0.4

HPLC analysis: 26% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH =

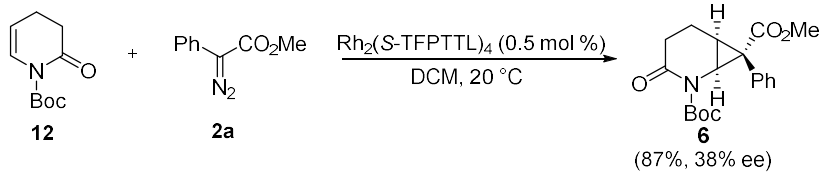
90/10, flow rate = 1.0 mL/min, λ = 225 nm, t_R = 11.21 min (minor) and 12.20 min (major). $[\alpha]_D^{20}$: -20.7 (c = 0.50, CH_2Cl_2; 26% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.36-7.27 (m, 3H), 7.15 (d, *J* = 6.6 Hz, 2H), 6.84-6.77 (m, 1H), 6.71-6.61 (m, 1H), 5.82 (d, *J* = 6.9 Hz, 1H), 5.75 (t, *J* = 7.3 Hz, 1H), 4.36-4.18 (m, 2H), 4.08 (t, *J* = 3.5 Hz, 1H), 3.58-3.51 (m, 1H), 1.54 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 171.9, 165.4, 150.0, 142.6, 137.8, 134.6, 134.5, 128.9, 128.2, 127.8, 126.8, 83.7, 61.5, 52.6, 49.2, 43.2, 28.0, 14.3.

HRMS (ESI): calculated for $C_{22}H_{25}NO_5Na$ [M+Na]+: 406.1625; Found: 406.1621.

Scheme 6-c



To a dry tube was added Rh_2(*S*-TFPTTL)$_4$ (1.5 mg, 0.001 mmol, 0.5 mol%), **12** (39.4 mg, 0.2 mmol, 1 equiv) and anhydrous DCM (2 mL), and then **2a** (70.4 mg, 0.4 mmol, 2.0 equiv) dissolved in anhydrous DCM (2 mL) was added via a syringe pump over 15 min under an argon atmosphere. The reaction mixture was stirred at 20 °C in a heating block for 15 min. The reaction mixture was concentrated. The residue was purified by silica gel chromatography (eluent: EtOAc/Petroleum ether = 1:5-1:2) to give **6** as colorless oil (60.0 mg, 87%, 38% ee). [Note: The racemic sample was prepared via general procedure by using $Rh_2(PTTL)_4$.]

R_f (Petroleum ether / EtOAc = 3:1) = 0.3

HPLC analysis: 38% ee; determined by HPLC: Daicel Chiralpak IA column, n-hexane/i-PrOH = 70/30, flow rate 1.0 mL/min, λ = 225 nm, t_R = 6.47 min (minor) and 7.23 min (major). $[\alpha]_D^{20}$: -60.1 (c = 0.50, CH_2Cl_2; 38% ee).

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 7.38-7.30 (m, 3H), 7.22 (d, *J* = 7.6 Hz, 2H), 3.92 (d, *J* = 9.1 Hz, 1H), 3.60 (s, 3H), 2.55 (dd, *J* = 15.9, 8.6 Hz, 1H), 2.48-2.35 (m, 1H), 2.33-2.21 (m, 1H), 2.04 (dt, *J* = 15.9, 4.2 Hz, 1H), 1.70-1.62 (m, 1H), 1.60 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) δ 172.7, 171.0, 152.7, 132.0, 131.2, 128.9, 128.0, 83.8, 52.8, 44.1, 38.6, 33.6, 28.0, 24.9, 18.0.

X-ray crystallographic data for 4b and 5a

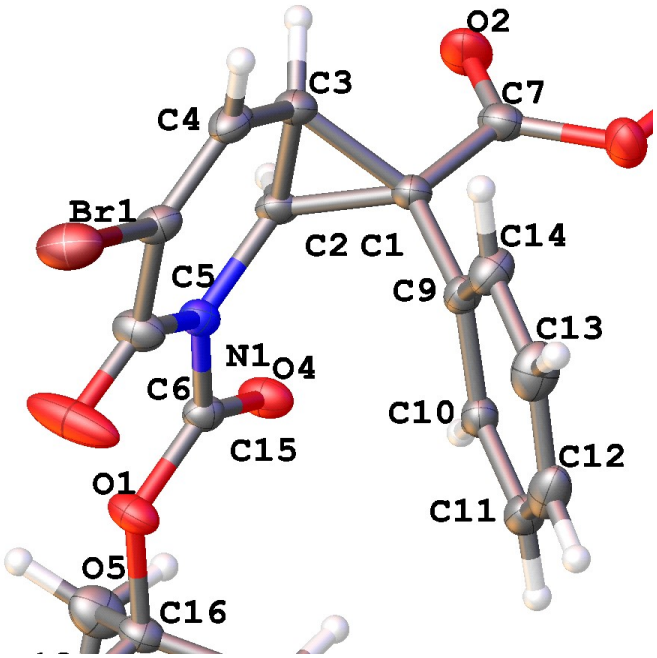
The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2141241 (**4b**) and CCDC 2141339 (**5a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/.

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 (2016/6).

X-ray crystallographic data for 4b

Method of crystallization: A purified compound **4b** was dissolved in a mixed solvent of dichloromethane and petroleum ether. This solution was placed in a cabinet to slowly evaporate.

Crystal data and structure for 4b



X-ray structure of **4b**. Thermal ellipsoids are shown at the 50% level

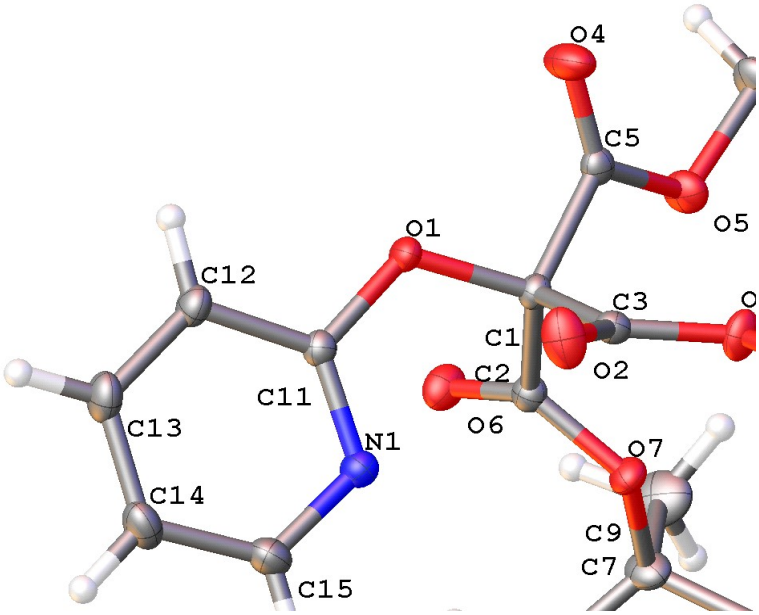
Empirical formula	$C_{19}H_{20}BrNO_5$	
Formula weight	422.27	
Temperature	213.00 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.1865(3) Å	a= 90 °
	b = 10.2193(3) Å	b= 90 °
	c = 18.5986(5) Å	g = 90 °
Volume	1936.09(10) $Å^3$	
Z	4	
Density (calculated)	1.449 Mg/m^3	
Absorption coefficient	2.069 mm^{-1}	
F(000)	864	
Crystal size	0.07 x 0.07 x 0.05 mm^3	
θ range for data collection	4.136 to 54.945°	
Index ranges	-12<=h<=12, -12<=k<=10, -22<=l<=22	
Reflections collected	20741	
Independent reflections	3683 [R(int) = 0.0627]	
Completeness to θ = 53.594°	100.0 %	
Max. and min. transmission	0.7508 and 0.5332	
Data / restraints / parameters	3683 / 0 / 239	
Goodness-of-fit on F^2	0.893	
Final R indices [I > 2σ(I)]	R1 = 0.0413, wR2 = 0.1084	

R indices (all data)	R1 = 0.0489, wR2 = 0.1201
Largest diff. peak and hole	0.305 and -0.923 e.Å^{-3}
Flack parameter	0.031(12)

X-ray crystallographic data for 5a

Method of crystallization: A purified compound **5a** was dissolved in a mixed solvent of dichloromethane and petroleum ether. This solution was placed in a cabinet to slowly evaporate.

Crystal data and structure for 5a



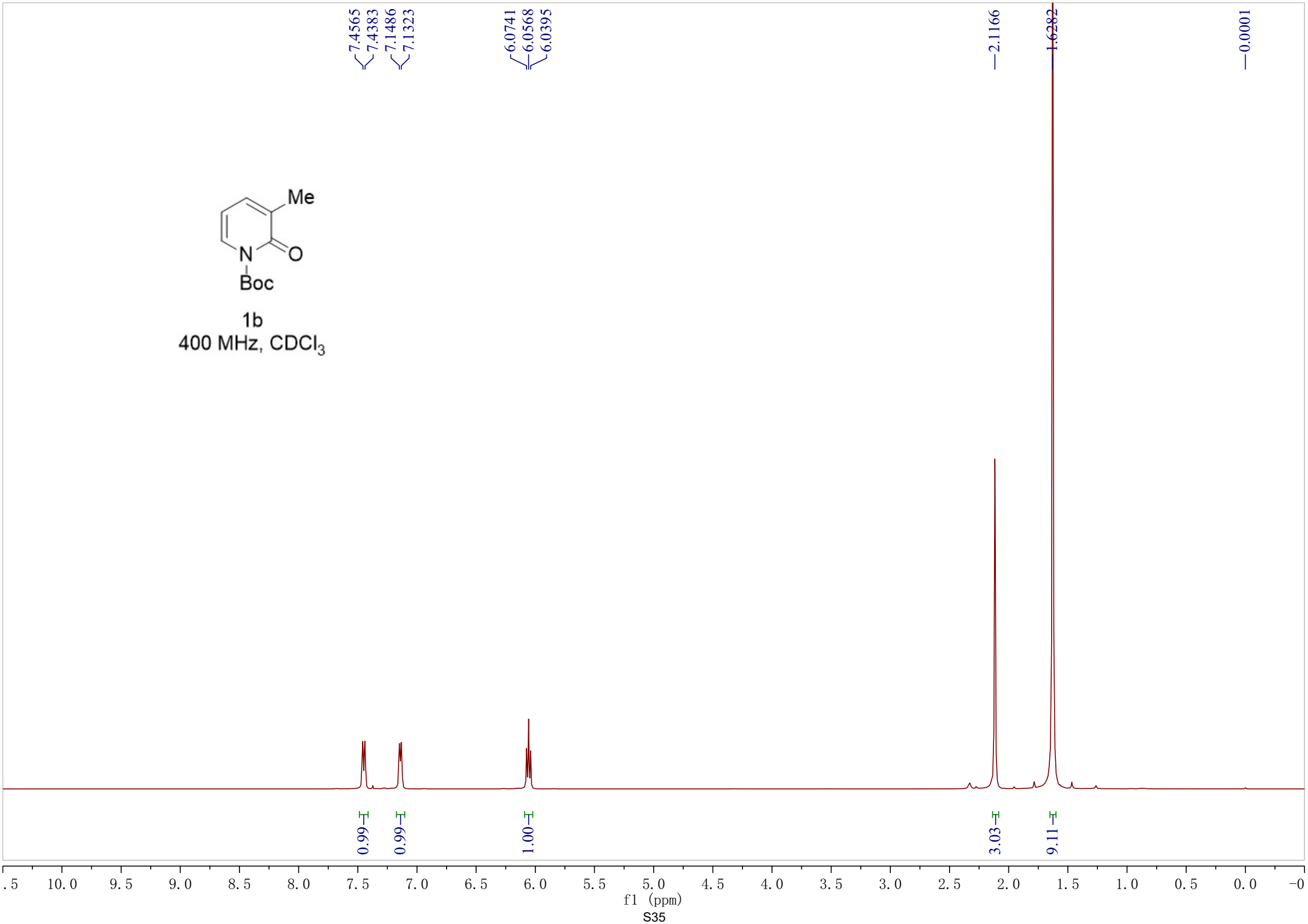
X-ray structure of **5a**. Thermal ellipsoids are shown at the 50% level

Empirical formula	$C_{15}H_{19}NO_7$	
Formula weight	325.31	
Temperature	212.98 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.39990(10) Å	a= 90 °
	b = 13.2871(2) Å	b= 90 °
	c = 16.8639(2) Å	g = 90 °
Volume	1658.11(4) Å^3	
Z	4	
Density (calculated)	1.303 Mg/m^3	
Absorption coefficient	0.562 mm^{-1}	
F(000)	688	
Crystal size	0.08 x 0.07 x 0.07 mm^3	
θ range for data collection	6.229 to 54.910°	
Index ranges	-7<=h<=9, -16<=k<=16, -20<=l<=20	
Reflections collected	17102	

Independent reflections	3127 [R(int) = 0.0315]
Completeness to θ = 53.594°	99.1 %
Max. and min. transmission	0.7508 and 0.5771
Data / restraints / parameters	3127 / 0 / 213
Goodness-of-fit on F^2	1.137
Final R indices [I > 2σ(I)]	R1 = 0.0335, wR2 = 0.0846
R indices (all data)	R1 = 0.0351, wR2 = 0.0861
Largest diff. peak and hole	0.212 and -0.223 e.$Å^{-3}$

References

1. (a) Davies, H. M. L.; Hansen, T.; Churchill, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 3063; (b) Wang, X.; Nozaki, K. *J. Am. Chem. Soc.* **2018**, *140*, 15635; (c) Ošeka, M.; Kimm, M.; Kaabel, S.; Järving, I.; Rissanen, K.; Kanger, T. *Org. Lett.* **2016**, *18*, 1358; (d) Zhu, S.-F.; Song, X.-G.; Li, Y.; Cai, Y.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2010**, *132*, 16374; (e) Denton, J. R.; Davies, H. M. L. *Org. Lett.* **2009**, *11*, 787; (f) Guptill, D. M.; Davies, H. M. L. *J. Am. Chem. Soc.* **2014**, *136*, 17718; (g) Chan, W.-W.; Yeung, S.-H.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. *Org. Lett* **2010,** *12*, 604; (h) Cheng, Q.-Q.; Zhu, S.-F.; Zhang, Y.-Z.; Xie, X.-L.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2013**, *135*, 14094; (i) Maurya, R. A.; Min, K.-I.; Kim, D.-P. *Green Chem.* **2014**, *16*, 116; (j) Sar, S.; Guha, S.; Prabakar, T.; Maiti, D.; Sen, S. *J. Org. Chem.* **2021**, *86*, 11736; (k) Thurow, S.; Fernandes, A. A. G.; Quevedo-Acosta, Y.; de Oliveira, M. F.; de Oliveira, M. G.; Jurberg, I. D. *Org. Lett.* **2019,** *21*, 6909; (l) Maier, T. C.; Fu, G. C. *J. Am. Chem. Soc.* **2006,** *128*, 4594;(m) Loy, N. S. Y.; Singh, A.; Xu, X.; Park, C.-M. *Angew. Chem. Int. Ed.* **2013,** *52*, 2212.
2. (a) Huang, L.; Gu, Y.; Fürstner, A. *Chem. Asian J.* **2019**, *14*, 4017; (b) Jana, S.; Rainier, J. D. *Org. Lett.* **2013**, *15*, 4426.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O
Boc
1b
400 MHz, CDCl3
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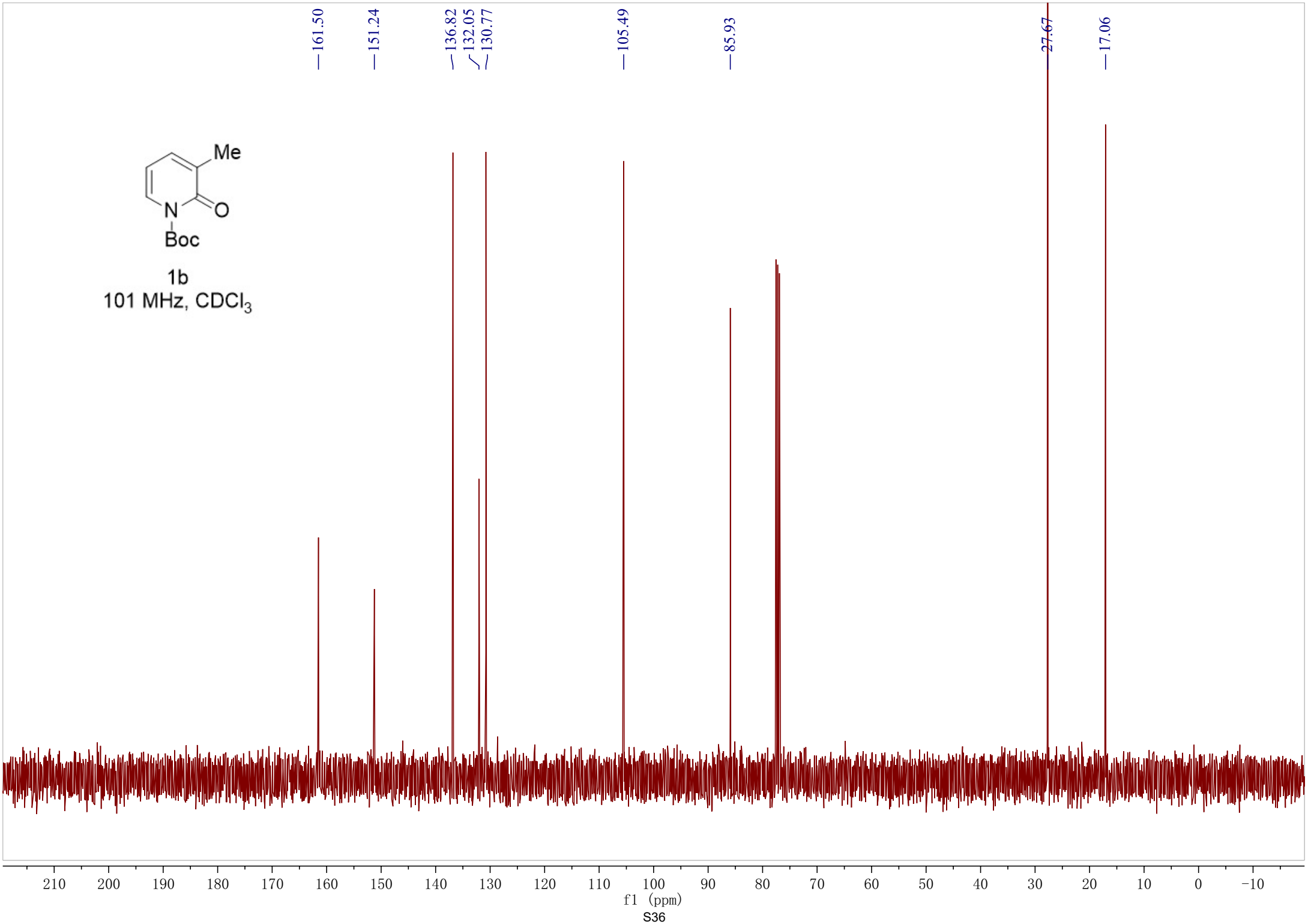
0.99
1.00
3.03
9.11
f1 (ppm)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200
190
180
170
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100
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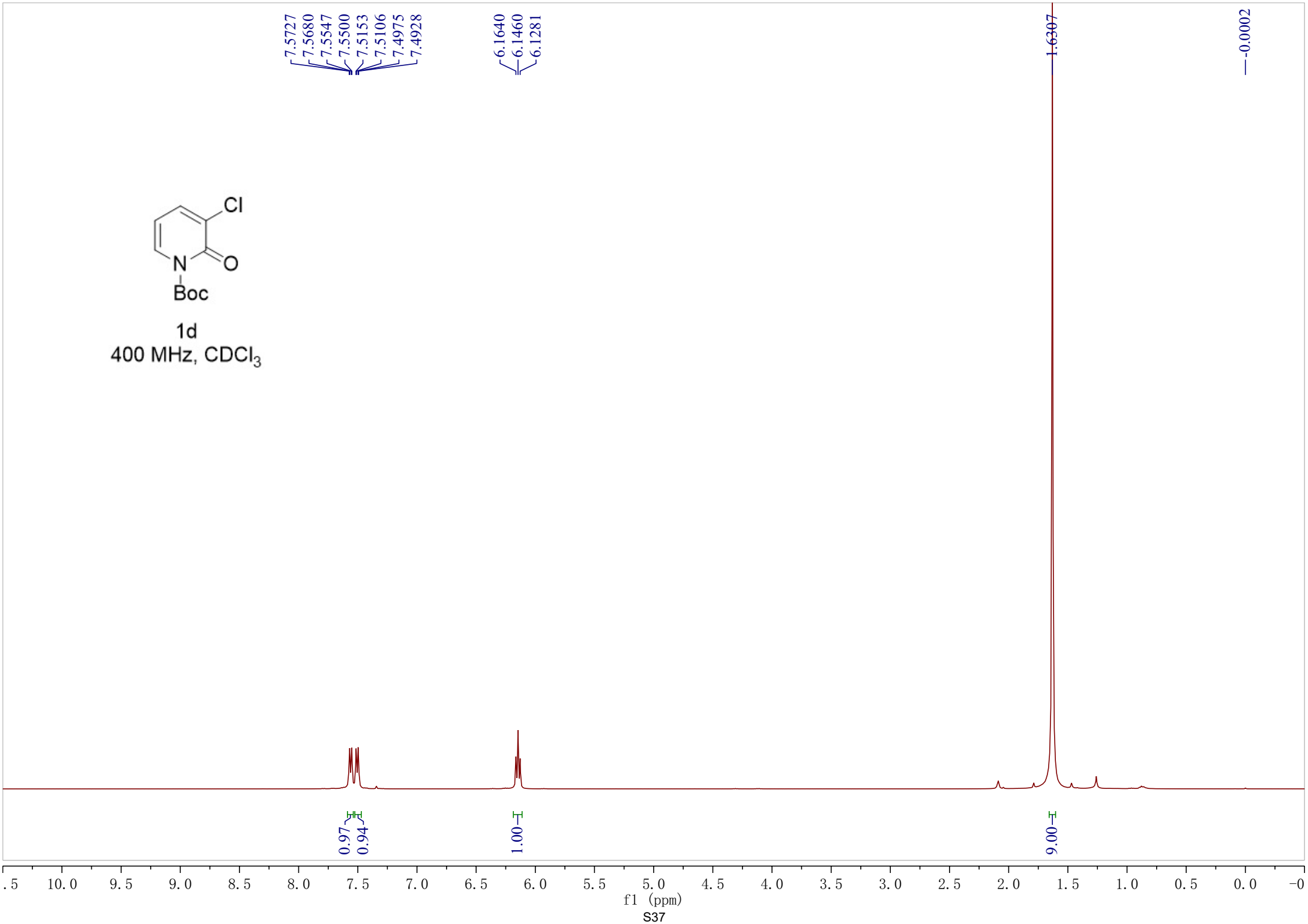
f1 (ppm)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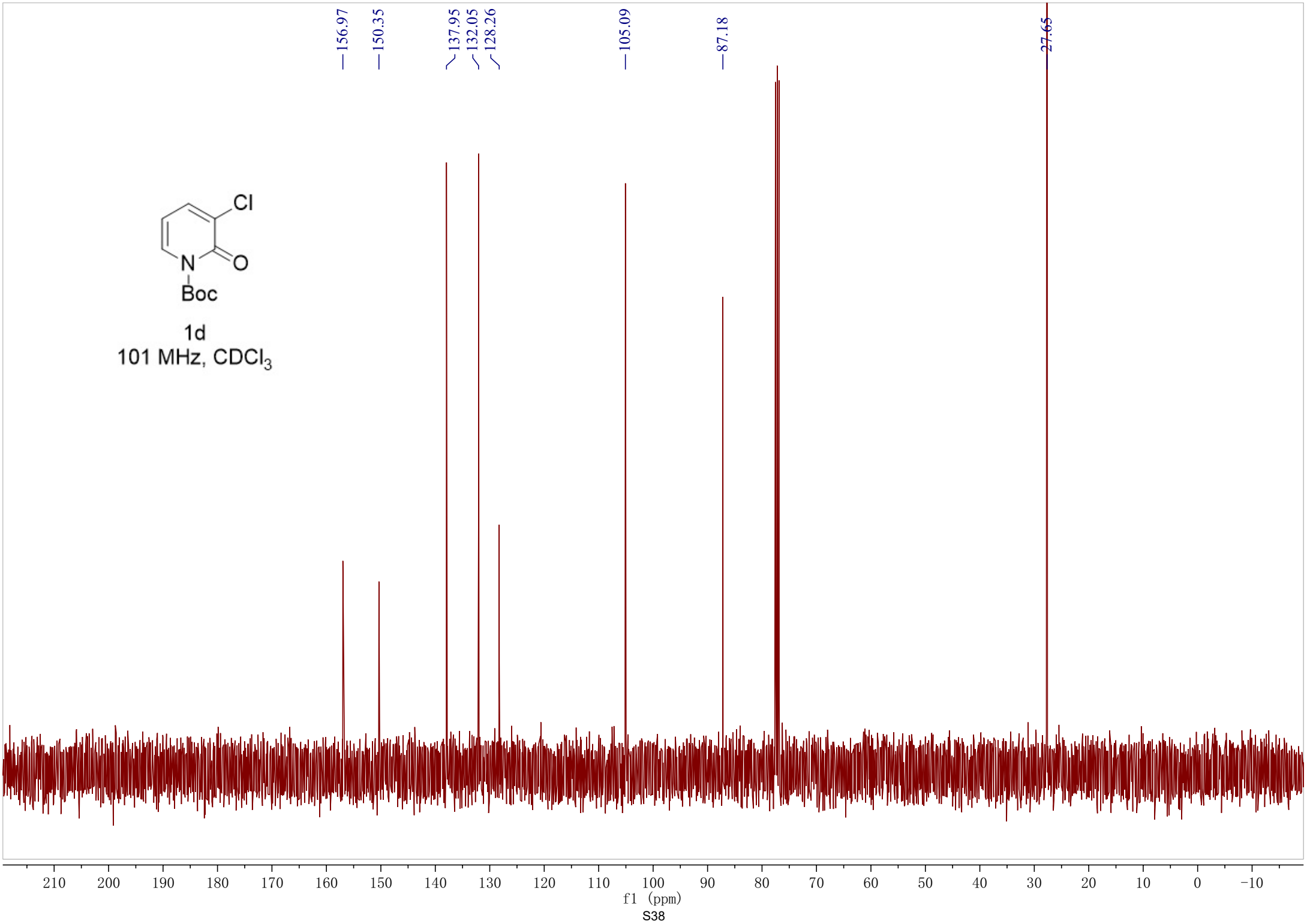
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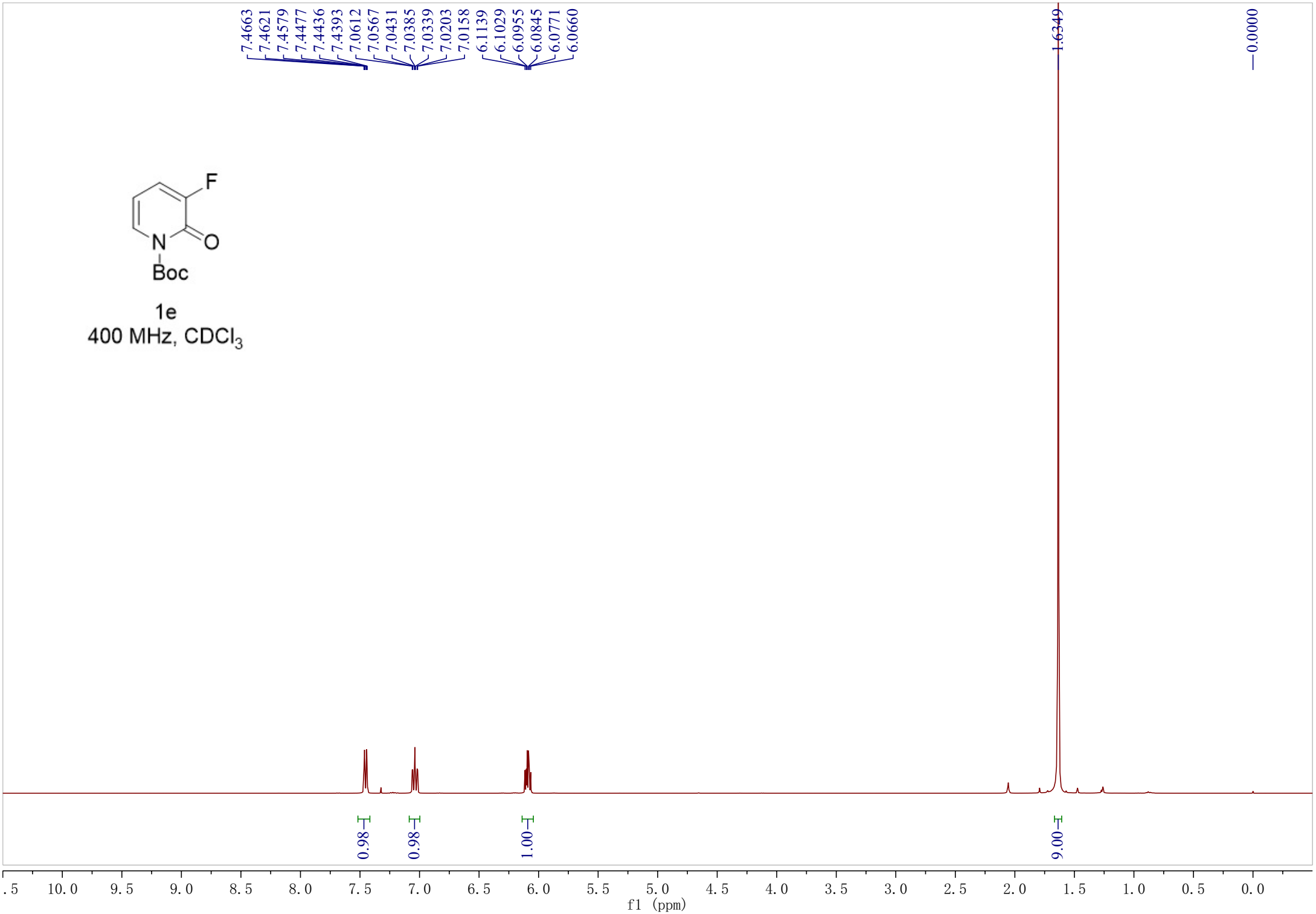
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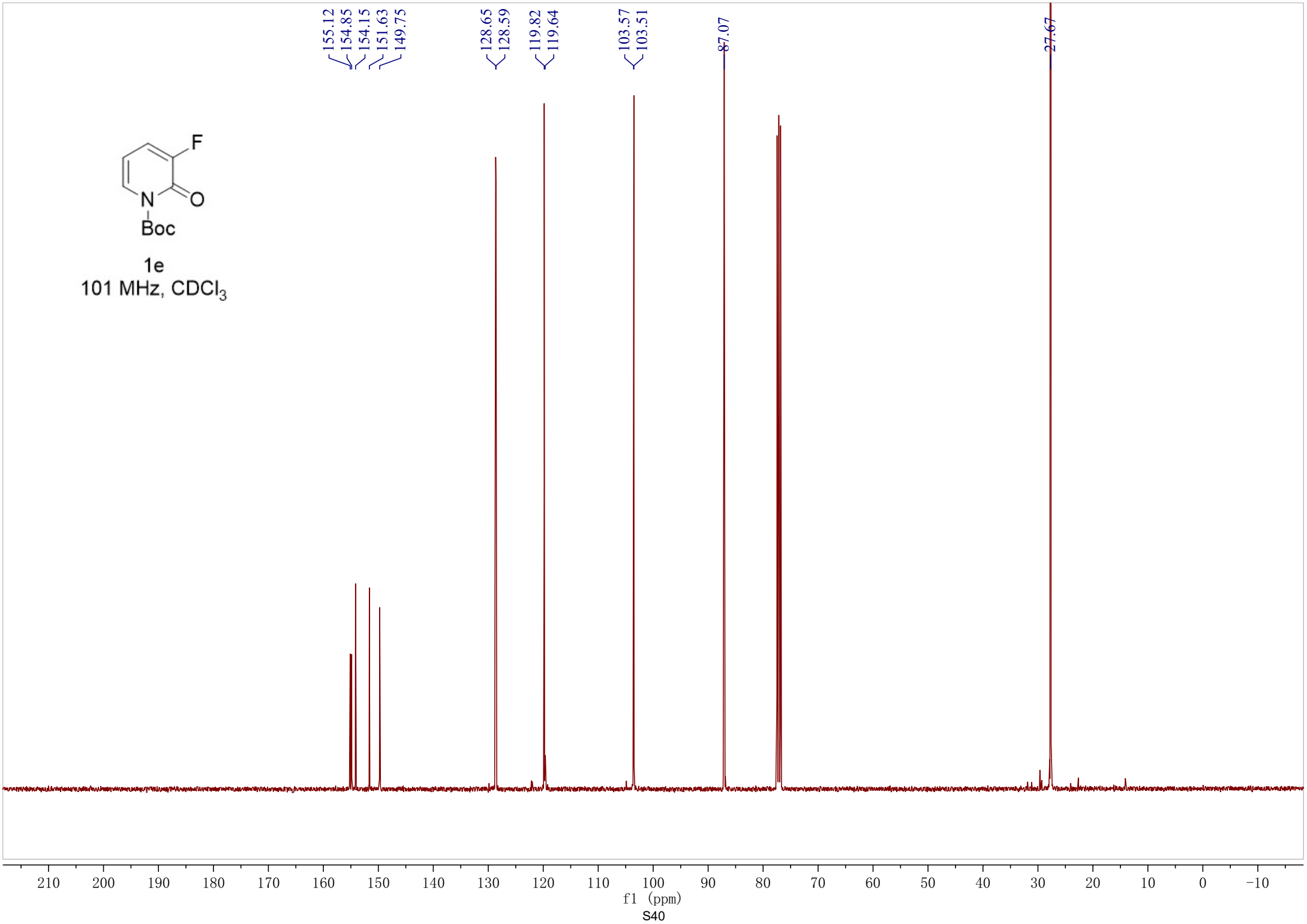
f1 (ppm)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O
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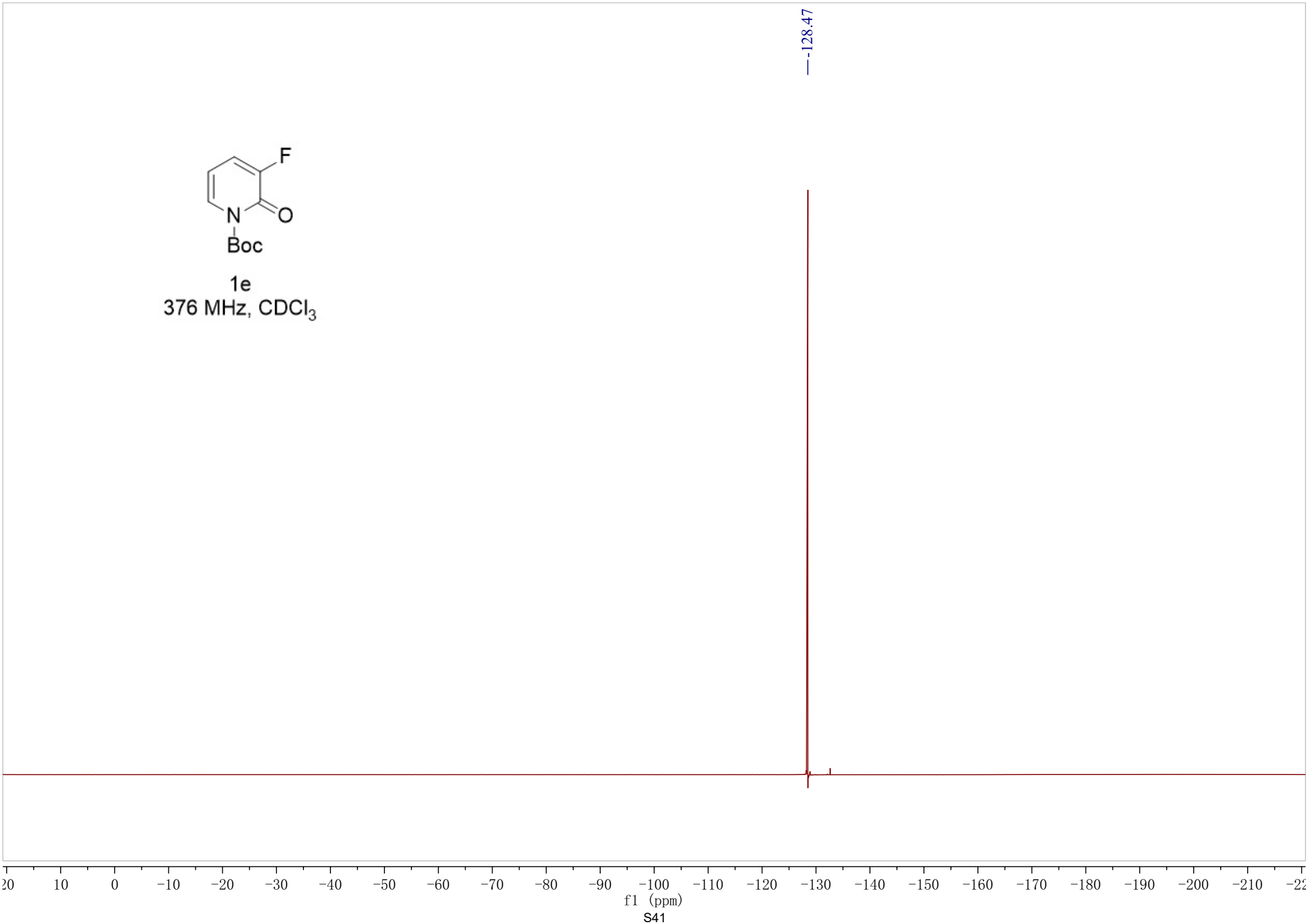
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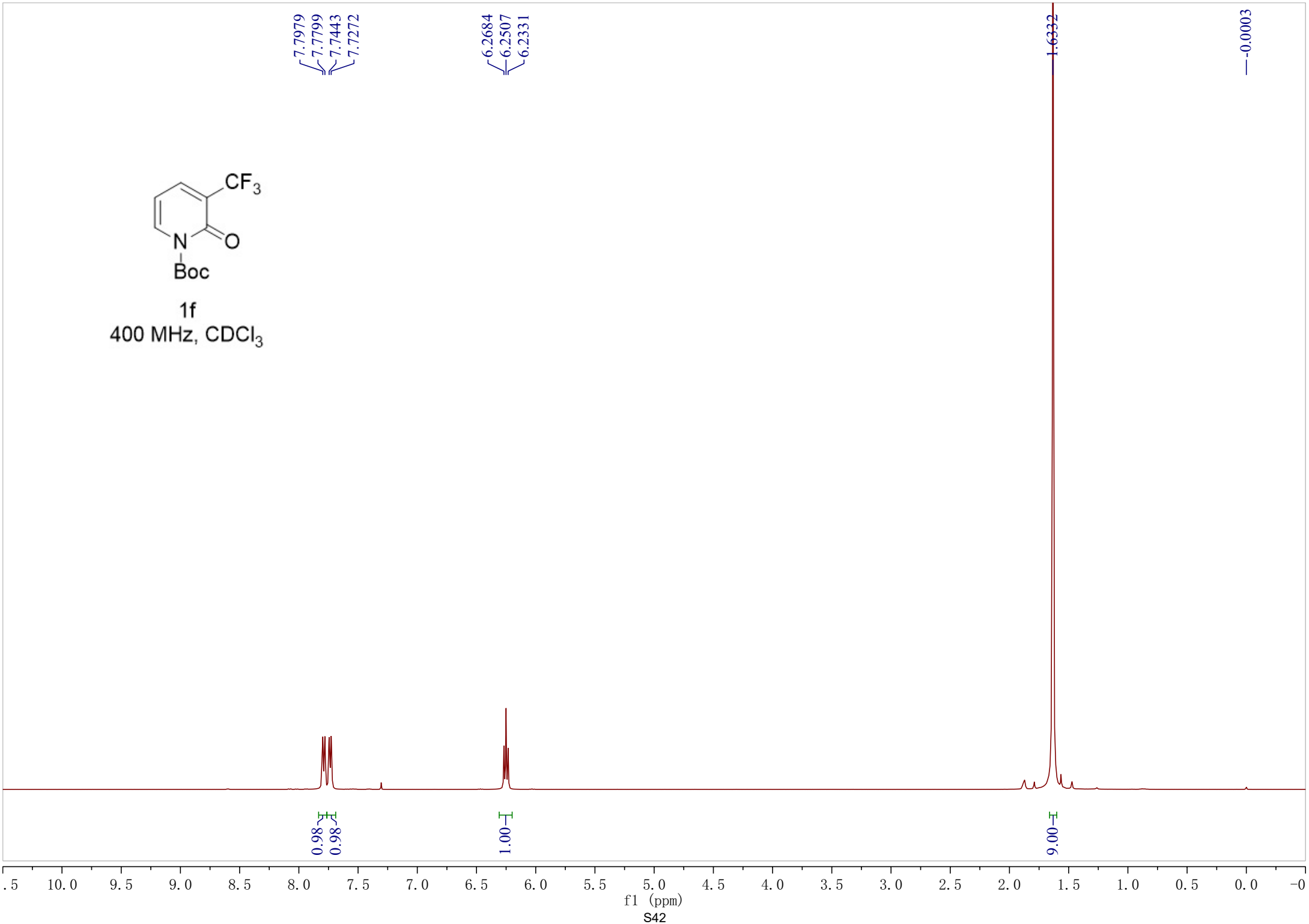
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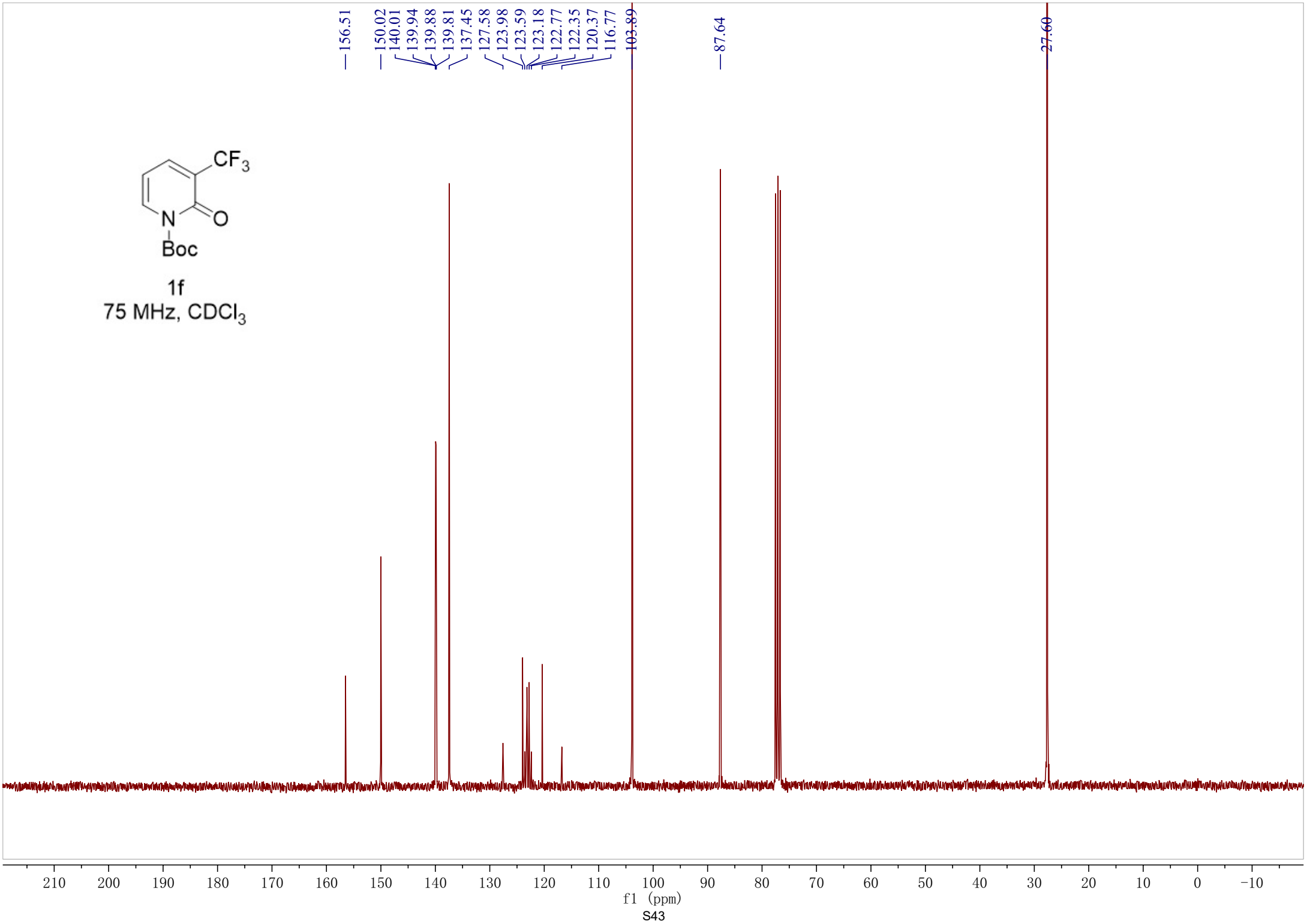
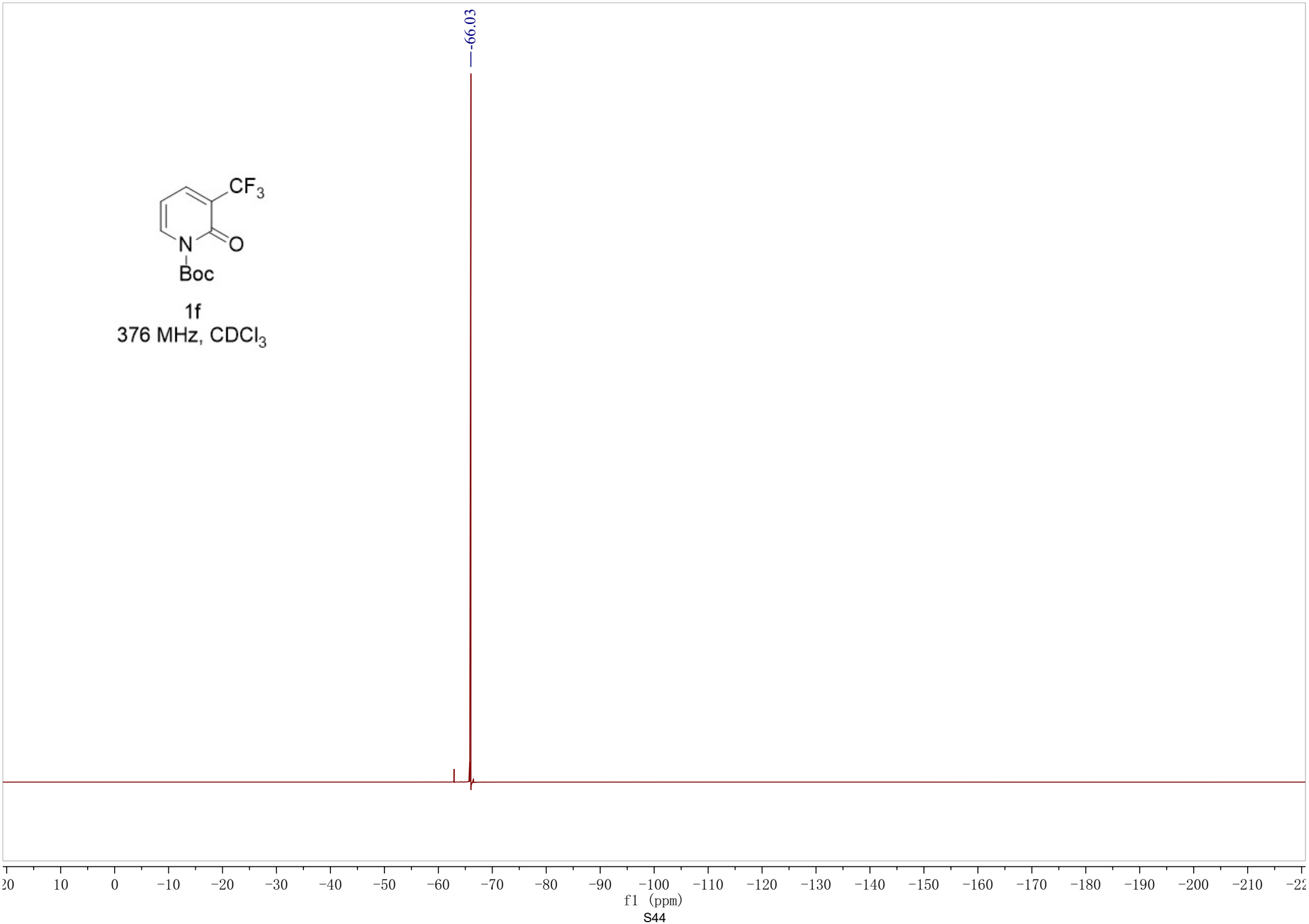
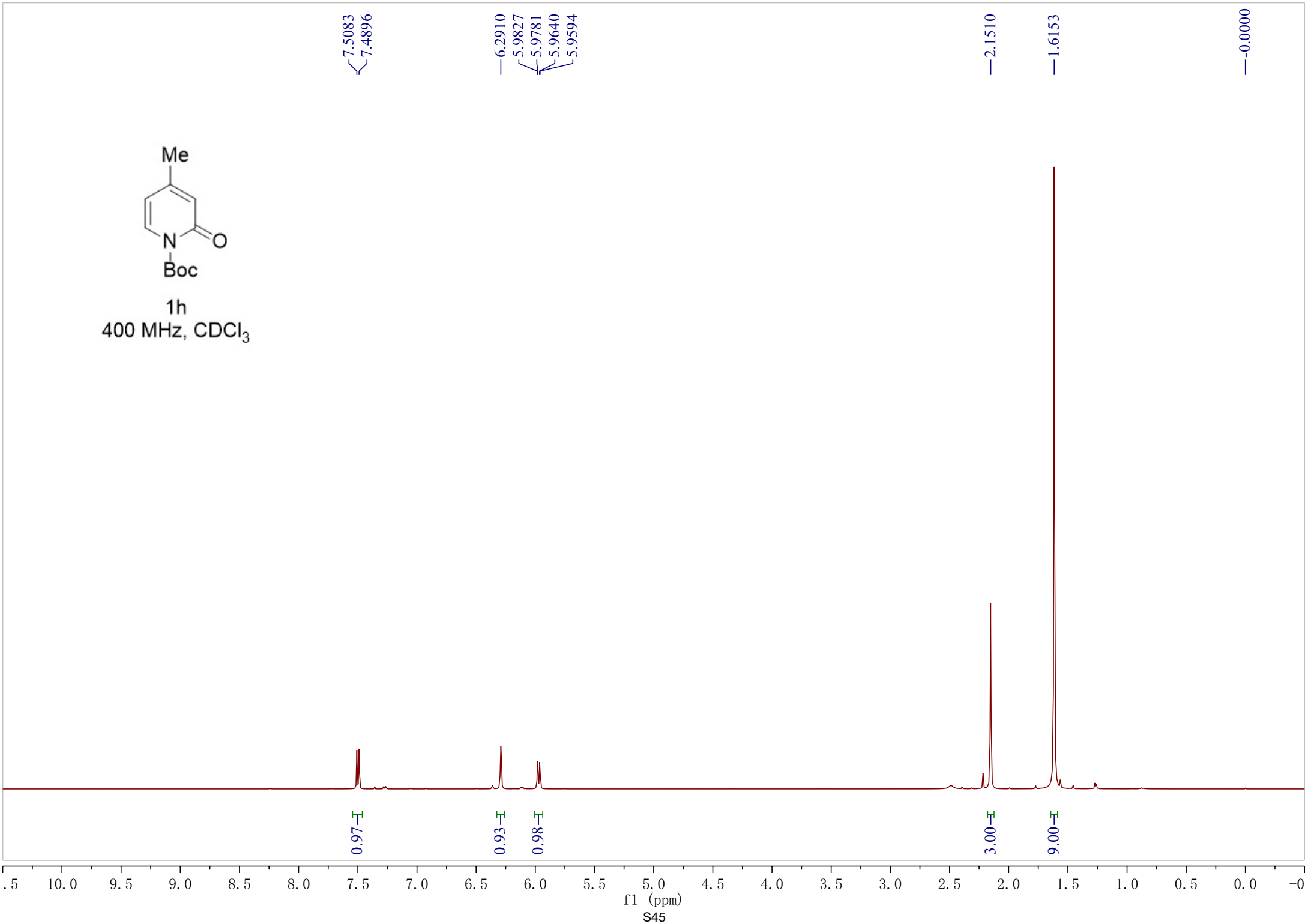
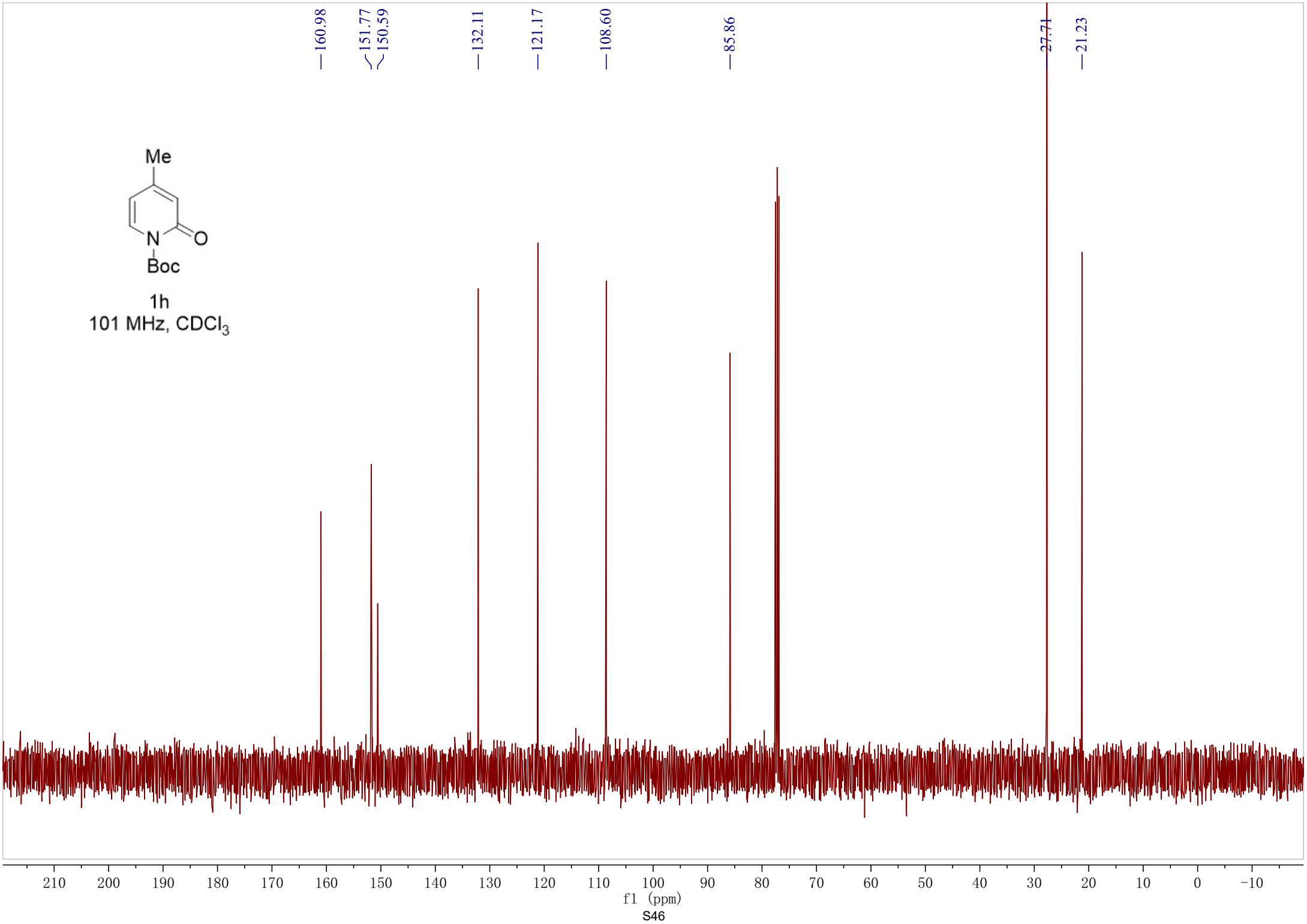
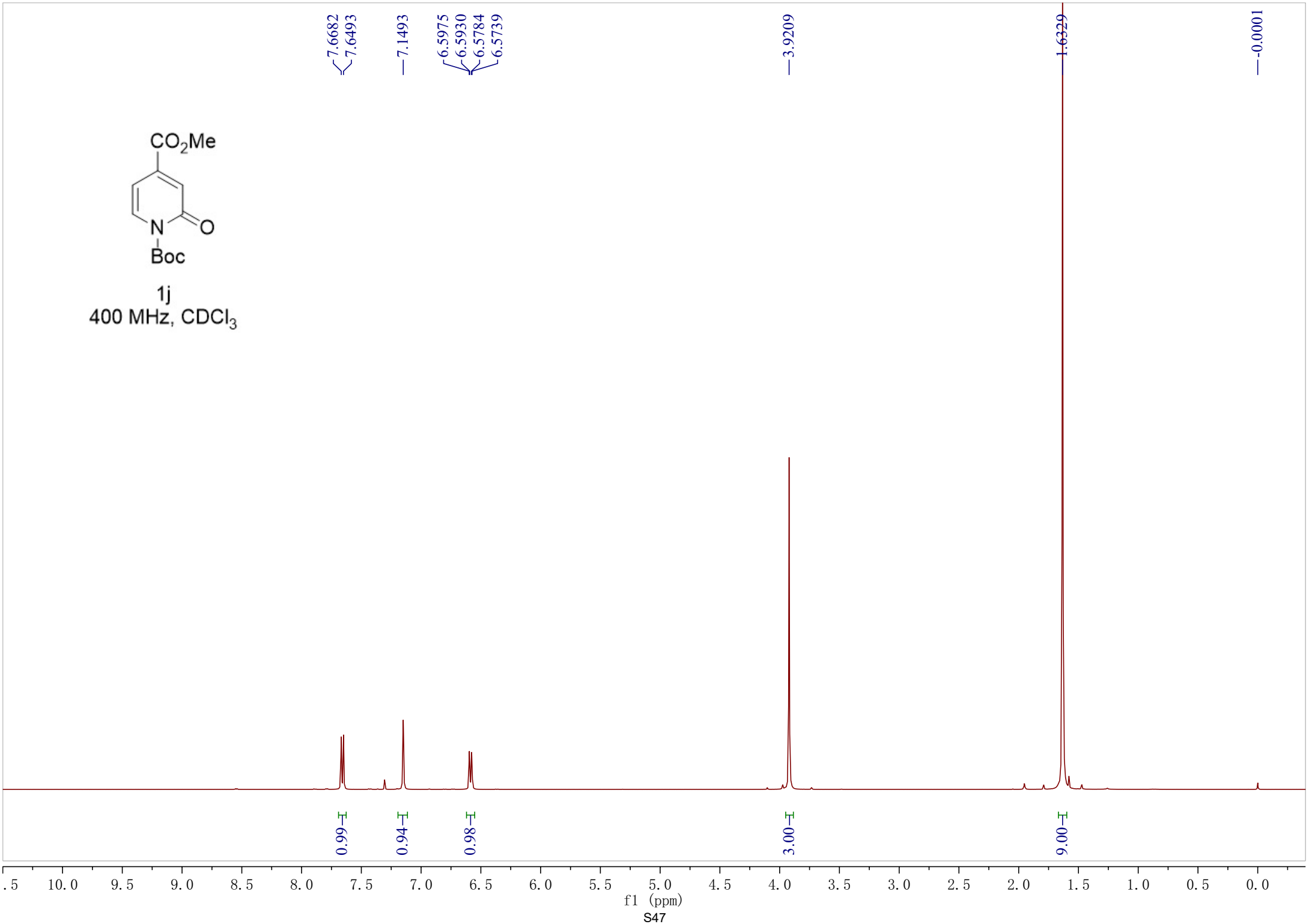
9.00
f1 (ppm)

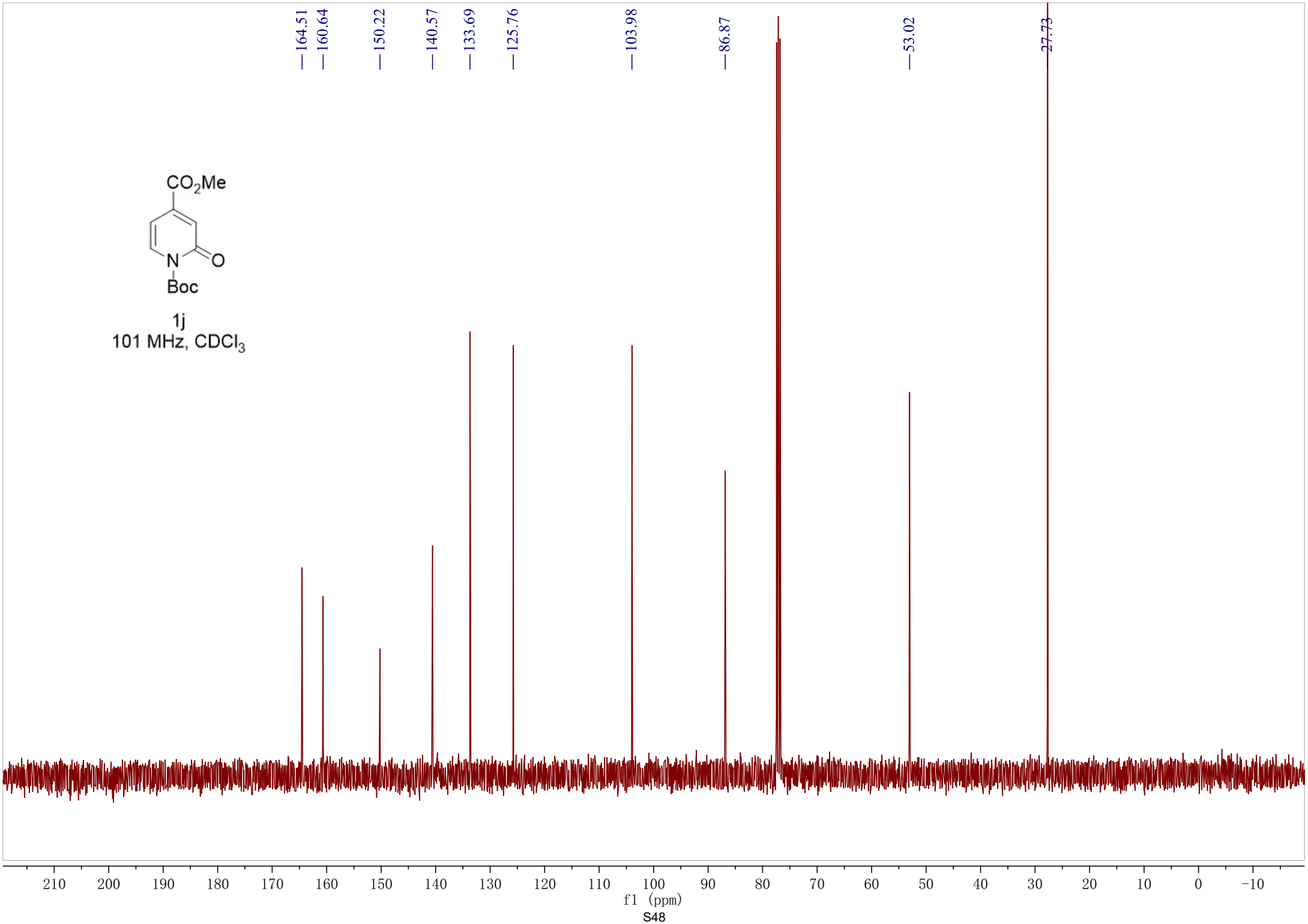

156.51
150.02
140.01
139.94
139.88
139.81
137.45
127.58
123.98
123.59
123.18
122.77
122.35
120.37
116.77
103.89
87.64
27.60
CF3
N
O
Boc
1f
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

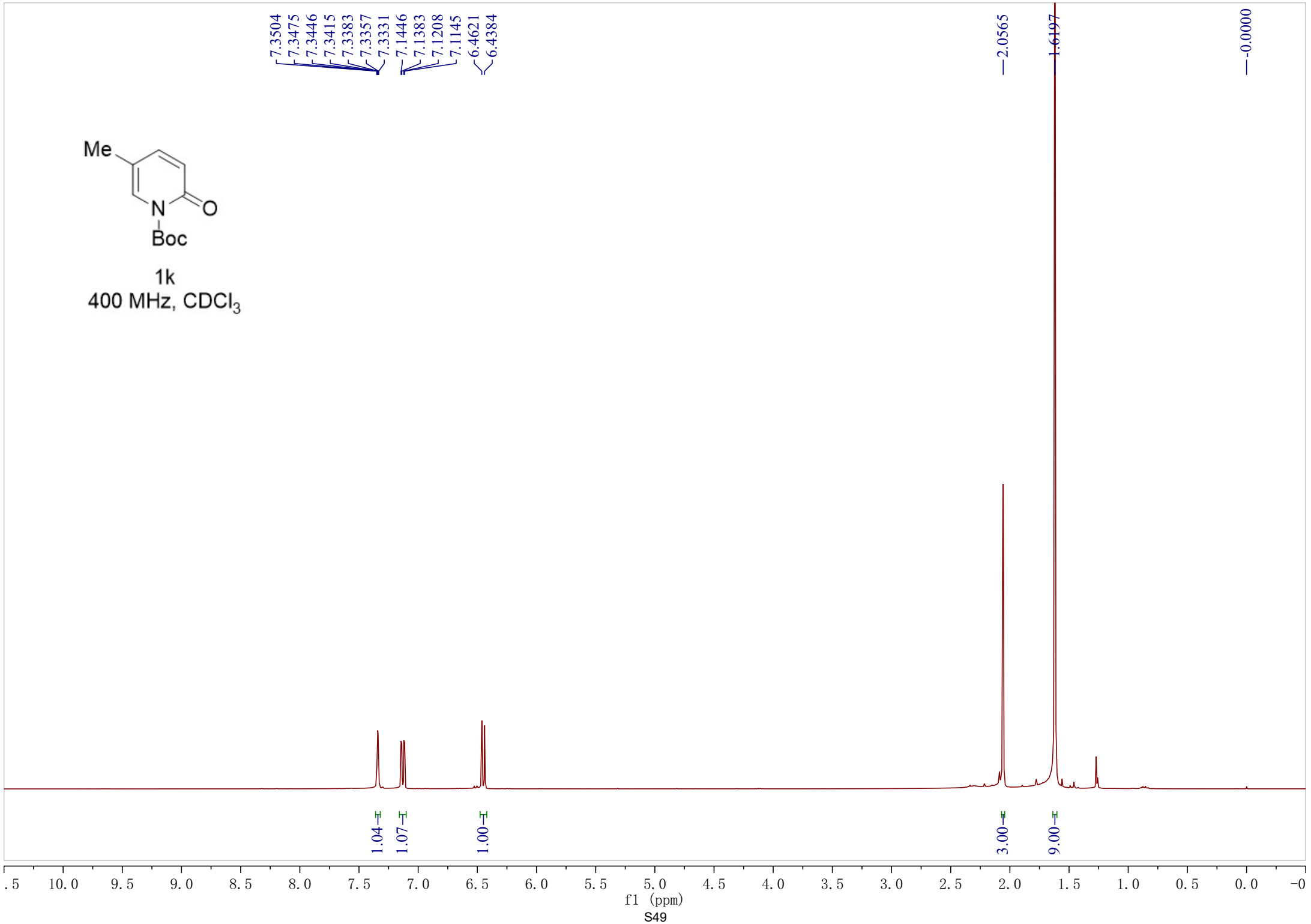

-66.03
CF3
N
O
Boc
1f
376 MHz, CDCl3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)

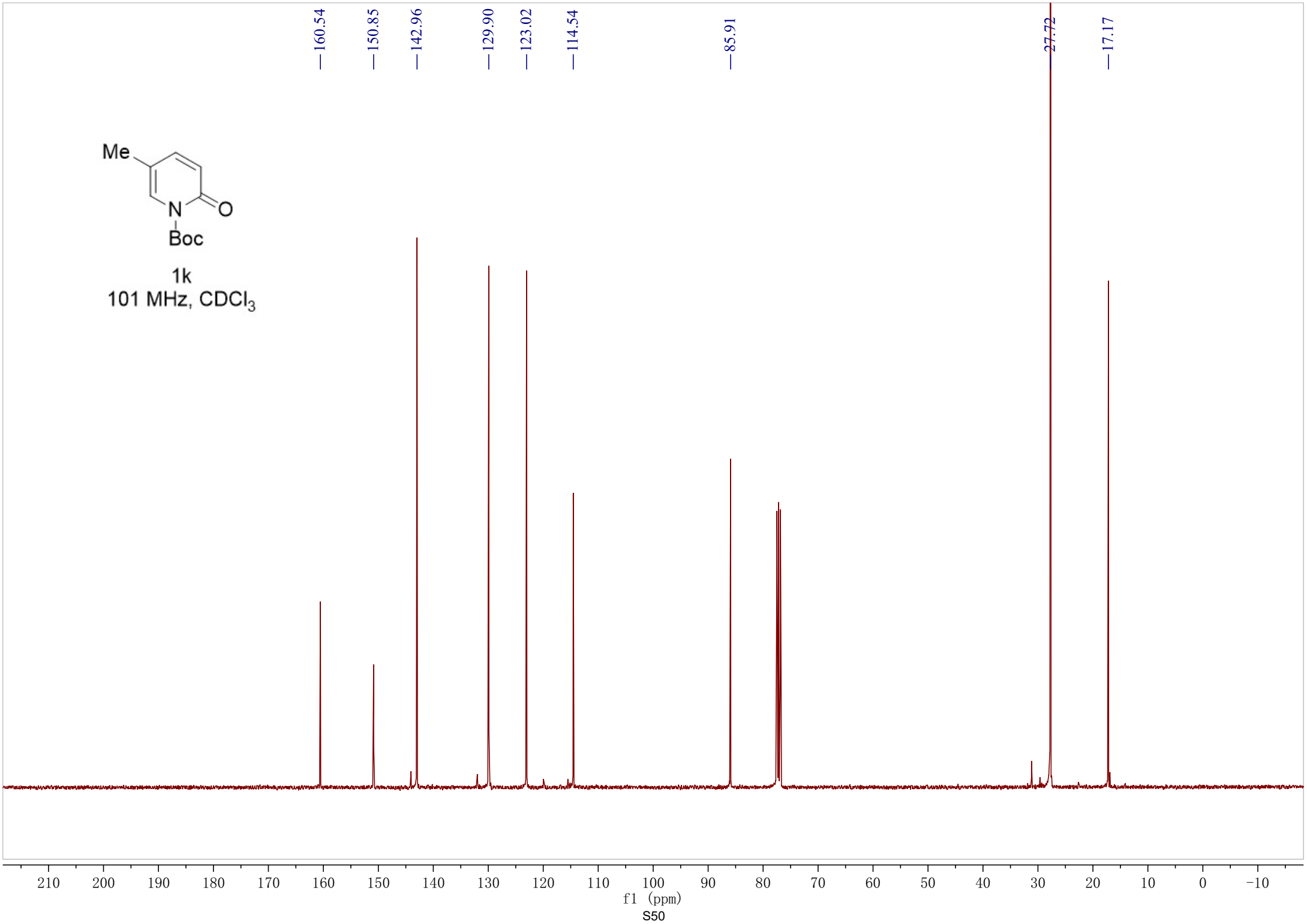

7.5083
7.4896
6.2910
5.9827
5.9781
5.9640
5.9594
2.1510
1.6153
-0.0000
Me
N
O
Boc
1h
400 MHz, CDCl3
0.97
0.93
0.98
3.00
9.00
f1 (ppm)

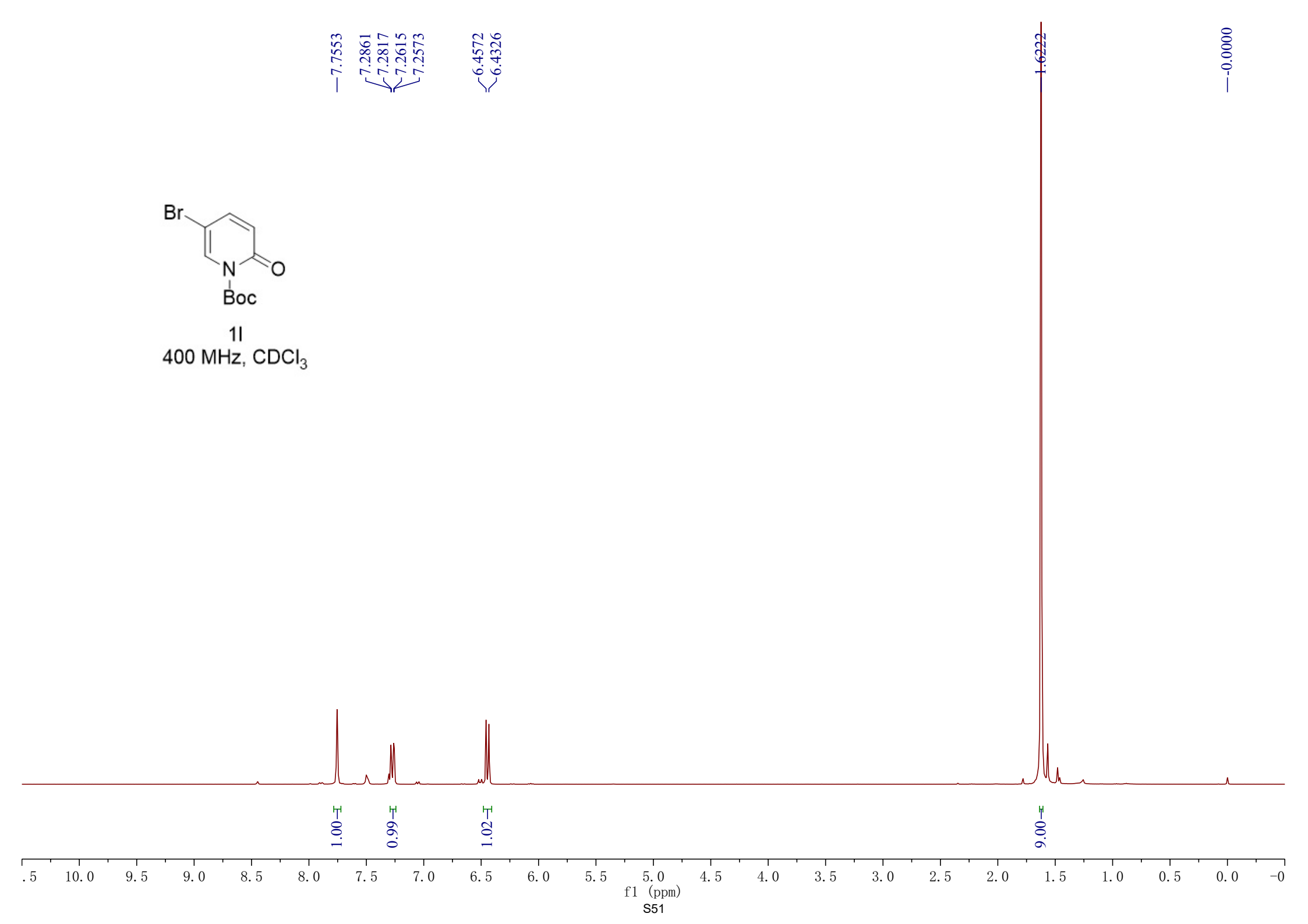

160.98
151.77
150.59
132.11
121.17
108.60
85.86
27.71
21.23
Me
N
O
Boc
1h
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

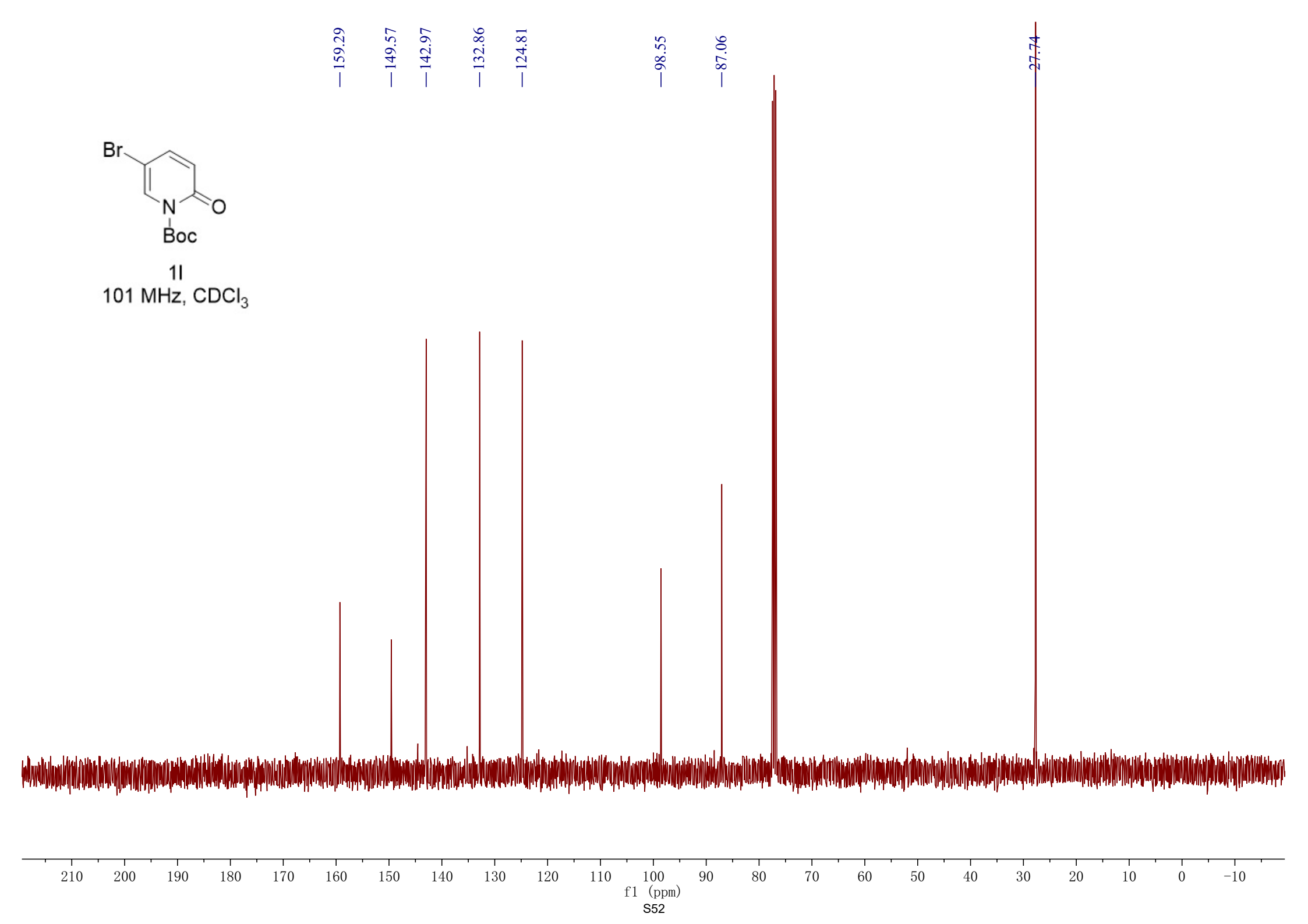

7.6682
7.6493
7.1493
6.5975
6.5930
6.5784
6.5739
3.9209
1.6329
-0.0001
CO2Me
N
O
Boc
1j
400 MHz, CDCl3
0.99
0.94
0.98
3.00
9.00
f1 (ppm)

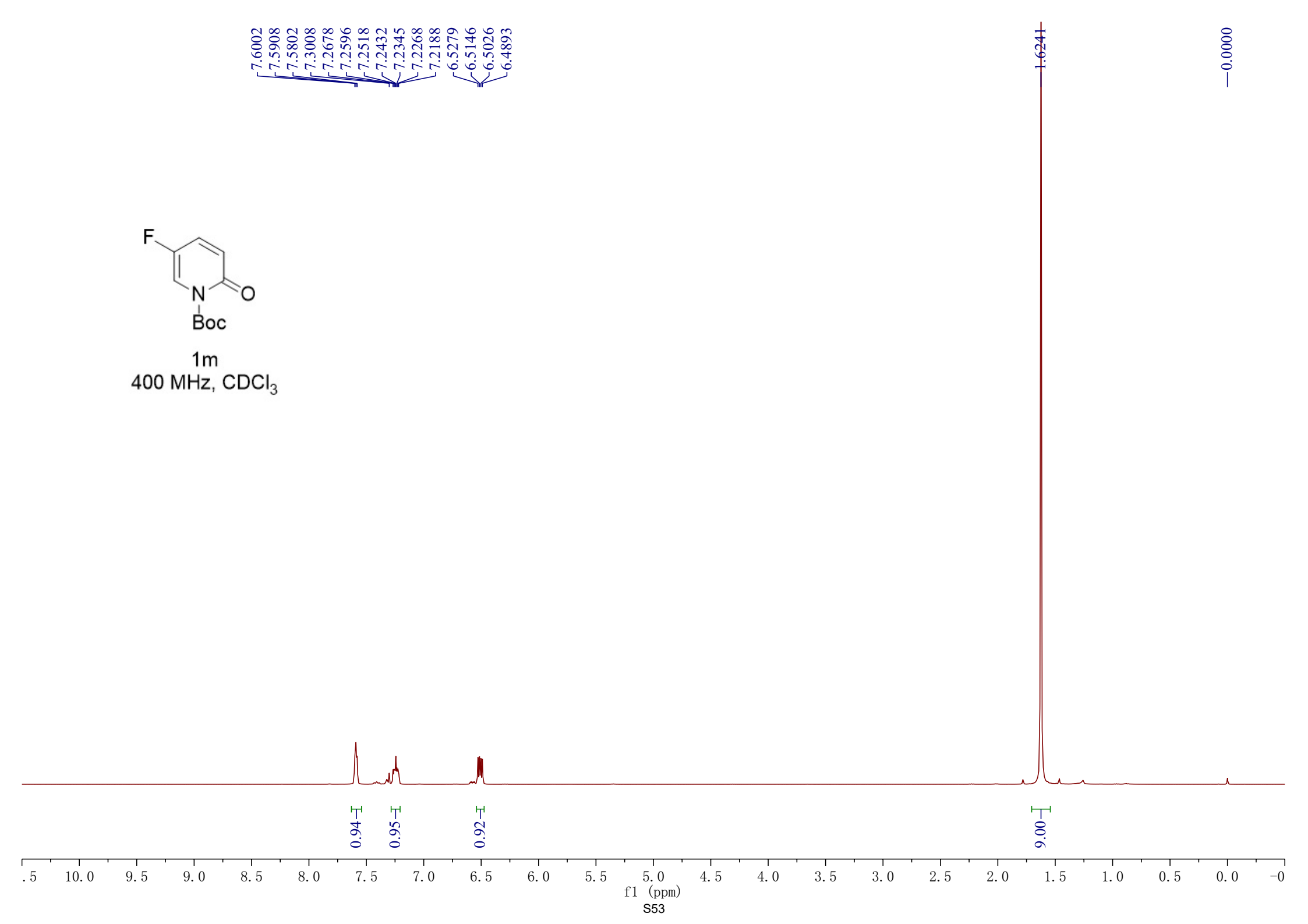

164.51
160.64
150.22
140.57
133.69
125.76
103.98
86.87
53.02
27.73
CO2Me
N
O
Boc
1j
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

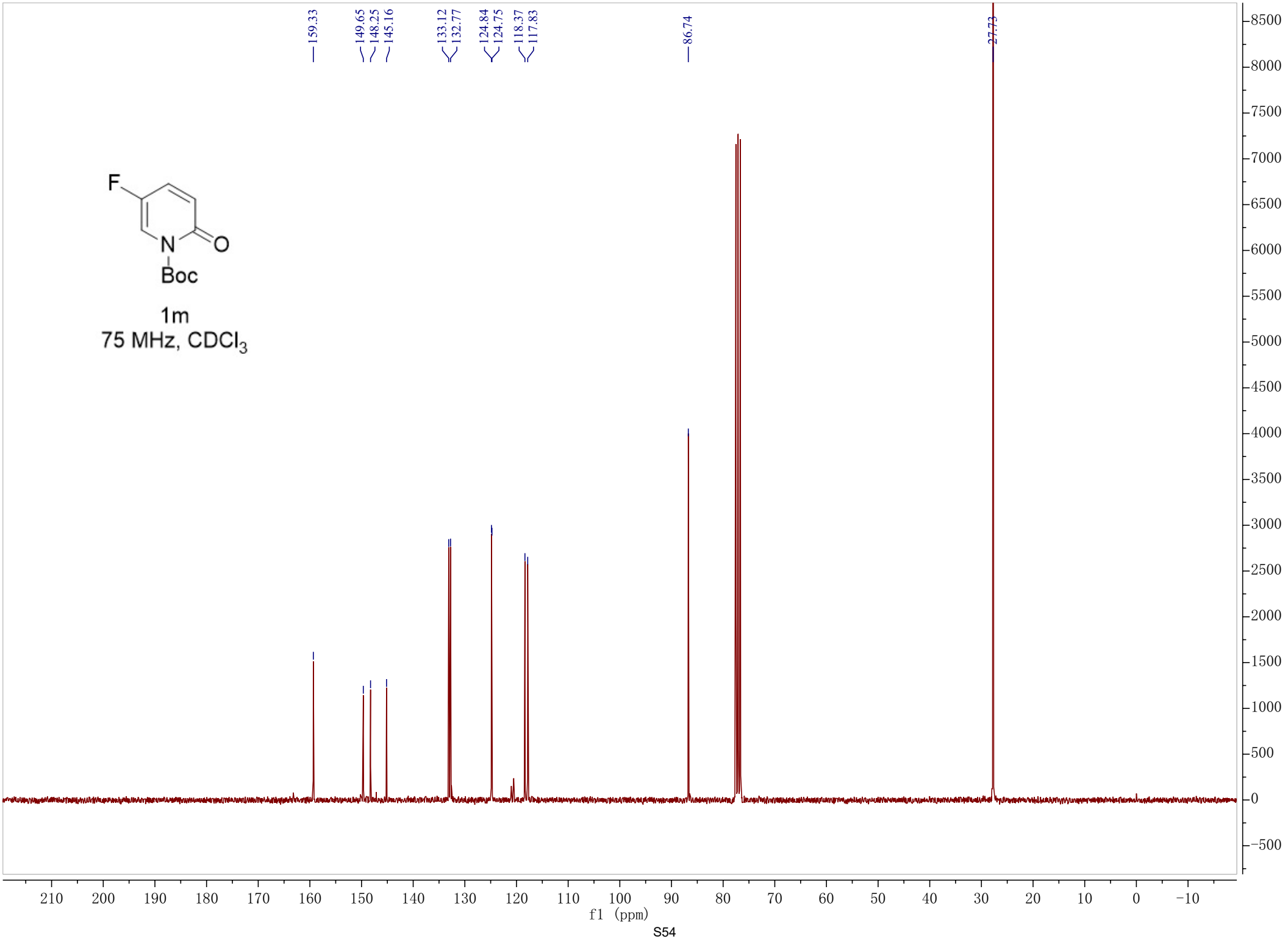

7.3504
7.3475
7.3446
7.3415
7.3383
7.3357
7.3331
7.1446
7.1383
7.1208
7.1145
6.4621
6.4384
2.0565
1.6197
-0.0000
Me
N
O
Boc
1k
400 MHz, CDCl3
1.04
1.07
1.00
3.00
9.00
f1 (ppm)

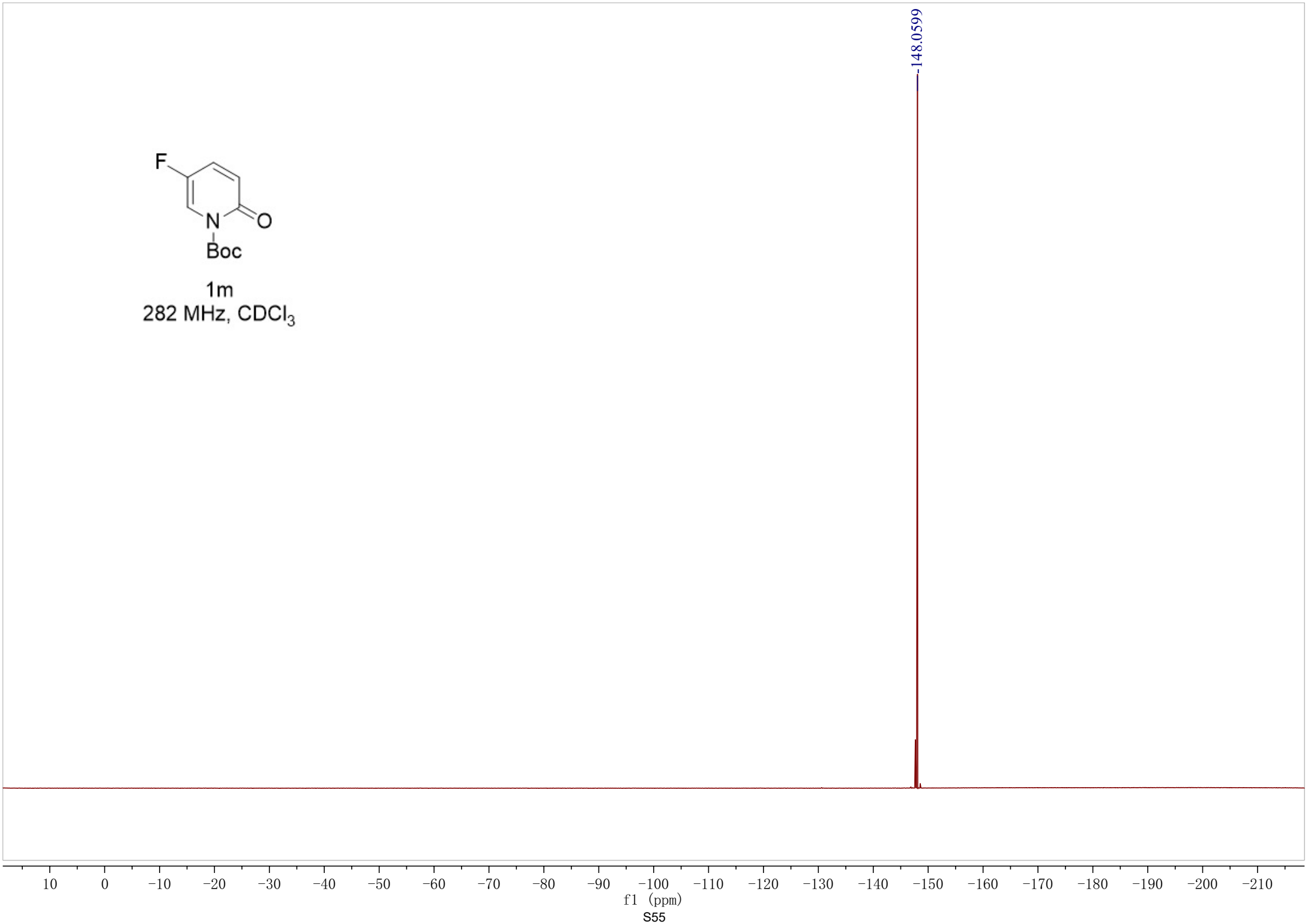

160.54
150.85
142.96
129.90
123.02
114.54
85.91
27.72
17.17
Me
N
O
Boc
1k
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

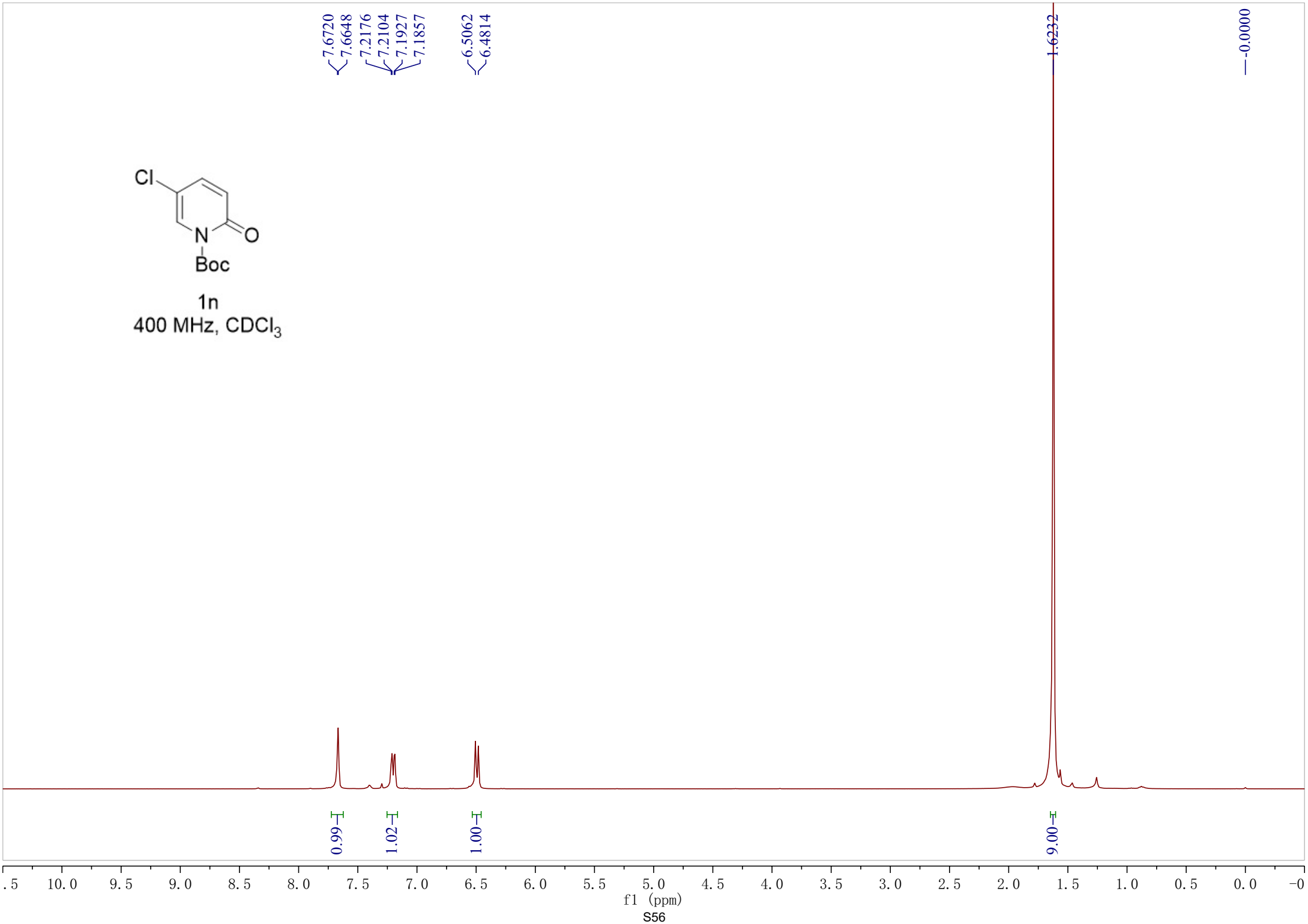

7.7553
7.2861
7.2817
7.2615
7.2573
6.4572
6.4326
1.6222
0.0000
Br
N
O
Boc
1l
400 MHz, CDCl3
1.00
0.99
1.02
9.00
f1 (ppm)

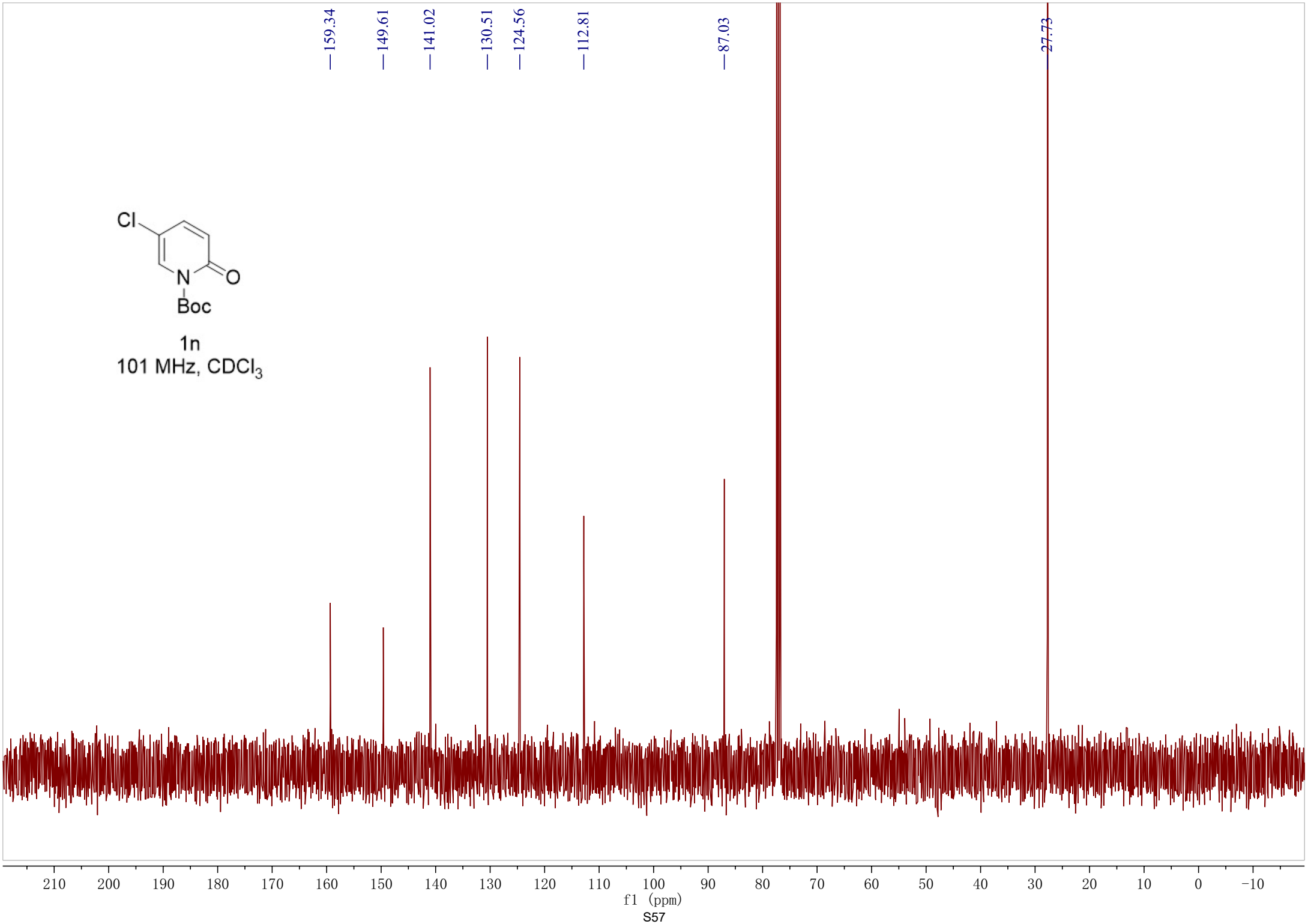

159.29
149.57
142.97
132.86
124.81
98.55
87.06
27.74
Br
N
O
Boc
1l
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

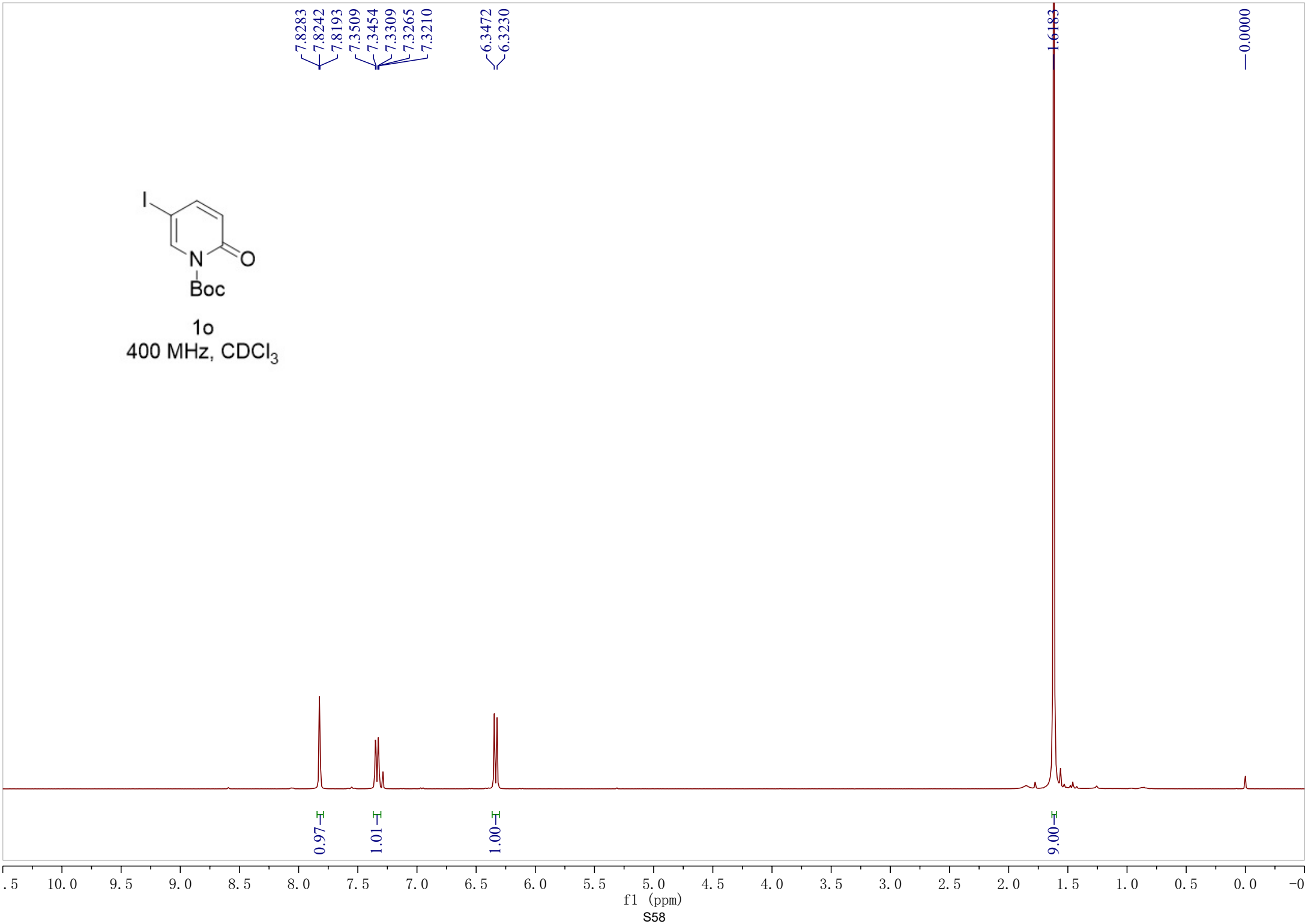

7.6002
7.5908
7.5802
7.3008
7.2678
7.2596
7.2518
7.2432
7.2345
7.2268
7.2188
6.5279
6.5146
6.5026
6.4893
1.6241
0.0000
F
N
O
Boc
1m
400 MHz, CDCl3
0.94
0.95
0.92
9.00
f1 (ppm)

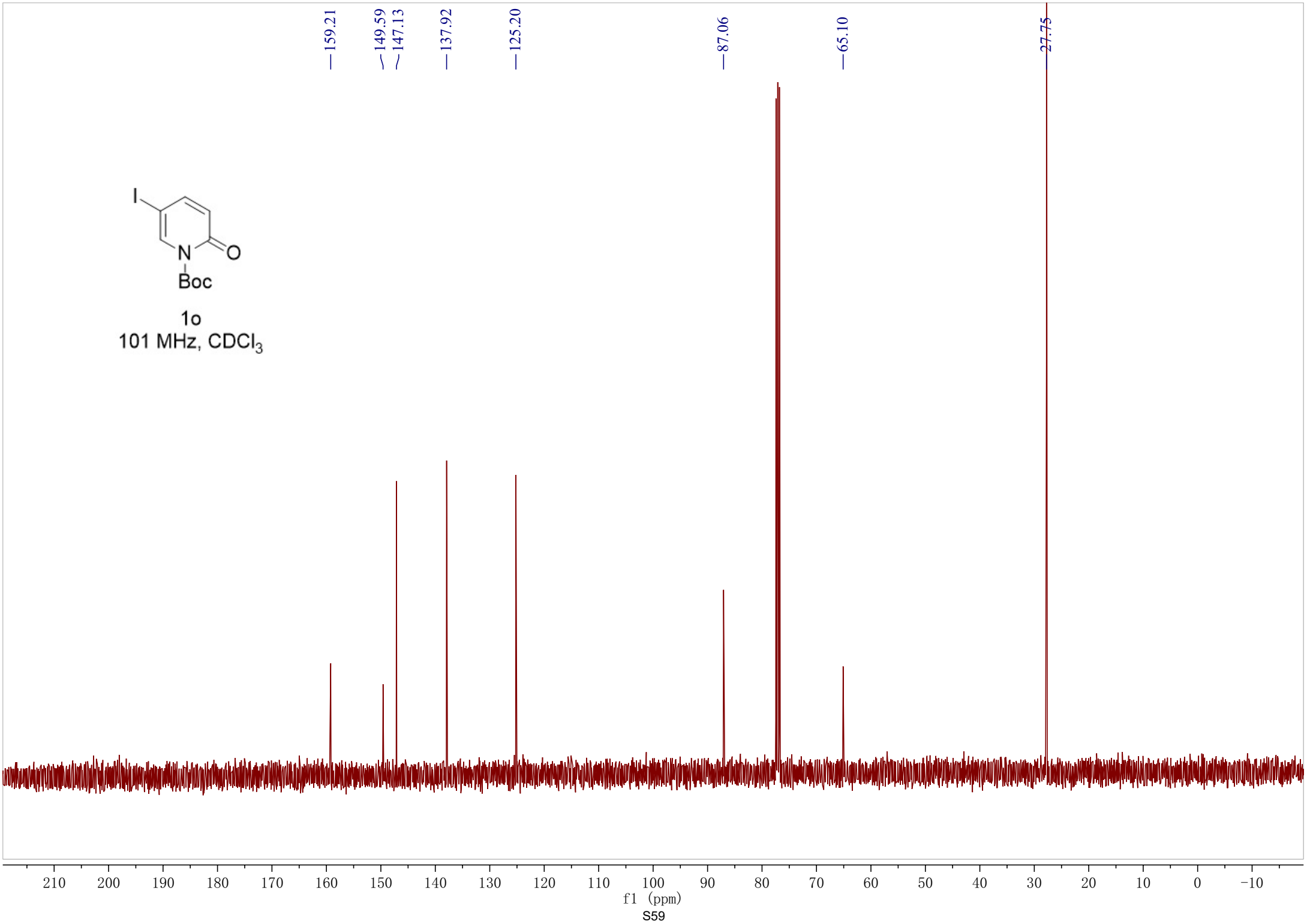

159.33
149.65
148.25
145.16
133.12
132.77
124.84
124.75
118.37
117.83
86.74
27.73
F
N
O
Boc
1m
75 MHz, CDCl3
f1 (ppm)

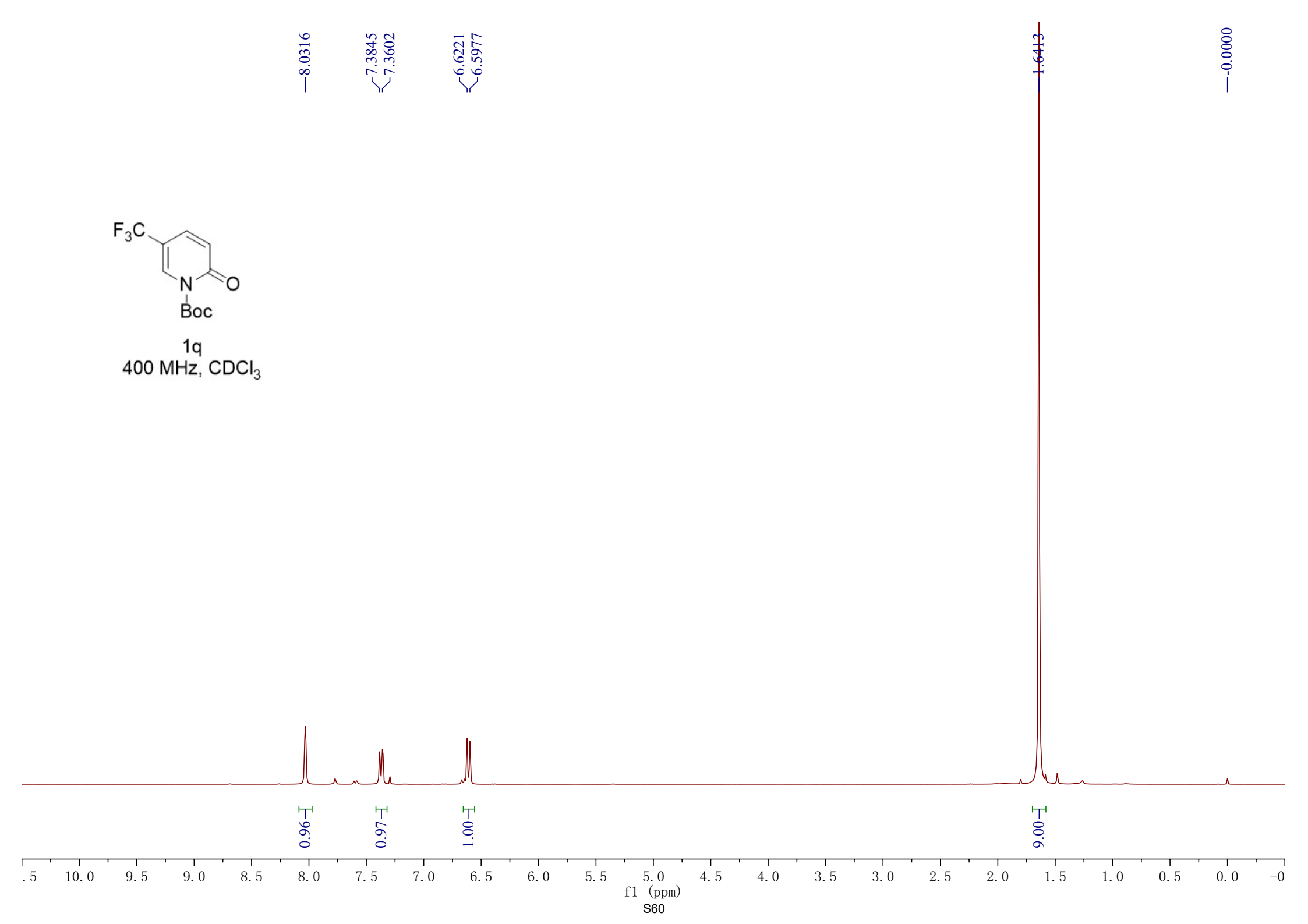

F
N
O
Boc
1m
282 MHz, CDCl3
-148.0599
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

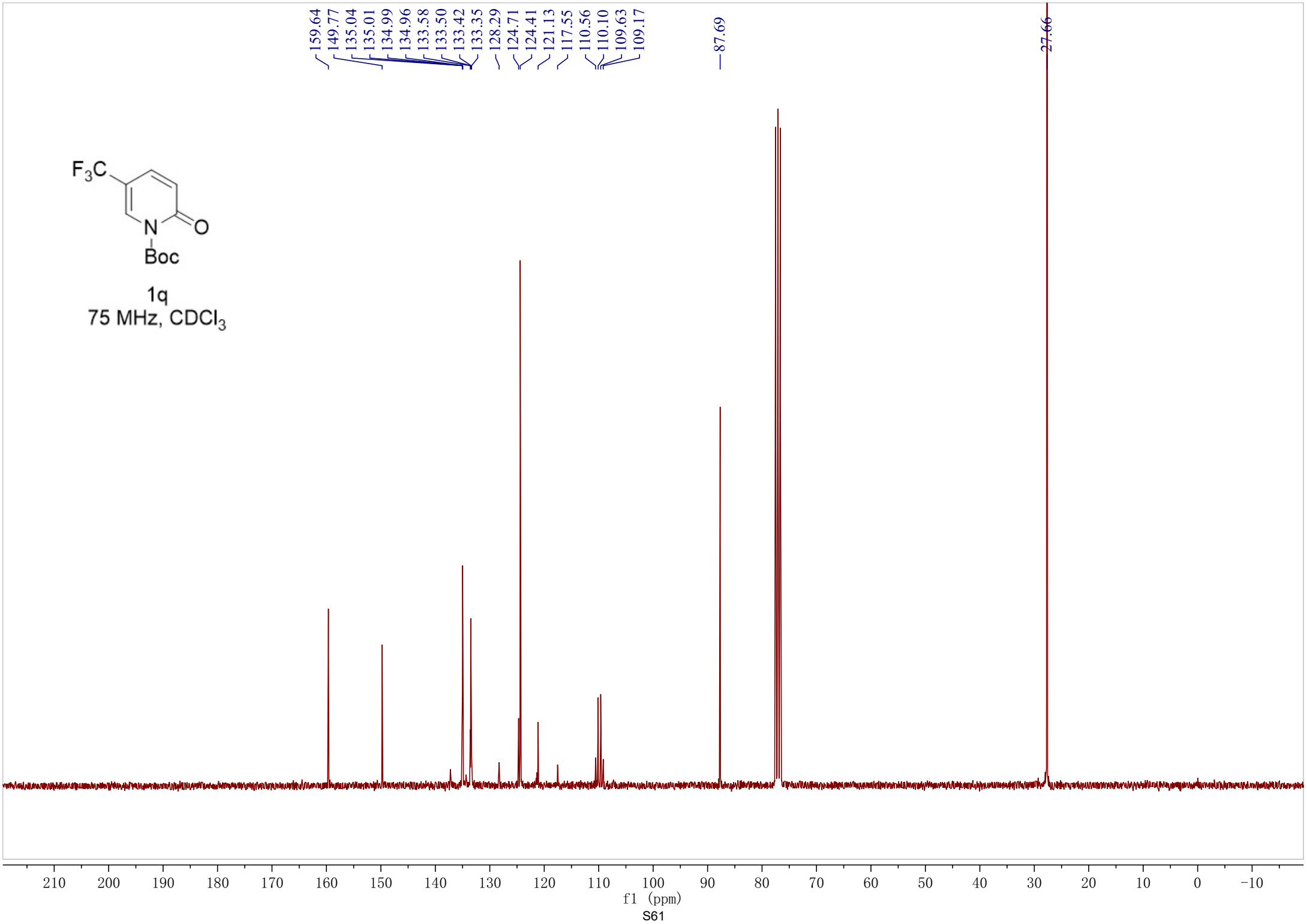

7.6720
7.6648
7.2176
7.2104
7.1927
7.1857
6.5062
6.4814
1.6232
-0.0000
Cl
N
O
Boc
1n
400 MHz, CDCl3
0.99
1.02
1.00
9.00
f1 (ppm)

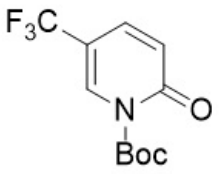

159.34
149.61
141.02
130.51
124.56
112.81
87.03
27.73
Cl
N
O
Boc
1n
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.8283
7.8242
7.8193
7.3509
7.3454
7.3309
7.3265
7.3210
6.3472
6.3230
1.6183
0.0000
I
N
O
Boc
1o
400 MHz, CDCl3
0.97
1.01
1.00
9.00
f1 (ppm)


159.21
149.59
147.13
137.92
125.20
87.06
65.10
27.75
I
N
O
Boc
1o
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.0316
7.3845
7.3602
6.6221
6.5977
1.6413
0.0000
F3C
N
O
Boc
1q
400 MHz, CDCl3
0.96
0.97
1.00
9.00
f1 (ppm)


159.64
149.77
135.04
135.01
134.99
134.96
133.58
133.50
133.42
133.35
128.29
124.71
124.41
121.13
117.55
110.56
110.10
109.63
109.17
87.69
27.66
F3C
N
O
Boc
1q
75 MHz, CDCl3
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)

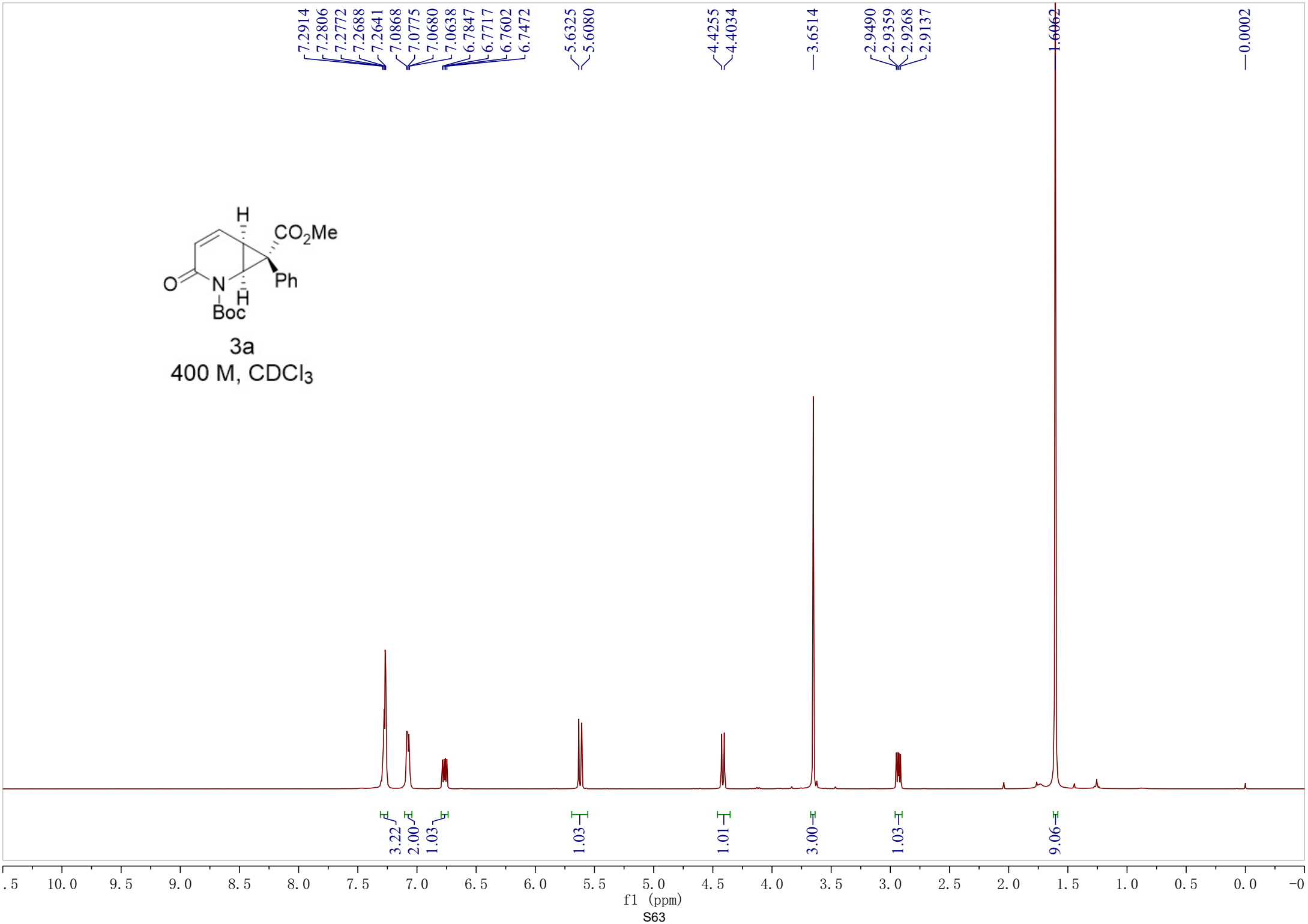


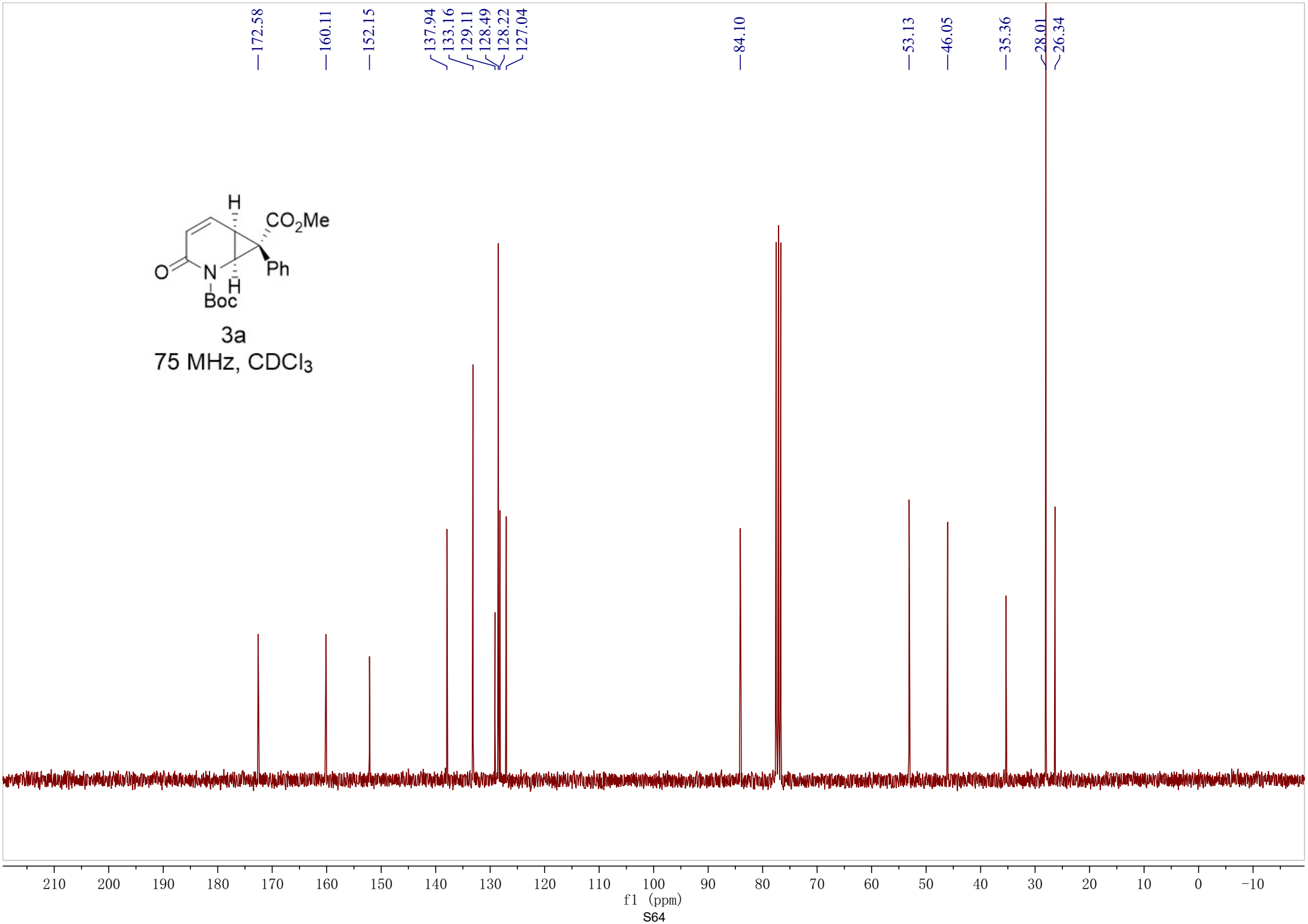
1q
282 MHz, $CDCl_3$

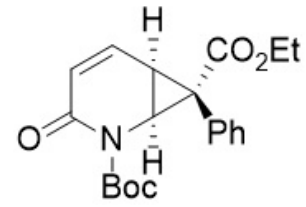
-63.5377

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

f1 (ppm)

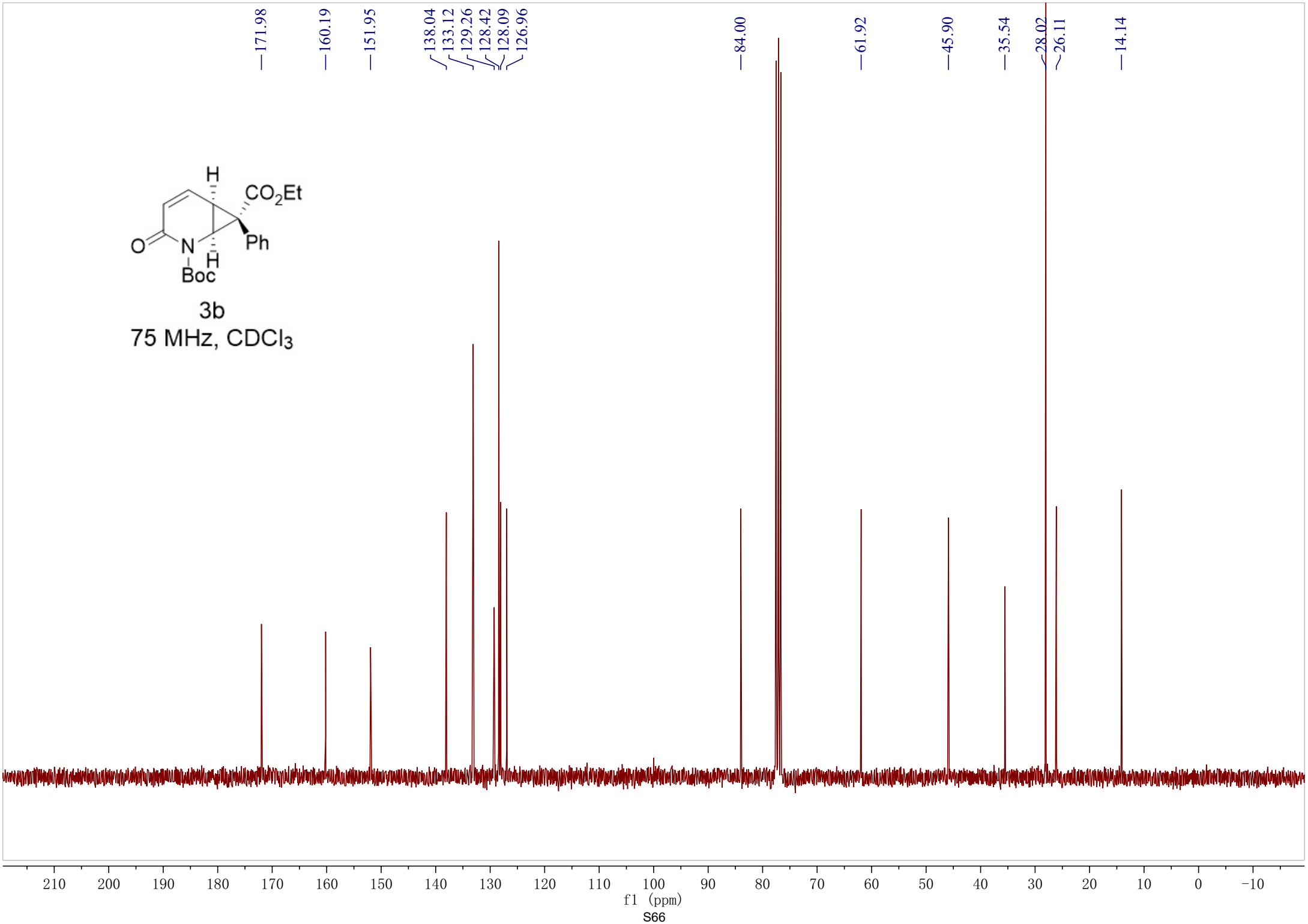

7.2914
7.2806
7.2772
7.2688
7.2641
7.0868
7.0775
7.0680
7.0638
6.7847
6.7717
6.7602
6.7472
5.6325
5.6080
4.4255
4.4034
3.6514
2.9490
2.9359
2.9268
2.9137
1.6062
0.0002
H
CO2Me
Ph
O
N
H
Boc
3a
400 M, CDCl3
3.22
2.00
1.03
1.03
1.01
3.00
1.03
9.06
f1 (ppm)

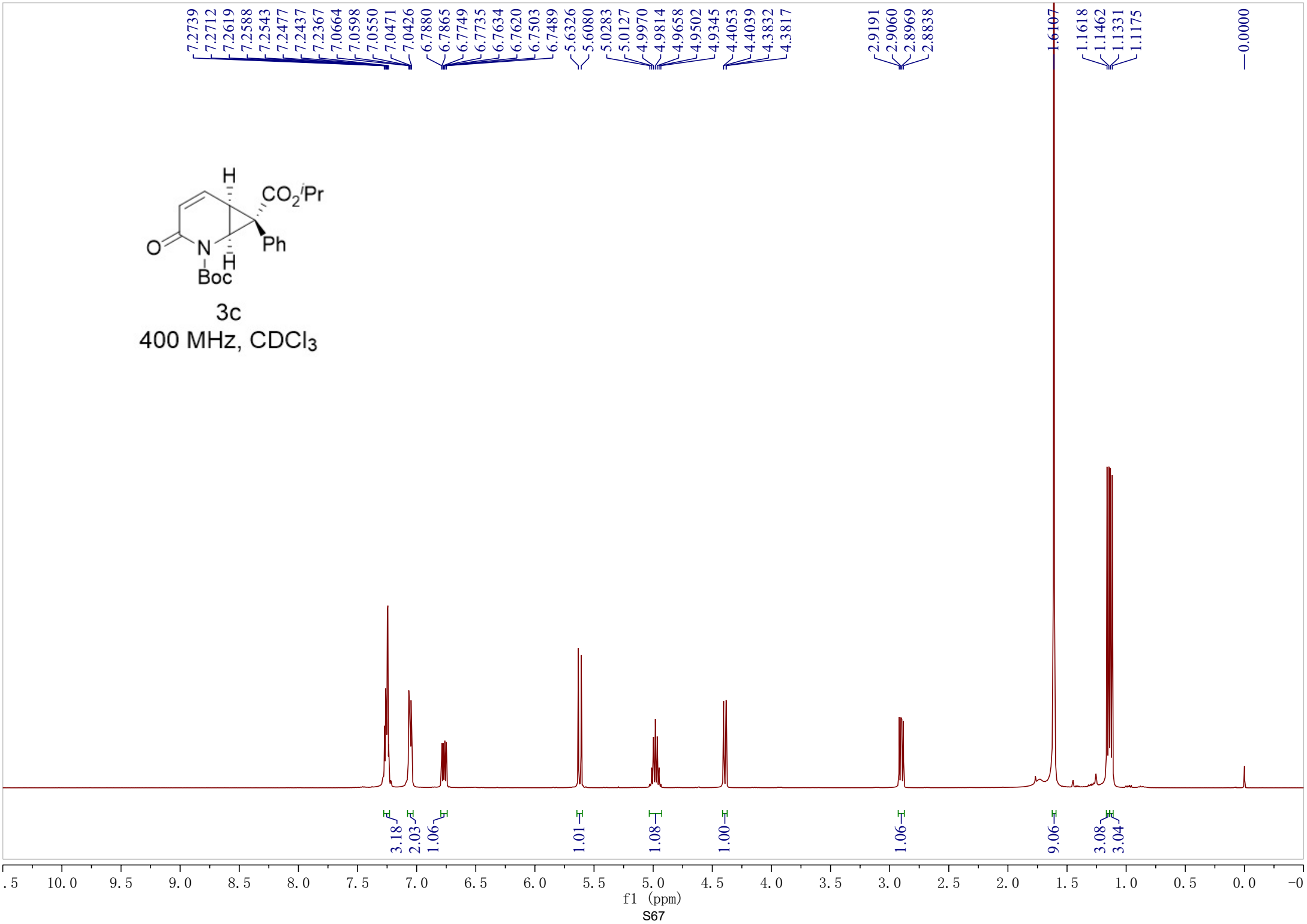

172.58
160.11
152.15
137.94
133.16
129.11
128.49
128.22
127.04
84.10
53.13
46.05
35.36
28.01
26.34
H
CO2Me
O
N
Ph
H
Boc
3a
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

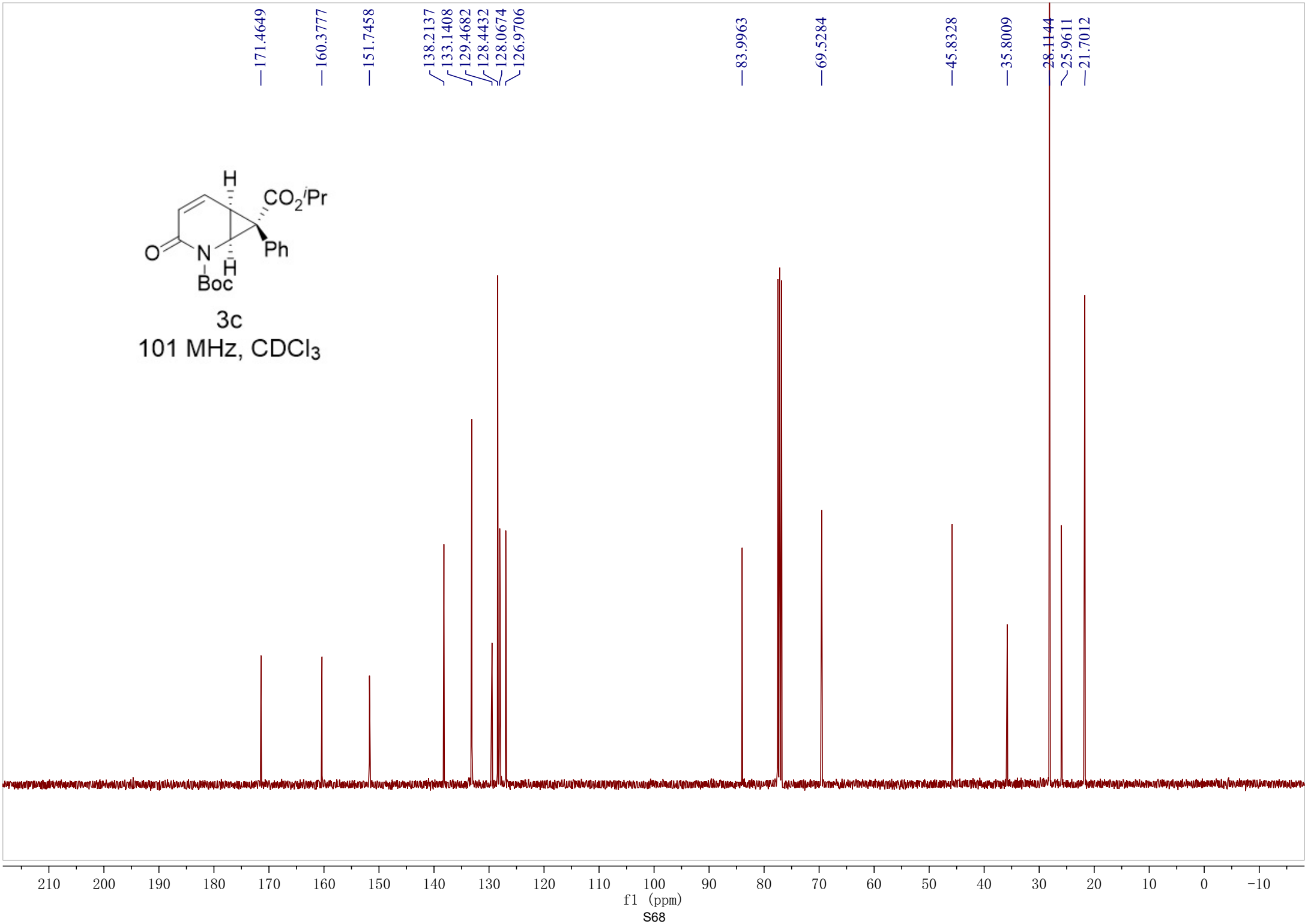


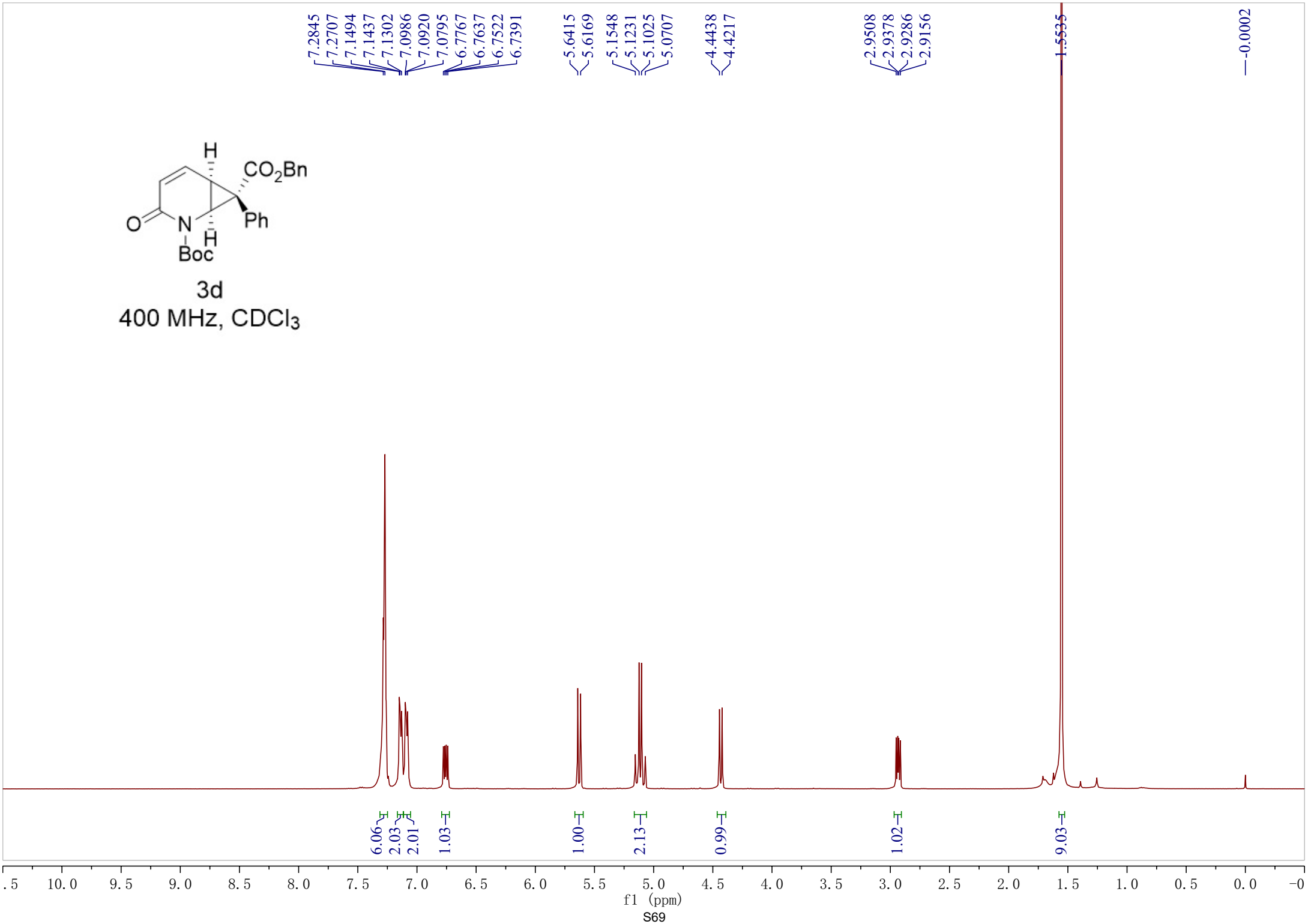
3b

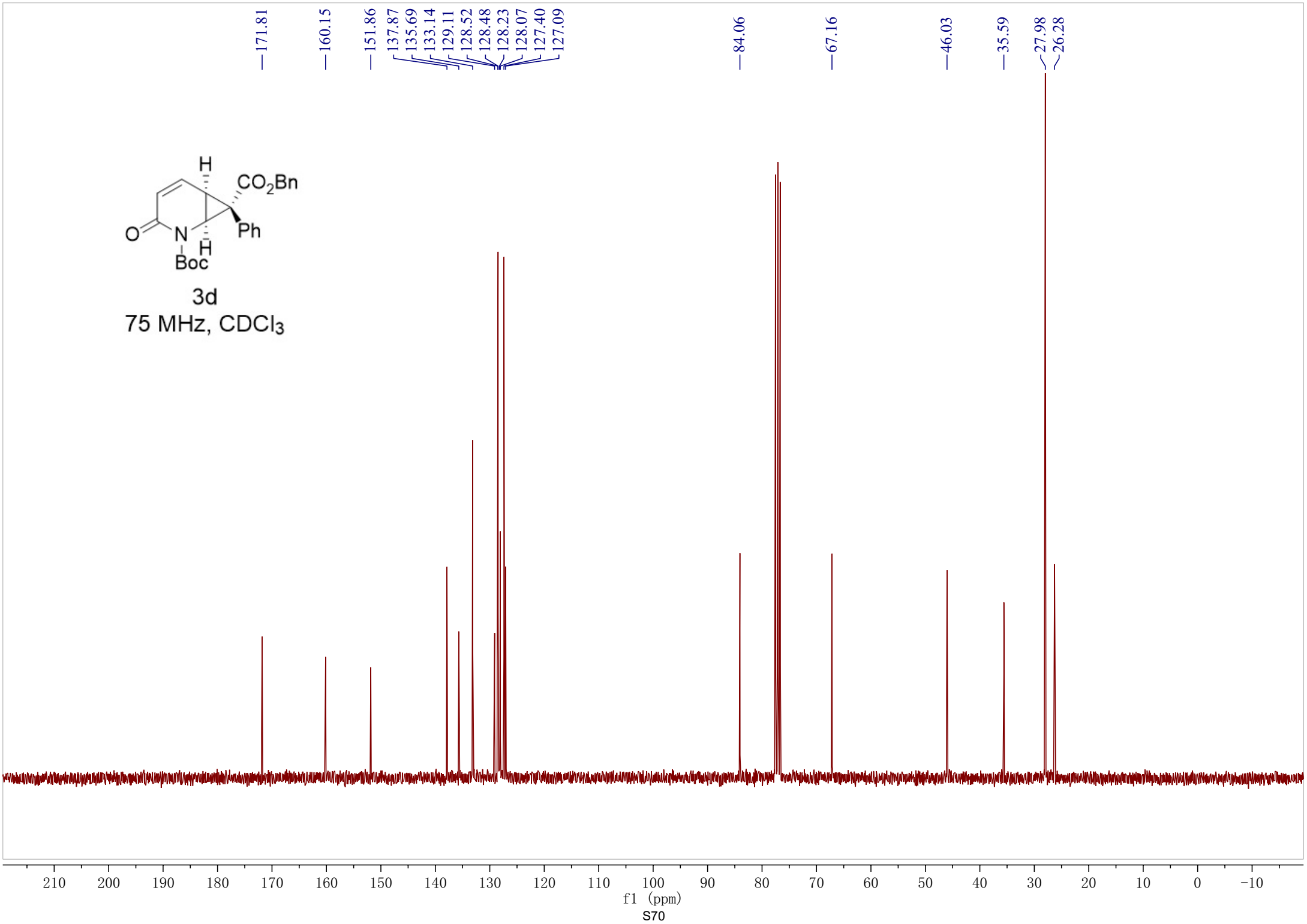
400 MHz, $CDCl_3$

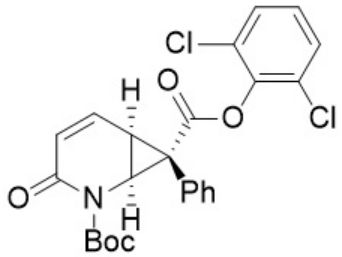

171.98
160.19
151.95
138.04
133.12
129.26
128.42
128.09
126.96
84.00
61.92
45.90
35.54
28.02
26.11
14.14
H
CO2Et
O
N
H
Ph
Boc
3b
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.2739
7.2712
7.2619
7.2588
7.2543
7.2477
7.2437
7.2367
7.0664
7.0598
7.0550
7.0471
7.0426
6.7880
6.7865
6.7749
6.7735
6.7634
6.7620
6.7503
6.7489
5.6326
5.6080
5.0283
5.0127
4.9970
4.9814
4.9658
4.9502
4.9345
4.4053
4.4039
4.3832
4.3817
2.9191
2.9060
2.8969
2.8838
1.6107
1.1618
1.1462
1.1331
1.1175
0.0000
H
CO2iPr
Ph
O
N
H
Boc
3c
400 MHz, CDCl3
3.18
2.03
1.06
1.01
1.08
1.00
1.06
9.06
3.08
3.04
f1 (ppm)


171.4649
160.3777
151.7458
138.2137
133.1408
129.4682
128.4432
128.0674
126.9706
83.9963
69.5284
45.8328
35.8009
28.1144
25.9611
21.7012
H
CO2iPr
O
N
H
Ph
Boc
3c
101 MHz, CDCl3
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)

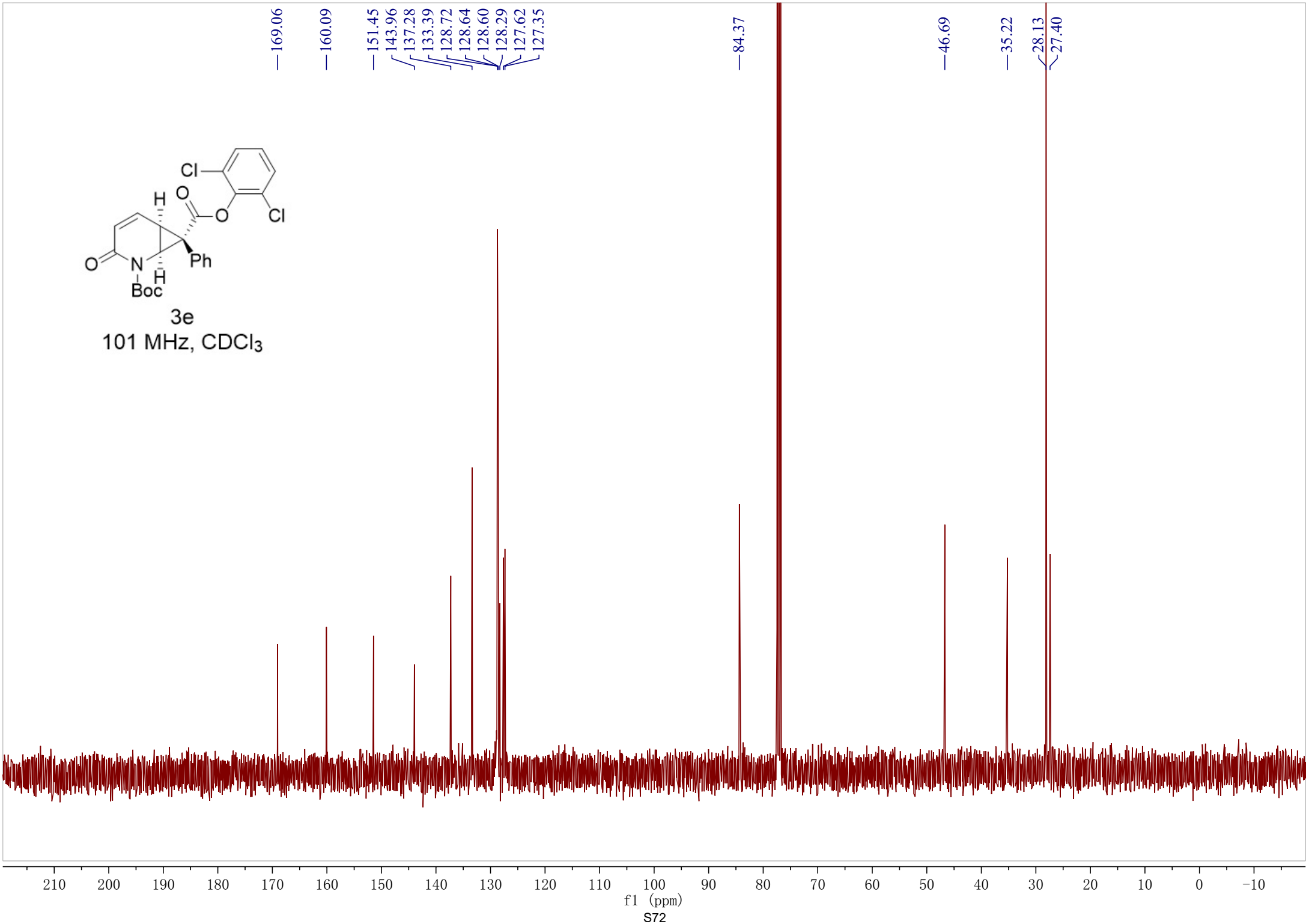

7.2845
7.2707
7.1494
7.1437
7.1302
7.0986
7.0920
7.0795
6.7767
6.7637
6.7522
6.7391
5.6415
5.6169
5.1548
5.1231
5.1025
5.0707
4.4438
4.4217
2.9508
2.9378
2.9286
2.9156
1.5535
-0.0002
H
CO2Bn
Ph
O
N
H
Boc
3d
400 MHz, CDCl3
6.06
2.03
2.01
1.03
1.00
2.13
0.99
1.02
9.03
f1 (ppm)

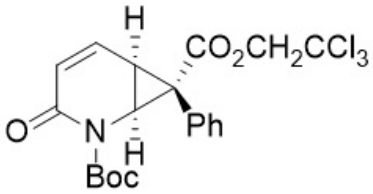

171.81
160.15
151.86
137.87
135.69
133.14
129.11
128.52
128.48
128.23
128.07
127.40
127.09
84.06
67.16
46.03
35.59
27.98
26.28
H
CO2Bn
O
N
H
Ph
Boc
3d
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3e

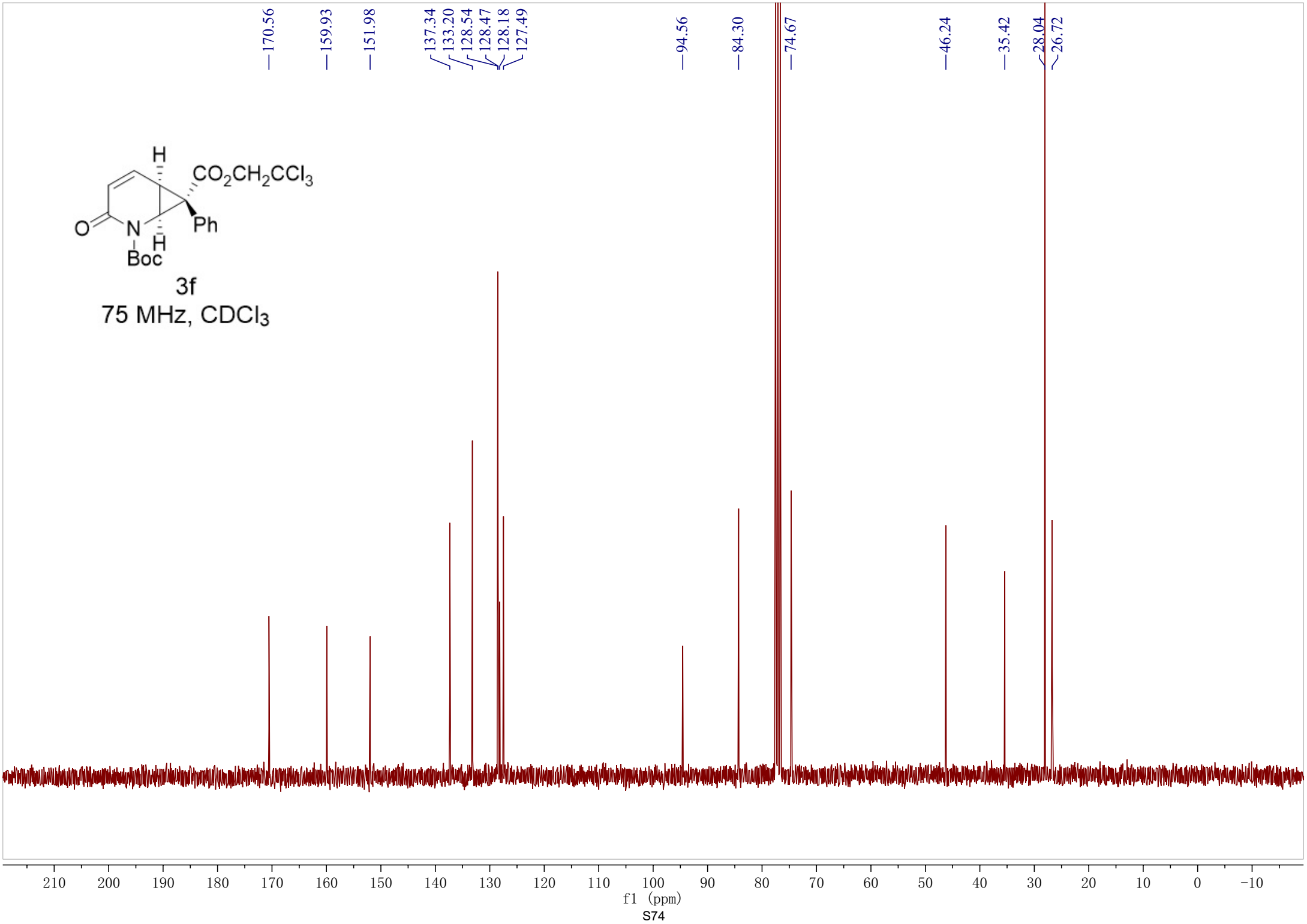
400 MHz, $CDCl_3$

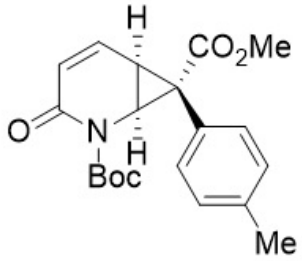

169.06
160.09
151.45
143.96
137.28
133.39
128.72
128.64
128.60
128.29
127.62
127.35
84.37
46.69
35.22
28.13
27.40
Cl
O
H
O
Cl
O
N
H
Ph
Boc
3e
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



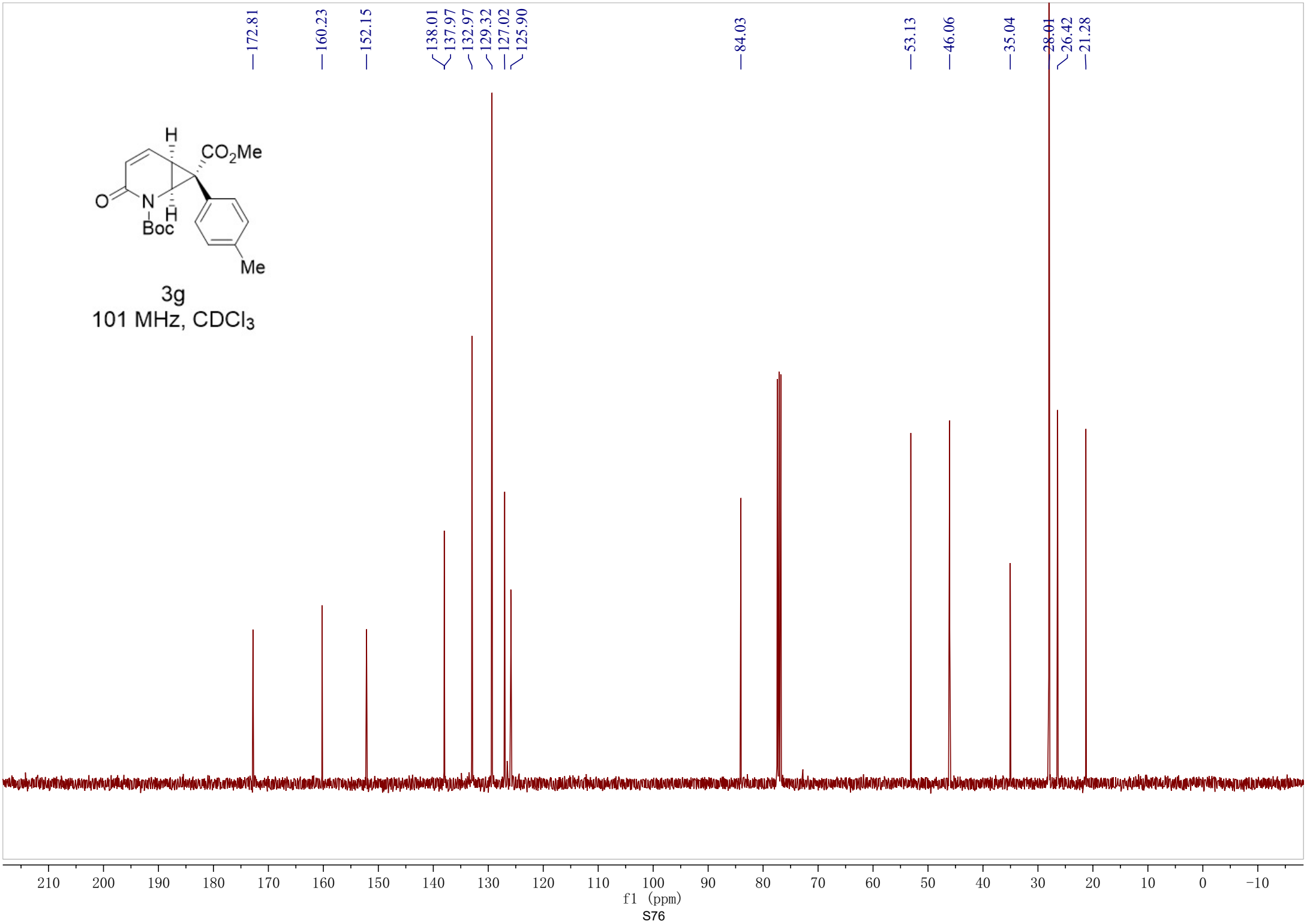
3f

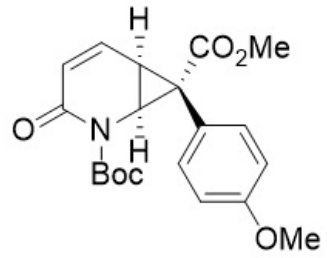
400 MHz, $CDCl_3$


170.56
159.93
151.98
137.34
133.20
128.54
128.47
128.18
127.49
94.56
84.30
74.67
46.24
35.42
28.04
26.72
H
CO2CH2CCl3
O
N
Ph
H
Boc
3f
75 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3g
400 MHz, $CDCl_3$


172.81
160.23
152.15
138.01
137.97
132.97
129.32
127.02
125.90
84.03
53.13
46.06
35.04
28.01
26.42
21.28
H
CO2Me
O
N
H
Boc
Me
3g
101 MHz, CDCl3
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)



3h

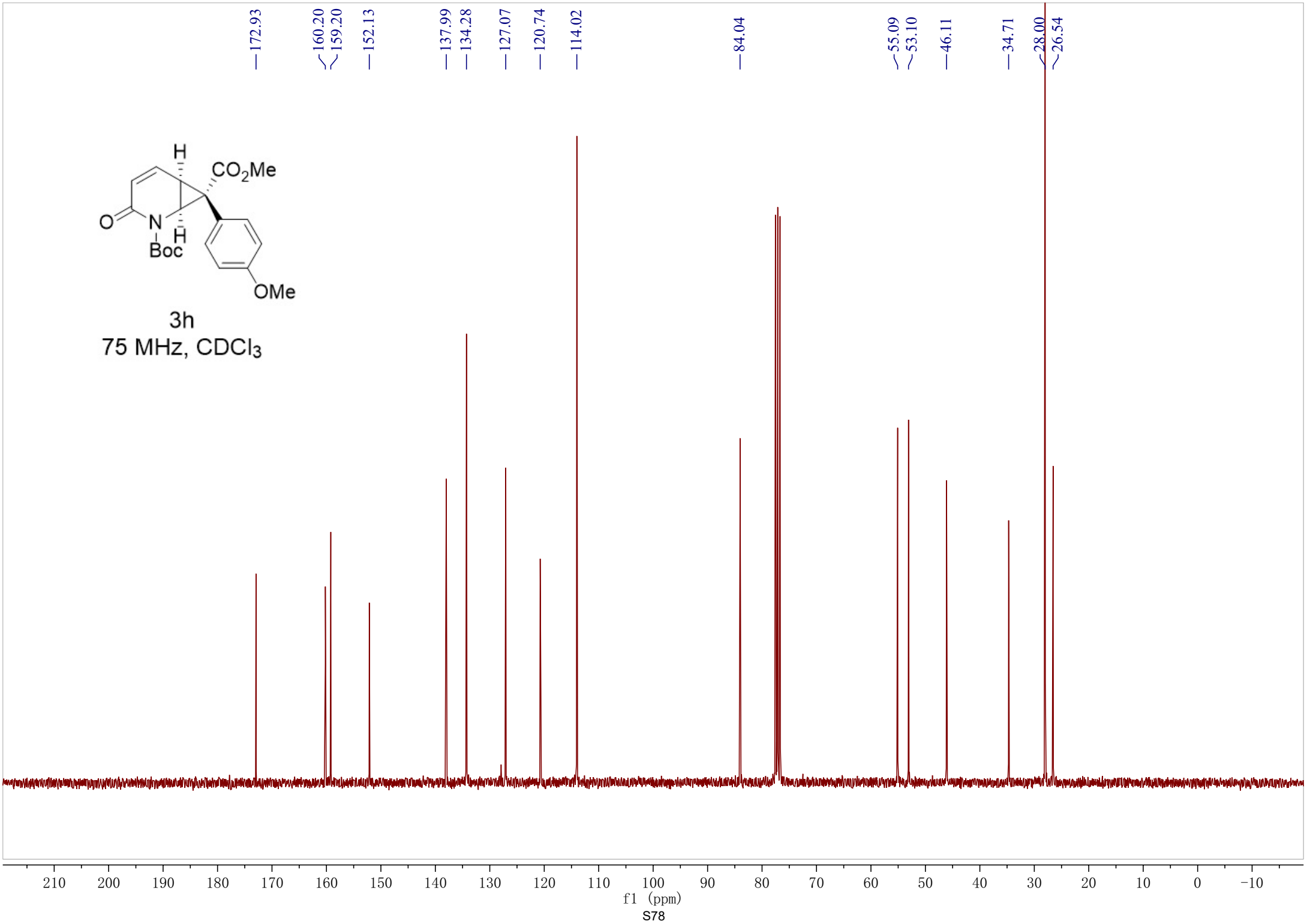
300 MHz, $CDCl_3$

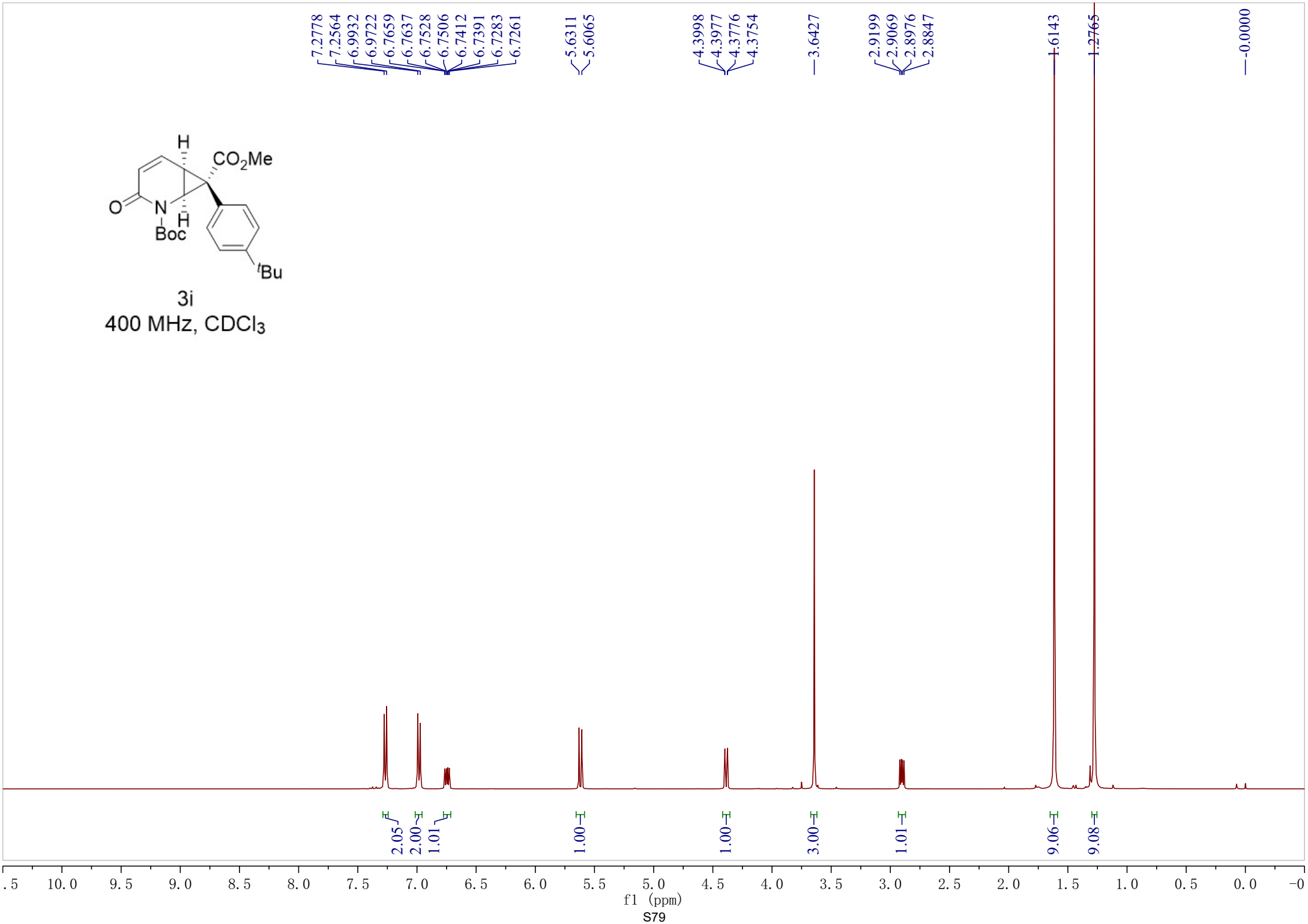
6.9958
6.9889
6.9738
6.9666
6.8100
6.8067
6.8007
6.7837
6.7800
6.7770
6.7622
6.7594
6.7470
6.7442
6.7296
6.7267
5.6577
5.6251
4.3944
4.3916
4.3647
4.3620
3.7601
3.6535
2.9248
2.9074
2.8952
2.8777
1.6046
-0.0000

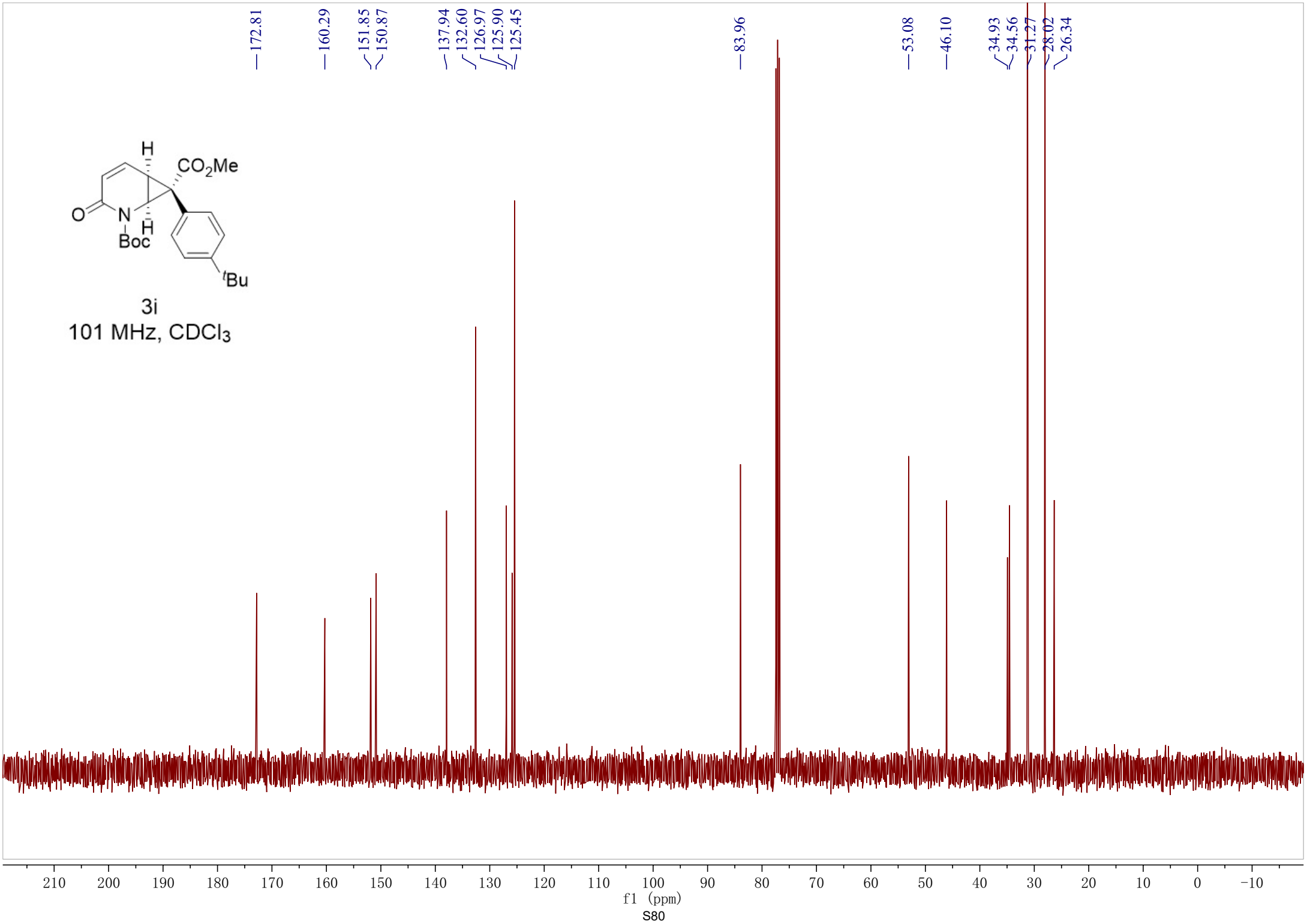
2.01
3.08
1.00
1.00
3.01
3.00
1.03
9.02

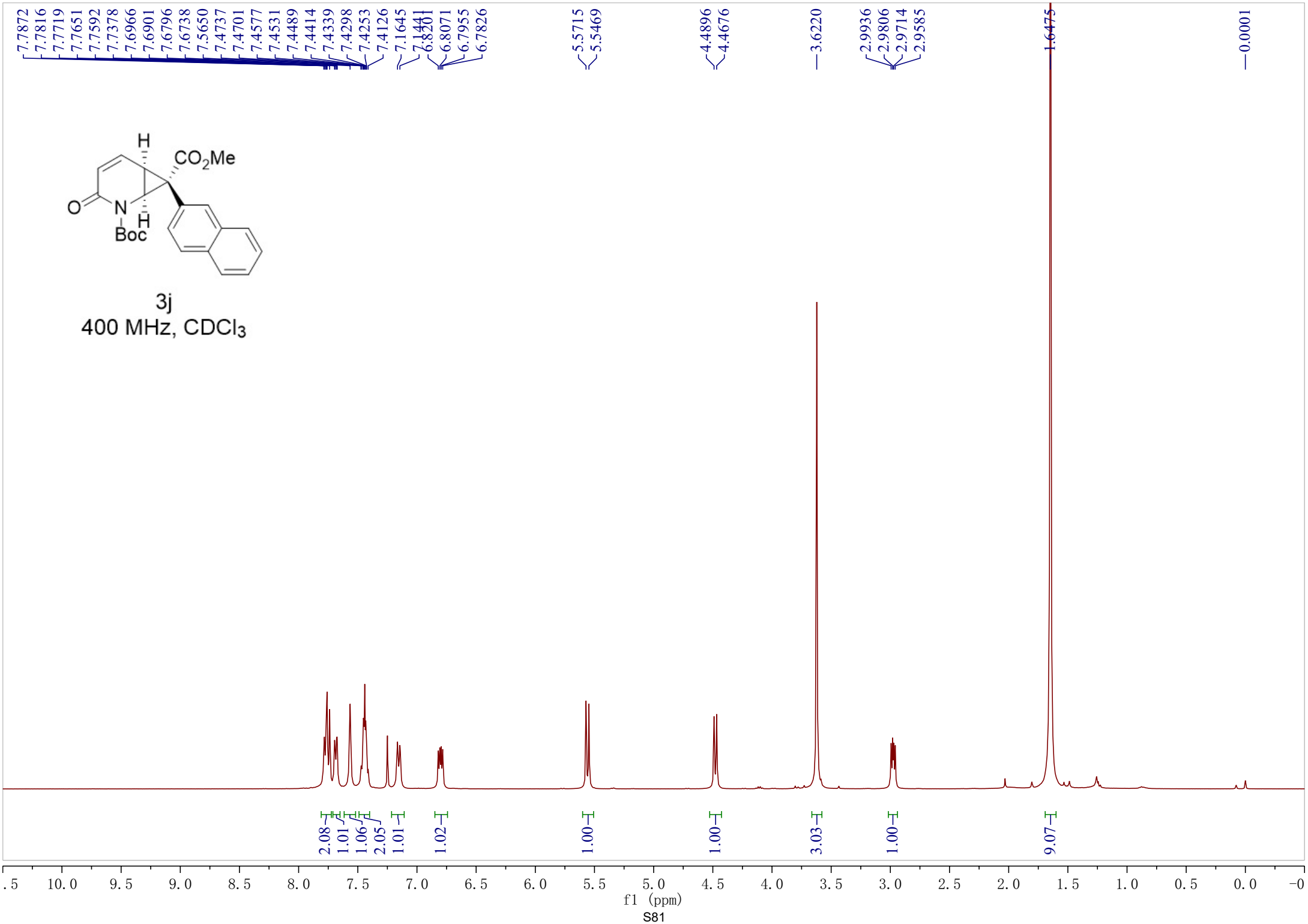
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

f1 (ppm)

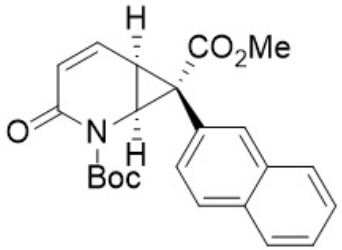

172.93
160.20
159.20
152.13
137.99
134.28
127.07
120.74
114.02
84.04
55.09
53.10
46.11
34.71
28.00
26.54
H
CO2Me
O
N
H
Boc
OMe
3h
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.2778
7.2564
6.9932
6.9722
6.7659
6.7637
6.7528
6.7506
6.7412
6.7391
6.7283
6.7261
5.6311
5.6065
4.3998
4.3977
4.3776
4.3754
3.6427
2.9199
2.9069
2.8976
2.8847
1.6143
1.2765
-0.0000
H
CO2Me
O
N
H
Boc
tBu
3i
400 MHz, CDCl3
2.05
2.00
1.01
1.00
1.00
3.00
1.01
9.06
9.08
f1 (ppm)


172.81
160.29
151.85
150.87
137.94
132.60
126.97
125.90
125.45
83.96
53.08
46.10
34.93
34.56
31.27
28.02
26.34
H
CO2Me
O
N
H
Boc
tBu
3i
101 MHz, CDCl3
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)


7.7872
7.7816
7.7719
7.7651
7.7592
7.7378
7.6966
7.6901
7.6796
7.6738
7.5650
7.4737
7.4701
7.4577
7.4531
7.4489
7.4414
7.4339
7.4298
7.4253
7.4126
7.1645
7.1441
7.1201
6.8071
6.7955
6.7826
5.5715
5.5469
4.4896
4.4676
3.6220
2.9936
2.9806
2.9714
2.9585
1.6475
0.0001
H
CO2Me
O
N
H
Boc
3j
400 MHz, CDCl3
2.08
1.01
1.06
2.05
1.01
1.02
1.00
1.00
3.03
1.00
9.07
f1 (ppm)

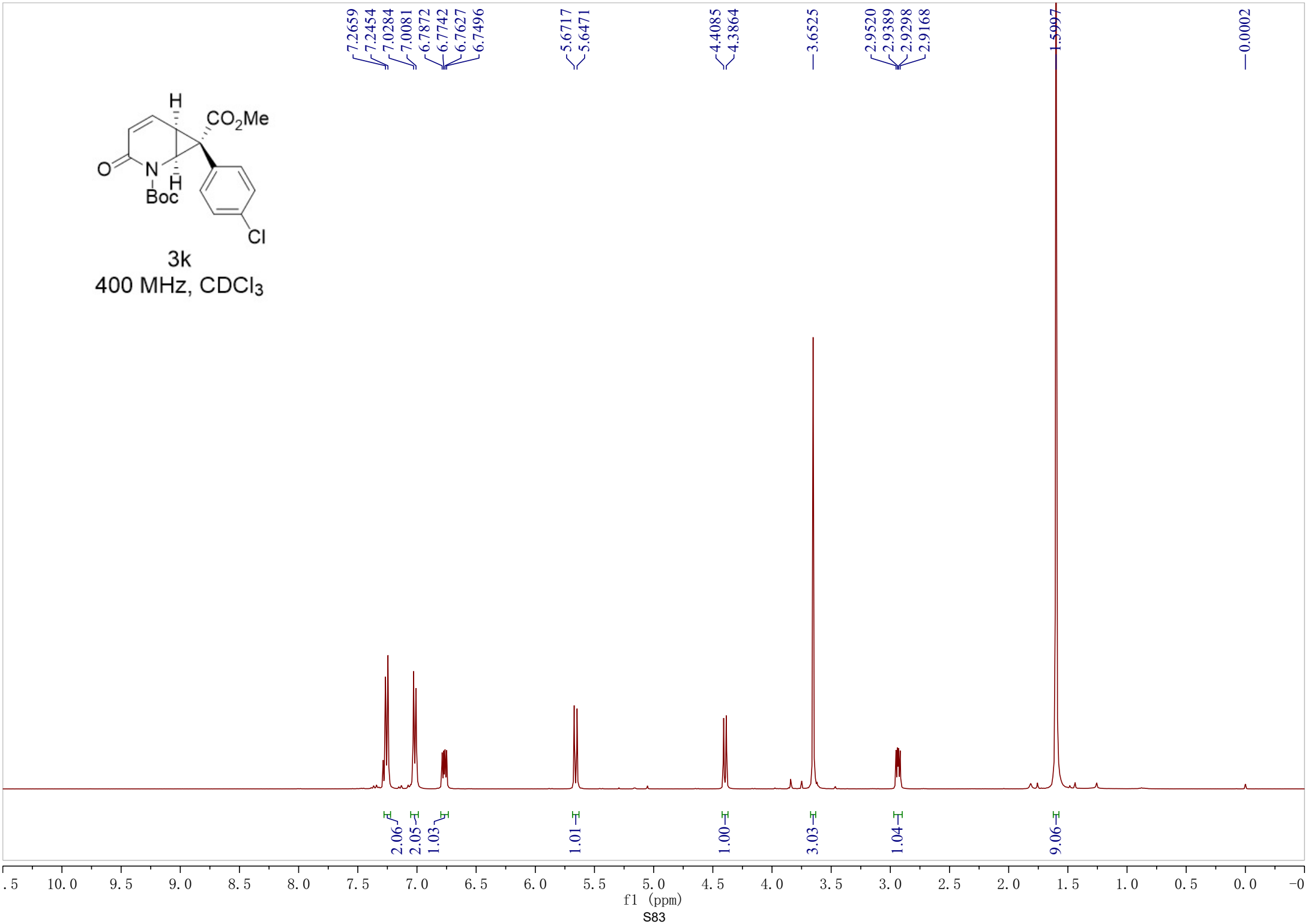
sjt01.96.fid
sjh-05-827

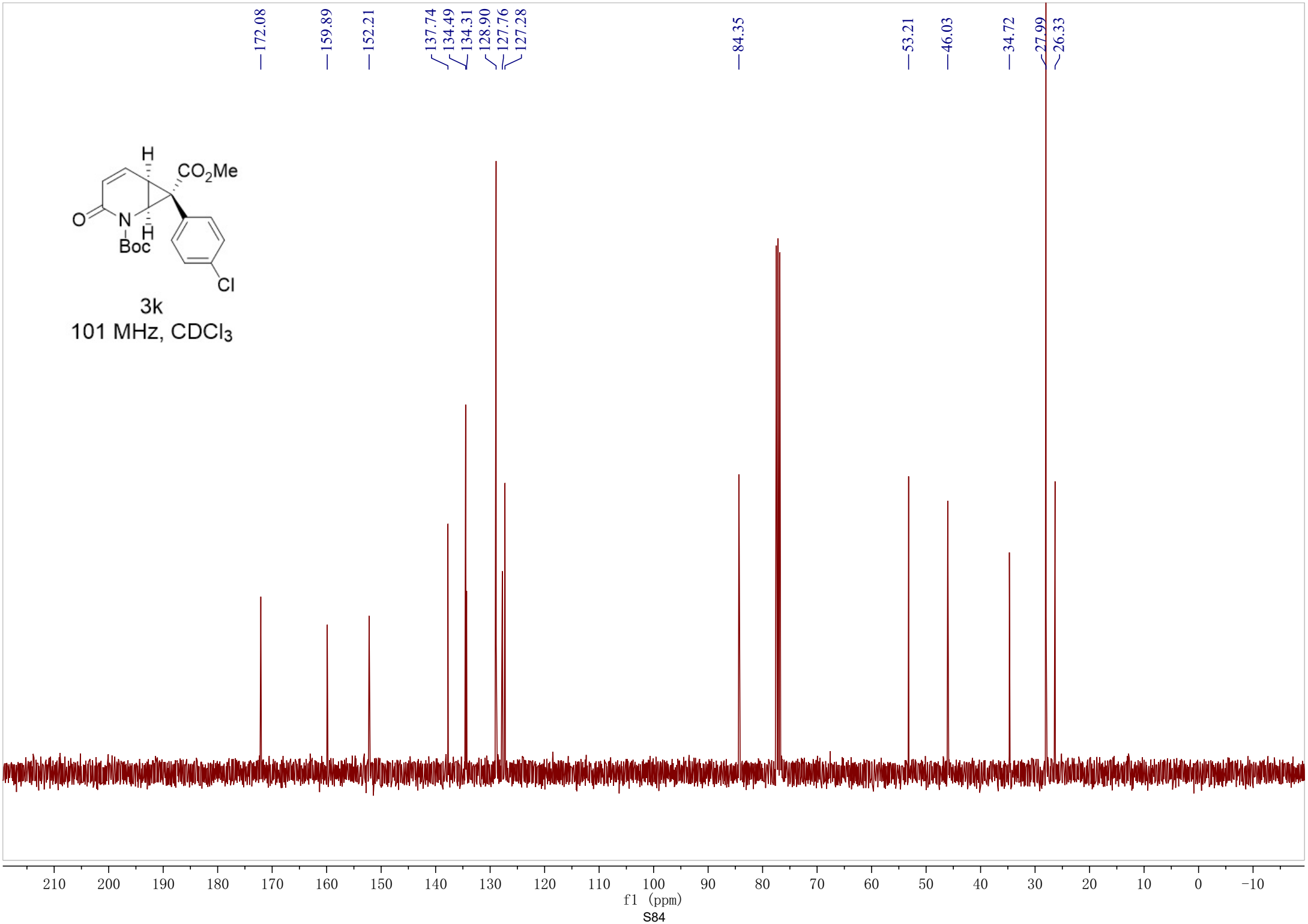


3j
101 MHz, $CDCl_3$

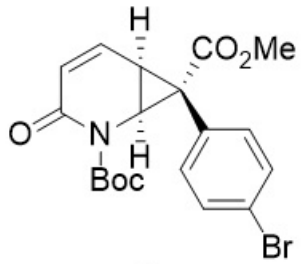
172.66
160.02
152.37
137.84
133.24
133.03
132.87
130.11
128.27
127.88
127.74
127.08
126.61
126.58
126.18
84.16
53.16
46.19
35.45
28.10
26.59

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)

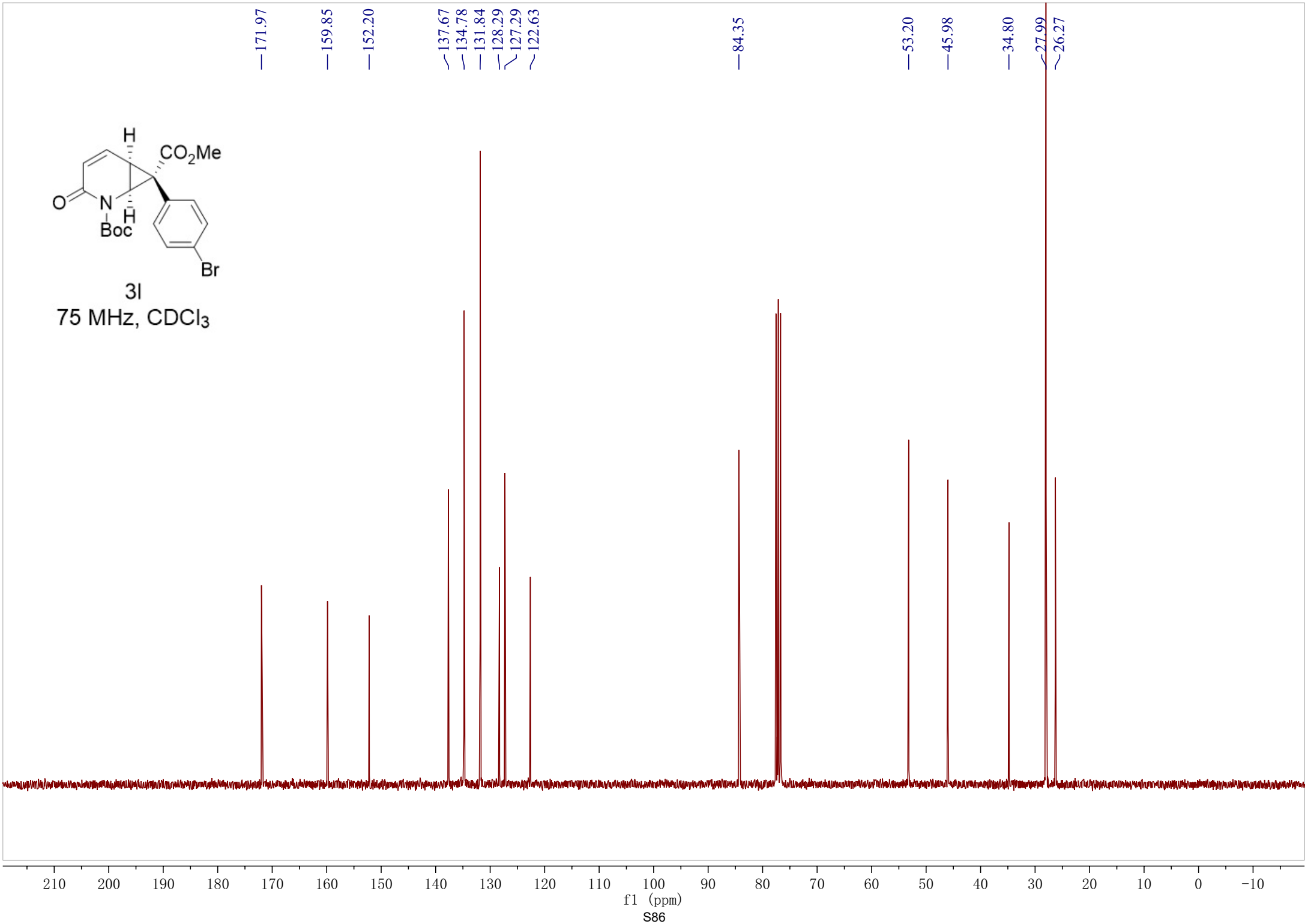

7.2659
7.2454
7.0284
7.0081
6.7872
6.7742
6.7627
6.7496
5.6717
5.6471
4.4085
4.3864
3.6525
2.9520
2.9389
2.9298
2.9168
1.5997
0.0002
H
CO2Me
O
N
H
Boc
Cl
3k
400 MHz, CDCl3
2.06
2.05
1.03
1.01
1.00
3.03
1.04
9.06
f1 (ppm)

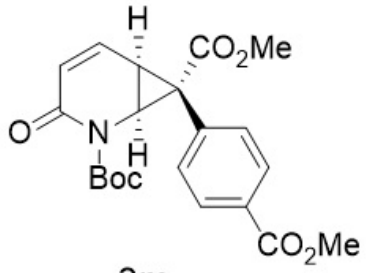

172.08
159.89
152.21
137.74
134.49
134.31
128.90
127.76
127.28
84.35
53.21
46.03
34.72
27.99
26.33
H
CO2Me
O
N
H
Boc
Cl
3k
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3sjtao.9885.fid
3sjtao 9885 sjh-04-709 1h cdcl3



3l
300 MHz, $CDCl_3$


171.97
159.85
152.20
137.67
134.78
131.84
128.29
127.29
122.63
84.35
53.20
45.98
34.80
27.99
26.27
H
CO2Me
O
N
H
Boc
Br
3l
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3m

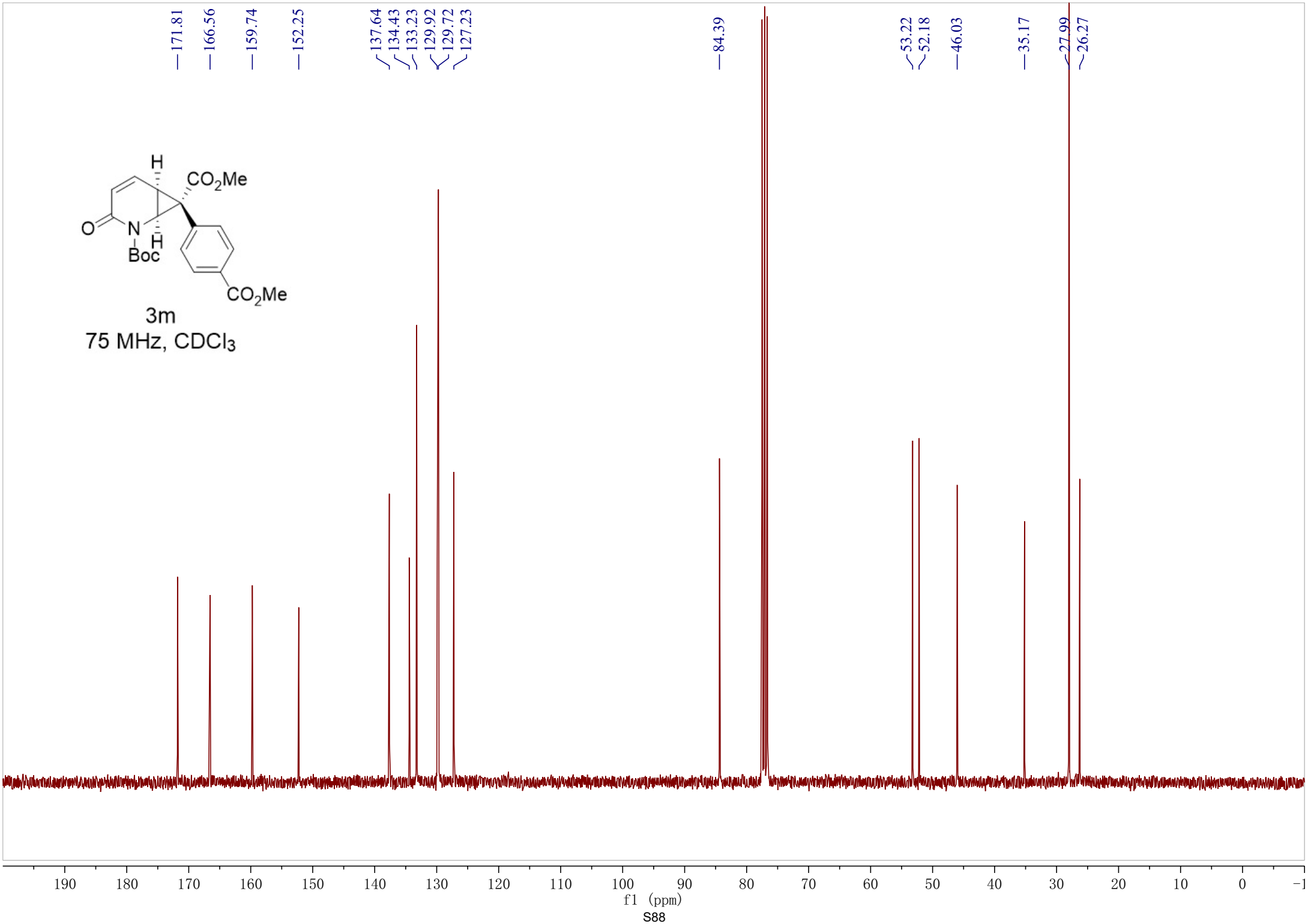
300 MHz, $CDCl_3$

7.9719
7.9437
7.1863
7.1584
6.8160
6.7985
6.7832
6.7658
5.6479
5.6152
4.4512
4.4216
3.8942
3.6542
2.9923
2.9748
2.9626
2.9452
1.6105
-0.0002

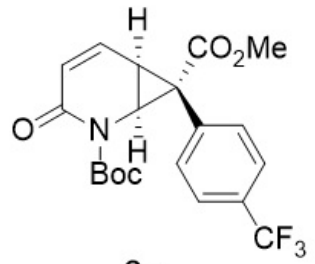
2.00
1.99
1.00
1.00
0.99
3.00
3.00
1.00
9.00

10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)

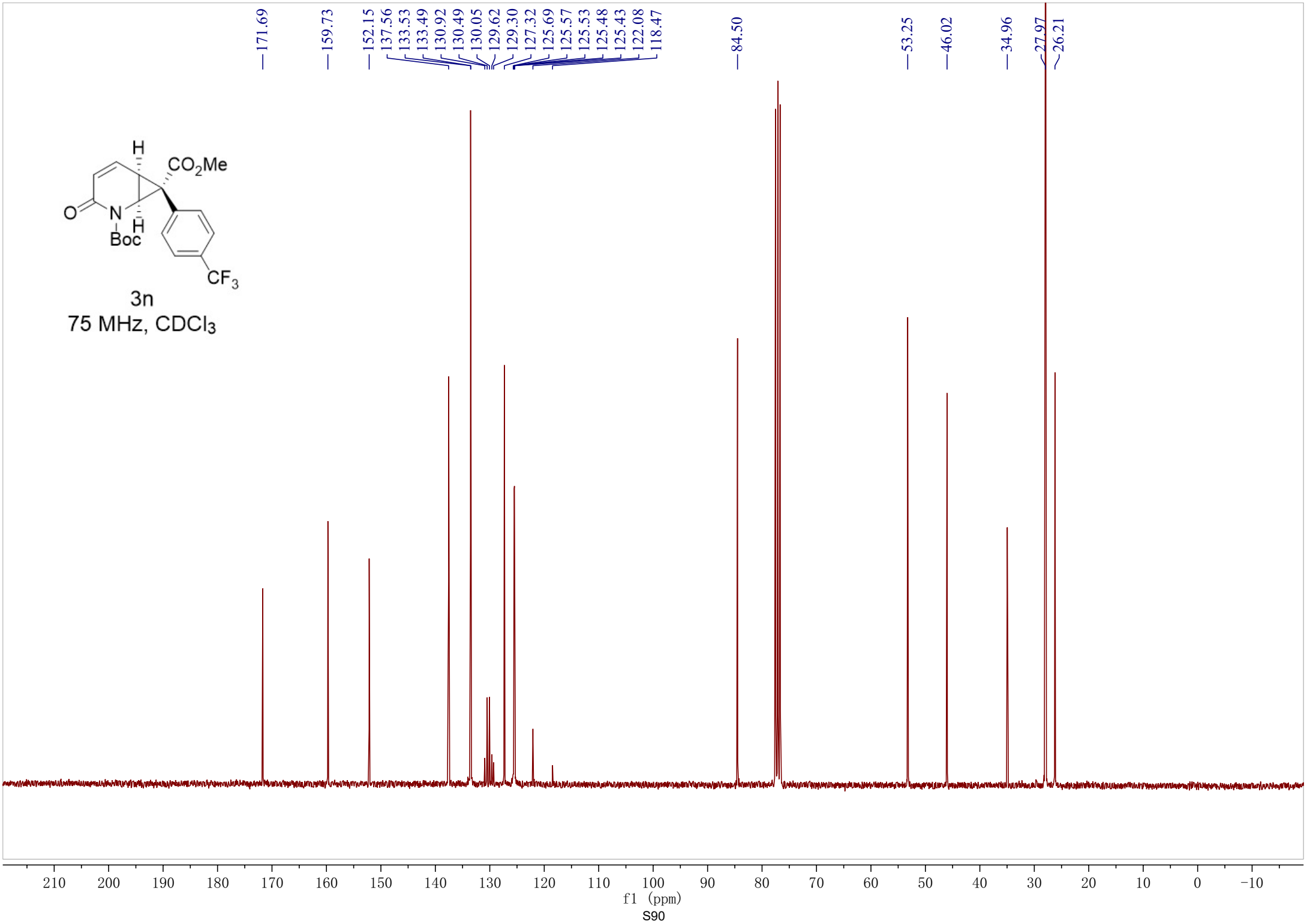

171.81
166.56
159.74
152.25
137.64
134.43
133.23
129.92
129.72
127.23
84.39
53.22
52.18
46.03
35.17
27.99
26.27
H
CO2Me
O
N
H
Boc
CO2Me
3m
75 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

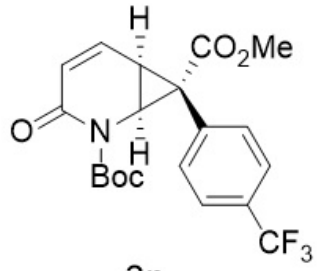
sjt02.52.fid
cq-04-49



3n

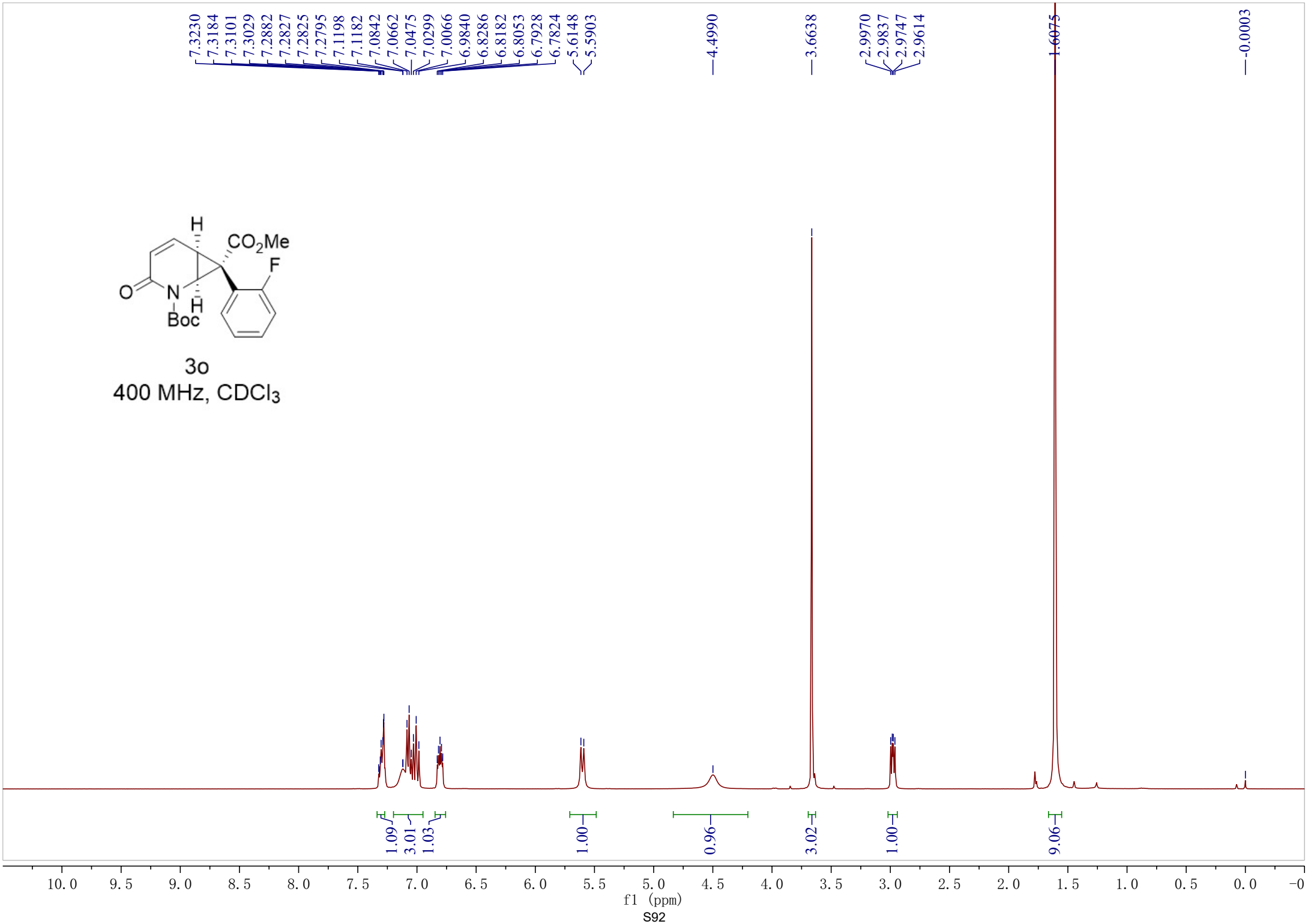
400 MHz, $CDCl_3$

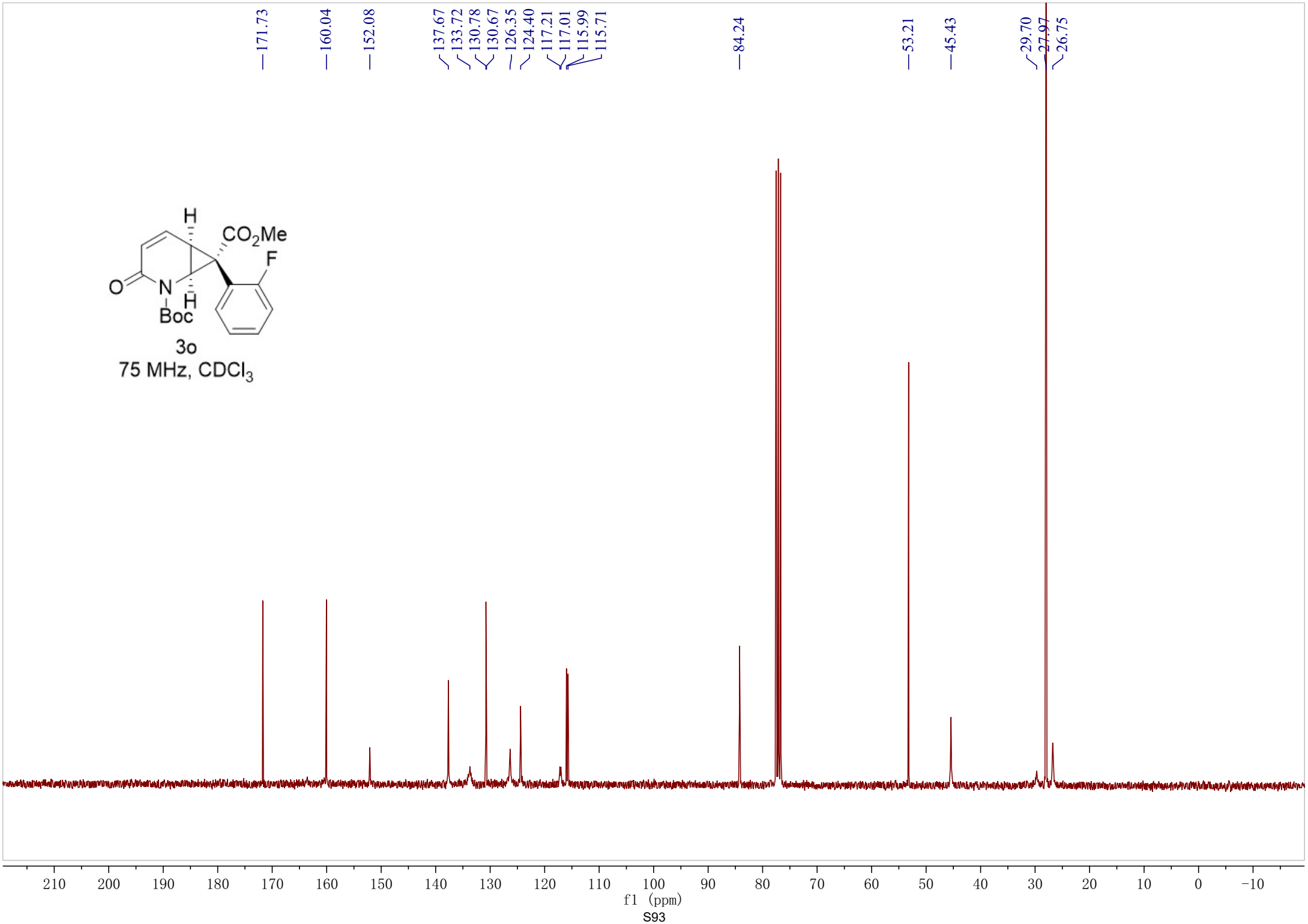

171.69
159.73
152.15
137.56
133.53
133.49
130.92
130.49
130.05
129.62
129.30
127.32
125.69
125.57
125.53
125.48
125.43
122.08
118.47
84.50
53.25
46.02
34.96
27.97
26.21
H
CO2Me
O
N
H
Boc
CF3
3n
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

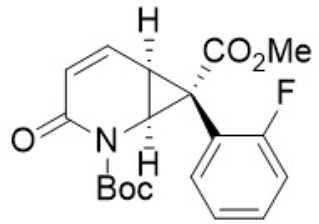


3n

282 MHz, $CDCl_3$


7.3230
7.3184
7.3101
7.3029
7.2882
7.2827
7.2825
7.2795
7.1198
7.1182
7.0842
7.0662
7.0475
7.0299
7.0066
6.9840
6.8286
6.8182
6.8053
6.7928
6.7824
5.6148
5.5903
4.4990
3.6638
2.9970
2.9837
2.9747
2.9614
1.6075
-0.0003
H
CO2Me
F
O
N
H
Boc
3o
400 MHz, CDCl3
1.09
3.01
1.03
1.00
0.96
3.02
1.00
9.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

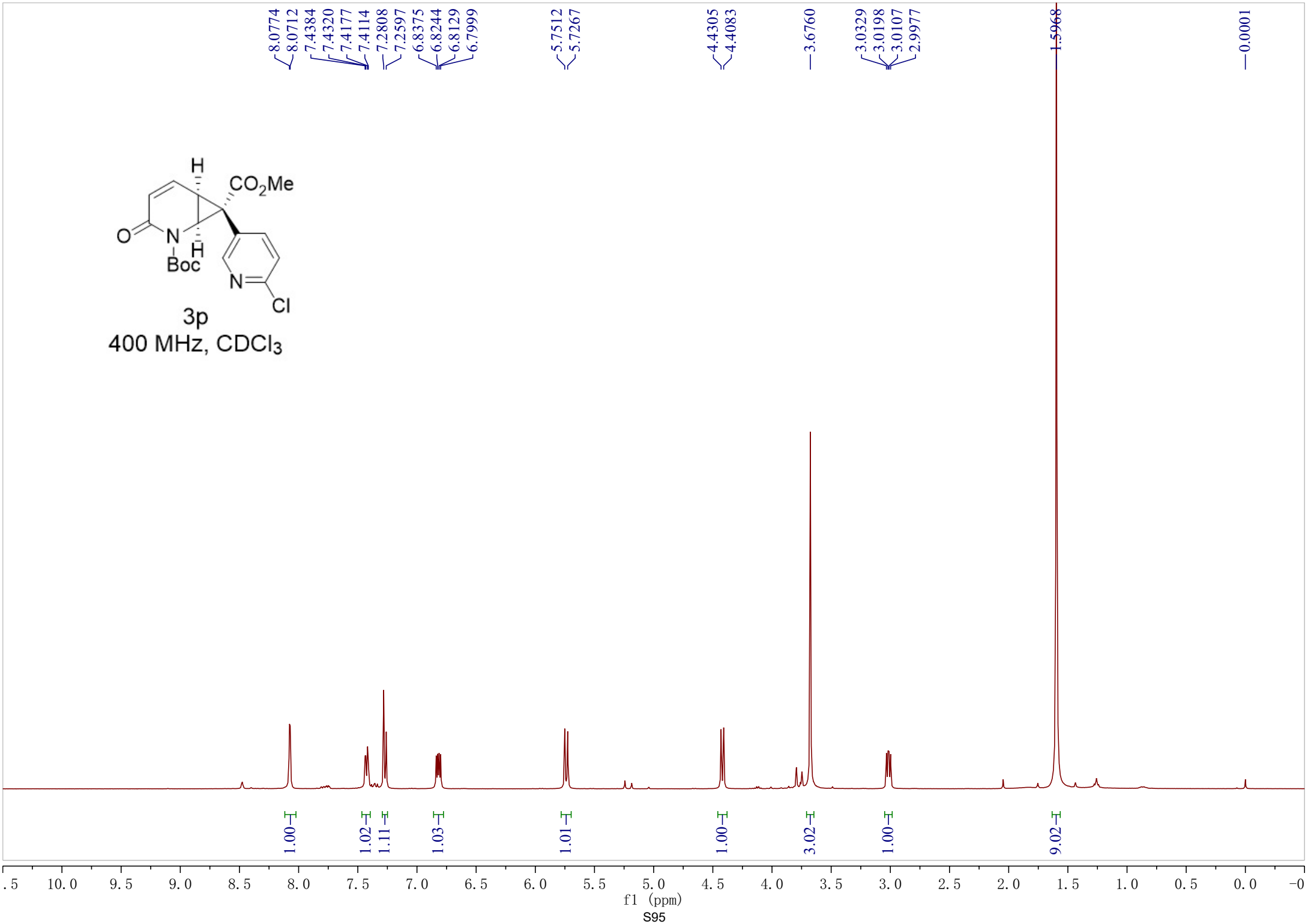

171.73
160.04
152.08
137.67
133.72
130.78
130.67
126.35
124.40
117.21
117.01
115.99
115.71
84.24
53.21
45.43
29.70
27.97
26.75
H
CO2Me
F
O
N
H
Boc
3o
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

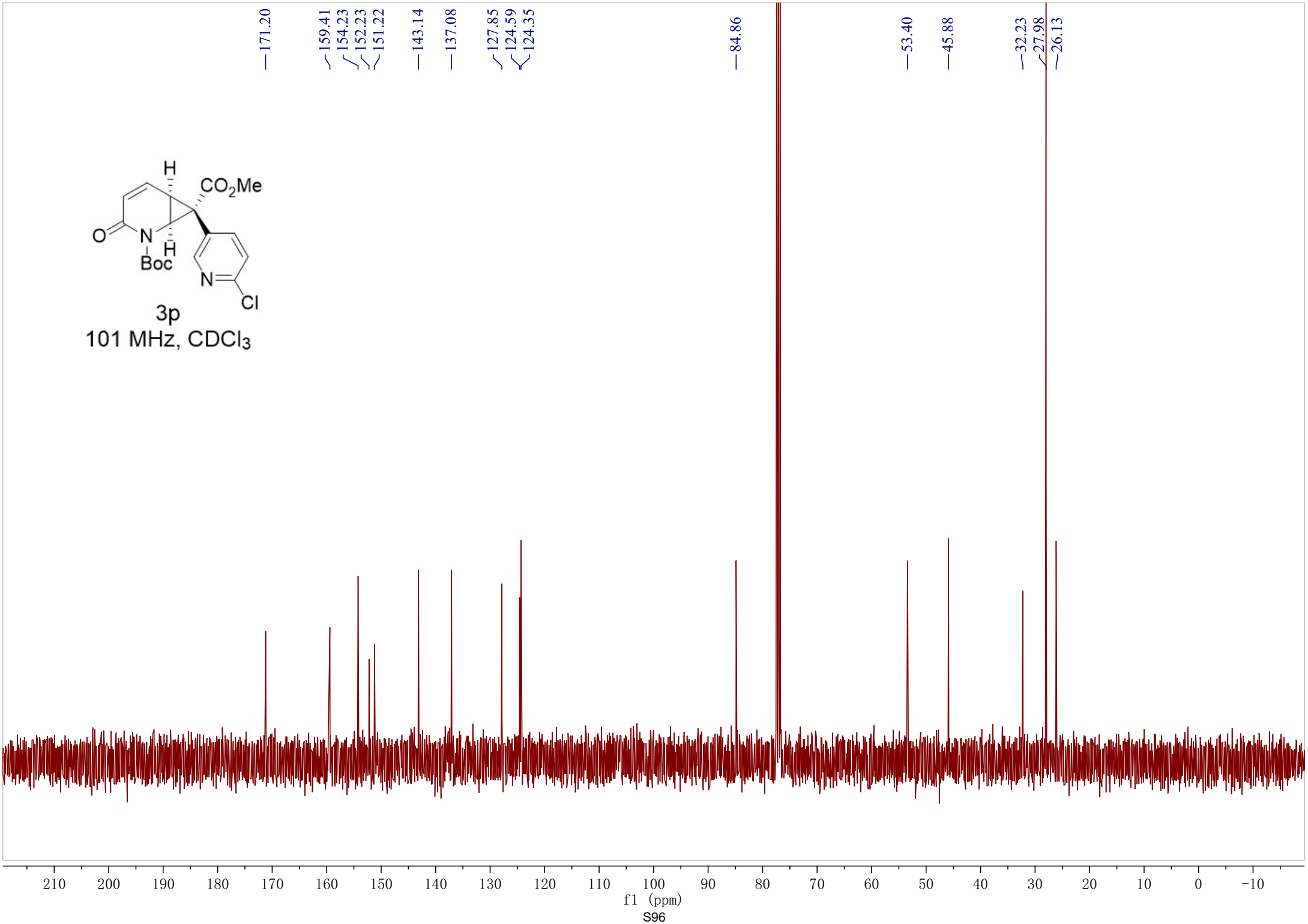


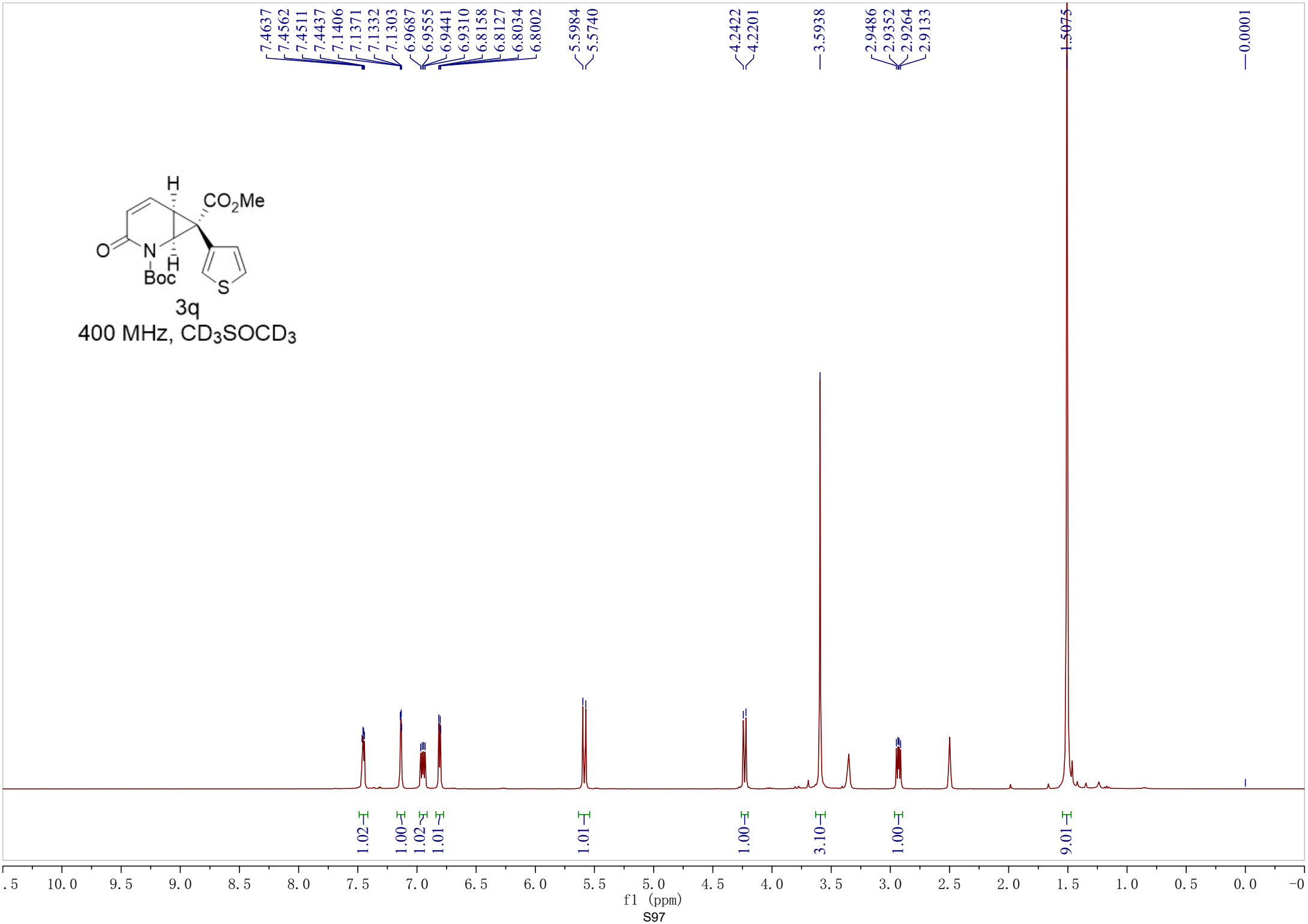
3o
282 MHz, $CDCl_3$

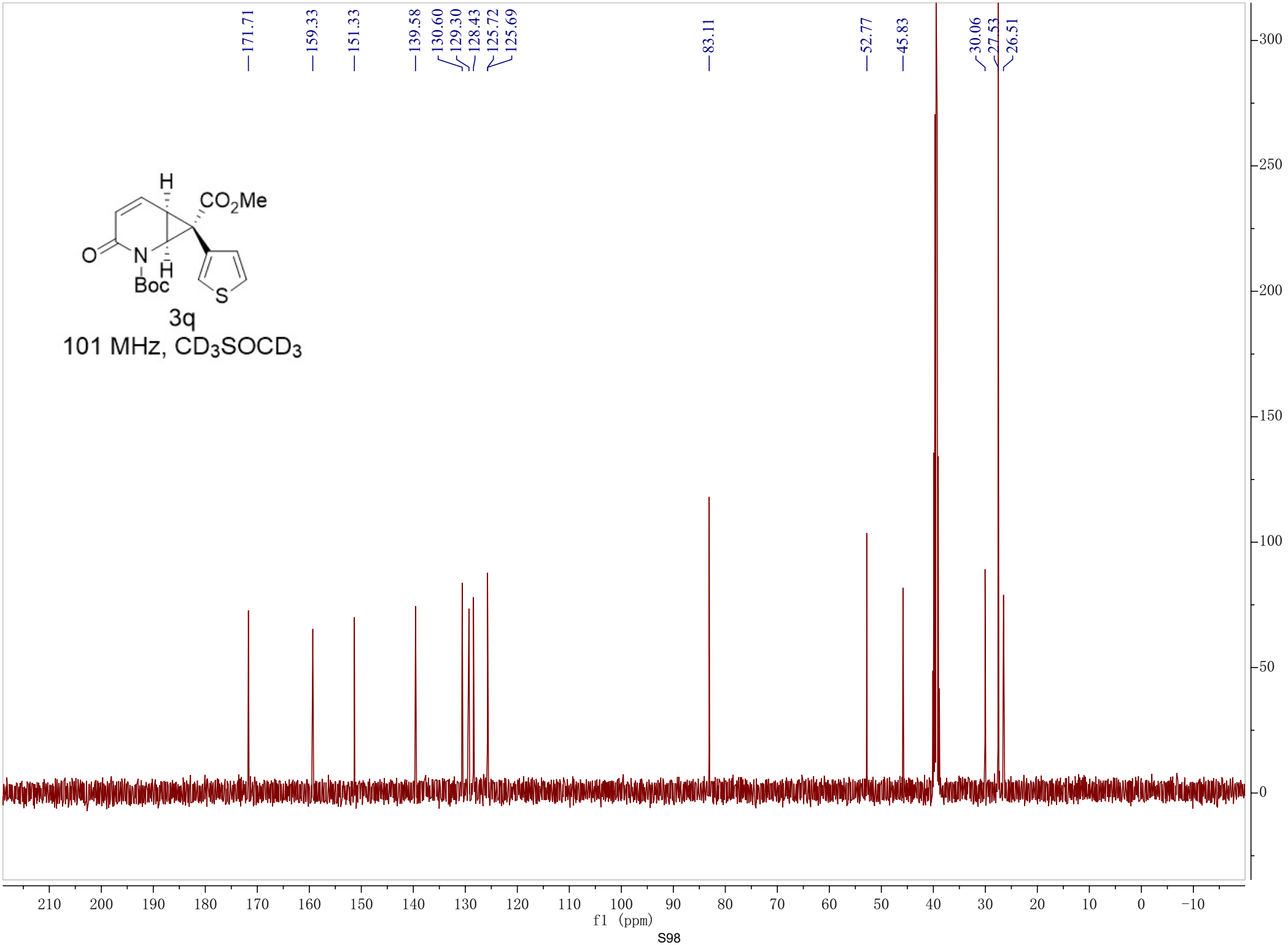
-112.80

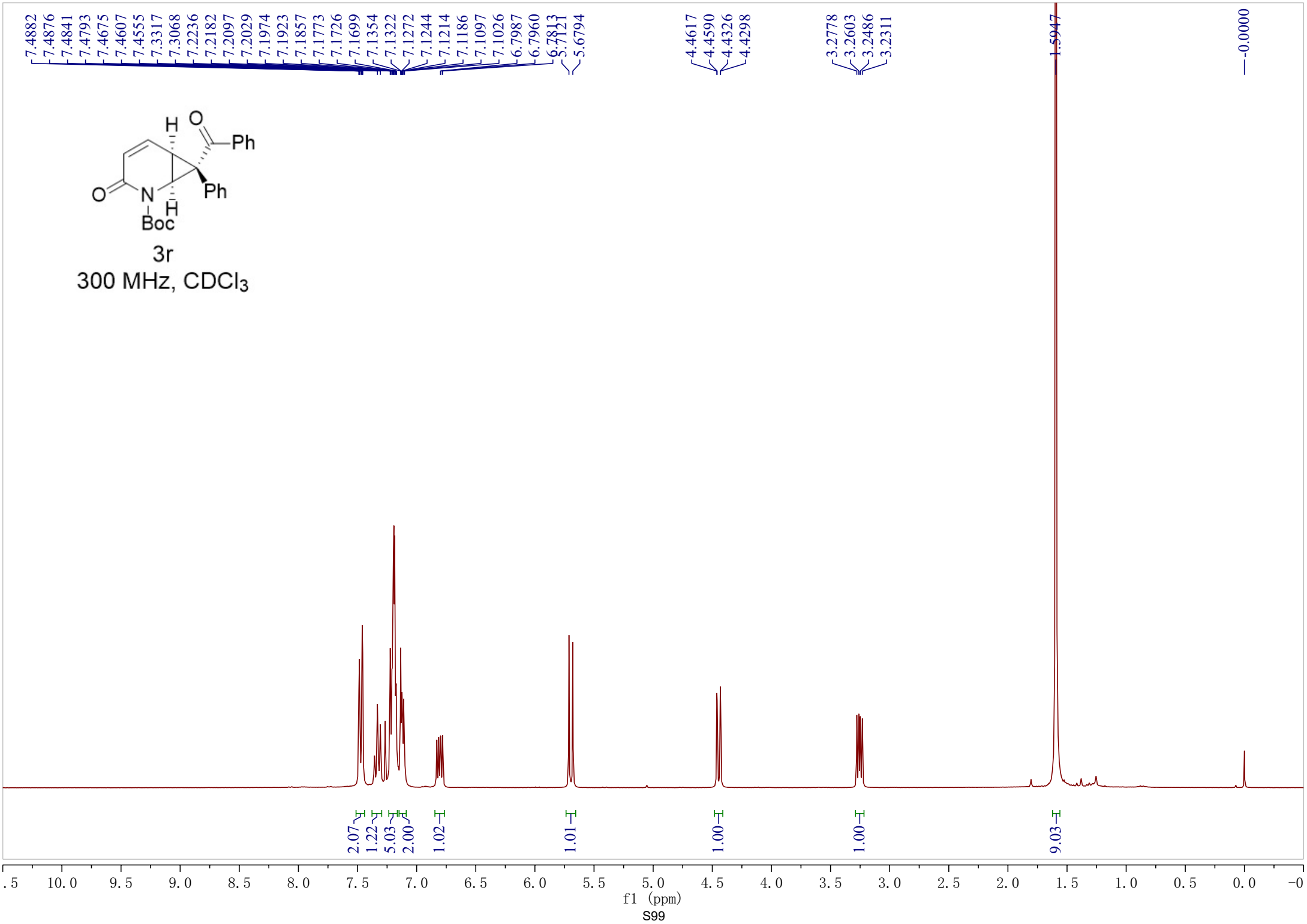
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

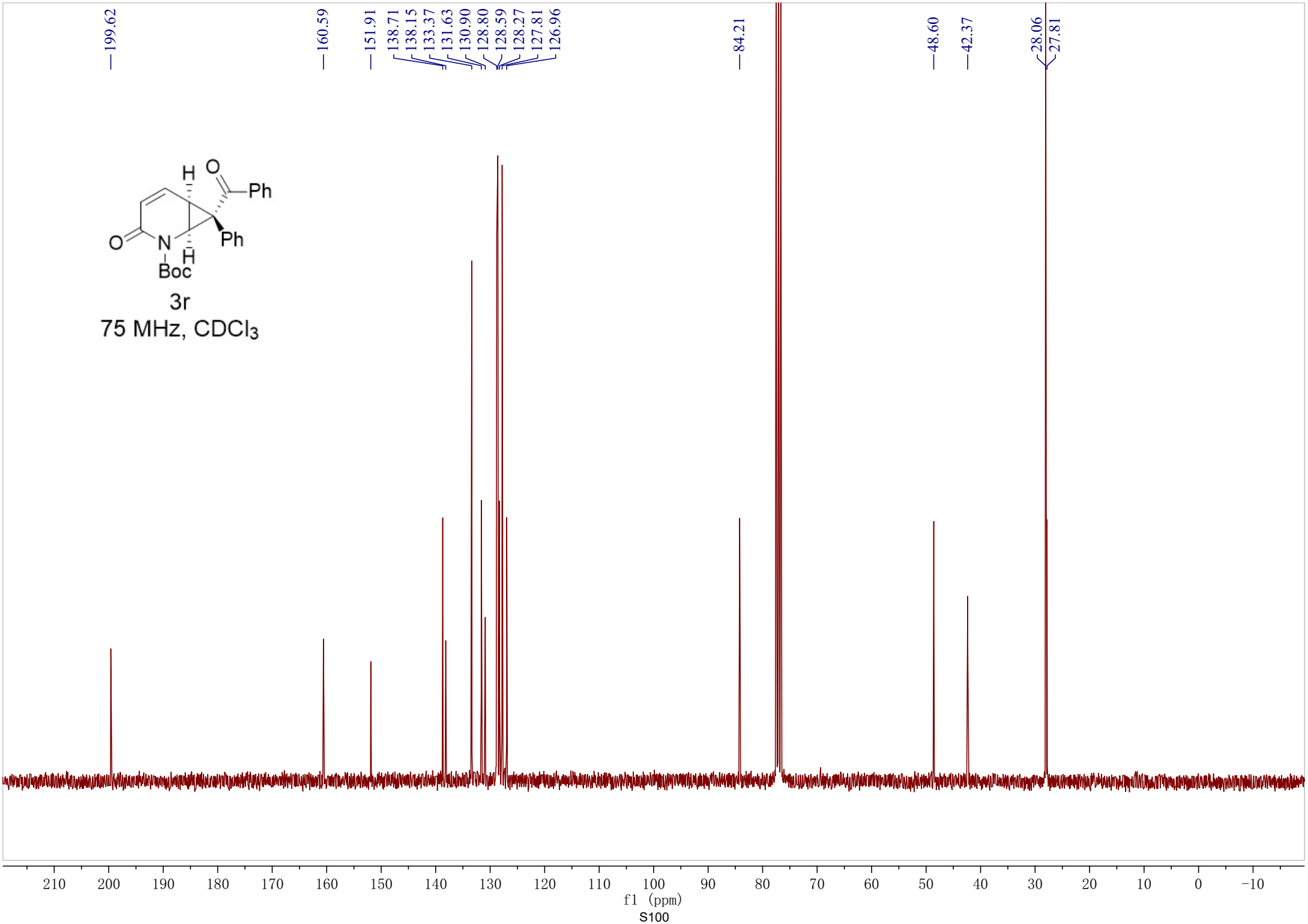

8.0774
8.0712
7.4384
7.4320
7.4177
7.4114
7.2808
7.2597
6.8375
6.8244
6.8129
6.7999
5.7512
5.7267
4.4305
4.4083
3.6760
3.0329
3.0198
3.0107
2.9977
1.5968
0.0001
H
CO2Me
O
N
H
Boc
N
Cl
3p
400 MHz, CDCl3
1.00
1.02
1.11
1.03
1.01
1.00
3.02
1.00
9.02
f1 (ppm)

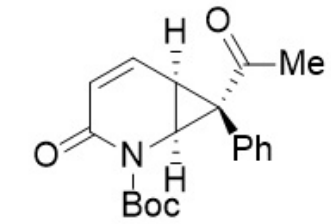

171.20
159.41
154.23
152.23
151.22
143.14
137.08
127.85
124.59
124.35
84.86
53.40
45.88
32.23
27.98
26.13
H
CO2Me
O
N
H
Boc
N
Cl
3p
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.4637
7.4562
7.4511
7.4437
7.1406
7.1371
7.1332
7.1303
6.9687
6.9555
6.9441
6.9310
6.8158
6.8127
6.8034
6.8002
5.5984
5.5740
4.2422
4.2201
3.5938
2.9486
2.9352
2.9264
2.9133
1.5075
0.0001
H
CO2Me
O
N
H
Boc
S
3q
400 MHz, CD3SOCD3
1.02
1.00
1.02
1.01
1.01
1.00
3.10
1.00
9.01
f1 (ppm)


171.71
159.33
151.33
139.58
130.60
129.30
128.43
125.72
125.69
83.11
52.77
45.83
30.06
27.53
26.51
H
CO2Me
O
N
H
Boc
S
3q
101 MHz, CD3SOCD3
300
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)

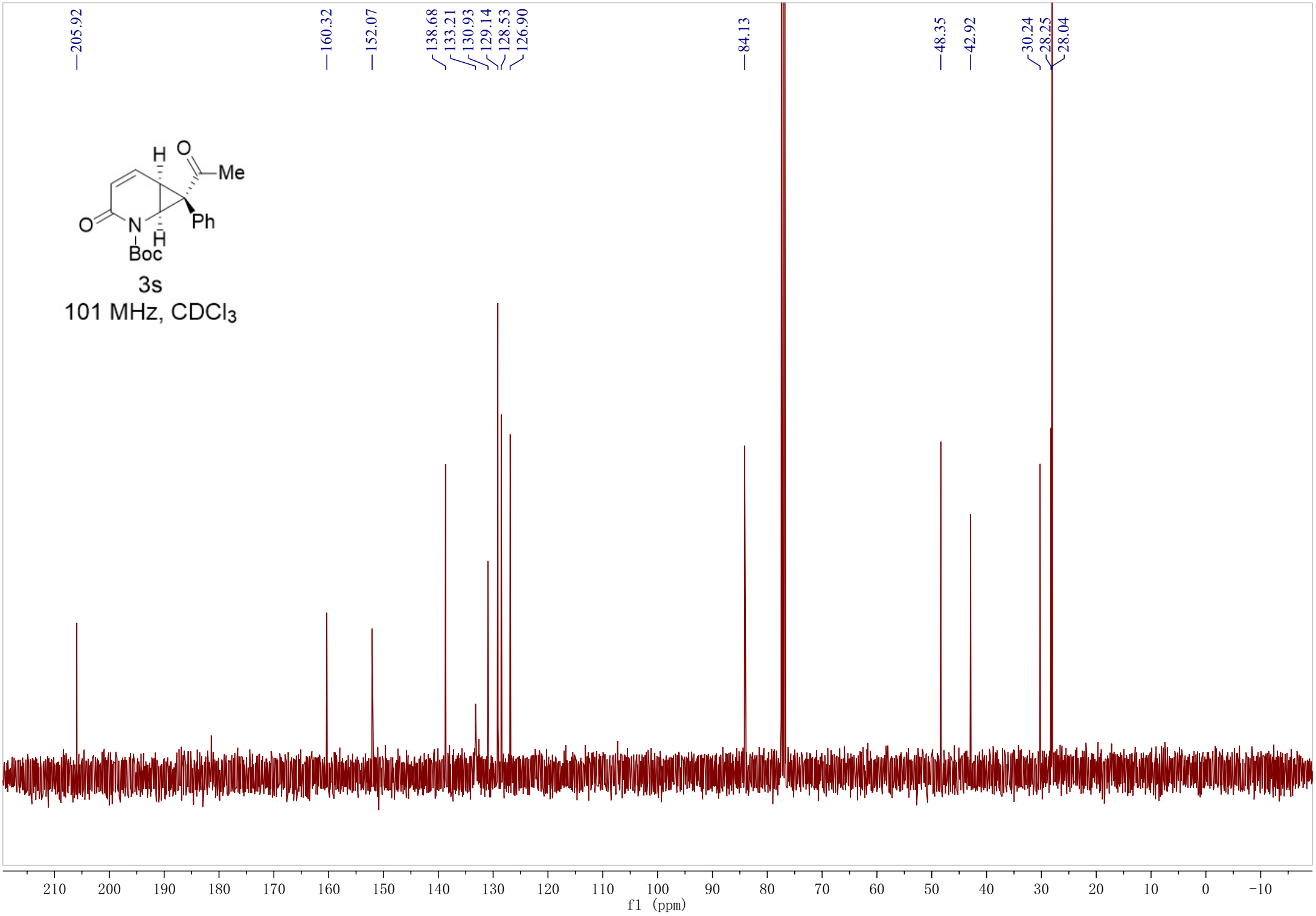

7.4882
7.4876
7.4841
7.4793
7.4675
7.4607
7.4555
7.3317
7.3068
7.2236
7.2182
7.2097
7.2029
7.1974
7.1923
7.1857
7.1773
7.1726
7.1699
7.1354
7.1322
7.1272
7.1244
7.1214
7.1186
7.1097
7.1026
6.7987
6.7960
6.7813
5.7121
5.6794
4.4617
4.4590
4.4326
4.4298
3.2778
3.2603
3.2486
3.2311
1.5947
0.0000
H
O
Ph
O
N
H
Ph
Boc
3r
300 MHz, CDCl3
2.07
1.22
5.03
2.00
1.02
1.01
1.00
1.00
9.03
f1 (ppm)

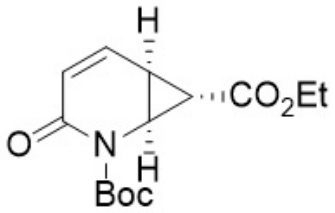

199.62
160.59
151.91
138.71
138.15
133.37
131.63
130.90
128.80
128.59
128.27
127.81
126.96
84.21
48.60
42.37
28.06
27.81
H
O
Ph
O
N
H
Ph
Boc
3r
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3s

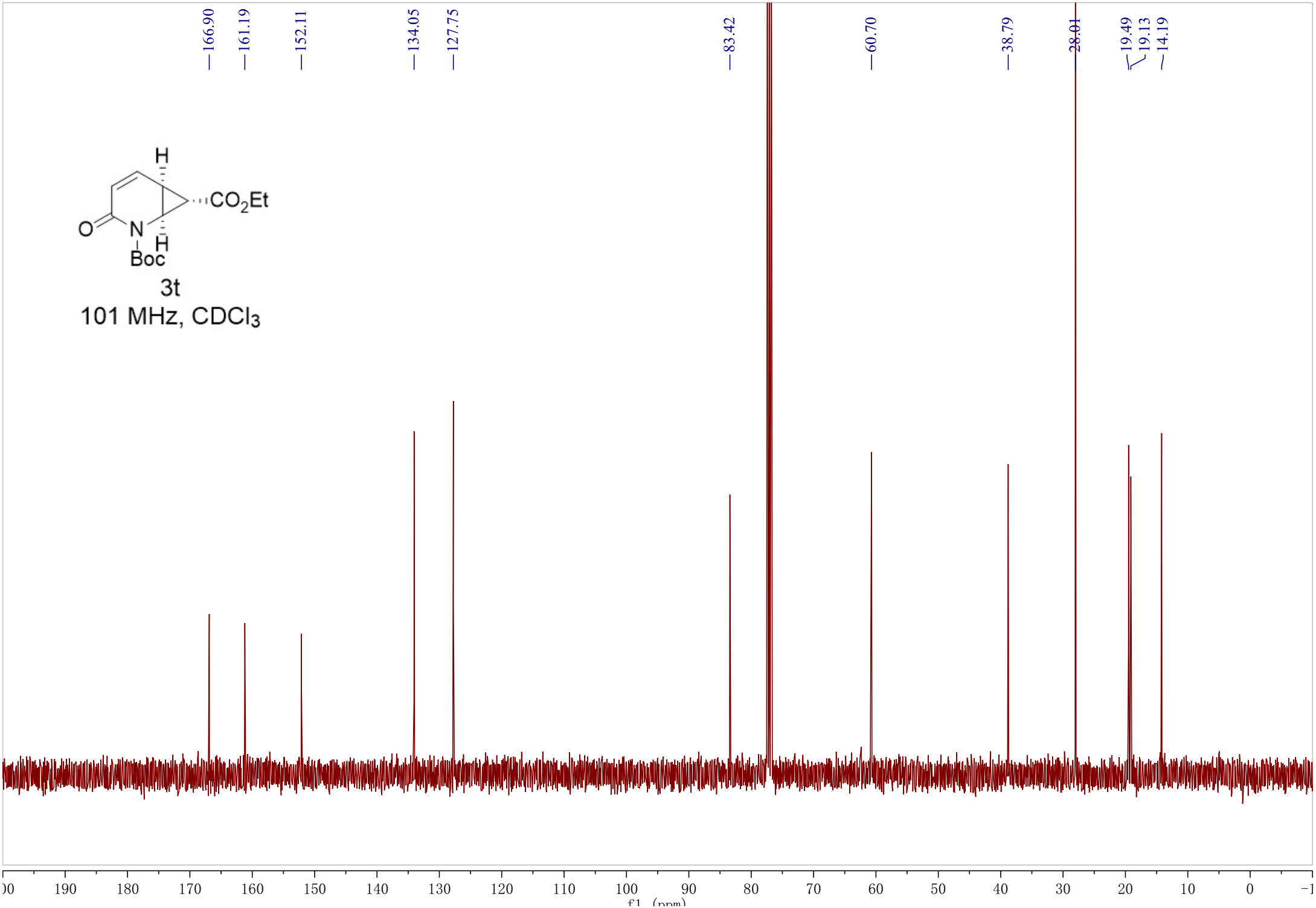
400 MHz, $CDCl_3$

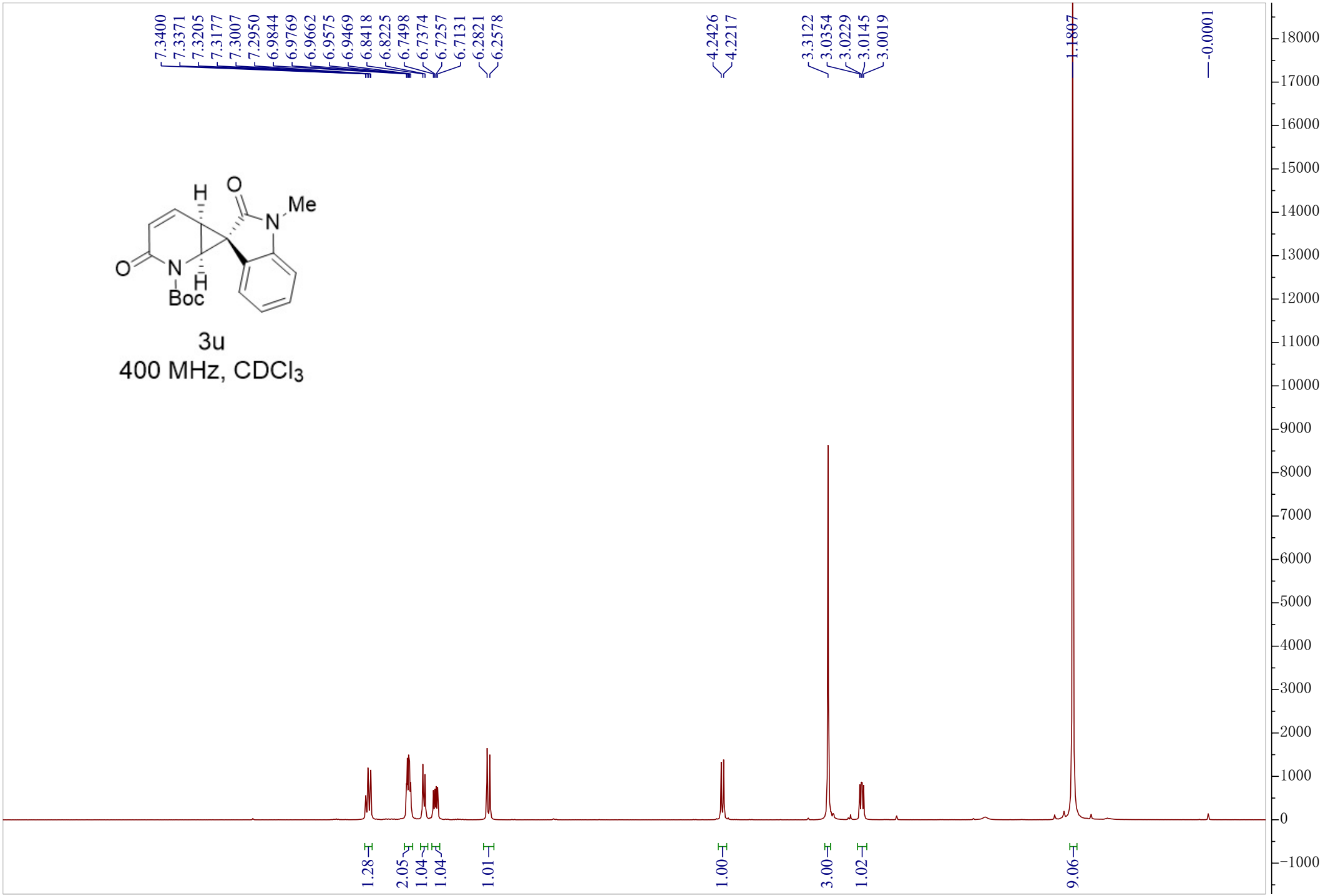

205.92
160.32
152.07
138.68
133.21
130.93
129.14
128.53
126.90
84.13
48.35
42.92
30.24
28.25
28.04
H
O
Me
O
N
H
Ph
Boc
3s
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

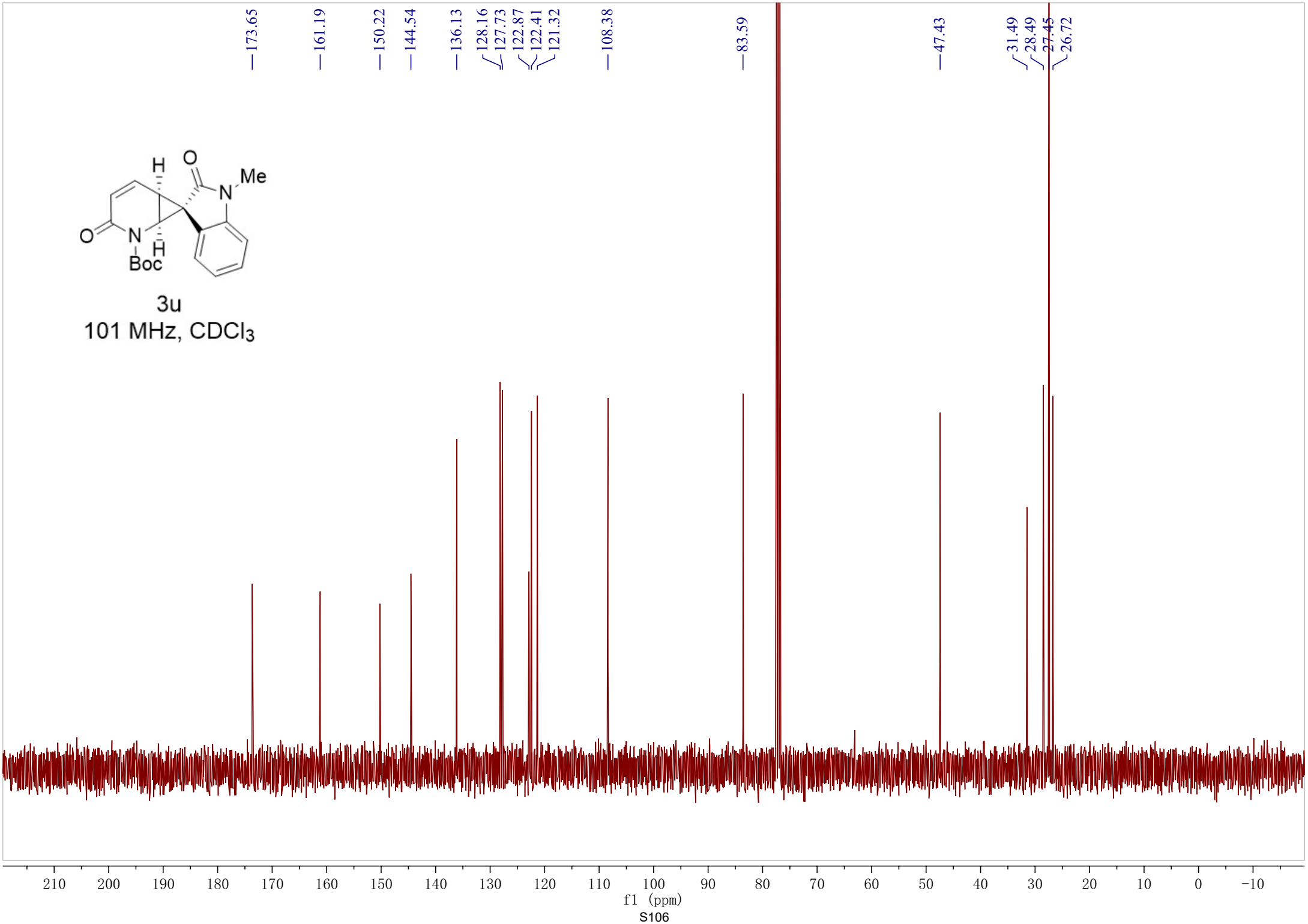


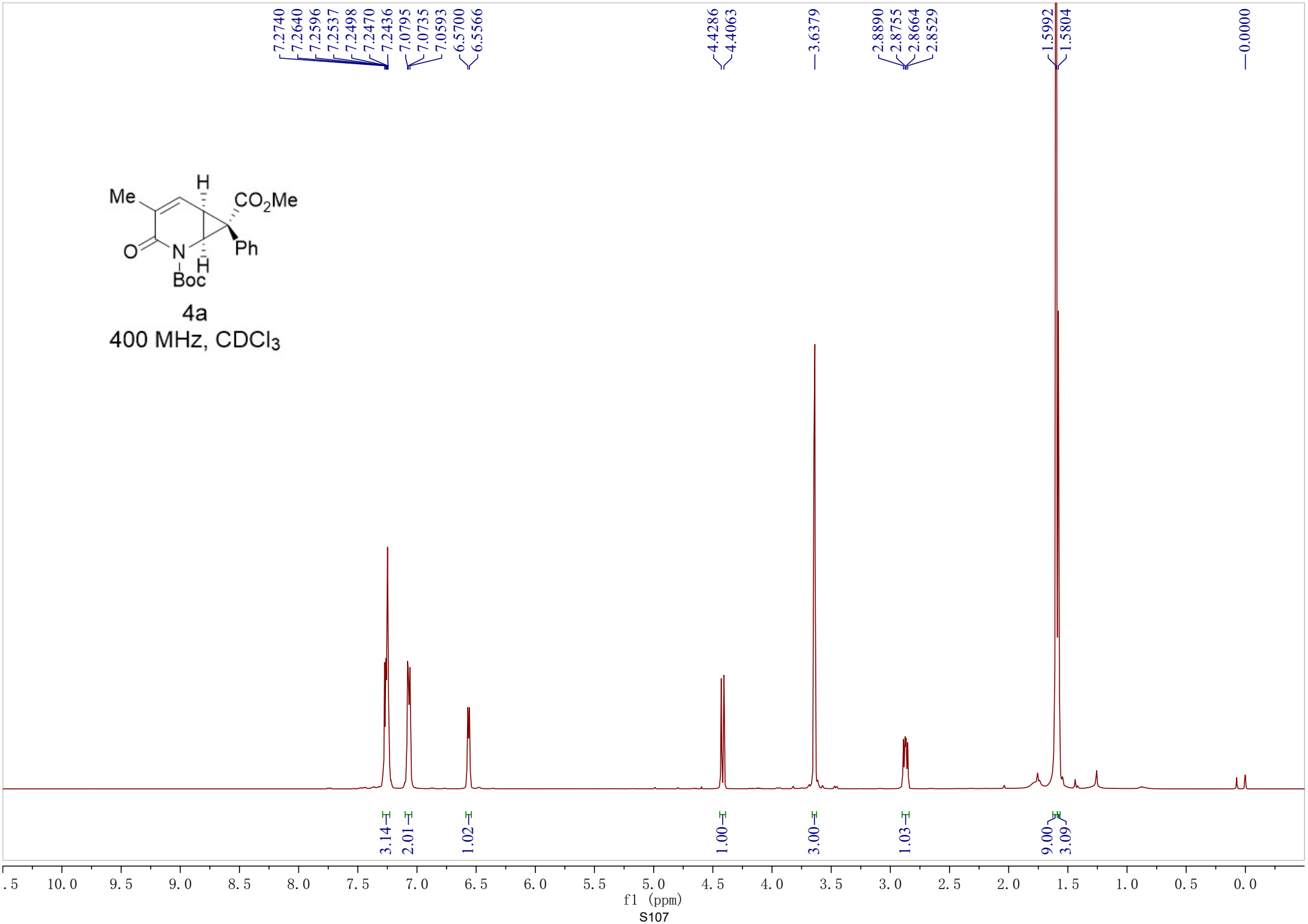
3t

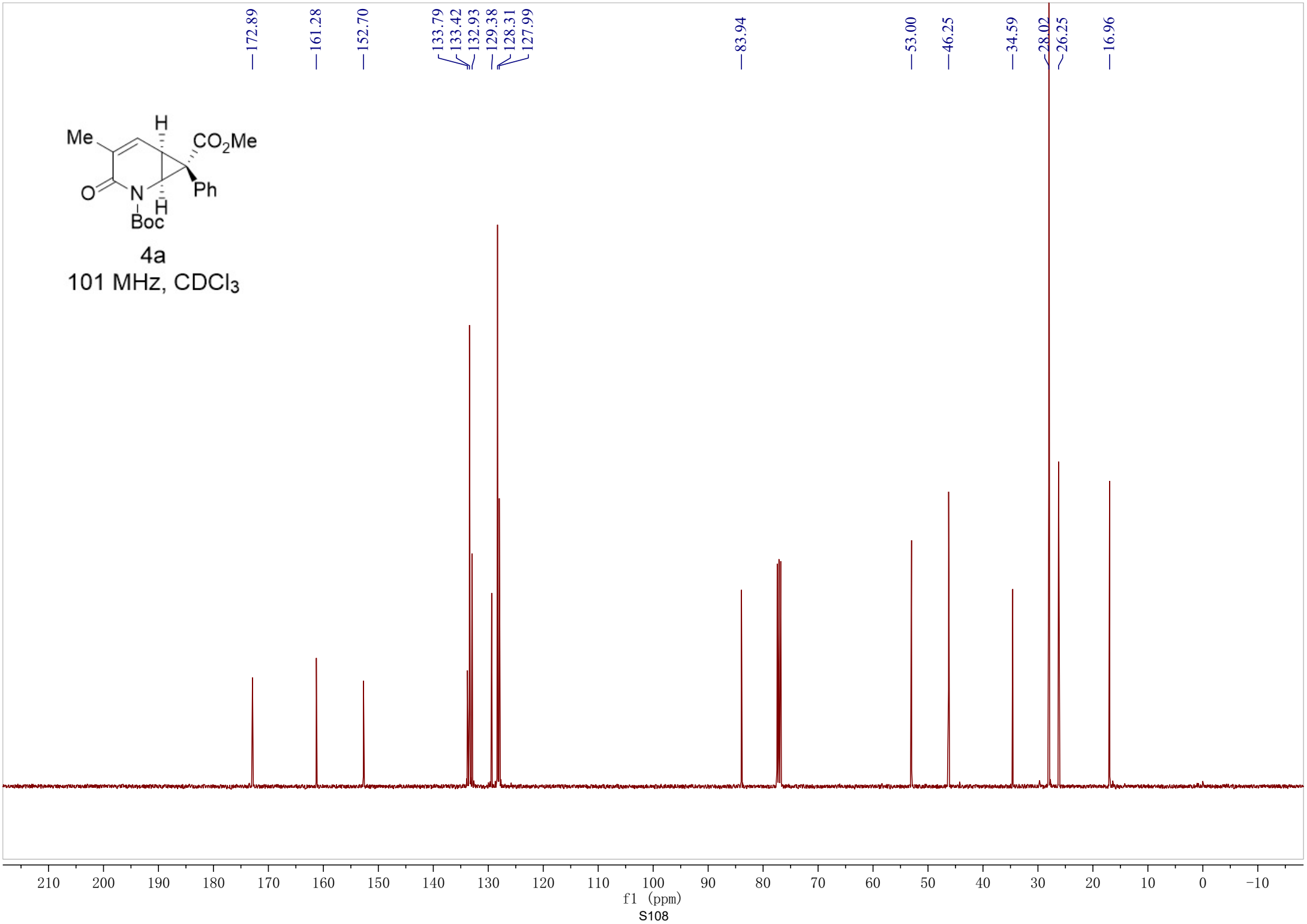
400 MHz, $CDCl_3$

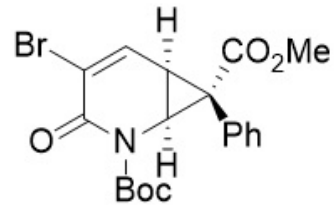

166.90
161.19
152.11
134.05
127.75
83.42
60.70
38.79
28.01
19.49
19.13
14.19
H
CO2Et
O
N
H
Boc
3t
101 MHz, CDCl3
f1 (ppm)


7.3400
7.3371
7.3205
7.3177
7.3007
7.2950
6.9844
6.9769
6.9662
6.9575
6.9469
6.8418
6.8225
6.7498
6.7374
6.7257
6.7131
6.2821
6.2578
4.2426
4.2217
3.3122
3.0354
3.0229
3.0145
3.0019
1.1807
-0.0001
H
O
Me
N
O
N
H
Boc
3u
400 MHz, CDCl3
1.28
2.05
1.04
1.04
1.01
1.00
3.00
1.02
9.06
f1 (ppm)


173.65
161.19
150.22
144.54
136.13
128.16
127.73
122.87
122.41
121.32
108.38
83.59
47.43
31.49
28.49
27.45
26.72
H
O
Me
N
O
N
H
Boc
3u
101 MHz, CDCl3
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)

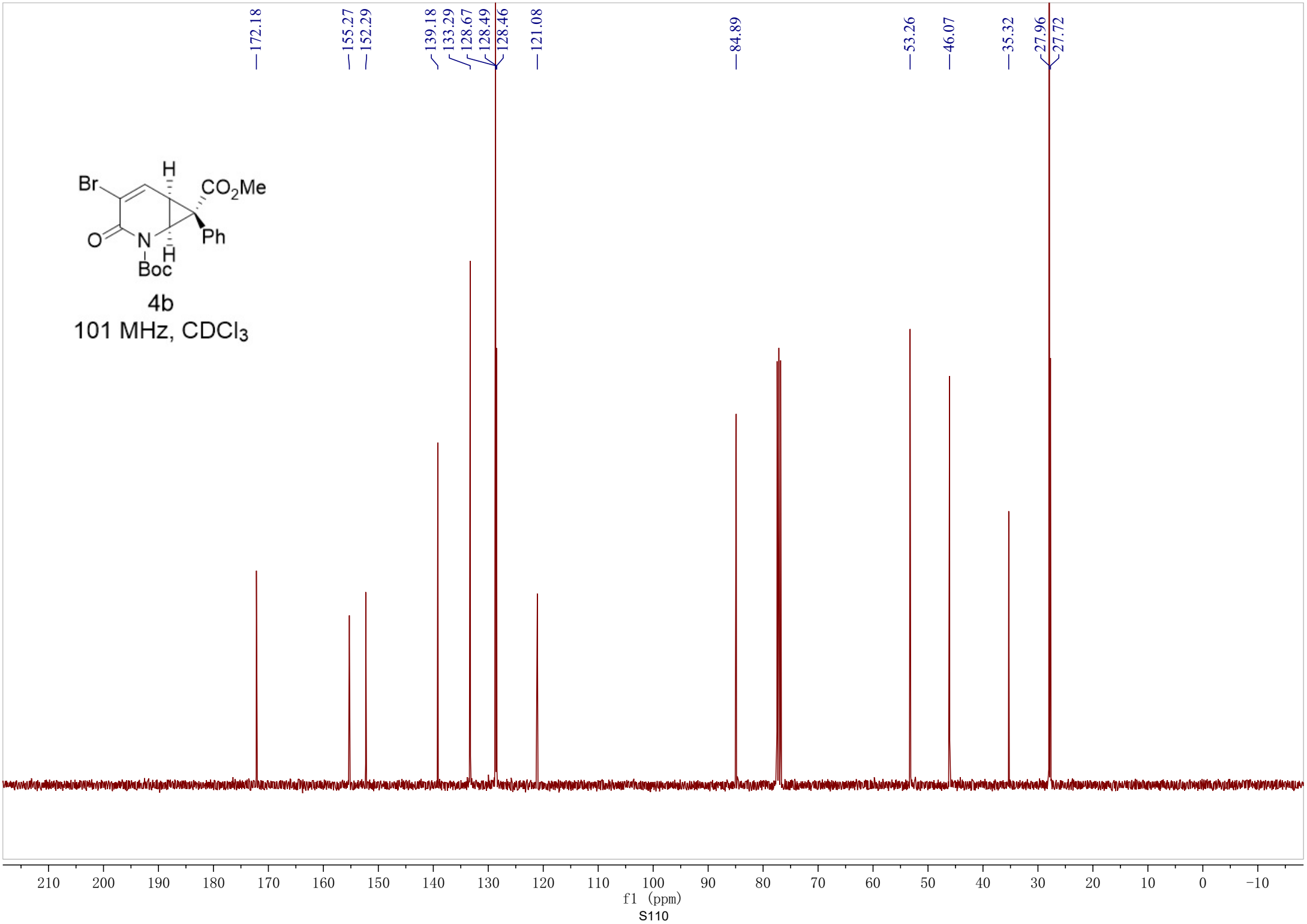

7.2740
7.2640
7.2596
7.2537
7.2498
7.2470
7.2436
7.0795
7.0735
7.0593
6.5700
6.5566
4.4286
4.4063
3.6379
2.8890
2.8755
2.8664
2.8529
1.5992
1.5804
0.0000
Me
H
CO2Me
O
N
H
Ph
Boc
4a
400 MHz, CDCl3
3.14
2.01
1.02
1.00
3.00
1.03
9.00
3.09
f1 (ppm)

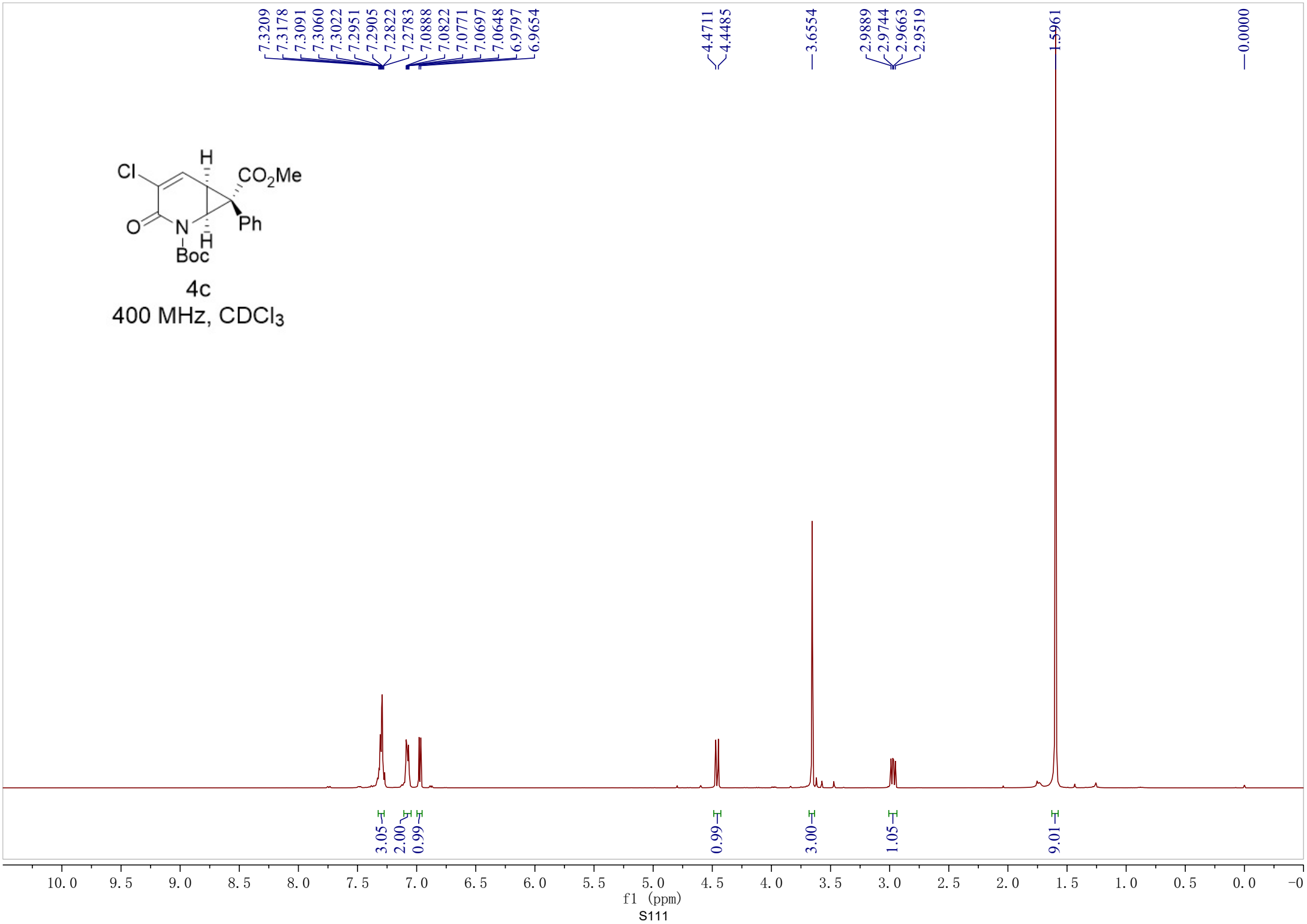

172.89
161.28
152.70
133.79
133.42
132.93
129.38
128.31
127.99
83.94
53.00
46.25
34.59
28.02
26.25
16.96
Me
H
CO2Me
O
N
Ph
H
Boc
4a
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

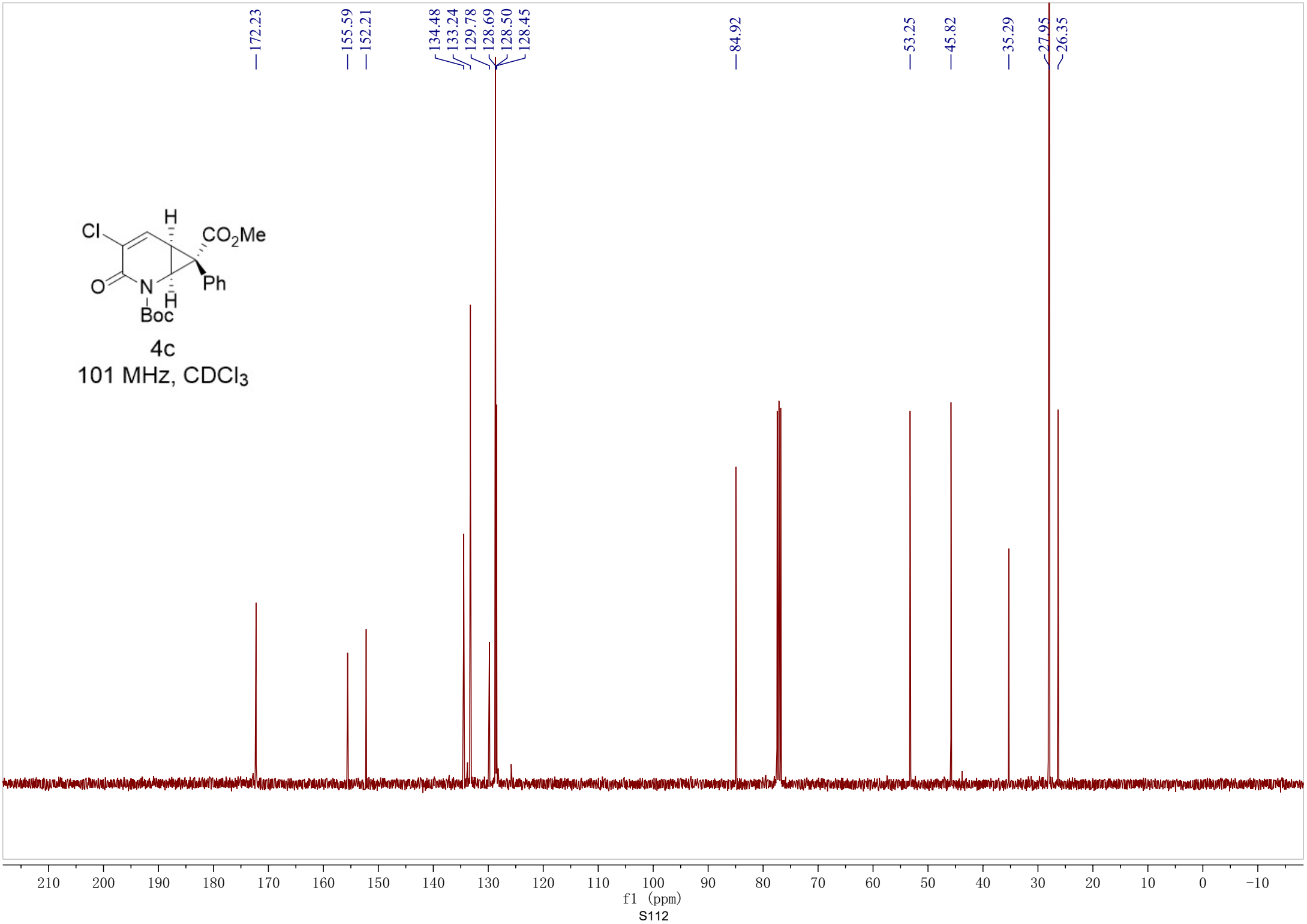


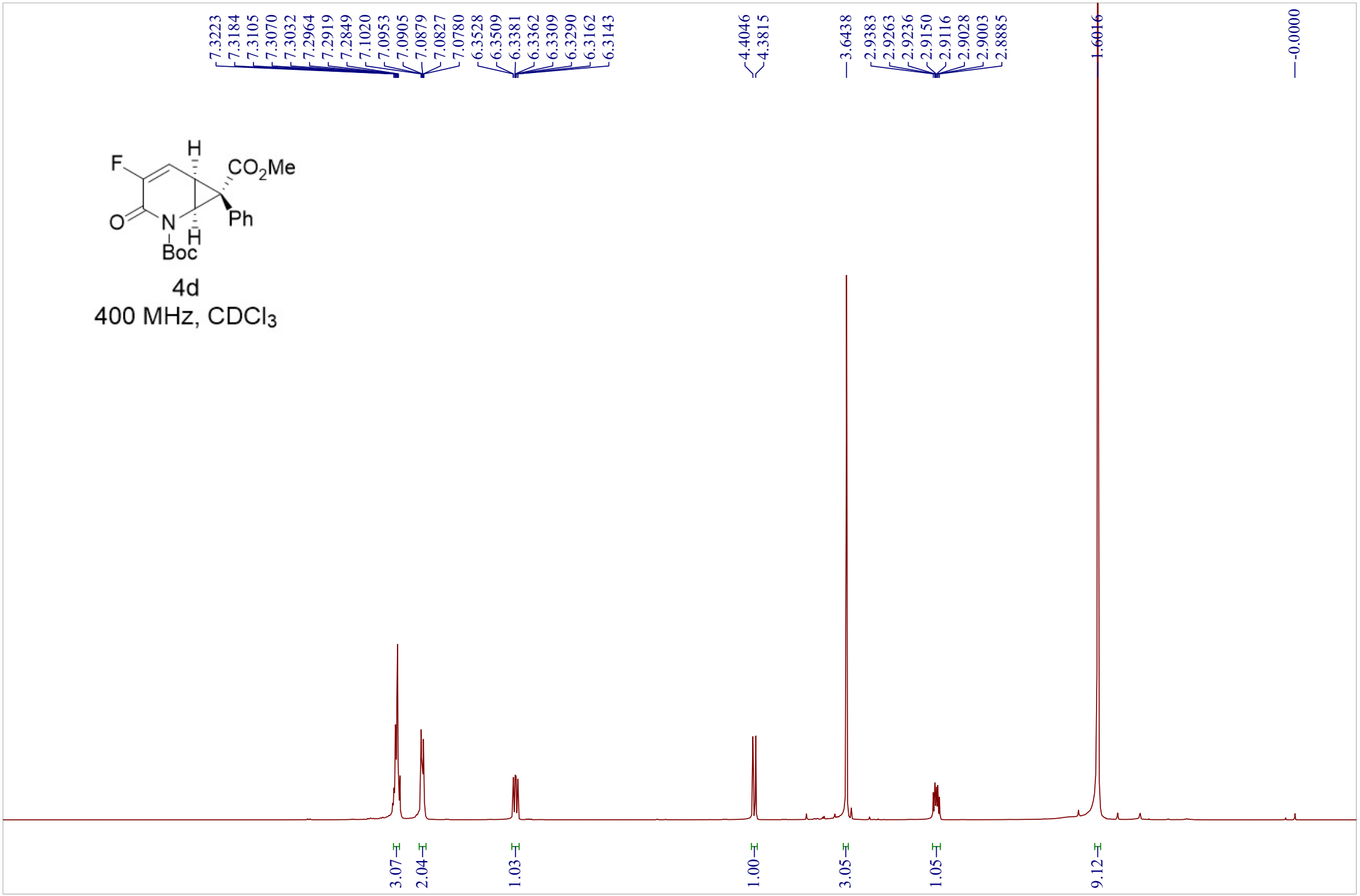
4b

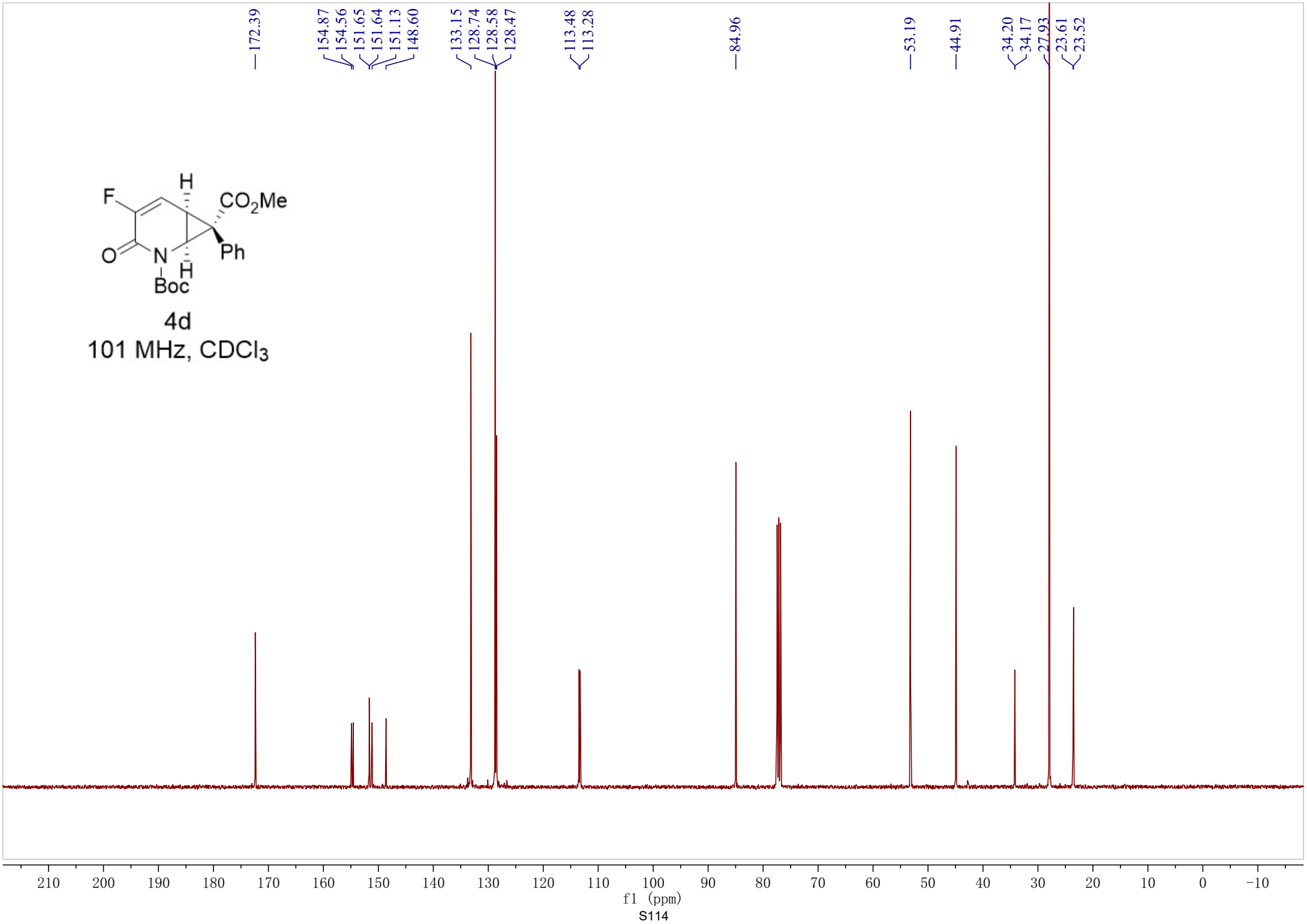
400 MHz, $CDCl_3$

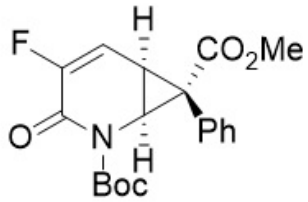

172.18
155.27
152.29
139.18
133.29
128.67
128.49
128.46
121.08
84.89
53.26
46.07
35.32
27.96
27.72
Br
H
CO2Me
O
N
Ph
H
Boc
4b
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


7.3209
7.3178
7.3091
7.3060
7.3022
7.2951
7.2905
7.2822
7.2783
7.0888
7.0822
7.0771
7.0697
7.0648
6.9797
6.9654
4.4711
4.4485
3.6554
2.9889
2.9744
2.9663
2.9519
1.5961
0.0000
Cl
H
CO2Me
O
N
Ph
H
Boc
4c
400 MHz, CDCl3
3.05
2.00
0.99
0.99
3.00
1.05
9.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.23
155.59
152.21
134.48
133.24
129.78
128.69
128.50
128.45
84.92
53.25
45.82
35.29
27.95
26.35
Cl
H
CO2Me
O
N
Ph
H
Boc
4c
101 MHz, CDCl3
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)

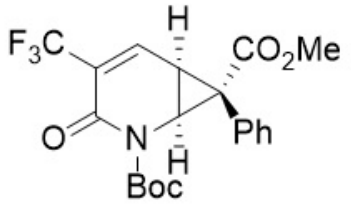

7.3223
7.3184
7.3105
7.3070
7.3032
7.2964
7.2919
7.2849
7.1020
7.0953
7.0905
7.0879
7.0827
7.0780
6.3528
6.3509
6.3381
6.3362
6.3309
6.3290
6.3162
6.3143
4.4046
4.3815
3.6438
2.9383
2.9263
2.9236
2.9150
2.9116
2.9028
2.9003
2.8885
1.6016
-0.0000
F
H
CO2Me
O
N
Ph
H
Boc
4d
400 MHz, CDCl3
3.07
2.04
1.03
1.00
3.05
1.05
9.12
f1 (ppm)


172.39
154.87
154.56
151.65
151.64
151.13
148.60
133.15
128.74
128.58
128.47
113.48
113.28
84.96
53.19
44.91
34.20
34.17
27.93
23.61
23.52
F
H
CO2Me
O
N
Ph
H
Boc
4d
101 MHz, CDCl3
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)



4d

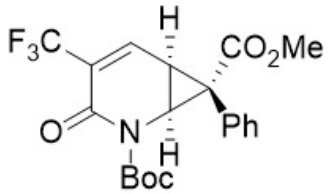
376 MHz, $CDCl_3$



4e

300 MHz, $CDCl_3$

3dkai.782.fid
sjh-04-717 13c cdcl3

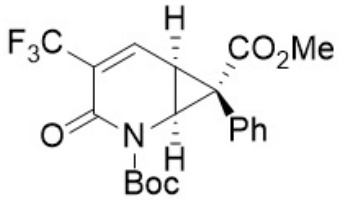


4e
75 MHz, $CDCl_3$

171.86
155.34
152.15
141.29
141.21
141.14
141.07
133.08
128.78
128.72
127.80
127.71
127.30
126.90
126.50
126.08
122.46
118.84
115.23
85.08
53.43
45.86
36.92
27.94
24.78

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)

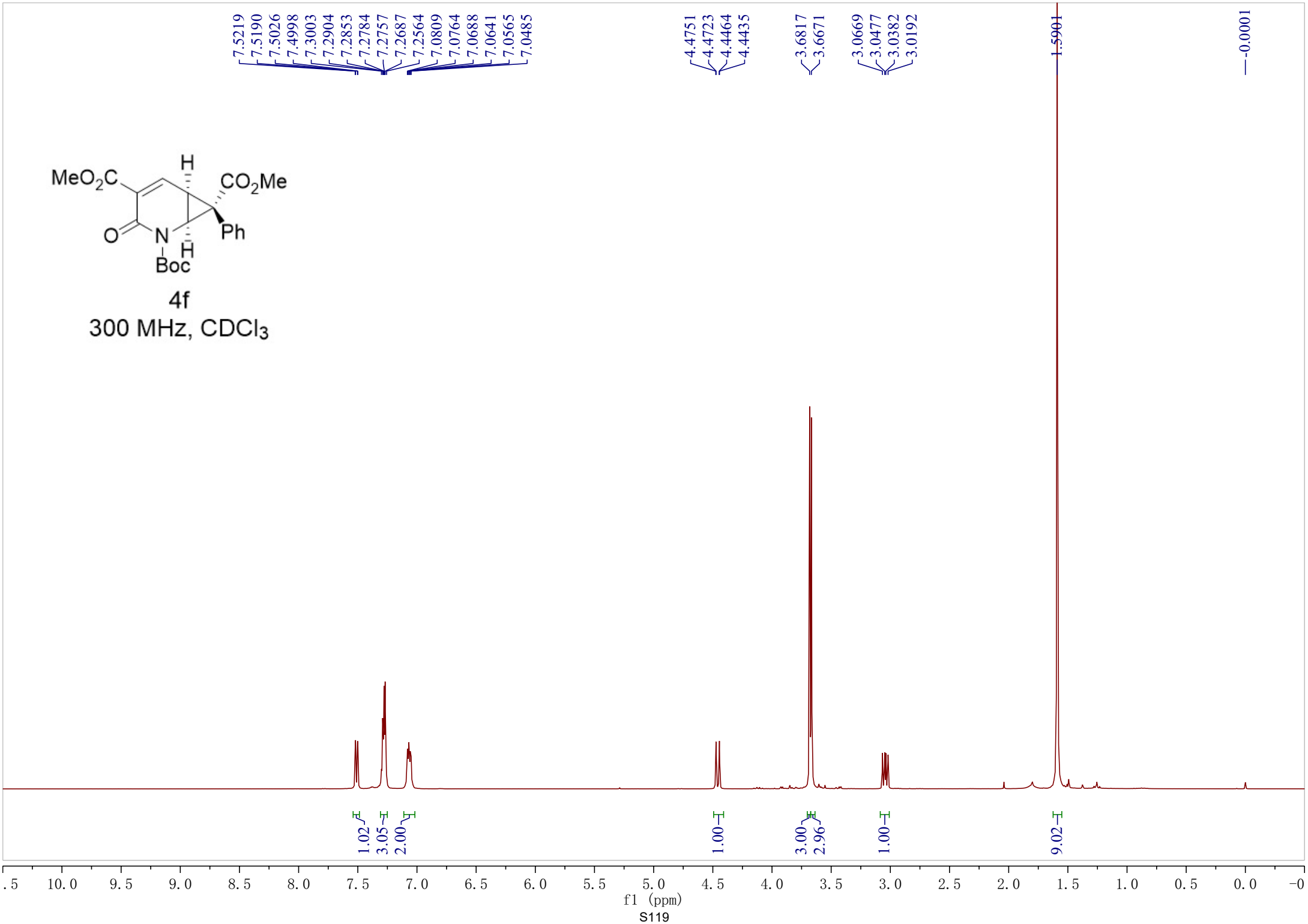
3dkai.781.fid
sjh-04-717 19f cdcl3

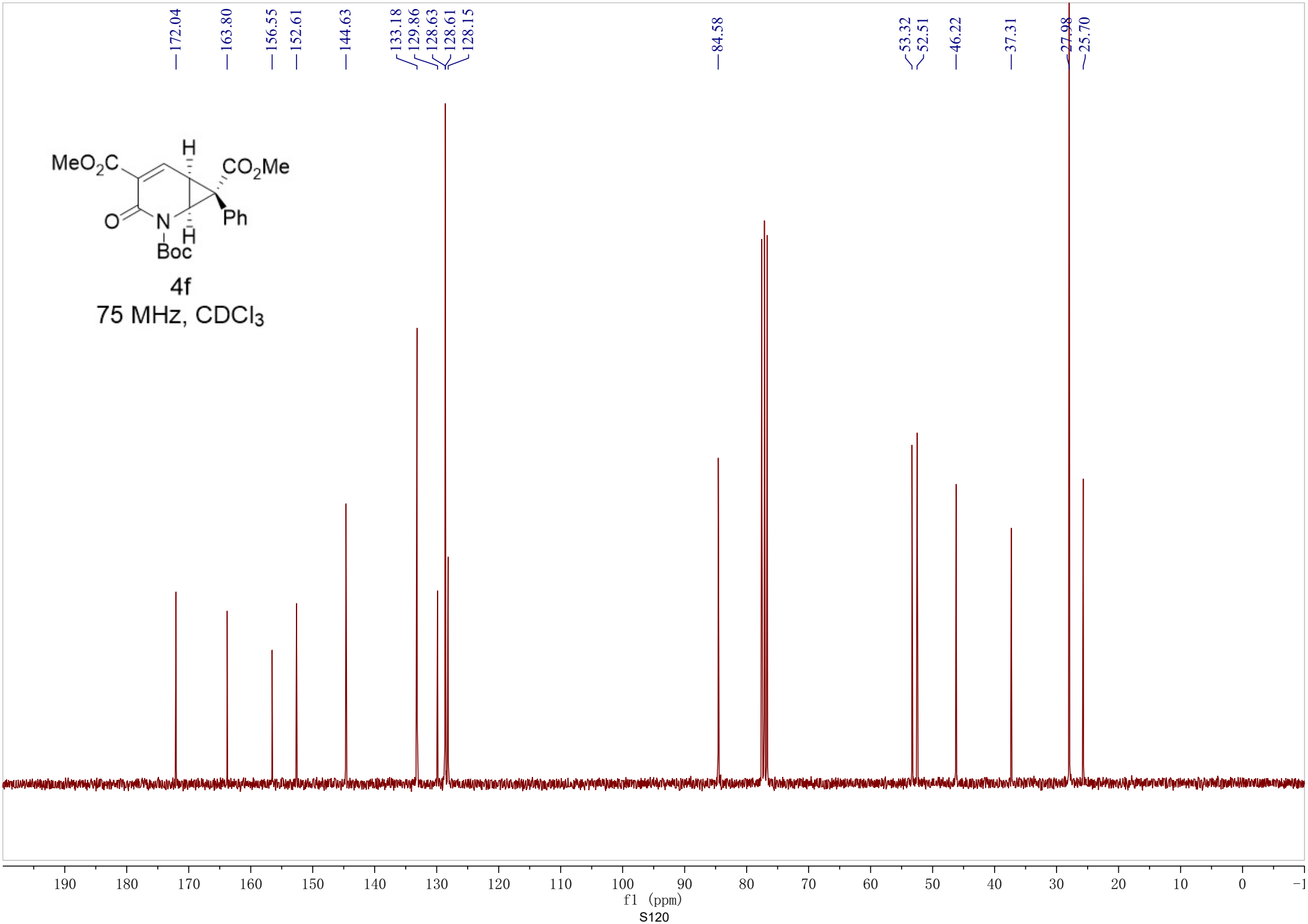


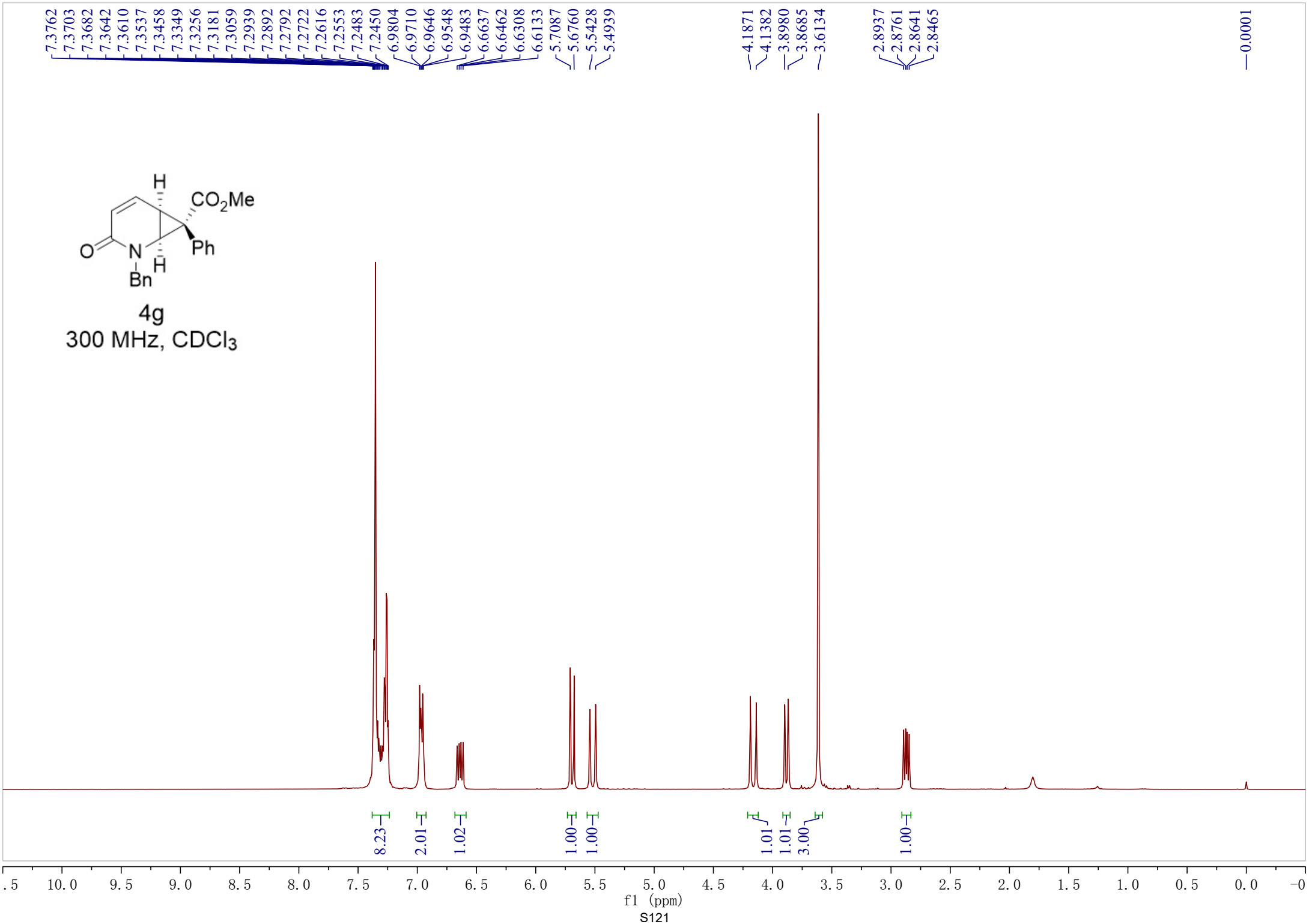
4e
282 MHz, $CDCl_3$

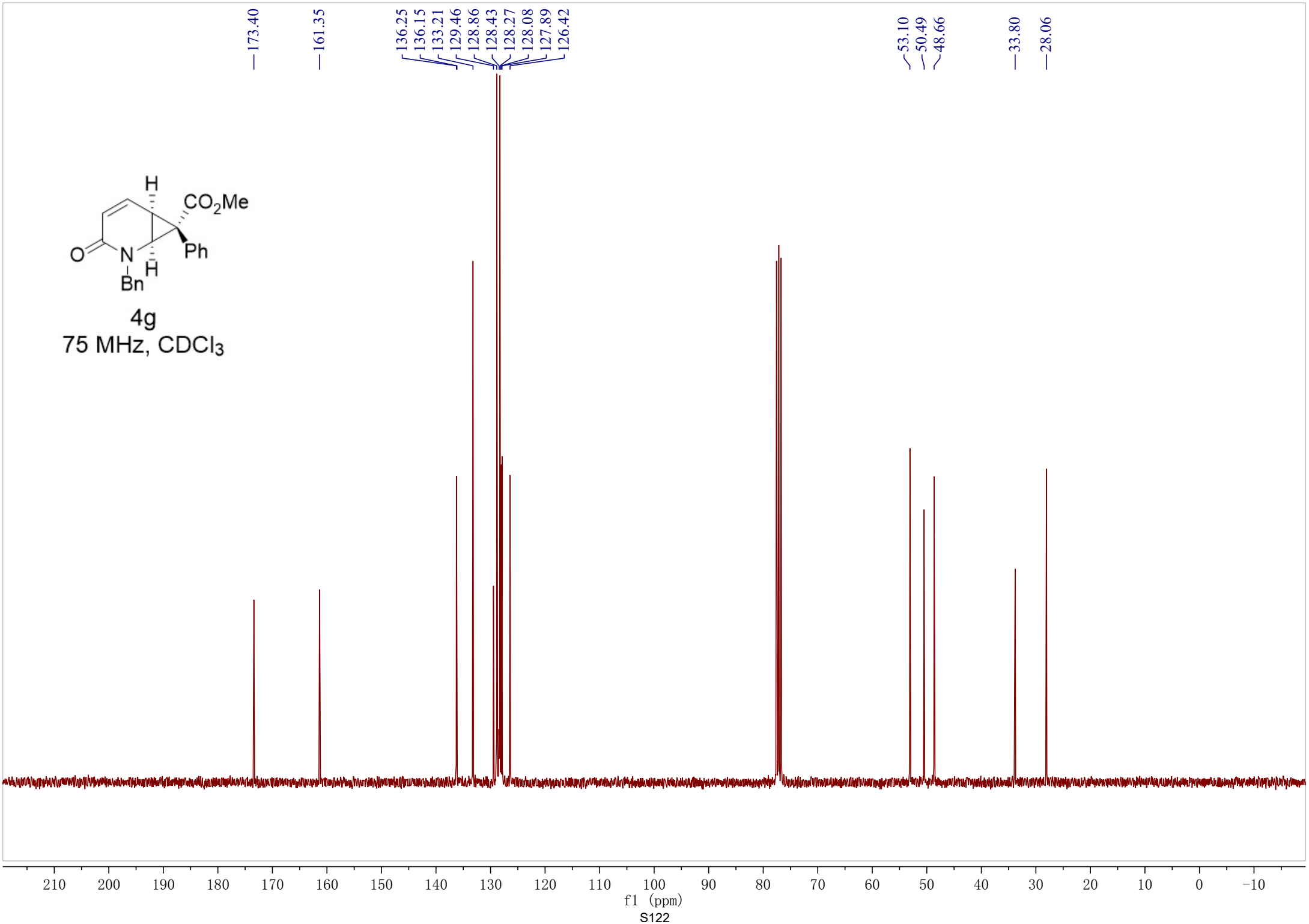
-65.78

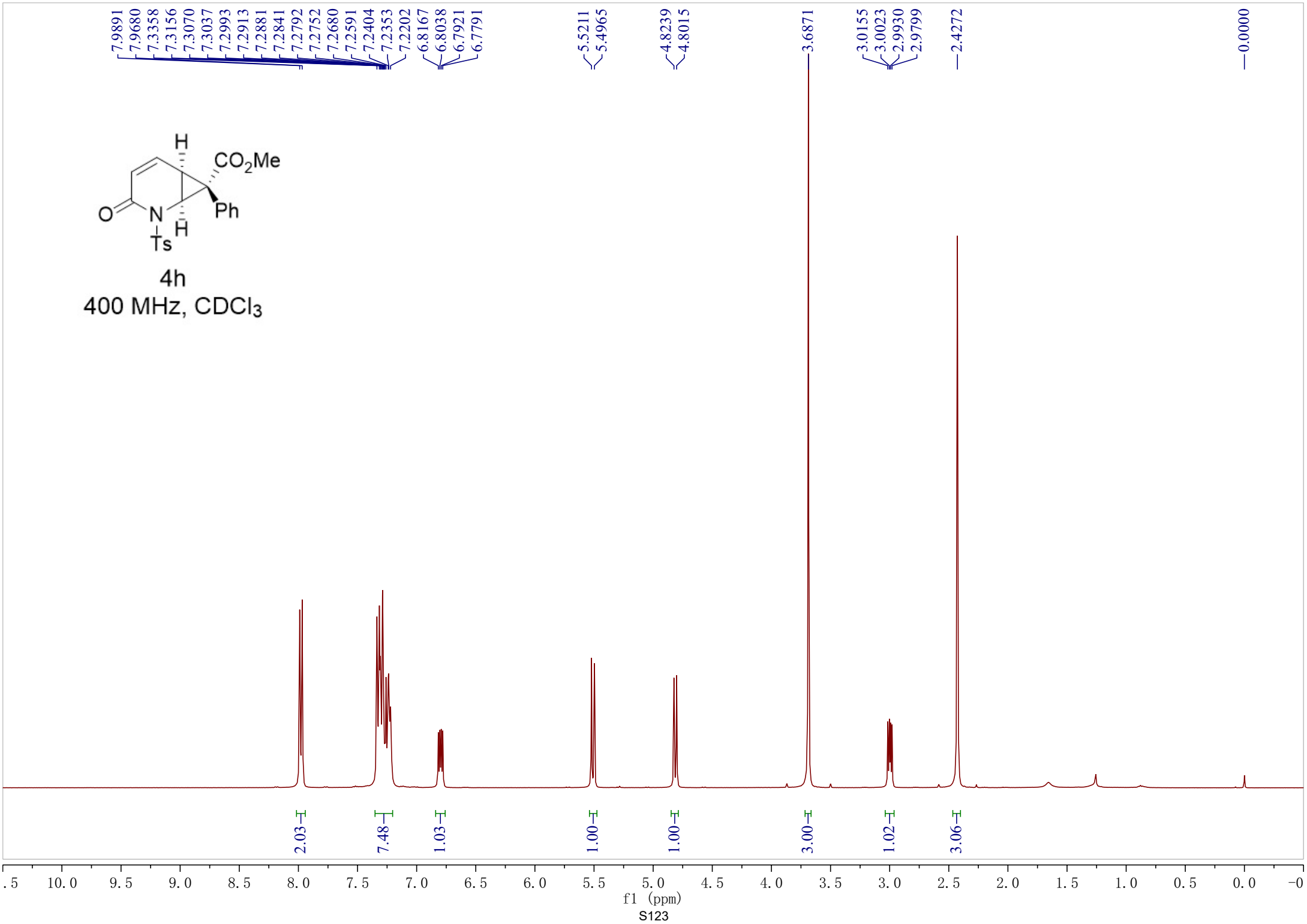
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

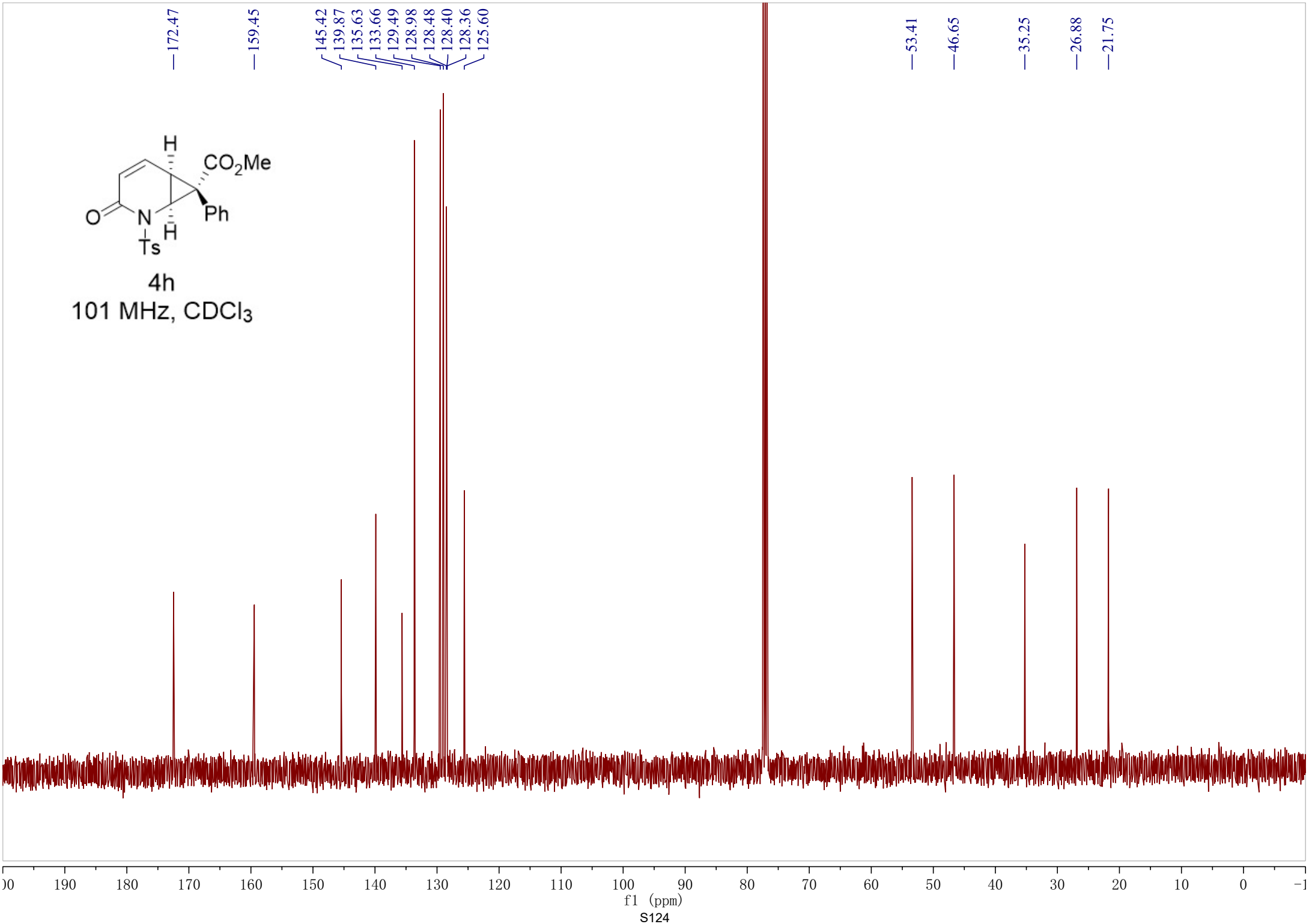

7.5219
7.5190
7.5026
7.4998
7.3003
7.2904
7.2853
7.2784
7.2757
7.2687
7.2564
7.0809
7.0764
7.0688
7.0641
7.0565
7.0485
4.4751
4.4723
4.4464
4.4435
3.6817
3.6671
3.0669
3.0477
3.0382
3.0192
1.5901
-0.0001
MeO2C
CO2Me
Ph
O
N
H
H
Boc
4f
300 MHz, CDCl3
1.02
3.05
2.00
1.00
3.00
2.96
1.00
9.02
f1 (ppm)

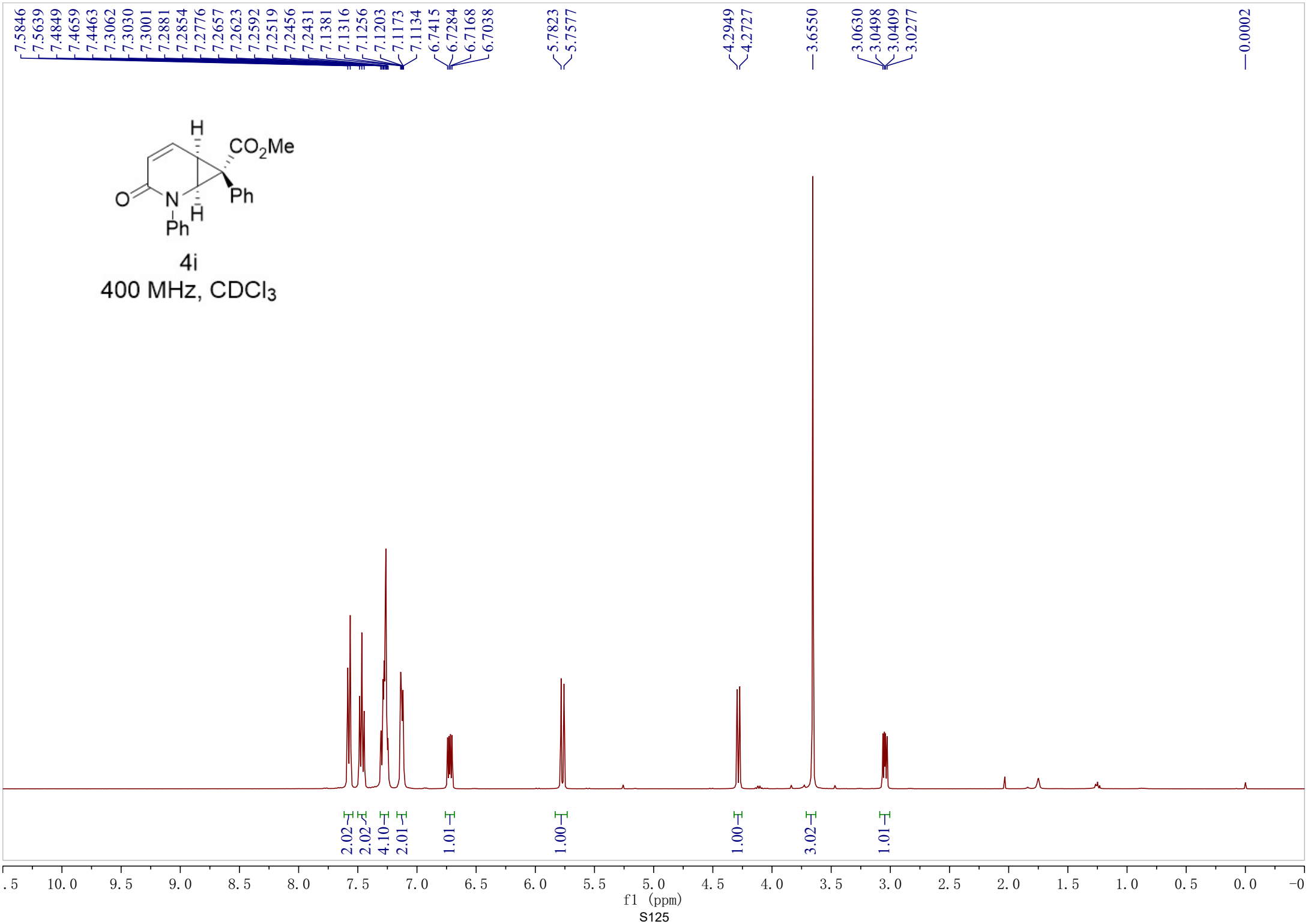

172.04
163.80
156.55
152.61
144.63
133.18
129.86
128.63
128.61
128.15
84.58
53.32
52.51
46.22
37.31
27.98
25.70
MeO2C
CO2Me
H
O
N
H
Boc
Ph
4f
75 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

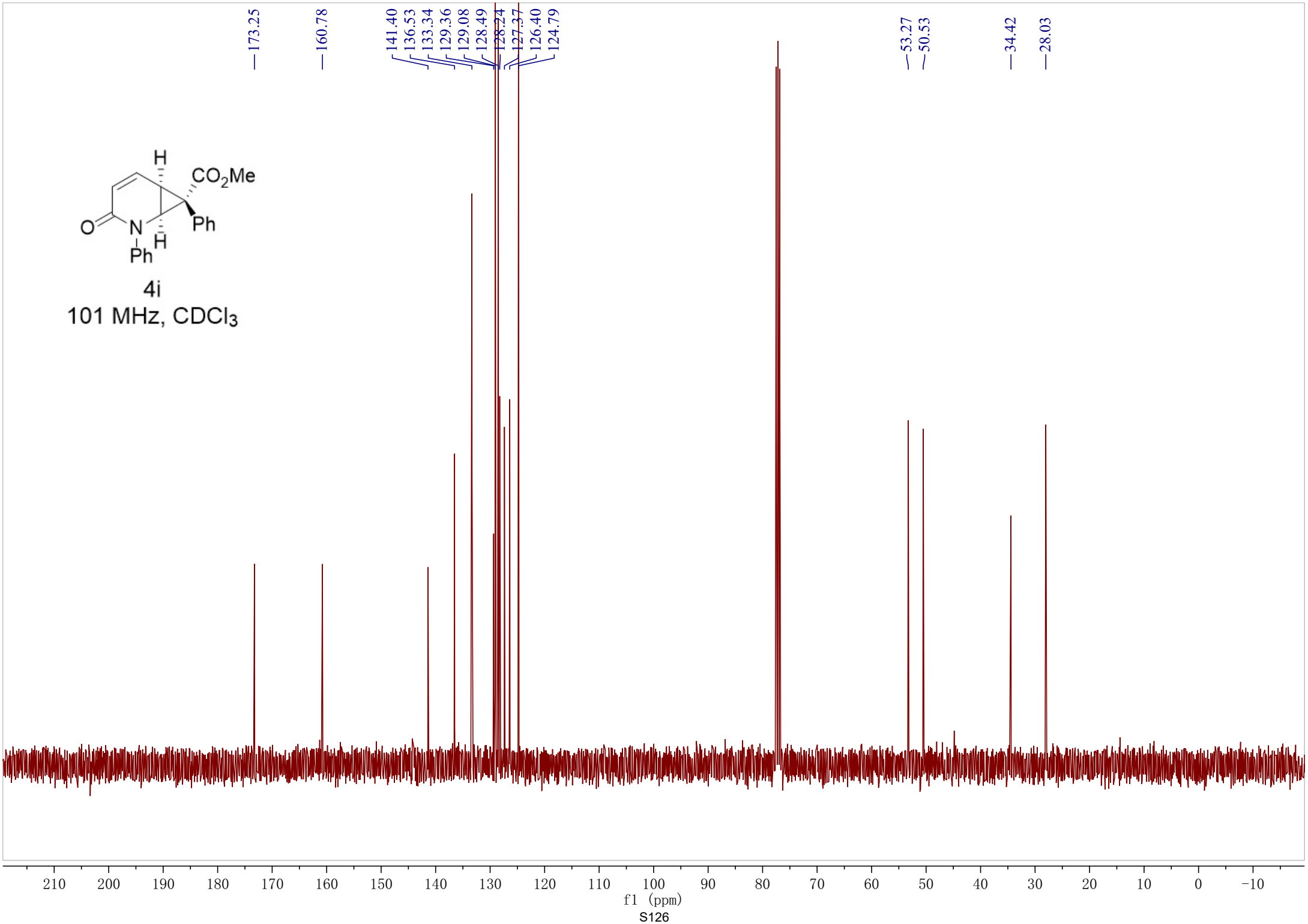

7.3762
7.3703
7.3682
7.3642
7.3610
7.3537
7.3458
7.3349
7.3256
7.3181
7.3059
7.2939
7.2892
7.2792
7.2722
7.2616
7.2553
7.2483
7.2450
6.9804
6.9710
6.9646
6.9548
6.9483
6.6637
6.6462
6.6308
6.6133
5.7087
5.6760
5.5428
5.4939
4.1871
4.1382
3.8980
3.8685
3.6134
2.8937
2.8761
2.8641
2.8465
0.0001
H
CO2Me
O
N
Ph
Bn
H
4g
300 MHz, CDCl3
8.23
2.01
1.02
1.00
1.00
1.01
1.01
3.00
1.00
f1 (ppm)

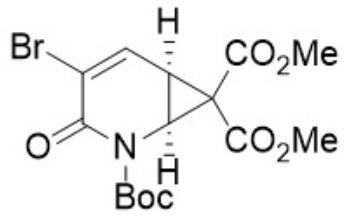

173.40
161.35
136.25
136.15
133.21
129.46
128.86
128.43
128.27
128.08
127.89
126.42
53.10
50.49
48.66
33.80
28.06
H
CO2Me
O
N
H
Ph
Bn
4g
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.9891
7.9680
7.3358
7.3156
7.3070
7.3037
7.2993
7.2913
7.2881
7.2841
7.2792
7.2752
7.2680
7.2591
7.2404
7.2353
7.2202
6.8167
6.8038
6.7921
6.7791
5.5211
5.4965
4.8239
4.8015
3.6871
3.0155
3.0023
2.9930
2.9799
2.4272
0.0000
H
CO2Me
O
N
Ph
H
Ts
4h
400 MHz, CDCl3
2.03
7.48
1.03
1.00
1.00
3.00
1.02
3.06
f1 (ppm)


172.47
159.45
145.42
139.87
135.63
133.66
129.49
128.98
128.48
128.40
128.36
125.60
53.41
46.65
35.25
26.88
21.75
H
CO2Me
O
N
H
Ph
Ts
4h
101 MHz, CDCl3
f1 (ppm)

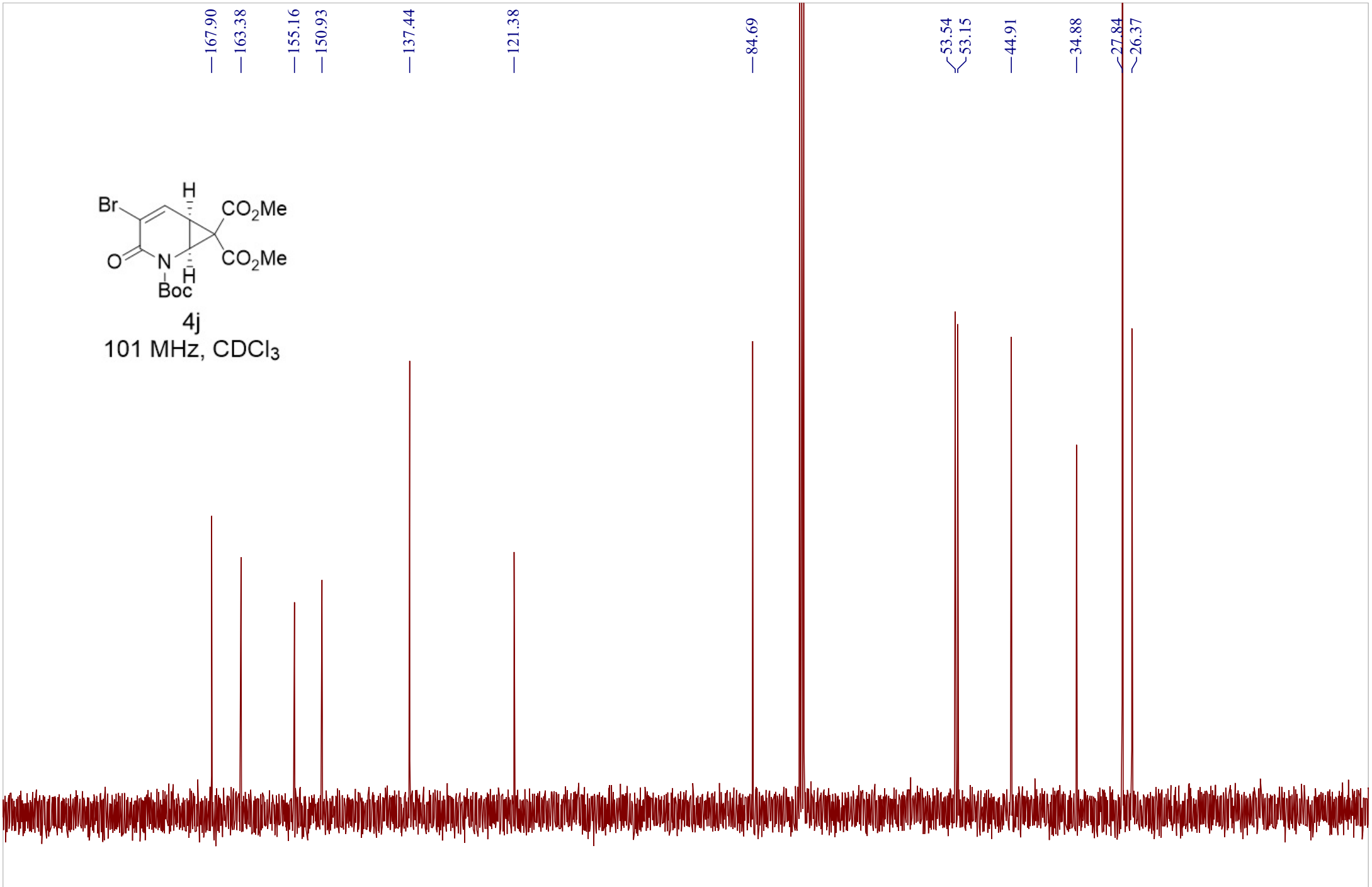

7.5846
7.5639
7.4849
7.4659
7.4463
7.3062
7.3030
7.3001
7.2881
7.2854
7.2776
7.2657
7.2623
7.2592
7.2519
7.2456
7.2431
7.1381
7.1316
7.1256
7.1203
7.1173
7.1134
6.7415
6.7284
6.7168
6.7038
5.7823
5.7577
4.2949
4.2727
3.6550
3.0630
3.0498
3.0409
3.0277
0.0002
H
CO2Me
O
N
Ph
H
Ph
4i
400 MHz, CDCl3
2.02
2.02
4.10
2.01
1.01
1.00
1.00
3.02
1.01
f1 (ppm)

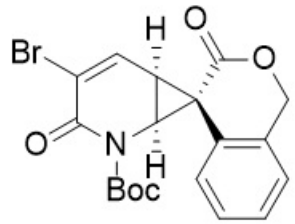

173.25
160.78
141.40
136.53
133.34
129.36
129.08
128.49
128.24
127.37
126.40
124.79
53.27
50.53
34.42
28.03
H
CO2Me
O
N
Ph
H
Ph
4i
101 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4j

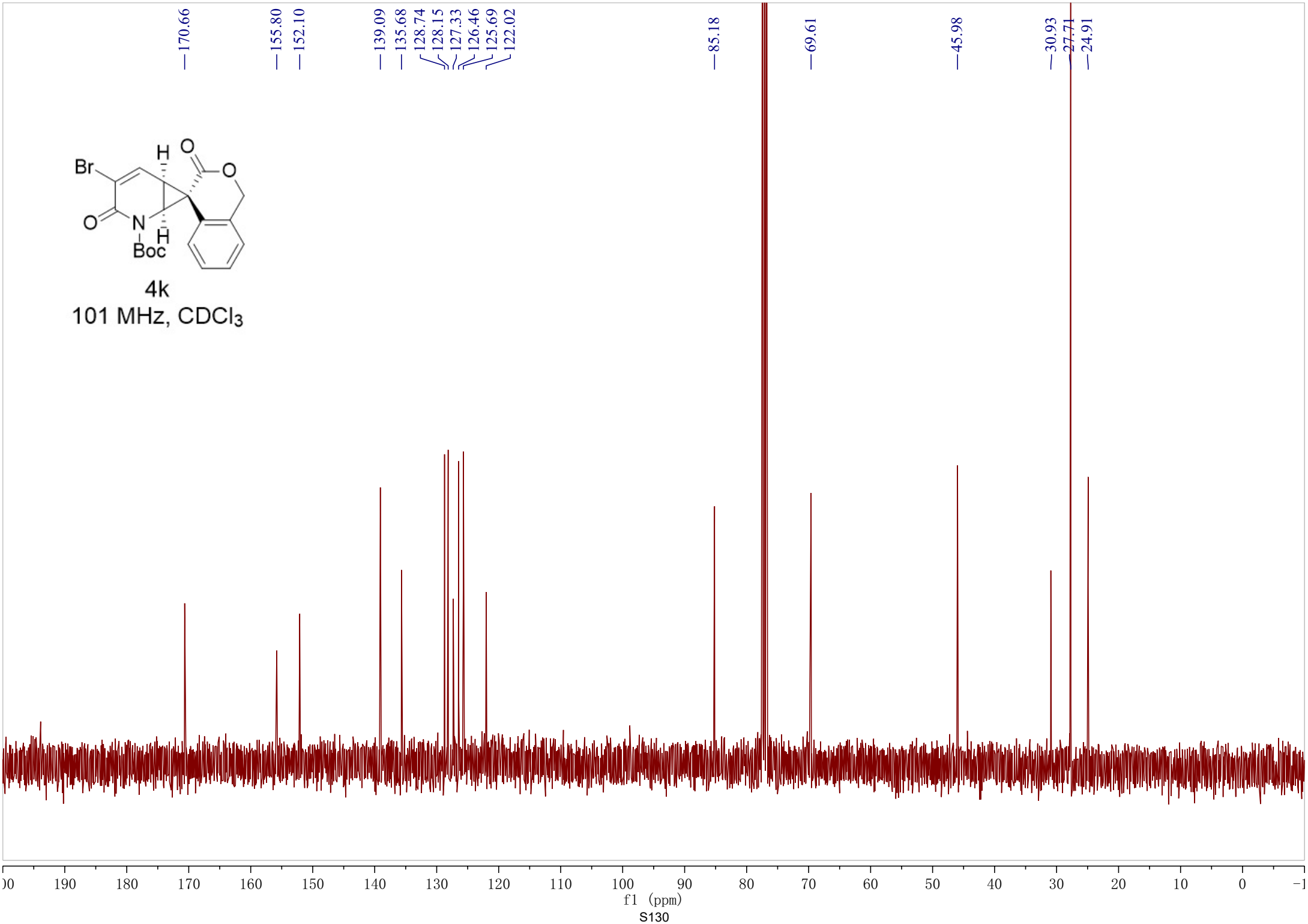
400 MHz, $CDCl_3$

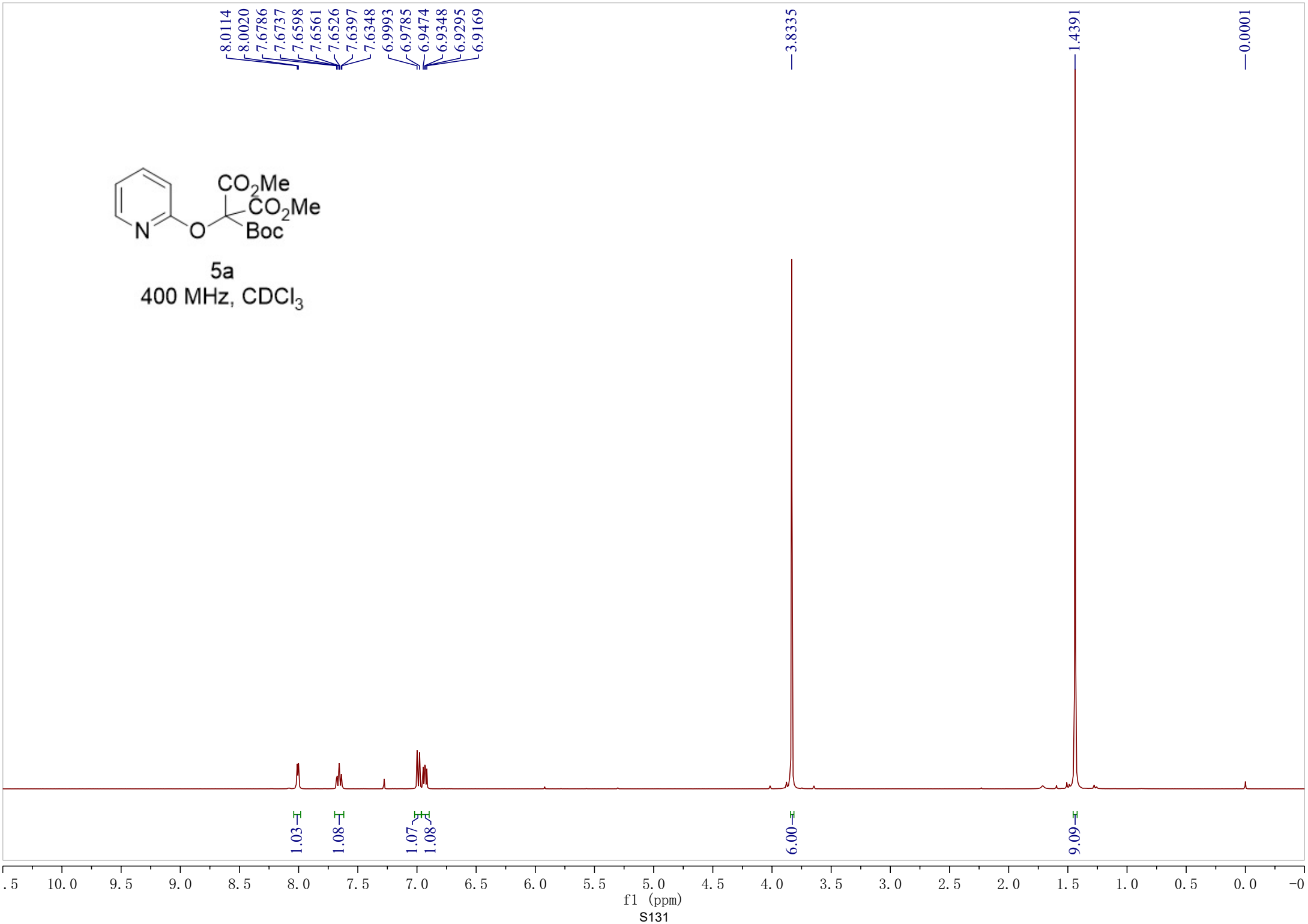

167.90
163.38
155.16
150.93
137.44
121.38
84.69
53.54
53.15
44.91
34.88
27.84
26.37
Br
H
CO2Me
CO2Me
O
N
H
Boc
4j
101 MHz, CDCl3
f1 (ppm)

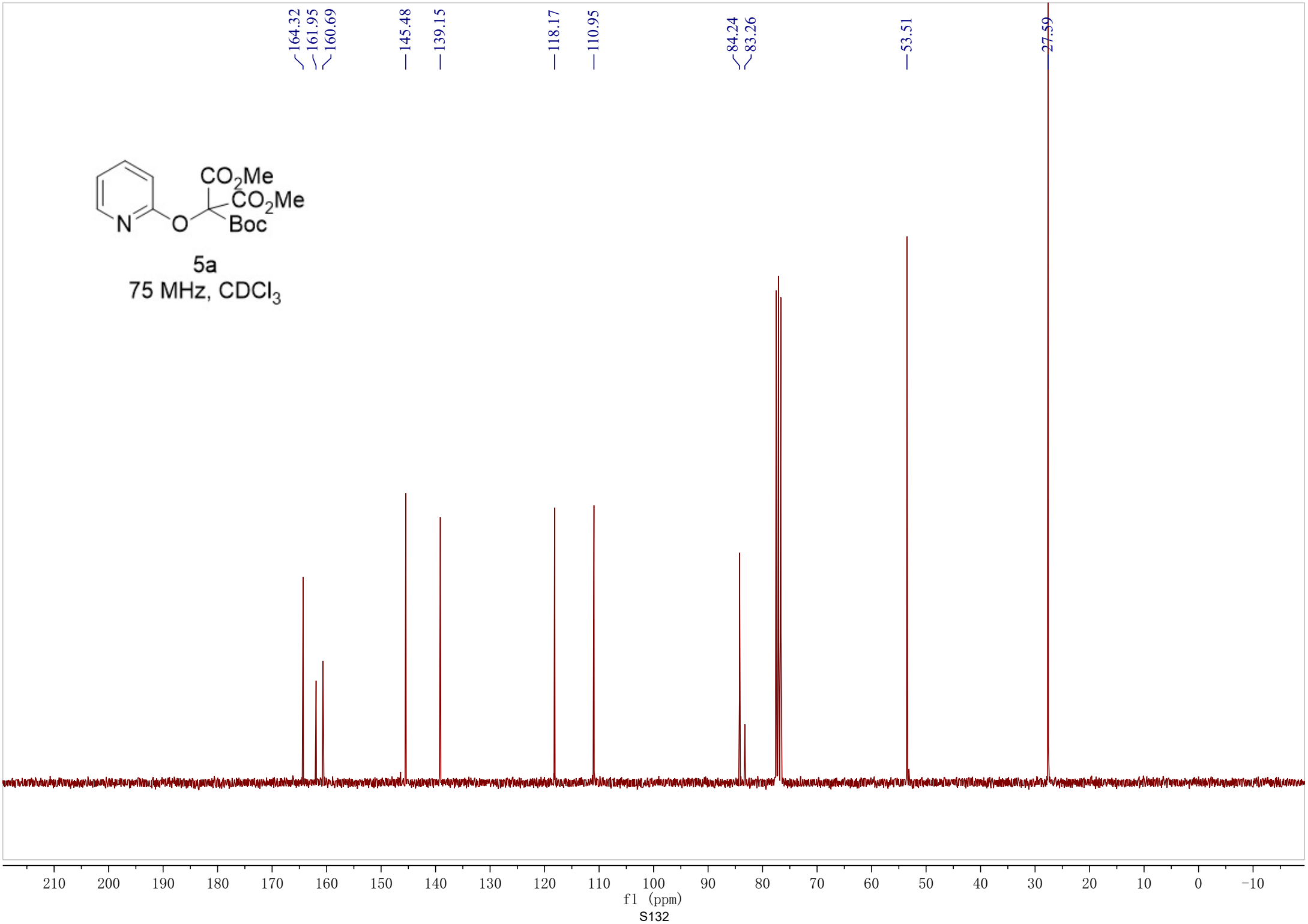


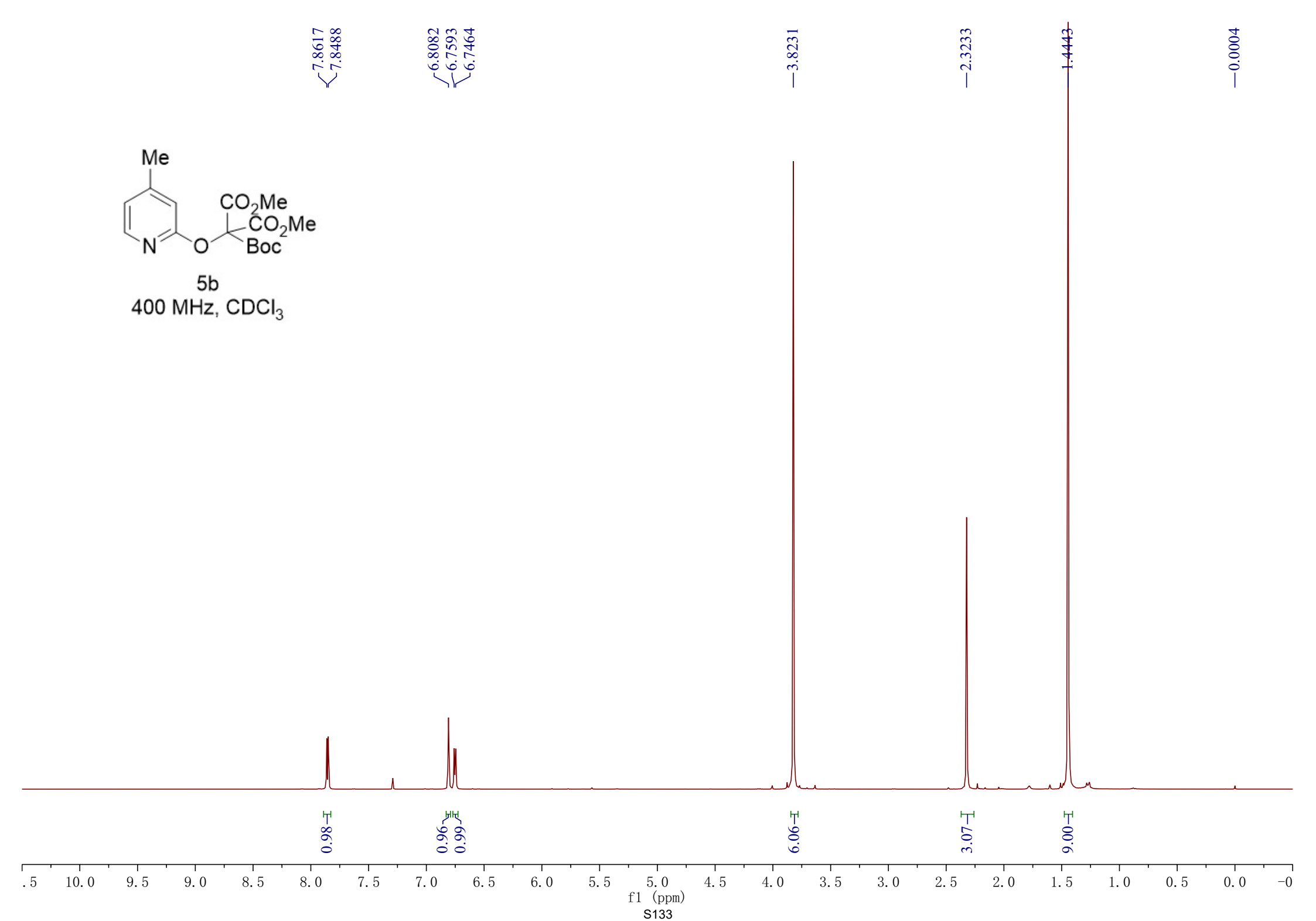
4k

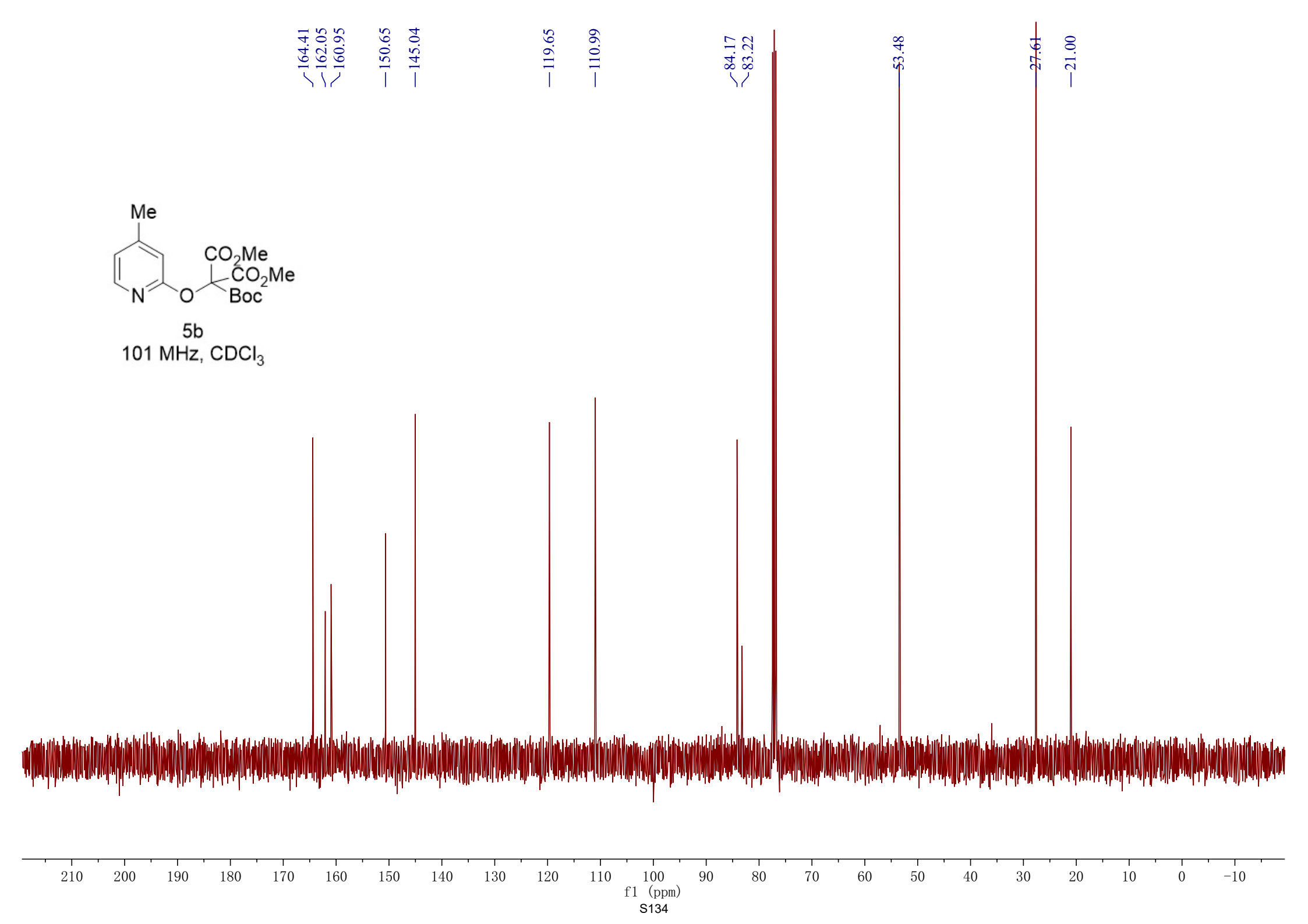
400 MHz, $CDCl_3$

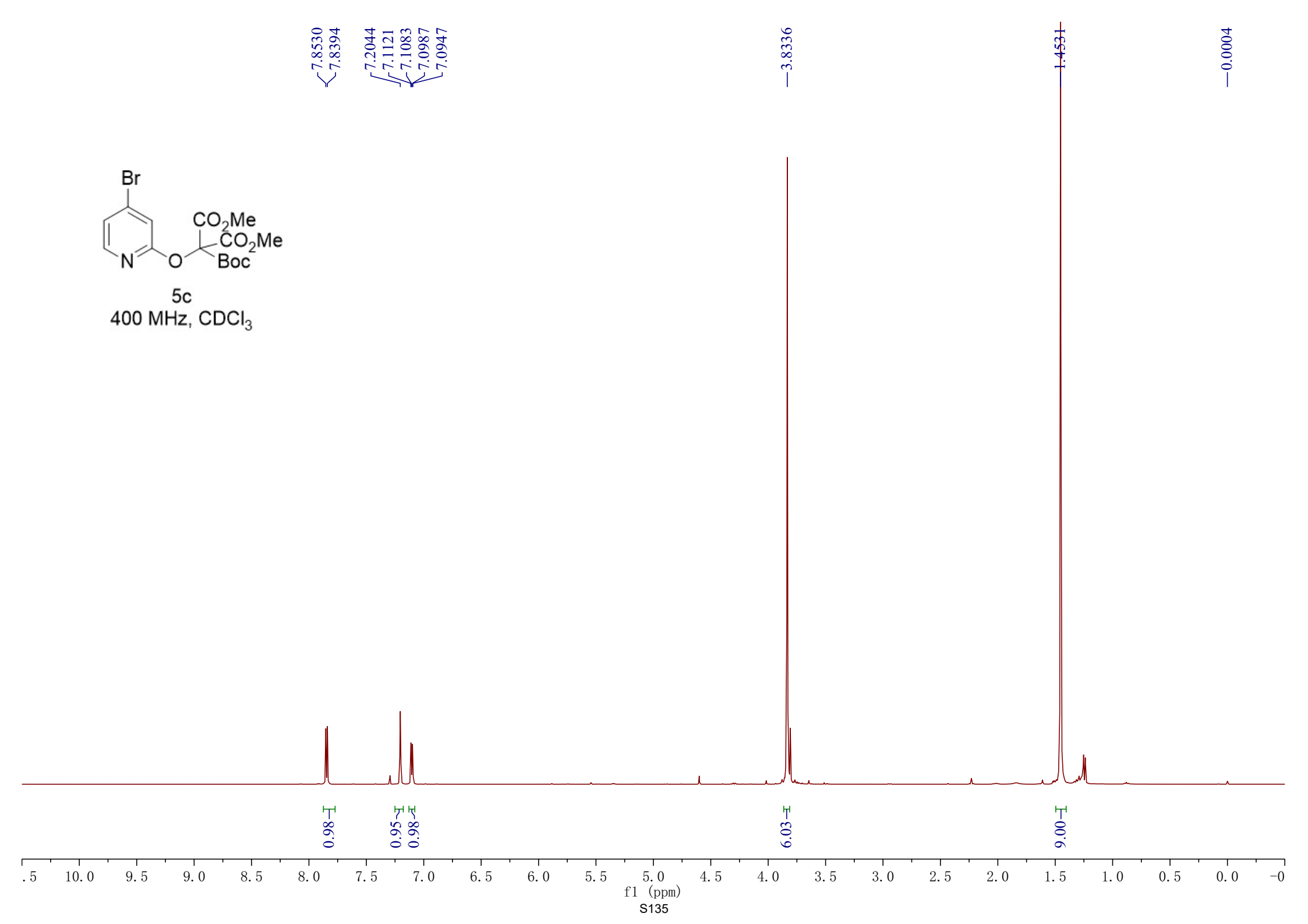

170.66
155.80
152.10
139.09
135.68
128.74
128.15
127.33
126.46
125.69
122.02
85.18
69.61
45.98
30.93
27.71
24.91
Br
O
H
O
O
N
H
Boc
4k
101 MHz, CDCl3
f1 (ppm)

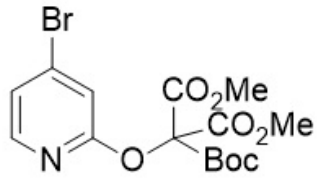

8.0114
8.0020
7.6786
7.6737
7.6598
7.6561
7.6526
7.6397
7.6348
6.9993
6.9785
6.9474
6.9348
6.9295
6.9169
3.8335
1.4391
0.0001
CO2Me
CO2Me
Boc
N
O
5a
400 MHz, CDCl3
1.03
1.08
1.07
1.08
6.00
9.09
f1 (ppm)


164.32
161.95
160.69
145.48
139.15
118.17
110.95
84.24
83.26
53.51
27.59
CO2Me
CO2Me
Boc
N
O
5a
75 MHz, CDCl3
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)


7.8617
7.8488
6.8082
6.7593
6.7464
3.8231
2.3233
1.4443
0.0004
Me
CO2Me
CO2Me
N
O
Boc
5b
400 MHz, CDCl3
0.98
0.96
0.99
6.06
3.07
9.00
f1 (ppm)

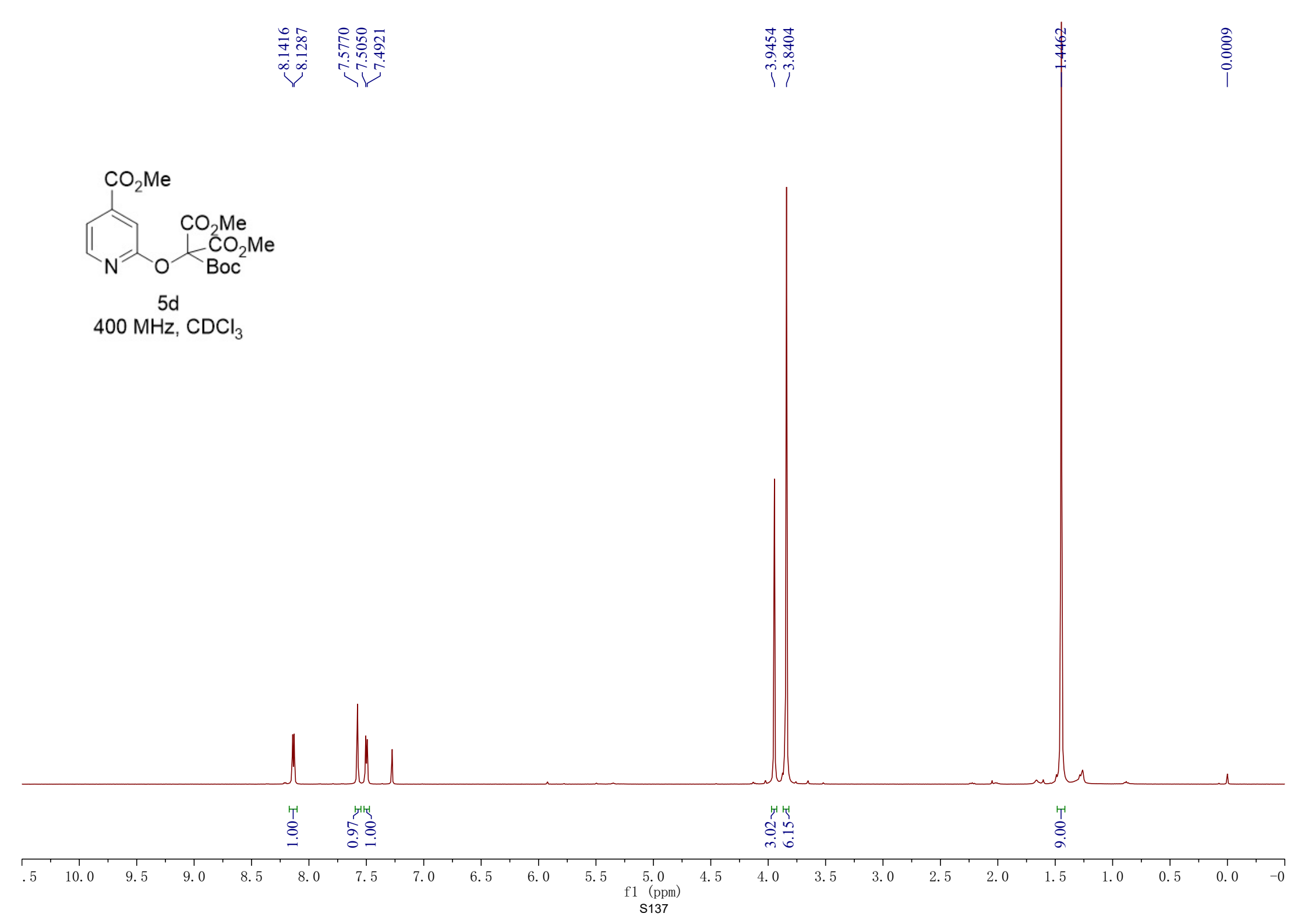

164.41
162.05
160.95
150.65
145.04
119.65
110.99
84.17
83.22
53.48
27.61
21.00
Me
CO2Me
CO2Me
Boc
N
O
5b
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

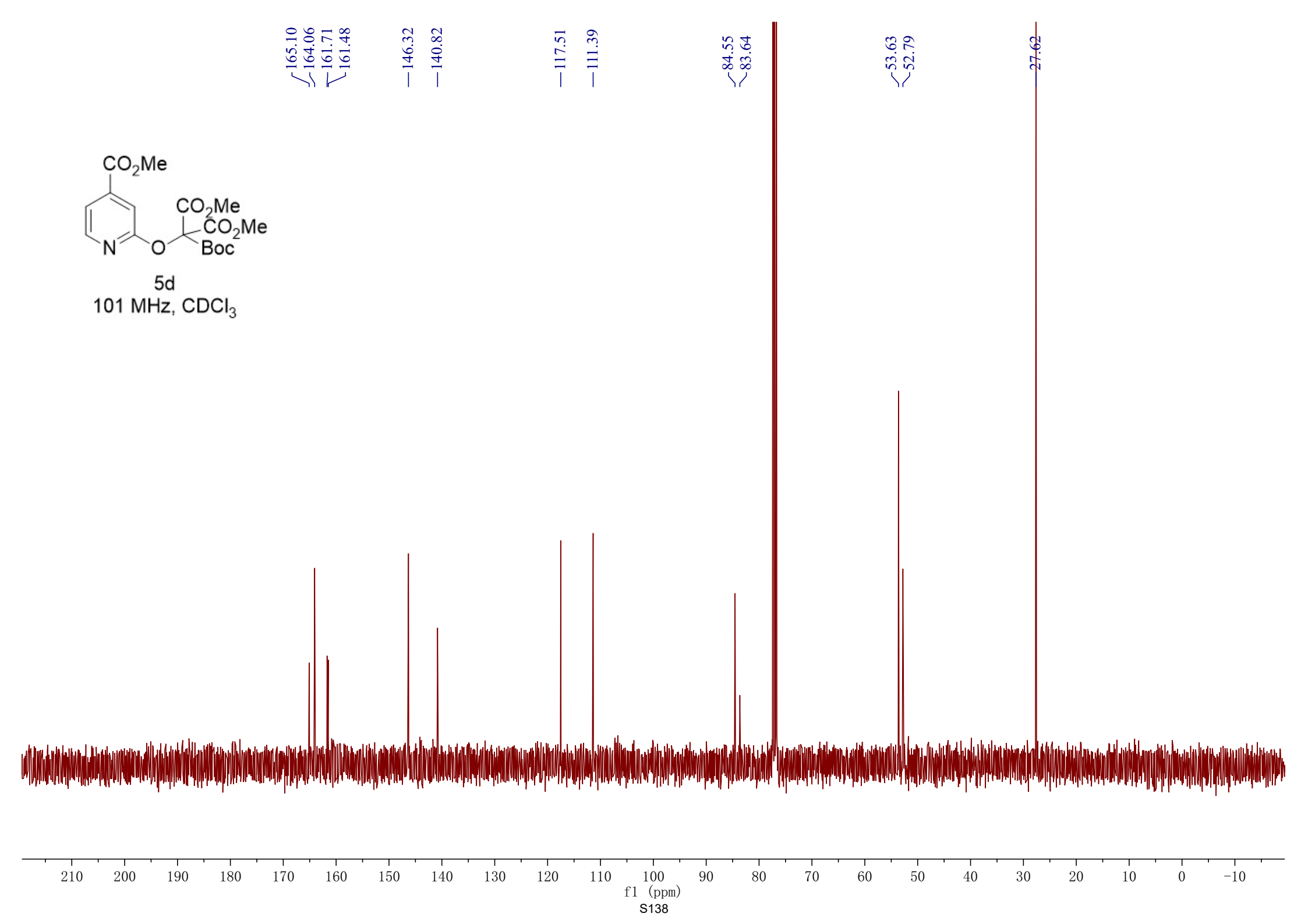

7.8530
7.8394
7.2044
7.1121
7.1083
7.0987
7.0947
3.8336
1.4531
0.0004
Br
CO2Me
CO2Me
N
O
Boc
5c
400 MHz, CDCl3
0.98
0.95
0.98
6.03
9.00
f1 (ppm)

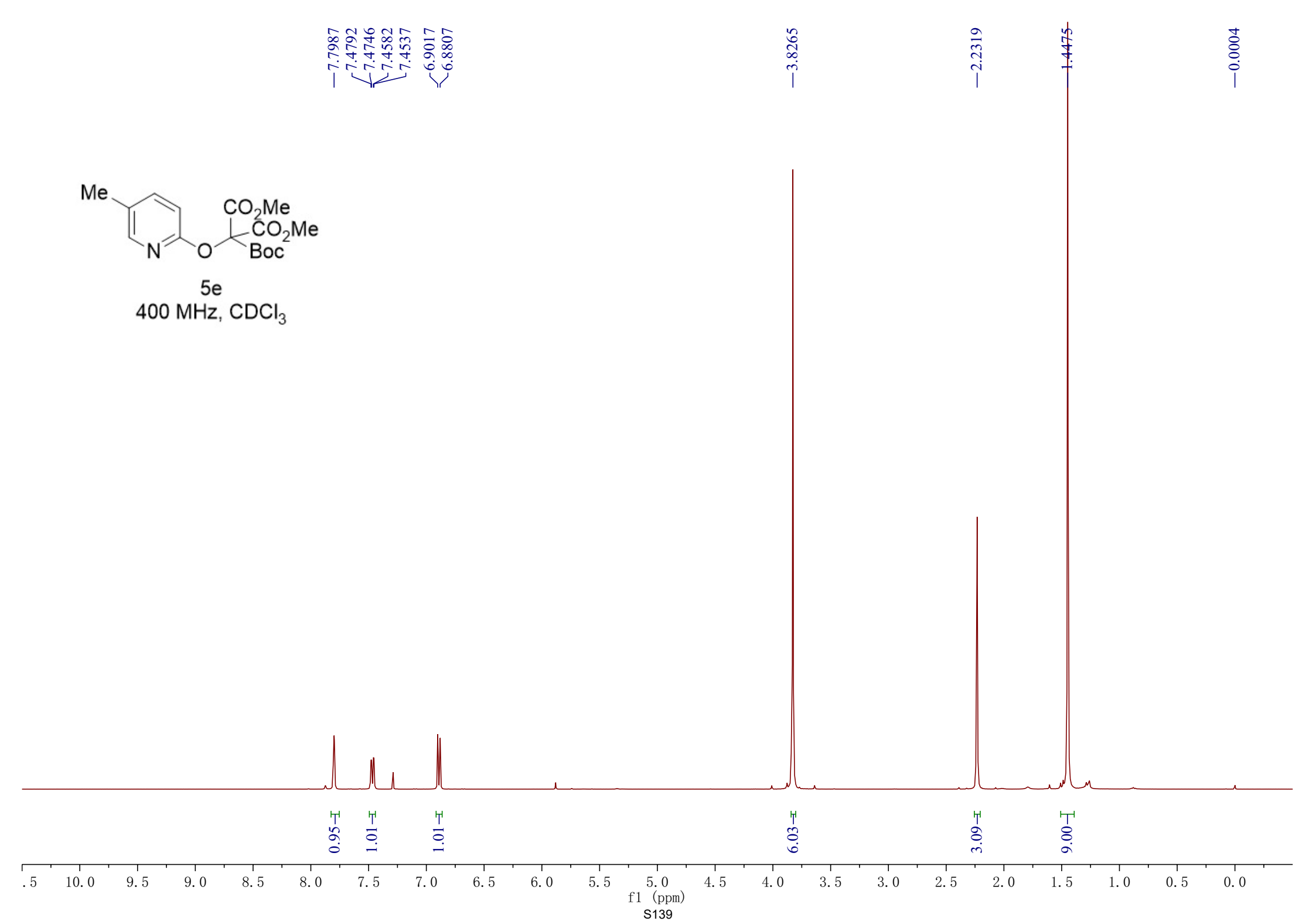


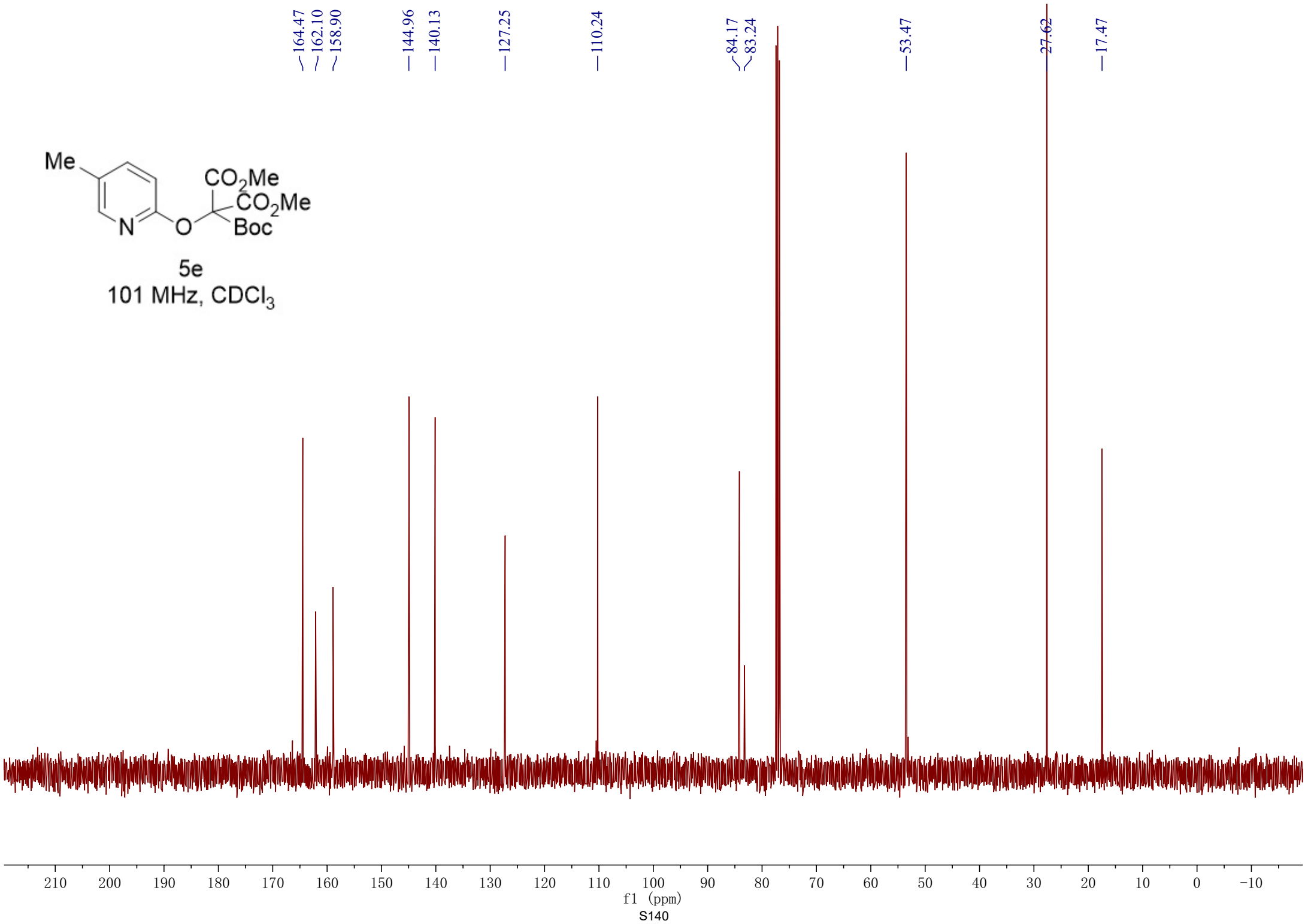
5c

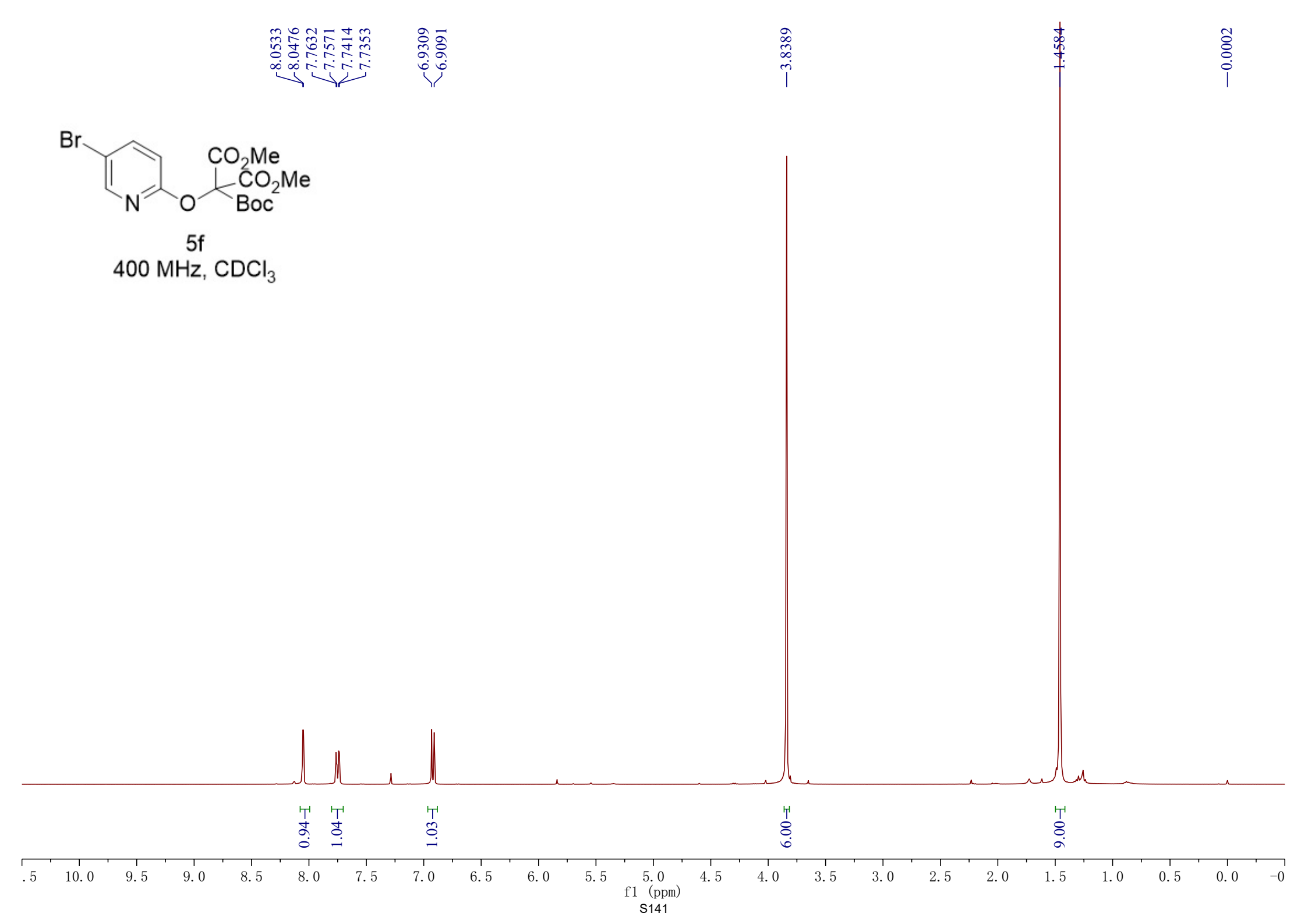
101 MHz, $CDCl_3$

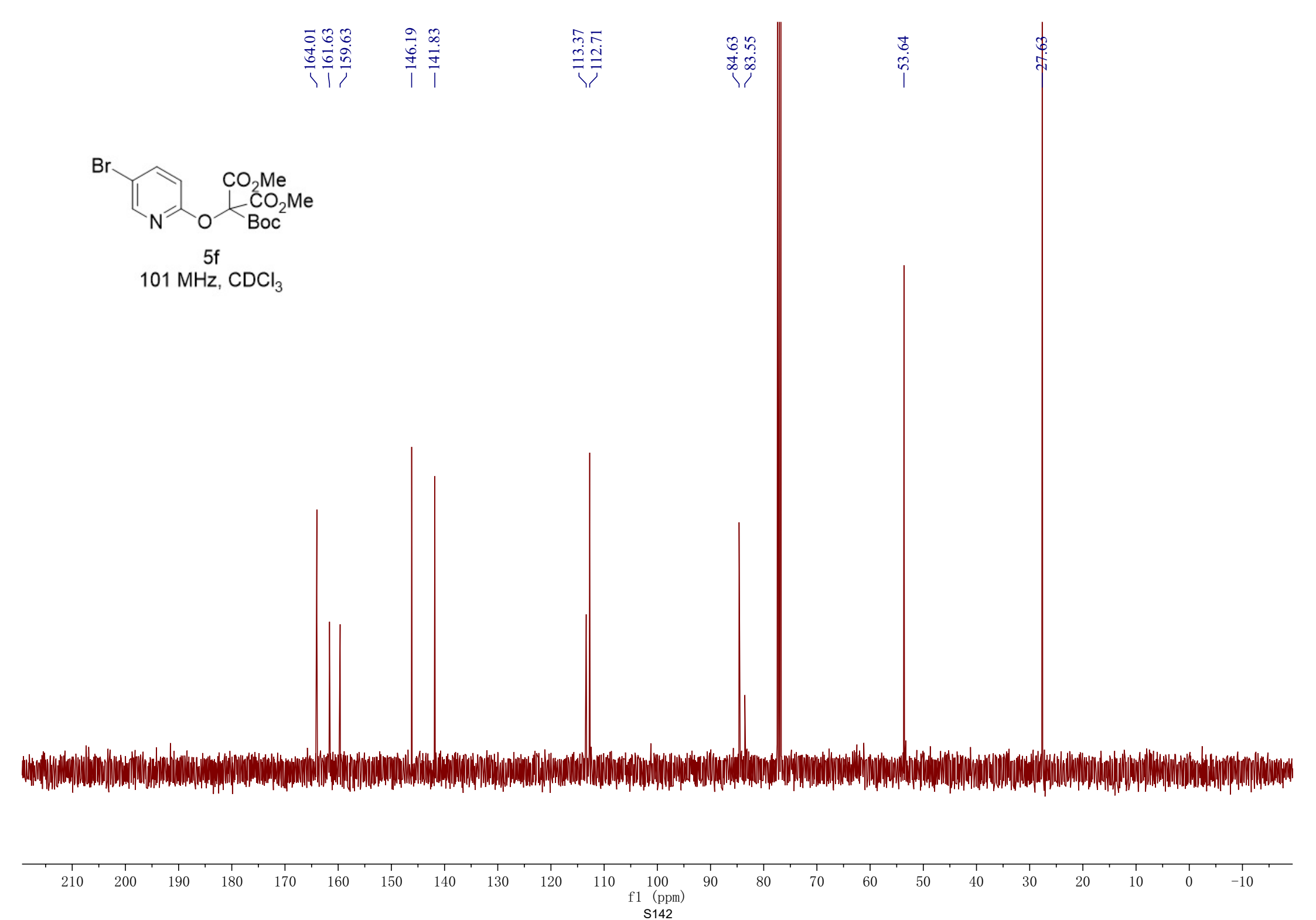

8.1416
8.1287
7.5770
7.5050
7.4921
3.9454
3.8404
1.4462
0.0009
CO2Me
CO2Me
CO2Me
N
O
Boc
5d
400 MHz, CDCl3
1.00
0.97
1.00
3.02
6.15
9.00
f1 (ppm)

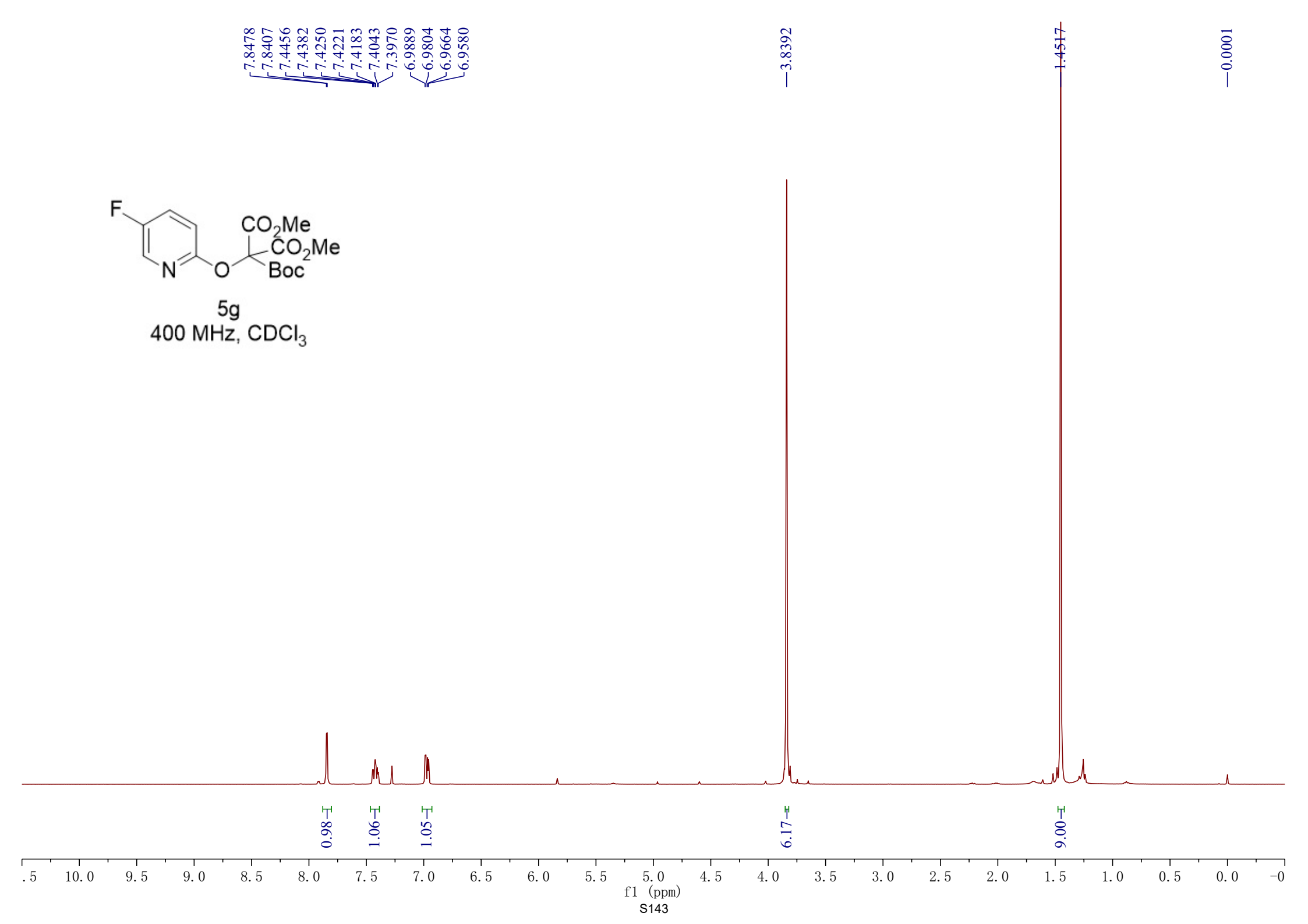

165.10
164.06
161.71
161.48
146.32
140.82
117.51
111.39
84.55
83.64
53.63
52.79
27.62
CO2Me
CO2Me
CO2Me
N
O
Boc
5d
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

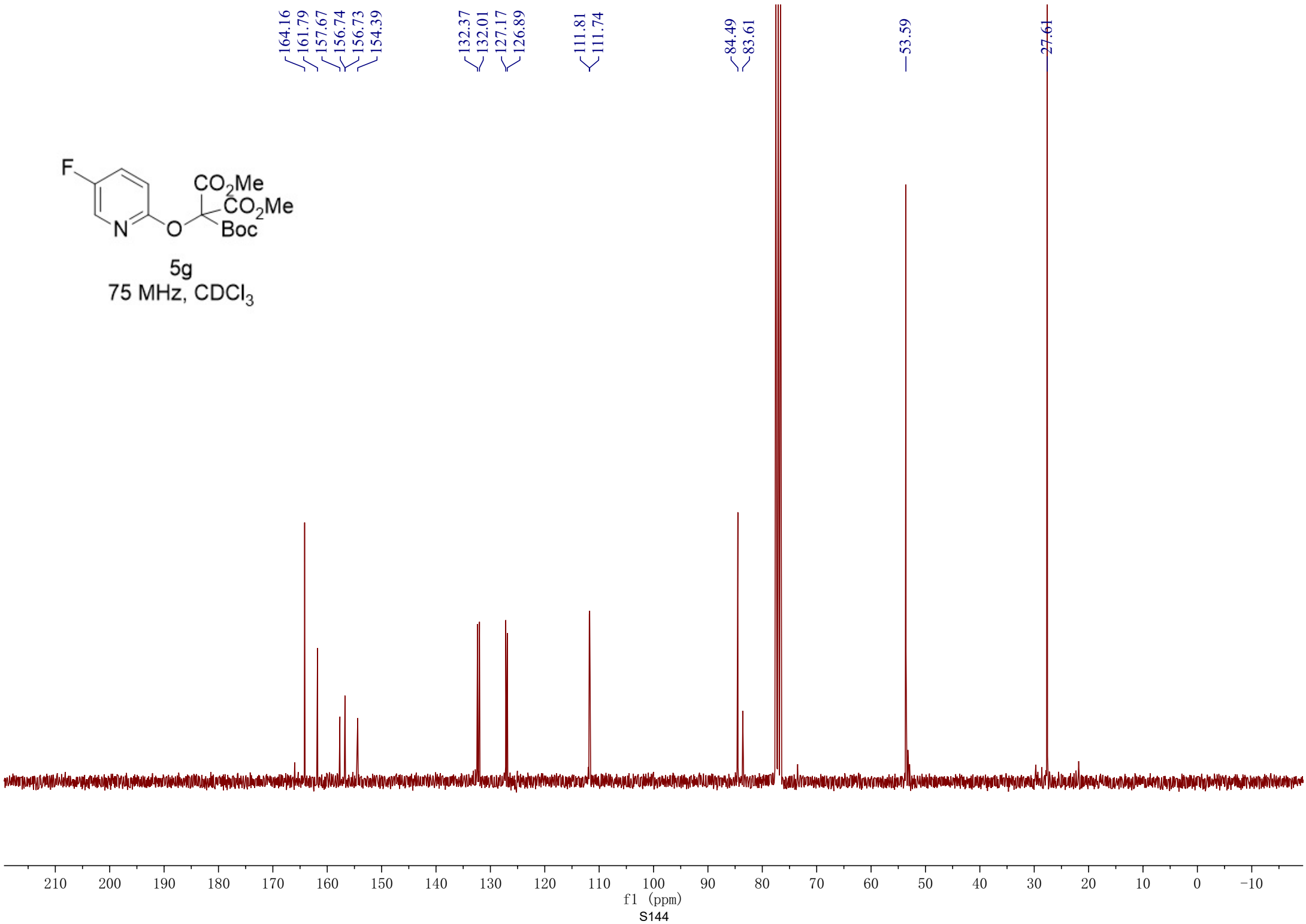

7.7987
7.4792
7.4746
7.4582
7.4537
6.9017
6.8807
3.8265
2.2319
1.4475
0.0004
Me
CO2Me
CO2Me
N
O
Boc
5e
400 MHz, CDCl3
0.95
1.01
1.01
6.03
3.09
9.00
f1 (ppm)

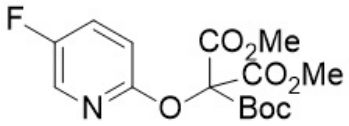

164.47
162.10
158.90
144.96
140.13
127.25
110.24
84.17
83.24
53.47
27.62
17.47
Me
CO2Me
CO2Me
N
O
Boc
5e
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


8.0533
8.0476
7.7632
7.7571
7.7414
7.7353
6.9309
6.9091
3.8389
1.4584
0.0002
Br
CO2Me
CO2Me
Boc
N
O
5f
400 MHz, CDCl3
0.94
1.04
1.03
6.00
9.00
f1 (ppm)

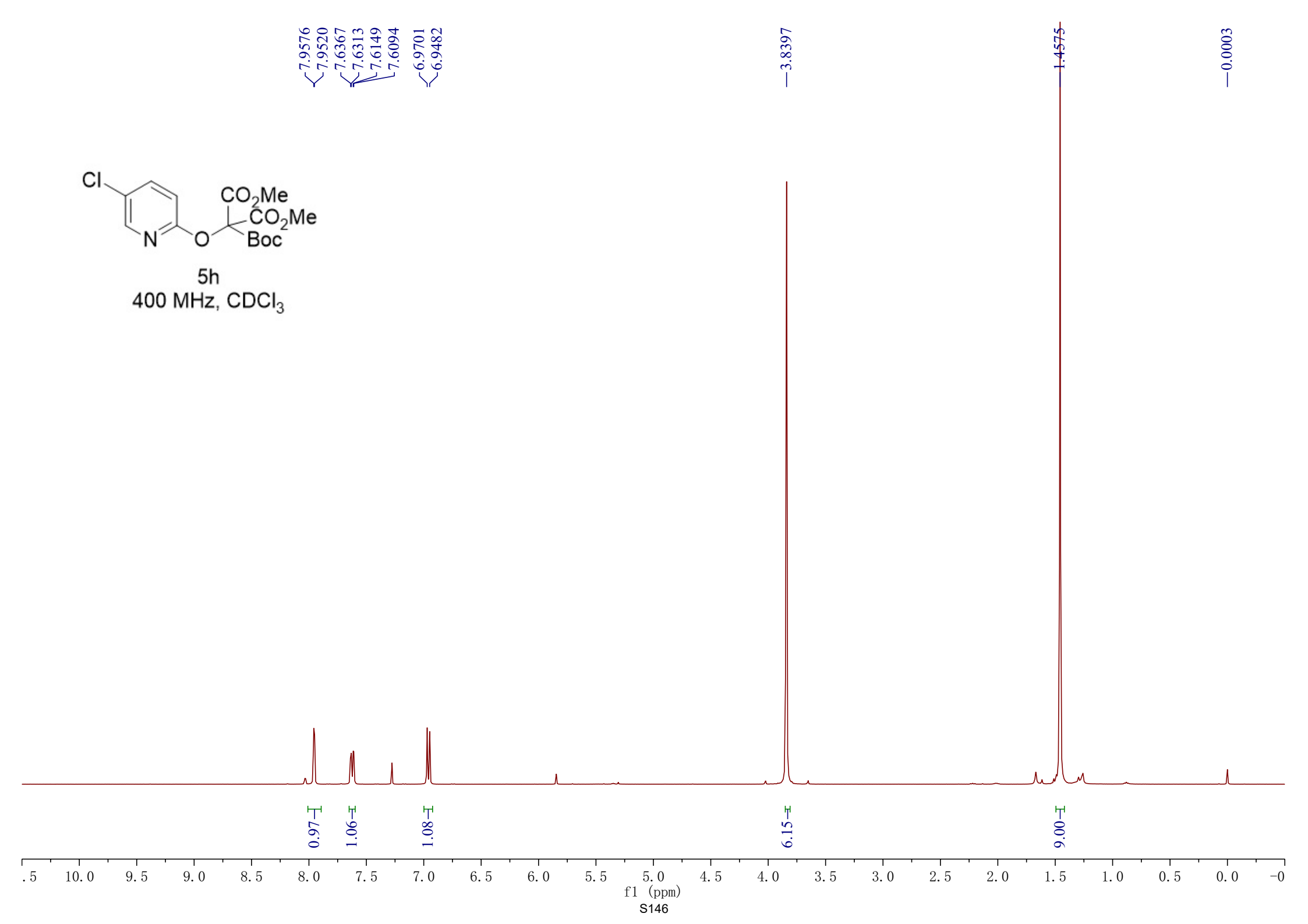

164.01
161.63
159.63
146.19
141.83
113.37
112.71
84.63
83.55
53.64
27.63
Br
CO2Me
CO2Me
N
O
Boc
5f
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

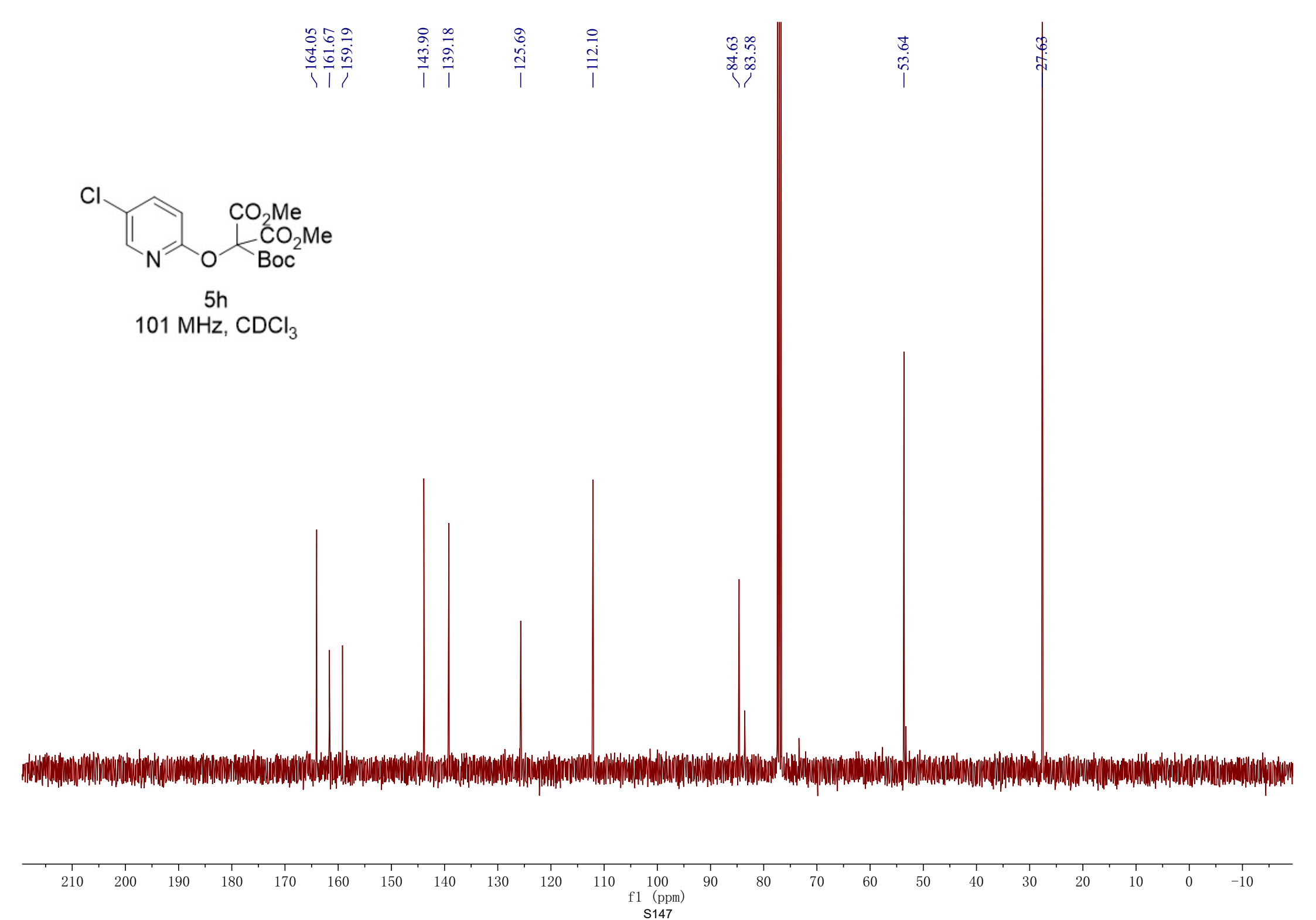

7.8478
7.8407
7.4456
7.4382
7.4250
7.4221
7.4183
7.4043
7.3970
6.9889
6.9804
6.9664
6.9580
3.8392
1.4517
0.0001
F
CO2Me
CO2Me
N
O
Boc
5g
400 MHz, CDCl3
0.98
1.06
1.05
6.17
9.00
f1 (ppm)

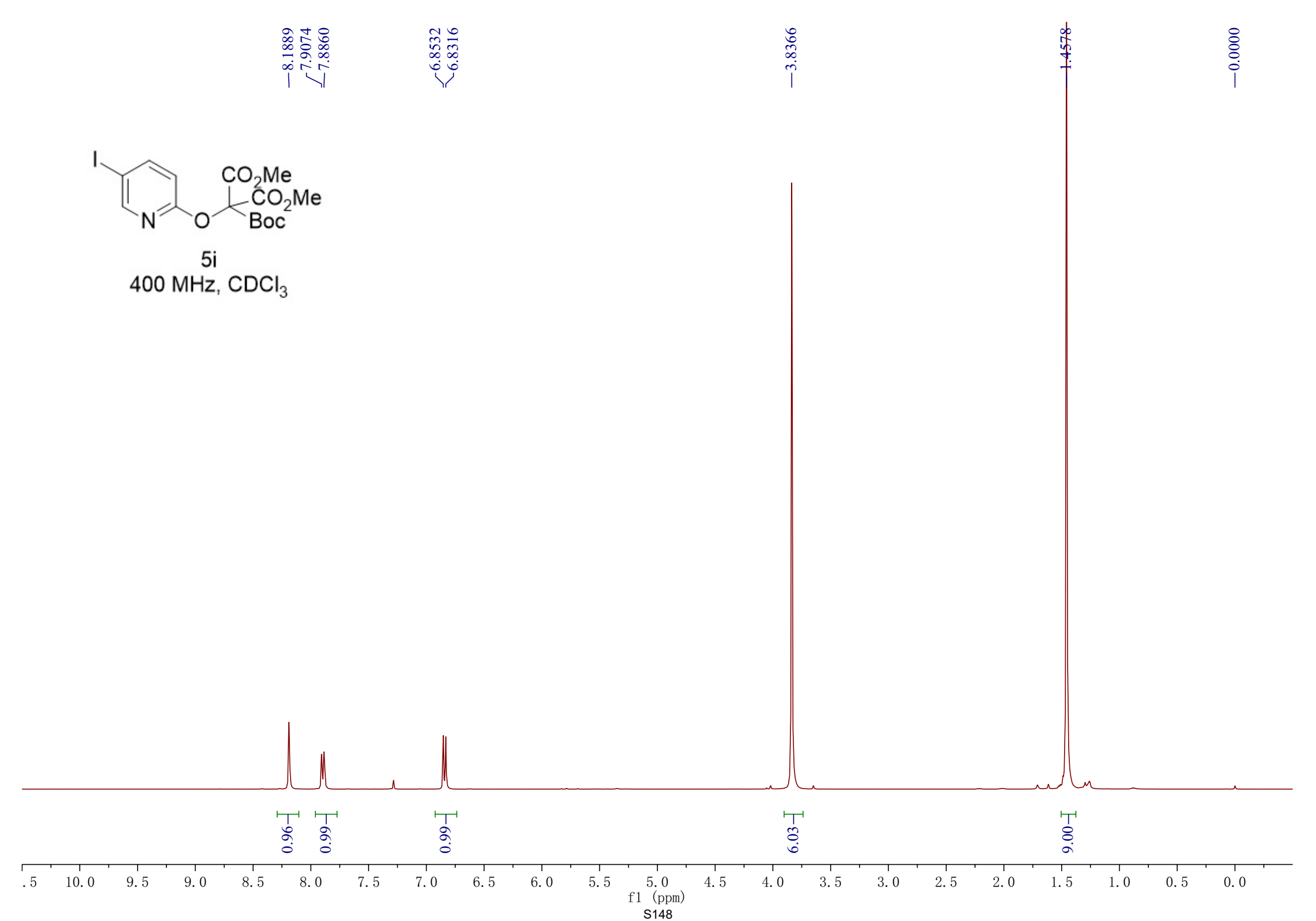

164.16
161.79
157.67
156.74
156.73
154.39
132.37
132.01
127.17
126.89
111.81
111.74
84.49
83.61
53.59
27.61
F
CO2Me
CO2Me
N
O
Boc
5g
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

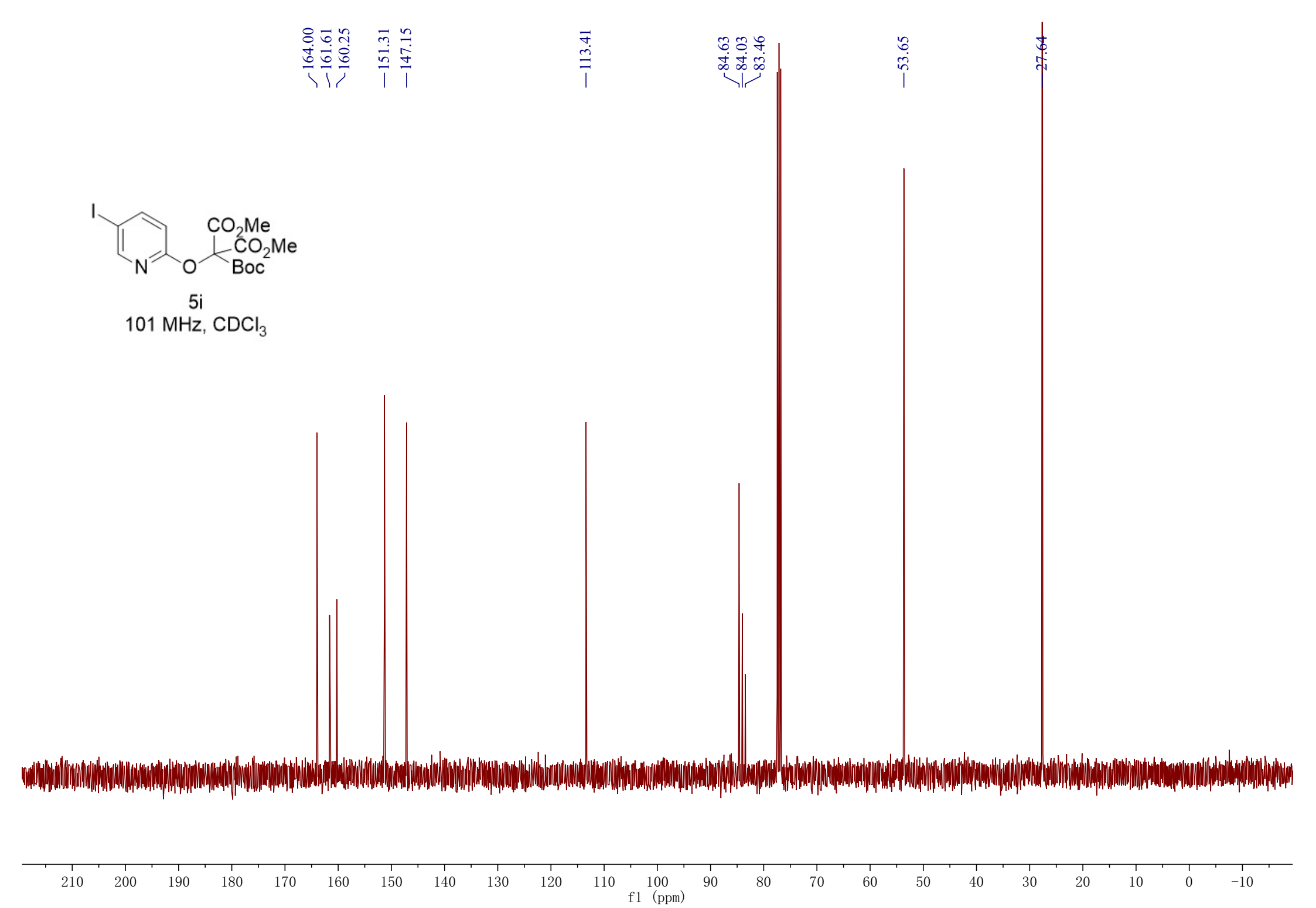


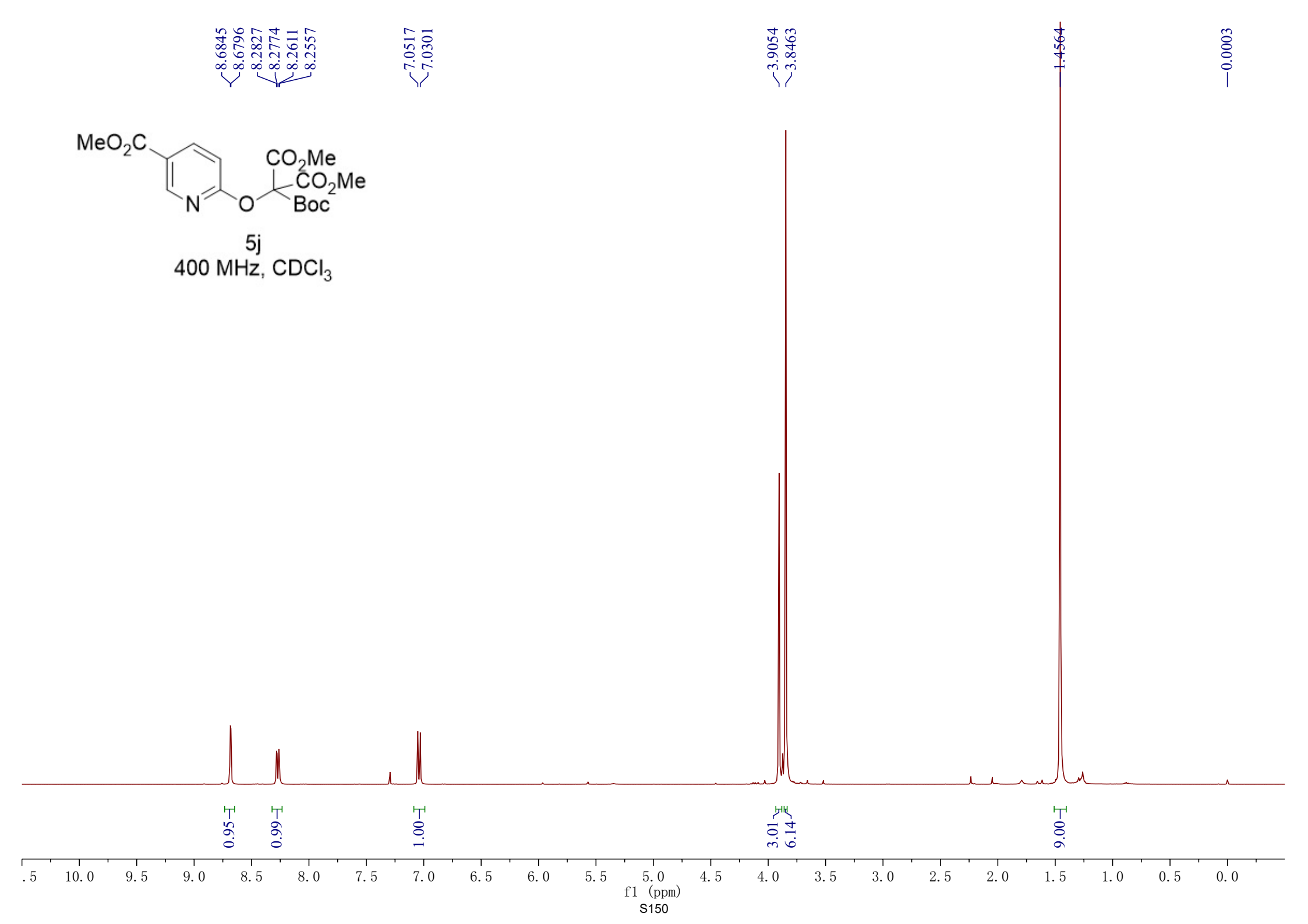
5g
282 MHz, $CDCl_3$

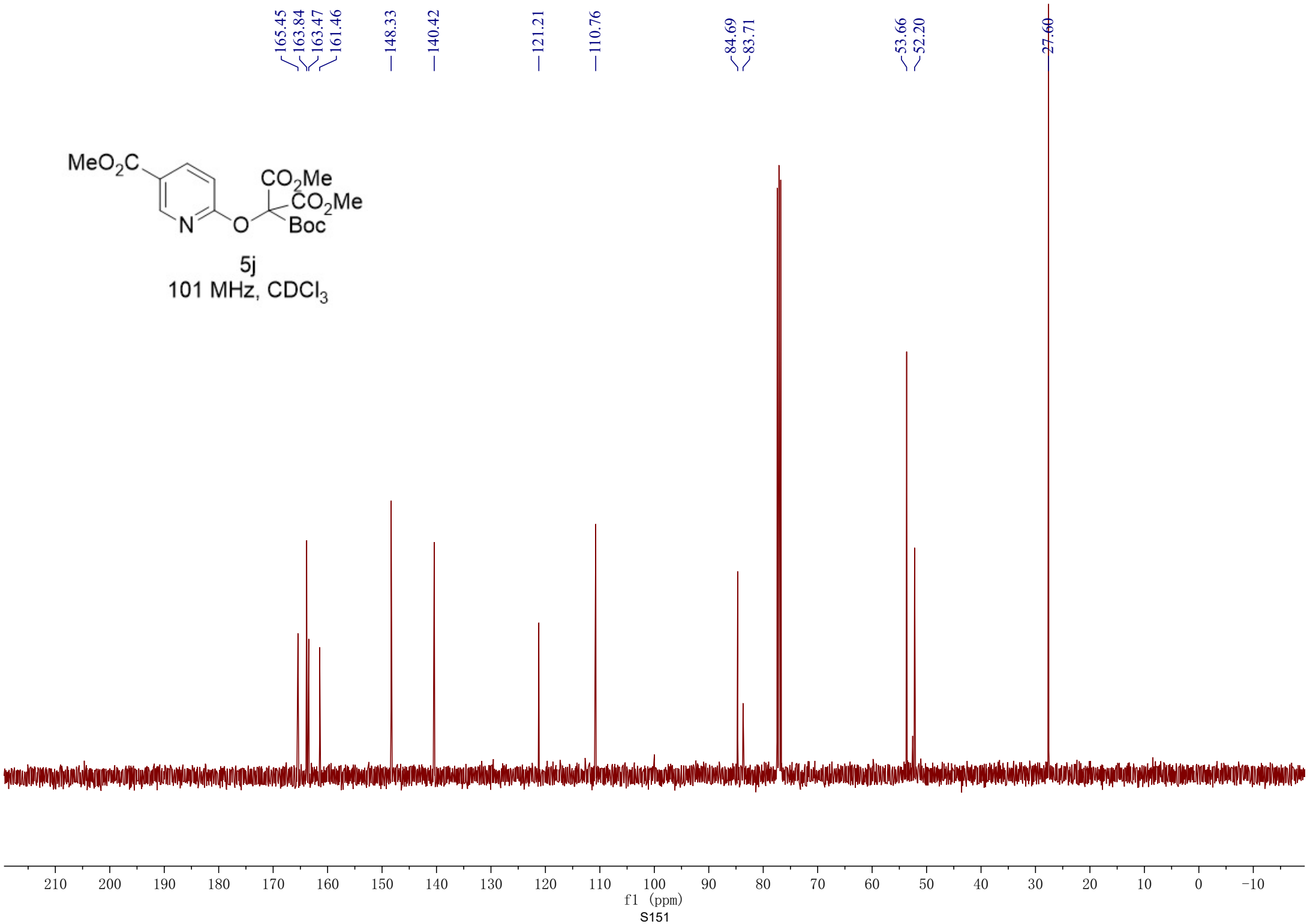

7.9576
7.9520
7.6367
7.6313
7.6149
7.6094
6.9701
6.9482
3.8397
1.4575
0.0003
Cl
N
O
CO2Me
CO2Me
Boc
5h
400 MHz, CDCl3
0.97
1.06
1.08
6.15
9.00
f1 (ppm)

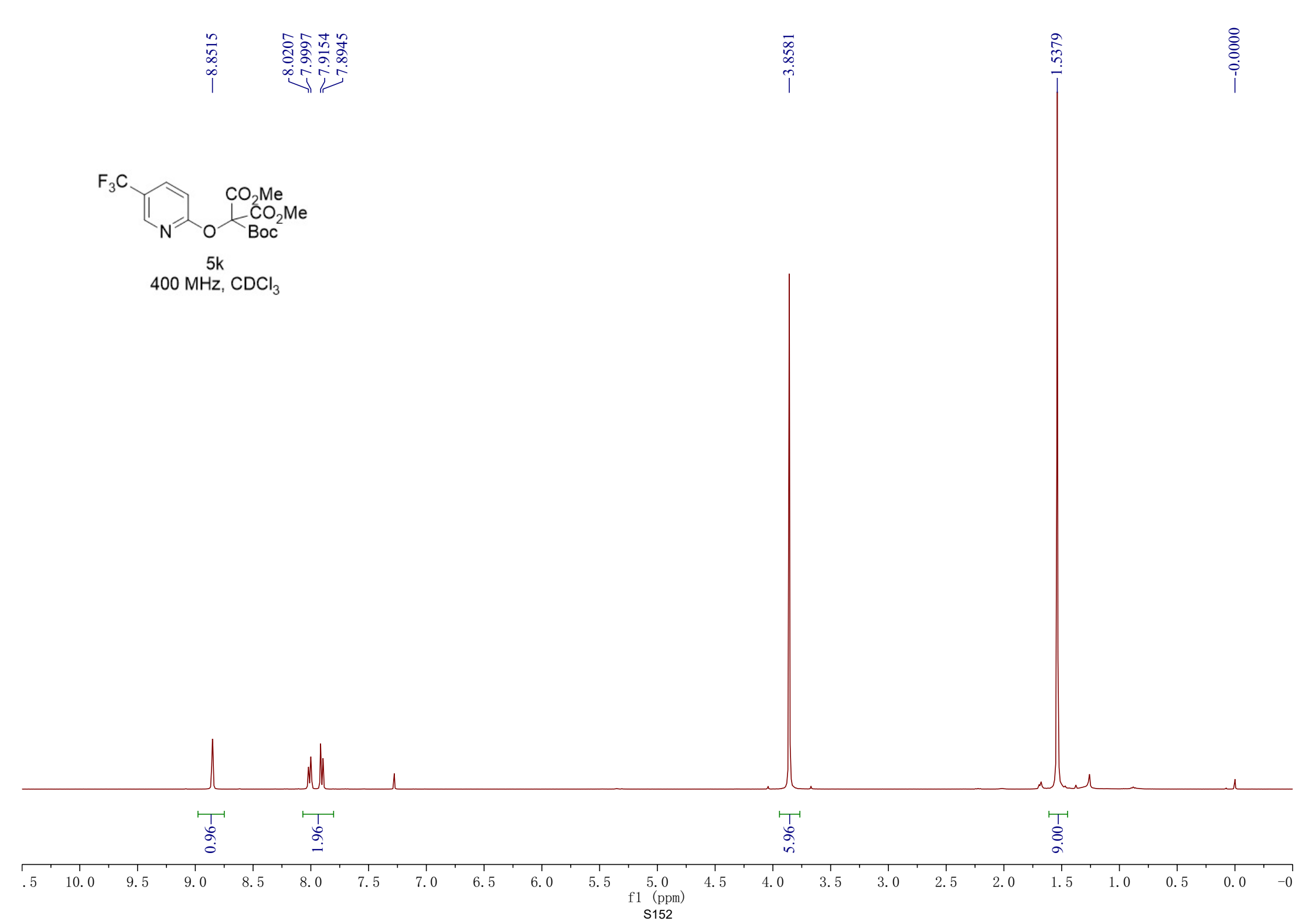

164.05
161.67
159.19
143.90
139.18
125.69
112.10
84.63
83.58
53.64
27.63
Cl
N
O
CO2Me
CO2Me
Boc
5h
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

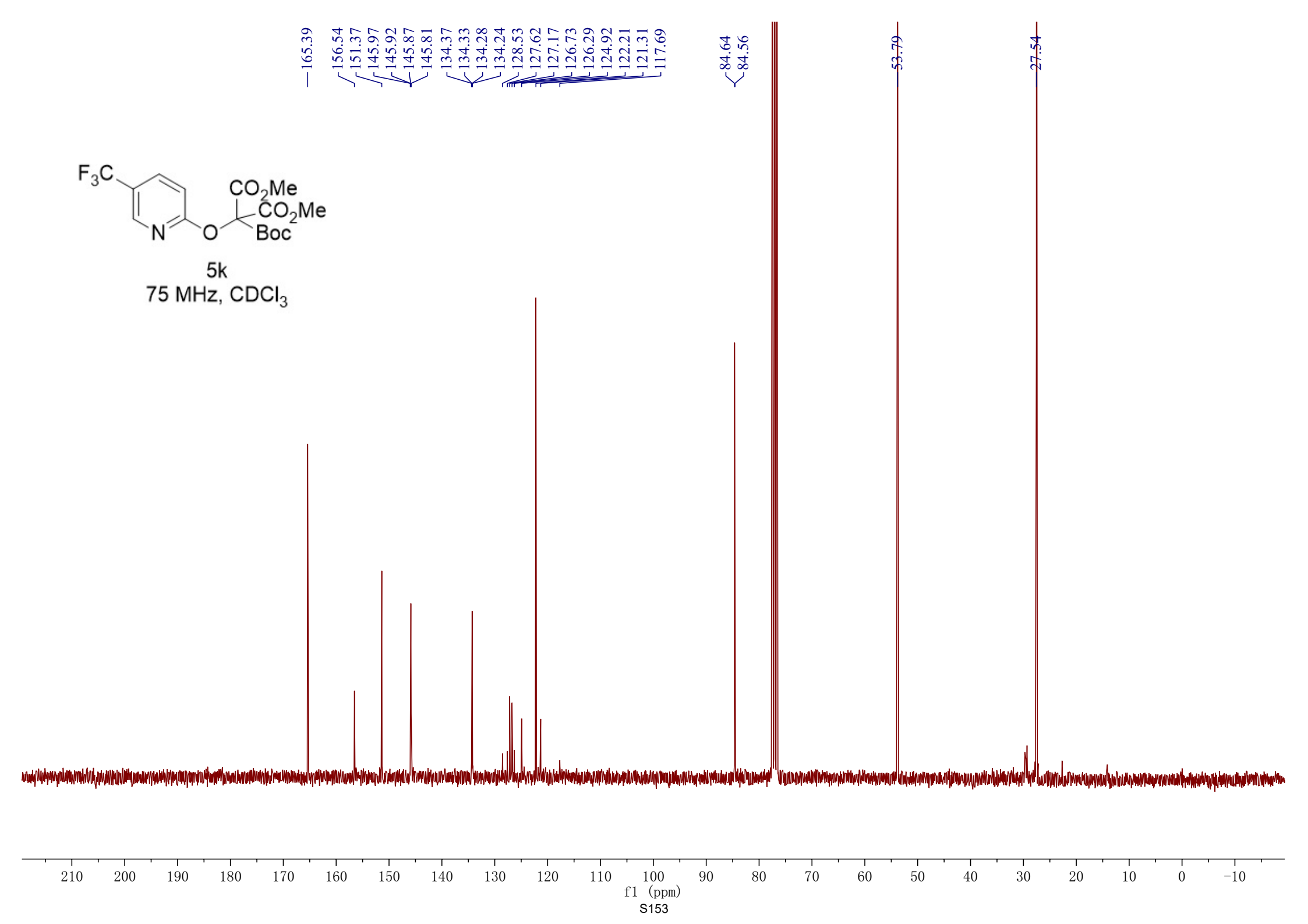

8.1889
7.9074
7.8860
6.8532
6.8316
3.8366
1.4578
0.0000
I
CO2Me
CO2Me
N
O
Boc
5i
400 MHz, CDCl3
0.96
0.99
0.99
6.03
9.00
f1 (ppm)

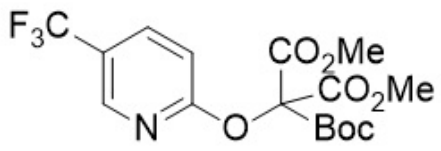

164.00
161.61
160.25
151.31
147.15
113.41
84.63
84.03
83.46
53.65
27.64
I
CO2Me
CO2Me
Boc
N
O
5i
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.6845
8.6796
8.2827
8.2774
8.2611
8.2557
7.0517
7.0301
3.9054
3.8463
1.4564
0.0003
MeO2C
CO2Me
CO2Me
N
O
Boc
5j
400 MHz, CDCl3
0.95
0.99
1.00
3.01
6.14
9.00
f1 (ppm)


165.45
163.84
163.47
161.46
148.33
140.42
121.21
110.76
84.69
83.71
53.66
52.20
27.60
MeO2C
CO2Me
CO2Me
N
O
Boc
5j
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

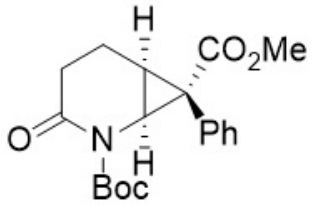

8.8515
8.0207
7.9997
7.9154
7.8945
3.8581
1.5379
-0.0000
F3C
CO2Me
CO2Me
Boc
N
O
5k
400 MHz, CDCl3
0.96
1.96
5.96
9.00
f1 (ppm)


165.39
156.54
151.37
145.97
145.92
145.87
145.81
134.37
134.33
134.28
134.24
128.53
127.62
127.17
126.73
126.29
124.92
122.21
121.31
117.69
84.64
84.56
53.79
27.54
F3C
CO2Me
CO2Me
Boc
N
O
5k
75 MHz, CDCl3
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)



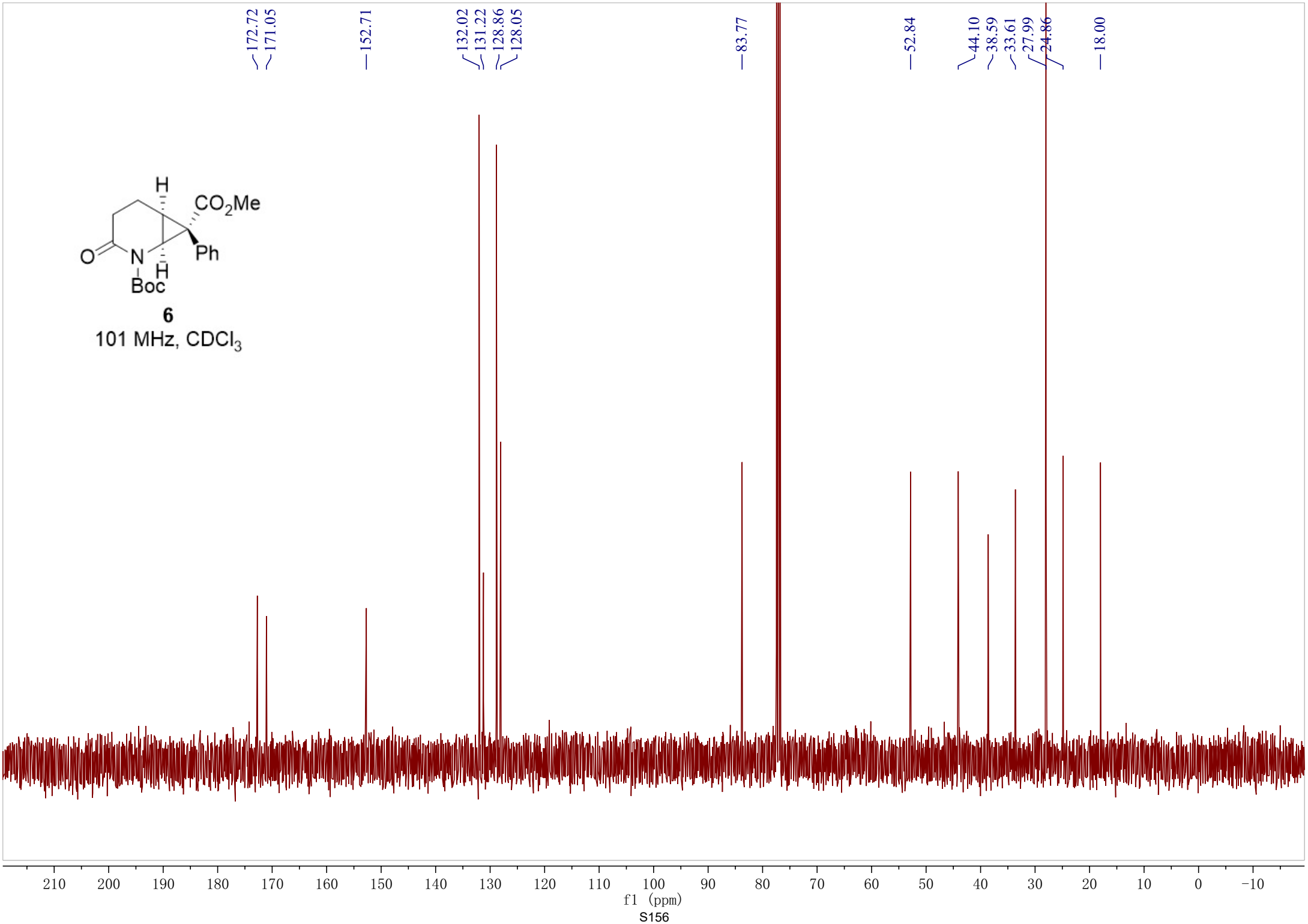
5k

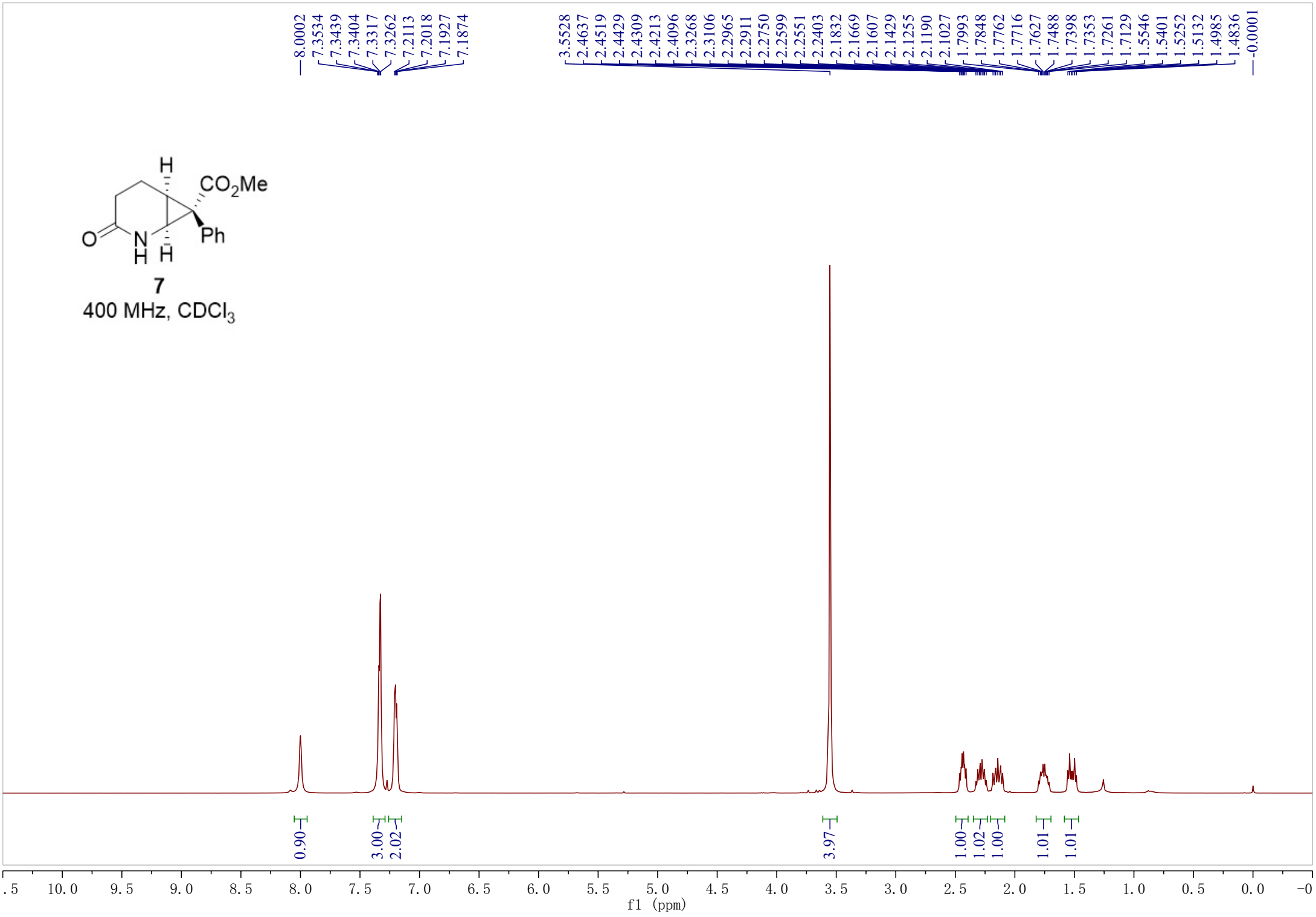
282 MHz, $CDCl_3$

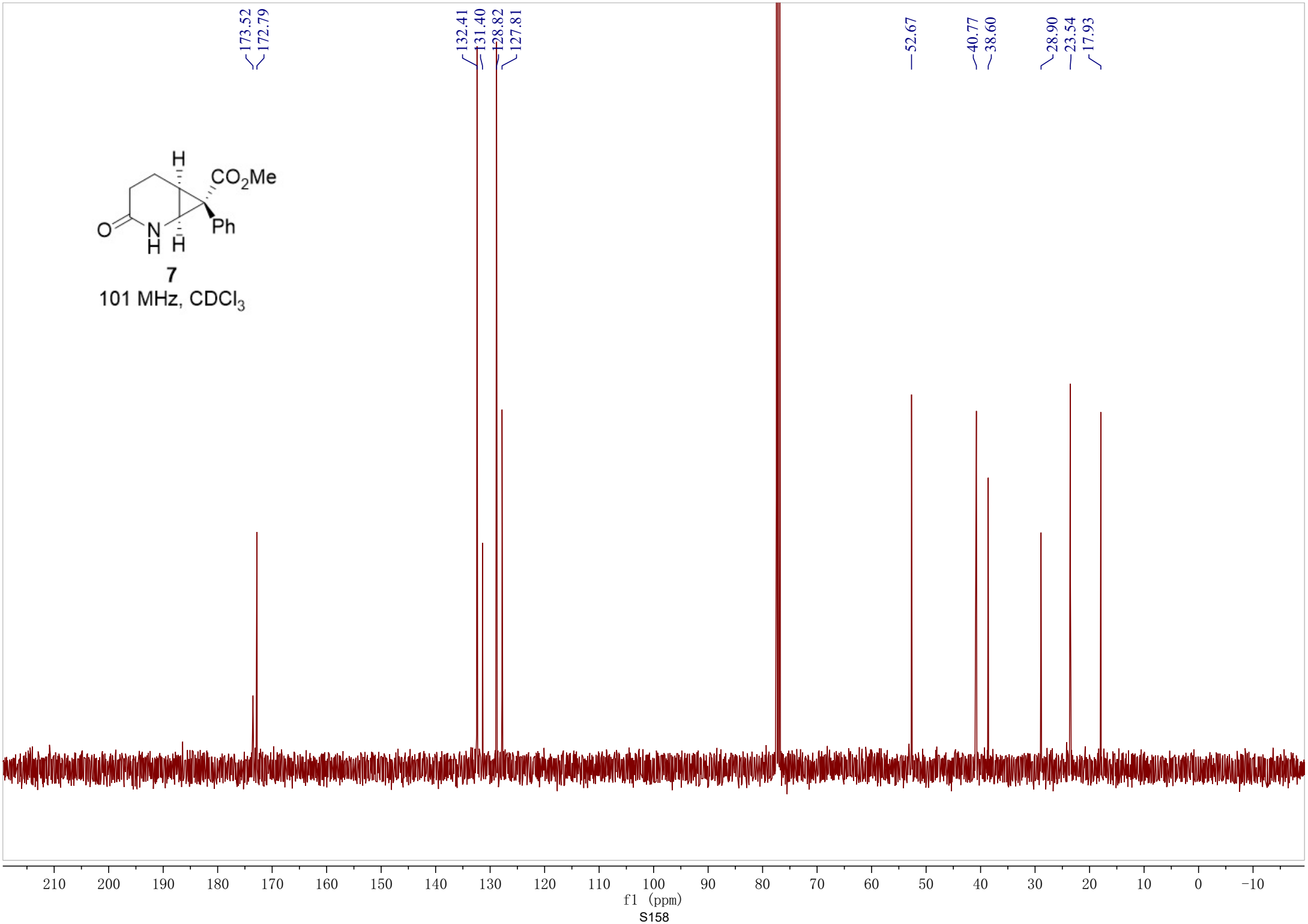


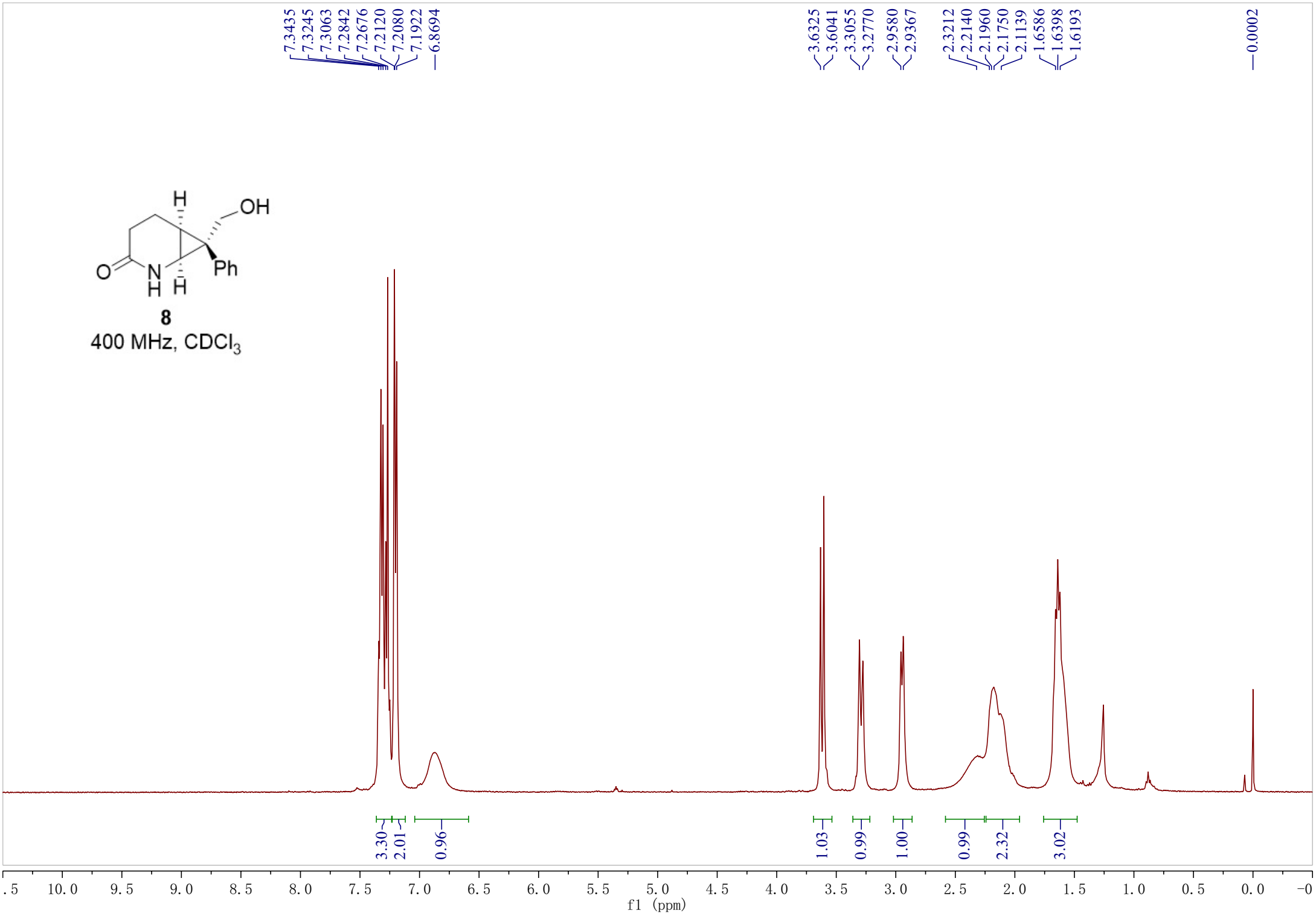
6

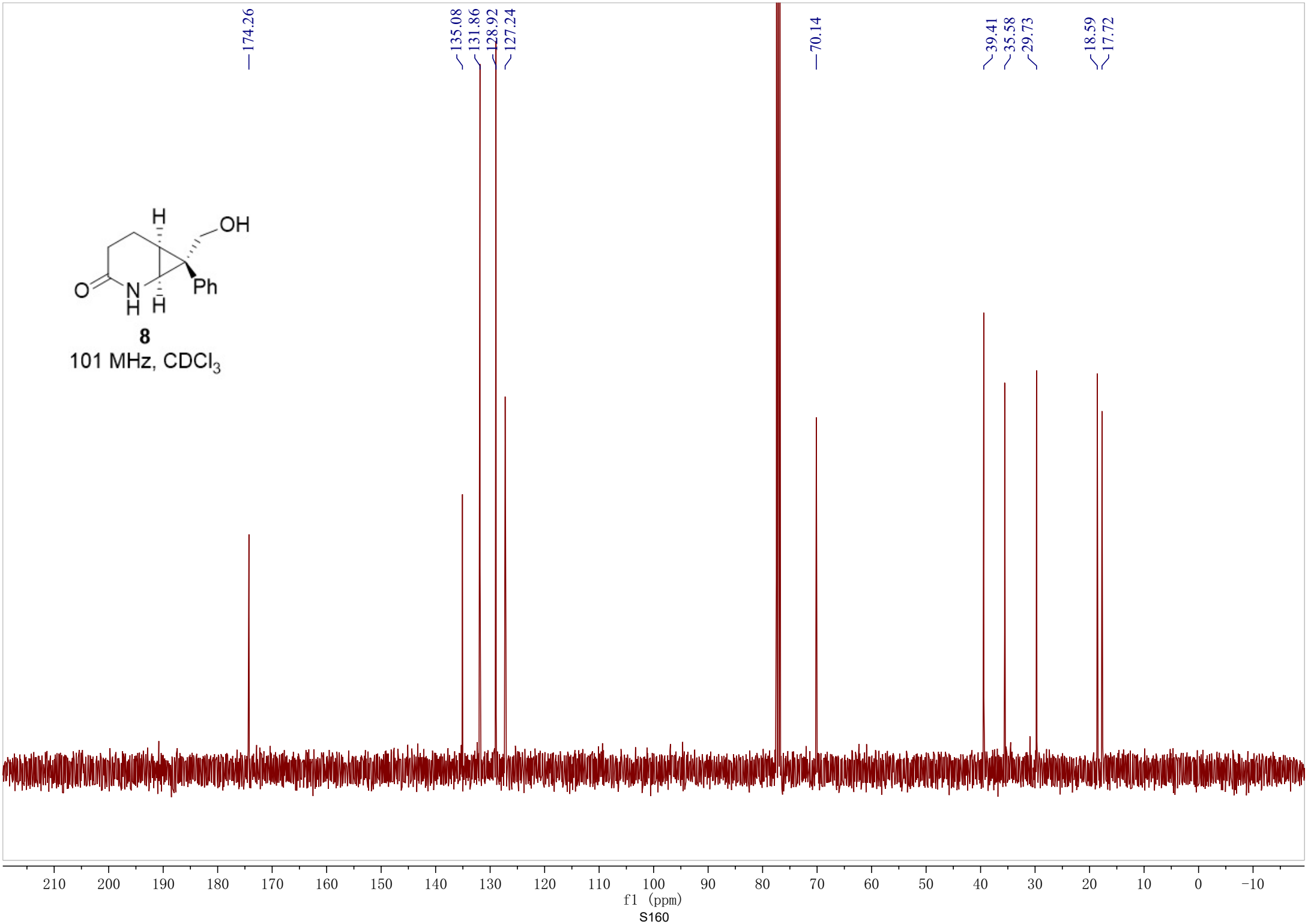
400 MHz, $CDCl_3$

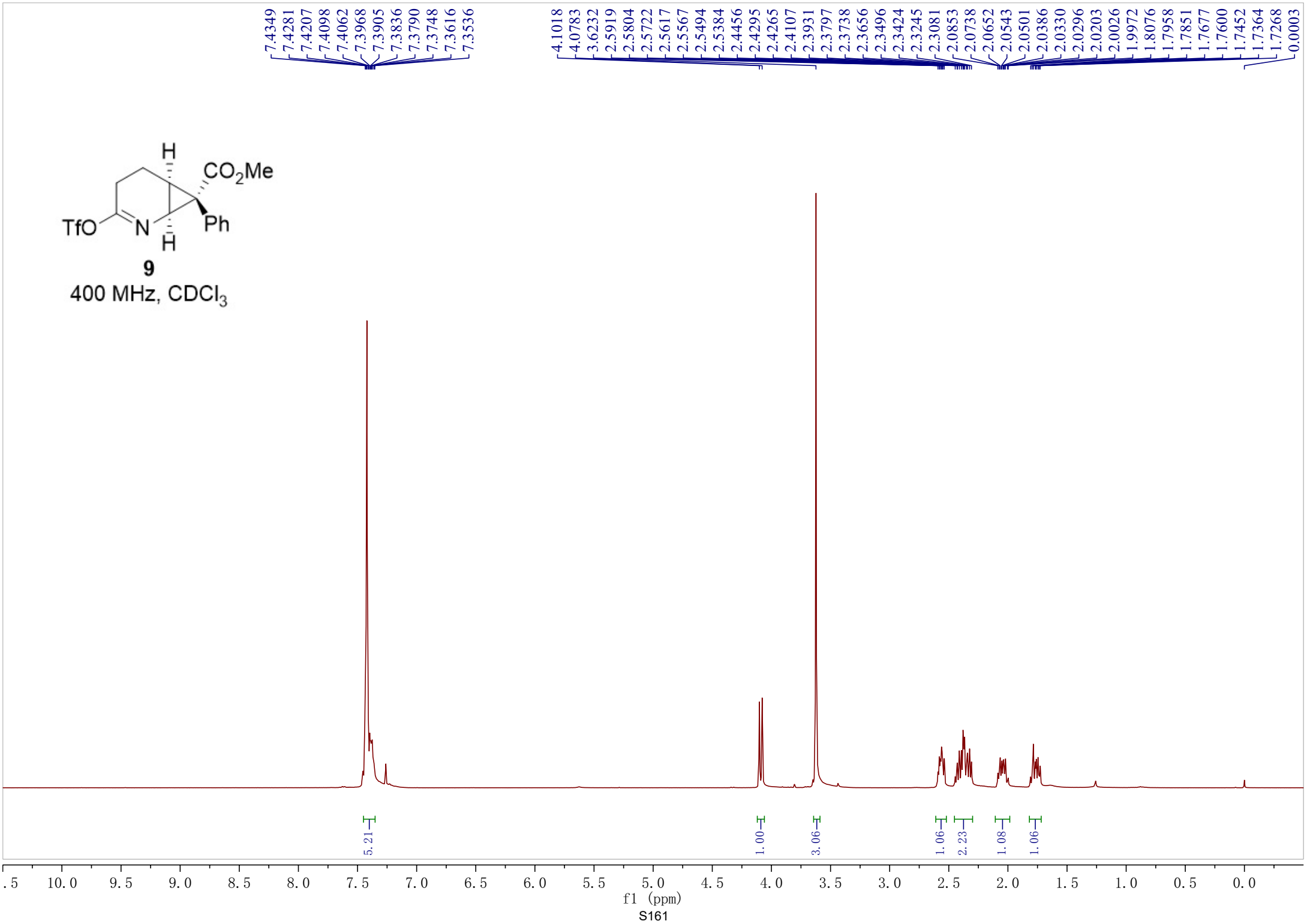

172.72
171.05
152.71
132.02
131.22
128.86
128.05
83.77
52.84
44.10
38.59
33.61
27.99
24.86
18.00
H
CO2Me
O
N
H
Ph
Boc
6
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

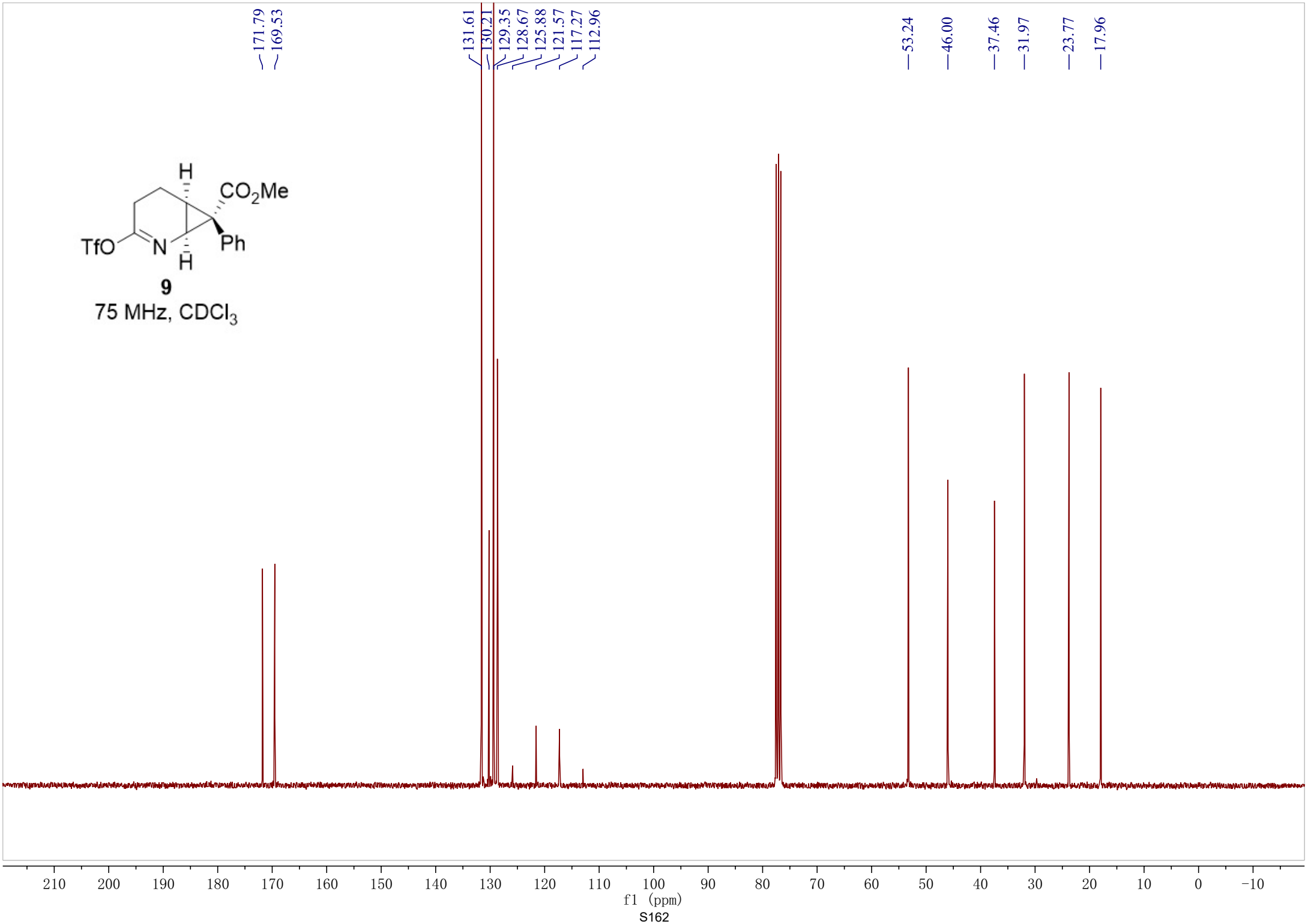

8.0002
7.3534
7.3439
7.3404
7.3317
7.3262
7.2113
7.2018
7.1927
7.1874
3.5528
2.4637
2.4519
2.4429
2.4309
2.4213
2.4096
2.3268
2.3106
2.2965
2.2911
2.2750
2.2599
2.2551
2.2403
2.1832
2.1669
2.1607
2.1429
2.1255
2.1190
2.1027
1.7993
1.7848
1.7762
1.7716
1.7627
1.7488
1.7398
1.7353
1.7261
1.7129
1.5546
1.5401
1.5252
1.5132
1.4985
1.4836
-0.0001
H
CO2Me
O
N
H
H
Ph
7
400 MHz, CDCl3
0.90
3.00
2.02
3.97
1.00
1.02
1.00
1.01
1.01
f1 (ppm)

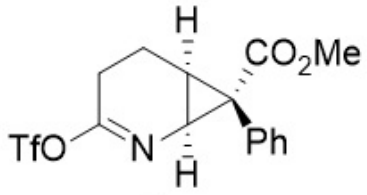

173.52
172.79
132.41
131.40
128.82
127.81
52.67
40.77
38.60
28.90
23.54
17.93
H
CO2Me
O
N
H
H
Ph
7
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.3435
7.3245
7.3063
7.2842
7.2676
7.2120
7.2080
7.1922
6.8694
3.6325
3.6041
3.3055
3.2770
2.9580
2.9367
2.3212
2.2140
2.1960
2.1750
2.1139
1.6586
1.6398
1.6193
0.0002
H
OH
O
N
H
H
Ph
8
400 MHz, CDCl3
3.30
2.01
0.96
1.03
0.99
1.00
0.99
2.32
3.02
f1 (ppm)


174.26
135.08
131.86
128.92
127.24
70.14
39.41
35.58
29.73
18.59
17.72
H
OH
O
N
H
H
Ph
8
101 MHz, CDCl3
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)

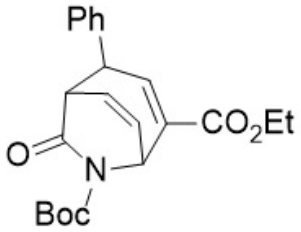

7.4349
7.4281
7.4207
7.4098
7.4062
7.3968
7.3905
7.3836
7.3790
7.3748
7.3616
7.3536
4.1018
4.0783
3.6232
2.5919
2.5804
2.5722
2.5617
2.5567
2.5494
2.5384
2.4456
2.4295
2.4265
2.4107
2.3931
2.3797
2.3738
2.3656
2.3496
2.3424
2.3245
2.3081
2.0853
2.0738
2.0652
2.0543
2.0501
2.0386
2.0330
2.0296
2.0203
2.0026
1.9972
1.8076
1.7958
1.7851
1.7677
1.7600
1.7452
1.7364
1.7268
0.0003
H
CO2Me
TfO
N
Ph
H
9
400 MHz, CDCl3
5.21
1.00
3.06
1.06
2.23
1.08
1.06
f1 (ppm)


171.79
169.53
131.61
130.21
129.35
128.67
125.88
121.57
117.27
112.96
53.24
46.00
37.46
31.97
23.77
17.96
H
CO2Me
TfO
N
Ph
H
9
75 MHz, CDCl3
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)



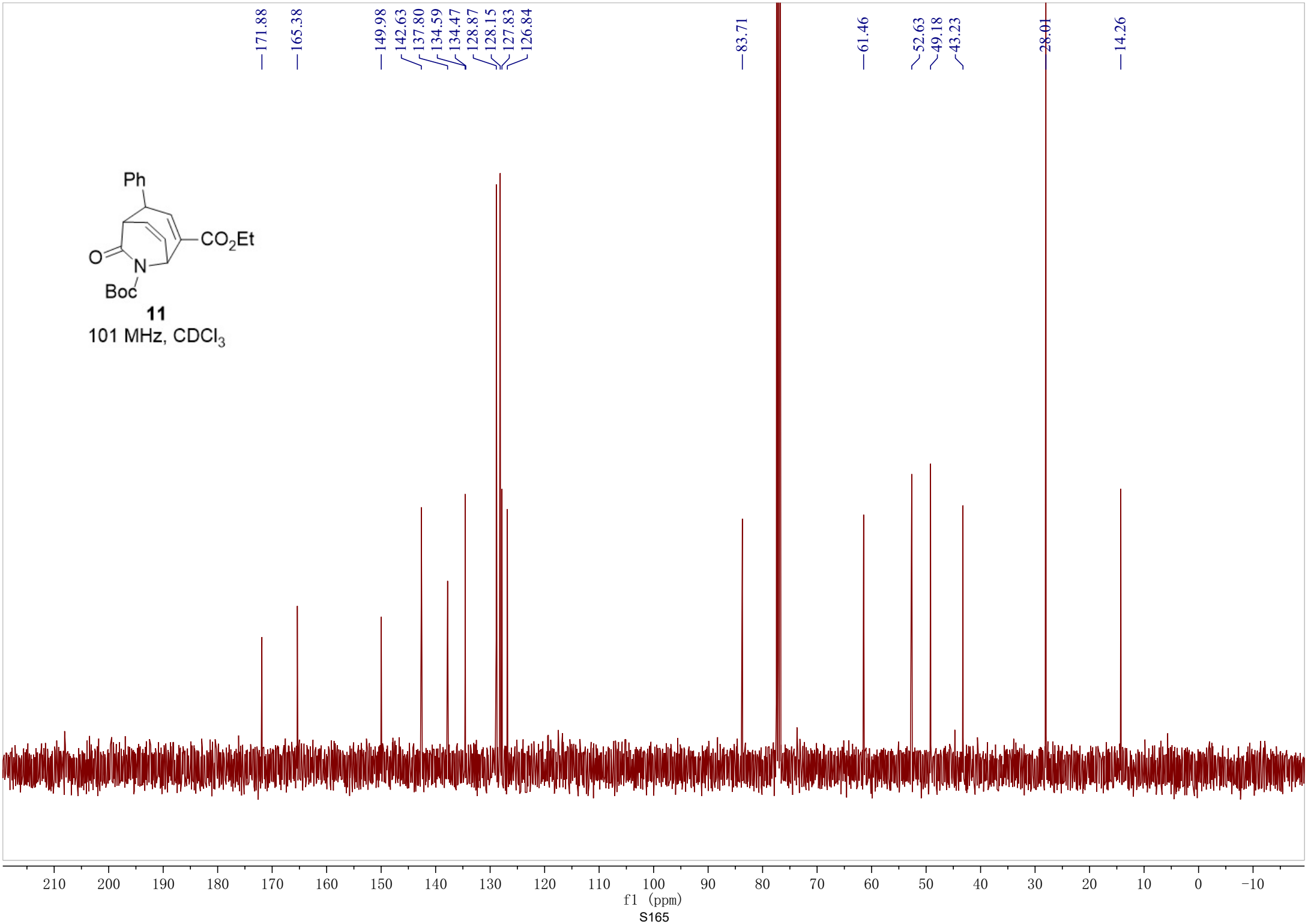
9

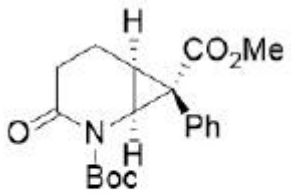
282 MHz, $CDCl_3$



11

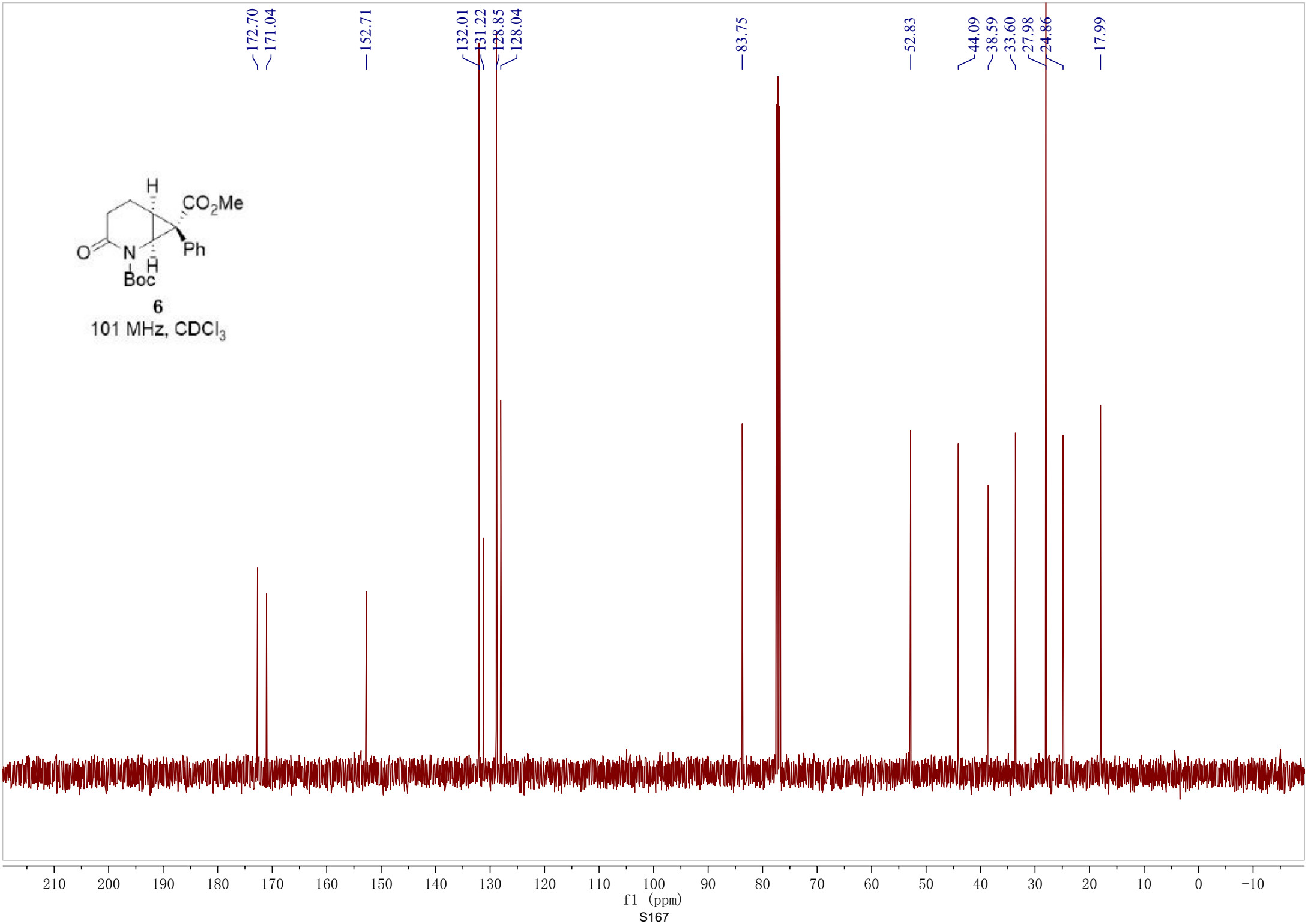
400 MHz, $CDCl_3$


171.88
165.38
149.98
142.63
137.80
134.59
134.47
128.87
128.15
127.83
126.84
83.71
61.46
52.63
49.18
43.23
28.01
14.26
Ph
CO2Et
O
N
Boc
11
101 MHz, CDCl3
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)

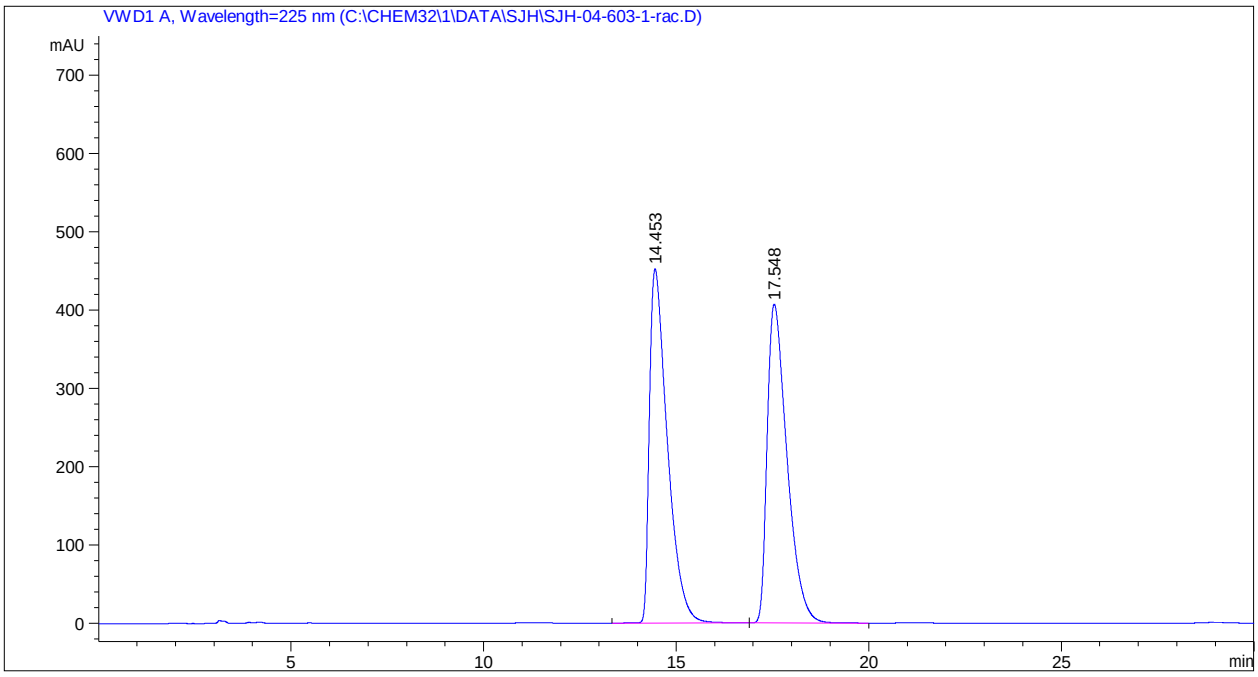


6

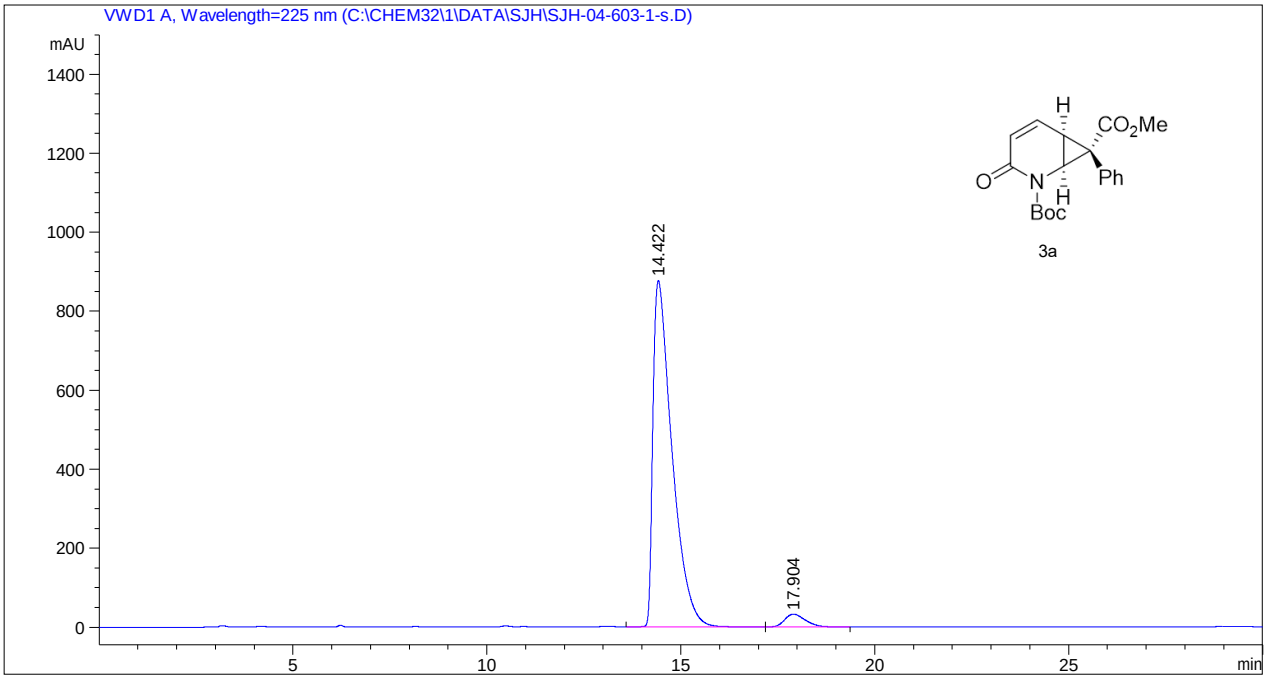
400 MHz, $CDCl_3$


172.70
171.04
152.71
132.01
131.22
128.85
128.04
83.75
52.83
44.09
38.59
33.60
27.98
24.86
17.99
H
CO2Me
O
N
Ph
H
Boc
6
101 MHz, CDCl3
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)

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 95/5, flow rate = 1.0 mL/min, λ= 225 nm

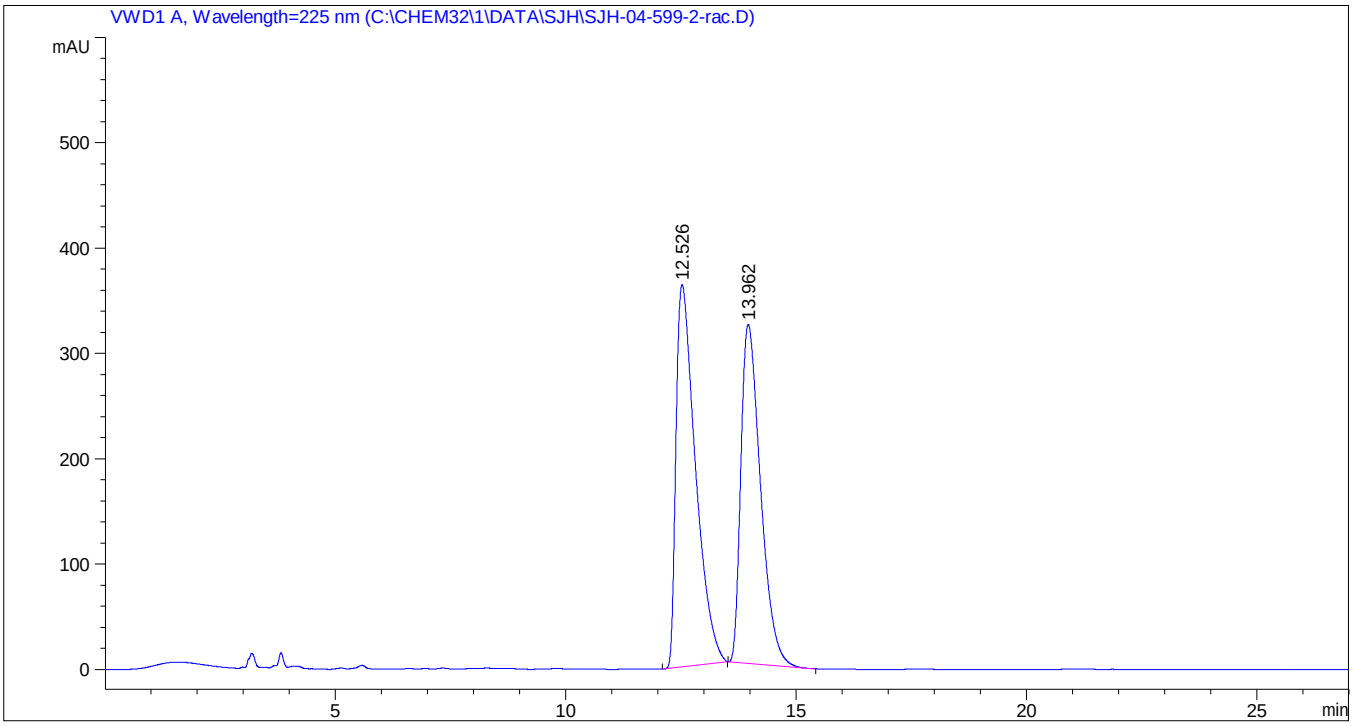


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.453	MM	0.5398	1.46504e4	452.36029	50.1466
2	17.548	MM	0.5969	1.45648e4	406.69696	49.8534

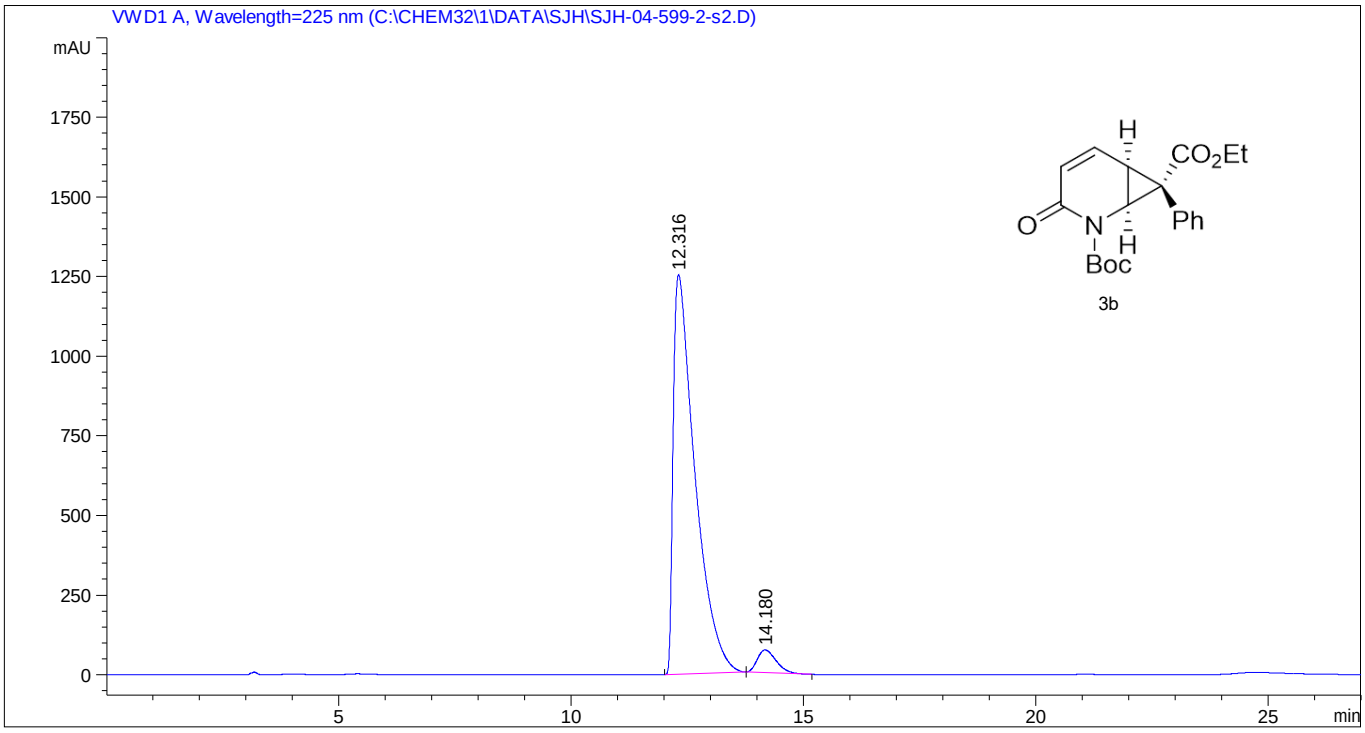


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.422	BB	0.5061	2.99153e4	876.68182	96.1688
2	17.904	BB	0.5619	1191.77148	32.42045	3.8312

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 95/5, flow rate = 1.0 mL/min, λ= 225 nm

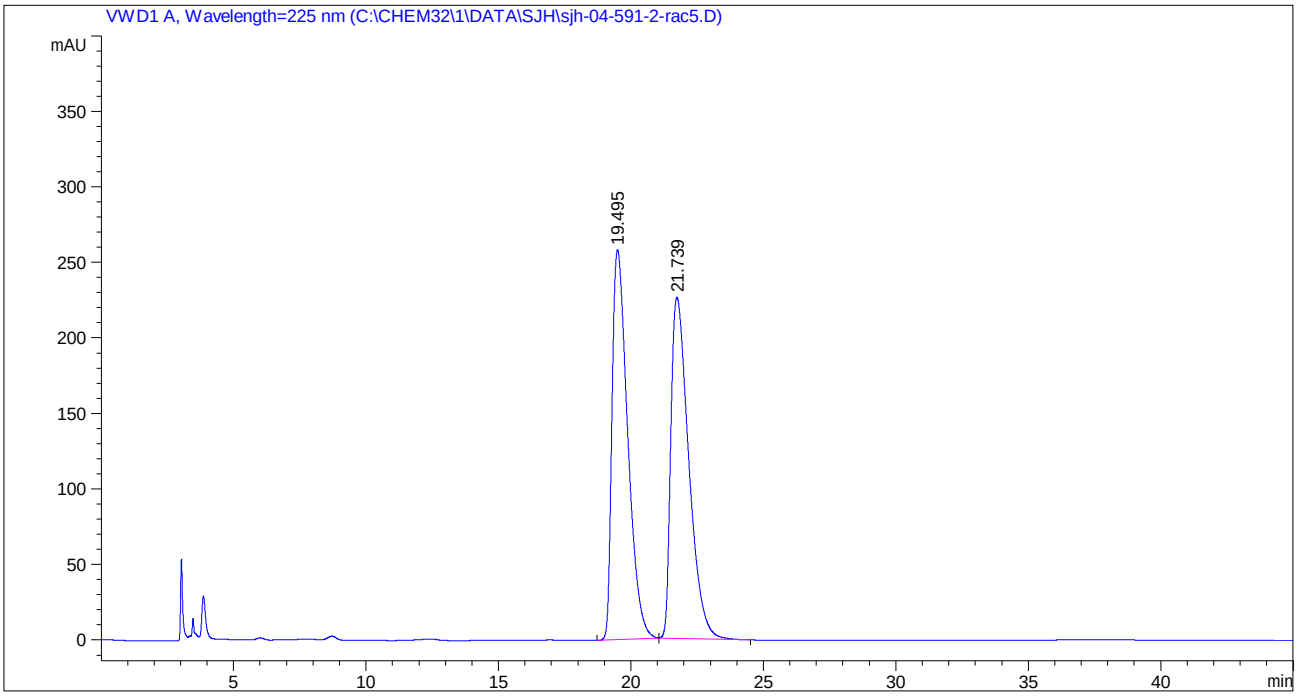


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.526	MM	0.4905	1.06739e4	362.71918	52.7604
2	13.962	MM	0.4951	9557.00098	321.74789	47.2396

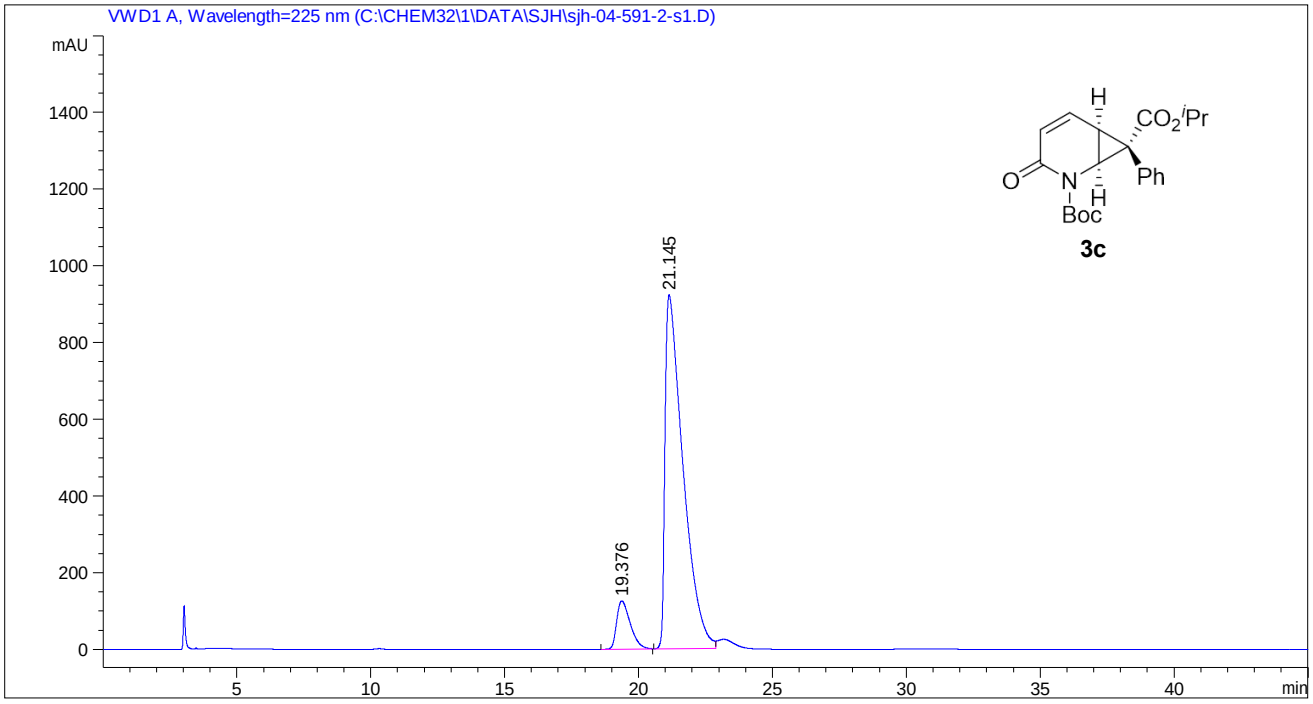


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.316	MM	0.5410	4.06711e4	1253.03271	95.2441
2	14.180	MM	0.4723	2030.84338	71.65865	4.7559

Daicel Chiralpak IA column, n-hexane/i-PrOH = 99/1, flow rate = 1.0 mL/min, λ= 225 nm

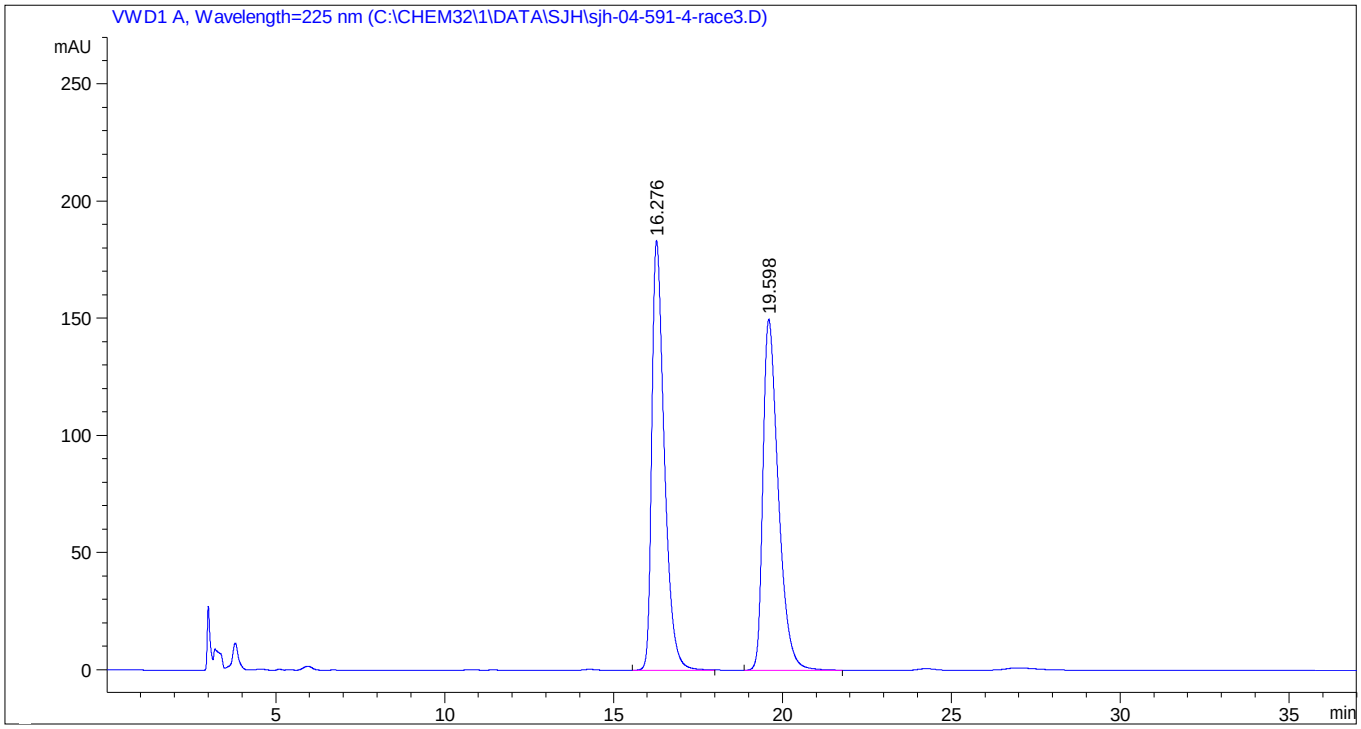


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.495	MM	0.6853	1.06142e4	258.13834	49.9752
2	21.739	MM	0.7846	1.06247e4	225.69656	50.0248

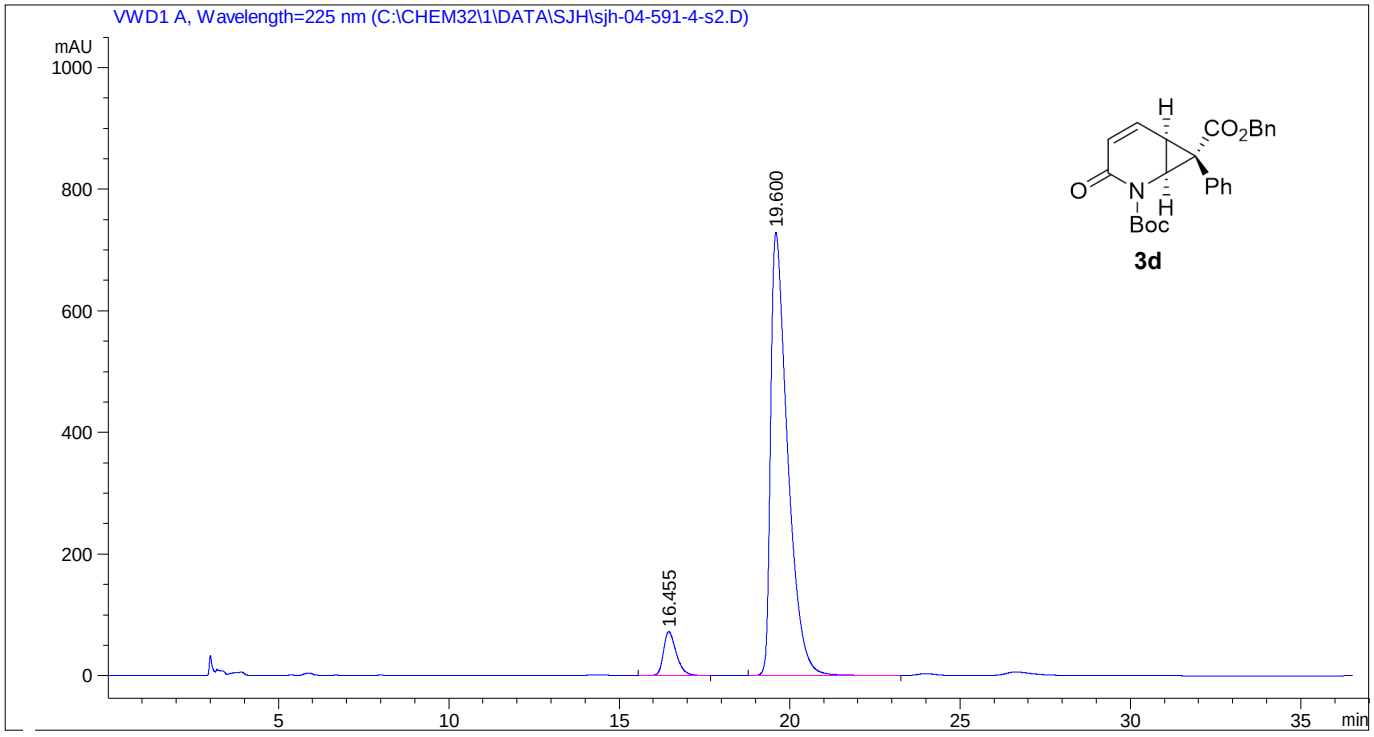


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.376	MM	0.5893	4455.73828	126.01668	9.3765
2	21.145	MM	0.7778	4.30647e4	922.80725	90.6235

Daicel Chiralpak IA column, n-hexane/i-PrOH = 95/5, flow rate = 1.0 mL/min, λ= 225 nm

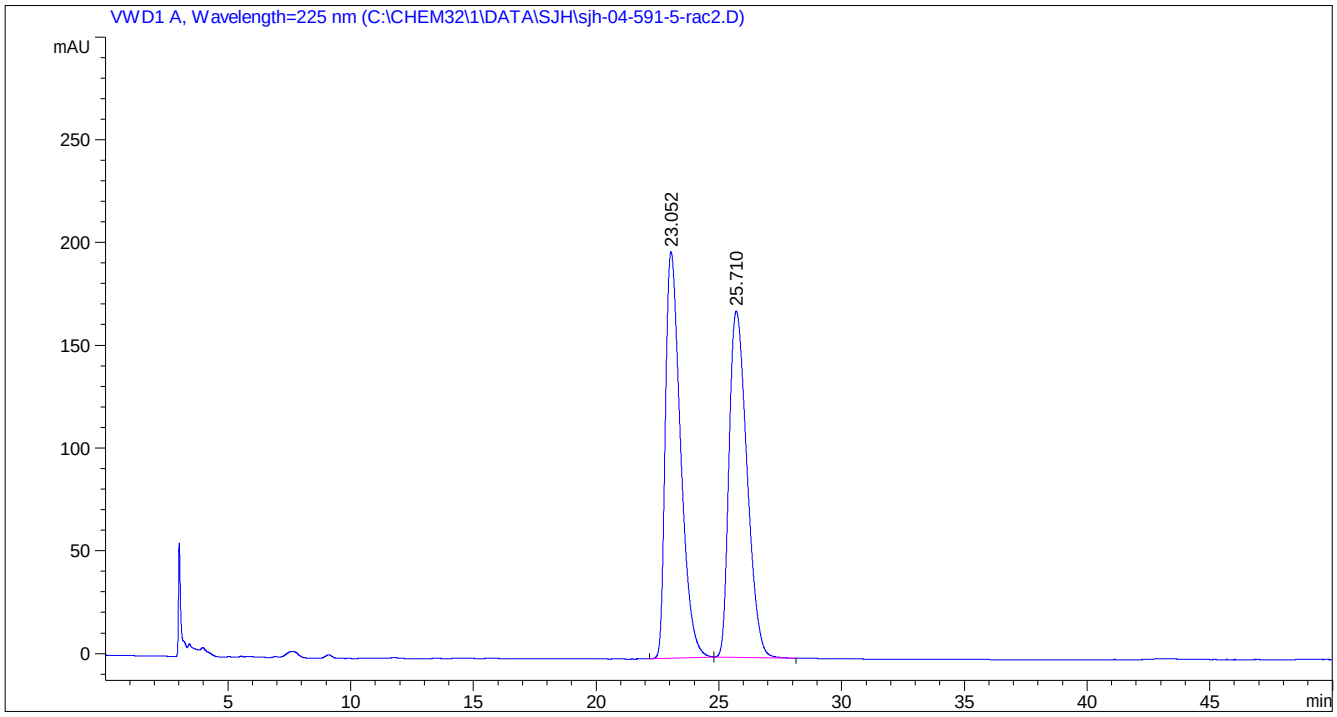


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.276	MM	0.4295	4726.71338	183.42010	49.9409
2	19.598	MM	0.5272	4737.90479	149.79068	50.0591

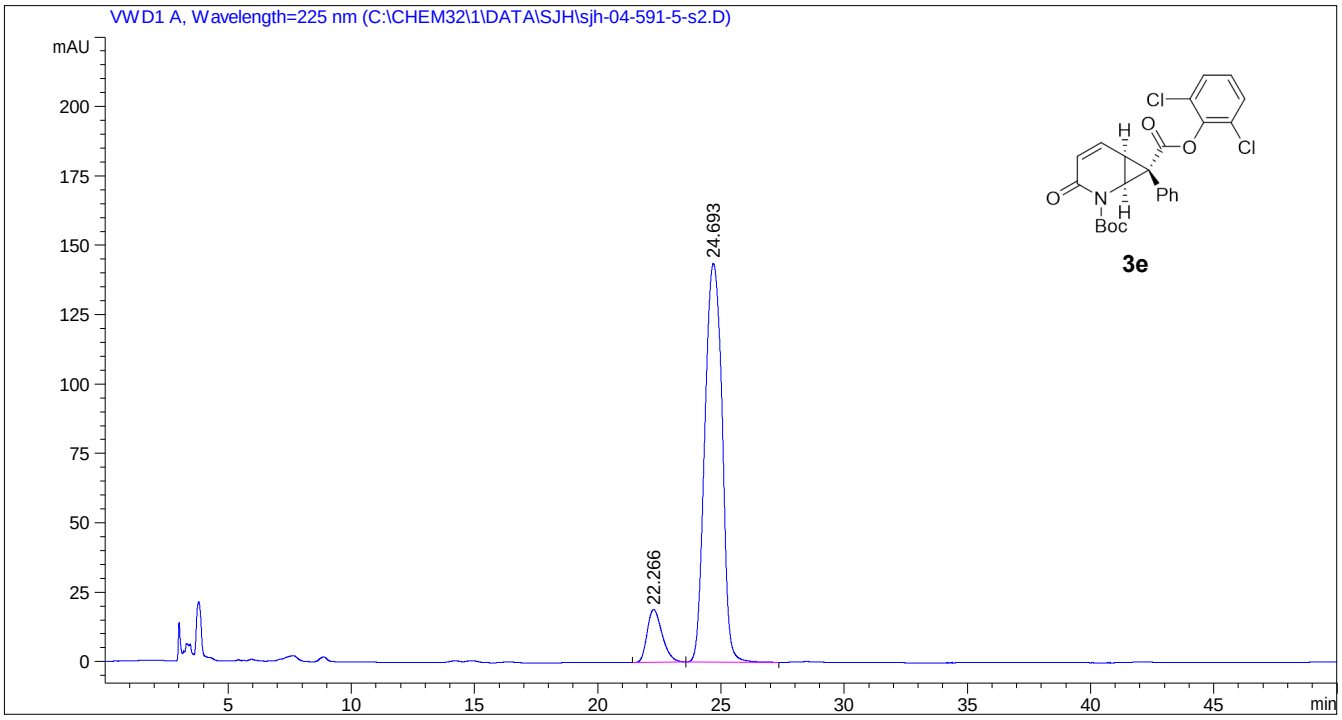


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.455	BB	0.3965	1890.60864	72.43559	6.9788
2	19.600	BB	0.5144	2.52002e4	728.76556	93.0212

Daicel Chiralpak IA column, n-hexane/i-PrOH = 97/3, flow rate = 1.0 mL/min, λ= 225 nm



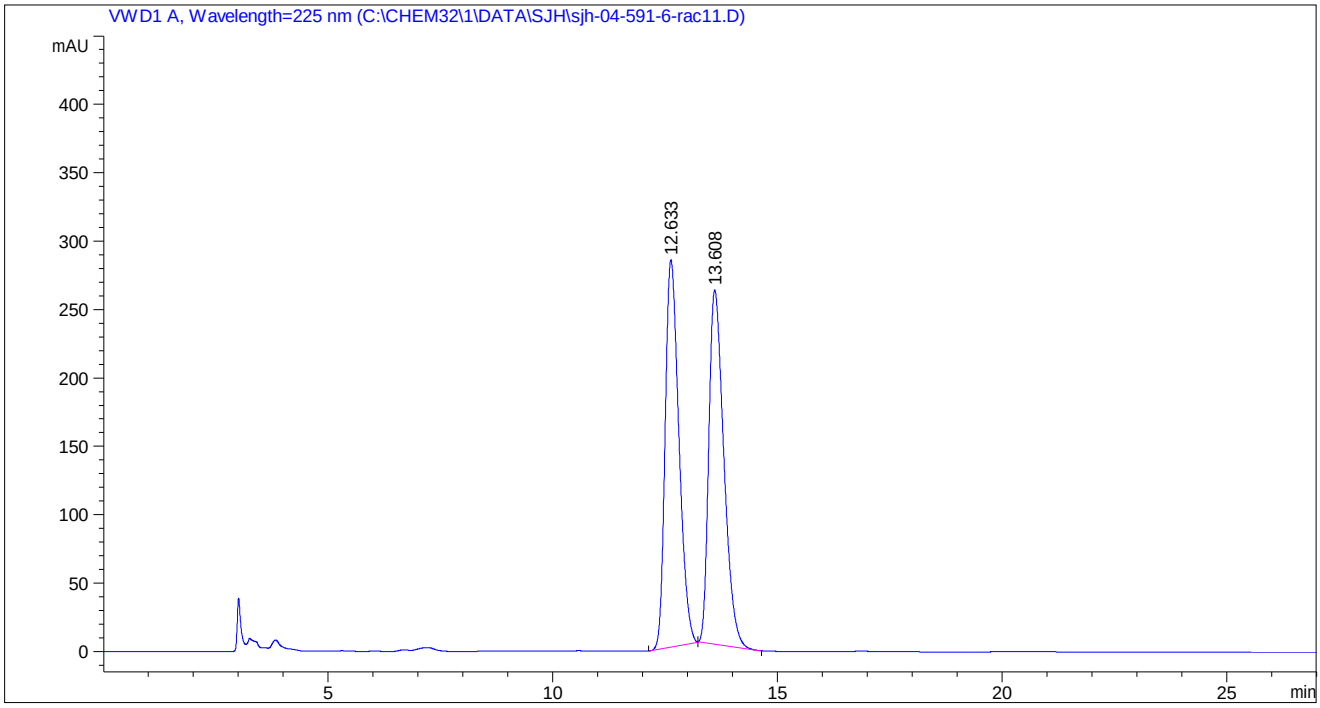
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.052	BB	0.6682	8531.91309	197.79977	49.9503
2	25.710	BB	0.8035	8548.90137	168.34212	50.0497



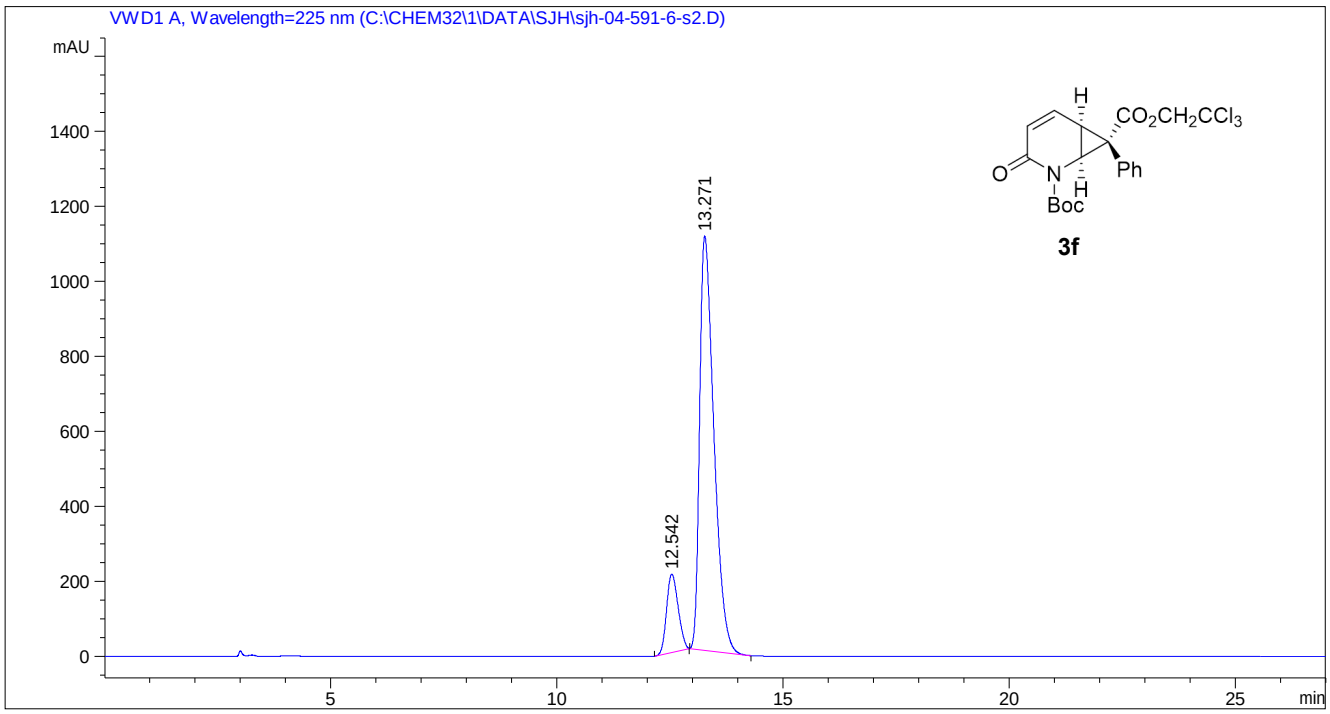
3e

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.266	BB	0.6520	805.72766	19.06608	10.3450
2	24.693	BB	0.8073	6982.86621	143.60544	89.6550

Daicel Chiralpak IA column, n-hexane/i-PrOH = 98/2, flow rate = 1.0 mL/min, λ= 225 nm

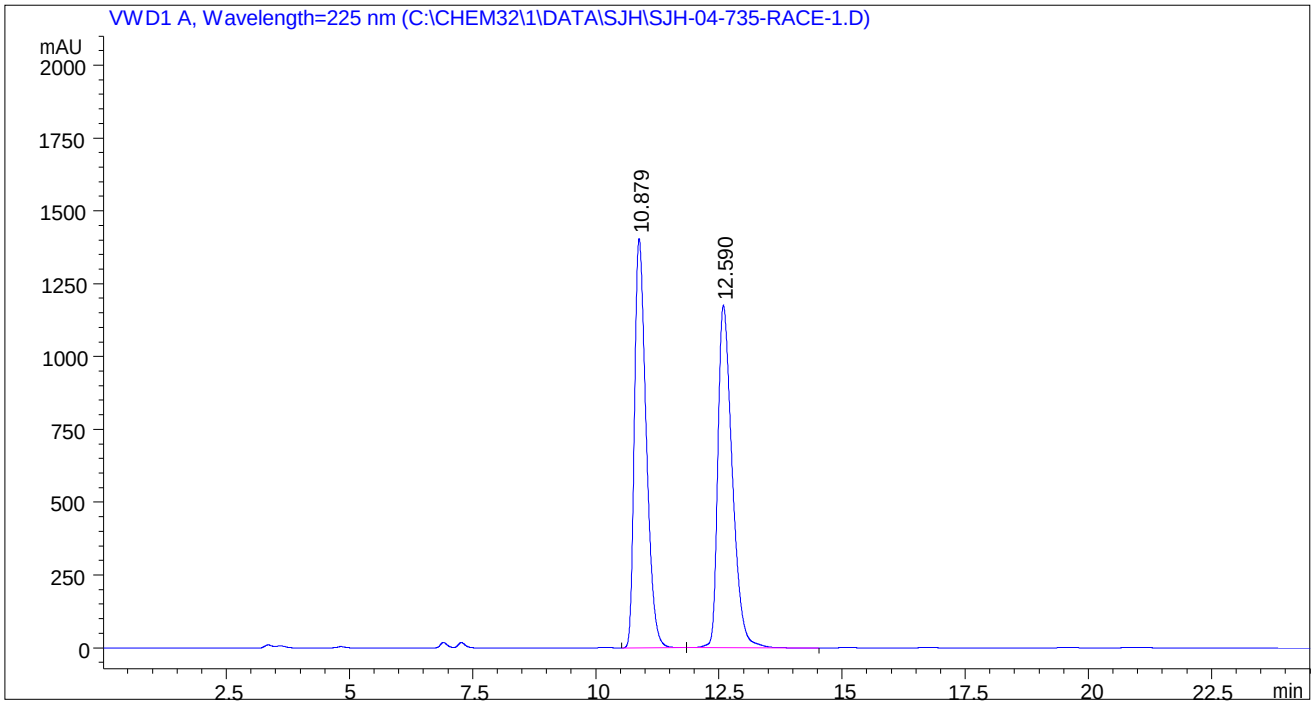


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.633	MM	0.3549	6025.06055	282.92834	50.0157
2	13.608	MM	0.3874	6021.27393	259.02838	49.9843

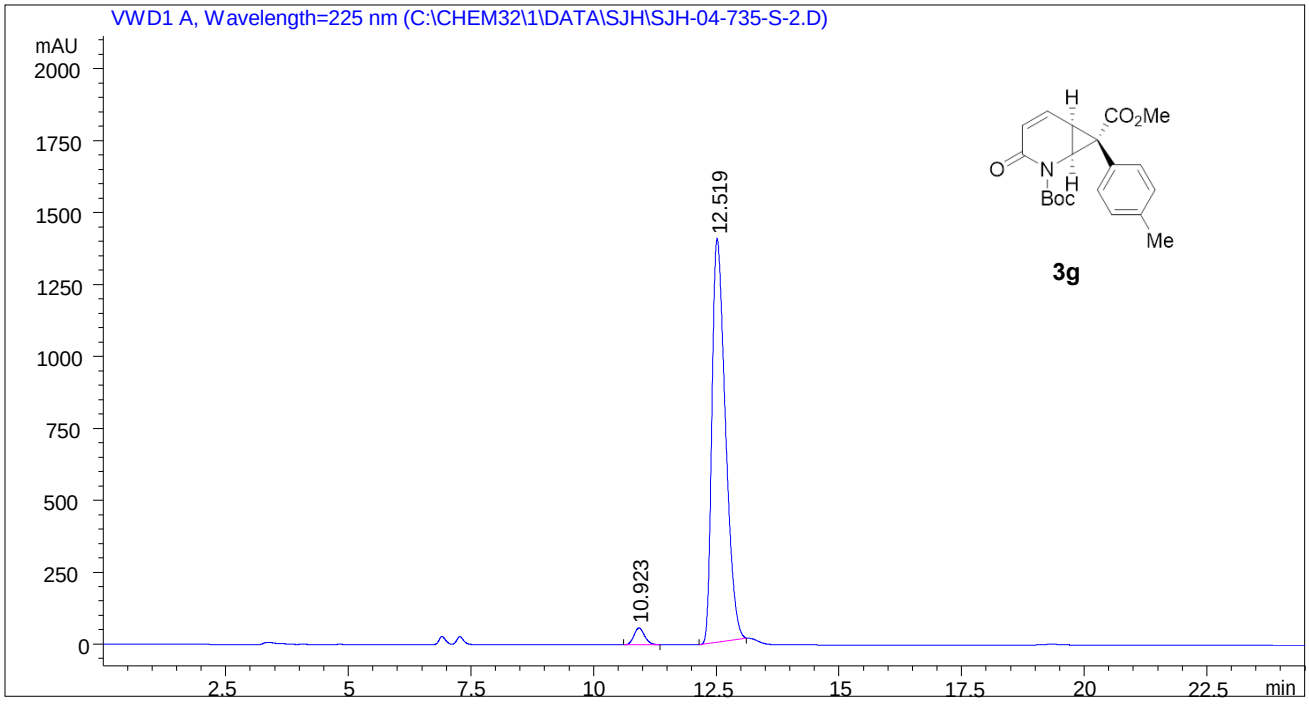


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.542	MM	0.2957	3713.64111	209.29031	13.3270
2	13.271	MM	0.3644	2.41520e4	1104.59241	86.6730

Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1 mL/min, λ = 225 nm

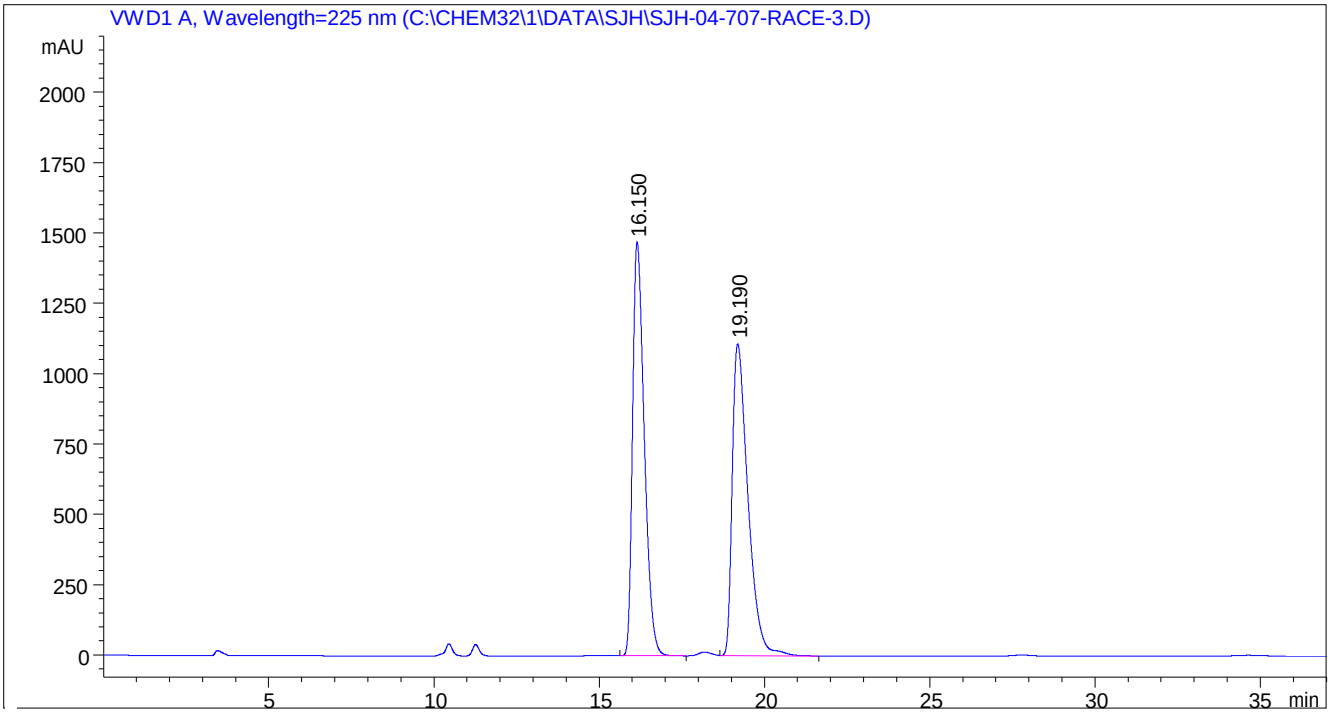


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.879	BB	0.2561	2.33820e4	1405.15918	49.5005
2	12.590	BB	0.3098	2.38538e4	1175.34033	50.4995

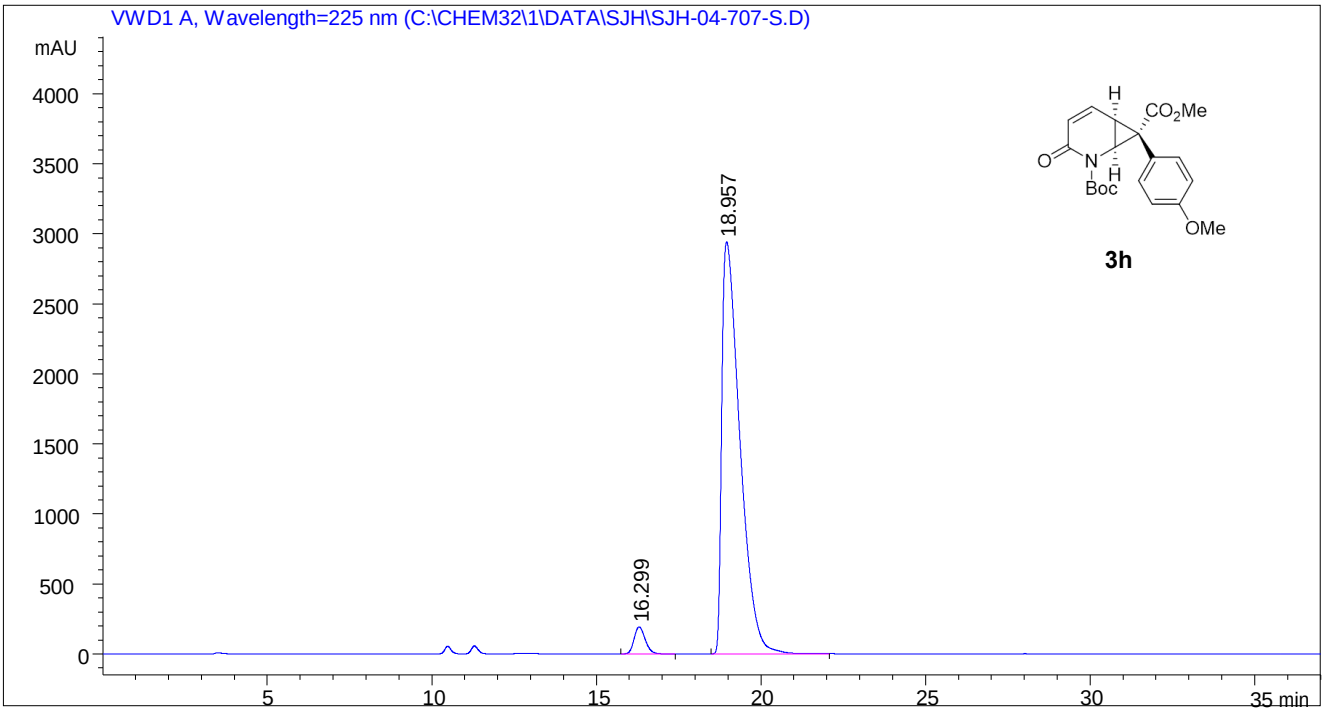


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.923	MM	0.2529	890.82404	58.71807	3.2080
2	12.519	MM	0.3194	2.68782e4	1402.57605	96.7920

Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1 mL/min, λ = 225 nm

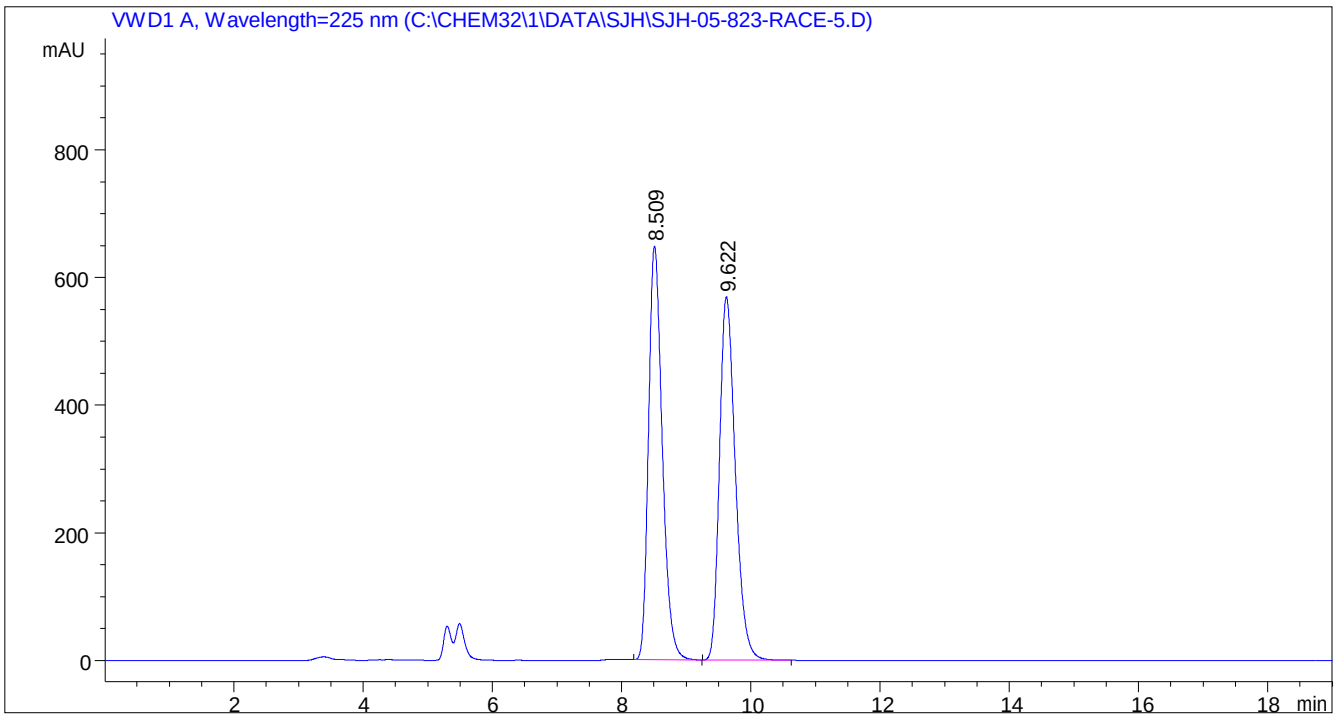


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.150	BB	0.3814	3.63522e4	1470.77710	49.7827
2	19.190	MM	0.5514	3.66695e4	1108.42358	50.2173

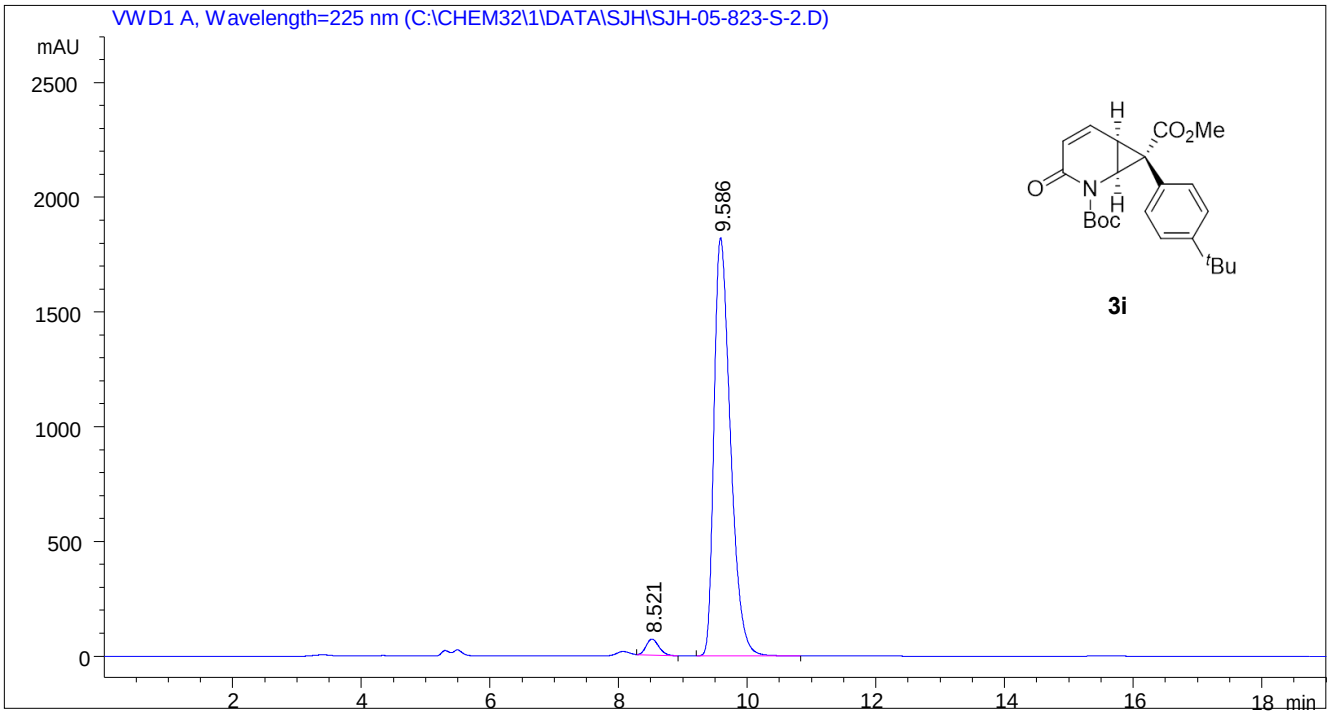


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.299	MM	0.3880	4502.83057	193.39685	3.8502
2	18.957	MM	0.6371	1.12448e5	2941.58960	96.1498

Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1 mL/min, λ = 225 nm



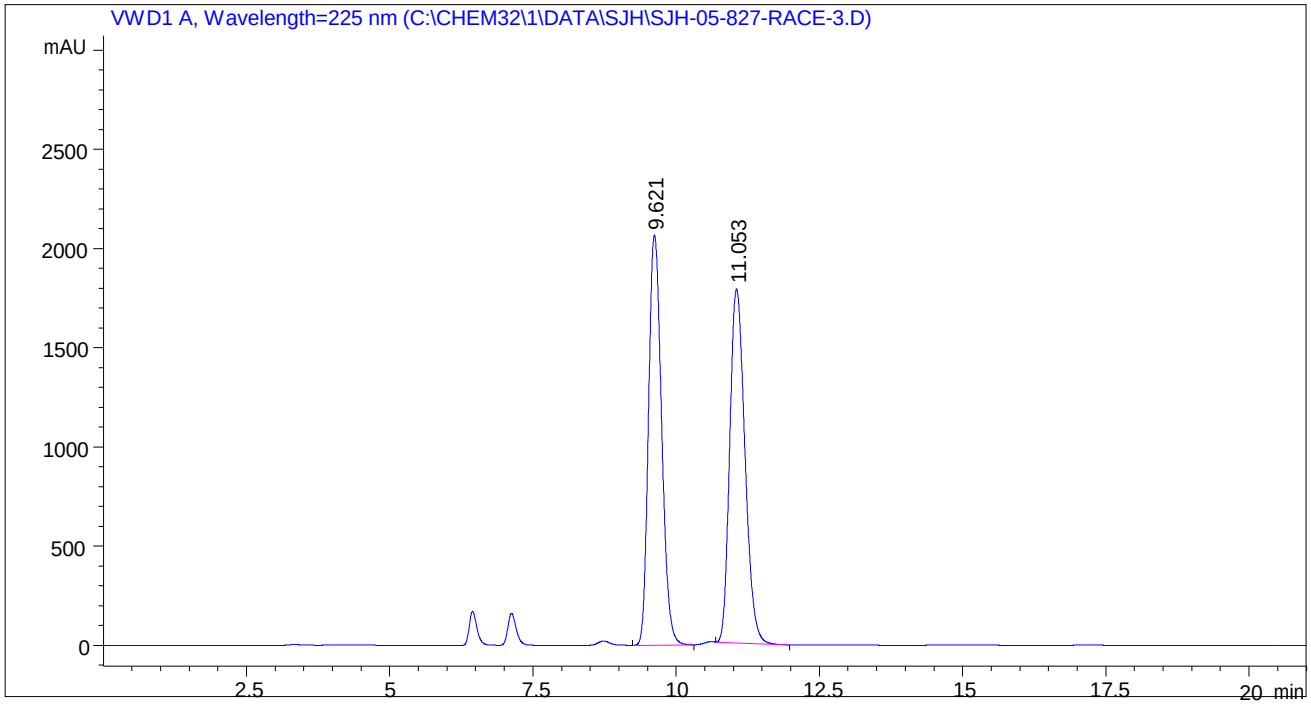
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.509	BB	0.2275	9577.28320	647.80591	49.6915
2	9.622	MM	0.2839	9696.18848	569.31964	50.3085



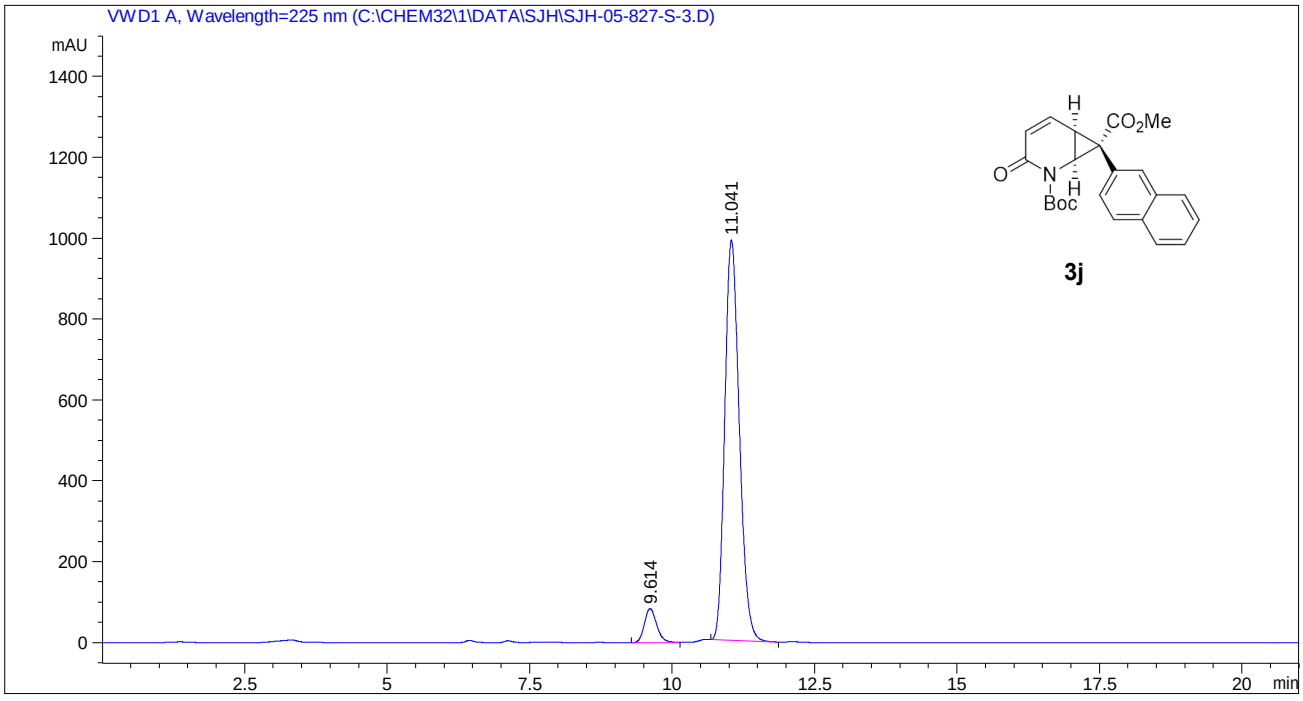
3i

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.521	MM	0.2300	968.63684	70.17899	2.9057
2	9.586	MM	0.2960	3.23671e4	1822.38806	97.0943

Daicel Chiralpak IE column,n-hexane/i-PrOH = 70/30, flow rate = 1mL/min,λ = 225 nm



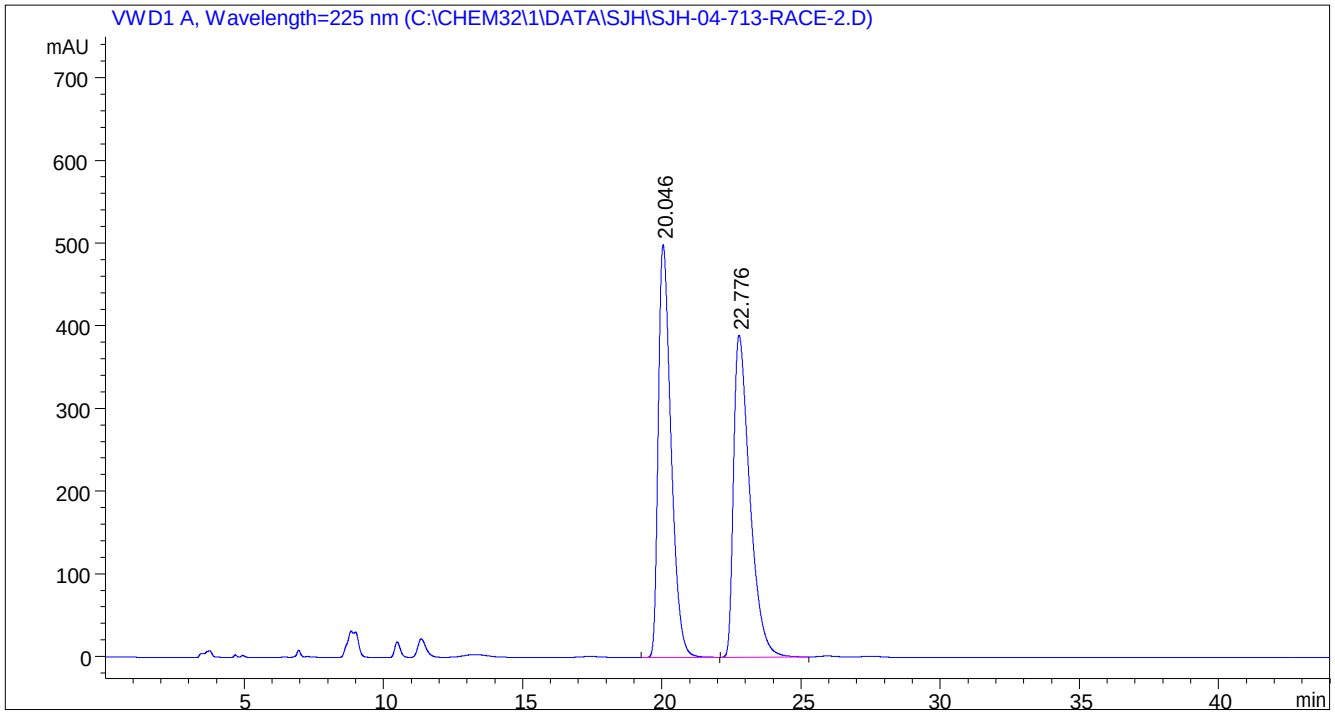
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.621	BB	0.2479	3.27844e4	2068.35645	49.9231
2	11.053	MM	0.3069	3.28853e4	1785.64282	50.0769



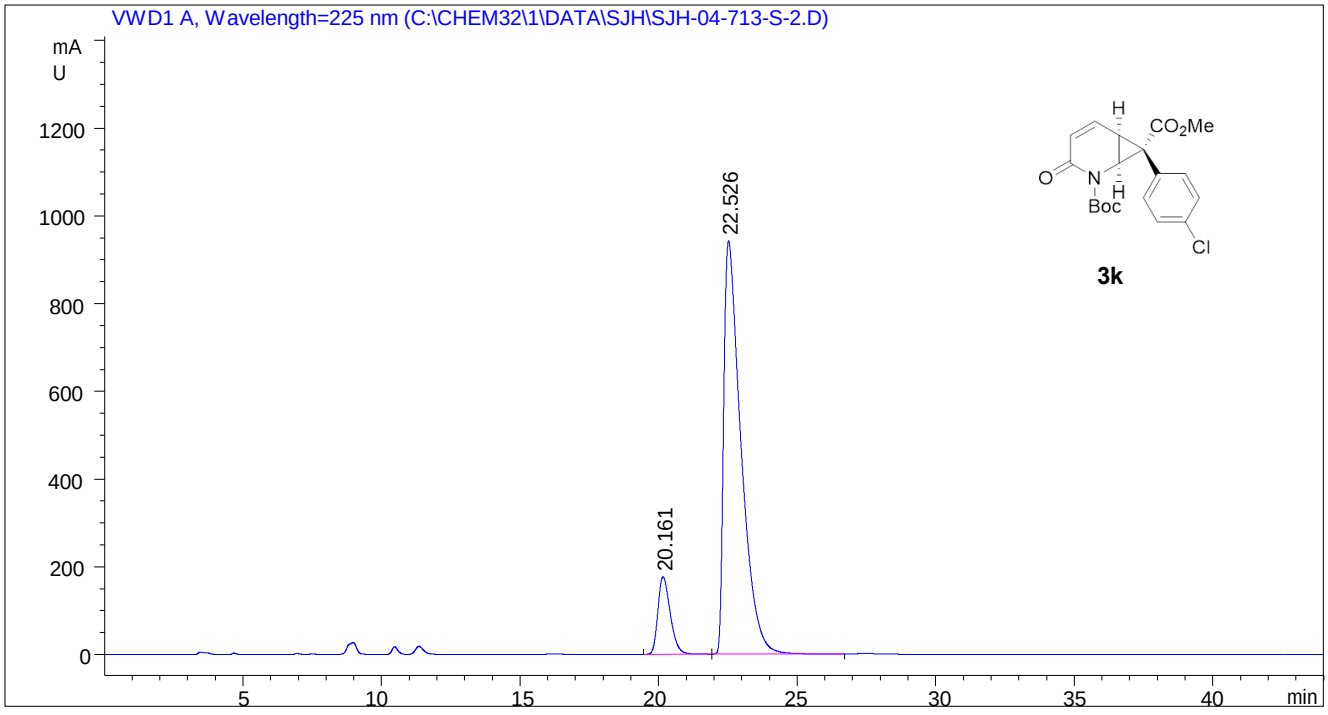
3j

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.614	MM	0.2517	1276.12012	84.49329	6.7557
2	11.041	MM	0.2966	1.76134e4	989.88690	93.2443

Daicel Chiralpak IE column, n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ = 225 nm

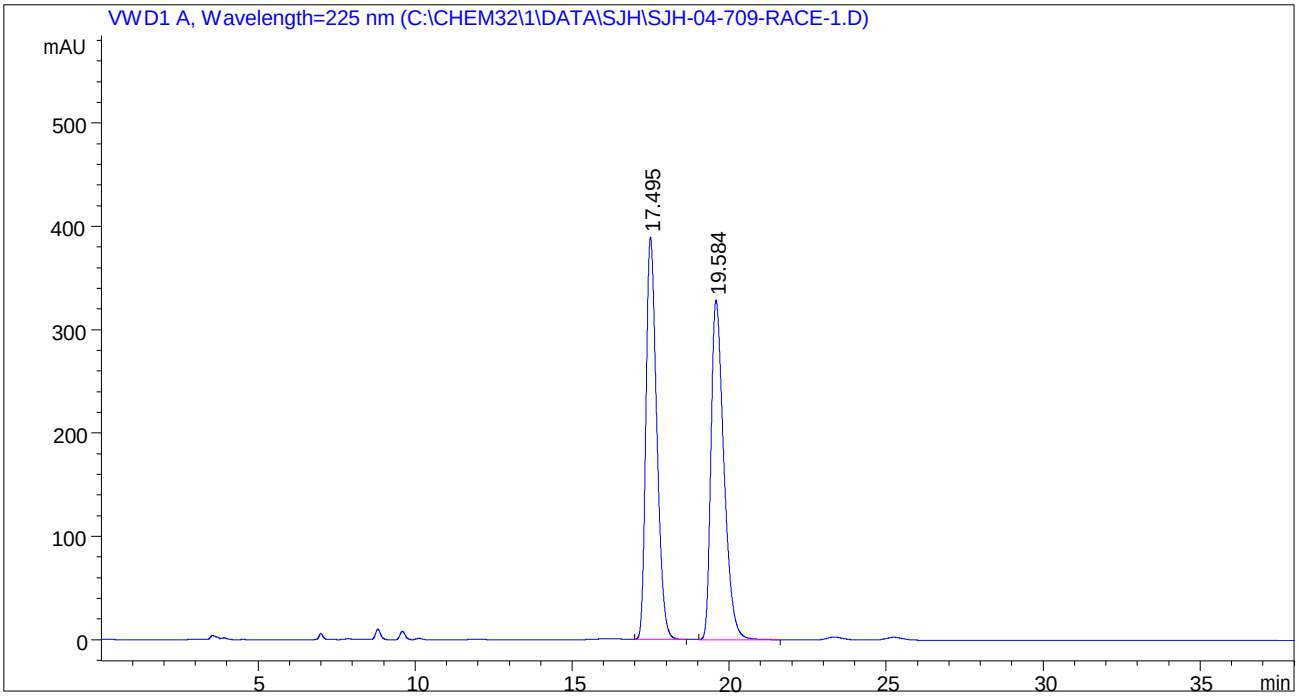


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.046	BB	0.4872	1.58764e4	498.92899	50.1210
2	22.776	BB	0.6131	1.57997e4	389.63635	49.8790

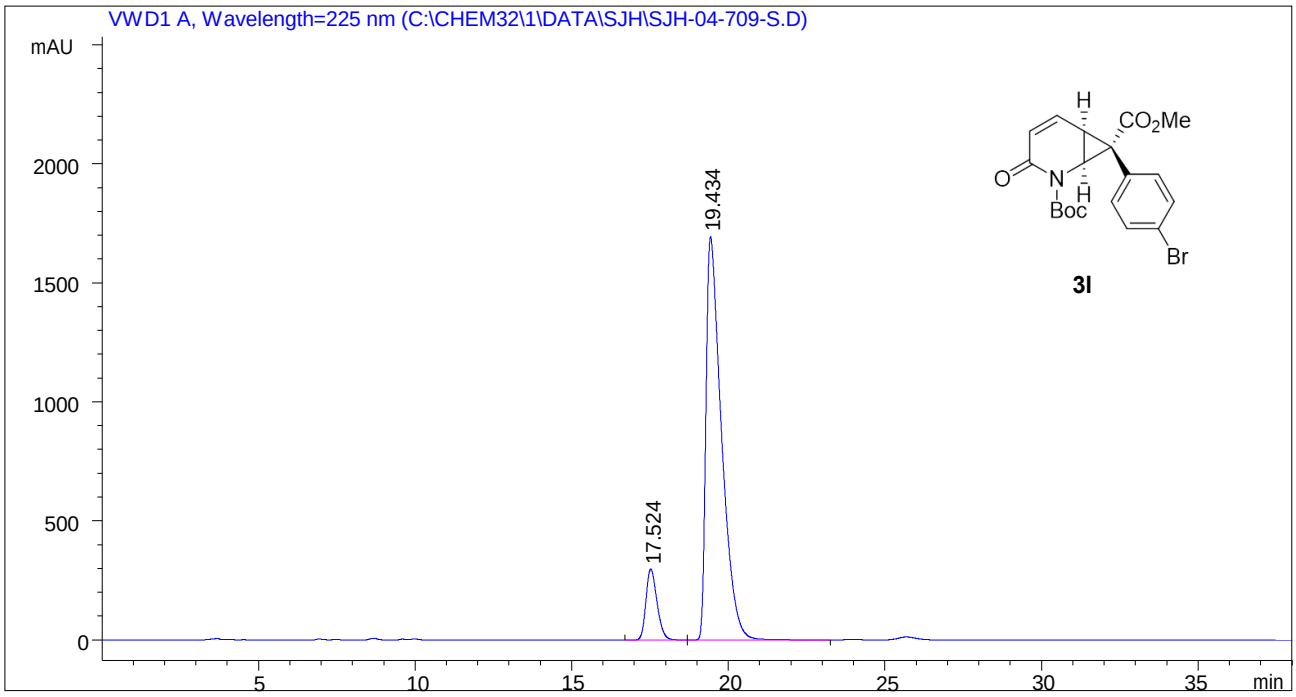


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.161	BB	0.4777	5473.23682	176.53435	11.7887
2	22.526	BB	0.6450	4.09547e4	942.45776	88.2113

Daicel Chiralpak IE column, n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ = 225 nm

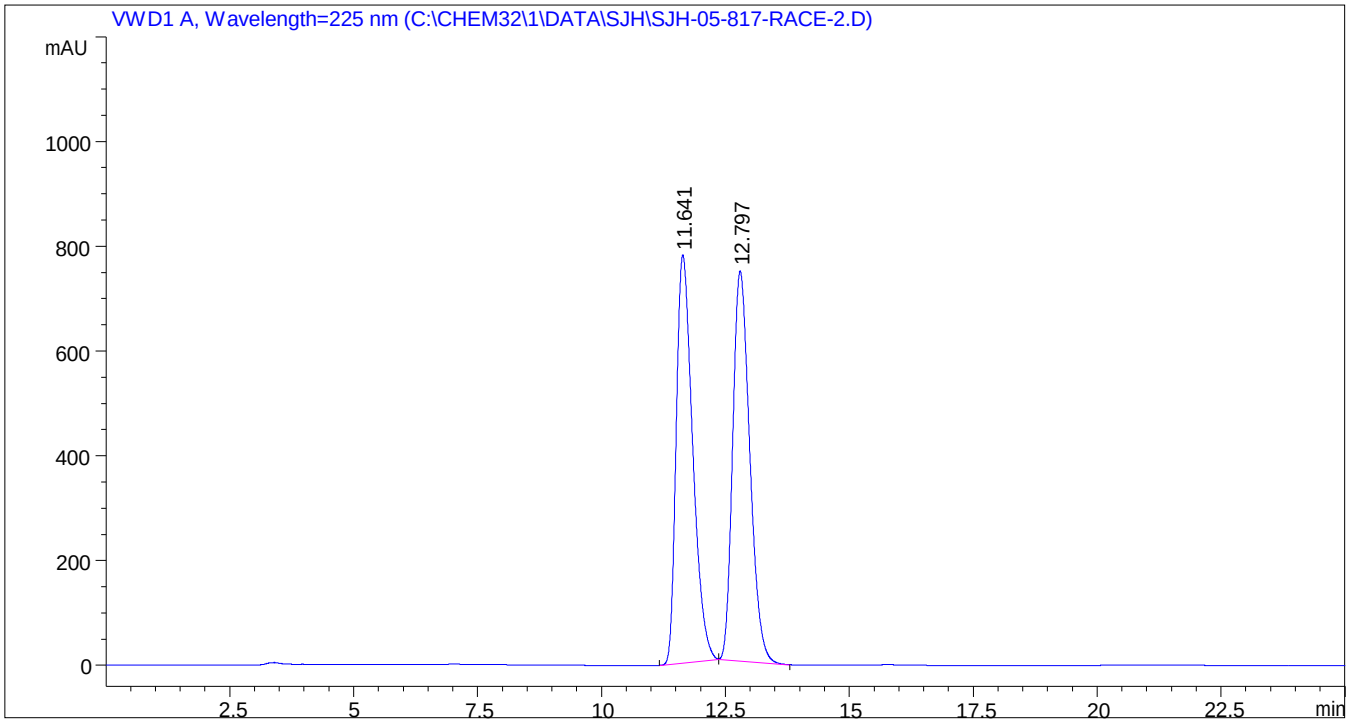


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.495	BB	0.3706	9326.06738	389.08344	49.7874
2	19.584	MM	0.4771	9405.70703	328.55307	50.2126

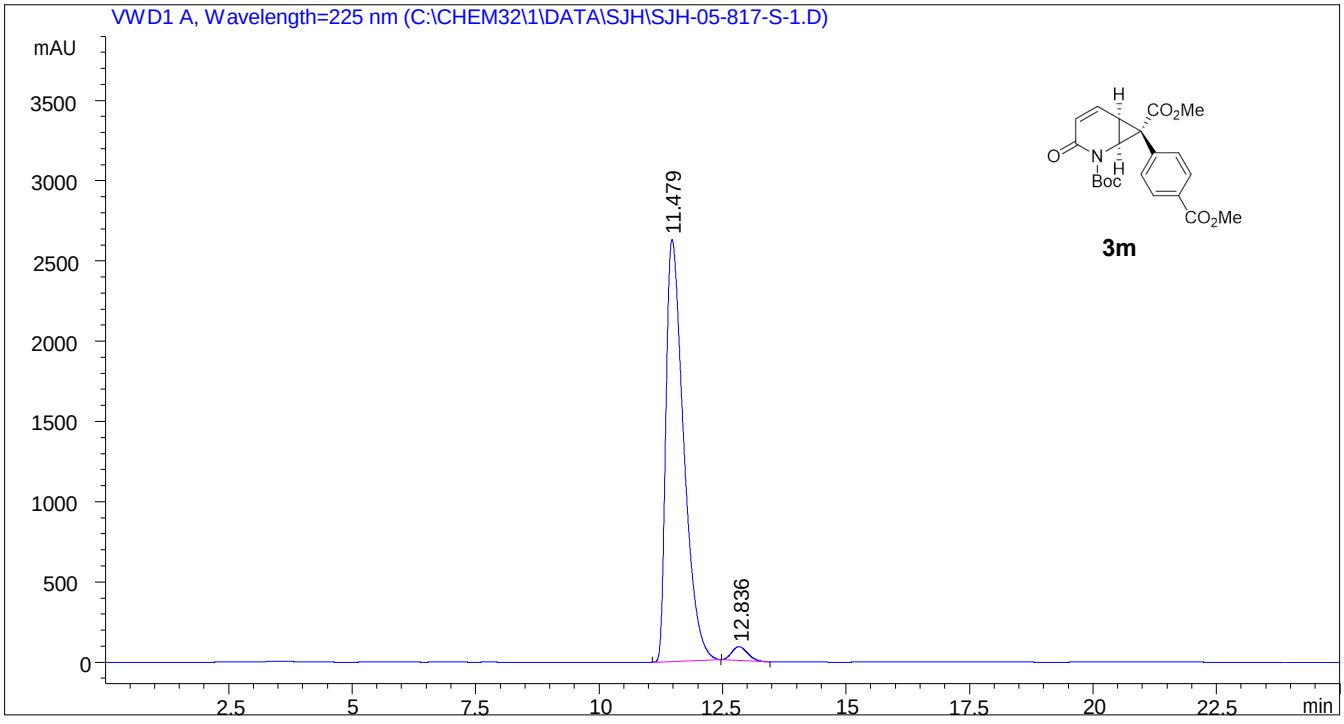


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.524	BB	0.3792	7320.87549	298.43396	11.1417
2	19.434	BB	0.5112	5.83863e4	1693.70227	88.8583

Daicel Chiralpak IE column, n-hexane/i-PrOH = 60/40, flow rate = 1mL/min, λ = 225 nm

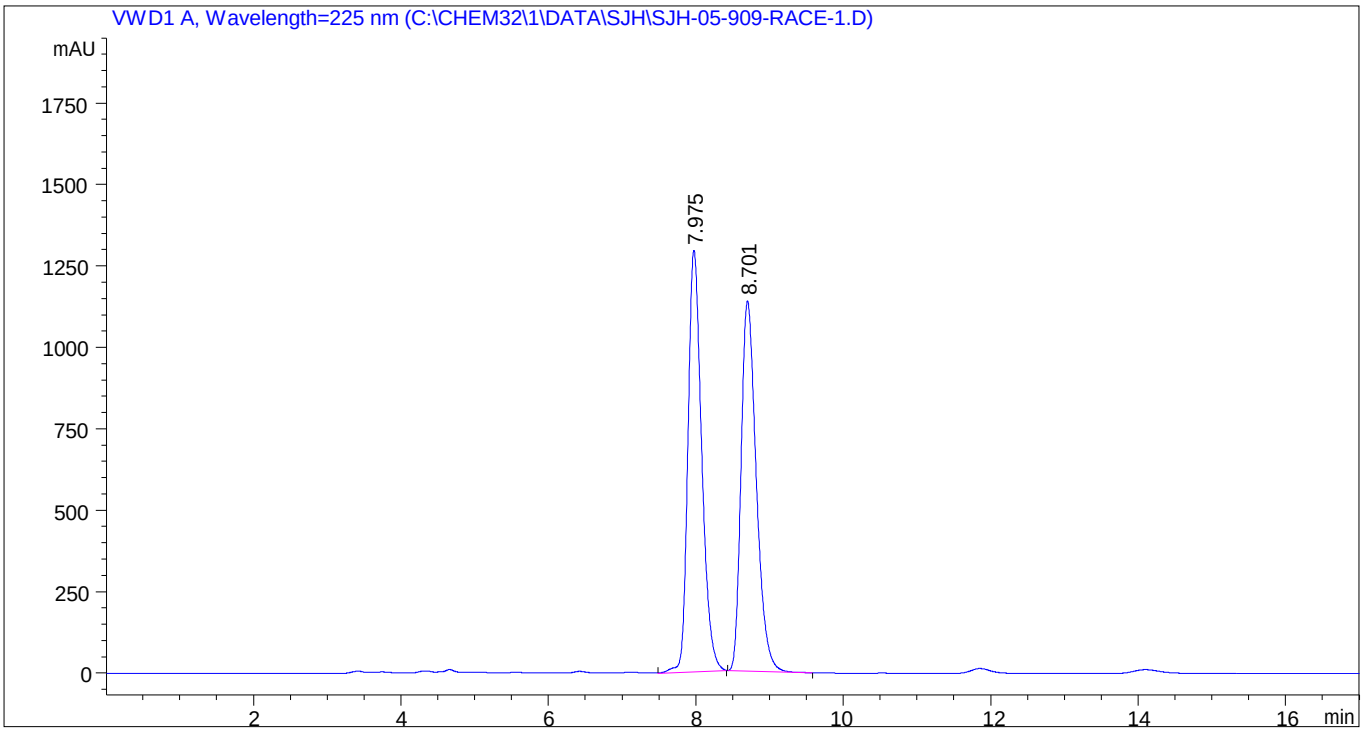


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.641	MM	0.3839	1.79409e4	778.91870	50.1297
2	12.797	MM	0.3996	1.78481e4	744.46631	49.8703

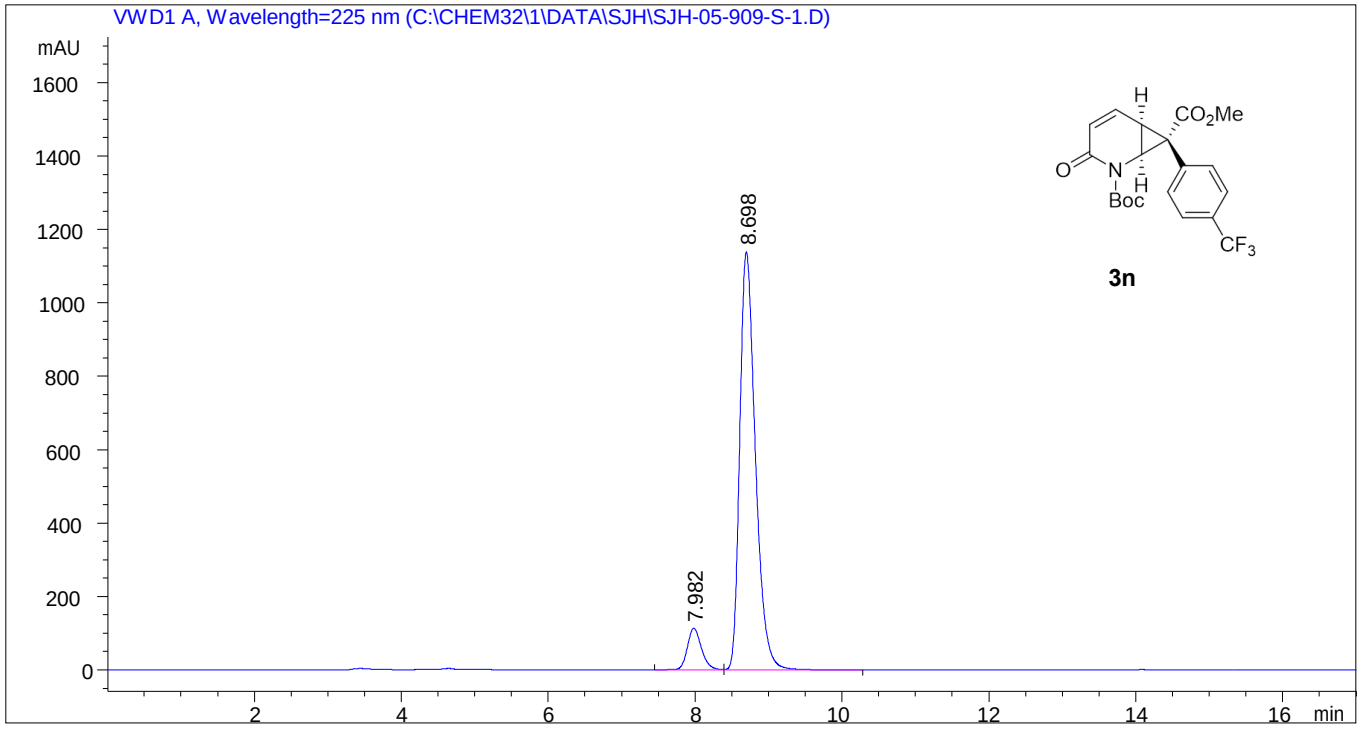


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.479	MM	0.4173	6.58148e4	2628.38281	97.1457
2	12.836	MM	0.3732	1933.75476	86.35349	2.8543

Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1 mL/min, λ = 225 nm

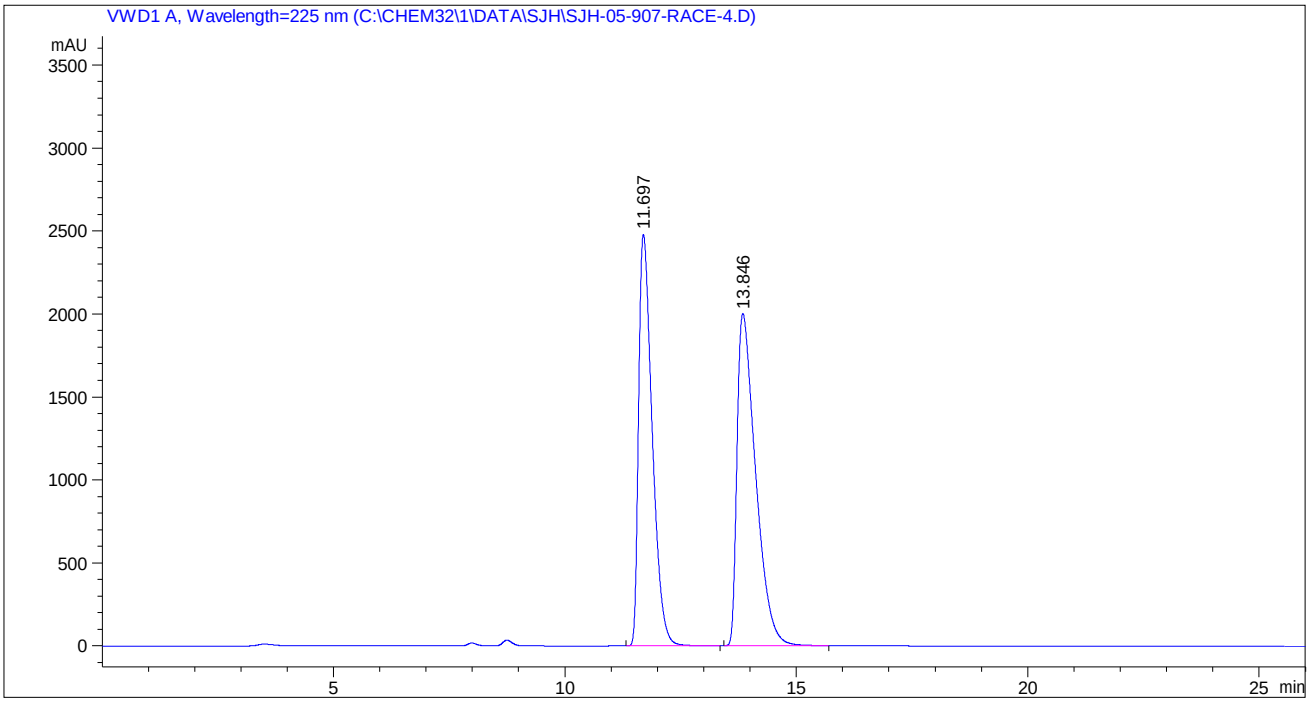


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.975	MM	0.2170	1.68543e4	1294.27600	50.8183
2	8.701	MM	0.2391	1.63115e4	1137.03247	49.1817

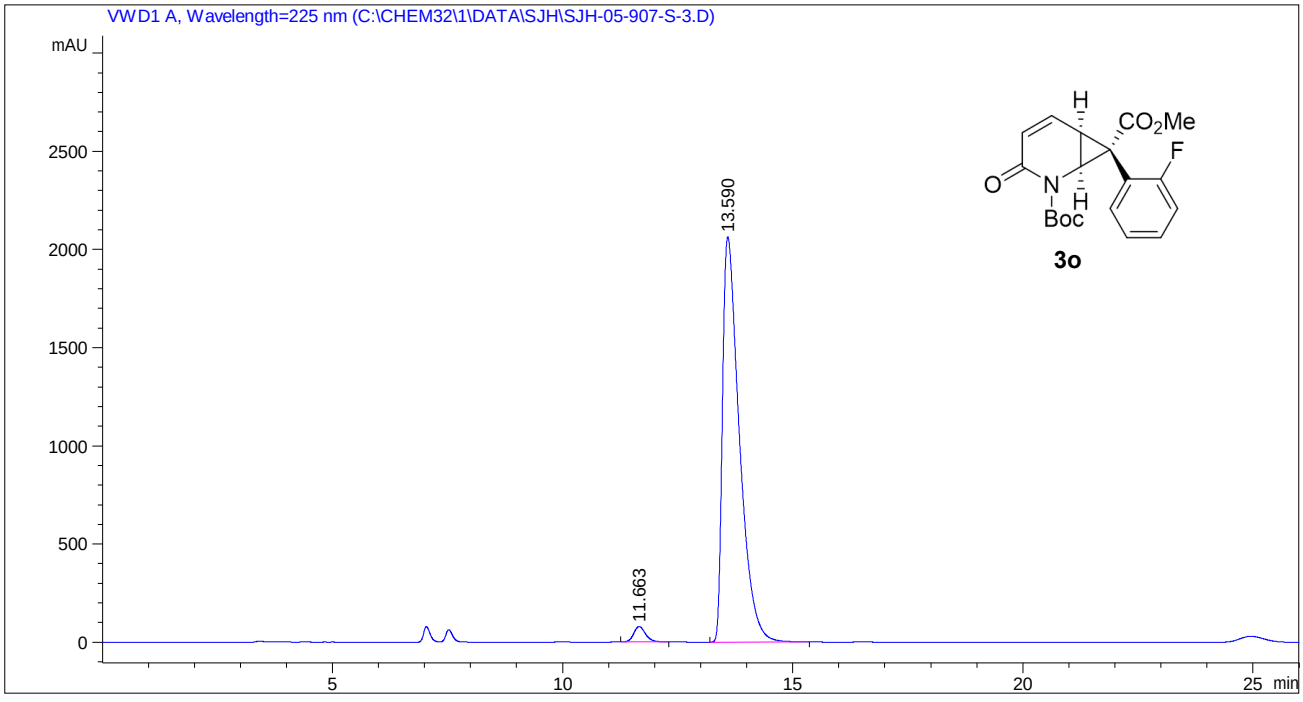


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.982	BV	0.2061	1527.15942	113.44385	8.3106
2	8.698	VB	0.2267	1.68488e4	1138.22668	91.6894

Daicel Chiralpak IE column, n-hexane/i-PrOH = 80/20, flow rate = 1mL/min, λ = 225 nm

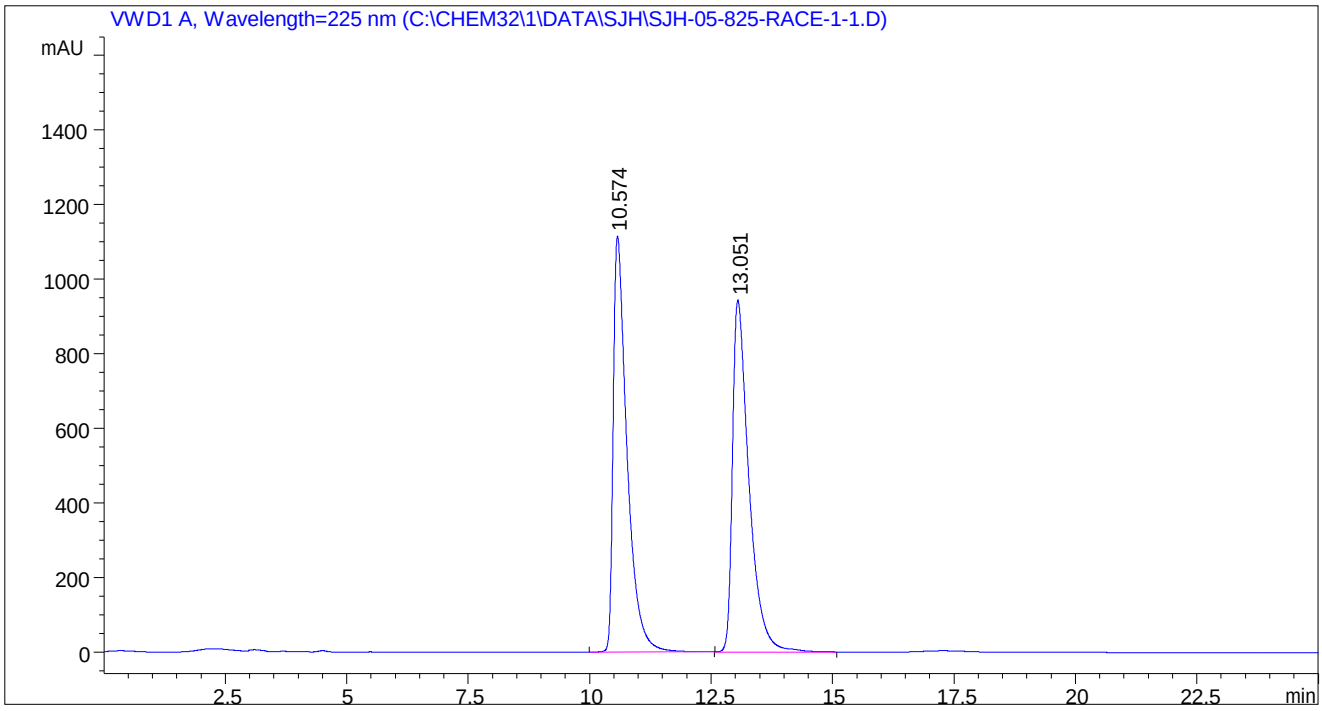


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.697	MM	0.3398	5.05625e4	2479.85132	47.4679
2	13.846	MM	0.4656	5.59567e4	2003.00562	52.5321

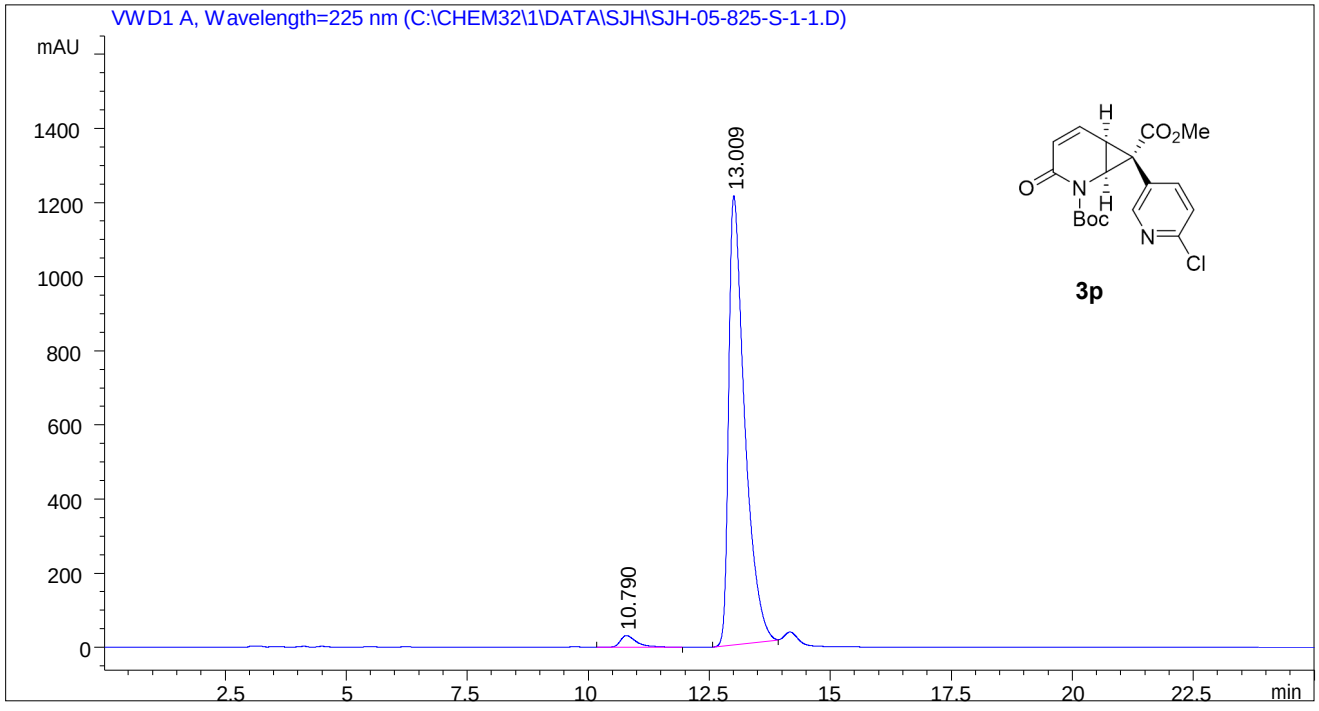


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.663	MM	0.2986	1411.80225	78.81175	2.6032
2	13.590	MM	0.4263	5.28208e4	2064.96338	97.3968

Daicel Chiralpak IA column, n-hexane/i-PrOH = 90/10, flow rate = 1mL/min, λ = 225 nm

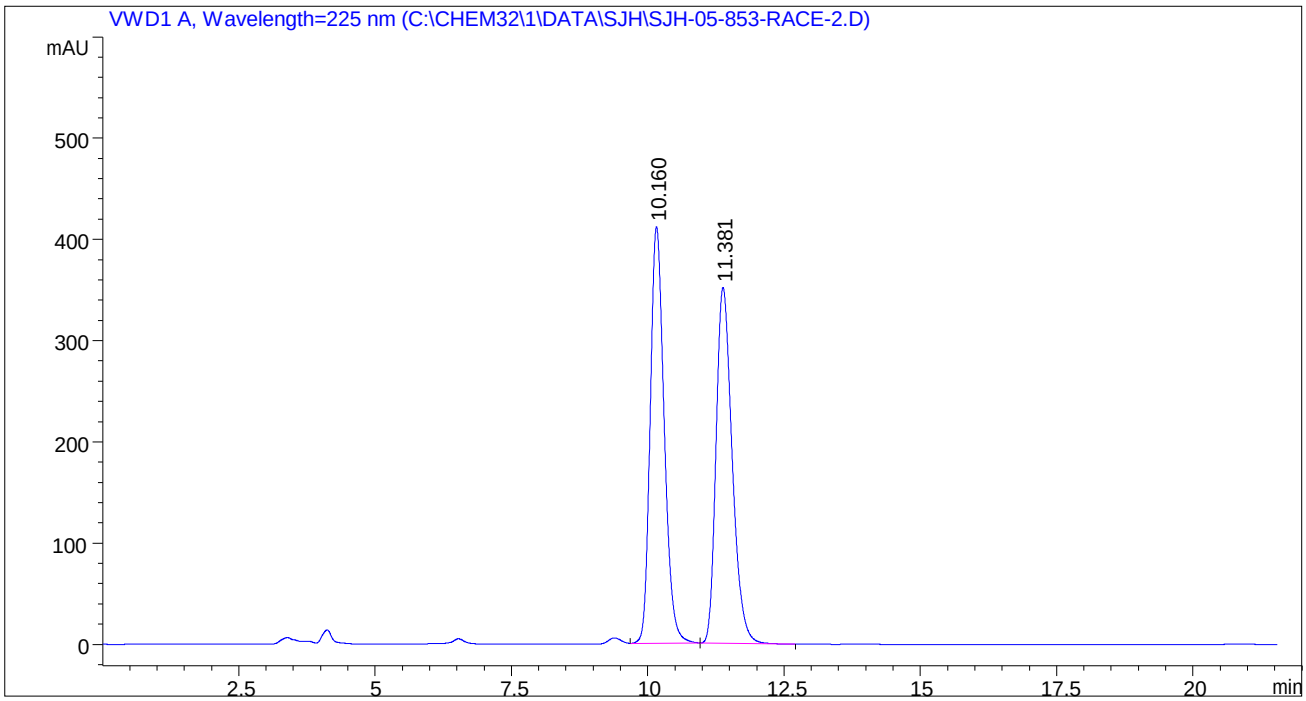


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.574	BB	0.2915	2.21357e4	1115.62512	49.8402
2	13.051	MM	0.3936	2.22776e4	943.40997	50.1598

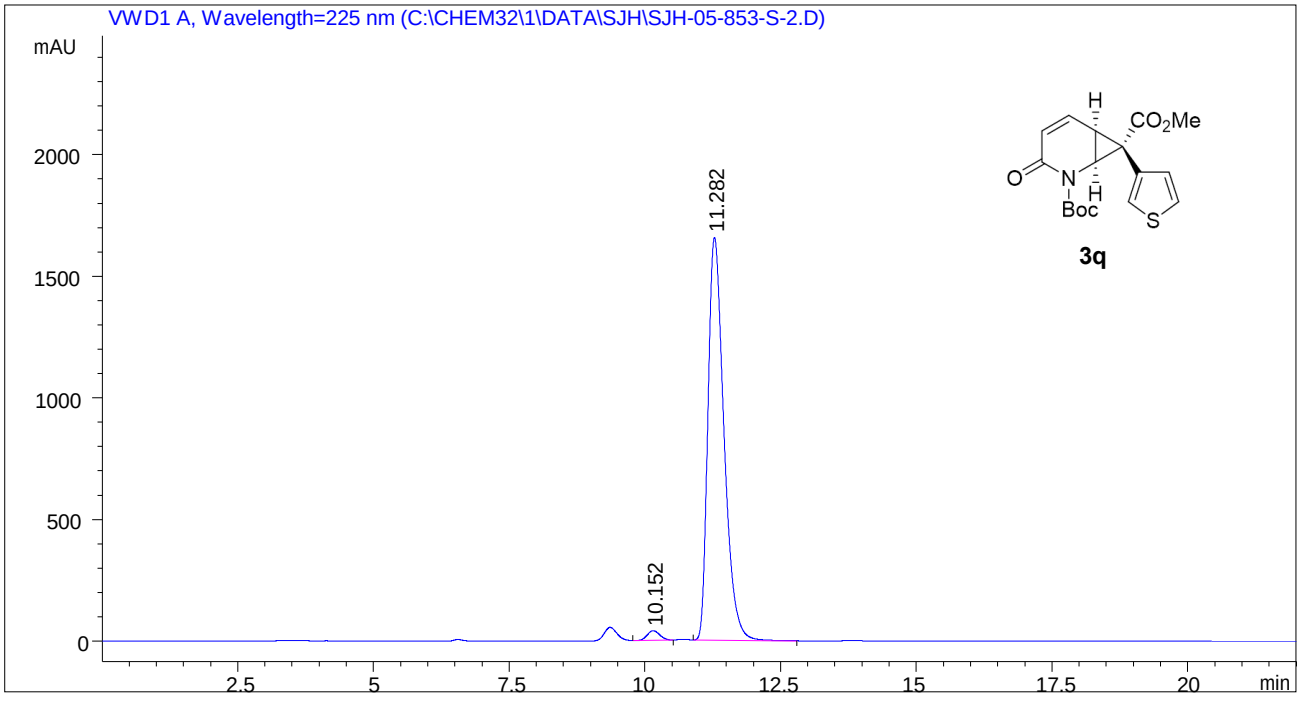


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.790	BB	0.3418	724.75726	31.56922	2.5283
2	13.009	MM	0.3841	2.79405e4	1212.24292	97.4717

Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm



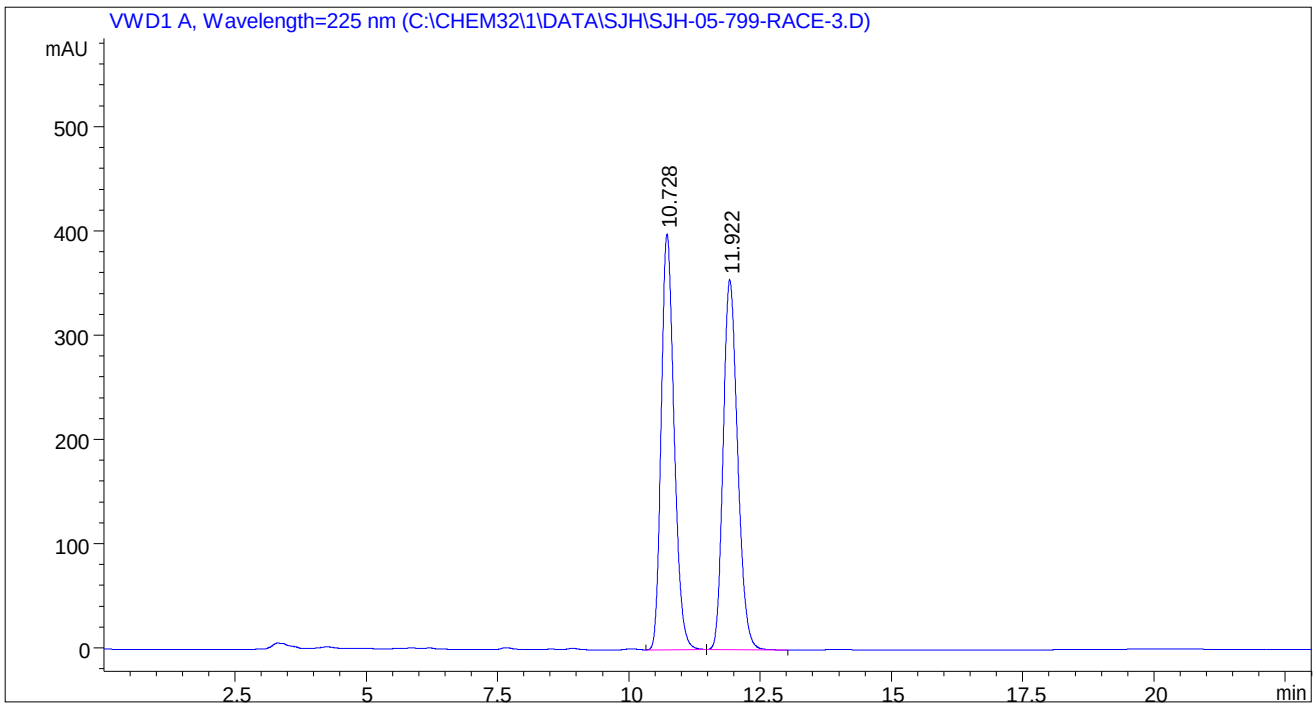
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.160	MM	0.2979	7356.22900	411.52200	50.3975
2	11.381	MM	0.3432	7240.18701	351.58508	49.6025



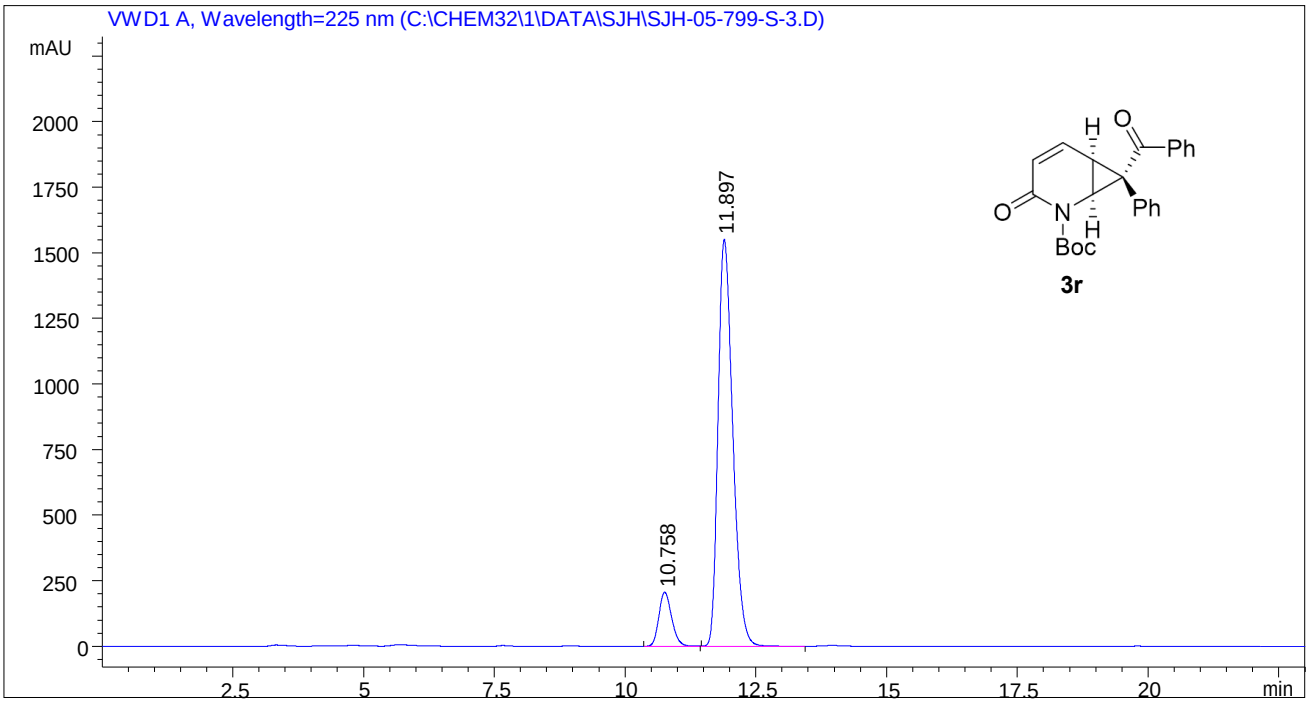
3q

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.152	MM	0.2732	664.59509	40.54438	1.9174
2	11.282	MM	0.3421	3.39972e4	1656.39783	98.0826

Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm



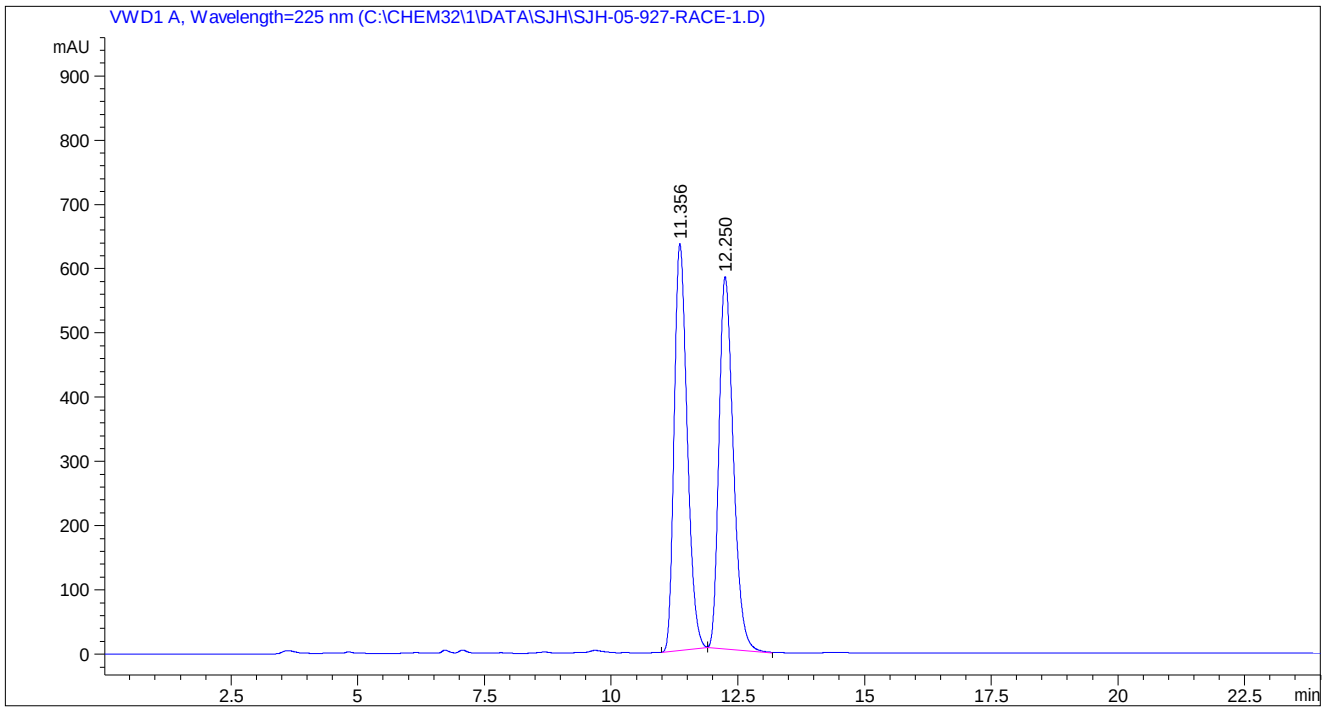
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.728	BB	0.2646	6816.74268	398.45349	50.0820
2	11.922	BB	0.2965	6794.41748	354.73389	49.9180



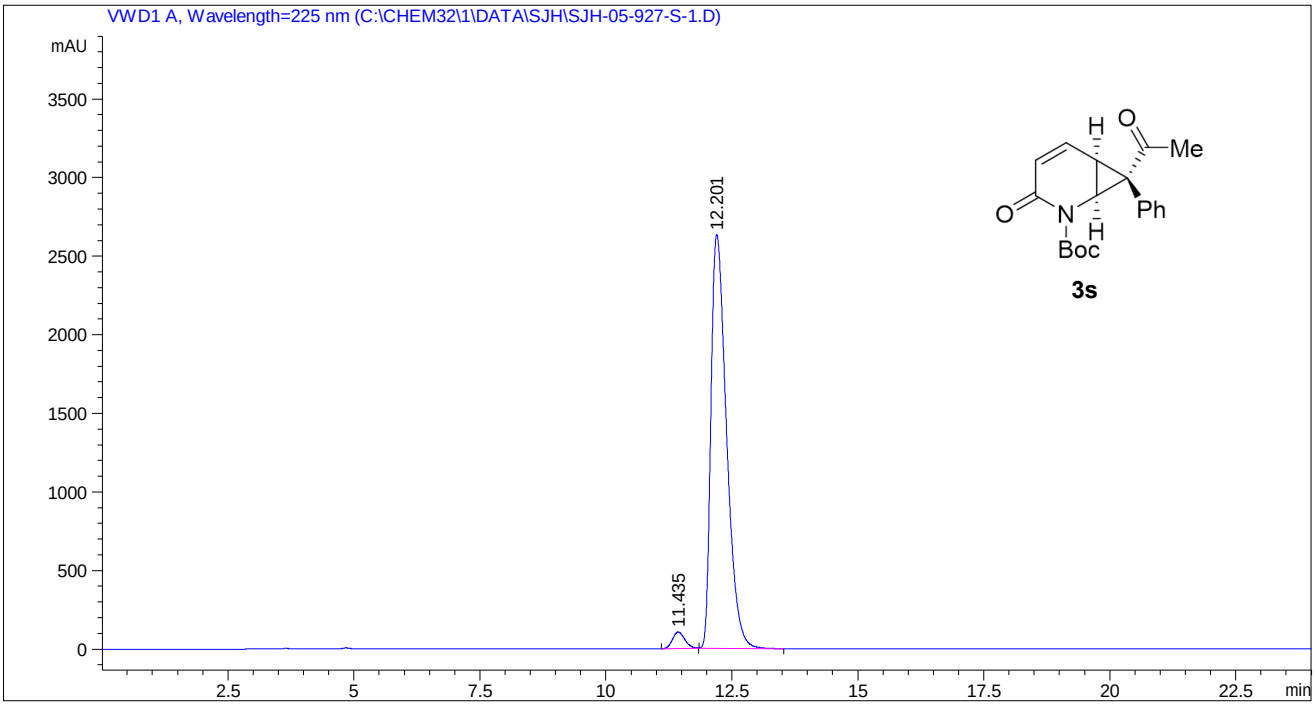
3r

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.758	MM	0.2824	3498.52515	206.47075	10.3338
2	11.897	VB	0.3022	3.03567e4	1552.04138	89.6662

Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 70/30, λ = 225 nm



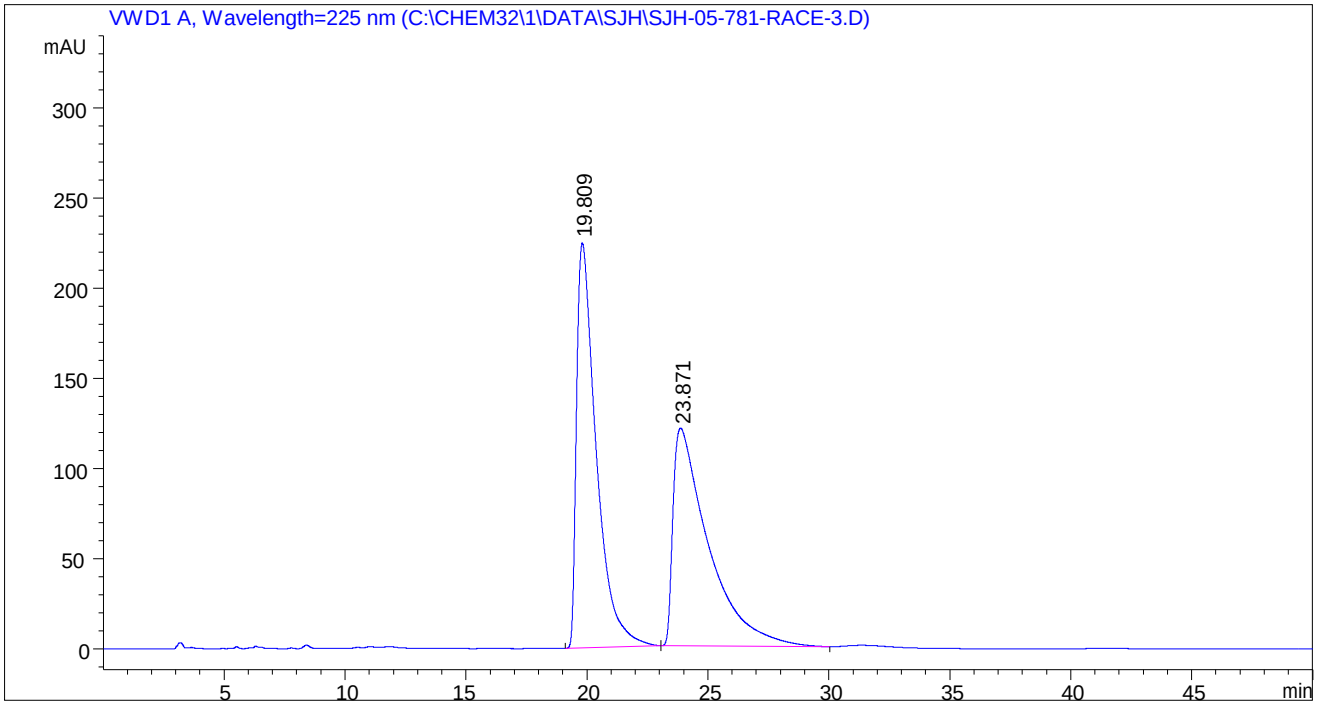
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.356	MM	0.2978	1.13147e4	633.20142	49.7739
2	12.250	MM	0.3285	1.14175e4	579.29535	50.2261



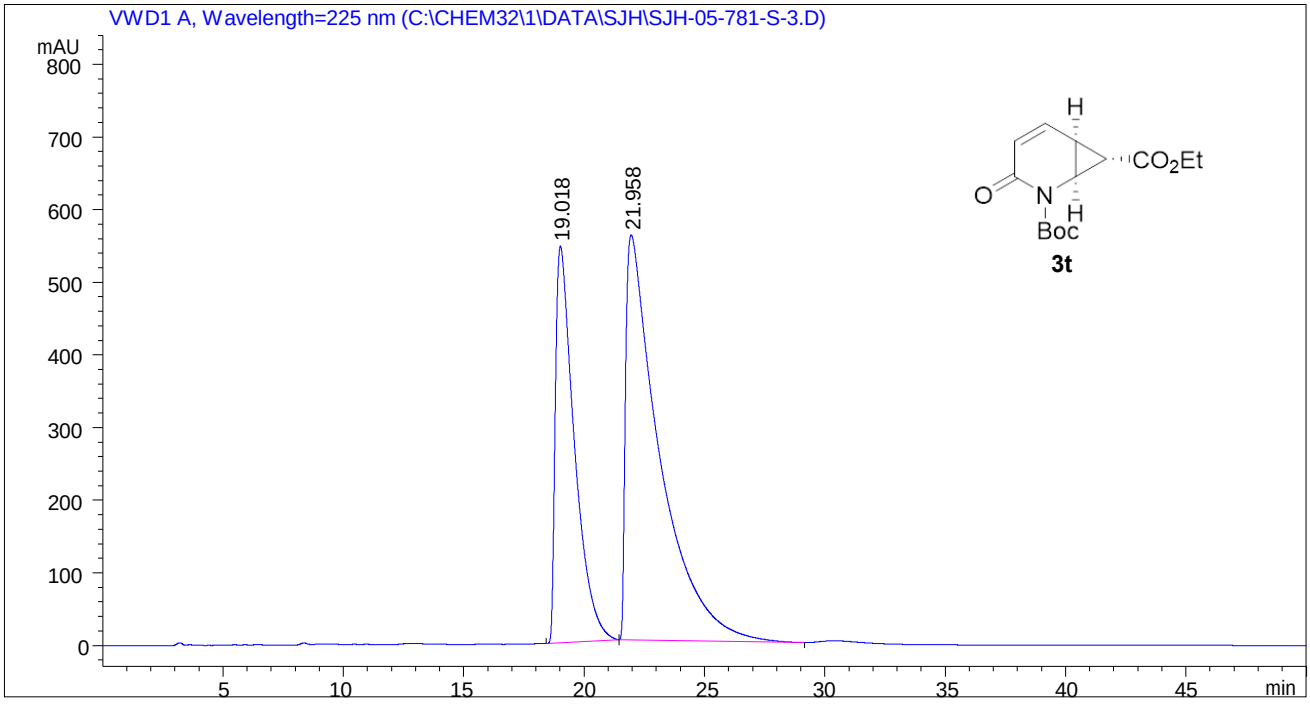
3s

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.435	MM	0.2829	1793.72400	105.67153	3.0732
2	12.201	MM	0.3582	5.65720e4	2632.28540	96.9268

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1mL/min, λ = 225 nm

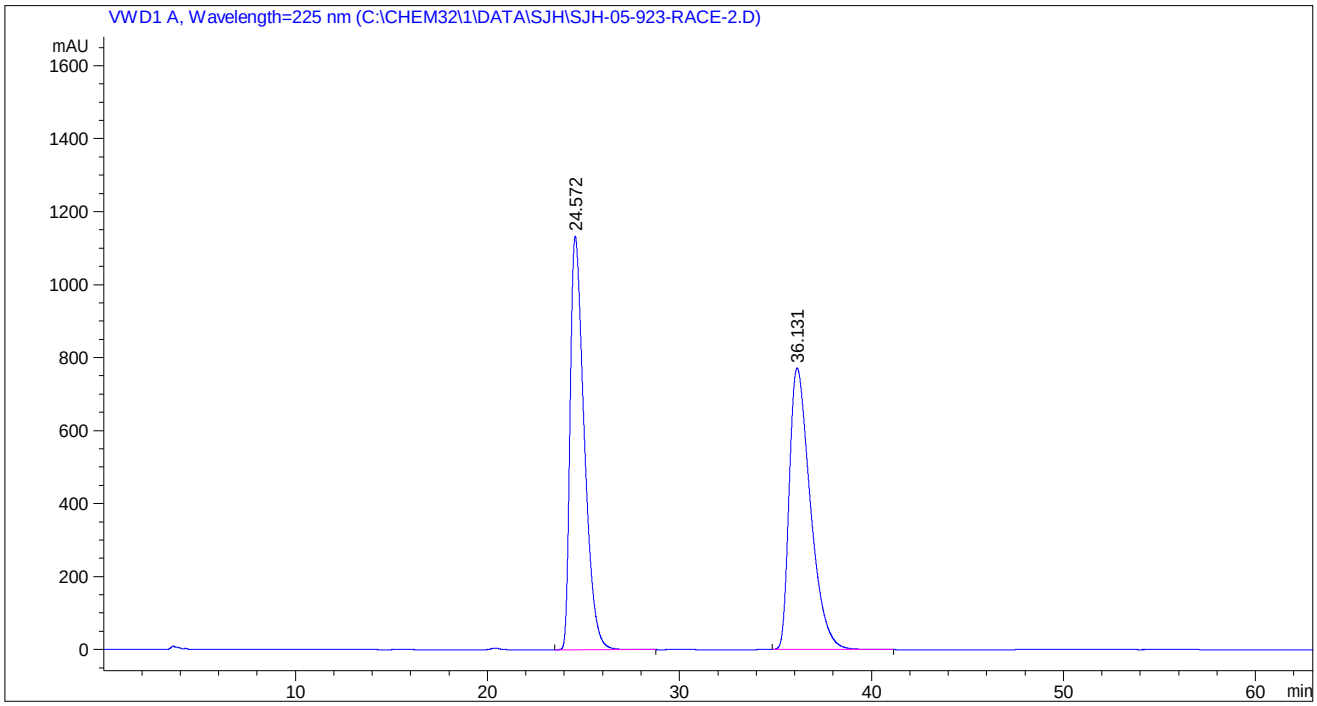


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.809	BB	0.8396	1.26902e4	224.45665	50.8124
2	23.871	BB	1.4262	1.22844e4	120.81619	49.1876

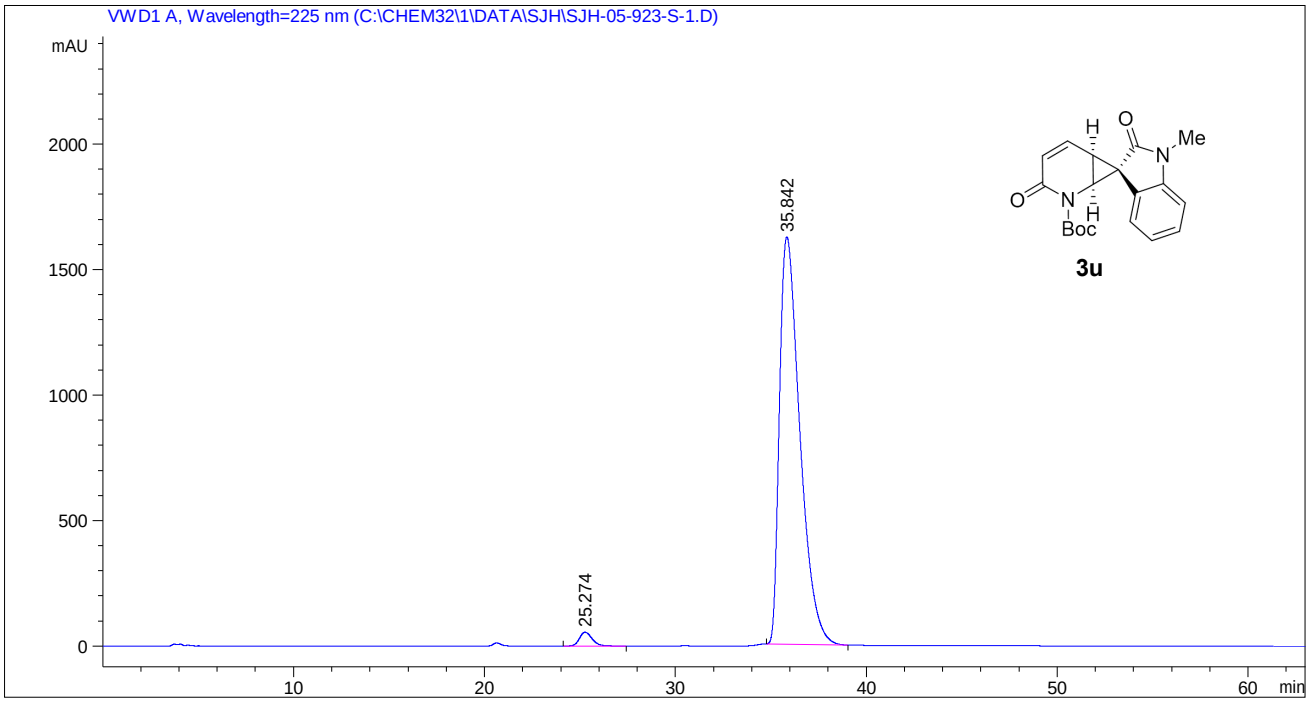


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.018	MM	0.9167	3.00303e4	546.00989	35.5006
2	21.958	MM	1.6306	5.45606e4	557.67621	64.4994

Daicel Chiralpak IE column, n-hexane/i-PrOH = 60/40, flow rate = 1mL/min, λ = 225 nm



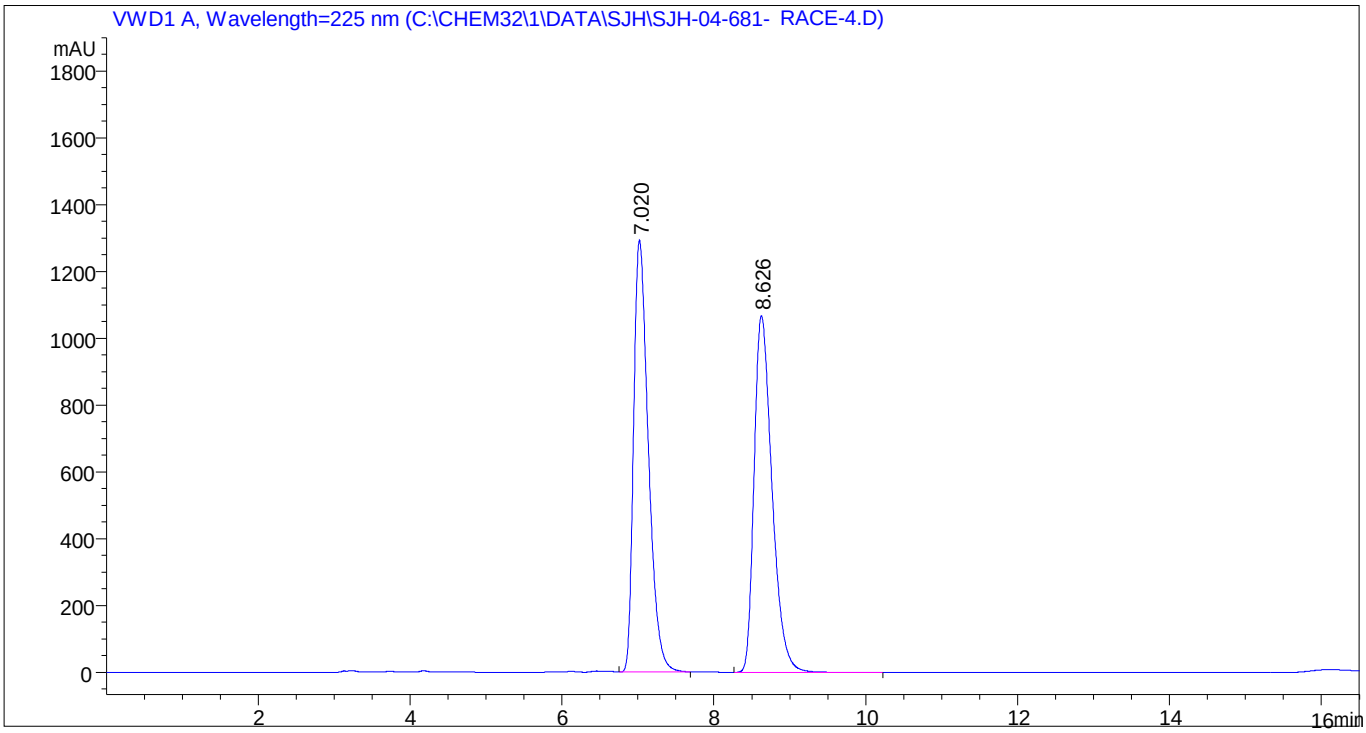
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.572	BB	0.7813	5.79280e4	1133.29517	49.6861
2	36.131	BB	1.1710	5.86601e4	770.67578	50.3139



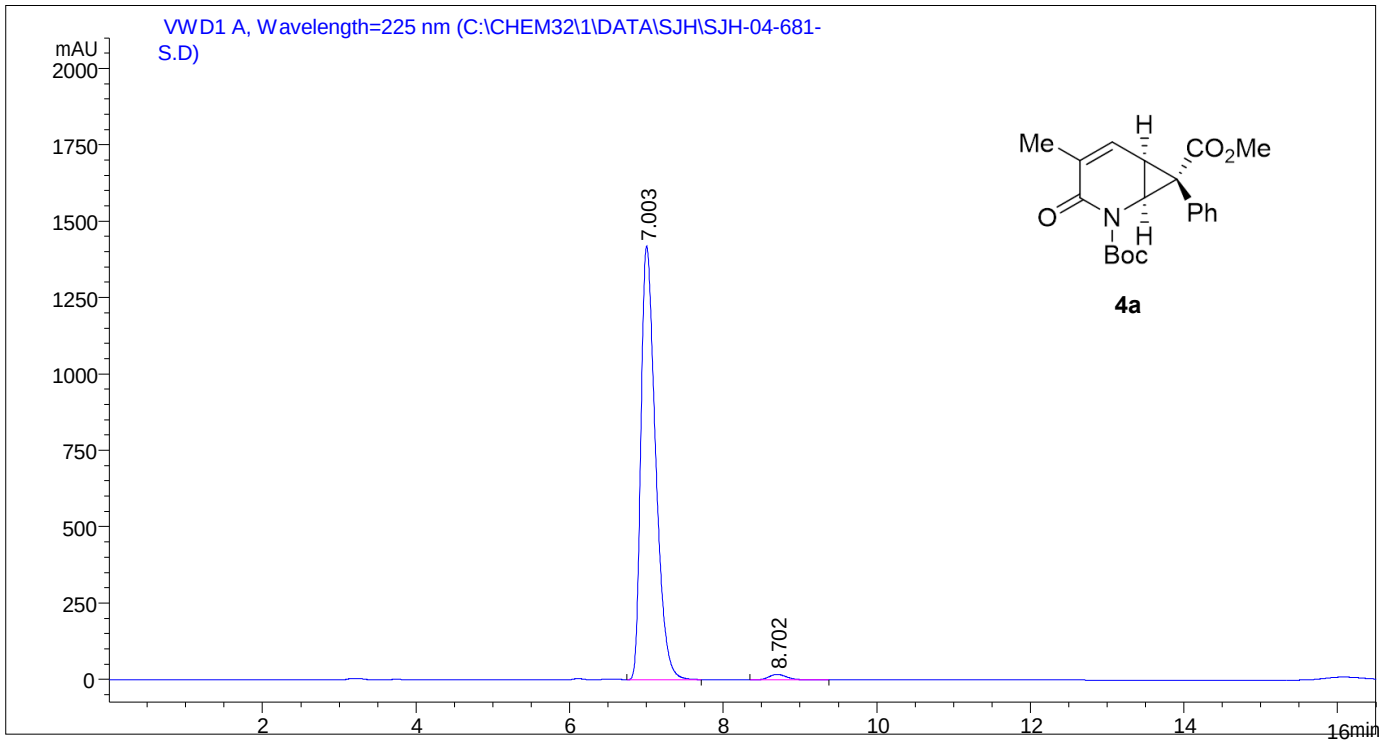
3u

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.274	BB	0.7108	2529.67676	54.98046	2.0541
2	35.842	MM	1.2380	1.20623e5	1623.84741	97.9459

Daicel Chiral OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ= 225 nm



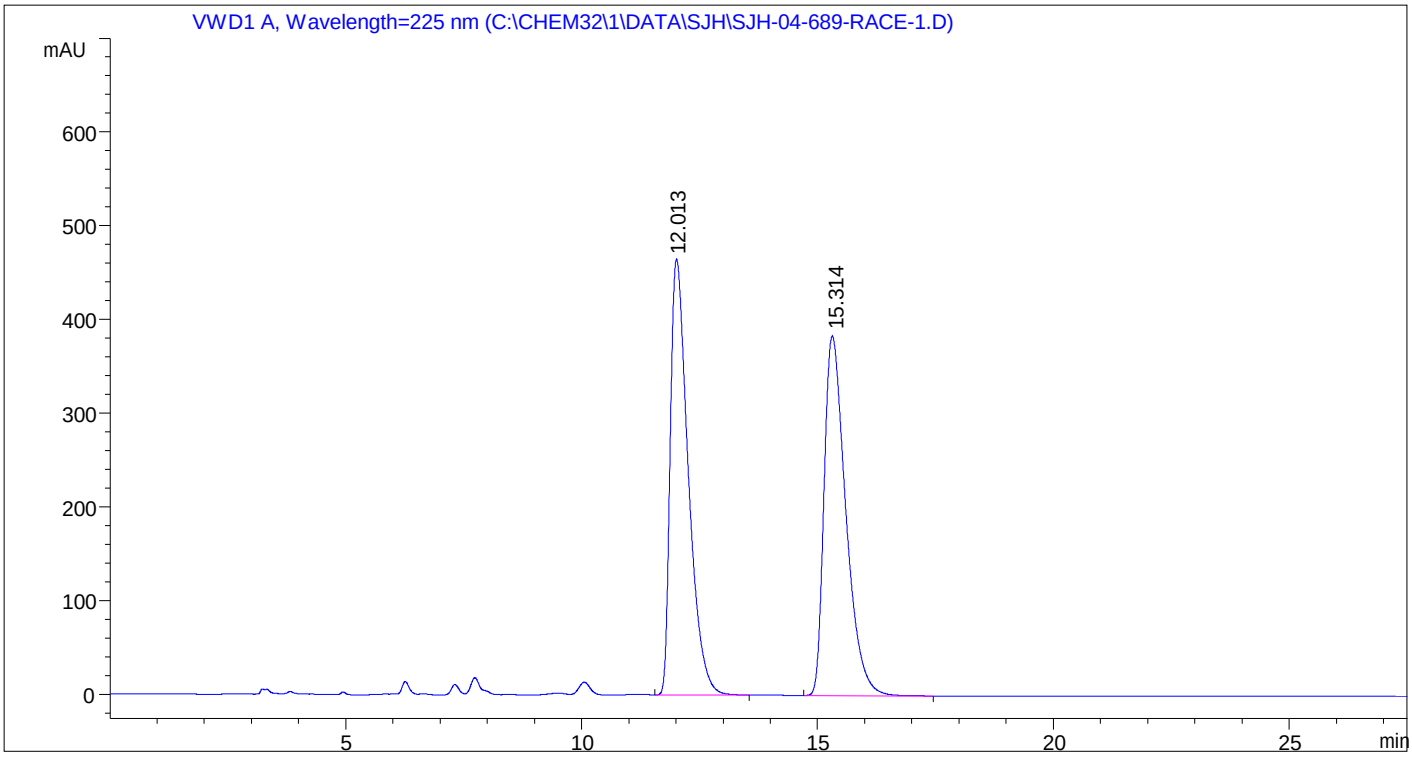
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.020	MM	0.2246	1.74229e4	1292.74377	49.9201
2	8.626	BB	0.2510	1.74787e4	1067.90869	50.0799



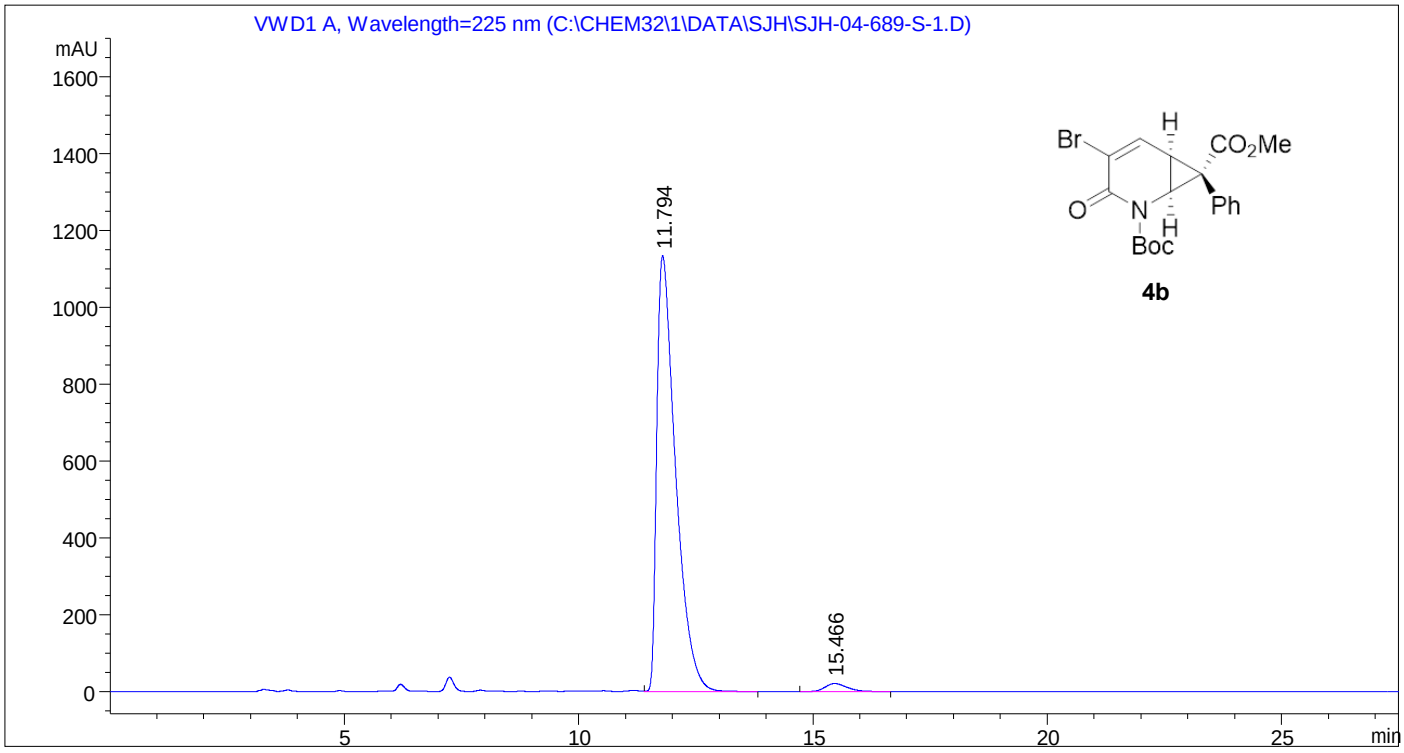
4a

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.003	BB	0.2038	1.88519e4	1420.38171	98.4307
2	8.702	BB	0.2528	300.56561	18.28523	1.5693

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1mL/min, λ= 225 nm

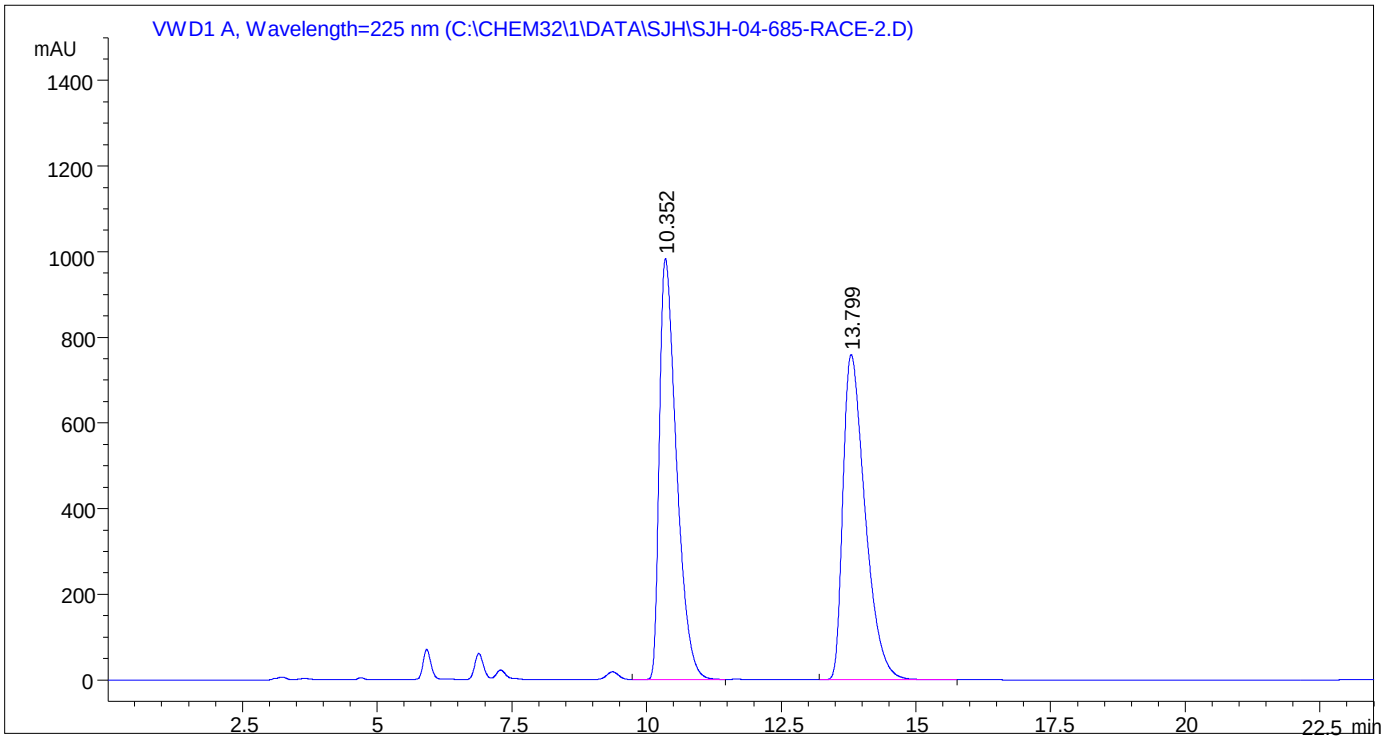


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.013	MM	0.4428	1.23570e4	465.14908	50.1172
2	15.314	MM	0.5342	1.22992e4	383.76050	49.8828

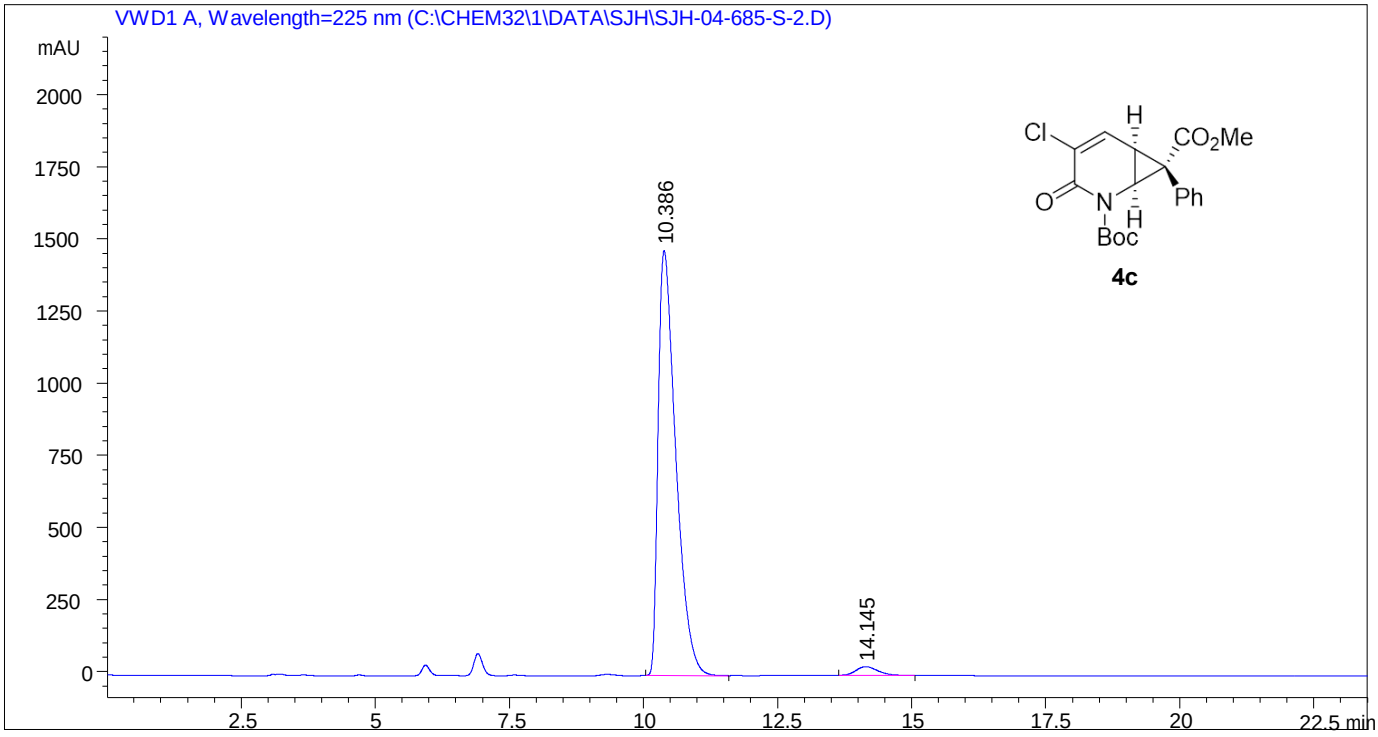


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.794	MM	0.4635	3.15341e4	1133.94006	97.8838
2	15.466	BB	0.5022	681.75842	20.81046	2.1162

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ= 225 nm

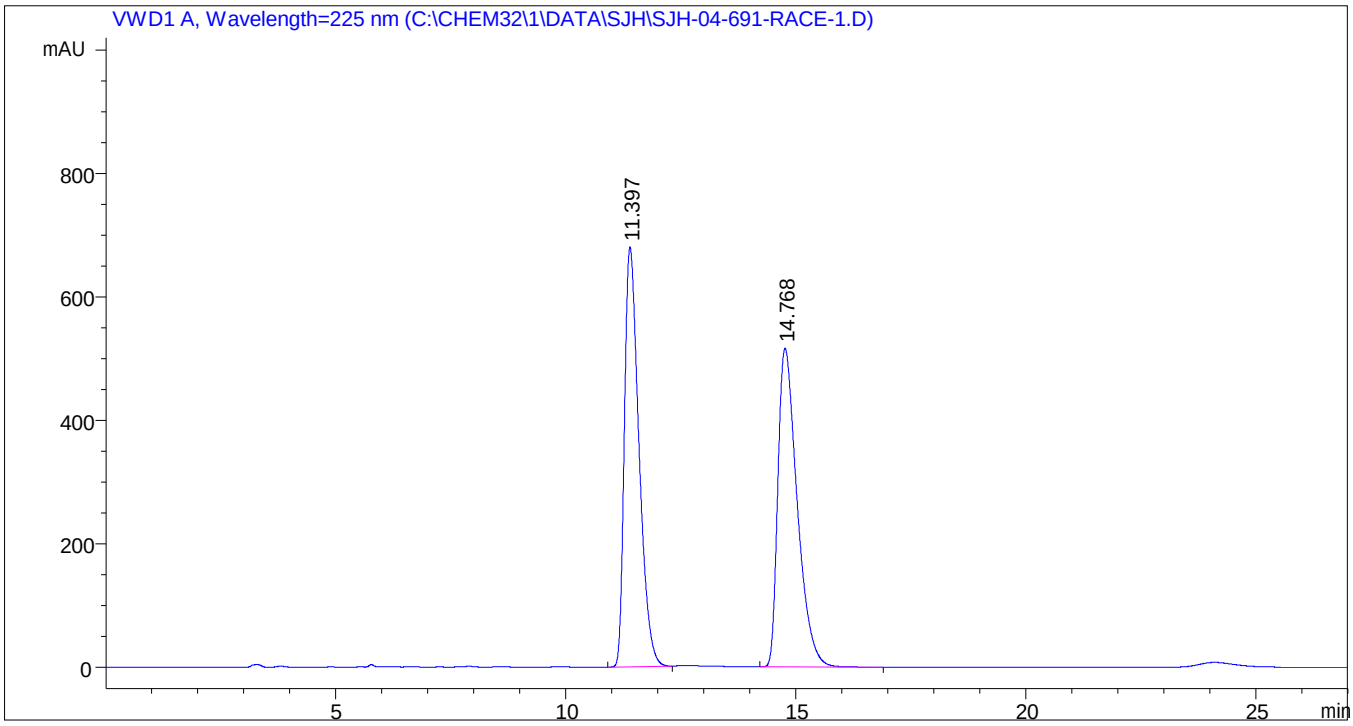


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.352	VB R	0.3354	2.16787e4	982.58807	49.9214
2	13.799	MM	0.4772	2.17470e4	759.50818	50.0786

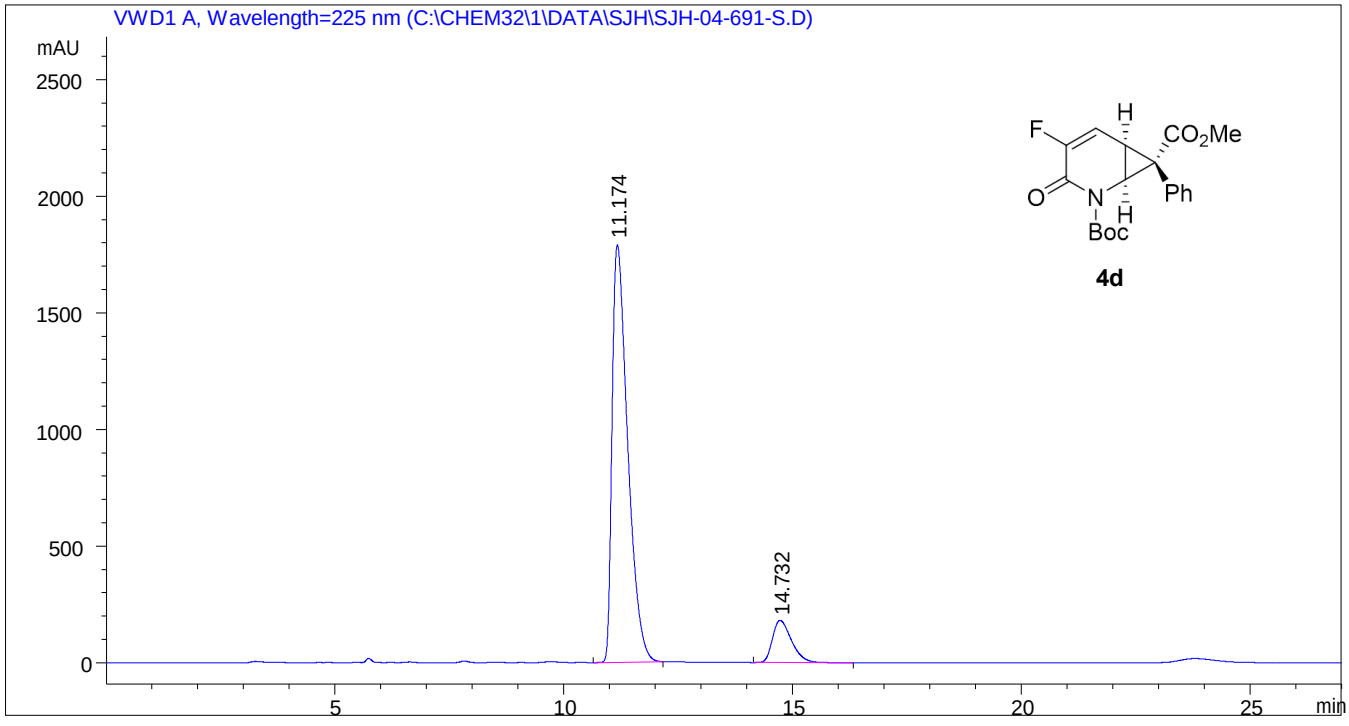


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.386	MM	0.3822	3.37804e4	1473.20068	97.5328
2	14.145	MM	0.4726	854.50903	30.13777	2.4672

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ = 225 nm



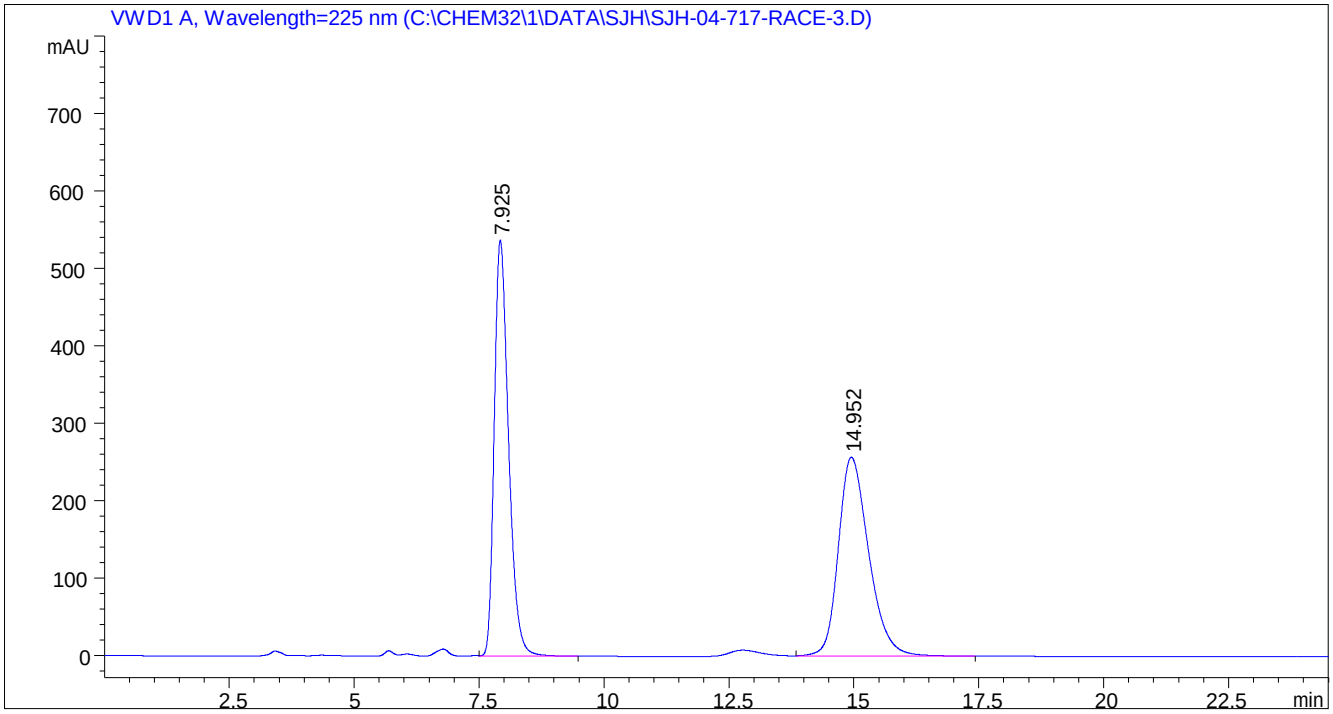
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.397	MM	0.3671	1.49730e4	679.85742	49.9008
2	14.768	BB	0.4447	1.50326e4	516.33838	50.0992



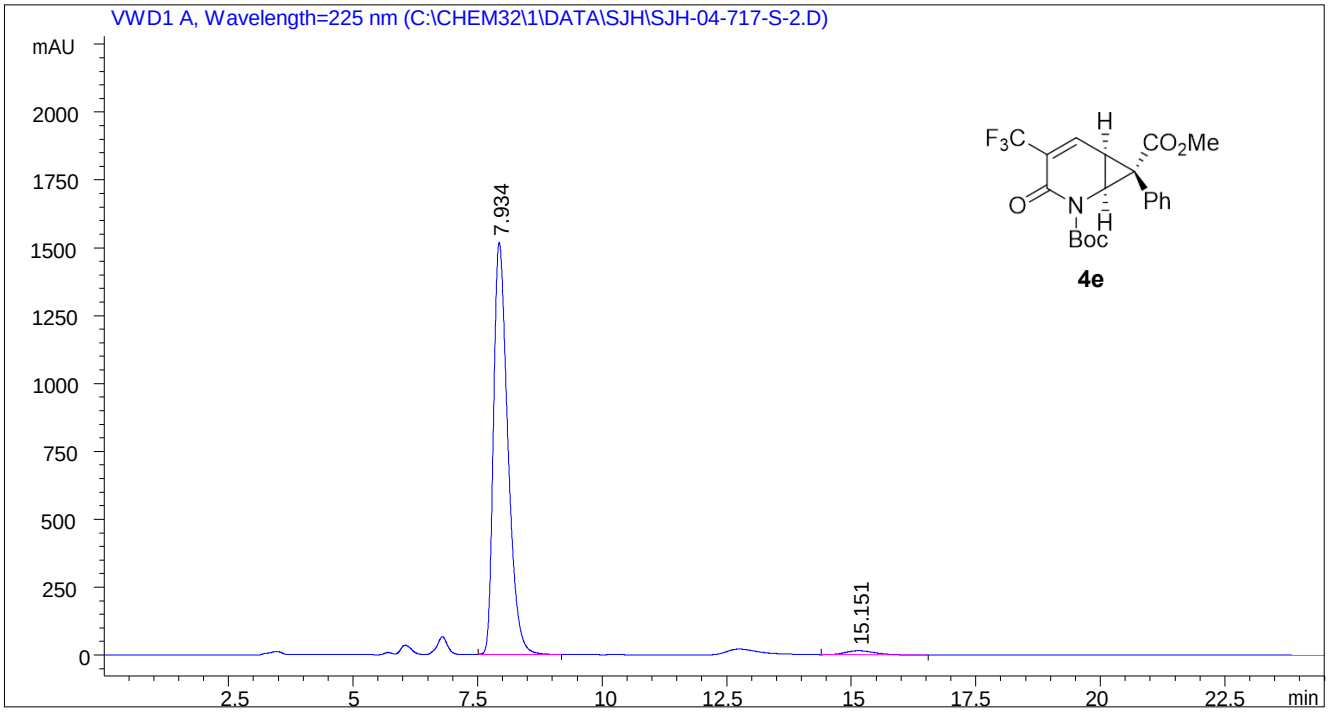
4d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.174	MM	0.3958	4.25069e4	1789.76392	89.0487
2	14.732	BB	0.4431	5227.56006	181.48271	10.9513

Daicel Chiralpak OD-H column, n-hexane/i-PrOH = 80/20， flow rate = 1 mL/min, λ = 225 nm



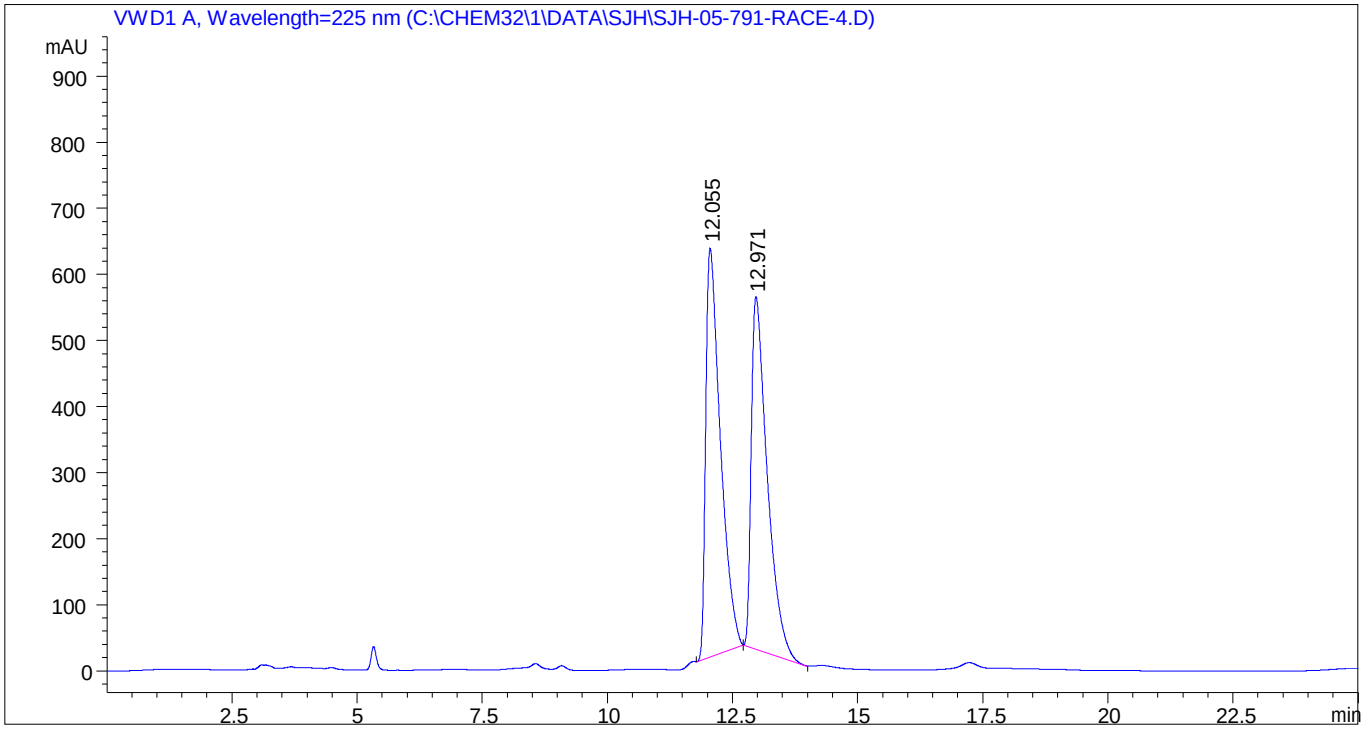
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.925	MM	0.3314	1.06705e4	536.56073	49.6241
2	14.952	MM	0.7036	1.08322e4	256.59656	50.3759



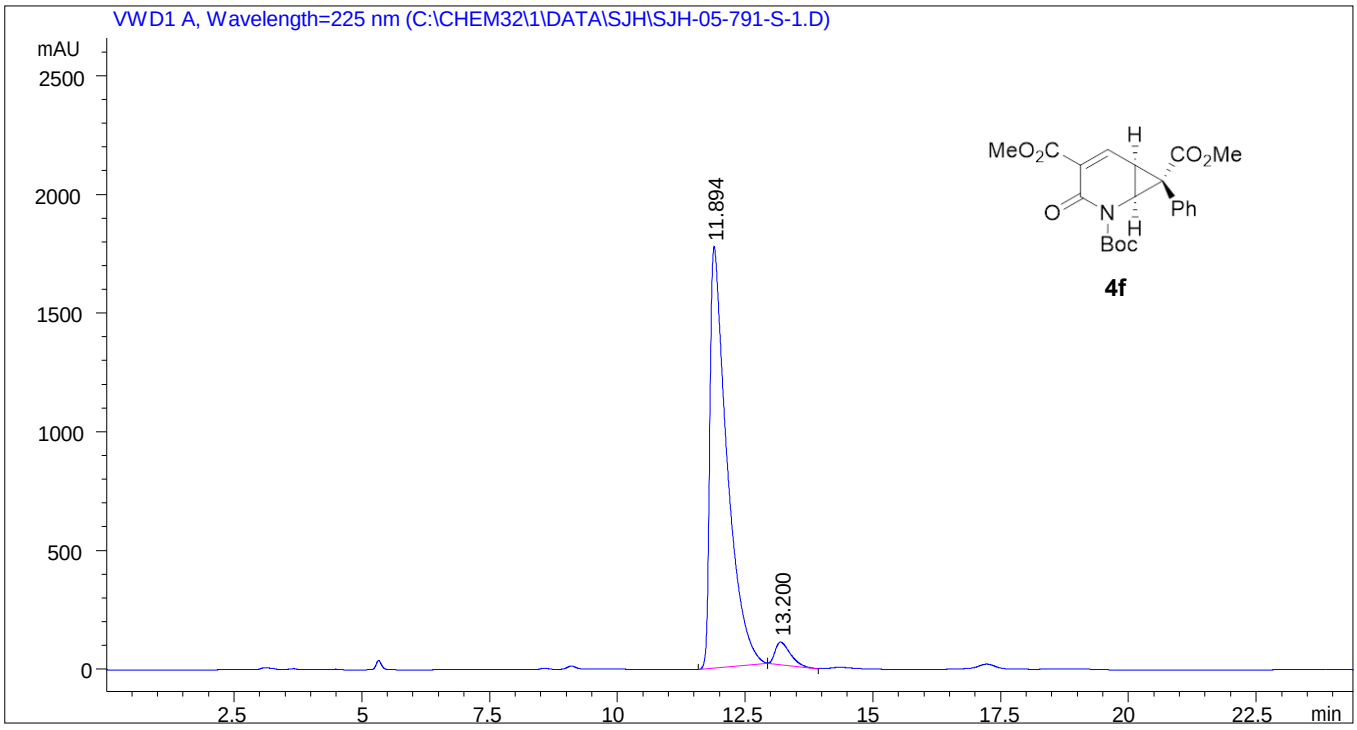
4e

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.934	MM	0.3342	3.04333e4	1517.79272	98.0041
2	15.151	BB	0.6403	619.77478	14.93005	1.9959

Daicel Chiralpak IA column, n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ = 225 nm

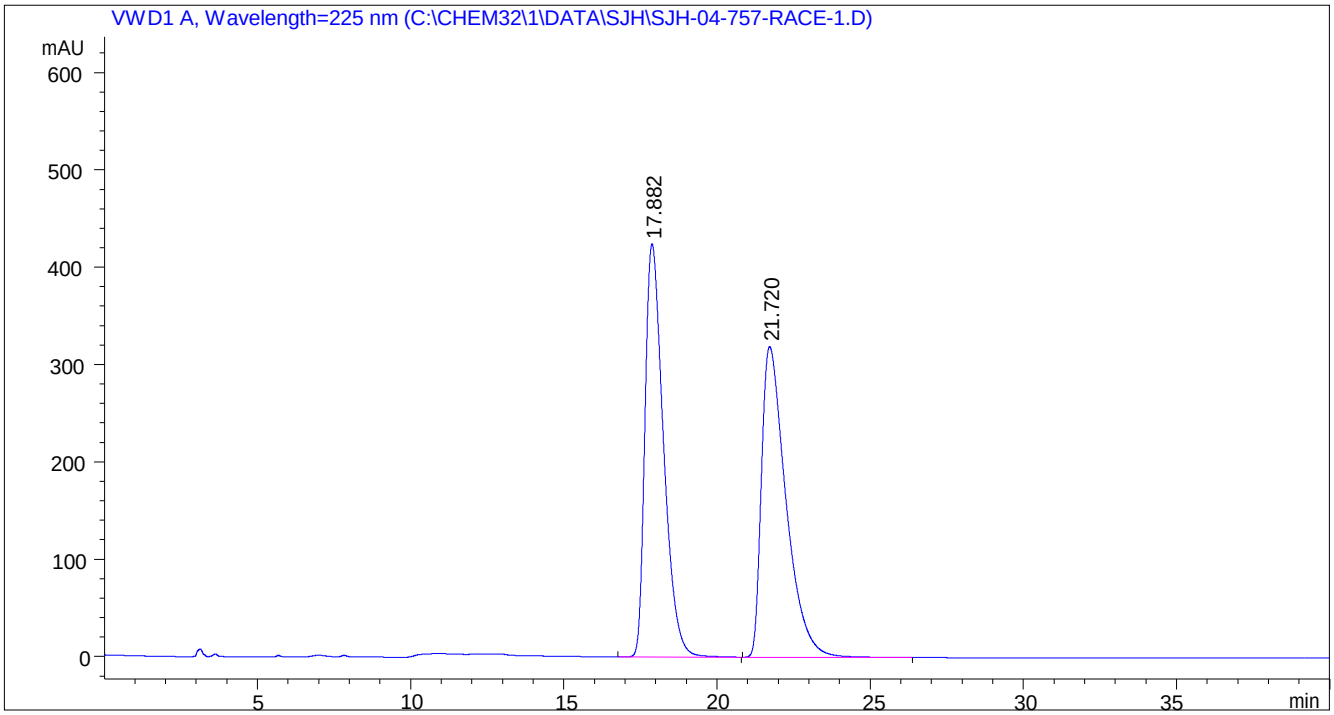


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.055	MM	0.3406	1.26478e4	618.94067	51.6020
2	12.971	MM	0.3705	1.18625e4	533.66229	48.3980

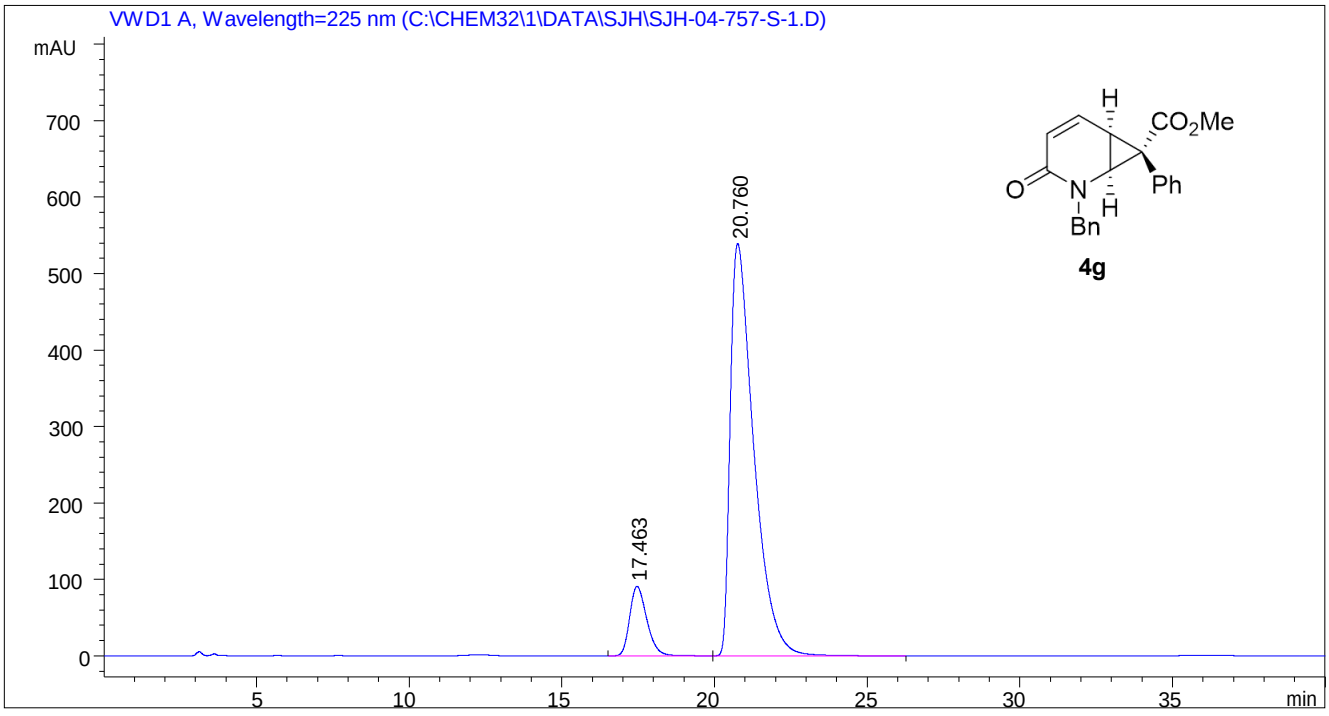


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.894	MM	0.3907	4.16621e4	1777.33081	95.4707
2	13.200	MM	0.3427	1976.52563	96.12506	4.5293

Daicel Chiralpak OD-H n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ = 225 nm

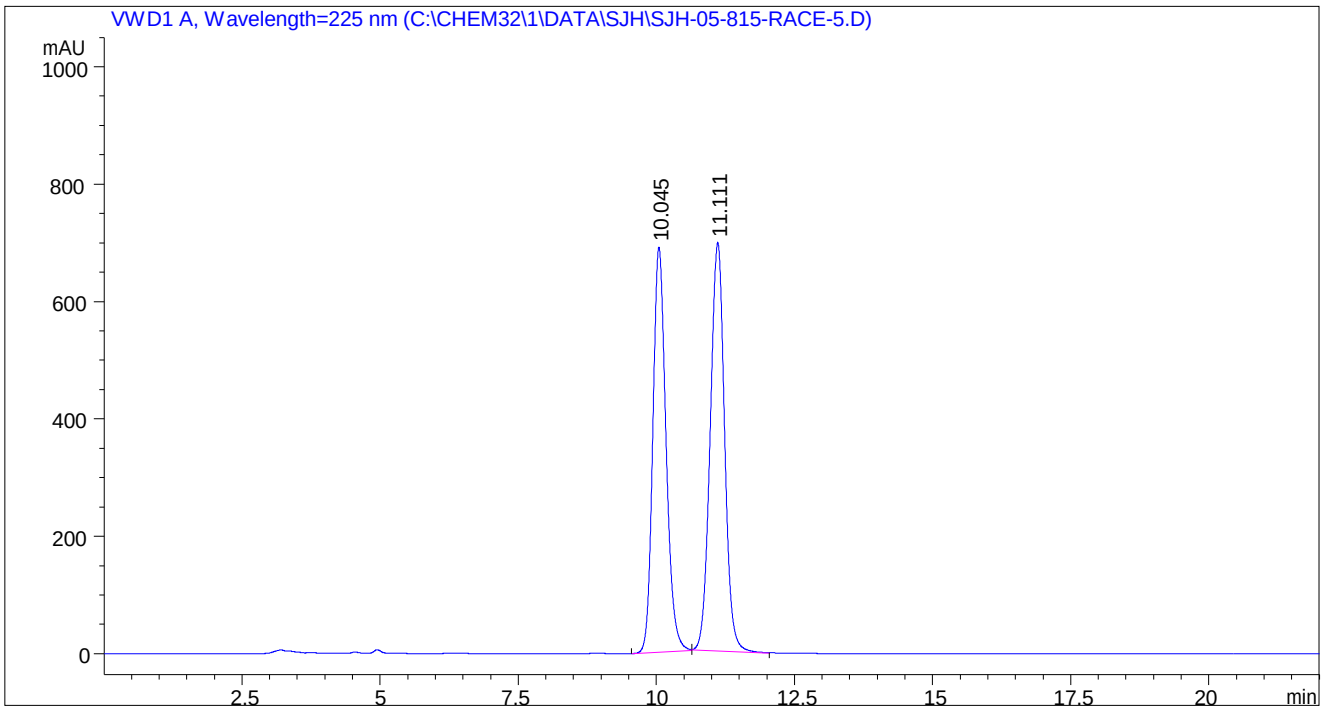


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.882	BB	0.6442	1.77967e4	424.40686	50.0324
2	21.720	BB	0.8404	1.77737e4	319.29681	49.9676

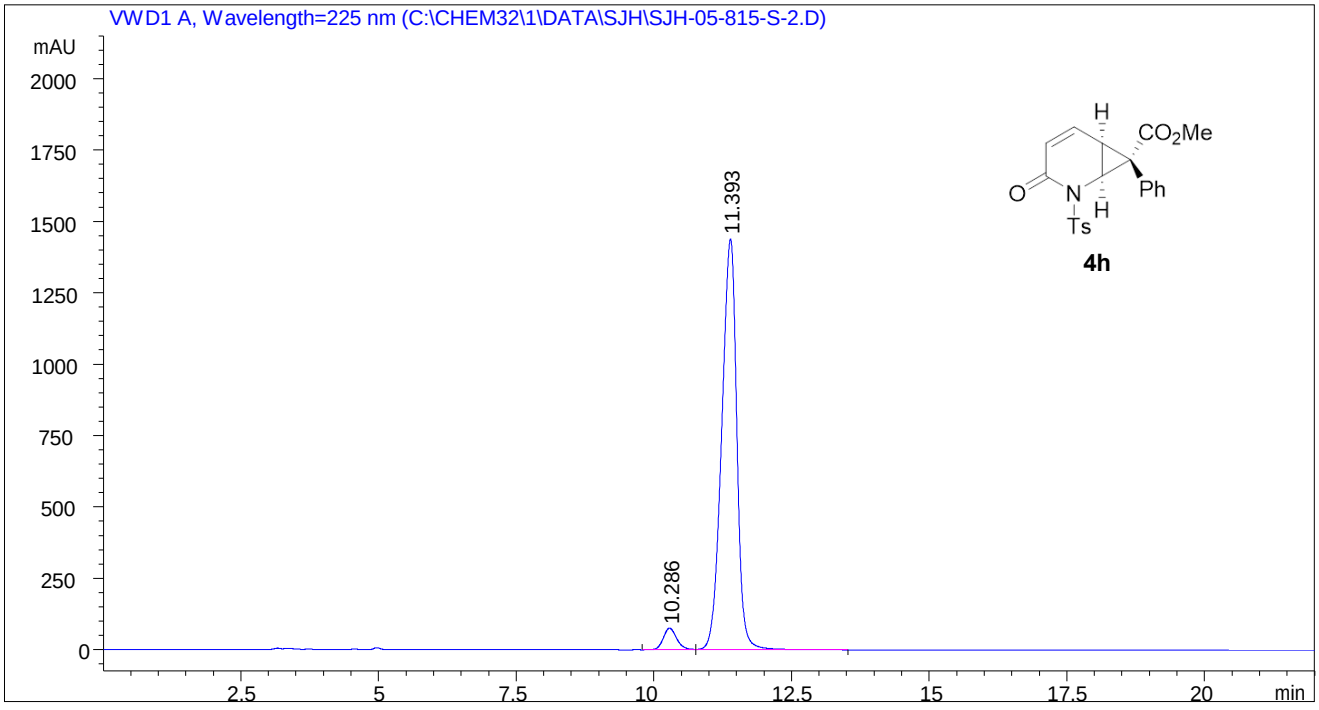


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.463	BB	0.6033	3556.08423	90.91541	10.9566
2	20.760	BB	0.8071	2.88999e4	539.40942	89.0434

Daicel Chiralpak IA column, n-hexane/i-PrOH = 60/40, flow rate = 1 mL/min, λ = 225 nm

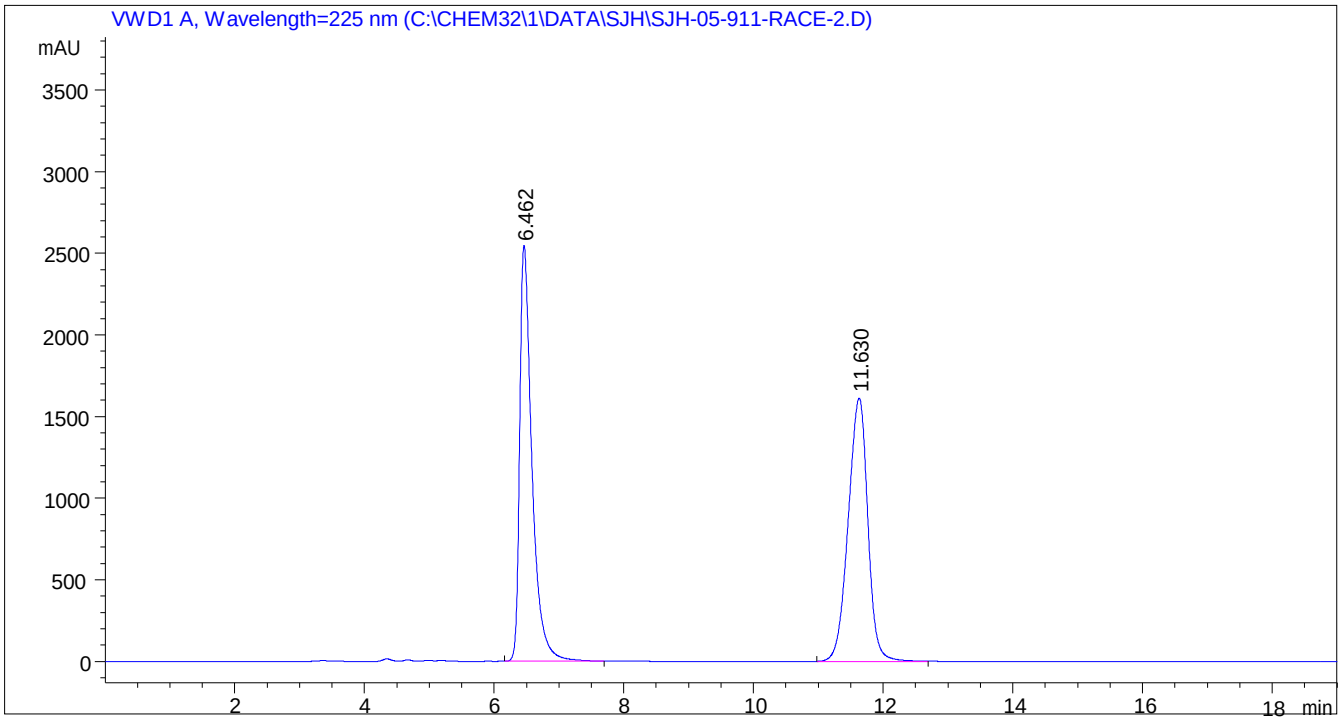


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.045	MM	0.2765	1.14623e4	690.95581	47.7178
2	11.111	MM	0.3007	1.25587e4	696.09619	52.2822

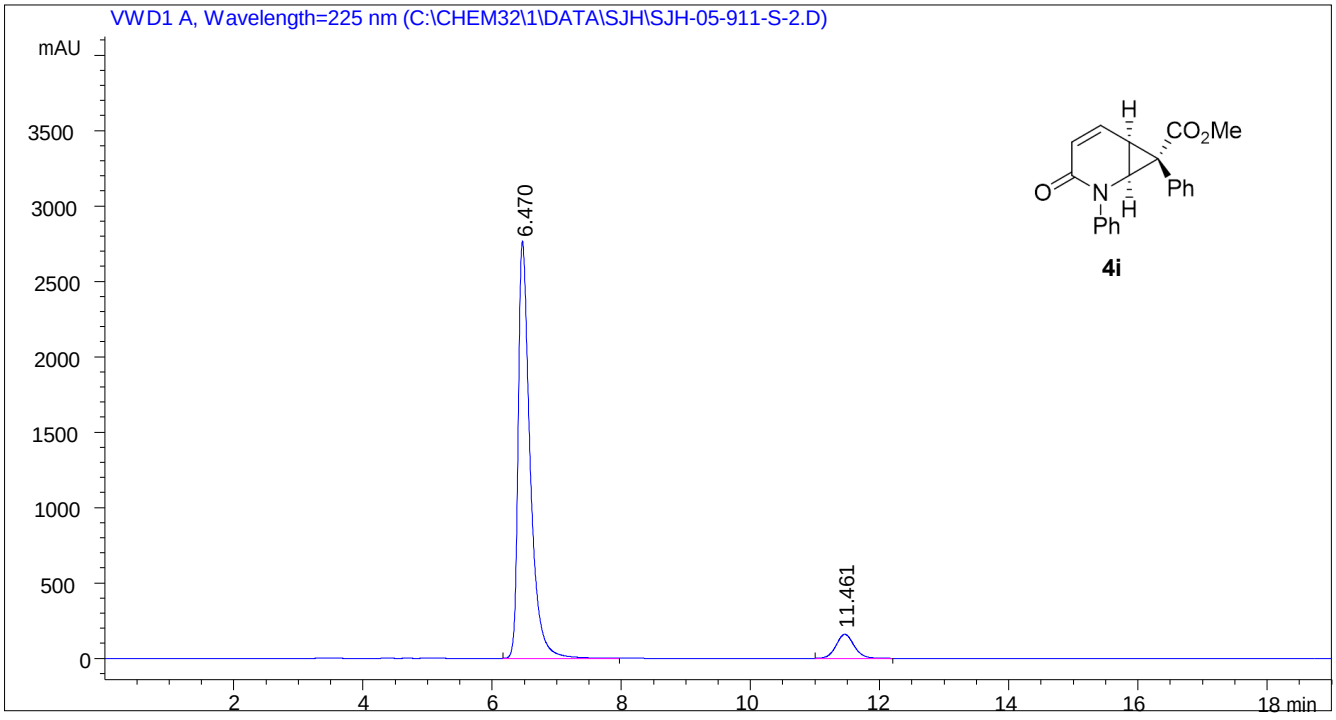


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.286	BV	0.2615	1300.01099	76.03944	4.4972
2	11.393	VB	0.2968	2.76069e4	1439.29773	95.5028

Daicel Chiralpak IA column, n-hexane/i-PrOH = 60/40, flow rate = 1 mL/min, λ = 225 nm



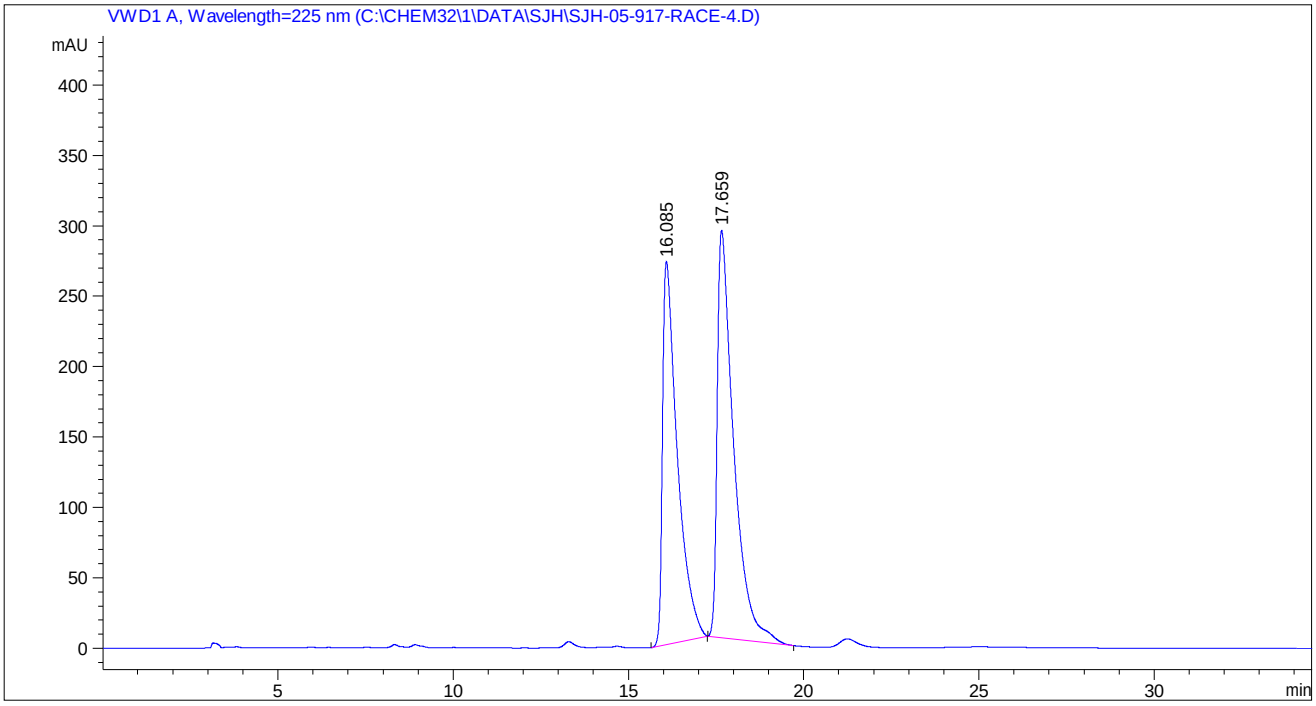
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.462	MM	0.2188	3.34281e4	2546.28906	49.6148
2	11.630	MM	0.3508	3.39471e4	1612.78674	50.3852



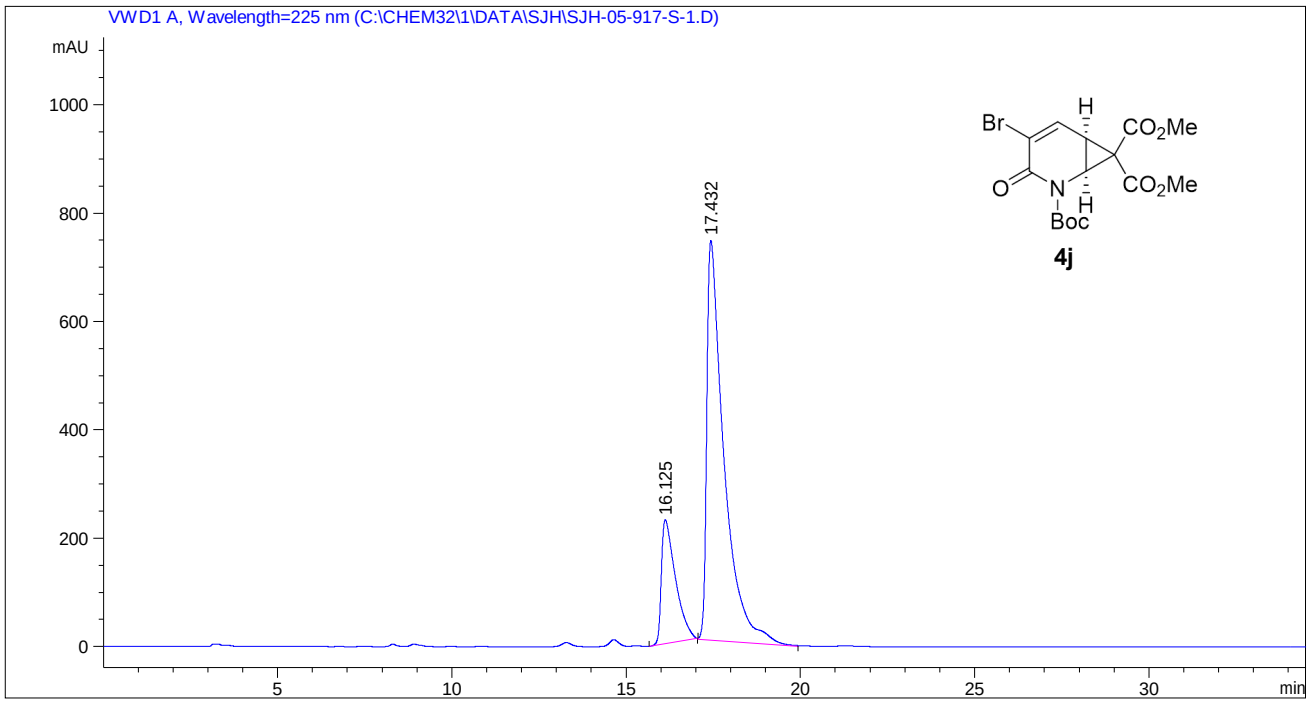
4i

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.470	MM	0.2152	3.57273e4	2766.41089	91.8266
2	11.461	MM	0.3304	3180.07031	160.42200	8.1734

Daicel Chiralpak IA column, n-hexane/i-PrOH = 95/5,flow rate = 1mL/min,λ = 225 nm



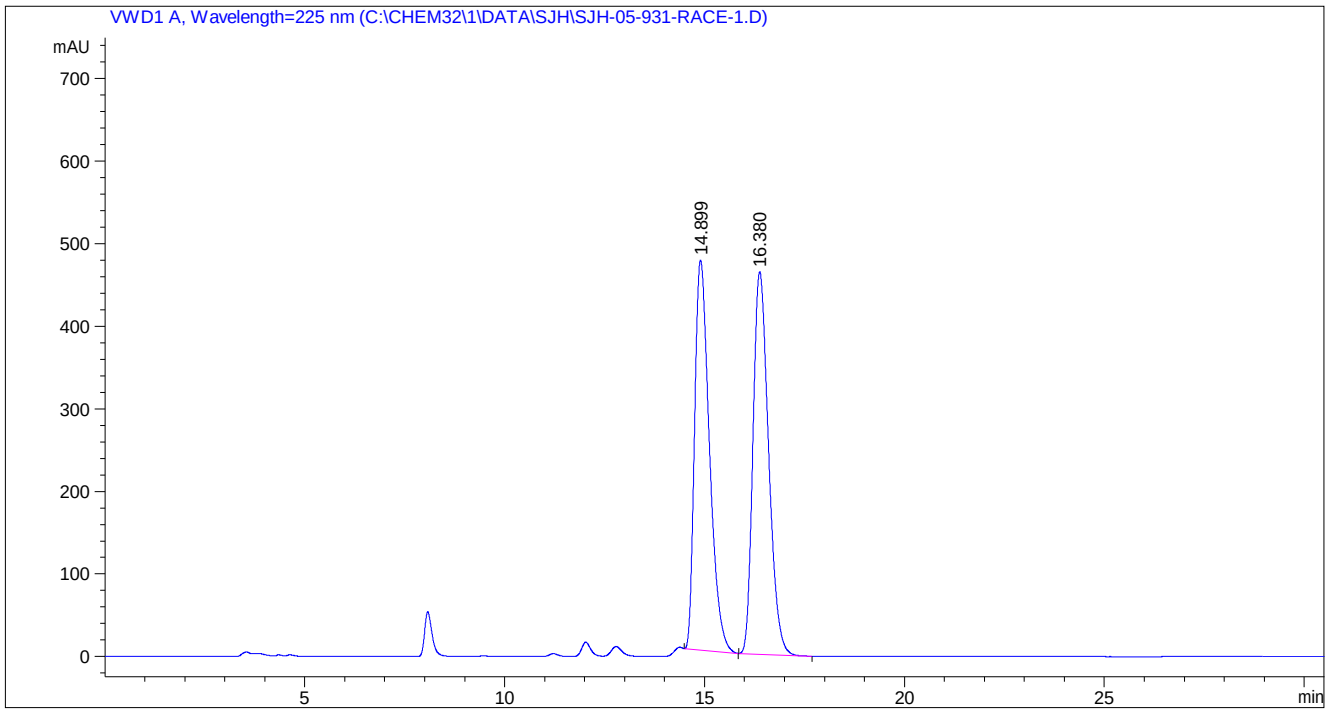
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.085	MM	0.4902	7999.53467	272.00464	45.8955
2	17.659	MM	0.5431	9430.37207	289.37720	54.1045



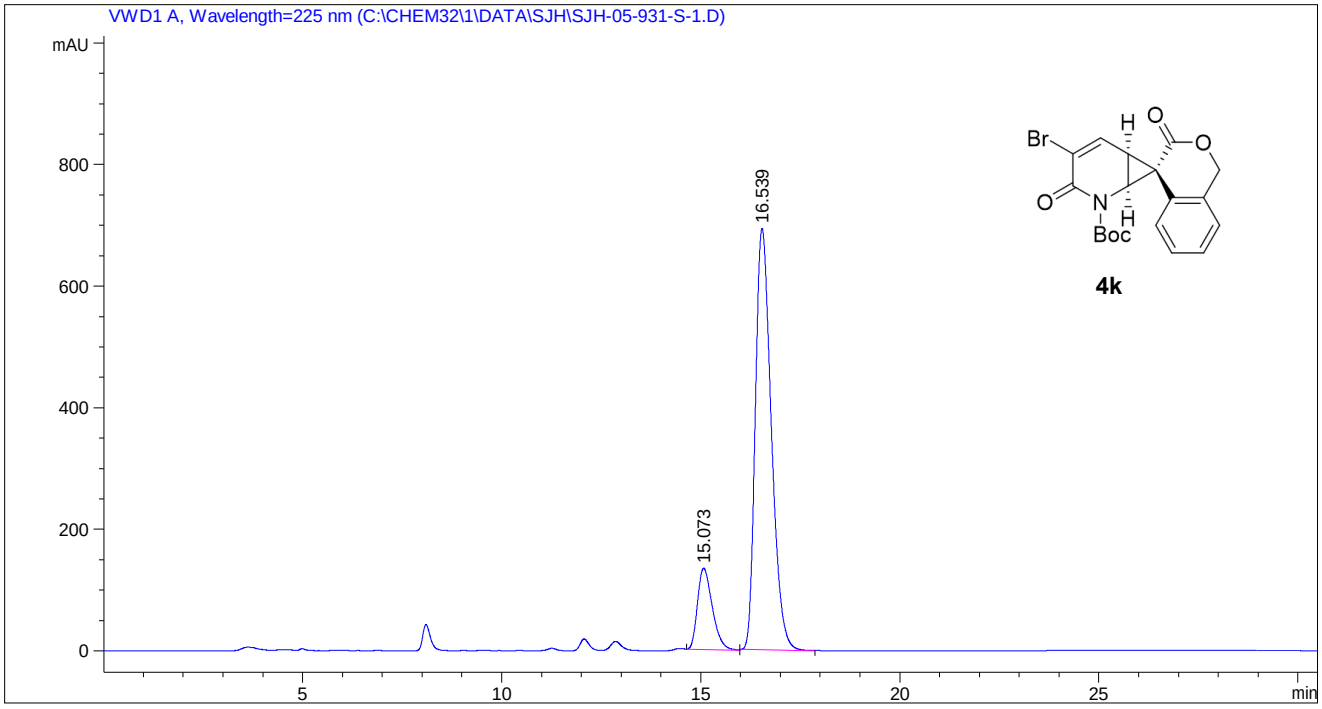
4j

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.125	MM	0.4675	6419.11279	228.84973	20.2605
2	17.432	MM	0.5707	2.52639e4	737.86743	79.7395

Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm



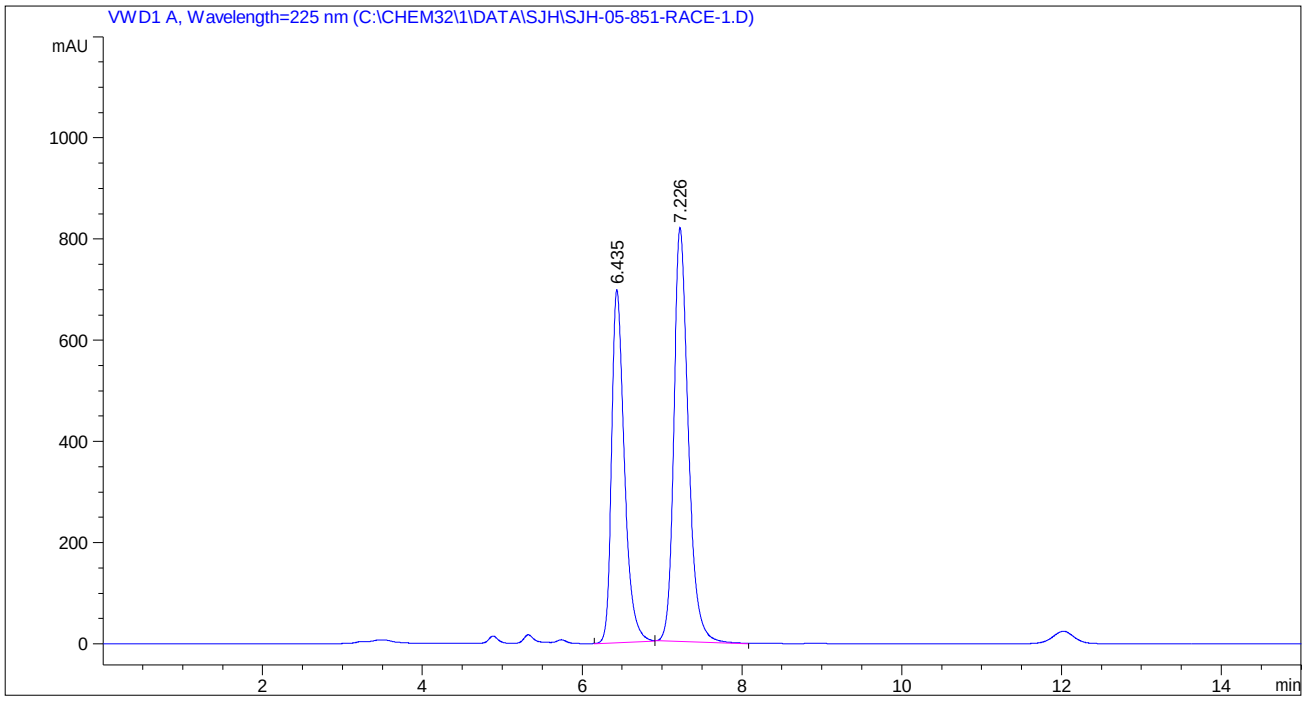
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.899	MM	0.4298	1.21909e4	472.78000	49.2686
2	16.380	MM	0.4513	1.25529e4	463.54794	50.7314



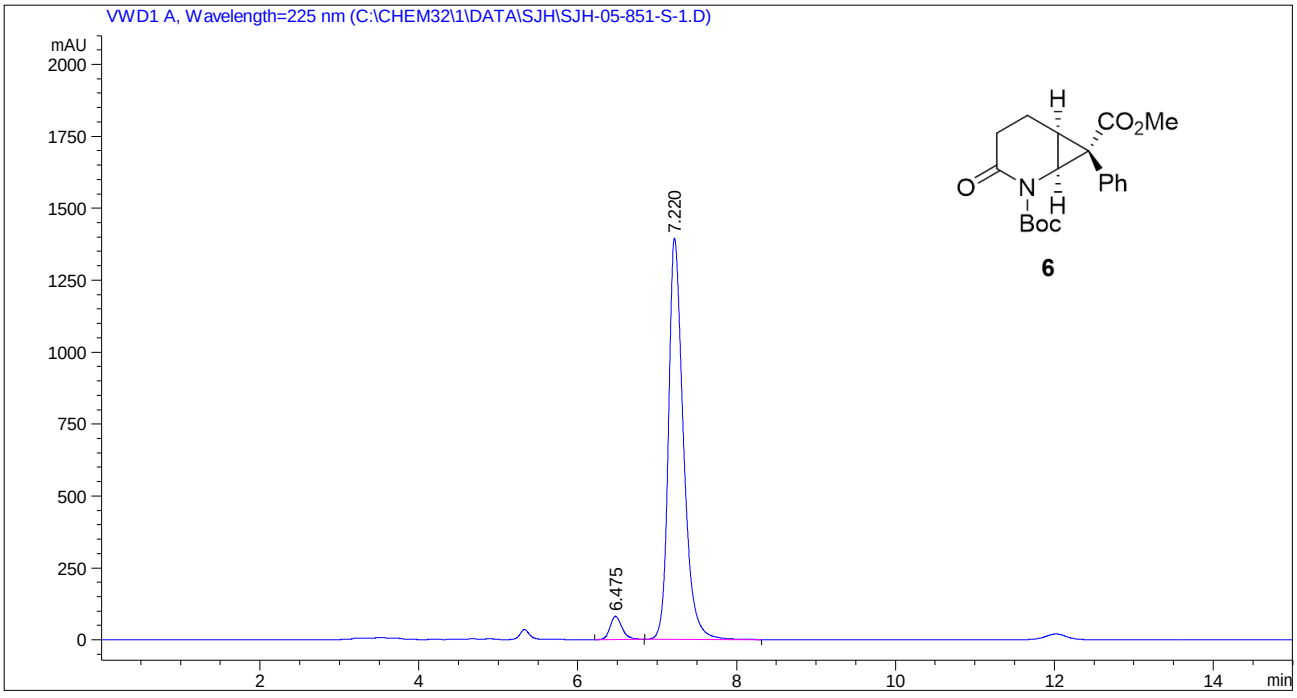
4k

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.073	MM	0.4309	3464.83447	134.01190	15.2032
2	16.539	MM	0.4644	1.93254e4	693.55530	84.7968

Daicel Chiralpak IA column, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm



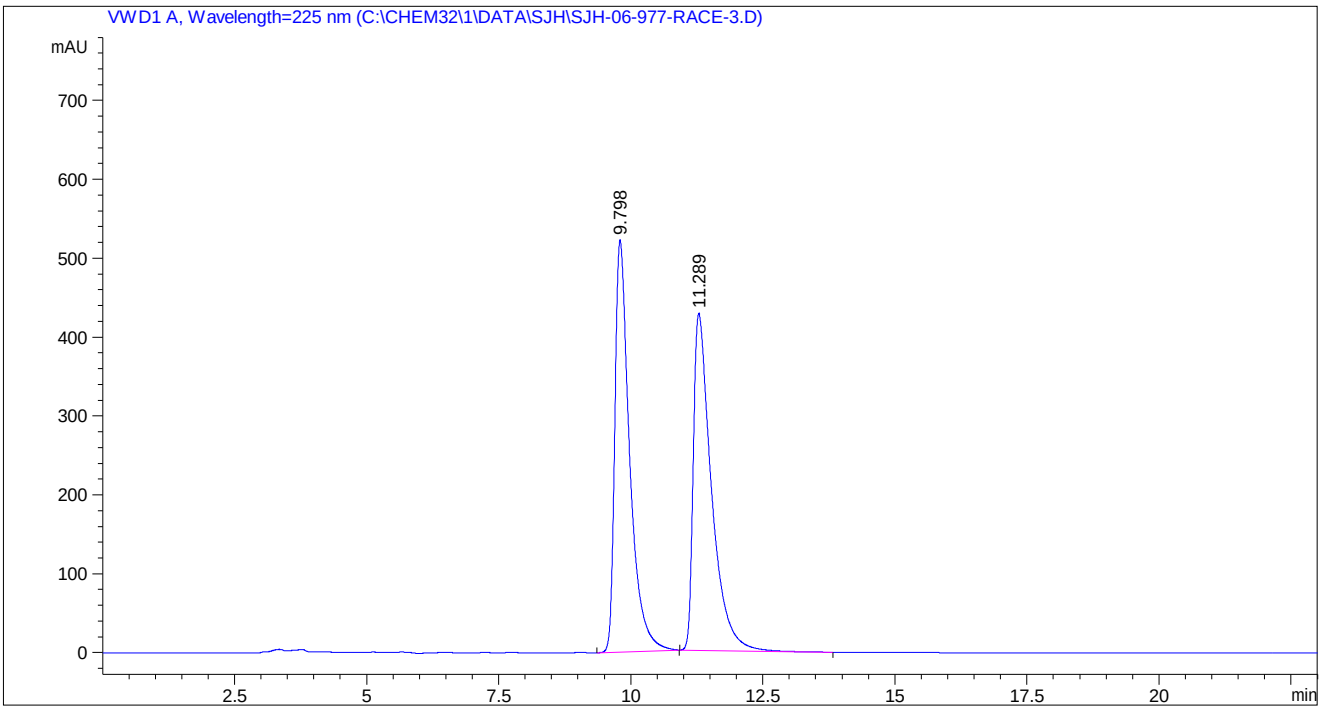
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.435	MM	0.1852	7757.58545	698.11932	43.0501
2	7.226	MM	0.2092	1.02623e4	817.77039	56.9499



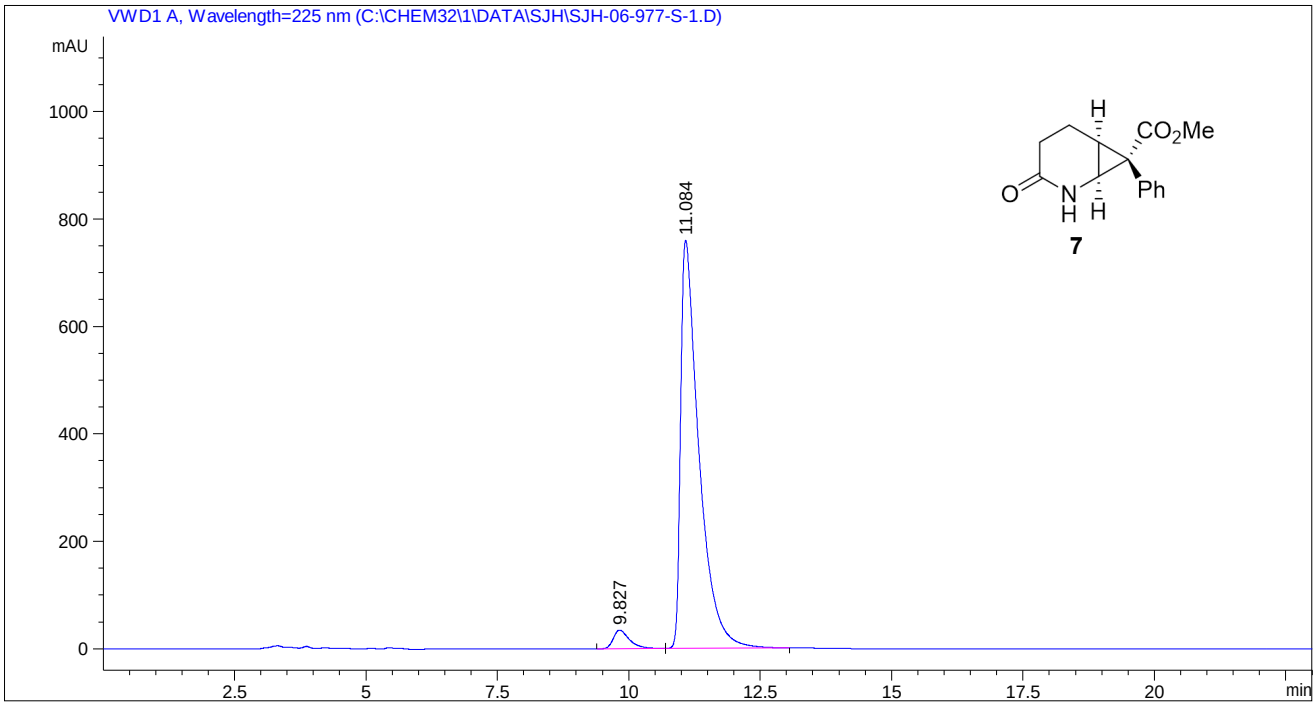
6

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.475	MM	0.1729	835.68524	80.57413	4.3849
2	7.220	MM	0.2178	1.82225e4	1394.40515	95.6151

Daicel Chiralpak IA column, n-hexane/i-PrOH = 80/20, flow rate = 1mL/min, λ = 225 nm

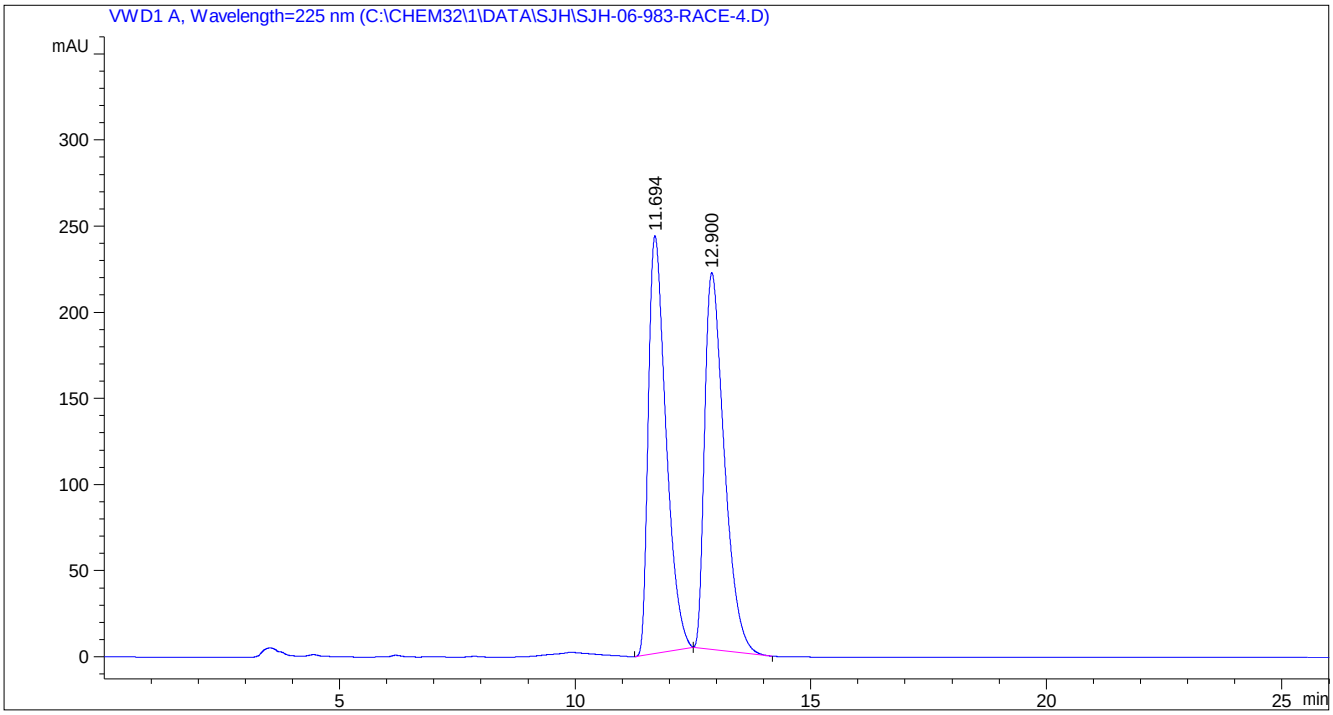


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.798	MM	0.3252	1.01977e4	522.67200	50.0148
2	11.289	MM	0.3974	1.01917e4	427.42496	49.9852

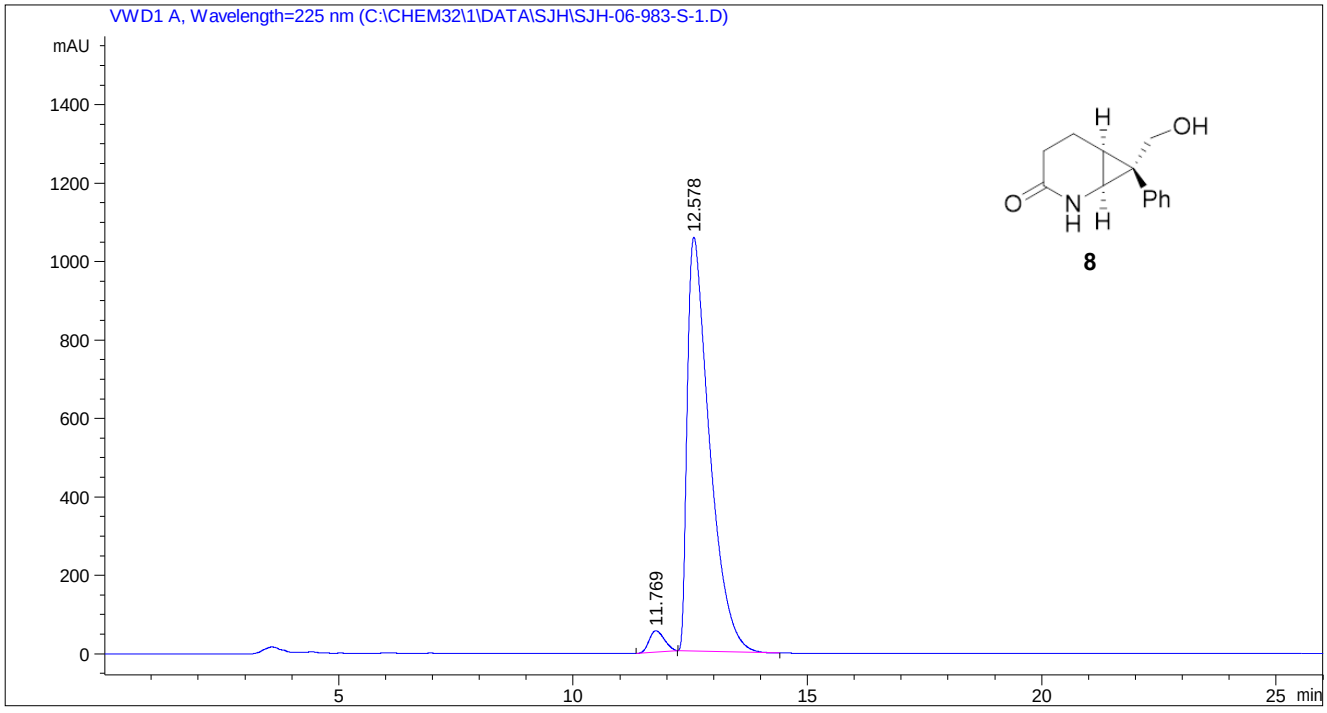


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.827	BV	0.3206	749.03339	34.87262	3.9058
2	11.084	VB	0.3520	1.84285e4	759.71979	96.0942

Daicel Chiralpak IE column, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm

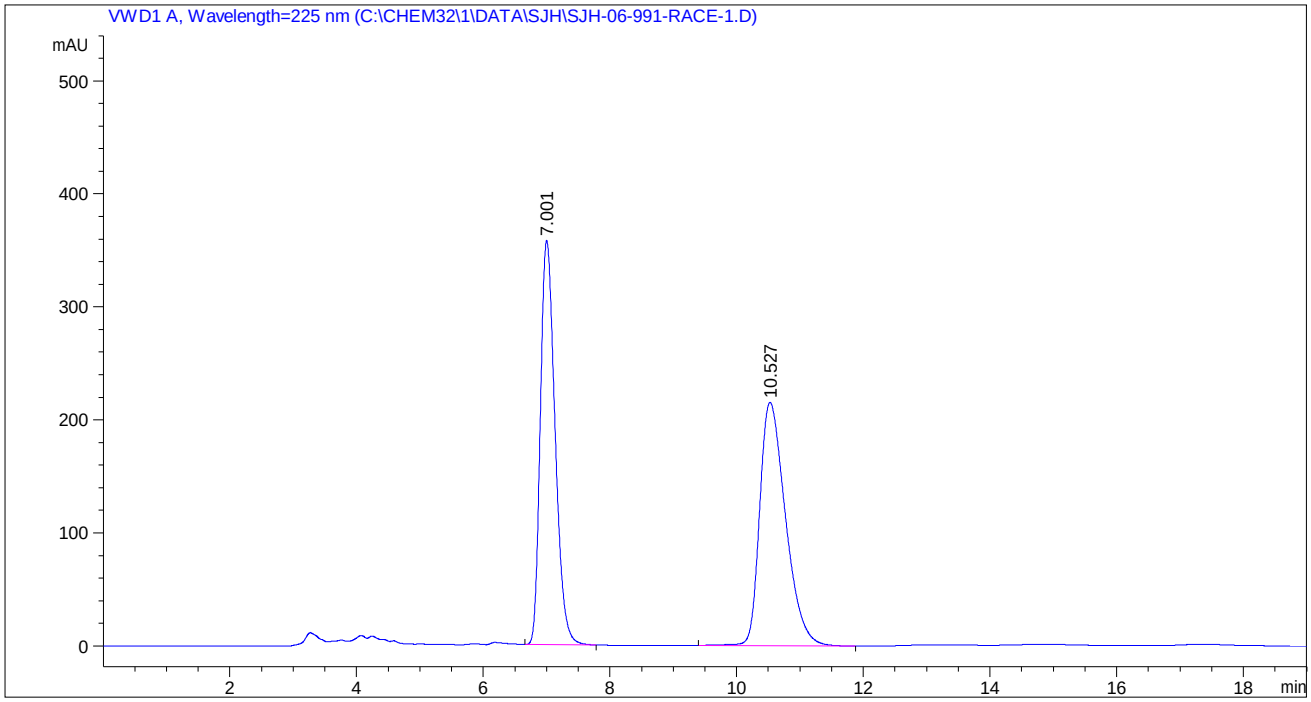


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.694	MM	0.4349	6328.07373	242.49071	49.9214
2	12.900	MM	0.4837	6347.98828	218.72670	50.0786

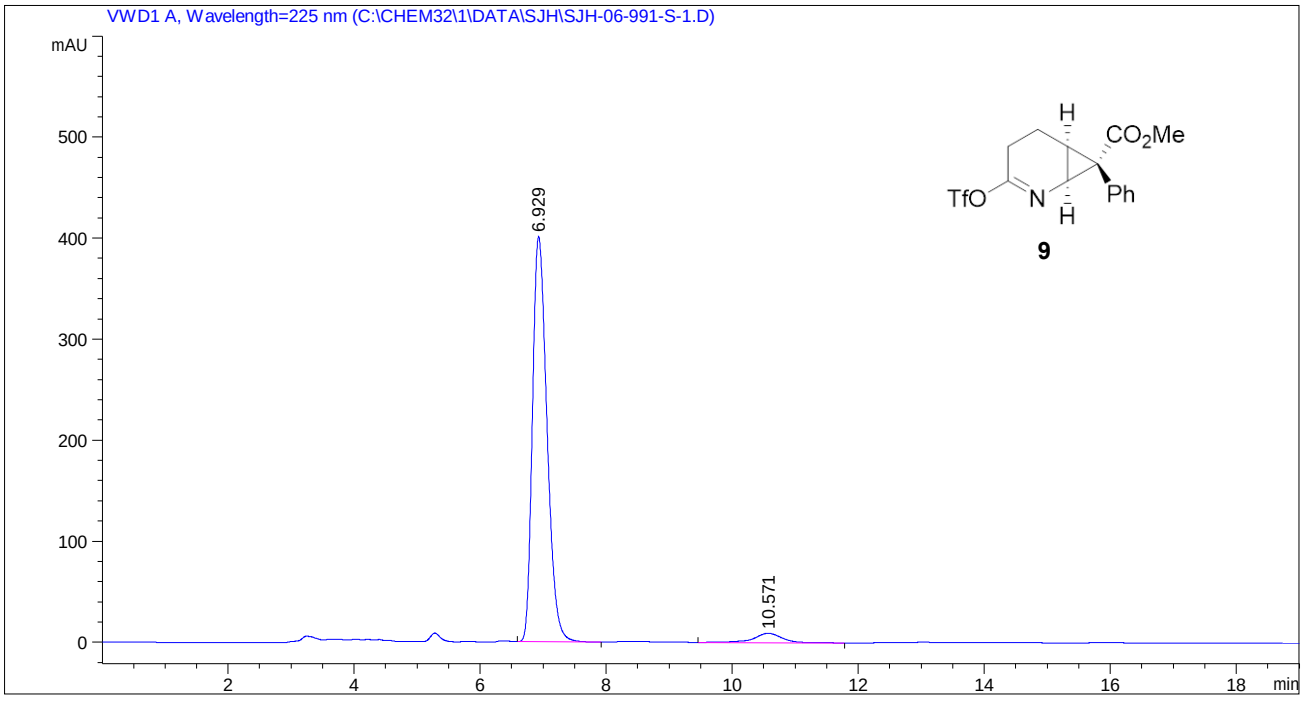


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.769	MM	0.3755	1238.15906	54.95762	3.4320
2	12.578	MM	0.5500	3.48386e4	1055.80042	96.5680

Daicel Chiralpak OD-H, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm

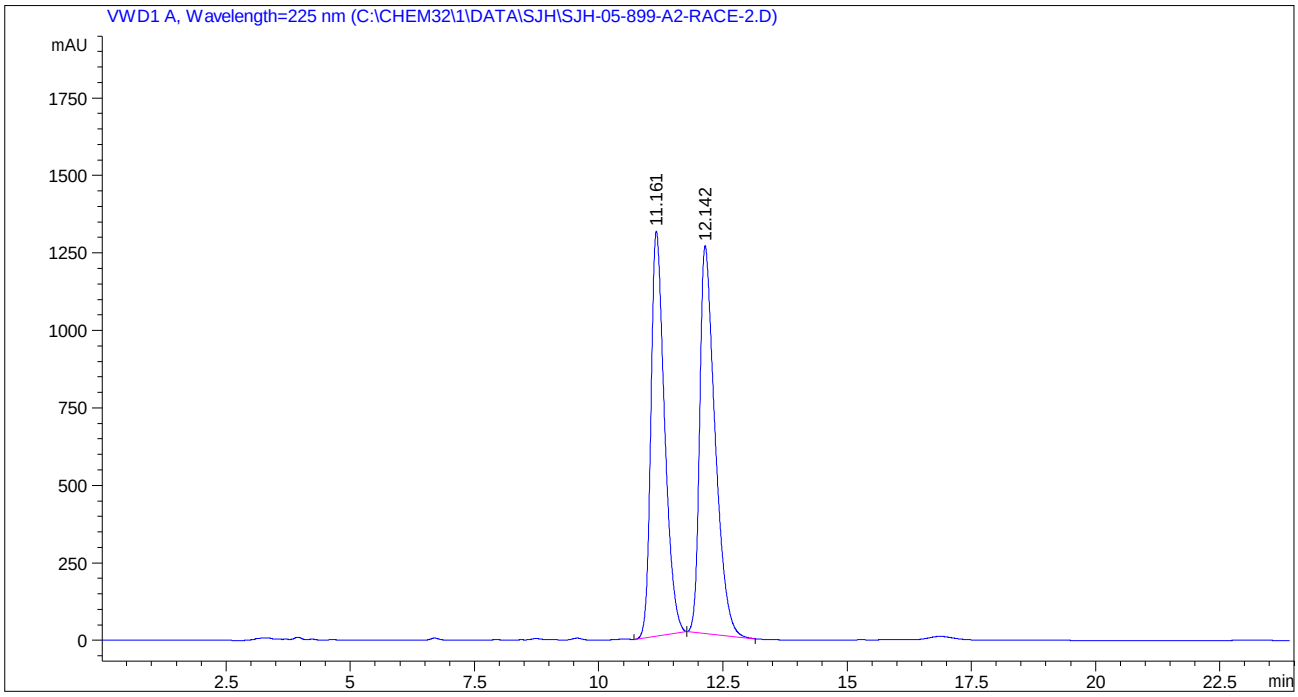


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.001	MM	0.2695	5782.83105	357.64136	48.5790
2	10.527	MM	0.4736	6121.14502	215.42709	51.4210

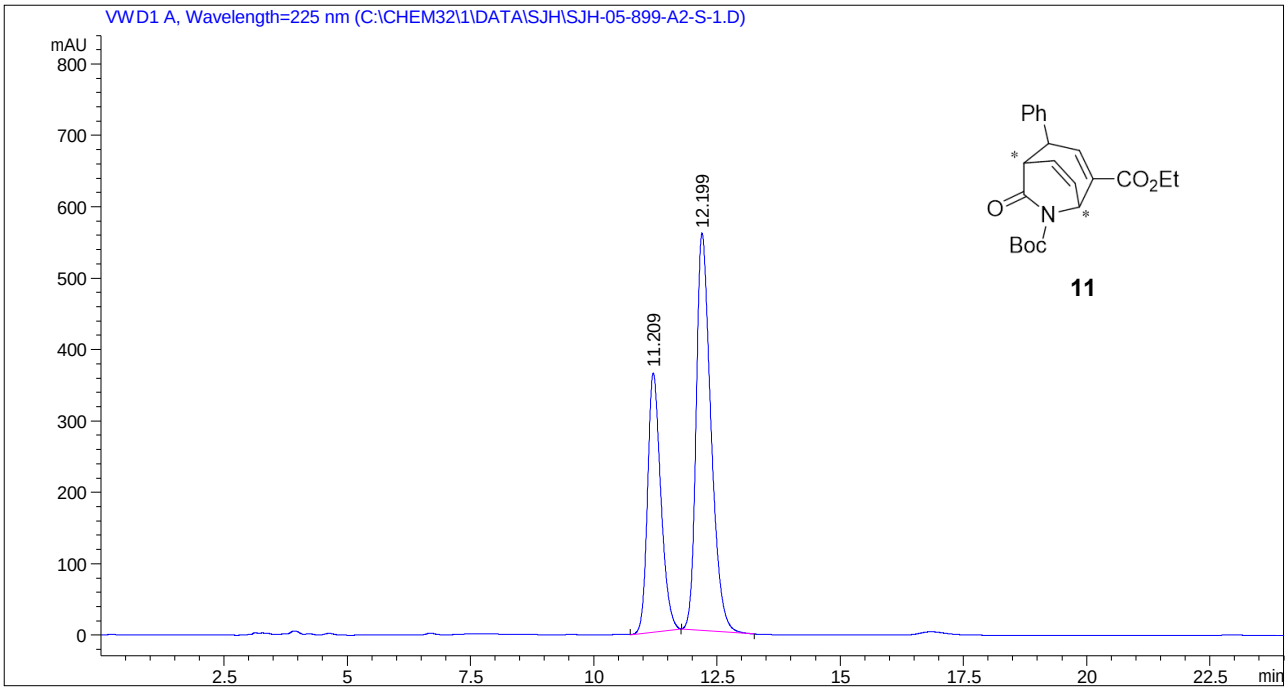


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.929	MM	0.2673	6431.05518	400.99155	95.7550
2	10.571	BB	0.4603	285.09976	9.23236	4.2450

Daicel Chiralpak IA column, n-hexane/i-PrOH = 90/10, flow rate = 1 mL/min, λ = 225 nm

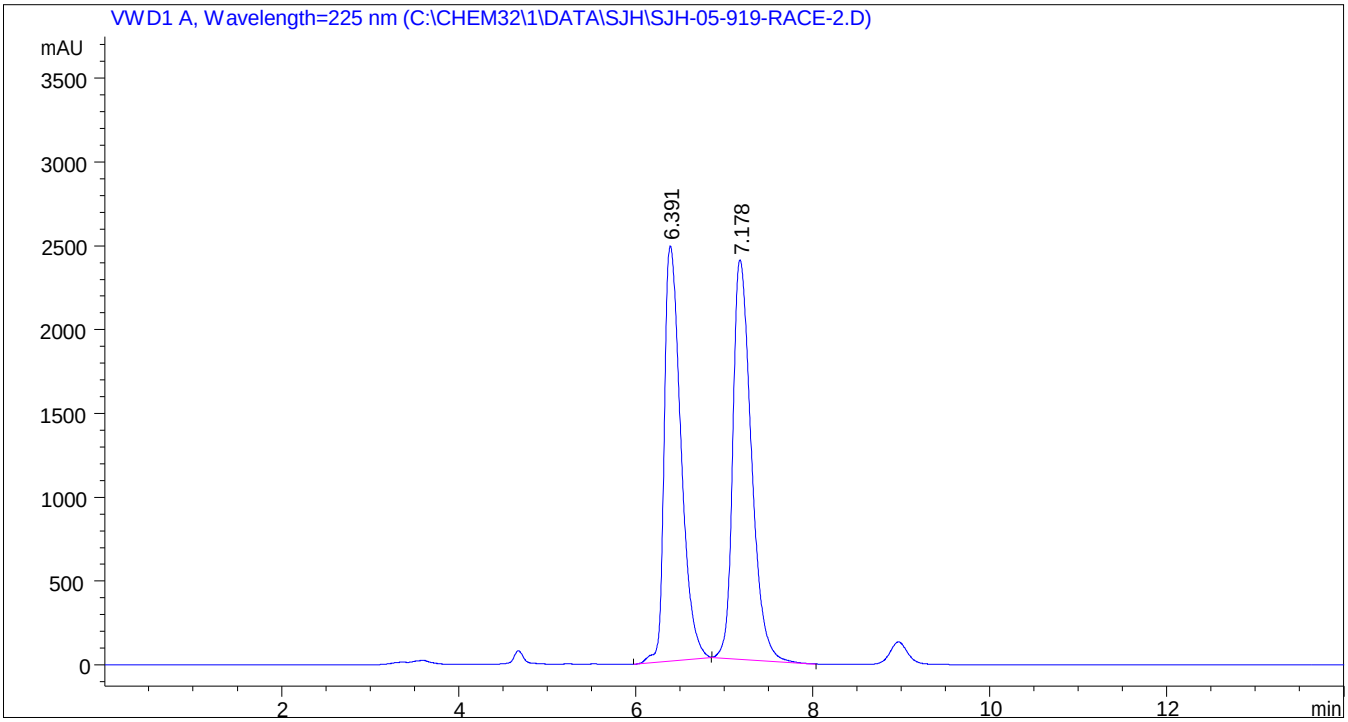


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.161	MM	0.3195	2.50631e4	1307.20911	48.1857
2	12.142	MM	0.3591	2.69505e4	1250.99670	51.8143

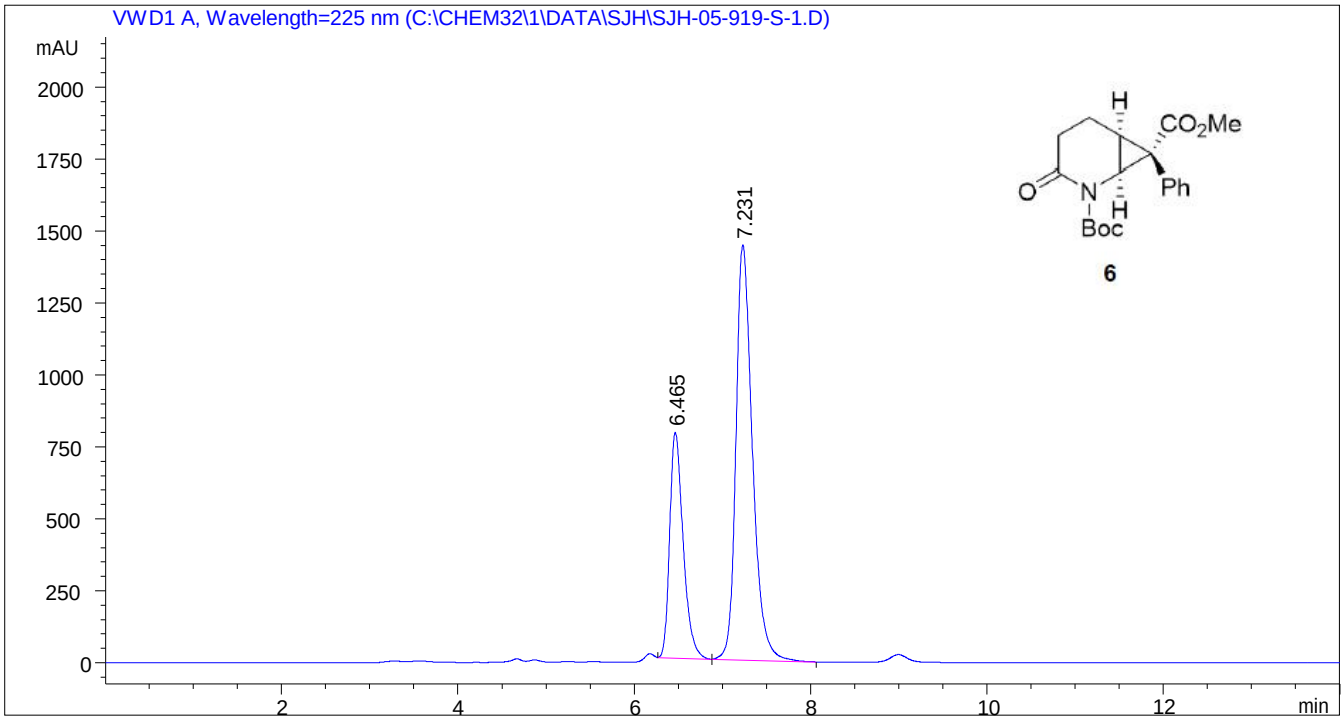


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.209	MM	0.3118	6797.37988	363.38104	36.9524
2	12.199	MM	0.3472	1.15976e4	556.65869	63.0476

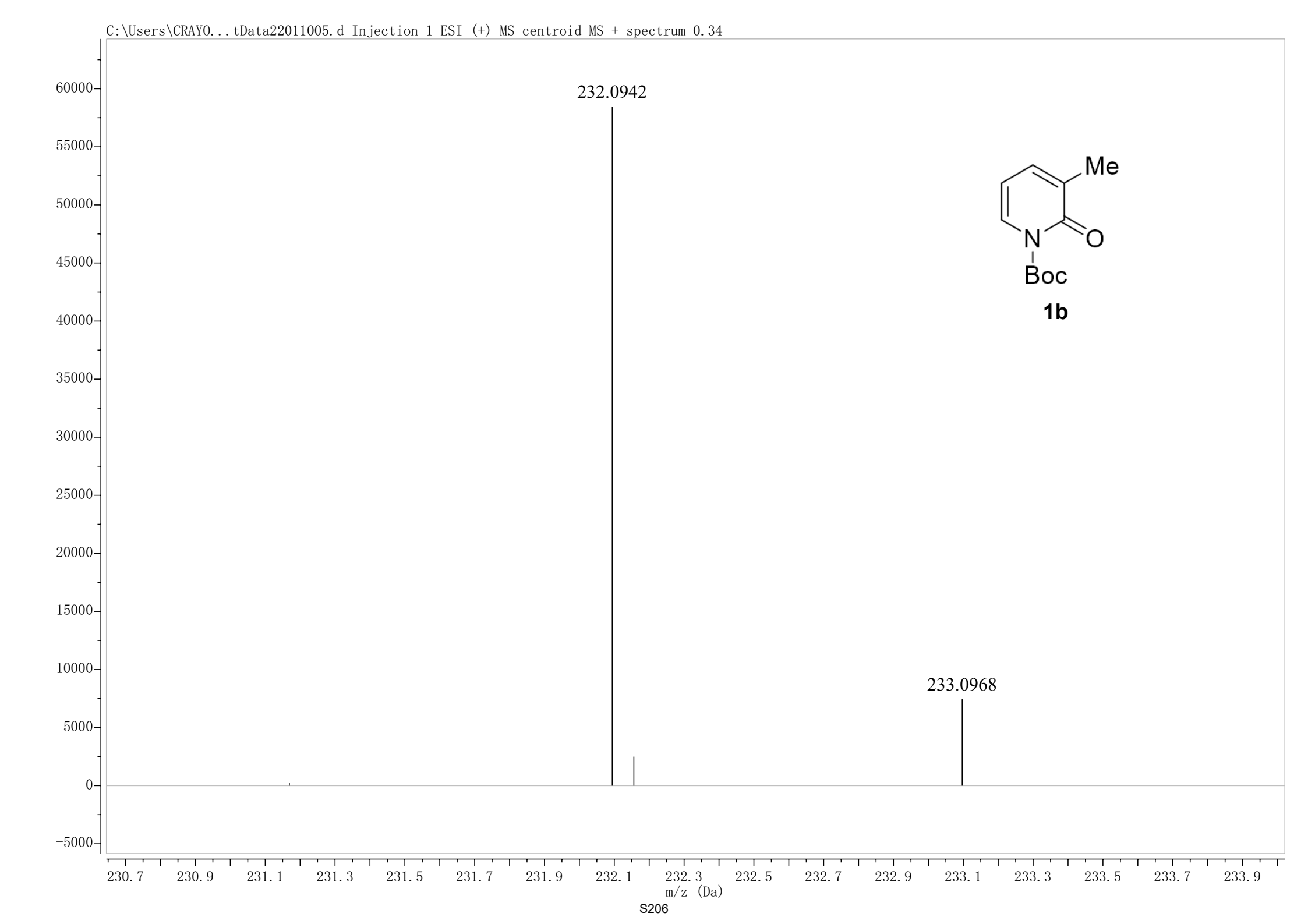
Daicel Chiralpak IA column, n-hexane/i-PrOH = 70/30, flow rate = 1mL/min, λ = 225 nm

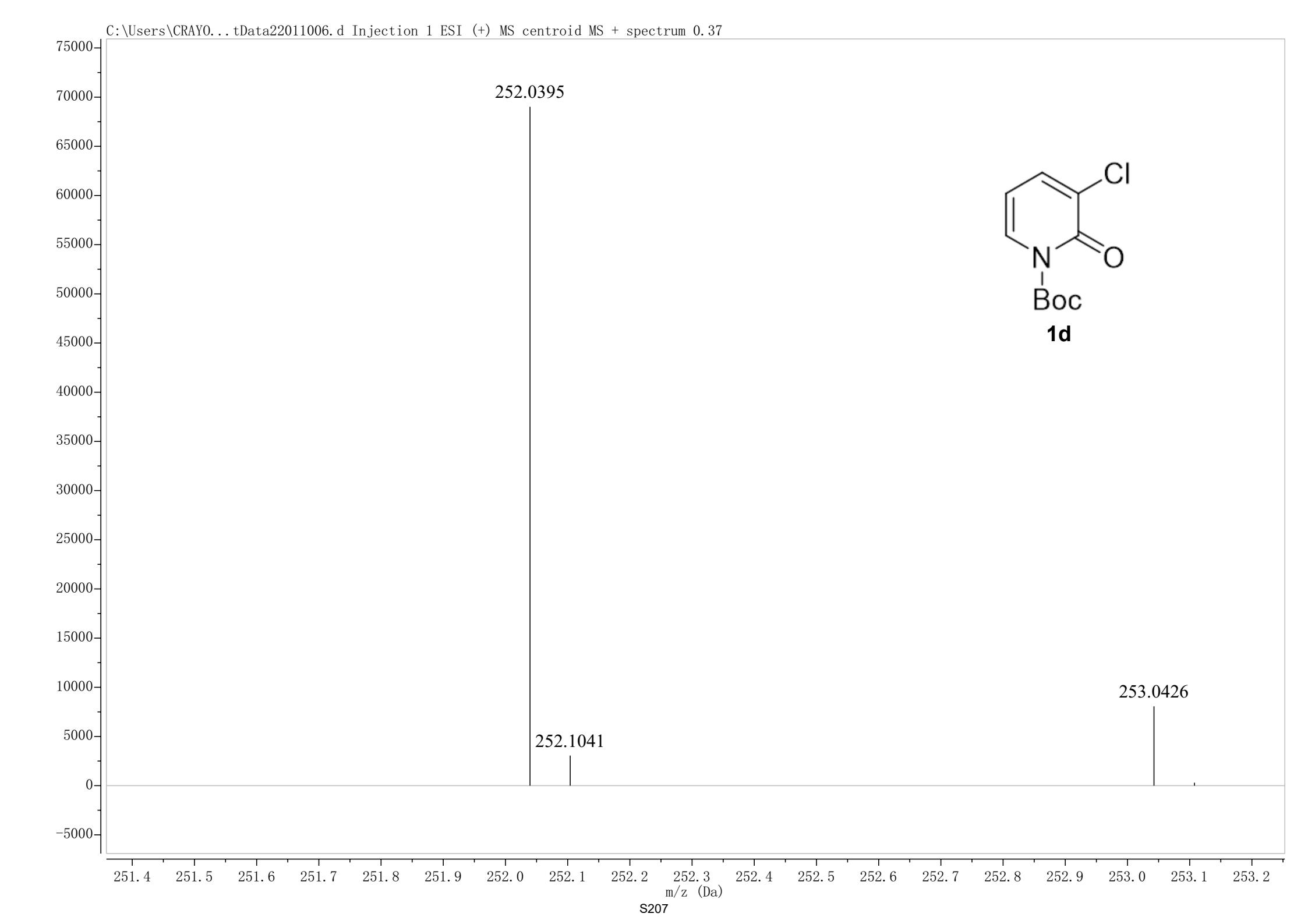


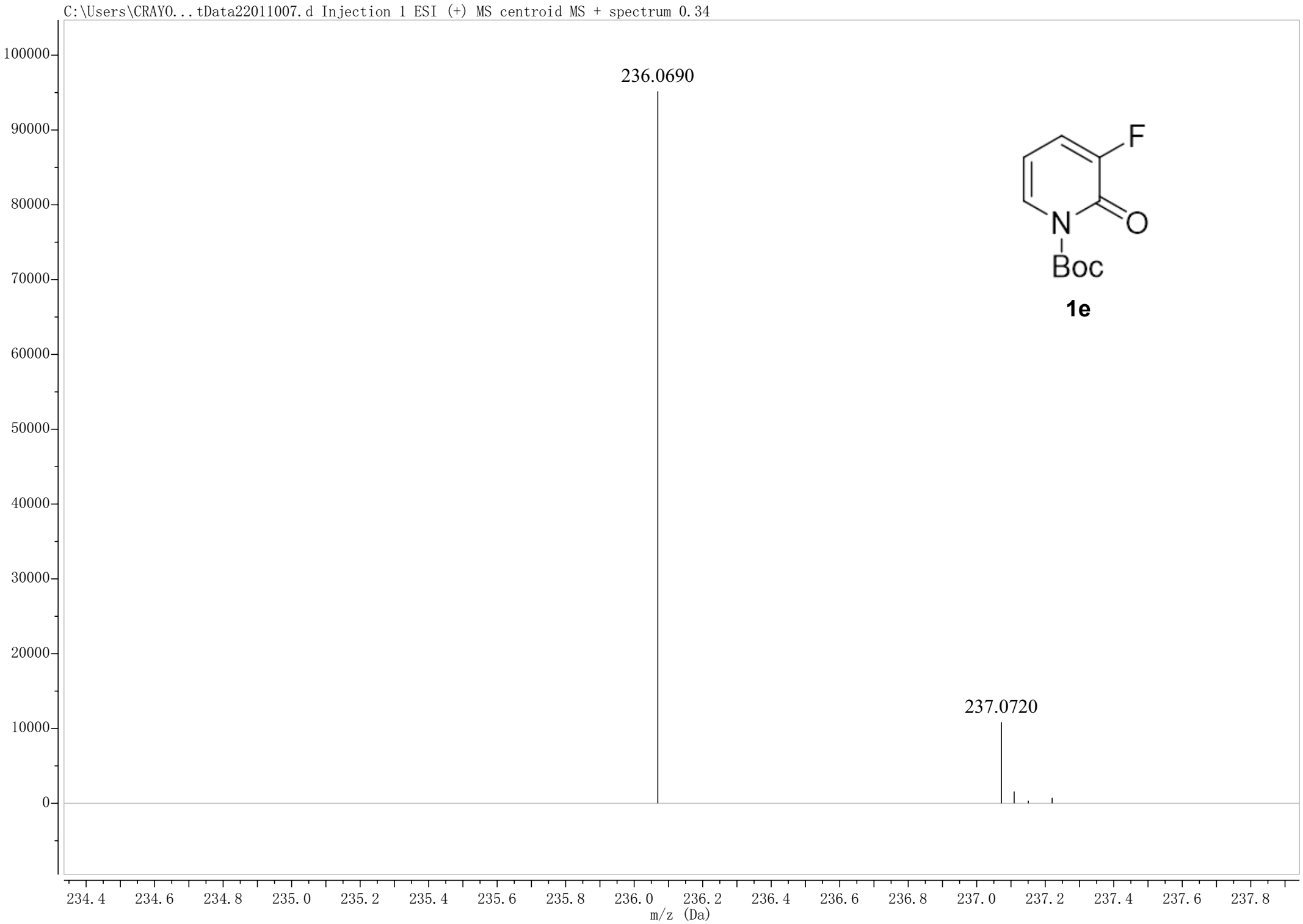
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.391	MM	0.2188	3.25323e4	2477.90186	48.3843
2	7.178	MM	0.2429	3.47050e4	2380.88013	51.6157

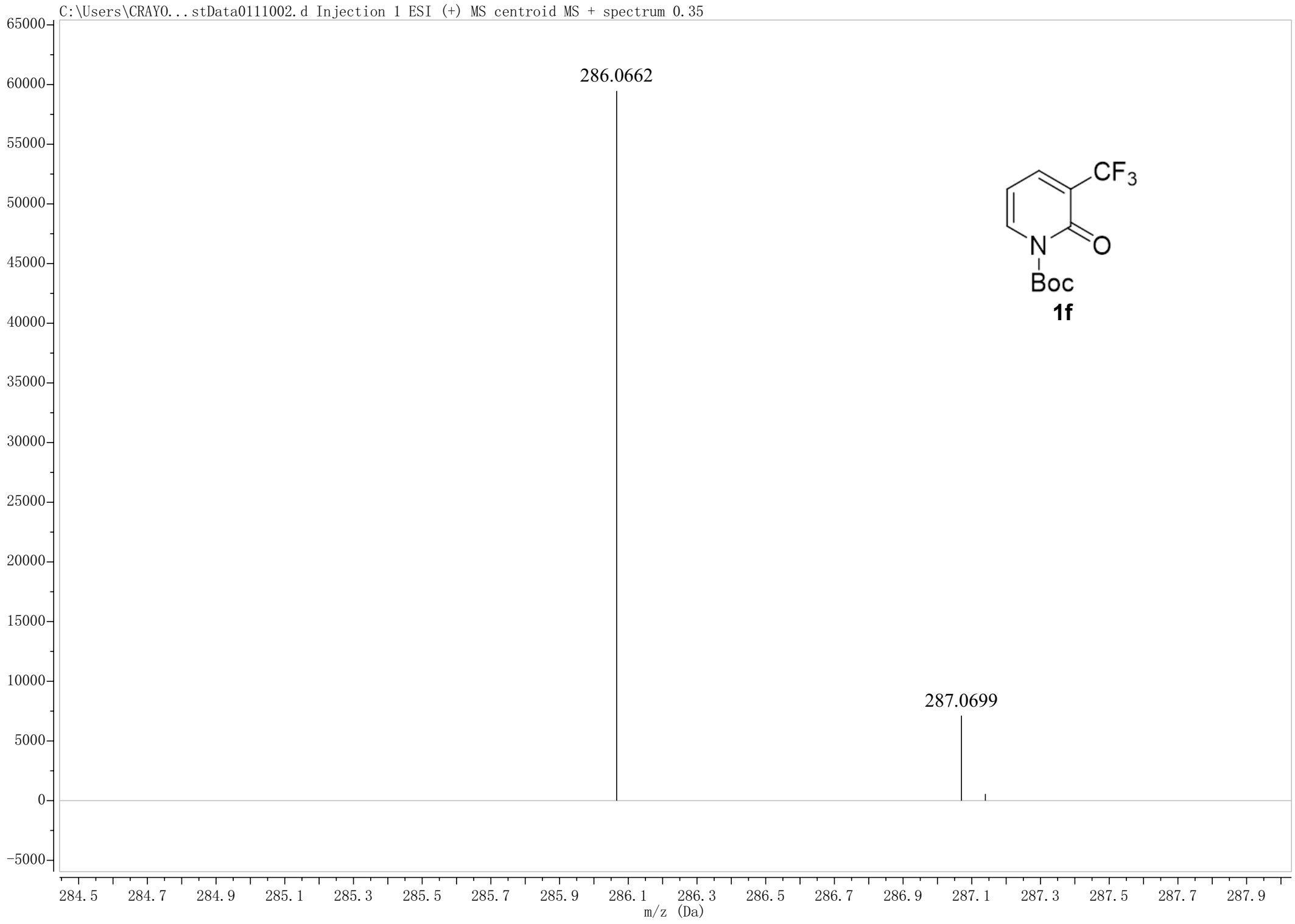


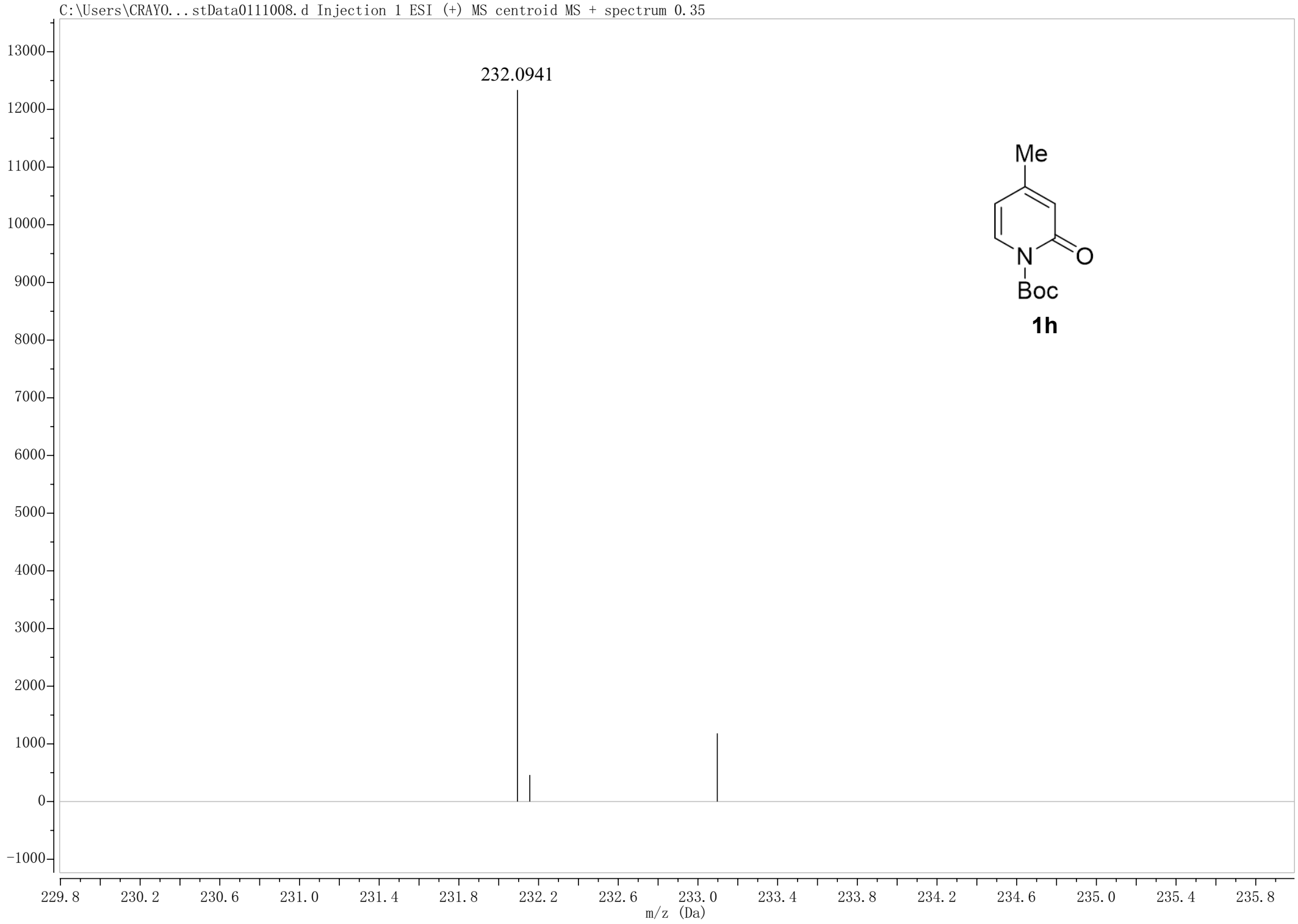
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.465	MM	0.1770	8327.48926	784.16614	30.7418
2	7.231	MM	0.2167	1.87610e4	1442.77917	69.2582

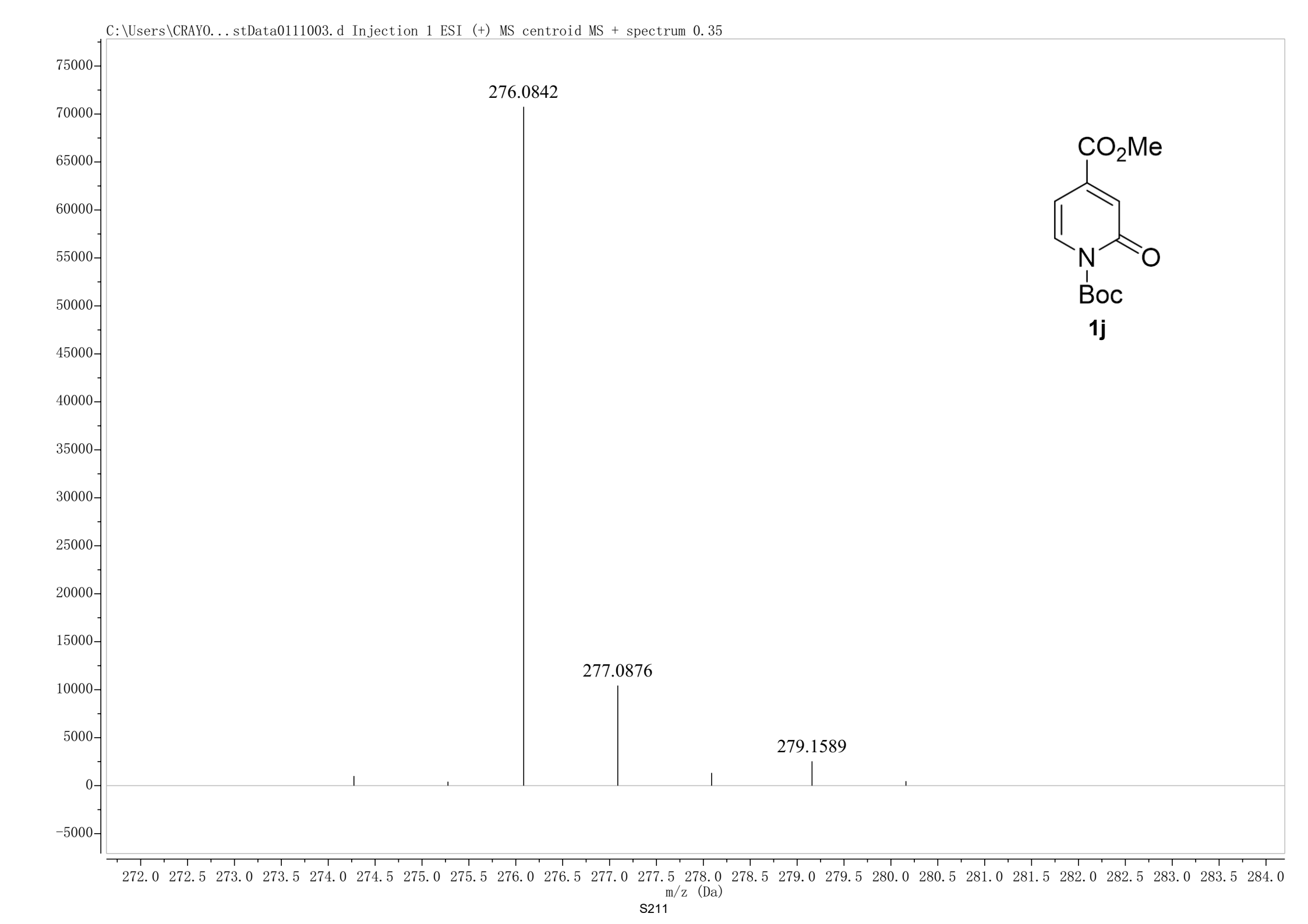

C:\Users\CRAYO...tData22011005.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
232.0942
233.0968
Me
N
O
Boc
1b
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
230.7
230.9
231.1
231.3
231.5
231.7
231.9
232.1
232.3
232.5
232.7
232.9
233.1
233.3
233.5
233.7
233.9
m/z (Da)

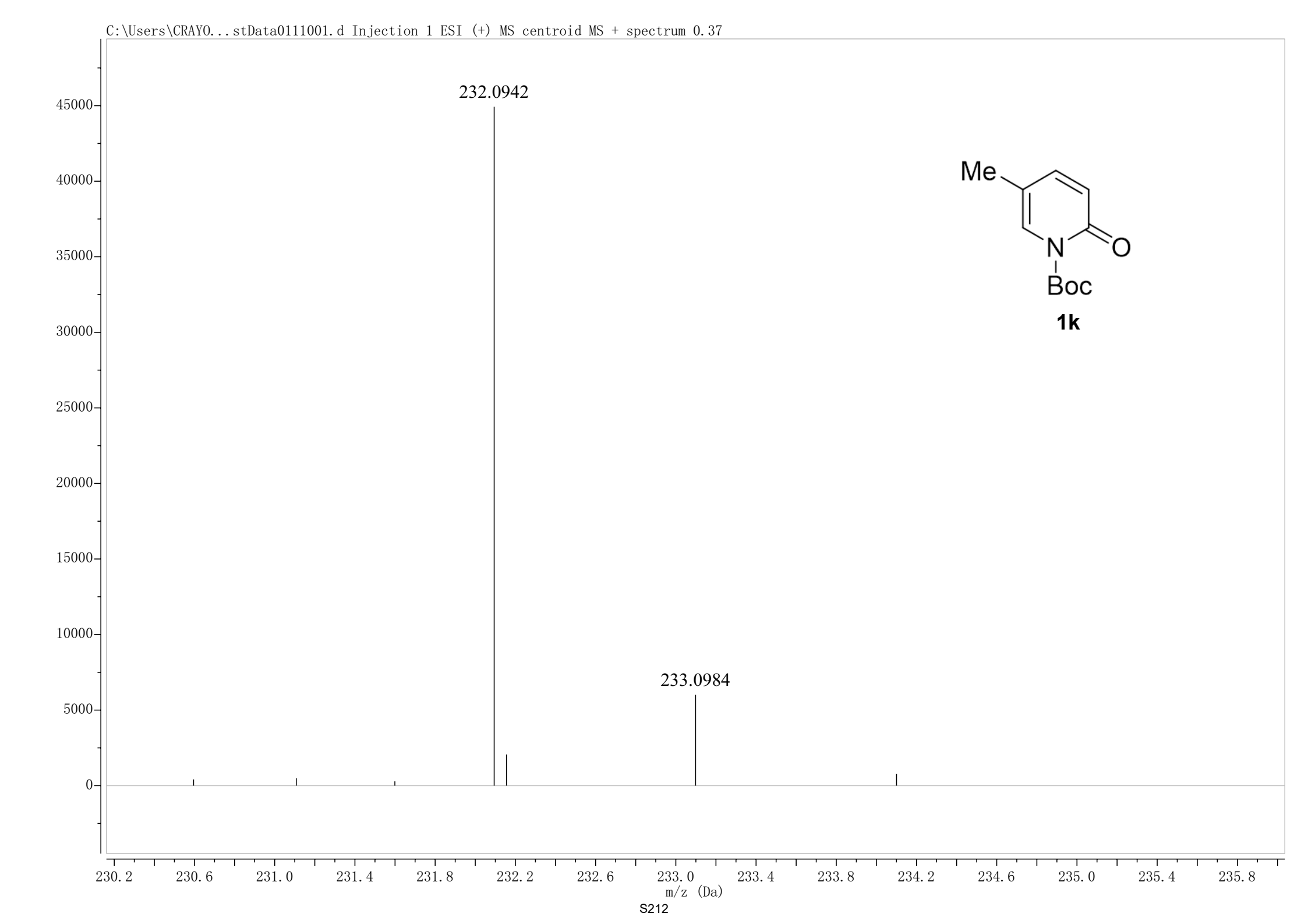

C:\Users\CRAYO...tData22011006.d Injection 1 ESI (+) MS centroid MS + spectrum 0.37
252.0395
252.1041
253.0426
Cl
N
O
Boc
1d
m/z (Da)

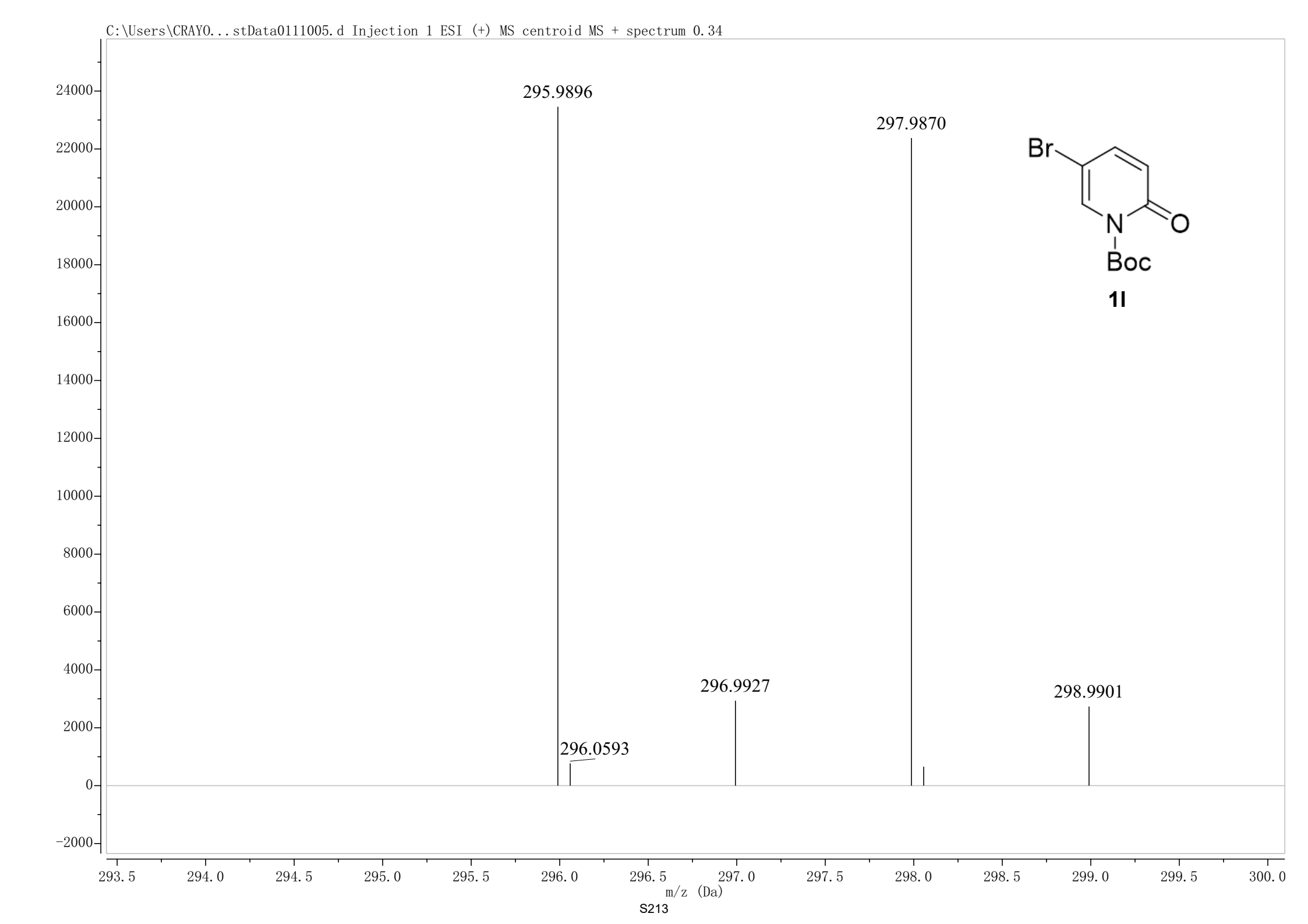

C:\Users\CRAYO...tData22011007.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
236.0690
237.0720
F
N
O
Boc
1e
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
234.4
234.6
234.8
235.0
235.2
235.4
235.6
235.8
236.0
236.2
236.4
236.6
236.8
237.0
237.2
237.4
237.6
237.8
m/z (Da)

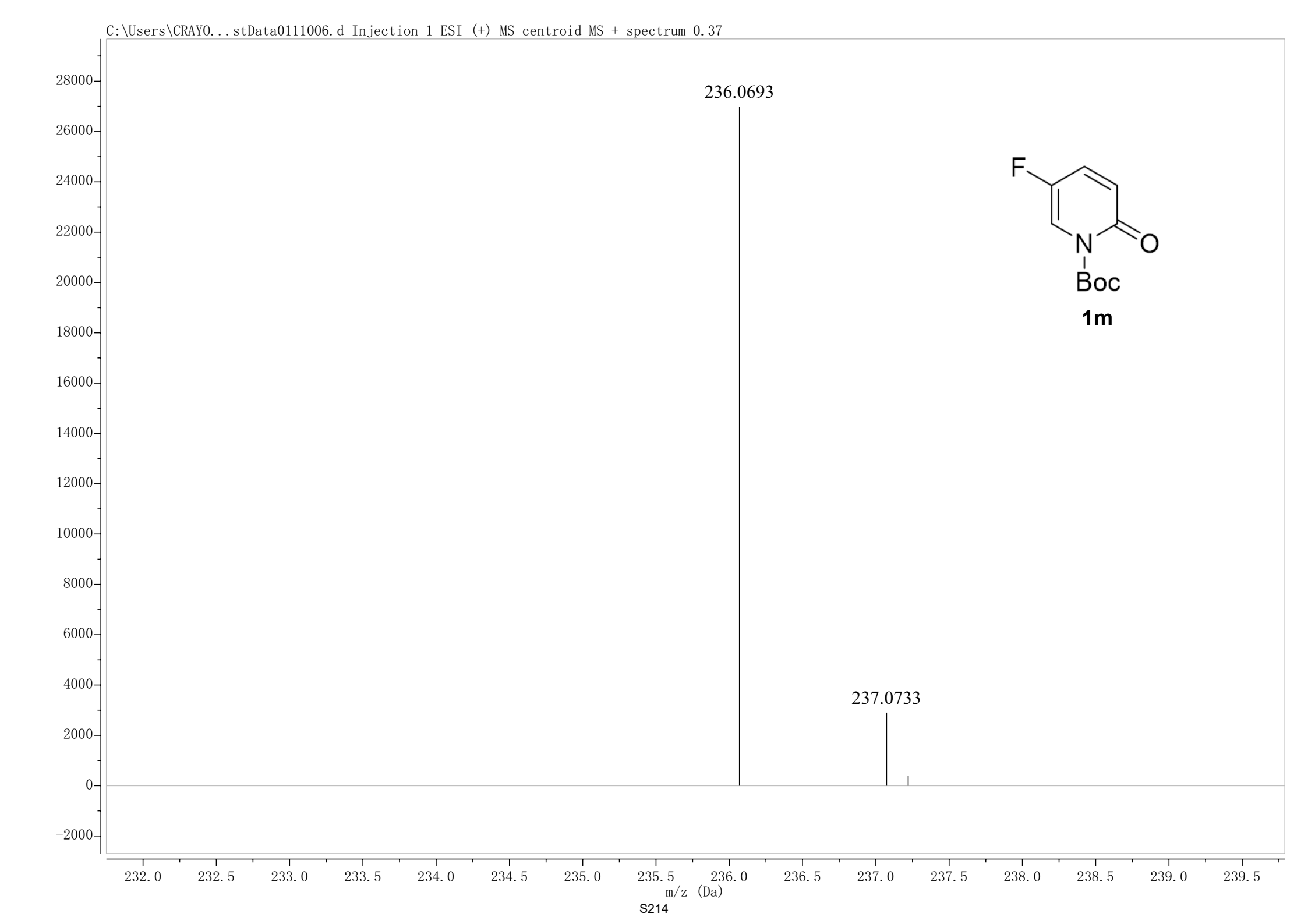

C:\Users\CRAYO...stData0111002.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
286.0662
287.0699
CF3
N
O
Boc
1f
m/z (Da)

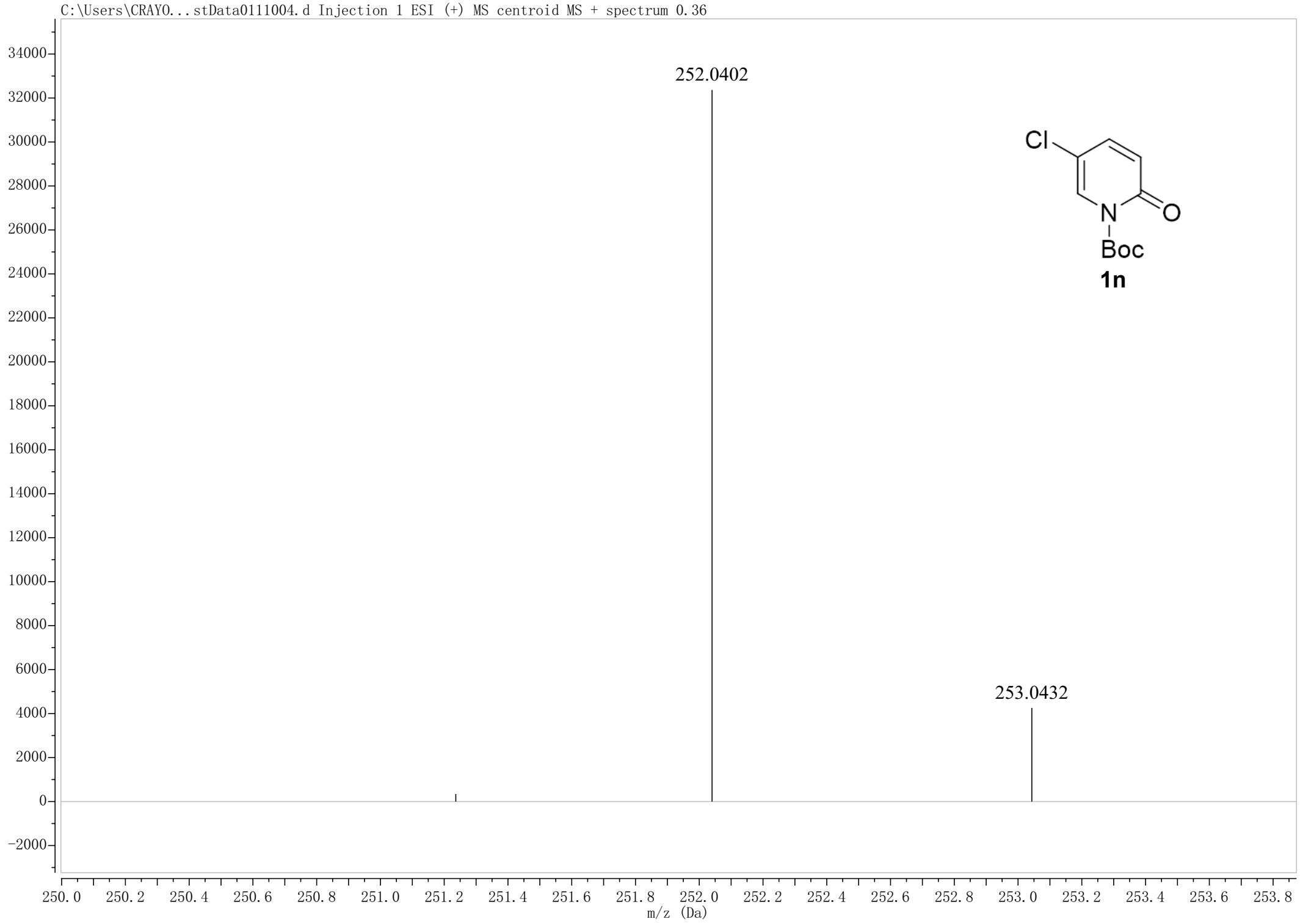

C:\Users\CRAYO...stData0111008.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
232.0941
Me
N
O
Boc
1h
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
229.8
230.2
230.6
231.0
231.4
231.8
232.2
232.6
233.0
233.4
233.8
234.2
234.6
235.0
235.4
235.8
m/z (Da)

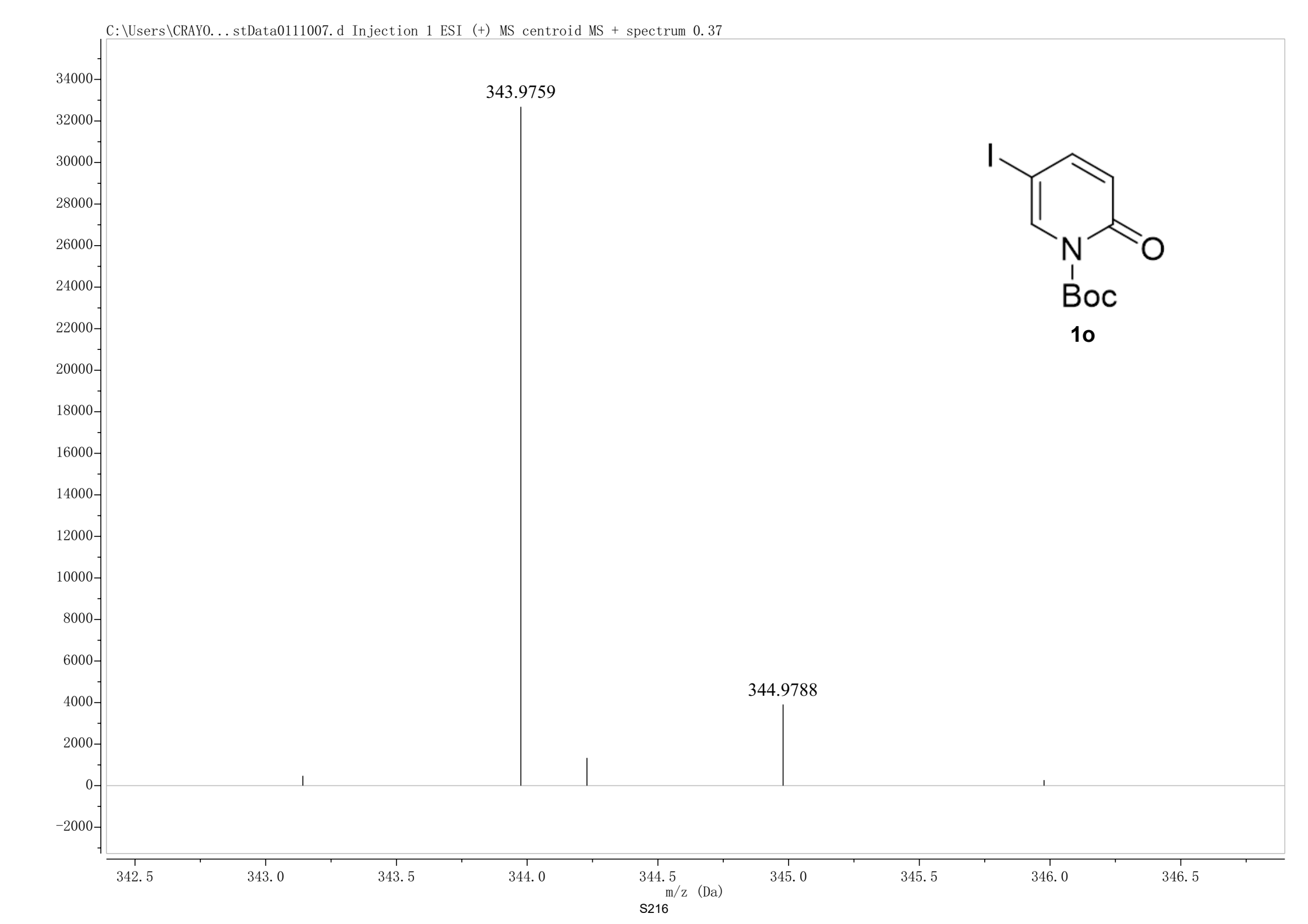

C:\Users\CRAYO...stData0111003.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
276.0842
277.0876
279.1589
CO2Me
N
O
Boc
1j
m/z (Da)

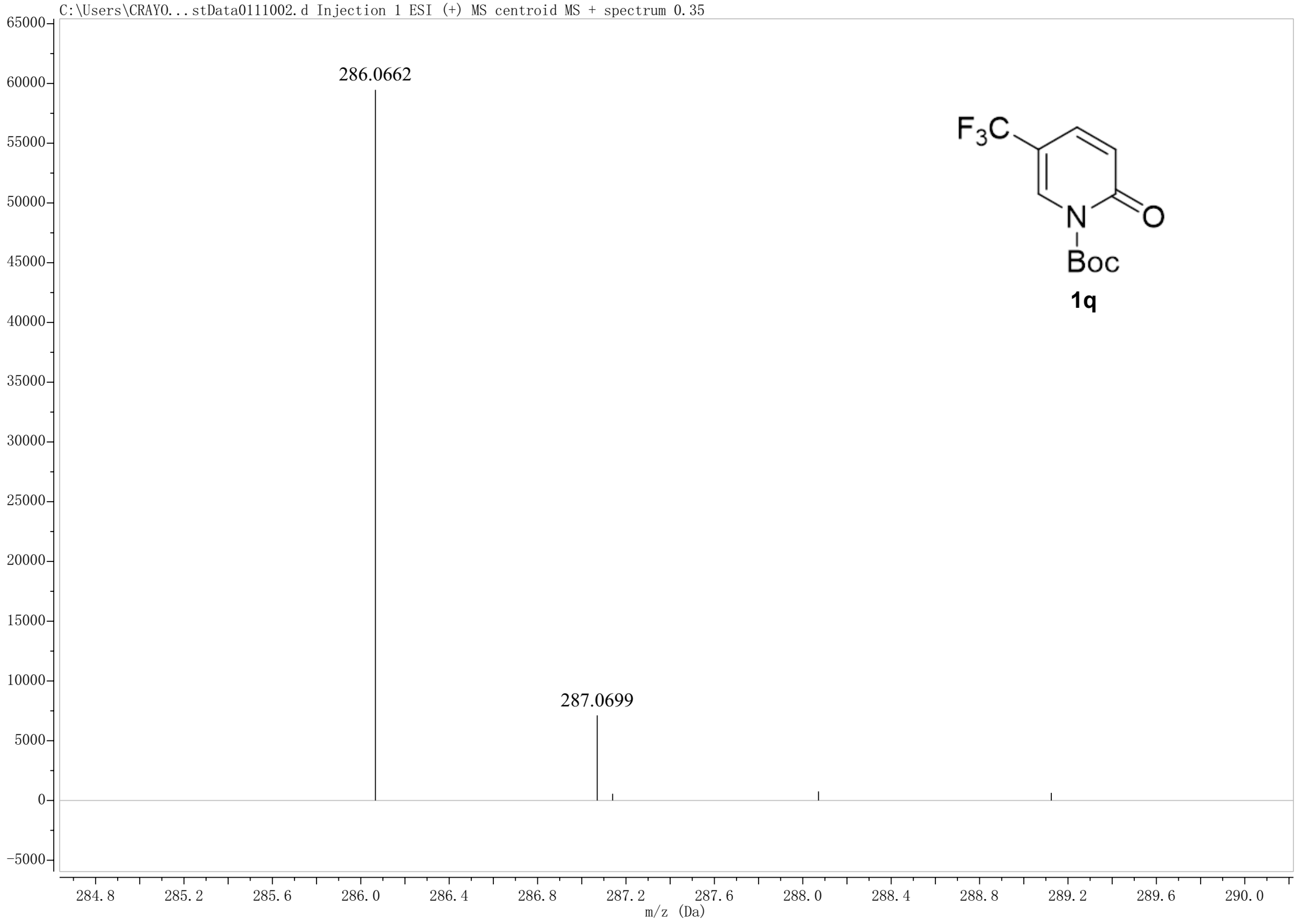

C:\Users\CRAYO...stData0111001.d Injection 1 ESI (+) MS centroid MS + spectrum 0.37
232.0942
233.0984
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
230.2
230.6
231.0
231.4
231.8
232.2
232.6
233.0
233.4
233.8
234.2
234.6
235.0
235.4
235.8
m/z (Da)
Me
N
O
Boc
1k


C:\Users\CRAYO...stData0111005.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
295.9896
297.9870
296.9927
298.9901
296.0593
Br
N
O
Boc
1l
m/z (Da)

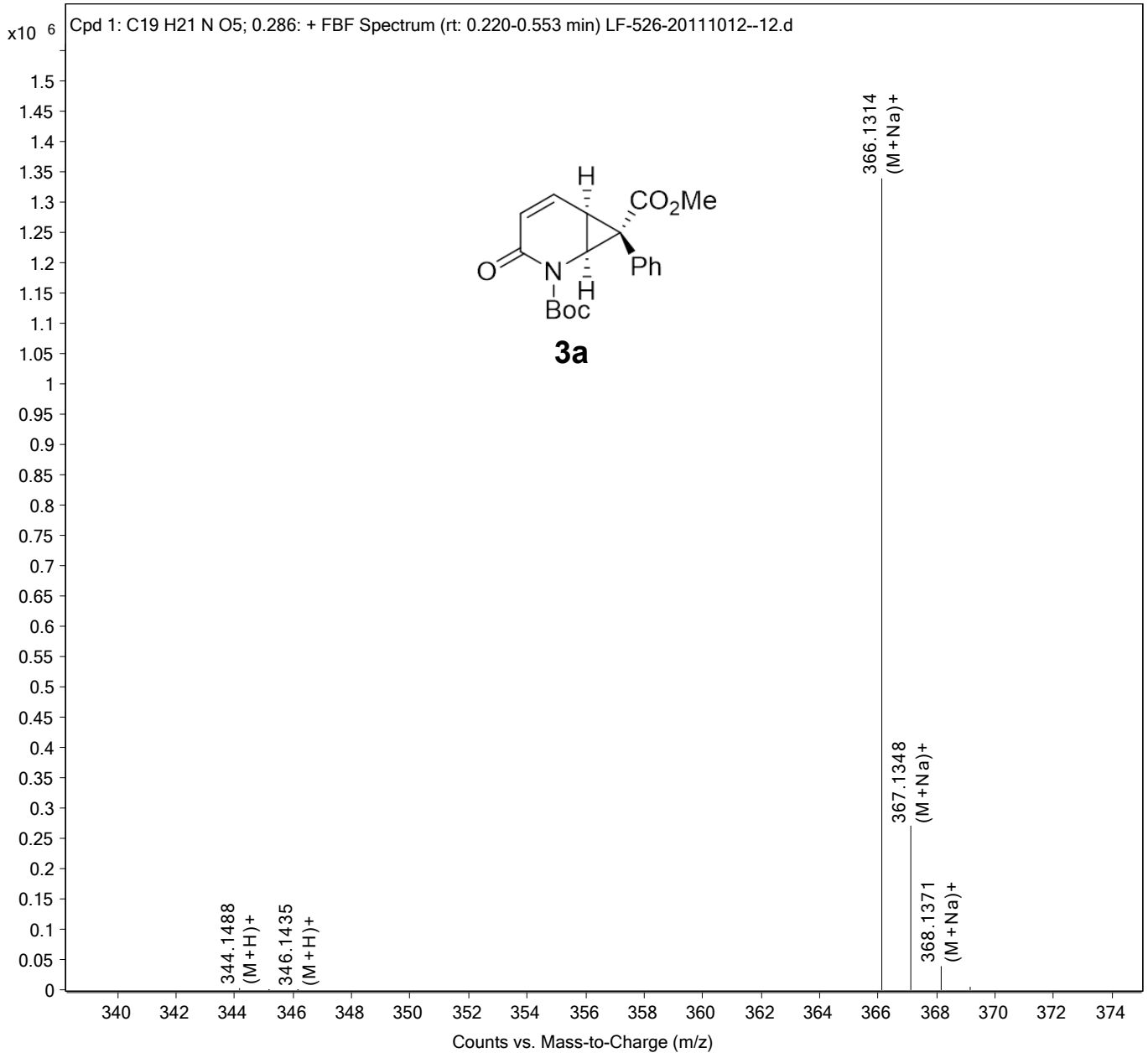

C:\Users\CRAYO...stData0111006.d Injection 1 ESI (+) MS centroid MS + spectrum 0.37
236.0693
237.0733
F
N
O
Boc
1m
m/z (Da)


C:\Users\CRAYO...stData0111004.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36
252.0402
253.0432
Cl
N
O
Boc
1n
m/z (Da)


C:\Users\CRAYO...stData0111007.d Injection 1 ESI (+) MS centroid MS + spectrum 0.37
343.9759
344.9788
I
N
O
Boc
1o
m/z (Da)

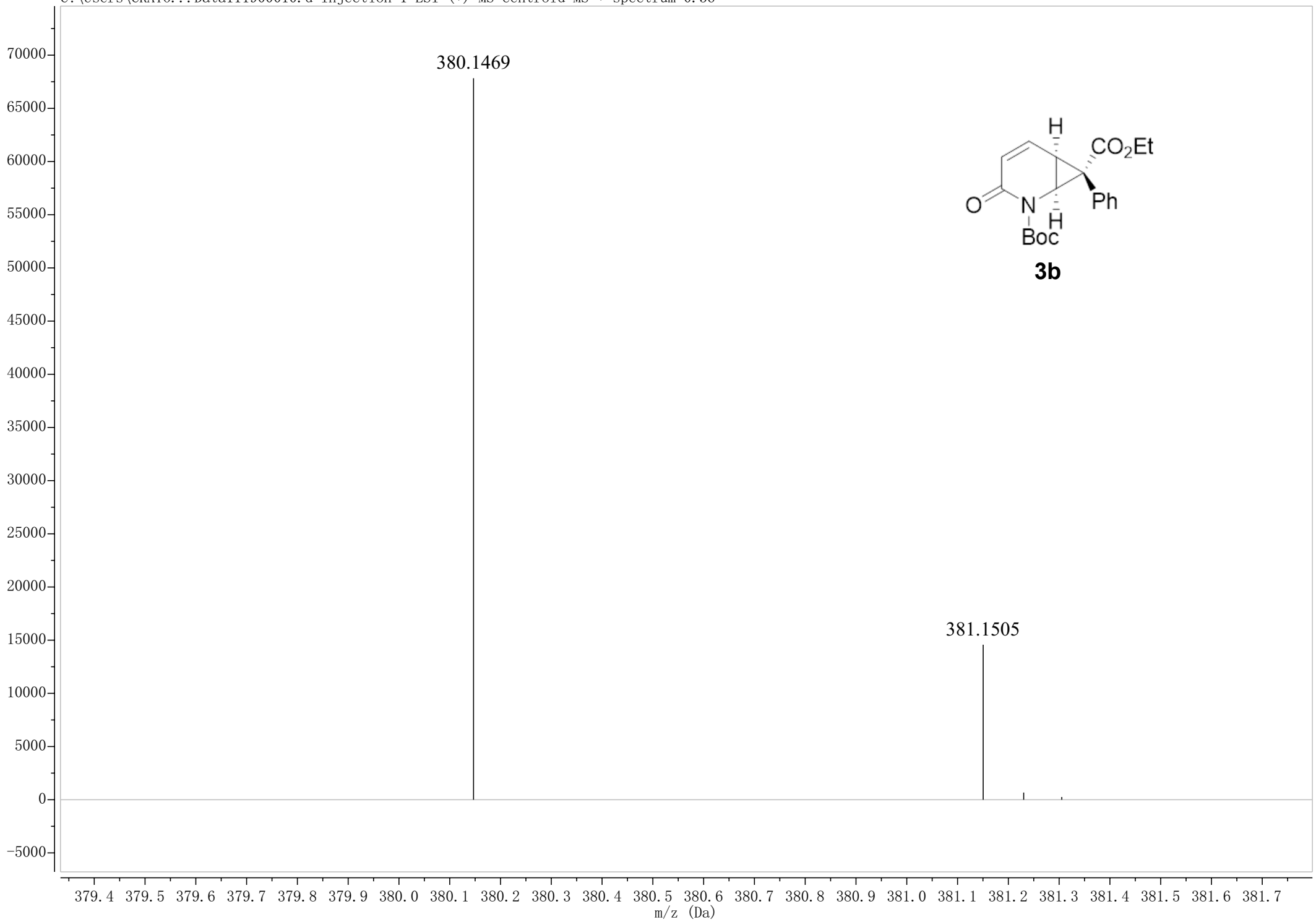

C:\Users\CRAYO...stData0111002.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
286.0662
287.0699
F3C
N
O
Boc
1q
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
284.8
285.2
285.6
286.0
286.4
286.8
287.2
287.6
288.0
288.4
288.8
289.2
289.6
290.0
m/z (Da)

Sample Name	Sample12	**Position**	P2-B1	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--12.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:33:58 AM (UTC+08:00)



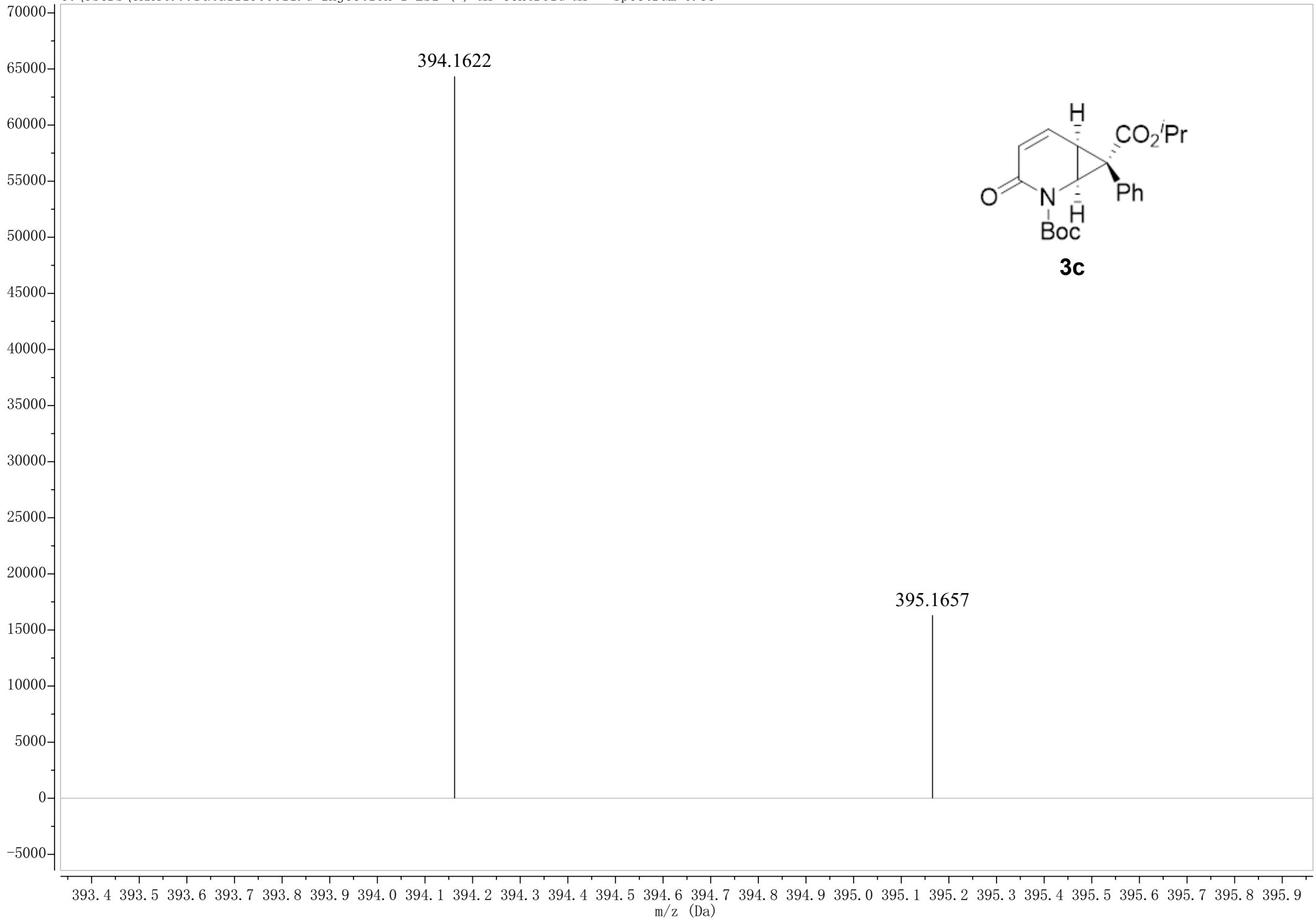
3a

C:\Users\CRAYO...Data111900010.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



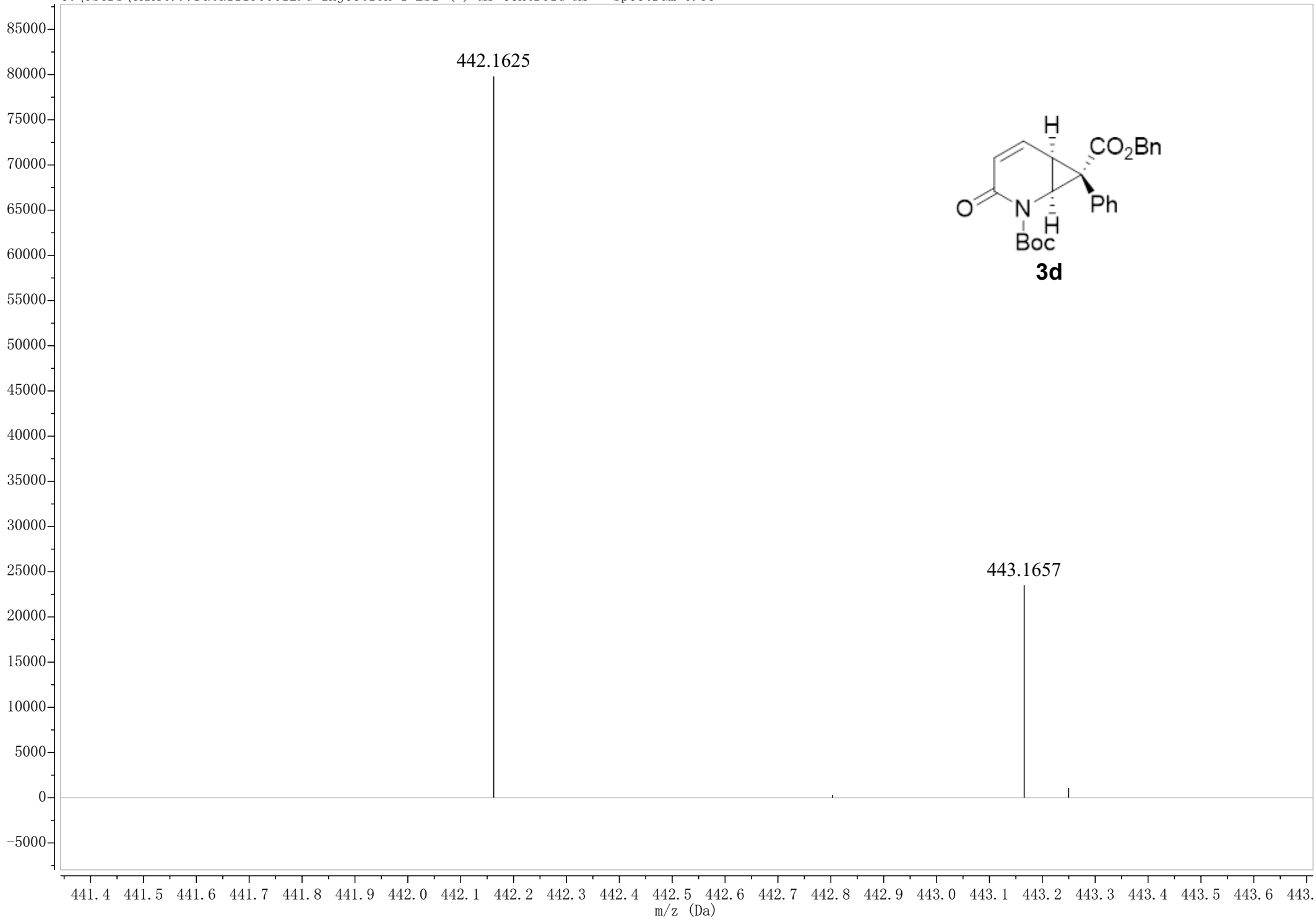
3b

C:\Users\CRAYO...Data111900011.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35

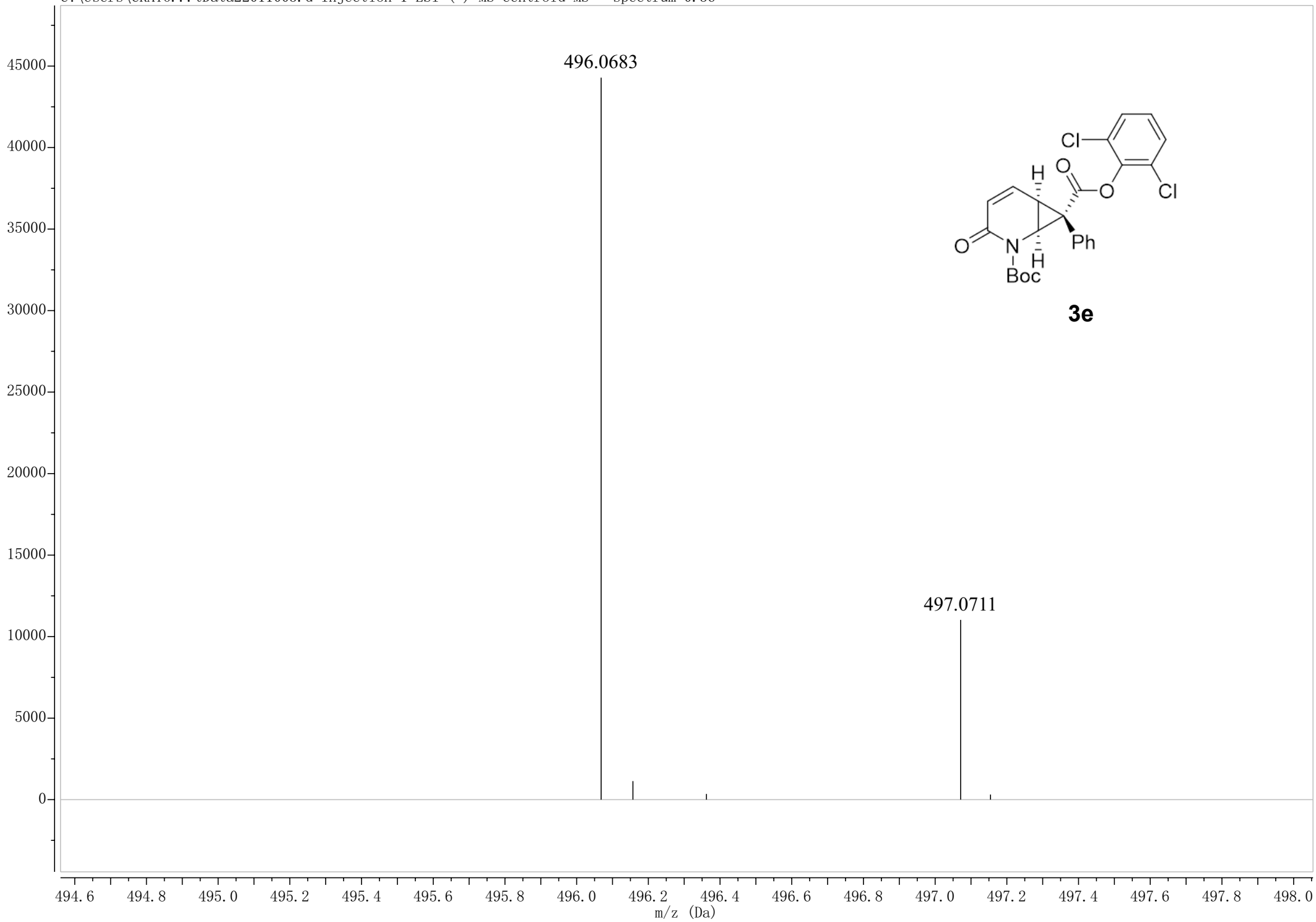


3c

C:\Users\CRAYO...Data111900012.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35

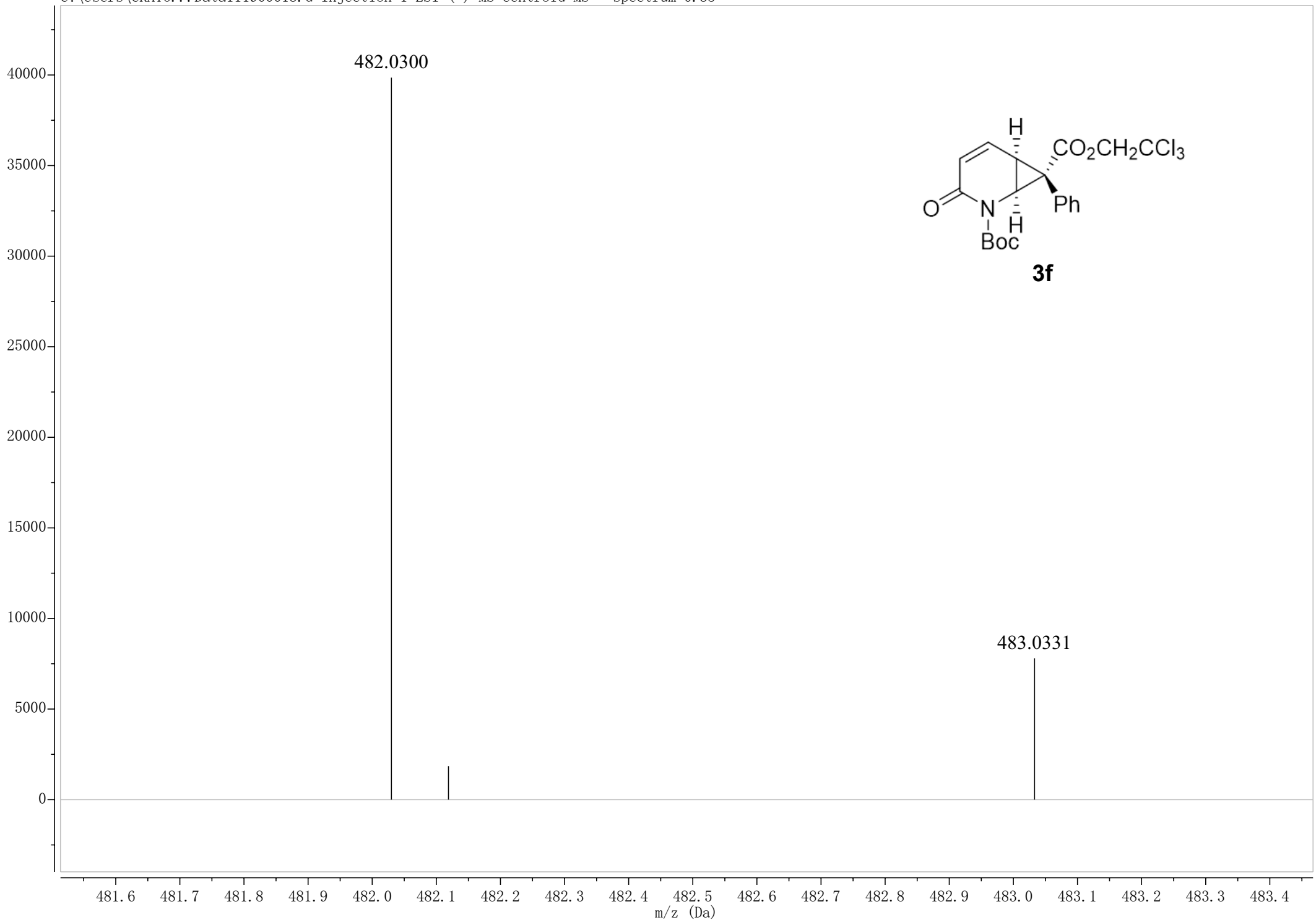


C:\Users\CRAYO...tData22011003.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



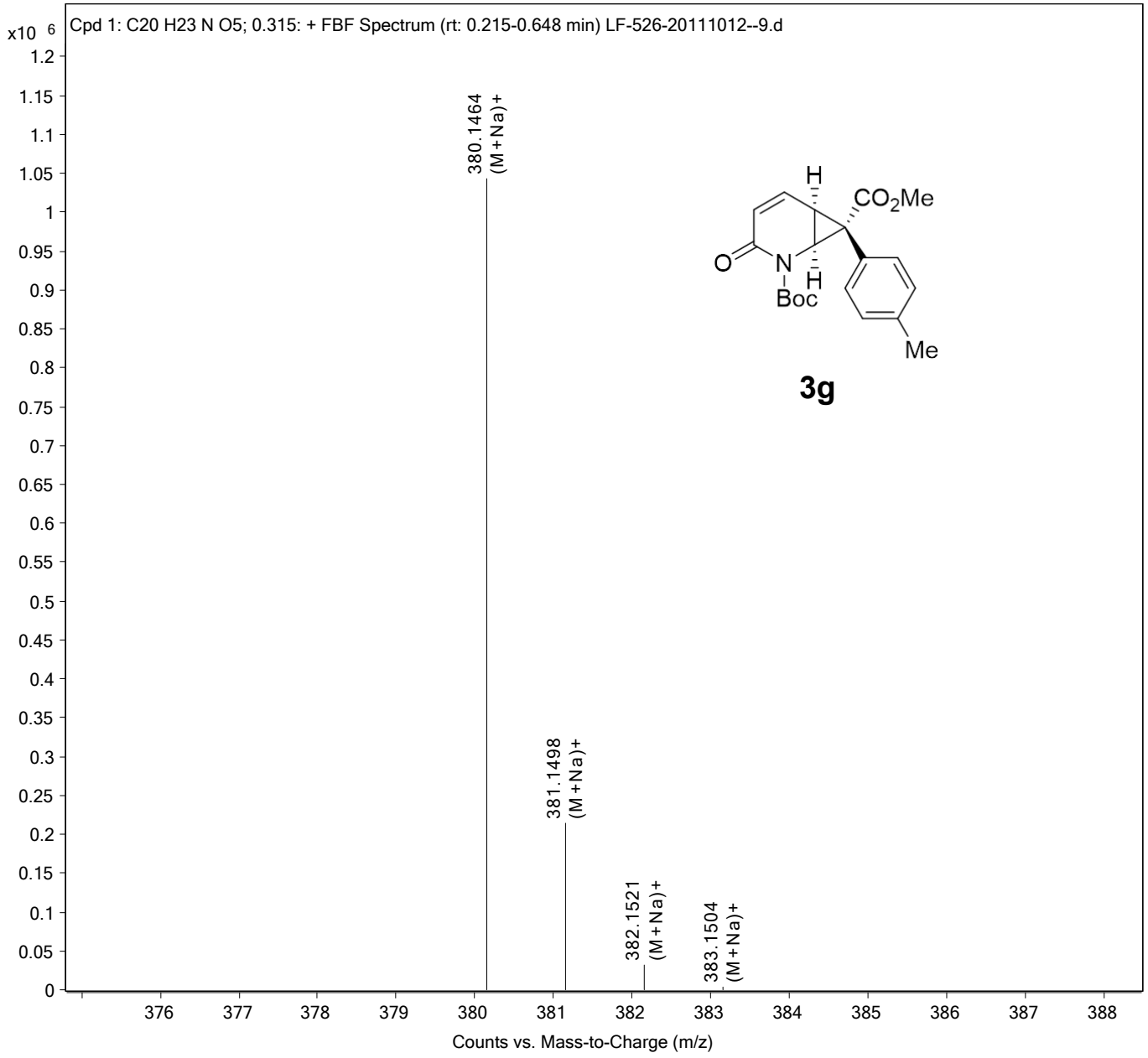
3e

C:\Users\CRAYO...Data111900013.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35

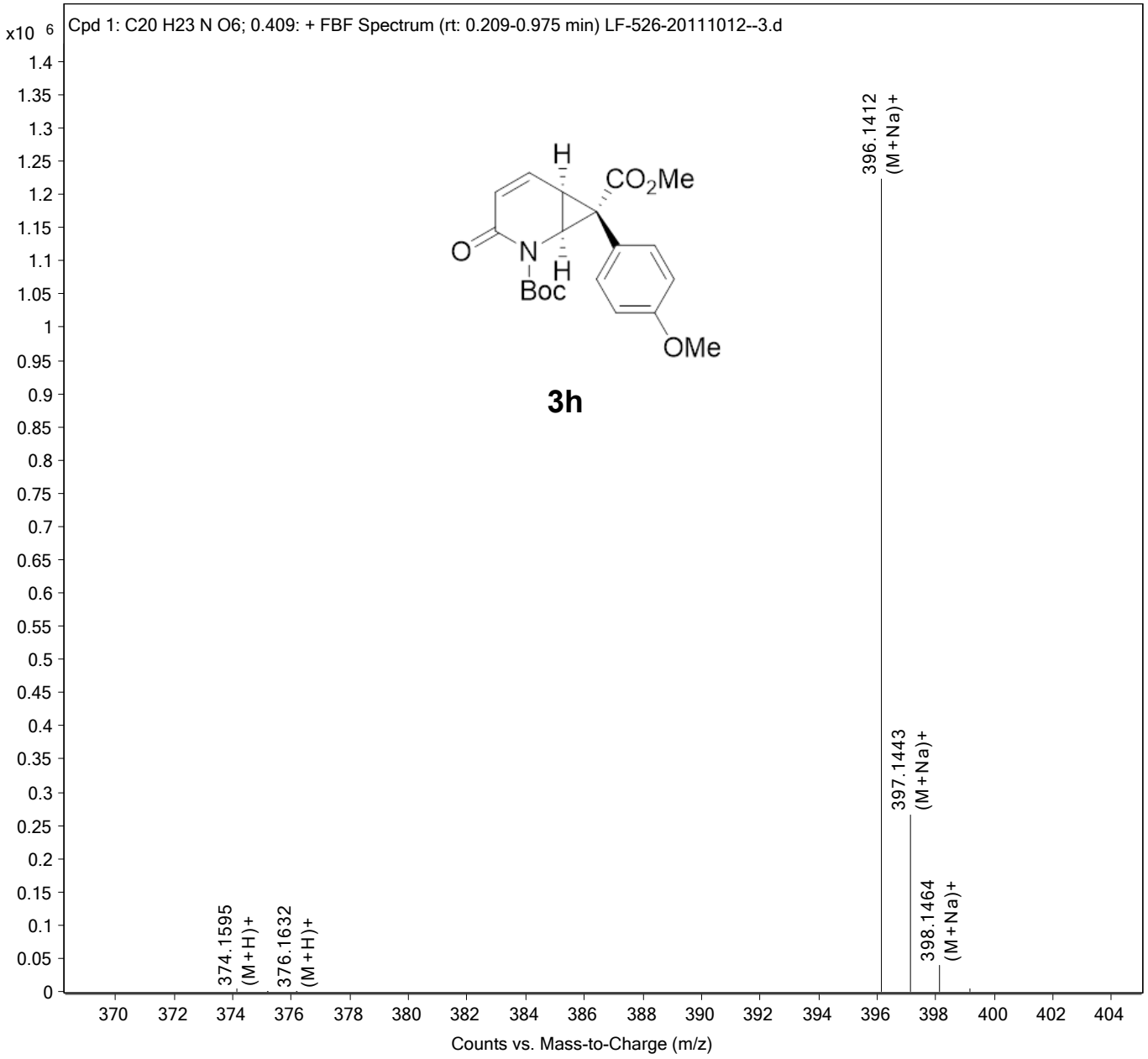


3f

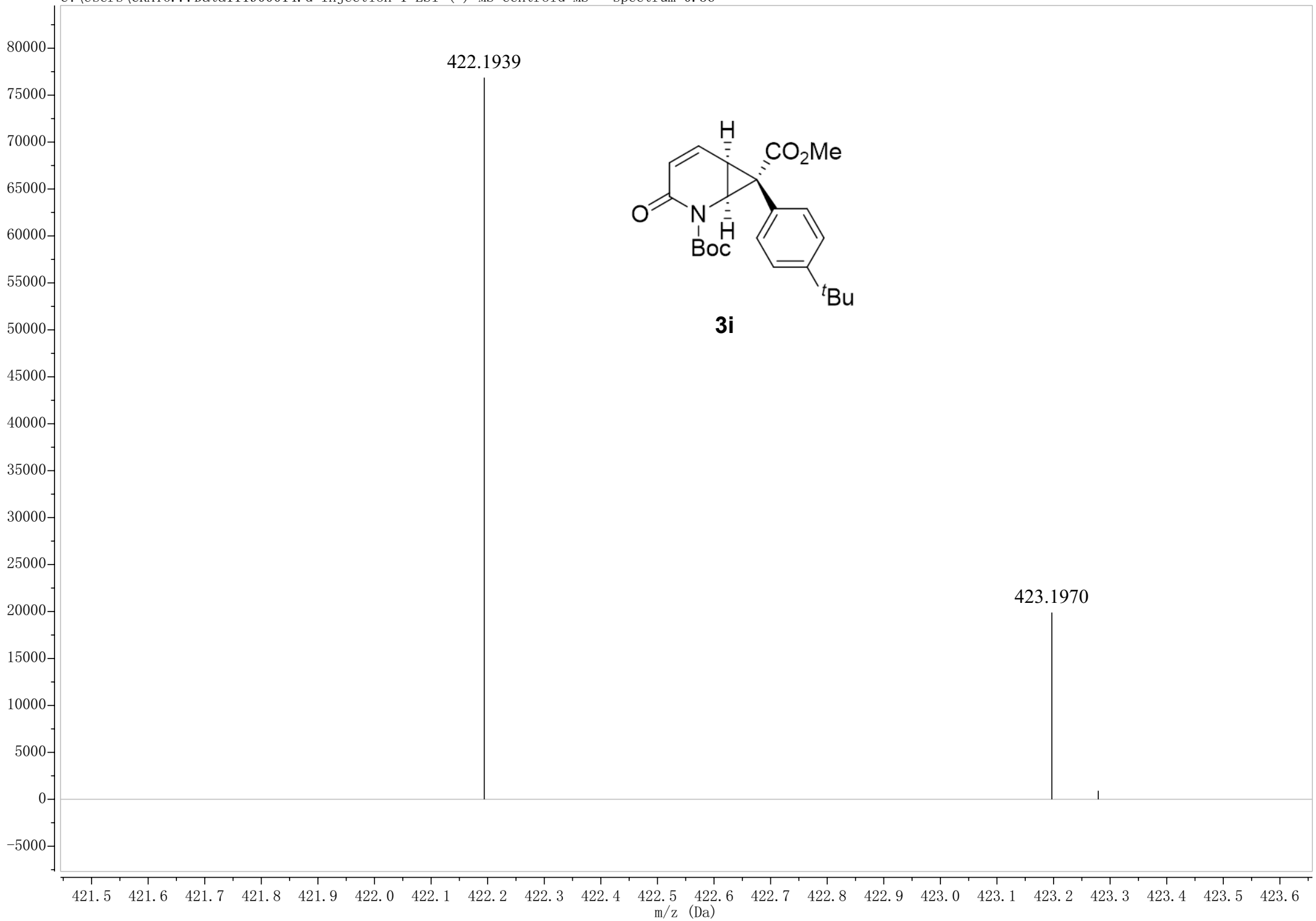
Sample Name	Sample9	**Position**	P2-C9	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--9.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:28:47 AM (UTC+08:00)



Sample Name	Sample3	**Position**	P2-C3	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--3.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:18:29 AM (UTC+08:00)

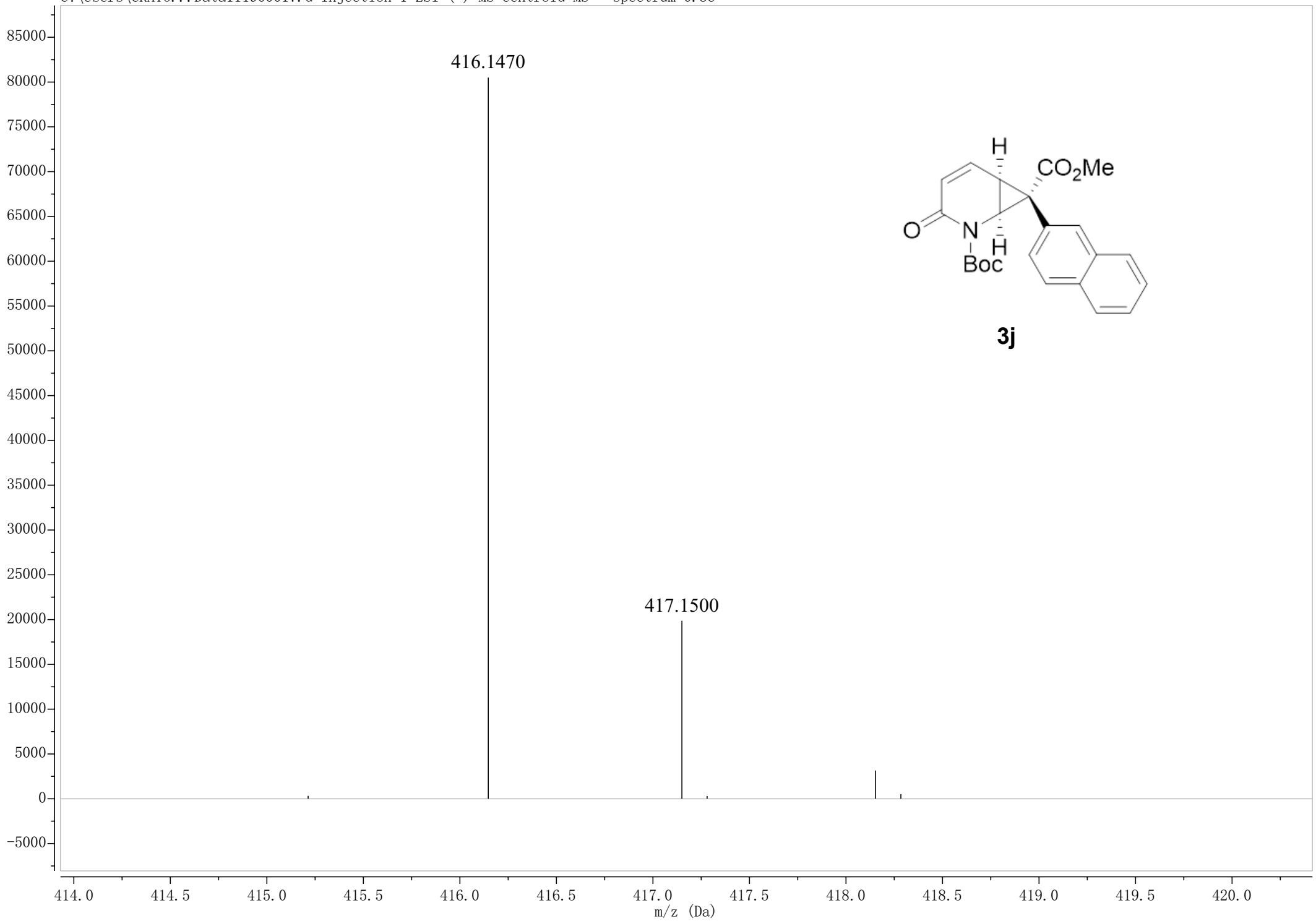


C:\Users\CRAYO...Data111900014.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



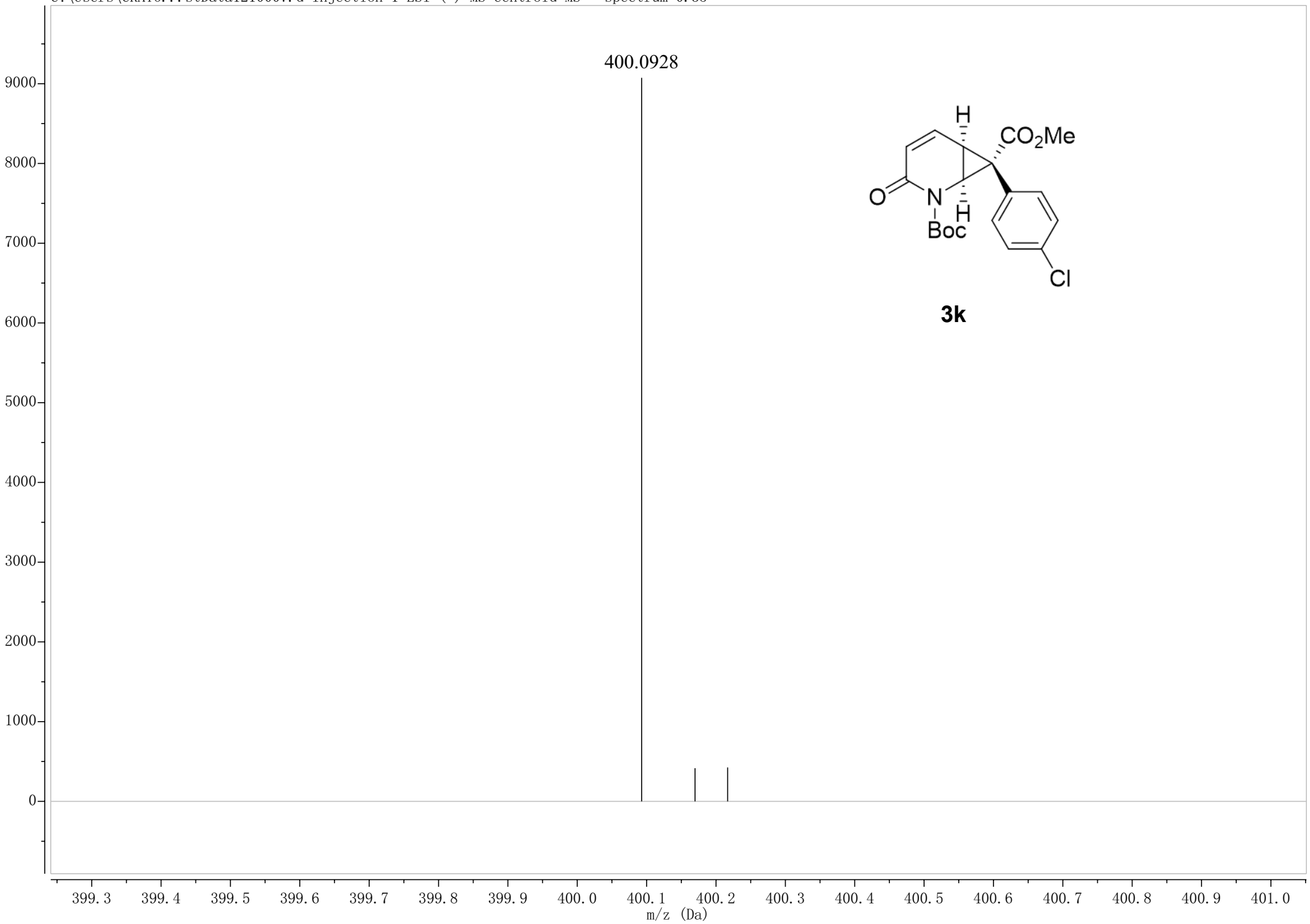
3i

C:\Users\CRAYO...Data111900017.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



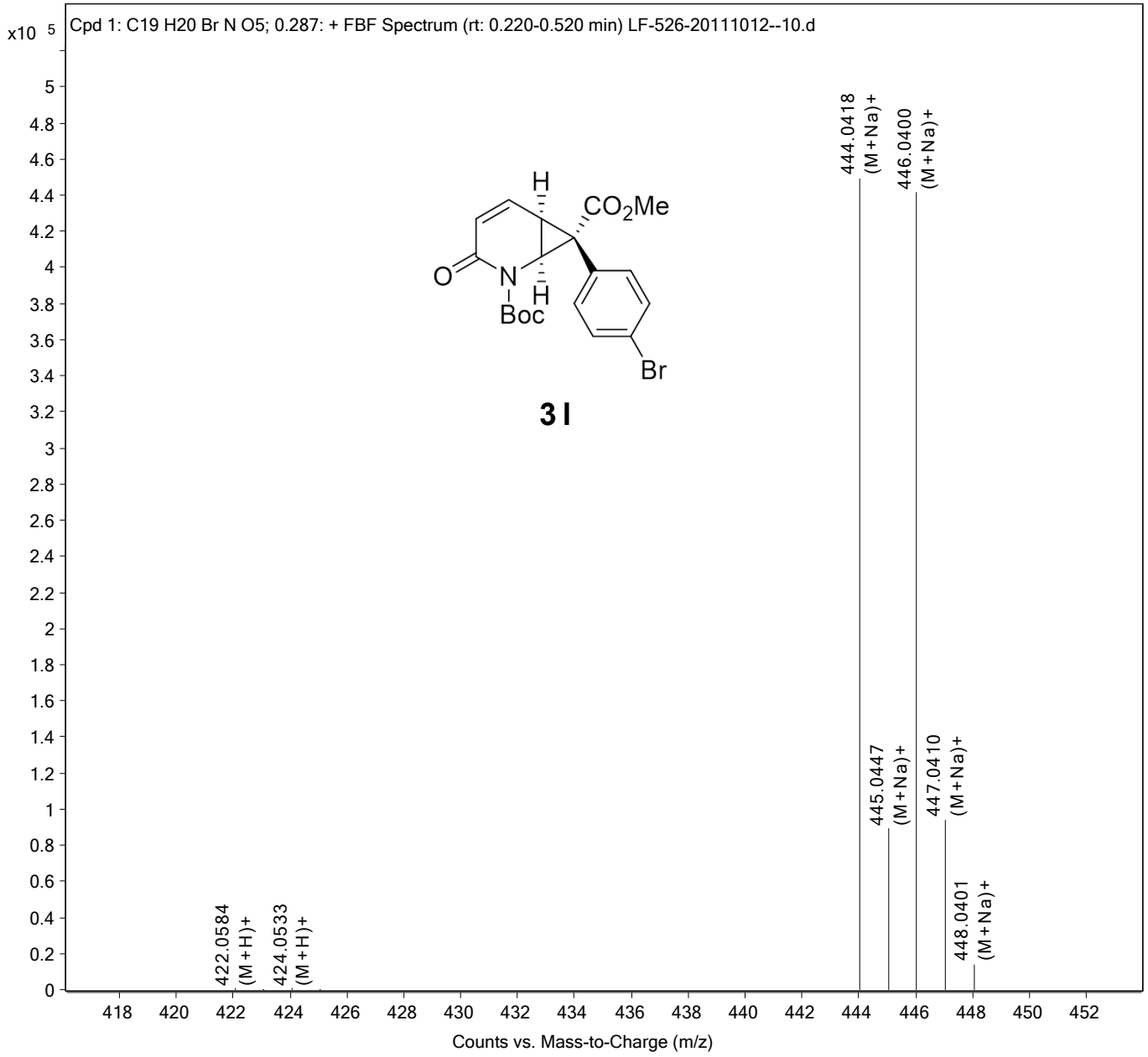
3j

C:\Users\CRAYO...stData1210007.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35

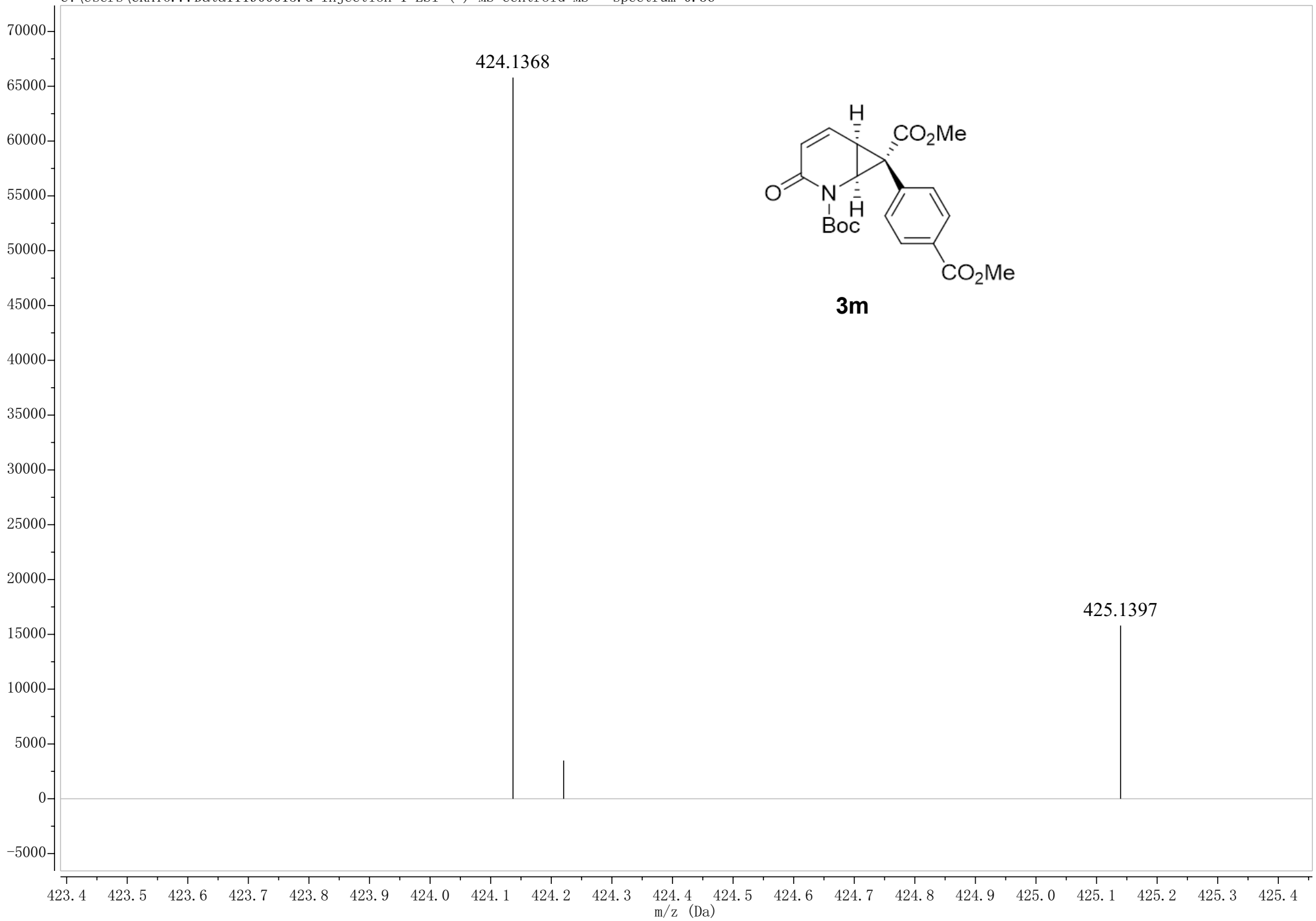


3k

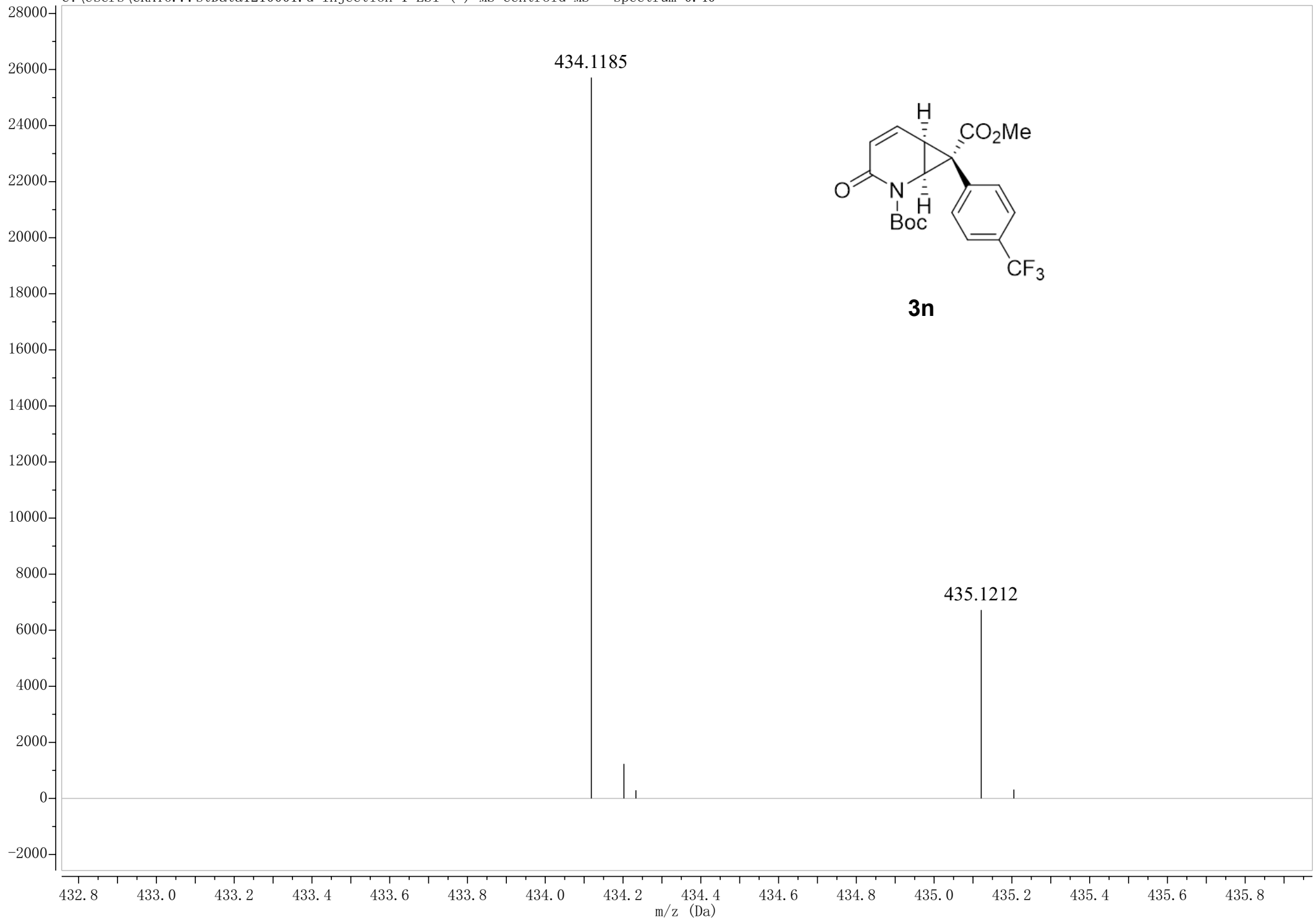
Sample Name	Sample10	**Position**	P2-C10	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--10.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:30:30 AM (UTC+08:00)



C:\Users\CRAYO...Data111900015.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36

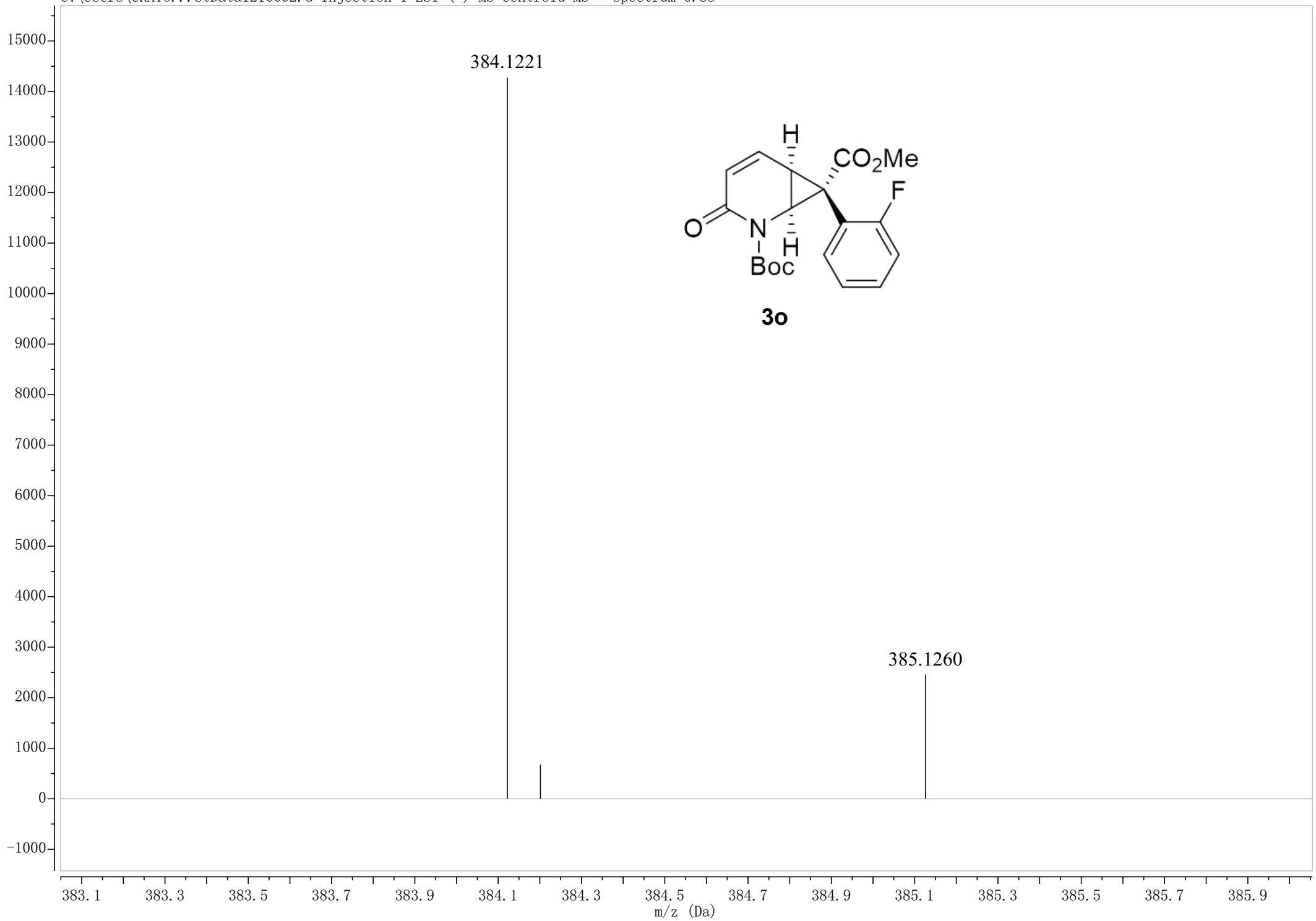


C:\Users\CRAYO...stData1210001.d Injection 1 ESI (+) MS centroid MS + spectrum 0.40



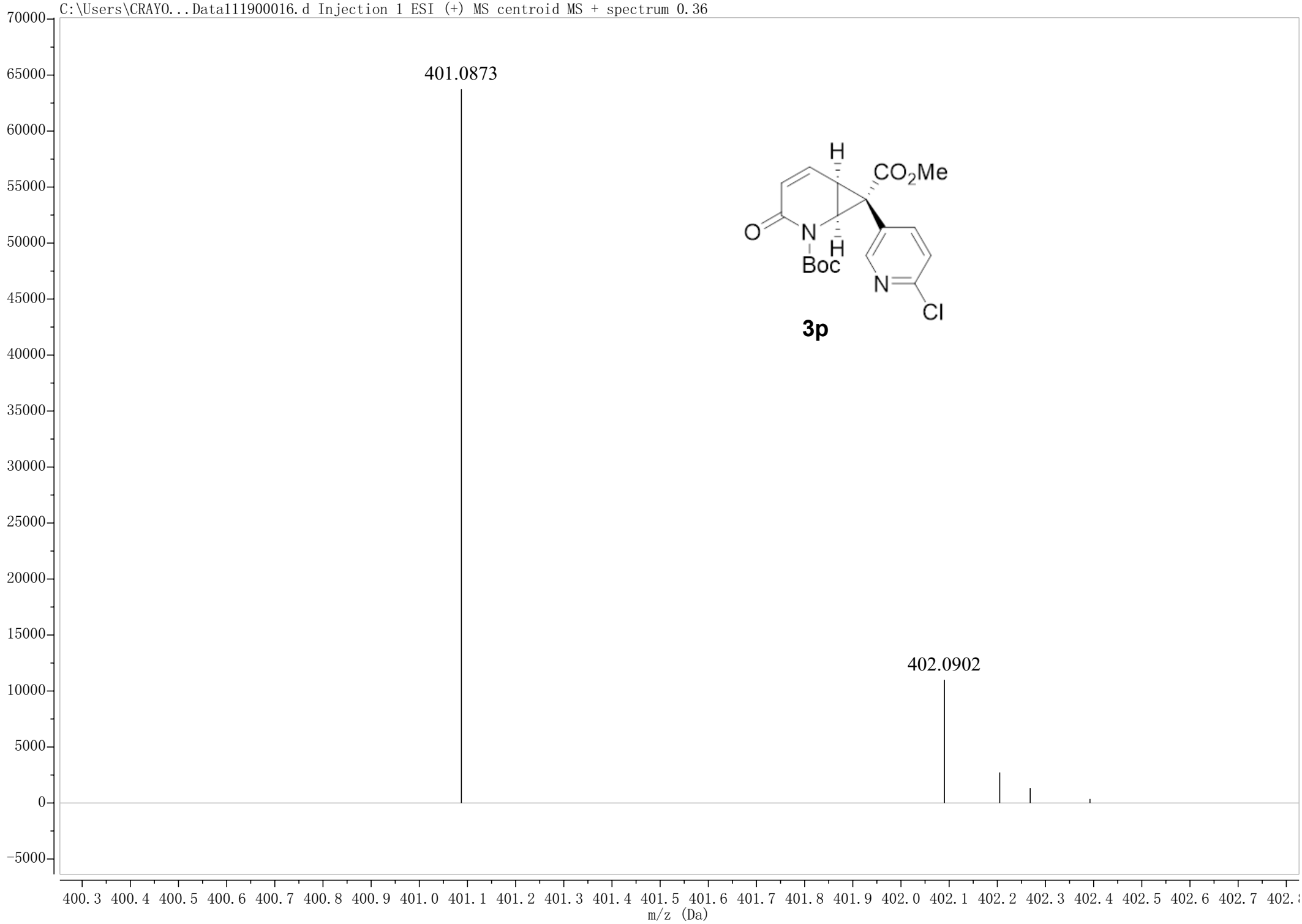
3n

C:\Users\CRAYO...stData1210002.d Injection 1 ESI (+) MS centroid MS + spectrum 0.38



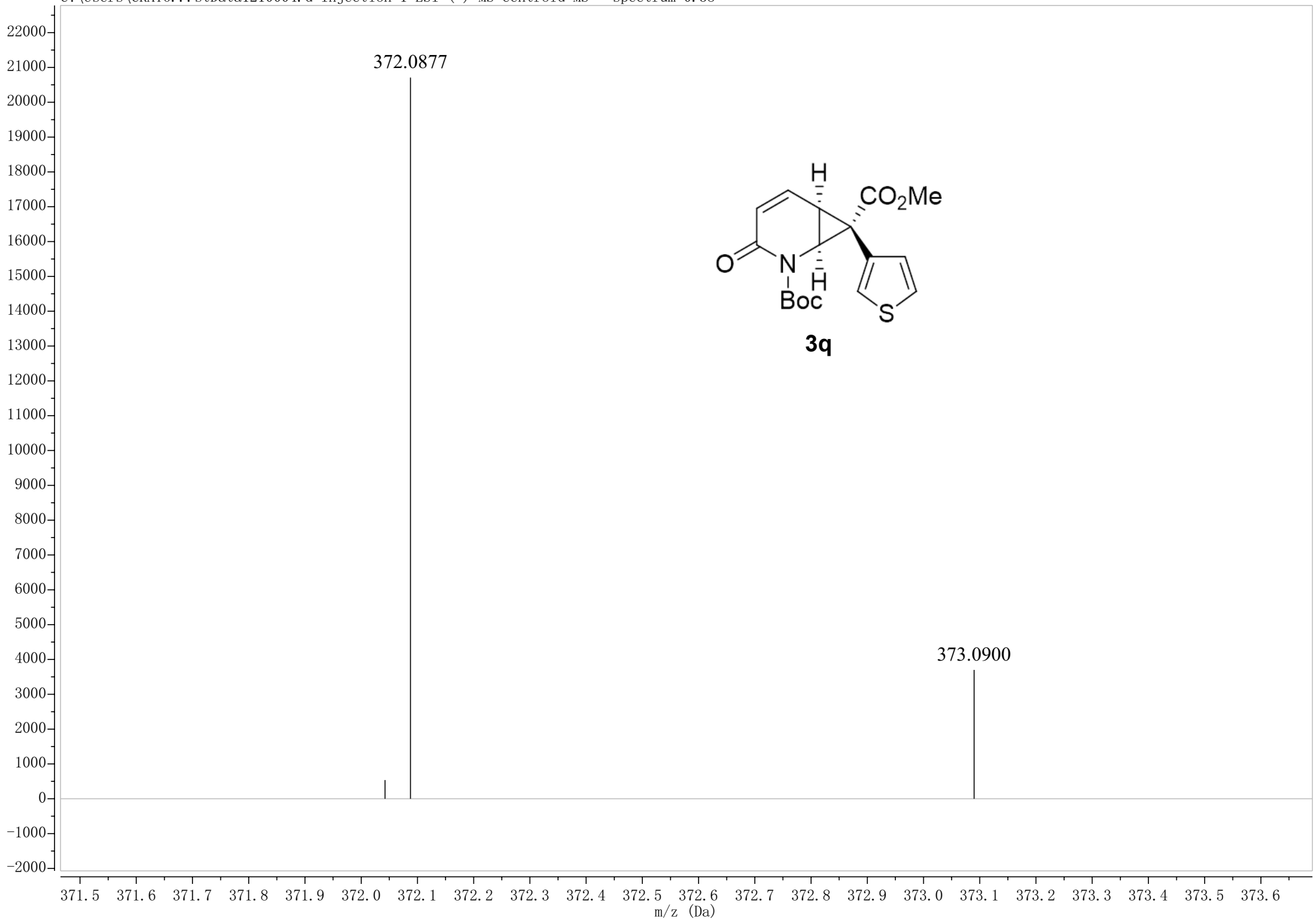
3o

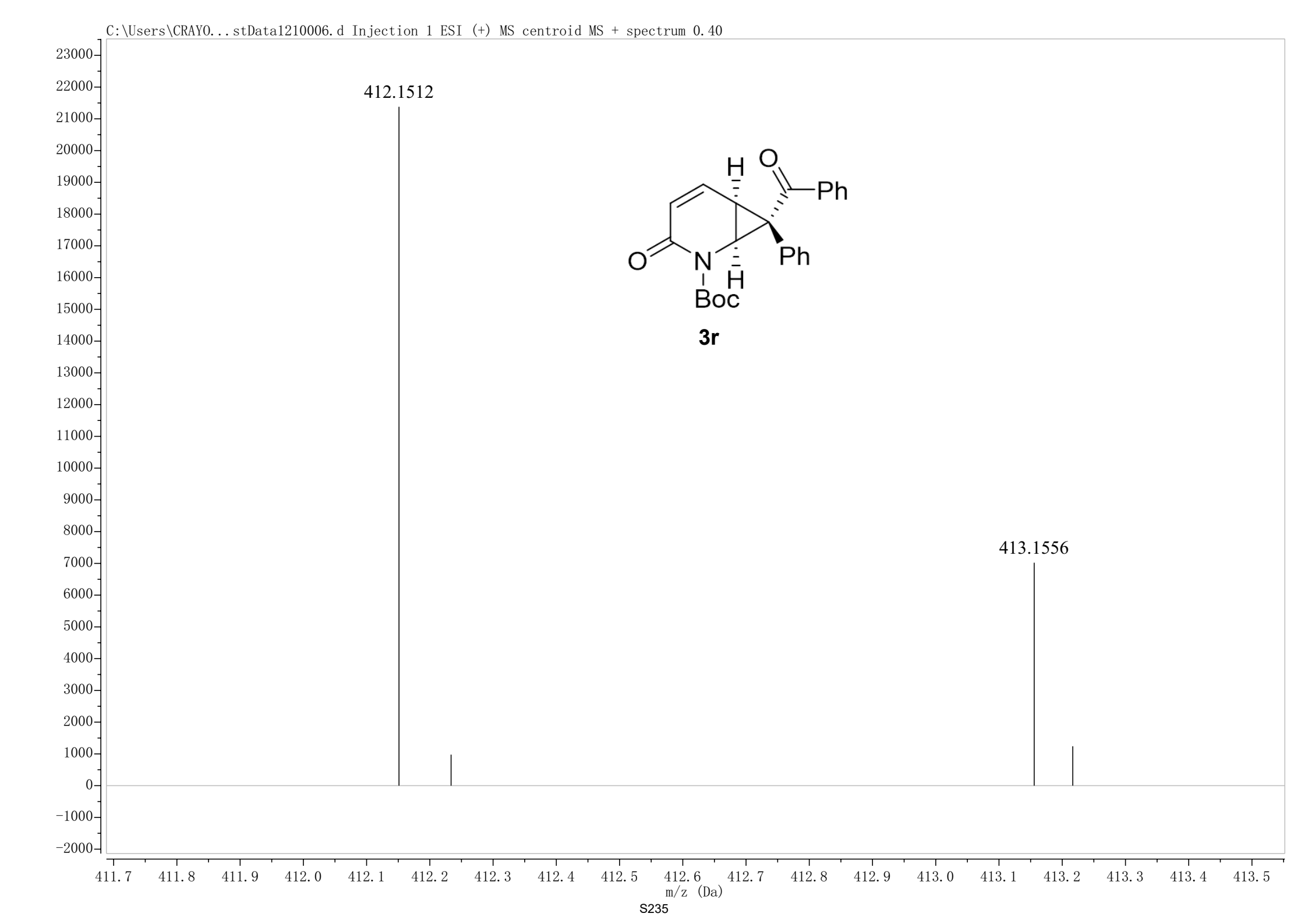
C:\Users\CRAYO...Data111900016.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



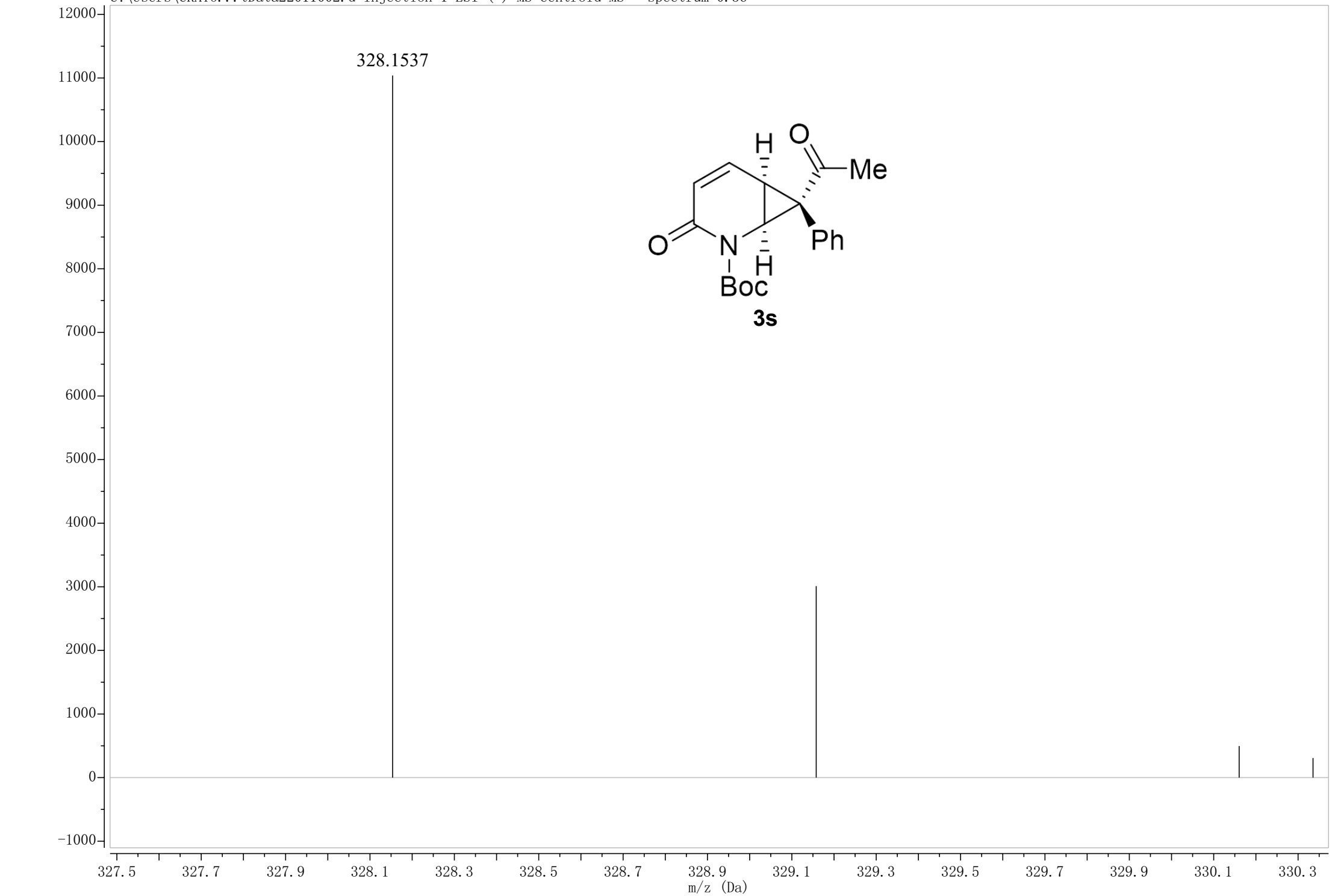
3p

C:\Users\CRAYO...stData1210004.d Injection 1 ESI (+) MS centroid MS + spectrum 0.38



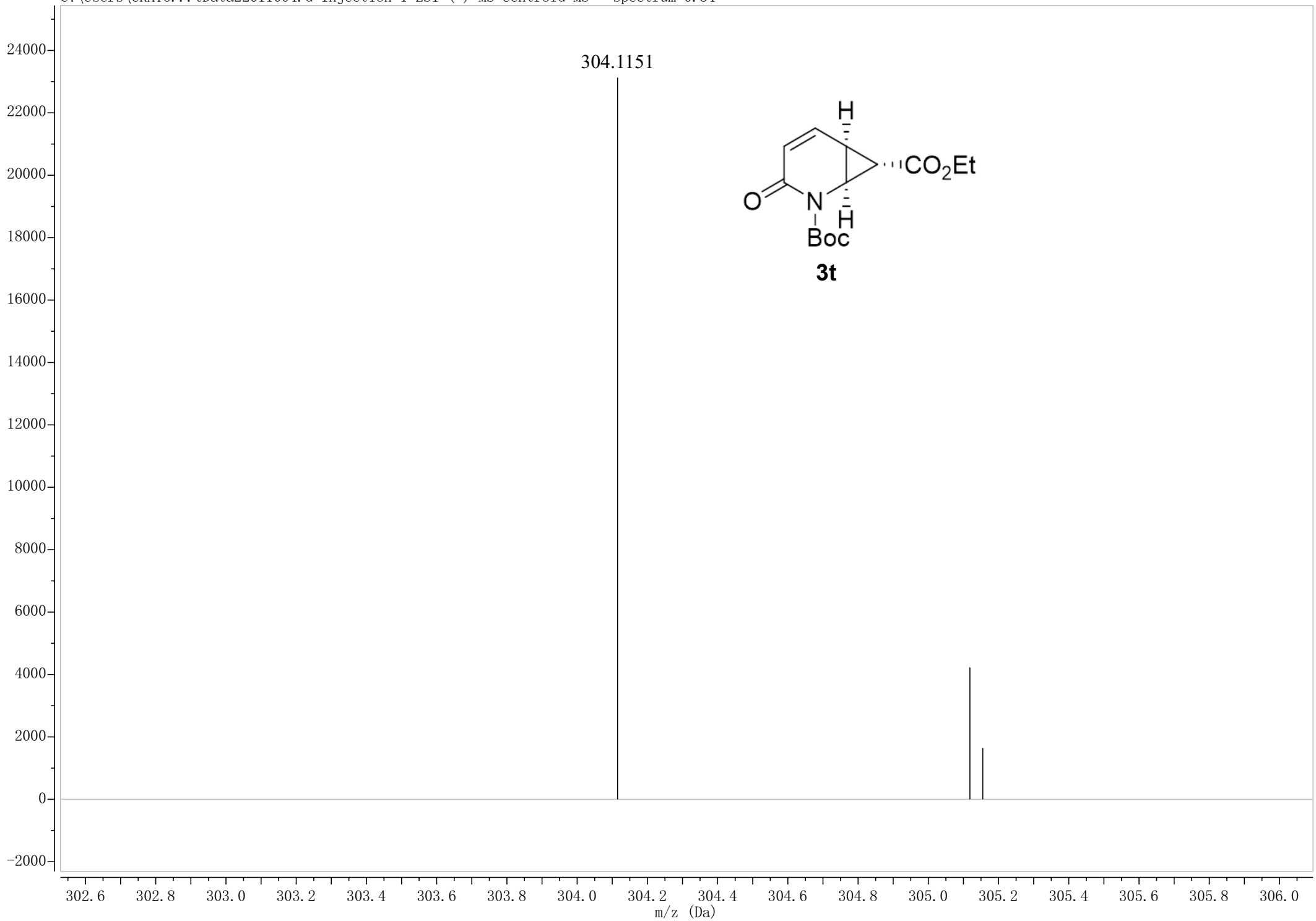

C:\Users\CRAYO...stData1210006.d Injection 1 ESI (+) MS centroid MS + spectrum 0.40
412.1512
413.1556
3r
m/z (Da)

C:\Users\CRAYO...tData22011002.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



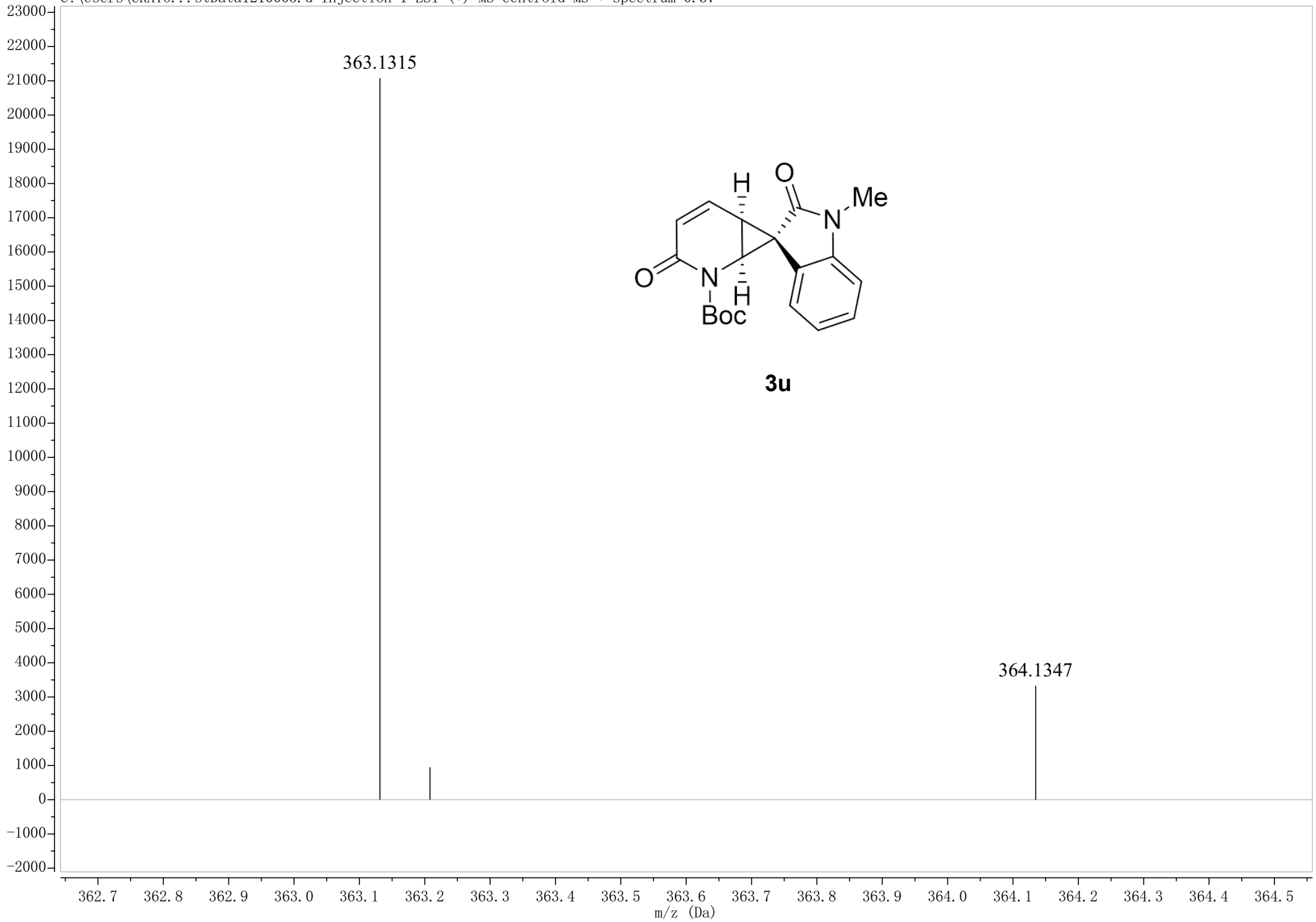
3s

C:\Users\CRAYO...tData22011004.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34



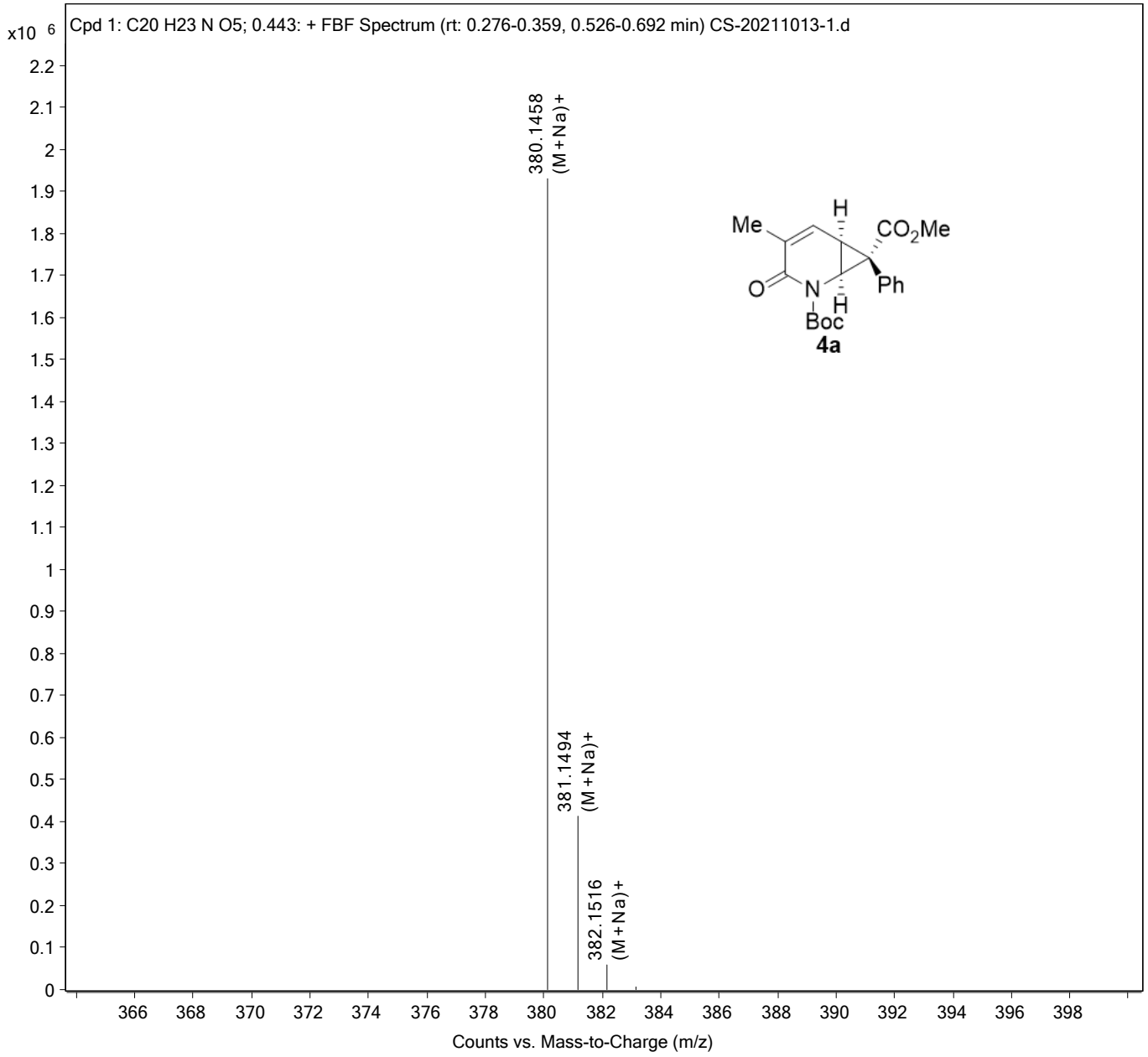
3t

C:\Users\CRAYO...stData1210005.d Injection 1 ESI (+) MS centroid MS + spectrum 0.37

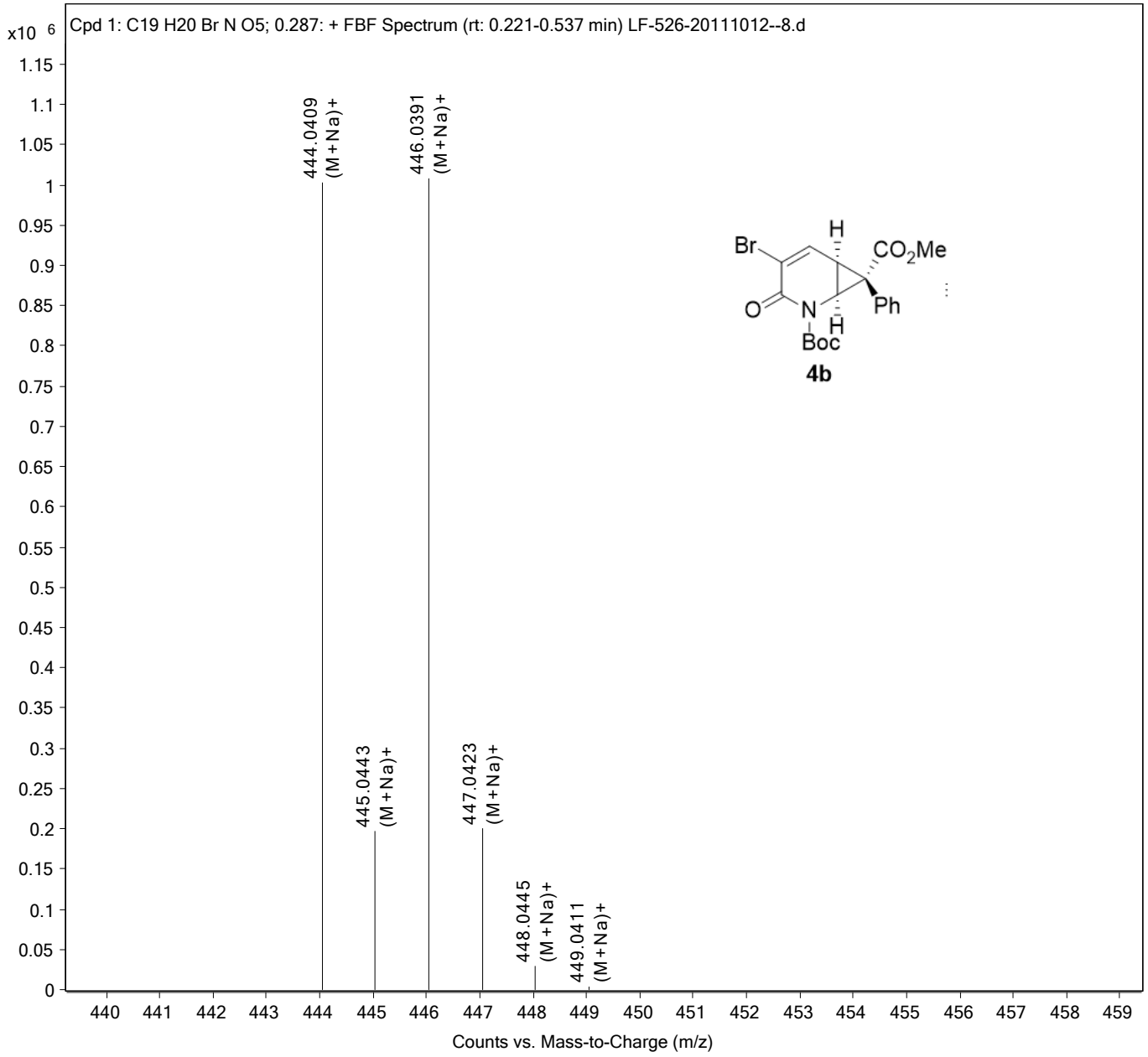


3u

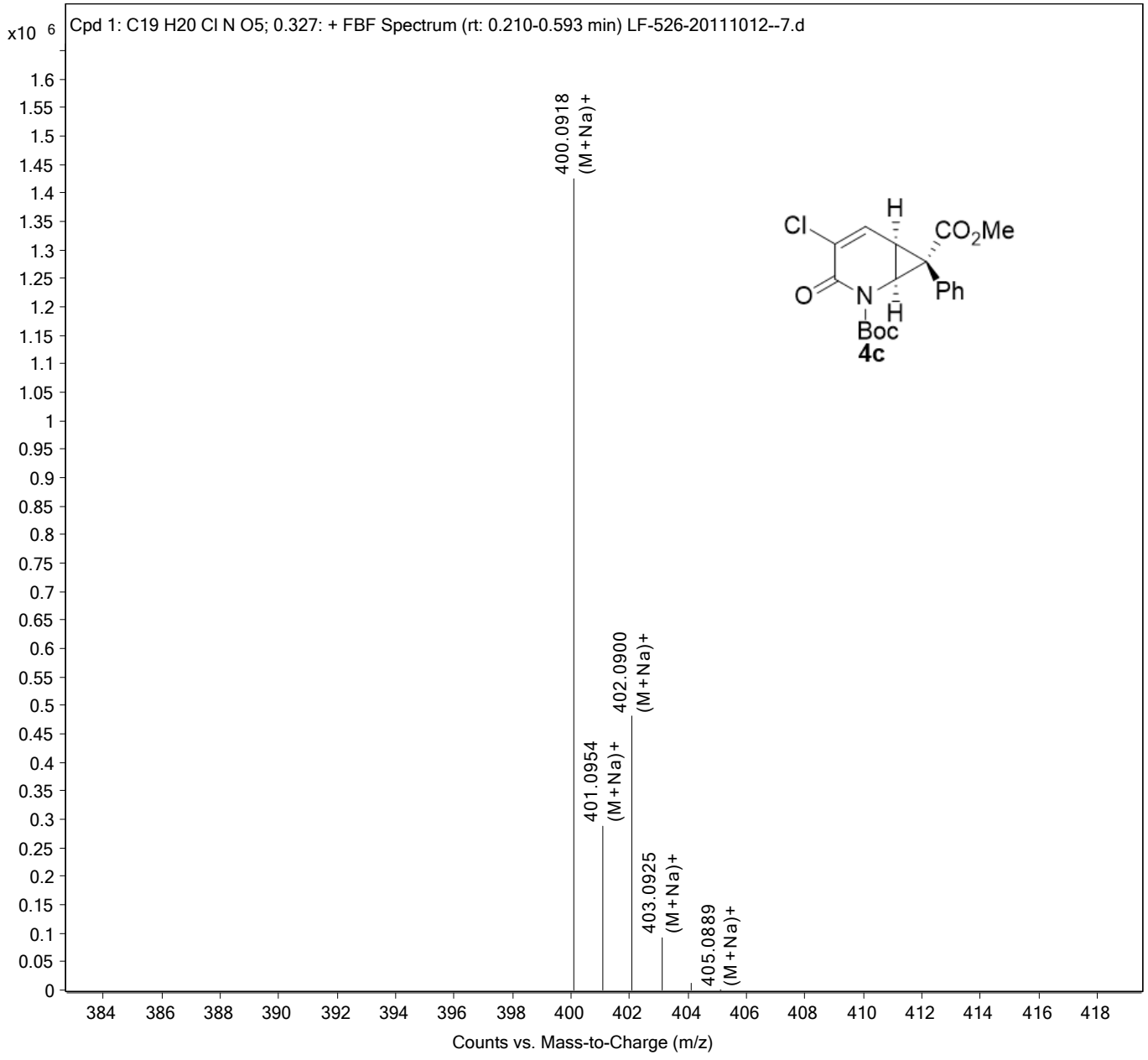
Sample Name	Sample46	**Position**	P2-D11	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	20	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CS-20211013-1.d
ACQ Method	100-1000.m	**Comment**		**Acquired Time**	10/13/2021 7:44:22 PM (UTC+08:00)



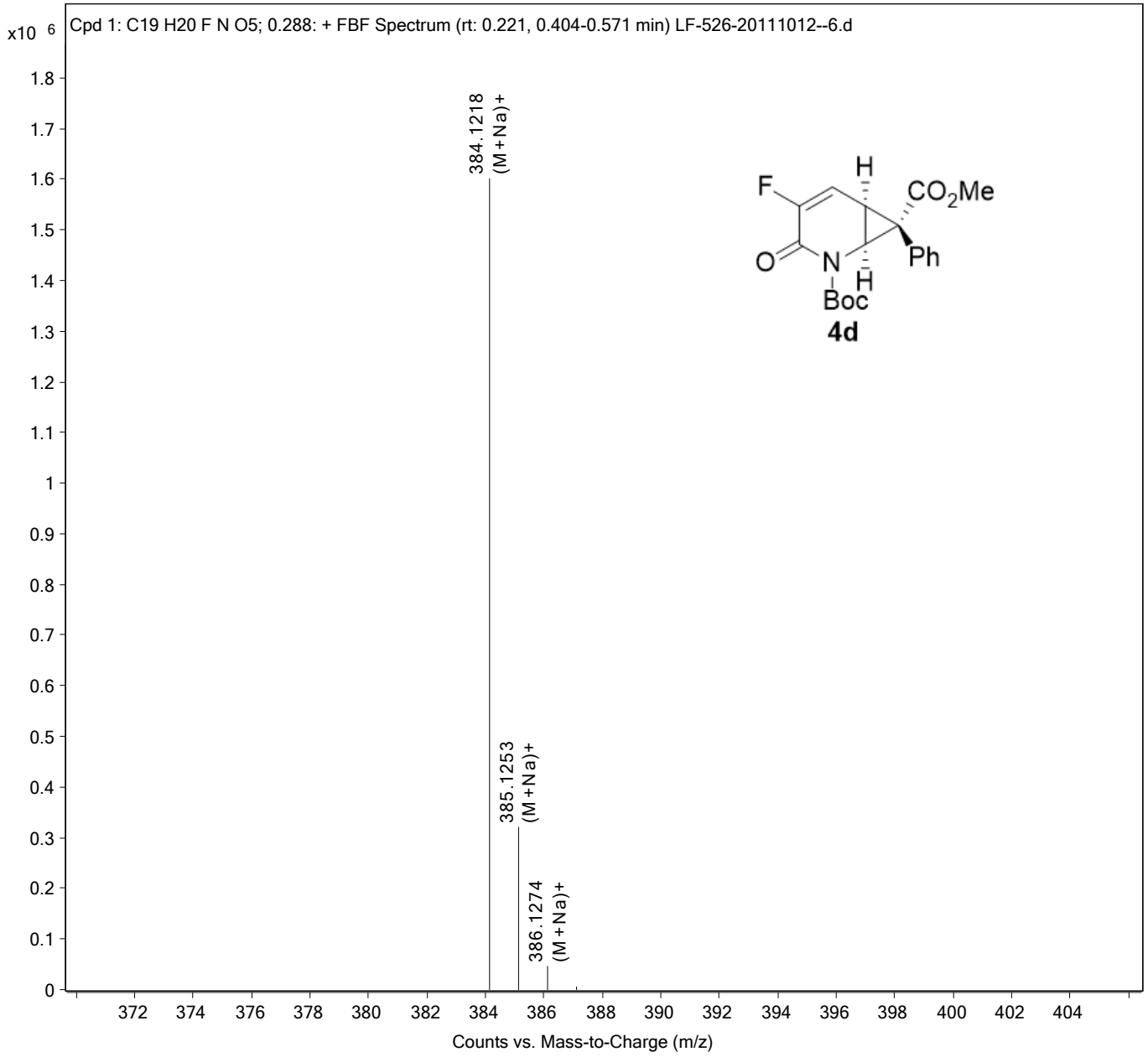
Sample Name	Sample8	**Position**	P2-C8	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--8.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:27:04 AM (UTC+08:00)



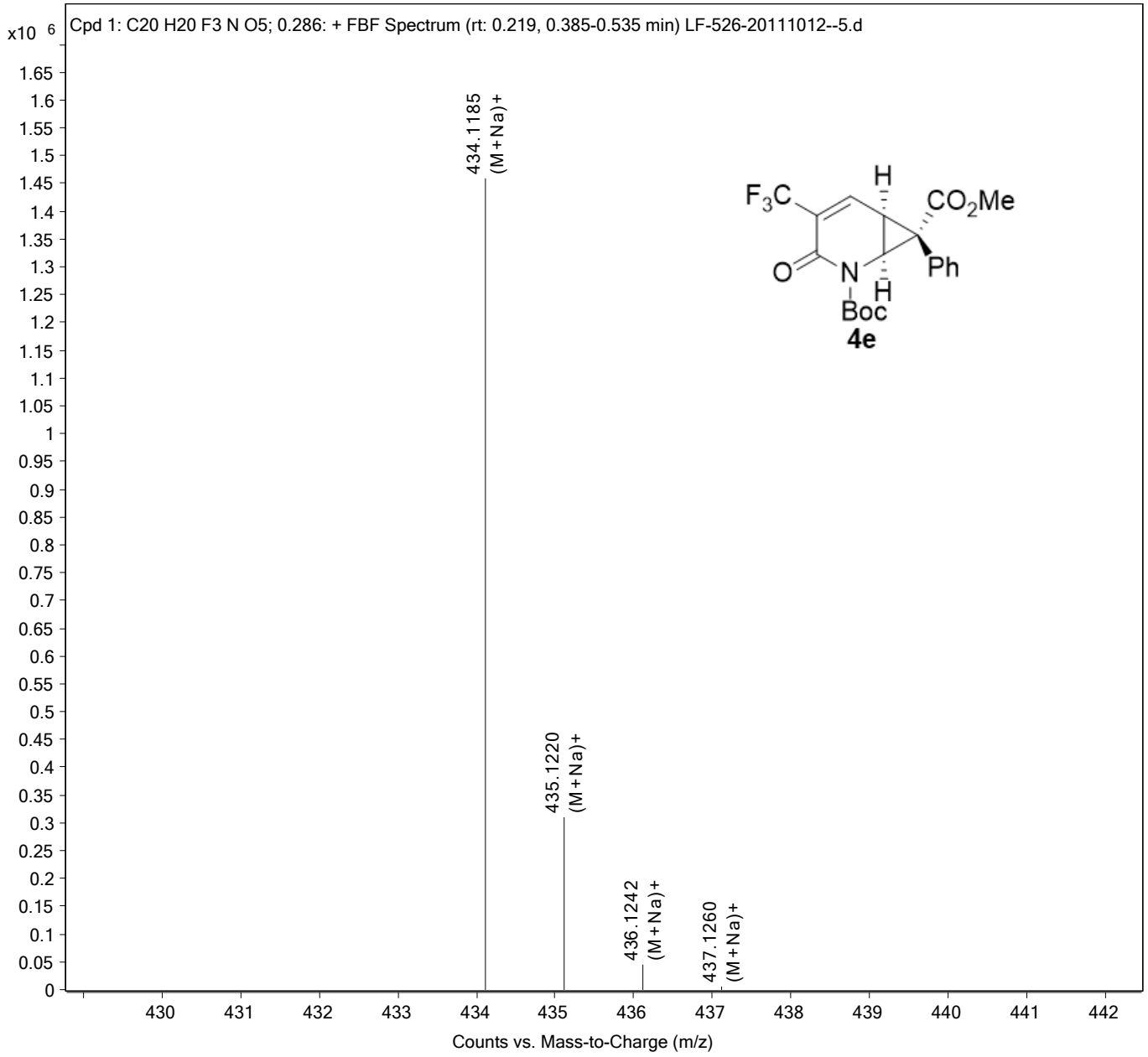
Sample Name	Sample7	**Position**	P2-C7	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--7.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:25:21 AM (UTC+08:00)



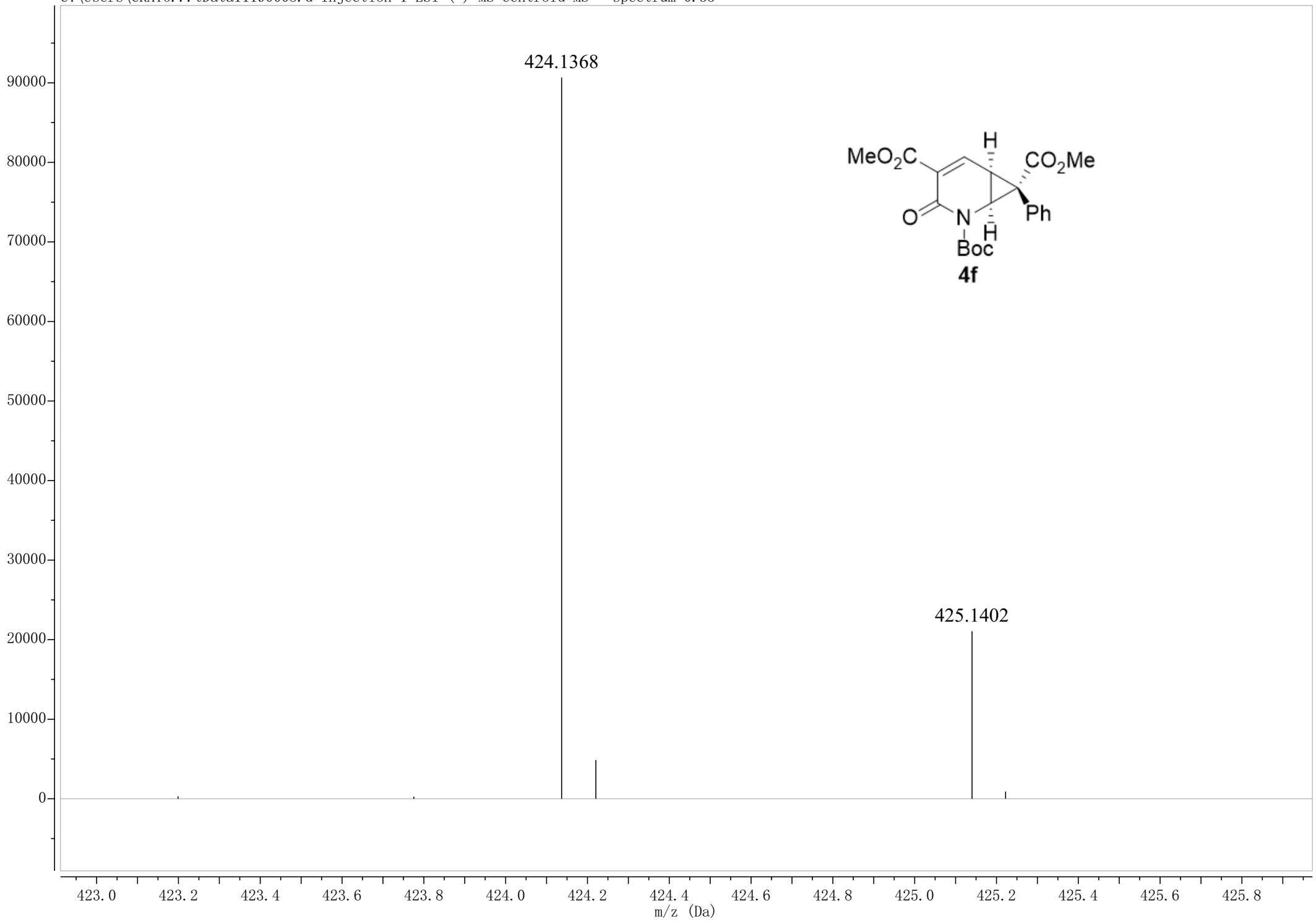
Sample Name	Sample6	**Position**	P2-C6	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--6.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:23:38 AM (UTC+08:00)



Sample Name	Sample5	**Position**	P2-C5	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--5.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:21:55 AM (UTC+08:00)

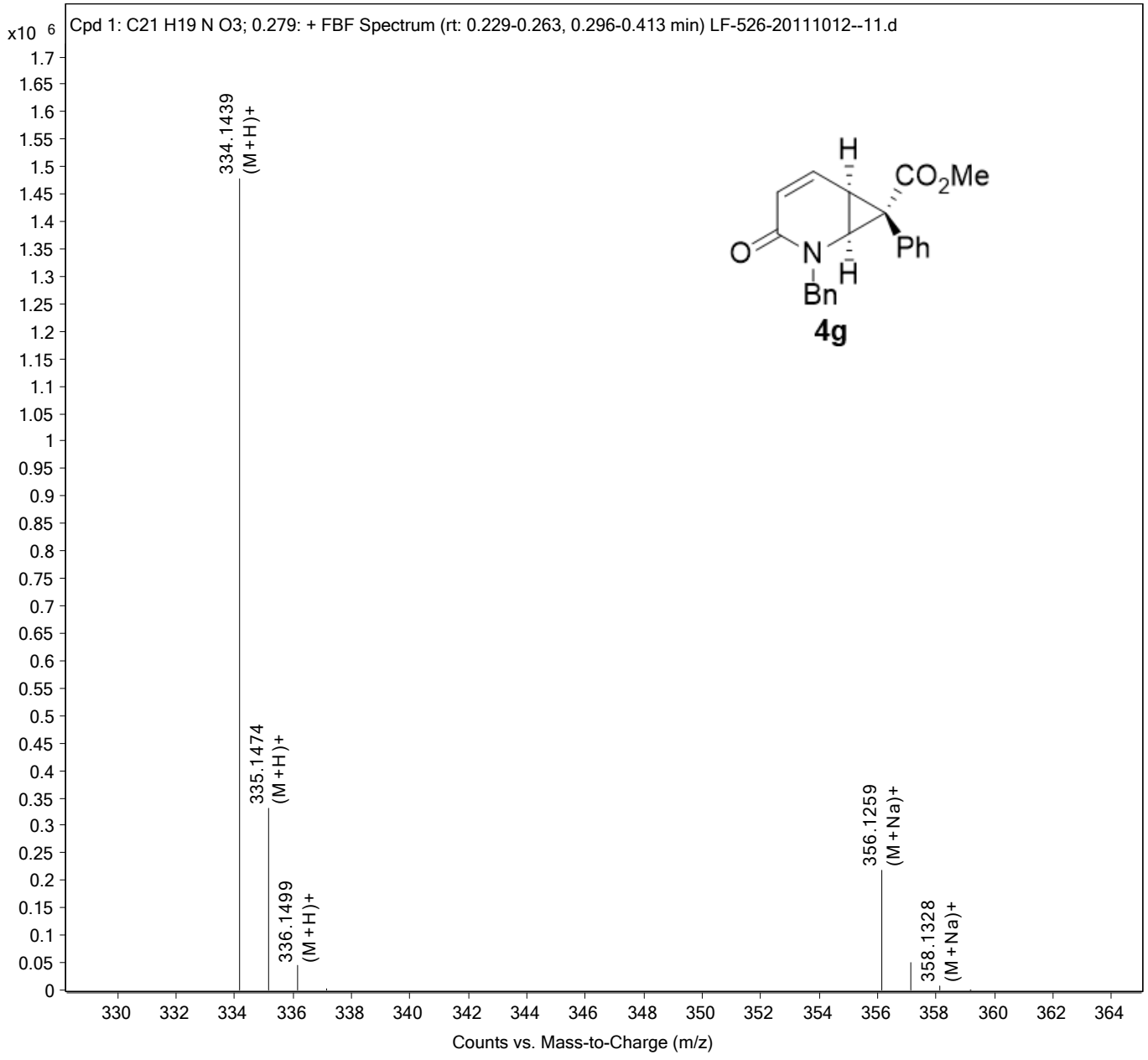


C:\Users\CRAYO...tData11190008.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35

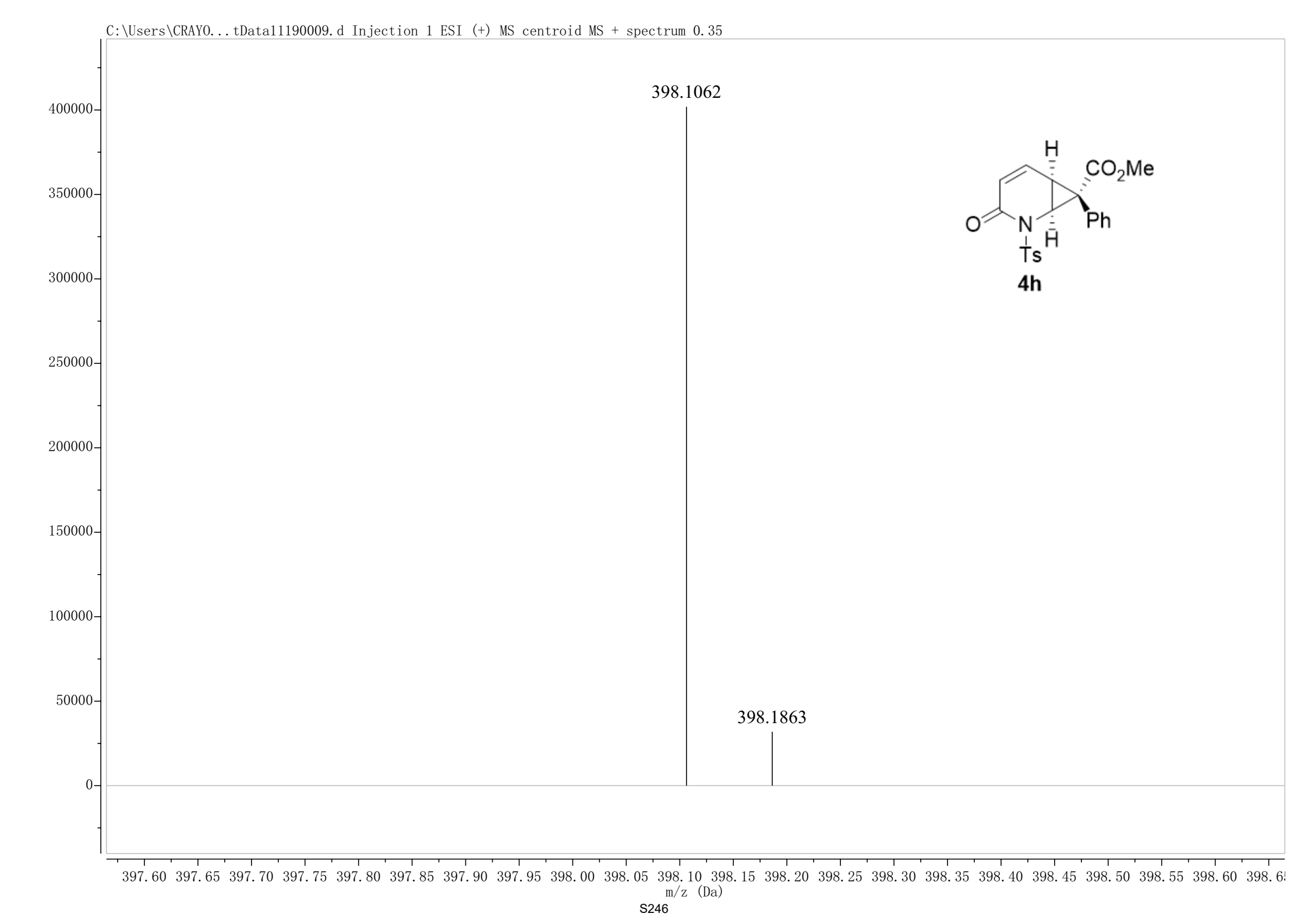


4f

Sample Name	Sample11	**Position**	P2-C11	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	10	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	LF-526-20111012--11.d
ACQ Method	CH3CN-100-1000.m	**Comment**		**Acquired Time**	10/12/2021 9:32:13 AM (UTC+08:00)

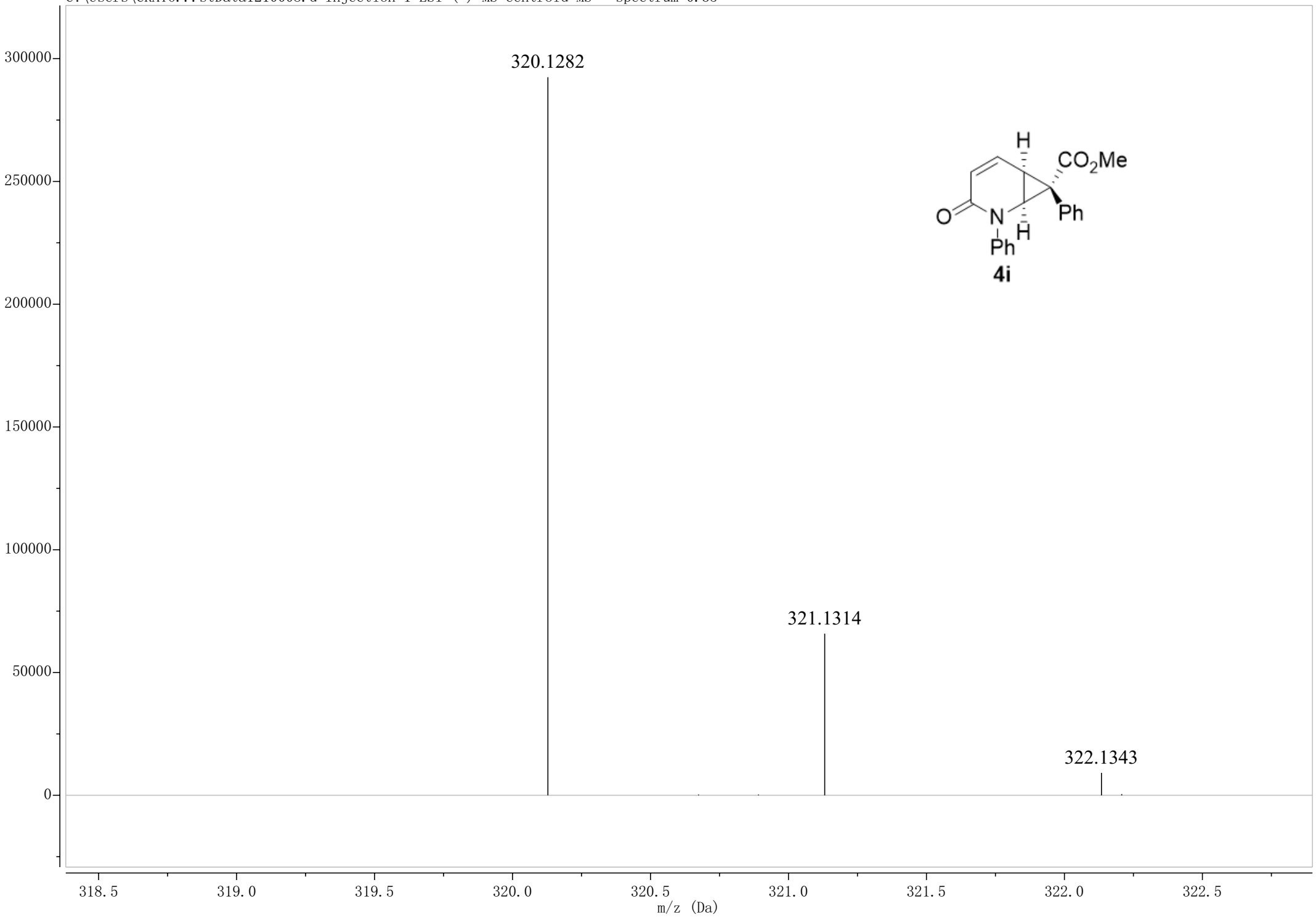


C:\Users\CRAYO...tData11190009.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35



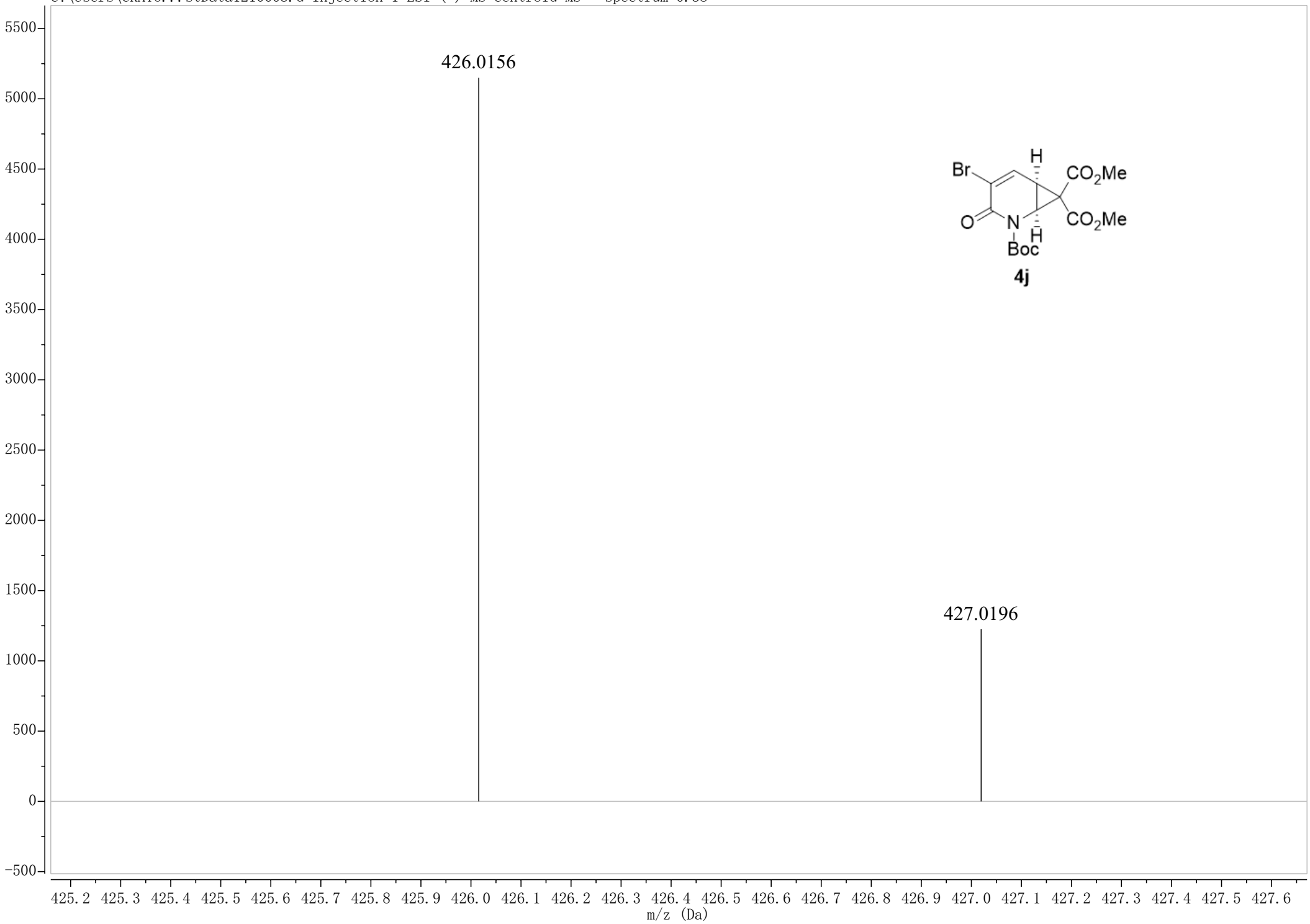
4h

C:\Users\CRAYO...stData1210008.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35



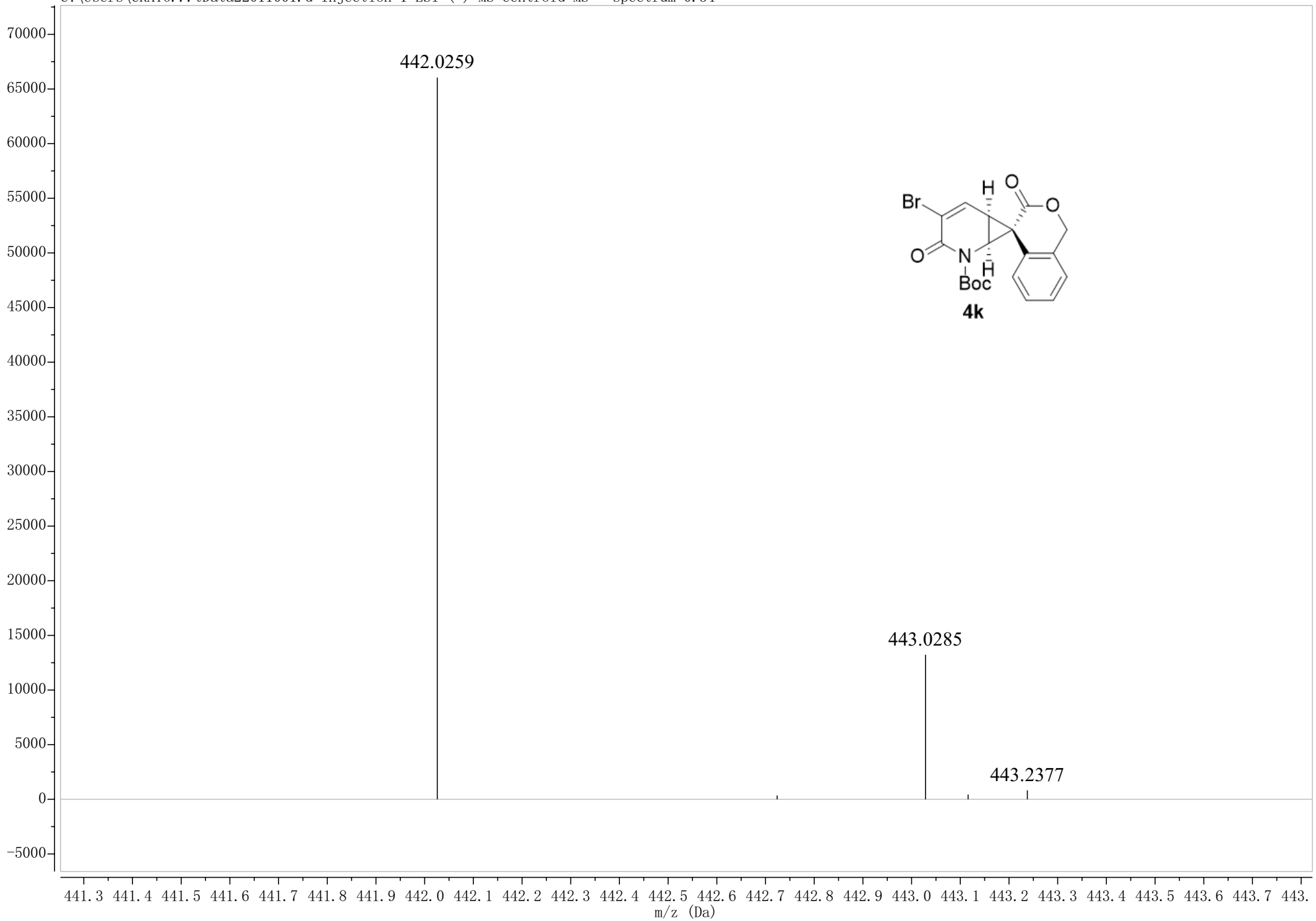
4i

C:\Users\CRAYO...stData1210003.d Injection 1 ESI (+) MS centroid MS + spectrum 0.38

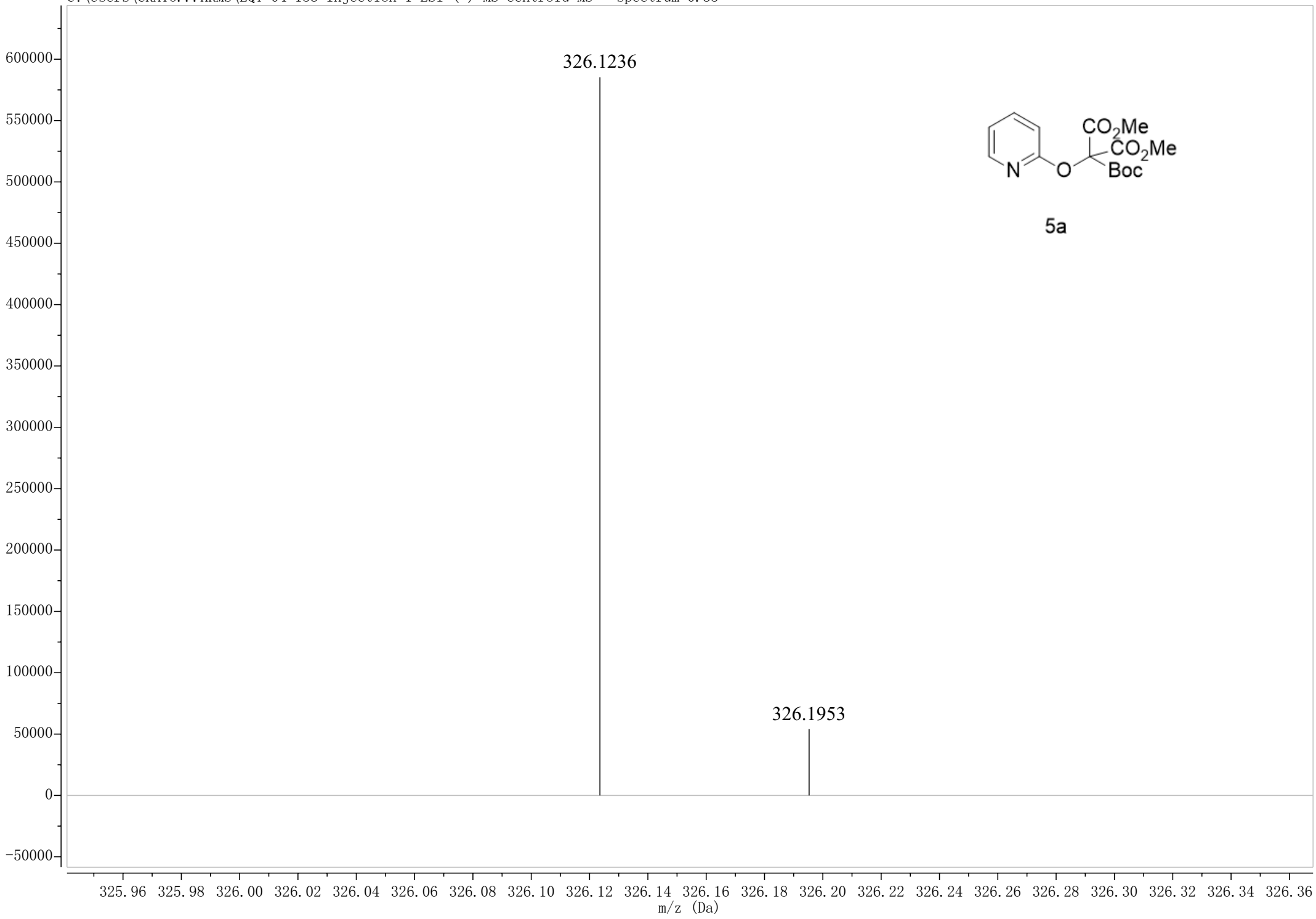


4j

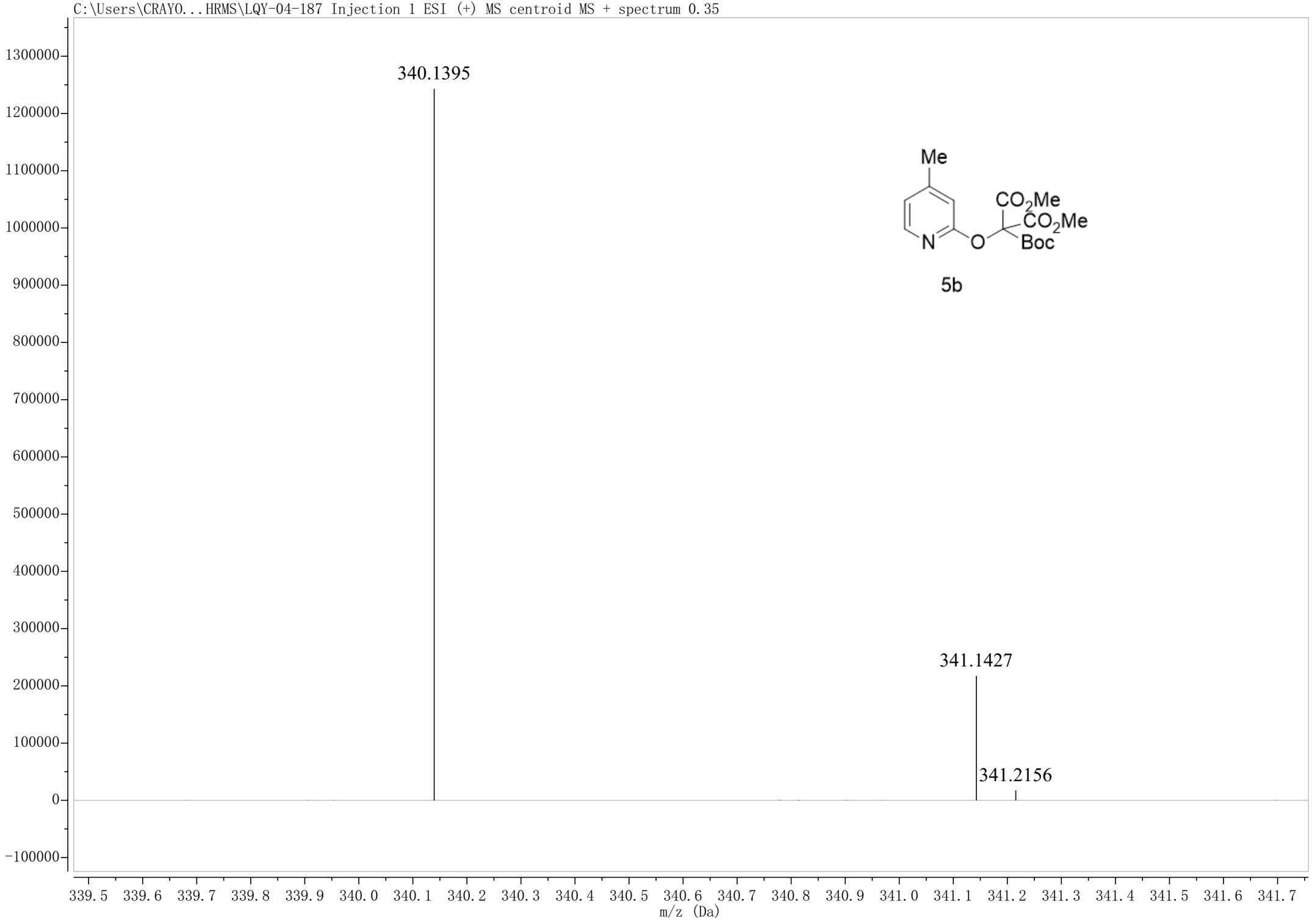
C:\Users\CRAYO...tData22011001.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34

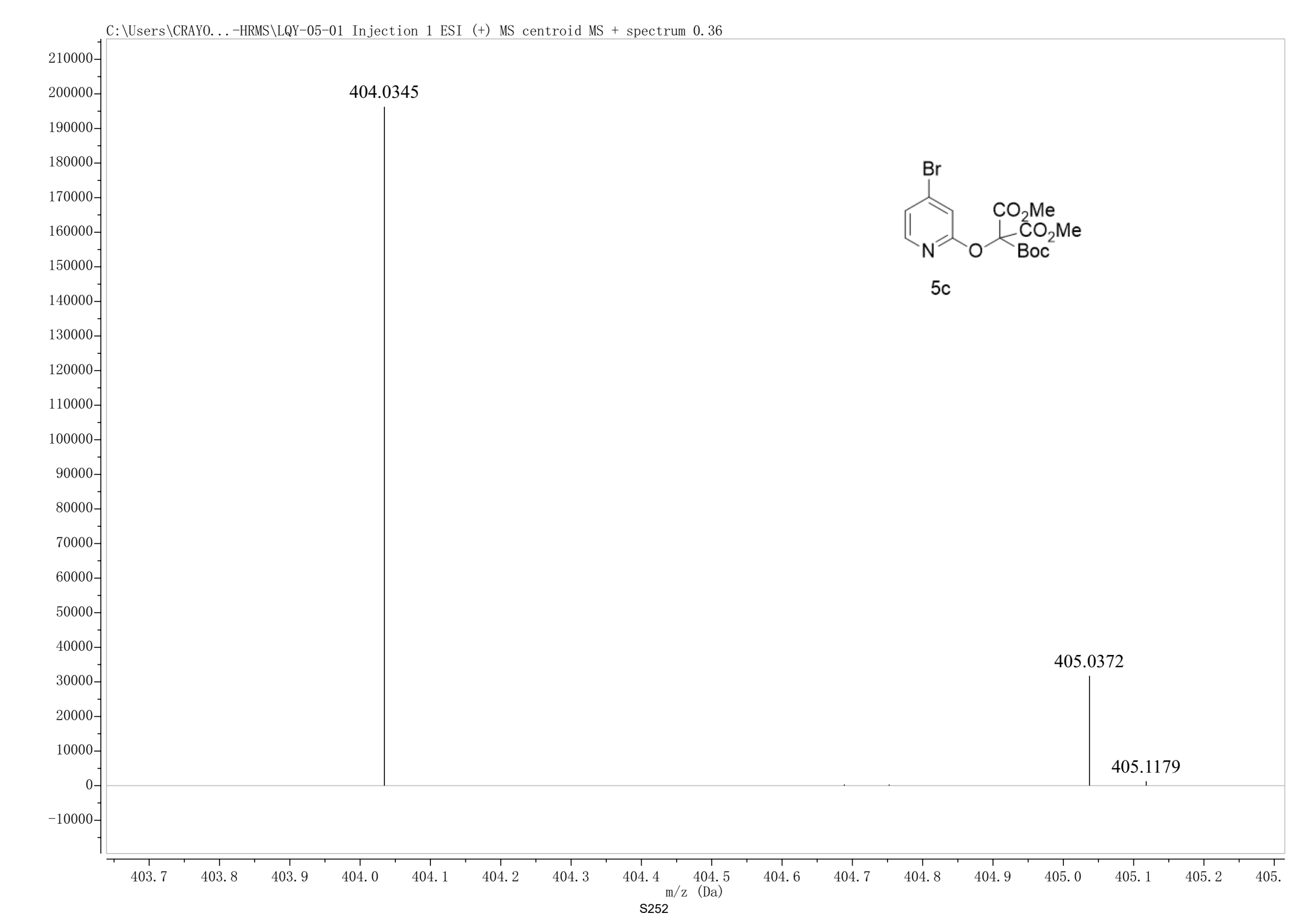


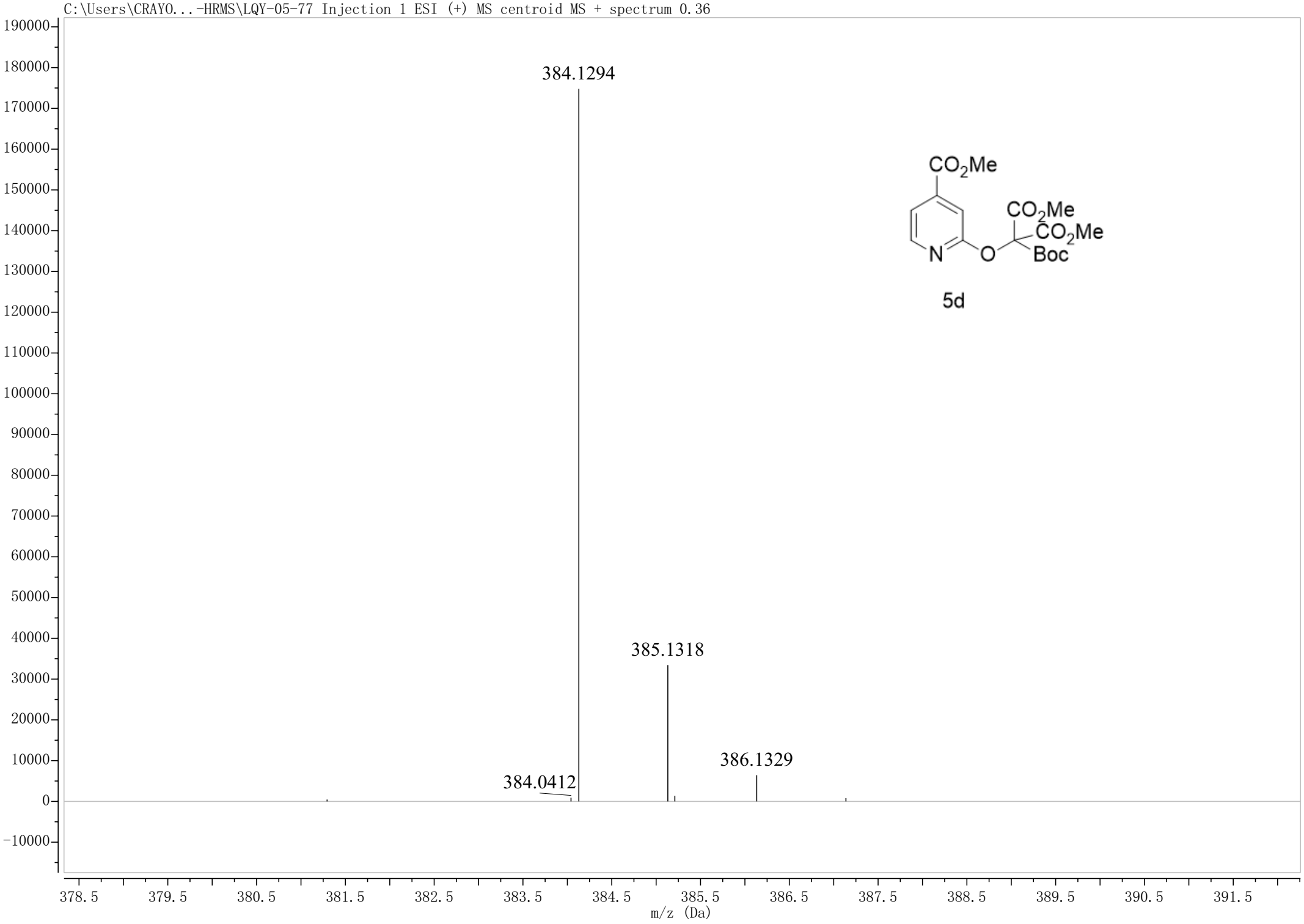
C:\Users\CRAYO...HRMS\LQY-04-153 Injection 1 ESI (+) MS centroid MS + spectrum 0.35

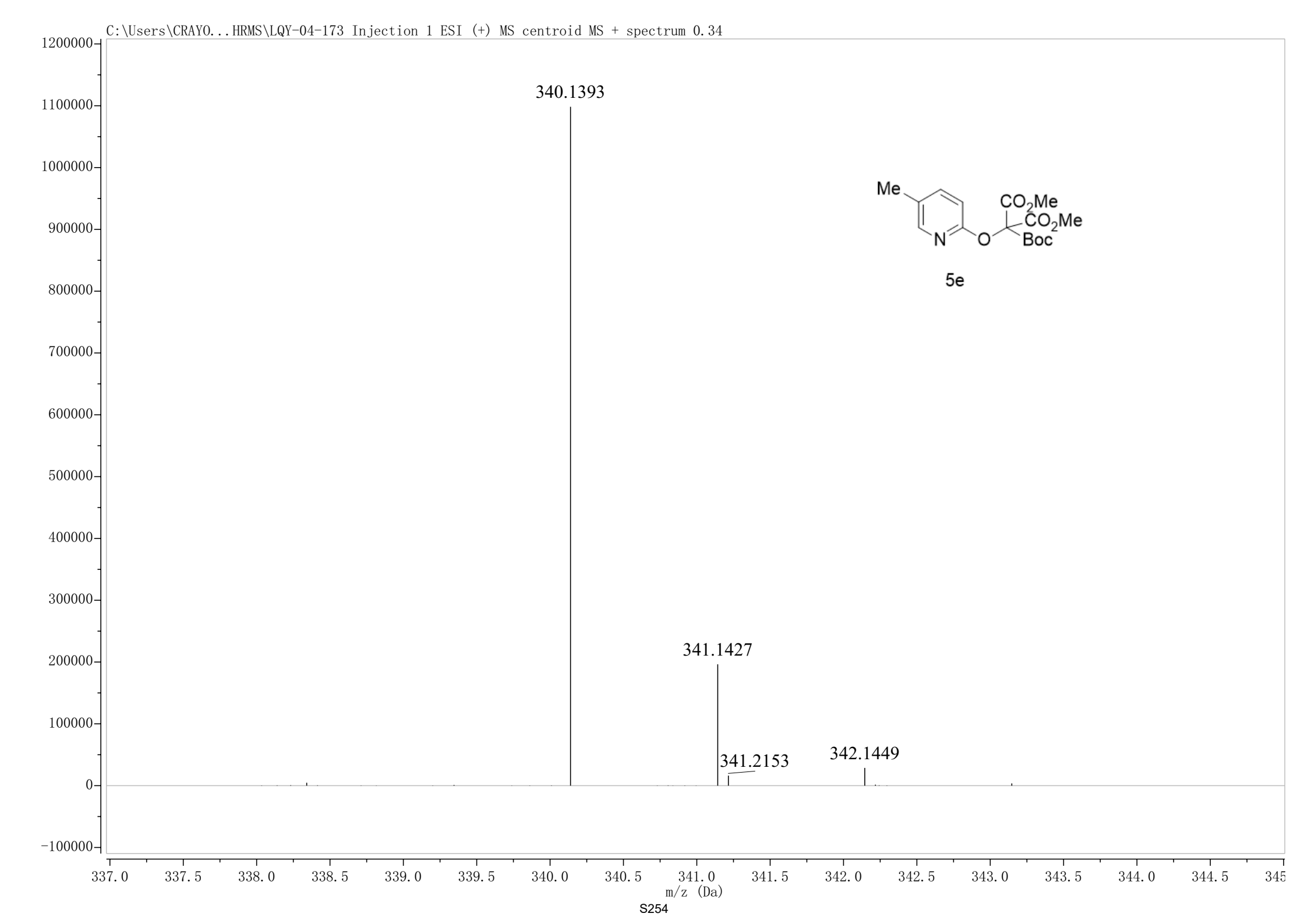


5a

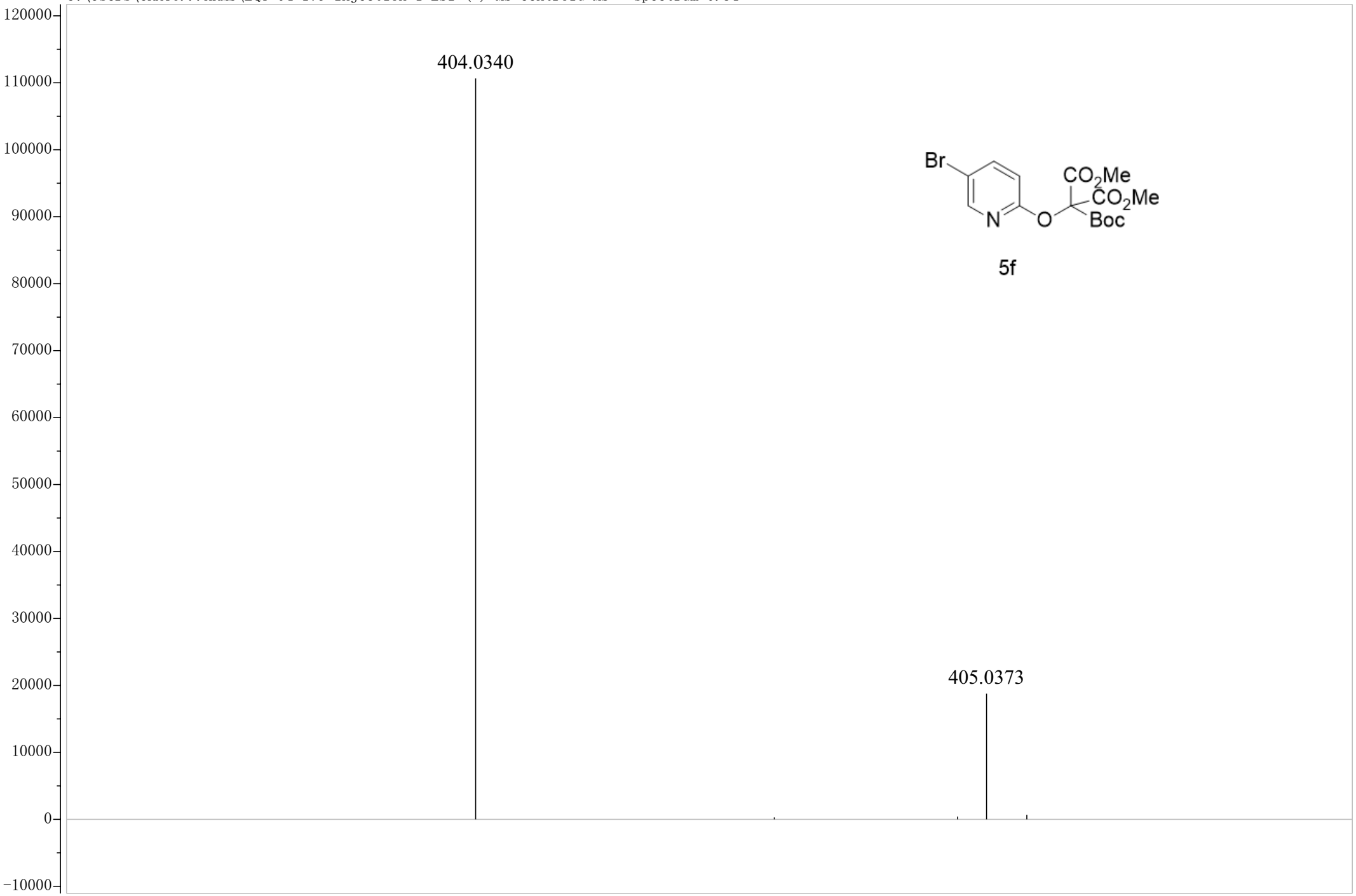

C:\Users\CRAYO...HRMS\LQY-04-187 Injection 1 ESI (+) MS centroid MS + spectrum 0.35
340.1395
341.1427
341.2156
Me
CO2Me
CO2Me
Boc
N
O
5b
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
339.5
339.6
339.7
339.8
339.9
340.0
340.1
340.2
340.3
340.4
340.5
340.6
340.7
340.8
340.9
341.0
341.1
341.2
341.3
341.4
341.5
341.6
341.7
m/z (Da)

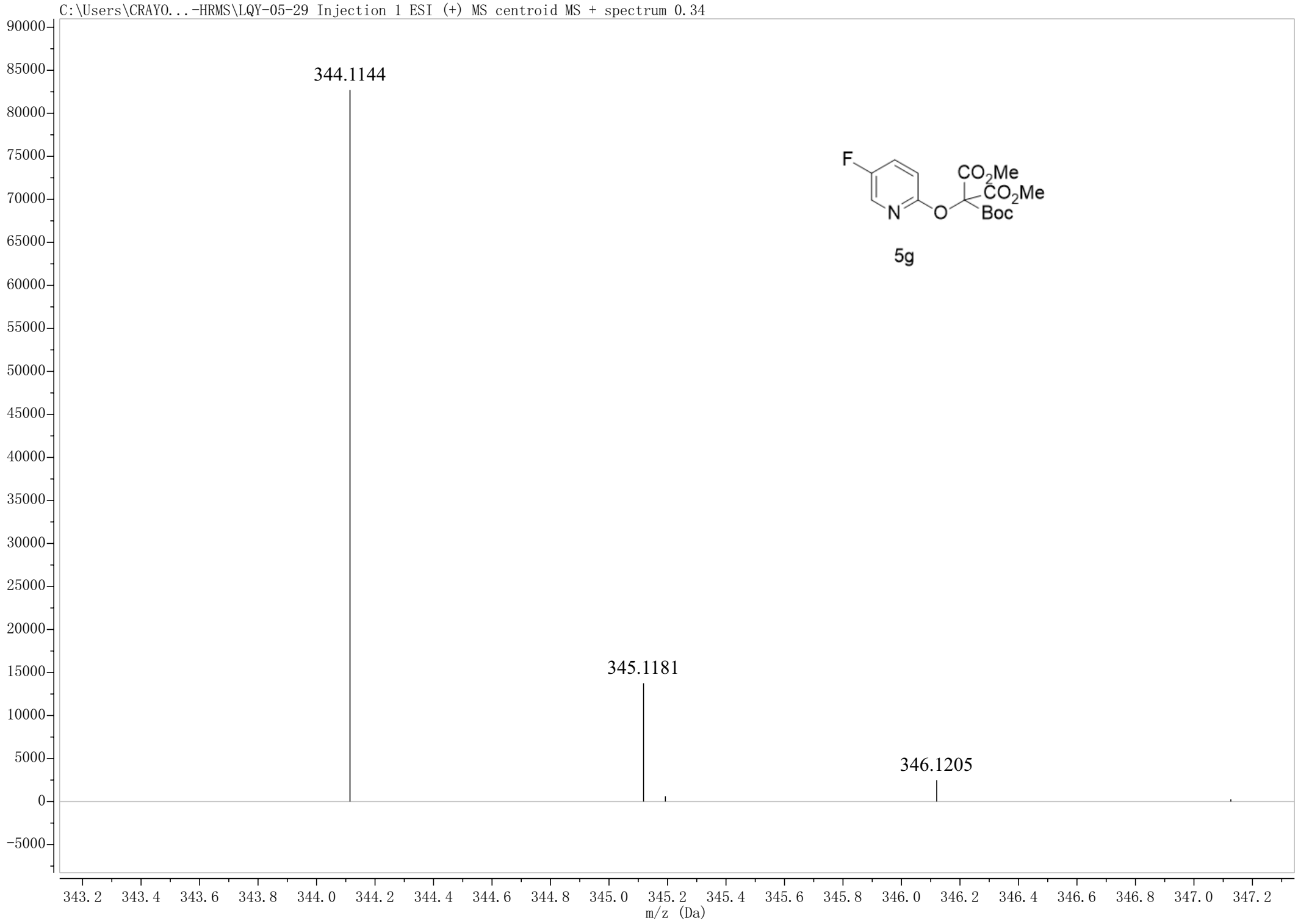

C:\Users\CRAYO...-HRMS\LQY-05-01 Injection 1 ESI (+) MS centroid MS + spectrum 0.36
404.0345
405.0372
405.1179
Br
CO2Me
CO2Me
N
O
Boc
5c
m/z (Da)

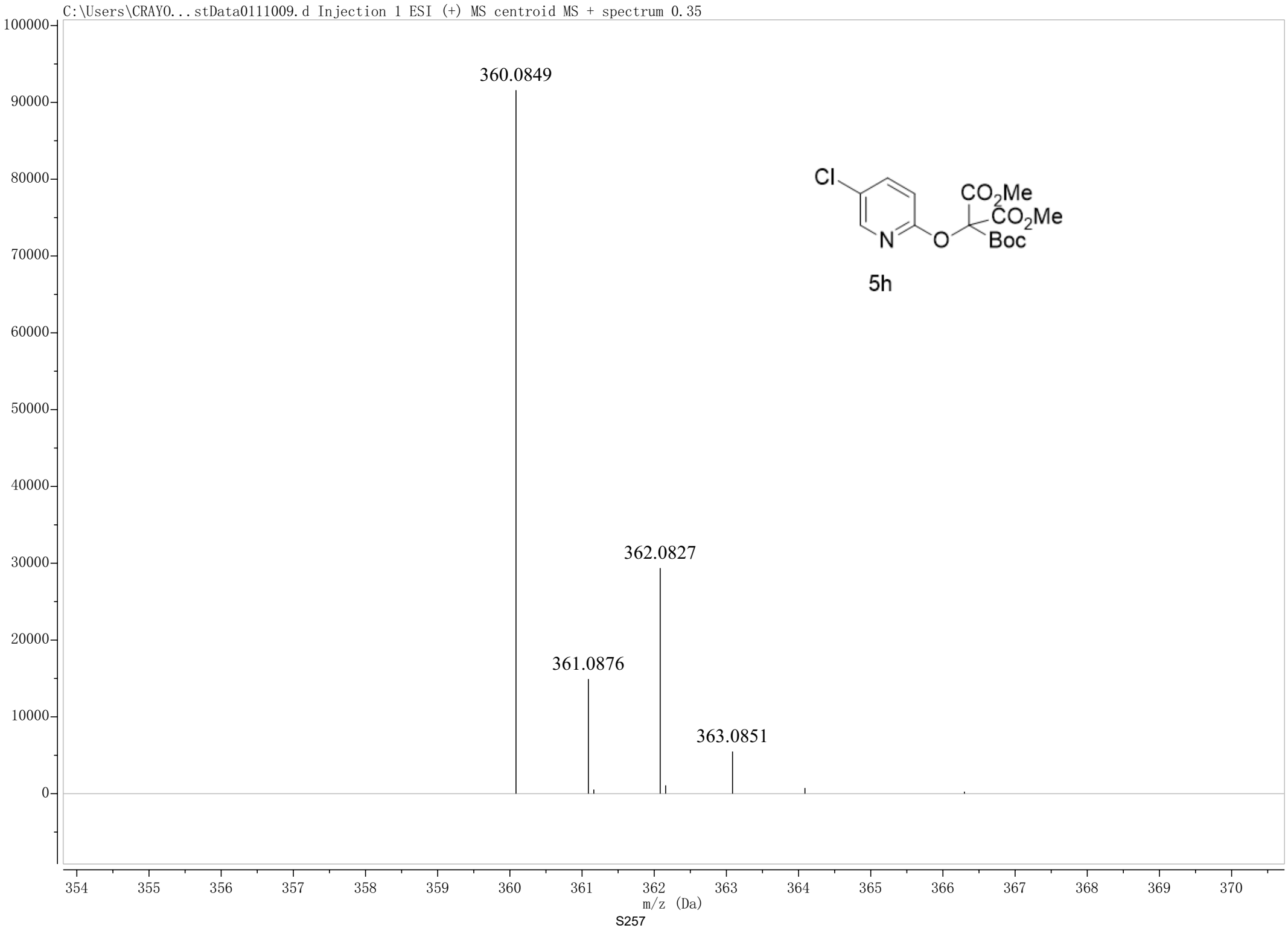

C:\Users\CRAYO...-HRMS\LQY-05-77 Injection 1 ESI (+) MS centroid MS + spectrum 0.36
384.1294
385.1318
386.1329
384.0412
CO2Me
CO2Me
CO2Me
N
O
Boc
5d
m/z (Da)


C:\Users\CRAYO...HRMS\LQY-04-173 Injection 1 ESI (+) MS centroid MS + spectrum 0.34
340.1393
341.1427
341.2153
342.1449
Me
CO2Me
CO2Me
Boc
N
O
5e
m/z (Da)

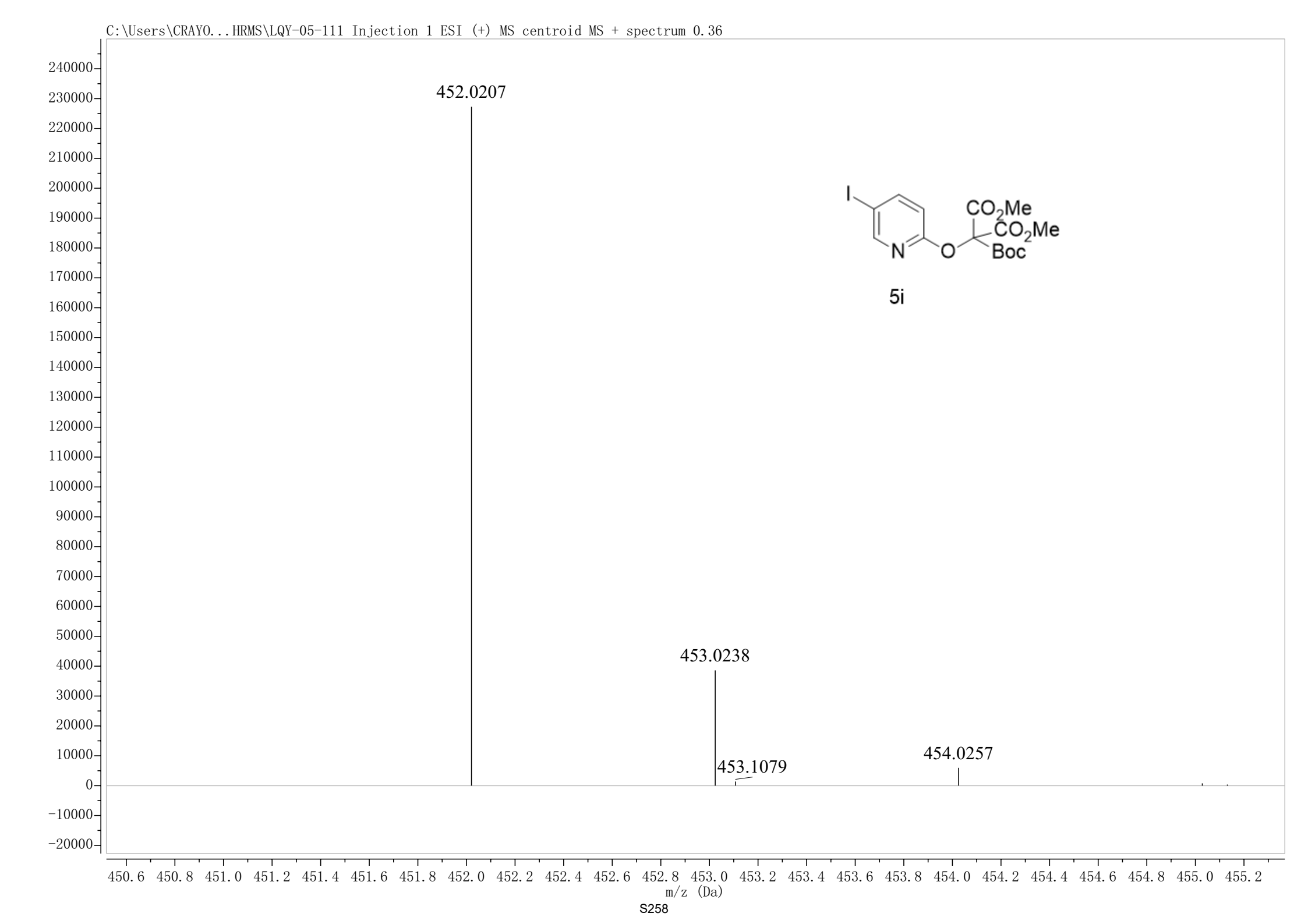
C:\Users\CRAYO...HRMS\LQY-04-179 Injection 1 ESI (+) MS centroid MS + spectrum 0.34



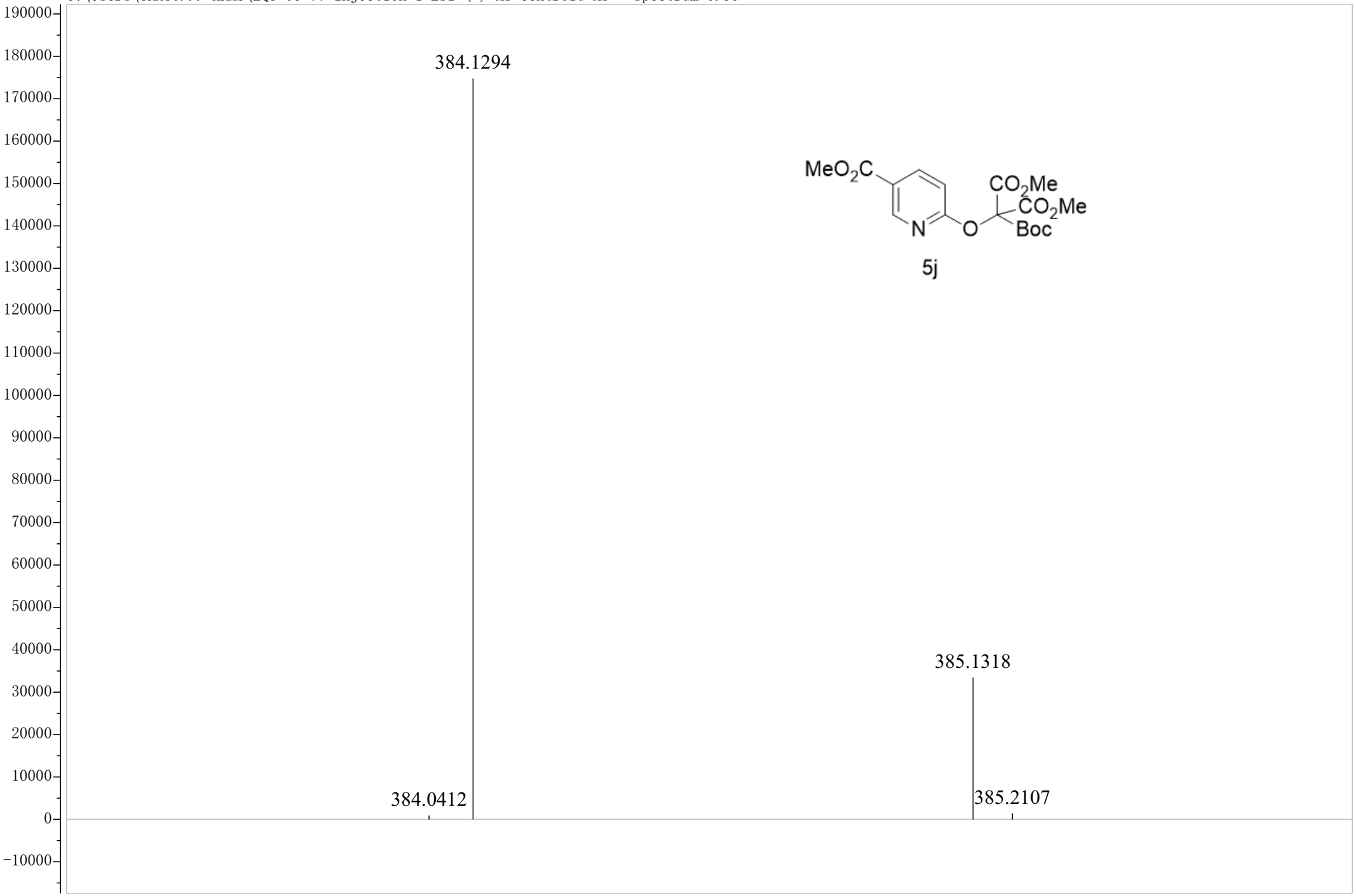

C:\Users\CRAYO...-HRMS\LQY-05-29 Injection 1 ESI (+) MS centroid MS + spectrum 0.34
344.1144
345.1181
346.1205
F
N
O
CO2Me
CO2Me
Boc
5g
m/z (Da)


C:\Users\CRAYO...stData0111009.d Injection 1 ESI (+) MS centroid MS + spectrum 0.35
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
360.0849
362.0827
361.0876
363.0851
Cl
N
O
CO2Me
CO2Me
Boc
5h
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
m/z (Da)

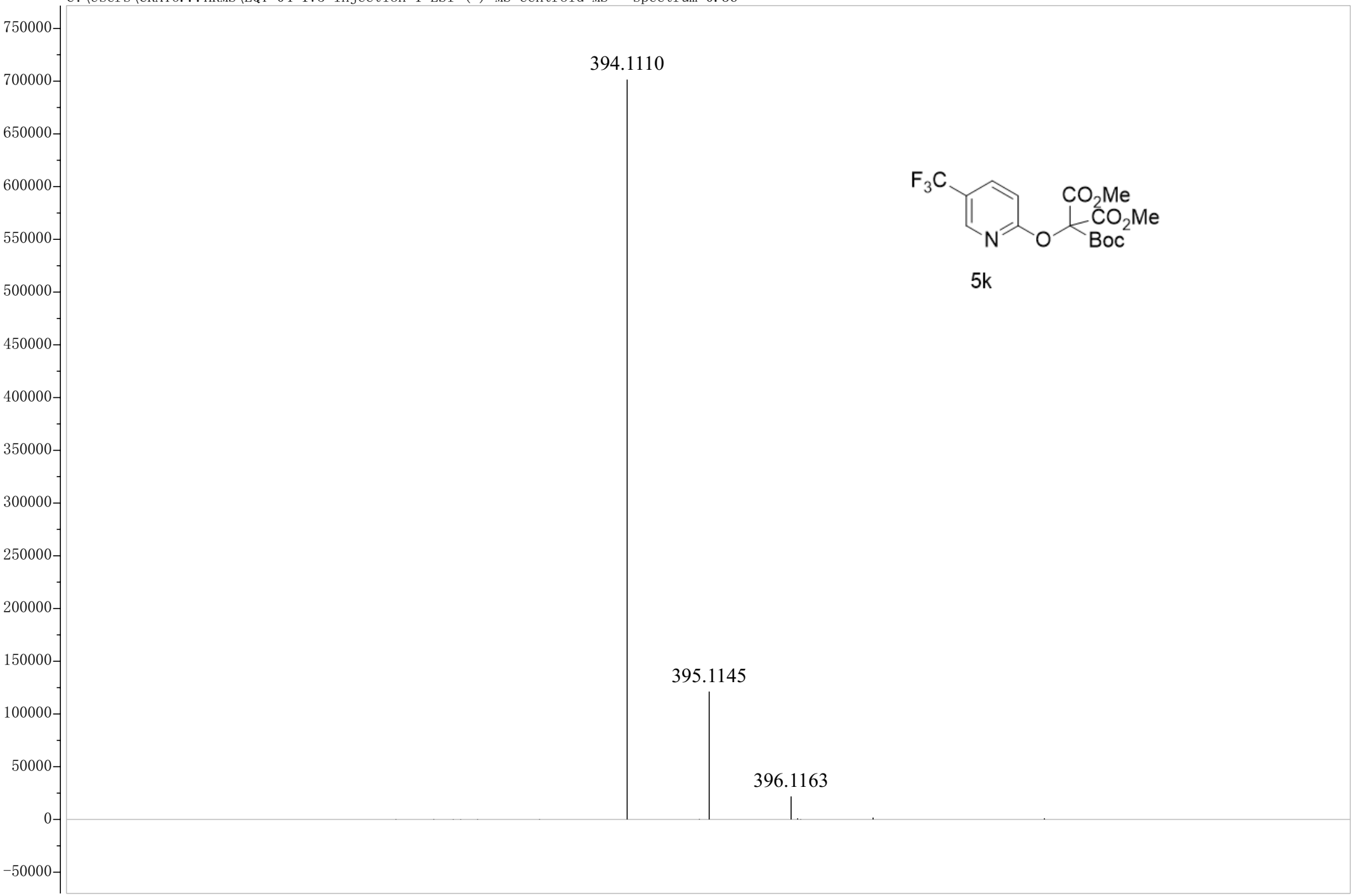
C:\Users\CRAYO...HRMS\LQY-05-111 Injection 1 ESI (+) MS centroid MS + spectrum 0.36



C:\Users\CRAYO...-HRMS\LQY-05-77 Injection 1 ESI (+) MS centroid MS + spectrum 0.36

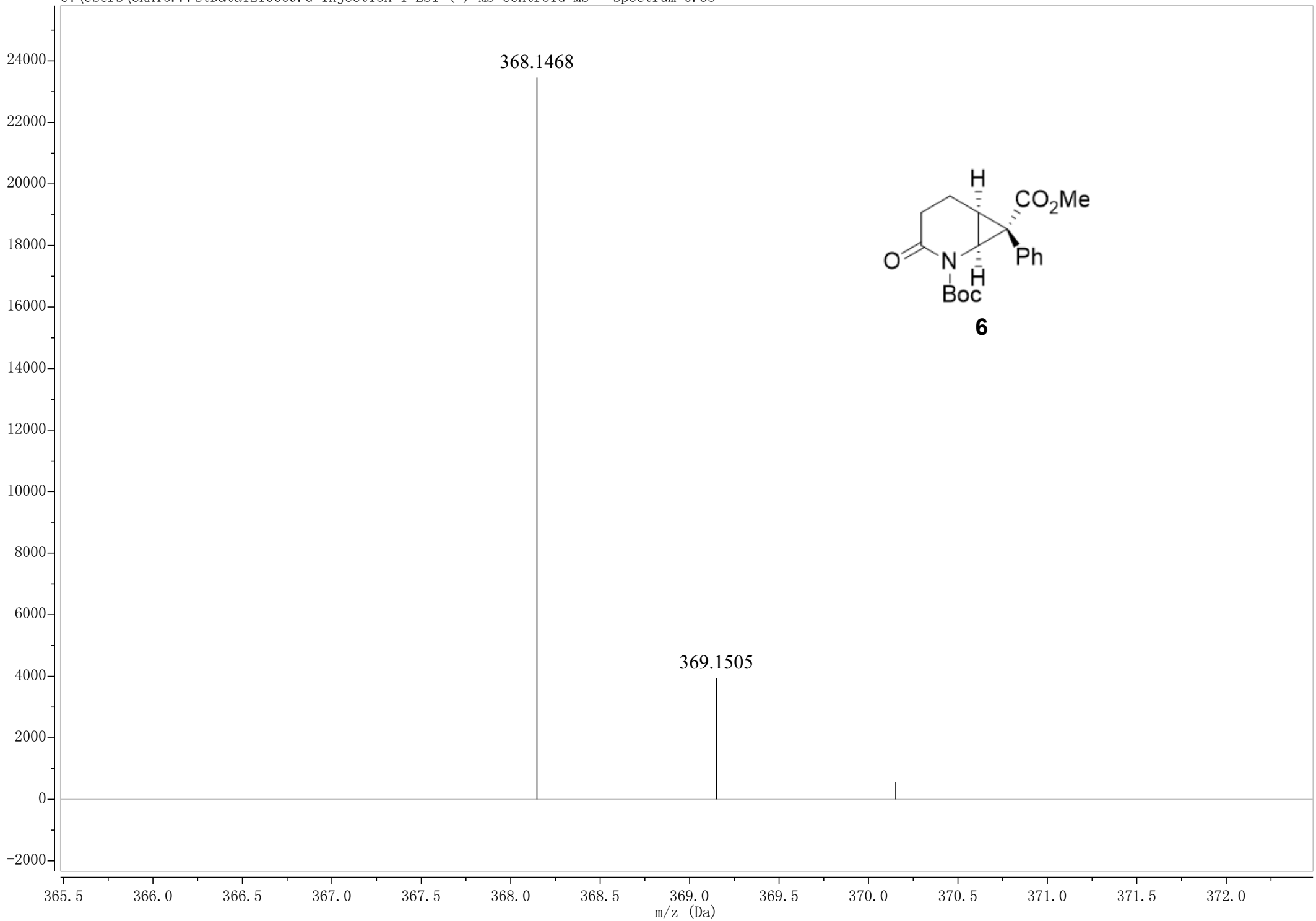


C:\Users\CRAYO...HRMS\LQY-04-175 Injection 1 ESI (+) MS centroid MS + spectrum 0.36

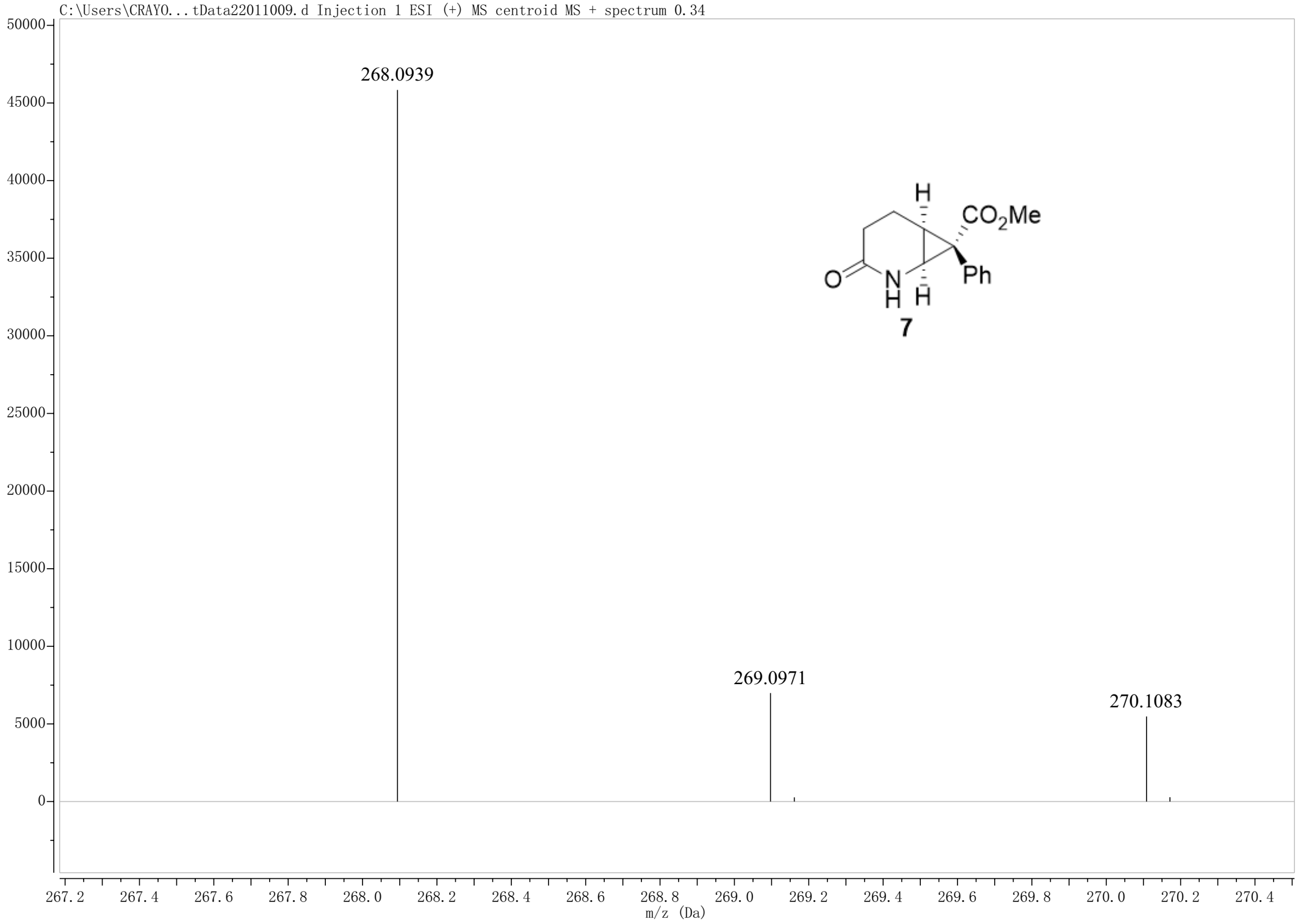


5k

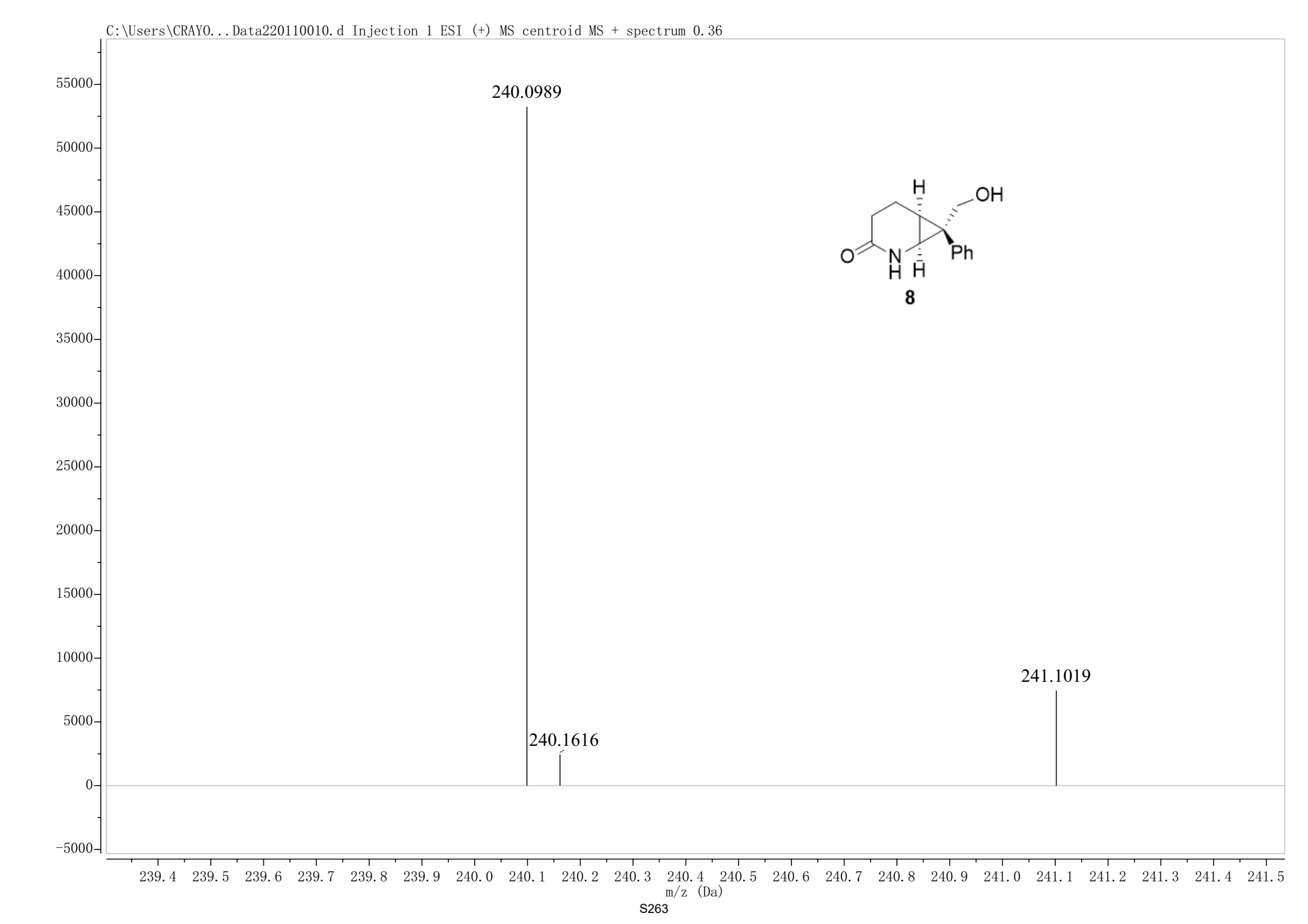
C:\Users\CRAYO...stData1210009.d Injection 1 ESI (+) MS centroid MS + spectrum 0.38



6

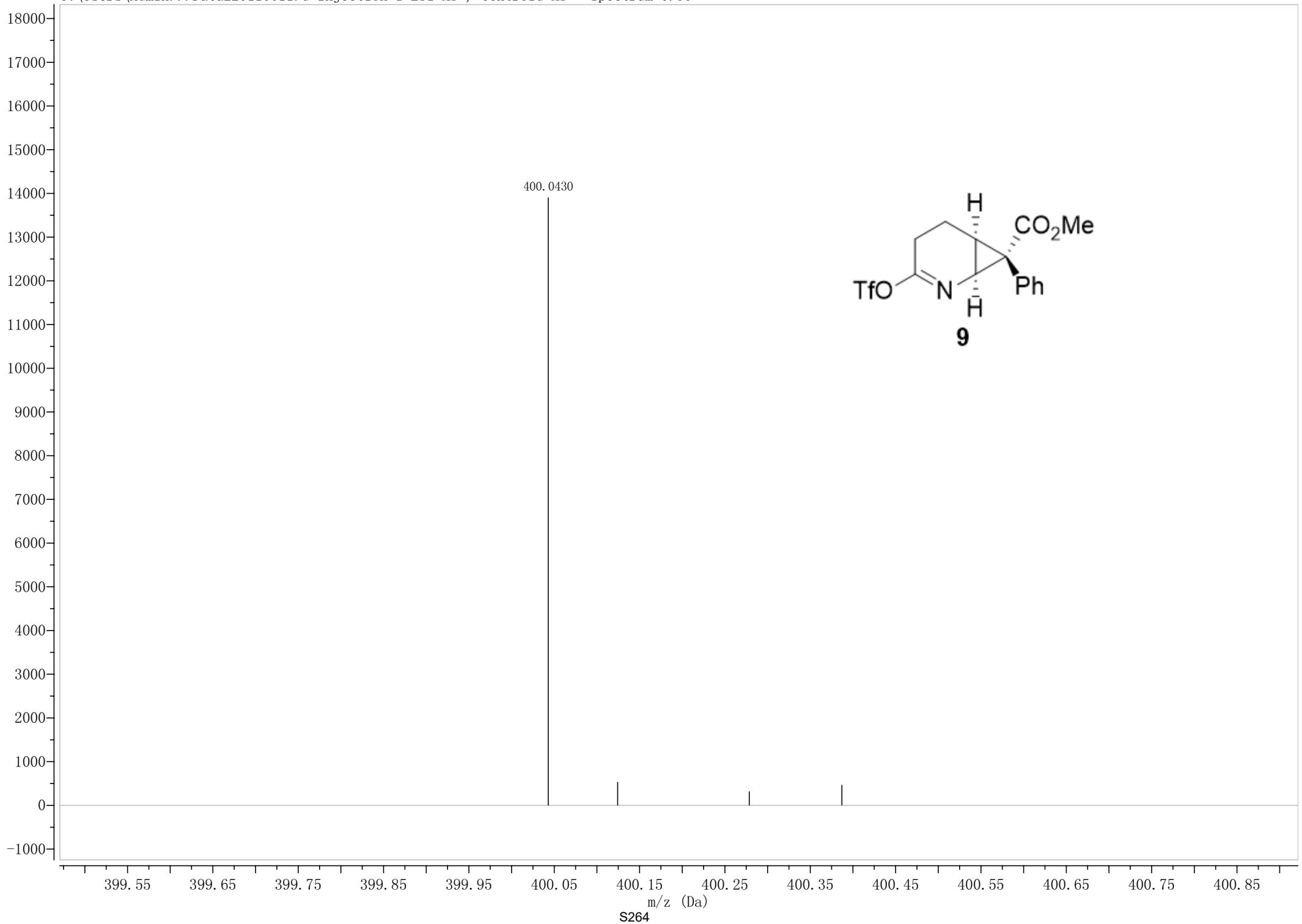

C:\Users\CRAYO...tData22011009.d Injection 1 ESI (+) MS centroid MS + spectrum 0.34
268.0939
269.0971
270.1083
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
267.2
267.4
267.6
267.8
268.0
268.2
268.4
268.6
268.8
269.0
269.2
269.4
269.6
269.8
270.0
270.2
270.4
m/z (Da)
H
CO2Me
O
N
H
H
Ph
7

C:\Users\CRAYO...Data220110010.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36



8

C:\Users\Admin...Data220110011.d Injection 1 ESI MS+, Centroid MS + spectrum 0.36



9

C:\Users\CRAYO...orklistData12.d Injection 1 ESI (+) MS centroid MS + spectrum 0.36