Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rhodium-Catalyzed Dearomative Rearrangement of 2-Oxypyridines with Cyclopropenes: Access to N-Alkylated 2-Pyridones

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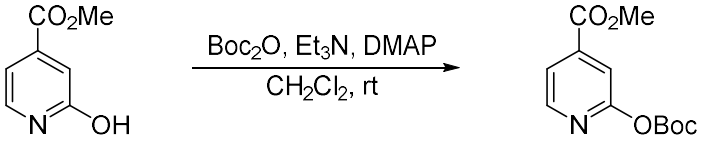
General information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F_{254} indicator. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz, 400 MHz spectrometer in $CDCl_3$. ^{13}C NMR were recorded on Bruker 75 MHz or 100 MHz spectrometer in $CDCl_3$. ^{19}F NMR were recorded on Bruker 282 MHz 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, 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.

Preparation of substrates

2-O-substituted pyridines (**1**)[1] and cyclopropenes (**2**)[2] were prepared according to literature procedures. Methyl 2-((tert-butoxycarbonyl)oxy)isonicotinate (**1f**) was new compound.



1f

To a solution of methyl 2-hydroxyisonicotinate (1 mmol) in CH_2Cl_2 (2.5 mL) was added Et_3N (2 mmol) and DMAP (0.1 mmol) at rt, then stirred for 5 min. Boc_2O (1.1 mmol) in CH_2Cl_2 (0.5 mL) was added dropwise to the reaction solution and stirred until consumption of the starting material. The reaction was diluted with CH_2Cl_2, washed with brine, dried over Na_2SO_4, filtered and concentrated under vacuum; the residue was purified by column chromatography (silica gel, eluted with EtOAc:Petroleum ether = 1:50-1:10, note: 20% Et_3N was added in the eluent.) to give **1f** as yellow solid (197.4 mg, 78%).

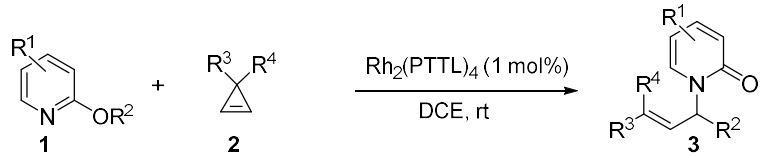
R_f (Petroleum ether/ EtOAc 5:1) = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.54 (d, *J* = 5.1 Hz, 1H), 7.78 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.67 (s, 1H), 3.97 (s, 3H), 1.58 (s, 9H).

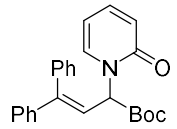
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 164.6, 158.7, 150.7, 149.2, 141.3, 121.4, 115.8, 84.5, 52.9, 27.7.

HRMS (ESI): calculated for $C_{12}H_{15}NO_5Na$ $[M+Na]^+$: 276.0842; Found: 276.0839.

General procedure for Scheme 2 and 3



To a dry sealable Schlenk tube was added $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%) under an argon atmosphere, then a solution of **1** (0.2 mmol, 1 equiv) and **2** (0.24 mmol, 1.2 equiv) in DCE (2 mL) was added. The resulting solution was stirred at rt for 4-8 h until consumption of the starting materials monitored by TLC. The reaction solution was concentrated under vacuum; the residue was purified by column chromatography on silica gel to give **3**.



tert-butyl 2-(2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3aa)

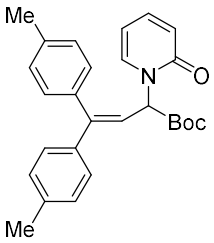
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (74.3 mg, 96%), mp: 108-110 °C.

R_f (Petroleum ether/ EtOAc 5:1) = 0.35.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42-7.34 (m, 3H), 7.34-7.25 (m, 6H), 7.22 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.18-7.11 (m, 2H), 6.52 (d, *J* = 9.3, 1H), 6.46 (d, *J* = 9.6 Hz, 1H), 6.13 (td, *J* = 6.8, 1.3 Hz, 1H), 5.38 (d, *J* = 9.6 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.3, 162.1, 149.5, 140.9, 139.6, 138.3, 136.2, 129.4, 128.8, 128.5, 128.4, 128.3, 127.7, 120.9, 120.1, 105.8, 82.7, 61.5, 28.0.

HRMS (ESI): calculated for $C_{25}H_{25}NO_3Na$ $[M+Na]^+$: 410.1727; Found: 410.1721.

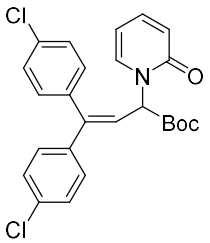


tert-butyl 2-(2-oxopyridin-1(2H)-yl)-4,4-di-p-tolylbut-3-enoate (3ab)

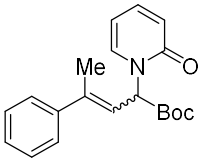
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(methylbenzene) (52.8 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (70.6 mg, 85%), mp: 89-90 °C.

R_f (Petroleum ether/ EtOAc 5:1) = 0.35.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.35-7.27 (m, 2H), 7.21-7.14 (m, 4H), 7.10 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.53 (dd, *J* = 9.9, 1.4 Hz, 1H), 6.34 (d, *J* = 9.9 Hz, 1H), 6.15 (td, *J* = 6.7, 1.4 Hz, 1H), 5.39 (d, *J* = 9.9 Hz, 1H), 2.37 (s, 3H), 2.34 (s, 3H), 1.47 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.4, 162.1, 149.7, 139.5, 138.4, 138.3, 137.9, 136.0, 135.3, 129.3, 129.2, 129.0, 127.7, 120.8, 118.5, 105.7, 82.5, 61.5, 28.0, 21.3, 21.2.
HRMS (ESI): calculated for $C_{27}H_{29}NO_3Na$ $[M+Na]^+$: 438.2040; Found: 438.2042.



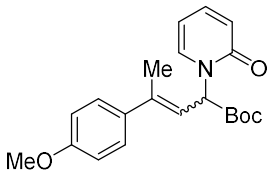
tert-butyl 4,4-bis(4-chlorophenyl)-2-(2-oxopyridin-1(2H)-yl)but-3-enoate (3ac)
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 4,4'-(cycloprop-2-ene-1,1-diyl)bis(chlorobenzene) (62.4 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (84.6 mg, 93%), mp: 181-183 ^{o}C.
R_f (Petroleum ether/ EtOAc 5:1) = 0.35.
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38 (d, *J* = 8.3 Hz, 2H), 7.35-7.23 (m, 3H), 7.20-7.14 (m, 3H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.53 (d, *J* = 9.1 Hz, 1H), 6.48 (d, *J* = 9.5 Hz, 1H), 6.15 (t, *J* = 6.4 Hz, 1H), 5.38 (d, *J* = 9.5 Hz, 1H), 1.46 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.8, 161.9, 146.7, 139.7, 138.9, 136.2, 136.1, 134.6, 134.5, 130.7, 129.1, 128.9, 128.6, 121.4, 121.0, 106.0, 83.0, 61.2, 27.9.
HRMS (ESI): calculated for $C_{25}H_{23}Cl_2NO_3Na$ $[M+Na]^+$: 478.0947; Found: 478.0946.



tert-butyl 2-(2-oxopyridin-1(2H)-yl)-4-phenylpent-3-enoate (3ad)
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and (1-methylcycloprop-2-en-1-yl)benzene (31.2 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (55. 9 mg, 86%, isomer ratio = 3:1).
R_f (Petroleum ether/ EtOAc 5:1) = 0.3.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (dt, *J* = 3.8, 1.9 Hz, 3H), 7.39-7.27 (m, 5.32H), 7.22 (dd, *J* = 6.8, 1.7 Hz, 0.33H), 7.17-7.11 (m, 0.66H), 6.60 (d, *J* = 9.1 Hz, 1H), 6.50 (d, *J* = 9.2 Hz, 0.33H), 6.29 (d, *J* = 8.8 Hz, 1H), 6.20 (td, *J* = 6.8, 1.3 Hz, 1H), 6.14 (td, *J* = 6.8, 1.4 Hz, 0.33H), 6.00-5.94 (m, 1H), 5.86 (dd, *J* = 9.7, 1.4 Hz, 0.33H), 5.30 (d, *J* = 9.7 Hz, 0.33H), 2.16 (d, *J* = 1.4 Hz, 1H), 2.13 (d, *J* = 1.3 Hz, 3H), 1.48 (s, 9H), 1.45 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.0, 168.6, 162.3, 162.0, 146.7, 145.1, 141.9, 140.0, 139.5, 139.4, 135.9, 135.5, 128.6, 128.5, 128.2, 127.8, 127.3, 126.0, 120.7, 120.4, 119.6, 118.8, 106.0, 105.5, 82.8, 82.4, 60.7, 56.9, 28.0, 27.9, 26.2, 17.1.

HRMS (ESI): calculated for $C_{20}H_{23}NO_3Na$ $[M+Na]^+$: 348.1570; Found: 348.1572.



tert-butyl 4-(4-methoxyphenyl)-2-(2-oxopyridin-1(2H)-yl)pent-3-enoate (3ae)

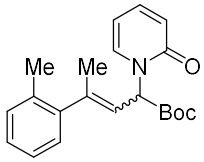
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 1-methoxy-4-(1-methylcycloprop-2-en-1-yl)benzene (38.4 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (65.3 mg, 92%, isomer ratio = 1.3:1).

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

^{1}H NMR (300 MHz, CDCl3): δ (ppm) 7.47-7.23 (m, 5.52H), 7.13-7.04 (m, 1.52H), 6.92-6.82 (m, 3.52H), 6.59 (d, *J* = 8.7 Hz, 1H), 6.54-6.45 (m, 0.76H), 6.25 (d, *J* = 8.8 Hz, 1H), 6.22-6.08 (m, 1.72H), 5.90 (dd, *J* = 8.8, 1.3 Hz, 1H), 5.78 (dd, *J* = 9.8, 1.4 Hz, 0.76H), 5.39 (d, *J* = 9.8 Hz, 0.76H), 3.82 (s, 3H), 3.80 (s, 2.28H), 2.15 (d, *J* = 1.4 Hz, 2.28H), 2.10 (d, *J* = 1.3 Hz, 3H), 1.48 (s, 9H), 1.45 (s, 6.84H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 169.2, 168.7, 162.3, 162.1, 159.7, 159.2, 146.5, 144.4, 139.5, 139.4, 135.8, 135.5, 134.2, 132.1, 128.5, 127.2, 120.7, 120.4, 118.1, 117.8, 114.0, 113.8, 105.9, 105.5, 82.7, 82.3, 60.6, 57.1, 55.4, 55.3, 28.0, 27.9, 26.3, 17.0.

HRMS (ESI): calculated for $C_{21}H_{25}NO_4Na$ $[M+Na]^+$: 378.1676; Found: 378.1680.



tert-butyl 2-(2-oxopyridin-1(2H)-yl)-4-(o-tolyl)pent-3-enoate (3af)

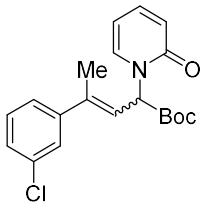
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 1-methyl-2-(1-methylcycloprop-2-en-1-yl)benzene (34.6 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (62.4 mg, 92%, isomer ratio = 1.3:1), mp: 123-124 ^{o}C.

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

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.31-7.03 (m, 9.10H), 6.91 (d, *J* = 5.8 Hz, 0.82H), 6.72 (d, *J* = 7.1 Hz, 1H), 6.46 (d, *J* = 9.1 Hz, 1.82H), 6.18-5.92 (m, 3.64H), 4.92 (d, *J* = 9.1 Hz, 0.82H), 4.77 (d, *J* = 9.4 Hz, 1H), 2.31 (s, 3H), 2.06 (s, 5.46H), 1.95 (s, 2.46H), 1.44 (s, 16.40H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 168.4, 162.0, 161.9, 146.9, 146.3, 139.7, 139.6, 139.4, 136.5, 136.2, 134.7, 130.5, 130.4, 127.9, 127.7, 127.1, 126.2, 126.0, 120.7, 120.0, 119.8, 105.4, 105.3, 82.3, 61.8, 61.5, 27.9, 25.4, 19.0, 18.8.

HRMS (ESI): calculated for $C_{21}H_{25}NO_3Na$ $[M+Na]^+$: 362.1727; Found: 362.1734.



tert-butyl 4-(3-chlorophenyl)-2-(2-oxopyridin-1(2H)-yl)pent-3-enoate (3ag)

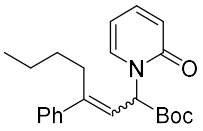
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 1-chloro-3-(1-methylcycloprop-2-en-1-yl)benzene (39.4 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (63.2 mg, 88%, isomer ratio = 1:1), mp:70-72 ºC.

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

^{1}H NMR (400 MHz, CDCl3): δ (ppm) 7.41-7.25 (m, 9H), 7.20 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.17-7.13 (m, 1H), 7.08-7.00 (m, 1H), 6.60 (d, *J* = 8.9 Hz, 1H), 6.50 (d, *J* = 8.7 Hz, 1H), 6.29 (d, *J* = 8.7 Hz, 1H), 6.21 (td, *J* = 6.9, 1.4 Hz, 1H), 6.15 (td, *J* = 6.9, 1.4 Hz, 1H), 6.00 (dd, *J* = 8.7, 1.4 Hz, 1H), 5.89 (dd, *J* = 9.6, 1.4 Hz, 1H), 5.31 (d, *J* = 9.6 Hz, 1H), 2.13 (d, *J* = 1.4 Hz, 3H), 2.12 (d, *J* = 1.4 Hz, 3H), 1.48 (s, 9H), 1.46 (s, 9H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 168.7, 168.3, 162.2, 161.9, 144.9, 143.8, 143.5, 141.8, 139.5, 139.4, 135.9, 135.5, 134.42, 134.4, 130.0, 129.7, 128.1, 127.9, 127.6, 126.2, 125.6, 124.2, 121.0, 120.8, 120.5, 120.0, 106.1, 105.7, 83.0, 82.7, 60.3, 56.7, 28.0, 27.9, 26.0, 17.1.

HRMS (ESI): calculated for $C_{20}H_{22}ClNO_3Na$ $[M+Na]^+$: 382.1180; Found: 382.1186.



tert-butyl 2-(2-oxopyridin-1(2H)-yl)-4-phenyloct-3-enoate (3ah)

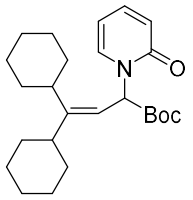
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and (1-butylcycloprop-2-en-1-yl)benzene (41.3 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (54.3 mg, 74%, isomer ratio = 2:1).

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

^{1}H NMR (300 MHz, CDCl3): δ (ppm) 7.45-7.40 (m, 1H), 7.39-7.24 (m, 8.0H), 7.23-7.16 (m, 0.5H), 7.14-7.08 (m, 1H), 6.59 (d, *J* = 9.2 Hz, 1H), 6.49 (d, *J* = 9.2 Hz, 0.5H), 6.25 (d, *J* = 9.4 Hz, 1H), 6.22-6.16 (m, 1H), 6.15-6.09 (m, 0.5H), 5.87-5.77 (m, 1.5H), 5.25 (d, *J* = 9.7 Hz, 0.5H), 2.66-2.49 (m, 2H), 2.48-2.39 (m, 1H), 1.49 (s, 9H), 1.46 (s, 4.5H), 1.37-1.15 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 1.5H), 0.81 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 169.1, 168.6, 162.3, 162.0, 151.0, 150.7, 141.4, 139.5, 139.4, 139.3, 135.9, 135.5, 128.5, 128.49, 128.1, 127.7, 127.6, 126.7, 120.7, 120.4, 119.5, 118.4, 105.8, 105.5, 82.7, 82.3, 60.7, 56.8, 39.3, 30.7, 30.5, 29.7, 28.0, 27.9, 22.5, 22.1, 13.9, 13.8.

HRMS (ESI): calculated for $C_{23}H_{29}NO_3Na$ $[M+Na]^+$: 390.2040; Found: 390.2044.



tert-butyl 4,4-dicyclohexyl-2-(2-oxopyridin-1(2H)-yl)but-3-enoate (3ai)

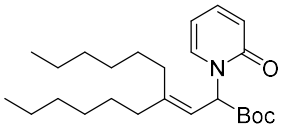
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldicyclohexane (48.9 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%) at 45 °C. The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (67.0 mg, 84%), mp: 113-114 °C.

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

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41-7.29 (m, 2H), 6.56 (d, *J* = 9.3 Hz, 1H), 6.17 (td, *J* = 6.8, 1.2 Hz, 1H), 6.01 (d, *J* = 9.6 Hz, 1H), 5.33 (d, *J* = 9.6 Hz, 1H), 2.52-2.39 (m, 1H), 2.08-1.97 (m, 1H), 1.82-1.53 (m, 9H), 1.45 (s, 9H), 1.38-1.10 (m, 11H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.7, 162.5, 161.5, 139.3, 135.1, 120.2, 114.4, 105.5, 82.1, 56.4, 41.6, 40.3, 34.9, 34.8, 30.4, 30.1, 27.9, 26.9, 26.1, 26.06, 26.0, 25.9.

HRMS (ESI): calculated for $C_{25}H_{37}NO_3Na$ $[M+Na]^+$: 422.2666; Found: 422.2669.



tert-butyl 4-hexyl-2-(2-oxopyridin-1(2H)-yl)dec-3-enoate (3aj)

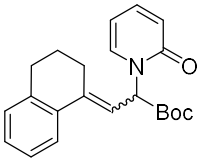
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 3,3-dihexylcycloprop-1-ene (49.9 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (74.2 mg, 92%).

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

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38 (dd, *J* = 6.8, 1.8 Hz, 1H), 7.34-7.27 (m, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 6.16 (td, *J* = 6.8, 1.2 Hz, 1H), 5.99 (d, *J* = 9.6 Hz, 1H), 5.36 (d, *J* = 9.6 Hz, 1H), 2.14-2.03 (m, 4H), 1.52-1.35 (m, 12H), 1.34-1.14 (m, 13H), 0.90-0.83 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.6, 162.3, 151.9, 139.3, 135.4, 120.3, 116.2, 105.5, 82.2, 56.6, 36.6, 31.7, 31.67, 30.9, 29.2, 28.9, 28.1, 27.9, 27.8, 22.6, 22.5, 14.1, 14.0.

HRMS (ESI): calculated for $C_{25}H_{41}NO_3Na$ $[M+Na]^+$: 426.2979; Found: 426.2981.



tert-butyl 3-(3,4-dihydronaphthalen-1(2H)-ylidene)-2-(2-oxopyridin-1(2H)-yl)propanoate (3ak)

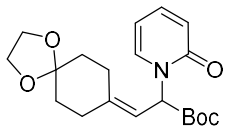
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 3',4'-dihydro-2'H-spiro[cyclopropane-1,1'-naphthalen]-2-ene (37.4 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (62.5 mg, 89%, isomer ratio = 1.25:1).

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

^{1}H NMR (400 MHz, CDCl3): δ (ppm) 7.67-7.60 (m, 0.82H), 7.50-7.41 (m, 1.82H), 7.38-7.29 (m, 1.82H), 7.26-7.09 (m, 6.46H), 6.58 (d, *J* = 9.2 Hz, 1.82H), 6.28 (d, *J* = 8.7 Hz, 0.82H), 6.23-6.11 (m, 2.64H), 5.93 (d, *J* = 10.0 Hz, 1H), 5.62 (d, *J* = 10.0 Hz, 1H), 2.90-2.74 (m, 3.64H), 2.71-2.49 (m, 2.82H), 2.44-2.34 (m, 0.82H), 2.03-1.91 (m, 2H), 1.88-1.73 (m, 1.64H), 1.48 (s, 7.38H), 1.45 (s, 9H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 169.3, 169.0, 162.4, 162.3, 146.8, 144.1, 139.6, 139.1, 138.6, 135.5, 135.3, 134.3, 133.9, 129.2, 128.8, 128.6, 128.4, 127.3, 126.3, 126.0, 124.3, 120.7, 120.4, 115.4, 115.0, 105.9, 105.7, 82.8, 82.4, 59.9, 56.6, 34.7, 30.2, 29.3, 28.0, 27.9, 27.2, 23.9, 22.7.

HRMS (ESI): calculated for $C_{22}H_{25}NO_3Na$ $[M+Na]^+$: 374.1727; Found: 374.1731.



tert-butyl 2-(2-oxopyridin-1(2H)-yl)-3-(1,4-dioxaspiro[4.5]decan-8-ylidene)propanoate (3al)

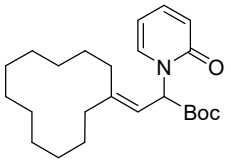
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 7,10-dioxadispiro[2.2.4^6.2^3]dodec-1-ene (39.8 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%) at 45 °C. The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (69.3 mg, 96%), mp: 128-129 °C.

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

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.37-7.28 (m, 1H), 6.57 (d, *J* = 8.7 Hz, 1H), 6.20 (td, *J* = 6.9, 1.5 Hz, 1H), 6.13 (d, *J* = 8.7 Hz, 1H), 5.46 (d, *J* = 8.7 Hz, 1H), 4.00-3.92 (m, 4H), 2.47-2.22 (m, 4H), 1.77-1.53 (m, 4H), 1.45 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.2, 162.2, 148.1, 139.5, 135.4, 120.3, 115.2, 108.2, 105.8, 82.6, 64.5, 64.4, 56.0, 36.0, 34.9, 33.5, 27.9, 26.3.

HRMS (ESI): calculated for $C_{20}H_{27}NO_5Na$ $[M+Na]^+$: 384.1781; Found: 384.1785.



tert-butyl 3-cyclododecylidene-2-(2-oxopyridin-1(2H)-yl)propanoate (3am)

Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and spiro[2.11]tetradec-1-ene (46.0 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%) at 45 °C. The crude product was

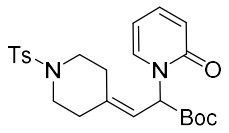
purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (49.6 mg, 64%), mp: 85-87 °C.

R_f (Petroleum ether/ EtOAc 5:1) = 0.35.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.35-7.26 (m, 1H), 6.56 (d, *J* = 9.1 Hz, 1H), 6.17 (td, *J* = 7.0, 1.2 Hz, 1H), 6.05 (d, *J* = 9.3 Hz, 1H), 5.49 (d, *J* = 9.3 Hz, 1H), 2.30-2.11 (m, 3H), 2.10-1.99 (m, 1H), 1.76-1.25 (m, 27H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.8, 162.3, 150.2, 139.3, 135.5, 120.4, 116.8, 105.5, 82.3, 56.5, 31.2, 30.0, 27.9, 25.2, 25.0, 24.0, 23.7, 23.6, 23.56, 23.1, 23.08, 22.2.

HRMS (ESI): calculated for $C_{24}H_{37}NO_3Na$ $[M+Na]^+$: 410.2666; Found: 410.2665.



tert-butyl 2-(2-oxopyridin-1(2H)-yl)-3-(1-tosylpiperidin-4-ylidene)propanoate (3an)

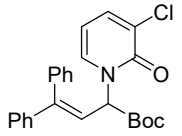
Prepared from tert-butyl pyridin-2-yl carbonate (39.0 mg, 0.2 mmol, 1.0 equiv) and 6-tosyl-6-azaspiro[2.5]oct-1-ene (63.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%) at 80 °C. The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 10:1 to 1:1) to give the desired product as a white solid (82.5 mg, 90%), mp: 186-188 °C.

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

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.62 (d, *J* = 8.4 Hz, 2H), 7.37-7.23 (m, 4H), 6.62-6.45 (m, 1H), 6.27-6.06 (m, 2H), 5.48 (d, *J* = 8.9 Hz, 1H), 3.19-2.93 (m, 4H), 2.53-2.30 (m, 7H), 1.38 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.5, 161.9, 143.7, 143.5, 139.5, 135.4, 133.2, 129.7, 127.6, 120.4, 117.5, 106.0, 82.9, 55.2, 47.4, 46.7, 35.1, 28.6, 27.8, 21.5.

HRMS (ESI): calculated for $C_{24}H_{30}N_2O_5SNa$ $[M+Na]^+$: 481.1768; Found: 481.1771.



tert-butyl 2-(3-chloro-2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ba)

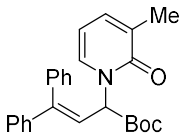
Prepared from tert-butyl (3-chloropyridin-2-yl) carbonate (45.8 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (72.4 mg, 86%), mp: 122-124 °C.

R_f (Petroleum ether/ EtOAc 5:1) = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.43-7.34 (m, 3H), 7.33-7.25 (m, 5H), 7.19-7.10 (m, 3H), 6.46 (d, *J* = 9.4 Hz, 1H), 6.10 (t, *J* = 7.1 Hz, 1H), 5.42 (d, *J* = 9.4 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.8, 158.5, 149.8, 140.8, 138.2, 137.7, 135.0, 129.3, 128.9, 128.6, 128.5, 128.4, 127.8, 126.4, 119.7, 105.0, 83.2, 62.5, 28.1.

HRMS (ESI): calculated for $C_{25}H_{24}ClNO_3Na$ $[M+Na]^+$: 444.1337; Found: 444.1334.



tert-butyl 2-(3-methyl-2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ca)

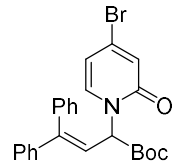
Prepared from tert-butyl (3-methylpyridin-2-yl) carbonate (41.8 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (69.0 mg, 86%), mp: 100-102 ºC.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40-7.33 (m, 3H), 7.32-7.25 (m, 5H), 7.18-7.13 (m, 3H), 7.07 (d, *J* = 6.8 Hz, 1H), 6.50 (d, *J* = 9.6 Hz, 1H), 6.05 (t, *J* = 6.8 Hz, 1H), 5.33 (d, *J* = 9.6 Hz, 1H), 2.10 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.4, 162.3, 148.8, 141.0, 138.3, 136.7, 133.6, 129.8, 129.4, 128.6, 128.3, 128.1, 127.7, 120.6, 105.4, 82.4, 61.9, 28.0, 17.2.

HRMS (ESI): calculated for $C_{26}H_{27}NO_3Na$ $[M+Na]^+$: 424.1883; Found: 424.1881.



tert-butyl 2-(4-bromo-2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3da)

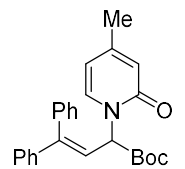
Prepared from tert-butyl (4-bromopyridin-2-yl) carbonate (54.6 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (78.2 mg, 84%).

R_f (Petroleum ether/ EtOAc 5:1) = 0.25.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41-7.37 (m, 3H), 7.33-7.24 (m, 5H), 7.16-7.05 (m, 3H), 6.75 (d, *J* = 2.2 Hz, 1H), 6.40 (d, *J* = 9.5 Hz, 1H), 6.29 (dd, *J* = 7.4, 2.2 Hz, 1H), 5.37 (d, *J* = 9.5 Hz, 1H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.9, 160.7, 150.1, 140.6, 138.0, 136.1, 135.8, 129.2, 128.8, 128.6, 128.4, 128.3, 127.7, 122.8, 119.3, 110.0, 83.0, 61.1, 28.0.

HRMS (ESI): calculated for $C_{25}H_{24}{}^{79}BrNO_3Na$ $[M+Na]^+$: 488.0832; Found: 488.0826. calculated for $C_{25}H_{24}{}^{81}BrNO_3Na$ $[M+Na]^+$: 490.0811; Found: 490.0809.



tert-butyl 2-(4-methyl-2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ea)

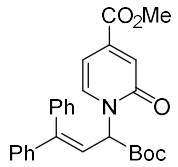
Prepared from tert-butyl (4-methylpyridin-2-yl) carbonate (41.8 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (68.2 mg, 85%).

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

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40-7.35 (m, 3H), 7.31-7.26 (m, 5H), 7.17-7.10 (m, 3H), 6.42 (d, *J* = 9.6 Hz, 1H), 6.32 (s, 1H), 5.99 (dd, *J* = 7.2, 1.6 Hz, 1H), 5.36 (d, *J* = 9.6 Hz, 1H), 2.16 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.4, 162.0, 151.2, 149.3, 140.9, 138.2, 134.9, 129.4, 128.6, 128.4, 128.3, 128.2, 127.7, 120.2, 119.2, 108.3, 82.5, 61.0, 28.0, 21.3.

HRMS (ESI): calculated for $C_{26}H_{27}NO_3Na$ $[M+Na]^+$: 424.1883; Found: 424.1887.



methyl 1-(1-(tert-butoxy)-1-oxo-4,4-diphenylbut-3-en-2-yl)-2-oxo-1,2-dihydropyridine-4-carboxylate (3fa)

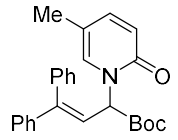
Prepared from methyl 2-((tert-butoxycarbonyl)oxy)isonicotinate (50.6 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (63.2 mg, 71%).

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

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41-7.35 (m, 3H), 7.32-7.26 (m, 6H), 7.17-7.09 (m, 3H), 6.63 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.47 (d, *J* = 9.5 Hz, 1H), 5.40 (d, *J* = 9.5 Hz, 1H), 3.89 (s, 3H), 1.47 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.8, 165.1, 161.7, 150.0, 140.6, 140.5, 138.1, 136.6, 129.2, 128.8, 128.6, 128.4, 128.3, 127.7, 122.6, 119.4, 104.1, 82.9, 61.6, 52.9, 27.9.

HRMS (ESI): calculated for $C_{27}H_{27}NO_5Na$ $[M+Na]^+$: 468.1781; Found: 468.1781.

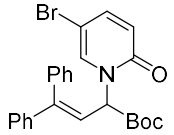


tert-butyl 2-(5-methyl-2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ga)

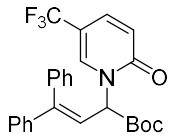
Prepared from tert-butyl (5-methylpyridin-2-yl) carbonate (41.8 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (71.4 mg, 89%), mp: 149-150 °C.

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

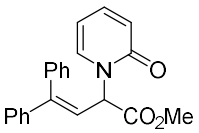
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42-7.34 (m, 3H), 7.31-7.25 (m, 5H), 7.19-7.11 (m, 3H), 6.93 (s, 1H), 6.47 (d, J = 9.6 Hz, 2H), 5.36 (d, J = 9.6 Hz, 1H), 2.04 (s, 3H), 1.47 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.4, 161.3, 149.1, 142.2, 140.9, 138.3, 133.6, 129.4, 128.7, 128.4, 128.3, 128.1, 127.7, 120.4, 120.37, 114.6, 82.6, 61.4, 28.0, 17.3.
HRMS (ESI): calculated for $C_{26}H_{27}NO_3Na$ $[M+Na]^+$: 424.1883; Found: 424.424.1885.



tert-butyl 2-(5-bromo-2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ha)
Prepared from tert-butyl (5-bromopyridin-2-yl) carbonate (54.6 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (79.1 mg, 85%). mp: 162-165 °C.
R_f (Petroleum ether/ EtOAc 5:1) = 0.25.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42-7.38 (m, 3H), 7.33-7.27 (m, 7H), 7.18-7.08 (m, 2H), 6.48-7.37 (m, 2H), 5.36 (d, J = 9.2 Hz, 1H), 1.47 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.8, 160.5, 150.3, 142.7, 140.7, 138.1, 136.3, 129.3, 128.9, 128.7, 128.5, 128.4, 127.8, 122.0, 119.4, 97.8, 83.1, 61.5, 28.0.
HRMS (ESI): calculated for $C_{25}H_{24}{}^{79}BrNO_3Na$ $[M+Na]^+$: 488.0832; Found: 488.0826. calculated for $C_{25}H_{24}{}^{81}BrNO_3Na$ $[M+Na]^+$: 490.0811; Found: 490.0809.



tert-butyl 2-(2-oxo-5-(trifluoromethyl)pyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ia)
Prepared from tert-butyl (5-(trifluoromethyl)pyridin-2-yl) carbonate (52.6 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (45.5 mg, 50%), mp: 156-157 °C.
R_f (Petroleum ether/ EtOAc 5:1) = 0.2.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.47 (s, 1H), 7.43-7.37 (m, 4H), 7.34-7.26 (m, 5H), 7.14-7.09 (m, 2H), 6.55 (d, J = 9.6 Hz, 1H), 6.48 (d, J = 9.1 Hz, 1H), 5.40 (d, J = 9.1 Hz, 1H), 1.47 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.51, 161.20, 150.34, 140.40, 137.99, 136.14 (q, J_{C-F} = 5.2 Hz), 135.14 (q, J_{C-F} = 2.3 Hz), 129.09, 128.89, 128.71, 128.45, 128.41, 127.64, 123.37 (q, J_{C-F} = 264.9 Hz), 121.25, 119.04, 109.32 (q, J_{C-F} = 34.9 Hz), 83.32, 61.77, 27.92.
^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -62.3.
HRMS (ESI): calculated for $C_{26}H_{24}F_3NO_3Na$ $[M+Na]^+$: 478.1600; Found: 478.1603.



methyl 2-(2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ja)

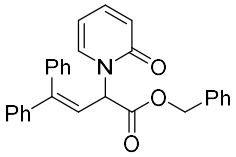
Prepared from methyl pyridin-2-yl carbonate (30.6 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(esp)_2$ (1.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (56.5 mg, 82%), mp: 144-146 ºC.

R_f (Petroleum ether/ EtOAc 5:1) = 0.15.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42-7.36 (m, 3H), 7.36-7.26 (m, 6H), 7.19-7.11 (m, 3H), 6.53 (d, *J* = 9.5 Hz, 2H), 6.15 (td, *J* = 6.7, 1.2 Hz, 1H), 5.40 (d, *J* = 9.5 Hz, 1H), 3.77 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.7, 162.0, 149.8, 140.5, 139.8, 138.0, 136.1, 129.3, 128.8, 128.6, 128.4, 128.3, 127.7, 121.0, 119.4, 106.1, 61.1, 53.0.

HRMS (ESI): calculated for $C_{22}H_{19}NO_3Na$ $[M+Na]^+$: 368.1257; Found: 368.1255.



benzyl 2-(2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enoate (3ka)

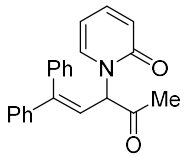
Prepared from benzyl pyridin-2-yl carbonate (45.8 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as colorless sticky oil (39.6 mg, 47%).

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

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38-7.21 (m, 14H), 7.18 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.12-7.06 (m, 2H), 6.54 (d, *J* = 9.2 Hz, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 6.14 (td, *J* = 6.7, 0.9 Hz, 1H), 5.46 (d, *J* = 9.6 Hz, 1H), 5.22 (q, *J* = 13.0 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.0, 162.1, 150.0, 140.6, 140.0, 138.0, 136.1, 135.6, 129.3, 128.8, 128.6, 128.4, 128.3, 128.27, 128.1, 127.7, 121.0, 119.3, 106.1, 67.4, 61.2.

HRMS (ESI): calculated for $C_{28}H_{23}NO_3Na$ $[M+Na]^+$: 444.1570; Found: 444.1567.



1-(4-oxo-1,1-diphenylpent-1-en-3-yl)pyridin-2(1H)-one (3la)

Prepared from pyridin-2-yl acetate (27.4 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was

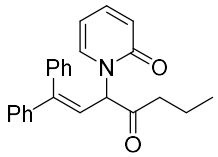
purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (54.6 mg, 83%), mp: 96-97 ºC.

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

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.44-7.38 (m, 3H), 7.37-7.26 (m, 7H), 7.16-7.01 (m, 2H), 6.58-6.51 (m, 1H), 6.27 (d, *J* = 10.2 Hz, 1H), 6.22 (td, *J* = 6.8, 1.5 Hz, 1H), 5.47 (d, *J* = 10.2 Hz, 1H), 2.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 202.2, 162.2, 151.7, 140.5, 140.0, 138.0, 135.9, 129.0, 128.9, 128.6, 128.5, 127.8 120.7, 118.6, 106.3, 66.8, 28.0.

HRMS (ESI): calculated for $C_{22}H_{19}NO_2Na$ $[M+Na]^+$: 352.1308; Found: 352.1306.



1-(4-oxo-1,1-diphenylhept-1-en-3-yl)pyridin-2(1H)-one (3ma)

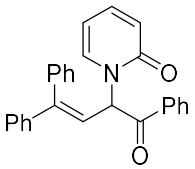
Prepared from pyridin-2-yl butyrate (33.0 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (55.7 mg, 78%), mp: 116-118 ºC.

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

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44-7.25 (m, 10H), 7.14-7.09 (m, 2H), 6.53 (d, *J* = 9.2 Hz, 1H), 6.27-6.17 (m, 2H), 5.52 (d, *J* = 10.4 Hz, 1H), 2.63-2.46 (m, 2H), 1.69-1.55 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 204.5, 162.1, 151.7, 140.6, 139.8, 138.0, 135.8, 129.0, 128.95, 128.8, 128.5, 128.49, 127.7, 120.6, 118.7, 106.1, 66.1, 42.6, 16.9, 13.7.

HRMS (ESI): calculated for $C_{24}H_{23}NO_2Na$ $[M+Na]^+$: 380.1621; Found: 380.1616.



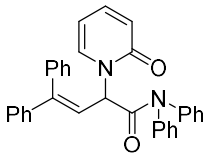
methyl 1-(1-(tert-butoxy)-1-oxo-4,4-diphenylbut-3-en-2-yl)-2-oxo-1,2-dihydropyridine-4-carbo xylate (3na)

Prepared from pyridin-2-yl benzoate (39.8 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give the desired product as a white solid (74.2 mg, 95%), mp: 102-104 ºC.

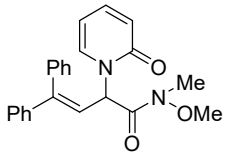
R_f (Petroleum ether/ EtOAc 3:1) = 0.2.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85-7.77 (m, 2H), 7.67 (dd, *J* = 6.8, 1.7 Hz, 1H), 7.53-7.45 (m, 1H), 7.43-7.33 (m, 6H), 7.31-7.24 (m, 3H), 7.23-7.18 (m, 2H), 7.11-7.04 (m, 2H), 6.66 (d, *J* = 10.3 Hz, 1H), 6.53 (d, *J* = 9.0 Hz, 1H), 6.28 (td, *J* = 6.8, 1.3 Hz, 1H), 6.18 (d, *J* = 10.3 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 195.0, 162.0, 152.1, 140.6, 139.8, 137.9, 135.7, 135.0, 133.6, 129.0, 128.96, 128.9, 128.8, 128.77, 128.6, 128.5, 127.9, 120.4, 118.9, 106.2, 61.2.
HRMS (ESI): calculated for $C_{27}H_{21}NO_2Na$ $[M+Na]^+$: 414.1465; Found: 414.1456.



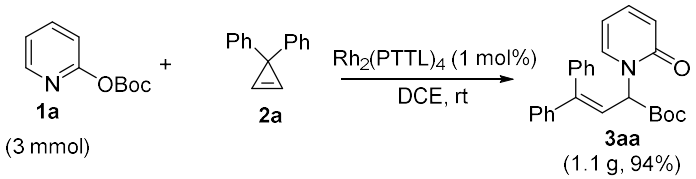
2-(2-oxopyridin-1(2H)-yl)-N,N,4,4-tetraphenylbut-3-enamide (3oa)
Prepared from pyridin-2-yl diphenylcarbamate (58.0 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 10:1 to 1:1) to give the desired product as a white solid (93.5 mg, 97%), mp: 143-146 °C.
R_f (Petroleum ether/ EtOAc 1:1) = 0.3.
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.63 (dd, *J* = 6.8, 1.6 Hz, 1H), 7.50-7.38 (m, 2H), 7.36-7.26 (m, 10H), 7.22-7.12 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.55-6.46 (m, 3H), 6.27 (d, *J* = 9.6 Hz, 1H), 6.22-6.17 (dt, *J* = 6.8, 1.0 Hz, 1H), 5.84 (d, *J* = 9.6Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.6, 162.3, 152.0, 142.7, 141.3, 140.9, 139.7, 137.0, 136.2, 129.6, 128.88, 128.85, 128.7, 128.5, 128.2, 128.0, 127.9, 126.4, 120.2, 118.6, 105.8, 59.0.
HRMS (ESI): calculated for $C_{33}H_{26}N_2O_2Na$ $[M+Na]^+$: 505.1886; Found: 505.1883.



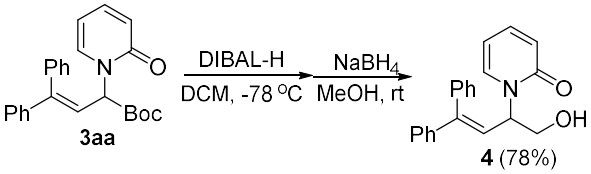
N-methoxy-N-methyl-2-(2-oxopyridin-1(2H)-yl)-4,4-diphenylbut-3-enamide (3pa)
Prepared from pyridin-2-yl methoxy(methyl)carbamate (36.4 mg, 0.2 mmol, 1.0 equiv) and cycloprop-2-ene-1,1-diyldibenzene (46.1 mg, 0.24 mmol, 1.2 equiv) according to the general procedure in the presence of $Rh_2(PTTL)_4$ (2.5 mg, 0.002 mmol, 1 mol%). The crude product was purified by flash chromatography on silica gel (Petroleum ether/ EtOAc = 10:1 to 1:1) to give the desired product as a white solid (65.8 mg, 88%), mp: 149-150 °C.
R_f (Petroleum ether/ EtOAc 1:1) = 0.3.
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.68 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.38-7.29 (m, 9H), 7.10-7.04 (m, 2H), 6.51 (d, *J* = 8.8 Hz, 1H), 6.28-6.15 (m, 3H), 3.50 (s, 3H), 3.19 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.2, 151.3, 140.6, 139.6, 138.1, 136.0, 129.1, 128.7, 128.5, 128.4, 128.3, 127.9, 120.2, 118.6, 105.9, 61.0, 56.6, 32.3.
HRMS (ESI): calculated for $C_{23}H_{22}N_2O_3Na$ $[M+Na]^+$: 397.1523; Found: 397.1521.

Further exploration for Scheme 4

Scheme 4-a



To a Schlenk flask was added $Rh_2(PTTL)_4$ (37.5 mg, 0.03 mmol, 1 mol%) under an argon atmosphere, then a solution of **1a** (0.585 g, 3 mmol, 1 equiv) and **2a** (0.691 g, 3.6 mmol, 1.2 equiv) in DCE (30 mL) was added. The resulting solution was stirred at rt for 4 h. The reaction solution was concentrated under vacuum; the residue was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 20:1 to 5:1) to give **3aa** as a white solid (1.1 g, 94%).



To a cold solution of **3aa** (77.4 mg, 0.2 mmol) in DCM (3 mL) was added dropwise DIBAL-H (0.3 mL, 0.3 mmol, 1 M in toluene) at -78 °C. After stirring at -78 °C for 30 min, MeOH (0.1 mL) was added dropwise to the reaction, followed by Na_2SO_4 (0.5 g), celite (0.5 g) and water (2 drops). The mixture was stirred at rt for 30 min, then filtered and washed the solid with DCM. The filtrate was washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The crude sticky residue was dissolved in MeOH (2 mL), then $NaBH_4$ (11.4 mg, 0.3 mmol) was added. The reaction was stirred at rt for 30 min. The solvent was removed under vacuum, the residue was added water and extracted with EtOAc. The layer was washed with brine, dried over Na_2SO_4, concentrated and purified by flash chromatography on silica gel (Petroleum ether/EtOAc = 10:1 to 2:1) to give **4** as colorless sticky oil (49.5 mg, 78%).

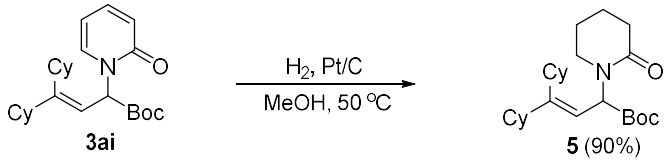
R_f (Petroleum ether/ EtOAc 1:1) = 0.2.

^{1}H NMR (300 MHz, CDCl3): δ (ppm) 7.39-7.23 (m, 9H), 7.16 (dd, *J* = 6.8, 1.1 Hz, 1H), 7.08-7.01 (m, 2H), 6.56 (d, *J* = 9.0 Hz, 1H), 6.49 (d, *J* = 9.0 Hz, 1H), 6.13 (td, *J* = 6.8, 1.1 Hz, 1H), 5.21-5.06 (m, 1H), 4.04-3.87 (m, 2H), 3.80 (s, 1H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 163.3, 147.9, 140.9, 139.4, 138.6, 136.7, 129.0, 128.6, 128.3, 128.2, 128.0, 127.5, 121.8, 121.0, 106.5, 65.0, 61.1.

HRMS (ESI): calculated for $C_{21}H_{19}NO_2Na$ $[M+Na]^+$: 340.1308; Found: 340.1309.

Scheme 4-b



To a solution of **3ai** (79.8 mg, 0.20 mmol) in anhydrous MeOH (3 mL) was added 10% Pt/C (19.5 mg), then degassed and refilled with H_2. The reaction mixture was stirred under H_2 balloon at 50 °C for 12 h. After the reaction was complete (monitored by TLC), the reaction mixture was filtrated through a pad of celite and washed with EtOAc. The filtrate was concentrated under reduced pressure and purified by silica gel column chromatography (EA/PE = 5:1) to afford **5**

(72.5 mg, 90%) as yellow oil.

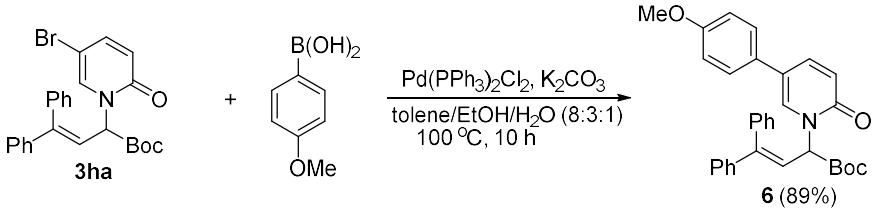
R_f (Petroleum ether/ EtOAc 5:1) = 0.3.

^{1}H NMR (300 MHz, CDCl3): δ (ppm) 5.83 (d, *J* = 8.7 Hz, 1H), 5.24 (d, *J* = 8.7 Hz, 1H), 3.25 (t, *J* = 5.4 Hz, 2H), 2.55-2.30 (m, 3H), 1.87-1.58 (m, 13H), 1.44 (s, 9H), 1.36-1.13 (m, 12H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 171.0, 169.4, 158.3, 115.0, 81.2, 54.2, 44.2, 41.2, 39.9, 35.2, 34.9, 32.4, 30.6, 30.4, 28.0, 27.1, 27.0, 26.2, 26.16, 26.15, 26.06, 23.3, 21.2.

HRMS (ESI): calculated for $C_{25}H_{41}NO_3Na$ $[M+Na]^+$: 426.2979; Found: 426.2979.

Scheme 4-c



Under an argon atmosphere, **3ha** (93.2 mg, 0.2 mmol), $PdCl_2(PPh_3)_2$ (7.8 mg, 0.01 mmol), 4-methoxyphenylboronic acid (36.5 mg, 0.24 mmol) and K_2CO_3 (82.8 mg, 0.6 mmol) were placed in a dry Schlenk tube, then toluene (8 mL), EtOH (3 mL) and H_2O (1 mL) were added. The resulted mixture was stirred at 100 °C for 10 h under argon atmosphere. Toluene and EtOH were removed under reduced pressure, the residual slurry was dissolved in H_2O and extracted with DCM. The combined layers were dried over $MgSO_4$, filtered and evaporated; the residue was purified by flash chromatography on silica gel **(**Petroleum ether/EtOAc = 15:1 to 5:1) to give **6** as colorless sticky oil (87.8 mg, 89%).

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

^{1}H NMR (300 MHz, CDCl3): δ (ppm) 7.56 (dd, *J* = 9.4, 2.0 Hz, 1H), 7.43-7.33 (m, 3H), 7.32-7.25 (m, 8H), 7.21-7.14 (m, 2H), 6.99-6.88 (m, 2H), 6.59 (d, *J* = 9.4 Hz, 1H), 6.54 (d, *J* = 9.4 Hz, 1H), 5.45 (d, J = 9.4 Hz, 1H), 3.82 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (75 MHz, CDCl3): δ (ppm) 168.2, 161.2, 159.1, 149.3, 140.9, 139.6, 138.3, 133.0, 129.4, 129.3, 128.7, 128.4, 128.3, 128.2, 127.7, 127.1, 120.7, 120.2, 119.7, 114.5, 82.76, 61.8, 55.4, 28.0.

HRMS (ESI): calculated for $C_{32}H_{31}NO_4Na$ $[M+Na]^+$: 516.2145; Found: 516.2143.

X-ray crystallographic data

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2131456, **3ha**). The data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/.

Method of crystallization: A solution of **3ha** in DCM and Petroleum ether was evaporated the solvent slowly at room temperature.

Crystal data and structure for 3ha

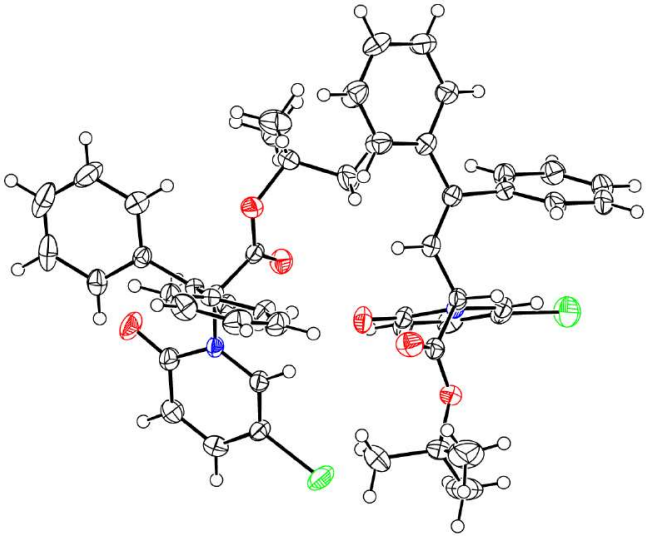


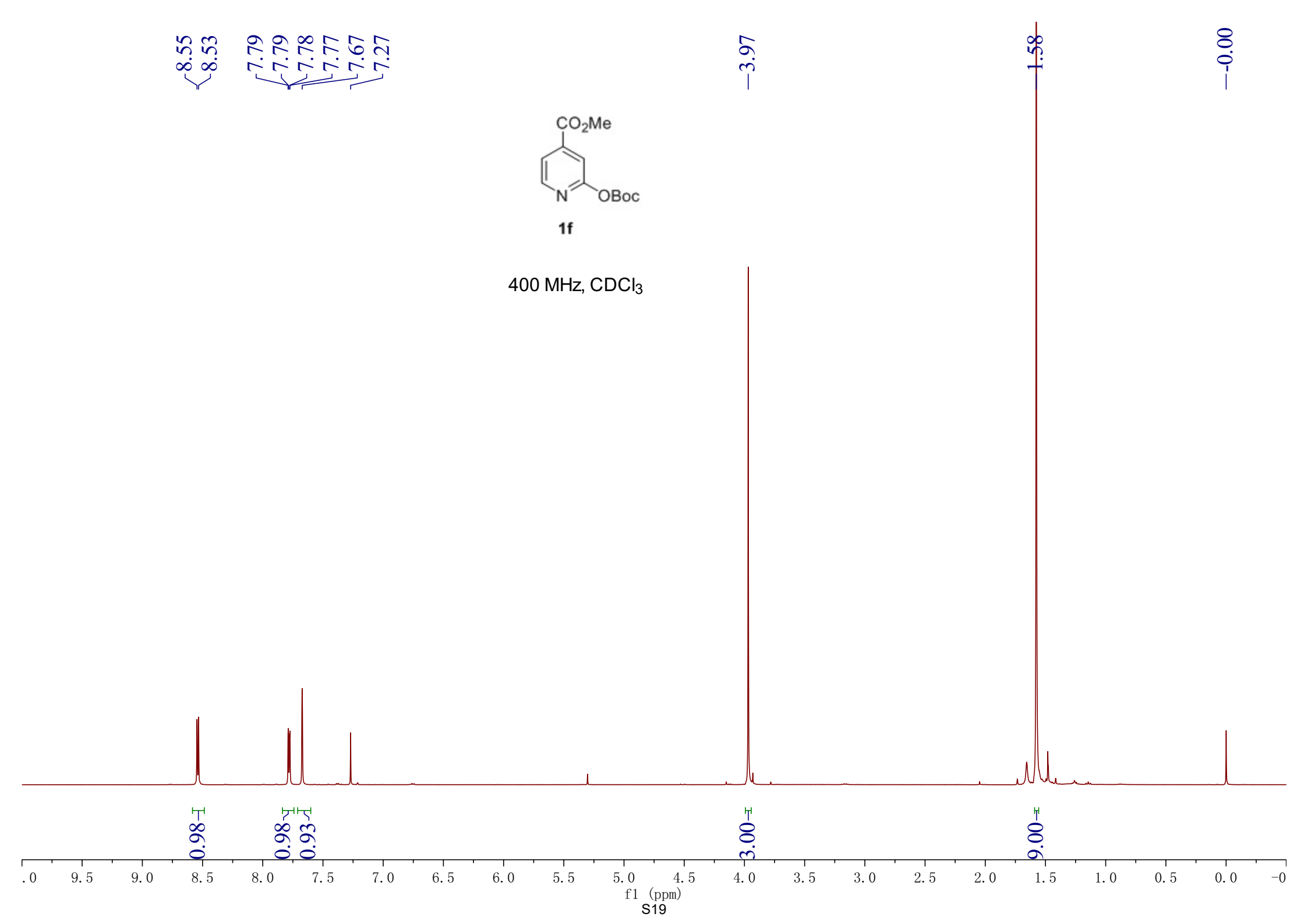
Figure 1. ORTEP diagram of **3ha**. Thermal ellipsoids are shown at the 50% level.

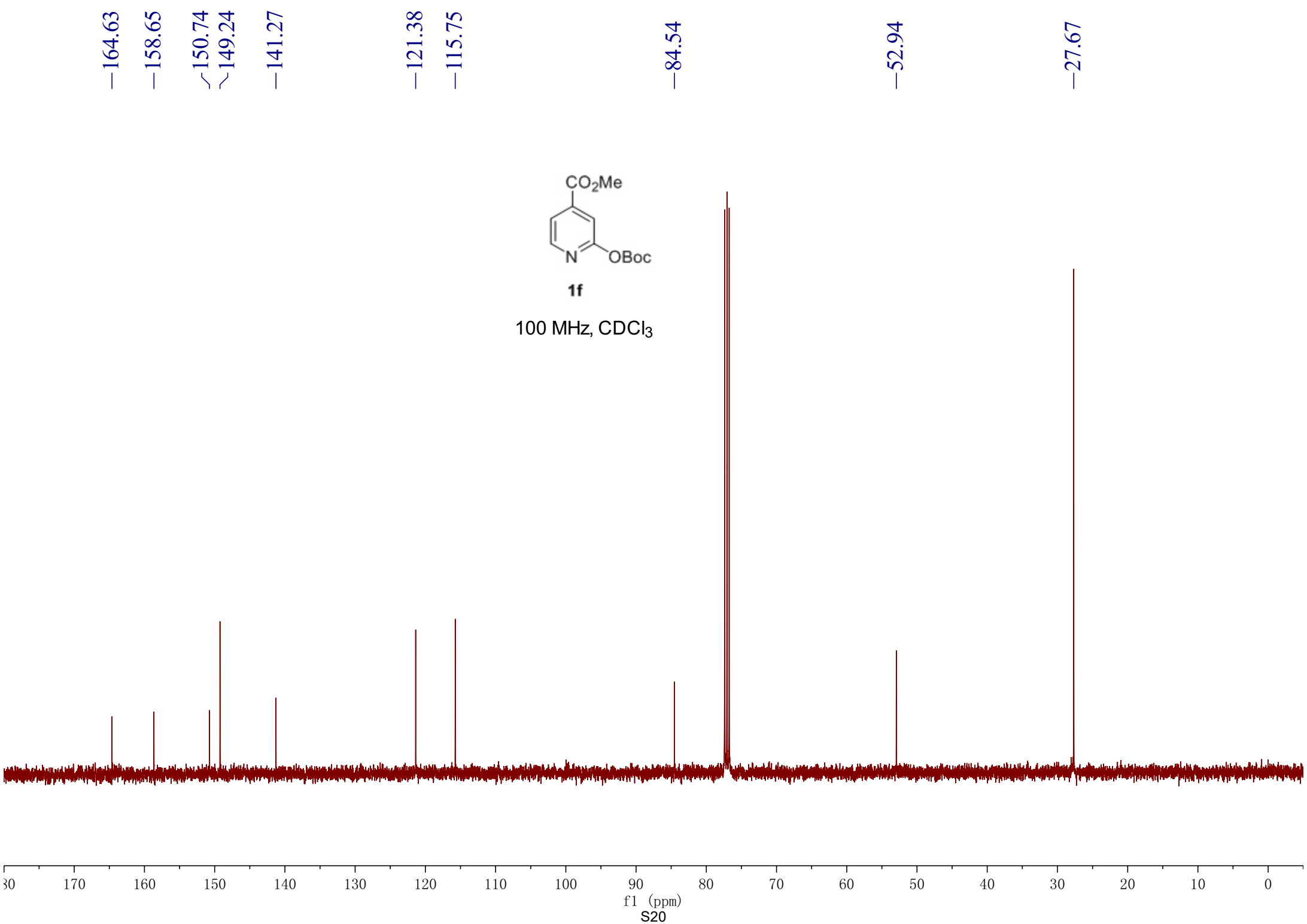
Empirical formula	$C_{25}H_{24}BrNO_3$	
Formula weight	466.38	
Temperature	296.15 K	
Wavelength	0.71703 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.6644 (6) Å	α = 75.708 (2) °
	b = 11.9643 (6) Å	β = 85.239 (2) °
	c = 19.4199 (9) Å	γ = 70.225 (2) °
Volume	2259.5 (2) $Å^3$	
Z	4	
Density (calculated)	1.371 g/cm^3	
Absorption coefficient	1.845 mm^{-1}	
F(000)	960	
Crystal size	0.12 x 0.12 x 0.1 mm^3	
θ range for data collection	1.921 to 27.504°	
Index ranges	$-11 \le h \le 13$, $-15 \le k \le 15$, $-25 \le l \le 25$	
Reflections collected	21000	
Independent reflections	10274 (R_{int} = 0.0571)	
Completeness to θ = 25.242 °	99.1 %	
Max. and min. transmission	0.7456 and 0.5741	
Data / restraints / parameters	10274 /18/547	
Goodness-of-fit on F^2	1.044	
Final R indices [I > 2σ(I)]	R_1 = 0.0563, wR_2 = 0.1399	
R indices (all data)	R_1 = 0.0823, wR_2 = 0.1511	
Largest diff. peak and hole	0.499 and -0.858 e.$Å^{-3}$	

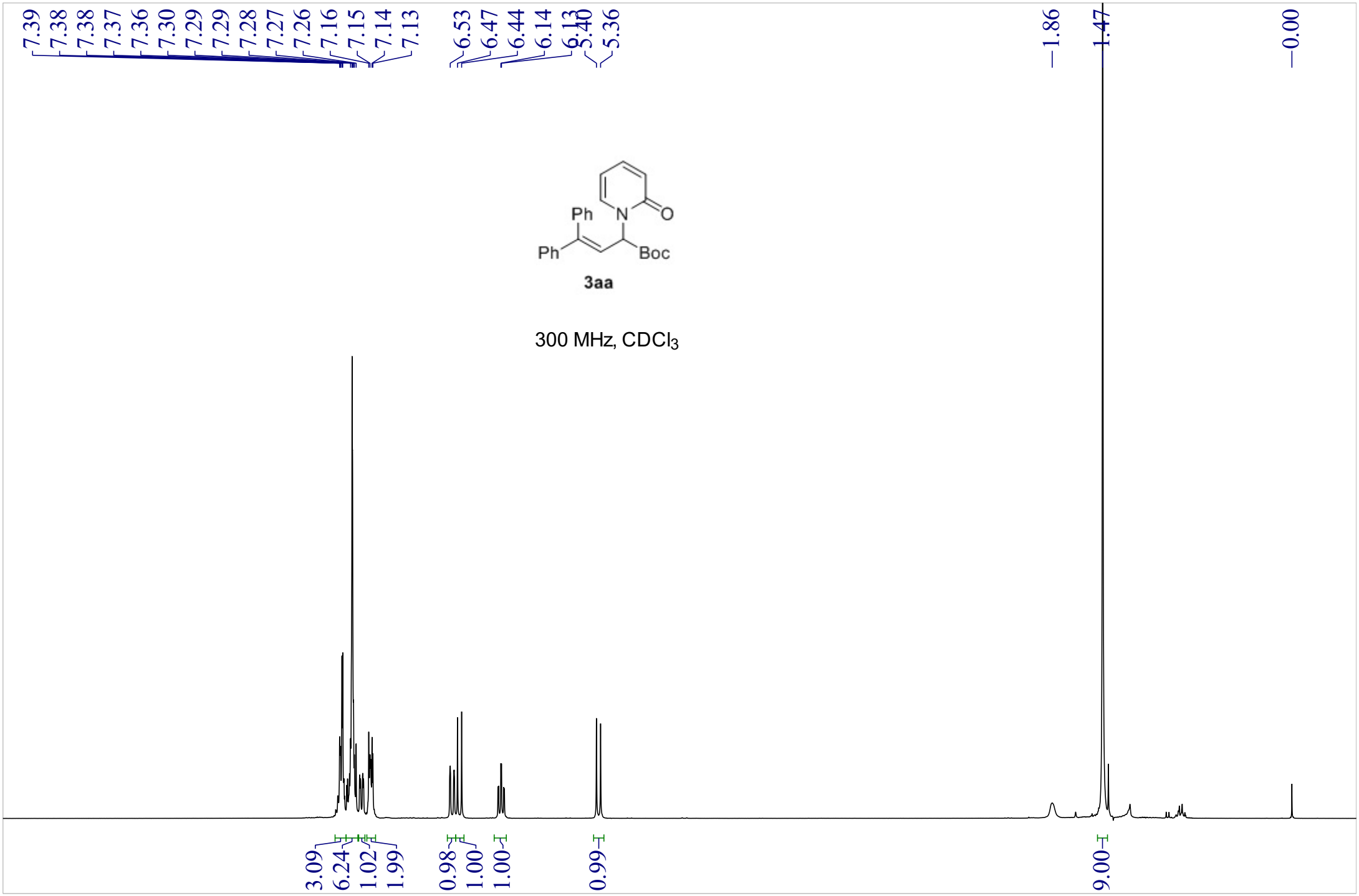
References

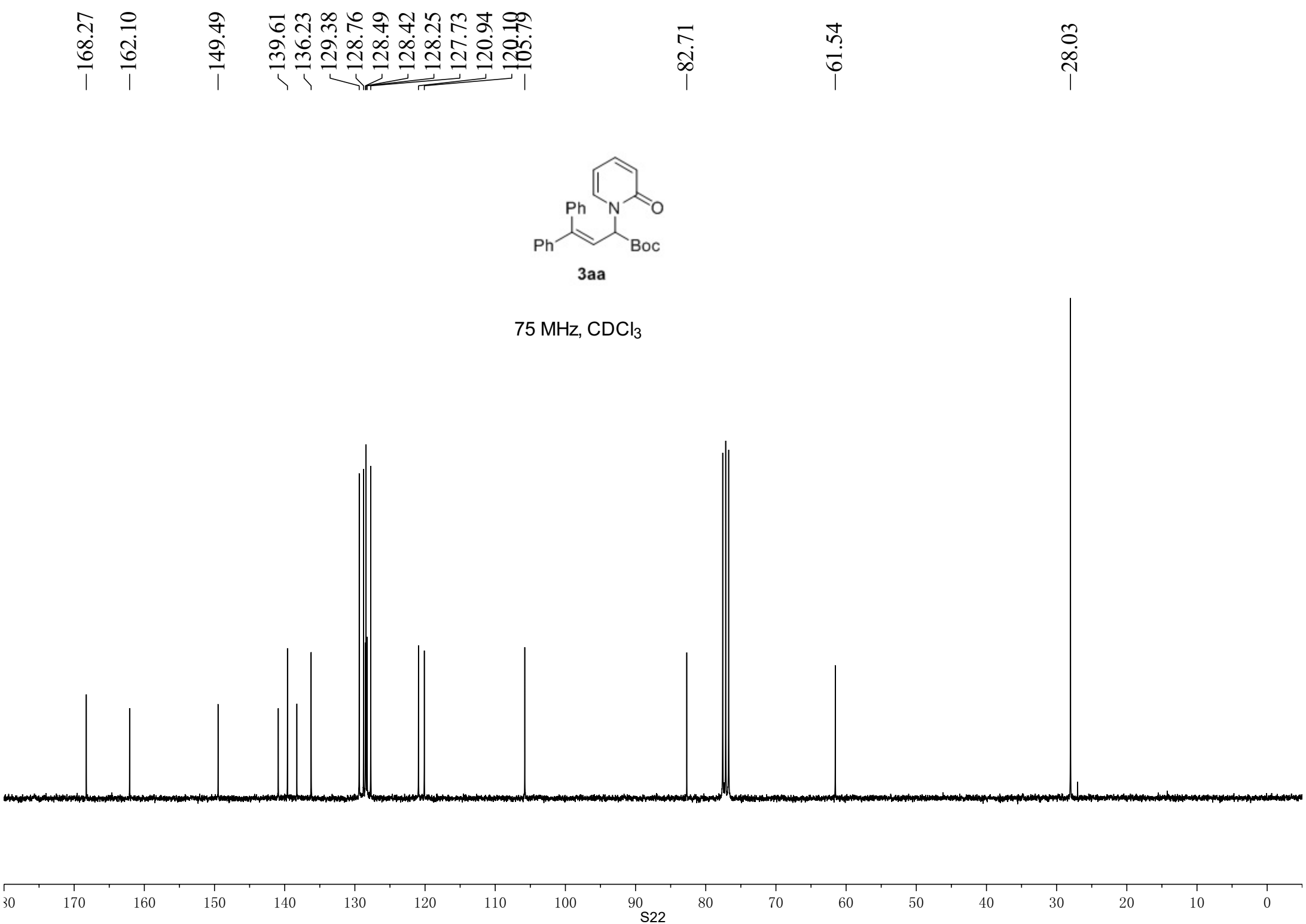
1. Xu, G.; Chen, P.; Liu, P.; Tang, S.; Zhang, X.; Sun, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 1980.

2. (a) Shintani, R.; Iino, R.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136*, 7849. (b) Zhang, H.; Wang, B.; Yi, H.; Zhang, Y.; Wang, J. *Org. Lett.* **2015**, *17,* 3322. (c) Chen, J.; Guo, P.; Zhang, J.; Rong, J.; Sun, W.; Jiang, Y.; Loh, T.-P. *Angew. Chem. Int. Ed.* **2019**, *58*, 12674. (d) Ross, R. J.; Jeyaseelan, R.; Lautens, M. *Org. Lett.* **2020**, *22,* 4838.


8.55
8.53
7.79
7.79
7.78
7.77
7.67
7.27
3.97
1.58
-0.00
CO2Me
N
OBoc
1f
400 MHz, CDCl3
0.98
0.98
0.93
3.00
9.00
f1 (ppm)


164.63
158.65
150.74
149.24
141.27
121.38
115.75
84.54
52.94
27.67
CO2Me
N
OBoc
1f
100 MHz, CDCl3
f1 (ppm)


7.39
7.38
7.38
7.37
7.36
7.30
7.29
7.29
7.28
7.27
7.26
7.16
7.15
7.14
7.13
6.53
6.47
6.44
6.14
6.13
5.40
5.36
1.86
1.47
0.00
Ph
N
O
Ph
Boc
3aa
300 MHz, CDCl3
3.09
6.24
1.02
1.99
0.98
1.00
1.00
0.99
9.00
f1 (ppm)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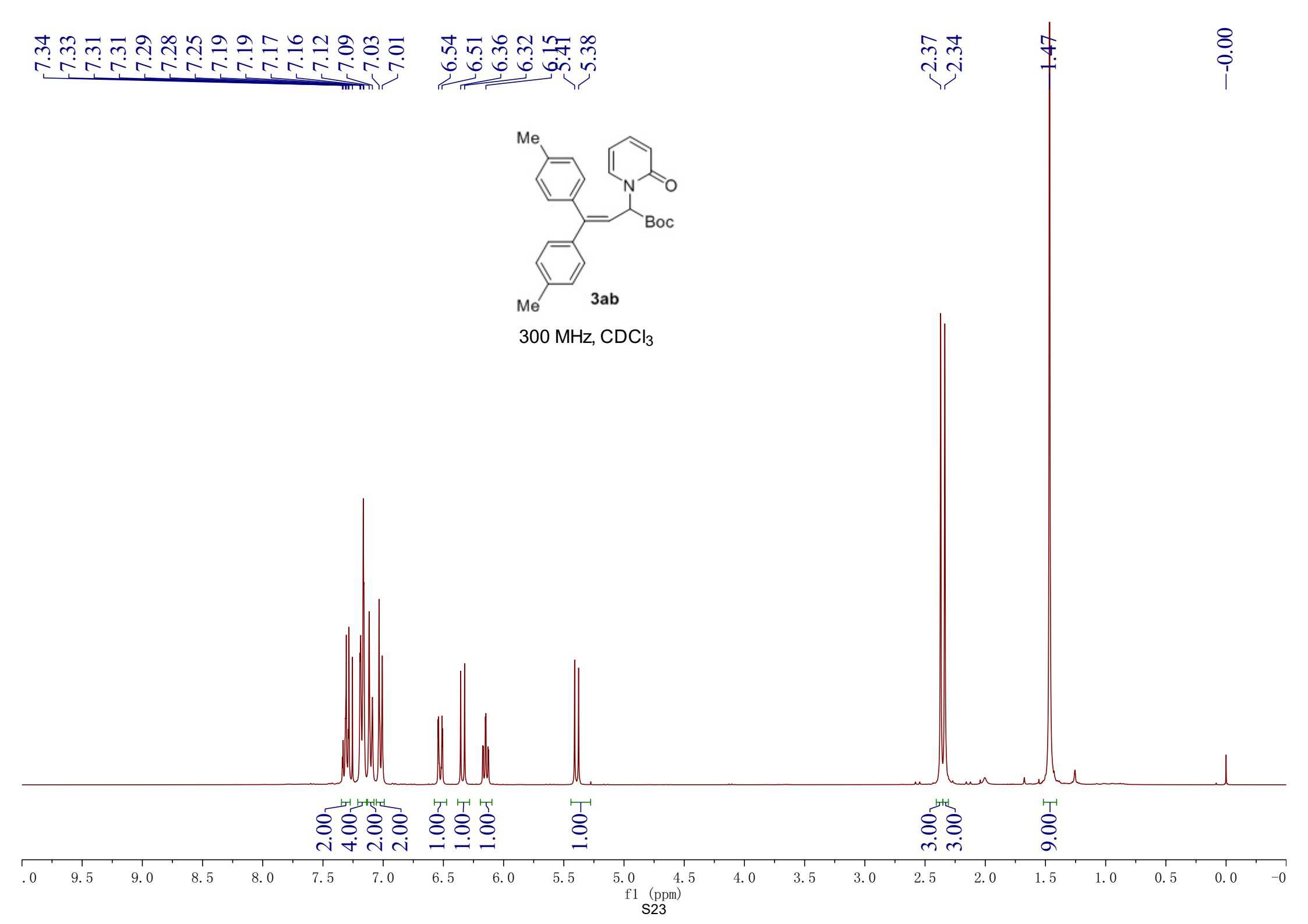
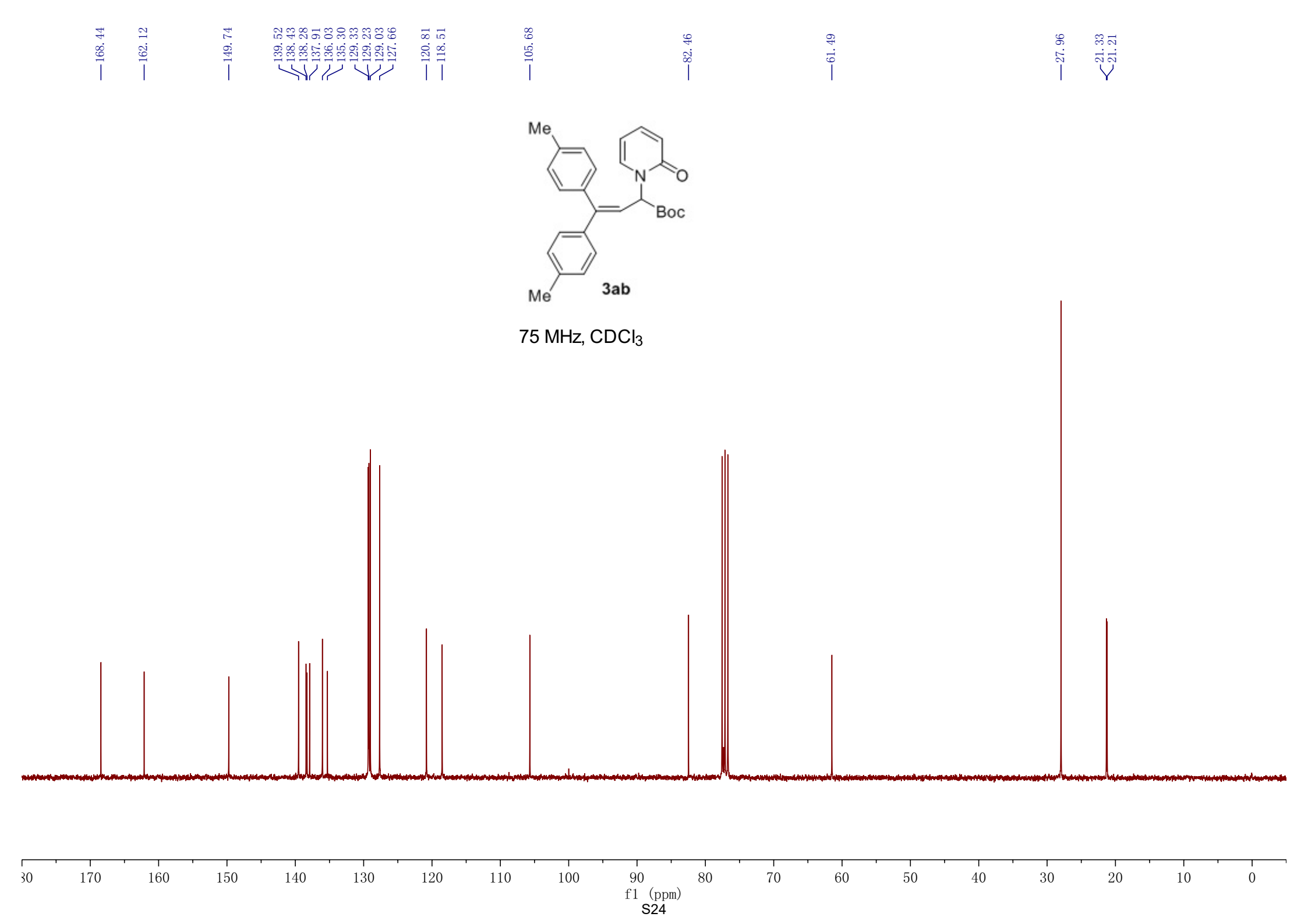
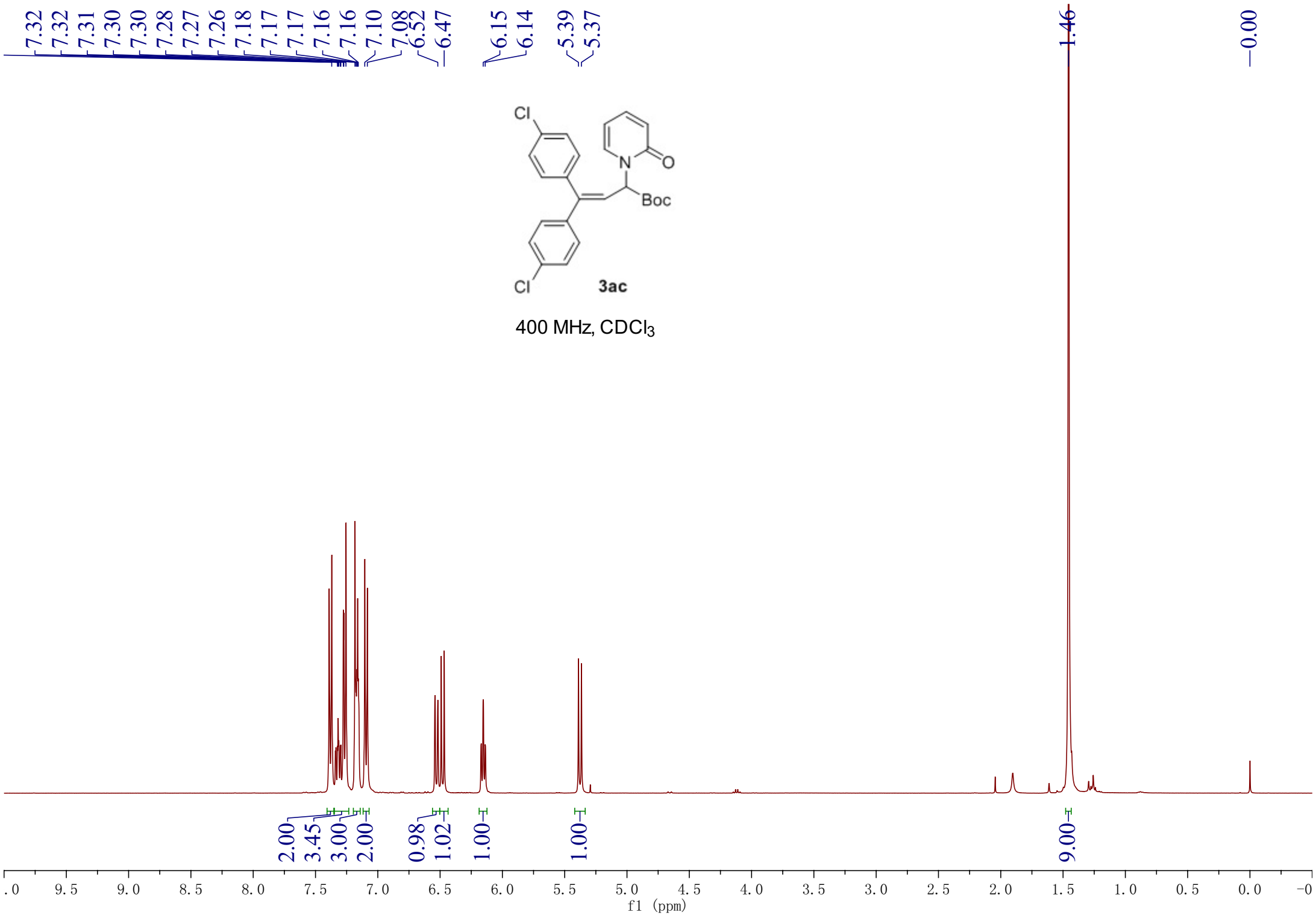
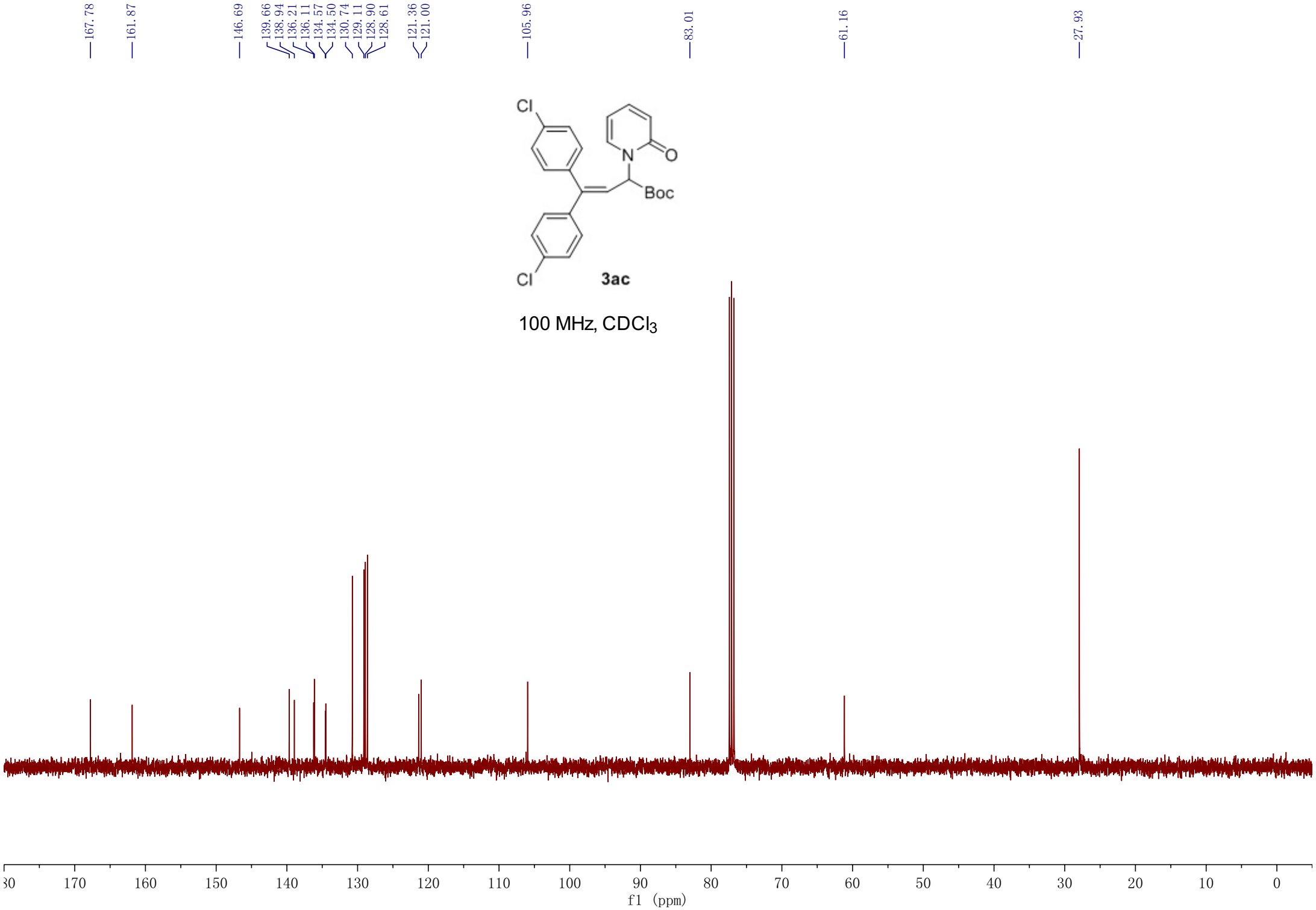
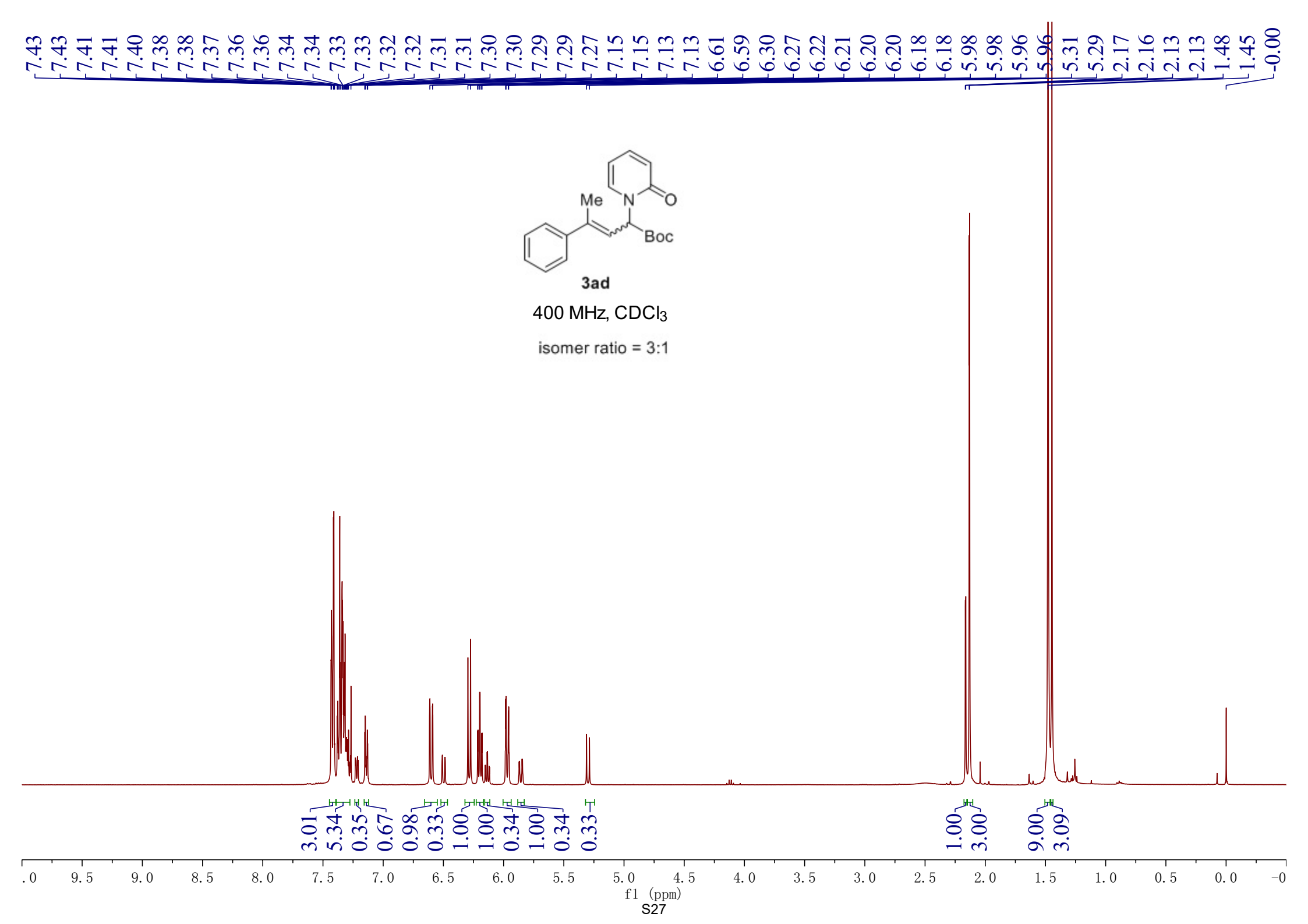
162.10
149.49
139.61
136.23
129.38
128.76
128.49
128.42
128.25
127.73
120.94
120.10
105.79
82.71
61.54
28.03
Ph
N
O
Ph
Boc
3aa
75 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

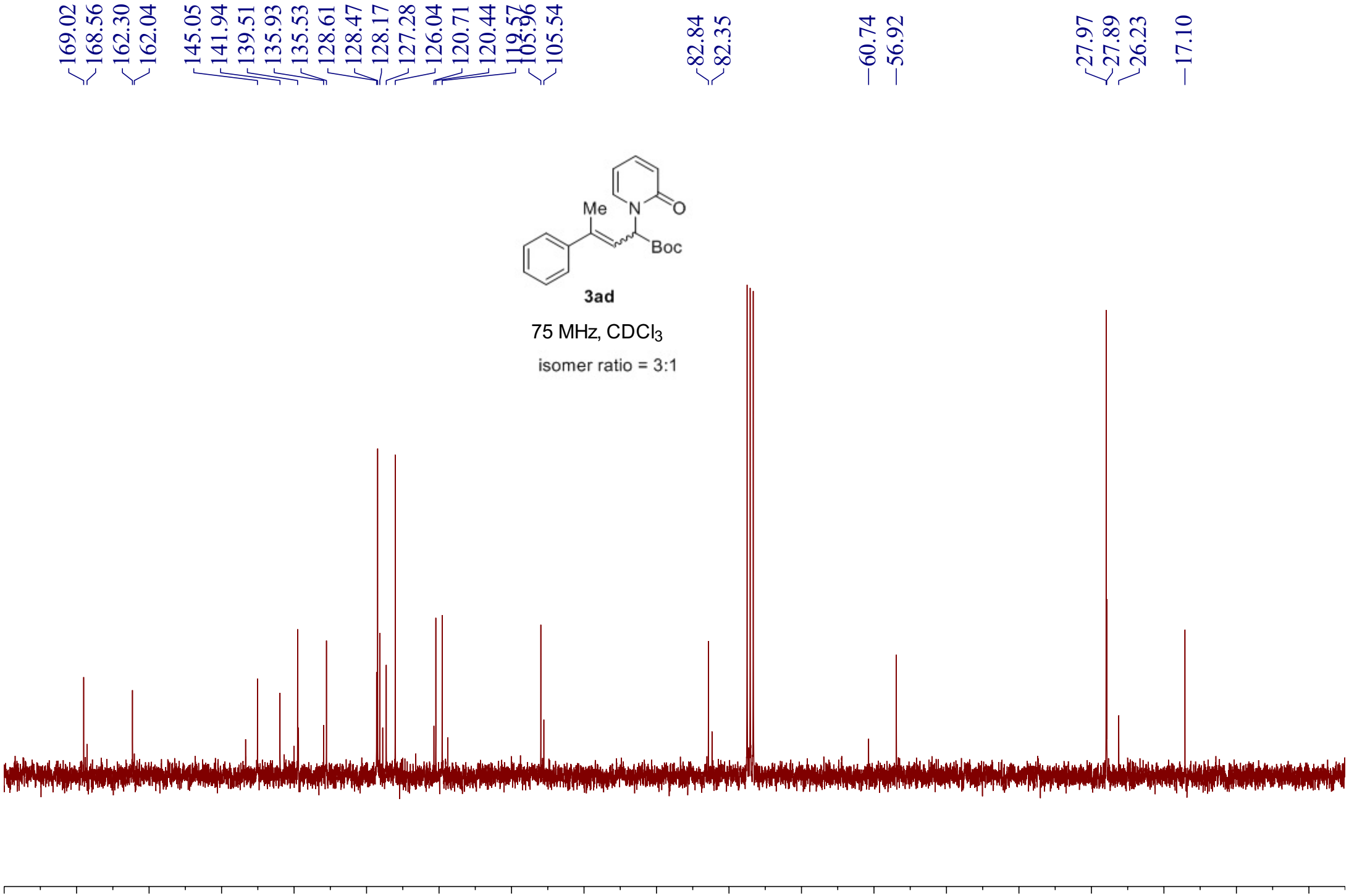

7.34
7.33
7.31
7.31
7.29
7.28
7.25
7.19
7.19
7.17
7.16
7.12
7.09
7.03
7.01
6.54
6.51
6.36
6.32
6.15
5.41
5.38
2.37
2.34
1.47
-0.00
Me
N
O
Boc
Me
3ab
300 MHz, CDCl3
2.00
4.00
2.00
2.00
1.00
1.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)

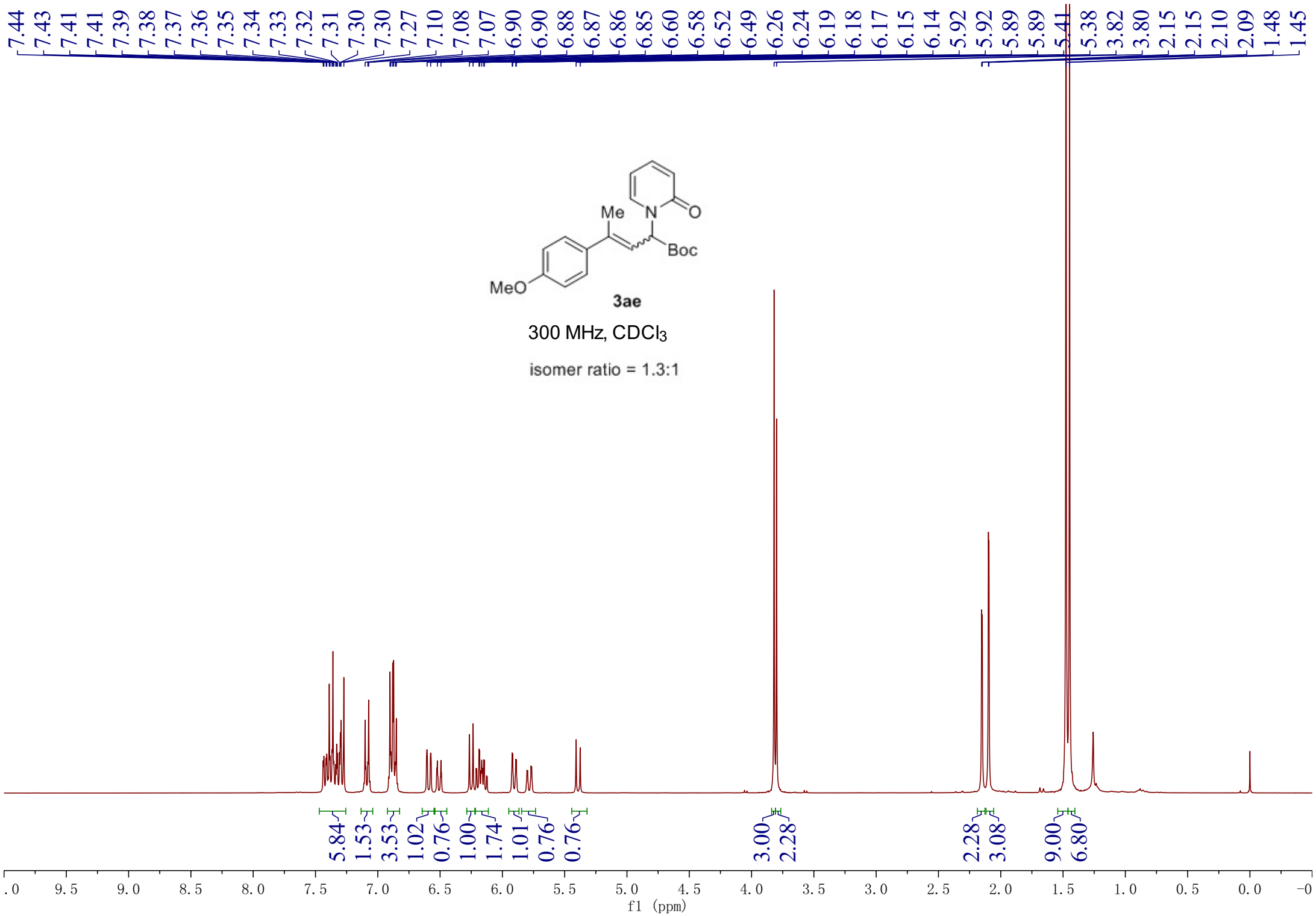

168.44
162.12
149.74
139.52
138.43
138.28
137.91
136.03
135.30
129.33
129.23
129.03
127.66
120.81
118.51
105.68
82.46
61.49
27.96
21.33
21.21
Me
N
O
Boc
Me
3ab
75 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.32
7.32
7.31
7.30
7.30
7.28
7.27
7.26
7.18
7.17
7.17
7.16
7.16
7.10
7.08
6.52
6.47
6.15
6.14
5.39
5.37
1.46
0.00
Cl
N
O
Boc
Cl
3ac
400 MHz, CDCl3
2.00
3.45
3.00
2.00
0.98
1.02
1.00
1.00
9.00
f1 (ppm)

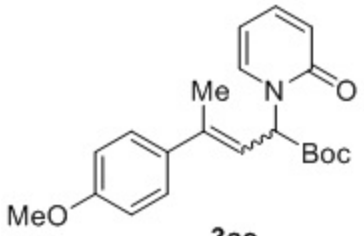

167.78
161.87
146.69
139.66
138.94
136.21
136.11
134.57
134.50
130.74
129.11
128.90
128.61
121.36
121.00
105.96
83.01
61.16
27.93
Cl
N
O
Boc
Cl
3ac
100 MHz, CDCl3
f1 (ppm)


7.43 7.43 7.41 7.41 7.40 7.38 7.38 7.37 7.36 7.36 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.29 7.27 7.15 7.15 7.13 7.13 6.61 6.59 6.30 6.27 6.22 6.21 6.20 6.20 6.18 6.18 5.98 5.98 5.96 5.96 5.31 5.29 2.17 2.16 2.13 2.13 1.48 1.45 -0.00
Me
N
O
Boc
3ad
400 MHz, CDCl3
isomer ratio = 3:1
3.01 5.34 0.35 0.67 0.98 0.33 1.00 1.00 0.34 1.00 0.34 0.33 1.00 3.00 9.00 3.09
f1 (ppm)


169.02
168.56
162.30
162.04
145.05
141.94
139.51
135.93
135.53
128.61
128.47
128.17
127.28
126.04
120.71
120.44
119.57
105.96
105.54
82.84
82.35
60.74
56.92
27.97
27.89
26.23
17.10
Me
N
O
Boc
3ad
75 MHz, CDCl3
isomer ratio = 3:1
f1 (ppm)


7.44 7.43 7.41 7.41 7.39 7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.30 7.27 7.10 7.08 7.07 6.90 6.90 6.88 6.87 6.86 6.85 6.60 6.58 6.52 6.49 6.26 6.24 6.19 6.18 6.17 6.15 6.14 5.92 5.92 5.89 5.89 5.41 5.38 3.82 3.80 2.15 2.15 2.10 2.09 1.48 1.45
Me
N
O
Boc
MeO
3ae
300 MHz, CDCl3
isomer ratio = 1.3:1
5.84 1.53 3.53 1.02 0.76 1.00 1.74 1.01 0.76 0.76 3.00 2.28 2.28 3.08 9.00 6.80
f1 (ppm)

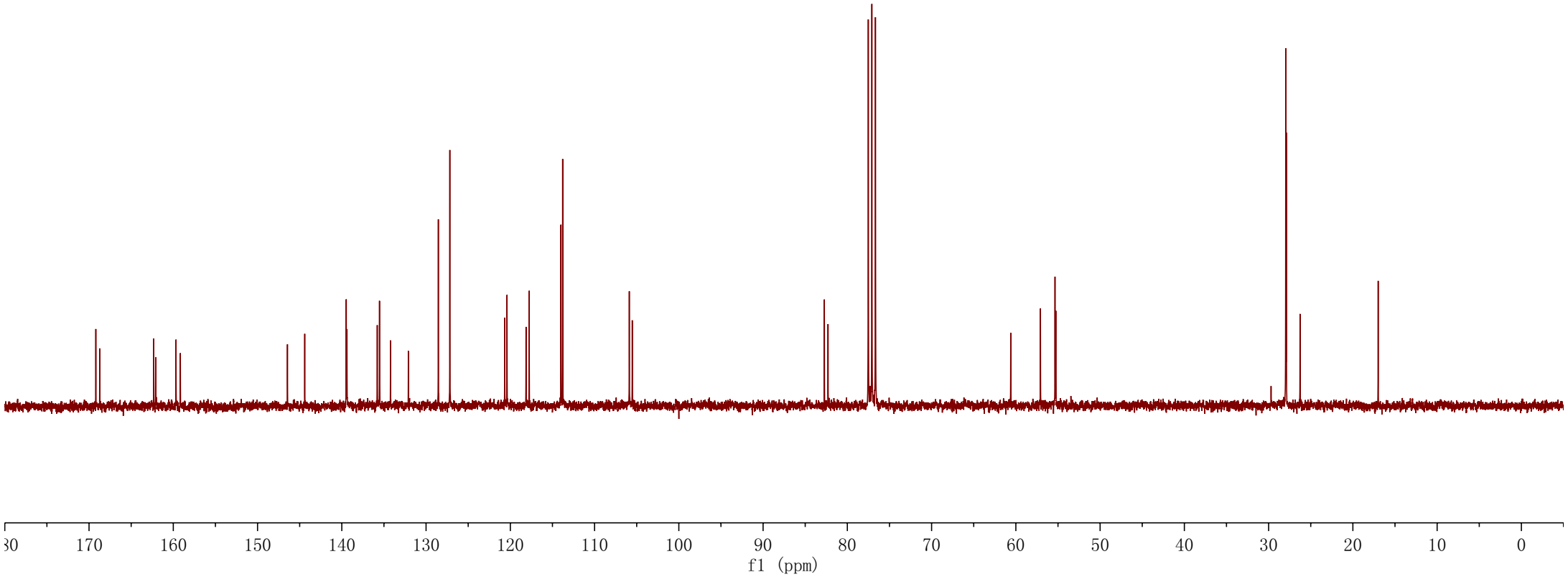
169.19
168.73
162.32
162.09
159.68
159.16
139.47
135.79
135.52
128.54
127.18
120.66
120.40
118.14
117.76
113.99
113.79
105.88
105.53
82.73
82.29
60.61
57.08
55.35
55.25
27.97
27.90
26.27
17.00

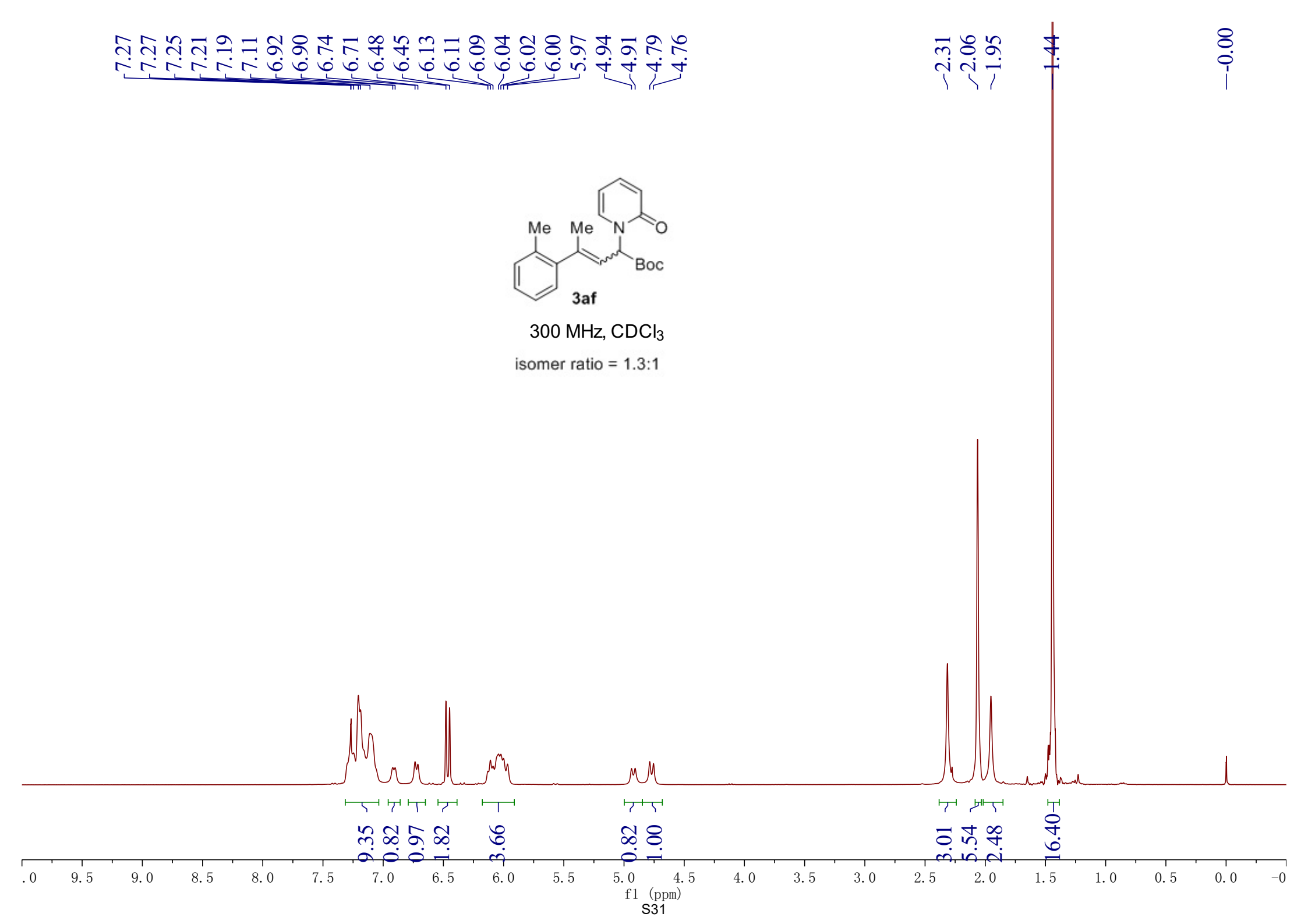


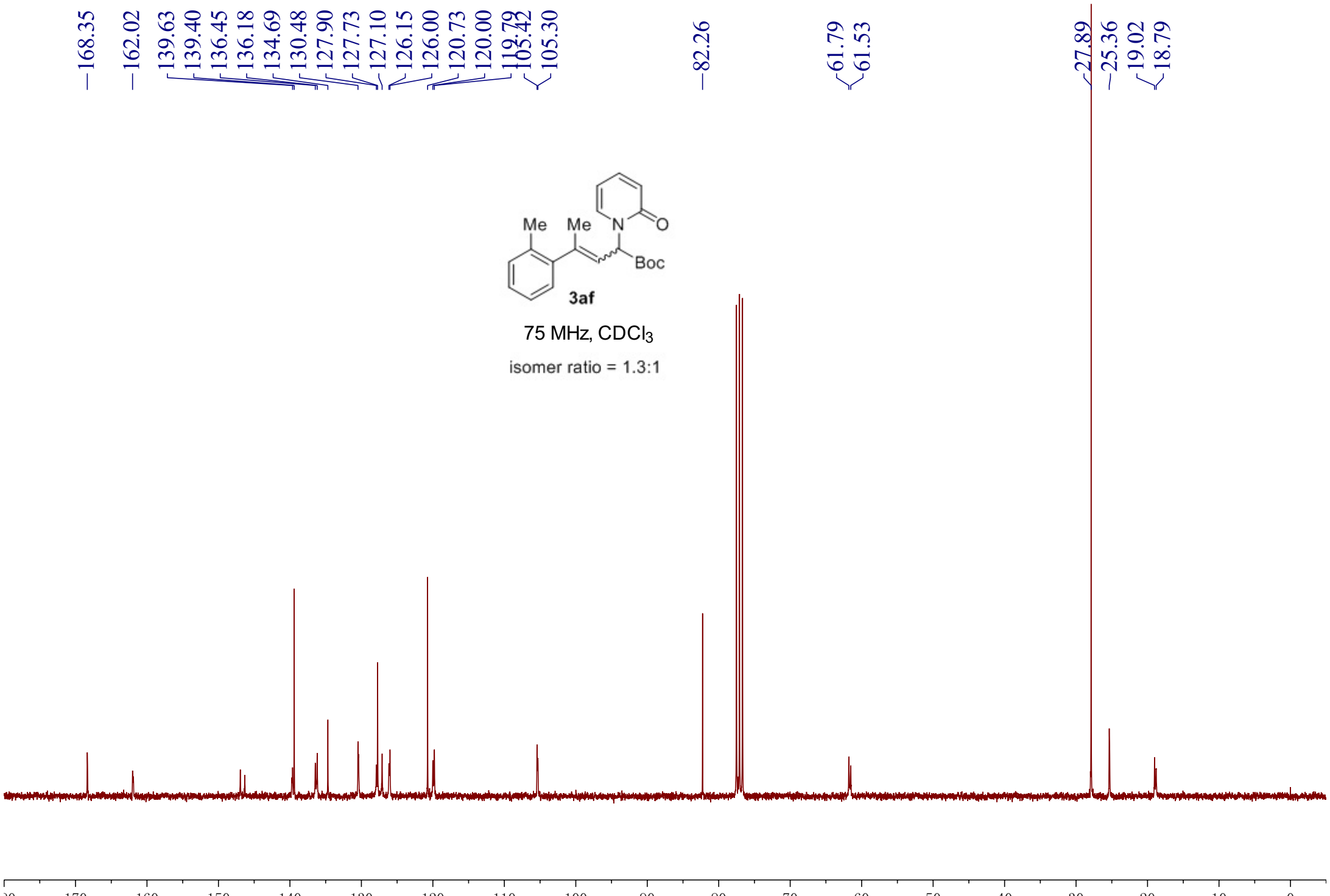
3ae

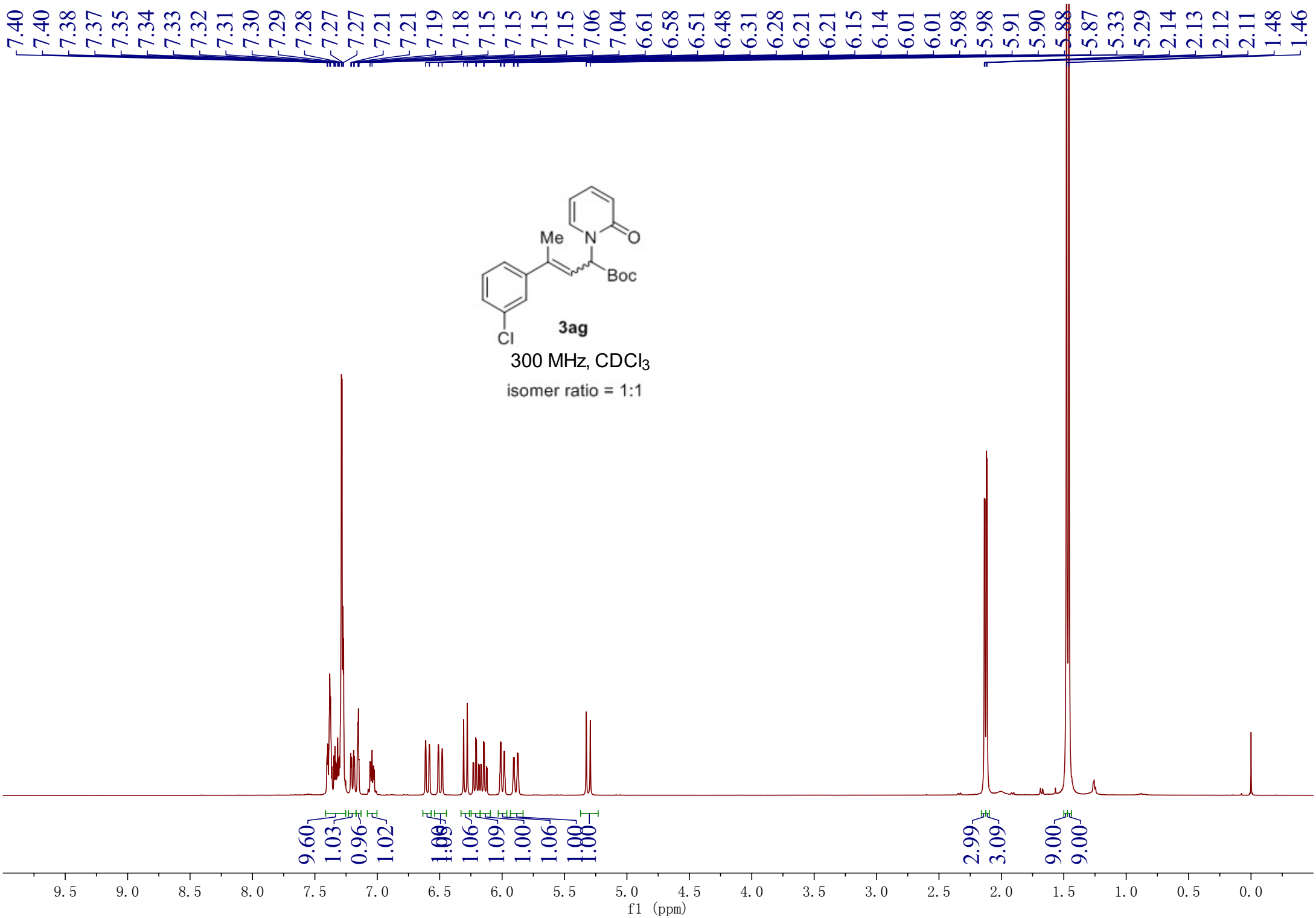
75 MHz, $CDCl_3$

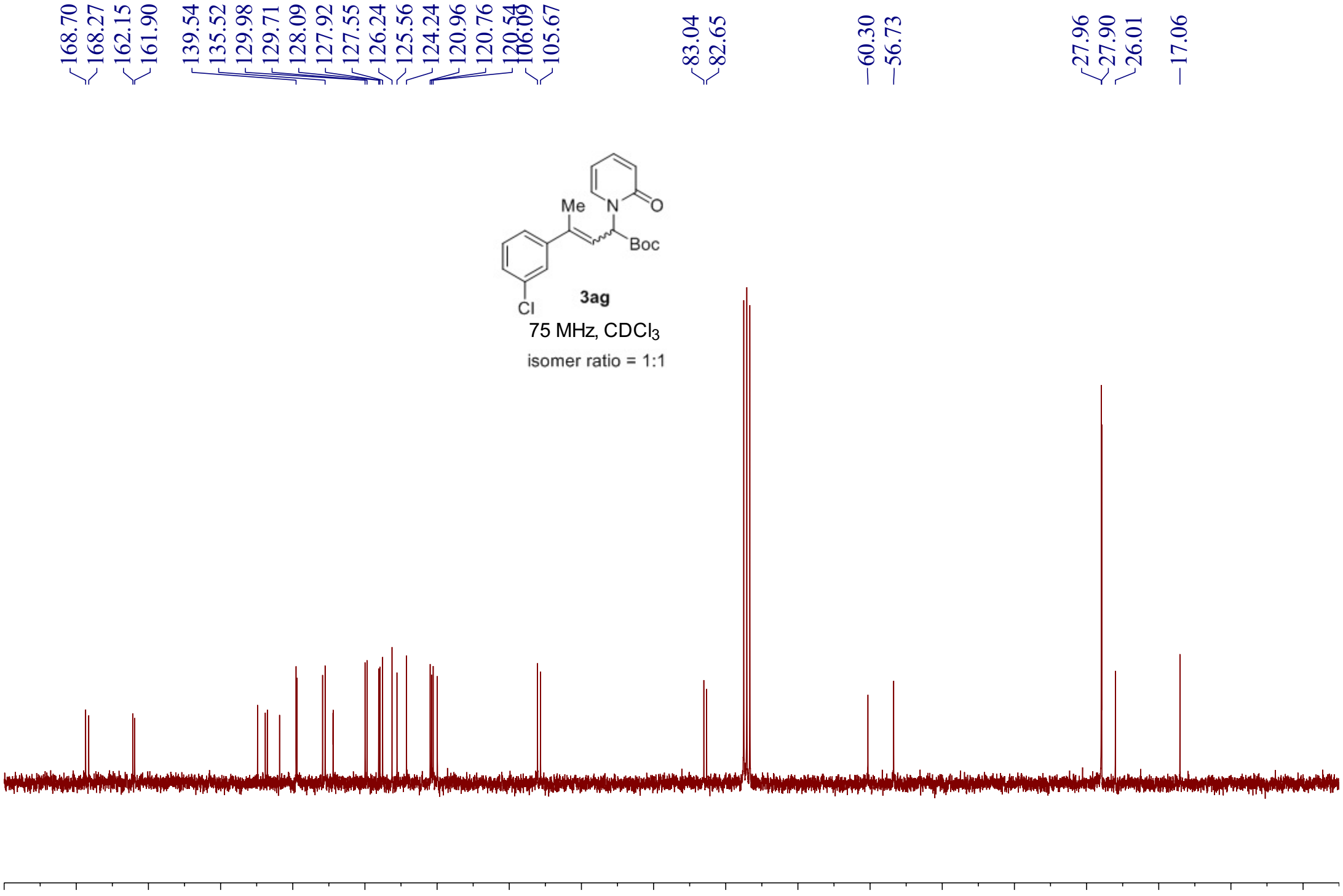
isomer ratio = 1.3:1

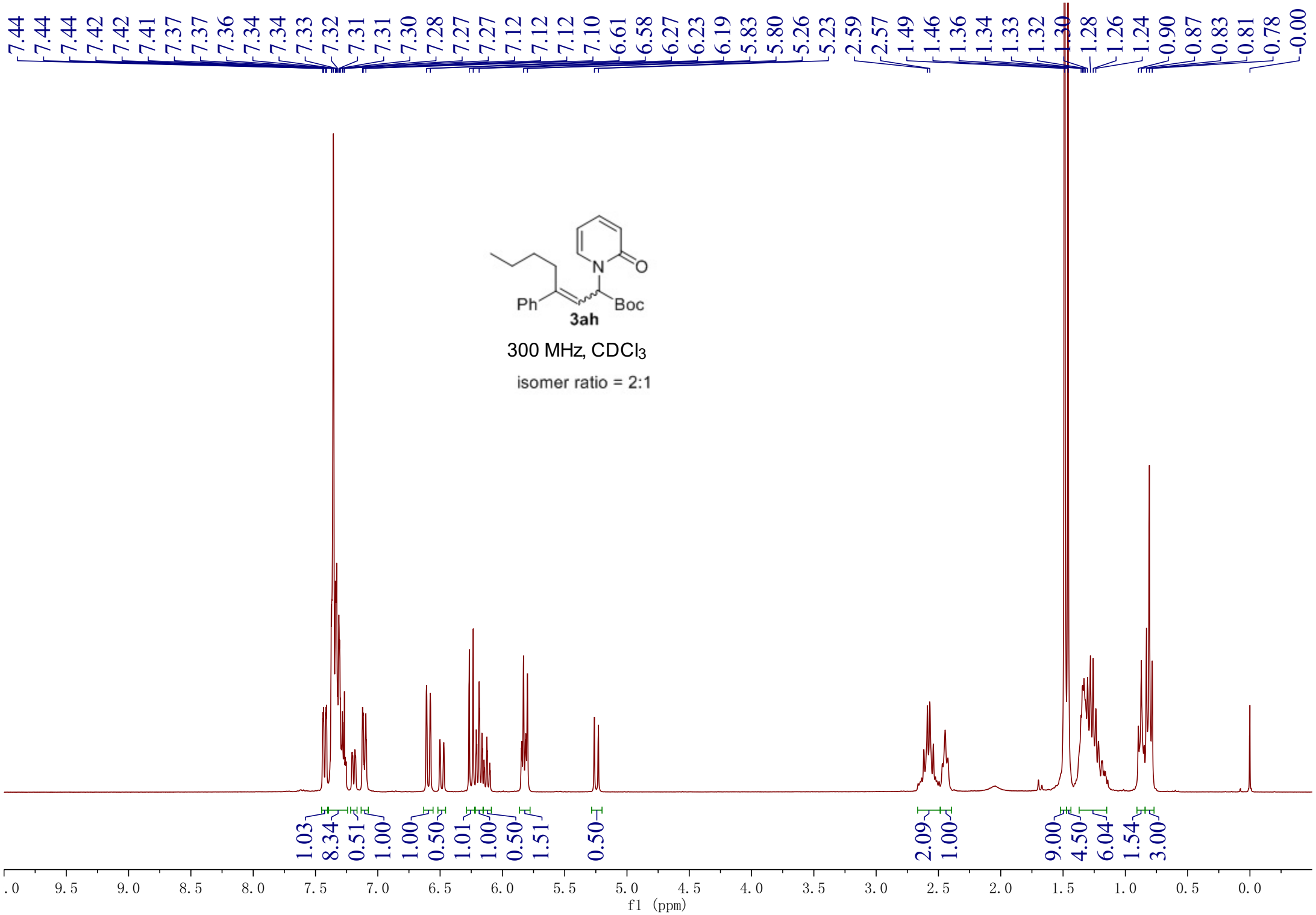


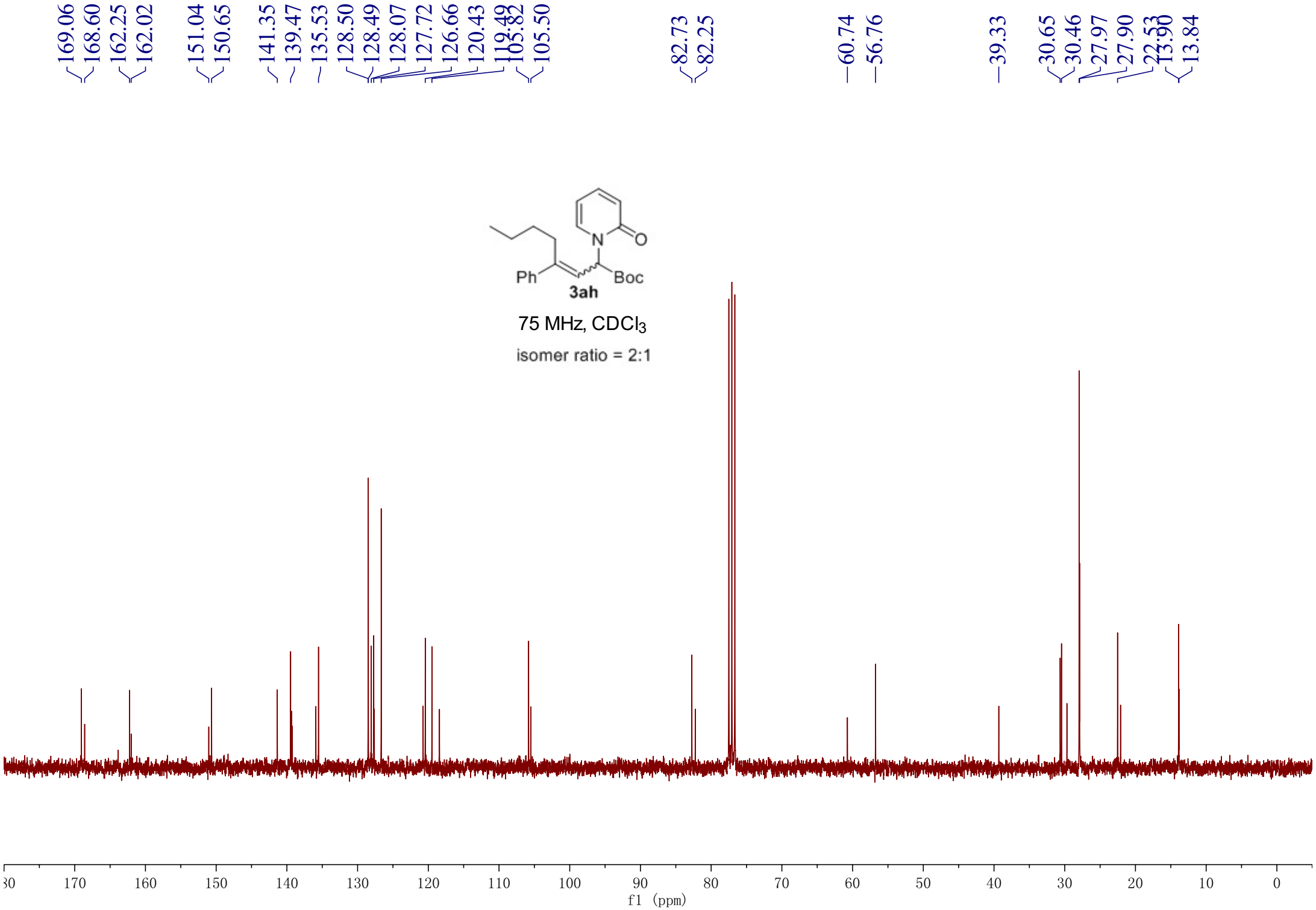

7.27
7.27
7.25
7.21
7.19
7.11
6.92
6.90
6.74
6.71
6.48
6.45
6.13
6.11
6.09
6.04
6.02
6.00
5.97
4.94
4.91
4.79
4.76
2.31
2.06
1.95
1.44
-0.00
Me
Me
N
O
Boc
3af
300 MHz, CDCl3
isomer ratio = 1.3:1
9.35
0.82
0.97
1.82
3.66
0.82
1.00
3.01
5.54
2.48
16.40
f1 (ppm)

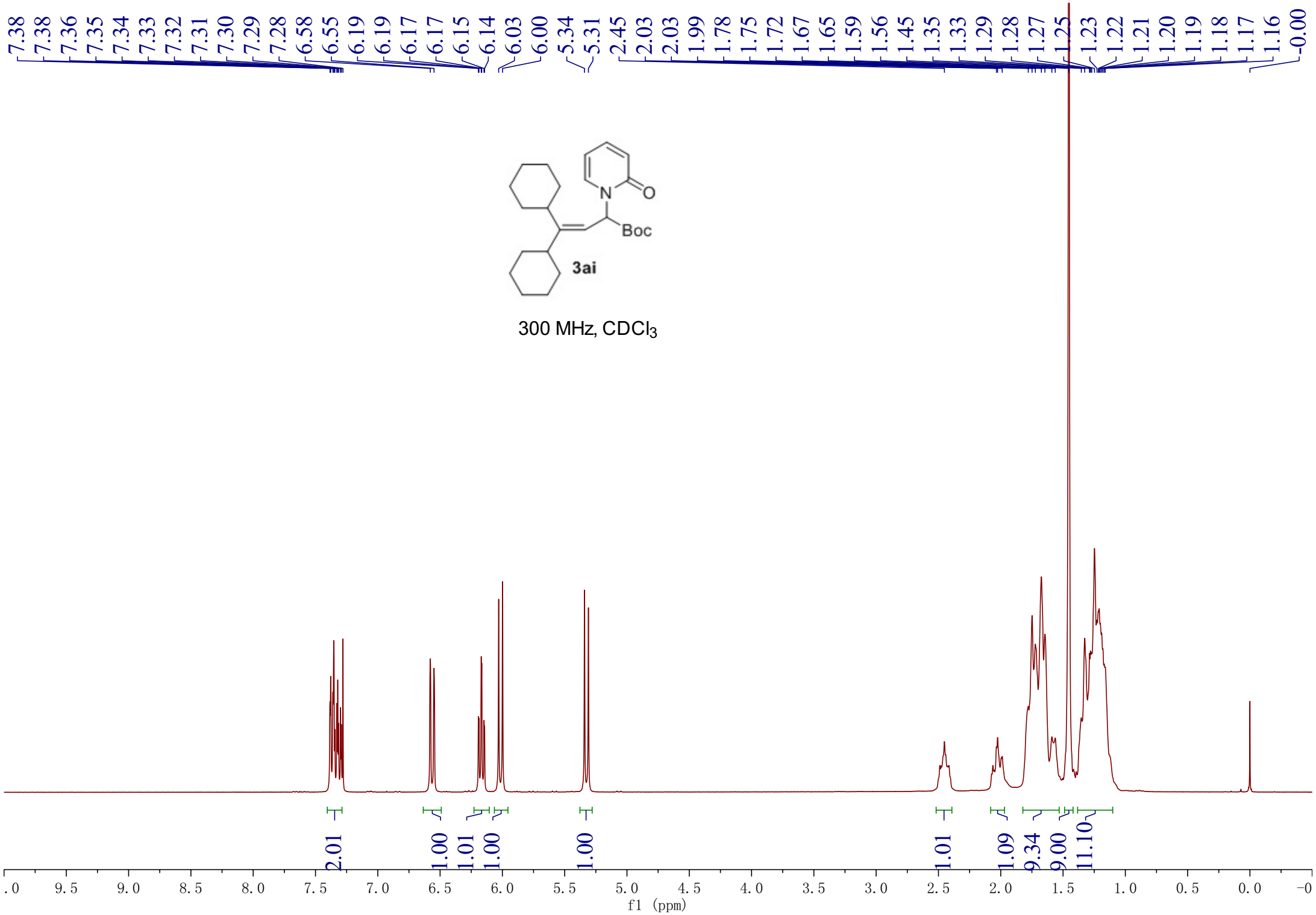

168.35
162.02
139.63
139.40
136.45
136.18
134.69
130.48
127.90
127.73
127.10
126.15
126.00
120.73
120.00
119.79
105.42
105.30
82.26
61.79
61.53
27.89
25.36
19.02
18.79
Me
Me
N
O
Boc
3af
75 MHz, CDCl3
isomer ratio = 1.3:1
f1 (ppm)

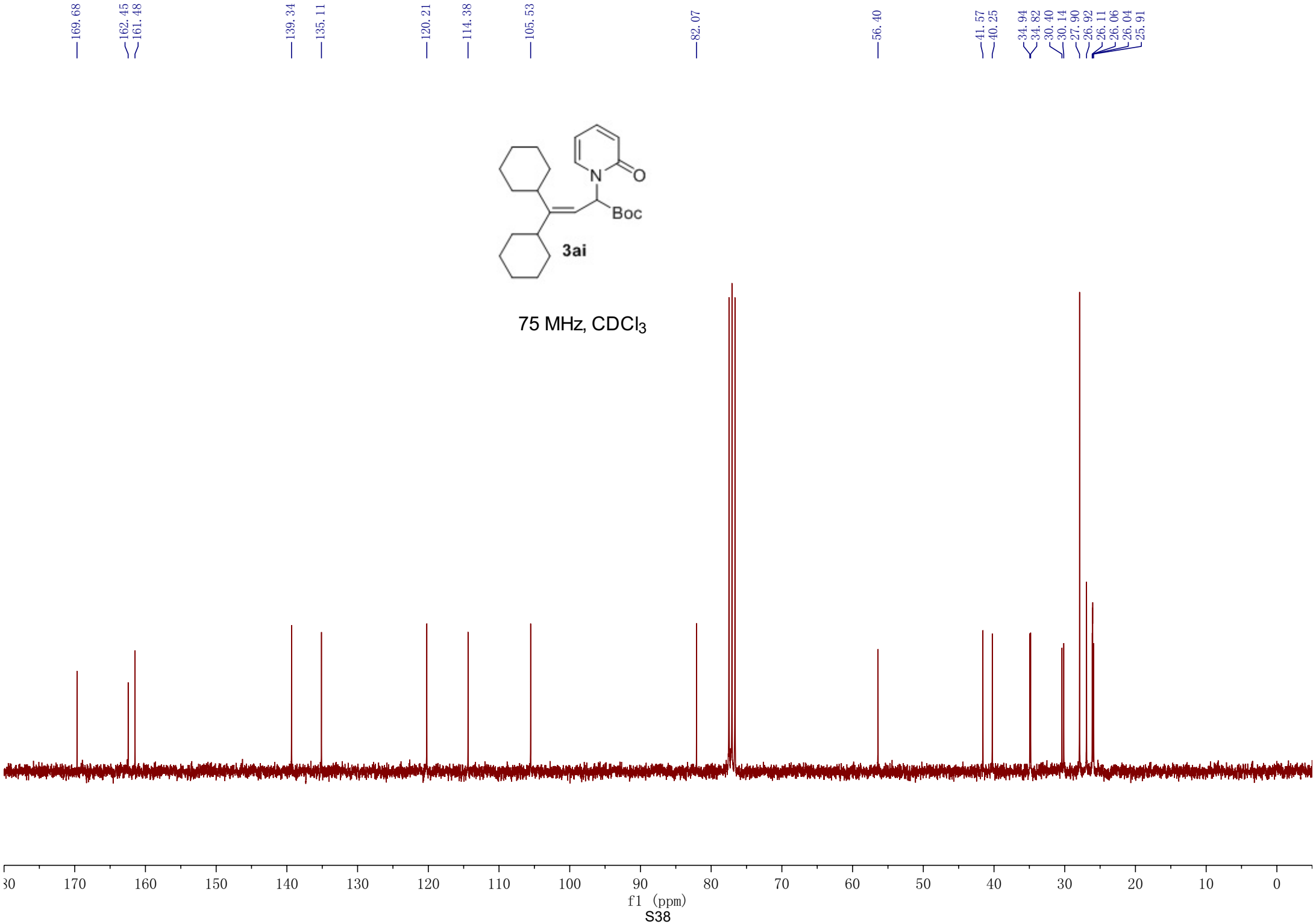

7.40 7.40 7.38 7.37 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.27 7.27 7.21 7.21 7.19 7.18 7.15 7.15 7.15 7.15 7.06 7.04 6.61 6.58 6.51 6.48 6.31 6.28 6.21 6.21 6.15 6.14 6.01 6.01 5.98 5.98 5.91 5.90 5.88 5.87 5.33 5.29 2.14 2.13 2.12 2.11 1.48 1.46
Me
N
O
Boc
Cl
3ag
300 MHz, CDCl3
isomer ratio = 1:1
9.60 1.03 0.96 1.02 1.00 1.06 1.09 1.00 1.06 1.00 2.99 3.09 9.00 9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

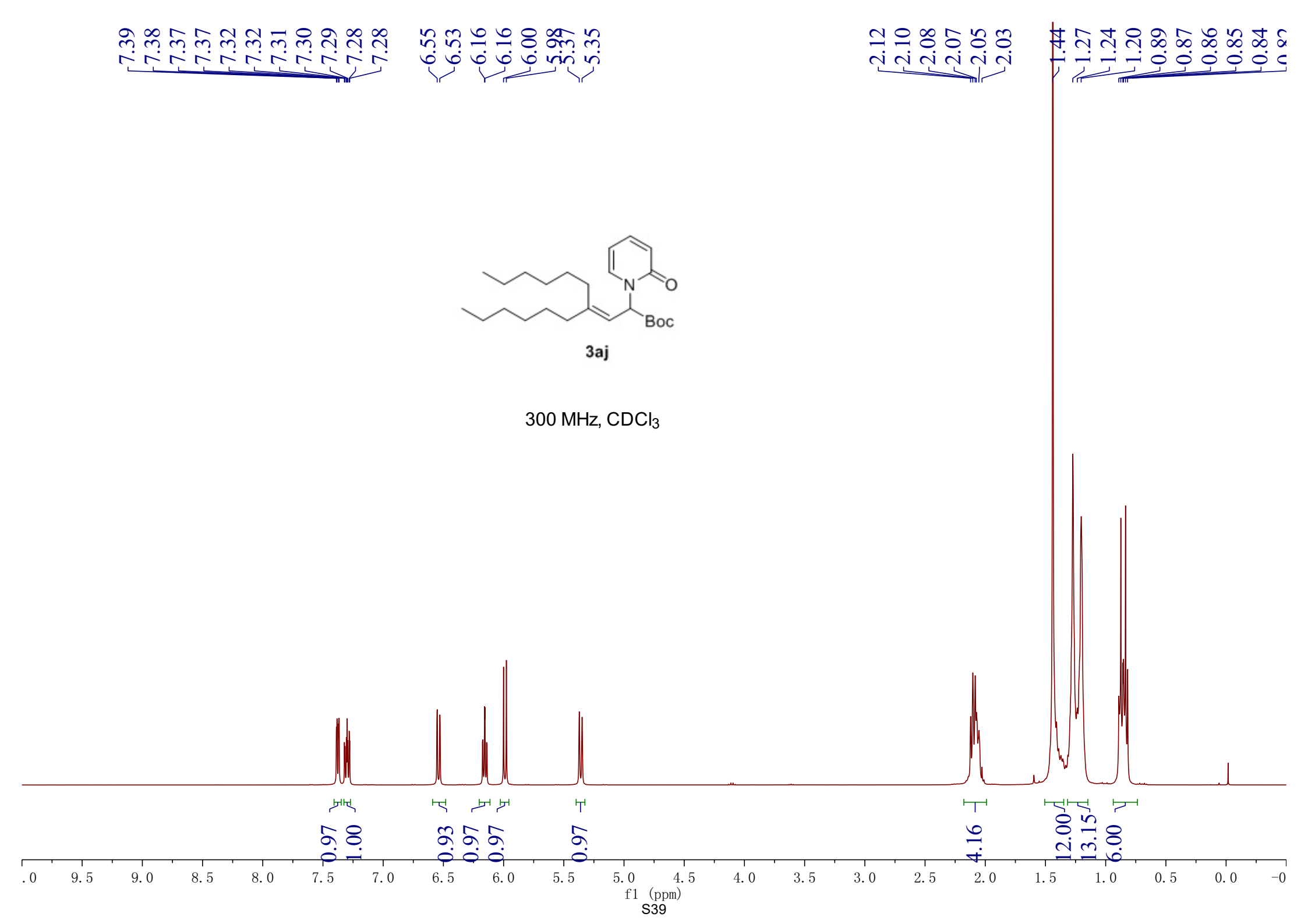

168.70
168.27
162.15
161.90
139.54
135.52
129.98
129.71
128.09
127.92
127.55
126.24
125.56
124.24
120.96
120.76
120.54
106.09
105.67
83.04
82.65
60.30
56.73
27.96
27.90
26.01
17.06
Me
N
O
Boc
Cl
3ag
75 MHz, CDCl3
isomer ratio = 1:1
f1 (ppm)


7.44 7.44 7.44 7.42 7.42 7.41 7.37 7.37 7.36 7.34 7.34 7.33 7.32 7.31 7.31 7.30 7.28 7.27 7.27 7.12 7.12 7.12 7.10 6.61 6.58 6.27 6.23 6.19 5.83 5.80 5.26 5.23 2.59 2.57 1.49 1.46 1.36 1.34 1.33 1.32 1.30 1.28 1.26 1.24 0.90 0.87 0.83 0.81 0.78 -0.00
N
O
Ph
Boc
3ah
300 MHz, CDCl3
isomer ratio = 2:1
1.03 8.34 0.51 1.00 1.00 0.50 1.01 1.00 0.50 1.51 0.50 2.09 1.00 9.00 4.50 6.04 1.54 3.00
f1 (ppm)


169.06
168.60
162.25
162.02
151.04
150.65
141.35
139.47
135.53
128.50
128.49
128.07
127.72
126.66
120.43
119.49
105.82
105.50
82.73
82.25
60.74
56.76
39.33
30.65
30.46
27.97
27.90
22.53
13.90
13.84
N
O
Ph
Boc
3ah
75 MHz, CDCl3
isomer ratio = 2:1
f1 (ppm)

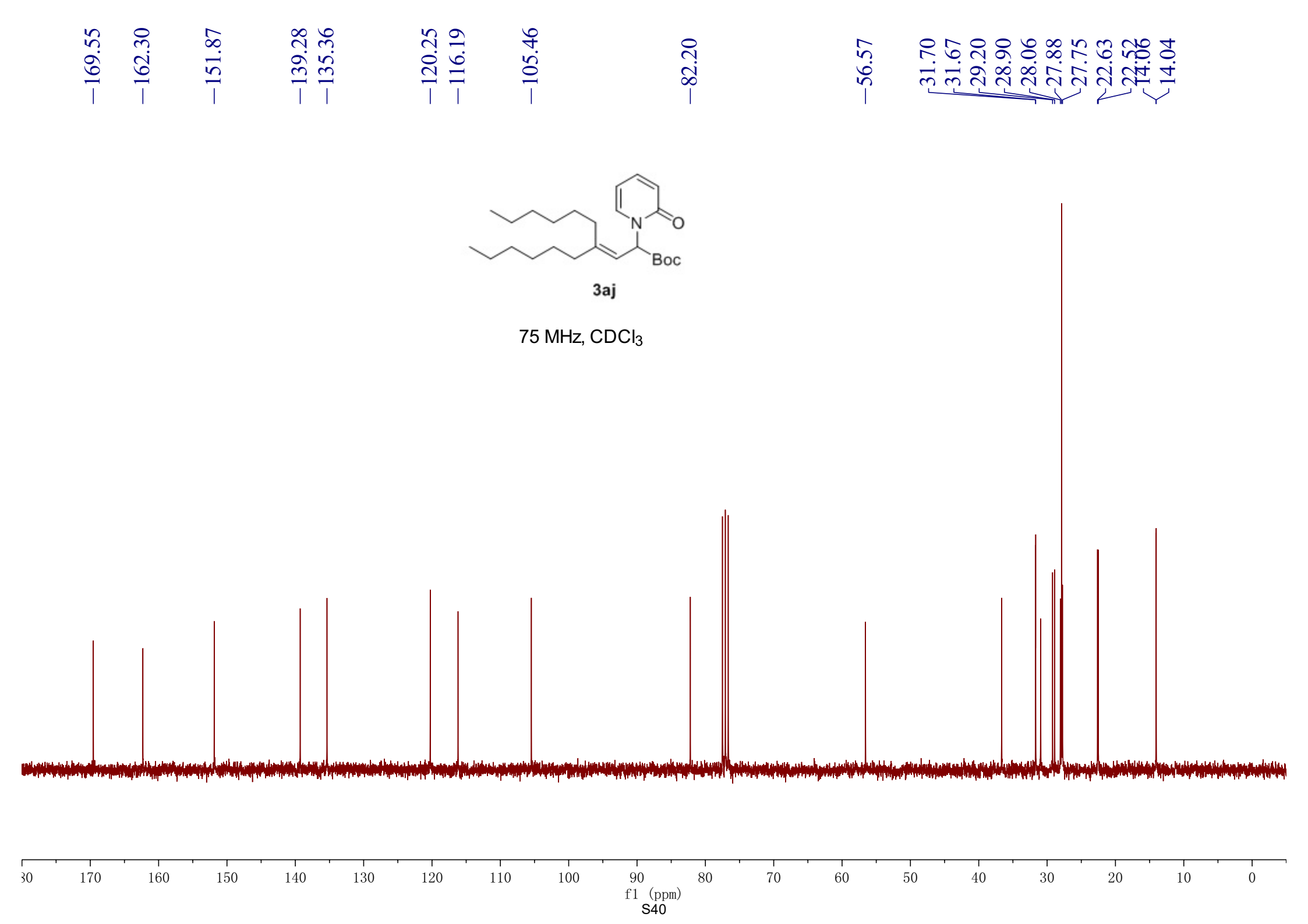

7.38
7.38
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.29
7.28
6.58
6.55
6.19
6.19
6.17
6.17
6.15
6.14
6.03
6.00
5.34
5.31
2.45
2.03
2.03
1.99
1.78
1.75
1.72
1.67
1.65
1.59
1.56
1.45
1.35
1.33
1.29
1.28
1.27
1.25
1.23
1.22
1.21
1.20
1.19
1.18
1.17
1.16
-0.00
N
O
Boc
3ai
300 MHz, CDCl3
2.01
1.00
1.01
1.00
1.00
1.01
1.09
9.34
9.00
11.10
f1 (ppm)

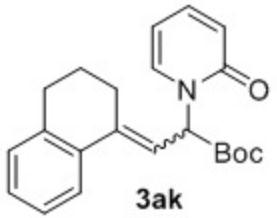

169.68
162.45
161.48
139.34
135.11
120.21
114.38
105.53
82.07
56.40
41.57
40.25
34.94
34.82
30.40
30.14
27.90
26.92
26.11
26.06
26.04
25.91
N
O
Boc
3ai
75 MHz, CDCl3
f1 (ppm)



3aj

300 MHz, $CDCl_3$

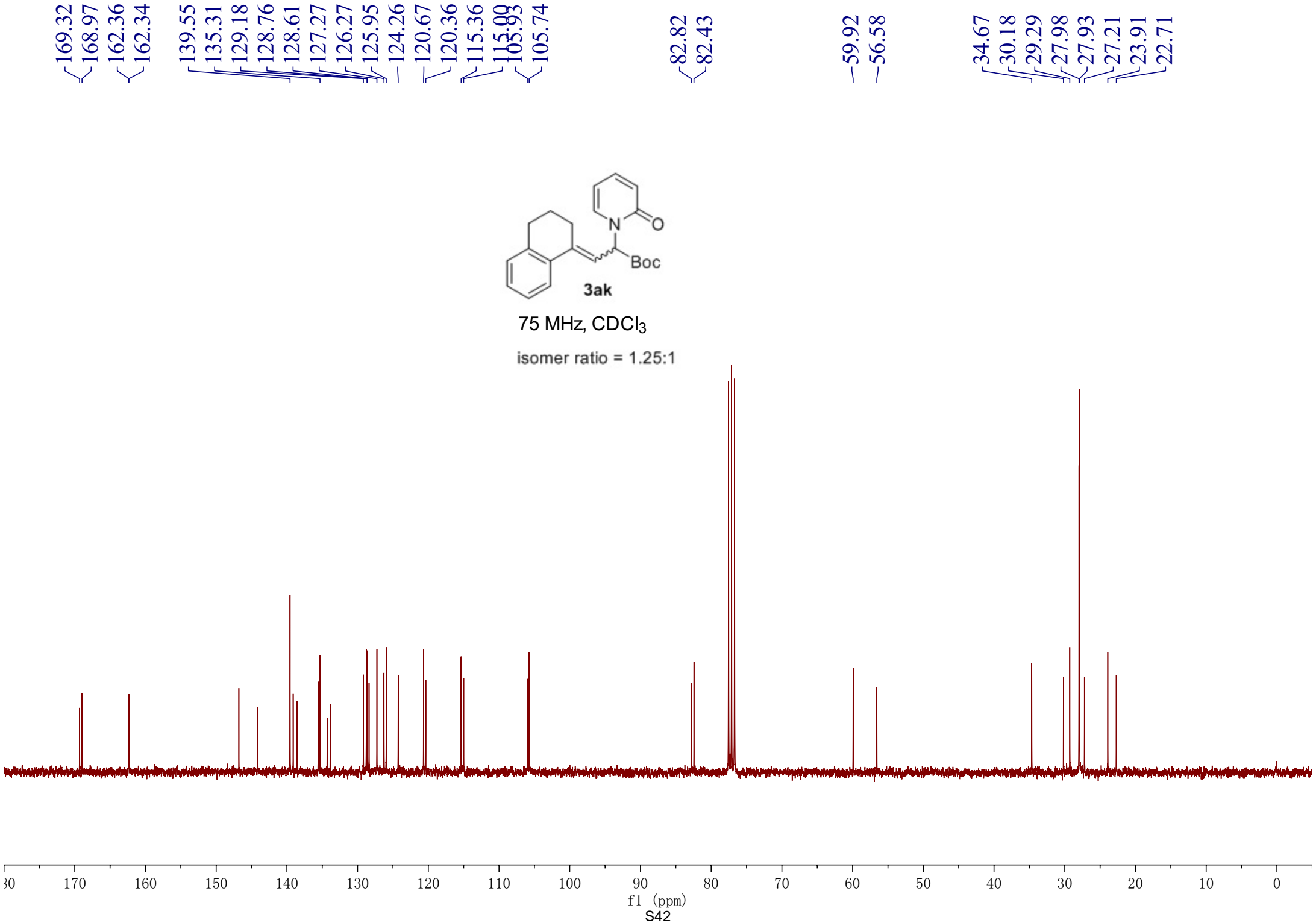

169.55
162.30
151.87
139.28
135.36
120.25
116.19
105.46
82.20
56.57
31.70
31.67
29.20
28.90
28.06
27.88
27.75
22.63
22.52
14.06
14.04
N
O
Boc
3aj
75 MHz, CDCl3
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

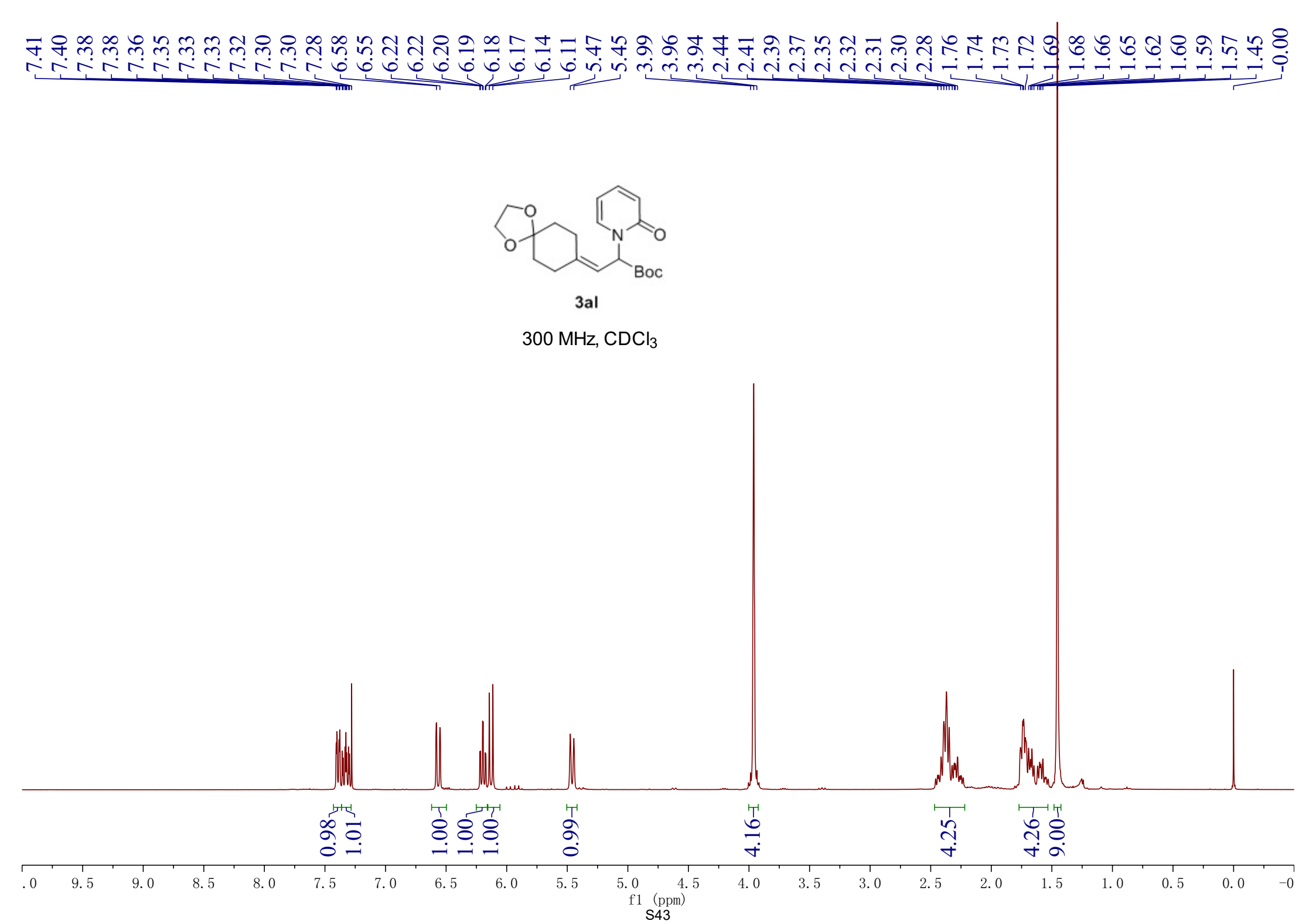


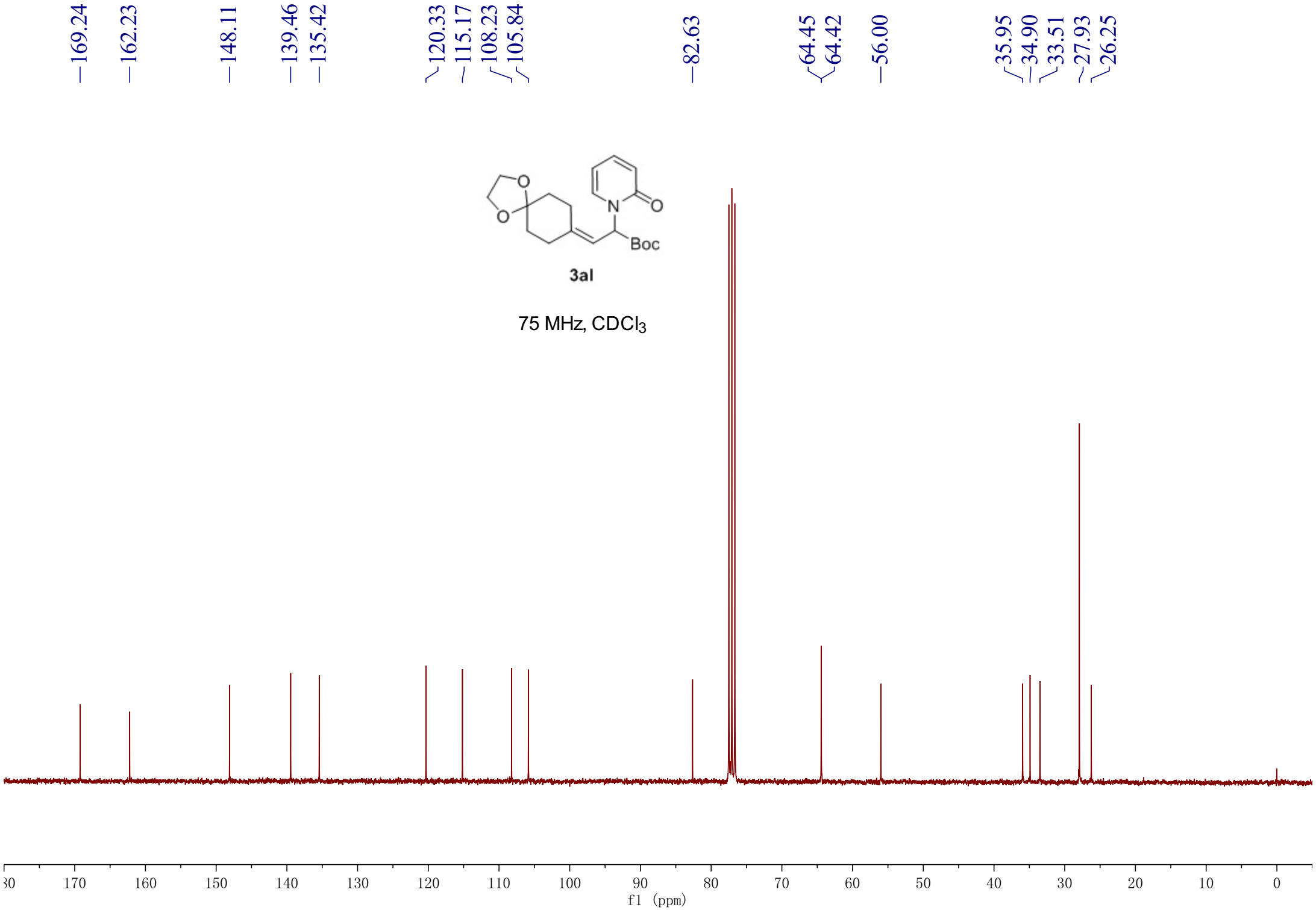
3ak

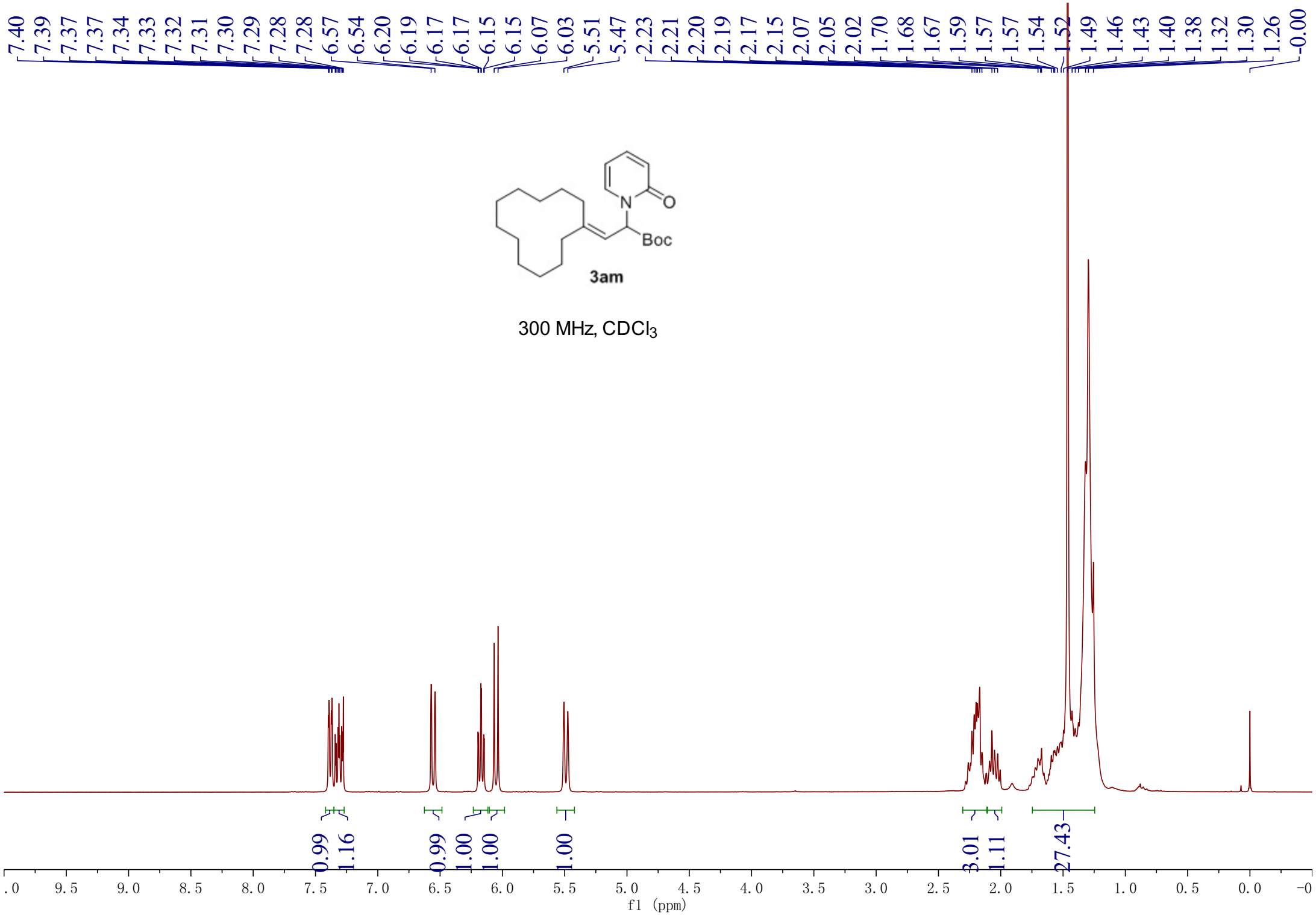
300 MHz, $CDCl_3$

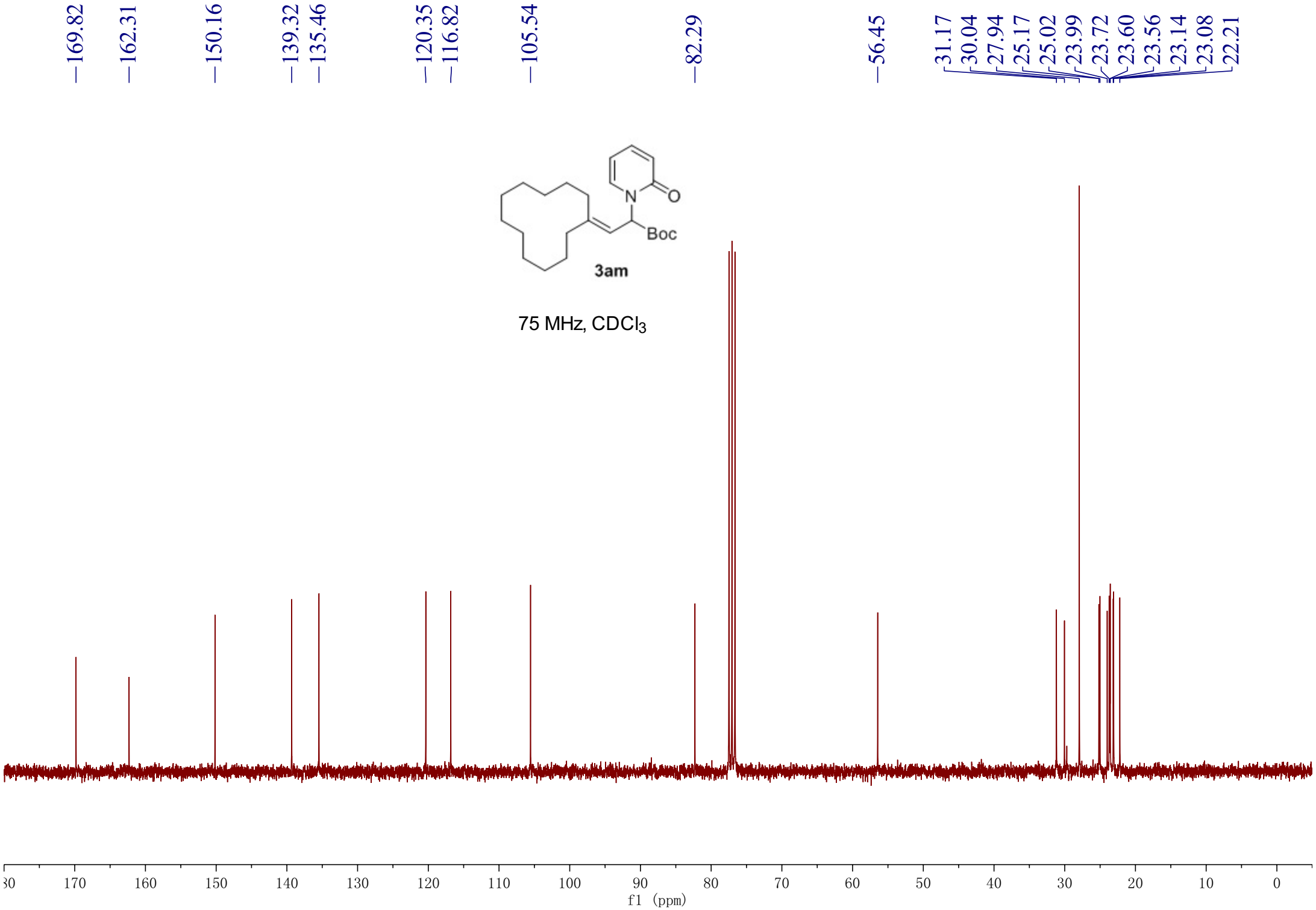
isomer ratio = 1.25:1

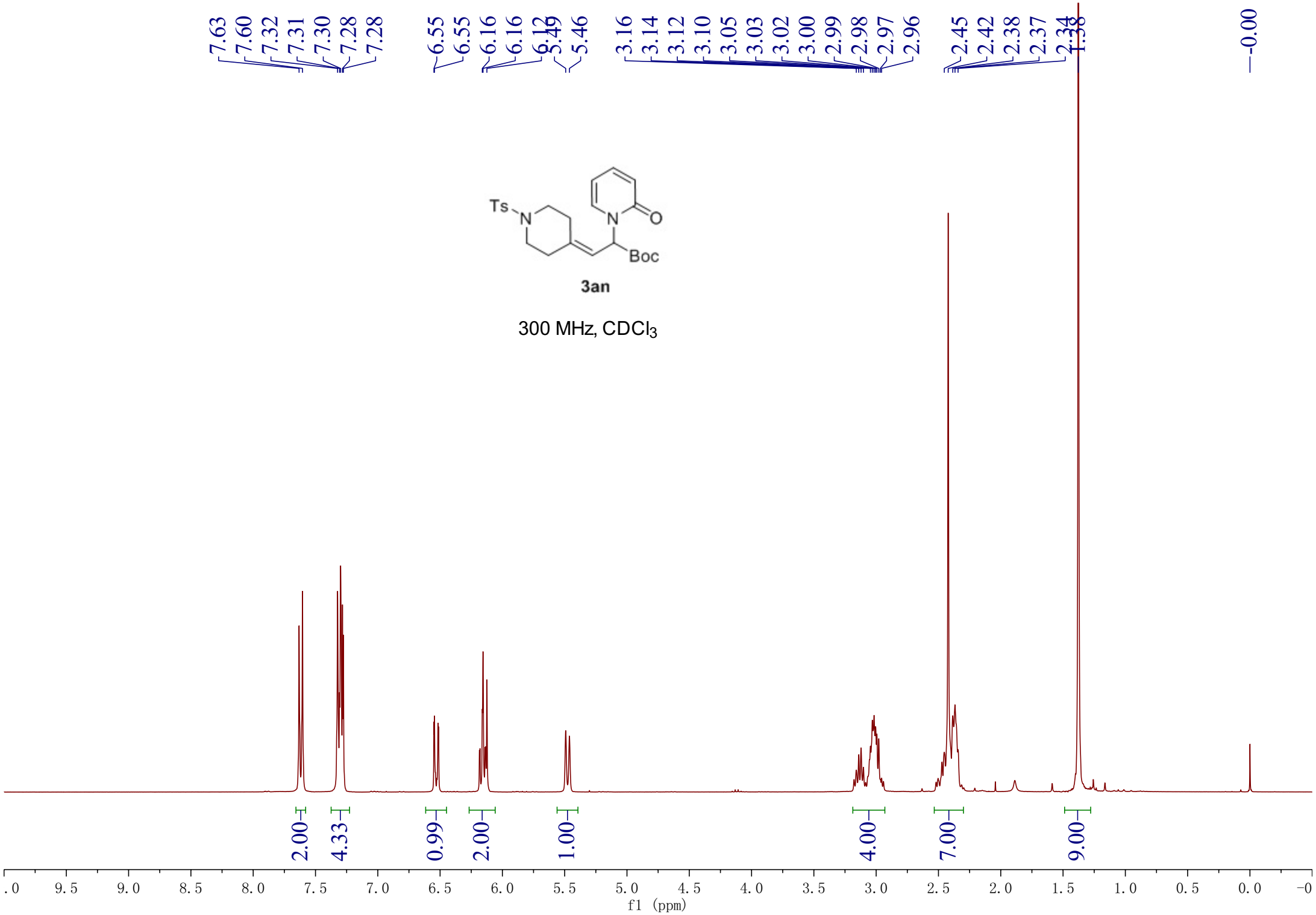

169.32
168.97
162.36
162.34
139.55
135.31
129.18
128.76
128.61
127.27
126.27
125.95
124.26
120.67
120.36
115.36
115.00
105.93
105.74
82.82
82.43
59.92
56.58
34.67
30.18
29.29
27.98
27.93
27.21
23.91
22.71
N
O
Boc
3ak
75 MHz, CDCl3
isomer ratio = 1.25:1
f1 (ppm)

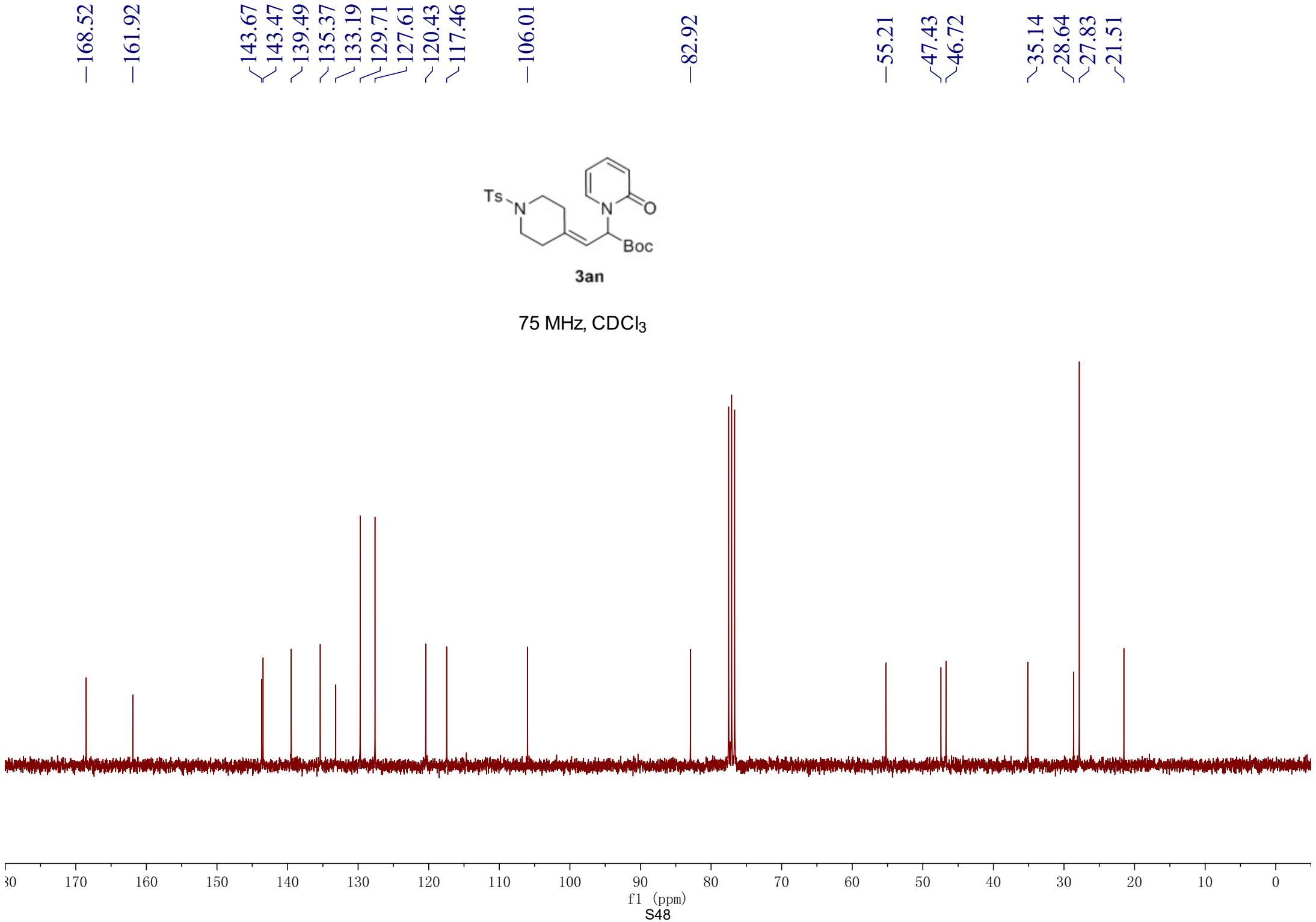

7.41
7.40
7.38
7.38
7.36
7.35
7.33
7.33
7.32
7.30
7.30
7.28
6.58
6.55
6.22
6.22
6.20
6.19
6.18
6.17
6.14
6.11
5.47
5.45
3.99
3.96
3.94
2.44
2.41
2.39
2.37
2.35
2.32
2.31
2.30
2.28
1.76
1.74
1.73
1.72
1.69
1.68
1.66
1.65
1.62
1.60
1.59
1.57
1.45
-0.00
O
O
N
O
Boc
3aI
300 MHz, CDCl3
0.98
1.01
1.00
1.00
1.00
0.99
4.16
4.25
4.26
9.00
f1 (ppm)

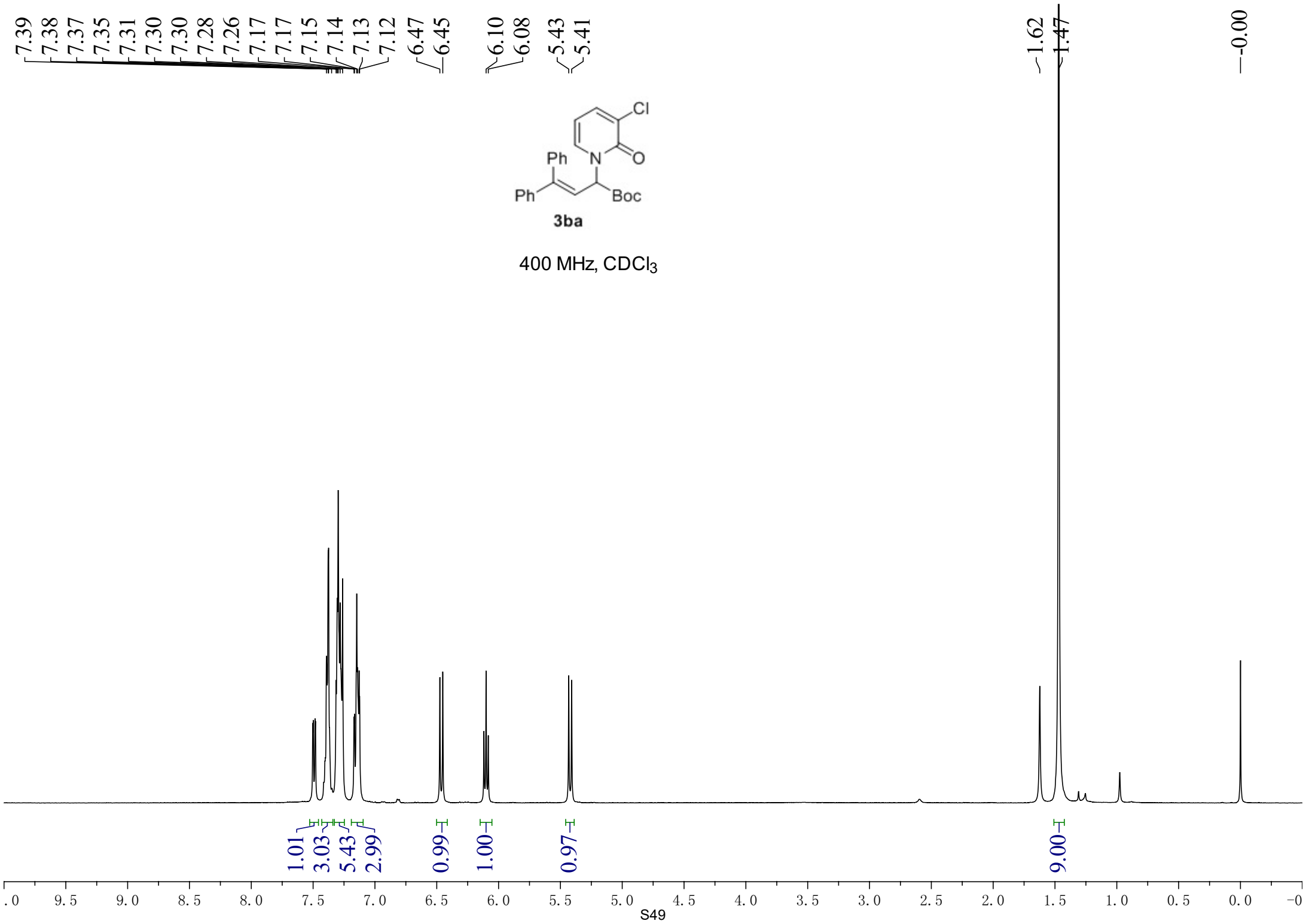

169.24
162.23
148.11
139.46
135.42
120.33
115.17
108.23
105.84
82.63
64.45
64.42
56.00
35.95
34.90
33.51
27.93
26.25
O
O
N
O
Boc
3al
75 MHz, CDCl3
f1 (ppm)

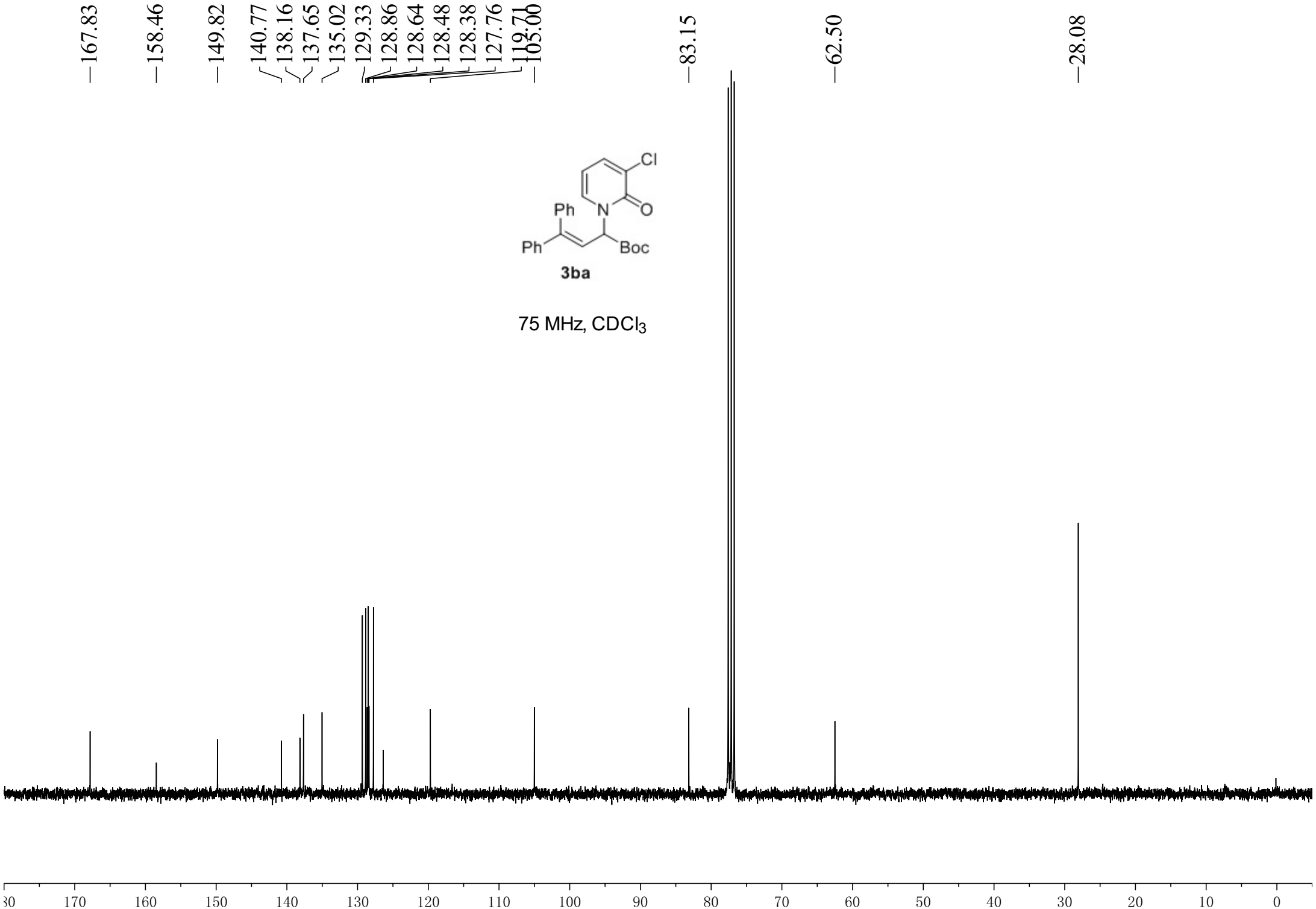

7.40 7.39 7.37 7.37 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.28 6.57 6.54 6.20 6.19 6.17 6.17 6.15 6.15 6.07 6.03 5.51 5.47 2.23 2.21 2.20 2.19 2.17 2.15 2.07 2.05 2.02 1.70 1.68 1.67 1.59 1.57 1.57 1.54 1.52 1.49 1.46 1.43 1.40 1.38 1.32 1.30 1.26 -0.00
N
O
Boc
3am
300 MHz, CDCl3
0.99 1.16 0.99 1.00 1.00 1.00 3.01 1.11 27.43
f1 (ppm)

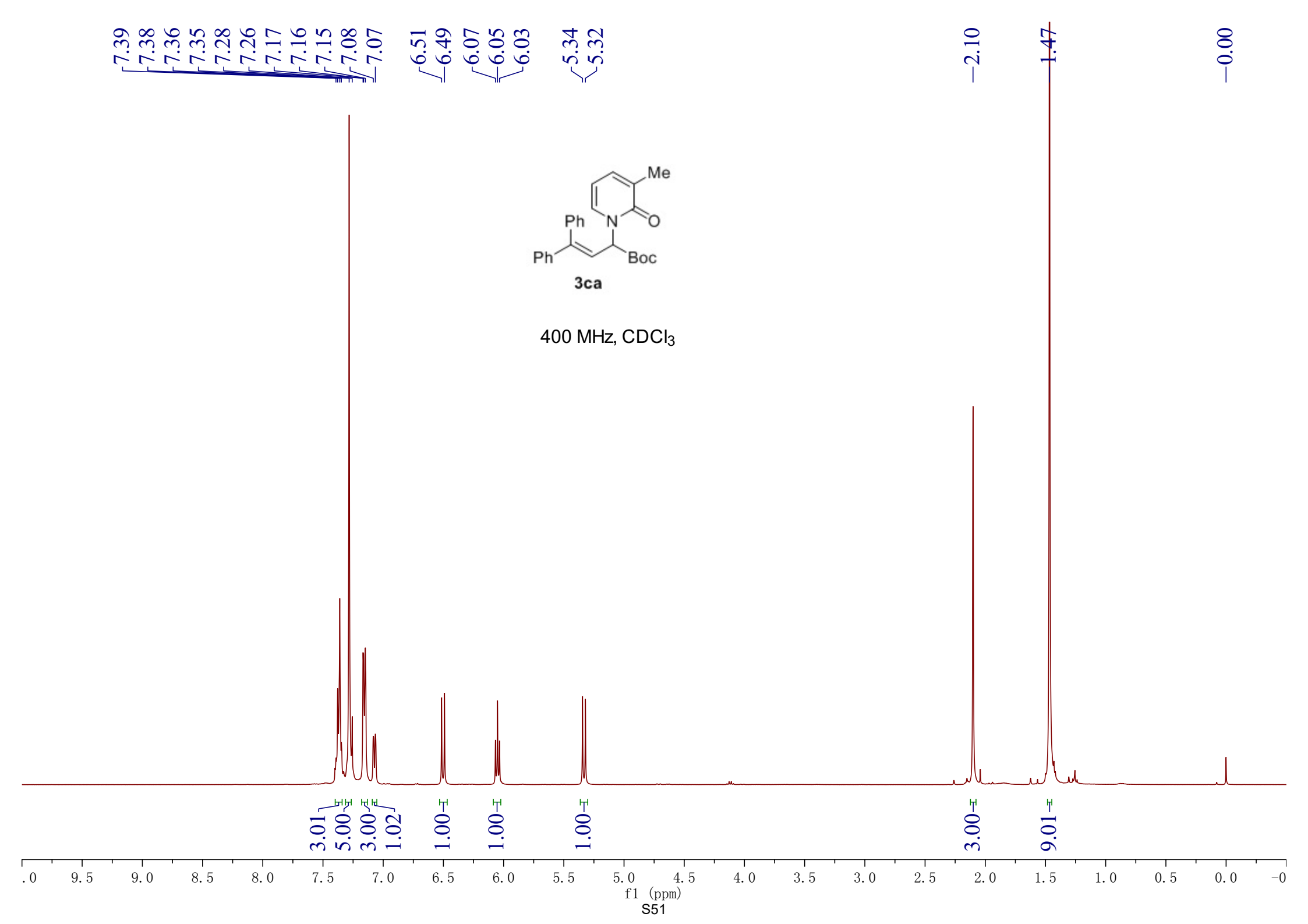

169.82
162.31
150.16
139.32
135.46
120.35
116.82
105.54
82.29
56.45
31.17
30.04
27.94
25.17
25.02
23.99
23.72
23.60
23.56
23.14
23.08
22.21
N
O
Boc
3am
75 MHz, CDCl3
f1 (ppm)

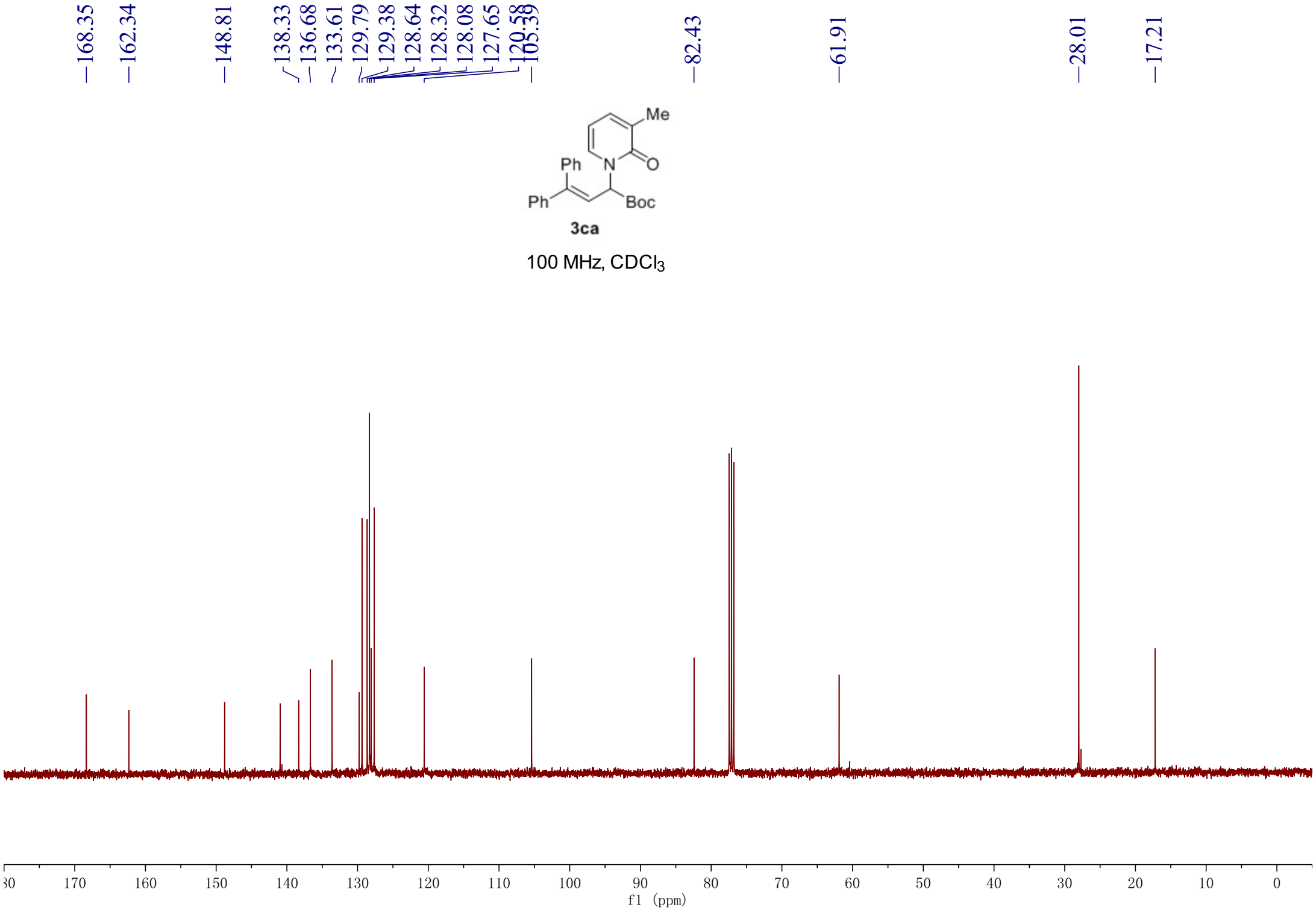

7.63
7.60
7.32
7.31
7.30
7.28
7.28
6.55
6.55
6.16
6.16
6.12
5.49
5.46
3.16
3.14
3.12
3.10
3.05
3.03
3.02
3.00
2.99
2.98
2.97
2.96
2.45
2.42
2.38
2.37
2.34
1.38
-0.00
Ts
N
N
O
Boc
3an
300 MHz, CDCl3
2.00
4.33
0.99
2.00
1.00
4.00
7.00
9.00
f1 (ppm)

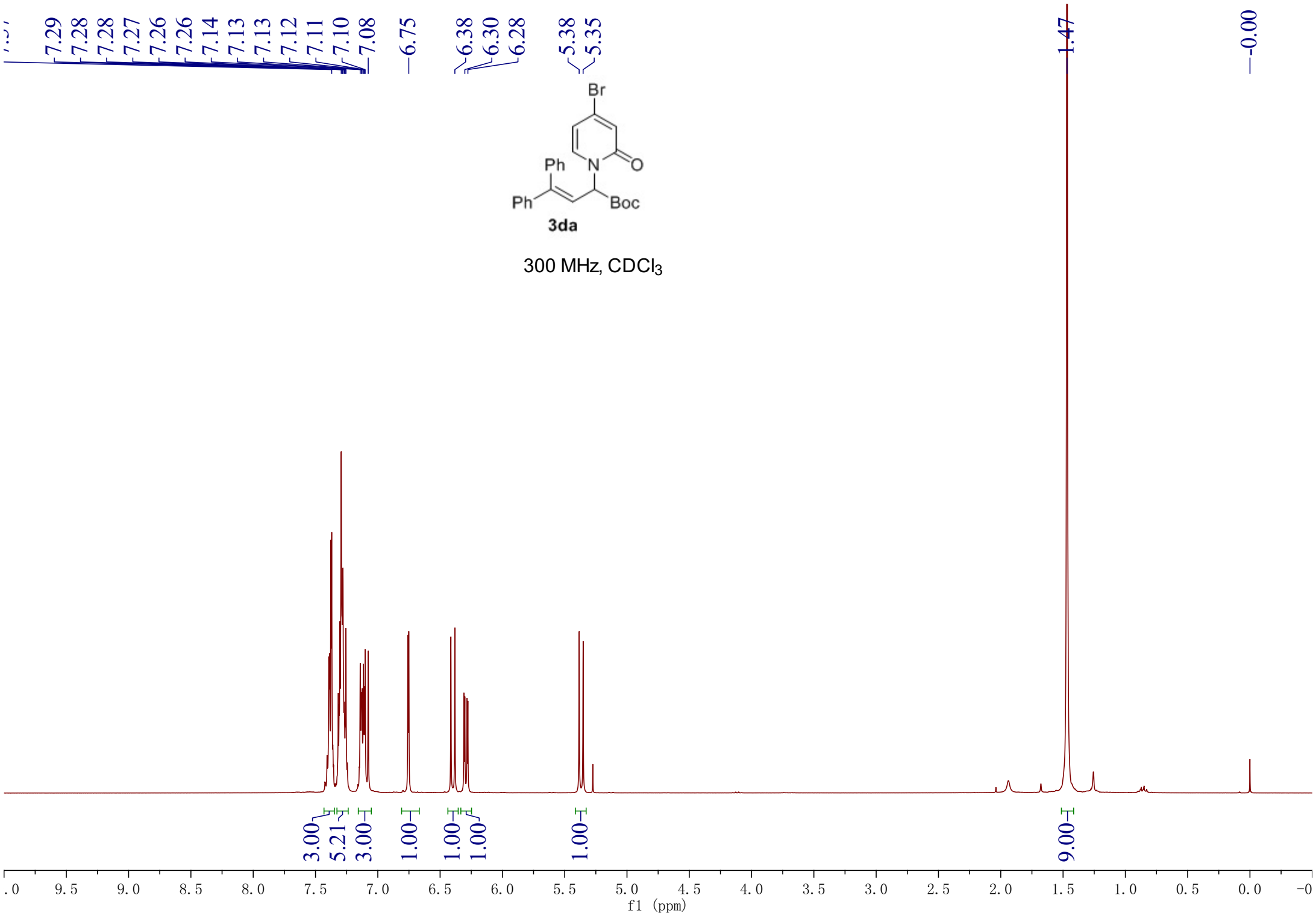

168.52
161.92
143.67
143.47
139.49
135.37
133.19
129.71
127.61
120.43
117.46
106.01
82.92
55.21
47.43
46.72
35.14
28.64
27.83
21.51
Ts
N
N
O
Boc
3an
75 MHz, CDCl3
f1 (ppm)

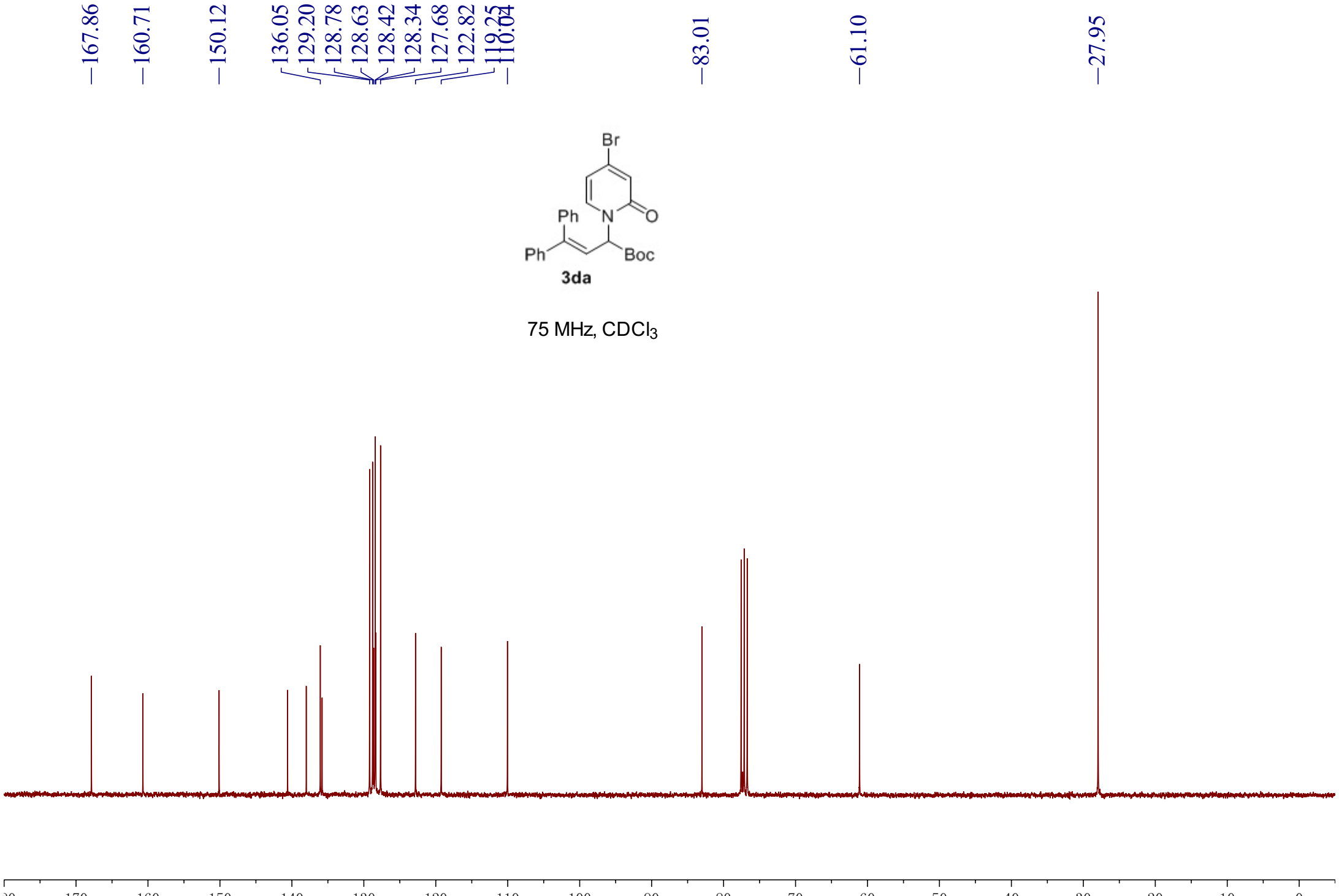

7.39
7.38
7.37
7.35
7.31
7.30
7.30
7.28
7.26
7.17
7.17
7.15
7.14
7.13
7.12
6.47
6.45
6.10
6.08
5.43
5.41
1.62
1.47
0.00
Cl
Ph
N
O
Ph
Boc
3ba
400 MHz, CDCl3
1.01
3.03
5.43
2.99
0.99
1.00
0.97
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

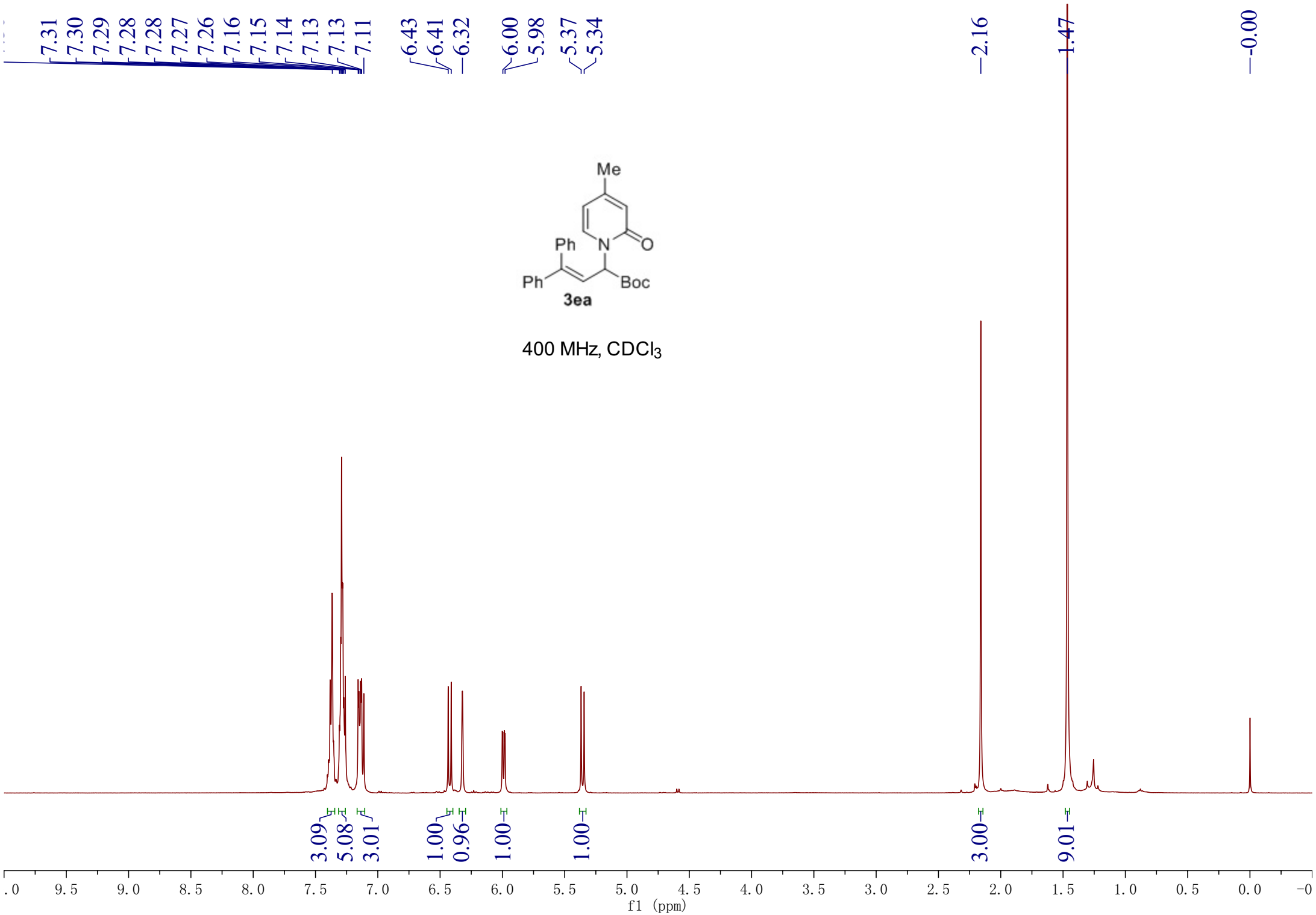

167.83
158.46
149.82
140.77
138.16
137.65
135.02
129.33
128.86
128.64
128.48
128.38
127.76
119.71
105.00
83.15
62.50
28.08
Cl
Ph
N
O
Ph
Boc
3ba
75 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

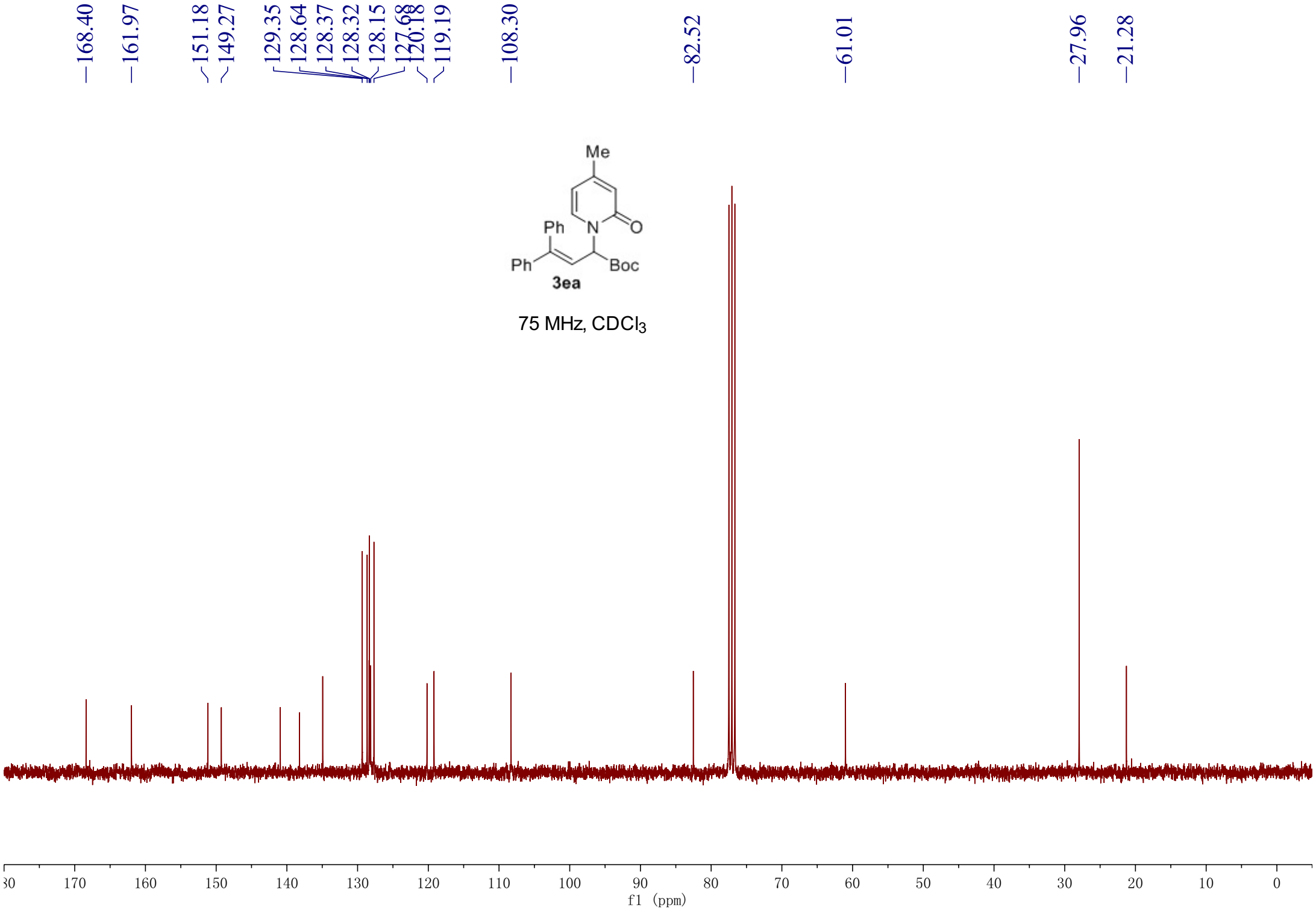

7.39
7.38
7.36
7.35
7.28
7.26
7.17
7.16
7.15
7.08
7.07
6.51
6.49
6.07
6.05
6.03
5.34
5.32
2.10
1.47
0.00
Me
Ph
N
O
Ph
Boc
3ca
400 MHz, CDCl3
3.01
5.00
3.00
1.02
1.00
1.00
1.00
3.00
9.01
f1 (ppm)

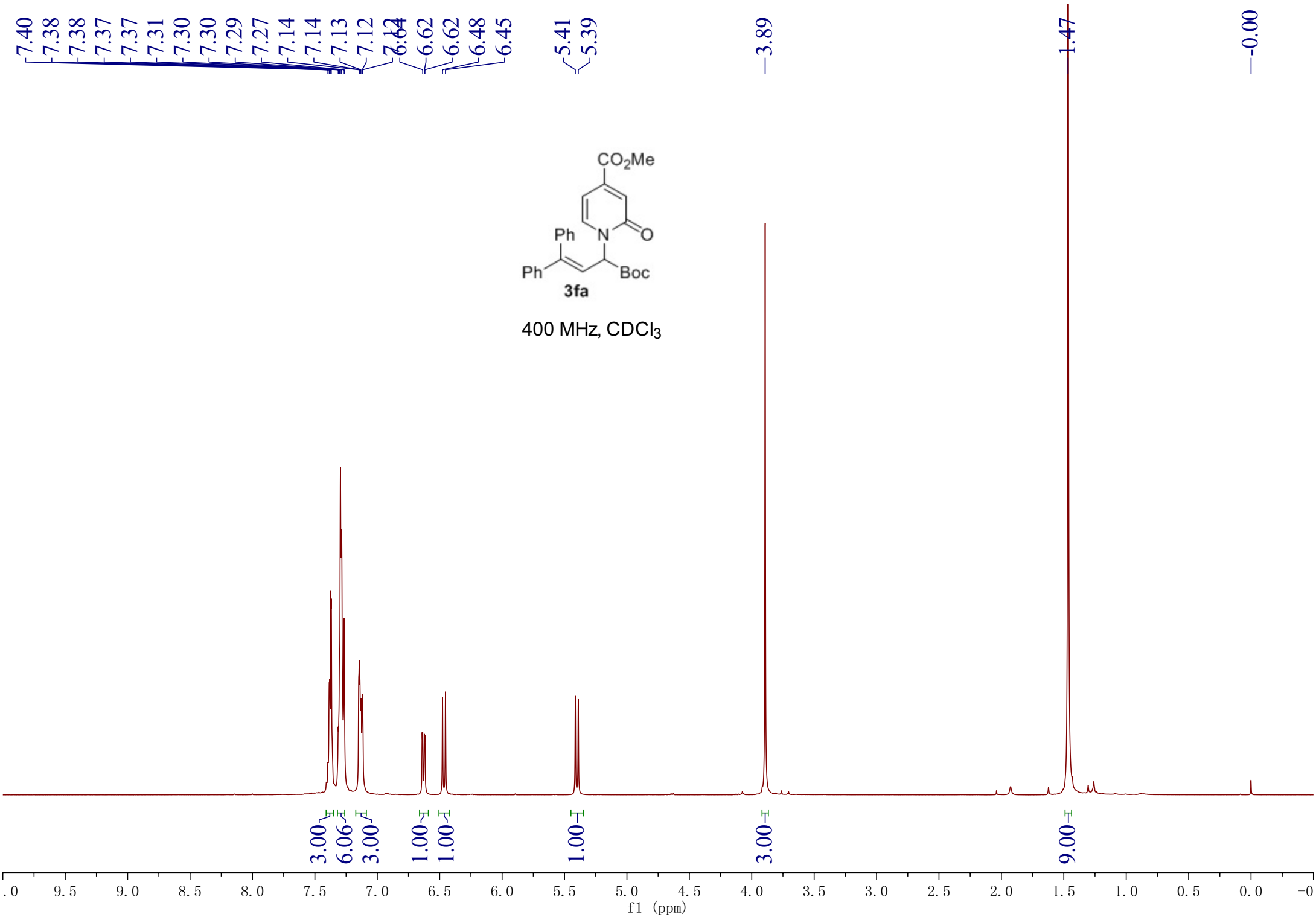

168.35
162.34
148.81
138.33
136.68
133.61
129.79
129.38
128.64
128.32
128.08
127.65
120.58
105.39
82.43
61.91
28.01
17.21
Me
Ph
N
O
Ph
Boc
3ca
100 MHz, CDCl3
f1 (ppm)

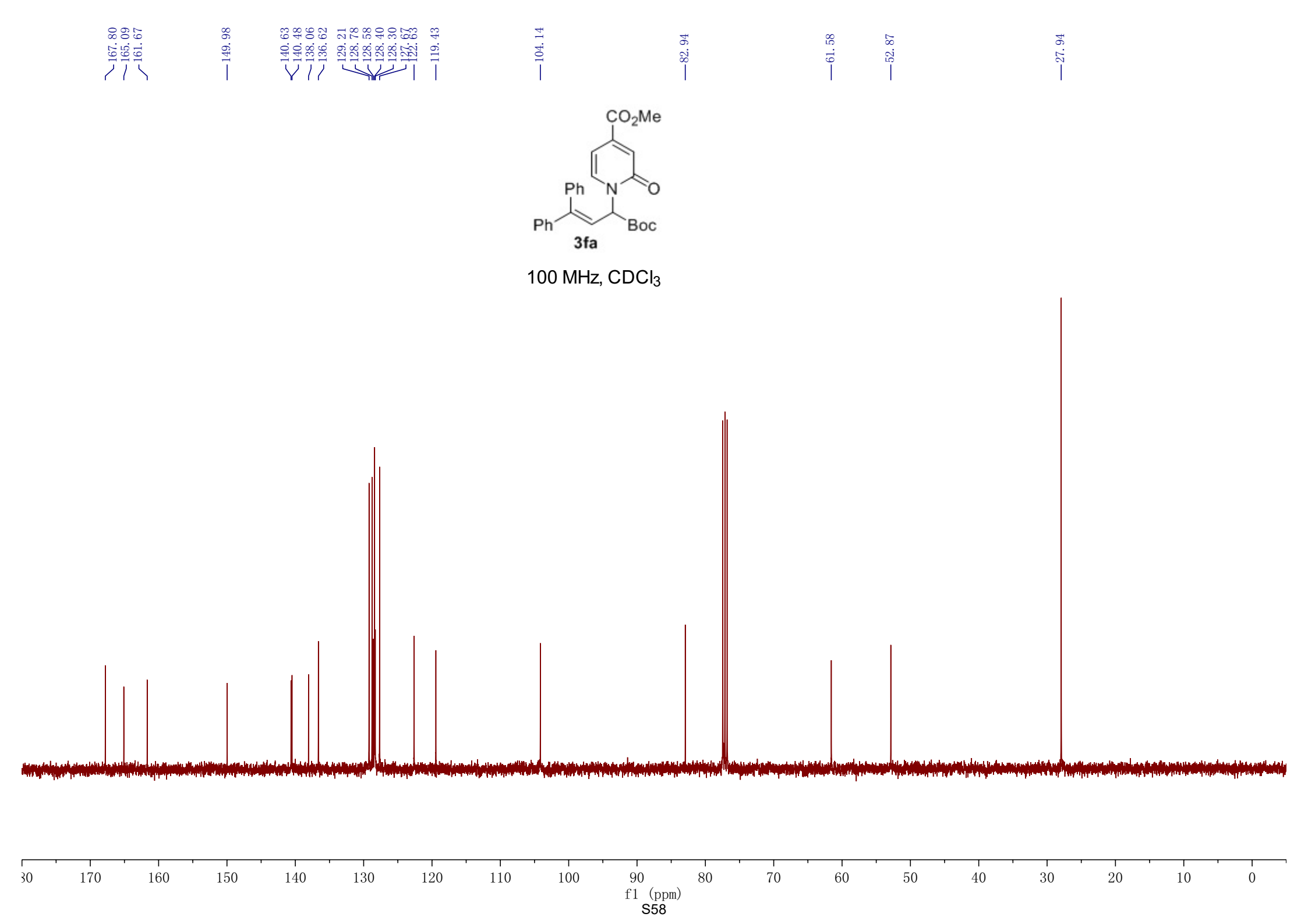

7.29
7.28
7.28
7.27
7.26
7.26
7.14
7.13
7.13
7.12
7.11
7.10
7.08
6.75
6.38
6.30
6.28
5.38
5.35
1.47
0.00
Br
Ph
N
O
Ph
Boc
3da
300 MHz, CDCl3
3.00
5.21
3.00
1.00
1.00
1.00
1.00
9.00
f1 (ppm)

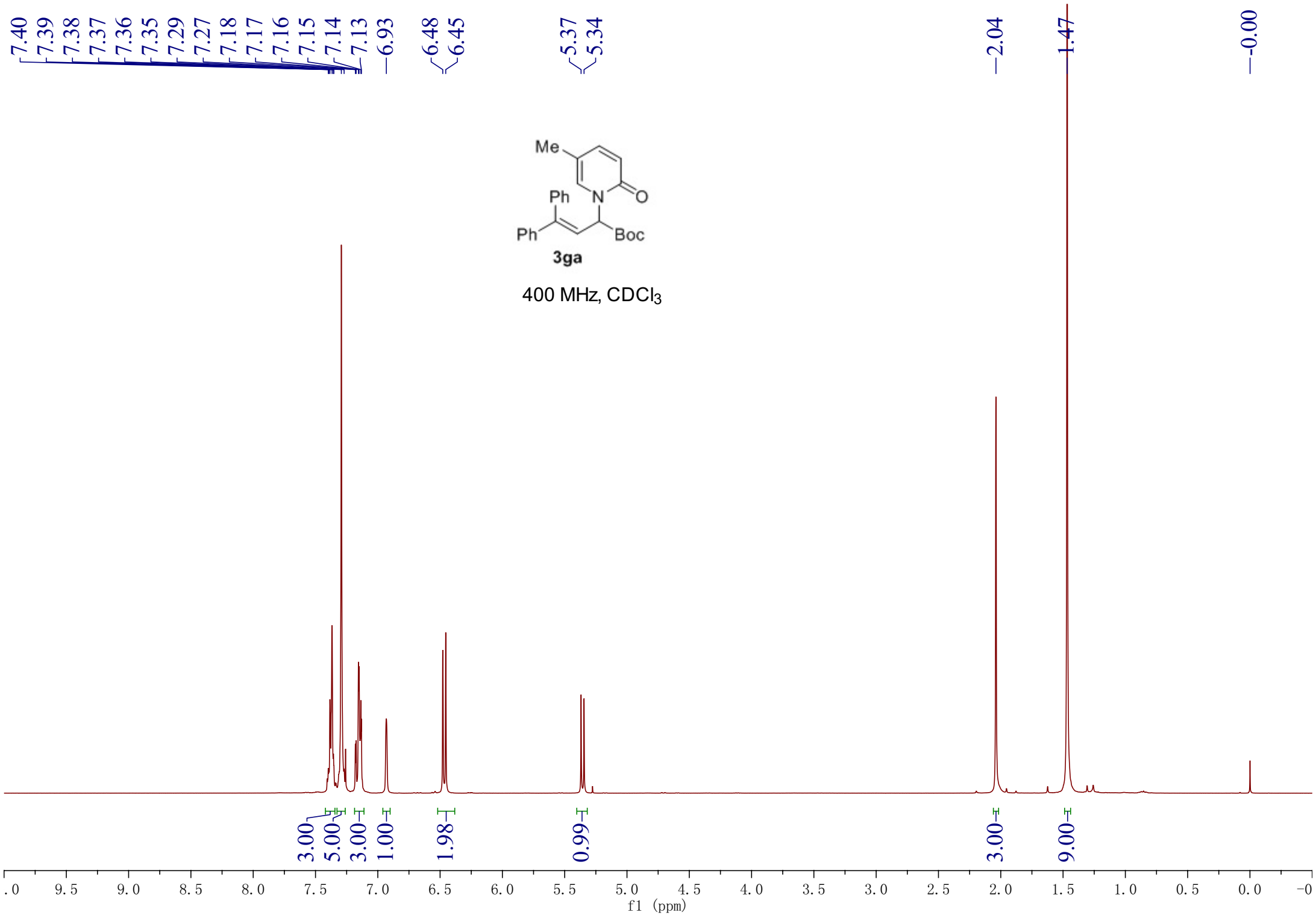

167.86
160.71
150.12
136.05
129.20
128.78
128.63
128.42
128.34
127.68
122.82
119.25
110.04
83.01
61.10
27.95
Br
Ph
N
O
Ph
Boc
3da
75 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.16
7.15
7.14
7.13
7.13
7.11
6.43
6.41
6.32
6.00
5.98
5.37
5.34
2.16
1.47
-0.00
Me
Ph
N
O
Ph
Boc
3ea
400 MHz, CDCl3
3.09
5.08
3.01
1.00
0.96
1.00
1.00
3.00
9.01
f1 (ppm)


168.40
161.97
151.18
149.27
129.35
128.64
128.37
128.32
128.15
127.68
120.18
119.19
108.30
82.52
61.01
27.96
21.28
Me
Ph
N
O
Ph
Boc
3ea
75 MHz, CDCl3
f1 (ppm)


7.40
7.38
7.38
7.37
7.37
7.31
7.30
7.30
7.29
7.27
7.14
7.14
7.13
7.12
6.64
6.62
6.62
6.48
6.45
5.41
5.39
3.89
1.47
0.00
CO2Me
Ph
N
O
Ph
Boc
3fa
400 MHz, CDCl3
3.00
6.06
3.00
1.00
1.00
1.00
3.00
9.00
f1 (ppm)


167.80
165.09
161.67
149.98
140.63
140.48
138.06
136.62
129.21
128.78
128.58
128.40
128.30
127.67
122.63
119.43
104.14
82.94
61.58
52.87
27.94
CO2Me
Ph
N
O
Ph
Boc
3fa
100 MHz, CDCl3
f1 (ppm)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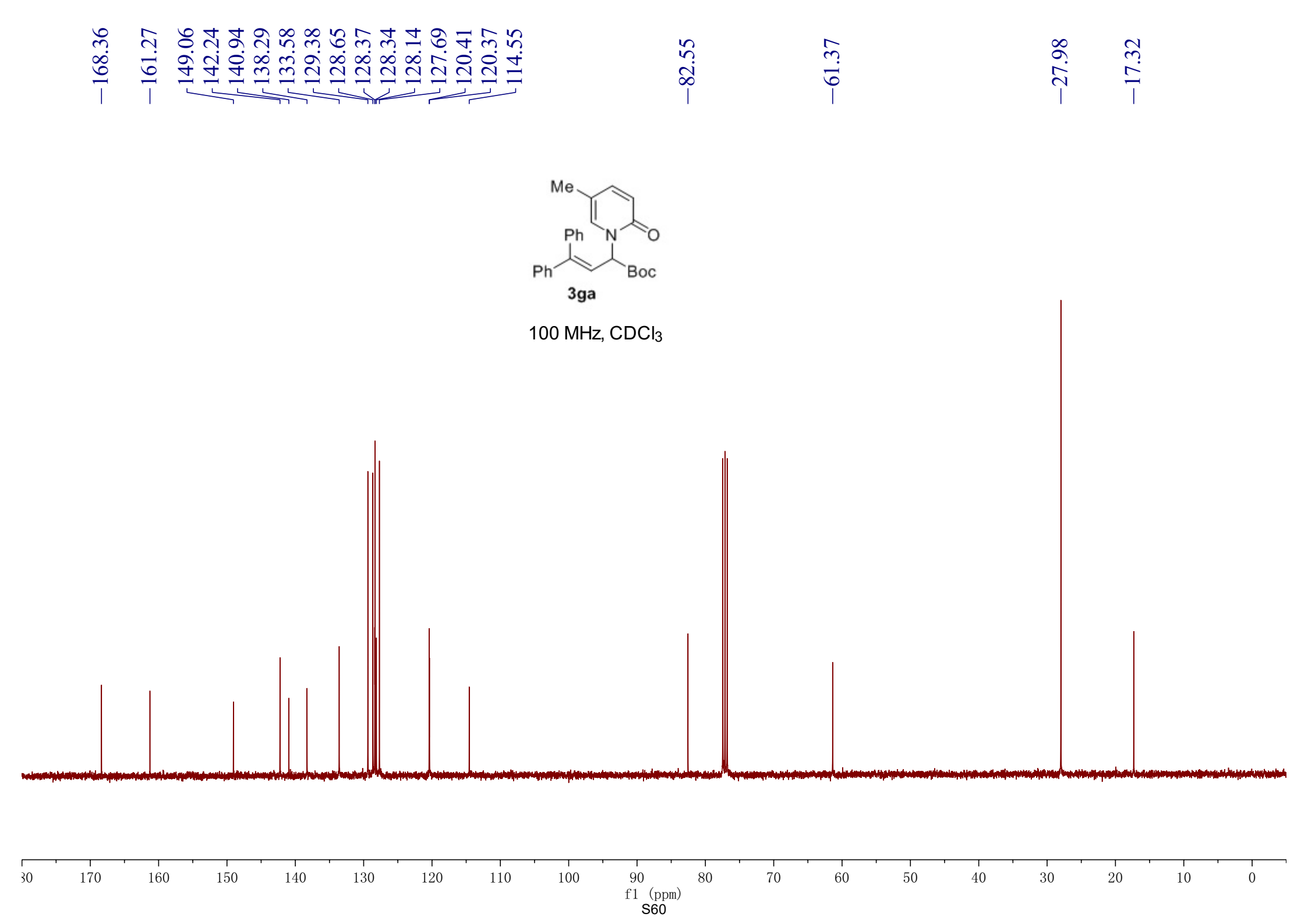
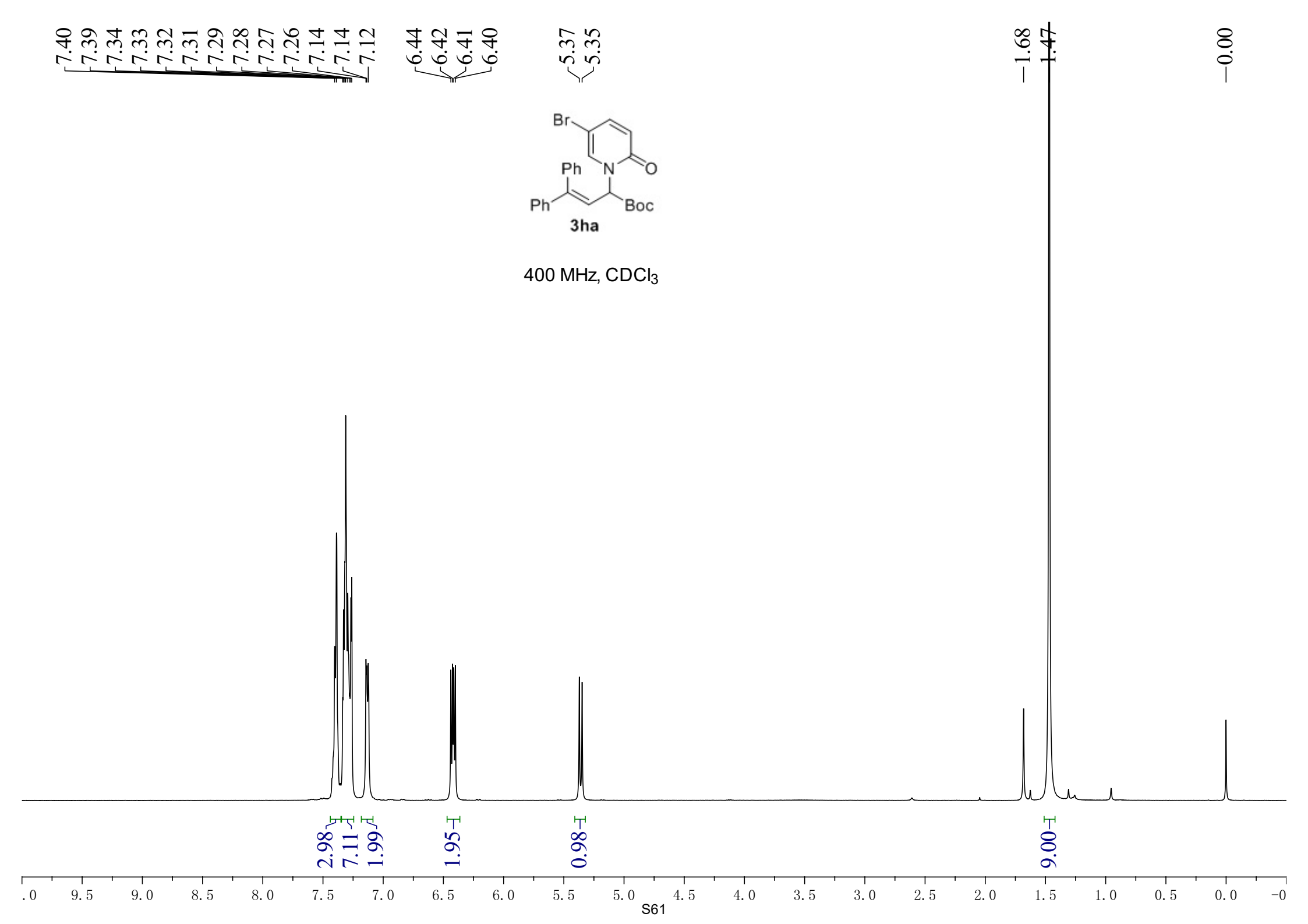
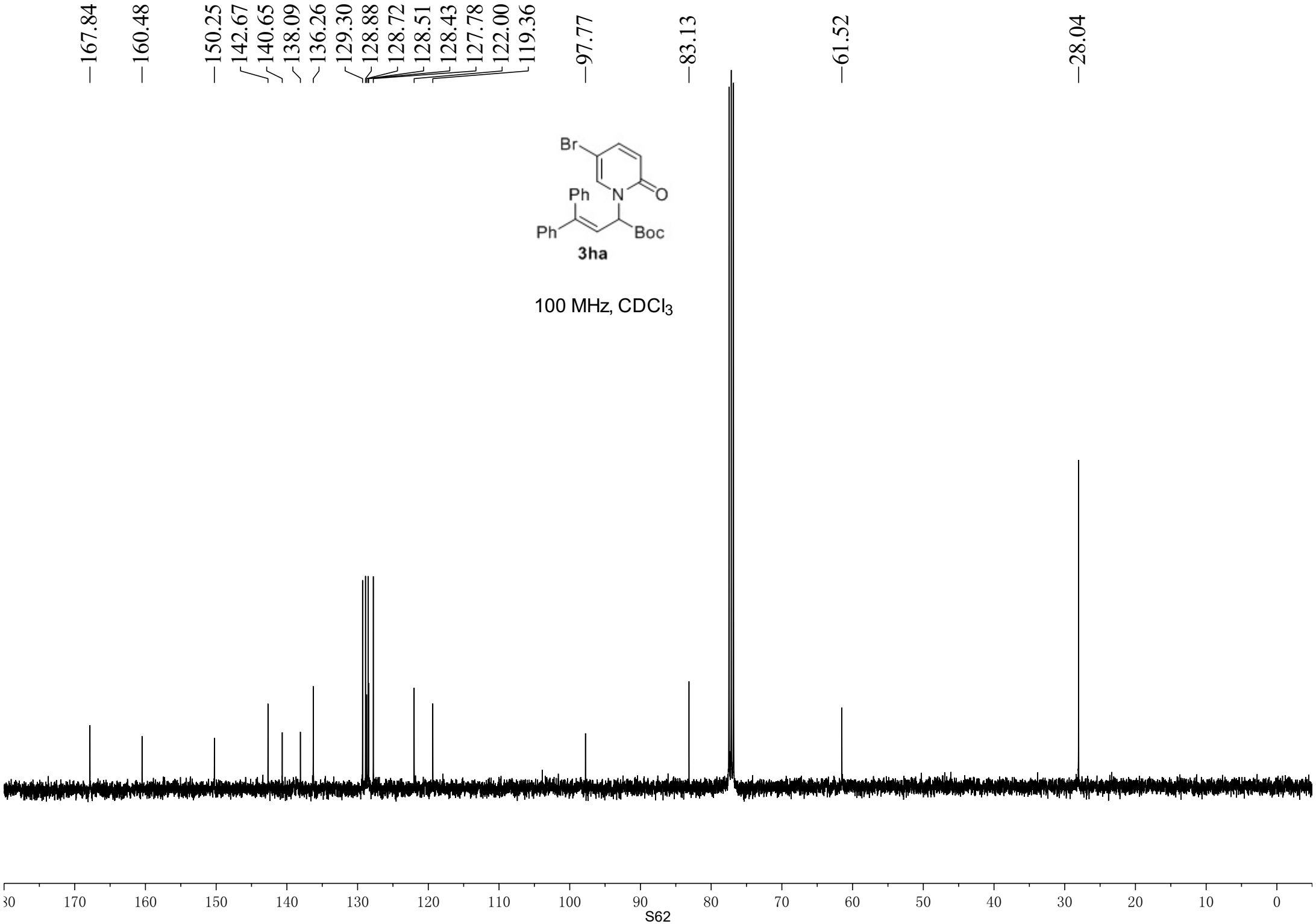
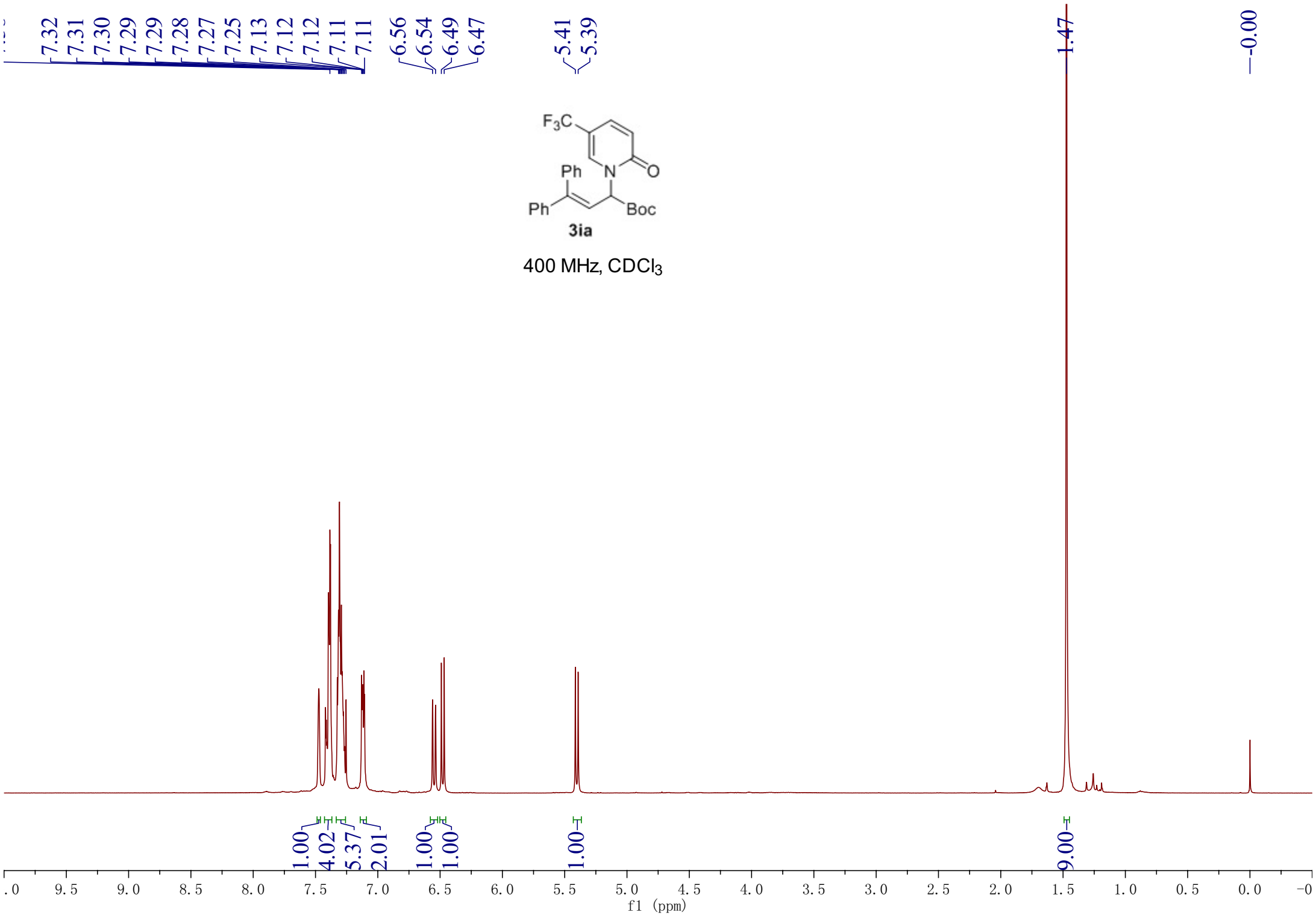
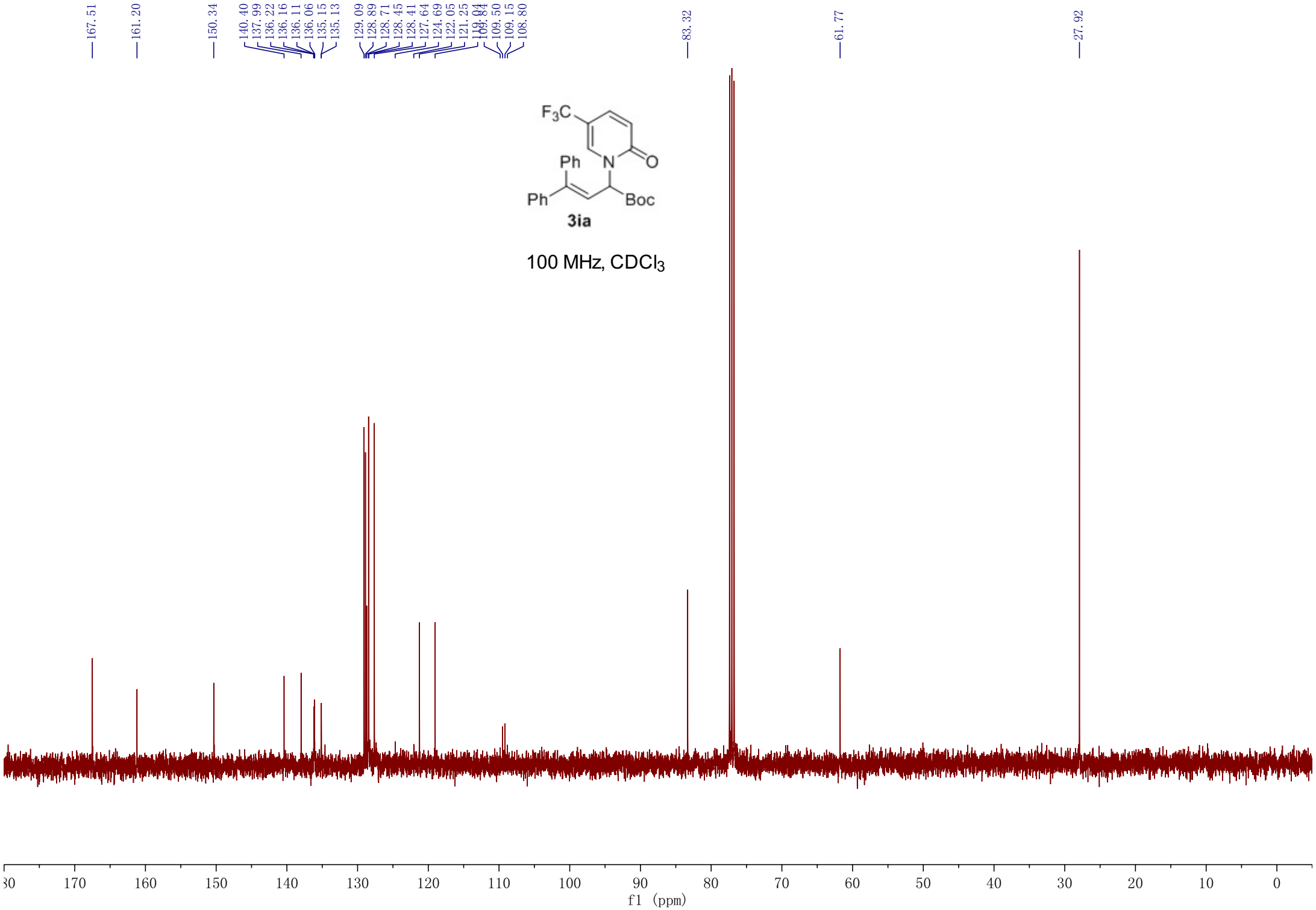
7.39
7.38
7.37
7.36
7.35
7.29
7.27
7.18
7.17
7.16
7.15
7.14
7.13
6.93
6.48
6.45
5.37
5.34
2.04
1.47
0.00
Me
Ph
N
O
Ph
Boc
3ga
400 MHz, CDCl3
3.00
5.00
3.00
1.00
1.98
0.99
3.00
9.00
f1 (ppm)

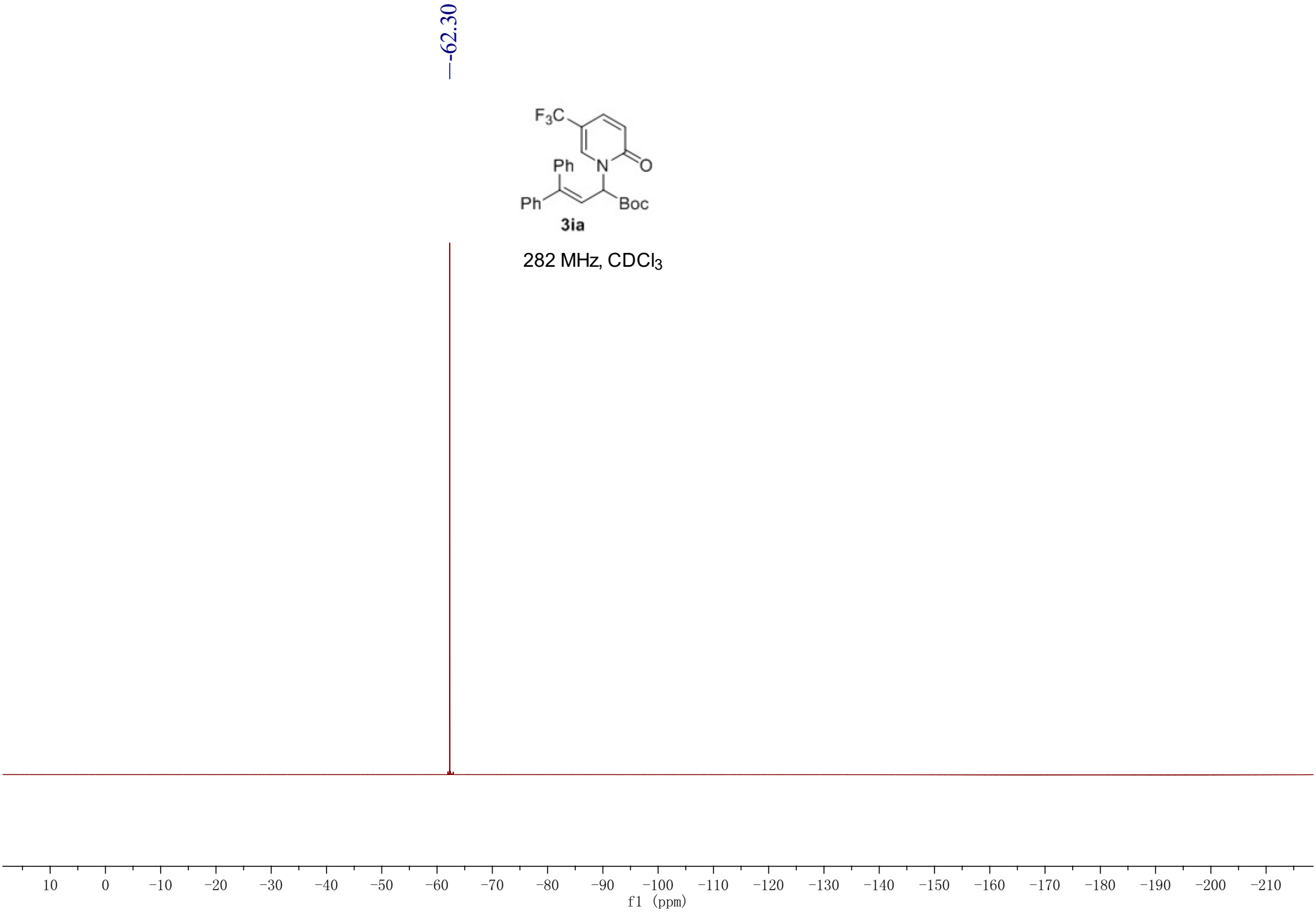

168.36
161.27
149.06
142.24
140.94
138.29
133.58
129.38
128.65
128.37
128.34
128.14
127.69
120.41
120.37
114.55
82.55
61.37
27.98
17.32
Me
Ph
N
O
Ph
Boc
3ga
100 MHz, CDCl3
f1 (ppm)

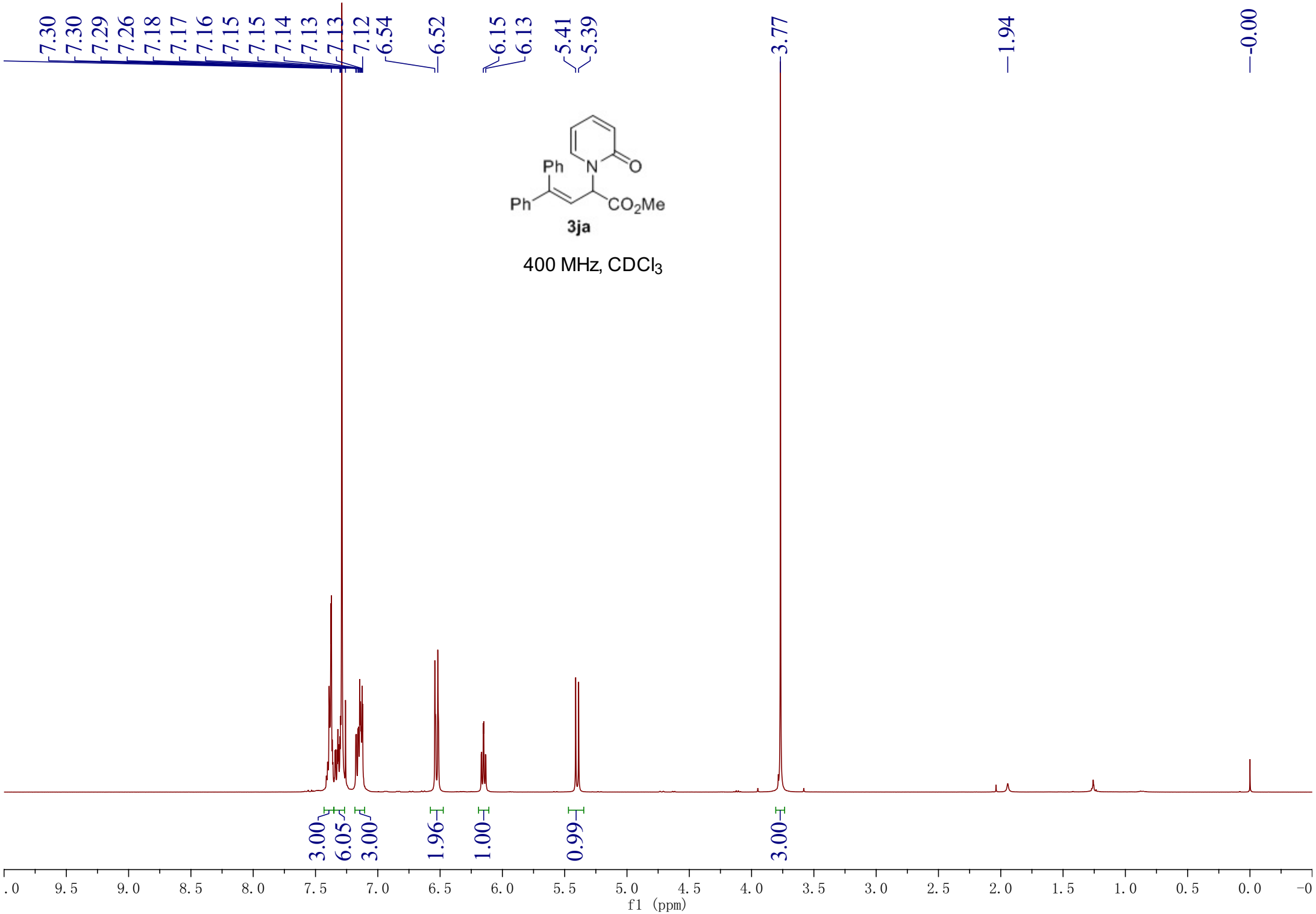

7.40
7.39
7.34
7.33
7.32
7.31
7.29
7.28
7.27
7.26
7.14
7.14
7.12
6.44
6.42
6.41
6.40
5.37
5.35
1.68
1.47
0.00
Br
Ph
N
O
Ph
Boc
3ha
400 MHz, CDCl3
2.98
7.11
1.99
1.95
0.98
9.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

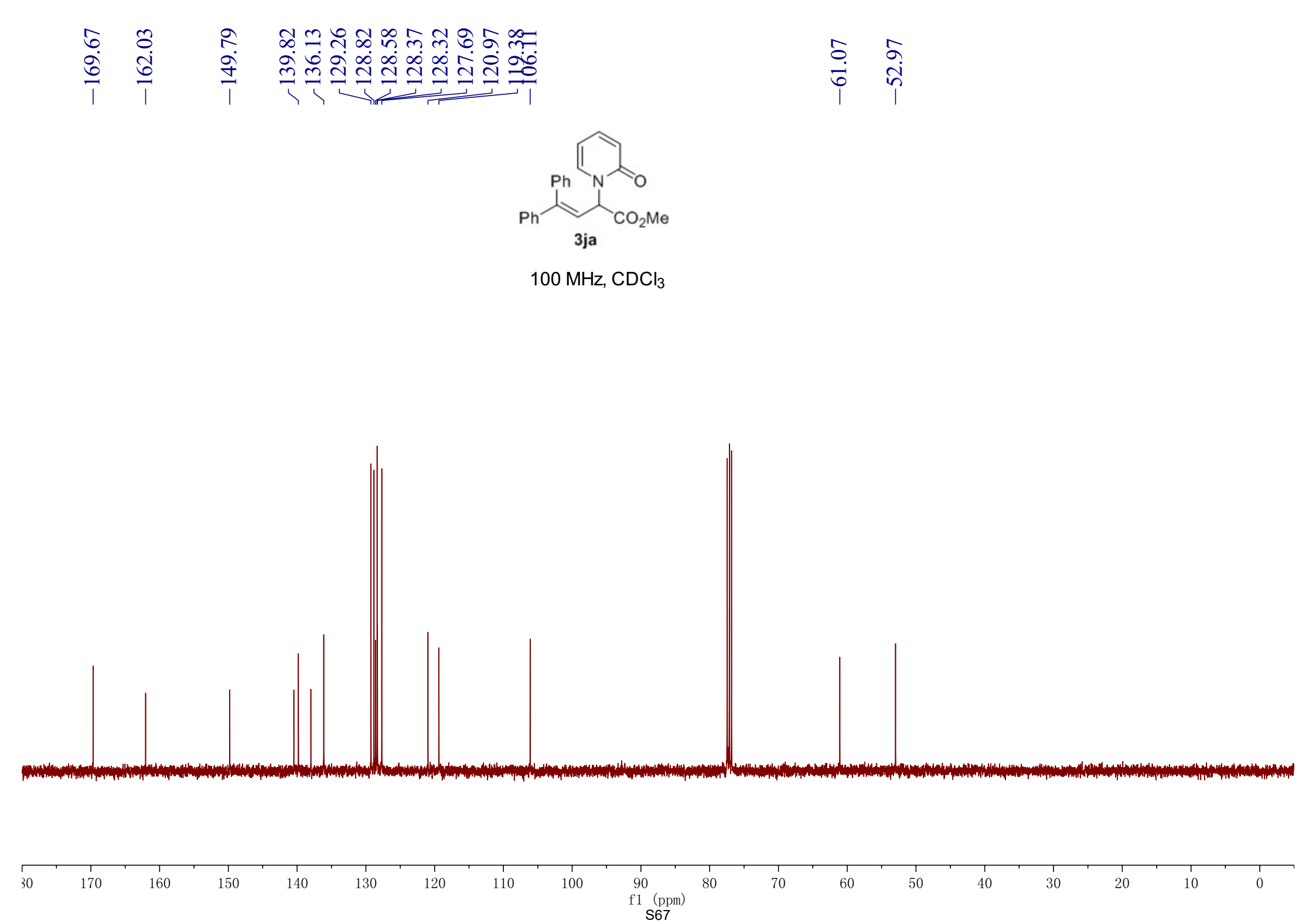

167.84
160.48
150.25
142.67
140.65
138.09
136.26
129.30
128.88
128.72
128.51
128.43
127.78
122.00
119.36
97.77
83.13
61.52
28.04
Br
Ph
N
O
Ph
Boc
3ha
100 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

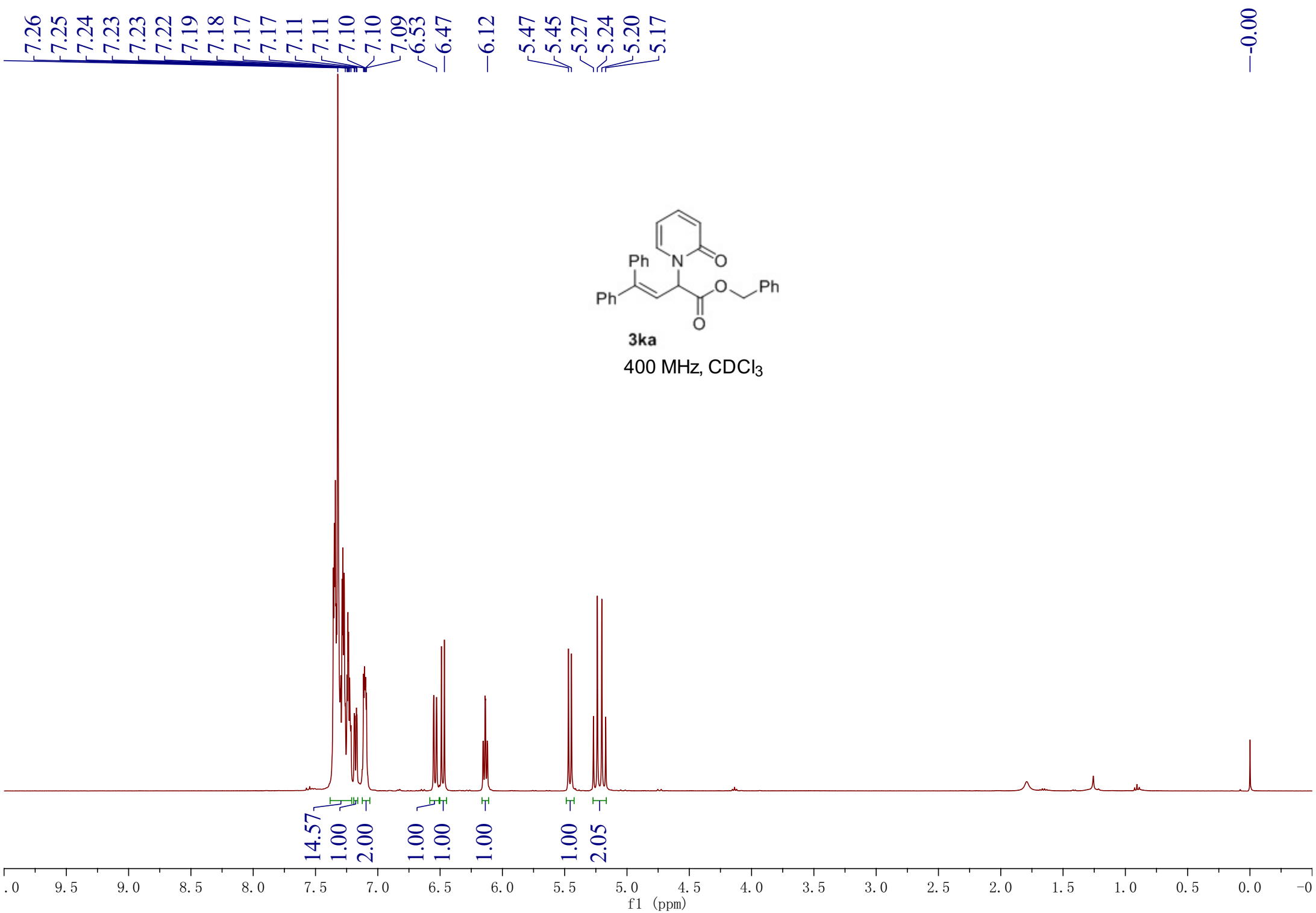

7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.25
7.13
7.12
7.12
7.11
7.11
6.56
6.54
6.49
6.47
5.41
5.39
1.47
0.00
F3C
Ph
N
O
Ph
Boc
3ia
400 MHz, CDCl3
1.00
4.02
5.37
2.01
1.00
1.00
1.00
9.00
f1 (ppm)


167.51
161.20
150.34
140.40
137.99
136.22
136.16
136.11
136.06
135.15
135.13
129.09
128.89
128.71
128.45
128.41
127.64
124.69
122.05
121.25
109.50
109.15
108.80
83.32
61.77
27.92
F3C
Ph
N
O
Ph
Boc
3ia
100 MHz, CDCl3
f1 (ppm)


-62.30
F3C
Ph
N
O
Ph
Boc
3ia
282 MHz, CDCl3
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)

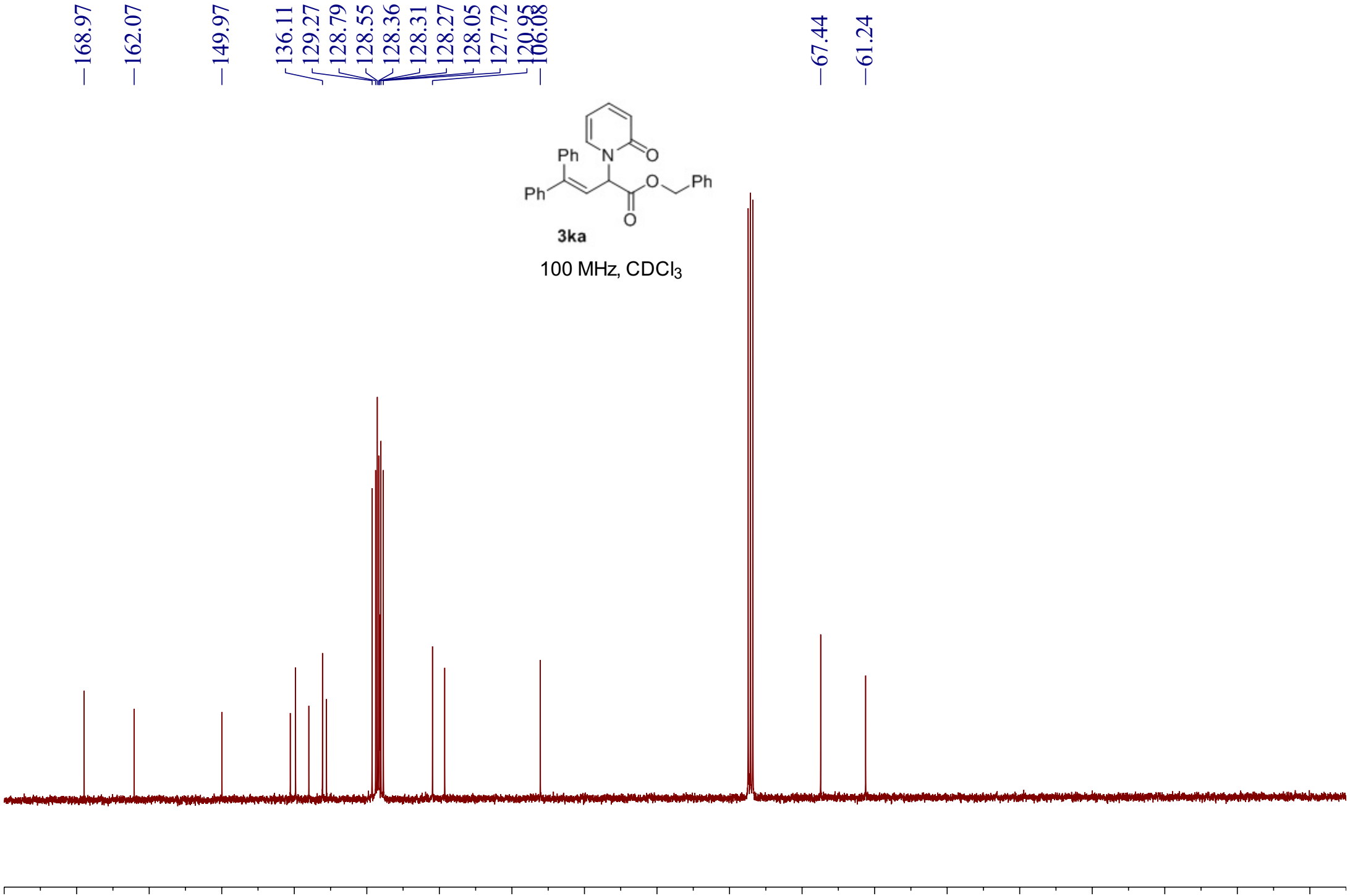

7.30
7.30
7.29
7.26
7.18
7.17
7.16
7.15
7.15
7.14
7.13
7.13
7.12
6.54
6.52
6.15
6.13
5.41
5.39
3.77
1.94
0.00
Ph
N
O
Ph
CO2Me
3ja
400 MHz, CDCl3
3.00
6.05
3.00
1.96
1.00
0.99
3.00
f1 (ppm)

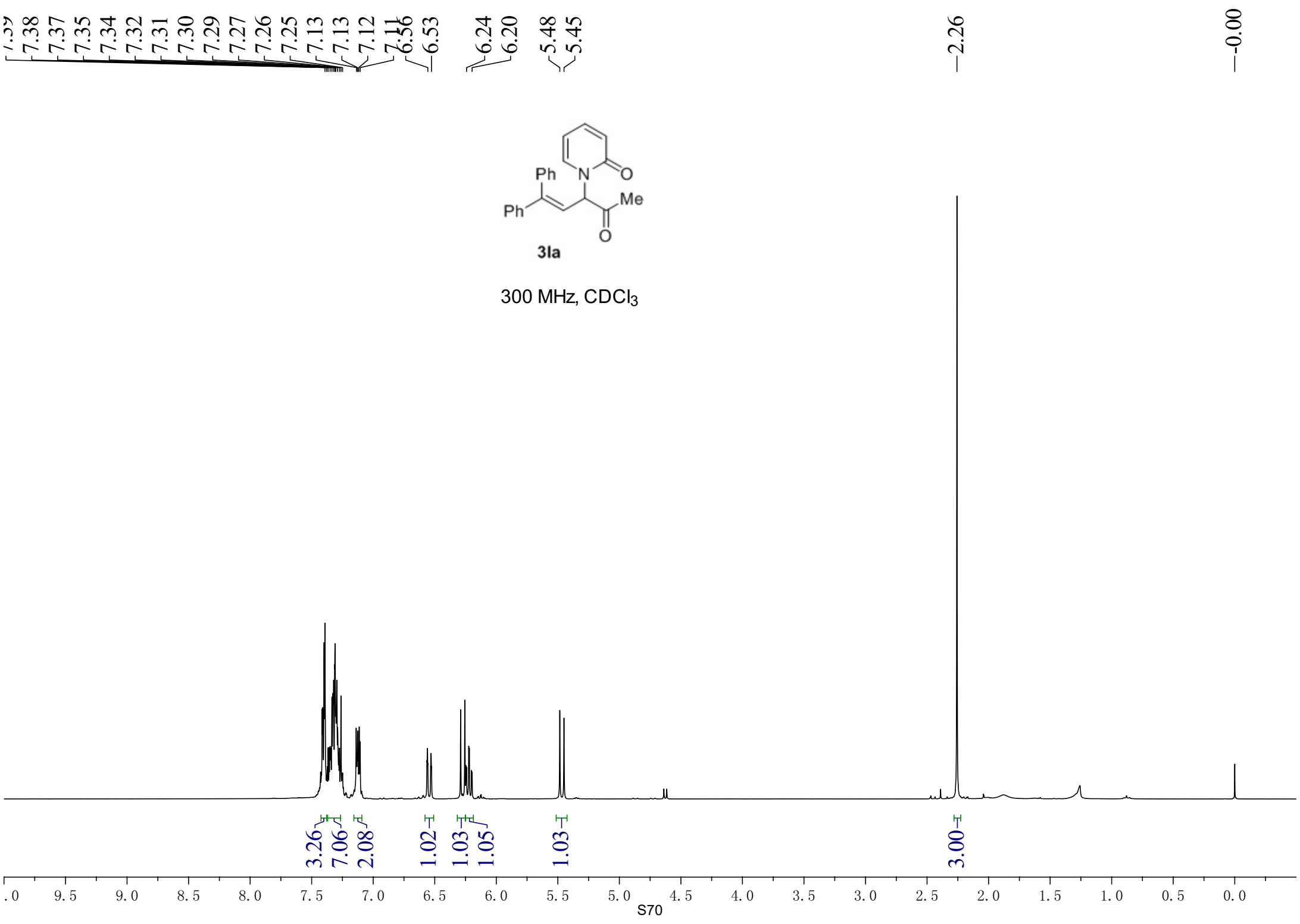

169.67
162.03
149.79
139.82
136.13
129.26
128.82
128.58
128.37
128.32
127.69
120.97
119.38
106.11
61.07
52.97
Ph
N
O
Ph
CO2Me
3ja
100 MHz, CDCl3
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3ka

400 MHz, $CDCl_3$


168.97
162.07
149.97
136.11
129.27
128.79
128.55
128.36
128.31
128.27
128.05
127.72
120.95
106.08
67.44
61.24
Ph
N
O
Ph
O
O
Ph
3ka
100 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.38
7.37
7.35
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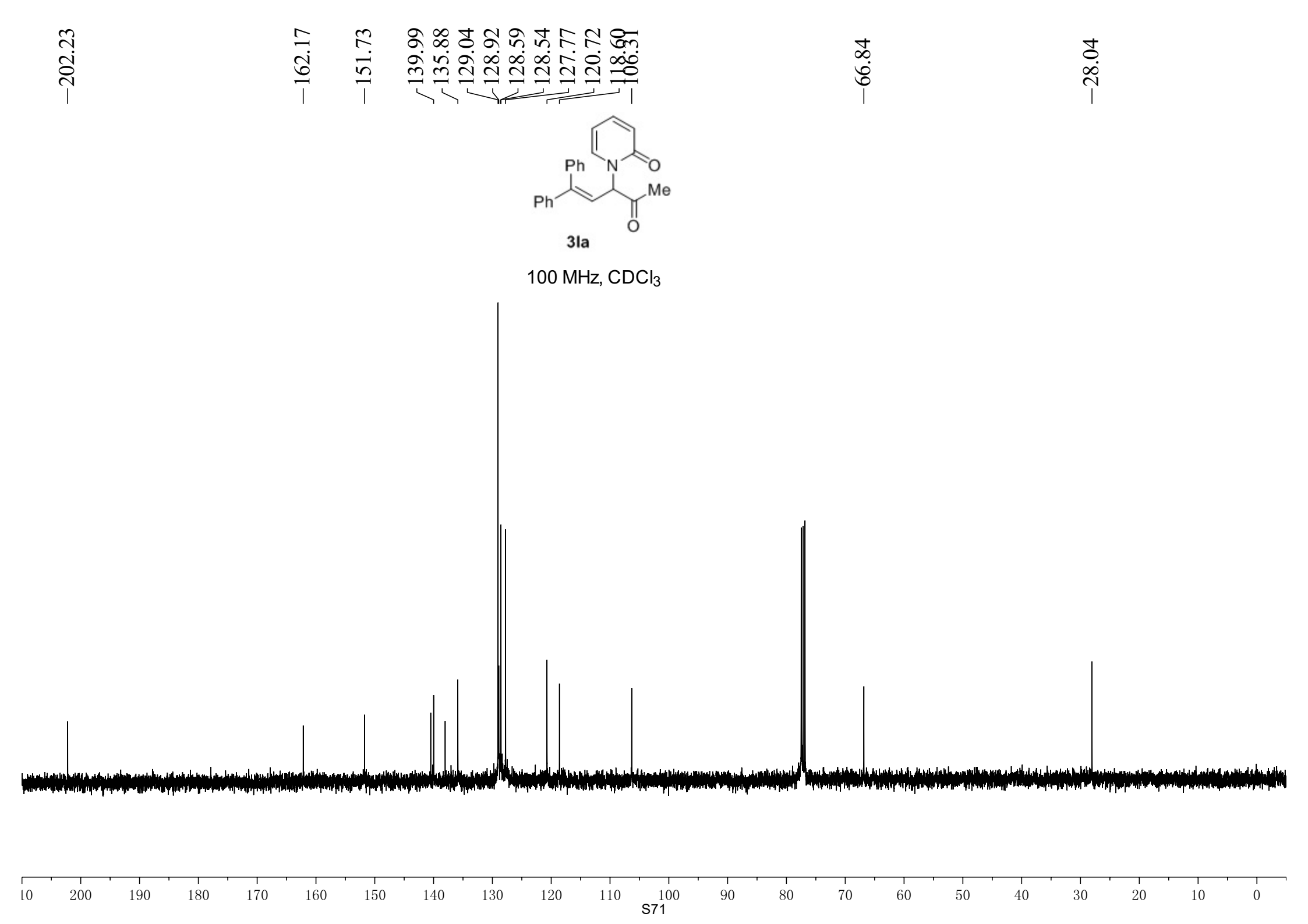
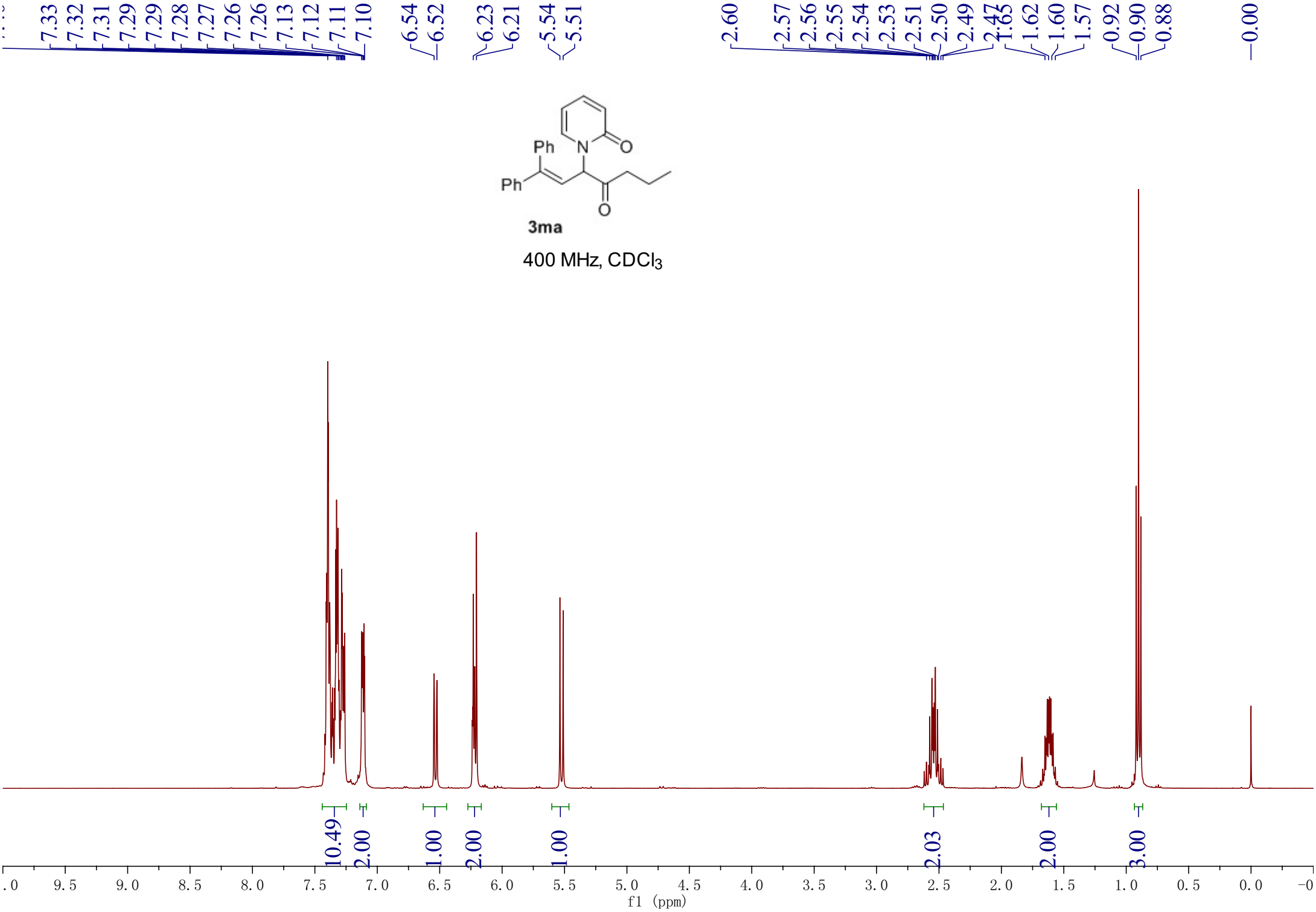
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.13
7.13
7.12
7.11
6.56
6.53
6.24
6.20
5.48
5.45
2.26
-0.00
Ph
N
O
Ph
Me
O
3la
300 MHz, CDCl3
3.26
7.06
2.08
1.02
1.03
1.05
1.03
3.00
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


202.23
162.17
151.73
139.99
135.88
129.04
128.92
128.59
128.54
127.77
120.72
118.60
106.31
66.84
28.04
Ph
N
O
Ph
Me
O
3la
100 MHz, CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.33
7.32
7.31
7.29
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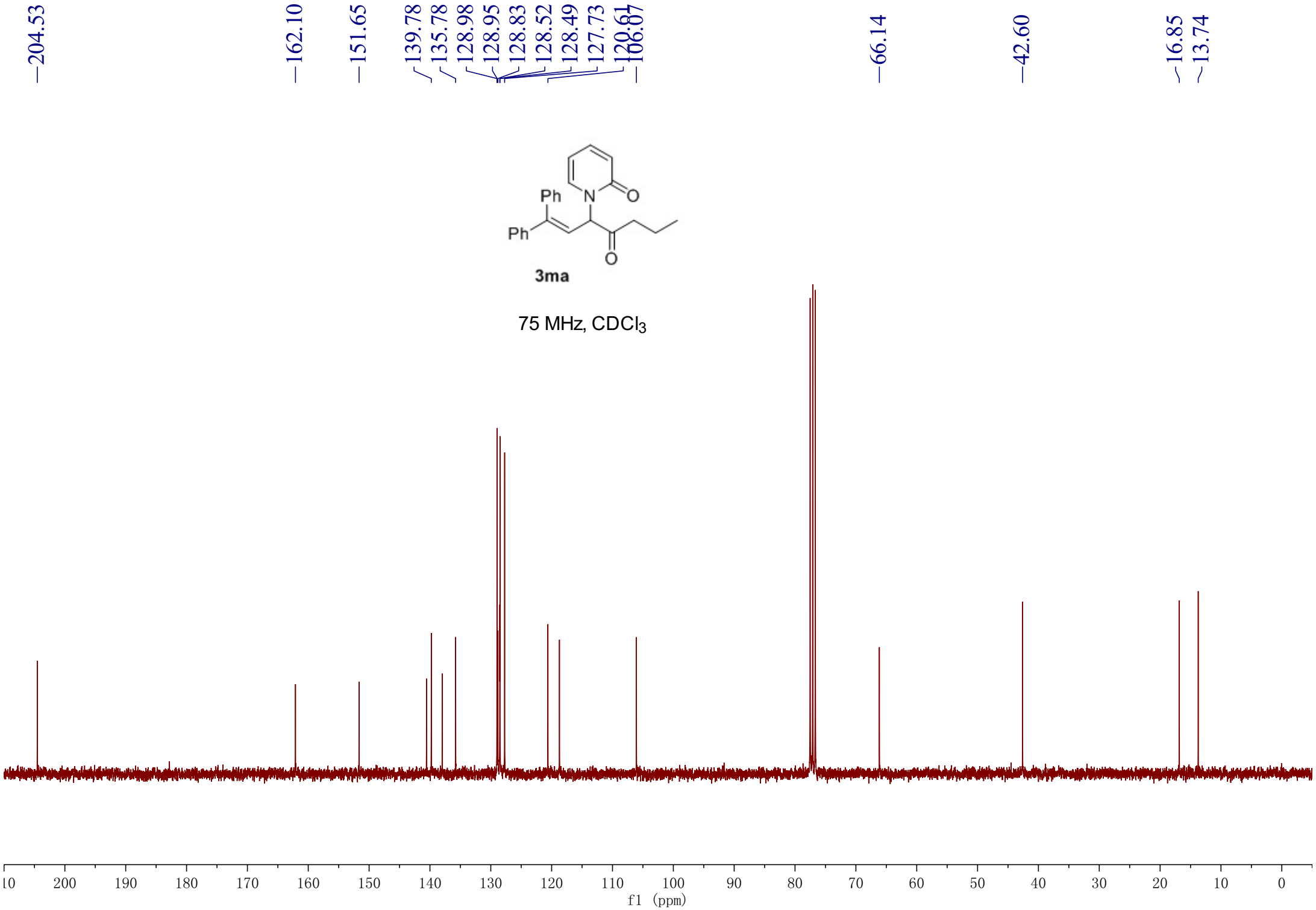
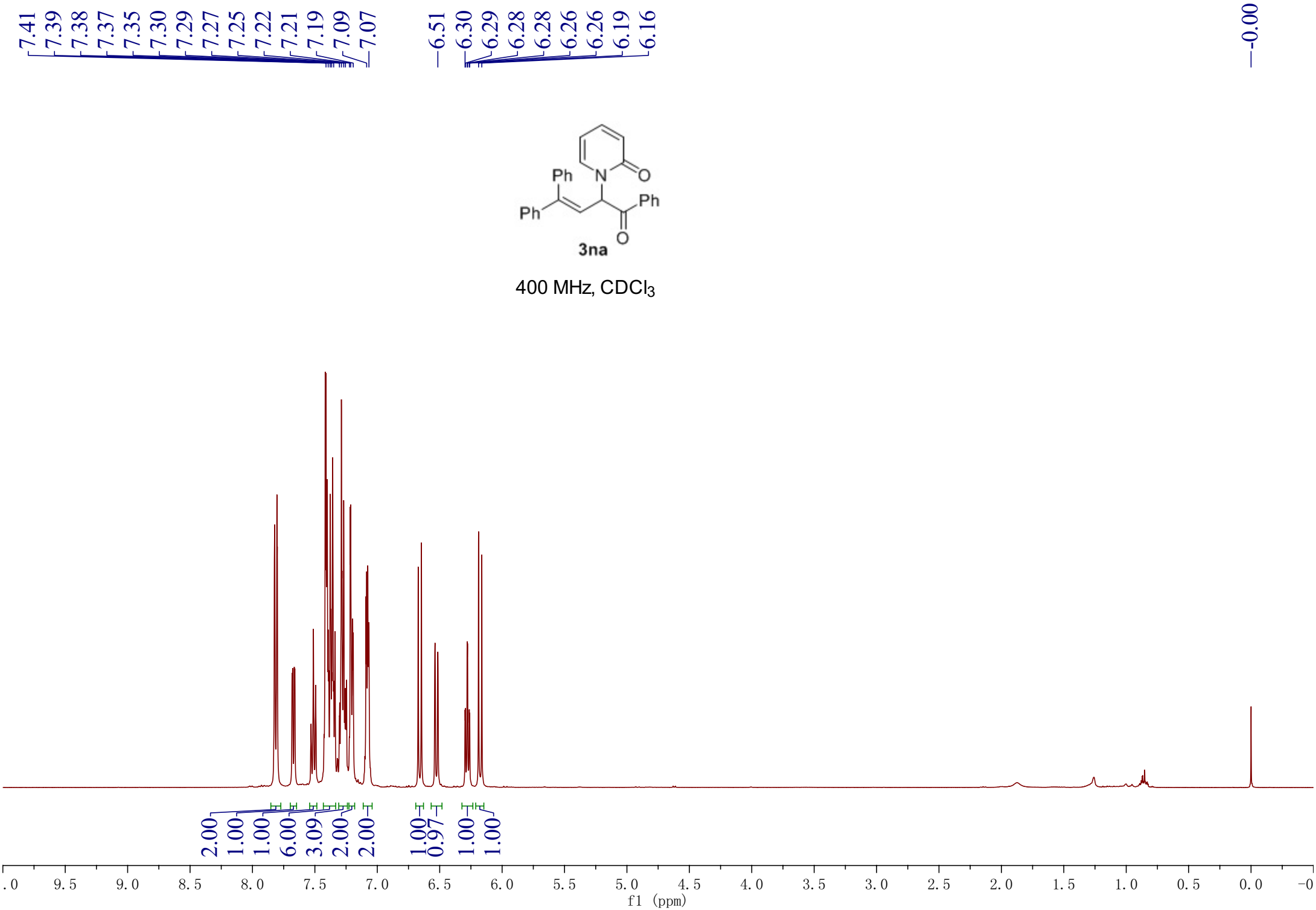
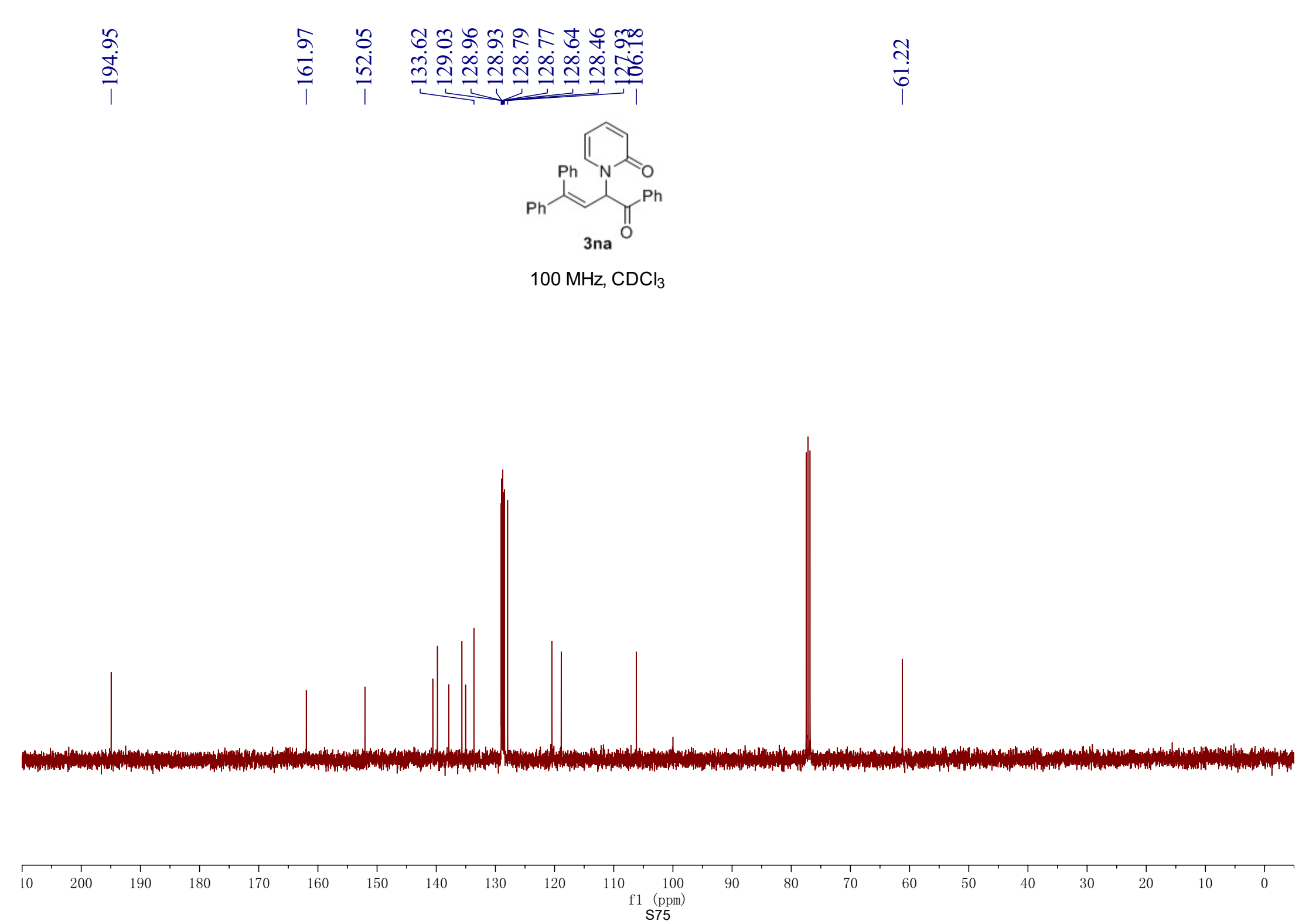
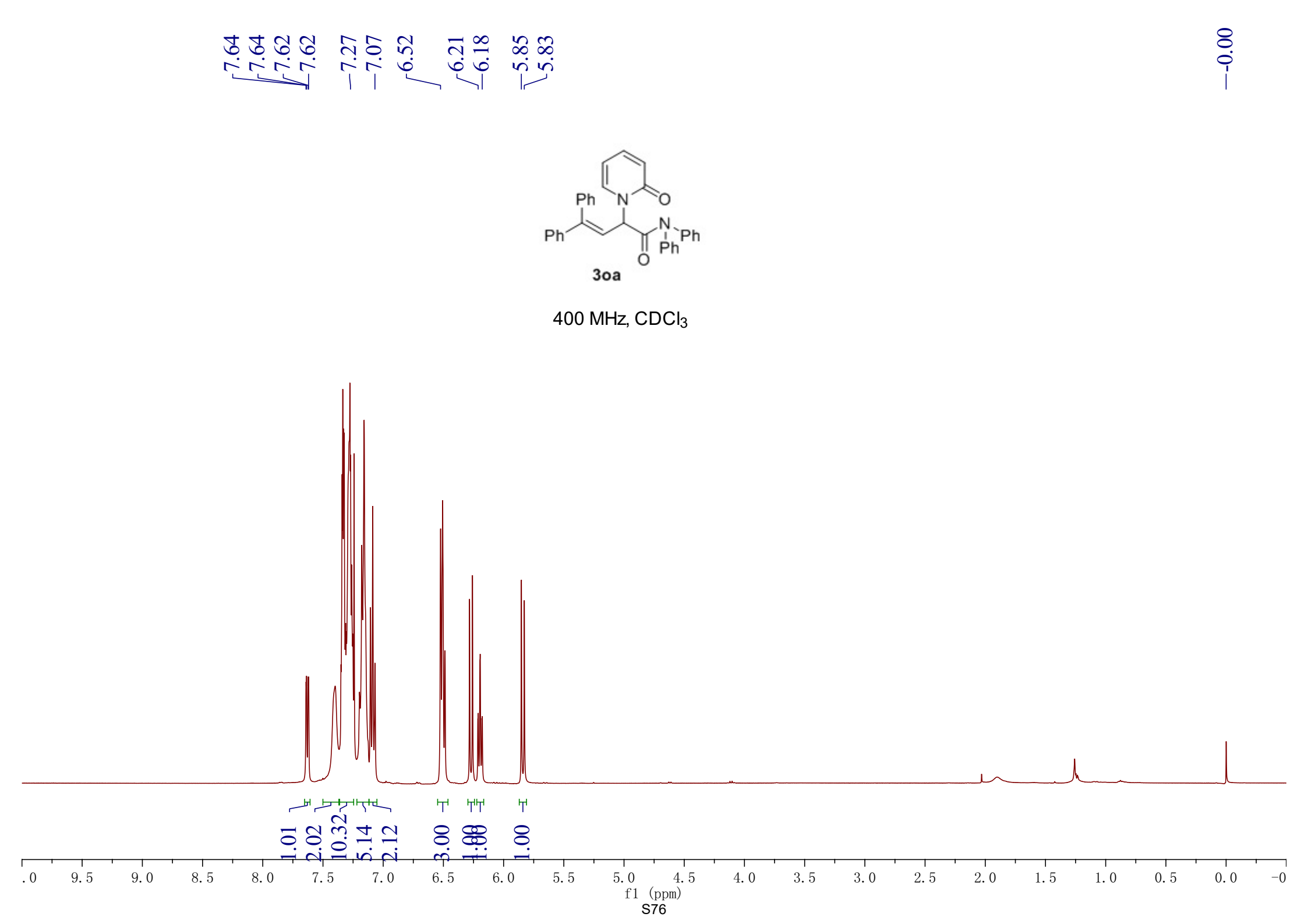
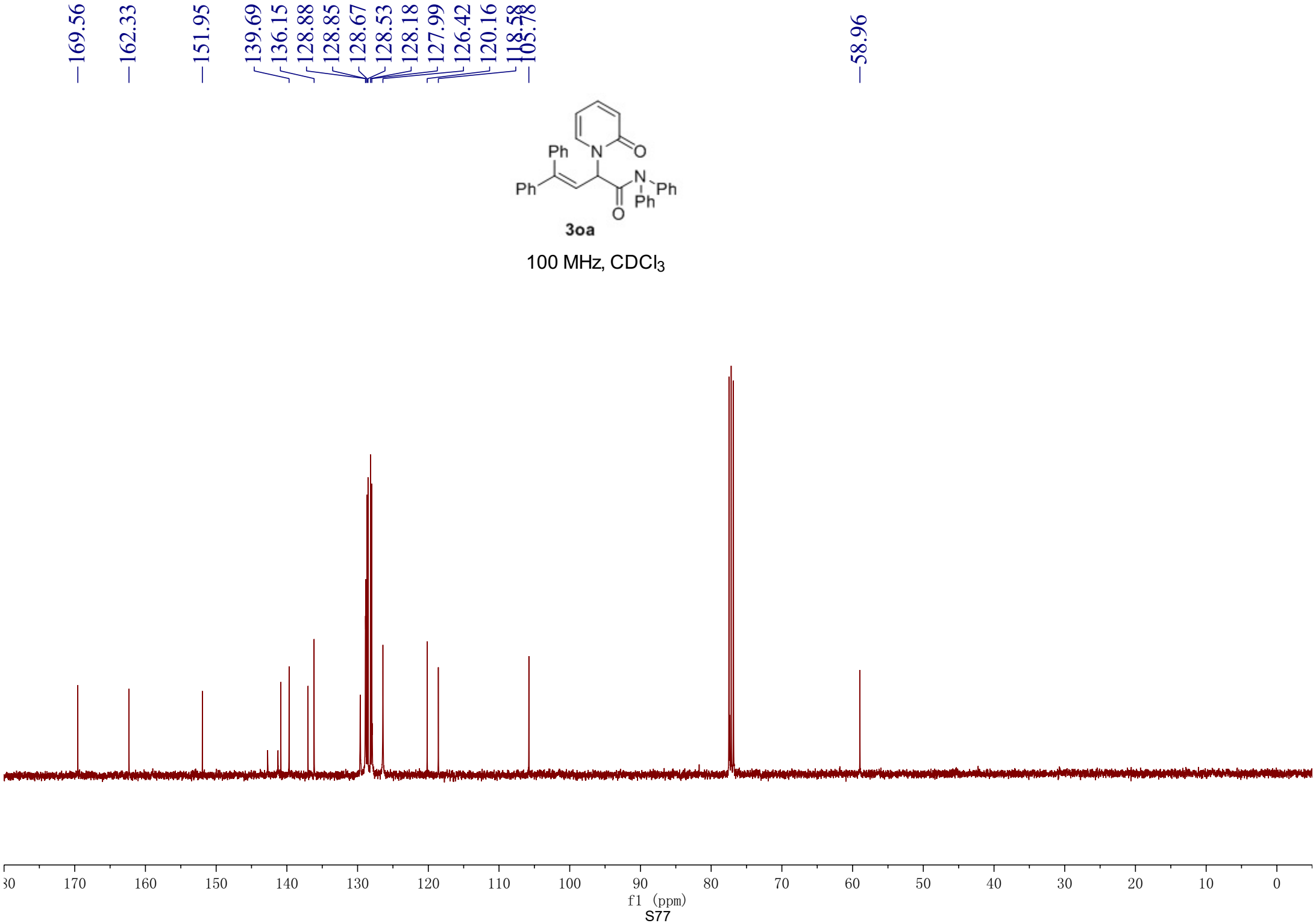
7.28
7.27
7.26
7.26
7.13
7.12
7.11
7.10
6.54
6.52
6.23
6.21
5.54
5.51
2.60
2.57
2.56
2.55
2.54
2.53
2.51
2.50
2.49
2.47
1.65
1.62
1.60
1.57
0.92
0.90
0.88
0.00
Ph
N
O
Ph
O
3ma
400 MHz, CDCl3
10.49
2.00
1.00
2.00
1.00
2.03
2.00
3.00
f1 (ppm)

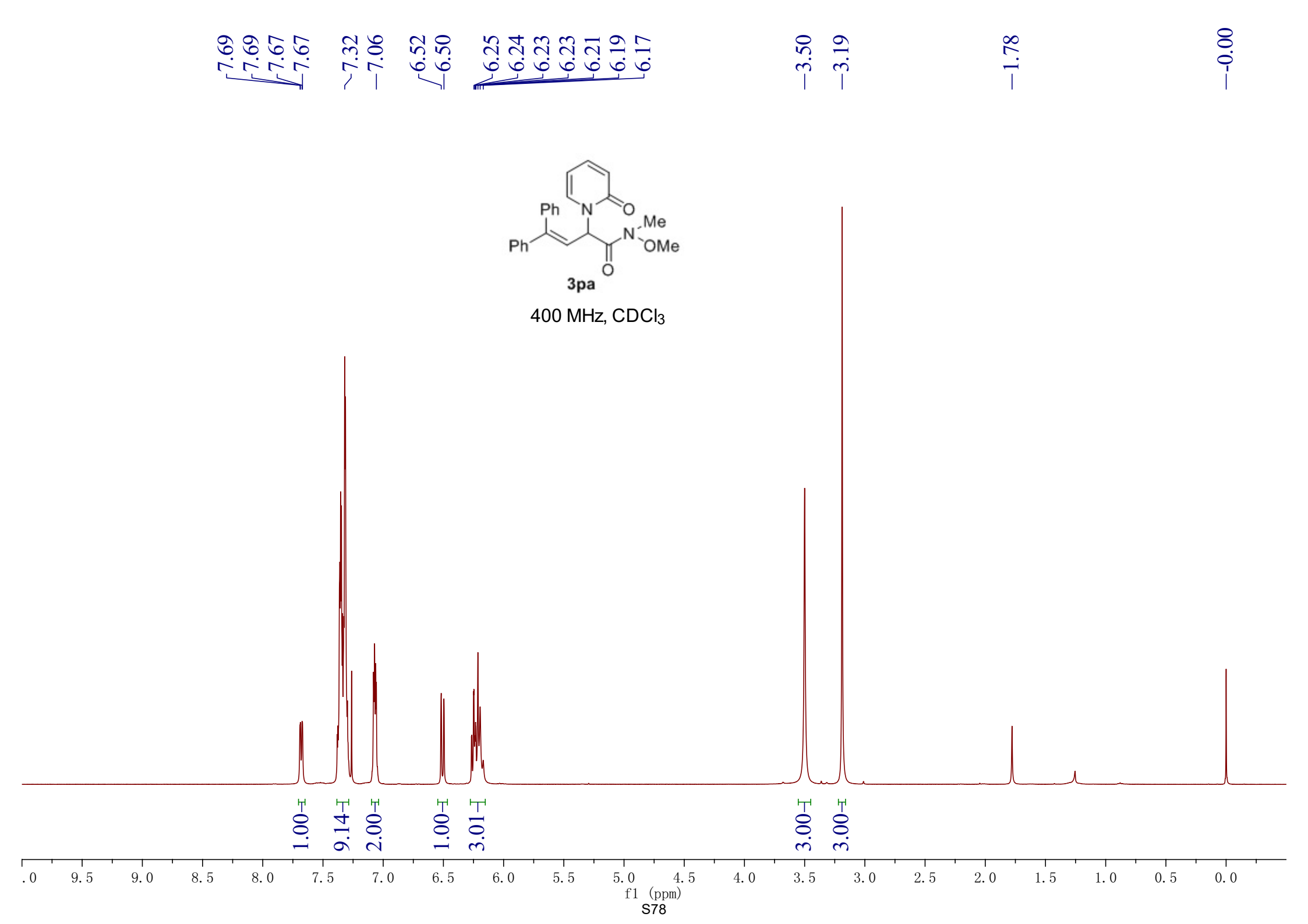

204.53
162.10
151.65
139.78
135.78
128.98
128.95
128.83
128.52
128.49
127.73
120.61
106.07
66.14
42.60
16.85
13.74
Ph
N
O
Ph
O
3ma
75 MHz, CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

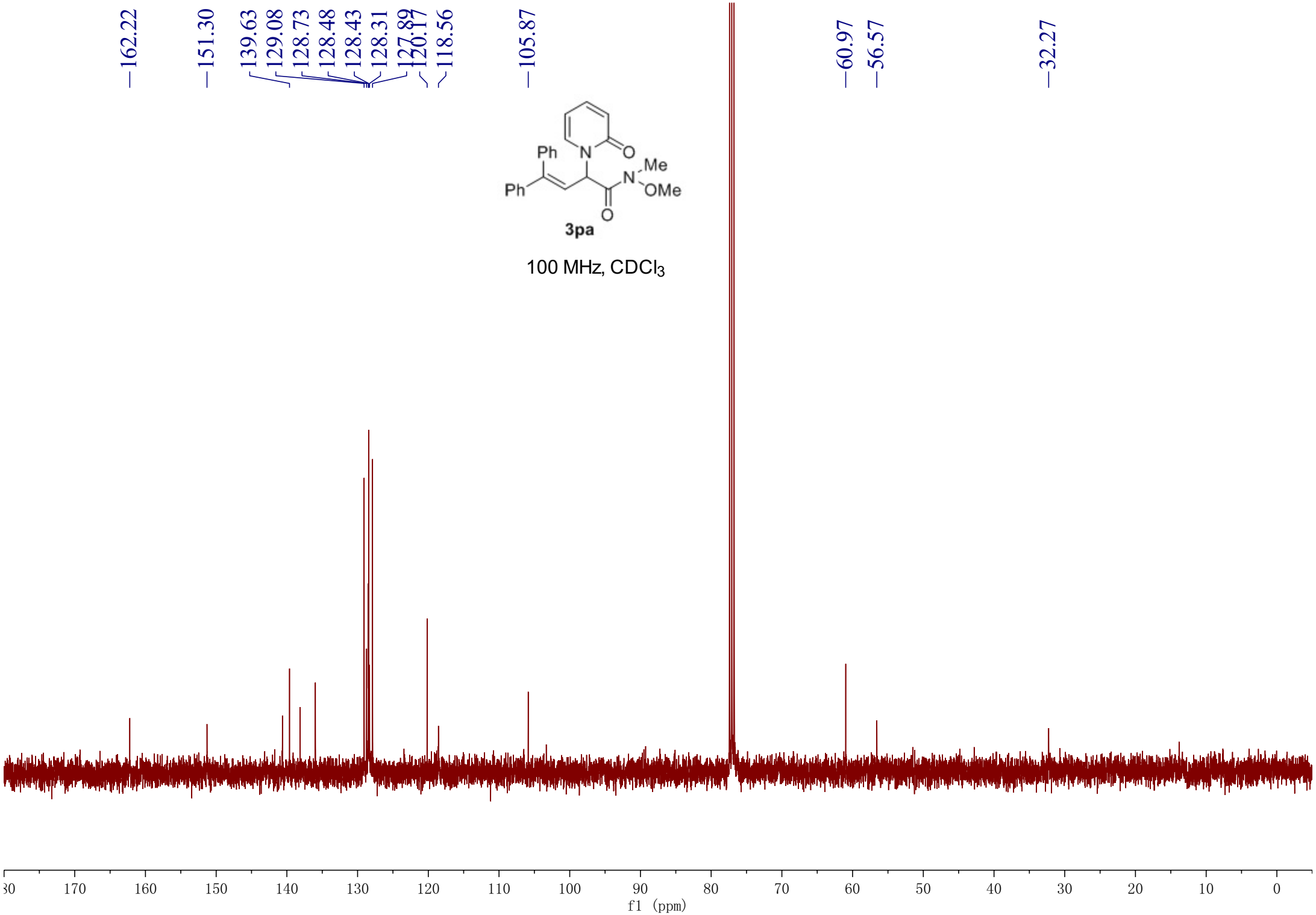

7.41
7.39
7.38
7.37
7.35
7.30
7.29
7.27
7.25
7.22
7.21
7.19
7.09
7.07
6.51
6.30
6.29
6.28
6.28
6.26
6.26
6.19
6.16
-0.00
Ph
N
O
Ph
Ph
O
3na
400 MHz, CDCl3
2.00
1.00
1.00
6.00
3.09
2.00
2.00
1.00
0.97
1.00
1.00
f1 (ppm)

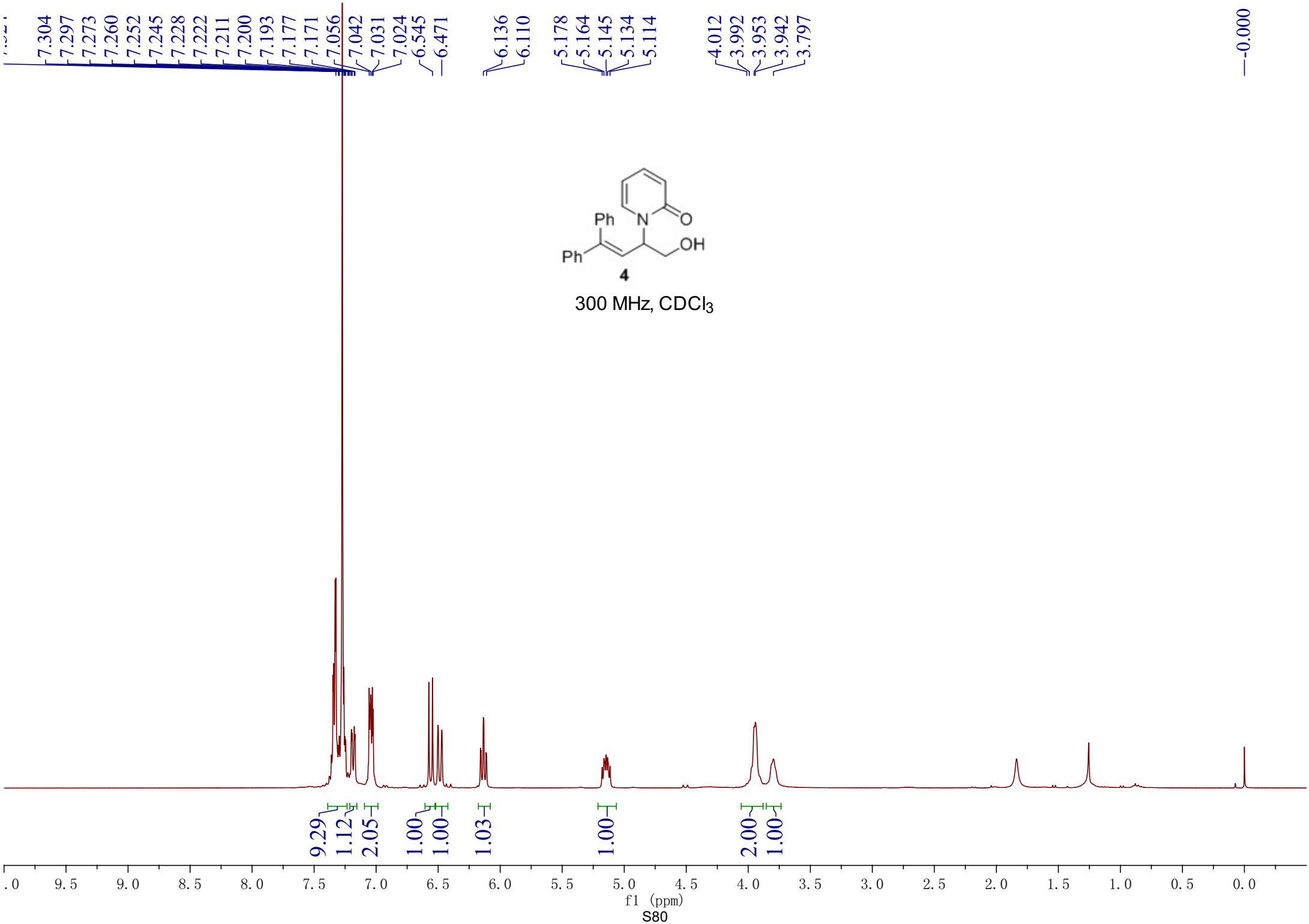

194.95
161.97
152.05
133.62
129.03
128.96
128.93
128.79
128.77
128.64
128.46
127.93
106.18
61.22
Ph
N
O
Ph
Ph
O
3na
100 MHz, CDCl3
f1 (ppm)

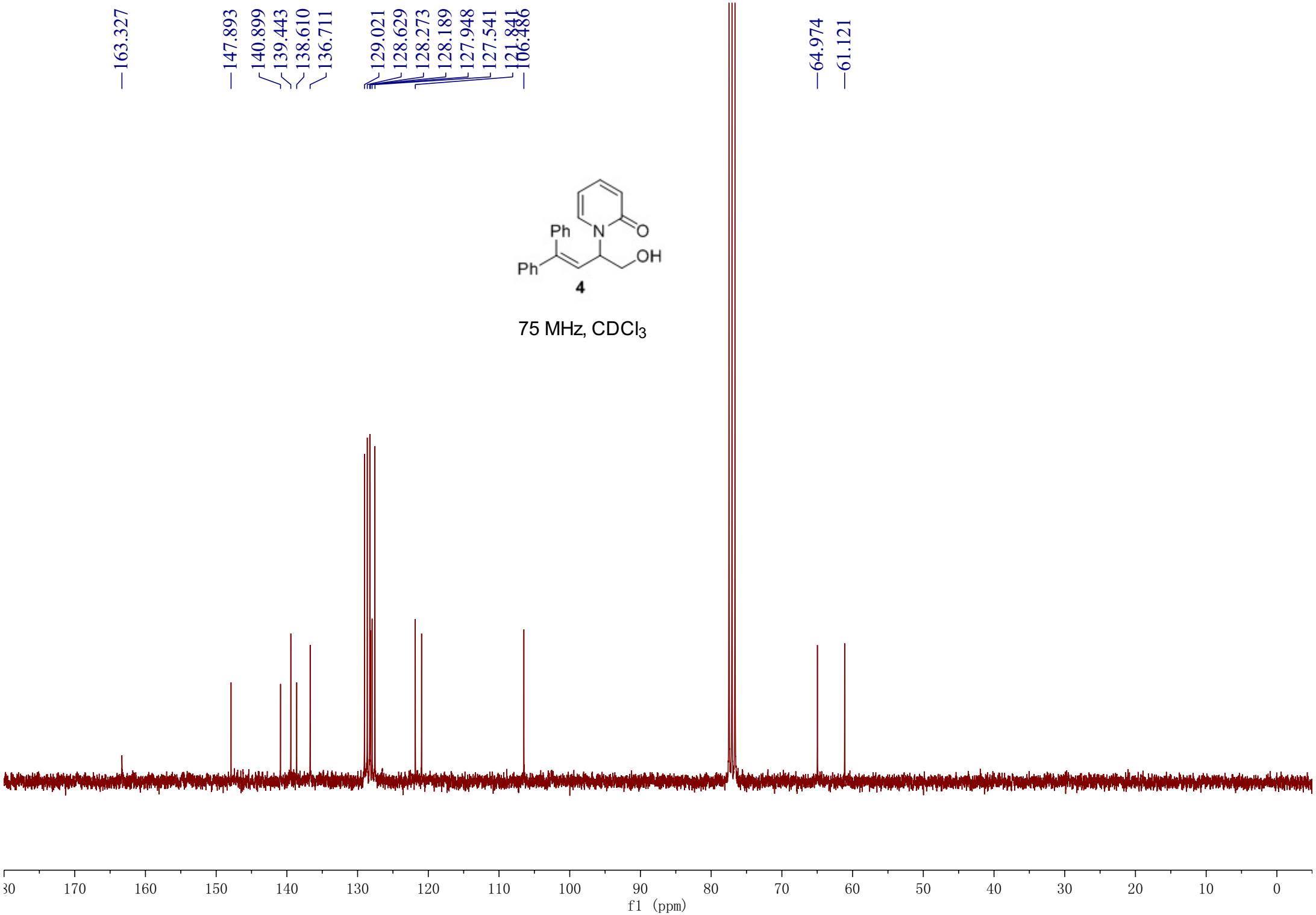

7.64
7.64
7.62
7.62
7.27
7.07
6.52
6.21
6.18
5.85
5.83
0.00
Ph
N
O
Ph
N
Ph
Ph
O
3oa
400 MHz, CDCl3
1.01
2.02
10.32
5.14
2.12
3.00
1.00
1.00
1.00
f1 (ppm)

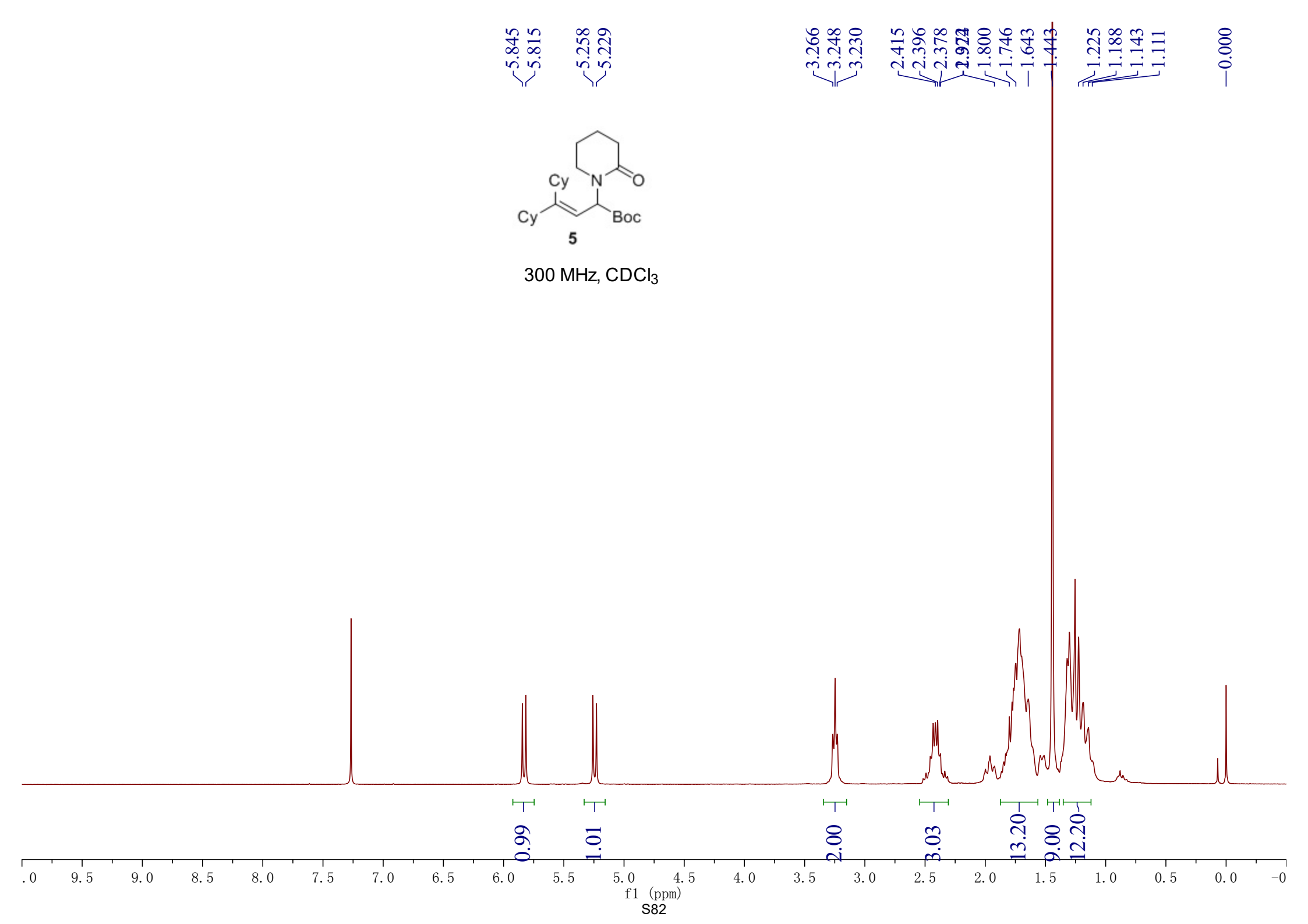

169.56
162.33
151.95
139.69
136.15
128.88
128.85
128.67
128.53
128.18
127.99
126.42
120.16
58.96
Ph
N
O
Ph
N
Ph
Ph
O
3oa
100 MHz, CDCl3
f1 (ppm)

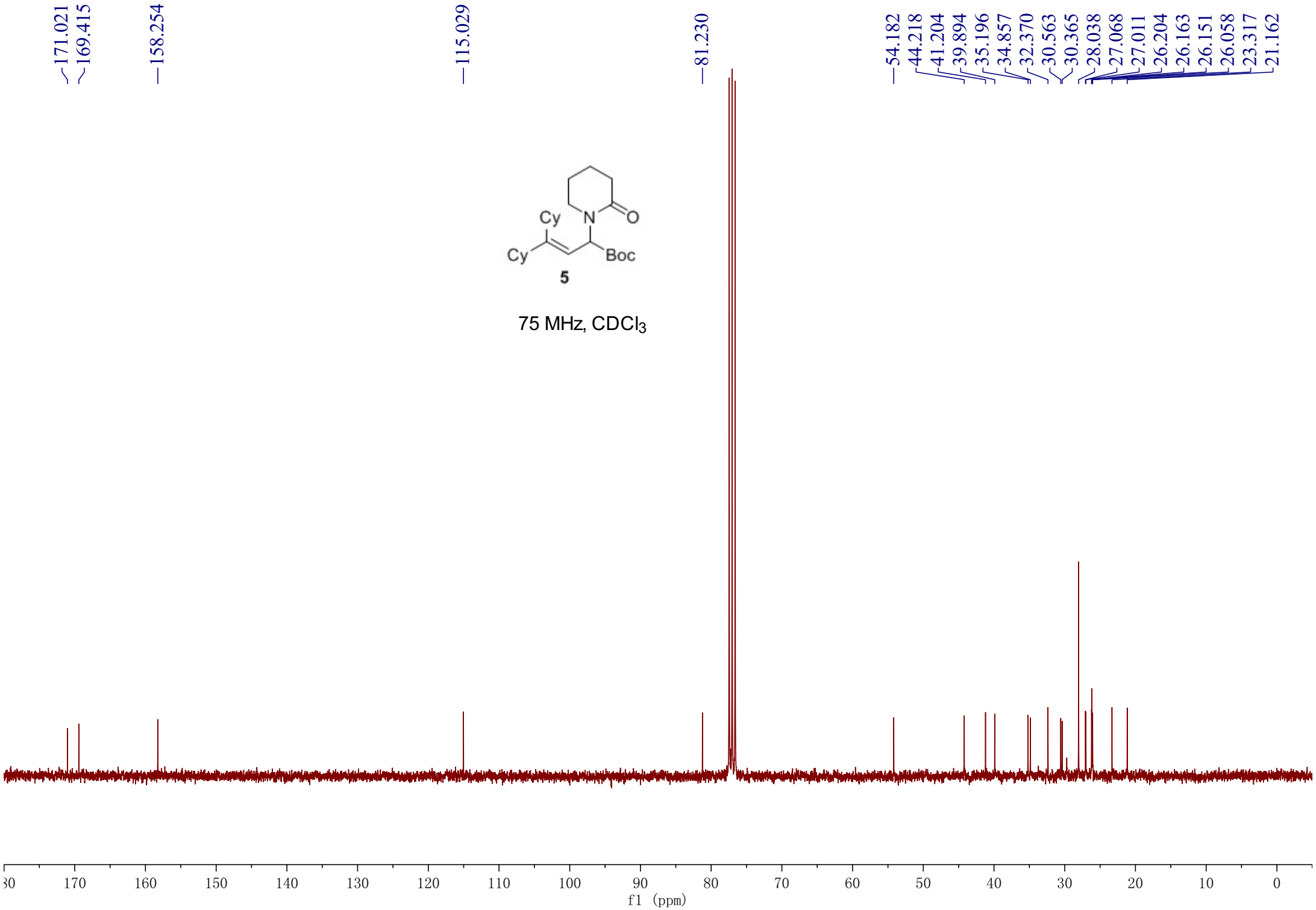

7.69
7.69
7.67
7.67
7.32
7.06
6.52
6.50
6.25
6.24
6.23
6.23
6.21
6.19
6.17
3.50
3.19
1.78
0.00
Ph
N
O
Me
N
OMe
Ph
O
3pa
400 MHz, CDCl3
1.00
9.14
2.00
1.00
3.01
3.00
3.00
f1 (ppm)

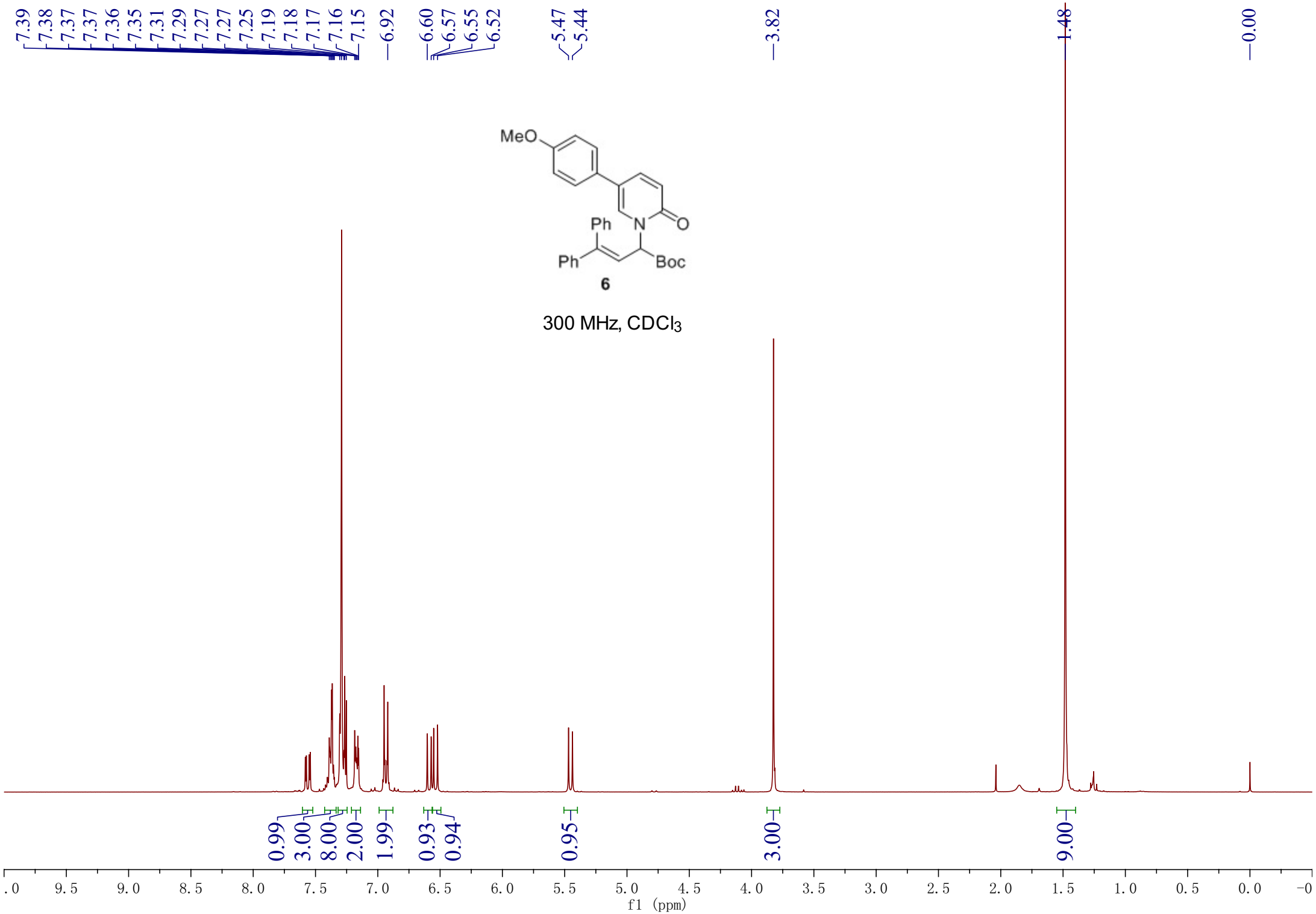

162.22
151.30
139.63
129.08
128.73
128.48
128.43
128.31
127.89
127.17
120.17
118.56
105.87
60.97
56.57
32.27
Ph
N
O
Me
N
OMe
Ph
O
3pa
100 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

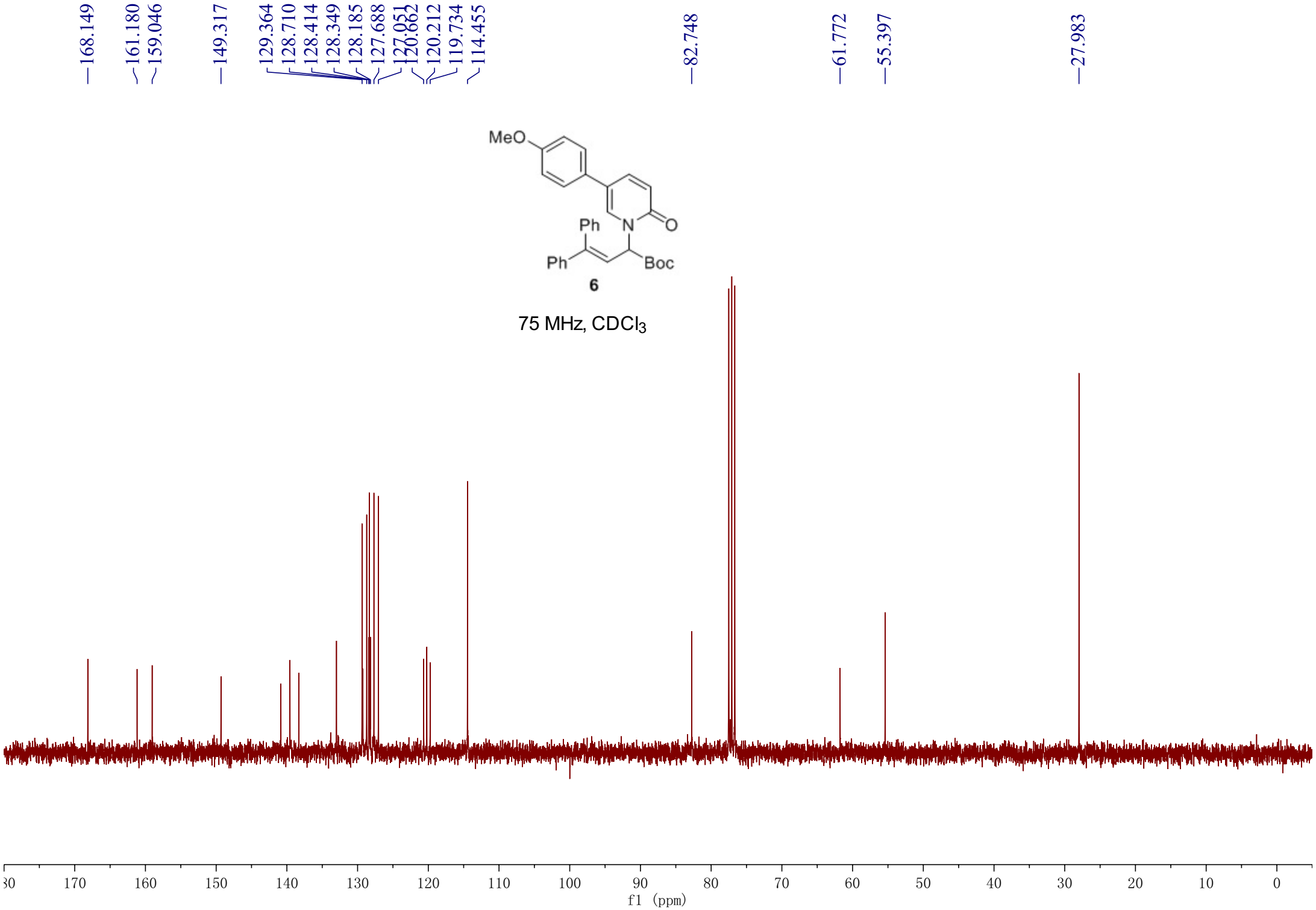

7.304
7.297
7.273
7.260
7.252
7.245
7.228
7.222
7.211
7.200
7.193
7.177
7.171
7.056
7.042
7.031
7.024
6.545
6.471
6.136
6.110
5.178
5.164
5.145
5.134
5.114
4.012
3.992
3.953
3.942
3.797
-0.000
Ph
N
O
OH
Ph
4
300 MHz, CDCl3
9.29
1.12
2.05
1.00
1.00
1.03
1.00
2.00
1.00
f1 (ppm)


163.327
147.893
140.899
139.443
138.610
136.711
129.021
128.629
128.273
128.189
127.948
127.541
121.841
106.486
64.974
61.121
Ph
N
O
OH
Ph
4
75 MHz, CDCl3
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

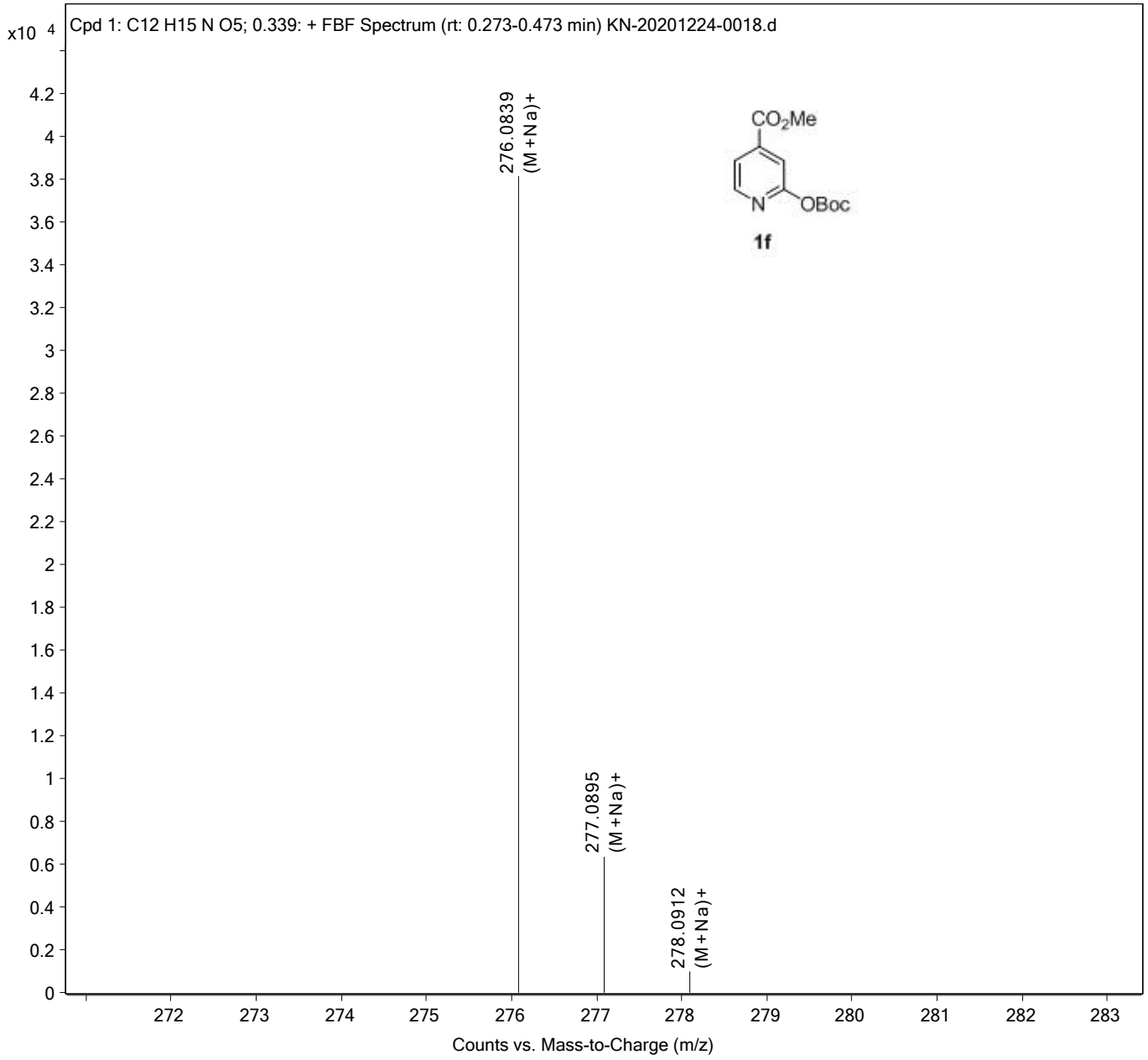

5.845
5.815
5.258
5.229
3.266
3.248
3.230
2.415
2.396
2.378
1.800
1.746
1.643
1.443
1.225
1.188
1.143
1.111
0.000
Cy
N
O
Cy
Boc
5
300 MHz, CDCl3
0.99
1.01
2.00
3.03
13.20
9.00
12.20
f1 (ppm)


171.021
169.415
158.254
115.029
81.230
54.182
44.218
41.204
39.894
35.196
34.857
32.370
30.563
30.365
28.038
27.068
27.011
26.204
26.163
26.151
26.058
23.317
21.162
Cy
N
O
Cy
Boc
5
75 MHz, CDCl3
f1 (ppm)

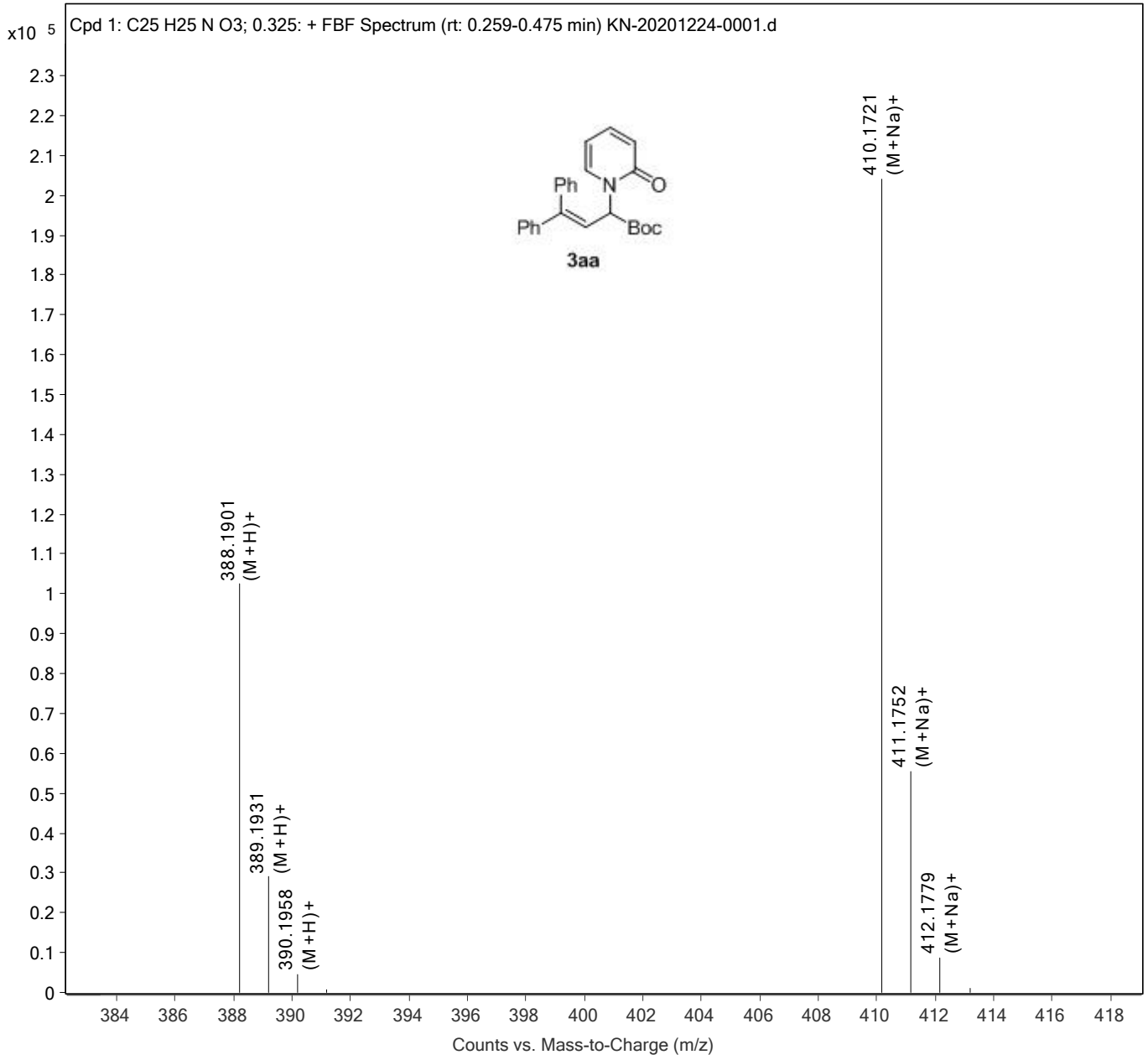

7.39
7.38
7.37
7.37
7.36
7.35
7.31
7.29
7.27
7.27
7.25
7.19
7.18
7.17
7.16
7.15
6.92
6.60
6.57
6.55
6.52
5.47
5.44
3.82
1.48
0.00
MeO
Ph
N
O
Ph
Boc
6
300 MHz, CDCl3
0.99
3.00
8.00
2.00
1.99
0.93
0.94
0.95
3.00
9.00
f1 (ppm)


168.149
161.180
159.046
149.317
129.364
128.710
128.414
128.349
128.185
127.688
127.051
120.862
120.212
119.734
114.455
82.748
61.772
55.397
27.983
MeO
Ph
N
O
Ph
Boc
6
75 MHz, CDCl3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

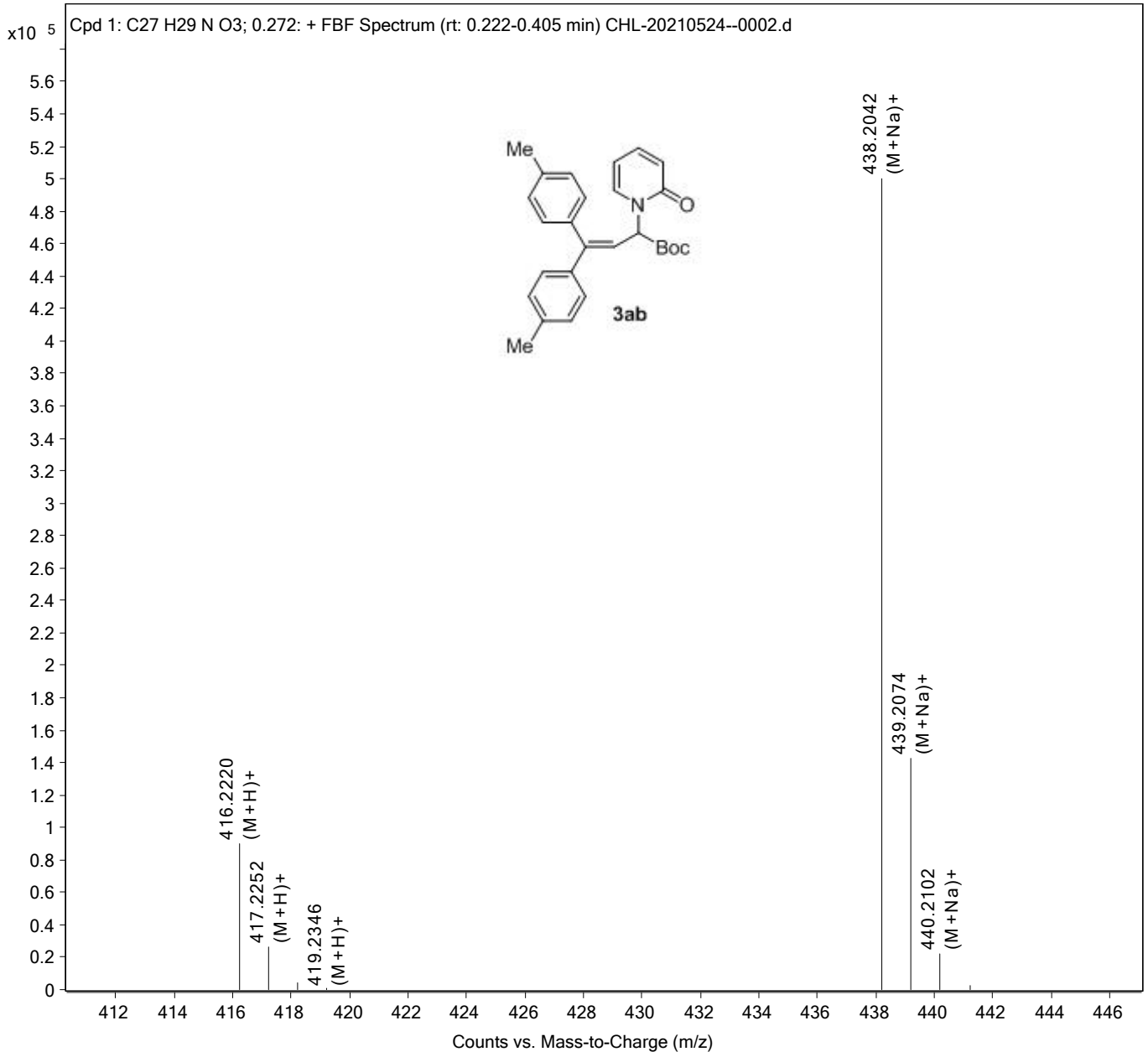
Sample Name	Sample62	**Position**	P1-F7	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0018.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:44:53 PM (UTC+08:00)



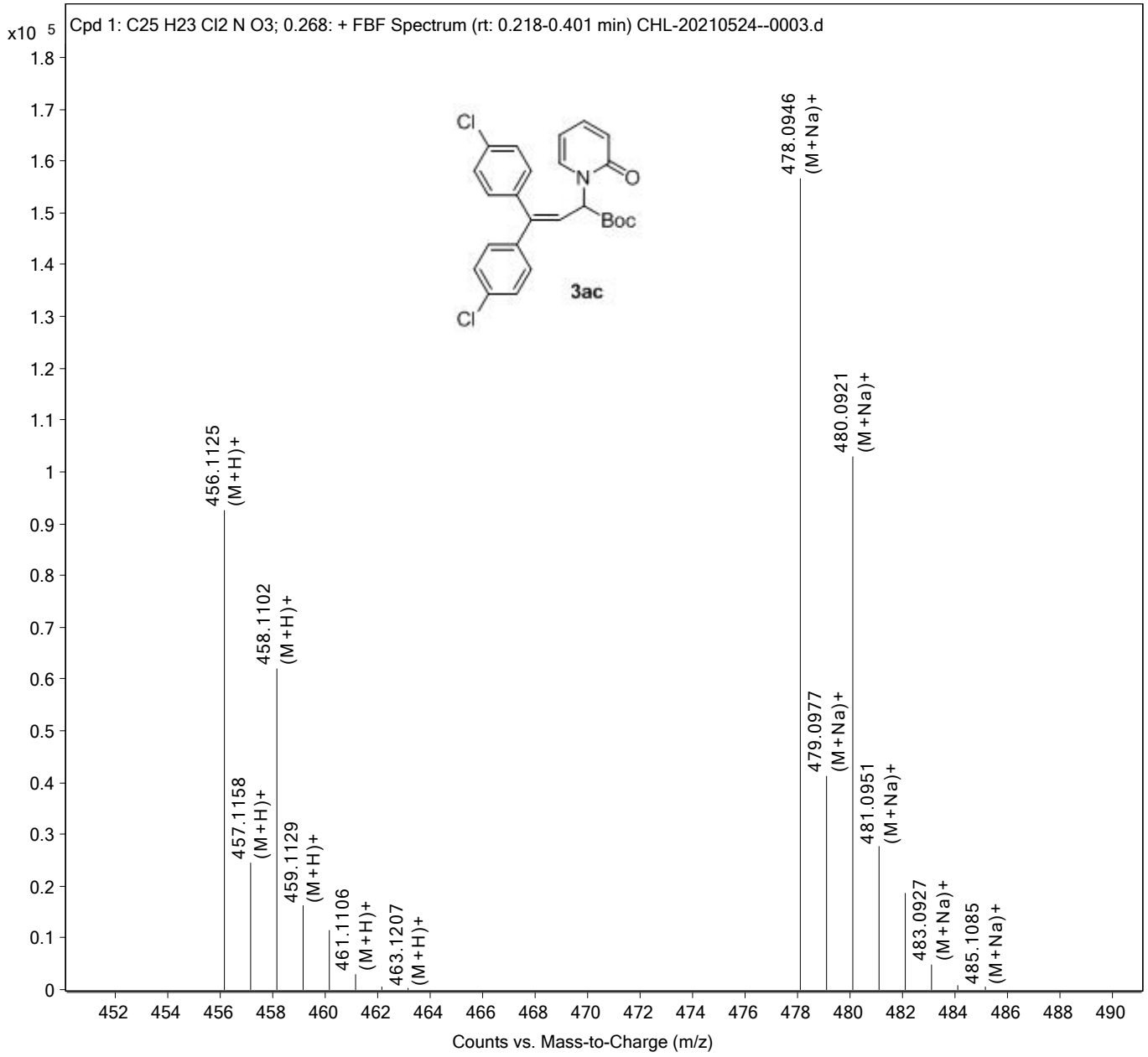
Sample Name	Sample45	**Position**	P1-E1	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0001.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:16:08 PM (UTC+08:00)



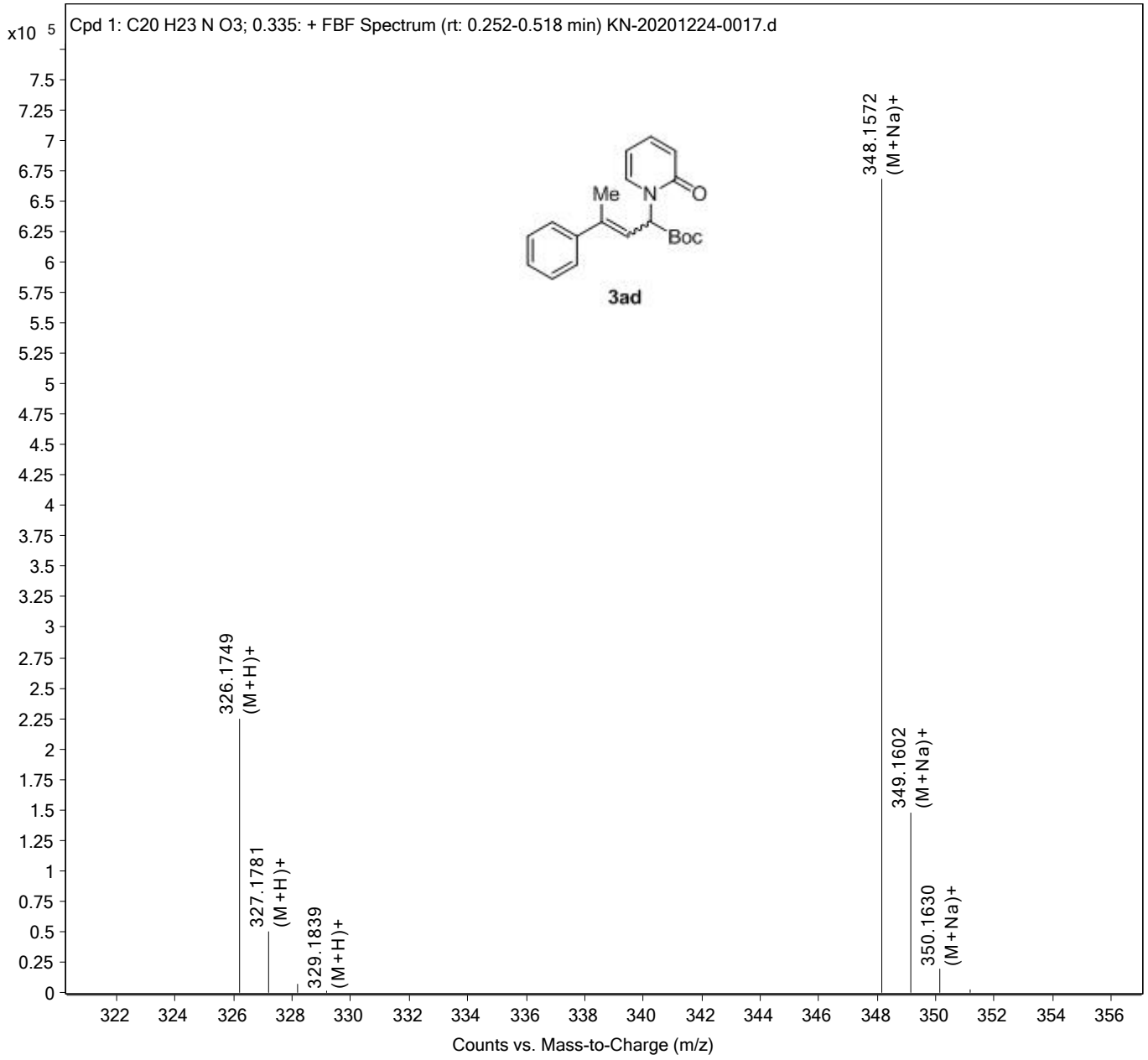
Sample Name	Sample12	**Position**	P2-B2	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0002.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:33:27 AM (UTC+08:00)



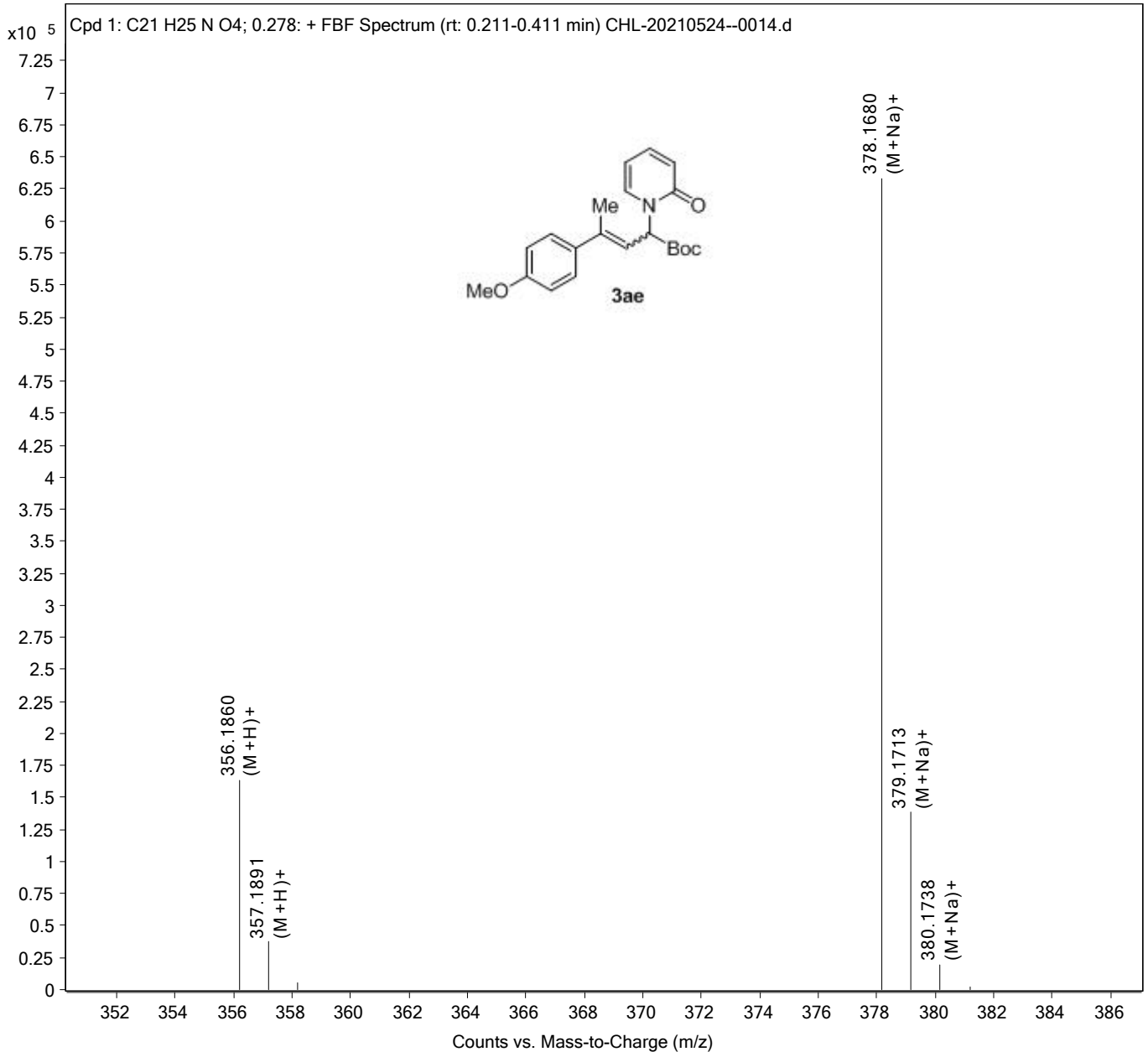
Sample Name	Sample13	**Position**	P2-B3	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0003.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:35:04 AM (UTC+08:00)



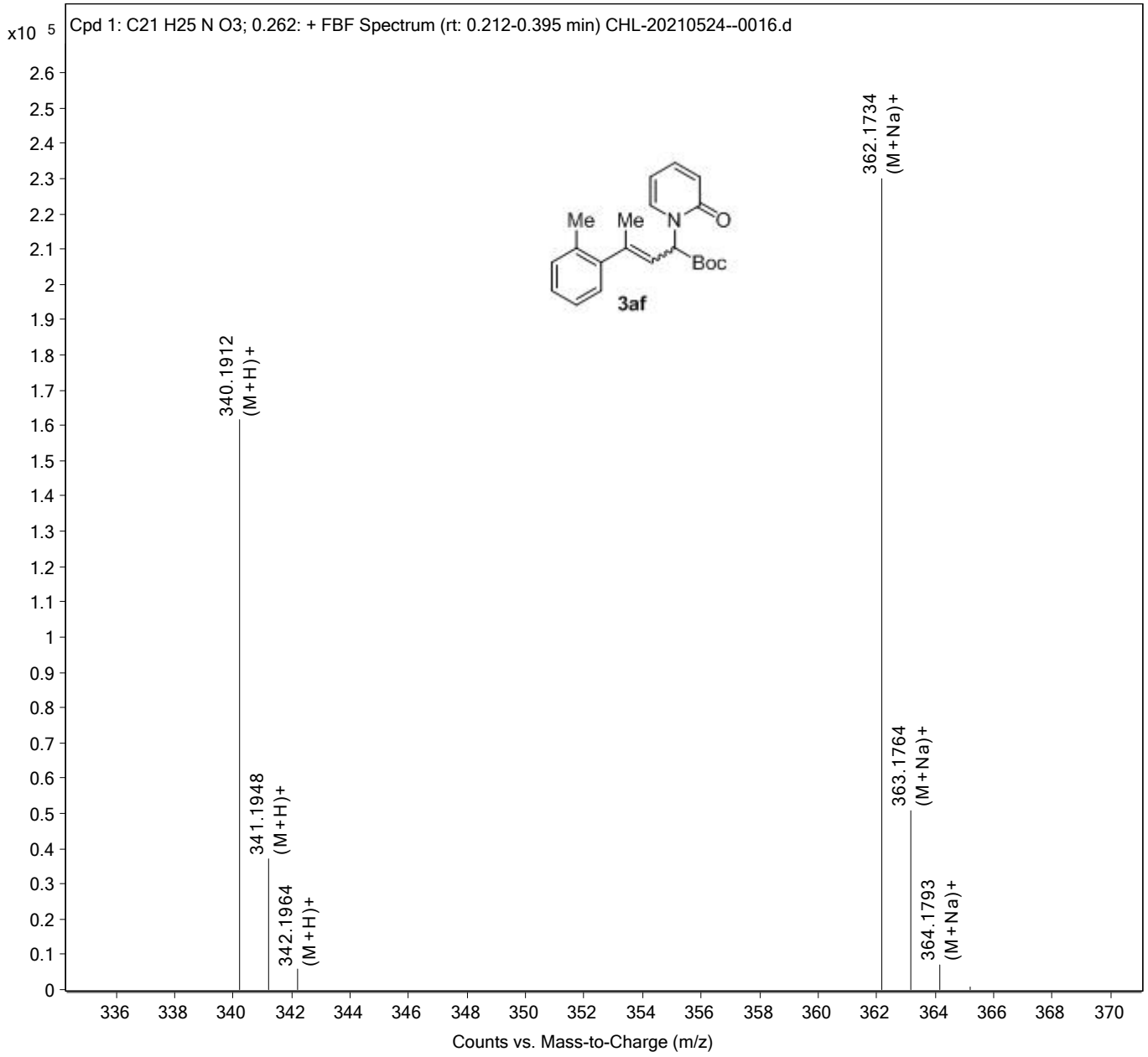
Sample Name	Sample61	**Position**	P1-F6	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0017.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:43:13 PM (UTC+08:00)



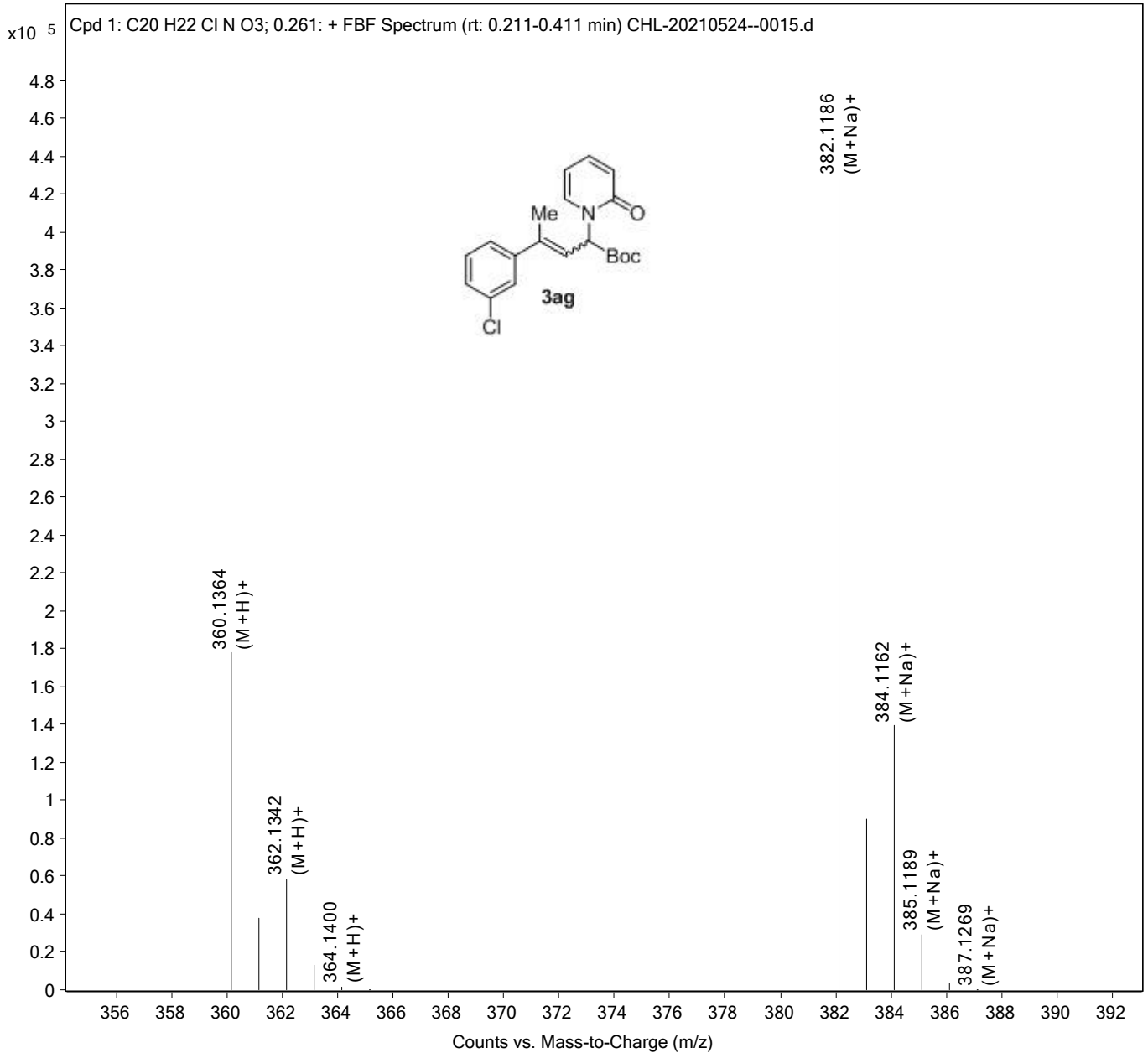
Sample Name	Sample24	**Position**	P2-C3	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0014.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:52:54 AM (UTC+08:00)



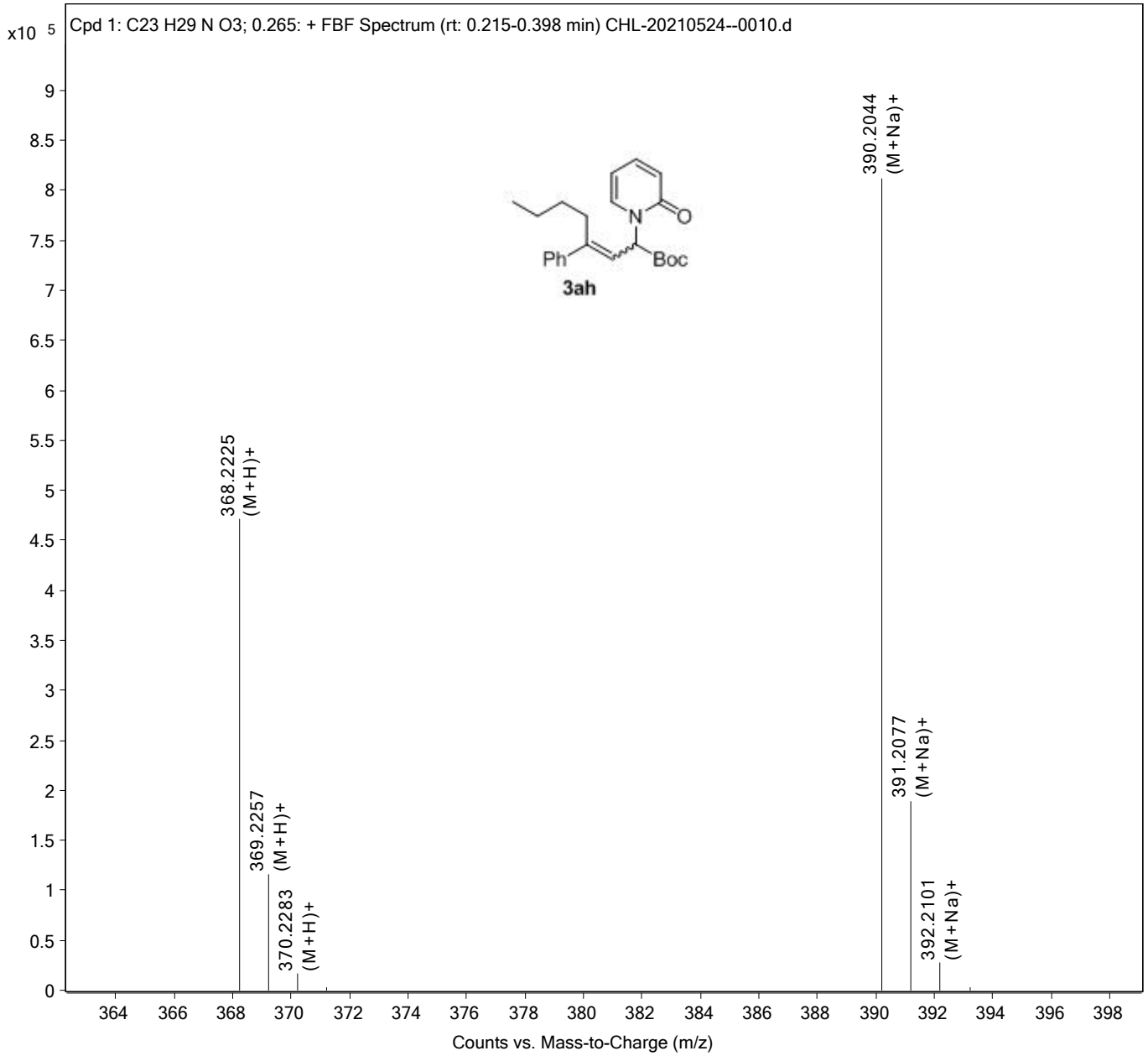
Sample Name	Sample26	**Position**	P2-C5	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0016.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:56:08 AM (UTC+08:00)



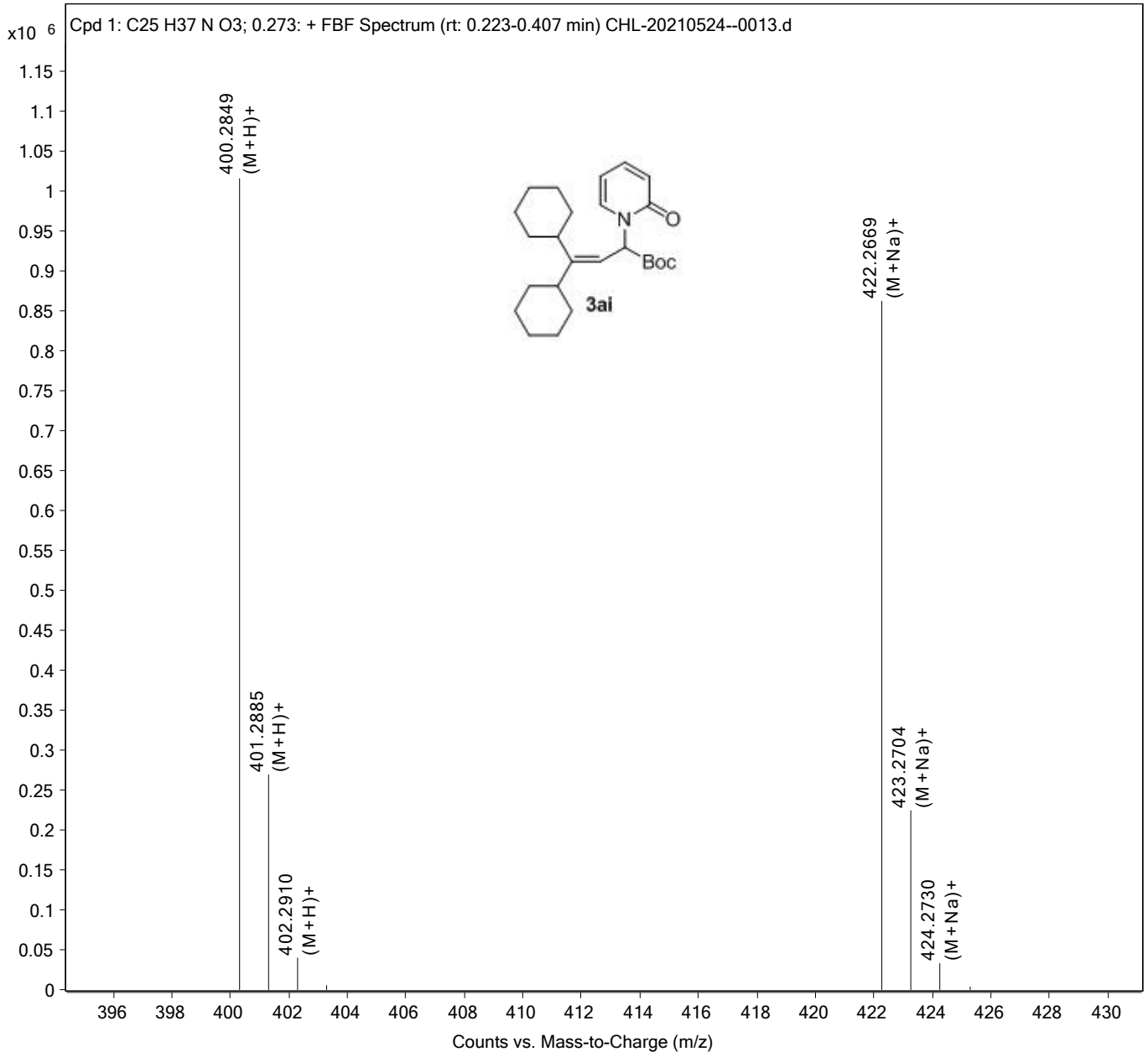
Sample Name	Sample25	**Position**	P2-C4	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0015.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:54:31 AM (UTC+08:00)



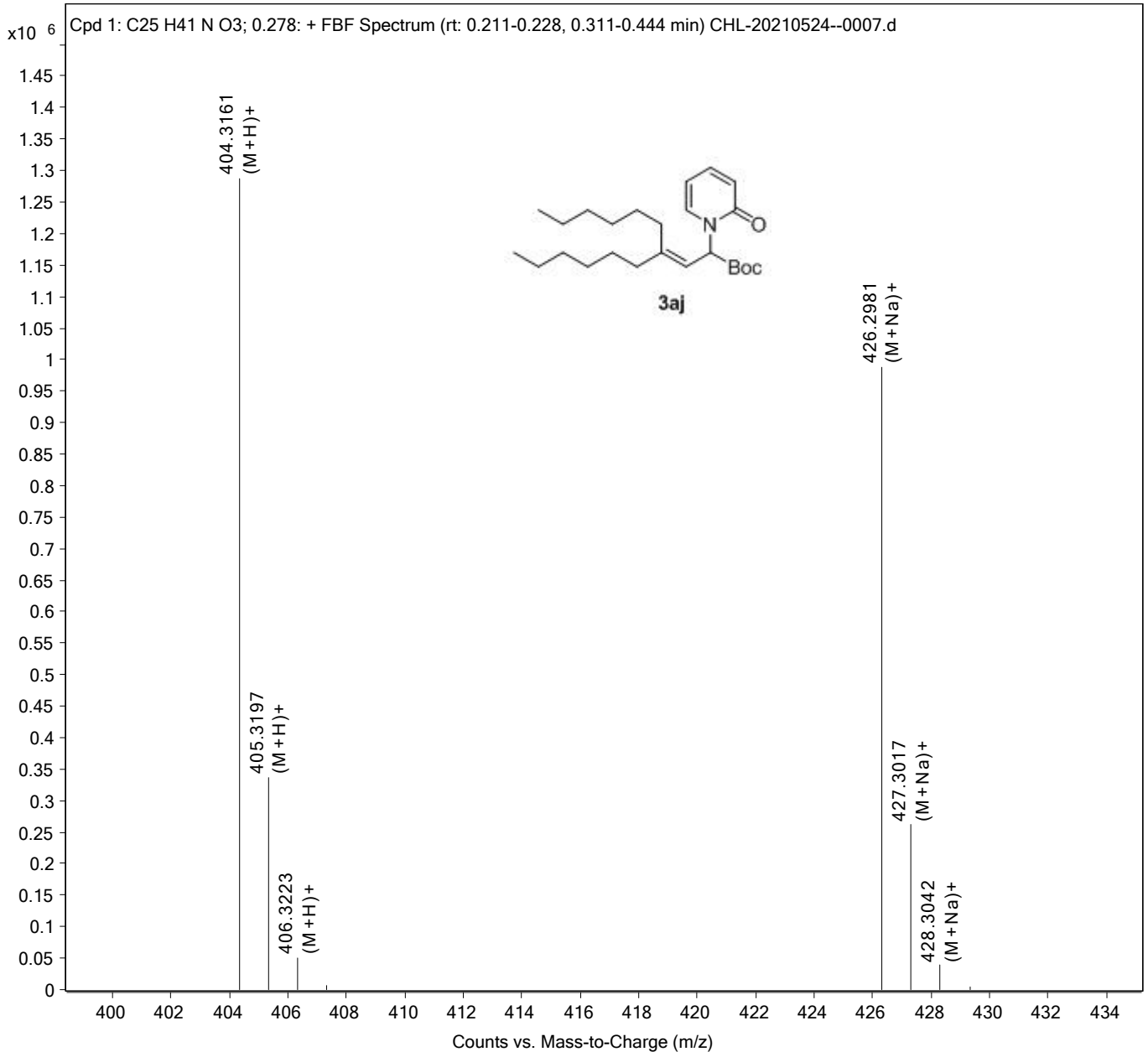
Sample Name	Sample20	**Position**	P2-B10	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0010.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:46:22 AM (UTC+08:00)



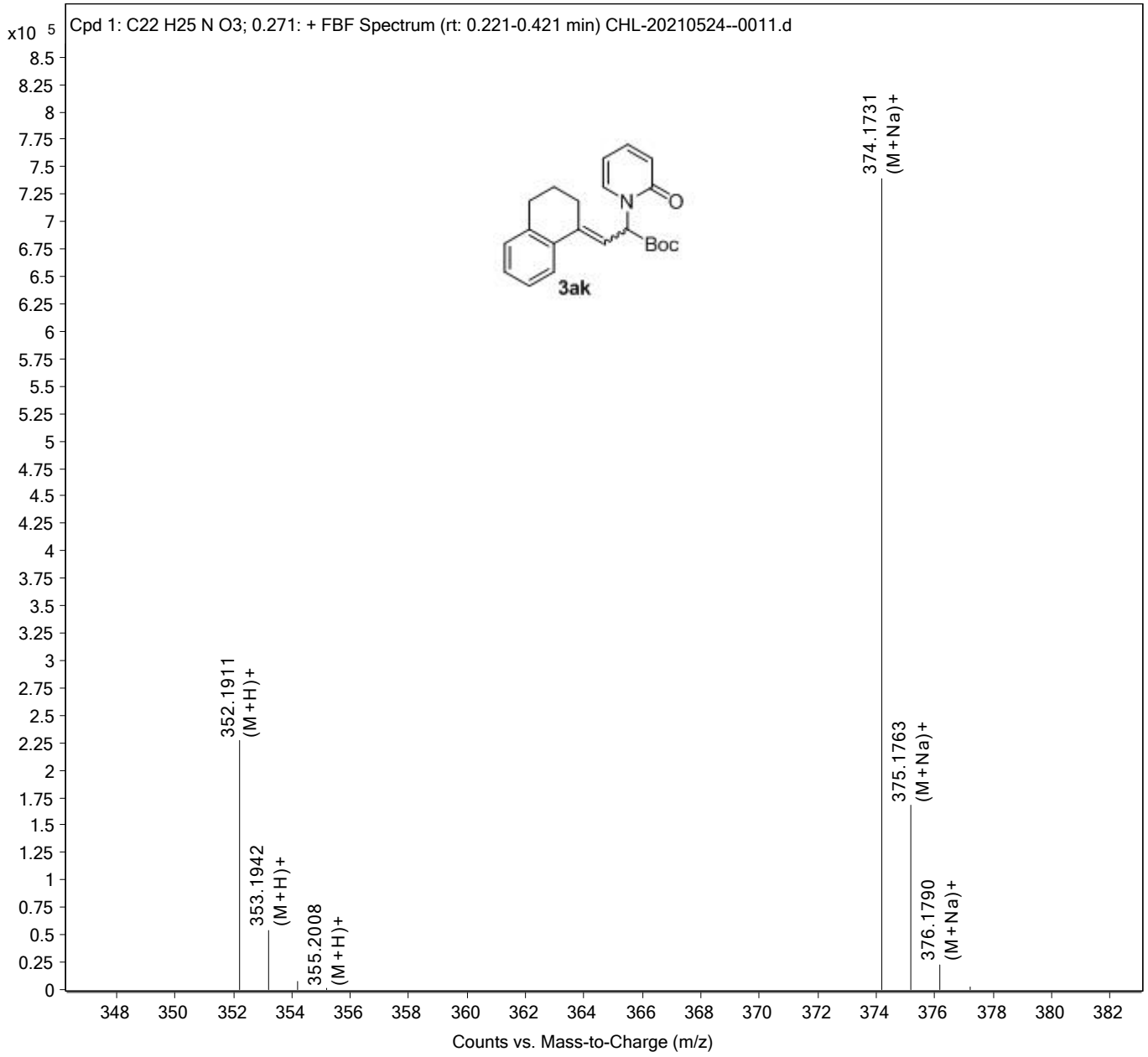
Sample Name	Sample23	**Position**	P2-C2	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0013.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:51:17 AM (UTC+08:00)



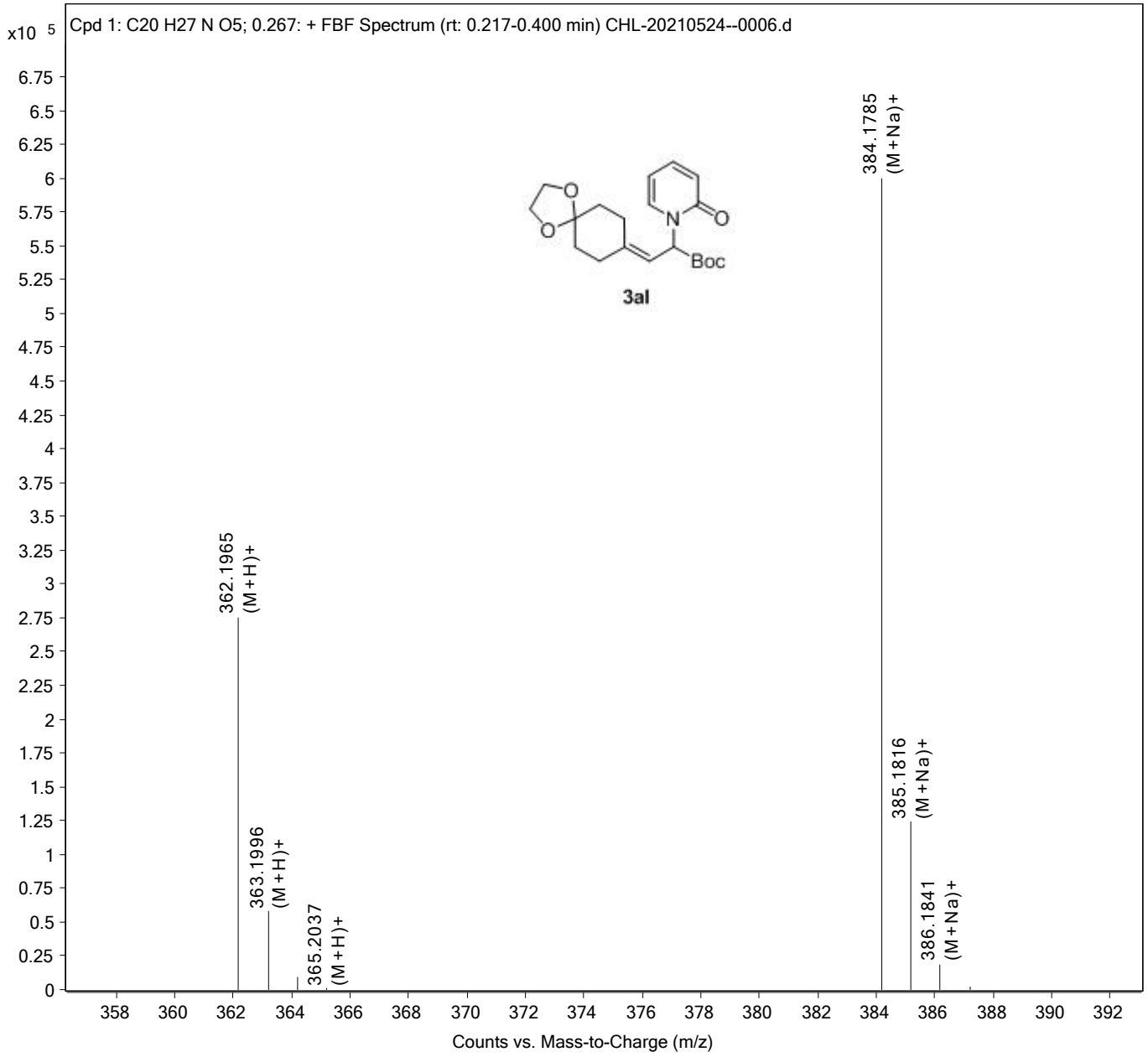
Sample Name	Sample17	**Position**	P2-B7	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0007.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:41:32 AM (UTC+08:00)



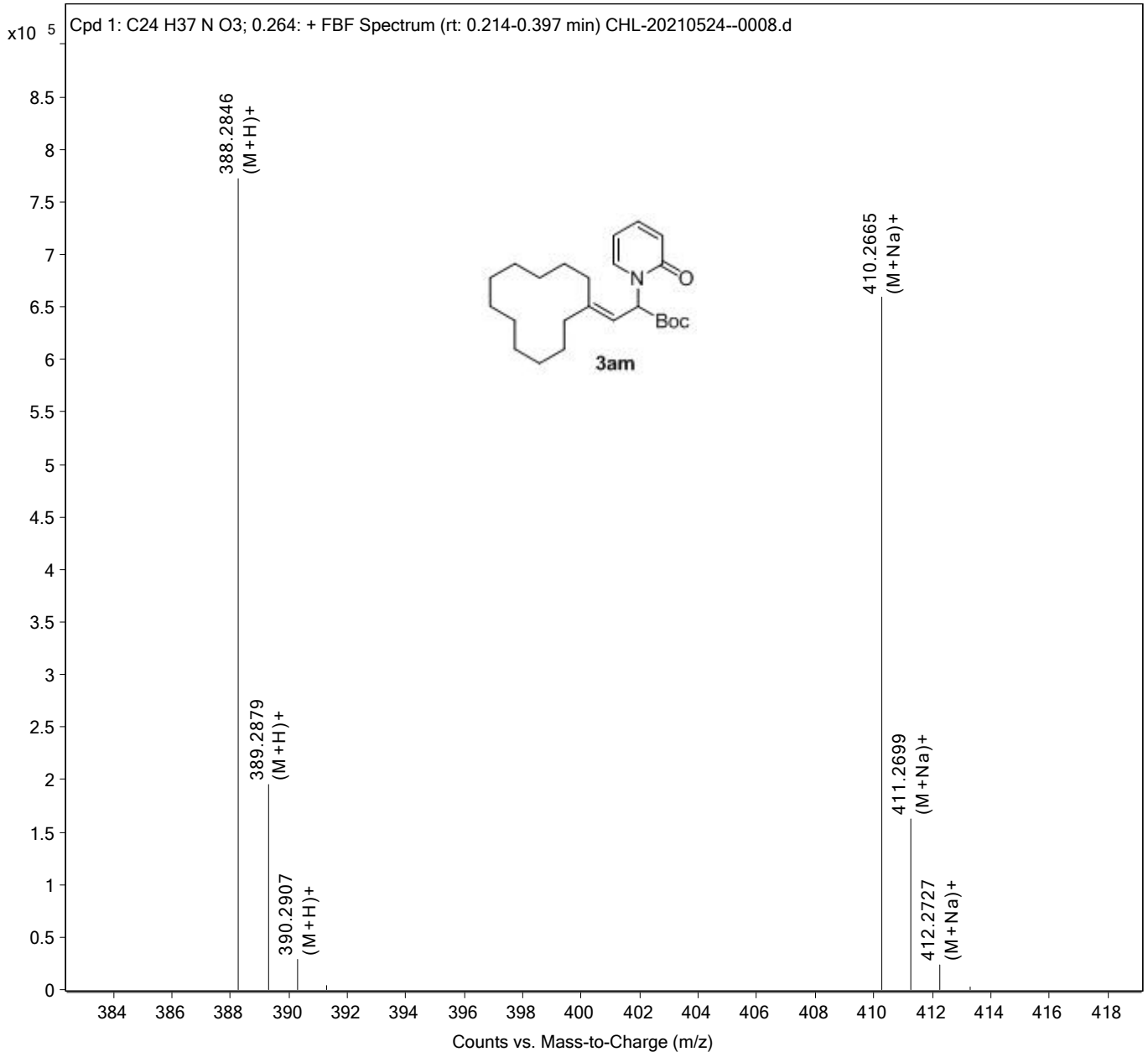
Sample Name	Sample21	**Position**	P2-B11	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0011.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:47:59 AM (UTC+08:00)



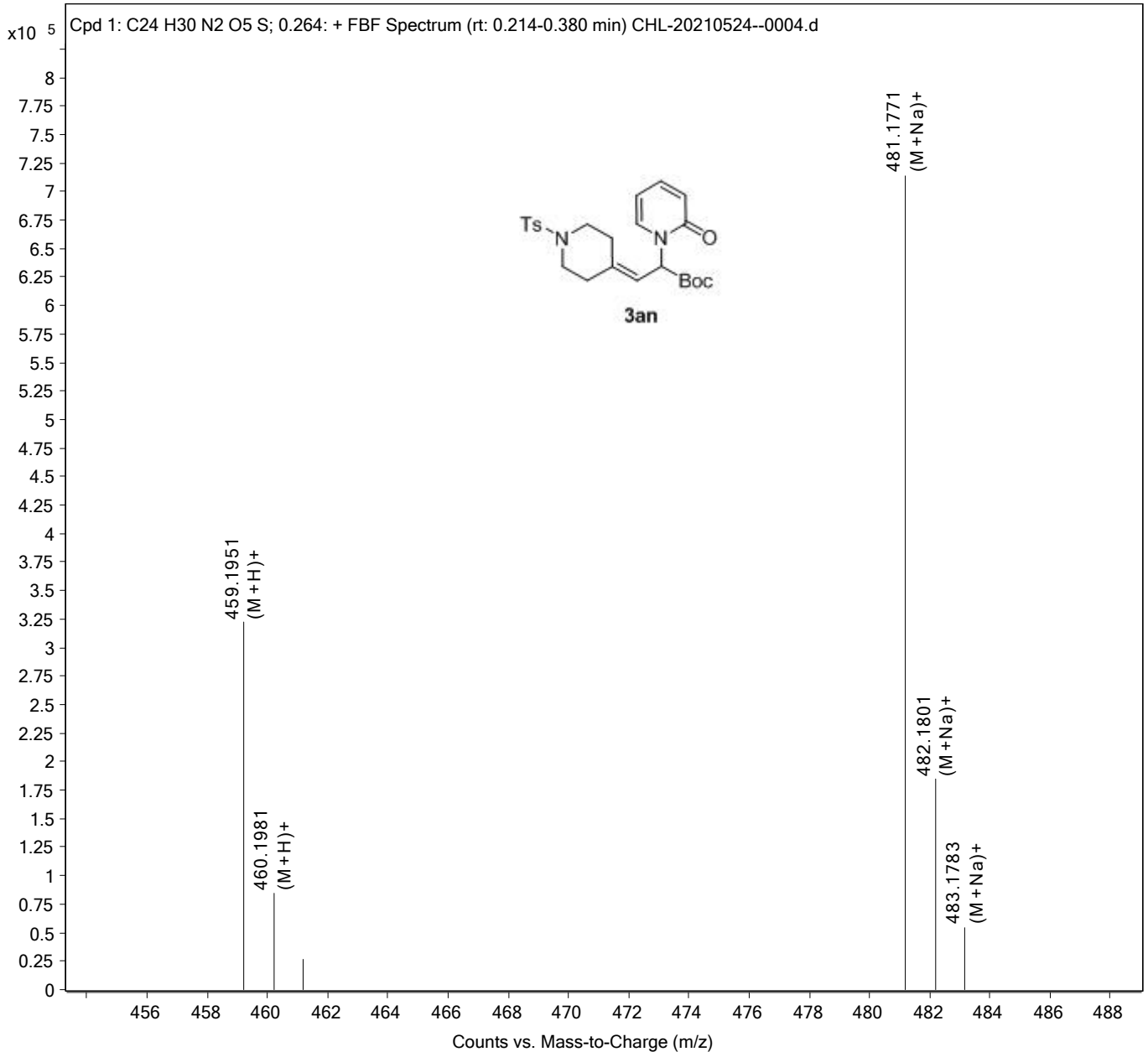
Sample Name	Sample16	**Position**	P2-B6	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0006.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:39:55 AM (UTC+08:00)



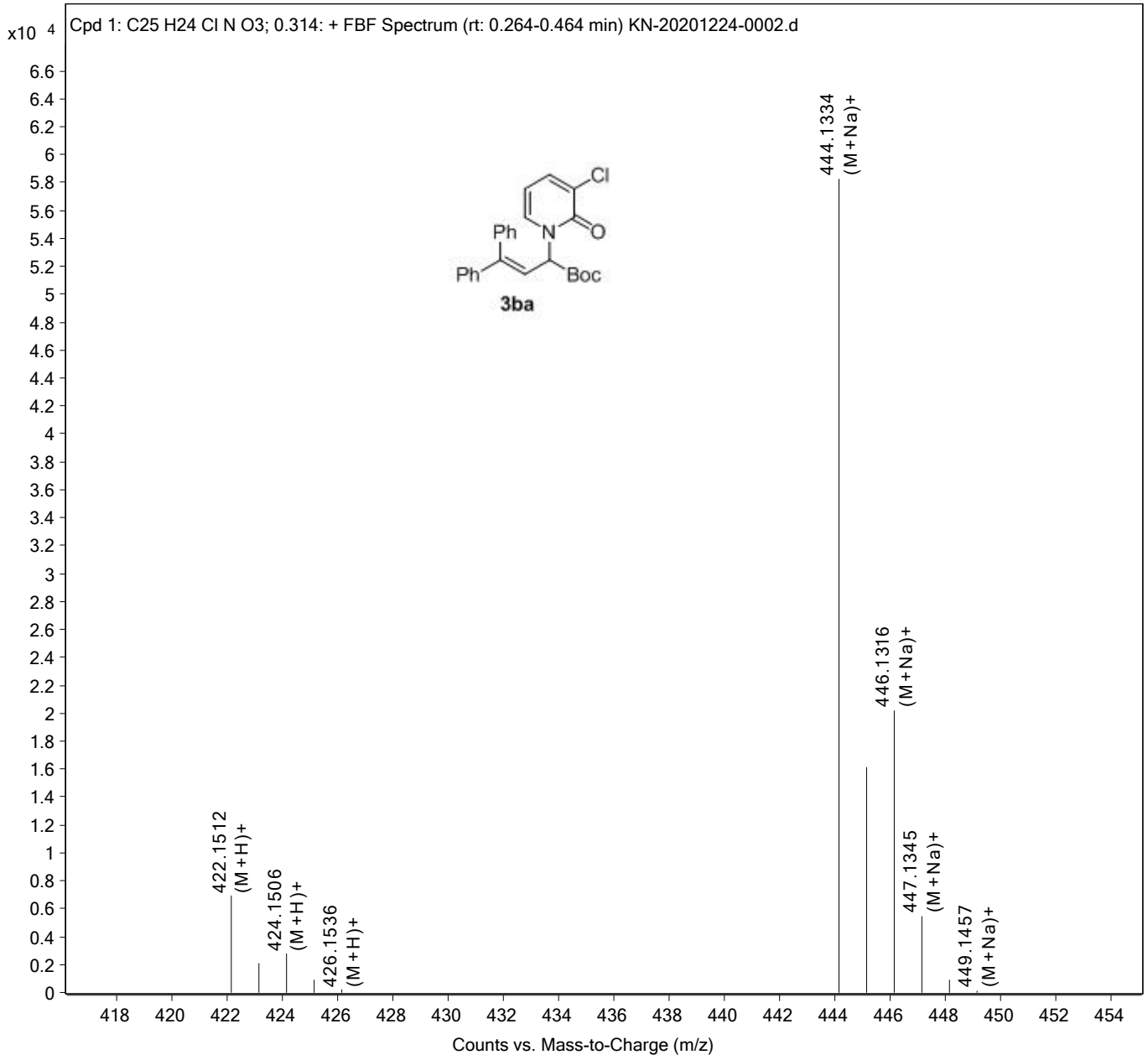
Sample Name	Sample18	**Position**	P2-B8	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0008.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:43:09 AM (UTC+08:00)



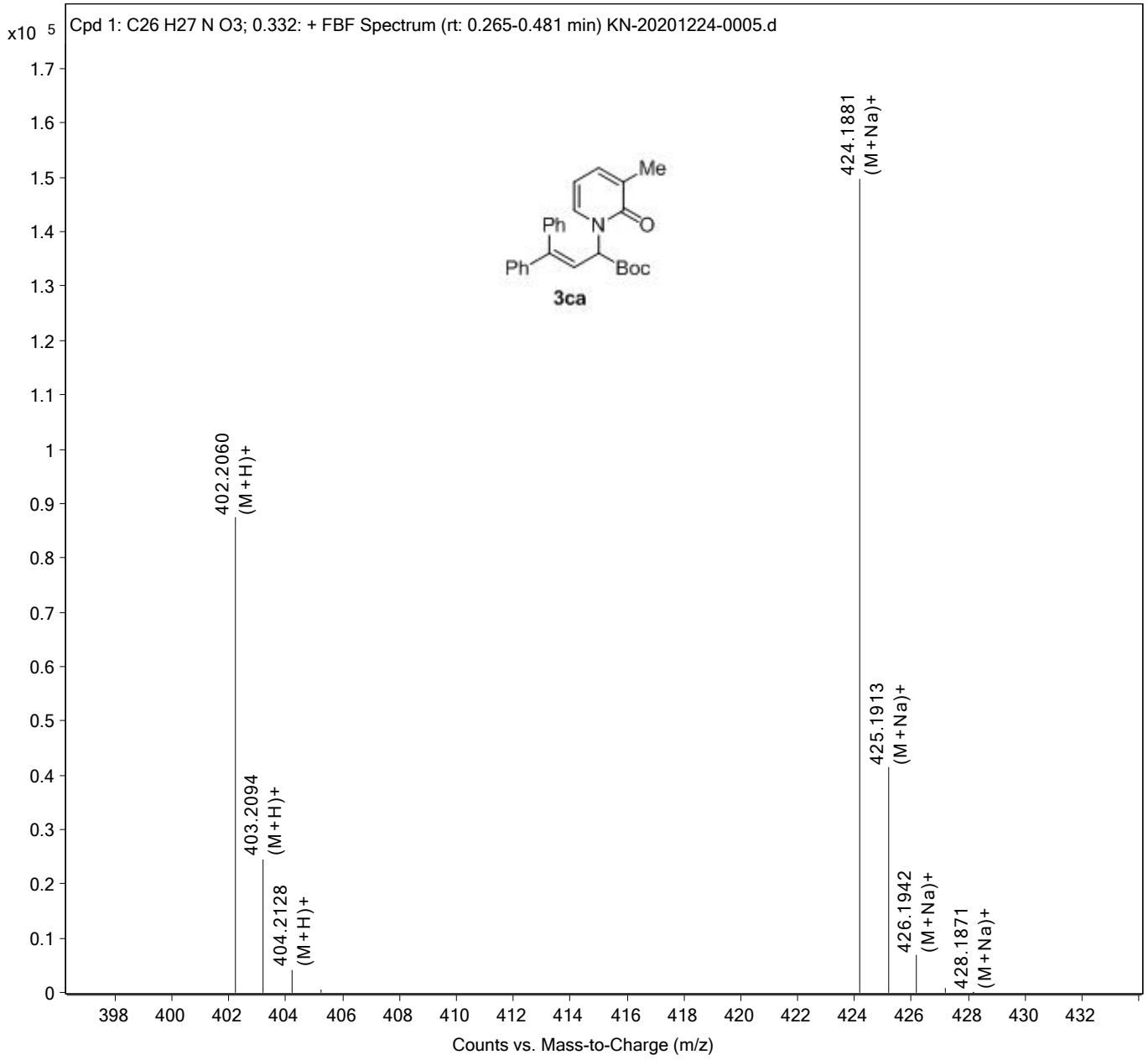
Sample Name	Sample14	**Position**	P2-B4	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0004.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:36:41 AM (UTC+08:00)



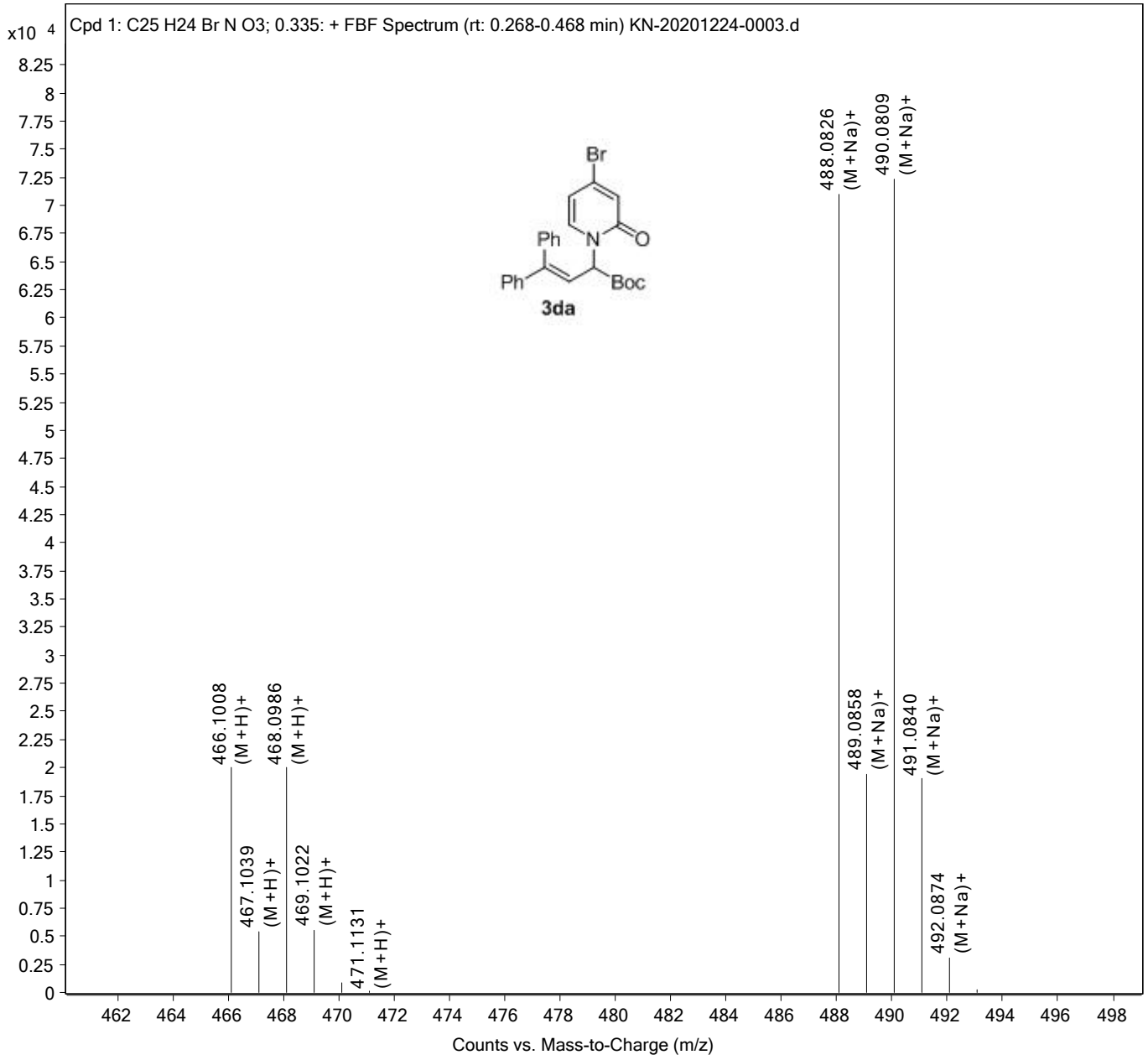
Sample Name	Sample46	**Position**	P1-E2	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0002.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:17:46 PM (UTC+08:00)



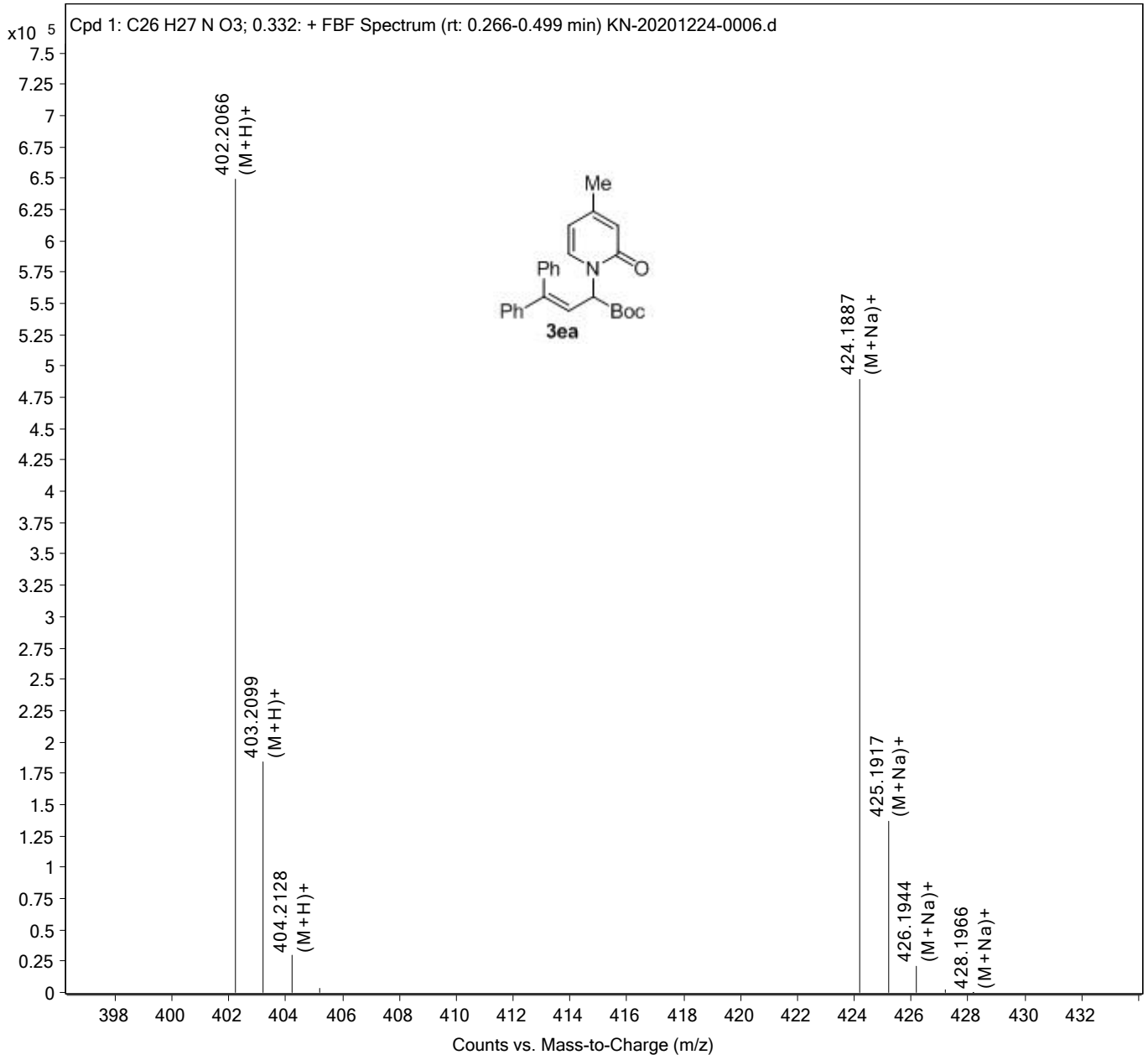
Sample Name	Sample49	**Position**	P1-E5	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0005.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:22:49 PM (UTC+08:00)



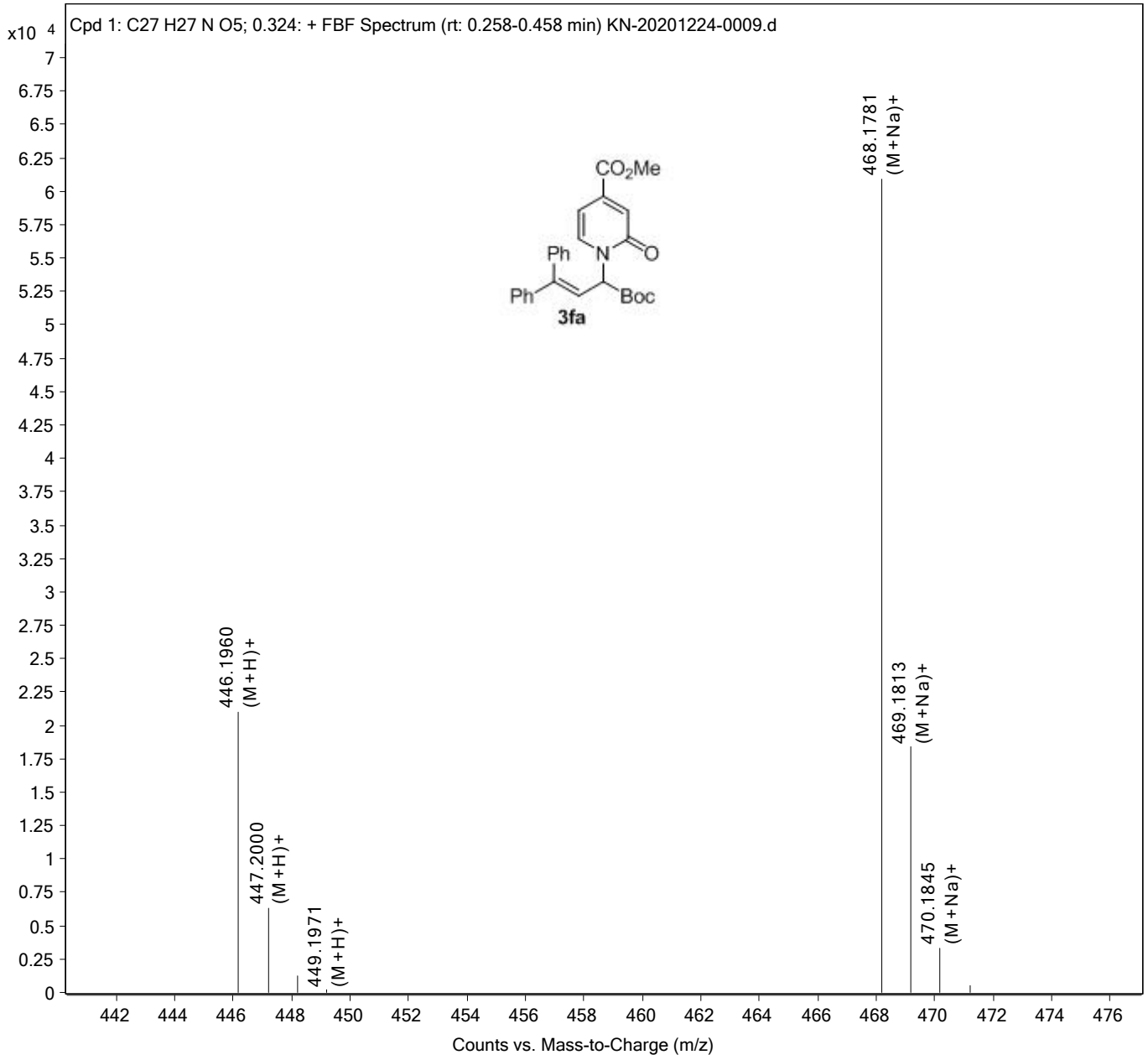
Sample Name	Sample47	**Position**	P1-E3	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0003.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:19:27 PM (UTC+08:00)



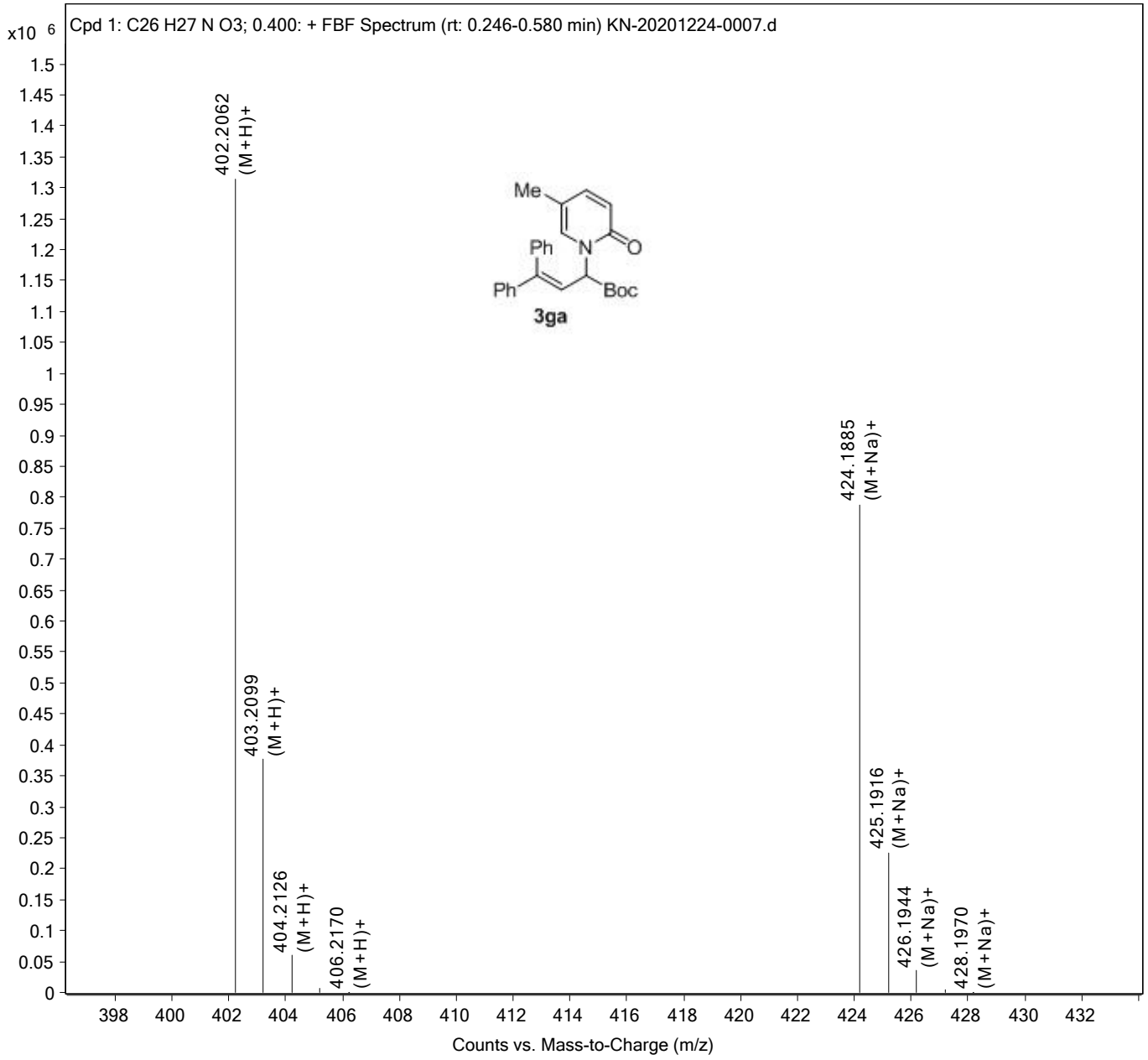
Sample Name	Sample50	**Position**	P1-E6	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0006.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:24:32 PM (UTC+08:00)



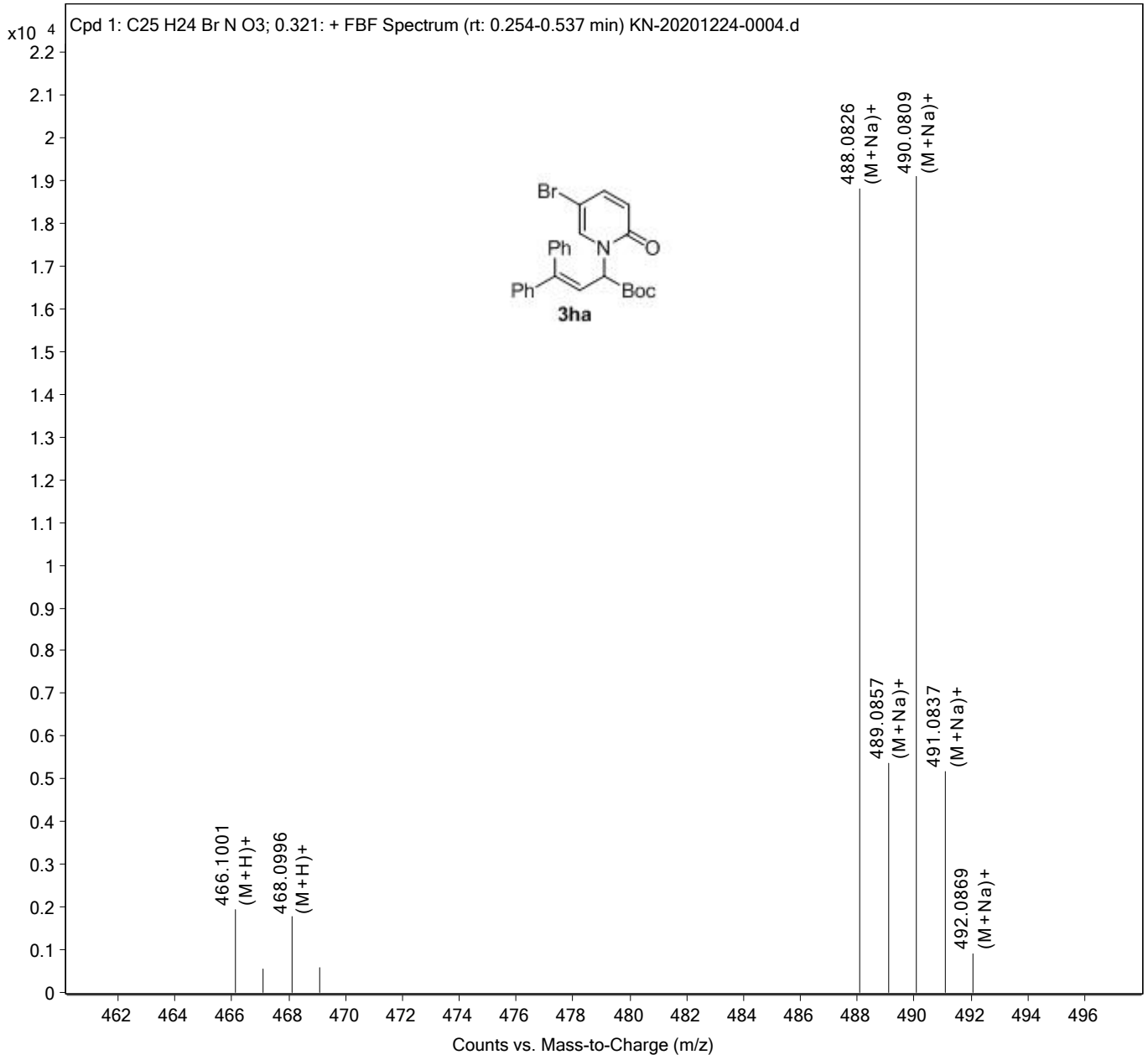
Sample Name	Sample53	**Position**	P1-E9	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0009.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:29:37 PM (UTC+08:00)



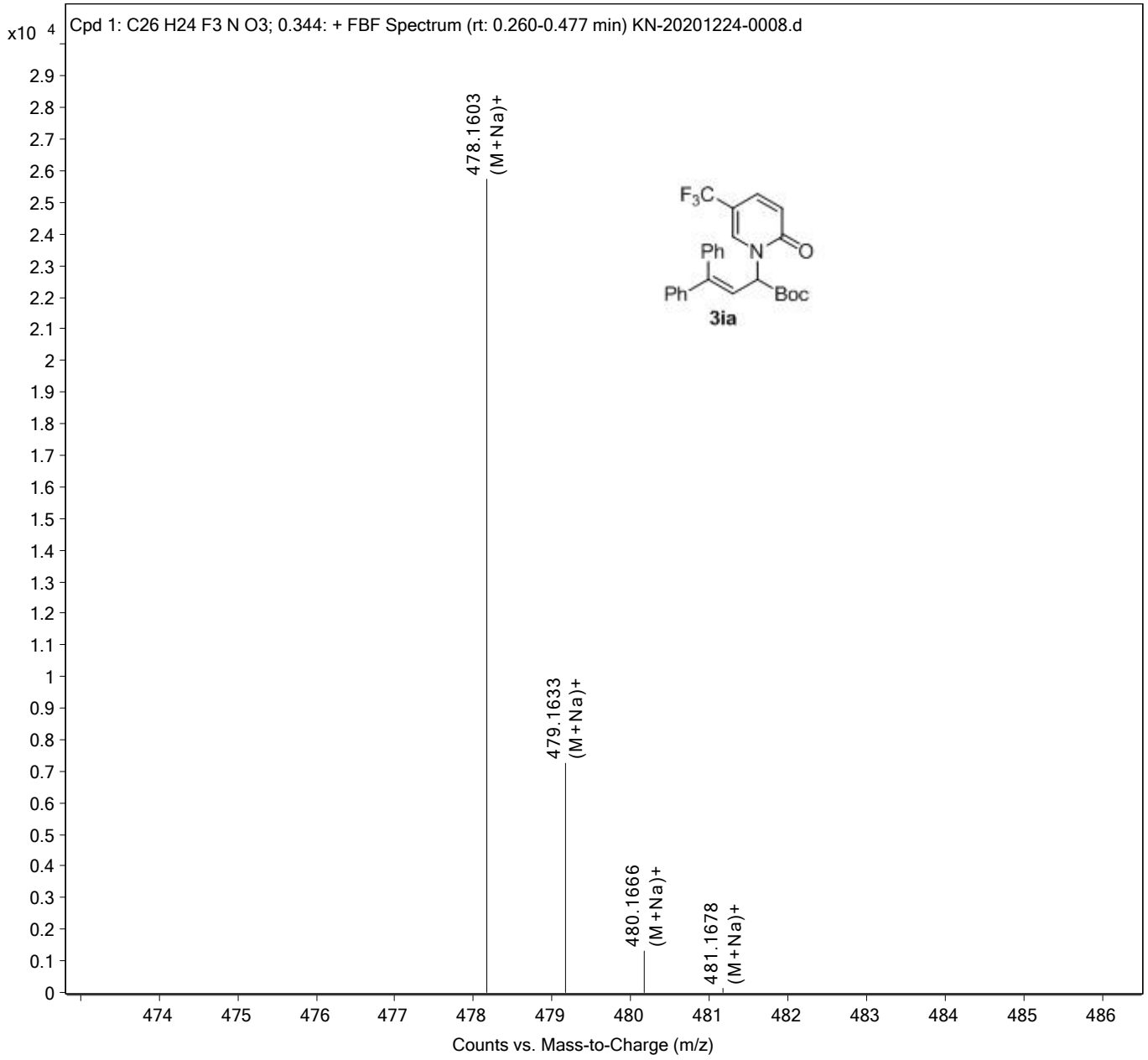
Sample Name	Sample51	**Position**	P1-E7	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0007.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:26:15 PM (UTC+08:00)



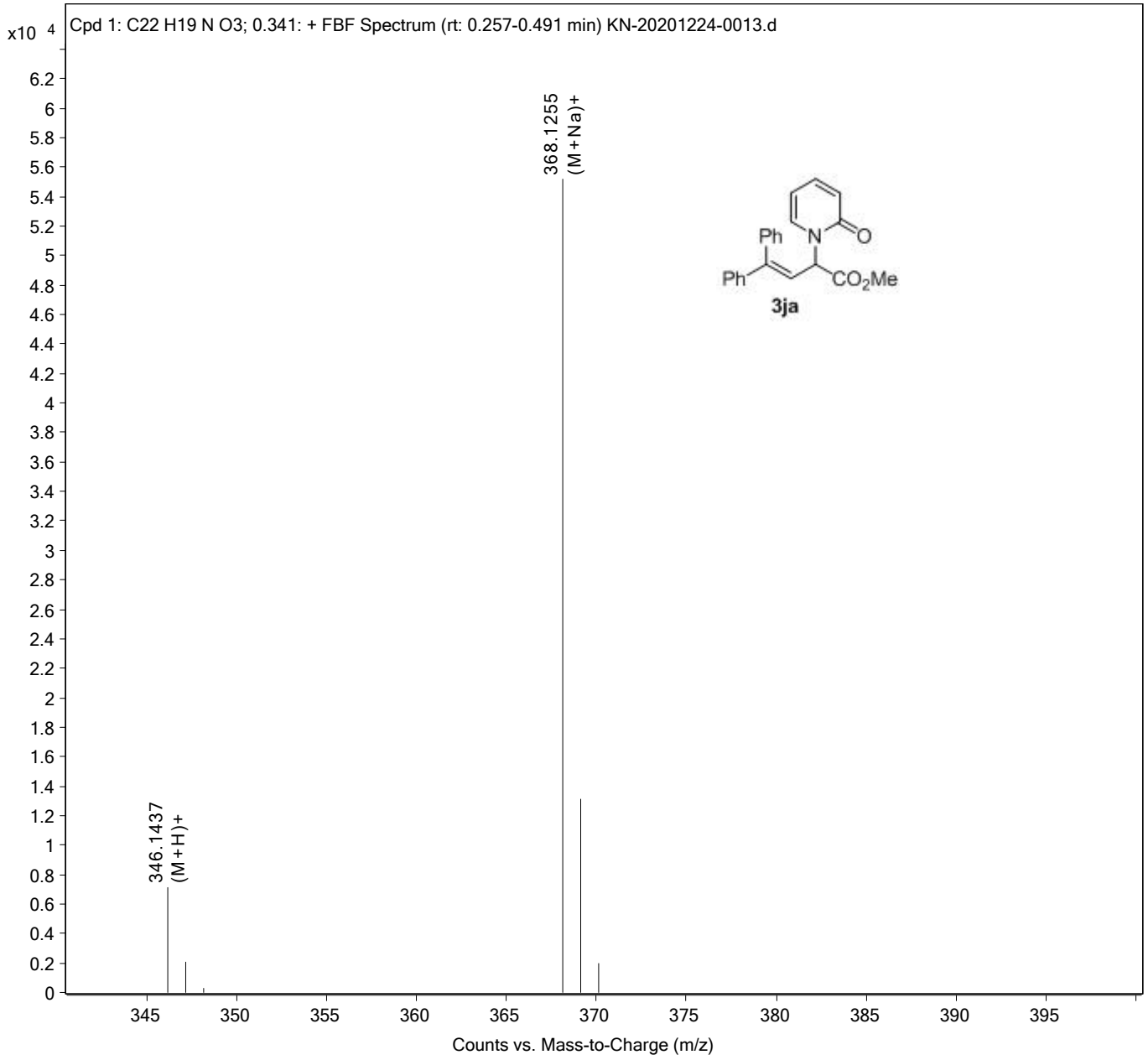
Sample Name	Sample48	**Position**	P1-E4	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0004.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:21:07 PM (UTC+08:00)



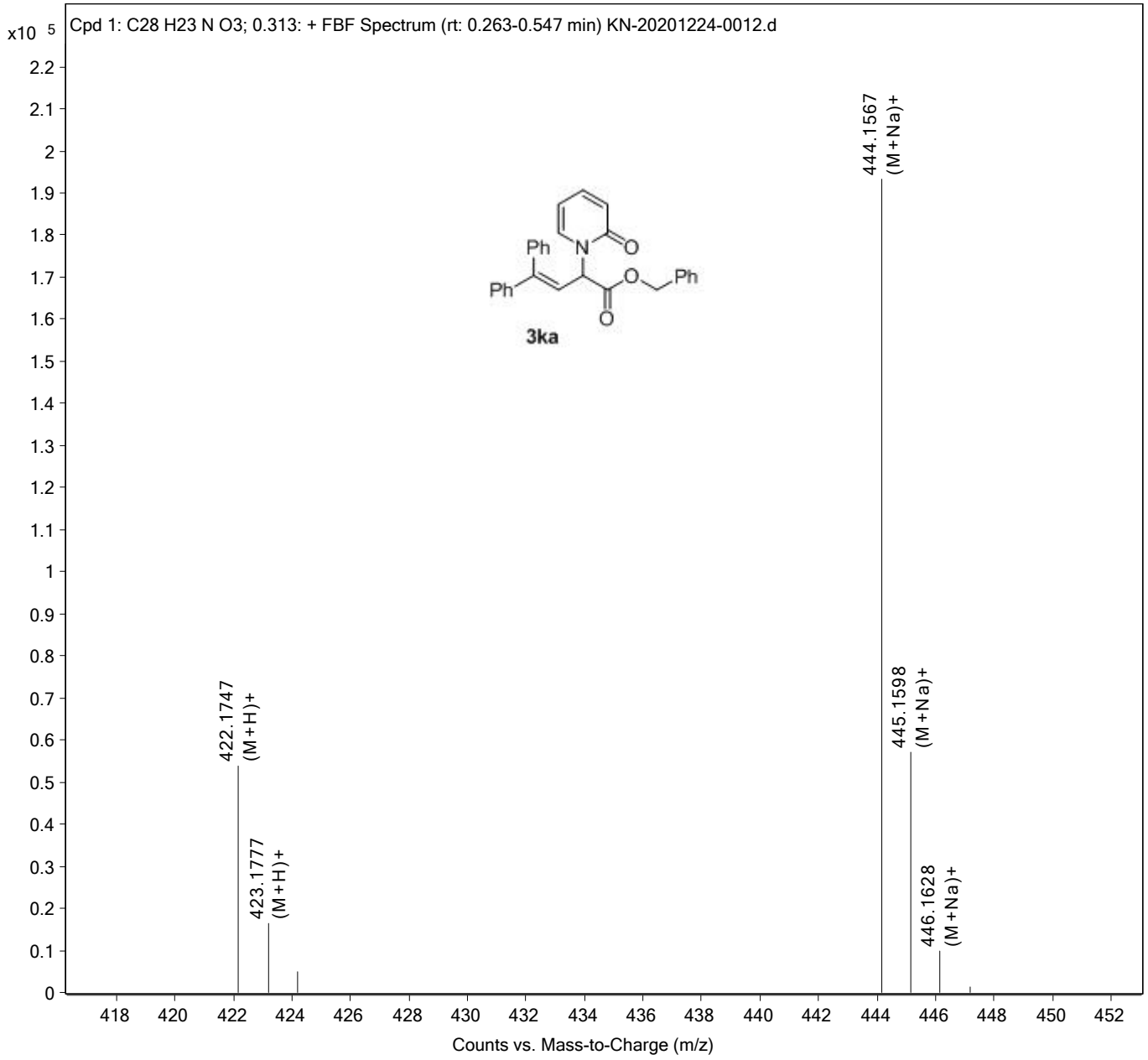
Sample Name	Sample52	**Position**	P1-E8	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0008.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:27:57 PM (UTC+08:00)



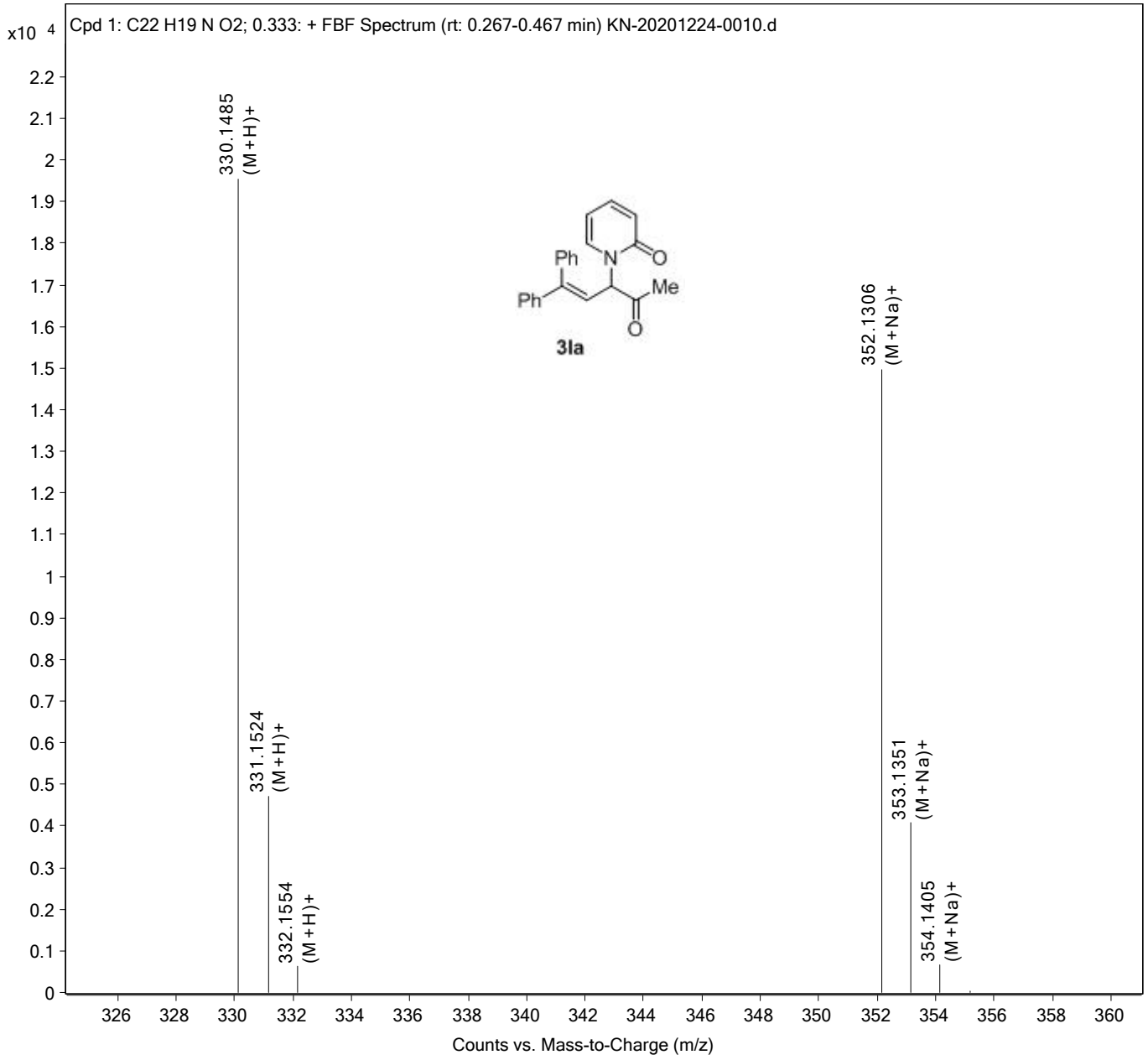
Sample Name	Sample57	**Position**	P1-F2	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0013.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:36:23 PM (UTC+08:00)



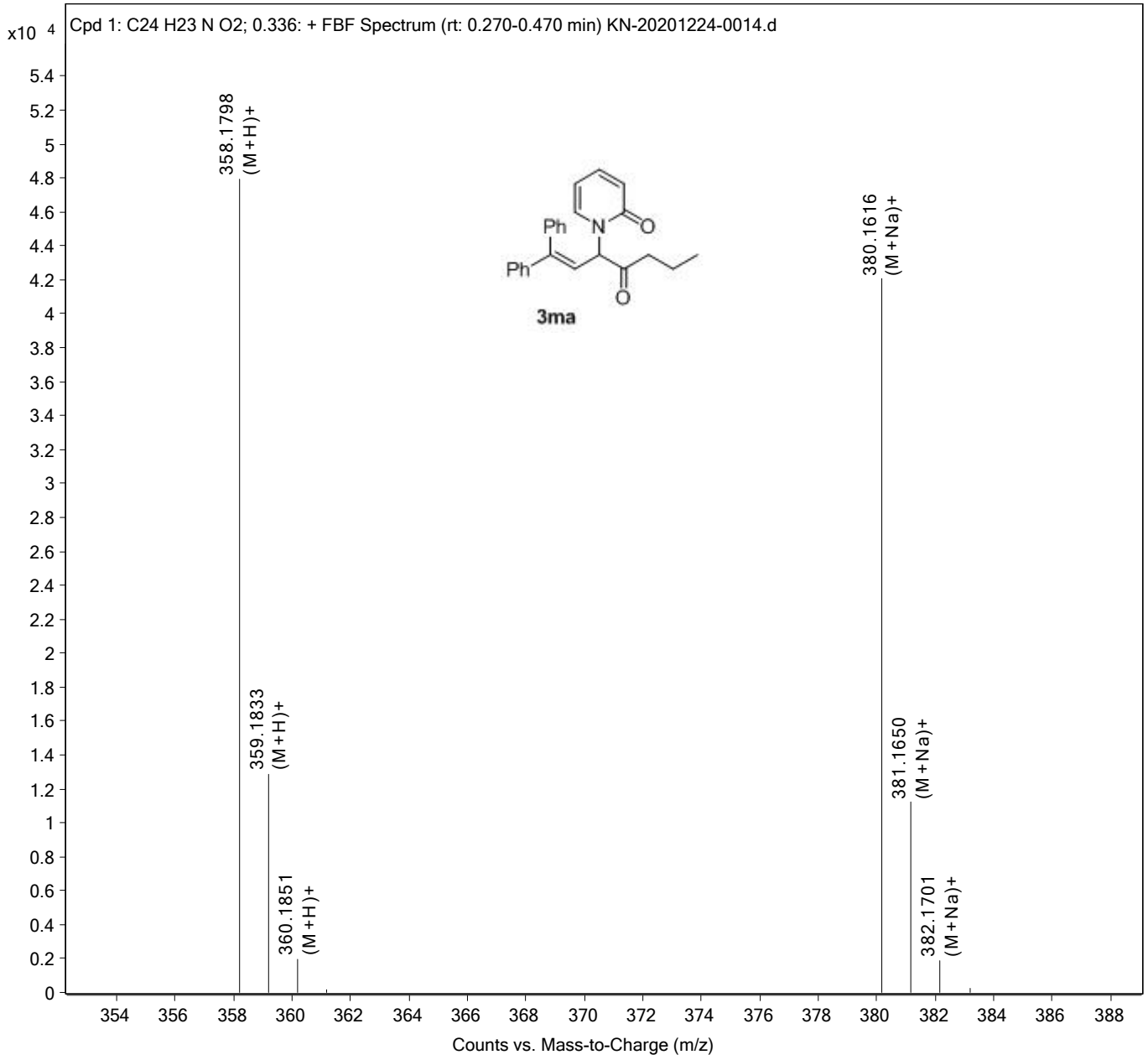
Sample Name	Sample56	**Position**	P1-F1	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0012.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:34:41 PM (UTC+08:00)



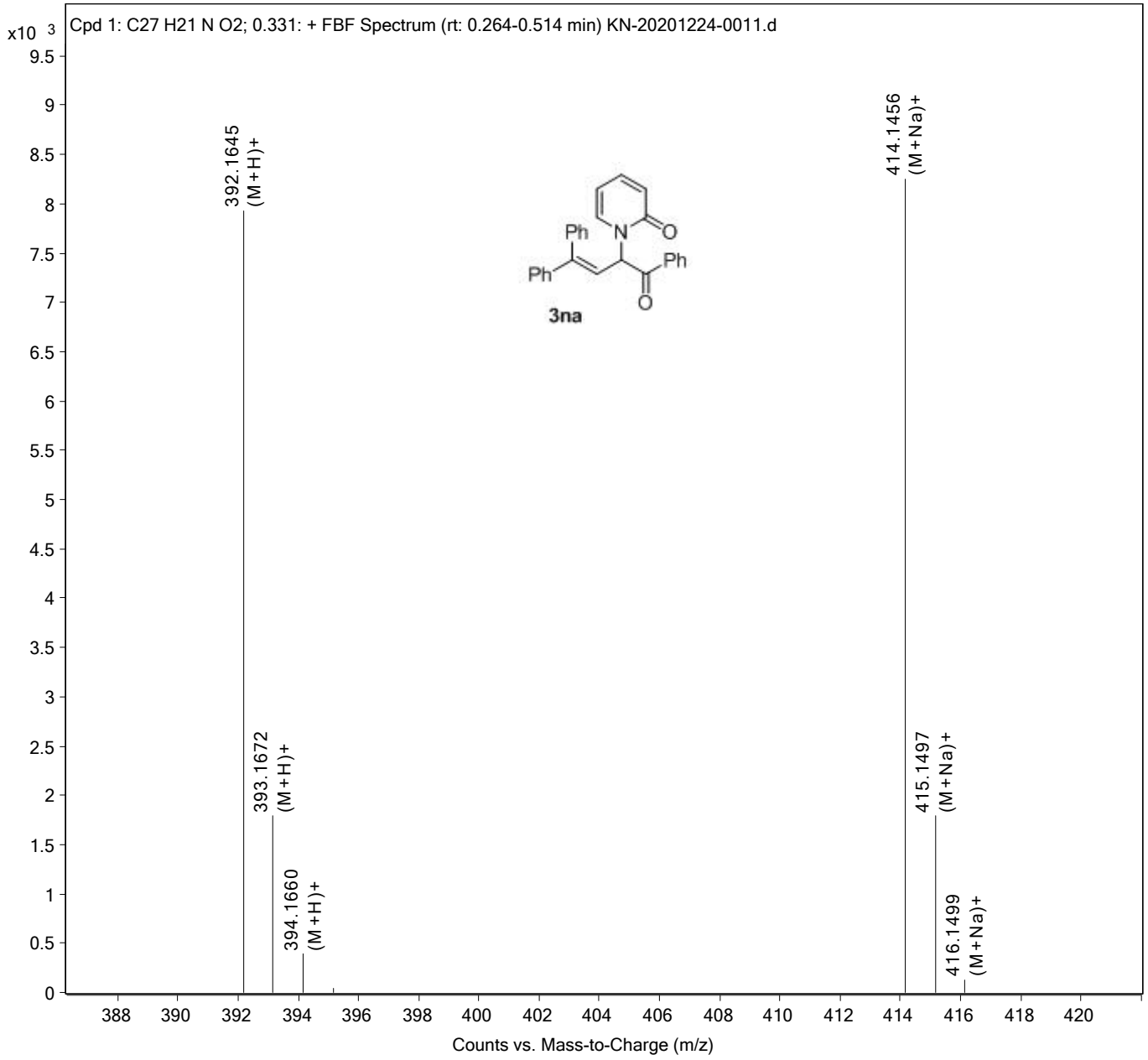
Sample Name	Sample54	**Position**	P1-E10	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0010.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:31:19 PM (UTC+08:00)



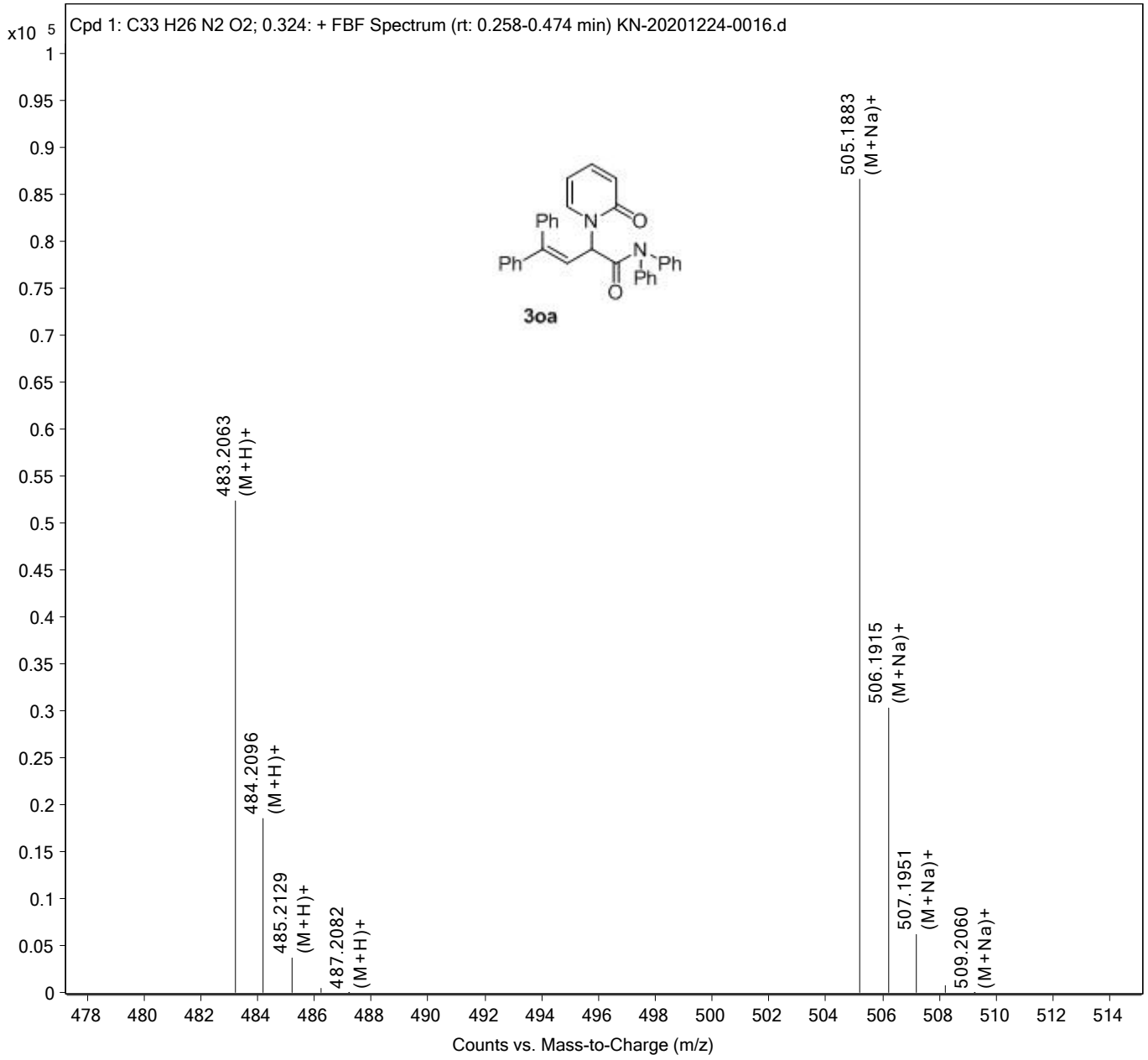
Sample Name	Sample58	**Position**	P1-F3	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0014.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:38:05 PM (UTC+08:00)



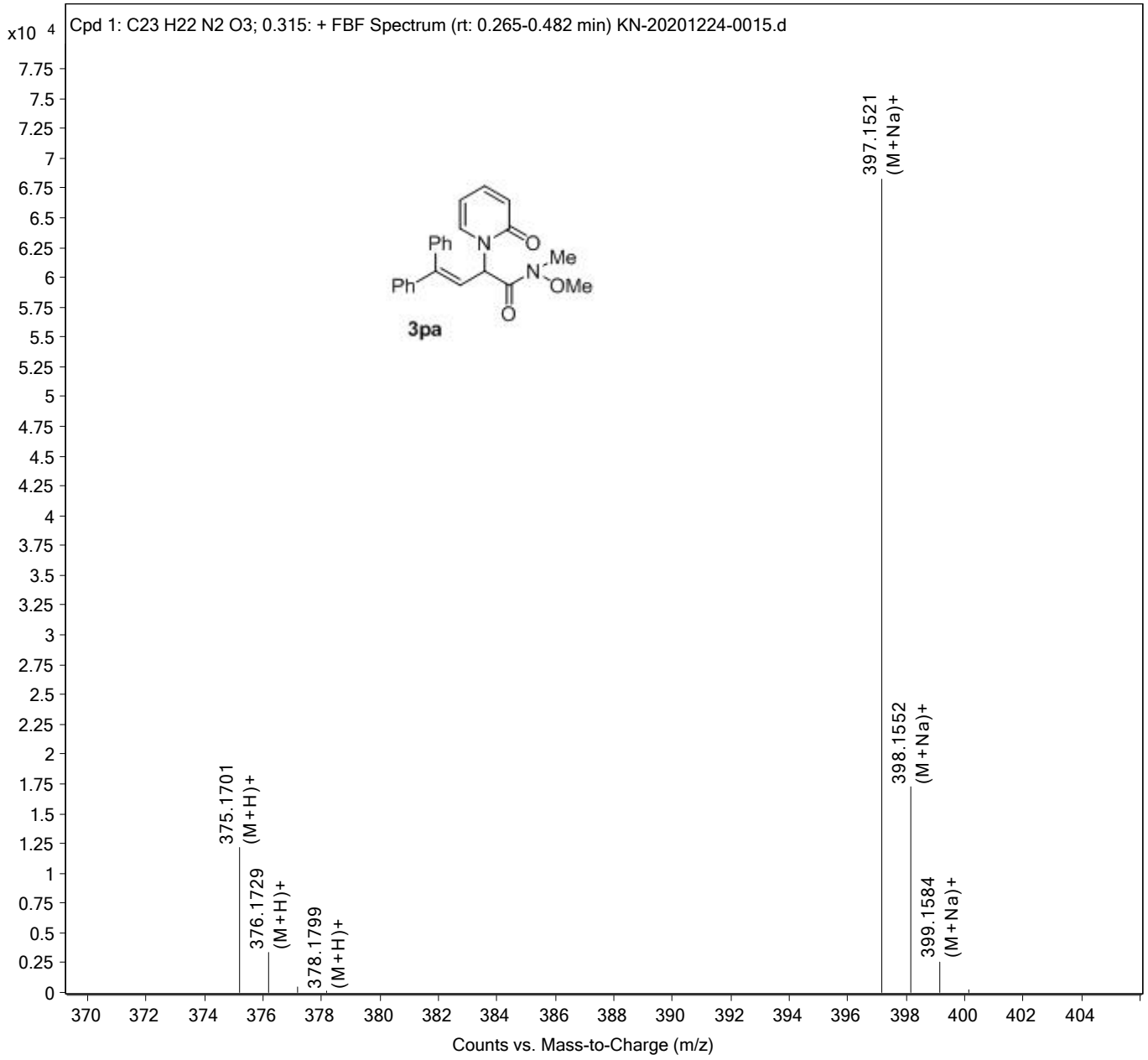
Sample Name	Sample55	**Position**	P1-E11	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0011.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:32:59 PM (UTC+08:00)



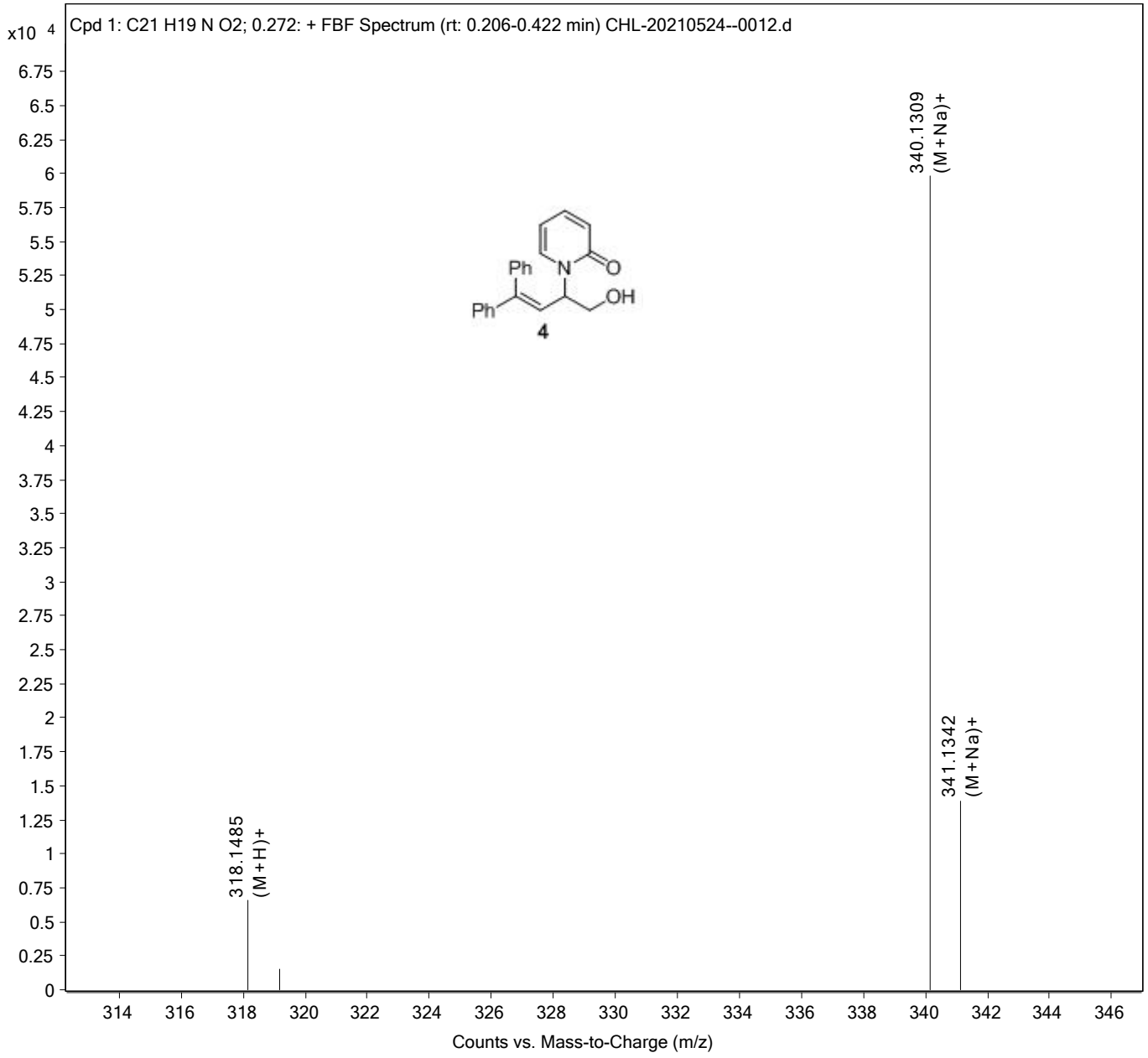
Sample Name	Sample60	**Position**	P1-F5	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0016.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:41:30 PM (UTC+08:00)



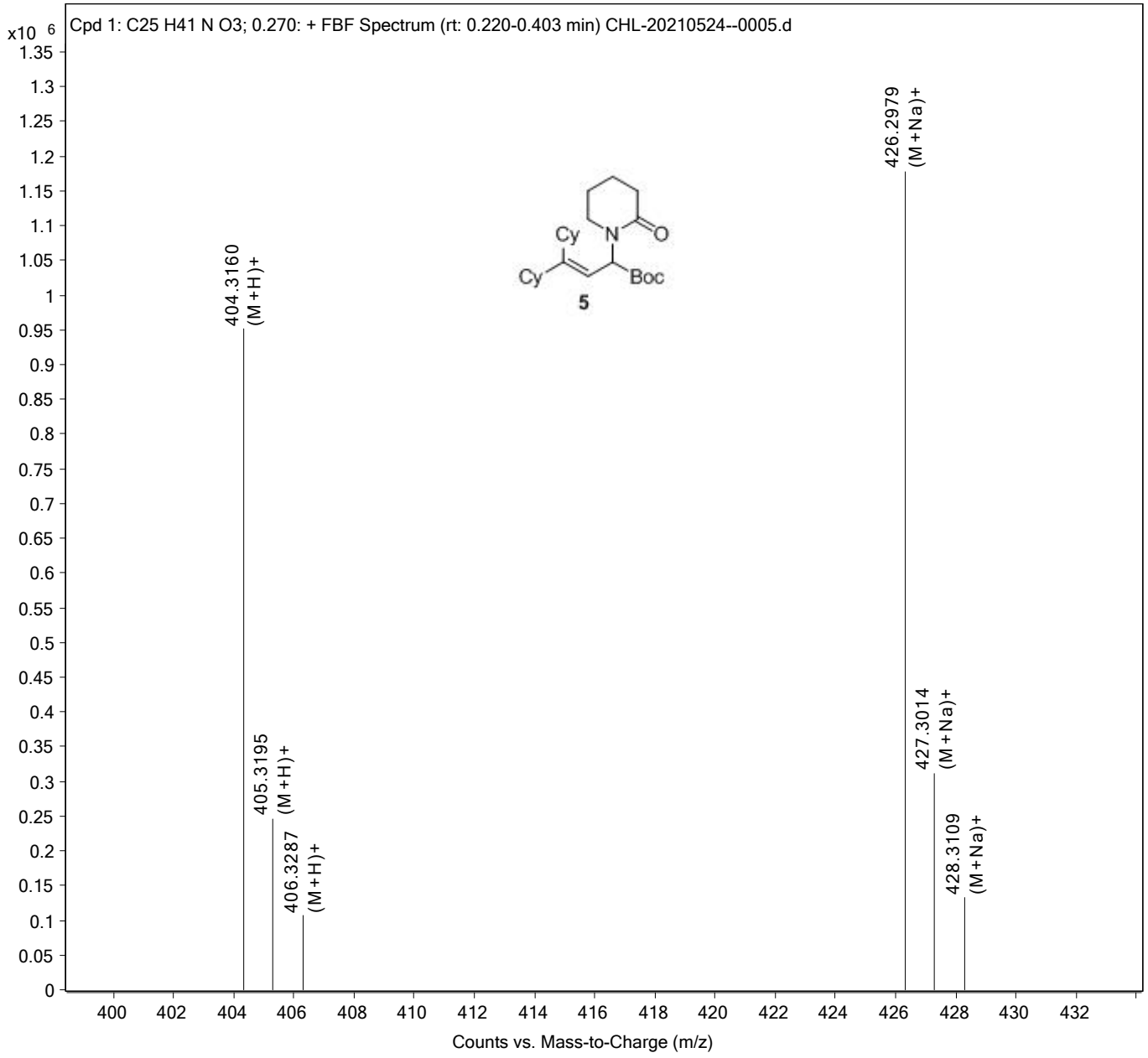
Sample Name	Sample59	**Position**	P1-F4	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	KN-20201224-0015.d
ACQ Method	NOZHUNOUV.m	**Comment**		**Acquired Time**	12/24/2020 1:39:48 PM (UTC+08:00)



Sample Name	Sample22	**Position**	P2-C1	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0012.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:49:36 AM (UTC+08:00)



Sample Name	Sample15	**Position**	P2-B5	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0005.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:38:18 AM (UTC+08:00)



Sample Name	Sample19	**Position**	P2-B9	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	1	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	CHL-20210524--0009.d
ACQ Method	NOZHU.m	**Comment**		**Acquired Time**	5/24/2021 11:44:45 AM (UTC+08:00)