Supporting Information

for

Rh(III)-Catalyzed C-H activation/cyclization of Oximes with alkenes for regioselective synthesis of isoquinolines

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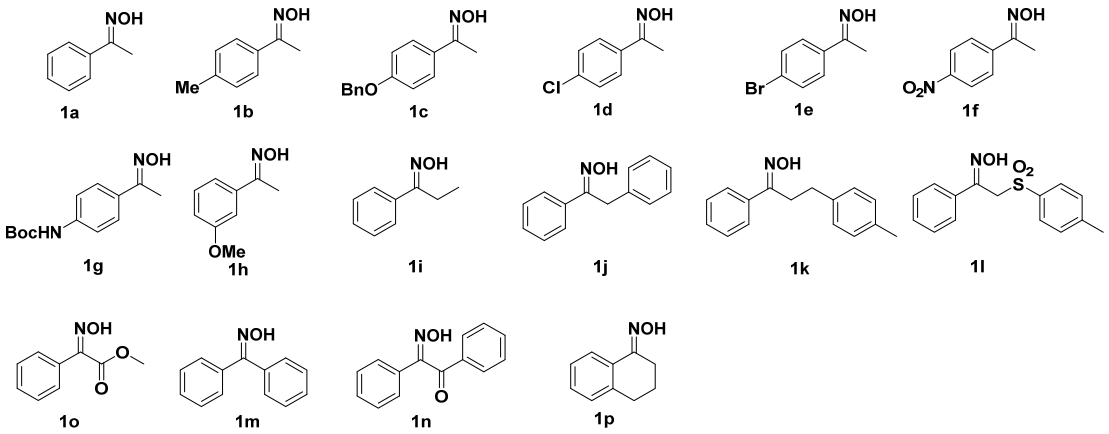
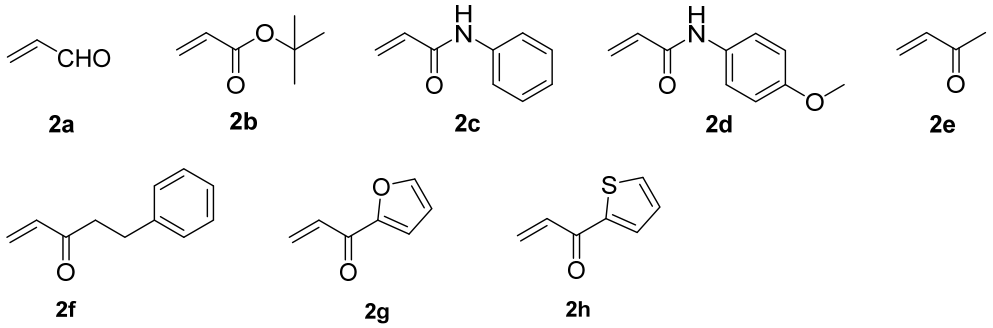
1. General Information:

Infrared spectra were obtained on a FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on BRUKER AVANCE III 400 spectrometer, BRUKER AVANCE III 500 spectrometer, BRUKER AVANCE III 600 spectrometer. $CDCl_3$ were used as solvent. Chemical shifts were referenced relative to residual solvent. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). HRMS were performed on Waters GCT Premier Time of Flight Mass Spectrometer (EI). Melting points were measured with micro melting point apparatus.

$[Cp^*RhCl_2]_2$, PivOH, CH_3CN, THF, CH_2Cl_2 were commercial available. The Oxime compounds **1** and the alkenes **2** were either commercial available, or easily prepared according the literature.

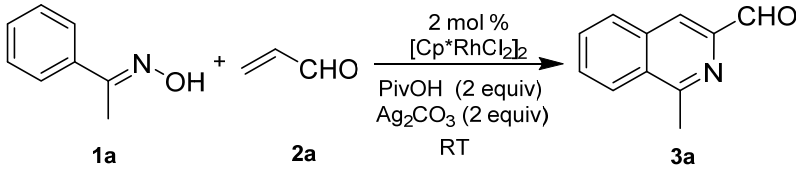




2a **2b** **2c** **2d** **2e**

2f **2g** **2h**

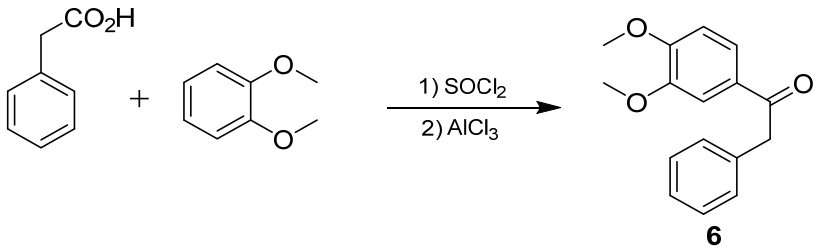
2. Typical Procedure for Synthesis of 3a:



1a **2a** **3a**

Under air, a vial equipped with a stir bar was charged with **1a** (27.0 mg, 0.2 mmol), acrolein **2a** (33.6 mg, 0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mg, 2 mol %), Ag_2CO_3 (110.3 mg, 0.4 mmol), PivOH (40.8 mg, 0.4 mmol), MeCN (1 mL). The reaction mixture was stirred at room temperature for 18 h. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as eluent to give **3a** as a white solid (28.7 mg, 84% yield).

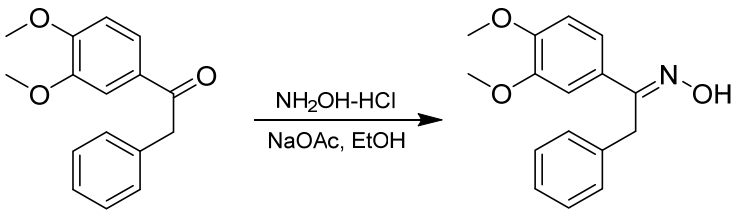
3. Procedure for Total Synthesis of Moxaverine:



6

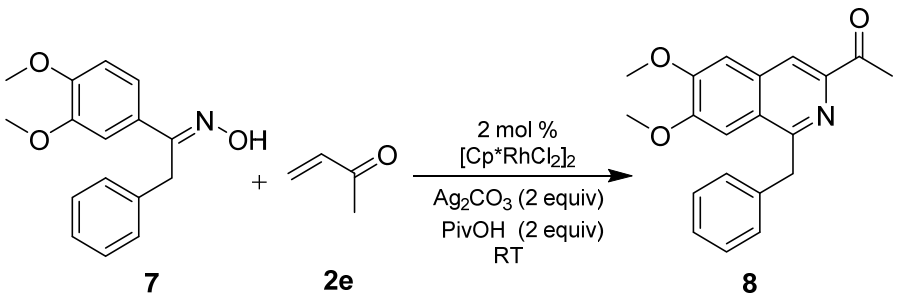
To a 100 mL flask containing phenylacetic acid (2.0 g, 14.7 mmol), 40 ml DCM, thionyl chloride (8.7 g, 73.5 mmol) was added and the

reaction mixture was heated to reflux for 3 h and then DCM and excess thionyl chloride were removed by distillation. The resulting oil was transferred to another two necked round bottom flask containing dry DCM (60 mL) and 1,2-dimethoxy benzene (1.7 g, 12.3 mmol). $AlCl_3$ (2.1 g, 15.9 mmol) was added in small portions and the mixture was stirred at room temperature for 3 h, after which the reaction was quenched by pouring into ice water (25 mL). The mixture was extracted with DCM and the combined organic layers were evaporated under vacuum. Recrystallization from ethyl alcohol gave the desired product **6** as yellow solid (2.5 g, 78.9% yield).



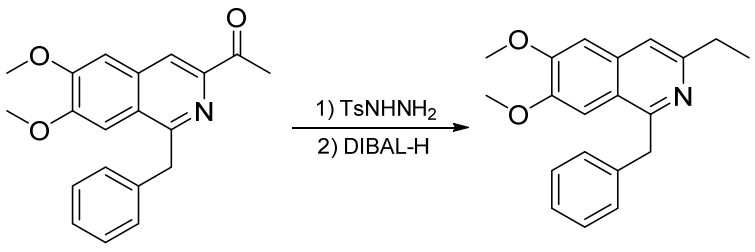
6 **7**

A mixture of **6** (2.5 g, 9.8 mmol), $NH_2OH{\cdot}HCl$ (1.4 g, 20.1 mmol), NaOAc (1.6 g, 20.1 mmol), ethyl alcohol (50 mL) were placed in a 100 mL round-bottom flask with a reflux condenser and stirred under reflux. After the completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic layers was dried by Na_2SO_4 and evaporated under vacuum to give the oxime **7** as pale yellow solid (2.6 g, 98% yield).



7 **2e** **8**

Under air, a vial equipped with a stir bar was charged with **7** (54.0 mg, 0.2 mmol), **2e** (66.1 mg, 0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mg, 2.0 mol%), Ag_2CO_3 (110.3 mg, 0.4 mmol), PivOH (40.8 mg, 0.4 mmol), MeCN (1 mL). The reaction mixture was stirred at room temperature for 18 h. After the completion of the reaction, the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to give **8** as a white solid (48.8 mg, 76.0% yield).



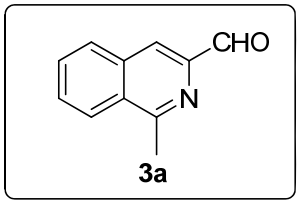
8 **Moxaverine**

The ketone 8 (48.8 mg, 0.15 mmol) was heated to boiling with *p*-Toluenesulfonyl hydrazide (27.9 mg, 0.15 mmol) in methanol (10 ml). After 12 h, the reaction mixture was evaporated to dryness under reduced pressure. The resulting product was transferred to a dry two necked round bottom flask in dry DCM (20 mL) was added DIBAL-H (45.0 µL, 1 M in Hexane, 0.45 mmol) drop-wise. The reaction mixture was stirred at RT for 1 h. After the completion of the reaction, the solvent was concentrated in

vacuum and the residue was purified by flash column chromatography on silica gel with ethyl acetate/petroleum ether (v/v, 1:5) as the eluent to give the product Moxaverine (29.9 mg, 64.9% yield).

4. Characterization of 3, 8, Moxaverine:

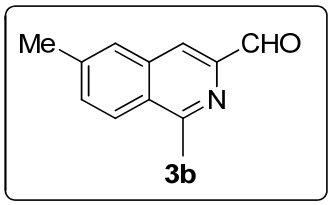
1-Methylisoquinoline-3-carbaldehyde (3a)



3a

White solid; m.p. 62-68 ºC; ^{1}H NMR ($CDCl_3$, 500MHz), δ: 10.23 (s, 1H), 8.25 (s, 1H), 8.21-8.20 (m, 1H), 8.02-8.01(m, 1H), 7.79-7.77 (m, 2H), 3.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.72, 160.00, 145.91, 135.41, 131.05, 130.17, 129.74, 129.54, 126.04, 121.31, 22.61; IR (KBr) *v*: 2957, 2925, 2850, 1702, 1656, 1389, 1261, 751, 707, 622 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_9NO$ (M^+): 171.0684; Found: 171.0686.

1,6-Dimethylisoquinoline-3-carbaldehyde (3b)

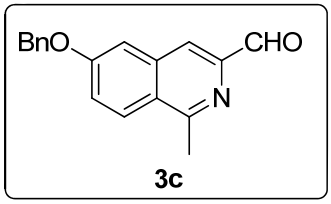


3b

White solid; m.p. 68-72 ºC; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.19 (s, 1H), 8.15 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.75 (s, 1H), 7.59 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 3.01 (s, 3H), 2.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.81, 159.60, 146.03, 141.56, 135.70, 132.34, 128.44, 128.11, 125.84,

120.95, 22.51, 21.96; IR (KBr) *v*: 3061, 2963, 2916, 2853, 1692, 1583, 1499, 1393, 1323, 1262, 1150, 800, 687, 610 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO$ (M^+):185.0841; Found: 185.0840.

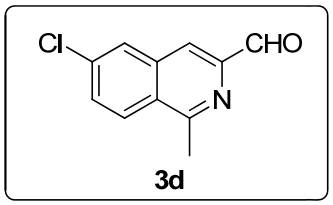
6-(Benzyloxy)-1-methylisoquinoline-3-carbaldehyde (3c)



3c

White solid; m.p. 105-112 ºC; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.18 (s, 1H), 8.11-8.09 (m, 2H), 7.49-7.29 (m, 7H), 5.23(s, 2H), 2.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.89, 160.32, 159.20, 146.47, 137.54, 135.93, 128.92, 125.36, 122.95, 120.41, 108.21, 70.51, 22.47; IR (KBr) *v*: 3423, 2962, 2361, 1707, 1618, 1500, 1414, 1232, 1189, 1138, 1007, 817, 714 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{15}NO_2$ (M^+): 277.1103; Found: 277.1102.

6-Chloro-1-methylisoquinoline-3-carbaldehyde (3d)

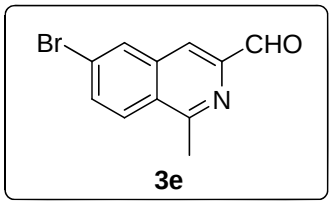


3d

White solid; m.p. 127-131 ºC; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.20 (s, 1H), 8.14-8.12 (m, 2H), 7.96 (d, J = 2 Hz, 1H), 7.69 (dd, J_1 = 8.8 Hz, J_2 = 2 Hz, 1H), 3.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.45, 160.01, 146.76, 137.36, 136.43, 130.93, 128.11, 127.87, 127.72, 119.80, 22.59; IR (KBr) *v*: 3071, 2960, 2921, 2870, 1703, 1609, 1583, 1389, 1172, 1146, 1090, 913,

813, 764 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_8ClNO$ (M^+): 205.0294; Found: 205.0295.

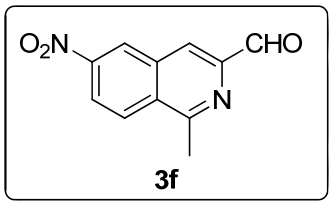
6-Bromo-1-methylisoquinoline-3-carbaldehyde (3e)



3e

White solid; m.p. 139-142 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.20 (s, 1H), 8.16 (d, *J* = 1.6 Hz, 1H), 8.14 (s, 1H), 8.06 (d, *J* = 9.2 Hz, 1H), 7.84 (dd, J_1 = 8.8 Hz, J_2 = 2 Hz, 1H), 3.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.46, 160.16, 146.72, 136.74, 133.52, 131.48, 128.10, 127.67, 125.86, 119.68, 22.57; IR (KBr) *v*: 2962, 2919, 2850, 1702, 1656, 1390, 1147, 994, 902, 810, 577, 506 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_8BrNO$ (M^+): 248.9789; Found: 248.9790.

1-Methyl-6-nitroisoquinoline-3-carbaldehyde (3f)

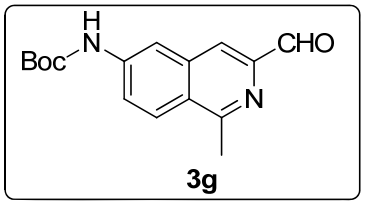


3f

White solid; m.p. 173-180 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.26 (s, 1H), 8.91 (d, *J*=2.4Hz, 1H), 8.51 (dd, J_1 = 9.2 Hz , J_2 = 2.4 Hz, 1H), 8.40-8.38 (m, 2H), 3.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 192.97, 160.60, 148.68, 147.41, 135.22, 131.29, 128.25, 125.39, 123.25, 121.13, 22.88; IR (KBr) *v*: 3109, 2962, 2923, 2865, 1704, 1623, 1538, 1375, 1349, 1147,

1092, 836, 737 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{11}H_8N_2O_3$ (M^+): 216.0535; Found: 216.0534.

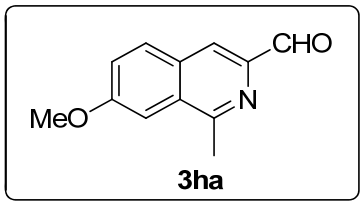
tert-Butyl (3-formyl-1-methylisoquinolin-6-yl)carbamate (3g)



3g

White solid; m.p. 170-173 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.17 (s, 1H), 8.12-8.08 (m, 3H), 7.64 (dd, J_1 = 9.2 Hz， J_2 = 2.4 Hz，1H), 7.01 (s, 1H), 2.98 (s, 3H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.67, 159.38, 152.48, 146.41, 140.67, 136.76, 127.20, 126.01, 122.42, 121.24, 114.74, 28.41, 27.22, 22.35; IR (KBr) *v*: 3631, 2977, 2358, 1695, 1656, 1399, 1241, 1156, 883, 818, 701, 686 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{18}N_2O_3$ (M^+): 286.1317; Found:286.1317.

7-Methoxy-1-methylisoquinoline-3-carbaldehyde (3ha)

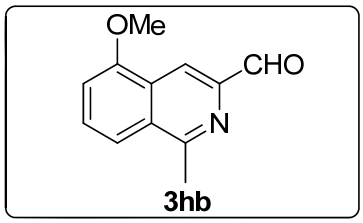


3ha

White solid; m.p. 100-104 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.19 (s, 1H), 8.64 (s, 1H), 7.73-7.65 (m, 2H), 7.08 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 4.04 (s, 3H), 3.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.47, 159.35, 156.71, 145.42, 130.59, 130.46, 127.95, 117.57, 116.79, 108.48, 56.00, 22.97; IR (KBr) *v*: 3022, 2957, 2924, 2850, 2368, 1691, 1615, 1584, 1496,

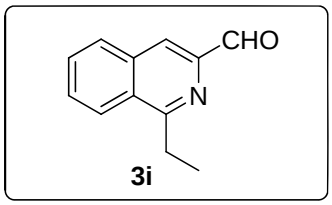
1387, 1368, 1323, 1267, 893, 804, 740 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO_2$ (M^+): 201.0790; Found: 201.0794.

5-Methoxy-1-methylisoquinoline-3-carbaldehyde (3hb)



White solid; m.p. 132-137 ºC ^1H NMR ($CDCl_3$, 400MHz), δ: 10.18 (s, 1H), 8.19 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.43 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.38 (d, J = 2.4 Hz, 1H), 4.01 (s, 3H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 192.39, 159.71, 156.84, 143.47, 130.20, 130.01, 129.43, 122.37, 120.06, 103.10, 54.64, 21.58; IR (KBr) *v*: 2963, 2921, 2361, 2026, 1625, 1499, 1405, 1261, 1089, 1029, 800, 679 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO_2$ (M^+): 201.0790; Found: 201.0786.

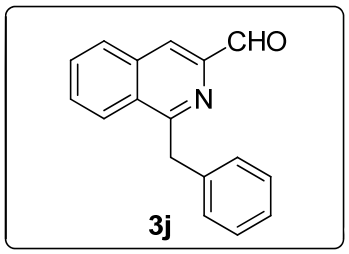
1-Ethylisoquinoline-3-carbaldehyde (3i)



White solid; m.p. 63-67 ºC; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.23 (s, 1H), 8.23-8.22 (m, 2H), 8.00-7.98 (m, 1H), 7.77-7.74 (m, 2H), 3.39 (q, J = 7.6 Hz, 2H), 1.48 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 194.06, 164.34, 145.96, 135.70, 130.77, 129.99, 129.69, 128.91, 125.57, 120.65, 28.65, 13.63; IR (KBr) *v*: 3068, 2974, 2937, 2881, 2827, 1704, 1503, 1444,

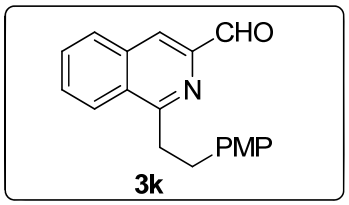
1385, 1126, 750, 722 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO$ (M^+): 185.0841; Found: 185.0838.

1-Benzylisoquinoline-3-carbaldehyde(3j)



Yellow solid; m.p. 80-86 ^oC; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.28 (s, 1H), 8.30 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8 Hz, 1H), 7.75-7.66 (m, 2H), 7.33-7.17 (m, 5H), 4.76 (s, 2H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.96, 161.32, 146.00, 138.90, 136.13, 130.92, 130.25, 129.69, 129.40, 128.74, 128.70, 126.62, 126.28, 121.26, 42.17; IR (KBr) *v*: 3058, 3023, 2925, 2873, 1697, 1583, 1494, 1452, 1126, 1026, 912, 749, 709 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{13}NO$ (M^+): 247.0997; Found: 247.0995.

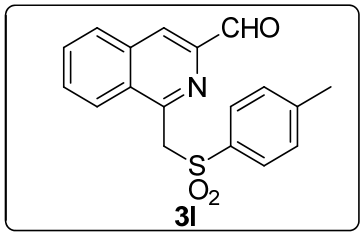
1-(4-Methoxyphenethyl)isoquinoline-3-carbaldehyde (3k)



White solid; m.p. 77-79 ^oC; ^1H NMR ($CDCl_3$, 400MHz), δ: 10.26 (s, 1H), 8.25 (s, 1H), 8.21-8.19 (m, 1H), 8..01 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1H), 7.77-7.73 (m, 2H), 7.25-7.22(m, 2H), 6.86-6.84 (m, 2H), 3.80 (s, 3H), 3.64 (t, *J* = 2 Hz, 2H), 3.20 (t, *J* = 2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 194.06, 162.27, 158.13, 145.98, 135.73, 133.76, 130.82, 130.08, 129.72, 129.52,

129.19, 125.46, 120.76, 114.01, 55.40, 37.41, 34.31; IR (KBr) *v*: 3004, 2929, 2830, 2809, 2367, 1703, 1613, 1583, 1511, 1446, 1386, 1238, 1177, 1032, 816, 746, 721 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{17}NO_2$ (M^+):291.1259; Found: 291.1264.

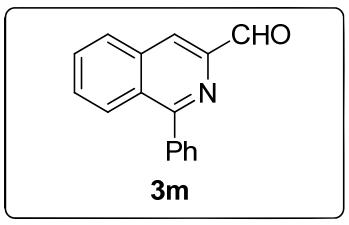
1-(Tosylmethyl)isoquinoline-3-carbaldehyde (3l)



3l

White solid; m.p. 196-197 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 9.87 (s, 1H), 8.38-8.35 (m, 1H), 8.31 (s, 1H), 8.05-8.03 (m, 1H), 7.87-7.83 (m, 2H), 7.87-7.81 (m, 2H), 7.23-7.13 (m, 2H), 5.15 (s, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.10, 150.44, 145.85, 145.21, 136.24, 135.27, 131.57, 130.96, 130.24, 129.67, 129.59, 128.82, 126.39, 121.73, 62.23, 21.77; IR (KBr) *v*: 3432, 2993, 2815, 2367, 2026, 1696, 1638, 1501, 1408, 1383, 1307, 1147, 1087, 685, 648 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{18}H_{15}NO_3S$ (M^+): 325.0773; Found: 325.0773.

1-Phenylisoquinoline-3-carbaldehyde (3m)

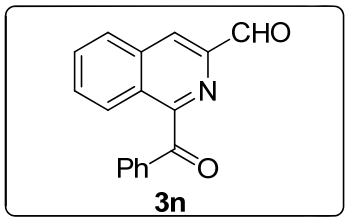


3m

White solid; m.p. 133-135 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.33 (s, 1H), 8.40 (s, 1H), 8.17 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 8.09 (d, J = 8 Hz,

1H), 7.83-7.79 (m, 1H), 7.75-7.69 (m, 3H), 7.61-7.55 (m, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 194.20, 161.77, 146.17, 138.84, 136.54, 131.09, 130.16, 130.06, 129.36, 129.28, 129.01, 128.73, 128.04, 120.44; IR (KBr) *v*: 3056, 2925, 2847, 2361, 1707, 1579, 1559, 1491, 1444, 1388, 1374, 1158, 1129, 931, 905, 770 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{16}H_{11}NO$ (M^+): 233.0841; Found: 233.0838.

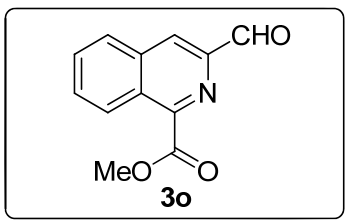
1-Benzoylisoquinoline-3-carbaldehyde (3n)



3n

White solid; m.p. 117-119 ^{o}C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.24 (s, 1H), 8.54 (s, 1H), 8.22 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 8.13 (d, J = 8 Hz, 1H), 7.99-7.97 (m, 2H), 7.88-7.84 (m, 1H), 7.80-7.76 (m, 1H), 7.67-7.63 (m, 1H), 7.52-7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 194.17, 193.26, 157.48, 145.21, 136.42, 136.13, 134.28, 131.82, 131.15, 130.94, 129.45, 128.75, 128.34, 126.63, 122.49; IR (KBr) *v*: 3068, 2931, 2832, 1709, 1666, 1597, 1448, 1290, 1244, 1162, 976, 908, 757, 744 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{11}NO_2$ (M^+): 261.0790; Found: 261.0791.

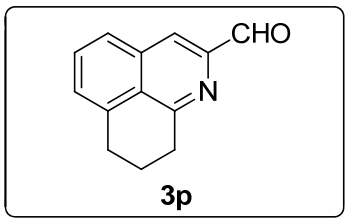
Methyl 3-formylisoquinoline-1-carboxylate (3o)



3o

White solid; m.p. 105-108 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.30 (s, 1H), 8.79-8.76 (m, 1H), 8.52 (d, *J* = 0.8 Hz, 1H), 8.08-8.06 (m, 1H), 7.85-7.83 (m, 2H), 4.13 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 192.85, 165.91, 149.66, 145.42, 136.69, 131.73, 131.58, 129.43, 128.55, 126.82, 123.94, 53.45; IR (KBr) *v*: 3428, 2959, 2856, 2026, 1720, 1701, 1500, 1444, 1292, 1249, 1206, 1157, 1127, 1037, 1020, 746, 738 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_9NO_3$ (M^+): 215.0582; Found: 215.0585.

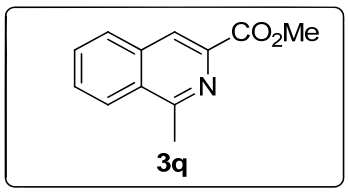
8,9-Dihydro-7*H*-benzo[*de*]quinoline-2-carbaldehyde (3p)



3p

White solid; m.p. 98-102 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.20 (s, 1H), 8.19 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69-7.65 (m, 1H), 7.51 (d, *J* = 6.8Hz, 1H), 3.34 (t, *J* = 6.4 Hz, 2H), 3.17 (t, *J* = 6.0 Hz, 2H), 2.23 (m, *J* = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 193.72, 161.58, 145.75, 139.28, 135.58, 131.04, 128.31, 127.35, 126.69, 121.24, 34.43, 30.45, 23.21; IR (KBr) *v*: 2925, 2338, 2027, 1690, 1586, 1492, 1413, 1348, 1153, 776, 731 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{13}H_{11}NO$ (M^+): 197.0841; Found: 197.0841.

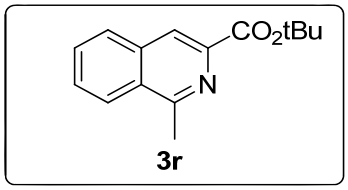
Methyl 1-methylisoquinoline-3-carboxylate (3q)



3q

White solid; m.p. 93-96 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.46 (s, 1H), 8.19-8.17 (m, 1H), 7.96-7.93 (m, 1H), 7.78-7.71 (m, 2H), 4.04 (s, 3H), 3.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 166.67, 159.52, 140.48, 135.59, 130.84, 129.56, 129.10, 128.86, 125.93, 123.17, 53.02, 22.85; IR (KBr) *v*: 3061, 2996, 2955, 2364, 1733, 1498, 1385, 1288, 1247, 1210, 1155, 811, 749 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO_2$ (M^+): 201.0790; Found: 201.0791.

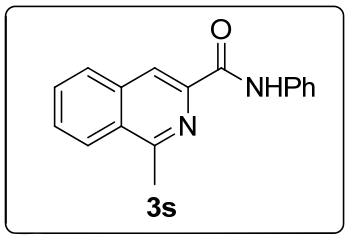
tert-Butyl 1-methylisoquinoline-3-carboxylate(3r)



3r

Pale yellow solid; m.p. 92-95 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 8.31 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.93-7.91(m, 1H), 7.75-7.67 (m, 1H), 3.03 (s, 3H), 1.66 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 164.91, 159.41, 141.74, 135.65, 130.60, 129.20, 128.88, 128.71, 125.88, 122.31, 81.89, 28.31, 22.79; IR (KBr) *v*: 3009, 2977, 2927, 2870, 2371, 1712, 1567, 1444, 1391, 1249, 1159, 1106, 979, 798, 767 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{17}NO_2$ (M^+): 243.1259; Found: 243.1257.

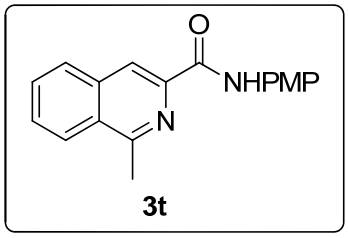
1-Methyl-*N*-phenylisoquinoline-3-carboxamide (3s)



3s

White solid; m.p. 160-163 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.32 (s, 1H), 8.56 (s, 1H), 8.18-8.16 (m, 1H), 7.99 (d, *J* = 7.2 Hz, 1H), 7.86-7.84 (m, 2H), 7.77-7.68 (m, 2H), 7.43-7.39 (m, 2H), 7.18-7.14 (m, 1H), 3.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 162.89, 157.77, 142.20, 138.15, 136.25, 130.83, 129.17, 129.04, 128.97, 128.82, 125.90, 124.25, 119.86, 119.58, 22.60; IR (KBr) *v*: 3333, 3061, 1683, 1599, 1435, 1311, 1194, 1024, 785, 768, 748, 689, 593 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{17}H_{14}N_2O$ (M^+): 262.1106; Found: 262.1103.

***N*-(4-methoxyphenyl)-1-methylisoquinoline-3-carboxamide (3t)**

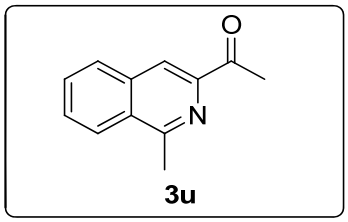


3t

White solid; m.p. 117-120 °C; ^{1}H NMR ($CDCl_3$, 400MHz), δ: 10.20 (s, 1H), 8.54(s, 1H), 8.16 (d. *J* = 8 Hz, 1H), 7.97 (d. *J* = 8 Hz, 1H), 7.78-7.66 (m, 4H), 6.96-6.92 (m, 2H), 3.82 (s, 3H), 3.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 162.61, 157.70, 156.37, 142.33, 136.25, 131.45, 130.77, 128.99, 128.88, 128.74, 125.88, 121.40, 119.36, 114.40, 55.60, 22.57; IR (KBr) *v*: 3351, 2993, 2921, 2838, 2365, 1672, 1610, 1568, 1523, 1410, 1246, 1184, 1034, 830, 811, 752 cm^{-1}; HRMS (EI) (*m/z*): calcd for

$C_{18}H_{16}N_2O_2$ (M^+): 292.1212; Found: 292.1213.

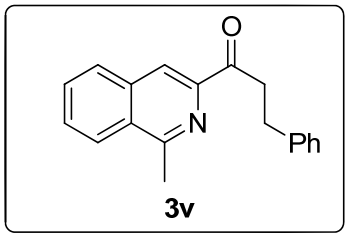
1-(1-Methylisoquinolin-3-yl)ethan-1-one (3u)



3u

White solid; m.p. 70-73 ^oC; ^1H NMR ($CDCl_3$, 400MHz), δ: 8.31 (s, 1H), 8.16-8.14 (m, 1H), 7.96-7.94 (m, 1H), 7.75-7.68 (m, 2H), 3.00 (s, 3H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 200.96, 158.47, 146.69, 135.62, 130.53, 129.48, 129.30, 129.16, 125.75, 119.12, 26.56, 22.73; IR (KBr) *v*: 3440, 2922, 2860, 2337, 1684, 1618, 1578, 1499, 1445, 1390, 1352, 1283, 1234, 1196, 757, 589 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{12}H_{11}NO$ (M^+): 185.0841; Found: 185.0844.

1-(1-Methylisoquinolin-3-yl)-3-phenylpropan-1-one (3v)

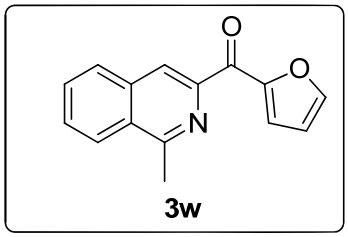


3v

White solid; m.p. 78-81 ^oC; ^1H NMR ($CDCl_3$, 400MHz), δ: 8.33 (s, 1H), 8.17-8.15 (m, 1H), 7.97 (dd, J_1 = 5.6 Hz, J_2 = 1.2 Hz, 1H), 7.75-7.69 (m, 2H), 7.34-7.29 (m, 4H), 7.22-7.19 (m, 1H), 3.68 (t, J = 6.4 Hz, 2H), 3.12 (t, J = 6.4 Hz, 2H), 2.99 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 201.82, 158.42, 146.43, 141.97, 135.71, 130.52, 129.51, 129.26, 128.69, 128.54, 126.05, 125.77, 119.13, 40.43, 30.38, 22.72; IR (KBr) *v*: 3440, 2981, 2918,

2856, 2362, 1687, 1618, 1562, 1496, 1442, 1392, 1377, 1168, 1133, 1058, 1024, 787, 754 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{19}H_{17}NO$ (M^+): 275.1310; Found: 275.1314.

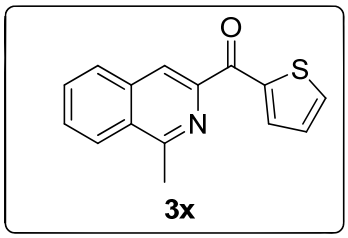
Furan-2-yl(1-methylisoquinolin-3-yl)methanone (3w)



3w

White solid; m.p. 117-119 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 8.49 (s, 1H), 8.26 (d, *J* = 3.2 Hz, 1H), 8.18-8.16 (m, 1H), 7.99-7.97 (m, 1H), 7.77-7.72 (m, 3H), 6.64 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1H), 3.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 179.57, 158.19, 151.93, 147.52, 146.72, 135.78, 130.68, 129.46, 129.30, 128.97, 125.74, 124.36, 121.66, 112.48, 22.72; IR (KBr) *v*: 3115, 2922, 2362, 1638, 1618, 1578, 1501, 1462, 1401, 1338, 1293, 1261, 802, 776, 742 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{11}NO_2$ (M^+): 237.0790; Found: 237.0796.

Methyl (1-methylisoquinolin-3-yl)(thiophen-2-yl)methanone (3x)

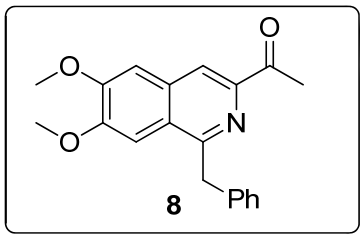


3x

White solid; m.p. 106-108 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 8.49-8.48 (m, 2H), 8.19-8.17 (m, 1H), 8.00-7.98 (m, 1H), 7.77-7.71 (m, 3H), 7.21-7.20 (m, 1H), 3.08(s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 183.78, 157.87,

146.58, 140.56, 136.58, 136.55, 135.95, 130.65, 129.44, 129.38, 129.03, 127.40, 125.72, 121.32, 22.18; IR (KBr) *v*: 2924, 2855, 2368, 1638, 1611, 1501, 1444, 1409, 1392, 1358, 1284, 1245, 1046, 783, 759, 713 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{15}H_{11}NOS(M^+)$: 253.0561; Found: 253.0560.

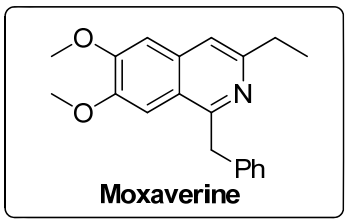
1-(1-Benzyl-6,7-dimethoxyisoquinolin-3-yl)ethan-1-one (8)



8

White solid; m.p. 143-145 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 8.25 (s, 1H), 7.33-7.18 (m, 7H), 4.83 (s, 2H), 4.01 (s, 3H), 3.90 (s, 3H), 2.80(s, 3H); ^{13}C NMR ($CDCl_3$, 150MHz), δ: 201.23, 157.11, 152.74, 151.65, 146.12, 139.46, 133.10, 128.79, 128.68, 126.52, 125.05, 118.34, 107.18, 104.35, 56.27, 56.11, 42.77, 26.43; IR (KBr) v: 3446, 2989, 2948, 2833, 1680, 1618, 1588, 1509, 1468, 1352, 1254, 1212, 1190, 1034, 888, 764, 749, 715 cm^{-1}; HRMS (EI) (m/z): calcd for $C_{20}H_{19}NO_3$ (M^+): 321.1365; Found: 321.1365.

1-Benzyl-3-ethyl-6,7-dimethoxyisoquinoline (Moxaverine)

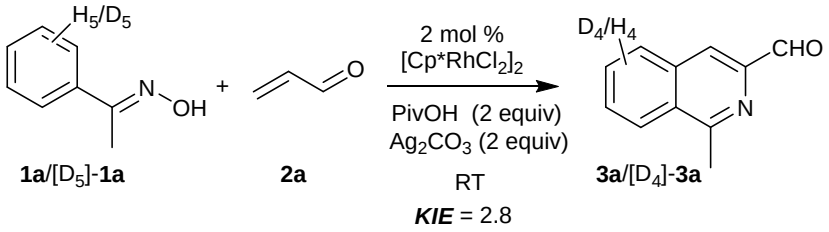


Moxaverine

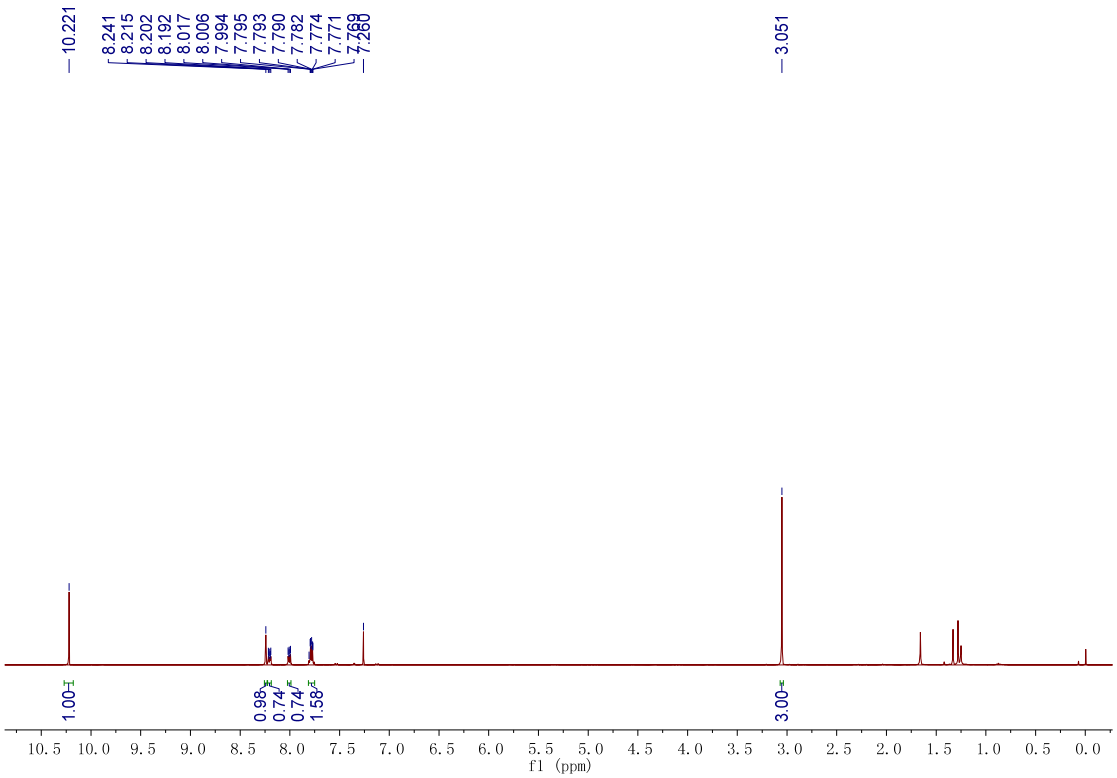
White solid; m.p. 65-67 °C; ^1H NMR ($CDCl_3$, 400MHz), δ: 7.20-7.07 (m, 7H), 6.91 (s, 1H), 4.51 (s, 2H), 3.90 (s, 3H), 3.75 (s, 3H), 2.88 (q, J = 7.2 Hz, 2H), 1.32(t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz), δ: 157.20,

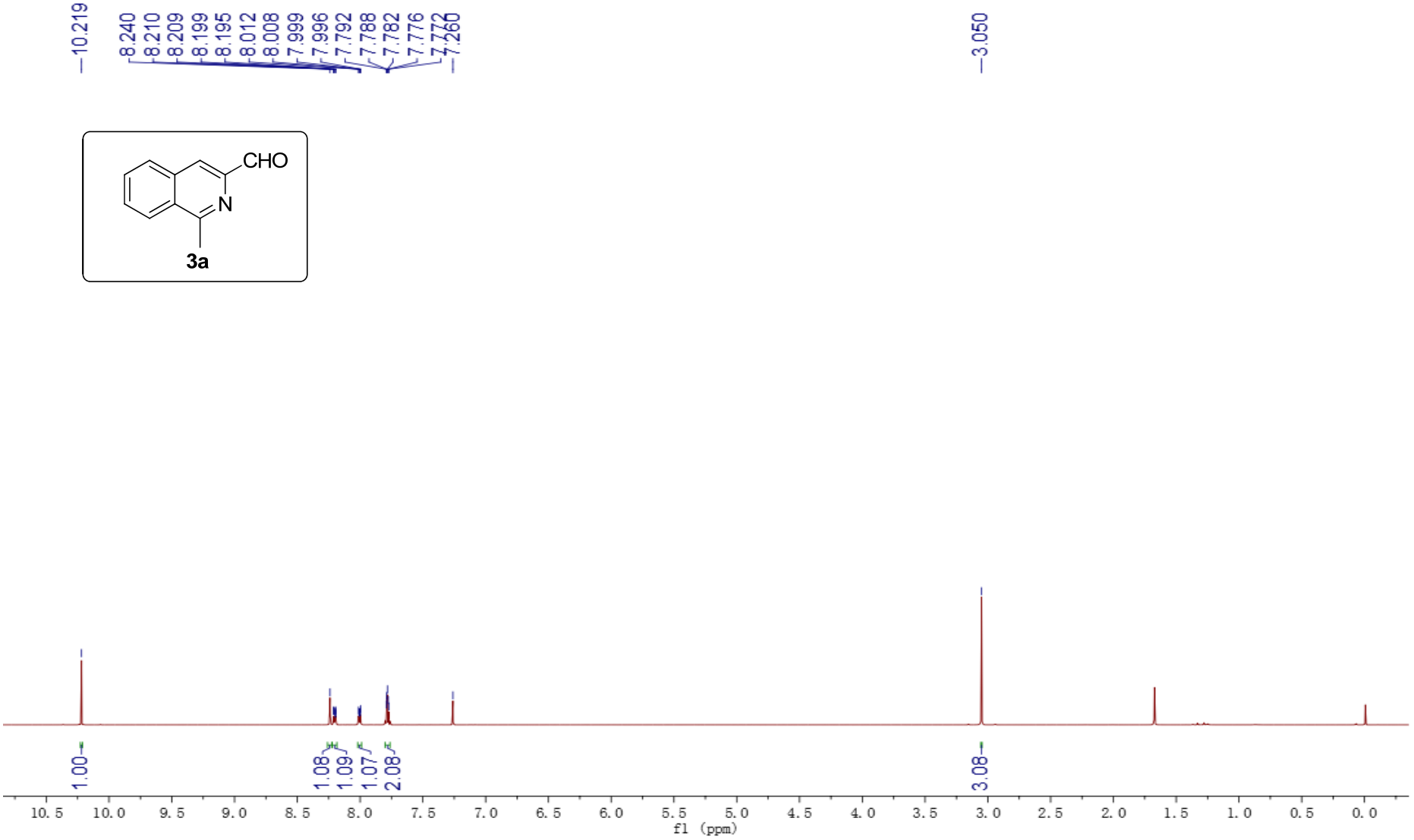
154.95, 152.45, 149.18, 139.99, 134.37, 128.61, 128.57, 126.25, 121.18, 115.54, 105.04, 104.45, 56.05, 55.89, 42.93, 31.16, 14.43; IR (KBr) v: 3022, 2961, 2927, 1622, 1598, 1571, 1508, 1451, 1428, 1216, 1159, 1043, 1028, 875, 848, 749, 707 cm^{-1}; HRMS (EI) (*m/z*): calcd for $C_{20}H_{21}NO_2$ (M^+): 307.1572; Found: 307.1572.

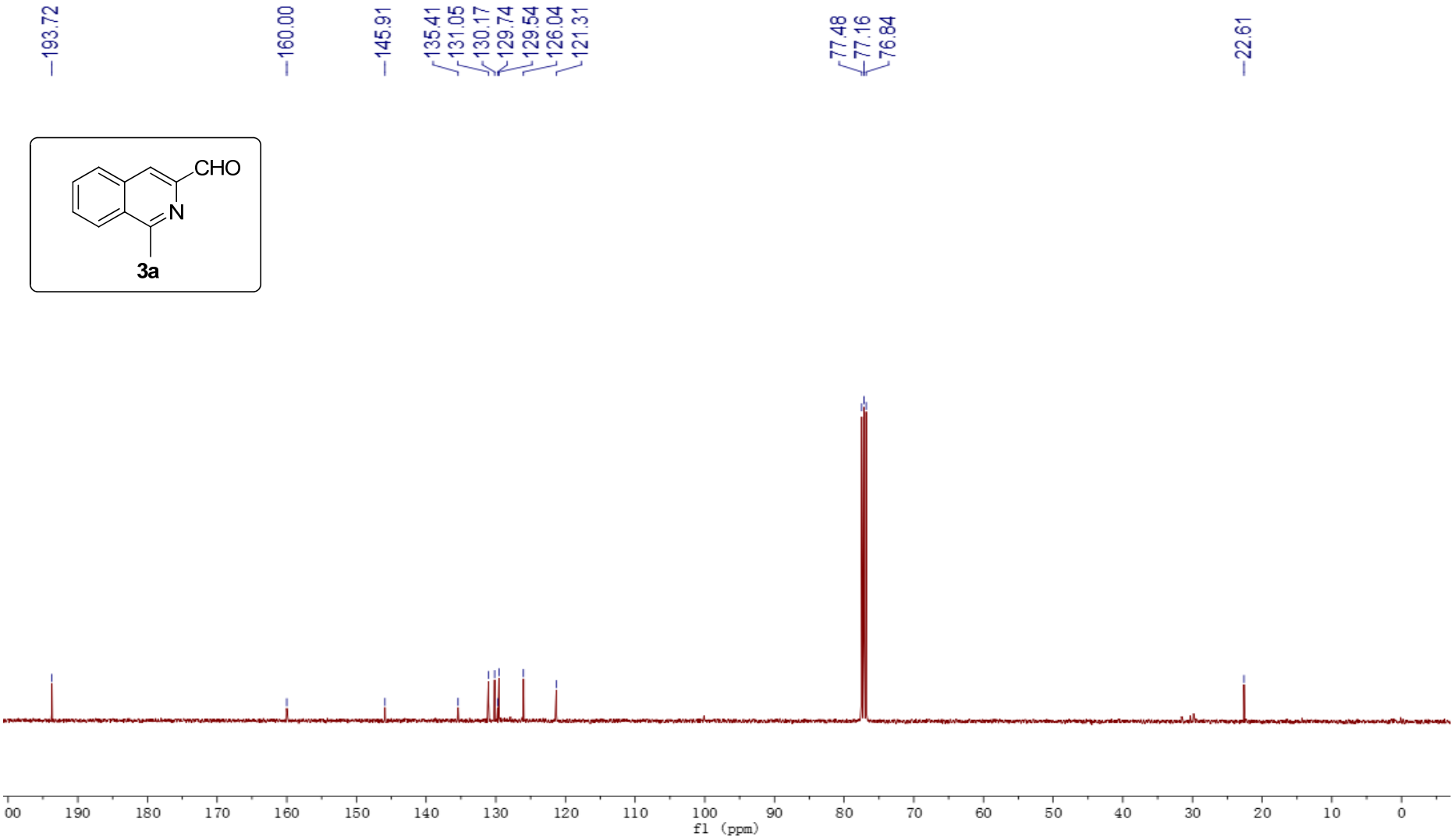
5. Kinetic Isotope Effect Study:

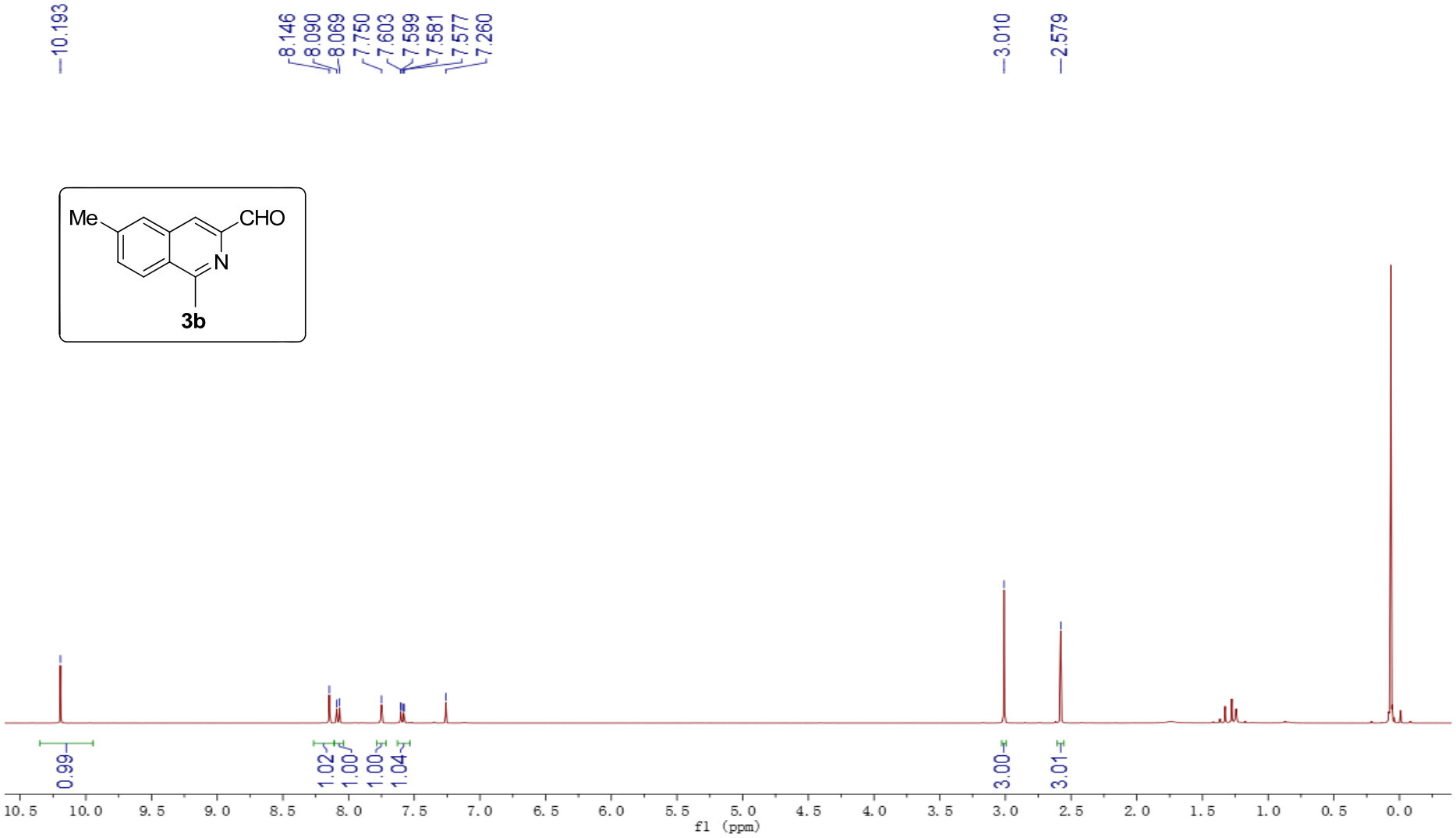


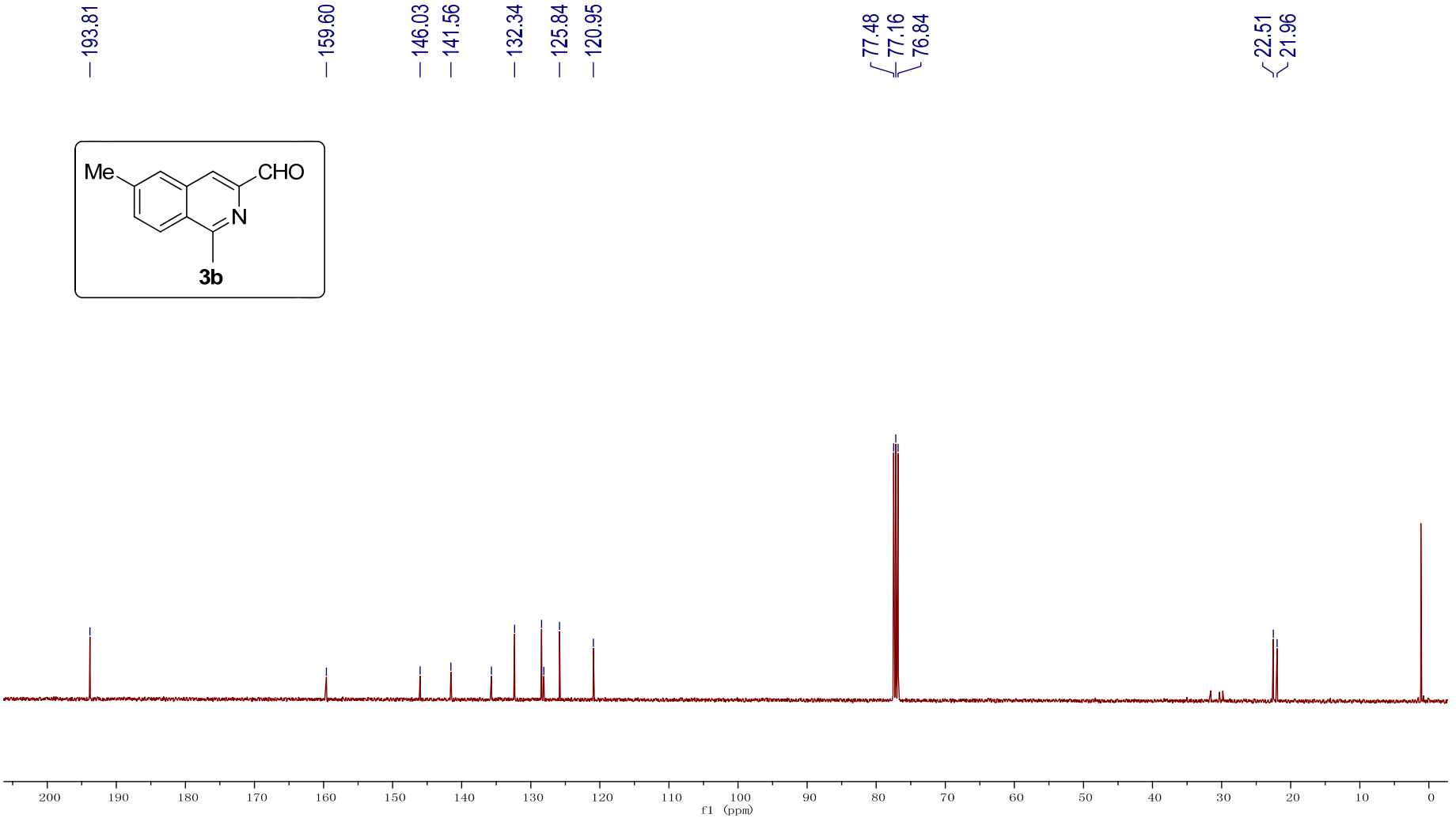
Following general procedure, a vial equipped with a stir bar was charged with **1a** (27.0 mg, 0.2 mmol), acrolein **2a** (33.6 mg, 0.6 mmol), $[Cp^*RhCl_2]_2$ (2.5 mg, 2 mol %), Ag_2CO_3 (110.3 mg, 0.4 mmol), PivOH (40.8 mg, 0.4 mmol), MeCN (1 mL). In another vial, $[D_5]$-1a (28.0 mg, 0.2 mmol) was used instead of 1a. The two reactions were allowed to stir at room temperature for 3 h. Afterwards, the reactions were combined and the solvent was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as eluent to give the product as a white solid (15 mg, 21.7% yield). The value of K_H/K_D was obtained based on ^{1}HNMR.

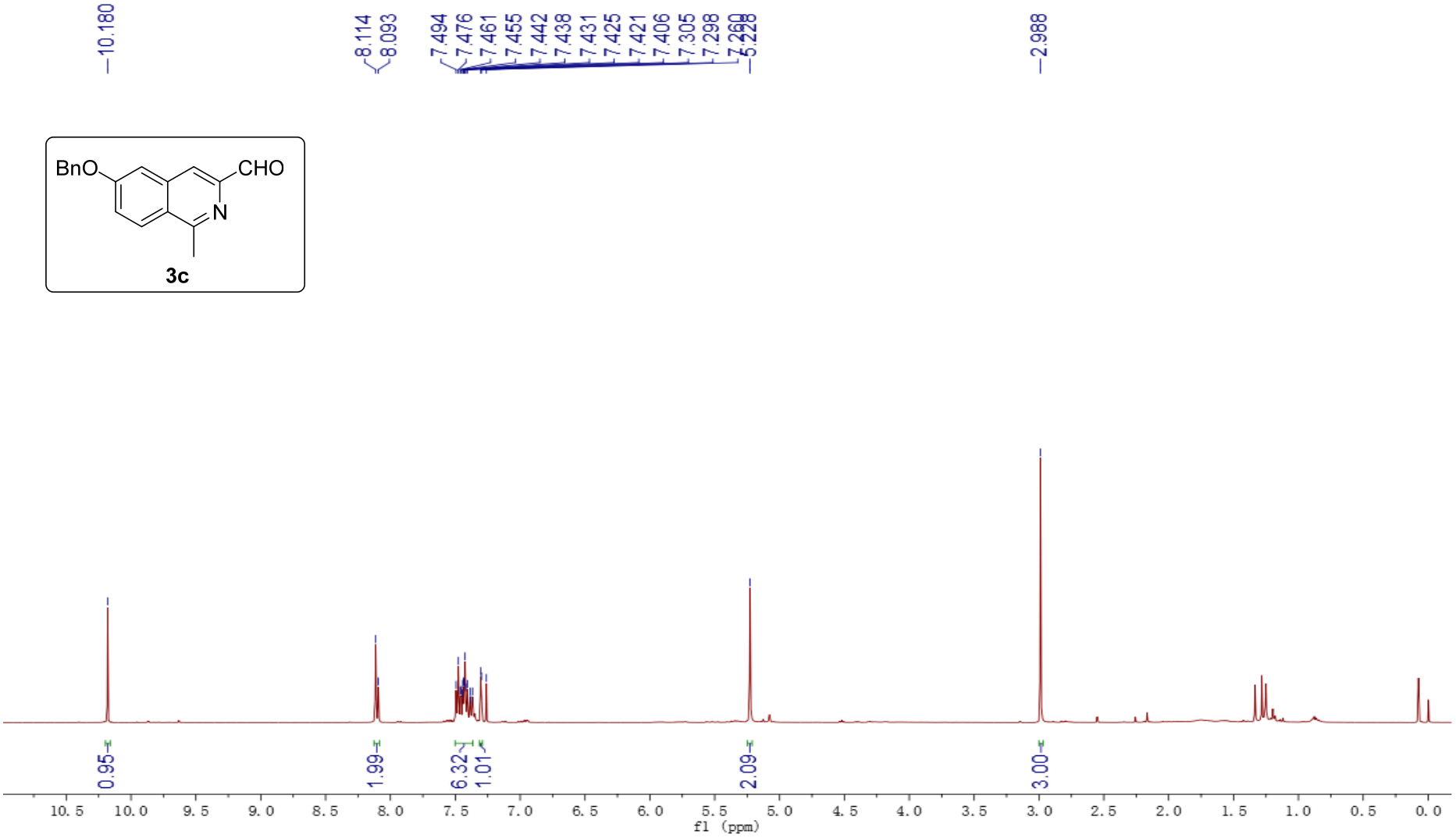

10.221
8.241
8.215
8.202
8.192
8.017
8.006
7.994
7.795
7.793
7.790
7.782
7.774
7.771
7.769
7.260
3.051
1.00
0.98
0.74
0.74
1.58
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

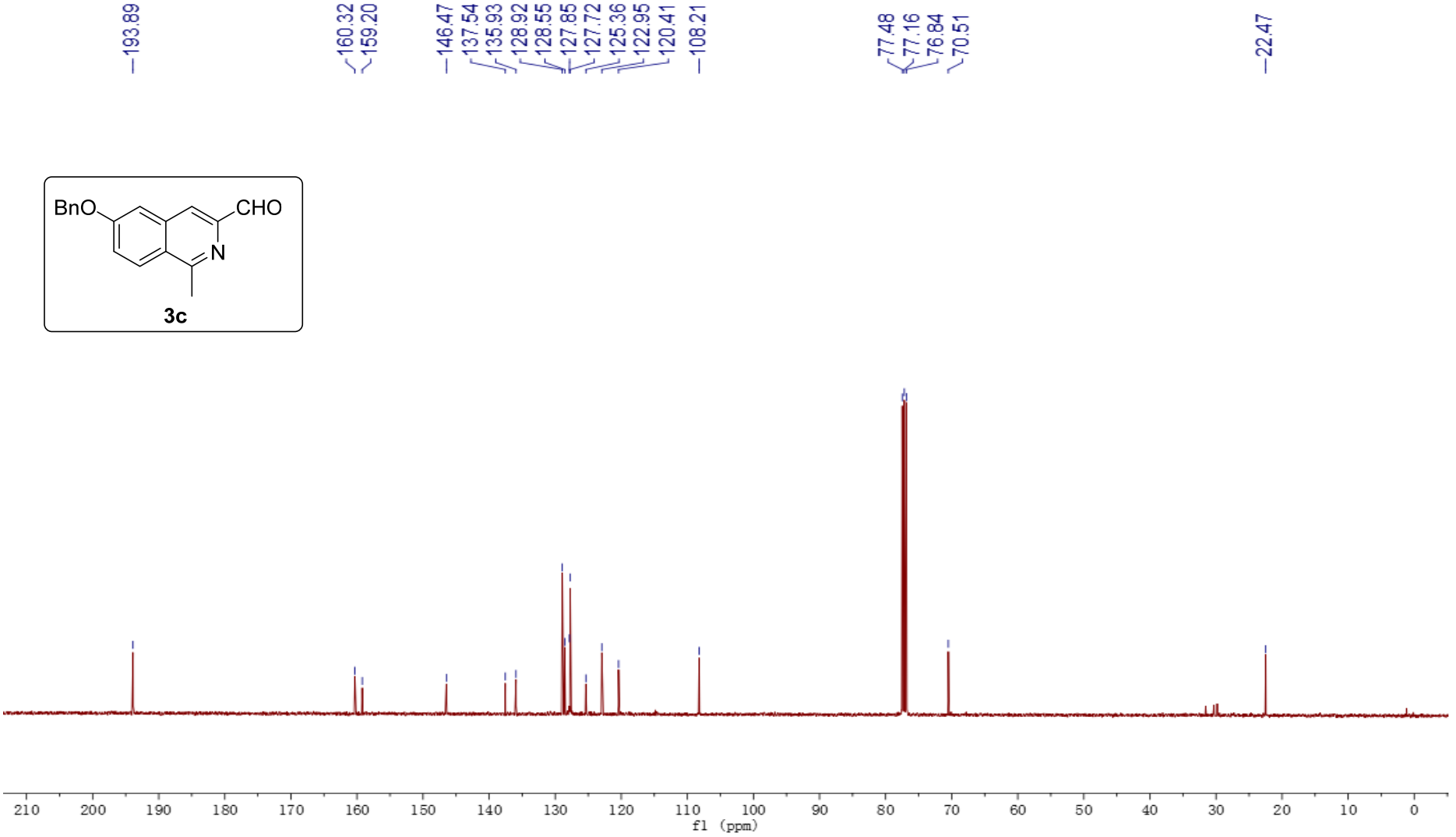

10.219
8.240
8.210
8.209
8.199
8.195
8.012
8.008
7.999
7.996
7.792
7.788
7.782
7.776
7.772
7.260
3.050
CHO
N
3a
1.00
1.08
1.09
1.07
2.08
3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

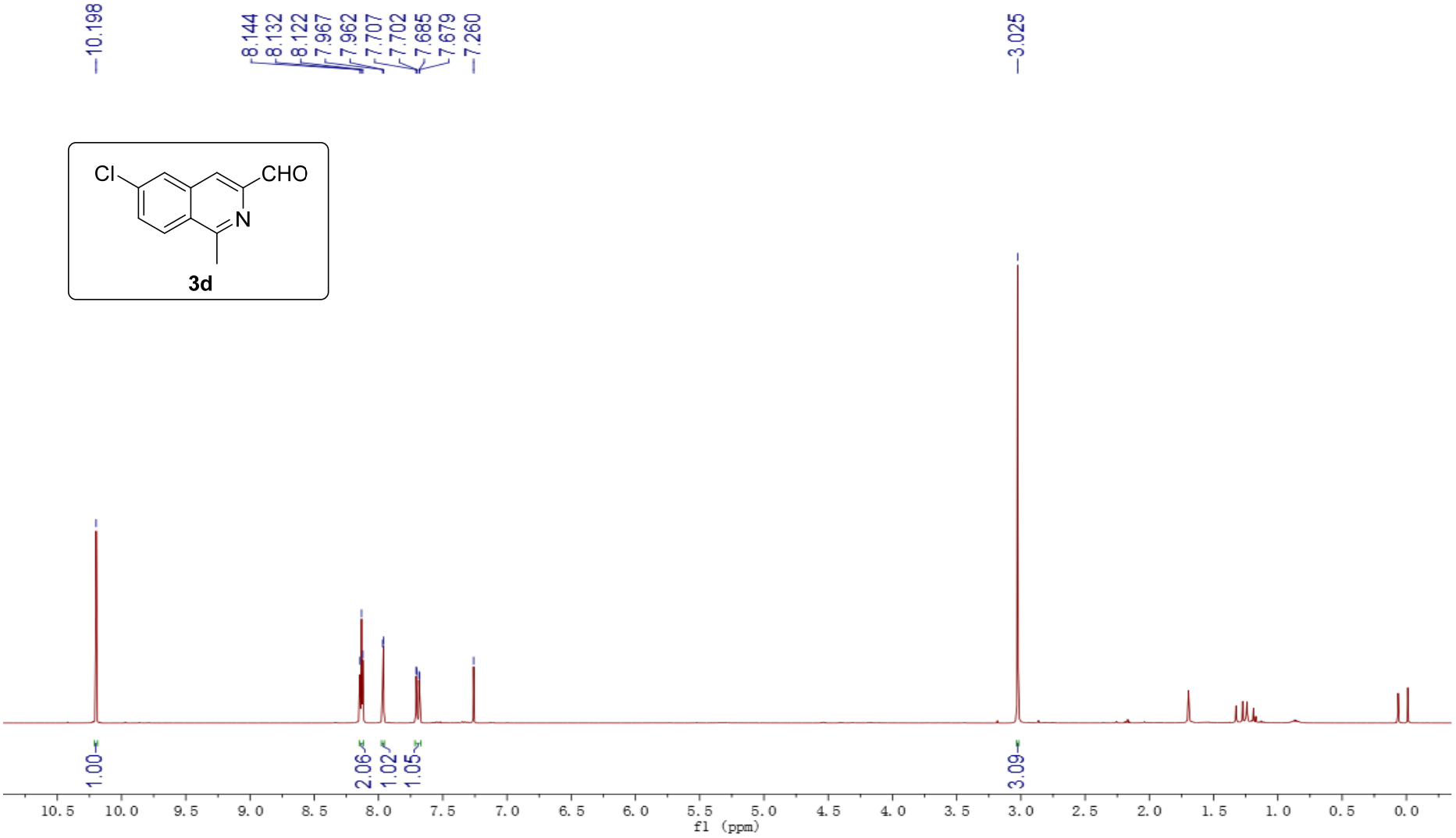

193.72
160.00
145.91
135.41
131.05
130.17
129.74
129.54
126.04
121.31
77.48
77.16
76.84
22.61
CHO
N
3a
f1 (ppm)

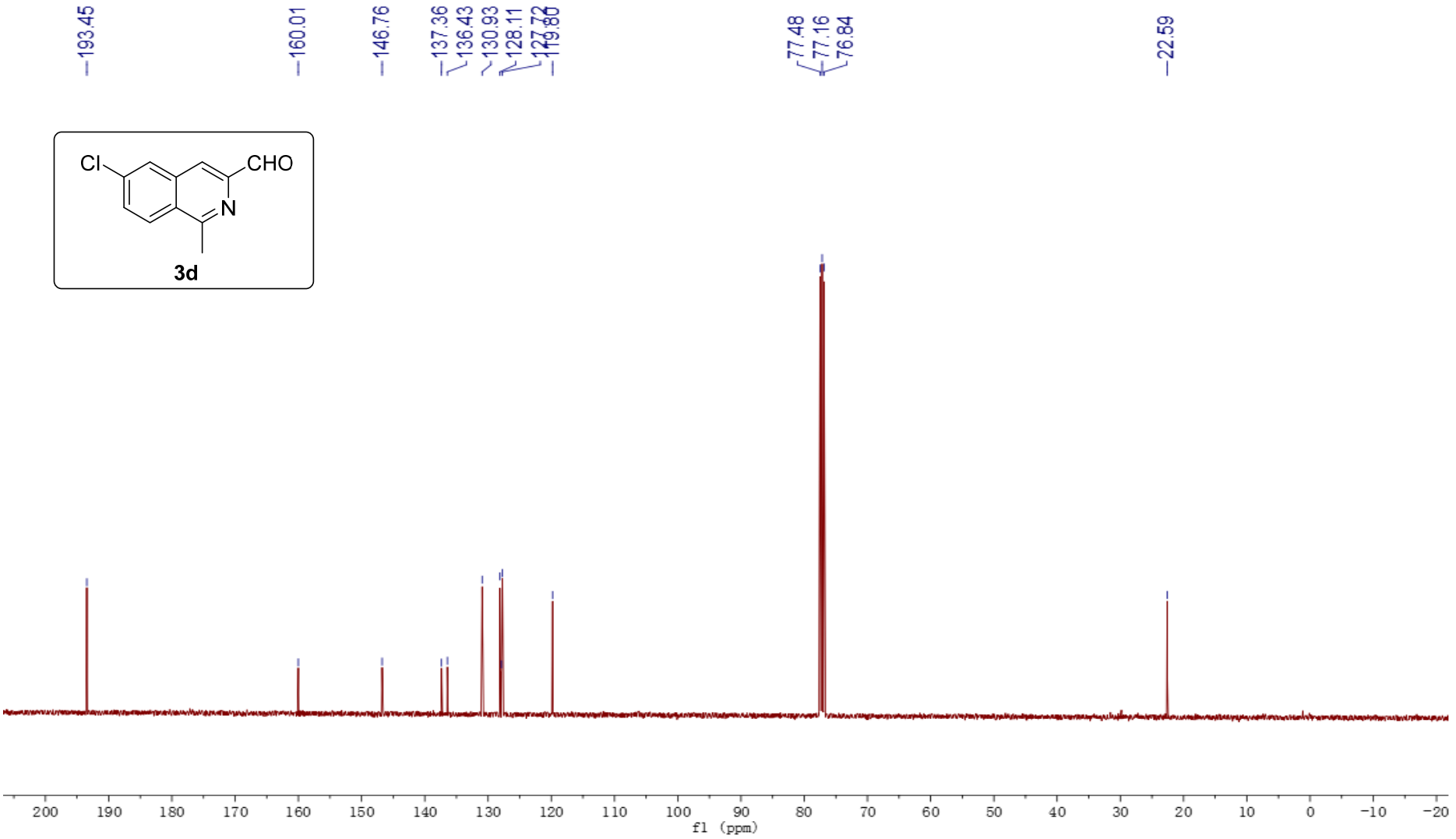

10.193
8.146
8.090
8.069
7.750
7.603
7.599
7.581
7.577
7.260
3.010
2.579
Me
CHO
N
3b
0.99
1.02
1.00
1.00
1.04
3.00
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

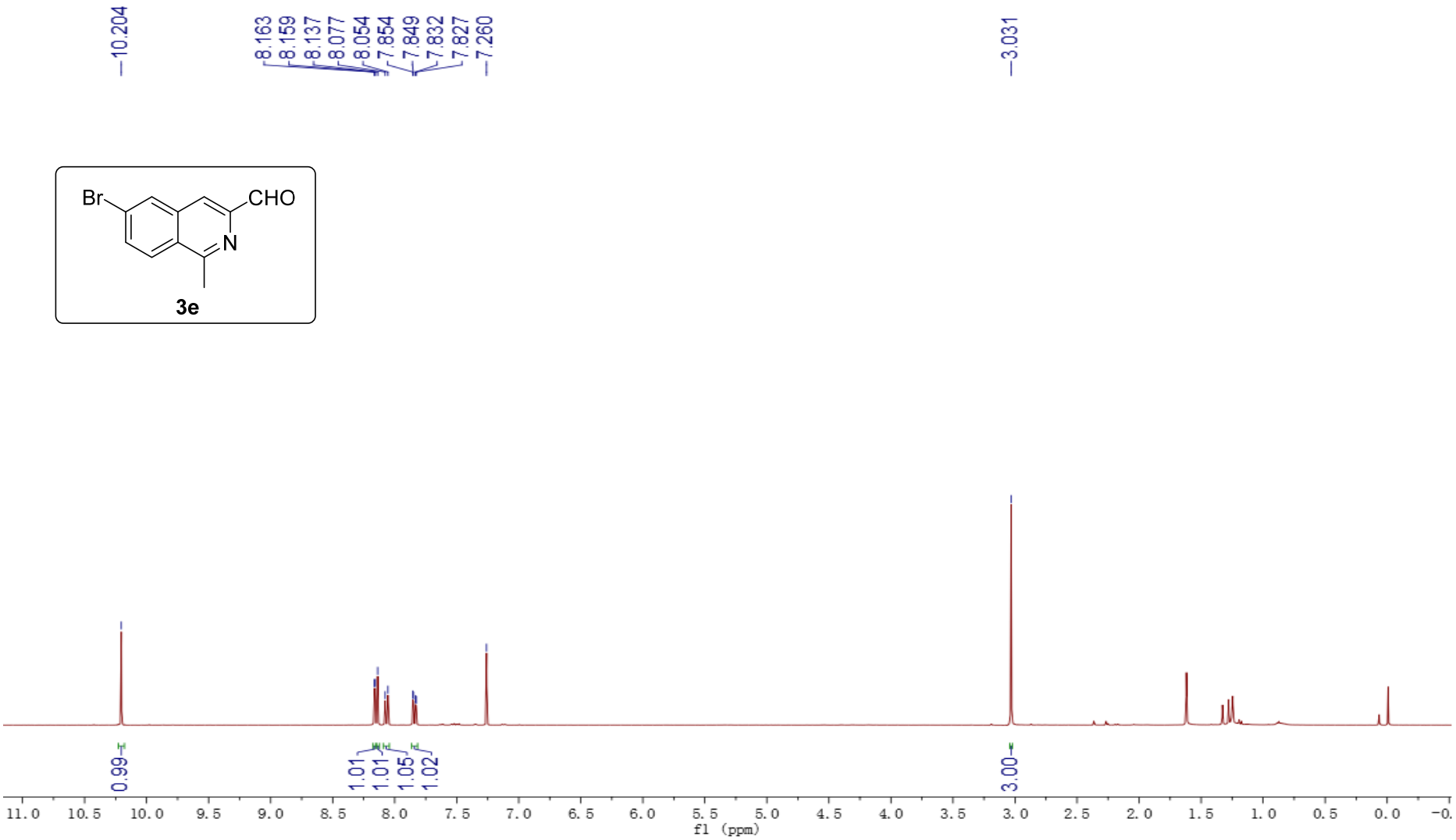

193.81
159.60
146.03
141.56
132.34
125.84
120.95
77.48
77.16
76.84
22.51
21.96
Me
CHO
N
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

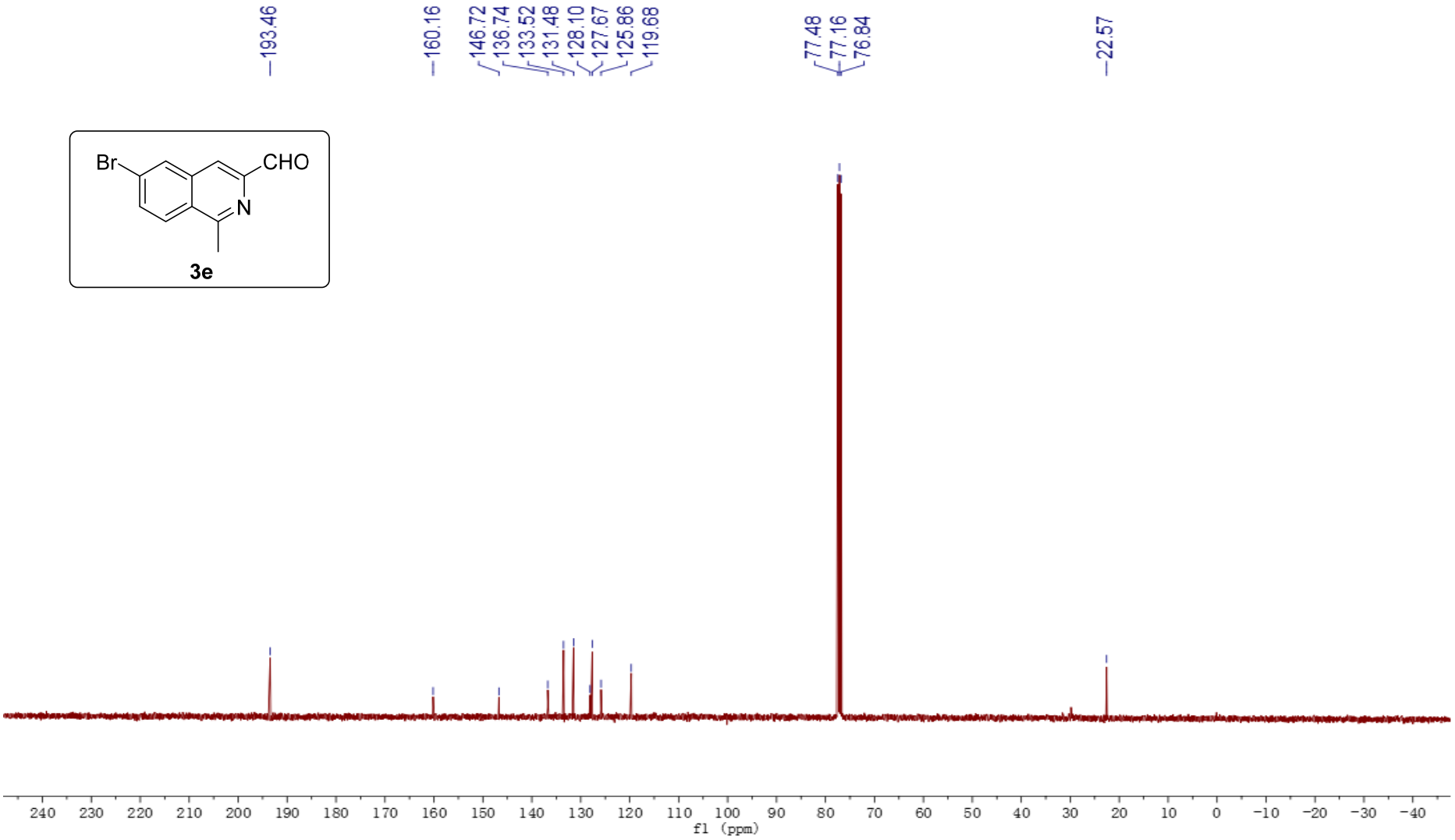

10.180
8.114
8.093
7.494
7.476
7.461
7.455
7.442
7.438
7.431
7.425
7.421
7.406
7.305
7.298
7.260
7.228
2.988
BnO
CHO
N
3c
0.95
1.99
6.32
1.01
2.09
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

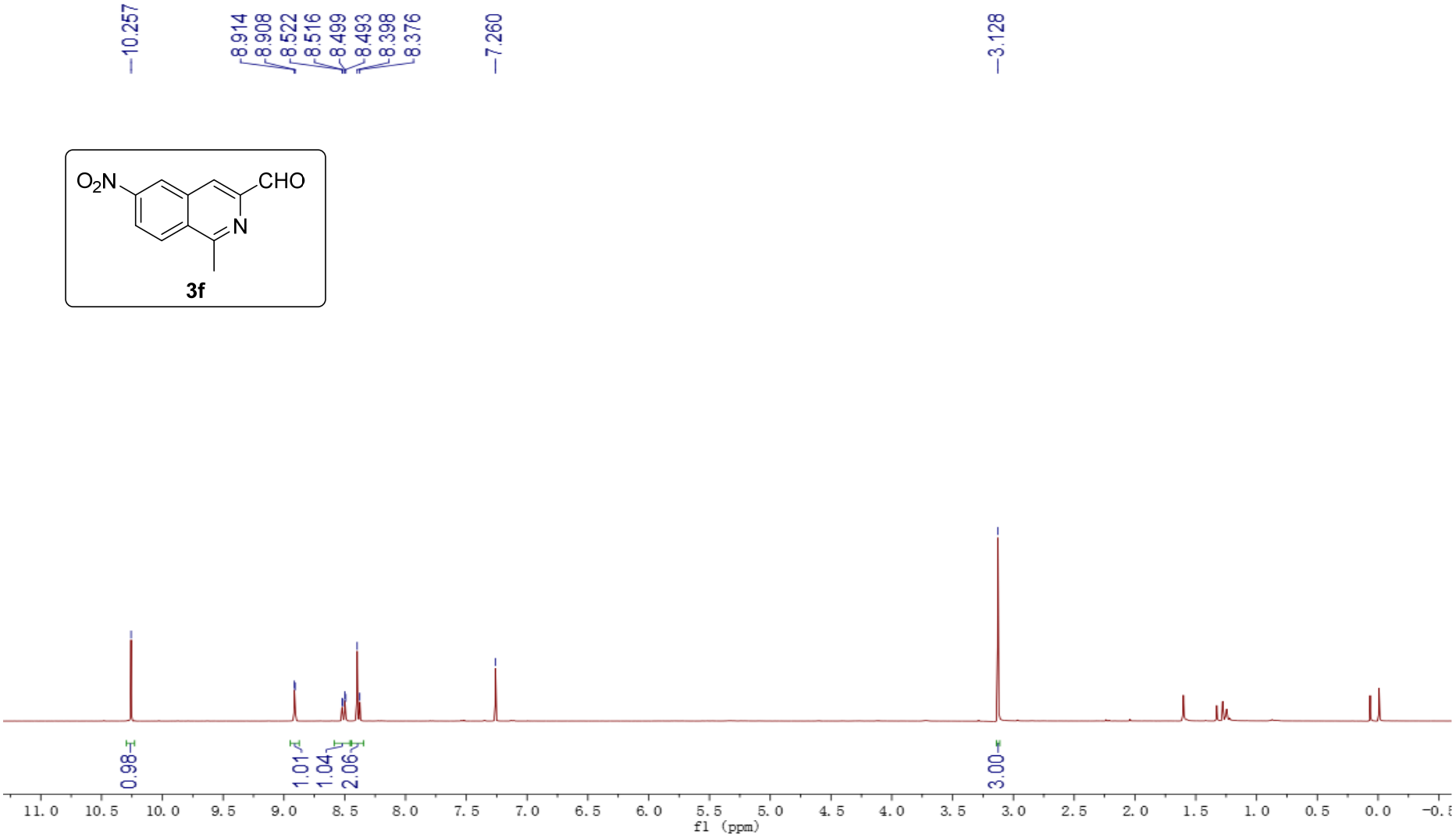

193.89
160.32
159.20
146.47
137.54
135.93
128.92
128.55
127.85
127.72
125.36
122.95
120.41
108.21
77.48
77.16
76.84
70.51
22.47
BnO
CHO
N
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

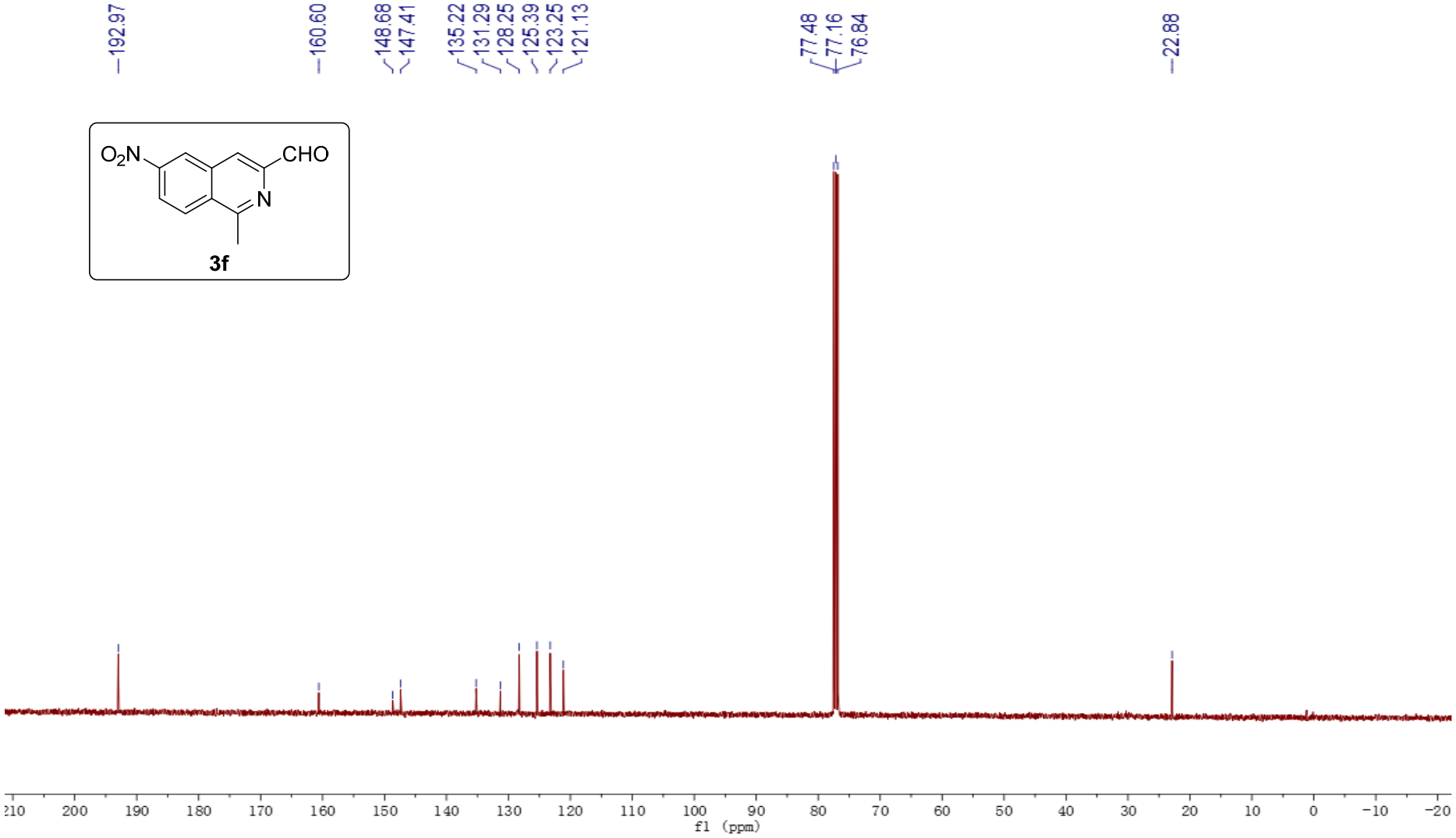

10.198
8.144
8.132
8.122
7.967
7.962
7.707
7.702
7.685
7.679
7.260
3.025
Cl
CHO
N
3d
1.00
2.06
1.02
1.05
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

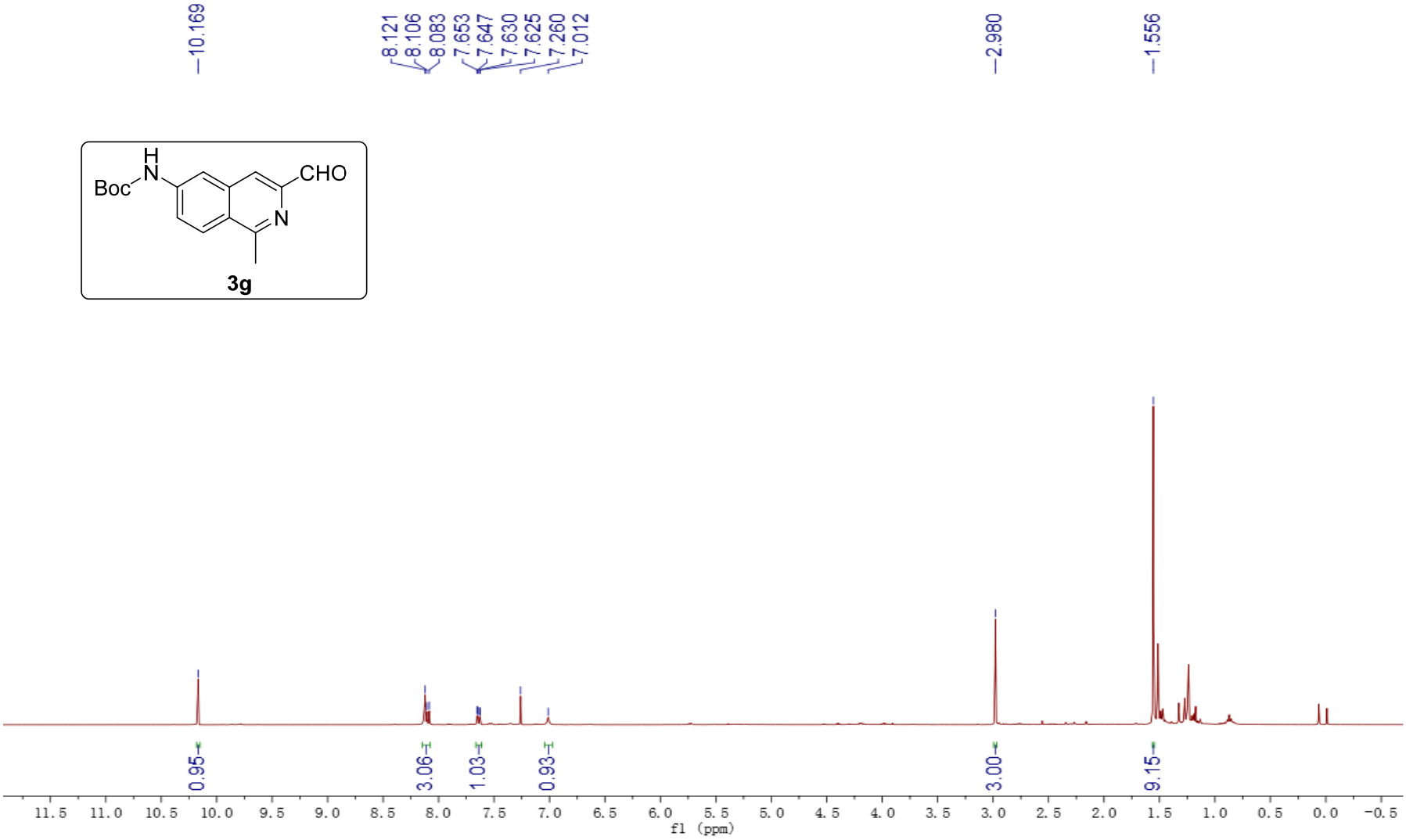

193.45
160.01
146.76
137.36
136.43
130.93
128.11
127.72
119.80
77.48
77.16
76.84
22.59
Cl
CHO
N
3d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

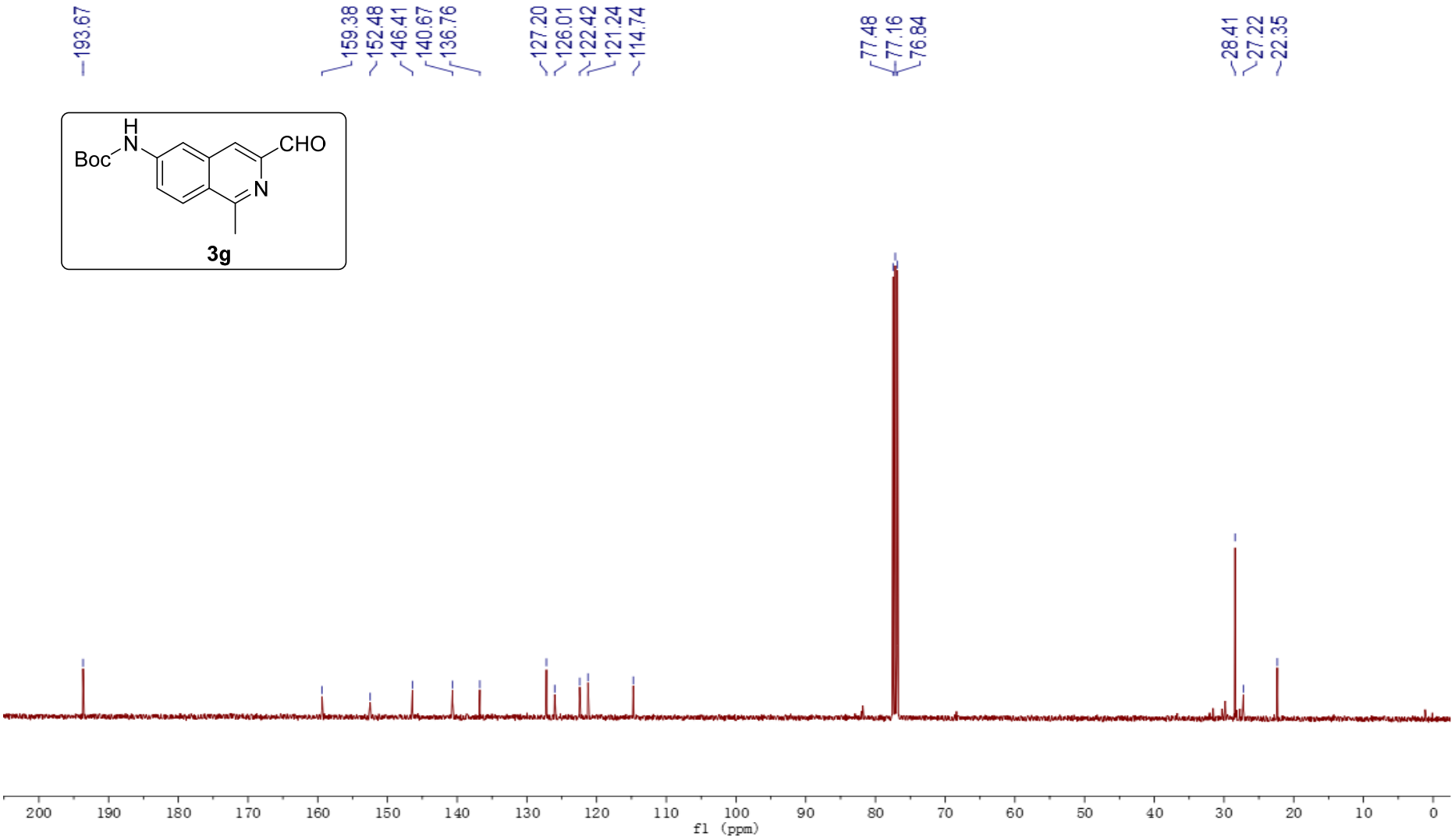

10.204
8.163
8.159
8.137
8.077
8.054
7.854
7.849
7.832
7.827
7.260
3.031
Br
CHO
N
3e
0.99
1.01
1.01
1.05
1.02
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

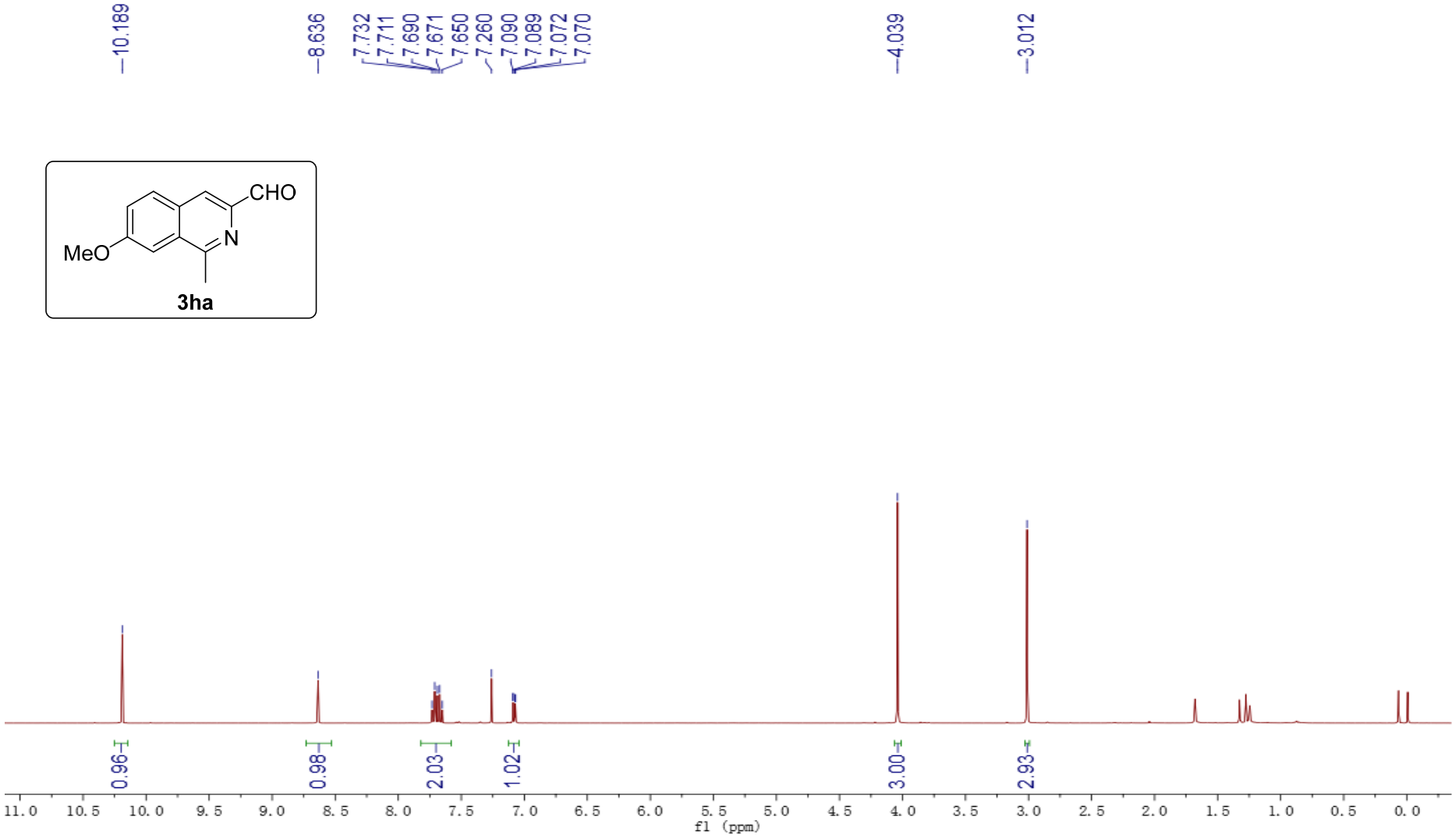

193.46
160.16
146.72
136.74
133.52
131.48
128.10
127.67
125.86
119.68
77.48
77.16
76.84
22.57
Br
CHO
N
3e
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)

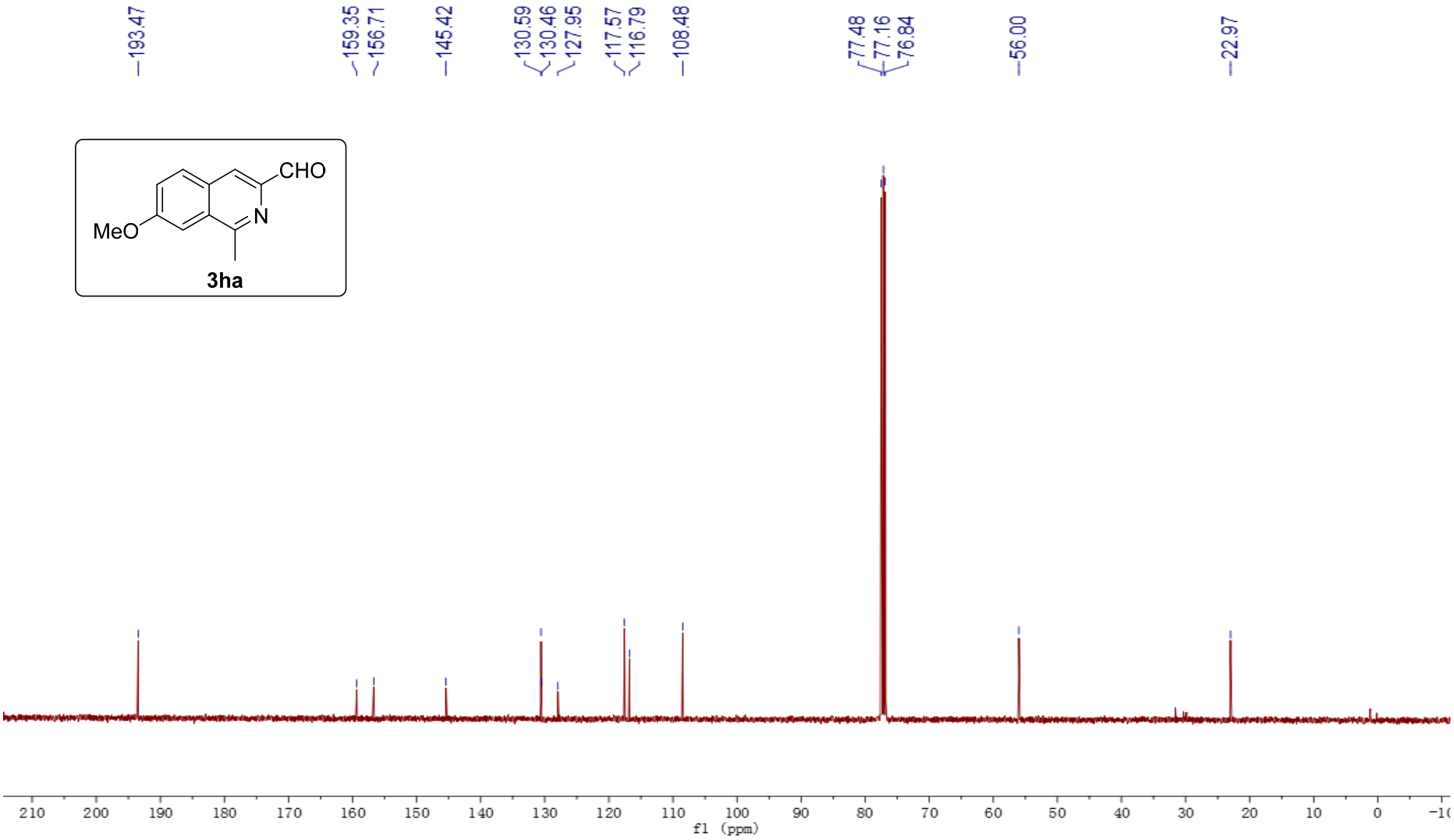

10.257
8.914
8.908
8.522
8.516
8.499
8.493
8.398
8.376
7.260
3.128
O2N
CHO
N
3f
0.98
1.01
1.04
2.06
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

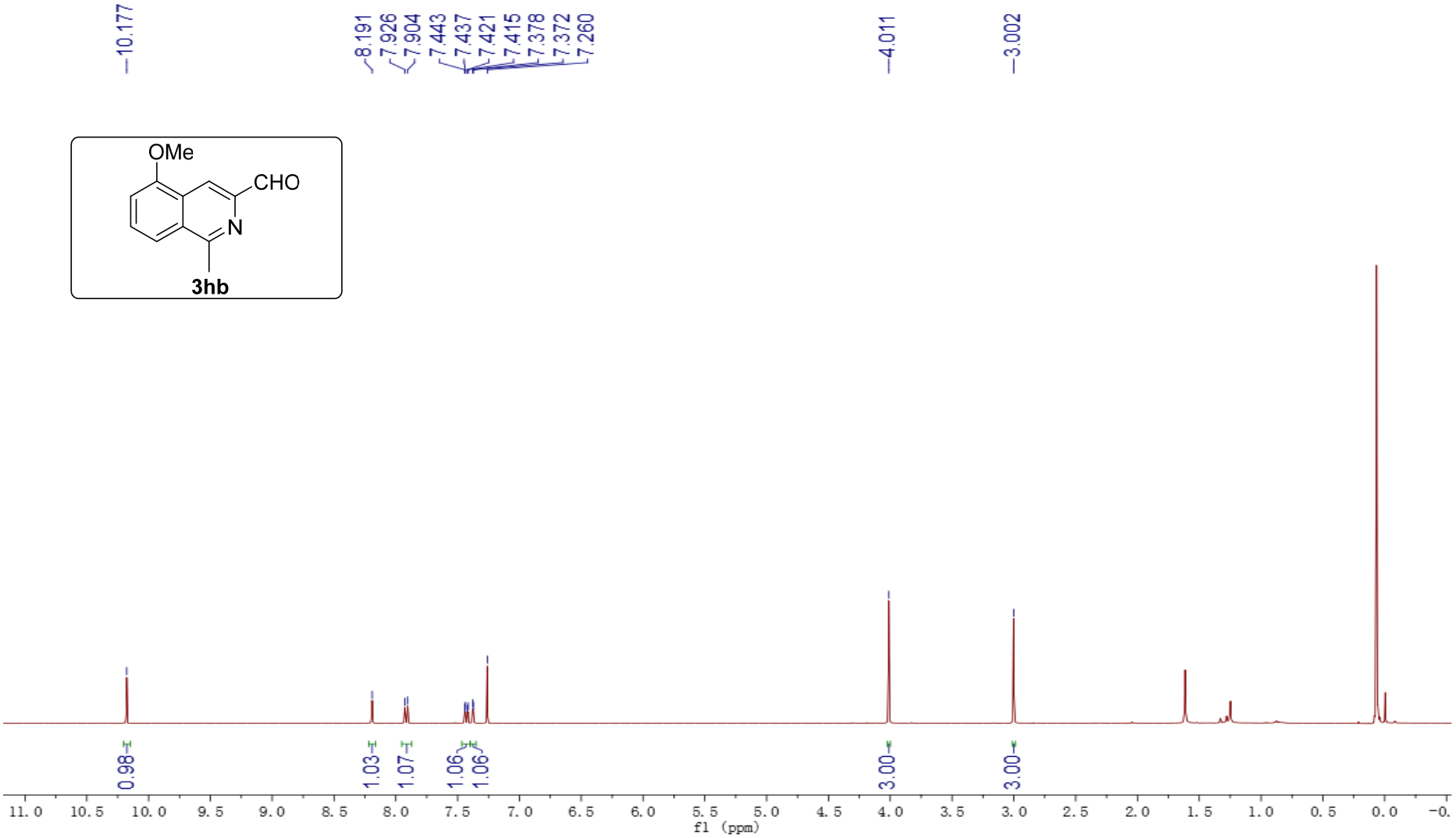

192.97
160.60
148.68
147.41
135.22
131.29
128.25
125.39
123.25
121.13
77.48
77.16
76.84
22.88
O2N
CHO
N
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

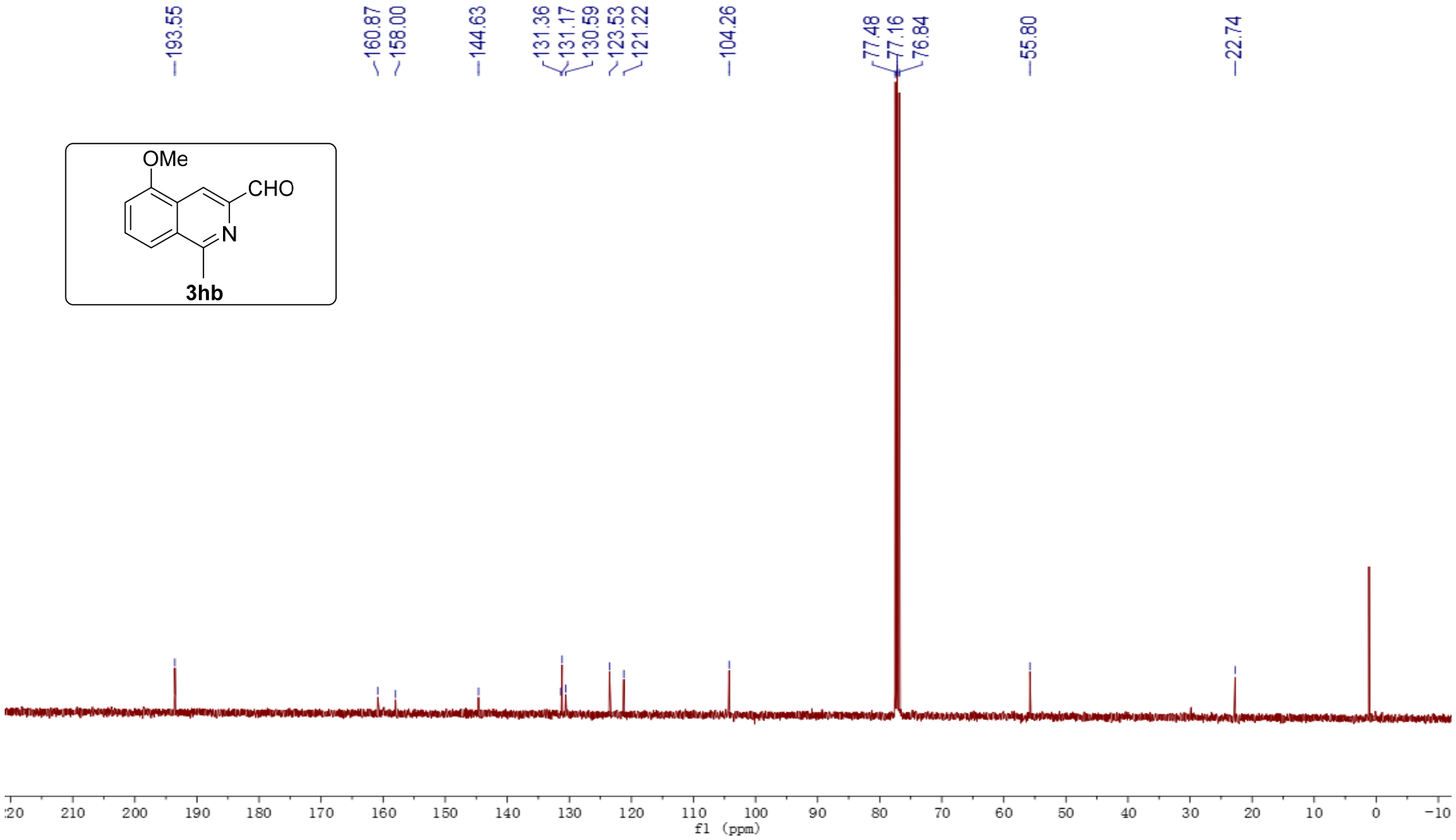

10.169
8.121
8.106
8.083
7.653
7.647
7.630
7.625
7.260
7.012
2.980
1.556
Boc
H
N
CHO
N
3g
0.95
3.06
1.03
0.93
3.00
9.15
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

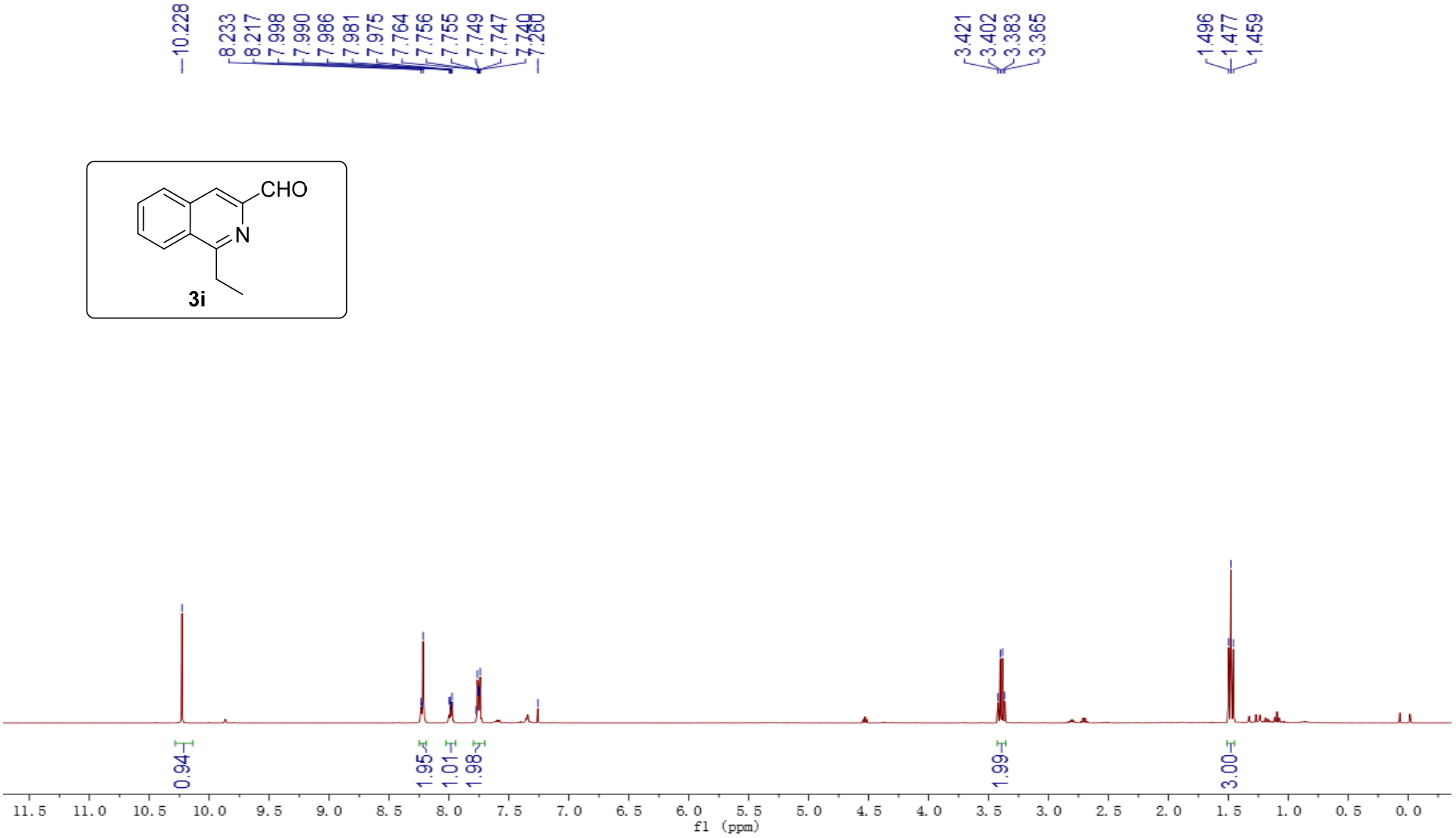

193.67
159.38
152.48
146.41
140.67
136.76
127.20
126.01
122.42
121.24
114.74
77.48
77.16
76.84
28.41
27.22
22.35
Boc
H
N
CHO
N
3g
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

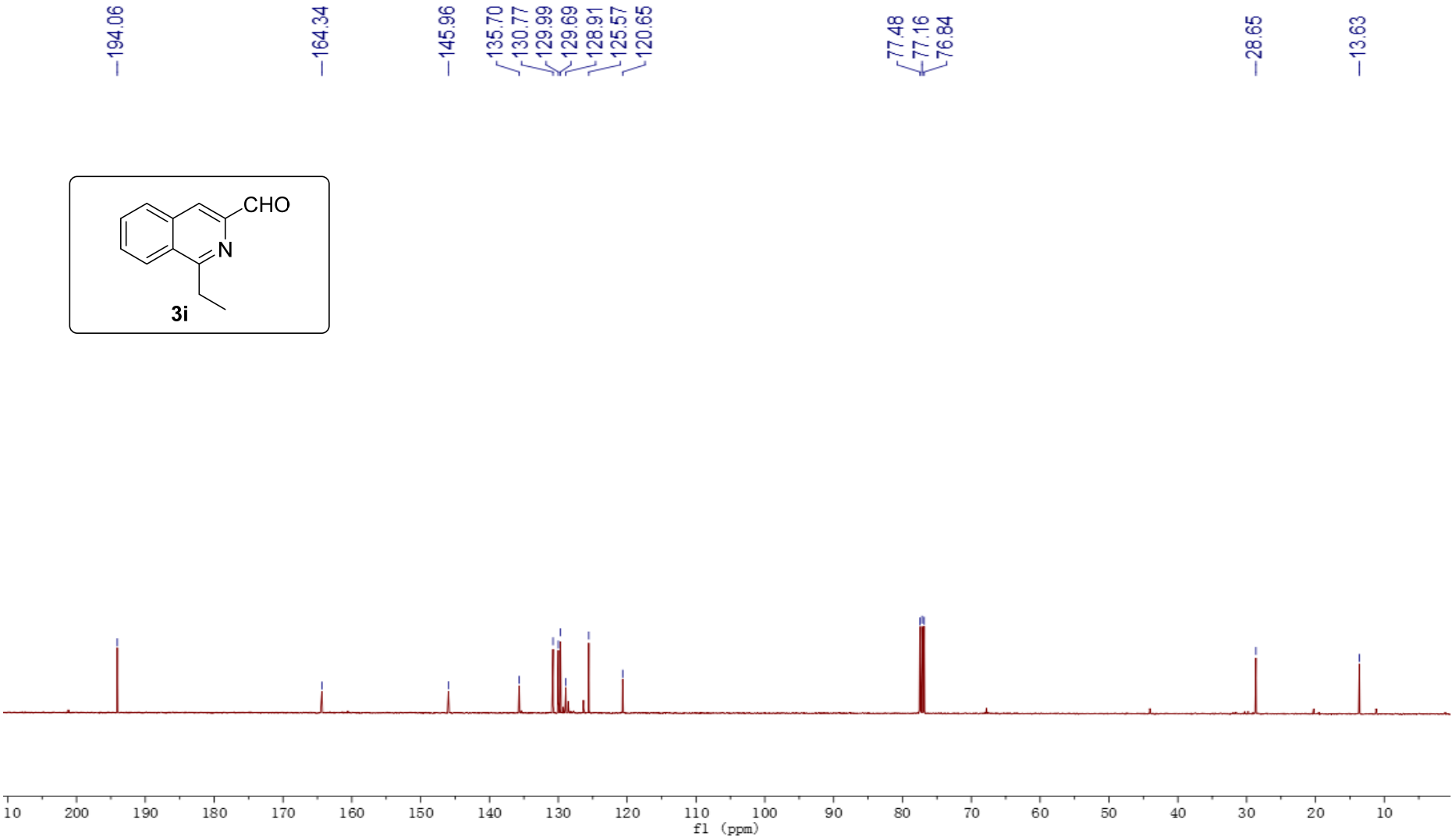

10.189
8.636
7.732
7.711
7.690
7.671
7.650
7.260
7.090
7.089
7.072
7.070
4.039
3.012
CHO
N
MeO
3ha
0.96
0.98
2.03
1.02
3.00
2.93
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


193.47
159.35
156.71
145.42
130.59
130.46
127.95
117.57
116.79
108.48
77.48
77.16
76.84
56.00
22.97
CHO
N
MeO
3ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

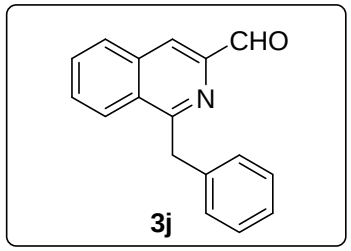

10.177
8.191
7.926
7.904
7.443
7.437
7.421
7.415
7.378
7.372
7.260
4.011
3.002
OMe
CHO
N
3hb
0.98
1.03
1.07
1.06
1.06
3.00
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


193.55
160.87
158.00
144.63
131.36
131.17
130.59
123.53
121.22
104.26
77.48
77.16
76.84
55.80
22.74
OMe
CHO
N
3hb
f1 (ppm)

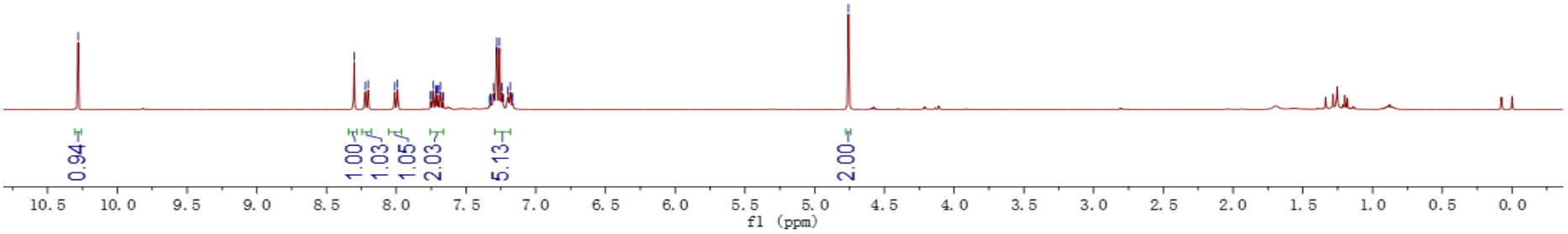

10.228
8.233
8.217
7.998
7.990
7.986
7.981
7.975
7.764
7.756
7.755
7.749
7.747
7.740
7.260
3.421
3.402
3.383
3.365
1.496
1.477
1.459
CHO
N
3i
0.94
1.95
1.01
1.98
1.99
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

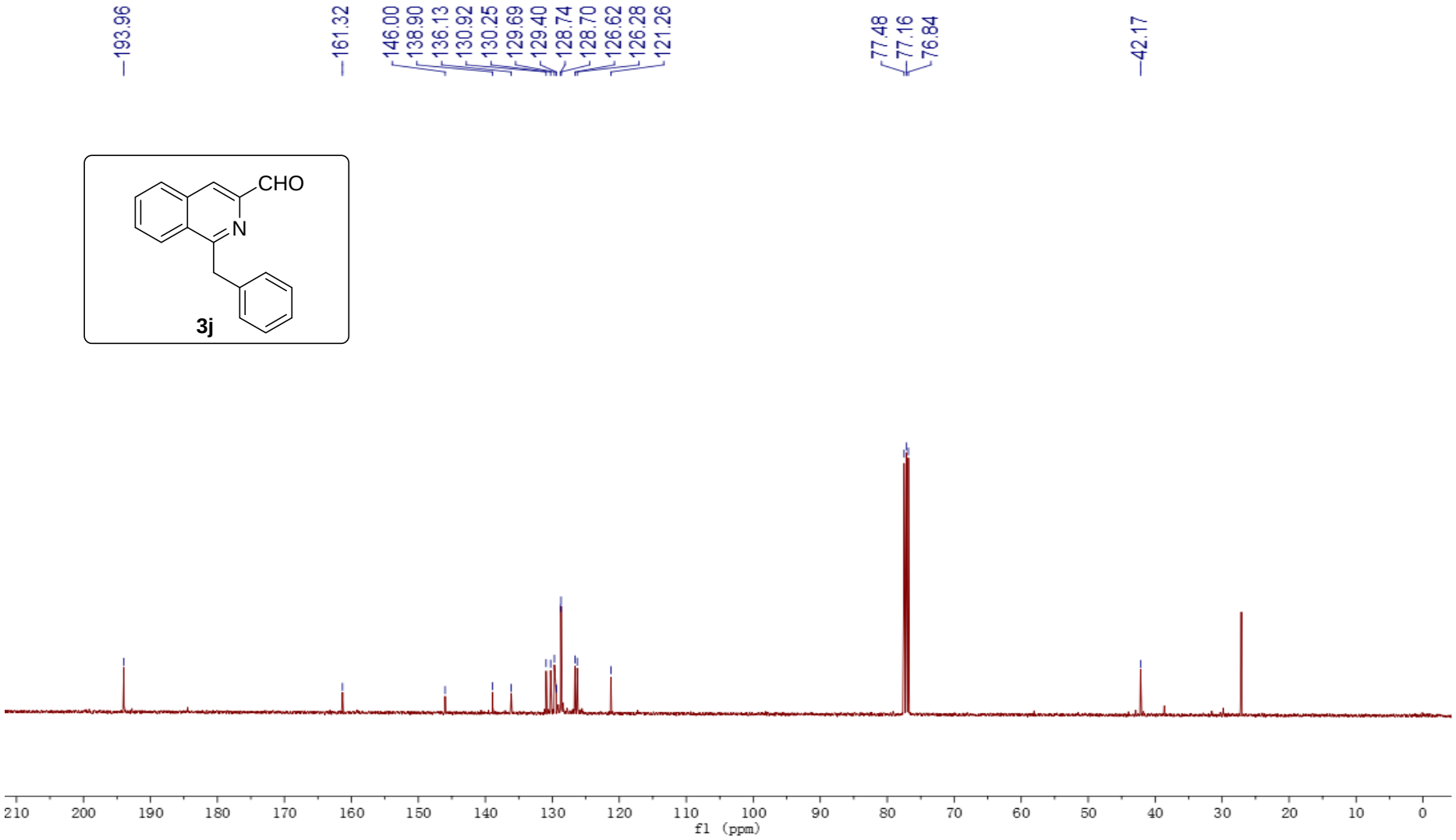

194.06
164.34
145.96
135.70
130.77
129.99
129.69
128.91
125.57
120.65
77.48
77.16
76.84
28.65
13.63
CHO
N
3i
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

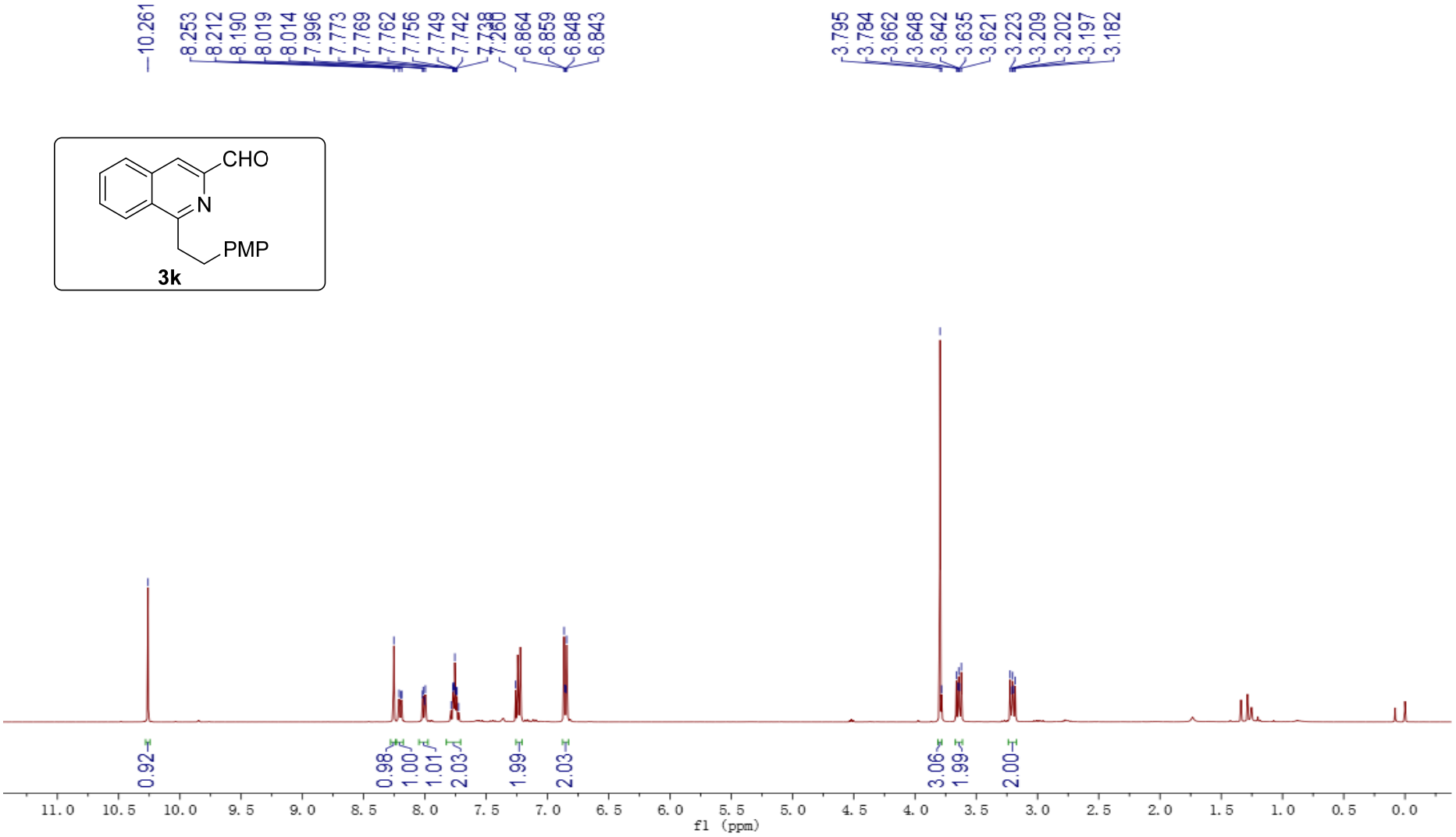

10.281
8.302
8.223
8.202
8.011
7.991
7.753
7.751
7.734
7.717
7.714
7.702
7.699
7.682
7.664
7.662
7.325
7.319
7.301
7.284
7.279
7.259
7.241
7.230
7.200
7.183
7.170

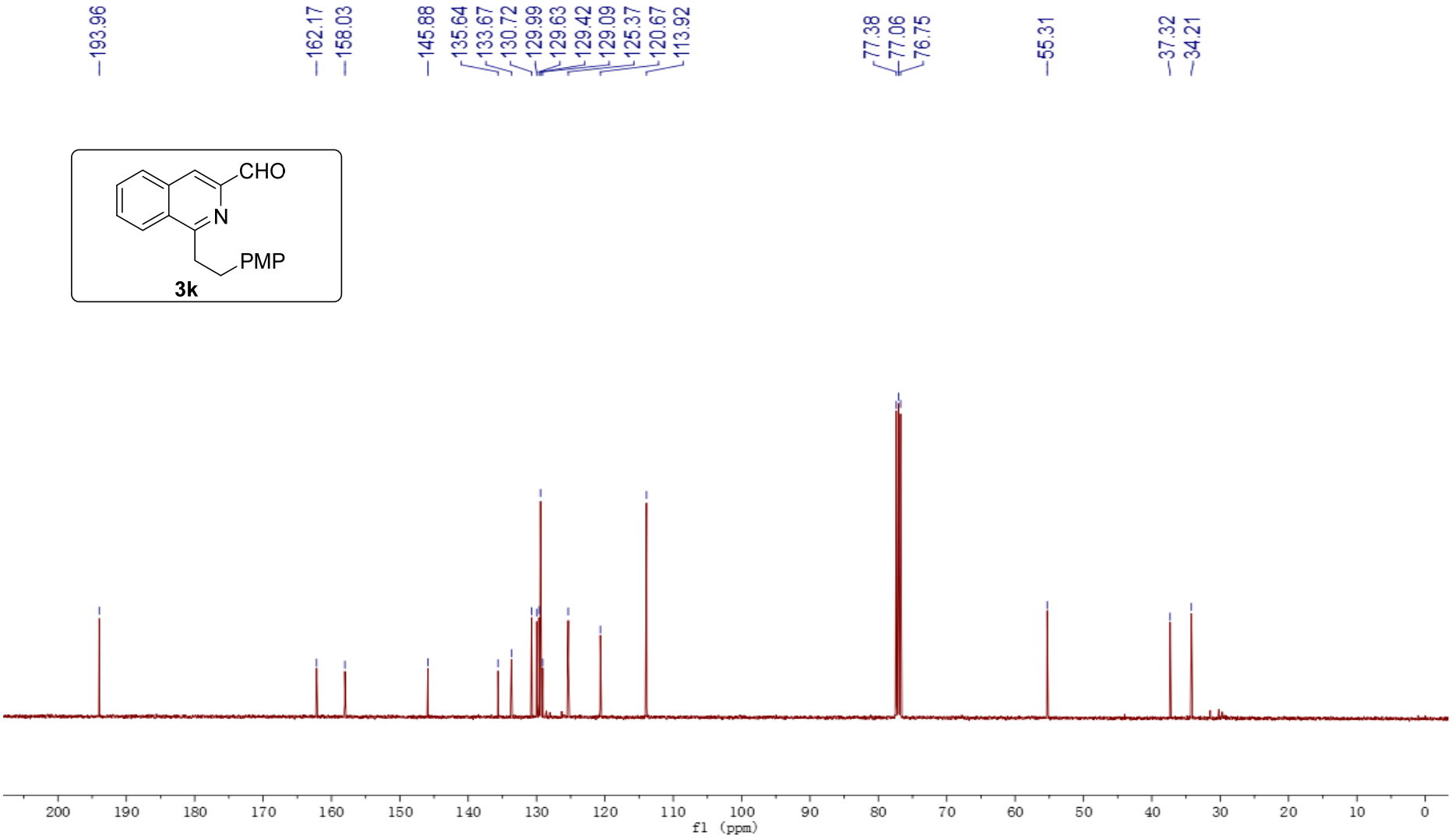

CHO
N

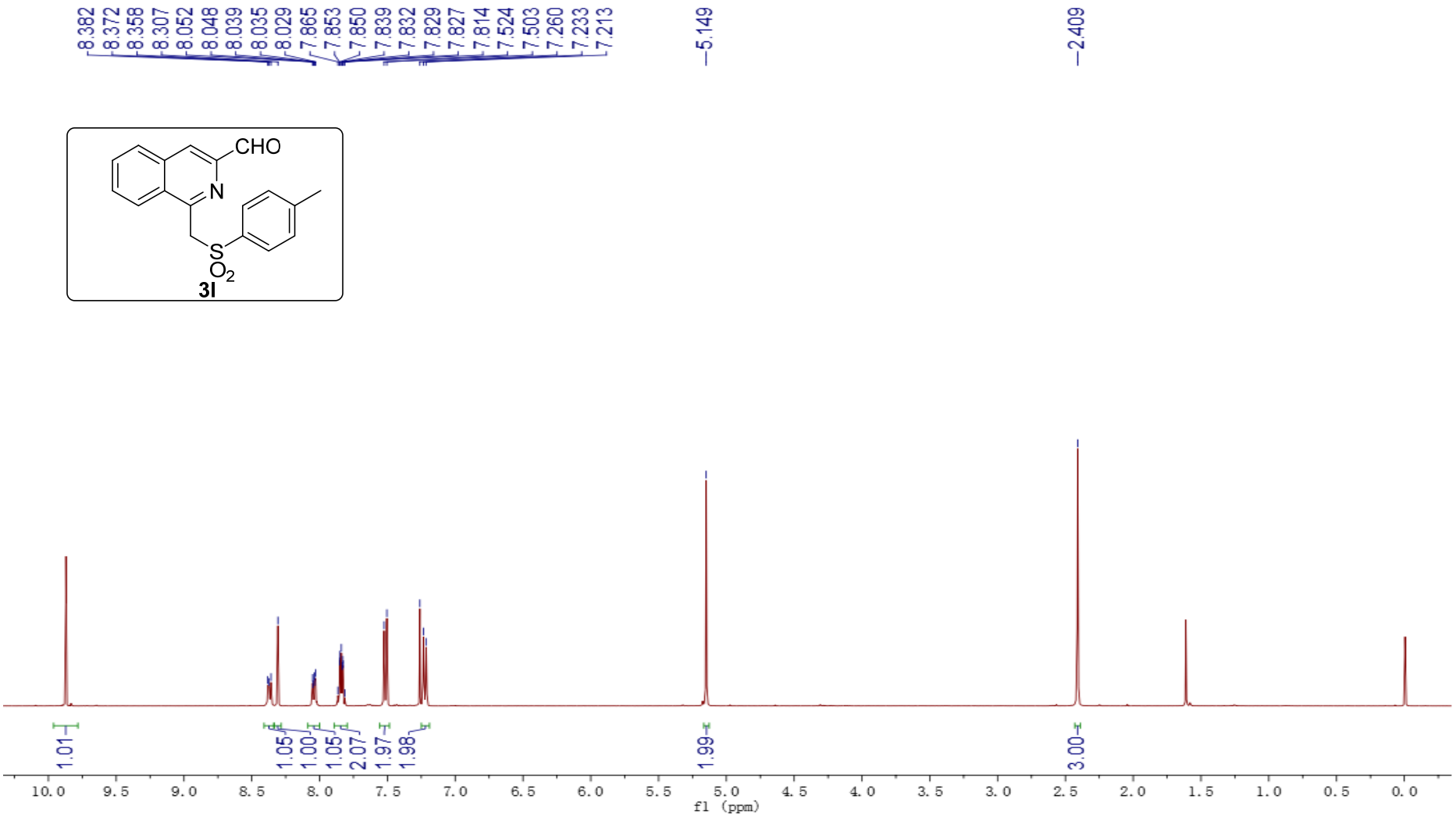
3j

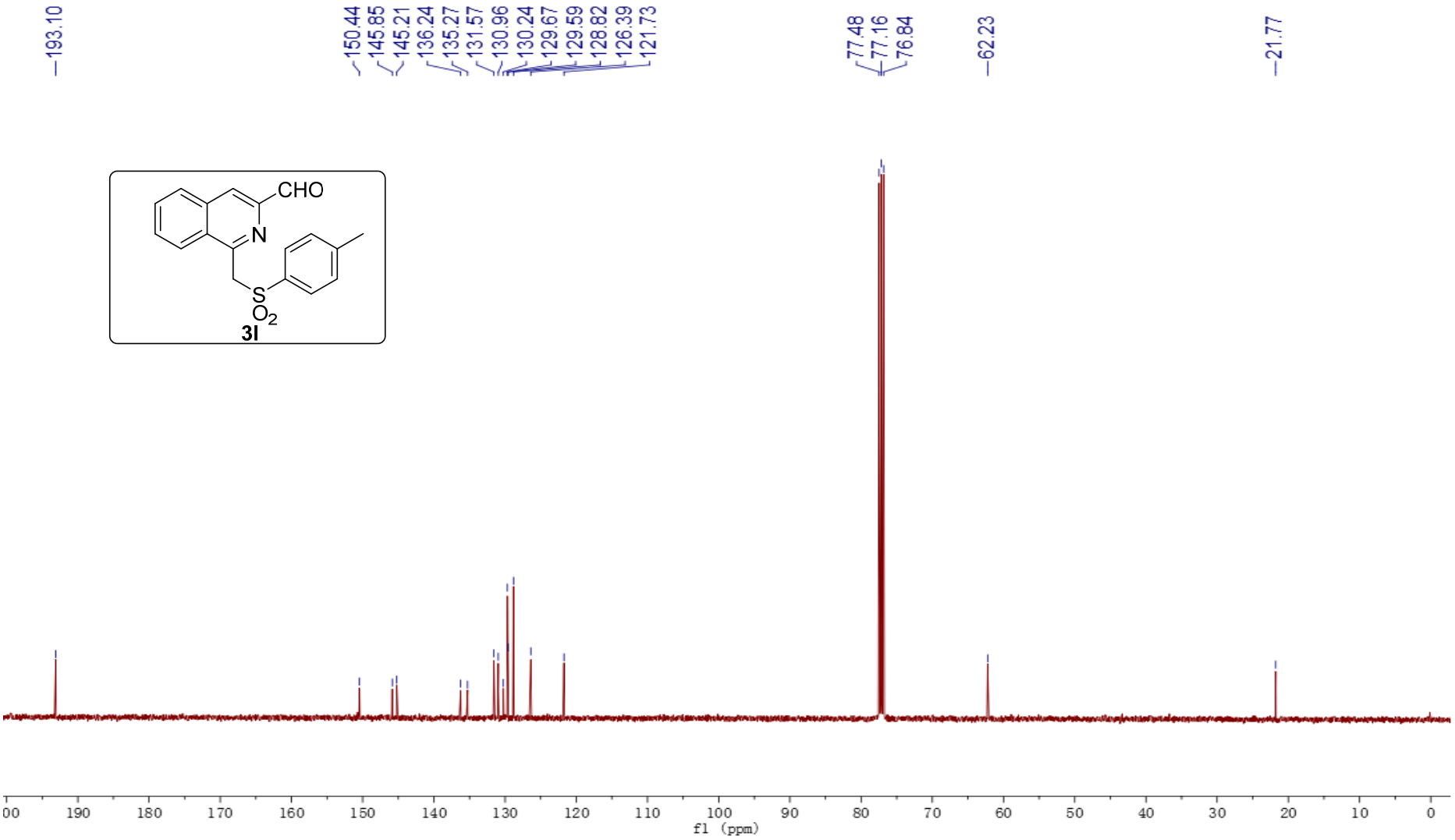

0.94
1.00
1.03
1.05
2.03
5.13
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.96
161.32
146.00
138.90
136.13
130.92
130.25
129.69
129.40
128.74
128.70
126.62
126.28
121.26
77.48
77.16
76.84
42.17
CHO
N
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

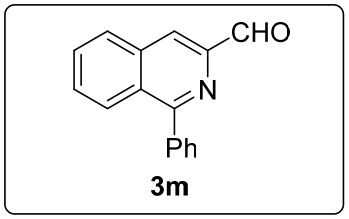

10.261
8.253
8.212
8.190
8.019
8.014
7.996
7.773
7.769
7.762
7.756
7.749
7.742
7.738
7.260
6.864
6.859
6.848
6.843
3.795
3.784
3.662
3.648
3.642
3.635
3.621
3.223
3.209
3.202
3.197
3.182
CHO
N
PMP
3k
0.92
0.98
1.00
1.01
2.03
1.99
2.03
3.06
1.99
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


193.96
162.17
158.03
145.88
135.64
133.67
130.72
129.99
129.63
129.42
129.09
125.37
120.67
113.92
77.38
77.06
76.75
55.31
37.32
34.21
CHO
N
PMP
3k
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

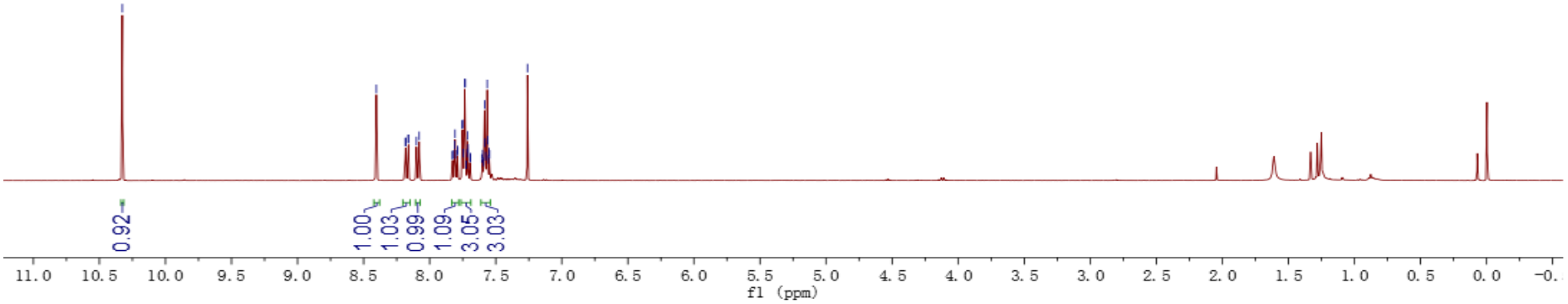

8.382
8.372
8.358
8.307
8.052
8.048
8.039
8.035
8.029
7.865
7.853
7.850
7.839
7.832
7.829
7.827
7.814
7.524
7.503
7.260
7.233
7.213
5.149
2.409
CHO
N
S
O2
3l
1.01
1.05
1.00
1.05
2.07
1.97
1.98
1.99
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

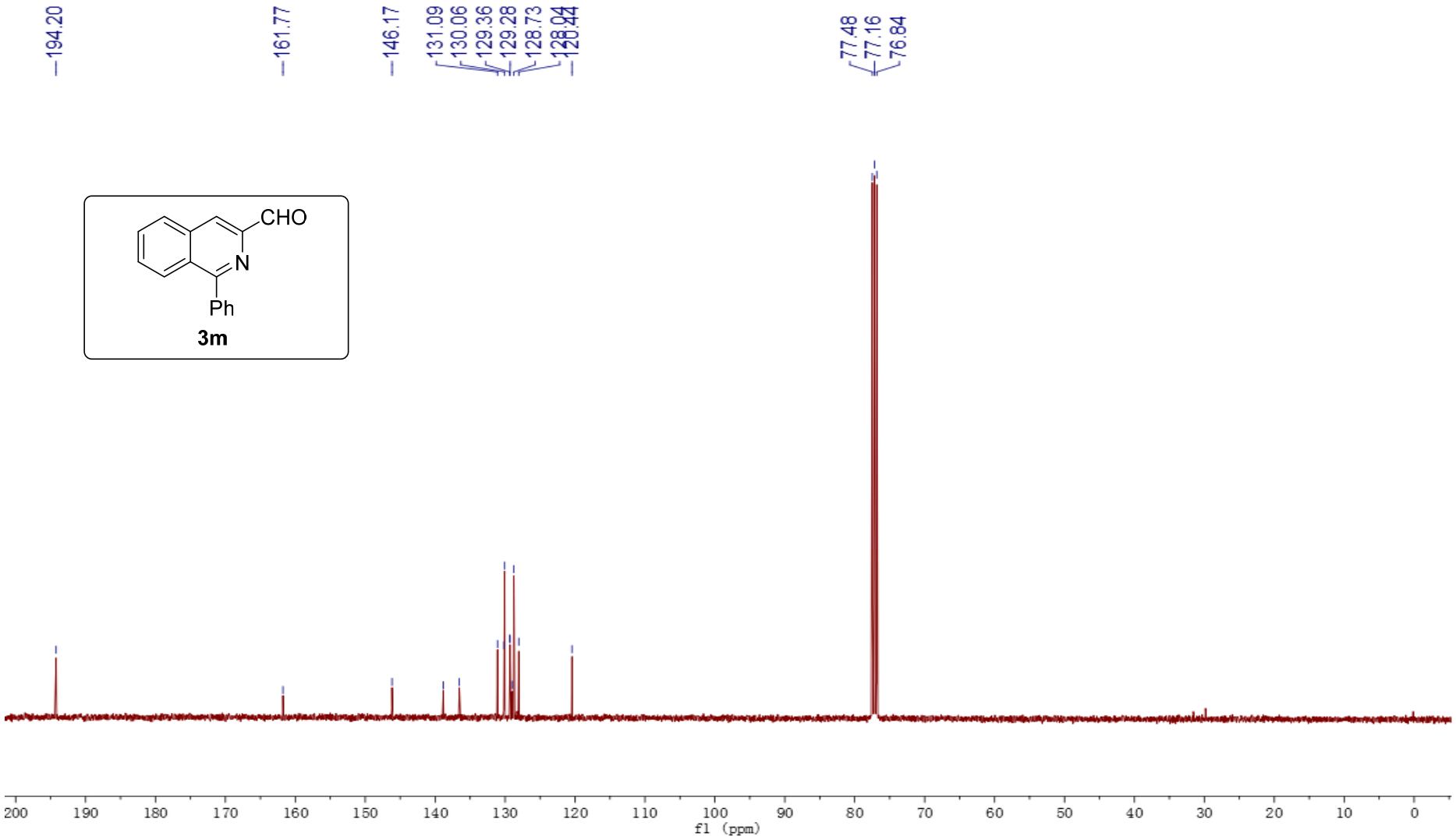

193.10
150.44
145.85
145.21
136.24
135.27
131.57
130.96
130.24
129.67
129.59
128.82
126.39
121.73
77.48
77.16
76.84
62.23
21.77
CHO
N
S
O2
3l
fl (ppm)

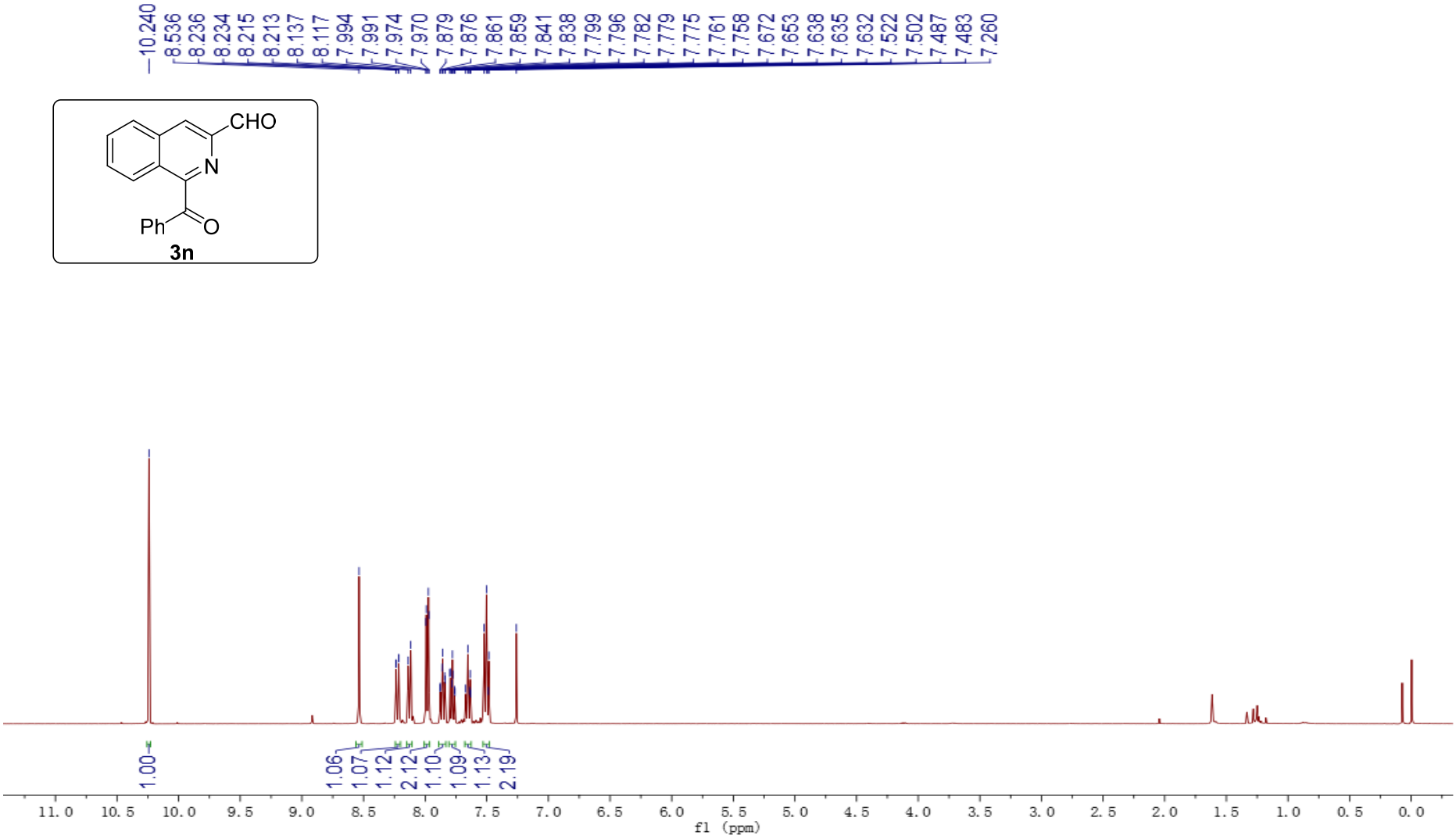

10.326
8.404
8.184
8.182
8.163
8.161
8.100
8.080
7.828
7.825
7.811
7.808
7.805
7.790
7.787
7.754
7.750
7.745
7.734
7.731
7.724
7.716
7.713
7.709
7.695
7.692
7.606
7.599
7.595
7.584
7.580
7.577
7.565
7.560
7.556
7.549
7.547
7.260


CHO
N
Ph

3m


0.92
1.00
1.03
0.99
1.09
3.05
3.03
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


194.20
161.77
146.17
131.09
130.06
129.36
129.28
128.73
128.04
120.44
77.48
77.16
76.84
CHO
N
Ph
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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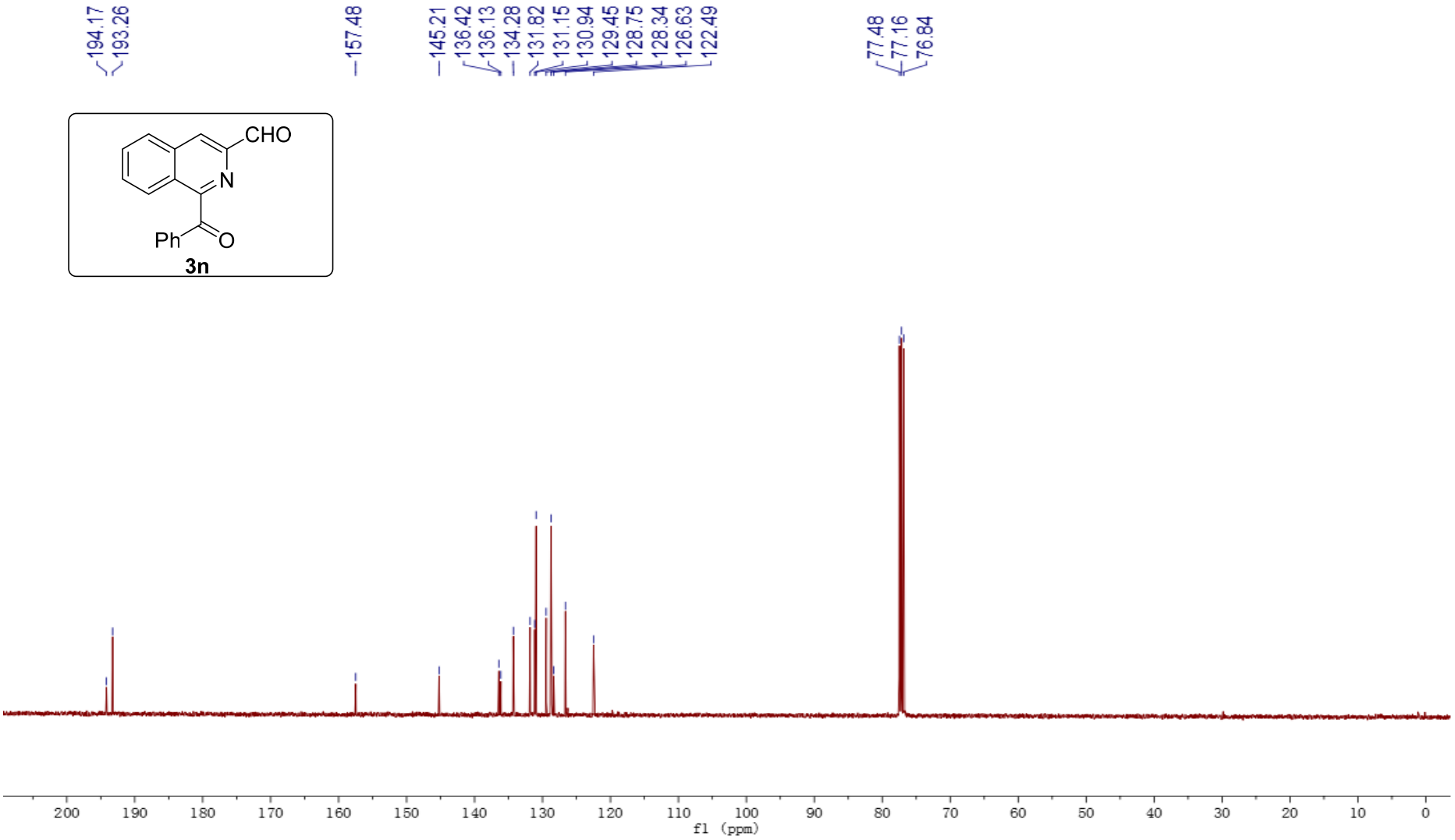
8.236
8.234
8.215
8.213
8.137
8.117
7.994
7.991
7.974
7.970
7.879
7.876
7.861
7.859
7.841
7.838
7.799
7.796
7.782
7.779
7.775
7.761
7.758
7.672
7.653
7.638
7.635
7.632
7.522
7.502
7.487
7.483
7.260
CHO
N
Ph
O
3n
1.00
1.06
1.07
1.12
2.12
1.10
1.09
1.13
2.19
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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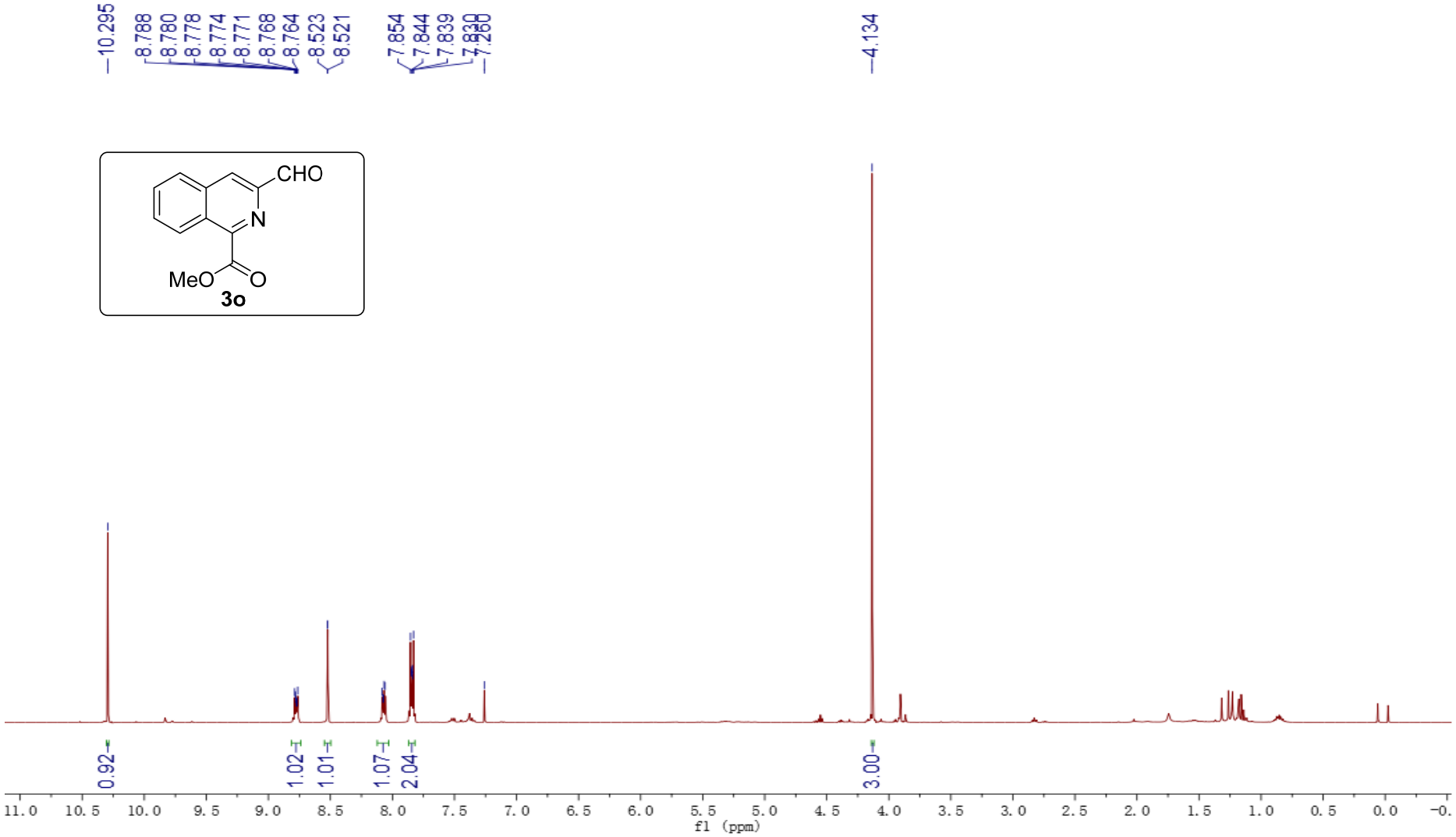
193.26
157.48
145.21
136.42
136.13
134.28
131.82
131.15
130.94
129.45
128.75
128.34
126.63
122.49
77.48
77.16
76.84
CHO
N
Ph
O
3n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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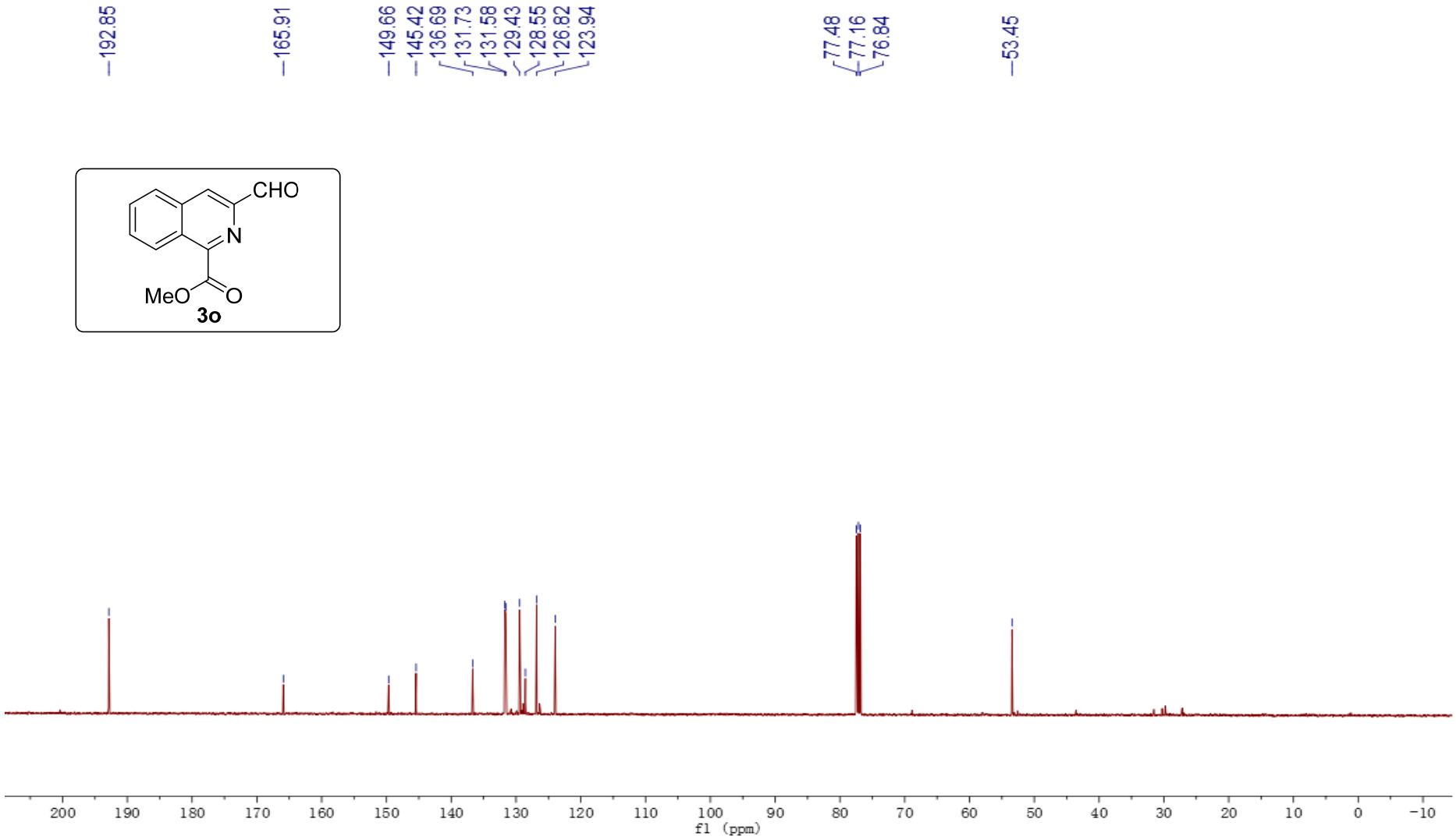
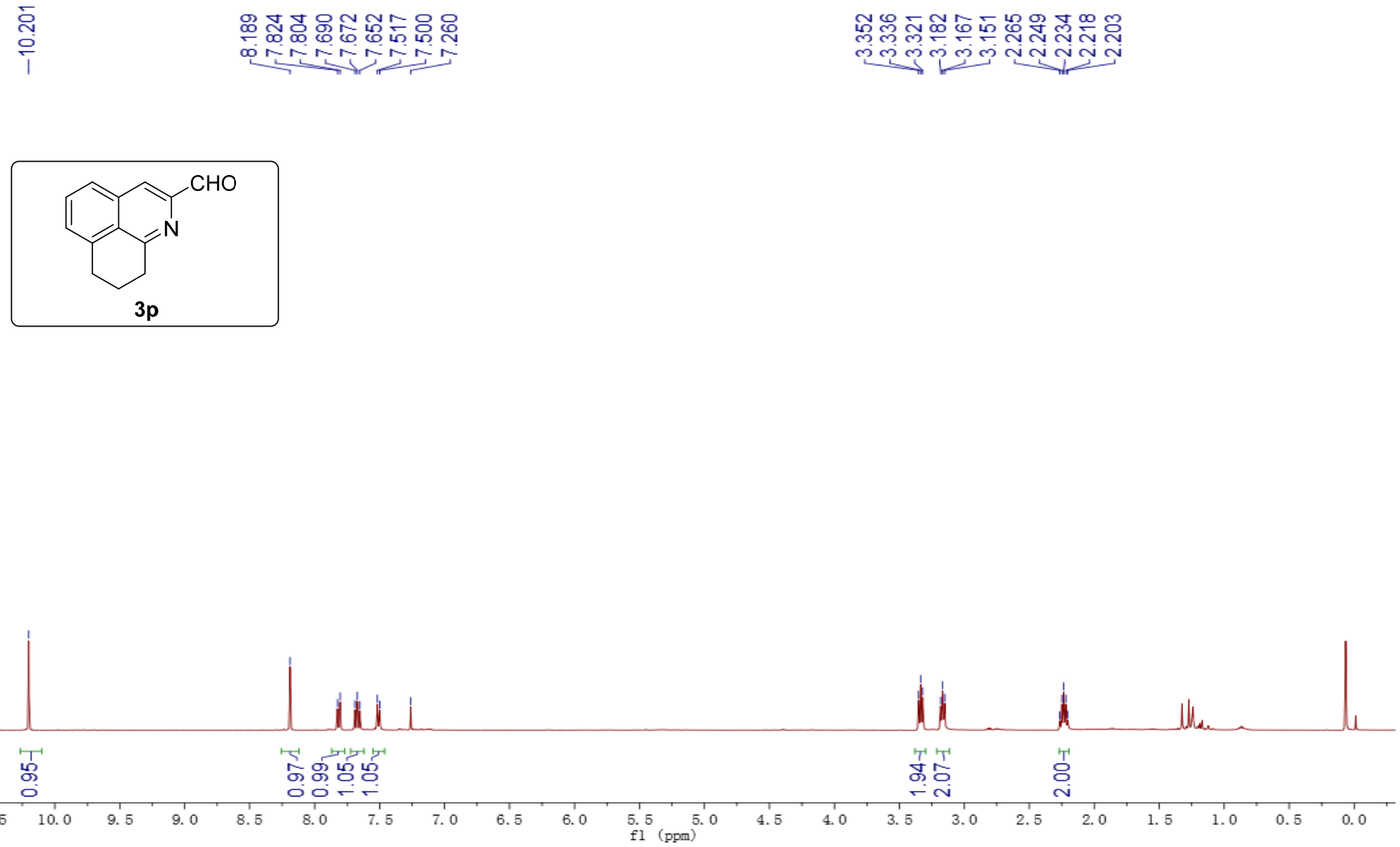
8.788
8.780
8.778
8.774
8.771
8.768
8.764
8.523
8.521
7.854
7.844
7.839
4.134
CHO
N
MeO
O
3o
0.92
1.02
1.01
1.07
2.04
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


192.85
165.91
149.66
145.42
136.69
131.73
131.58
129.43
128.55
126.82
123.94
77.48
77.16
76.84
53.45
CHO
N
MeO
O
3o
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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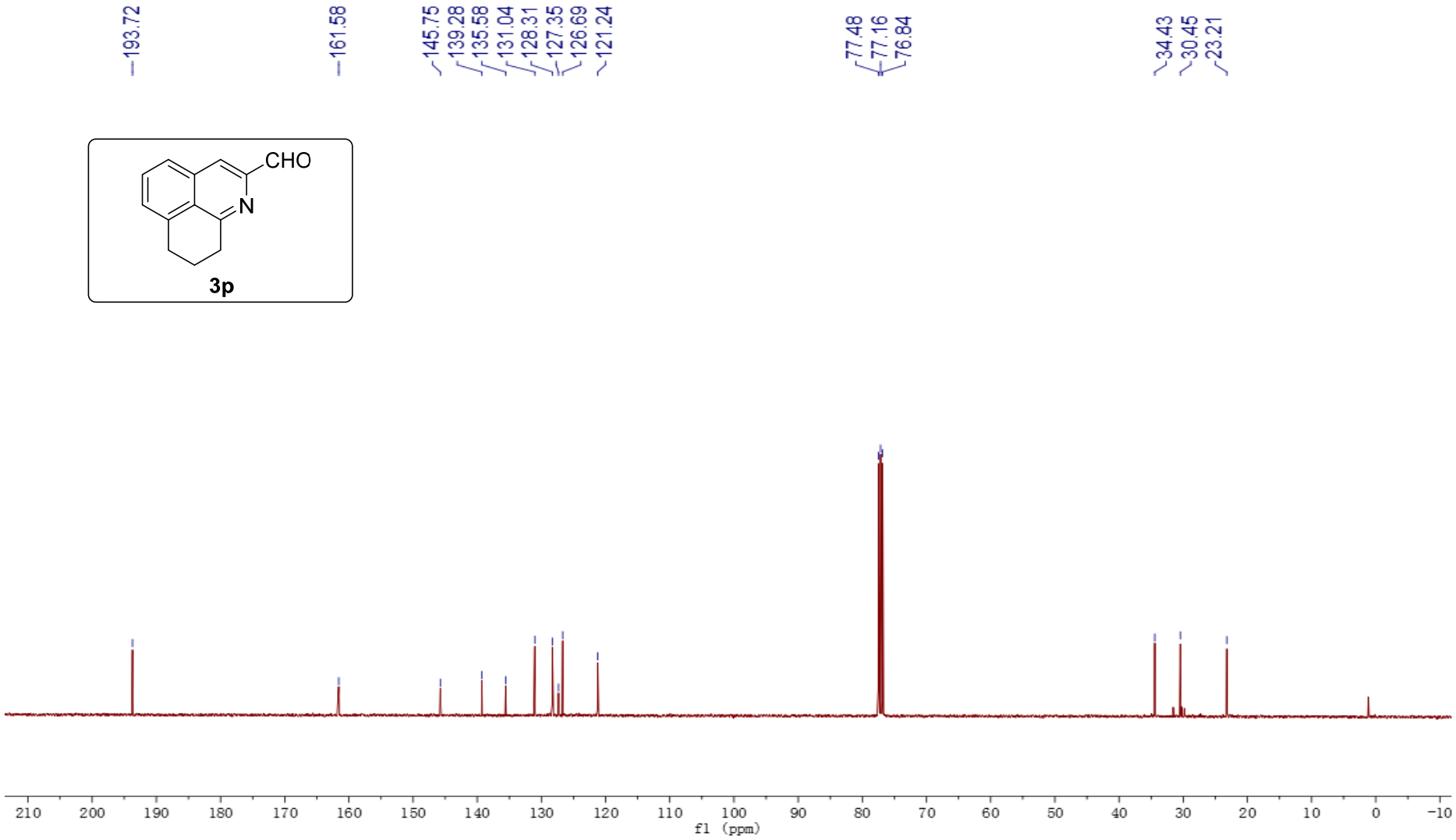
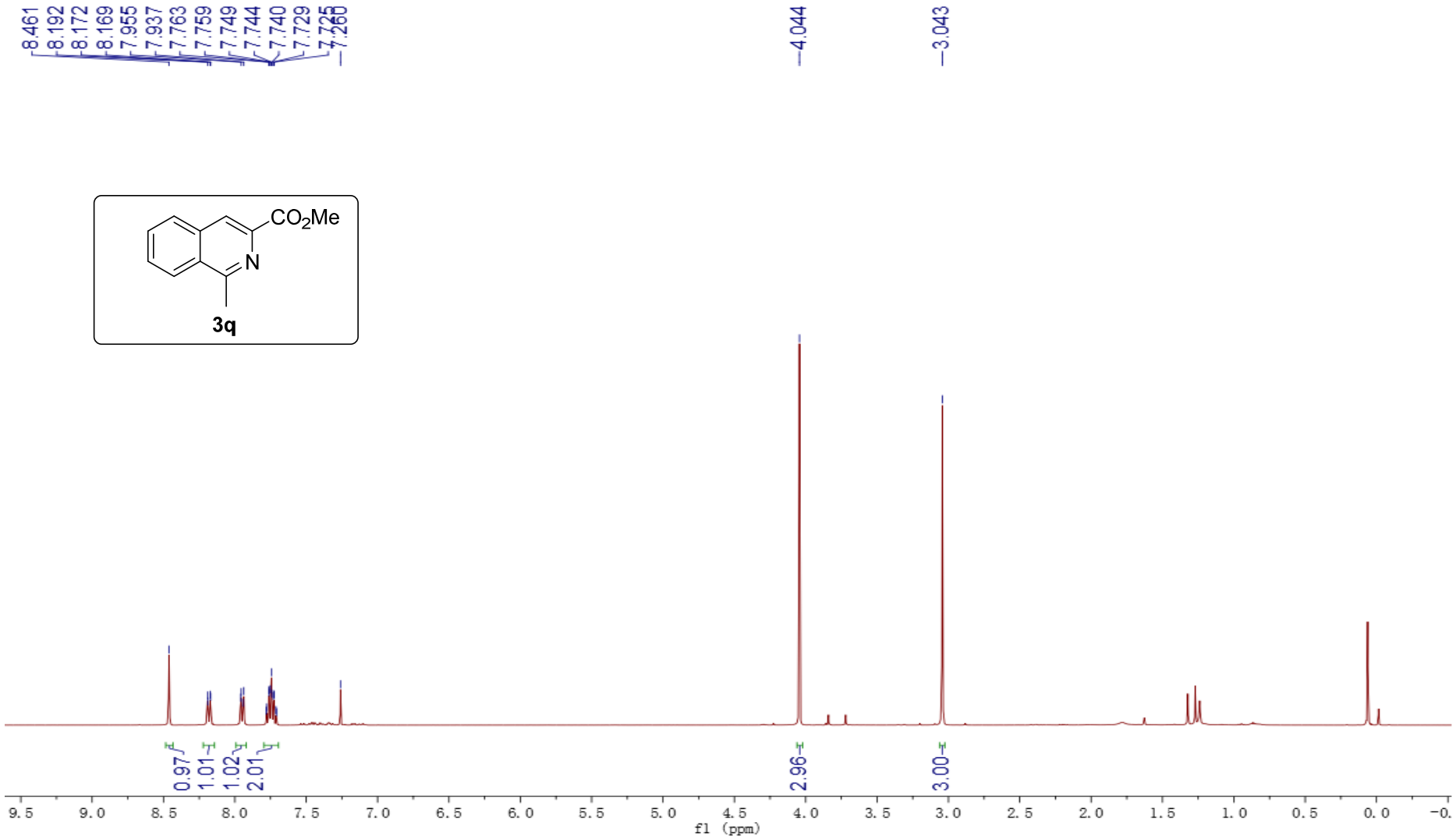
8.189
7.824
7.804
7.690
7.672
7.652
7.517
7.500
7.260
3.352
3.336
3.321
3.182
3.167
3.151
2.265
2.249
2.234
2.218
2.203
CHO
N
3p
0.95
0.97
0.99
1.05
1.05
1.94
2.07
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


193.72
161.58
145.75
139.28
135.58
131.04
128.31
127.35
126.69
121.24
77.48
77.16
76.84
34.43
30.45
23.21
CHO
N
3p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)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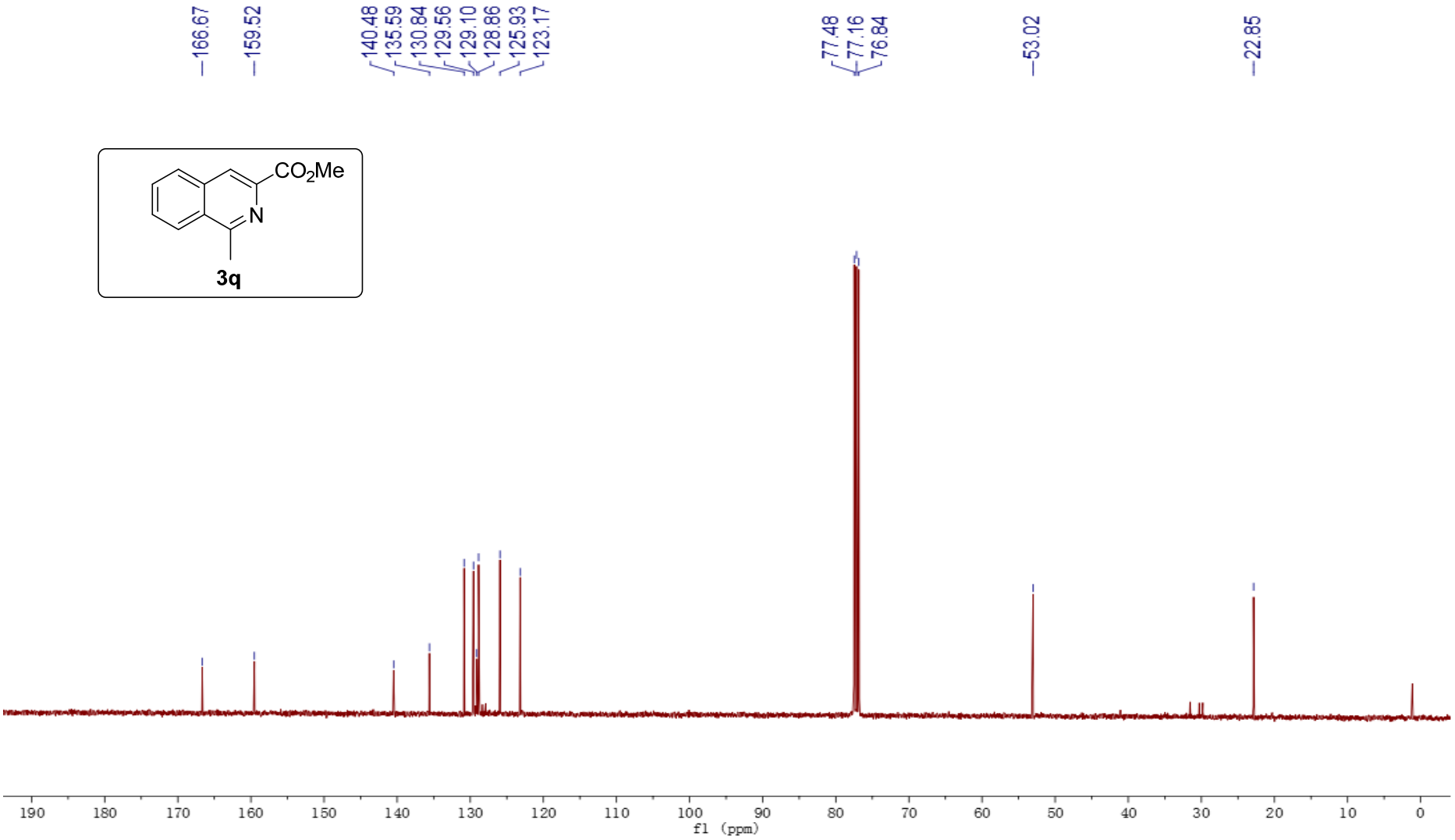
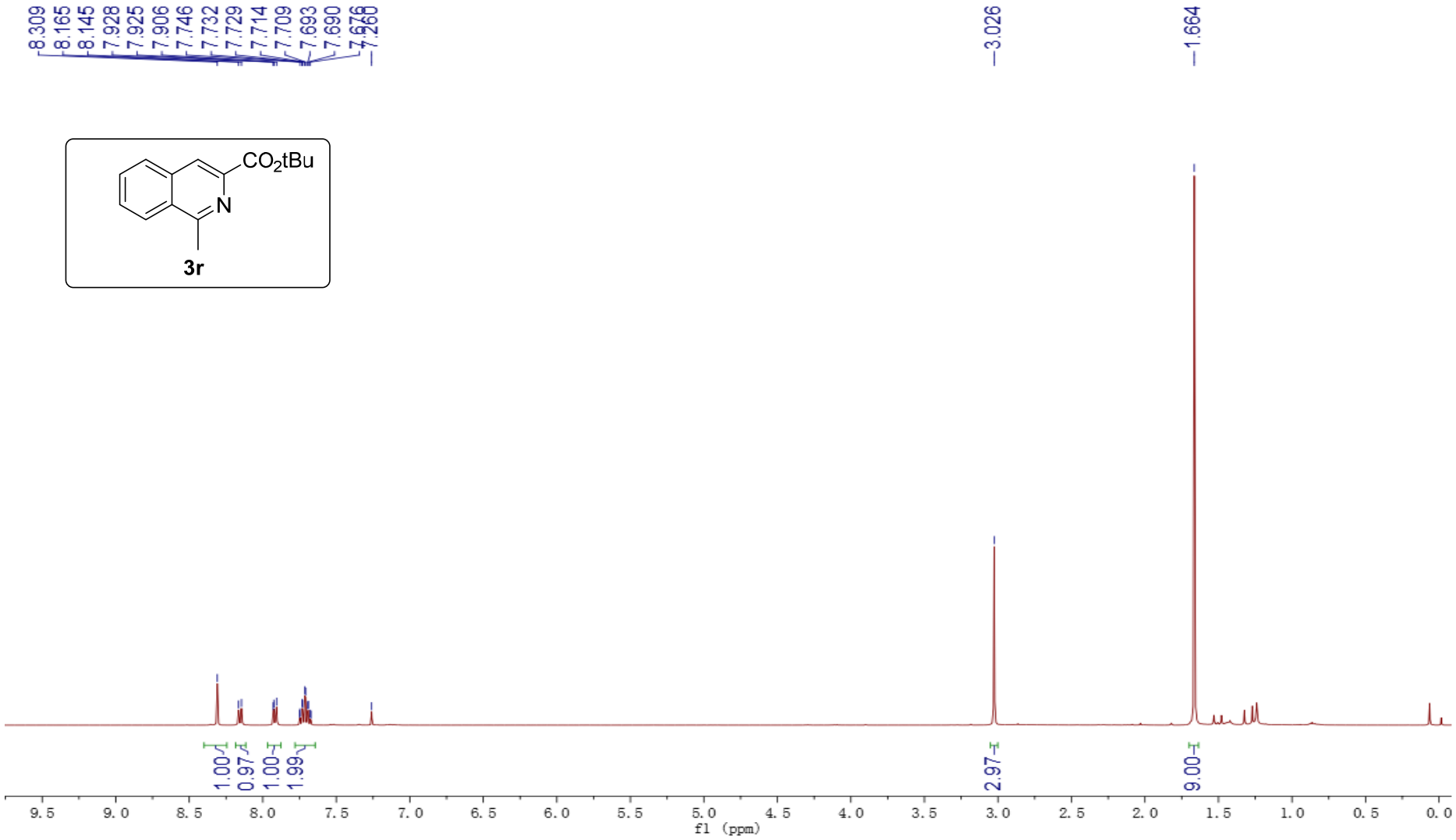
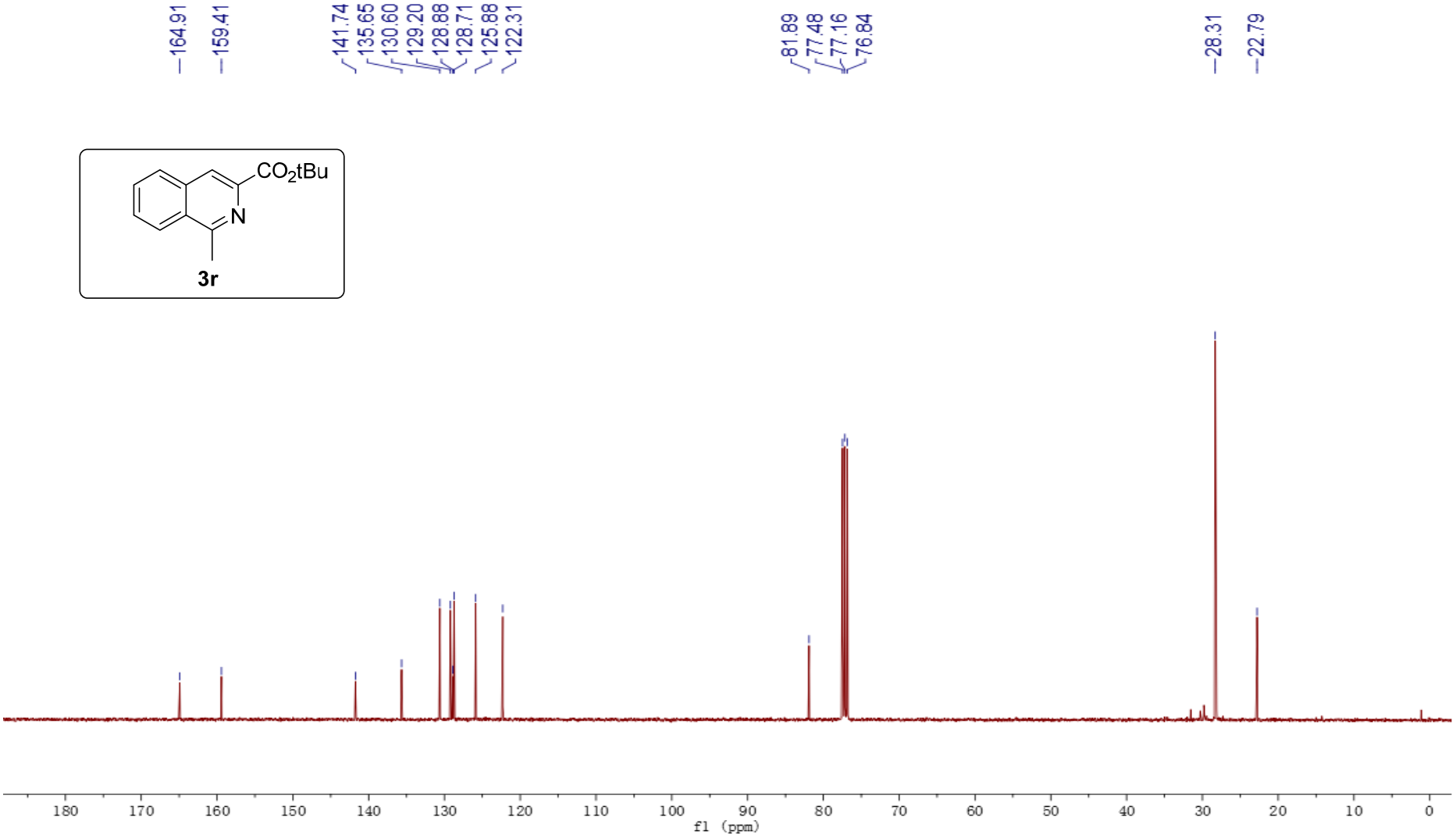
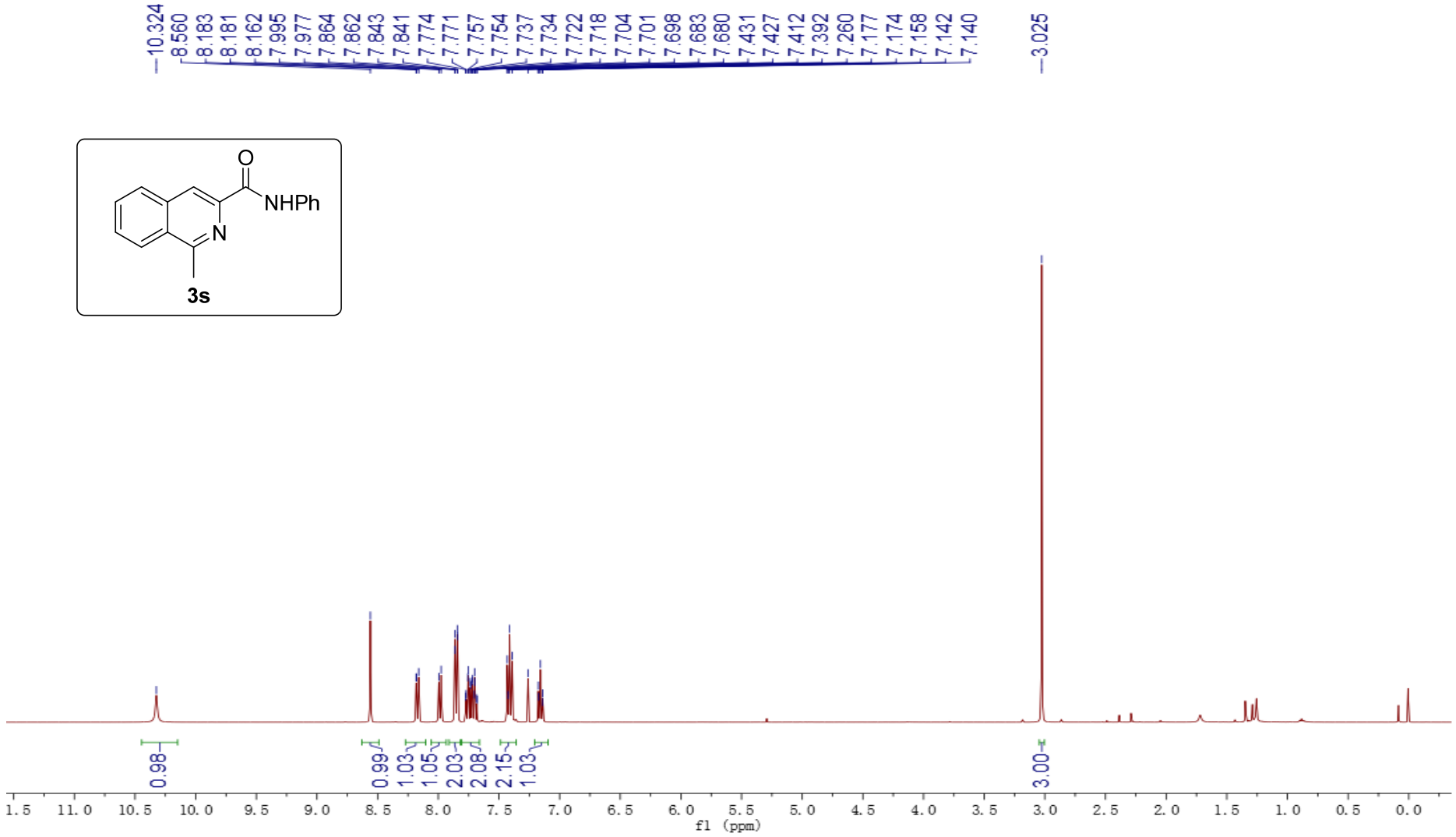
8.192
8.172
8.169
7.955
7.937
7.763
7.759
7.749
7.744
7.740
7.729
7.725
7.260
4.044
3.043
CO2Me
N
3q
0.97
1.01
1.02
2.01
2.96
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


166.67
159.52
140.48
135.59
130.84
129.56
129.10
128.86
125.93
123.17
77.48
77.16
76.84
53.02
22.85
CO2Me
N
3q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.309
8.165
8.145
7.928
7.925
7.906
7.746
7.732
7.729
7.714
7.709
7.693
7.690
7.676
7.260
3.026
1.664
CO2tBu
N
3r
1.00
0.97
1.00
1.99
2.97
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
f1 (ppm)


164.91
159.41
141.74
135.65
130.60
129.20
128.88
128.71
125.88
122.31
81.89
77.48
77.16
76.84
28.31
22.79
CO2tBu
N
3r
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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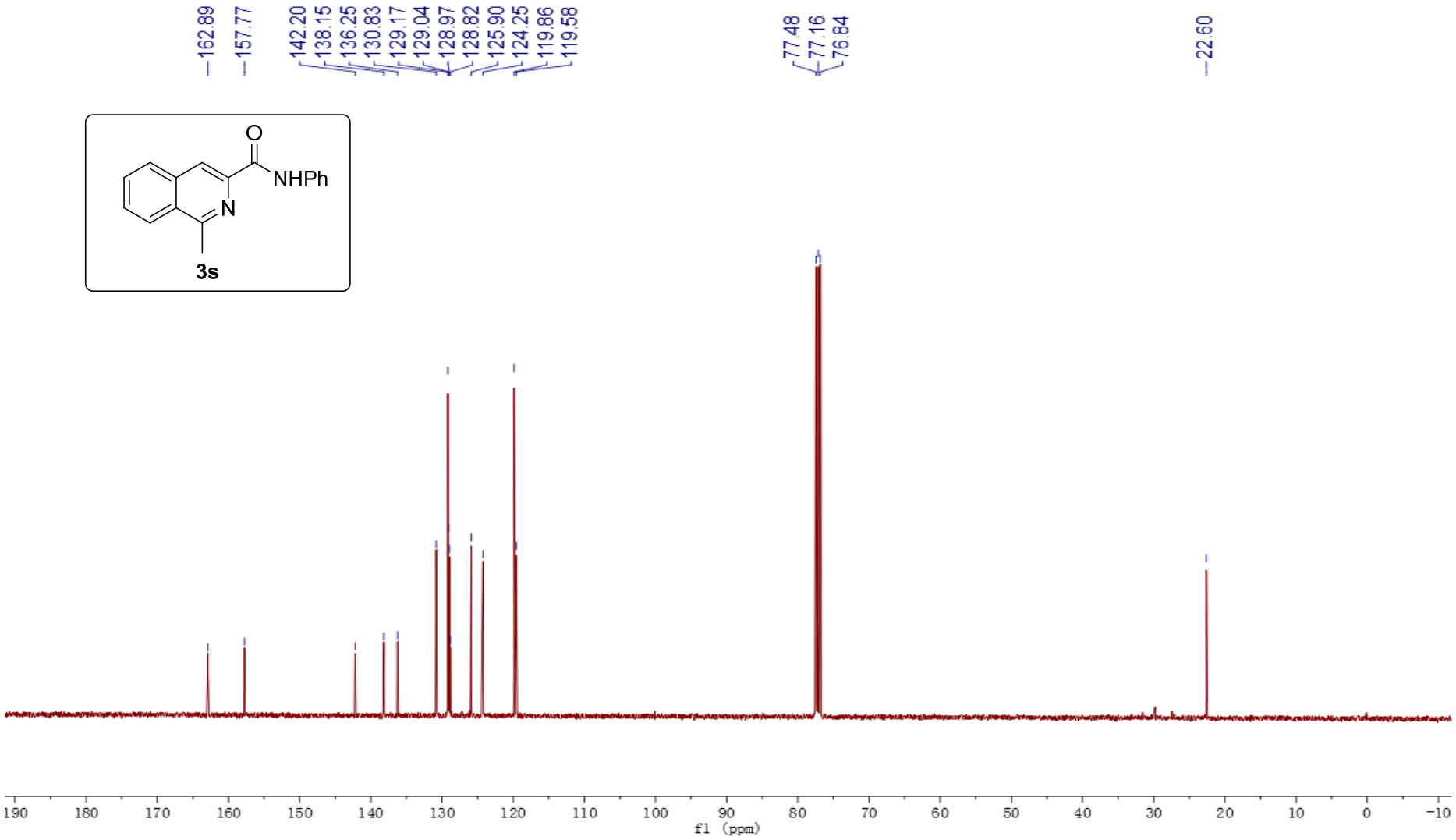
8.183
8.181
8.162
7.995
7.977
7.864
7.862
7.843
7.841
7.774
7.771
7.757
7.754
7.737
7.734
7.722
7.718
7.704
7.701
7.698
7.683
7.680
7.431
7.427
7.412
7.392
7.260
7.177
7.174
7.158
7.142
7.140
3.025
O
NHPh
N
3s
0.98
0.99
1.03
1.05
2.03
2.08
2.15
1.03
3.00
f1 (ppm)


162.89
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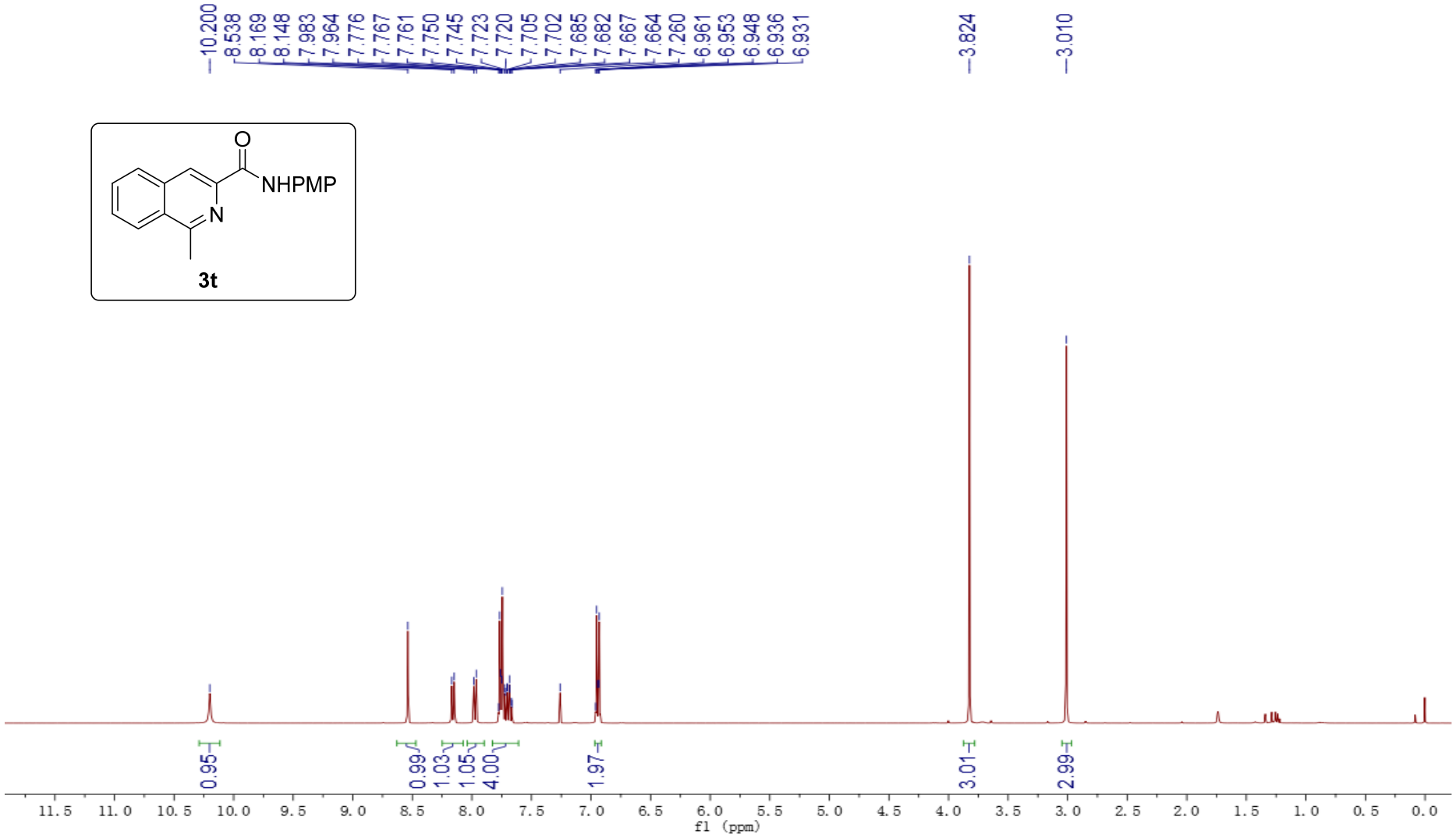
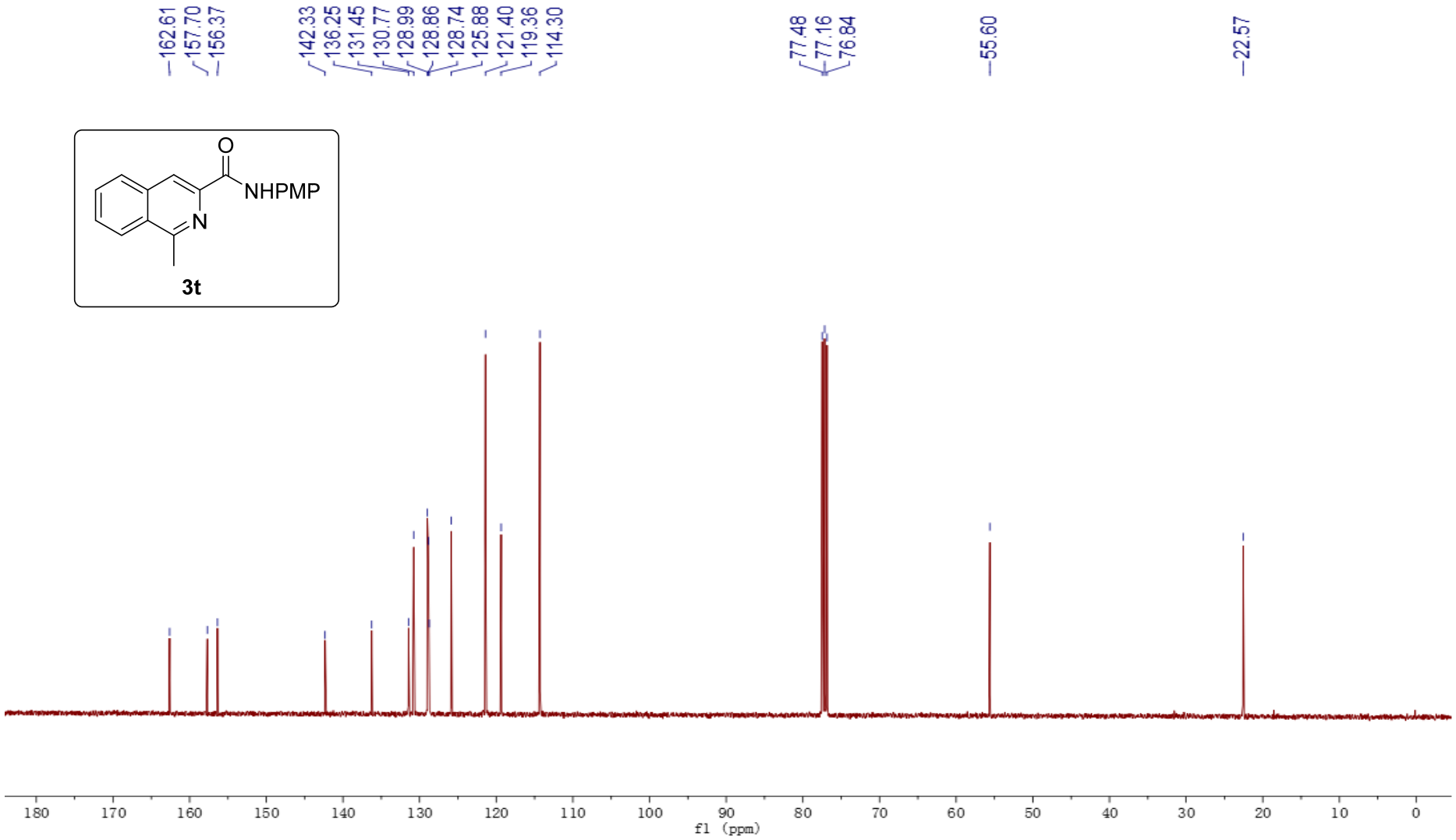
142.20
138.15
136.25
130.83
129.17
129.04
128.97
128.82
125.90
124.25
119.86
119.58
77.48
77.16
76.84
22.60
O
NHPh
N
3s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


10.200
8.538
8.169
8.148
7.983
7.964
7.776
7.767
7.761
7.750
7.745
7.723
7.720
7.705
7.702
7.685
7.682
7.667
7.664
7.260
6.961
6.953
6.948
6.936
6.931
3.824
3.010
O
NHPMP
N
3t
0.95
0.99
1.03
1.05
4.00
1.97
3.01
2.99
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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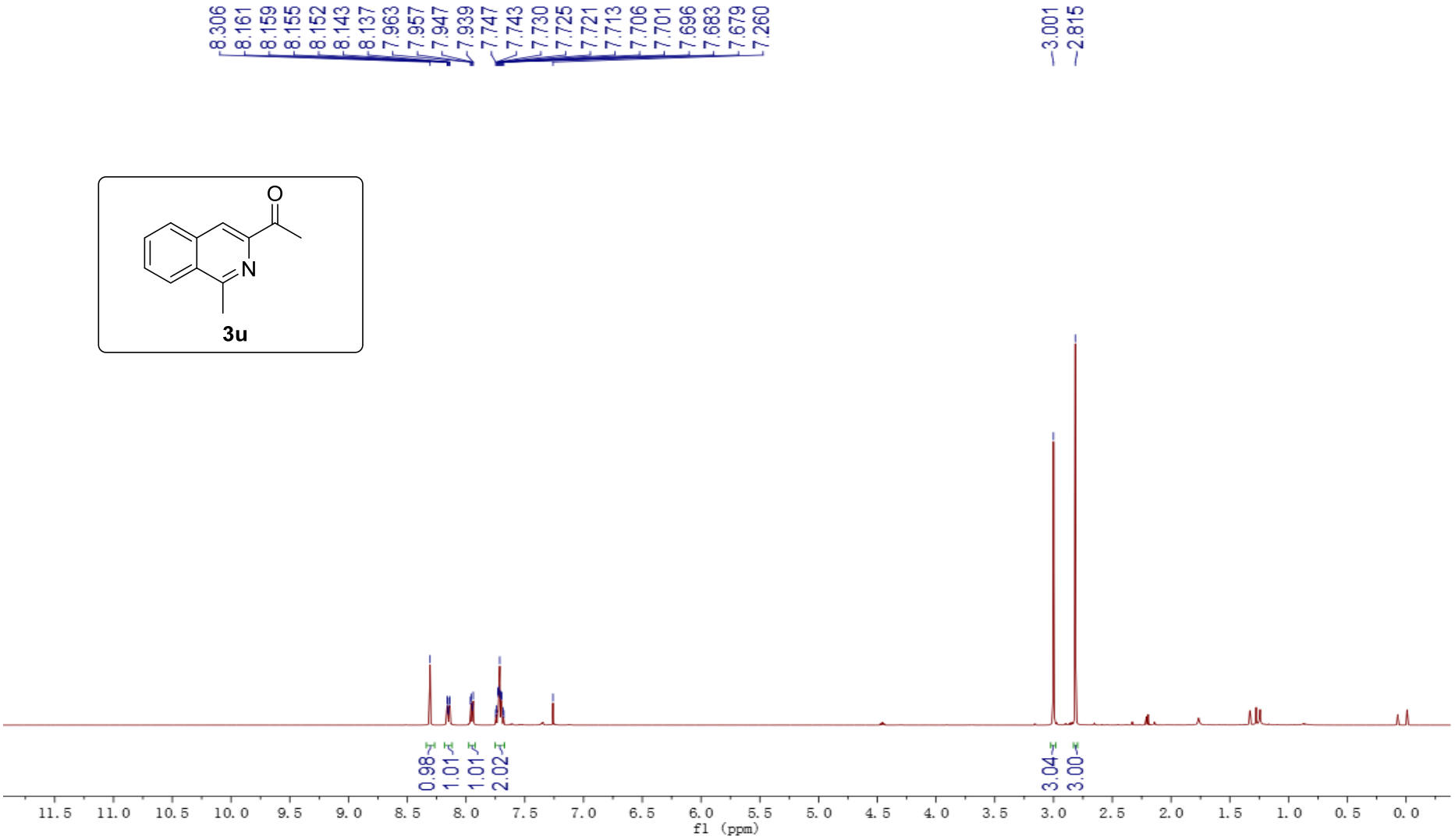
157.70
156.37
142.33
136.25
131.45
130.77
128.99
128.86
128.74
125.88
121.40
119.36
114.30
77.48
77.16
76.84
55.60
22.57
O
NHPMP
N
3t
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.155
8.152
8.143
8.137
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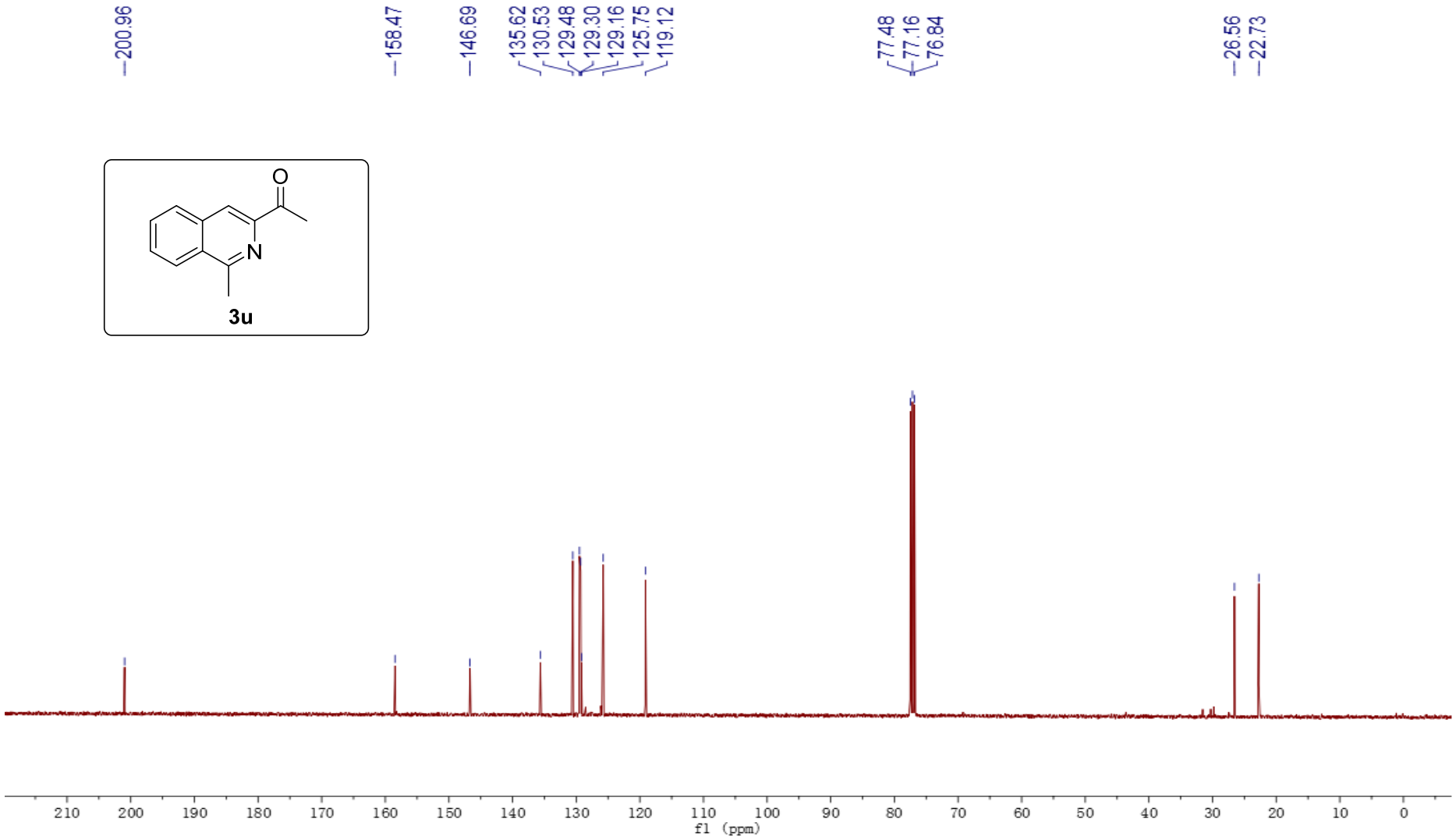
7.957
7.947
7.939
7.747
7.743
7.730
7.725
7.721
7.713
7.706
7.701
7.696
7.683
7.679
7.260
3.001
2.815
O
N
3u
0.98
1.01
1.01
2.02
3.04
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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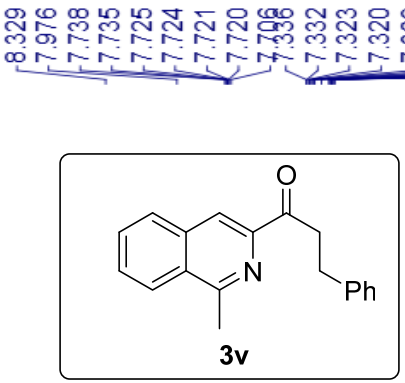
146.69
135.62
130.53
129.48
129.30
129.16
125.75
119.12
77.48
77.16
76.84
26.56
22.73
O
N
3u
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
Ph

3v

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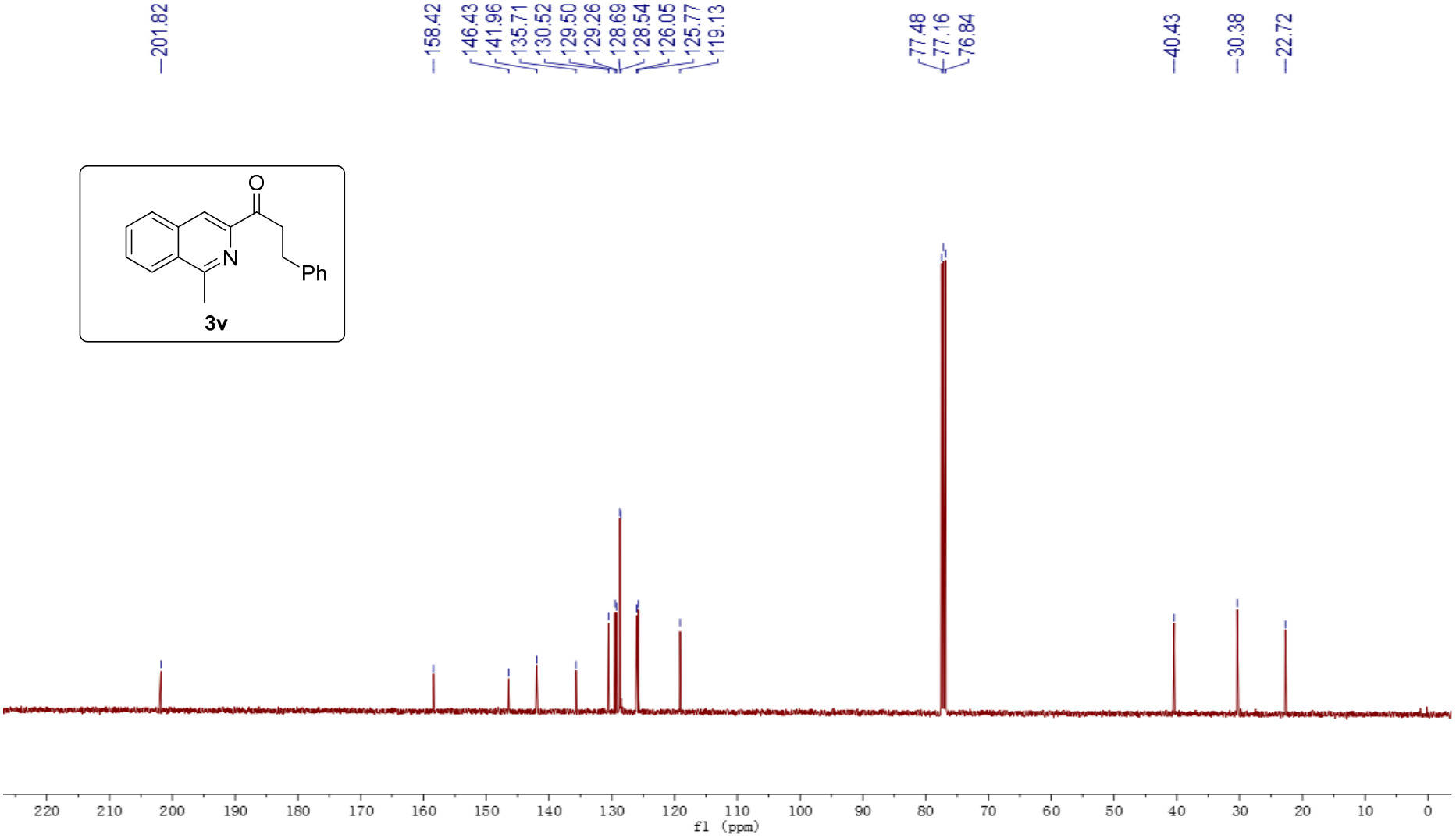
7.738
7.735
7.725
7.724
7.721
7.720
7.706
7.338
7.332
7.323
7.320
7.309
7.305
7.297
7.293
7.260
7.224
7.220
7.211
7.210
7.206
7.203
7.193
3.691
3.675
3.673
3.659
3.138
3.122
3.107
2.994
0.97
1.00
1.00
2.04
4.04
1.01
2.03
2.07
3.00
f1 (ppm)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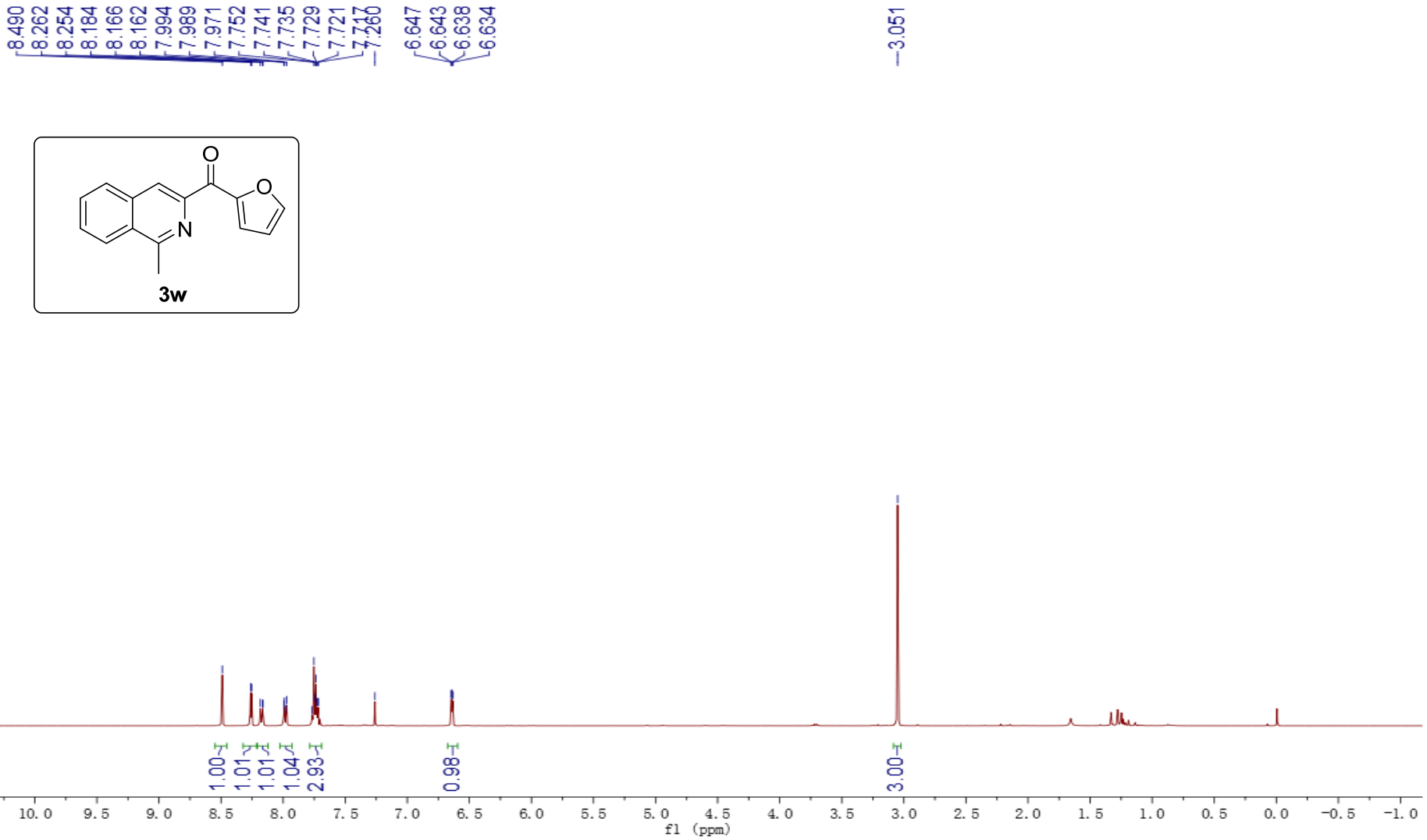
135.71
130.52
129.50
129.26
128.69
128.54
126.05
125.77
119.13
77.48
77.16
76.84
40.43
30.38
22.72
O
N
Ph
3v
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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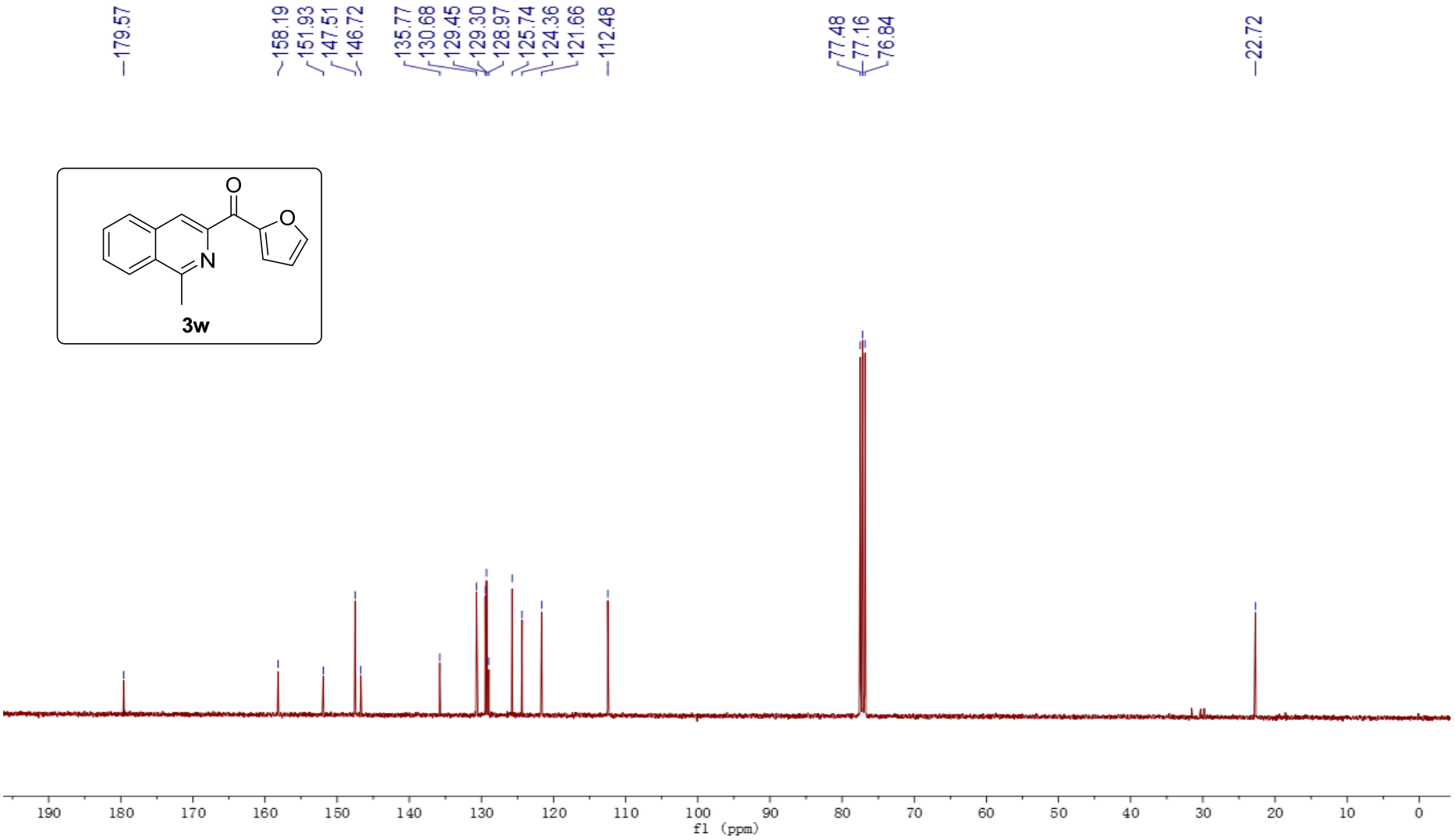
8.184
8.166
8.162
7.994
7.989
7.971
7.752
7.741
7.735
7.729
7.721
7.717
7.260
6.647
6.643
6.638
6.634
3.051
O
O
N
3w
1.00
1.01
1.01
1.04
2.93
0.98
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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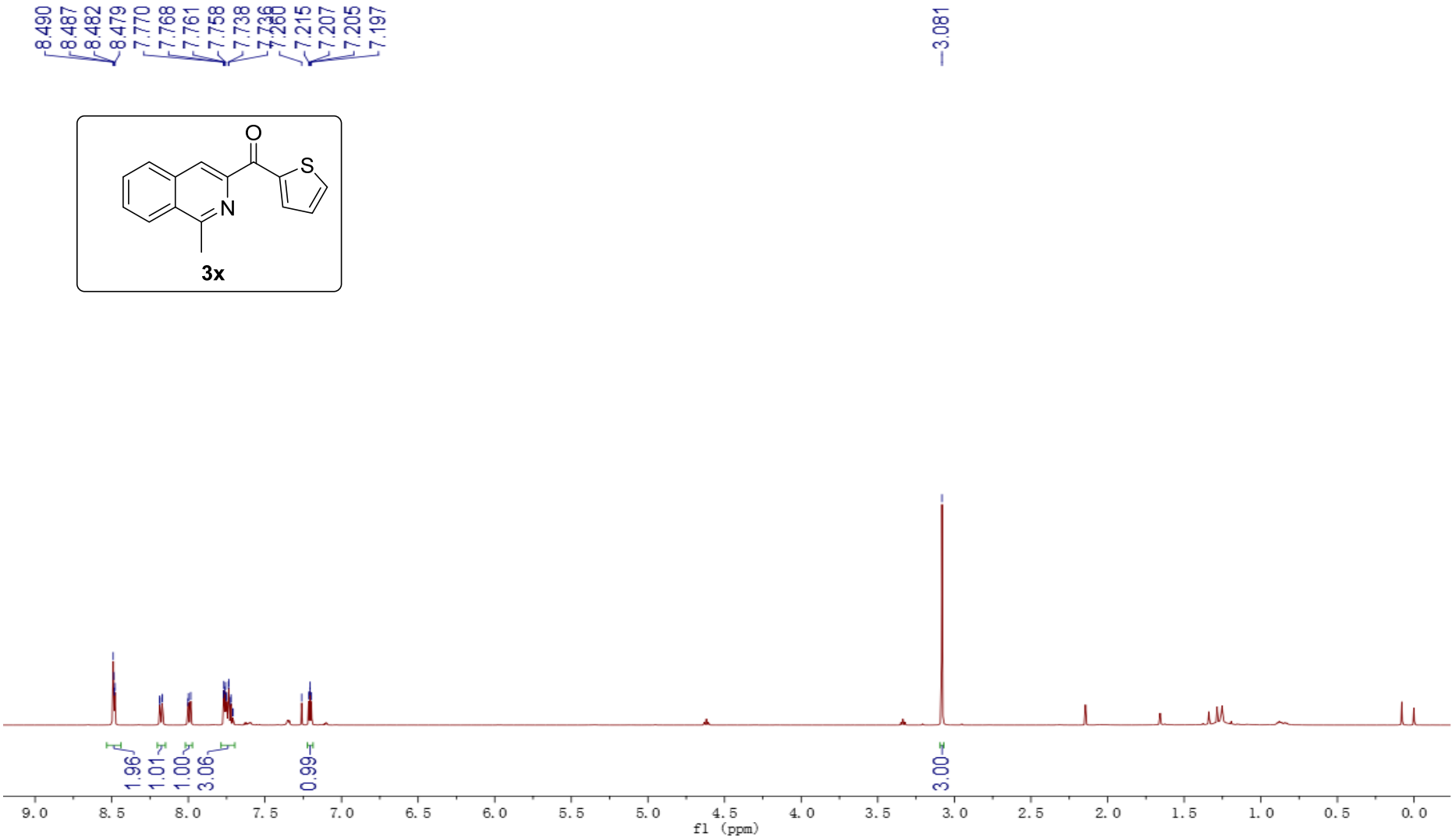
147.51
146.72
135.77
130.68
129.45
129.30
128.97
125.74
124.36
121.66
112.48
77.48
77.16
76.84
22.72
O
O
N
3w
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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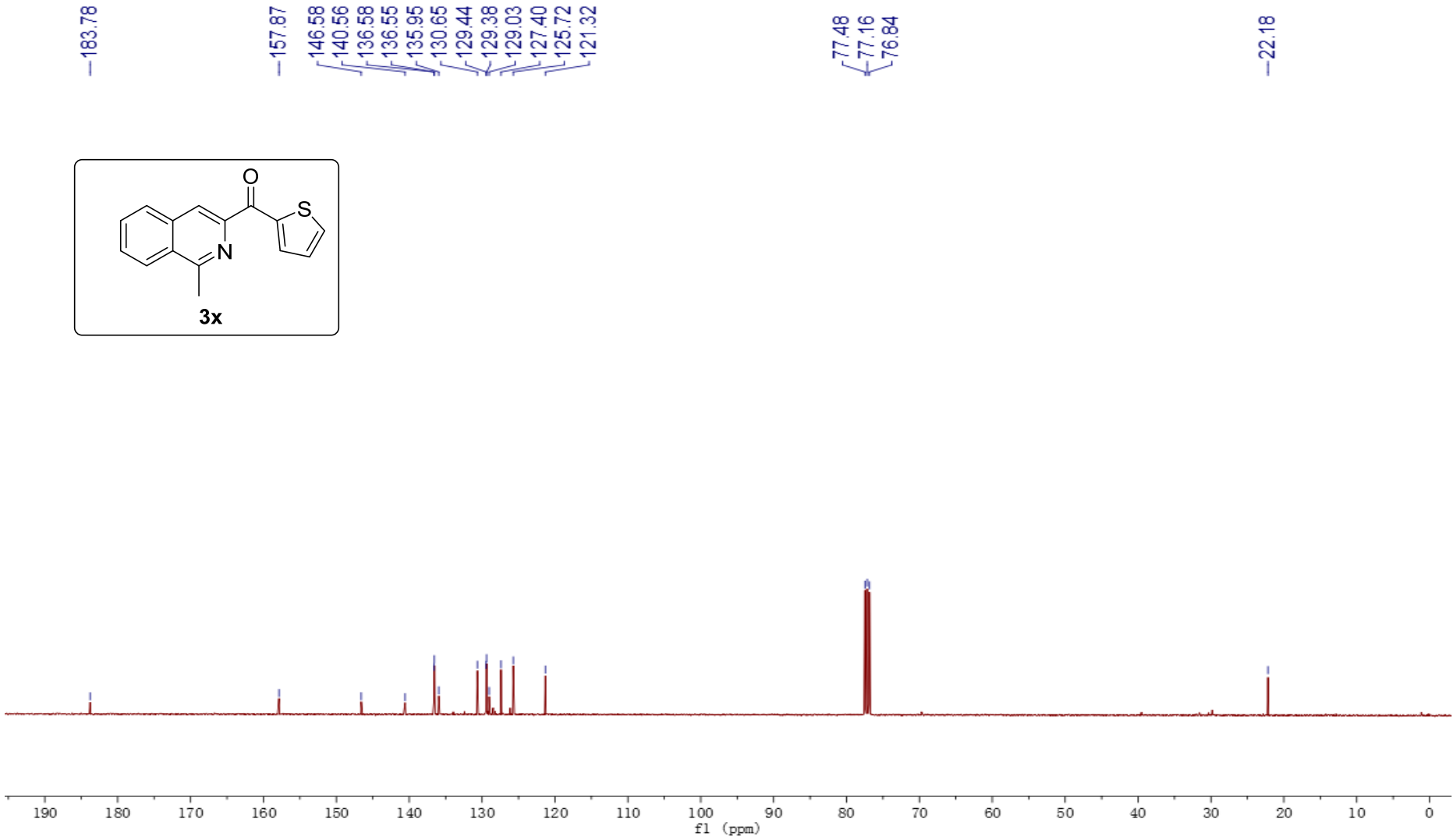
8.479
7.770
7.768
7.761
7.758
7.738
7.736
7.260
7.215
7.207
7.205
7.197
3.081
O
S
N
3x
1.96
1.01
1.00
3.06
0.99
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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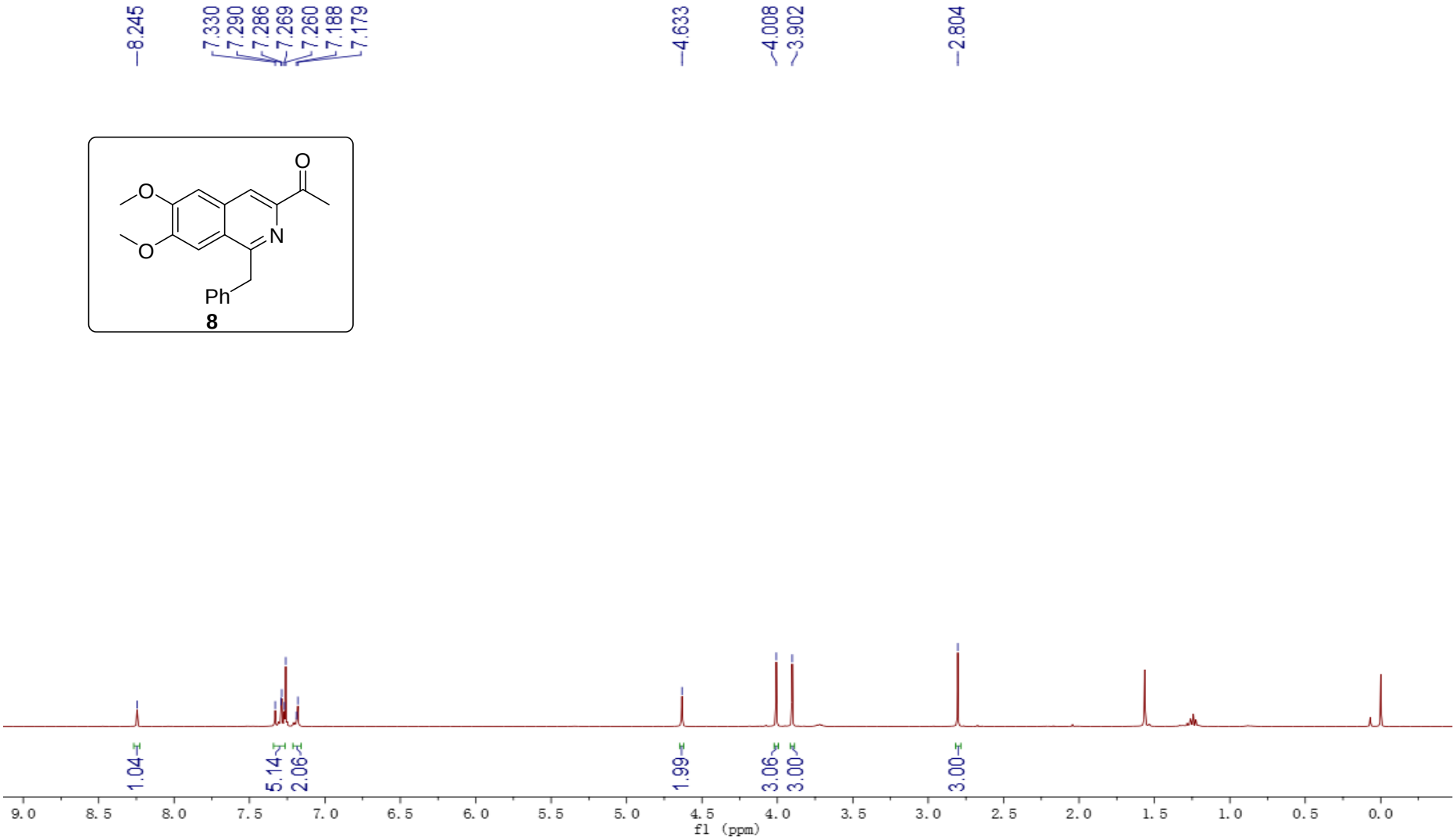
136.55
135.95
130.65
129.44
129.38
129.03
127.40
125.72
121.32
77.48
77.16
76.84
22.18
O
S
N
3x
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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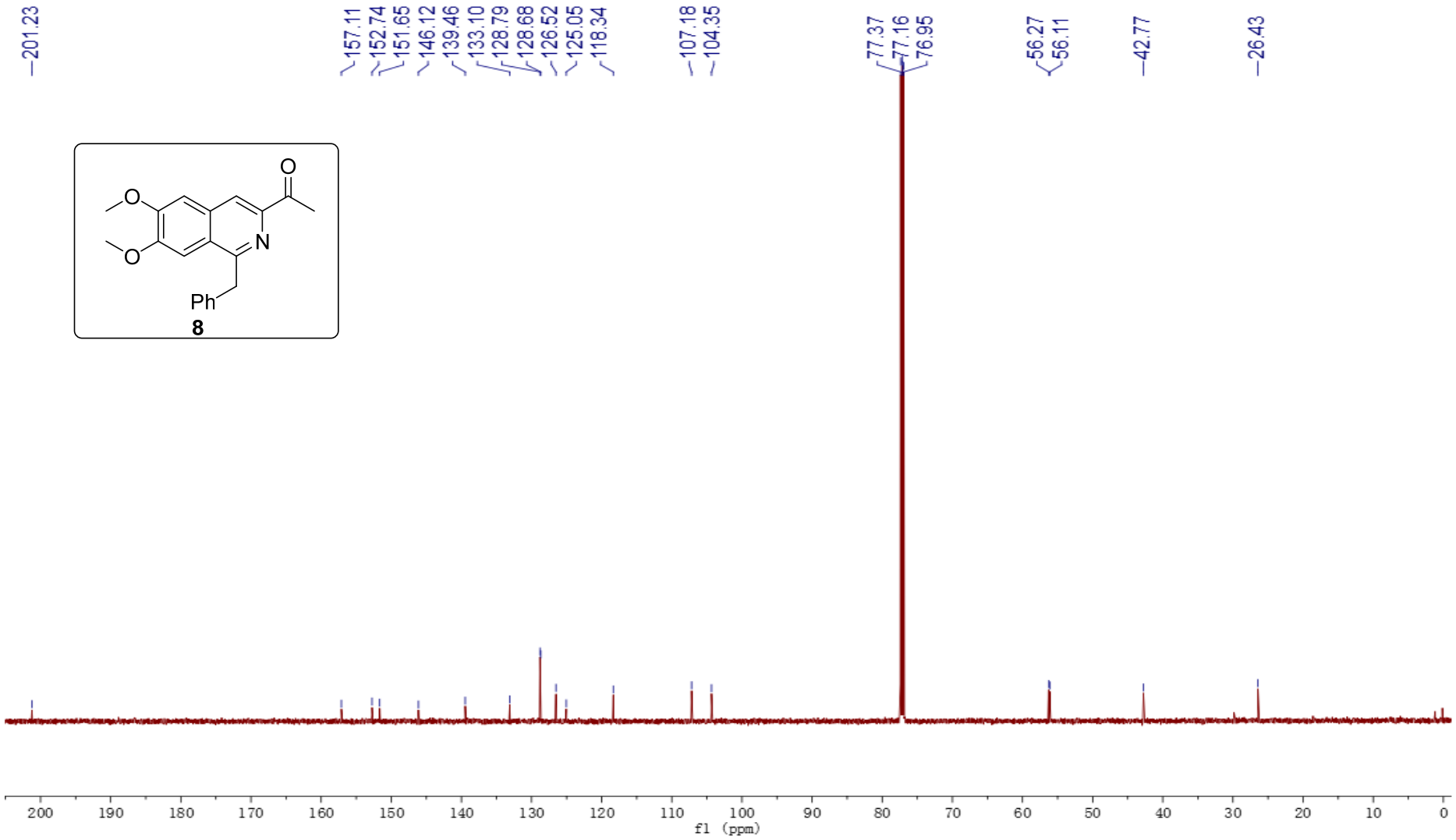
7.188
7.179
4.633
4.008
3.902
2.804
O
O
O
N
Ph
8
1.04
5.14
2.06
1.99
3.06
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


201.23
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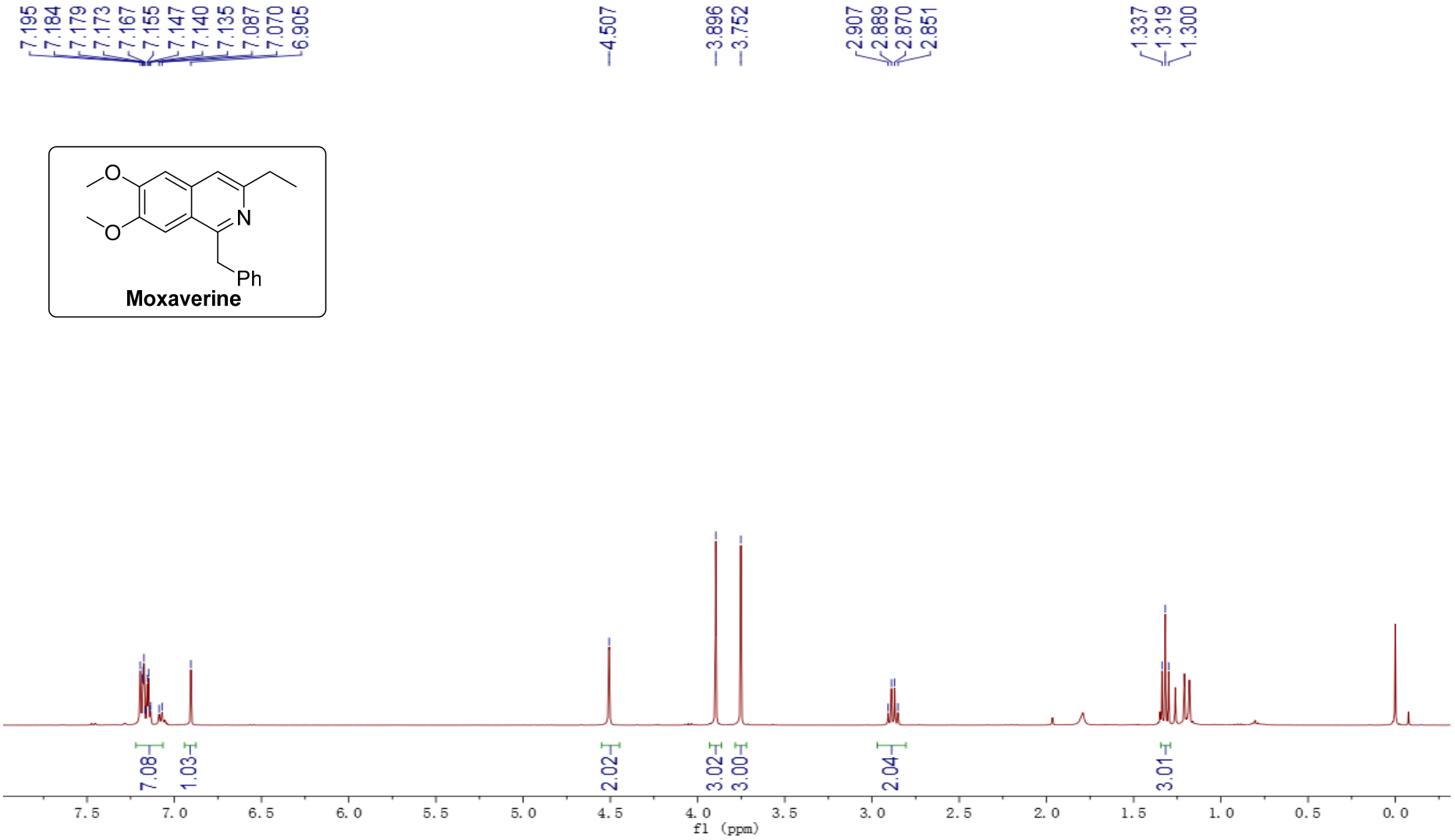
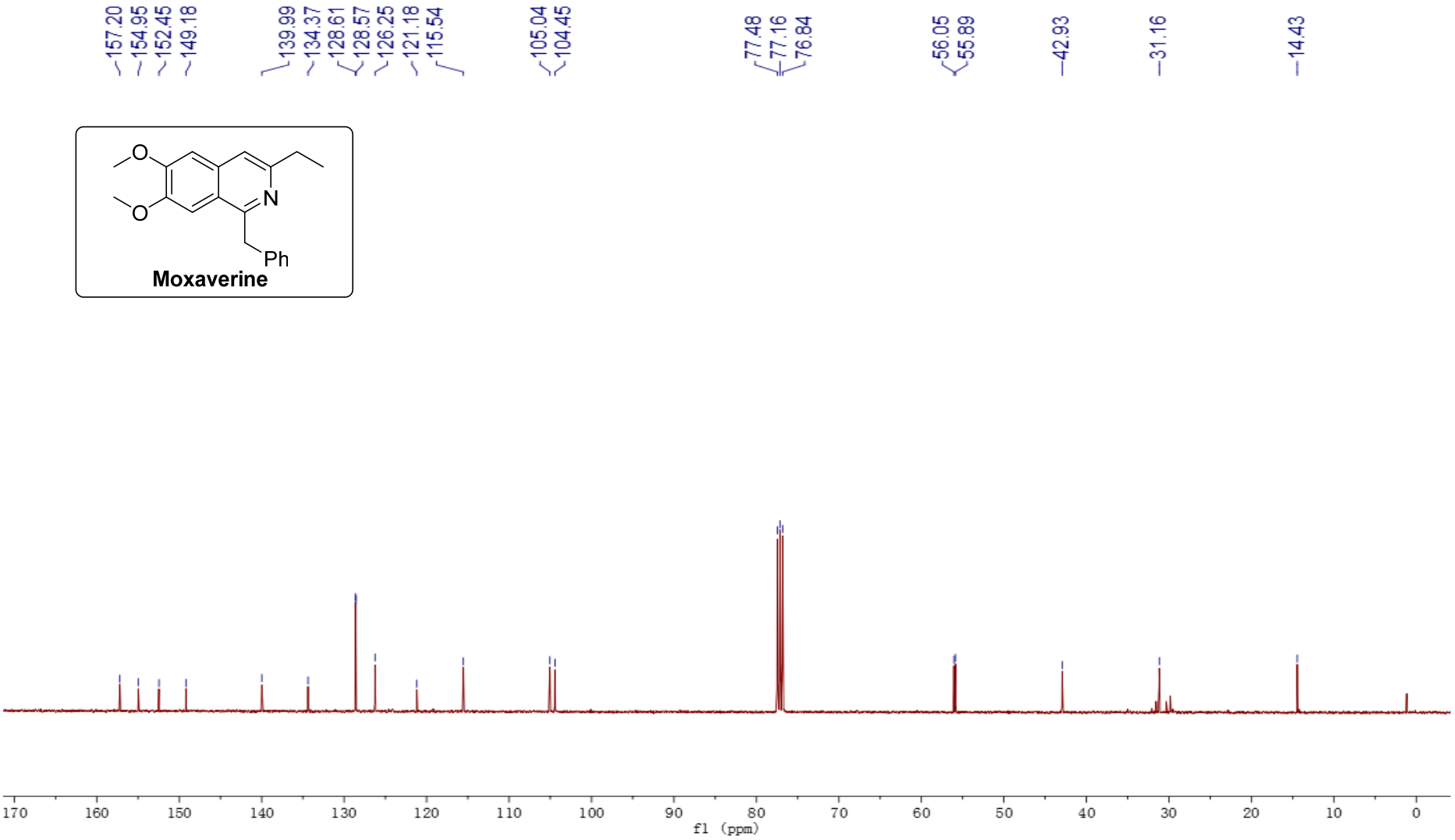
152.74
151.65
146.12
139.46
133.10
128.79
128.68
126.52
125.05
118.34
107.18
104.35
77.37
77.16
76.95
56.27
56.11
42.77
26.43
O
O
O
N
Ph
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.195
7.184
7.179
7.173
7.167
7.155
7.147
7.140
7.135
7.087
7.070
6.905
4.507
3.896
3.752
2.907
2.889
2.870
2.851
1.337
1.319
1.300
O
O
N
Ph
Moxaverine
7.08
1.03
2.02
3.02
3.00
2.04
3.01
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)


157.20
154.95
152.45
149.18
139.99
134.37
128.61
128.57
126.25
121.18
115.54
105.04
104.45
77.48
77.16
76.84
56.05
55.89
42.93
31.16
14.43
O
O
N
Ph
Moxaverine
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)