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Supporting Information

Divergent Synthesis from Reactions of 2-Trifluoromethyl-1, 3-Conjugated Enynes with *N*-Acetylated 2-Aminomalonates

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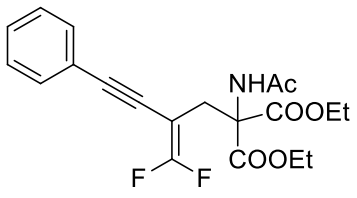
1. General information.

^{1}H NMR spectra, ^{13}C NMR spectra, ^{19}F NMR spectra were recorded on a Bruker 300 MHz, 400 MHz or 500 MHz spectrometer in chloroform-d3. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All reactions were carried out in

flame-dried glassware with magnetic stirring. DCM, DMF were freshly distilled from CaH_2; THF was freshly distilled from sodium metal prior to use. 4 Å molecular sieves were powdered and dried at 300 ºC in muffle furnace for 8-10 hours prior to use. All substrates and catalysts were prepared according to the literatures.[1-3]

2. General procedure for the synthesis of gem-Difluoro-1, 3-Conjugated Enynes derivatives 3

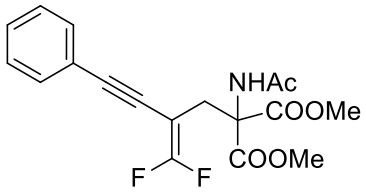
To a flame-dried flask equipped with a magnetic stir bar were added K_2CO_3(1.0 equiv). Then under N_2, 2-trifluoromethyl-1, 3-conjugated enyne compounds **1**(0.2 mmol), dialkyl 2-acetamidomalonate compounds **2**(0.3 mmol) in DMF(2.0 mL) were successively added into the flask. The reaction mixture was stirred at 25 ℃ for 5~10 h. After **1** was completely consumed, which was determined by TLC analysis, the reaction was quenched with H_2O (2.0 mL), then extracted with ethyl acetate (3x2.0 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated, purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 10:1~2:1) to afford the desired products **3**.



3aa

83% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). White

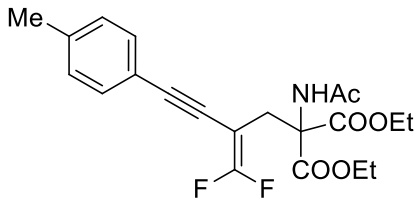
solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, *J* = 5.4, 2.1 Hz, 2H), 7.32 – 7.27 (m, 3H), 6.88 (s, 1H), 4.35 – 4.12 (m, 4H), 3.27 (s, 2H), 1.97 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -75.57 – -75.76 (m, 1F), -81.79 – -81.96 (m, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.35, 167.18, 160.19 (dd, *J* = 298.2, 297.2 Hz), 131.29, 128.62, 128.38, 122.50, 93.53 (dd, *J* = 5.8, 5.9Hz), 80.55 (dd, *J* = 7.8, 4.4 Hz), 73.59 (dd, *J* = 33.7, 18.3 Hz), 65.31 (dd, *J* = 3.3, 2.3 Hz), 62.83, 30.49, 22.79, 13.80. HRMS(ESI) calcd for $C_{20}H_{21}F_2NNaO_5$ [M+Na$^+$]: 416.1280, found: 416.1286.



3ab

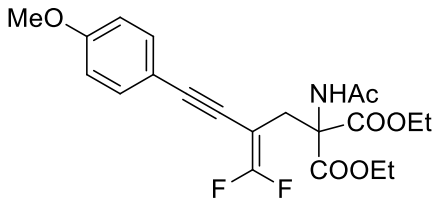
87% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.35-7.28 (m, 3H), 6.88 (s, 1H), 3.76 (s, 6H), 3.28 (dd, *J* = 2.0, 2.0 Hz, 2H), 1.99 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -75.34 (d, *J* = 6.8 Hz, 1F), -82.04 (d, *J* = 6.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 167.63, 160.26 (dd, *J* = 298.4, 297.2 Hz), 131.29, 128.67, 128.41, 122.38, 93.54 (dd, *J* = 5.9, 5.9 Hz), 80.40 (dd, *J* = 7.7, 4.5 Hz), 73.40 (dd, *J* = 33.8, 18.4 Hz), 65.09 (dd, *J* = 3.3, 2.3 Hz), 53.63, 30.80, 22.75. HRMS(ESI) calcd for $C_{18}H_{17}F_2NNaO_5$ [M+Na$^+$]: 388.0967, found:

388.0976.



3ba

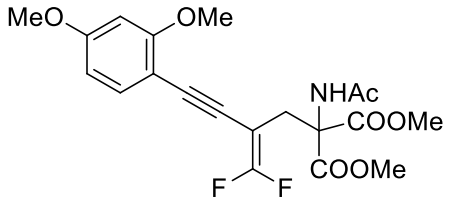
91% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.95 (s, 1H), 4.62 – 4.07 (m, 4H), 3.24 (s, 2H), 2.29 (s, 3H), 1.95 (s, 3H), 1.34 – 1.08 (m, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -74.92 – -77.86 (m, 1F), -82.54 – -82.55 (m, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.15, 166.98, 159.89 (dd, *J* = 297.1, 297.4 Hz), 138.63, 130.96, 128.94, 119.21, 93.51 (dd, *J* = 5.8, 5.8 Hz), 79.62 (dd, *J* = 7.6, 4.4 Hz), 73.49 (dd, *J* = 33.7, 18.3 Hz), 65.06 (dd, *J* = 2.7, 2.5 Hz), 62.55, 30.36, 22.51, 21.18, 13.57. HRMS(ESI) calcd for $C_{21}H_{23}F_2NNaO_5$ [M+Na^+]: 430.1436, found: 430.1446.



3ca

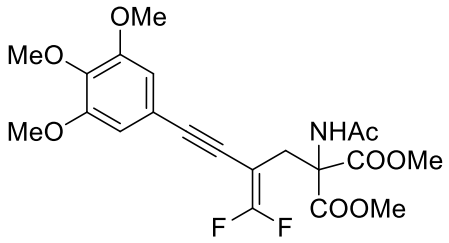
80% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.9 Hz, 2H), 6.87 (s, 1H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.56 – 4.10 (m, 4H), 3.79 (s, 3H), 3.25

(s, 2H), 1.97 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -76.37 (dd, *J* = 9.5, 2.4 Hz, 1F), -82.73 (dd, *J* = 9.4, 2.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.20, 167.18, 159.97 (dd, *J* = 297.1, 297.2 Hz), 159.79, 132.74, 114.53, 113.97, 93.47 (dd, *J* = 5.8, 5.8 Hz), 79.06 (dd, *J* = 7.6, 4.3 Hz), 73.63 (dd, *J* = 33.6, 18.4 Hz), 65.21 (dd, *J* = 3.3, 2.3 Hz), 62.75, 55.22, 30.53, 22.78, 13.77. HRMS(ESI) calcd for $C_{21}H_{23}F_2NNaO_6$ [M+Na$^+$]: 446.1386, found: 446.1395.



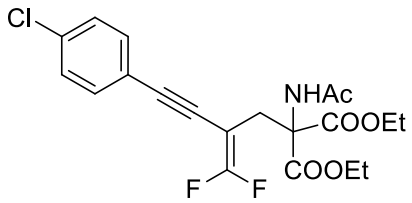
3db

56% isolated yield (silica gel, petroleum ether: ethyl acetate = 2:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 6.98 (s, 1H), 6.42-6.37 (m, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 3.72 (s, 6H), 3.22 (dd, *J* = 2.0, 2.0 Hz, 2H), 1.93 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.23 (d, *J* = 9.1 Hz, 1F), -83.27 (d, *J* = 9.0 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.33, 167.60, 161.46, 161.02, 159.85 (dd, *J* = 297.2, 297.0 Hz), 134.04, 104.90, 104.21, 98.40, 90.21 (dd, *J* = 5.8, 5.9 Hz), 82.56 (dd, *J* = 7.4, 4.4 Hz), 73.80 (dd, *J* = 33.5, 18.5 Hz), 65.19 (dd, *J* = 3.3, 2.3 Hz), 55.62 (d, *J* = 1.2 Hz), 55.37 (d, *J* = 1.1 Hz), 53.48 (d, *J* = 1.1 Hz), 30.87, 22.55. HRMS(ESI) calcd for $C_{20}H_{21}F_2NNaO_7$ [M+Na$^+$]: 448.1178, found: 448.1160.



3eb

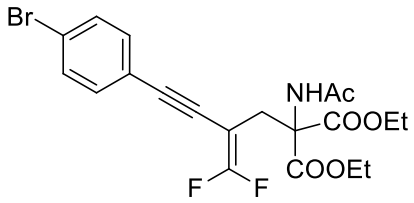
55% isolated yield (silica gel, petroleum ether: ethyl acetate = 2:1). White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.61 (d, *J* = 3.3 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 6H), 3.74 (s, 3H), 3.73 (s, 3H), 3.24 (s, 2H), 1.97 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -75.53 (dd, *J* = 14.6, 7.5 Hz, 1F), -82.26 (dd, *J* = 12.0, 7.5 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.30, 167.55, 160.06 (dd, *J* = 297.7, 297.9 Hz), 153.01, 139.01, 117.26, 108.43, 93.56 (dd, *J* = 5.7, 5.8 Hz), 79.39 (dd, *J* = 7.6, 4.5 Hz), 73.32 (dd, *J* = 33.8, 18.4 Hz), 65.00 (dd, *J* = 2.6, 2.8 Hz), 60.80, 56.03, 53.57, 30.73, 22.71. HRMS(ESI) calcd for $C_{21}H_{23}F_2NNaO_8$ [M+Na^+]: 478.1284, found: 478.1280.



3fa

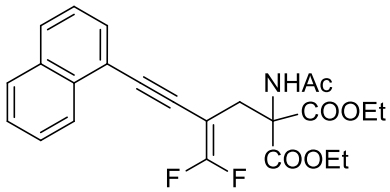
68% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.86 (s, 1H), 4.60 – 3.82 (m, 4H), 3.26 (s, 2H),

1.96 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -75.11 (d, *J* = 6.9 Hz, 1F), -81.43 (d, *J* = 6.8 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.23, 167.10, 160.15 (dd, *J* = 298.4, 297.8 Hz), 134.65, 132.42, 128.72, 120.89, 92.25 (dd, *J* = 5.8, 5.8 Hz), 81.54 (dd, *J* = 7.9, 4.5 Hz), 73.42 (dd, *J* = 33.9, 18.1 Hz), 65.16 (dd, *J* = 3.3, 2.3 Hz), 62.78, 30.35, 22.74, 13.75. HRMS(ESI) calcd for $C_{20}H_{20}ClF_2NNaO_5$ [M+Na$^+$]: 450.0890, found: 450.0889.



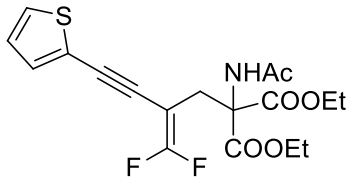
3ga

78% isolated yield (silica gel, petroleum ether: ethyl acetate = 4:1). White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.86 (s, 1H), 4.81 – 3.97 (m, 4H), 3.25 (s, 2H), 1.95 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.96 (dd, *J* = 6.1, 2.0 Hz, 1F), -81.12 (dd, *J* = 6.2, 1.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.16, 167.07, 160.13 (dd, *J* = 297.9, 298.2 Hz), 132.59, 131.63, 122.86, 121.36, 92.31 (dd, *J* = 5.8, 5.8 Hz), 81.75 (dd, *J* = 7.8, 4.5 Hz), 73.46 (dd, *J* = 33.9, 18.1 Hz), 65.17 (dd, *J* = 3.1, 2.3 Hz), 62.74, 30.32, 22.71, 13.73. HRMS(ESI) calcd for $C_{20}H_{20}BrF_2NNaO_5$ [M+Na$^+$]: 494.0385, found: 494.0376.



3ha

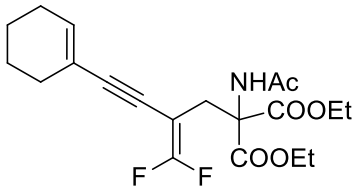
87% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.64 (d, *J* = 7.1 Hz, 1H), 7.60 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45 – 7.37 (m, 1H), 6.92 (s, 1H), 4.34 – 4.10 (m, 4H), 3.38 (s, 2H), 1.94 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -75.18 (d, *J* = 7.2 Hz, 1F), -81.55 (d, *J* = 7.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.36, 167.23, 160.28 (dd, *J* = 298.1, 297.6 Hz), 133.10, 132.86, 130.25, 129.14, 128.28, 127.05, 126.58, 125.94, 125.13, 120.09, 91.70 (dd, *J* = 5.8, 5.9 Hz), 85.36 (dd, *J* = 7.8, 4.6 Hz), 73.82 (dd, *J* = 33.8, 18.3 Hz), 65.35 (dd, *J* = 3.1, 2.4 Hz), 62.87, 30.63, 22.84, 13.81. HRMS(ESI) calcd for $C_{24}H_{23}F_2NNaO_5$ [M+Na^+]: 466.1436, found: 466.1437.



3ia

60% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 5.2, 1.1 Hz, 1H), 7.15 (dd, *J* = 3.6, 1.1 Hz, 1H), 6.95 – 6.91 (m, 1H), 6.90 (s, 1H),

4.28-4.11 (m, 4H), 3.23 (s, 2H), 1.97 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.74 (d, *J* = 5.3 Hz, 1F), -81.14 (d, *J* = 5.2 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.20, 166.99, 160.04 (dd, *J* = 298.4, 298.4 Hz), 132.11, 127.61, 127.01, 122.14, 86.54 (dd, *J* = 5.8, 5.9 Hz), 83.88 (dd, *J* = 7.8, 4.6 Hz), 73.45 (dd, *J* = 34.0, 18.1 Hz), 65.10 (dd, *J* = 3.2, 2.3 Hz), 62.74, 30.25, 22.65, 13.70. HRMS(ESI) calcd for $C_{18}H_{19}F_2NNaO_5S$ [M+Na^+]: 422.0844, found: 422.0858.

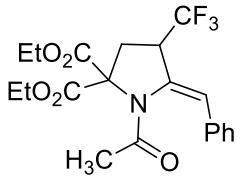


3ja

78% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (s, 1H), 6.06 (s, 1H), 4.40 – 4.08 (m, 4H), 3.15 (s, 2H), 2.25 – 2.00 (m, 4H), 1.99 (s, 3H), 1.62-1.50 (m, 4H), 1.23 (t, *J* = 7.0 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.06 (d, *J* = 10.1 Hz, 1F), -83.21 (d, *J* = 10.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.11, 167.13, 159.85 (dd, *J* = 296.8, 296.9 Hz), 135.54, 120.25, 95.34 (dd, *J* = 5.8, 6.0 Hz), 77.70 (dd, *J* = 7.5, 4.4 Hz), 73.61 (dd, *J* = 33.3, 18.5 Hz), 65.18 (dd, *J* = 3.0, 2.4 Hz), 62.67, 30.50, 28.87, 25.57, 22.71, 22.11, 21.31, 13.75. HRMS(ESI) calcd for $C_{20}H_{25}F_2NNaO_5$ [M+Na^+]: 420.1593, found: 420.1562.

3. General procedure for the synthesis of 4-Trifluoromethyl Pyrrolidines derivatives 4

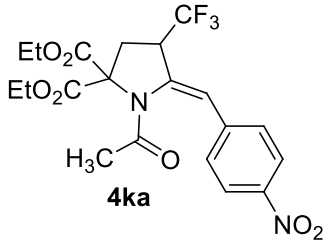
Under N_2, to a flame-dried flask equipped with a magnetic stir bar were added 2-trifluoromethyl-1, 3-conjugated enyne compounds **1**(0.2 mmol), dialkyl 2-acetamidomalonate compounds 2(0.3 mmol) and DMF(2.0 mL). Then DBU (20 mol %) or DBU (1.5 equiv)/CsF(1.2 equiv) was added into the flask. The reaction mixture was stirred at 25 ℃ for 2~5 h. After **1** was completely consumed, which was determined by TLC analysis, the reaction was quenched with H_2O (2.0 mL), then extracted with ethyl acetate (3x2.0 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated, purified by column chromatography (silica gel, petroleum ether: ethyl acetate = 5:1~2:1) to afford the desired products **4**.



4aa

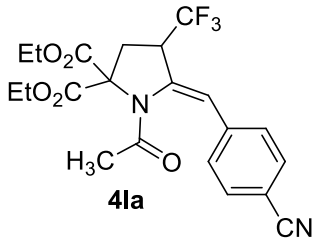
DBU (1.5 equiv)/CsF(1.2 equiv) was used, 46% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). White solid. Mp 80-82 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.22 (s, 1H), 4.38-4.22 (m, 4H), 3.73 – 3.36 (m, 1H), 2.93 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.61 (dd, *J* = 14.0, 7.5 Hz, 1H), 1.68

(s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -70.11 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.12, 168.56, 167.17, 134.89, 131.58 (q, *J* = 2.2 Hz), 128.99, 128.08, 127.84, 125.60 (q, *J* = 278.4 Hz), 118.31, 71.43, 62.70, 62.56, 46.29 (q, *J* = 29.7 Hz), 32.12, 22.32, 13.93, 13.81. HRMS(ESI) calcd for $C_{20}H_{22}F_3NNaO_5$ [M+Na$^+$]: 436.1342, found: 436.1353.



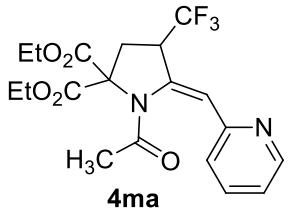
4ka

DBU (20 mol%) was used, 88% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). Yellow solid. Mp 132-133 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 6.26 (s, 1H), 4.61 – 4.20 (m, 4H), 3.84 – 3.44 (m, 1H), 2.93 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.63 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.67 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.81 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.76, 168.19, 166.87, 146.74, 141.82, 135.15, 128.55, 125.24 (q, *J* = 279.1 Hz), 124.34, 115.34, 71.61, 62.97, 62.83, 46.39 (q, *J* = 29.9 Hz), 31.86, 22.35, 13.93, 13.83. HRMS(ESI) calcd for $C_{20}H_{21}F_3N_2NaO_7$ [M+Na$^+$]: 481.1193, found: 481.1192.



4la

DBU (20 mol%) was used, 85% isolated yield (silica gel, petroleum ether: ethyl acetate = 2:1). Yellow solid. Mp 90-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 6.20 (s, 1H), 4.58 – 4.19 (m, 4H), 3.86 – 3.50 (m, 1H), 2.92 (dd, *J* = 14.0, 9.3 Hz, 1H), 2.61 (dd, *J* = 14.0, 7.6 Hz, 1H), 1.66 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -69.91 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.79, 168.21, 166.89, 139.75, 134.54, 132.77, 128.36, 125.25 (q, *J* = 278.8 Hz), 118.44, 115.84, 111.25, 71.53, 62.91, 62.78, 46.32 (q, *J* = 30.4 Hz), 31.86, 22.30, 13.91, 13.80. HRMS(ESI) calcd for $C_{21}H_{21}F_3N_2NaO_5$ [M+Na$^+$]: 461.1295, found: 461.1297.



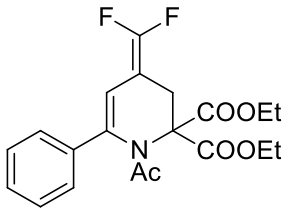
4ma

DBU (20 mol%) was used, 79% isolated yield (silica gel, petroleum ether: ethyl acetate = 2:1). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.63 (td, *J* = 7.8, 1.6 Hz, 1H), 7.11 (dd, *J* = 7.1, 5.1 Hz, 1H), 6.35 (s, 1H), 4.42 – 4.20 (m, 4H),

3.66 – 3.50 (m, 1H), 2.90 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.60 (dd, *J* = 13.9, 7.4 Hz, 1H), 1.71 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -69.98 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.51, 168.29, 167.04, 154.17, 149.75, 136.63, 134.25 (q, *J* = 2.1 Hz), 125.35 (q, *J* = 278.5 Hz), 122.73, 122.25, 118.03, 71.56, 62.67, 62.57, 46.31 (q, *J* = 29.8 Hz), 31.80, 22.23, 13.84, 13.77. HRMS(ESI) calcd for $C_{19}H_{21}F_3N_2NaO_5$ [M+Na^+]: 437.1295, found: 437.1301.

4. General procedure for the synthesis of 4-(difluoromethylene)-1,2,3,4-tetrahydropyridine derivatives 5

To a flame-dried vial equipped with a magnetic stir bar was added $IprAuNTf_2$ (5 mol %). Then under argon, **3** (0.3 mmol) in DCE (3 mL) were added into the vial. The reaction mixture was stirred at 25 ℃ for 24~72 h. After **3** was completely consumed as indicated by TLC, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography(silica gel, first, DCM: PE = 10:1, then PE: EA = 10:1~2:1) to afford the desired the products **5**.

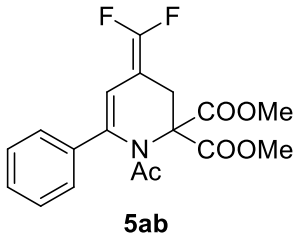


5aa

98% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1).

Colorless oil.

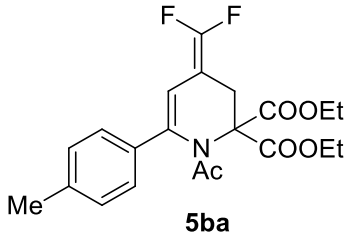
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.4 Hz, 2H), 7.42-7.30 (m, 3H), 6.12 (s, 1H), 4.31 – 4.11 (m, 4H), 3.21 (dd, *J* = 2.4 Hz, *J* = 2.5 Hz, 2H), 1.66 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (377 MHz, $CDCl_3$) δ -87.75 (d, *J* = 23.7 Hz, 1F), -88.55 (d, *J* = 23.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.82, 166.51, 152.75 (dd, *J* = 297.3, 293.7 Hz), 140.01 (dd, *J* = 13.2, 4.8 Hz), 137.68, 128.81, 128.77, 109.84, 85.16 (dd, *J* = 25.8, 17.5 Hz), 69.50, 62.32, 28.42 (d, *J* = 2.0 Hz), 24.80, 13.74. HRMS(ESI) calcd for $C_{20}H_{21}F_2NNaO_5$ [M+Na^+]: 416.1280, found: 416.1274.



5ab

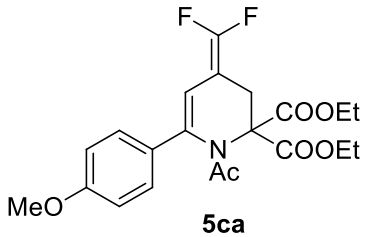
93% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.44-7.32 (m, 3H), 6.13 (dd, *J* = 1.5, 1.5 Hz, 1H), 3.77 (s, 6H), 3.23 (dd, *J* = 2.7, 2.7 Hz, 2H), 1.67 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.24 (dd, *J* = 22.6, 1.8 Hz, 1F), -88.18 (d, *J* = 22.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.02, 167.09, 152.84 (dd, *J* = 297.4, 294.0 Hz), 139.94 (dd, *J* = 13.2, 4.8 Hz), 137.65, 128.93, 126.26, 110.11, 85.06 (dd, *J* = 25.8, 17.6 Hz), 69.36 (d, *J* = 1.3 Hz), 53.39, 28.57 (d, *J* = 2.1 Hz), 24.82.

HRMS(ESI) calcd for $C_{18}H_{17}F_2NNaO_5$ [M+Na^+]: 388.0967, found: 388.0972.



5ba

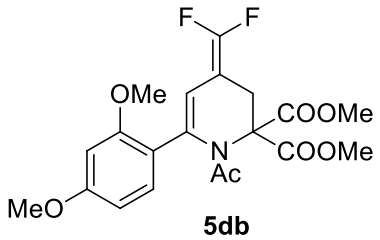
81% isolated yield (silica gel, petroleum ether: ethyl acetate = 4:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.48 – 3.92 (m, 4H), 3.20 (t, *J* = 2.3 Hz, 2H), 2.36 (s, 3H), 1.67 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -88.34 (d, *J* = 24.7 Hz, 1F), -89.04 (d, *J* = 24.6 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.91, 166.53, 152.64 (dd, *J* = 296.9, 293.4 Hz), 140.09 (dd, *J* = 13.1, 4.8 Hz), 138.91, 134.86, 129.45, 126.19, 109.05, 85.17 (dd, *J* = 25.7, 17.5 Hz), 69.51 (d, *J* = 1.1 Hz), 62.29, 28.43 (d, *J* = 2.0 Hz), 24.78, 21.16, 13.75. HRMS(ESI) calcd for $C_{21}H_{23}F_2NNaO_5$ [M+Na^+]: 430.1436, found: 430.1430.



5ca

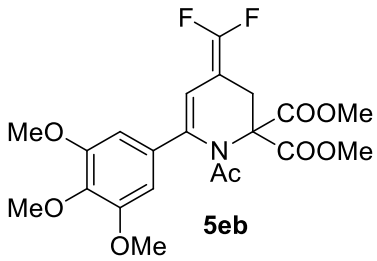
87% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 2H),

6.92 (d, *J* = 8.8 Hz, 2H), 6.02 (s, 1H), 4.47 – 4.08 (m, 4H), 3.83 (s, 3H), 3.20 (dd, *J* = 2.5, 2.6 Hz, 2H), 1.68 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -88.60 (d, *J* = 25.4 Hz, 1F), -89.28 (d, *J* = 25.3 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.03, 166.56, 160.15, 152.60 (dd, *J* = 296.7, 293.2 Hz), 139.87 (dd, *J* = 13.2, 4.7 Hz), 130.25, 127.70, 114.19, 108.34, 85.19 (dd, *J* = 25.6, 17.6 Hz), 69.62 (d, *J* = 1.1 Hz), 62.33, 55.31, 28.42 (d, *J* = 2.0 Hz), 24.76, 13.80. HRMS(ESI) calcd for $C_{21}H_{23}F_2NNaO_6$ [M+Na$^+$]: 446.1386, found: 446.1380.



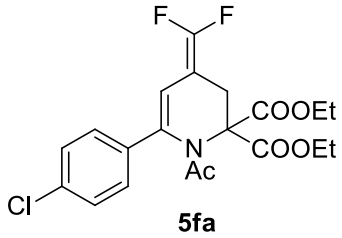
5db

90% isolated yield (silica gel, petroleum ether: ethyl acetate = 2:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.7 Hz, 1H), 6.55 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.30 (t, *J* = 1.5 Hz, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.76 (s, 6H), 3.20 (s, 2H), 1.66 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -88.84 (d, *J* = 25.2 Hz, 1F), -89.38 (d, *J* = 25.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.36, 160.97, 157.82, 152.50 (dd, *J* = 296.8, 292.7 Hz), 134.46 (dd, *J* = 13.2, 4.9 Hz), 130.65, 118.79, 111.15, 104.81, 98.86, 85.15 (dd, *J* = 25.3, 17.5 Hz), 69.30 (d, *J* = 1.2 Hz), 55.50, 55.42, 53.32, 28.57 (d, *J* = 2.0 Hz), 23.98. HRMS(ESI) calcd for $C_{20}H_{21}F_2NNaO_7$ [M+Na$^+$]: 448.1178, found: 448.1159.



5eb

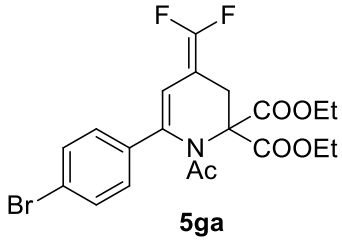
91% isolated yield (silica gel, petroleum ether: ethyl acetate = 2:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (s, 2H), 6.02 (s, 1H), 3.89 (s, 6H), 3.86 (s, 3H), 3.77 (s, 6H), 3.20 (dd, *J* = 2.6, 2.6 Hz, 2H), 1.73 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -87.70 (dd, *J* = 23.4, 1.6 Hz, 1F), -88.49 (d, *J* = 23.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.12, 167.09, 153.61, 152.65 (dd, *J* = 297.3, 293.7 Hz), 139.70 (dd, *J* = 13.1, 4.8 Hz), 138.85, 133.49, 109.19, 103.64, 84.90 (dd, *J* = 25.7, 17.7 Hz), 69.25, 60.93, 56.26, 53.40, 28.71 (d, *J* = 2.0 Hz), 24.74. HRMS(ESI) calcd for $C_{21}H_{23}F_2NNaO_8$ [M+Na$^+$]: 478.1284, found: 478.1277.



5fa

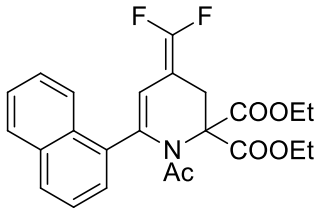
80% isolated yield (silica gel, petroleum ether: ethyl acetate = 5:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.13 (dd, *J* = 1.4, 1.5 Hz, 1H), 4.49 – 4.05 (m, 4H), 3.21 (dd, *J* = 2.6, 2.7 Hz, 2H), 1.68 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.82 (d, *J* = 21.2 Hz, 1F), -87.77 (d, *J* =

21.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.72, 166.40, 152.98 (dd, *J* = 297.9, 294.5 Hz), 139.03 (dd, *J* = 13.3, 4.8 Hz), 136.22, 134.75, 129.11, 127.57, 110.61, 85.19 (dd, *J* = 25.9, 17.3 Hz), 69.61 (d, *J* = 1.0 Hz), 62.46, 28.30 (d, *J* = 1.9 Hz), 24.77, 13.81. HRMS(ESI) calcd for $C_{20}H_{20}ClF_2NNaO_5$ [M+Na$^+$]: 450.0890, found: 450.0881.



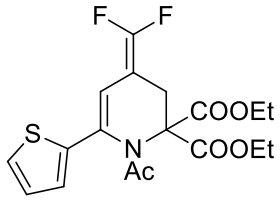
5ga

84% isolated yield (silica gel, petroleum ether: ethyl acetate = 4:1). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 6.14 (s, 1H), 4.51 – 3.92 (m, 4H), 3.21 (dd, *J* = 2.1, 2.4 Hz, 2H), 1.68 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ -86.72 (d, *J* = 19.9 Hz, 1F), -87.66 (d, *J* = 20.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.70, 166.37, 152.96 (dd, *J* = 298.0, 294.5 Hz), 139.07 (dd, *J* = 13.2, 4.8 Hz), 136.66, 132.04, 127.81, 122.93, 110.67, 85.19 (dd, *J* = 26.0, 17.3 Hz), 69.58 (d, *J* = 1.2 Hz), 62.45, 28.26 (d, *J* = 1.9 Hz), 24.77, 13.80. HRMS(ESI) calcd for $C_{20}H_{20}BrF_2NNaO_5$ [M+Na$^+$]: 494.0385, found: 494.0361.



5ha

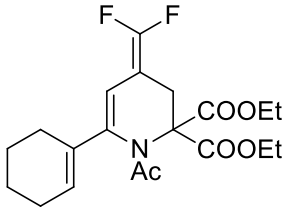
53% isolated yield (silica gel, petroleum ether: ethyl acetate = 4:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.4 Hz, 1H), 8.06 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.45 (m, 3H), 5.94 (s, 1H), 4.51 – 4.14 (m, 4H), 3.42 (s, 2H), 1.50 (s, 3H), 1.32 (t, *J* = 6.8 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.05 (d, *J* = 26.4 Hz), -90.29 (d, *J* = 26.4 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.63, 167.11, 152.28 (dd, *J* = 296.6, 292.8 Hz), 135.62 (dd, *J* = 12.8, 5.0 Hz), 135.37, 134.19, 130.84, 129.06, 128.84, 127.00, 126.41, 126.10, 125.32, 124.49, 110.08, 84.68 (dd, *J* = 25.6, 18.5 Hz), 69.11 (d, *J* = 0.9 Hz), 62.47, 29.51 (d, *J* = 2.3 Hz), 25.12, 13.89. HRMS(ESI) calcd for $C_{24}H_{23}F_2NNaO_5$ [M+Na^+]: 466.1436, found: 466.1429.



5ia

99% isolated yield (silica gel, petroleum ether: ethyl acetate = 10:1). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 3.4 Hz, 1H), 7.30 (d, *J* = 5.0 Hz, 1H), 7.03 (dd, *J* = 4.8, 3.9 Hz, 1H), 6.13 (s, 1H), 4.70 – 3.92 (m, 4H), 3.19 (dd, *J* = 2.5, 2.6 Hz, 2H), 1.84 (s, 3H), 1.21 (t, *J* =

7.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.78 (d, *J* = 21.1 Hz, 1F), -87.72 (d, *J* = 21.1 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.08, 166.24, 152.82 (dd, *J* = 298.0, 294.4 Hz), 141.27, 134.52 (dd, *J* = 13.3, 5.0 Hz), 127.59, 126.24, 126.18, 109.81, 85.06 (dd, *J* = 26.2, 17.5 Hz), 69.57 (d, *J* = 1.2 Hz), 62.36, 28.07 (d, *J* = 2.0 Hz), 23.98, 13.74. HRMS(ESI) calcd for $C_{18}H_{19}F_2NNaO_5S$ [M+Na^+]: 422.0844, found: 422.0820.

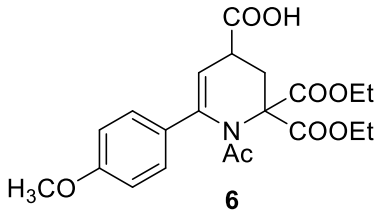


5ja

74% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44 (s, 1H), 5.85 (s, 1H), 4.37 – 4.03 (m, 4H), 3.14 (s, 2H), 2.22-2.20 (m, 4H), 1.99 (s, 3H), 1.77-1.69 (m, 2H), 1.68-1.60 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.89 (d, *J* = 24.5 Hz, 1F), -88.87 (d, *J* = 24.5 Hz, 1F). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.55, 166.37, 152.76 (dd, *J* = 296.8, 293.5 Hz), 141.86 (dd, *J* = 13.1, 4.5 Hz), 133.15, 129.77, 107.12, 85.21 (dd, *J* = 25.5, 17.1 Hz), 69.62 (d, *J* = 1.3 Hz), 62.19, 27.91 (d, *J* = 1.9 Hz), 25.70, 25.42, 23.67, 22.53, 22.07, 13.82. HRMS(ESI) calcd for $C_{20}H_{25}F_2NNaO_5$ [M+Na^+]: 420.1593, found: 420.1576.

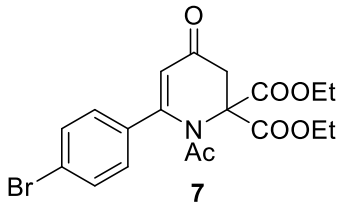
5. Derivatization of **5ca** and **5ga**

To a solution of **5ca** or **5ga** (0.2 mmol) in DMF (2mL), Bu_4OAc (0.4 mmol) was added at room temperature. The reaction mixture was stirred at room temperature over 8 h. After **5ca** or **5ga** was completely consumed, which was determined by TLC analysis, the reaction was quenched with H_2O (5.0 mL), then extracted with ethyl acetate (3x5.0 mL). The organic layer was washed with brine, dried over $MgSO_4$ and concentrated, purified by column chromatography.



6

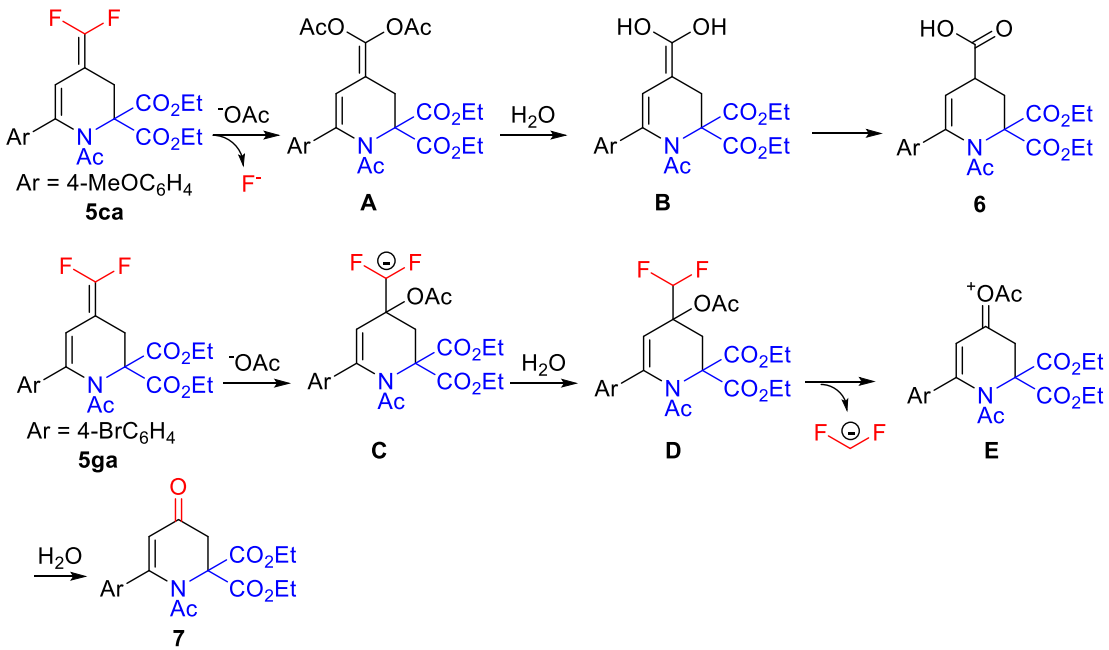
35% isolated yield (silica gel, EA). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.71 (d, *J* = 4.0 Hz, 1H), 4.38 – 4.09 (m, 4H), 3.79 (s, 3H), 3.64 – 3.46 (m, 1H), 2.93 (dd, *J* = 14.0, 6.3 Hz, 1H), 2.53 (dd, *J* = 14.0, 10.2 Hz, 1H), 1.65 (s, 3H), 1.25 (dt, *J* = 16.9, 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.02, 172.20, 167.91, 167.25, 160.01, 141.32, 130.54, 127.62, 114.17, 69.37, 62.35, 62.25, 55.30, 38.18, 34.76, 25.20, 13.88. HRMS(ESI) calcd for $C_{21}H_{25}NNaO_8$ [M+Na^+]: 442.1472, found: 442.1469.



7

49% isolated yield (silica gel, petroleum ether: ethyl acetate = 3:1). Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 5.66 (s, 1H), 4.28 (q, *J* = 3.7 Hz, 4H), 3.33 (s, 2H), 1.70 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 190.85, 171.74, 166.50, 155.74, 135.48, 132.66, 128.98, 126.00, 113.99, 73.37, 63.09, 44.70, 26.73, 13.84. HRMS (ESI) calcd for $C_{19}H_{20}BrNNaO_6$ [M+Na$^+$]: 460.0366, found: 460.0333.

6. Proposed mechanism for the formation of compound 6 and 7



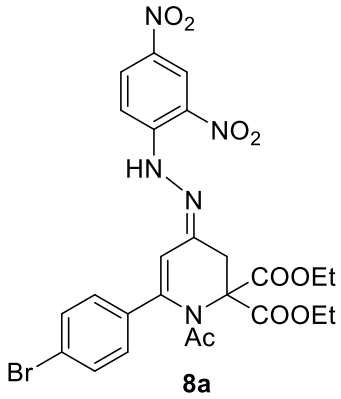
*Scheme 1 Plausible mechanism for the formation of compound **6** and **7***

We suggest that both terminal and internal position of carbon-carbon

double bond of difluorovinyl group can be attacked by nucleophiles, which depends on electronic nature of Aryl group. **5ca** bearing electron-donating aryl groups undergoes double consecutive addition-elimination process with nucleophile ($^{-}$OAc) at terminal carbon-carbon double bond of difluorovinyl group yielding intermediate **A**, followed by hydrolysis and isomerization to give finally the acid **6**. However, **5ga** bearing electron-withdrawing aryl groups undergoes nucleophilic addition with nucleophile ($^{-}$OAc) at internal carbon-carbon double bond of difluorovinyl group leading difluoromethyl anion intermediate **C**. The protonation of intermediate **C** by water would produce difluoromethyl substituted intermediate **D**. Subsequent heterolysis of carbon-carbon bond of difluoromethyl moiety of intermediate **D**, followed by hydrolysis to give 2,3-Dihydropyridin-4-one **7**.

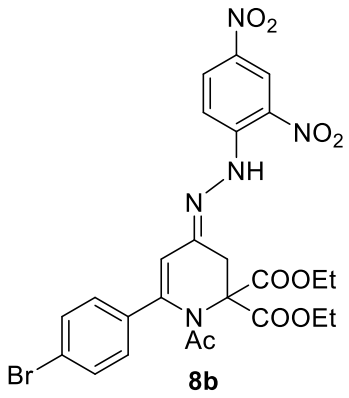
7. Synthesis of 2,4-dinitrophenyl hydrazones 8

To a solution of ketone substrate **7** (0.1 mmol, 43.8mg) and 2,4-dinitrophenyl hydrazine (0.11 mmol, 22 mg) in 2 mL MeOH was added 20 μL HCl (conc.) at room temperature. The reaction was stirred for overnight. Upon done, the solvent was removed in vacuo. The residue was purified by flash column chromatography (silica gel, Hex/EA 4:1) to give *Z*- or *E*- isomers of hydrazone **8a** or **8b** in total 80% isolated yield.



8a

(*Z*)-diethyl 1-acetyl-6-(4-bromophenyl)-4-(2-(2,4-dinitrophenyl) hydrazono)-3,4-dihydropyridine-2,2(1H)-dicarboxylate **8a**. 32% isolated yield. Orange solid. Mp 189-191 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.51 (s, 1H), 9.11 (d, *J* = 2.5 Hz, 1H), 8.33 (dd, *J* = 9.6, 2.5 Hz, 1H), 7.97 (d, *J* = 9.6 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 2H), 7.63 (d, *J* = 9.2 Hz, 2H), 6.10 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 4H), 3.56 (s, 2H), 1.71 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.38, 166.53, 149.03, 145.26, 144.47, 138.31, 136.17, 132.74, 130.16, 129.39, 128.91, 125.62, 123.37, 116.46, 102.82, 71.50, 62.95, 38.95, 26.40, 13.89. MS (ESI) m/z (%) 620.06 ($M+H^+$(^{81}Br), 54), 617.98 ($M+H^+$(^{79}Br), 49), 575.99 (100). HRMS (ESI) calcd for $C_{25}H_{24}N_5O_9Na^{79}Br$ [$M+Na^+$]: 640.0655, found: 640.0653.



8b

(*E*)-diethyl 1-acetyl-6-(4-bromophenyl)-4-(2-(2,4-dinitrophenyl) hydrazono)-3,4-dihydropyridine-2,2(1H)-dicarboxylate **8b**. 48% isolated yield. Orange solid. Mp 208-210 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.32 (s, 1H), 9.15 (d, *J* = 2.1 Hz, 1H), 8.35 (dd, *J* = 9.4, 1.9 Hz, 1H), 8.00 (d, *J* = 9.5 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 6.39 (s, 1H), 4.48 – 3.95 (m, 4H), 3.53 (s, 2H), 1.74 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.54, 166.00, 147.44, 145.44, 144.13, 138.84, 135.43, 132.42, 130.23, 130.07, 128.40, 124.64, 123.33, 116.62, 116.58, 70.51, 63.13, 31.80, 25.06, 13.82. MS (ESI) m/z (%) 620.00 ($M+H^+$(^{81}Br), 84), 618.05 ($M+H^+$(^{79}Br), 81), 576.06 (100). HRMS (ESI) calcd for $C_{25}H_{24}N_5O_9Na^{79}Br$ [$M+Na^+$]: 640.0655, found: 640.0629.

8. X-ray structures for 3aa and 4aa

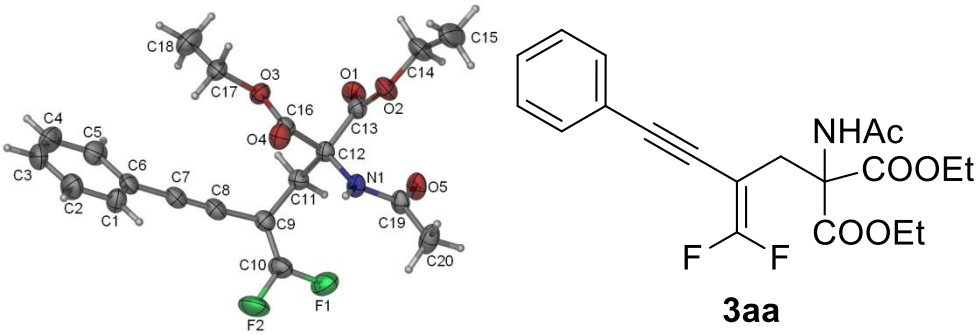


Figure 1. ORTEP depiction of compound **3aa**, CCDC 1465337

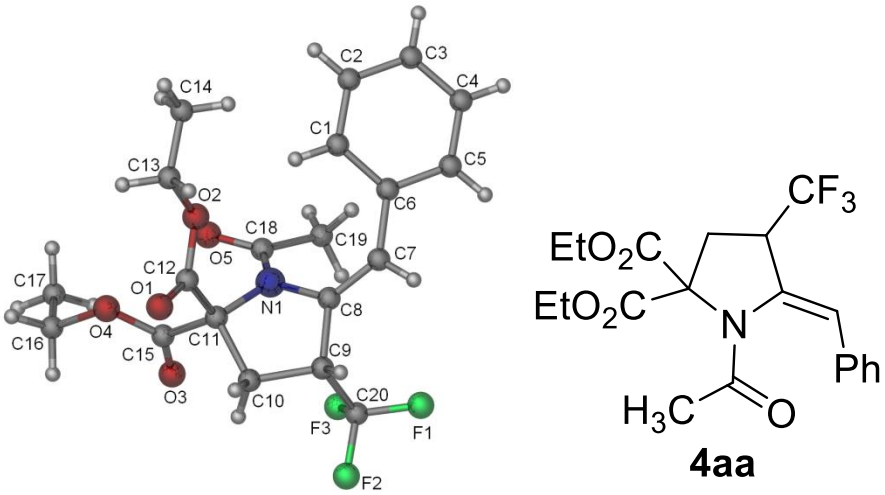


Figure 2. ORTEP depiction of compound **4aa**, CCDC 1465336

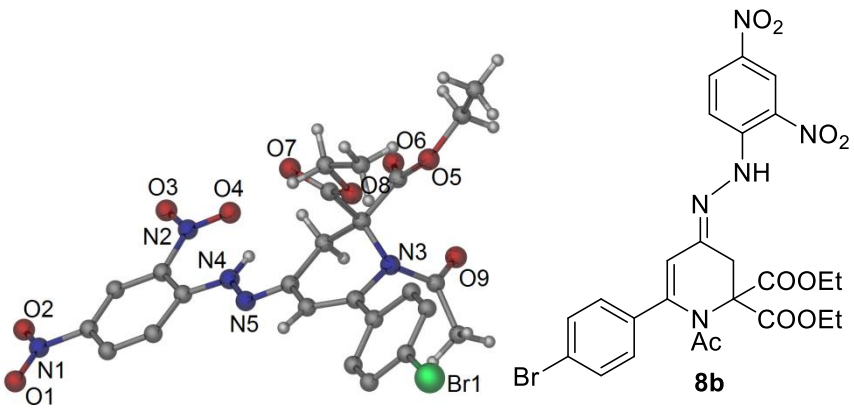


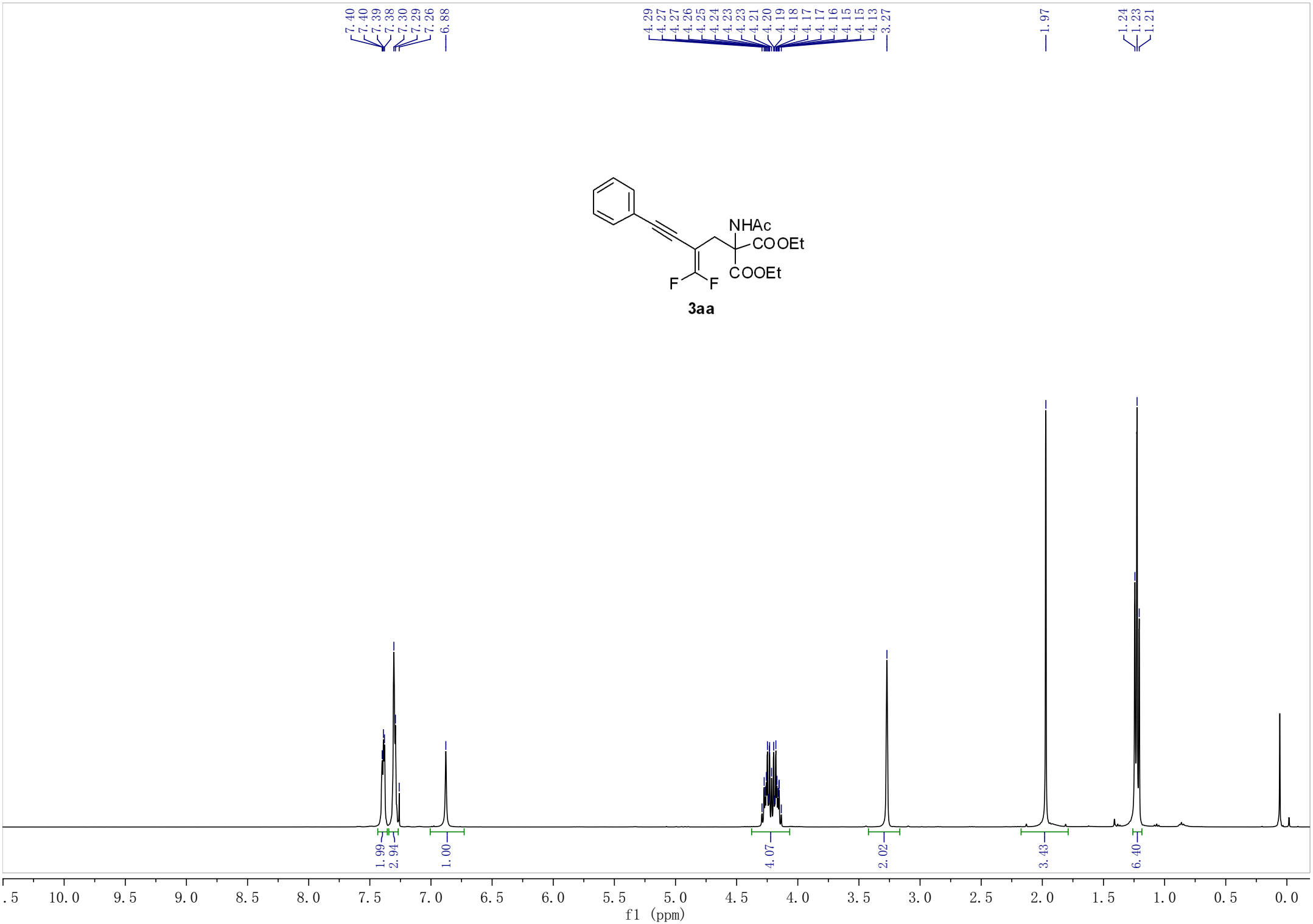
Figure 3. ORTEP depiction of compound **8b**, CCDC 1477180

9. Reference

[1] C. Hu, F. Hong, Y. Xu, *J. Fluorine. Chem*. **1993**, *64*, 1.

[2] L. Ye, Y. Wang, L. Zhang, *J. Am. Chem. Soc*. **2012**, *134*, 31.

[3] Q. Zeng, L. Zhang, J. Yang, B. Xu, Y. Xiao, J. Zhang, *Chem. Commun*. **2014**, *50*, 4203.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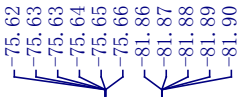
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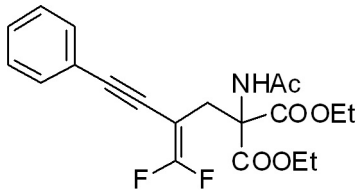
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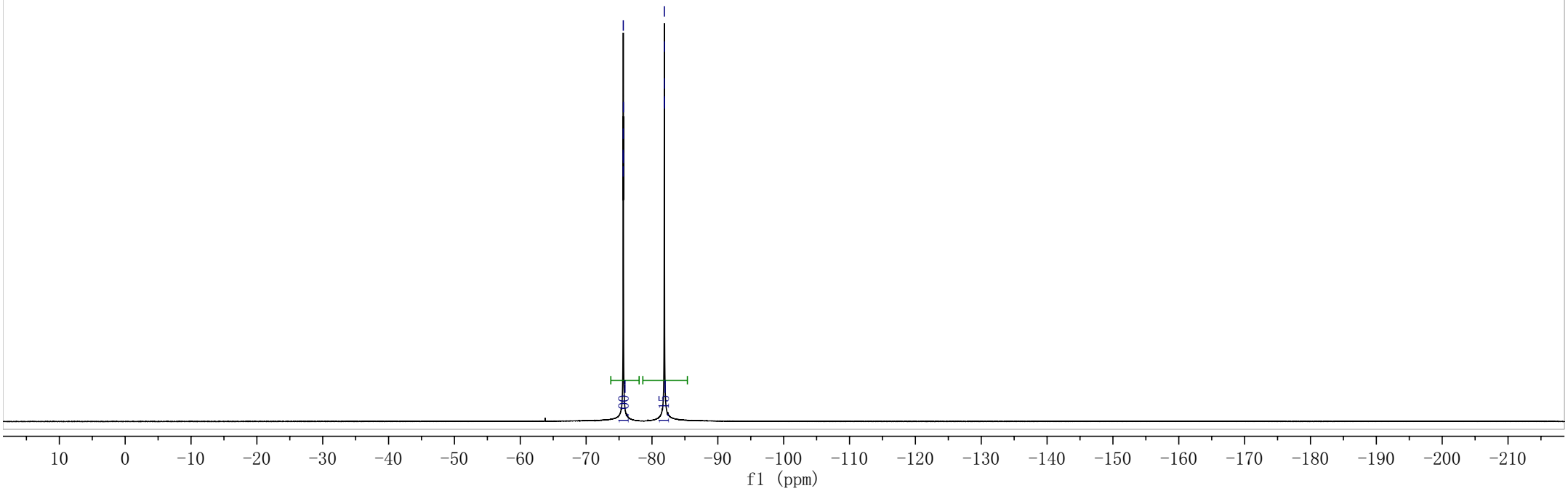
3aa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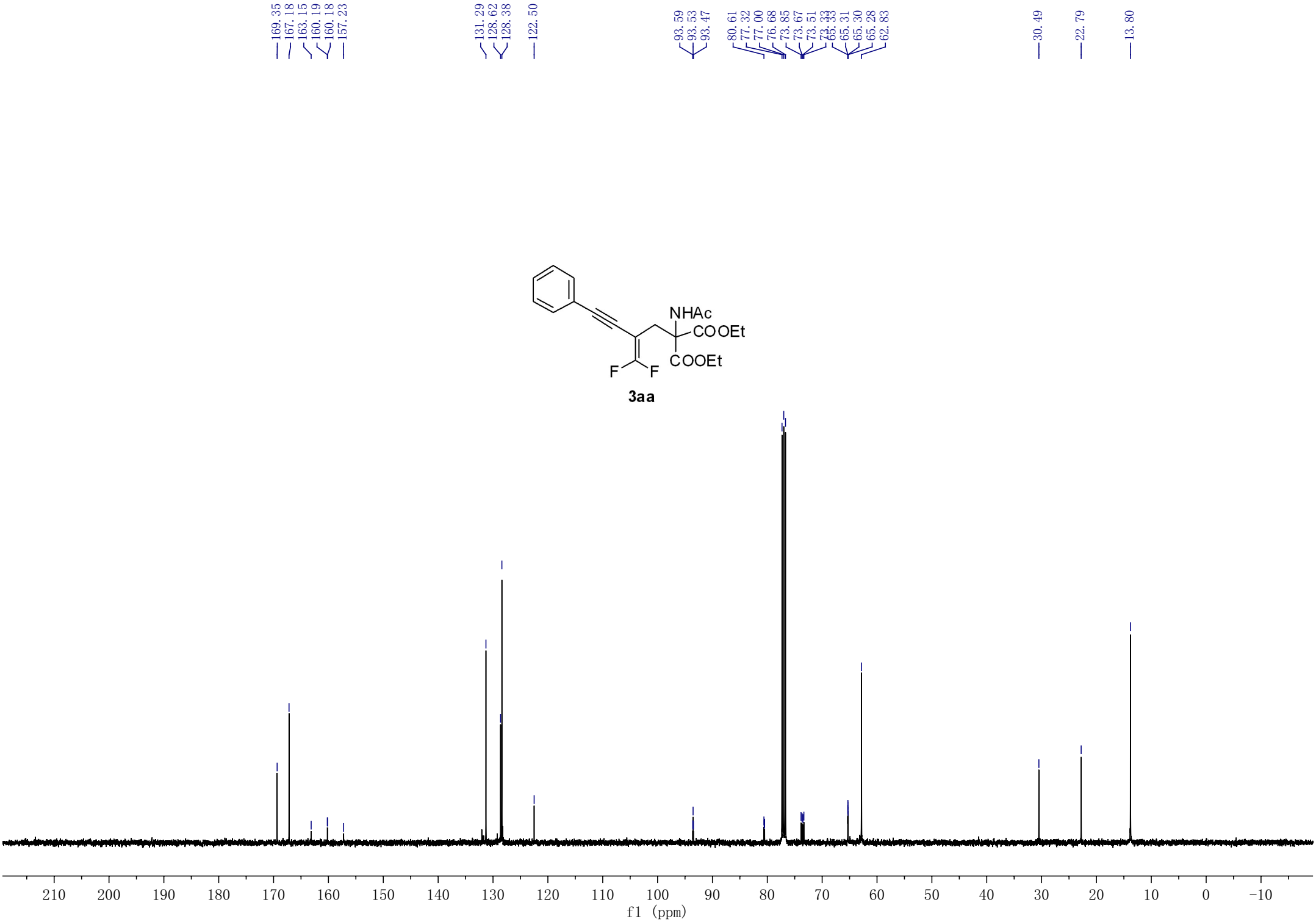
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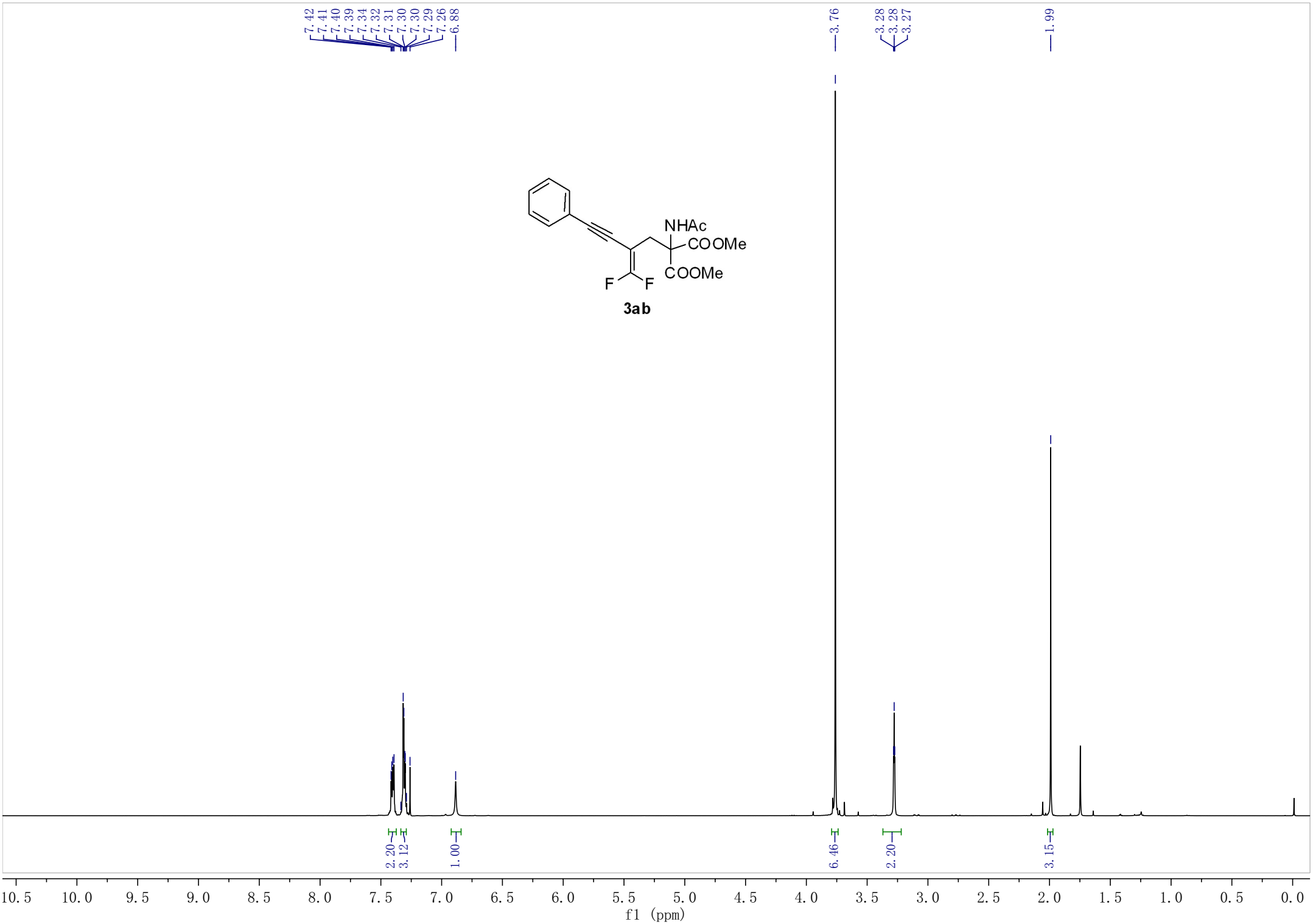
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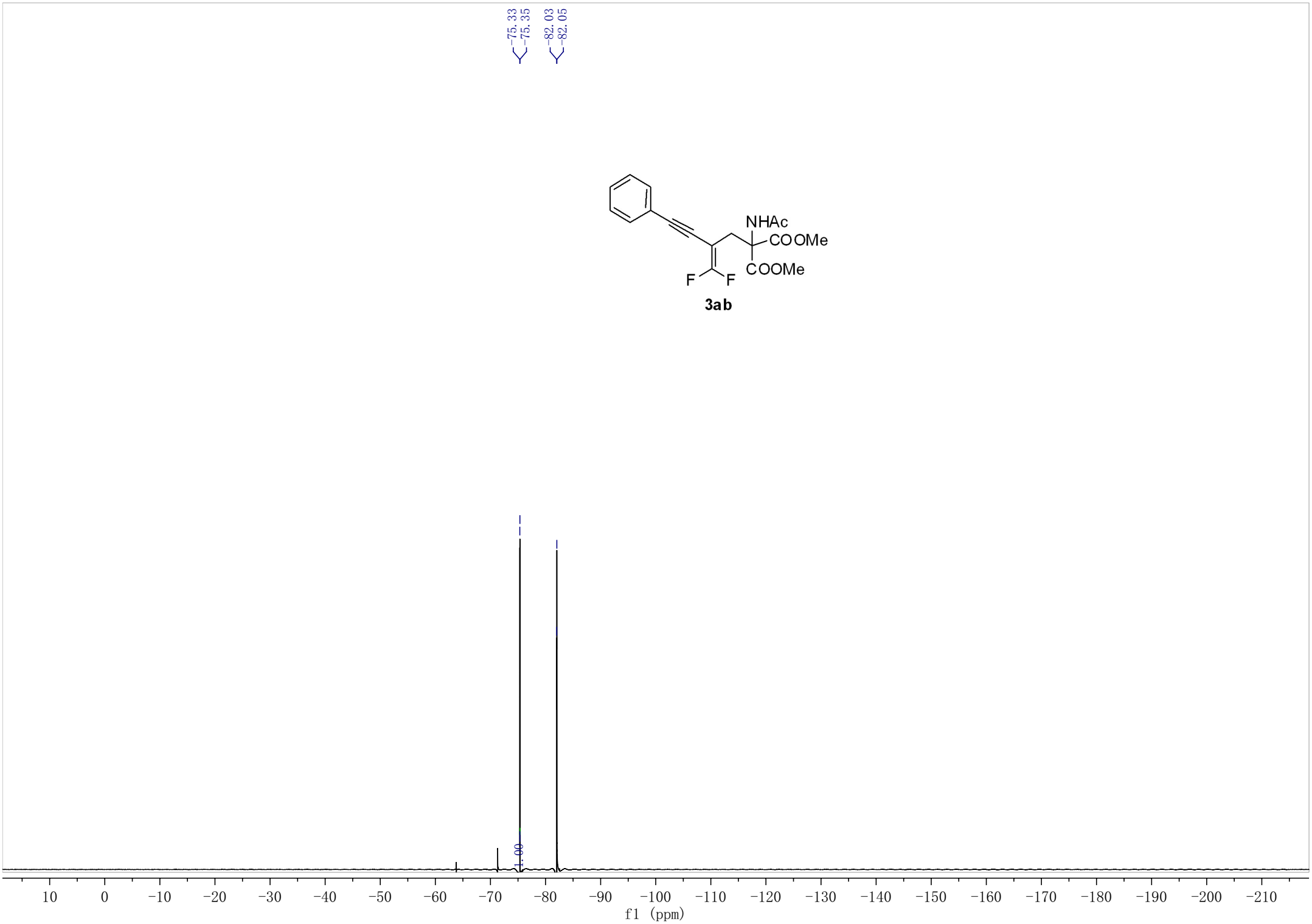
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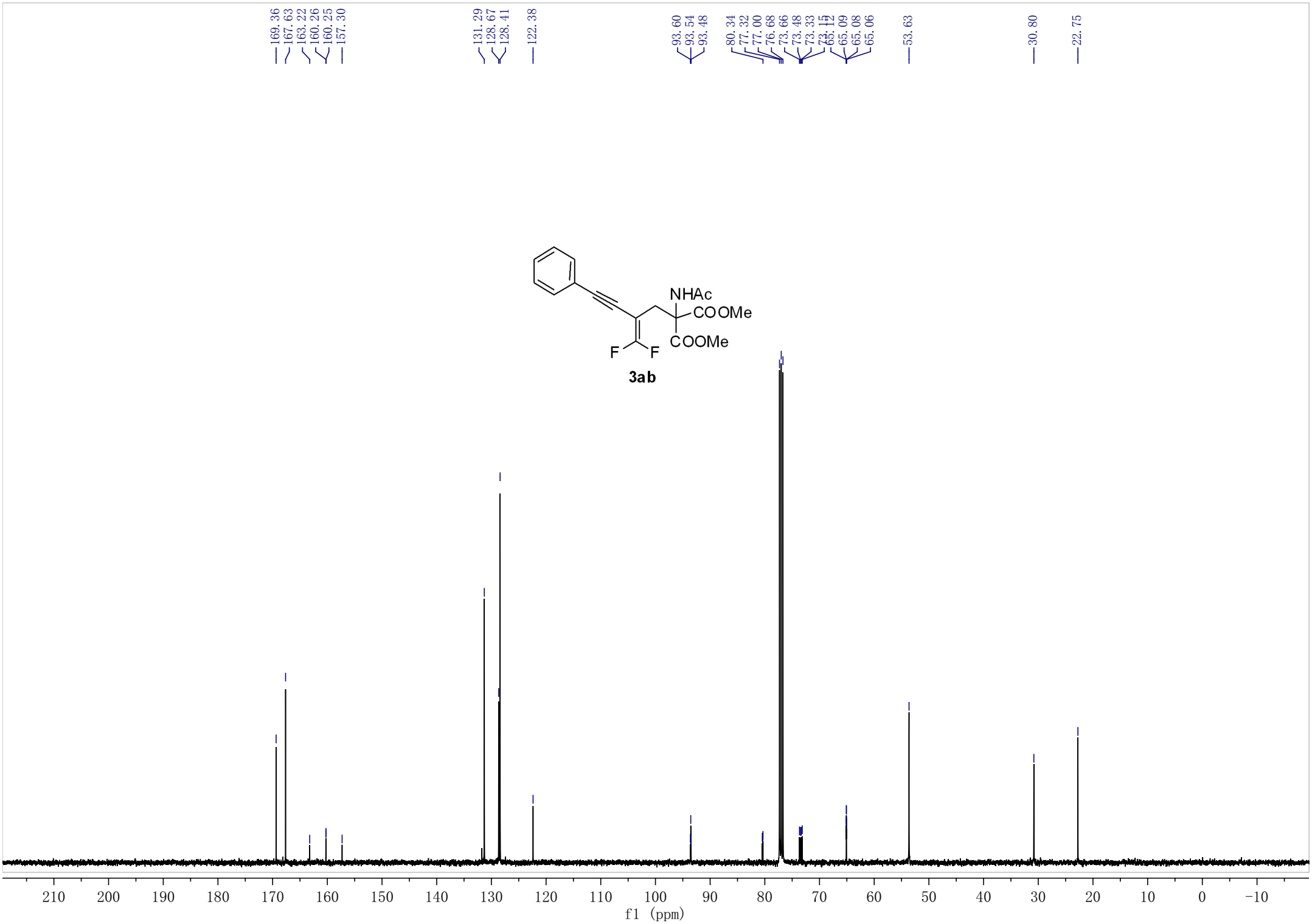
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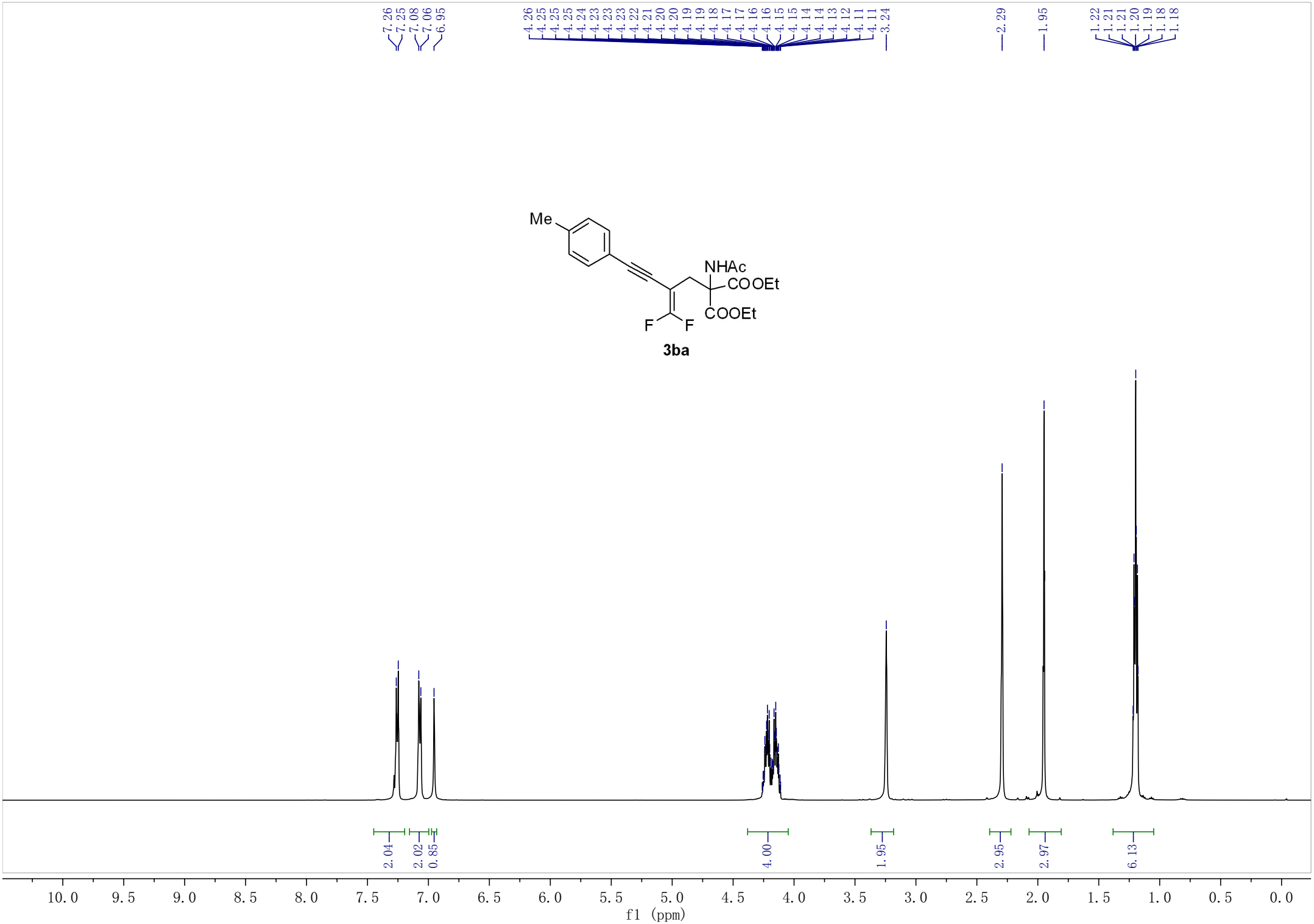
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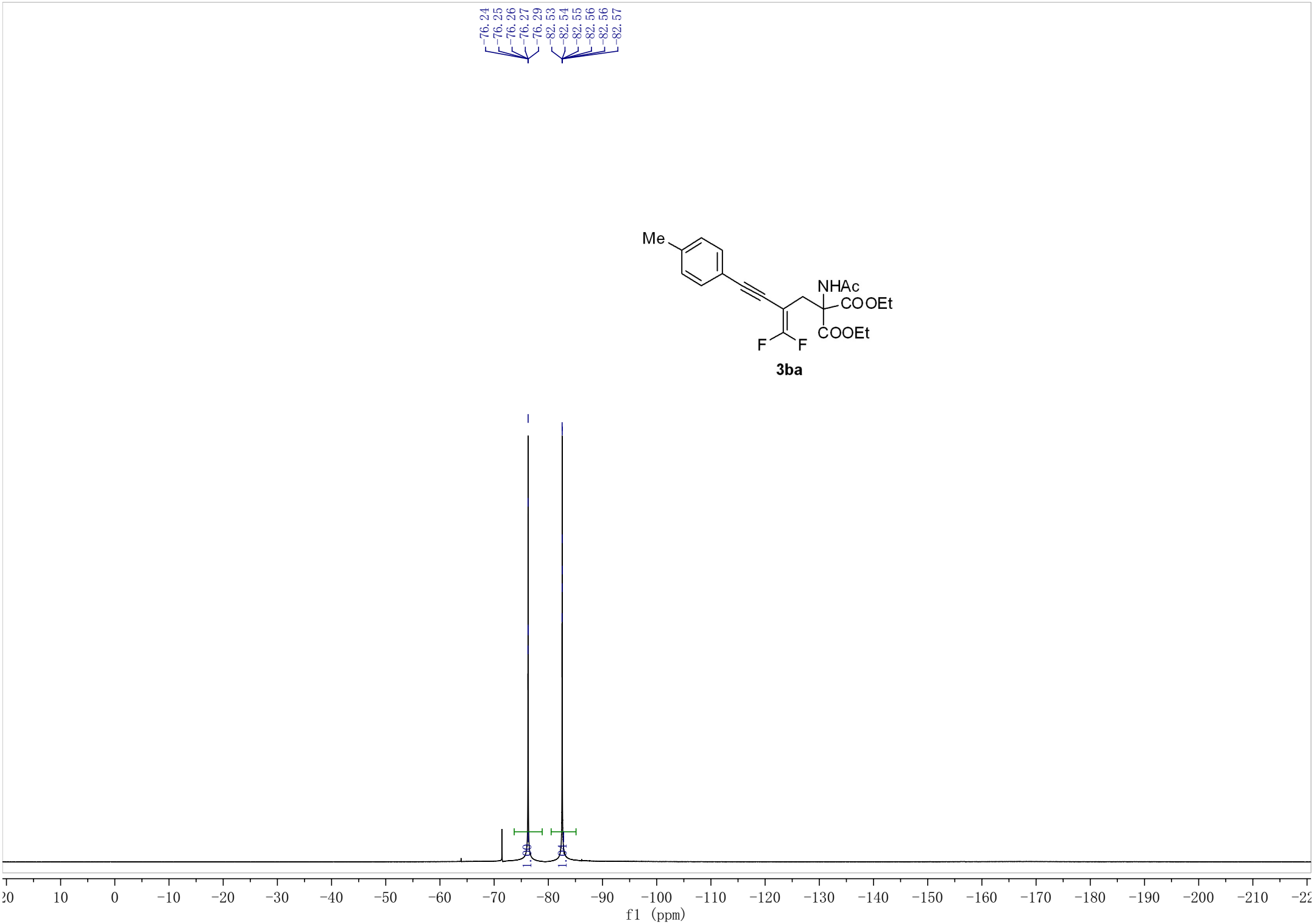
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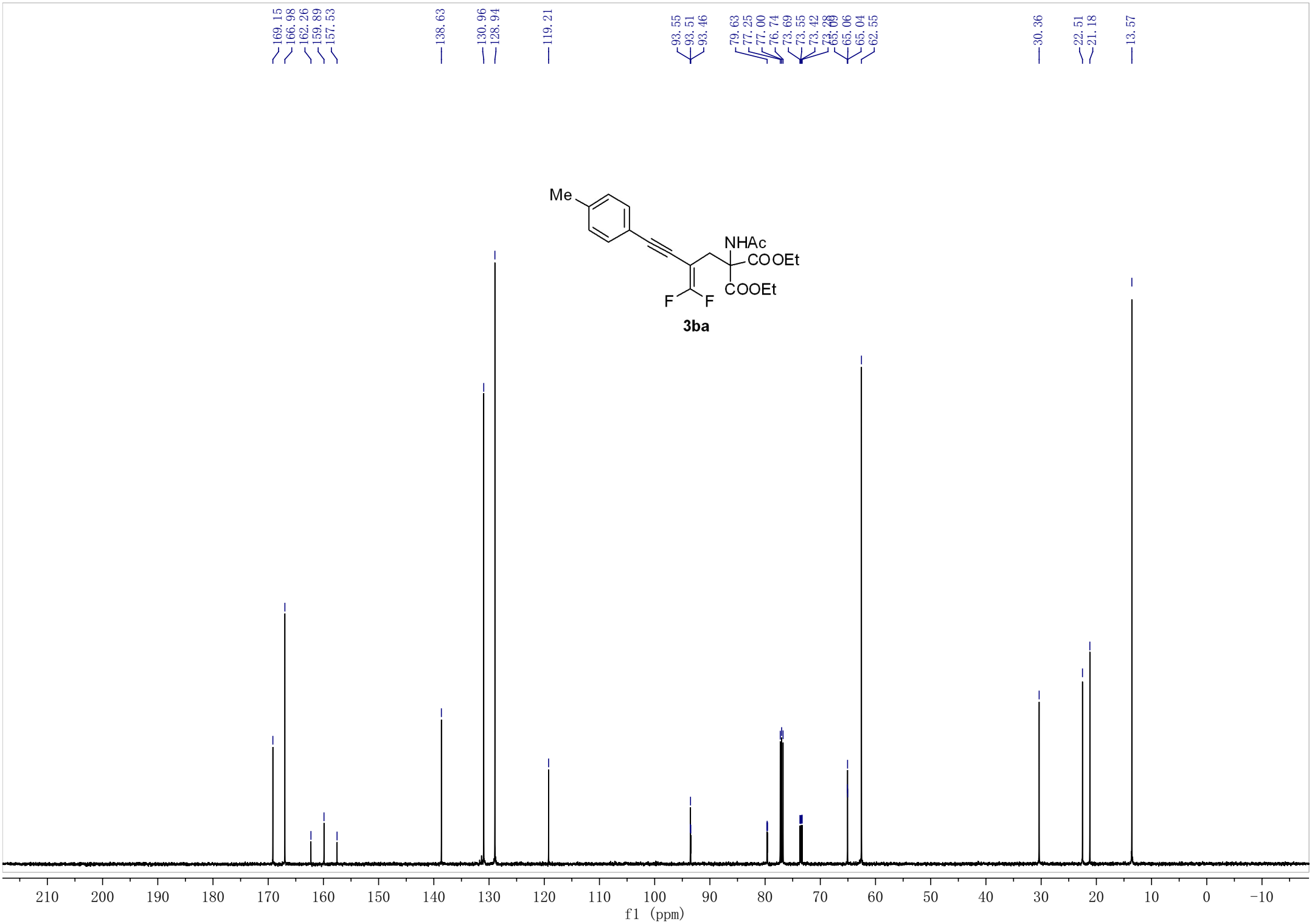
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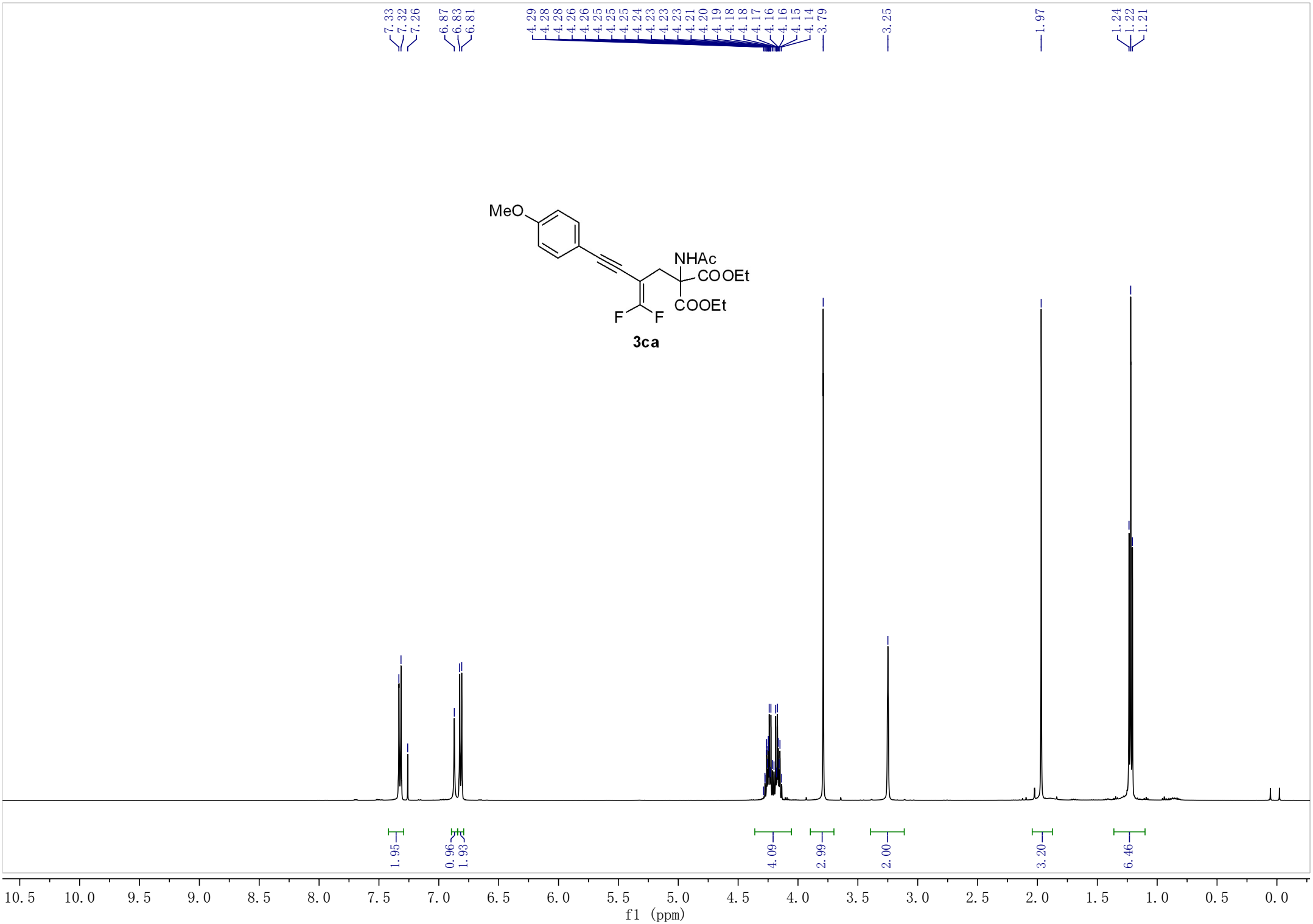
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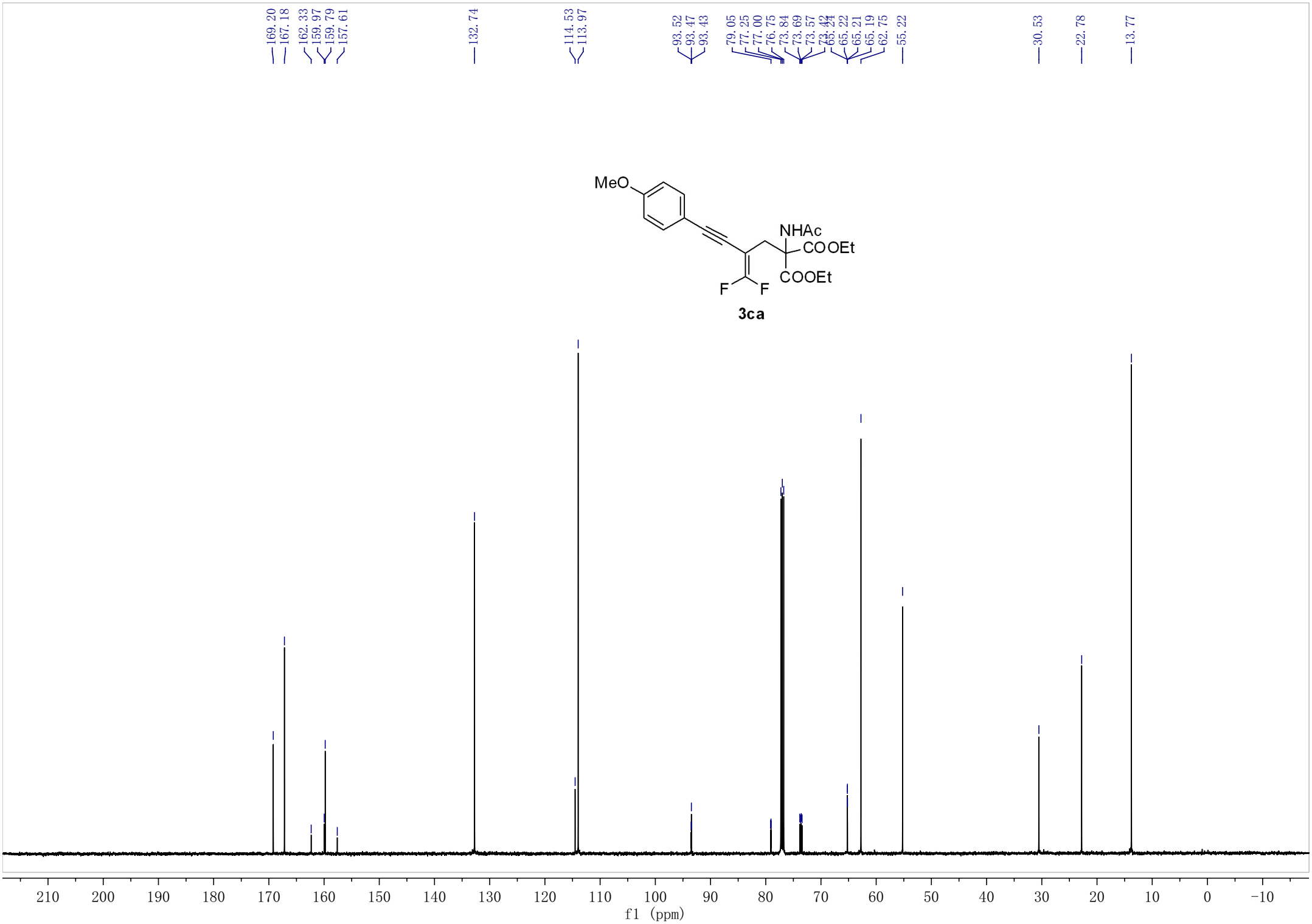
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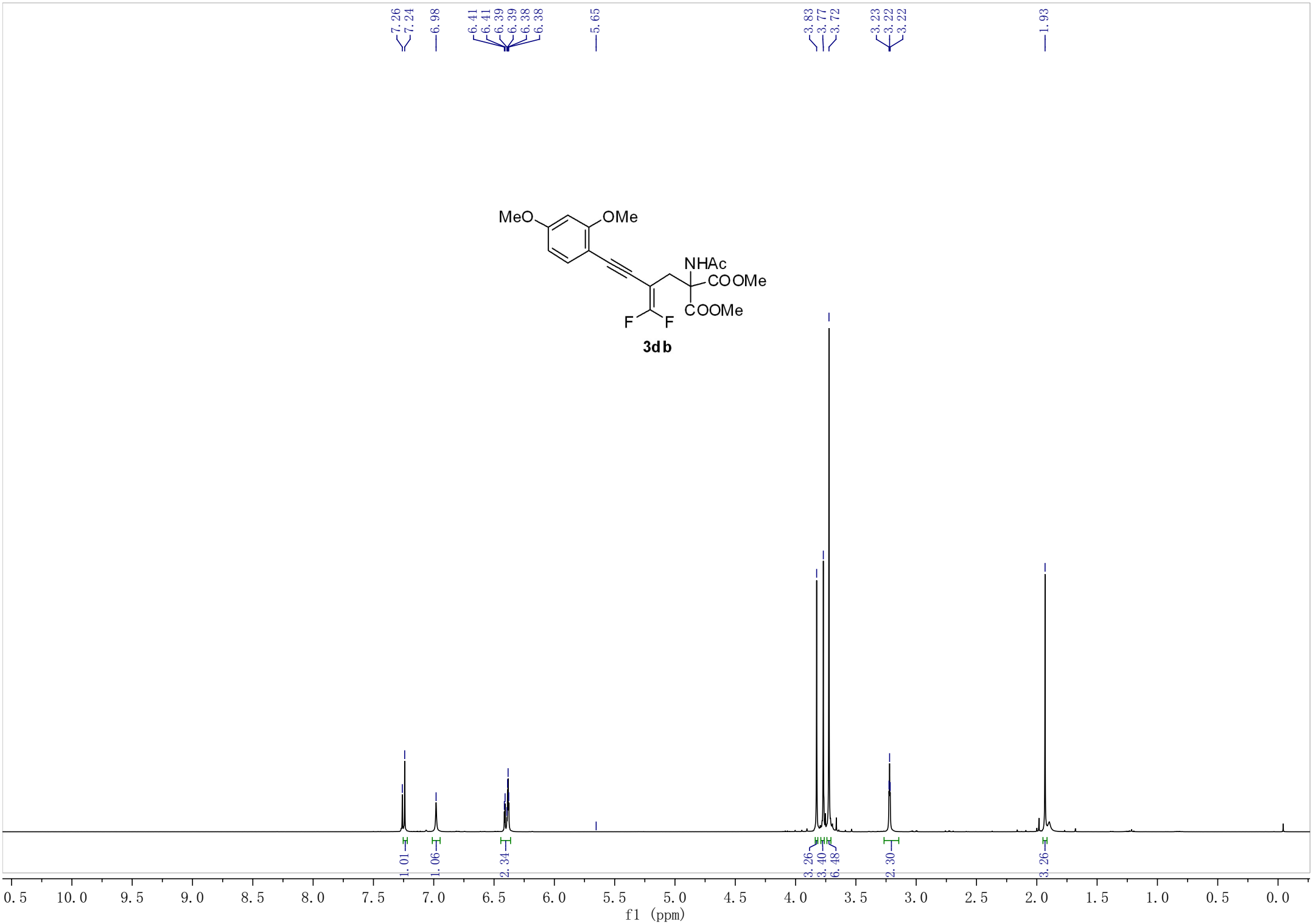
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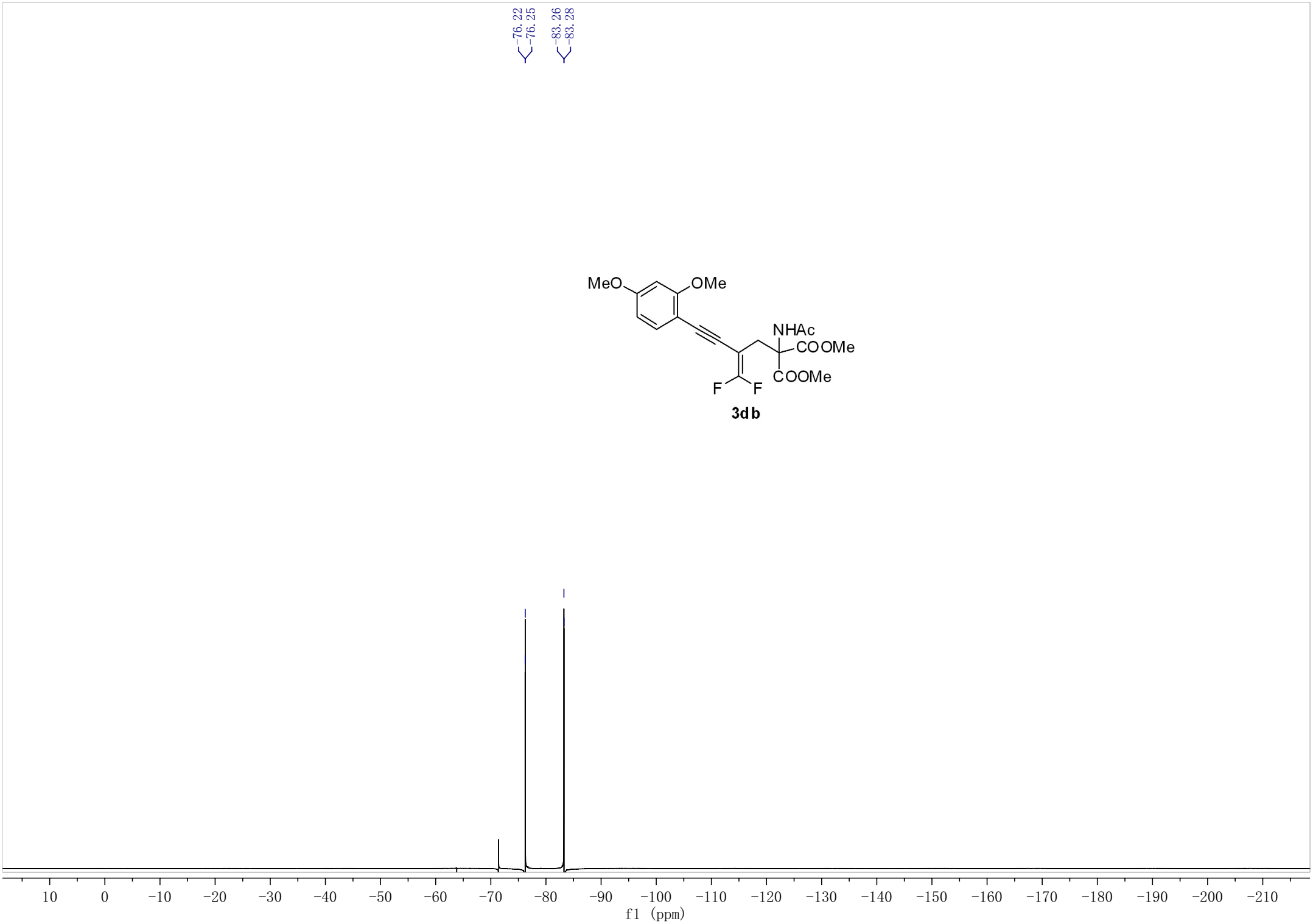
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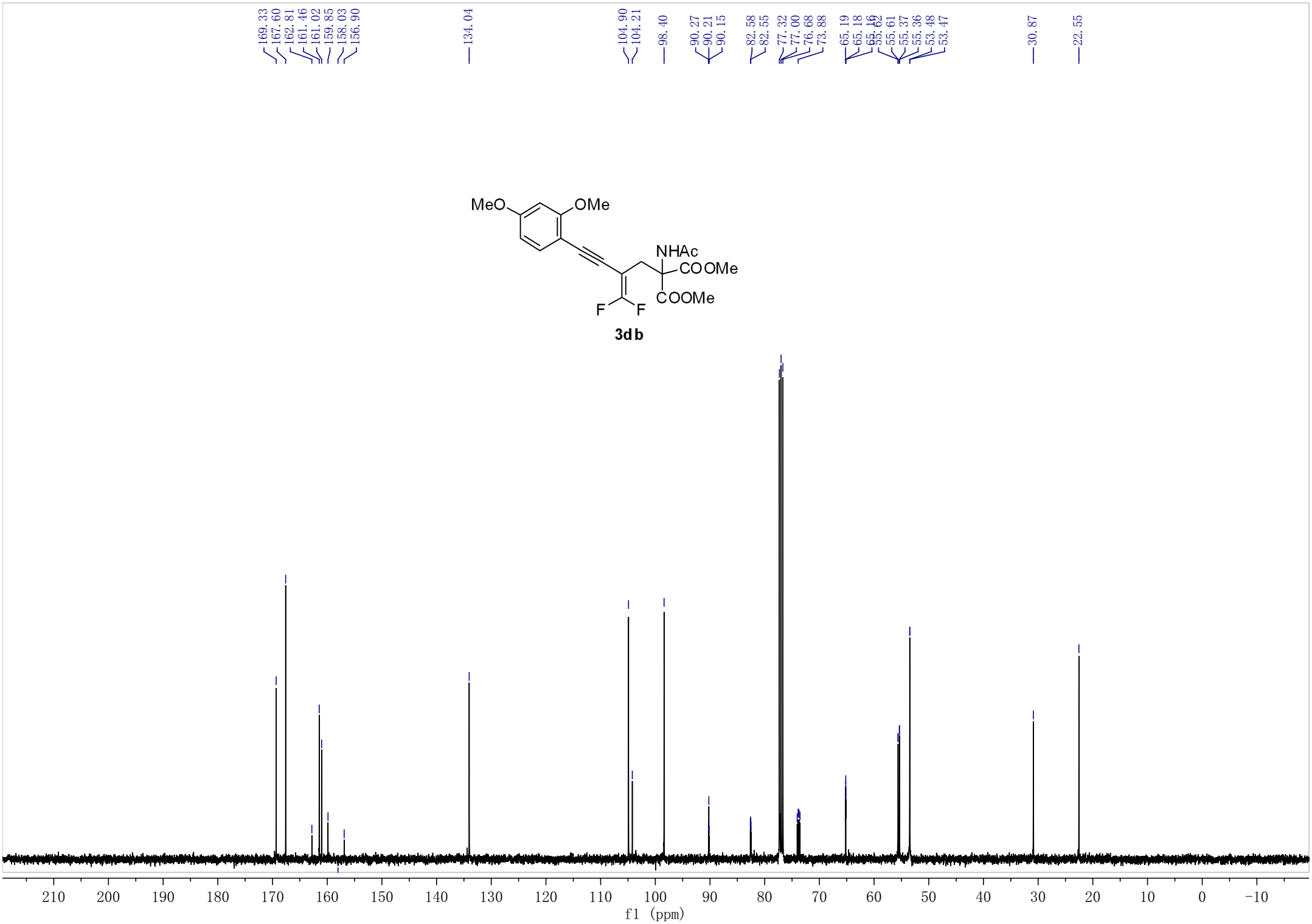
f1 (ppm)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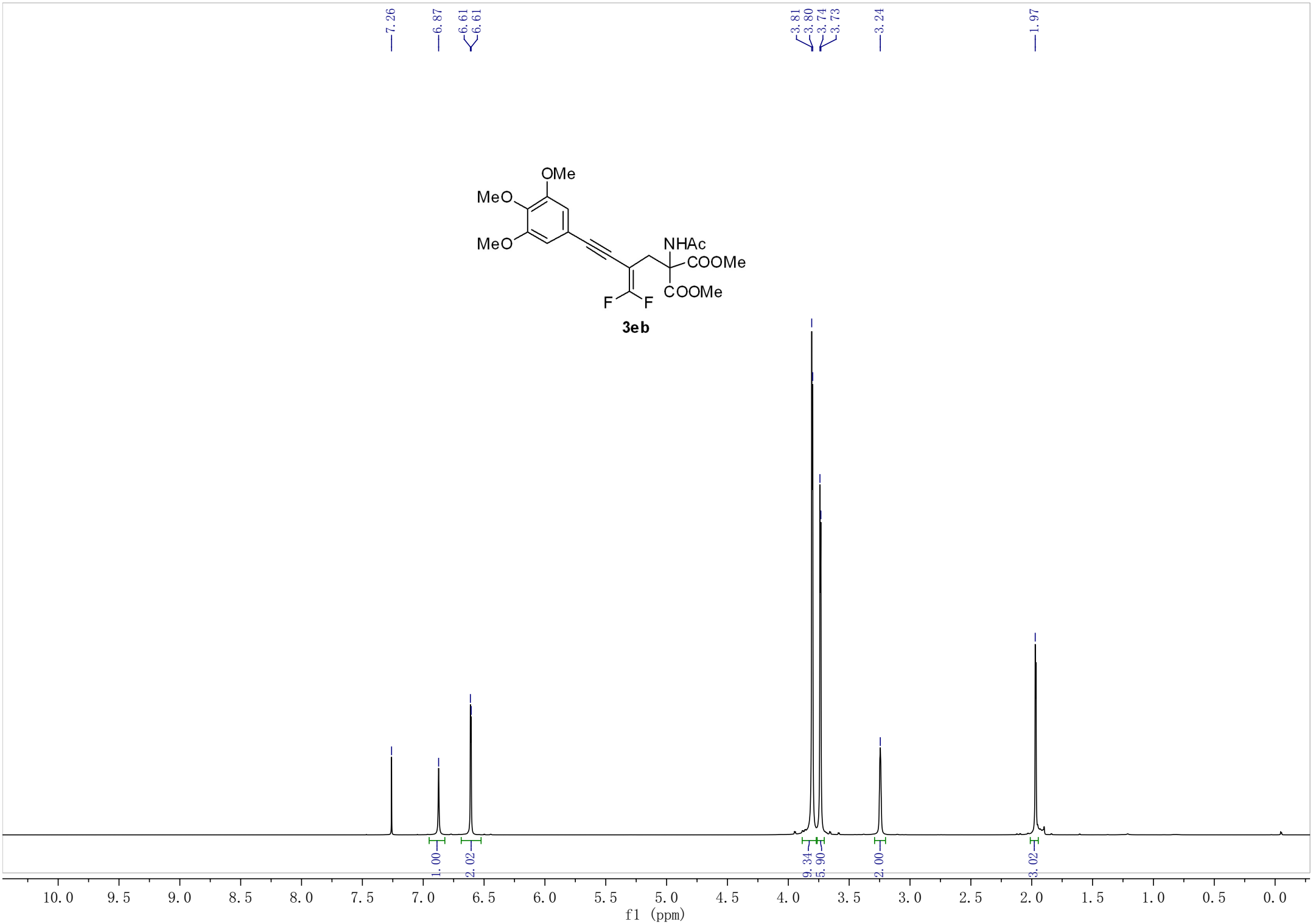
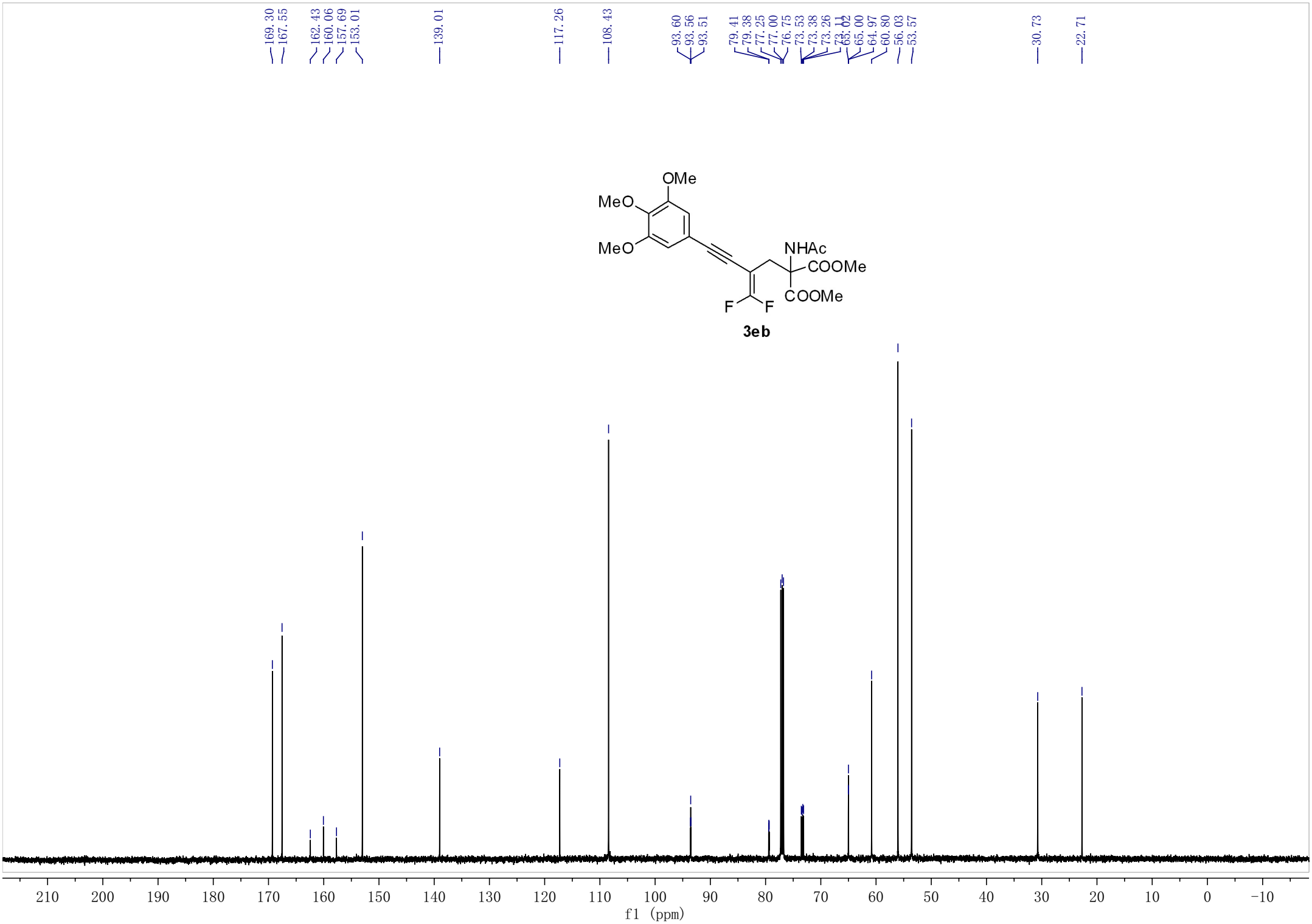
f1 (ppm)


7.26
6.87
6.61
6.61
3.81
3.80
3.74
3.73
3.24
1.97
OMe
MeO
MeO
NHAc
COOMe
COOMe
F
F
3eb
1.00
2.02
9.34
5.90
2.00
3.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-75.51
-75.52
-75.54
-75.55
-82.24
-82.26
-82.27
-82.29
OMe
MeO
MeO
NHAc
COOMe
COOMe
F
F
3eb
1.00
1.0
f1 (ppm)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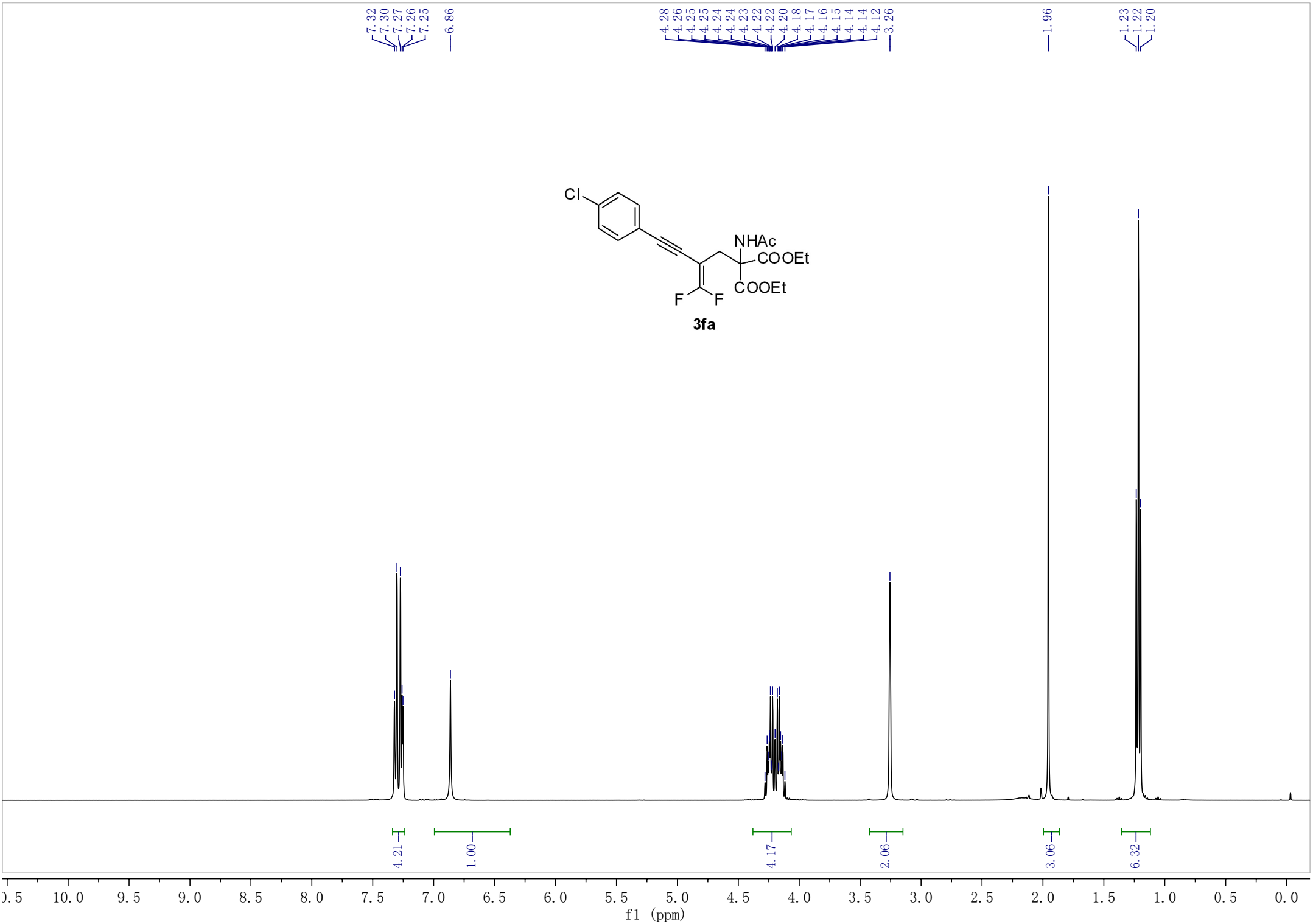
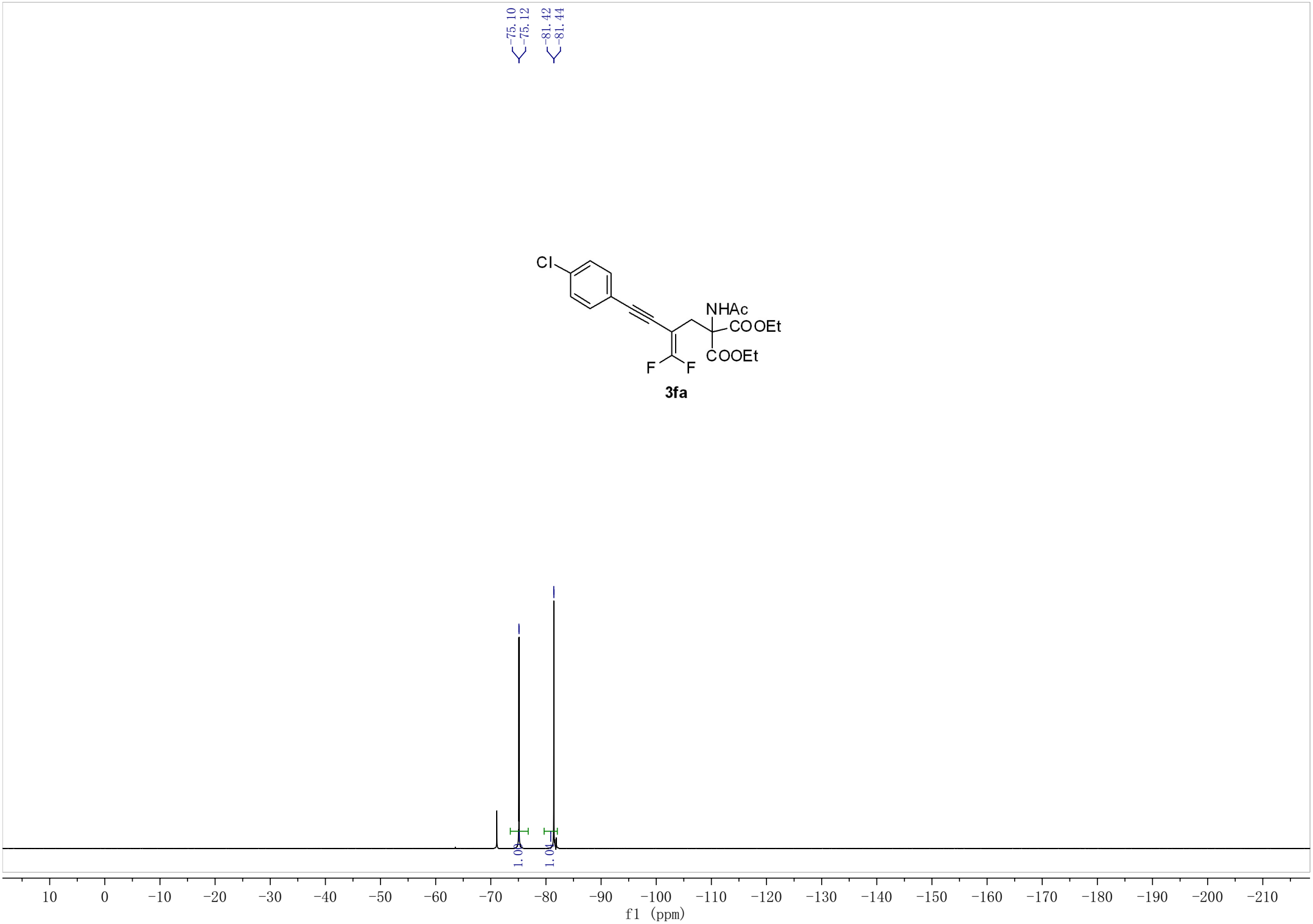
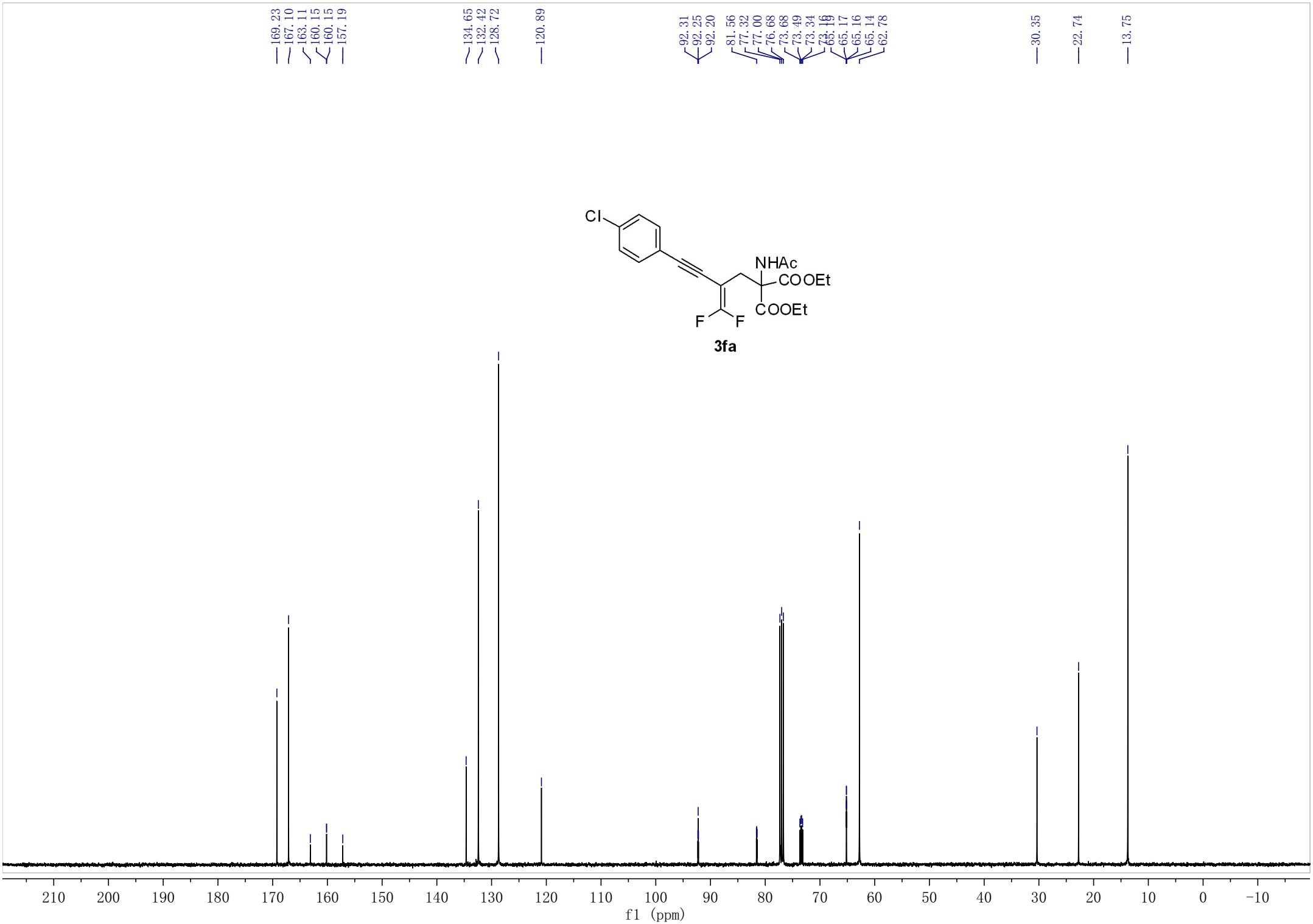
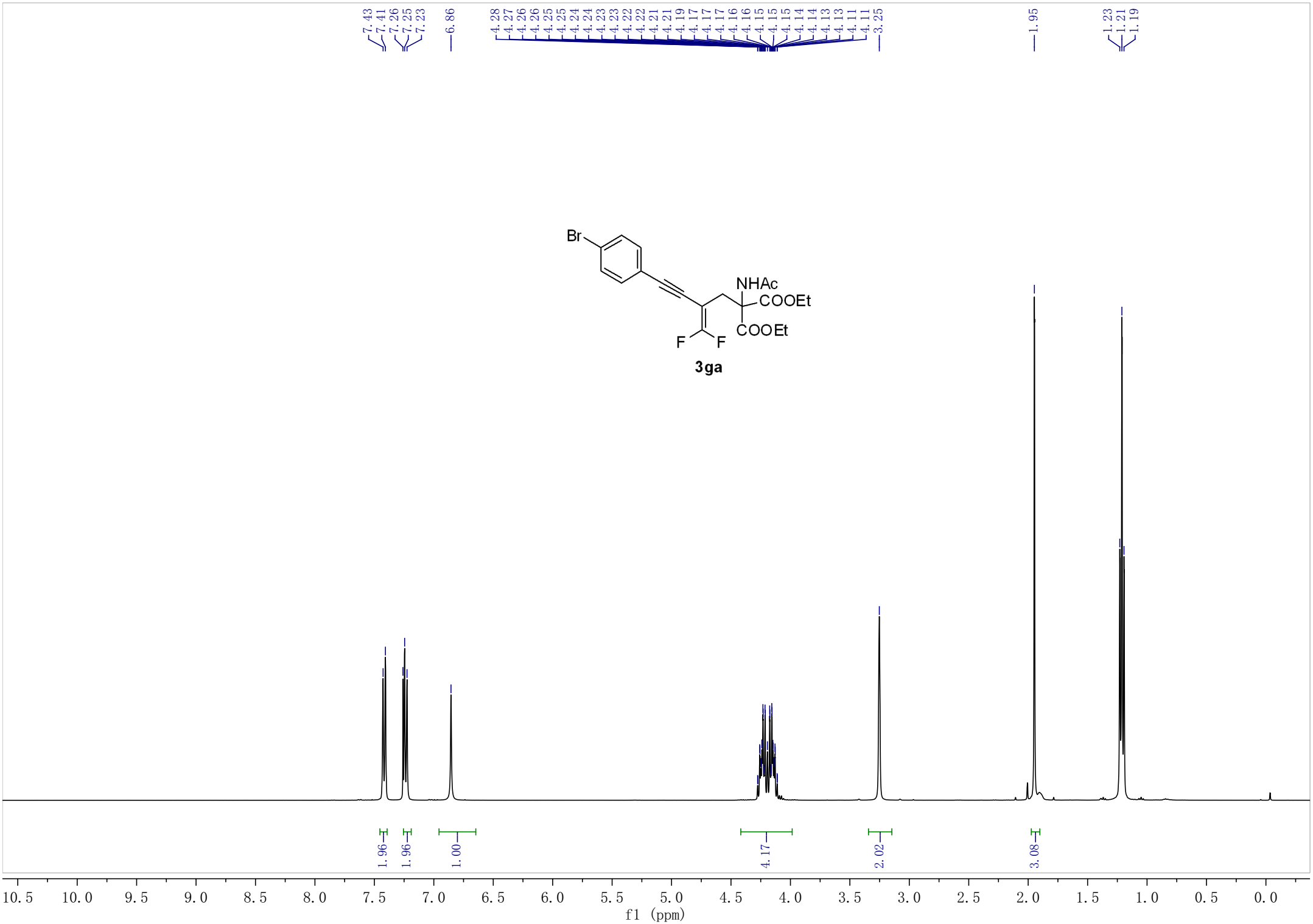
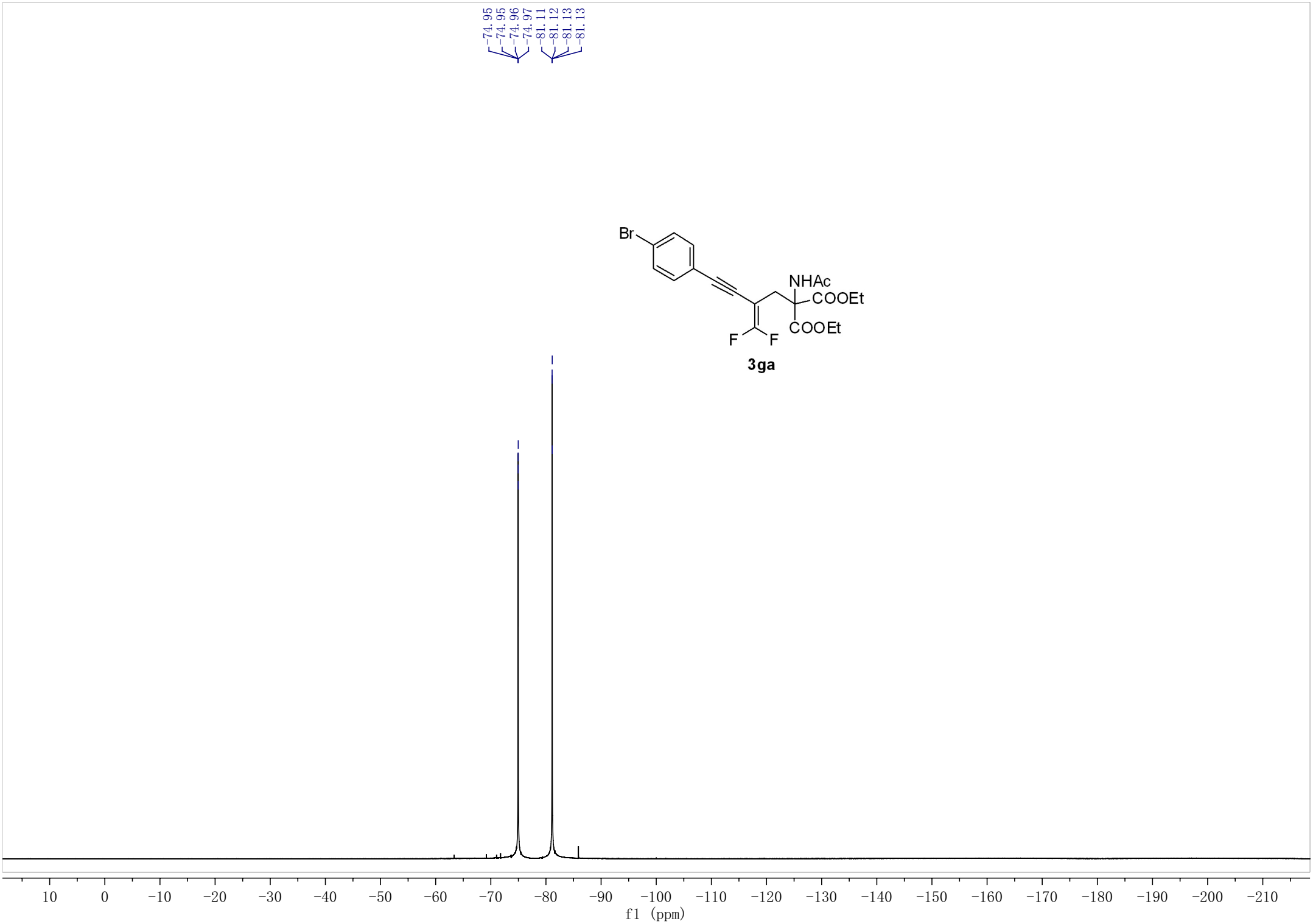
167.55
162.43
160.06
157.69
153.01
139.01
117.26
108.43
93.60
93.56
93.51
79.41
79.38
77.25
77.00
76.75
73.53
73.38
73.26
65.02
65.00
64.97
60.80
56.03
53.57
30.73
22.71
OMe
MeO
MeO
NHAc
COOMe
COOMe
F
F
3eb
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

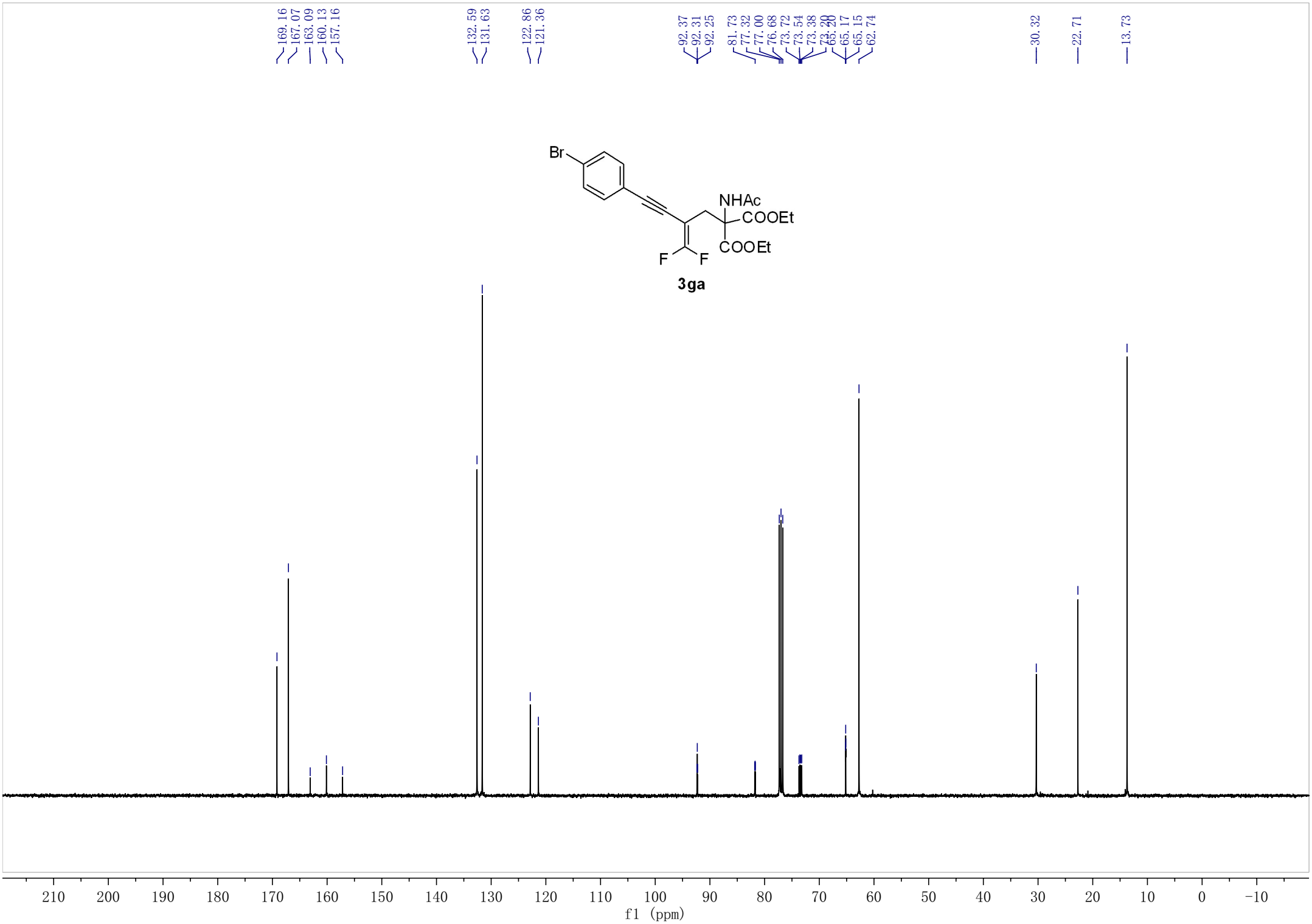

7.32
7.30
7.27
7.26
7.25
6.86
4.28
4.26
4.25
4.25
4.24
4.24
4.23
4.22
4.22
4.20
4.18
4.17
4.16
4.15
4.14
4.14
4.12
3.26
1.96
1.23
1.22
1.20
Cl
NHAc
COOEt
COOEt
F
F
3fa
4.21
1.00
4.17
2.06
3.06
6.32
f1 (ppm)

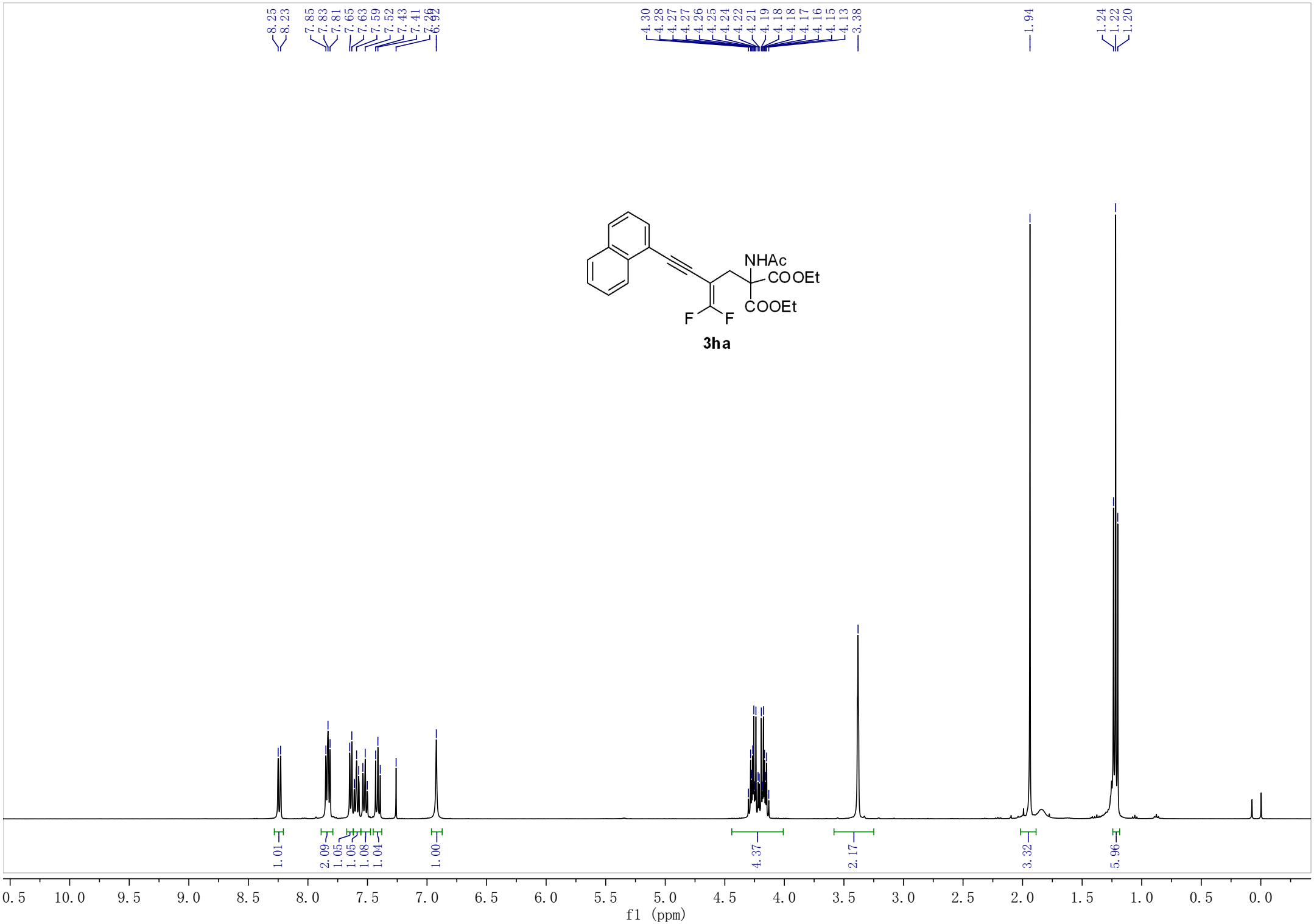

-75.10
-75.12
-81.42
-81.44
Cl
NHAc
COOEt
COOEt
F
F
3fa
1.00
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


169.23
167.10
163.11
160.15
160.15
157.19
134.65
132.42
128.72
120.89
92.31
92.25
92.20
81.56
77.32
77.00
76.68
73.68
73.49
73.34
65.17
65.16
65.14
62.78
30.35
22.74
13.75
Cl
NHAc
COOEt
COOEt
F
F
3fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.43
7.41
7.26
7.25
7.23
6.86
4.28
4.27
4.26
4.26
4.25
4.25
4.24
4.24
4.23
4.23
4.22
4.22
4.21
4.21
4.19
4.17
4.17
4.17
4.16
4.16
4.15
4.15
4.15
4.14
4.14
4.13
4.13
4.11
4.11
3.25
1.95
1.23
1.21
1.19
Br
NHAc
COOEt
COOEt
F
F
3ga
1.96
1.96
1.00
4.17
2.02
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)


-74.95
-74.95
-74.96
-74.97
-81.11
-81.12
-81.13
-81.13
Br
NHAc
COOEt
COOEt
F
F
3ga
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)


169.16
167.07
163.09
160.13
157.16
132.59
131.63
122.86
121.36
92.37
92.31
92.25
81.73
77.32
77.00
76.68
73.72
73.54
73.38
73.20
65.17
65.15
62.74
30.32
22.71
13.73
Br
NHAc
COOEt
COOEt
F
F
3ga
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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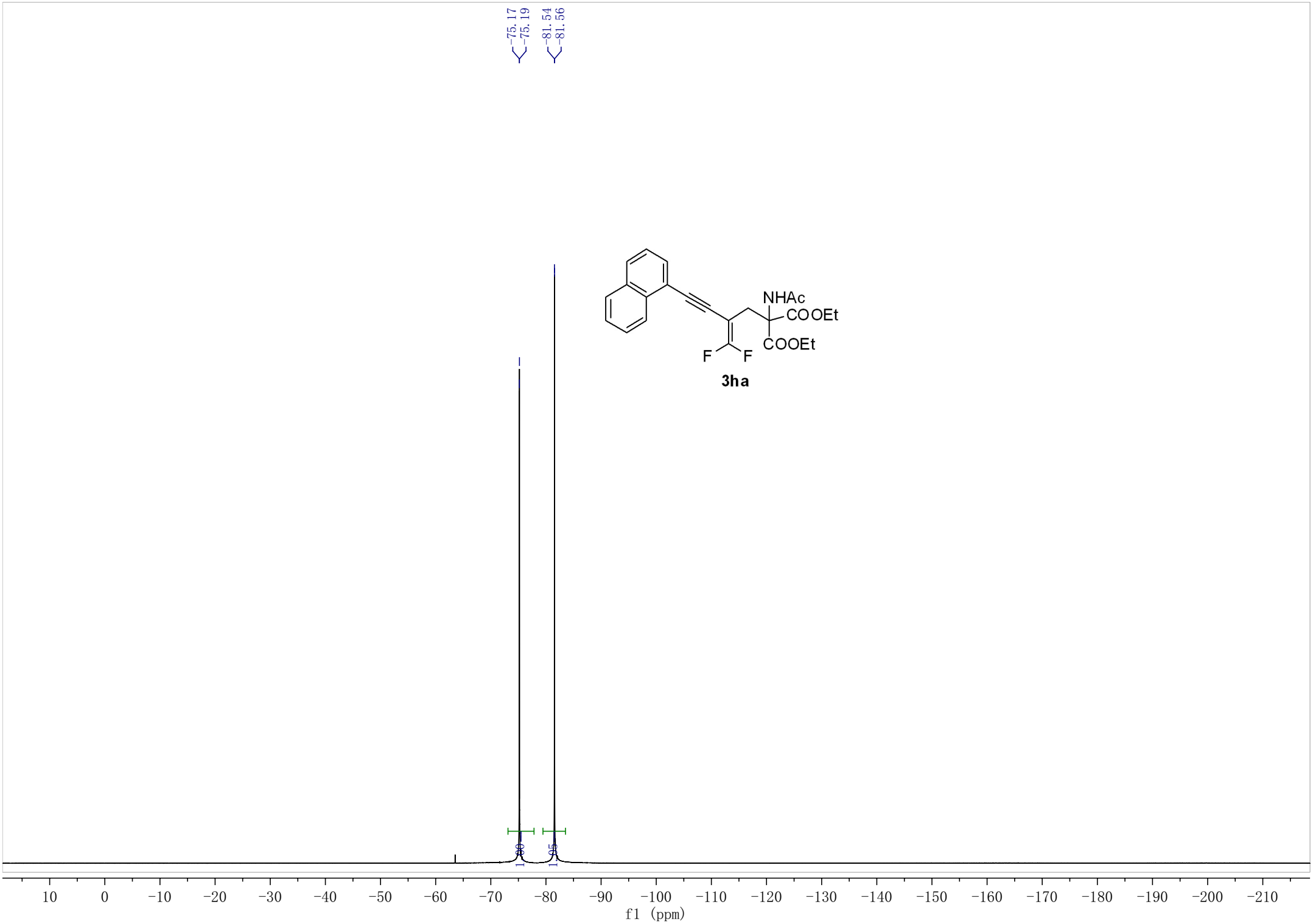
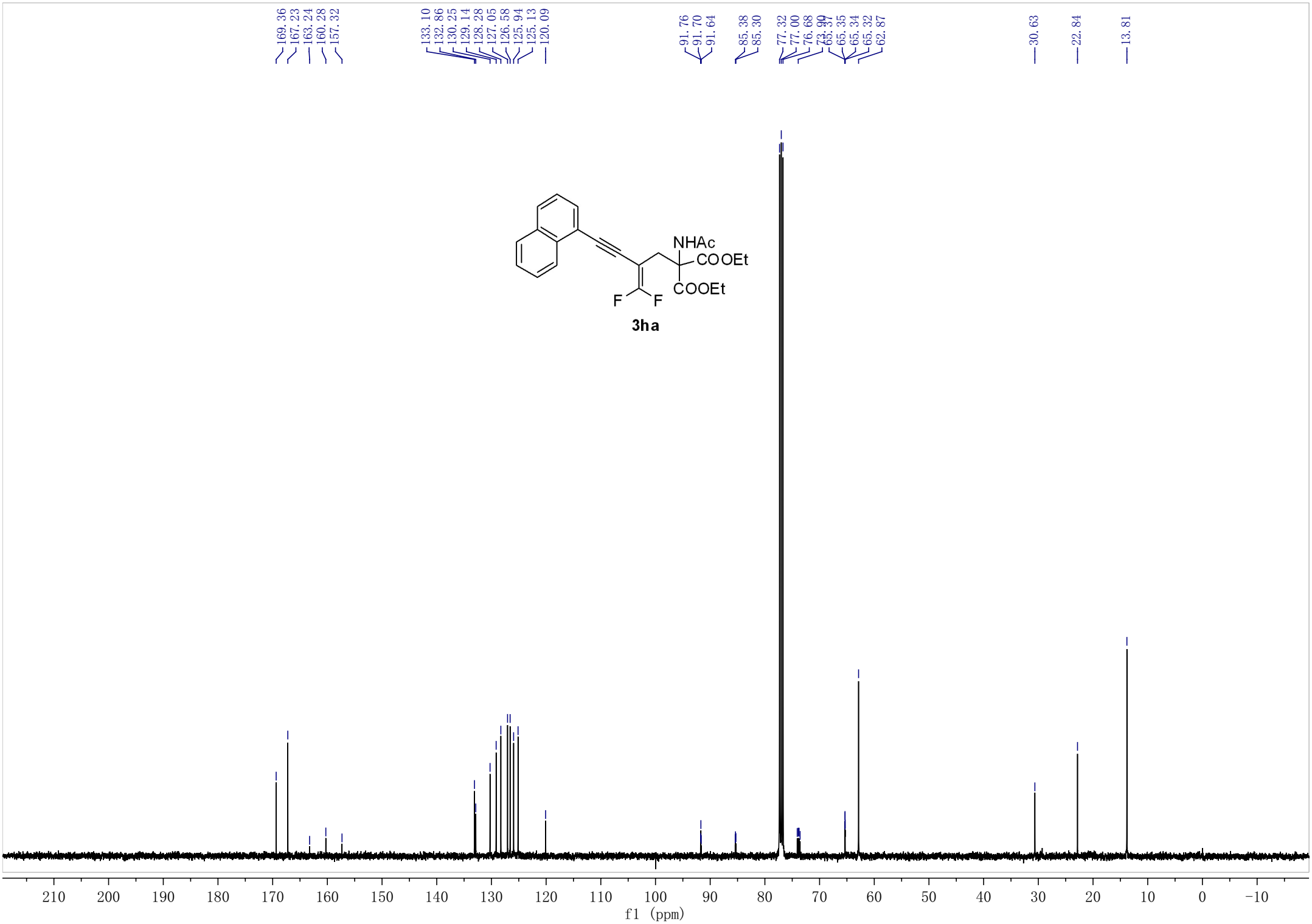
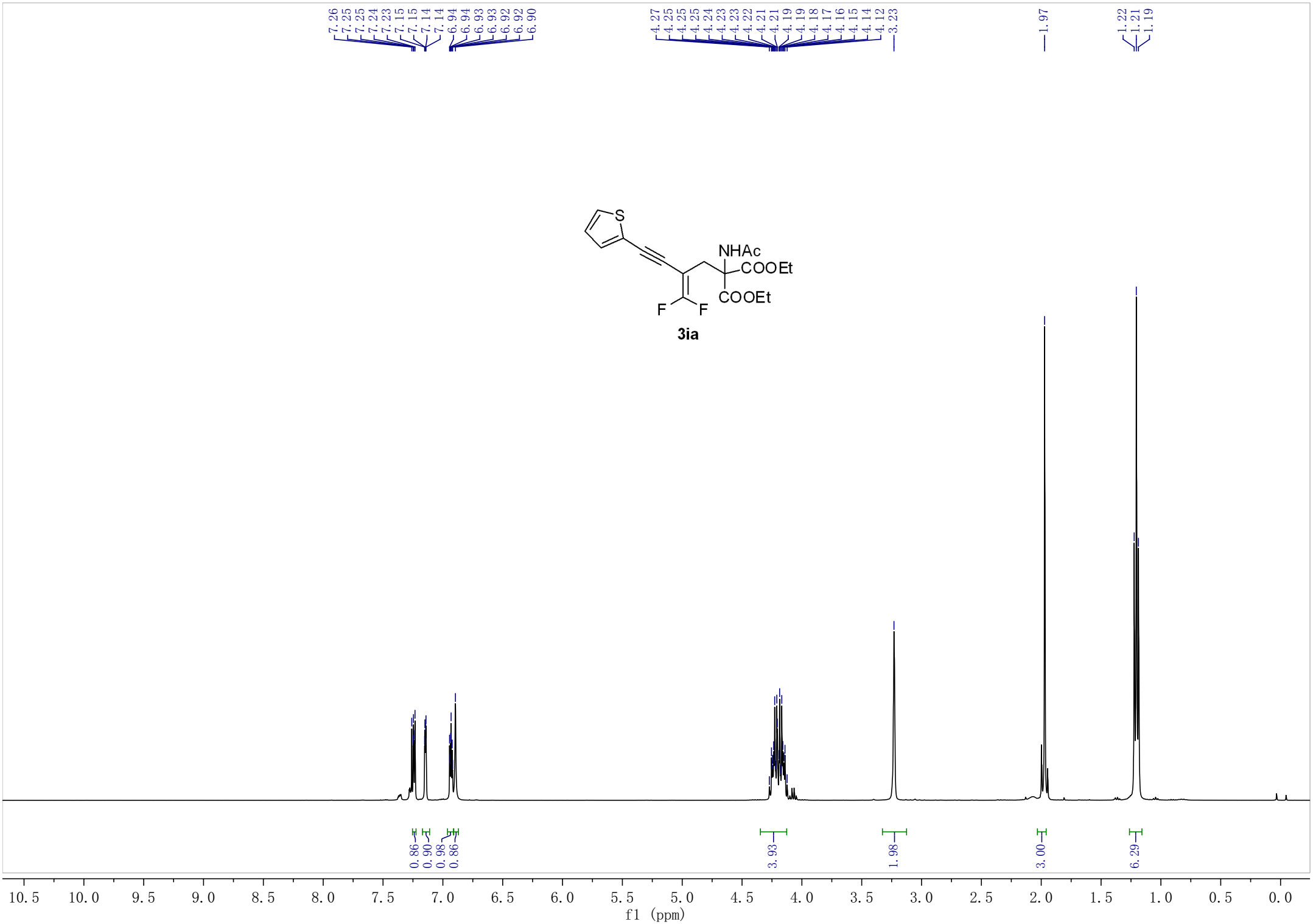
8.23
7.85
7.83
7.81
7.65
7.63
7.59
7.52
7.43
7.41
6.92
4.30
4.28
4.27
4.27
4.26
4.25
4.24
4.22
4.21
4.19
4.18
4.18
4.17
4.16
4.15
4.13
3.38
1.94
1.24
1.22
1.20
NHAc
COOEt
COOEt
F
F
3ha
1.01
2.09
1.05
1.05
1.08
1.04
1.00
4.37
2.17
3.32
5.96
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-75.17
-75.19
-81.54
-81.56
NHAc
COOEt
COOEt
F
F
3ha
1.00
1.05
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)


169.36
167.23
163.24
160.28
157.32
133.10
132.86
130.25
129.14
128.28
127.05
126.58
125.94
125.13
120.09
91.76
91.70
91.64
85.38
85.30
77.32
77.00
76.68
65.37
65.35
65.34
65.32
62.87
30.63
22.84
13.81
NHAc
COOEt
COOEt
F
F
3ha
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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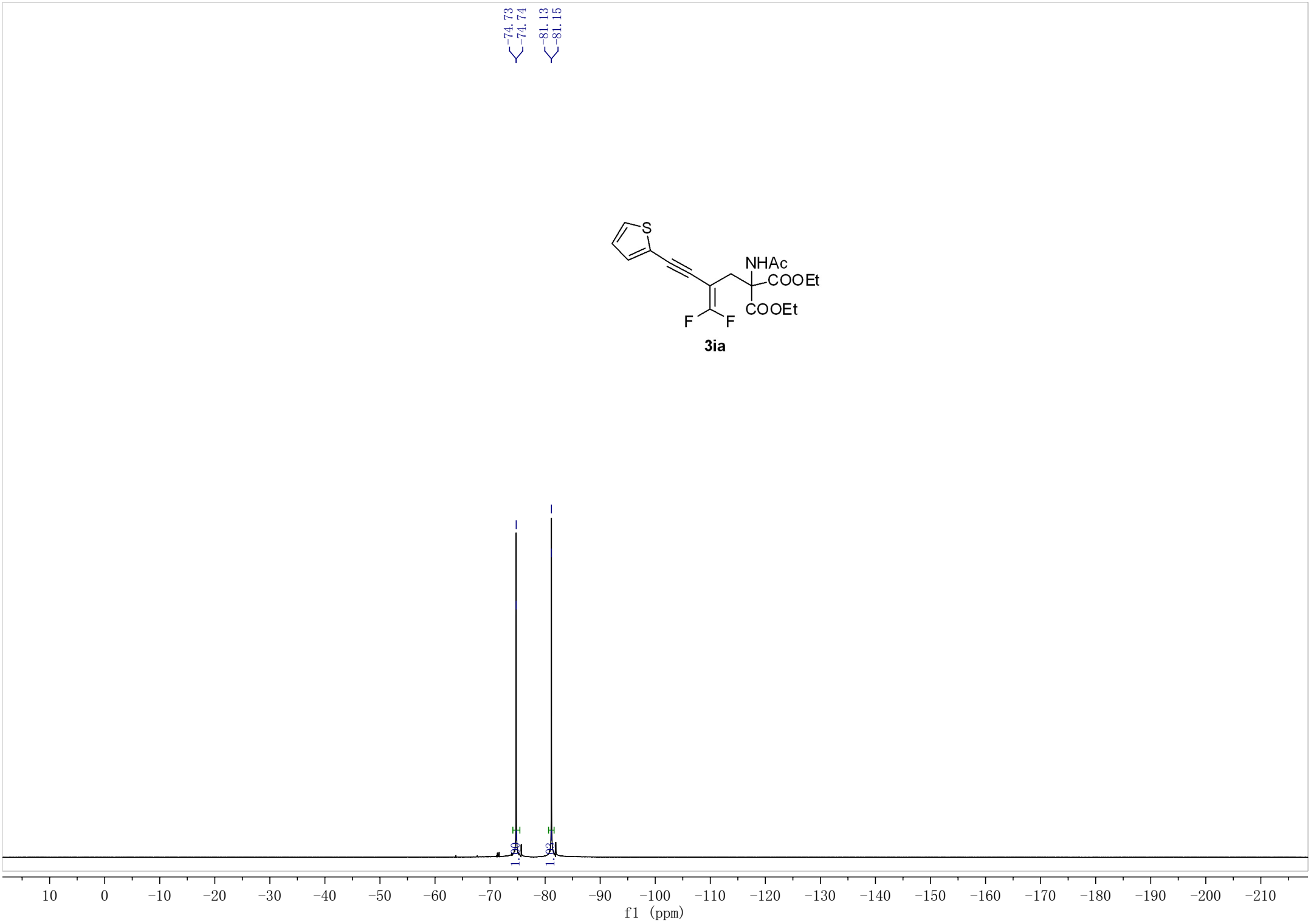
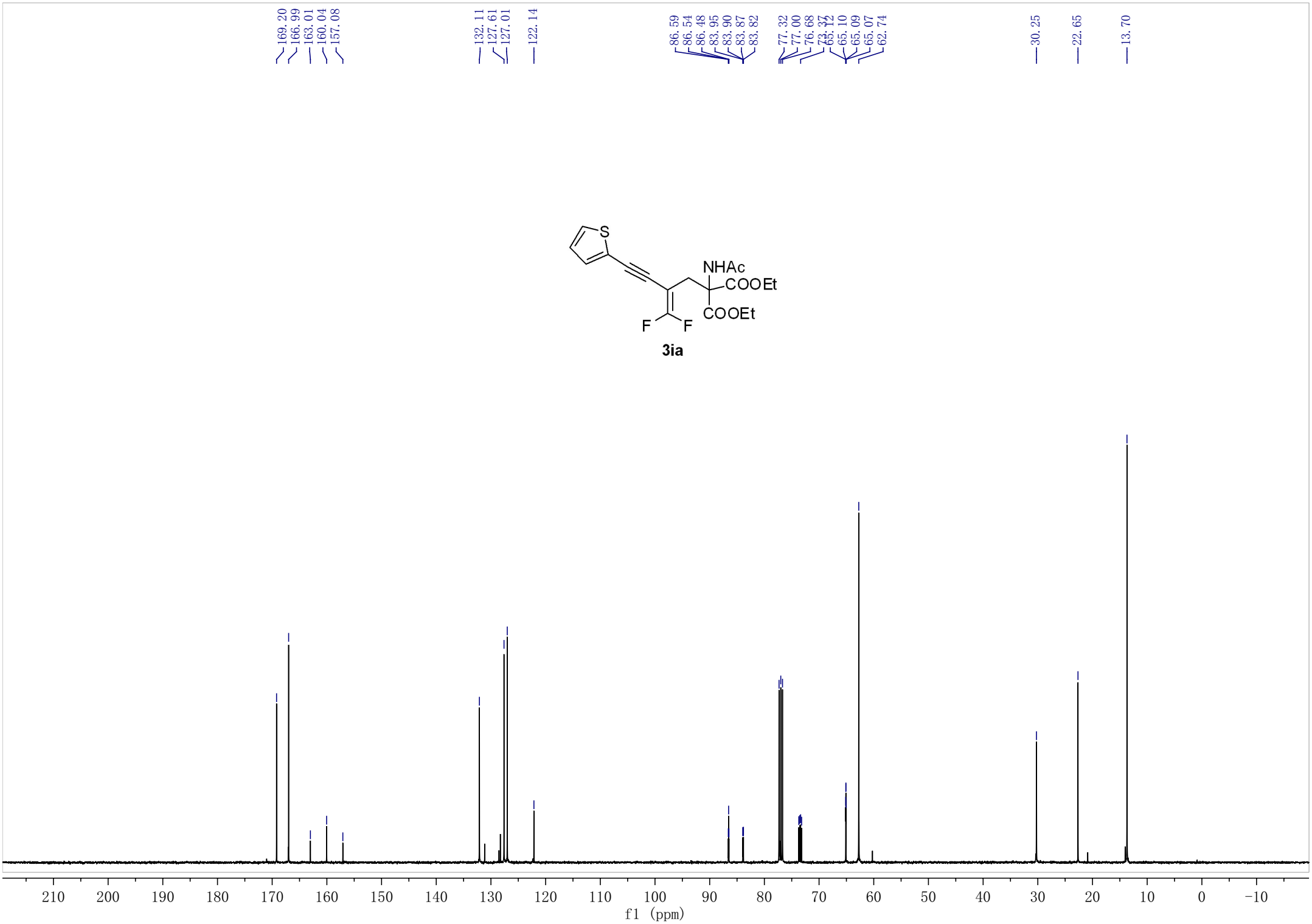
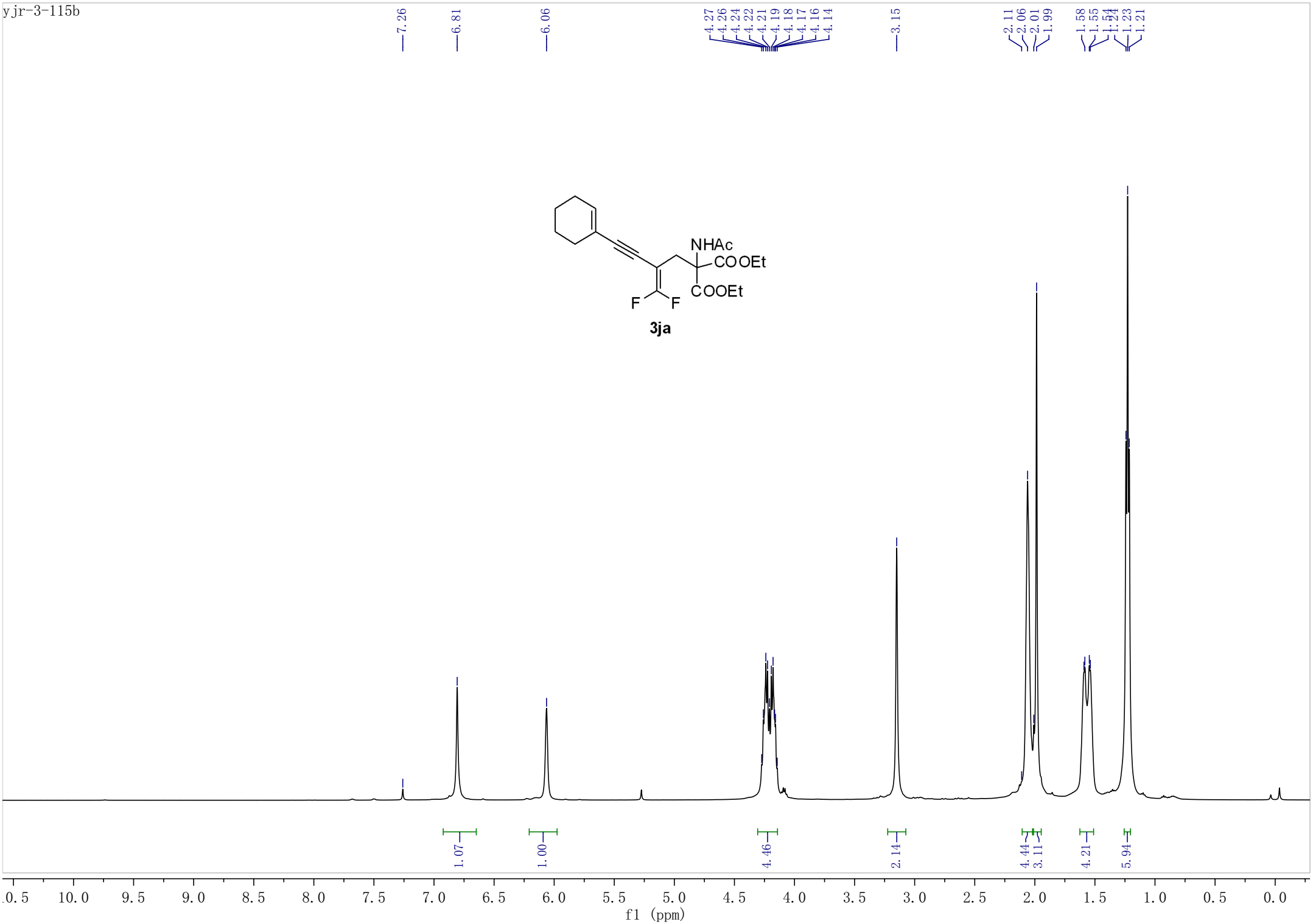
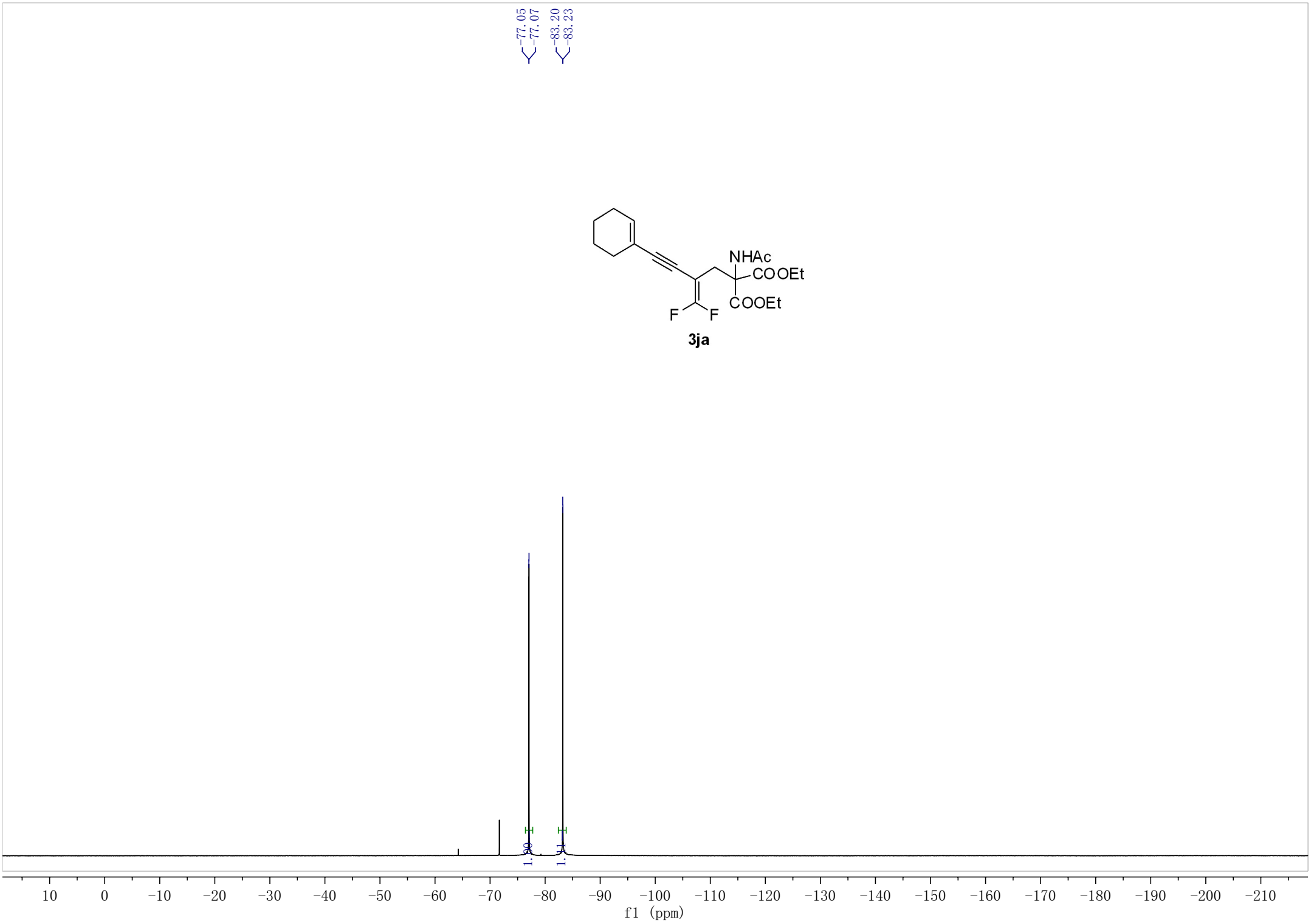
7.25
7.25
7.24
7.23
7.15
7.14
7.14
6.94
6.94
6.93
6.93
6.92
6.92
6.90
4.27
4.25
4.25
4.25
4.24
4.23
4.23
4.22
4.21
4.21
4.19
4.19
4.18
4.17
4.16
4.15
4.14
4.12
3.23
1.97
1.22
1.21
1.19
S
NHAc
COOEt
COOEt
F
F
3ia
0.86
0.90
0.98
0.86
3.93
1.98
3.00
6.29
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

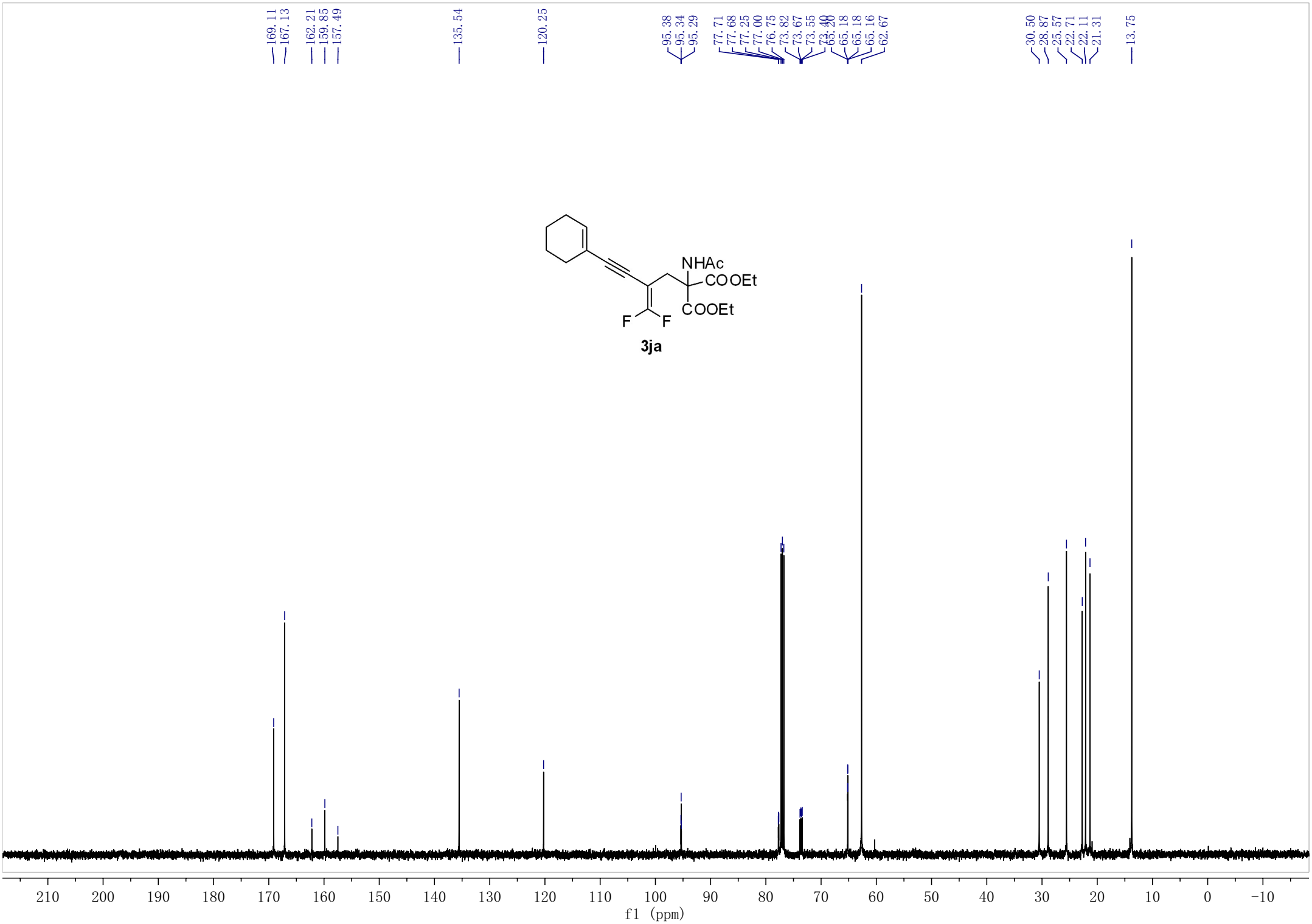

-74.73
-74.74
-81.13
-81.15
S
NHAc
COOEt
COOEt
F
F
3ia
1.00
1.02
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


169.20
166.99
163.01
160.04
157.08
132.11
127.61
127.01
122.14
86.59
86.54
86.48
83.95
83.90
83.87
83.82
77.32
77.00
76.68
73.37
65.12
65.10
65.09
65.07
62.74
30.25
22.65
13.70
S
NHAc
COOEt
COOEt
F
F
3ia
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)

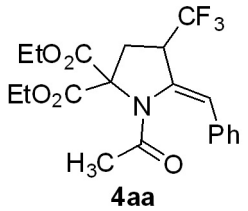
yjr-3-115b


7.26
6.81
6.06
4.27
4.26
4.24
4.22
4.21
4.19
4.18
4.17
4.16
4.14
3.15
2.11
2.06
2.01
1.99
1.58
1.55
1.54
1.23
1.21
NHAc
COOEt
COOEt
F
F
3ja
1.07
1.00
4.46
2.14
4.44
3.11
4.21
5.94
f1 (ppm)

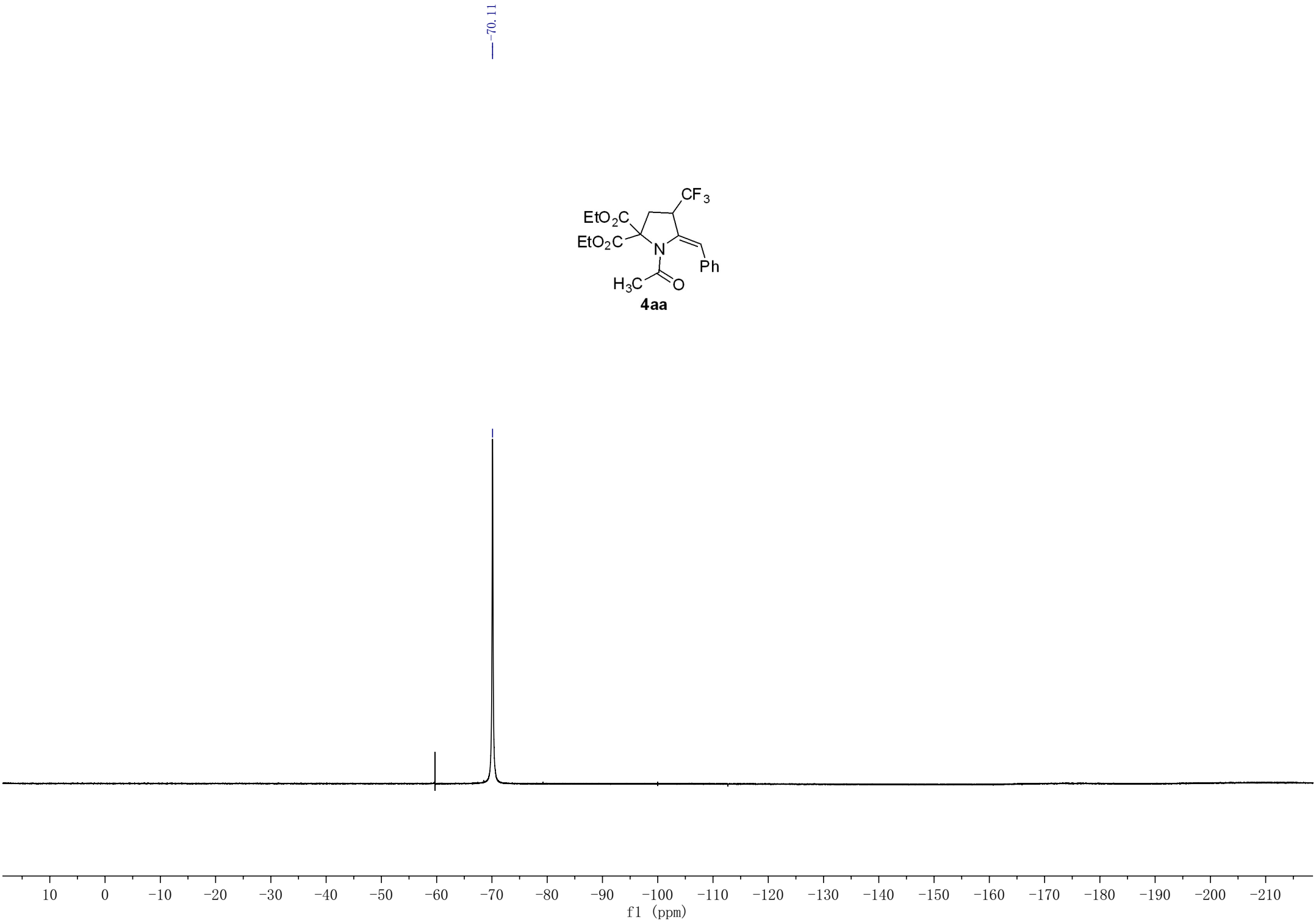

-77.05
-77.07
-83.20
-83.23
NHAc
COOEt
COOEt
F
F
3ja
1.00
1.11
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


169.11
167.13
162.21
159.85
157.49
135.54
120.25
95.38
95.34
95.29
77.71
77.68
77.25
77.00
76.75
73.82
73.67
73.55
65.18
65.16
62.67
30.50
28.87
25.57
22.71
22.11
21.31
13.75
NHAc
COOEt
COOEt
F
F
3ja
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)

lsy-1-31
lsy-1-31

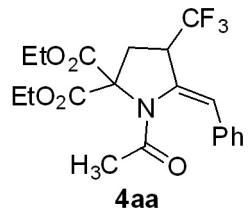


4aa

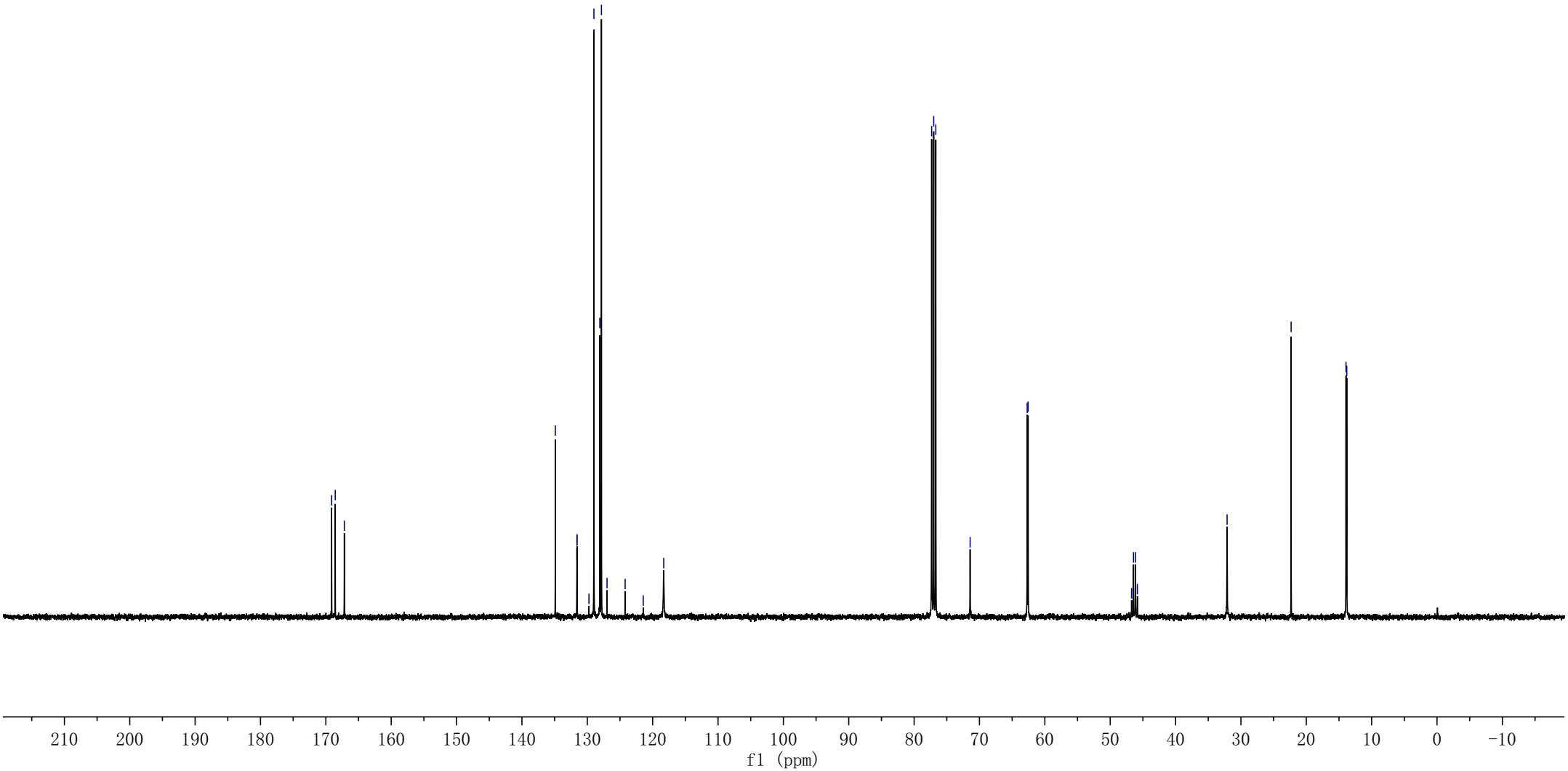

-70.11
CF3
EtO2C
EtO2C
N
Ph
H3C
O
4aa
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

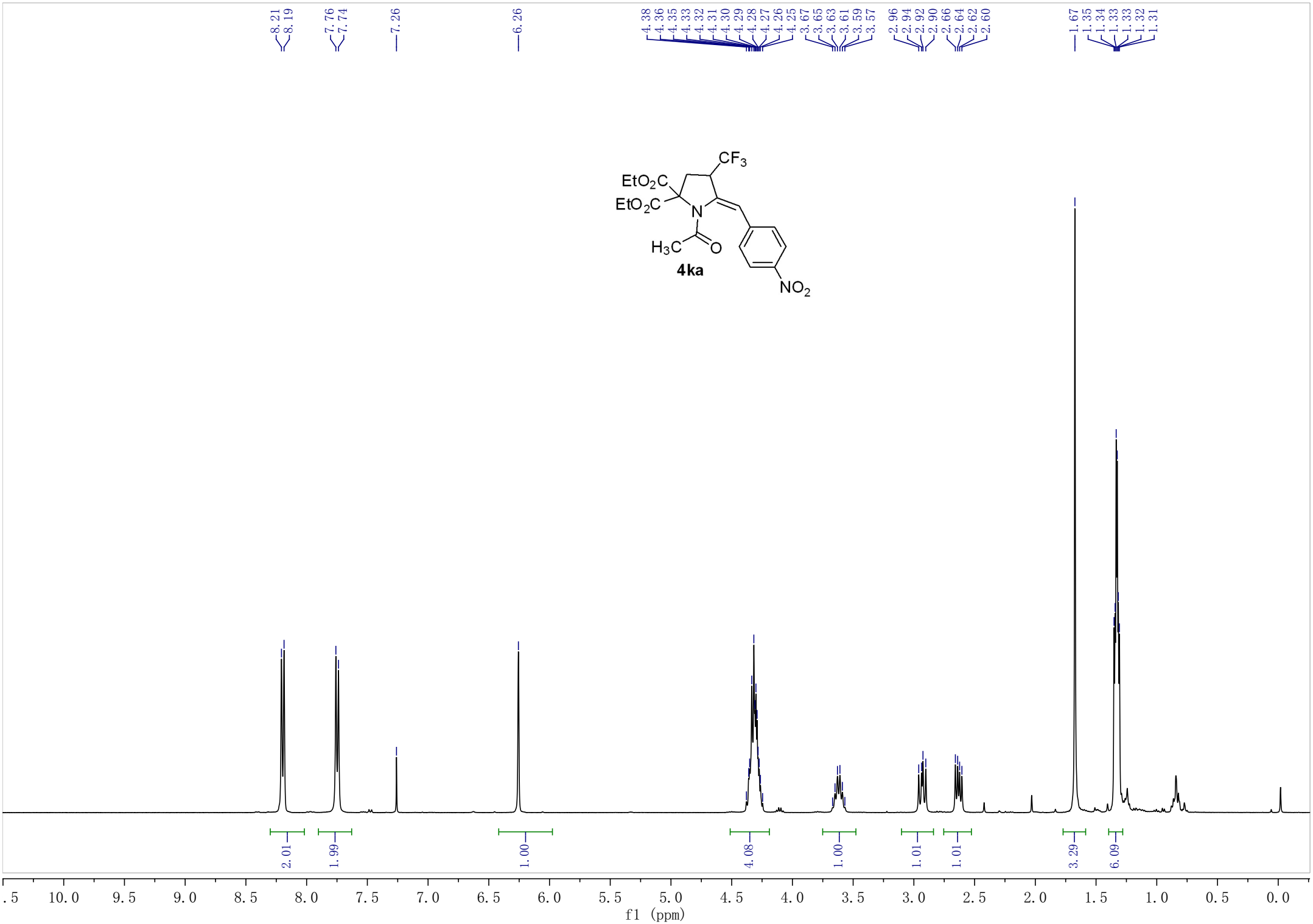
lsy-1-31
lsy-1-31

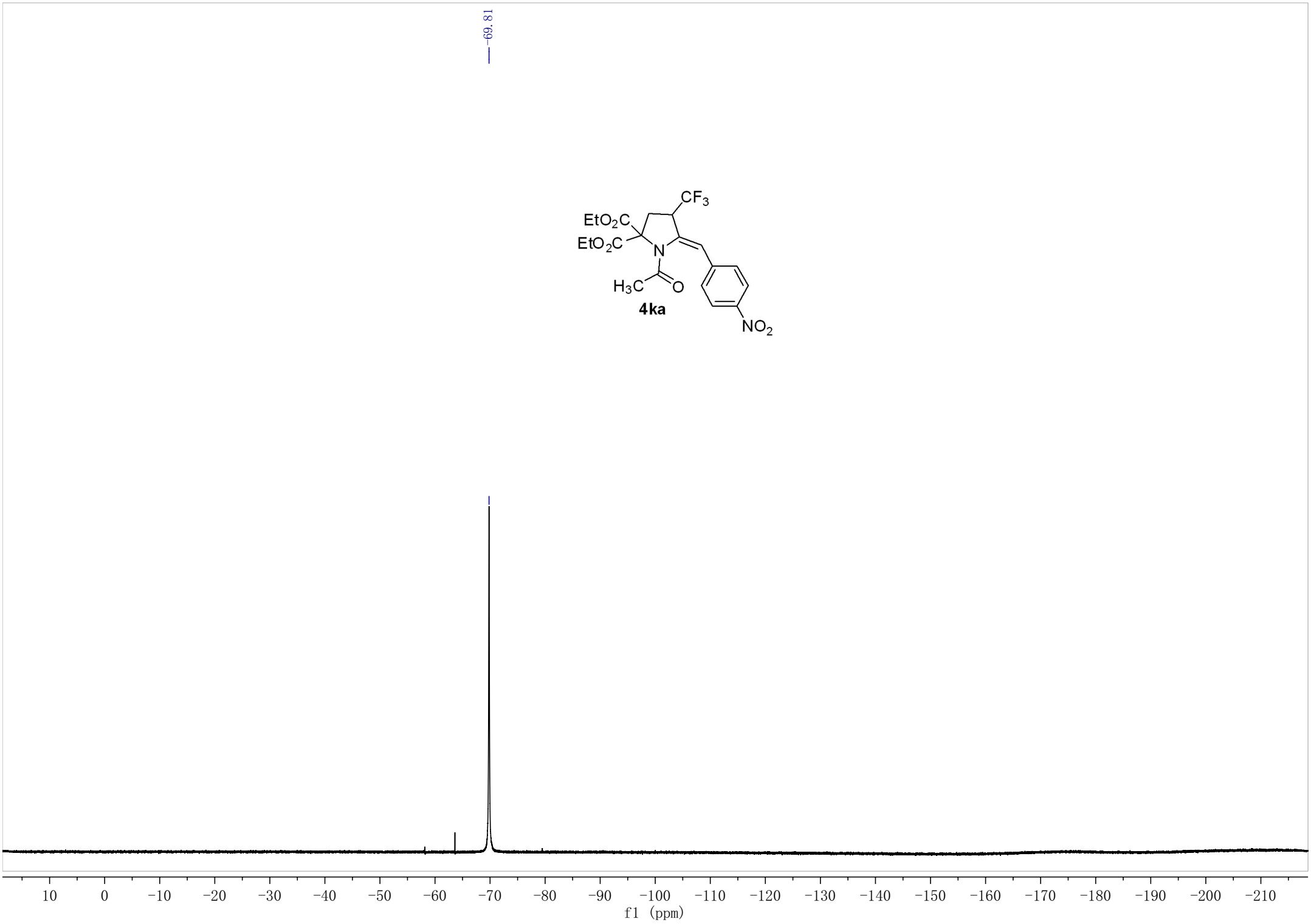
169.12
168.56
167.17
134.89
131.59
131.57
129.75
128.99
128.08
127.84
126.98
124.21
121.44
118.31
77.32
77.00
76.68
71.43
62.70
62.56
46.73
46.43
46.14
45.85
32.12
22.32
13.93
13.81

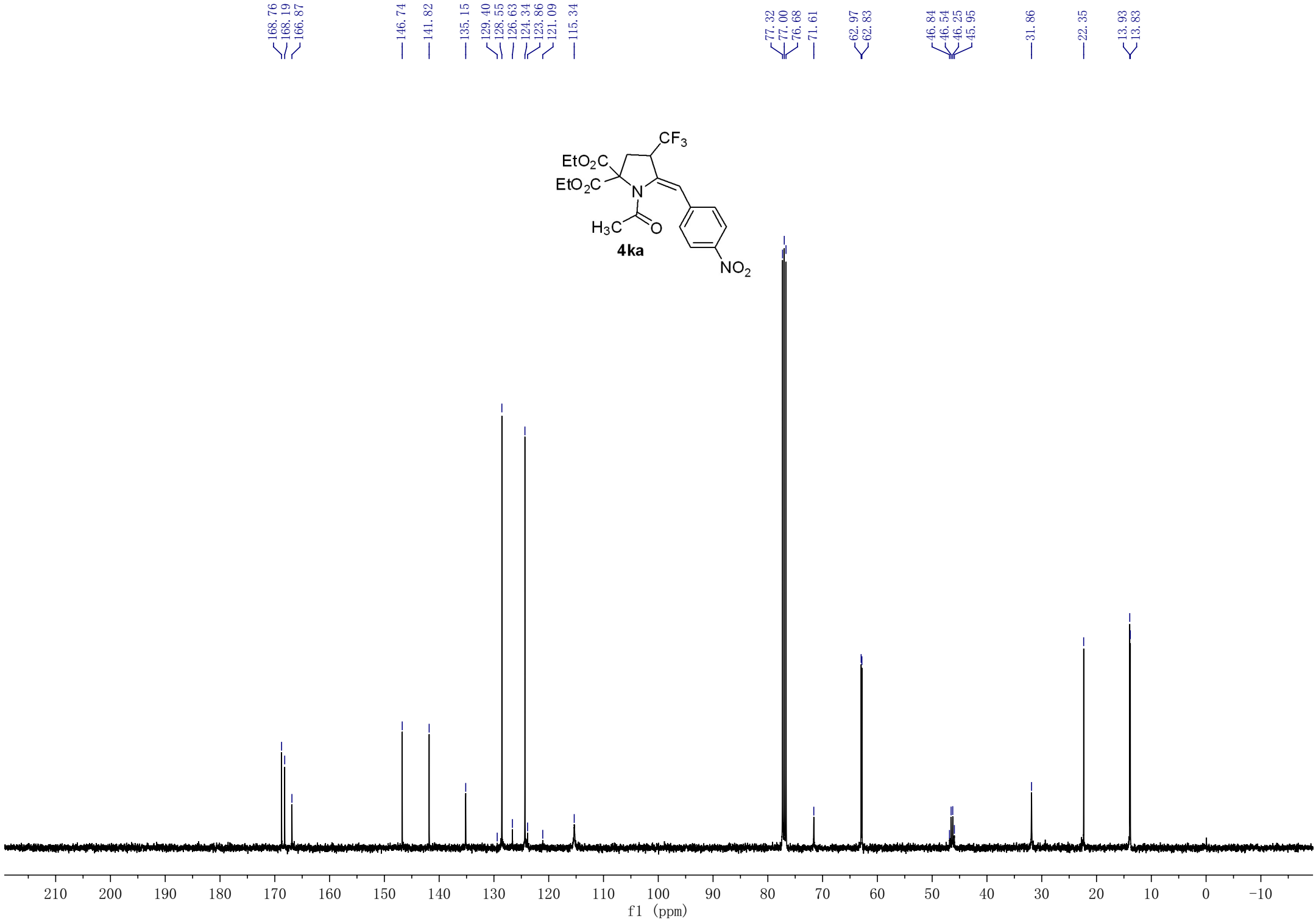


4aa




8.21
8.19
7.76
7.74
7.26
6.26
4.38
4.36
4.35
4.33
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.25
3.67
3.65
3.63
3.61
3.59
3.57
2.96
2.94
2.92
2.90
2.66
2.64
2.62
2.60
1.67
1.35
1.34
1.33
1.33
1.32
1.31
CF3
EtO2C
EtO2C
N
H3C
O
4ka
NO2
2.01
1.99
1.00
4.08
1.00
1.01
1.01
3.29
6.09
.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)


-69.81
CF3
EtO2C
EtO2C
N
H3C
O
4ka
NO2
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)


168.76
168.19
166.87
146.74
141.82
135.15
129.40
128.55
126.63
124.34
123.86
121.09
115.34
77.32
77.00
76.68
71.61
62.97
62.83
46.84
46.54
46.25
45.95
31.86
22.35
13.93
13.83
CF3
EtO2C
EtO2C
N
H3C
O
4ka
NO2
210
200
190
180
170
160
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140
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120
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100
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80
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60
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40
30
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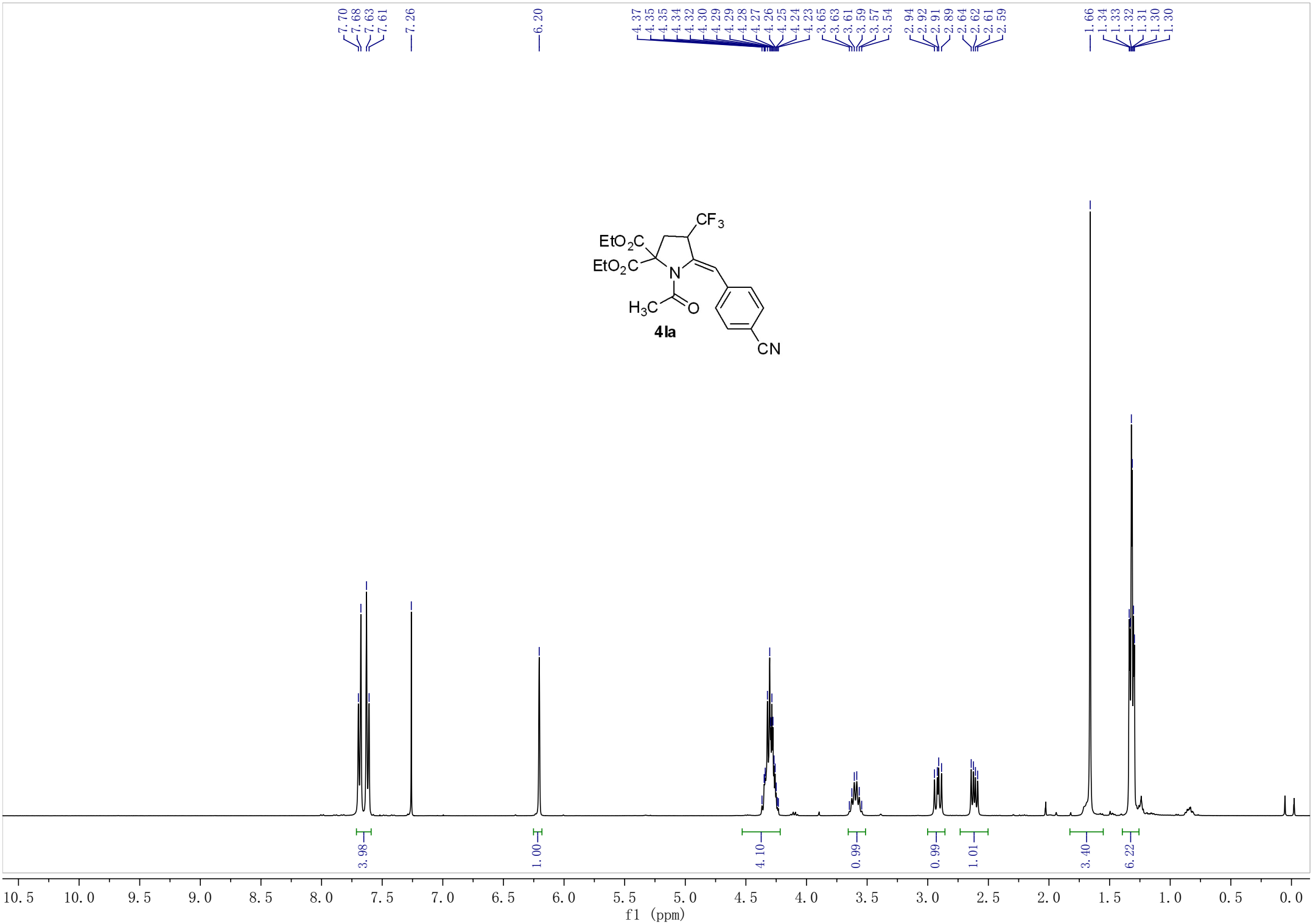
0
-10
f1 (ppm)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7.61
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4.35
4.35
4.34
4.32
4.30
4.29
4.29
4.28
4.27
4.26
4.25
4.24
4.23
3.65
3.63
3.61
3.59
3.57
3.54
2.94
2.92
2.91
2.89
2.64
2.62
2.61
2.59
1.66
1.34
1.33
1.32
1.31
1.30
1.30
CF3
EtO2C
EtO2C
N
H3C
O
4la
CN
3.98
1.00
4.10
0.99
0.99
1.01
3.40
6.22
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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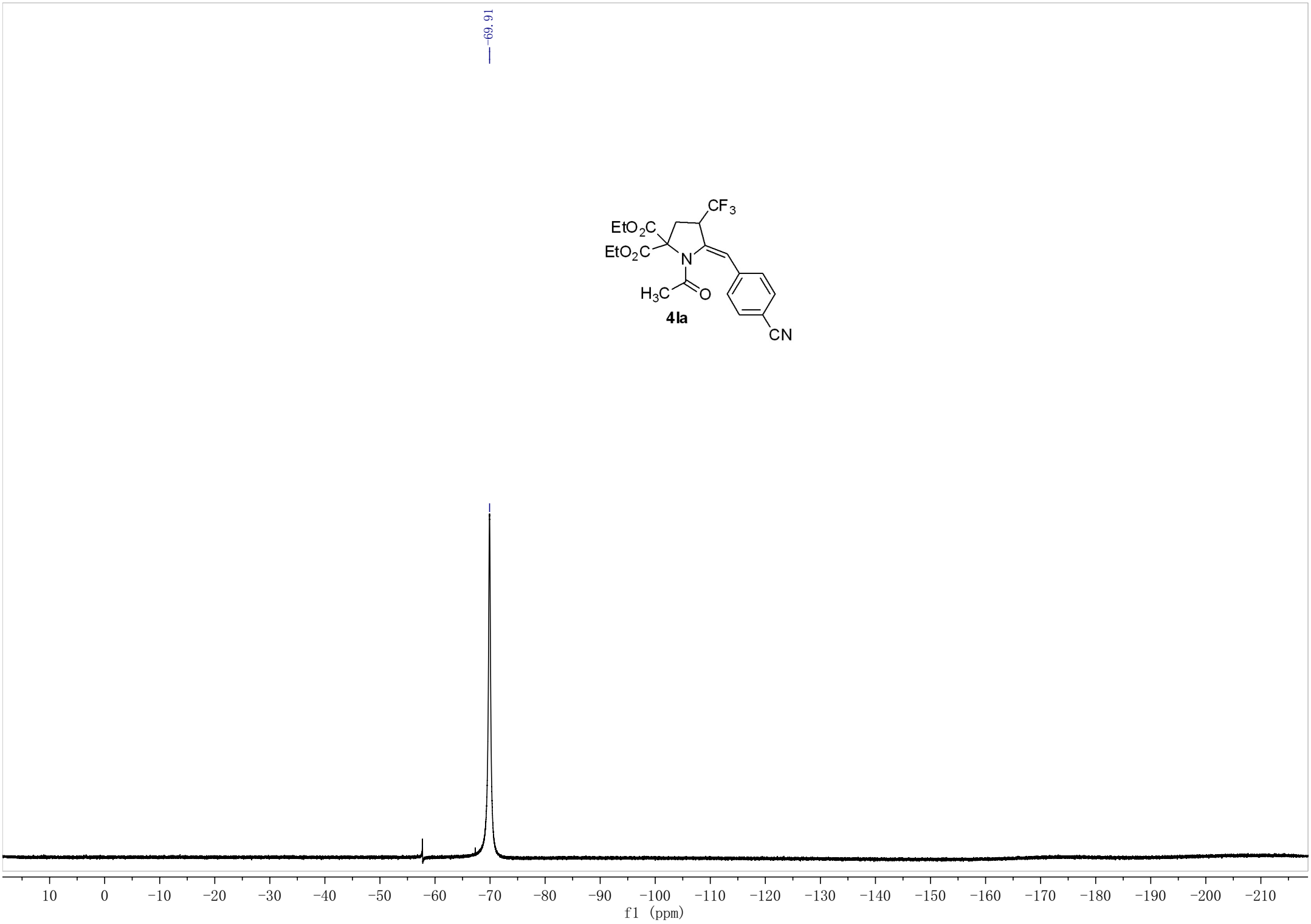
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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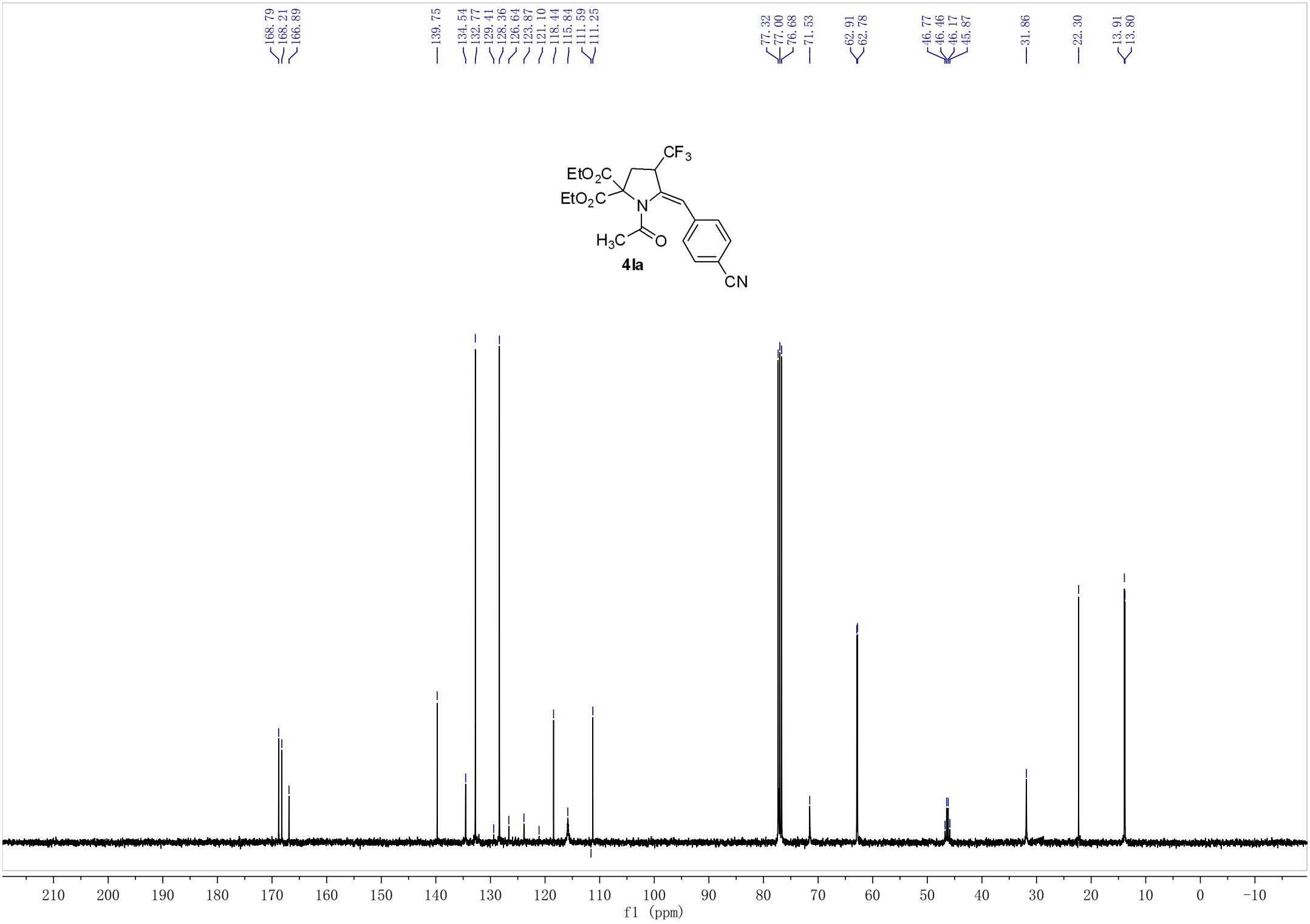
EtO2C
EtO2C
N
H3C
O
CN
4la
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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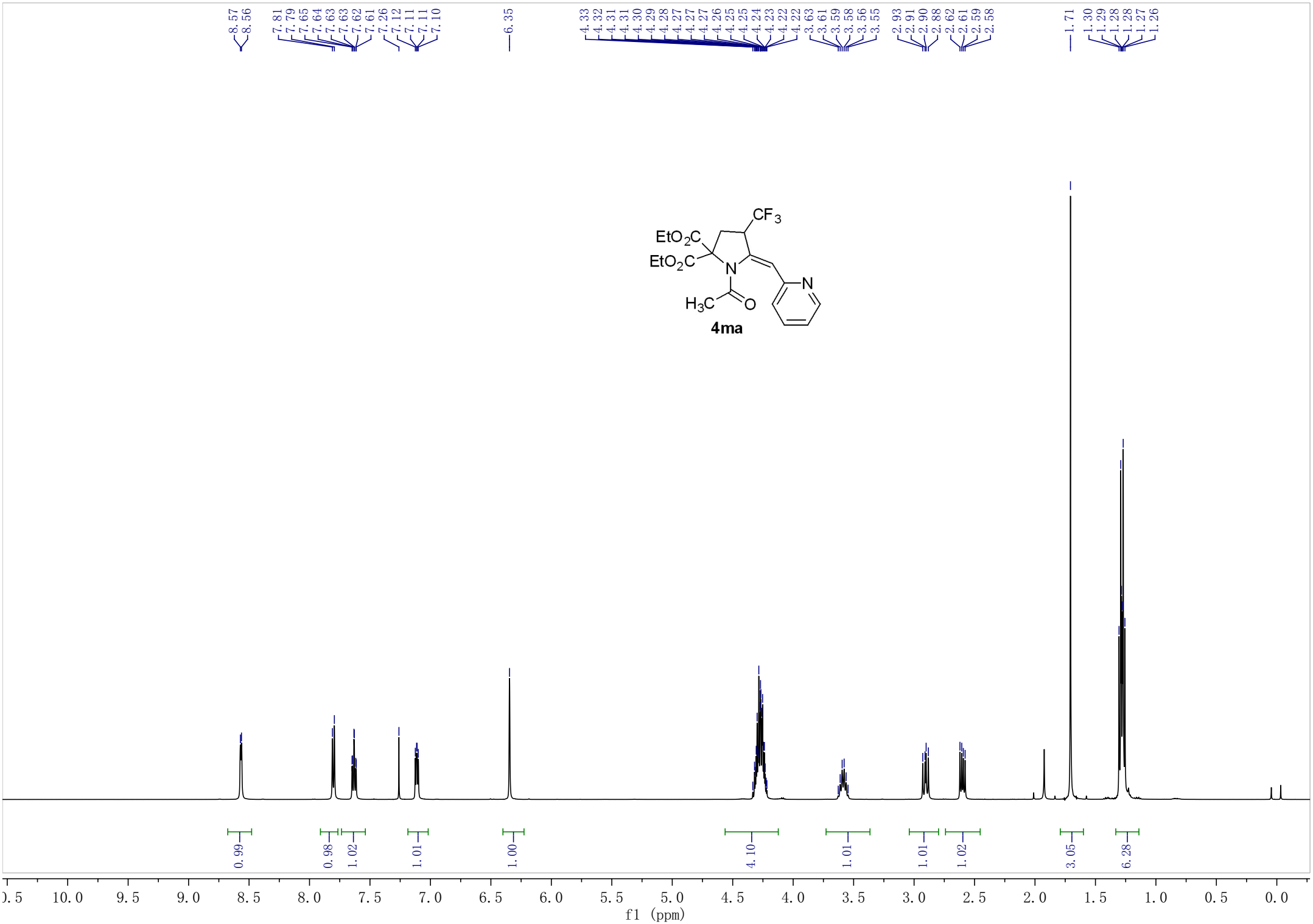
132.77
129.41
128.36
126.64
123.87
121.10
118.44
115.84
111.59
111.25
77.32
77.00
76.68
71.53
62.91
62.78
46.77
46.46
46.17
45.87
31.86
22.30
13.91
13.80
CF3
EtO2C
EtO2C
N
H3C
O
CN
4la
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.56
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7.79
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7.64
7.63
7.63
7.62
7.61
7.26
7.12
7.11
7.11
7.10
6.35
4.33
4.32
4.31
4.31
4.30
4.29
4.28
4.27
4.27
4.27
4.26
4.25
4.25
4.24
4.23
4.22
4.22
3.63
3.61
3.59
3.58
3.56
3.55
2.93
2.91
2.90
2.88
2.62
2.61
2.59
2.58
1.71
1.30
1.29
1.28
1.28
1.27
1.26
CF3
EtO2C
EtO2C
N
H3C
O
N
4ma
0.99
0.98
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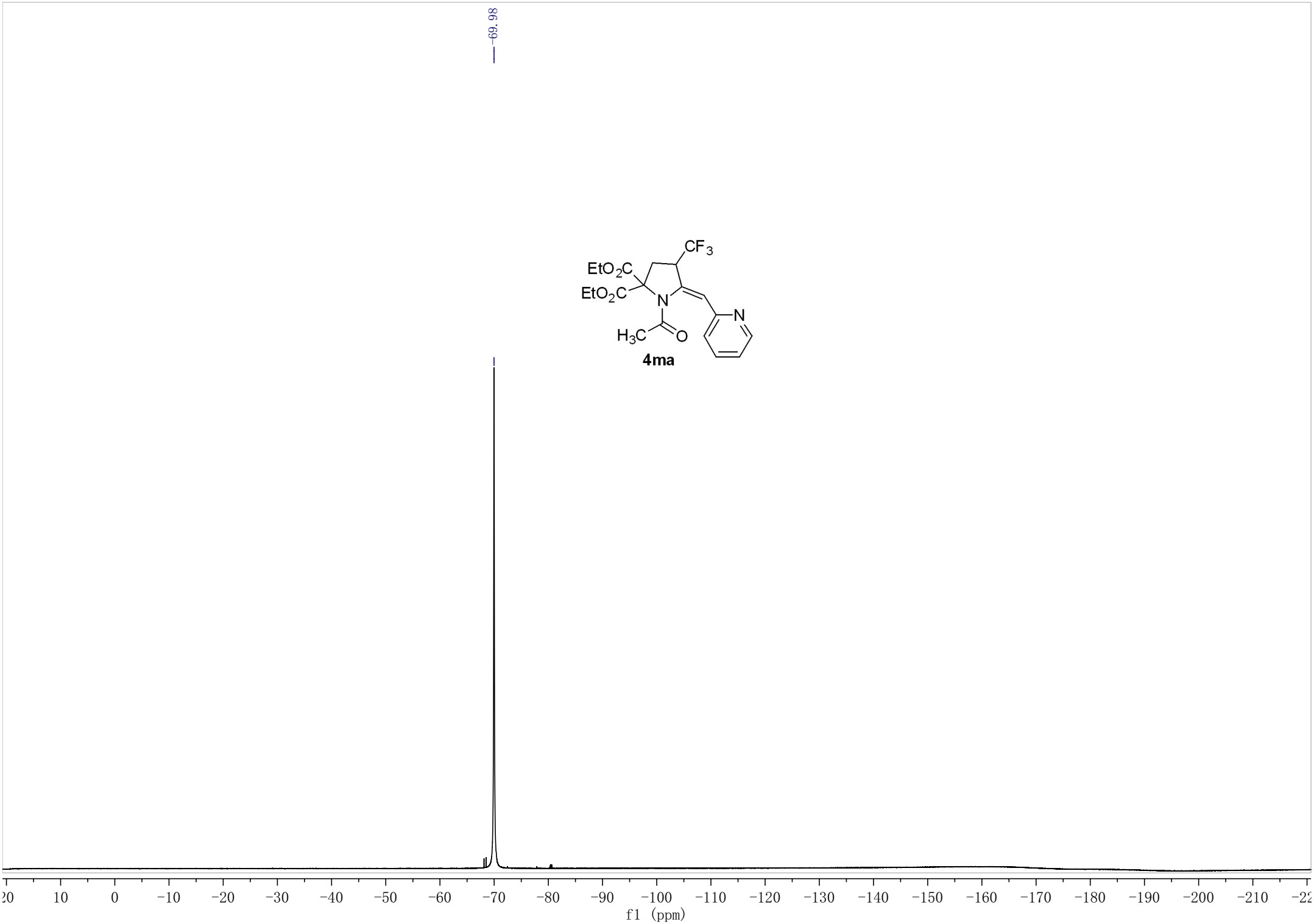
1.01
1.00
4.10
1.01
1.01
1.02
3.05
6.28
f1 (ppm)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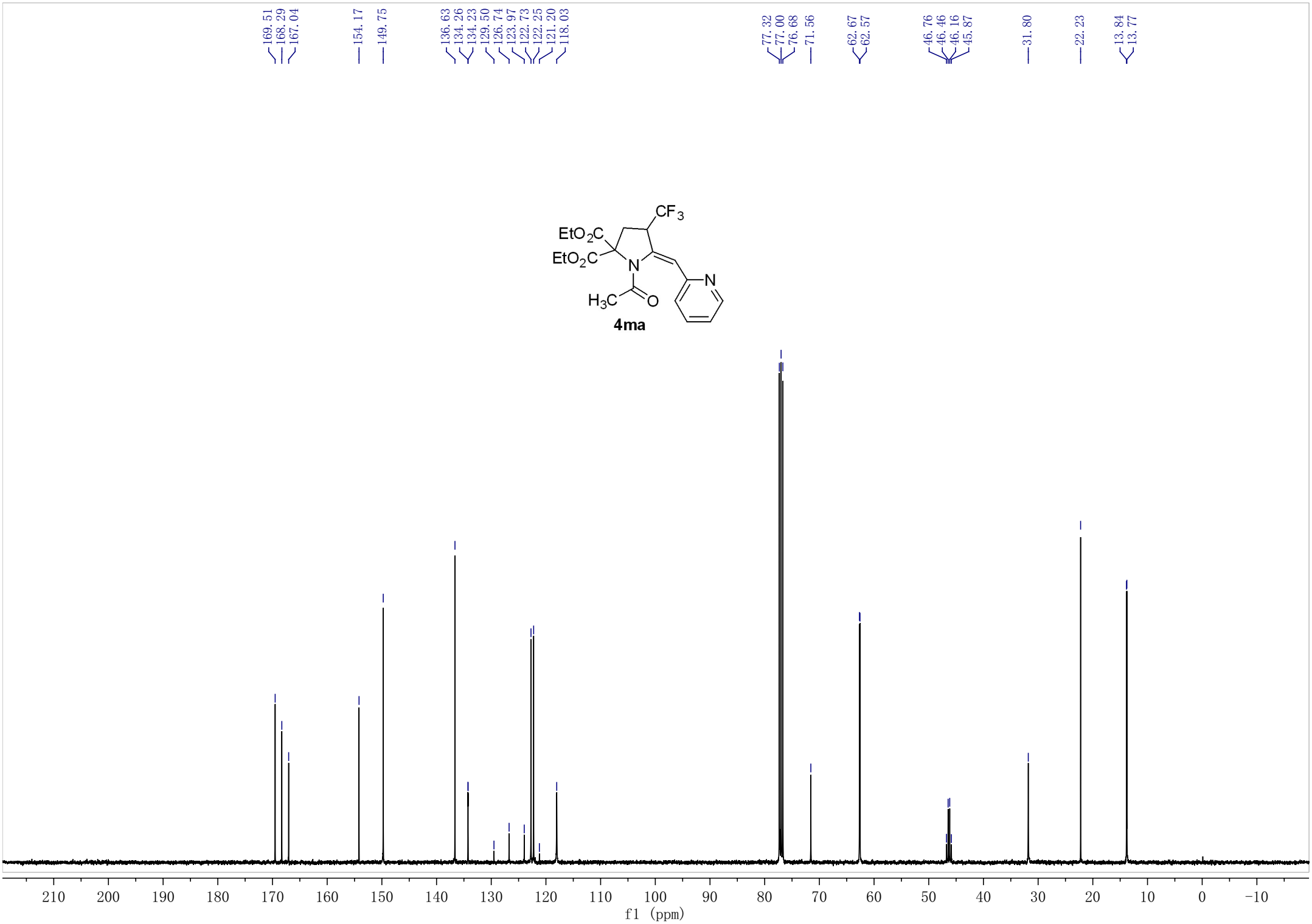
CF3
EtO2C
EtO2C
N
H3C
O
N
4ma
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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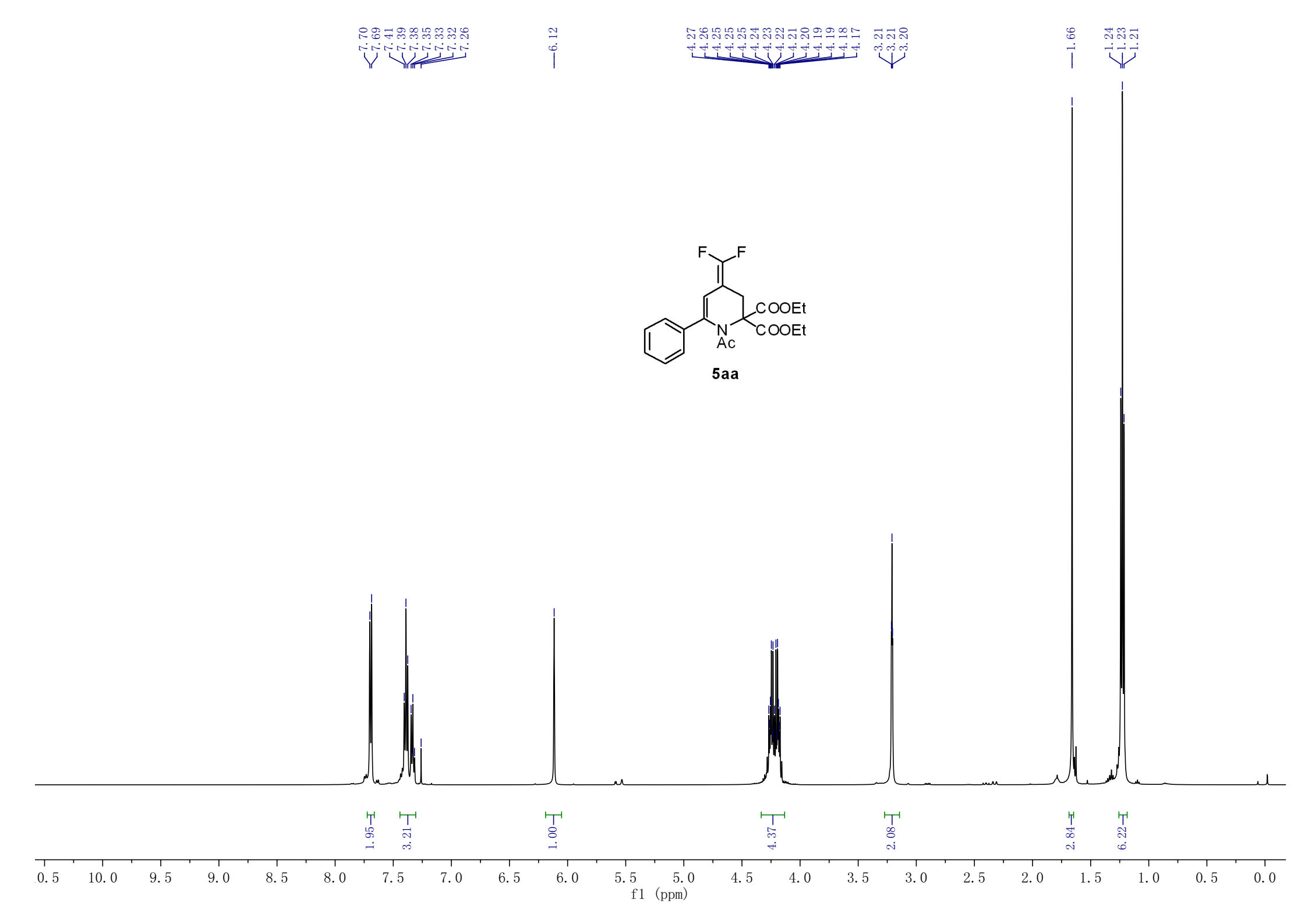
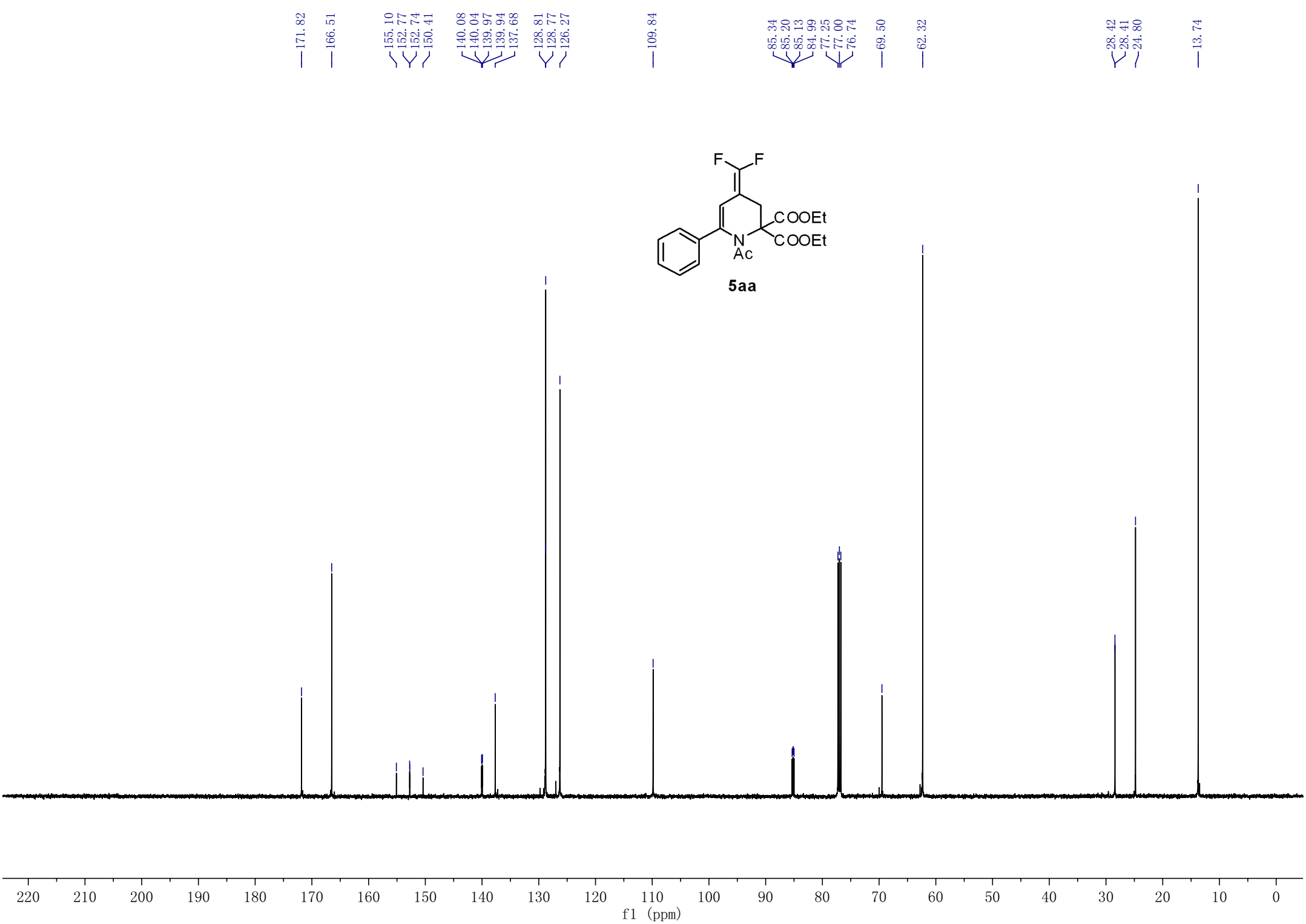
167.04
154.17
149.75
136.63
134.26
134.23
129.50
126.74
123.97
122.73
122.25
121.20
118.03
77.32
77.00
76.68
71.56
62.67
62.57
46.76
46.46
46.16
45.87
31.80
22.23
13.84
13.77
CF3
EtO2C
EtO2C
N
H3C
O
N
4ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.70
7.69
7.41
7.39
7.38
7.35
7.33
7.32
7.26
6.12
4.27
4.26
4.25
4.25
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.19
4.18
4.17
3.21
3.21
3.20
1.66
1.24
1.23
1.21
F
F
COOEt
COOEt
N
Ac
5aa
1.95
3.21
1.00
4.37
2.08
2.84
6.22
f1 (ppm)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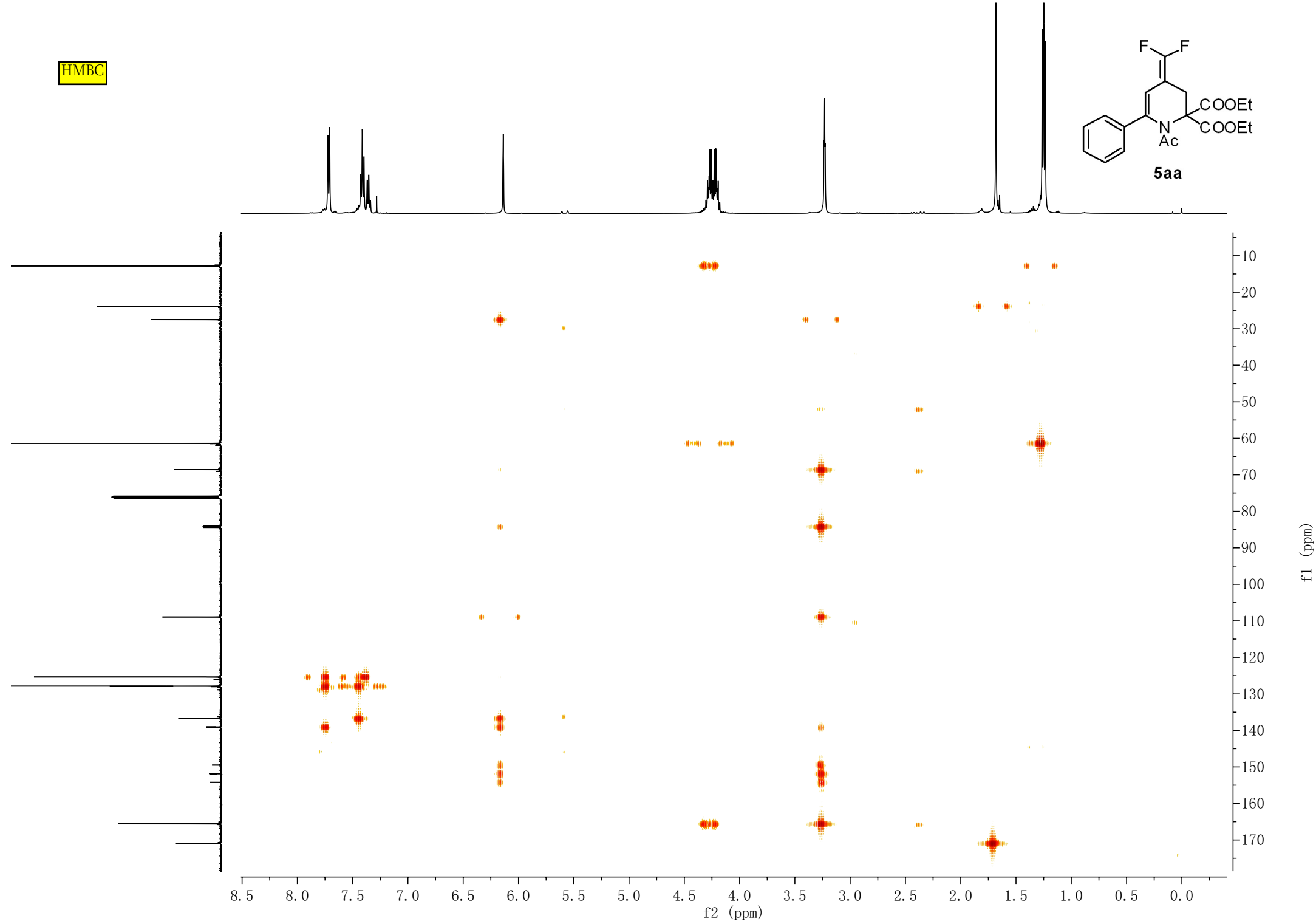
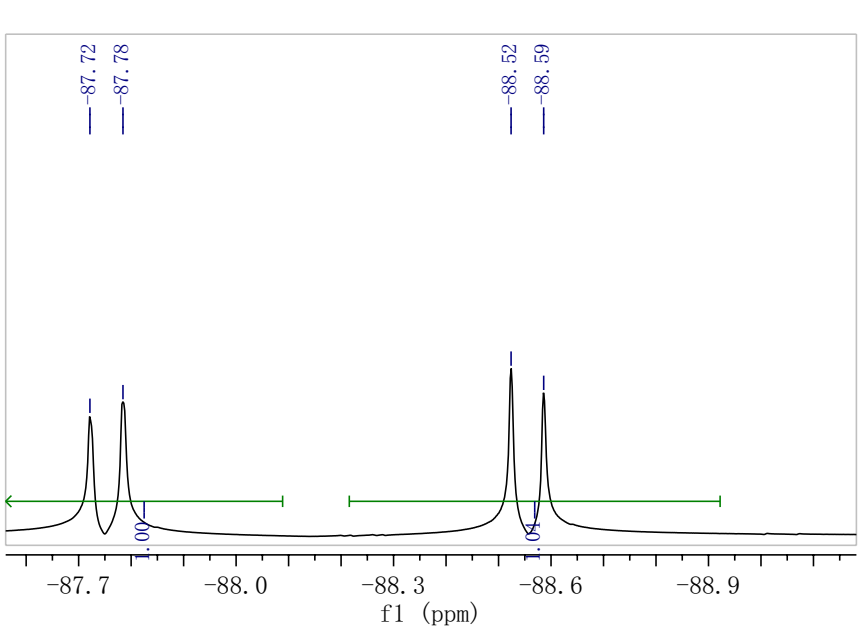
155.10
152.77
152.74
150.41
140.08
140.04
139.97
139.94
137.68
128.81
128.77
126.27
109.84
85.34
85.20
85.13
84.99
77.25
77.00
76.74
69.50
62.32
28.42
28.41
24.80
13.74
F
F
COOEt
COOEt
N
Ac
5aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HMBC
F
F
COOEt
COOEt
N
Ac
5aa
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
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
f1 (ppm)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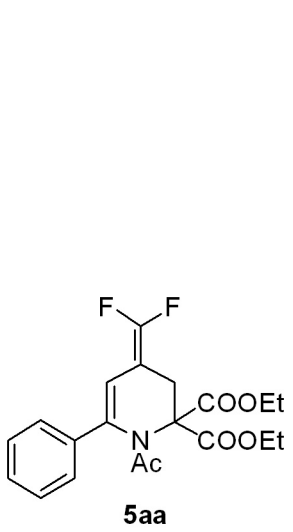
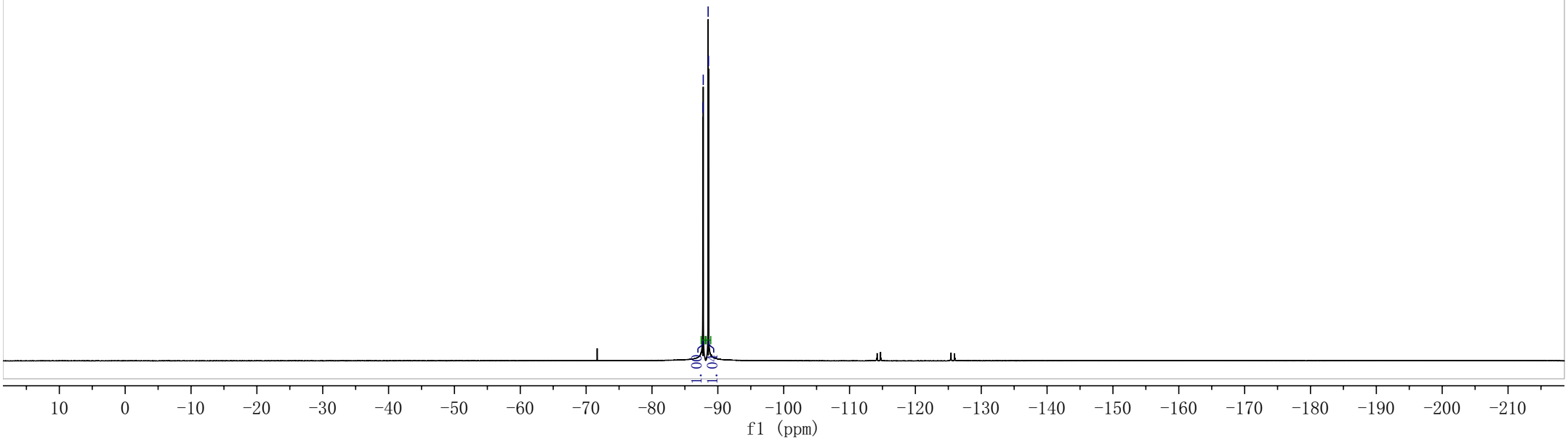
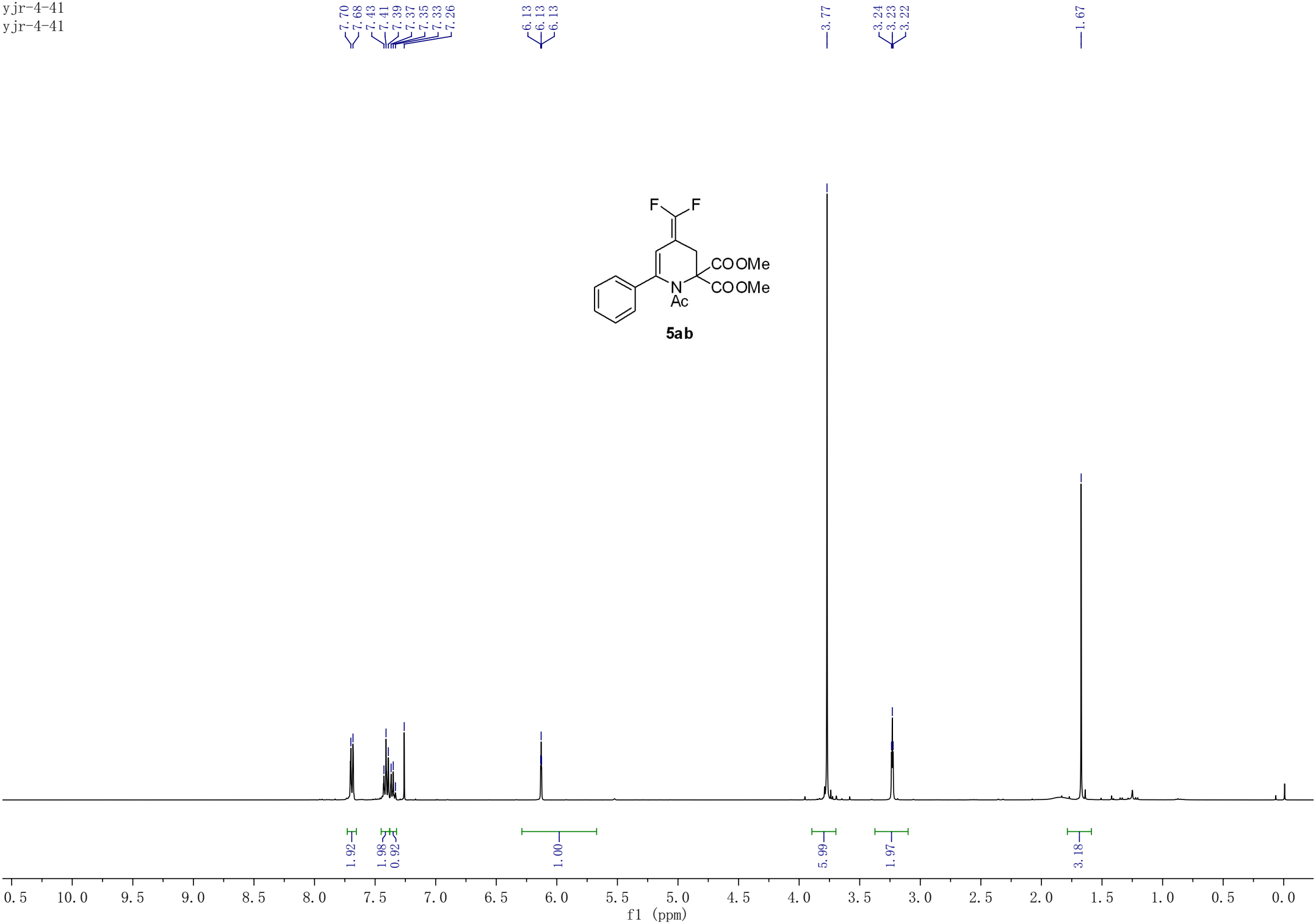
-87.78
-88.52
-88.59
1.00
1.01
-87.7
-88.0
-88.3
-88.6
-88.9
f1 (ppm)

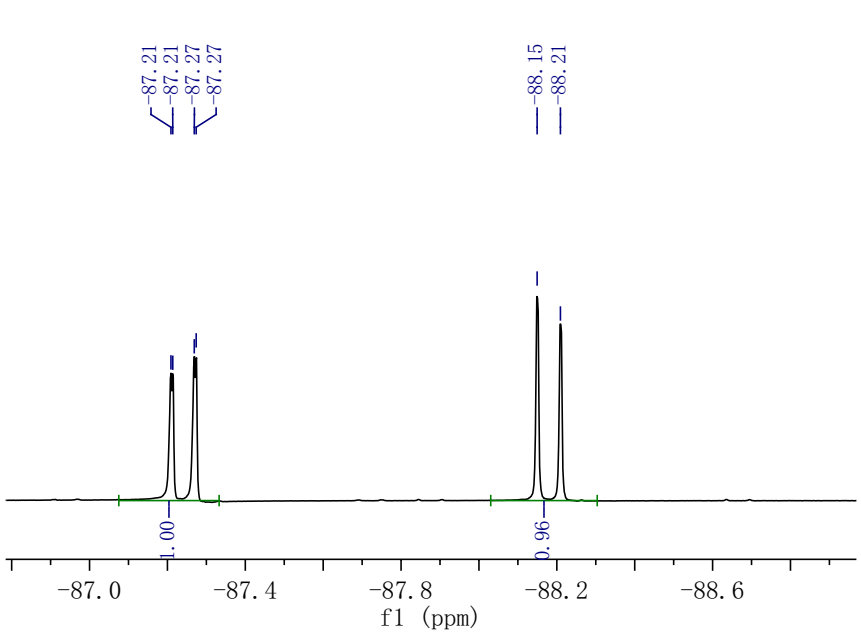

F
F
COOEt
COOEt
N
Ac

5aa


1.00
1.02
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)

yjr-4-41
yjr-4-41

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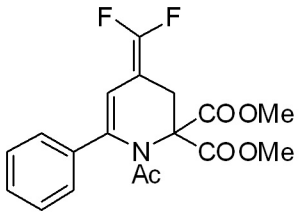
-87.21
-87.27
-87.27
-88.15
-88.21
1.00
0.96
-87.0
-87.4
-87.8
-88.2
-88.6
f1 (ppm)


F
F
COOMe
COOMe
N
Ac

5ab

-87.21
-87.21
-87.27
-87.27
-88.15
-88.21
1.00
0.96
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)

yjr-4-41
yjr-4-41

172.02
167.09
155.78
152.86
152.83
149.91
140.03
139.98
139.90
139.85
137.65
128.93
126.26
110.11
85.27
85.10
85.02
84.84
77.32
77.00
76.68
69.37
69.36
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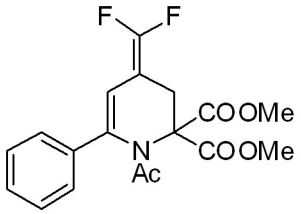
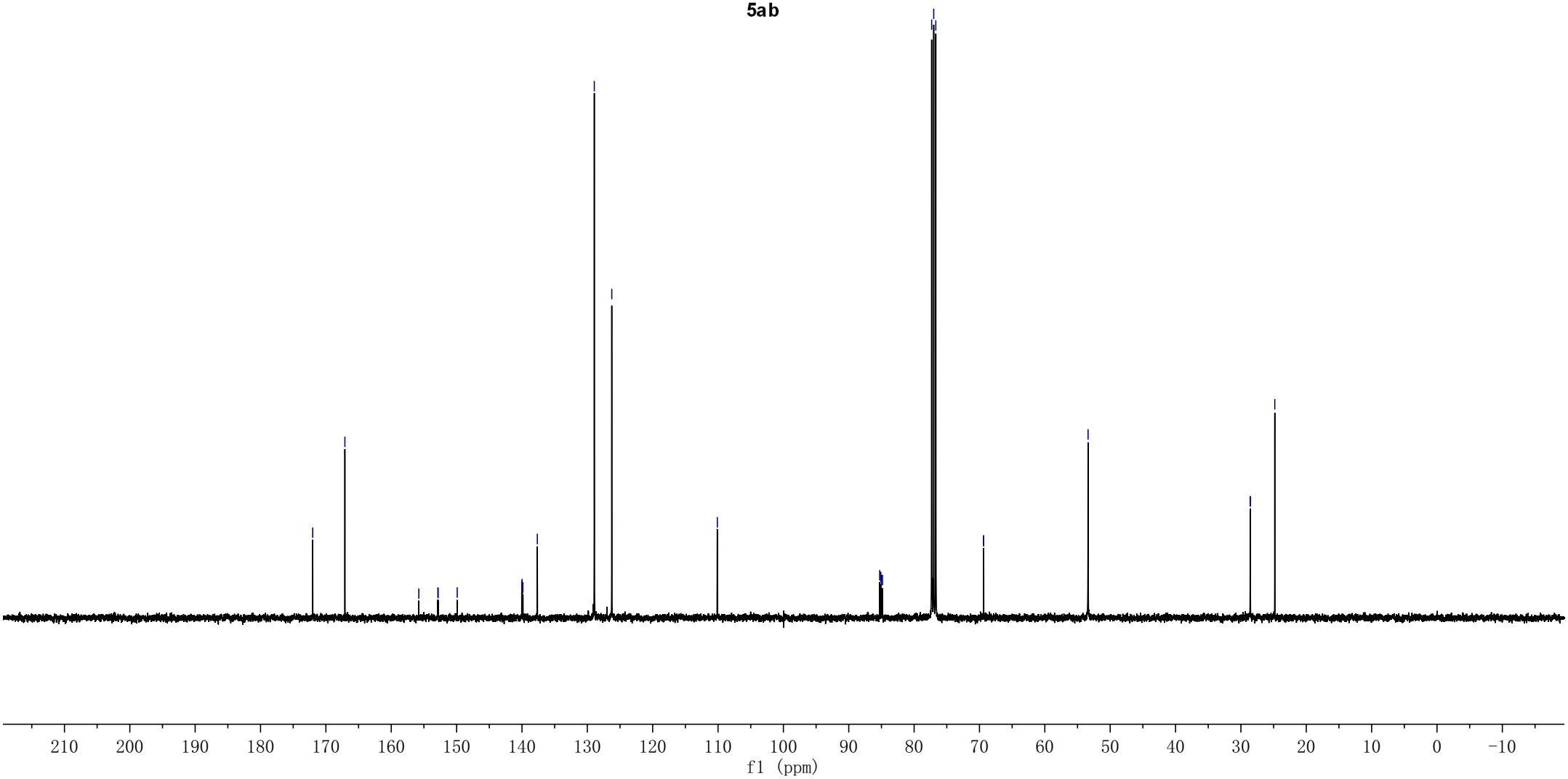
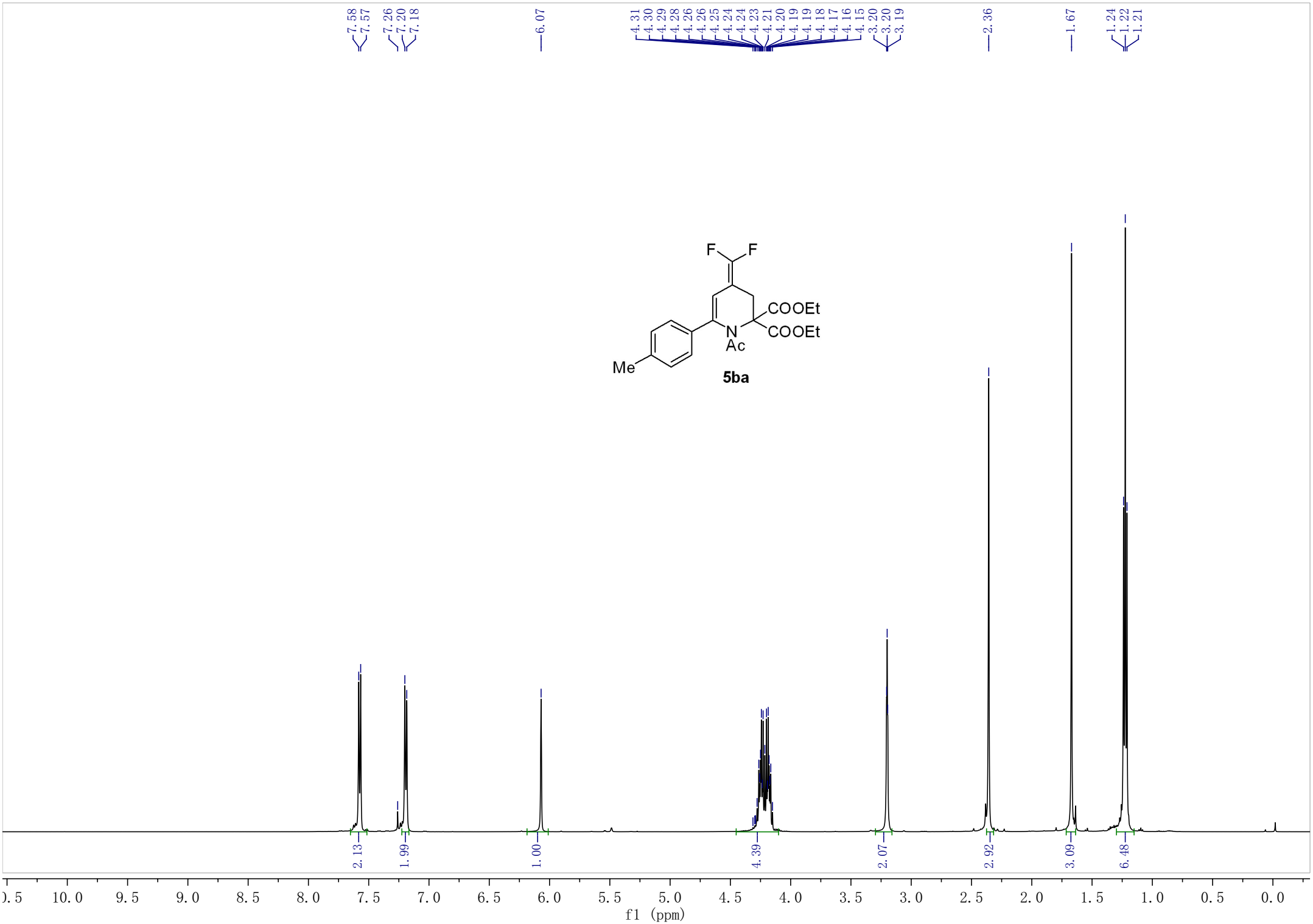
28.58
28.56
24.82



5ab

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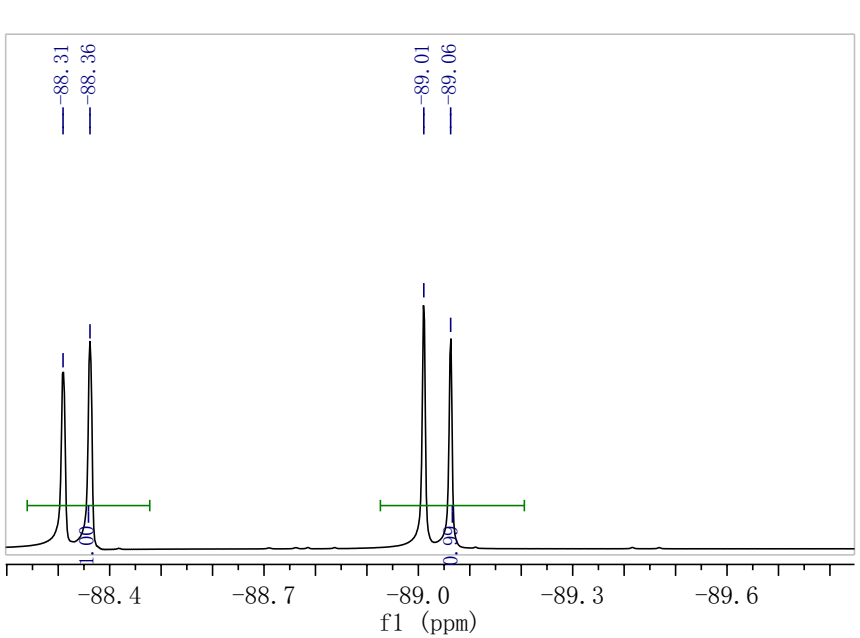
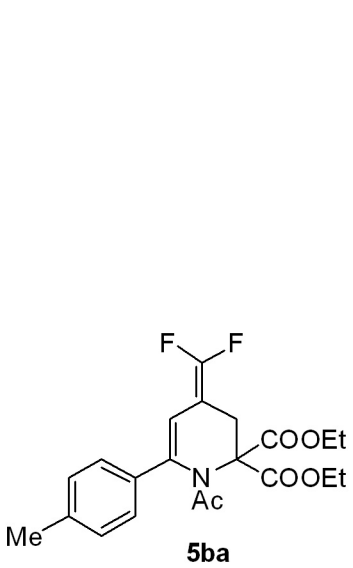
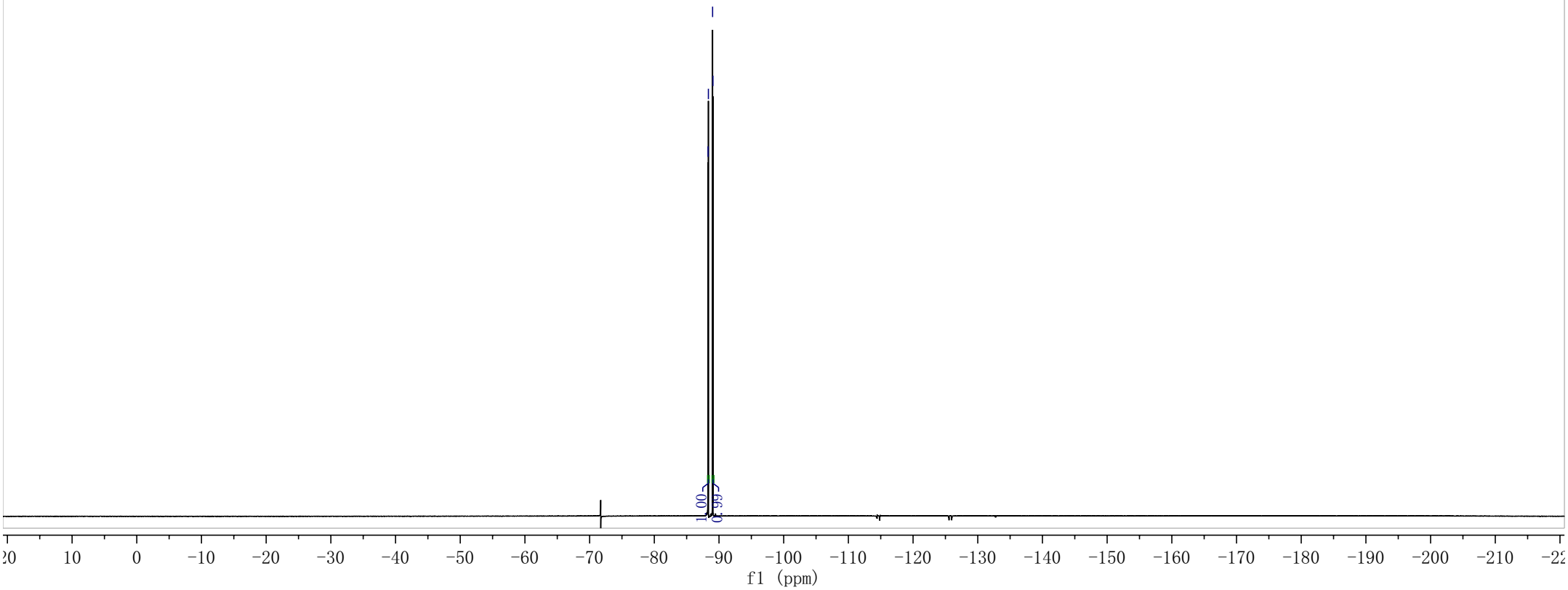
4.28
4.26
4.26
4.25
4.24
4.24
4.23
4.21
4.20
4.19
4.19
4.18
4.17
4.16
4.15
3.20
3.20
3.19
2.36
1.67
1.24
1.22
1.21
F
F
COOEt
COOEt
N
Ac
Me
5ba
2.13
1.99
1.00
4.39
2.07
2.92
3.09
6.48
f1 (ppm)


-88.31
-88.36
-89.01
-89.06
1.00
0.98
-88.4
-88.7
-89.0
-89.3
-89.6
f1 (ppm)


F
F
COOEt
COOEt
N
Ac
Me

5ba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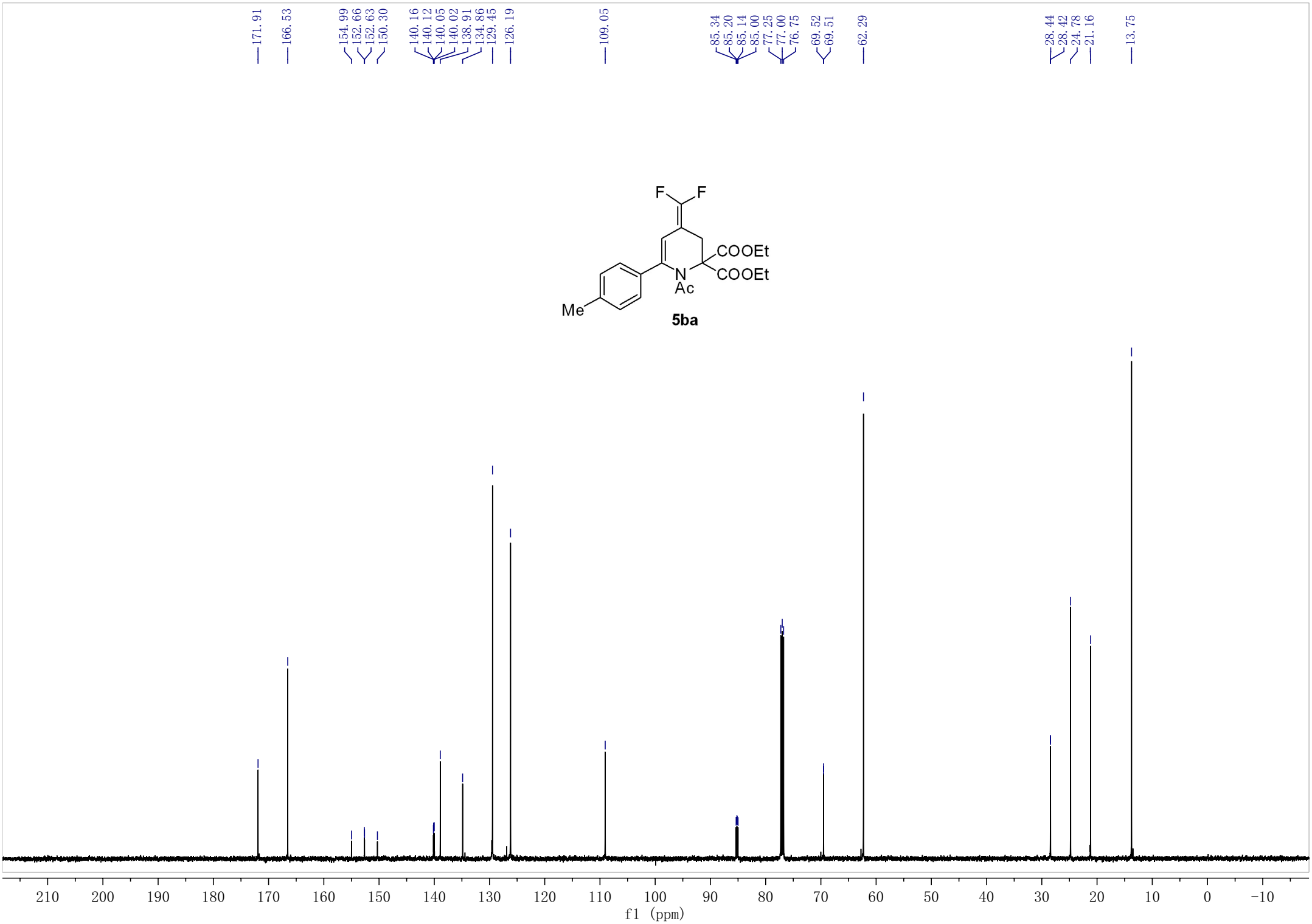
0.99
f1 (ppm)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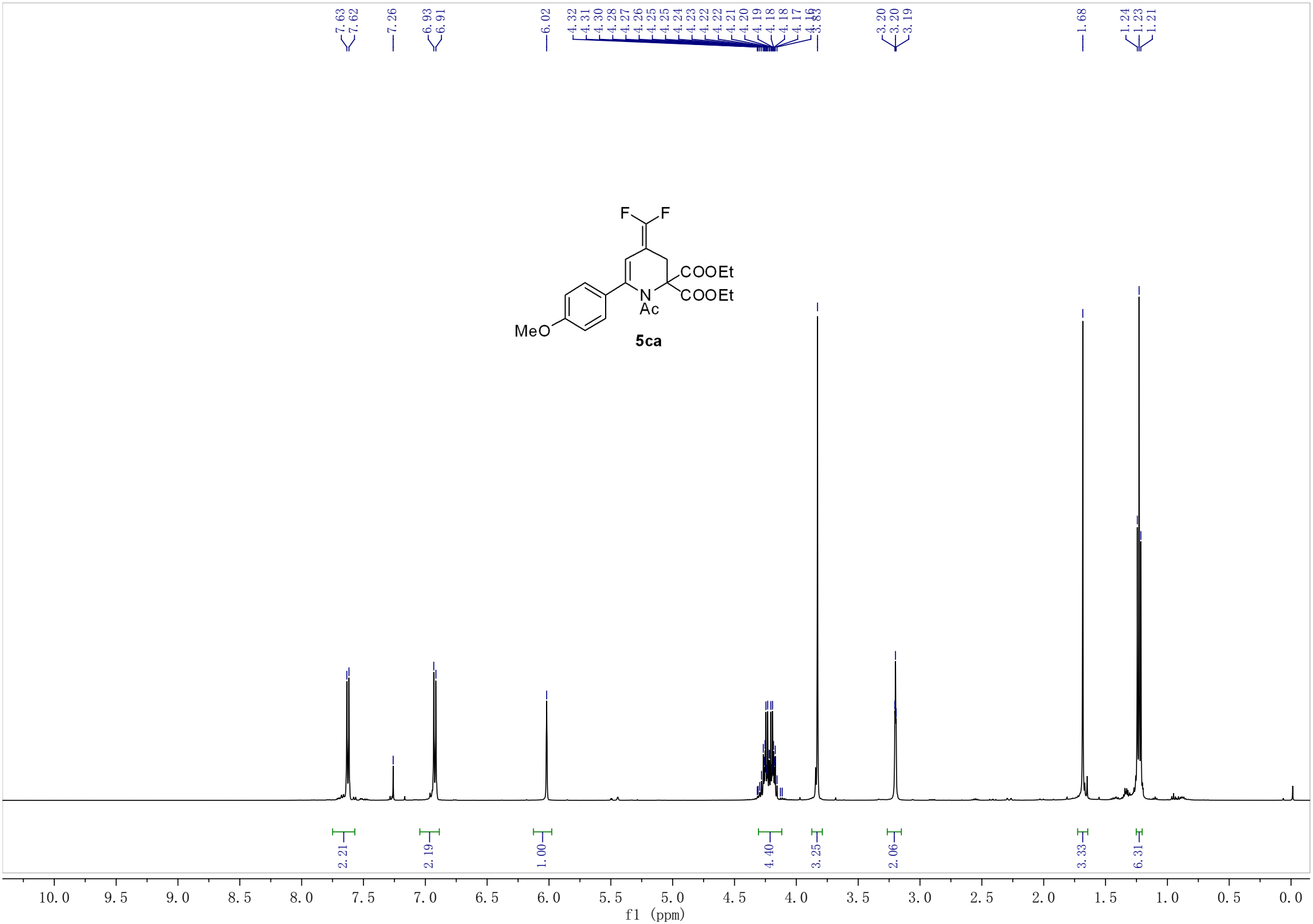
166.53
154.99
152.66
152.63
150.30
140.16
140.12
140.05
140.02
138.91
134.86
129.45
126.19
109.05
85.34
85.20
85.14
85.00
77.25
77.00
76.75
69.52
69.51
62.29
28.44
28.42
24.78
21.16
13.75
F
F
COOEt
COOEt
N
Ac
Me
5ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.63
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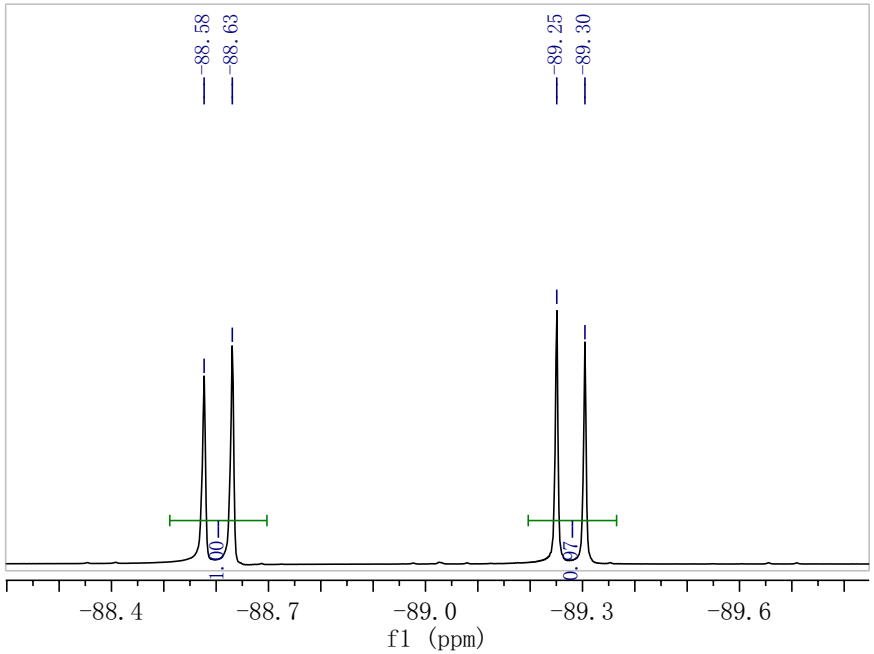
6.93
6.91
6.02
4.32
4.31
4.30
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.22
4.22
4.21
4.20
4.19
4.18
4.18
4.17
4.16
3.83
3.20
3.20
3.19
1.68
1.24
1.23
1.21
F
F
COOEt
COOEt
N
Ac
MeO
5ca
2.21
2.19
1.00
4.40
3.25
2.06
3.33
6.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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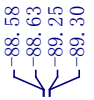
1.00
0.97
-88.4
-88.7
-89.0
-89.3
-89.6
f1 (ppm)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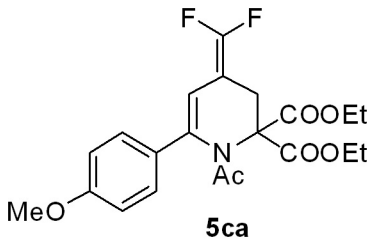
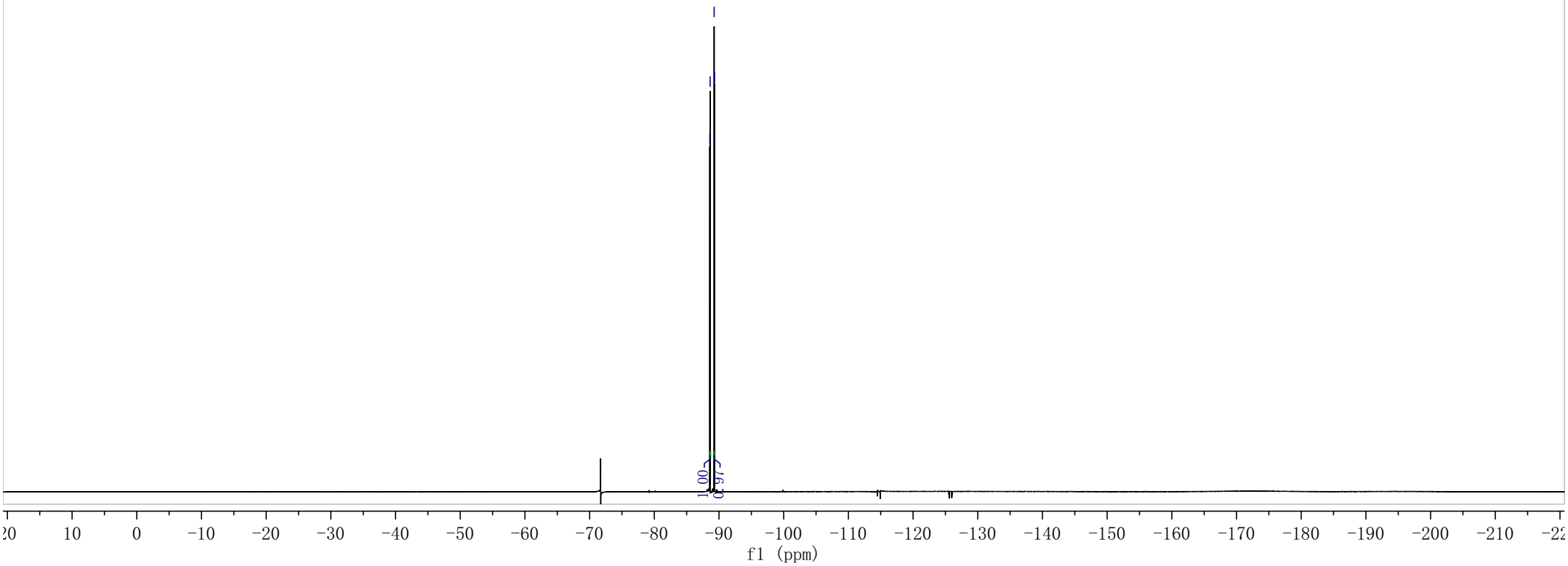
-88.63
-89.25
-89.30


F
F
COOEt
COOEt
N
Ac
MeO

5ca


1.00
0.97
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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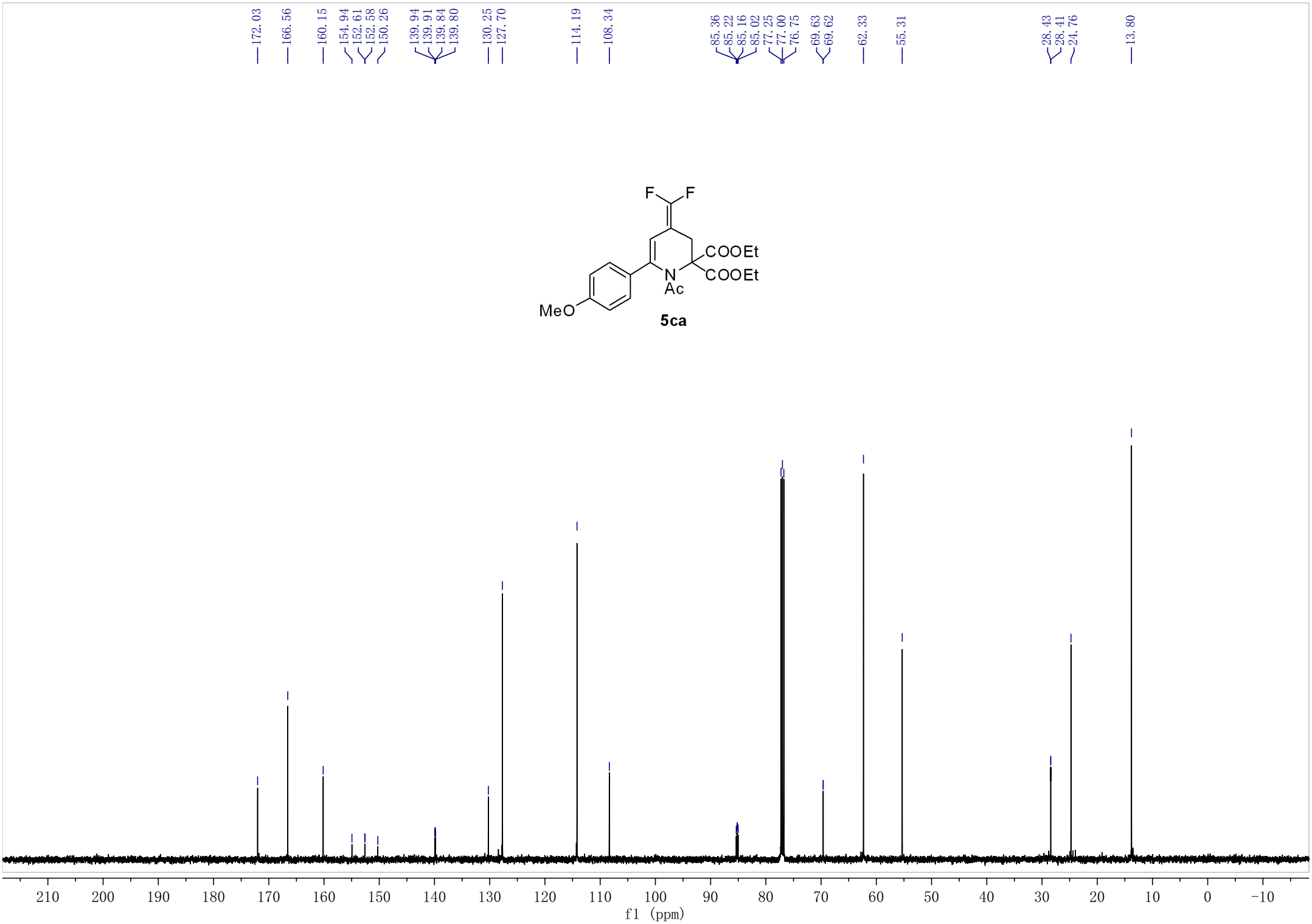
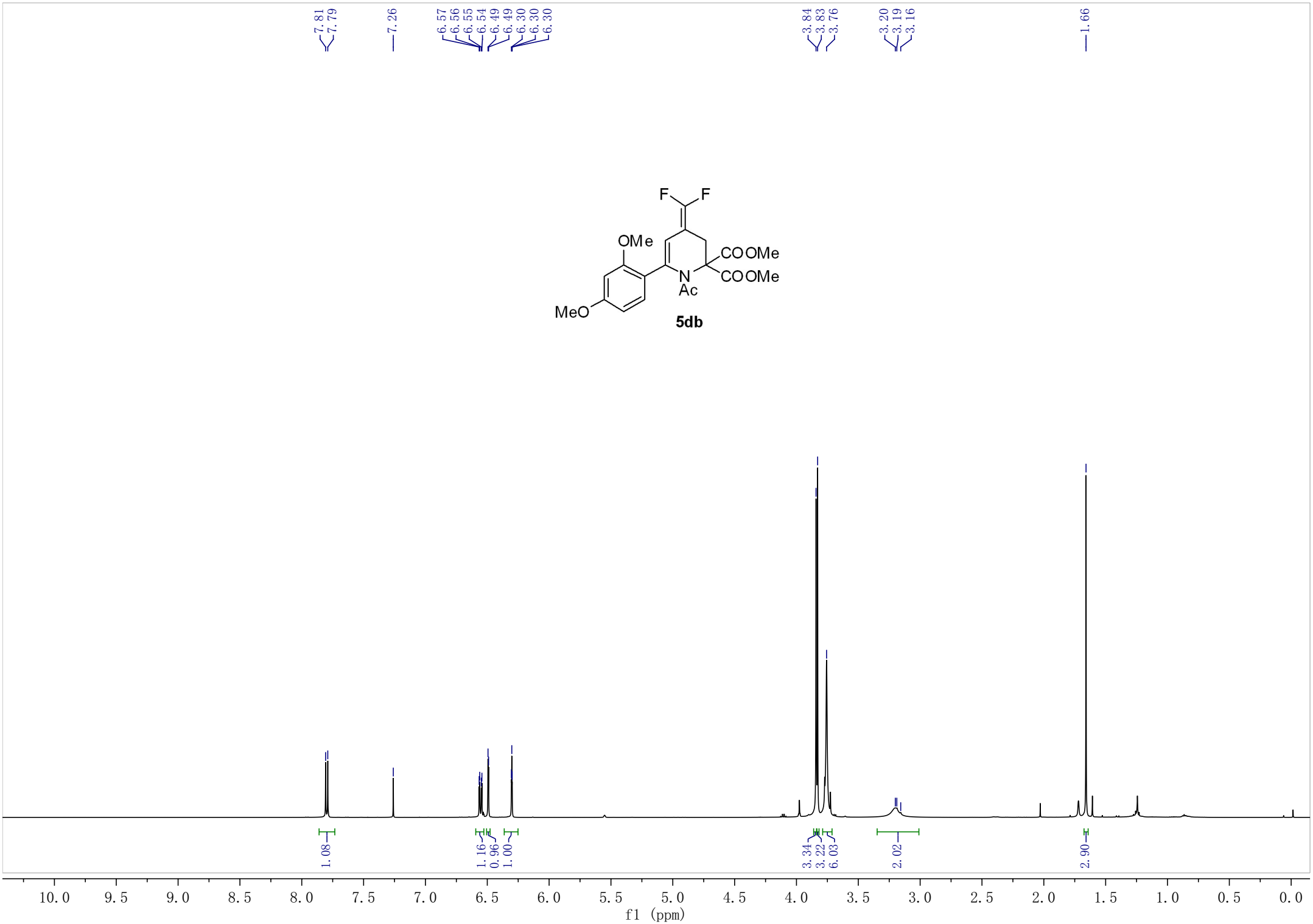
-170
-180
-190
-200
-210
f1 (ppm)


172.03
166.56
160.15
154.94
152.61
152.58
150.26
139.94
139.91
139.84
139.80
130.25
127.70
114.19
108.34
85.36
85.22
85.16
85.02
77.25
77.00
76.75
69.63
69.62
62.33
55.31
28.43
28.41
24.76
13.80
F
F
COOEt
COOEt
N
Ac
MeO
5ca
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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6.30
6.30
6.30
3.84
3.83
3.76
3.20
3.19
3.16
1.66
F
F
OMe
COOMe
COOMe
N
Ac
MeO
5db
1.08
1.16
0.96
1.00
3.34
3.22
6.03
2.02
2.90
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
1.5
1.0
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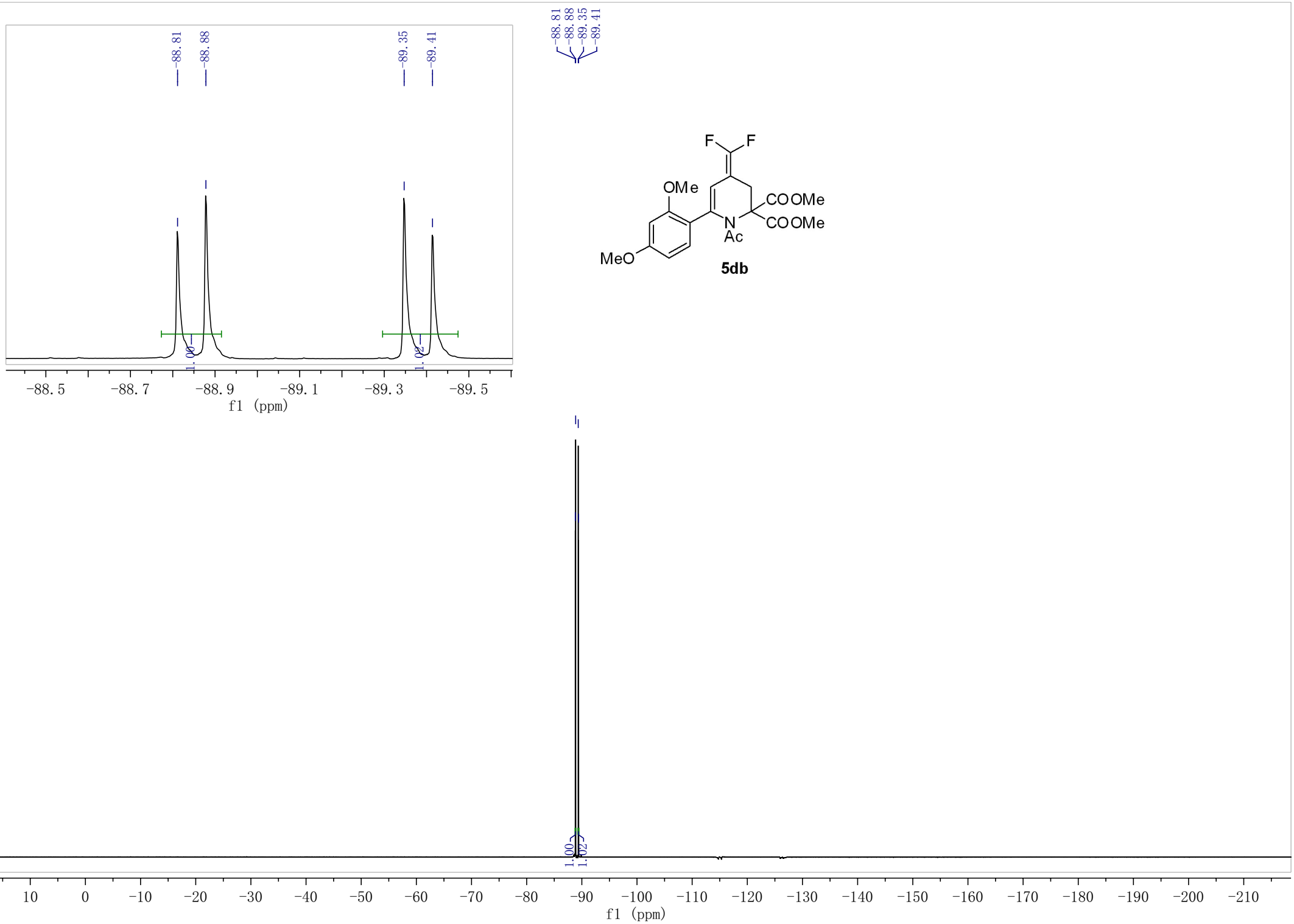
0.0
f1 (ppm)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-88.7
-88.9
-89.1
-89.3
-89.5
f1 (ppm)
F
F
OMe
COOMe
COOMe
N
Ac
MeO
5db
1.00
1.02
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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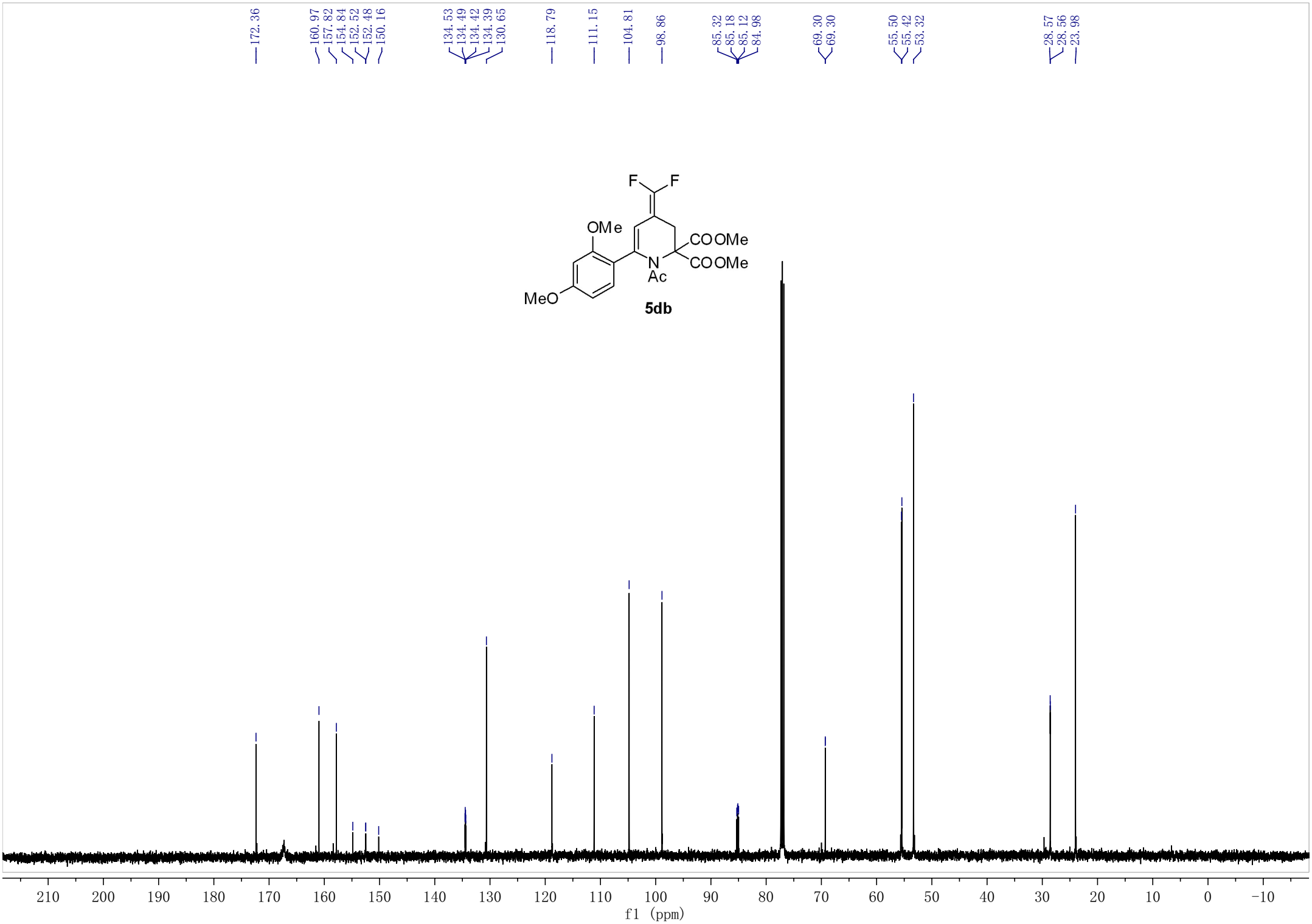
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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130.65
118.79
111.15
104.81
98.86
85.32
85.18
85.12
84.98
69.30
69.30
55.50
55.42
53.32
28.57
28.56
23.98
F
F
OMe
COOMe
COOMe
N
Ac
MeO
5db
210
200
190
180
170
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100
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80
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40
30
20
10
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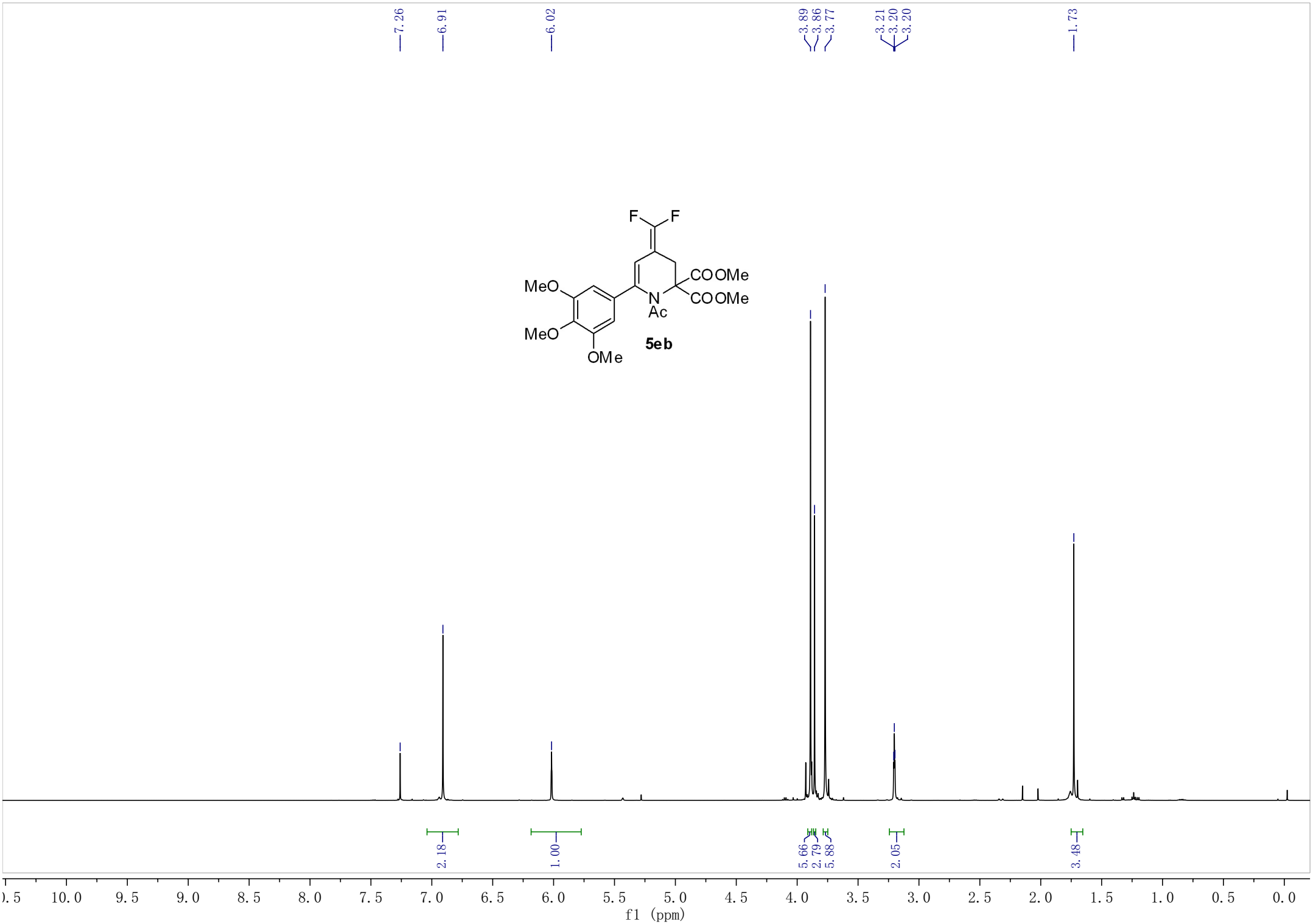
-10
f1 (ppm)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6.91
6.02
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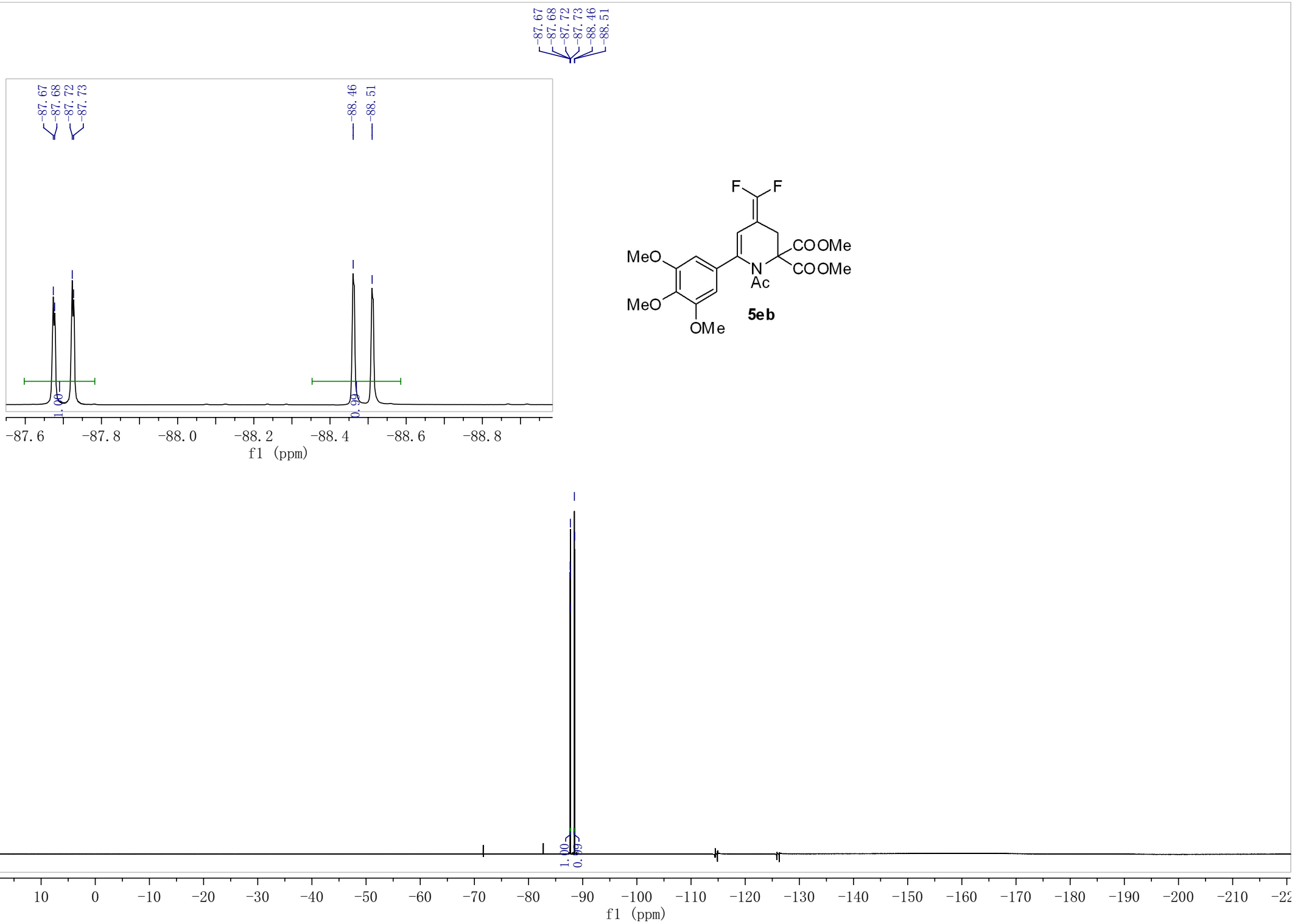
3.21
3.20
3.20
1.73
F
F
COOMe
COOMe
N
Ac
MeO
MeO
OMe
5eb
2.18
1.00
5.66
2.79
5.88
2.05
3.48
f1 (ppm)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-88.2
-88.4
-88.6
-88.8
f1 (ppm)
F
F
MeO
MeO
OMe
N
Ac
COOMe
COOMe
5eb
1.00
0.69
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-100
-110
-120
-130
-140
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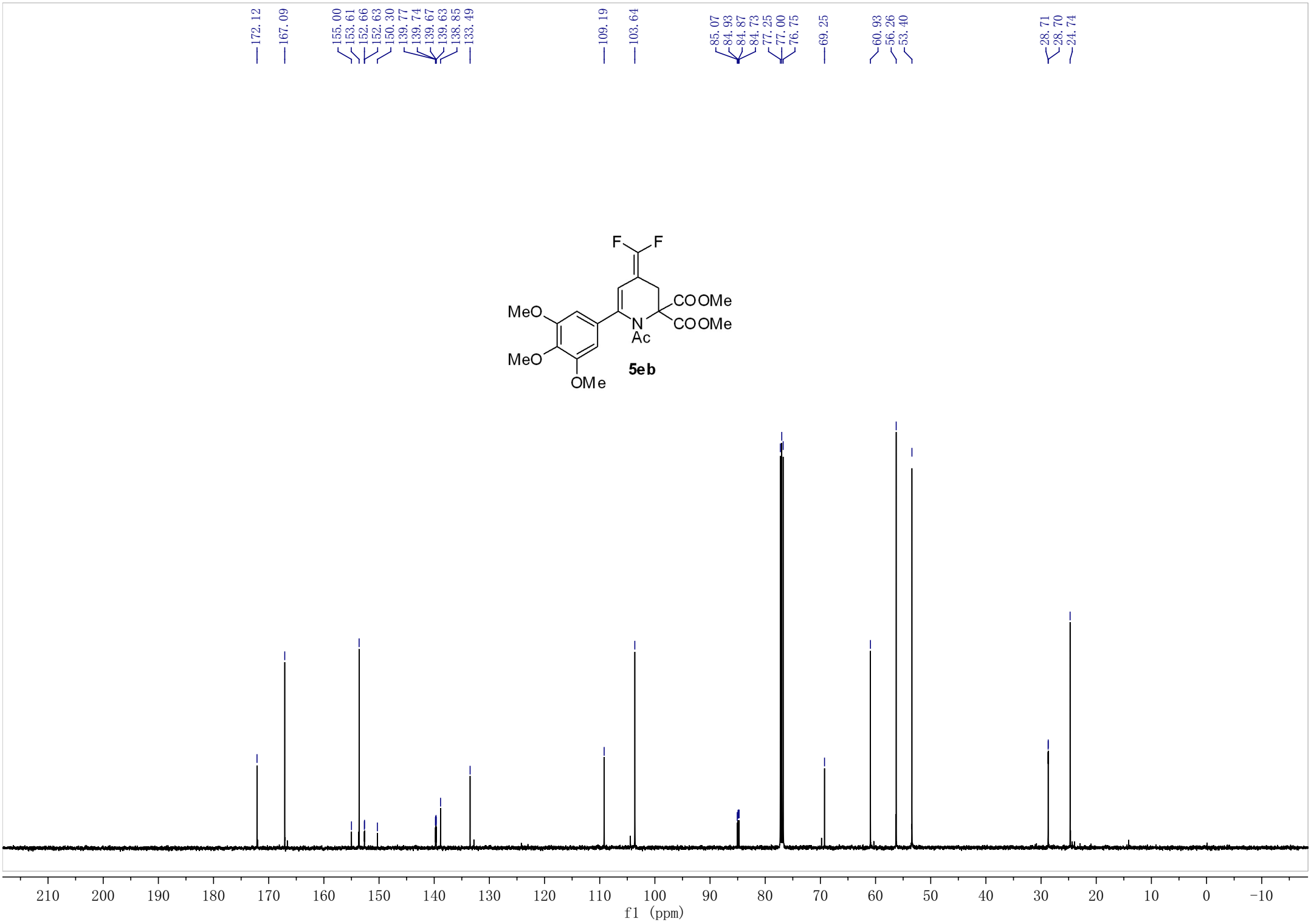
-170
-180
-190
-200
-210
f1 (ppm)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138.85
133.49
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103.64
85.07
84.93
84.87
84.73
77.25
77.00
76.75
69.25
60.93
56.26
53.40
28.71
28.70
24.74
F
F
COOMe
COOMe
N
Ac
MeO
MeO
OMe
5eb
210
200
190
180
170
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140
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120
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100
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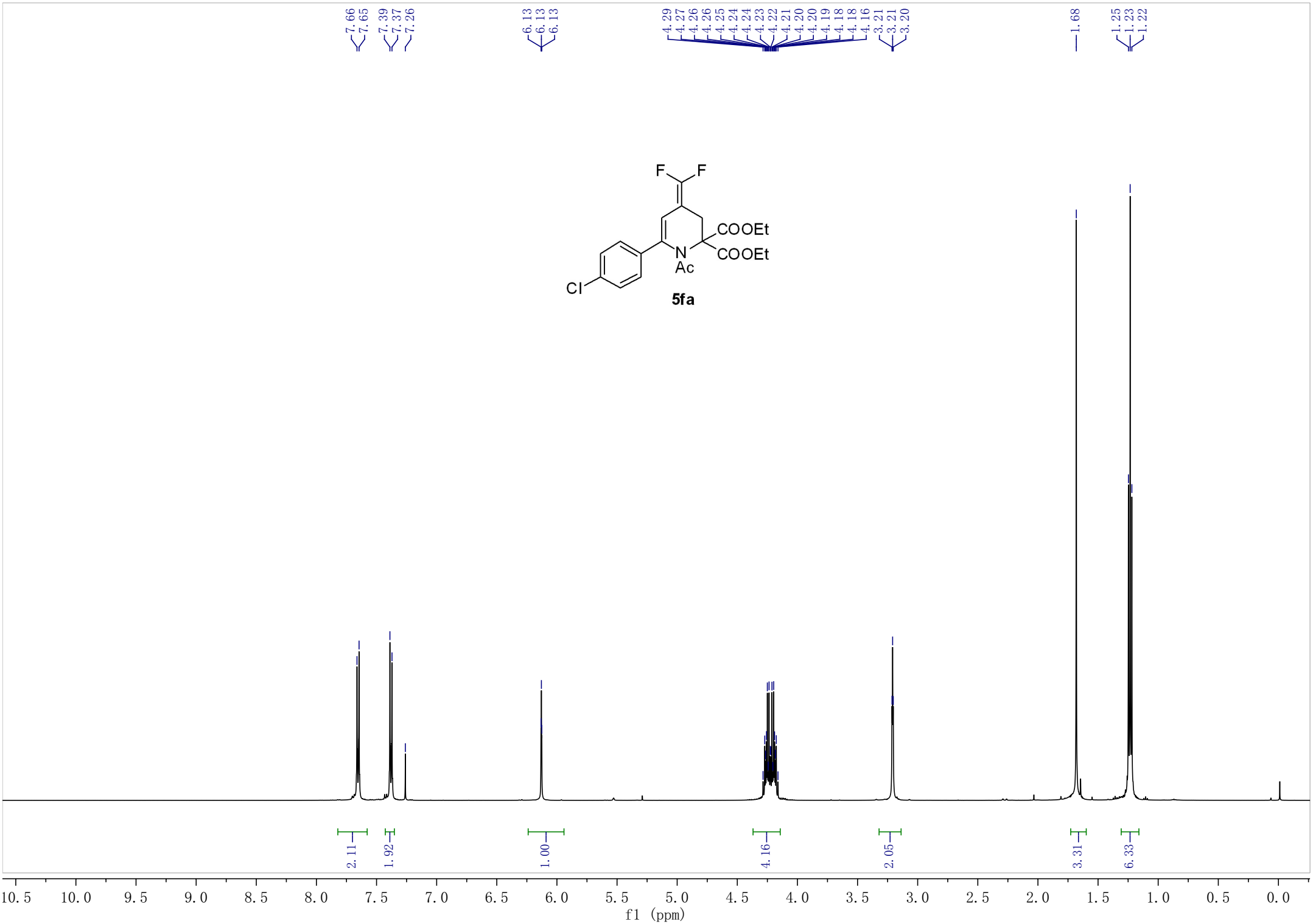
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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6.13
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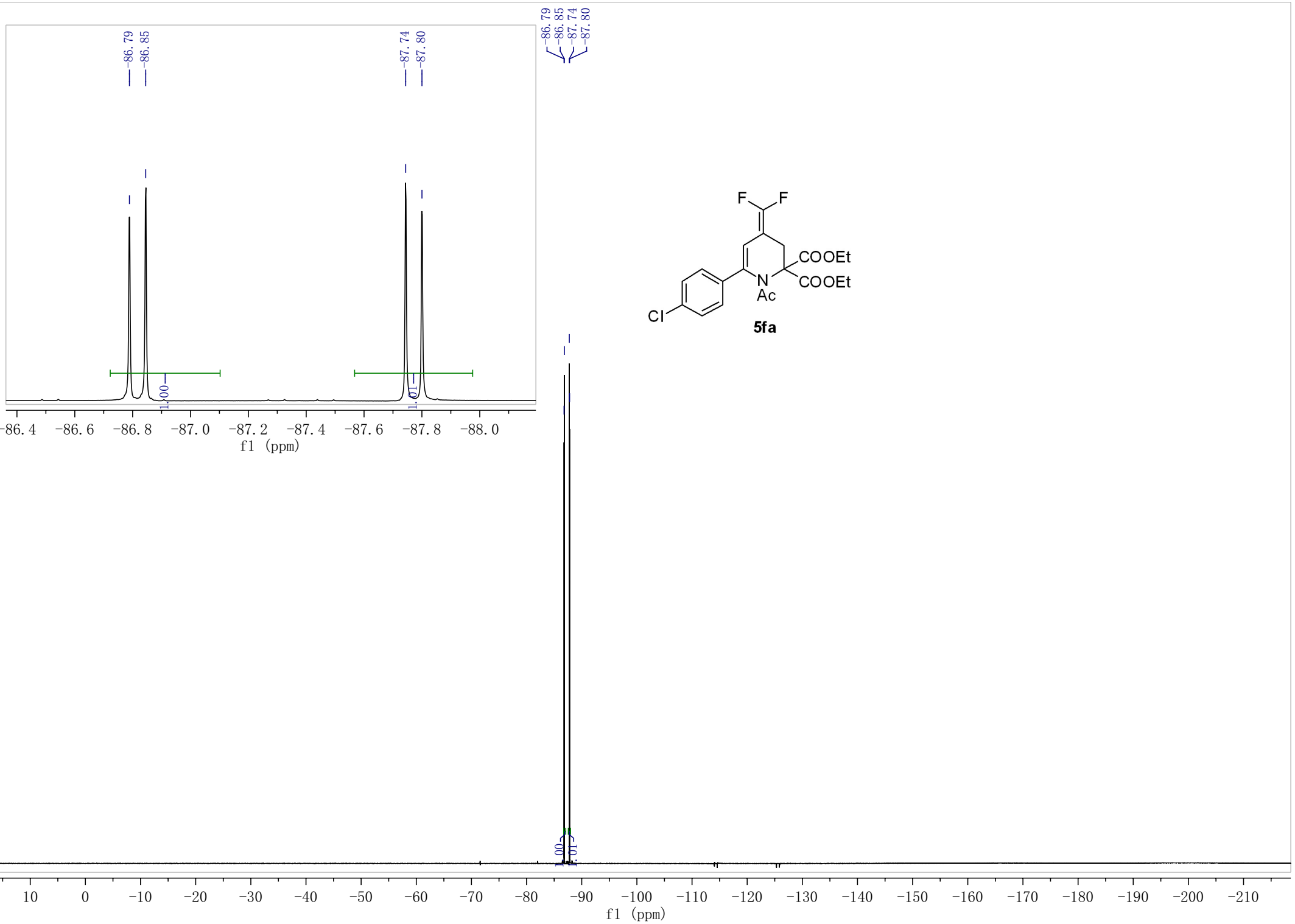
4.26
4.25
4.24
4.24
4.23
4.22
4.21
4.20
4.20
4.19
4.18
4.18
4.16
3.21
3.21
3.20
1.68
1.25
1.23
1.22
F
F
COOEt
COOEt
N
Ac
Cl
5fa
2.11
1.92
1.00
4.16
2.05
3.31
6.33
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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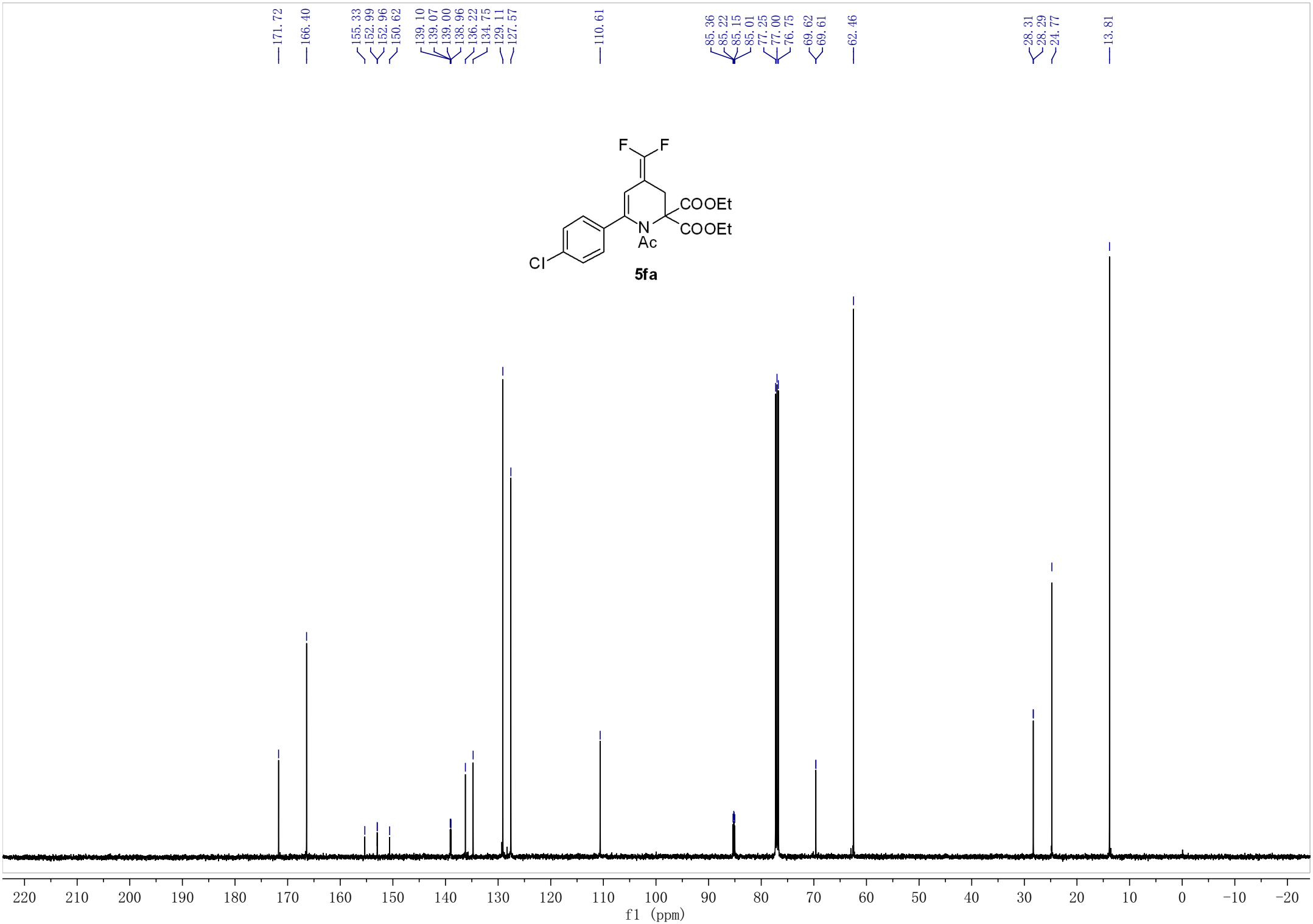
1.01
-86.4
-86.6
-86.8
-87.0
-87.2
-87.4
-87.6
-87.8
-88.0
f1 (ppm)
F
F
COOEt
COOEt
N
Ac
Cl
5fa
1.00
1.10
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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166.40
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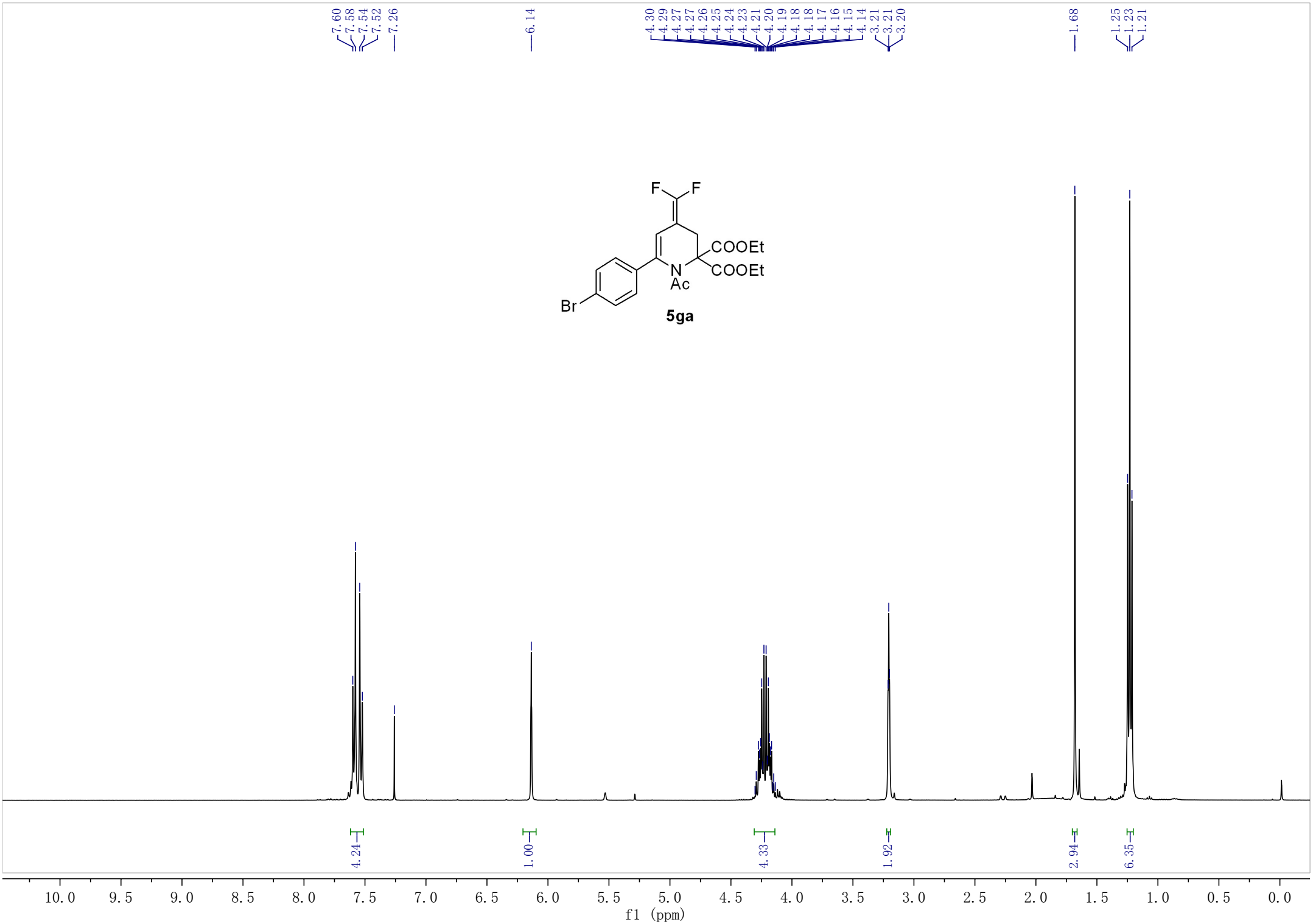
152.96
150.62
139.10
139.07
139.00
138.96
136.22
134.75
129.11
127.57
110.61
85.36
85.22
85.15
85.01
77.25
77.00
76.75
69.62
69.61
62.46
28.31
28.29
24.77
13.81
F
F
COOEt
COOEt
N
Ac
Cl
5fa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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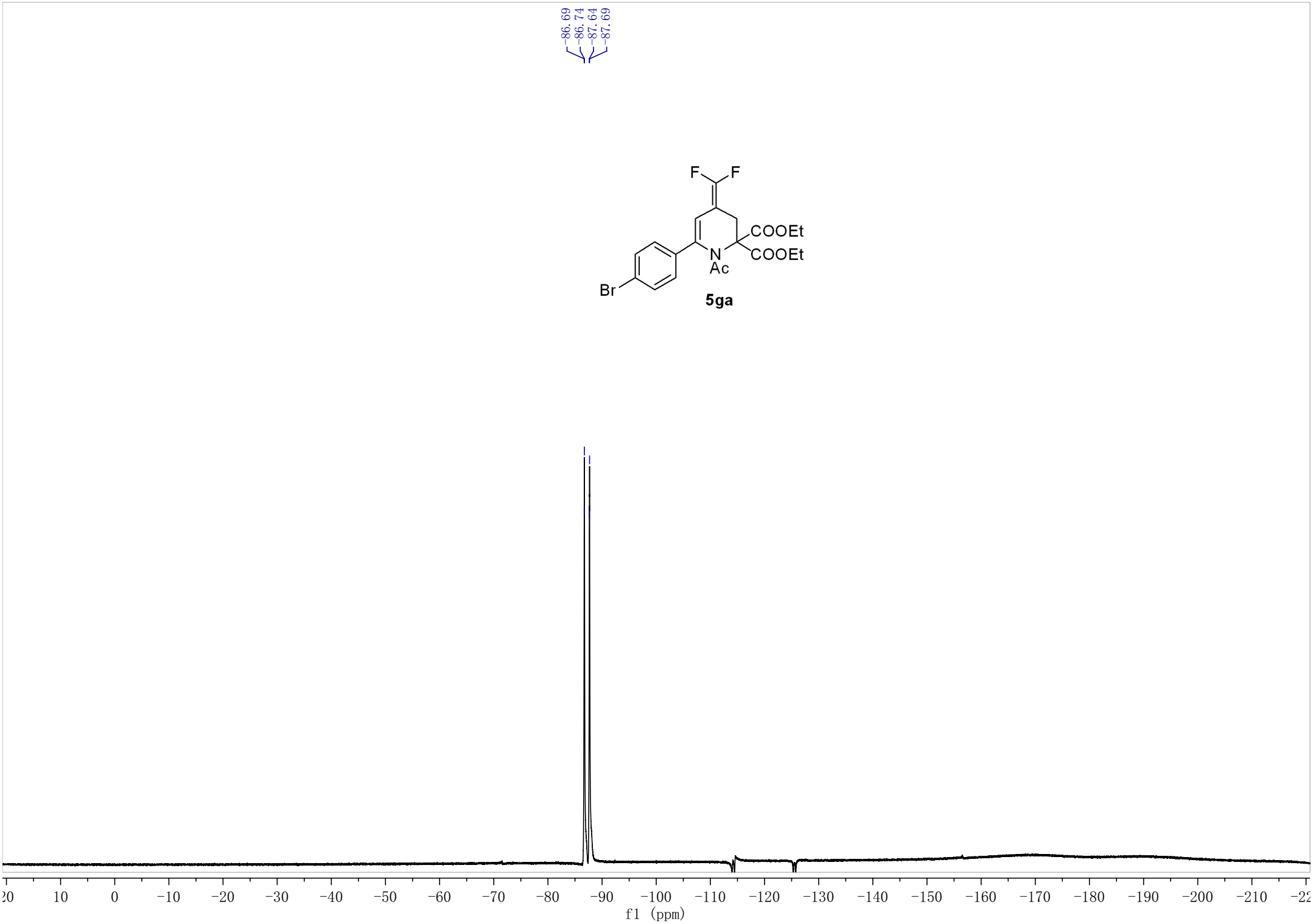
6.14
4.30
4.29
4.27
4.27
4.26
4.25
4.24
4.23
4.21
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
3.21
3.20
1.68
1.25
1.23
1.21
F
F
COOEt
COOEt
N
Ac
Br
5ga
4.24
1.00
4.33
1.92
2.94
6.35
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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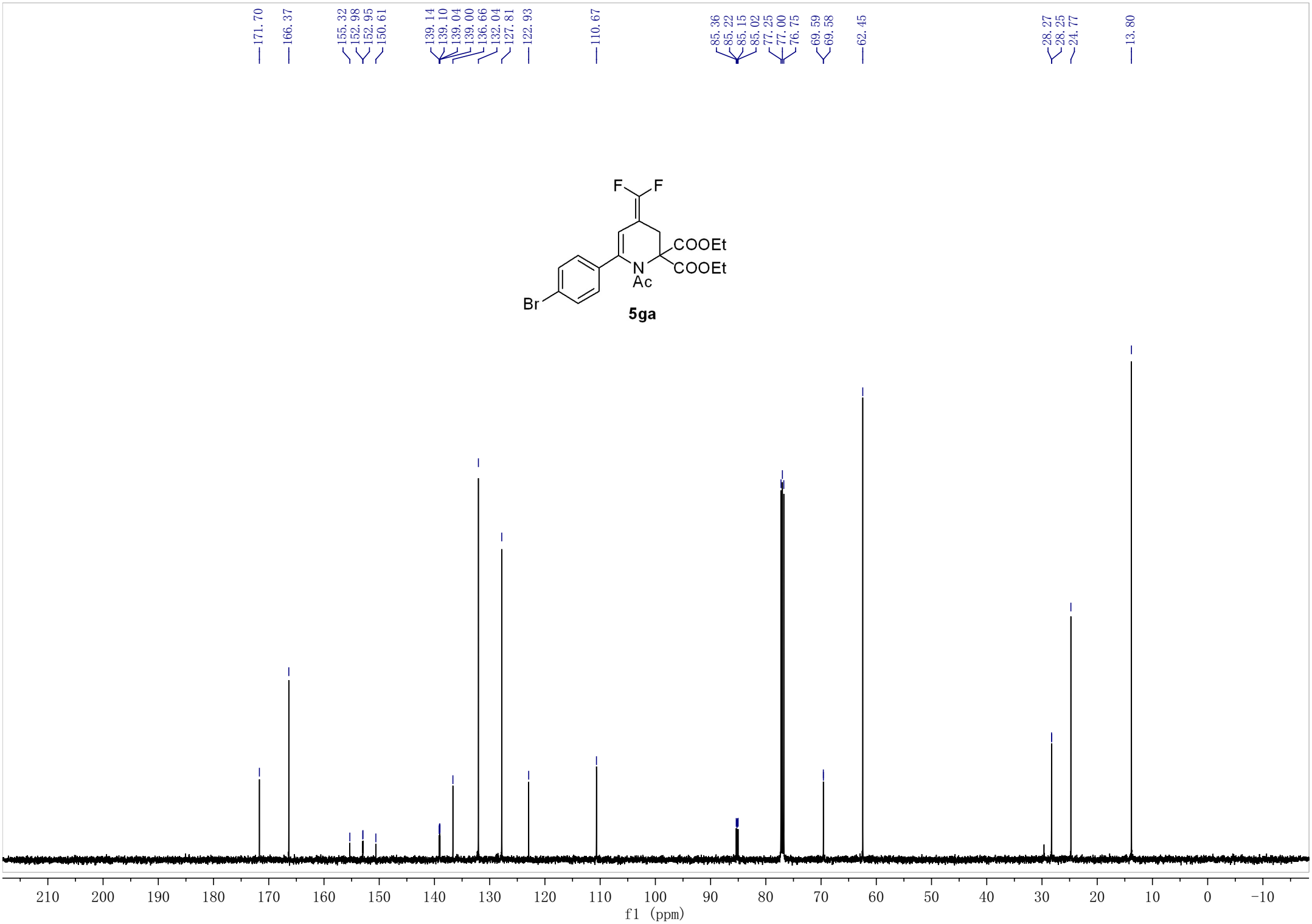
-86.74
-87.64
-87.69
F
F
COOEt
COOEt
N
Ac
Br
5ga
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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139.10
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139.00
136.66
132.04
127.81
122.93
110.67
85.36
85.22
85.15
85.02
77.25
77.00
76.75
69.59
69.58
62.45
28.27
28.25
24.77
13.80
F
F
COOEt
COOEt
N
Ac
Br
5ga
210
200
190
180
170
160
150
140
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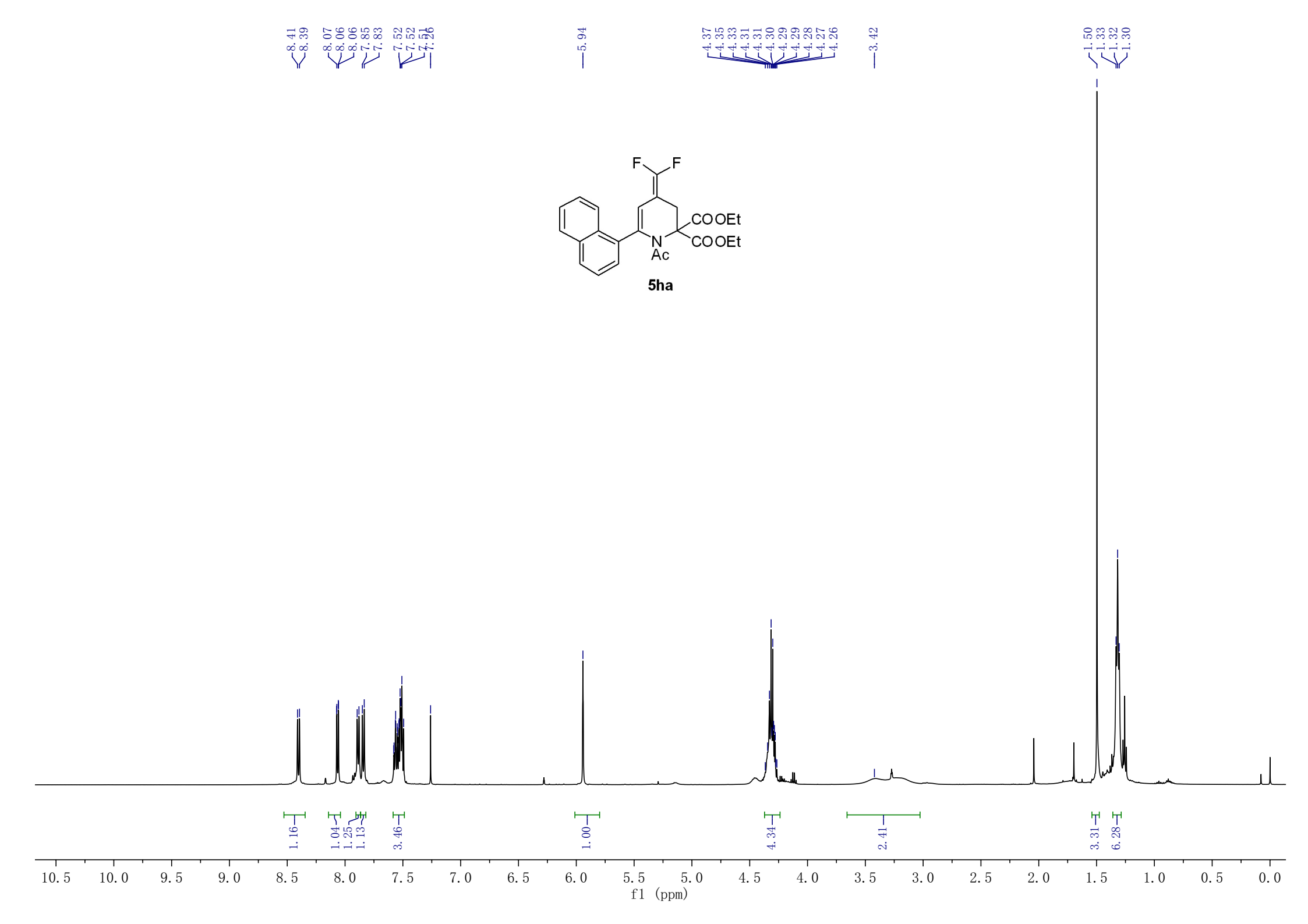
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.51
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4.35
4.33
4.31
4.31
4.30
4.29
4.29
4.28
4.27
4.26
3.42
1.50
1.33
1.32
1.30
F
F
COOEt
COOEt
N
Ac
5ha
1.16
1.04
1.25
1.13
3.46
1.00
4.34
2.41
3.31
6.28
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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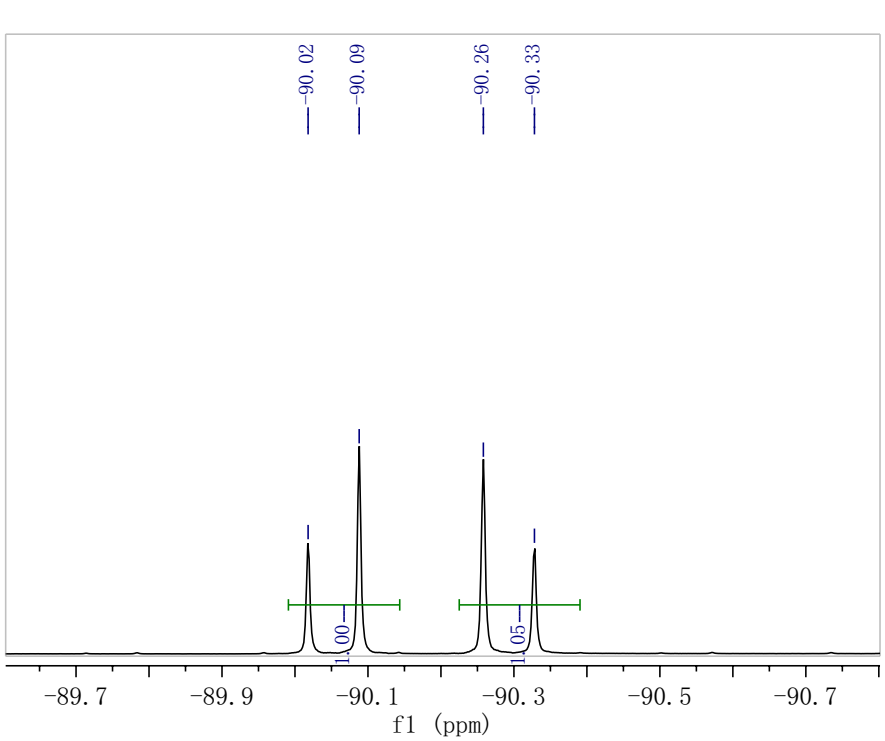
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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-90.09
-90.26
-90.33
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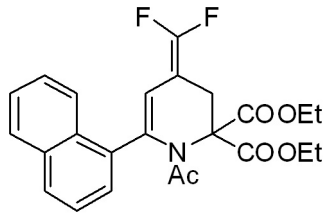
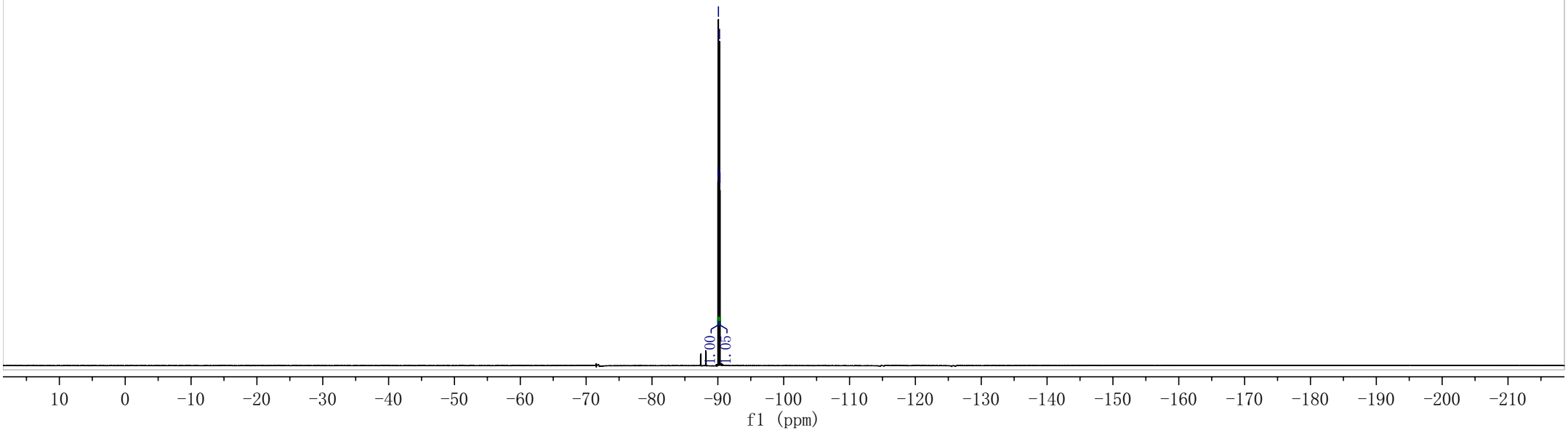
1.05
-89.7
-89.9
-90.1
-90.3
-90.5
-90.7
f1 (ppm)


F
F
COOEt
COOEt
N
Ac

5ha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1.05
10
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-20
-30
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-50
-60
-70
-80
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-100
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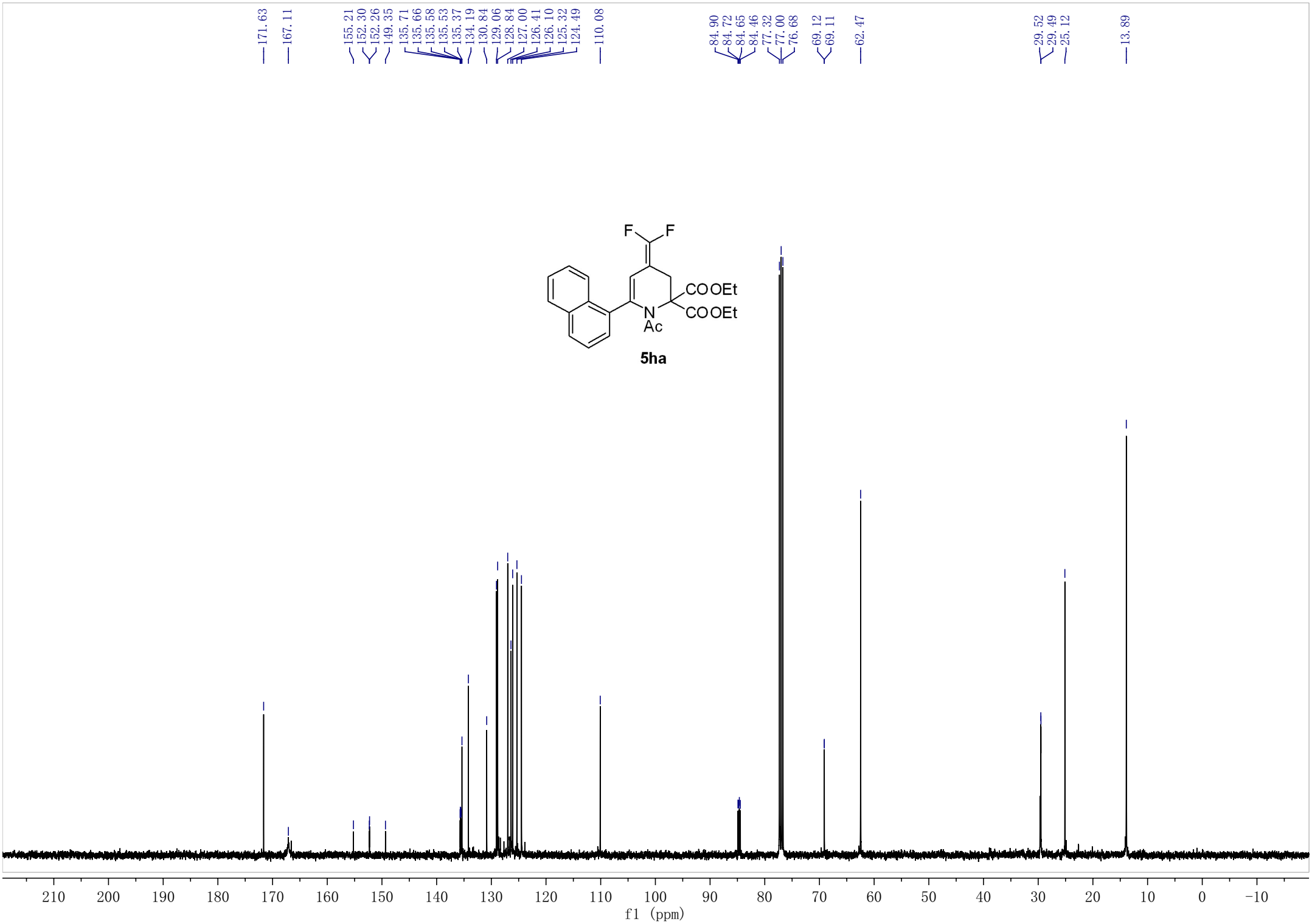
-170
-180
-190
-200
-210
f1 (ppm)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135.58
135.53
135.37
134.19
130.84
129.06
128.84
127.00
126.41
126.10
125.32
124.49
110.08
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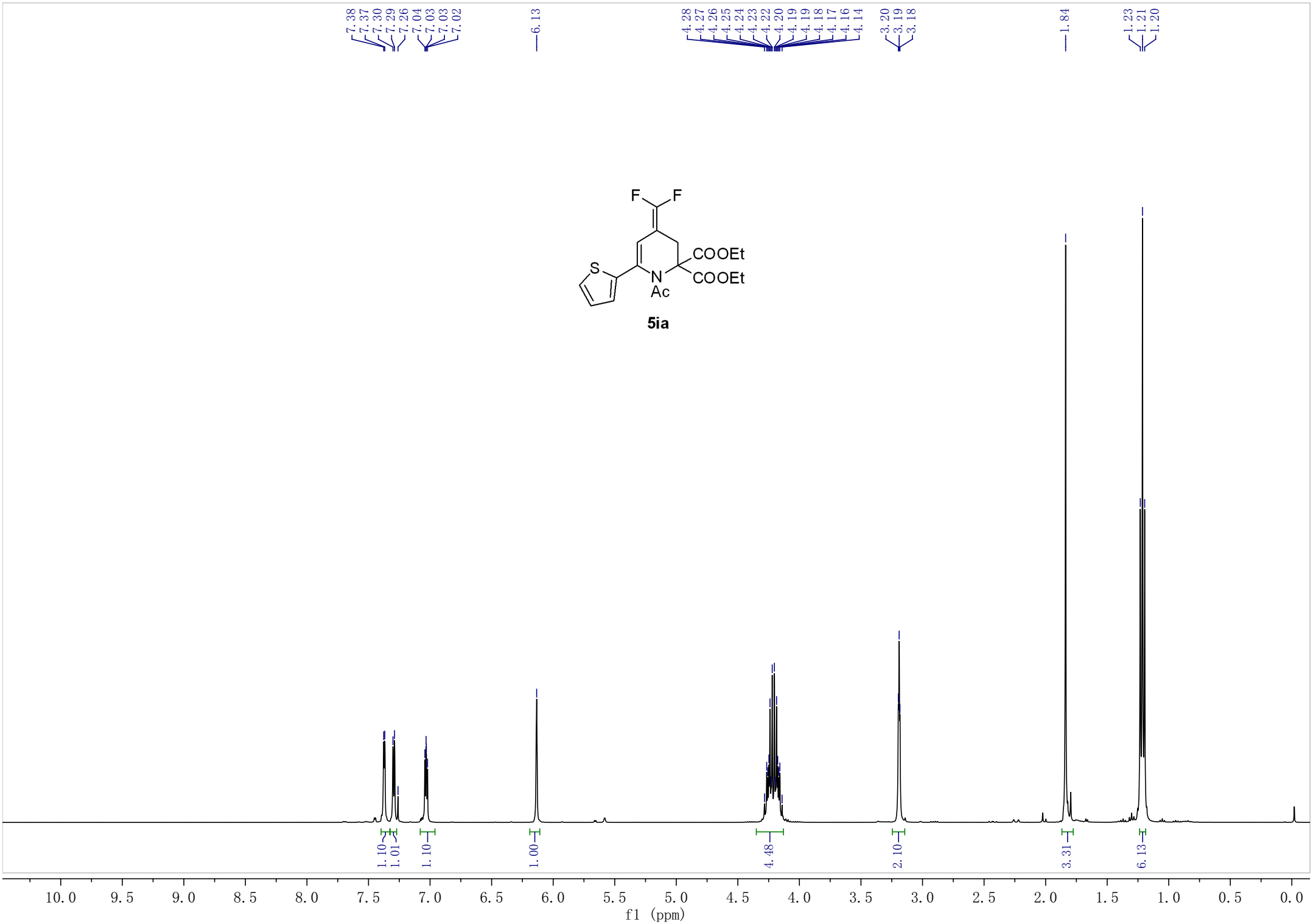
84.72
84.65
84.46
77.32
77.00
76.68
69.12
69.11
62.47
29.52
29.49
25.12
13.89
F
F
COOEt
COOEt
N
Ac
5ha
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.03
7.03
7.02
6.13
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.20
4.19
4.18
4.17
4.16
4.14
3.20
3.19
3.18
1.84
1.23
1.21
1.20
F
F
COOEt
COOEt
S
N
Ac
5ia
1.10
1.01
1.10
1.00
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2.10
3.31
6.13
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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3.0
2.5
2.0
1.5
1.0
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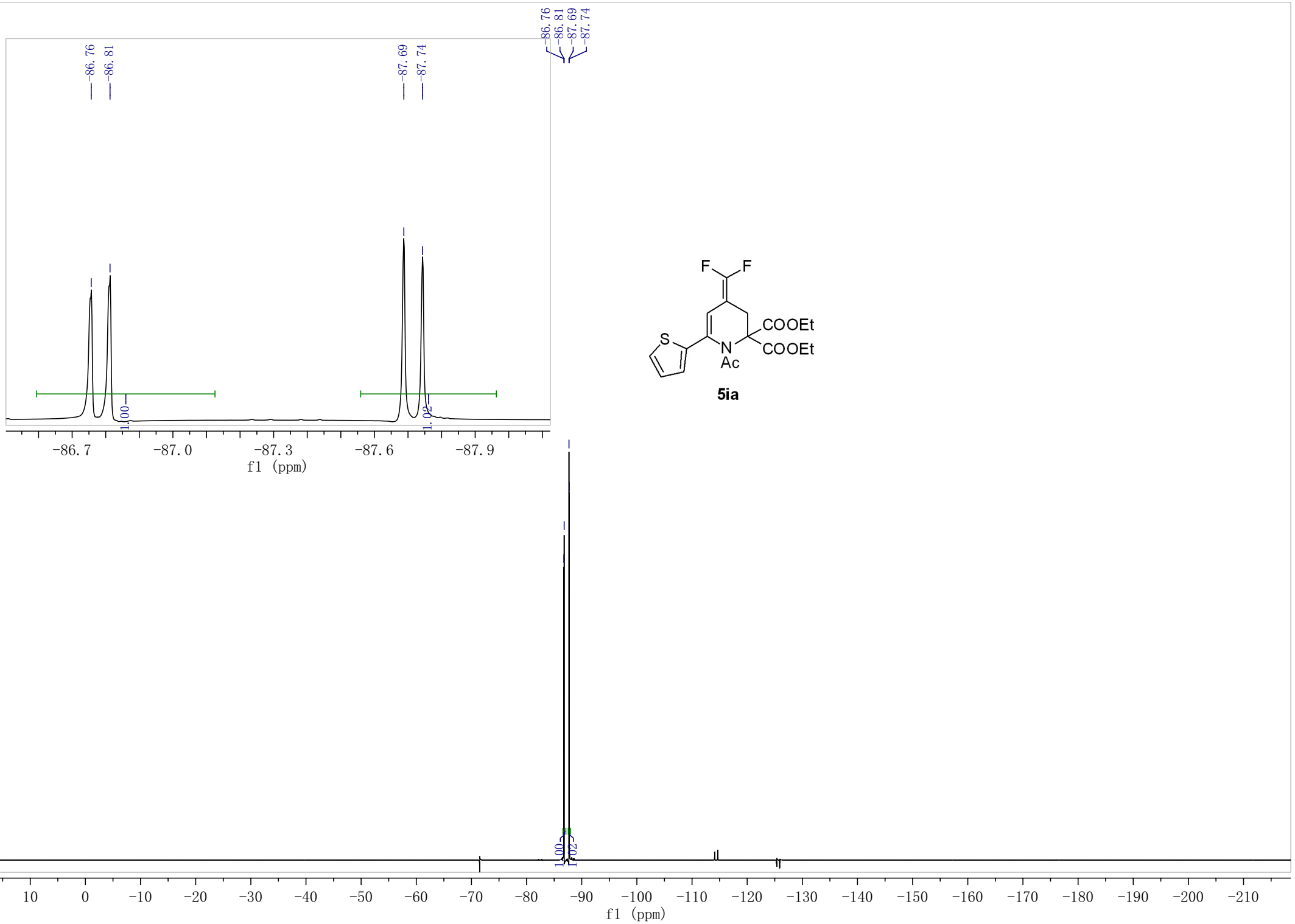
0.0
f1 (ppm)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1.02
-86.7
-87.0
-87.3
-87.6
-87.9
f1 (ppm)
F
F
COOEt
COOEt
S
N
Ac
5ia
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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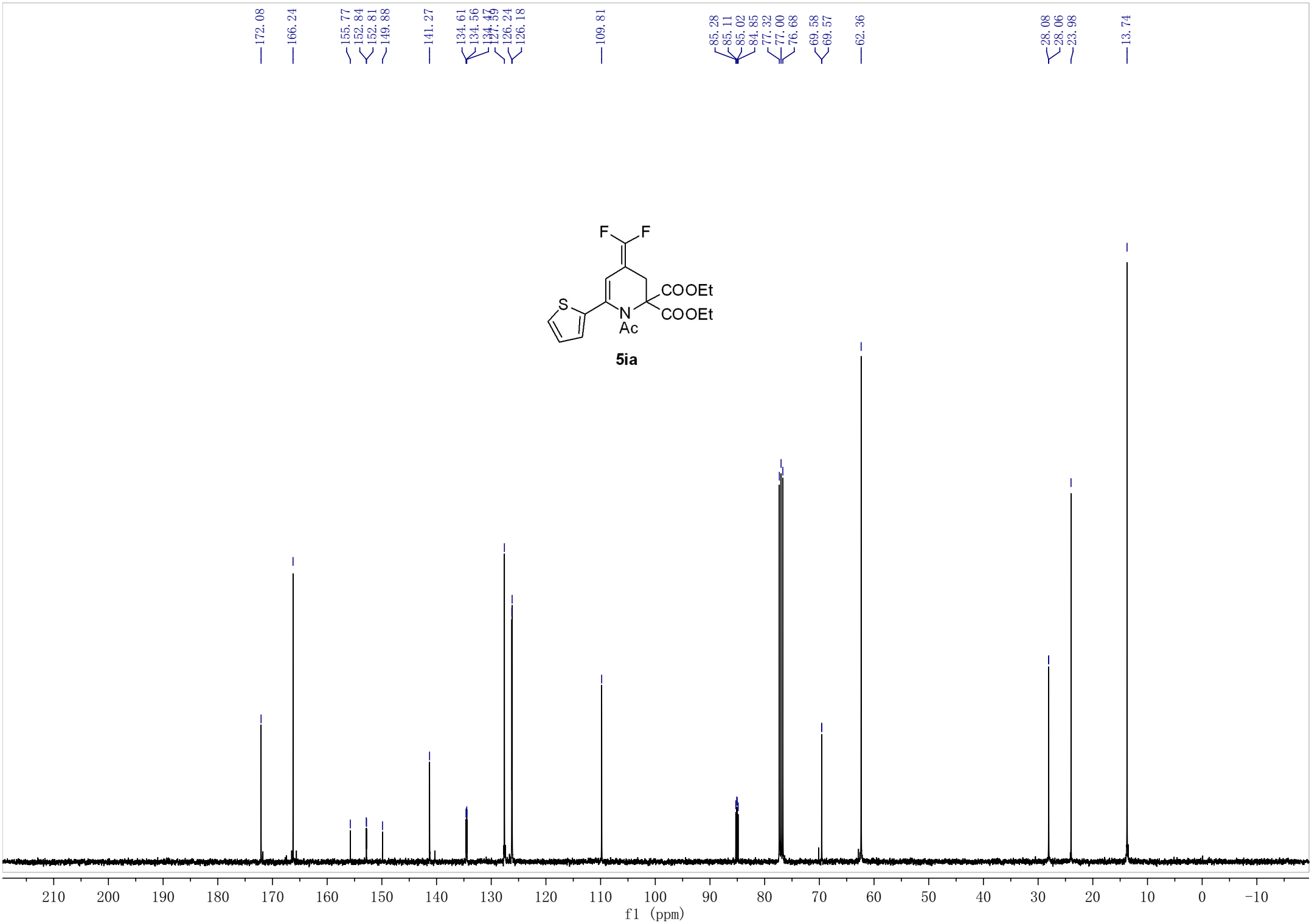
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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134.56
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126.18
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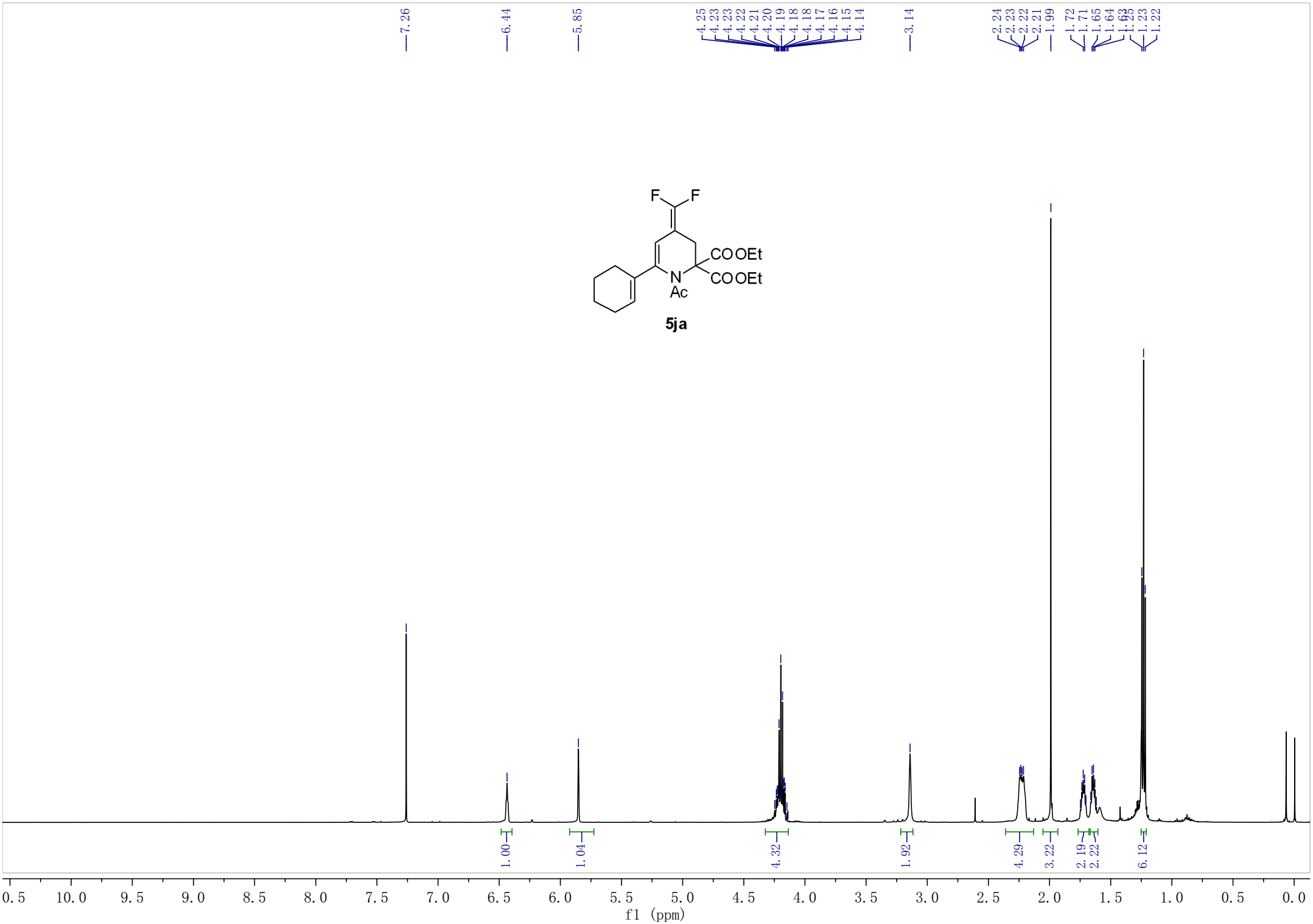
85.11
85.02
84.85
77.32
77.00
76.68
69.58
69.57
62.36
28.08
28.06
23.98
13.74
F
F
COOEt
COOEt
S
N
Ac
5ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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4.23
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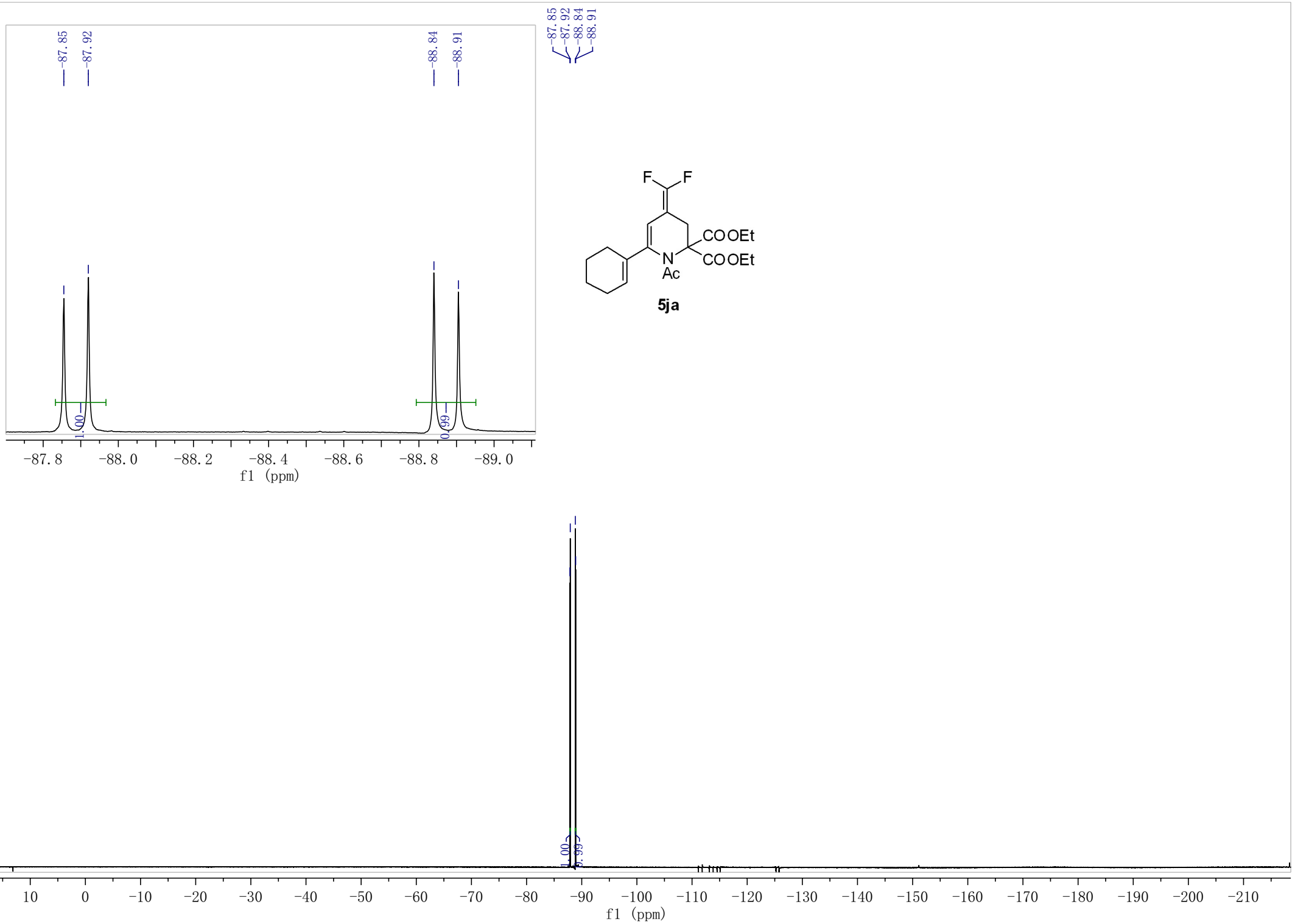
4.21
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
3.14
2.24
2.23
2.22
2.21
1.99
1.72
1.71
1.65
1.64
1.23
1.22
F
F
COOEt
COOEt
N
Ac
5ja
1.00
1.04
4.32
1.92
4.29
3.22
2.19
2.22
6.12
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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-87.8
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-88.2
-88.4
-88.6
-88.8
-89.0
f1 (ppm)
F
F
COOEt
COOEt
N
Ac
5ja
1.00
0.99
10
0
-10
-20
-30
-40
-50
-60
-70
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-130
-140
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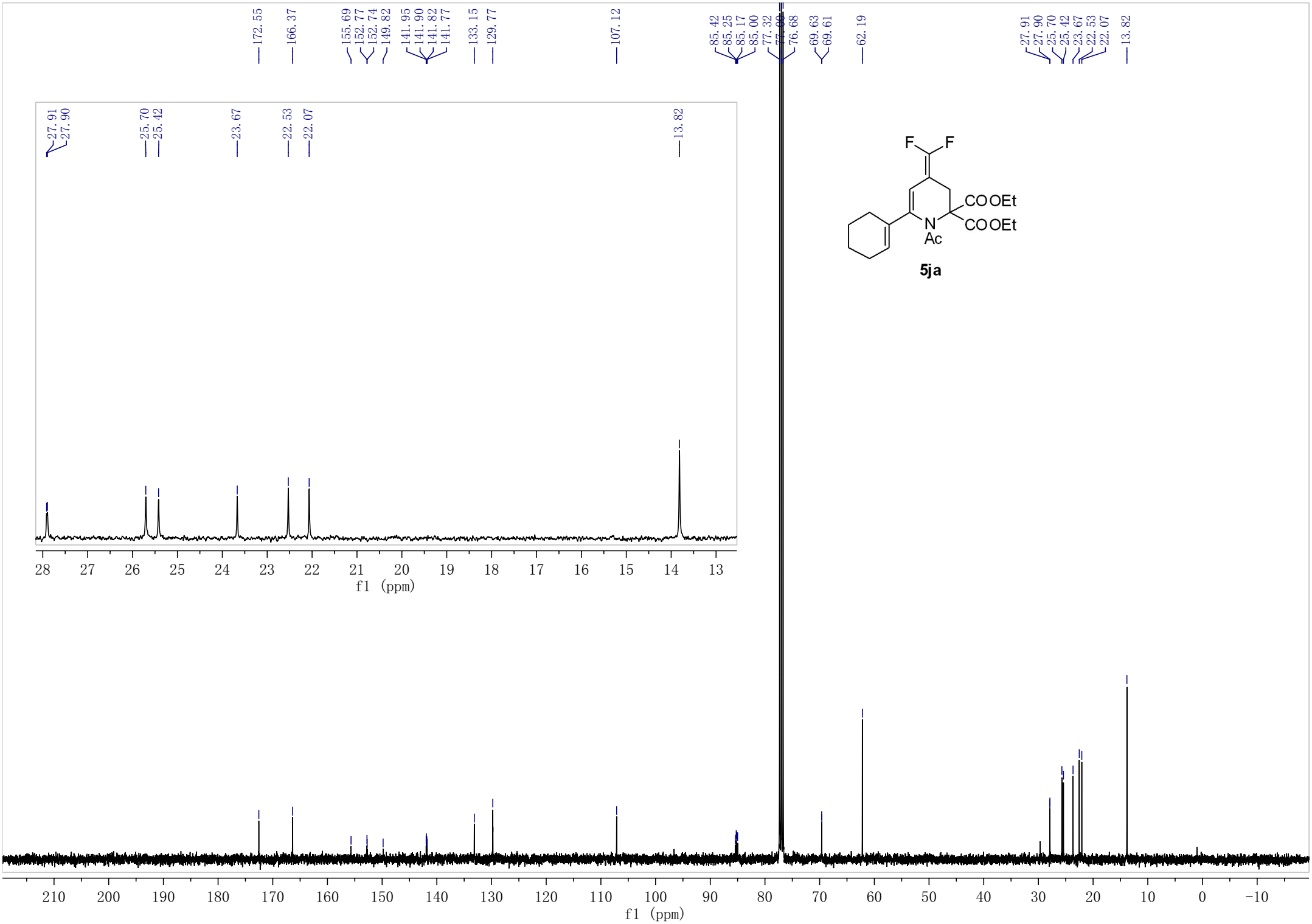
-170
-180
-190
-200
-210
f1 (ppm)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107.12
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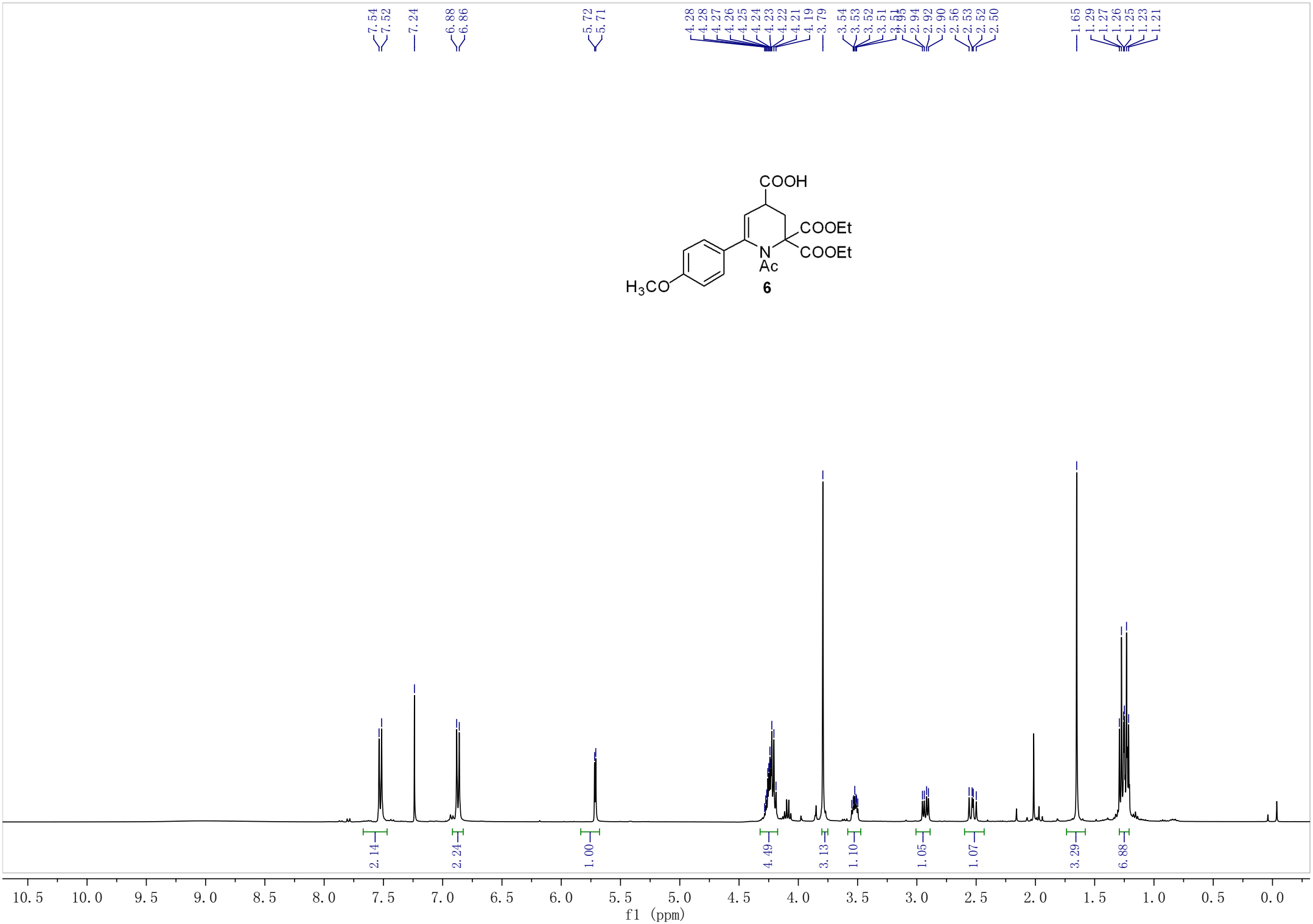
85.25
85.17
85.00
77.32
77.00
76.68
69.63
69.61
62.19
27.91
27.90
25.70
25.42
23.67
22.53
22.07
13.82
f1 (ppm)
F
F
COOEt
COOEt
N
Ac
5ja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7.24
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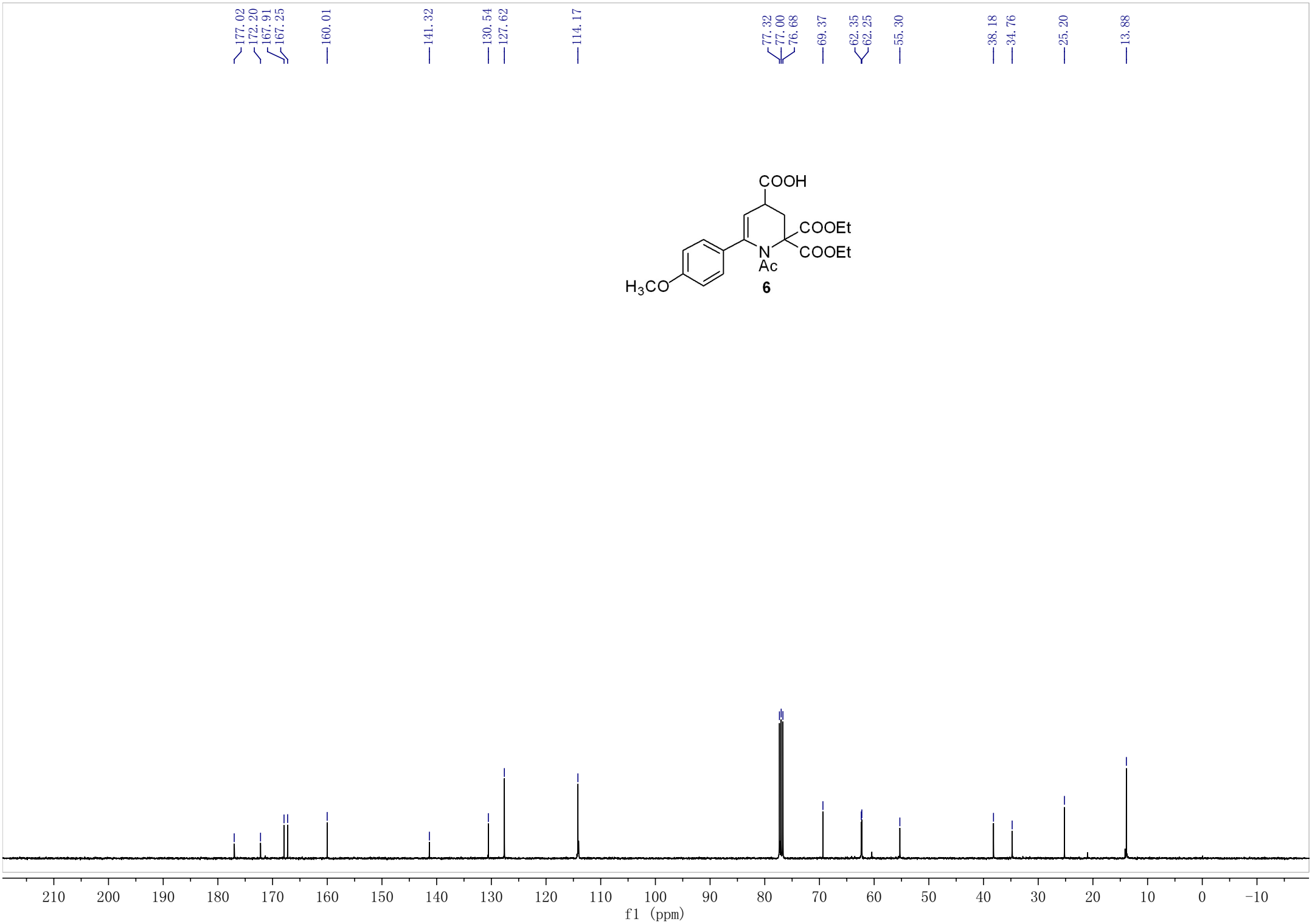
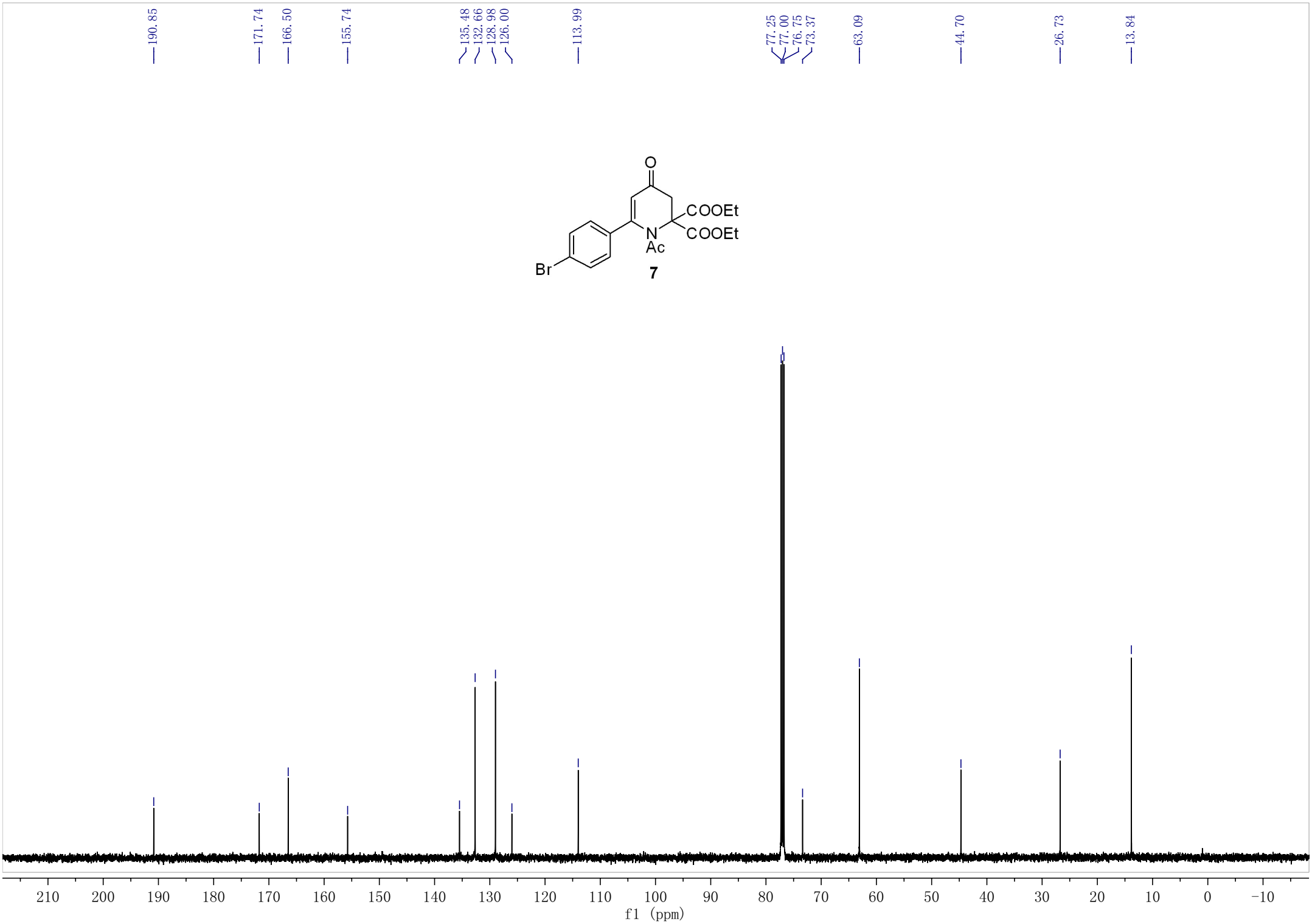
5.71
4.28
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.21
4.19
3.79
3.54
3.53
3.52
3.51
2.94
2.92
2.90
2.56
2.53
2.52
2.50
1.65
1.29
1.27
1.26
1.25
1.23
1.21
COOH
COOEt
COOEt
N
Ac
H3CO
6
2.14
2.24
1.00
4.49
3.13
1.10
1.05
1.07
3.29
6.88
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.02
172.20
167.91
167.25
160.01
141.32
130.54
127.62
114.17
77.32
77.00
76.68
69.37
62.35
62.25
55.30
38.18
34.76
25.20
13.88
COOH
COOEt
COOEt
N
Ac
H3CO
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.63
7.61
7.58
7.56
7.26
5.66
4.29
4.29
4.28
4.27
3.33
1.70
1.30
1.28
1.27
O
COOEt
COOEt
N
Ac
Br
7
2.15
2.16
1.00
4.42
2.10
3.46
6.01
0.5
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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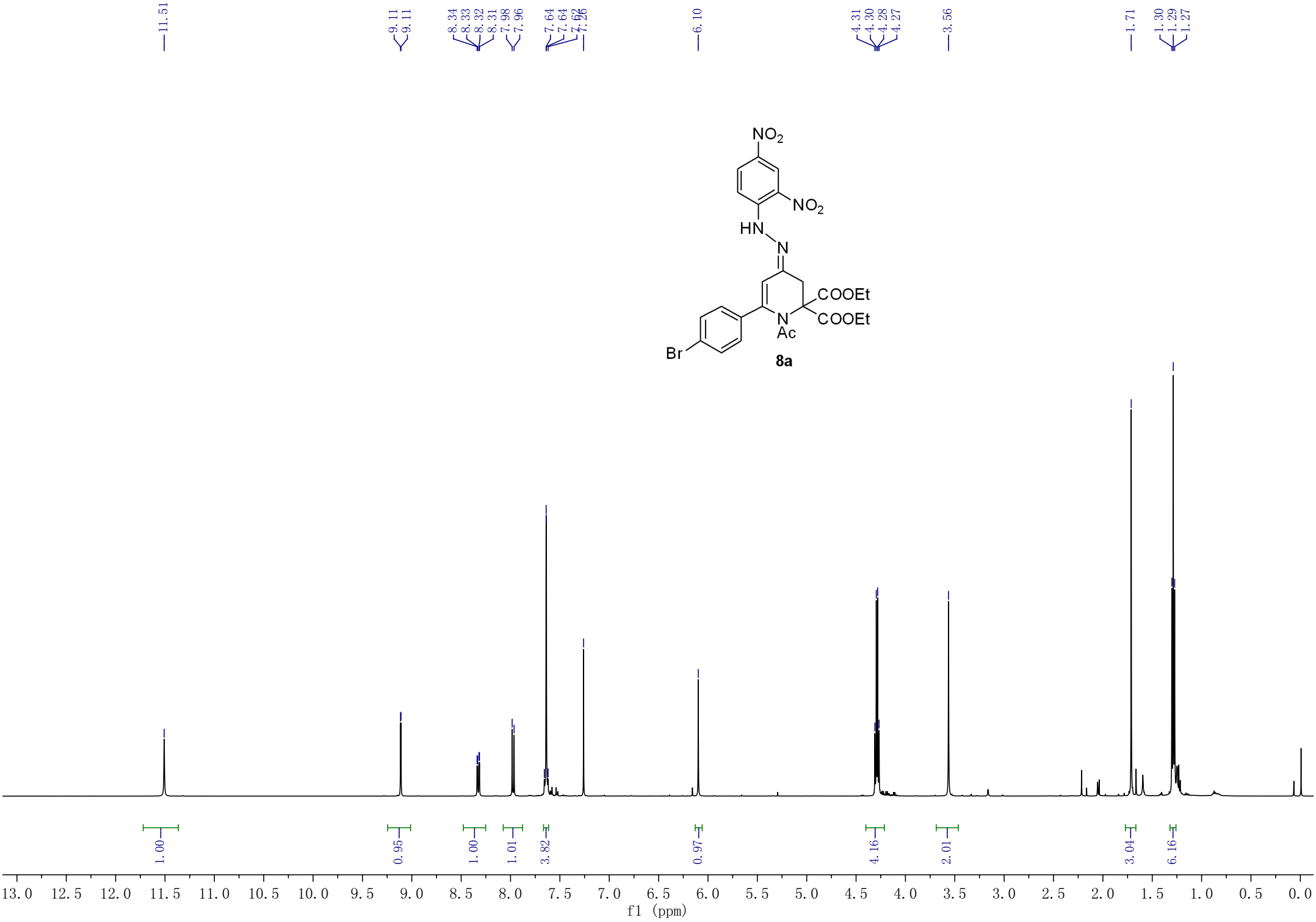
155.74
135.48
132.66
128.98
126.00
113.99
77.25
77.00
76.75
73.37
63.09
44.70
26.73
13.84
O
COOEt
COOEt
N
Ac
Br
7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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9.11
9.11
8.34
8.33
8.32
8.31
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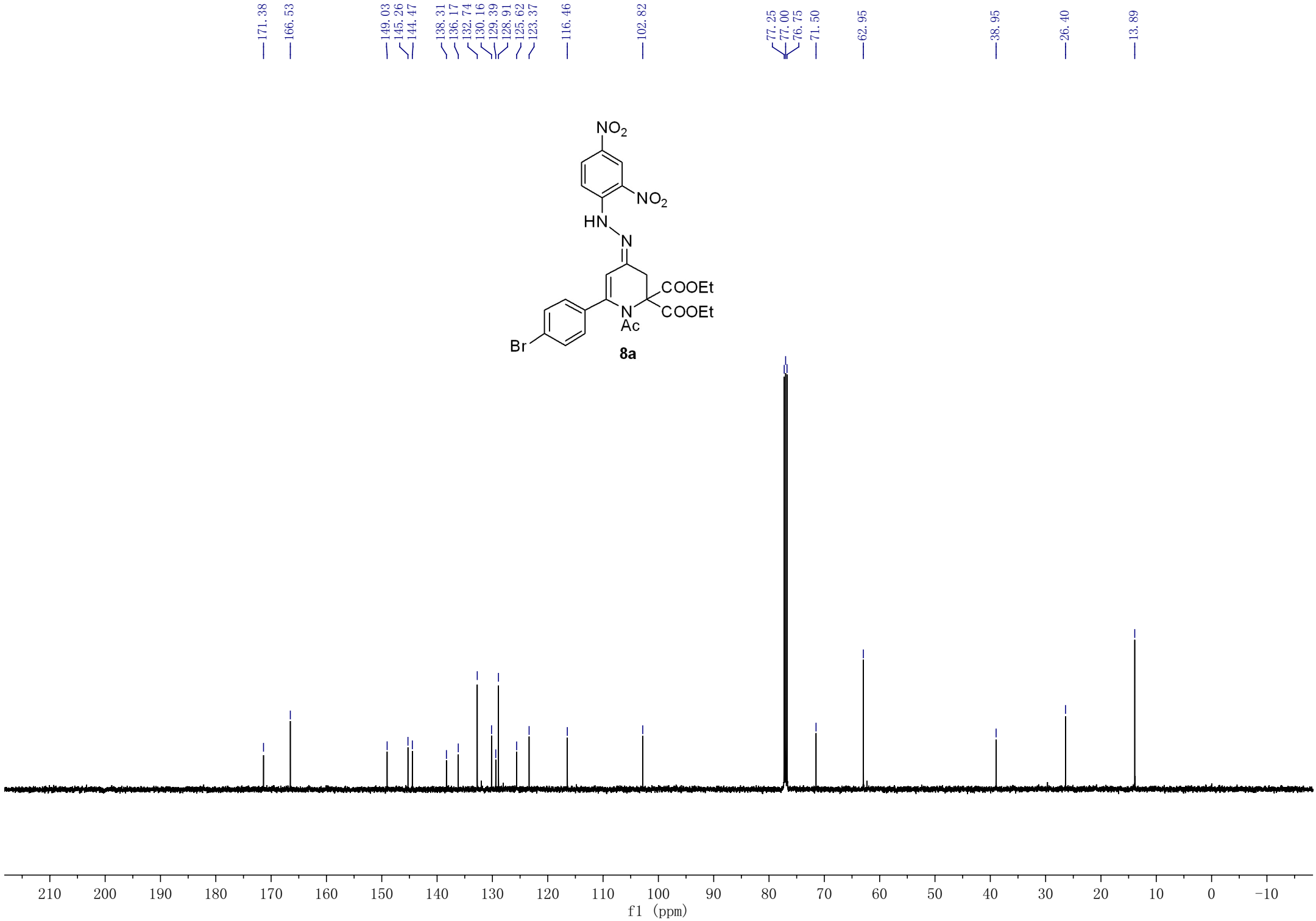
7.96
7.64
7.64
7.62
7.26
6.10
4.31
4.30
4.28
4.27
3.56
1.71
1.30
1.29
1.27
NO2
NO2
HN
N
COOEt
COOEt
N
Ac
Br
8a
1.00
0.95
1.00
1.01
3.82
0.97
4.16
2.01
3.04
6.16
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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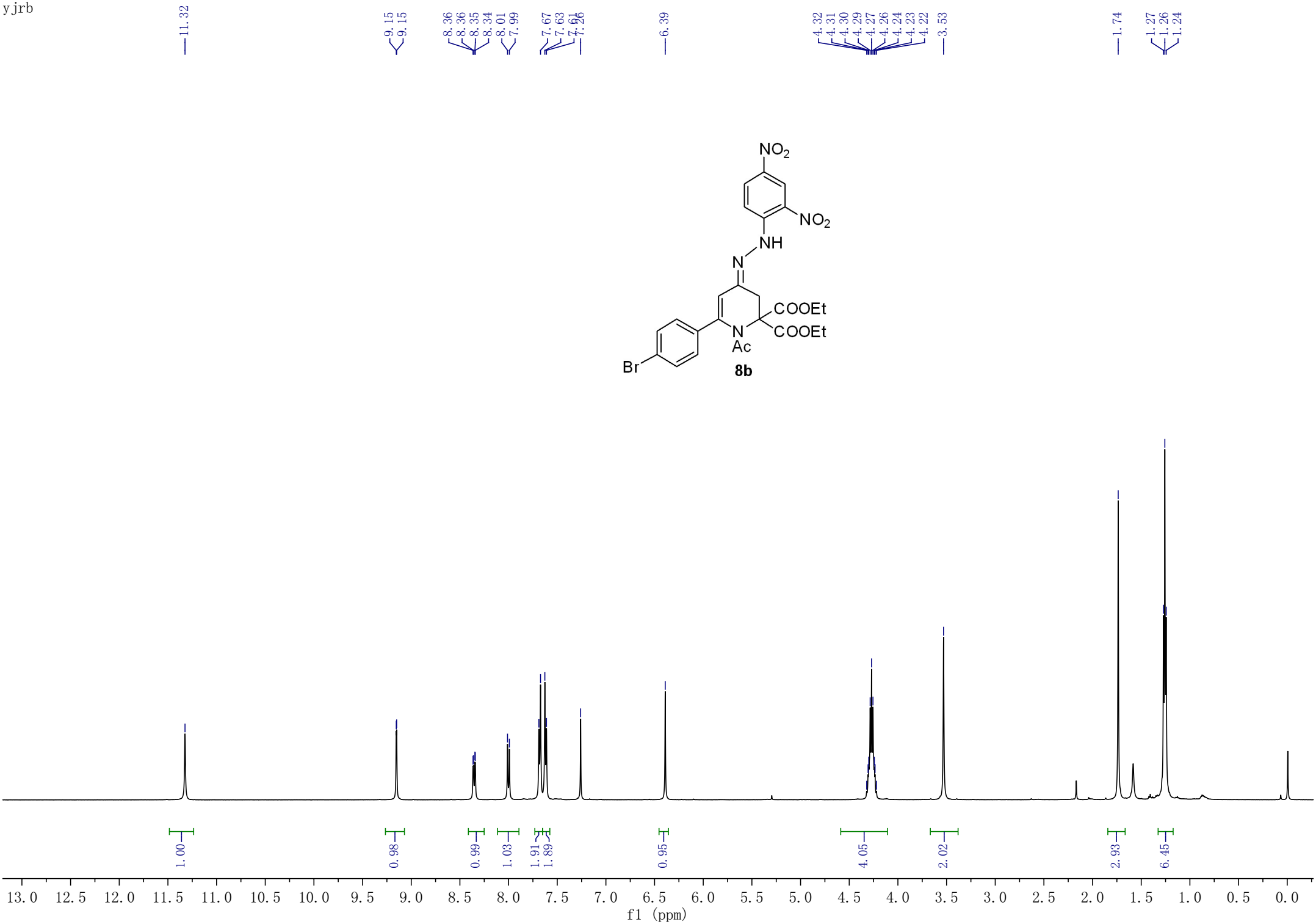
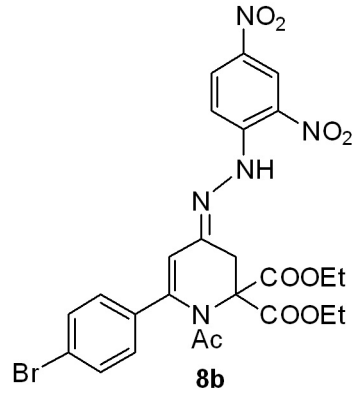
149.03
145.26
144.47
138.31
136.17
132.74
130.16
129.39
128.91
125.62
123.37
116.46
102.82
77.25
77.00
76.75
71.50
62.95
38.95
26.40
13.89
NO2
NO2
HN
N
COOEt
COOEt
N
Ac
Br
8a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

yjrb


11.32
9.15
9.15
8.36
8.36
8.35
8.34
8.01
7.99
7.67
7.63
7.61
7.26
6.39
4.32
4.31
4.30
4.29
4.27
4.26
4.24
4.23
4.22
3.53
1.74
1.27
1.26
1.24
NO2
NO2
NH
N
COOEt
COOEt
N
Ac
Br
8b
1.00
0.98
0.99
1.03
1.91
1.89
0.95
4.05
2.02
2.93
6.45
13.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

yjrb

171.54
166.00
147.44
145.44
144.13
138.84
135.43
132.42
130.23
130.07
128.40
124.64
123.33
116.62
116.58
77.25
77.00
76.75
70.51
63.13
31.80
25.06
13.82



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