Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Synthesis of 2-fluoro-2-pyrrolines via tandem reaction of α-trifluoromethyl-α,β-unsaturated carbonyl compounds with *N*-tosylated 2-aminomalonates [**]

Jieru Yang, Xiaofan Zhou, Yu Zeng, Chaoqian Huang,
Yuanjing Xiao* and Junliang Zhang*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes,

Department of Chemistry, East China Normal University, 3663 N.

Zhongshan Road, Shanghai 200062 (P. R. China).

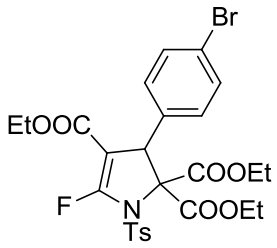
E-mail: yjxiao@chem.ecnu.edu.cn, jlzhang@chem.ecnu.edu.cn

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 under an atmosphere of argon in flame-dried glassware with magnetic stirring. MeOH, 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 ℃ in muffle furnace for 8-10 hours prior to use. All substrates were prepared according to the literatures.[1-6]

2. General procedure for the synthesis of 2-fluoro-2-pyrrolines 3

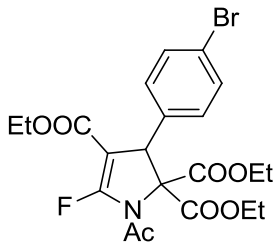
To a flame-dried vial equipped with a magnetic stir bar were added 4 Å molecular sieves (100 mg), K_2CO_3 (1.2 equiv). Then under argon, α-trifluoromethyl-α, β-unsaturated compounds **1** (0.45 mmol), diethyl 2-(4-methylphenylsulfonamido) malonate **2** (0.3 mmol) in DMF (3.0 mL) were successively added into the vial. The reaction mixture was stirred at room temperature for 5~10 h. After **2** 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 (silica gel, petroleum ether: ethyl acetate = 5:1~3:1) to afford the desired 2-fluoro-2-pyrrolines **3** and related by-products **4** or **5**.



3aa

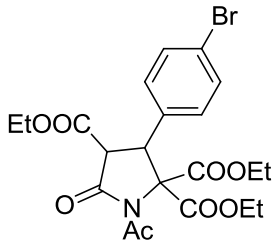
82% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.12 (brs, 2H), 4.82 (d, *J* = 5.7 Hz, 1H), 4.63 – 4.32 (m, 2H), 4.18 – 3.92 (m, 2H), 3.89 – 3.55 (m, 2H), 2.46 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J*

= 7.1 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.19. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.13, 163.52, 161.81 (d, *J* = 5.7 Hz), 156.16 (d, *J* = 295.0 Hz), 145.41, 136.42, 135.11, 135.10, 131.13, 129.52, 129.09 (d, *J* = 1.8 Hz), 122.33, 85.87 (d, *J* = 3.9 Hz), 77.40, 63.49, 62.75, 60.32, 50.42 (d, *J* = 1.8 Hz), 21.62, 14.00, 13.93, 13.31. HRMS(ESI) calcd for $C_{26}H_{27}BrFNNaO_8S$ [M+Na^+]: 634.0517, found: 634.0520.



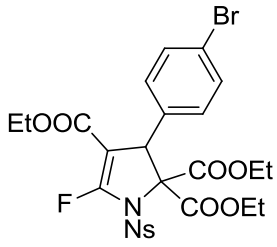
3ab

12% isolated yield. 13% NMR yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.6 Hz, 2H), 7.12 (brs, 2H), 4.60 (d, *J* = 2.9 Hz, 1H), 4.39-4.33 (m, 2H), 4.21 – 3.96 (m, 1H), 3.74 – 3.44 (m, 1H), 2.40 (d, *J* = 4.9 Hz, 3H), 1.37 (t, *J* = 5.9 Hz, 3H), 1.12 (t, *J* = 5.9 Hz, 3H), 0.89 (t, *J* = 6.0 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -99.39. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.72 (d, *J* = 3.7 Hz), 166.45, 162.74, 162.05 (d, *J* = 5.8 Hz), 155.34 (d, *J* = 295.4 Hz), 135.40, 135.39, 131.17, 122.24, 88.03 (d, *J* = 5.0 Hz), 73.80, 63.12, 62.17, 60.51, 48.93, 23.71 (d, *J* = 11.2 Hz), 14.02, 13.94, 13.33. HRMS(ESI) calcd for $C_{21}H_{23}BrFNNaO_7$ [M+Na^+]: 522.0534, found: 522.0541.



4ab

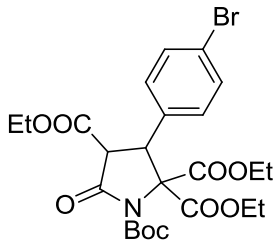
27% isolated yield. 33% NMR yield. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 4.43 – 4.07 (m, 6H), 4.01-3.92 (m, 1H), 3.89-3.81 (m, 1H), 2.56 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.91, 168.19, 166.18, 165.60, 165.15, 131.70, 131.68, 130.13, 122.99, 72.57, 62.65, 62.54, 62.46, 53.21, 47.14, 24.97, 13.93, 13.83, 13.44. HRMS(ESI) calcd for $C_{21}H_{24}BrNNaO_8$ [M+Na^+]: 520.0577, found: 520.0590.



3ac

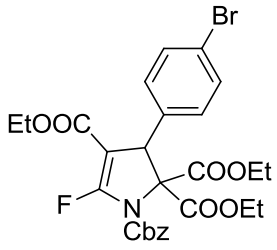
41% isolated yield. 36% NMR yield. Yellow oil.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 4H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.11 (brs,2H), 4.83 (d, *J* = 5.9 Hz, 1H), 4.65 – 4.36 (m, 2H), 4.28 – 3.93 (m, 2H), 3.91 – 3.60 (m, 2H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.2 Hz,

3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -97.31. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 163.36, 161.41 (d, *J* = 5.7 Hz), 155.09 (d, *J* = 295.0 Hz), 150.75, 144.51, 134.44, 131.29, 130.62, 130.60, 124.08, 122.64, 87.07 (d, *J* = 3.8 Hz), 77.73, 63.8, 63.15, 60.69, 50.35, 13.99, 13.96, 13.35. HRMS(ESI) calcd for $C_{25}H_{24}BrFN_2NaO_{10}S$ [M+Na^+]: 665.0211, found: 665.0219.



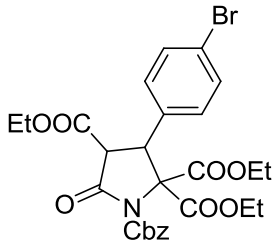
4ad

49% isolated yield. 54% NMR yield. White solid. Mp 86-88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.08 (d, *J* = 8.5 Hz, 2H), 4.33-4.25 (m, 2H), 4.23 – 4.02 (m, 4H), 3.97-3.88 (m, 2H), 1.44 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.31, 166.26, 165.94, 165.28, 148.60, 132.24, 131.56, 130.34, 122.83, 84.80, 72.86, 62.55, 62.35, 62.29, 53.24, 47.01, 27.57, 13.87, 13.84, 13.52. HRMS(ESI) calcd for $C_{24}H_{30}BrNNaO_9$ [M+Na^+]: 578.0996, found: 578.0998.



3ae

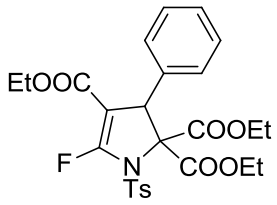
10% isolated yield. 15% NMR yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.33 (s, 5H), 7.13 (brs, 2H), 5.22 (q, *J* = 12.1 Hz, 2H), 4.70 (d, *J* = 5.5 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 4.19 – 3.96 (m, 2H), 3.64 – 3.14 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 163.02, 162.07 (d, *J* = 5.7 Hz), 156.26 (d, *J* = 301.8 Hz), 149.96 (d, *J* = 3.6 Hz), 135.48, 135.47, 134.55, 131.15, 128.56, 128.49, 128.25, 122.21, 87.32 (d, *J* = 3.4 Hz), 74.34, 68.82, 63.21, 62.26, 60.36, 49.64, 14.02, 13.84, 13.19. HRMS(ESI) calcd for $C_{27}H_{27}BrFNNaO_8$ [M+Na^+]: 614.0796, found: 614.0801.



4ae

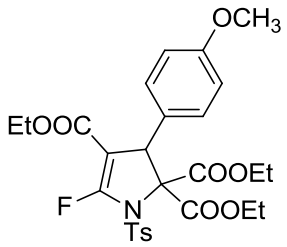
34% isolated yield. 40% NMR yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.40 – 7.27 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 5.29 (d, *J* = 12.2 Hz, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 4.29 – 4.06

(m, 6H), 3.91 – 3.75 (m, 2H), 1.24 (t, *J* = 7.4 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.20, 166.16, 165.83, 165.27, 150.48, 134.38, 132.08, 131.66, 130.44, 128.48, 128.46, 128.19, 123.01, 73.02, 69.13, 62.78, 62.62, 62.49, 53.19, 47.35, 13.94, 13.75, 13.40. HRMS(ESI) calcd for $C_{27}H_{28}BrNNaO_9$ [M+Na^+]: 612.0840, found: 612.0848.



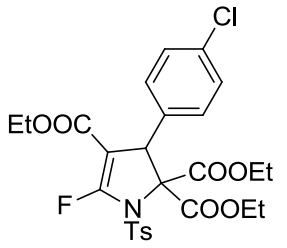
3ba

88% isolated yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 5H), 4.86 (d, *J* = 5.7 Hz, 1H), 4.57 – 4.37 (m, 2H), 4.16 – 3.88 (m, 2H), 3.79 – 3.47 (m, 2H), 2.44 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -97.11. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.23 (s), 163.55 (s), 161.85 (d, *J* = 5.7 Hz), 155.90 (d, *J* = 294.8 Hz), 145.21, 136.51, 135.93，135.92, 129.42, 128.99 (d, *J* = 1.8 Hz), 128.09, 127.89, 86.24 (d, *J* = 3.4 Hz), 77.63, 63.31, 62.45, 60.10, 50.98 (d, *J* = 1.7 Hz), 21.52, 13.88, 13.85, 13.18. HRMS(ESI) calcd for $C_{26}H_{28}FNNaO_8S$ [M+Na^+]: 556.1412, found: 556.1418.



3ca

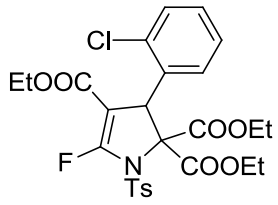
47% isolated yield. Yellow solid. Mp 93-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.15 (brs, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.81 (d, *J* = 5.7 Hz, 1H), 4.62 – 4.33 (m, 2H), 4.18 – 3.88 (m, 2H), 3.76 (s, 3H), 3.81 – 3.62 (m, 2H), 2.46 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -97.22. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.38, 163.71, 162.02 (d, *J* = 5.7 Hz), 159.46, 155.85 (d, *J* = 294.7 Hz), 145.23, 136.62, 129.48, 129.09 (d, *J* = 1.8 Hz), 127.89, 127.88, 113.37, 86.45 (d, *J* = 3.3 Hz), 77.75, 63.32, 62.55, 60.19, 55.15, 50.58 (d, *J* = 1.6 Hz), 21.63, 14.02, 13.95, 13.35. HRMS(ESI) calcd for $C_{27}H_{30}FNNaO_9S$ [M+Na^+]: 586.1518, found: 586.1530.



3da

84% isolated yield. White solid. Mp 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* =

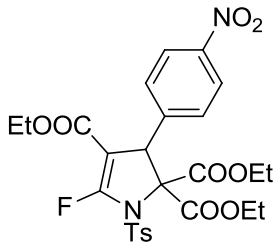
7.3 Hz, 2H), 7.18 (brs, 2H), 4.83 (d, *J* = 5.7 Hz, 1H), 4.56 – 4.33 (m, 2H), 4.16 – 3.92 (m, 2H), 3.84 – 3.61 (m, 2H), 2.46 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.25. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.14, 163.53, 161.82 (d, *J* = 5.7 Hz), 156.14 (d, *J* = 294.9 Hz), 145.41, 136.41, 134.57, 134.56, 134.13, 129.51, 129.09 (d, *J* = 1.8 Hz), 128.17, 85.93 (d, *J* = 3.8 Hz), 77.47, 63.48, 62.73, 60.31, 50.35 (d, *J* = 1.8 Hz), 21.62, 13.99, 13.93, 13.31. HRMS(ESI) calcd for $C_{26}H_{27}ClFNNaO_8S$ [M+Na^+]: 590.1022, found: 590.1028.



3ea

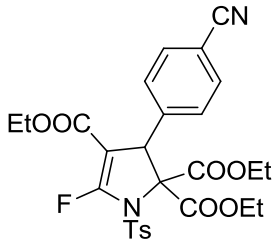
81% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.21-7.09 (m, 2H), 7.01 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.45 (d, *J* = 5.0 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 1H), 4.16 – 3.76 (m, 3H), 3.63-3.53 (m, 1H), 2.45 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -97.76. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.49, 163.49, 161.49 (d, *J* = 5.6 Hz), 156.28 (d, *J* = 295.7 Hz), 145.32, 136.41, 135.04, 134.53 (d, *J* = 2.0 Hz), 129.52, 129.34, 129.29, 129.26, 128.86 (d, *J* = 1.4 Hz), 126.44, 87.00 (d, *J* = 3.0 Hz), 77.20, 63.41, 62.61,

60.14, 47.28 (d, *J* = 2.1 Hz), 21.58, 13.78(2C), 13.20. HRMS calcd for $C_{26}H_{27}ClFNNaO_8S$: 590.1022, found: 590.1021.



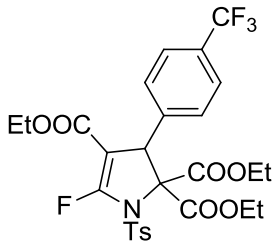
3fa

93% isolated yield. Yellow solid. Mp 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.44 (brs, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 4.96 (d, *J* = 5.5 Hz, 1H), 4.54 – 4.37 (m, 2H), 4.14 – 3.92 (m, 2H), 3.86 – 3.64 (m, 2H), 2.45 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -95.17. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.80, 163.30, 161.57 (d, *J* = 5.6 Hz), 156.34 (d, *J* = 295.4 Hz), 147.55, 145.61, 143.39, 136.02, 129.53(2C), 129.00, 123.00, 85.38 (d, *J* = 4.4 Hz), 77.07, 63.67, 62.87, 60.43, 50.17 (d, *J* = 0.6 Hz), 21.54, 13.90, 13.85, 13.25. HRMS(ESI) calcd for $C_{26}H_{27}FN_2NaO_{10}S$ [M+Na^+]: 601.1263, found: 601.1270.



3ga

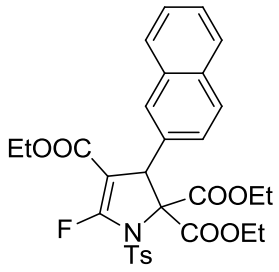
94% isolated yield. White solid. Mp 109-111 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 4H), 4.90 (d, *J* = 5.6 Hz, 1H), 4.57 – 4.38 (m, 2H), 4.18 – 3.89 (m, 2H), 3.88 – 3.53 (m, 2H), 2.47 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -95.20. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.94, 163.42, 161.70 (d, *J* = 5.7 Hz), 156.40 (d, *J* = 295.4 Hz), 145.64, 141.53, 136.13, 131.73, 129.58, 129.14, 129.13, 118.38, 112.06, 85.35 (d, *J* = 4.4 Hz), 77.20, 63.72, 62.92, 60.50, 50.54 (d, *J* = 1.6 Hz), 21.67, 13.99, 13.95, 13.34. HRMS(ESI) calcd for $C_{27}H_{27}FN_2NaO_8S$ [M+Na^+]: 581.1364, found: 581.1365.



3ha

84% isolated yield. White solid. Mp 157-158 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 4H), 4.92 (d, *J* = 5.6 Hz, 1H), 4.69 – 4.36 (m, 2H), 4.18 – 3.93 (m,

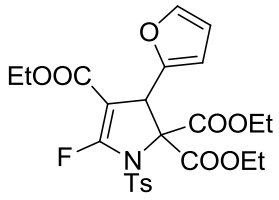
2H), 3.85 – 3.50 (m, 2H), 2.46 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.67 (s, 3F), -95.78 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.05, 163.50, 161.78 (d, *J* = 5.7 Hz), 156.27 (d, *J* = 295.1 Hz), 145.54, 140.16, 136.26, 130.36 (q, *J* = 32.5 Hz), 129.55, 129.11, 129.10, 124.90 (q, *J* = 3.5 Hz), 123.88 (q, *J* = 272.1 Hz), 85.67 (d, *J* = 4.1 Hz), 77.37, 63.61, 62.79, 60.40, 50.49, 21.61, 13.95, 13.92, 13.16. HRMS(ESI) calcd for $C_{27}H_{27}F_4NNaO_8S$ [M+Na^+]: 624.1286, found: 624.1293.



3ia

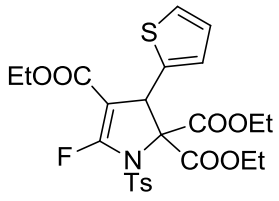
73% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.4 Hz, 2H), 7.85 – 7.69 (m, 4H), 7.50 – 7.42 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 2H), 5.05 (d, *J* = 5.4 Hz, 1H), 4.64 – 4.35 (m, 2H), 4.16 – 3.86 (m, 2H), 3.69 – 3.38 (m, 2H), 2.48 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H), 0.79 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.86. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.40, 163.61, 162.02 (d, *J* = 5.7 Hz), 156.13 (d, *J* = 295.0 Hz), 145.33, 136.64, 133.46, 133.11, 132.93, 129.54, 129.16, 129.14, 127.97, 127.61, 127.55, 126.20, 126.10, 86.43 (d, *J* = 3.2 Hz), 77.84, 63.50, 62.54, 60.27, 51.21, 21.67, 14.01(2C), 13.10.

HRMS(ESI) calcd for $C_{30}H_{30}FNNaO_8S$ [M+Na^+]: 606.1568, found: 606.1575.



3ja

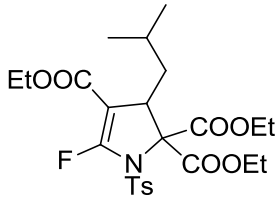
89% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.32 (brs, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.18 (d, *J* = 3.2 Hz, 1H), 4.98 (d, *J* = 5.2 Hz, 1H), 4.62 – 4.34 (m, 2H), 4.17 – 3.88 (m, 4H), 2.43 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 5.3 Hz, 3H), 1.11 (t, *J* = 5.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.94. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82, 163.55, 161.65 (d, *J* = 5.7 Hz), 155.95 (d, *J* = 294.9 Hz), 149.32 (d, *J* = 2.6 Hz), 145.24, 142.39, 136.43, 129.46, 128.86 (d, *J* = 1.5 Hz), 110.67, 109.29, 84.53 (d, *J* = 4.5 Hz), 76.71, 63.42, 62.97, 60.19, 45.05 (d, *J* = 2.6 Hz), 21.52, 13.96, 13.79, 13.43. HRMS(ESI) calcd for $C_{24}H_{26}FNNaO_9S$ [M+Na^+]: 546.1205, found: 546.1210.



3ka

78% isolated yield. White solid. Mp 103-105 ^{o}C. ^{1}H NMR (400 MHz,

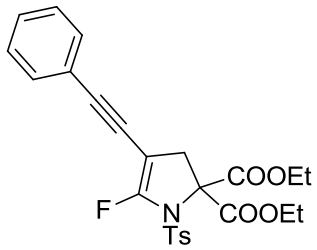
$CDCl_3$) δ 8.08 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.22 (dd, *J* = 3.9, 2.4 Hz, 1H), 6.93 (d, *J* = 4.0 Hz, 2H), 5.15 (d, *J* = 5.5 Hz, 1H), 4.61 – 4.34 (m, 2H), 4.16 – 3.97 (m, 2H), 3.96 – 3.76 (m, 2H), 2.45 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.2Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.85. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.98, 163.35, 161.74 (d, *J* = 5.6 Hz), 156.20 (d, *J* = 295.5 Hz), 145.31, 139.64, 136.48, 129.51, 129.00 (d, *J* = 1.6 Hz), 127.43, 126.67, 125.74, 86.95 (d, *J* = 4.0 Hz), 77.89, 63.48, 62.82, 60.30, 46.23 (d, *J* = 2.5 Hz), 21.61, 13.99, 13.89, 13.38. HRMS(ESI) calcd for $C_{24}H_{26}FNNaO_8S_2$ [M+Na^+]: 562.0976, found: 562.0984.



3la

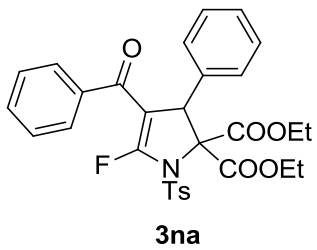
95% isolated yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.55 – 4.24 (m, 4H), 4.23 – 3.97 (m, 2H), 3.74-3.66 (m, 1H), 2.44 (s, 3H), 1.77 – 1.66 (m, 1H), 1.57 – 1.41 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.1 Hz, 3H), 0.86 (d, *J* = 6.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -98.76. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.19, 164.90, 162.41 (d, *J* = 5.7 Hz), 154.56 (d, *J* = 295.2 Hz), 145.16, 136.54, 129.51, 128.98 (d, *J* = 1.6 Hz), 87.44 (d, *J* = 1.0 Hz), 76.72, 63.20, 63.11,

60.23, 44.00, 39.21 (d, J = 0.8 Hz), 25.41, 23.42, 21.66, 21.16, 14.18, 13.87, 13.77. HRMS(ESI) calcd for $C_{24}H_{32}FNNaO_8S$ [M+Na^+]: 536.1725, found: 536.1737.



3ma

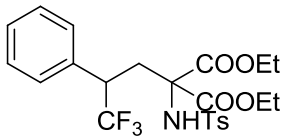
87% isolated yield. Yellow solid. Mp 76-78 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.31 – 7.26 (m, 3H), 4.55 – 4.19 (m, 4H), 3.30 (d, J = 5.4 Hz, 2H), 2.43 (s, 3H), 1.38 (t, J = 7.1 Hz, 6H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.86. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.52(2C), 151.67 (d, J = 285.6 Hz), 144.80, 136.79, 131.10, 129.37, 128.51, 128.50, 128.22, 122.65, 94.28 (d, J = 3.4 Hz), 78.68 (d, J = 5.1 Hz), 73.99 (d, J = 10.0 Hz), 72.71, 63.19(2C), 37.82, 21.51, 13.78(2C). HRMS(ESI) calcd for $C_{25}H_{24}FNNaO_6S$ [M+Na^+]: 508.1201, found: 508.1199.



3na

45% or 28% isolated yield (When Z or E material was used). Yellow oil.

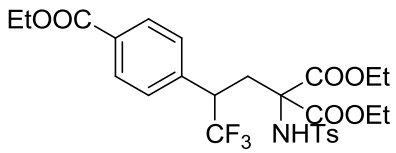
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39-7.29 (m, 4H), 7.27 – 7.20 (m, 3H), 5.13 (d, *J* = 5.5 Hz, 1H), 4.83 – 4.12 (m, 2H), 3.94 – 3.39 (m, 2H), 2.41 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -95.22. ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.59 (d, *J* = 4.7 Hz), 167.29, 163.95, 154.64 (d, *J* = 291.4 Hz), 145.38, 138.48, 136.39, 135.48, 132.38, 129.47, 129.15, 129.13, 128.34, 128.31, 128.21, 128.08, 95.20 (d, *J* = 6.1 Hz), 77.57, 63.36, 62.64, 51.50 (d, *J* = 2.9 Hz), 21.63, 14.02, 13.33. HRMS(ESI) calcd for $C_{30}H_{28}FNNaO_7S$ [M+Na^+]: 588.1463, found: 588.1478.



5oa

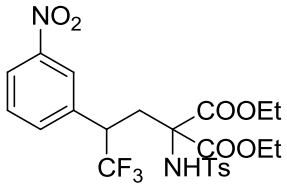
9% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.31–7.27 (m, 3H), 7.24-7.19 (m, 2 H), 5.93 (s, 1H), 4.02-3.92 (m, 1H), 3.68 – 3.52 (m, 2H), 3.52 – 3.37 (m, 1H), 3.26 – 3.07 (m, 2H), 2.79 (dd, *J* = 15.0, 11.6 Hz, 1H), 2.42 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.72, 166.16, 143.89, 137.83, 132.72, 129.97, 129.56, 128.61, 128.24, 127.17, 126.49 (q, *J* = 279.0 Hz), 65.98, 62.95, 62.51, 45.37 (q, *J* = 27.3 Hz), 31.99 (q, *J* = 2.0

Hz), 21.48, 13.50, 13.28. HRMS(ESI) calcd for $C_{23}H_{26}F_3NNaO_6S$ [M+Na^+]: 524.1325, found: 524.1336.



5pa

93% isolated yield. White solid. Mp 150-152 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 5.93 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.98-3.89 (m, 1H), 3.74 – 3.38 (m, 3H), 3.34 – 3.09 (m, 2H), 2.80 (dd, *J* = 15.1, 11.3 Hz, 1H), 2.40 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.35. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.55, 165.89, 165.84, 143.96, 137.66, 137.49, 130.75, 129.93, 129.51, 129.33, 127.15, 126.16 (q, *J* = 281.0 Hz), 65.73, 63.00, 62.57, 61.09, 45.31 (q, *J* = 27.5 Hz), 31.82, 21.42, 14.20, 13.42, 13.23. HRMS(ESI) calcd for $C_{26}H_{30}F_3NNaO_8S$ [M+Na^+]: 596.1536, found: 596.1534.



5qa

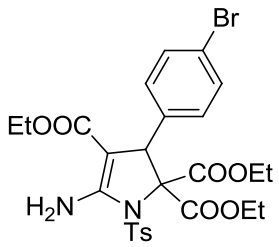
85% isolated yield. Yellow solid. Mp 125-126 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ8.18 (dd, *J* = 10.7, 1.1 Hz, 1H), 8.11 (s, 1H), 7.71 (d, *J* = 8.7 Hz,

2H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 2H), 5.90 (s, 1H), 4.00-3.90 (m, 1H), 3.75-3.69 (m, 1H), 3.62-3.52 (m, 2H), 3.40 – 3.18 (m, 2H), 2.85 (dd, *J* = 15.6, 11.1 Hz, 1H), 2.41 (s, 3H), 1.03 (t, *J* = 7.3 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -69.44. ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.49 (s), 165.67, 148.04, 144.13, 137.22, 136.48, 135.02, 129.55, 129.44, 127.18, 125.95 (q, *J* = 280.4 Hz), 124.28, 123.67, 65.64, 63.11, 62.79, 45.19 (q, *J* = 27.8 Hz), 31.78, 21.42, 13.42, 13.18. HRMS(ESI) calcd for $C_{23}H_{25}F_3N_2NaO_8S$ [M+Na^+]: 569.1176, found: 569.1183.

3. Synthetic transformations of 2-fluoro-2-pyrroline 3aa

Synthesis of 6

To a ace glass heavy-wall pressure tube equipped with a magnetic stir bar were added **3aa** (0.2 mmol, 122.4 mg). Then under N_2, NH_3 solution (0.4 M in 1,4-dioxane, 2 mL) was added into the tube. Then the reaction mixture was warmed to 50 ^{o}C, until the disappearance of substrate **3aa** as indicated by TLC over 7 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, petroleum ether: ethyl acetate = 3:1) to afford ammonia incorporated 2-pyrroline **6**.



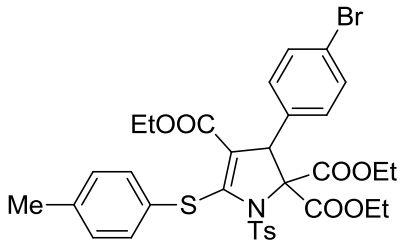
6

119.2 mg, 98% isolated yield. White solid. Mp 152-154 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 6.96 (brs, 2H), 6.73 (brs, 2H), 4.75 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 4.03 – 3.83 (m, 2H), 3.79 – 3.43 (m, 2H), 2.42 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.94 (brs, 3H), 0.81 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.84, 163.65, 144.40, 137.95, 137.80, 130.81, 129.41, 127.26, 121.48, 80.31, 77.20, 63.25, 62.33, 58.97, 51.35, 21.49, 14.14, 13.82, 13.12. HRMS(ESI) calcd for $C_{26}H_{29}BrN_2NaO_8S$ [M+Na^+]: 631.0720, found: 631.0725.

Synthesis of 7

To a flame-dried vial equipped with a magnetic stir bar were added 4A molecular sieves (100.0 mg), K_2CO_3 (0.4 mmol, 55.0 mg). Then 4-methylBenzenethiol (0.24 mmol, 30.0 mg) in DMF (2 mL) were added into the vial. After stirring for 30 min at room temperature, **3aa** (0.2 mmol, 122.4 mg) was added into the vial. Then the reaction mixture was warmed to 50 ^{o}C, until the disappearance of substrate **3aa** as indicated by TLC over 3h, 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 (silica gel, PE:EA = 5:1) to afford thiophenol incorporated 2-pyrroline **7**.



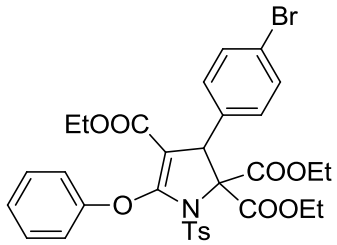
7

140.0 mg, 98% isolated yield. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 6H), 4.95 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 4.01 – 3.56 (m, 4H), 2.38 (s, 3H), 2.27 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.98, 164.34, 161.97, 147.75, 144.23, 138.02, 137.24, 136.33, 131.06, 130.78, 129.67, 129.61, 129.33, 129.03, 121.95, 115.73, 80.22, 77.20, 63.31, 62.50, 60.18, 54.97, 21.47, 20.95, 13.83, 13.68, 13.38. HRMS(ESI) calcd for $C_{33}H_{34}BrNNaO_8S_2$ [M+Na^+]: 738.0801, found: 738.0795.

Synthesis of 8

To a flame-dried vial equipped with a magnetic stir bar were added 4A molecular sieves (100.0 mg), K_2CO_3 (0.4 mmol, 55.0 mg). Then under

N_2, phenol (0.4 mmol, 37.6 mg) in DMF (2 mL) were added into the vial. After stirring for 30 min at 50 ^oC, **3aa** (0.2 mmol, 122.4 mg) was added into the vial. Until the disappearance of substrate **3aa** as indicated by TLC over 4h, 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 (silica gel, PE:EA = 5:1) to afford phenol incorporated 2-pyrroline **8**.

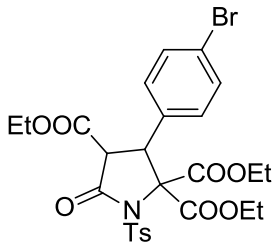


8

135.6 mg, 99% isolated yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.31-7.25 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.89 (s, 1H), 4.60-4.44 (m, 2H), 3.99 – 3.33 (m, 4H), 2.38 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.65 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.78, 164.20, 161.98, 156.68, 155.75, 144.70, 136.70, 136.22, 131.10, 129.44, 129.29, 128.99, 123.53, 122.05, 115.67, 91.58, 77.02, 63.37, 62.58, 59.81, 52.21, 21.51, 13.98, 13.47, 13.36. HRMS(ESI) calcd for $C_{32}H_{32}BrNNaO_9S$ [$M+Na^+$]: 708.0873, found: 708.0870.

Synthesis of pyrrolidinone 4aa

To a solution of monofluorinated **3aa** (0.2 mmol, 122.4 mg) in DMF (2mL), Bu_4OAc (0.5 mmol, 150.5 mg), H_2O(10 μL) was added at room temperature. The reaction mixture was stirred at 50 ^oC over 5 h. Until the disappearance of substrate **3aa** as indicated by TLC, 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 (silica gel, petroleum ether: ethyl acetate = 4:1) to afford pyrrolidinone **4aa**.

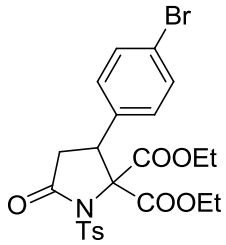


4aa

117.0 mg, 96% isolated yield, dr: 8:1. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 4.45-4.37 (m, 2H), 4.33 (d, *J* = 11.7 Hz, 1H), 4.23 – 3.88 (m, 4H), 4.02 (d, *J* = 11.7 Hz, 1H), 2.44 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.82, 165.99, 165.74, 165.30, 145.67, 134.44, 131.71, 131.64, 130.32, 130.08, 129.03, 123.15, 74.84, 63.21, 63.06, 62.51, 52.06, 49.01, 21.69, 13.87, 13.86, 13.49. HRMS(ESI) calcd for $C_{26}H_{28}BrNNaO_9S$ [$M+Na^+$]: 632.0560, found: 632.0571.

Synthesis of 9

Under N_2, to a sealed tube equipped with a magnetic stir bar were added **3aa** (0.2 mmol, 122.4 mg), phenol (0.2 g), HBr (40% aqueous solution, 2.4 mL) and CH_3COOH (0.8 mL). After stirring for 1 h at 90 ^oC, acetic acid was evaporated under reduced pressure. To the residue was added 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 (silica gel, PE:EA = 3:1) to afford the desired product **9**.



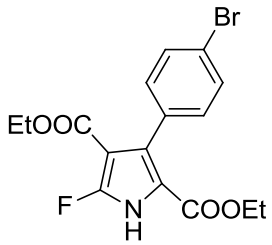
9

60.3 mg, 56% isolated yield. Colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.12 – 3.94 (m, 2H), 3.91-3.81 (m, 1H), 2.84 (dd, *J* = 8.4, 5.7 Hz, 2H), 2.45 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70, 166.96, 164.90, 145.35, 135.10, 134.47, 131.60, 129.98, 129.89, 128.96, 122.69, 77.08, 63.29, 62.70, 46.10, 36.15, 21.71, 13.91, 13.46. ^{13}C NMR DEPT 135 (126 MHz, $CDCl_3$) δ 131.69, 130.06, 129.98, 129.04, 63.36, 62.76, 46.19, 36.25, 21.77, 13.98, 13.53. HRMS(ESI)

calcd for $C_{23}H_{24}BrNNaO_7S$ [M+Na^+]: 560.0349, found: 560.0356.

Synthesis of 10

To a flame-dried flask equipped with a magnetic stir bar was added LiCl (0.25 mmol, 10.8 mg). Then under O_2, **3aa** (0.2 mmol, 122.4 mg) in DMF (2.0 mL) were added into the vial. Then the reaction mixture was warmed to 165 ^oC, until the disappearance of substrate **3aa** as indicated by TLC over 1.5 h, 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 (silica gel, PE:EA = 3:1) to afford the desired product **10**.



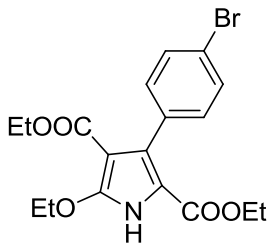
10

58.2 mg, 76% isolated yield. Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 10.11 (s, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -119.37. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.87 (d, *J* = 4.9 Hz), 160.83 (d, *J* = 1.9 Hz), 150.01 (d, *J* = 281.4 Hz), 132.11, 131.77, 130.41, 130.20, 121.70, 111.14, 97.31 (d, *J* = 3.2 Hz), 61.08,

60.12, 13.97, 13.81. HRMS(ESI) calcd for $C_{16}H_{15}BrFNNaO_4$ [M+Na^+]: 406.0061, found: 406.0075.

Synthesis of 11

To a solution of **3a** (0.2 mmol, 122.4 mg) in EtOH (6.0 mL) was added NaOH (1.0 mmol, 40.0 mg) at 70 ℃. After stirring for 1 h, the solvents were evaporated and DCM was added to the residue. The residue was washed with water, dried over $MgSO_4$ and the solvent evaporated. Flash column chromatography (silica gel, petroleum ether: ethyl acetate = 3:1) gave **11**.



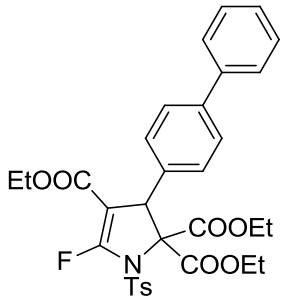
11

67.0 mg, 82% isolated yield. White solid. Mp 108-110 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.33 (q, *J* = 7.0 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.46 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.24, 160.90, 151.19, 133.66, 131.64, 131.55, 130.00, 121.06, 111.53, 100.51, 69.36, 60.45, 59.58, 14.95, 13.87, 13.81. HRMS(ESI) calcd for $C_{18}H_{20}BrNNaO_5$ [M+Na^+]:

432.0417, found: 432.0420.

Synthesis of 12

Under N_2, a mixture of phenylboronic acid (0.86 mmol, 104.9 mg), **3aa** (0.945 mmol, 578.3 mg), K_2CO_3 (1.72 mmol, 237.4 mg) and $Pd(PPh_3)_2Cl_2$ (0.017 mmol, 11.9 mg) in THF (2 mL) and H2O (1 mL) was heated at 95 °C in a sealed tube for 13 h. The mixture was cooled to rt and 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 (silica gel, PE:EA = 3:1) to afford the desired product **12**.



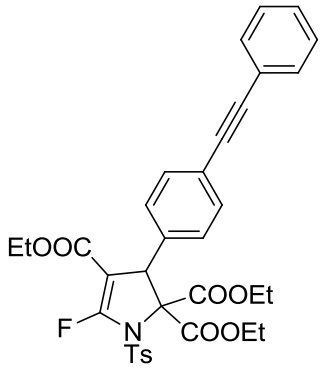
12

549.0 mg, 95% isolated yield. White solid. Mp 68-70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.50 – 7.30 (m, 5H), 4.94 (d, *J* = 5.7 Hz, 1H), 4.50 (q, *J* = 6.8 Hz, 2H), 4.29 – 3.89 (m, 2H), 3.90 – 3.56 (m, 2H), 2.47 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H),

0.99 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.66. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.26, 163.66, 161.98 (d, *J* = 5.6 Hz), 155.91 (d, *J* = 294.7 Hz), 145.31, 140.89, 140.39, 136.37, 134.89, 129.46, 129.06, 129.05, 128.67, 127.32, 126.89, 126.60, 86.14 (d, *J* = 3.5 Hz), 77.62, 63.41, 62.61, 60.25, 50.68 (d, *J* = 1.1 Hz), 21.61, 13.98, 13.93, 13.22. HRMS(ESI) calcd for $C_{32}H_{32}FNNaO_8S$ [M+Na^+]: 632.1725, found: 632.1734.

Synthesis of 13

Under N_2, to a flame-dried sealed tube equipped with a magnetic stir bar were successively added **3aa** (0.5 mmol, 306.0 mg), $Pd(PPh_3)_2Cl_2$ (0.01 mmol, 7.0 mg) and CuI (0.02 mmol, 3.8 mg), THF(0.75 mL) , Et_3N(0.2 mL), phenylacetylene(1.5 mmol, 0.17 mL). Then the reaction mixture was warmed to 60 ^oC. After stirring for 24 h, $Pd(PPh_3)_2Cl_2$ (0.01 mmol, 7.0 mg), phenylacetylene (0.5 mmol) were added for another two times every 4 h and the heating was continued for next 4 h. The mixture was cooled to rt and 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 (silica gel, PE:EA = 5:1) to afford the desired product **13**.



13

183.6 mg, 58% isolated yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.52 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.34 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.16 (brs, 2H), 4.88 (d, *J* = 5.6 Hz, 1H), 4.52-4.44 (m, 2H), 4.24 – 3.91 (m, 2H), 3.85 – 3.63 (m, 2H), 2.47 (s, 3H), 1.46 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.44. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.25, 163.56, 161.89 (d, *J* = 5.7 Hz), 156.12 (d, *J* = 295.0 Hz), 145.42, 136.35, 136.15, 136.14, 131.55, 131.21, 129.54, 129.15, 129.14, 128.33, 123.17, 123.00, 89.91, 88.98, 85.97 (d, *J* = 3.4 Hz), 77.55, 63.54, 62.80, 60.34, 50.75, 21.70, 14.03, 13.99, 13.41. HRMS(ESI) calcd for $C_{34}H_{32}FNNaO_8S$ [M+Na^+]: 656.1725, found: 656.1734.

4. X-ray structures for 3da

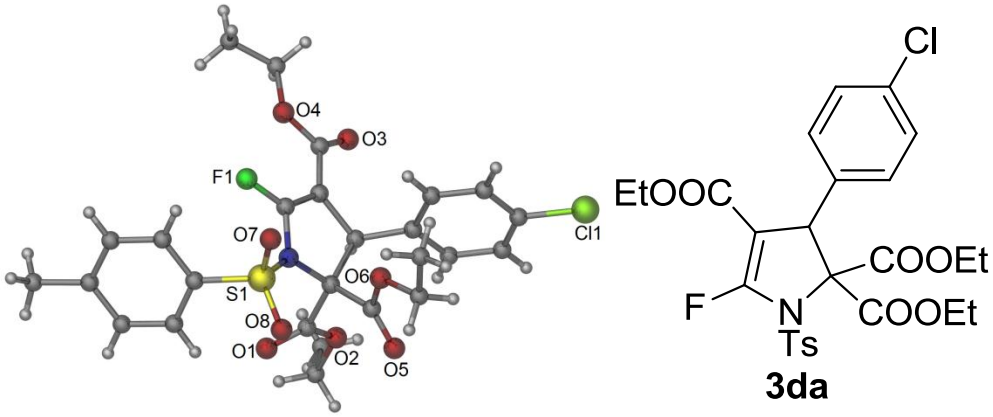


Figure 1. ORTEP depiction of compound **3da**, CCDC 1445375

5. Reference

[1] S. Roy, A. Basak. *Tetrahedron*. **2013**, *69*, 2184-2192.

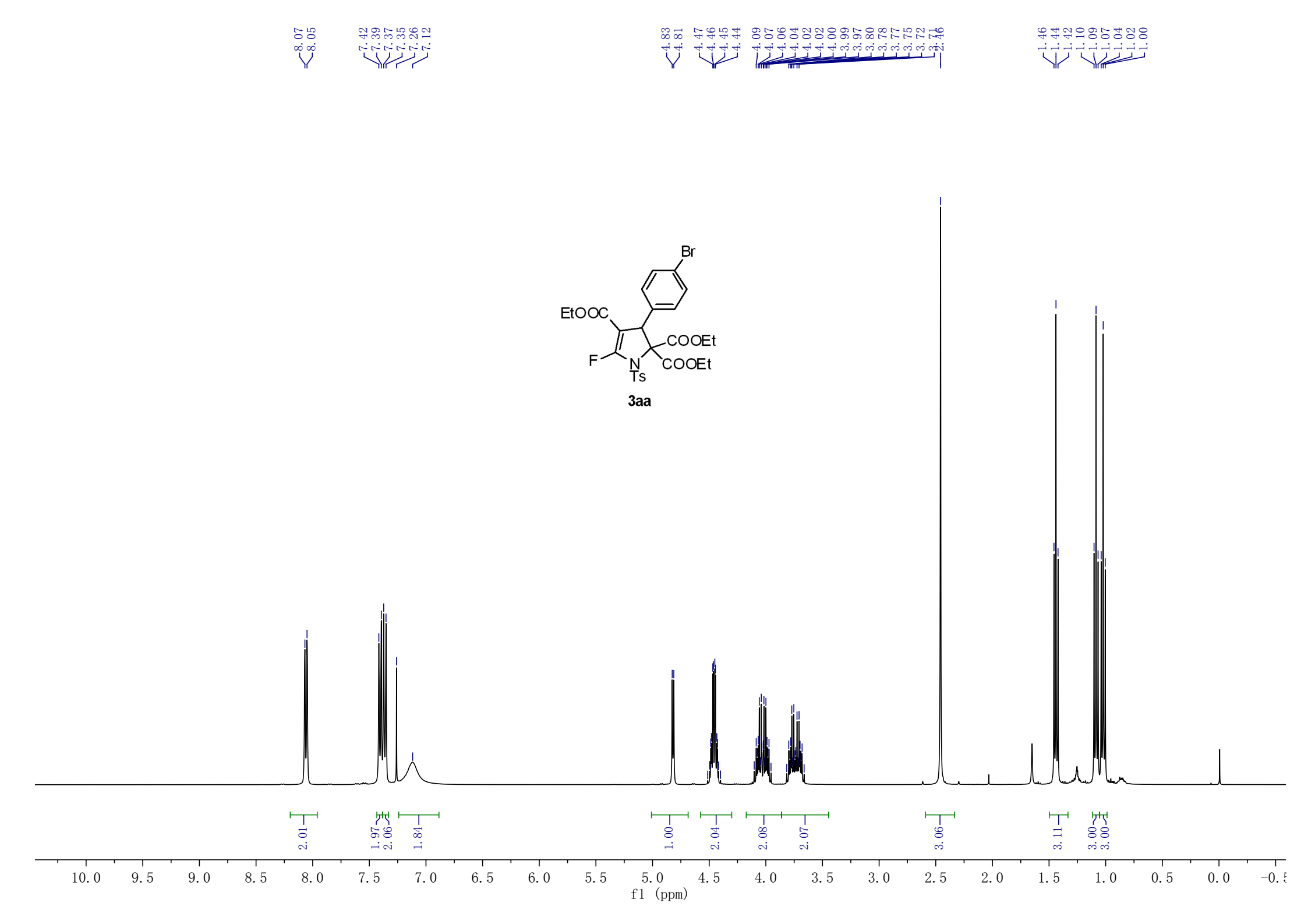
[2] X. Zhang, F. Qing, Y. Peng. *J. Fluorine Chem*. **2001**, *108*, 79-82.

[3] Y. Le Bigot, R. ElGharbi, M. Delmas, A. Gaset. *Tetrahedron*. **1986**, *42*, 3813-3823.

[4] R. Pan, X. Liu, M. Deng. *J. Fluorine Chem*. **1999**, *95*, 167-170.

[5] X. Zhang, F. Qing, Y. Yang, J. Yu and X. Fu. *Tetrahedron Lett*. **2000**, *41*, 2953-2955.

[6] T. Ichitsuka, T. Fujita, T. Arita, and J. Ichikawa. *Angew. Chem*. **2014**, *126*, 7694 –7698(*Angew. Chem., Int. Ed*. 2014, 53, 7564-7568).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1.46
1.44
1.42
1.10
1.09
1.07
1.04
1.02
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COOEt
F
N
Ts
COOEt
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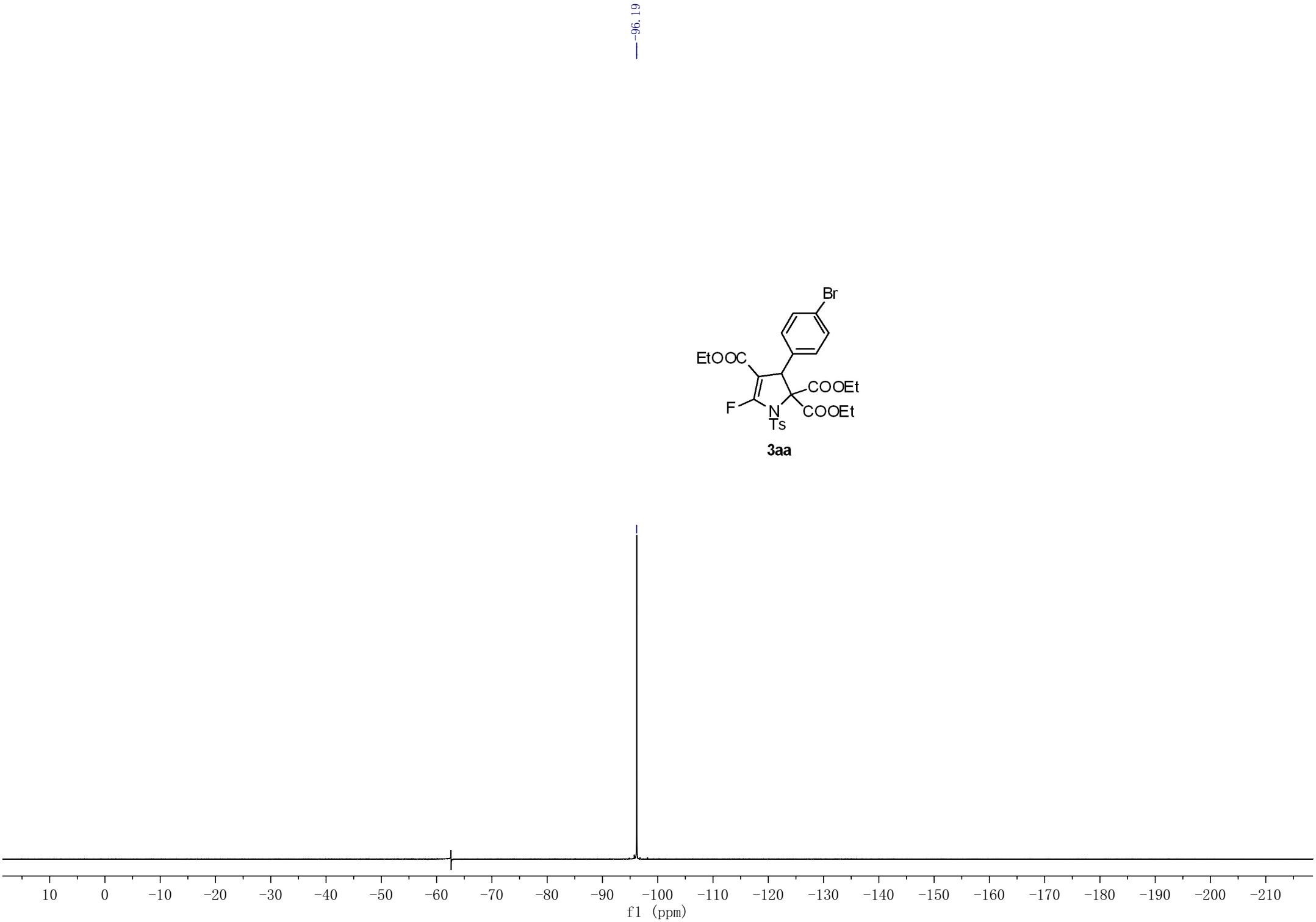
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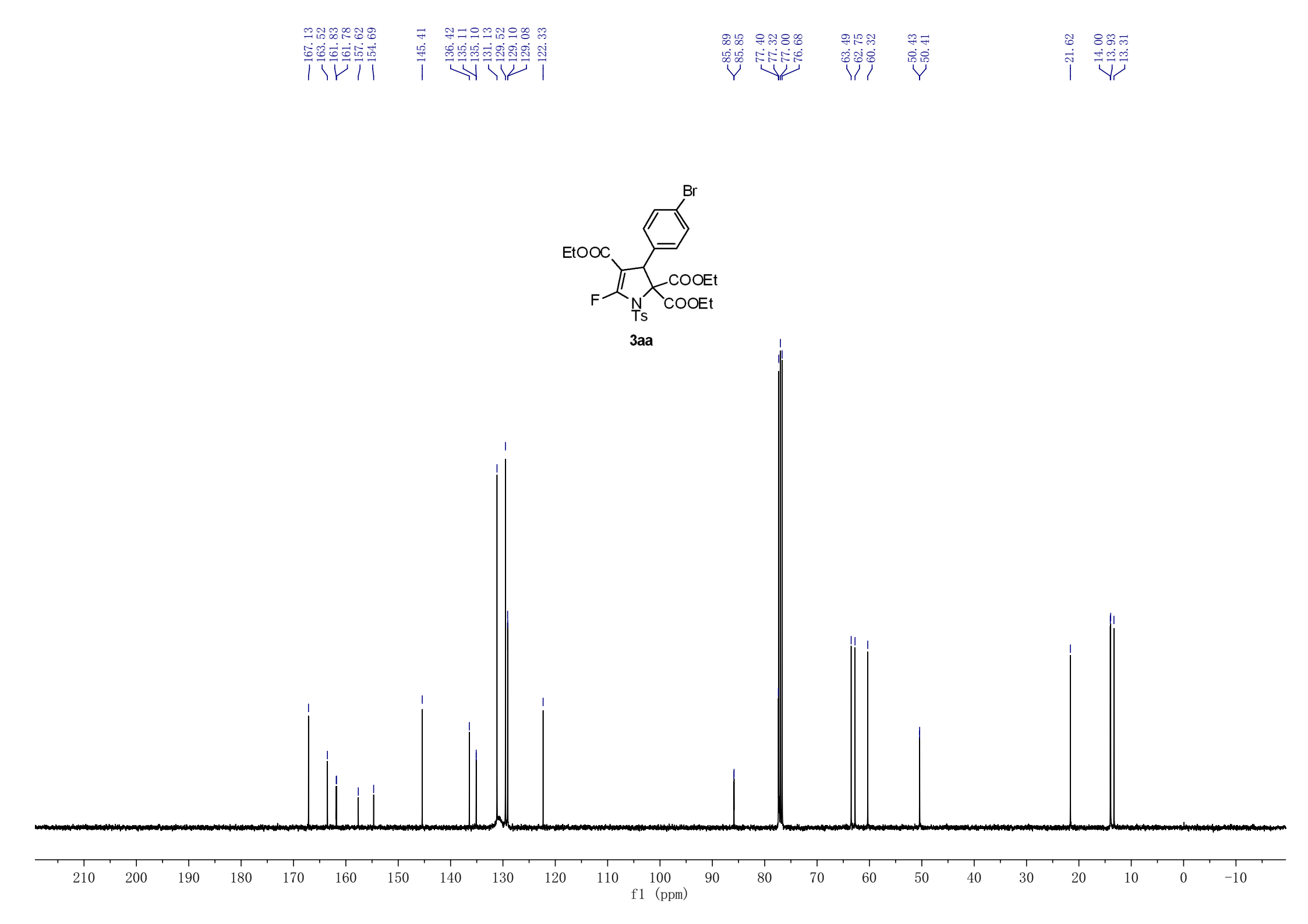
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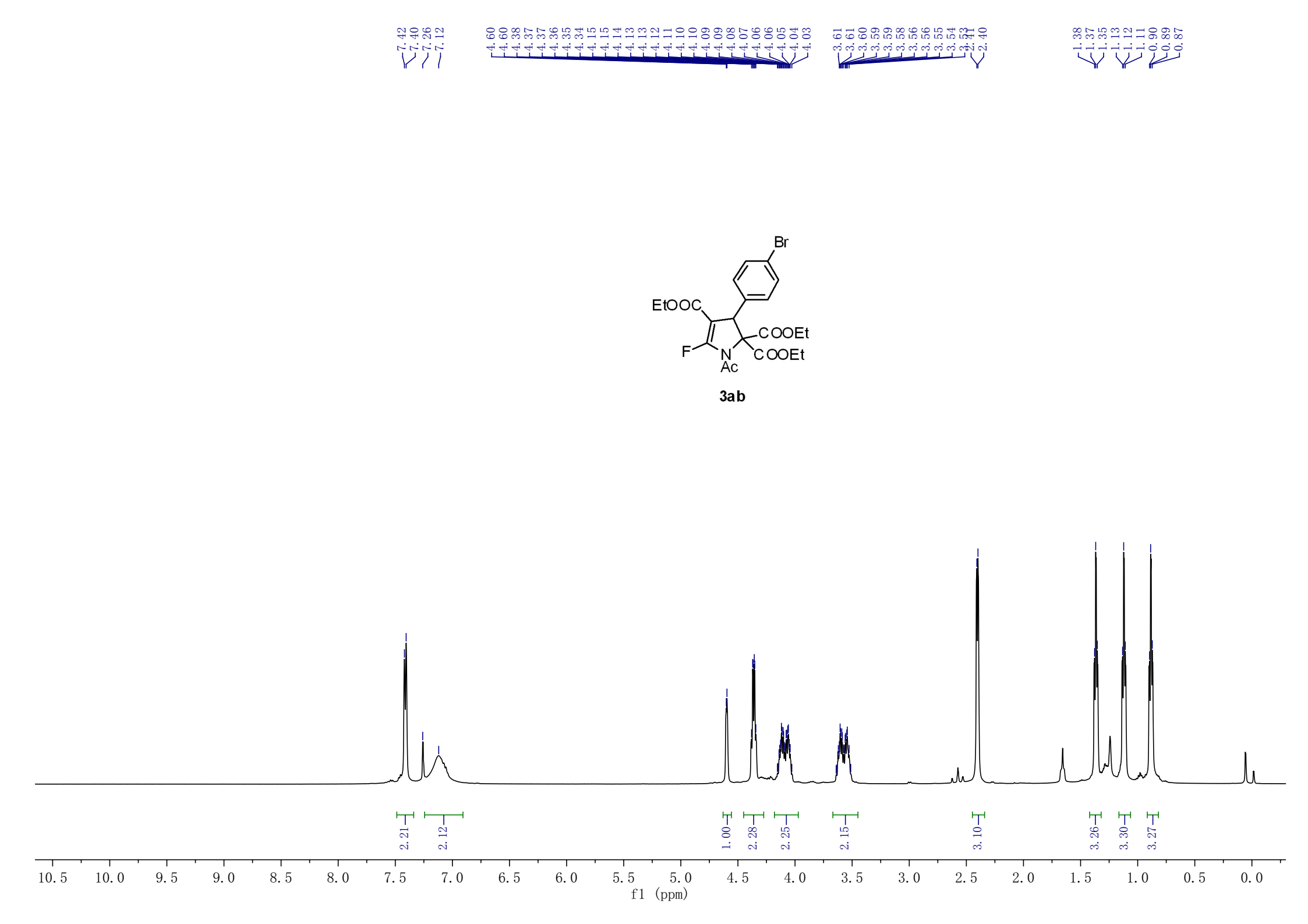
f1 (ppm)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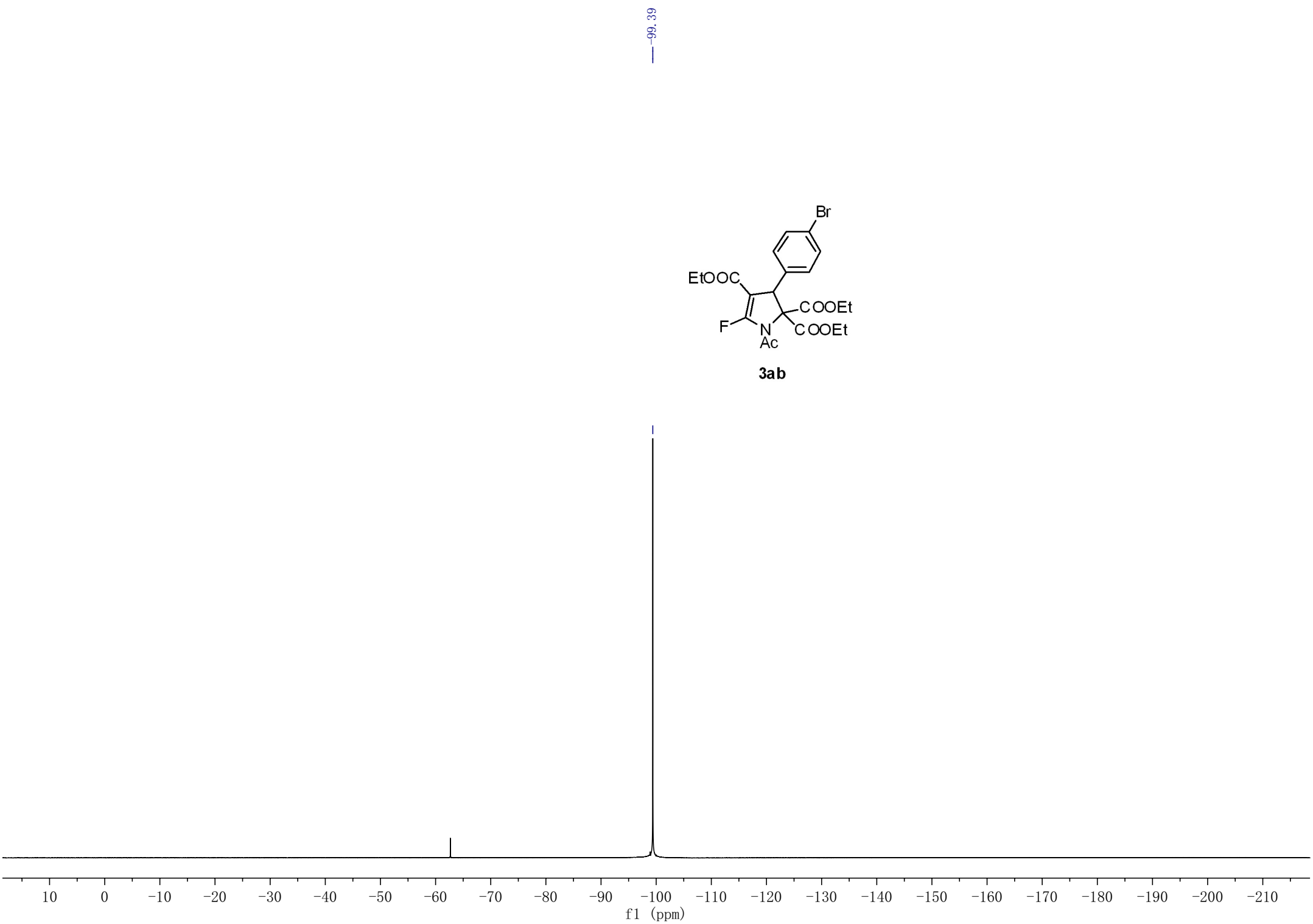
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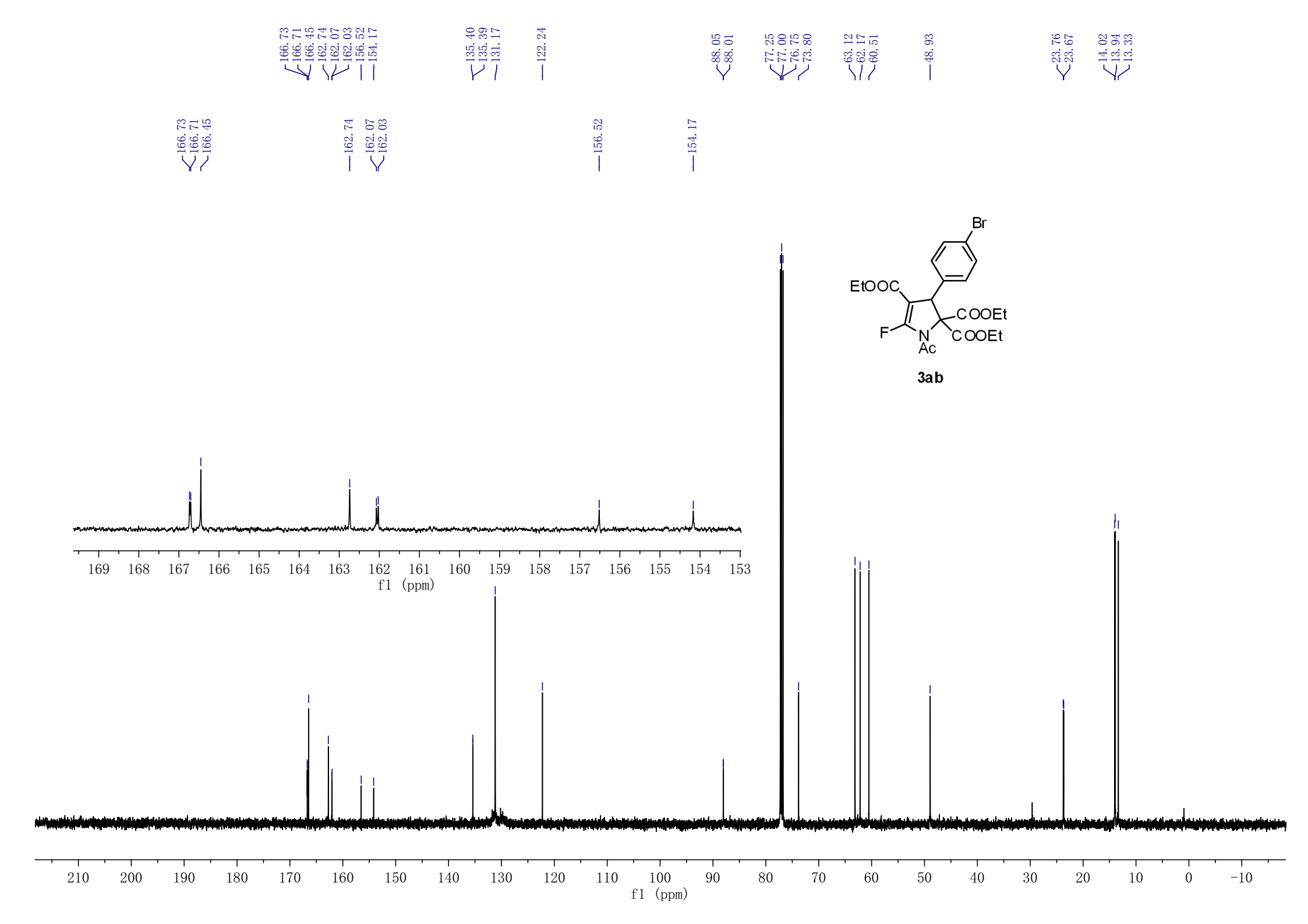
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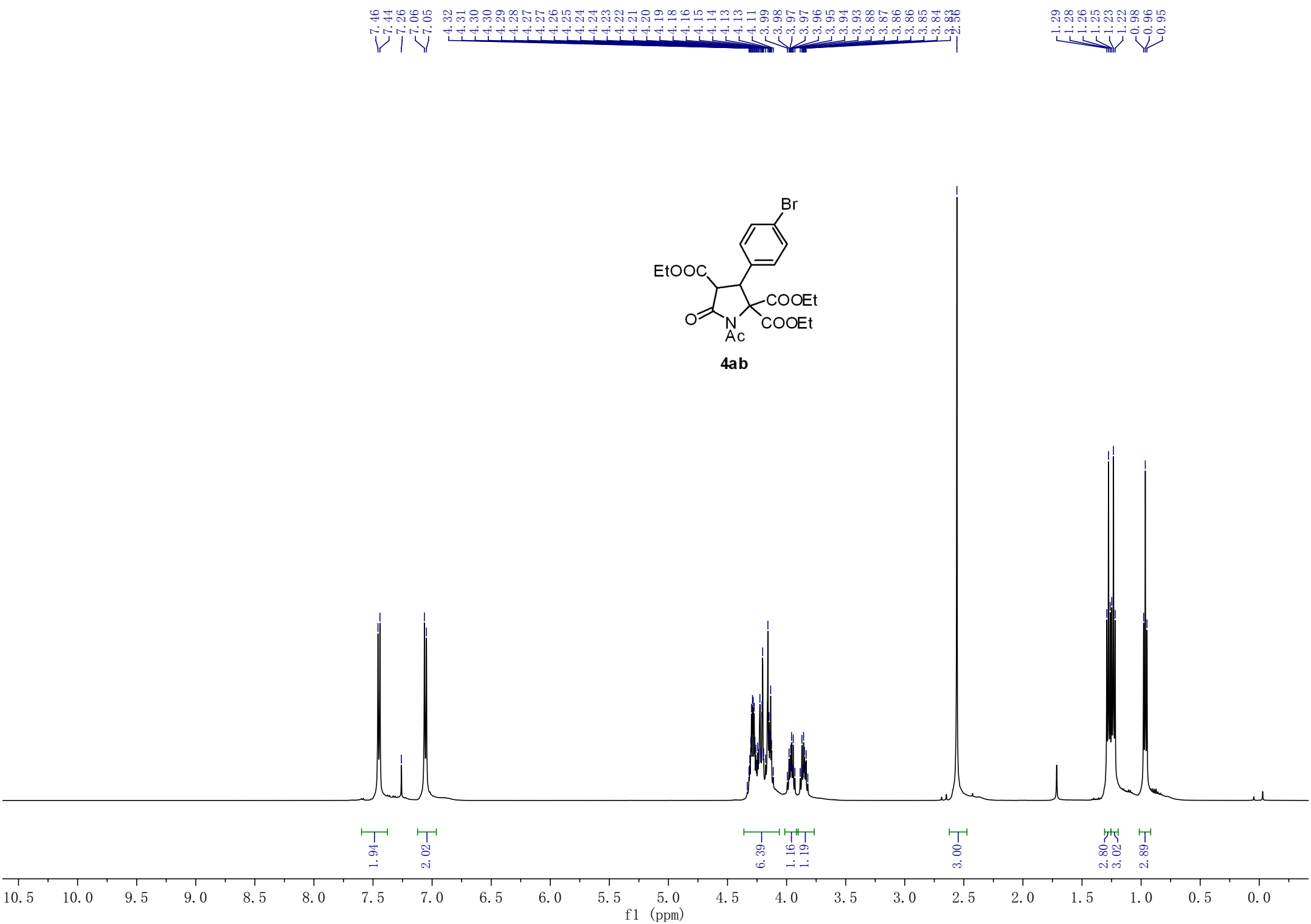
f1 (ppm)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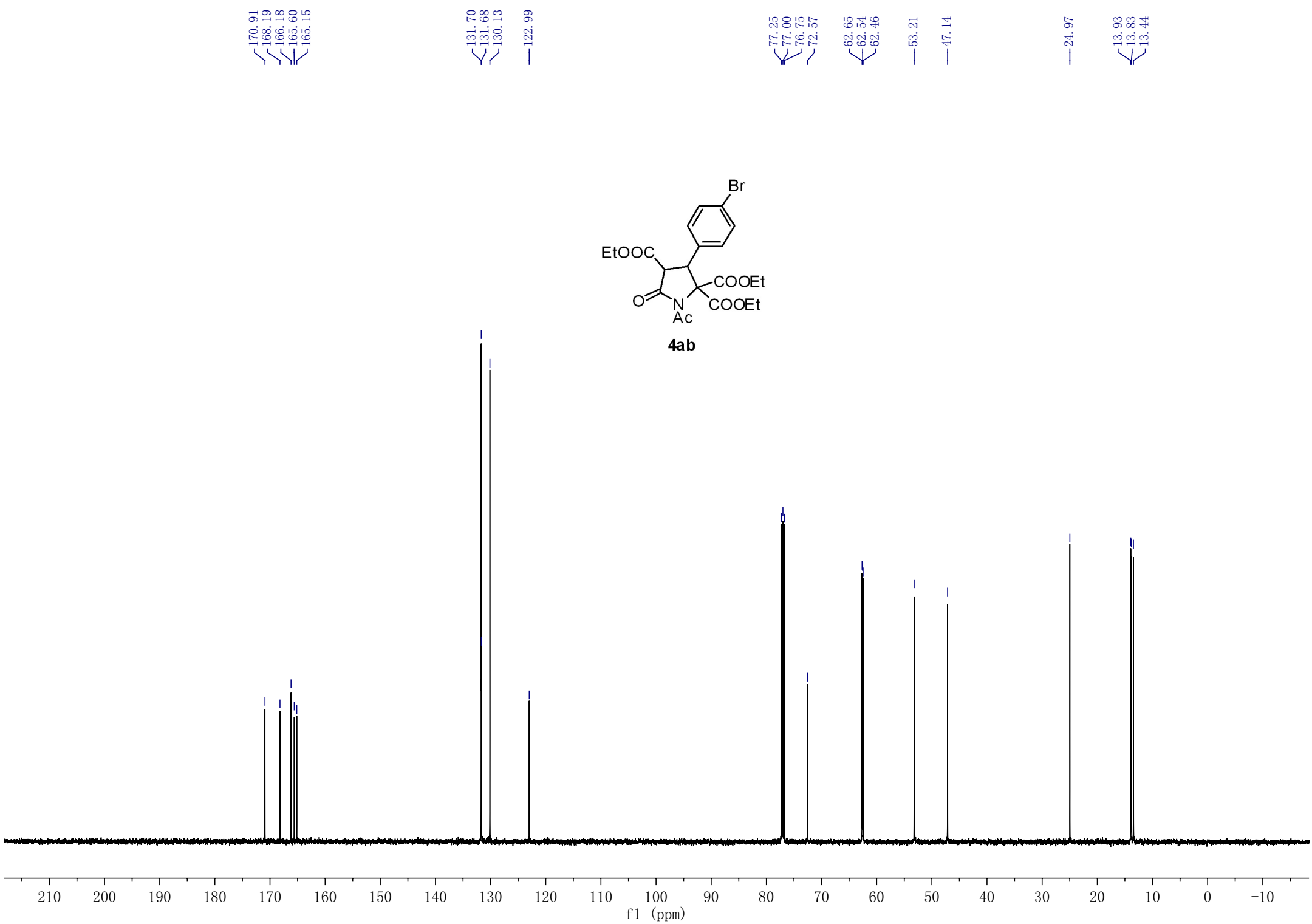
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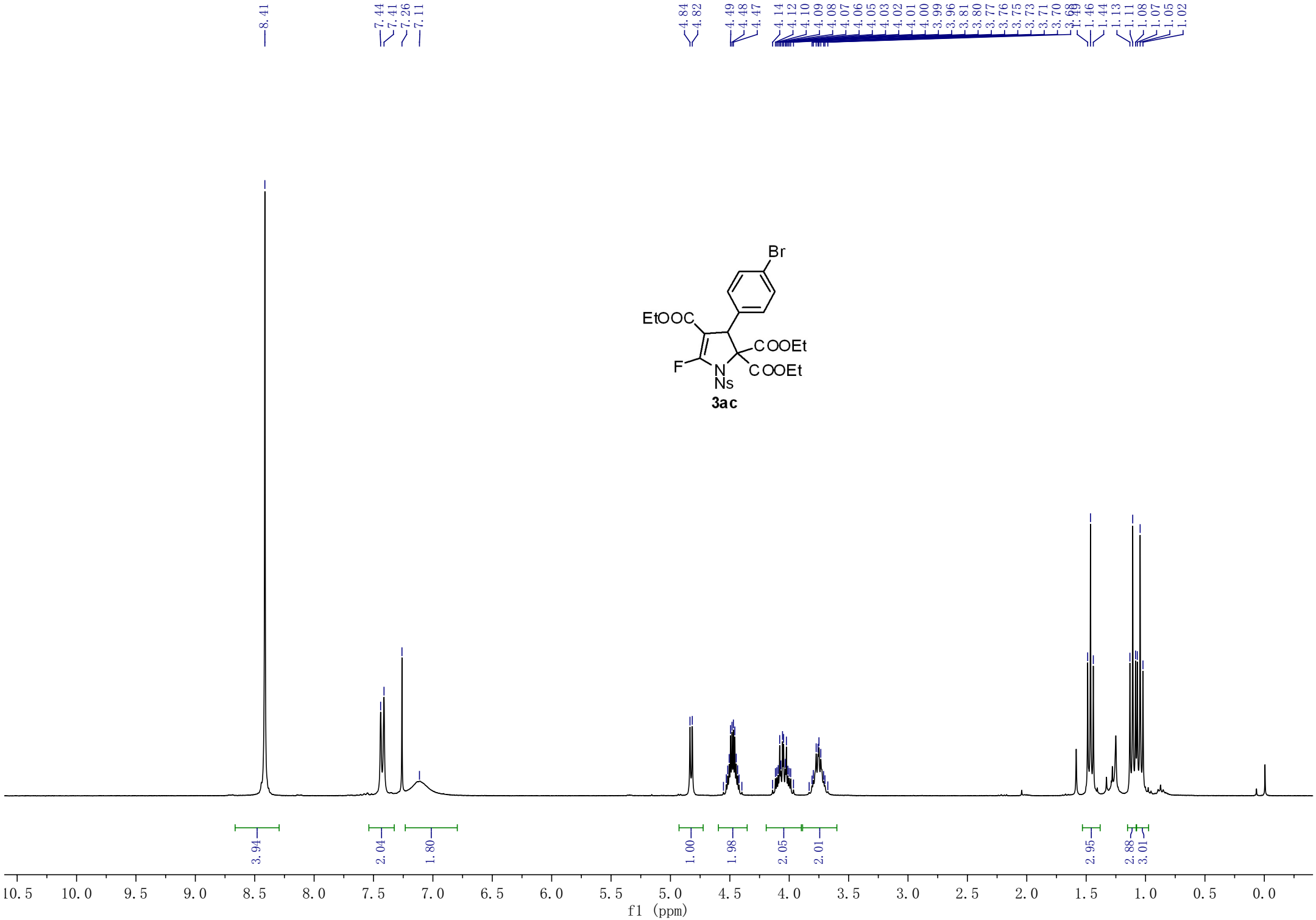
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2.88
3.01
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9.0
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6.0
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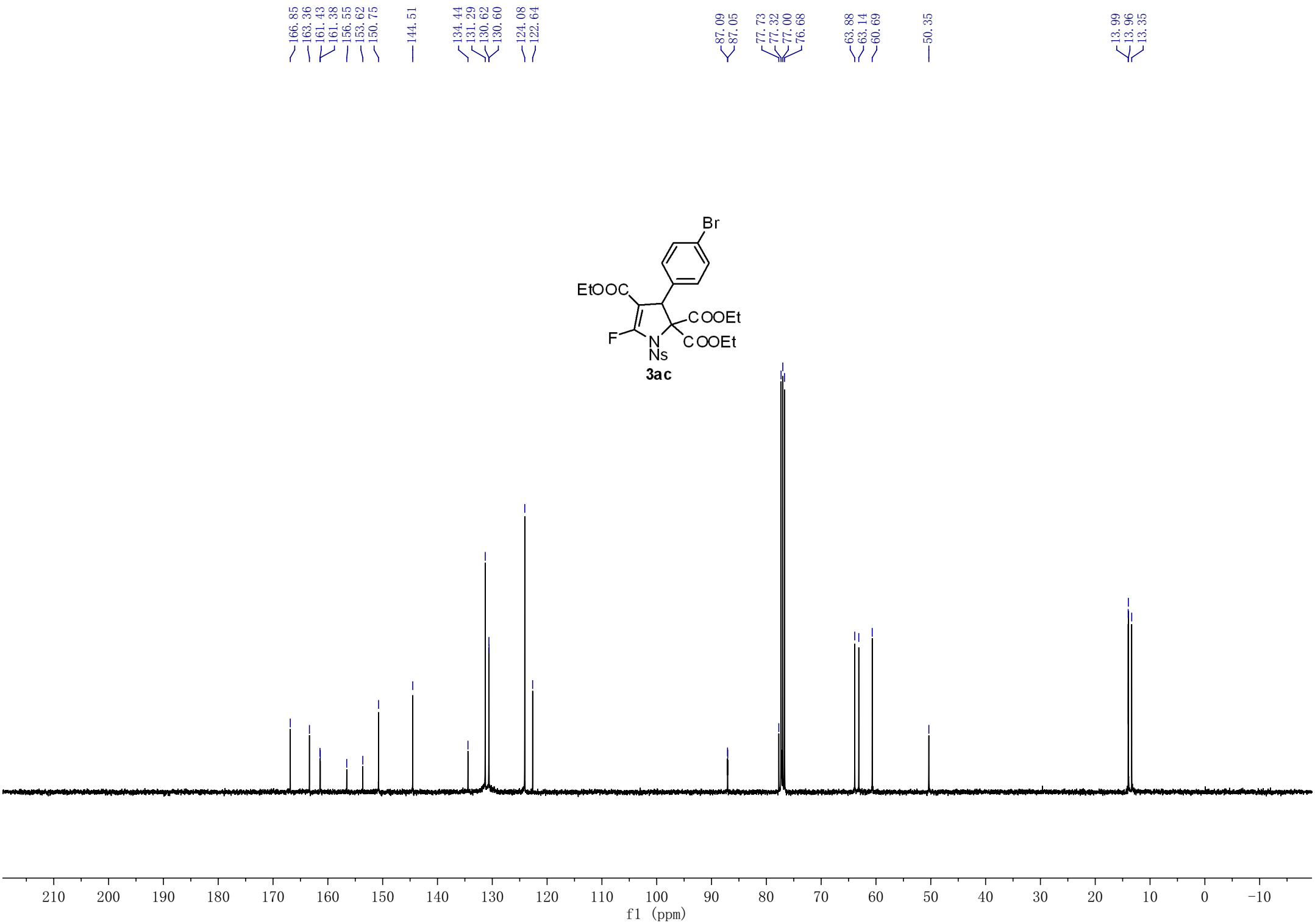
f1 (ppm)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122.64
87.09
87.05
77.73
77.32
77.00
76.68
63.88
63.14
60.69
50.35
13.99
13.96
13.35
Br
EtOOC
COOEt
F
N
COOEt
Ns
3ac
210
200
190
180
170
160
150
140
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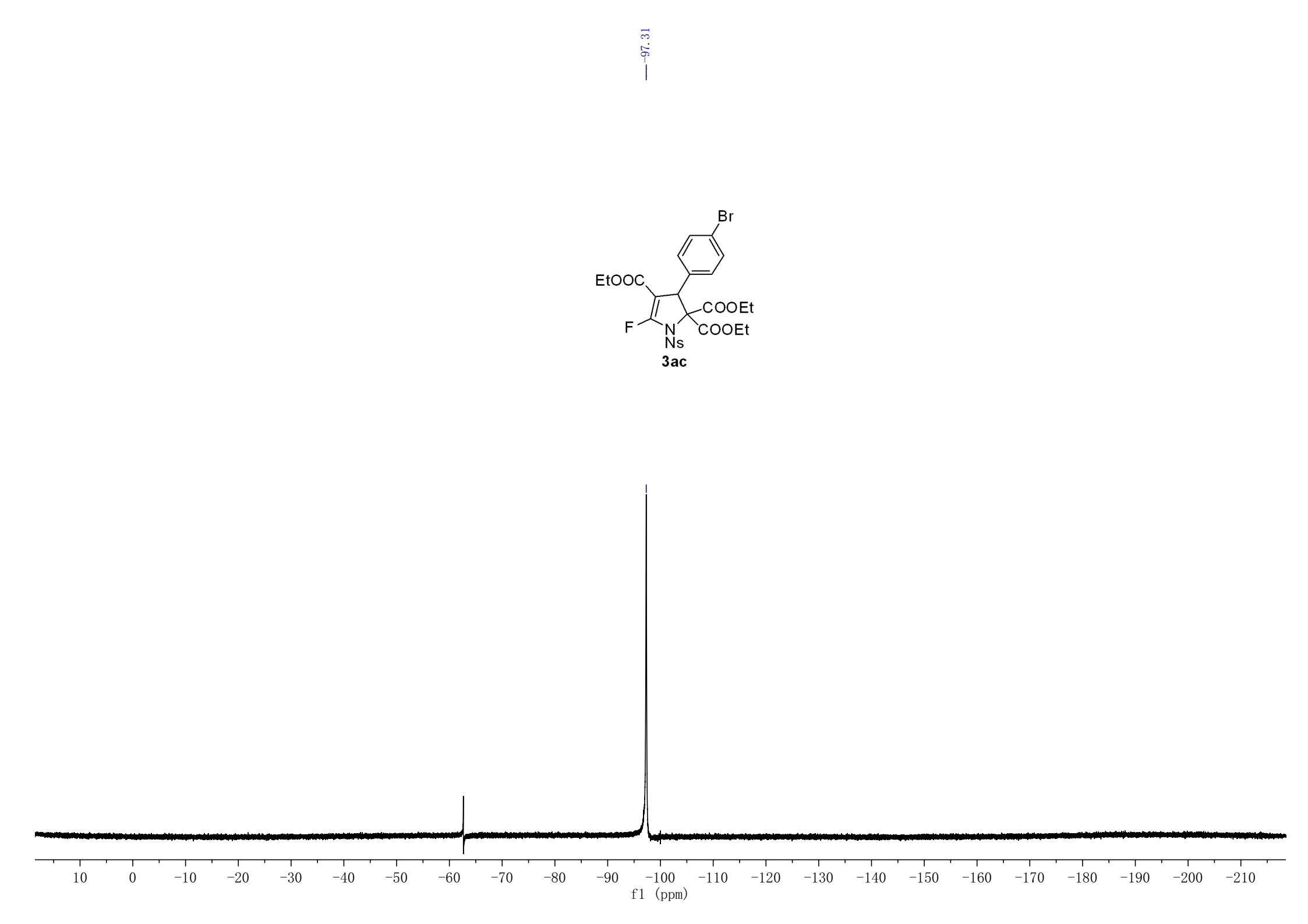
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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-60
-70
-80
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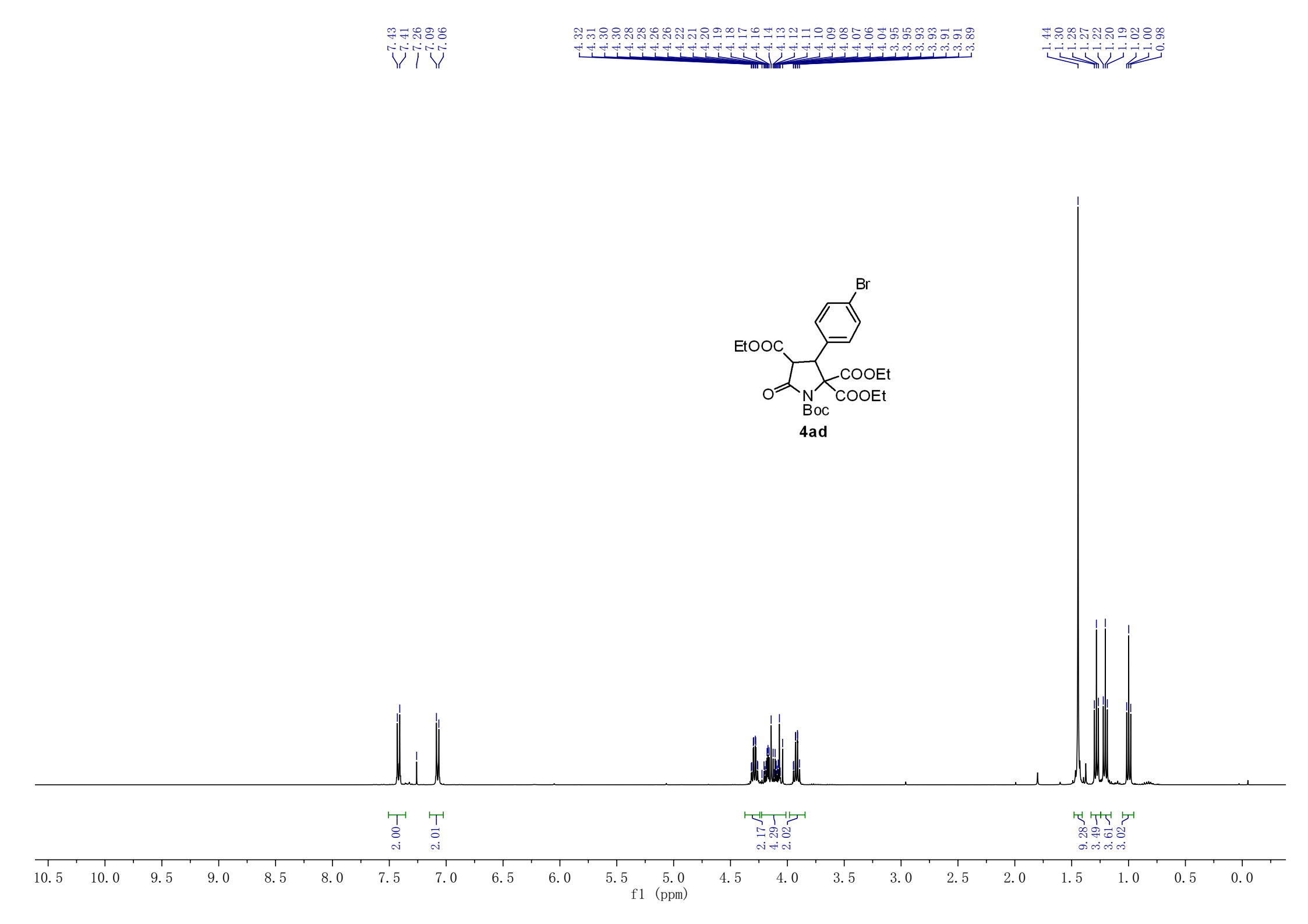
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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4.21
4.20
4.19
4.18
4.17
4.16
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.07
4.06
4.04
3.95
3.95
3.93
3.93
3.91
3.91
3.89
1.44
1.30
1.28
1.27
1.22
1.20
1.19
1.02
1.00
0.98
Br
EtOOC
COOEt
O
N
COOEt
Boc
4ad
2.00
2.01
2.17
4.29
2.02
9.28
3.49
3.61
3.02
10.5
10.0
9.5
9.0
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8.0
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7.0
6.5
6.0
5.5
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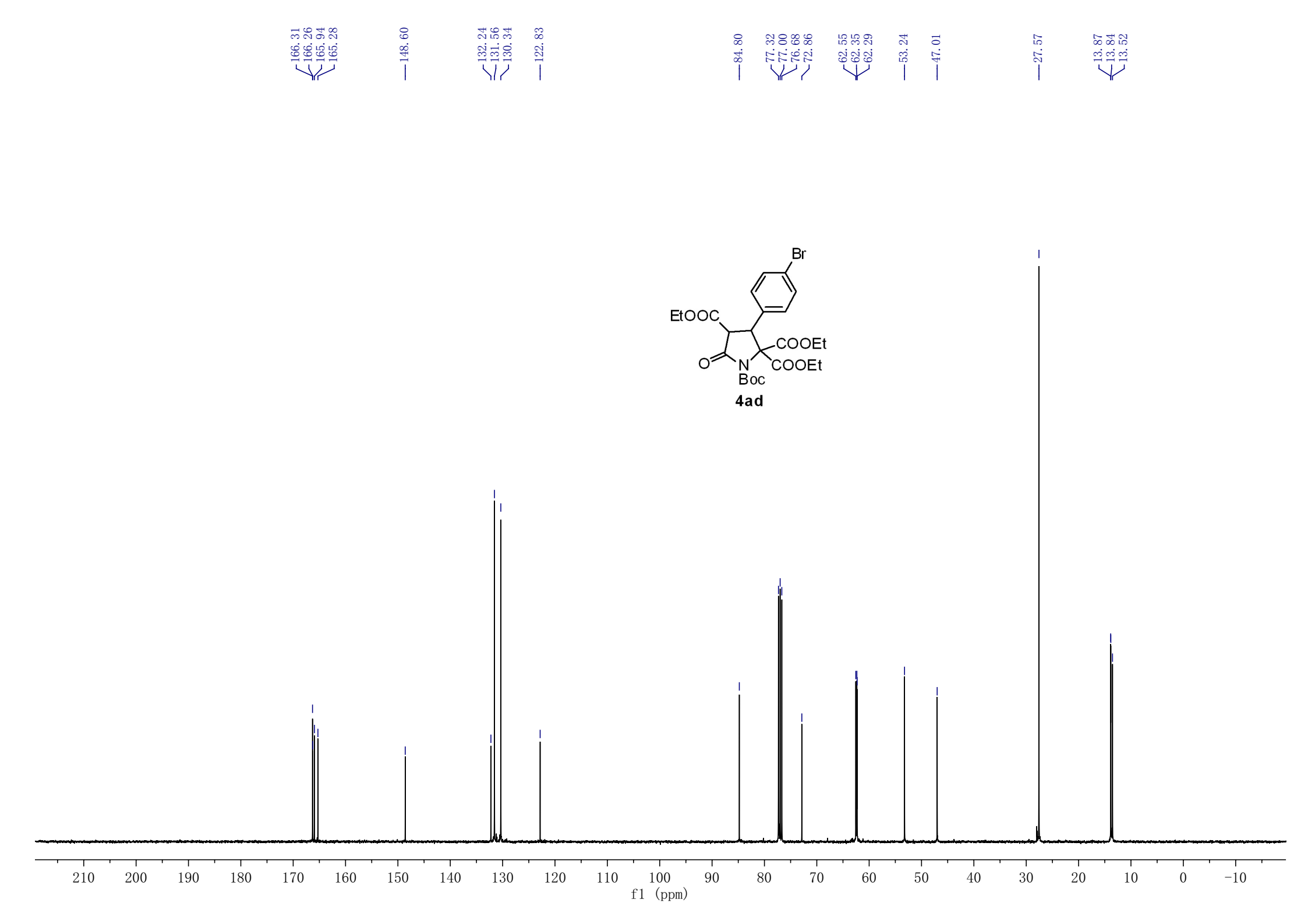
0.0
f1 (ppm)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77.00
76.68
72.86
62.55
62.35
62.29
53.24
47.01
27.57
13.87
13.84
13.52
Br
EtOOC
COOEt
O
N
COOEt
Boc
4ad
210
200
190
180
170
160
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100
90
80
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60
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40
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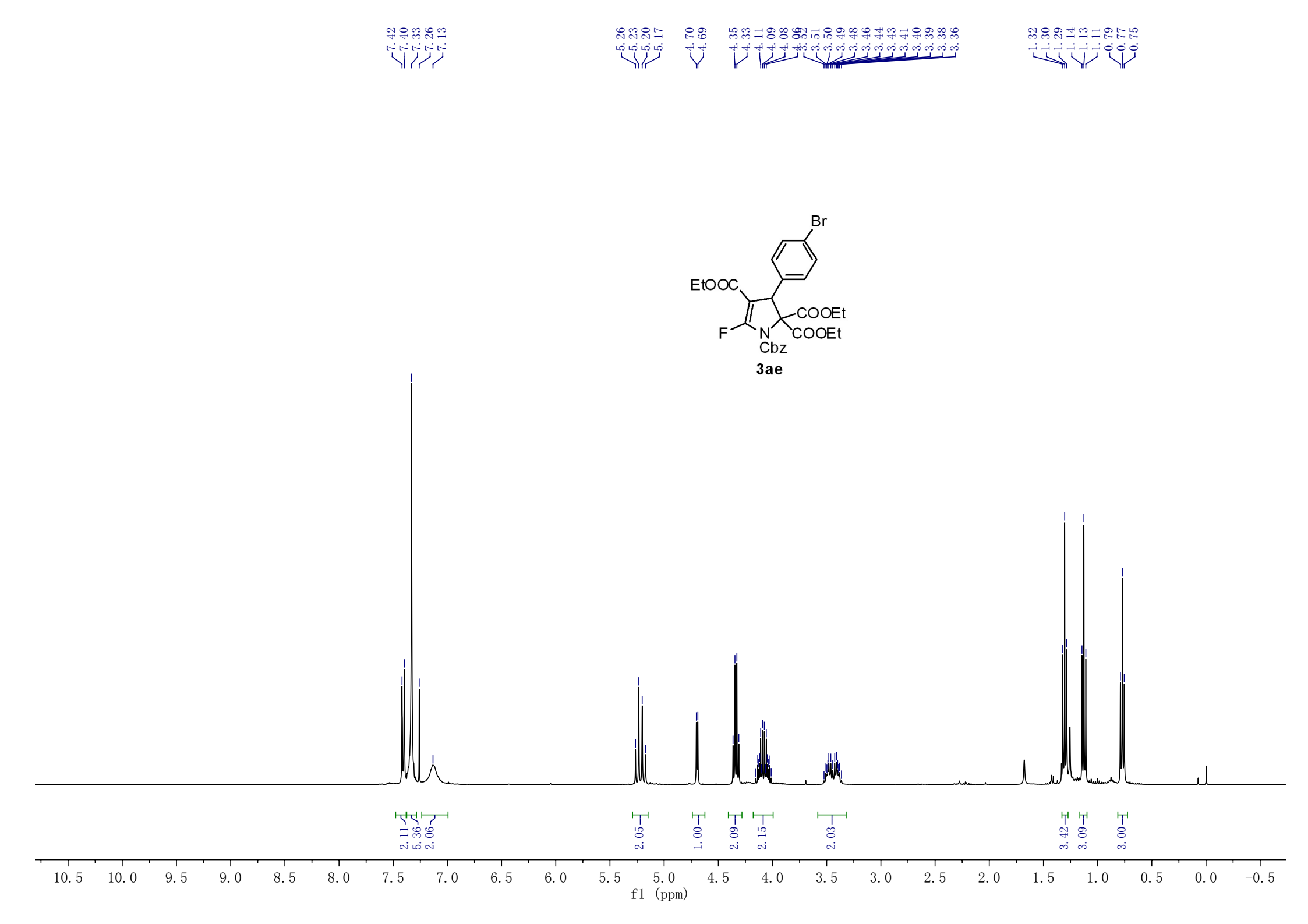
-10
f1 (ppm)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4.33
4.11
4.09
4.08
3.51
3.50
3.49
3.48
3.46
3.44
3.43
3.41
3.40
3.39
3.38
3.36
1.32
1.30
1.29
1.14
1.13
1.11
0.79
0.77
0.75
Br
EtOOC
COOEt
F
N
COOEt
Cbz
3ae
2.11
5.36
2.06
2.05
1.00
2.09
2.15
2.03
3.42
3.09
3.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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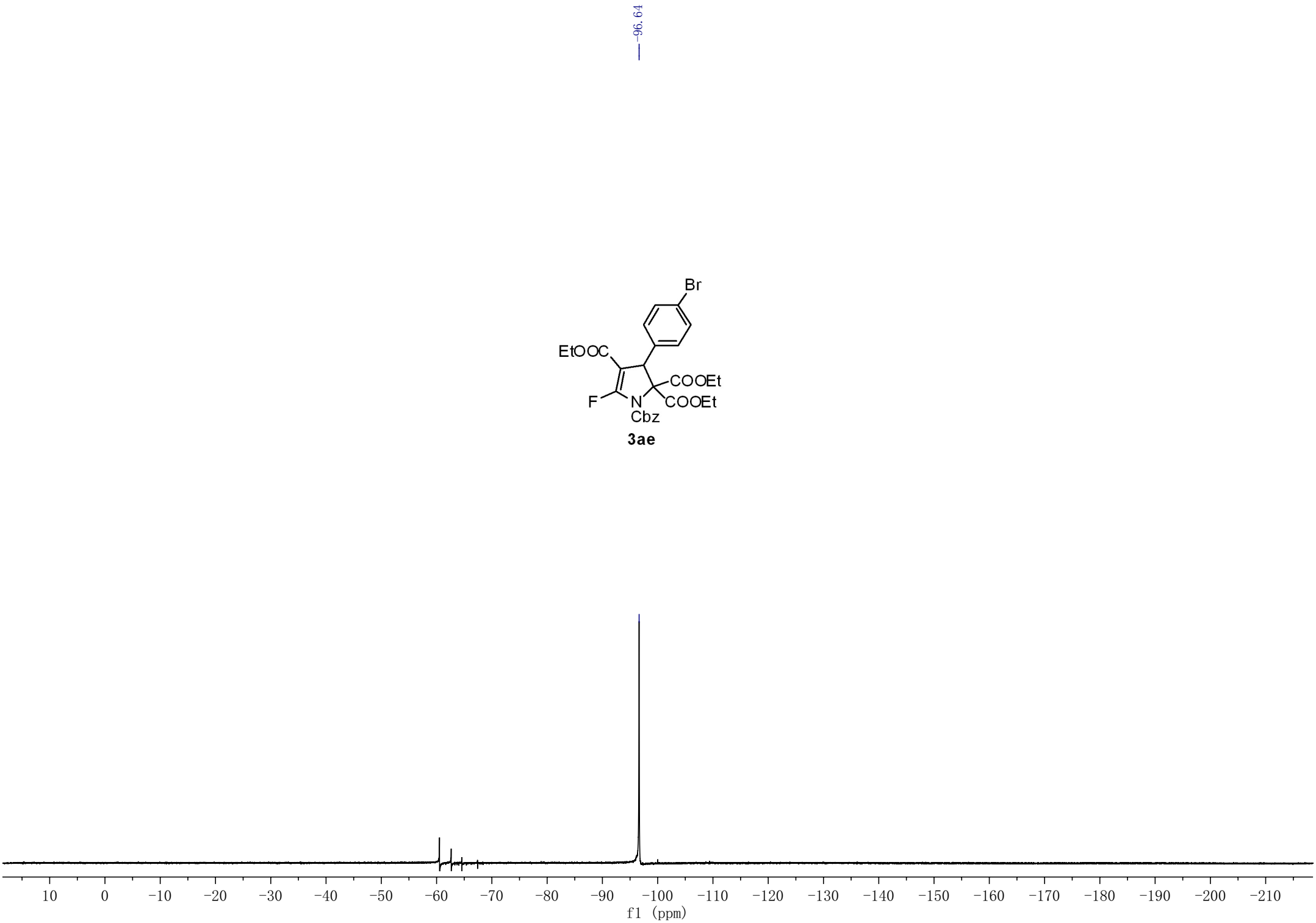
0.0
-0.5
f1 (ppm)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COOEt
Cbz
3ae
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-10
-20
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-40
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-60
-70
-80
-90
-100
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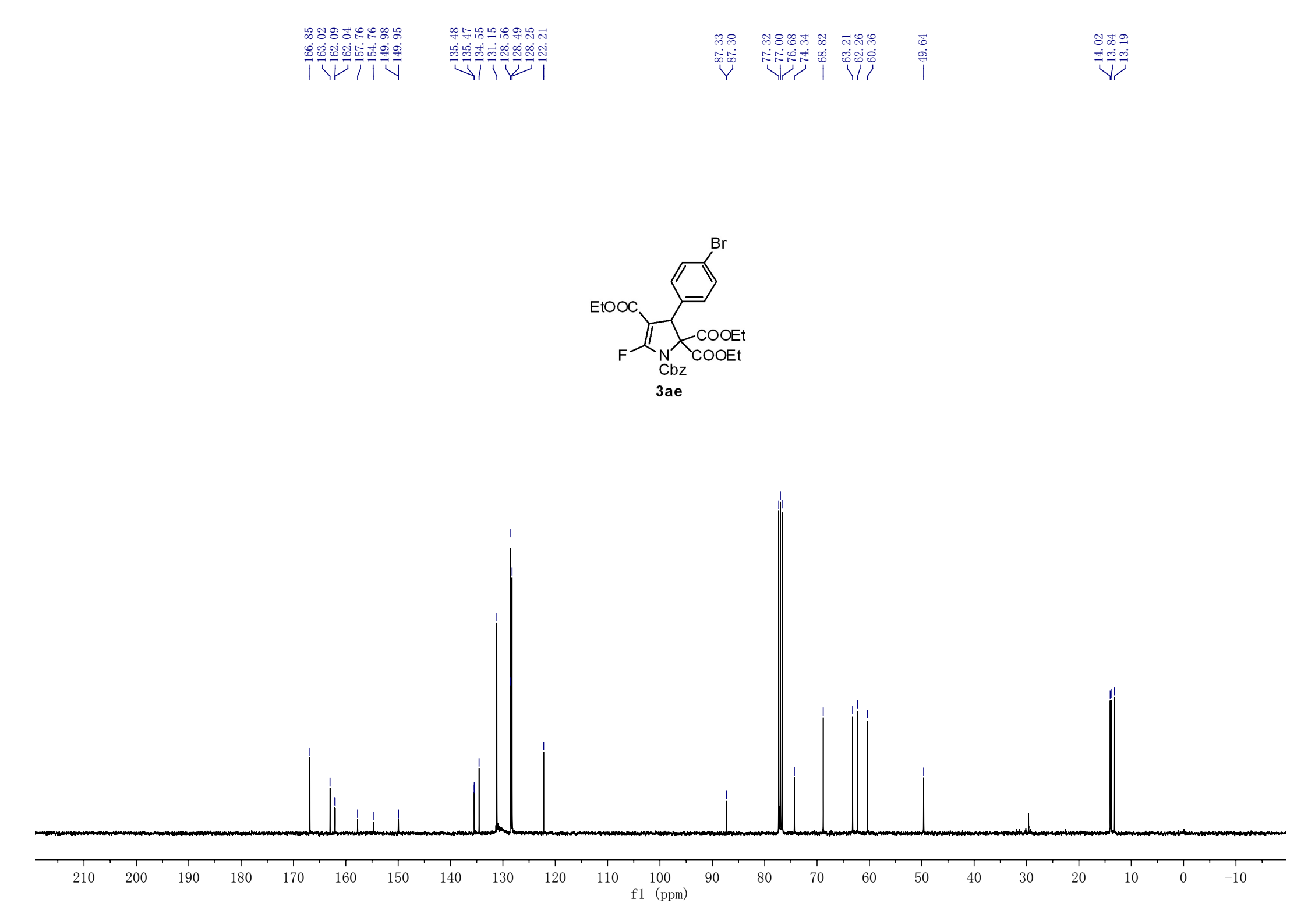
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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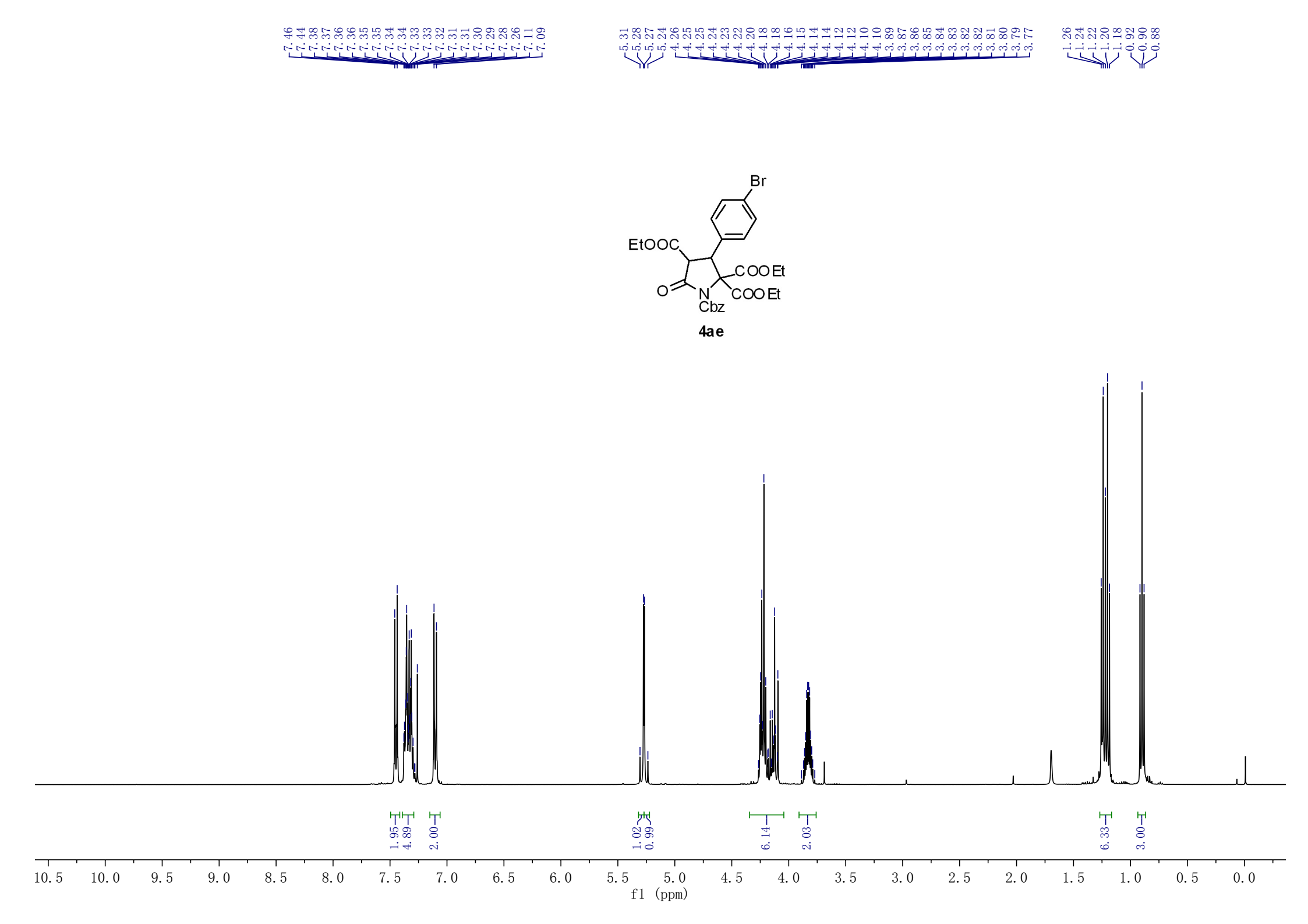
149.95
135.48
135.47
134.55
131.15
128.56
128.49
128.25
122.21
87.33
87.30
77.32
77.00
76.68
74.34
68.82
63.21
62.26
60.36
49.64
14.02
13.84
13.19
Br
EtOOC
COOEt
F
N
COOEt
Cbz
3ae
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.31
7.30
7.29
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7.11
7.09
5.31
5.28
5.27
5.24
4.26
4.25
4.25
4.24
4.23
4.22
4.20
4.18
4.18
4.16
4.15
4.14
4.14
4.12
4.12
4.10
4.10
3.89
3.87
3.86
3.85
3.84
3.83
3.82
3.82
3.81
3.80
3.79
3.77
1.26
1.24
1.22
1.20
1.18
0.92
0.90
0.88
Br
EtOOC
COOEt
COOEt
O
N
Cbz
4ae
1.95
4.89
2.00
1.02
0.99
6.14
2.03
6.33
3.00
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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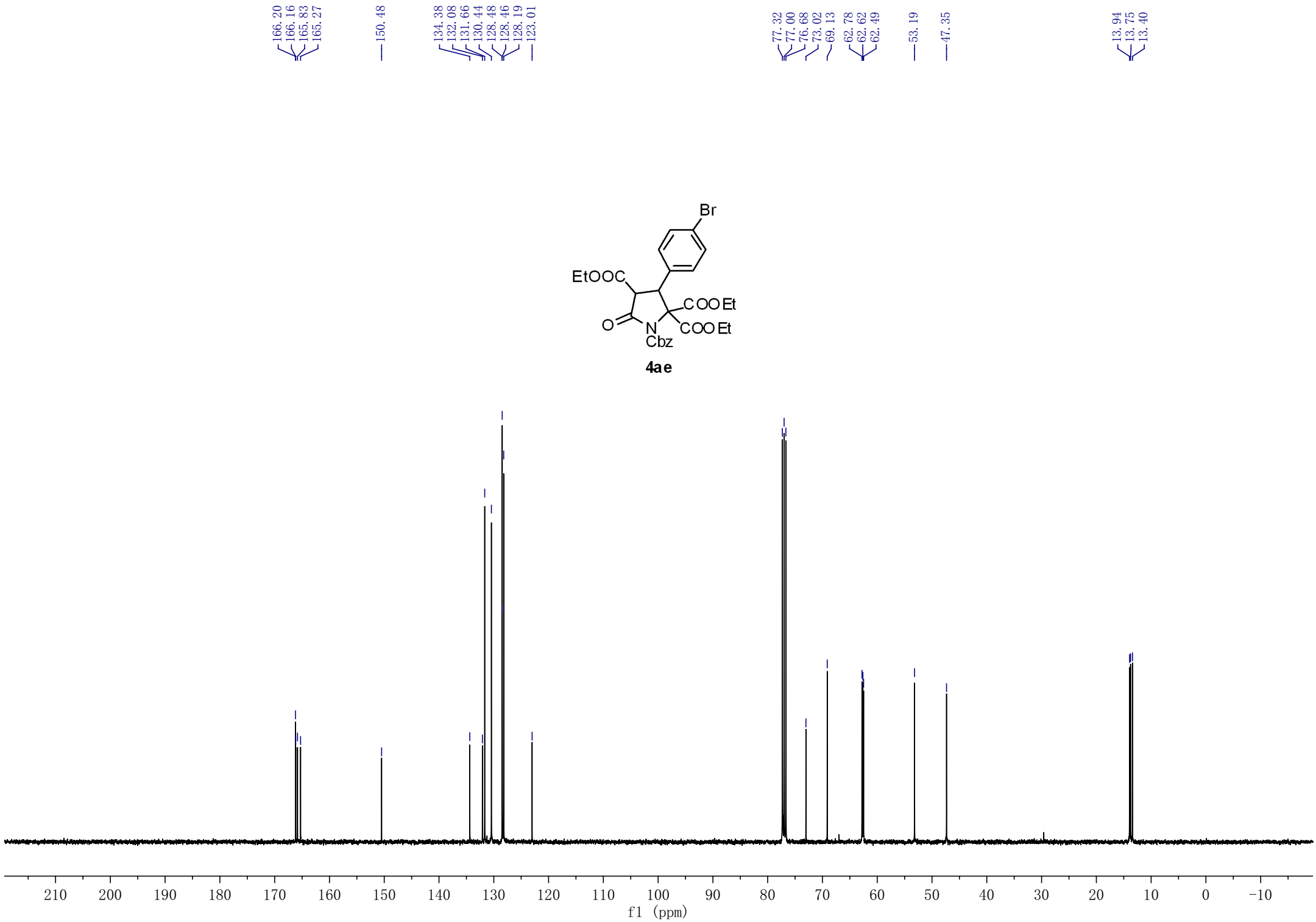
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.08
131.66
130.44
128.48
128.46
128.19
123.01
77.32
77.00
76.68
73.02
69.13
62.78
62.62
62.49
53.19
47.35
13.94
13.75
13.40
Br
EtOOC
COOEt
O
N
COOEt
Cbz
4ae
210
200
190
180
170
160
150
140
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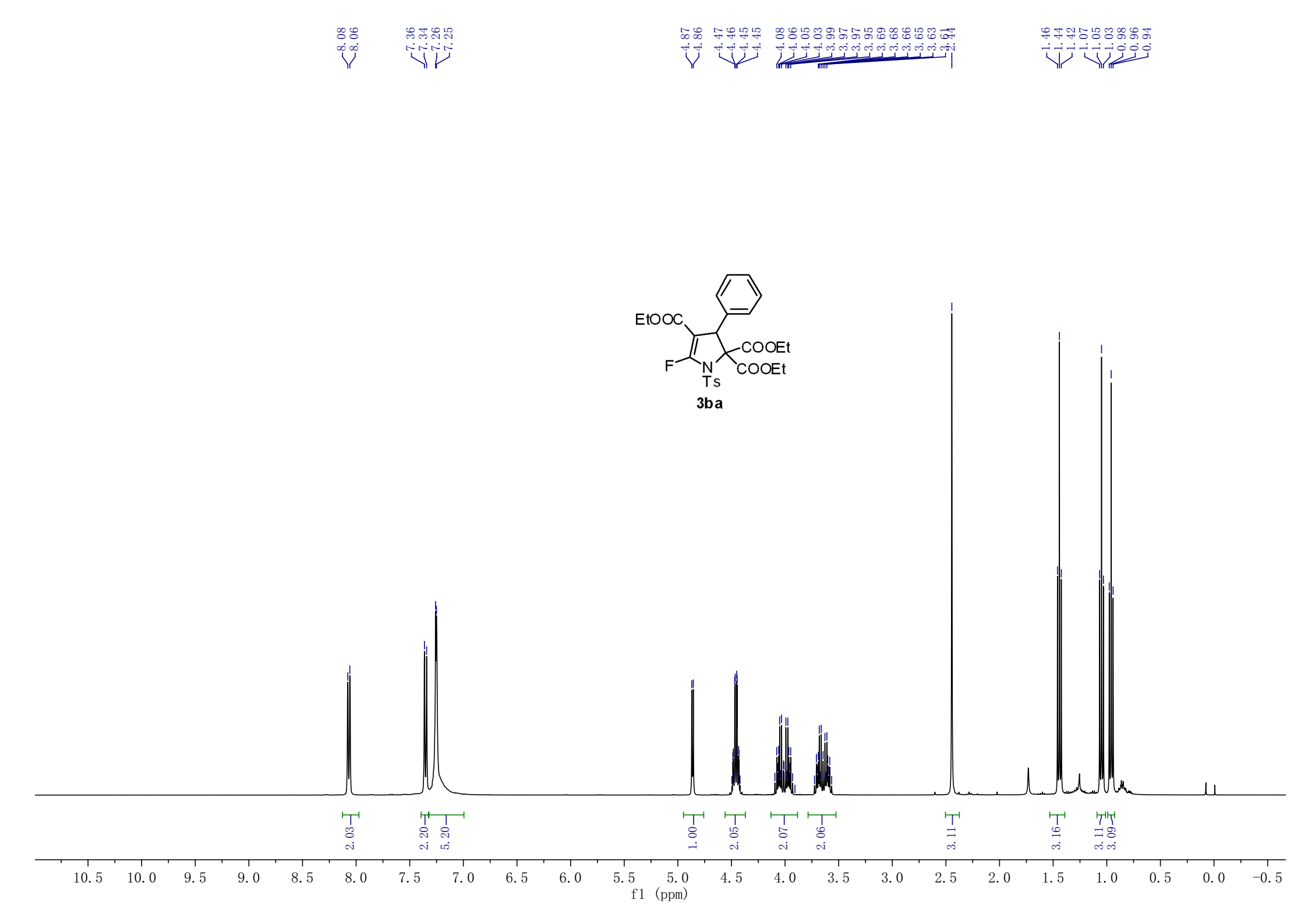
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.06
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7.34
7.26
7.25
4.87
4.86
4.47
4.46
4.45
4.45
4.08
4.06
4.05
4.03
3.99
3.97
3.97
3.95
3.69
3.68
3.66
3.65
3.63
3.61
3.44
1.46
1.44
1.42
1.07
1.05
1.03
0.98
0.96
0.94
EtOOC
COOEt
F
N
COOEt
Ts
3ba
2.03
2.20
5.20
1.00
2.05
2.07
2.06
3.11
3.16
3.11
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
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3.0
2.5
2.0
1.5
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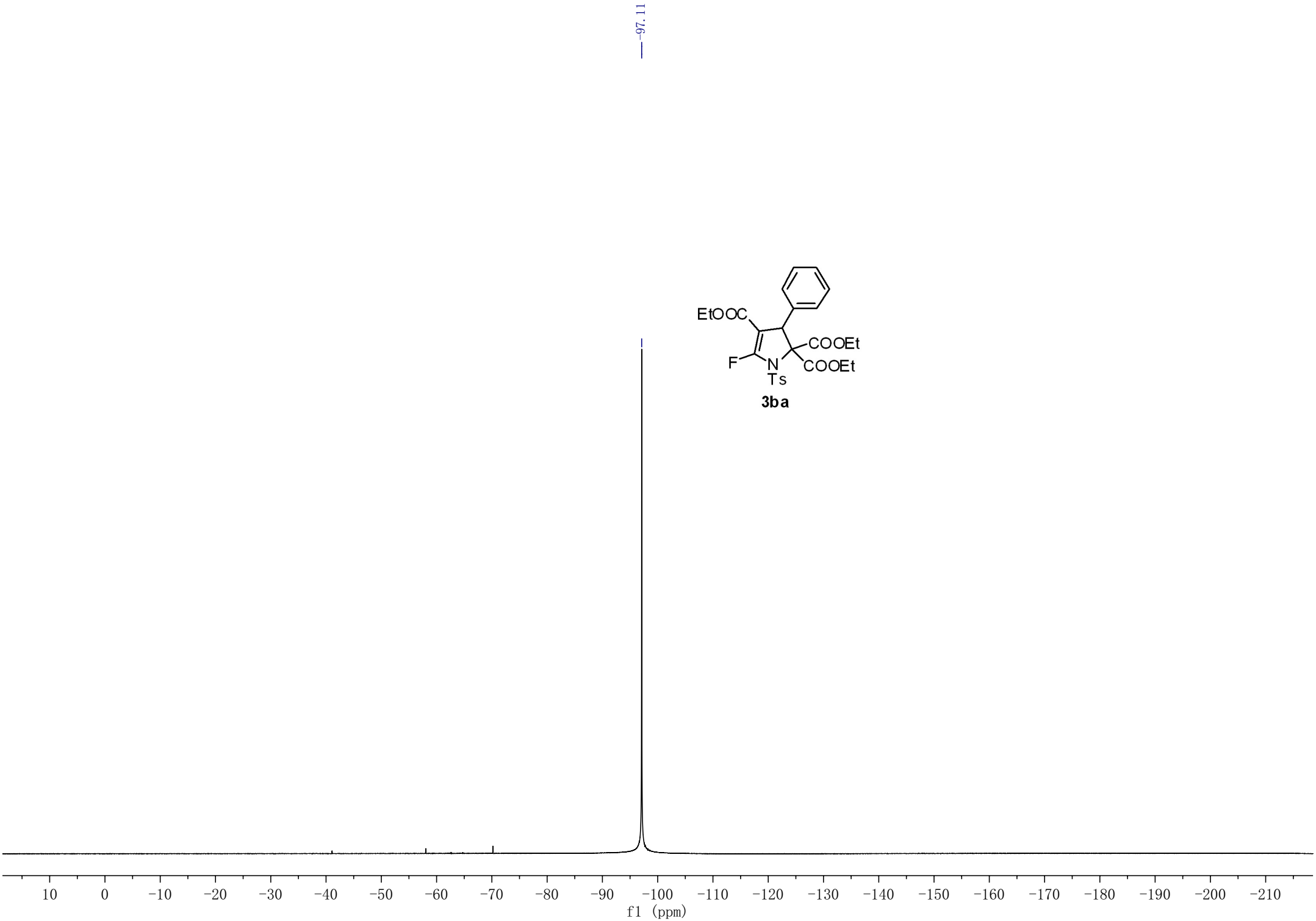
0.5
0.0
-0.5
f1 (ppm)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F
N
COOEt
Ts
3ba
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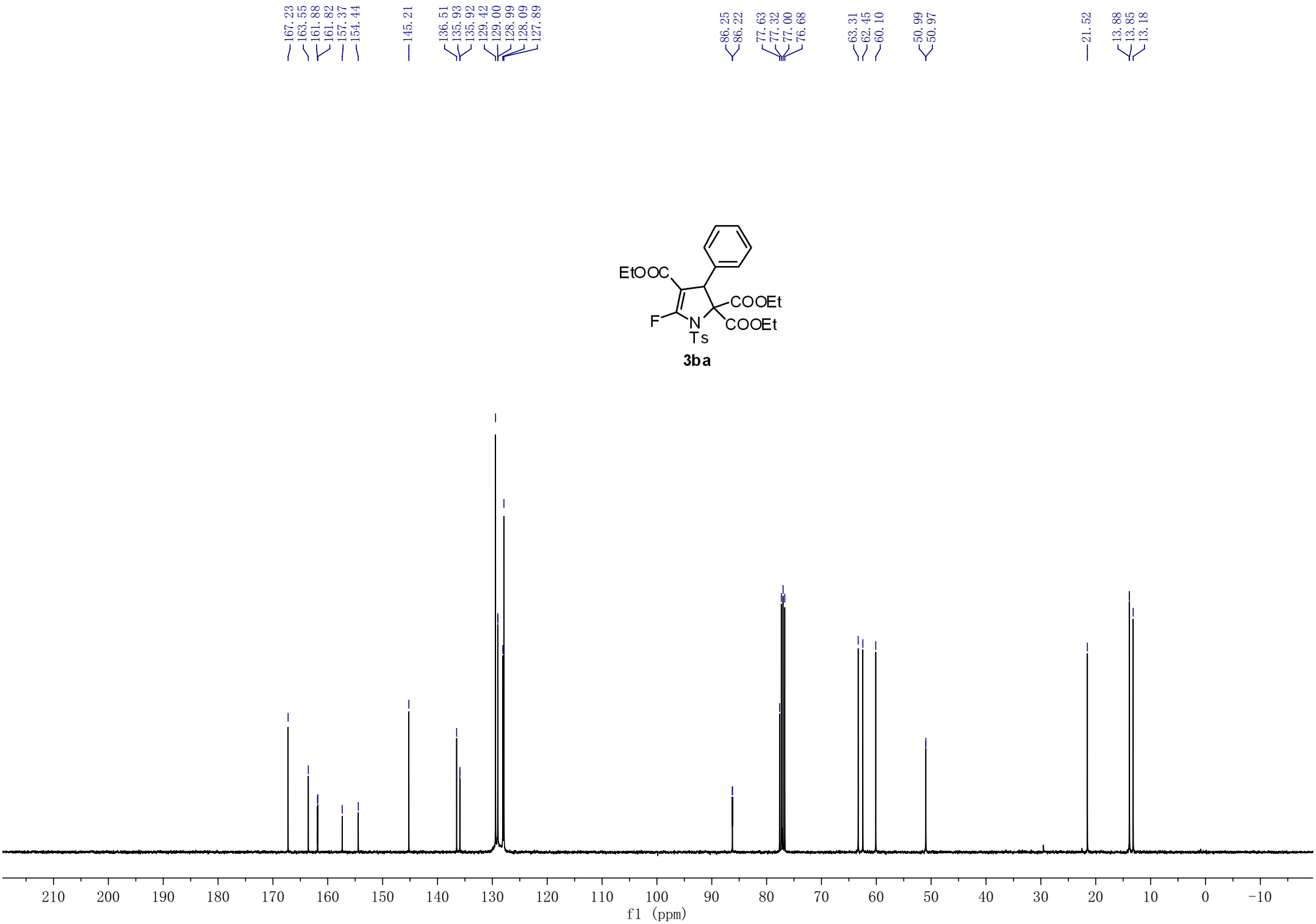
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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136.51
135.93
135.92
129.42
129.00
128.99
128.09
127.89
86.25
86.22
77.63
77.32
77.00
76.68
63.31
62.45
60.10
50.99
50.97
21.52
13.88
13.85
13.18
EtOOC
COOEt
F
N
COOEt
Ts
3ba
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
50
40
30
20
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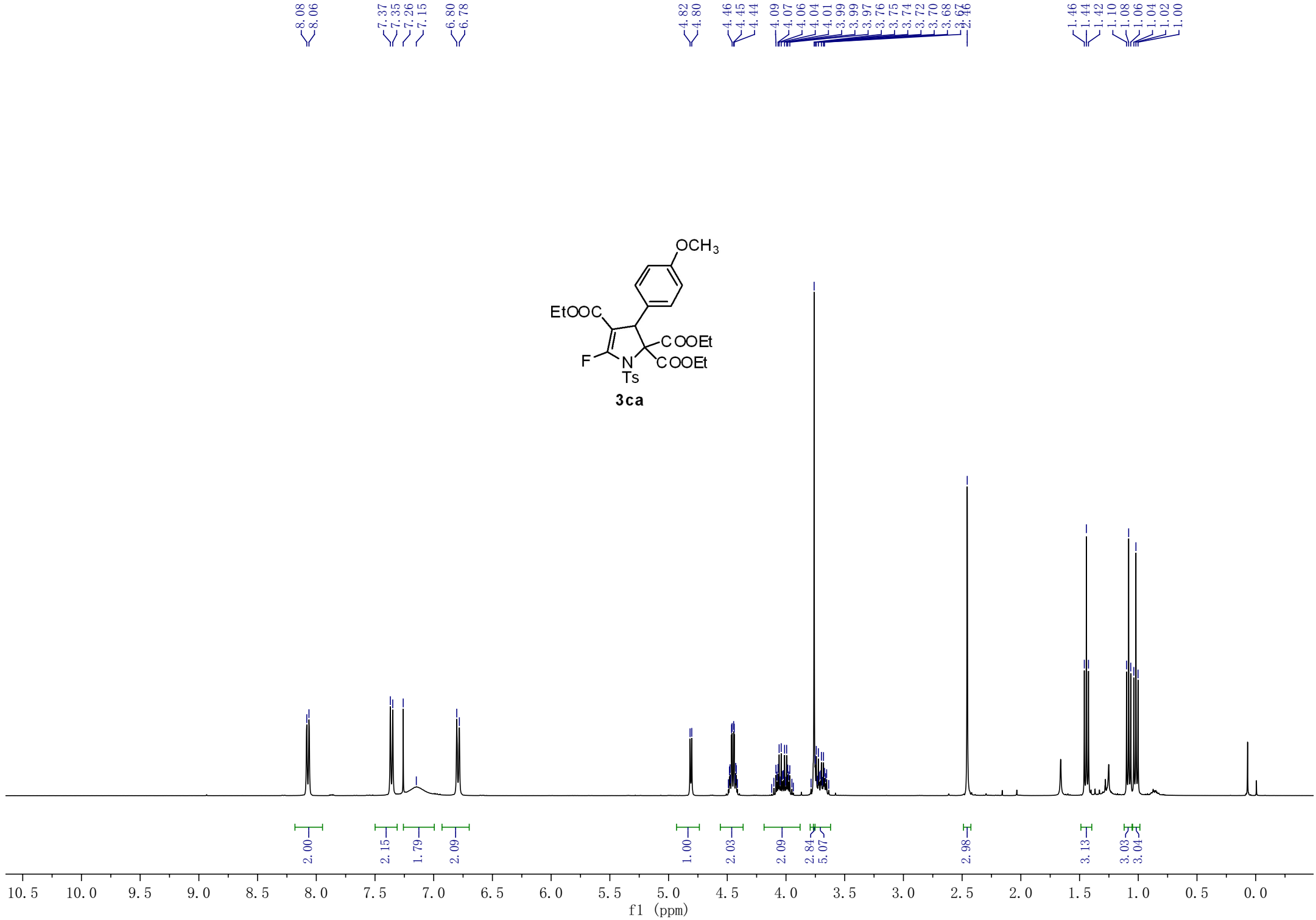
0
-10
f1 (ppm)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4.80
4.46
4.45
4.44
4.09
4.07
4.06
4.04
4.01
3.99
3.99
3.97
3.76
3.75
3.74
3.72
3.70
3.68
3.67
3.66
2.46
1.46
1.44
1.42
1.10
1.08
1.06
1.04
1.02
1.00
OCH3
EtOOC
COOEt
F
N
COOEt
Ts
3ca
2.00
2.15
1.79
2.09
1.00
2.03
2.09
2.84
5.07
2.98
3.13
3.03
3.04
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
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3.5
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2.5
2.0
1.5
1.0
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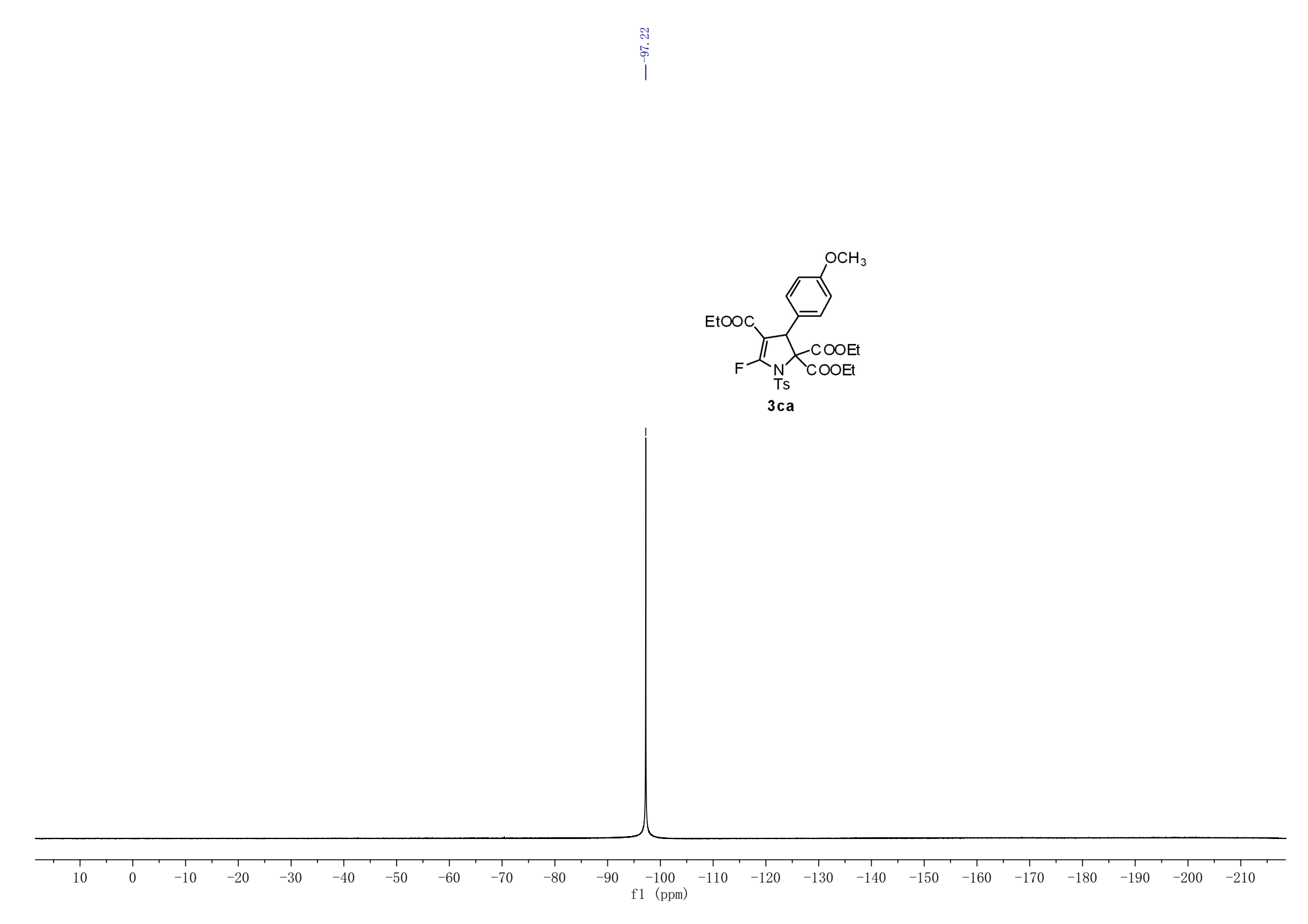
0.0
f1 (ppm)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F
N
COOEt
Ts
3ca
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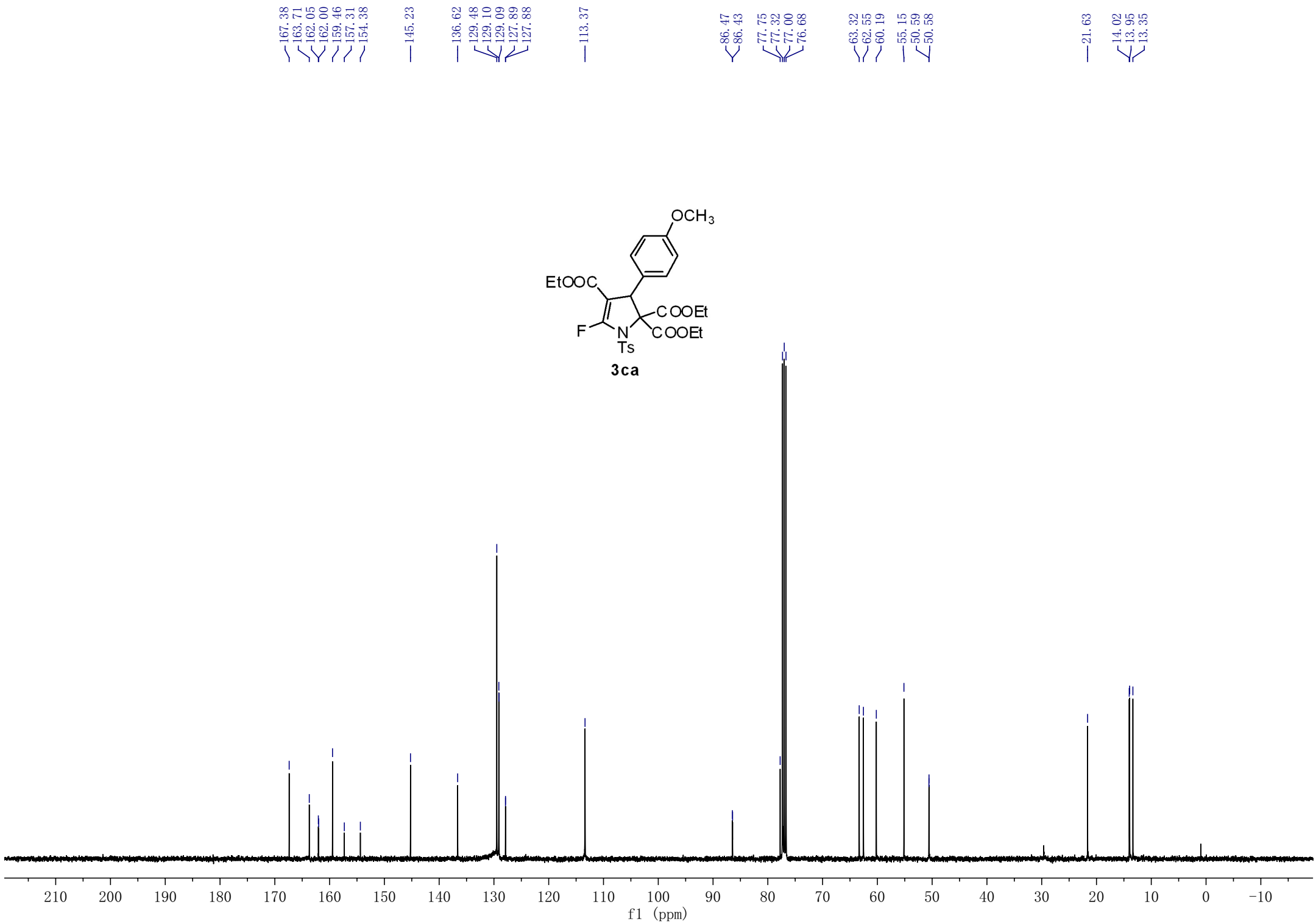
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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136.62
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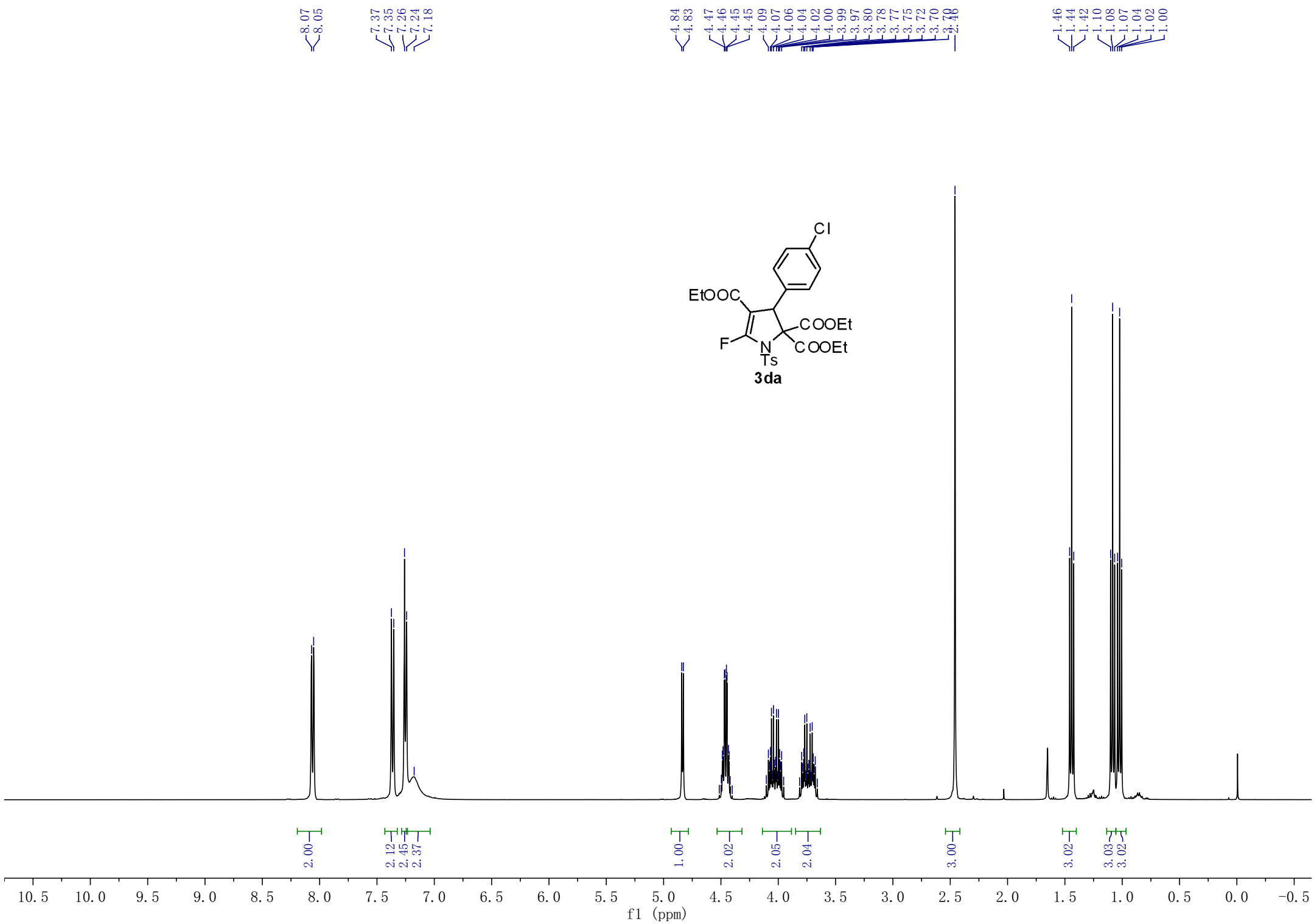
129.10
129.09
127.89
127.88
113.37
86.47
86.43
77.75
77.32
77.00
76.68
63.32
62.55
60.19
55.15
50.59
50.58
21.63
14.02
13.95
13.35
OCH3
EtOOC
COOEt
F
N
COOEt
Ts
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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4.83
4.47
4.46
4.45
4.45
4.09
4.07
4.06
4.04
4.02
4.00
3.99
3.97
3.80
3.78
3.77
3.75
3.72
3.70
2.48
1.46
1.44
1.42
1.10
1.08
1.07
1.04
1.02
1.00
Cl
EtOOC
COOEt
F
N
COOEt
Ts
3da
2.00
2.12
2.45
2.37
1.00
2.02
2.05
2.04
3.00
3.02
3.03
3.02
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
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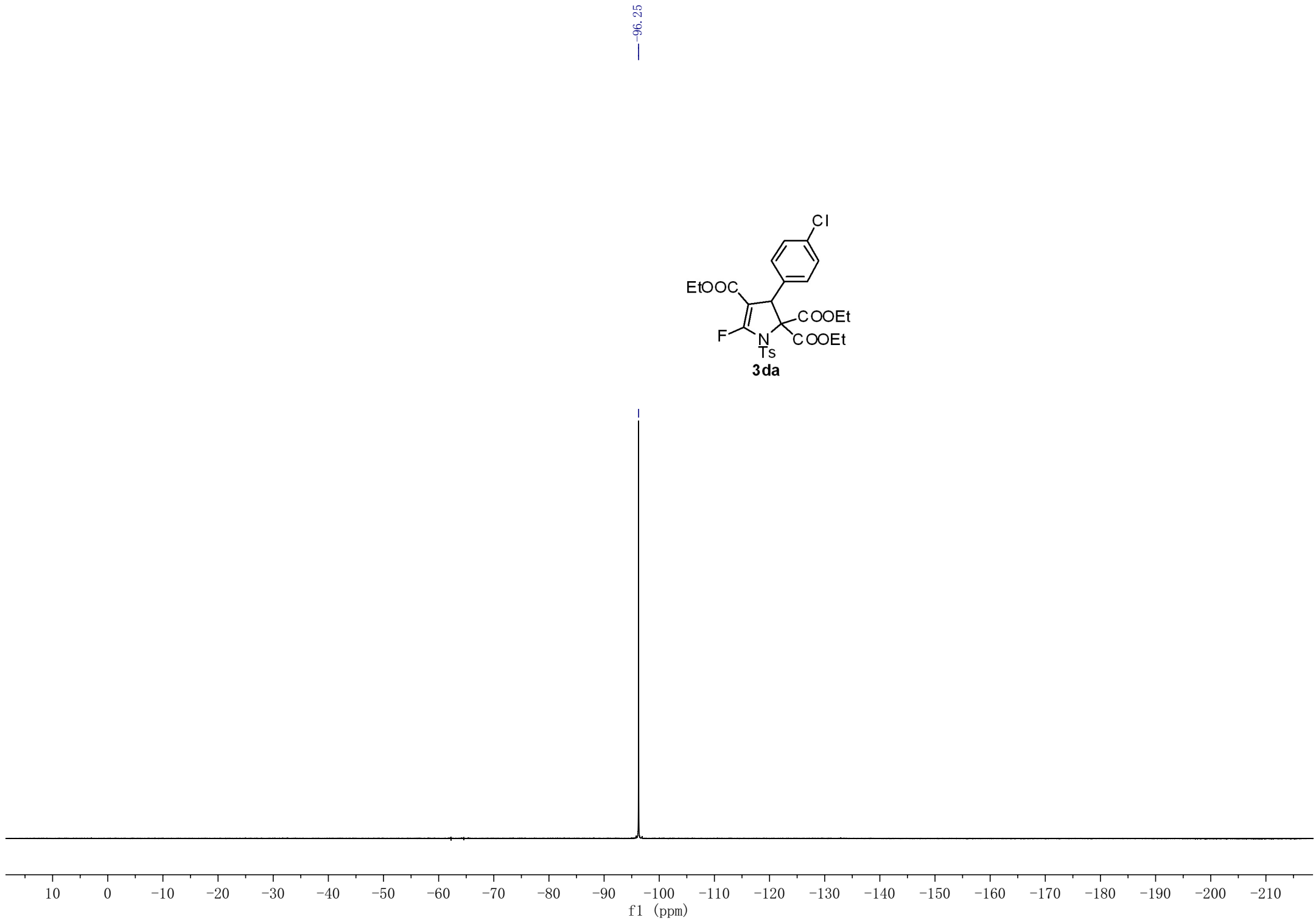
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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COOEt
Ts
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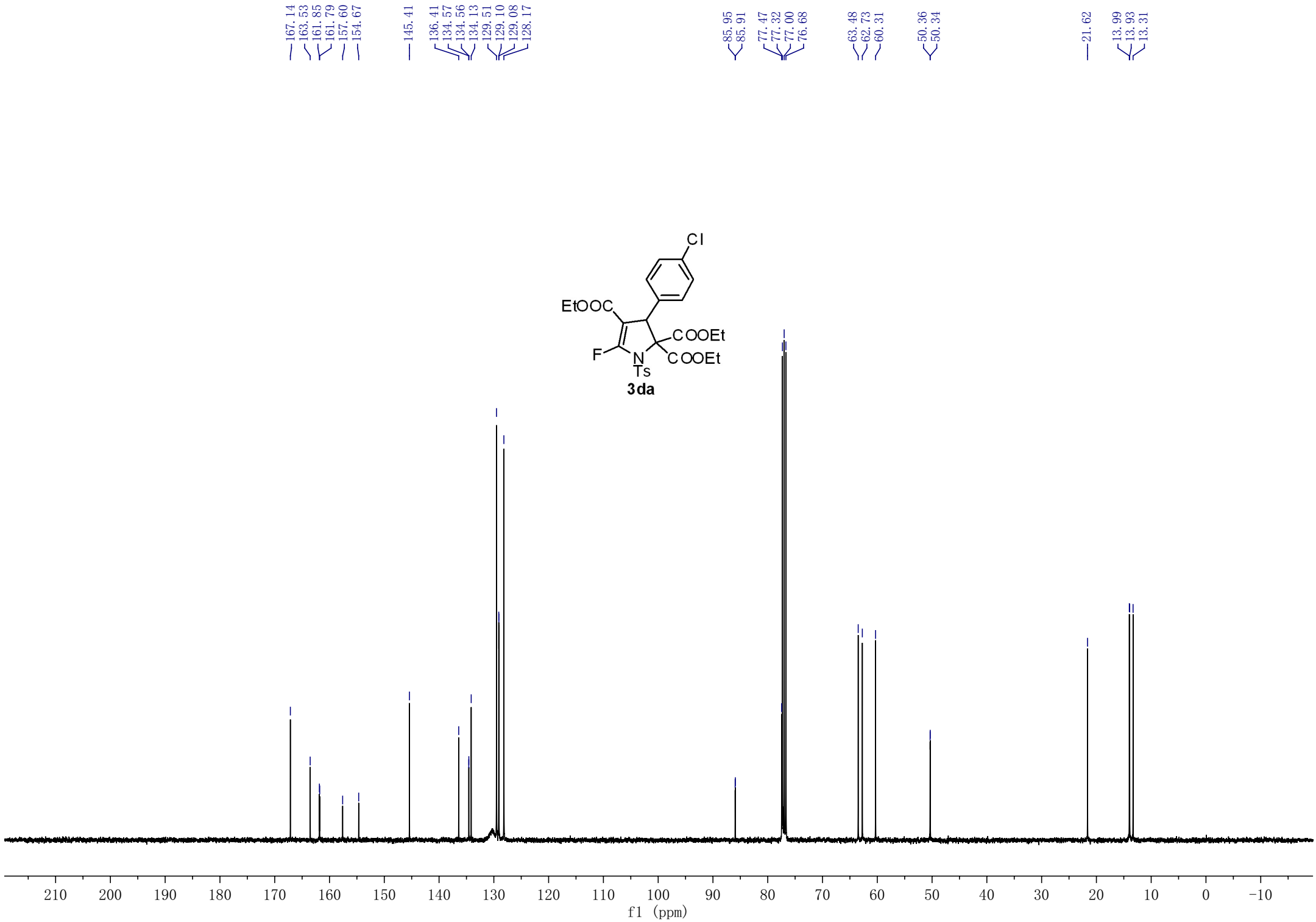
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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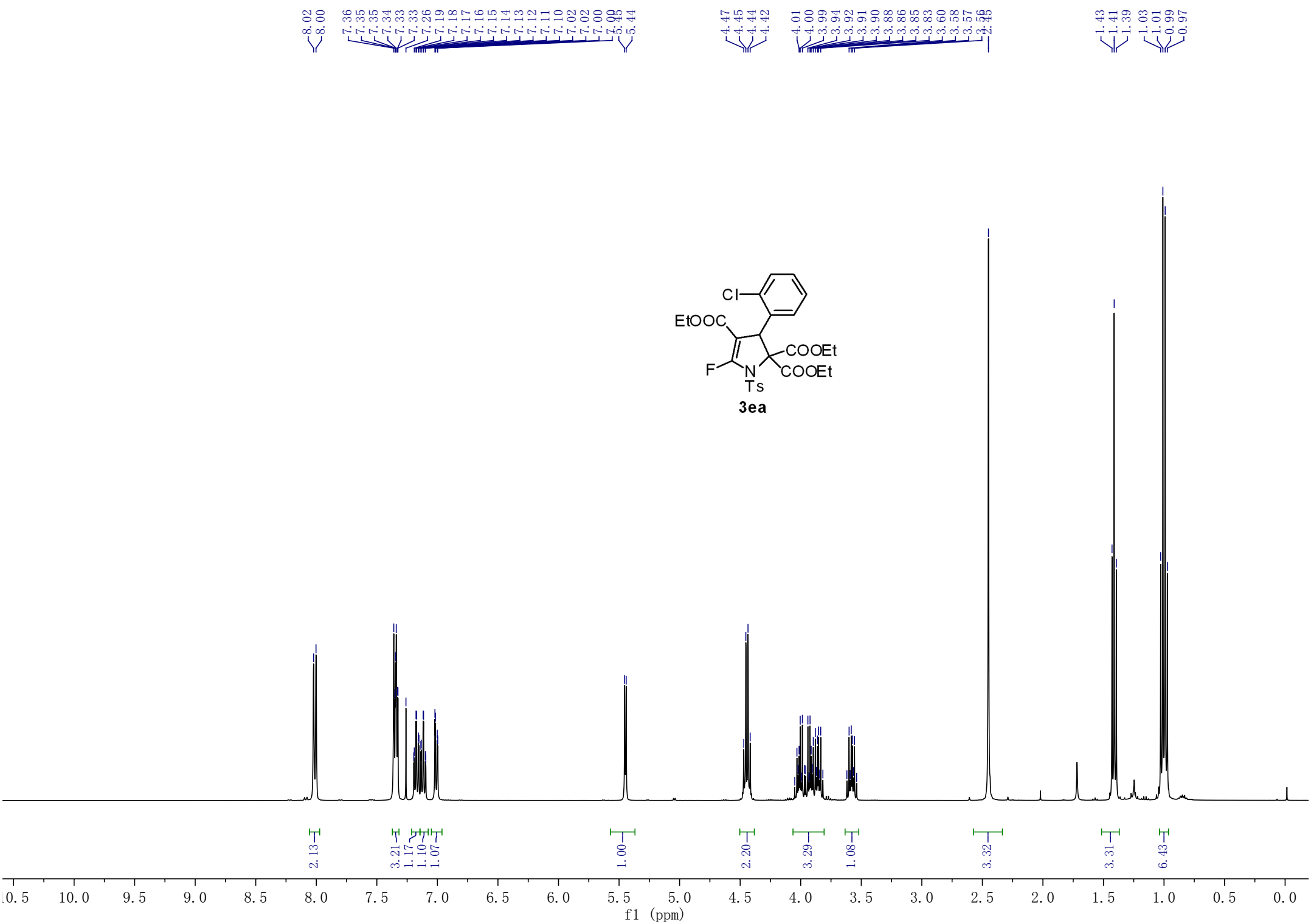
136.41
134.57
134.56
134.13
129.51
129.10
129.08
128.17
85.95
85.91
77.47
77.32
77.00
76.68
63.48
62.73
60.31
50.36
50.34
21.62
13.99
13.93
13.31
Cl
EtOOC
COOEt
F
N
COOEt
Ts
3da
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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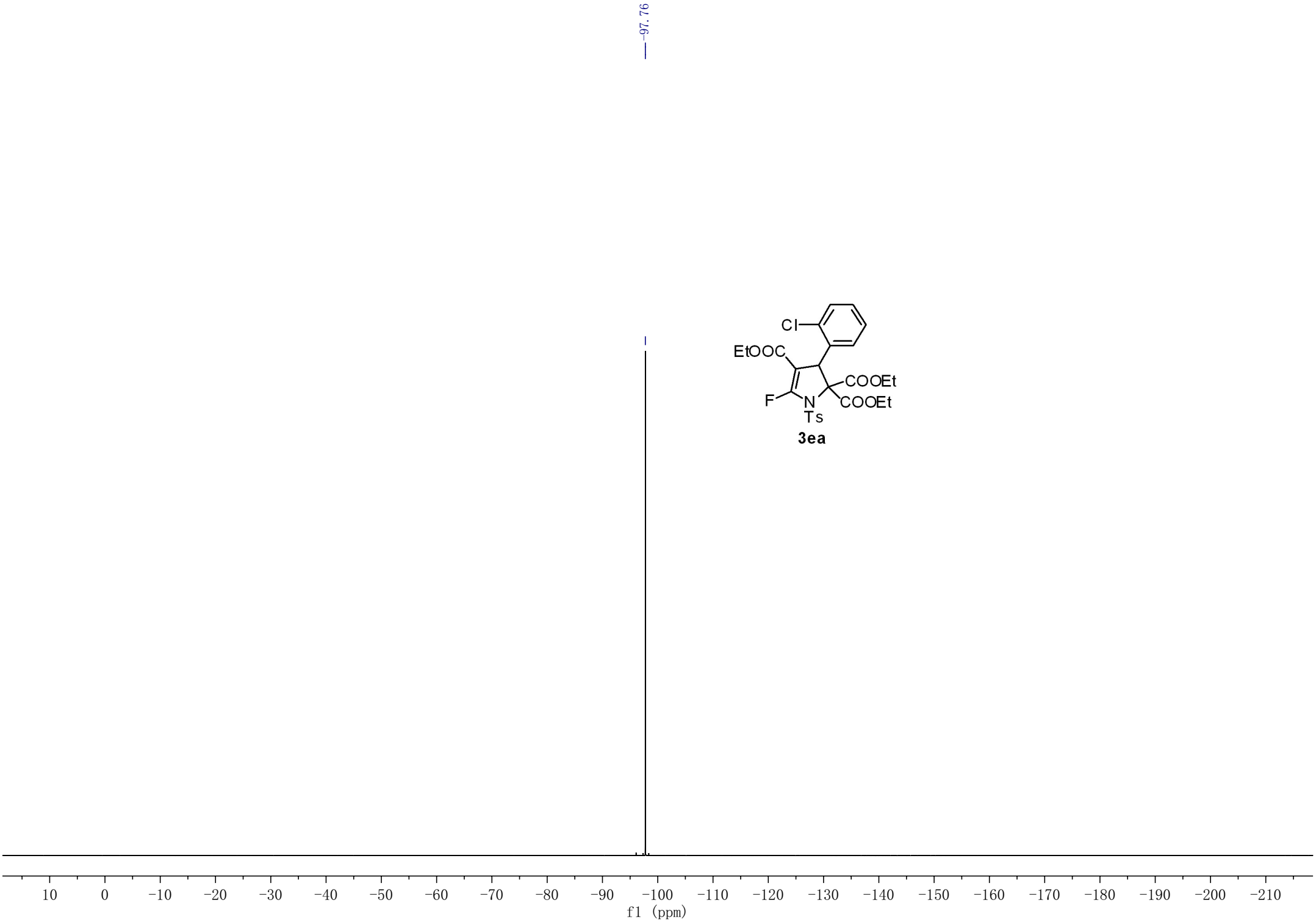
7.34
7.33
7.33
7.26
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.10
7.02
7.02
7.00
7.00
5.45
5.44
4.47
4.45
4.44
4.42
4.01
4.00
3.99
3.94
3.92
3.91
3.90
3.88
3.86
3.85
3.83
3.60
3.58
3.57
3.56
2.45
1.43
1.41
1.39
1.03
1.01
0.99
0.97
Cl
EtOOC
COOEt
F
N
COOEt
Ts
3ea
2.13
3.21
1.17
1.10
1.07
1.00
2.20
3.29
1.08
3.32
3.31
6.43
f1 (ppm)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F
N
COOEt
Ts
3ea
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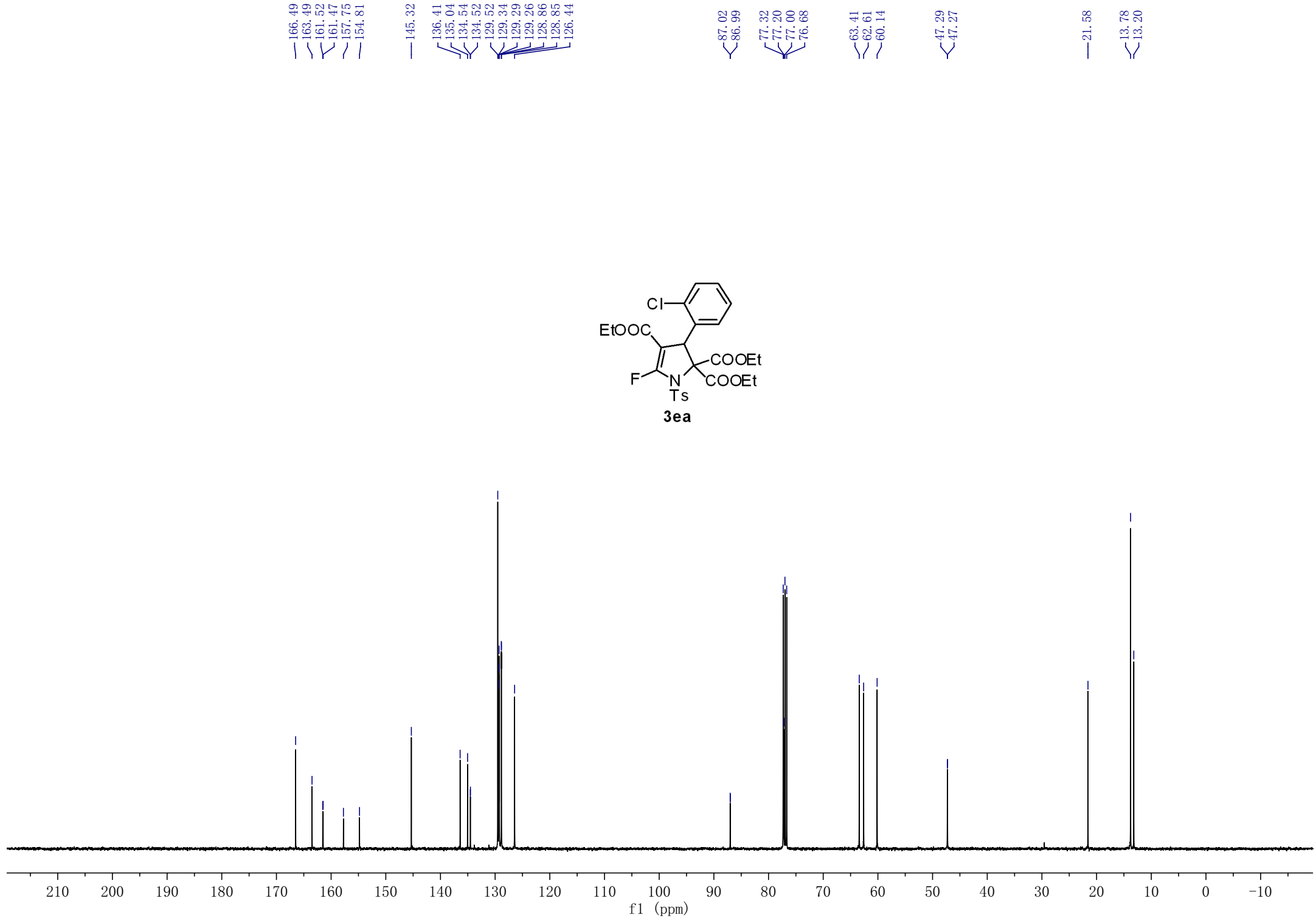
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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136.41
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134.54
134.52
129.52
129.34
129.29
129.26
128.86
128.85
126.44
87.02
86.99
77.32
77.20
77.00
76.68
63.41
62.61
60.14
47.29
47.27
21.58
13.78
13.20
Cl
EtOOC
COOEt
F
N
COOEt
Ts
3ea
210
200
190
180
170
160
150
140
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120
110
100
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80
70
60
50
40
30
20
10
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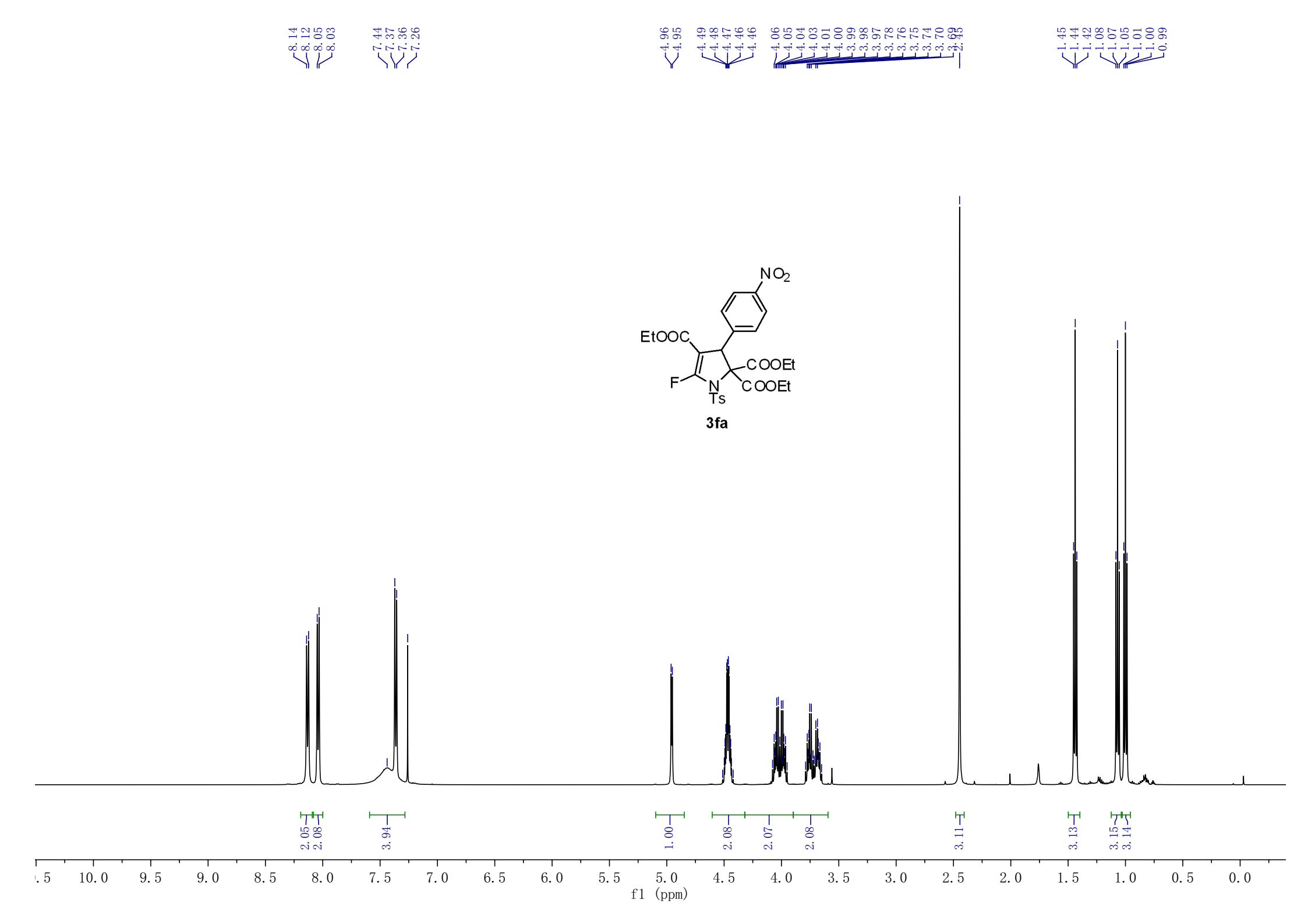
-10
f1 (ppm)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8.05
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7.44
7.37
7.36
7.26
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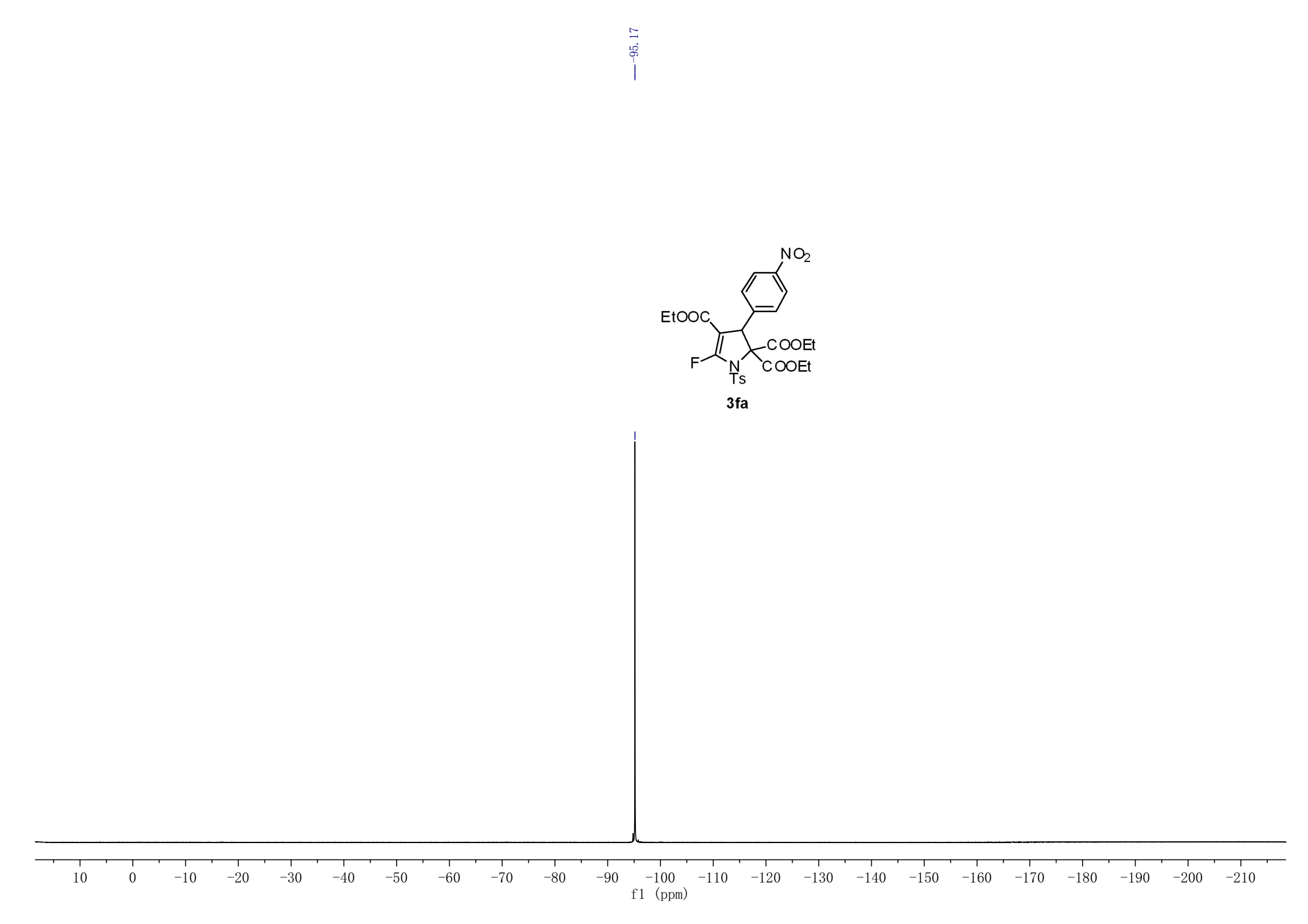
4.95
4.49
4.48
4.47
4.46
4.46
4.06
4.05
4.04
4.03
4.01
4.00
3.99
3.98
3.97
3.78
3.76
3.75
3.74
3.70
3.69
2.43
1.45
1.44
1.42
1.08
1.07
1.05
1.01
1.00
0.99
NO2
EtOOC
COOEt
F
N
COOEt
Ts
3fa
2.05
2.08
3.94
1.00
2.08
2.07
2.08
3.11
3.13
3.15
3.14
f1 (ppm)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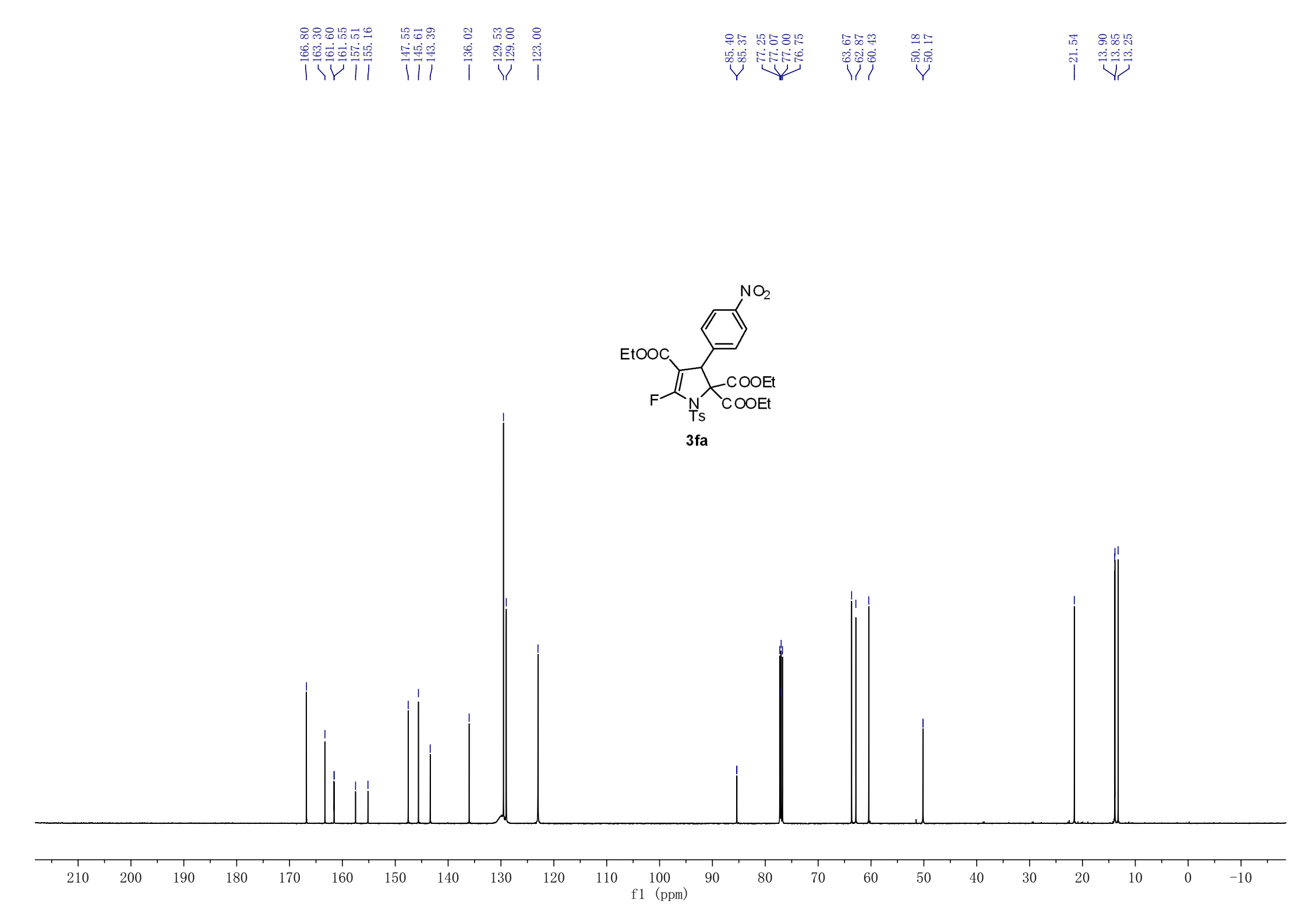
F
N
Ts
COOEt
3fa
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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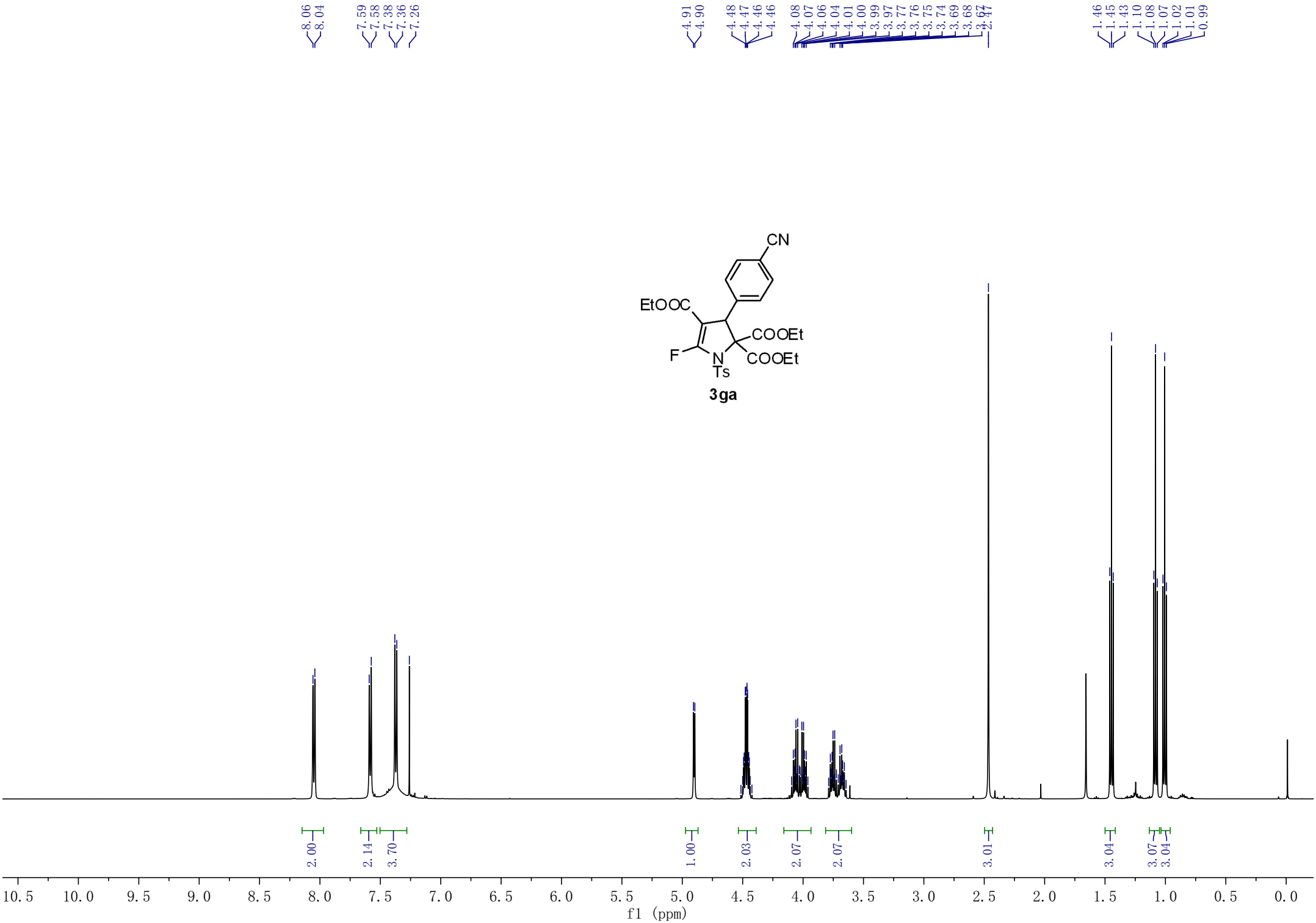
155.16
147.55
145.61
143.39
136.02
129.53
129.00
123.00
85.40
85.37
77.25
77.07
77.00
76.75
63.67
62.87
60.43
50.18
50.17
21.54
13.90
13.85
13.25
NO2
EtOOC
COOEt
F
N
COOEt
Ts
3fa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.59
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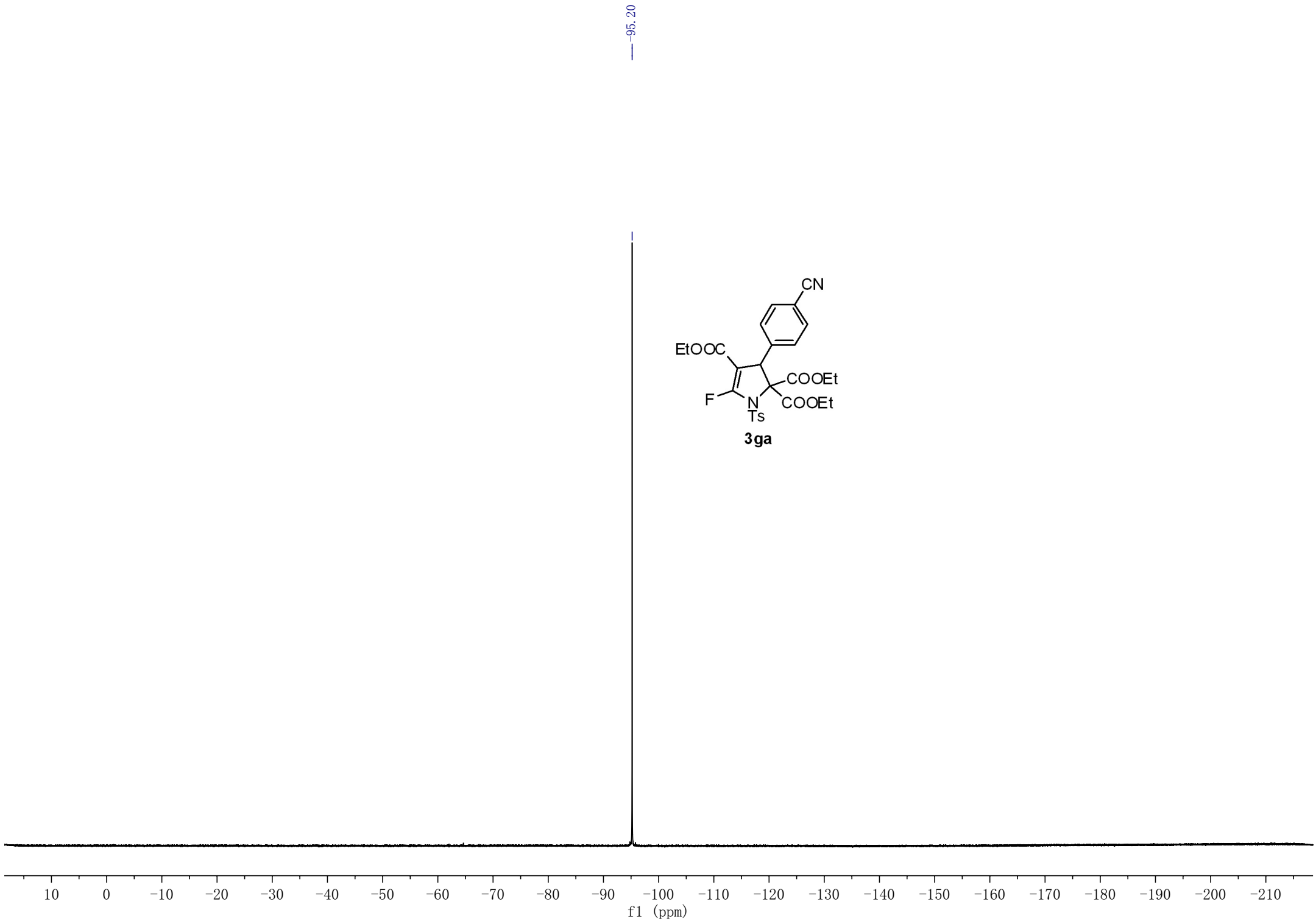
7.36
7.26
4.91
4.90
4.48
4.47
4.46
4.46
4.08
4.07
4.06
4.04
4.01
4.00
3.99
3.97
3.77
3.76
3.75
3.74
3.69
3.68
3.67
2.47
1.46
1.45
1.43
1.10
1.08
1.07
1.02
1.01
0.99
CN
EtOOC
COOEt
F
N
Ts
COOEt
3ga
2.00
2.14
3.70
1.00
2.03
2.07
2.07
3.01
3.04
3.07
3.04
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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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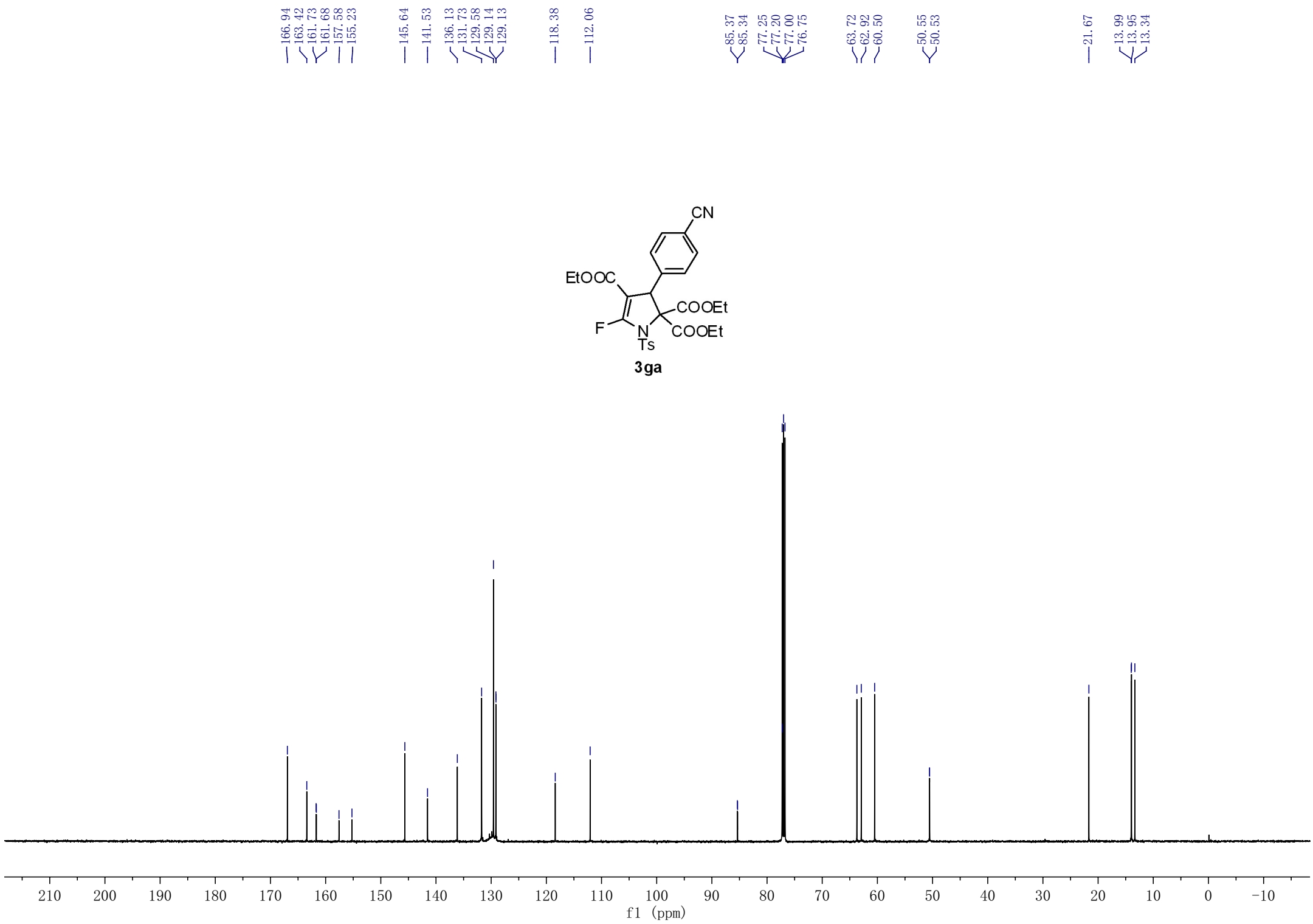
EtOOC
COOEt
F
N
Ts
COOEt
3ga
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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155.23
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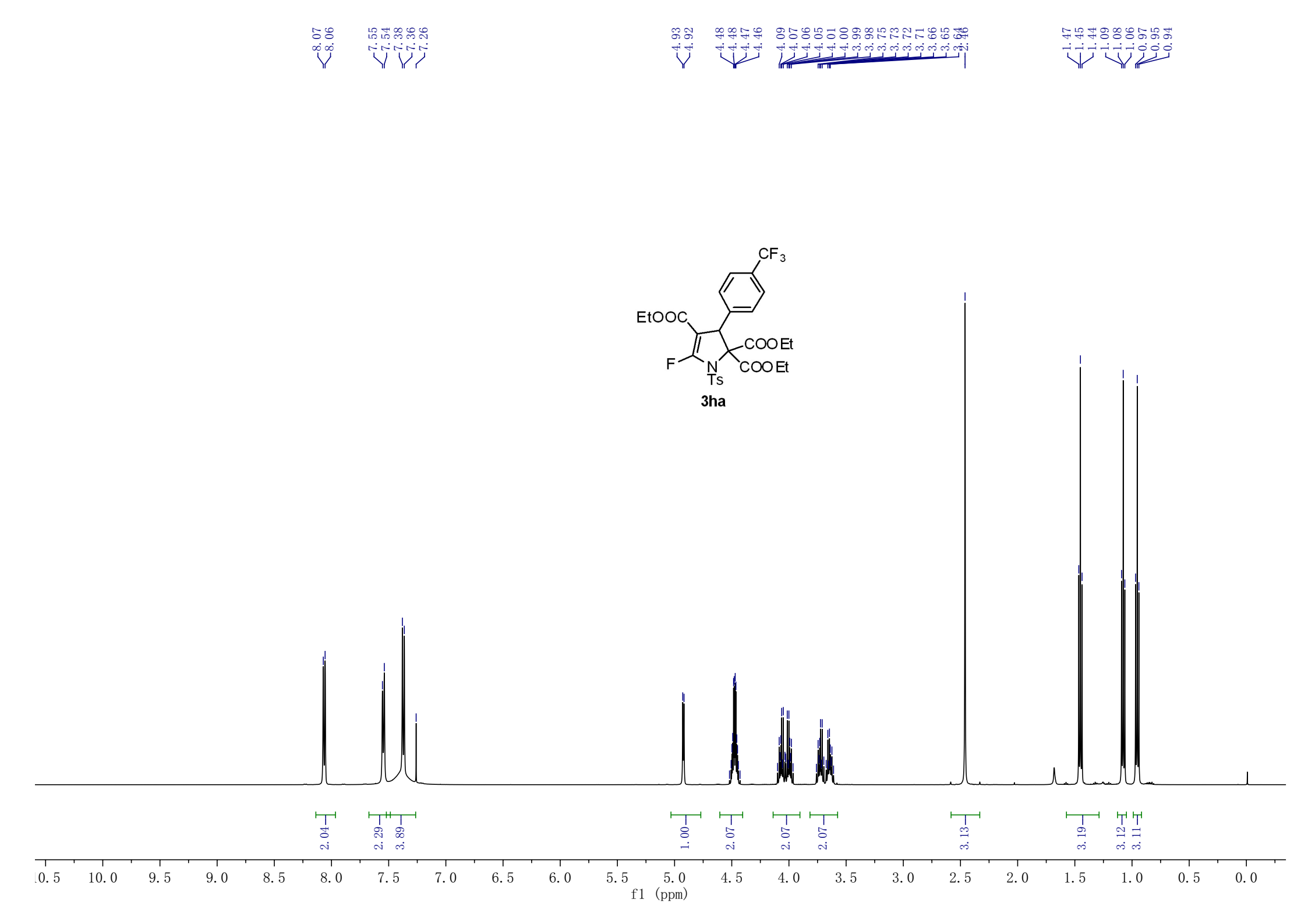
141.53
136.13
131.73
129.58
129.14
129.13
118.38
112.06
85.37
85.34
77.25
77.20
77.00
76.75
63.72
62.92
60.50
50.55
50.53
21.67
13.99
13.95
13.34
CN
EtOOC
COOEt
F
N
Ts
COOEt
3ga
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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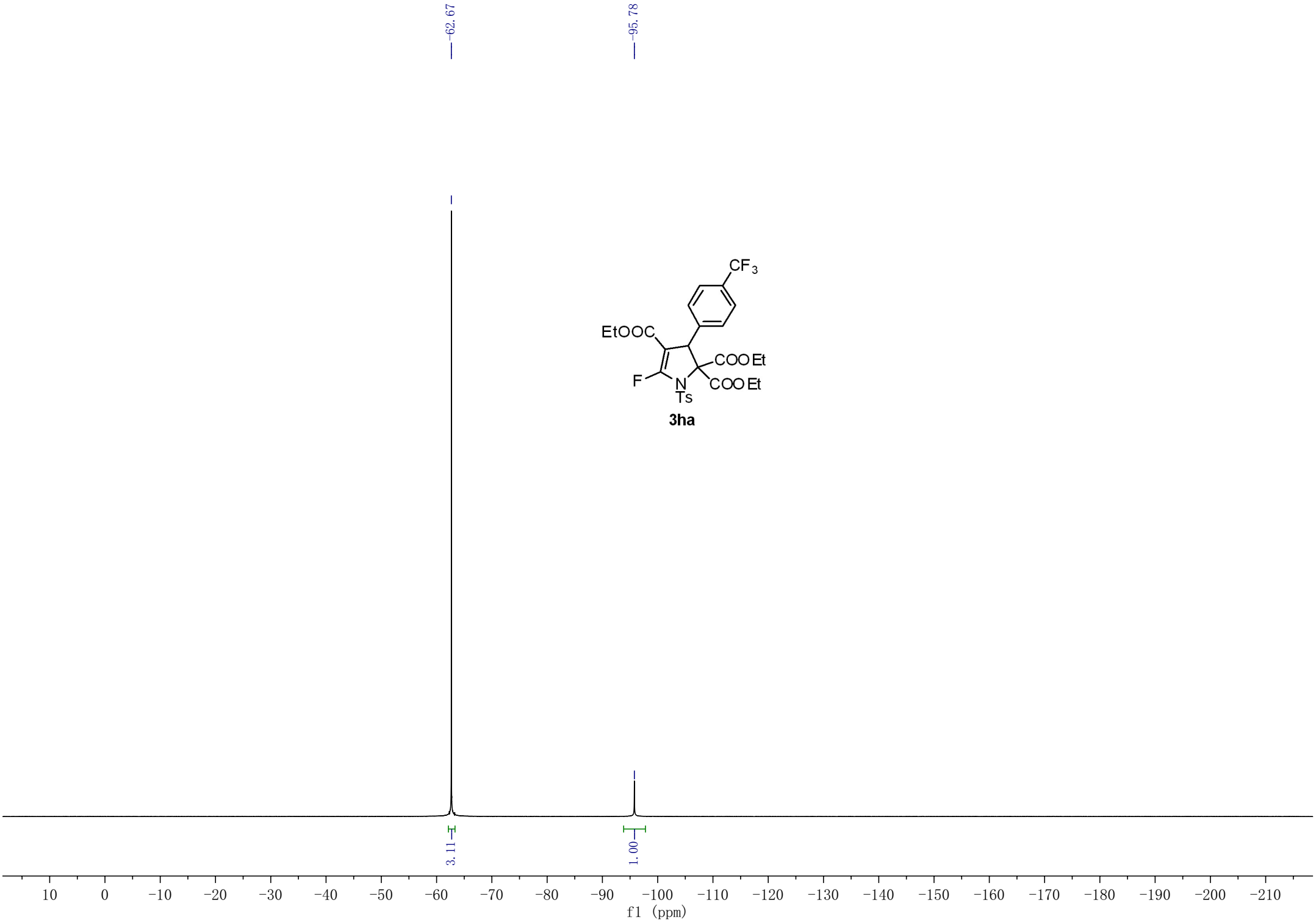
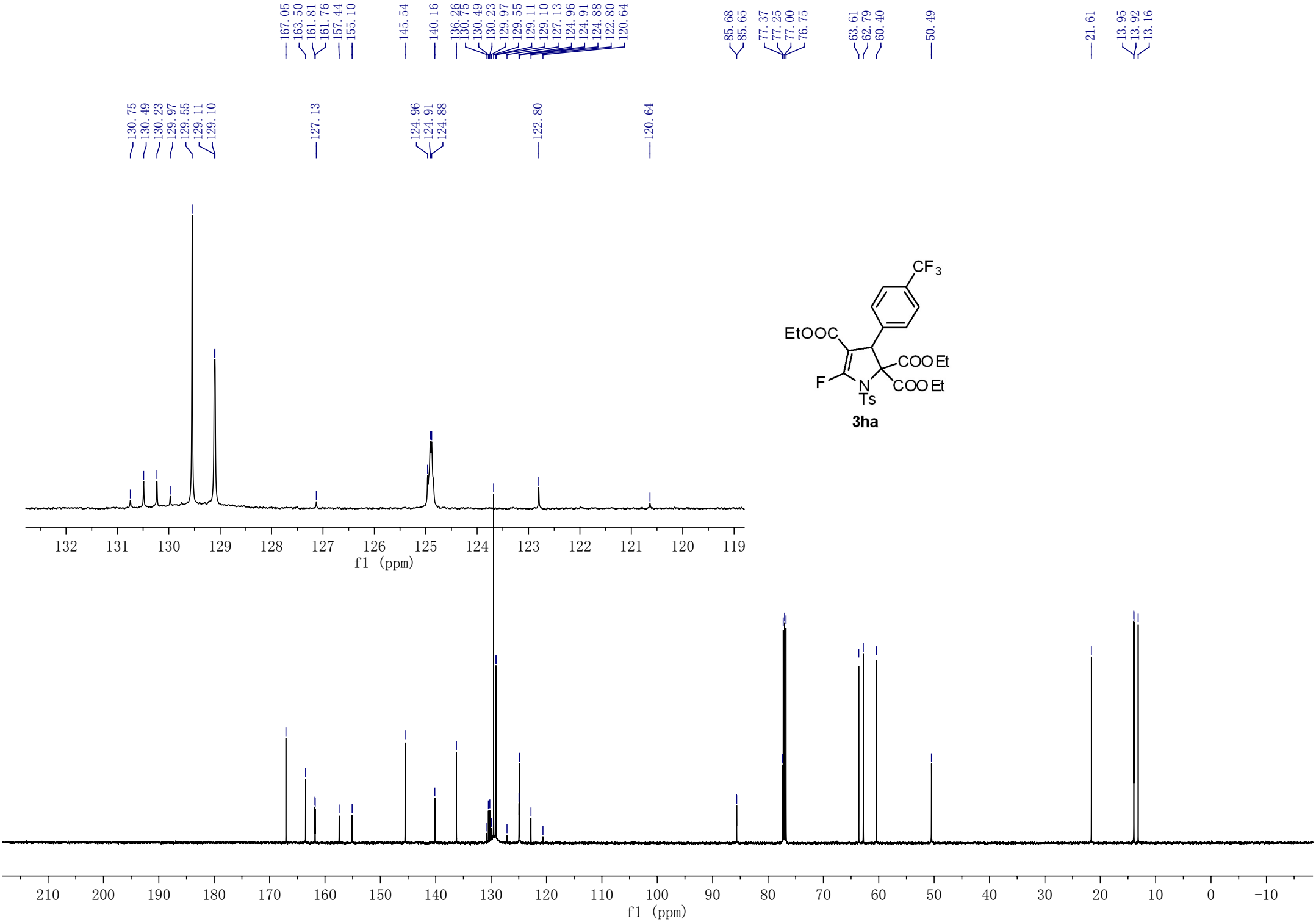
8.06
7.55
7.54
7.38
7.36
7.26
4.93
4.92
4.48
4.48
4.47
4.46
4.09
4.07
4.06
4.05
4.01
4.00
3.99
3.98
3.75
3.73
3.72
3.71
3.66
3.65
2.46
1.47
1.45
1.44
1.09
1.08
1.06
0.97
0.95
0.94
CF3
EtOOC
COOEt
F
N
COOEt
Ts
3ha
2.04
2.29
3.89
1.00
2.07
2.07
2.07
3.13
3.19
3.12
3.11
f1 (ppm)


-62.67
-95.78
CF3
EtOOC
COOEt
F
N
Ts
COOEt
3ha
3.11
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)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163.50
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161.76
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155.10
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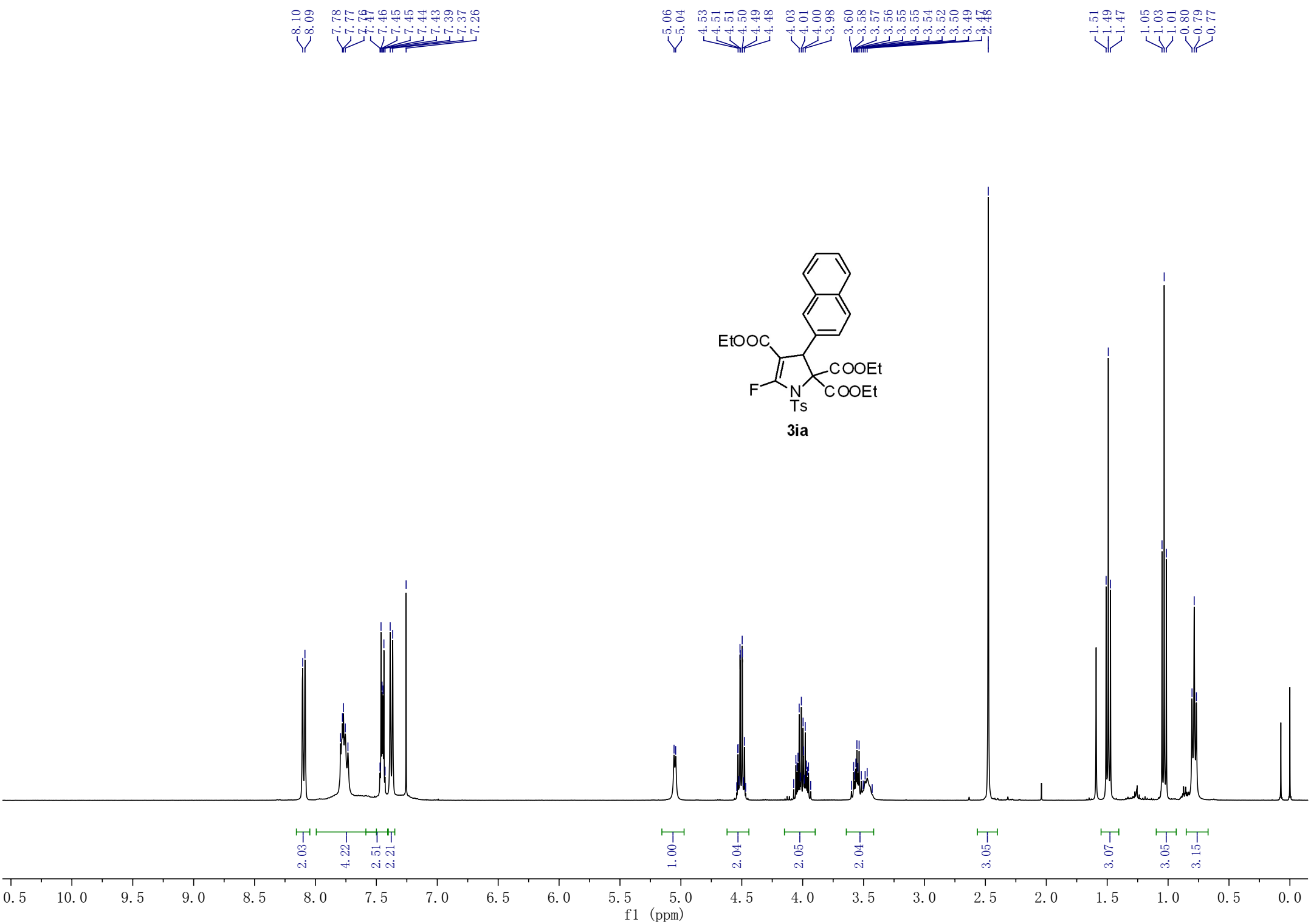
140.16
136.26
130.75
130.49
130.23
129.97
129.55
129.11
129.10
127.13
124.96
124.91
124.88
122.80
120.64
85.68
85.65
77.37
77.25
77.00
76.75
63.61
62.79
60.40
50.49
21.61
13.95
13.92
13.16
CF3
EtOOC
COOEt
F
N
Ts
COOEt
3ha
f1 (ppm)
f1 (ppm)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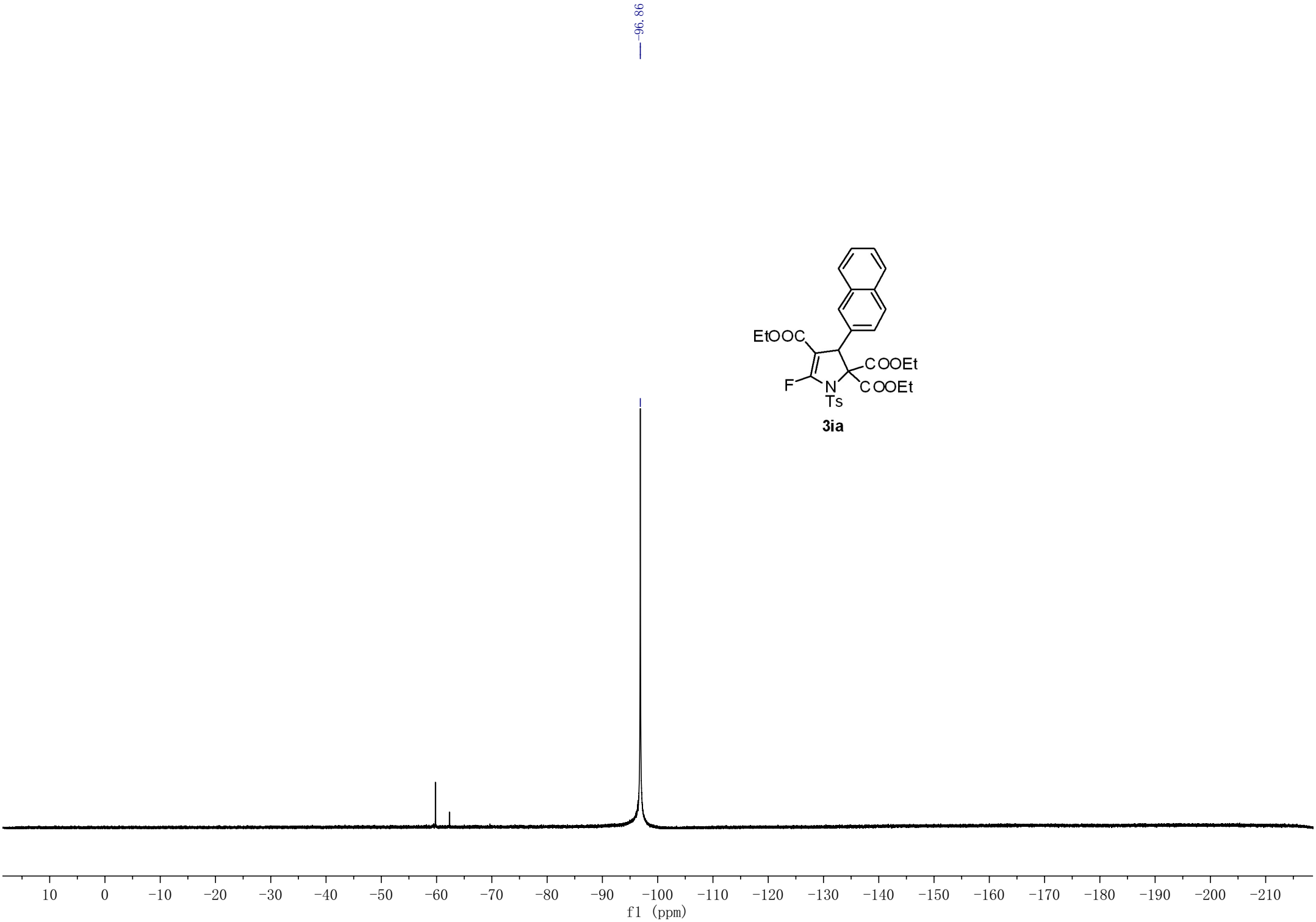
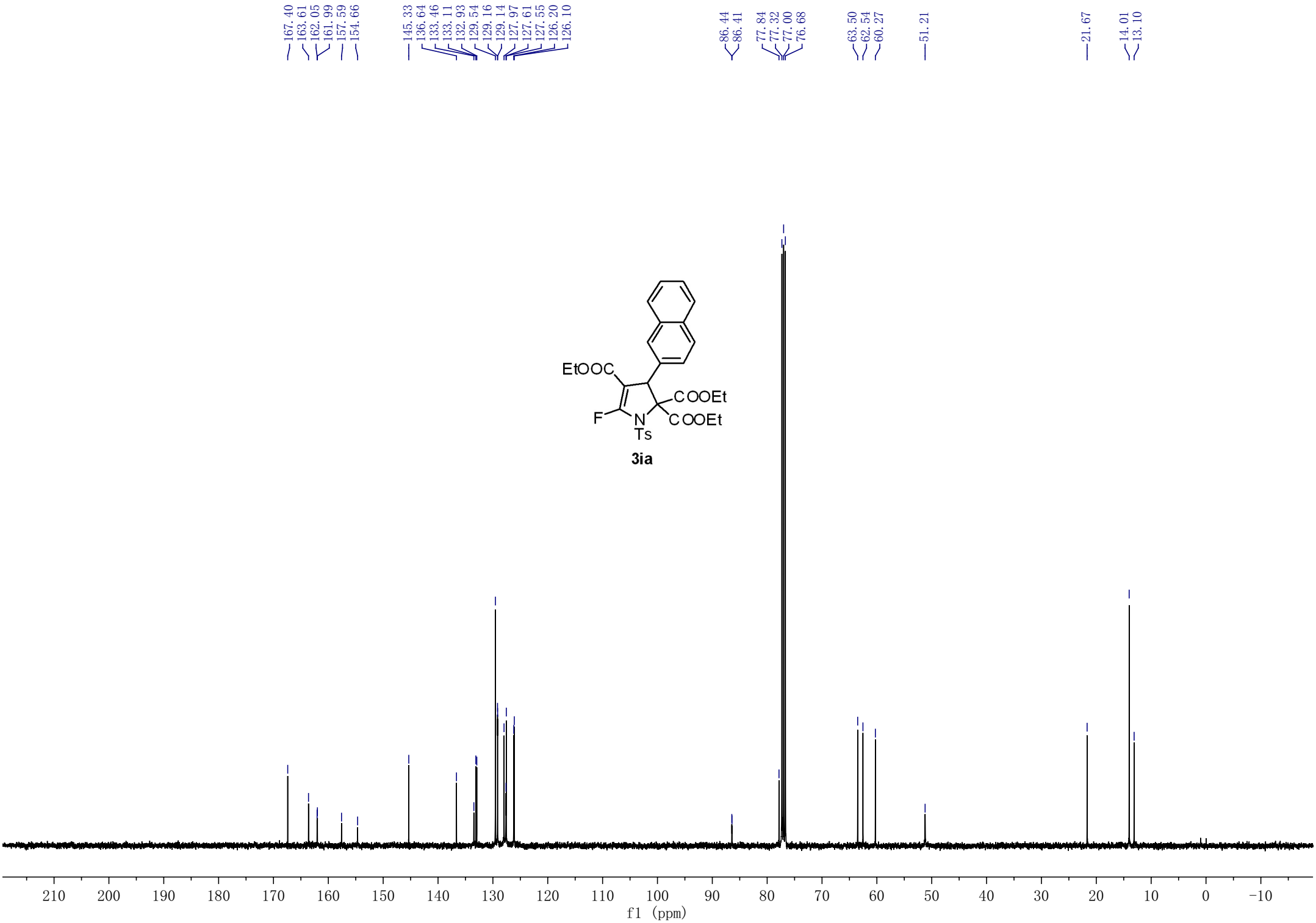
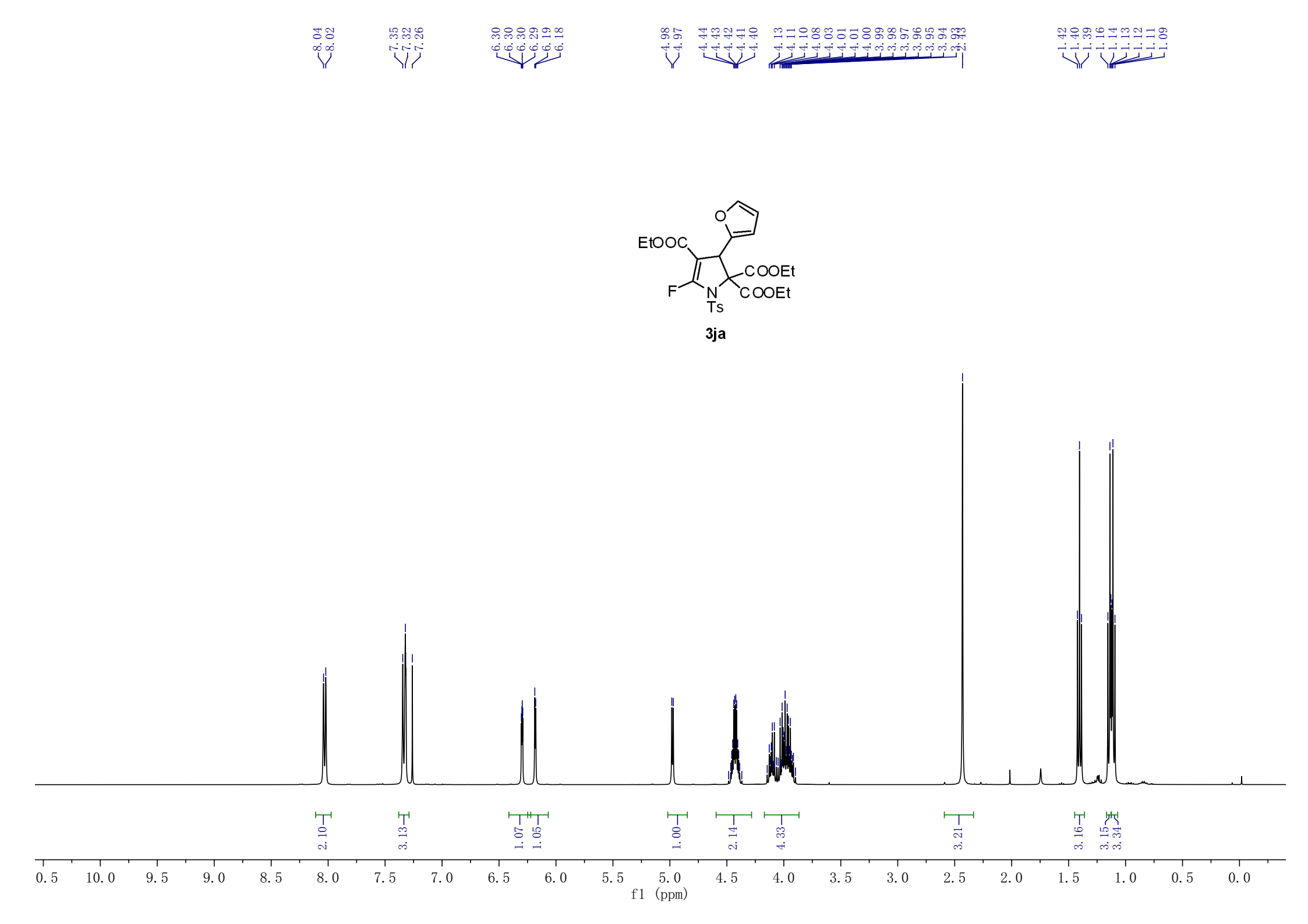
8.09
7.78
7.77
7.76
7.47
7.46
7.45
7.44
7.43
7.39
7.37
7.26
5.06
5.04
4.53
4.51
4.51
4.50
4.49
4.48
4.03
4.01
4.00
3.98
3.60
3.58
3.57
3.56
3.55
3.55
3.54
3.52
3.50
3.49
2.48
1.51
1.49
1.47
1.05
1.03
1.01
0.80
0.79
0.77
EtOOC
COOEt
F
N
COOEt
Ts
3ia
2.03
4.22
2.51
2.21
1.00
2.04
2.05
2.04
3.05
3.07
3.05
3.15
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)


-96.86
EtOOC
COOEt
F
N
COOEt
Ts
3ia
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)


167.40
163.61
162.05
161.99
157.59
154.66
145.33
136.64
133.46
133.11
132.93
129.54
129.16
129.14
127.97
127.61
127.55
126.20
126.10
86.44
86.41
77.84
77.32
77.00
76.68
63.50
62.54
60.27
51.21
21.67
14.01
13.10
EtOOC
COOEt
F
N
COOEt
Ts
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)


8.04
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7.32
7.26
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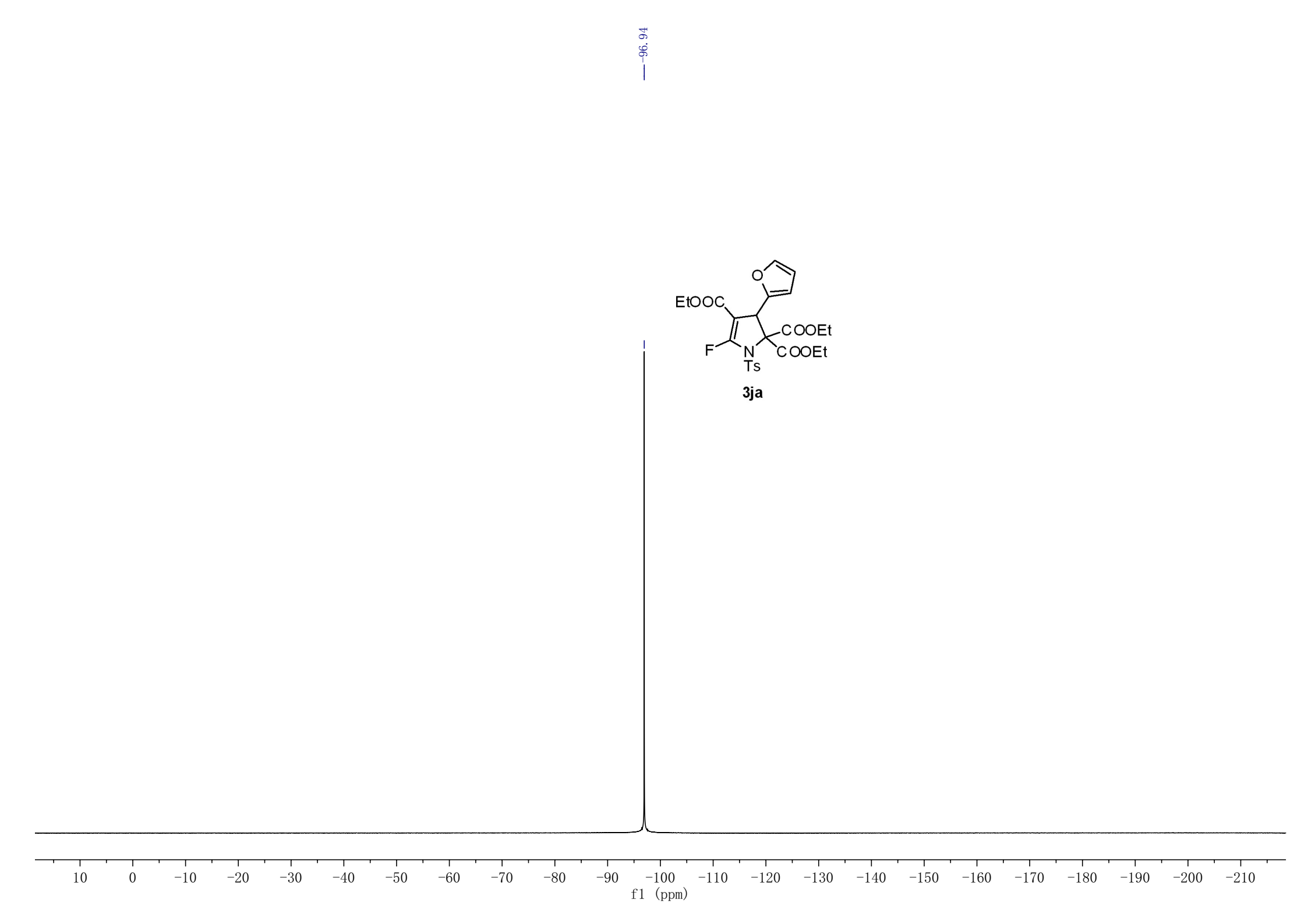
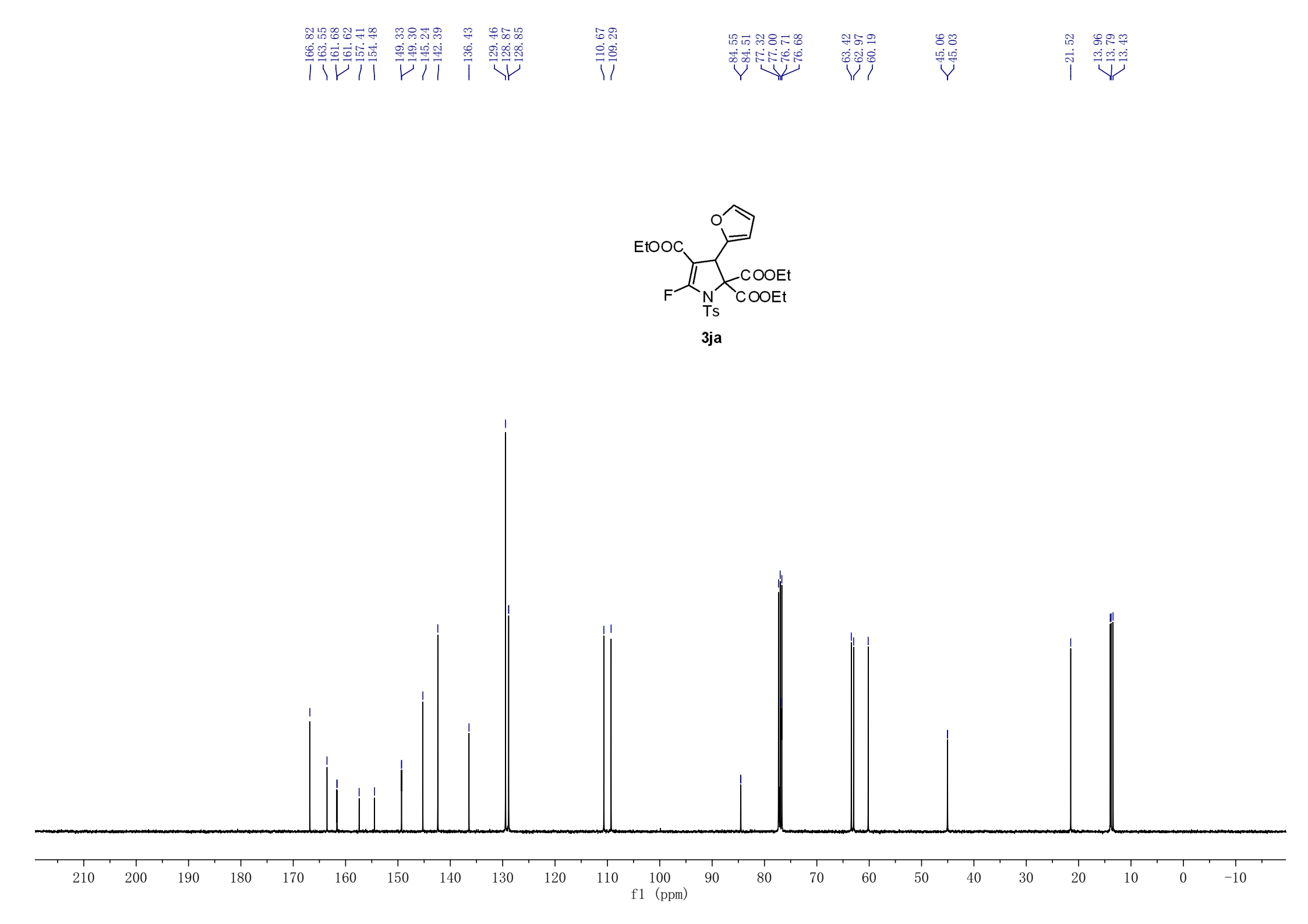
6.30
6.30
6.29
6.19
6.18
4.98
4.97
4.44
4.43
4.42
4.41
4.40
4.13
4.11
4.10
4.08
4.03
4.01
4.01
4.00
3.99
3.98
3.97
3.96
3.95
3.94
3.93
2.43
1.42
1.40
1.39
1.16
1.14
1.13
1.12
1.11
1.09
EtOOC
COOEt
F
N
COOEt
Ts
O
2.10
3.13
1.07
1.05
1.00
2.14
4.33
3.21
3.16
3.15
3.34
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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)

3ja


-96.94
EtOOC
COOEt
F
N
COOEt
Ts
3ja
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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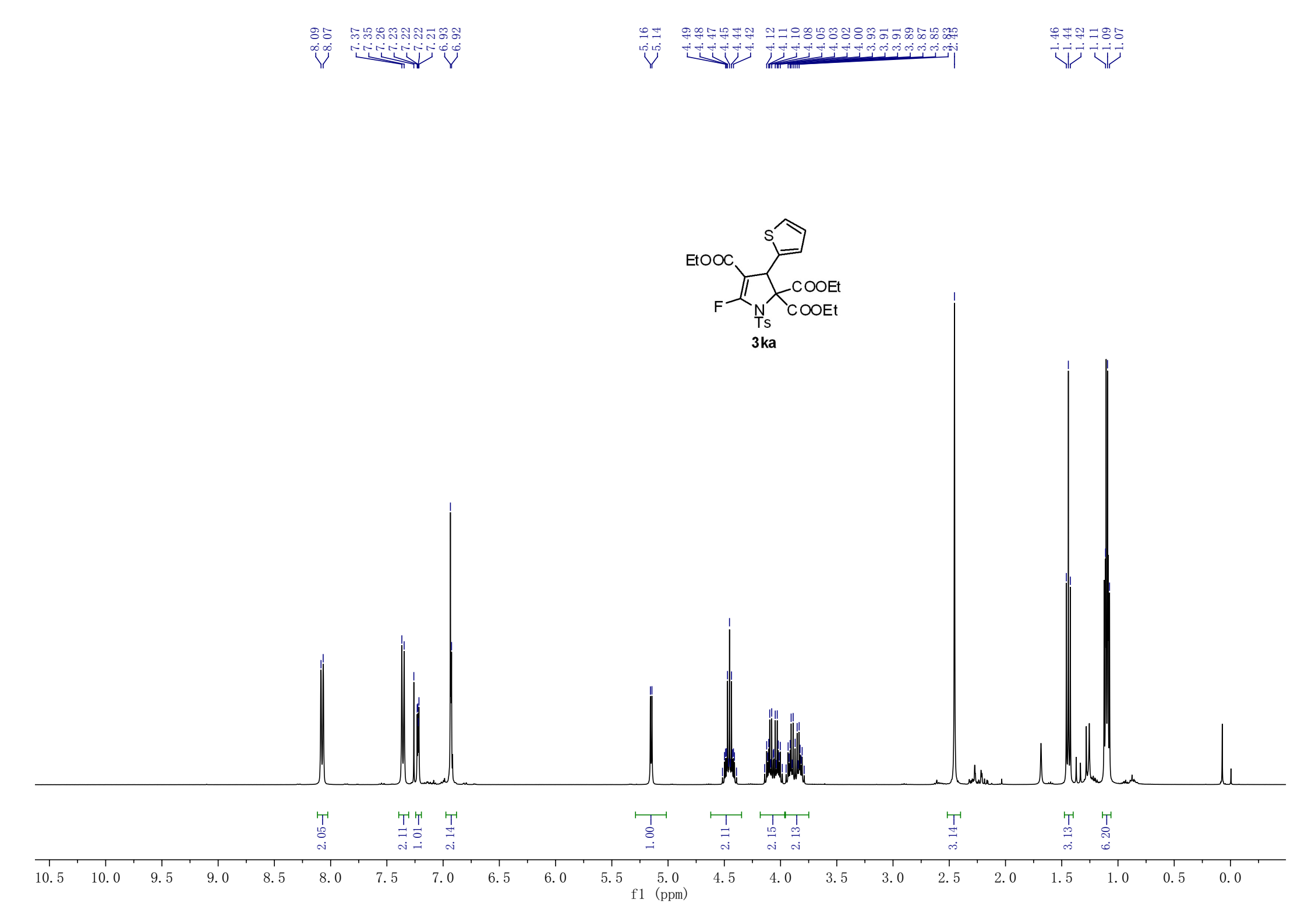
154.48
149.33
149.30
145.24
142.39
136.43
129.46
128.87
128.85
110.67
109.29
84.55
84.51
77.32
77.00
76.71
76.68
63.42
62.97
60.19
45.06
45.03
21.52
13.96
13.79
13.43
EtOOC
O
COOEt
F
N
COOEt
Ts
3ja
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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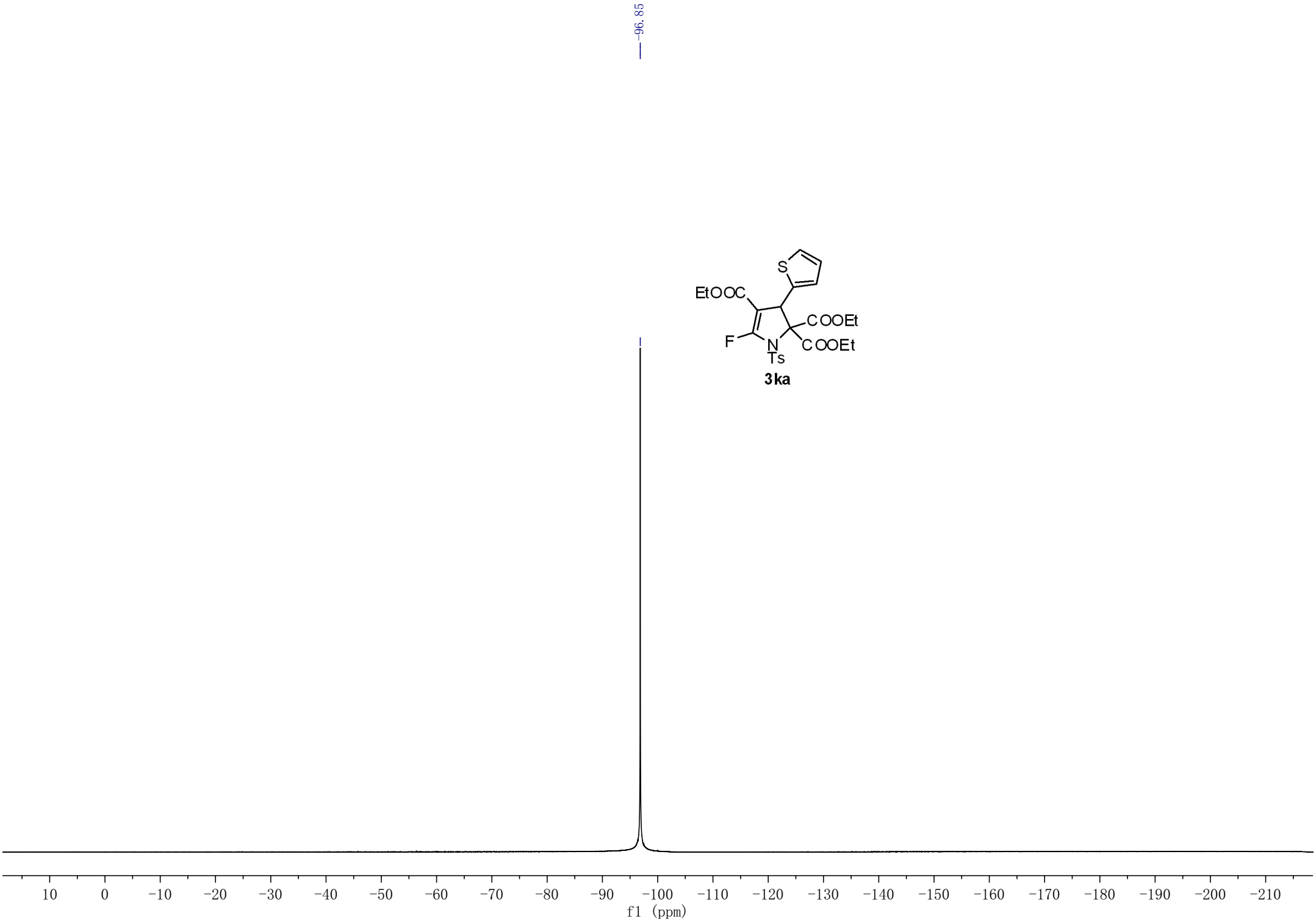
7.35
7.26
7.23
7.22
7.22
7.21
6.93
6.92
5.16
5.14
4.49
4.48
4.47
4.45
4.44
4.42
4.12
4.11
4.10
4.08
4.05
4.03
4.02
4.00
3.93
3.91
3.91
3.89
3.87
3.85
3.83
2.45
1.46
1.44
1.42
1.11
1.09
1.07
S
EtOOC
COOEt
F
N
Ts
COOEt
3ka
2.05
2.11
1.01
2.14
1.00
2.11
2.15
2.13
3.14
3.13
6.20
10.5
10.0
9.5
9.0
8.5
8.0
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)


-96.85
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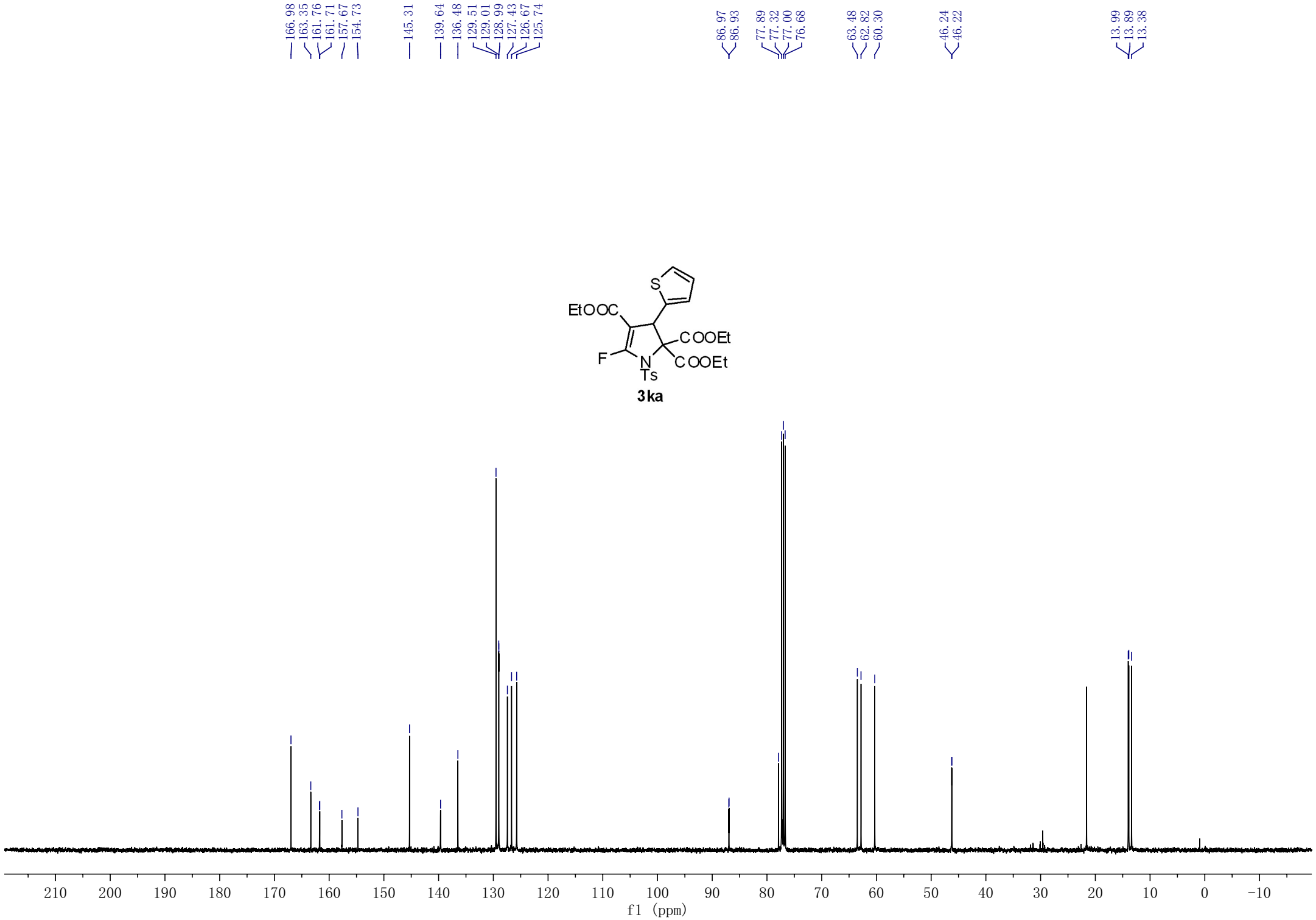
COOEt
F
N
Ts
COOEt
3ka
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


166.98
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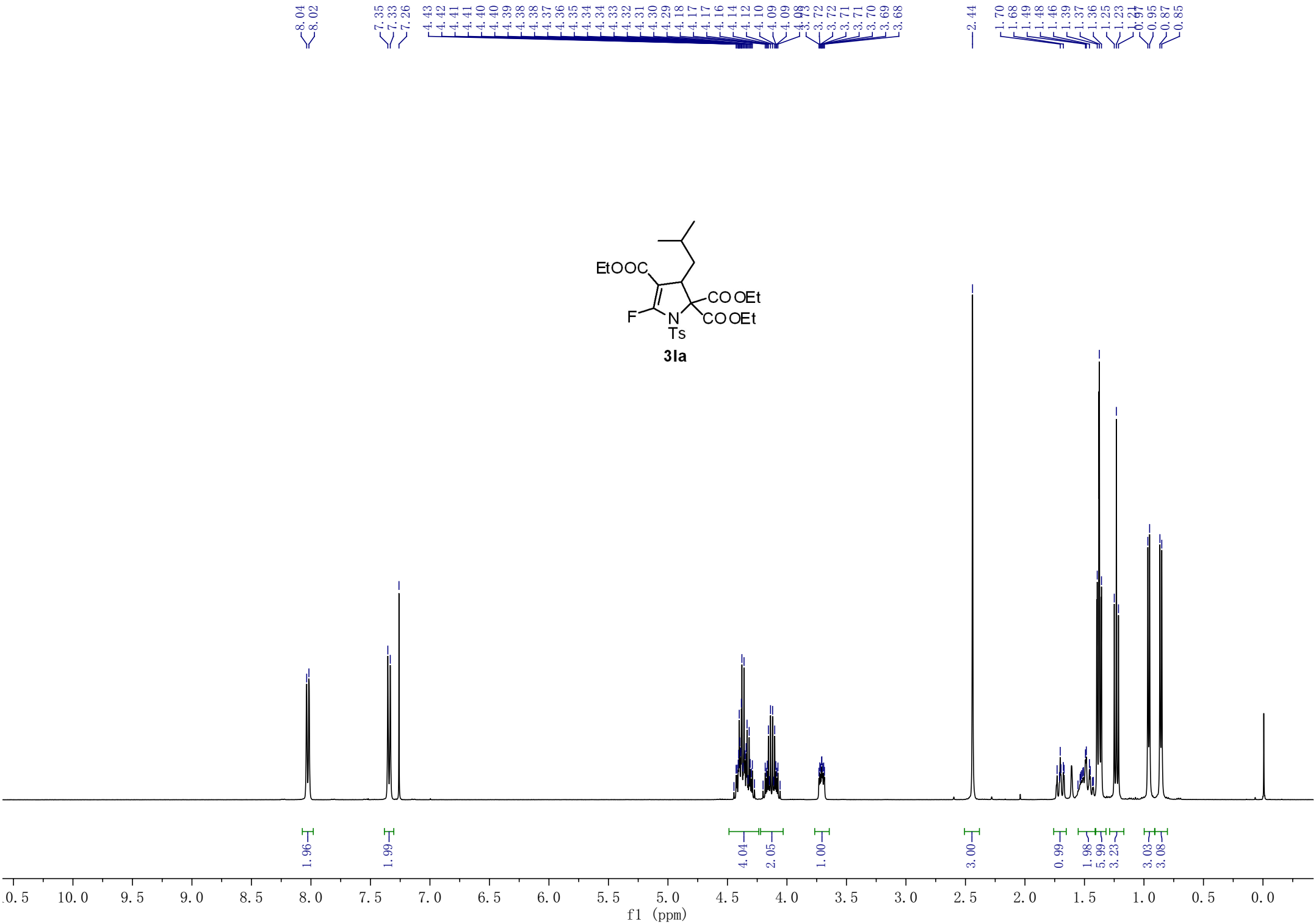
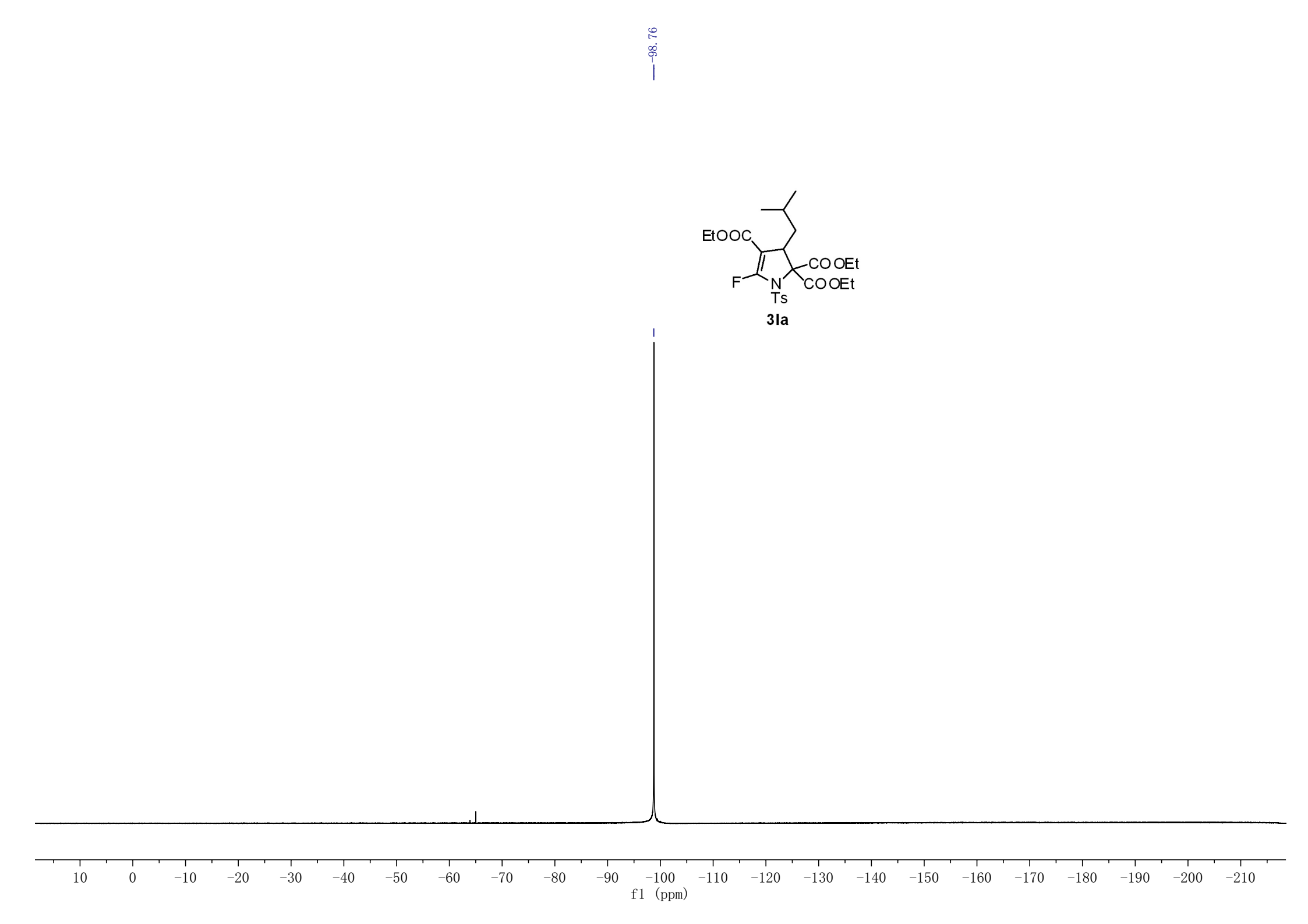
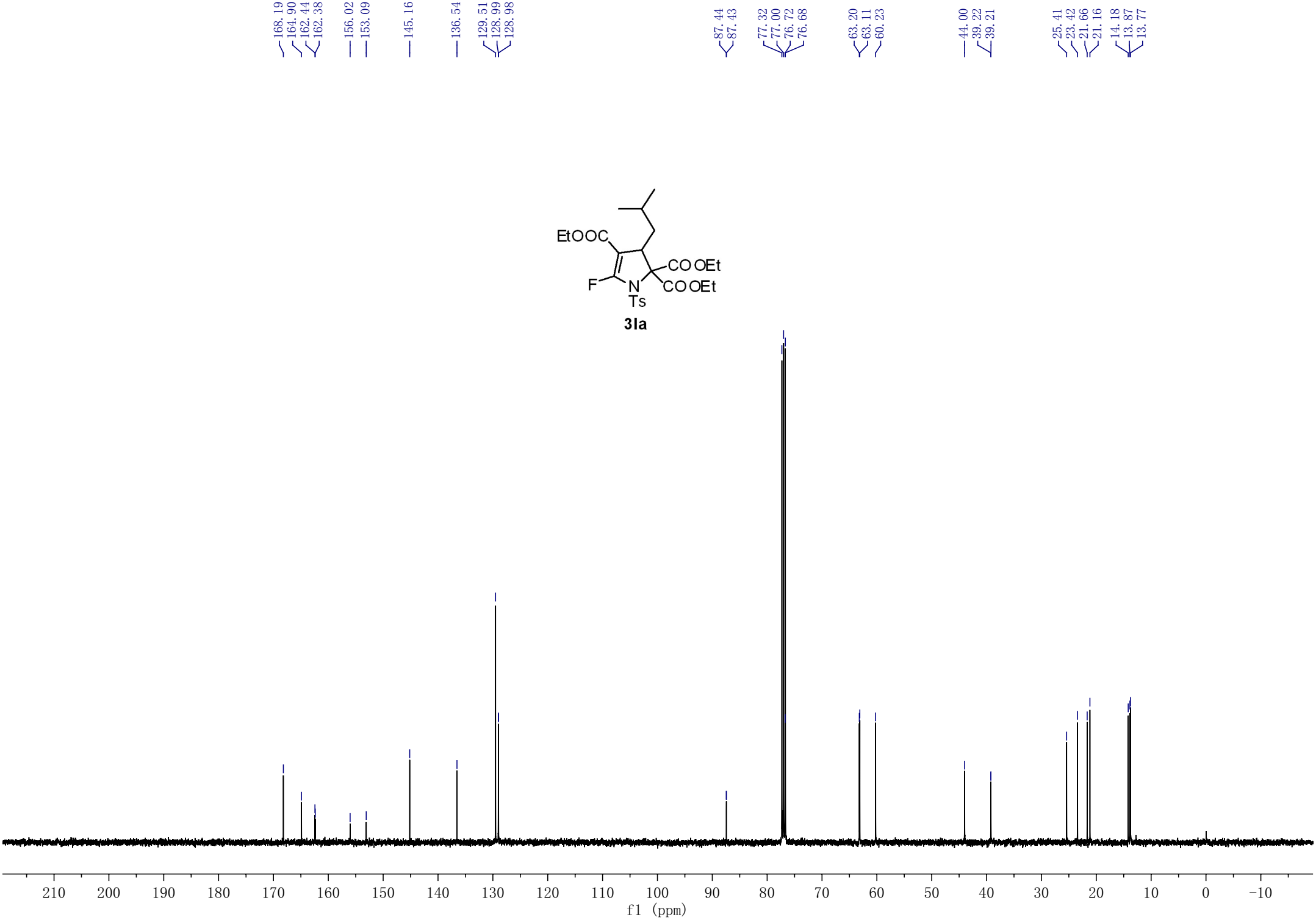
161.71
157.67
154.73
145.31
139.64
136.48
129.51
129.01
128.99
127.43
126.67
125.74
86.97
86.93
77.89
77.32
77.00
76.68
63.48
62.82
60.30
46.24
46.22
13.99
13.89
13.38
EtOOC
S
COOEt
F
N
COOEt
Ts
3ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.04
8.02
7.35
7.33
7.26
4.43
4.42
4.41
4.41
4.40
4.40
4.39
4.38
4.38
4.37
4.36
4.35
4.34
4.34
4.33
4.32
4.31
4.30
4.29
4.18
4.17
4.17
4.16
4.14
4.12
4.10
4.09
4.09
3.72
3.72
3.71
3.70
3.69
3.68
2.44
1.70
1.68
1.49
1.48
1.46
1.39
1.37
1.36
1.25
1.23
0.95
0.87
0.85
EtOOC
CO OEt
F
N
COOEt
Ts
3Ia
1.96
1.99
4.04
2.05
1.00
3.00
0.99
1.98
5.99
3.23
3.03
3.08
f1 (ppm)


-98.76
EtOOC
CO OEt
F
N
CO OEt
Ts
3Ia
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)


168.19
164.90
162.44
162.38
156.02
153.09
145.16
136.54
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128.98
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87.43
77.32
77.00
76.72
76.68
63.20
63.11
60.23
44.00
39.22
39.21
25.41
23.42
21.66
21.16
14.18
13.87
13.77
EtOOC
CO OEt
F
N
CO OEt
Ts
3Ia
210
200
190
180
170
160
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100
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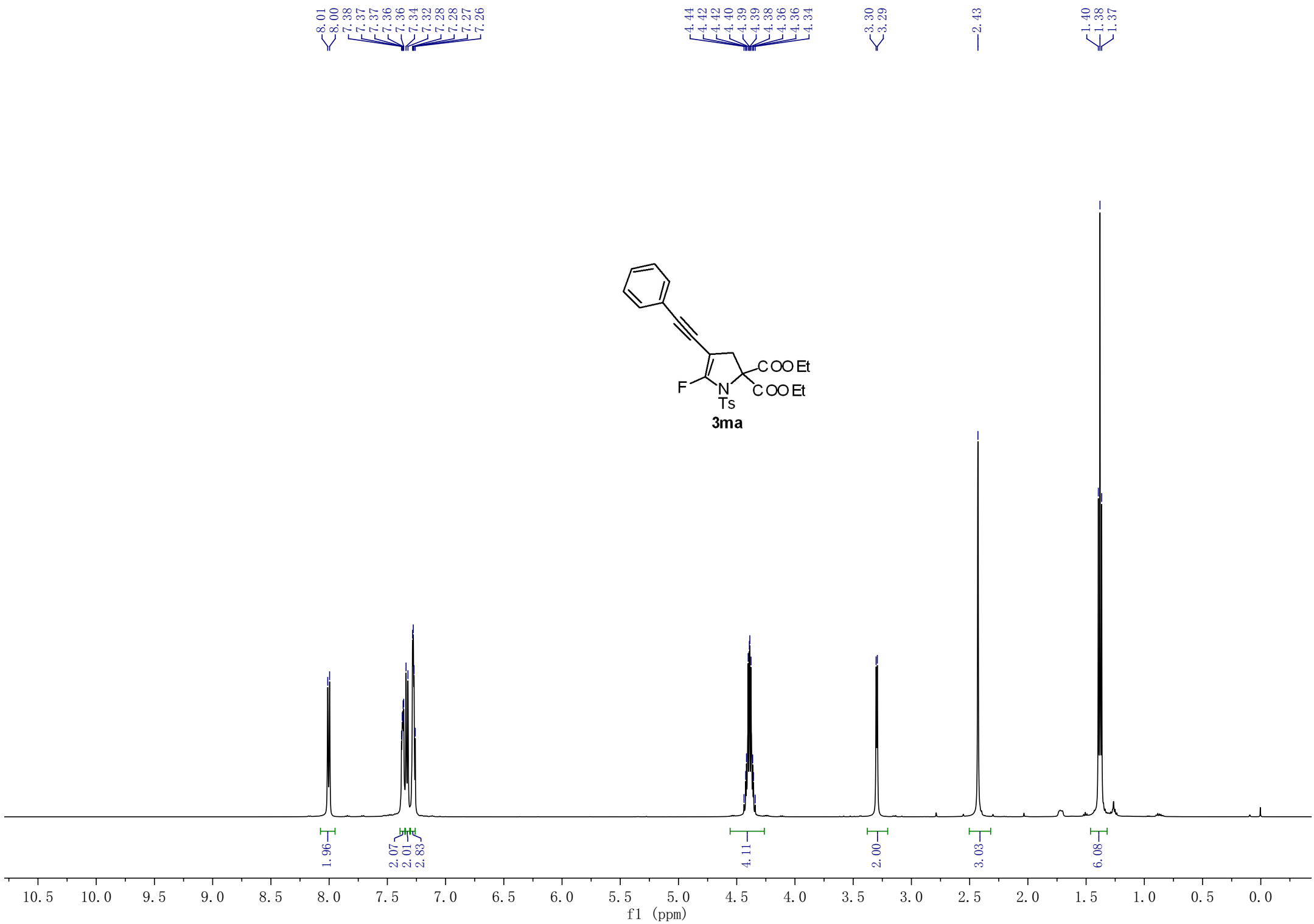
-10
f1 (ppm)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8.00
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7.34
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7.28
7.28
7.27
7.26
4.44
4.42
4.42
4.40
4.39
4.39
4.38
4.36
4.36
4.34
3.30
3.29
2.43
1.40
1.38
1.37
COOEt
F
N
COOEt
Ts
3ma
1.96
2.07
2.01
2.83
4.11
2.00
3.03
6.08
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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1.0
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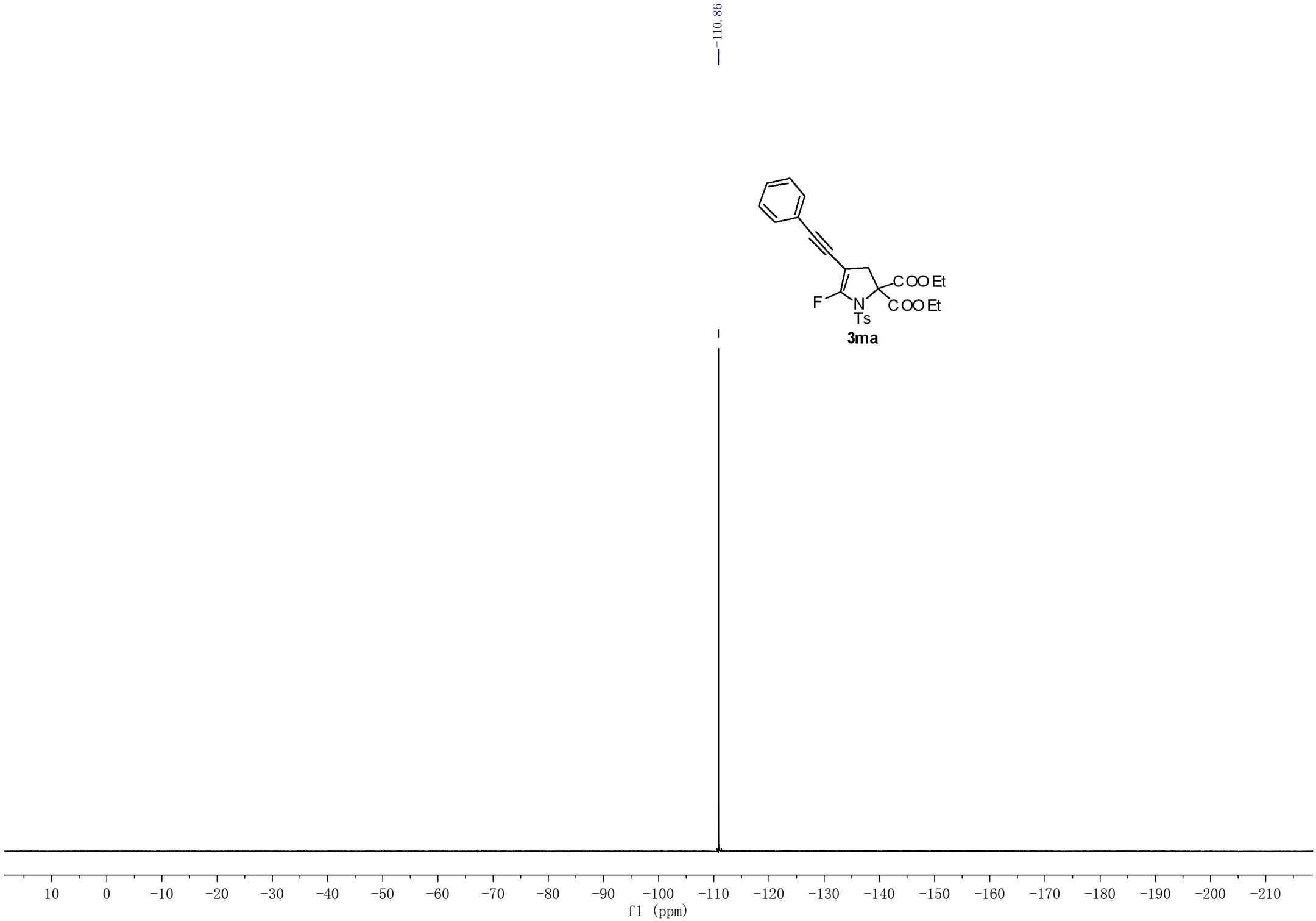
f1 (ppm)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COOEt
F
N
Ts
3ma
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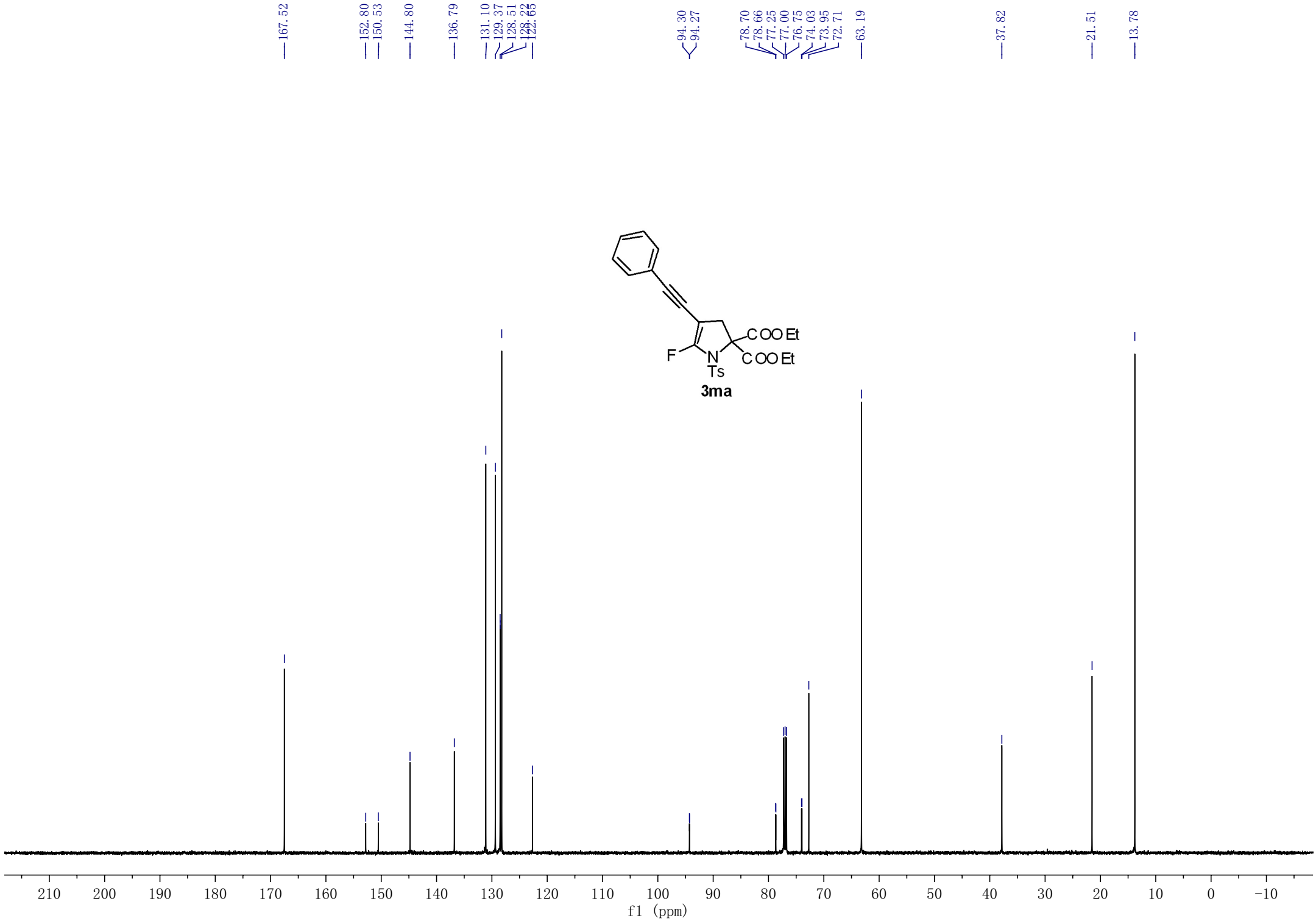
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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128.51
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94.27
78.70
78.66
77.25
77.00
76.75
74.03
73.95
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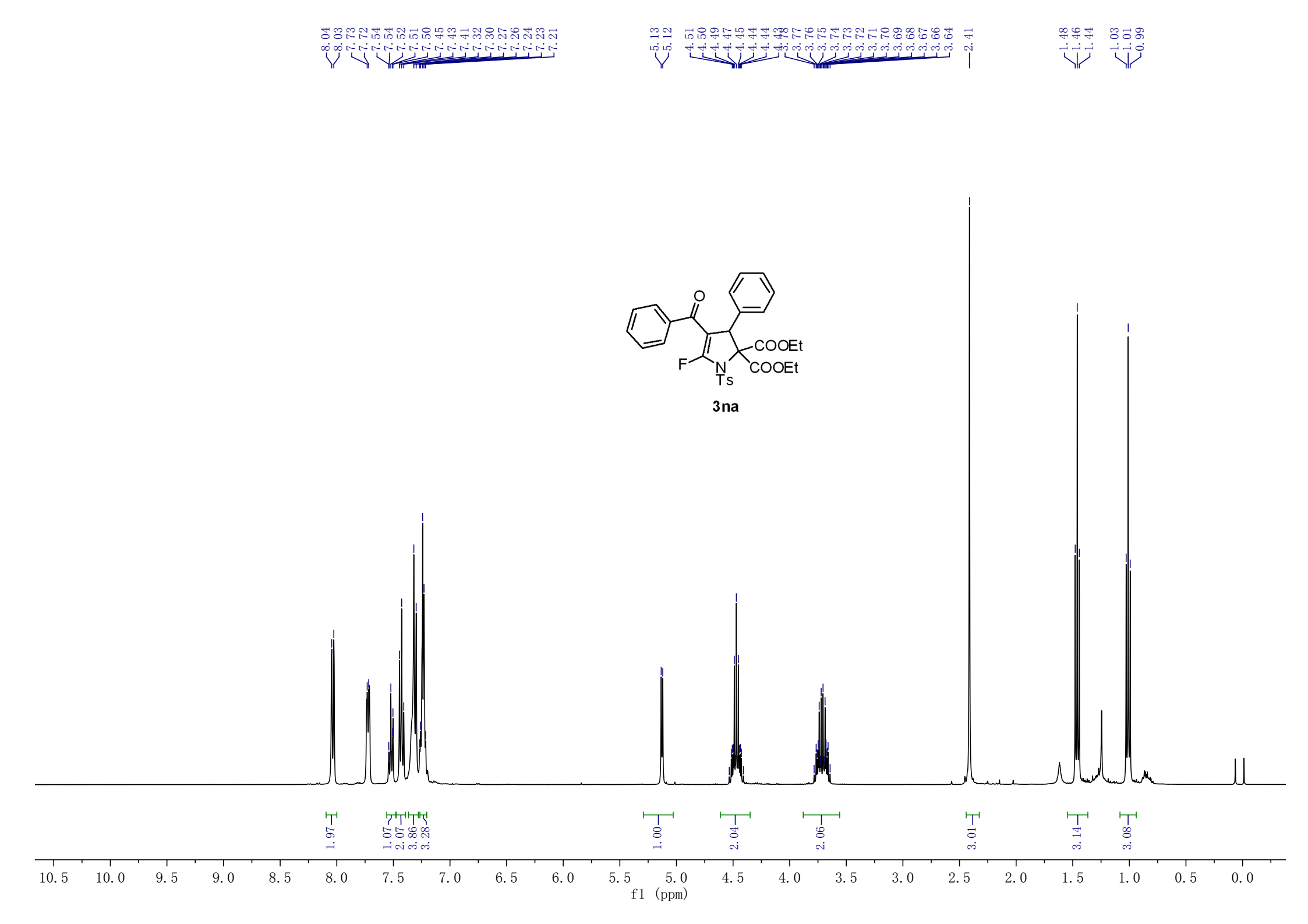
63.19
37.82
21.51
13.78
COOEt
COOEt
F
N
Ts
3ma
f1 (ppm)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7.45
7.43
7.41
7.32
7.30
7.27
7.26
7.24
7.23
7.21
5.13
5.12
4.51
4.50
4.49
4.47
4.45
4.44
4.44
3.77
3.76
3.75
3.74
3.73
3.72
3.71
3.70
3.69
3.68
3.67
3.66
3.64
2.41
1.48
1.46
1.44
1.03
1.01
0.99
O
COOEt
F
N
COOEt
Ts
3na
1.97
1.07
2.07
3.86
3.28
1.00
2.04
2.06
3.01
3.14
3.08
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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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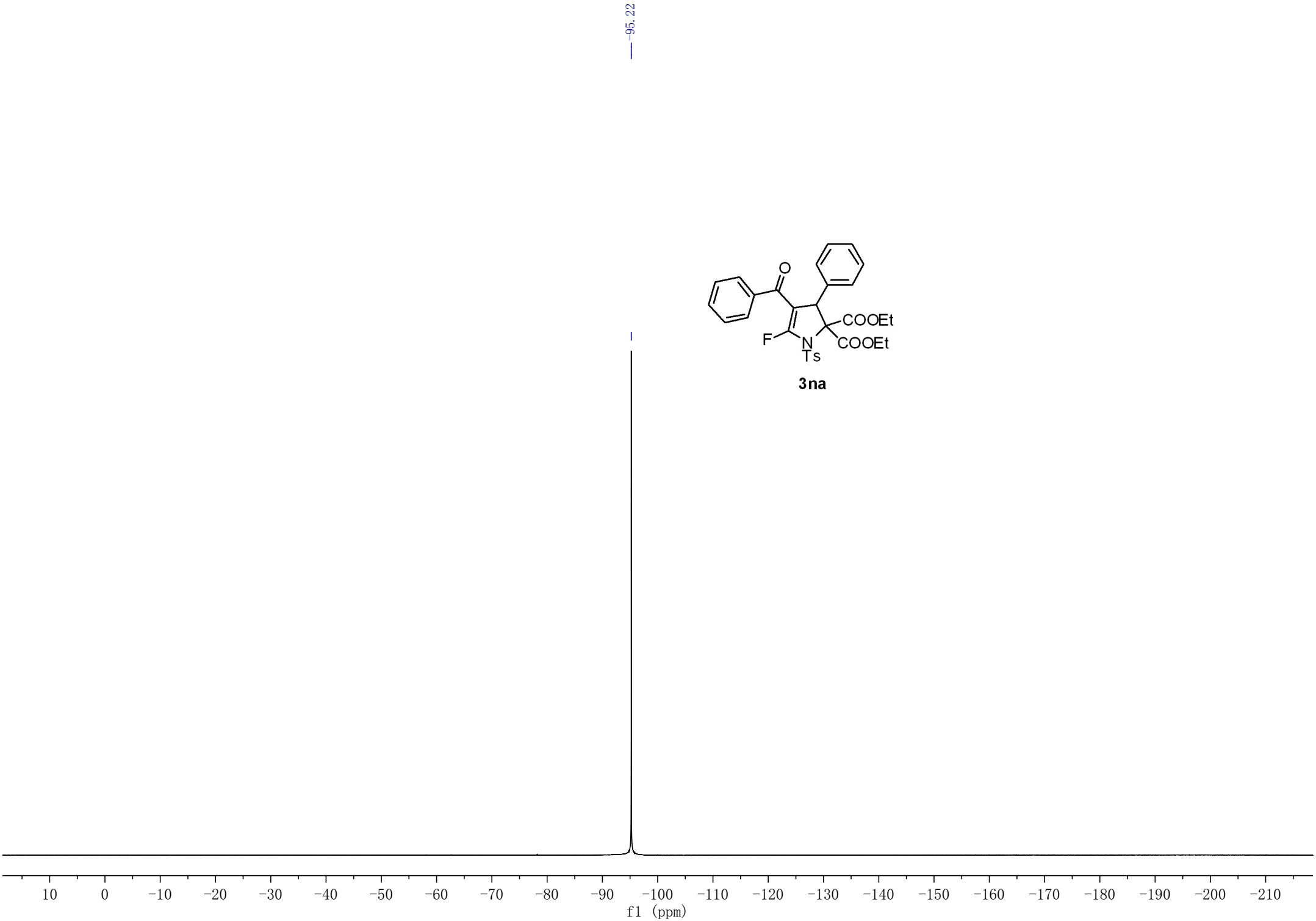
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


-95.22
O
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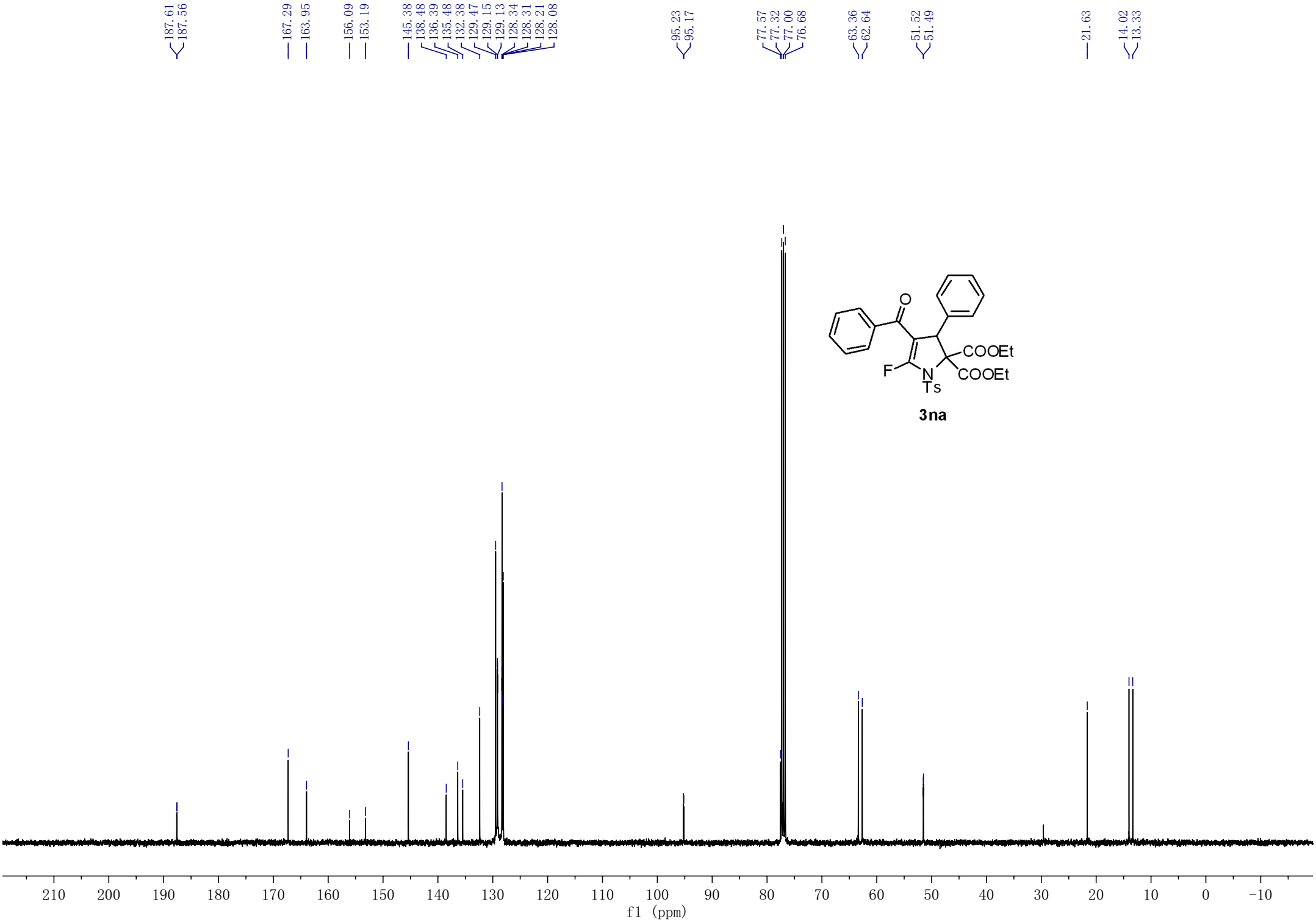
F
N
COOEt
Ts
3na
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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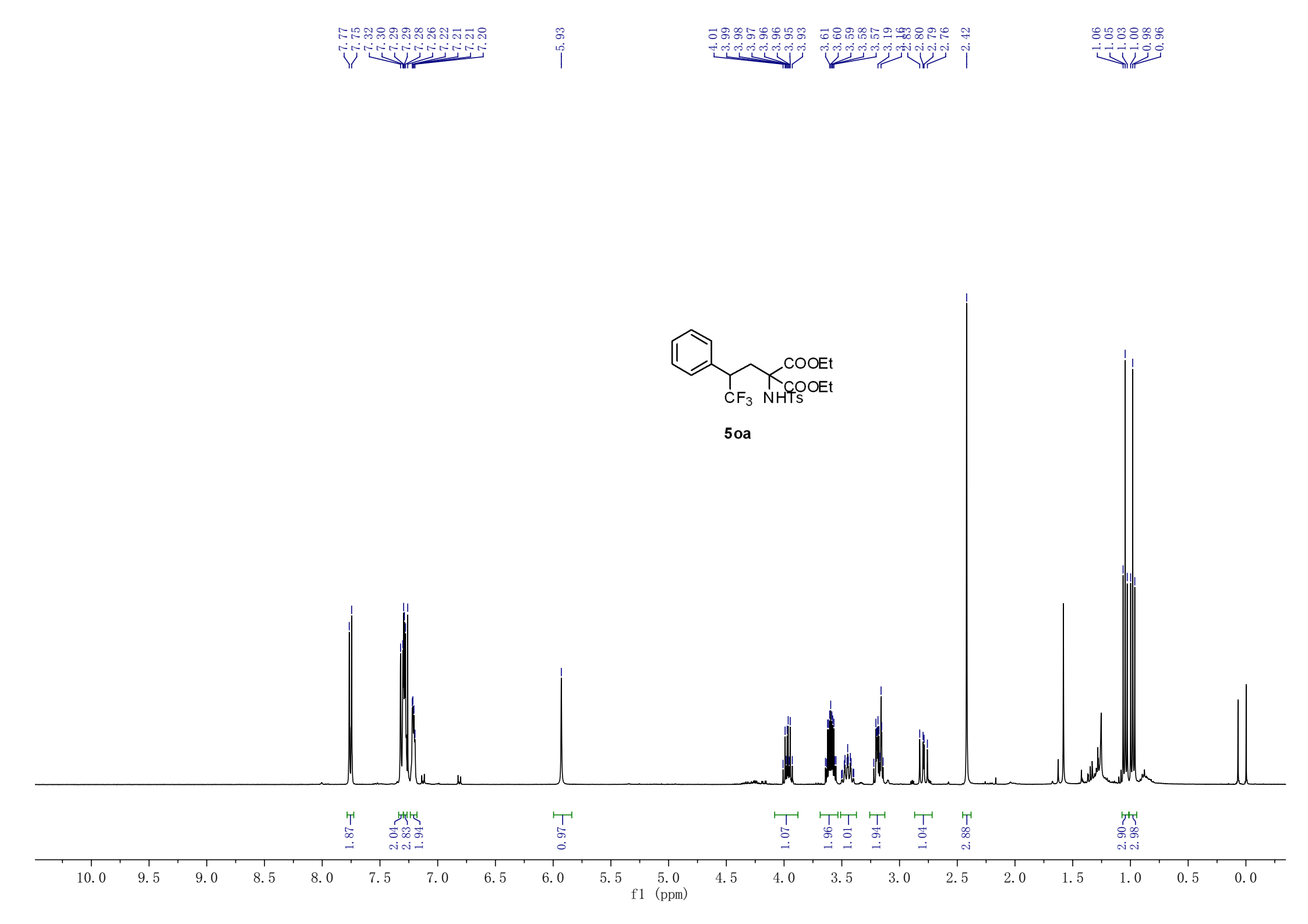
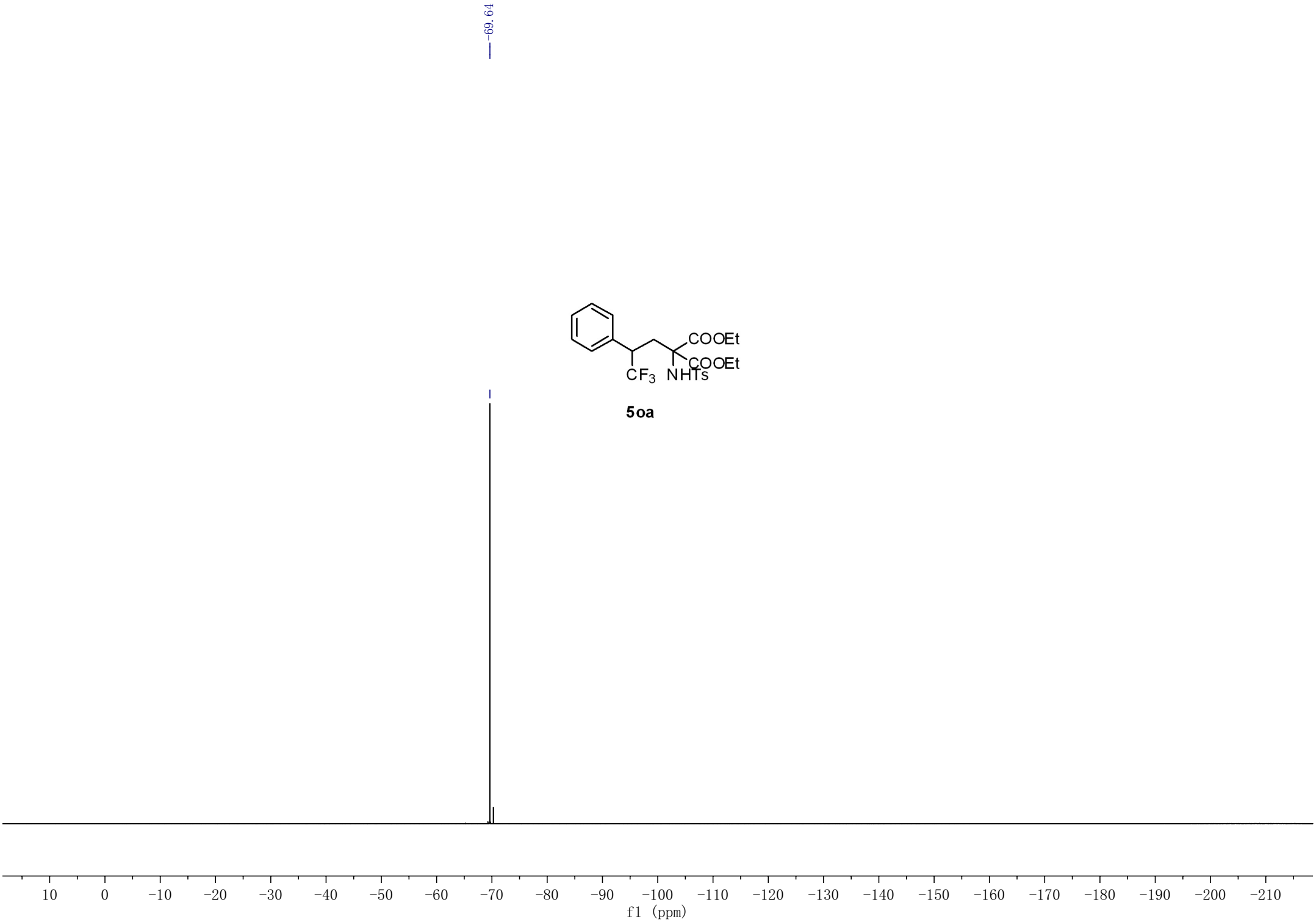
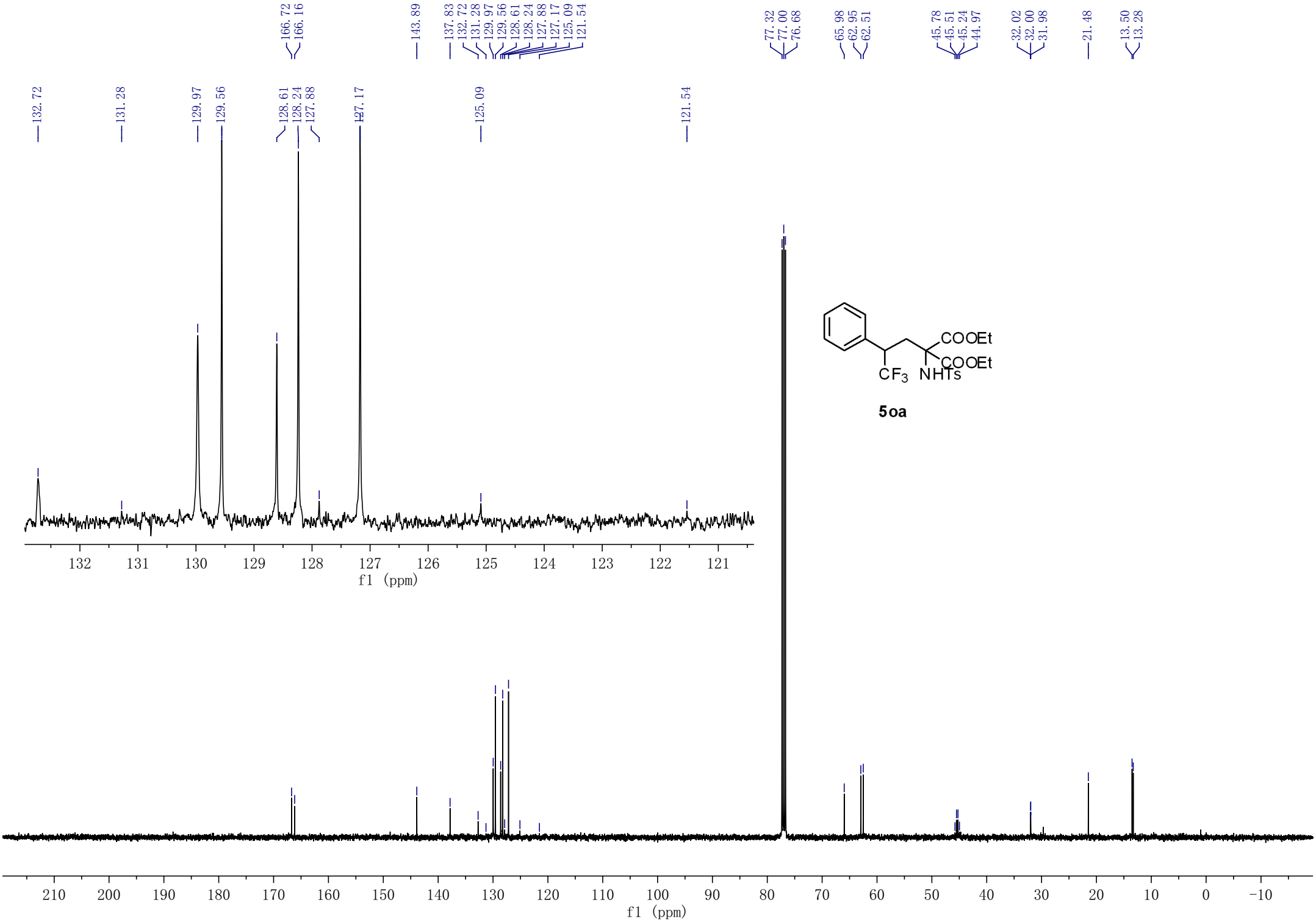
132.38
129.47
129.15
129.13
128.34
128.31
128.21
128.08
95.23
95.17
77.57
77.32
77.00
76.68
63.36
62.64
51.52
51.49
21.63
14.02
13.33
O
COOEt
F
N
COOEt
Ts
3na
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.77
7.75
7.32
7.30
7.29
7.29
7.28
7.26
7.22
7.21
7.21
7.20
5.93
4.01
3.99
3.98
3.97
3.96
3.96
3.95
3.93
3.61
3.60
3.59
3.58
3.57
3.19
3.16
2.83
2.80
2.79
2.76
2.42
1.06
1.05
1.03
1.00
0.98
0.96
COOEt
COOEt
CF3
NHTs
5oa
1.87
2.04
2.83
1.94
0.97
1.07
1.96
1.01
1.94
1.04
2.88
2.90
2.98
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)


-69.64
COOEt
COOEt
CF3 NHTs
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)

5oa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166.16
143.89
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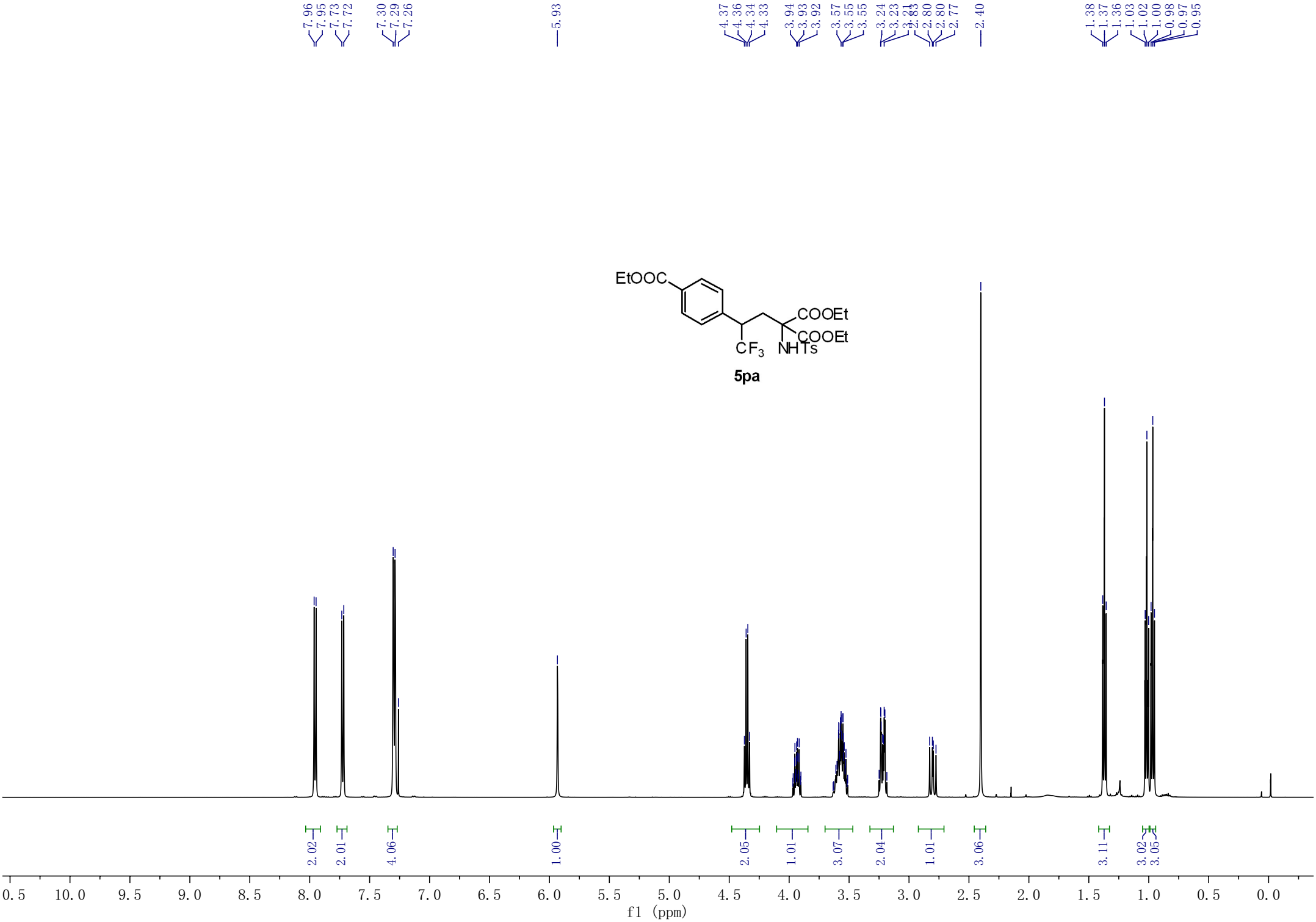
132.72
131.28
129.97
129.56
128.61
128.24
127.88
127.17
125.09
121.54
77.32
77.00
76.68
65.98
62.95
62.51
45.78
45.51
45.24
44.97
32.02
32.00
31.98
21.48
13.50
13.28
COOEt
COOEt
CF3
NHTs
5oa
f1 (ppm)
f1 (ppm)


7.96
7.95
7.73
7.72
7.30
7.29
7.26
5.93
4.37
4.36
4.34
4.33
3.94
3.93
3.92
3.57
3.55
3.55
3.24
3.23
3.21
2.83
2.80
2.80
2.77
2.40
1.38
1.37
1.36
1.03
1.02
1.00
0.98
0.97
0.95
EtOOC
COOEt
COOEt
CF3
NHTs
5pa
2.02
2.01
4.06
1.00
2.05
1.01
3.07
2.04
1.01
3.06
3.11
3.02
3.05
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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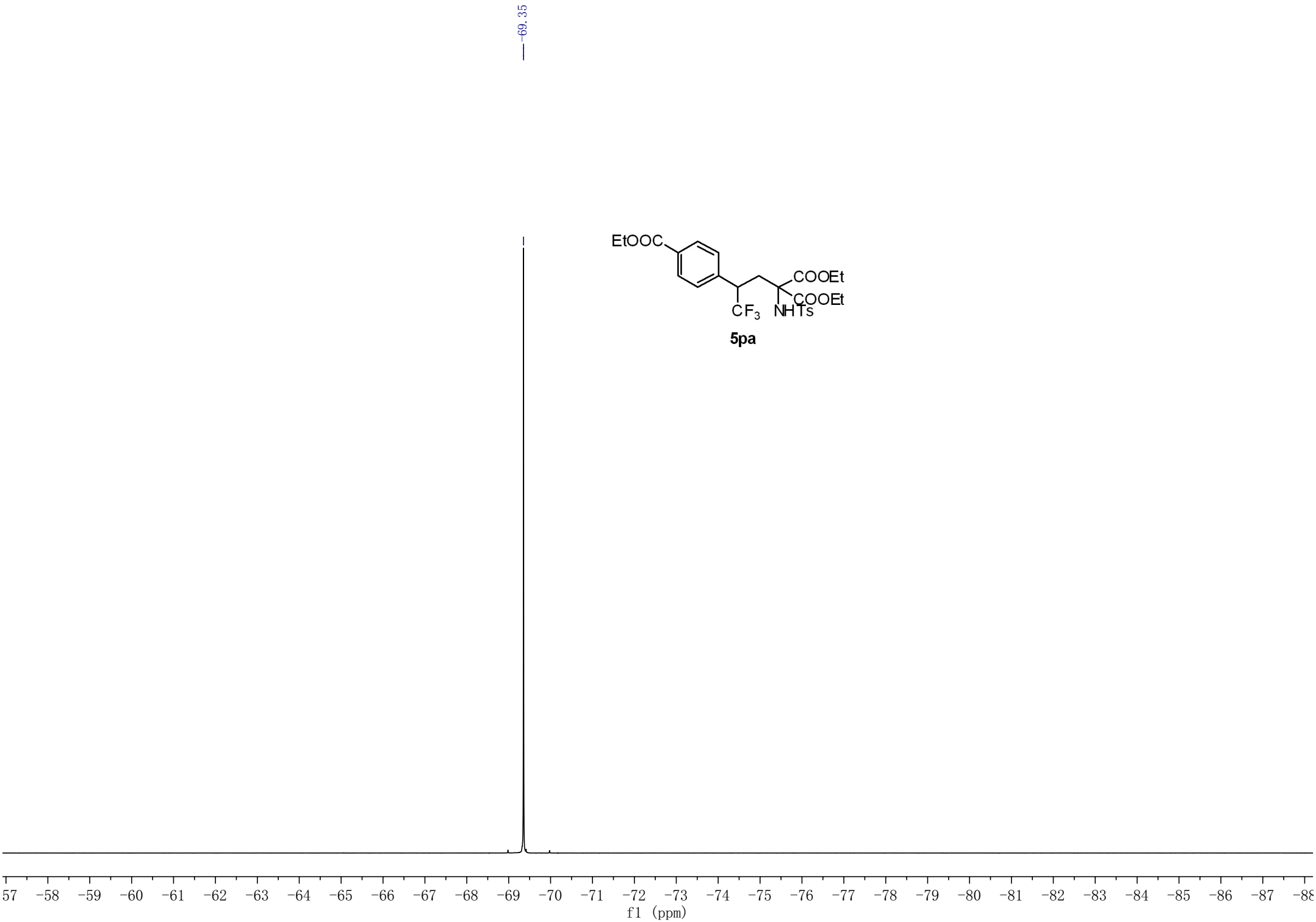
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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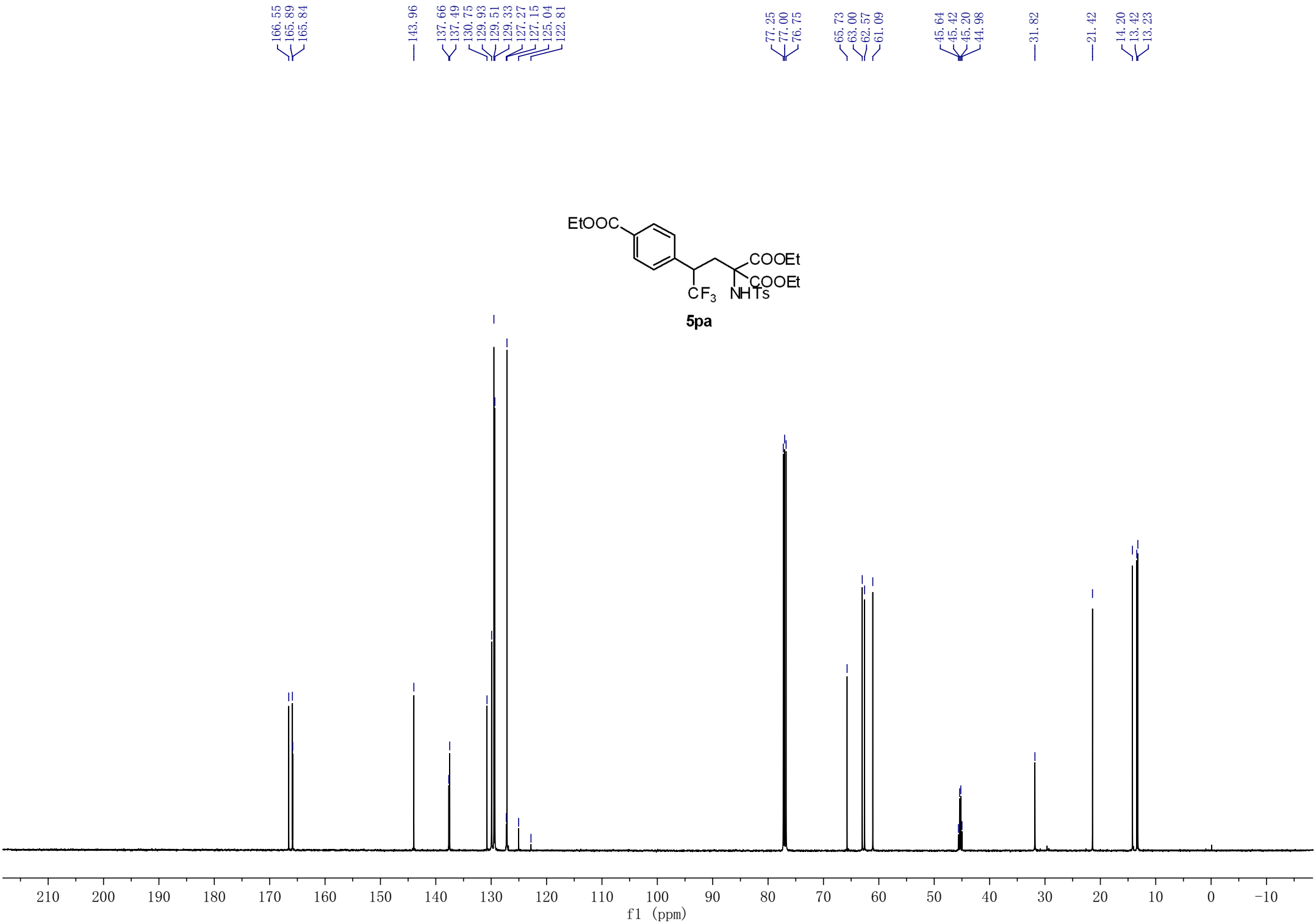
COOEt
COOEt
CF3
NHTs
5pa
57 -58 -59 -60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79 -80 -81 -82 -83 -84 -85 -86 -87 -88
f1 (ppm)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165.84
143.96
137.66
137.49
130.75
129.93
129.51
129.33
127.27
127.15
125.04
122.81
77.25
77.00
76.75
65.73
63.00
62.57
61.09
45.64
45.42
45.20
44.98
31.82
21.42
14.20
13.42
13.23
EtOOC
COOEt
COOEt
CF3
NHTs
5pa
210
200
190
180
170
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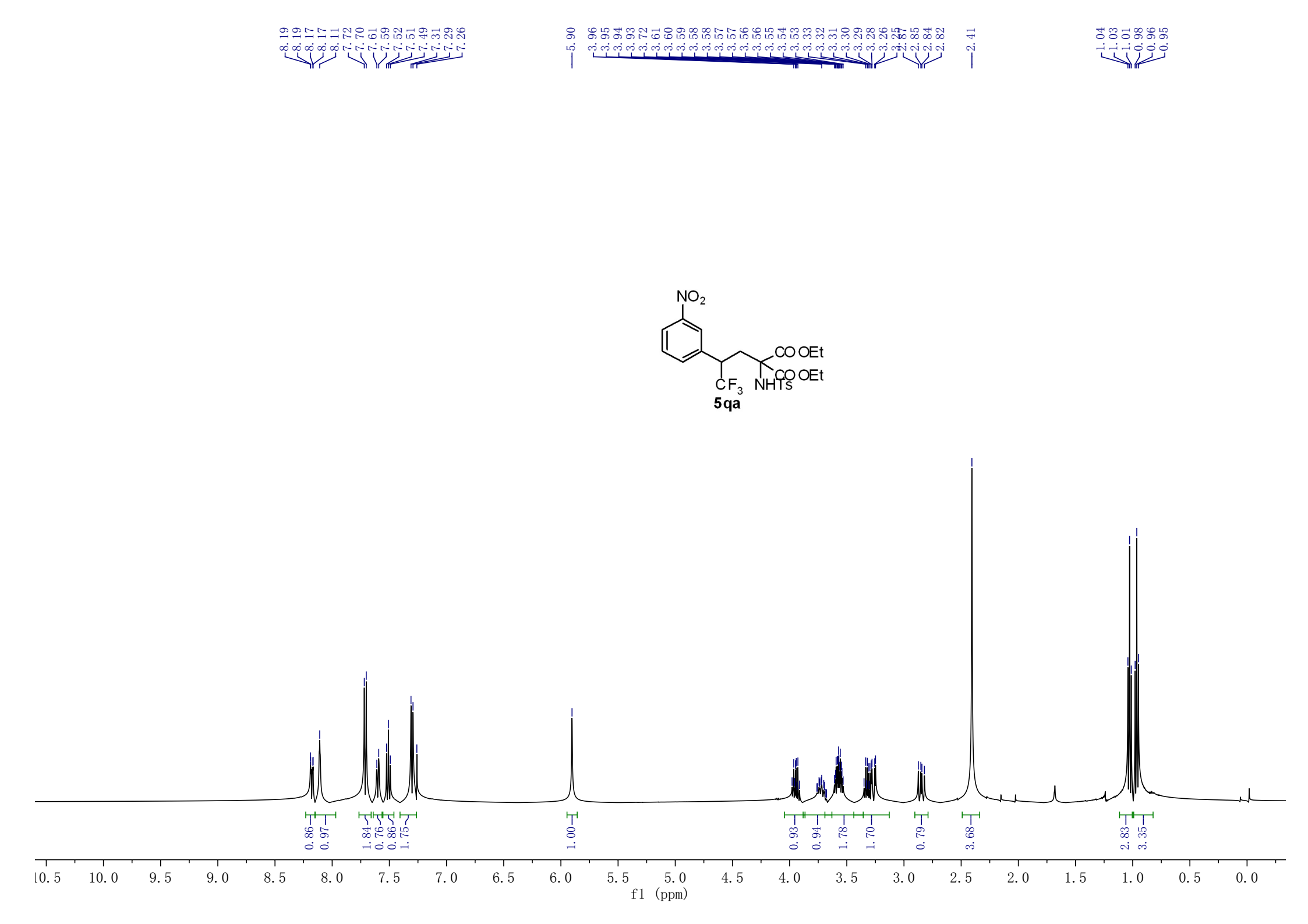
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.61
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7.52
7.51
7.49
7.31
7.29
7.26
5.90
3.96
3.95
3.94
3.93
3.72
3.61
3.60
3.59
3.58
3.58
3.57
3.57
3.56
3.56
3.55
3.54
3.53
3.33
3.32
3.31
3.30
3.29
3.28
3.26
2.85
2.84
2.82
2.41
1.04
1.03
1.01
0.98
0.96
0.95
NO2
CO OEt
CO OEt
CF3
NHTs
5qa
0.86
0.97
1.84
0.76
0.86
1.75
1.00
0.93
0.94
1.78
1.70
0.79
3.68
2.83
3.35
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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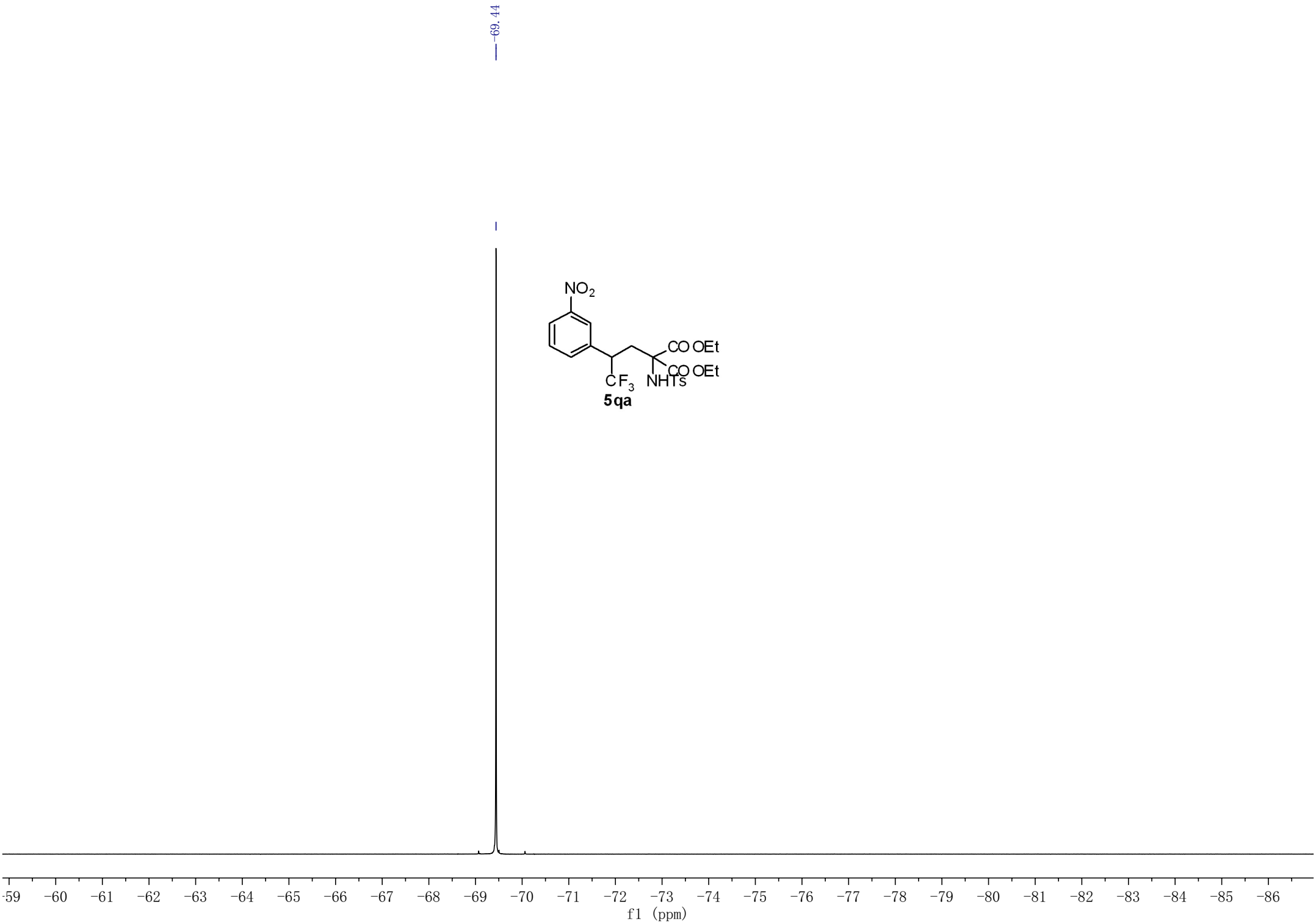
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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CO OEt
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5qa
-59
-60
-61
-62
-63
-64
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-67
-68
-69
-70
-71
-72
-73
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-75
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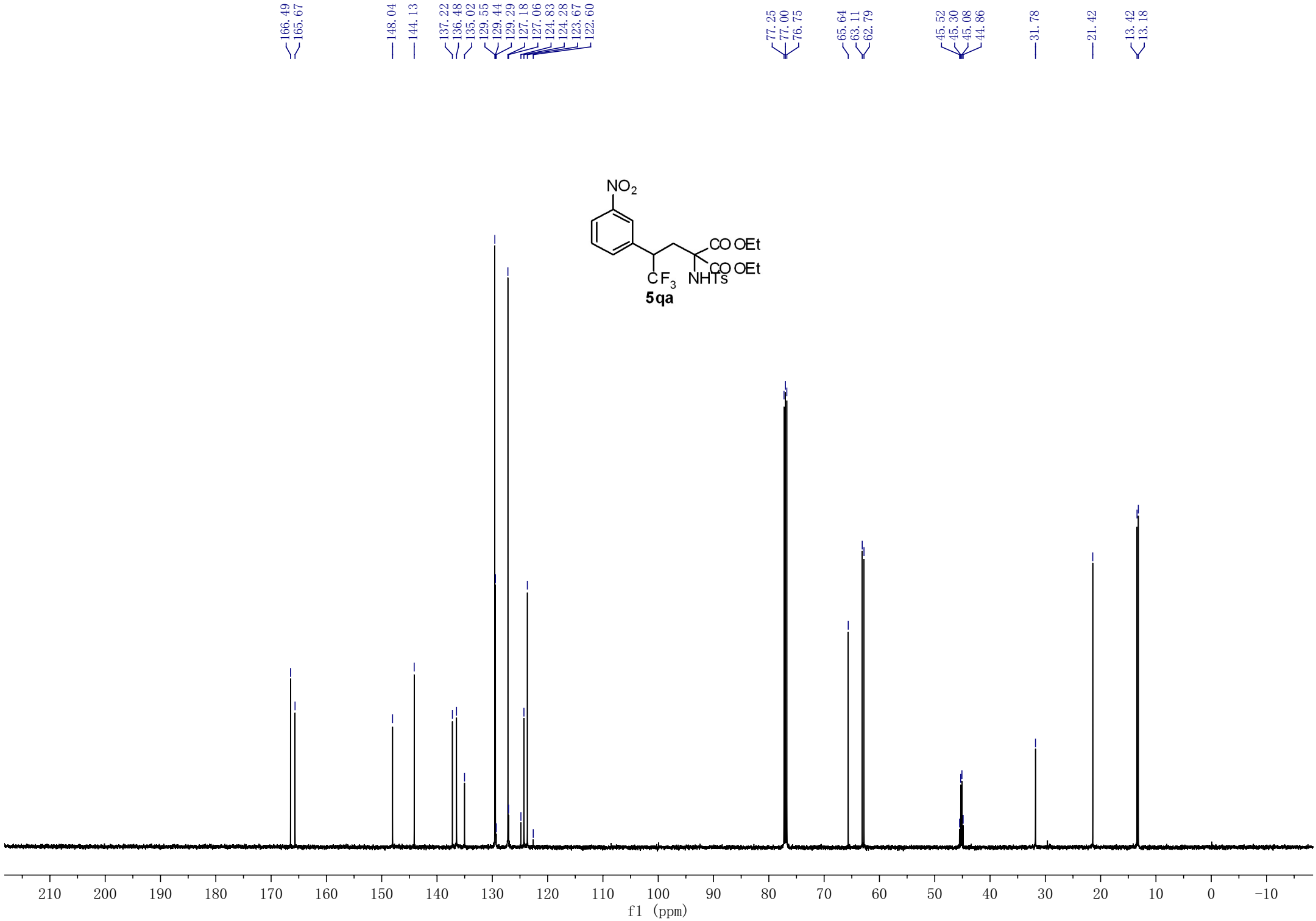
-77
-78
-79
-80
-81
-82
-83
-84
-85
-86
f1 (ppm)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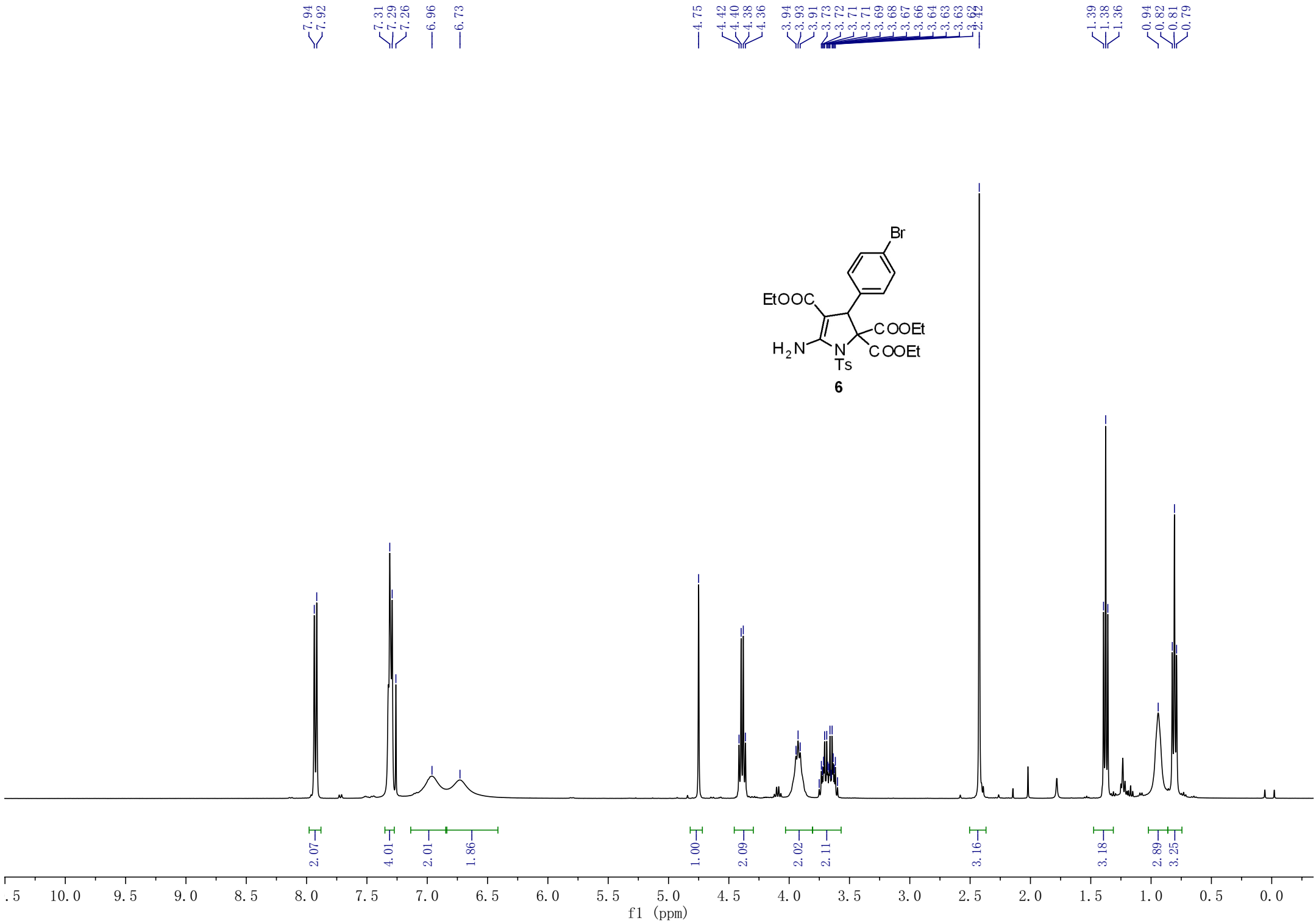
127.06
124.83
124.28
123.67
122.60
77.25
77.00
76.75
65.64
63.11
62.79
45.52
45.30
45.08
44.86
31.78
21.42
13.42
13.18
NO2
CO OEt
CO OEt
CF3
NHTs
5qa
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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4.40
4.38
4.36
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3.93
3.91
3.73
3.72
3.71
3.71
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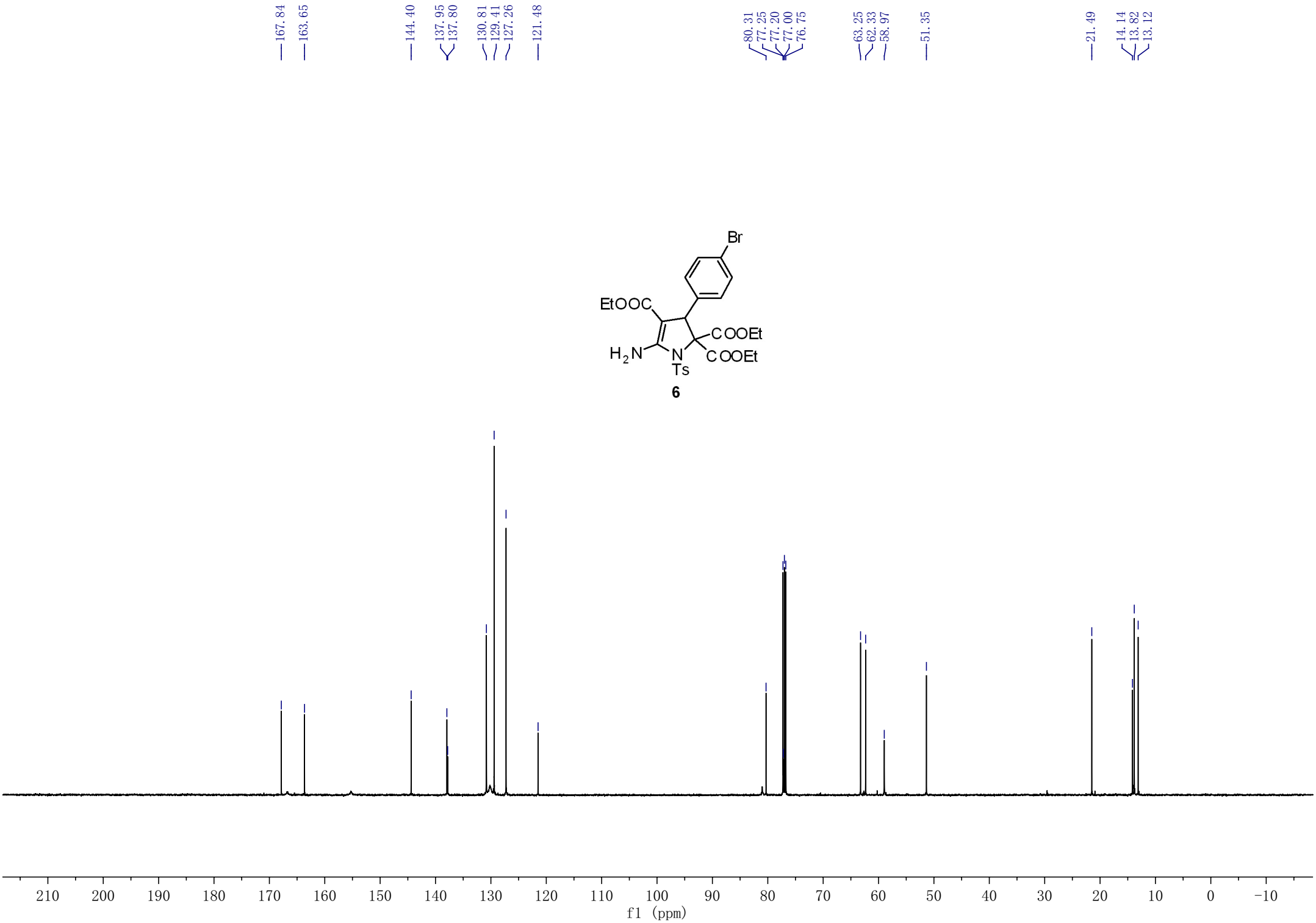
3.68
3.67
3.66
3.64
3.63
3.63
3.62
3.42
1.39
1.38
1.36
0.94
0.82
0.81
0.79
Br
EtOOC
COOEt
H2N
N
COOEt
Ts
6
2.07
4.01
2.01
1.86
1.00
2.09
2.02
2.11
3.16
3.18
2.89
3.25
f1 (ppm)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80.31
77.25
77.20
77.00
76.75
63.25
62.33
58.97
51.35
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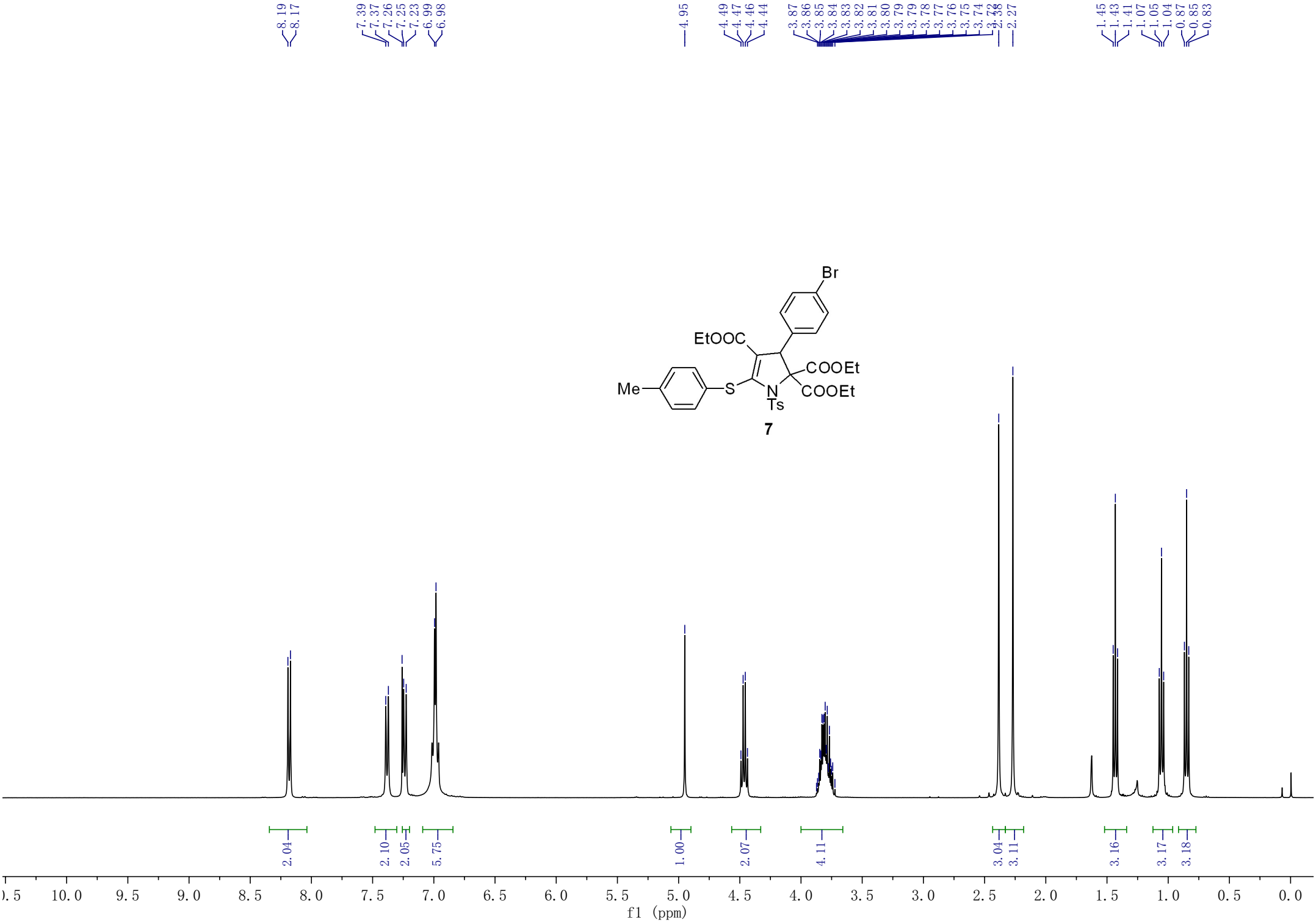
13.82
13.12
Br
EtOOC
COOEt
COOEt
H2N
N
Ts
6
f1 (ppm)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4.44
3.87
3.86
3.85
3.84
3.83
3.82
3.81
3.80
3.79
3.79
3.78
3.77
3.76
3.75
3.74
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2.27
1.45
1.43
1.41
1.07
1.05
1.04
0.87
0.85
0.83
Br
EtOOC
COOEt
COOEt
Me
S
N
Ts
7
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2.05
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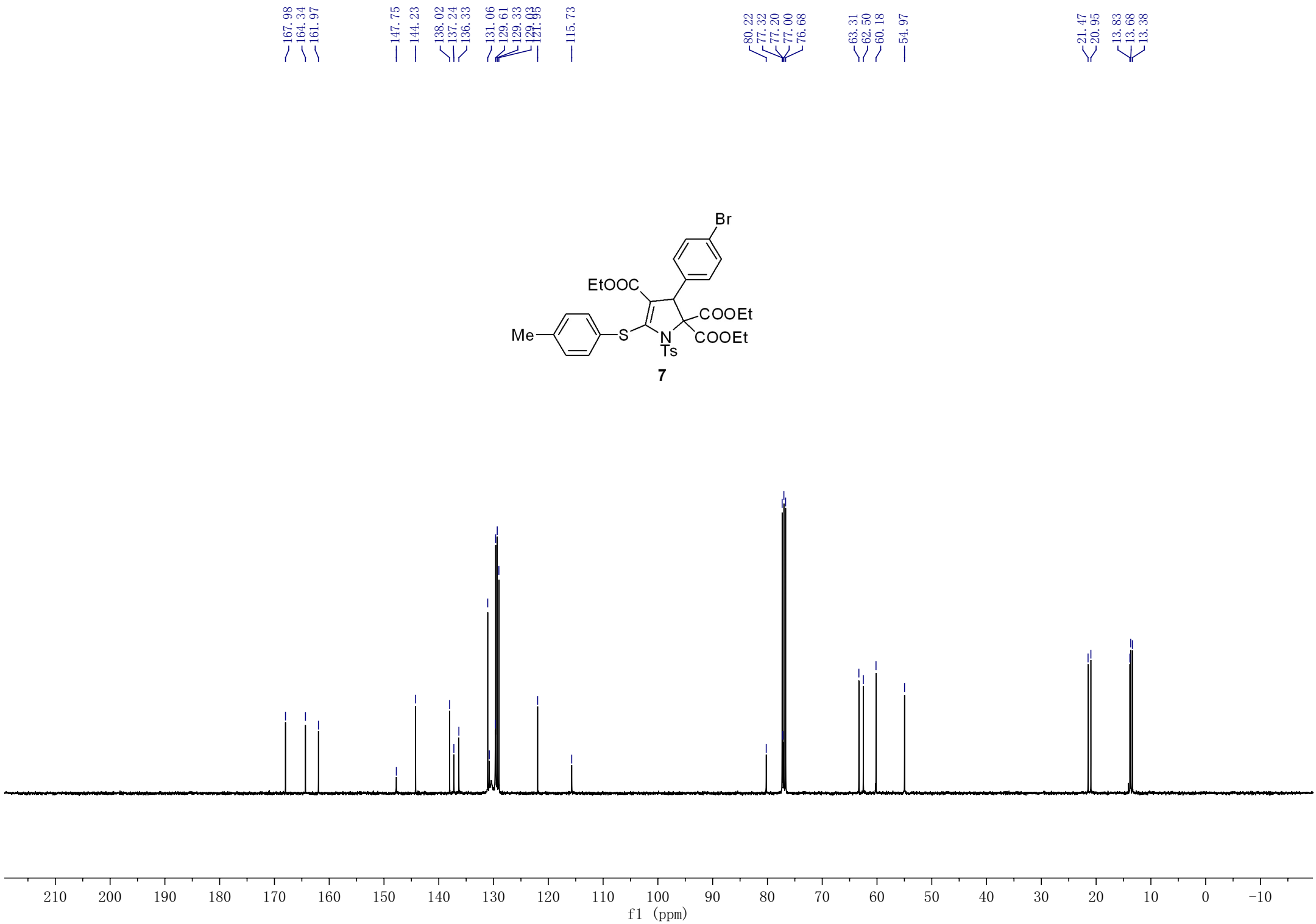
1.00
2.07
4.11
3.04
3.11
3.16
3.17
3.18
f1 (ppm)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131.06
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129.33
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77.32
77.20
77.00
76.68
63.31
62.50
60.18
54.97
21.47
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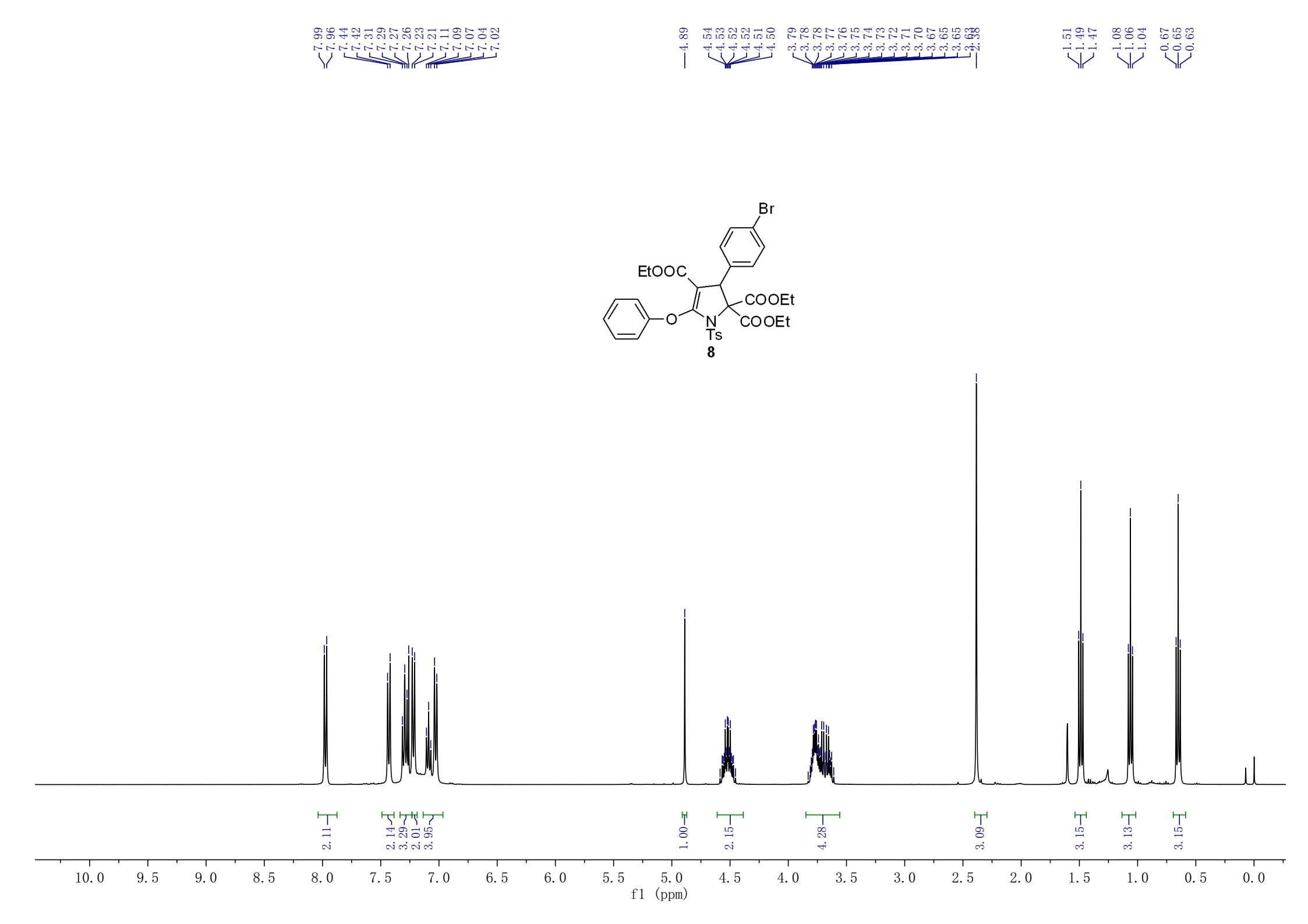
13.68
13.38
Br
EtOOC
COOEt
COOEt
Me
S
N
Ts
7
f1 (ppm)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7.27
7.26
7.23
7.21
7.11
7.09
7.07
7.04
7.02
4.89
4.54
4.53
4.52
4.52
4.51
4.50
3.79
3.78
3.78
3.77
3.76
3.75
3.74
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3.67
3.65
3.65
3.63
1.51
1.49
1.47
1.08
1.06
1.04
0.67
0.65
0.63
Br
EtOOC
COOEt
COOEt
O
N
Ts
8
2.11
2.14
3.29
2.01
3.95
1.00
2.15
4.28
3.09
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7.5
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6.5
6.0
5.5
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4.5
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3.5
3.0
2.5
2.0
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1.0
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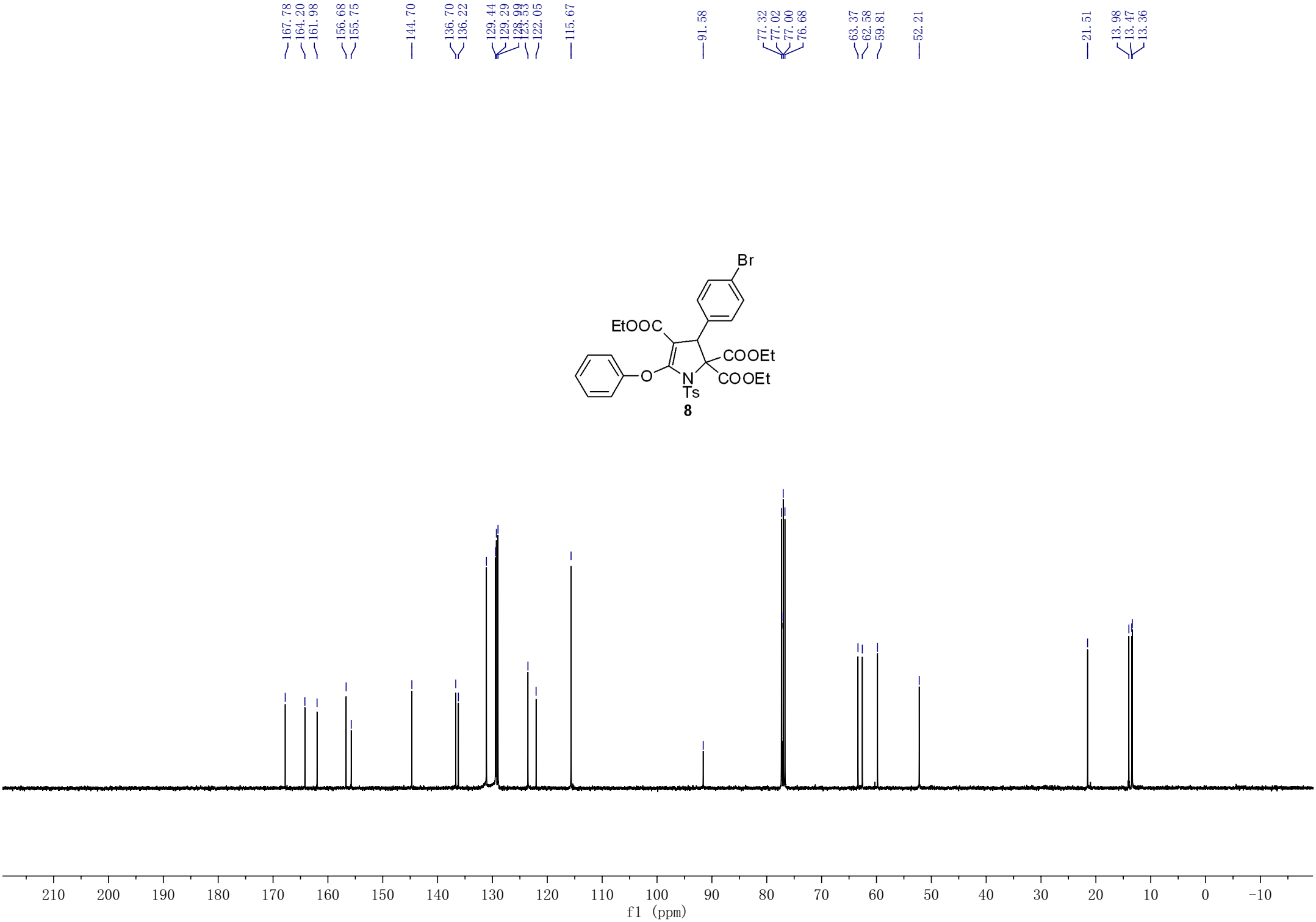
0.0
f1 (ppm)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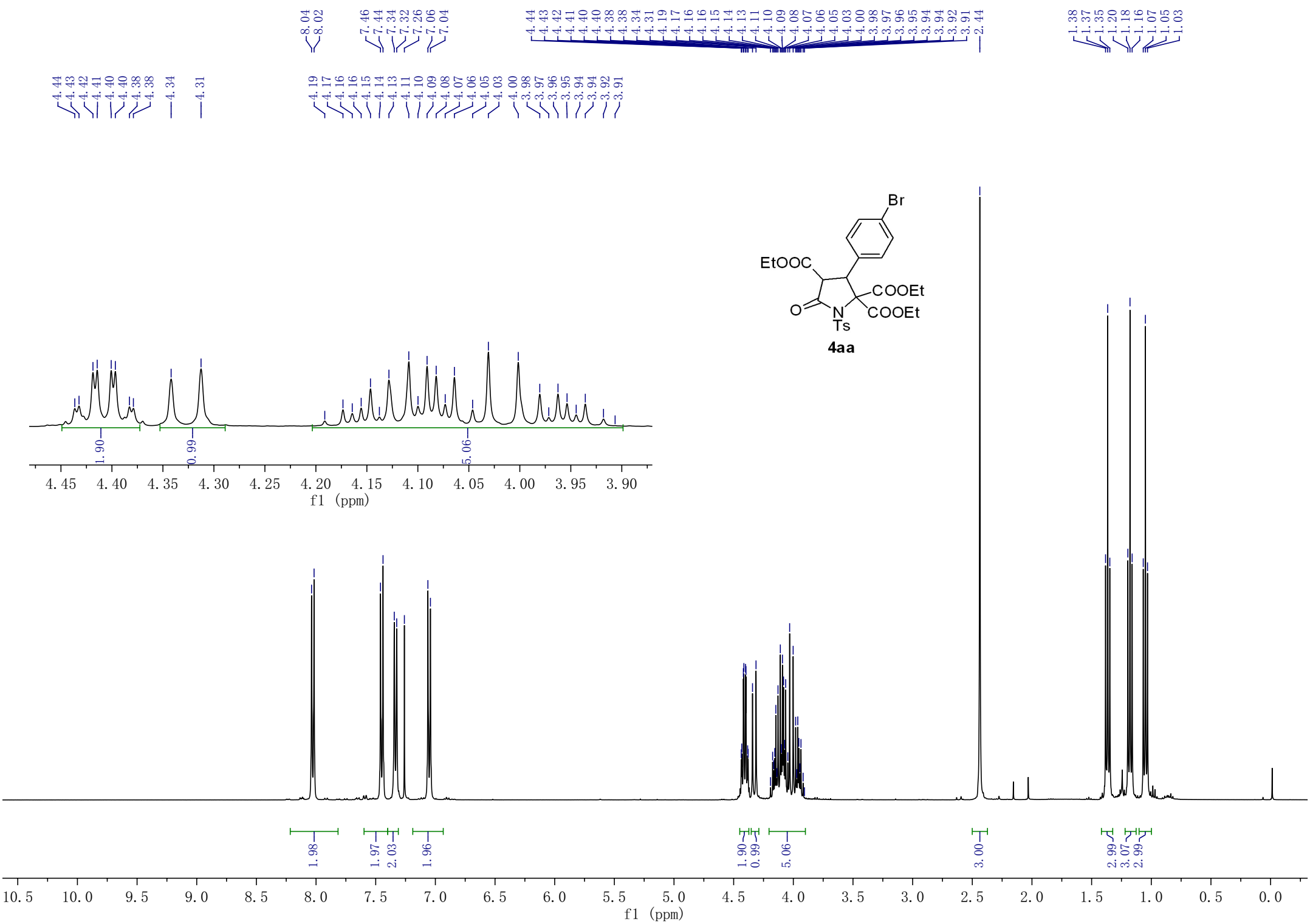
136.70
136.22
129.44
129.29
122.05
115.67
91.58
77.32
77.02
77.00
76.68
63.37
62.58
59.81
52.21
21.51
13.98
13.47
13.36
Br
EtOOC
COOEt
COOEt
O
N
Ts
8
f1 (ppm)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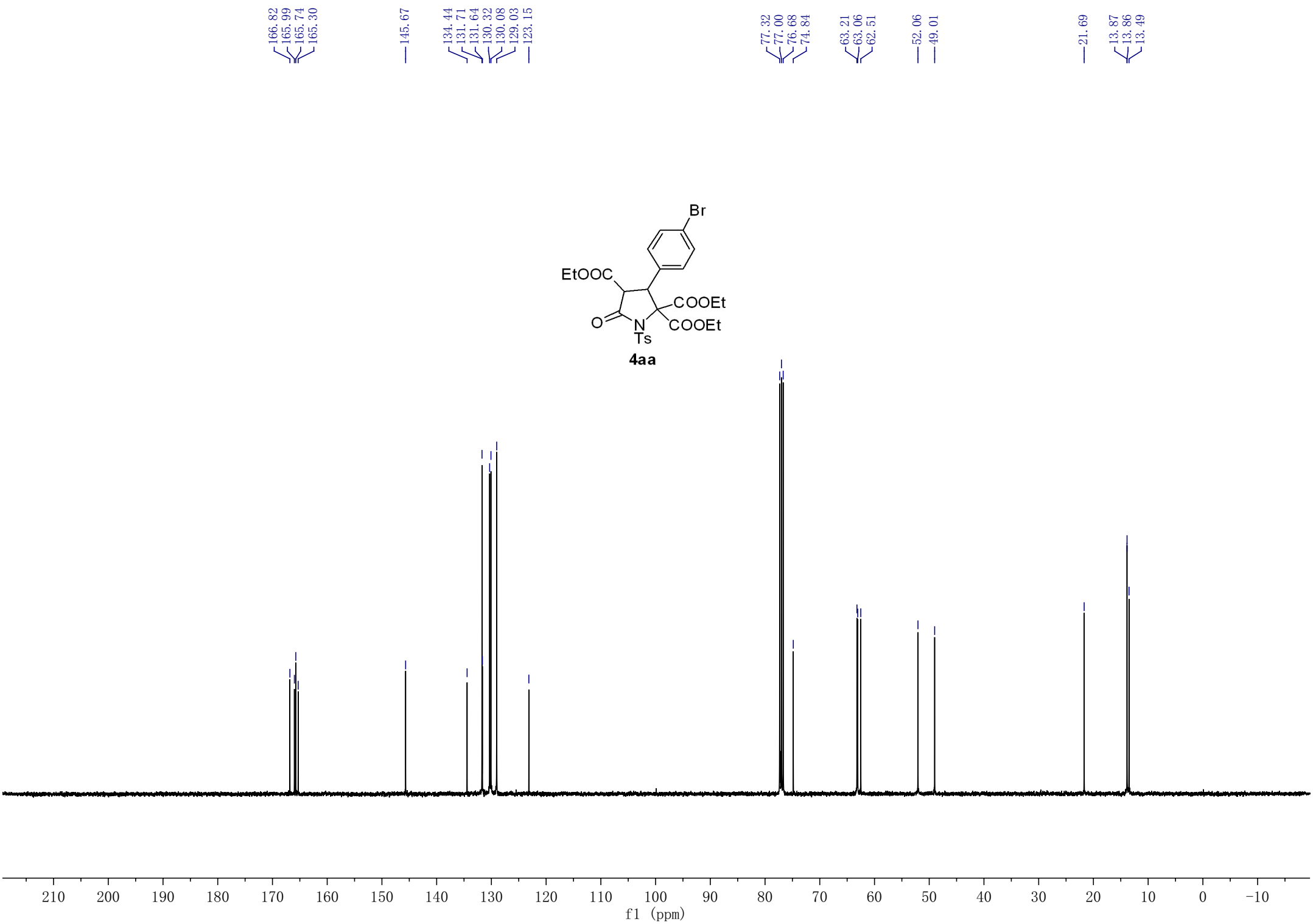
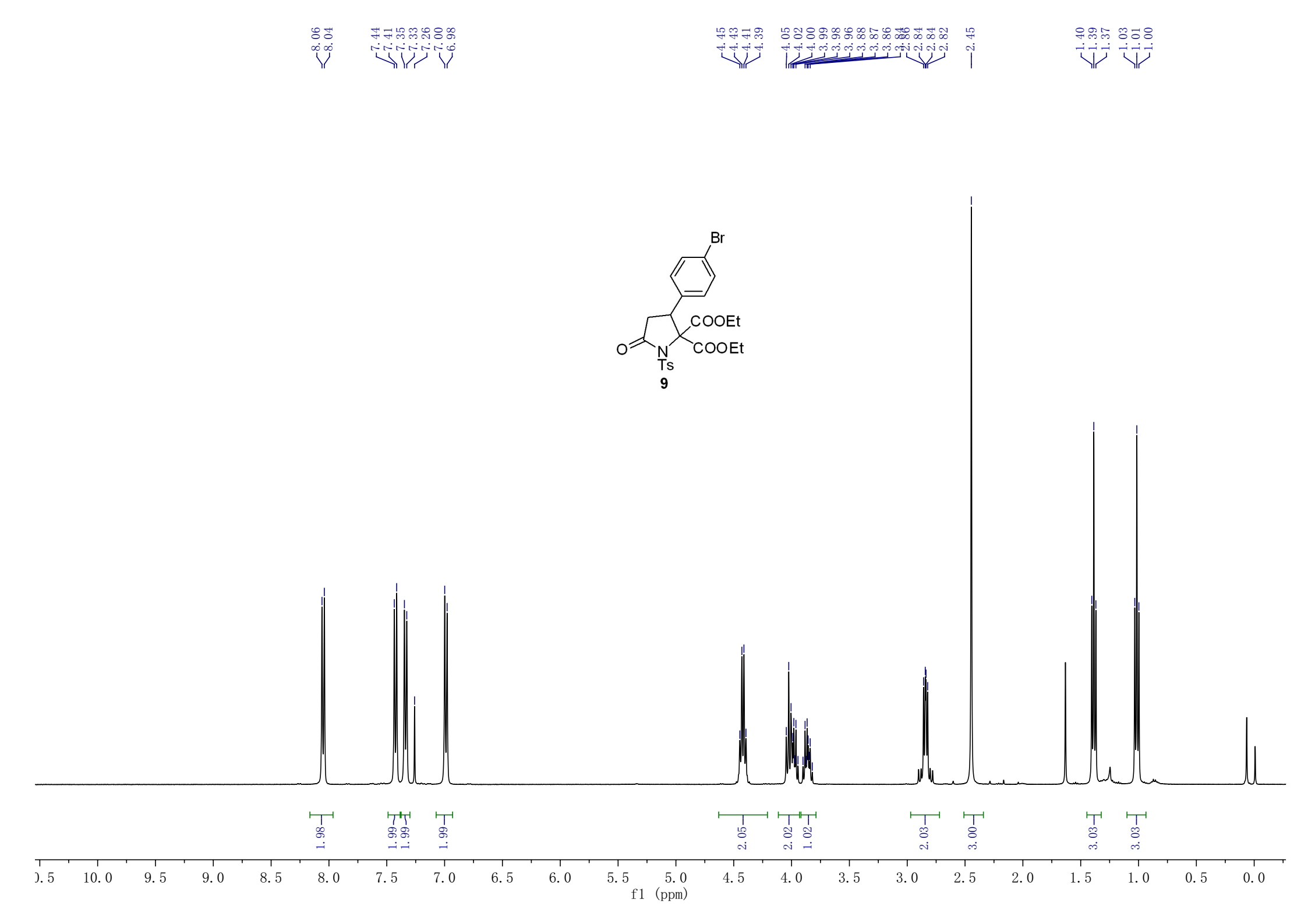
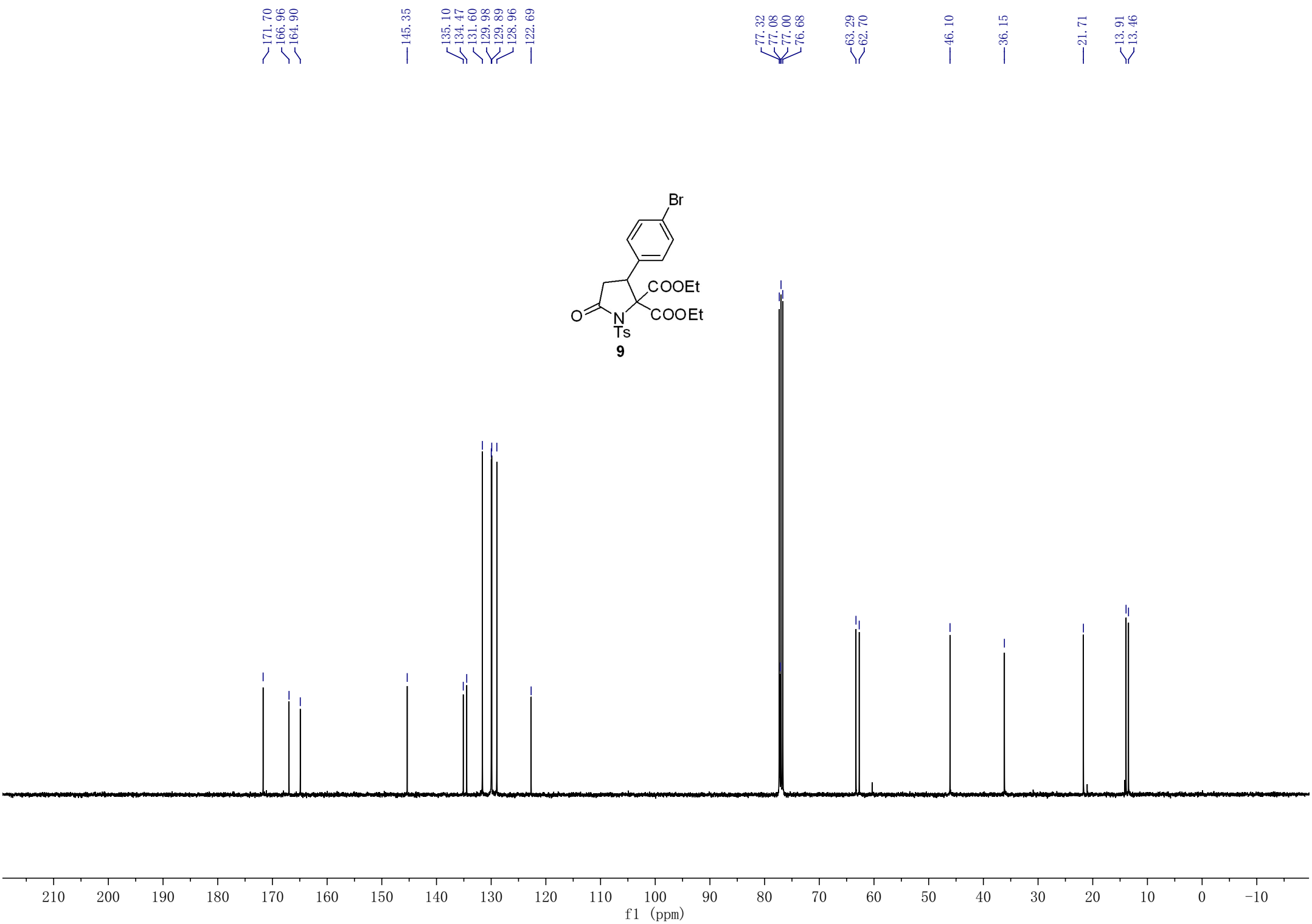
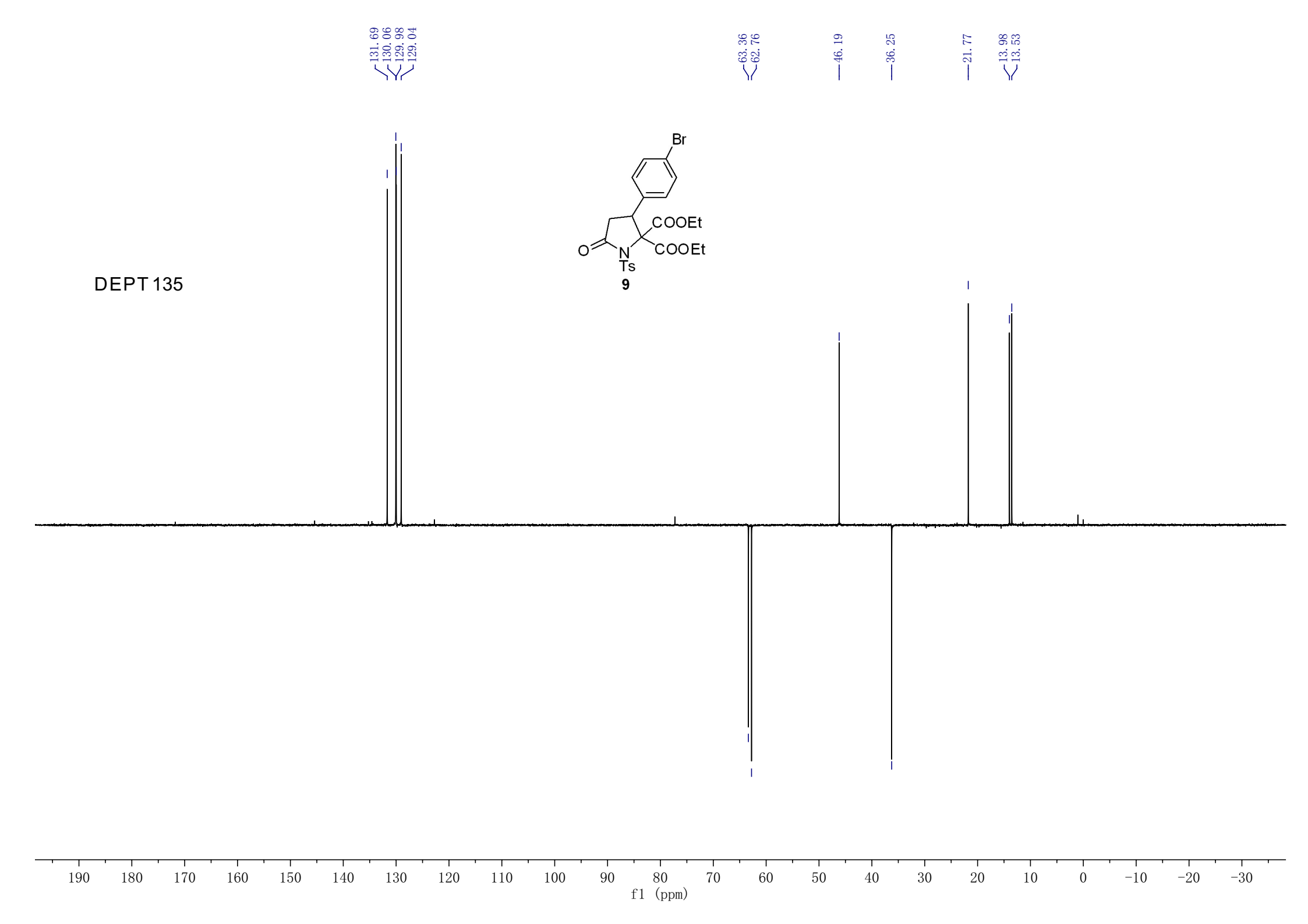
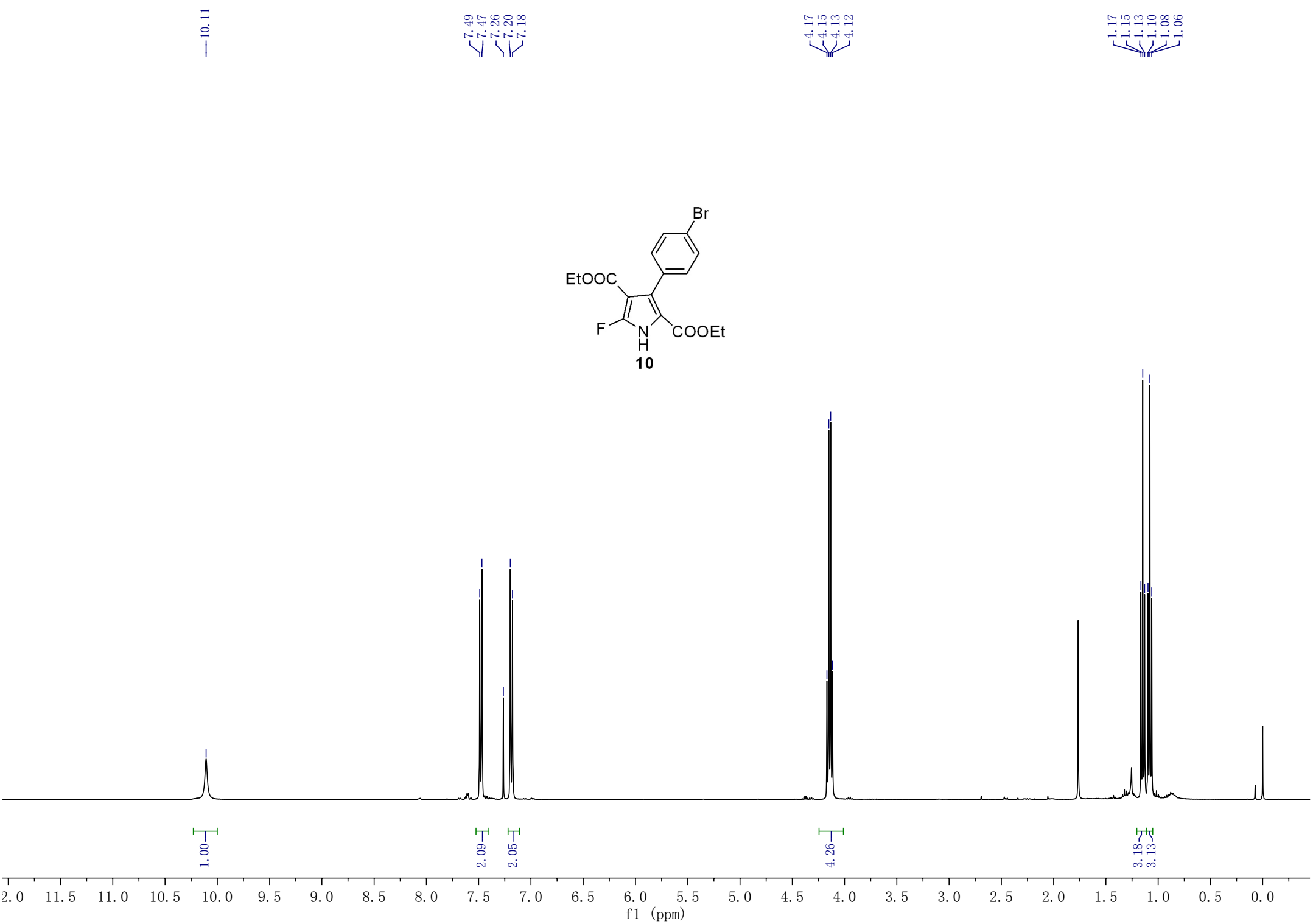
8.02
7.46
7.44
7.34
7.32
7.26
7.06
7.04
4.44
4.43
4.42
4.41
4.40
4.40
4.38
4.38
4.34
4.31
4.19
4.17
4.16
4.16
4.15
4.14
4.13
4.11
4.10
4.09
4.08
4.07
4.06
4.05
4.03
4.00
3.98
3.97
3.96
3.95
3.94
3.94
3.92
3.91
2.44
1.38
1.37
1.35
1.20
1.18
1.16
1.07
1.05
1.03
Br
EtOOC
COOEt
O
N
COOEt
Ts
4aa
1.90
0.99
5.06
4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90
f1 (ppm)
1.98
1.97
2.03
1.96
1.90
0.99
5.06
3.00
2.99
3.07
2.99
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)

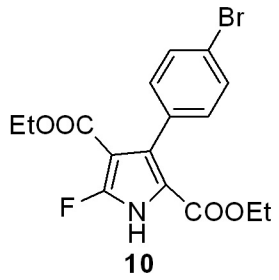

166.82
165.99
165.74
165.30
145.67
134.44
131.71
131.64
130.32
130.08
129.03
123.15
77.32
77.00
76.68
74.84
63.21
63.06
62.51
52.06
49.01
21.69
13.87
13.86
13.49
Br
EtOOC
COOEt
COOEt
O
N
Ts
4aa
f1 (ppm)


8.06
8.04
7.44
7.41
7.35
7.33
7.26
7.00
6.98
4.45
4.43
4.41
4.39
4.05
4.02
4.00
3.99
3.98
3.96
3.88
3.87
3.86
2.84
2.82
2.45
1.40
1.39
1.37
1.03
1.01
1.00
Br
COOEt
COOEt
O
N
Ts
9
1.98
1.99
1.99
1.99
2.05
2.02
1.02
2.03
3.00
3.03
3.03
f1 (ppm)


171.70
166.96
164.90
145.35
135.10
134.47
131.60
129.98
129.89
128.96
122.69
77.32
77.08
77.00
76.68
63.29
62.70
46.10
36.15
21.71
13.91
13.46
Br
COOEt
COOEt
O
N
Ts
9
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)

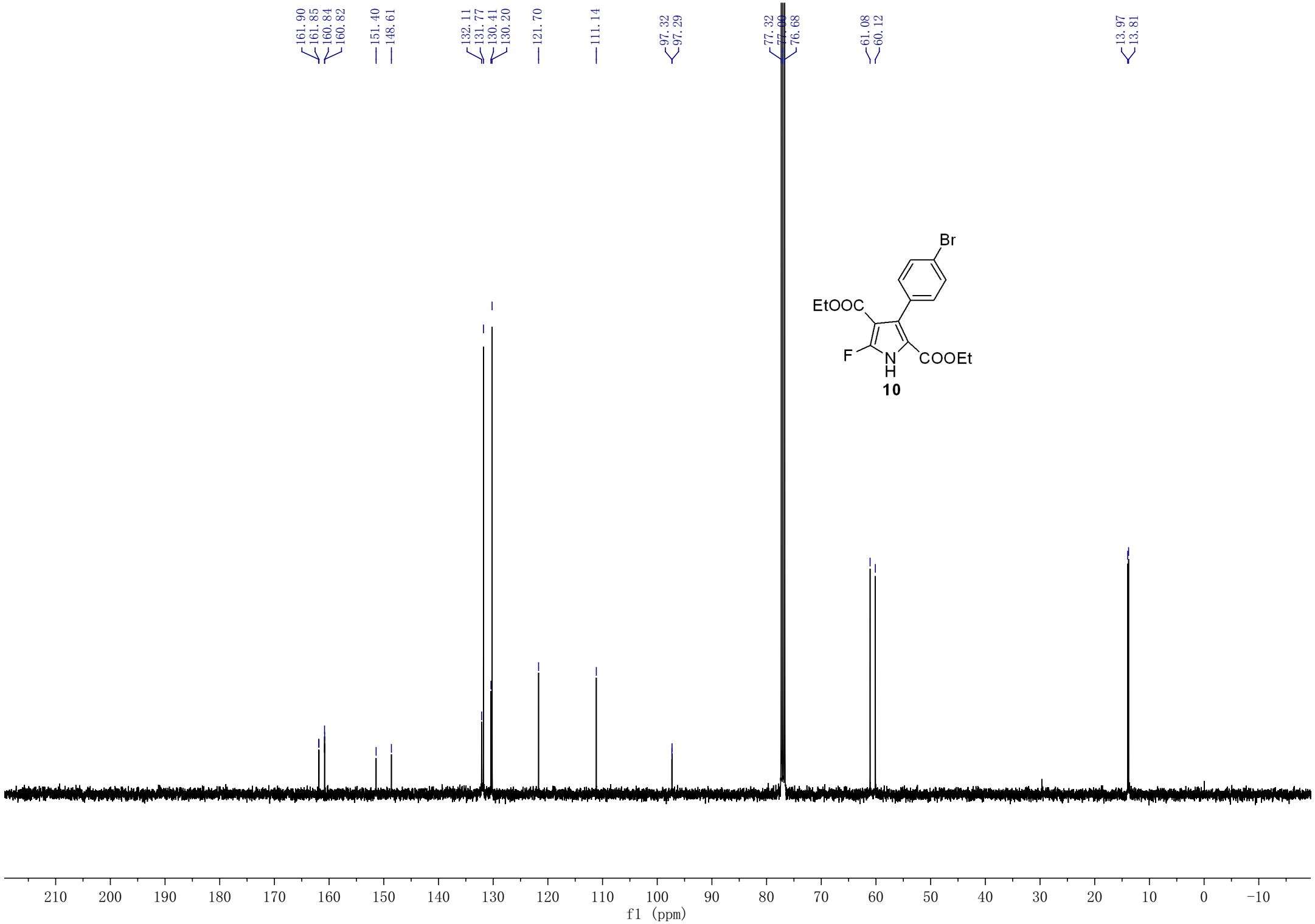

131.69
130.06
129.98
129.04
63.36
62.76
46.19
36.25
21.77
13.98
13.53
Br
COOEt
COOEt
O
N
Ts
9
DEPT 135
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

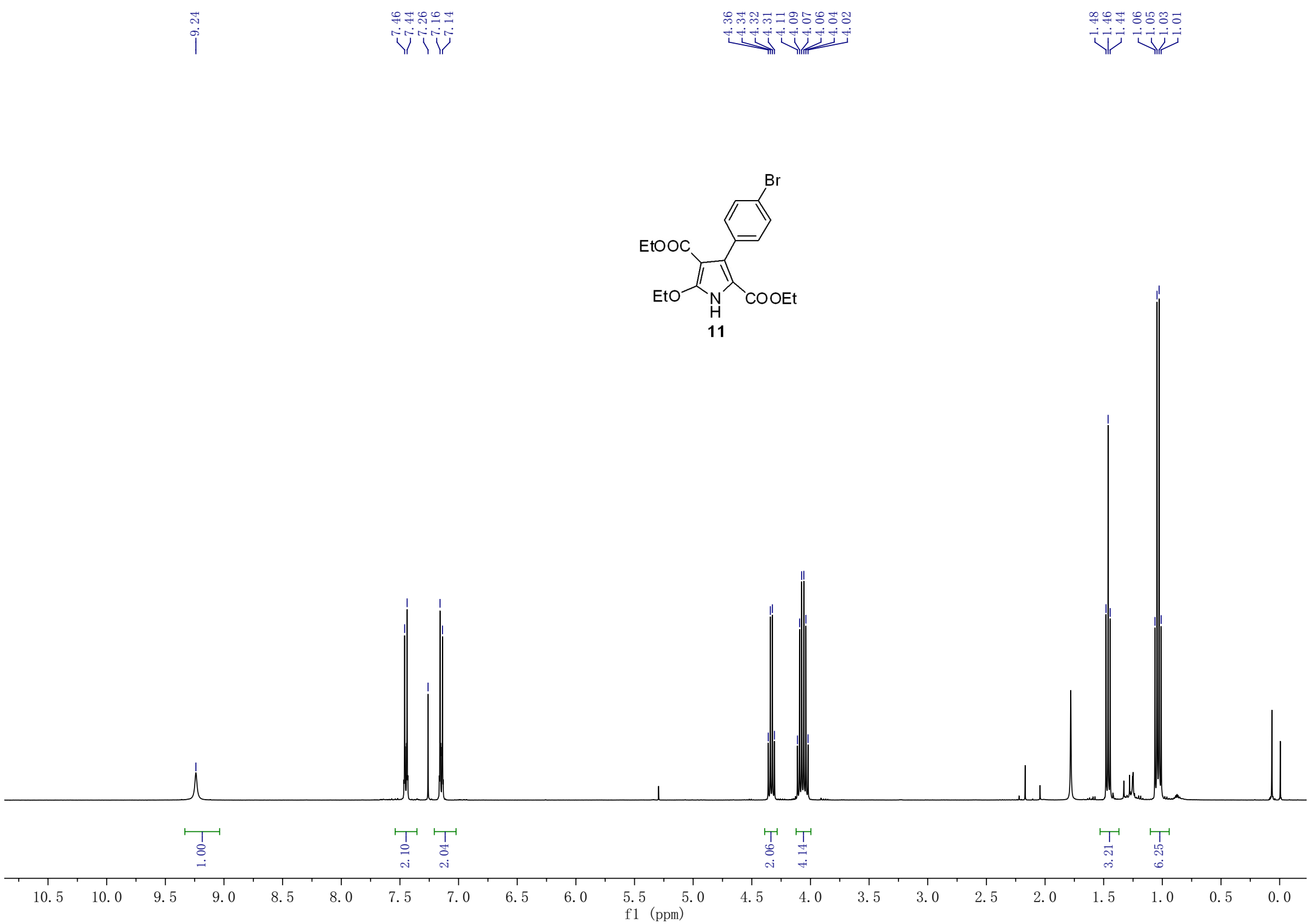

10.11
7.49
7.47
7.26
7.20
7.18
4.17
4.15
4.13
4.12
1.17
1.15
1.13
1.10
1.08
1.06
Br
EtOOC
F
N
H
COOEt
10
1.00
2.09
2.05
4.26
3.18
3.13
f1 (ppm)

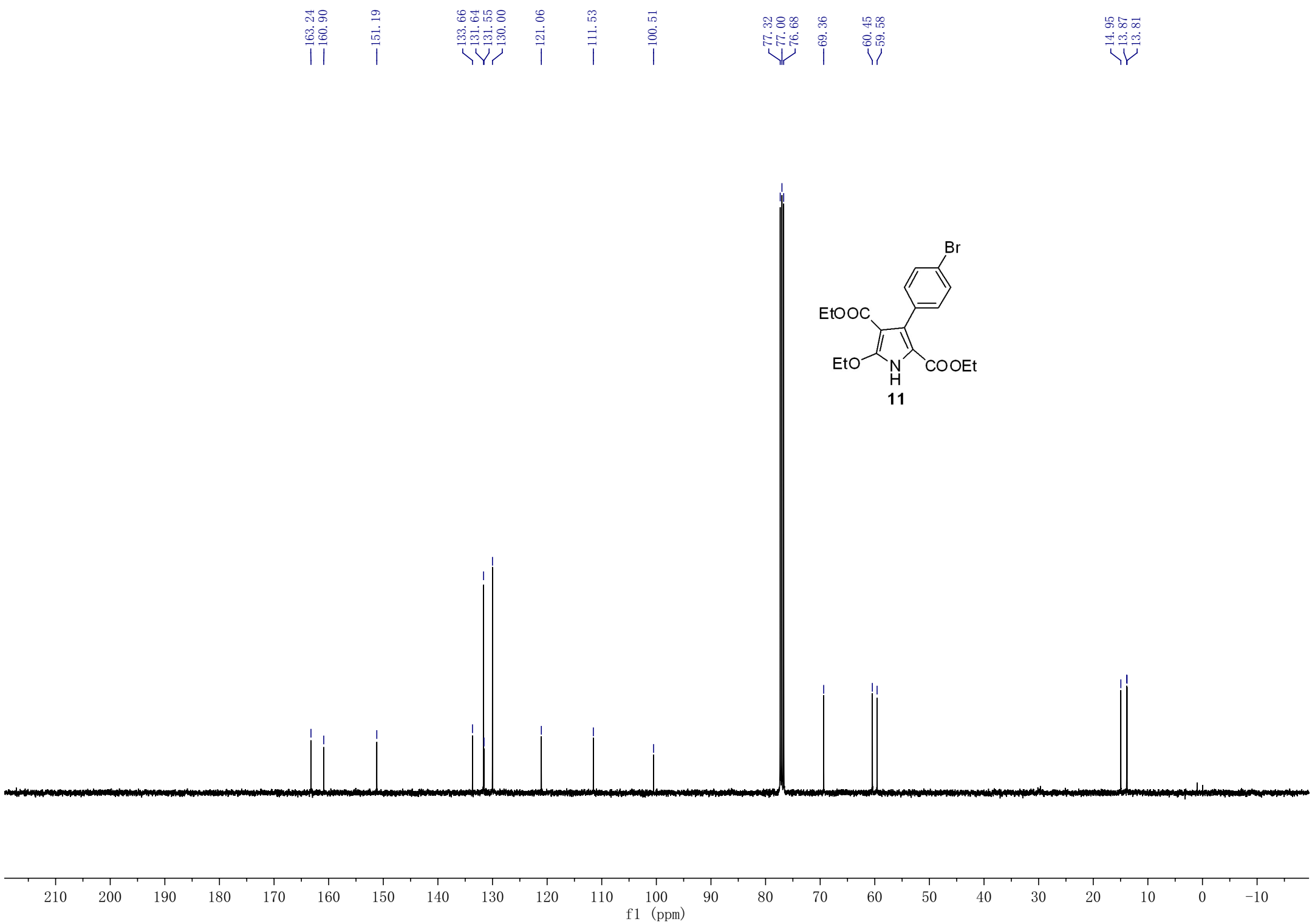

Br
EtOOC
F
N
H
COOEt

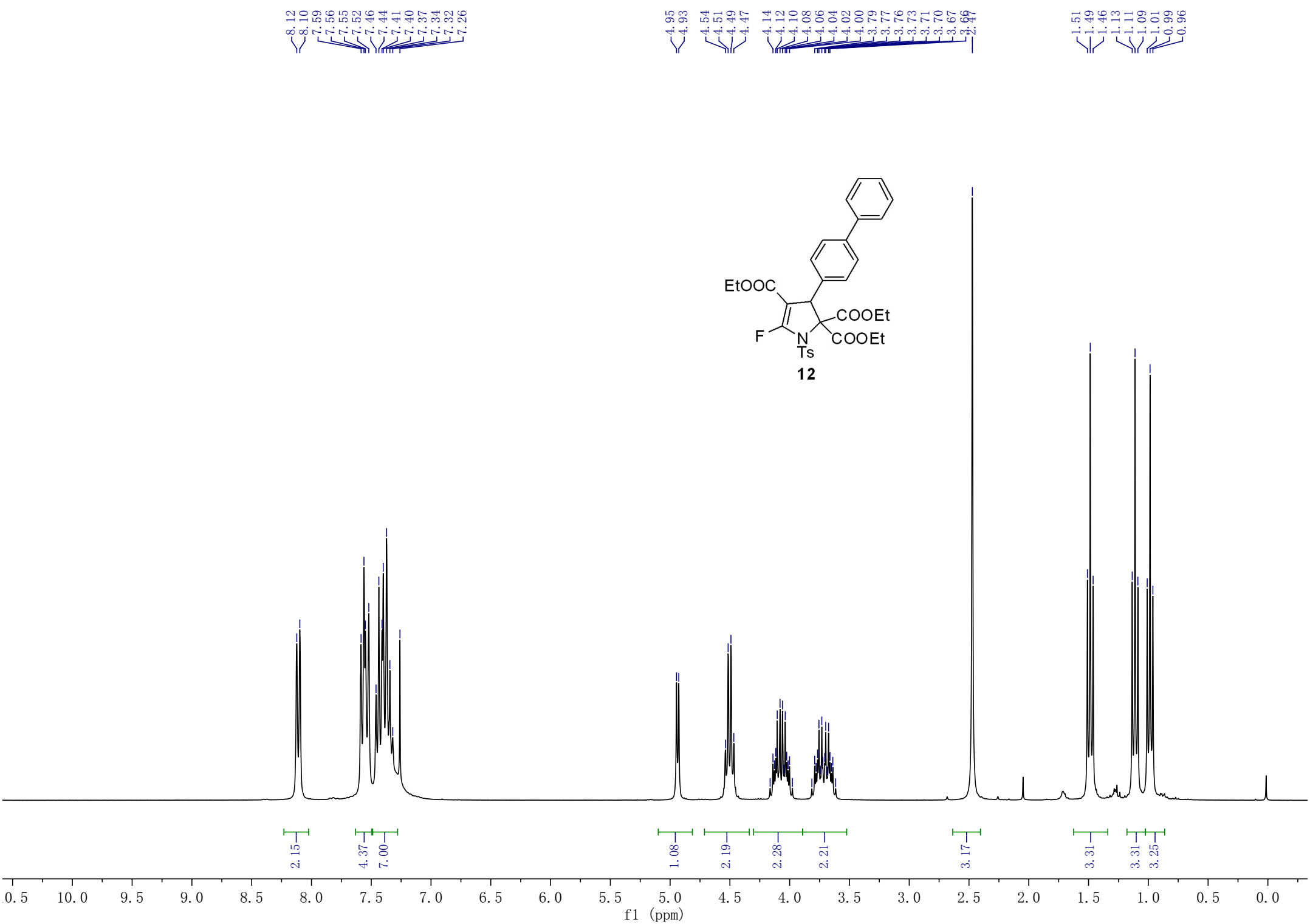
10

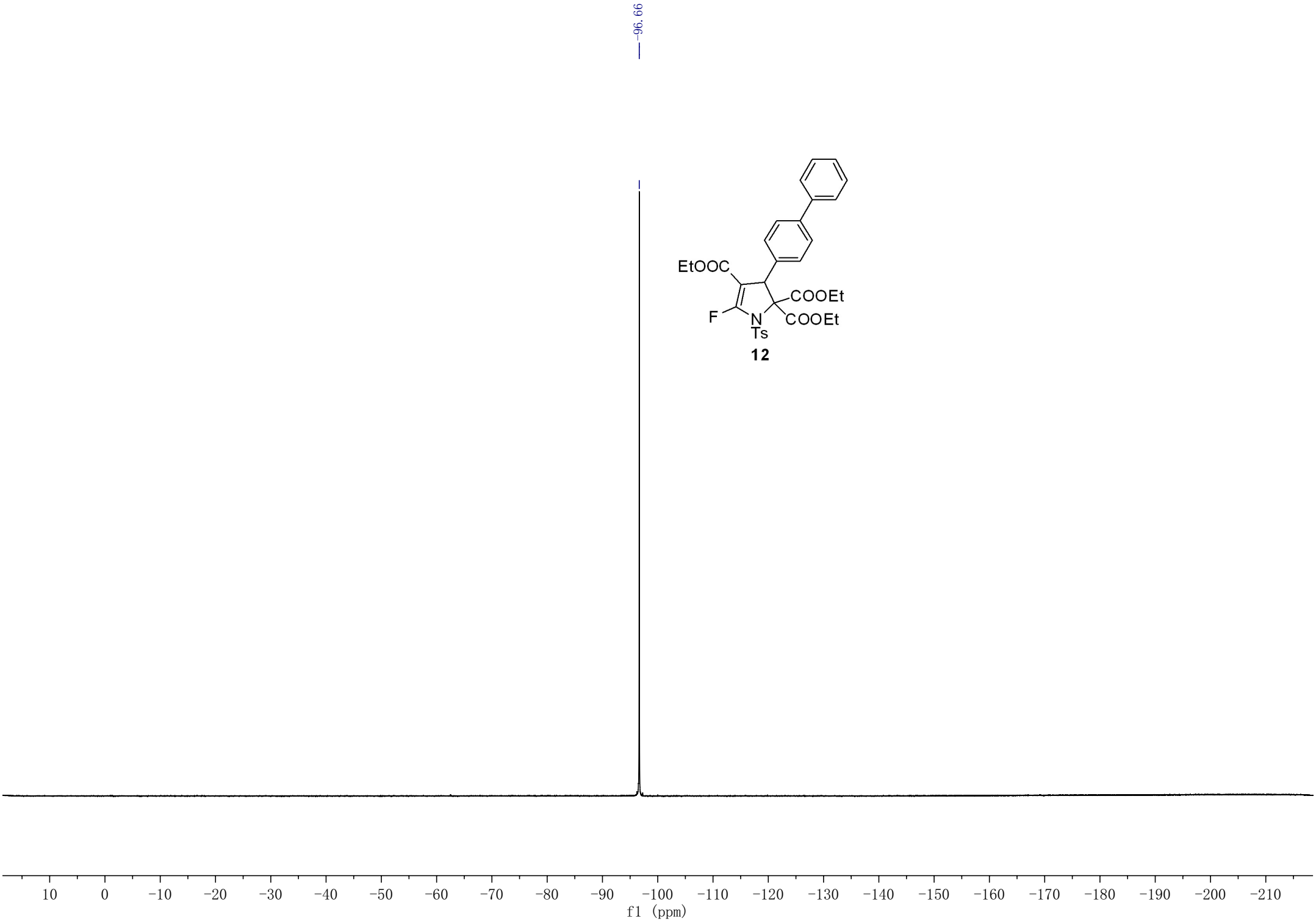
-119.37
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

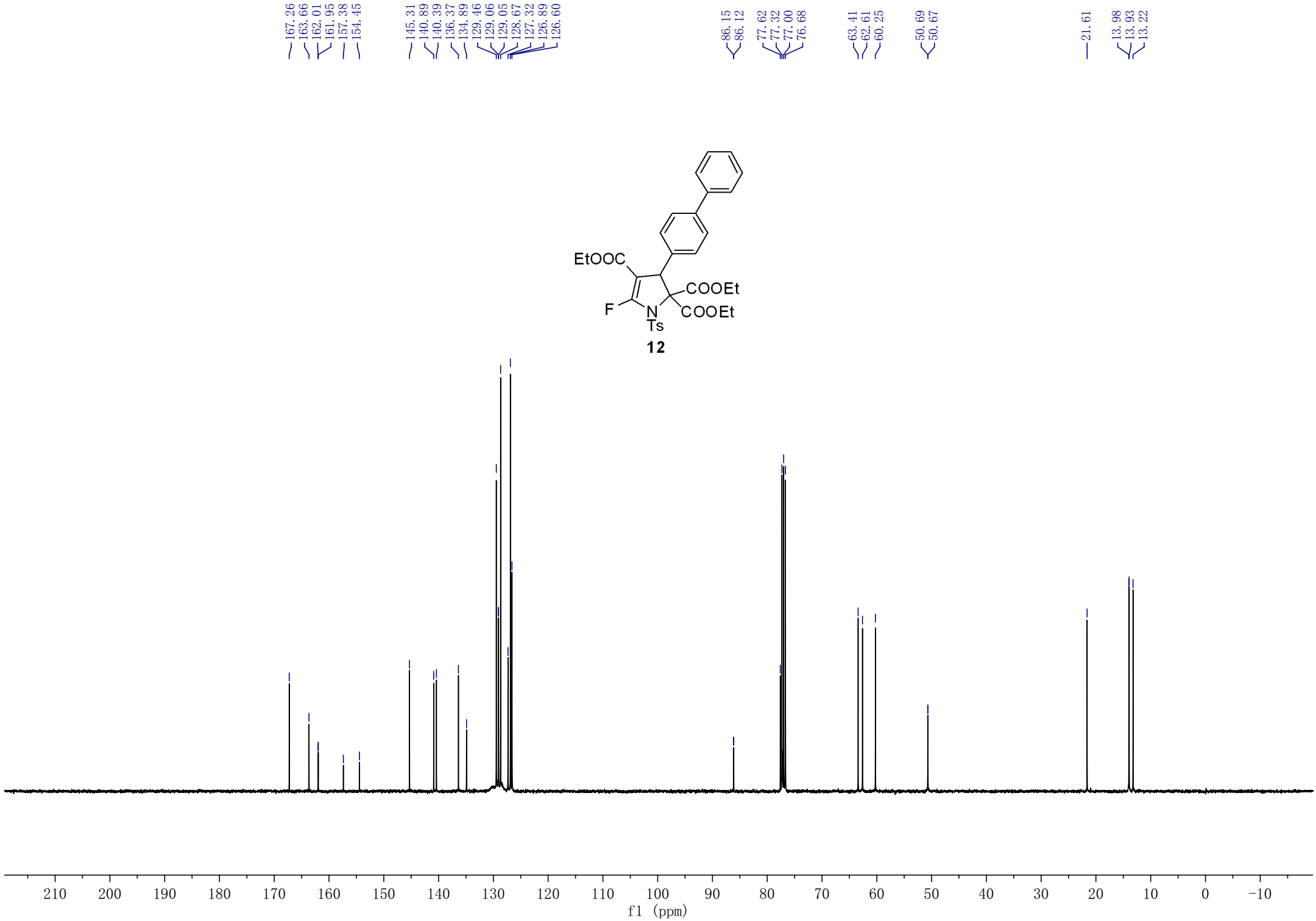

161.90
161.85
160.84
160.82
151.40
148.61
132.11
131.77
130.41
130.20
121.70
111.14
97.32
97.29
77.32
77.00
76.68
61.08
60.12
13.97
13.81
Br
EtOOC
F
N
H
COOEt
10
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

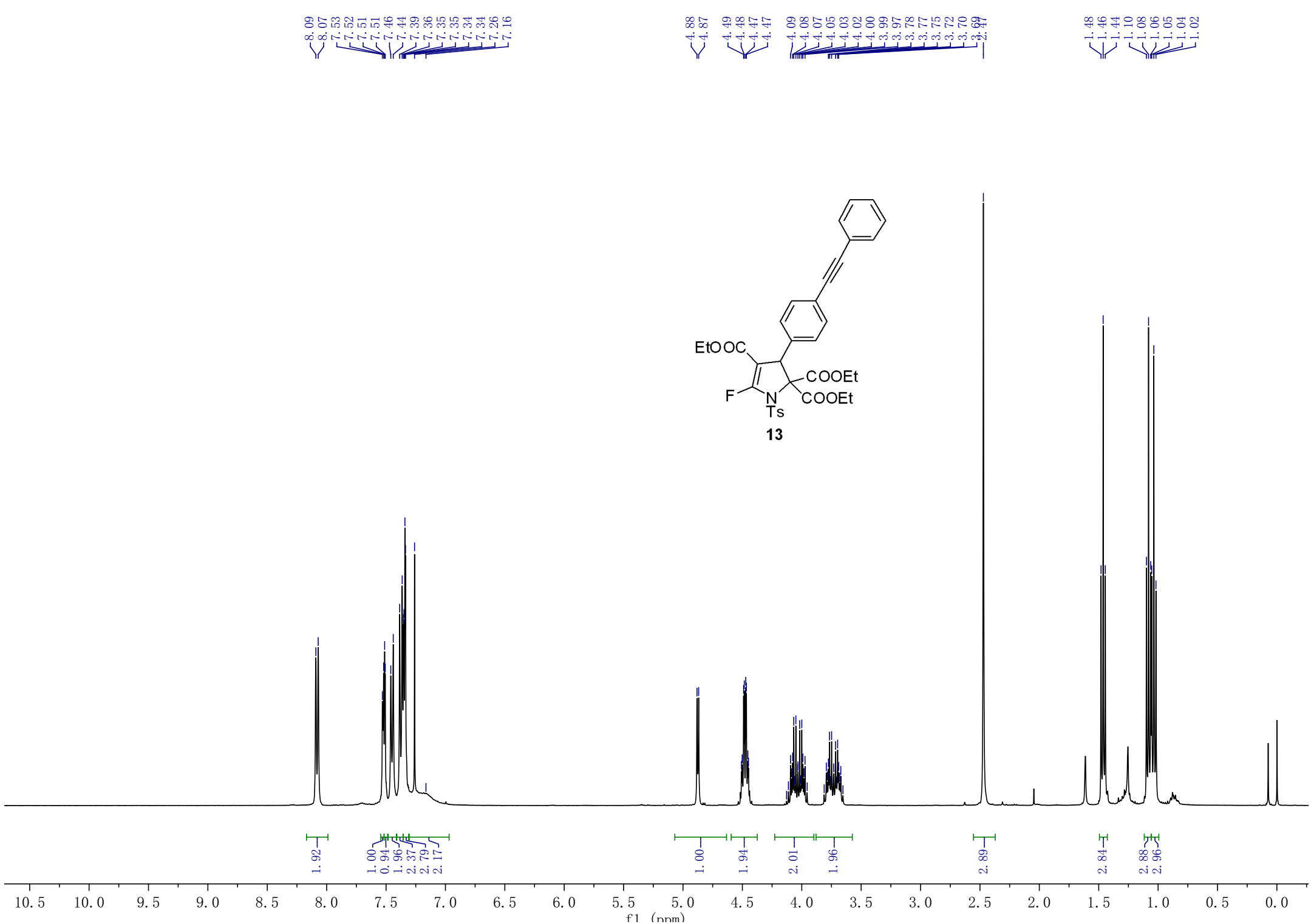

9.24
7.46
7.44
7.26
7.16
7.14
4.36
4.34
4.32
4.31
4.11
4.09
4.07
4.06
4.04
4.02
1.48
1.46
1.44
1.06
1.05
1.03
1.01
Br
EtOOC
EtO
N
H
COOEt
11
1.00
2.10
2.04
2.06
4.14
3.21
6.25
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

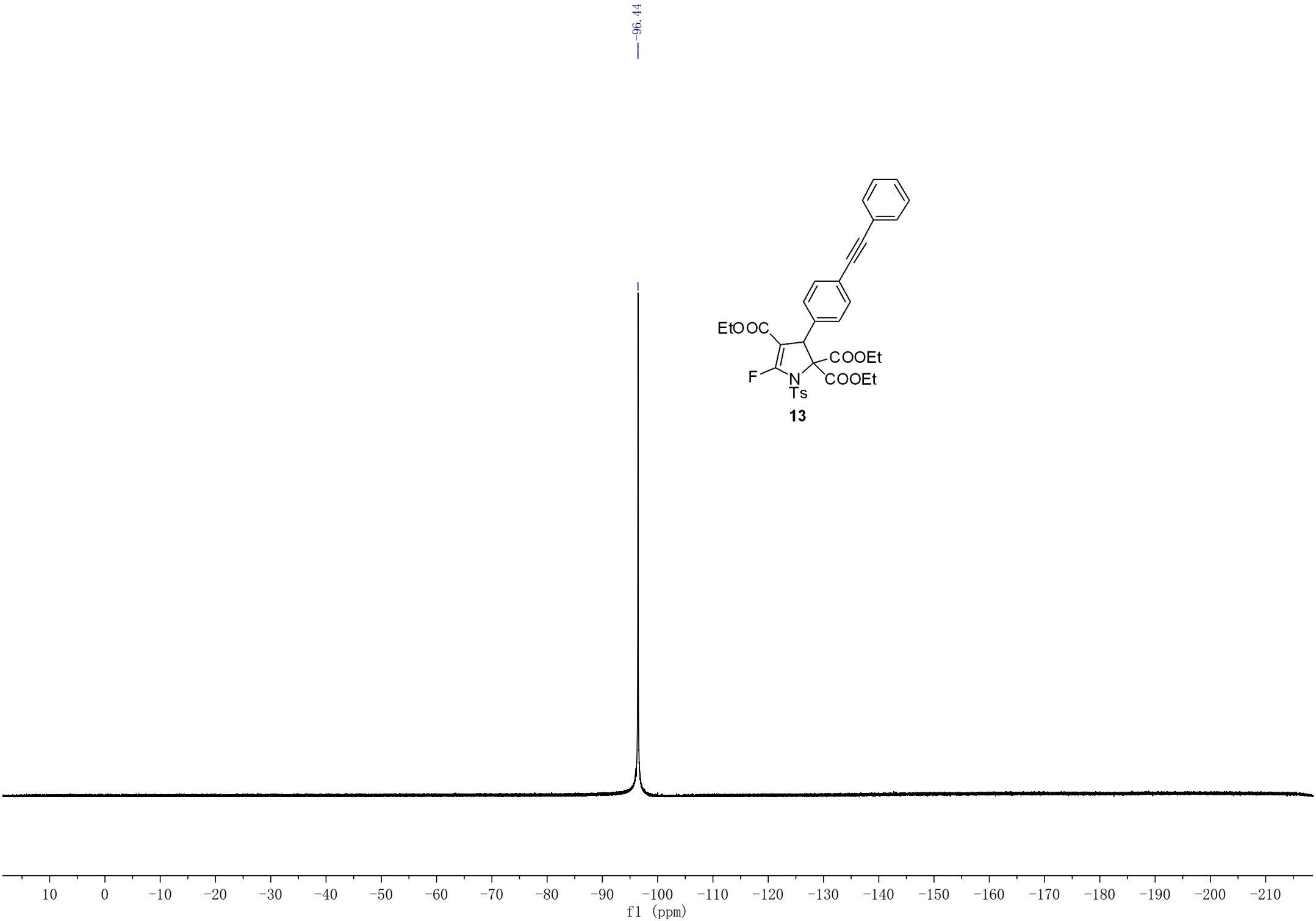

163.24
160.90
151.19
133.66
131.64
131.55
130.00
121.06
111.53
100.51
77.32
77.00
76.68
69.36
60.45
59.58
14.95
13.87
13.81
Br
EtOOC
EtO
N
H
COOEt
11
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

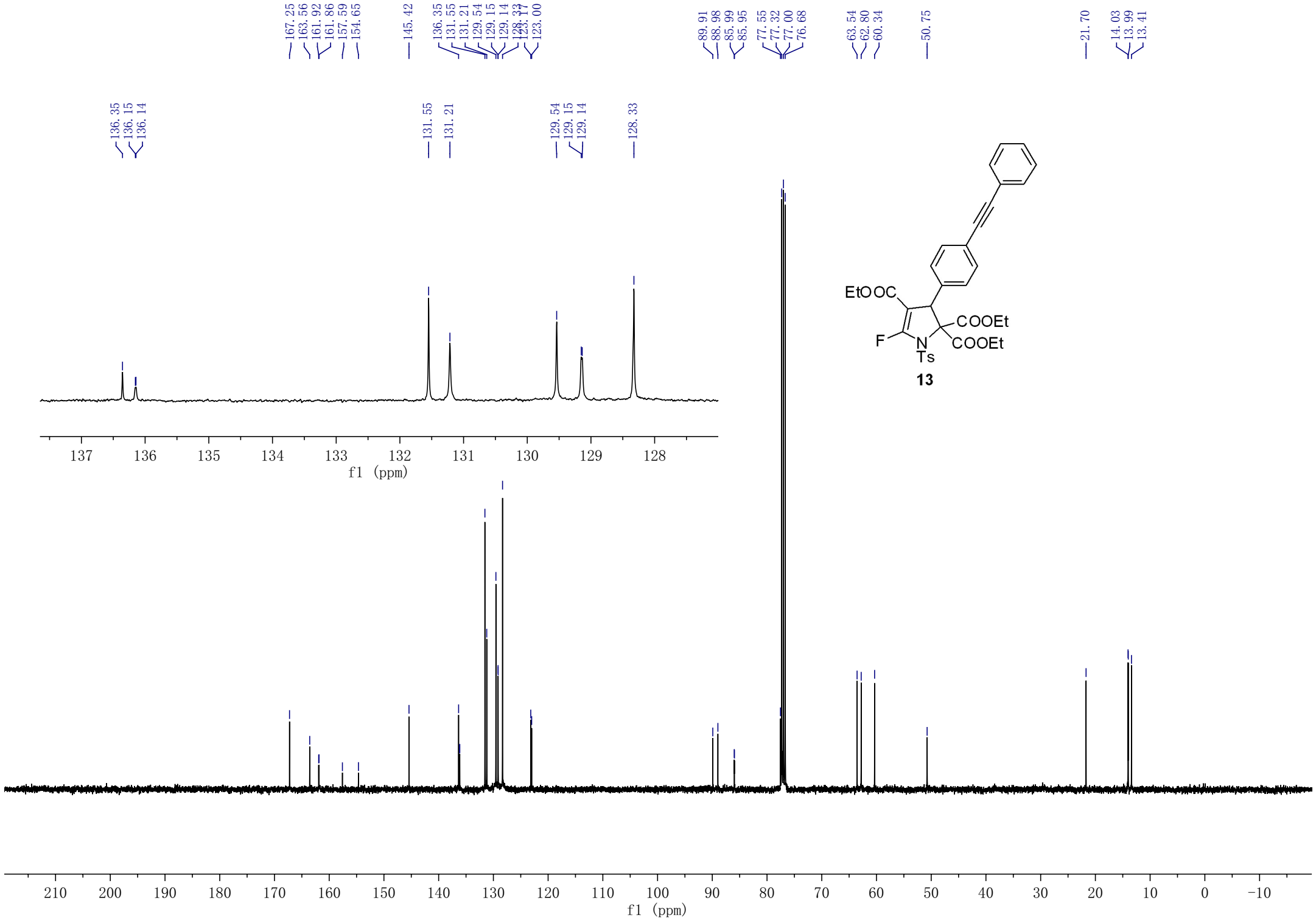

8.12
8.10
7.59
7.56
7.55
7.52
7.46
7.44
7.41
7.40
7.37
7.34
7.32
7.26
4.95
4.93
4.54
4.51
4.49
4.47
4.14
4.12
4.10
4.08
4.06
4.04
4.02
4.00
3.79
3.77
3.76
3.73
3.71
3.70
3.67
2.47
1.51
1.49
1.46
1.13
1.11
1.09
1.01
0.99
0.96
EtOOC
COOEt
F
N
COOEt
Ts
12
2.15
4.37
7.00
1.08
2.19
2.28
2.21
3.17
3.31
3.31
3.25
f1 (ppm)


-96.66
EtOOC
COOEt
F
N
Ts
COOEt
12
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)


167.26
163.66
162.01
161.95
157.38
154.45
145.31
140.89
140.39
136.37
134.89
129.46
129.06
129.05
128.67
127.32
126.89
126.60
86.15
86.12
77.62
77.32
77.00
76.68
63.41
62.61
60.25
50.69
50.67
21.61
13.98
13.93
13.22
EtOOC
COOEt
F
N
COOEt
Ts
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.09
8.07
7.53
7.52
7.51
7.51
7.46
7.44
7.39
7.36
7.35
7.35
7.34
7.34
7.26
7.16
4.88
4.87
4.49
4.48
4.47
4.47
4.09
4.08
4.07
4.05
4.03
4.02
4.00
3.99
3.97
3.78
3.77
3.75
3.72
3.70
3.69
3.47
1.48
1.46
1.44
1.10
1.08
1.06
1.05
1.04
1.02
EtOOC
COOEt
F
N
COOEt
Ts
13
1.92
1.00
0.94
1.96
2.37
2.79
2.17
1.00
1.94
2.01
1.96
2.89
2.84
2.88
2.96
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)


-96.44
EtOOC
COOEt
F
N
COOEt
Ts
13
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)


167.25
163.56
161.92
161.86
157.59
154.65
145.42
136.35
131.55
131.21
129.54
129.15
129.14
128.33
123.17
123.00
89.91
88.98
85.99
85.95
77.55
77.32
77.00
76.68
63.54
62.80
60.34
50.75
21.70
14.03
13.99
13.41
136.35
136.15
136.14
131.55
131.21
129.54
129.15
129.14
128.33
EtOOC
COOEt
F
N
Ts
COOEt
13
137
136
135
134
133
132
131
130
129
128
f1 (ppm)
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)