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A controlled selective synthesis of dihydropyrans through tandem reaction of alkynes with diazo compounds

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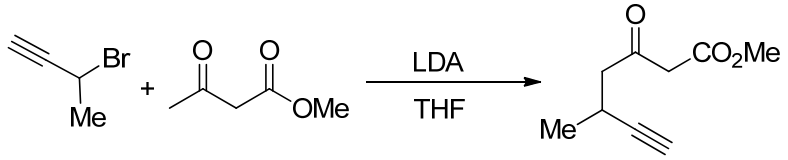
General Information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and ^{13}C NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in $CDCl_3$. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus. All of the diazo compounds were known and prepared according to the literature procedures. [1] 6,6'-dimethoxy-2,2'-bipyridine (**L4**) was prepared according to the literature procedures,[2] the other ligands were commercial available.

Preparation of substrates

Alkynes (**1a-1d** and **1f-1g**) were known compounds and prepared according to the literature procedures.[3] The unreported alkynes were showing as below.

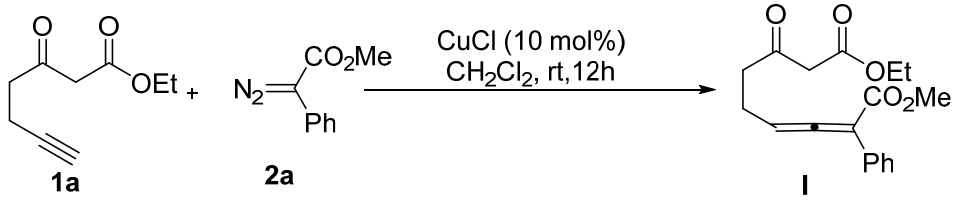


1e

To a solution of $^{i}Pr_2NH$ (3.4 g, 33 mmol) in THF(25 mL) was added dropwise 2.5 M n-BuLi in hexane (13.5 mL, 33 mmol) at -15 °C under argon atmosphere. After addition, the solution was stirred for 20min and methyl acetoacetate(1.7 g, 14.5 mmol) was added; the mixture was stirred for 30min, then 3-bromobut-1-yne (2.1 g, 16 mmol) was added slowly. The mixture was stirred at 0 °C for 10h. The reaction was quenched with H_2O and extracted with ethyl acetate, the organic layer was dried over Na_2SO_4 and concentration; the residue was purified by column chromatography (petroleum ether: EtOAc = 65:1) to give **1e** (1.8 g, yield: 74%) as colorless oil, ^{1}H NMR showed it was contained 10% of enol form in $CDCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.49 (s, 2H), 3.06-2.92 (m, 1H), 2.81 (dd, J = 17.1, 6.9 Hz, 1H), 2.66 (dd, J = 17.1, 6.9 Hz, 1H), 2.07 (s, 1H), 1.24 (d, J = 6.8 Hz, 3H). ^{13}C NMR (75

MHz, $CDCl_3$) δ 200.30, 167.37, 87.20, 68.85, 52.42, 49.34, 49.34, 21.15, 20.56. HRMS (ESI) calcd. for $C_9H_{13}O_3$ $[M+H]^+$: 169.0859, found: 169.0856.

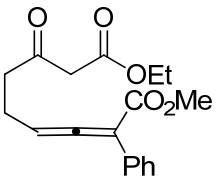
Preparation of intermediate allenoate I



1a **2a** **I**

Condition 1: To a schlenk tube was added CuCl (4.7 mg, 0.047 mol) and anhydrous CH_2Cl_2 (2 mL) under argon atmosphere, after stirring for 45min, a solution of **1a** (80 mg, 0.47 mmol) and **2a** (100 mg, 0.57 mmol) in CH_2Cl_2 (2 mL) was added under argon atmosphere, then the resulting solution was stirred at room temperature for 12h. The reaction mixture was concentrated under vacuum at low temperature, the residue was purified by column chromatography (silica gel, eluted with EtOAc: petroleum ether=1:30). The target intermediate was obtained as yellow oil (56 mg, yield: 37%) at 0 ^oC, which was extremely unstable at room temperature.

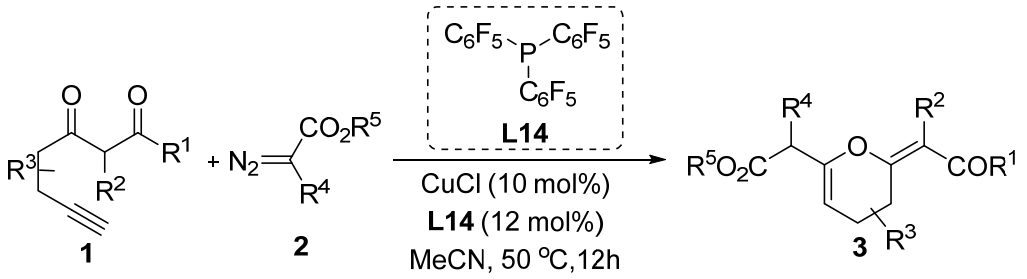
Condition 2: The addition of ligand **L4** to the above reaction system can furnish the allenoate intermediate in 74% yield.



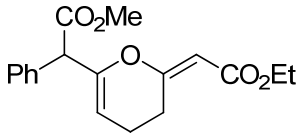
9-ethyl 1-methyl 7-oxo-2-phenylnona-2,3-dienedioate(I):

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 5H), 4.87 (s, 1H), 4.36 (tt, *J* = 10.5, 5.3 Hz, 2H), 3.78 (s, 3H), 2.73-2.64 (m, 1H), 2.52-2.43 (m, 1H), 2.43-2.33 (m, 1H), 2.09 (dt, *J* = 10.2, 5.3 Hz, 1H), 2.03-1.94 (m, 1H), 1.93-1.82 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.46, 170.31, 166.38, 157.84, 134.81, 134.48, 128.98, 128.37, 128.07, 61.66, 55.35, 52.62, 37.26, 26.74, 21.94, 14.19. HRMS (ESI) calcd. for $C_{18}H_{21}O_5$ $[M+H]^+$:317.1384, found:317.1388.

General procedure for Table 2



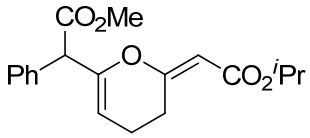
To a schlenk tube was added CuCl (2 mg, 0.02 mol), $P(C_6F_5)_3$ (12.8 mg, 0.024 mmol) and anhydrous MeCN (2 mL) under argon atmosphere, after stirring for 45min, a solution of **1** (0.2 mmol) and **2** (0.24 mmol) in MeCN (1 mL) was added under argon atmosphere, then the resulting solution was stirred at 50 °C for 12h. The reaction mixture was cooled and concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: petroleum ether=1:30 ~ 1:10) to give desired product **3**.



***(E)-methyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl acetate (3a)*:**

Colorless oil (44 mg, yield: 70%).

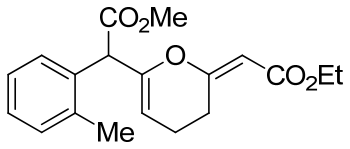
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.46 (s, 1H), 4.88 (t, *J* = 4.3 Hz, 1H), 4.42 (d, *J* = 1.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.22-3.05 (m, 2H), 2.17-2.06 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.89, 167.70, 167.46, 149.23, 134.76, 128.93, 128.64, 127.91, 102.67, 98.32, 59.60, 55.17, 52.49, 21.97, 17.99, 14.35. HRMS (ESI) calcd. for $C_{18}H_{21}O_5$ $[M+H]^+$: 317.1384, found: 317.1387.



***(E)-methyl 2-(2-(2-isopropoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-phenylacetate (3b)*:**

A white solid (43 mg, yield: 65%), mp: 104-105 °C.

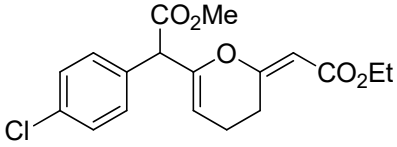
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.30 (m, 5H), 5.44 (s, 1H), 5.06-4.97 (m, 1H), 4.88 (t, *J* = 4.3 Hz, 1H), 4.41 (d, *J* = 1.0 Hz, 1H), 3.73 (s, 3H), 3.20-3.05 (m, 2H), 2.17-2.07 (m, 2H), 1.23 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.89, 166.41, 165.97, 148.13, 133.69, 127.89, 127.60, 126.88, 101.56, 97.75, 65.65, 54.12, 51.50, 20.95, 20.87, 16.94. HRMS (ESI) calcd. for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540, found: 331.1538.



***(E)-methyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-(o-tolyl) acetate (3c)*:**

Colorless oil (53 mg, yield: 81 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (m, 4H), 5.46 (s, 1H), 4.77 (t, *J* = 4.3 Hz, 1H), 4.62 (d, *J* = 1.0 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.25-3.04 (m, 2H), 2.33 (s, 3H), 2.17-2.07 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.32, 167.87, 167.53, 148.64, 136.64, 133.16, 130.66, 127.96, 127.89, 126.33, 102.86, 98.23, 59.62, 52.52, 51.39, 22.01, 19.56, 17.97, 14.38. HRMS (ESI) calcd. for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540, found: 331.1543.

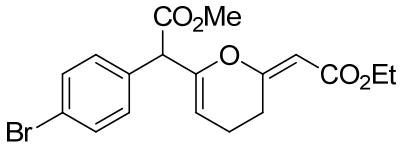


***(E)-methyl 2-(4-chlorophenyl)-2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)acetate (3d)*:**

Colorless oil (54 mg, yield: 77%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.26 (m, 4H), 5.45 (s, 1H), 4.91 (t, *J* = 4.3 Hz, 1H), 4.39 (d, *J* = 0.7 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.19-3.04 (m, 2H), 2.19-2.10 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.54,

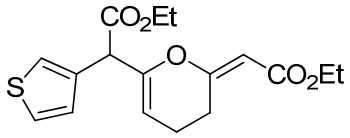
167.47, 167.39, 148.71, 133.92, 133.29, 130.31, 128.82, 102.77, 98.49, 59.68, 54.48, 52.67, 21.87, 17.98, 14.35. HRMS (ESI) calcd. for $C_{18}H_{20}ClO_5$ $[M+H]^+$: 351.0994, found: 351.0991.



***(E)-methyl 2-(4-bromophenyl)-2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)acetate (3e)*:**

Colorless oil (54 mg, yield: 68%).

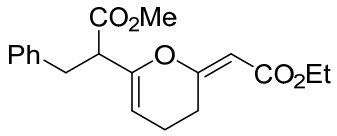
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 5.45 (s, 1H), 4.91 (t, *J* = 4.3 Hz, 1H), 4.37 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.21-3.02 (m, 2H), 2.19-2.08 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.47, 167.46, 167.40, 148.61, 133.81, 131.78, 130.66, 122.09, 102.80, 98.51, 59.69, 54.56, 52.69, 21.86, 17.98, 14.36. HRMS (ESI) calcd. for $C_{18}H_{20}BrO_5$ $[M+H]^+$: 395.0489, found: 395.0488.



***(E)-ethyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-(thiophen-3-yl)acetate (3f)*:**

Colorless oil (43 mg, yield: 64%).

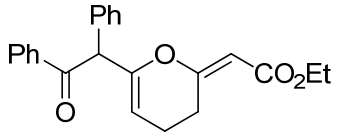
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.26-7.21 (m, 1H), 7.09 (dd, *J* = 4.9, 1.3 Hz, 1H), 5.47 (s, 1H), 4.90 (t, *J* = 4.2 Hz, 1H), 4.51 (s, 1H), 4.26-4.17 (m, 2H), 4.17-4.09 (m, 2H), 3.20-3.03 (m, 2H), 2.20-2.08 (m, 2H), 1.27 (td, *J* = 7.1, 0.5 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.19, 167.75, 167.51, 148.99, 134.61, 128.09, 125.70, 123.68, 102.21, 98.28, 61.50, 59.66, 50.75, 21.94, 17.96, 14.36, 14.16. HRMS (ESI) calcd. for $C_{17}H_{21}O_5S$ $[M+H]^+$: 337.1104, found: 337.1108.



***(E)-methyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-3-phenyl propanoate (3g)*:**

Colorless oil (39 mg, yield: 59%).

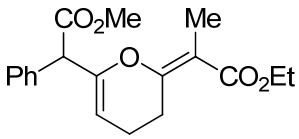
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.11 (m, 5H), 5.52 (s, 1H), 4.89 (t, *J* = 4.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.68 (s, 3H), 3.36-3.29 (m, 1H), 3.14 (dt, *J* = 14.3, 7.0 Hz, 2H), 3.08-2.94 (m, 2H), 2.13-1.96 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.74, 167.75, 167.53, 147.77, 138.50, 128.94, 128.38, 126.51, 102.39, 98.31, 59.65, 52.26, 51.46, 35.14, 21.94, 17.94, 14.37. HRMS (ESI) calcd. for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540, found: 331.1541.



***(E)-ethyl 2-(6-(2-oxo-1,2-diphenylethyl)-3,4-dihydro-2H-pyran-2-ylidene)acetate (3h)*:**

Colorless oil (40 mg, yield: 56%).

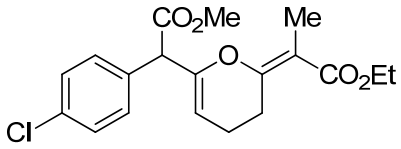
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.56-7.49 (m, 1H), 7.45 -7.28 (m, 7H), 5.41 (s, 2H), 4.77 (t, *J* = 4.3 Hz, 1H), 4.17-4.06 (m, 2H), 3.25-3.03 (m, 2H), 2.20-2.02 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.70, 168.01, 167.55, 150.26, 136.30, 134.88, 133.22, 129.40, 128.90, 128.84, 128.64, 127.84, 103.87, 98.08, 59.58, 57.18, 22.08, 18.07, 14.37. HRMS (ESI) calcd. for $C_{23}H_{23}O_4$ $[M+H]^+$: 363.1591, found: 363.1594.



***(E)-ethyl 2-(6-(2-methoxy-2-oxo-1-phenylethyl)-3,4-dihydro-2H-pyran-2-ylidene) propanoate (3i)*:**

Colorless oil (49 mg, yield: 74%).

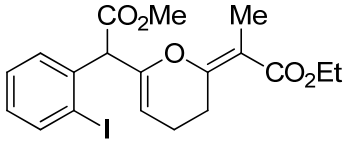
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 4.86 (t, *J* = 4.2 Hz, 1H), 4.46 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.06 (t, *J* = 6.8 Hz, 2H), 2.14-2.07 (m, 2H), 1.80 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.13, 168.99, 160.26, 149.35, 135.04, 129.02, 128.59, 127.86, 106.48, 101.98, 60.07, 55.42, 52.49, 22.89, 18.92, 14.36, 11.51. HRMS (ESI) calcd. for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540, found: 331.1544.



***(E)-ethyl 2-(6-(1-(4-chlorophenyl)-2-methoxy-2-oxoethyl)-3,4-dihydro-2H-pyran-2-ylidene)propanoate (3j)*:**

Colorless oil (55 mg, yield: 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 4H), 4.88 (t, *J* = 4.2 Hz, 1H), 4.43 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.12-2.97 (m, 2H), 2.14-2.06 (m, 2H), 1.78 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.73, 168.89, 159.99, 148.90, 133.84, 133.63, 130.38, 128.74, 106.70, 102.09, 60.12, 54.75, 52.60, 22.83, 18.93, 14.34, 11.52. HRMS (ESI) calcd. for $C_{19}H_{22}ClO_5$ $[M+H]^+$: 365.1150, found: 365.1153.

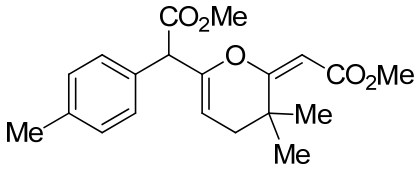


***(E)-ethyl 2-(6-(1-(2-iodophenyl)-2-methoxy-2-oxoethyl)-3,4-dihydro-2H-pyran-2-ylidene)propanoate (3k)*:**

Colorless oil (62 mg, yield: 68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.35 (td, *J* = 7.9, 1.2 Hz, 1H), 7.00 (td, *J* = 7.8, 1.6 Hz, 1H), 4.92 (d, *J* = 4.3 Hz, 1H), 4.89 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 3.15-3.00 (m, 2H), 2.17- 2.09

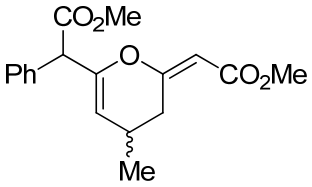
(m, 2H), 1.80 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.58, 168.93, 160.08, 148.12, 139.75, 138.28, 129.44, 129.42, 128.43, 106.70, 102.90, 101.83, 60.09, 59.55, 52.65, 22.85, 19.03, 14.35, 11.58. HRMS (ESI) calcd. for $C_{19}H_{22}IO_5$ $[M+H]^+$: 457.0506, found: 457.0509.



***(E)-methyl 2-(2-(2-methoxy-2-oxoethylidene)-3,3-dimethyl-3,4-dihydro-2H-pyran-6-yl)-2-(p-tolyl)acetate (3l)*:**

Colorless oil (42 mg, yield: 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.85 (d, J = 10.1 Hz, 1H), 4.90 (s, 1H), 4.22 (d, J = 10.1 Hz, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 2.54 (d, J = 15.5 Hz, 1H), 2.38 (d, J = 15.5 Hz, 1H), 2.32 (s, 3H), 1.26 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.44, 172.80, 165.95, 154.52, 137.16, 135.32, 129.44, 127.49, 101.95, 88.11, 52.40, 51.10, 49.41, 42.41, 38.66, 27.38, 27.34, 21.07. HRMS (ESI) calcd. for $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1697, found: 345.1699.

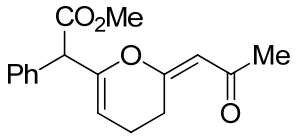


***(E)-methyl 2-(2-(2-methoxy-2-oxoethylidene)-4-methyl-3,4-dihydro-2H-pyran-6-yl)-2-phenylacetate (3m)*:**

Colorless oil (31 mg, yield: 49%), dr value was 1:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.30 (m, 5H), 5.49 (s, 1H), 4.82 (d, J = 3.2 Hz, 0.5H), 4.79 (d, J = 3.2 Hz, 0.5H), 4.41 (s, 1H), 3.73 (s, 3H), 3.67 (s, 3H), 3.44 (dd, J = 15.1, 5.6 Hz, 0.5H), 3.35 (dd, J = 15.1, 5.6 Hz, 0.5H), 2.68 (dd, J = 15.1, 9.4 Hz, 0.5H), 2.58 (dd, J = 15.1, 9.1 Hz, 0.5H), 2.43-2.32 (m, 1H), 1.02 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.92, 167.95, 167.65, 167.50, 148.17, 148.14, 134.70,

134.68, 128.92, 128.67, 127.95, 127.93, 109.22, 108.99, 98.50, 98.30, 54.99, 54.92, 52.55, 51.00, 30.15, 30.03, 24.38, 24.32, 20.56, 20.53. HRMS (ESI) calcd. for $C_{18}H_{21}O_5$ $[M+H]^+$: 317.1384, found: 317.1386.

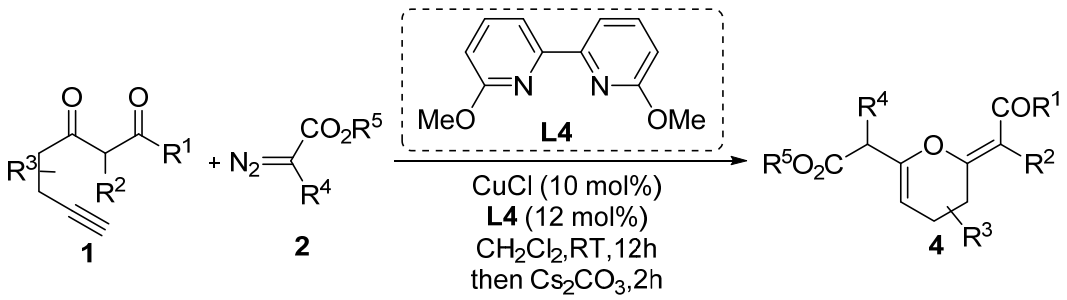


***(E)-methyl 2-(2-(2-oxopropylidene)-3,4-dihydro-2H-pyran-6-yl)-2-phenylacetate (3n)*:**

Colorless oil (31 mg, yield: 55%).

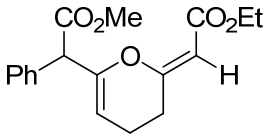
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 5.88 (s, 1H), 4.92 (t, *J* = 4.4 Hz, 1H), 4.42 (s, 1H), 3.74 (s, 3H), 3.18-3.07 (m, 2H), 2.15 (s, 3H), 2.12-2.06 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.99, 170.87, 167.18, 148.97, 134.63, 128.90, 128.68, 127.96, 105.81, 103.44, 55.14, 52.53, 32.13, 22.14, 17.58. HRMS (ESI) calcd. for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1278, found: 287.12781.

General procedure for Table 3



To a schlenk tube was added CuCl (2 mg, 0.02 mol), **L4** (5.2 mg, 0.024 mmol) and anhydrous CH_2Cl_2 (2 mL) under argon atmosphere, after stirring for 45min, a solution of **1** (0.2 mmol) and **2** (0.24 mmol) in CH_2Cl_2 (1 mL) was added under argon atmosphere, then the resulting solution was stirred at room temperature for 12h. Cs_2CO_3 (78 mg, 0.24 mmol) was added, the mixture was stirred for another 2h. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: petroleum ether=1:15 ~ 1:8) to give

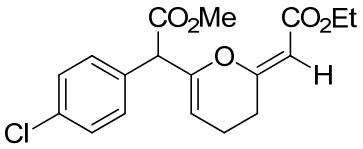
desired product **4**.



***(Z)-methyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-phenyl acetate (4a)*:**

Colorless oil (41 mg, yield: 65%).

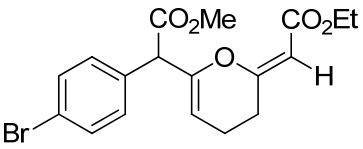
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.30 (m, 5H), 4.94 (s, 1H), 4.84 (t, *J* = 4.3 Hz, 1H), 4.53 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.49-2.38 (m, 2H), 2.20 – 2.08 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.98, 164.82, 162.14, 150.05, 134.84, 129.12, 128.60, 127.87, 102.00, 97.21, 59.50, 55.08, 52.51, 26.97, 18.76, 14.34. HRMS (ESI) calcd. for $C_{18}H_{21}O_5$ $[M+H]^+$: 317.1384, found: 317.1381.



***(Z)-methyl 2-(4-chlorophenyl)-2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)acetate (4b)*:**

Colorless oil (49 mg, yield: 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 4.95 (s, 1H), 4.89 (t, *J* = 4.3 Hz, 1H), 4.48 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.19-2.09 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.63, 164.71, 161.99, 149.46, 133.87, 133.40, 130.56, 128.76, 102.08, 97.35, 59.55, 54.43, 52.70, 26.87, 18.73, 14.36. HRMS (ESI) calcd. for $C_{18}H_{20}ClO_5$ $[M+H]^+$: 351.0994, found: 351.0996.

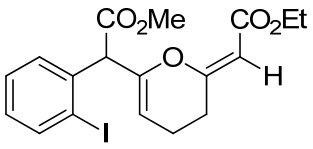


(Z)-methyl 2-(4-bromophenyl)-2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-

***pyran-6-yl)acetate (4c)*:**

Colorless oil (56 mg, yield: 71%).

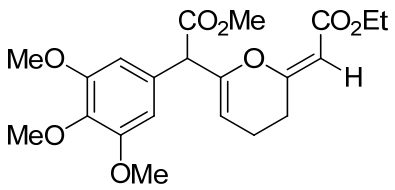
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.35-7.30 (m, 2H), 4.95 (s, 1H), 4.89 (t, *J* = 4.3 Hz, 1H), 4.47 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.20-2.11 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.53, 164.69, 161.93, 149.40, 133.98, 131.72, 130.91, 122.06, 102.08, 97.39, 59.55, 54.53, 52.68, 26.88, 18.75, 14.35. HRMS (ESI) calcd. for $C_{18}H_{20}BrO_5$ $[M+H]^+$: 395.0489, found: 395.0491.



***(Z)-methyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-(2-iodo phenyl)acetate (4d)*:**

A white solid (50 mg, yield: 57%), mp: 89-90 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.62 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.36 (td, *J* = 7.9, 1.2 Hz, 1H), 7.03-6.95 (m, 1H), 4.95 (s, 2H), 4.89 (t, *J* = 4.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.45 (t, *J* = 6.9 Hz, 2H), 2.21-2.12 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.45, 164.81, 161.82, 148.57, 139.66, 138.01, 129.86, 129.44, 128.48, 102.84, 101.89, 97.52, 59.58, 59.37, 52.73, 26.87, 18.86, 14.36. HRMS (ESI) calcd. for $C_{18}H_{20}IO_5$ $[M+H]^+$: 443.0350, found: 443.0353.

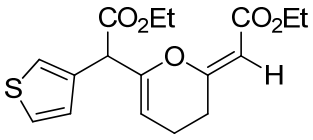


***(Z)-methyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-(3,4,5-trimethoxyphenyl)acetate (4e)*:**

Colorless oil (51 mg, yield: 63%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (s, 2H), 4.96 (s, 1H), 4.93 (t, *J* = 4.3 Hz, 1H), 4.44

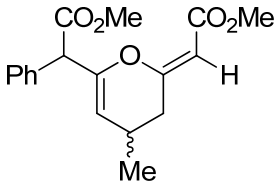
(s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 3.77 (s, 3H), 2.49-2.40 (m, 2H), 2.21-2.11 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.97, 164.65, 162.34, 153.21, 149.84, 137.60, 130.23, 106.26, 101.90, 97.09, 60.80, 59.43, 56.16, 55.15, 52.60, 26.94, 18.72, 14.35. HRMS (ESI) calcd. for $C_{21}H_{27}O_8$ $[M+H]^+$: 407.1700, found: 407.1702.



***(Z)-ethyl 2-(2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2H-pyran-6-yl)-2-(thiophen-3-yl)acetate (4f)*:**

Yellow oil (33 mg, yield: 49%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.29 (d, J = 4.4 Hz, 1H), 7.18 (d, J = 4.4 Hz, 1H), 4.94 (s, 1H), 4.89 (t, J = 4.3 Hz, 1H), 4.61 (s, 1H), 4.26-4.18 (m, 2H), 4.18 -4.12 (m, 2H), 2.47-2.40 (m, 2H), 2.18-2.11 (m, 2H), 1.29-1.24 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.27, 164.78, 162.19, 149.68, 134.76, 128.36, 125.51, 123.84, 101.56, 97.13, 61.49, 59.53, 50.63, 26.99, 18.69, 14.36, 14.06. HRMS (ESI) calcd. for $C_{17}H_{21}O_5S$ $[M+H]^+$: 337.1104, found:337.1106.

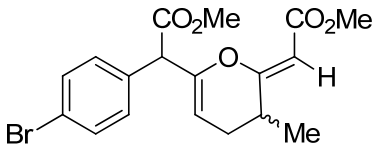


***(Z)-methyl 2-(2-(2-methoxy-2-oxoethylidene)-4-methyl-3,4-dihydro-2H-pyran-6-yl)-2-phenylacetate (4g)*:**

Colorless oil (38 mg, yield: 61%), dr value was 1.2:1.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.31 (m, 5H), 4.95 (d, J = 0.6 Hz, 1H), 4.78 (d, J = 3.1 Hz, 1H), 4.53 (s, 1H), 3.75 (s, 1.35H), 3.75 (s, 1.65H), 3.67 (s, 1.35H), 3.66 (s, 1.65H), 2.54-2.43 (m, 1.1H), 2.43-2.33 (m, 0.9H), 2.18-2.13 (m, 0.55H), 2.13-2.06 (m, 0.45H), 1.00 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.02, 171.01, 165.22, 165.18, 162.15, 161.98, 148.99, 134.81, 134.73, 129.19, 129.14, 128.61, 127.90,

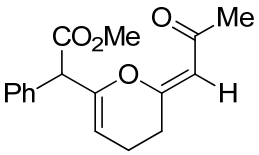
127.87, 108.33, 108.13, 97.31, 97.15, 54.96, 54.84, 52.57, 52.56, 50.88, 35.25, 35.16, 24.97, 24.91, 20.41, 20.38. HRMS (ESI) calcd. for $C_{18}H_{21}O_5$ $[M+H]^+$: 317.1384, found:317.1386.



***(Z)-methyl 2-(4-bromophenyl)-2-(2-(2-methoxy-2-oxoethylidene)-3-methyl-3,4-dihydro-2H-pyran-6-yl)acetate (4h)*:**

Colorless oil (52 mg, yield: 66%), dr value was 1.3:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 8.2, 4.5 Hz, 2H), 5.03 (s, 1H), 4.89-4.78 (m, 1H), 4.47 (d, *J* = 6.3 Hz, 1H), 3.75 (s, 1.3H), 3.75 (s, 1.7H), 3.67 (s, 1.3H), 3.67 (s, 1.7H), 2.60-2.48 (m, 1H), 2.30-2.18 (m, 1H), 1.94-1.81 (m, 1H), 1.17 (t, *J* = 6.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.53, 166.63, 166.56, 165.36, 165.34, 148.74, 148.58, 134.04, 133.91, 131.71, 131.67, 130.94, 130.90, 122.04, 122.01, 100.70, 95.34, 95.29, 54.46, 54.44, 52.64, 50.91, 30.93, 30.89, 26.78, 26.74, 17.81, 17.78. HRMS (ESI) calcd. for $C_{18}H_{20}BrO_5$ $[M+H]^+$: 395.0489, found: 395.0492.



***(Z)-methyl 2-(2-(2-oxopropylidene)-3,4-dihydro-2H-pyran-6-yl)-2-phenylacetate (4i)*:**

Colorless oil (26 mg, yield: 45%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 5H), 5.13 (s, 1H), 4.95 (t, *J* = 4.3 Hz, 1H), 4.52 (s, 1H), 3.74 (s, 3H), 2.51-2.41 (m, 2H), 2.23 (s, 3H), 2.22 – 2.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.69, 170.84, 161.42, 149.58, 134.39, 128.94, 128.77, 128.13, 109.17, 102.66, 55.08, 52.58, 31.28, 27.02, 18.68. HRMS (ESI) calcd. for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1278, found: 287.1281.

X-ray structure of 3b

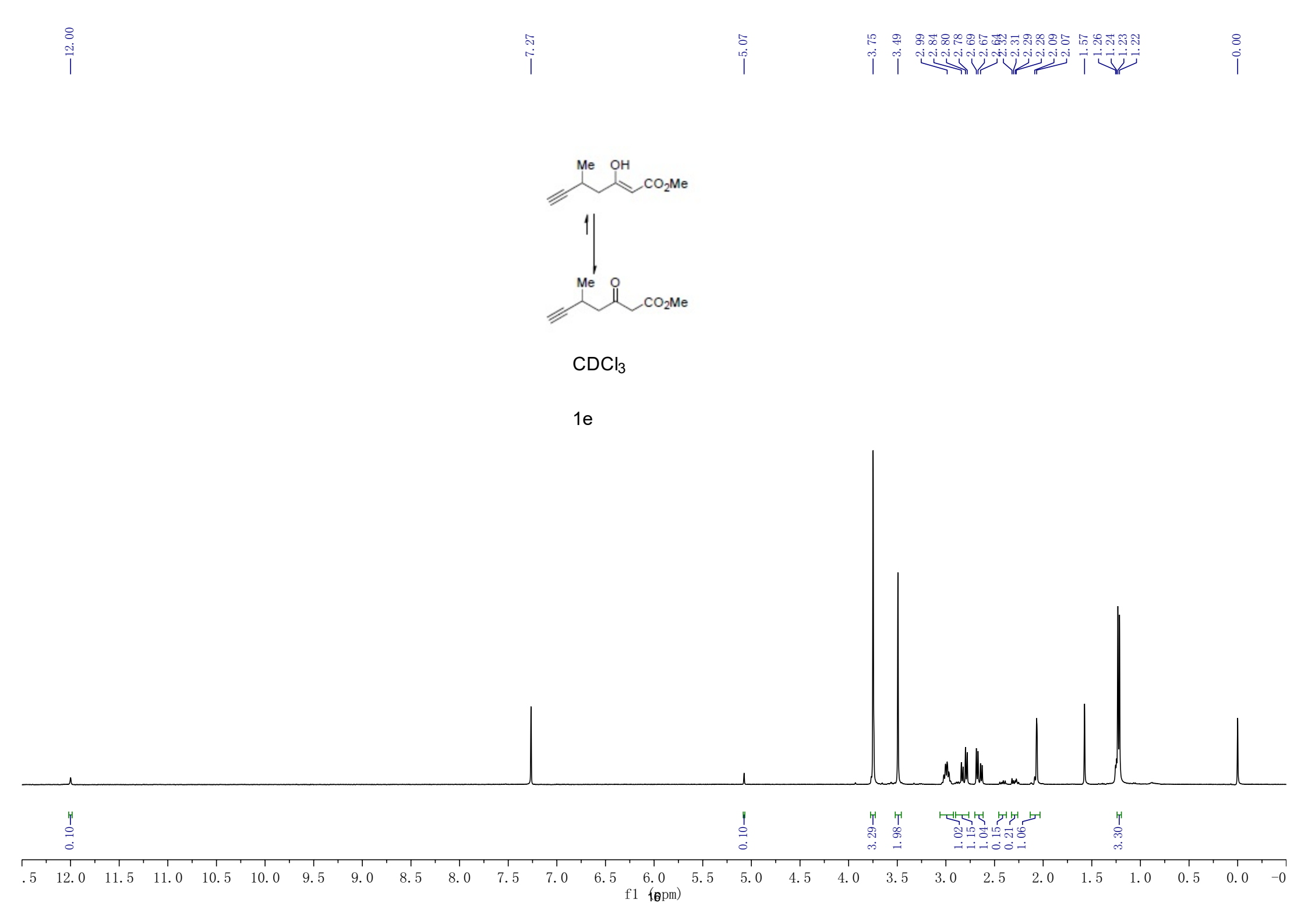
The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1528333, **3b**). The data can be obtained free of charge via the internet at www.ccdc.cam.ac.uk/data_request/cif.

References:

(1) (a) Zhu, C.; Xu, G.; Ding, D.; Qiu, L.; Sun, J. *Org. Lett.* **2015**, *17*, 4244. (b) Xu, G.; Zhu, C.; Gu, W.; Li, J.; Sun, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 883. (c) Zhu, Y.; Liu, X.; Dong, S.; Zhou, Y.; Li, W.; Lin, L.; Feng, X. *Angew. Chem. Int. Ed.* **2014**, *53*, 1636. (d) Nicolle, S. M.; Lewis, W.; Hayes, C. J.; Moody, C. J. *Angew. Chem. Int. Ed.* **2015**, *54*, 8485.

(2) Dai, X.-J.; Li, C.-J. *J. Am. Chem. Soc.* **2016**, *138*, 5433.

(3) (a) Li, Z.; Hao, P.; Li, L.; Tan, C. Y. J.; Cheng, X.; Chen, G. Y. J.; Sze, S. K.; Shen, H.-M.; Yao, S. Q. *Angew. Chem. Int. Ed.* **2013**, *52*, 8551. (b) Hayakawa, K.; Yodo, M.; Ohsuki, S.; Kanematsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 6735. (c) Presset, M.; Michelet, B.; Guillot, R.; Bour, C.; Bezzenine-Lafollee, S.; Gandon, V. *Chem. Commun.* **2015**, *51*, 5318. (d) Qian, H.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 2056. (e) Bucher, J.; Wurm, T.; Nalivela, K. S.; Rudolph, M.; Rominger, F.; Hashmi, A. St. K. *Angew. Chem. Int. Ed.* **2014**, *53*, 3854.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2.29
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2.07
1.57
1.26
1.24
1.23
1.22
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Me
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CO2Me
Me
O
CO2Me
CDCl3
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0.10
3.29
1.98
1.02
1.15
1.04
0.15
0.21
1.06
3.30
f1 (ppm)

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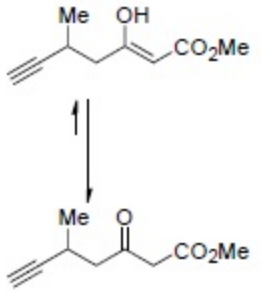
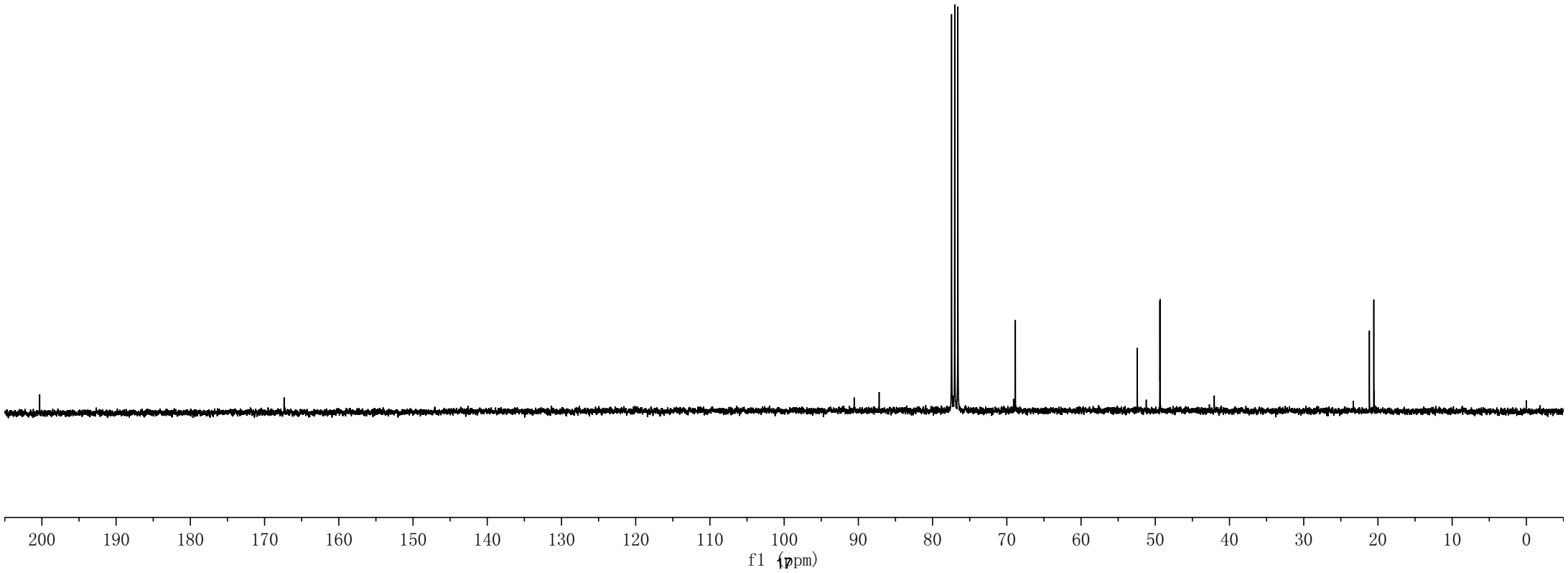
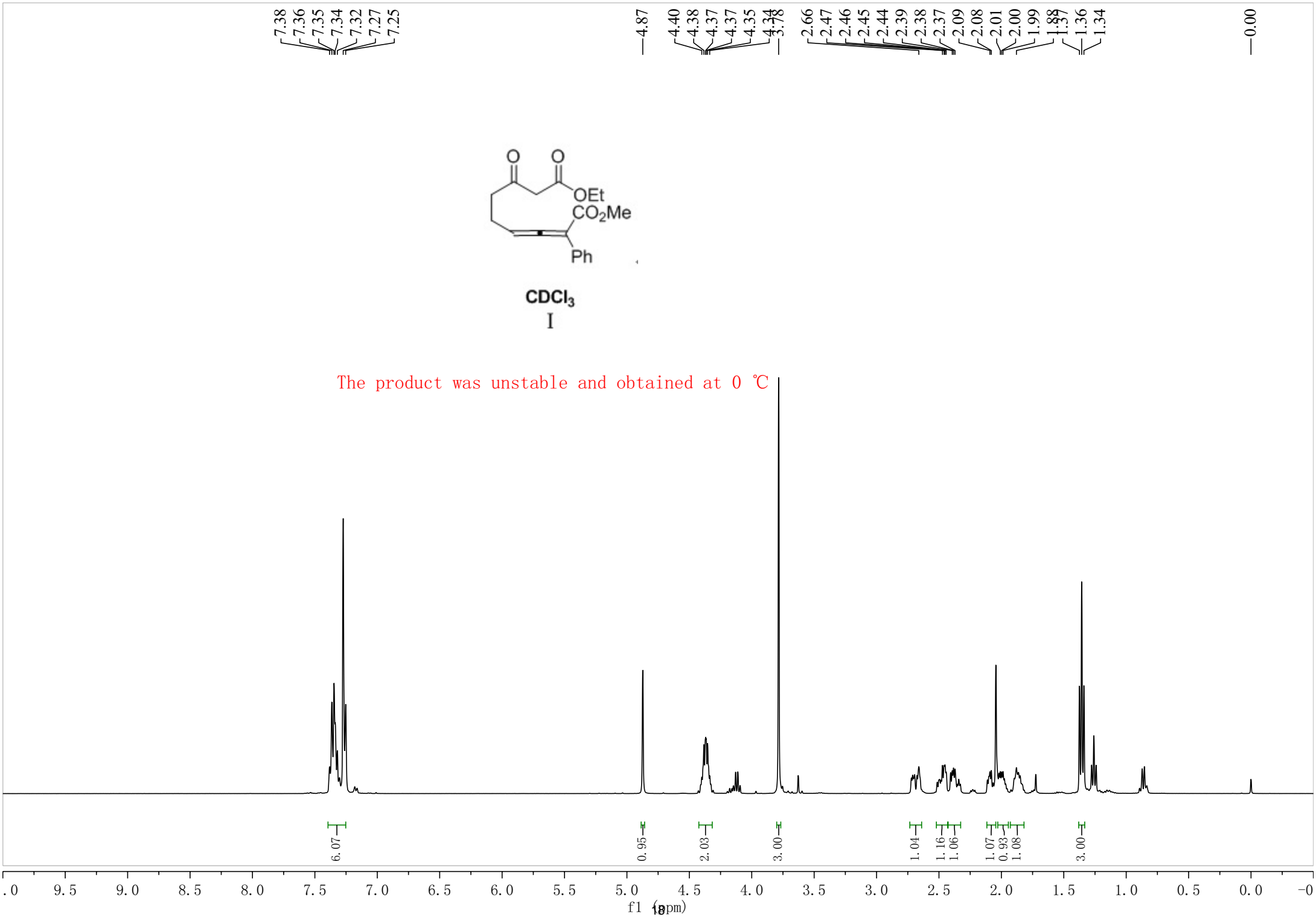
20.56



$CDCl_3$

1e

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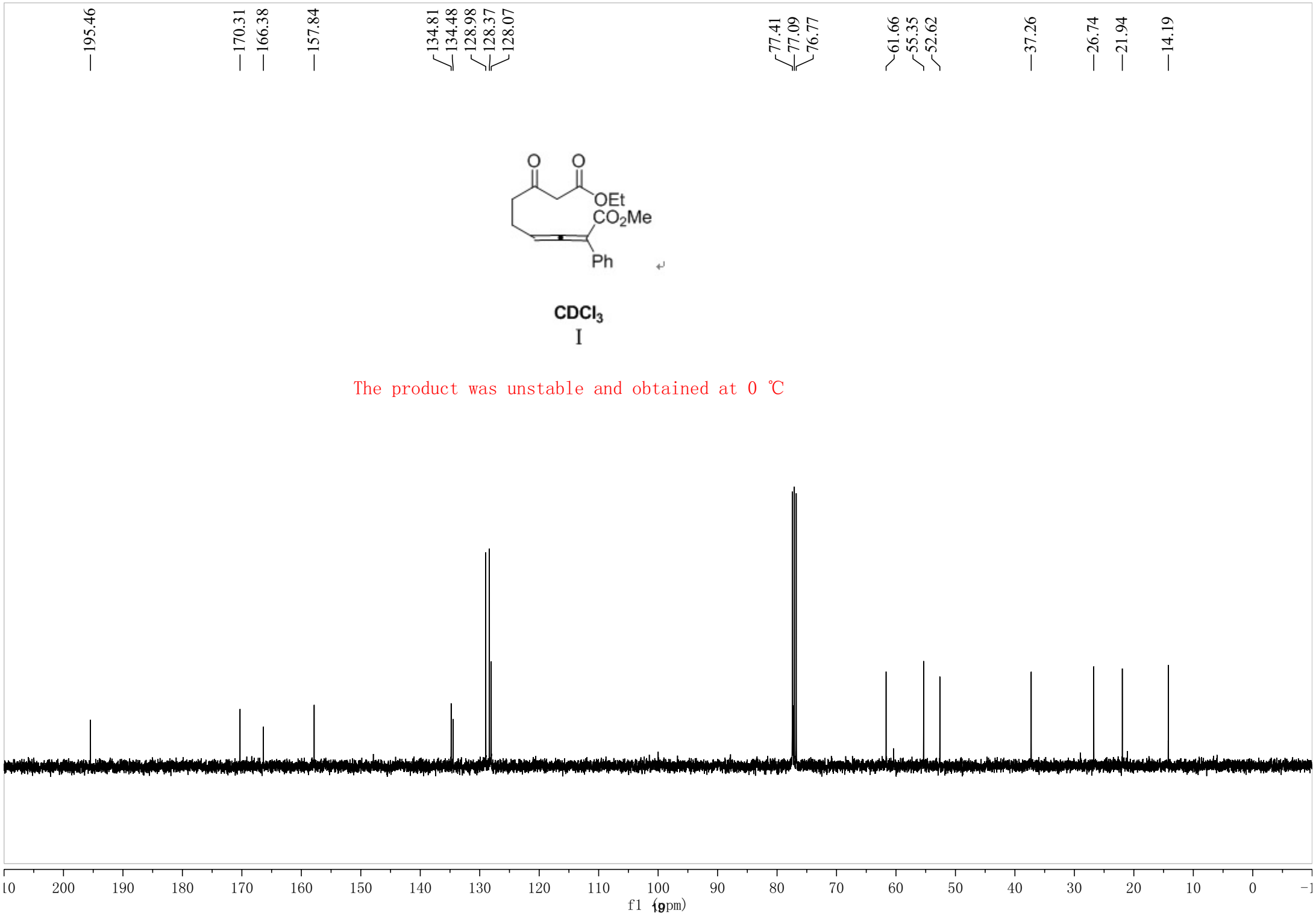
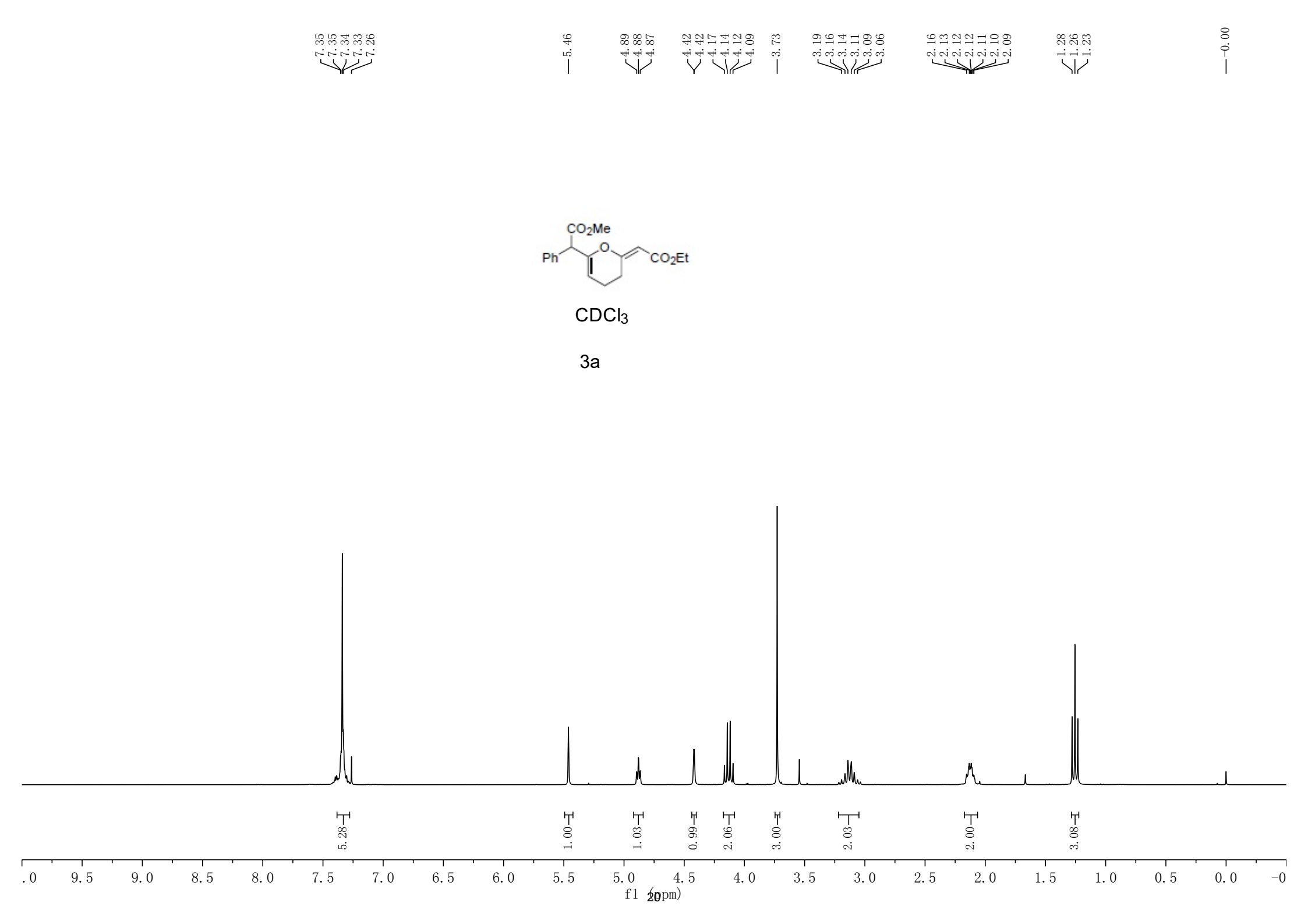
2.00
1.99
1.88
1.37
1.36
1.34
0.00
O
O
OEt
CO2Me
Ph
CDCl3
I
The product was unstable and obtained at 0 ℃
6.07
0.95
2.03
3.00
1.04
1.16
1.06
1.07
0.93
1.08
3.00
f1 (ppm)



I

The product was unstable and obtained at 0 ℃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1.23
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Ph
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CO2Et
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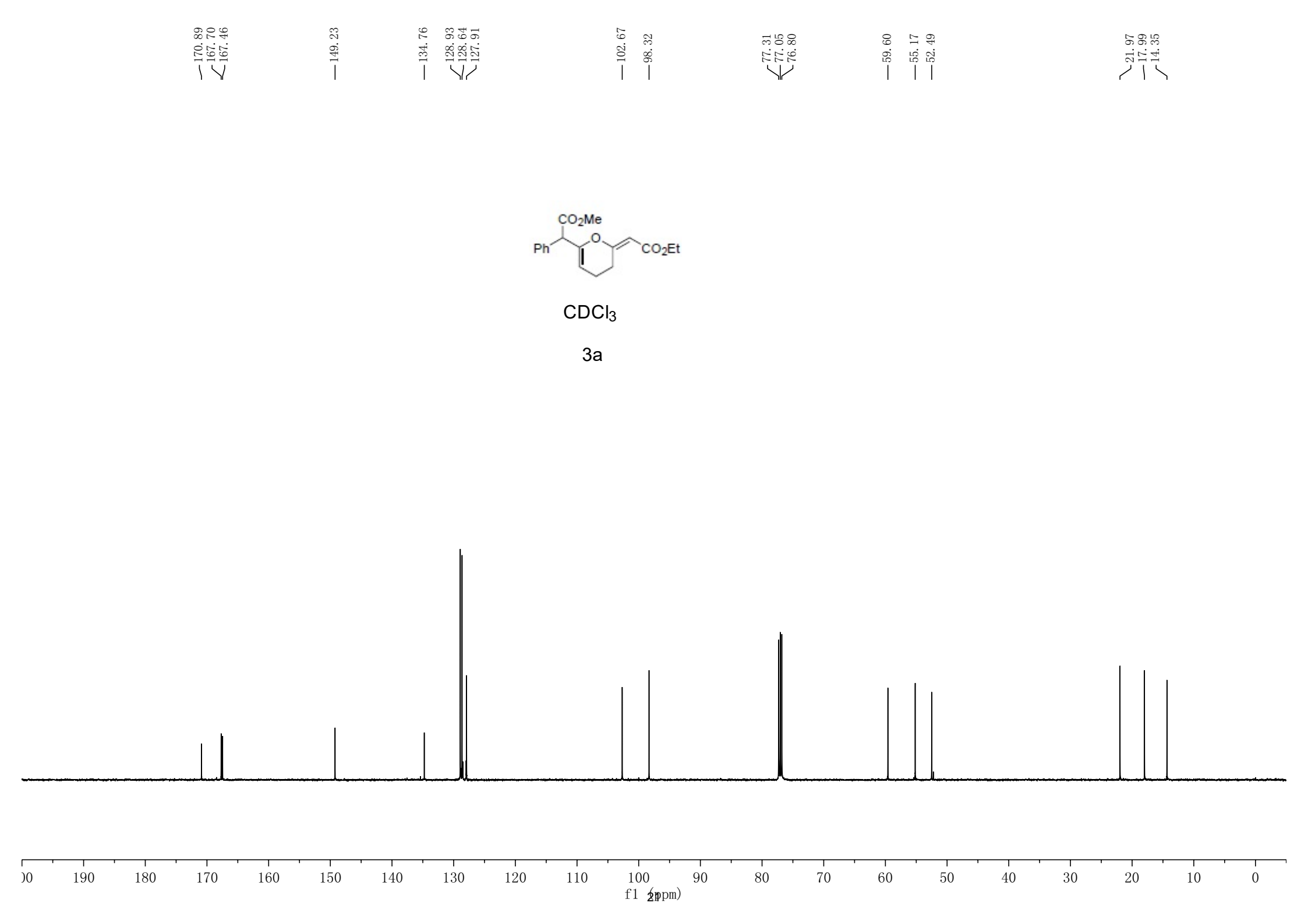
f1 (ppm)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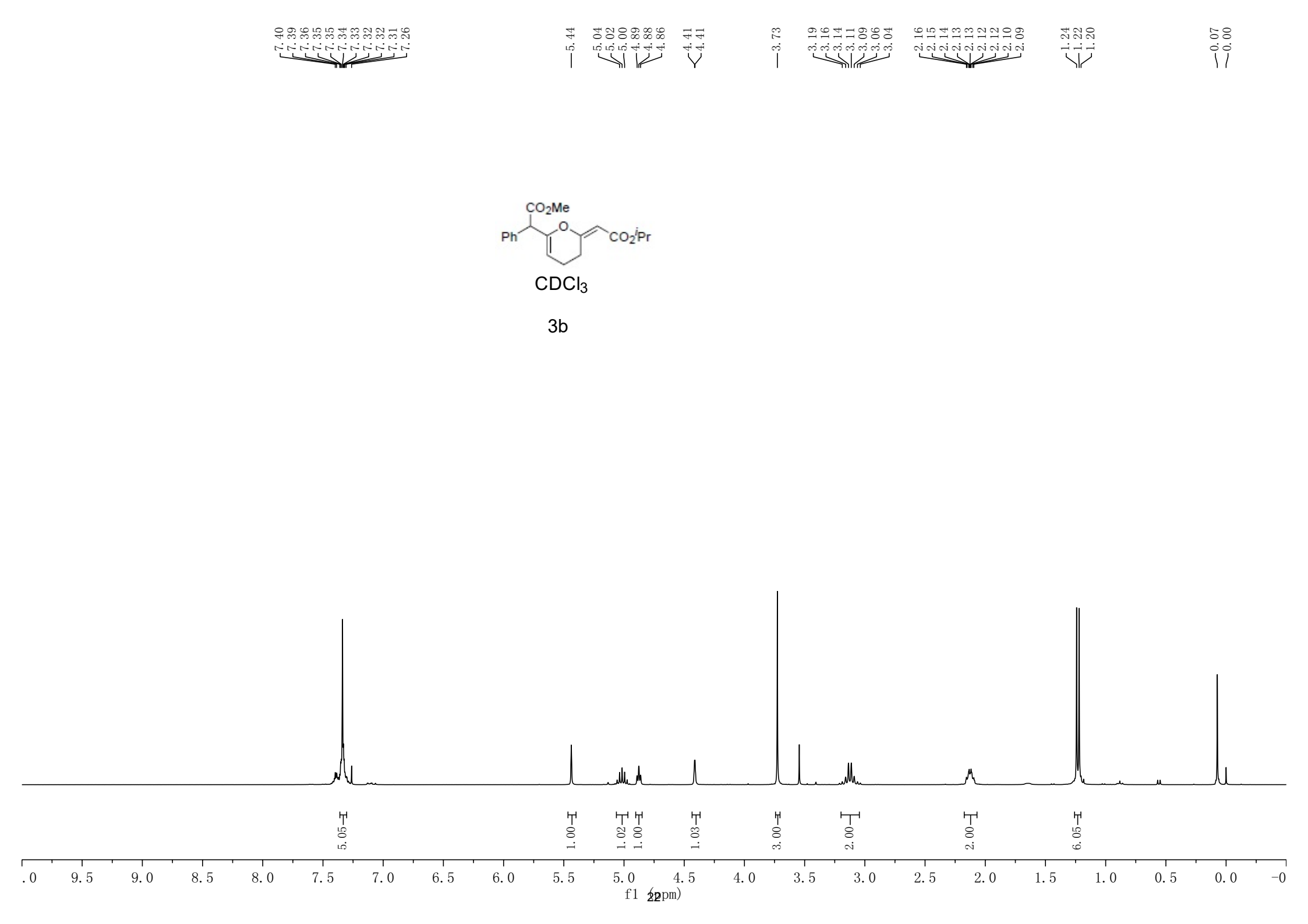
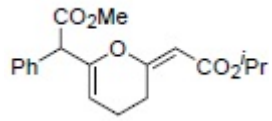
52.49
21.97
17.99
14.35
CO2Me
Ph
O
CO2Et
CDCl3
3a
f1 (ppm)

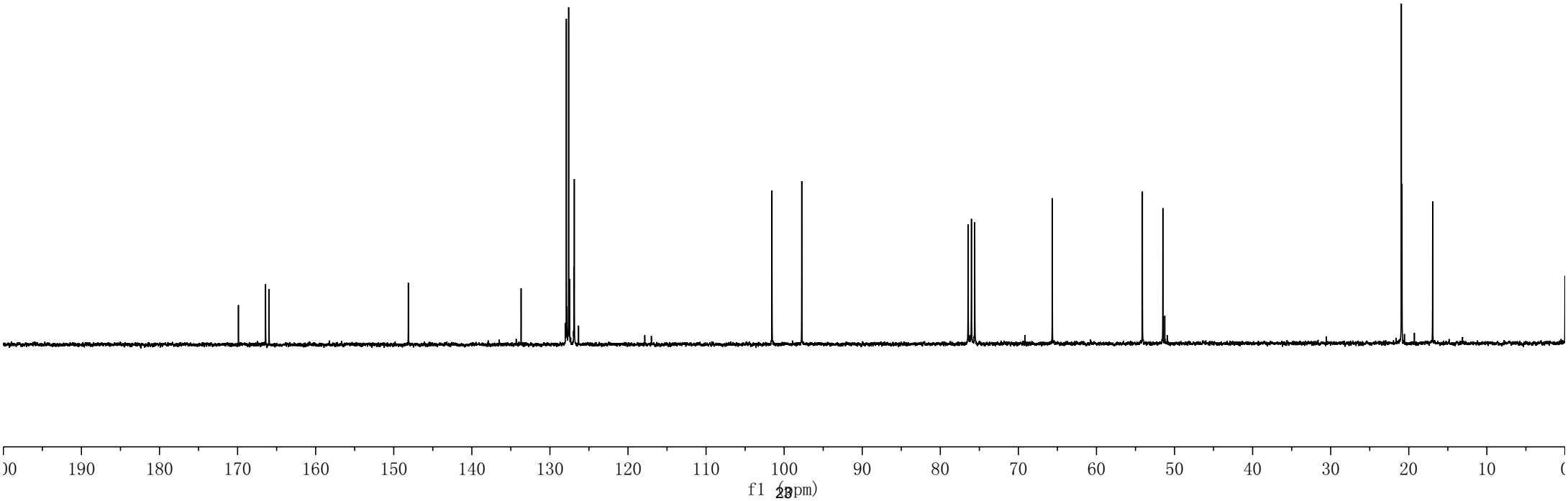

7.40
7.39
7.36
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.26
5.44
5.04
5.02
5.00
4.89
4.88
4.86
4.41
4.41
3.73
3.19
3.16
3.14
3.11
3.09
3.06
3.04
2.16
2.15
2.14
2.13
2.13
2.12
2.12
2.10
2.09
1.24
1.22
1.20
0.07
0.00
CO2Me
Ph
O
CO2iPr
CDCl3
3b
5.05
1.00
1.02
1.00
1.03
3.00
2.00
2.00
6.05
f1 (ppm)

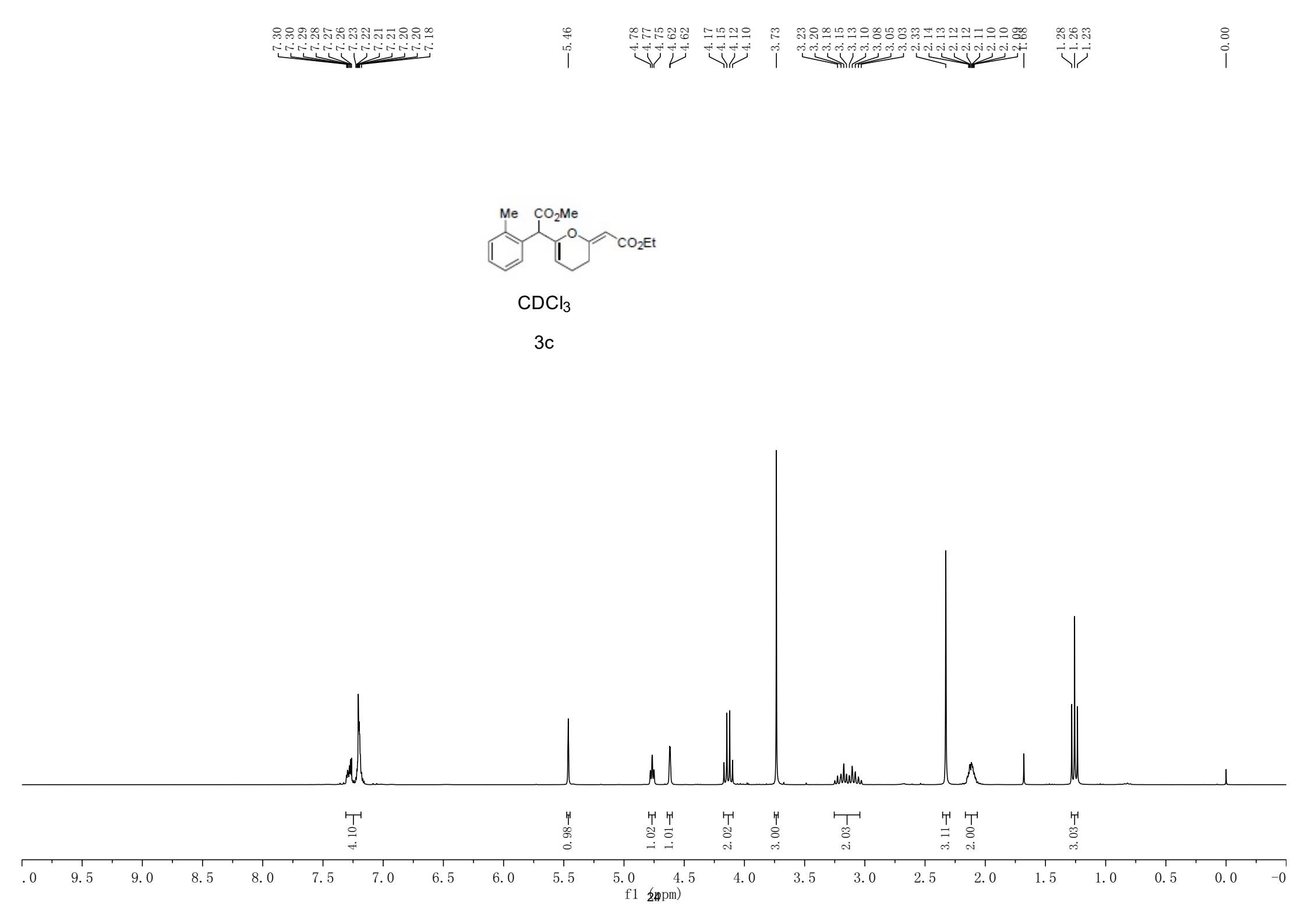
169.89
166.41
165.97
148.13
133.69
127.89
127.60
126.88
101.56
97.75
76.44
76.01
75.59
65.65
54.12
51.50
20.95
20.87
16.94



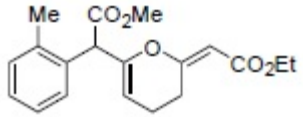
$CDCl_3$

3b



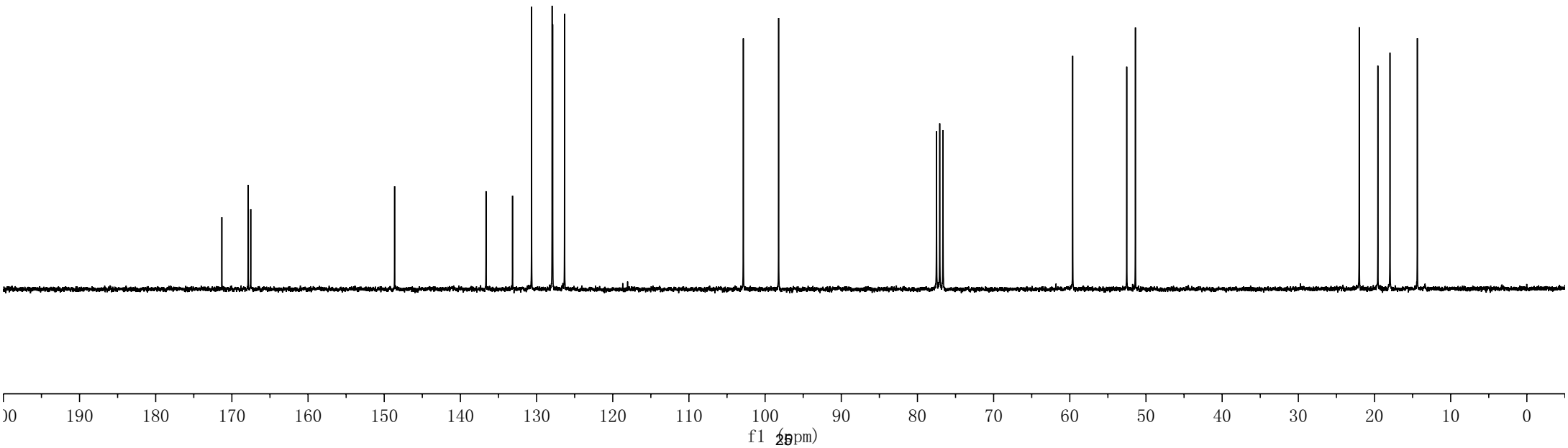

7.30
7.30
7.29
7.28
7.27
7.26
7.23
7.22
7.21
7.21
7.20
7.20
7.18
5.46
4.78
4.77
4.75
4.62
4.62
4.17
4.15
4.12
4.10
3.73
3.23
3.20
3.18
3.15
3.13
3.10
3.08
3.05
3.03
2.33
2.14
2.13
2.12
2.12
2.11
2.10
2.10
1.28
1.26
1.23
0.00
Me
CO2Me
O
CO2Et
CDCl3
3c
4.10
0.98
1.02
1.01
2.02
3.00
2.03
3.11
2.00
3.03
f1 (ppm)

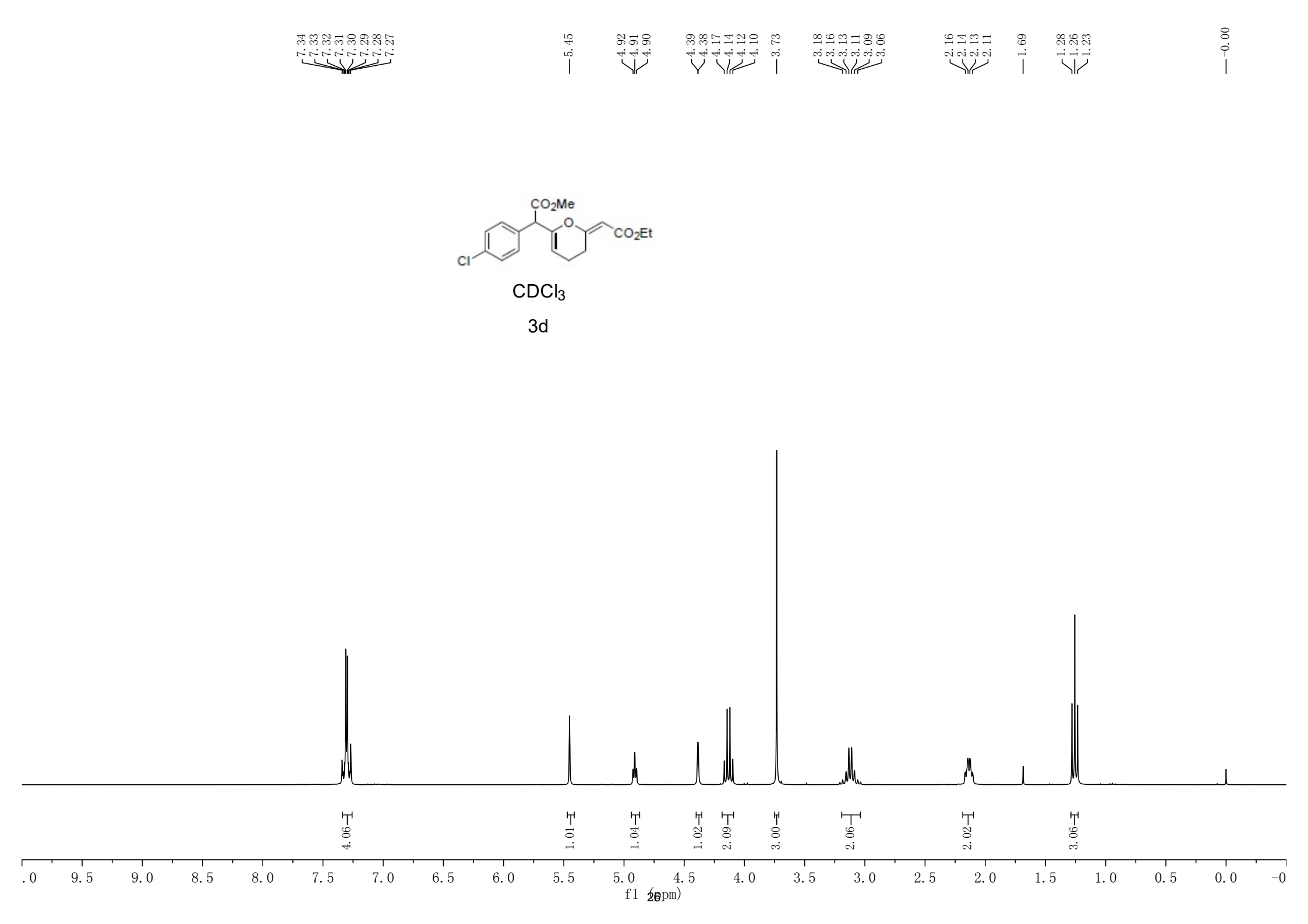
171.32
167.87
167.53
148.64
136.64
133.16
130.66
127.96
127.89
126.33
102.86
98.23
77.50
77.07
76.65
59.62
52.52
51.39
22.01
19.56
17.97
14.38



$CDCl_3$

3c

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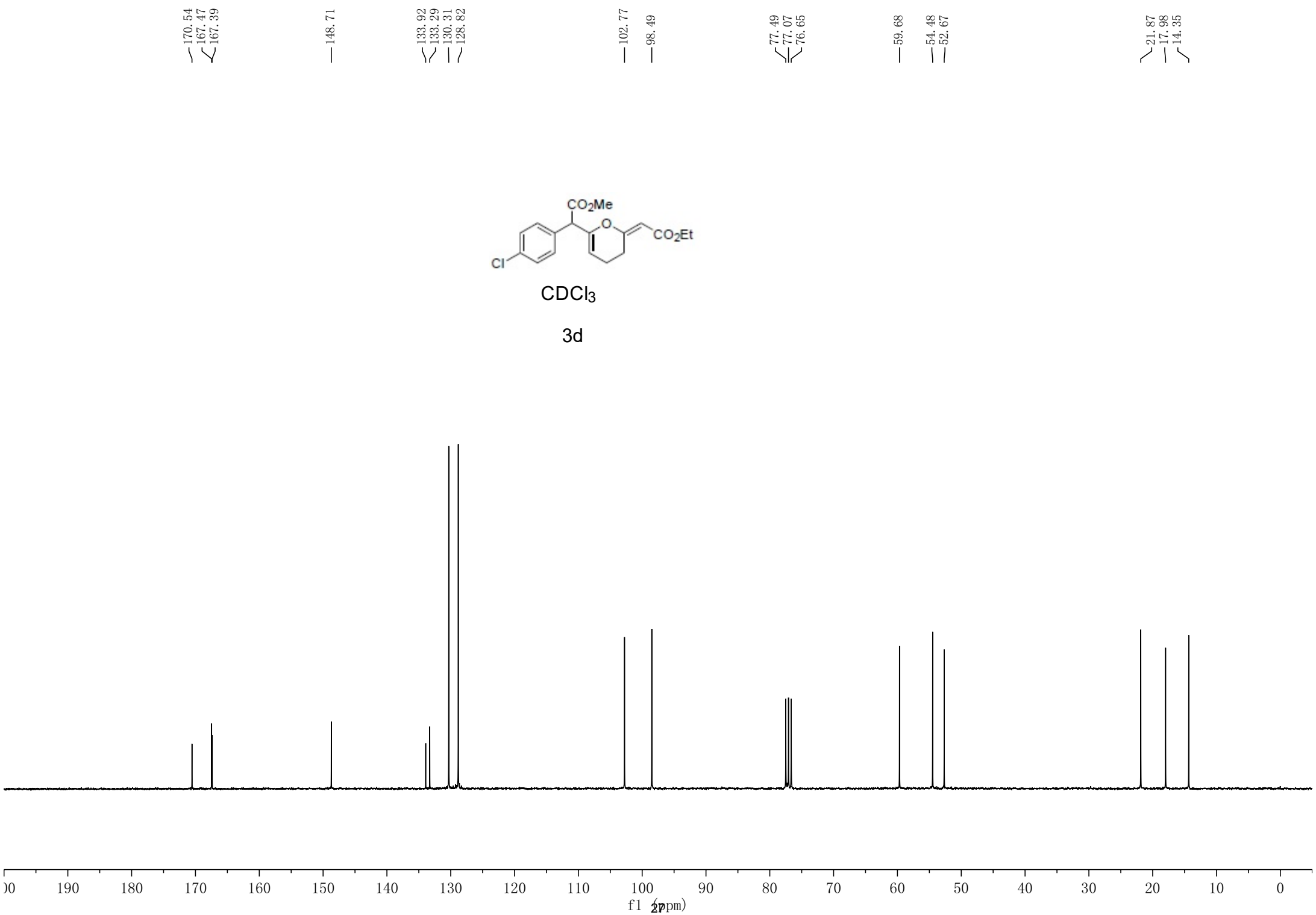
7.33
7.32
7.31
7.30
7.29
7.28
7.27
5.45
4.92
4.91
4.90
4.39
4.38
4.17
4.14
4.12
4.10
3.73
3.18
3.16
3.13
3.11
3.09
3.06
2.16
2.14
2.13
2.11
1.69
1.28
1.26
1.23
0.00
CO2Me
O
CO2Et
Cl
CDCl3
3d
4.06
1.01
1.04
1.02
2.09
3.00
2.06
2.02
3.06
f1 (ppm)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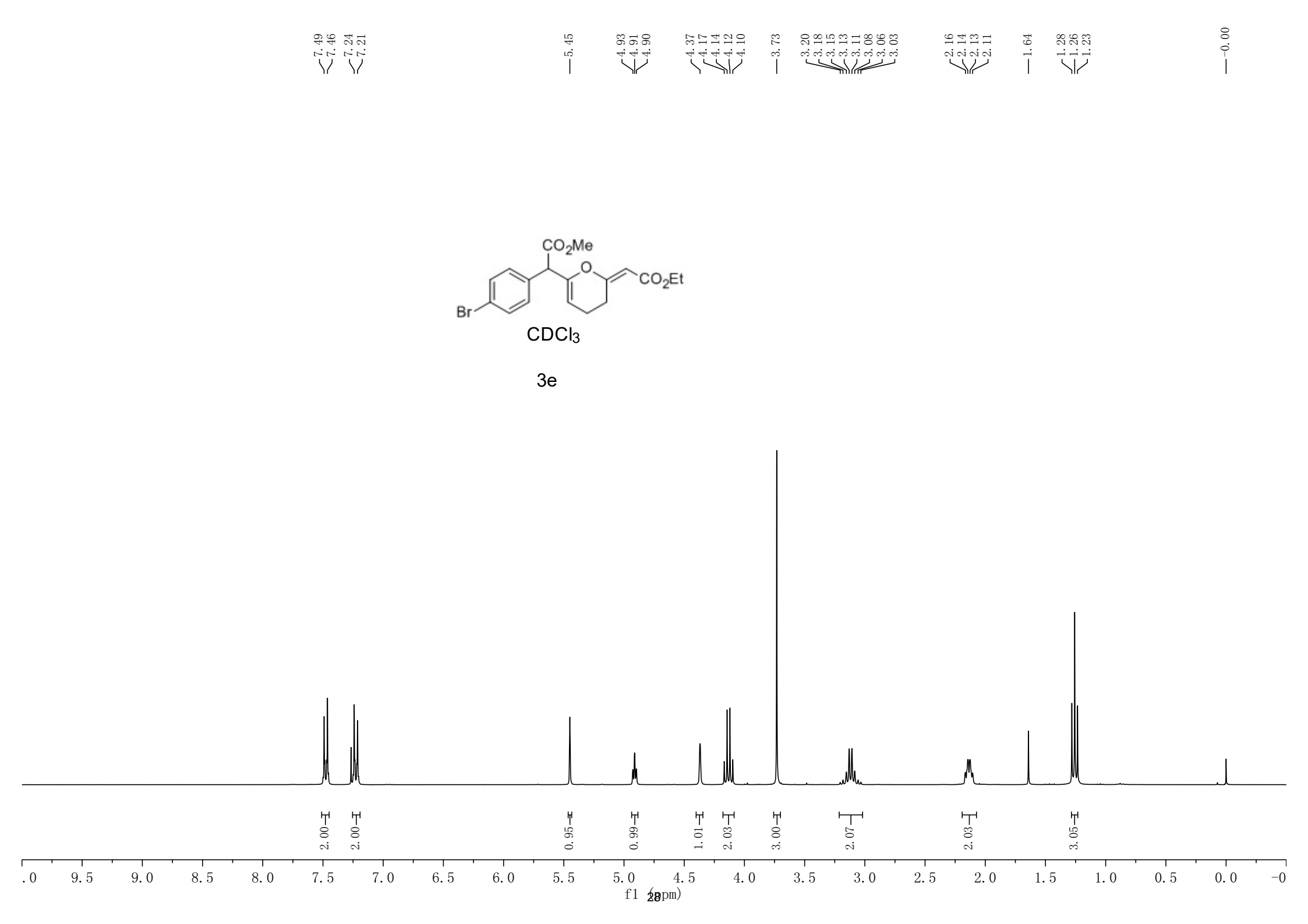
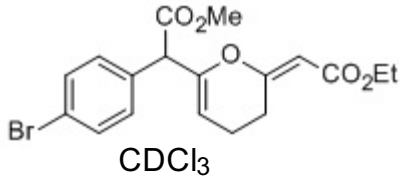
167.47
167.39
148.71
133.92
133.29
130.31
128.82
102.77
98.49
77.49
77.07
76.65
59.68
54.48
52.67
21.87
17.98
14.35
CO2Me
O
CO2Et
Cl
CDCl3
3d
f1 (ppm)

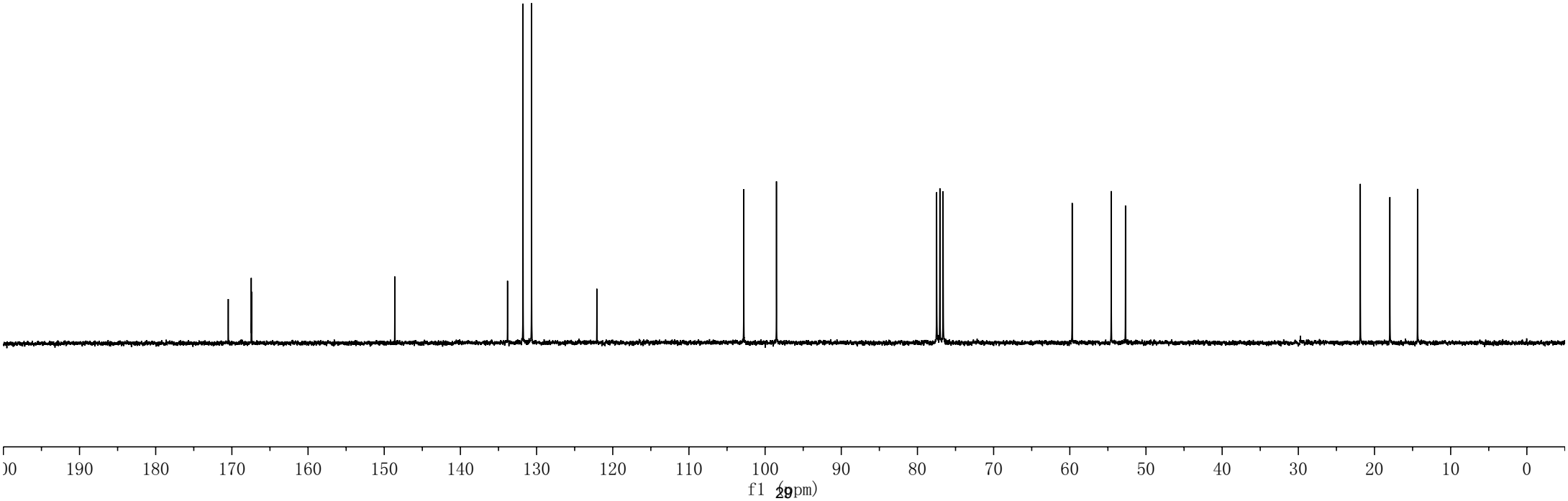

7.49
7.46
7.24
7.21
5.45
4.93
4.91
4.90
4.37
4.17
4.14
4.12
4.10
3.73
3.20
3.18
3.15
3.13
3.11
3.08
3.06
3.03
2.16
2.14
2.13
2.11
1.64
1.28
1.26
1.23
0.00
CO2Me
O
CO2Et
Br
CDCl3
3e
2.00
2.00
0.95
0.99
1.01
2.03
3.00
2.07
2.03
3.05
f1 (ppm)

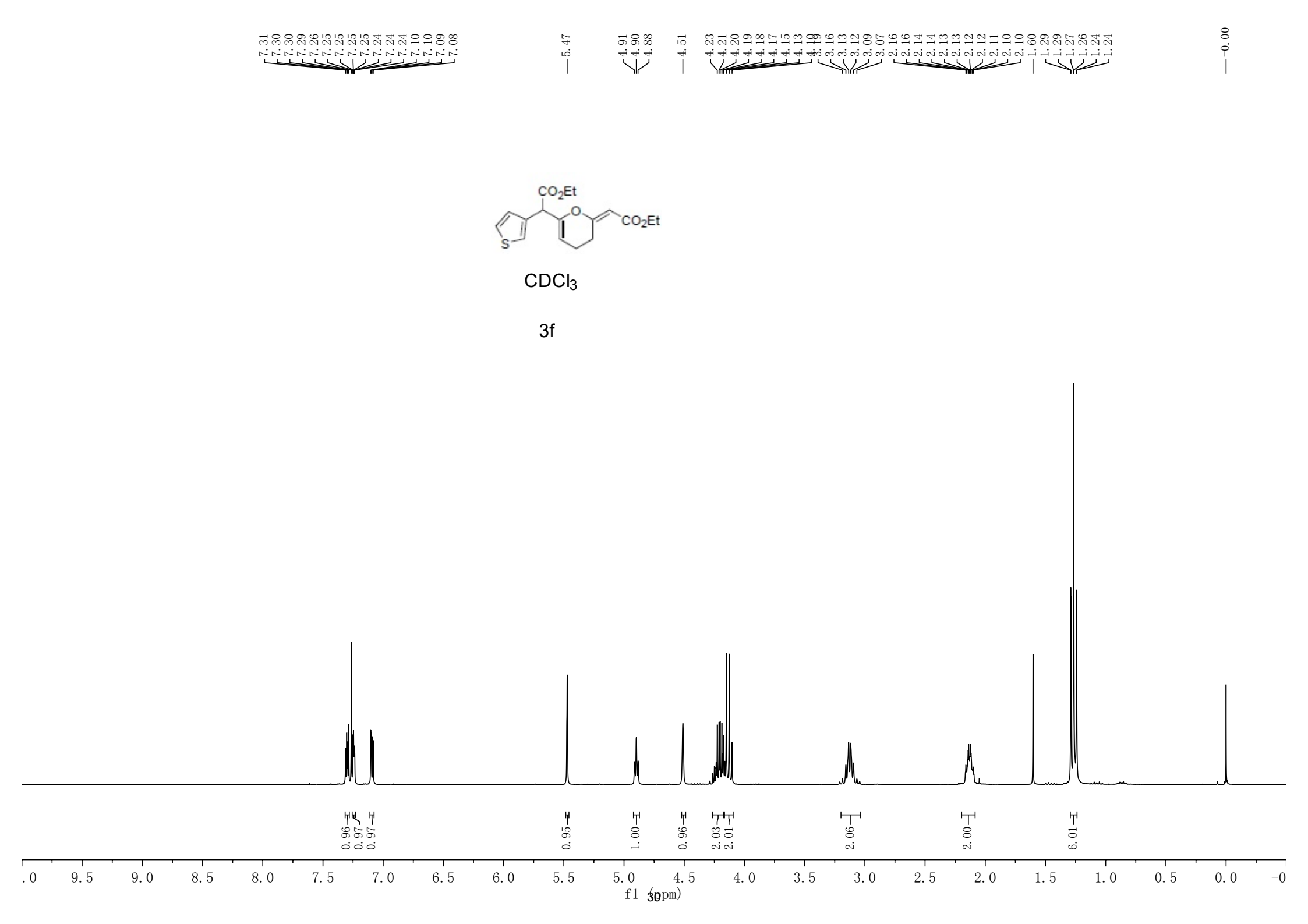
170.47
167.46
167.40
148.61
133.81
131.78
130.66
122.09
102.80
98.51
77.48
77.06
76.63
59.69
54.56
52.69
21.86
17.98
14.36



$CDCl_3$

3e

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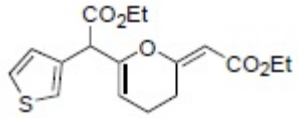
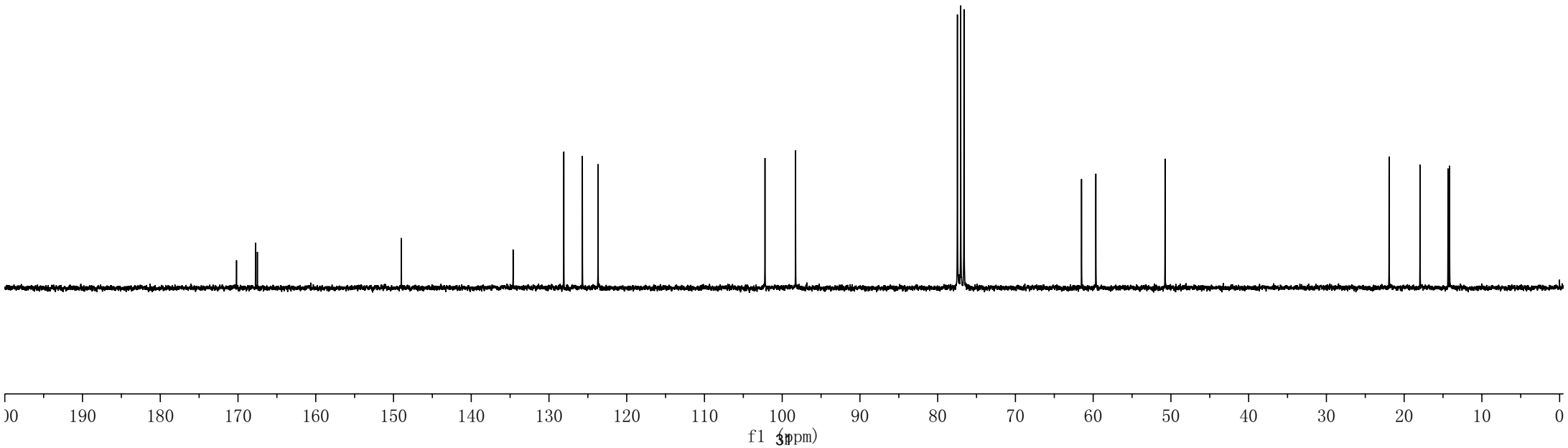
7.25
7.25
7.24
7.24
7.24
7.10
7.10
7.09
7.08
5.47
4.91
4.90
4.88
4.51
4.23
4.21
4.20
4.19
4.18
4.17
4.15
4.13
3.19
3.16
3.13
3.12
3.09
3.07
2.16
2.16
2.14
2.14
2.13
2.13
2.12
2.12
2.11
2.10
2.10
1.60
1.29
1.29
1.27
1.26
1.24
1.24
-0.00
CO2Et
O
CO2Et
S
CDCl3
3f
0.96
0.97
0.97
0.95
1.00
0.96
2.03
2.01
2.06
2.00
6.01
f1 (ppm)

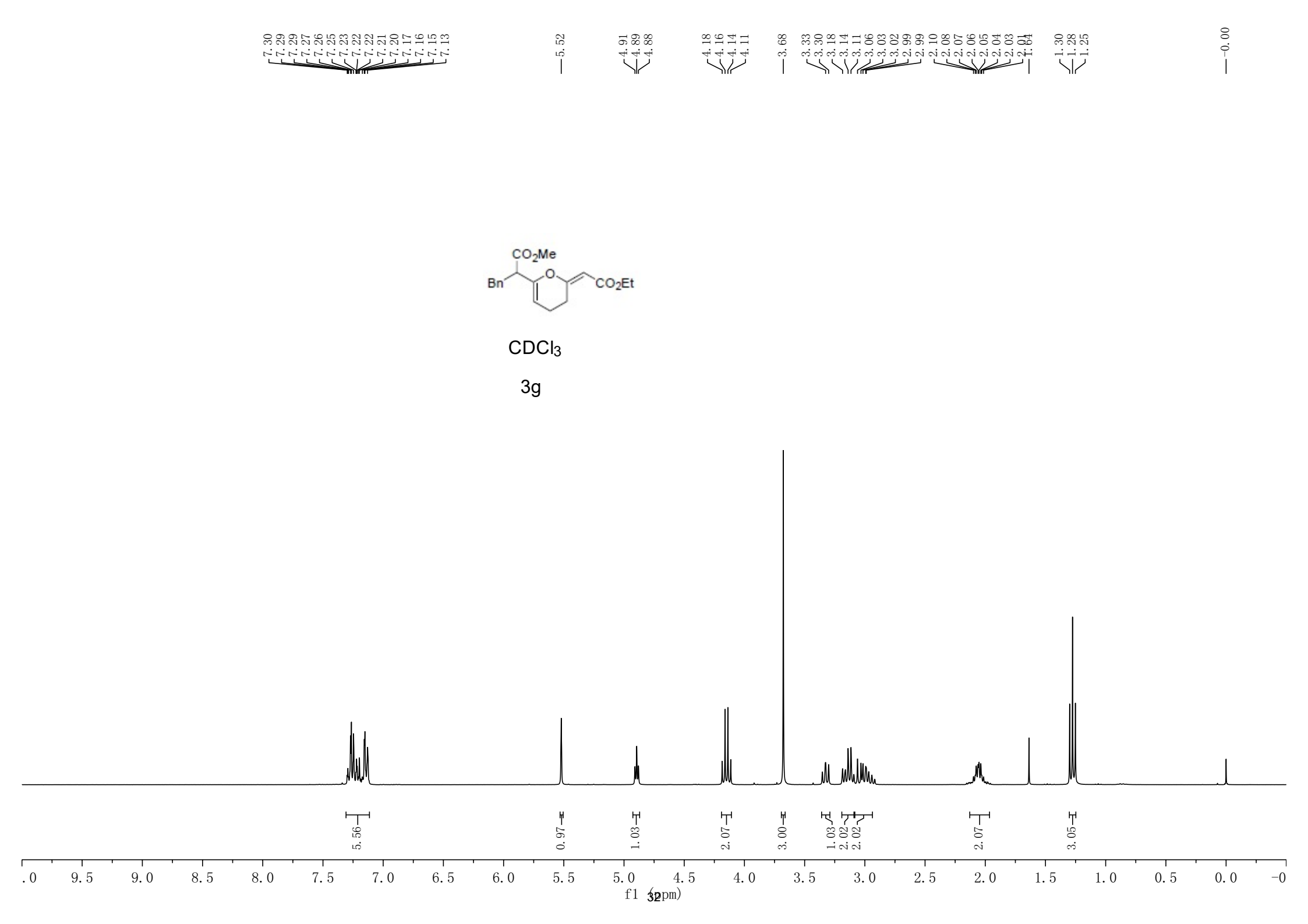
170.19
167.75
167.51
148.99
134.61
128.09
125.70
123.68
102.21
98.28
77.46
77.04
76.62
61.50
59.66
50.75
21.94
17.96
14.36
14.16



$CDCl_3$

3f

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7.25
7.23
7.22
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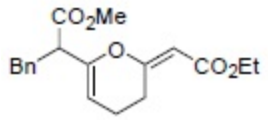
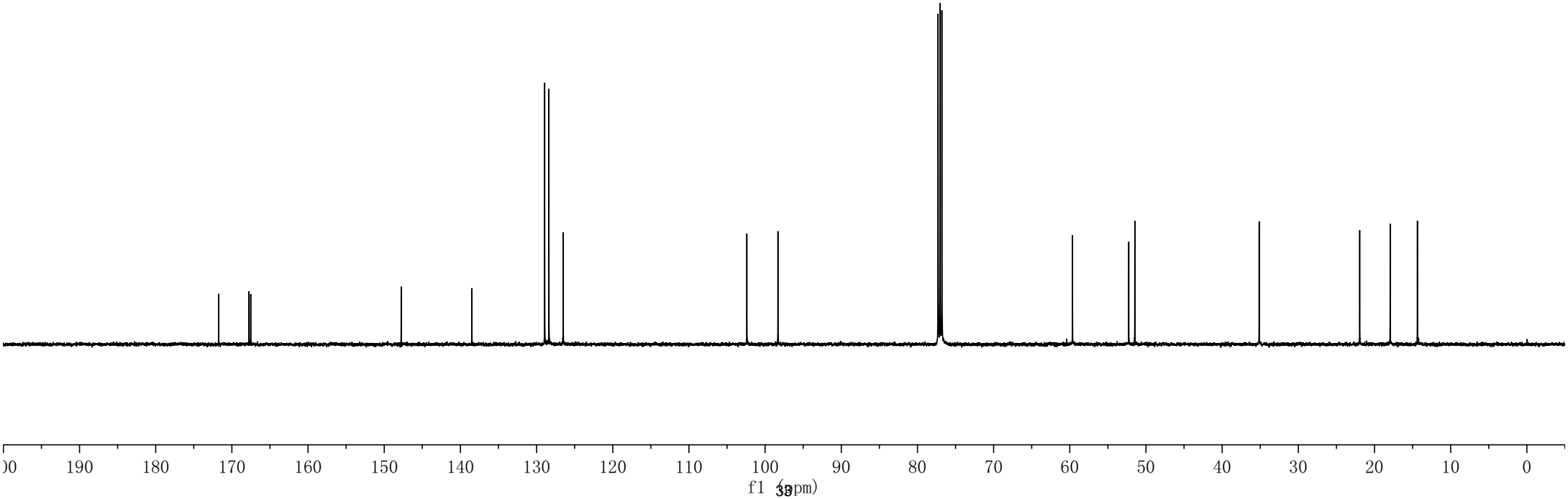
7.21
7.20
7.17
7.16
7.15
7.13
5.52
4.91
4.89
4.88
4.18
4.16
4.14
4.11
3.68
3.33
3.30
3.18
3.14
3.11
3.06
3.03
3.02
2.99
2.99
2.10
2.08
2.07
2.06
2.05
2.04
2.03
2.01
1.64
1.30
1.28
1.25
0.00
CO2Me
Bn
O
CO2Et
CDCl3
3g
5.56
0.97
1.03
2.07
3.00
1.03
2.02
2.02
2.07
3.05
f1 (ppm)

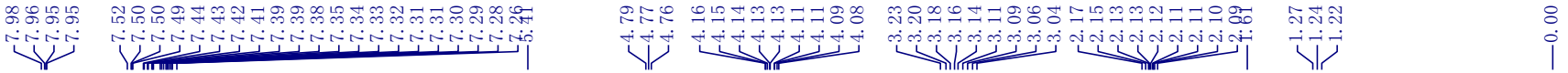
171.74
167.75
167.53
147.77
138.50
128.94
128.38
126.51
102.39
98.31
77.30
77.04
76.79
59.65
52.26
51.46
35.14
21.94
17.94
14.37



$CDCl_3$

3g

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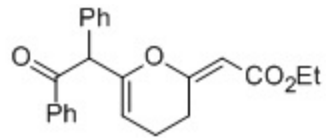
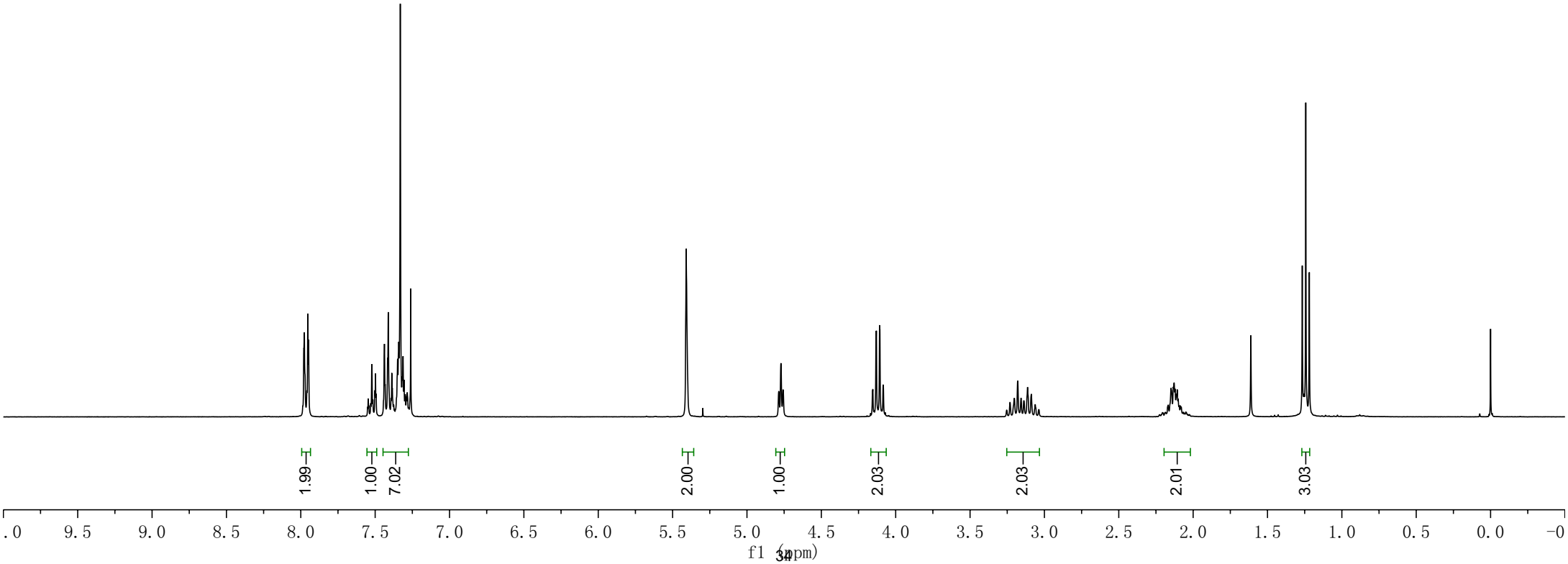
7.96
7.95
7.95
7.52
7.50
7.50
7.49
7.44
7.43
7.42
7.41
7.39
7.39
7.38
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.26
5.41
4.79
4.77
4.76
4.16
4.15
4.14
4.13
4.13
4.11
4.11
4.09
4.08
3.23
3.20
3.18
3.16
3.14
3.11
3.09
3.06
3.04
2.17
2.15
2.13
2.12
2.11
2.10
2.09
1.61
1.27
1.24
1.22
0.00


Ph
O
O
CO2Et
Ph

$CDCl_3$

3h


1.99
1.00
7.02
2.00
1.00
2.03
2.03
2.01
3.03
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

195.70
168.01
167.55
150.26
136.30
134.88
133.22
129.40
128.90
128.84
128.64
127.84
103.87
98.08
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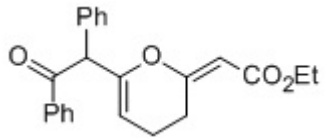
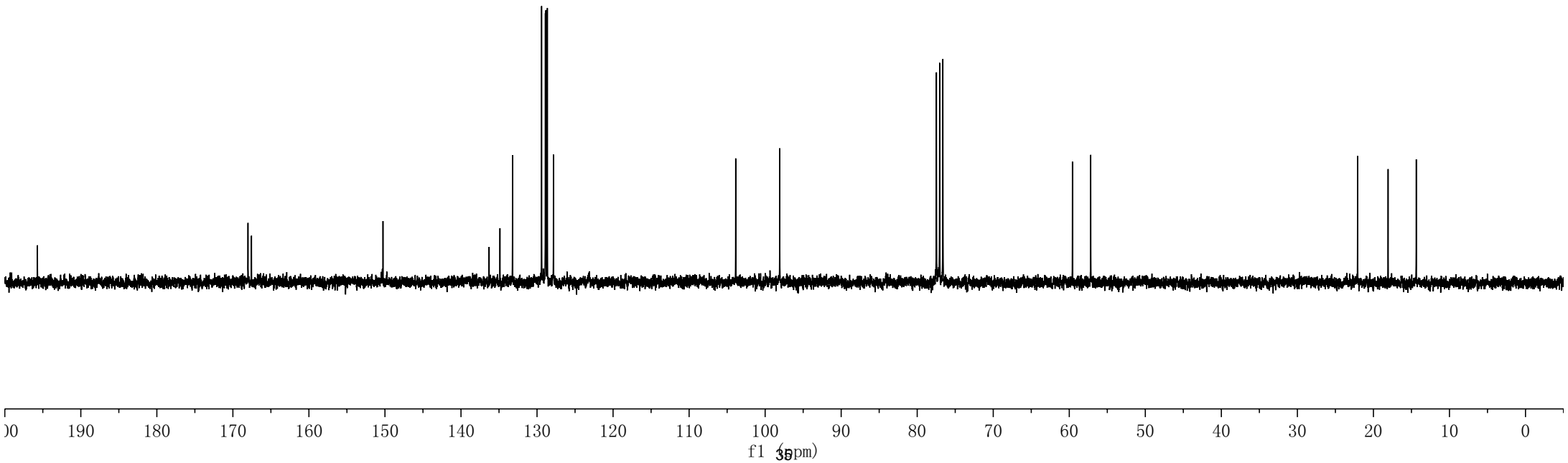
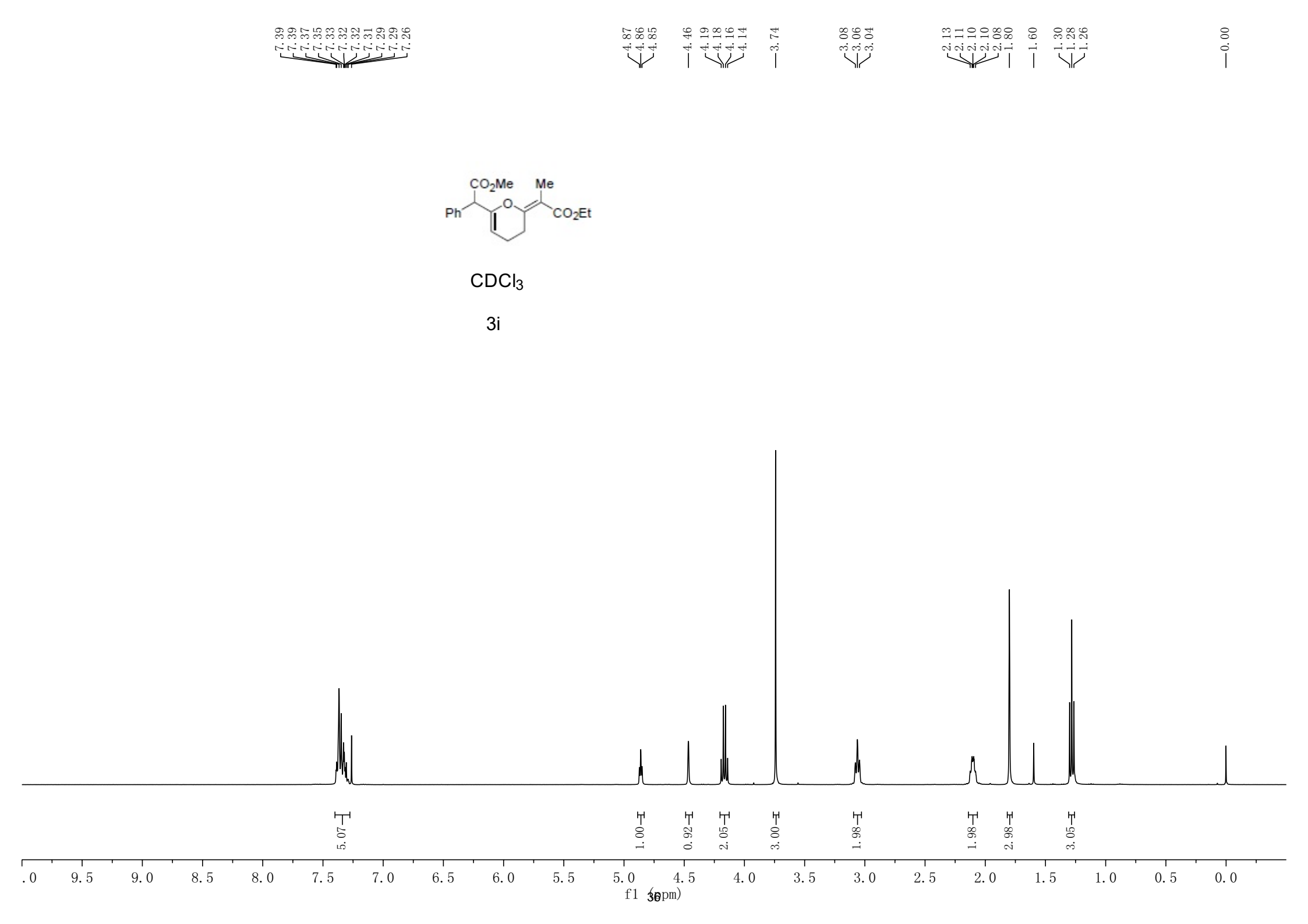
76.63
59.58
57.18
22.08
18.07
14.37



$CDCl_3$

3h




7.39
7.39
7.37
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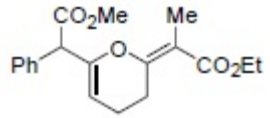
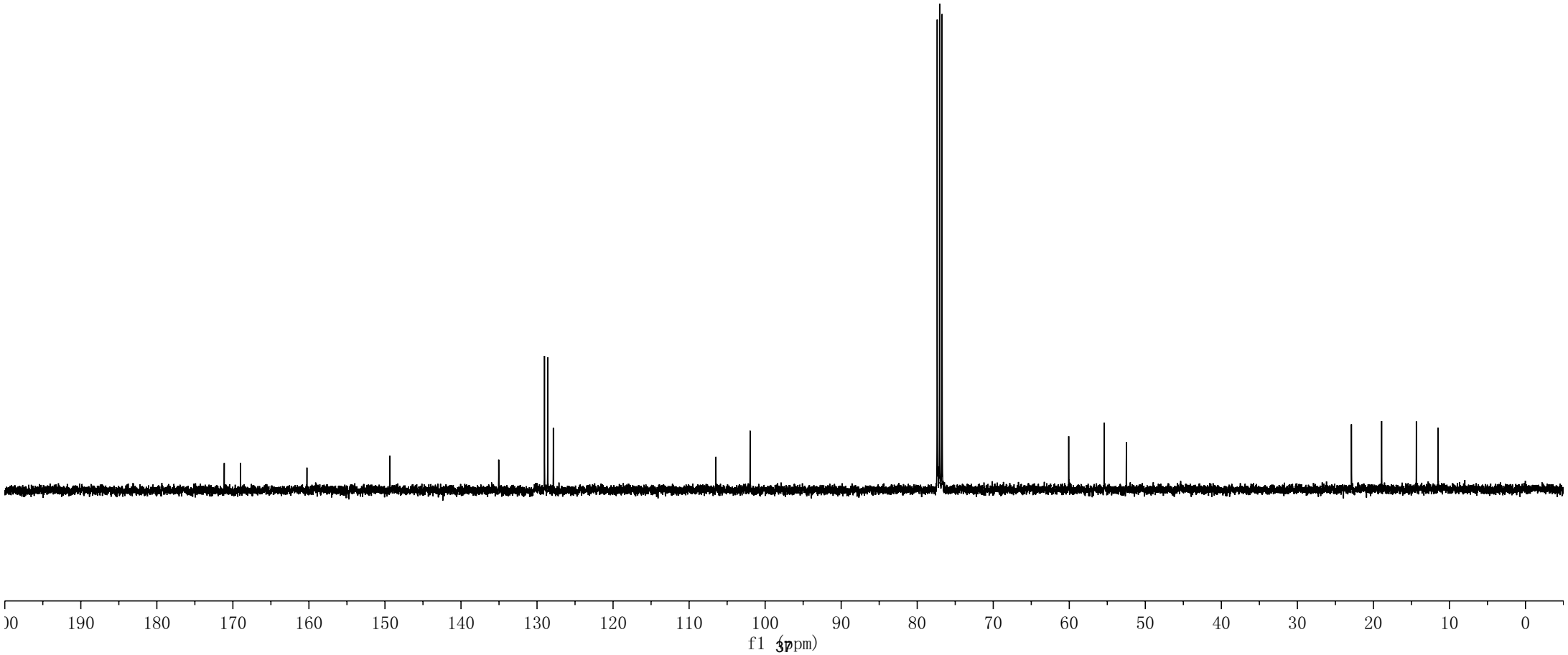
7.33
7.32
7.32
7.31
7.29
7.29
7.26
4.87
4.86
4.85
4.46
4.19
4.18
4.16
4.14
3.74
3.08
3.06
3.04
2.13
2.11
2.10
2.10
2.08
1.80
1.60
1.30
1.28
1.26
0.00
CO2Me
Me
Ph
O
CO2Et
CDCl3
3i
5.07
1.00
0.92
2.05
3.00
1.98
1.98
2.98
3.05
f1 (ppm)

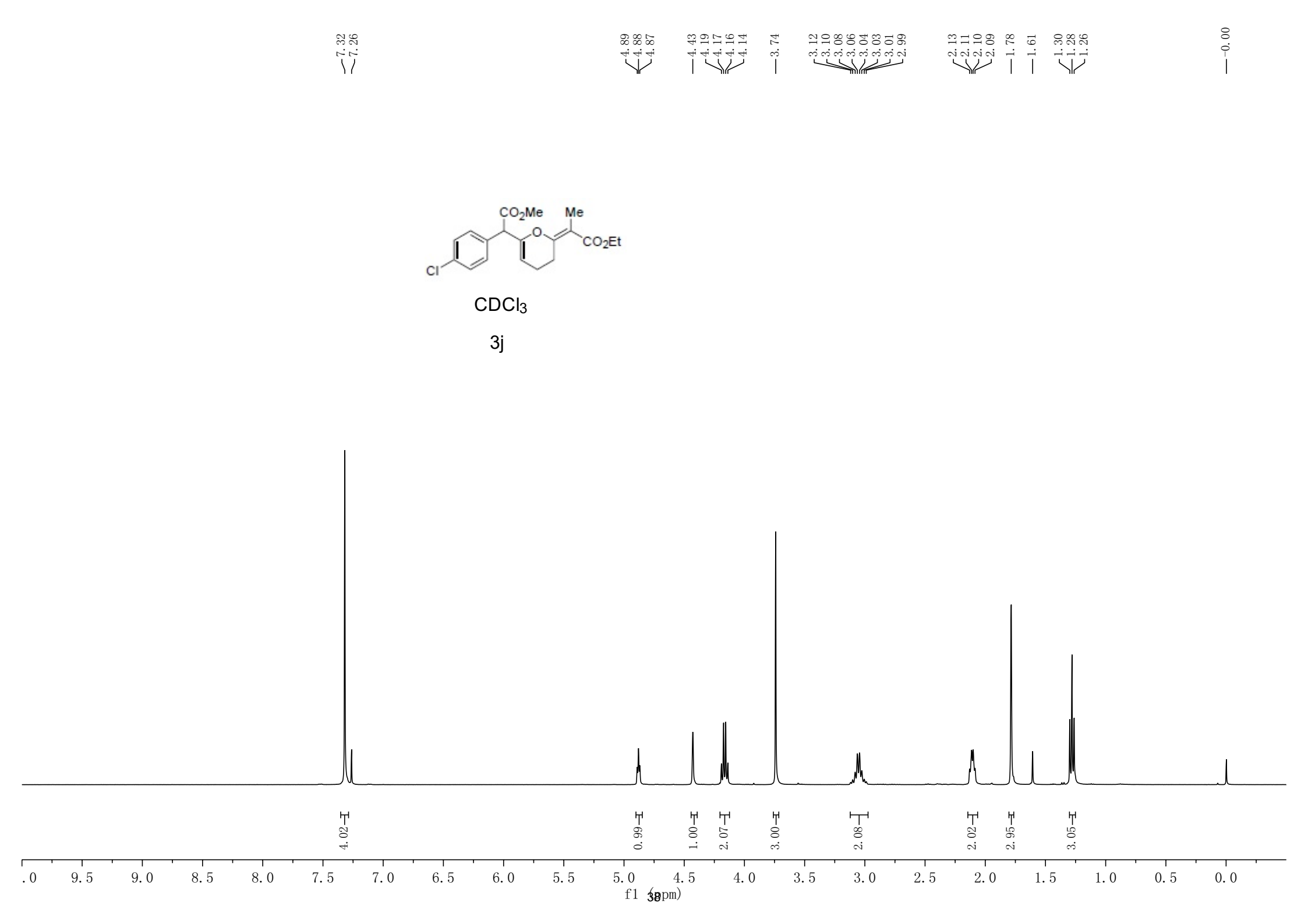
171.13
168.99
160.26
149.35
135.04
129.02
128.59
127.86
106.48
101.98
77.37
77.05
76.74
60.07
55.42
52.49
22.89
18.92
14.36
11.51



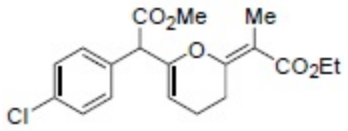
$CDCl_3$

3i



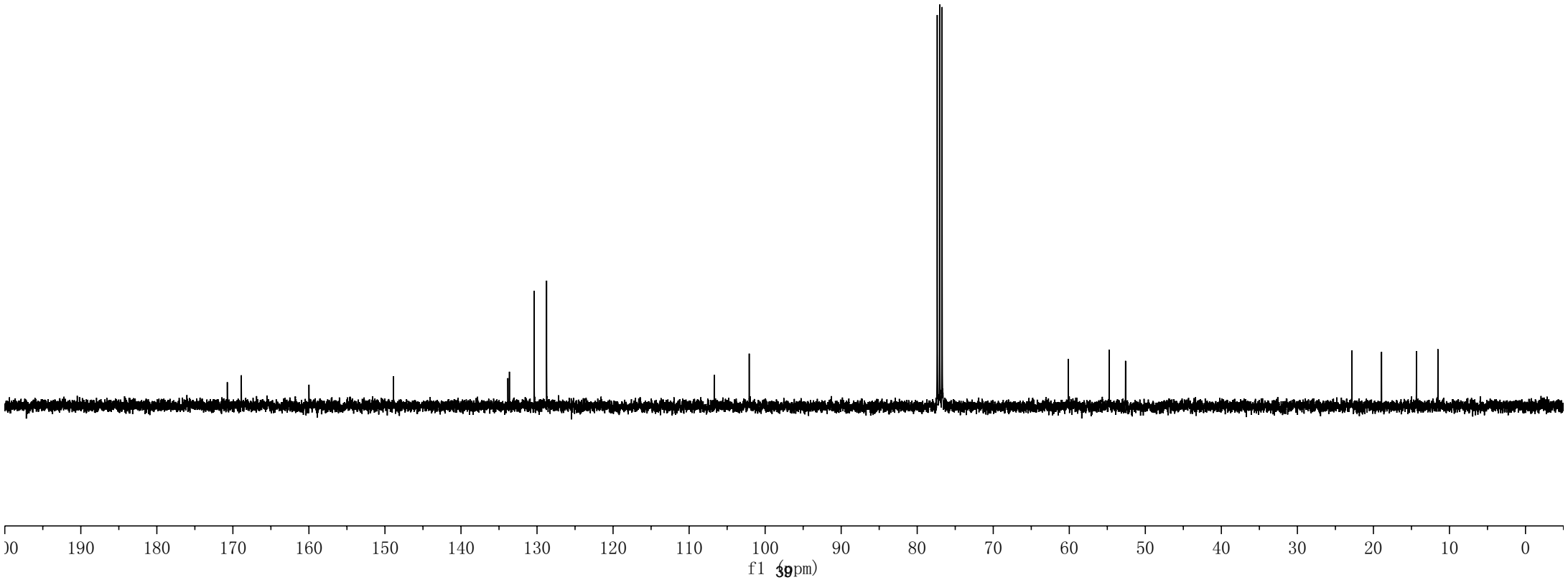

7.32
7.26
4.89
4.88
4.87
4.43
4.19
4.17
4.16
4.14
3.74
3.12
3.10
3.08
3.06
3.04
3.03
3.01
2.99
2.13
2.11
2.10
2.09
1.78
1.61
1.30
1.28
1.26
0.00
CO2Me
Me
O
CO2Et
Cl
CDCl3
3j
4.02
0.99
1.00
2.07
3.00
2.08
2.02
2.95
3.05
f1 (ppm)

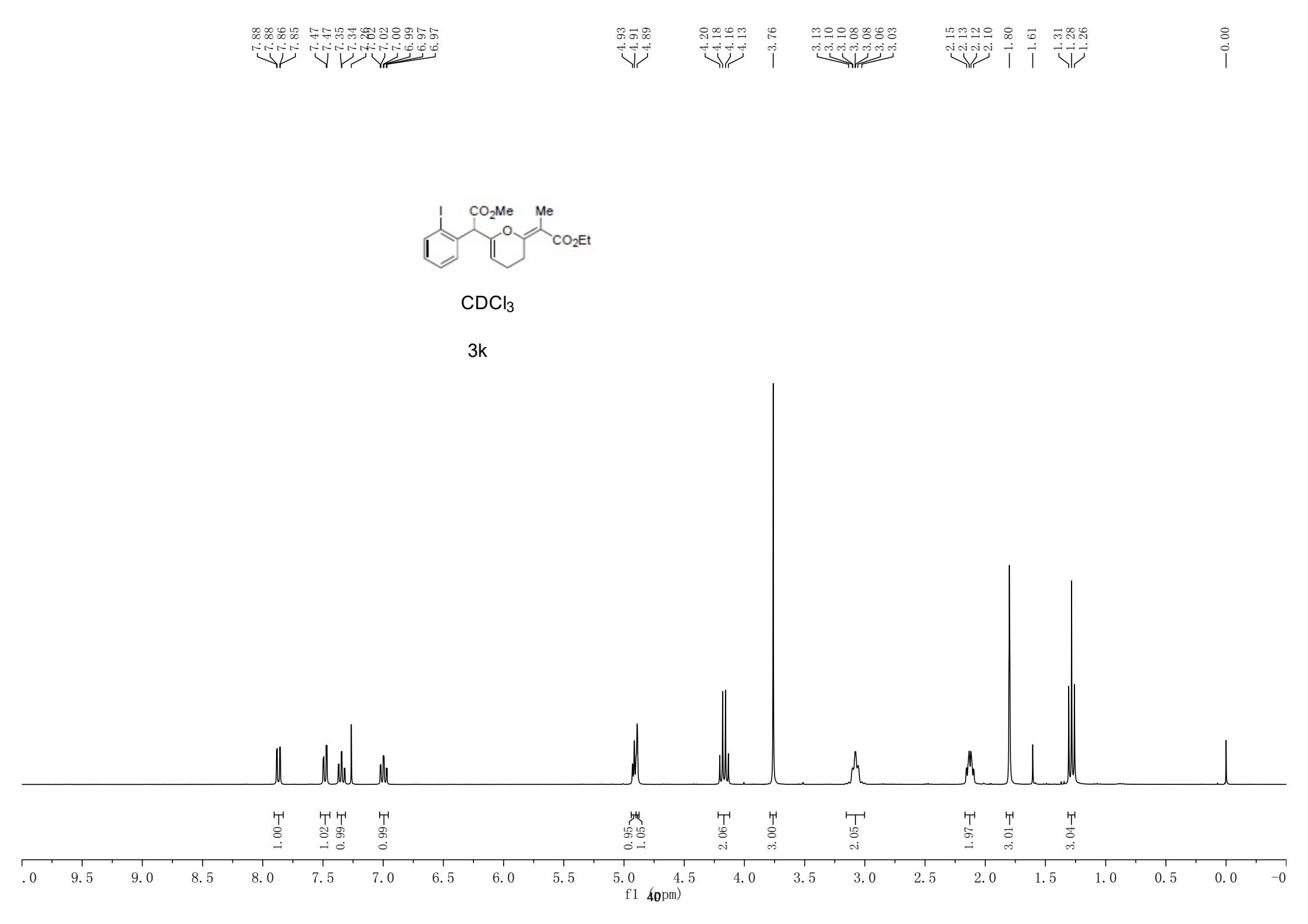
170.73
168.89
159.99
148.90
133.84
133.63
130.38
128.74
106.70
102.09
77.37
77.05
76.73
60.12
54.75
52.60
22.83
18.93
14.34
11.52



$CDCl_3$

3j

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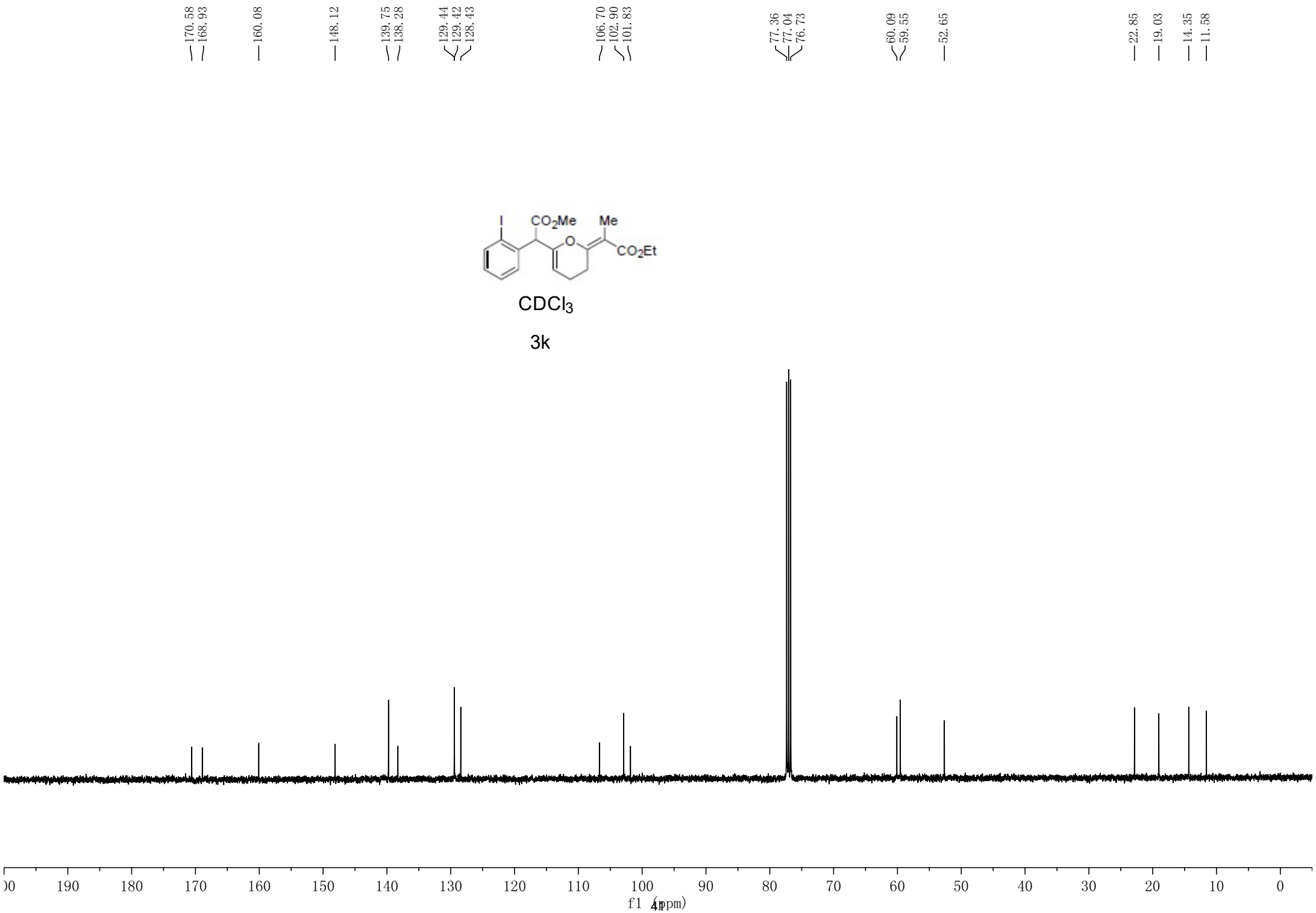
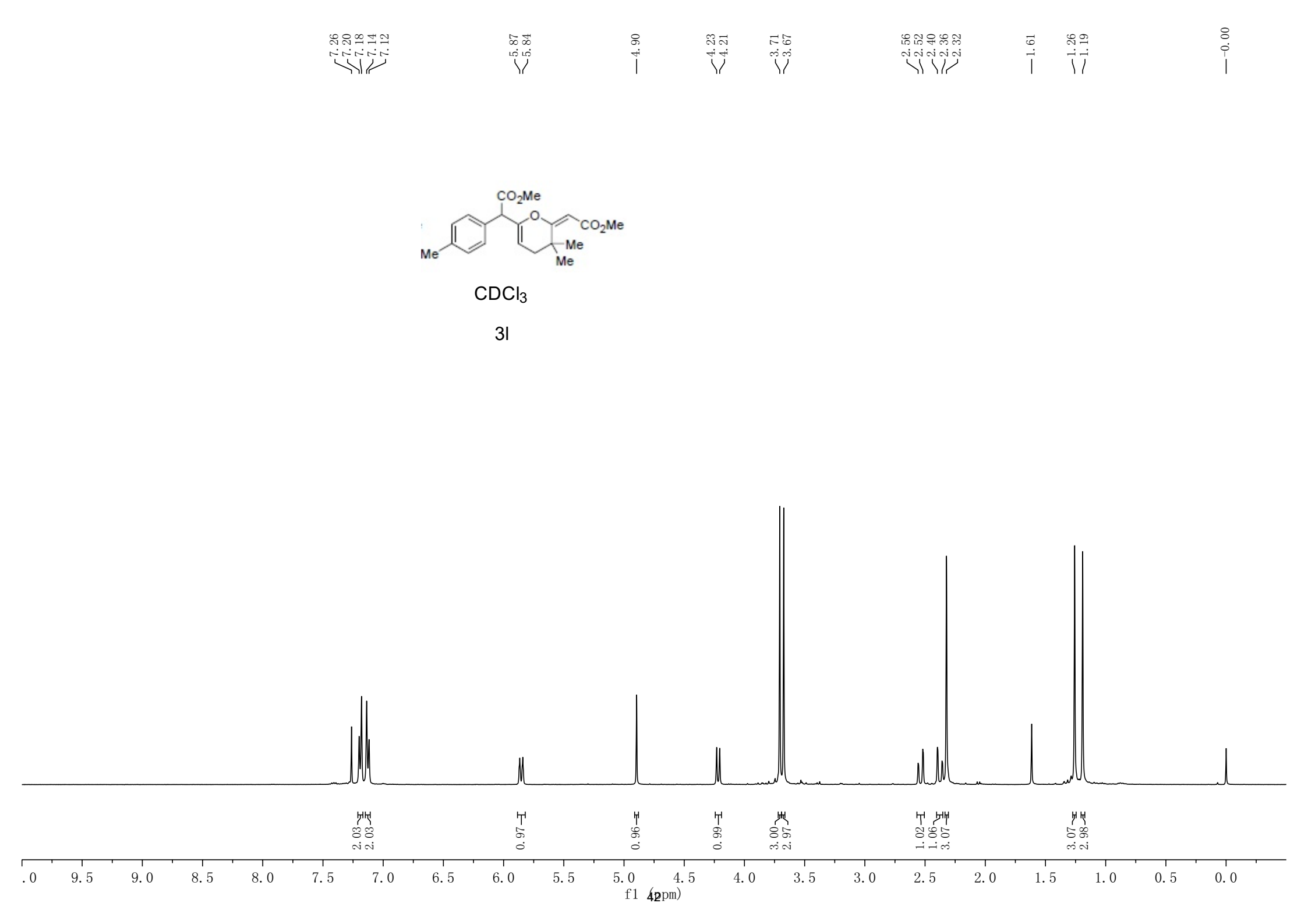
7.88
7.86
7.85
7.47
7.47
7.35
7.34
7.02
7.00
6.99
6.97
6.97
4.93
4.91
4.89
4.20
4.18
4.16
4.13
3.76
3.13
3.10
3.10
3.08
3.08
3.06
3.03
2.15
2.13
2.12
2.10
1.80
1.61
1.31
1.28
1.26
0.00
I
CO2Me
Me
O
CO2Et
CDCl3
3k
1.00
1.02
0.99
0.99
0.95
1.05
2.06
3.00
2.05
1.97
3.01
3.04
f1 (ppm)


170.58
168.93
160.08
148.12
139.75
138.28
129.44
129.42
128.43
106.70
102.90
101.83
77.36
77.04
76.73
60.09
59.55
52.65
22.85
19.03
14.35
11.58
I
CO2Me
Me
O
CO2Et
CDCl3
3k
f1 (ppm)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2.52
2.40
2.36
2.32
1.61
1.26
1.19
0.00
CO2Me
CO2Me
Me
Me
Me
CDCl3
3l
2.03
2.03
0.97
0.96
0.99
3.00
2.97
1.02
1.06
3.07
3.07
2.98
f1 (ppm)

176.44
172.80
165.95
154.52
137.16
135.32
129.44
127.49
101.95
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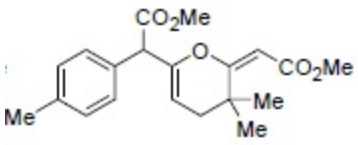
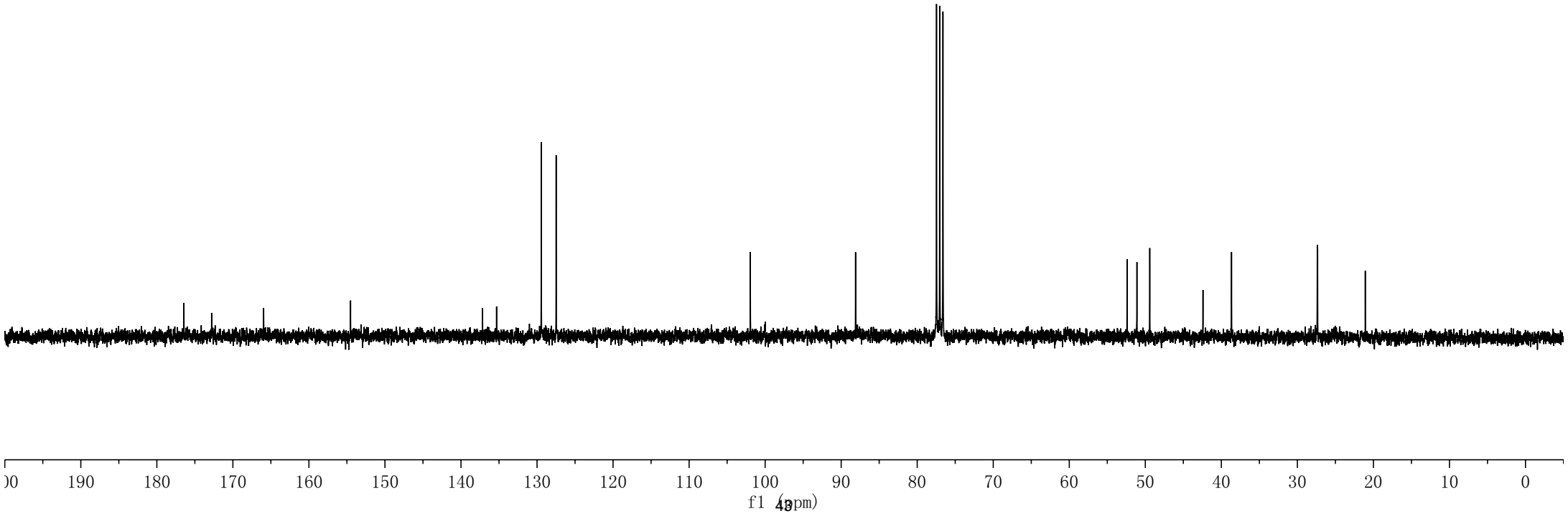
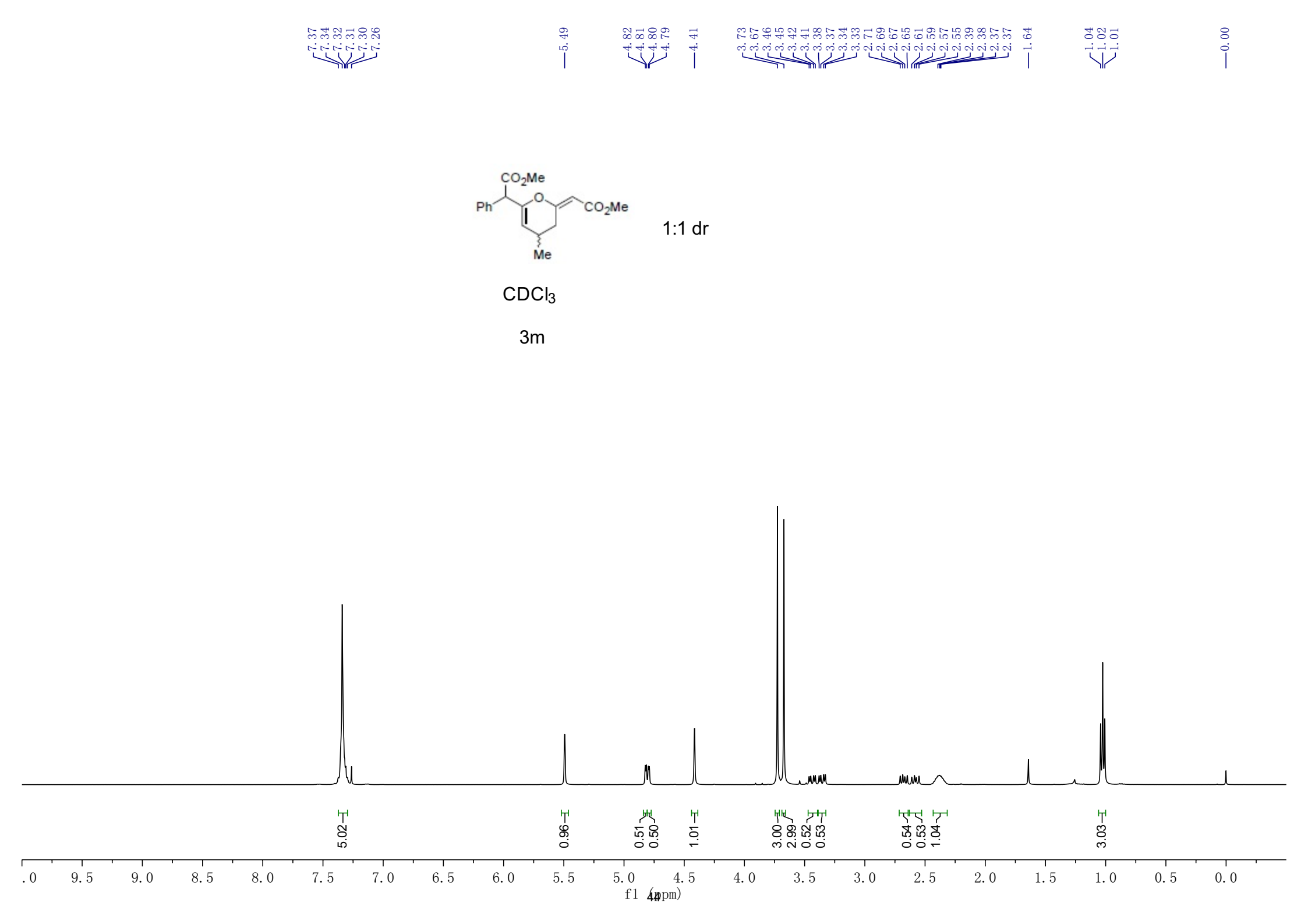


$CDCl_3$

3l

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4.41
3.73
3.67
3.46
3.45
3.42
3.41
3.38
3.37
3.34
3.33
2.71
2.69
2.67
2.65
2.61
2.59
2.57
2.55
2.39
2.38
2.37
2.37
1.64
1.04
1.02
1.01
0.00
CO2Me
Ph
O
CO2Me
Me
1:1 dr
CDCl3
3m
5.02
0.96
0.51
0.50
1.01
3.00
2.99
0.52
0.53
0.54
0.53
1.04
3.03
f1 (ppm)

170.92
167.95
167.65
167.50
148.17
148.14
134.70
134.68
128.92
128.67
127.95
127.93
109.22
108.99
98.50
98.30
77.48
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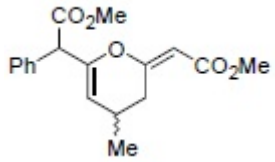
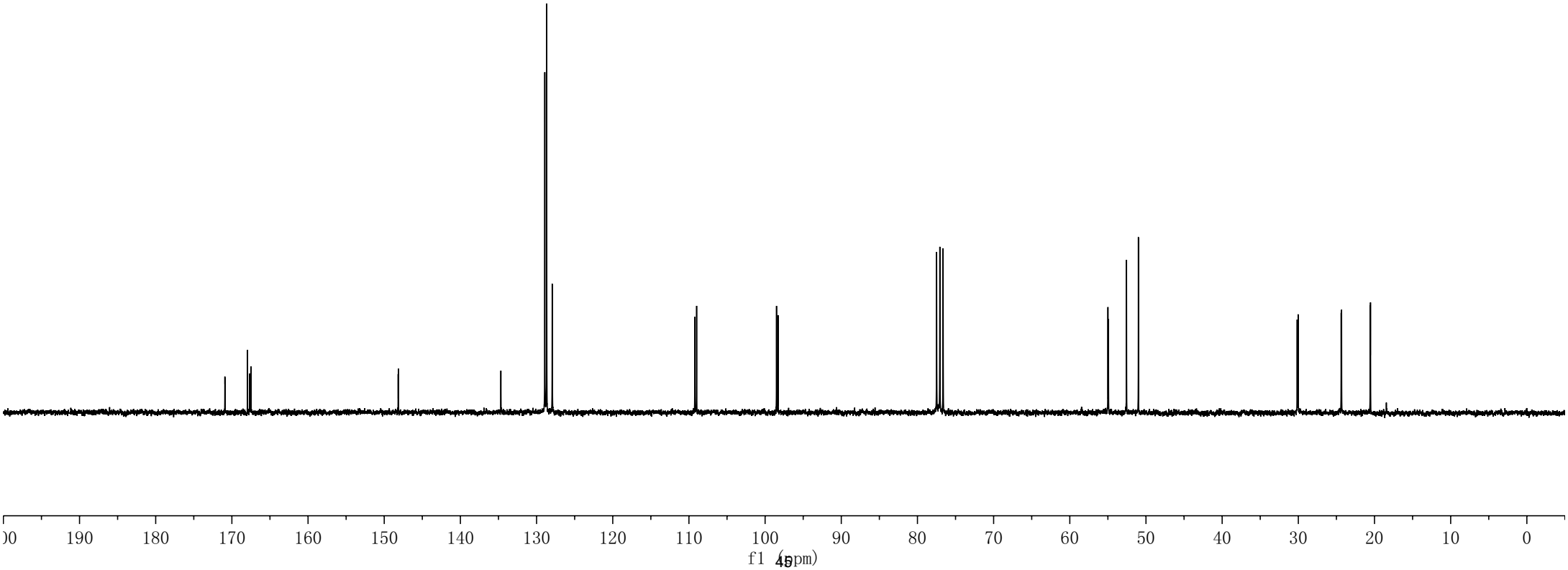
20.53

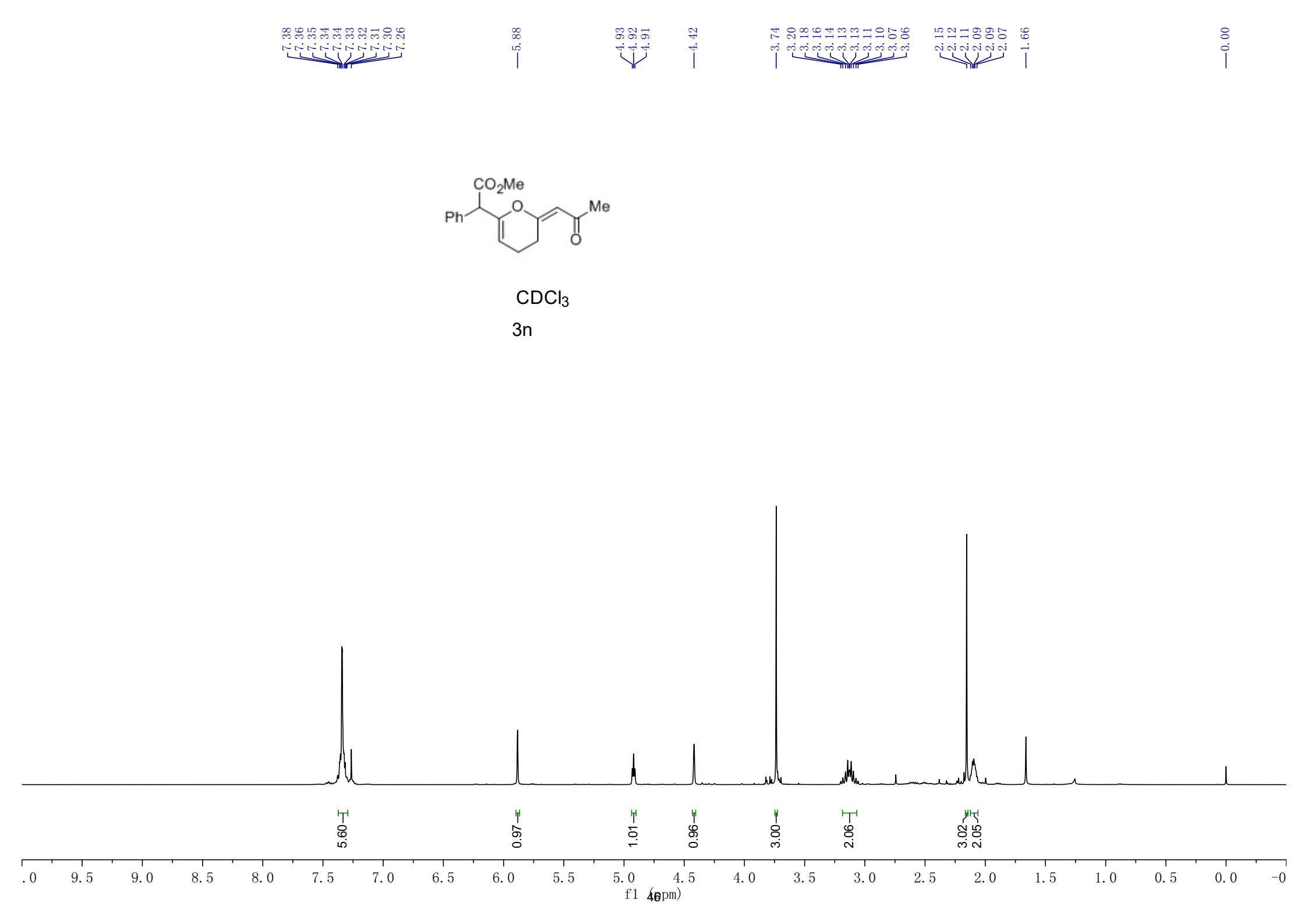


1:1 dr

$CDCl_3$

3m

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7.33
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7.31
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7.26
5.88
4.93
4.92
4.91
4.42
3.74
3.20
3.18
3.16
3.14
3.13
3.13
3.11
3.10
3.07
3.06
2.15
2.12
2.11
2.09
2.09
2.07
1.66
0.00
CO2Me
Ph
O
Me
O
CDCl3
3n
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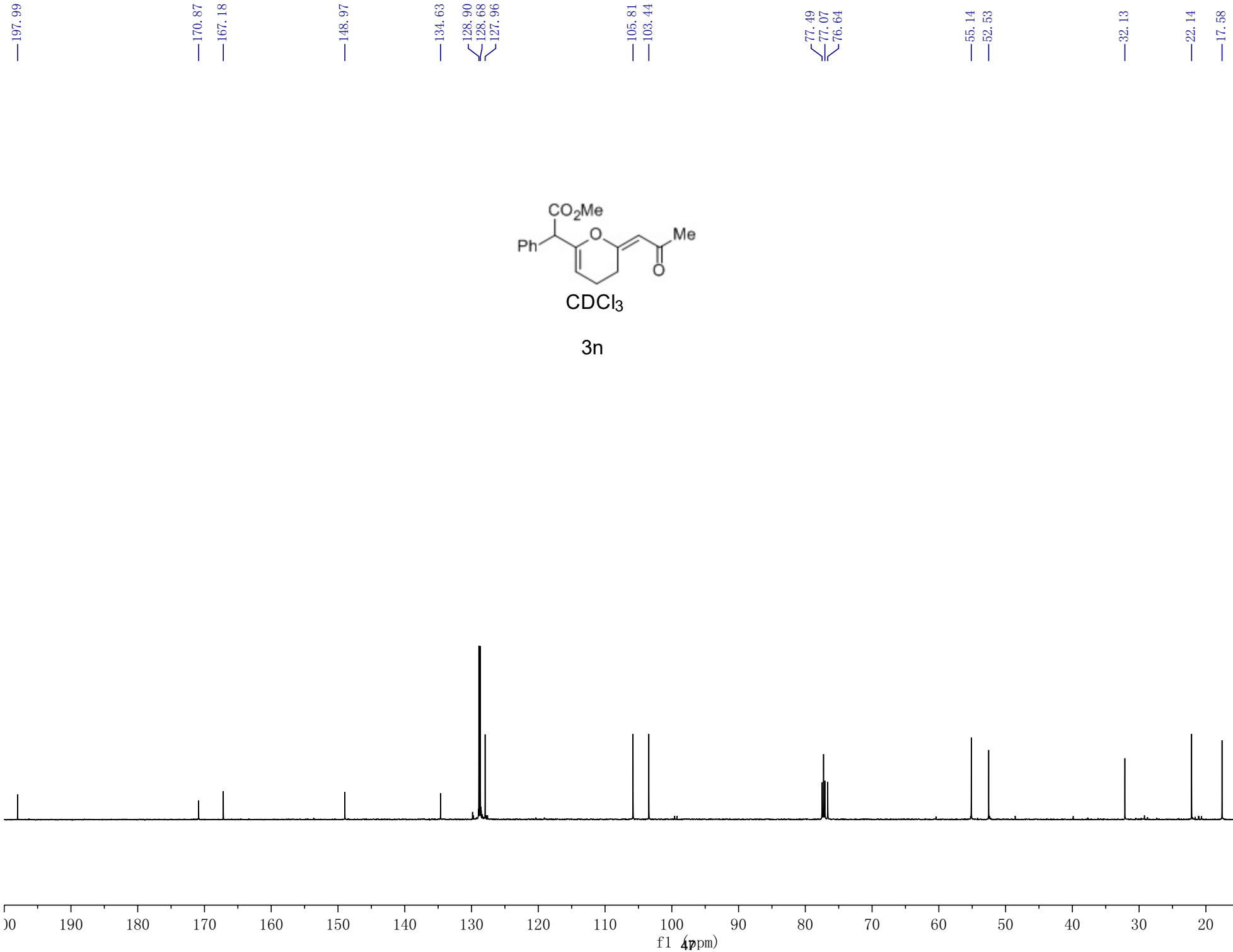
0.97
1.01
0.96
3.00
2.06
3.02
2.05
f1 (ppm)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127.96
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103.44
77.49
77.07
76.64
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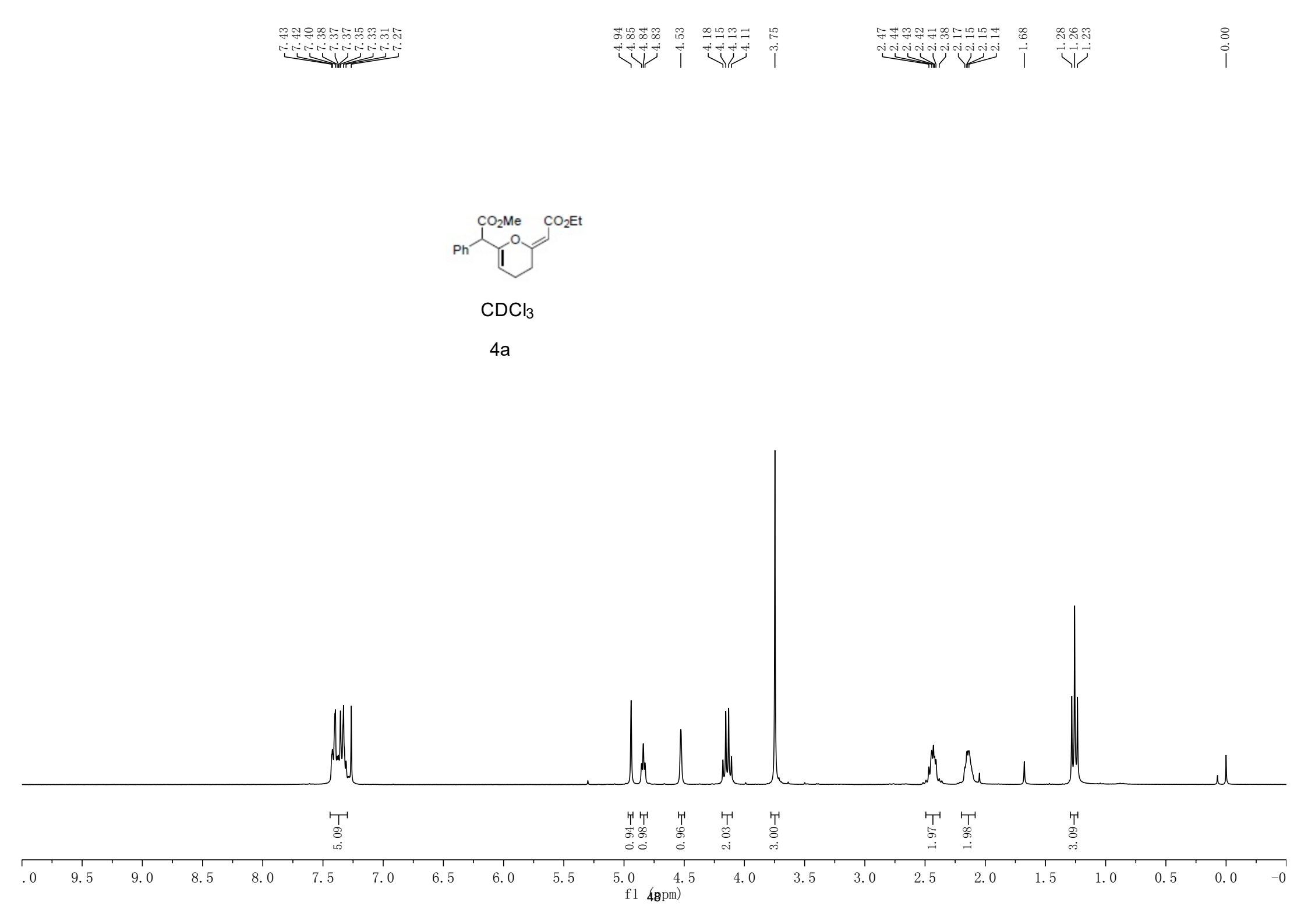
52.53
32.13
22.14
17.58
CO2Me
Ph
O
Me
O
CDCl3
3n
f1 (ppm)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7.27
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4.85
4.84
4.83
4.53
4.18
4.15
4.13
4.11
3.75
2.47
2.44
2.43
2.42
2.41
2.38
2.17
2.15
2.15
2.14
1.68
1.28
1.26
1.23
0.00
CO2Me
CO2Et
Ph
O
CDCl3
4a
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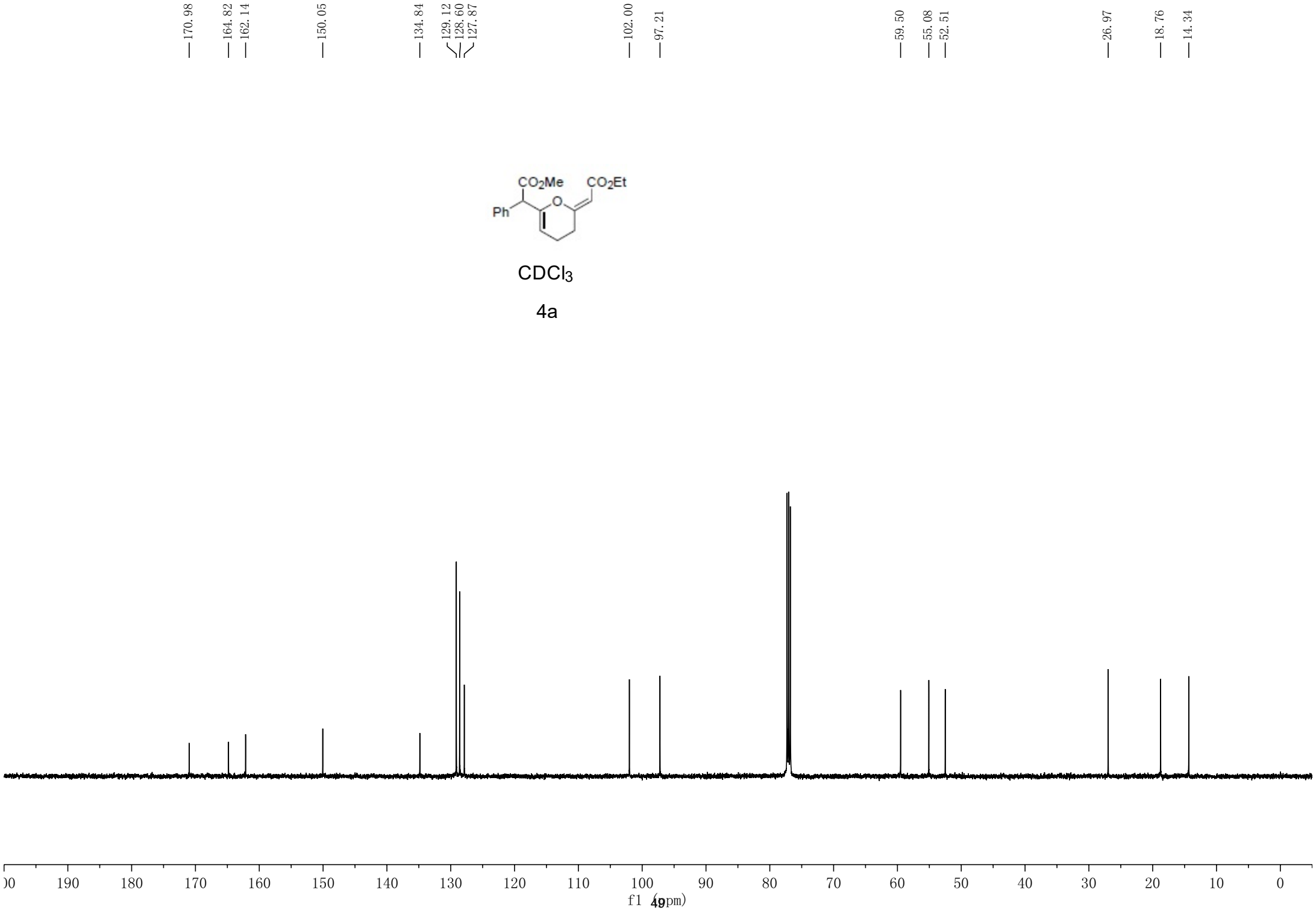
0.94
0.98
0.96
2.03
3.00
1.97
1.98
3.09
f1 (ppm)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97.21
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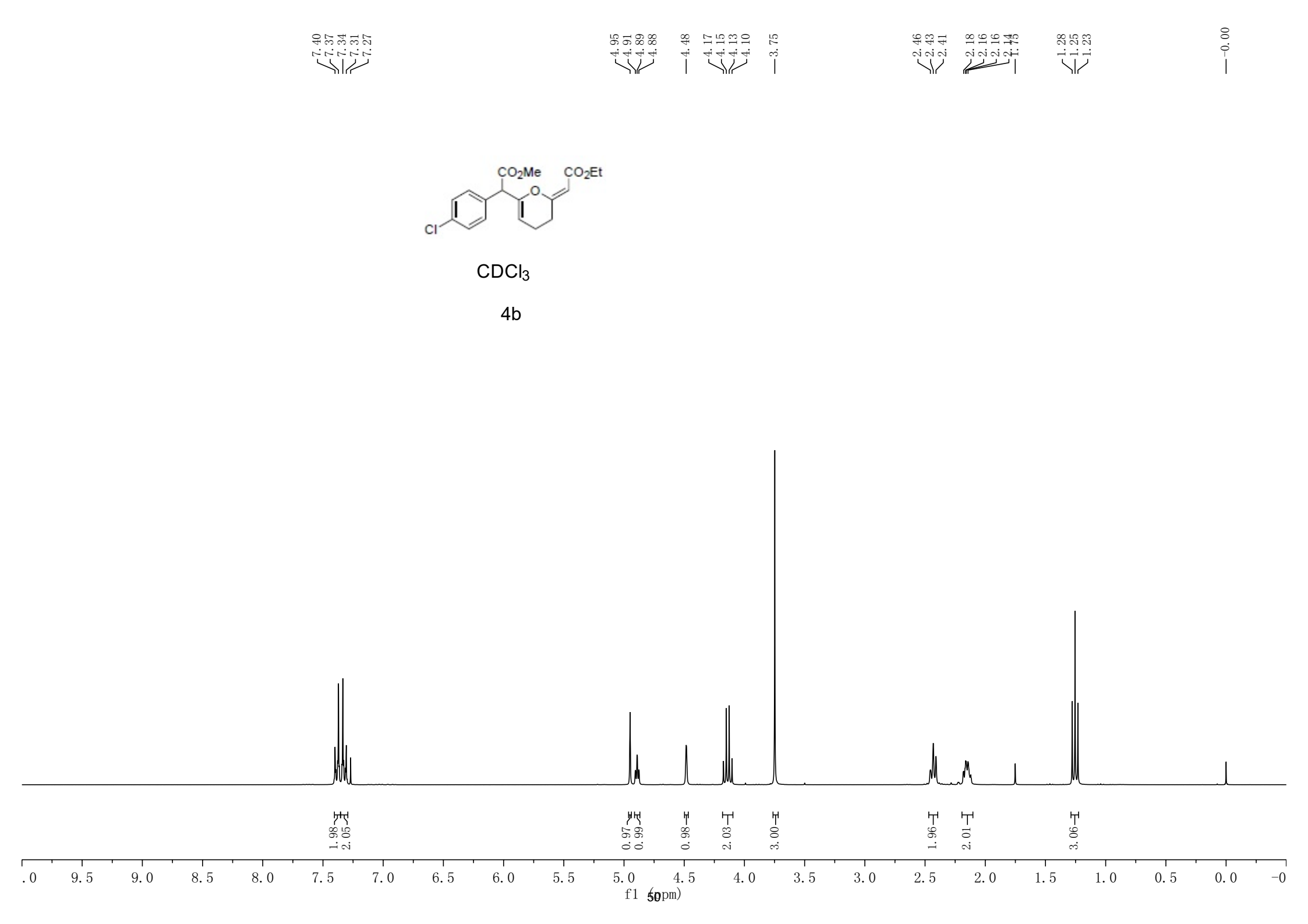
55.08
52.51
26.97
18.76
14.34
CO2Me
CO2Et
Ph
O
CDCl3
4a
f1 (ppm)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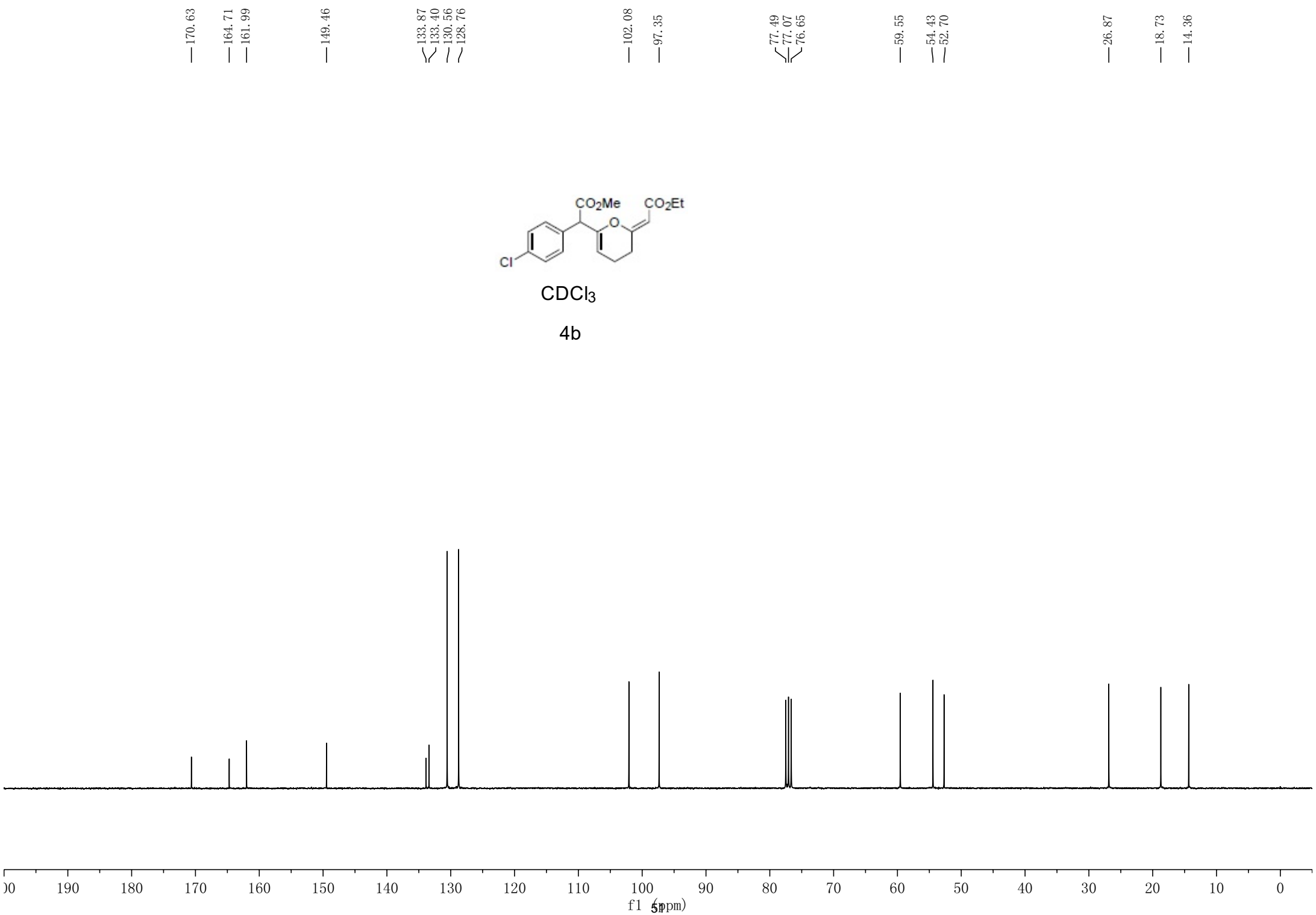
4.88
4.48
4.17
4.15
4.13
4.10
3.75
2.46
2.43
2.41
2.18
2.16
2.16
2.14
1.75
1.28
1.25
1.23
0.00
CO2Me
CO2Et
O
Cl
CDCl3
4b
1.98
2.05
0.97
0.99
0.98
2.03
3.00
1.96
2.01
3.06
f1 (ppm)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97.35
77.49
77.07
76.65
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54.43
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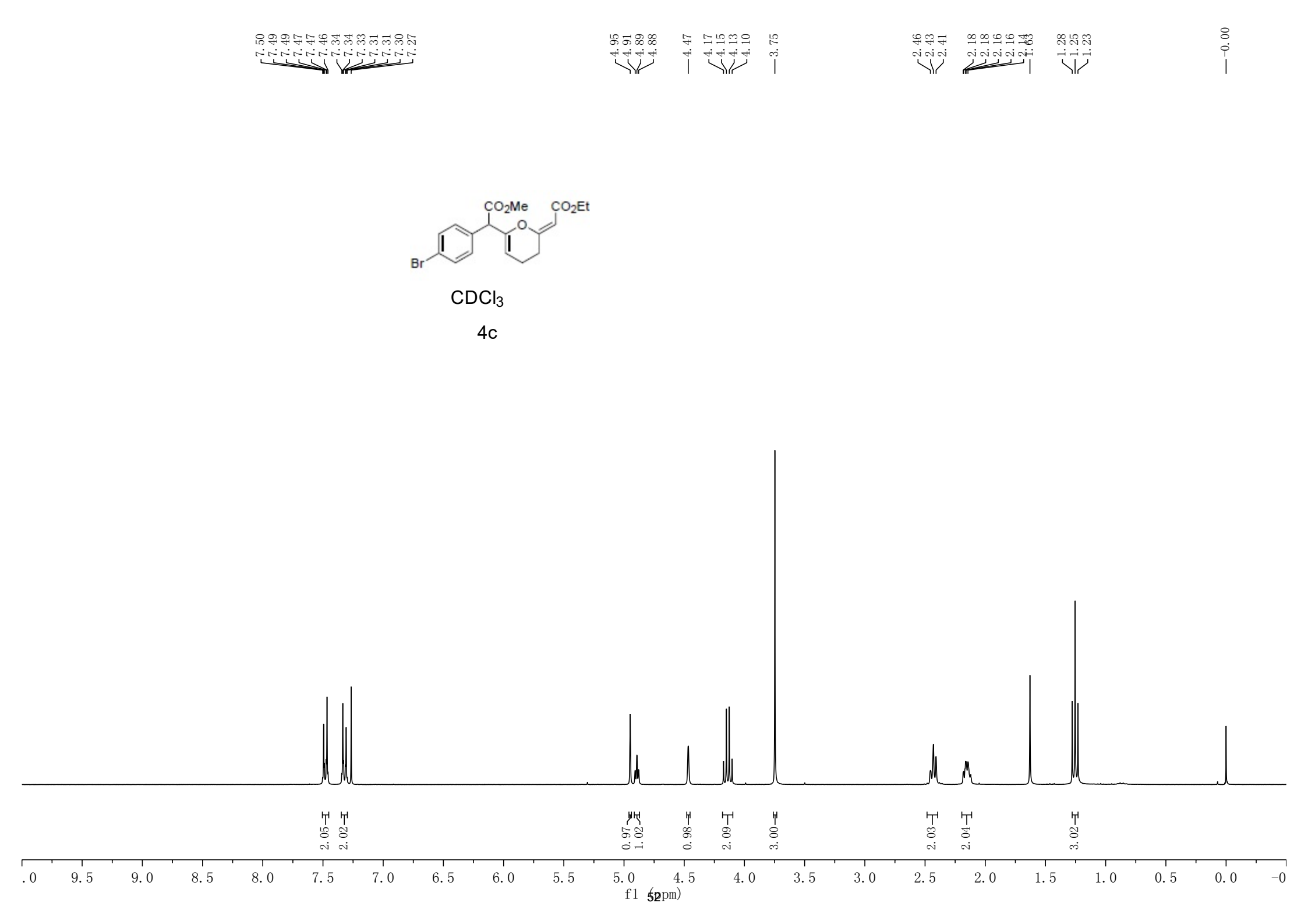
26.87
18.73
14.36
CO2Me
CO2Et
O
Cl
CDCl3
4b
f1 (ppm)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7.46
7.34
7.34
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7.31
7.31
7.30
7.27
4.95
4.91
4.89
4.88
4.47
4.17
4.15
4.13
4.10
3.75
2.46
2.43
2.41
2.18
2.18
2.16
2.16
1.63
1.28
1.25
1.23
0.00
CO2Me
CO2Et
O
Br
CDCl3
4c
2.05
2.02
0.97
1.02
0.98
2.09
3.00
2.03
2.04
3.02
f1 (ppm)

170.53
164.69
161.93
149.40
133.98
131.72
130.91
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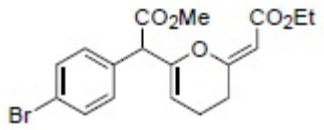

$CDCl_3$

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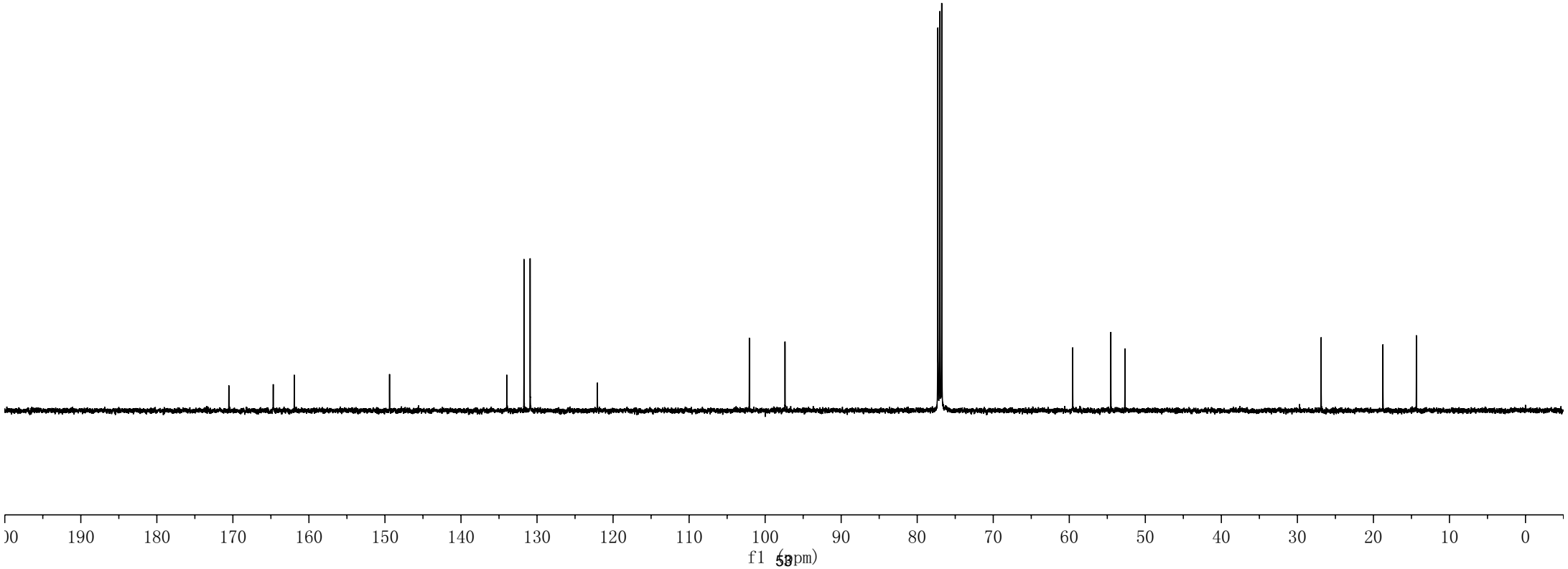

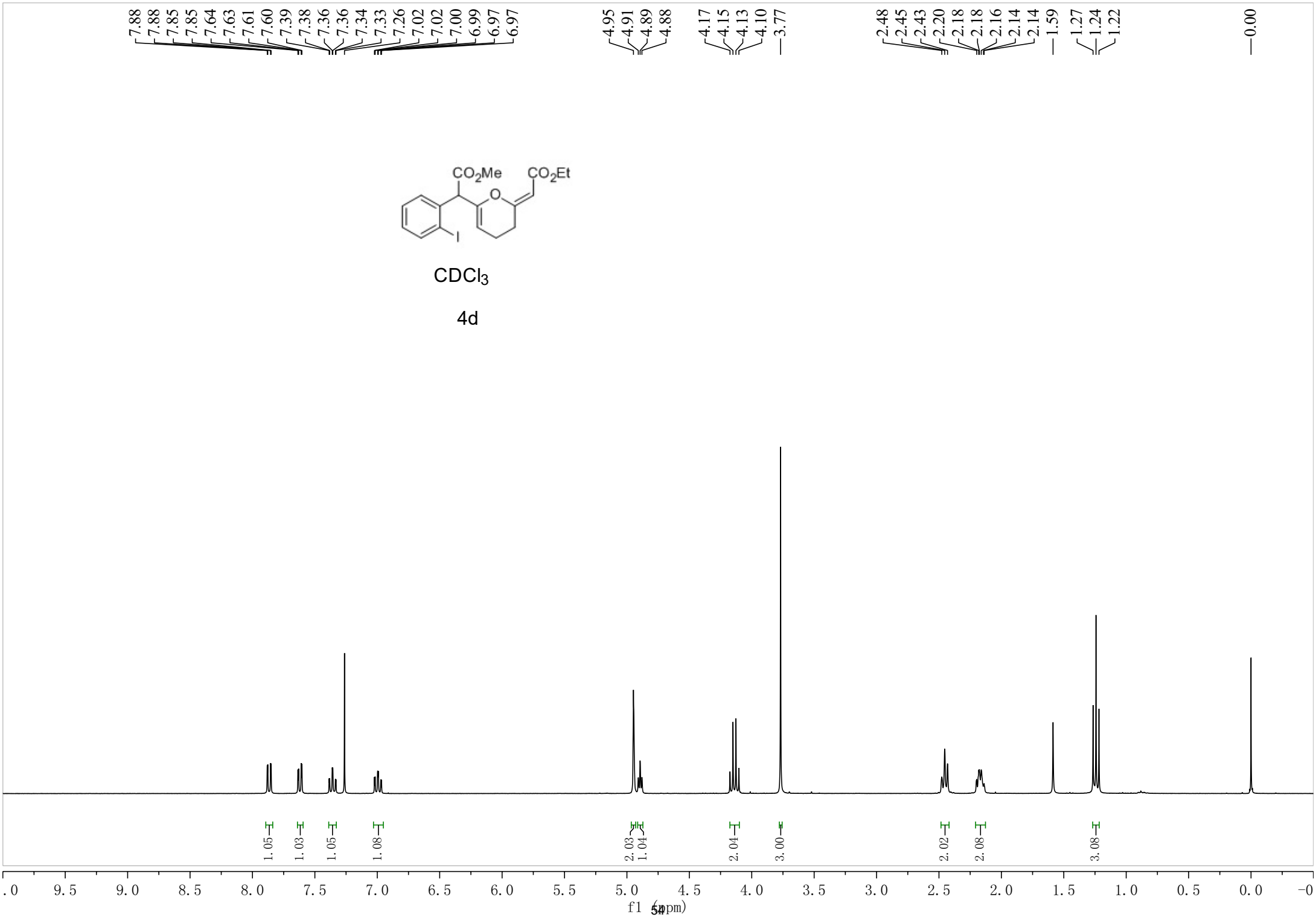
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7.38
7.36
7.36
7.34
7.33
7.26
7.02
7.02
7.00
6.99
6.97
6.97
4.95
4.91
4.89
4.88
4.17
4.15
4.13
4.10
3.77
2.48
2.45
2.43
2.20
2.18
2.18
2.16
2.14
2.14
1.59
1.27
1.24
1.22
0.00
CO2Me
CO2Et
O
I
CDCl3
4d
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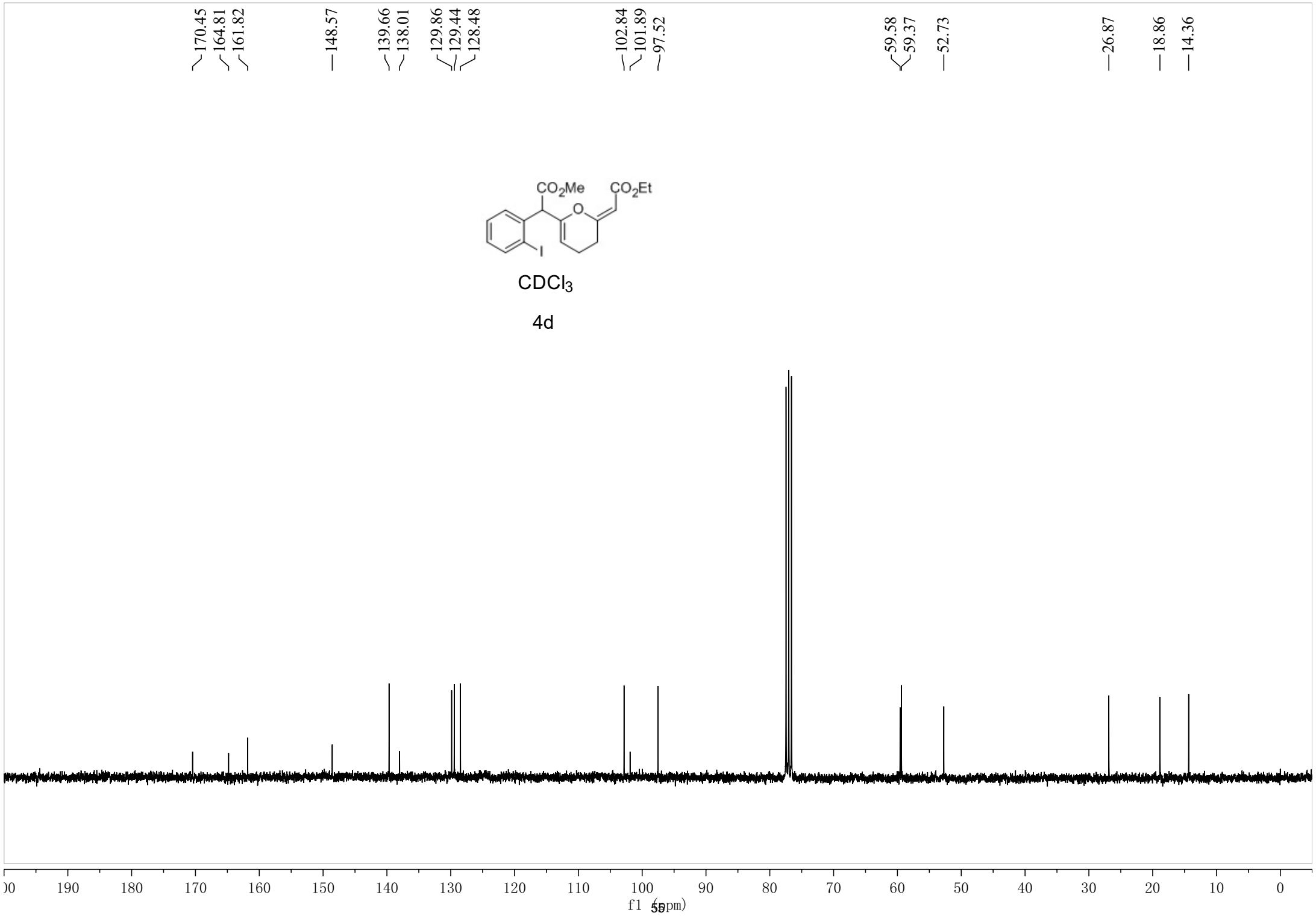
1.03
1.05
1.08
2.03
1.04
2.04
3.00
2.02
2.08
3.08
f1 (ppm)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129.44
128.48
102.84
101.89
97.52
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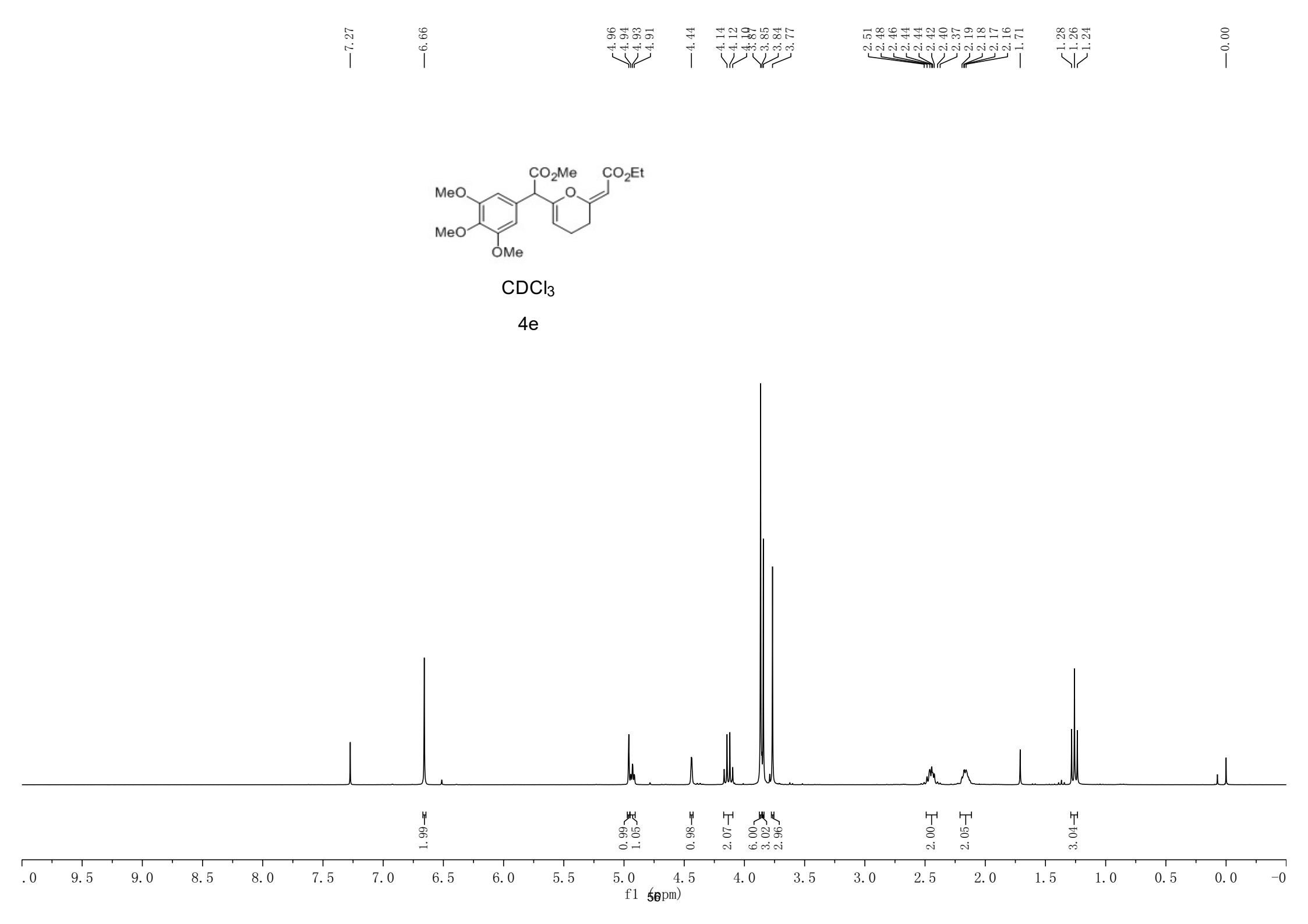
59.37
52.73
26.87
18.86
14.36
CO2Me
CO2Et
O
I
CDCl3
4d
f1 (ppm)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3.84
3.77
2.51
2.48
2.46
2.44
2.42
2.40
2.37
2.19
2.18
2.17
2.16
1.71
1.28
1.26
1.24
0.00
CO2Me
CO2Et
MeO
MeO
OMe
O
CDCl3
4e
1.99
0.99
1.05
0.98
2.07
6.00
3.02
2.96
2.00
2.05
3.04
f1 (ppm)

170.97
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162.34
153.21
149.84
137.60
130.23
106.26
101.90
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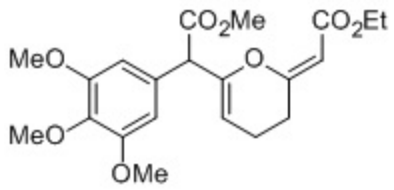
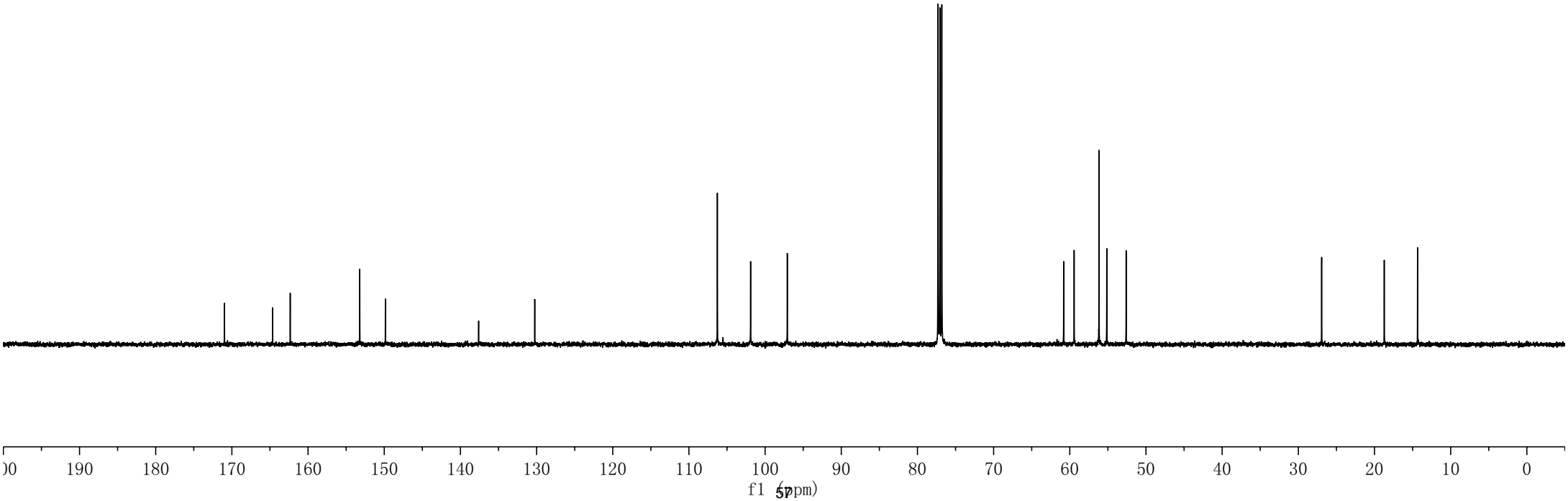
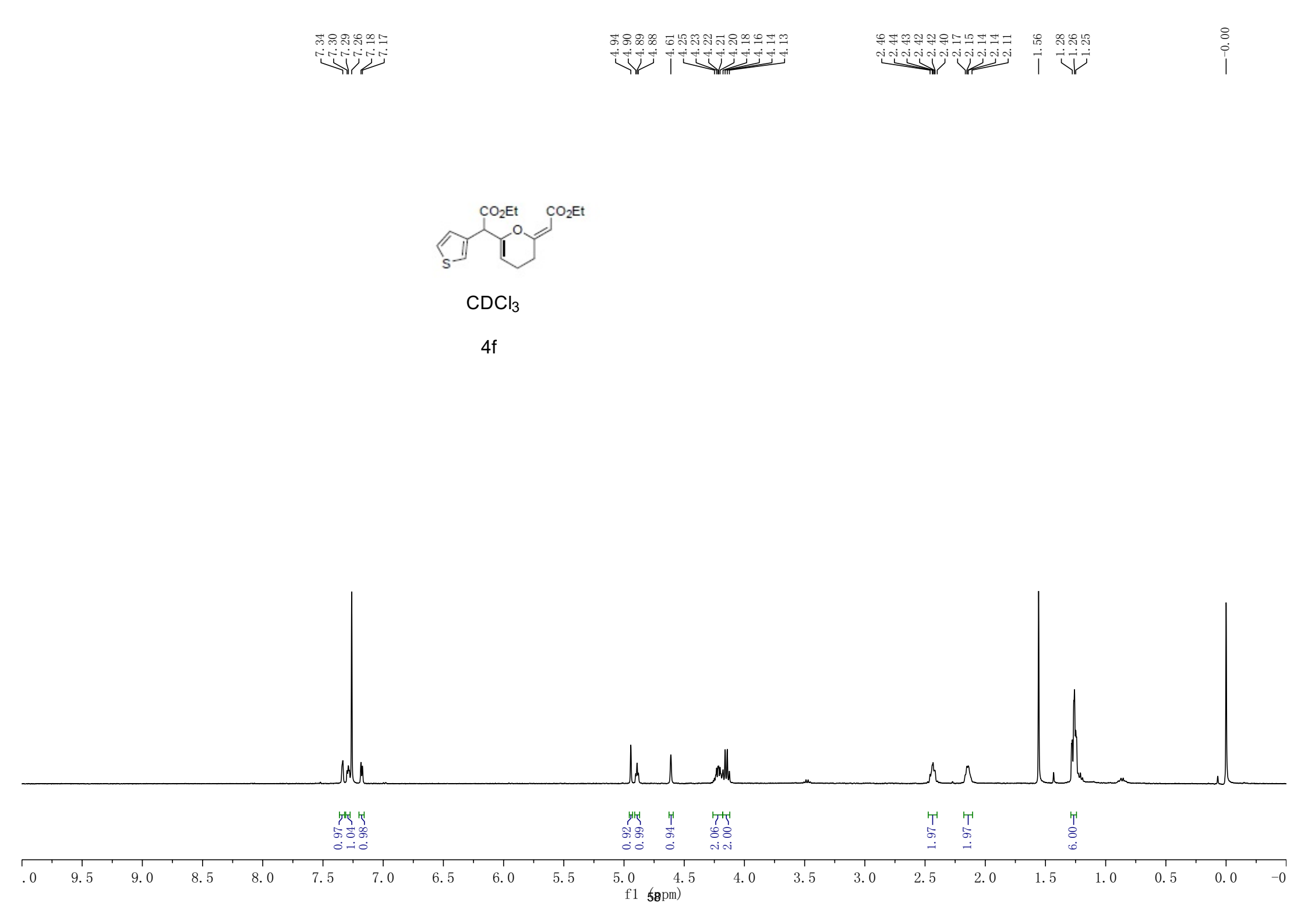
18.72
14.35



$CDCl_3$

4e

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4.23
4.22
4.21
4.20
4.18
4.16
4.14
4.13
2.46
2.44
2.43
2.42
2.42
2.40
2.17
2.15
2.14
2.14
2.11
1.56
1.28
1.26
1.25
0.00
CO2Et
CO2Et
O
S
CDCl3
4f
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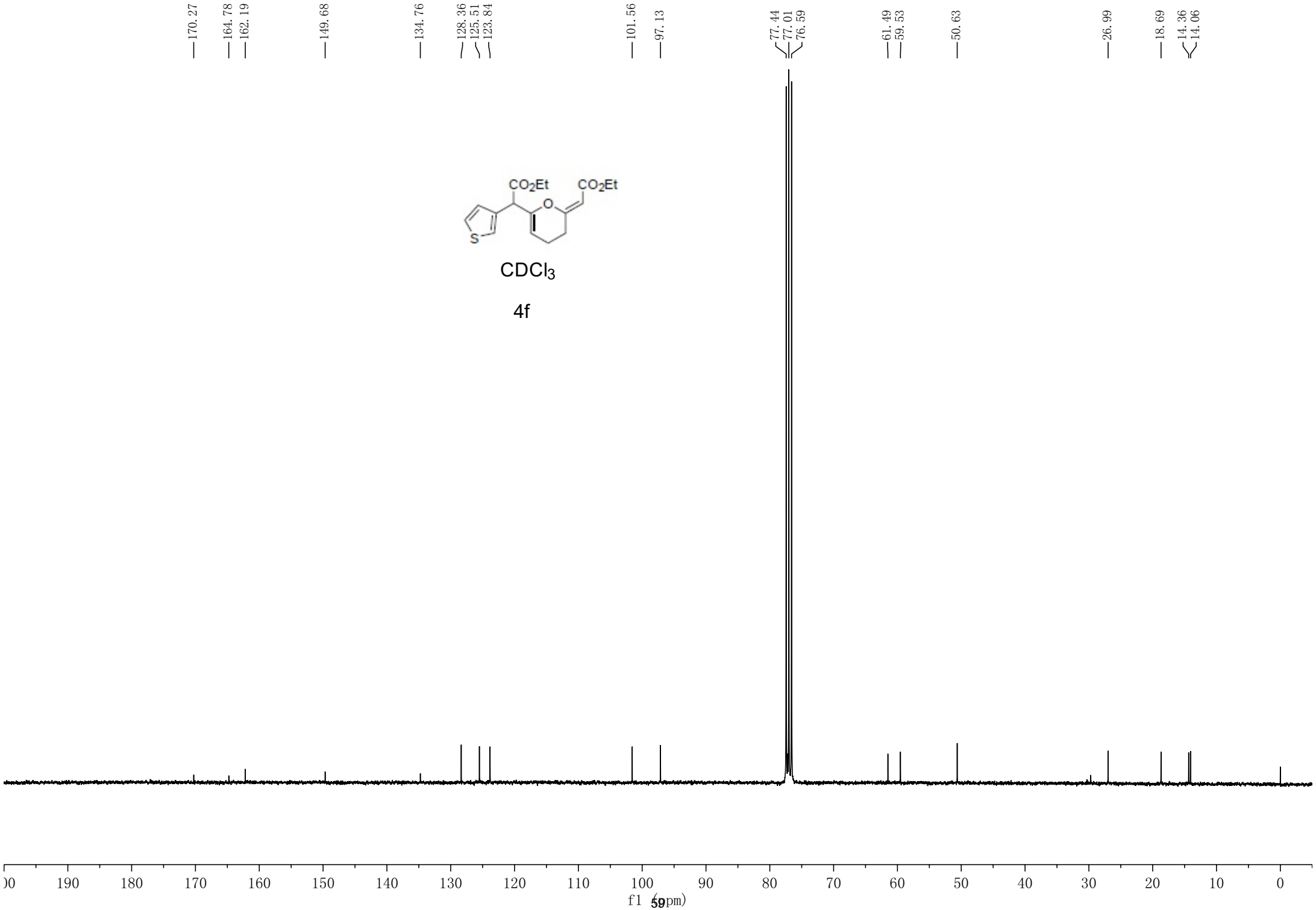
0.92
0.99
0.94
2.06
2.00
1.97
1.97
6.00
f1 (ppm)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77.44
77.01
76.59
61.49
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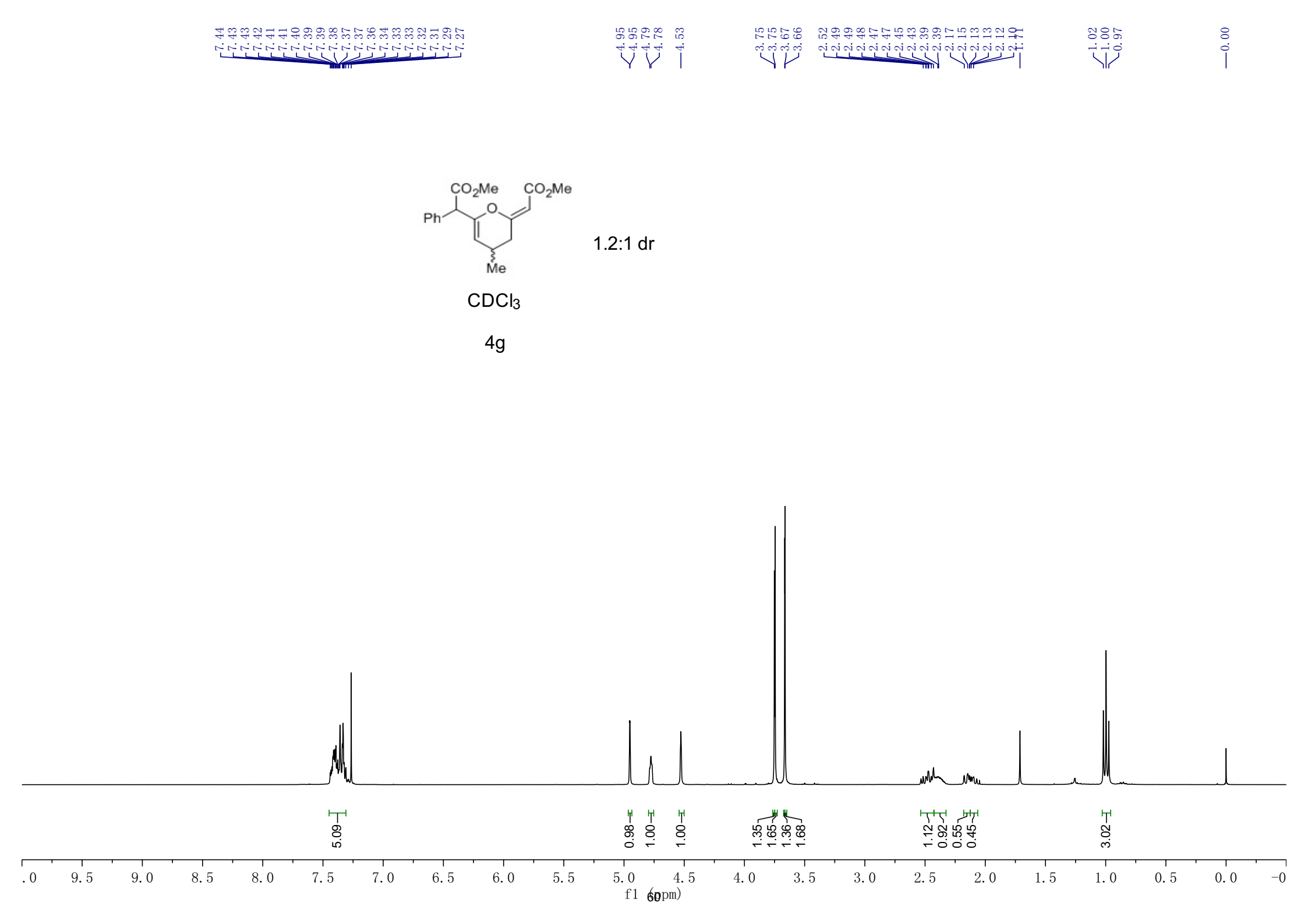
14.36
14.06
CO2Et
CO2Et
O
S
CDCl3
4f
f1 (ppm)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7.33
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7.29
7.27
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2.45
2.43
2.39
2.39
2.17
2.15
2.13
2.13
2.12
1.71
1.02
1.00
0.97
0.00
CO2Me
CO2Me
Ph
O
Me
1.2:1 dr
CDCl3
4g
5.09
0.98
1.00
1.00
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1.65
1.36
1.68
1.12
0.92
0.55
0.45
3.02
f1 (ppm)

171.02
171.01
165.22
165.18
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161.98
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134.81
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129.14
128.61
127.90
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108.33
108.13
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97.15
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77.06
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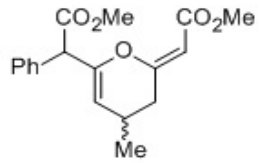
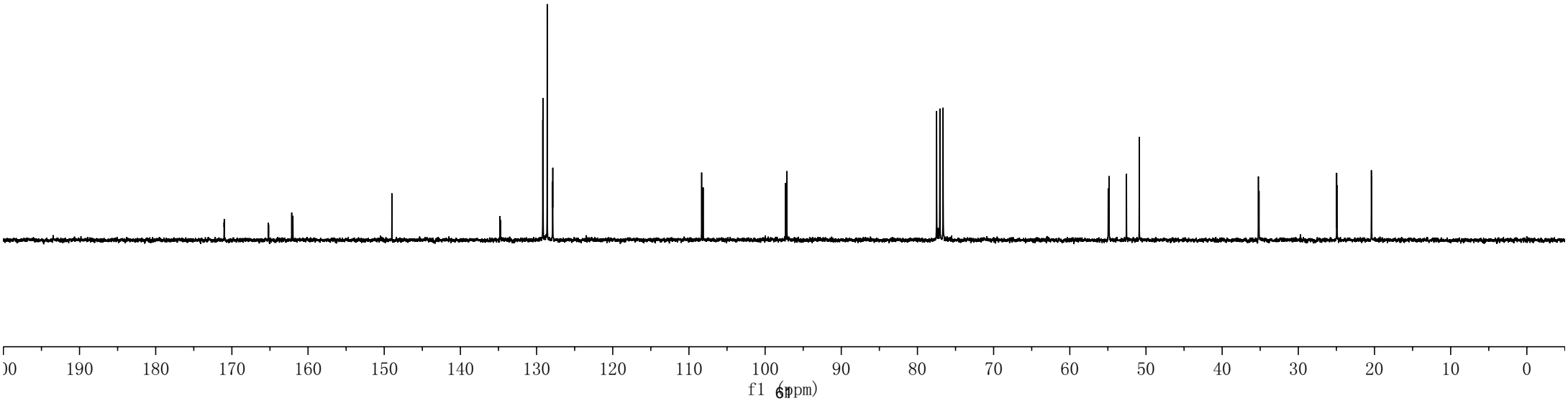
20.38

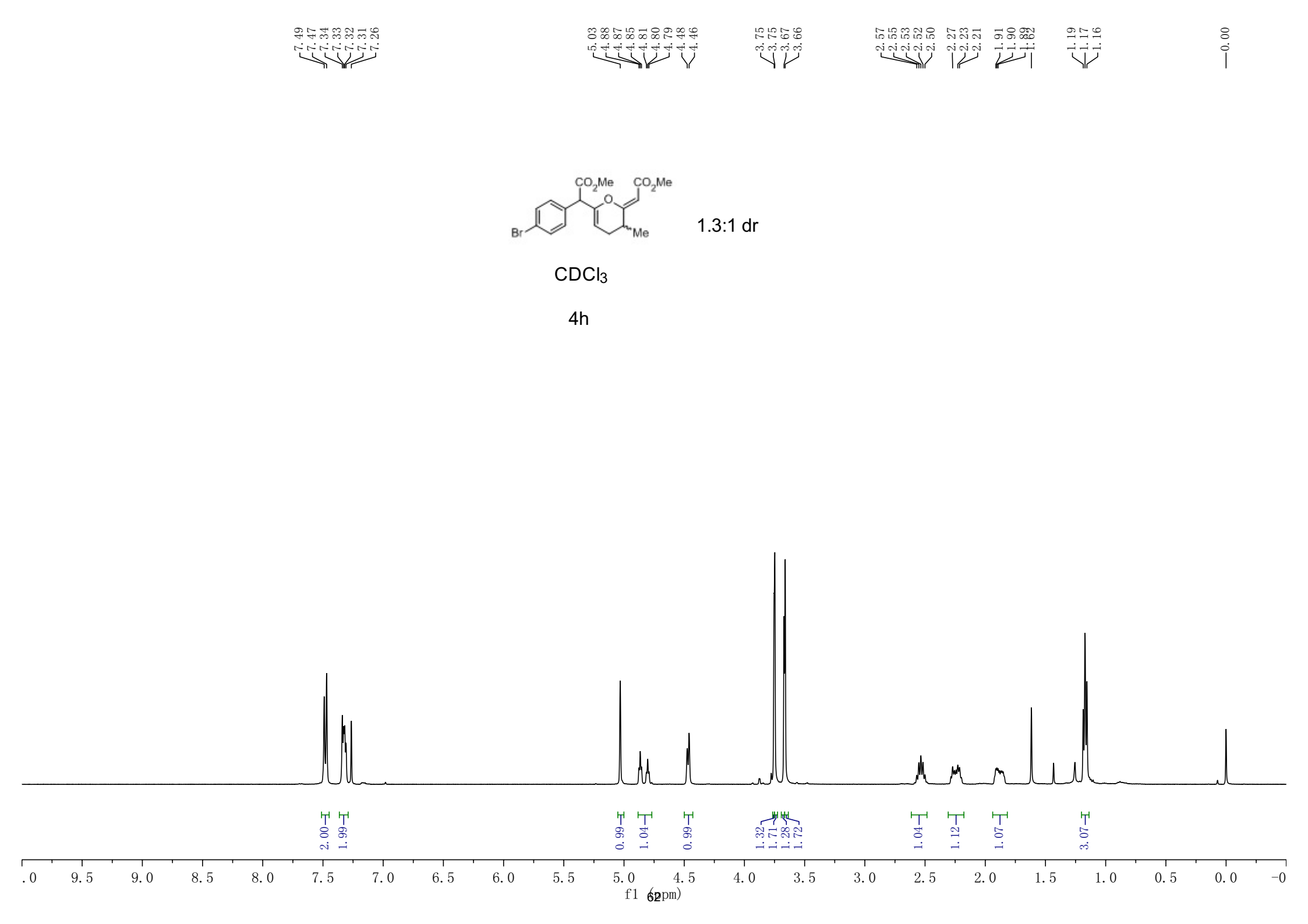


1.2:1 dr

$CDCl_3$

4g

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4.48
4.46
3.75
3.75
3.67
3.66
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2.52
2.50
2.27
2.23
2.21
1.91
1.90
1.62
1.19
1.17
1.16
0.00
CO2Me
CO2Me
O
Br
Me
1.3:1 dr
CDCl3
4h
2.00
1.99
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1.32
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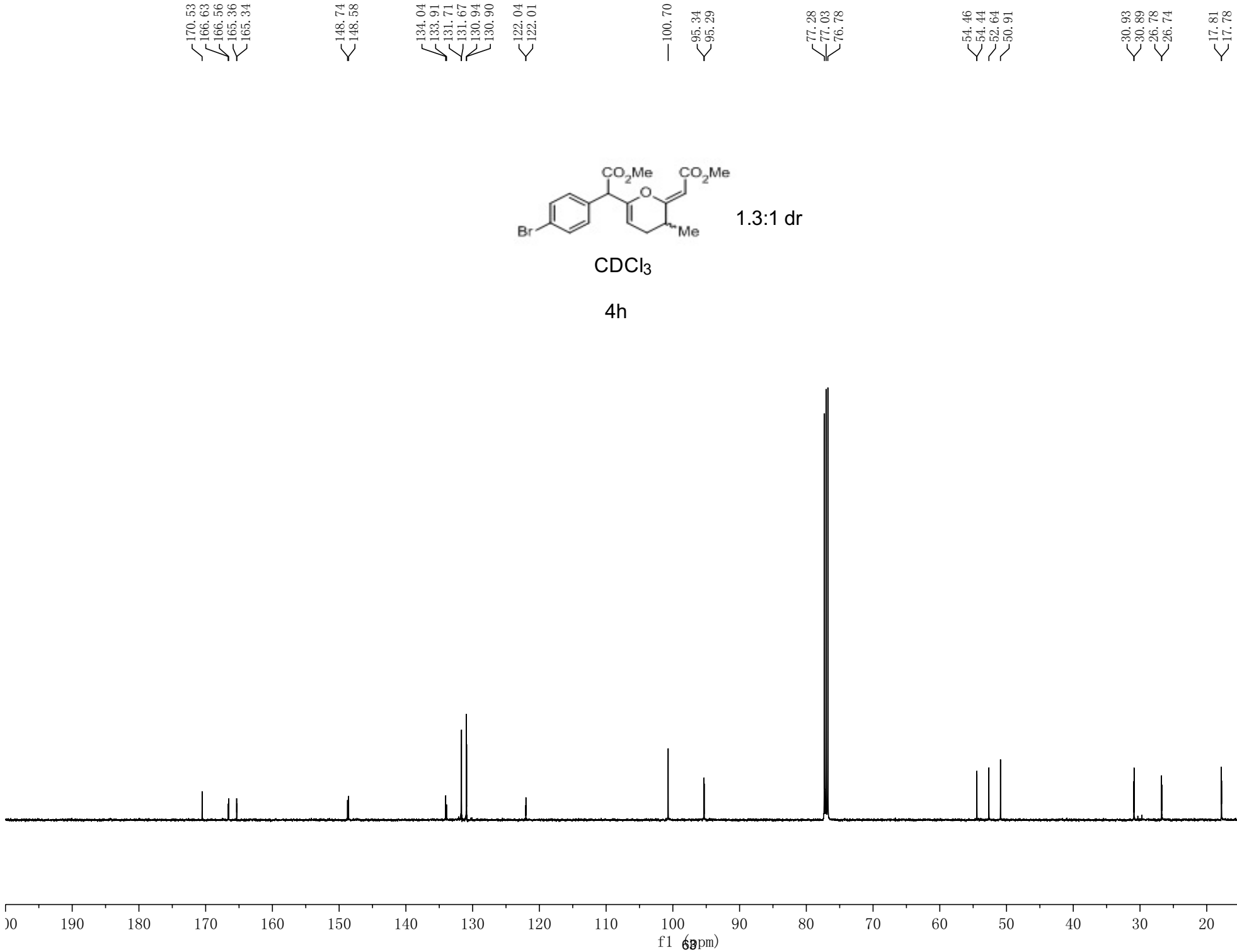
1.28
1.72
1.04
1.12
1.07
3.07
f1 (ppm)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131.67
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130.90
122.04
122.01
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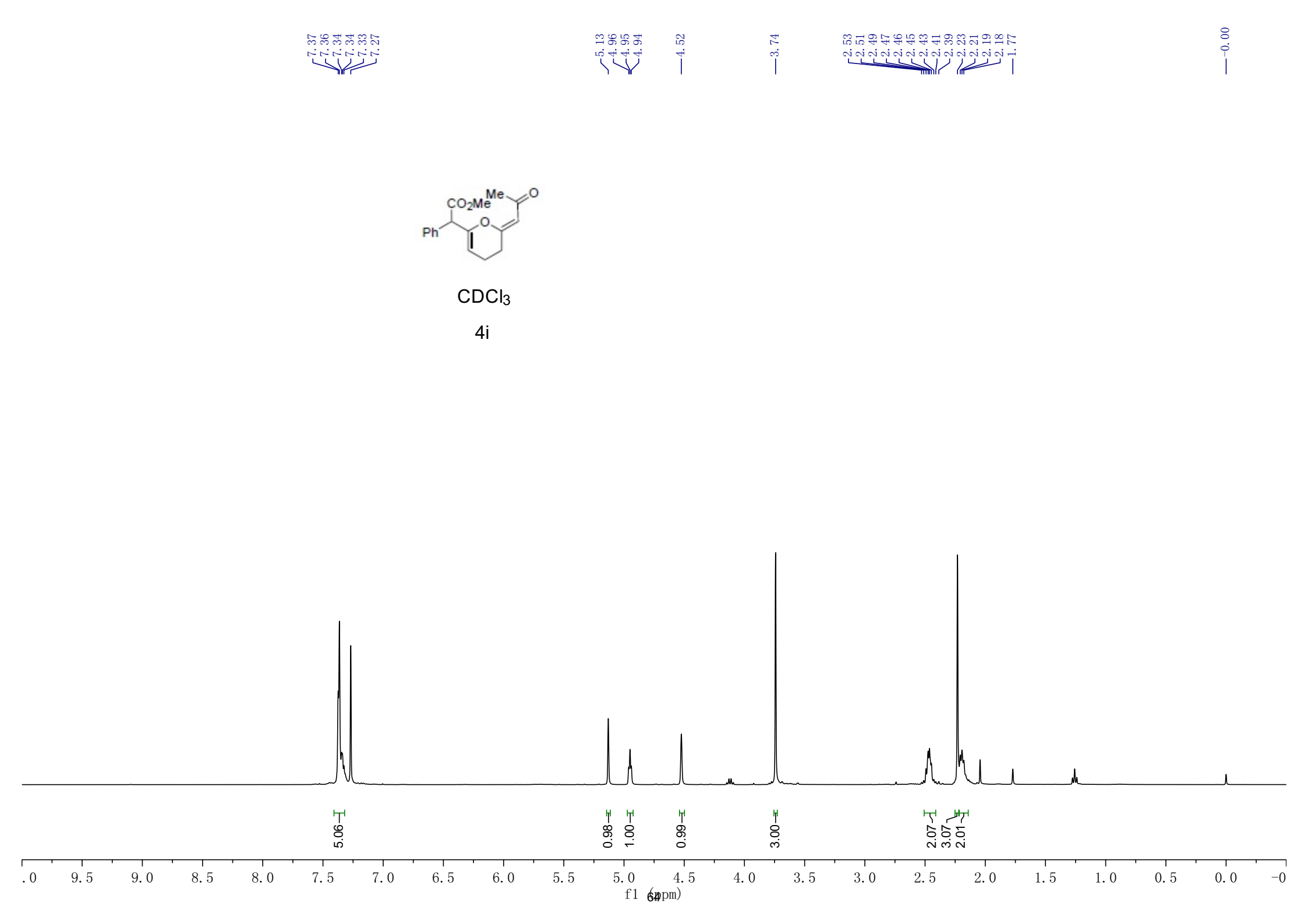
95.29
77.28
77.03
76.78
54.46
54.44
52.64
50.91
30.93
30.89
26.78
26.74
17.81
17.78
CO2Me
CO2Me
O
Br
Me
1.3:1 dr
CDCl3
4h
f1 (ppm)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2.23
2.21
2.19
2.18
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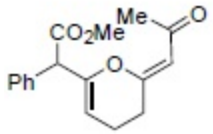
Me
O
CO2Me
O
Ph
CDCl3
4i
5.06
0.98
1.00
0.99
3.00
2.07
3.07
2.01
f1 (ppm)

197.69
170.84
161.42
149.58
134.39
128.94
128.77
128.13
109.17
102.66
77.48
77.06
76.64
55.08
52.58
31.28
27.02
18.68



$CDCl_3$

4i