Supporting Information

Metal Free Biomimetic Deaminative Direct C-C Coupling of Unprotected Primary Amines with Active Methylene Compounds

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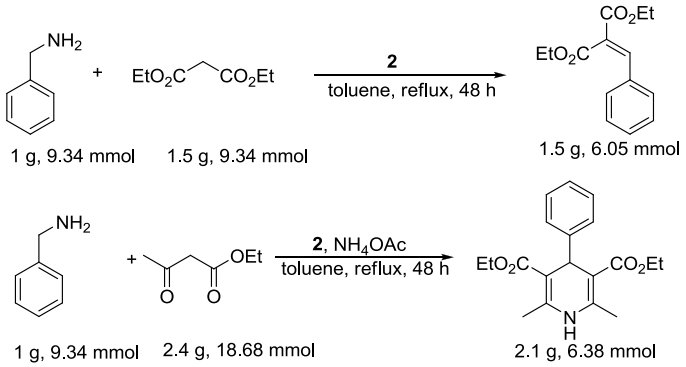
Experimental:

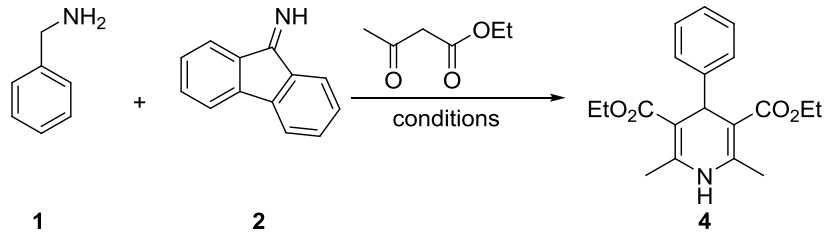
General: All reactions involving air- or moisture-sensitive reagents or intermediates were carried out in oven-dried glassware under an argon atmosphere. Dichloromethane (CH_2Cl_2) was freshly distilled from phosphorus (V) oxide (P_2O_5). Commercial grade xylene, benzene and toluene were distilled over CaH_2 before use. All other solvents and reagents were purified according to standard procedures or were used as received from Aldrich, Acros, Merck and Spectrochem. ^1H, ^{13}C NMR spectroscopy: *Varian Mercury plus 400 MHz, Bruker 600 MHz* (at 298 K), *Bruker 400 MHz* (at 298 K). Chemical shifts, δ (in ppm), are reported relative to TMS δ (^1H) 0.0 ppm, δ (^{13}C) 0.0 ppm) which was used as the inner reference. Otherwise the solvents residual proton resonance and carbon resonance ($CDCl_3$, δ (^1H) 7.26 ppm, δ (^{13}C) 77.2 ppm; DMSO-d_6, (^1H) 2.50 ppm, δ (^{13}C) 39.6 ppm) were used for calibration. Column chromatography: Merck or Spectrochem silica gel 60-120 under gravity. MS (ESI-HRMS): Mass spectra were recorded on an Agilent Accurate-Mass Q-TOF LC/MS 6520, and peaks are given in *m/z* (% of basis peak).

Scheme s1: Gram scale synthesis



The major byproduct of the reaction, 9-Fluorenone, which was isolated easily, can be recycled after its conversion to 9-Fluorenone imine.

Table s1: Optimization of the reaction conditions for the synthesis of dihydropyridines.[a]



1 **2** **4**

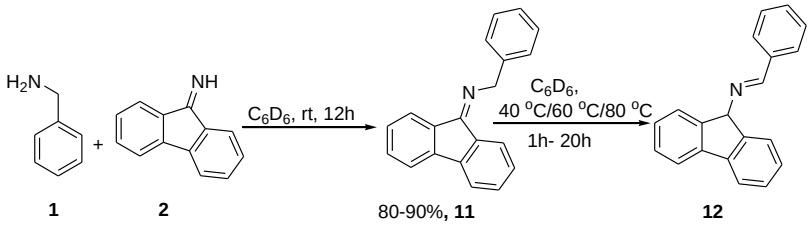
entry	conditions	yield[b]
1	toluene, rt, 12 h	0
2	toluene, reflux, 12 h	10
3	toluene, reflux, 24 h	12
4	toluene, reflux, 48 h	13
5	toluene, close tube, 48 h	45
6	neat, close tube, 48 h	51
7	neat, close tube, 60 h	50
8	toluene, reflux, 48 h, NH_4OAc (1 eq)	63
9	**toluene, reflux, 48 h, NH_4OAc (2 eq)**	**68**
10	toluene, reflux, 48 h, NH_4OAc (3 eq)	67
11	toluene, reflux, 60 h, NH_4OAc (2 eq)	69

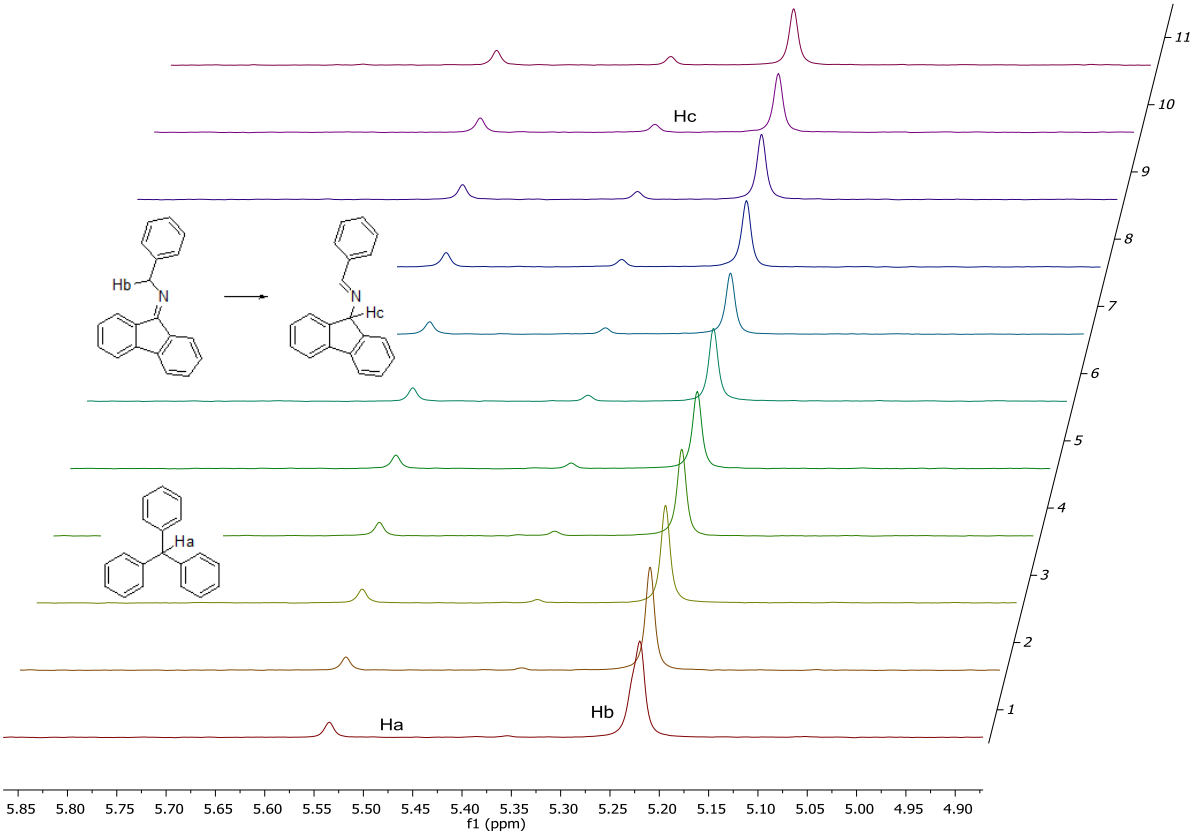
12	toluene, reflux, 36 h, NH_4OAc (2 eq)	53
13	toluene, reflux, 24 h, NH_4OAc (2 eq)	45
14	toluene, reflux, 12 h, NH_4OAc (2 eq)	35
15	xylene, reflux, 48 h, NH_4OAc (2 eq)	68
16	xylene, reflux, 24 h, NH_4OAc (2 eq)	48
17	DCE, reflux, 48 h, NH_4OAc (2 eq)	40
18	MeOH, reflux, 48 h, NH_4OAc (2 eq)	25
19	DMF, reflux, 48 h, NH_4OAc (2 eq)	50
20	benzene, reflux, 48 h, NH_4OAc (2 eq)	48
21	DCM, reflux, 48 h, NH_4OAc (2 eq)	12
22	neat, 130 ^oC, 48 h, NH_4OAc (2 eq)	67
23	neat, 130 ^oC, 48 h, NH_4OAc (1 eq)	64
24	neat, MW, 120 ^oC, 45 min, NH_4OAc (2 eq)	60
25	toluene, MW, 120 ^oC, 45 min, NH_4OAc (2 eq)	58
26	THF, reflux, 48 h, NH_4OAc (2 eq)	35

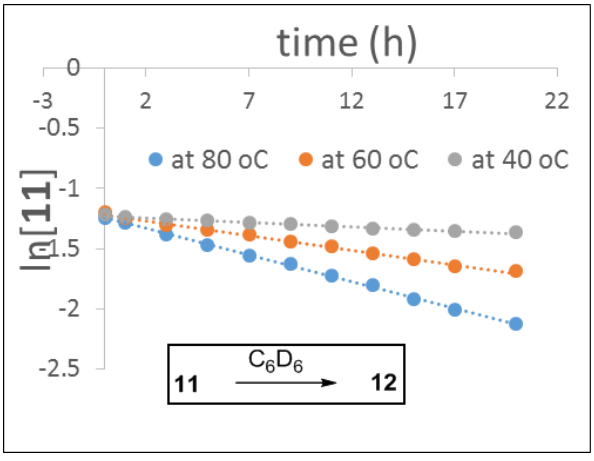
[a]1eq (0.56 mmol) benzyl amine, 1eq 9-fluuorneone imine (0.56 mmol), and 2 eq ethylacetoacetate (1.12 mmol) were reacted in 2 mL solvent. [b]Isolated yield.

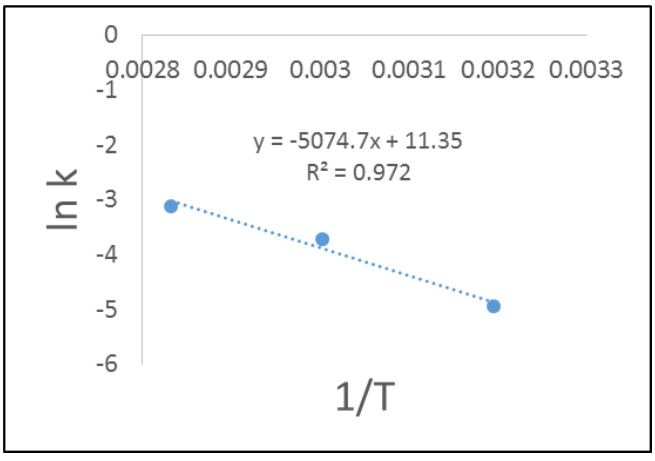
Kinetic experiments:

In a NMR tube, benzylamine (30 mg, 0.28 mmol) was added to a solution of 9-fluorenone imine **2** (50 mg, 0.28 mmol) and tripheylmethane (13.8 mg, 0.056 mmol) in benzene-d_6 (0.75 mL) and the solution was kept 12 h in room temperature. The yield of the imine **11** was calculated to be 80-90% form the ^1H NMR experiment. Then the mixture was heated and the time dependent concentrations of **11** was calculated using ^1H-NMR experiments.


H2N
NH
C6D6, rt, 12h
N
C6D6,
40 °C/60 °C/80 °C
1h- 20h
N
1
2
80-90%, 11
12


Hb
N
N
Hc
Ha
Hc
Hb
Ha
11
10
9
8
7
6
5
4
3
2
1
5.85 5.80 5.75 5.70 5.65 5.60 5.55 5.50 5.45 5.40 5.35 5.30 5.25 5.20 5.15 5.10 5.05 5.00 4.95 4.90
f1 (ppm)


time (h)
0
-3
2
7
12
17
22
-0.5
-1
-1.5
-2
-2.5
ln[11]
at 80 oC
at 60 oC
at 40 oC
C6D6
11
12


0
0.0028 0.0029 0.003 0.0031 0.0032 0.0033
-1
-2
-3
-4
-5
-6
ln k
y = -5074.7x + 11.35
R² = 0.972
1/T

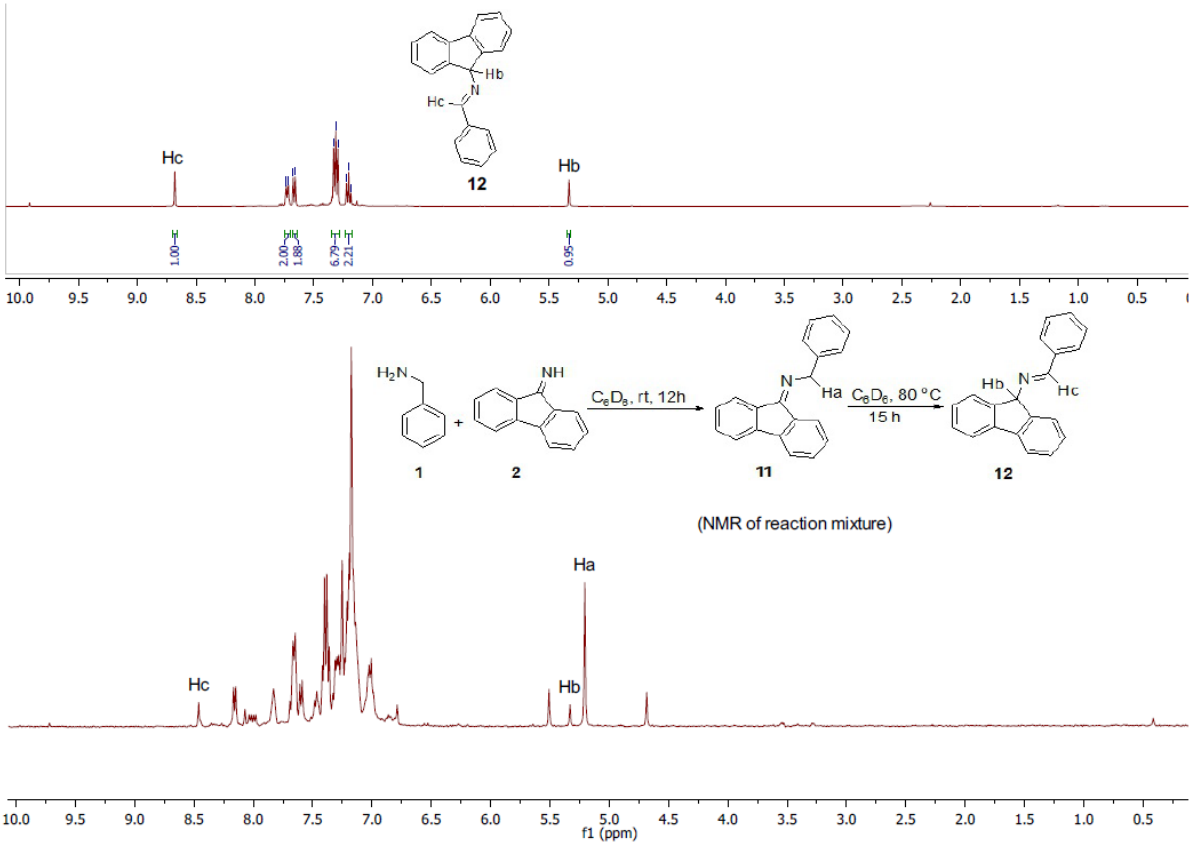
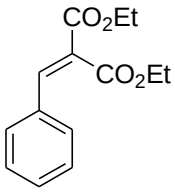
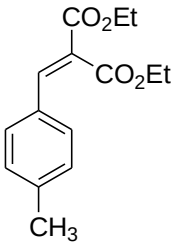
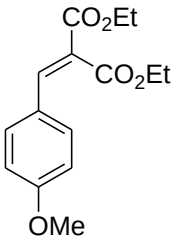


Figure s1: Identification of **12**.

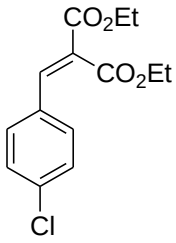
General procedure for the synthesis of olefin (GP I): Amine (0.56 mmol) was added to a solution of 9-fluorenone imine (0.56 mmol) in toluene (2 mL) and the mixture was stirred at room temperature for 1 h. Active methylene compound (0.56 mmol) was then added to the mixture and the reaction mixture was refluxed for 48 h under argon atmosphere (placing argon balloon). After disappearance of starting materials (indicated by TLC) solvent was evaporated under reduced pressure. The crude mixture was subjected to column chromatography (silica) to afford analytically pure products.

Diethyl 2-benzylidenemalonate (3a)[1b]: According to GP I, benzylamine (60 mg, 0.56 mmol),  9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3a** as a colorless oil (97 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.46 - 73 (m, 2H), 7.39 - 7.34 (m, 3H), 4.35 - 4.27 (m, 4H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 164.3, 142.3, 133.1, 130.7, 129.6, 129.0, 126.5, 61.9, 61.8, 14.3, 14.1 ppm.

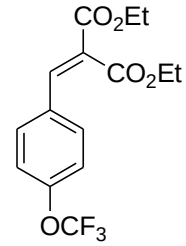
Diethyl 2-(4-methylbenzylidene)malonate (3b)[1b]: According to GP I, 4-methylbenzylamine  (68 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3b** as a colorless oil (99 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.37 - 4.27 (m, 4H), 2.36 (s, 3H), 1.34 - 1.29 (m, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.2, 164.5, 142.4, 141.4, 130.3, 129.8, 129.8, 125.4, 61.9, 61.6, 21.7, 14.4, 14.1 ppm.

Diethyl 2-(4-methoxybenzylidene)malonate (3c)[1b]: According to GP I, 4-methoxybenzylamine  (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3c** as a colorless oil (0.10 g, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (s, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.34 - 1.31 (m, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.4, 164.6, 161.7, 141.9, 131.7, 125.5, 123.7, 114.4, 61.8, 61.6, 55.5, 14.3, 14.1 ppm.

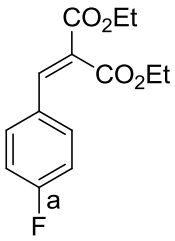
Diethyl 2-(4-chlorobenzylidene)malonate (3d)[1b]: According to GP I, 4-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3d** as a colorless oil (0.11 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.40 - 7.34 (m, , 4H), 4.36 - 4.28 (m, 4H), 1.35 - 1.28 (m, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.6, 164.1, 140.9, 136.8, 131.6, 130.8, 129.3, 127.1, 62.1, 62.0, 14.3, 14.1 ppm.



Diethyl 2-(4-(trifluoromethoxy)benzylidene)malonate (3e): According to GP I, 4-trifluoromethoxybenzylamine (0.11 g, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3e** as a colorless oil (0.13 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.70 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.36 - 4.29 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.5, 164.1, 150.7 (4 peaks, CF_3), 140.5, 131.7, 131.2, 127.4, 121.1, 62.1, 62.1, 14.3, 14.1 ppm. HRMS: Exact mass calculated for $C_{15}H_{15}F_3O_5$ ($[M+H]^+$): 333.0944, Found: 333.0961.



Diethyl 2-(4-fluorobenzylidene)malonate (3f)[1b]: According to GP I, 4-Fluorobenzylamine (70 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.03 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3f** as a colorless oil (0.10 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (s, 1H), 7.47 - 7.44 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 4.35 - 4.28 (m, 4H), 1.34 - 1.28 (m, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.8, 164.9 (a), 164.2, 163.2 (a), 141.0, 131.8, 131.6, 129.6, 129.3, 129.3, 129.0, 126.3, 126.3, 116.3, 116.2, 62.0, 61.9, 14.3, 14.1 ppm.

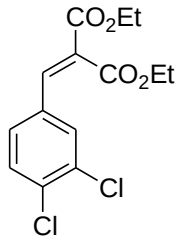


Diethyl 2-(2-fluorobenzylidene)malonate (3g)[1c]: According to GP I, 2-fluorobenzylamine (70 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3g** as a colorless oil (89 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.39 - 7.34 (m, 1H), 7.13 - 7.06 (m, 2H), 4.33 - 4.26 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.1, 163.8, 162.1 (a), 159.6 (a), 134.8, 134.6, 132.4, 132.3, 129.4, 129.4, 128.2, 128.2, 124.3, 124.3, 121.4, 121.2, 116.0, 115.8, 61.8, 61.7, 14.1, 13.9 ppm.

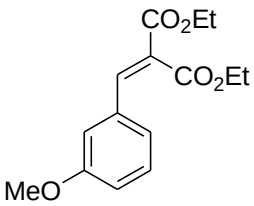
Diethyl 2-(2-chlorobenzylidene)malonate (3h)[1c]: According to GP I, 2-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3h** as a colorless oil (0.10 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.03 (s, 1H), 7.44 - 7.42 (m, 2H), 7.33 - 7.30 (m, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.18 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.1, 163.9, 139.5, 134.9, 132.2, 131.4, 130.1, 129.5, 129.0, 127.0, 62.1, 61.9, 14.3, 14.0 ppm.

Diethyl 2-(2-methoxybenzylidene)malonate (3i)[1f]: According to GP I, 2-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3i** as a colorless oil (0.11 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 7.38 - 7.33 (m, 2H), 6.90 - 6.87 (m, 2H), 4.30 - 4.24 (m, 4H), 3.83 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 164.5, 158.1, 138.4, 132.1, 129.3, 126.3, 122.4, 120.6, 110.9, 61.6, 61.5, 55.6, 14.3, 14.0 ppm.

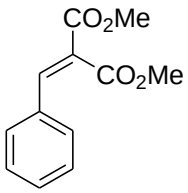
Diethyl 2-(3,4-dichlorobenzylidene)malonate (3j)[1d]: According to GP I, 3,4-dichlorobenzylamine (98 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3j** as a colorless oil (0.12 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.61 (s, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.1 Hz, 1H), 4.38 - 4.29 (m, 4H), 1.33 (q, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.2, 163.8, 139.4, 134.9, 133.4, 133.1, 131.2, 131.0, 128.6, 128.3, 62.2, 62.2, 14.3, 14.2 ppm.



Diethyl 2-(3-methoxybenzylidene)malonate (3k)[1f]: According to GP I, 3-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3k** as a colorless oil (0.1 g, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.73 (s, 1H), 7.32 - 7.29 (m, 1H), 7.08 - 7.06 (m, 1H), 7.02 - 7.01 (m, 1H), 6.97-6.96 (m, 1H), 4.38 - 4.31 (m, 4H), 3.82 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.9, 164.3, 159.9, 142.2, 134.4, 130.0, 126.8, 122.2, 116.7, 114.5, 61.9, 61.9, 55.5, 14.4, 14.1 ppm.



Dimethyl 2-benzylidenemalonate (3l)[1e]: According to GP I, benzylamine (60 mg, 0.36 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and dimethylmalonate (64 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:15) of crude product gave **3l** as a colorless oil (77 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.78 (s, 1H), 7.43 - 7.37 (m, 5H), 3.84 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.4, 164.7, 143.2, 132.9, 130.9, 129.6, 129.1, 125.6, 53.0, 52.9 ppm.



Dimethyl 2-(2-methoxybenzylidene)malonate (3m)[1g]: According to GP I, 2-methoxybenzylamine (77, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and dimethylmalonate (64 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:15) of crude product gave **3m** as a colorless oil (88 mg, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.11 (s, 1H), 7.38 - 7.32 (m, 2H), 6.93 - 6.89 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.4, 164.9, 158.2, 139.3, 132.4, 129.2, 125.4, 122.3, 120.7, 111.1, 55.7, 52.7, 52.6 ppm.

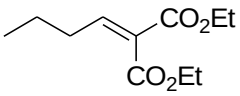
Dibenzyl 2-benzylidenemalonate (3n)[1c]: According to GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and dibenzylmalonate (0.14 mL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:10) of crude product gave **3n** as a colorless oil (0.13 g, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.82 (s, 1H), 7.39 - 7.28 (m, 15H), 5.313 (s, 2H), 5.309 (s, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.5, 164.1, 143.4, 135.7, 135.0, 132.8, 130.8, 129.7, 129.0, 128.97, 128.78, 128.73, 128.65, 128.48,128.22, 125.8, 67.8, 67.4 ppm.

Dibenzyl 2-(2-methoxybenzylidene)malonate (3o): According to GP I, 2-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and dibenzylmalonate (0.14 mL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:10) of crude product gave **3o** as a colorless oil (0.16 g, 72%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.17 (s, 1H), 7.37 - 7.23 (m, 12H), 6.89 - 6.75 (m, 2H), 5.29 (s, 2H), 5.24 (s, 2H), 3.82 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.6, 164.3, 158.2, 139.7, 135.8, 135.2, 132.3, 129.4, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 125.6, 122.2, 120.7, 111.0, 67.5, 67.2, 55.6 ppm. HRMS: Exact mass calculated for $C_{25}H_{22}O_2$ ($[M+H]^+$): 403.1540, Found: 403.1555.

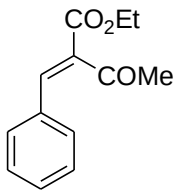
Diethyl 2-((furan-2-yl)methylene)malonate (3p)[1a]: According to GP I, furfurylamine (54 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 µL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3p** as a colorless oil (80 mg,

60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 1.9 Hz, 1H), 7.39 (s, 1H), 6.71 (d, *J* = 3.6 Hz, 1H), 6.44 - 6.43 (m, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 166.3, 164.2, 149.03, 146.2, 127.5, 122.0, 118.0, 112.7, 61.7, 61.6, 14.2, 14.1 ppm.

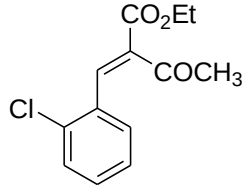
Diethyl 2-butylidenemalonate (3q): According to GP I, butylamine (40 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and diethylmalonate (85 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave **3q** as a colourless oil (61 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 6.99 (t, *J* = 7.8 Hz, 1H), 4.31 - 4.28 (m, 2H), 4.25 - 4.21 (m, 2H), 2.29 - 2.25 (m, 2H), 1.55 - 1.48 (m, 2H), 1.34 - 1.31 (m, 3H), 1.30 - 1.28 (m, 3H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 165.7, 164.0, 149.3, 128.8, 61.3, 61.2, 31.7, 21.7, 14.2, 14.1, 13.8 ppm.



***(E/Z)*-ethyl 2-benzylidene-3-oxobutanoate (3r)[1j]:** According to GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol)) and Ethyl acetoacetate (71 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave a mixture of E/Z (1.3:1) isomer of **3r** as a colorless oil (76 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.67 (s, 1H), 7.57 (s, 1H), 7.46 - 7.44 (m, 1H), 7.41 - 7.37 (m, 8H), 4.35 - 4.28 (m, 4H), 2.43 (s, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 203.8, 194.9, 168.0, 164.6, 141.5, 140.7, 134.8, 134.2, 133.1, 133.06, 130.9, 130.6, 129.9, 129.7, 129.1, 129.1, 62.0, 61.8, 31.5, 26.8, 14.4, 14.1 ppm.

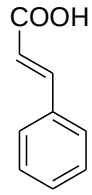


***(E/Z)*-ethyl 2-(2-chlorobenzylidene)-3-oxobutanoate (3s):** According to GP I, 2-Chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and Ethyl acetoacetate (71 μL, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:20) of crude product gave a mixture of E/Z (1.5:1) isomer of **3s** as a colorless oil (91 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.85 (s, 1H), 7.78 (s, 1H), 7.36 - 7.32 (m, 4H), 7.25

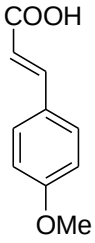


- 7.20 (m, 3H), 7.17 - 7.11 (m, 2H), 4.25 - 4.19 (m, 2H), 4.16 - 4.11 (m, 2H), 2.36 (s, 2H), 2.14 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 4H), 1.07 (t, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.0, 194.6, 166.8, 164.1, 138.3, 137.5, 136.8, 136.5, 134.7, 134.4, 132.1, 131.9, 131.4, 131.2, 130.2, 129.9, 129.9, 129.3, 127.1, 127.0, 61.8, 6.7, 31.3, 26.8, 14.2, 13.9 ppm.

Cinnamic acid (3t)[(3h)]: According to GP I: Benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and malonic acid (58 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave **3t** as a white solid (58 mg, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 16.0 Hz, 1H), 7.58 - 7.56 (m, 2H), 7.42 - 7.41 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 172.9, 147.3, 134.2, 131.0, 129.2, 128.6, 117.5 ppm.

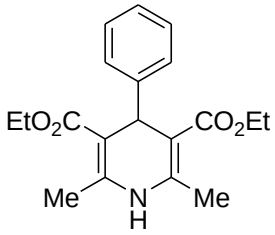


***(E)*-3-(4-methoxyphenyl)acrylic acid (3u)[(3i)]:** According to GP I: 4-Methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and malonic acid (58 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave **3u** as a white solid (68 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 15.9 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 3.85 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 172.1, 162.0, 146.9, 130.3, 127.1, 114.8, 114.6, 55.6 ppm.



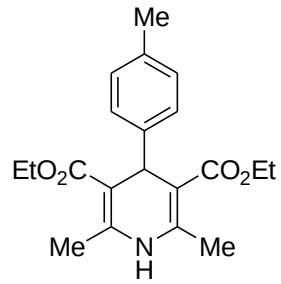
General procedure for the synthesis of dihydropyridine (GP II): Amine (0.56 mmol) was added to a solution of 9-fluorenone imine (0.56 mmol) in toluene (2 mL) and the mixture was stirred at room temperature for 1 h. Active methylene compound (1.12 mmol) and ammonium acetate (1.12 mmol) was then added to the mixture and the reaction mixture was refluxed for 48 h under argon atmosphere (placing argon balloon). After disappearance of starting materials (indicated by TLC) solvent was evaporated under reduced pressure. The crude mixture was subjected to column chromatography (silica) to afford analytically pure products.

Diethyl-1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6a)[2a]: According to



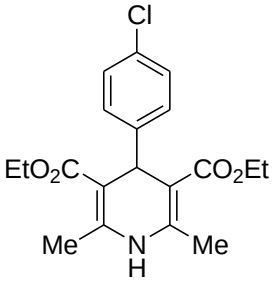
GP II, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6a** as a yellow gum (0.13 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 - 7.26 (m, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 5.96 (s, 1H), 4.99 (s, 1H), 4.14 - 4.02 (m, 4H), 2.30 (s, 6H), 1.22 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.7, 147.8, 144.1, 128.0, 127.8, 126.1, 104.0, 59.7, 39.7, 19.5, 14.3 ppm.

Diethyl-1,4-dihydro-2,6-dimethyl-4-p-tolylpyridine-3,5-dicarboxylate (6b)[2c]: According to



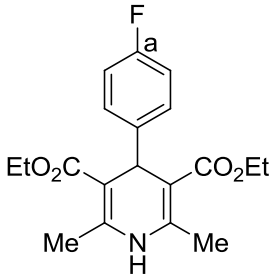
GP II, 4-methylbenzylamine (68 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6b** as a yellow gum (0.13 g, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.17 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 5.73 (s, 1H), 4.94 (s, 1H), 4.11 - 4.05 (m, 4H), 2.31 (s, 6H), 2.27 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.9, 145.1, 144.0, 135.7, 128.7, 128.0, 104.4, 59.9, 39.3, 21.3, 19.8, 14.5 ppm.

Diethyl-4-(4-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6c)[2a]:



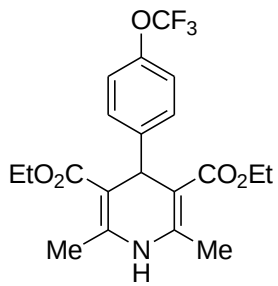
According to GP II, 4-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6c** as a yellow gum (0.13 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.22 - 7.20 (m, 2H), 7.17 - 7.15 (m, 2H), 5.66 (s, 1H), 4.95 (s, 1H), 4.123 - 4.04 (m, 4H), 2.32 (s, 6H), 1.21 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.6, 146.5, 144.2, 131.9, 129.6, 128.1, 104.1, 60.0, 39.5, 19.8, 14.5 ppm.

Diethyl-4-(4-fluorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6d)[2c]:

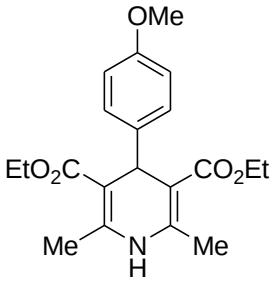


According to GP II, 4-fluorobenzylamine (0.70 g, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6d** as a yellow gum (0.12 g, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.24 - 7.22 (m, 2H), 6.90 - 6.86 (m, 2H), 5.67 (s, 1H), 4.95 (s, 1H), 4.14 - 4.03 (m, 4H), 2.32 (s, 6H), 1.21 (t, *J* = 7.2 Hz, 6H). ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.7, 162.3 (a), 160.7 (a), 144.0, 143.9, 143.8, 129.7, 129.6, 114.8, 114.6, 104.4, 60.0, 39.2, 19.8, 14.5 ppm.

Diethyl-1,4-dihydro-2,6-dimethyl-4-(4-(trifluoromethoxy)phenyl)pyridine-3,5dicarboxylate (6e): According to GP II, 4-trifluoromethoxybenzylamine (107 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6e** as a yellow gum (0.16 g, 68%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 5.82 (s, 1H), 4.99 (s, 1H), 4.13 - 4.03 (m, 4H), 2.32 (s, 6H), 1.20 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl3) δ = 167.3, 151.6, 144.3, 128.4, 128.3, 128.1, 124.89 (CF_3), 124.86 (CF_3), 124.82 (CF_3), 124.78 (CF_3), 103.6, 59.9, 19.7, 19.6, 14.3 ppm. HRMS: Exact mass calculated for $C_{20}H_{22}F_3NO_5$ ($[M+H]^+$): 414.1523, Found: 414.1514.

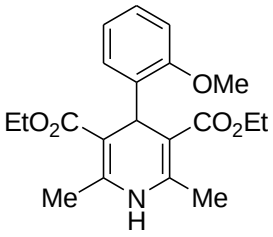


Diethyl-1,4-dihydro-4-(4-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6f)[2b]:



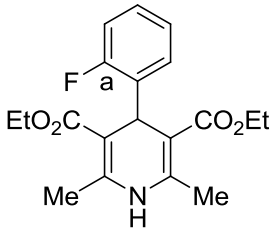
According to GP II, 4-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6f** as a yellow gum (0.14 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.19 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 2H), 5.97 (br. s, 1H), 4.93 (s, 1H), 4.13 - 4.04 (m, 4H), 3.74 (s, 3H), 2.29 (s, 6H), 1.22 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.9, 158.0, 143.9, 140.5, 129.1, 113.3, 104.5, 59.9, 55.3, 38.9, 19.7, 14.5 ppm.

Diethyl-1,4-dihydro-4-(2-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6g)[2d]:



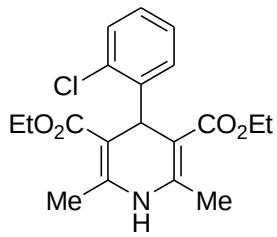
According to GP II, 2-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6g** as a yellow gum (0.14 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.21 - 7.19 (m, 1H), 7.11 - 7.07(m, 1H), 6.82 - 6.77 (m, 2H), 5.74 (br. s, 1H), 5.27 (s, 1H), 4.04 (q, *J* = 7.2 Hz, 4H), 3.77 (s, 3H), 2.27 (s, 6H), 1.18 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.3, 157.3, 143.9, 135.5, 130.8, 127.5, 120.2, 110.8, 103.3, 59.7, 55.5, 35.5, 19.7, 14.4 ppm.

Diethyl-4-(2-fluorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6h)[2b]:



According to GP II, 2-fluorobenzylamine (70 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6h** as a yellow gum (0.12 g, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.31 - 7.28 (m, 1H), 7.10 - 7.07 (m, 1H), 7.00 - 6.97 (m, 1H), 6.91 - 6.88 (m, 1H), 5.77 (s, 1H), 5.23 (s, 1H), 4.09 - 4.00 (m, 4H), 2.30 (s, 6H), 1.19 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.8, 160.8 (a), 159.1 (a), 144.5, 135.2, 135.1, 131.3, 131.3, 127.90, 127.9, 123.8, 123.8, 115.2, 115.0, 103.2, 59.9, 34.3, 19.7, 14.2 ppm.

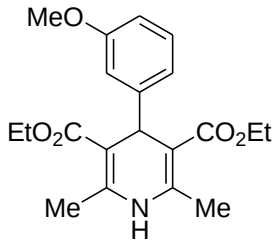
Diethyl-4-(2-chlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6i)[2c]:



According to GP II, 2-chlorobenzylamine (79 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6i** as a yellow gum (0.13 g, 65%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.36 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.21 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.10 (td, *J* = 7.6, 1.4 Hz, 1H), 7.01 (td, *J* = 7.6, 1.7 Hz, 1H), 6.25 (s, 1H), 5.38 (s, 1H), 4.08-4.04 (m, 4H), 2.24 (s, 6H), 1.18

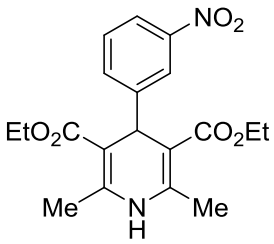
(t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.0, 145.8, 144.5, 132.5, 131.7, 129.4, 127.4, 126.8, 103.7, 59.9, 37.6, 19.4, 14.4 ppm.

Diethyl-1,4-dihydro-4-(3-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6j)[2h]:



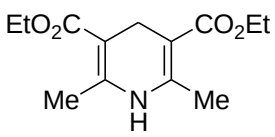
According to GP II, 3-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mm ol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6j** as a yellow gum (0.14 g, 71%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.11 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.84 - 6.83 (m, 1H), 6.68 - 6.65 (m, 1H), 6.03 (s, 1H), 4.98 (s, 1H), 4.12 - 4.05 (m, 4H), 3.75 (s, 3H), 2.29 (s, 6H), 1.22 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.8, 159.4, 149.5, 144.2, 128.9, 120.7, 114.4, 111.0, 104.2, 60.0, 55.3, 39.7, 19.8, 14.5 ppm.

Diethyl-1,4-dihydro-2,6-dimethyl-4-(3-nitrophenyl)pyridine-3,5-dicarboxylate (6k)[2d]:



According to GP II: 3-Nitrobenzylamine (85 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6k** as a yellow gum (0.13 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.06 (s, 1H), 7.93 (d, *J* = 8 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 8 Hz, 1H), 5.69 (s, 1H), 5.02 (s, 1H), 4.025-3.97 (m, 4H), 2.29 (s, 6H), 1.15 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.3, 150.1, 148.3, 144.9, 134.7, 128.8, 123.3, 121.5, 103.6, 60.2, 40.2, 19.9, 14.4 ppm.

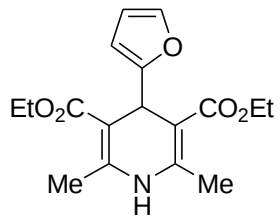
Diethyl 1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6l)[2c]: According to GP II,



methylamine hydrochloride (38 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:2) of crude product gave **6l** as a yellow solid (22 mg, 15%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.40 (s, 1H), 4.14 (q, *J* = 7.2 Hz, 4H), 3.24 (s,

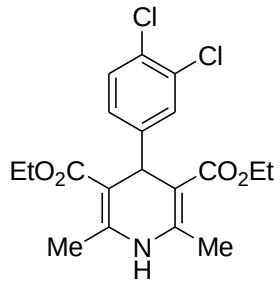
2H), 2.17 (s, 6H), 1.26 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.3, 145.2, 99.6, 59.9, 25.0, 19.3, 14.7 ppm.

Diethyl 4-(furan-2-yl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6m)[2a]:



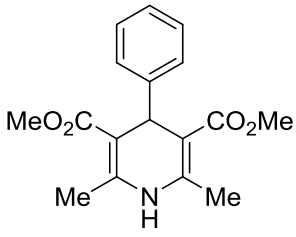
According to GP II, furfurylamine (54 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6m** as a yellow gum (0.12 g, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.20 (s, 1H), 6.20 - 6.19 (m, 1H), 6.01 (s, 1H), 5.93 (d, *J* = 3.0 Hz, 1H), 5.19 (s, 1H), 4.20 - 4.09 (m, 4H), 2.31 (s, 6H), 1.25 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.7, 158.8, 145.4, 141.0, 110.2, 104.6, 100.8, 60.0, 33.5, 19.7, 14.5 ppm.

Diethyl-4-(3,4-dichlorophenyl)-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (6n)[2f]:



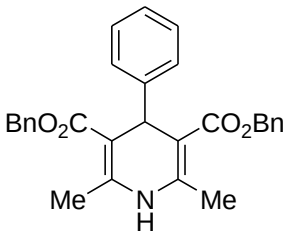
According to GP II, 3,4-dichlorobenzylamine (98 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6n** as a yellow gum (0.14 g, 63%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 1.8 Hz, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.70 (s, 1H), 4.92 (s, 1H), 4.14 - 4.03 (m, 4H), 2.32 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.4, 148.2, 144.5, 131.8, 130.3, 130.0, 129.9, 127.8, 103.6, 60.2, 39.5, 19.9, 14.5 ppm.

Dimethyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6o)[2a]: According to GP II, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), methyl acetoacetate (1.2 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6o** as a yellow gum (0.12 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 - 7.17 (m, 2H), 7.16 - 7.12 (m, 2H), 7.08-7.04 (m, 1H), 5.60 (s, 1H), 4.93 (s, 1H), 3.57 (s, 6H),

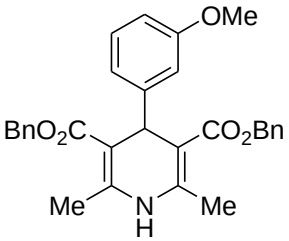


2.27 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.2, 147.6, 144.4, 128.2, 127.8, 126.4, 104.1, 51.2, 39.4, 19.9 ppm.

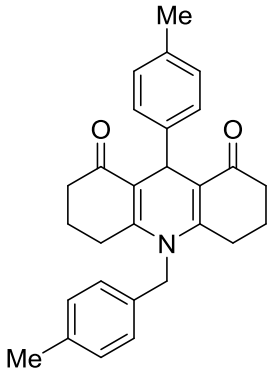
Dibenzyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (6p)[(2g)]: According to GP II, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), benzyl acetoacetate (1.9 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6p** as a yellow gum (0.18 g, 70%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 - 7.28 (m, 5H), 7.20 - 7.19 (m, 6H), 7.17 - 7.11 (m, 4H), 5.77 (s, 1H), 5.11 - 5.04 (m, 5H), 2.33 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.5, 147.6, 144.6, 144.6, 136.7, 128.5, 128.3, 128.2, 128.0, 127.9, 126.4, 104.1, 65.8, 39.7, 19.9 ppm.



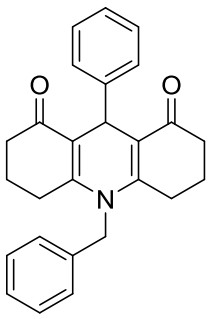
Dibenzyl 1,4-dihydro-4-(3-methoxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (6q): According to GP I: According to GP II, 3-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), benzyl acetoacetate (1.9 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **6q** as a yellow gum (0.18 g, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 - 7.20 (m, 10H), 7.07 (t, *J* = 8 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.76 - 6.75 (m, 1H), 6.68 - 6.65 (m, 1H), 5.73 (s, 1H), 5.12 - 5.04 (m, 5H), 3.57 (s, 3H), 2.32 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.5, 159.5, 149.2, 144.8, 136.7, 129.0, 128.5, 128.0, 127.9, 120.7, 114.1, 111.7, 103.9, 65.8, 55.1, 39.7, 19.8 ppm. HRMS: Exact mass calculated for $C_{30}H_{29}NO_5$ ($[M+H]^+$): 484.2118, Found: 484.2130.



10-(4-Methylbenzyl)-9-(p-tolyl)decahydroacridine-1,8(*2H,5H*)-dione (6r)[2e]: According to GP I, 4-methylbenzylamine (0.135 g, 1.12 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and 1,2-cyclohexanedione (0.13 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave **6r** as a white solid (0.14 g, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.20 - 7.18 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 7.8 Hz, 2H), 5.35 (s, 1H), 4.89 (s, 2H), 2.68 - 2.64 (m, 2H), 2.50 – 2.45 (m, 2H), 2.37 (s, 3H), 2.37 - 2.34 (m, 2H), 2.31 - 2.28 (m, 2H), 2.26 (s, 3H), 1.98 - 1.94 (m, 2H), 1.91 - 1.87 (m, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 196.12, 152.43, 143.50, 137.84, 135.49, 133.99, 130.09, 128.92, 127.88, 125.41, 116.49, 48.83, 36.68, 31.48, 26.87, 21.64, 21.27, 21.25 ppm.

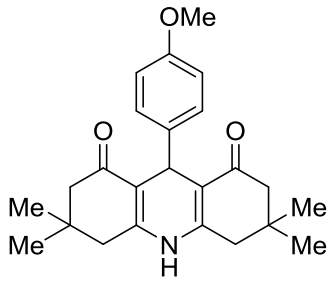


10-Benzyl-decahydro-9-phenylacridine-1,8(*5H,8aH*)-dione(6s)[2e]: According to GP I, benzylamine (0.12 g, 1.12 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and cyclohexanedione (0.13 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave **6s** as a white solid (0.13 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (t, J = 7.4 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.31 - 7.30 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.2 Hz, 2H), 7.14 - 7.11 (m, 1H), 5.44 (s, 1H), 4.96 (s, 2H), 2.72 - 2.67 (m, 2H), 2.53-2.48 (m, 2H), 2.44 - 2.40 (m, 2H), 2.35 - 2.30 (m, 2H), 2.03 - 1.98 (m, 2H), 1.96 - 1.89 (m, 2H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 196.1, 152.5, 146.3, 137.1, 129.5, 128.3, 128.1, 128.0, 126.2, 125.5, 116.5, 49.1, 36.7, 31.8, 26.9, 21.7 ppm.



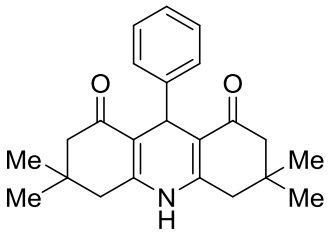
Decahydro-9-(4-methoxyphenyl)-3,3,6,6-tetramethylacridine-1,8(*5H,8aH*)-dione(6t)[2e]:

According to GP I, 4-methoxybenzylamine (77 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (0.16 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave **6t** as a white solid (0.115 g, 54%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.85 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 5.02 (s, 1H), 3.63 (s, 3H), 2.24 - 2.09 (m, 8H), 1.03 (s, 6H), 0.92 (s, 6H) ppm. ^{13}C NMR



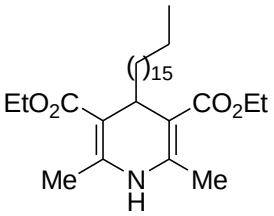
(151 MHz, $CDCl_3$) δ = 196.5, 157.7, 150.2, 139.4, 129.0, 113.3, 113.1, 55.1, 51.0, 40.4, 32.9, 32.7, 29.7, 27.1 ppm.

Decahydro-3,3,6,6-tetramethyl-9-phenylacridine-1,8(*5H,8aH*)-dione (6u)[2e]: According to



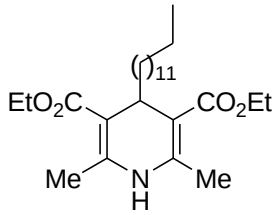
GP I, benzylamine (60 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (0.16 g, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:1) of crude product gave **6u** as a white solid (97 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (s, 1H), 7.34 (d, *J* = 6.8 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 5.10 (s, 1H), 2.28 - 2.11 (m, 8H), 1.05 (s, 6H), 0.94 (s, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 195.5, 147.5, 146.5, 128.3, 128.2, 126.2, 114.1, 50.9, 41.5, 33.8, 32.9, 29.7, 27.4 ppm.

Diethyl-4-heptadecyl-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (7a): According



to GP II, octadecylamine (0.151 g, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:5) of crude product gave **7a** as a yellow gum (0.16 g, 58%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.54 (s, 1H), 4.23 - 4.11 (m, 4H), 3.91 (t, *J* = 6 Hz, 1H), 2.27 (s, 6H), 1.30 - 1.21 (m, 38H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.4, 144.8, 103.6, 59.8, 37.1, 33.1, 32.1, 30.2, 30.0, 29.97, 29.93, 29.88, 29.58, 25.1, 22.9, 19.7, 14.6, 14.4 ppm (Less no carbon observed due to overlapping in aliphatic region). HRMS: Exact mass calculated for $C_{30}H_{53}NO_4$ ($[M+H]^+$): 492.4047, Found: 492.4031.

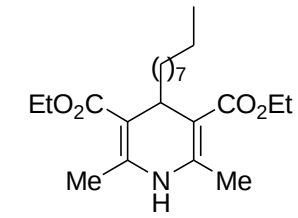
Diethyl-1,4-dihydro-2,6-dimethyl-4-tridecylpyridine-3,5-dicarboxylate (7b): According to GP



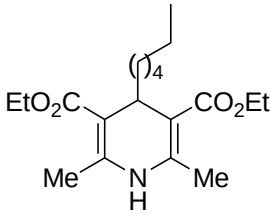
II, tetradecylamine (0.119 g, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:5) of crude product gave **7b** as a yellow gum (0.15 g, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.51 (s, 1H), 4.24 - 4.12 (m, 4H), 3.91 (t, *J* = 6 Hz, 1H), 2.28 (s, 6H), 1.30 - 1.18 (m, 30H), 0.87 (t, *J* =

7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.4, 144.7, 103.6, 59.8, 37.1, 33.1, 32.1, 30.2, 30.01, 29.96, 29.93, 29.92, 29.88, 29.58, 25.1, 22.9, 19.7, 14.6, 14.4 ppm (Less no carbon observed due to overlapping in aliphatic region). HRMS: Exact mass calculated for $C_{26}H_{45}NO_4$ ($[M+H]^+$): 436.3421, Found: 436.3434.

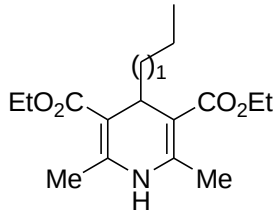
Diethyl-1,4-dihydro-2,6-dimethyl-4-nonylpyridine-3,5-dicarboxylate (7c)[2i]: According to GP II, decylamine (88 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:5) of crude product gave **7c** as a yellow gum (0.131 g, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.60 (s, 1H), 4.23 - 4.18 (m, 2H), 4.16 - 4.11 (m, 2H), 3.91 (t, *J* = 6.4 Hz, 1H), 2.27 (s, 6H), 1.30 - 1.18 (m, 22H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.4, 144.8, 103.6, 59.8, 37.1, 33.1, 32.1, 30.2, 30.0, 29.9, 29.6, 25.1, 22.9, 19.7, 14.6, 14.3 ppm.



Diethyl-4-hexyl-1,4-dihydro-2,6-dimethylpyridine-3,5-dicarboxylate (7d)[2j]: According to GP II, heptylamine (64 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **7d** as a yellow gum (0.116 g, 56%). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 5.51 (s, 1H), 4.24 - 4.11 (m, 4H), 3.91 (t, *J* = 6.0 Hz, 1H), 2.28 (s, 6H), 1.30 - 1.19 (m, 16H), 0.85 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.4, 144.8, 103.6, 59.8, 37.1, 33.1, 32.2, 29.8, 25.1, 23.0, 19.7, 14.6, 14.4 ppm.



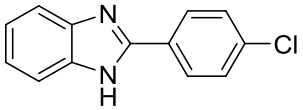
Diethyl-1,4-dihydro-2,6-dimethyl-4-propylpyridine-3,5-dicarboxylate (7e)[2k]: According to GP II, butylamine (41 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol), ethyl acetoacetate (1.4 mL, 1.12 mmol) and ammonium acetate (86 mg, 1.12 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:4) of crude product gave **7e** as a yellow gum (89 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.50 (s, 1H), 4.23 - 4.12 (m,



4H), 3.93 (t, *J* = 5.6 Hz, 1H), 2.28 (s, 6H), 1.30 - 1.18 (m, 10H), 0.84 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 168.4, 144.8, 103.6, 59.8, 39.4, 32.9, 19.7, 18.2, 14.6, 14.5 ppm.

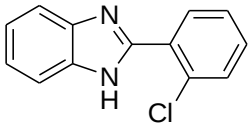
General procedure for the synthesis of benzimidazole (GP III): Amine (0.56 mmol) was added to a solution of 9-fluorenone imine (0.56 mmol) in toluene (2 mL) and the mixture was stirred at room temperature for 1 h. o-Phenylenediamine (1.12 mmol) then added to the mixture and the reaction mixture was refluxed for 48 h under argon atmosphere (placing argon balloon). After disappearance of starting materials (indicated by TLC) solvent was evaporated under reduced pressure. The crude mixture was subjected to column chromatography (silica) to afford analytically pure products.

2-(4-methylphenyl)-*1H*-benzo*[d]*imidazole (9a)[3a]: According to GP III, 4-Chloroenzylamine



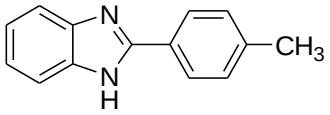
(79 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and o-phenylenediamine (60 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:3) of crude product gave **9a** as a pale yellow solid (84 mg, 66%). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 13.03 (s, 1H), 8.23 (d, *J* = 8.6 Hz, 2H), 7.70 (s, 1H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.57 (s, 1H), 7.26 - 7.21 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ = 150.3, 143.9, 135.2, 134.6, 129.1, 128.2, 122.8, 121.9, 119.0, 111.5, 99.6 ppm.

2-(2-chlorophenyl)-*1H*-benzo*[d]*imidazole (9b)[3a]: According to GP III, 2-chloroenzylamine (79

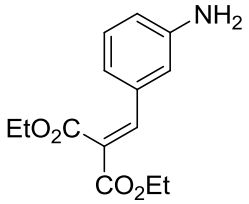


mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and o-phenylenediamine (60 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:3) of crude product gave **9c** as a white solid (80 mg, 63%). ^{1}H NMR (400 MHz, DMSO-D_6) δ = 12.78 (s, 1H), 7.93 - 7.90 (m, 1H), 7.72 (s, 1H), 7.67 - 7.65 (m, 1H), 7.64 - 7.51 (m, 3H), 7.28 - 7.25 (m, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-D_6) δ = 149.6, 143.6, 135.1, 132.5, 132.1, 131.7, 130.8, 130.3, 127.9, 123.3, 122.2, 119.5, 112.2 ppm.

2-p-tolyl-*1H*-benzo*[d]*imidazole (9c)[3a]: According to GP III, 4-methylenzylamine (68 mg, 0.56 mmol), 9-fluorenone imine **2** (0.10 g, 0.56 mmol) and o-phenylenediamine (60 mg, 0.56 mmol) were reacted for 48 h and column chromatography (silica gel; EtOAc:hexane, 1:3) of crude product gave **9b** as a white solid (72 mg, 62%). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.88 (s, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.66 (s, 1H), 7.66 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 4.4 Hz, 2H), 2.38 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ = 150.3, 143.9, 135.2, 134.6, 129.1, 128.2, 122.8, 121.9, 119.0, 111.5, 99.6 ppm.



Diethyl 2-(3-aminobenzylidene) malonate (16): According to GP I, 2-aminobenzylamine (0.10 g, 0.82 mmol), 9-fluorenone imine **2** (0.22 g, 1.23 mmol) and diethylmalonate (0.13 mL, 0.82 mmol) were reacted for 48 h and solvent was evaporated after cooling down the reaction mixture. Then crude mixture was dissolved in methanol and 1 (N) aq HCl was added to it. After 3 h stirring at rt, solvent was evaporated and reaction mixture was diluted by $NaHCO_3$ (10 mL) and the mixture was extracted with ethyl acetate (3 X 20 mL). The combined organic layers were washed successively with water (20 mL) and brine (10 mL). The organic layer was dired over sodium sulphate and the solvents were evaporated to get the crude reaction mixture which was subjected to column chromatography (silica gel; EtOAc: hexane, 1:4) to obtain analytically pure product (**16**) as a pale yellow oil (0.12 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (s, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.85 – 6.84 (m, 1H), 6.82 – 6.79 (m, 1H), 4.35 – 4.27 (m, 4H), 2.52 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ = 167.0, 164.3, 144.6, 142.3, 134.2, 123.0, 126.6, 121.4, 118.6, 116.9, 62.0, 61.9, 14.4, 14.1 ppm.



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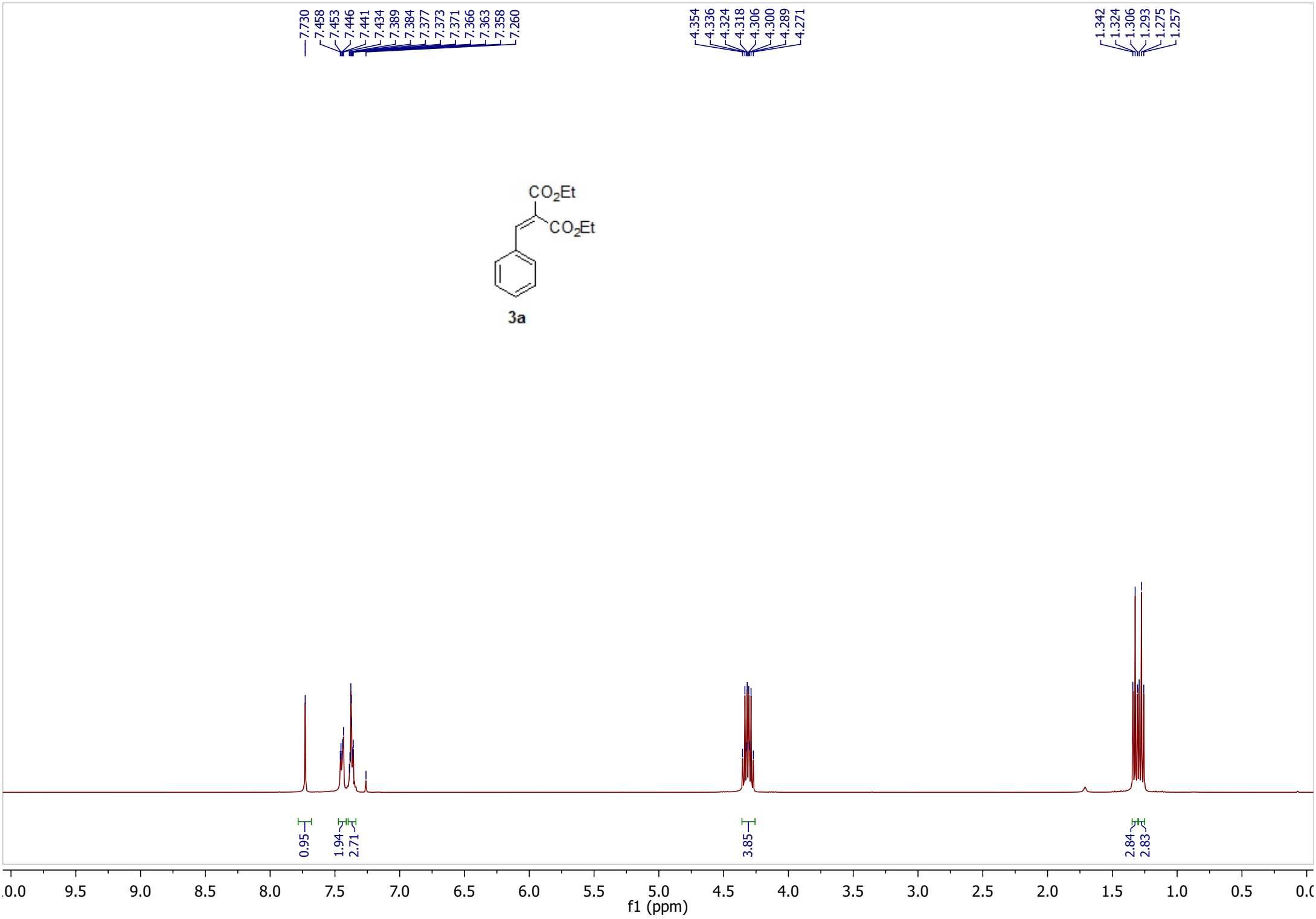
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7.441
7.434
7.389
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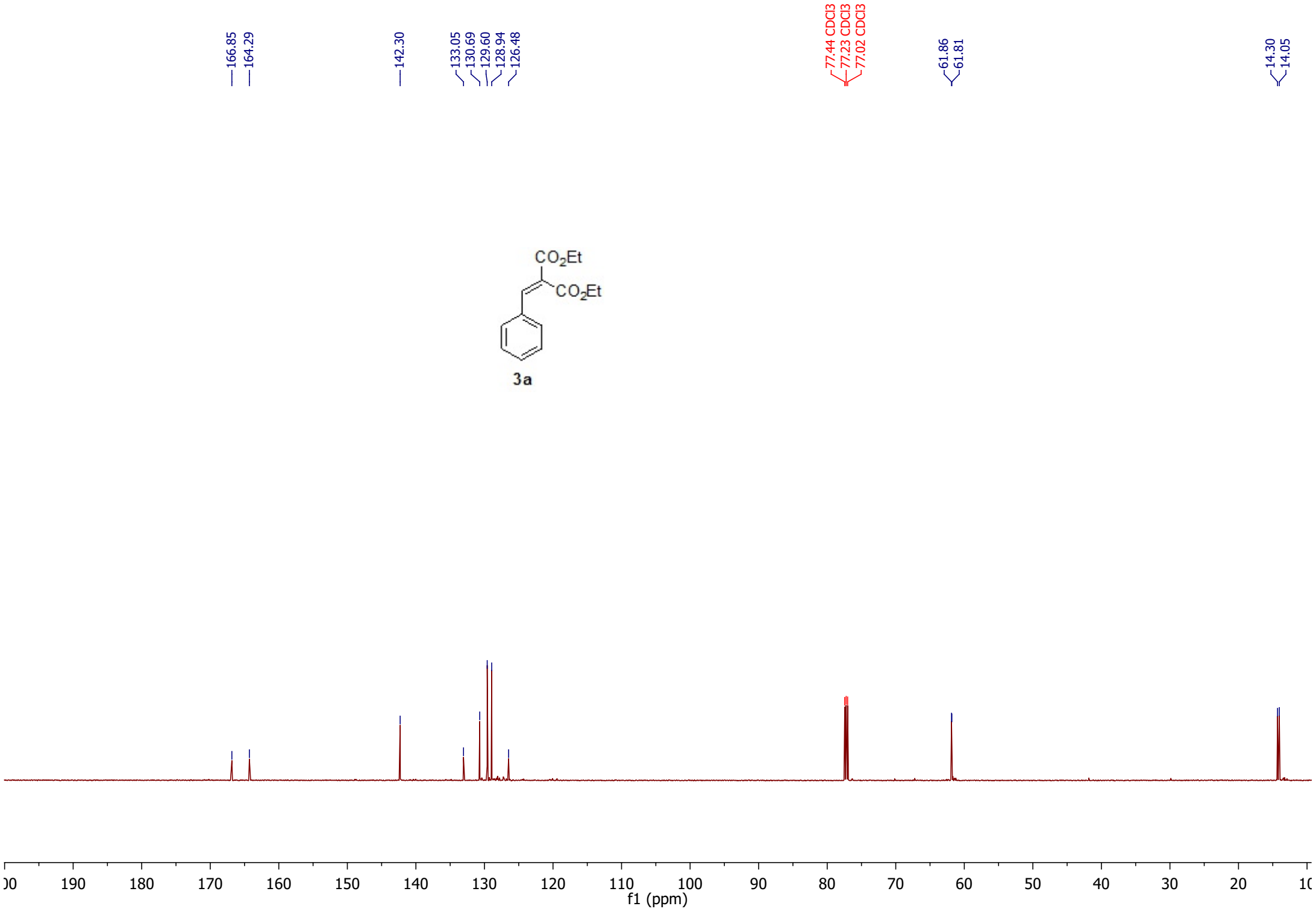
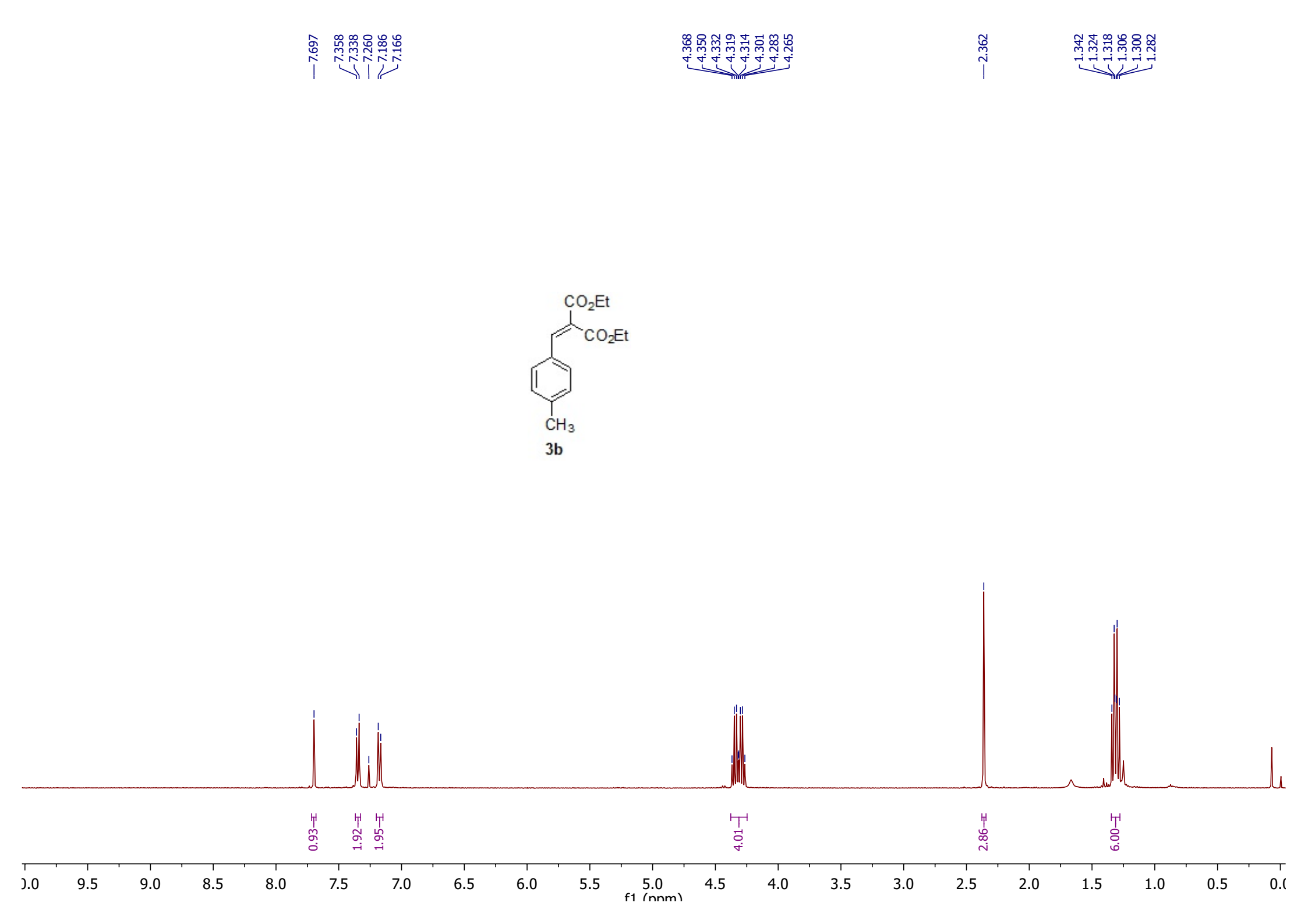
7.377
7.373
7.371
7.366
7.363
7.358
7.260
4.354
4.336
4.324
4.318
4.306
4.300
4.289
4.271
1.342
1.324
1.306
1.293
1.275
1.257
CO2Et
CO2Et
3a
0.95
1.94
2.71
3.85
2.84
2.83
f1 (ppm)


166.85
164.29
142.30
133.05
130.69
129.60
128.94
126.48
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
61.86
61.81
14.30
14.05
CO2Et
CO2Et
3a
f1 (ppm)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7.260
7.186
7.166
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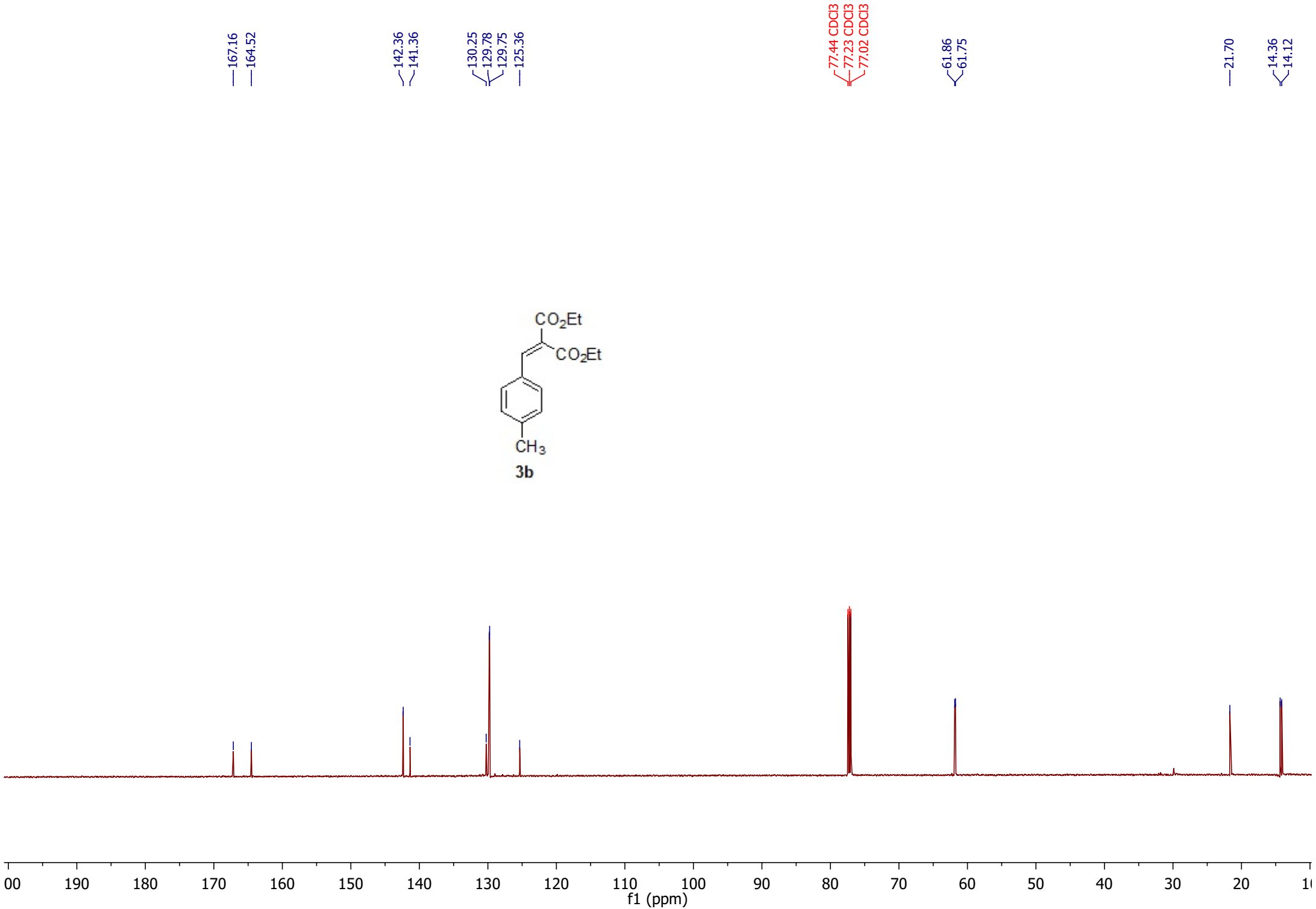
4.350
4.332
4.319
4.314
4.301
4.283
4.265
2.362
1.342
1.324
1.318
1.306
1.300
1.282
CO2Et
CO2Et
CH3
3b
0.93
1.92
1.95
4.01
2.86
6.00
f1 (ppm)


167.16
164.52
142.36
141.36
130.25
129.78
129.75
125.36
77.44 CDCl3
77.23 CDCl3
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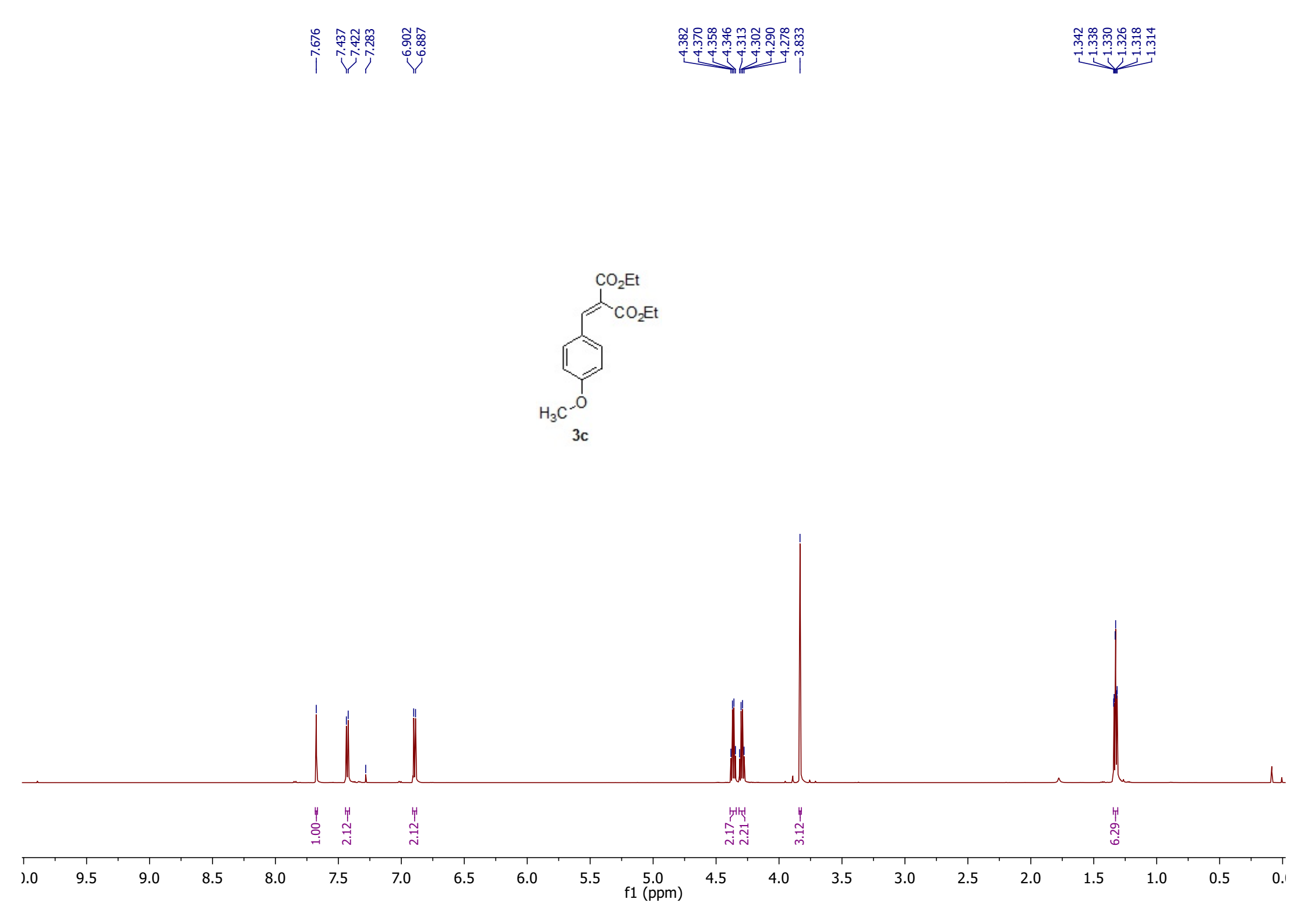
61.86
61.75
21.70
14.36
14.12
CO2Et
CO2Et
CH3
3b
f1 (ppm)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7.422
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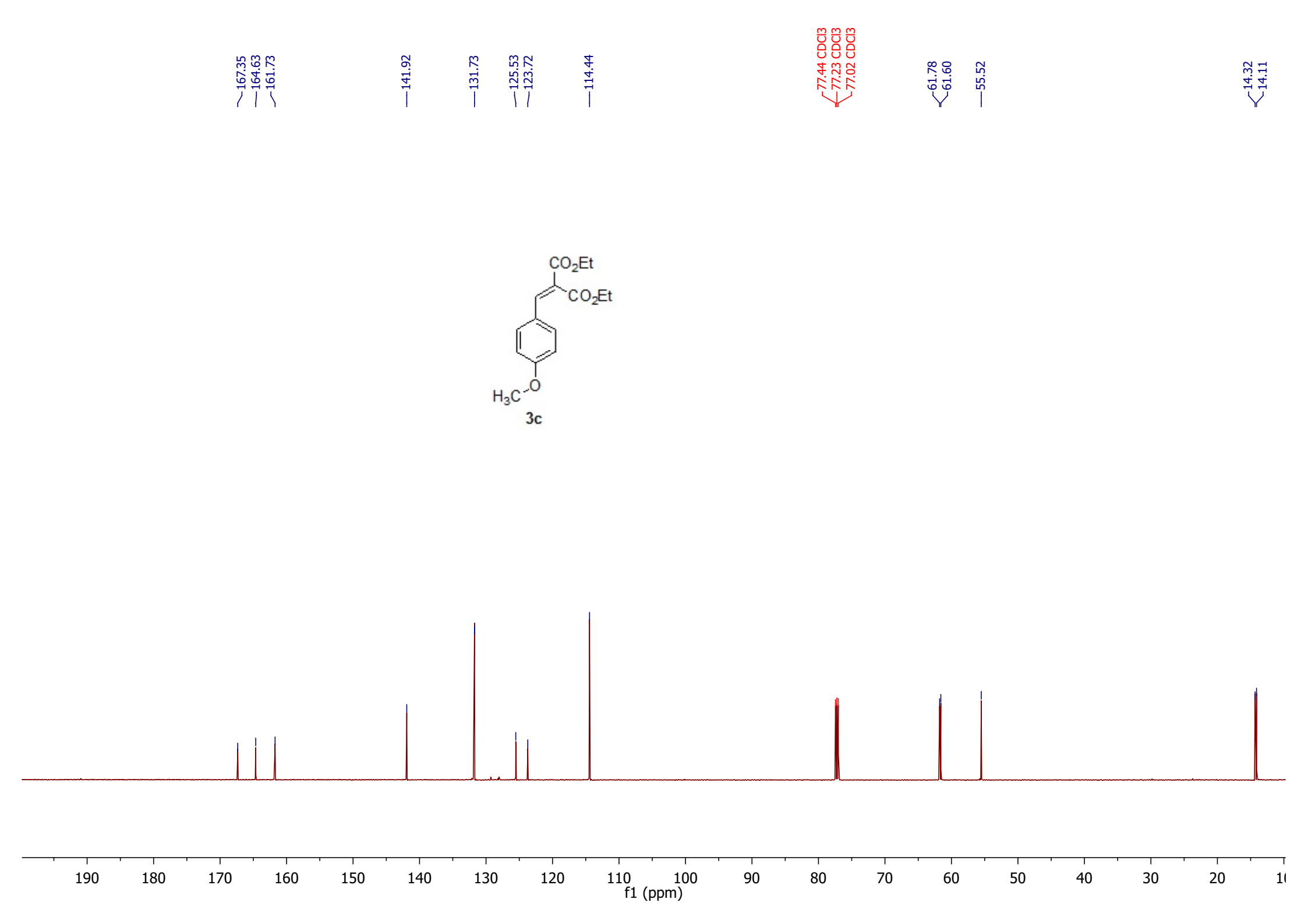
4.382
4.370
4.358
4.346
4.313
4.302
4.290
4.278
3.833
1.342
1.338
1.330
1.326
1.318
1.314
CO2Et
CO2Et
H3C-O
3c
1.00
2.12
2.12
2.17
2.21
3.12
6.29
f1 (ppm)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164.63
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125.53
123.72
114.44
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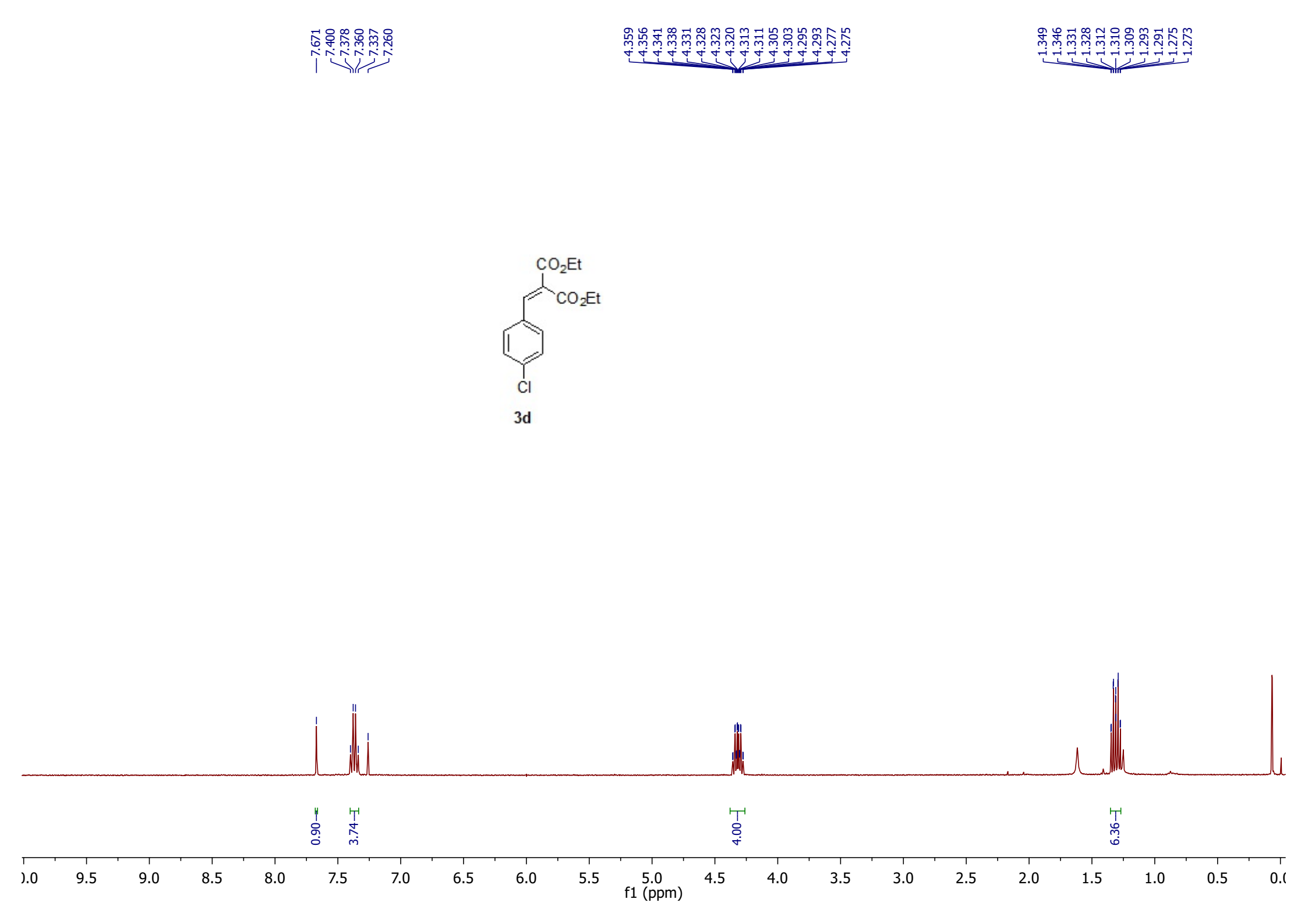
77.23 CDCl3
77.02 CDCl3
61.78
61.60
55.52
14.32
14.11
CO2Et
CO2Et
H3C
O
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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4.356
4.341
4.338
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4.323
4.320
4.313
4.311
4.305
4.303
4.295
4.293
4.277
4.275
1.349
1.346
1.331
1.328
1.312
1.310
1.309
1.293
1.291
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1.273
CO2Et
CO2Et
Cl
3d
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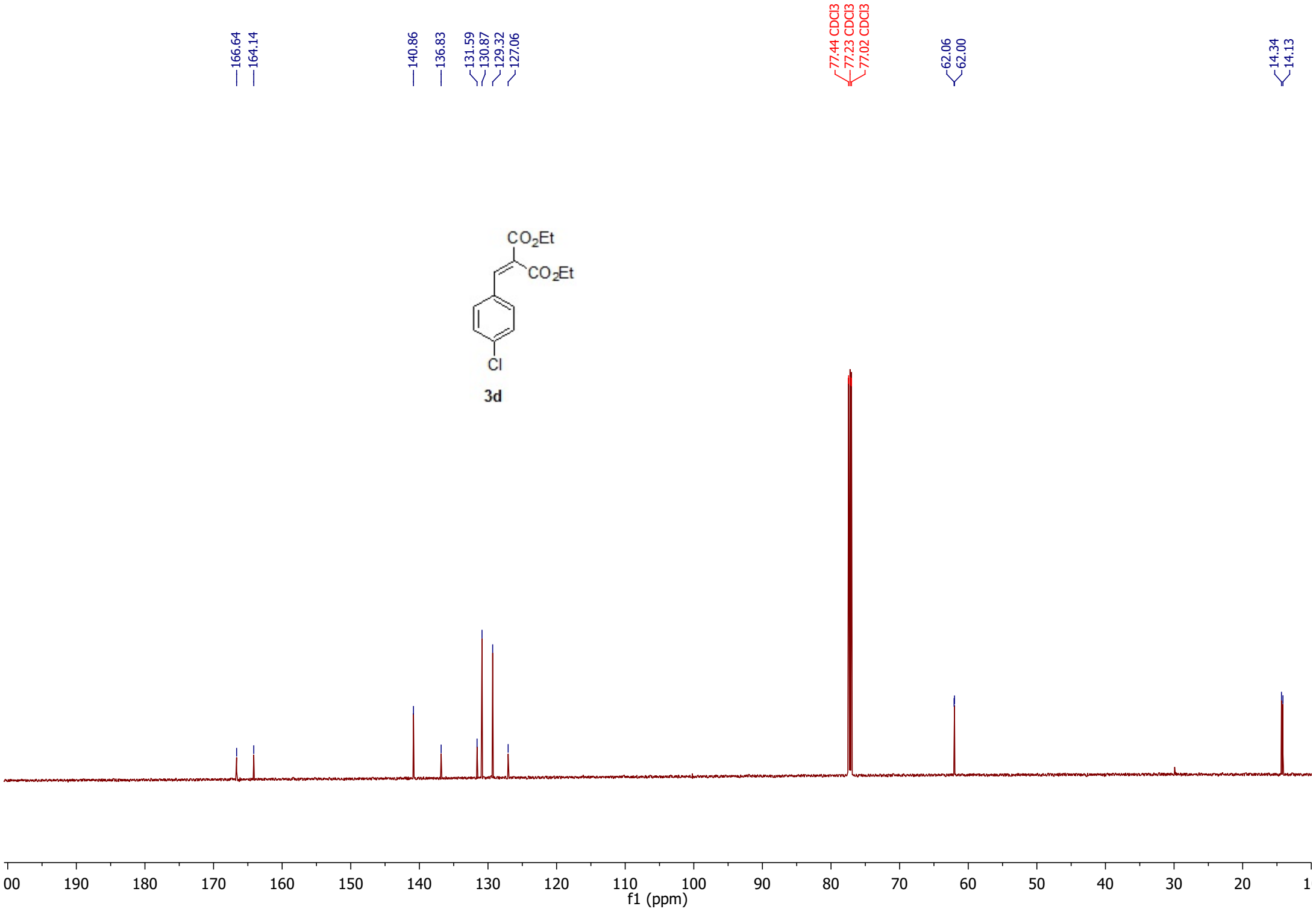
6.36
f1 (ppm)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129.32
127.06
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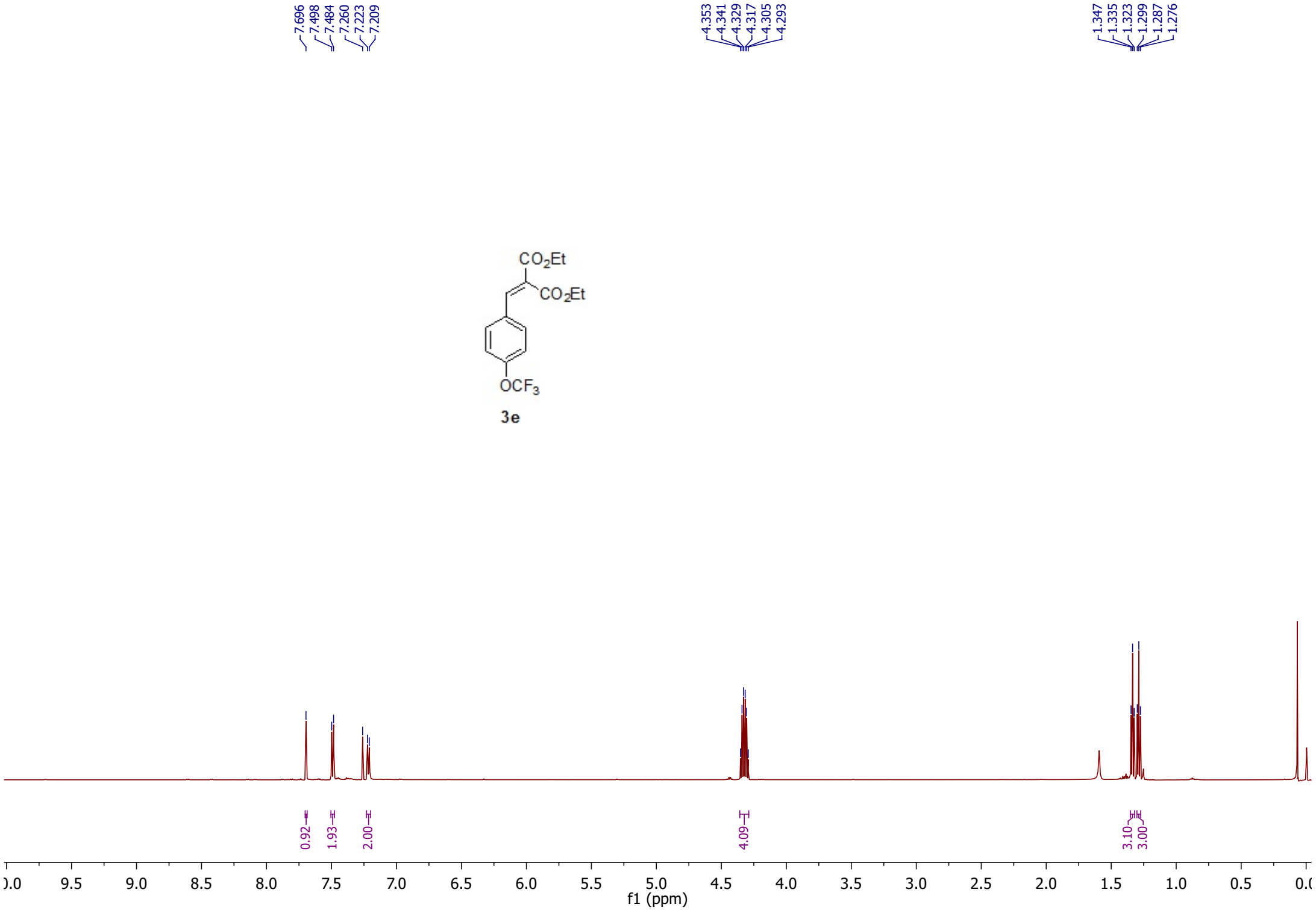
62.00
14.34
14.13
CO2Et
CO2Et
Cl
3d
f1 (ppm)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1.335
1.323
1.299
1.287
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OCF3
3e
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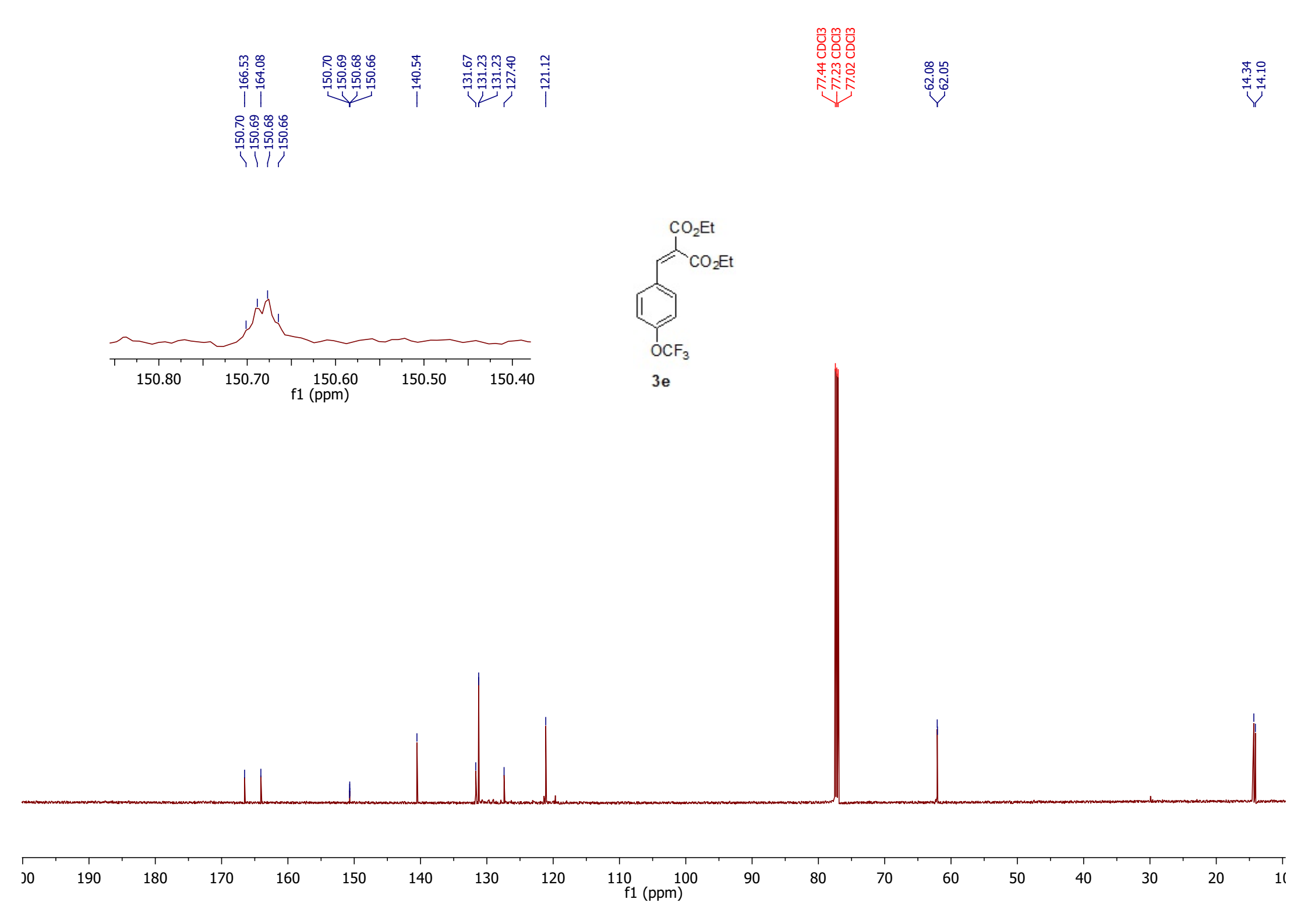
4.09
3.10
3.00
f1 (ppm)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140.54
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131.23
131.23
127.40
121.12
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
62.08
62.05
14.34
14.10
150.80
150.70
150.60
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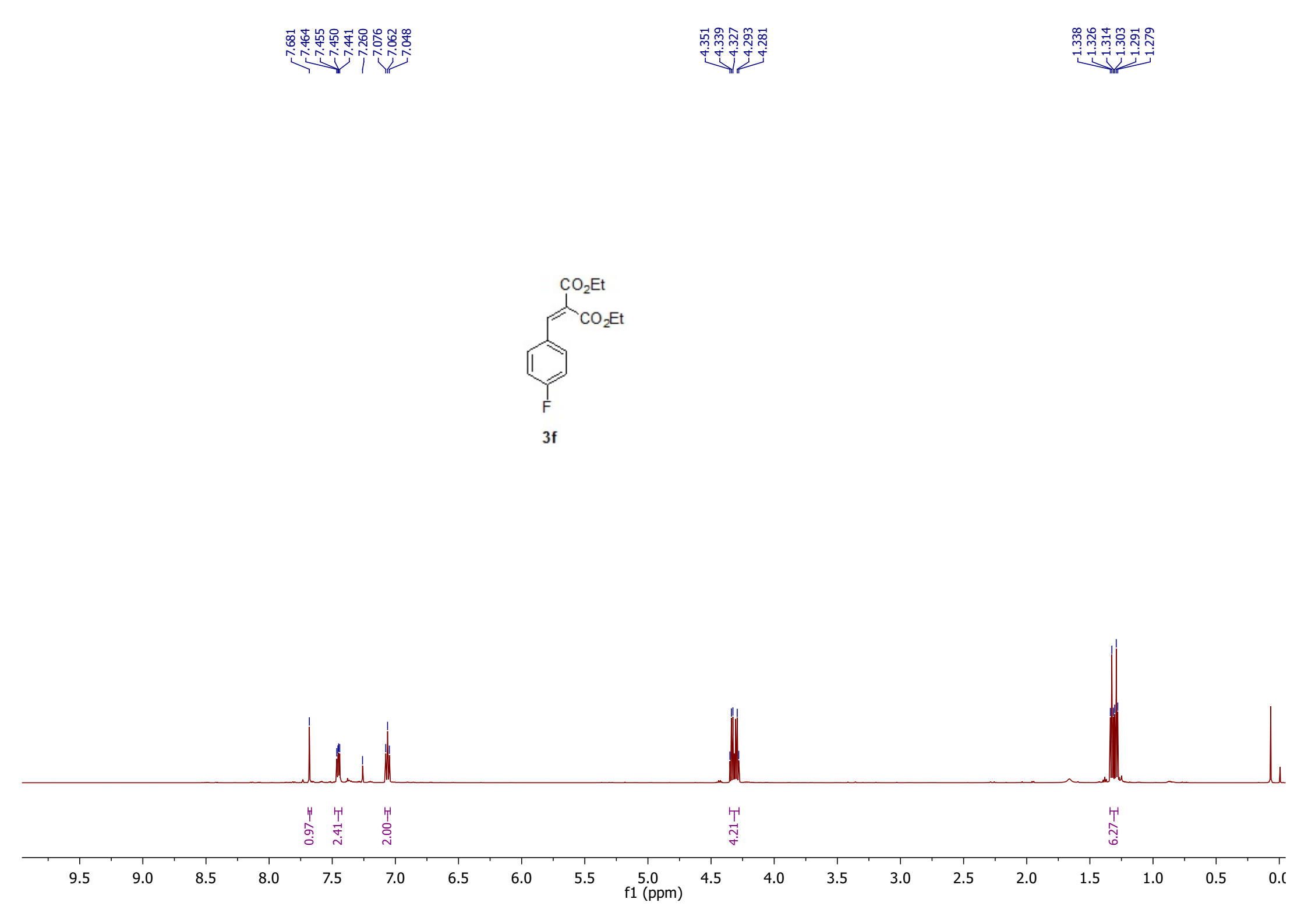
150.40
f1 (ppm)
CO2Et
CO2Et
OCF3
3e
f1 (ppm)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4.281
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1.326
1.314
1.303
1.291
1.279
CO2Et
CO2Et
F
3f
0.97
2.41
2.00
4.21
6.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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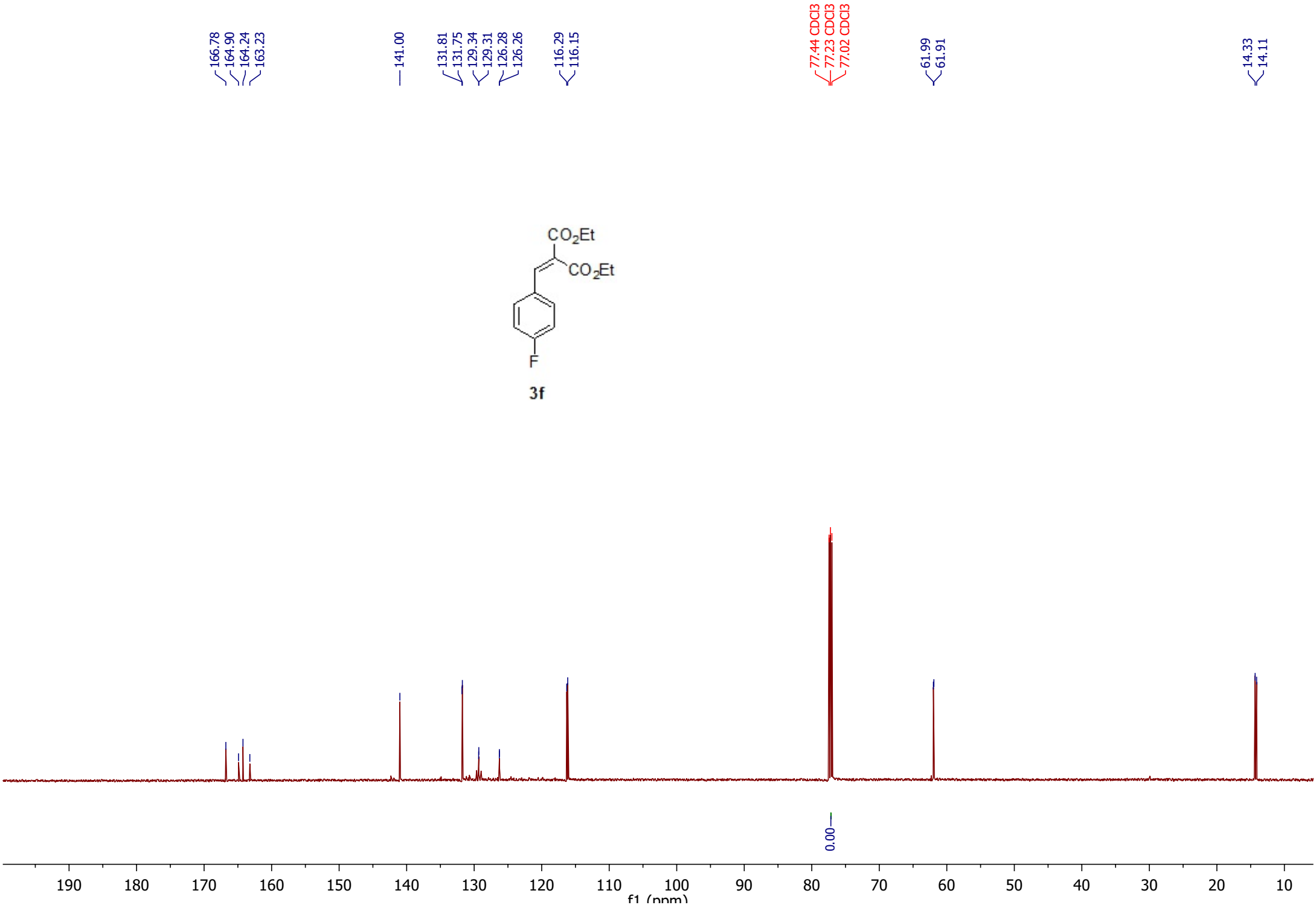
f1 (ppm)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77.23 CDCl3
77.02 CDCl3
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61.91
14.33
14.11
CO2Et
CO2Et
F
3f
0.00
190
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140
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120
110
100
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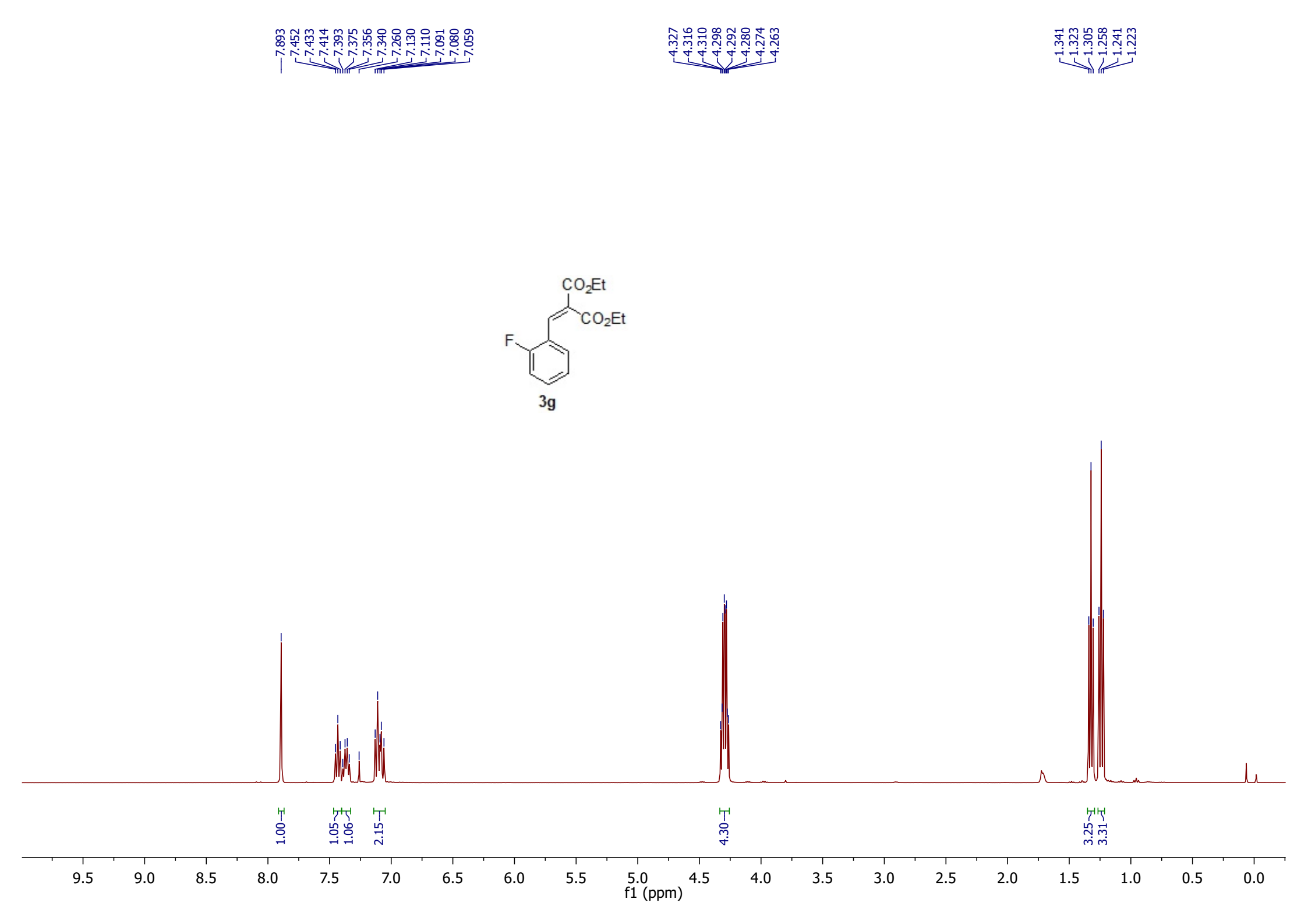
80
70
60
50
40
30
20
10
f1 (ppm)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4.316
4.310
4.298
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1.323
1.305
1.258
1.241
1.223
CO2Et
CO2Et
F
3g
1.00
1.05
1.06
2.15
4.30
3.25
3.31
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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1.0
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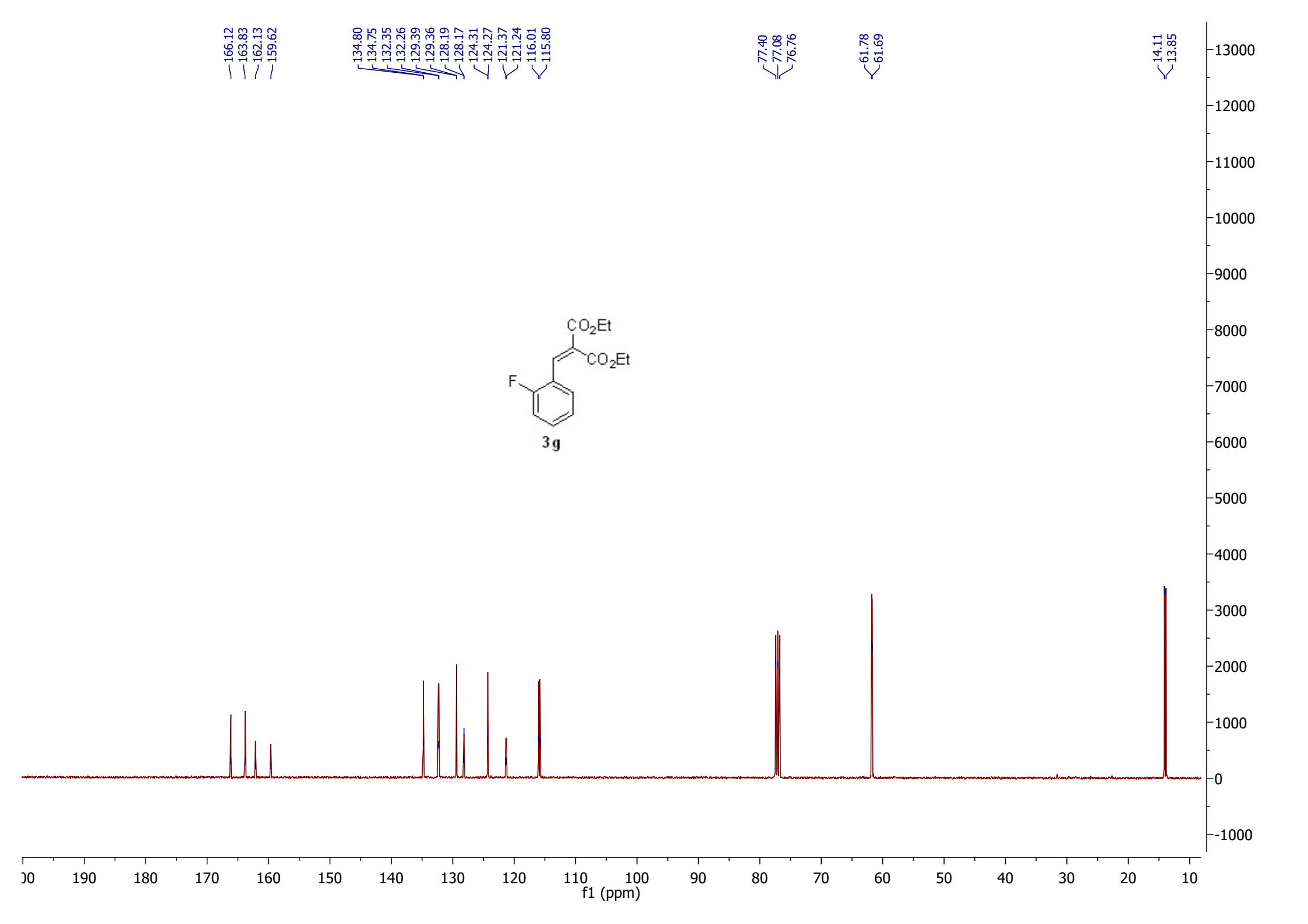
f1 (ppm)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124.31
124.27
121.37
121.24
116.01
115.80
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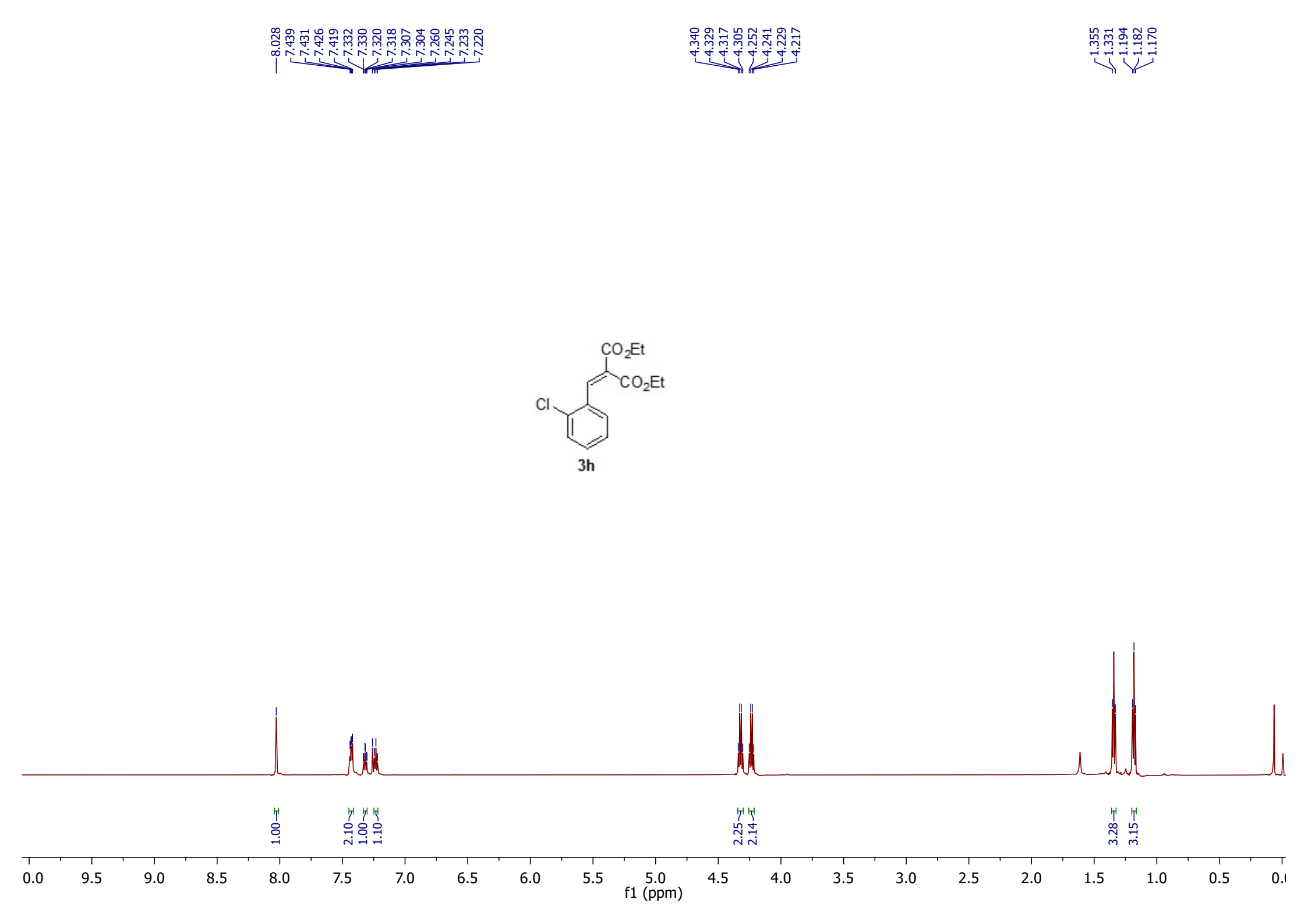
76.76
61.78
61.69
14.11
13.85
CO2Et
CO2Et
F
3g
f1 (ppm)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7.419
7.332
7.330
7.320
7.318
7.307
7.304
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7.245
7.233
7.220
4.340
4.329
4.317
4.305
4.252
4.241
4.229
4.217
1.355
1.331
1.194
1.182
1.170
CO2Et
CO2Et
Cl
3h
1.00
2.10
1.00
1.10
2.25
2.14
3.28
3.15
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.5
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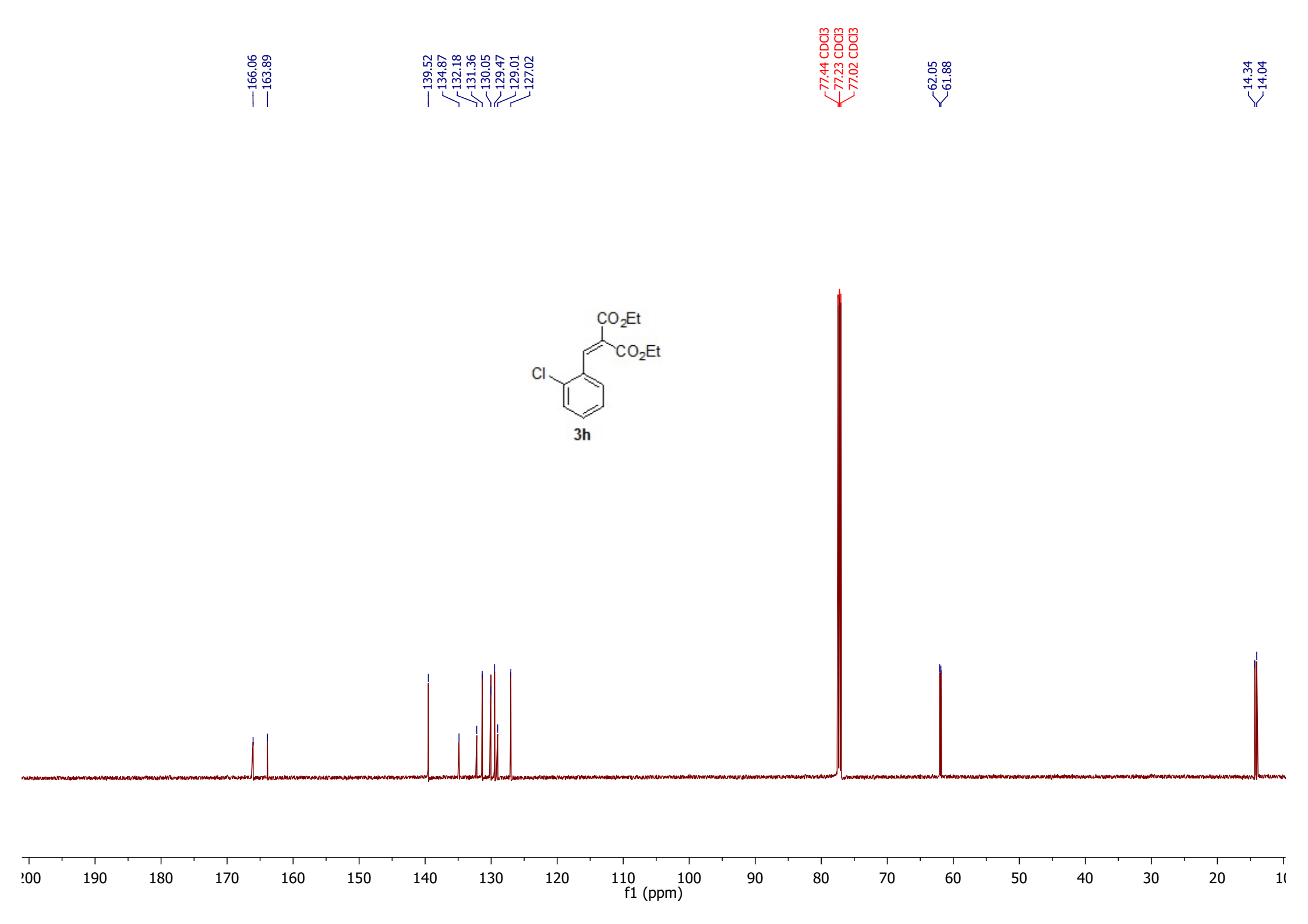
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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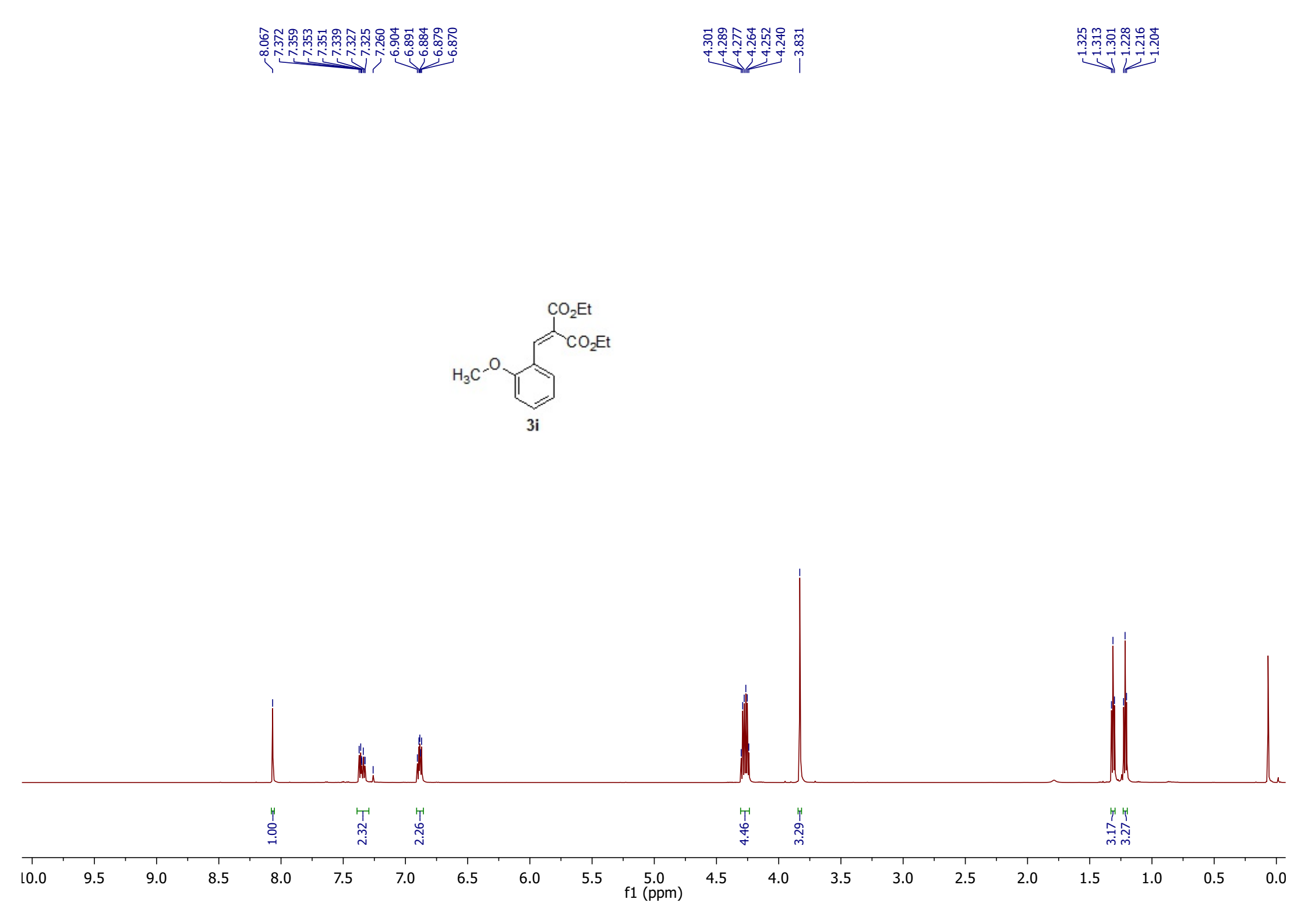
163.89
139.52
134.87
132.18
131.36
130.05
129.47
129.01
127.02
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
62.05
61.88
14.34
14.04
CO2Et
CO2Et
Cl
3h
f1 (ppm)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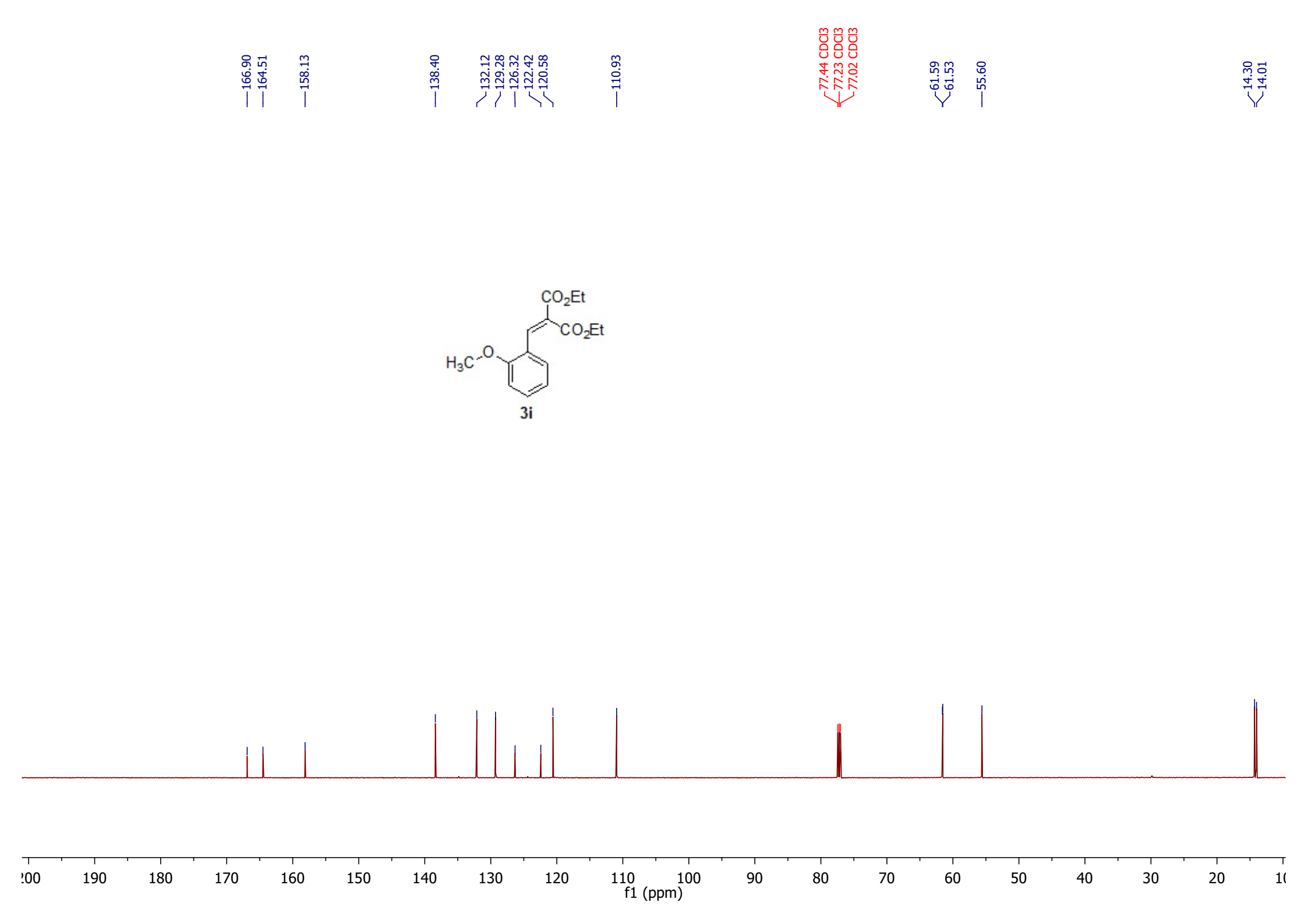
7.327
7.325
7.260
6.904
6.891
6.884
6.879
6.870
4.301
4.289
4.277
4.264
4.252
4.240
3.831
1.325
1.313
1.301
1.228
1.216
1.204
CO2Et
CO2Et
H3C
O
3i
1.00
2.32
2.26
4.46
3.29
3.17
3.27
f1 (ppm)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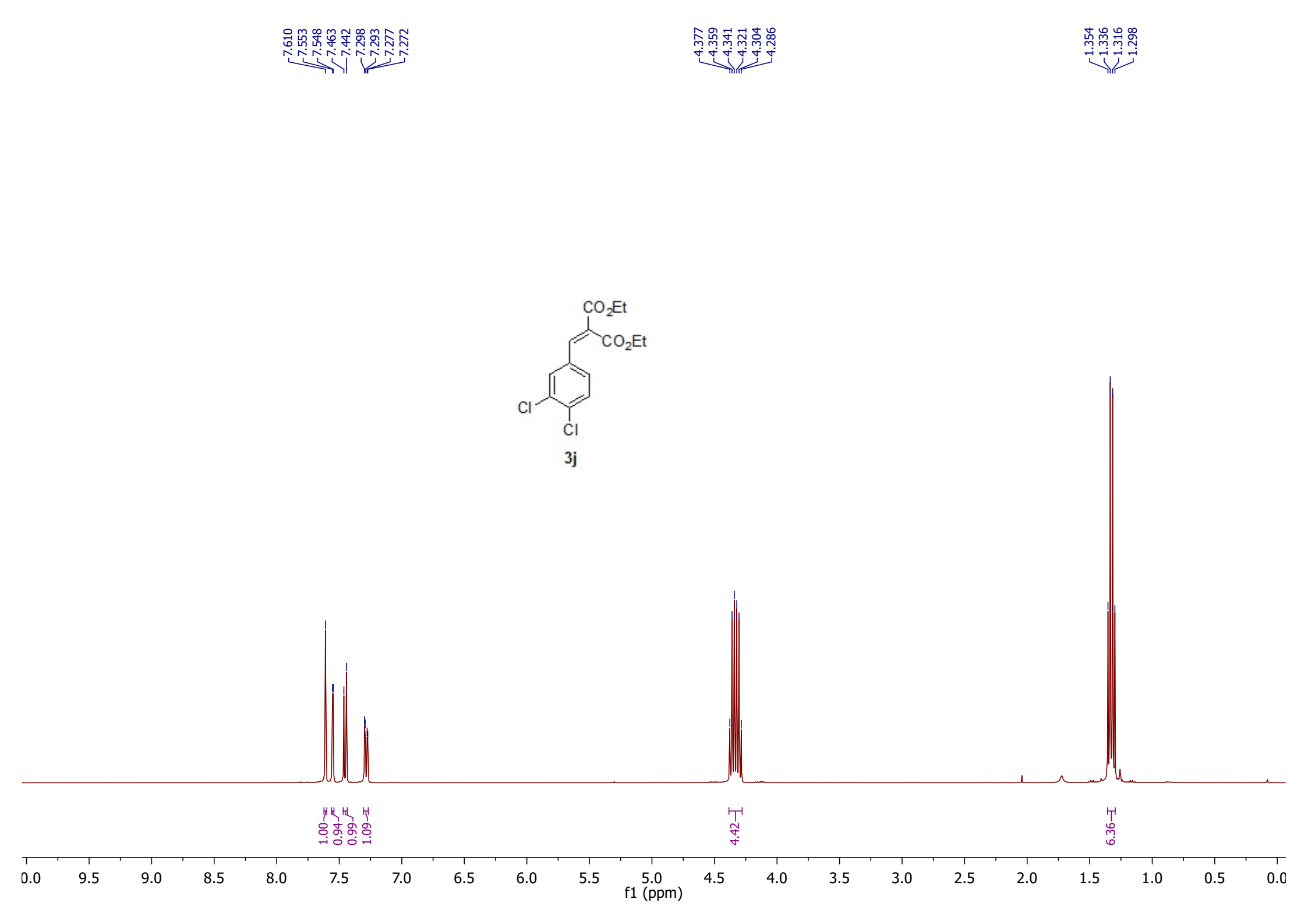
132.12
129.28
126.32
122.42
120.58
110.93
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
61.59
61.53
55.60
14.30
14.01
CO2Et
CO2Et
H3C
O
3i
f1 (ppm)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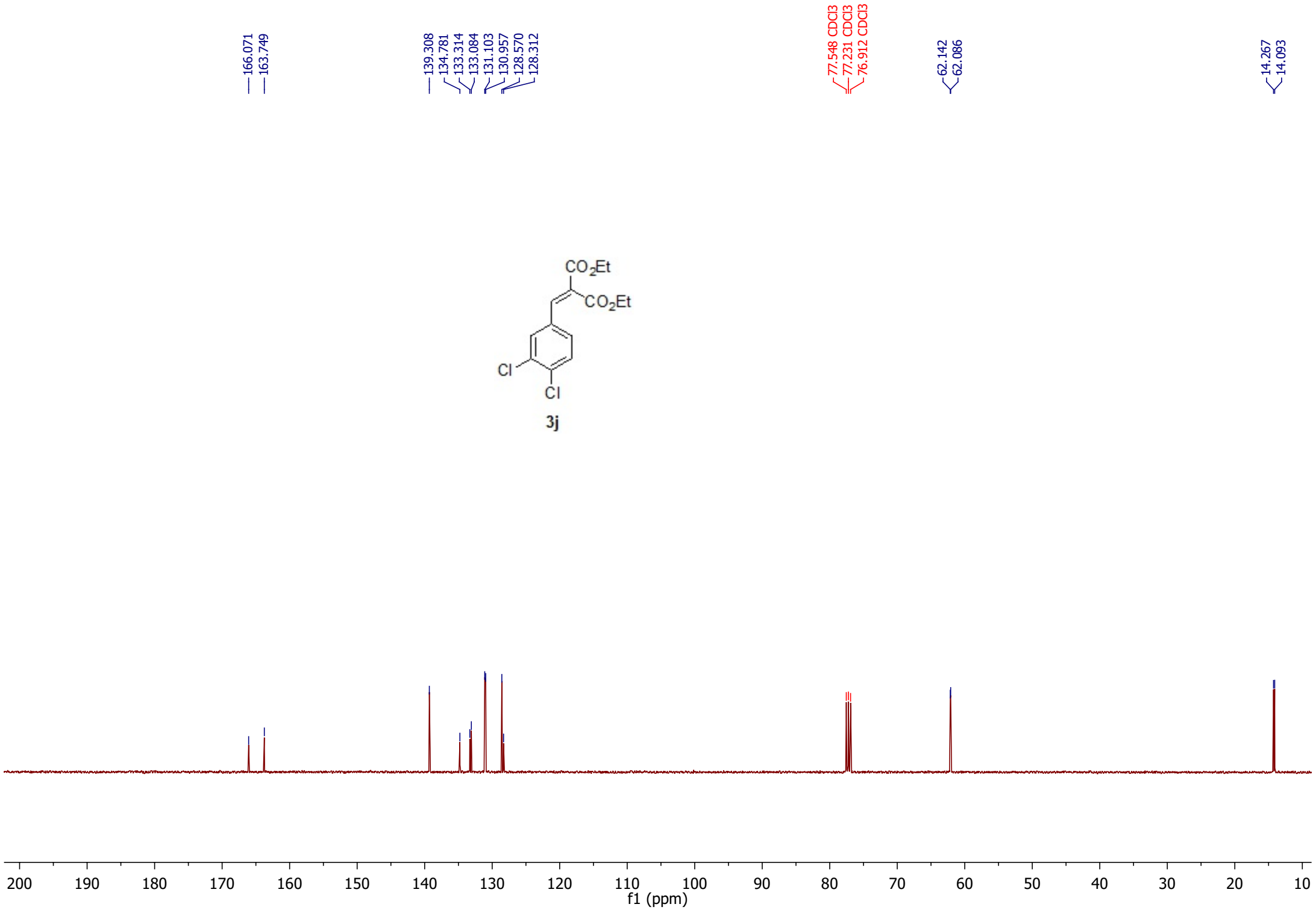
7.548
7.463
7.442
7.298
7.293
7.277
7.272
4.377
4.359
4.341
4.321
4.304
4.286
1.354
1.336
1.316
1.298
CO2Et
CO2Et
Cl
Cl
3j
1.00
0.94
0.99
1.09
4.42
6.36
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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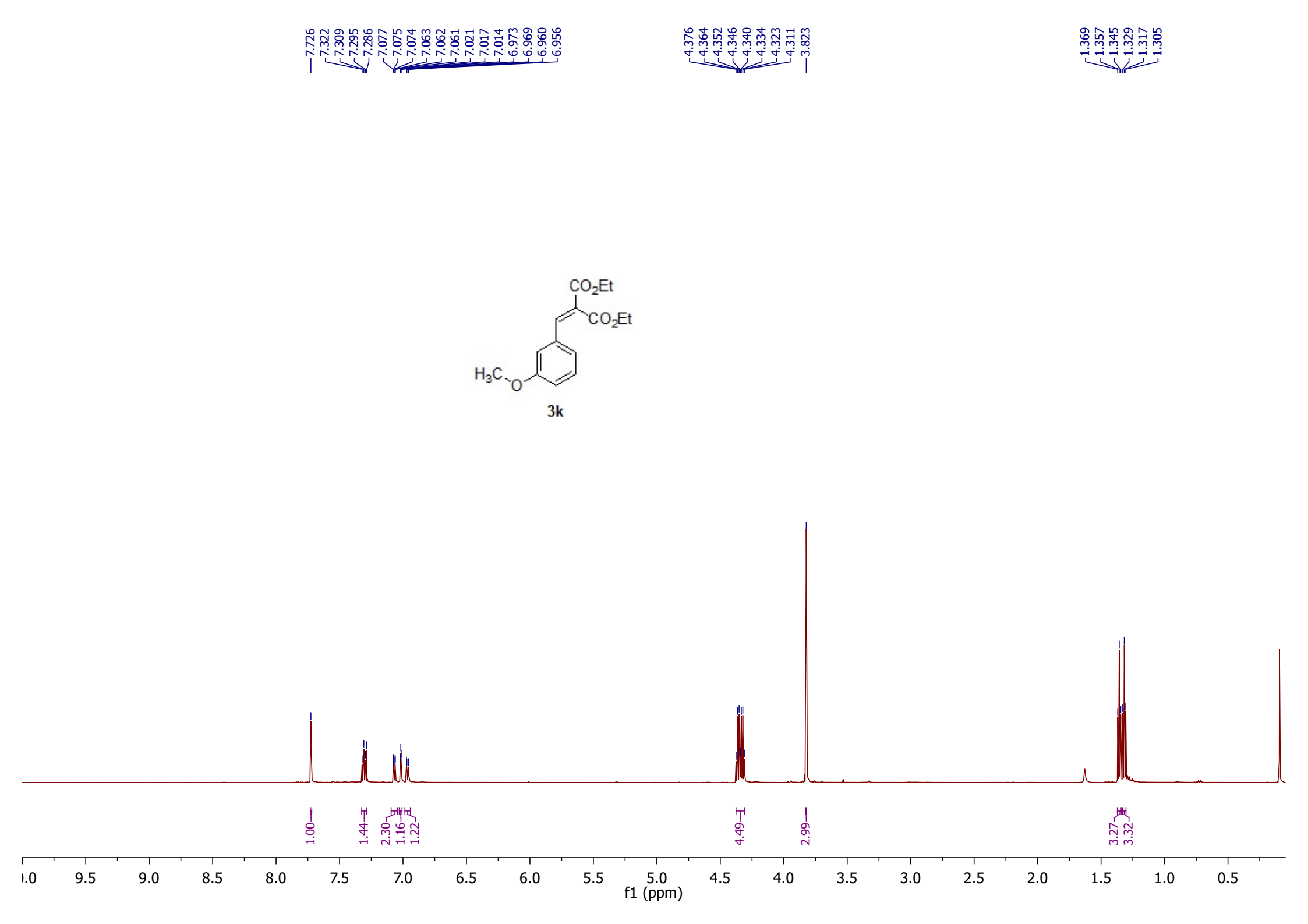
163.749
139.308
134.781
133.314
133.084
131.103
130.957
128.570
128.312
77.548 CDCl3
77.231 CDCl3
76.912 CDCl3
62.142
62.086
14.267
14.093
CO2Et
CO2Et
Cl
Cl
3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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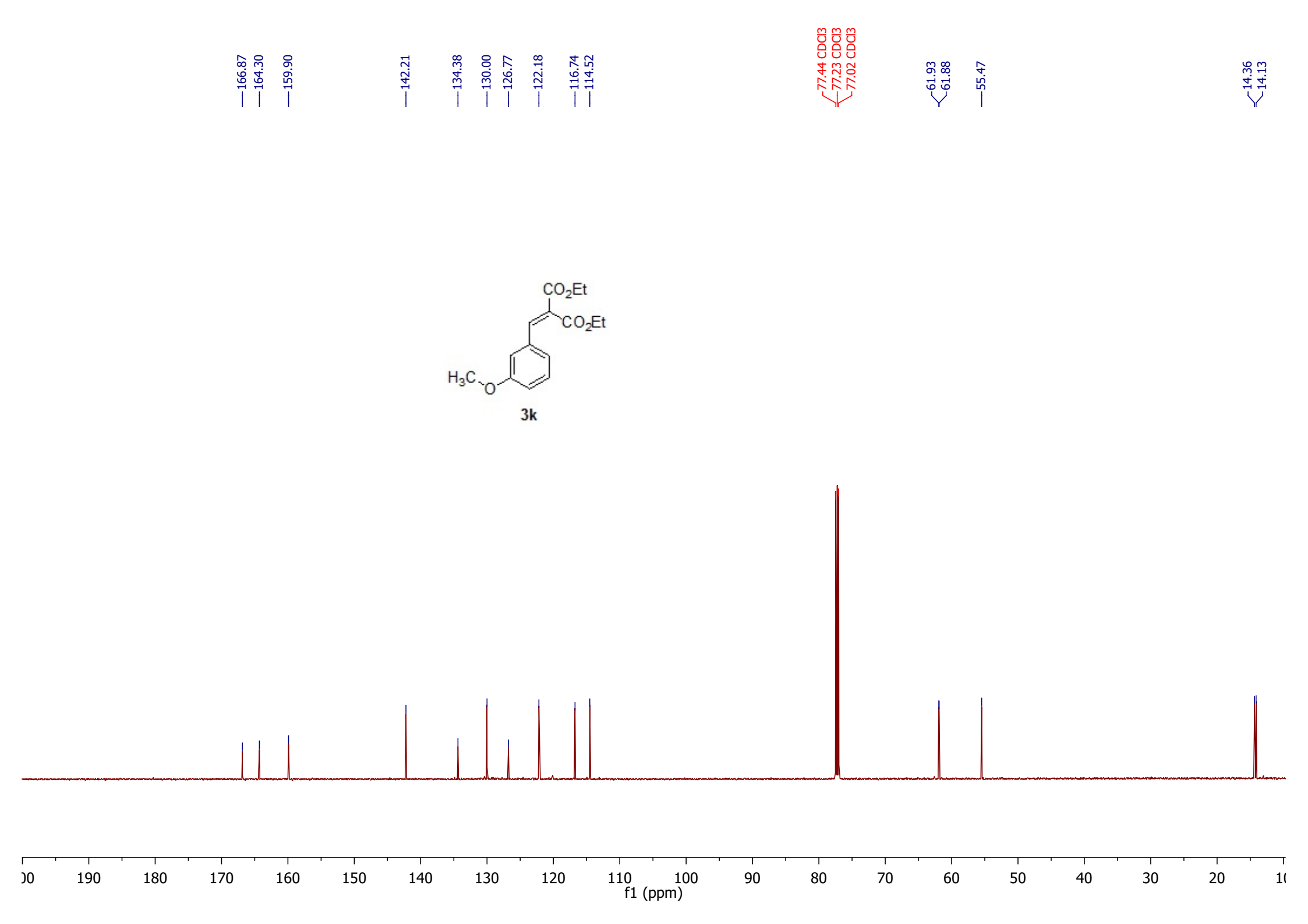
7.309
7.295
7.286
7.077
7.075
7.074
7.063
7.062
7.061
7.021
7.017
7.014
6.973
6.969
6.960
6.956
4.376
4.364
4.352
4.346
4.340
4.334
4.323
4.311
3.823
1.369
1.357
1.345
1.329
1.317
1.305
CO2Et
CO2Et
H3C
O
3k
1.00
1.44
2.30
1.16
1.22
4.49
2.99
3.27
3.32
f1 (ppm)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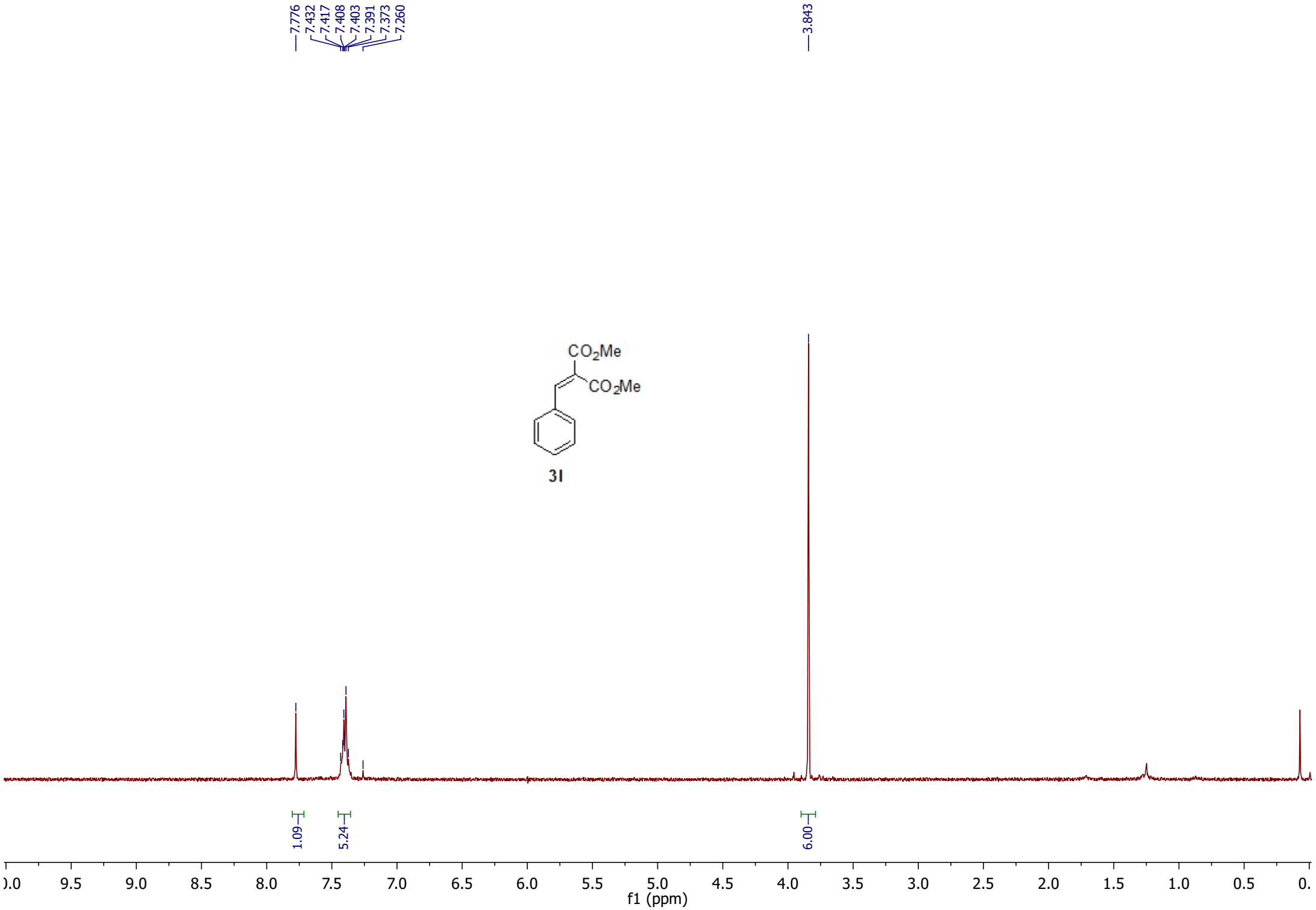
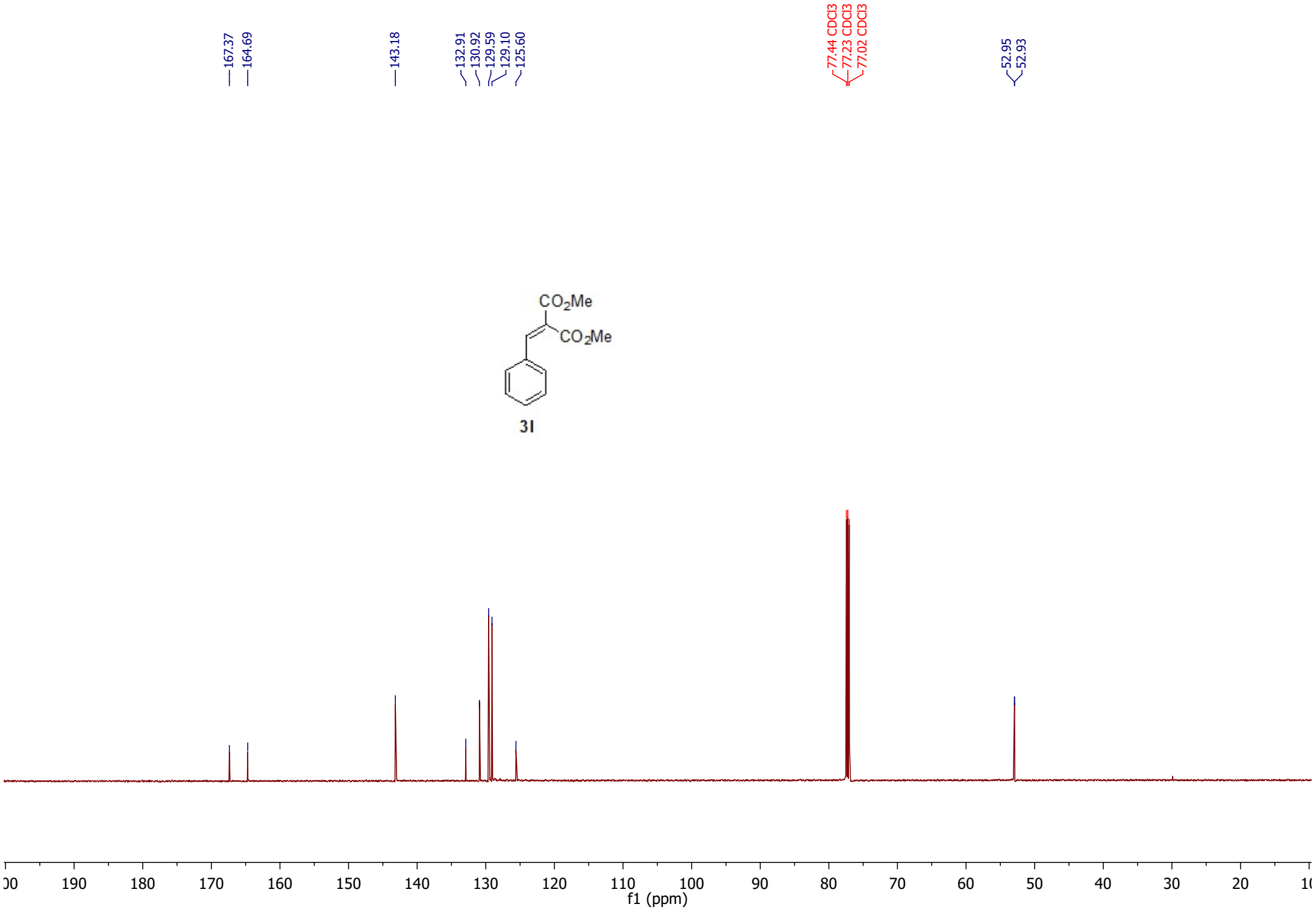
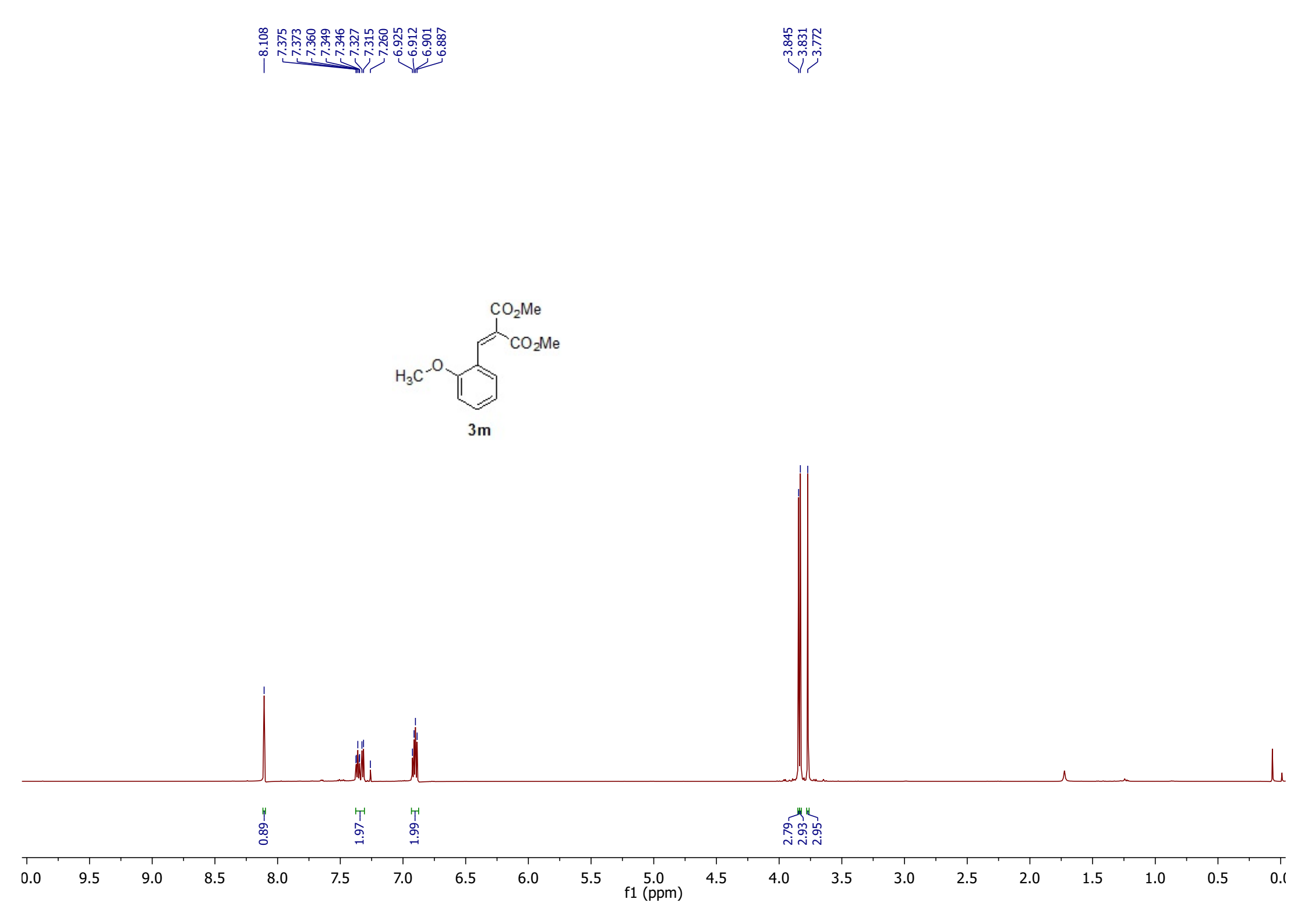
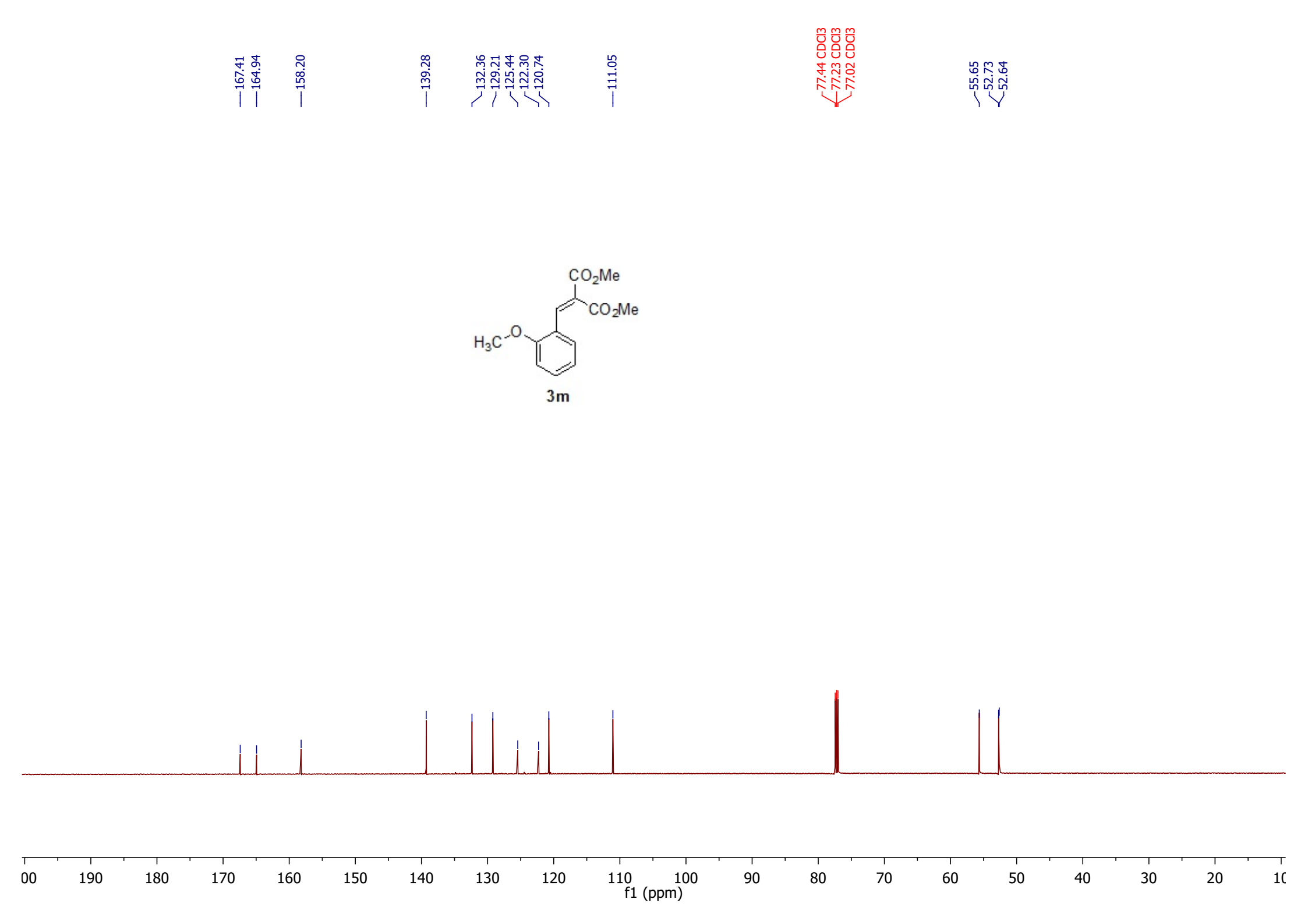
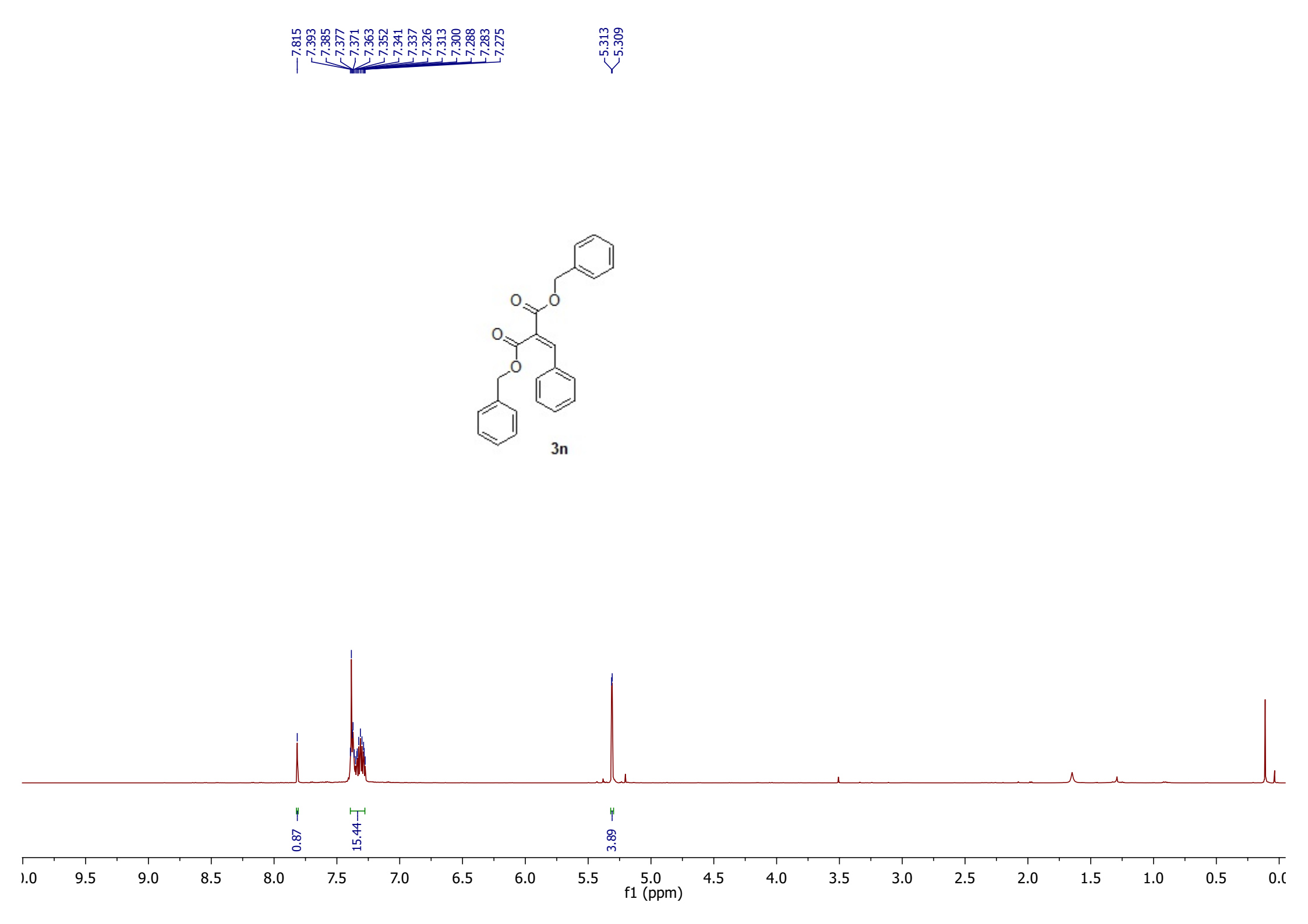
164.30
159.90
142.21
134.38
130.00
126.77
122.18
116.74
114.52
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
61.93
61.88
55.47
14.36
14.13
CO2Et
CO2Et
H3C
O
3k
f1 (ppm)

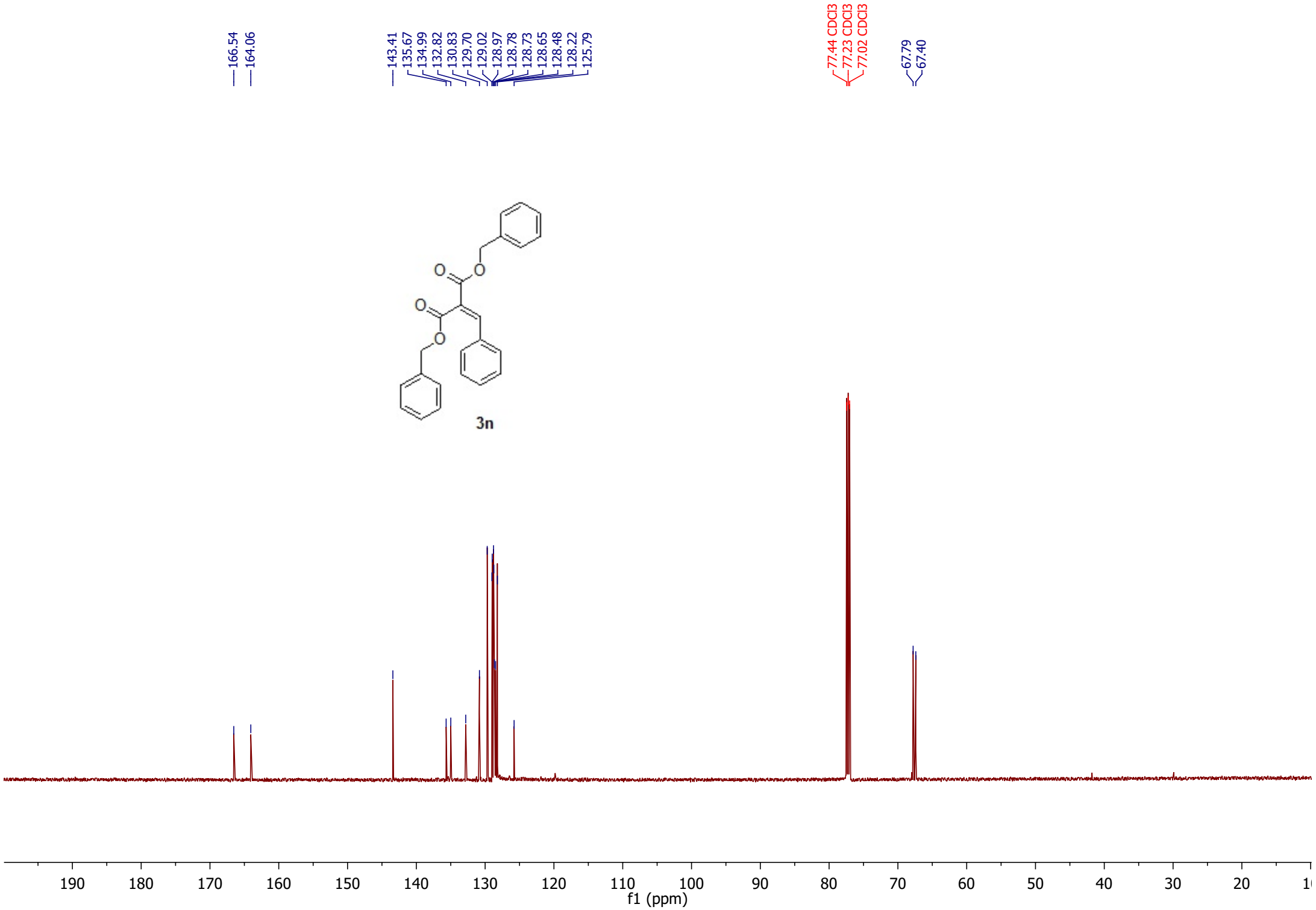

7.776
7.432
7.417
7.408
7.403
7.391
7.373
7.260
3.843
CO2Me
CO2Me
3l
1.09
5.24
6.00
f1 (ppm)

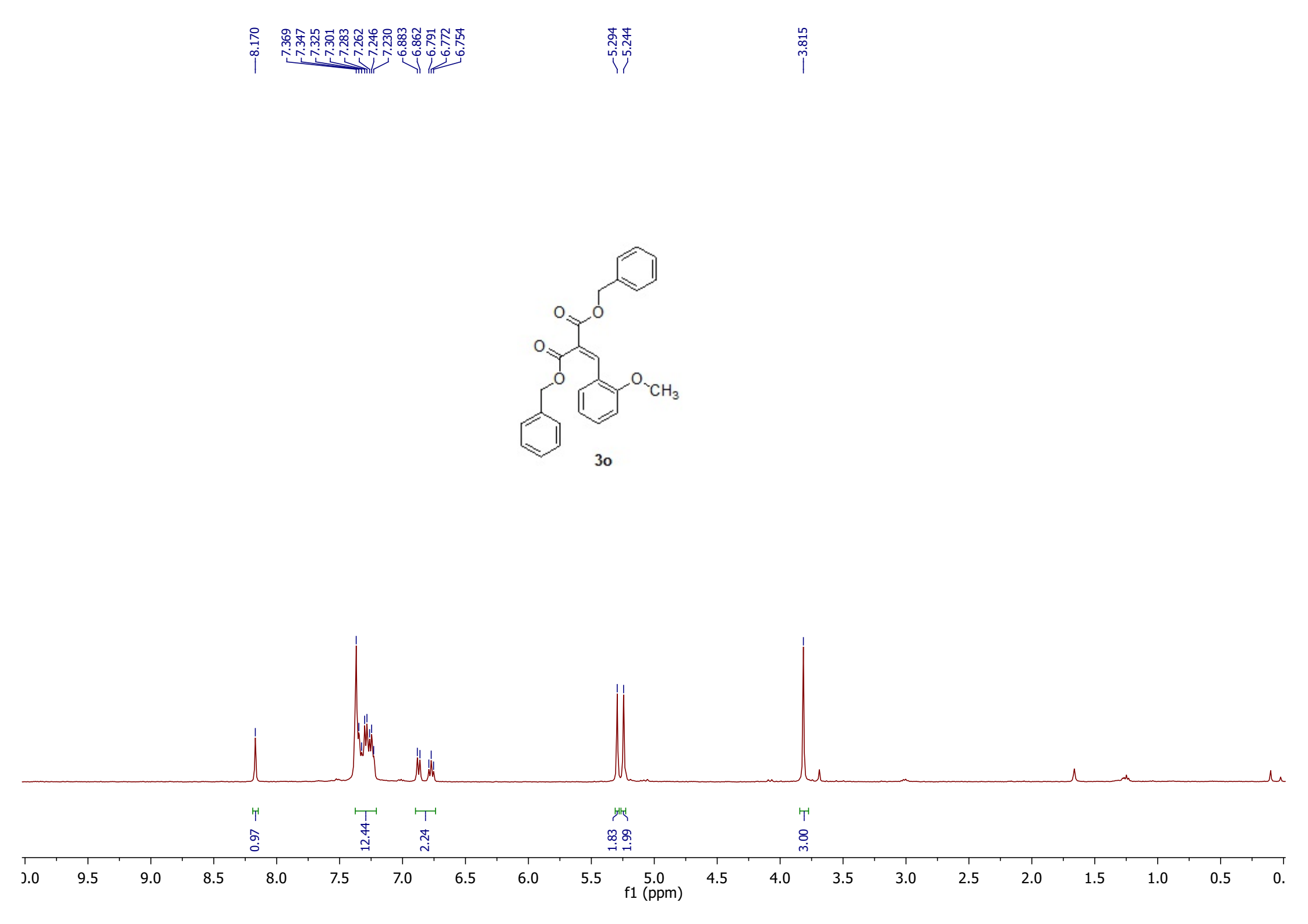

167.37
164.69
143.18
132.91
130.92
129.59
129.10
125.60
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
52.95
52.93
CO2Me
CO2Me
3l
f1 (ppm)


8.108
7.375
7.373
7.360
7.349
7.346
7.327
7.315
7.260
6.925
6.912
6.901
6.887
3.845
3.831
3.772
CO2Me
CO2Me
H3C
O
3m
0.89
1.97
1.99
2.79
2.93
2.95
f1 (ppm)


167.41
164.94
158.20
139.28
132.36
129.21
125.44
122.30
120.74
111.05
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
55.65
52.73
52.64
CO2Me
CO2Me
H3C
O
3m
f1 (ppm)


7.815
7.393
7.385
7.377
7.371
7.363
7.352
7.341
7.337
7.326
7.313
7.300
7.288
7.283
7.275
5.313
5.309
O
O
O
O
3n
0.87
15.44
3.89
f1 (ppm)


166.54
164.06
143.41
135.67
134.99
132.82
130.83
129.70
129.02
128.97
128.78
128.73
128.65
128.48
128.22
125.79
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
67.79
67.40
O
O
O
O
3n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


8.170
7.369
7.347
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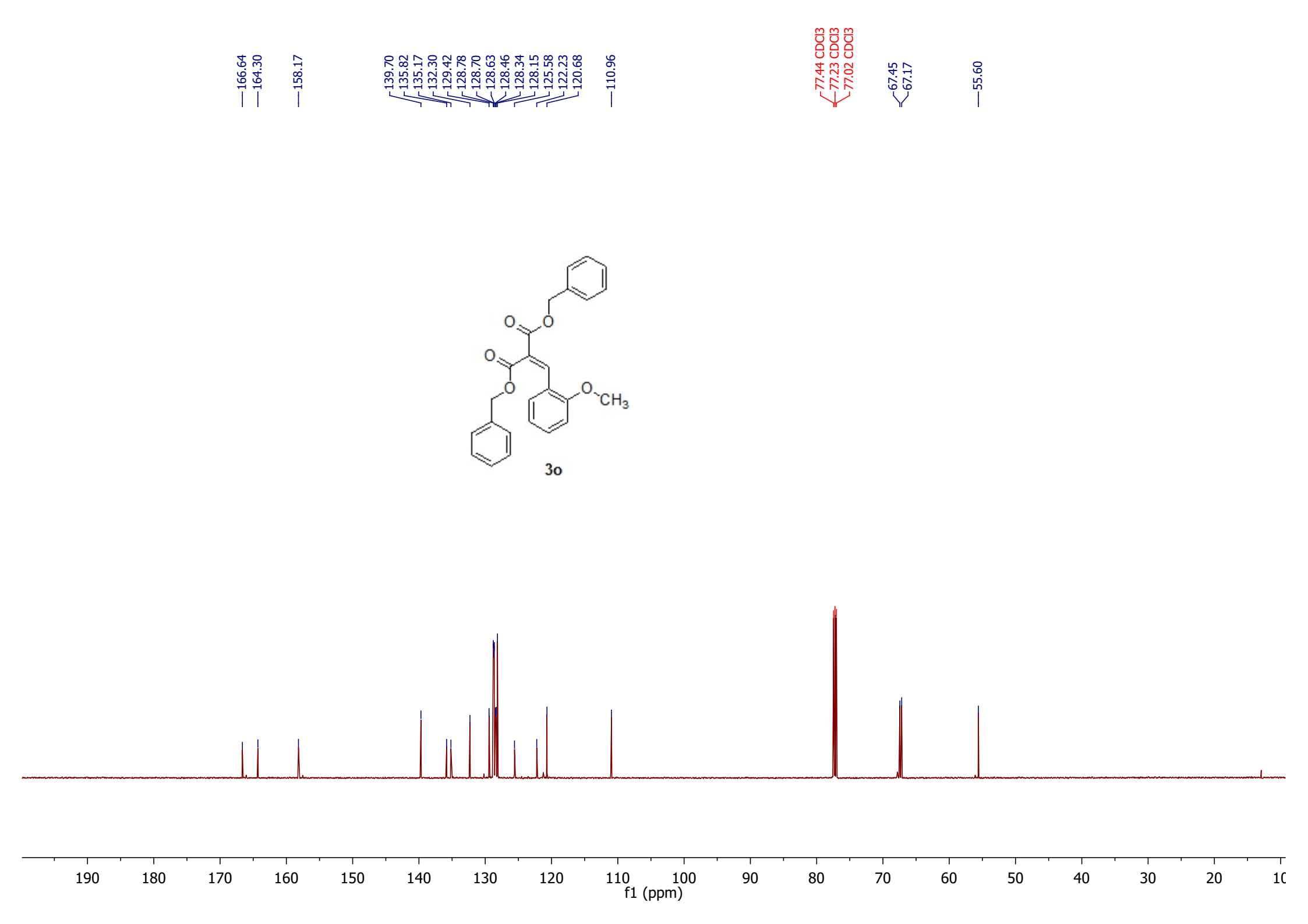
7.301
7.283
7.262
7.246
7.230
6.883
6.862
6.791
6.772
6.754
5.294
5.244
3.815
O
O
O
O
O
CH3
3o
0.97
12.44
2.24
1.83
1.99
3.00
f1 (ppm)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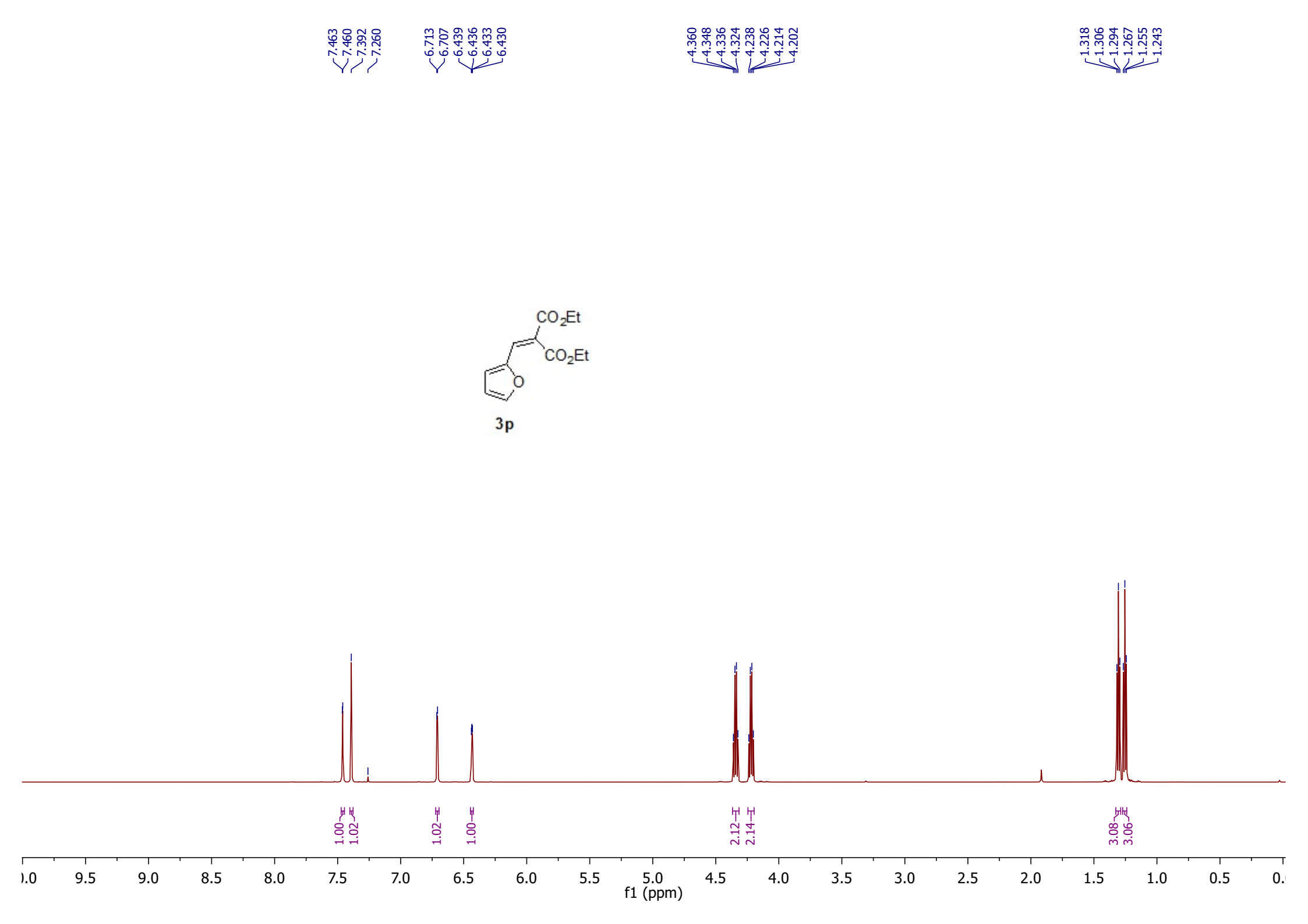
164.30
158.17
139.70
135.82
135.17
132.30
129.42
128.78
128.70
128.63
128.46
128.34
128.15
125.58
122.23
120.68
110.96
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
67.45
67.17
55.60
O
O
O
O
O
CH3
3o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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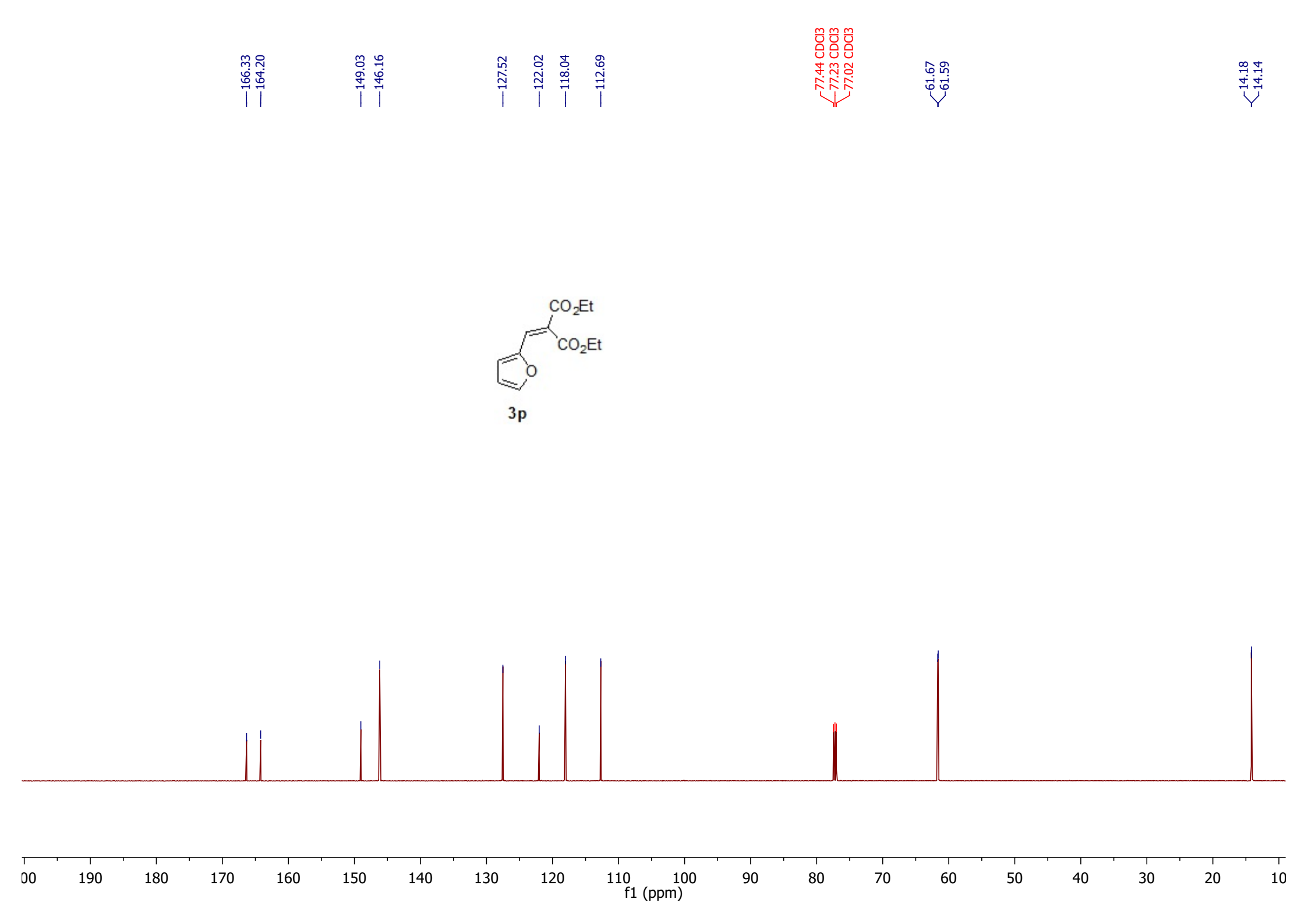
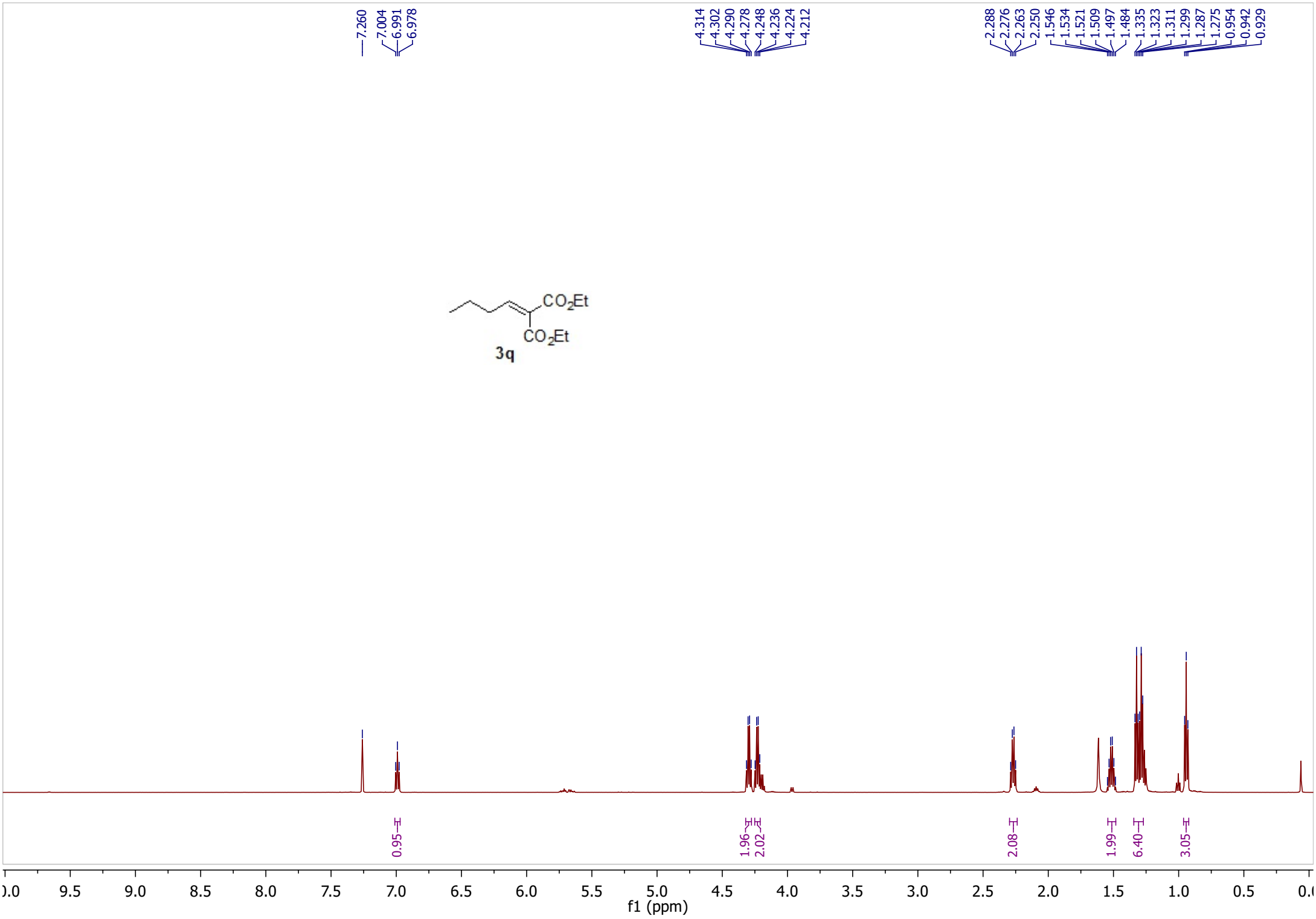
7.392
7.260
6.713
6.707
6.439
6.436
6.433
6.430
4.360
4.348
4.336
4.324
4.238
4.226
4.214
4.202
1.318
1.306
1.294
1.267
1.255
1.243
CO2Et
CO2Et
O
3p
1.00
1.02
1.02
1.00
2.12
2.14
3.08
3.06
f1 (ppm)


166.33
164.20
149.03
146.16
127.52
122.02
118.04
112.69
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
61.67
61.59
14.18
14.14
CO2Et
CO2Et
O
3p
f1 (ppm)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6.991
6.978
4.314
4.302
4.290
4.278
4.248
4.236
4.224
4.212
2.288
2.276
2.263
2.250
1.546
1.534
1.521
1.509
1.497
1.484
1.335
1.323
1.311
1.299
1.287
1.275
0.954
0.942
0.929
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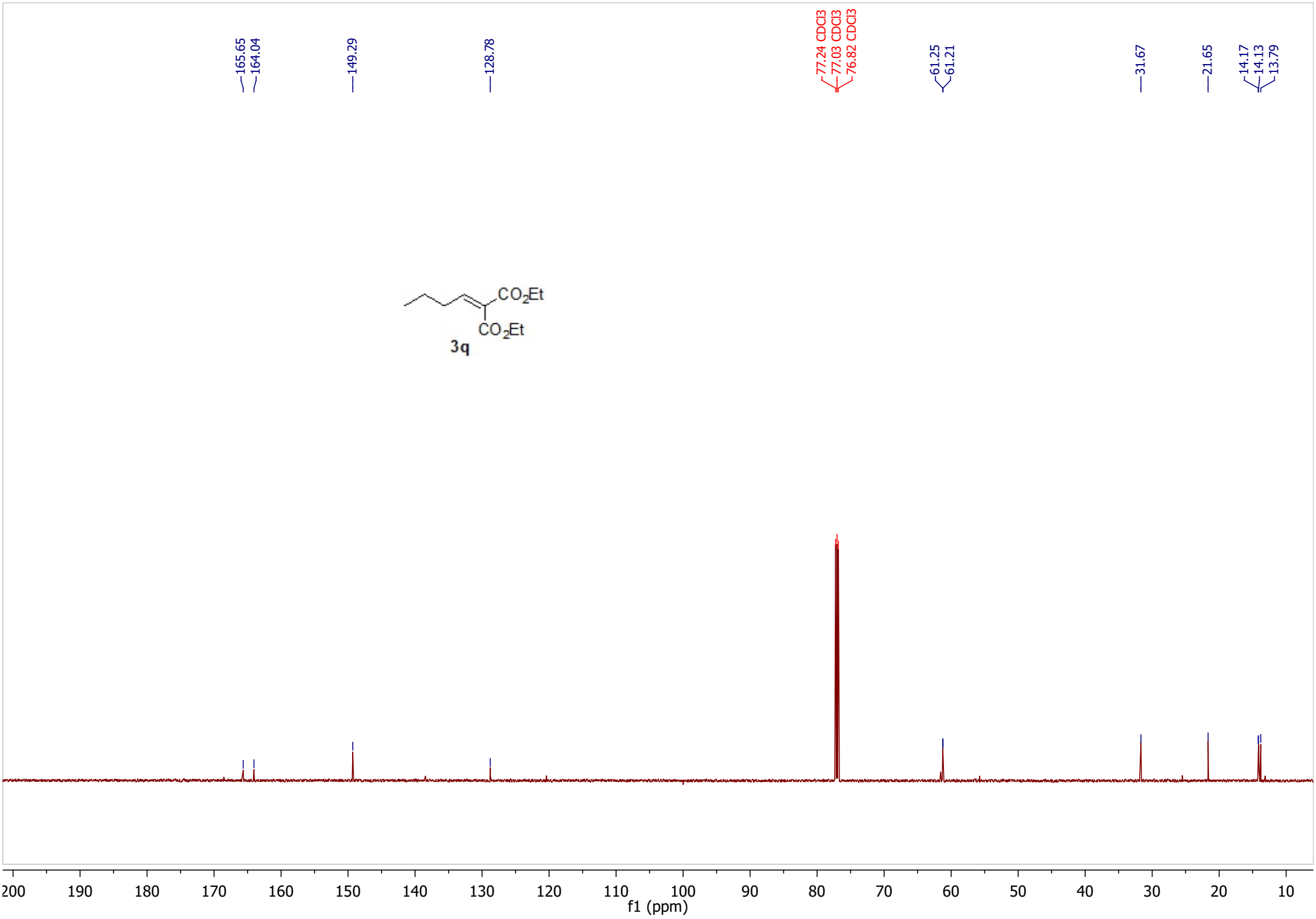
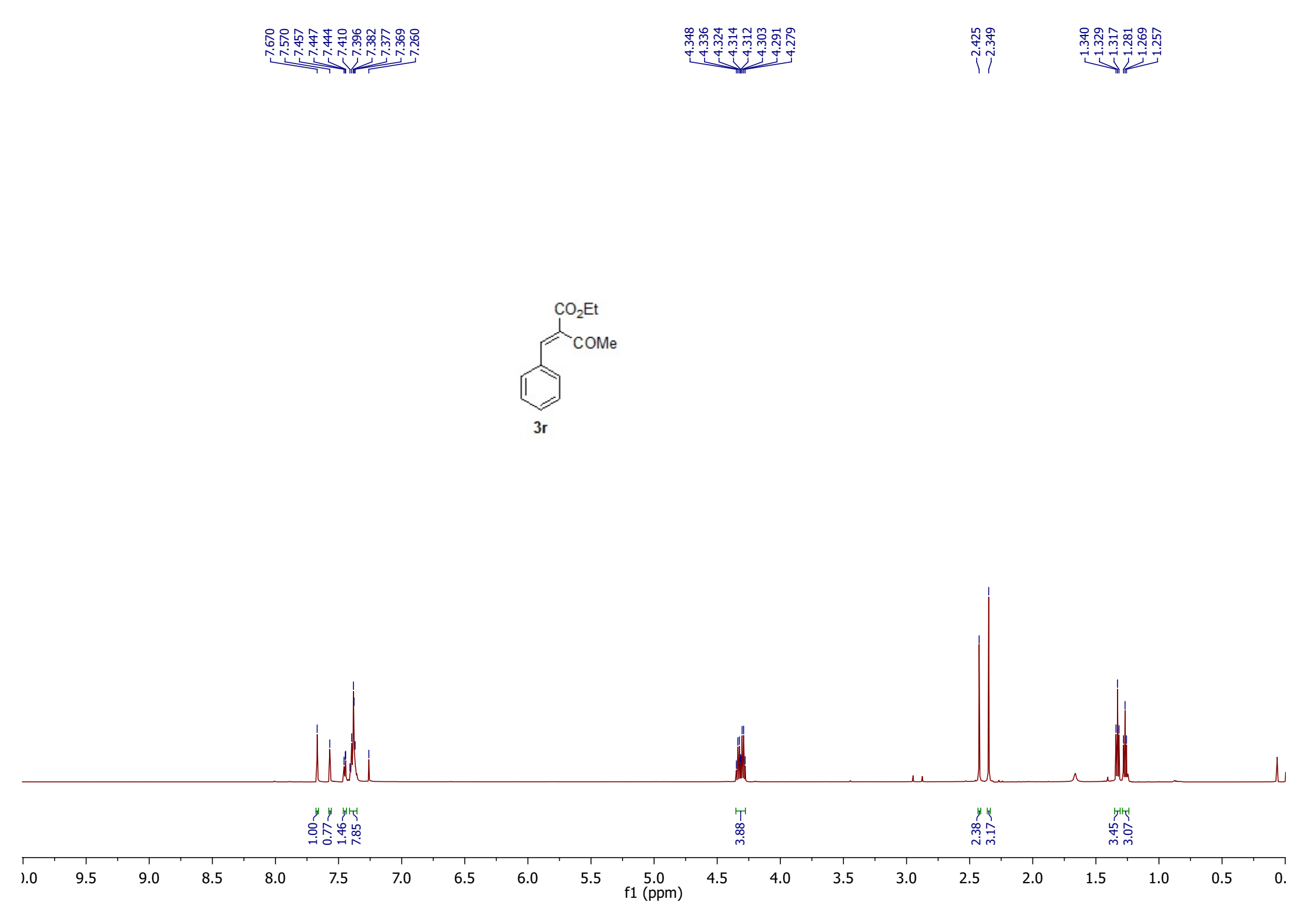
CO2Et
3q
0.95
1.96
2.02
2.08
1.99
6.40
3.05
f1 (ppm)


165.65
164.04
149.29
128.78
77.24 CDCl3
77.03 CDCl3
76.82 CDCl3
61.25
61.21
31.67
21.65
14.17
14.13
13.79
CO2Et
CO2Et
3q
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.444
7.410
7.396
7.382
7.377
7.369
7.260
4.348
4.336
4.324
4.314
4.312
4.303
4.291
4.279
2.425
2.349
1.340
1.329
1.317
1.281
1.269
1.257
CO2Et
COMe
3r
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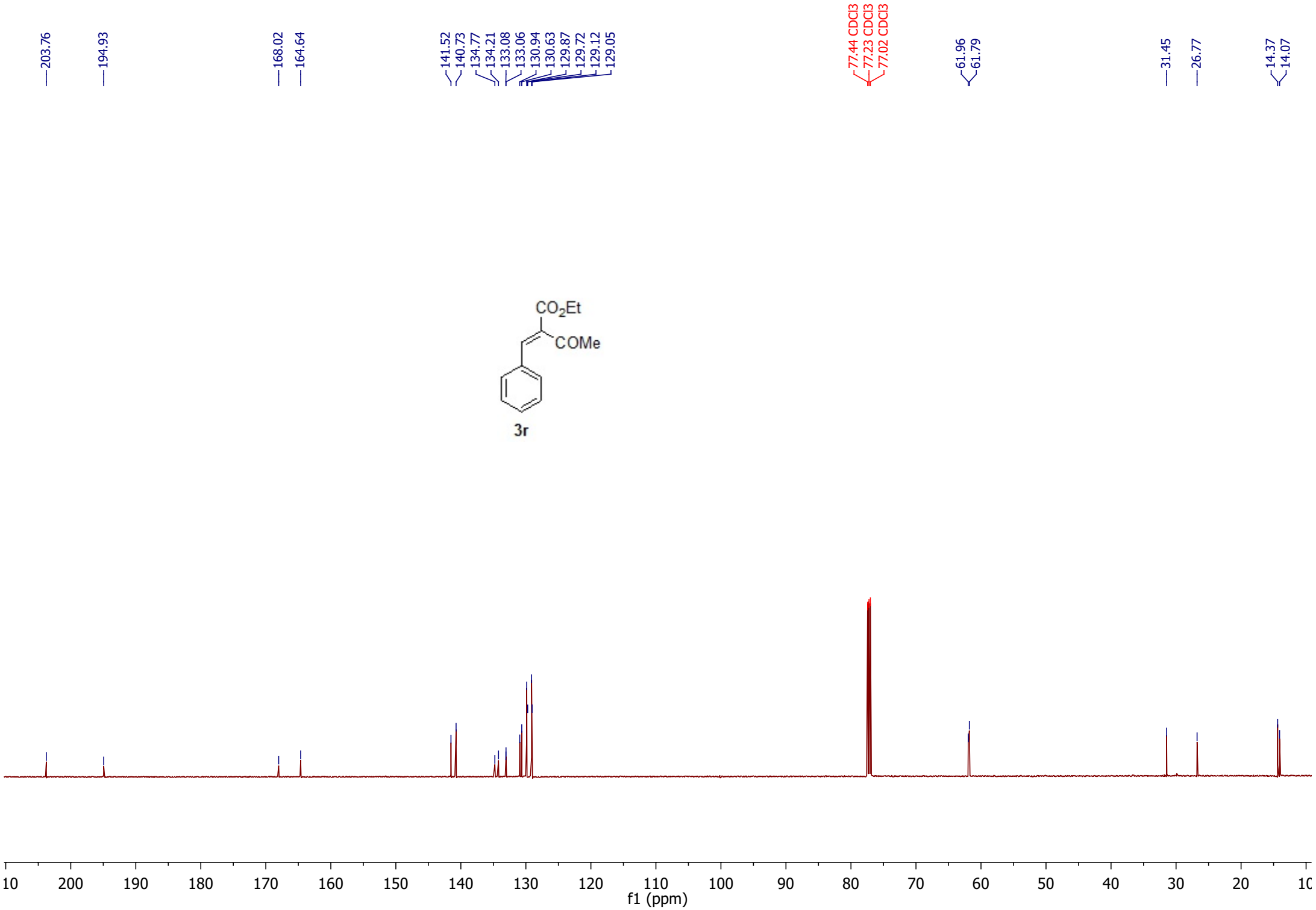
0.77
1.46
7.85
3.88
2.38
3.17
3.45
3.07
f1 (ppm)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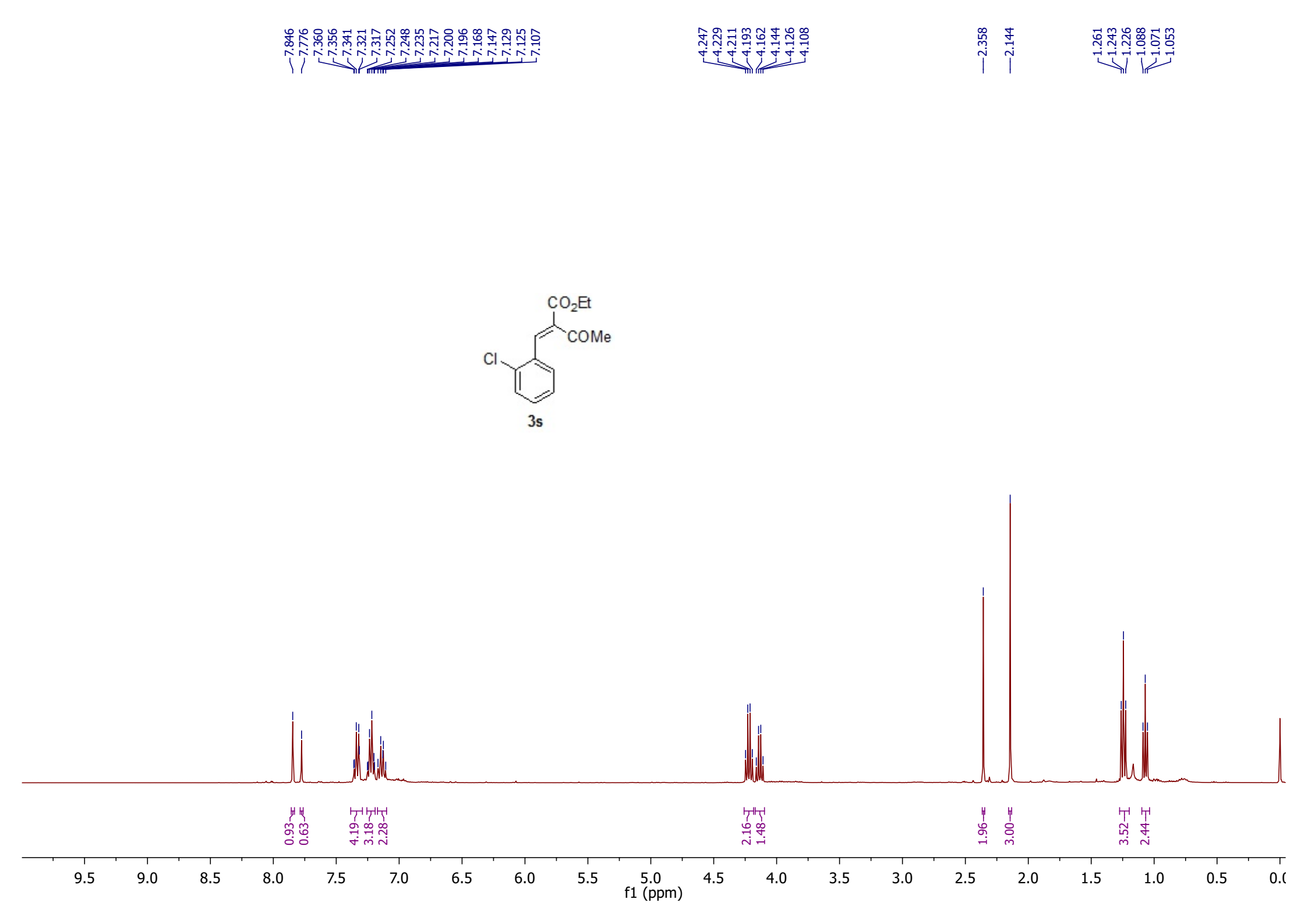
194.93
168.02
164.64
141.52
140.73
134.77
134.21
133.08
133.06
130.94
130.63
129.87
129.72
129.12
129.05
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
61.96
61.79
31.45
26.77
14.37
14.07
CO2Et
COMe
3r
f1 (ppm)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7.341
7.321
7.317
7.252
7.248
7.235
7.217
7.200
7.196
7.168
7.147
7.129
7.125
7.107
4.247
4.229
4.211
4.193
4.162
4.144
4.126
4.108
2.358
2.144
1.261
1.243
1.226
1.088
1.071
1.053
CO2Et
COMe
Cl
3s
0.93
0.63
4.19
3.18
2.28
2.16
1.48
1.96
3.00
3.52
2.44
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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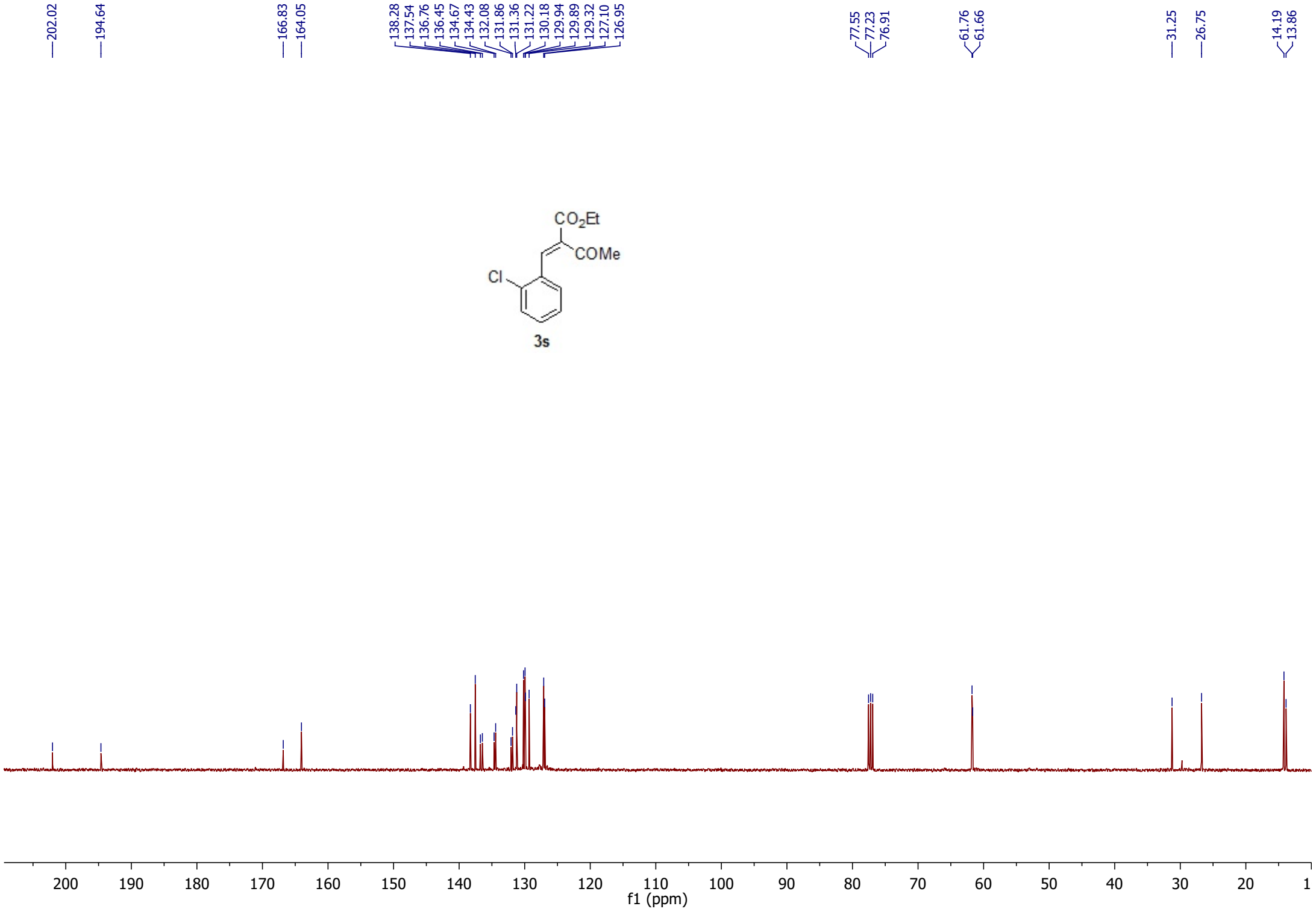
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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166.83
164.05
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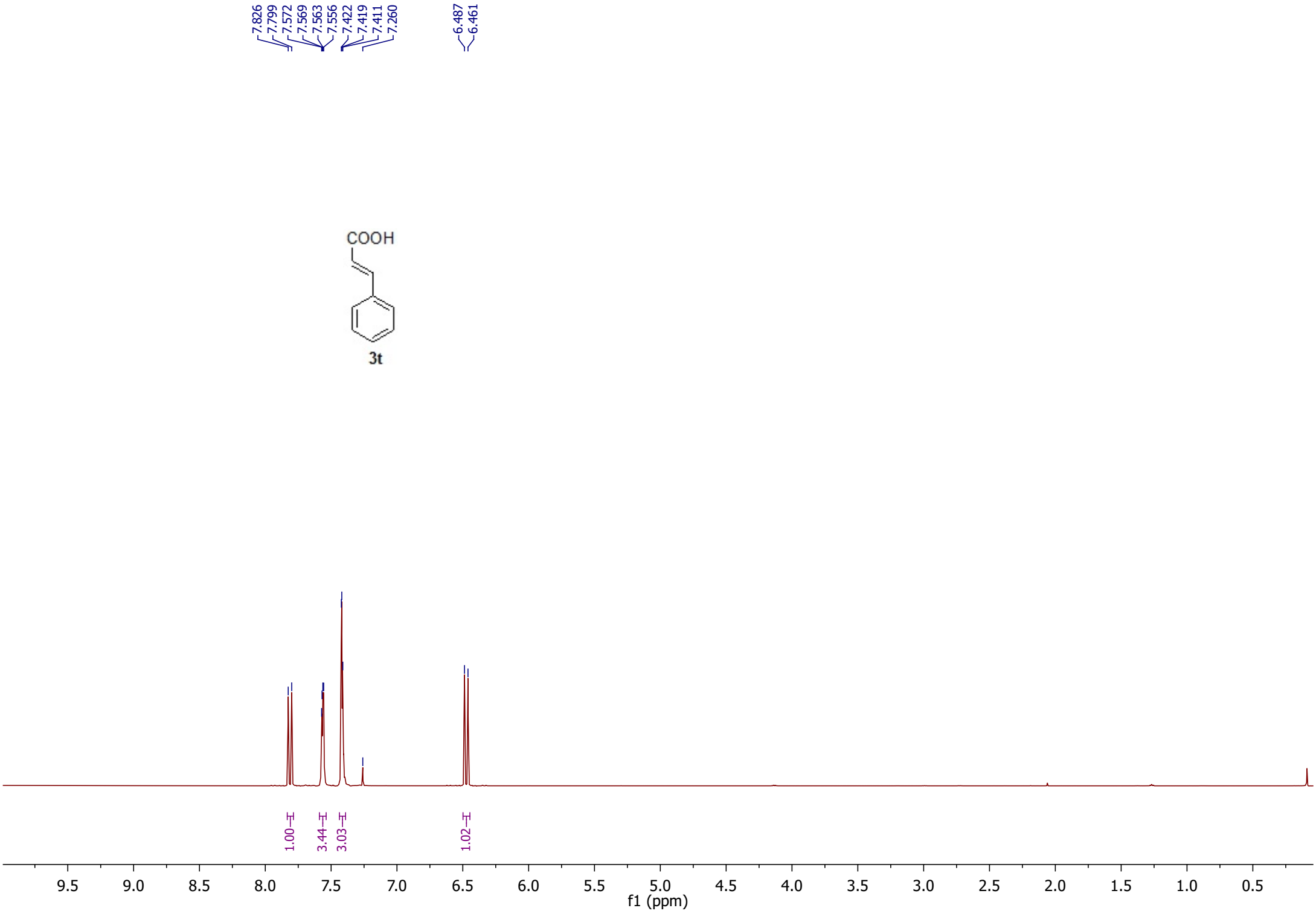
137.54
136.76
136.45
134.67
134.43
132.08
131.86
131.36
131.22
130.18
129.94
129.89
129.32
127.10
126.95
77.55
77.23
76.91
61.76
61.66
31.25
26.75
14.19
13.86
CO2Et
COMe
Cl
3s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
1
f1 (ppm)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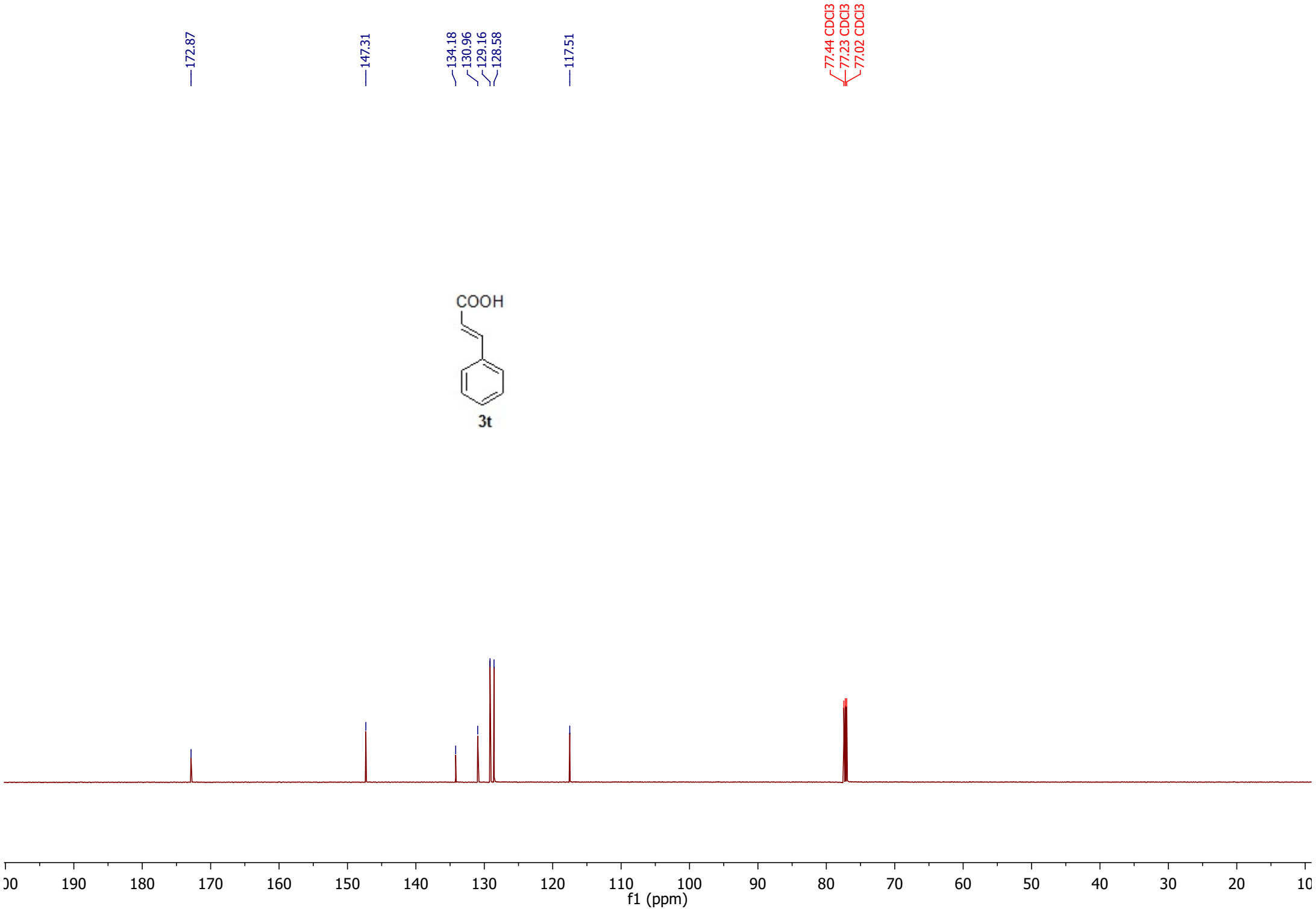
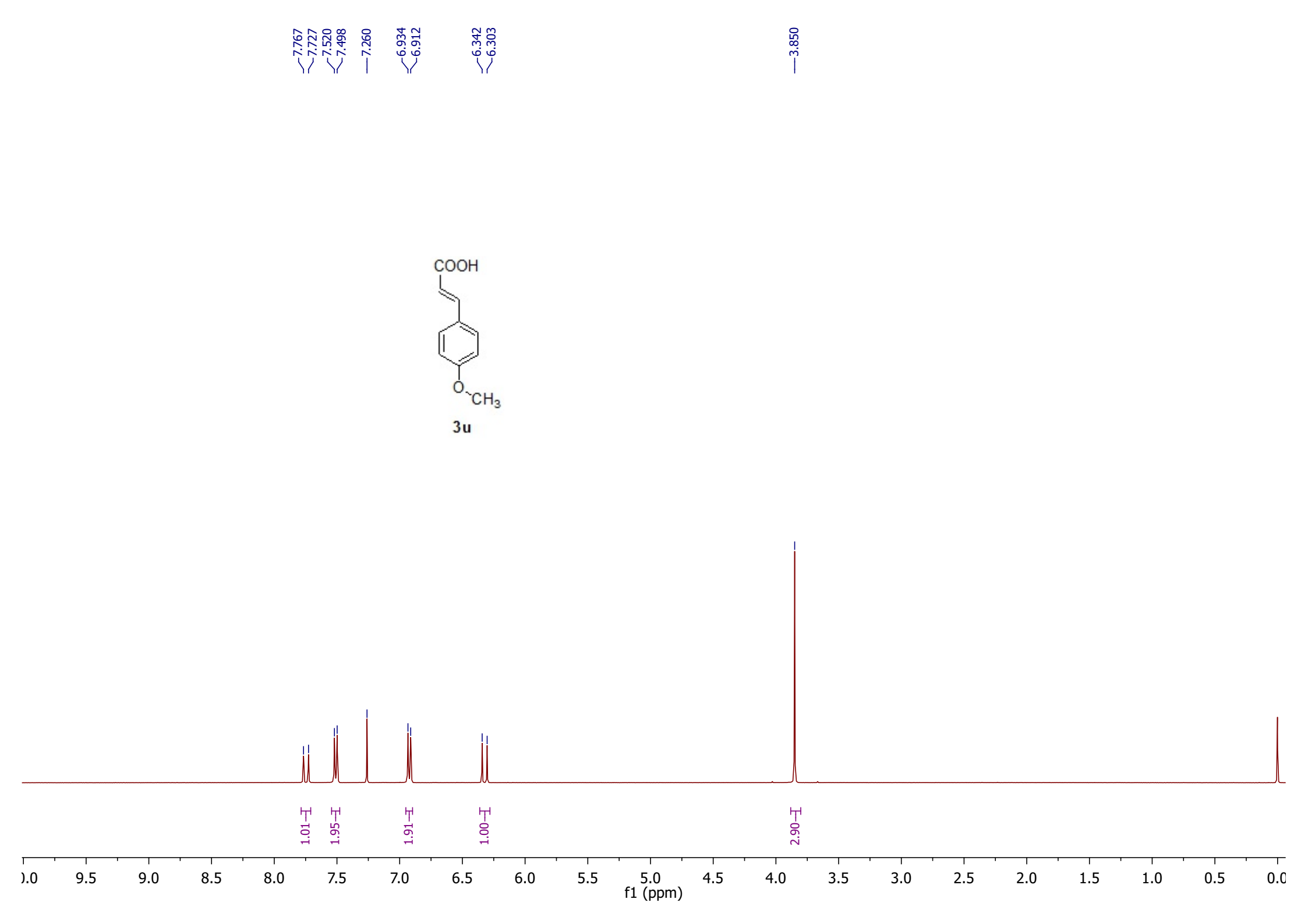
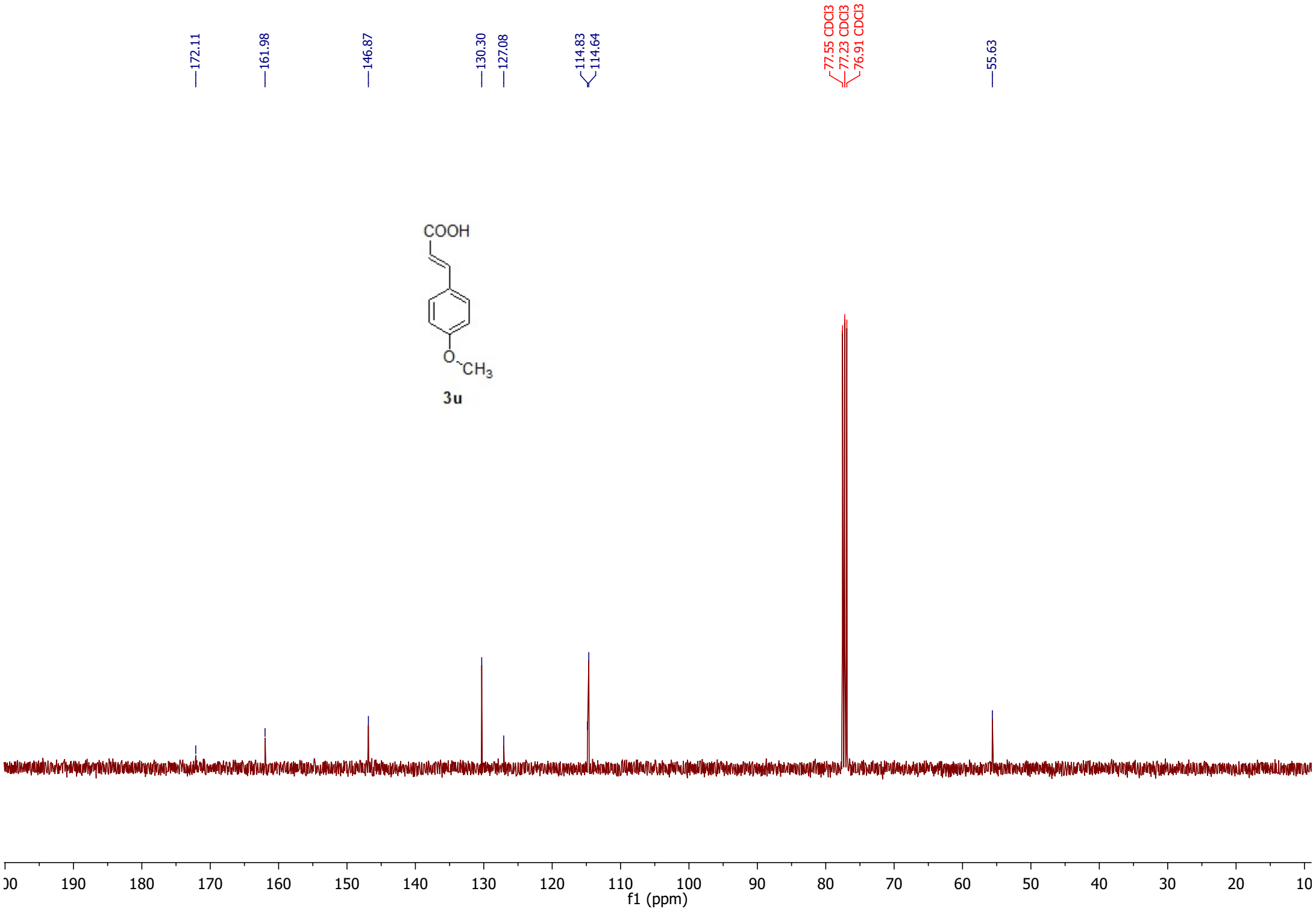
7.572
7.569
7.563
7.556
7.422
7.419
7.411
7.260
6.487
6.461
COOH
3t
1.00
3.44
3.03
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


172.87
147.31
134.18
130.96
129.16
128.58
117.51
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
COOH
3t
f1 (ppm)


7.767
7.727
7.520
7.498
7.260
6.934
6.912
6.342
6.303
3.850
COOH
O
CH3
3u
1.01
1.95
1.91
1.00
2.90
f1 (ppm)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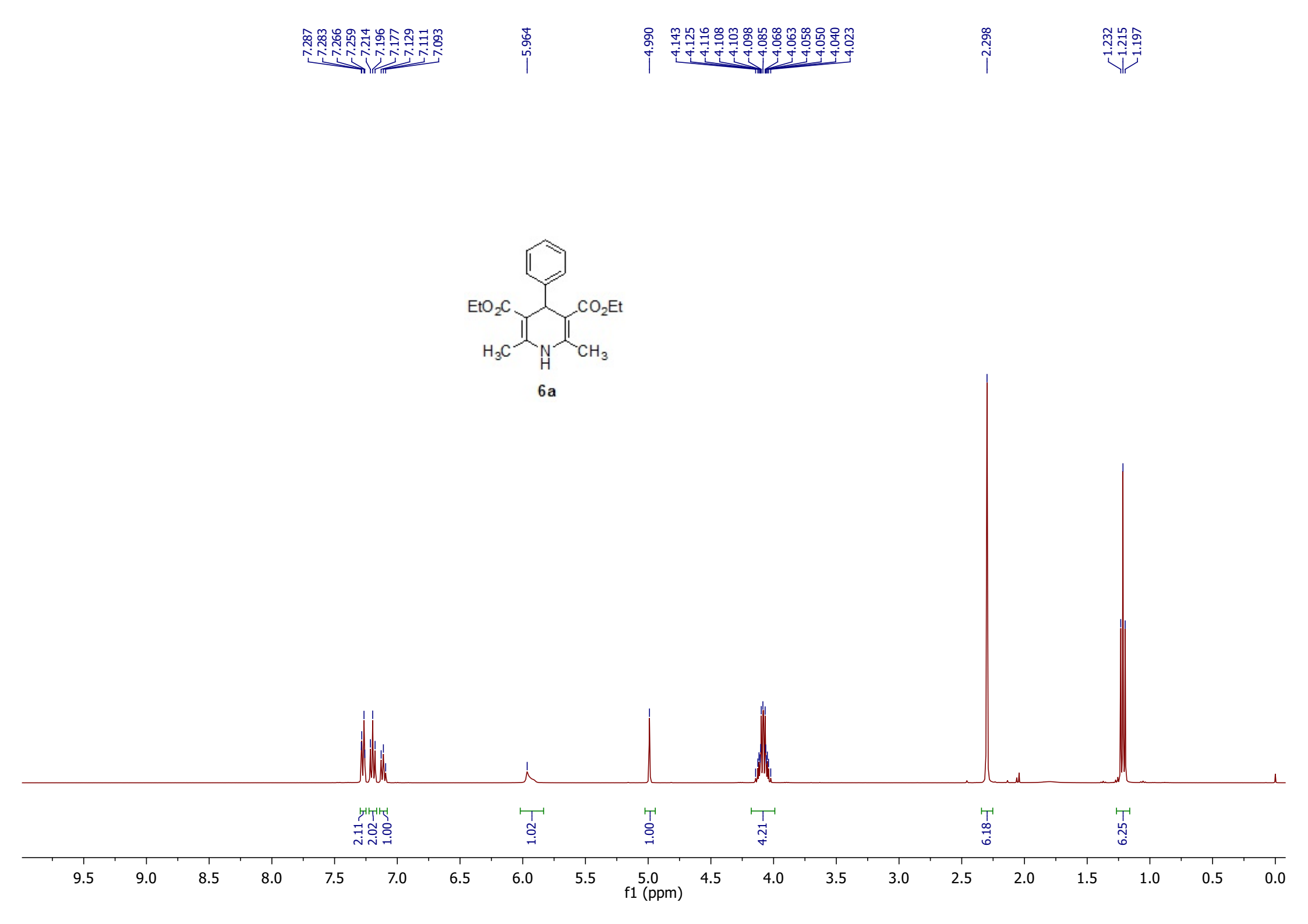
161.98
146.87
130.30
127.08
114.83
114.64
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
55.63
COOH
O
CH3
3u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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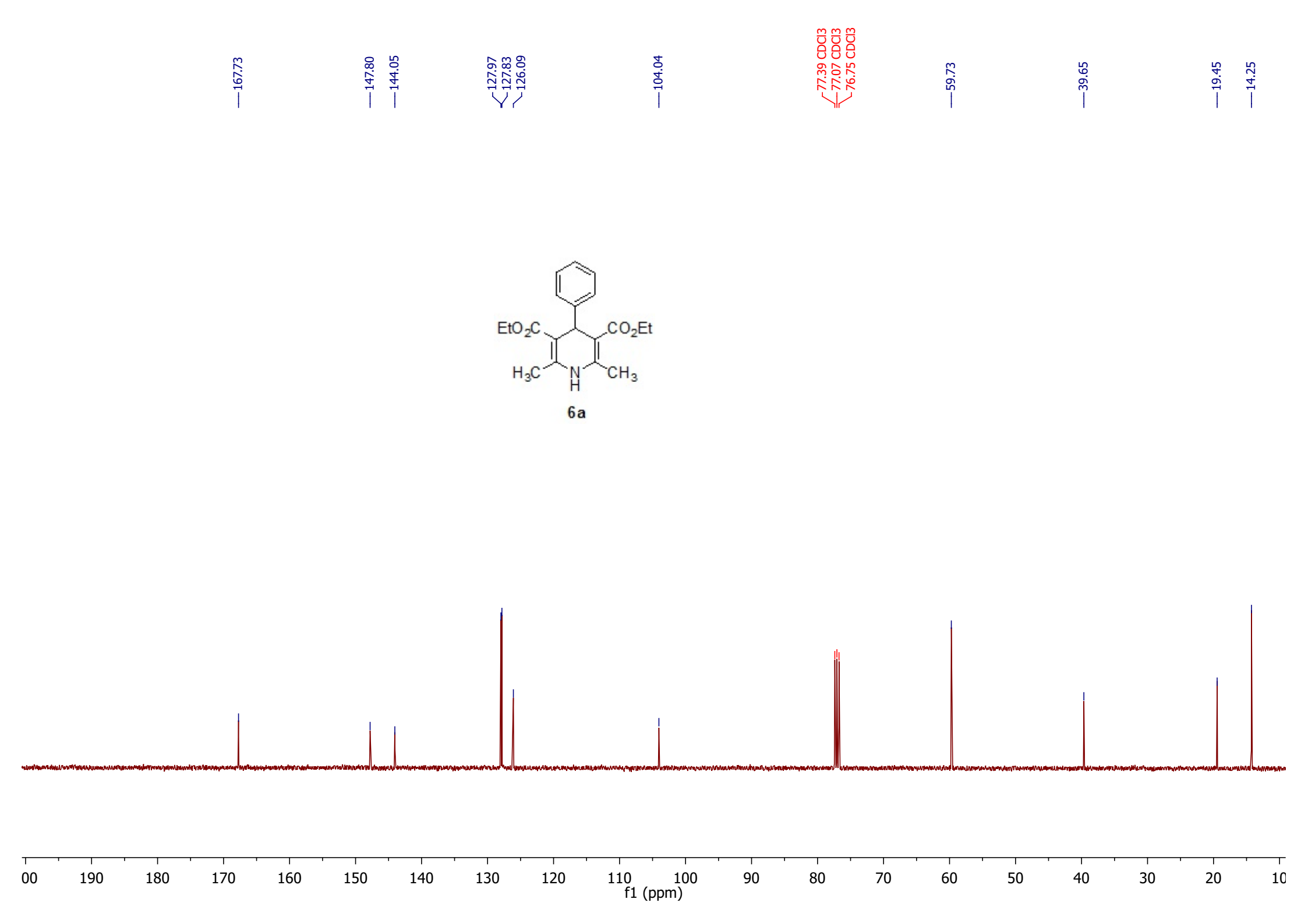
7.259
7.214
7.196
7.177
7.129
7.111
7.093
5.964
4.990
4.143
4.125
4.116
4.108
4.103
4.098
4.085
4.068
4.063
4.058
4.050
4.040
4.023
2.298
1.232
1.215
1.197
EtO2C
CO2Et
H3C
CH3
N
H
6a
2.11
2.02
1.00
1.02
1.00
4.21
6.18
6.25
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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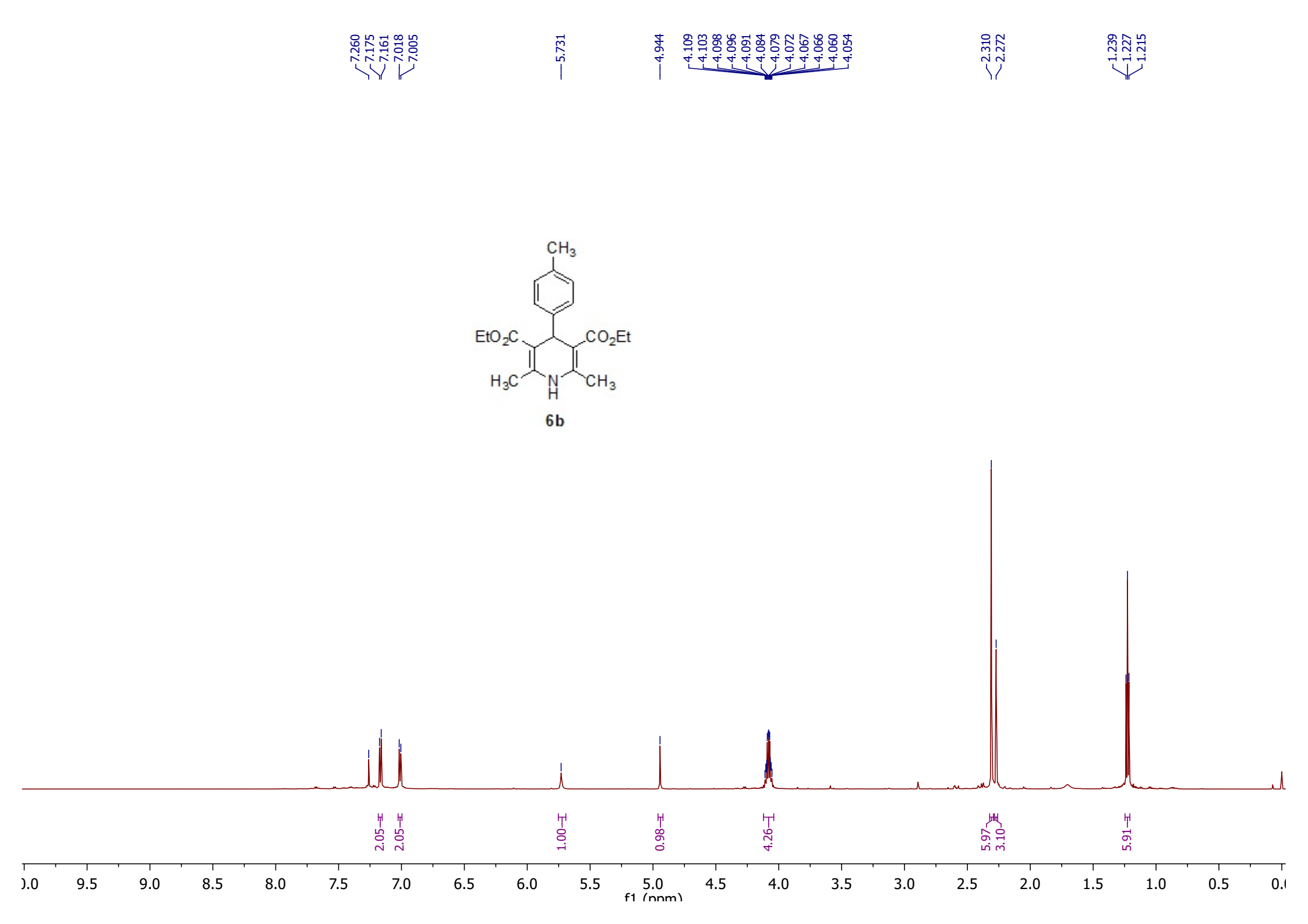
147.80
144.05
127.97
127.83
126.09
104.04
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
59.73
39.65
19.45
14.25
EtO2C
CO2Et
H3C
CH3
N
H
6a
f1 (ppm)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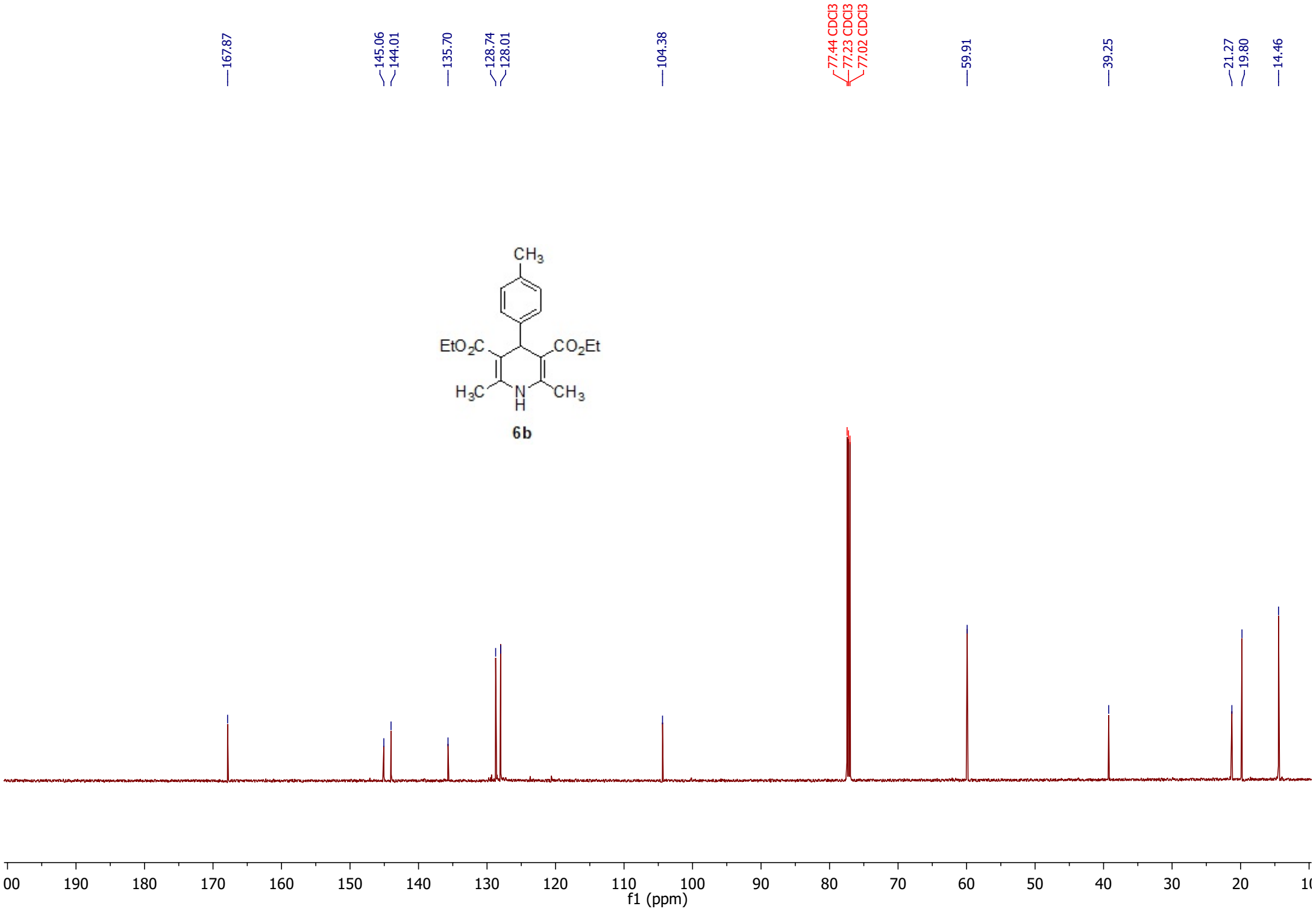
7.175
7.161
7.018
7.005
5.731
4.944
4.109
4.103
4.098
4.096
4.091
4.084
4.079
4.072
4.067
4.066
4.060
4.054
2.310
2.272
1.239
1.227
1.215
CH3
EtO2C
CO2Et
H3C
N
H
CH3
6b
2.05
2.05
1.00
0.98
4.26
5.97
3.10
5.91
f1 (ppm)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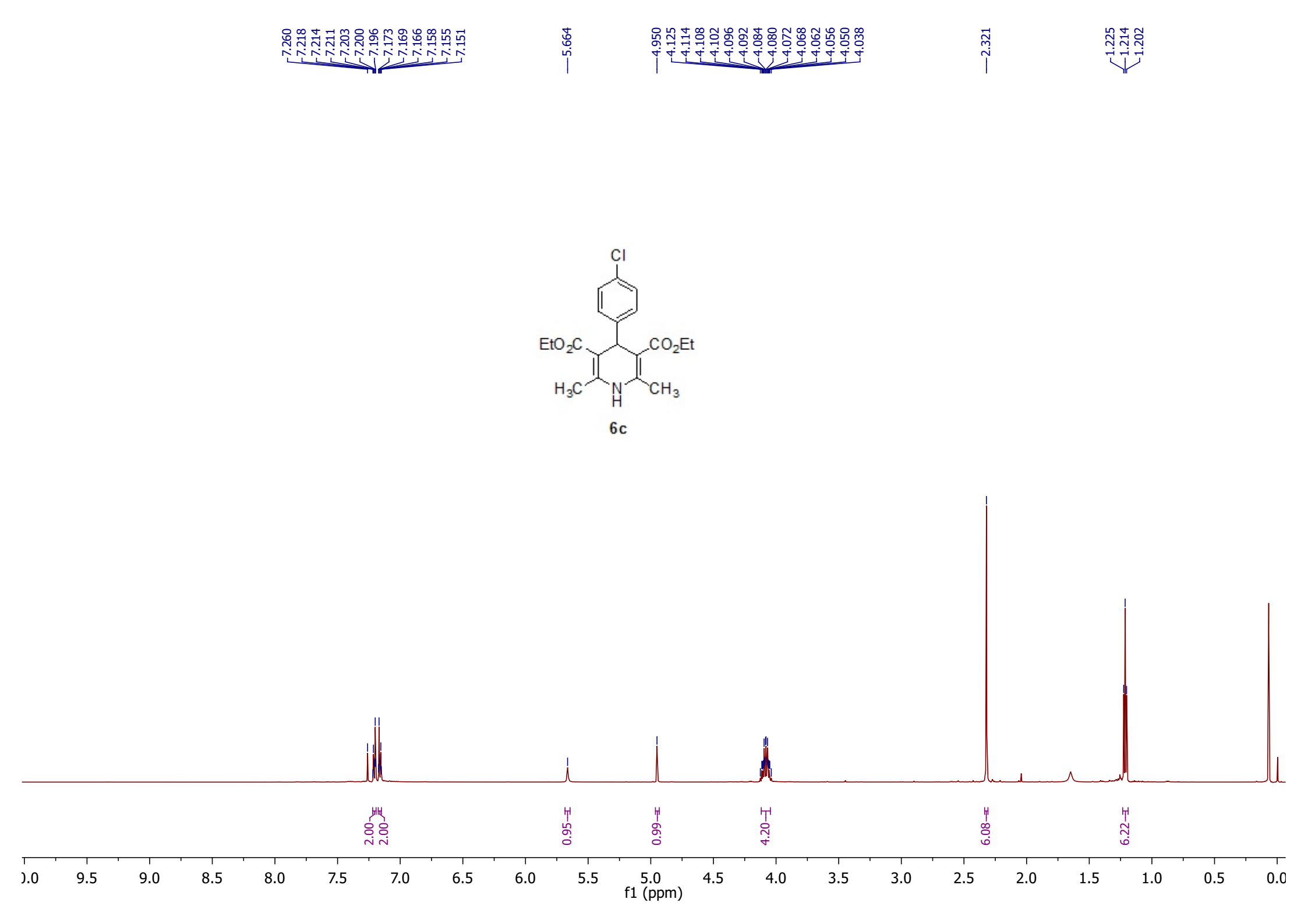
144.01
135.70
128.74
128.01
104.38
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.91
39.25
21.27
19.80
14.46
CH3
EtO2C
CO2Et
H3C
N
H
CH3
6b
f1 (ppm)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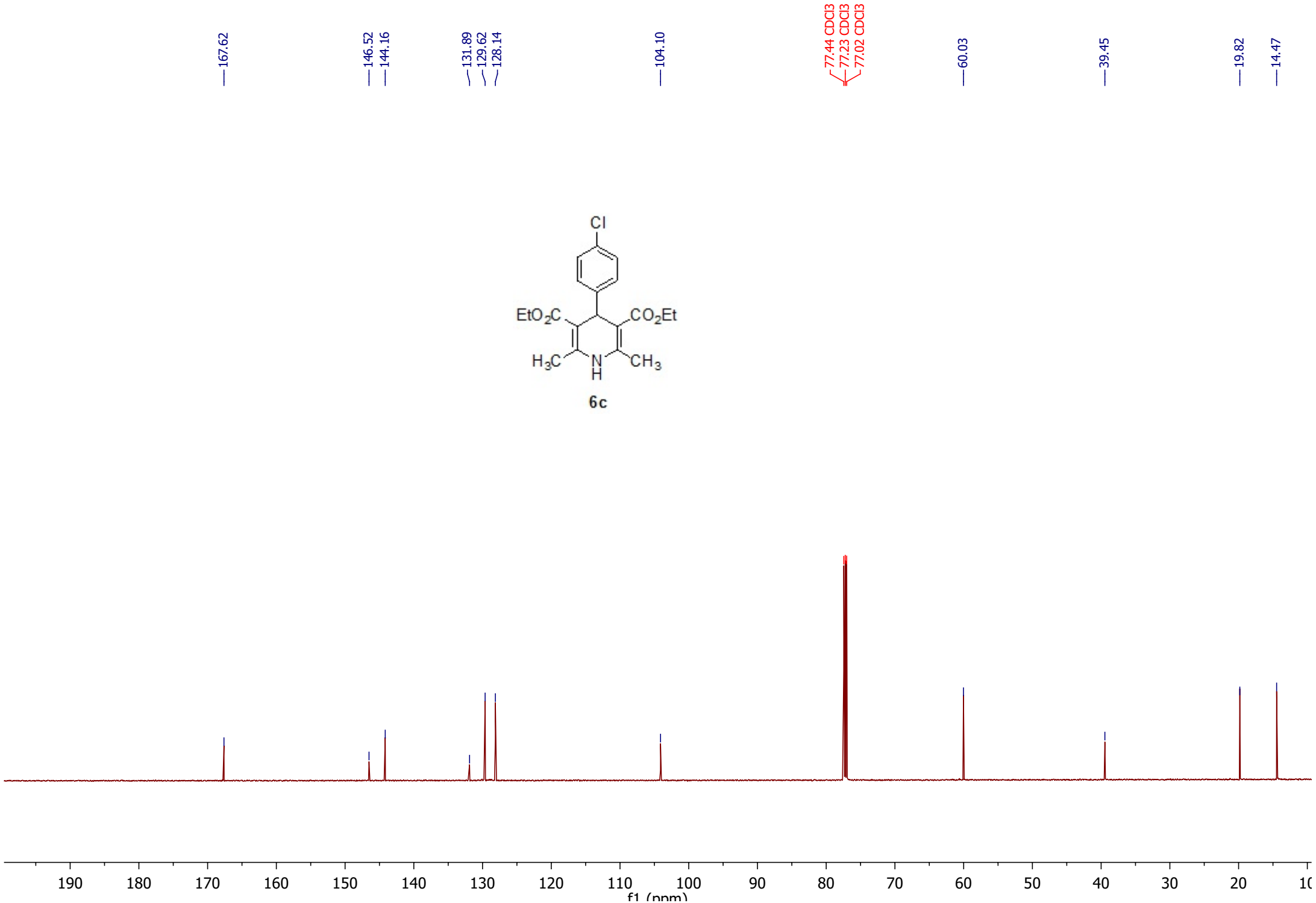
7.218
7.214
7.211
7.203
7.200
7.196
7.173
7.169
7.166
7.158
7.155
7.151
5.664
4.950
4.125
4.114
4.108
4.102
4.096
4.092
4.084
4.080
4.072
4.068
4.062
4.056
4.050
4.038
2.321
1.225
1.214
1.202
Cl
EtO2C
CO2Et
H3C
N
H
CH3
6c
2.00
2.00
0.95
0.99
4.20
6.08
6.22
f1 (ppm)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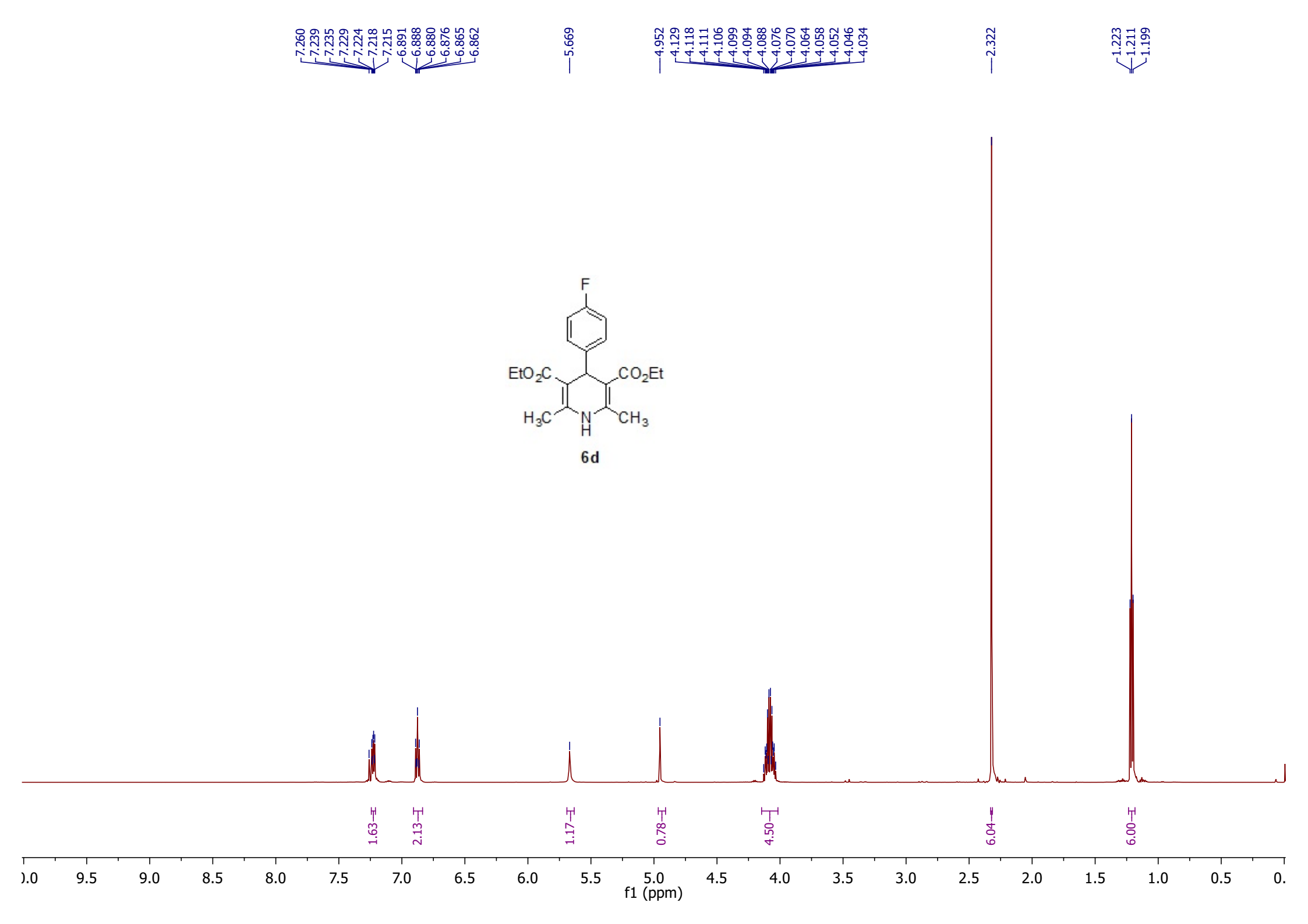
146.52
144.16
131.89
129.62
128.14
104.10
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
60.03
39.45
19.82
14.47
Cl
EtO2C
CO2Et
H3C
N
H
CH3
6c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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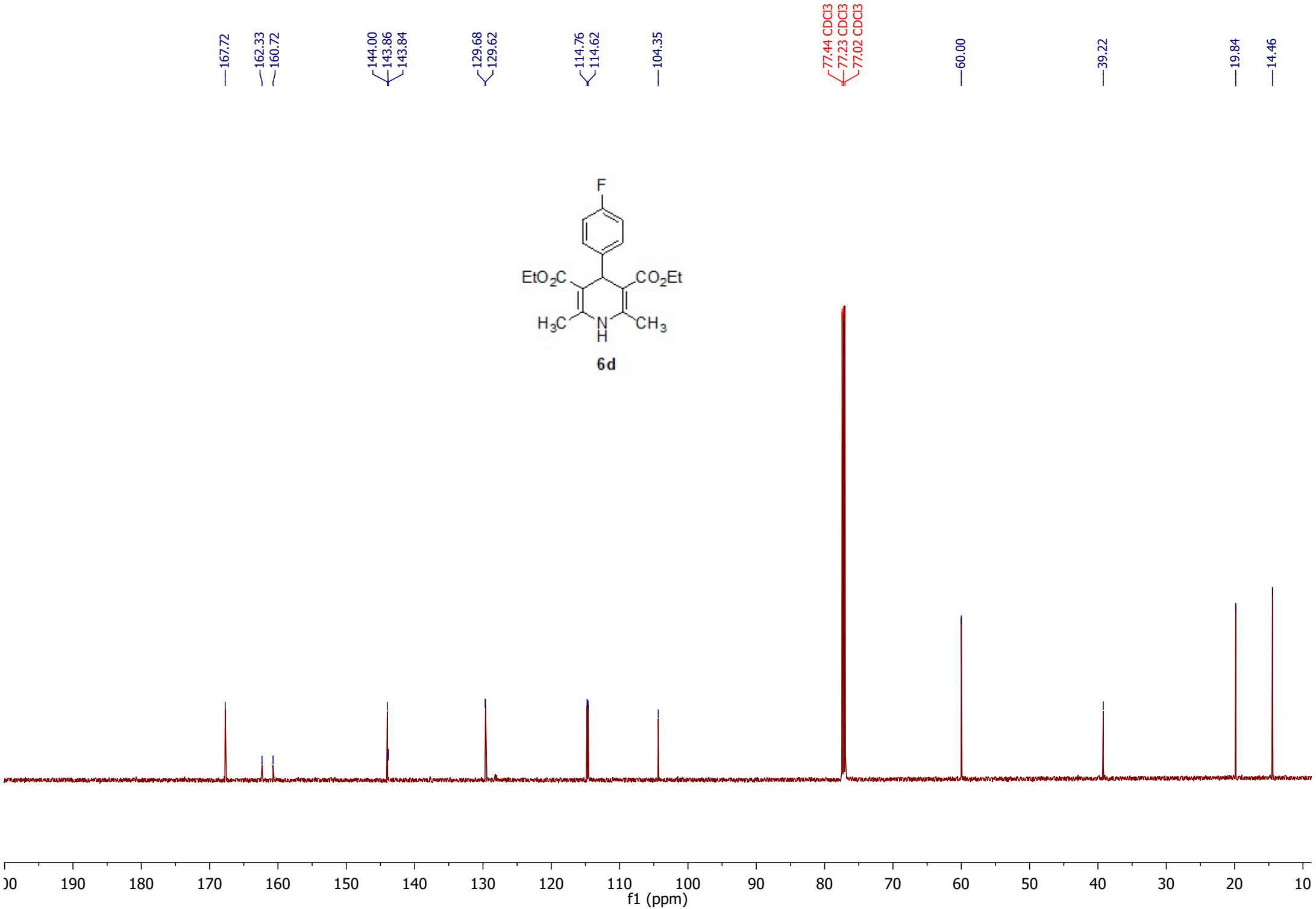
7.239
7.235
7.229
7.224
7.218
7.215
6.891
6.888
6.880
6.876
6.865
6.862
5.669
4.952
4.129
4.118
4.111
4.106
4.099
4.094
4.088
4.076
4.070
4.064
4.058
4.052
4.046
4.034
2.322
1.223
1.211
1.199
F
EtO2C
CO2Et
H3C
N
H
CH3
6d
1.63
2.13
1.17
0.78
4.50
6.04
6.00
f1 (ppm)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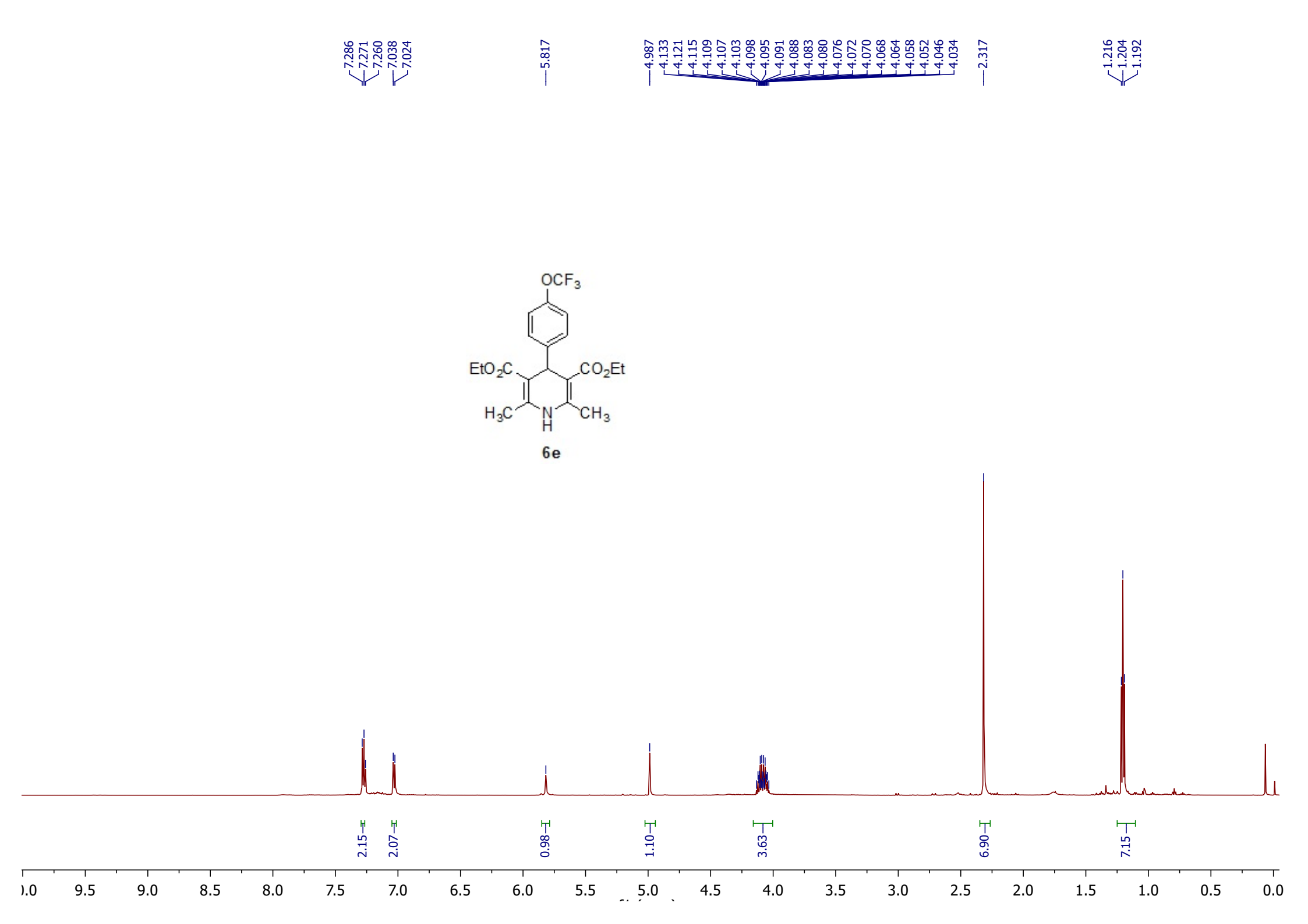
162.33
160.72
144.00
143.86
143.84
129.68
129.62
114.76
114.62
104.35
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
60.00
39.22
19.84
14.46
F
EtO2C
CO2Et
H3C
CH3
N
H
6d
f1 (ppm)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7.271
7.260
7.038
7.024
5.817
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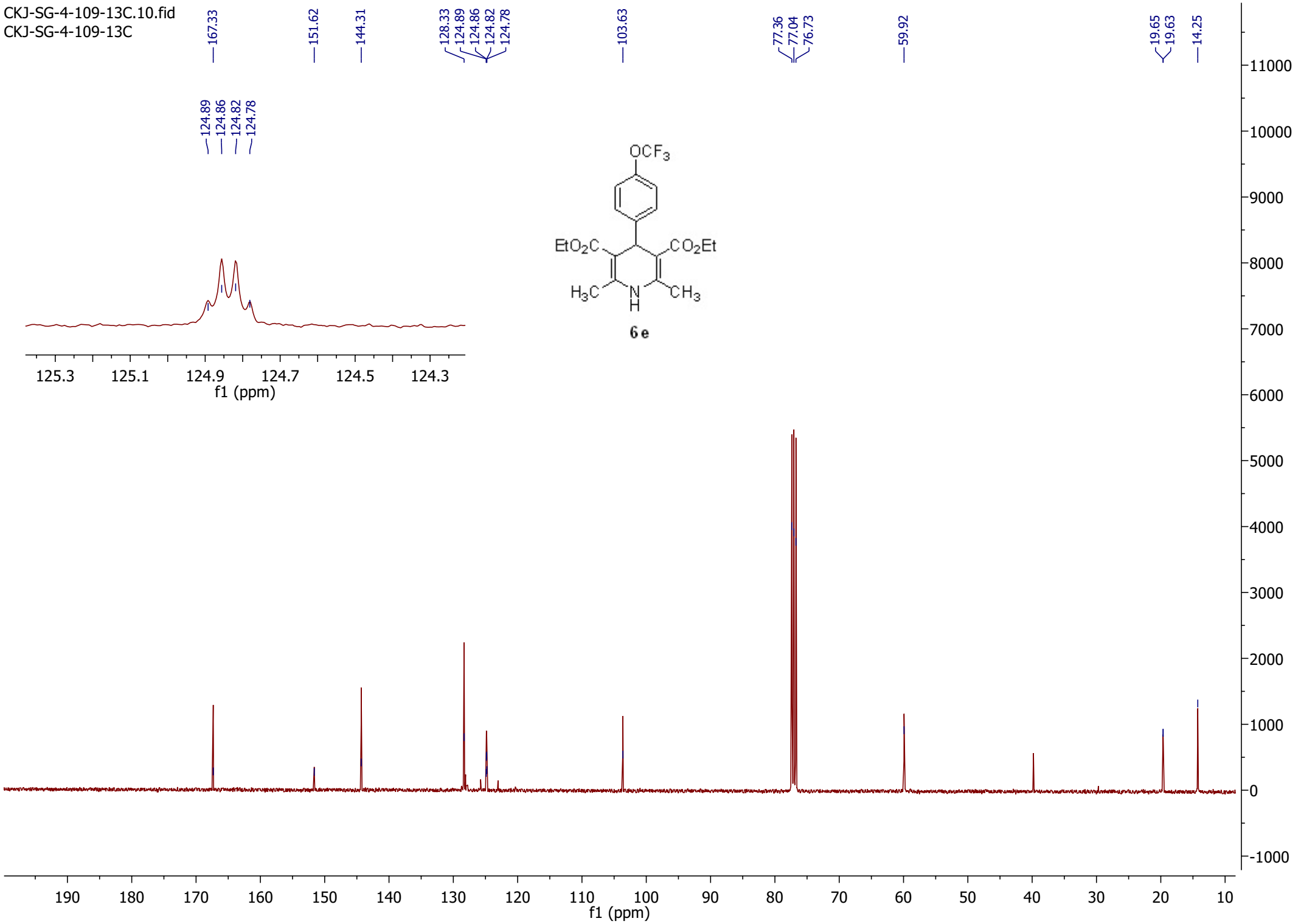
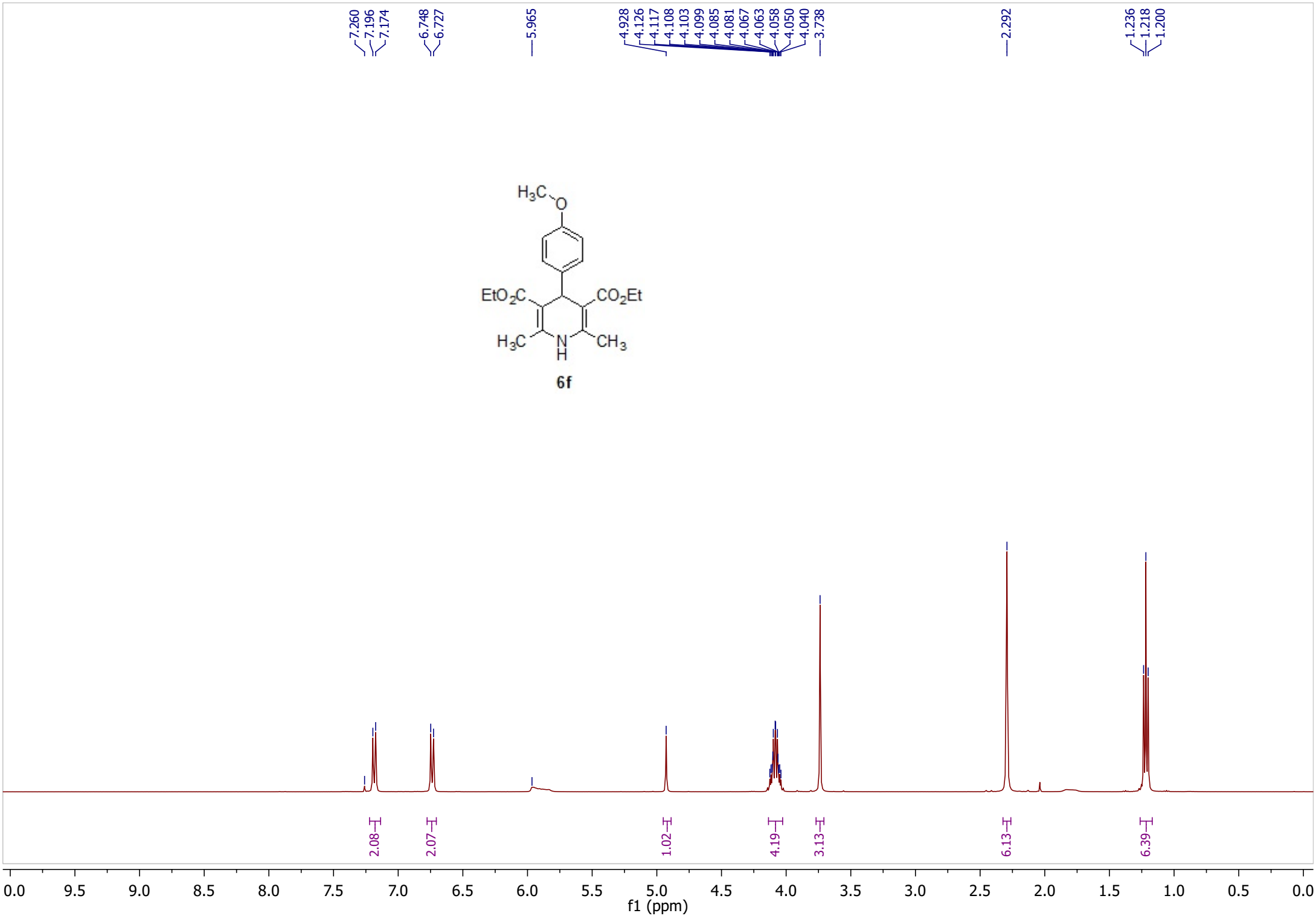
4.133
4.121
4.115
4.109
4.107
4.103
4.098
4.095
4.091
4.088
4.083
4.080
4.076
4.072
4.070
4.068
4.064
4.058
4.052
4.046
4.034
2.317
1.216
1.204
1.192
OCF3
EtO2C
CO2Et
H3C
N
H
CH3
6e
2.15
2.07
0.98
1.10
3.63
6.90
7.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

CKJ-SG-4-109-13C.10.fid
CKJ-SG-4-109-13C

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7.174
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6.727
5.965
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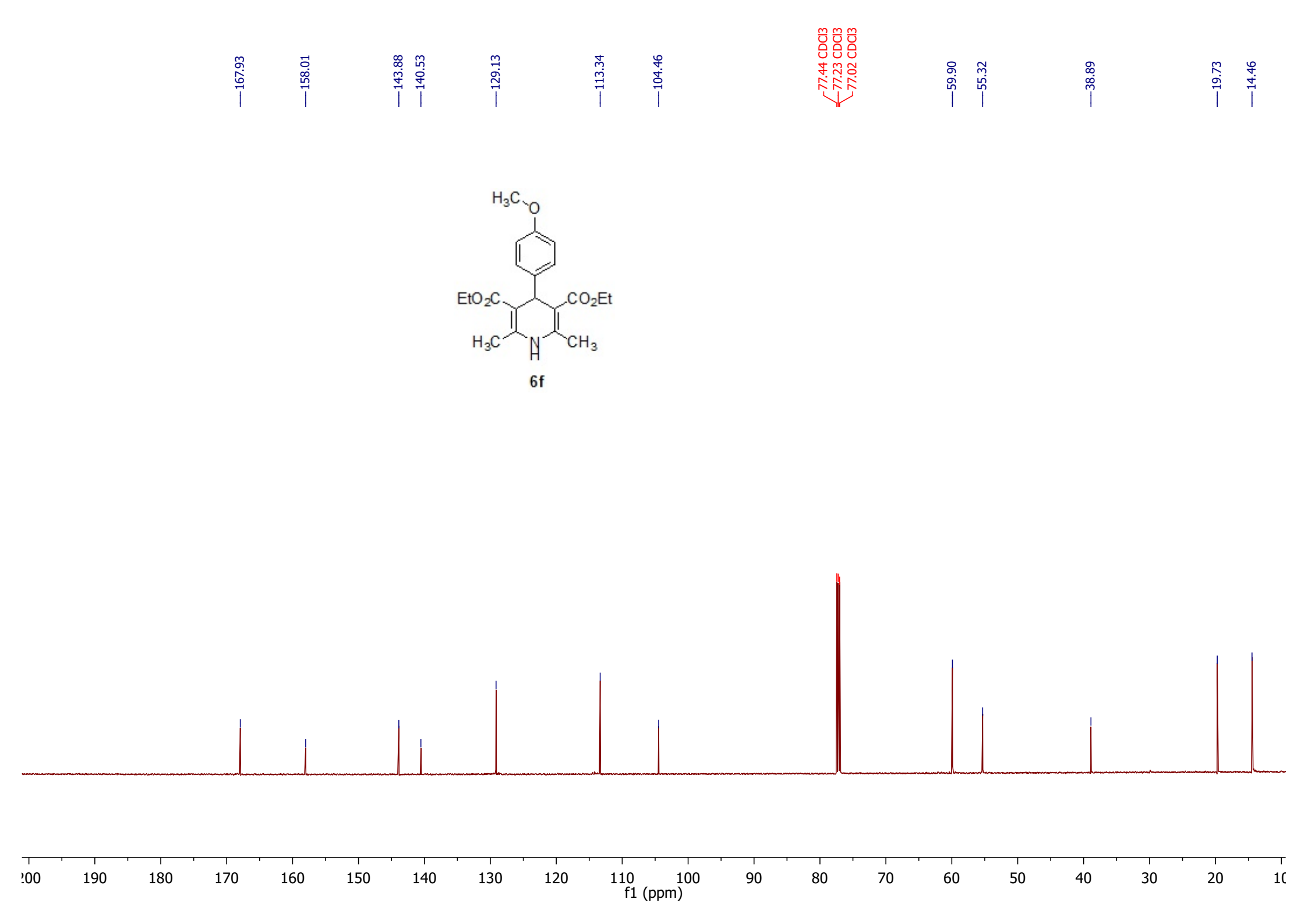
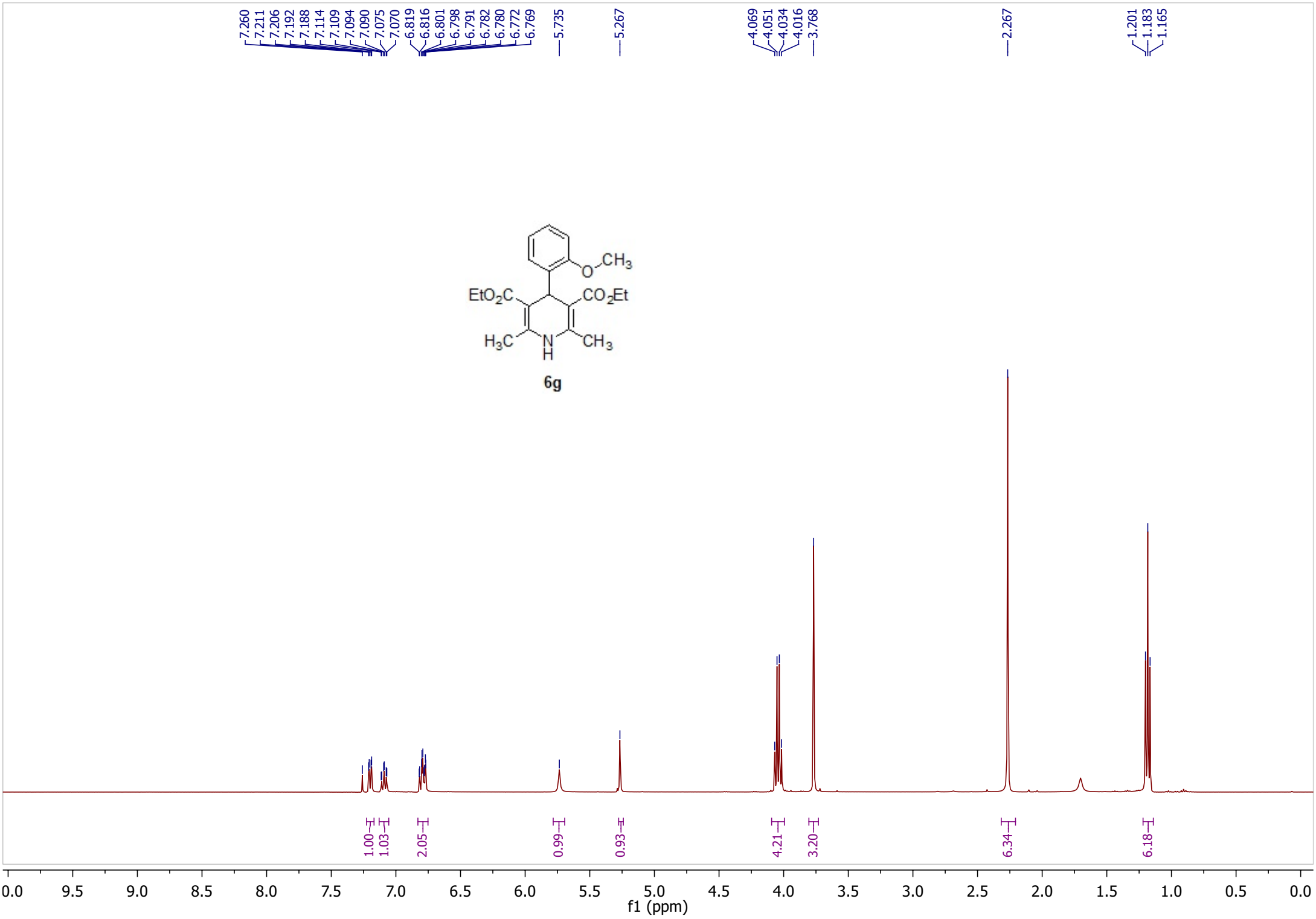
4.126
4.117
4.108
4.103
4.099
4.085
4.081
4.067
4.063
4.058
4.050
4.040
3.738
2.292
1.236
1.218
1.200
H3C
O
EtO2C
CO2Et
H3C
N
H
CH3
6f
2.08
2.07
1.02
4.19
3.13
6.13
6.39
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.93
158.01
143.88
140.53
129.13
113.34
104.46
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.90
55.32
38.89
19.73
14.46
H3C
O
EtO2C
CO2Et
H3C
CH3
N
H
6f
f1 (ppm)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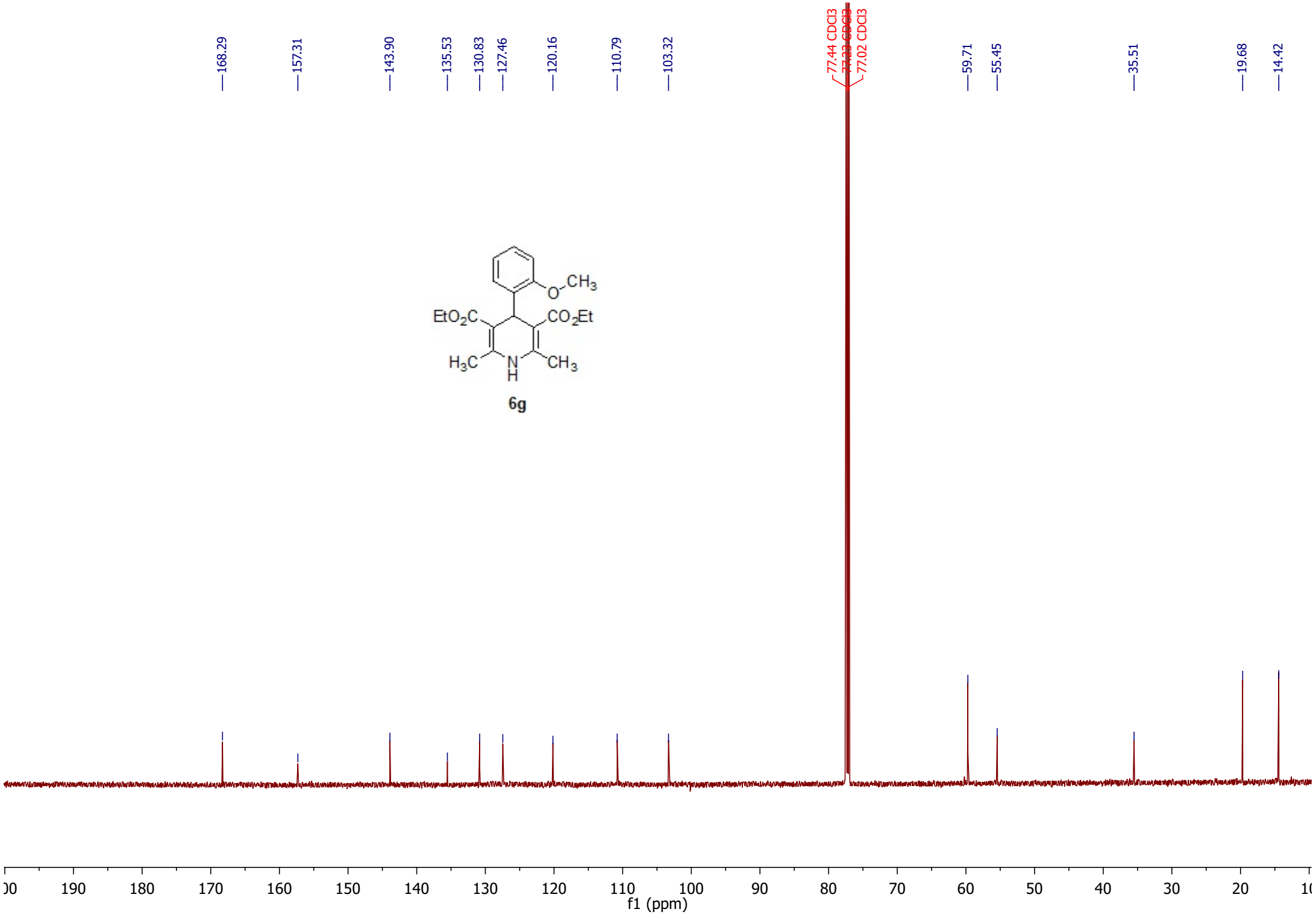
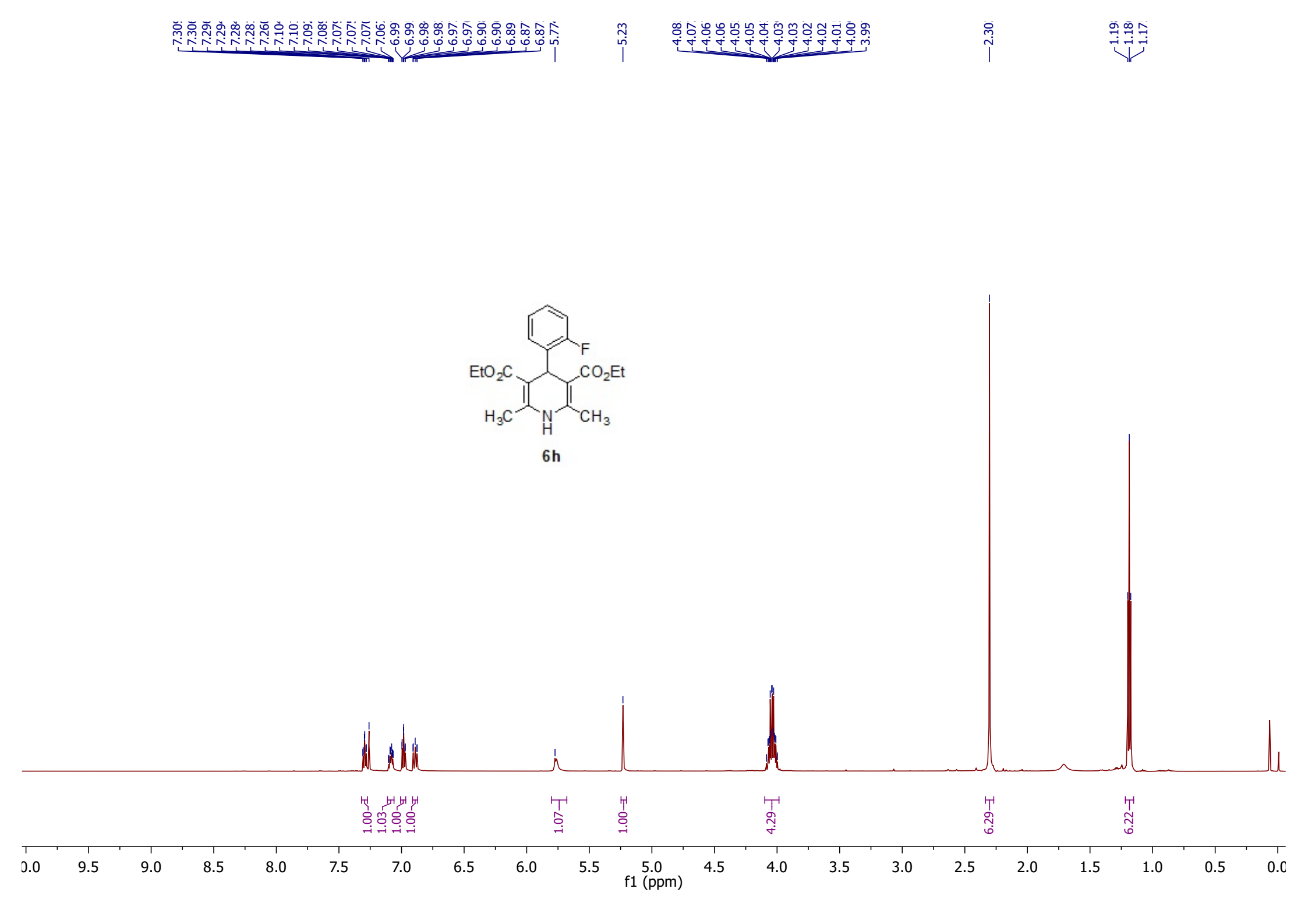
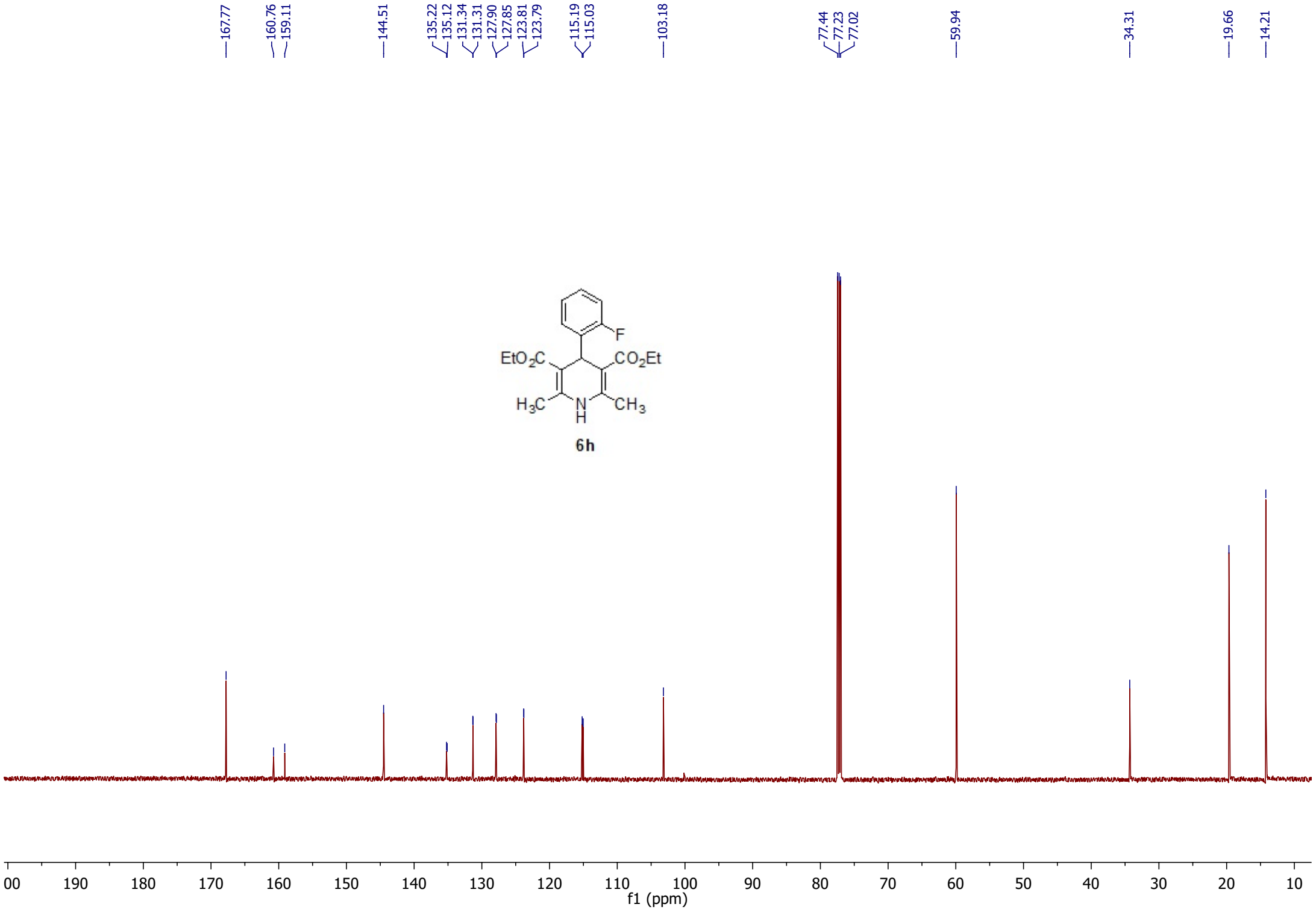
7.211
7.206
7.192
7.188
7.114
7.109
7.094
7.090
7.075
7.070
6.819
6.816
6.801
6.798
6.791
6.782
6.780
6.772
6.769
5.735
5.267
4.069
4.051
4.034
4.016
3.768
2.267
1.201
1.183
1.165
EtO2C
CO2Et
H3C
CH3
O
CH3
N
H
6g
1.00
1.03
2.05
0.99
0.93
4.21
3.20
6.34
6.18
f1 (ppm)


168.29
157.31
143.90
135.53
130.83
127.46
120.16
110.79
103.32
77.44 CDCl3
77.33 CDCl3
77.02 CDCl3
59.71
55.45
35.51
19.68
14.42
O
CH3
EtO2C
CO2Et
H3C
N
H
CH3
6g
f1 (ppm)


F
EtO2C
CO2Et
H3C
N
H
CH3
6h
f1 (ppm)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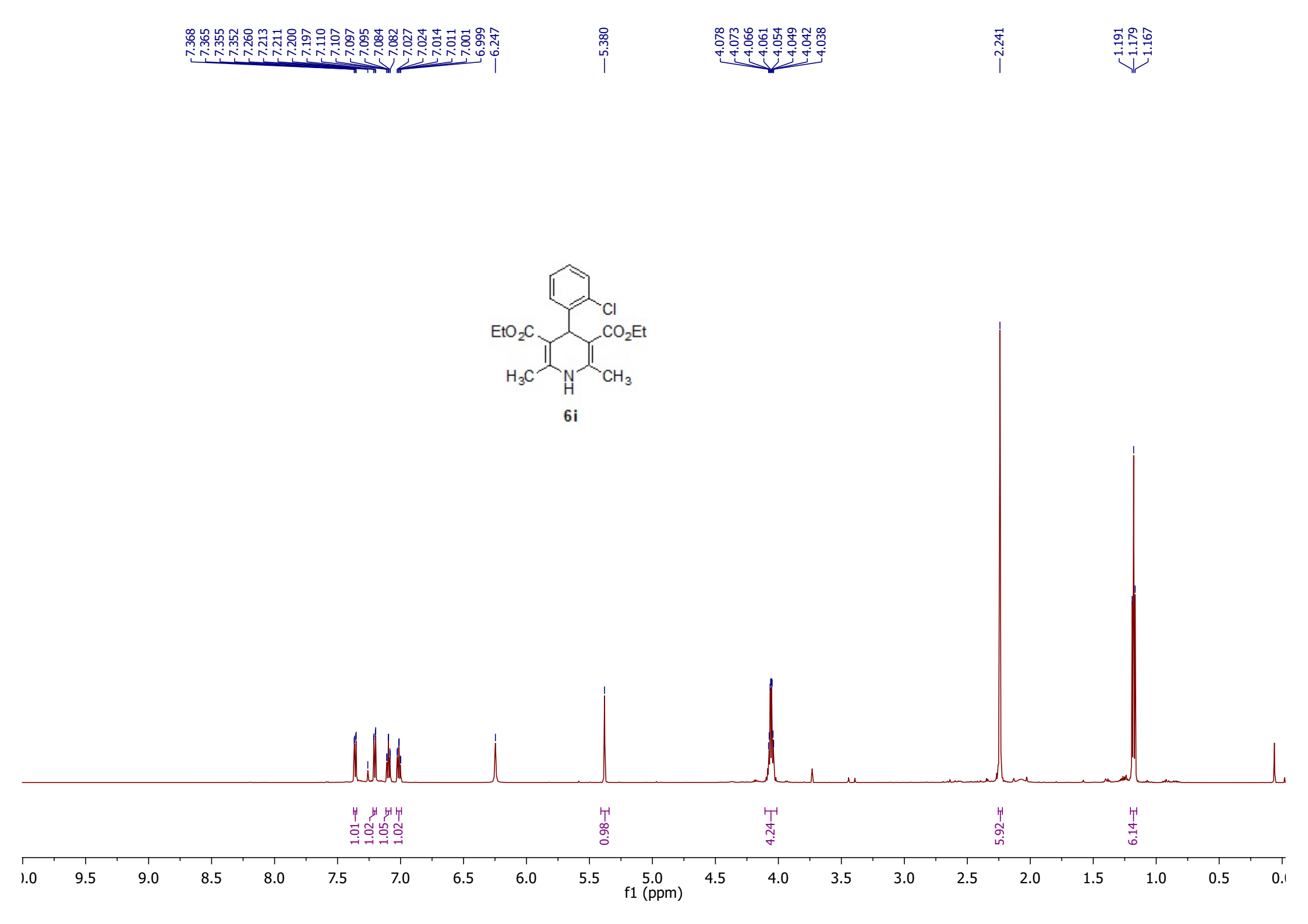
160.76
159.11
144.51
135.22
135.12
131.34
131.31
127.90
127.85
123.81
123.79
115.19
115.03
103.18
77.44
77.23
77.02
59.94
34.31
19.66
14.21
F
EtO2C
CO2Et
H3C
N
H
CH3
6h
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.365
7.355
7.352
7.260
7.213
7.211
7.200
7.197
7.110
7.107
7.097
7.095
7.084
7.082
7.027
7.024
7.014
7.011
7.001
6.999
6.247
5.380
4.078
4.073
4.066
4.061
4.054
4.049
4.042
4.038
2.241
1.191
1.179
1.167
Cl
EtO2C
CO2Et
H3C
N
H
CH3
6i
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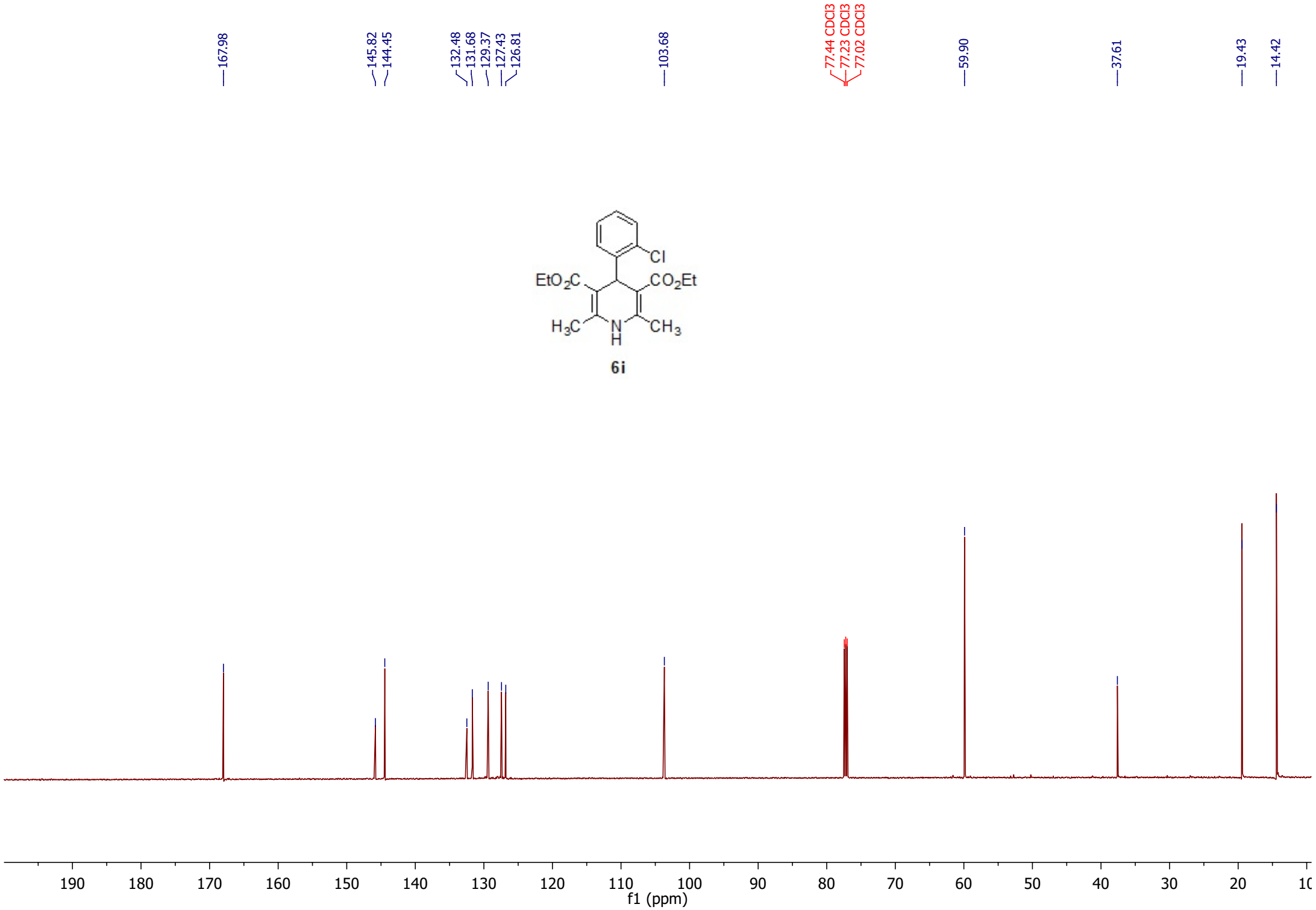
1.02
1.05
1.02
0.98
4.24
5.92
6.14
f1 (ppm)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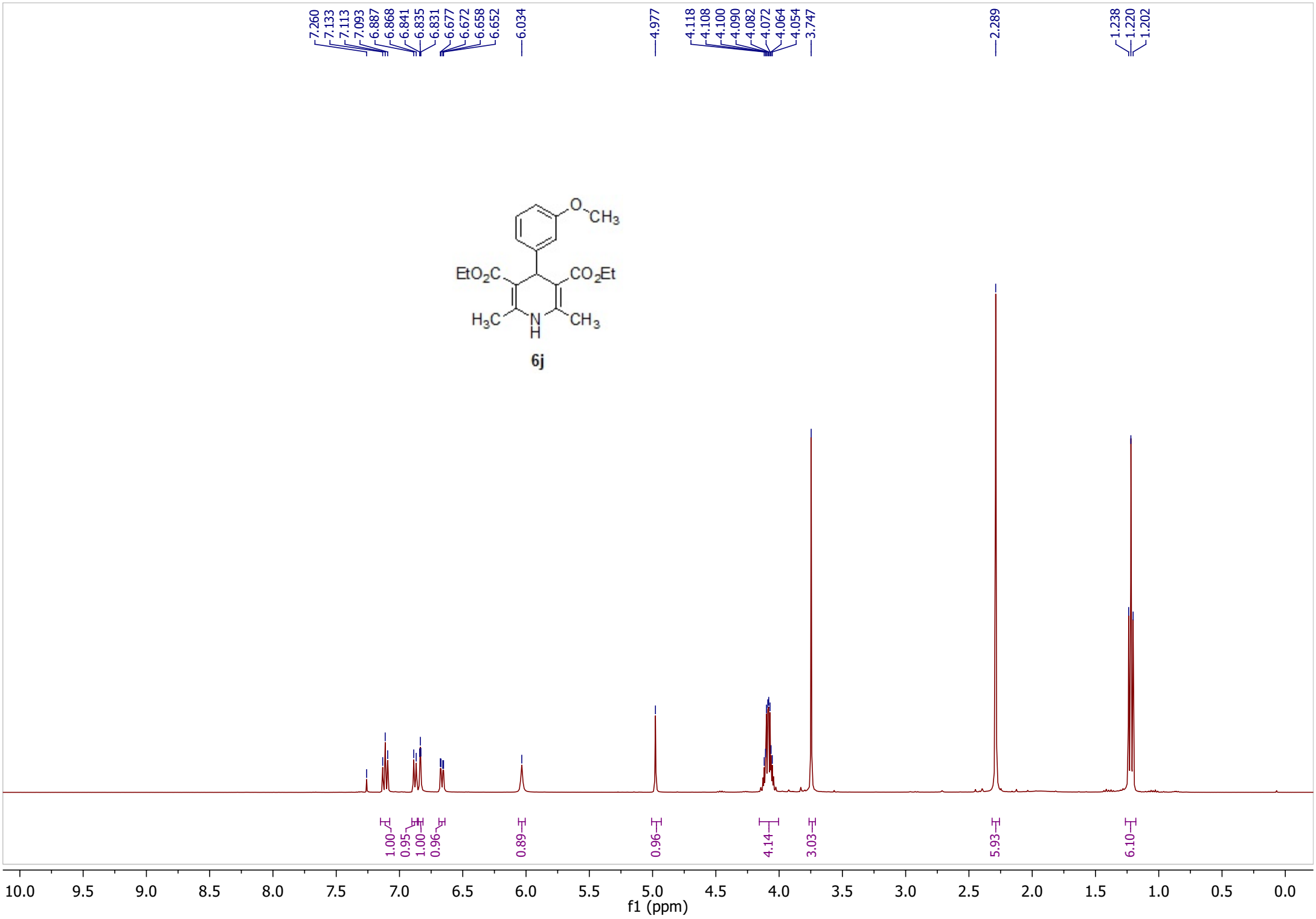
144.45
132.48
131.68
129.37
127.43
126.81
103.68
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.90
37.61
19.43
14.42
Cl
EtO2C
CO2Et
H3C
CH3
N
H
6i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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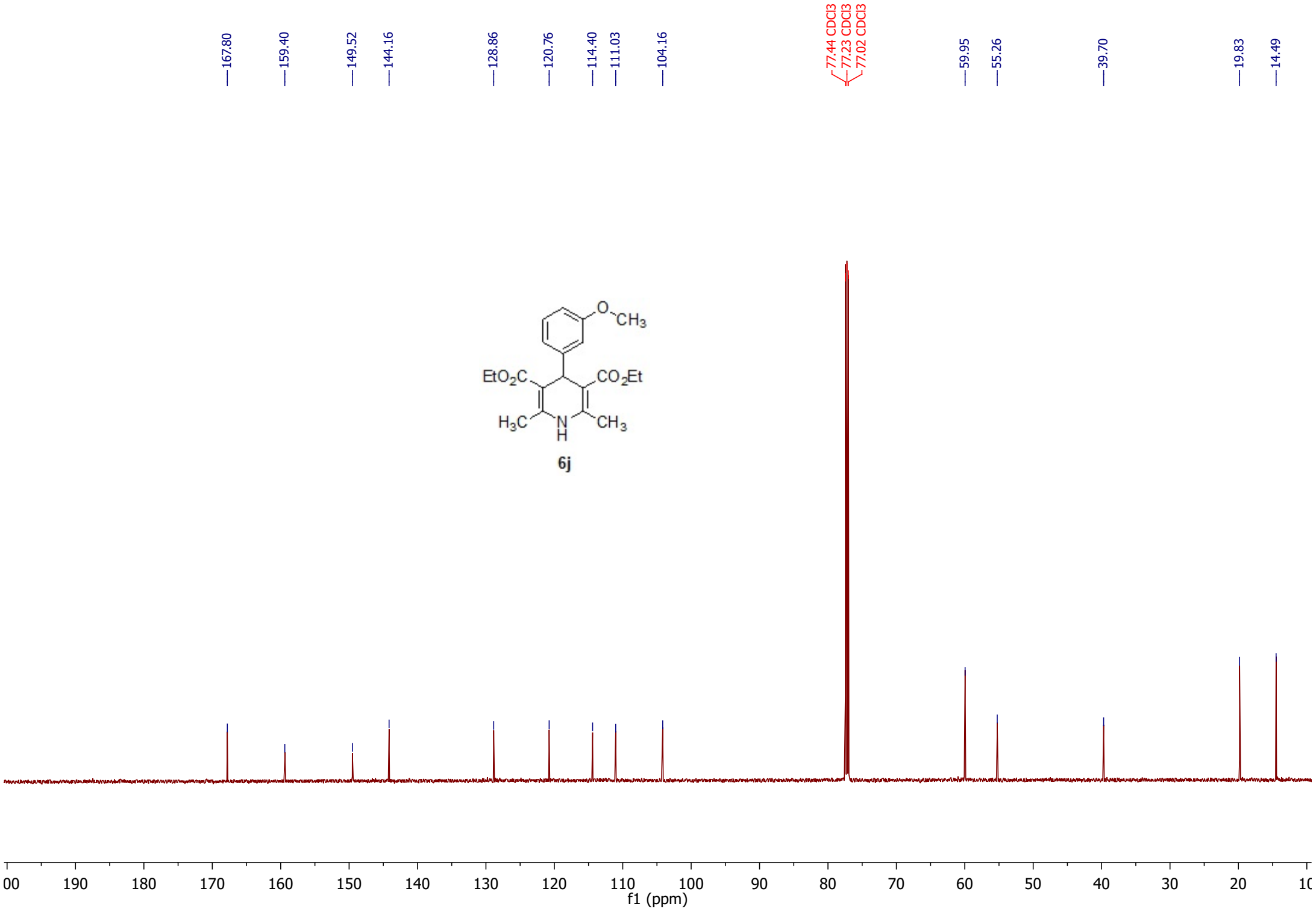
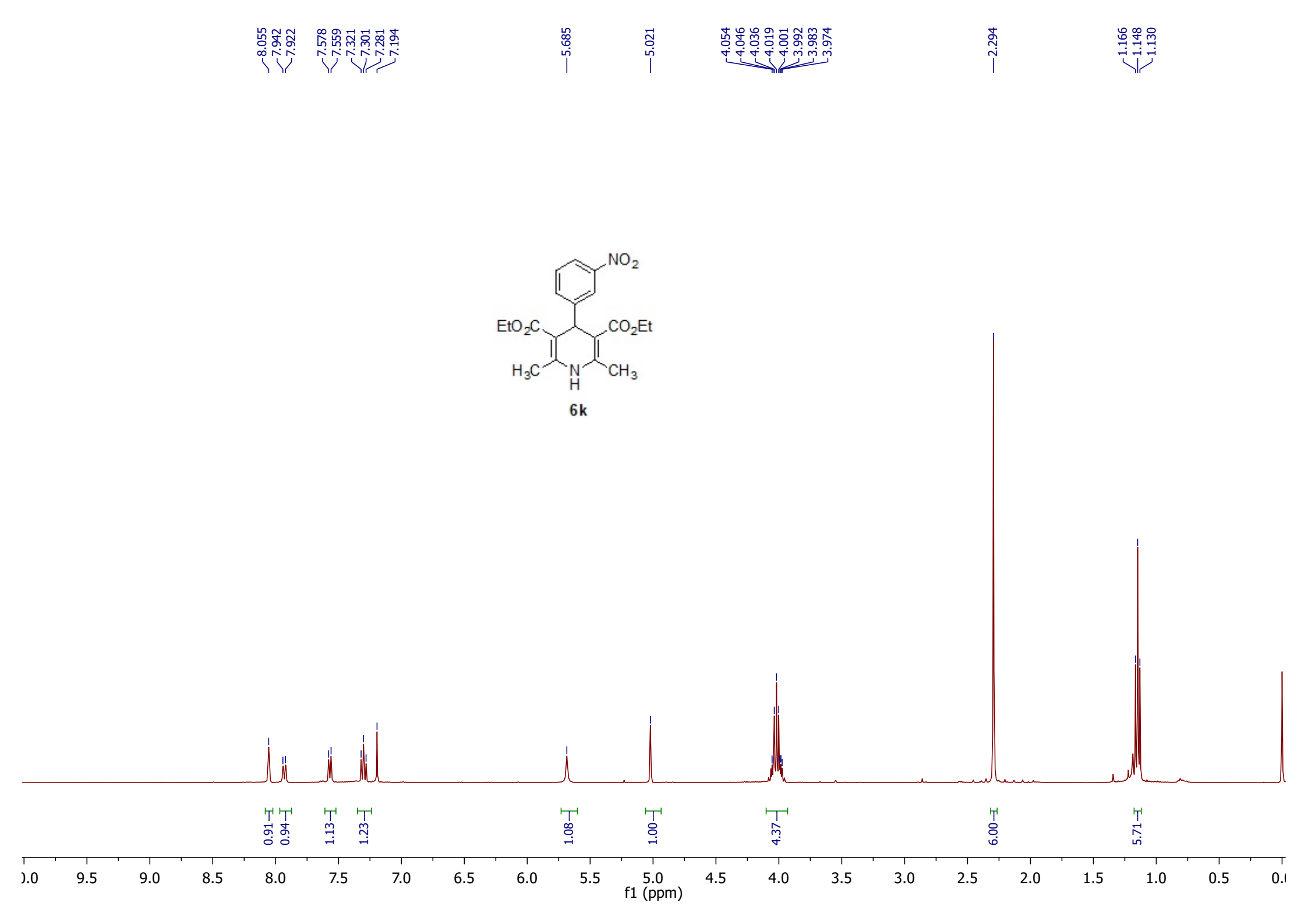
6.868
6.841
6.835
6.831
6.677
6.672
6.658
6.652
6.034
4.977
4.118
4.108
4.100
4.090
4.082
4.072
4.064
4.054
3.747
2.289
1.238
1.220
1.202
O
CH3
EtO2C
CO2Et
H3C
N
H
CH3
6j
1.00
0.95
1.00
0.96
0.89
0.96
4.14
3.03
5.93
6.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.80
159.40
149.52
144.16
128.86
120.76
114.40
111.03
104.16
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.95
55.26
39.70
19.83
14.49
O
CH3
EtO2C
CO2Et
H3C
N
H
CH3
6j
f1 (ppm)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7.281
7.194
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4.054
4.046
4.036
4.019
4.001
3.992
3.983
3.974
2.294
1.166
1.148
1.130
NO2
EtO2C
CO2Et
H3C
N
H
CH3
6k
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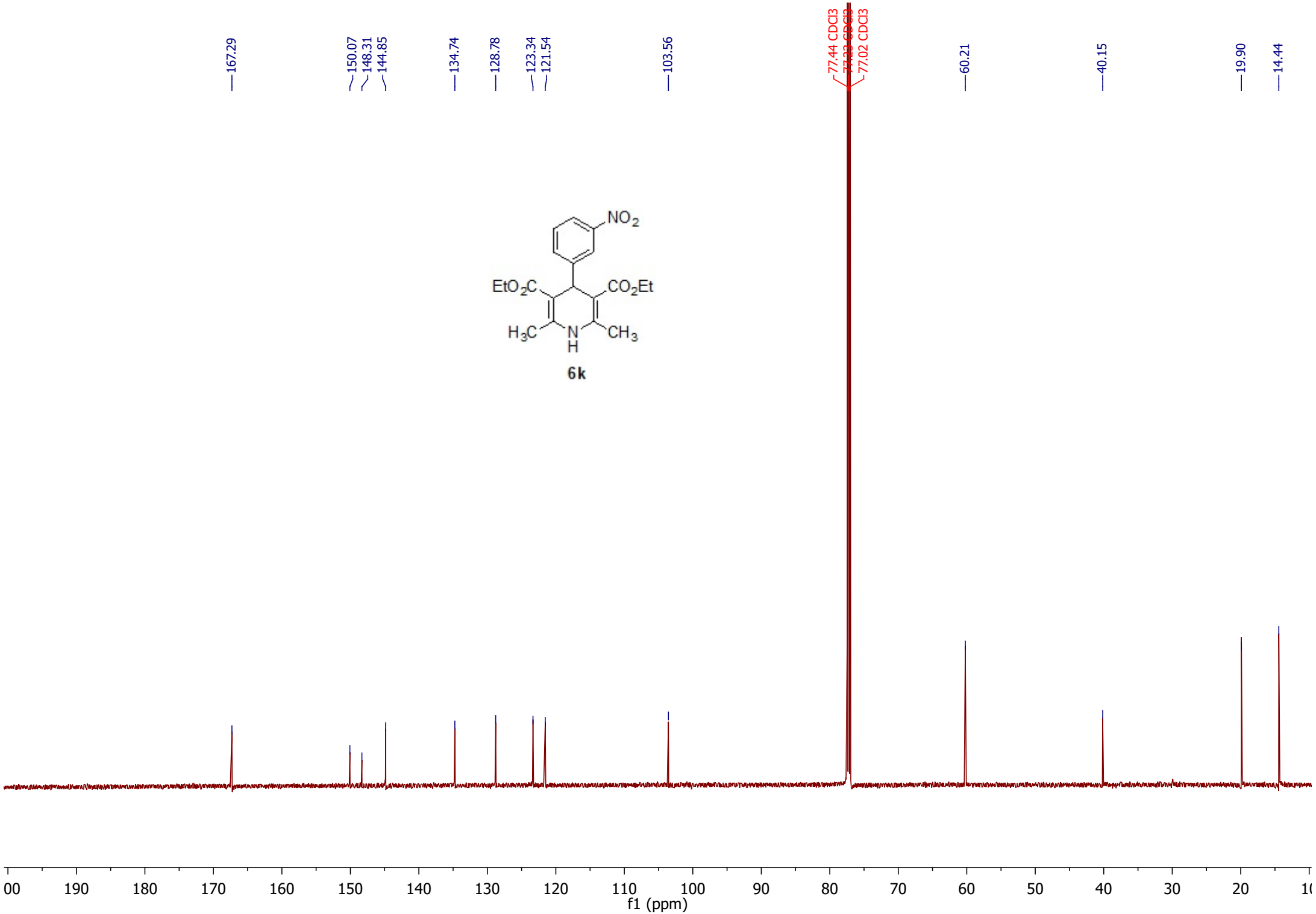
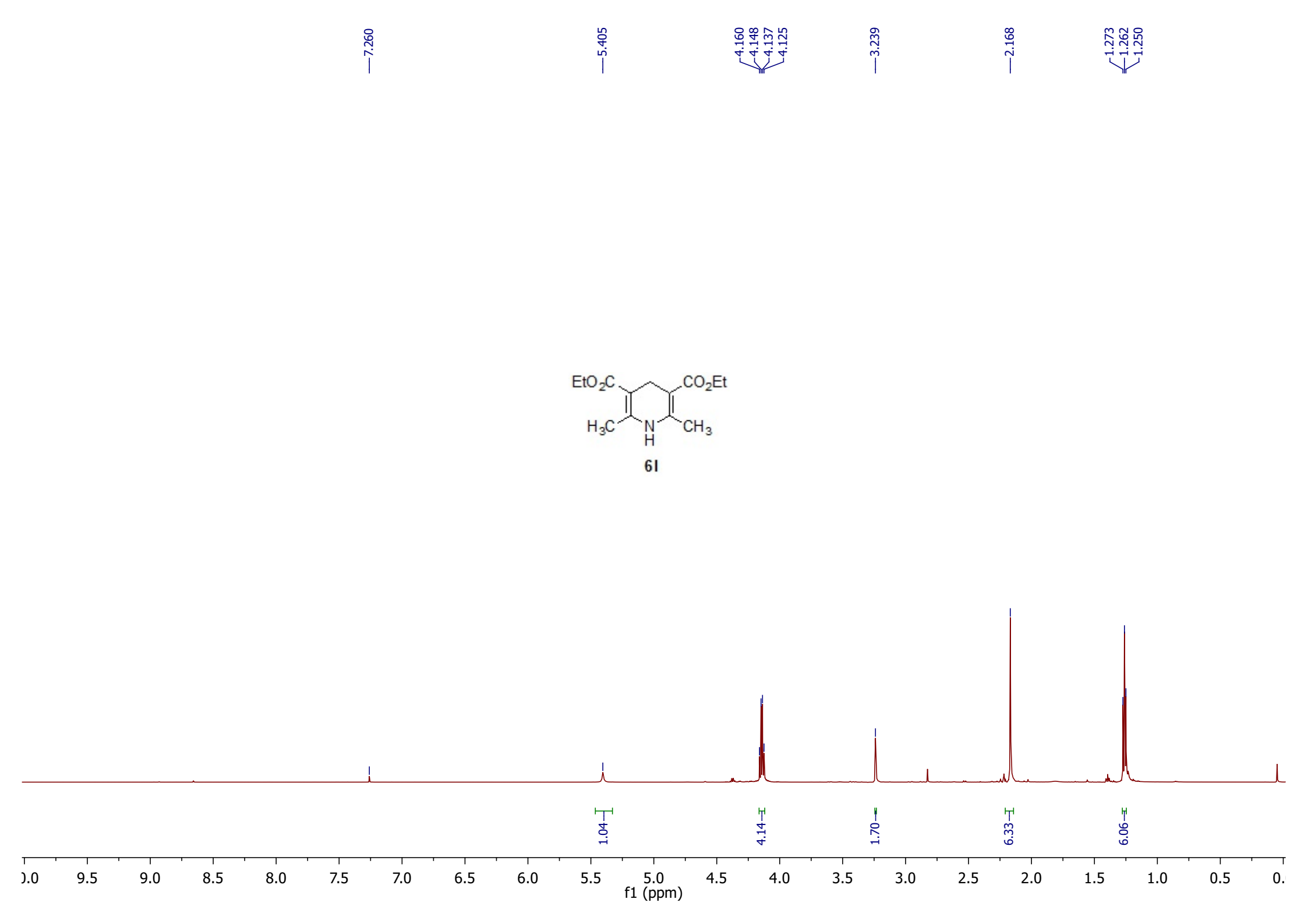
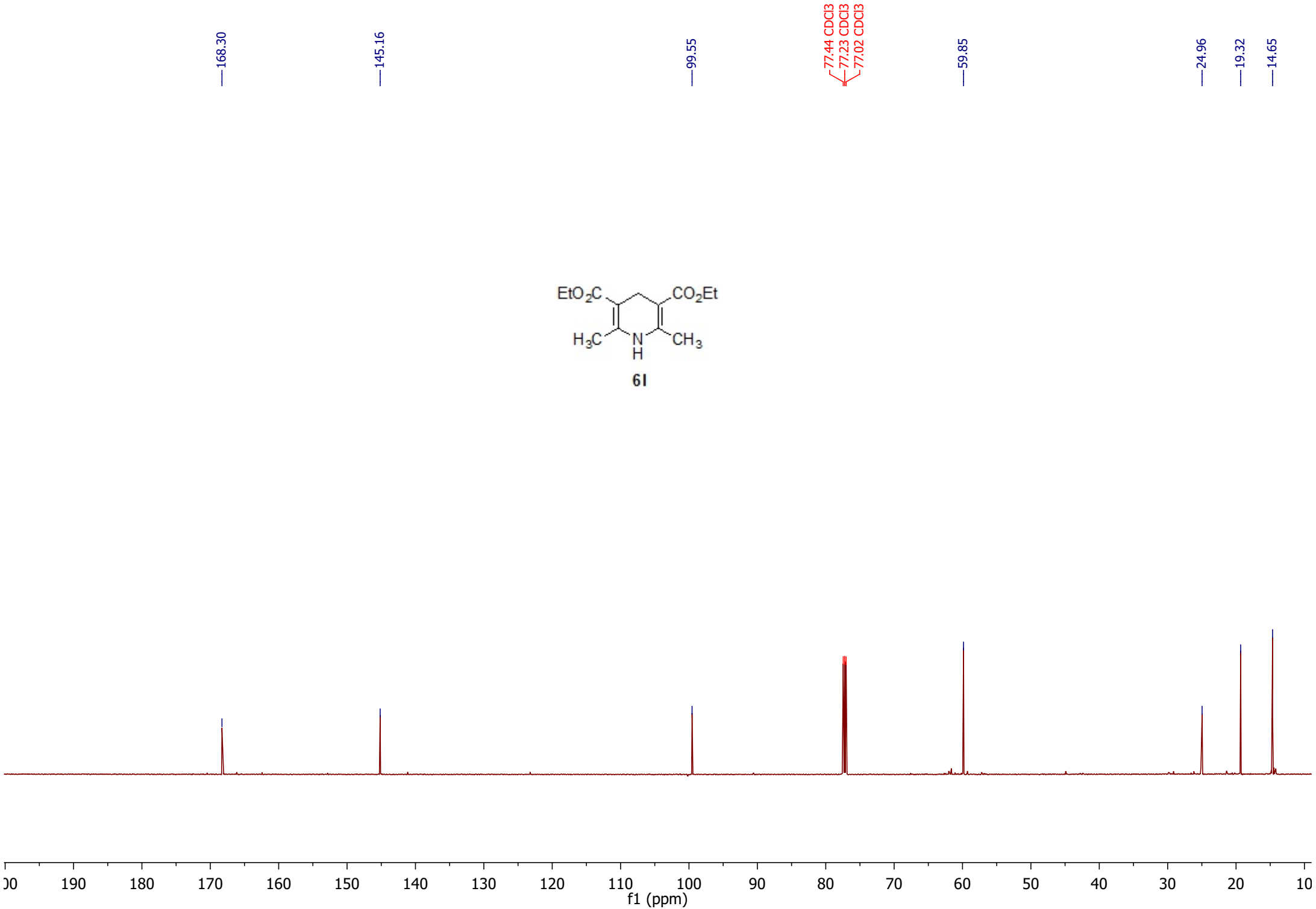
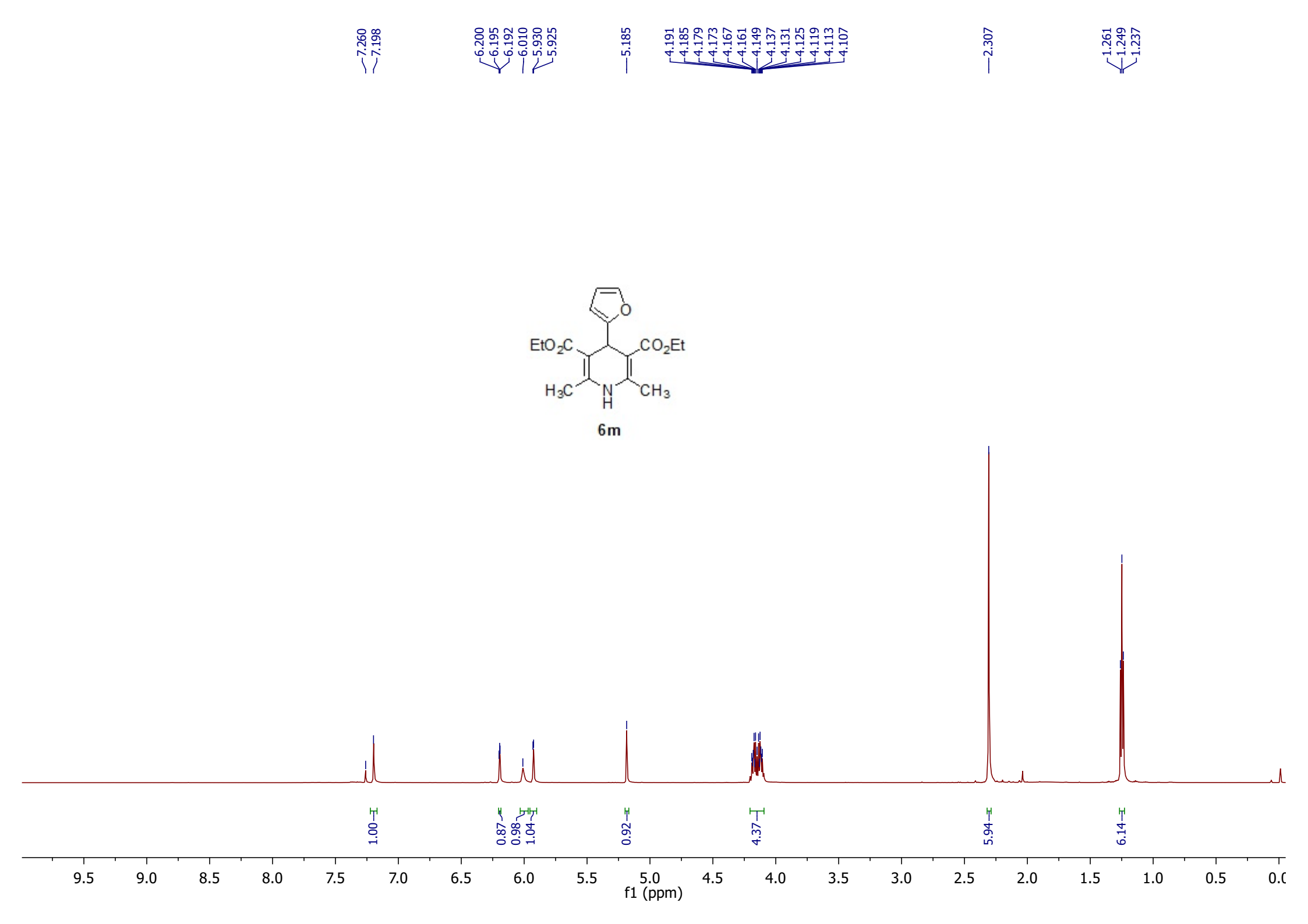
0.94
1.13
1.23
1.08
1.00
4.37
6.00
5.71
f1 (ppm)


167.29
150.07
148.31
144.85
134.74
128.78
123.34
121.54
103.56
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
60.21
40.15
19.90
14.44
NO2
EtO2C
CO2Et
H3C
N
H
CH3
6k
f1 (ppm)


7.260
5.405
4.160
4.148
4.137
4.125
3.239
2.168
1.273
1.262
1.250
EtO2C
CO2Et
H3C
N
H
CH3
6l
1.04
4.14
1.70
6.33
6.06
f1 (ppm)


168.30
145.16
99.55
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.85
24.96
19.32
14.65
EtO2C
CO2Et
H3C
N
H
CH3
6l
f1 (ppm)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7.198
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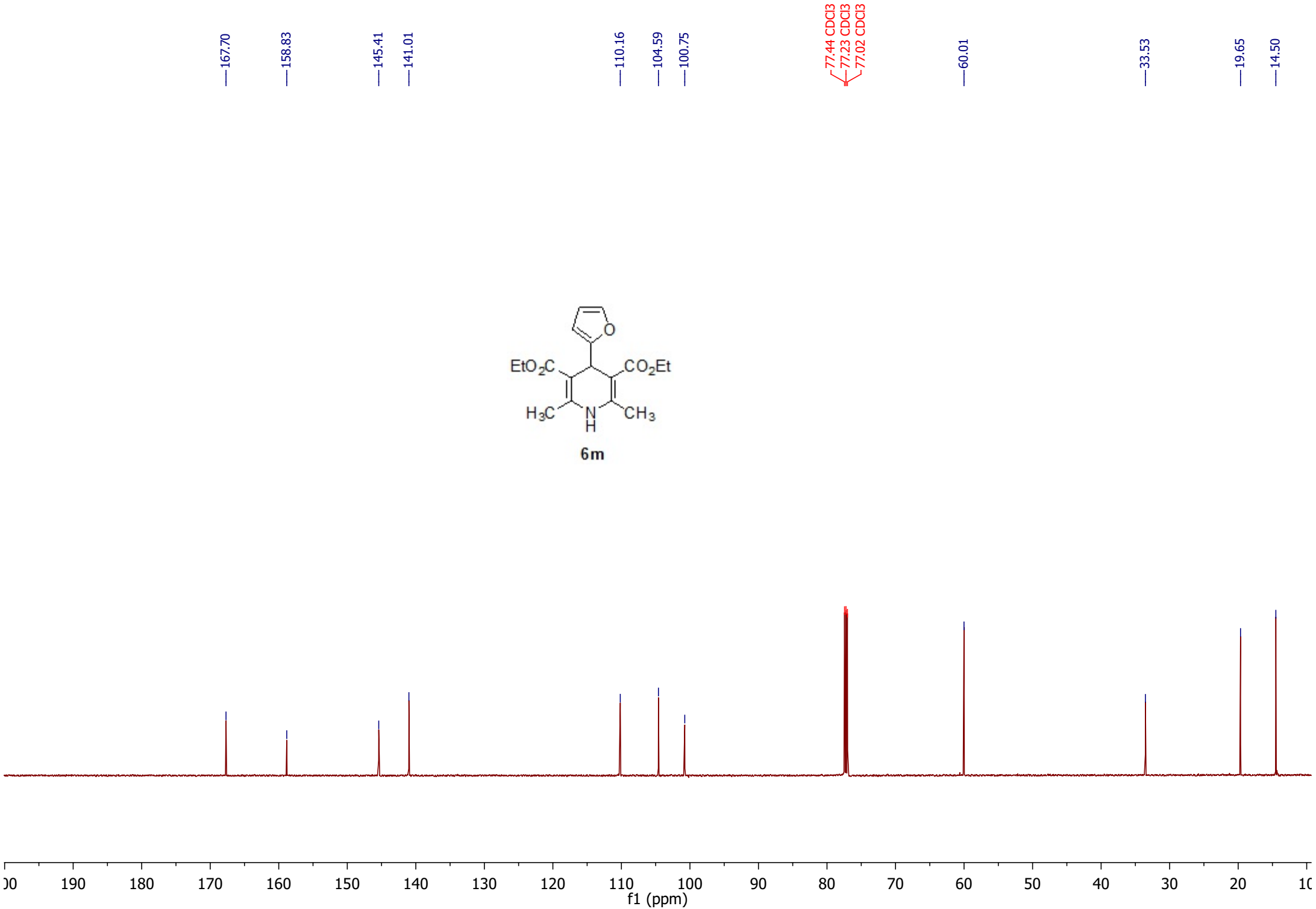
6.195
6.192
6.010
5.930
5.925
5.185
4.191
4.185
4.179
4.173
4.167
4.161
4.149
4.137
4.131
4.125
4.119
4.113
4.107
2.307
1.261
1.249
1.237
O
EtO2C
CO2Et
H3C
CH3
N
H
6m
1.00
0.87
0.98
1.04
0.92
4.37
5.94
6.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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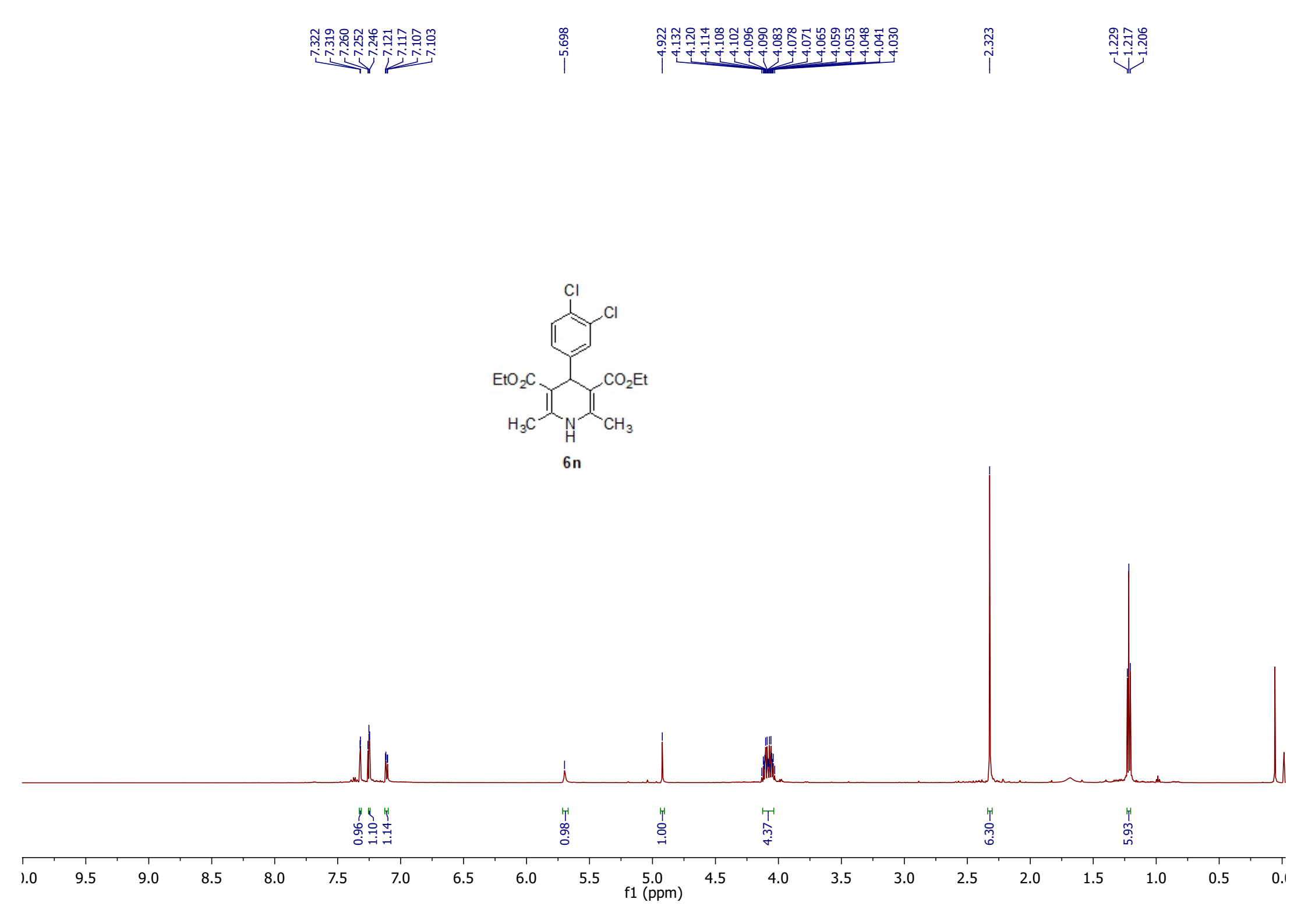
158.83
145.41
141.01
110.16
104.59
100.75
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
60.01
33.53
19.65
14.50
O
EtO2C
CO2Et
H3C
N
H
CH3
6m
f1 (ppm)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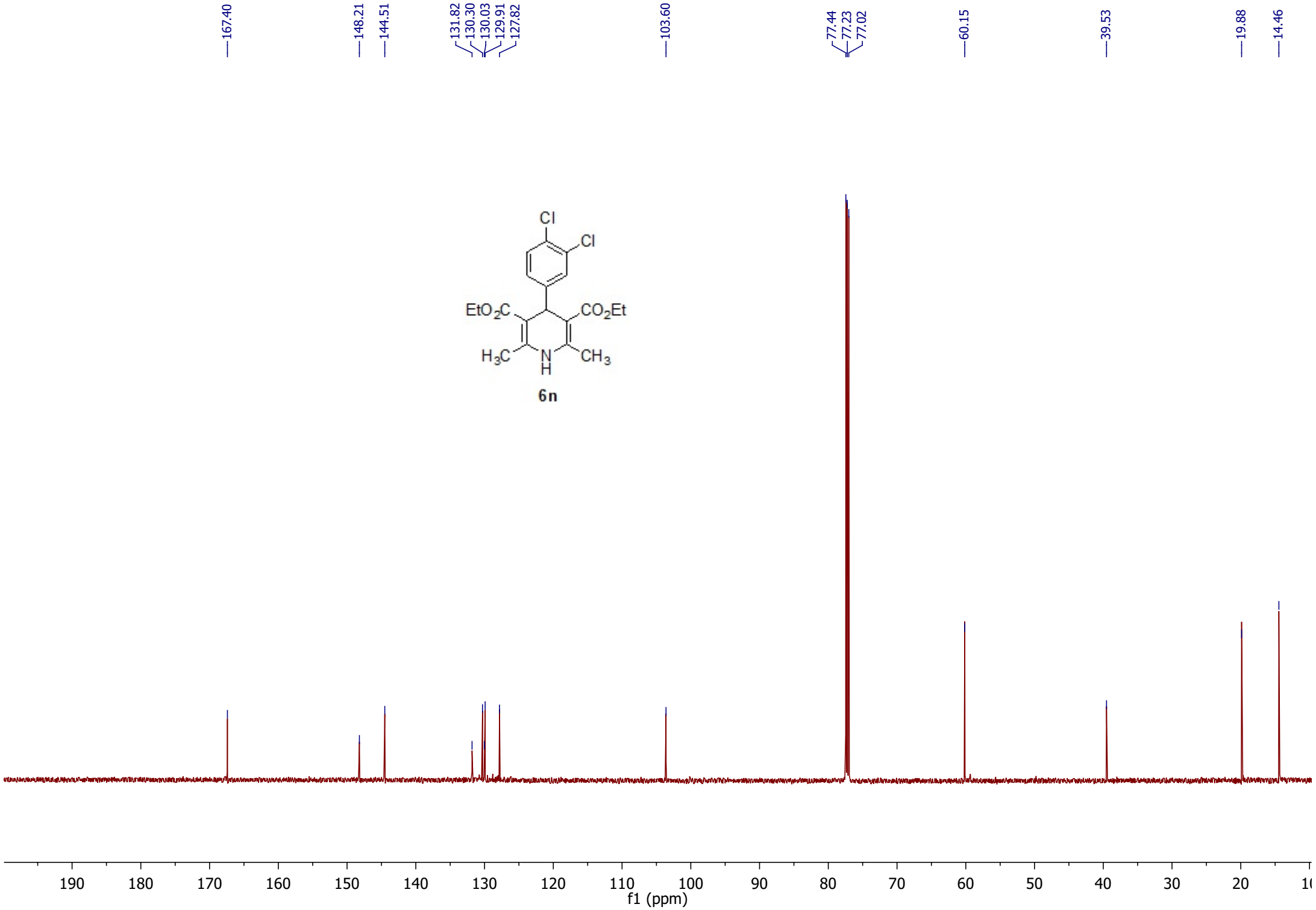
7.319
7.260
7.252
7.246
7.121
7.117
7.107
7.103
5.698
4.922
4.132
4.120
4.114
4.108
4.102
4.096
4.090
4.083
4.078
4.071
4.065
4.059
4.053
4.048
4.041
4.030
2.323
1.229
1.217
1.206
Cl
Cl
EtO2C
CO2Et
H3C
N
H
CH3
6n
0.96
1.10
1.14
0.98
1.00
4.37
6.30
5.93
f1 (ppm)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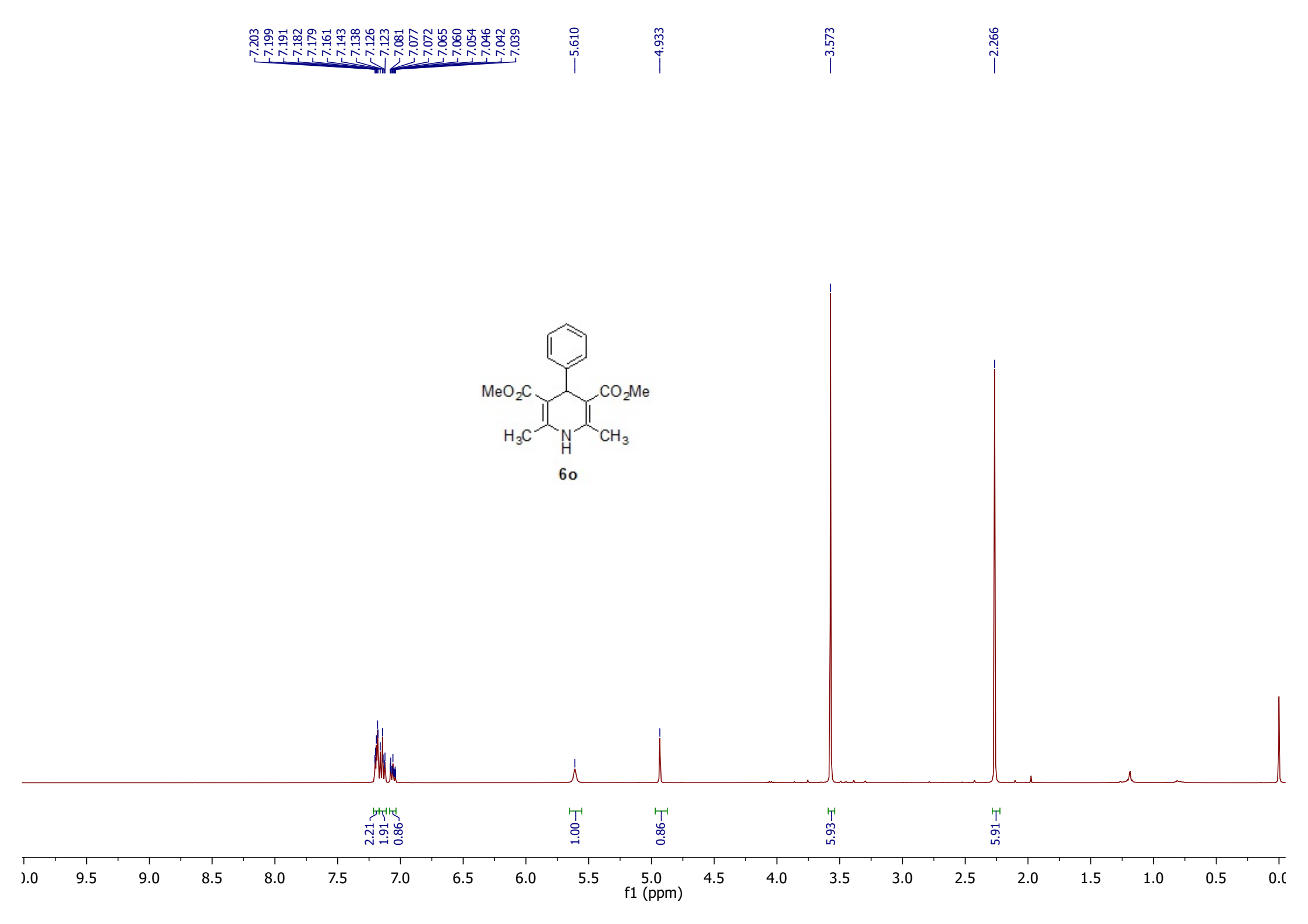
148.21
144.51
131.82
130.30
130.03
129.91
127.82
103.60
77.44
77.23
77.02
60.15
39.53
19.88
14.46
Cl
Cl
EtO2C
CO2Et
H3C
N
H
CH3
6n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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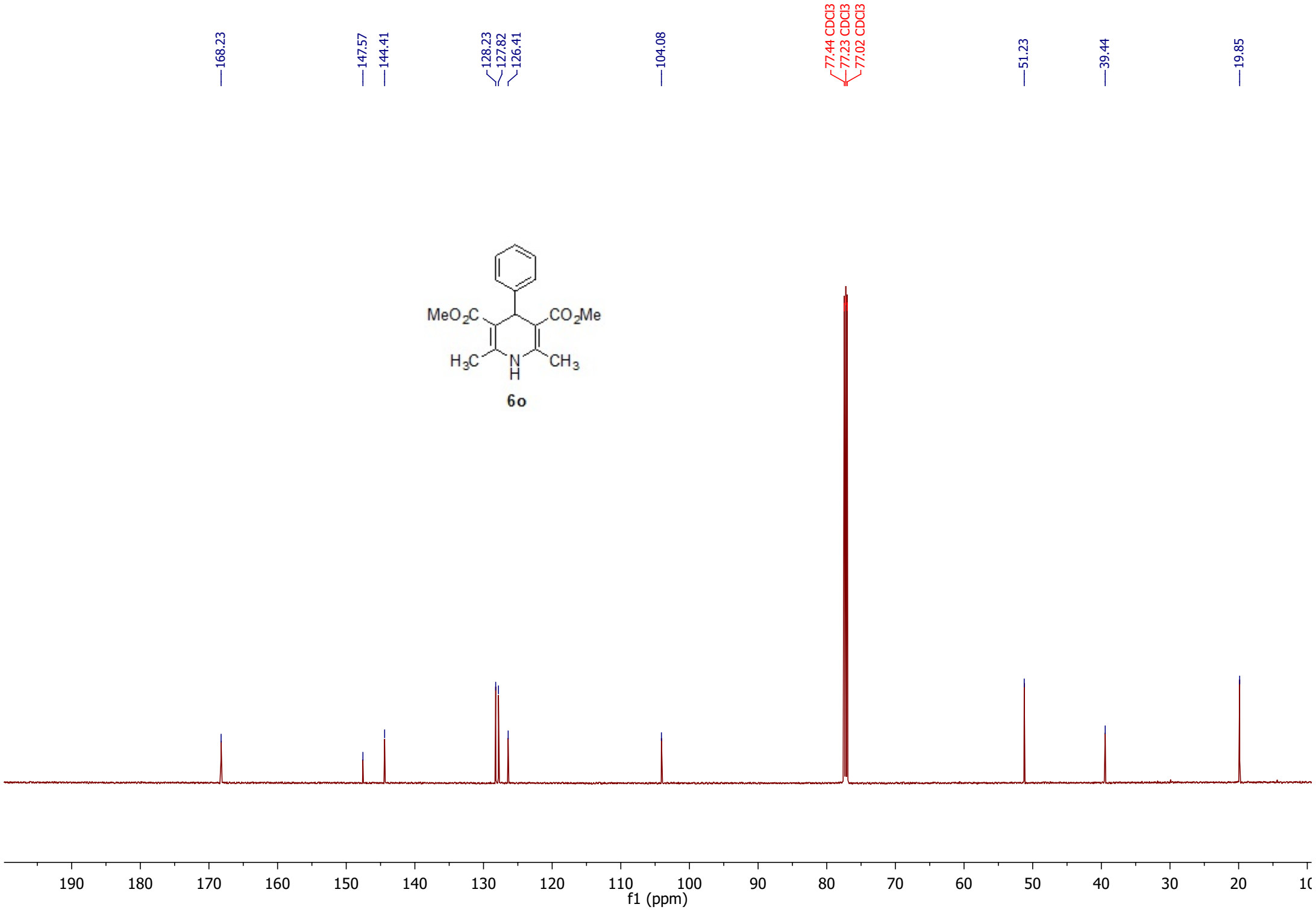
7.199
7.191
7.182
7.179
7.161
7.143
7.138
7.126
7.123
7.081
7.077
7.072
7.065
7.060
7.054
7.046
7.042
7.039
5.610
4.933
3.573
2.266
MeO2C
CO2Me
H3C
CH3
N
H
6o
2.21
1.91
0.86
1.00
0.86
5.93
5.91
f1 (ppm)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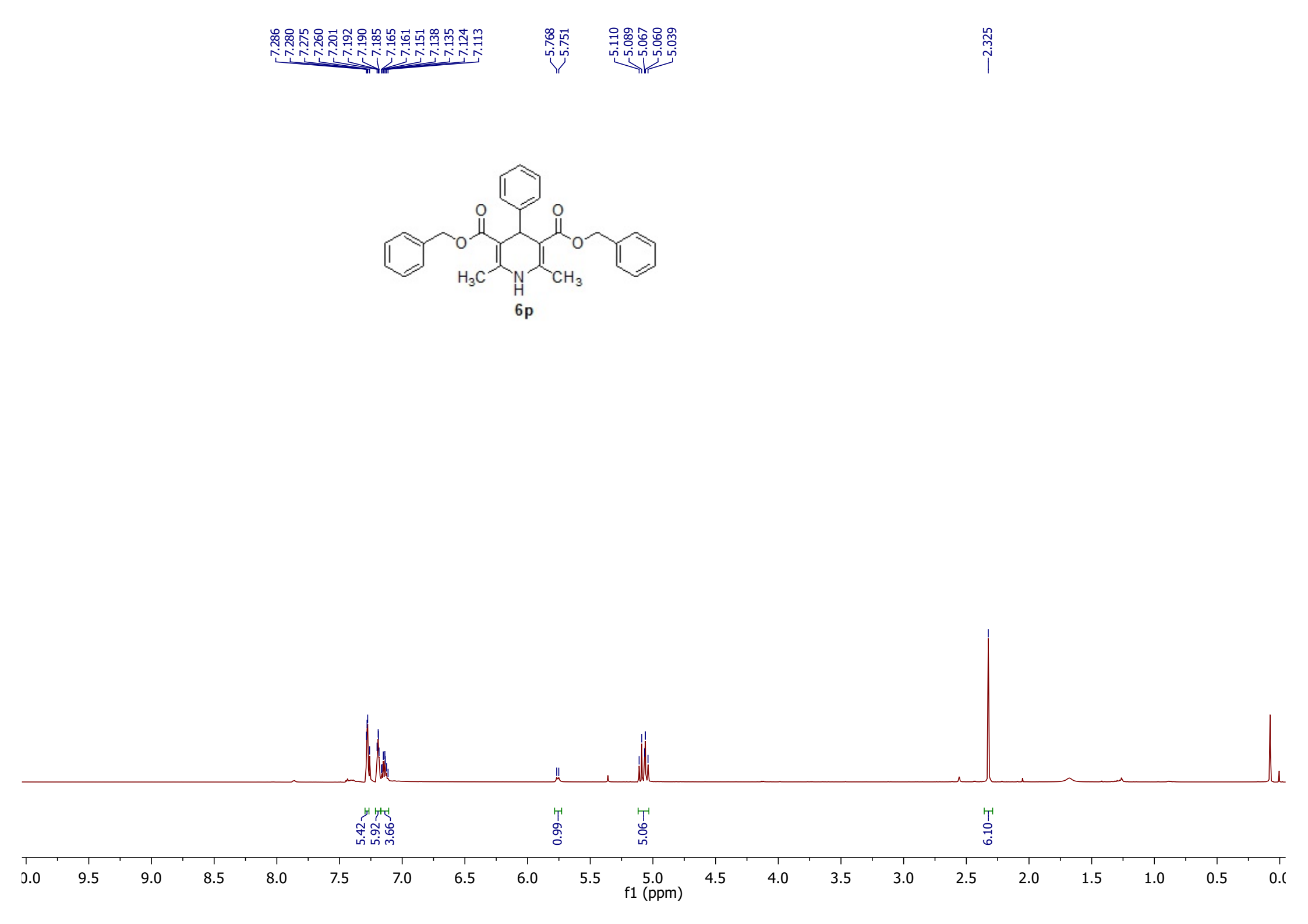
147.57
144.41
128.23
127.82
126.41
104.08
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
51.23
39.44
19.85
MeO2C
CO2Me
H3C
CH3
N
H
6o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)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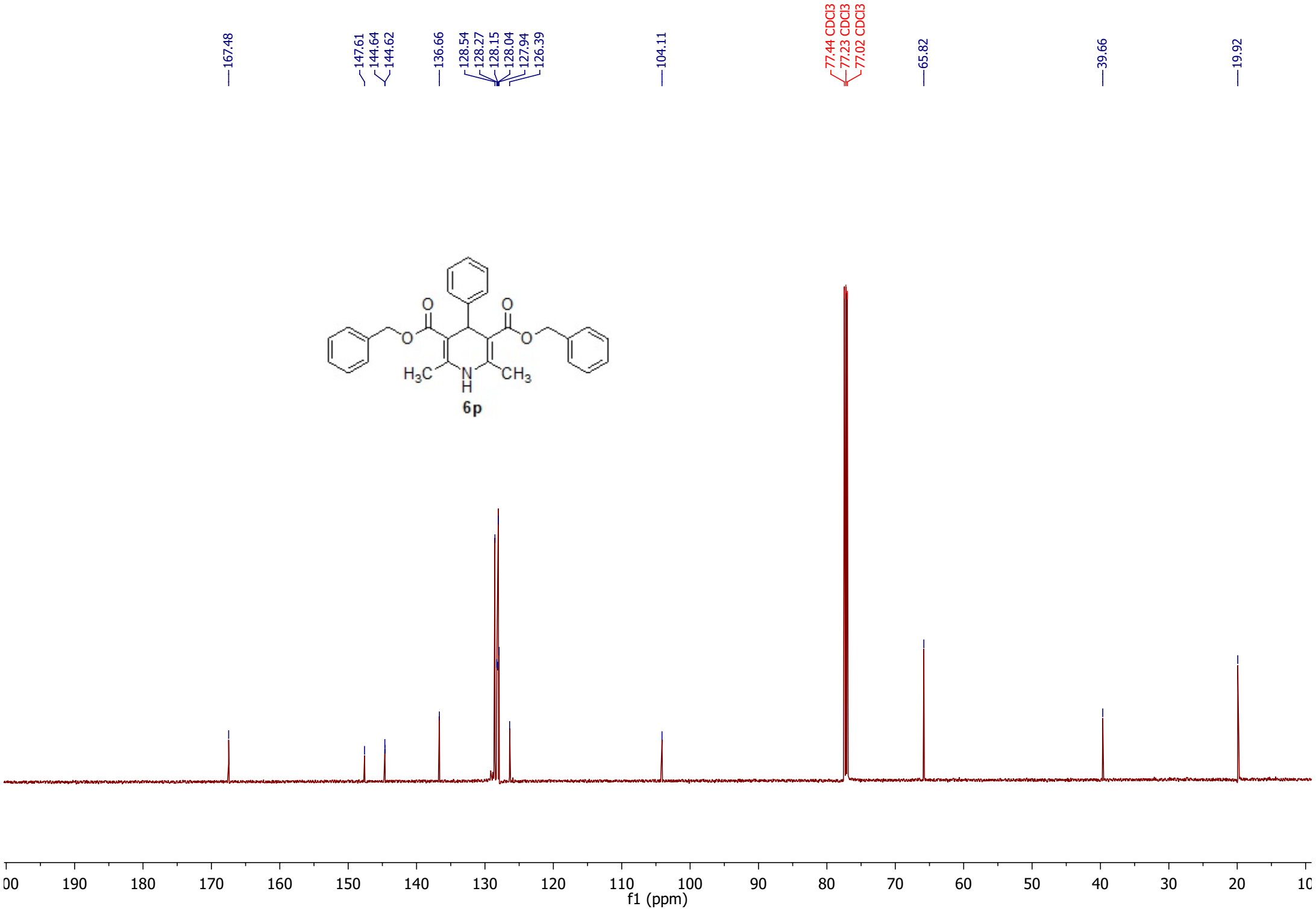
7.280
7.275
7.260
7.201
7.192
7.190
7.185
7.165
7.161
7.151
7.138
7.135
7.124
7.113
5.768
5.751
5.110
5.089
5.067
5.060
5.039
2.325
O
O
O
O
H3C
N
H
CH3
6p
5.42
5.92
3.66
0.99
5.06
6.10
f1 (ppm)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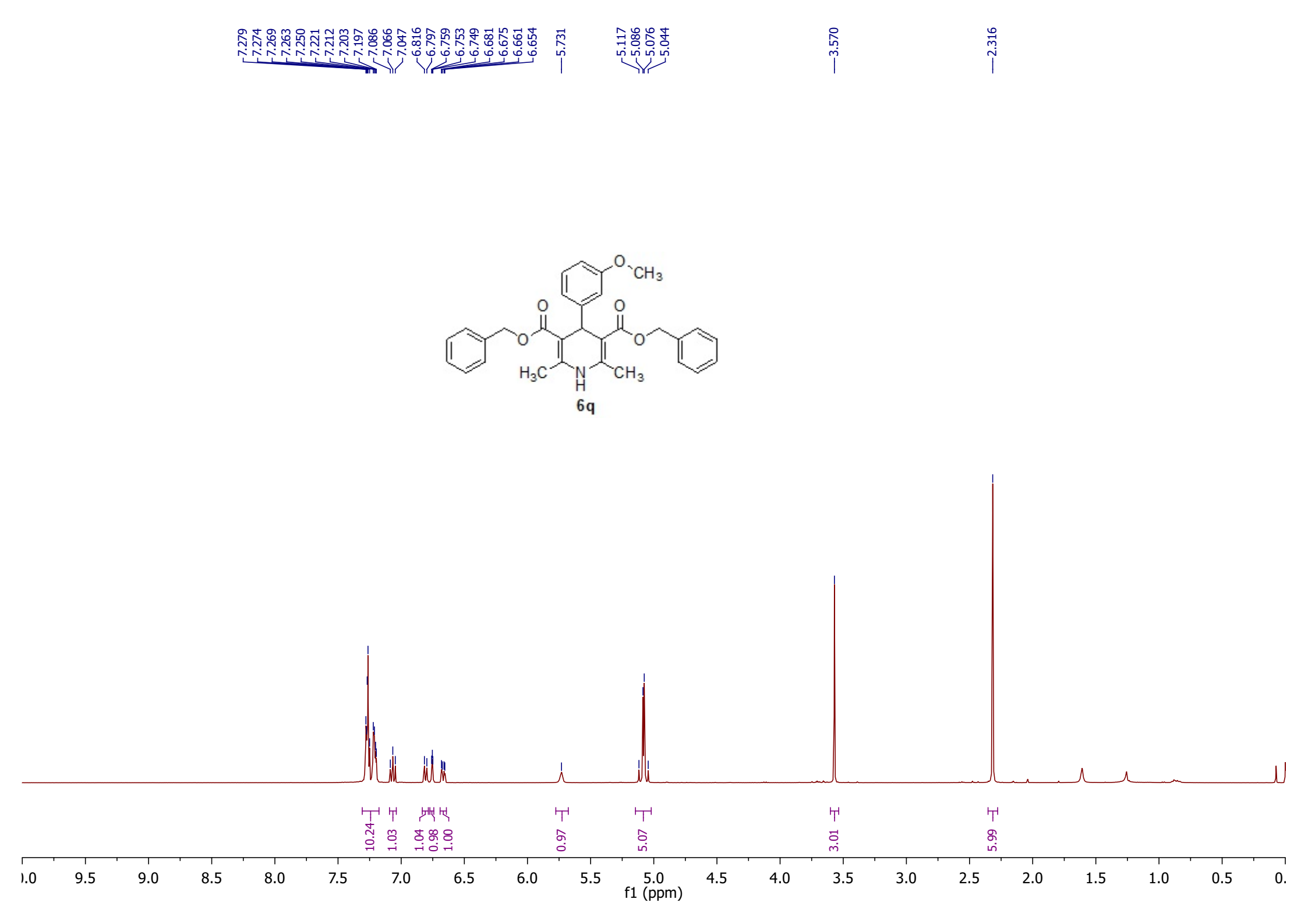
147.61
144.64
144.62
136.66
128.54
128.27
128.15
128.04
127.94
126.39
104.11
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
65.82
39.66
19.92
O
O
O
O
H3C
N
H
CH3
6p
f1 (ppm)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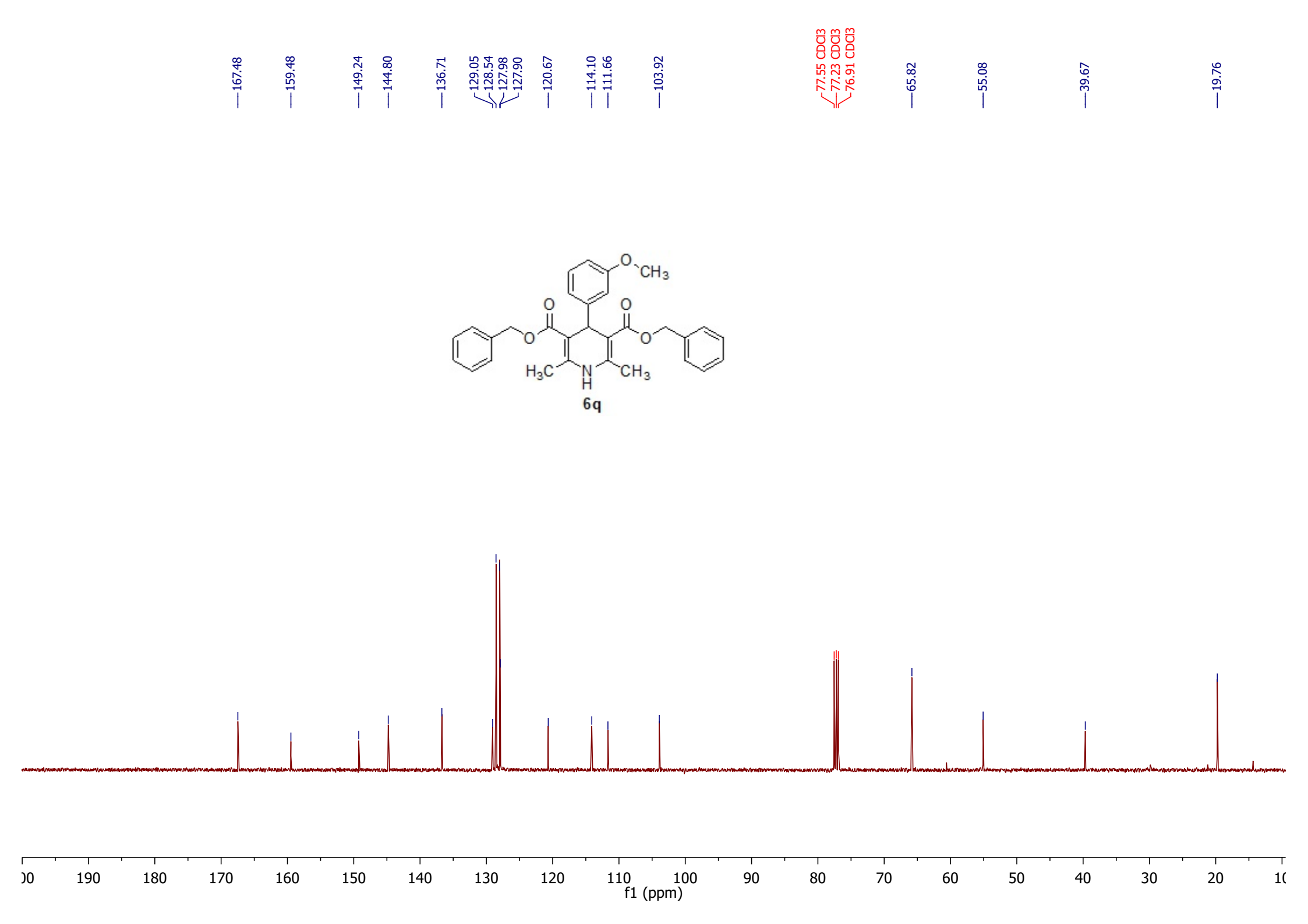
7.274
7.269
7.263
7.250
7.221
7.212
7.203
7.197
7.086
7.066
7.047
6.816
6.797
6.759
6.753
6.749
6.681
6.675
6.661
6.654
5.731
5.117
5.086
5.076
5.044
3.570
2.316
O
CH3
O
O
O
O
H3C
N
H
CH3
6q
10.24
1.03
1.04
0.98
1.00
0.97
5.07
3.01
5.99
f1 (ppm)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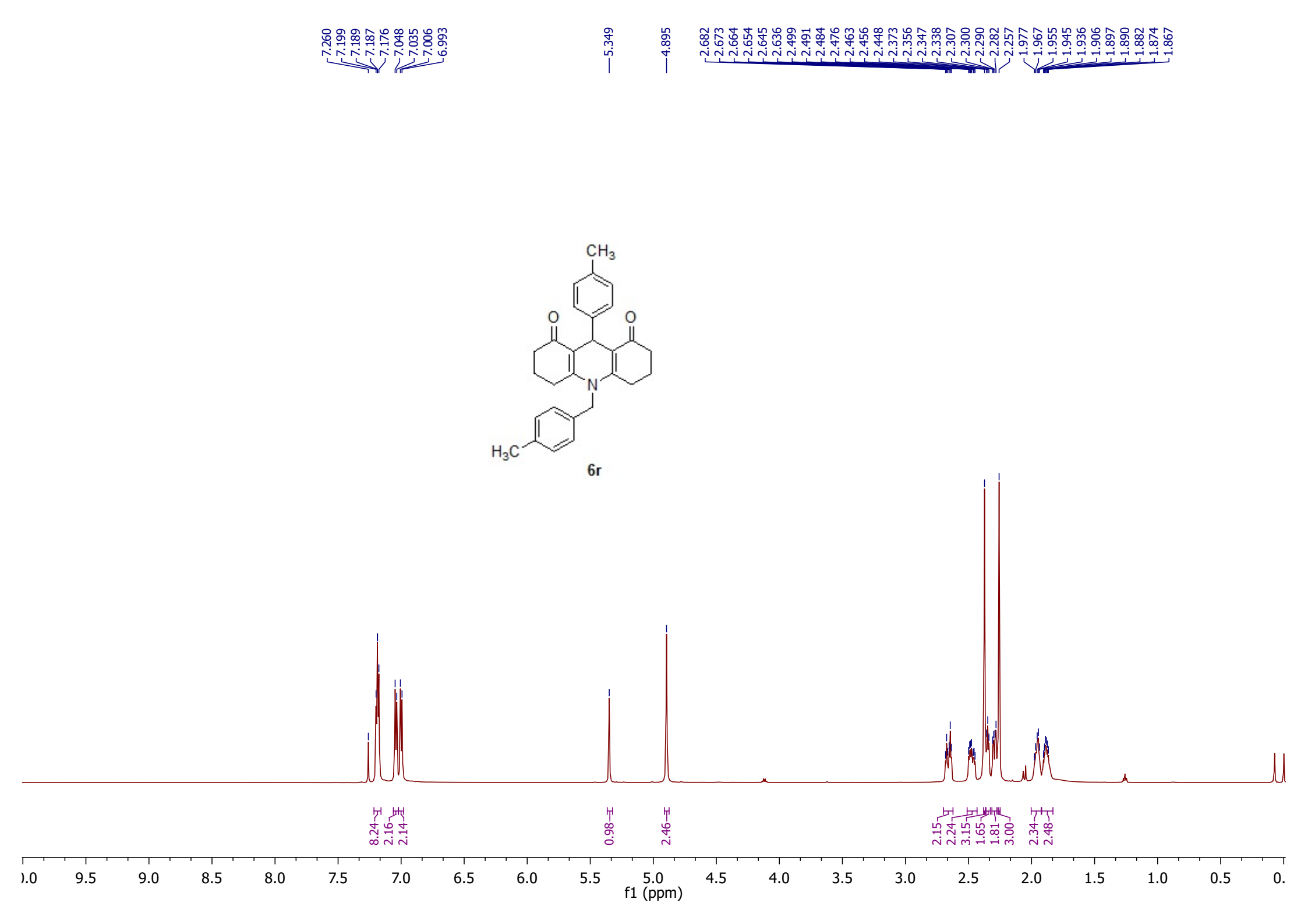
159.48
149.24
144.80
136.71
129.05
128.54
127.98
127.90
120.67
114.10
111.66
103.92
77.55 CDCl3
77.23 CDCl3
76.91 CDCl3
65.82
55.08
39.67
19.76
O
CH3
O
O
O
O
H3C
N
H
CH3
6q
f1 (ppm)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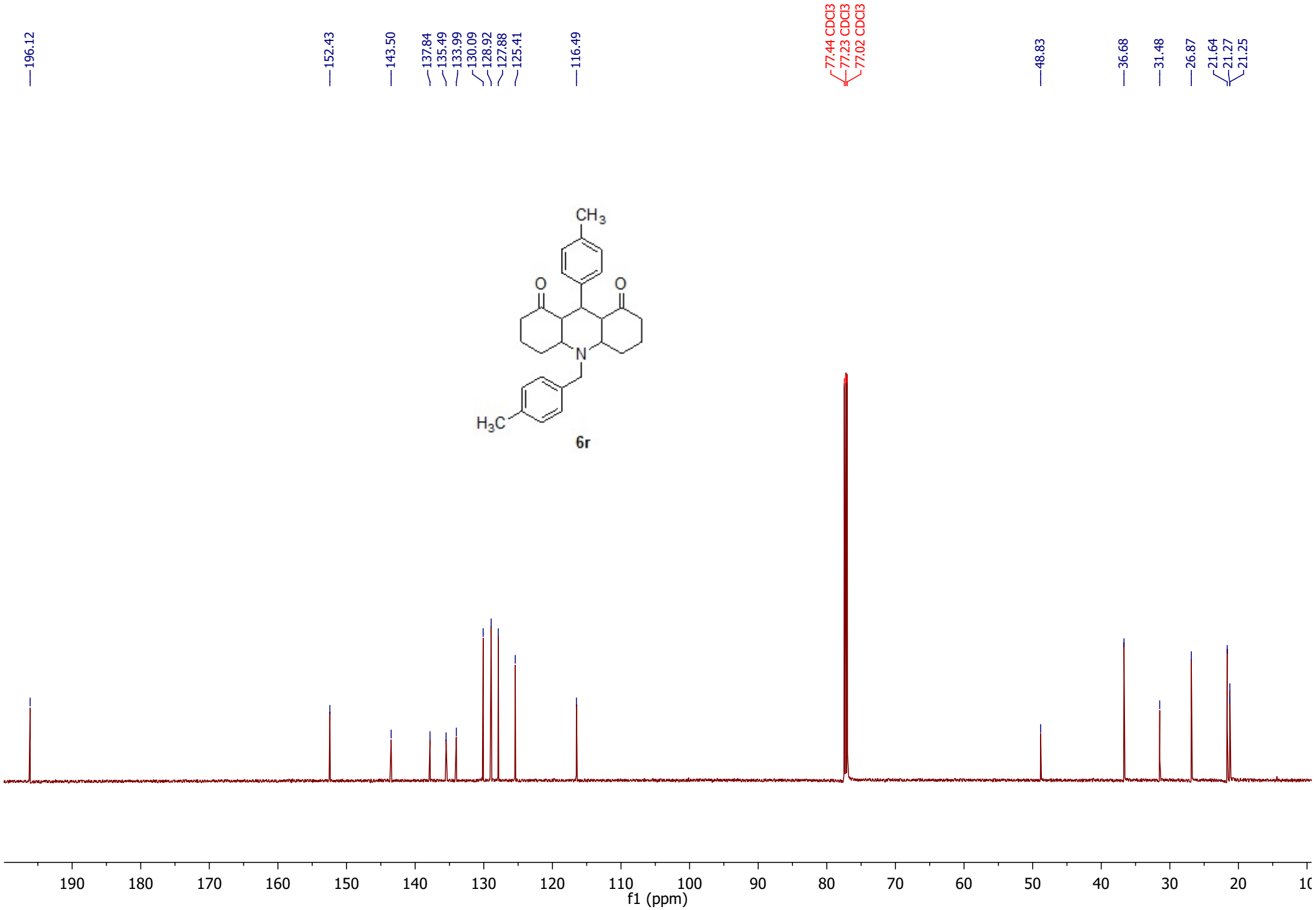
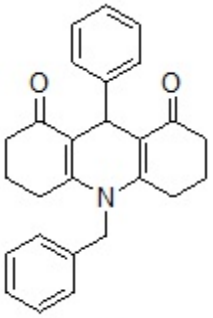
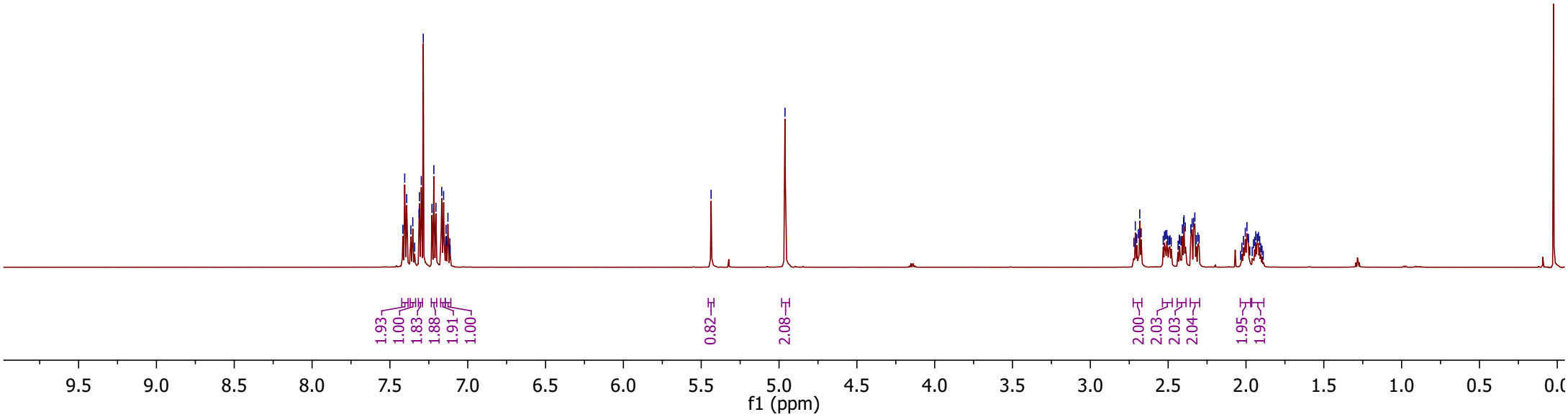
7.199
7.189
7.187
7.176
7.048
7.035
7.006
6.993
5.349
4.895
2.682
2.673
2.664
2.654
2.645
2.636
2.499
2.491
2.484
2.476
2.463
2.456
2.448
2.373
2.356
2.347
2.338
2.307
2.300
2.290
2.282
2.257
1.977
1.967
1.955
1.945
1.936
1.906
1.897
1.890
1.882
1.874
1.867
CH3
O
O
N
H3C
6r
8.24
2.16
2.14
0.98
2.46
2.15
2.24
3.15
1.65
1.81
3.00
2.34
2.48
f1 (ppm)


196.12
152.43
143.50
137.84
135.49
133.99
130.09
128.92
127.88
125.41
116.49
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
48.83
36.68
31.48
26.87
21.64
21.27
21.25
CH3
O
O
N
H3C
6r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.417
7.405
7.392
7.365
7.353
7.341
7.313
7.310
7.298
7.286
7.230
7.218
7.204
7.167
7.155
7.141
7.139
7.137
7.127
7.117
7.115
7.113
5.437
4.962
2.720
2.711
2.702
2.692
2.683
2.674
2.532
2.524
2.517
2.509
2.504
2.495
2.488
2.480
2.436
2.429
2.426
2.418
2.409
2.401
2.398
2.390
2.354
2.346
2.337
2.329
2.319
2.309
2.301
2.035
2.026
2.016
2.004
1.994
1.984
1.976
1.960
1.952
1.944
1.937
1.927
1.920
1.912
1.905
1.897
1.889


O
O
N

6s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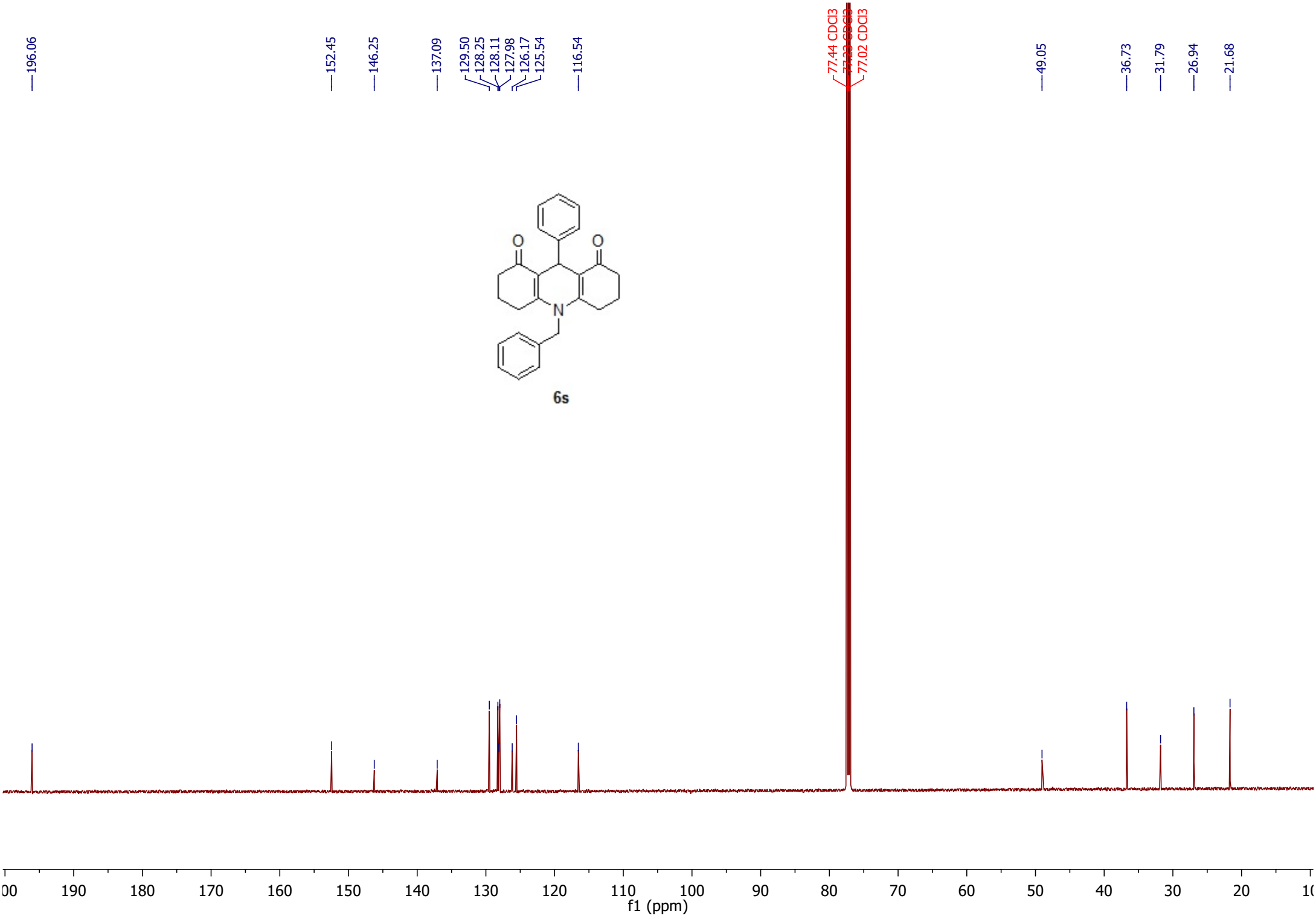
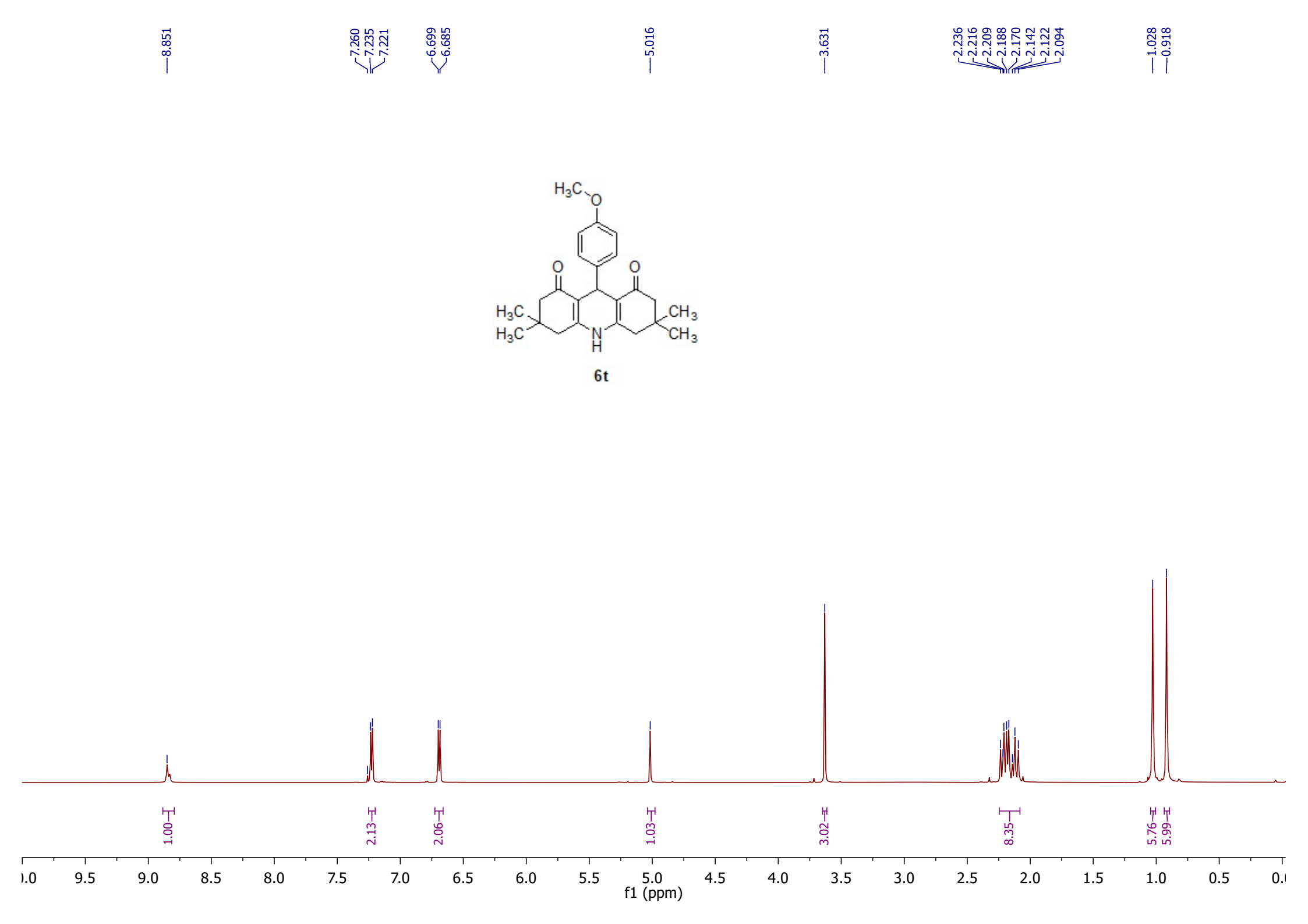
1.00
1.83
1.88
1.91
1.00
0.82
2.08
2.00
2.03
2.03
2.04
1.95
1.93
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


196.06
152.45
146.25
137.09
129.50
128.25
128.11
127.98
126.17
125.54
116.54
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
49.05
36.73
31.79
26.94
21.68
O
O
N
6s
f1 (ppm)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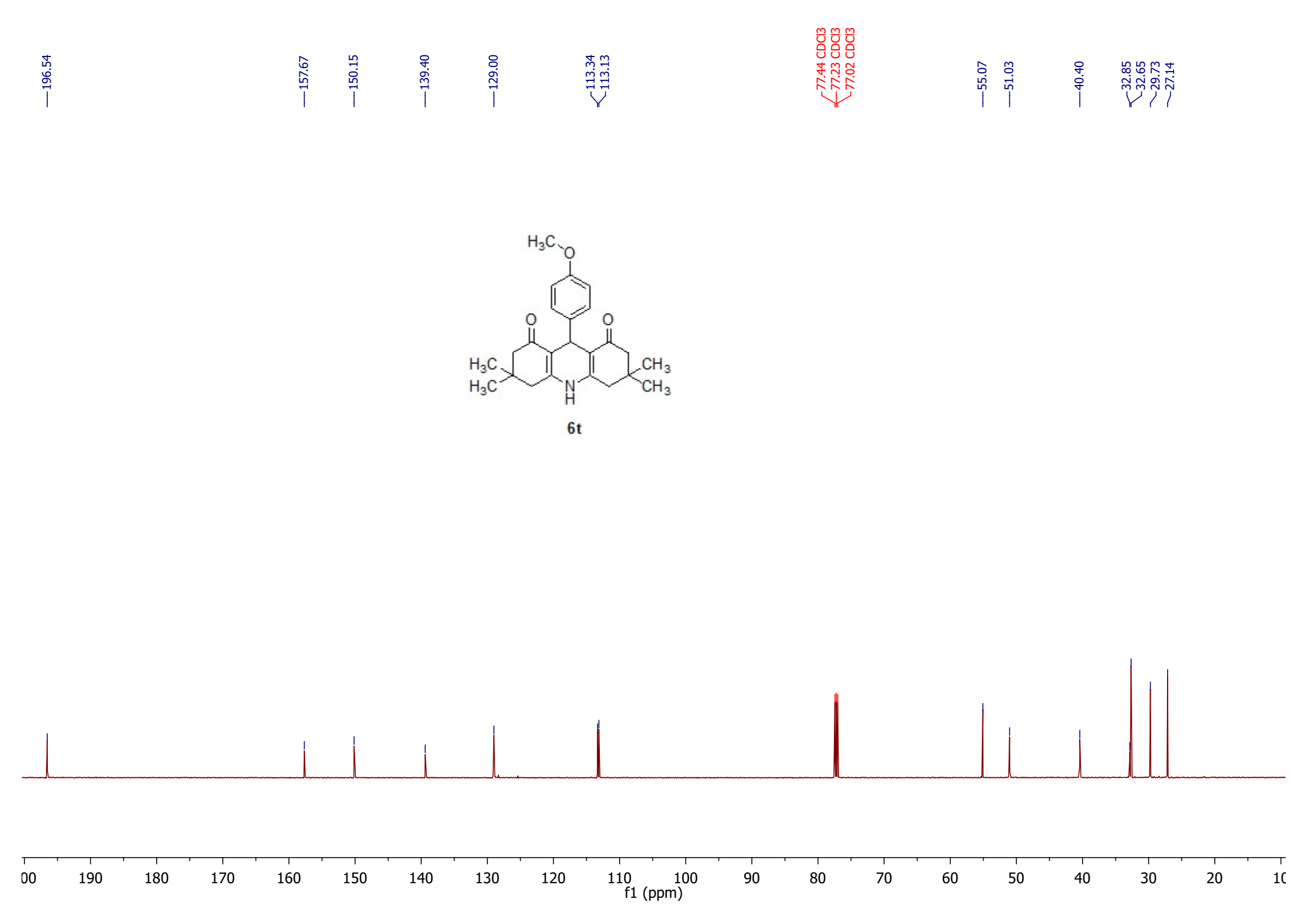
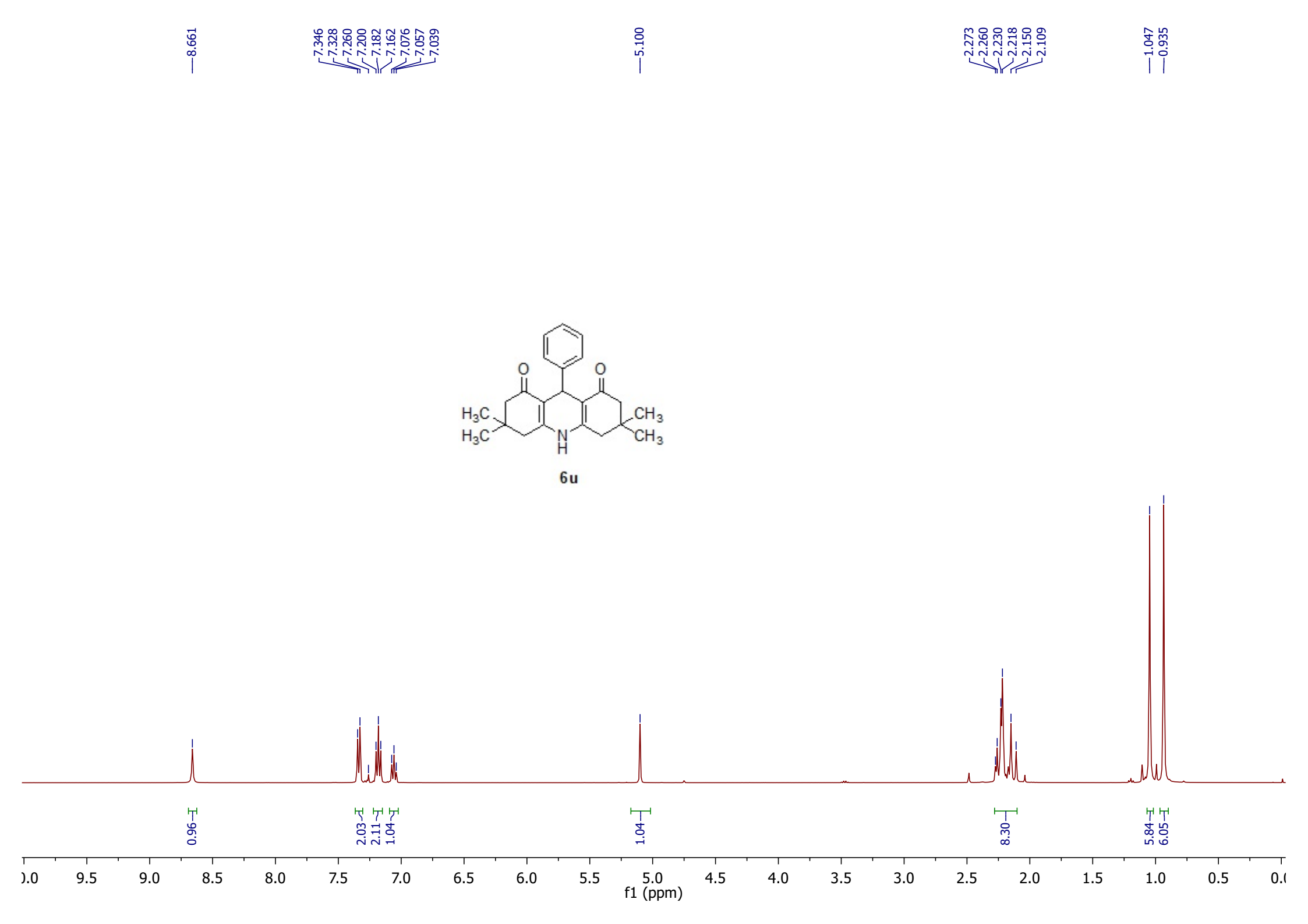
6.685
5.016
3.631
2.236
2.216
2.209
2.188
2.170
2.142
2.122
2.094
1.028
0.918
H3C
O
O
O
H3C
H3C
CH3
CH3
N
H
6t
1.00
2.13
2.06
1.03
3.02
8.35
5.76
5.99
f1 (ppm)


196.54
157.67
150.15
139.40
129.00
113.34
113.13
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
55.07
51.03
40.40
32.85
32.65
29.73
27.14
H3C
O
O
O
H3C
H3C
CH3
CH3
N
H
6t
f1 (ppm)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7.328
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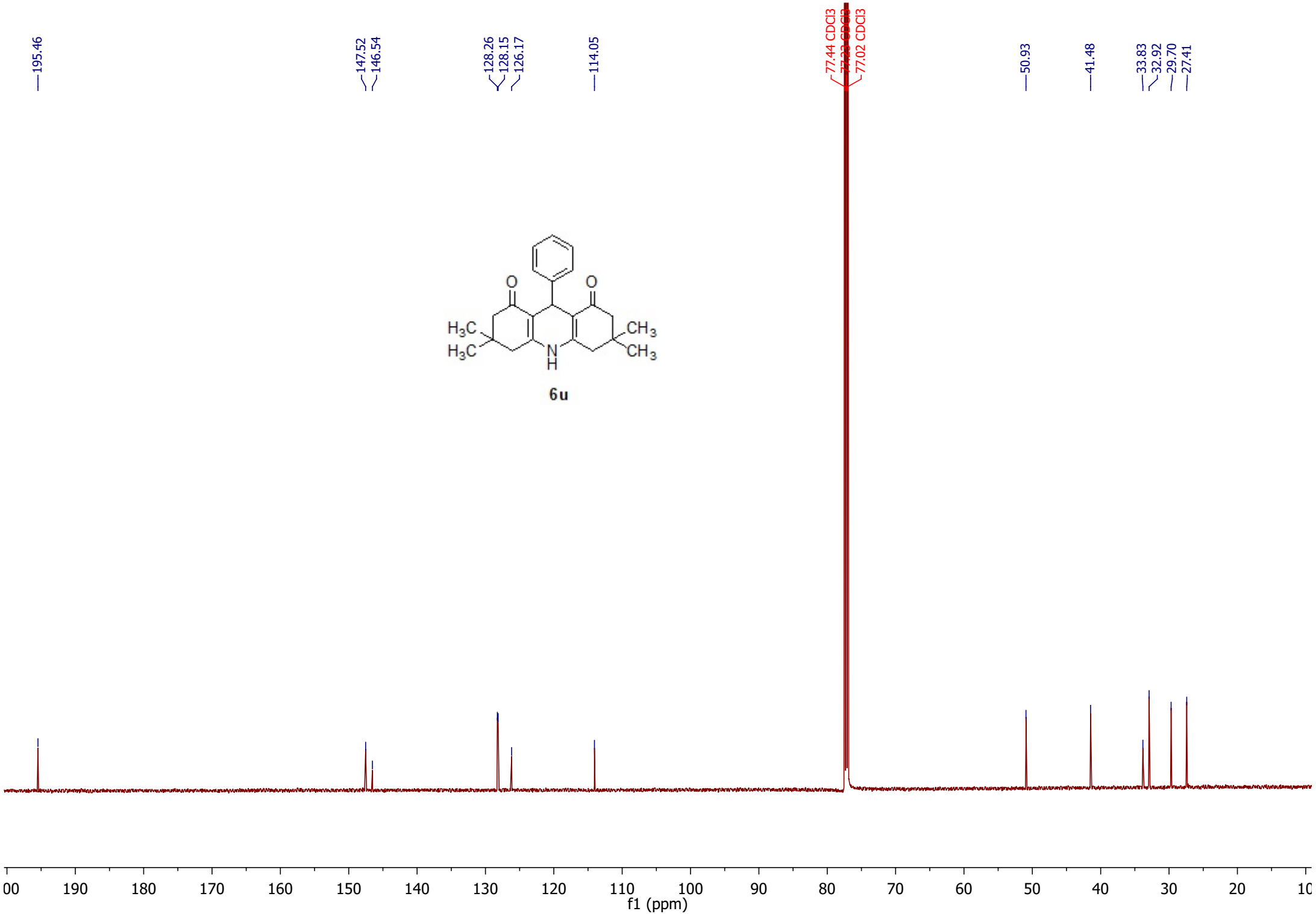
7.200
7.182
7.162
7.076
7.057
7.039
5.100
2.273
2.260
2.230
2.218
2.150
2.109
1.047
0.935
O
O
H3C
H3C
CH3
CH3
N
H
6u
0.96
2.03
2.11
1.04
1.04
8.30
5.84
6.05
f1 (ppm)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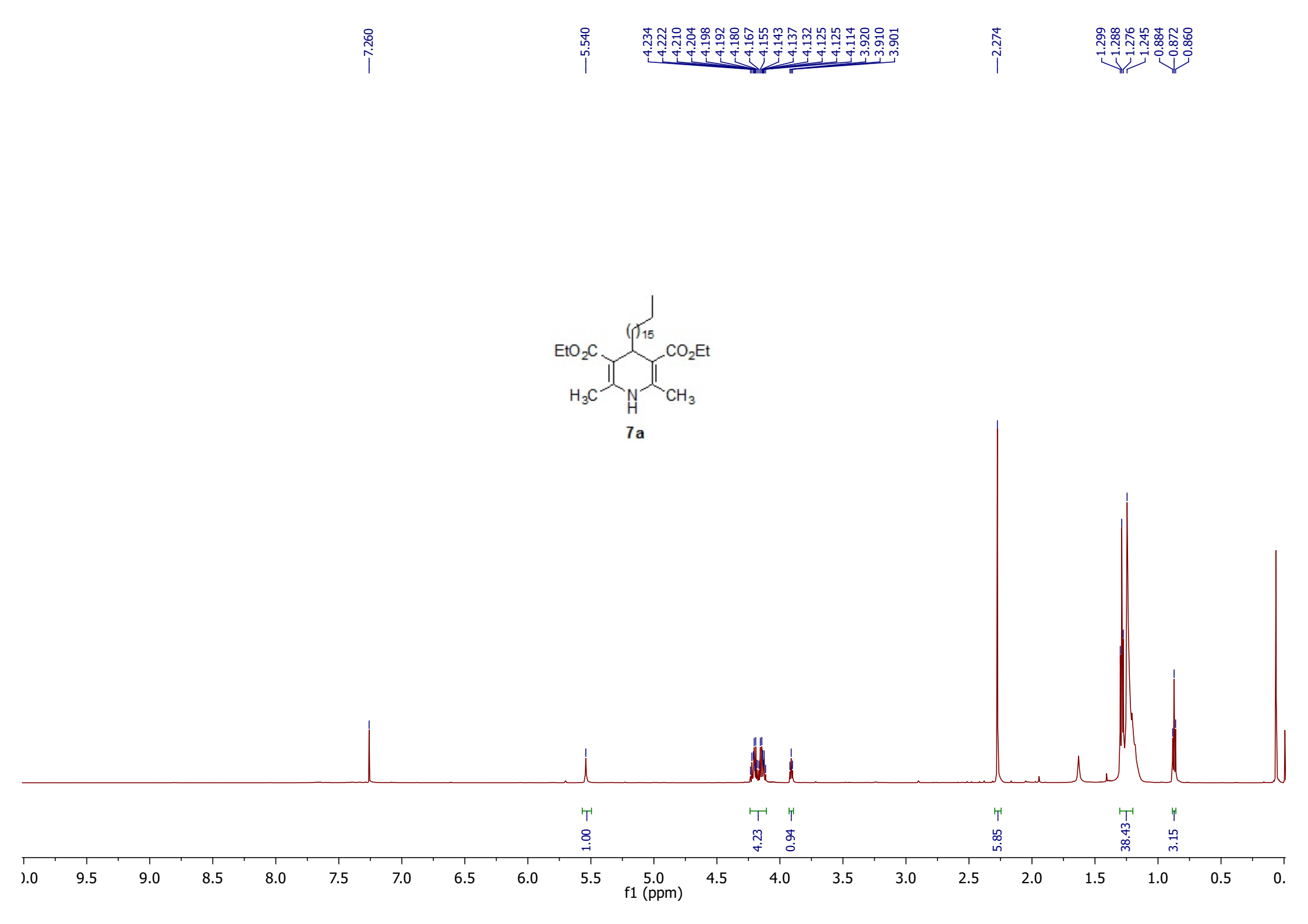
147.52
146.54
128.26
128.15
126.17
114.05
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
50.93
41.48
33.83
32.92
29.70
27.41
O
O
H3C
H3C
CH3
CH3
N
H
6u
f1 (ppm)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4.204
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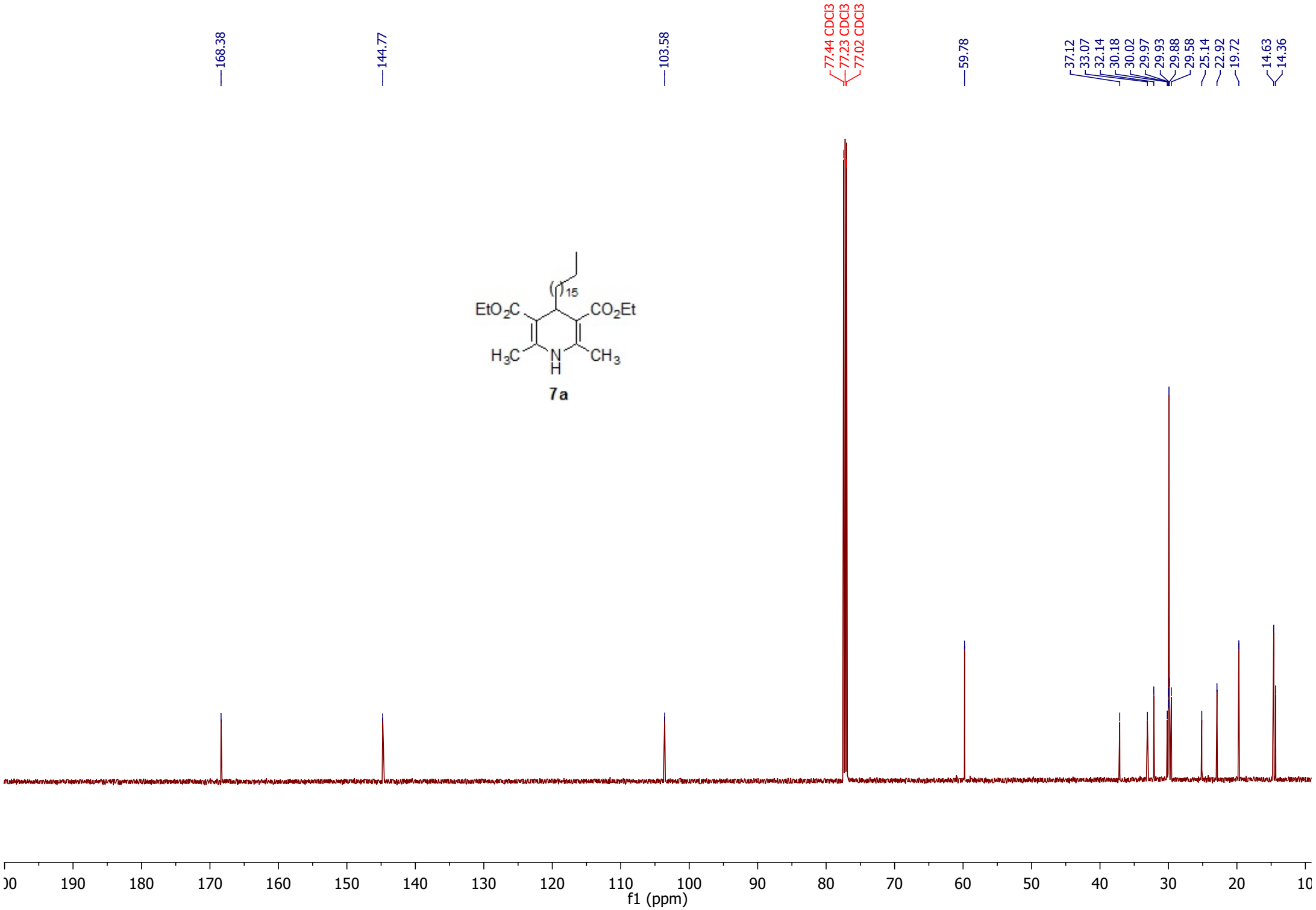
4.192
4.180
4.167
4.155
4.143
4.137
4.132
4.125
4.125
4.114
3.920
3.910
3.901
2.274
1.299
1.288
1.276
1.245
0.884
0.872
0.860
EtO2C
CO2Et
H3C
CH3
N
H
15
7a
1.00
4.23
0.94
5.85
38.43
3.15
f1 (ppm)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103.58
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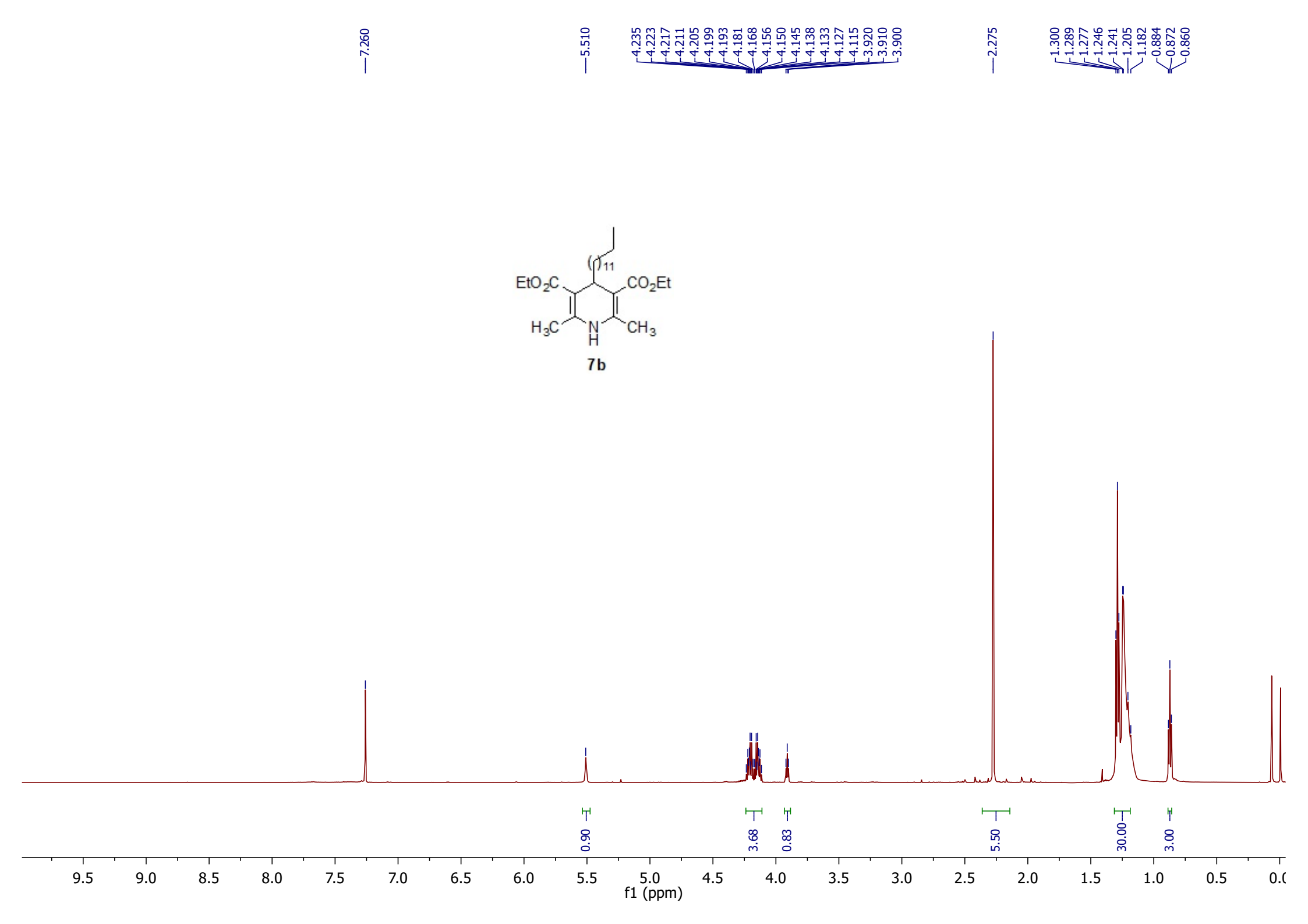
77.23 CDCl3
77.02 CDCl3
59.78
37.12
33.07
32.14
30.18
30.02
29.97
29.93
29.88
29.58
25.14
22.92
19.72
14.63
14.36
EtO2C
CO2Et
H3C
CH3
N
H
15
7a
f1 (ppm)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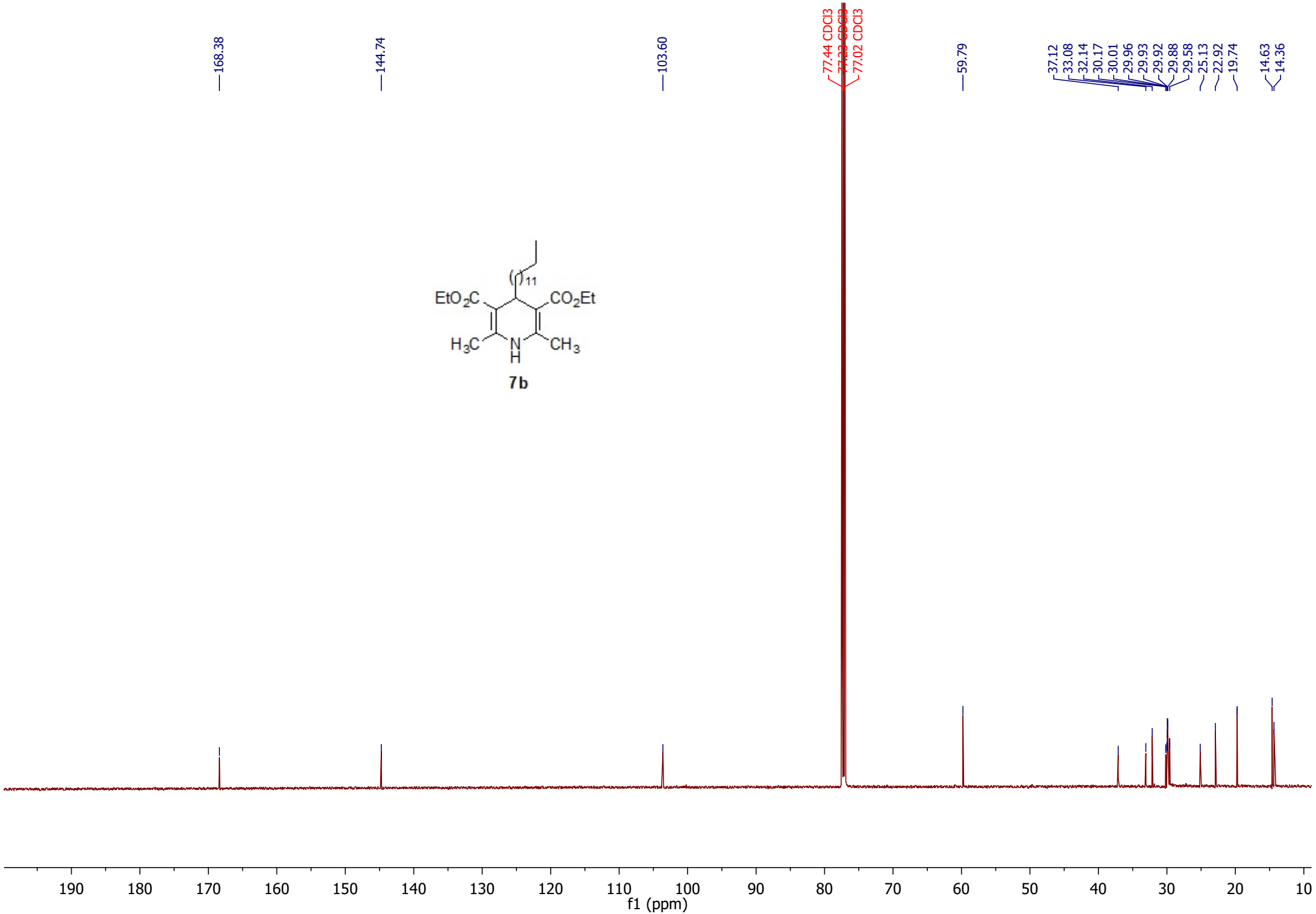
4.235
4.223
4.217
4.211
4.205
4.199
4.193
4.181
4.168
4.156
4.150
4.145
4.138
4.133
4.127
4.115
3.920
3.910
3.900
2.275
1.300
1.289
1.277
1.246
1.241
1.205
1.182
0.884
0.872
0.860
EtO2C
CO2Et
H3C
CH3
N
H
11
7b
0.90
3.68
0.83
5.50
30.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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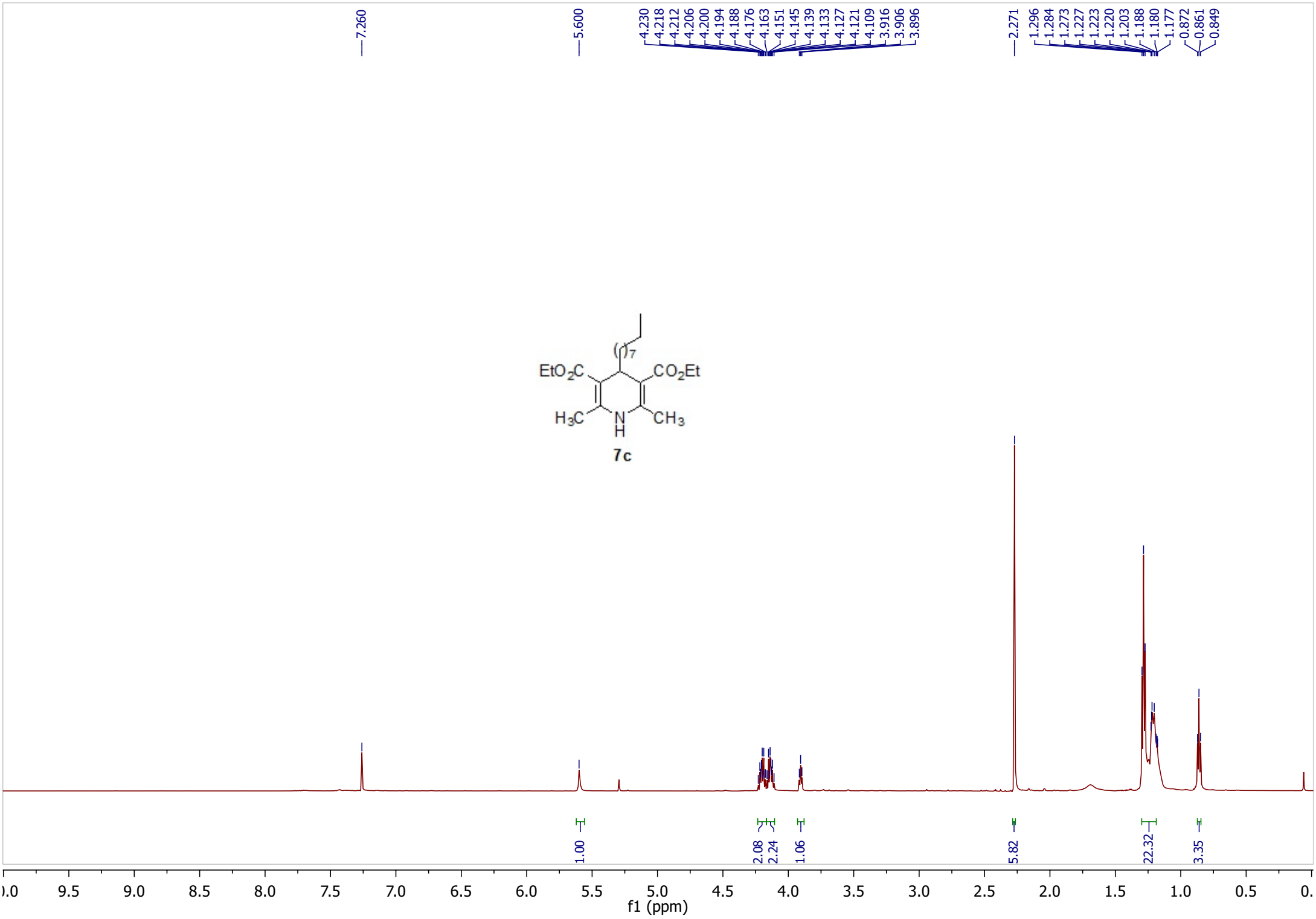
144.74
103.60
77.44 CDCl3
77.33 CDCl3
77.02 CDCl3
59.79
37.12
33.08
32.14
30.17
30.01
29.96
29.93
29.92
29.88
29.58
25.13
22.92
19.74
14.63
14.36
11
EtO2C
CO2Et
H3C
N
H
CH3
7b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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5.600
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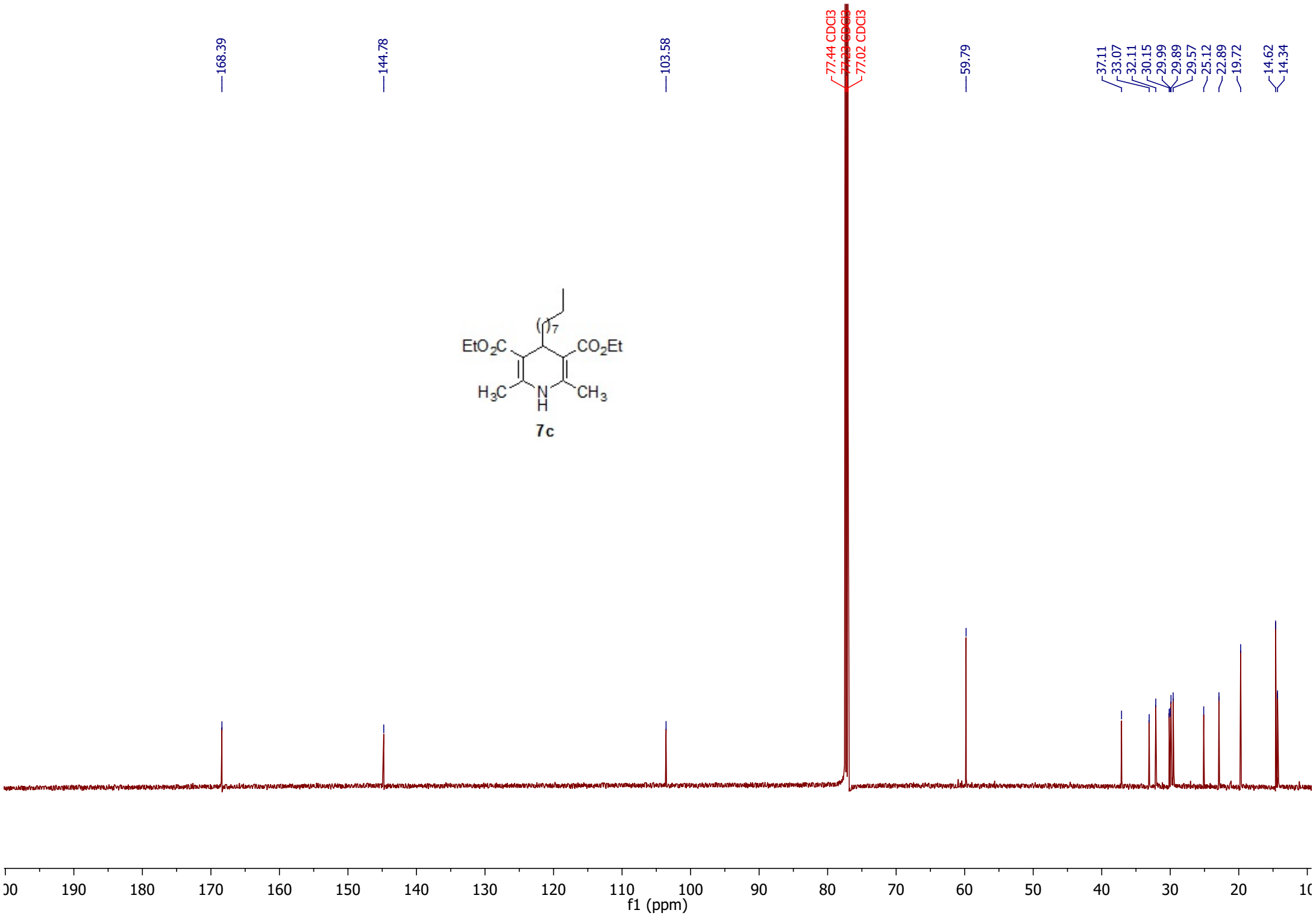
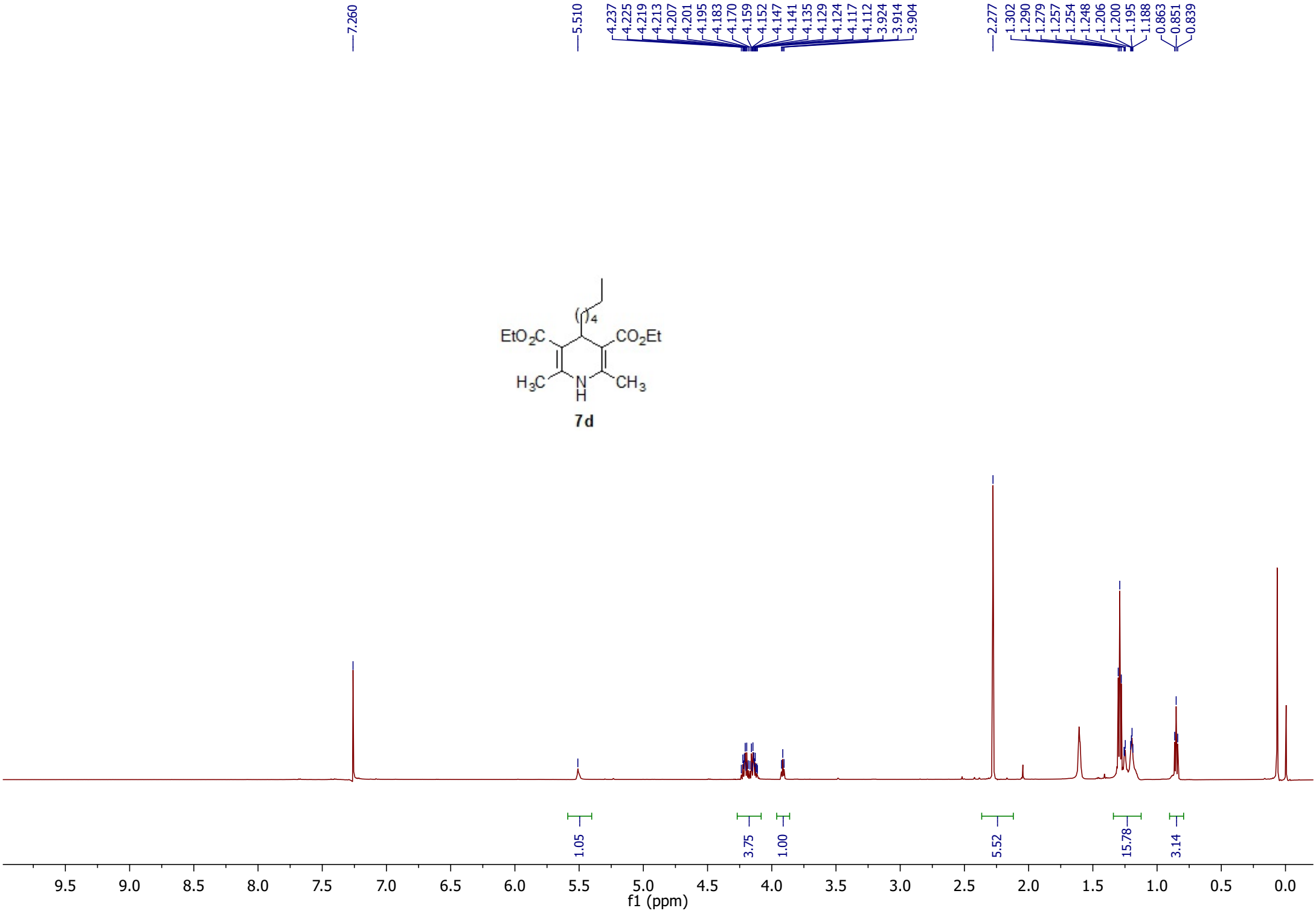
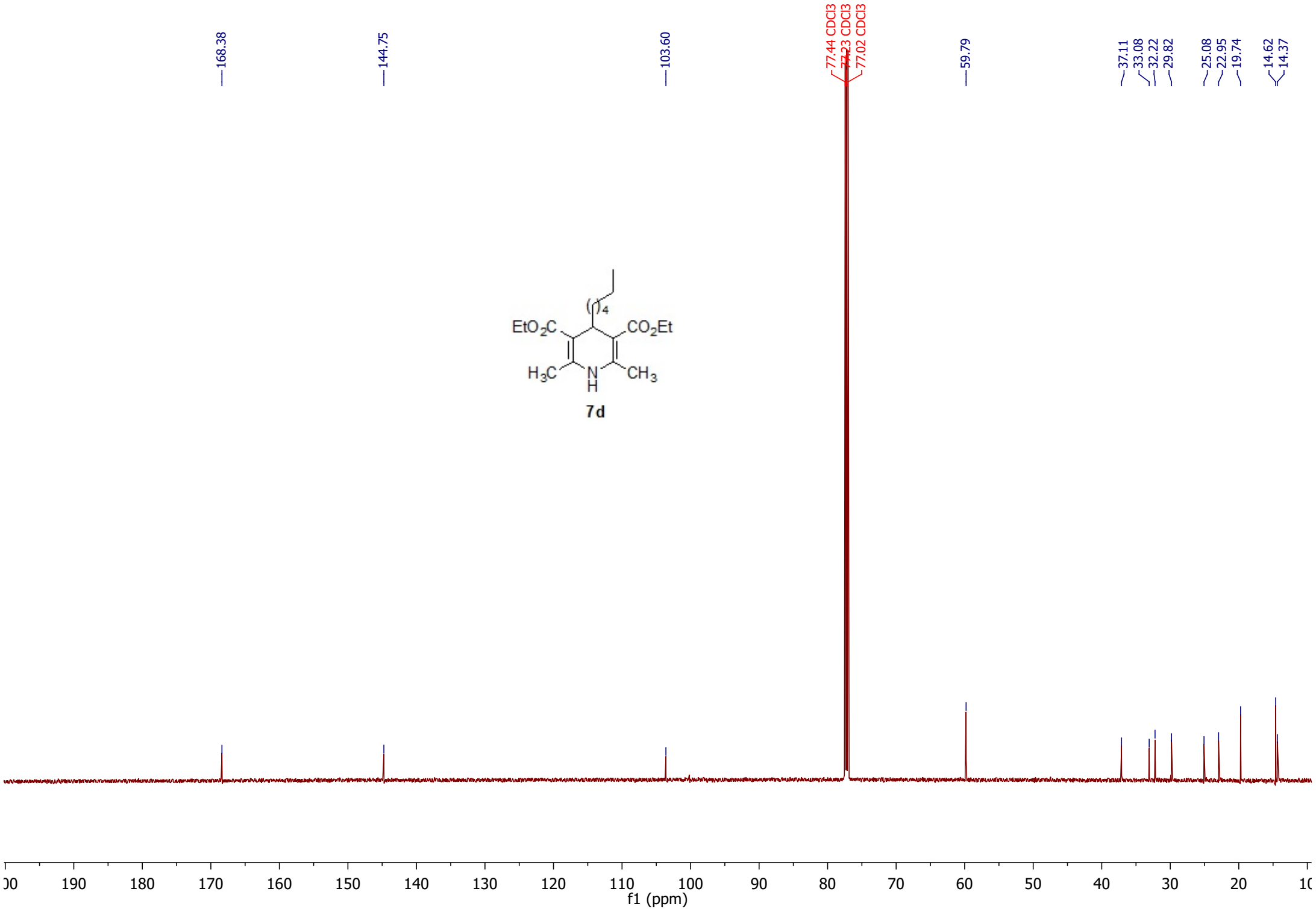
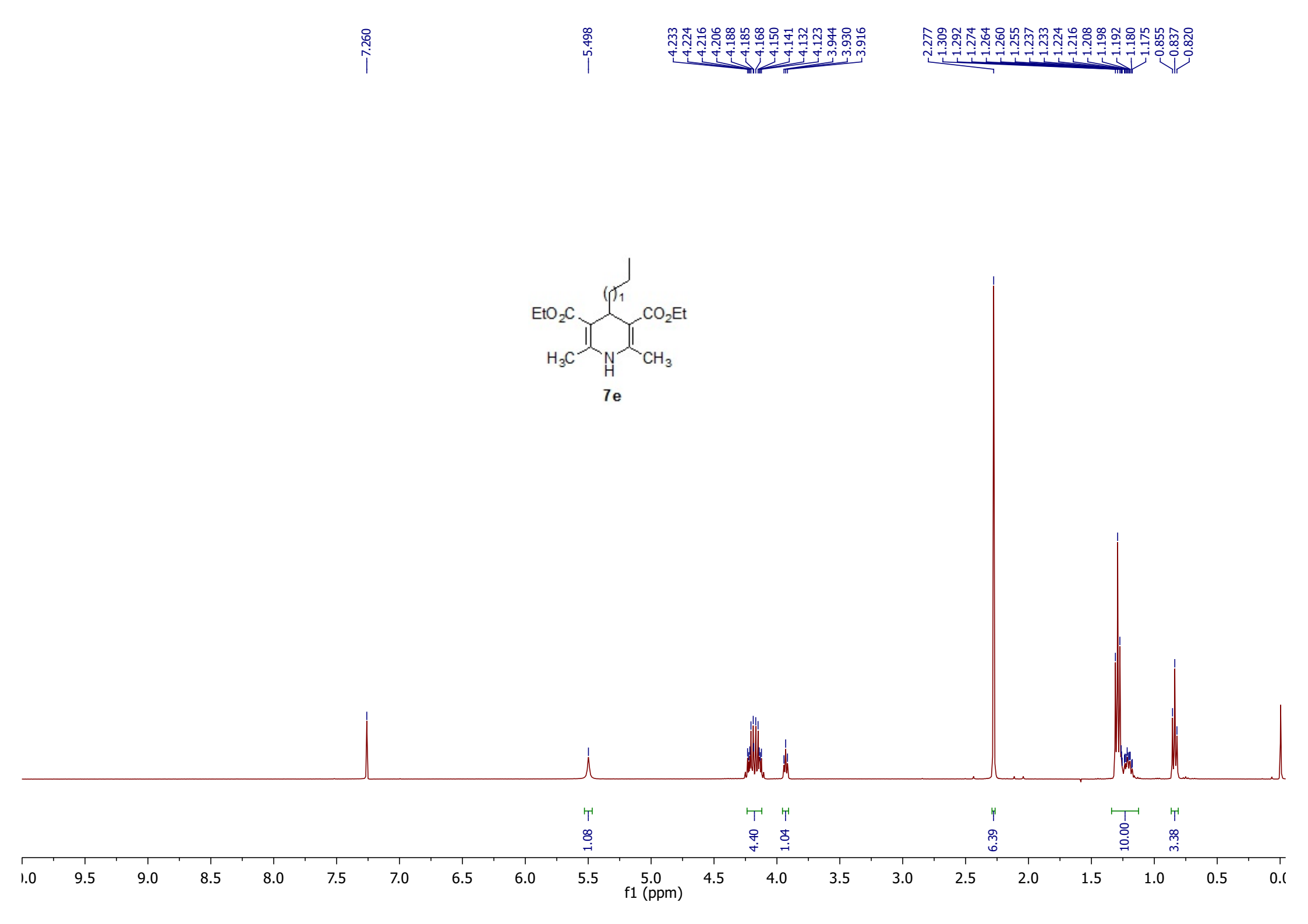
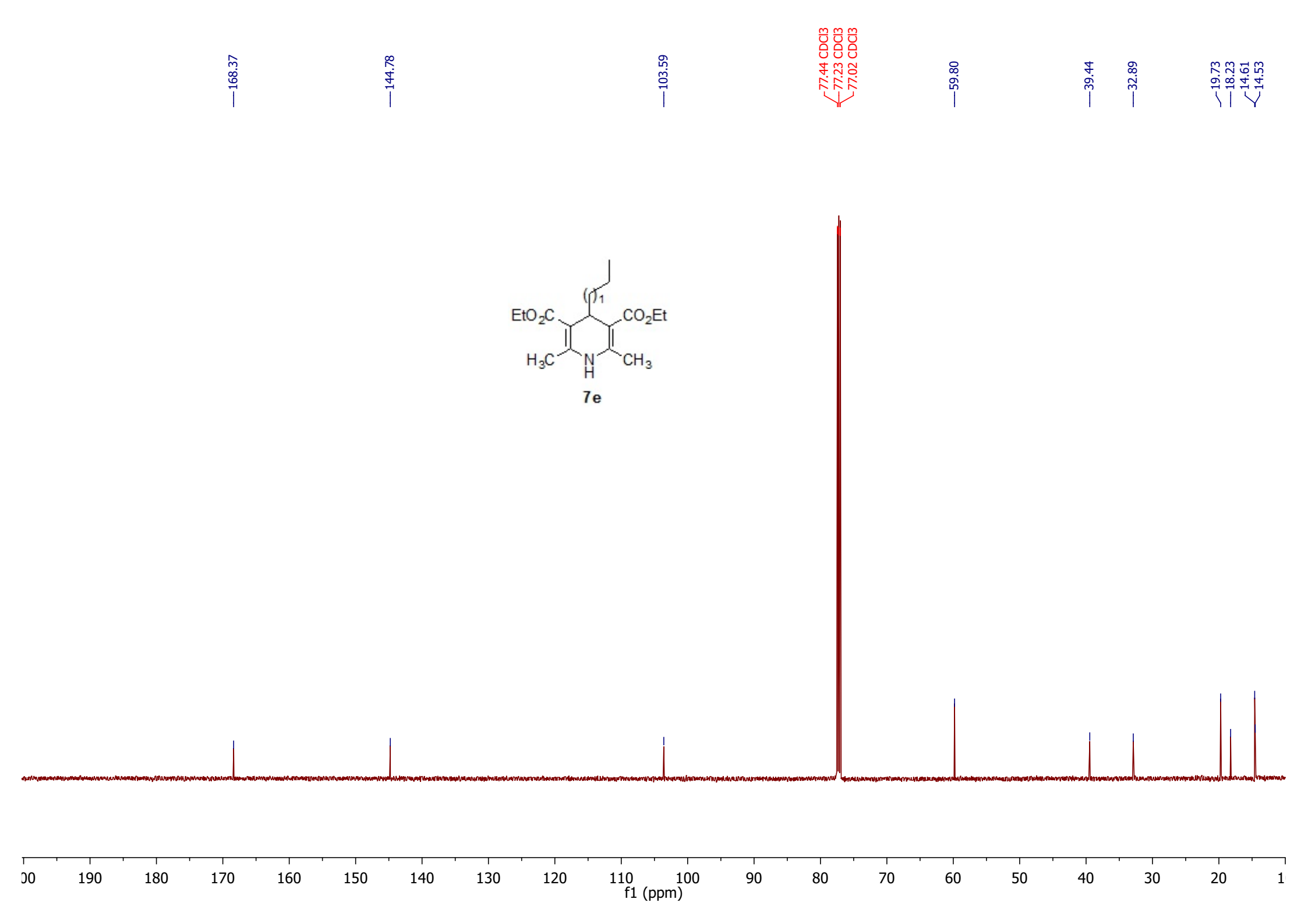
4.212
4.206
4.200
4.194
4.188
4.176
4.163
4.151
4.145
4.139
4.133
4.127
4.121
4.109
3.916
3.906
3.896
2.271
1.296
1.284
1.273
1.227
1.223
1.220
1.203
1.188
1.180
1.177
0.872
0.861
0.849
EtO2C
CO2Et
H3C
CH3
N
H
7
7c
1.00
2.08
2.24
1.06
5.82
22.32
3.35
f1 (ppm)

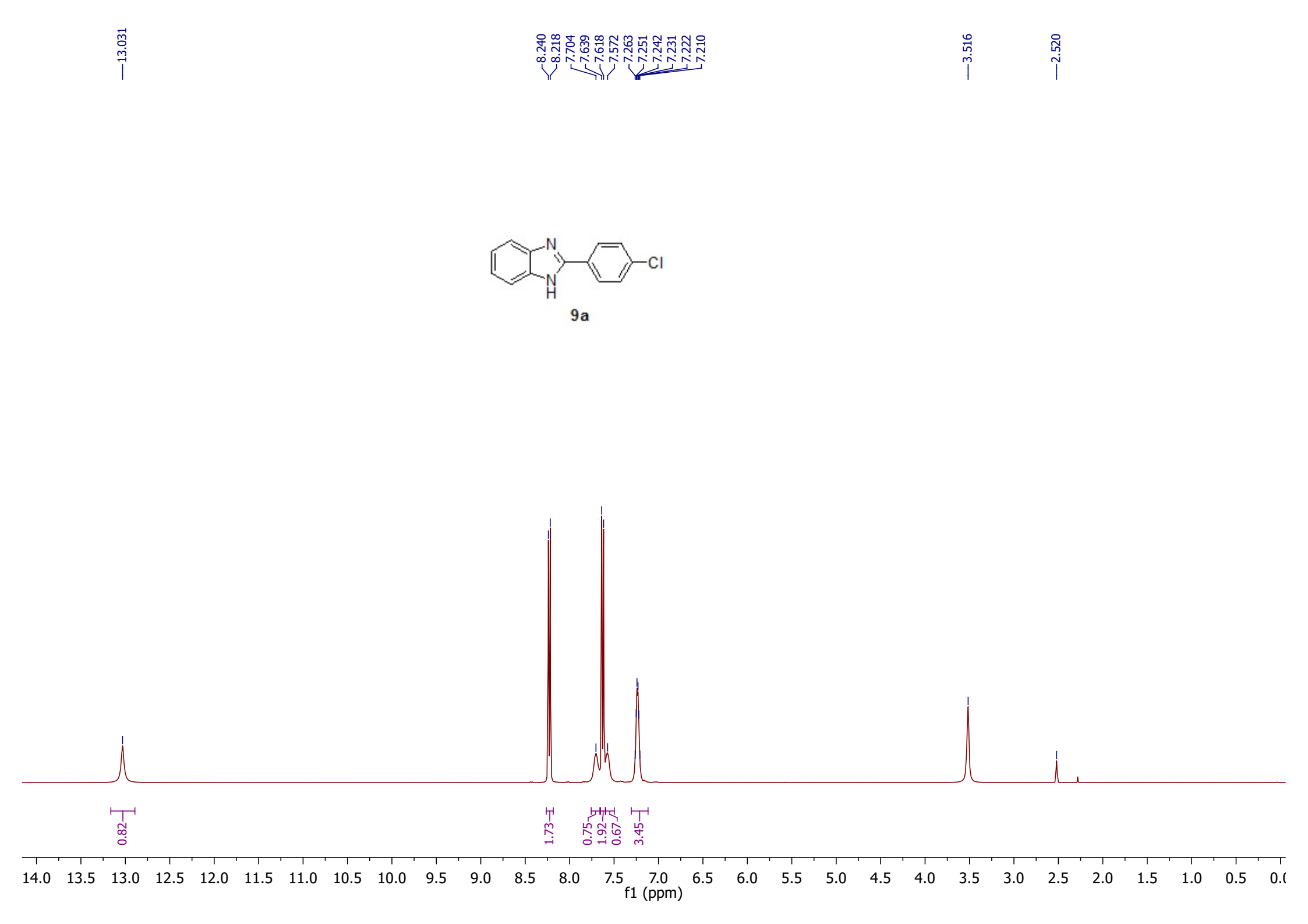

168.39
144.78
103.58
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.79
37.11
33.07
32.11
30.15
29.99
29.89
29.57
25.12
22.89
19.72
14.62
14.34
EtO2C
CO2Et
H3C
CH3
N
H
7
7c
f1 (ppm)

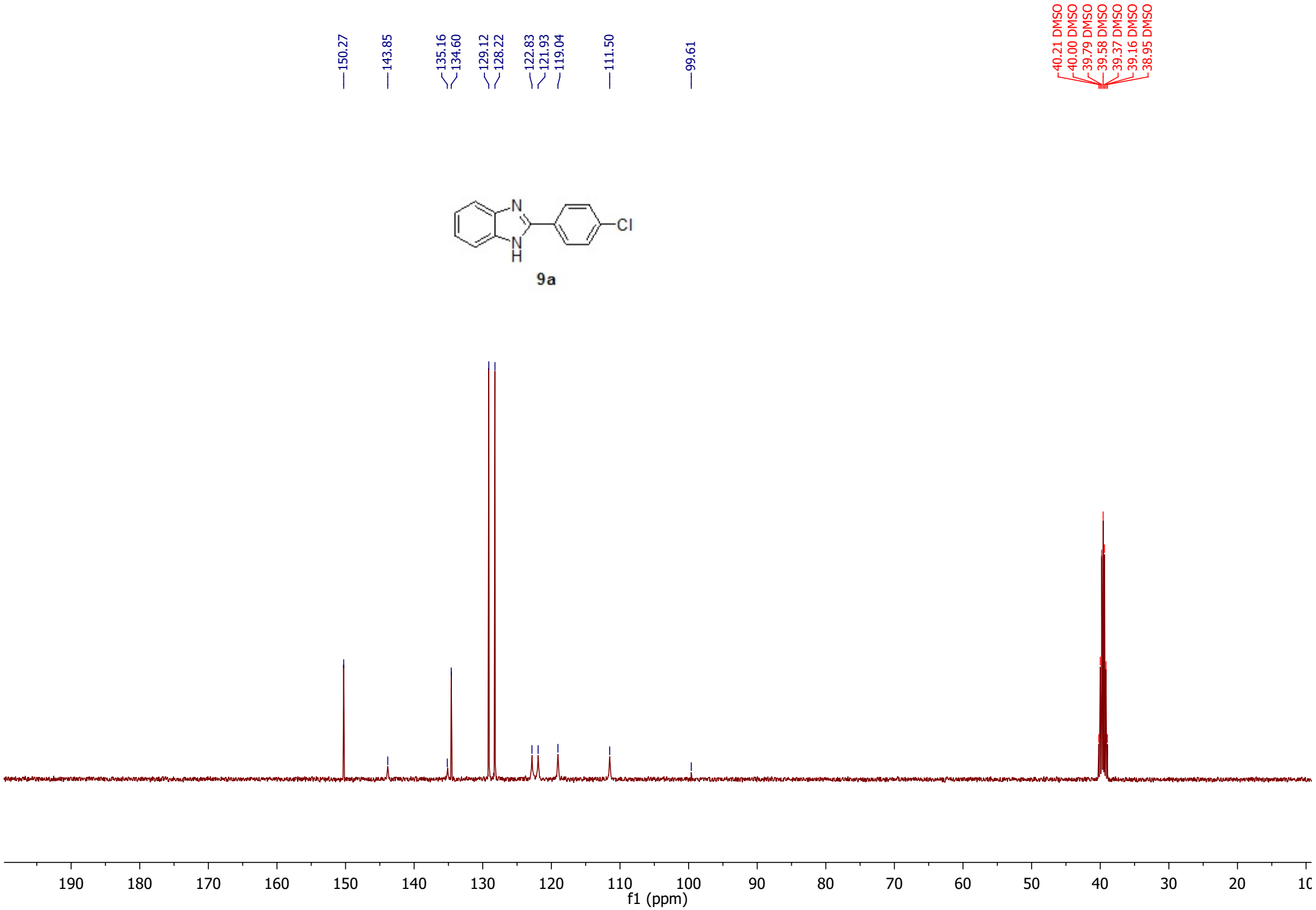

7.260
5.510
4.237
4.225
4.219
4.213
4.207
4.201
4.195
4.183
4.170
4.159
4.152
4.147
4.141
4.135
4.129
4.124
4.117
4.112
3.924
3.914
3.904
2.277
1.302
1.290
1.279
1.257
1.254
1.248
1.206
1.200
1.195
1.188
0.863
0.851
0.839
EtO2C
CO2Et
H3C
CH3
N
H
4
7d
1.05
3.75
1.00
5.52
15.78
3.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

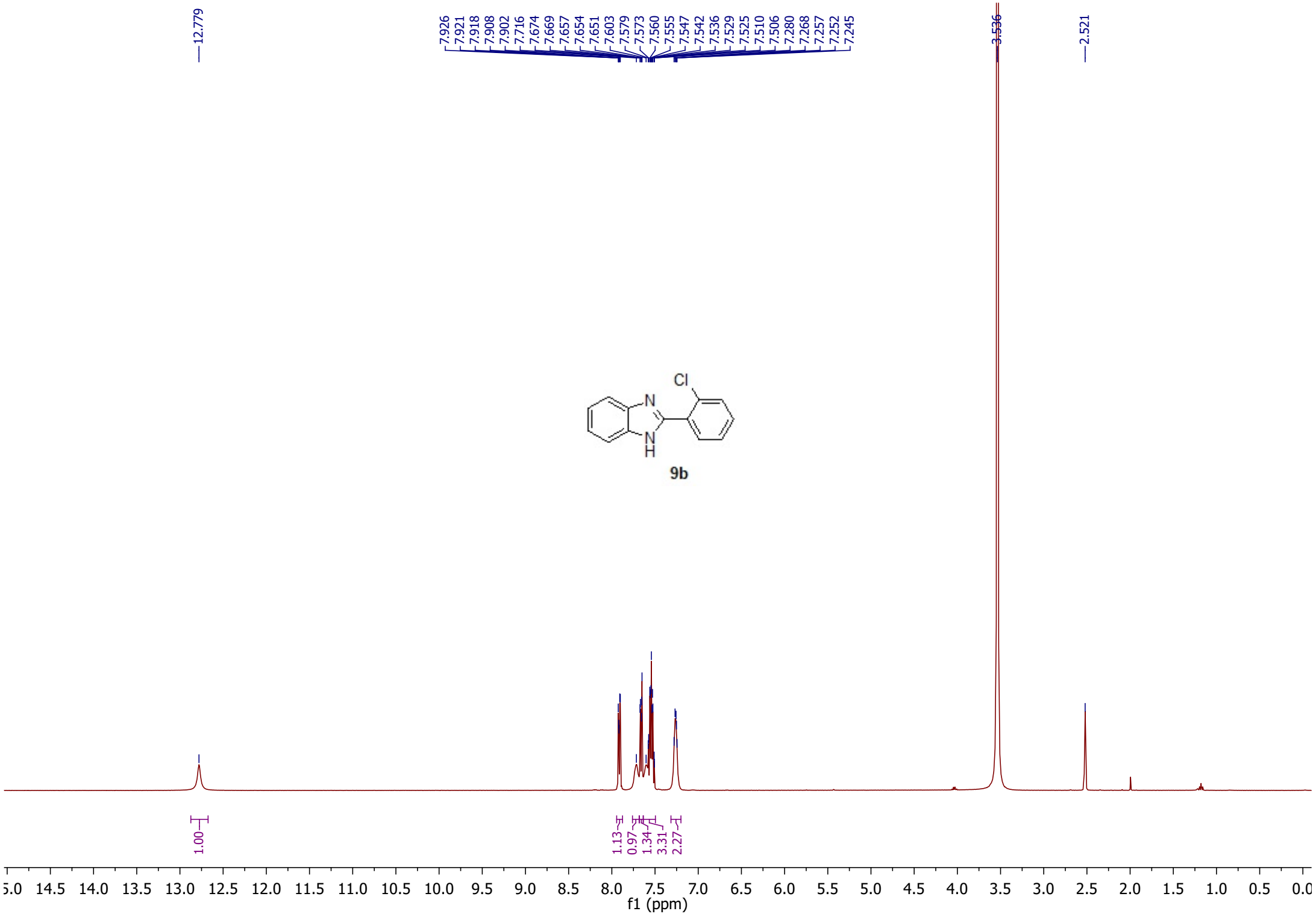

168.38
144.75
103.60
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.79
37.11
33.08
32.22
29.82
25.08
22.95
19.74
14.62
14.37
EtO2C
CO2Et
H3C
CH3
N
H
4
7d
f1 (ppm)

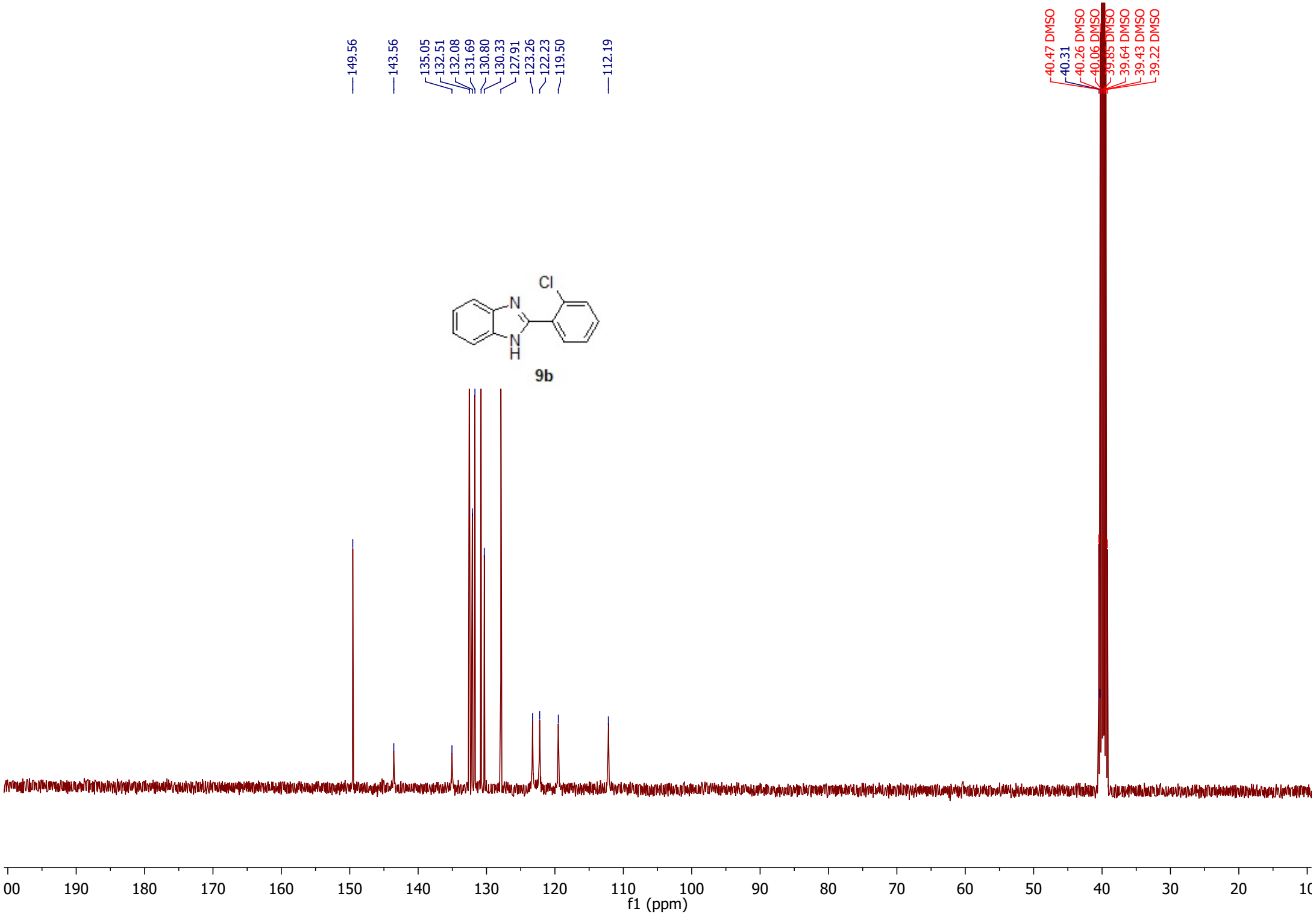

7.260
5.498
4.233
4.224
4.216
4.206
4.188
4.185
4.168
4.150
4.141
4.132
4.123
3.944
3.930
3.916
2.277
1.309
1.292
1.274
1.264
1.260
1.255
1.237
1.233
1.224
1.216
1.208
1.198
1.192
1.180
1.175
0.855
0.837
0.820
EtO2C
CO2Et
H3C
CH3
N
H
7e
1.08
4.40
1.04
6.39
10.00
3.38
f1 (ppm)

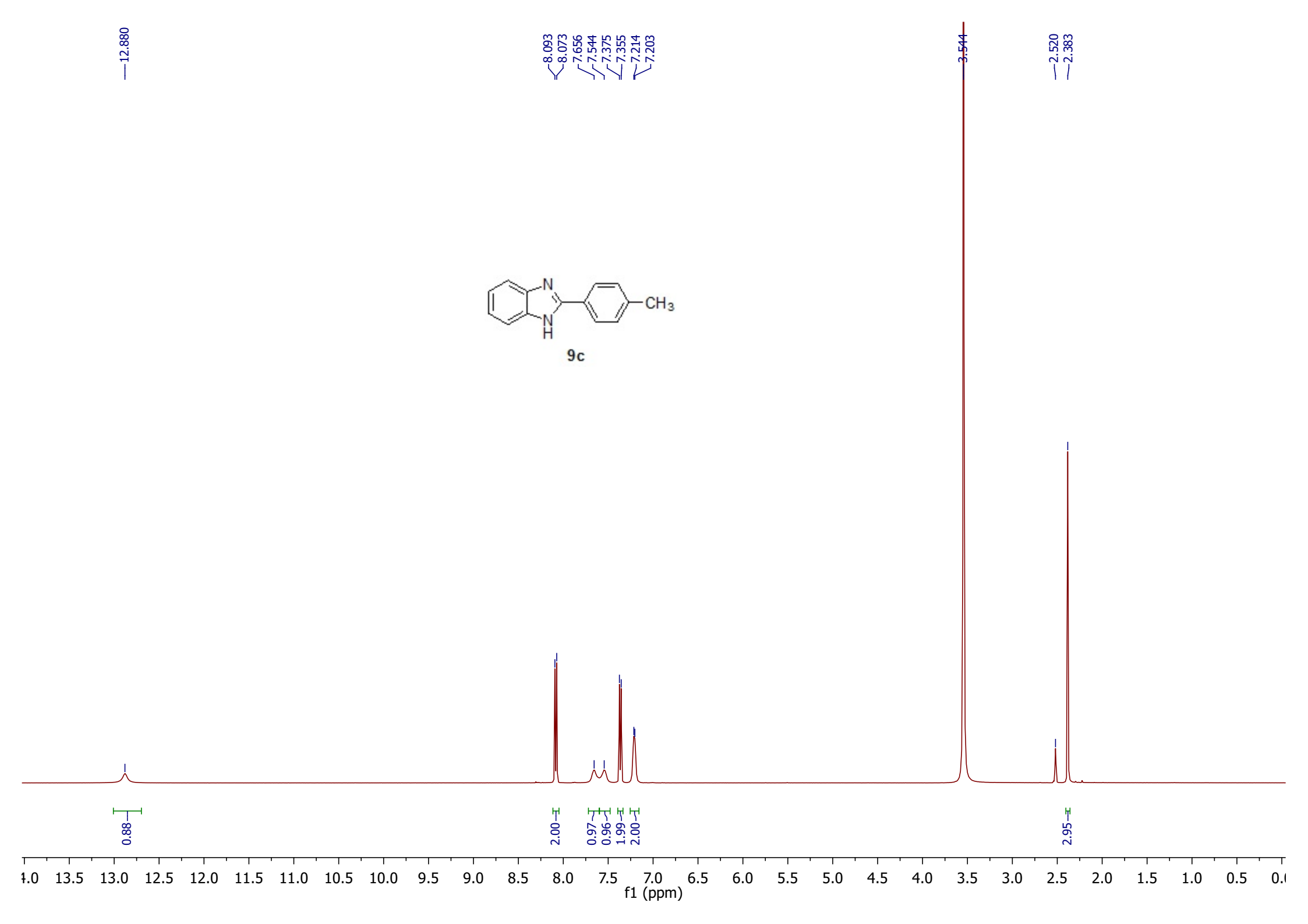

168.37
144.78
103.59
77.44 CDCl3
77.23 CDCl3
77.02 CDCl3
59.80
39.44
32.89
19.73
18.23
14.61
14.53
EtO2C
CO2Et
H3C
CH3
N
H
7e
f1 (ppm)

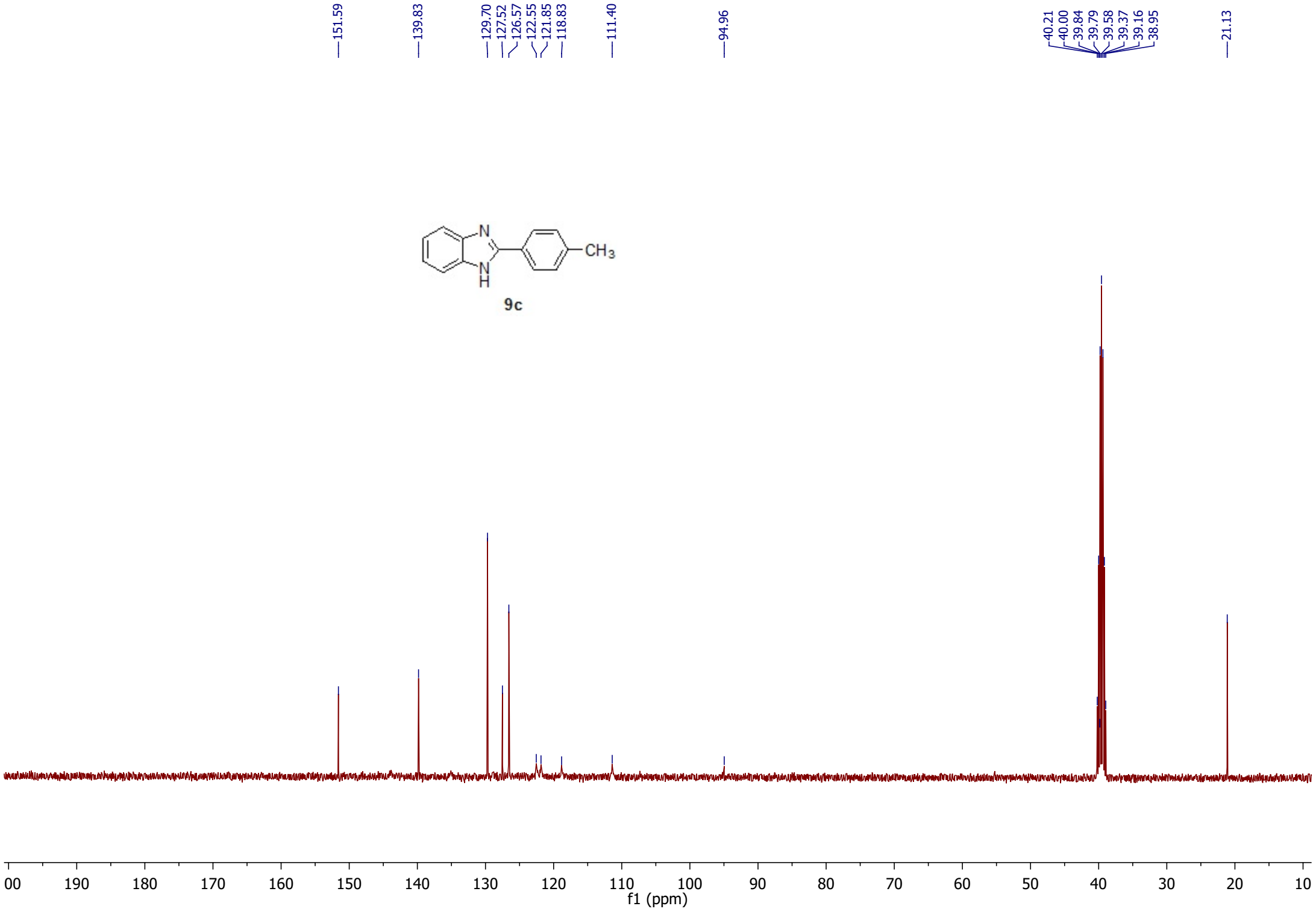

13.031
8.240
8.218
7.704
7.639
7.618
7.572
7.263
7.251
7.242
7.231
7.222
7.210
3.516
2.520
N
N
H
Cl
9a
0.82
1.73
0.75
1.92
0.67
3.45
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

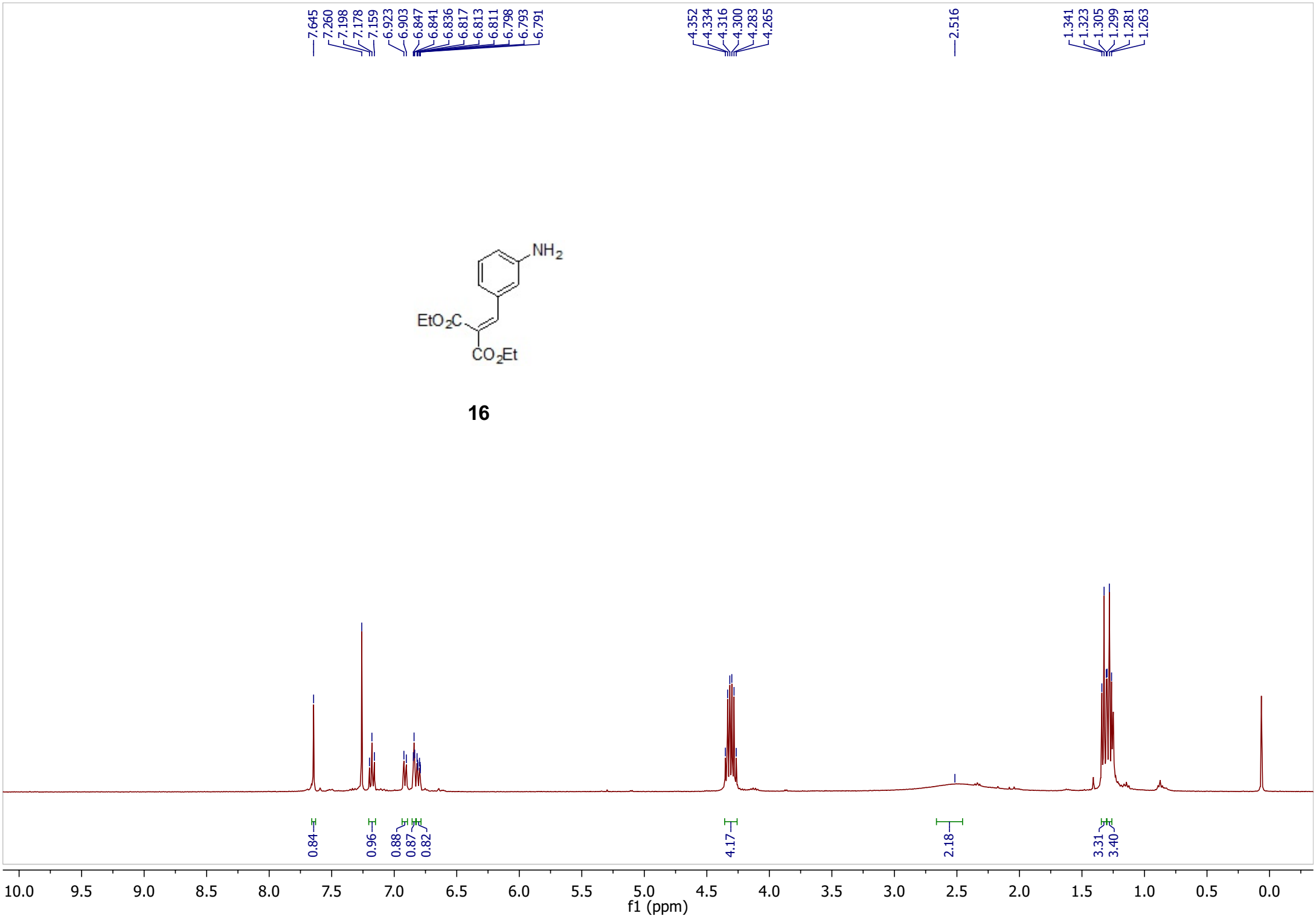

150.27
143.85
135.16
134.60
129.12
128.22
122.83
121.93
119.04
111.50
99.61
40.21 DMSO
40.00 DMSO
39.79 DMSO
39.58 DMSO
39.37 DMSO
39.16 DMSO
38.95 DMSO
N
N
H
Cl
9a
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


12.779
7.926
7.921
7.918
7.908
7.902
7.716
7.674
7.669
7.657
7.654
7.651
7.603
7.579
7.573
7.560
7.555
7.547
7.542
7.536
7.529
7.525
7.510
7.506
7.280
7.268
7.257
7.252
7.245
3.536
2.521
Cl
N
N
H
9b
1.00
1.13
0.97
1.34
3.31
2.27
f1 (ppm)

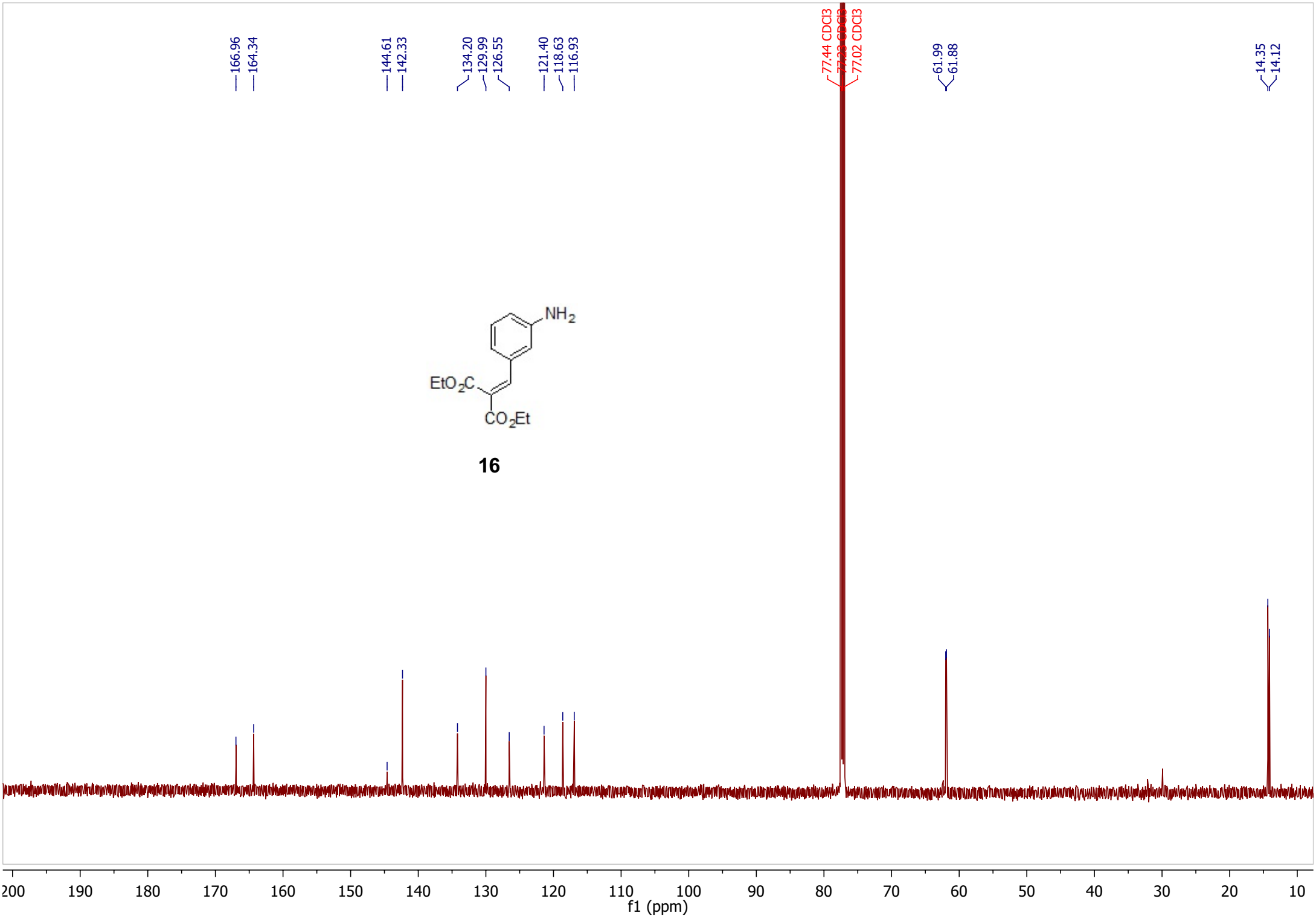

149.56
143.56
135.05
132.51
132.08
131.69
130.80
130.33
127.91
123.26
122.23
119.50
112.19
40.47 DMSO
40.31
40.26 DMSO
40.06 DMSO
39.85 DMSO
39.64 DMSO
39.43 DMSO
39.22 DMSO
Cl
N
N
H
9b
f1 (ppm)


12.880
8.093
8.073
7.656
7.544
7.375
7.355
7.214
7.203
3.544
2.520
2.383
N
N
H
CH3
9c
0.88
2.00
0.97
0.96
1.99
2.00
2.95
f1 (ppm)


151.59
139.83
129.70
127.52
126.57
122.55
121.85
118.83
111.40
94.96
40.21
40.00
39.84
39.79
39.58
39.37
39.16
38.95
21.13
N
N
H
CH3
9c
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.645
7.260
7.198
7.178
7.159
6.923
6.903
6.847
6.841
6.836
6.817
6.813
6.811
6.798
6.793
6.791
4.352
4.334
4.316
4.300
4.283
4.265
2.516
1.341
1.323
1.305
1.299
1.281
1.263
NH2
EtO2C
CO2Et
0.84
0.96
0.88
0.87
0.82
4.17
2.18
3.31
3.40
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)

16


166.96
164.34
144.61
142.33
134.20
129.99
126.55
121.40
118.63
116.93
77.44 CDCl3
77.02 CDCl3
61.99
61.88
14.35
14.12
NH2
EtO2C
CO2Et
16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)