Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

A mild and highly efficient laccase-mediator system for aerobic oxidation of alcohols

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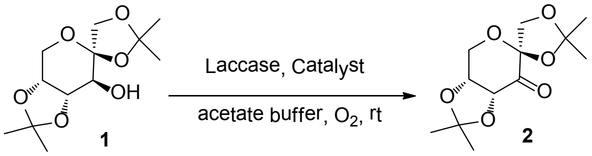
1. *General experimental remarks*

Laccase from *Trametes versicolor*, *Rhus vernicifera*, and *Agaricus bisporus* were purchased from Sigma-Aldrich as light brown lyophilized powder and used without modification. ABNO and Nor-AZADO were synthesized according to reported procedures.[1,2] Other reagents were ACS reagent grade and used without further purification. NMR spectra were recorded on a Bruker Ascend 400 MHz NMR spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR). Chemical shifts are reported in parts per million (ppm). ^{1}H and ^{13}C chemical shifts are referenced relative to the tetramethylsilane. GC-MS were recorded on a Thermo Trace DSQ GC-MS spectrometer using a TRB-5MS (30 m×0.25 mm×0.25 mm) column. ESI-MS were recorded on a Thermal Finnigan TSQ Quantum ultra AM spectrometer using a TRB-5MS (30 m×0.25 mm×0.25 mm) column. Melting points were determined in an open capillary tube with a Mel-temp II melting point apparatus. Infrared spectra were recorded as a KBr pellet on a Perkin-Elmer 1600 series FT-IR spectrophotometer.

2. *Optimization study* for the aerobic oxidation of 1.

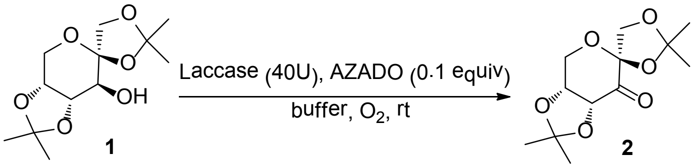
Table S1 The effect of different laccase and nitroxyl radicals.[a]



Entry	Laccase (U)	Nitroxyl radical (equiv)	Yield[b]
1	*Trametes versicolor* (40)	TEMPO (0.2)	< 10
2	*Trametes versicolor* (40)	AZADO (0.2)	63
3	--	AZADO (0.2)	--
4	*Trametes versicolor* (40)	--	--
5	*Trametes versicolor* (40, heat killed)	AZADO (0.2)	--
6	*Rhus vernicifera* (40)	AZADO (0.2)	56
7	*Agaricus bisporus* (40)	AZADO (0.2)	49
8	*Trametes versicolor* (30)	AZADO (0.2)	52
9	*Trametes versicolor*(50)	AZADO (0.2)	67
10	*Trametes versicolor*(40)	Nor-AZADO (0.2)	60
11	*Trametes versicolor*(40)	ABNO (0.2)	46

[a] Reaction conditions: **1** (1 mmol), laccase, nitroxyl radical, under O_2 atmosphere at room temperature for 12h unless otherwise noted. [b] NMR yields using 1,1,2,2-tetrachloroethane as an internal standard.

Table S2 The solvent effect.[a]



Entry	Buffer and PH	Co-solvent (mL)	Yield[b]
1	Acetate (0.2 mol/L, 5.0 mL), PH=5.0	--	58
2	Phosphate (0.2 mol/L, 5.0 mL), PH=5.0	--	49
3	Citrate (0.1 mol/L, 5.0 mL), PH=5.0	--	53
4	Acetate (0.2 mol/L, 5.0 mL), PH=5.5	--	55
5	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	--	63
6	Acetate (0.2 mol/L, 5.0 mL), PH=4.0	--	60
7	Acetate (0.2 mol/L, 5.0 mL), PH=3.5	--	57
8	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	Cyclohexane (1.0)	69
9	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	THF (1.0)	24
10	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	Hexane (1.0)	61
11	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	Dioxane (1.0)	68
12	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	Ethyl acetate (1.0)	36
13	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	Ph (1.0)	74
14	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	PhMe (1.0)	77
15	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	PhF (1.0)	76
16	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	$PhCF_3$ (1.0)	87
17	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	Hexafluorobenzene (1.0)	72
18	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	TFE (1.0)	23
19	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	HFIP (1.0)	39
20	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	$PhCF_3$ (1.5)	78
21	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	$PhCF_3$ (2.0)	75
22	Acetate (0.2 mol/L, 5.0 mL), PH=4.5	$PhCF_3$ (0.5)	82

[a] Reaction conditions: **1** (1 mmol), laccase (40U), AZADO (0.1 equiv), under O_2 atmosphere at room temperature for 12h unless otherwise noted. [b] NMR yields using 1,1,2,2-tetrachloroethane as an internal standard.

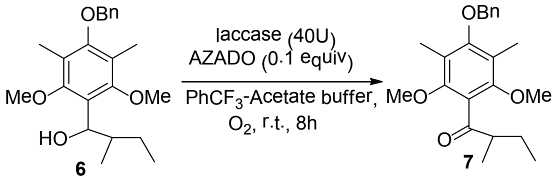
3. General procedure for the green oxidation of alcohols (Table 2)

To a stirred solution of alcohol (1 mmol), AZADO (0.1 mmol) in acetate buffer (0.2 M, pH 4.5, 5mL)-$PhCF_3$ (1 mL), laccase from *Trametes versicolor* (4 mg, 10U/mg) was added. The solution was stirred at room temperature under oxygen atmoshere (balloon) for several hours while checking the reaction progress by using gas or thin-layer chromatography. After completion, the mixture was extracted with diethyl ether (3×5 mL). The organic phase was concentrated under vacuum and the crude product was purified by column chromatography (hexane:EtOAc = 10:1) to provide the analytically pure product, which was characterized by using NMR and MS. The oxidation of alcohols with laccase-TEMPO system was using a similar procedure except for using 30mol% TEMPO as catalyst.

4. Kinetic isotope effect studies

α-monodeutero-*p*-methylbenzyl alcohol was synthesized according to reported literature[3,4] and used as the substrate (2 mmol) in the above procedure. After completion (monitored with GC after 12h), the reaction mixture was quenched with MTBE and dried over Na_2SO_4. The organic phase was concentrated under vacuum, and the crude product (both labelled and unlabelled aldehydes) were isolated and purified by column chromatography (hexane:EtOAc = 10:1). The k_H/k_D value was determined by ^{1}H NMR by measuring the intensity of the α-proton.

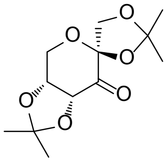
5. Preparation of 1-(4-(benzyloxy)-2,6-dimethoxy-3,5-dimethylphenyl)-2-methylbutan-1-one 7 using laccase-AZADO system



1-(4-(benzyloxy)-2,6-dimethoxy-3,5-dimethylphenyl)-2-methylbutan-1-ol **6** was synthesized according to reported literature[5] and used as the substrate (1 mmol) in the above procedure. The reaction mixture was stirred for 8h at room temperature. After completion, the mixture was extracted with EtOAc (2×10 mL). The organic phase was concentrated under vacuum and the crude product was purified by column chromatography (hexane:EtOAc = 10:1) to provide the ketone **7**, isolated as yellow oil (76%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34-7.47 (m, 5H), 4.80 (s, 2H), 3.72 (s, 6H), 2.83-2.95 (m, 1H), 2.21 (s, 6H), 1.73-1.87 (m, 1H), 1.16-1.47 (m, 4H), 0.95 (t, *J* = 10 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 208.52, 157.15, 153.37, 136.84, 128.08, 127.41, 127.01, 126.93, 120.38, 74.07, 62.02, 48.88, 24.76, 14.79, 11.23, 9.18.

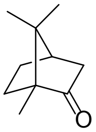
6. *Spectral data of products*

1,2:4,5-di-*O*-isopropylidene-β-D-*erythro*-2,3-hexadiulo-2,6-pyranose(Shi Epoxidation Catalyst).



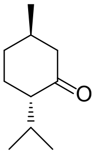
Reaction of 1,2:4,5-di-*O*-isopropylidene-*β*-D-fructopyranose (1 mmol) according to the general procedure afforded 220 mg (85%) of product using laccase-AZADO system, isolated as white solid, mp 102-104 °C (lit.[6] mp 101-103 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 4.72 (d, *J* = 5.6 Hz, 1H), 4.60 (d, *J* = 9.5 Hz, 1H), 4.54 (dd, *J* = 5.6, 1.3 Hz, 1H), 4.38 (dd, *J* = 13.5, 2.2 Hz, 1H), 4.11 (d, *J* = 13.5 Hz, 1H), 3.98 (d, *J* = 9.5 Hz, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.39 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.94, 112.81, 109.64, 103.13, 76.92, 74.88, 69.01, 59.09, 26.14, 25.51, 25.05, 25.00.

D(+)-Camphor.



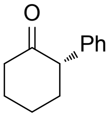
Reaction of (+)-borneol (1 mmol) according to the general procedure afforded 140 mg (92%) of product using laccase-AZADO system and 93 mg (61%) of product using laccase-TEMPO system, isolated as white solid, mp 178-179 °C (lit.[7] mp 177-178 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.29-2.35 (m, 1H), 2.06 (t, *J* = 4.5 Hz, 1H), 1.89-1.96 (m, 1H), 1.79-1.84 (m, 1H), 1.62-1.69 (m, 1H), 1.28-1.41 (m, 2H), 0.93 (s, 3H), 0.88 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 219.42, 57.64, 46.73, 43.26, 43.06, 29.91, 27.03, 19.73, 19.10, 9.19.

(-)-Menthone.



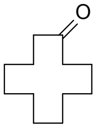
Reaction of (-)-menthol (1.0 mmol) according to the general procedure afforded 130 mg (84%) of product using laccase-AZADO system, isolated as colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (ddd, *J* = 12.9, 3.9, 2.2 Hz, 1H), 1.82-2.12 (m, 6H), 1.29-1.38 (m, 2H), 0.98 (d, *J* = 6.3 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.37, 55.92, 50.89, 35.49, 33.96, 27.90, 25.94, 22.30, 21.22, 18.72.

(S)-2-Phenylcyclohexanone.



Reaction of (*1R, 2S*)-*trans*-2-phenyl-1-cyclohexanol (1.0 mmol) according to the general procedure afforded 156 mg (90%) of product using laccase-AZADO system and 40 mg (23%) of product using laccase-TEMPO system, isolated as colorless crystal, mp 58-60 °C (lit.[8] mp 56-59 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.29 (m, 2H), 7.28-7.22 (m, 1H), 7.14 (dd, *J* = 5.2, 3.3 Hz, 2H), 3.60 (dd, *J* = 12.2, 5.4 Hz, 1H), 2.61-2.36 (m, 2H), 2.35-2.20 (m, 1H), 2.20-1.91 (m, 3H), 1.91-1.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.40, 138.75, 128.53, 128.34, 126.88, 57.37, 42.17, 35.08, 27.81, 25.30.

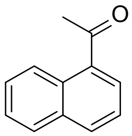
Cyclododecanone.



Reaction of cyclododecanol (1.0 mmol) according to the general procedure afforded 131 mg (72%) of product using laccase-AZADO system and 64 mg (35%) of product using laccase-TEMPO system, isolated as a colorless crystal; mp 59-61 °C (lit.[8] mp 59-61 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44-2.47 (m, 4H), 1.69-1.72 (m, 4H), 1.24-1.31(m, 14H);

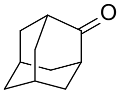
^{13}C NMR (100 MHz, CDCl$_3$): δ 212.88, 40.41, 24.79, 24.65, 24.27, 22.59, 22.40.

1-Acetonaphthone



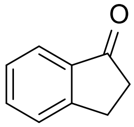
Reaction of (*S*)-(-)-α-methyl-1-naphthalenemethanol (1 mmol) according to the general procedure afforded 157 mg (92%) of product using laccase-AZADO system and 124 mg (73%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.77 (d, *J* = 8.8 Hz, 1H), 7.92-7.99 (m, 3H), 7.47-7.88 (m, 3H), 2.74 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 201.82, 135.47, 134.01, 133.04, 130.18, 128.70, 128.44, 128.07, 126.46, 126.05, 124.36, 29.98.

2-Adamantanone.



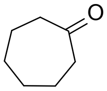
Reaction of 2-adamantanol (1 mmol) according to the general procedure afforded 135 mg (90%) of product using laccase-AZADO system and 101 mg (67%) of product using laccase-TEMPO system, isolated as white solid, mp 256-258 °C (lit.[9] mp 256-259 °C); ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.52 (s, 2H), 1.91-2.08 (m, 12H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 217.39, 45.98, 38.26, 35.30, 26.46.

1-Indanone.



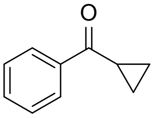
Reaction of 2,3-dihydro-1*H*-inden-1-ol (1 mmol) according to the general procedure afforded 116 mg (88%) of product using laccase-AZADO system and 86 mg (65%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.67 (d, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.28 (s, 1H), 3.04-3.07 (m, 2H), 2.58-2.61 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 207.00, 155.15, 137.09, 134.58, 127.27, 126.70, 123.69, 36.21, 25.80.

Cycloheptanone.



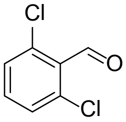
Reaction of cycloheptanol (1.0 mmol) according to the general procedure afforded 85 mg (76%) of product using laccase-AZADO system and 53 mg (47%) of product using laccase-TEMPO system, isolated as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43-2.46 (m, 4H), 1.61-1.69 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.26, 43.84, 30.39, 24.32.

Cyclopropyl phenyl ketone.



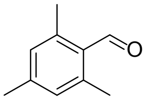
Reaction of α-cyclopropylbenzyl alcohol (1.0 mmol) according to the general procedure afforded 136 mg (93%) of product using laccase-AZADO system and 124 mg (85%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (dd, J = 5.2, 3.3 Hz, 2H), 7.54 -7.58 (m, 1H), 7.47 (t, J = 7.5 Hz, 2H), 2.68 (tt, J = 7.9, 4.6 Hz, 1H), 1.23-1.26 (m, 2H), 1.04 (dq, J = 7.2, 3.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.63, 137.01, 131.69, 127.47, 126.98, 16.12, 10.59.

2,6-Dichlorobenzaldehyde.



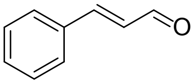
Reaction of 2,6-dichlorobenzyl alcohol (1.0 mmol) according to the general procedure afforded 136 mg (78%) of product using laccase-AZADO system and 42 mg (24%) of product using laccase-TEMPO system, isolated as yellow solid, mp 68-70 °C (lit.[10] mp 69-71 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.49 (s, 1H), 7.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.01, 135.75, 132.66, 129.46, 128.74.

Mesitaldehyde.



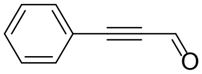
Reaction of mesitylmethanol (1.0 mmol) according to the general procedure afforded 122 mg (82%) of product using laccase-AZADO system and 67 mg (45%) of product using laccase-TEMPO system, isolated as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.47 (s, 1H), 6.80 (s, 2H), 2.49 (s, 6H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.96, 143.81, 141.47, 130.52, 130.00, 21.44, 20.46.

Cinnamaldehyde.



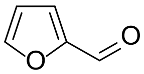
Reaction of cinnamyl alcohol (1.0 mmol) according to the general procedure afforded 122 mg (92%) of product using laccase-AZADO system and 118 mg (90%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 (d, J = 7.7 Hz, 1H), 7.42-7.55 (m, 6H), 6.72 (dd, J = 16.0, 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.64, 151.72, 133.01, 130.25, 128.09, 127.60, 127.47.

Phenylpropargyl aldehyde.



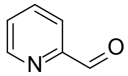
Reaction of 3-phenyl-2-propyn-1-ol (1.0 mmol) according to the general procedure afforded 103 mg (79%) of product using laccase-AZADO system and 92 mg (71%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43 (s, 1H), 7.26-7.62 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.76, 133.40, 131.45, 128.89, 119.71, 95.09, 88.61.

Furfural.



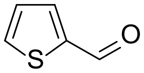
Reaction of furfuryl alcohol (1.0 mmol) according to the general procedure afforded 88 mg (92%) of product using laccase-AZADO system and 81 mg (85%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.68 (s, 1H), 7.24 (d, J = 3.6 Hz, 1H), 6.59 (dd, J = 3.6, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.90, 153.04, 148.09, 120.96, 112.60.

2-Pyridinecarboxaldehyde.



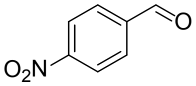
Reaction of 2-pyridinemethanol (1.0 mmol) according to the general procedure afforded 92 mg (86%) of product using laccase-AZADO system and 85 mg (80%) of product using laccase-TEMPO system, isolated as yellow yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.01 (d, *J* = 0.7 Hz, 1H), 8.72-8.74 (m, 1H), 7.84-7.91 (m, 1H), 7.80-7.82 (m, 1H), 7.45-7.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.38, 151.81, 149.20, 136.05, 126.85, 120.67.

2-Thiophenecarboxaldehyde.



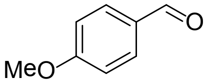
Reaction of 2-thiophenemethanol (1.0 mmol) according to the general procedure afforded 105 mg (94%) of product using laccase-AZADO system and 97 mg (87%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.73-7.77 (m, 2H), 7.18-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.00, 144.04, 136.36, 135.12, 128.35.

***p*-Nitrobenzaldehyde.**



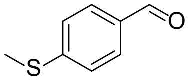
Reaction of *p*-nitrobenzyl alcohol (1.0 mmol) according to the general procedure afforded 141 mg (93%) of product using laccase-AZADO system and 136 mg (90%) of product using laccase-TEMPO system, isolated as yellow solid, mp 106-107 °C (lit.[11] mp 106-108 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (s, 1H), 8.39 (d, *J* = 8.7 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.24, 150.15, 139.06, 129.47, 123.30.

***p*-Anisaldehyde.**



Reaction of *p*-methoxylbenzyl alcohol (1.0 mmol) according to the general procedure afforded 133 mg (98%) of product using laccase-AZADO system and 130 mg (96%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 7.81-7.84 (m, 2H), 6.98-7.00 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.76, 163.61, 130.95, 128.98, 113.31, 54.56.

4-(Methylthio)benzaldehyde.



Reaction of 4-(methylthio)benzyl alcohol (1.0 mmol) according to the general procedure afforded 143 mg (94%) of product using laccase-AZADO system and 133 mg (88%) of product using laccase-TEMPO system, isolated as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.17, 146.88, 131.96, 128.96, 124.19, 13.67.

7. References

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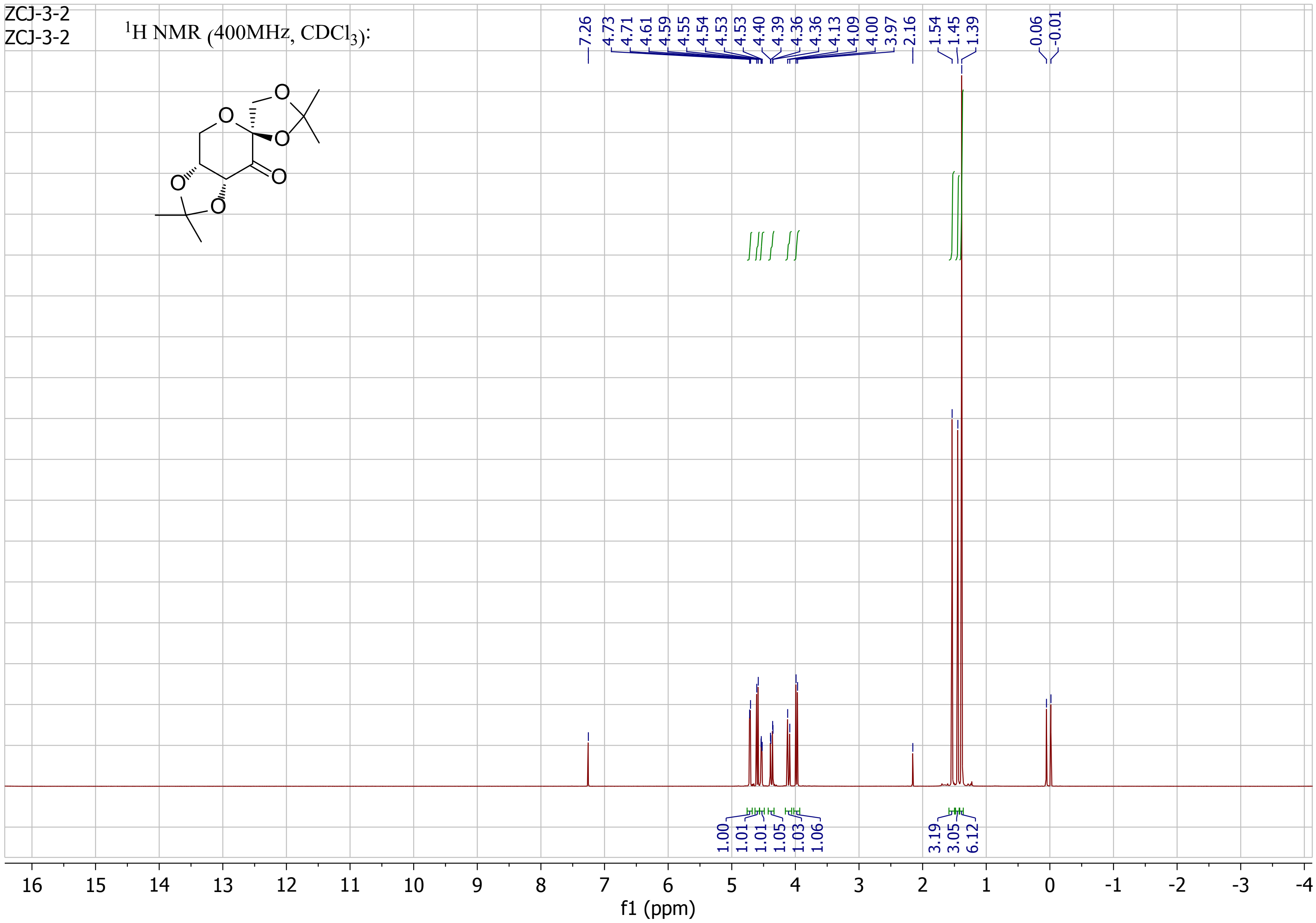
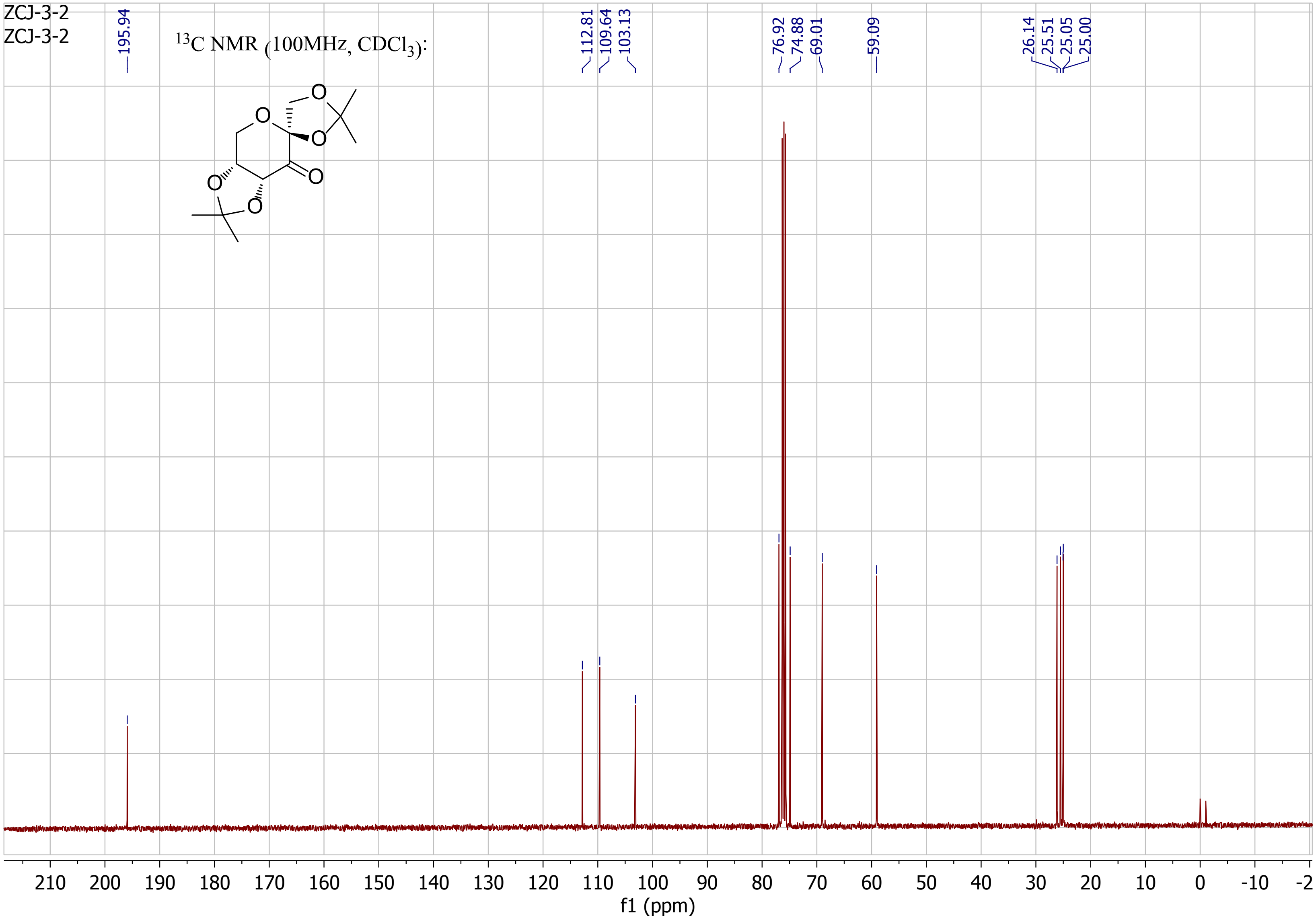
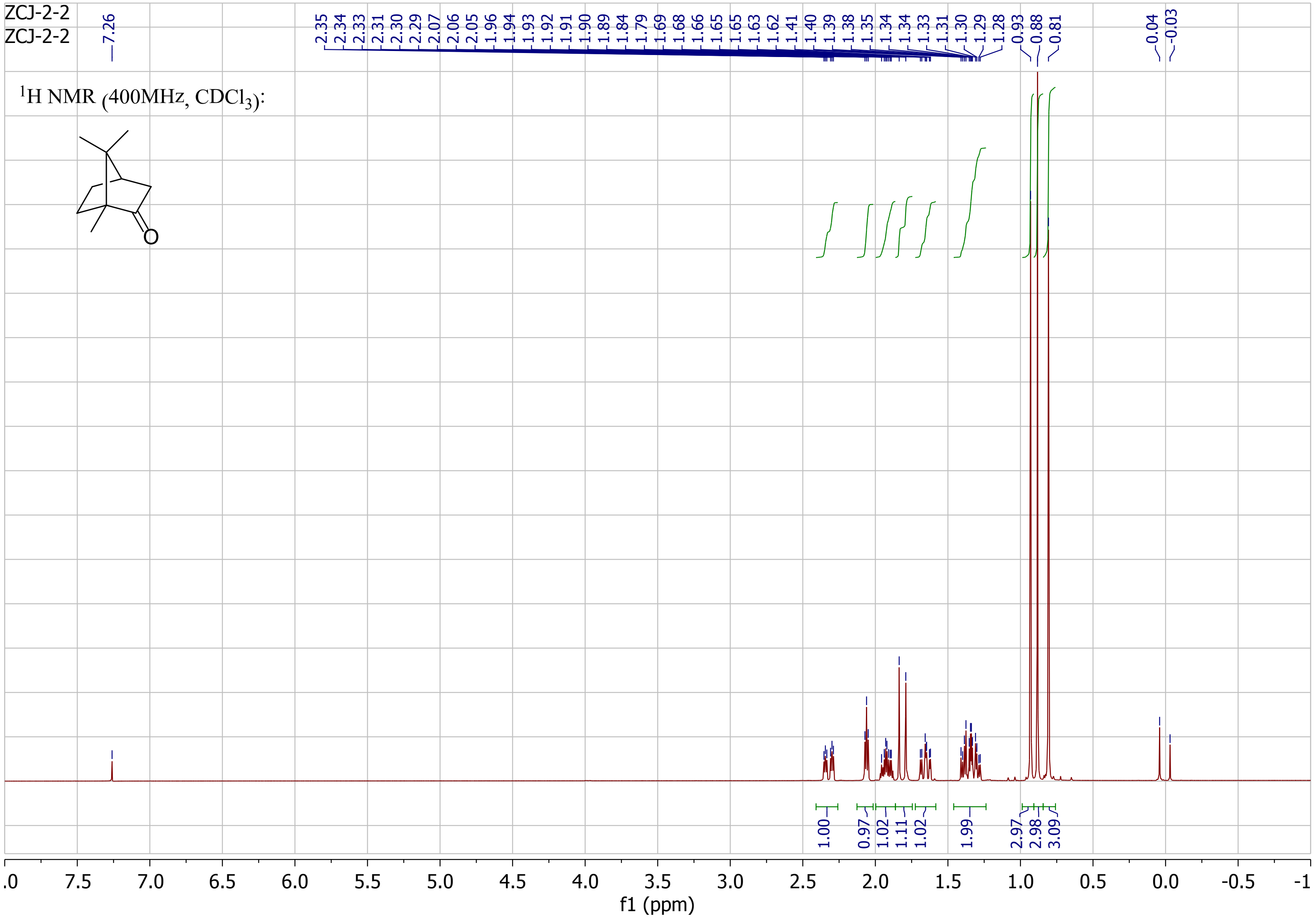
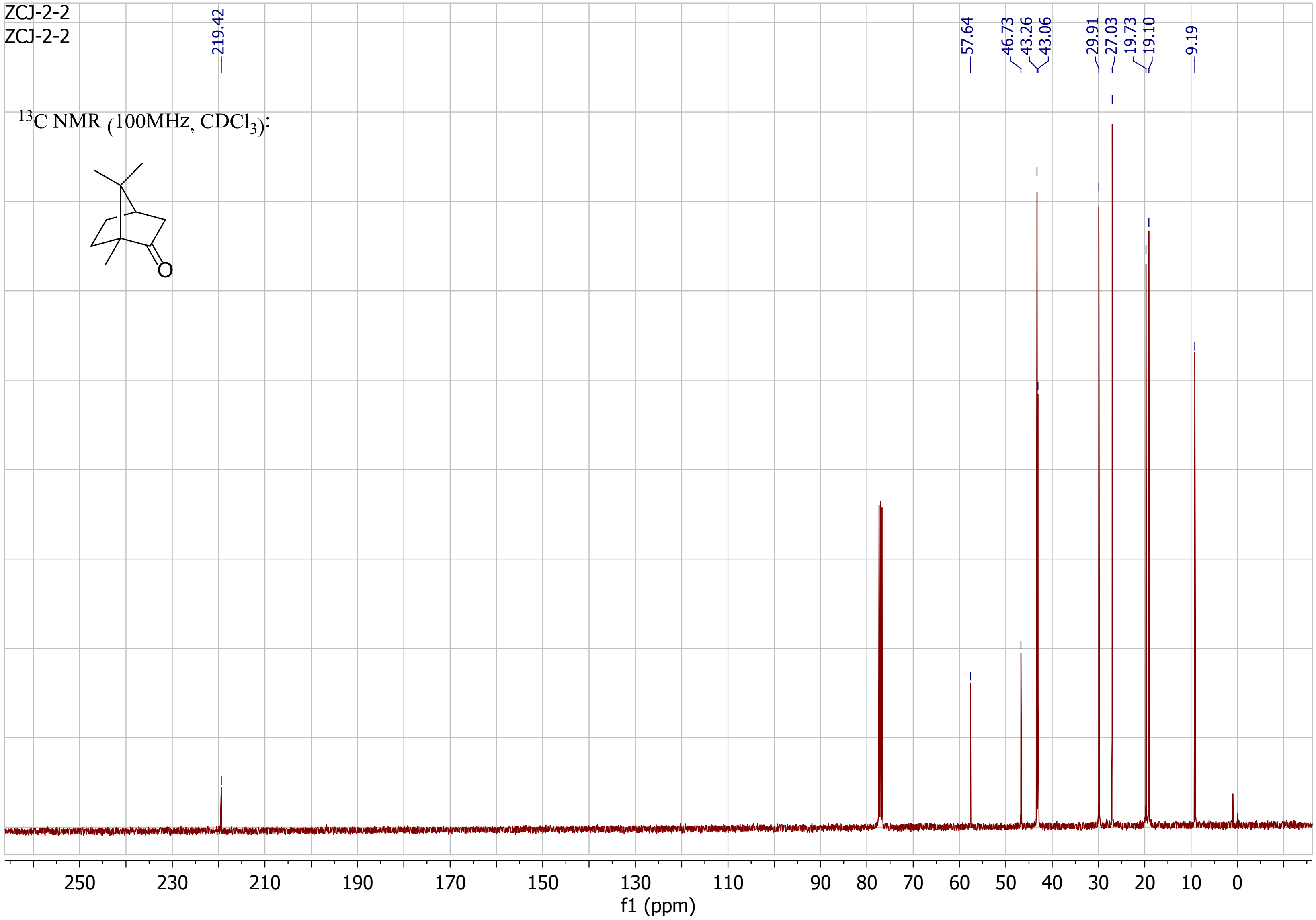
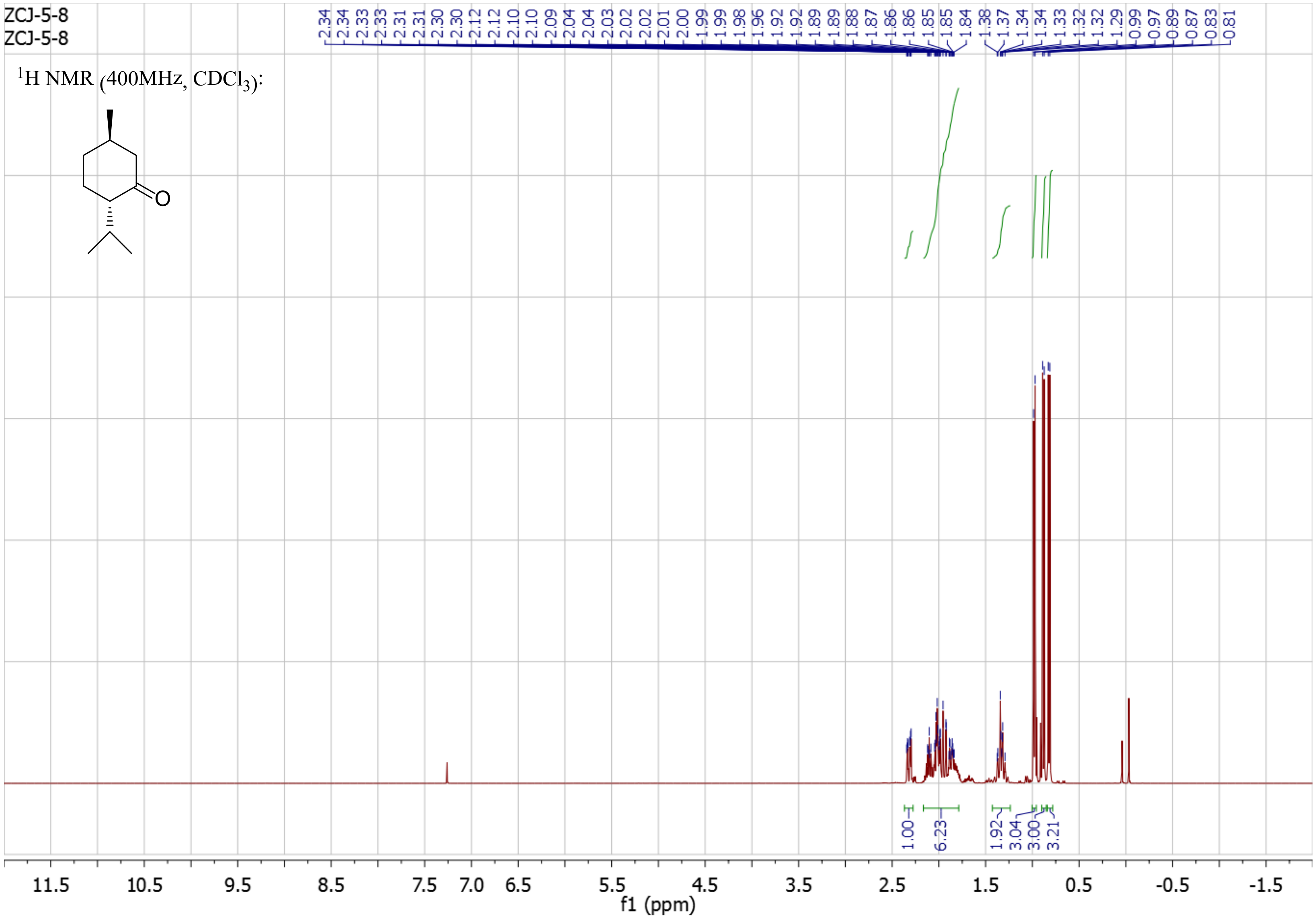
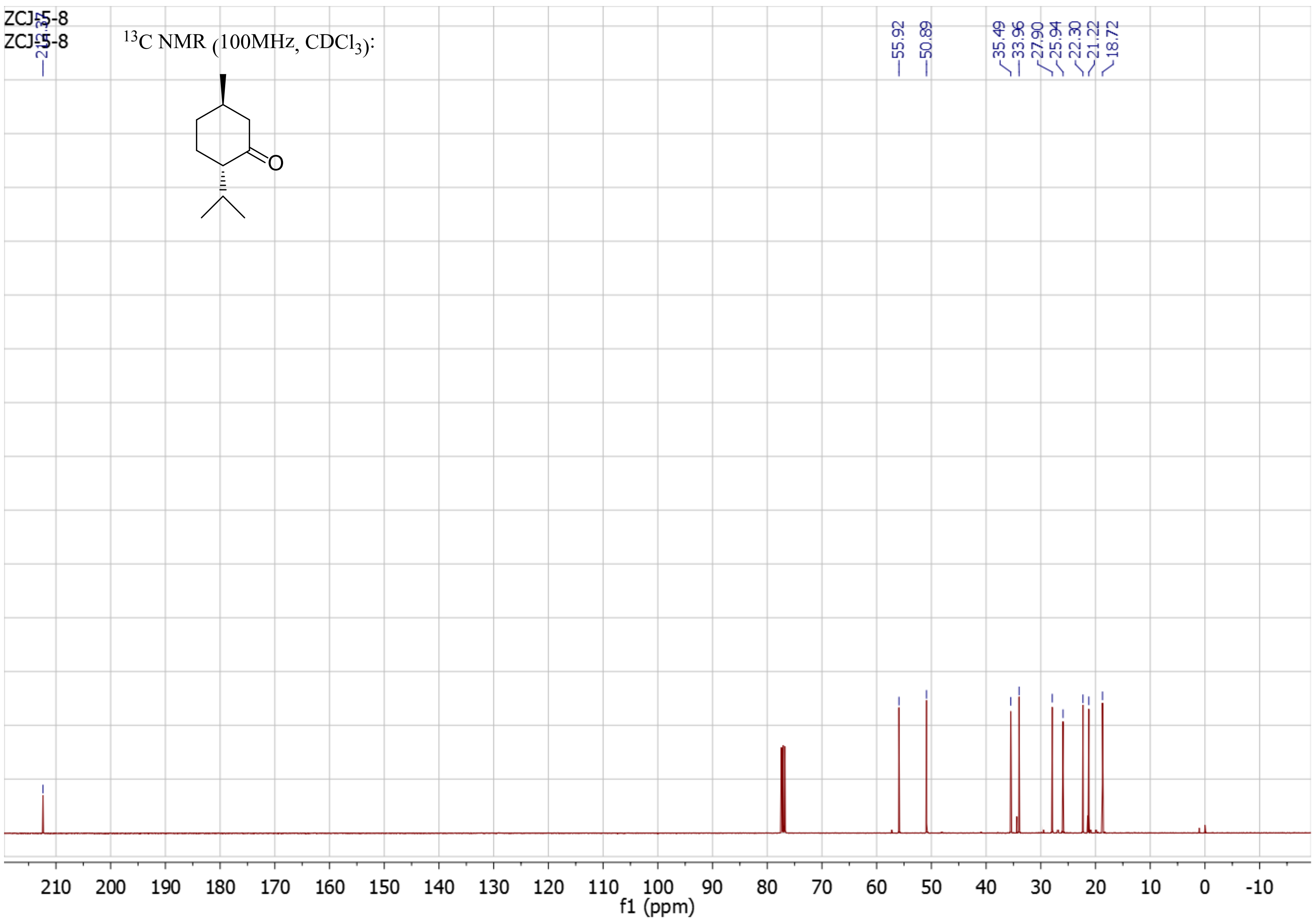

ZCJ-3-2
ZCJ-3-2
^{1}H NMR (400MHz, CDCl$_3$):
7.26
4.73
4.71
4.61
4.59
4.55
4.54
4.53
4.53
4.40
4.39
4.36
4.36
4.13
4.09
4.00
3.97
2.16
1.54
1.45
1.39
0.06
-0.01
1.00
1.01
1.01
1.05
1.03
1.06
3.19
3.05
6.12
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

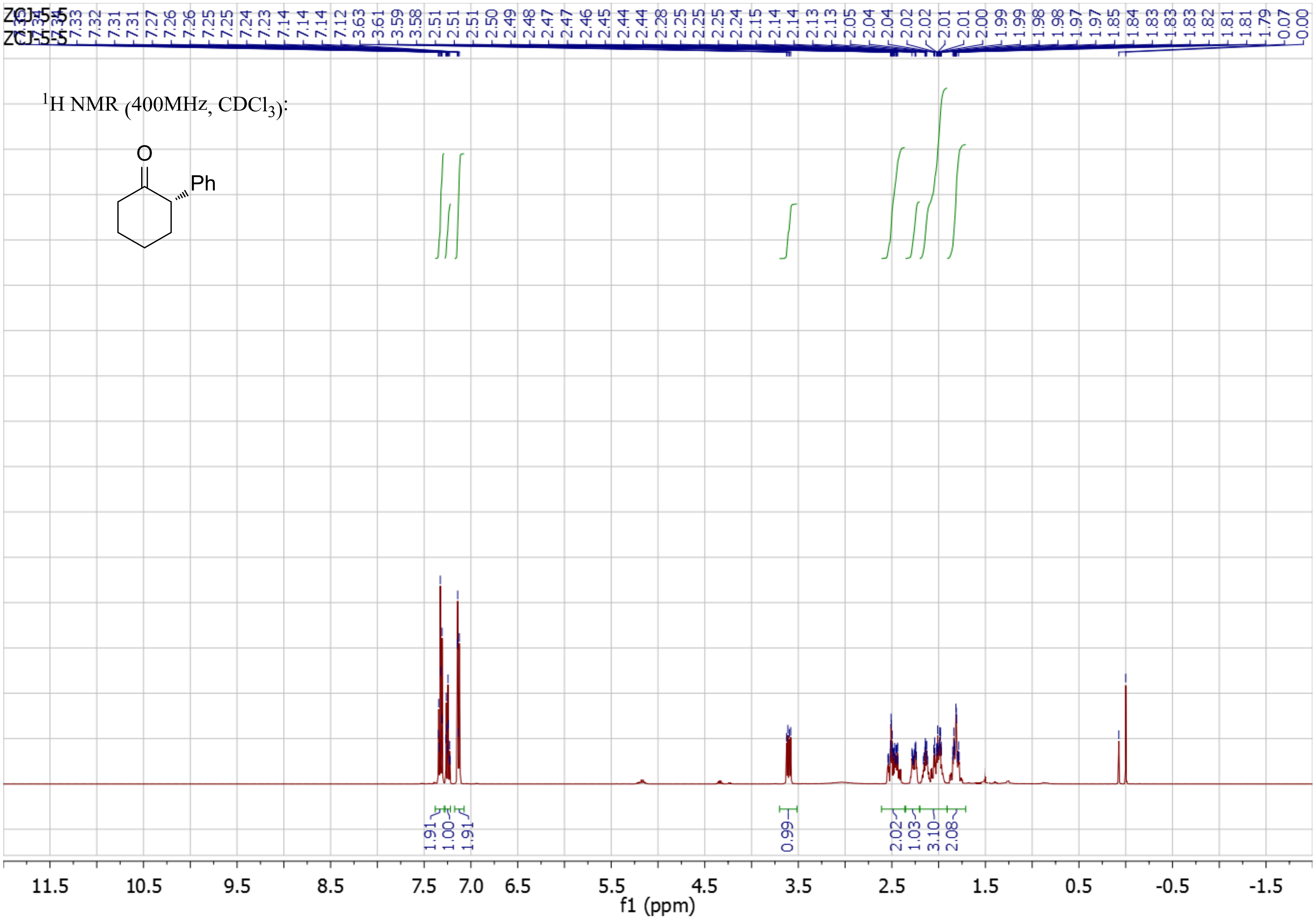

ZCJ-3-2
ZCJ-3-2
195.94
13C NMR (100MHz, CDCl3):
112.81
109.64
103.13
76.92
74.88
69.01
59.09
26.14
25.51
25.05
25.00
O
O
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

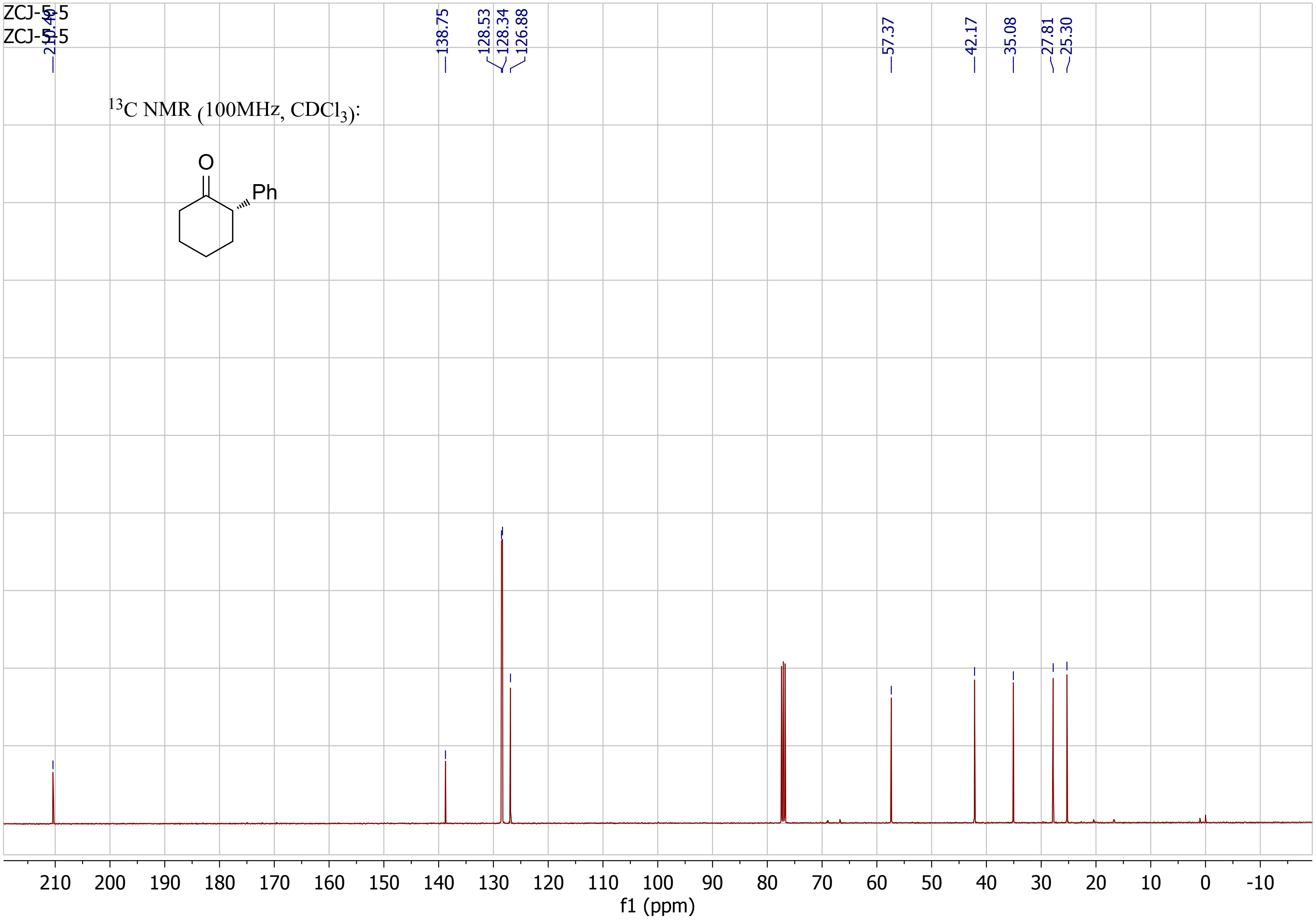

ZCJ-2-2
ZCJ-2-2
7.26
2.35
2.34
2.33
2.31
2.30
2.29
2.07
2.06
2.05
1.96
1.94
1.93
1.92
1.91
1.90
1.89
1.84
1.79
1.69
1.68
1.66
1.65
1.63
1.62
1.41
1.40
1.39
1.38
1.35
1.34
1.34
1.33
1.31
1.30
1.29
1.28
0.93
0.88
0.81
0.04
-0.03
^{1}H NMR (400MHz, CDCl$_3$):
O
1.00
0.97
1.02
1.11
1.02
1.99
2.97
2.98
3.09
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

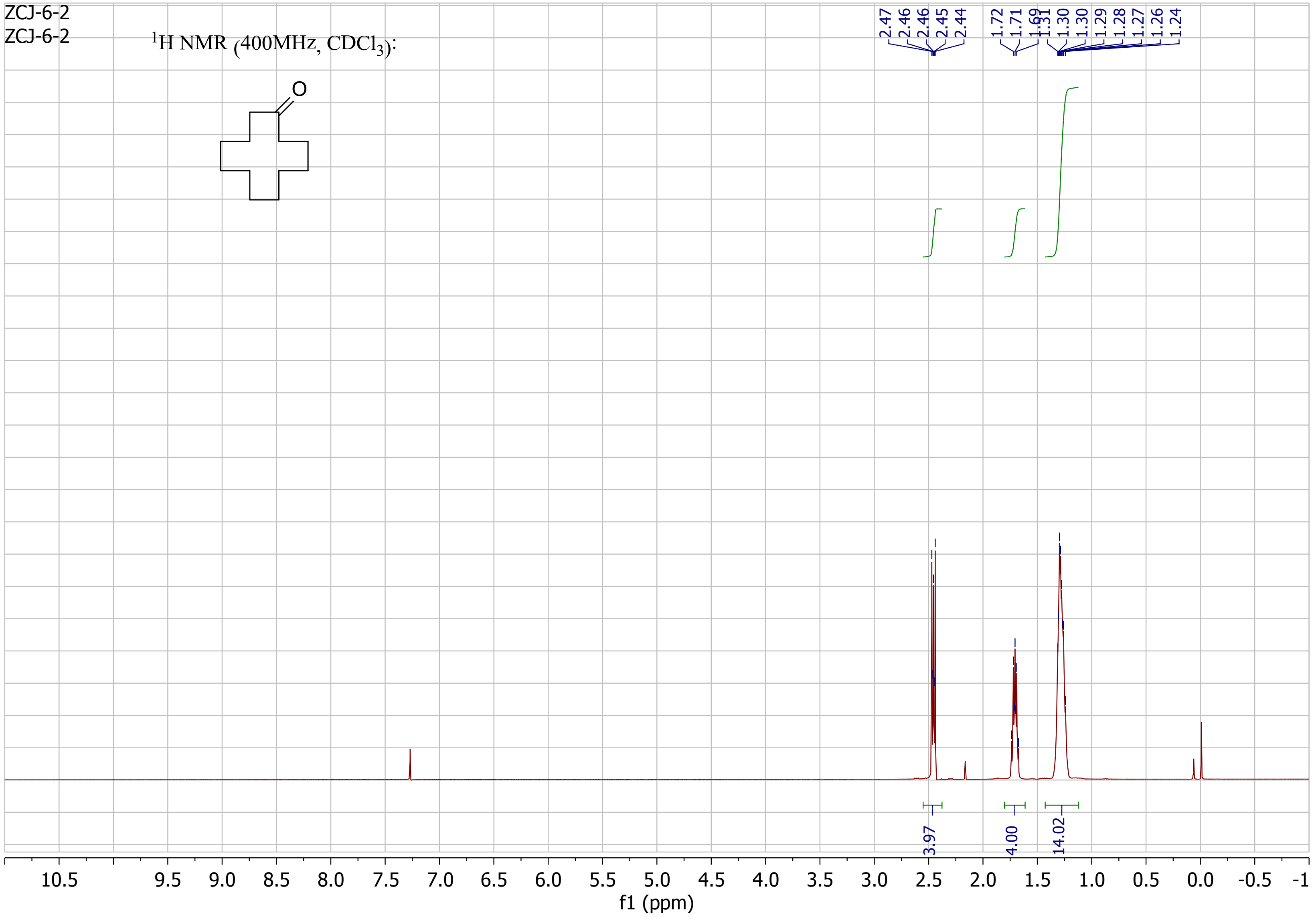

ZCJ-2-2
ZCJ-2-2
^{13}C NMR (100MHz, CDCl$_3$):
O
219.42
57.64
46.73
43.26
43.06
29.91
27.03
19.73
19.10
9.19
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

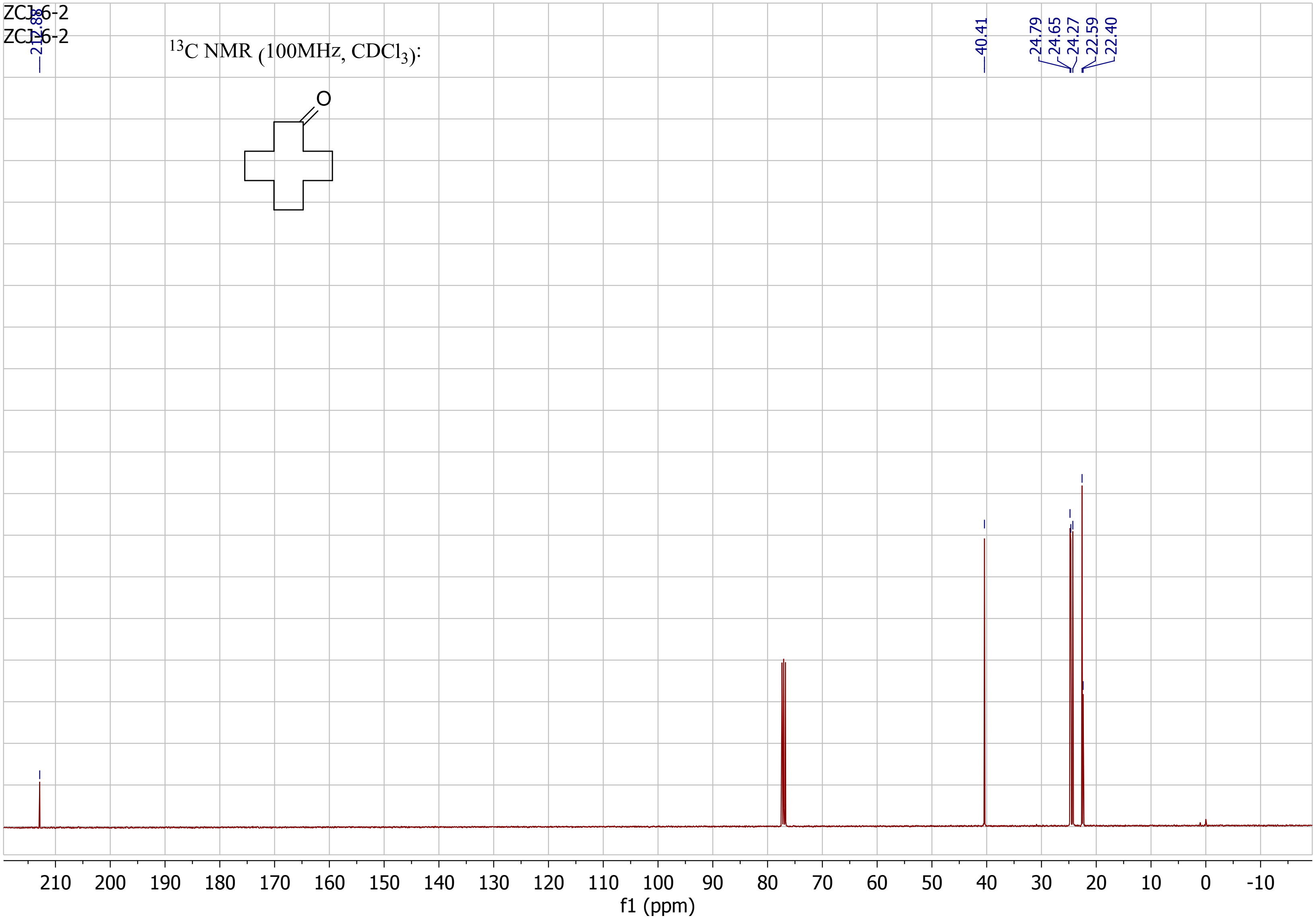

ZCJ-5-8
ZCJ-5-8
^{1}H NMR (400MHz, $CDCl_3$):
O
2.34
2.34
2.33
2.33
2.31
2.31
2.30
2.12
2.12
2.10
2.10
2.09
2.04
2.04
2.03
2.02
2.02
2.01
2.00
1.99
1.99
1.98
1.96
1.92
1.92
1.89
1.89
1.88
1.87
1.86
1.86
1.85
1.85
1.84
1.38
1.37
1.34
1.34
1.33
1.32
1.32
1.29
0.99
0.97
0.89
0.87
0.83
0.81
1.00
6.23
1.92
3.04
3.00
3.21
11.5
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

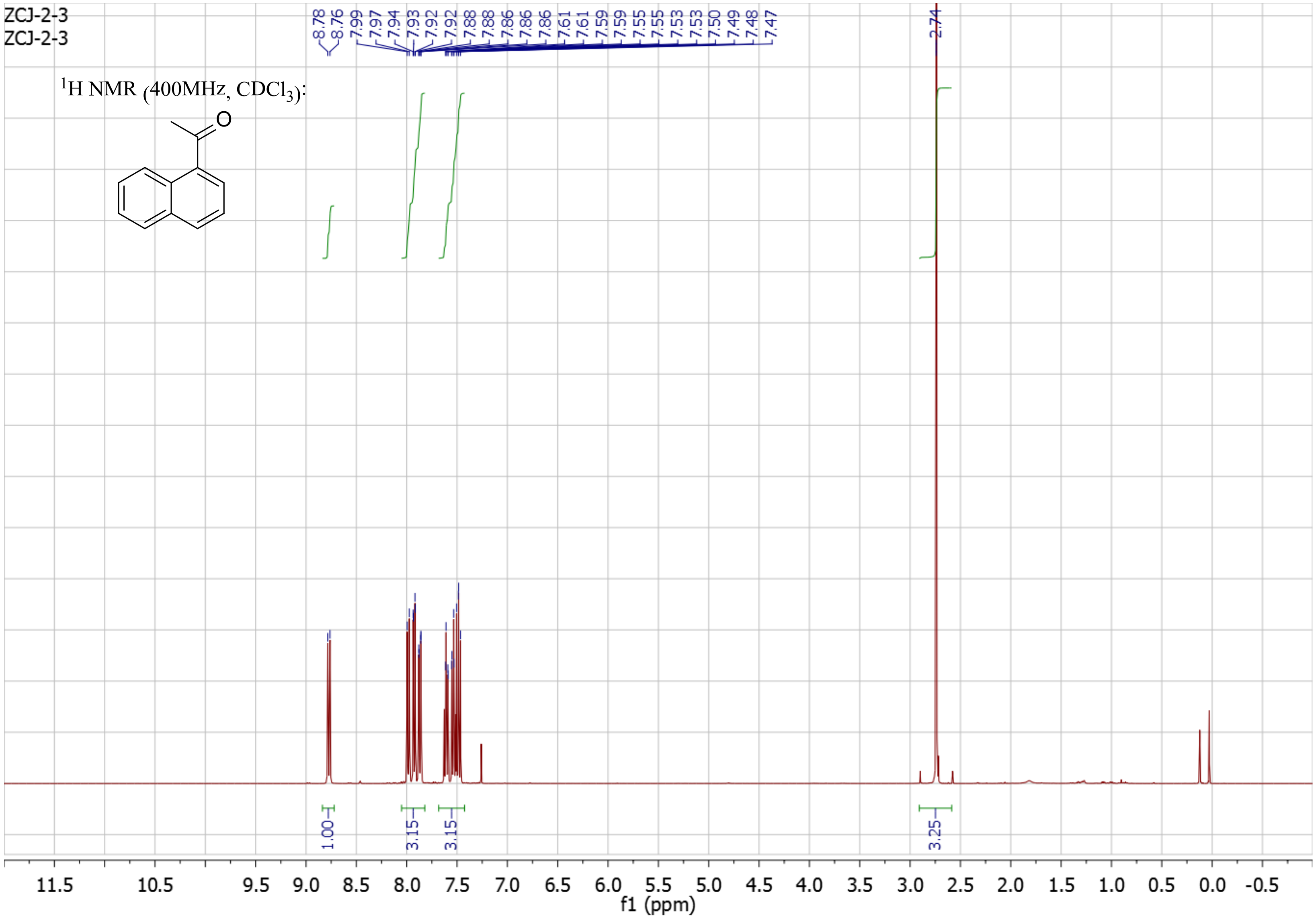

ZCJ-5-8
ZCJ-5-8
^{13}C NMR (100MHz, CDCl$_3$):
O
212.37
55.92
50.89
35.49
33.96
27.90
25.94
22.30
21.22
18.72
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


ZCJ-5-5
ZCJ-5-5
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.27
7.26
7.26
7.25
7.25
7.24
7.23
7.14
7.14
7.14
7.12
3.63
3.61
3.59
3.58
2.51
2.51
2.51
2.50
2.49
2.48
2.47
2.47
2.46
2.45
2.44
2.44
2.28
2.25
2.25
2.25
2.24
2.15
2.14
2.14
2.13
2.13
2.05
2.04
2.04
2.02
2.02
2.01
2.01
2.00
1.99
1.99
1.98
1.98
1.97
1.97
1.85
1.84
1.83
1.83
1.83
1.82
1.81
1.81
1.79
0.07
0.00
¹H NMR (400MHz, CDCl₃):
O
Ph
1.91
1.00
1.91
0.99
2.02
1.03
3.10
2.08
11.5
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)


ZCJ-5-5
ZCJ-5-5
210.40
138.75
128.53
128.34
126.88
57.37
42.17
35.08
27.81
25.30
^{13}C NMR (100MHz, CDCl$_3$):
O
Ph
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


ZCJ-6-2
ZCJ-6-2
¹H NMR (400MHz, CDCl₃):
O
2.47
2.46
2.46
2.45
2.44
1.72
1.71
1.69
1.31
1.30
1.30
1.29
1.28
1.27
1.26
1.24
3.97
4.00
14.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


ZCJ-6-2
ZCJ-6-2
212.88
^{13}C NMR (100MHz, CDCl$_3$):
O
40.41
24.79
24.65
24.27
22.59
22.40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


ZCJ-2-3
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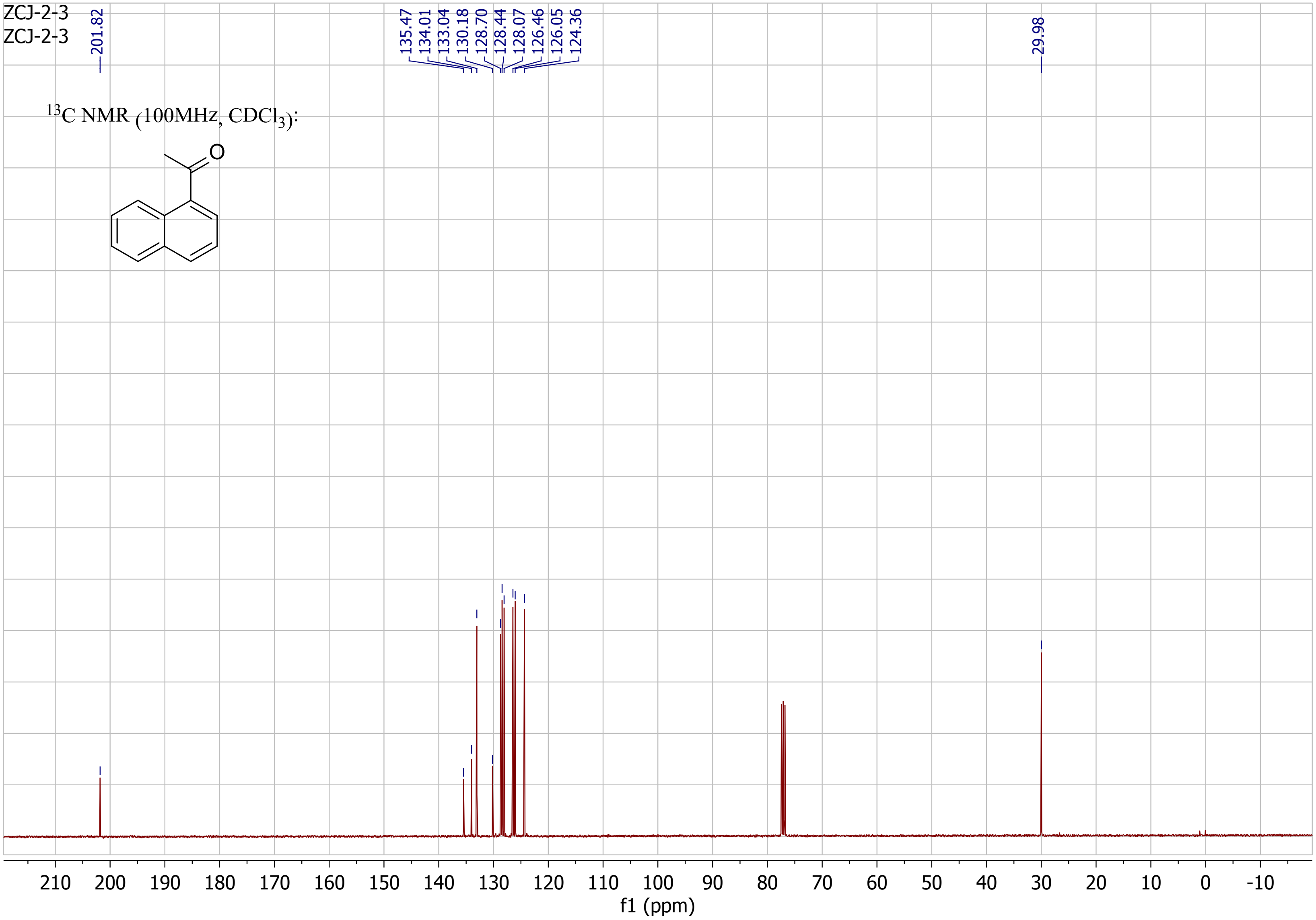
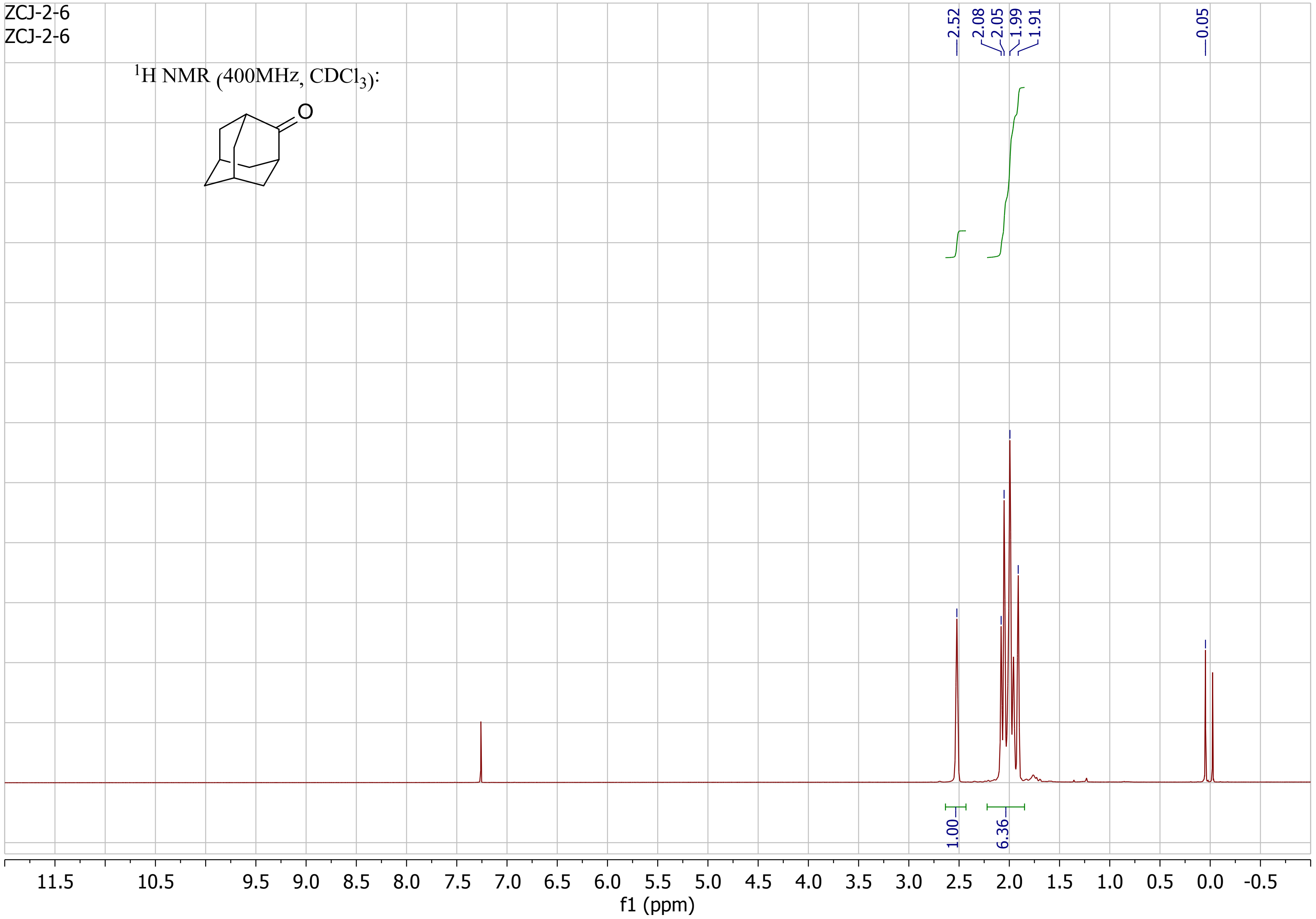
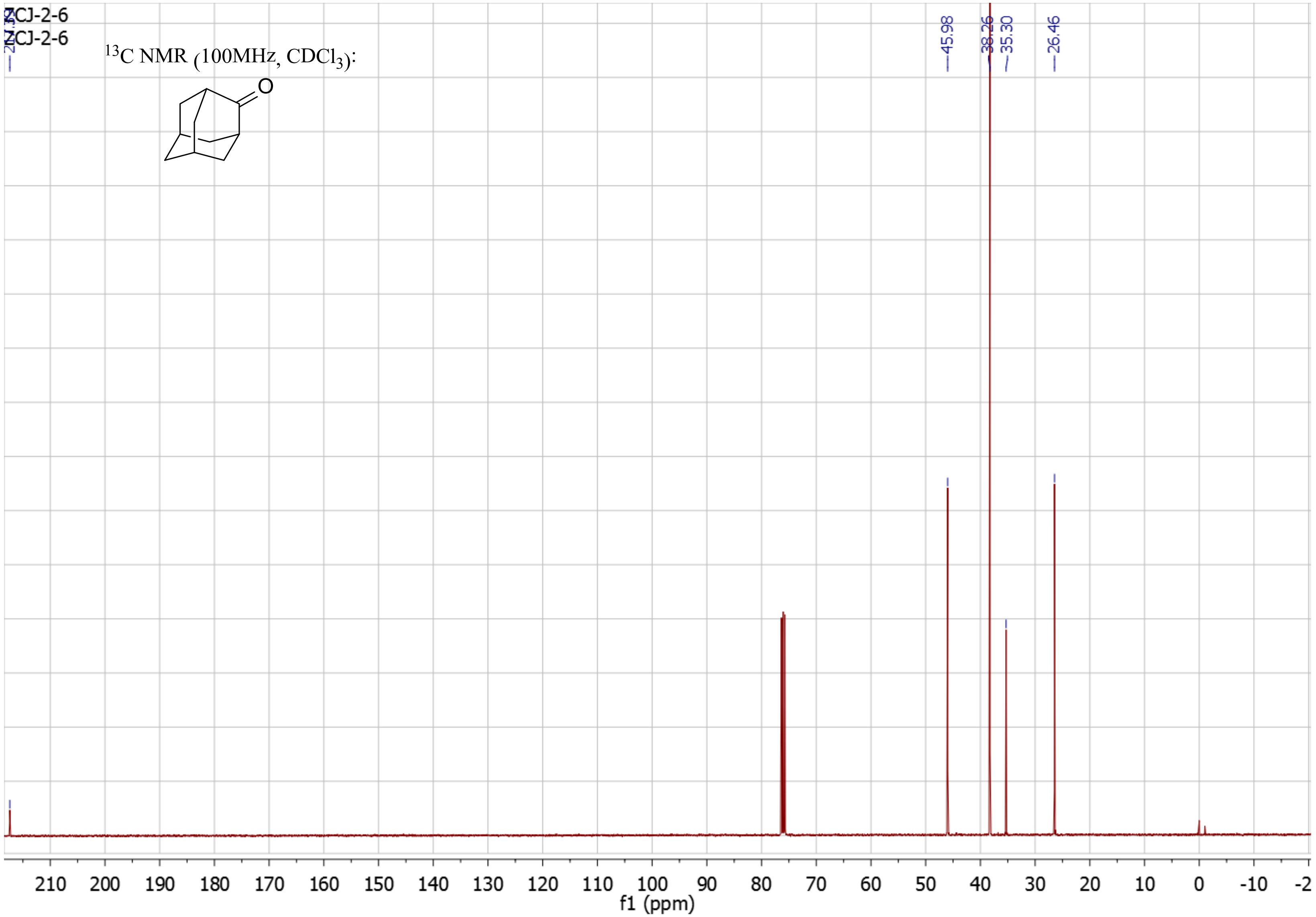
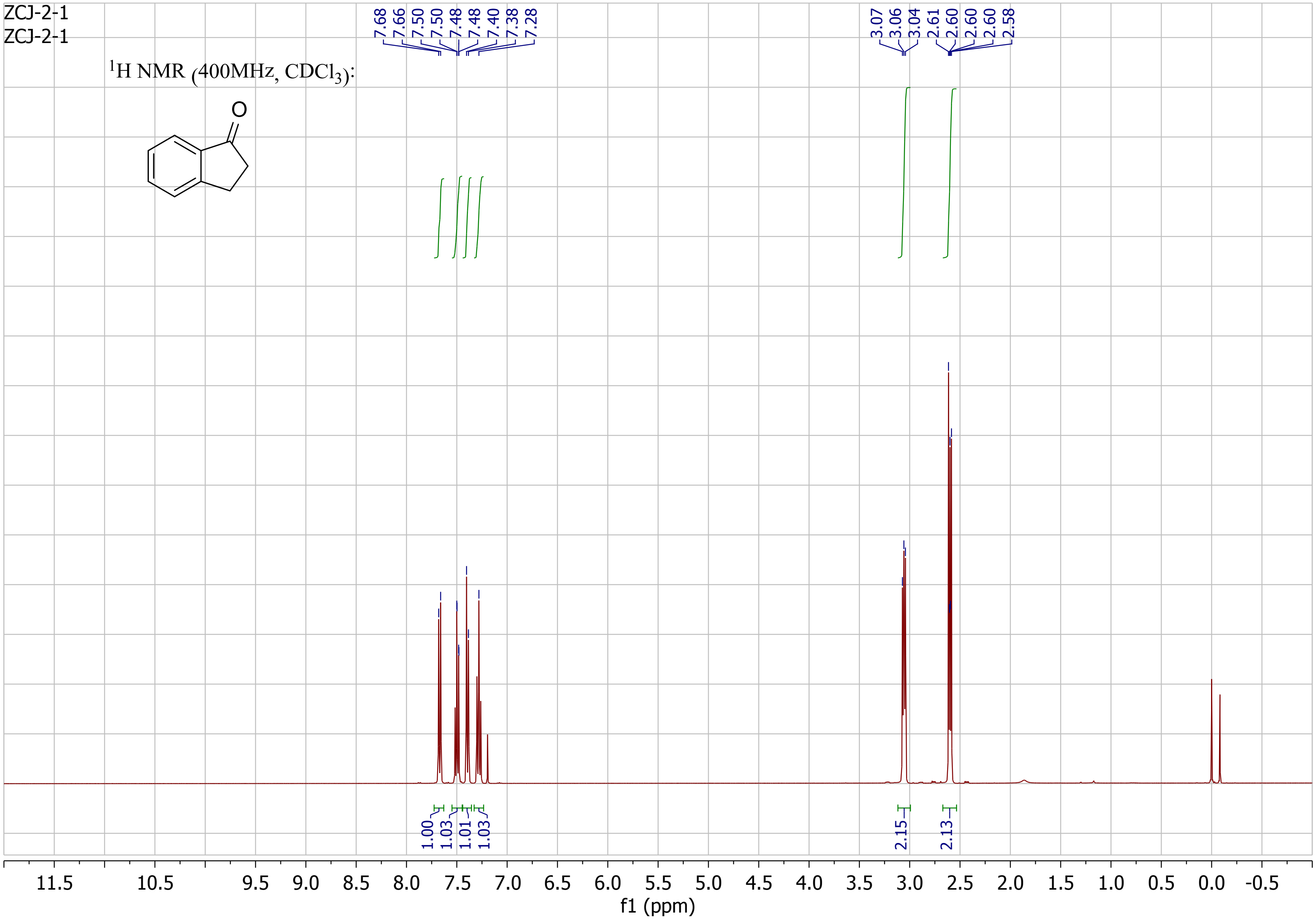
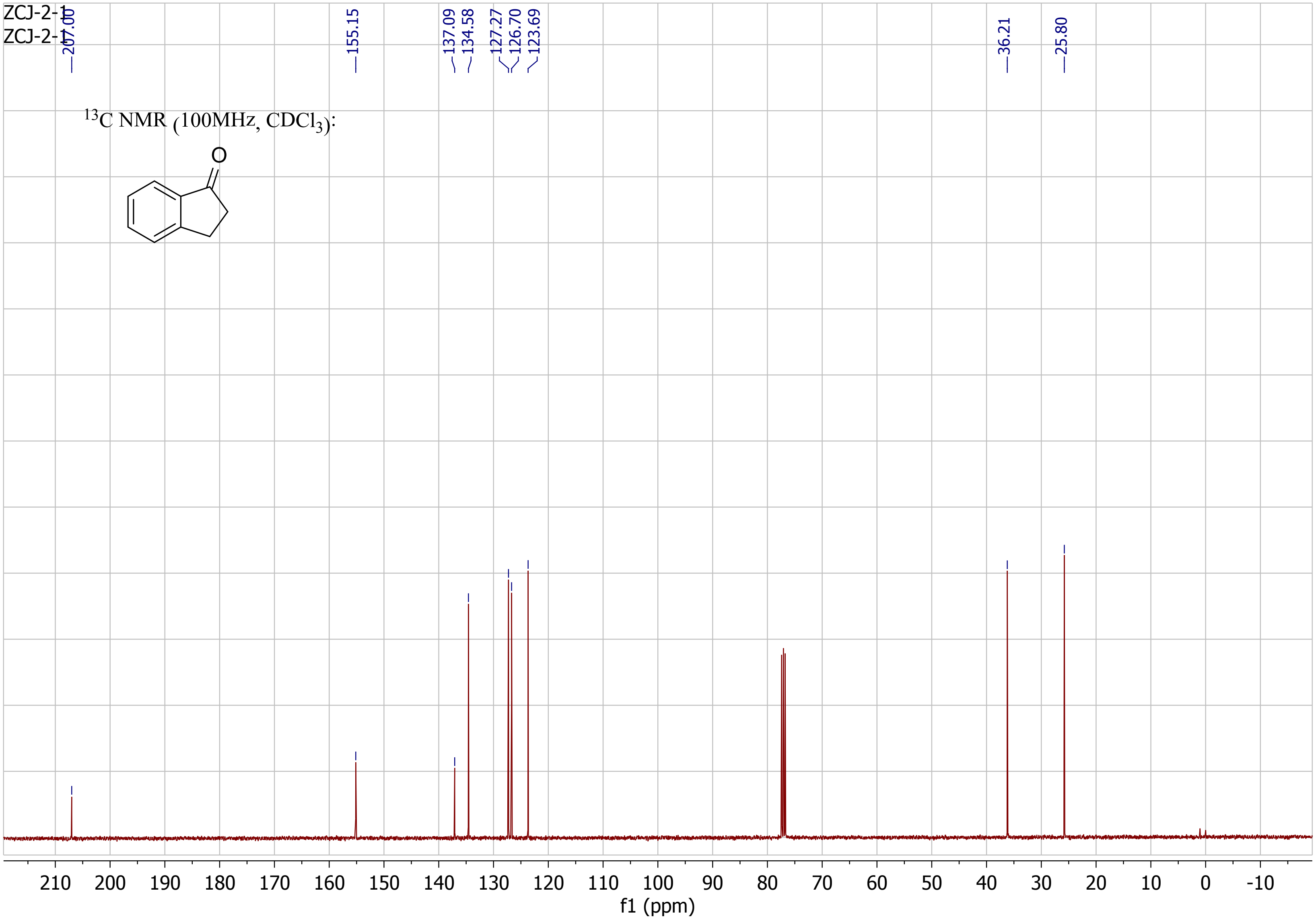
^{1}H NMR (400MHz, $CDCl_3$):
O
8.78
8.76
7.99
7.97
7.94
7.93
7.92
7.92
7.88
7.88
7.86
7.86
7.61
7.61
7.59
7.59
7.55
7.55
7.53
7.53
7.50
7.49
7.48
7.47
2.74
1.00
3.15
3.15
3.25
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


ZCJ-2-3
ZCJ-2-3
201.82
135.47
134.01
133.04
130.18
128.70
128.44
128.07
126.46
126.05
124.36
29.98
^{13}C NMR (100MHz, CDCl$_3$):
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

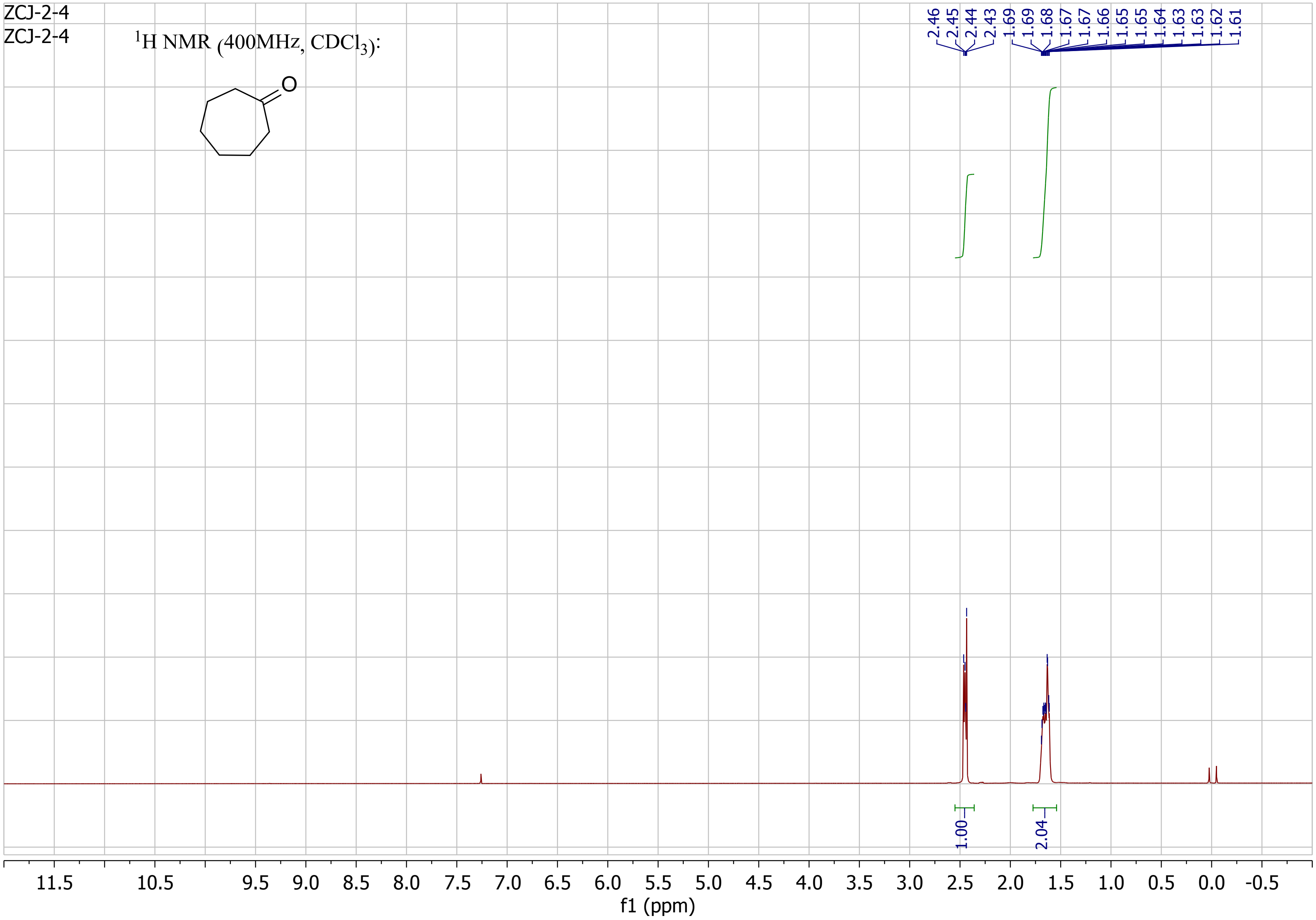

ZCJ-2-6
ZCJ-2-6
^{1}H NMR (400MHz, CDCl$_3$):
O
2.52
2.08
2.05
1.99
1.91
0.05
1.00
6.36
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

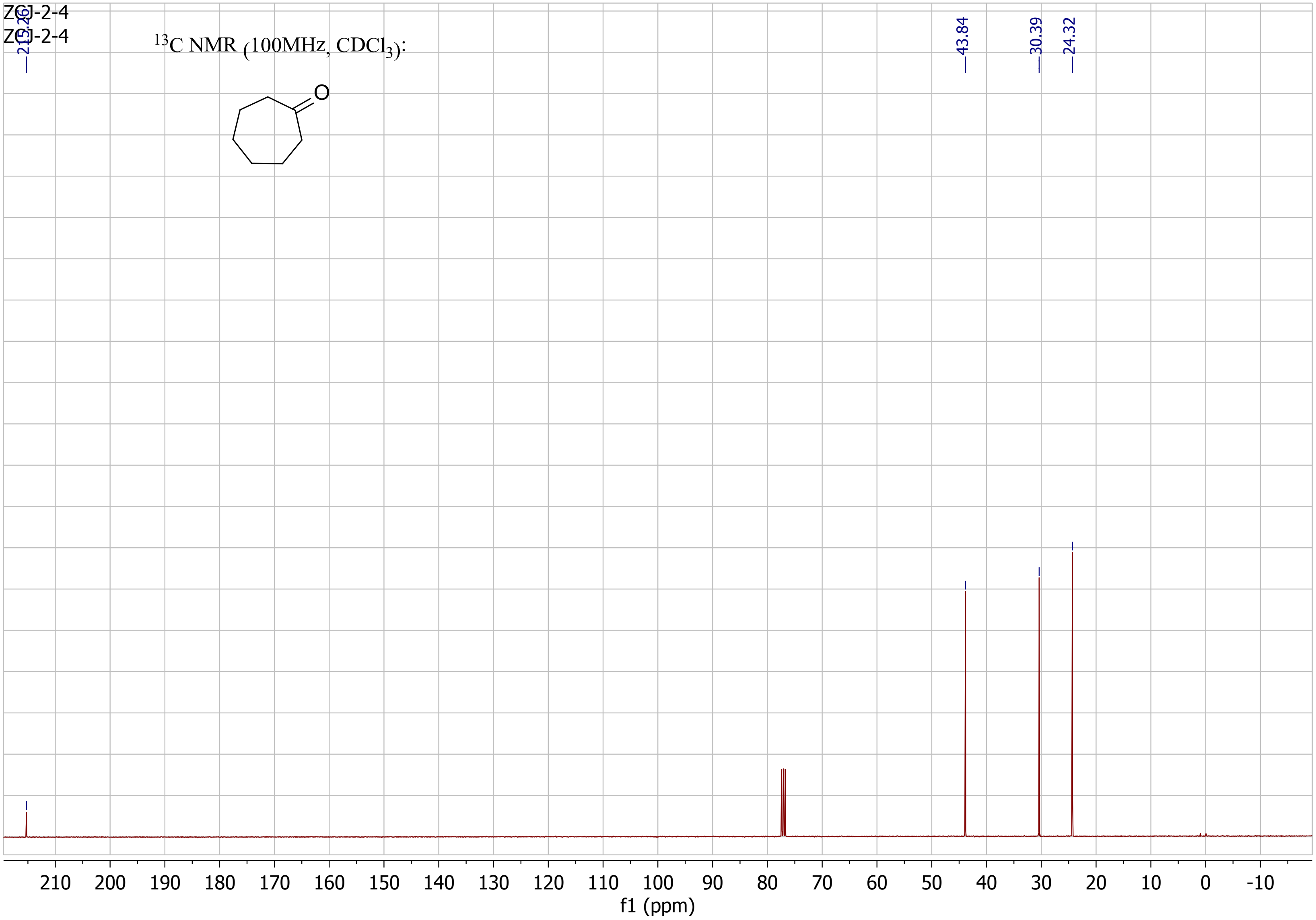

ZCJ-2-6
ZCJ-2-6
^{13}C NMR (100MHz, CDCl$_3$):
O
217.39
45.98
38.26
35.30
26.46
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


ZCJ-2-1
ZCJ-2-1
^{1}H NMR (400MHz, CDCl$_3$):
O
7.68
7.66
7.50
7.50
7.48
7.48
7.40
7.38
7.28
3.07
3.06
3.04
2.61
2.60
2.60
2.60
2.58
1.00
1.03
1.01
1.03
2.15
2.13
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

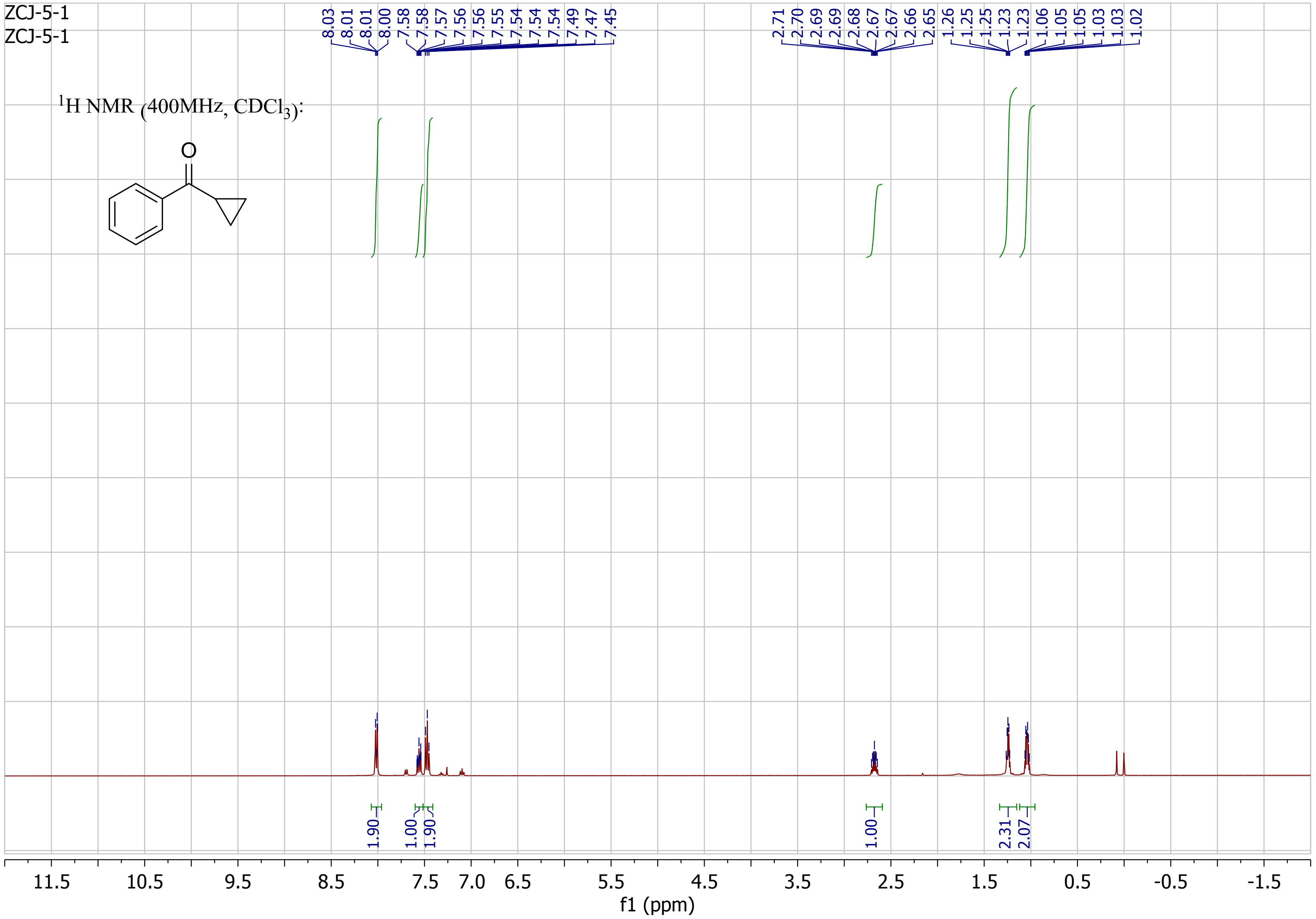


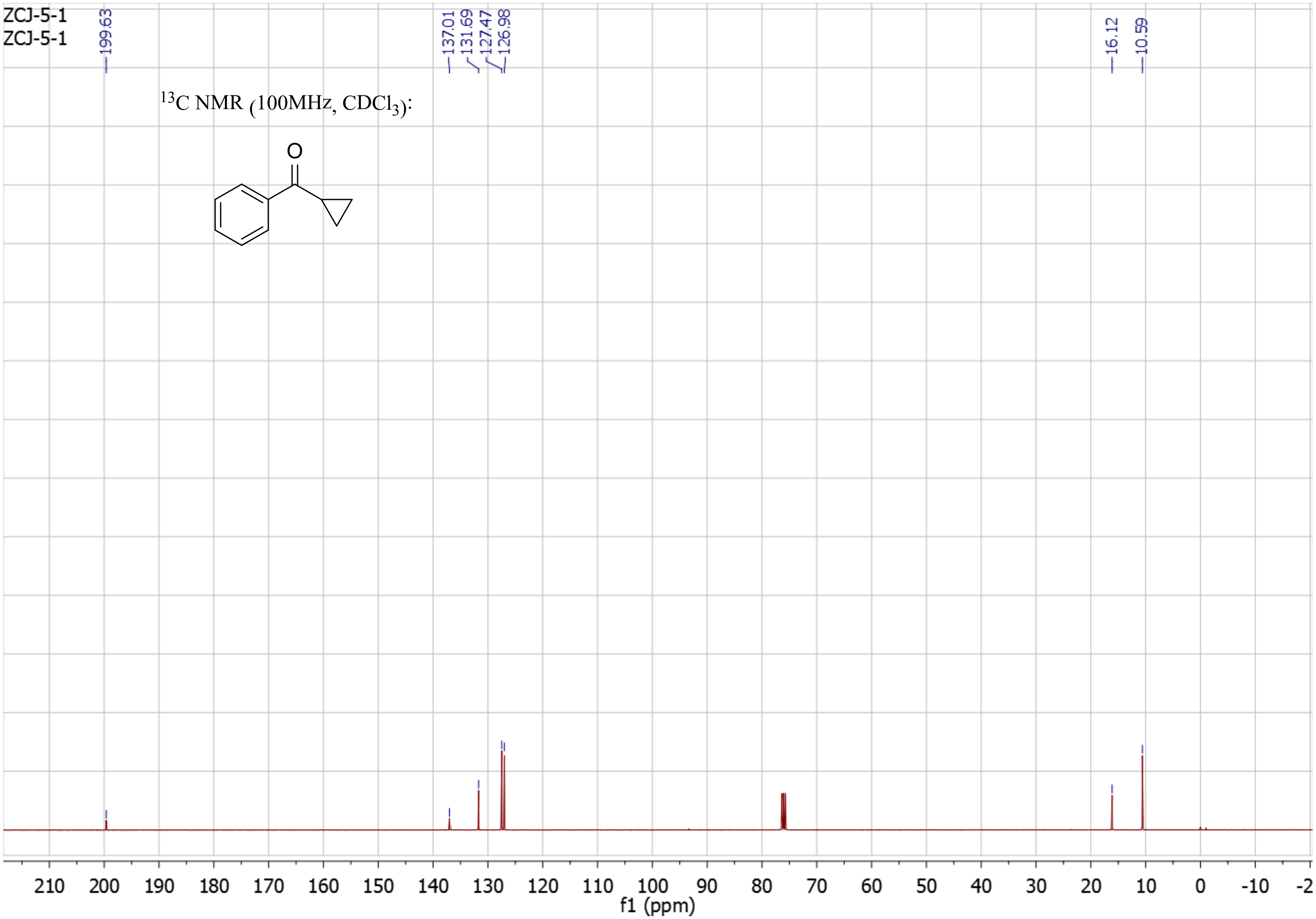
^{13}C NMR (100MHz, $CDCl_3$):

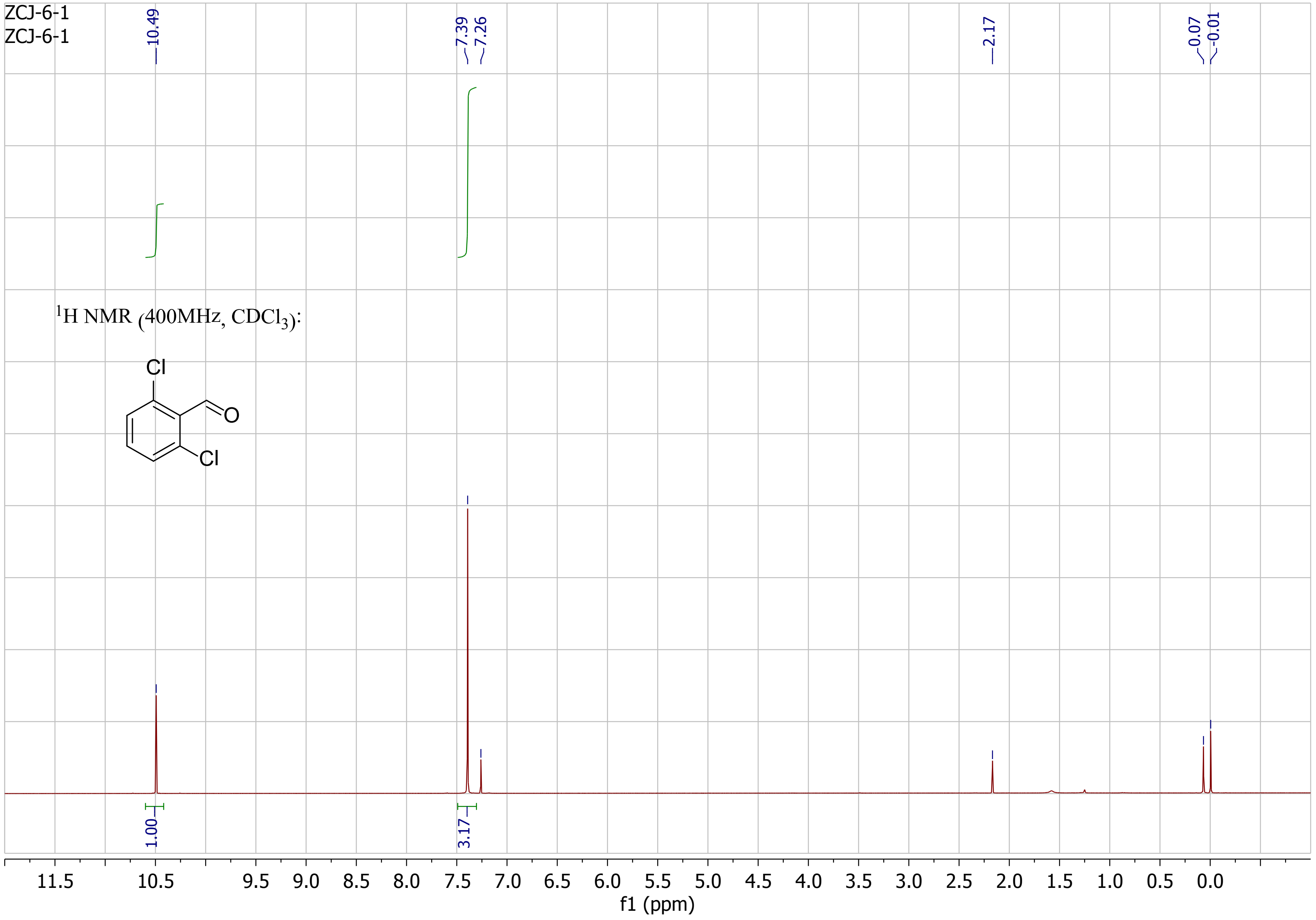

ZCJ-2-4
ZCJ-2-4
^{1}H NMR (400MHz, CDCl$_3$):
O
2.46
2.45
2.44
2.43
1.69
1.69
1.68
1.67
1.67
1.66
1.65
1.65
1.64
1.63
1.63
1.62
1.61
1.00
2.04
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

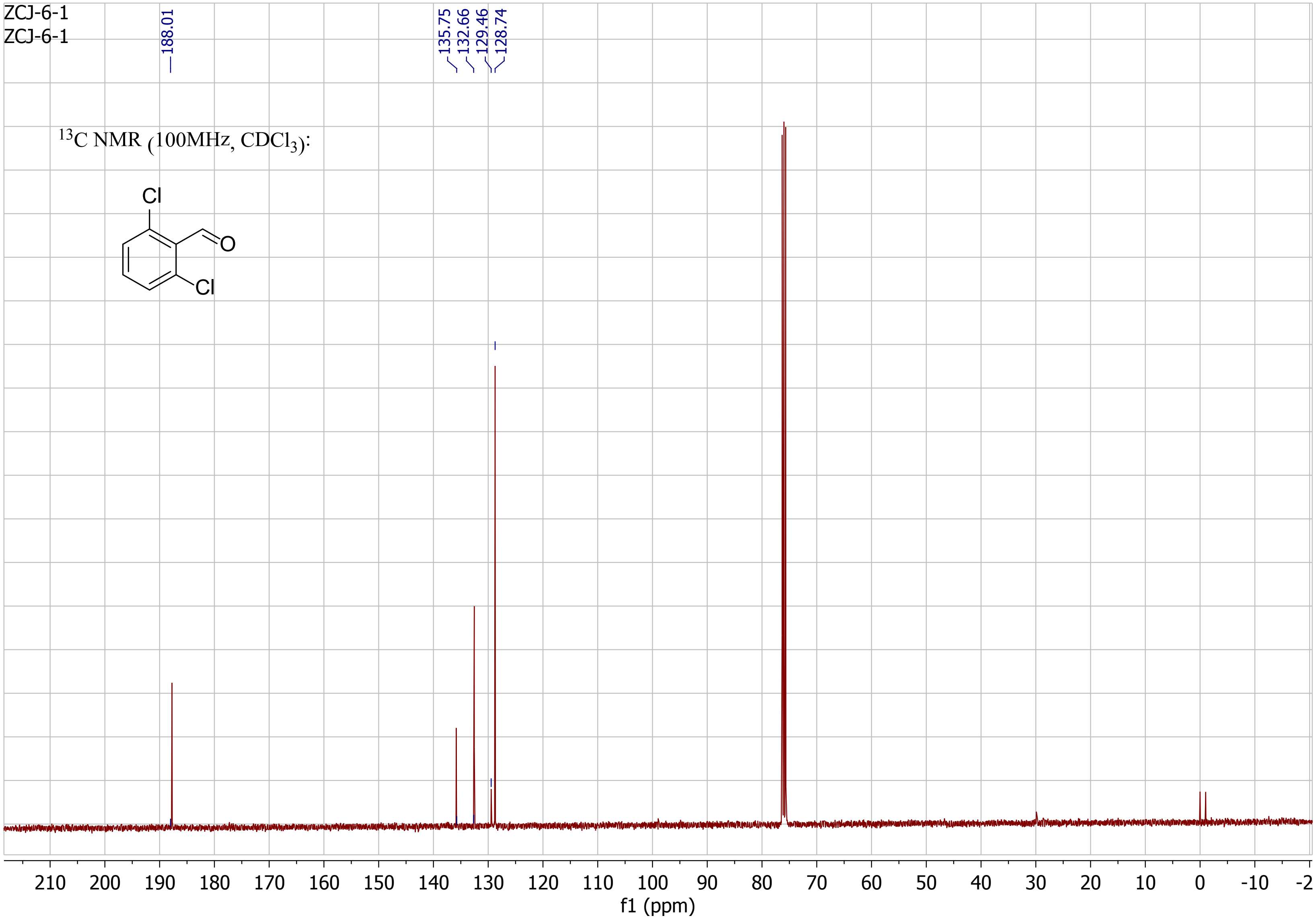


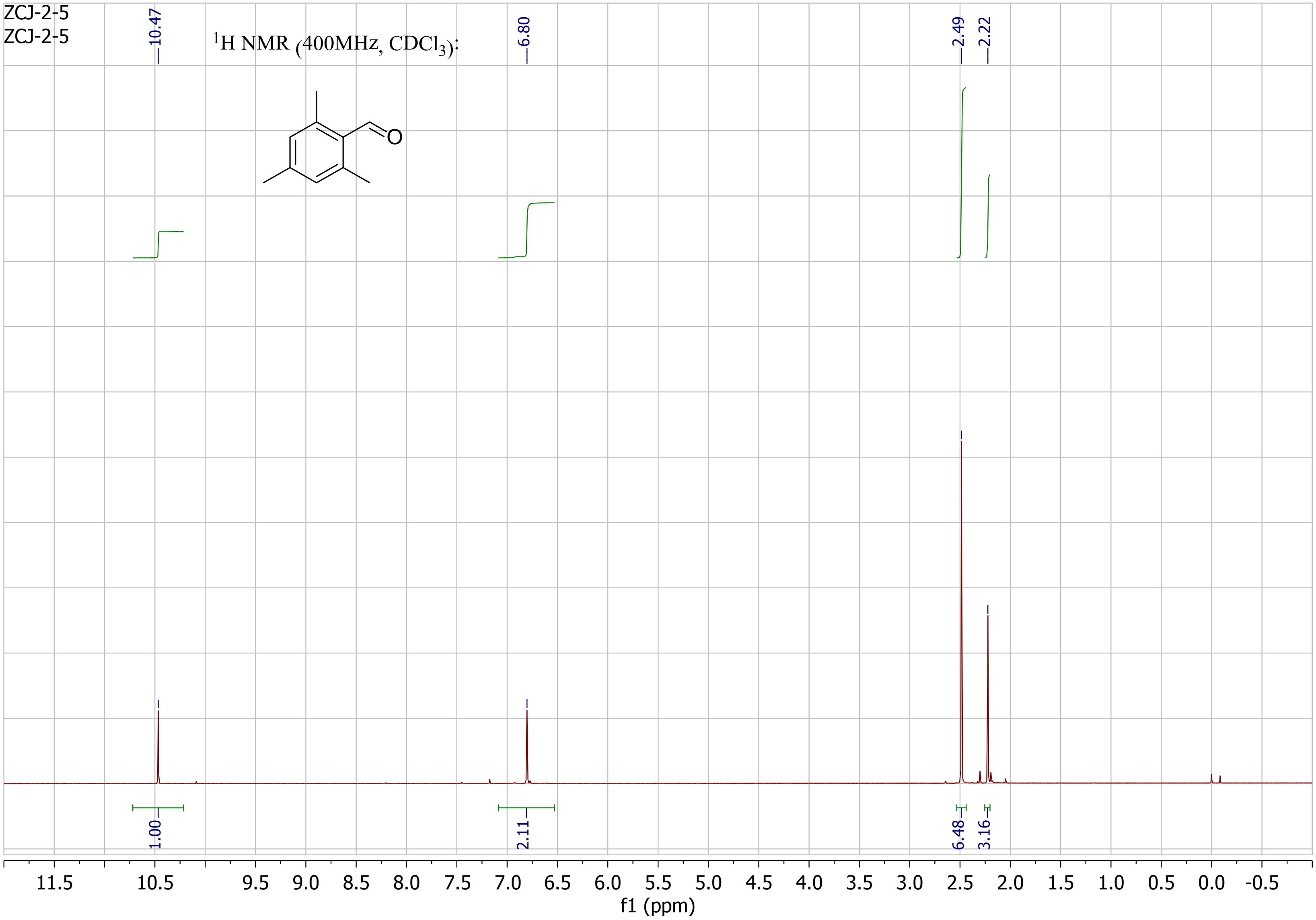
^{13}C NMR (100MHz, $CDCl_3$):

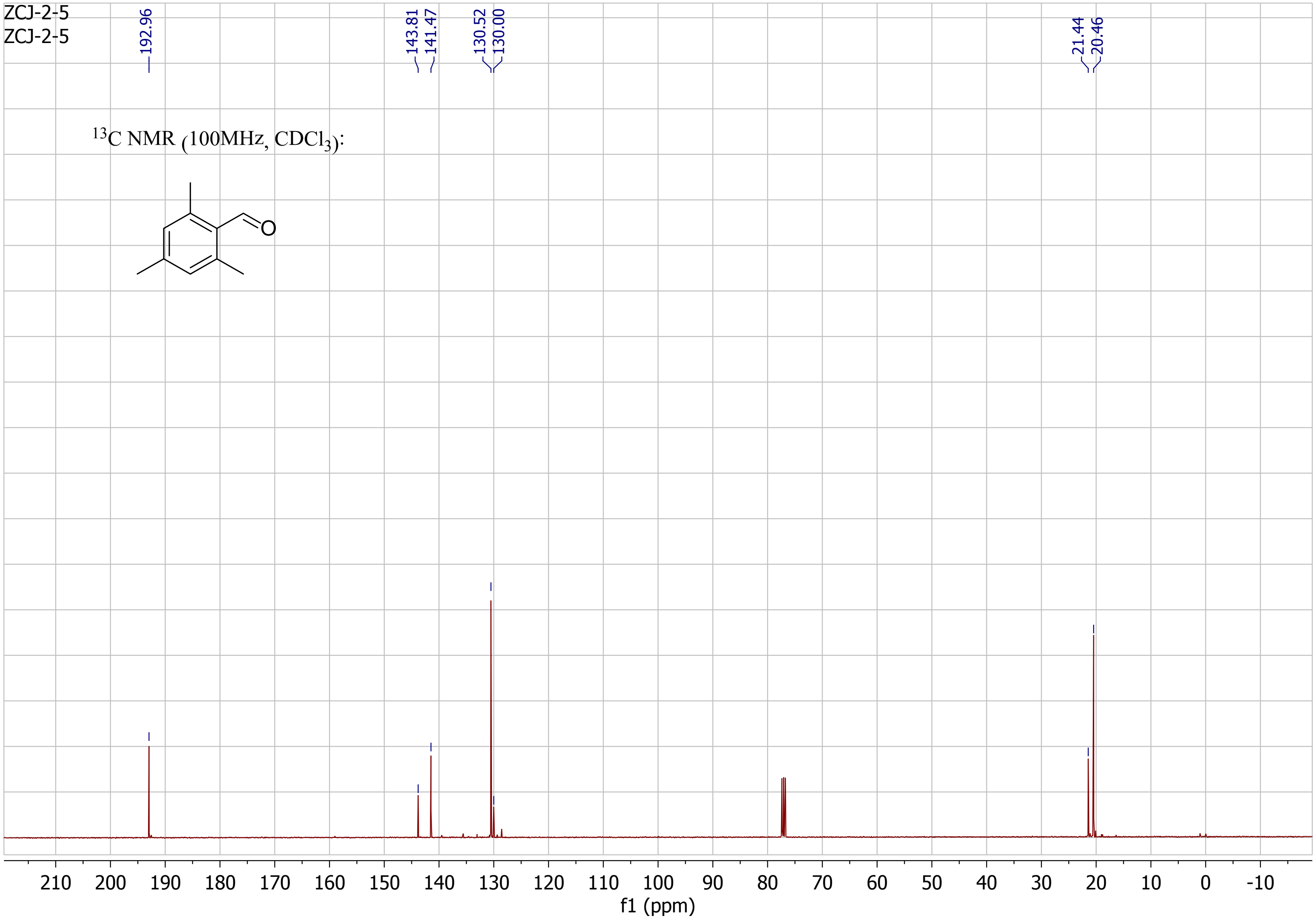

ZCJ-5-1
ZCJ-5-1
^{1}H NMR (400MHz, CDCl$_3$):
O
8.03
8.01
8.01
8.00
7.58
7.58
7.57
7.56
7.55
7.54
7.54
7.54
7.49
7.47
7.45
2.71
2.70
2.69
2.69
2.68
2.67
2.67
2.66
2.65
1.26
1.25
1.25
1.23
1.23
1.06
1.05
1.05
1.03
1.03
1.02
1.90
1.00
1.90
1.00
2.31
2.07
11.5
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

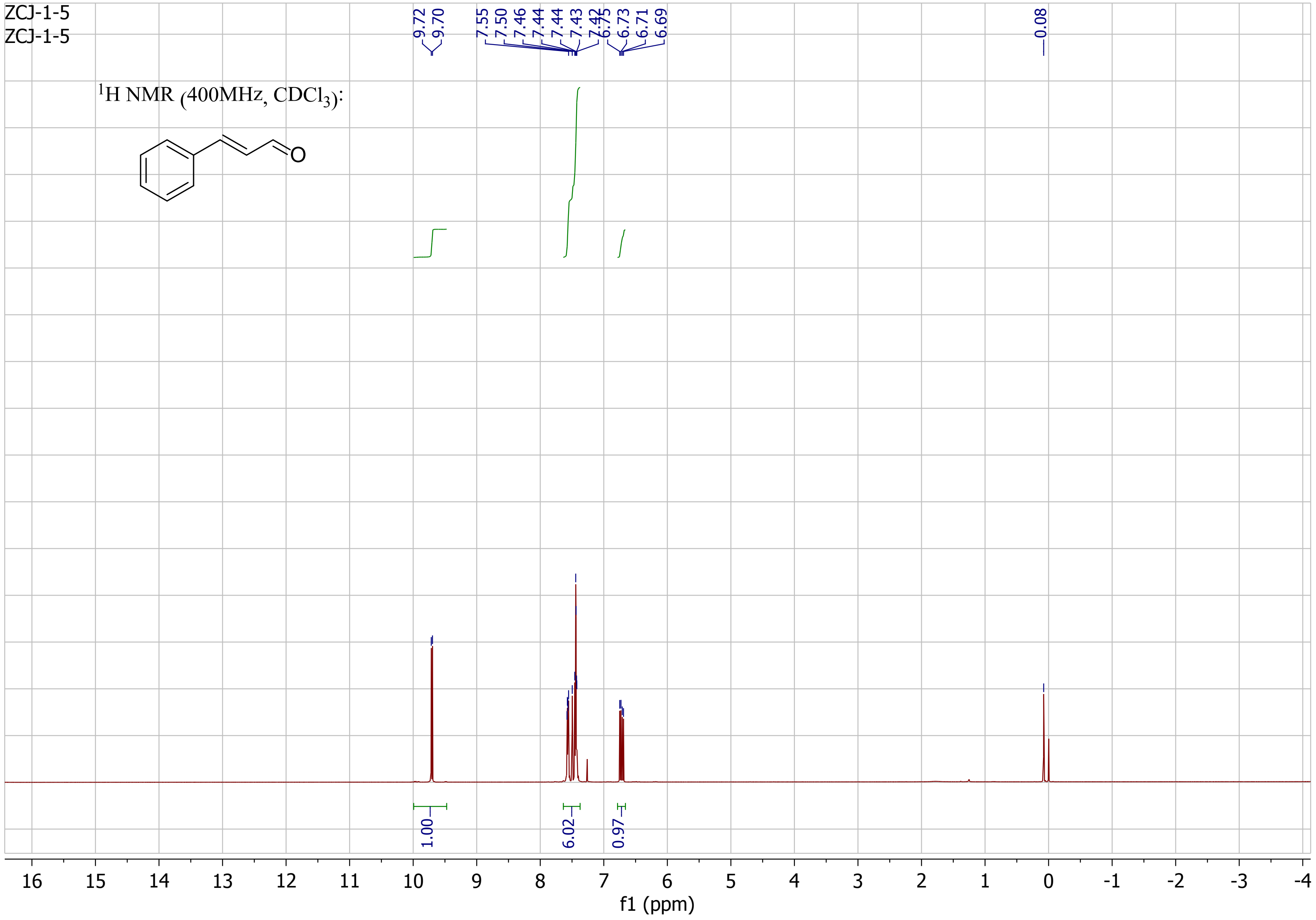

^{13}C NMR (100MHz, $CDCl_3$):

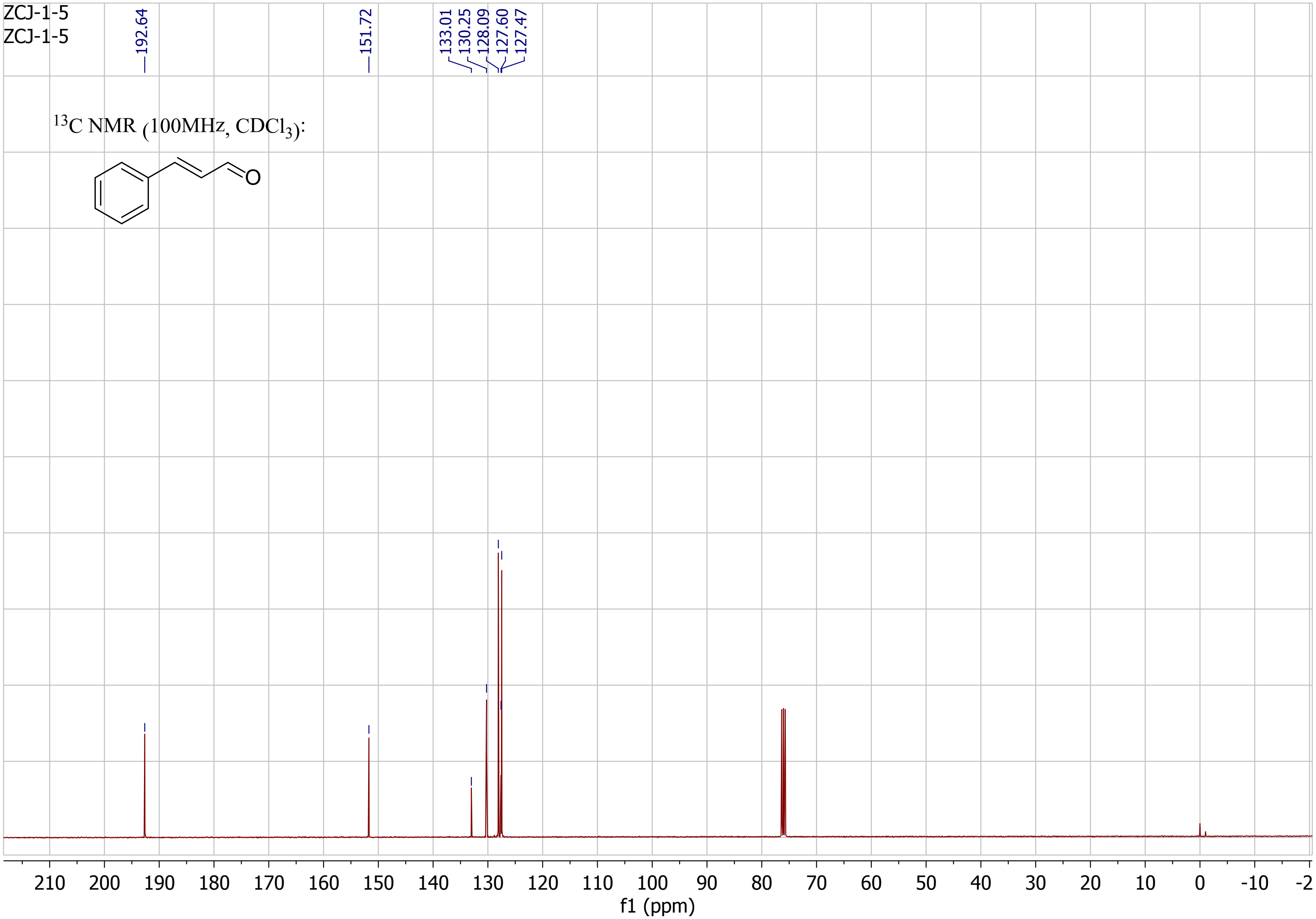

ZCJ-6-1
ZCJ-6-1
10.49
7.39
7.26
2.17
0.07
-0.01
^{1}H NMR (400MHz, $CDCl_3$):
Cl
O
Cl
1.00
3.17
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

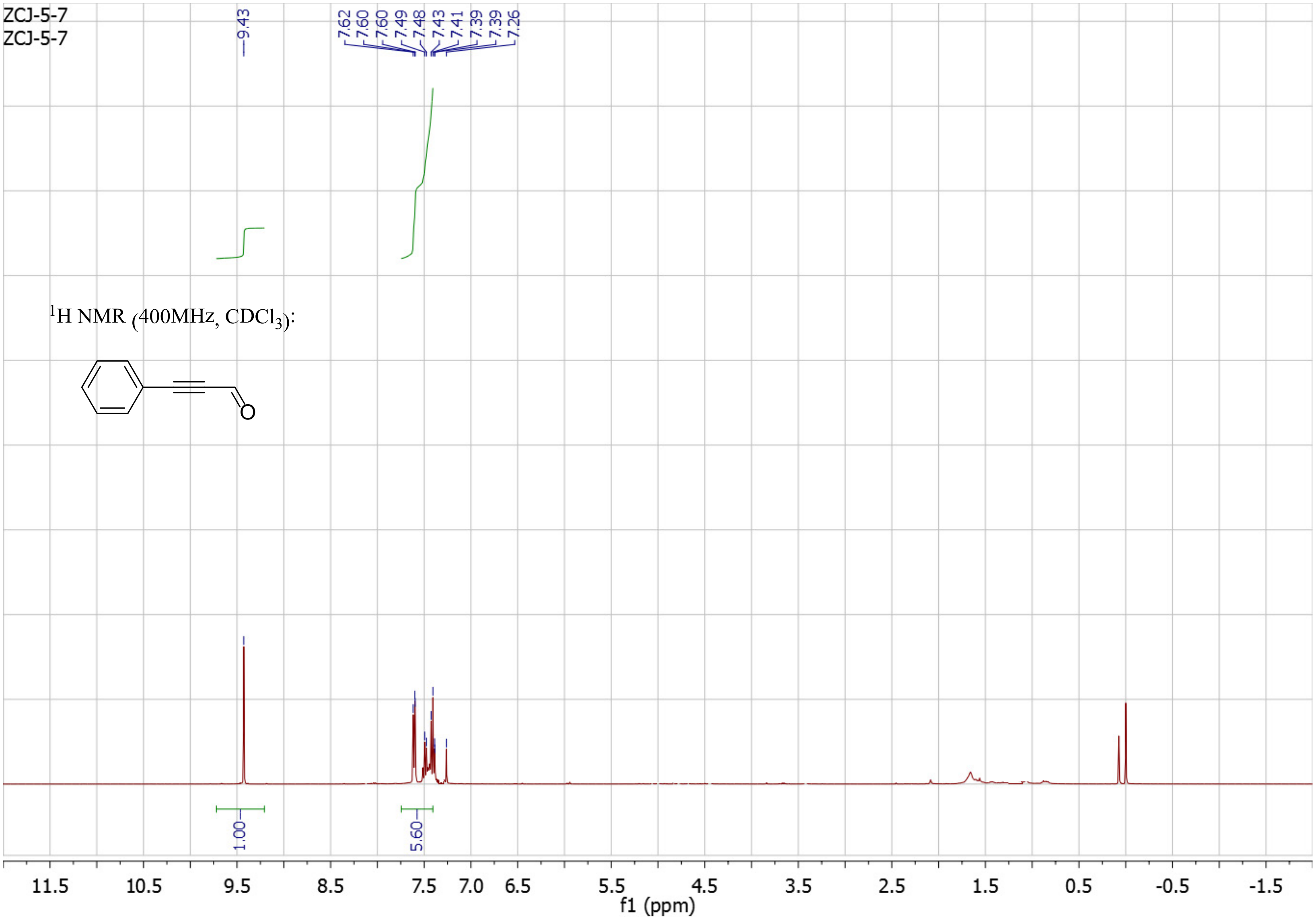

ZCJ-6-1
ZCJ-6-1
188.01
135.75
132.66
129.46
128.74
^{13}C NMR (100MHz, CDCl$_3$):
Cl
O
Cl
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

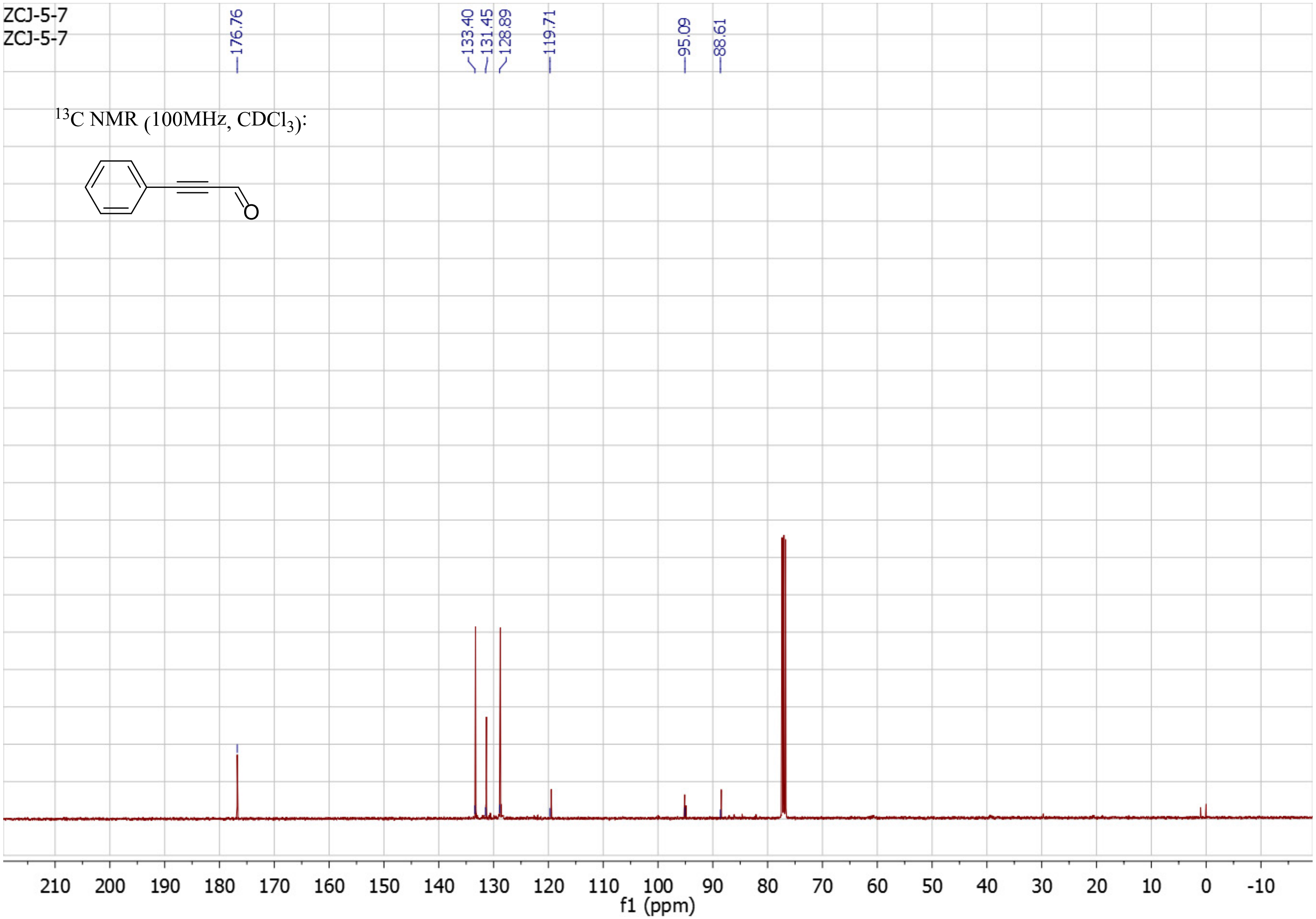

ZCJ-2-5
ZCJ-2-5
10.47
^{1}H NMR (400MHz, CDCl$_3$):
6.80
2.49
2.22
O
1.00
2.11
6.48
3.16
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

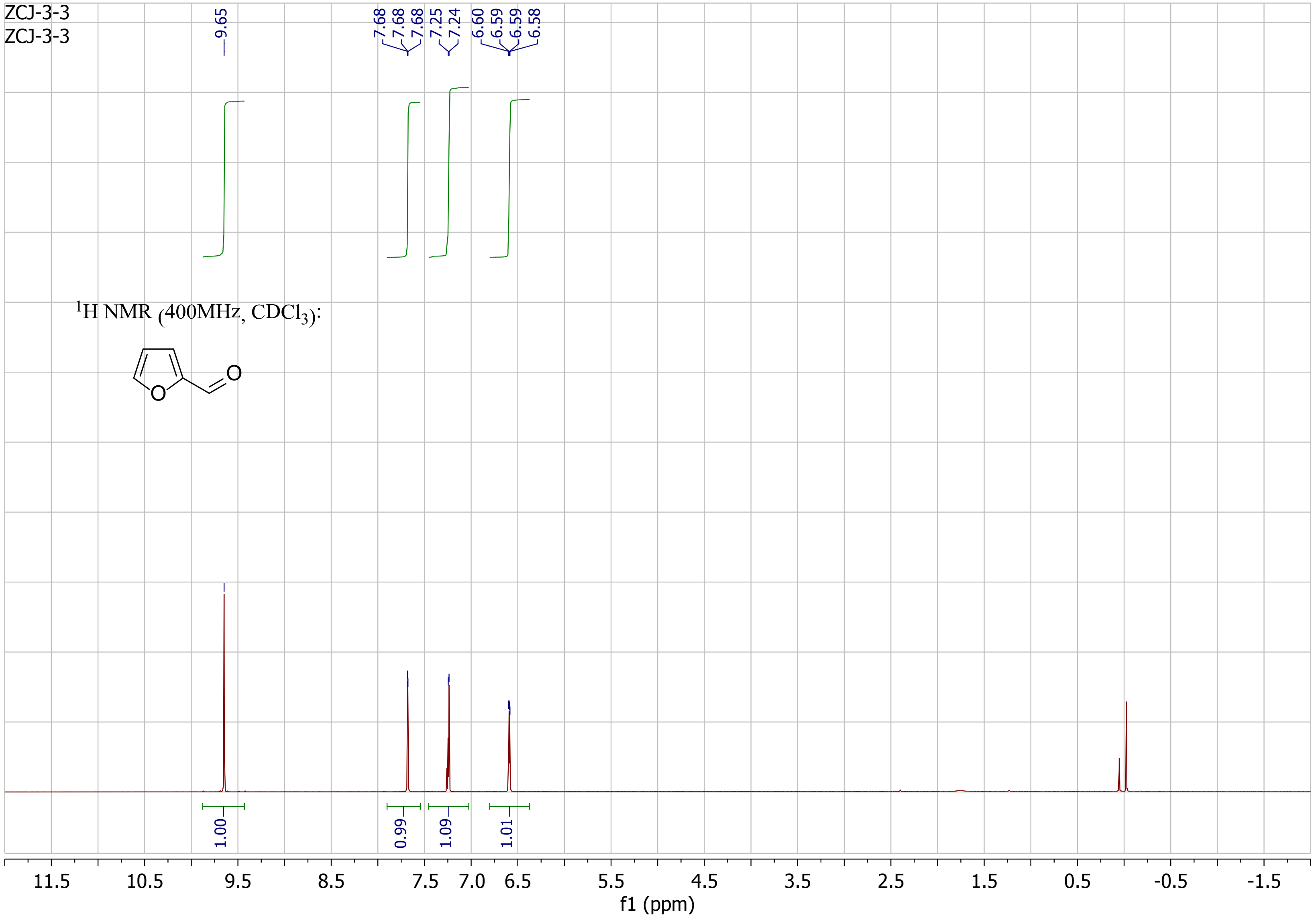

ZCJ-2-5
ZCJ-2-5
192.96
143.81
141.47
130.52
130.00
21.44
20.46
^{13}C NMR (100MHz, CDCl$_3$):
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

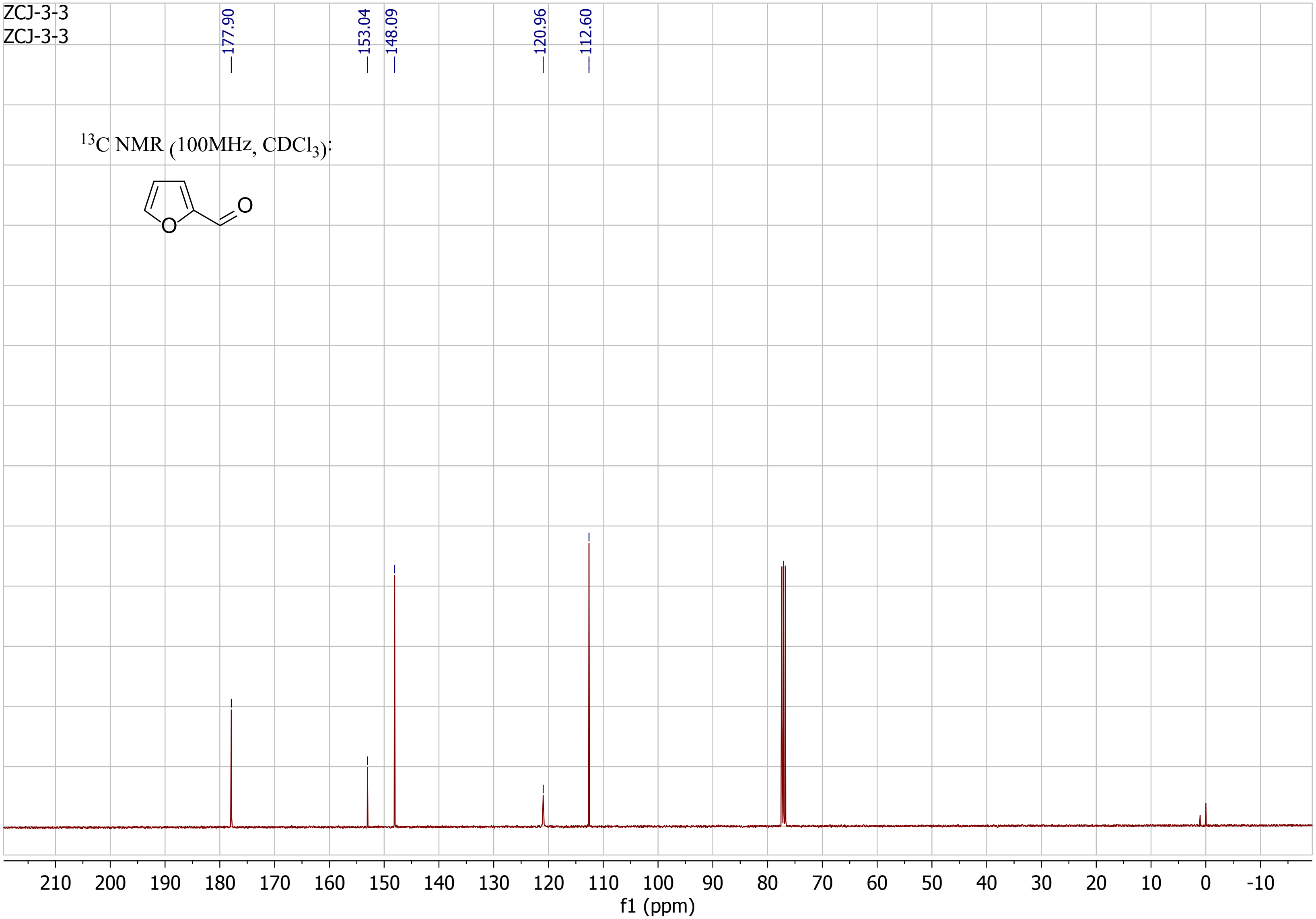

ZCJ-1-5
ZCJ-1-5
^{1}H NMR (400MHz, $CDCl_3$):
O
9.72
9.70
7.55
7.50
7.46
7.44
7.44
7.43
7.42
6.75
6.73
6.71
6.69
0.08
1.00
6.02
0.97
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

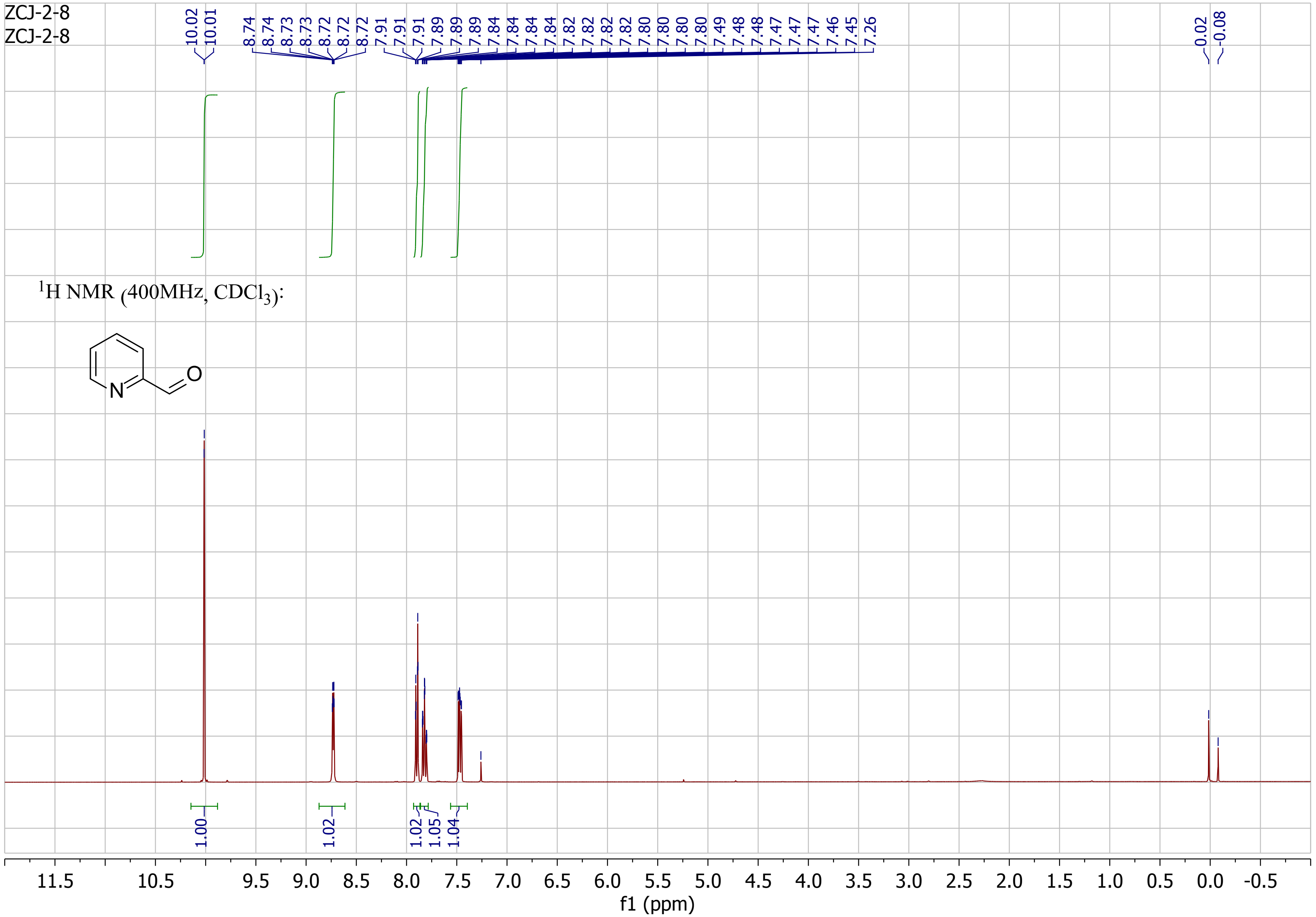

ZCJ-1-5
ZCJ-1-5
192.64
151.72
133.01
130.25
128.09
127.60
127.47
^{13}C NMR (100MHz, CDCl$_3$):
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

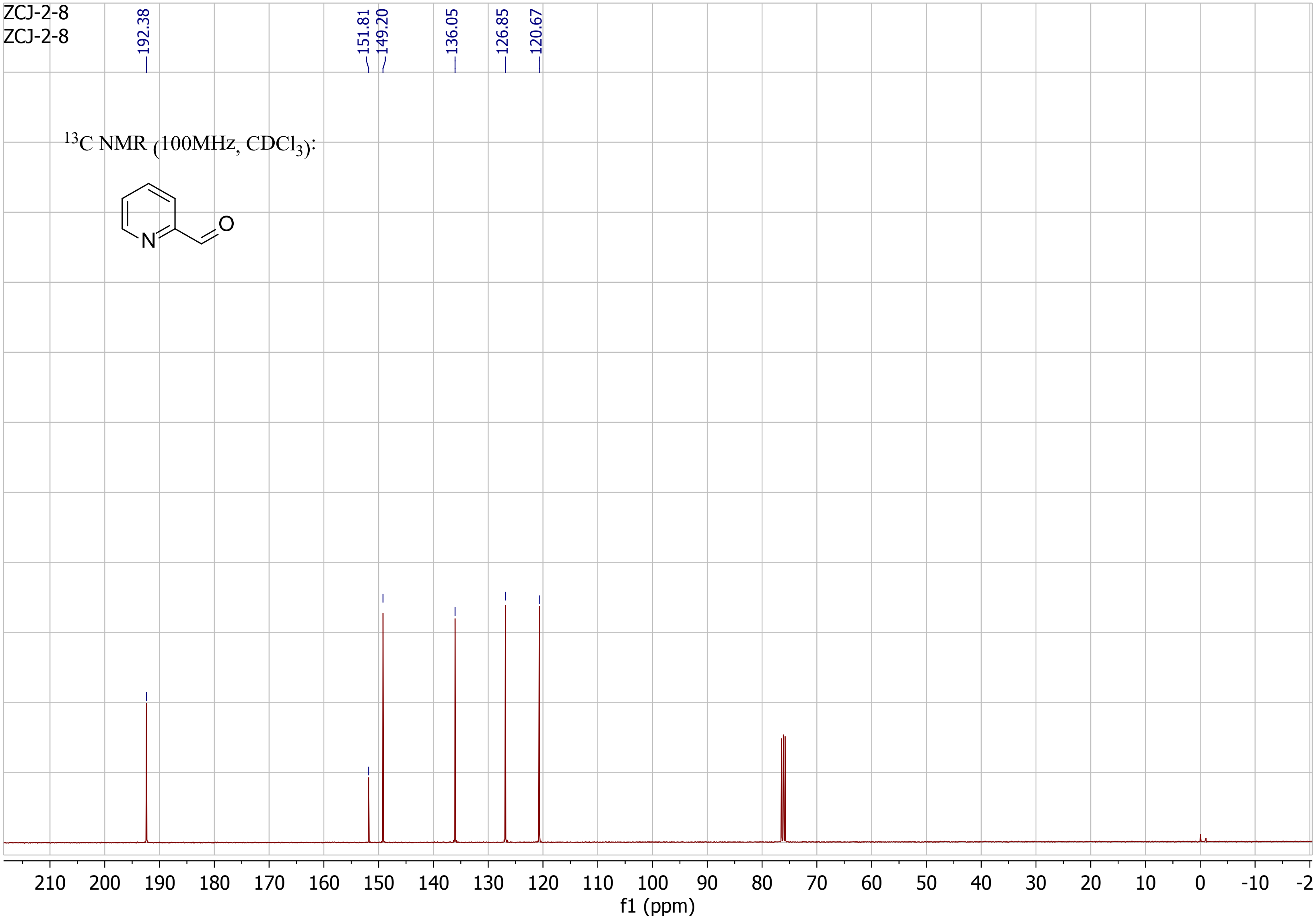

ZCJ-5-7
ZCJ-5-7
9.43
7.62
7.60
7.60
7.49
7.48
7.43
7.41
7.39
7.39
7.26
^{1}H NMR (400MHz, $CDCl_3$):
O
1.00
5.60
11.5
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

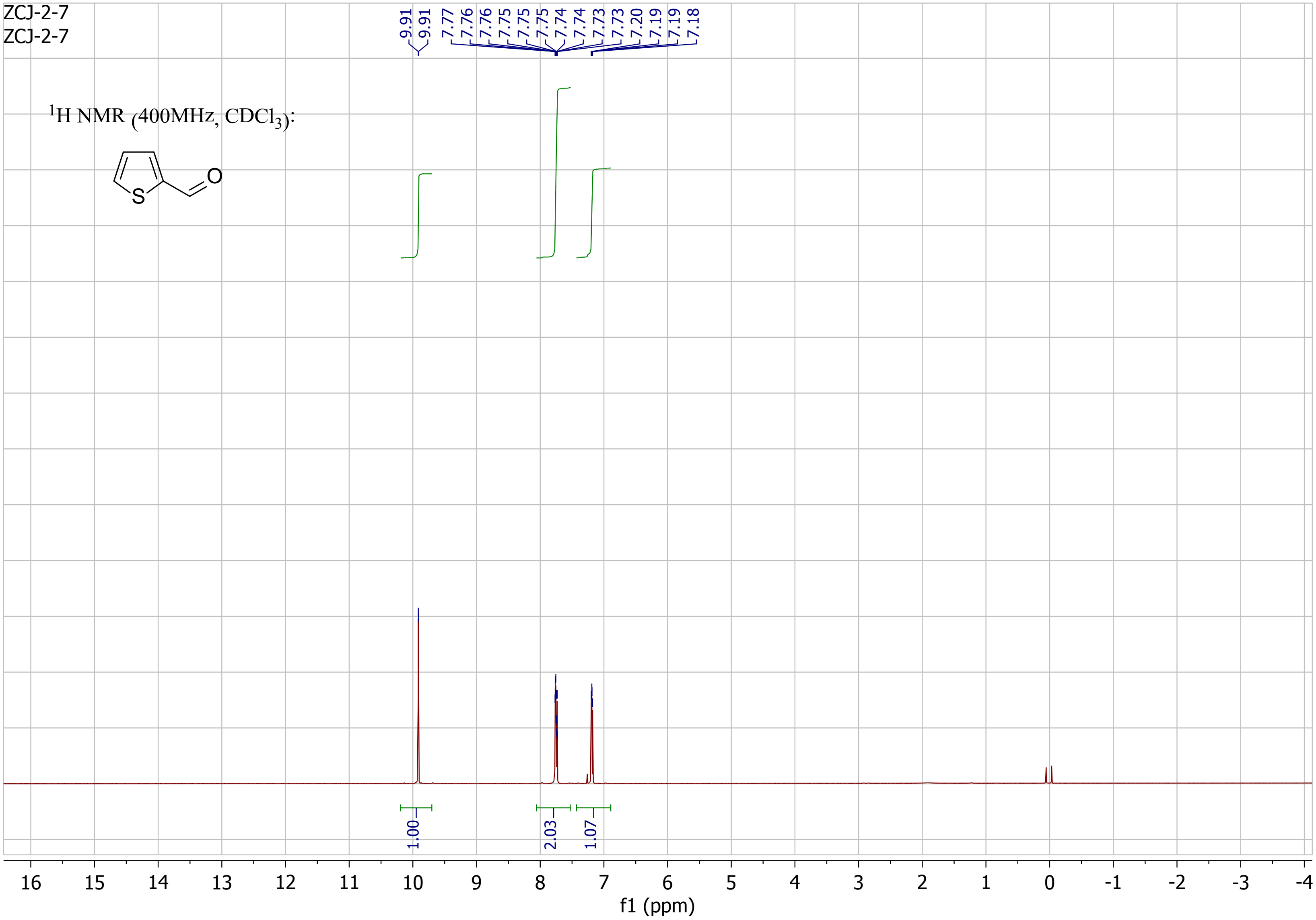

ZCJ-5-7
ZCJ-5-7
176.76
133.40
131.45
128.89
119.71
95.09
88.61
^{13}C NMR (100MHz, CDCl$_3$):
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

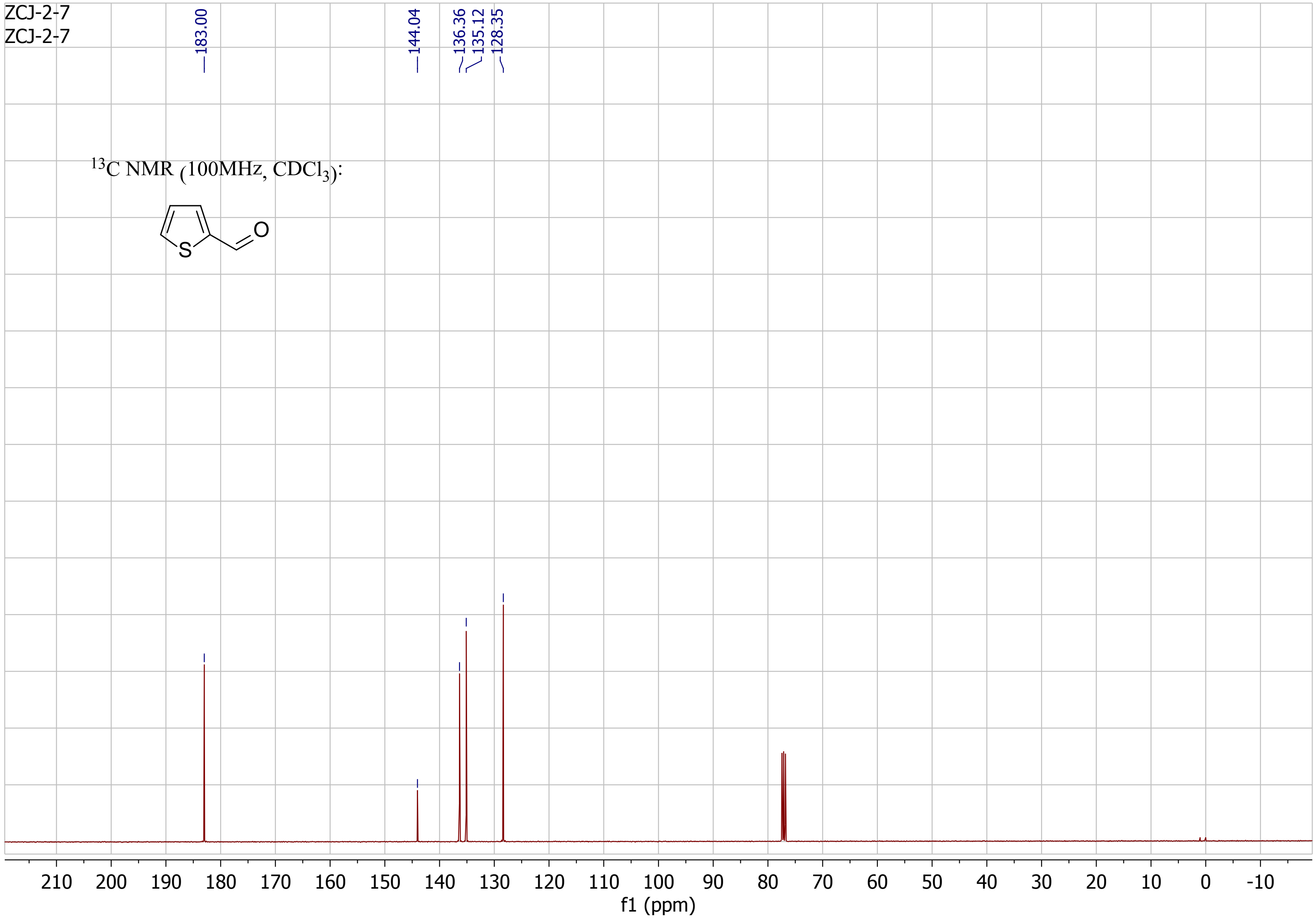

ZCJ-3-3
ZCJ-3-3
9.65
7.68
7.68
7.68
7.25
7.24
6.60
6.59
6.59
6.58
^{1}H NMR (400MHz, CDCl$_3$):
O
O
1.00
0.99
1.09
1.01
11.5
10.5
9.5
8.5
7.5
7.0
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

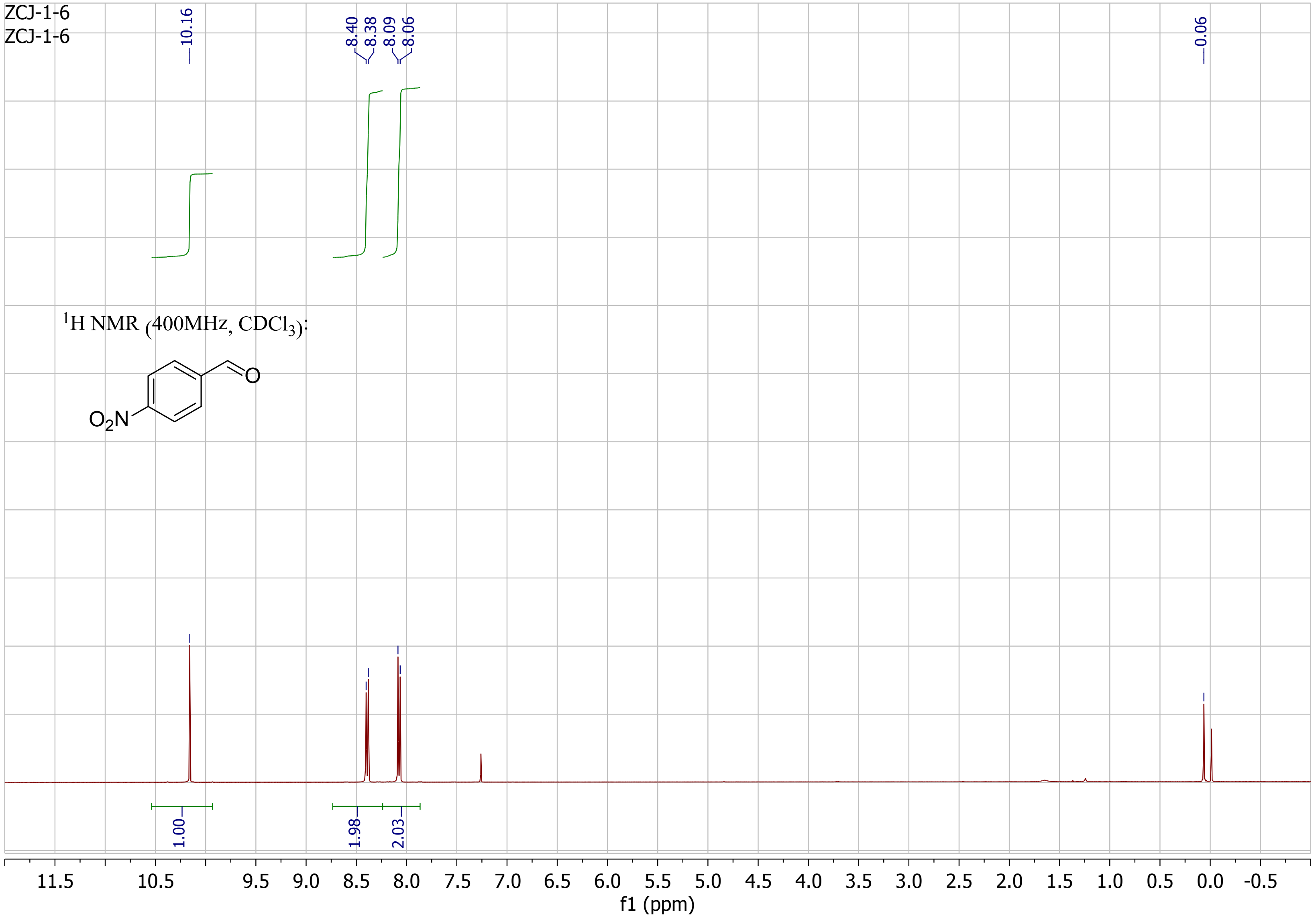

ZCJ-3-3
ZCJ-3-3
177.90
153.04
148.09
120.96
112.60
^{13}C NMR (100MHz, CDCl$_3$):
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

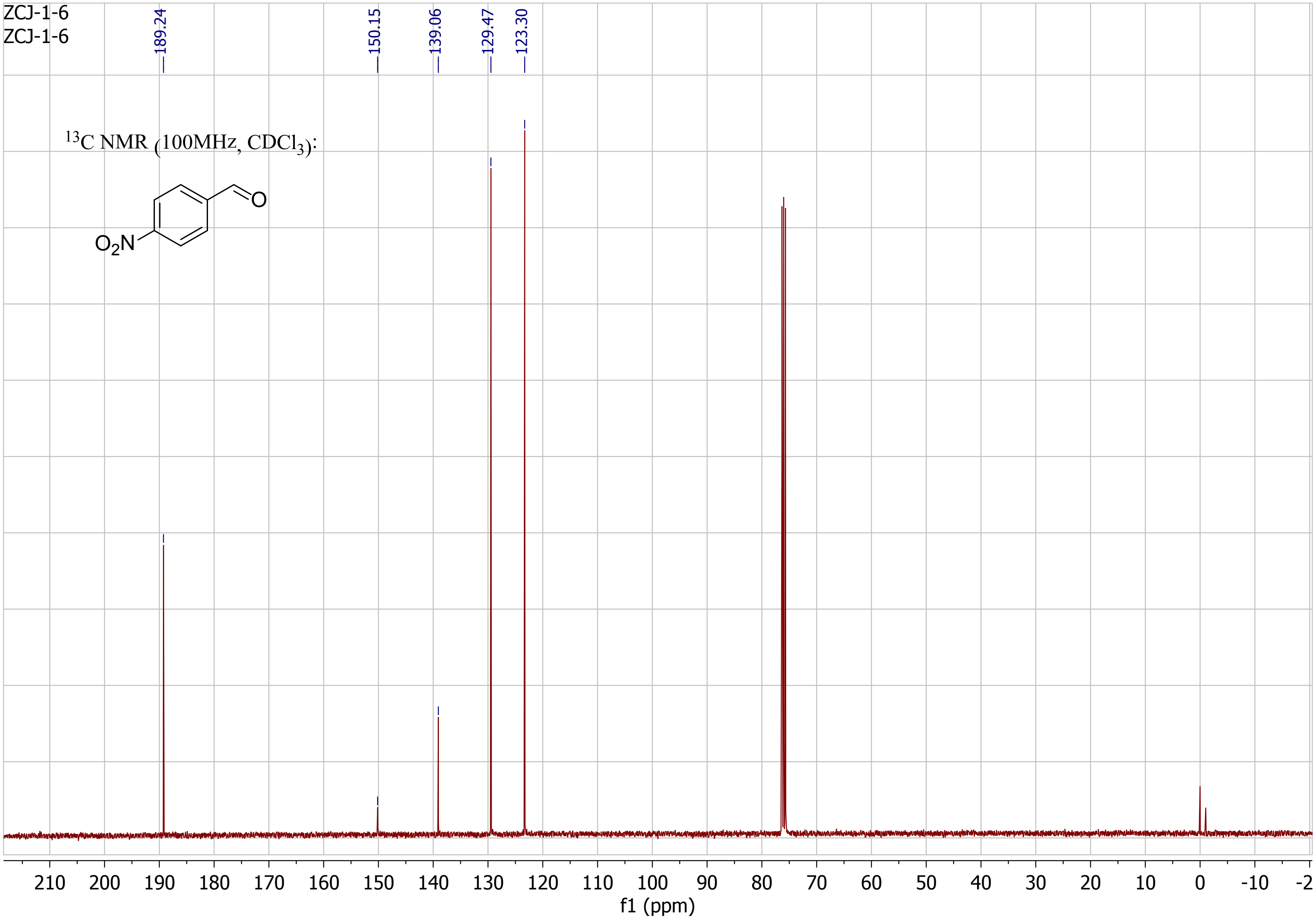

ZCJ-2-8
ZCJ-2-8
10.02
10.01
8.74
8.74
8.73
8.73
8.72
8.72
8.72
7.91
7.91
7.91
7.89
7.89
7.89
7.84
7.84
7.84
7.84
7.82
7.82
7.82
7.82
7.80
7.80
7.80
7.80
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.45
7.26
0.02
-0.08
^{1}H NMR (400MHz, CDCl$_3$):
N
O
1.00
1.02
1.02
1.05
1.04
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

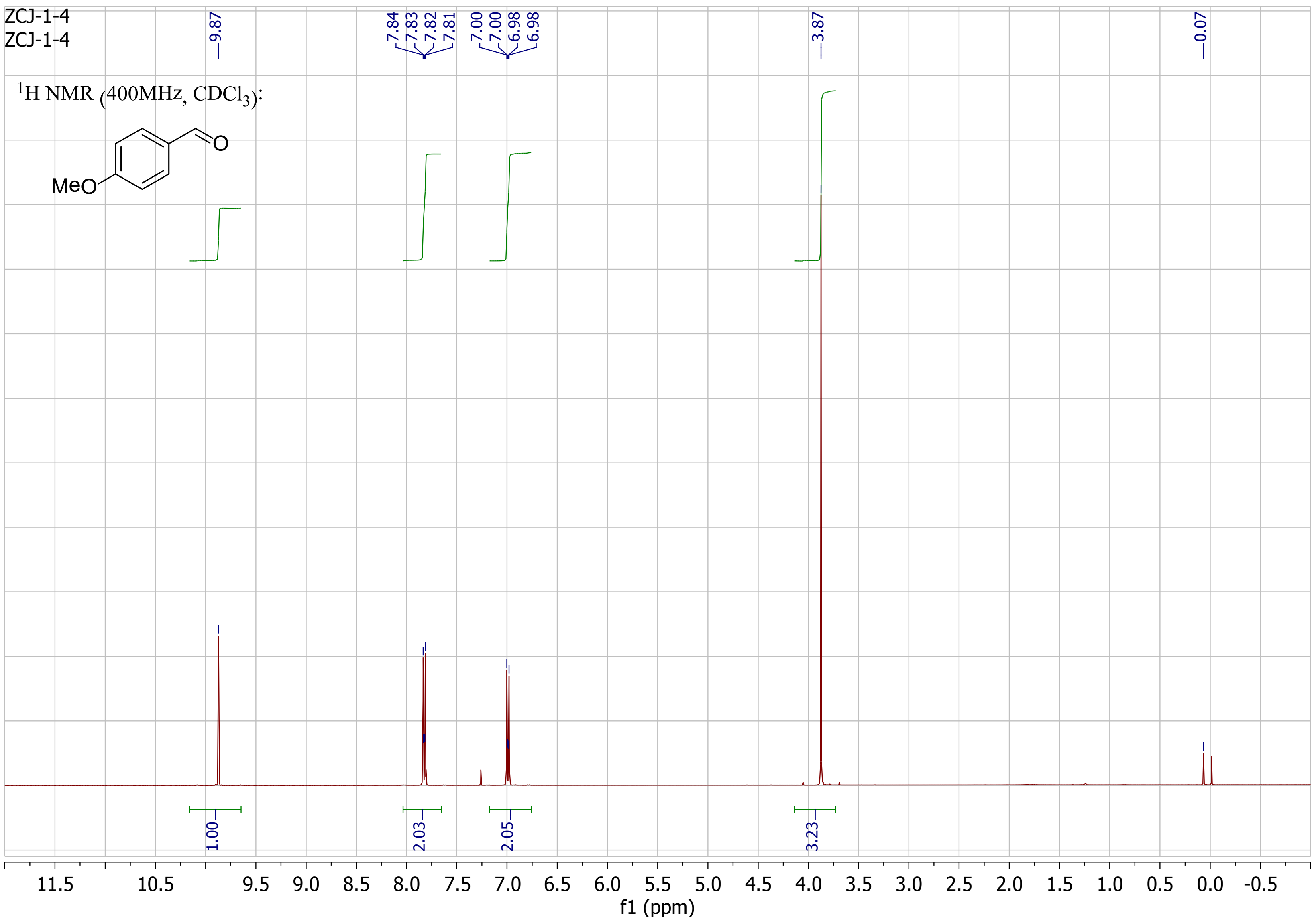

ZCJ-2-8
ZCJ-2-8
192.38
151.81
149.20
136.05
126.85
120.67
^{13}C NMR (100MHz, $CDCl_3$):
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

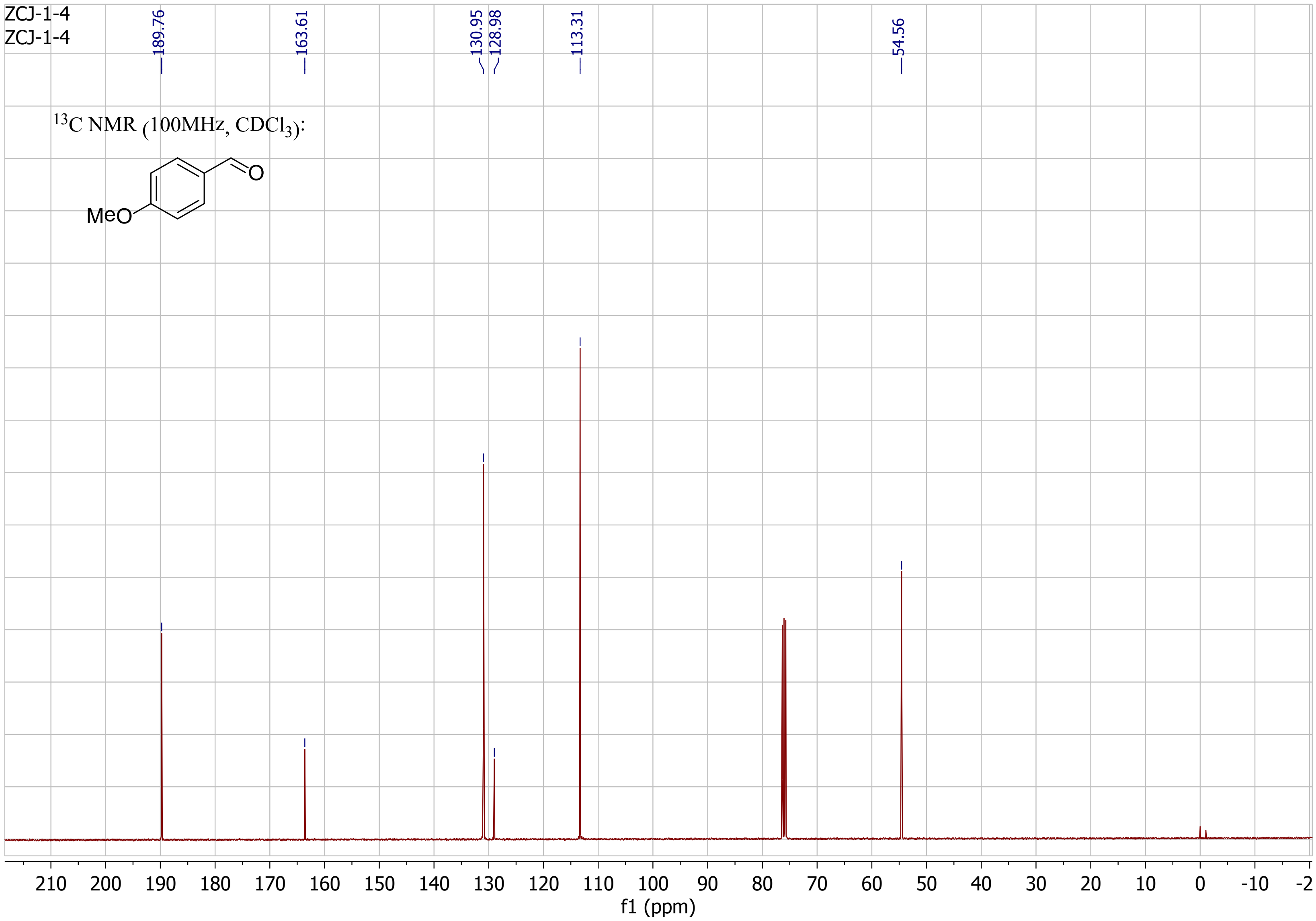

ZCJ-2-7
ZCJ-2-7
^{1}H NMR (400MHz, CDCl$_3$):
S
O
9.91
9.91
7.77
7.76
7.76
7.75
7.75
7.75
7.74
7.74
7.73
7.73
7.20
7.19
7.19
7.18
1.00
2.03
1.07
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)

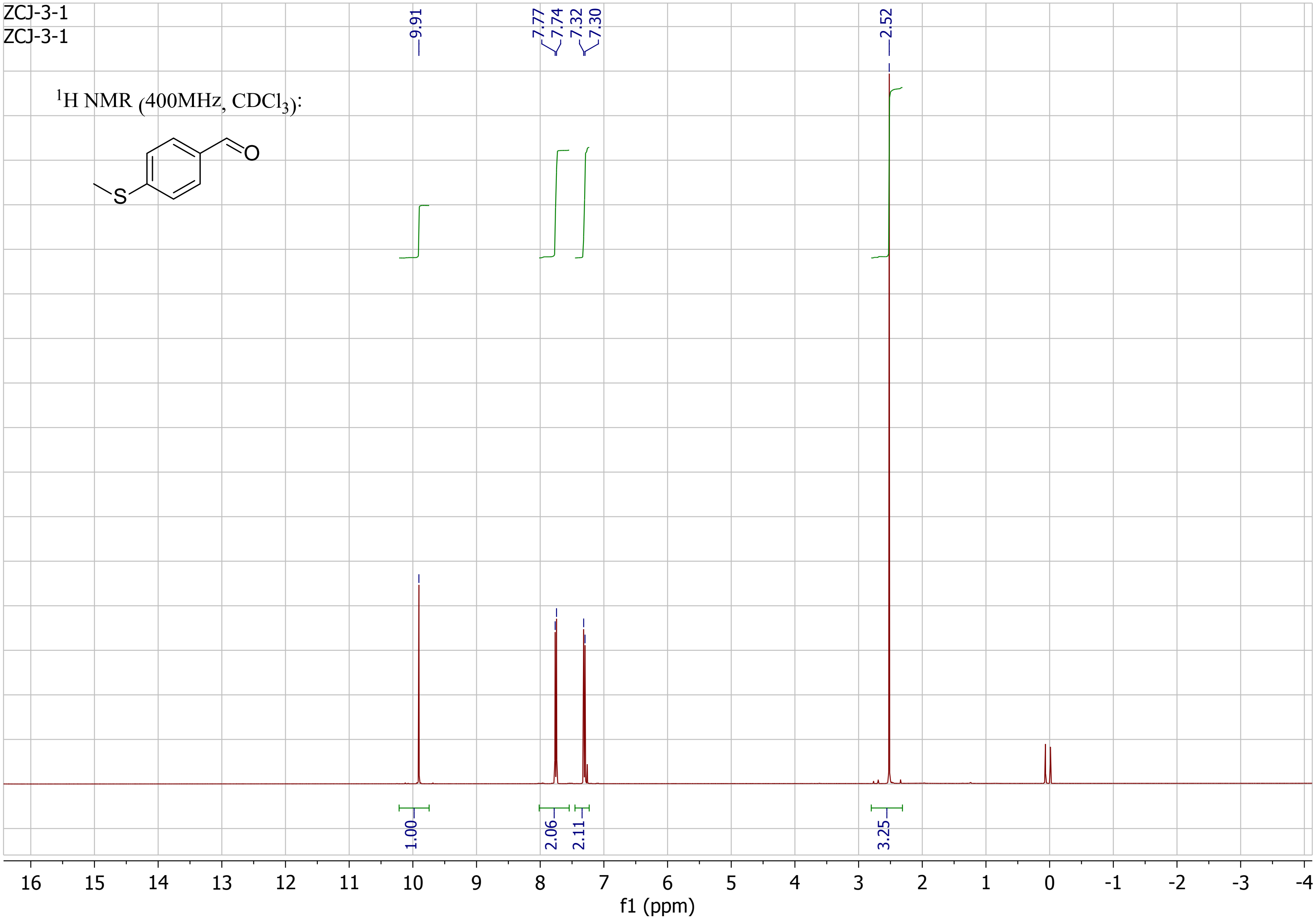

ZCJ-2-7
ZCJ-2-7
183.00
144.04
136.36
135.12
128.35
^{13}C NMR (100MHz, CDCl$_3$):
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

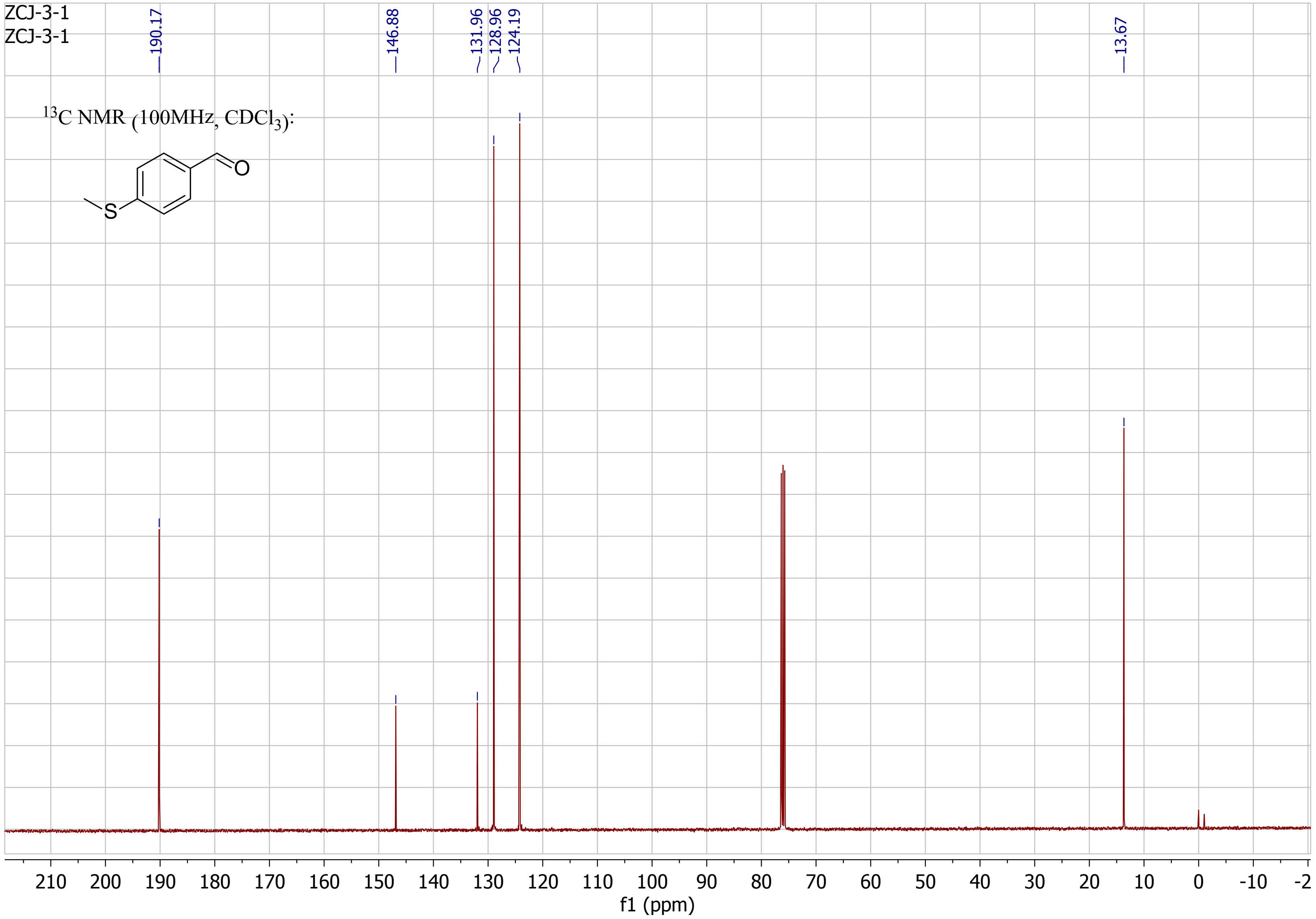

ZCJ-1-6
ZCJ-1-6
10.16
8.40
8.38
8.09
8.06
0.06
¹H NMR (400MHz, CDCl₃):
O
O₂N
1.00
1.98
2.03
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


ZCJ-1-6
ZCJ-1-6
189.24
150.15
139.06
129.47
123.30
^{13}C NMR (100MHz, CDCl$_3$):
O
O_2N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


ZCJ-1-4
ZCJ-1-4
^{1}H NMR (400MHz, CDCl$_3$):
MeO
O
9.87
7.84
7.83
7.82
7.81
7.00
7.00
6.98
6.98
3.87
0.07
1.00
2.03
2.05
3.23
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


ZCJ-1-4
ZCJ-1-4
189.76
163.61
130.95
128.98
113.31
54.56
^{13}C NMR (100MHz, CDCl$_3$):
MeO
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)


ZCJ-3-1
ZCJ-3-1
^{1}H NMR (400MHz, CDCl$_3$):
S
O
9.91
7.77
7.74
7.32
7.30
2.52
1.00
2.06
2.11
3.25
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
f1 (ppm)


ZCJ-3-1
ZCJ-3-1
190.17
146.88
131.96
128.96
124.19
13.67
^{13}C NMR (100MHz, CDCl$_3$):
S
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)