Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Unprecedented Enantioselective Copper Catalyzed Conjugate Addition to Trisubstituted Cyclohexenones. Construction of Chiral Quaternary Centers.

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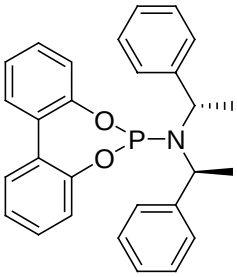
General Procedures. ^{1}H (500 or 400 MHz) and ^{13}C (125 or 100 MHz) NMR spectra were recorded in $CDCl_3$, and chemical shift (δ) are given in ppm relative to residual $CHCl_3$. Evolution of reaction was followed by GC-MS Hewlett Packard (EI mode) HP6890-5973. Optical rotations were measured at 20°C in a 10 cm cell in the stated solvent ; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1} (concentration c given as g/100 mL). Enantiomeric excesses were determined by chiral-GC (capillary column, 10 psi H_2). Temperature programs are described as follows: initial temperature (°C) – initial time (min) – temperature gradient (°C/min) – final temperature (°C) ; retention time (R_T) are given in min. Flash chromatography were performed using silica gel 32-63 μm, 60 Å and a pentane-diethylether mixture as eluant.

All reactions were conducted under argon atmosphere. THF and diethylether were distilled from sodium-benzophenone ketyl under nitrogen. Substituted cyclohexenones (**3**, **4**, **7**, **9** and **11**) were synthesized by the reaction of corresponding Grignard reagent with 3-ethoxycyclohex-2-en-1-one (commercially avaible) in THF. All Grignard reagents were synthesized in THF by addition of the corresponding bromide onto magnesium. 3-methylcyclohex-2-en-1-one (**1**) (Aldrich), trimethylaluminium 2.0M in heptane (Fluka or Aldrich), triethylaluminium 0.9M in hexane (Fluka) and Copperthiophene carboxylate (FrontierScientific) were purchased and used without any further purification.

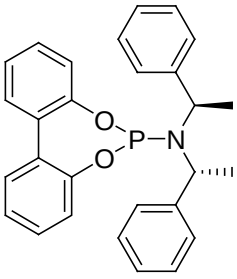
Typical procedure for ligand (L1 to L11) synthesis:

To a stirred mixture of Et_3N (111.1 mmol, 15.5 mL) and PCl_3 (22.2 mmol, 1.9 mL) at 0°C, a solution of amine (22.2 mmol) in THF (10 mL) was added and the reaction mixture was stirred for 3h at room temperature. Biphenol or binaphthol (22.2 mmol) in a solution of THF (5 mL) was slowly added to the reaction mixture at 0°C and then the suspension was stirred at RT overnight. The suspension was diluted in toluene (8 mL) and filtered on neutral alumina, the solution was concentrated and purified by flash chromatography through neutral alumina using dry toluene as eluent, to give the pure ligand as a white solid or a colorless oil.



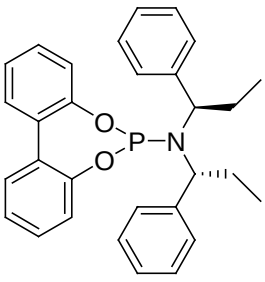
Ligand **L1** : see ref. [1].

^{1}H NMR (400 MHz, $CDCl_3$) : 7.49-7.45 (m, 2H), 7.38-7.10 (m, 16H), 4.60 (q, 1H, J = 7.0 Hz), 4.58 (q, 1H, J = 7.0 Hz), 1.73 (d, 6H, J = 7 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 152.0, 151.9, 151.1, 151.0, 143.0, 131.2, 130.0, 129.8, 129.1, 129.0, 128.9, 128.2, 127.9, 127.7, 126.6, 125.3, 124.0, 122.5, 122.0, 52.7, 52.6, 22.2.
^{31}P (162 MHz, $CDCl_3$) : 147.0.
$[\alpha]_D$: - 236 (c = 3.0 in toluene).



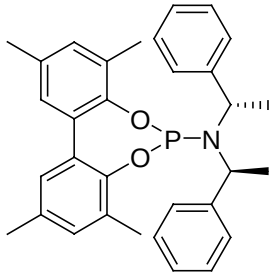
Ligand **L2** : see ref. [1].

^{1}H NMR (400 MHz, $CDCl_3$) : 7.49-7.45 (m, 2H), 7.38-7.10 (m, 16H), 4.60 (q, 1H, J = 7.0 Hz), 4.58 (q, 1H, J = 7.0 Hz), 1.73 (d, 6H, J = 7 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 152.0, 151.9, 151.1, 151.0, 143.0, 131.2, 130.0, 129.8, 129.1, 129.0, 128.9, 128.2, 127.9, 127.7, 126.6, 125.3, 124.0, 122.5, 122.0, 52.7, 52.6, 22.2.
^{31}P (162 MHz, $CDCl_3$) : 147.0.
$[\alpha]_D$: + 236 (c = 3.0, toluene).



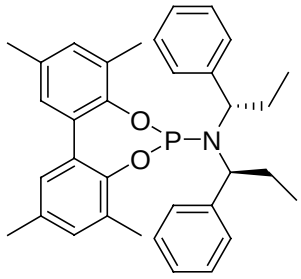
Ligand **L3** : see ref. [1]

^{1}H NMR (400 MHz, $CDCl_3$) : 7.51-7.54 (m, 2H), 7.42-7.36 (m, 2H), 7.32-7.19 (m, 4H), 7.07-7.00 (m, 10H), 4.28 (t, 1H, J = 10.3 Hz), 4.27 (t, 1H, J = 10.3 Hz), 2.32-2.24 (m, 2H), 2.17-2.10 (m, 2H), 0.83 (t, 6H, J = 7.3 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 151.9, 151.8, 150.9, 141.0, 131.4, 129.9, 129.7, 129.1, 129.0, 128.3, 127.5, 126.2, 124.6, 123.7, 122.5, 121.7, 59.8, 59.7, 29.6, 28?3, 11.6.
^{31}P (162 MHz, $CDCl_3$) : 144.4.
$[\alpha]_D$: + 231 (c = 3.5, toluene).



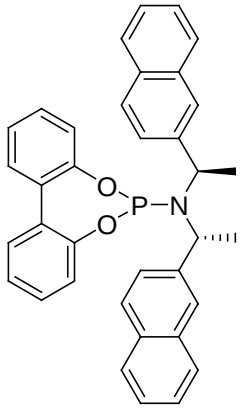
Ligand **L4** : see ref. [1]

^{1}H NMR (400 MHz, $CDCl_3$) : 7.30-6.98 (m, 14H), 4.78-4.58 (m, 2H), 2.47 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.09 (s, 3H), 1.71 (d, 6H, J = 7Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 148.0, 147.9, 147.1, 143.5, 137.5, 133.3, 132.6, 131.0, 130.9, 130.2, 129.3, 129.0, 128.2, 128.1, 127.9, 127.8, 127.6, 126.5, 125.3, 109.6, 52.5, 20.8, 17.3, 16.3.
^{31}P (162 MHz, $CDCl_3$) : 144.4.
$[\alpha]_D$: - 221 (c = 2.2, toluene).



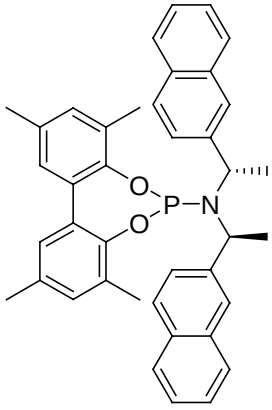
Ligand **L5** :

^{1}H NMR (400 MHz, $CDCl_3$) : 7.10-7.03 (m, 14H), 4.32 (s, 2H), 2.49 (s, 3H), 2.36 (s, 6H), 2.28 (m, 2H), 2.07 (s, 2H), 1.99 (s, 3H), 0.78 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) : 147.9, 147.3, 133.2, 132.7, 131.2, 131.1, 130.9, 130.4, 130.3, 129.3, 128.7, 128.2, 127.6, 126.4, 60.2, 23.2, 20.9, 20.8, 17.2, 16.4, 11.9.
^{31}P (162 MHz, $CDCl_3$) : 144.4.
$[\alpha]_D$: - 215 (c = 1.06, $CHCl_3$).



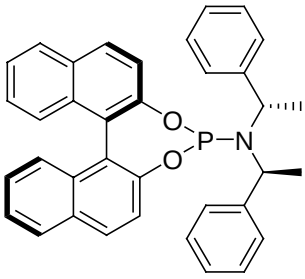
Ligand **L6** : see ref. [2]

^{1}H NMR (500 MHz, $CDCl_3$) : 7.53–7.17 (m, 22H), 4.82–4.78 (m, 2H), 1.90 (d, 6H, J = 7.0 Hz).
^{13}C NMR (125MHz, $CDCl_3$) : 151.9, 151.8, 151.0, 140.4, 132.9, 132.4, 131.2, 130.0, 129.8, 129.2, 129.0, 128.2, 127.9, 127.3, 127.0, 126.1, 125.7, 125.6, 125.3, 124.7, 124.1, 122.5, 122.1, 52.8, 52.7, 22.1.
^{31}P NMR (203 MHz; $CDCl_3$) : 146.3.
$[\alpha]_D$: + 405 (c = 1.12, $CHCl_3$).



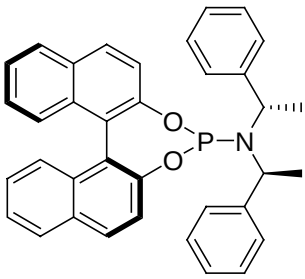
Ligand **L7** : see ref. [2]

^{1}H NMR (400 MHz, $CDCl_3$) : 7.67 (d, 2H, J = 6,8 Hz), 7.52–7.02 (m, 16H), 4.89 (m, 2H), 2.55 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.11 (s, 3H), 1.85 (d, 6H, J = 4,0 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 147.5, 141.2, 133.8, 133.3, 133.1, 132.7, 131.4, 130.6, 130.5, 129.7, 128.6, 128.2, 127.7, 127.6, 127.2, 126.6, 126.0, 125.8, 53.1, 53.0, 21.2, 17.8, 16.9.
^{31}P NMR (162MHz, $CDCl_3$) : 142.0.
$[\alpha]_D$: - 435 (c = 1.0, $CHCl_3$).



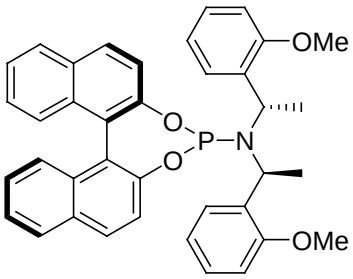
Ligand **L8** : see ref. [3]

All analysis are in accordance with reported data [3].



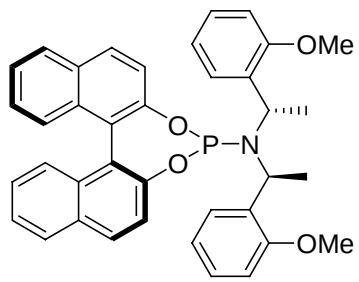
Ligand **L9** : see ref. [3]

All analysis are in accordance with reported data [3].



Ligand **L10** : see ref. [4]

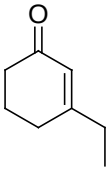
^{1}H NMR (400 MHz, $CDCl_3$) : 8.05-5.03 (m, 20H), 5.07 (dq, 2H, J_1 = 1.04 Hz, J_2 = 7.08 Hz), 3.52 (s, 6H), 1.61 (d, 6H, J = 7.08 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 155.9, 150.7, 150.16, 133.0, 132.3, 131.4, 130.5, 129.5, 128.4, 128.2, 127.5, 127.4, 127.3, 127.2, 126.0, 125.8, 124.7, 124.4, 124.4, 124.3, 122.8, 122.5, 121.8, 119.4, 109.3, 65.9, 54.6, 48.3, 48.2, 22.2, 15.3.
^{31}P NMR (162 MHz, $CDCl_3$) : 152.15.
$[\alpha]_D$ = - 272.2 (c 1.0, CHCl3).



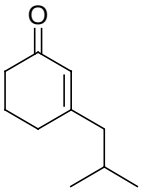
Ligand **L11** : see ref. [4]

^{1}H NMR (400 MHz, $CDCl_3$) : 8.04-6.52 (m, 20H), 4.99 (dq, 2H, J_1 = 1.24 Hz, J_2 = 7.08 Hz), 3.58 (s, 6H), 1.55 (d, 6H, J = 7.08 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 156.1, 149.9, 132.8, 132.5, 131.4, 130.3, 129.2, 128.3, 128.0, 127.7, 127.6, 127.4, 127.3, 125.9, 125.6, 124.7, 124.5, 124.2, 122.7, 1212.5, 119.6, 109.2, 54.6, 50.3, 50.2, 22.6, 22.5.
^{31}P NMR (162 MHz, $CDCl_3$) : 155.25.
$[\alpha]_D$ = + 144.3 (c 1.1, $CHCl_3$).

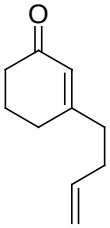
Typical procedure for 3-substituted cyclohex-2-en-1-ones synthesis. A flame-dried flask was charged with Grignard reagent (2.0 eq.) and cooled to 0°C. The ethoxycyclohex-2-en-1-one (50 mmol) in THF (40mL) was added dropwise. Once the addition was complete the reaction mixture was left at room temperature until complete disappearance of the starting material. The reaction was hydrolyzed by addition of aqueous sulfuric acid (5% w/w). Diethyl ether (50 mL) was added and the aqueous phase was separated and extracted further with diethyl ether (3 x 20mL). The combined organic fractions were washed with $NaHCO_3$, brine and water, dried over sodium sulfate, filtered and concentrated *in vacuo*. The oily residue was purified by Kugelrohr distillation under reduced pressure.



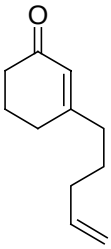
3-ethylcyclohex-2-enone (3) [5]:
^{1}H NMR (500 MHz, $CDCl_3$) : 5.87 (t, 1H, J = 1.4 Hz), 2.36 (t, 2H, J = 3.3 Hz), 2.29 (t, 2H, J = 5.7 Hz), 2.27-2.22 (m, 2H), 1.99 (m, 2H), 1,1 (t, 3H, J = 7.4 Hz).
^{13}C NMR (125 MHz, $CDCl_3$) : 200, 167.8, 124.5, 37.4, 30.8, 29.7, 22.7, 11.2.



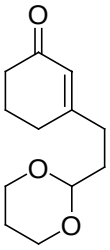
3-*isobutyl*-butylcyclohex-2-enone (4) [6]:
^{1}H NMR (400 MHz, $CDCl_3$) : 5.84 (s, 1H), 2.35 (t, 2H, J = 6.7 Hz), 2.25 (t, 2H, J = 5.9 Hz), 2.07 (d, 2H, J = 7.3 Hz), 1.97 (quint., 2H, J = 6.4 Hz), 1.87 (m, 1H), 0.9 (d, 6H, J = 6.6 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 199.9, 165.7, 126.9, 47.7, 37.3, 29.7, 26.4, 22.8, 22.5.



3-(3-butenyl)cyclohex-2-enone (7) [7]:
^{1}H NMR (500 MHz, $CDCl_3$) : 5.80 (s, 1H), 5.75-5.67 (m, 1H), 4.98 (dd, 1H, J_1 = 17.1 Hz, J_2 = 1.5 Hz), 4.92 (dd, 1H, J_1 = 9.4 Hz, J_2 = 1.6 Hz), 2.29-2.19 (m, 8H), 1.94-1.89 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) : 199.9, 165.6, 137.1, 126.1, 115.7, 37.5, 37.4, 31.1, 29.9, 22.8.

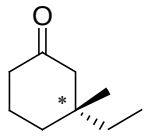


3-(3-pentenyl)cyclohex-2-enone (9) [8]:
^{1}H NMR (400 MHz, $CDCl_3$) : 5.82 (s, 1H), 5.78-5.68 (m, 1H), 4.99-4.91 (m, 2H), 2.31-1.90 (m, 10H), 1.59-1.51 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) : 200.0, 166.5, 138.0, 125.9, 115.5, 37.5, 37.5, 33.4, 29.9, 26.2, 22.9.

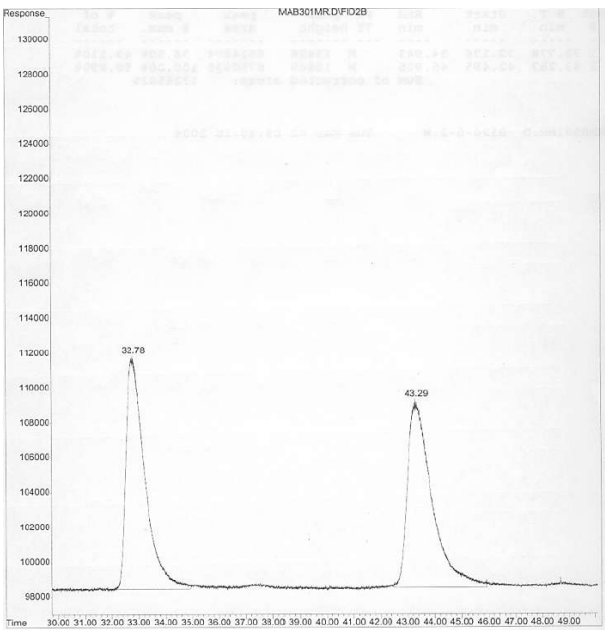


3-[2-(1-3-dioxan-2-yl)ethyl]cyclohex-2-enone (11) [8]:
^{1}H NMR (400 MHz, $CDCl_3$) : 5.70 (s, 1H), 4.39 (t, 1H, J= 5.0Hz), 3.93 (dd, 2H, J_1 = 10.6Hz, J_2 = 5.0Hz), 3.60 (td, 2H, J_1 = 12.4Hz, J_2 = 2.3Hz), 2.21-2.14 (m, 6H), 1.86-1.80 (m, 2H), 1.65-1.60 (m, 2H), 1.20 (dt, 2H, J_1 = 13.4Hz, J_2 = 1.2Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 199.6, 165.8, 125.4, 101.0, 66.7, 37.2, 32.1, 32.0, 29.6, 25.6, 22.6.

Typical procedure for enantioselective copper catalyzed conjugate addition with trialkylaluminium reagent. A flame-dried Schlenk tube was charged with copper salt (2.0 mol%) and the chiral ligand (4.0 mol%). Solvent (2 mL) was added and the mixture was stirred at room temperature for 30 min before being cooled to –30°C in an ethanol cold bath. The trialkylaluminium (2.0 eq. for Me_3Al, 1.0mL of a 2M solution in heptane, or 1.4 eq. for Et_3Al, 1.6 mL of a 0.9M in hexane) was introduced dropwise at such rate that the temperaure did not rise above –30°C, and the reaction mixture was stirred at -30°C for a further 5 min. Then the Michael acceptor (1.0 eq., 1.0 mmol) in diethylether or THF (0.5 mL) was added dropwise. Once the addition was complete the reaction mixture was left at –30°C overnight. The reaction was hydrolyzed by addition of MeOH at –30°C, followed by NH_4Cl sat. or HCl 2N (3mL) at room temperature. Diethyl ether (10 mL) was added and the aqueous layer was separated and extracted further with diethyl ether (3 x 3mL). The combined organic fractions were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The oily residue was purified by flash column chromatography (eluent = pentane : diethylether) to yield the 1,4-adduct. Gas Chromatography on a chiral stationary phase indicated the enantiomeric excess of 1-4adduct.



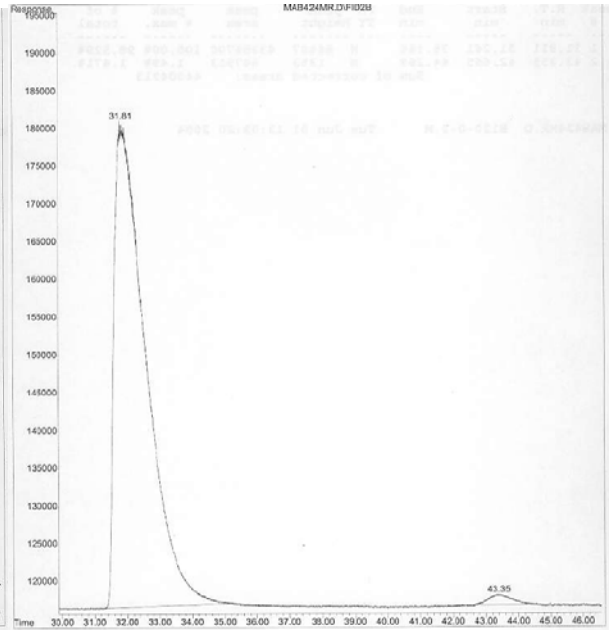
3-ethyl-3-methylcyclohexanone (2) [9]:
^{1}H NMR (400 MHz, $CDCl_3$) : 2.26 (t, 2H, J = 6.6 Hz), 2.16 (d of AB sys., 1H, J = 13.6 Hz), 2.08 (d of AB sys., 1H, J = 13.6 Hz), 1.88-1.81 (m, 2H), 1.64-1.48 (2m, 2H), 1.33 (q, 2H, J = 7.3 Hz), 0.88 (s, 3H), 0.83 (t, 3H, J = 7.6 Hz).
^{13}C NMR (100 MHz, $CDCl_3$) : 212.8, 53.7, 41.4, 39.0, 35.7, 34.3, 24.7, 22.5, 8.1.
$[\alpha]_D$: +5.45 ($CHCl_3$, c = 1.64, ee = 92% ***R***. Absolute configuration was assigned in analogy with **13**). Enantiomeric excess was measured by chiral GC (lipodex E, isotherm 60°C, Rt_1 = 32.8 (*R*), Rt_2 = 43.3 (*S*)).



Signal : MAB301MR.D\FID2B

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	32.778	32.176	34.943	M	13426	6514894	96.50%	49.110%
2	43.287	42.495	45.905	M	10849	6750935	100.00%	50.890%

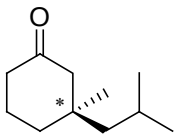
Sum of corrected areas: 13265829



Signal : MAB424MR.D\FID2B

peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	31.811	31.261	35.146	M	64487	43356700	100.00%	98.529%
2	43.355	42.665	44.269	M	1353	647513	1.49%	1.471%

Sum of corrected areas: 44004213



3-*i*-butyl-3-methylcyclohexanone (5):

The crude mixture was purified by flash chromatography (pentane : Et_2O, 80:20, Rf = 0.53, anisaldehyde as revelator) to afford the title compound as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) : 2.29-2.23 (m, 2H), 2.19 (d of AB sys., 1H, J = 13.4 Hz), 2.09 (d of AB sys., 1H, J = 13.4 Hz), 1.93-1.51 (3m, 5H), 1.19 (t, 2H, J = 5.0 Hz), 0.93 (s, 3H), 0.91 (dd, 6H, J_1 = 6.6 Hz, J_2 = 1.0 Hz).

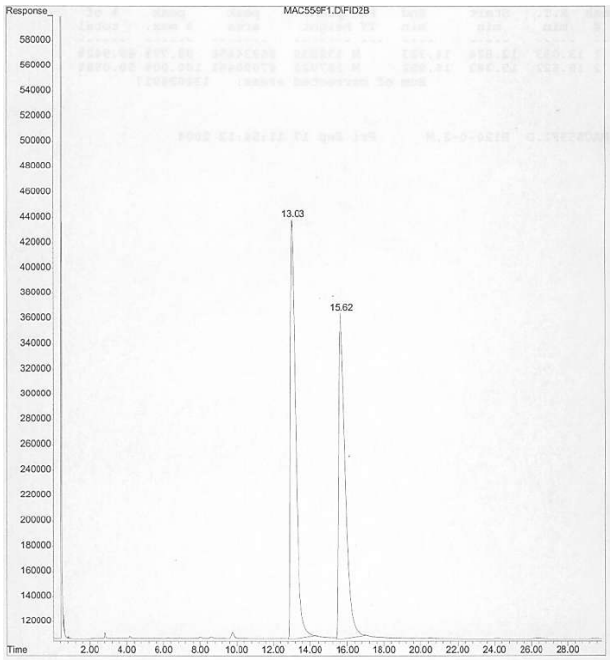
^{13}C NMR (100 MHz, $CDCl_3$) : 212.7, 54.6, 51.2, 41.3, 39.7, 36.8, 25.8, 25.7, 25.6, 24.2, 22.5.

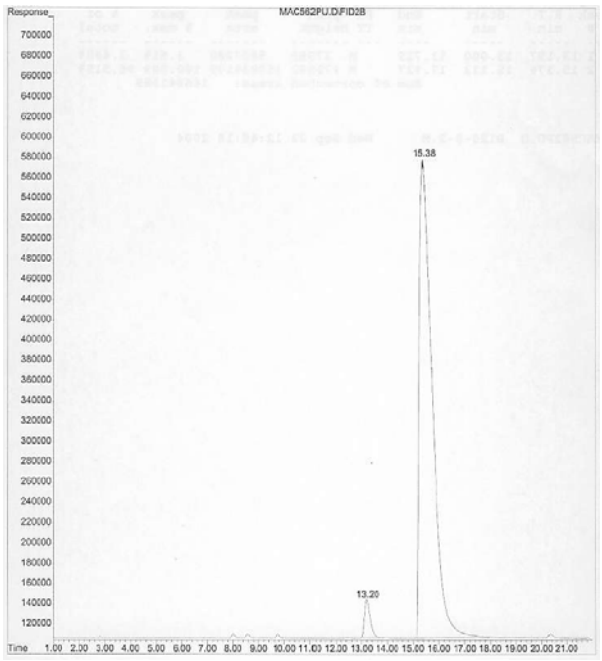
IR (neat, cm^{-1}) : 2956, 1716, 1467.

MS (IE) : 153(2), 125 (9), 112 (9), 111 (100), 110 (3), 107 (2), 98 (2), 97 (9), 95 (7), 93 (2), 85 (1), 84 (2), 83 (22), 82 (4), 81 (2), 79 (2), 77 (1), 71 (2), 70 (6), 69 (25), 68 (3), 67 (6), 65 (1), 58 (1), 57 (5), 56 (15), 55 (98), 54 (2), 53 (5).

HRMS (ESI-MS) : $[M+Na]^+$ found 191.1408390, calcld. for $C_{11}H_{20}ONa$: 191.1406364.

$[\alpha]_D$: -5.25 ($CHCl_3$, c = 1.73, ee = 93% *R*. Absolute configuration was assigned in analogy with **13**). Enantiomeric excess was measured by chiral GC (lipodex E, isotherm 80°C, Rt_1 = 13.0 (*S*), Rt_2 = 15.6 (*R*)).





Signal : MAC559F1.D\FID2B

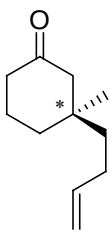
peak #	R.T. min	Start min	End min	PK	peak TY	peak height	peak area	% max.	% of total
1	13.033	12.824	14.323		M	332036	66934456	99.77%	49.942%
2	15.622	15.383	16.952		M	257923	67090461	100.00%	50.058%

Sum of corrected areas: 134024917

Signal : MAC562PU.D\FID2B

peak #	R.T. min	Start min	End min	PK	peak TY	peak height	peak area	% max.	% of total
1	13.197	13.000	13.719		M	37989	5807280	3.61%	3.485%
2	15.376	15.133	17.927		M	472582	160834109	100.00%	96.515%

Sum of corrected areas: 166641389

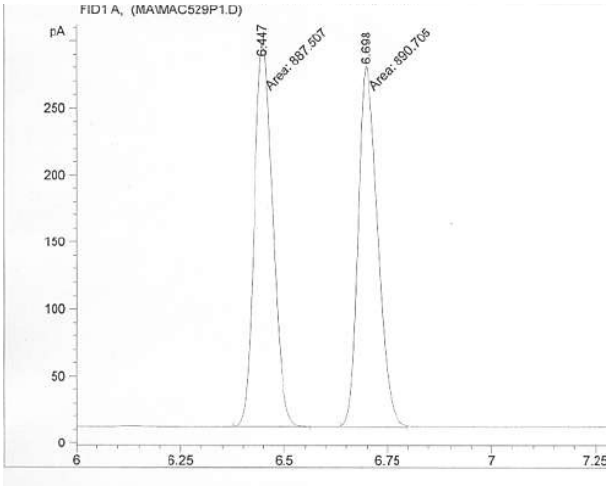


3-(3-butenyl)-3-methylcyclohexanone (8) [7]:

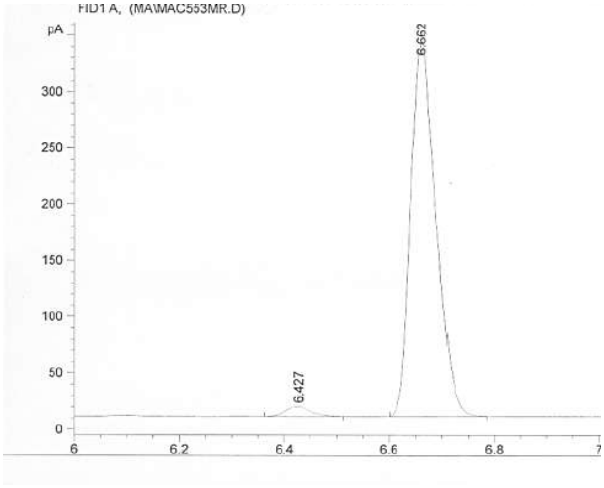
^{1}H NMR (500 MHz, $CDCl_3$) : 5.83-5.75 (m, 1H), 5.00 (dd, 1H, J_1 = 17.0 Hz, J_2 = 1.7 Hz), 4.93 (dd, 1H, J_1 = 10.3 Hz, J_2 = 1.3 Hz), 2.32-2.24 (m, 2H), 2.20 (d of AB sys., 1H, J = 13.4 Hz), 2.12 (d of AB sys., 1H, J = 13.4 Hz), 2.05-1.98 (m, 2H), 1.90-1.83 (m, 2H), 1.66-1.53 (m, 2H), 1.39-1.34 (m, 2H), 0.93 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) : 212.5, 139.1, 114.7, 54.0, 41.3, 41.2, 38.9, 36.2, 28.2, 25.2, 22.4.

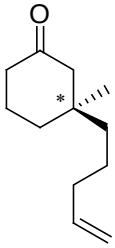
$[\alpha]_D$: +0.90 ($CHCl_3$, c = 1.71, ee = 93% *R*. Absolute configuration was assigned in analogy with **13**). Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, Rt_1 = 6.4 (*S*), Rt_2 = 6.7 (*R*)).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.447	MM	0.0517	887.50702	285.96204	49.91007
2	6.698	MM	0.0553	890.70526	268.21765	50.08993
Totals :				1778.21228	554.17969	



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	6.427	BB	0.0477	29.00474	8.70781	2.52924
2	6.662	BB	0.0496	1117.77417	332.44604	97.47076
Totals :				1146.77891	341.15385	

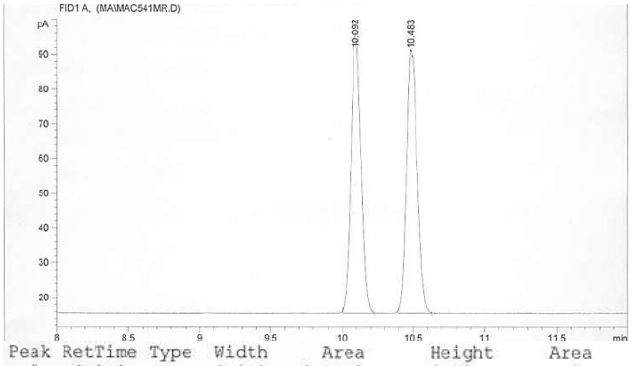


3-(3-pentenyl)-3-methylcyclohexanone (10) [10]:

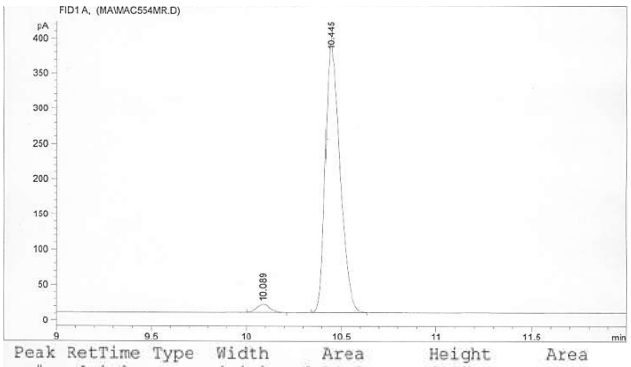
^{1}H NMR (400 MHz, $CDCl_3$) : 5.82-5.72 (m, 1H), 5.00-4.91 (m, 2H), 2.25 (t, 2H, J = 6.8 Hz), 2.18 (d of AB sys., 1H, J = 13.4 Hz), 2.09 (d of AB sys., 1H, J = 13.4 Hz), 2.03-1.98 (m, 2H), 1.87-1.81 (m, 2H), 1.65-1.49 (2m, 2H), 1.36-1.23 (m, 4H), 0.90 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) : 212.6, 138.9, 115.0, 54.1, 41.3, 38.9, 36.1, 34.6, 25.4, 23.0, 22.4.

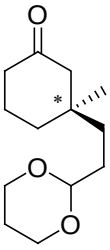
$[\alpha]_D$: -1.67 ($CHCl_3$, c = 1.70, ee = 93% *S*. Absolute configuration was assigned in analogy with **13**). Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, Rt_1 = 10.1 (*R*), Rt_2 = 10.5 (*S*)).



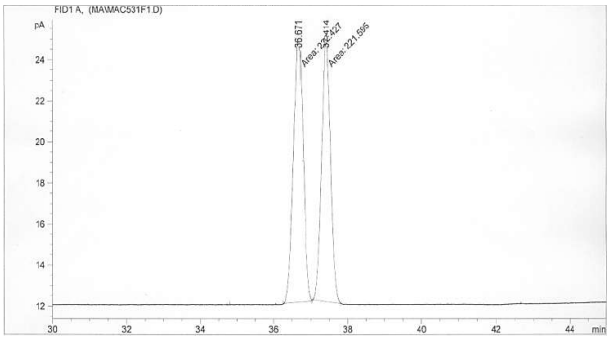
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.092	BB	0.0636	392.97452	80.18492	49.99425
2	10.483	BB	0.0696	393.06488	75.36453	50.00575
Totals :				786.03940	155.54945	



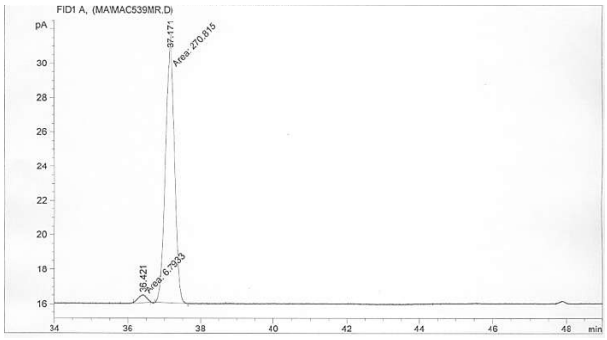
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	10.089	BB	0.0668	53.32511	11.18465	2.56836
2	10.445	BB	0.0722	2022.90344	392.11273	97.43164
Totals :				2076.22855	403.29739	



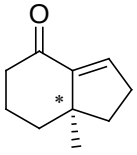
3-[2-(1-3-dioxan-2-yl)ethyl]-3-methylcyclohex-2-enone (12) [11, 12]:
^{1}H NMR (500 MHz, $CDCl_3$) : 4.46 (t, 1H, J = 5.0 Hz), 4.08 (dd, 2H, J_1 = 10.6 Hz, J_2 = 4.9 Hz), 3.73 (tt, 2H, J_1 = 12.3 Hz, J_2 = 2.4 Hz), 2.29-2.22 (m, 2H), 2.17-2.00 (m, 3H), 1.89-1.78 (m, 2H), 1.63-1.49 (m, 4H), 1.38-1.30 (m, 3H), 0.89 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) : 212.4, 102.9, 67.2, 54.1, 41.3, 38.4, 35.9, 35.8, 29.7, 26.1, 25.1, 22.4.
$[\alpha]_D$: +0.08 ($CHCl_3$, c = 1.25, ee = 94% *R.* Absolute configuration was assigned in analogy with **13**). Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, Rt_1 = 36.7 (*S*), Rt_2 = 37.4 (*R*)).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	36.671	MM	0.2894	222.42731	12.81153	50.09367
2	37.414	MM	0.2830	221.59549	13.05064	49.90633
Totals :				444.02280	25.86216	

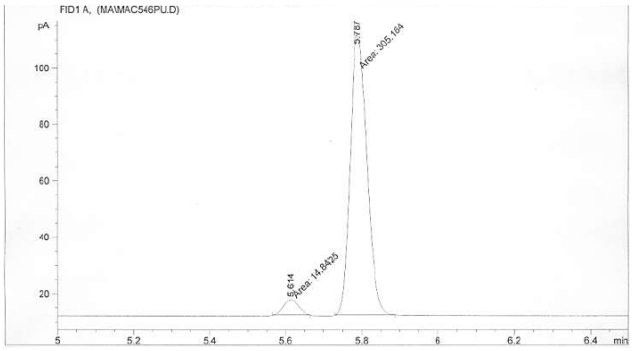


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	36.421	MM	0.2559	6.79330	4.42467e-1	2.44708
2	37.171	MM	0.2882	270.81500	15.66130	97.55292
Totals :				277.60830	16.10377	

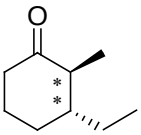


1,2,5,6,7,7a-hexahydro-7a-methylinden-4-one (13) [12, 13]**:**
According to litterature references [12,13], the 1,4-adduct **12** (565.8 mg, 2.5 mmol) was dissolved in a 6N HCl solution in THF (10 mL) at room temperature. After being stirred at room temperature for 18 hours, the mixture was neutralized at 0°C with a sodium bicarbonate saturated solution, diluted with diethylether, washed with three portions of water, and one of brine, dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude mixture was purified by flash chromatography (pentane : dietheylether) to afford 255.2 mg (68% yield) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) : 6.43 (t, 1H, J = 3.0 Hz), 2.54-2.18 (3m, 5H), 2.03-1.79 (m, 6H), 1.57 (td, 1H, J_1 = 13.9 Hz, J_2 = 4.8 Hz), 1.07 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) : 200.8, 149.7, 136.4, 47.7, 42.5, 40.0, 38.5, 30.1, 24.2, 21.5.
$[\alpha]_D$: -74.6 ($CHCl_3$, c = 1.53, ee = 90% *R.* Absolute configuration was attributed in comparison with litterature data[12]). Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 130°C, Rt_1 = 36.7 (*S*), Rt_2 = 37.4 (*R*)).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	5.614	MM	0.0453	14.84254	5.46614	4.63820
2	5.787	MM	0.0514	305.16388	98.97114	95.36180
Totals :				320.00642	104.43728	



3-ethyl-2-methylcyclohexanone (15) [14]:

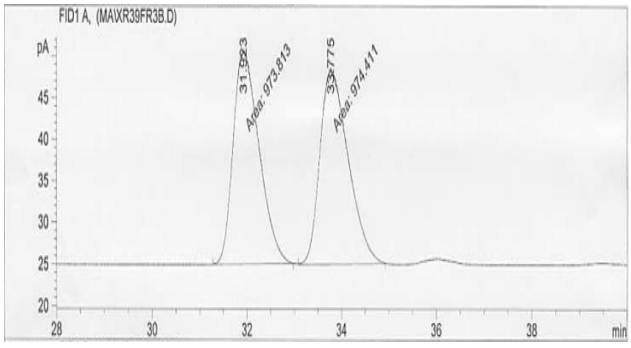
^{1}H NMR (500 MHz, $CDCl_3$) : 2.37 (m, 1H), 2.26 (m, 1H), 2.16 (m, 1H), 2.04 (m, 1H), 1.89 (m, 1H), 1.62 (m, 2H), 1.36 (m, 3H), 1.02 (d, 3H, J = 6.7 Hz), 0.90 (t, 3H, J = 7.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$) *trans* diastereoisomer : 213.8, 49.5, 46.7, 41.5, 29.7, 26.2, 25.9, 11.8, 10.2.

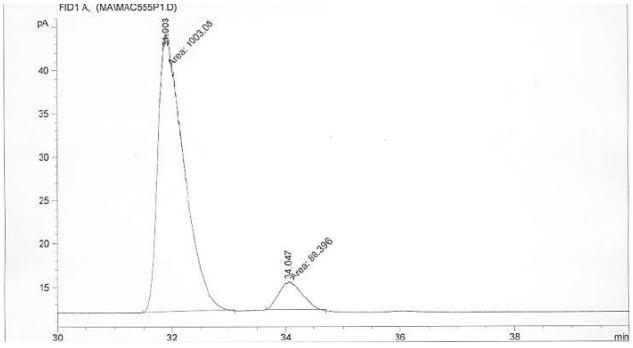
^{13}C NMR (125 MHz, $CDCl_3$) *cis* diastereoisomer : 214.8, 48.8, 43.9, 39.7, 26.5, 23.9, 21.9, 11.6, 11.3.

$[\alpha]_D$: -12.7 ($CHCl_3$, c = 1.29, ee = 82% (2S, 3*R*)). Enantiomeric excess was measured by chiral GC (Hydrodex B-3P, isotherm 70°C, Rt_1 = 31.9 (2*S*, 3*R*), Rt_2 = 33.8 (2*R*, 3*S*)).

Trans-adduct after separation by flash-chromatography :



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.923	MM	0.6289	973.81287	25.80717	49.98466
2	33.775	MM	0.6886	974.41077	23.58534	50.01534
Totals :				1948.22363	49.39251	



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.903	MM	0.5183	1003.08112	32.25285	91.90125
2	34.047	MM	0.4631	88.39598	3.18121	8.09875
Totals :				1091.47710	35.43405	

References :

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PALAIS L PROTON CDCl3 u guest 1

*** Current Data Parameters ***

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PROCNO : 1

*** Acquisition Parameters ***

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*** Processing Parameters ***

SF : 500.1300080 MHz

*** 1D NMR Plot Parameters ***

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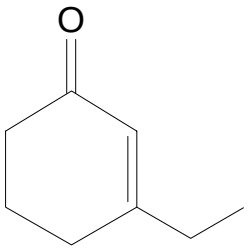

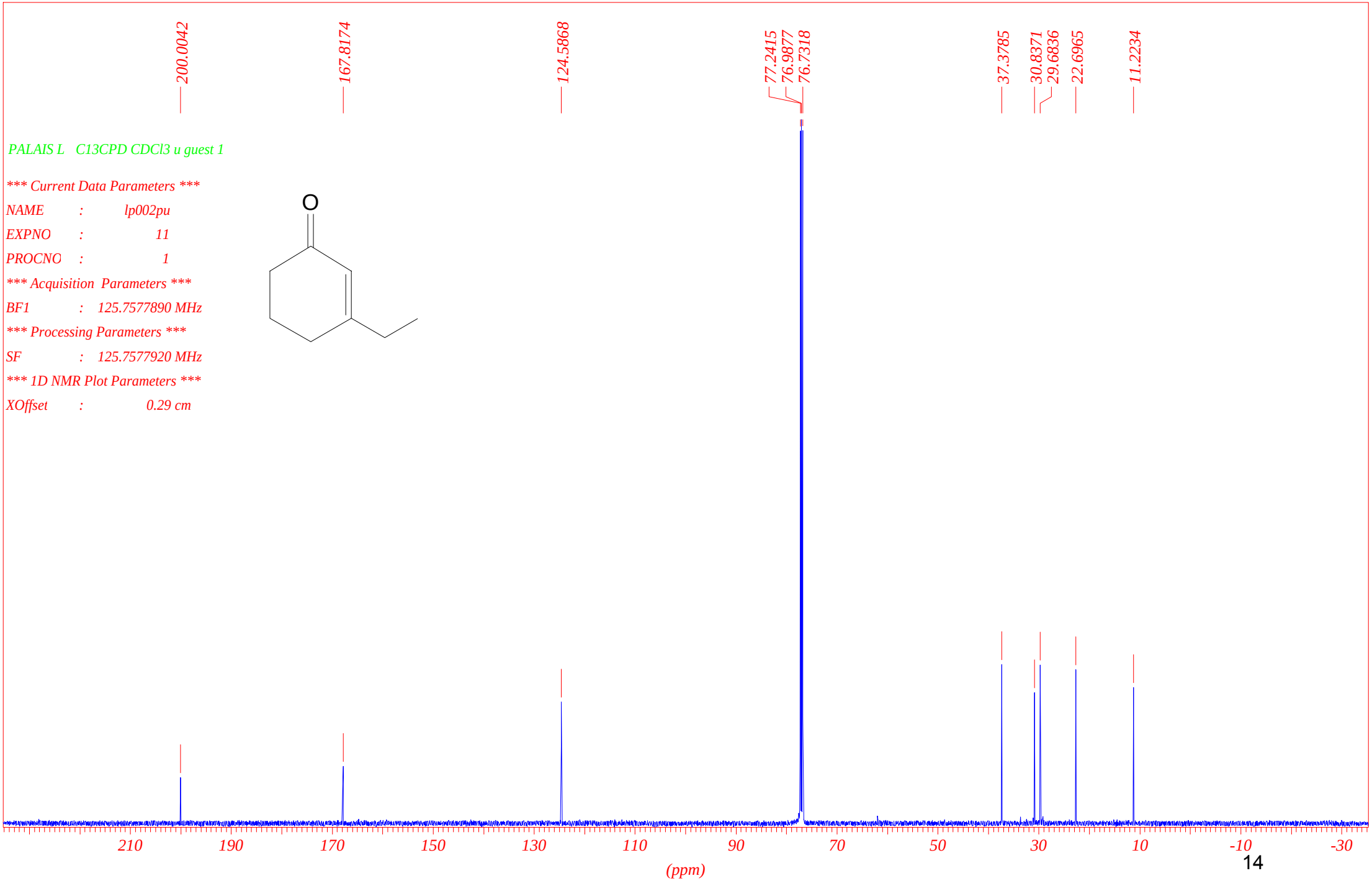
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PALAIS L C13CPD CDCl3 u guest 1
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150
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110
90
70
50
30
10
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(ppm)

PALAIS L C13DEPT135 CDCl3 u gues

*** Current Data Parameters ***

NAME : lp002pu

EXPNO : 12

PROCNO : 1

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*** Processing Parameters ***

SF : 125.7577920 MHz

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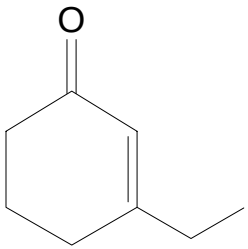

Laetitia PROTON CDCl3 u guest 6

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*** 1D NMR Plot Parameters ***

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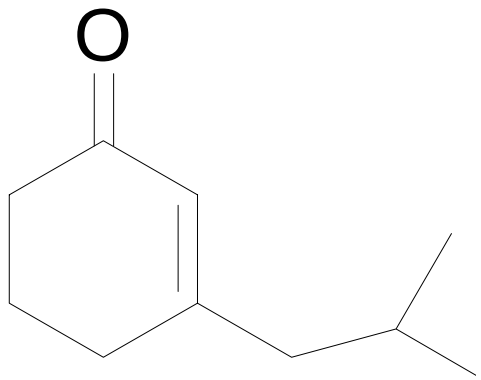

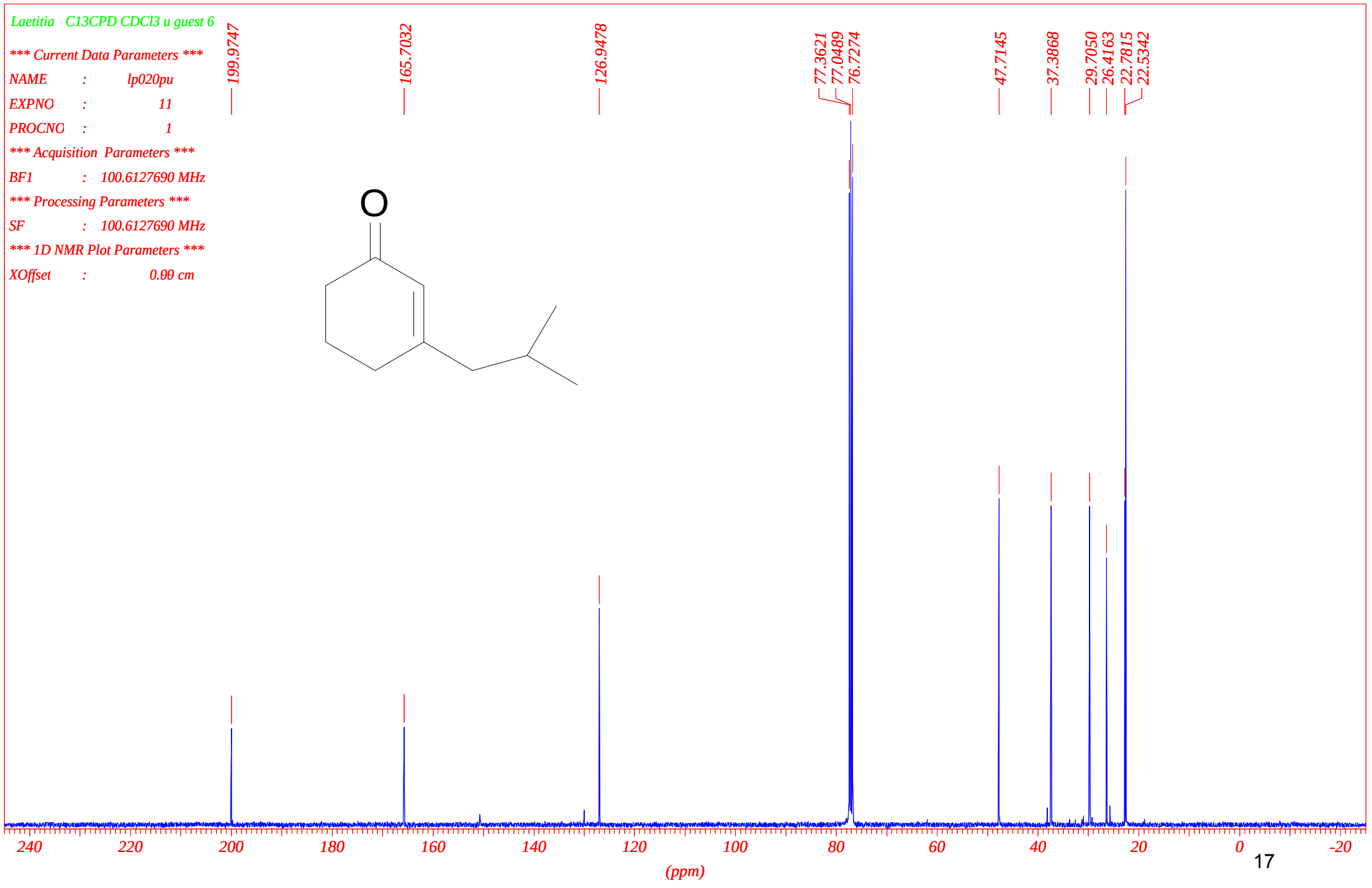
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29.7050
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O
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
(ppm)


Laetitia C13DEPT135 CDCl3 u guest (
*** Current Data Parameters ***
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PROCNO : 1
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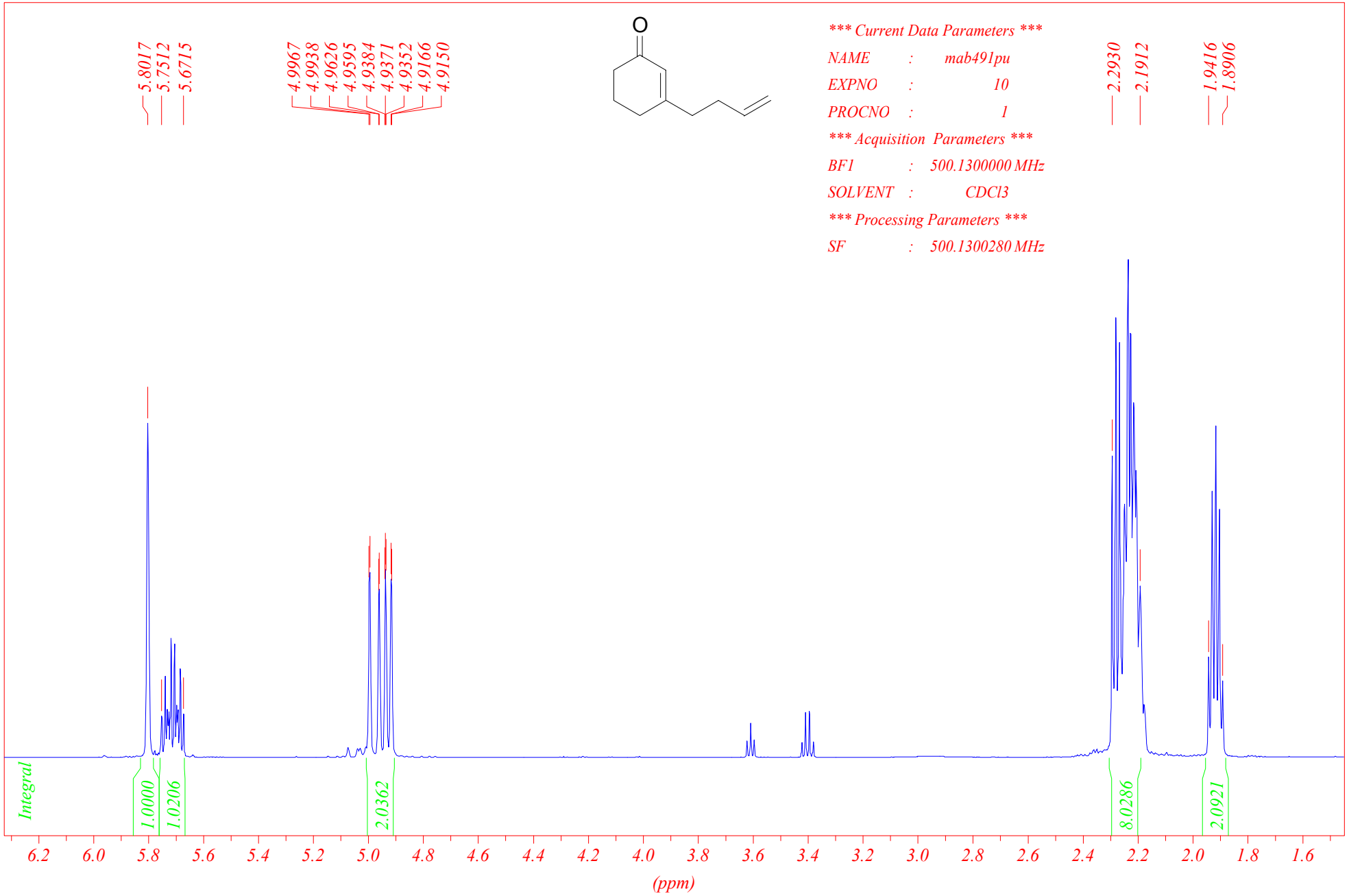
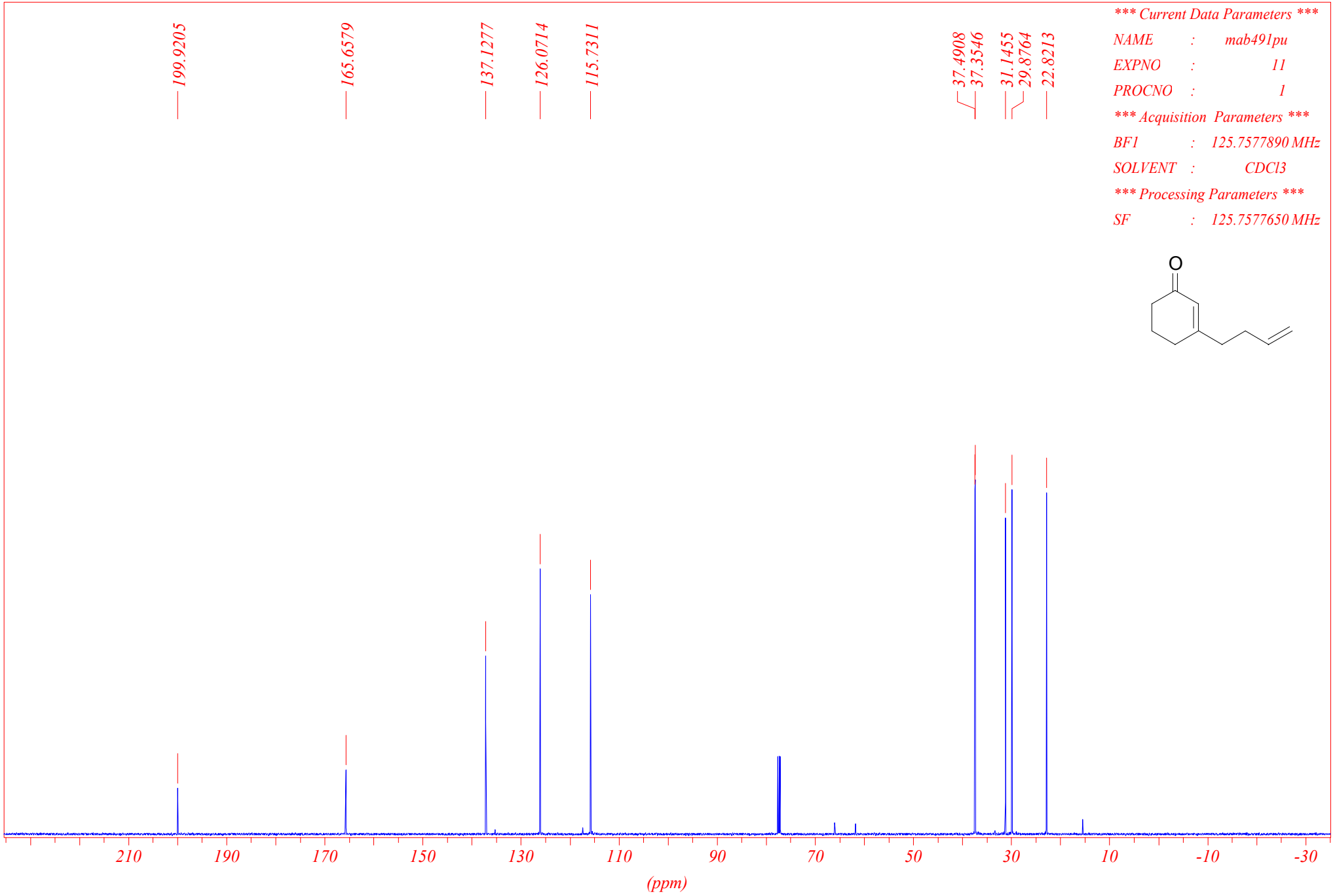
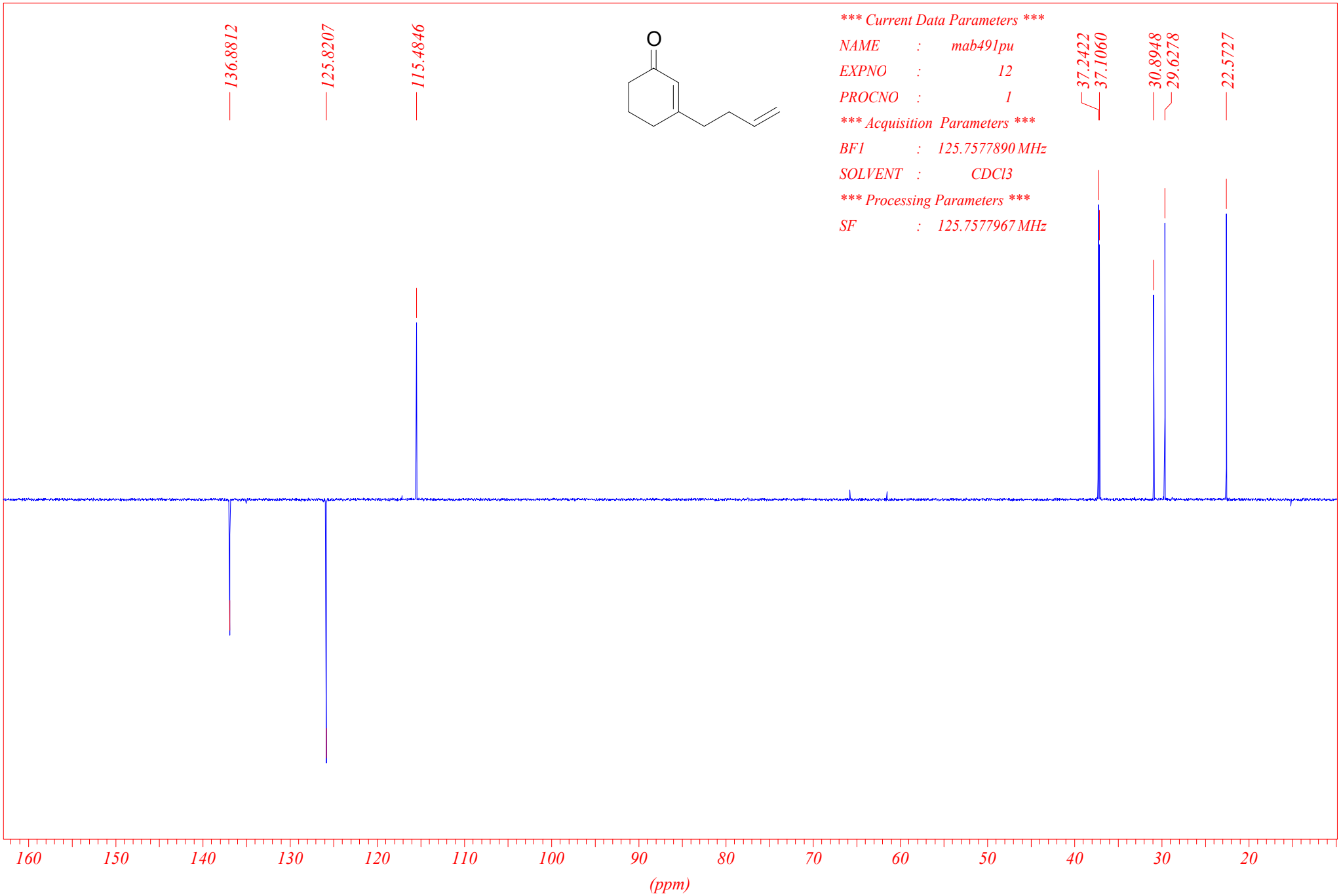
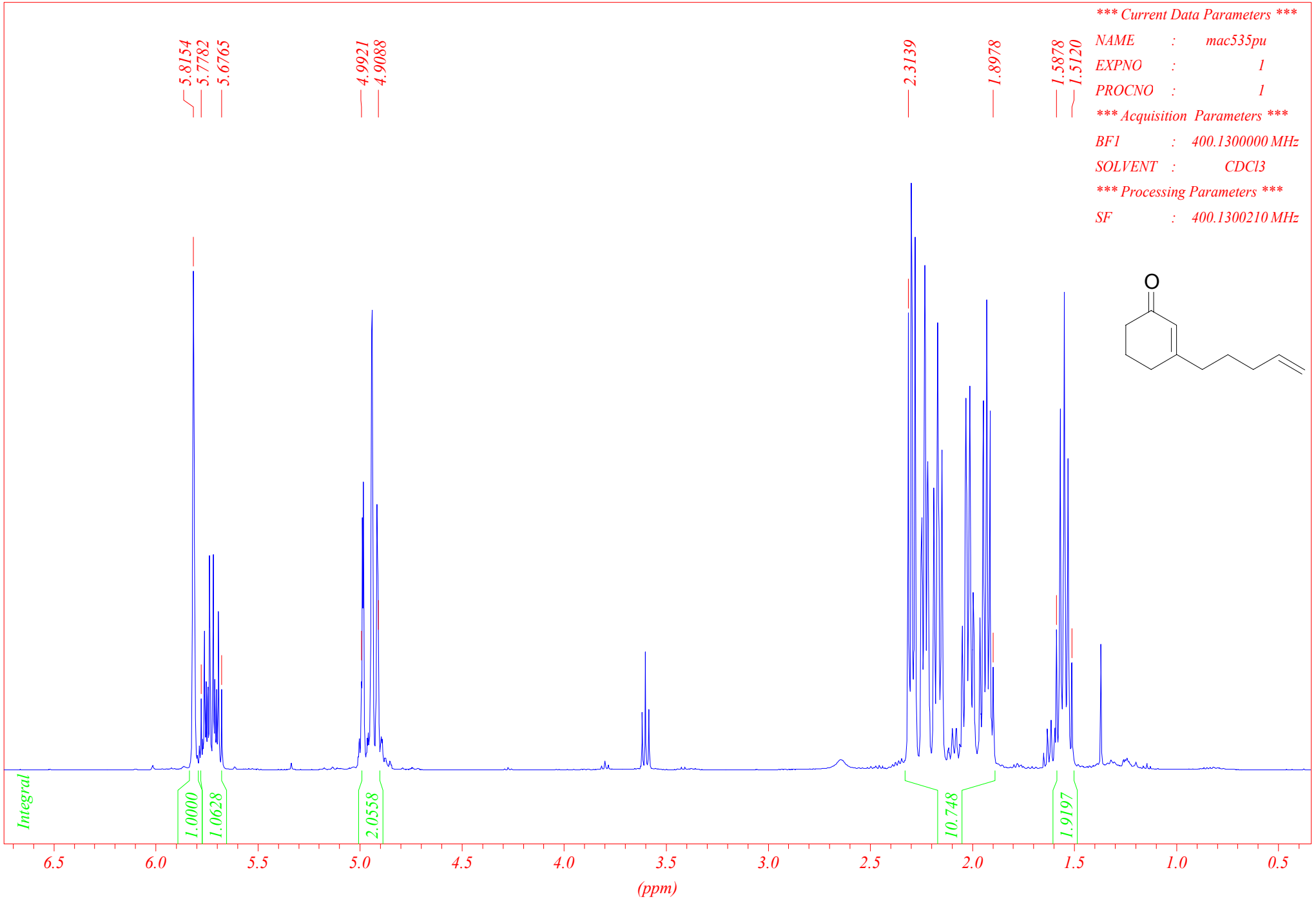
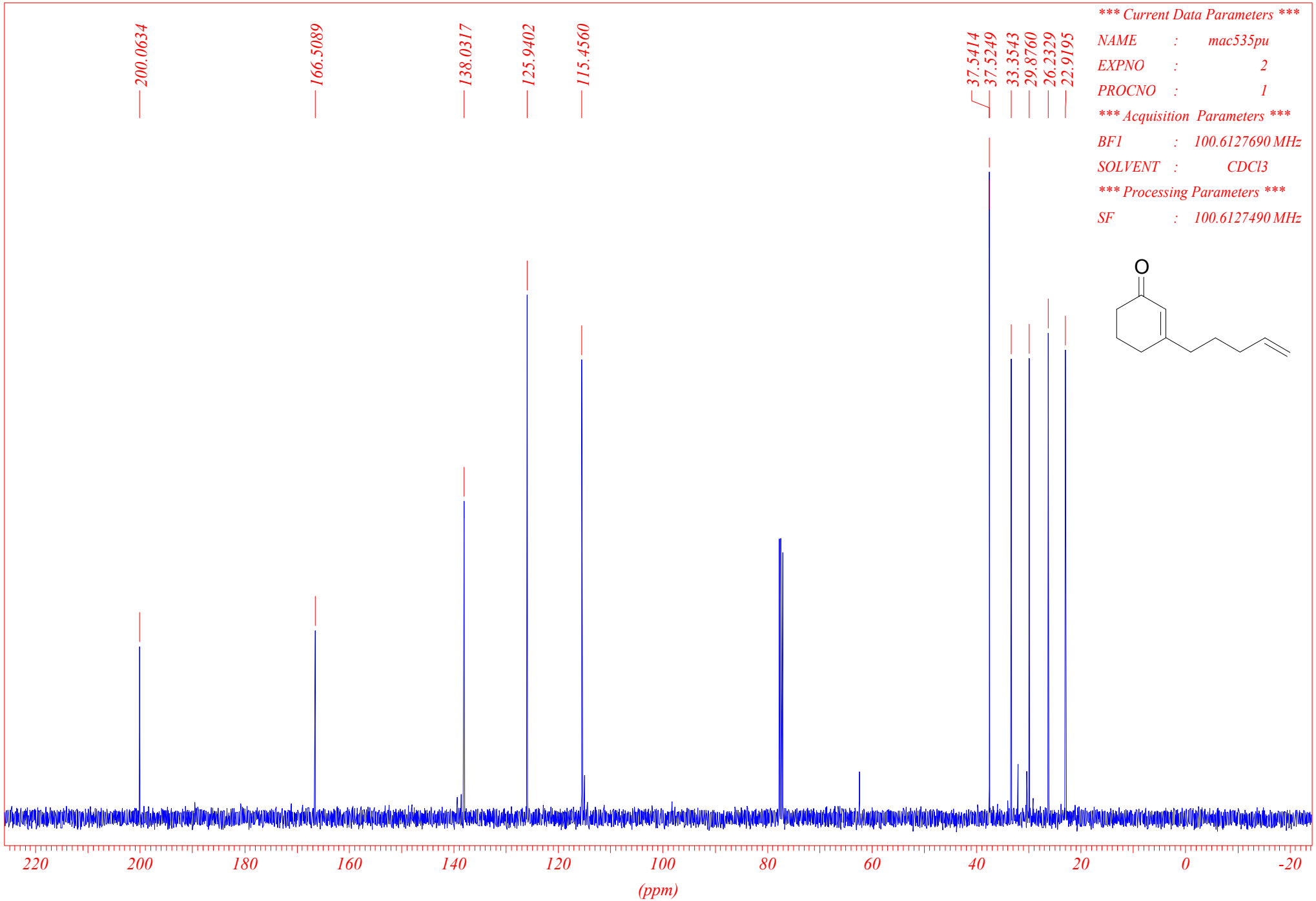
-20
(ppm)

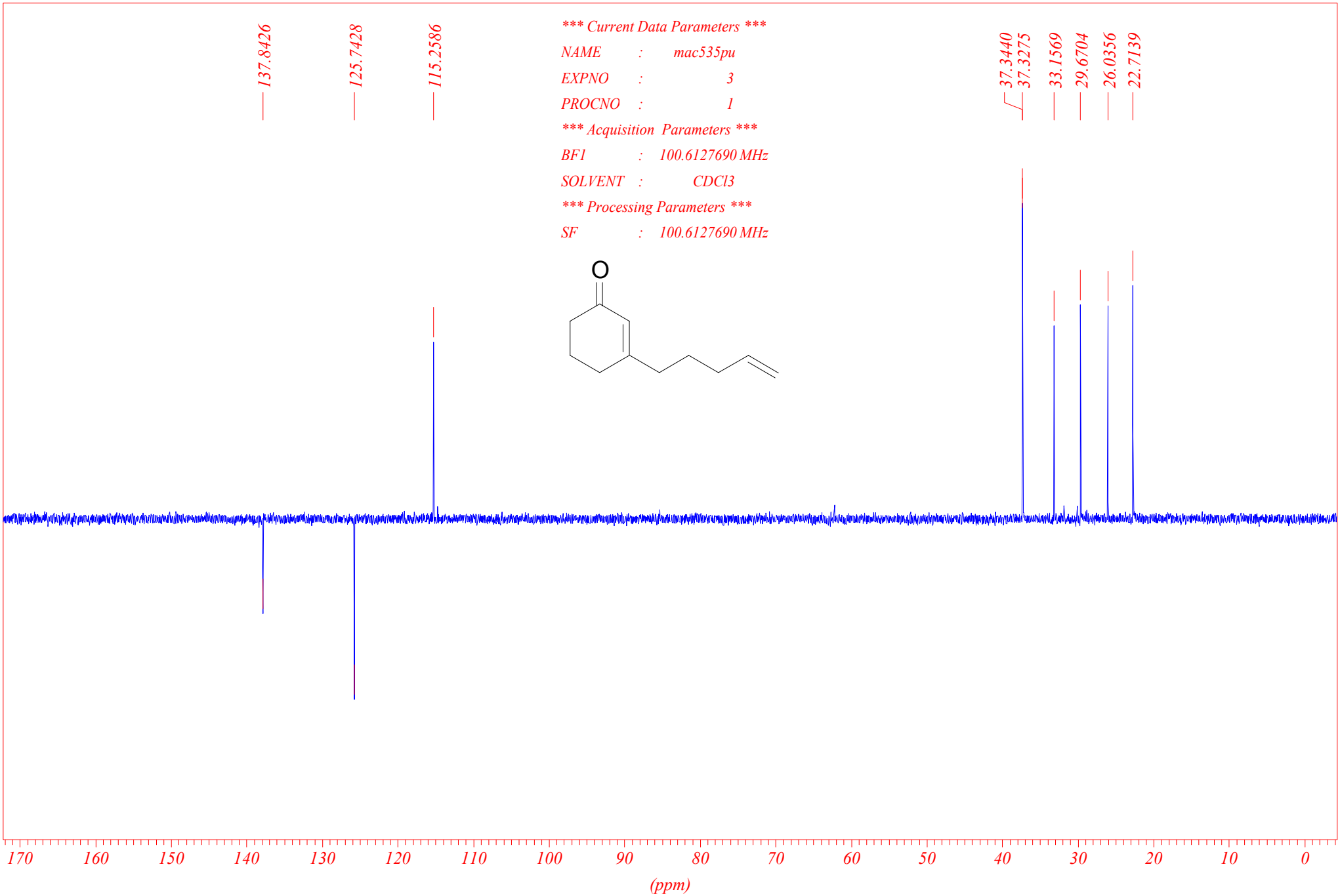

5.8017
5.7512
5.6715
4.9967
4.9938
4.9626
4.9595
4.9384
4.9371
4.9352
4.9166
4.9150
2.2930
2.1912
1.9416
1.8906
O
*** Current Data Parameters ***
NAME : mab491pu
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 500.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300280 MHz
Integral
1.0000
1.0206
2.0362
8.0286
2.0921
6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6
(ppm)

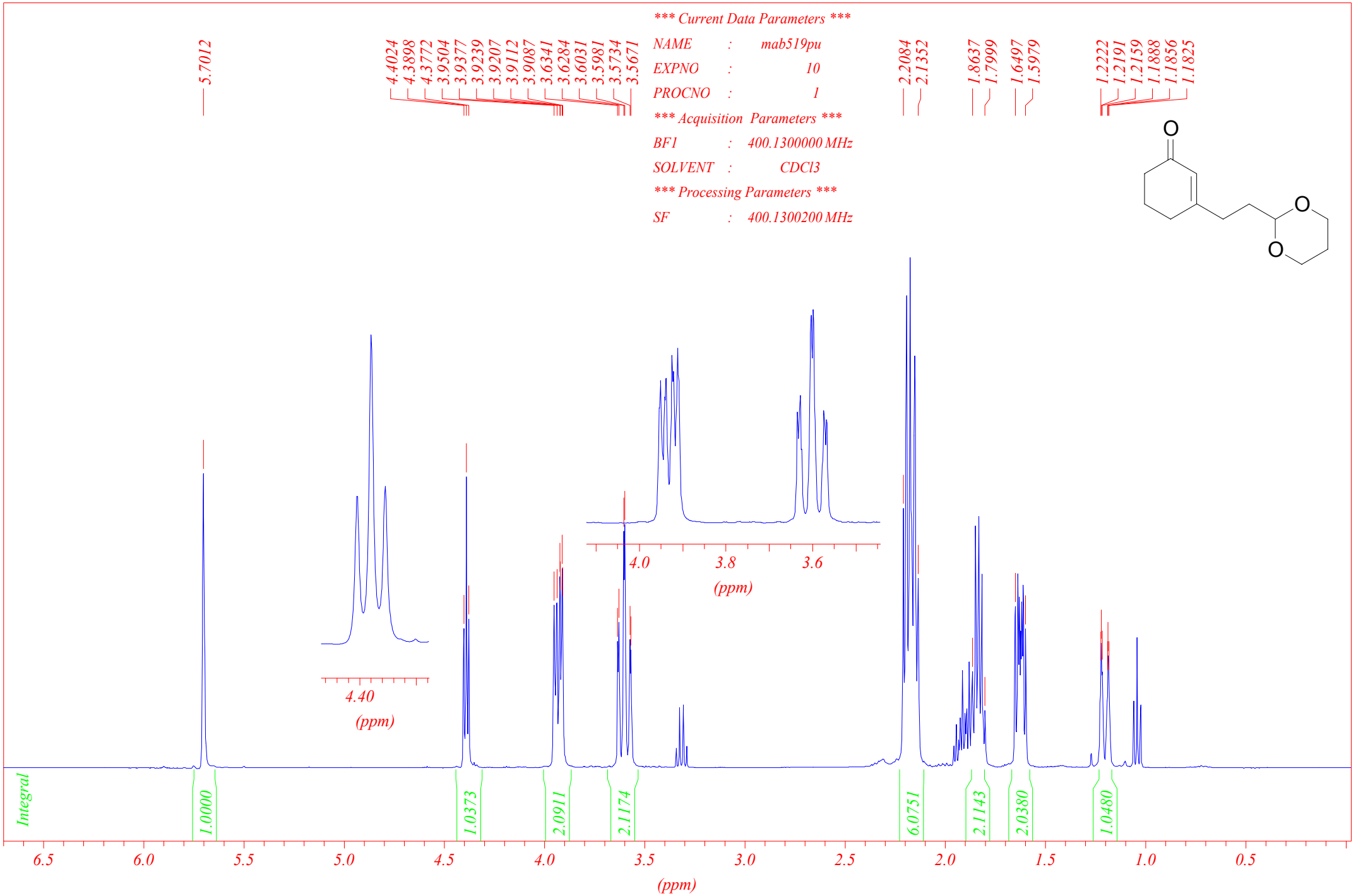

199.9205
165.6579
137.1277
126.0714
115.7311
37.4908
37.3546
31.1455
29.8764
22.8213
*** Current Data Parameters ***
NAME : mab491pu
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577650 MHz
O
210
190
170
150
130
110
90
70
50
30
10
-10
-30
(ppm)

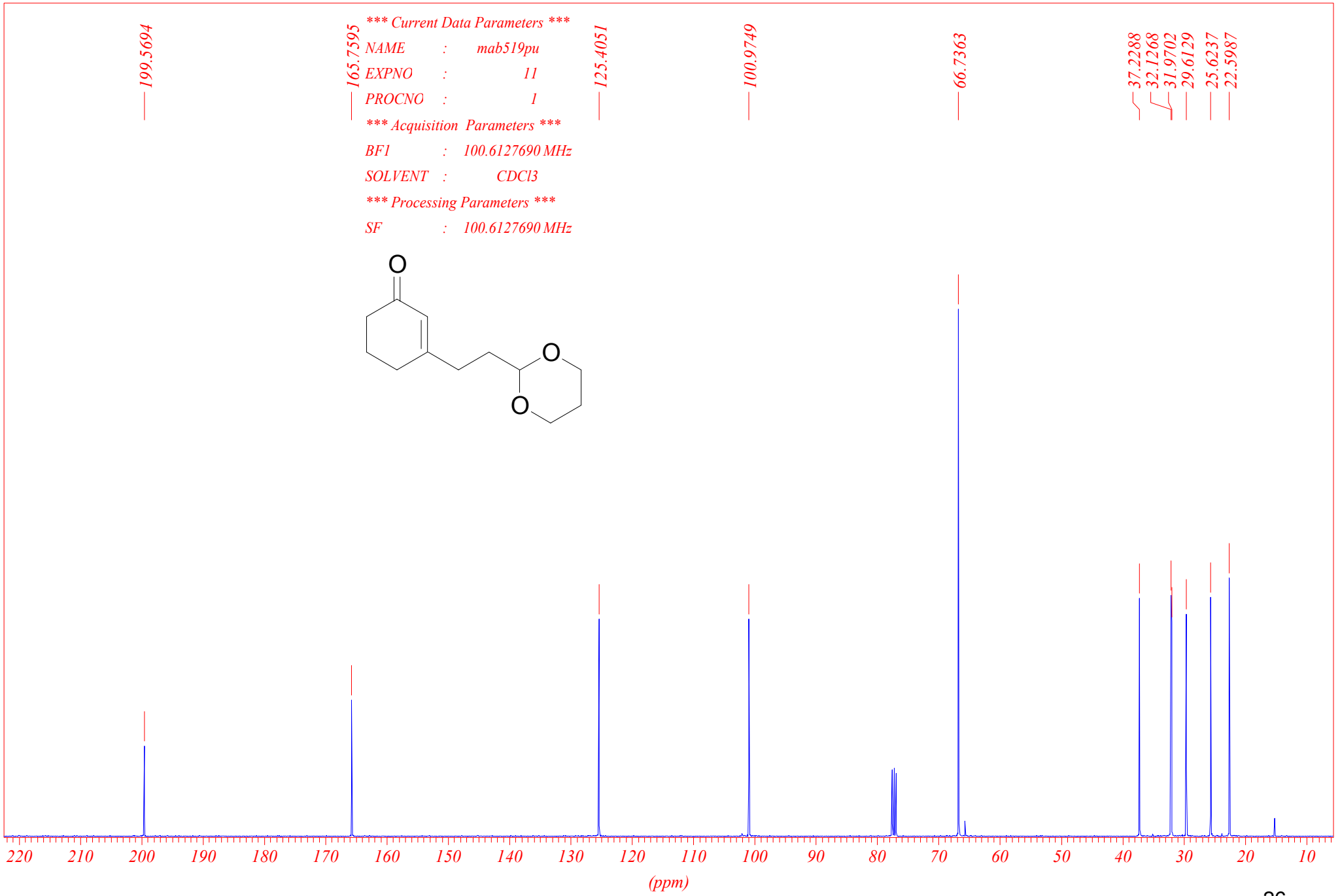

136.8812
125.8207
115.4846
37.2422
37.1060
30.8948
29.6278
22.5727
O
*** Current Data Parameters ***
NAME : mab491pu
EXPNO : 12
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577967 MHz
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

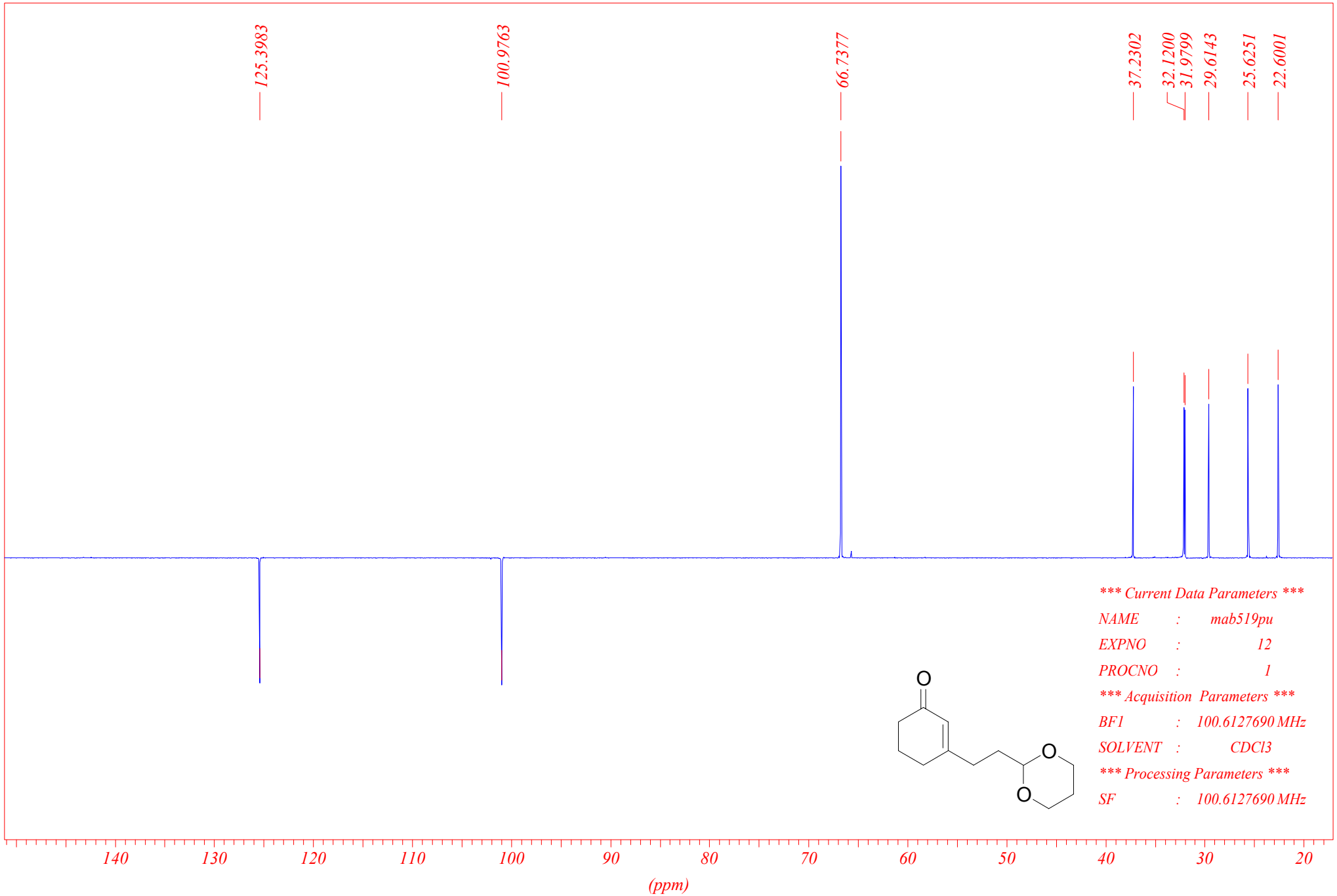

*** Current Data Parameters ***
NAME : mac535pu
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 400.1300210 MHz
5.8154
5.7782
5.6765
4.9921
4.9088
2.3139
1.8978
1.5878
1.5120
O
Integral
1.0000
1.0628
2.0558
10.748
1.9197
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

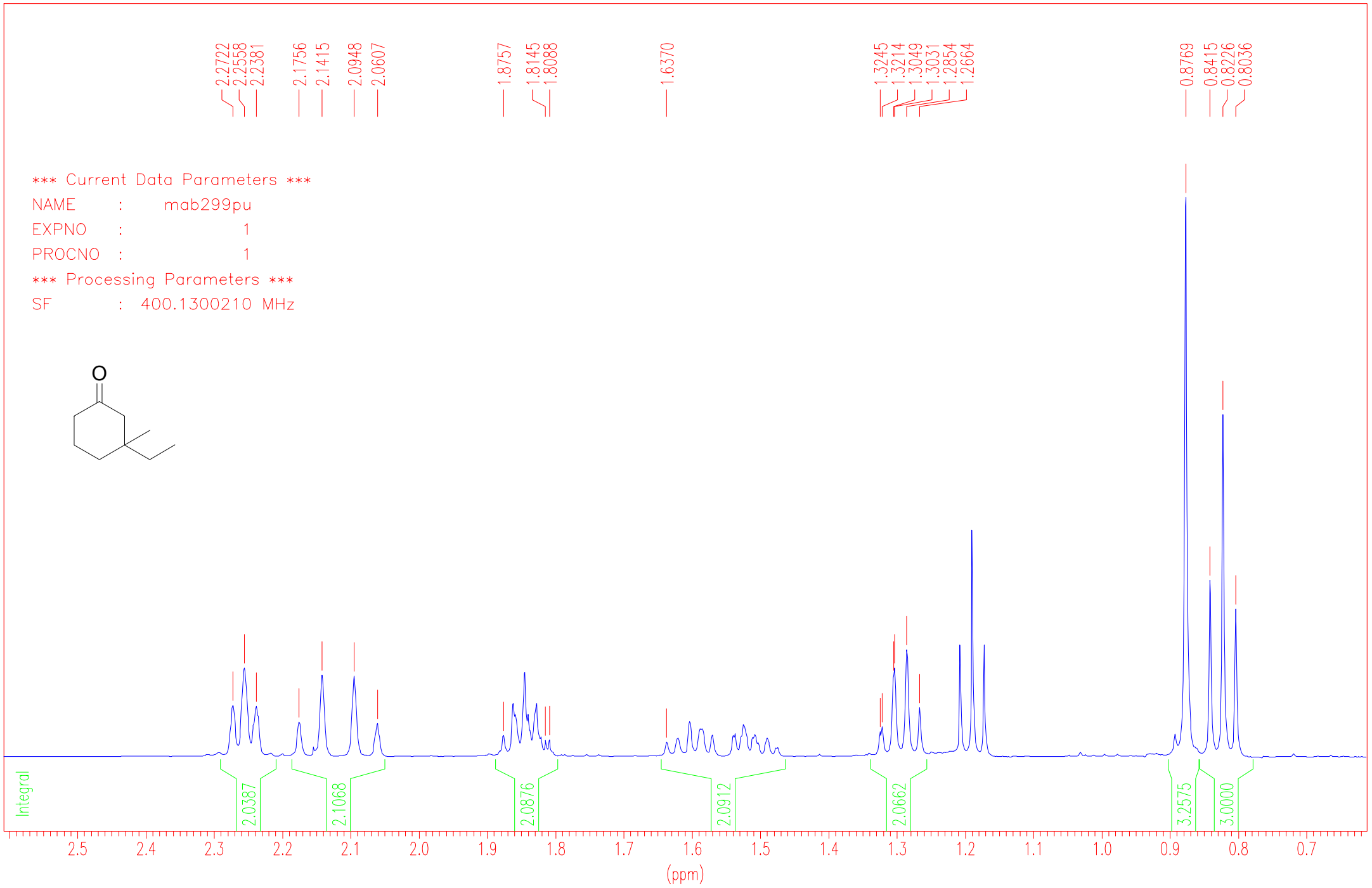

200.0634
166.5089
138.0317
125.9402
115.4560
37.5414
37.5249
33.3543
29.8760
26.2329
22.9195
*** Current Data Parameters ***
NAME : mac535pu
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127490 MHz
O
220
200
180
160
140
120
100
80
60
40
20
0
-20
(ppm)

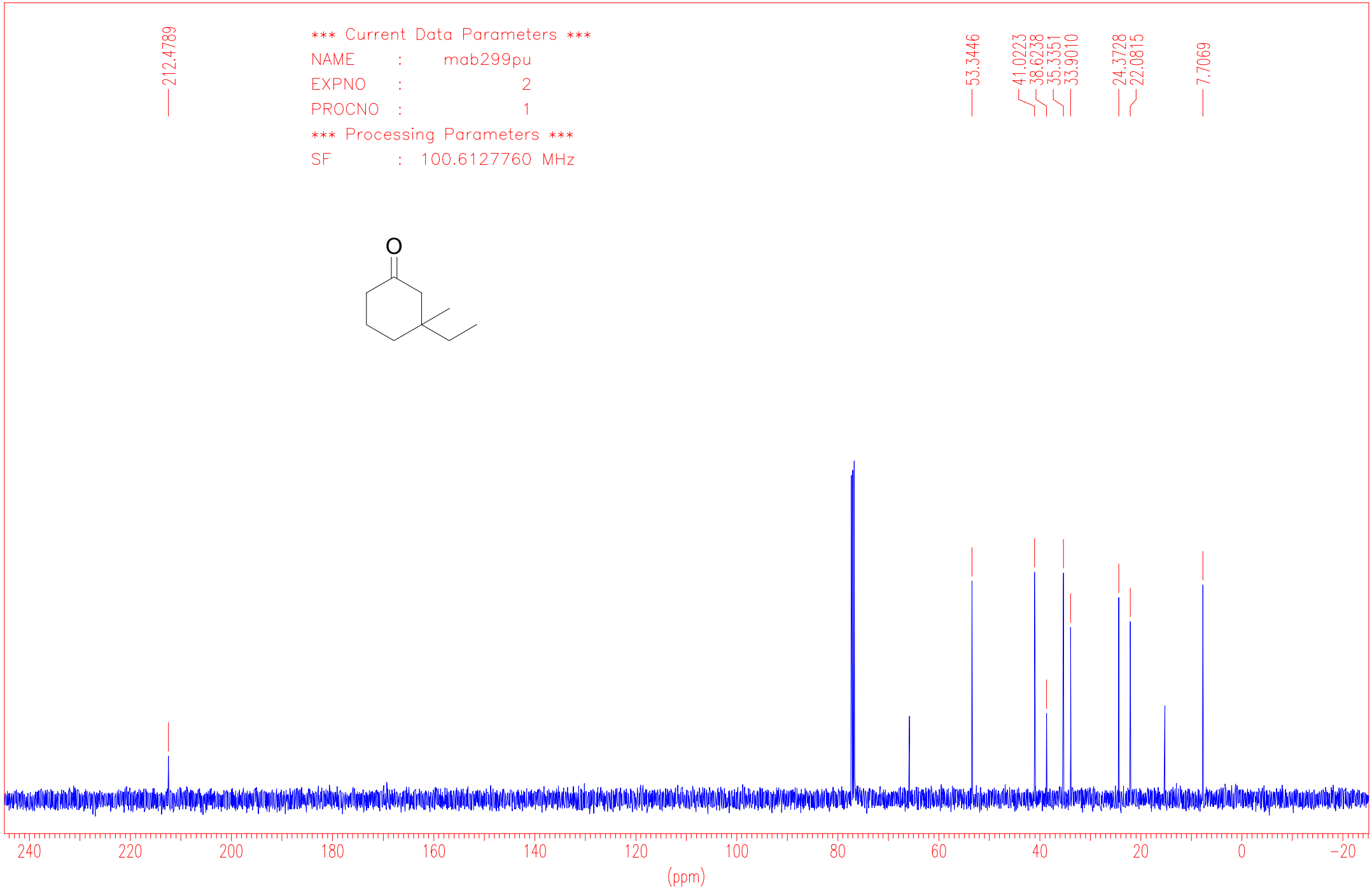

137.8426
125.7428
115.2586
37.3440
37.3275
33.1569
29.6704
26.0356
22.7139
*** Current Data Parameters ***
NAME : mac535pu
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127690 MHz
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

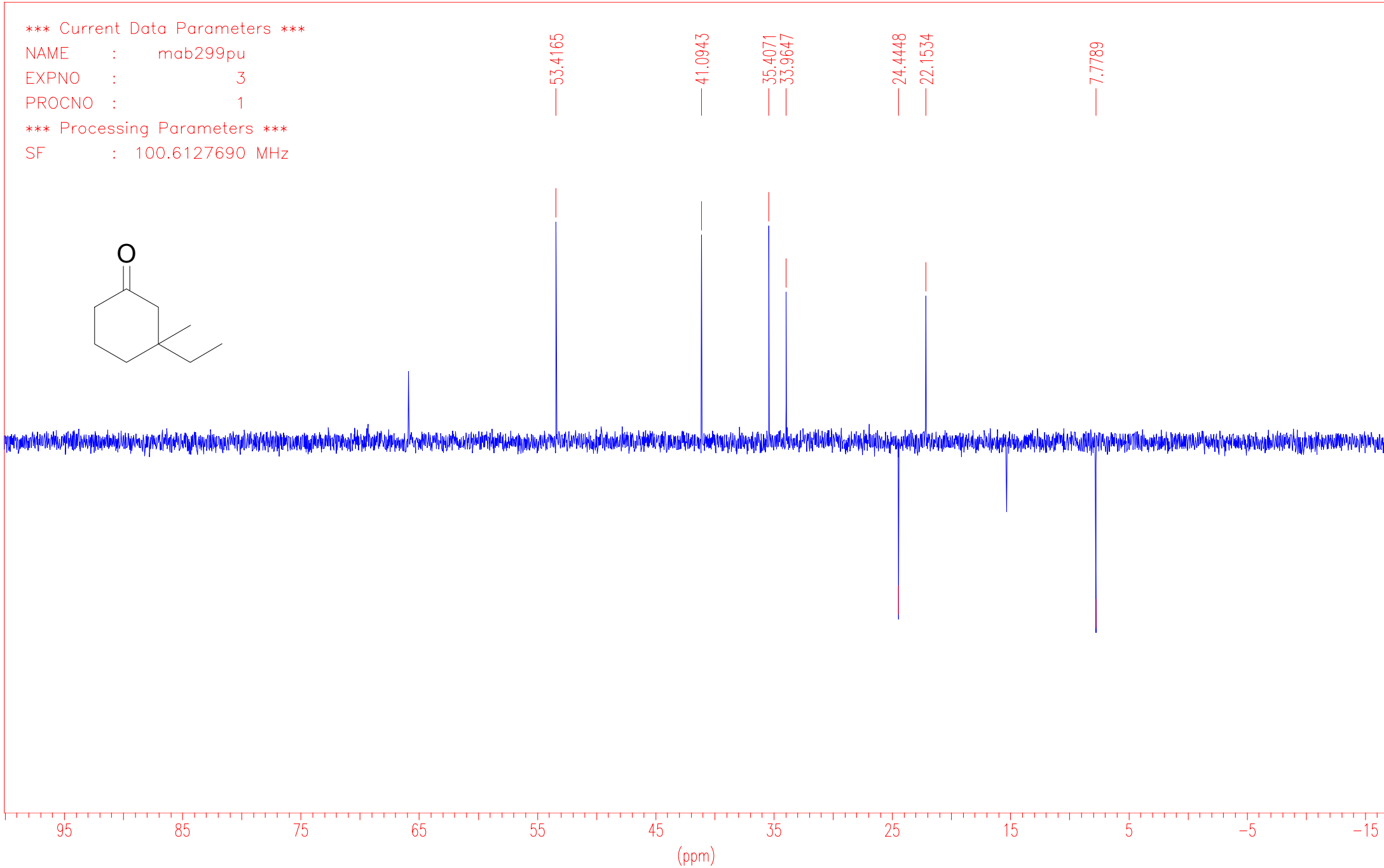

*** Current Data Parameters ***
NAME : mab519pu
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 400.1300200 MHz
5.7012
4.4024
4.3898
4.3772
3.9504
3.9377
3.9239
3.9207
3.9112
3.9087
3.6341
3.6284
3.6031
3.5981
3.5734
3.5671
2.2084
2.1352
1.8637
1.7999
1.6497
1.5979
1.2222
1.2191
1.2159
1.1888
1.1856
1.1825
O
O
O
4.40
(ppm)
4.0
3.8
3.6
(ppm)
Integral
1.0000
1.0373
2.0911
2.1174
6.0751
2.1143
2.0380
1.0480
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
(ppm)

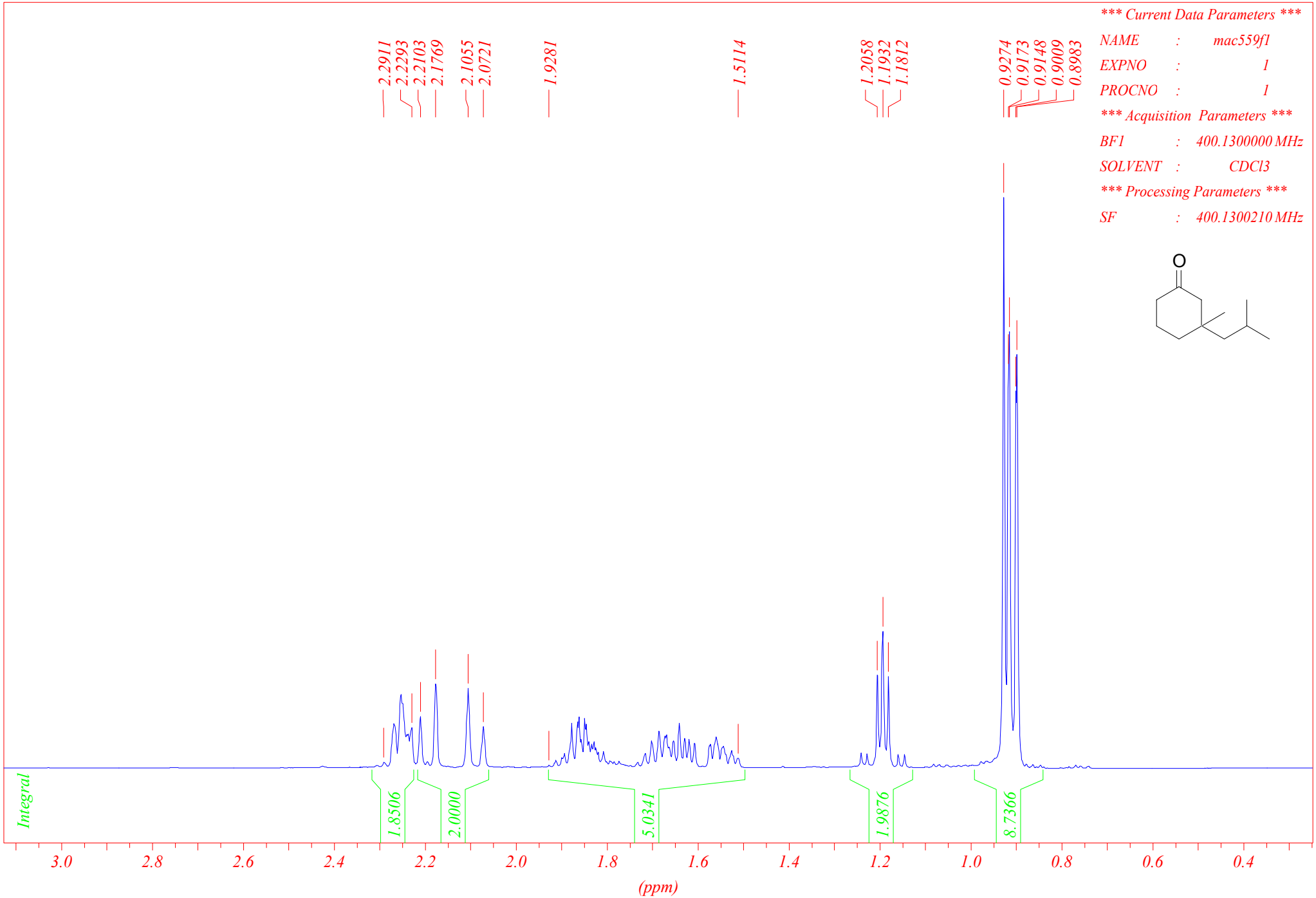

199.5694
165.7595
125.4051
100.9749
66.7363
37.2288
32.1268
31.9702
29.6129
25.6237
22.5987
*** Current Data Parameters ***
NAME : mab519pu
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127690 MHz
O
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

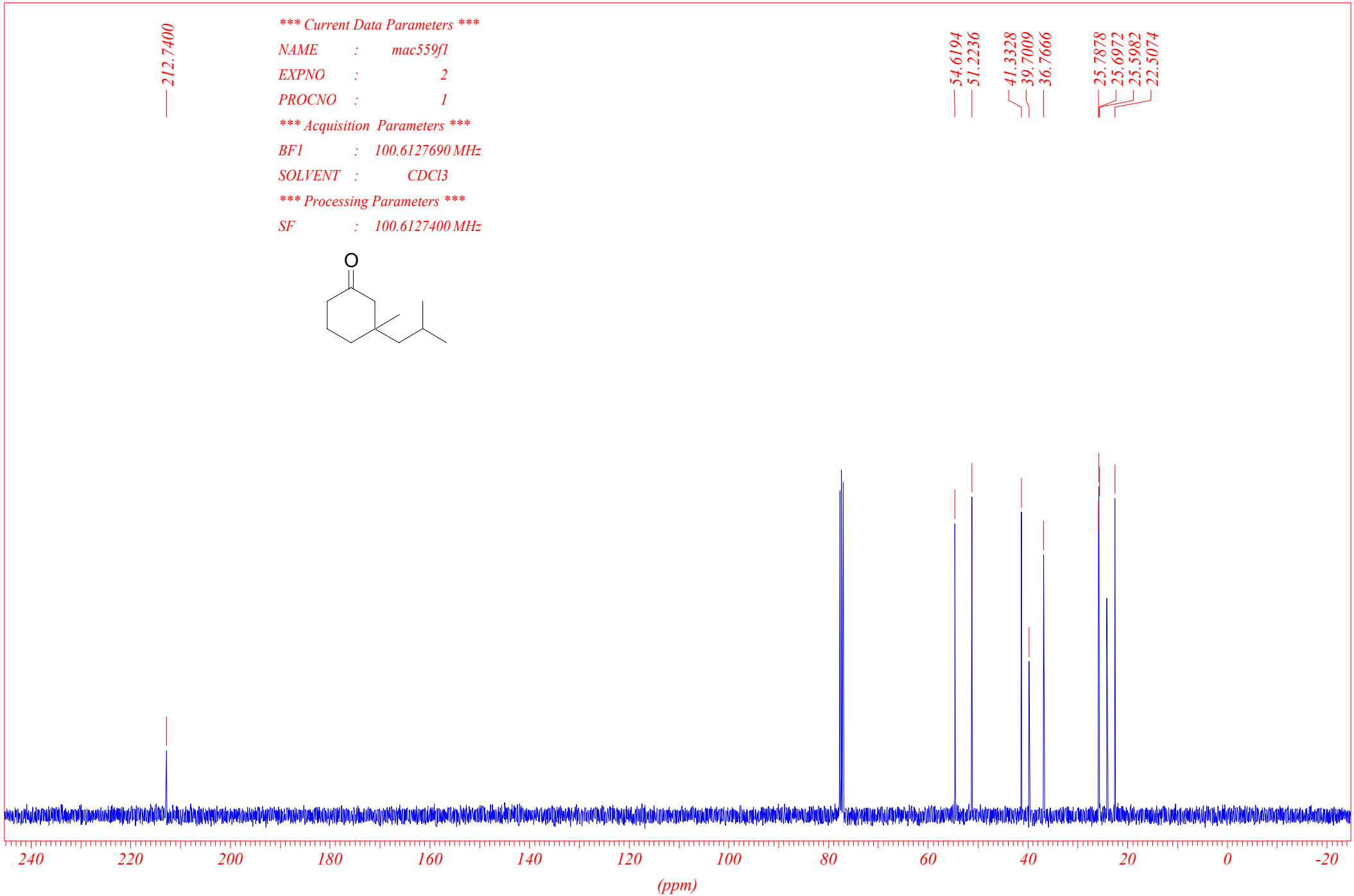

125.3983
100.9763
66.7377
37.2302
32.1200
31.9799
29.6143
25.6251
22.6001
*** Current Data Parameters ***
NAME : mab519pu
EXPNO : 12
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127690 MHz
O
O
O
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

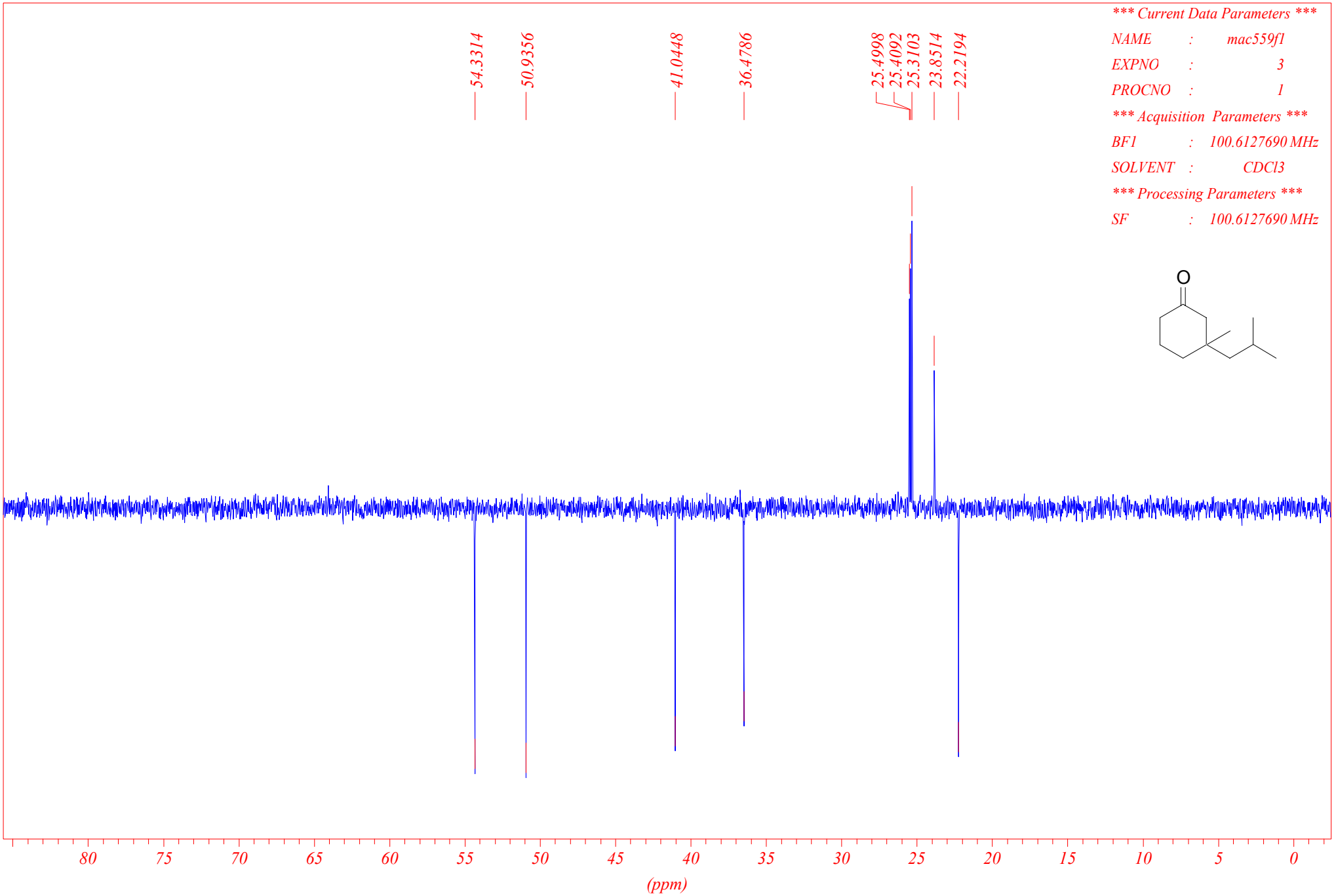

2.2722
2.2558
2.2381
2.1756
2.1415
2.0948
2.0607
1.8757
1.8145
1.8088
1.6370
1.3245
1.3214
1.3049
1.3031
1.2854
1.2664
0.8769
0.8415
0.8226
0.8036
*** Current Data Parameters ***
NAME : mab299pu
EXPNO : 1
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300210 MHz
O
Integral
2.0387
2.1068
2.0876
2.0912
2.0662
3.2575
3.0000
2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
(ppm)

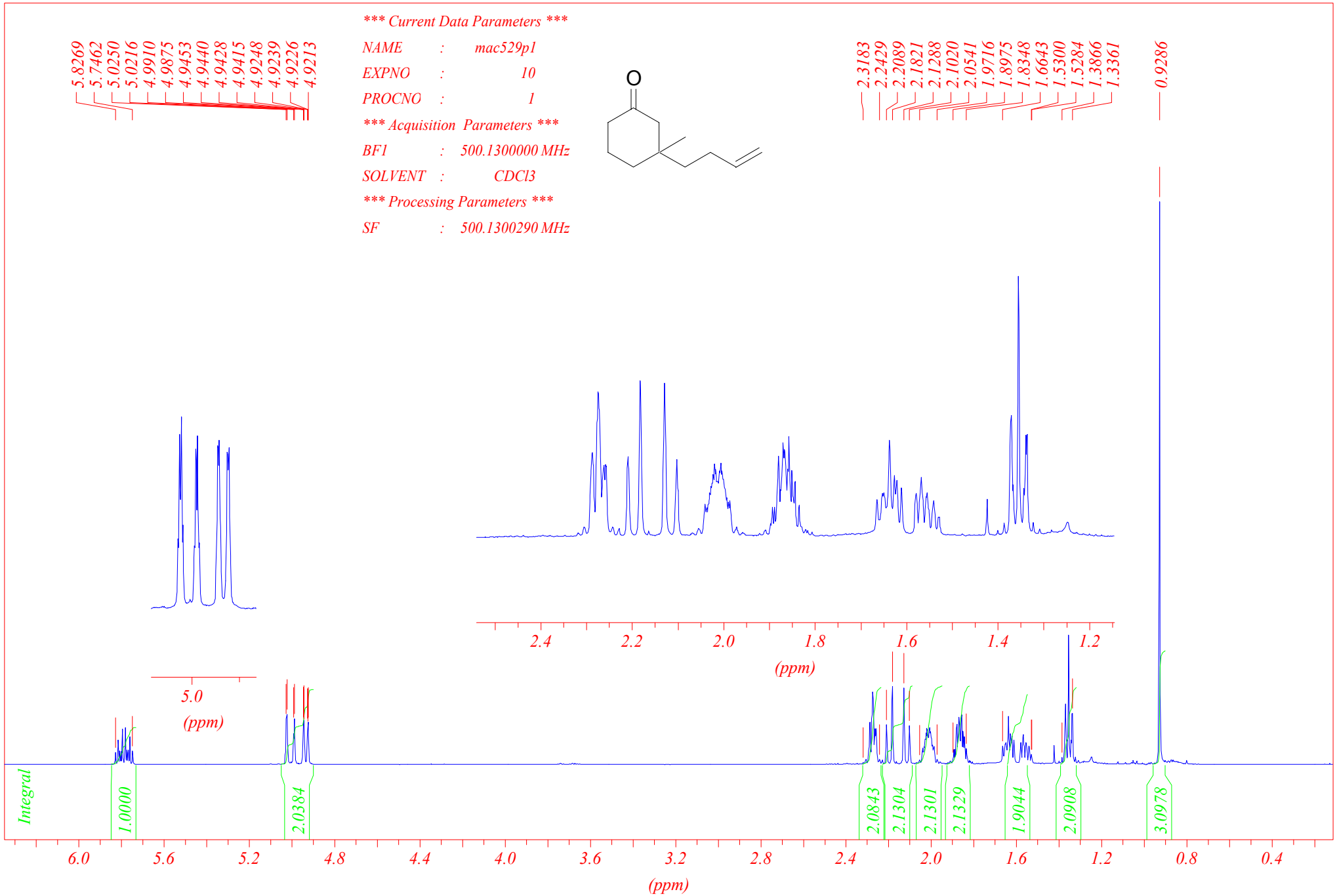

212.4789
*** Current Data Parameters ***
NAME : mab299pu
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127760 MHz
O
53.3446
41.0223
38.6238
35.3351
33.9010
24.3728
22.0815
7.7069
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
(ppm)

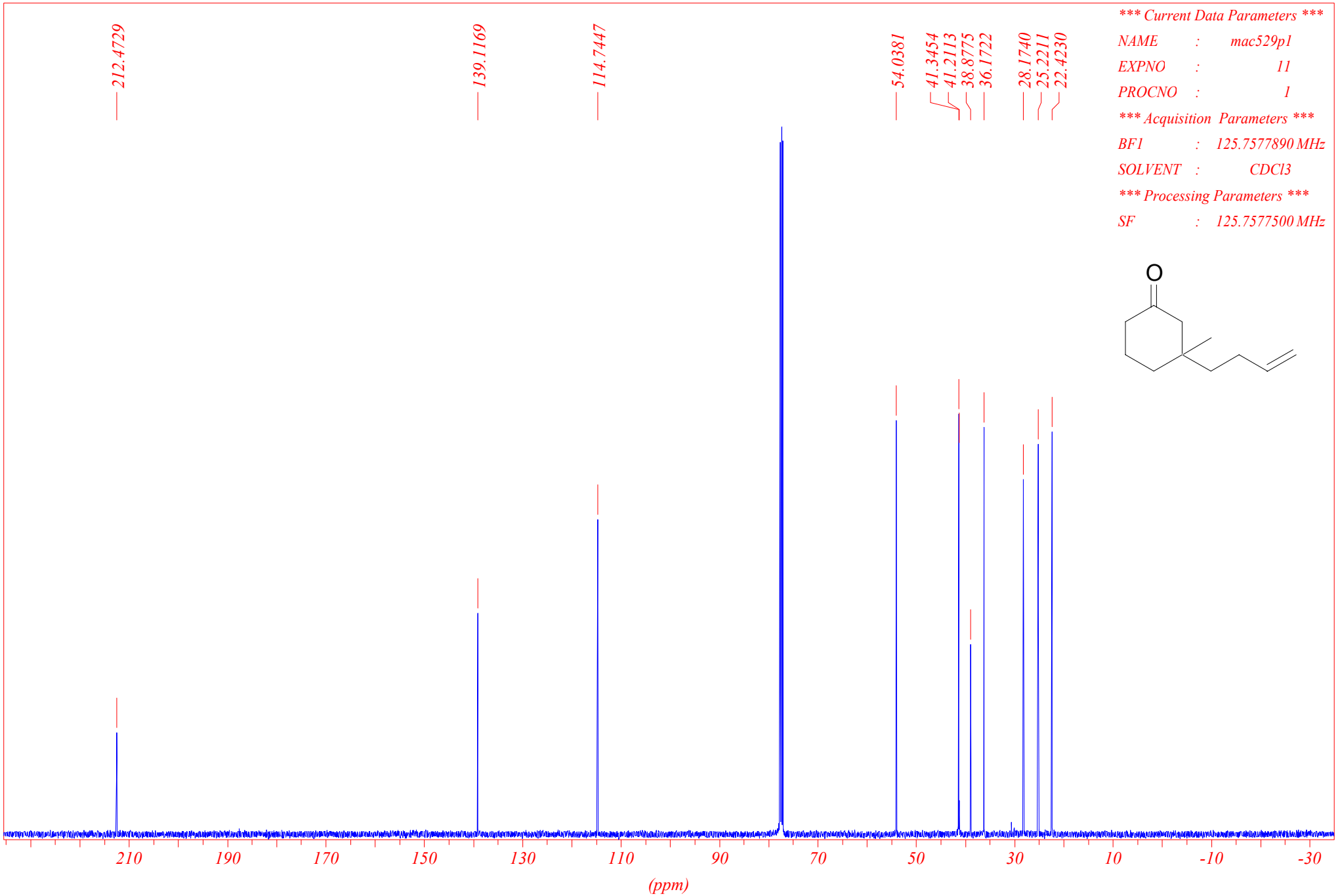

*** Current Data Parameters ***
NAME : mab299pu
EXPNO : 3
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127690 MHz
53.4165
41.0943
35.4071
33.9647
24.4448
22.1534
7.7789
O
95
85
75
65
55
45
35
25
15
5
−5
−15
(ppm)

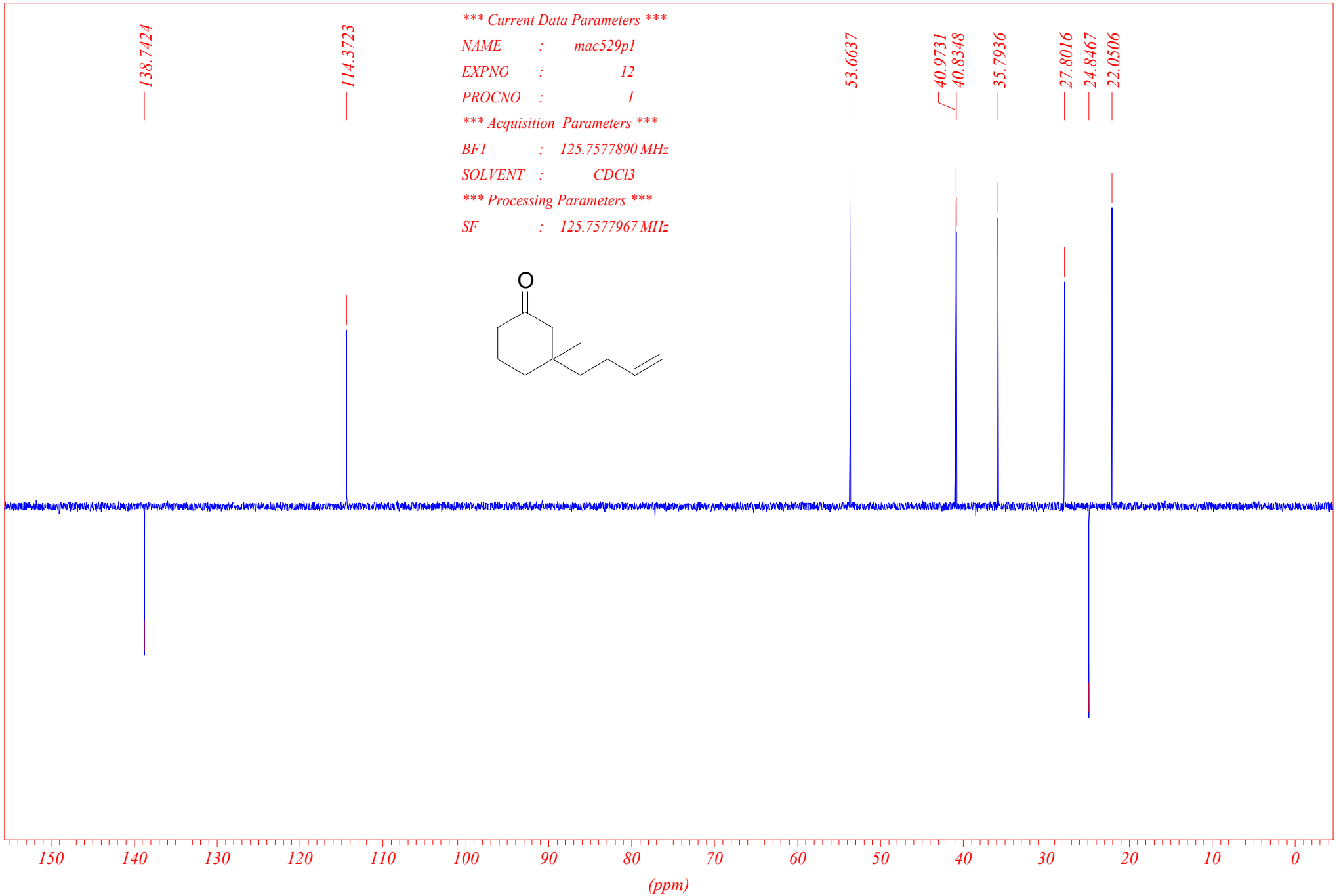

*** Current Data Parameters ***
NAME : mac559f1
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 400.1300210 MHz
2.2911
2.2293
2.2103
2.1769
2.1055
2.0721
1.9281
1.5114
1.2058
1.1932
1.1812
0.9274
0.9173
0.9148
0.9009
0.8983
O
Integral
1.8506
2.0000
5.0341
1.9876
8.7366
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
(ppm)

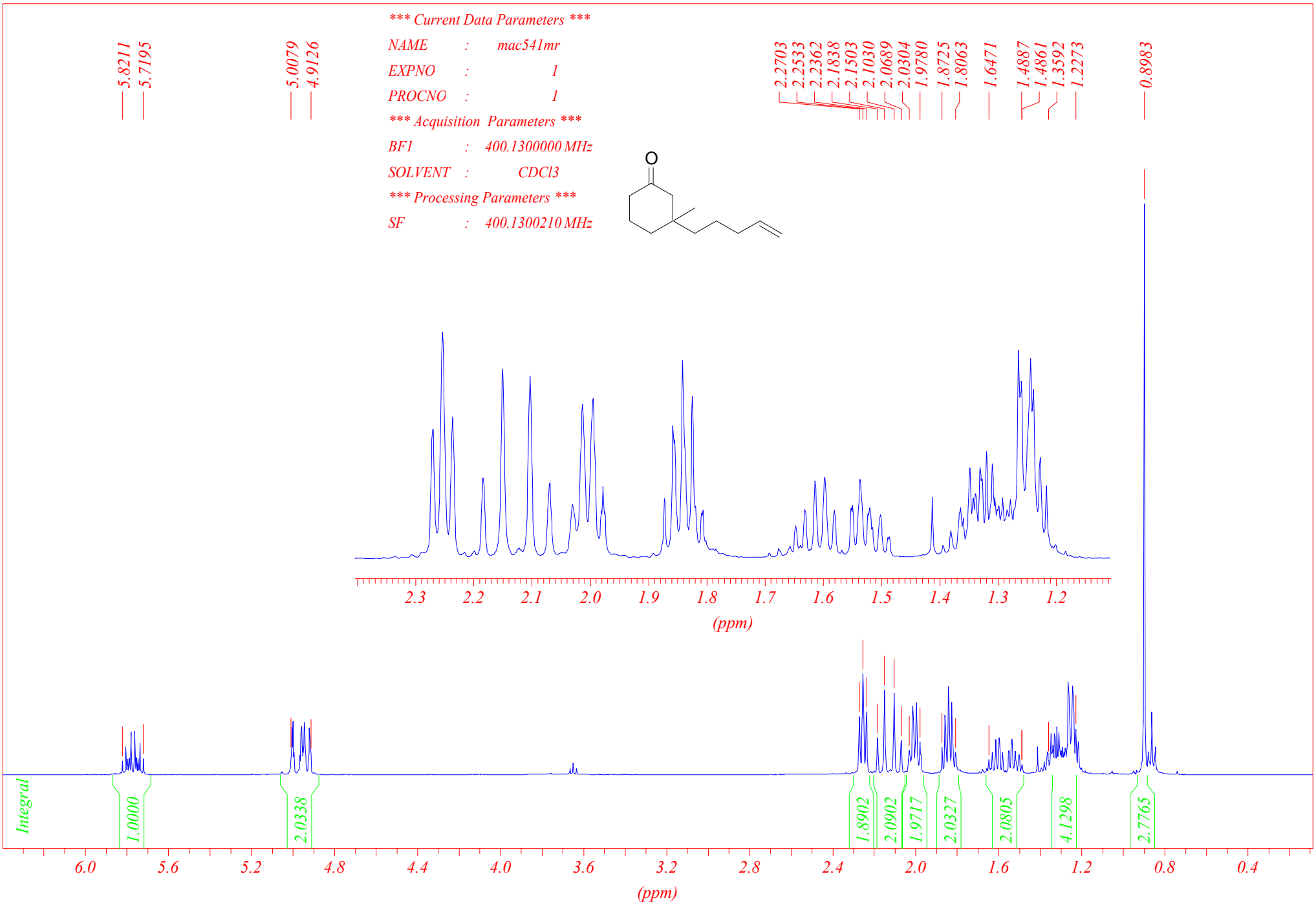

212.7400
*** Current Data Parameters ***
NAME : mac559f1
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127400 MHz
O
54.6194
51.2236
41.3328
39.7009
36.7666
25.7878
25.6972
25.5982
22.5074
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
(ppm)

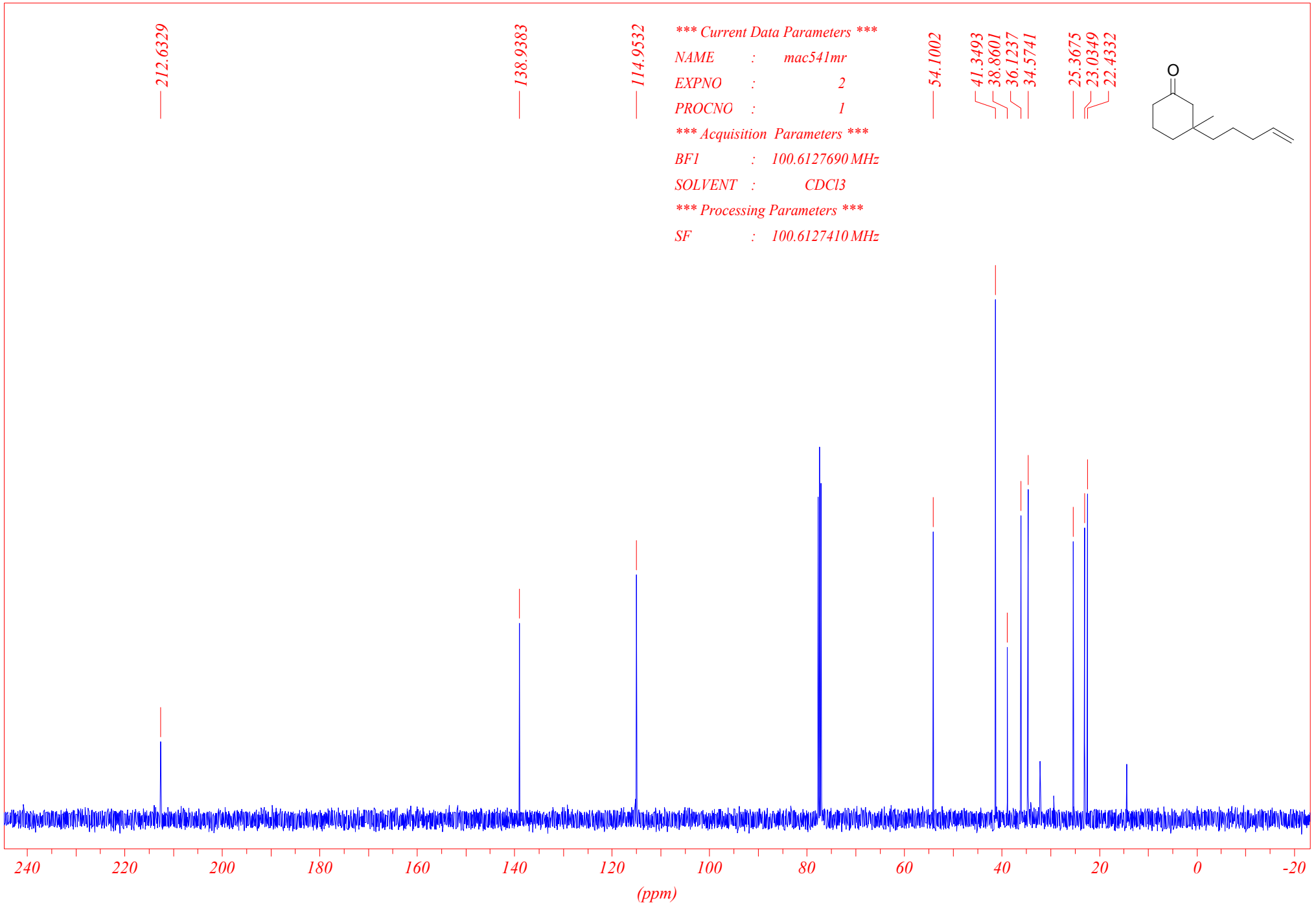

54.3314
50.9356
41.0448
36.4786
25.4998
25.4092
25.3103
23.8514
22.2194
*** Current Data Parameters ***
NAME : mac559f1
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127690 MHz
O
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
(ppm)

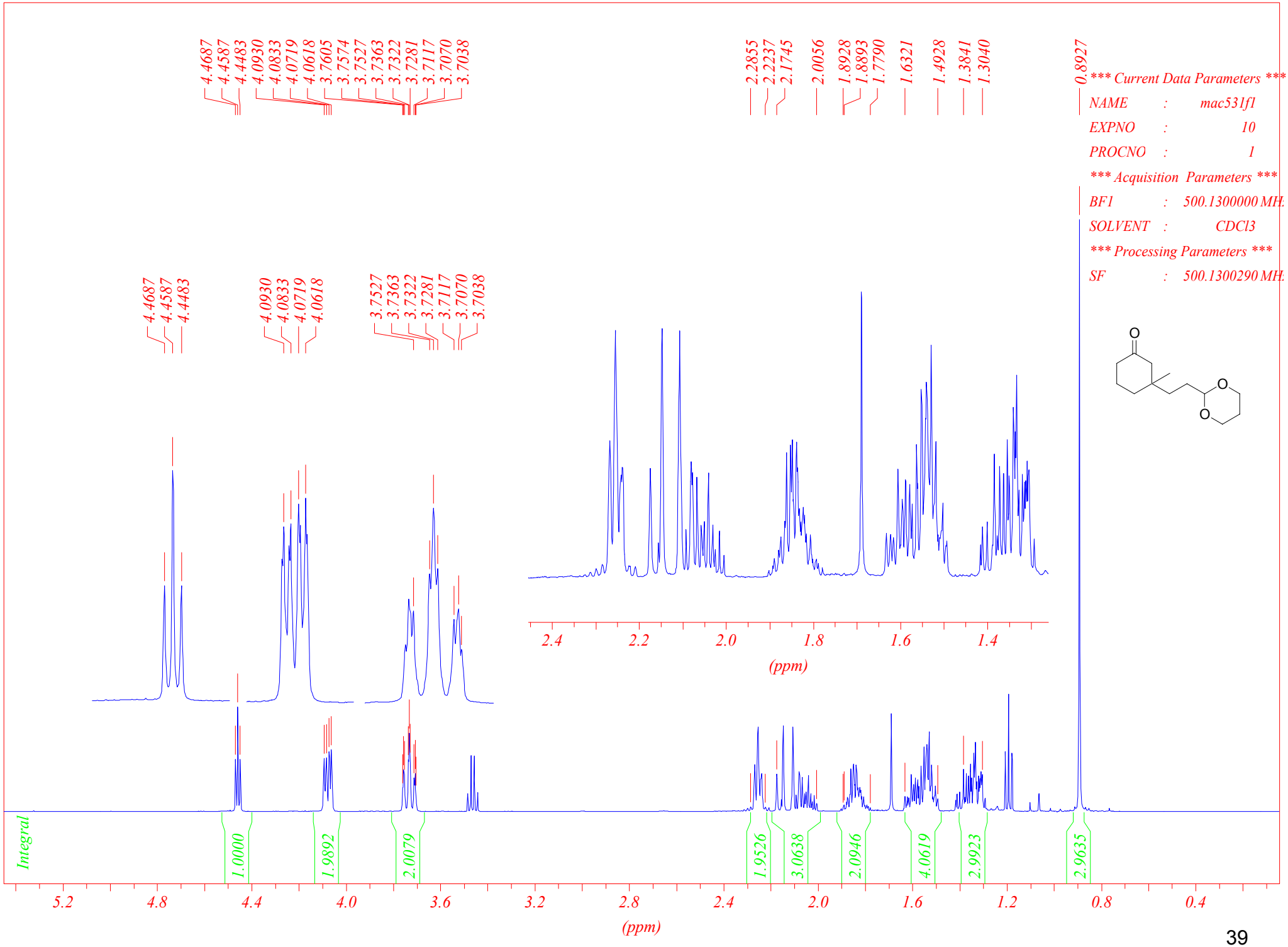

*** Current Data Parameters ***
NAME : mac529p1
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 500.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300290 MHz
5.8269
5.7462
5.0250
5.0216
4.9910
4.9875
4.9453
4.9440
4.9428
4.9415
4.9248
4.9239
4.9226
4.9213
2.3183
2.2429
2.2089
2.1821
2.1288
2.1020
2.0541
1.9716
1.8975
1.8348
1.6643
1.5300
1.5284
1.3866
1.3361
0.9286
O
5.0
(ppm)
2.4
2.2
2.0
1.8
1.6
1.4
1.2
(ppm)
Integral
1.0000
2.0384
2.0843
2.1304
2.1301
2.1329
1.9044
2.0908
3.0978
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
(ppm)

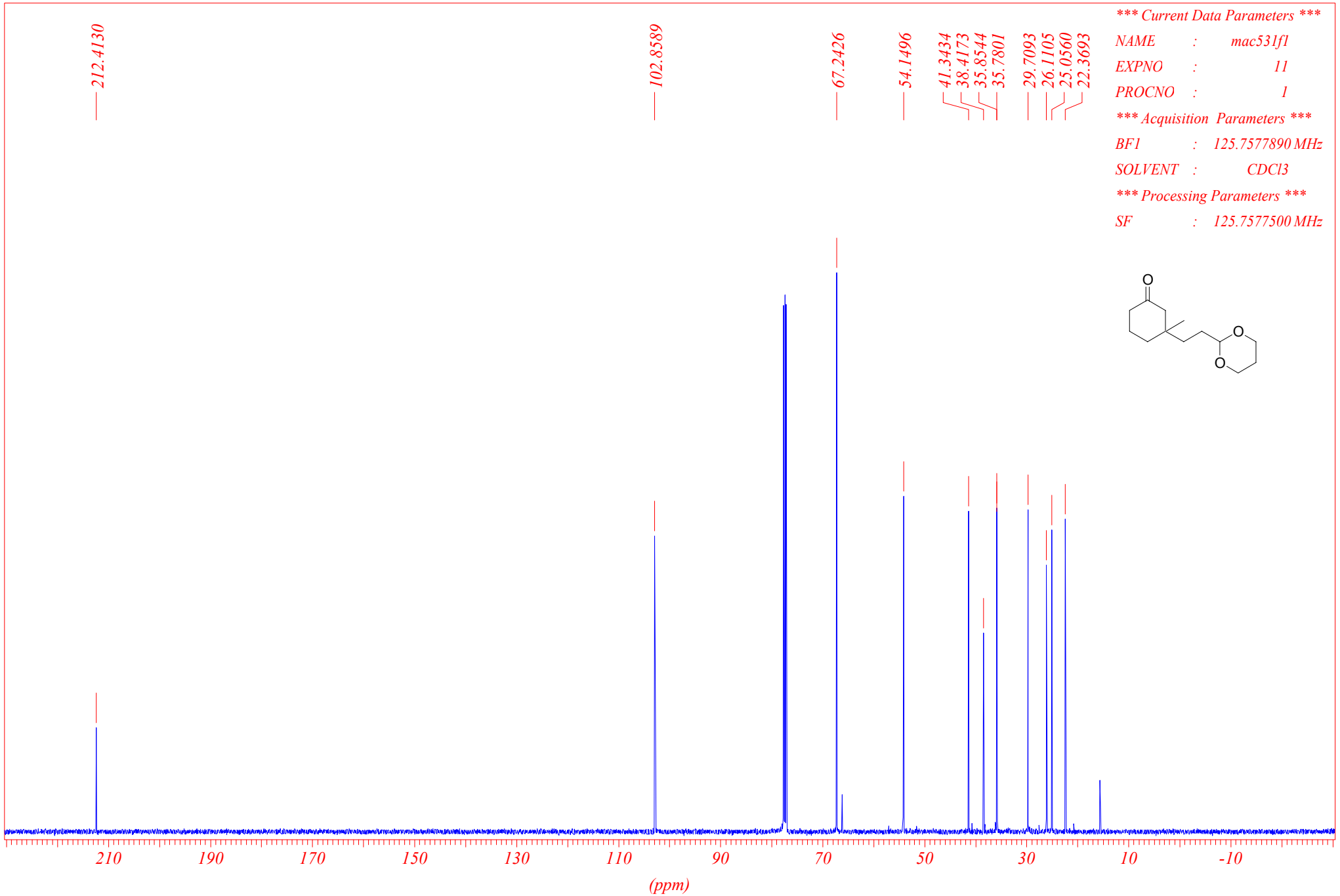

212.4729
139.1169
114.7447
54.0381
41.3454
41.2113
38.8775
36.1722
28.1740
25.2211
22.4230
*** Current Data Parameters ***
NAME : mac529p1
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577500 MHz
O
210
190
170
150
130
110
90
70
50
30
10
-10
-30
(ppm)

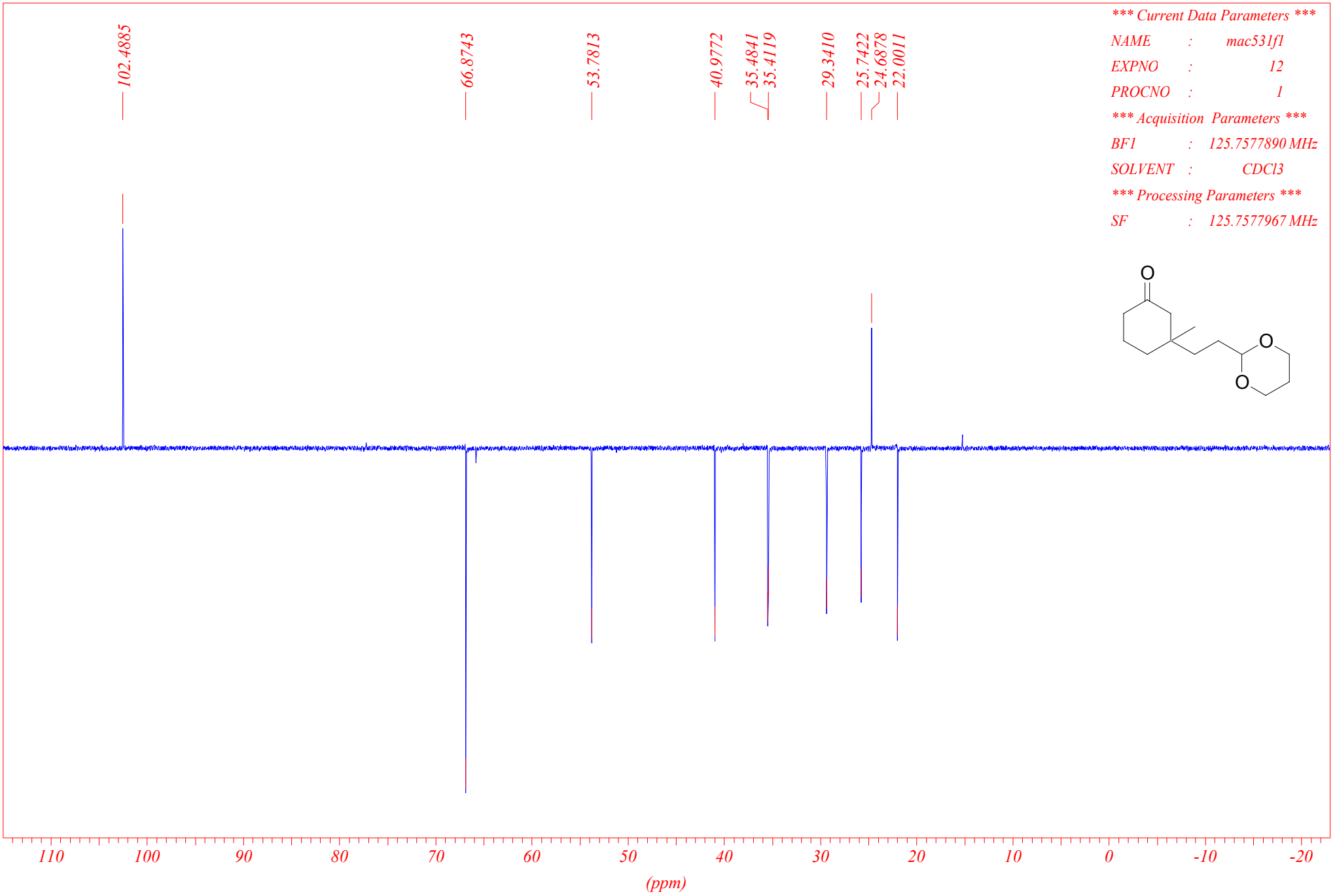

138.7424
114.3723
53.6637
40.9731
40.8348
35.7936
27.8016
24.8467
22.0506
*** Current Data Parameters ***
NAME : mac529p1
EXPNO : 12
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577967 MHz
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

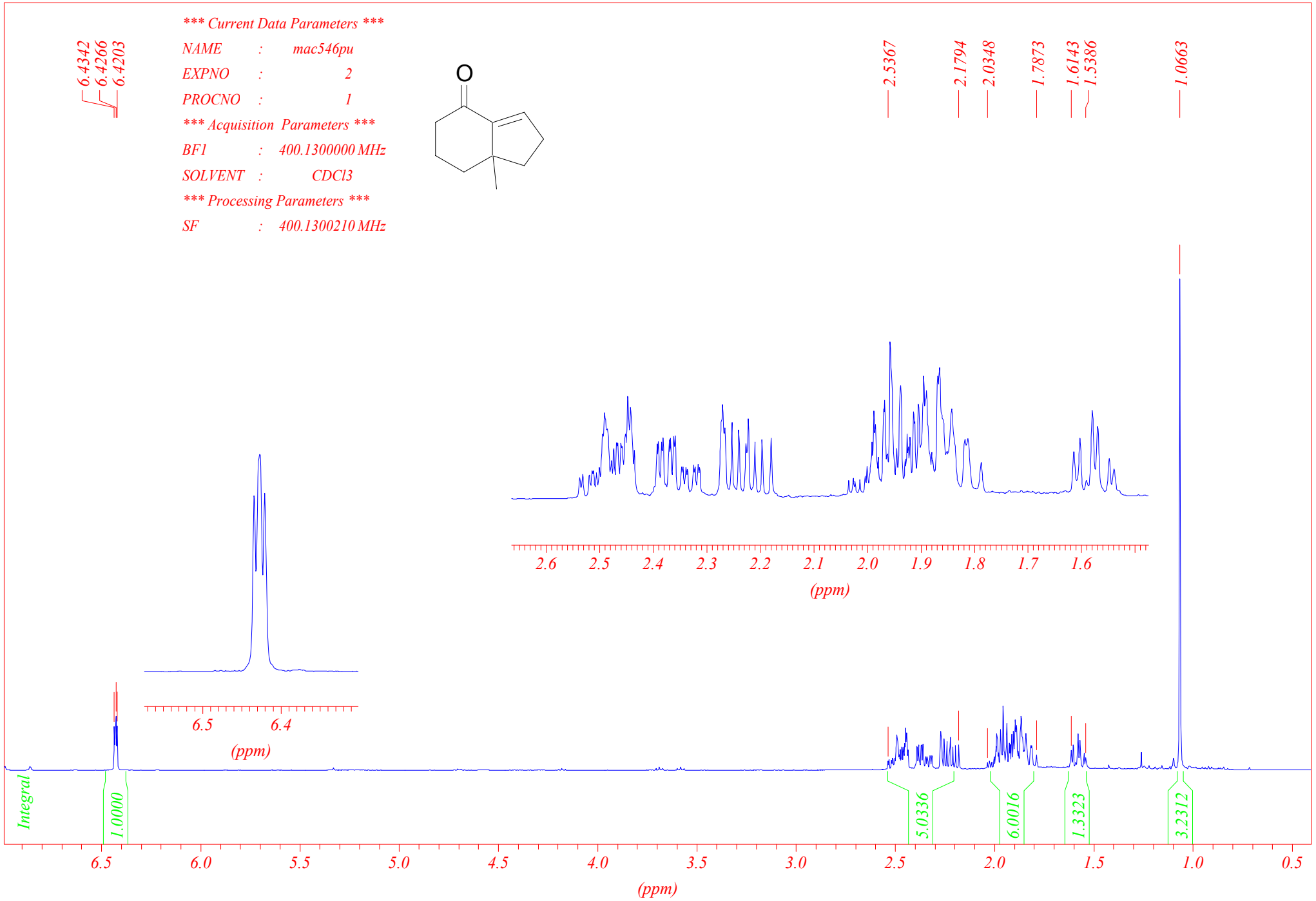

*** Current Data Parameters ***
NAME : mac541mr
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 400.1300210 MHz
5.8211
5.7195
5.0079
4.9126
2.2703
2.2533
2.2362
2.1838
2.1503
2.1030
2.0689
2.0304
1.9780
1.8725
1.8063
1.6471
1.4887
1.4861
1.3592
1.2273
0.8983
O
2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2
(ppm)
Integral
1.0000
2.0338
1.8902
2.0902
1.9717
2.0327
2.0805
4.1298
2.7765
6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4
(ppm)

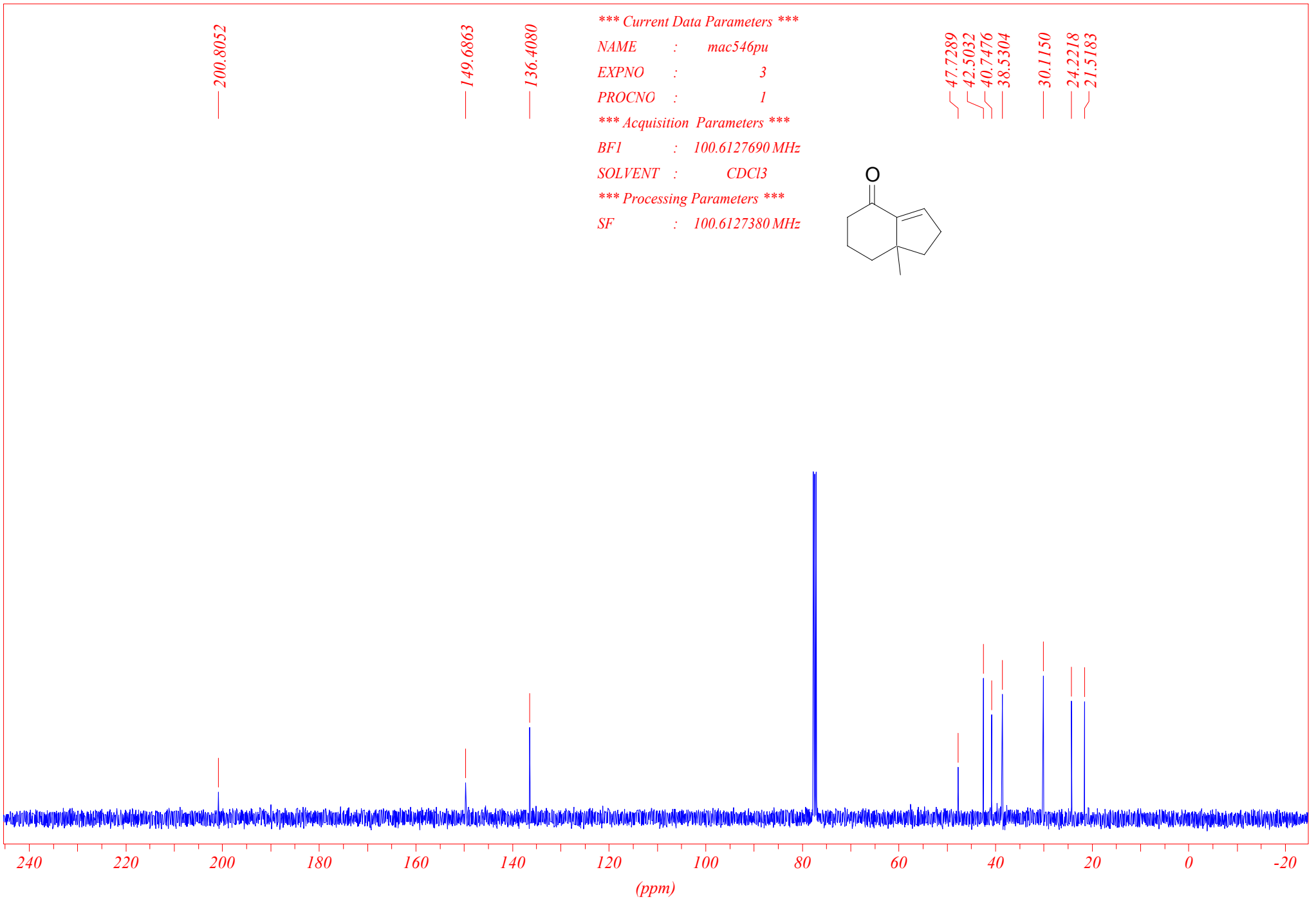

212.6329
138.9383
114.9532
54.1002
41.3493
38.8601
36.1237
34.5741
25.3675
23.0349
22.4332
*** Current Data Parameters ***
NAME : mac541mr
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127410 MHz
O
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
(ppm)

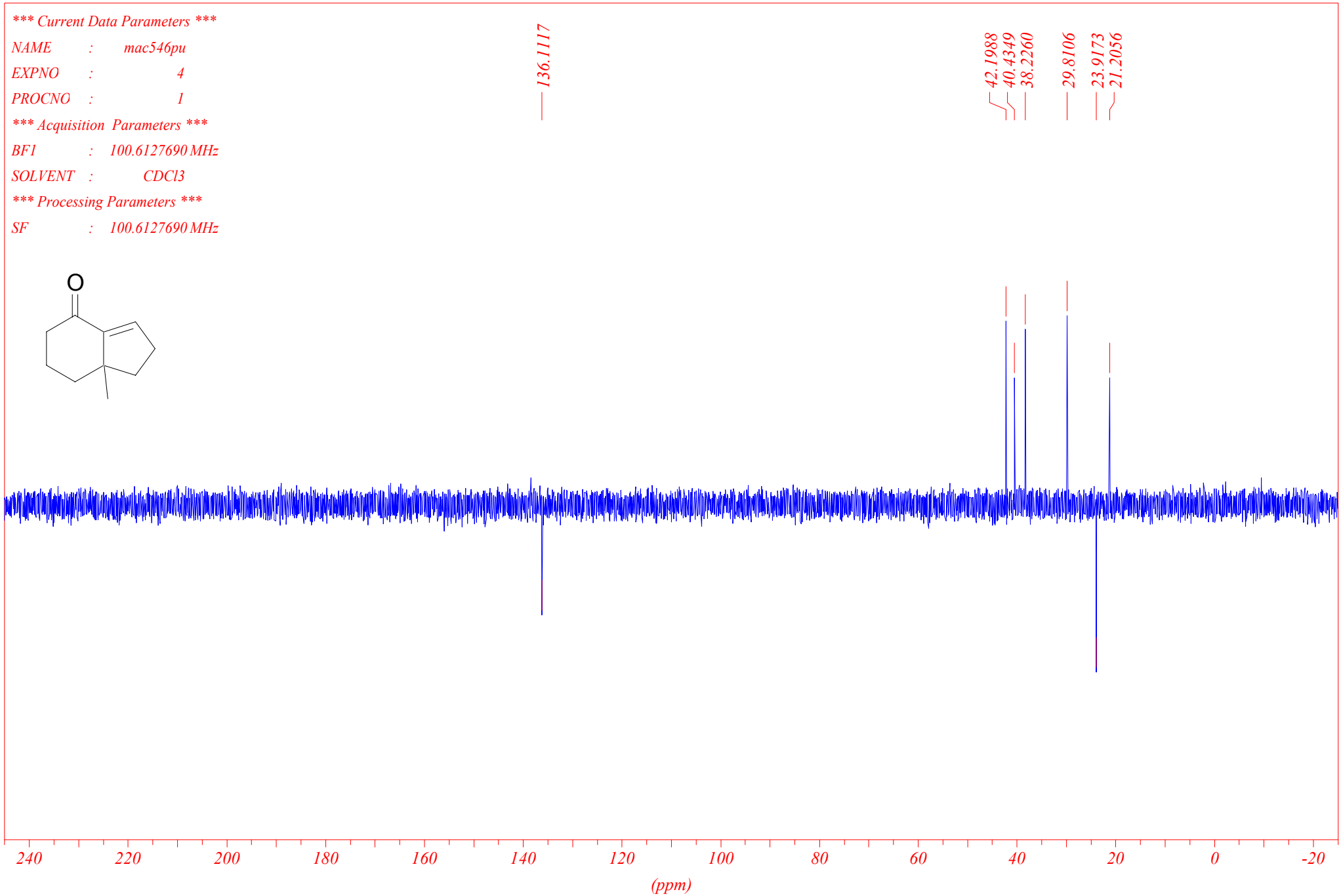

4.4687
4.4587
4.4483
4.0930
4.0833
4.0719
4.0618
3.7605
3.7574
3.7527
3.7363
3.7322
3.7281
3.7117
3.7070
3.7038
2.2855
2.2237
2.1745
2.0056
1.8928
1.8893
1.7790
1.6321
1.4928
1.3841
1.3040
0.8927
*** Current Data Parameters ***
NAME : mac531f1
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 500.1300000 MH
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300290 MH
O
O
O
2.4
2.2
2.0
1.8
1.6
1.4
(ppm)
Integral
1.0000
1.9892
2.0079
1.9526
3.0638
2.0946
4.0619
2.9923
2.9635
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
(ppm)

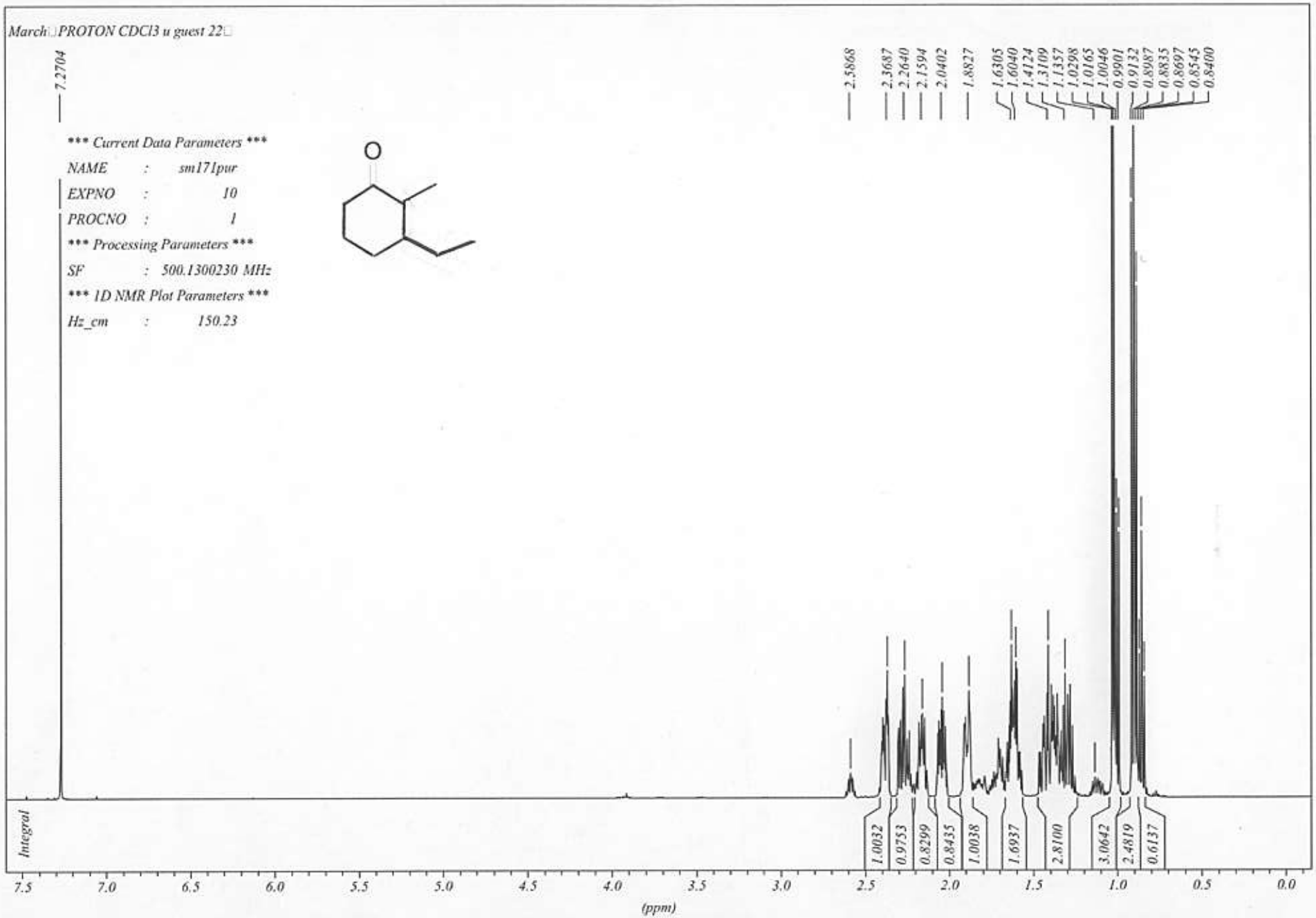

212.4130
102.8589
67.2426
54.1496
41.3434
38.4173
35.8544
35.7801
29.7093
26.1105
25.0560
22.3693
*** Current Data Parameters ***
NAME : mac531f1
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577500 MHz
O
O
O
210
190
170
150
130
110
90
70
50
30
10
-10
(ppm)

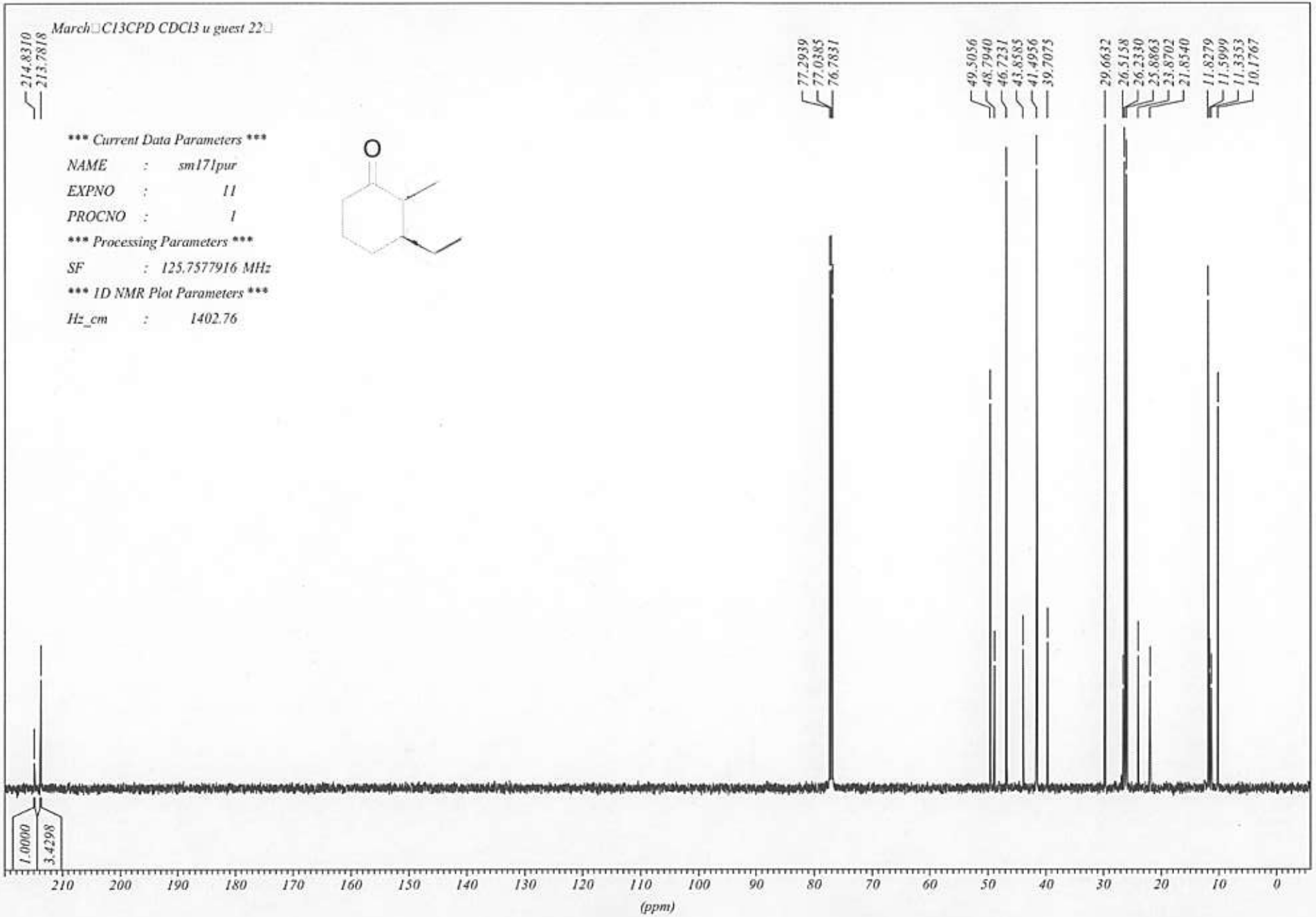

102.4885
66.8743
53.7813
40.9772
35.4841
35.4119
29.3410
25.7422
24.6878
22.0011
*** Current Data Parameters ***
NAME : mac531f1
EXPNO : 12
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 125.7577890 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577967 MHz
O
O
O
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
(ppm)

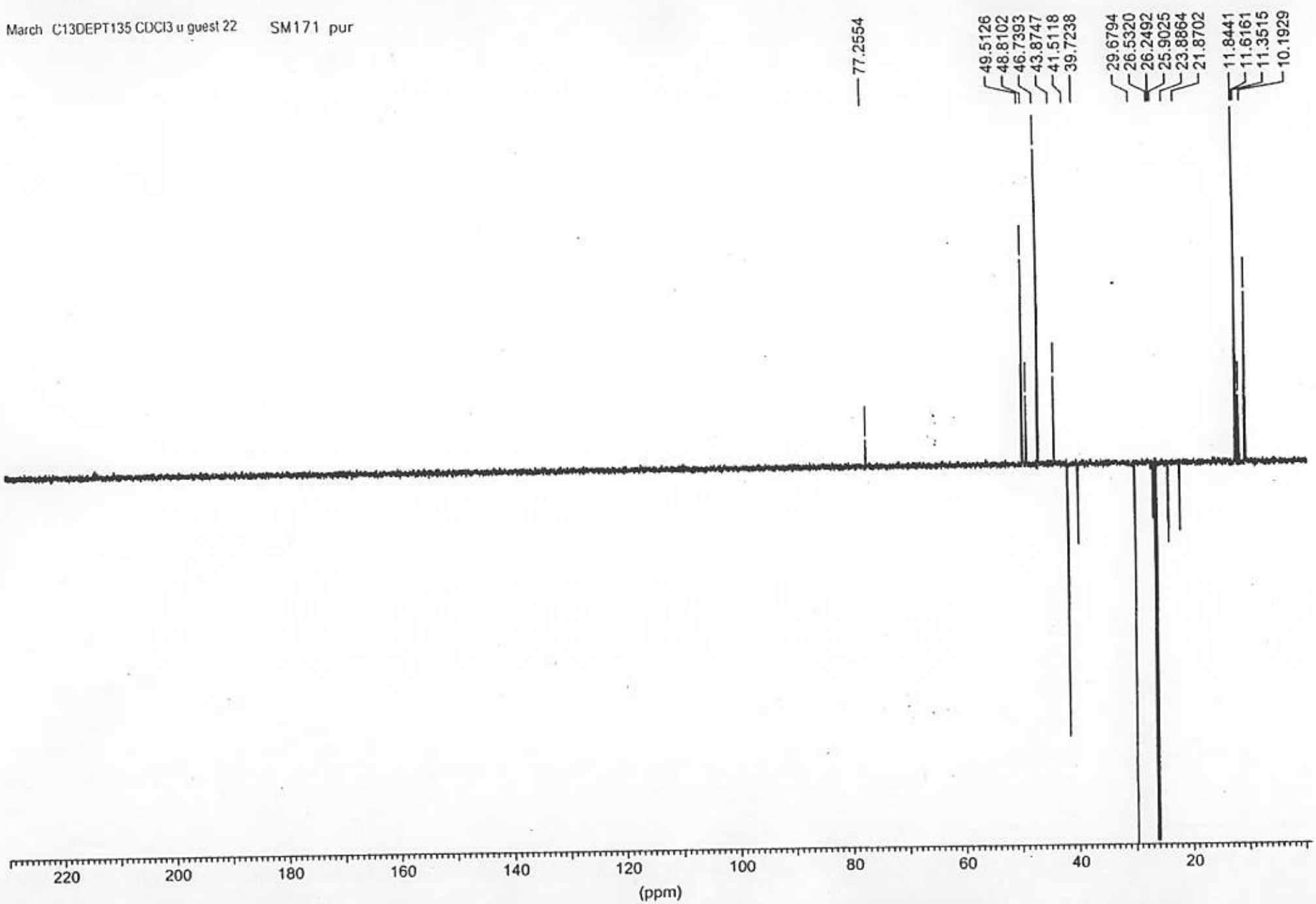

*** Current Data Parameters ***
NAME : mac546pu
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 400.1300210 MHz
6.4342
6.4266
6.4203
2.5367
2.1794
2.0348
1.7873
1.6143
1.5386
1.0663
O
6.5
6.4
(ppm)
2.6
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
(ppm)
Integral
1.0000
5.0336
6.00016
1.3323
3.2312
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
(ppm)


200.8052
149.6863
136.4080
47.7289
42.5032
40.7476
38.5304
30.1150
24.2218
21.5183
*** Current Data Parameters ***
NAME : mac546pu
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127380 MHz
O
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
(ppm)


*** Current Data Parameters ***
NAME : mac546pu
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 100.6127690 MHz
O
136.1117
42.1988
40.4349
38.2260
29.8106
23.9173
21.2056
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
(ppm)


March PROTON CDCl3 u guest 22
7.2704
2.5868
2.3687
2.2640
2.1594
2.0402
1.8827
1.6305
1.6040
1.4124
1.3109
1.1357
1.0298
1.0165
1.0046
0.9901
0.9132
0.8987
0.8835
0.8697
0.8545
0.8400
*** Current Data Parameters ***
NAME : sm171pur
EXPNO : 10
PROCNO : 1
*** Processing Parameters ***
SF : 500.1300230 MHz
*** 1D NMR Plot Parameters ***
Hz_cm : 150.23
O
Integral
1.0032
0.9753
0.8299
0.8435
1.0038
1.6937
2.8100
3.0642
2.4819
0.6137
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
(ppm)


March□C13CPD CDCl3 u guest 22□
214.8310
213.7818
77.2939
77.0385
76.7831
49.5056
48.7940
46.7231
43.8585
41.4956
39.7075
29.6632
26.5158
26.2330
25.8863
23.8702
21.8540
11.8279
11.5999
11.3353
10.1767
*** Current Data Parameters ***
NAME : sm171pur
EXPNO : 11
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577916 MHz
*** 1D NMR Plot Parameters ***
Hz_cm : 1402.76
O
1.0000
3.4298
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)


March C13DEPT135 CDCl3 u guest 22 SM171 pur
77.2554
49.5126
48.8102
46.7393
43.8747
41.5118
39.7238
29.6794
26.5320
26.2492
25.9025
23.8864
21.8702
11.8441
11.6161
11.3515
10.1929
220
200
180
160
140
120
100
80
60
40
20
(ppm)