Supporting Information

A Concise Total Synthesis of Melithiazole C

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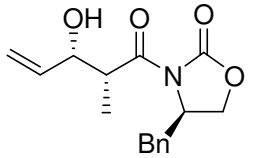
General: All reactions were performed under an argon atmosphere in anhydrous solvents (CH_2Cl_2 was distilled from CaH_2, THF and Et_2O were distilled from sodium/benzophenone). TLC was performed on Merck $60F_{254}$ silica gel plates and visualized with a UV lamp (254 nm) and a $KMnO_4/K_2CO_3$/AcOH solution in H_2O followed by heating. Flash chromatography was performed with Merck Geduran Si60 silica gel (40-63 μM). Optical rotations were determined with a Perkin Elmer 343 polarimeter. Infrared (IR) spectra were recorded on a Bruker TENSOR^{TM} 27 (IRFT) and wave-numbers are indicated in cm^{-1}. ^1H NMR spectra were recorded on a Bruker AVANCE 400 at 400 MHz and data are reported as follows: chemical shift in ppm relative to the residual solvent peak, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet or overlap of non equivalent resonances), integral. ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 at 100 MHz and data are reported as follows: chemical shift in ppm relative to the residual solvent peak, multiplicity with respect to proton (deduced from DEPT experiments, s = C_q, d = CH, t = CH_2, q = CH_3). Mass spectra with electronic impact (MS) were recorded with a Hewlett-Packard tandem 5890A/5971 GC-MS (70 eV). High resolution mass spectra (HRMS) were performed by the Groupe de Spectrométrie de Masse de l'Université Pierre et Marie Curie (Paris).

(*R*)-4-Benzyl-3-[(2*R*,3*S*)-3-hydroxy-2-methyl-pent-4-enoyl]-oxazolidin-2-one (6)[1]

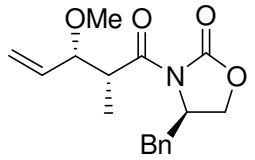


To a solution of oxazolidinone **4** (4.67 g, 20 mmol) in CH_2Cl_2 (60 mL) were added *n*-Bu_2BOTf 24 mL, 1.0 M in CH_2Cl_2, 24 mmol) and $^iPr_2NEt$ (4.8 mL, 27.6 mmol) dropwise at 0 °C. After

[1] Nicolaou, K. C.; Brenzovich, W. E.; Bulger, P. G.; Francis, T. M. *Org. Biomol. Chem.* **2006**, *4*, 2119-2157.

10 min the mixture was cooled to -78 °C and freshly distilled acrolein (7.0 mL, 105 mmol) was added dropwise over 5 min. The mixture was stirred at -78 °C for 45 min and allowed to warm to 0 °C over 30 min before a pH 7 aqueous buffer solution (30 mL) and MeOH (100 mL) were added. A MeOH/35% H_2O_2 mixture (2/1, 100 mL) was then added slowly over 20 min and the mixture was stirred for a further 20 min at 0 °C before it was concentrated *in vacuo*. The residue was partitioned between Et_2O (200 mL) and H_2O (200 mL) and the aqueous phase was extracted with Et_2O (2 x 200 mL). The combined organic phases were washed with a saturated aqueous $NaHCO_3$ solution (150 mL) and brine (150 mL). Drying over $MgSO_4$, evaporation of the solvent and purification of the residue by flash chromatography (SiO_2; 30% EtOAc in hexane) gave **6** (5.39 g, 93%) as a white solid.

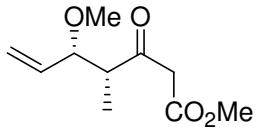
(*R*)-4-Benzyl-3-[(2*R*,3*S*)-3-methoxy-2-methyl-pent-4-enoyl]-oxazolidin-2-one (7)



To a solution of alcohol **6** (1.8 g, 6.2 mmol) and 2,6-ditertbutyl pyridine (11.5 g, 60 mmol) in CH_2Cl_2 (30 mL) was added methyl triflate (8.2 g, 50 mmol) dropwise and the mixture was stirred for 40 h at rt. The reaction was quenched with a saturated aqueous $NaHCO_3$ solution (100 mL), extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic phases were dried over $MgSO_4$. Evaporation of the solvent and purification of the residue by flash chromatography (SiO_2; hexane to ether/hexane : 1/1) gave **7** (1.6 g, 85%) as a colourless viscous oil.

R*f* = 0.28 (ether/hexane : 1/1); $[\alpha]^{20}_{D}$ – 69.0 (*c* 1.0, $CHCl_3$); **IR**: 2981, 2922, 1773, 1694, 1454, 1379, 1192, 1092, 980, 928, 745, 700 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.40-7.29 (m, 3H), 7.28-7.19 (m, 2H), 5.82 (m, 1H), 5.31-5.27 (m, 2H), 4.66 (m, 1H), 4.19 (quint, *J* = 7 Hz, 2H), 4.11 (m, 1H), 3.77 (t_{app}, *J* = 7.0 Hz, 1H), 3.31 (s, 3H), 3.30 (m, 1H), 2.78 (dd, *J* = 9.8 and 13.3 Hz, 1H), 1.29 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 174.6 (s), 153.2 (s), 136.0 (d), 135.3 (s), 129.5 (2 x d), 128.9 (2 x d), 127.3 (d), 119.0 (t), 84.1 (d), 66.0 (t), 56.8 (q), 55.5 (d), 42.3 (d), 37.8 (t), 13.3 (q); **MS** (EI, 70 eV): *m/z* (%): 303 (2), 272 (10), 256 (2), 156 (3), 127 (28), 117 (12), 99 (8), 91 (18), 71 (100); **HRMS** (ESI): calcd for $C_{17}H_{21}NNaO_4$ $[M + Na]^+$: 326.1363, found: 326.1357.

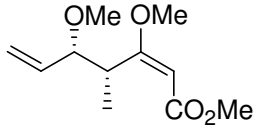
(4*R*,5*S*)-5-Methoxy-4-methyl-3-oxo-hept-6-enoic acid methyl ester (8)



To a solution of oxazolidinone **7** (607 mg, 2 mmol) in THF/H_2O (4/1, 5 mL) at 0 °C was added a 35% aqueous H_2O_2 solution (0.8 mL, 8 mmol) dropwise followed by LiOH•H_2O (168 mg, 4 mmol). After 1 h the mixture was treated with a saturated aqueous $Na_2S_2O_5$ solution (5 mL), diluted with H_2O (20 mL) and washed with CH_2Cl_2 (3 x 20 mL). The aqueous phase was then acidified with 3M HCl (8 mL) and extracted with EtOAc (4 x 30 mL). Drying of the combined organic phases over $MgSO_4$ and evaporation of the solvent gave the crude acid which was dissolved in THF (10 mL) and treated with carbonyl diimidazole (357 mg, 2.2 mmol) at 0 °C. After 2 h at rt the mixture was added dropwise to a solution of $LiCH_2CO_2Me$ prepared from AcOMe (444 mg, 6 mmol), $^{i}Pr_2NH$ (610 mg, 6 mmol) and *n*-BuLi (6 mmol, 2M in cyclohexane) at -78 °C and stirring was continued for 2 h at -78 °C. The reaction was quenched with 2N HCl (20 mL) and the aqueous phase was extracted with Et_2O (3 x 20 mL). Drying of the combined organic phases over $MgSO_4$, evaporation of the solvent and purification of the residue by flash chromatography (SiO_2; ether/hexane : 1/4) gave **8** (300 mg, 75%) as a colourless oil [ratio keto/enol-form = 9/1).

R*f* = 0.18 (ether/hexane : 1/4); $[\alpha]^{20}_{D}$ – 41.8 (*c* 1.0, $CHCl_3$); **IR**: 2983, 2939, 2825, 1747, 1713, 1629, 1437, 1311, 1238, 1160, 1087, 997, 930, 841, 656 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz, keto-form): δ = 5.64 (m, 1H), 5.33-5.24 (m, 2H), 3.77 (m, 1H), 3.75 (s, 3H), 3.61 (d, *J* = 15.8 Hz, 2H), 3.57 (d, *J* = 15.8 Hz, 2H), 3.28 (s, 3H), 2.94 (dq, *J* = 5.5 and 7.0 Hz, 1H), 1.12 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz, keto-form): δ = 204.6 (s), 167.8 (s), 134.9 (d), 119.4 (t), 83.8 (d), 56.6 (q), 52.2 (d), 50.8 (q), 49.4 (t), 11.8 (q); **MS** (EI, 70 eV): *m/z* (%): 168 (2), 127 (4), 101 (12), 95 (6), 71 (100), 59 (8); **HRMS** (ESI): calcd for $C_{10}H_{16}NaO_4$ $[M + Na]^+$: 223.0946, found: 223.0941.

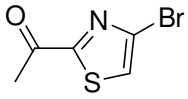
(*E*)-(4*R*,5*S*)-3,5-Dimethoxy-4-methyl-hepta-2,6-dienoic acid methyl ester (2)



To a solution of keto ester **8** (200 mg, 1.0 mmol) and trimethyl orthoformate (424 mg, 4.0 mmol) in MeOH (5 mL) was added concentrated sulphuric acid (20 mg, 0.2 mmol) and the mixture was stirred for 48 h at rt. After dilution with Et_2O (80 ml) the organic phase was washed with a saturated aqueous $NaHCO_3$ solution (10 mL), dried over $MgSO_4$ and concentrated. Purification of the residue by flash chromatography (SiO_2; ether/hexane : 1/5) gave **2** (180 mg, 84%) as a colourless oil.

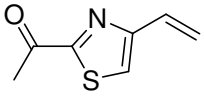
R*f* = 0.25 (ether/hexane : 1/5); $[\alpha]^{20}_D$ + 171.0 (*c* 1.0, $CHCl_3$); **IR**: 2940, 2821, 1710, 1621, 1436, 1382, 1270, 1193, 1138, 1093, 1038, 993, 923, 824, 696 cm^{-1}; **^{1}H NMR** (C_6D_6, 400 MHz): δ = 5.97 (ddd, *J* = 8.0, 10.3 and 16.9 Hz, 1H), 5.22-5.13 (m, 2H), 5.11 (s, 1H), 4.79 (dq, *J* = 6.8 and 8.5 Hz, 1H), 3.75 (t_{app}, *J* = 8.3 Hz, 1H), 3.58 (s, 3H), 3.27 (s, 3H), 3.03 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (C_6D_6, 100 MHz): δ = 176.5 (s), 167.3 (s), 137.7 (d), 117.2 (t), 91.4 (d), 85.4 (d), 56.2 (q), 54.5 (q), 50.2 (q), 39.7 (d), 14.5 (q); **MS** (EI, 70 eV): *m/z* (%): 199 (2), 182 (14), 169 (8), 155 (7), 123 (12), 111 (3), 71 (100); **HRMS** (ESI): calcd for $C_{11}H_{18}NaO_4$ $[M + Na]^+$: 237.1103, found: 237.1097.

1-(4-Bromo-thiazol-2-yl)-ethanone (9)[2]



To a solution of dibromthiazole **5** (1.2 g, 5 mmol) in THF (10 mL) was added *n*-BuLi (2.75 mL, 5.5 mmol) dropwise at -78 °C. After 30 min *N*-acetyl morpholine was added dropwise and the mixture was stirred for 2 h at -78 °C before being diluted with Et_2O (100 ml) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL). Drying of the organic phase over $MgSO_4$, evaporation of the solvent and purification of the residue by flash chromatography (SiO_2; 10% ether in hexane) gave **9** (835 mg, 81%) as a white solid.

1-(4-Vinyl-thiazol-2-yl)-ethanone (3)

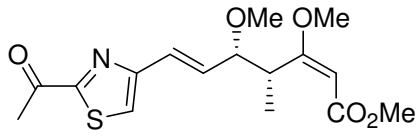


[2] Ung, A. T.; Pyne, S. G. *Tetrahedron: Asymmetry* **1998**, *9*, 1395-1407.

To a solution of bromide **9** (410 mg, 2 mmol) and $PdCl_2(PPh_3)_2$ (30 mg, 0.04 mmol) in dioxane (10 mL) was added vinyl tributyltin (700 mg, 2.2 mmol) dropwise and the mixture was stirred for 16 h at 100 °C. After dilution with Et_2O (100 mL) the organic phase was washed with H_2O (2 x 20 mL), dried over $MgSO_4$ and concentrated. Purification of the residue by flash chromatography (SiO_2; pentane to 5% ether in pentane) gave **3** (280 mg, 91%) as a yellow oil.

R*f* = 0.13 (5% ether in pentane); **IR**: 3099, 1685, 1483, 1451, 1357, 1275, 1054, 984, 946, 924, 780, 735 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.36 (s, 1H), 6.70 (dd, *J* = 10.8 and 17 Hz, 1H), 6.08 (dd, *J* = 1.5 and 17.0 Hz, 1H), 5.40 (dd, *J* = 1.5 and 10.8 Hz, 1H), 2.67 (s, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 191.9 (s), 166.7 (s), 156.2 (s), 129.4 (d), 121.9 (d), 118.0 (t), 26.0 (q); **MS** (EI, 70 eV): *m/z* (%): 153 (100), 138 (22), 125 (34), 111 (25), 84 (32), 69 (4), 58 (15); **HRMS** (ESI): calcd for C_7H_7NNaOS $[M + Na]^+$: 176.0141, found: 176.0140.

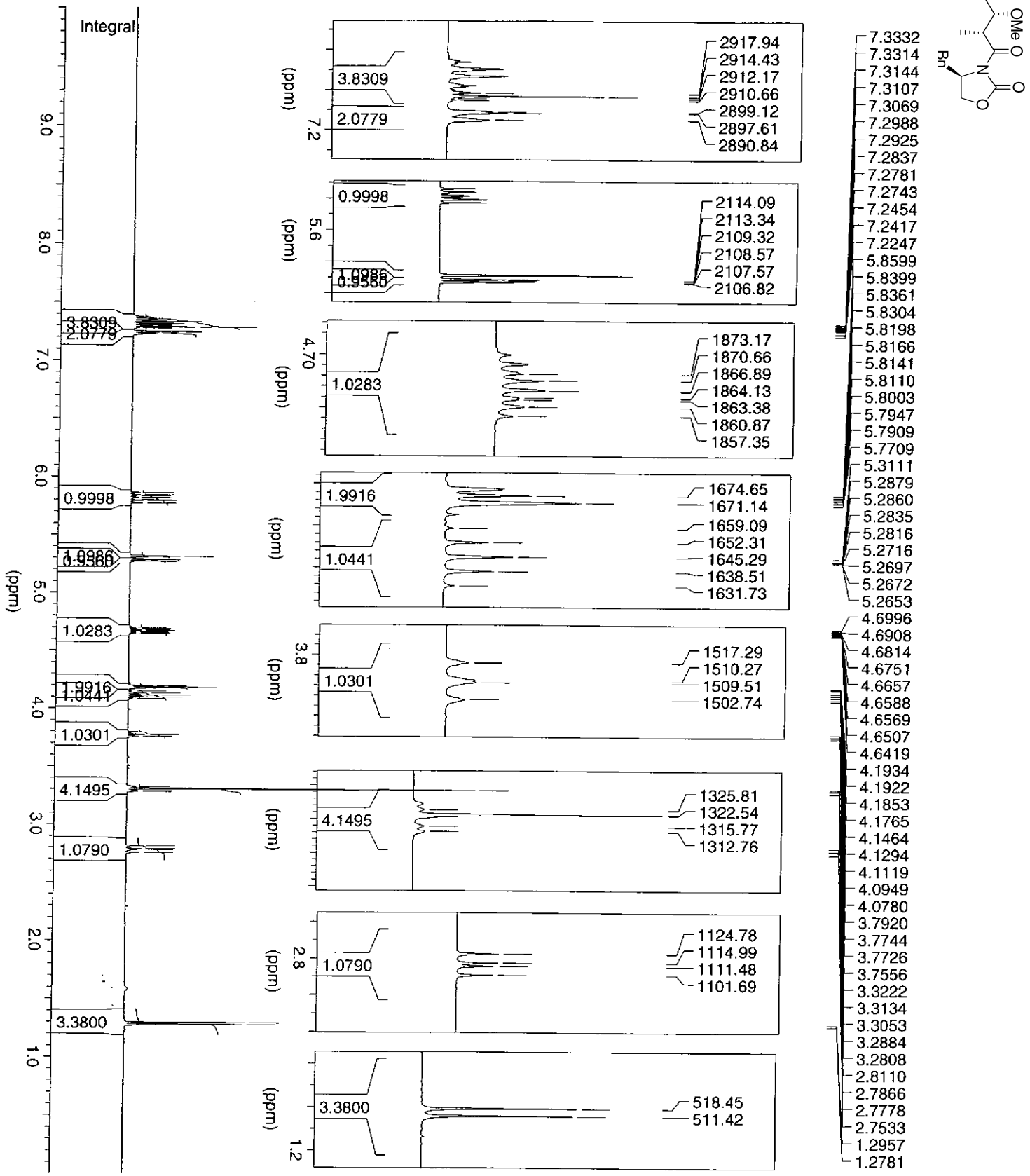
Melithiazole C (1)[3]



To a solution of **2** (21 mg, 0.1 mmol) and **3** (31 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) was added Grubbs 2nd generation catalyst (25 mg, 0.03 mmol) and the mixture was stirred for 60 h at 40 °C. Evaporation of the solvent, purification of the residue by flash chromatography (SiO_2; 2% acetone in CH_2Cl_2) and recrystallization from ether/hexane gave **1** (19 mg, 56%) as a white solid.

R*f* = 0.23 (2% acetone in CH_2Cl_2); **Mp**: 97-99 °C **$[\alpha]^{20}_D$** + 167.0 (*c* 0.3, MeOH); **IR**: 2933, 1709, 1688, 1622, 1438, 1383, 1359, 1272, 1145, 1093, 1054, 972, 928, 826 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 7.31 (s, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.40 (dd, *J* = 7.5 and 15.8 Hz, 1H), 4.90 (s, 1H), 4.11 (dq, *J* = 7.0 and 7.5 Hz, 1H), 3.75 (t_{app}, *J* = 7.5, 1H), 3.59 (s, 3H), 3.54 (s, 3H), 3.27 (s, 3H), 2.64 (s, 3H), 1.14 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** ($CDCl_3$, 100 MHz): δ = 191.9 (s), 176.5 (s), 167.7 (s), 166.5 (s), 155.6 (s), 133.2 (d), 124.7 (d), 121.4 (d), 91.1 (d), 84.2 (d), 57.1 (q), 55.5 (q), 50.8 (q), 39.8 (d), 26.0 (q), 13.9 (q); **MS** (EI, 70 eV): *m/z* (%): 307 (4), 276 (6), 196 (100), 181 (12), 154 (15), 123 (4); **HRMS** (ESI): calcd for $C_{16}H_{21}NNaO_5S$ $[M + Na]^+$: 362.1033, found: 362.1027.

[3] Söker, U.; Sasse, F.; Kunze, B.; Höfle, G. *Eur. J. Org. Chem.* **2000**, *11*, 2021-2026.



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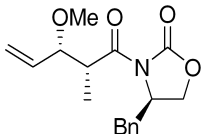

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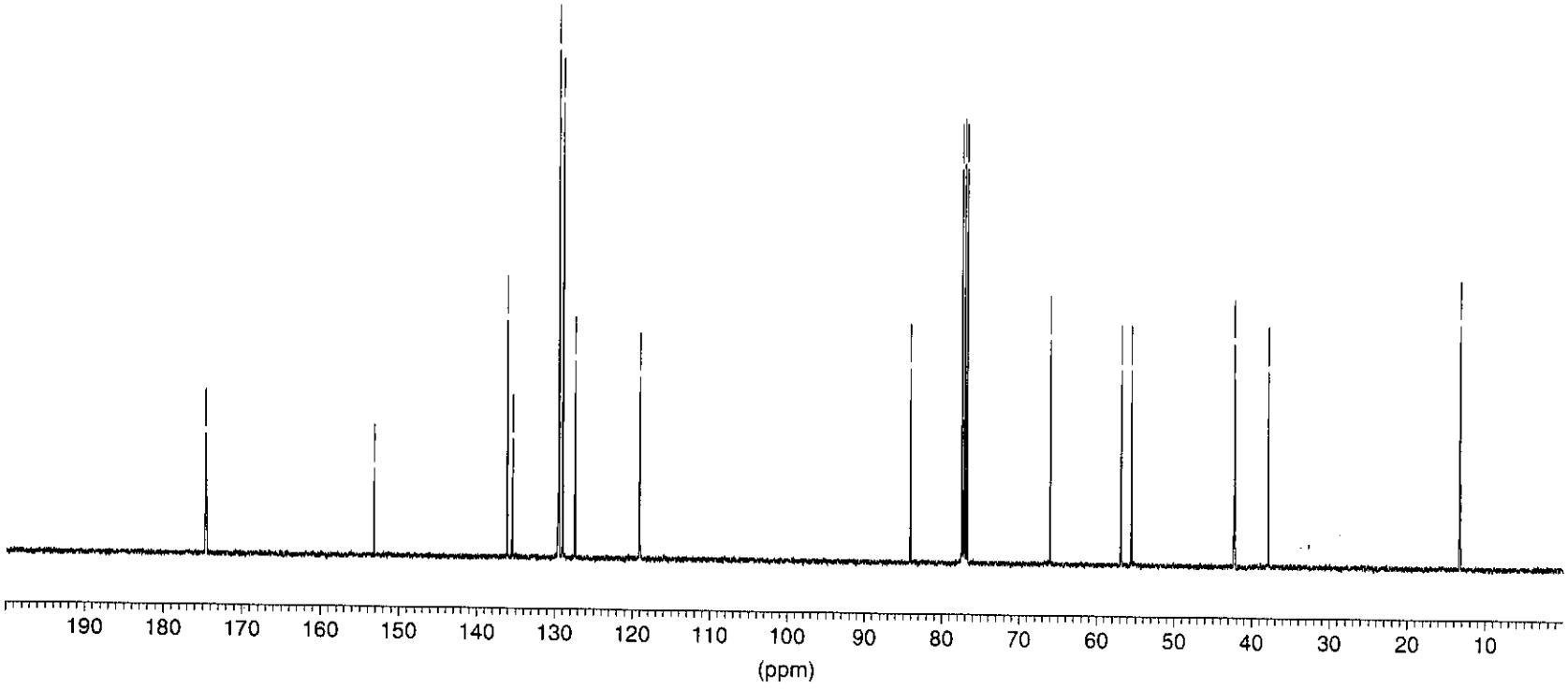

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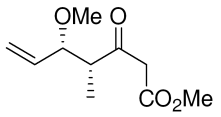

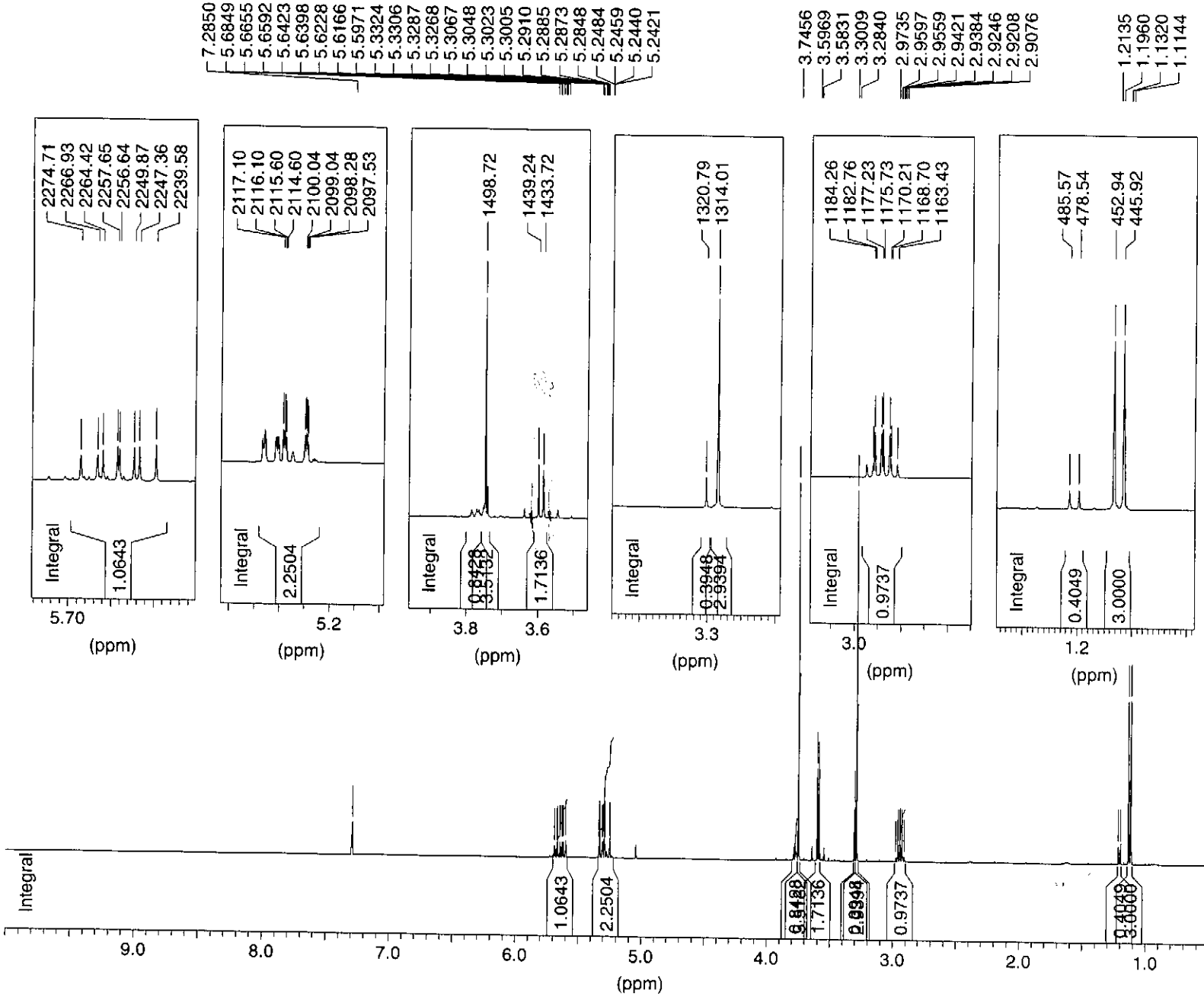

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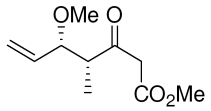

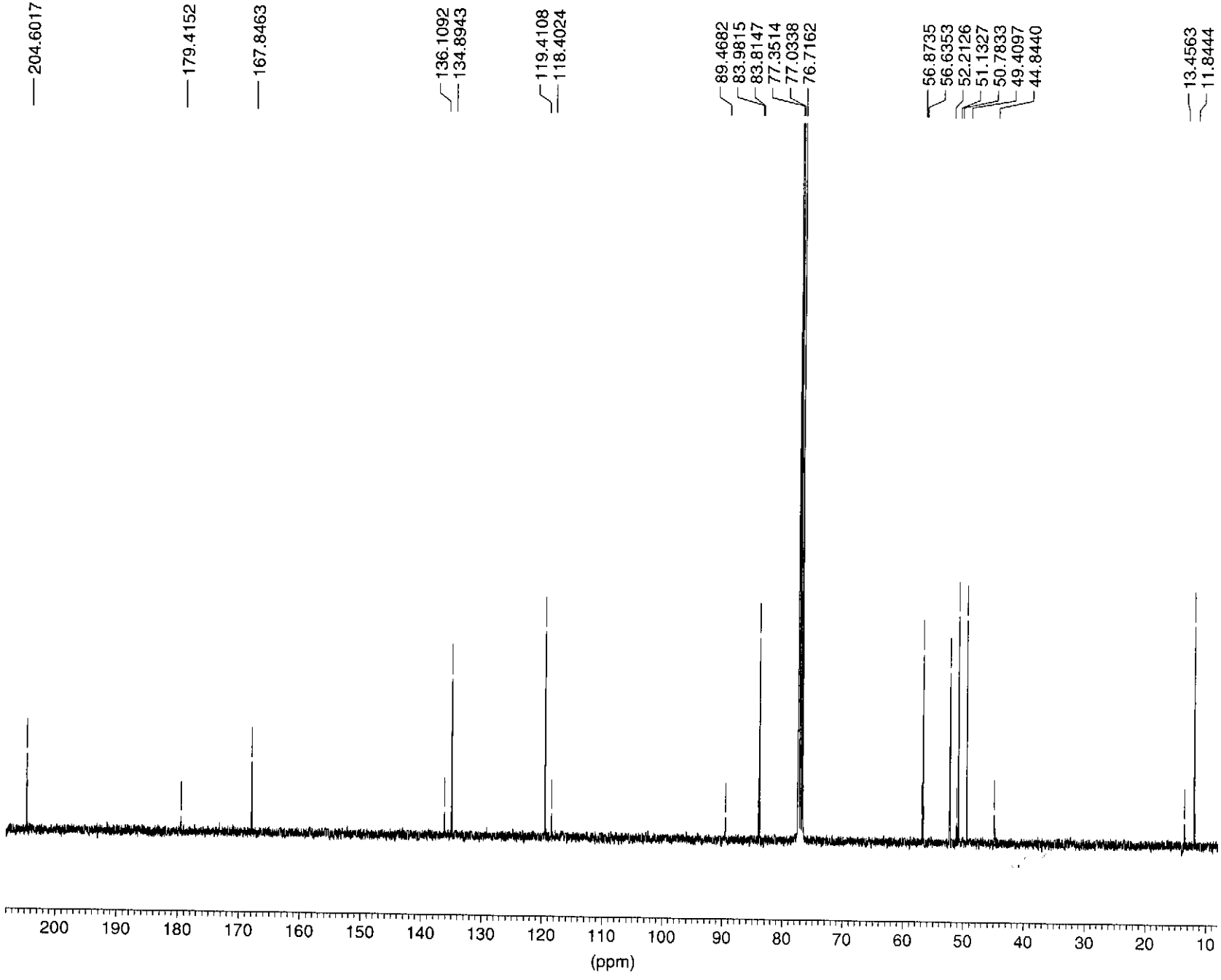

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*** 1D NMR Plot Parameters ***

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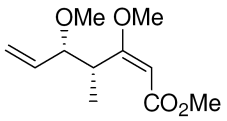

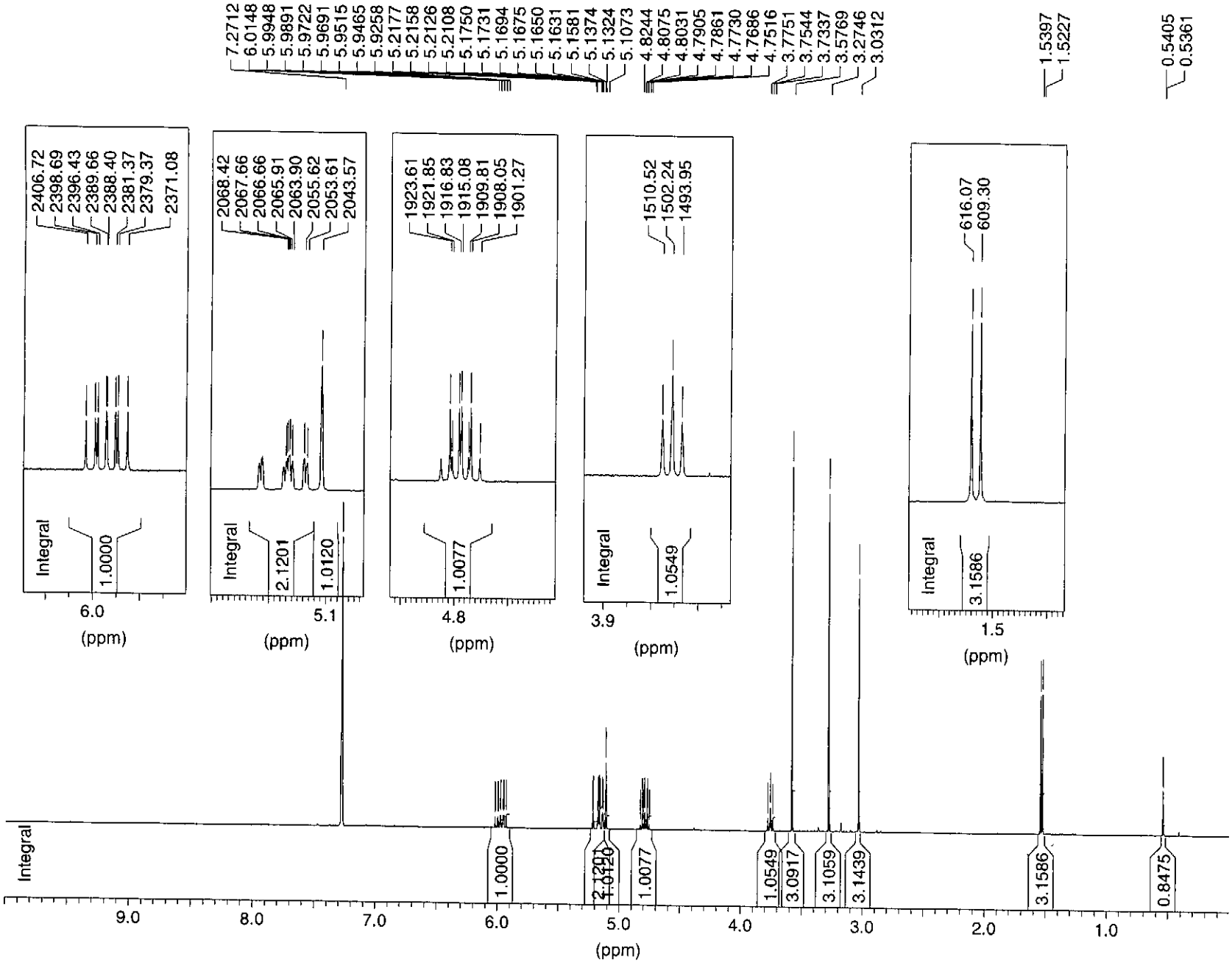

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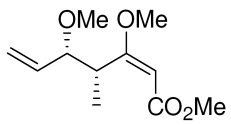
BF1	:	400.1300000 MHz
BF2	:	400.1300000 MHz
DECSTAT	:	DO
DS	:	2
FW	:	90000.00 Hz
INSTRUM	:	spect
LOCNUC	:	2H
NS	:	16
NUCLEUS	:	off
O1	:	2470.97 Hz
O2	:	2470.97 Hz
PULPROG	:	zg30
RO	:	20 Hz
SFO1	:	400.1324710 MHz
SOLVENT	:	C6D6
SW	:	20.5524 ppm
SW_h	:	8223.684 Hz
TD	:	65536
TE	:	296.7 K
VD	:	0.0000000 sec
YMAX_a	:	1220843520.0000000
YMIN_a	:	-928552704.0000000

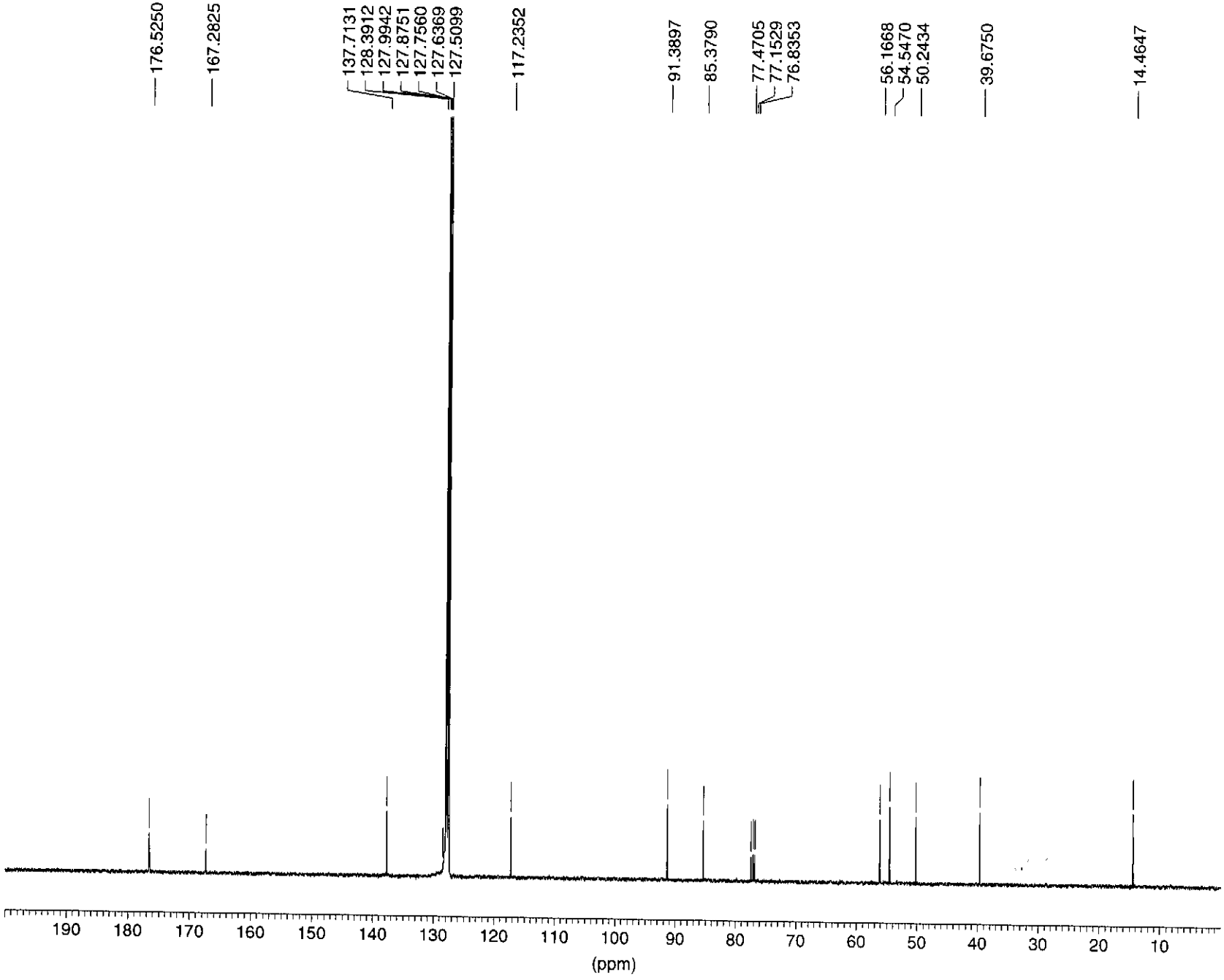
*** Processing Parameters ***

NC_proc	:	-3
OFFSET	:	16.452 ppm
SF	:	400.1300000 MHz
SI	:	32768

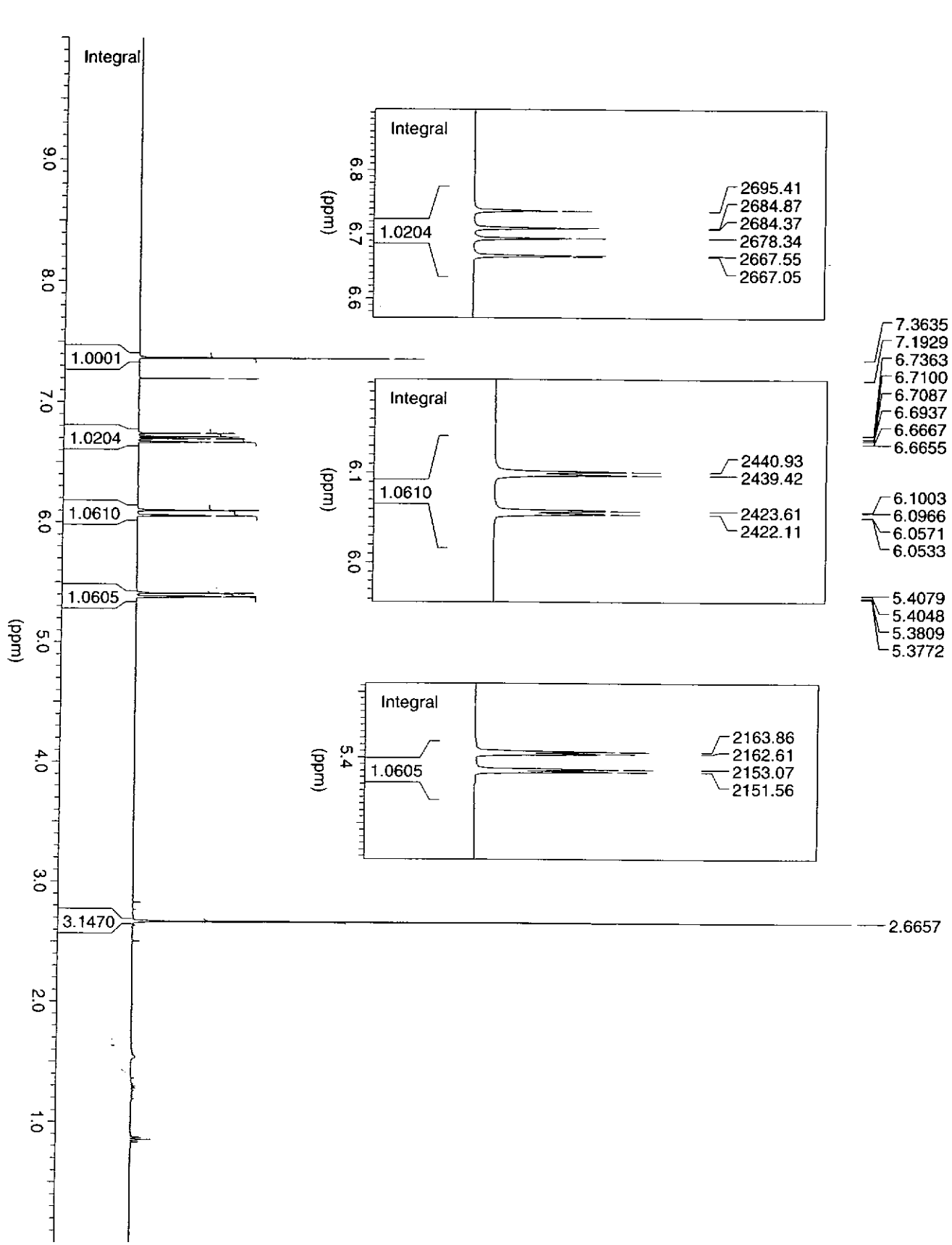
*** 1D NMR Plot Parameters ***

NC_proc	:	-3
NUCLEUS	:	off

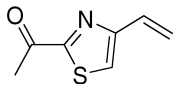




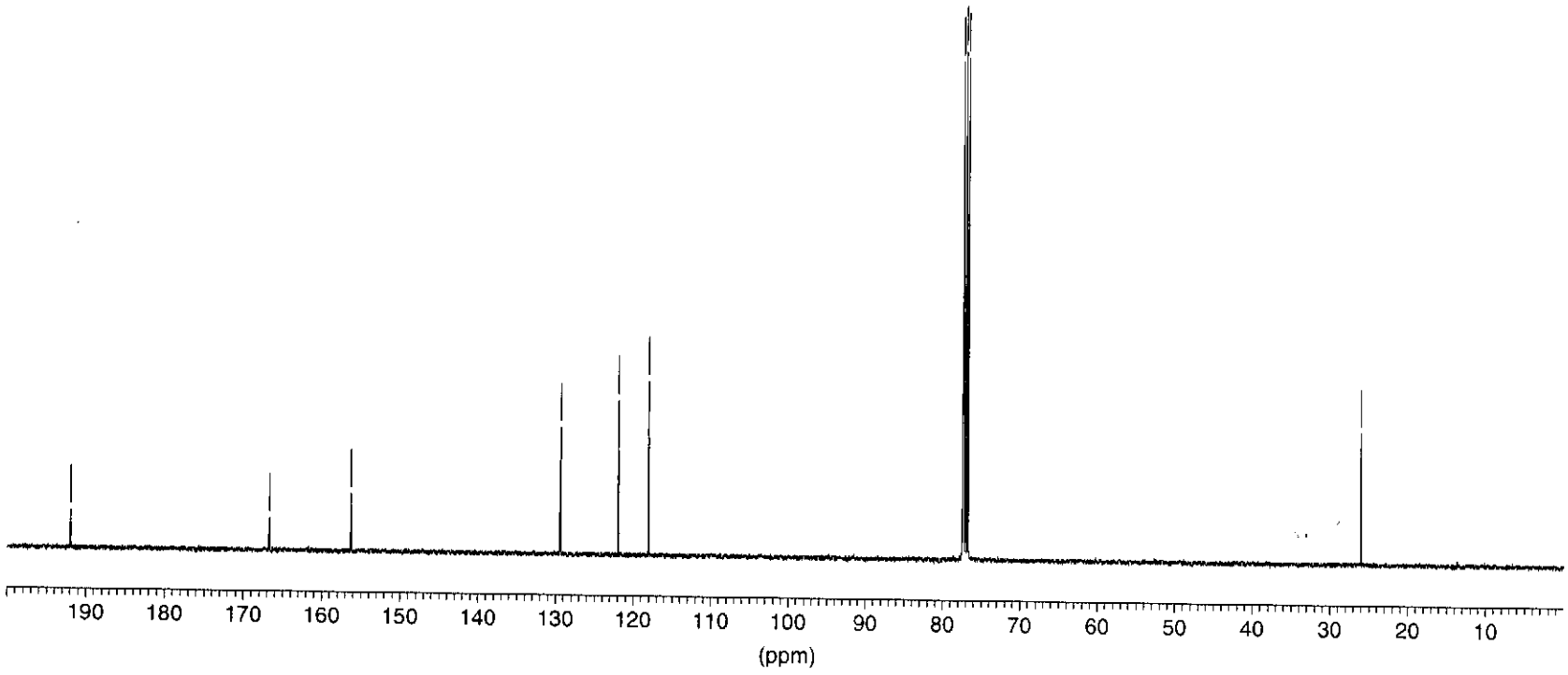
*** Current Data Parameters ***		
NAME	:	20070503
EXPNO	:	460
PROCNO	:	1
*** Acquisition Parameters ***		
AQ_mod	:	qsim
AUNM	:	au_zg
BF1	:	100.6127690 MHz
BF2	:	400.1300000 MHz
DECSTAT	:	DO
DS	:	4
FW	:	90000.00 Hz
INSTRUM	:	spect
LOCNUC	:	2H
NS	:	512
NUCLEUS	:	off
O1	:	10060.17 Hz
O2	:	1600.52 Hz
PULPROG	:	zgpg30
RO	:	20 Hz
SFO1	:	100.6228292 MHz
SOLVENT	:	CDCl3
SW	:	260.1598 ppm
SW_h	:	26178.010 Hz
TD	:	65536
TE	:	297.5 K
VD	:	0.0000000 sec
YMAX_a	:	1250301056.0000000
YMIN_a	:	-897187840.0000000
*** Processing Parameters ***		
NC_proc	:	2
OFFSET	:	230.082 ppm
SF	:	100.6127690 MHz
SI	:	32768
*** 1D NMR Plot Parameters ***		
NC_proc	:	2
NUCLEUS	:	off




```
*** Current Data Parameters ***
NAME                  :          20070320
EXPNO                 :               300
PROCNO                :                 1
*** Acquisition Parameters ***
AQ_mod                :               dqd
AUNM                  :             au_zg
BF1                   :  400.1300000 MHz
BF2                   :  400.1300000 MHz
DECSTAT               :                DO
DS                    :                 2
FW                    :       90000.00 Hz
INSTRUM               :              spect
LOCNUC                :                2H
NS                    :                16
NUCLEUS               :               off
O1                    :        2470.97 Hz
O2                    :        2470.97 Hz
PULPROG               :              zg30
RO                    :         21 Hz
SFO1                  :  400.1324710 MHz
SOLVENT               :              CDCl3
SW                    :       20.5524 ppm
SW_h                  :       8223.684 Hz
TD                    :             65536
TE                    :           295.9 K
VD                    :       0.0000000 sec
YMAX_a                : 1220888576.0000000
YMIN_a                : -92961264.0000000
*** Processing Parameters ***
NC_proc               :                -1
OFFSET                :       16.361 ppm
SF                    :  400.1300363 MHz
SI                    :             32768
*** 1D NMR Plot Parameters ***
NC_proc               :                -1
NUCLEUS               :               off
```



191.9290
166.6711
156.1980
129.3520
121.8882
118.0213
77.3514
77.2323
77.0338
76.7162
26.0336



*** Current Data Parameters ***

NAME	:	20070321
EXPNO	:	600
PROCNO	:	1

*** Acquisition Parameters ***

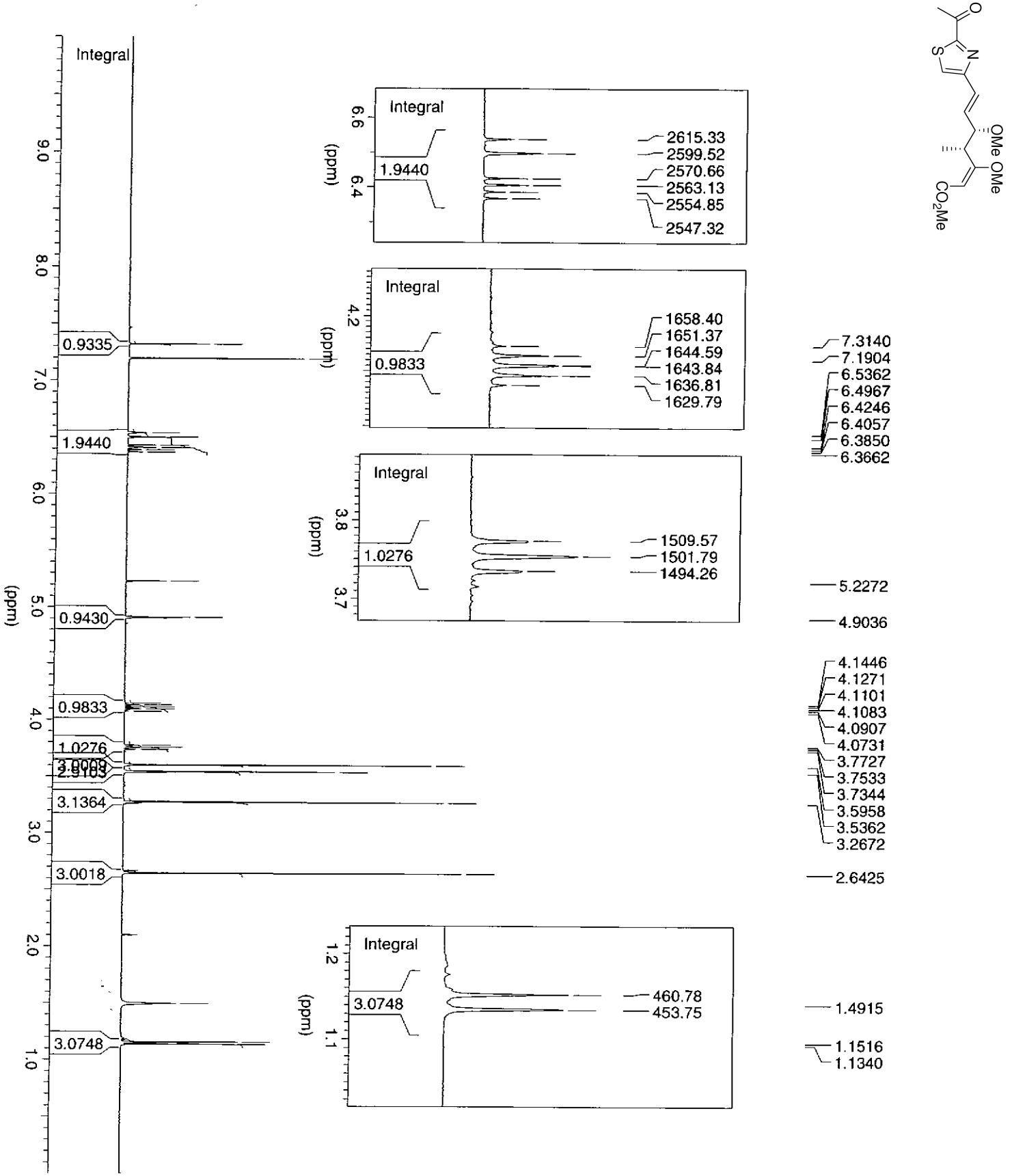
AQ_mod	:	qsim
AUNM	:	au_zg
BF1	:	100.6127690 MHz
BF2	:	400.1300000 MHz
DECSTAT	:	DO
DS	:	4
FW	:	90000.00 Hz
INSTRUM	:	spect
LOCNUC	:	2H
NS	:	1000
NUCLEUS	:	off
O1	:	10060.17 Hz
O2	:	1600.52 Hz
PULPROG	:	zgpg30
RO	:	20 Hz
SFO1	:	100.6228292 MHz
SOLVENT	:	CDCl3
SW	:	260.1598 ppm
SW_h	:	26178.010 Hz
TD	:	65536
TE	:	297.0 K
VD	:	0.0000000 sec
YMAX_a	:	1241264128.0000000
YMIN_a	:	-906857088.0000000

*** Processing Parameters ***

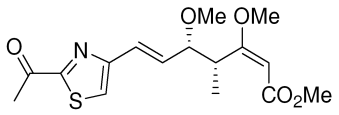
NC_proc	:	1
OFFSET	:	230.082 ppm
SF	:	100.6127690 MHz
SI	:	32768

*** 1D NMR Plot Parameters ***

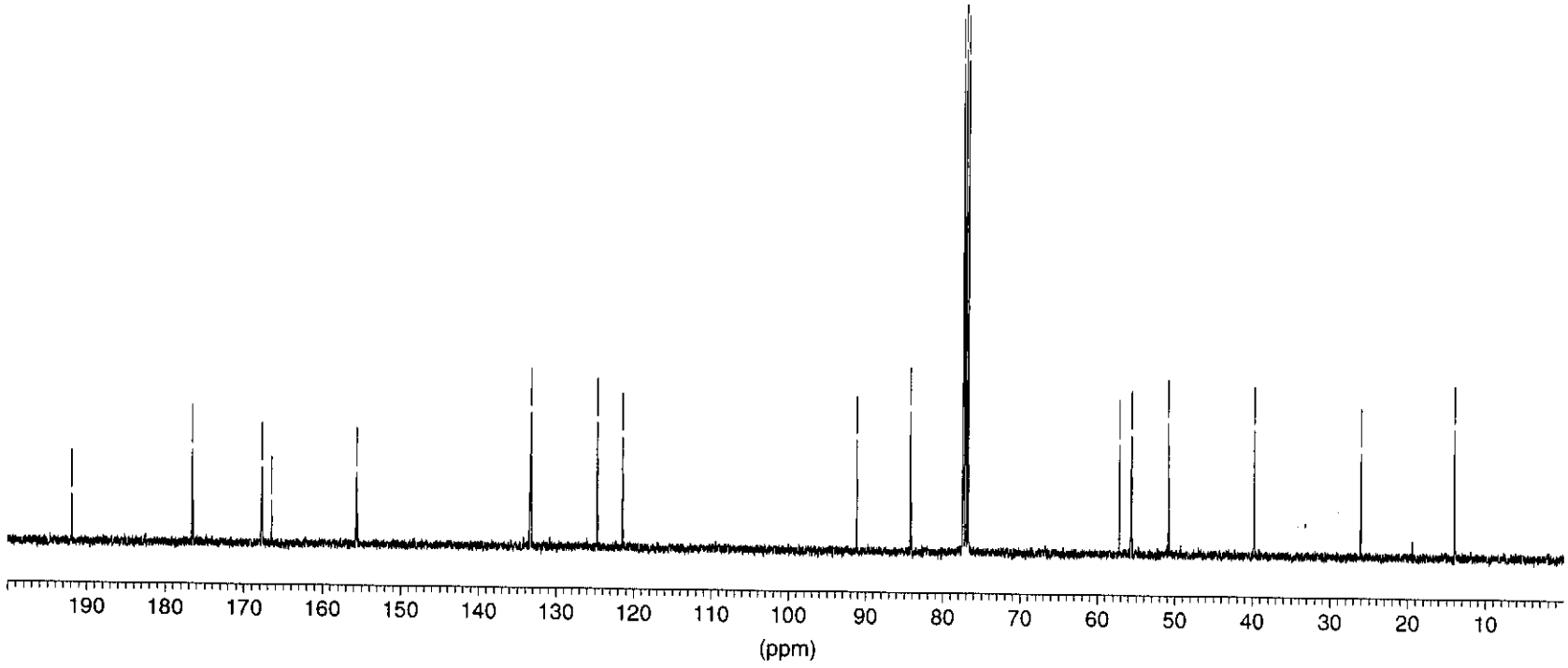
NC_proc	:	1
NUCLEUS	:	off




```
*** Current Data Parameters ***
NAME                  :  20070605
EXPNO                 :         120
PROCNO                :           1
*** Acquisition Parameters ***
AQ_mod                :         dqd
AUNM                  :       au_zg
BF1                   :  400.1300000 MHz
BF2                   :  400.1300000 MHz
DECSTAT               :          DO
DS                    :           2
FW                    :    90000.00 Hz
INSTRUM               :        spect
LOCNUC                :          2H
NS                    :          16
NUCLEUS               :         off
O1                    :  2470.97 Hz
O2                    :  2470.97 Hz
PULPROG               :        zg30
RO                    :       20 Hz
SFO1                  :  400.1324710 MHz
SOLVENT               :        CDCl3
SW                    :  20.5524 ppm
SW_h                  :  8223.684 Hz
TD                    :       65536
TE                    :       303.2 K
VD                    :  0.0000000 sec
YMAX_a                :  121749248.0000000
YMIN_a                : -935623616.0000000
*** Processing Parameters ***
NC_proc               :          -3
OFFSET                :  16.358 ppm
SF                    :  400.1300376 MHz
SI                    :       32768
*** 1D NMR Plot Parameters ***
NC_proc               :          -3
NUCLEUS               :         off
```



191.8814
176.5488
167.7034
166.4885
155.5786
133.2269
124.6593
121.3959
91.1118
84.1800
77.3593
77.2402
77.0417
76.7241
57.1435
55.5395
50.8310
39.7544
26.0257
13.9406



*** Current Data Parameters ***
NAME : 20070410
EXPNO : 270
PROCNO : 1
*** Acquisition Parameters ***
AQ_mod : qsim
AUNM : au_zg
BF1 : 100.6127690 MHz
BF2 : 400.1300000 MHz
DECSTAT : DO
DS : 4
FW : 90000.00 Hz
INSTRUM : spect
LOCNUC : 2H
NS : 256
NUCLEUS : off
O1 : 10060.17 Hz
O2 : 1600.52 Hz
PULPROG : zgpg30
RO : 20 Hz
SFO1 : 100.6228292 MHz
SOLVENT : CDCl3
SW : 260.1598 ppm
SW_h : 26178.010 Hz
TD : 65536
TE : 297.2 K
VD : 0.0000000 sec
YMAX_a : 1229099776.0000000
YMIN_a : -918446592.0000000
*** Processing Parameters ***
NC_proc : 0
OFFSET : 230.082 ppm
SF : 100.6127690 MHz
SI : 32768
*** 1D NMR Plot Parameters ***
NC_proc : 0
NUCLEUS : off