^{13}C NMR Spectroscopy for Quantitative Determination of Compound Ratios and Polymer End-Groups

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Supporting Information

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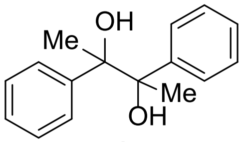
General Experimental Information:

All solvents were dried by filtration through alumina according to the method of Grubbs unless otherwise noted.[1] Dichloromethane and 2-methyl-2-oxazoline were stirred over calcium hydride and distilled under argon prior to use. Ethanol was heated at reflux over sodium-benzophenone and distilled under argon prior to use. Methyl triflate was distilled prior to use. L-Lactide was recrystallized from toluene and stored under argon. All synthetic procedures were run under an atmosphere of nitrogen in glassware that was flame-dried under vacuum and cooled under a stream of nitrogen unless otherwise stated. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on silica gel (SiO_2) 60 (230-400 mesh). ^{1}H and ^{13}C NMR spectra were acquired at ambient temperature using a BBO probehead on both the 400 and 500 MHz, and QXI probehead on the 600 MHz spectrometers, as indicated and were referenced to residual protio solvent.[1] The proton 90 degree pulse widths for the 400, 500, and 600 MHz are 7.75, 9.95, and 9.8 μs, respectively. The carbon 90 degree pulse widths for the 400, 500, and 600 MHz are 11.4, 10.25, and 11.25 μs, respectively. The data are reported as follows: chemical shifts are reported in parts per million (δ), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qu = quintet, m = multiplet, app = apparent), coupling constants (J) in Hertz (Hz), and integration. Resonances in the ^{13}C NMR spectra were assigned by HSQC data so the appropriate peaks can be compared. A Waltz-16 decoupling scheme with a pulse of 90 μsec was employed. Baseline correction was performed using the 5th order polynomial functions from -10 to 240 ppm range. MALDI-ToF spectra were acquired on a MALDI tandem mass spectrometer in positive ion mode. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (for PLA and P(Ox)) or 1,8,9-anthracenetriol (dithranol) (for P(NO)) in THF was used as the matrix. A saturated sodium trifluoroacetate solution in acetone was spotted on top of the matrix layer as dopant salt and the compound of interest was applied in its respective deuterated solvent. For analysis, a "Synthetic Polymer Analysis Kit" was used to calculate degrees of polymerization from the mass peaks obtained. Infrared (IR) spectra were obtained using an FT-IR spectrometer. High resolution mass spectra (HRMS) were acquired on a time-of-flight spectrometer. Analytical gas chromatography (GC) was performed on a chromatograph equipped with an auto-sampler and flame-ionization detector. A fused silica capillary column (30 m x 0.320 mm x 0.25 mm) wall-coated with DB-1 was used with helium gas carrier (25 psi column head pressure). Unless otherwise noted, all reagents and substrates were commercially available.

General Information Related to the Processing of ^{13}C NMR Spectra:

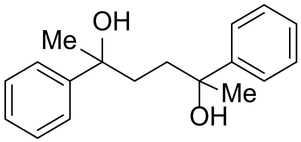
For the acquisition of ^{13}C NMR spectra associated with molecules with similar connectivity (i.e. diastereomers) or for ratios greater than 9:1 (i.e., polymer end-group analysis with DP > 10), broadband decoupled pulse programs were used. For the acquisition of ^{13}C NMR spectra associated with molecules of dissimilar connectivity (i.e., constitutional isomers, unrelated molecules, etc) inverse-gated decoupled pulse programs were used. Relaxation delays were limited to either 2 sec (short) or 30 sec (long) for comparison purposes, sweep width was set to 24k Hz on a 400 MHz spectrometer, the total number of data points collected was 64k, and the number of scans varied from 16 to 8000 (512 was used most commonly). When processing data, line broadening (LB) was set to 0.0, SI was set to 128k (2 x TD), and all mathematical fits employed during the deconvolution procedure were 100% Lorentzian in nature. If LB is set to 0.0 and SI is not 2 x TD, peak widths at half-height of 0.0 may cause the deconvolution procedure to terminate prematurely. Note, end-group analysis of polymers required line LB > 0 to improve signal to noise.

Synthetic Procedures:



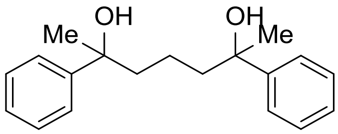
1

2,3-Diphenylbutane-2,3-diol (1): Synthesis was performed according to a previously reported literature procedure, and characterization data matched those reported in the literature.[2]



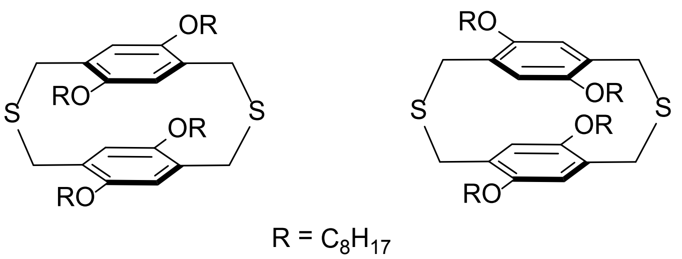
2

2,5-Diphenylhexane-2,5-diol (2): Synthesis was performed according to a previously reported literature procedure for the synthesis of **1**[3], and characterization data matched those reported in the literature.[4]

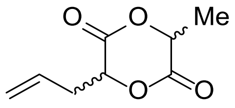


3

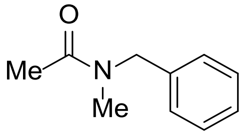
2,6-Diphenylheptane-2,6-diol (3): Synthesis was performed according to a previously reported literature procedure for the synthesis of **1**[5]. Crude diastereomeric mixture with residual EtOAc: colorless oil; ^{1}H (400 MHz, $CDCl_3$) δ 7.30 (m, 10H), 1.75 (m, 6H), 1.49 (s, 3H), 1.48 (s, 3H), 1.20 (m, 2H); ^{13}C (400 MHz, $CDCl_3$) δ 148.125, 148.116, 128.26, 128.25, 126.64, 126.63, 124.81, 124.80, 74.8, 44.3, 44.2, 30.3, 30.1, 18.6, 18.5; IR (ATR) 3409, 2972 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{19}H_{24}O_2$ $[M + Na]^+$ 307.1674, found 307.1679.



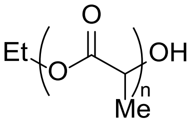
5,8,14,17-Tetraoctyloxy-2,11-dithia[3.3]paracyclophane and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane: Synthesis of the two regioisomers was performed according to a previously reported literature procedure and characterization data matched those reported in the literature.[6]



Allyl lactide: Synthesis was performed according to a previously reported literature procedure[7] and characterization data matched those reported in the literature.[8]

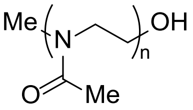


***N*-Benzyl-*N*-methylacetamide**: Synthesis was performed according to a previously reported literature procedure and characterization data matched those reported in the literature. [9]



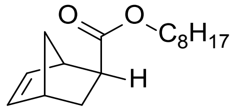
PLA

Poly(lactic acid) (P(LA)): Synthesis was performed according to a previously reported literature procedure except that ethanol was used as the initiator.[10]

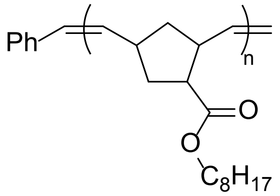


P(Ox)

Poly(4-methyl-oxazoline) (P(Ox)): Synthesis was performed according to a modified procedure previously reported in the literature.[11] A representative procedure affording a polymer with DP = 10 is described. A stock solution of methyl triflate (0.200 mL, 1.83 mmol) in MeCN (1.8 mL) was prepared. To a Schlenk reactor under an atmosphere of argon was added 2-methyl-2-oxazoline (0.311 g, 3.66 mmol), chlorobenzene (0.300 mL), and methyl triflate stock solution (0.414 mL, 0.37 mmol). The reactor was then heated (70°C) in an oil bath. Per repeat unit monomer one hour of polymerization time was assumed, so that the polymerization reaction described was heated for ten hours. Water (ca. 1 mL) was added to terminate the polymerization and the reaction mixture was stirred for two hours. The mixture was concentrated *in vacuo*, yielding a yellow oil. The crude product was dissolved in $CHCl_3$ (0.5 mL) and precipitated into cold Et_2O. Following centrifugation at 4000 rpm for 20 minutes, the supernatant was decanted and the process repeated two additional times, affording the desired poly(4-methyl-oxazoline) (0.077 g, 25% yield) as a white solid.



Octyl (1*R*,2*S*,4*R*)-bicyclo[2.2.1]hept-5-ene-2-carboxylate: To a cooled (0°C) mixture of bicyclo[2.2.1]hept-5-ene-exo-2-carboxylic acid (norbornene exo acid)[12] (1.5 g, 11 mmol), one spatula tip of 4-dimethylaminopyridine (DMAP), and *n*-octanol (2.23 mL, 14.1 mmol) in anhydrous CH_2Cl_2 (11 mL) was added 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC, 2.71 g, 14.1 mmol) portion-wise. The mixture was allowed to warm to room temperature over 12 h before being diluted with CH_2Cl_2 (40 mL) and extracted with 0.5 N HCl (2 x 100 mL). The organic layers were combined, washed with saturated aqueous $NaHCO_3$ (100 mL), dried over magnesium sulfate, and concentrated *in vacuo*, yielding a yellow oil. Purification by silica gel column chromatography (9:1 hexanes:EtOAc) afforded the desired product (2.28 g, 84% yield) as a clear oil. Analytical data were in accordance with the literature.[13]



P(NO)

Poly(norbornene octanoate) (P(NO): Synthesis was performed according to a modified procedure previously reported in the literature.[14] In two separate Schlenk reactors under an atmosphere of argon, *exo*-norbornene octanoate (0.300 g, 1.19 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL), and Grubbs 1st generation catalyst (0.098 g, 0.12 mmol) was dissolved in anhydrous CH_2Cl_2 (1 mL). The dissolved Grubbs 1st generation catalyst was transferred to the Schlenk reactor containing *exo*-norbornene octanoate using a syringe. The reaction mixture was stirred for 5 min. before an excess of ethyl vinyl ether (1 mL) was added to terminate the polymerization. After stirring for one hour, the mixture was concentrated *in vacuo*, yielding a black oil. Purification by preparative thin layer chromatography on silica (1:80 MeOH: CH_2Cl_2; 50 mg crude product per plate) afforded the desired product (0.222 g, 74% yield) as a light brown oil. Analytical data were in accordance with the literature,[15] yet with a methylene end-group rather than a cyanuric acid.

References:

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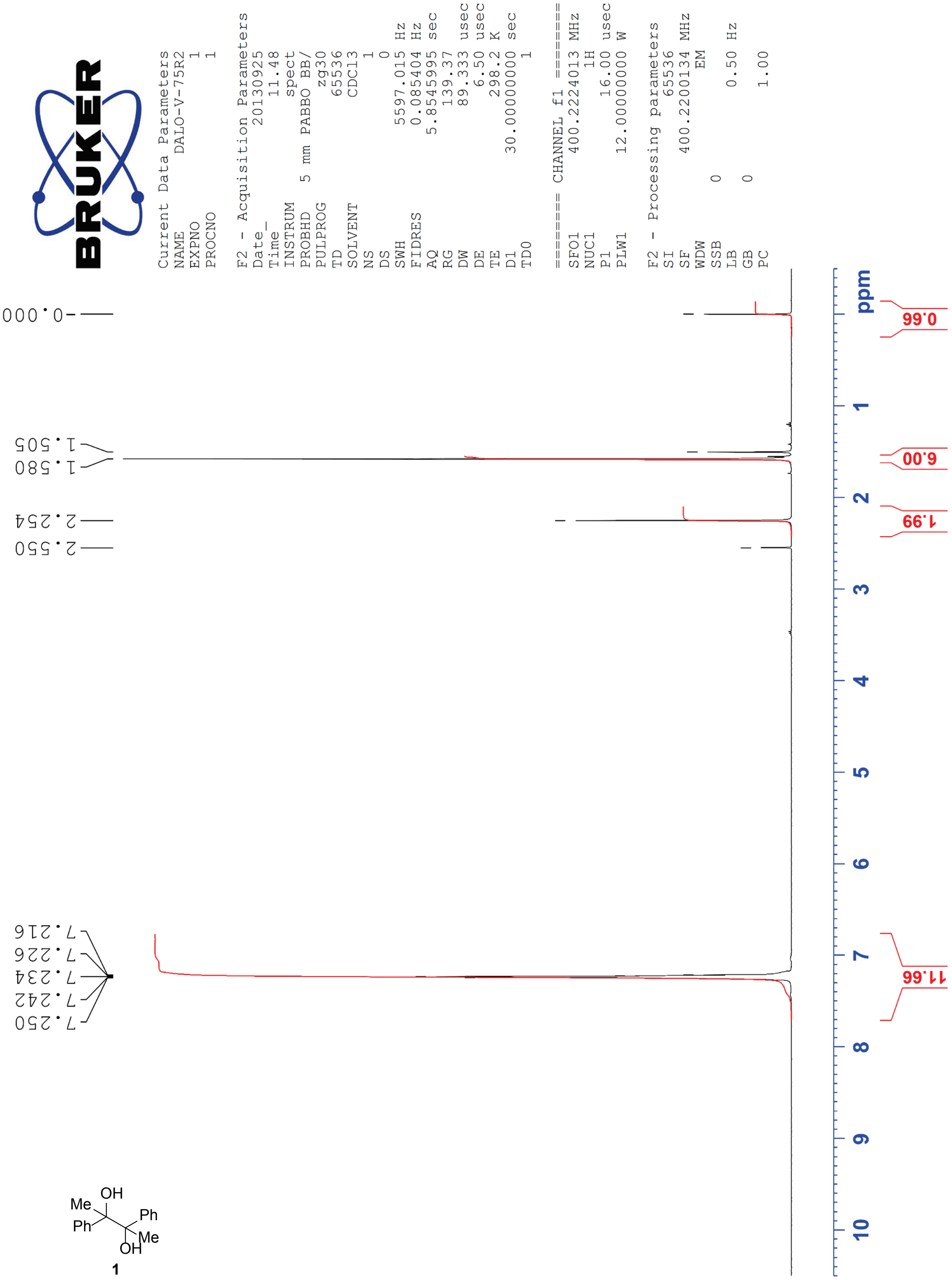
[1] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512—7515; Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stolz, B. M.; Bercaw, J. E.; Goldberg, K. I. *Organometallics* **2010**, *29*, 2176—2179.
[2] Lemiègre, L.; Lesetre, F.; Combret, J.-C.; Maddaluno, J. *Tetrahedron*, **2004**, *60*, 415.
[3] Lemiègre, L.; Lesetre, F.; Combret, J.-C.; Maddaluno, J. *Tetrahedron*, **2004**, *60*, 415.
[4] Carta, M; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. *Science*, **2013**, *339*, 303.
[5] Lemiègre, L.; Lesetre, F.; Combret, J.-C.; Maddaluno, J. *Tetrahedron*, **2004**, *60*, 415.
[6] Yu, C.-Y.; Helliwell, M.; Raftery, J.; Turner, M. L. *Chem. - Eur. J.* **2011**, *17*, 6991.
[7] Zou, J.; Hew, C. C.; Themistou, E.; Li, Y.; Chen, C.-K.; Alexandridis, P.; Cheng, C. *Adv. Mater.* **2011**, *23*, 4274.
[8] Leemhuis, M.; Akeroyd, N.; Kruijtzer, J. A. W.; van Nostrum, C. F.; Hennink, W. E. *Eur. Polym. J.* **2008**, *44*, 308; Zou, J.; Hew, C. C.; Themistou, E.; Li, Y.; Chen, C.-K.; Alexandridis, P.; Cheng, C. *Adv. Mater.* **2011**, *23*, 4274.
[9] Nishiwaki, K.; Ogawa, T.; Shigeta, K.; Takahashi, K.; Matsuo, K. *Tetrahedron* **2006**, *62*, 7034.
[10] Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2006**, *128*, 4556.
[11] Liu, Y.; Wang, Y.; Wang, Y.; Lu, J.; Piñón, V.; Weck, M. *J. Am. Chem. Soc.* **2011**, *133*, 14260.
[12] Manning, D. D.; Strong, L. E.; Hu, X.; Beck, P. J.; Kiessling, L. L. *Tetrahedron* **1997**, *53*, 11937.
[13] Kriegel, R. M.; Rees, W. S.; Weck, M. *Macromolecules* **2004**, *37*, 6644.
[14] Kriegel, R. M.; Rees, W. S.; Weck, M. *Macromolecules* **2004**, *37*, 6644.
[15] Yang, S. K.; Ambade, A. V.; Weck, M. *J. Am. Chem. Soc.* **2010**, *132*, 1637.

NMR Spectra:



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FIDRES           0.085404 Hz
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RG                 139.37
DW                 89.333 usec
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TE                  298.2 K
D1            30.00000000 sec
TD0                     1

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NUC1                   1H
P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
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WDW                    EM
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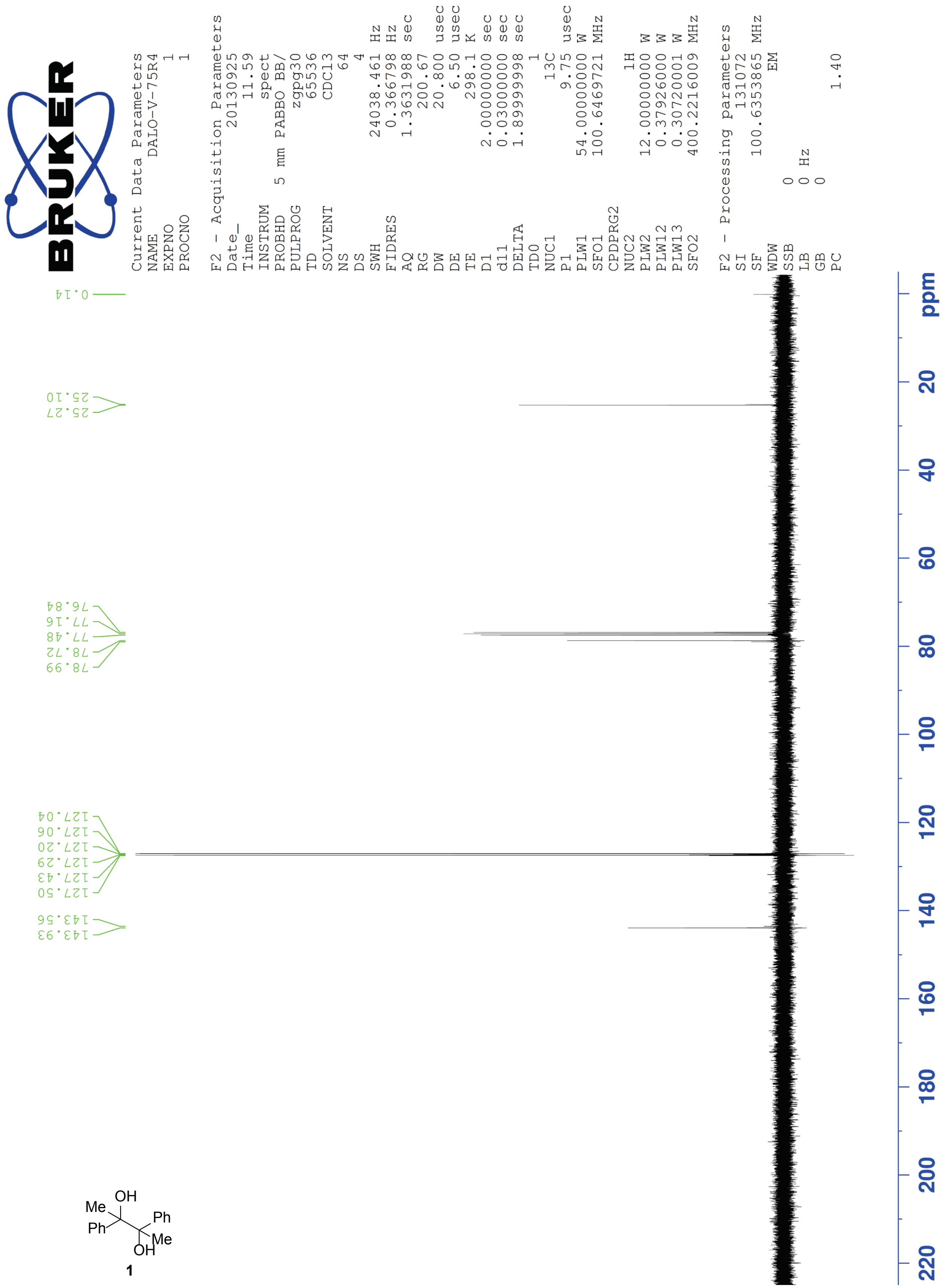
Spectrum S-1: ^{1}H NMR spectrum of **1** from Scheme 1.



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RG              200.67
DW              20.800 usec
DE                6.50 usec
TE               298.1 K
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TD0                  1
NUC1               13C
P1                9.75 usec
PLW1       54.00000000 W
SFO1       100.6469721 MHz
CPDPRG2
NUC2                1H
PLW2       12.00000000 W
PLW12       0.37926000 W
PLW13       0.30720001 W
SFO2       400.2216009 MHz

F2 - Processing parameters
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WDW                 EM
SSB      0
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GB       0
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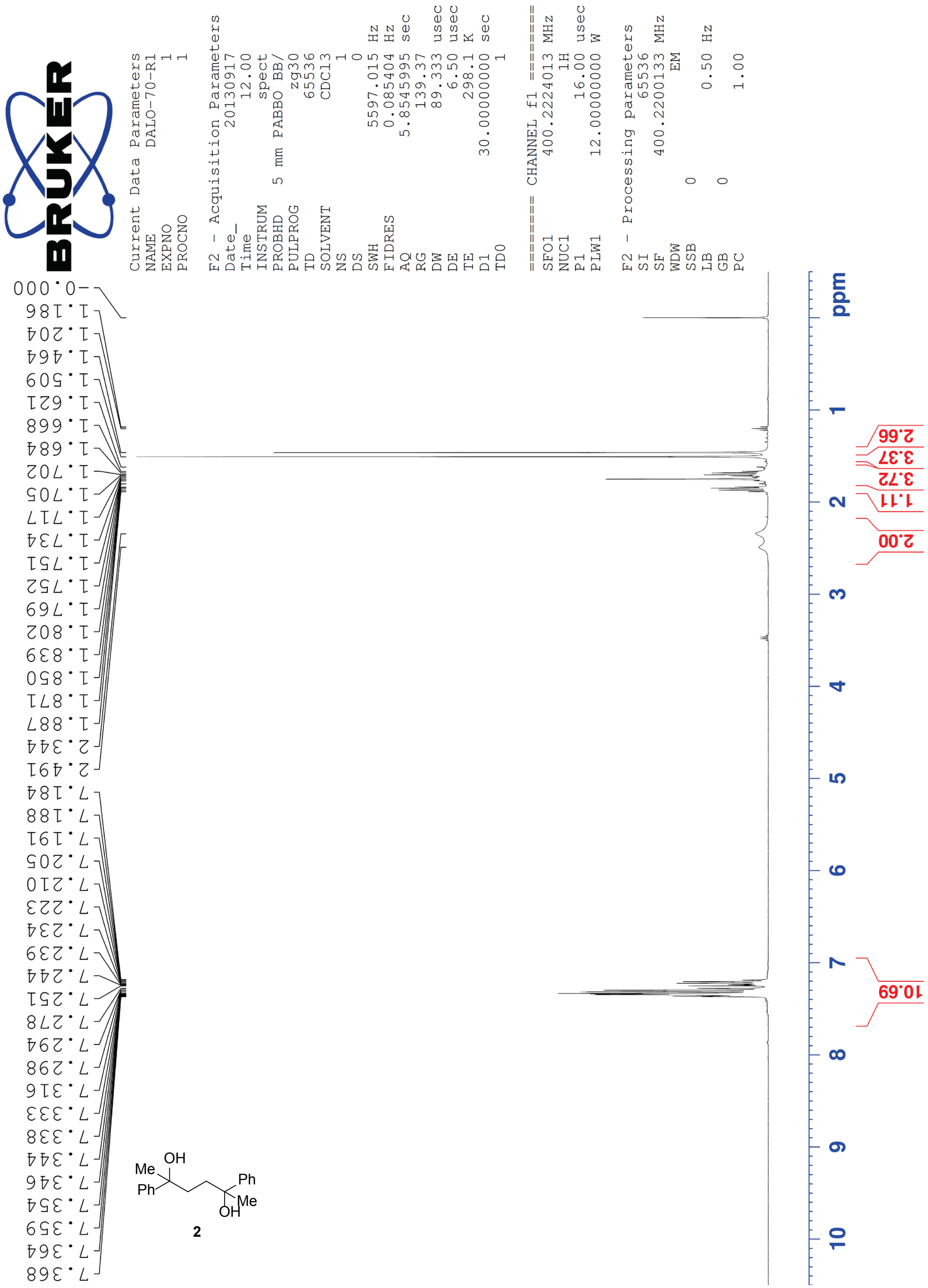
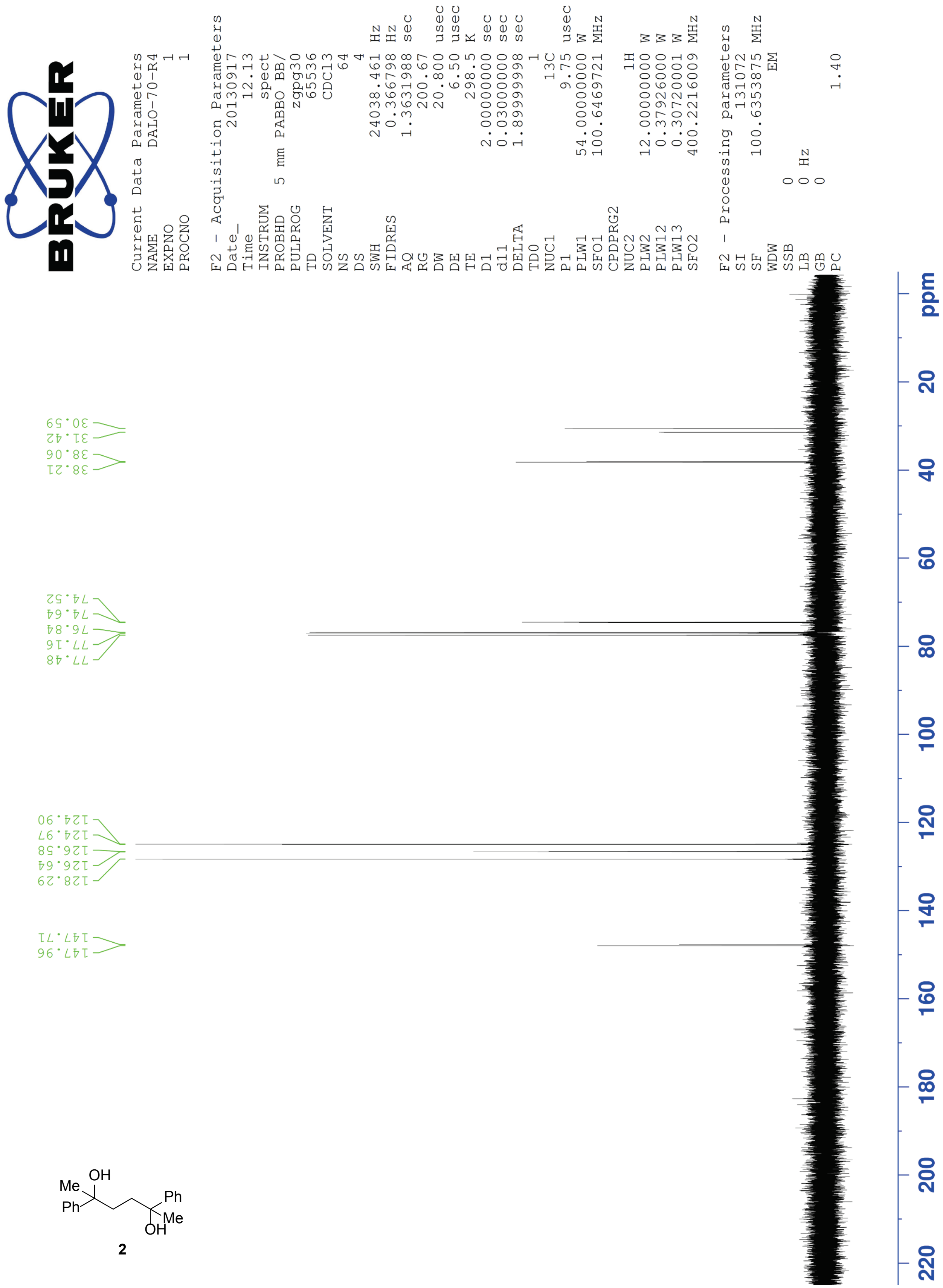
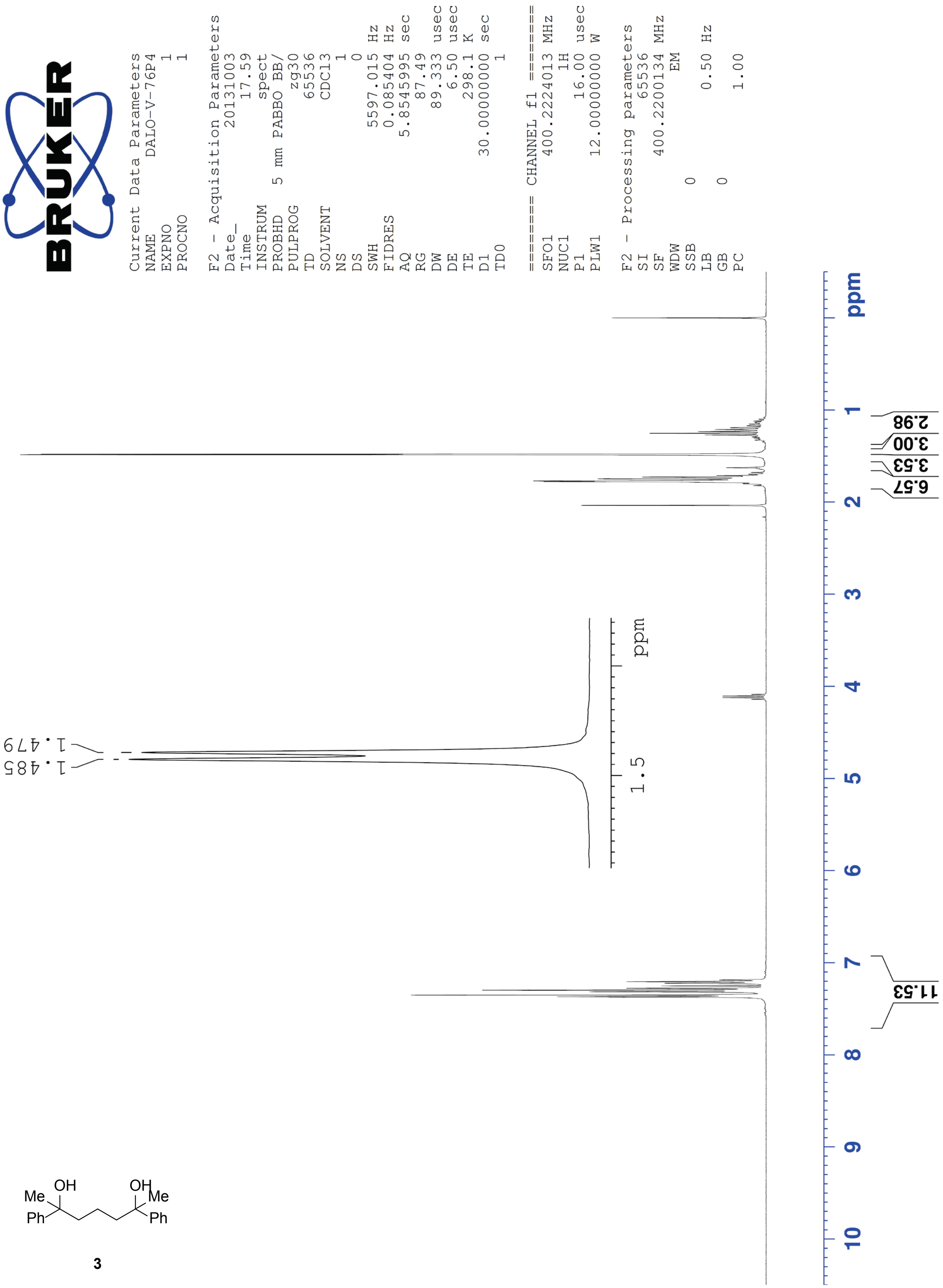
Spectrum S-2: ^{13}C NMR spectrum of **1** from Scheme 1.



Spectrum S-3: ^{1}H NMR spectrum of **2** from Scheme 1 and Table 1.



Spectrum S-4: ^{13}C NMR spectrum of **2** from Scheme 1 and Table 1.



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DS                      0
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FIDRES           0.085404 Hz
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DE                   6.50 usec
TE                  298.1 K
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TD0                     1

======== CHANNEL f1 ========
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P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
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GB                      0
PC                   1.00
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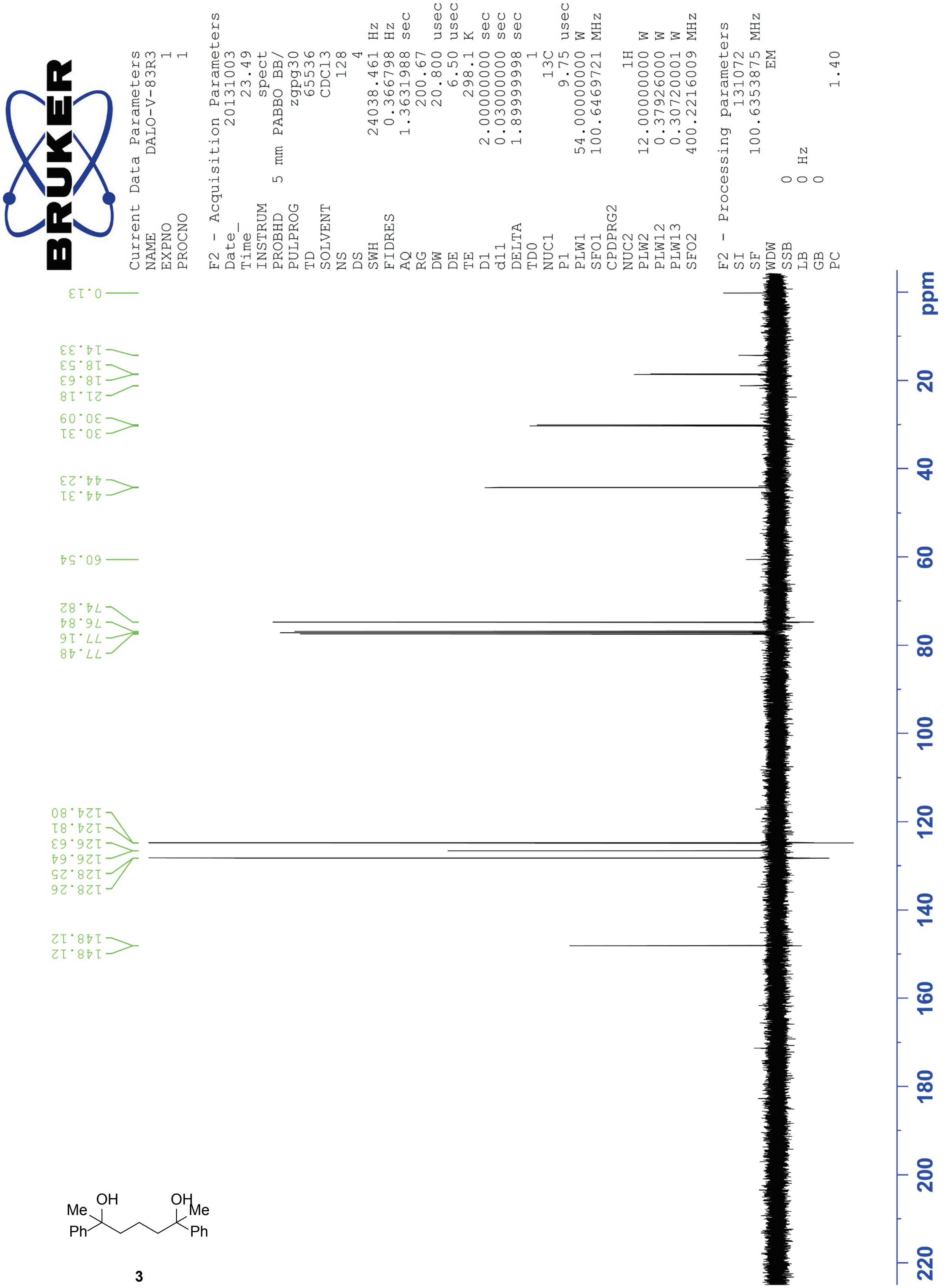
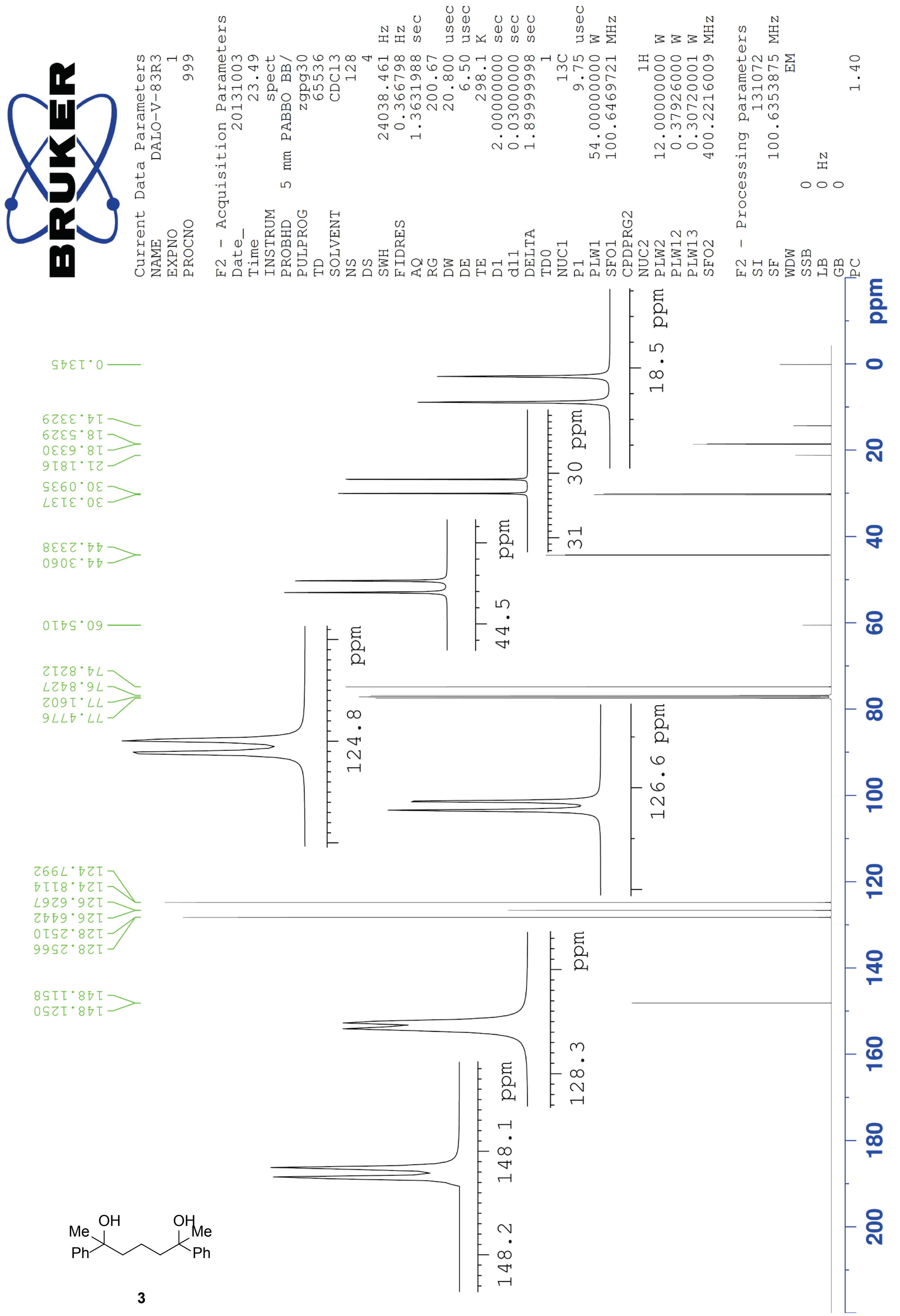
3

Spectrum S-5: Crude ^{1}H NMR spectrum of **3** from Scheme 1.



Spectrum S-6: Crude ^{13}C NMR spectrum of **3** from Scheme 1.



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PROCNO               999

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RG               200.67
DW               20.800 usec
DE                 6.50 usec
TE                298.1 K
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d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1
NUC1                13C
P1                 9.75 usec
PLW1        54.00000000 W
SFO1        100.6469721 MHz
CPDPRG2
NUC2                 1H
PLW2        12.00000000 W
PLW12        0.37926000 W
PLW13        0.30720001 W
SFO2        400.2216009 MHz

F2 - Processing parameters
SI               131072
SF          100.6353875 MHz
WDW                  EM
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PC                 1.40
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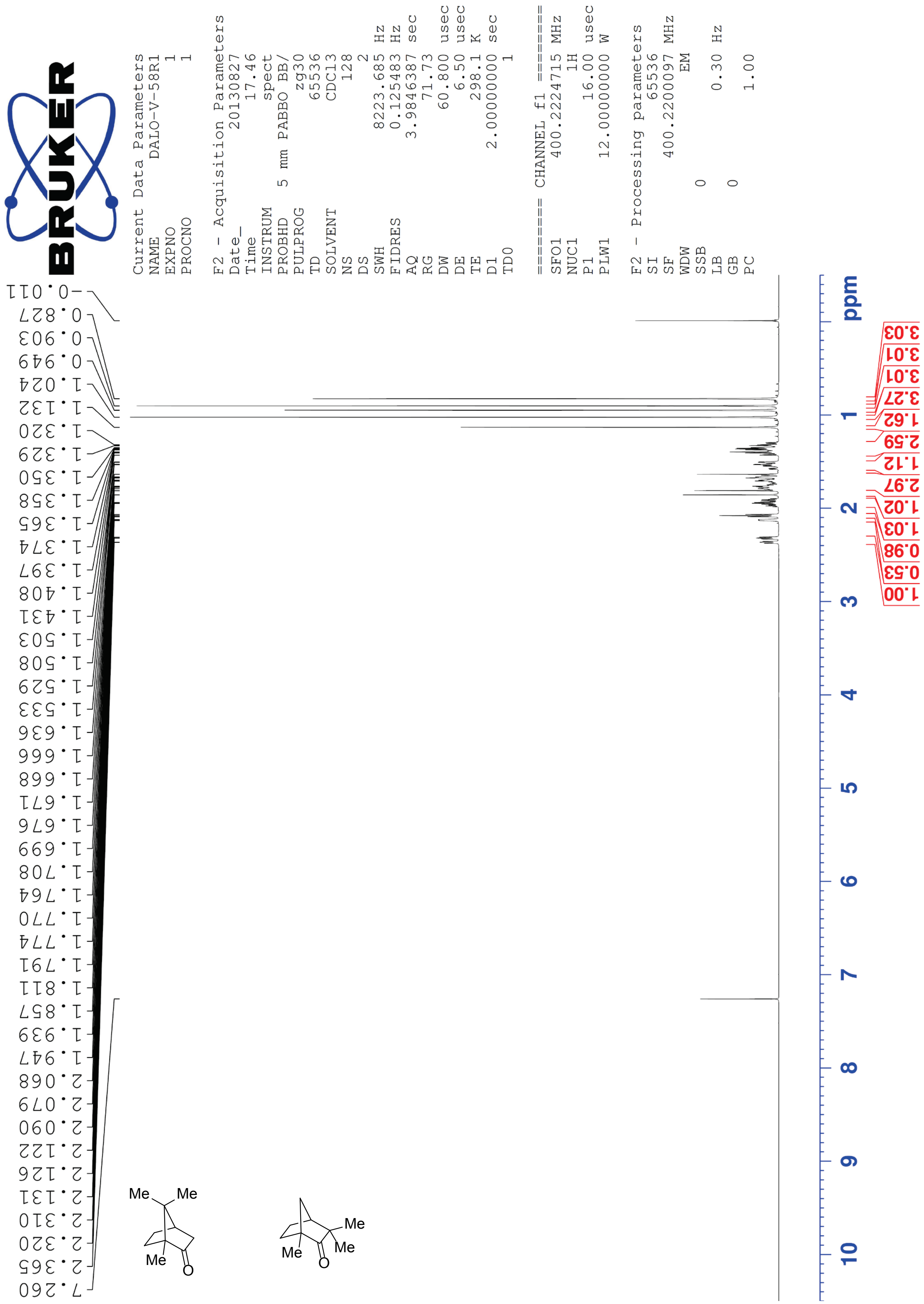
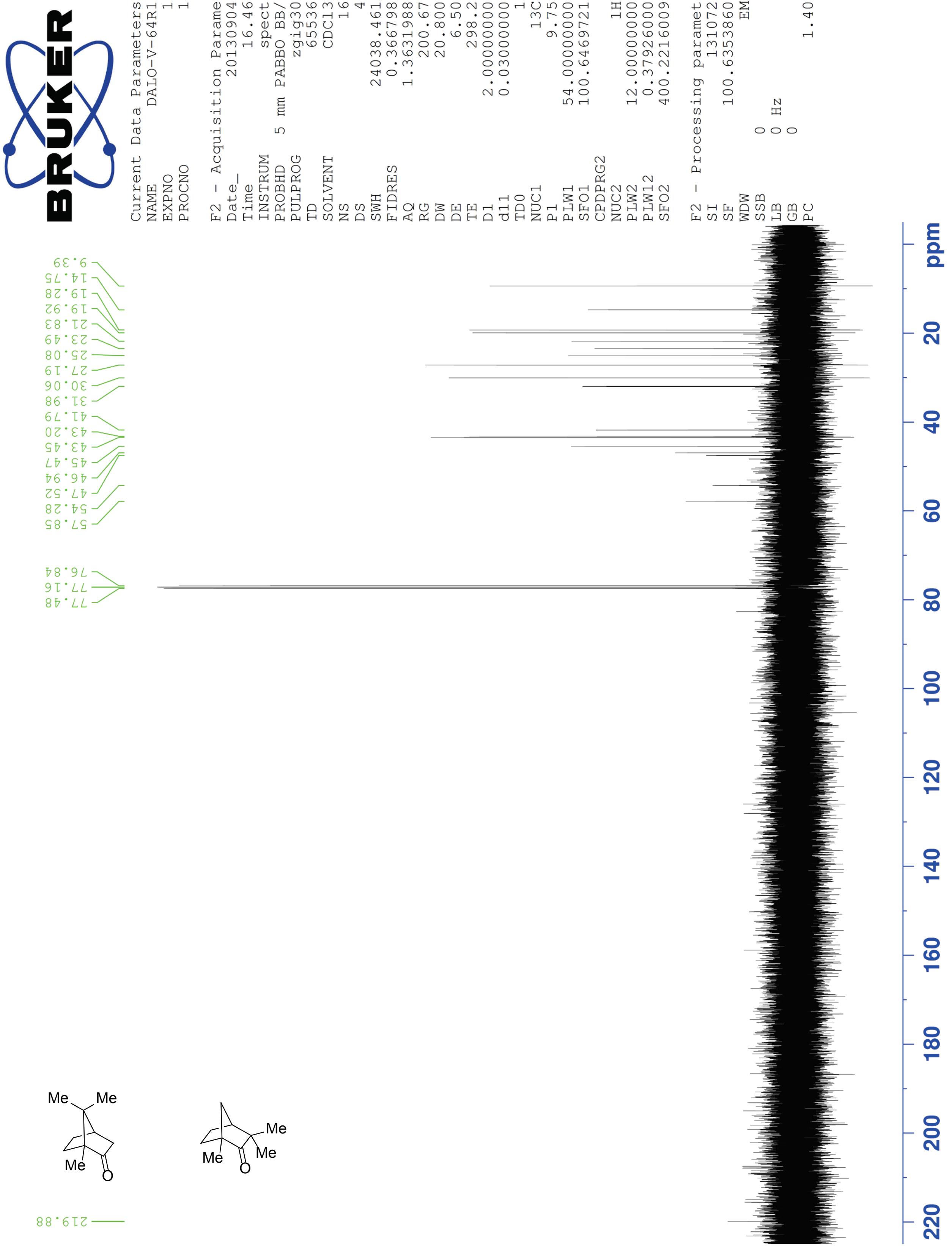
Spectrum S-7: Deconvoluted crude ^{13}C NMR spectrum of **3** from Scheme 1.



Spectrum S-8: ^{1}H NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Table 2.



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DW               20.800 usec
DE                 6.50 usec
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NUC2                 1H
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SFO2        400.2216009 MHz

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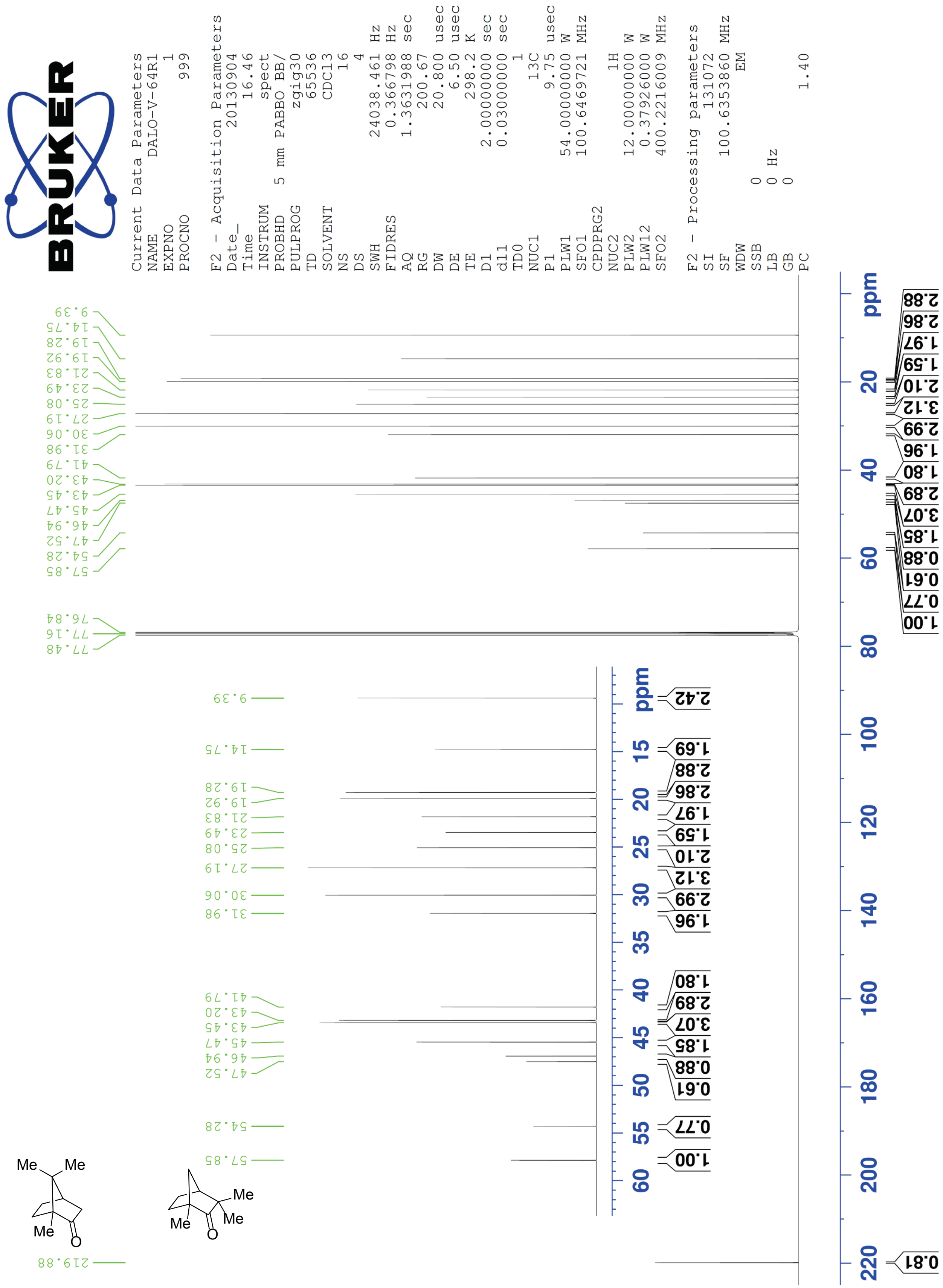
Spectrum S-9: ^{13}C NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Table 2.



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FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
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P1                  9.75 usec
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SFO1         100.6469721 MHz
CPDPRG2
NUC2                  1H
PLW2         12.00000000 W
PLW12         0.37926000 W
SFO2         400.2216009 MHz

F2 - Processing parameters
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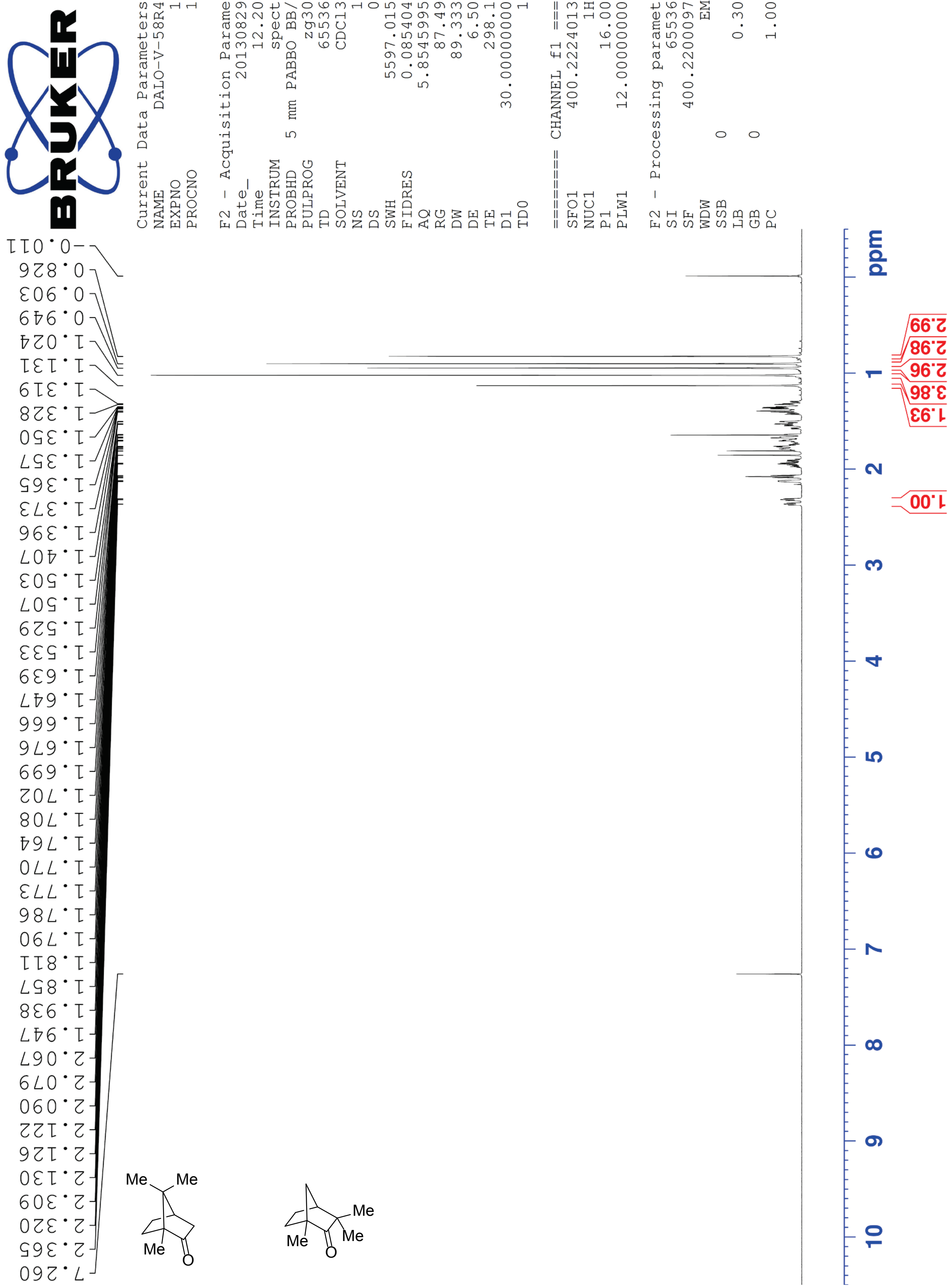
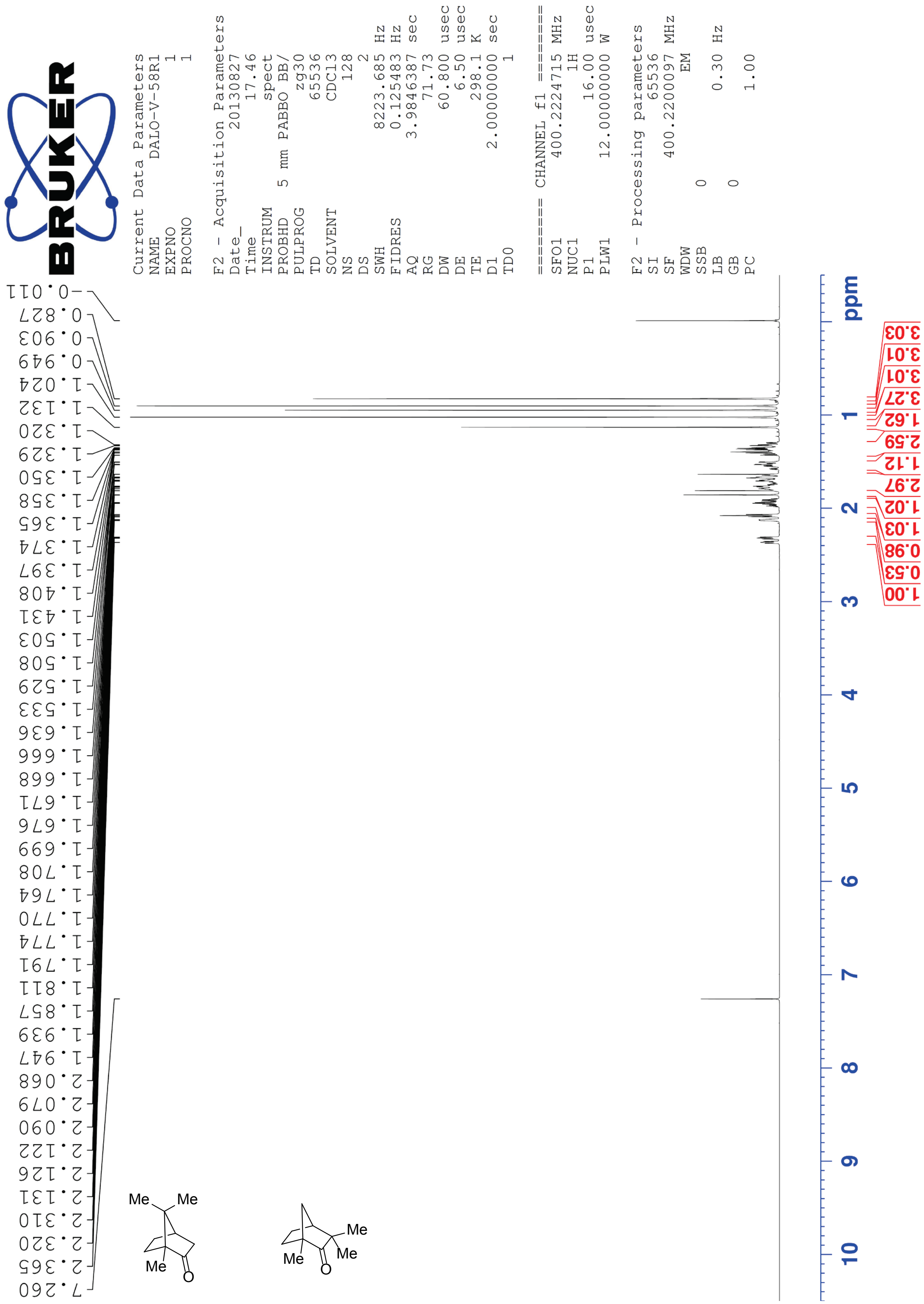
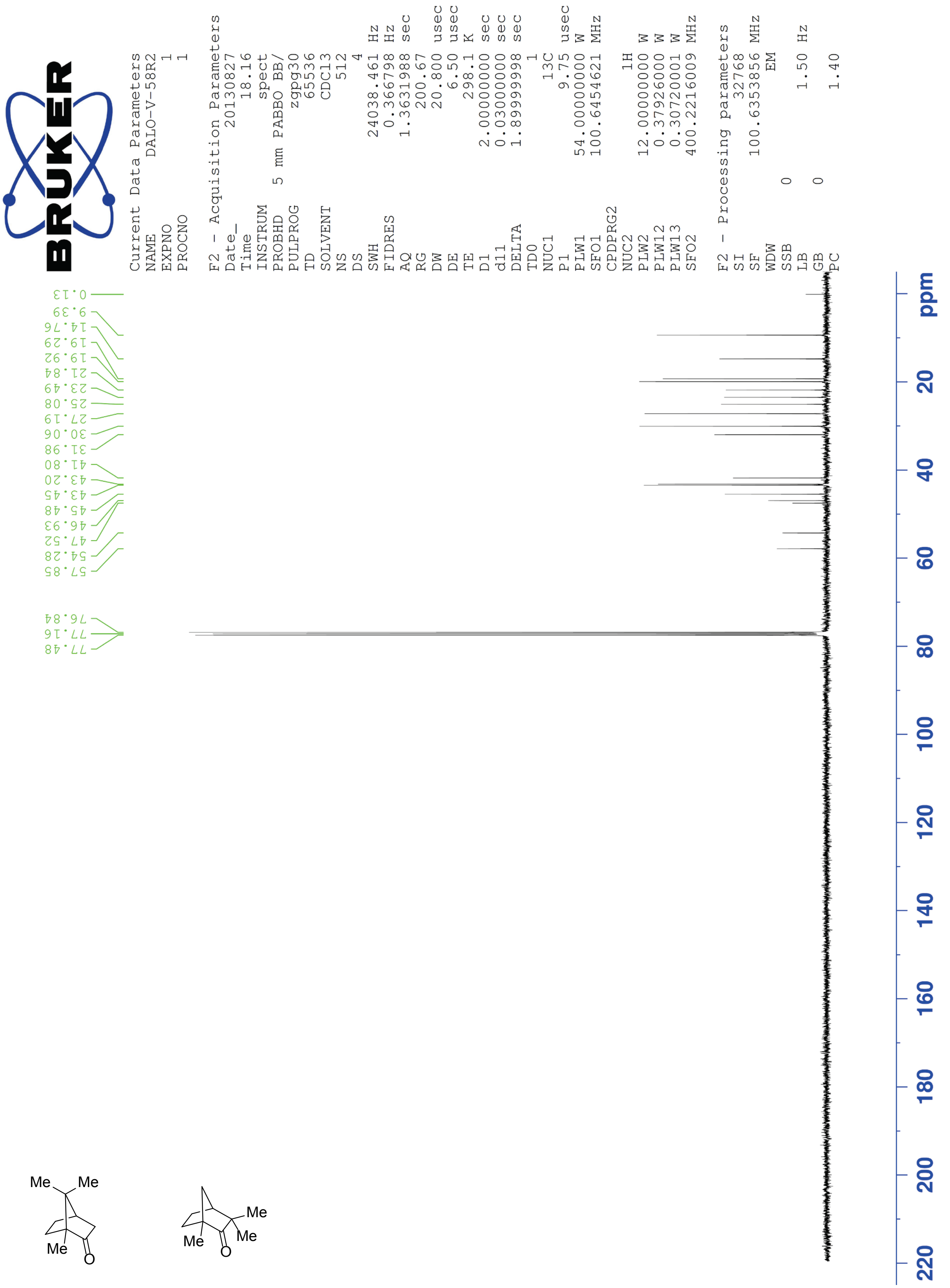
Spectrum S-10: Deconvoluted ^{13}C NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Table 2. See Table SI-2 for tabulated integrals.



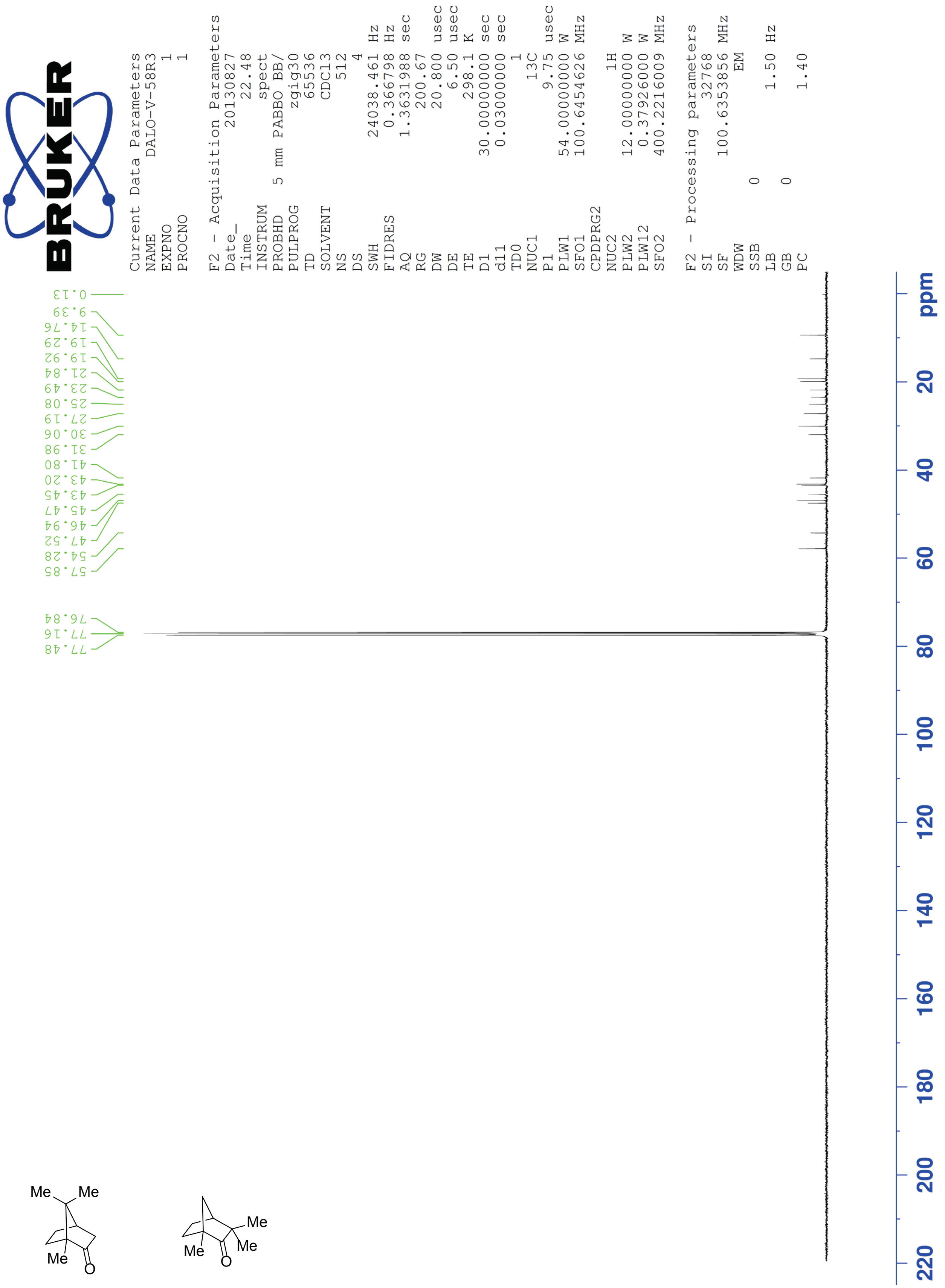
Spectrum S-11: Single-pulse ^{1}H NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Figure 1.



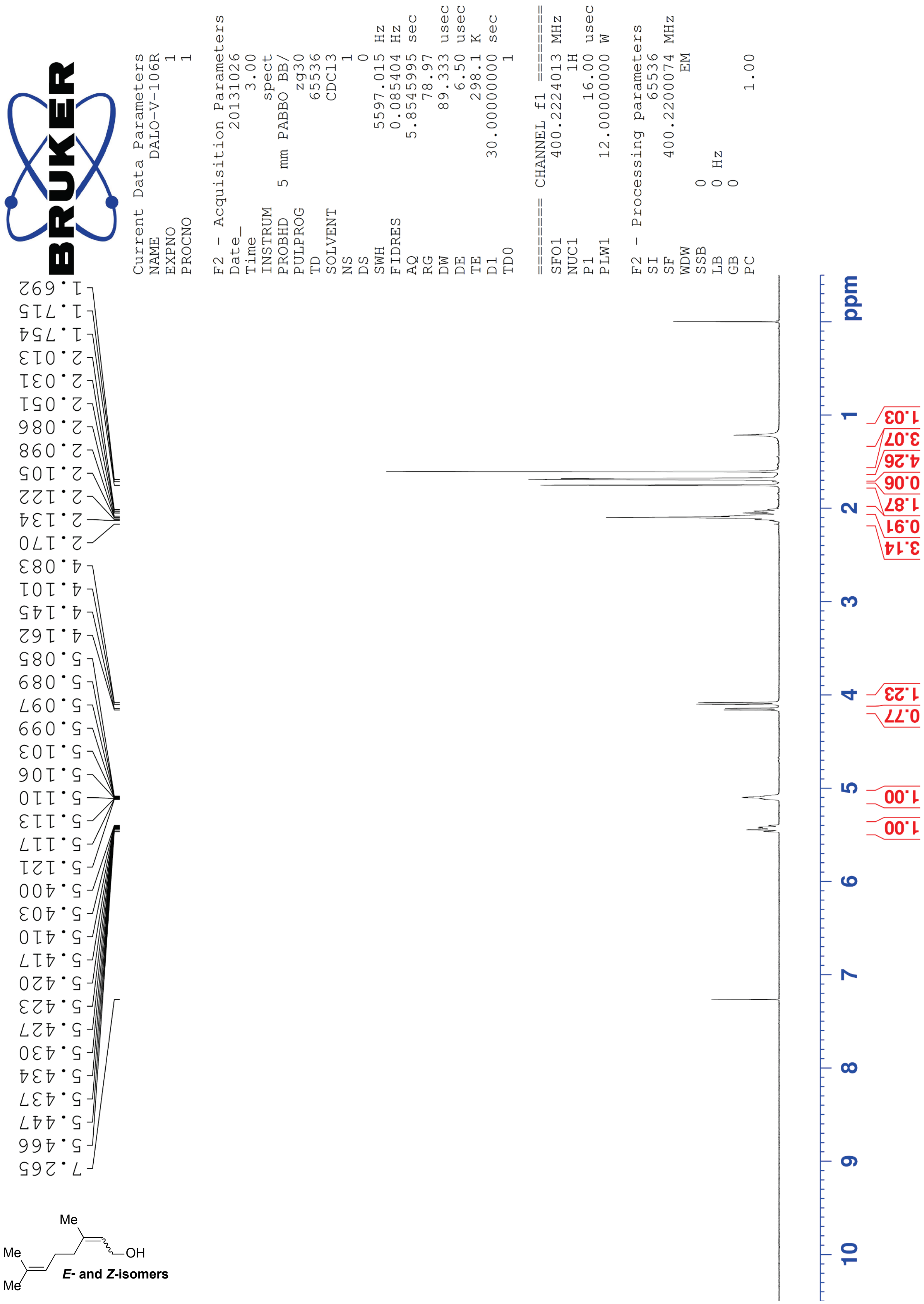
Spectrum S-12: 128-Scan ^{1}H NMR spectrum of camphor:fenchone (mol % fenchone = 39.2%) from Figure 1.


```
Current Data Parameters
NAME          DALO-V-58R2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130827
Time                18.16
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 200.67
DW                 20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1
NUC1                  13C
P1                   9.75 usec
PLW1          54.00000000 W
SFO1          100.6454621 MHz
CPDPRG2
NUC2                   1H
PLW2          12.00000000 W
PLW12          0.37926000 W
PLW13          0.30720001 W
SFO2          400.2216009 MHz

F2 - Processing parameters
SI                  32768
SF            100.6353856 MHz
WDW                    EM
SSB      0
LB                   1.50 Hz
GB       0
PC                   1.40
```

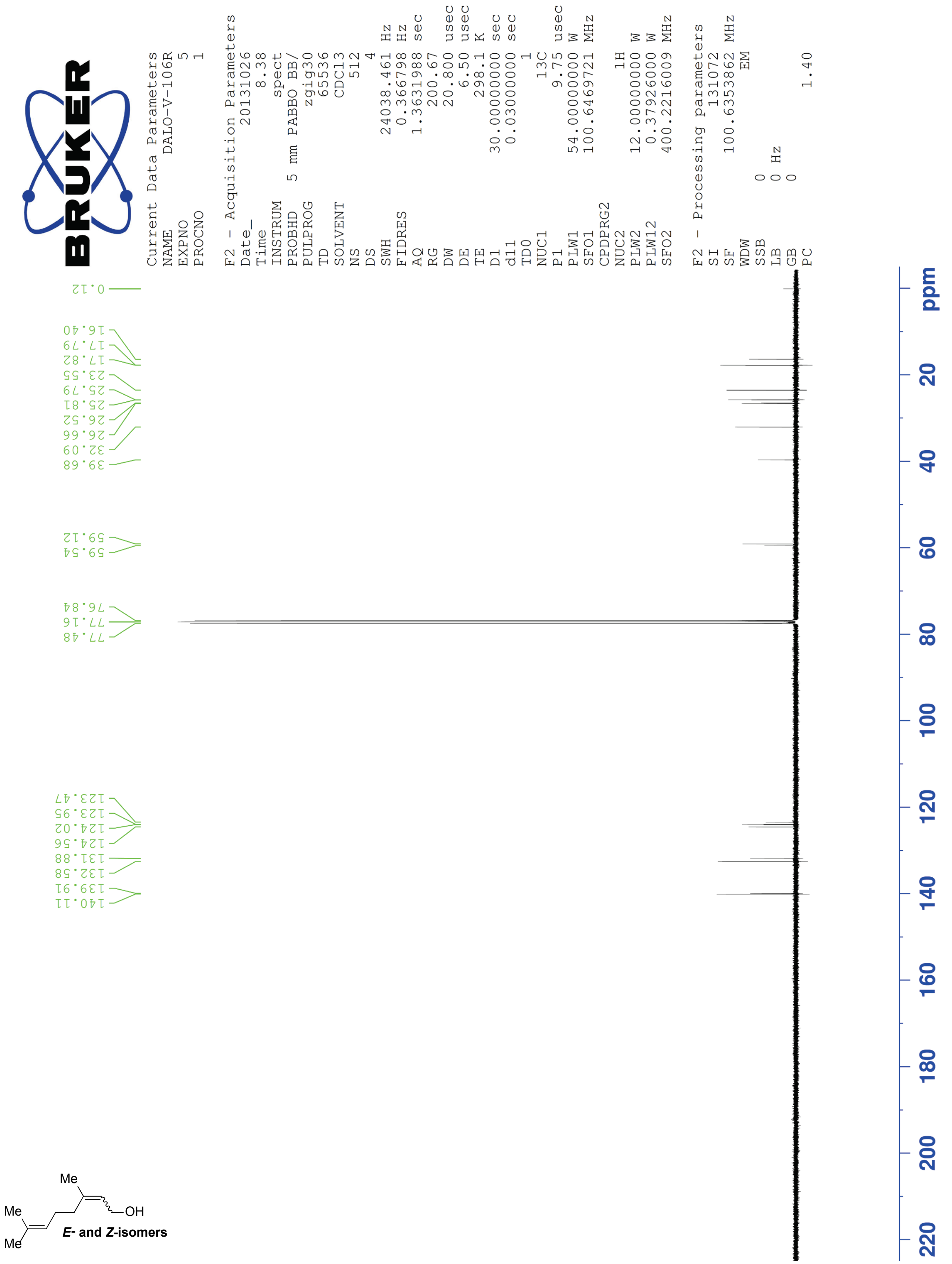
Spectrum S-13: BBD ^{13}C NMR spectrum of camphor:fenchone (mol% fenchone=39.2%) from Figure 1.



Spectrum S-14: IGD ^{13}C NMR spectrum of camphor:fenchone (mol % fenchone=39.2%) from Figure 1.

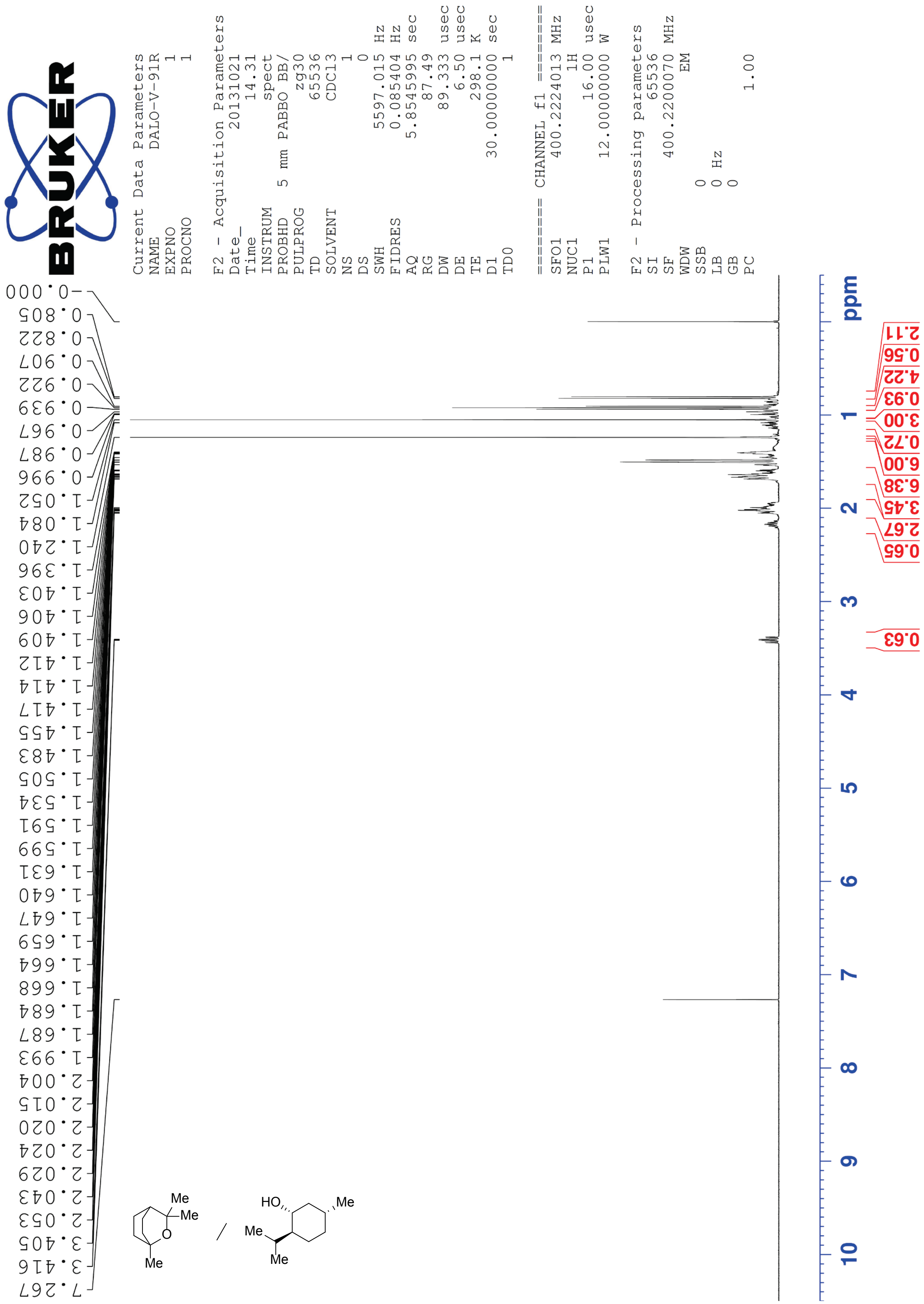


Spectrum S-15: ^{1}H NMR spectrum from Table 3.

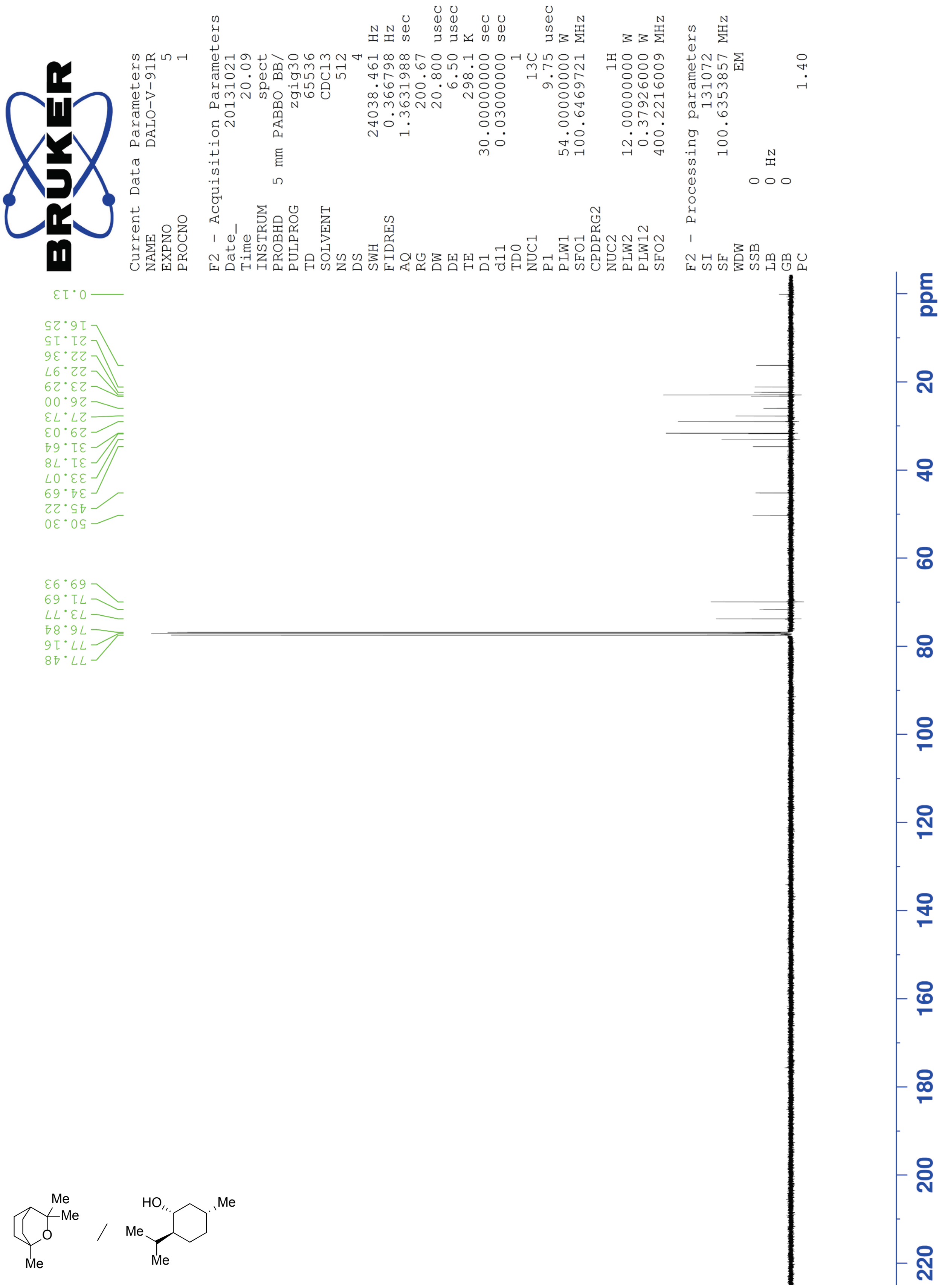


```
Current Data Parameters
NAME          DALO-V-106R
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131026
Time                 8.38
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1           30.00000000 sec
d11           0.03000000 sec
TD0                    1
NUC1                 13C
P1                  9.75 usec
PLW1         54.00000000 W
SFO1         100.6469721 MHz
CPDPRG2
NUC2                  1H
PLW2         12.00000000 W
PLW12         0.37926000 W
SFO2         400.2216009 MHz

F2 - Processing parameters
SI                131072
SF           100.6353862 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.40
```

Spectrum S-16: ^{13}C NMR spectrum from Table 3.

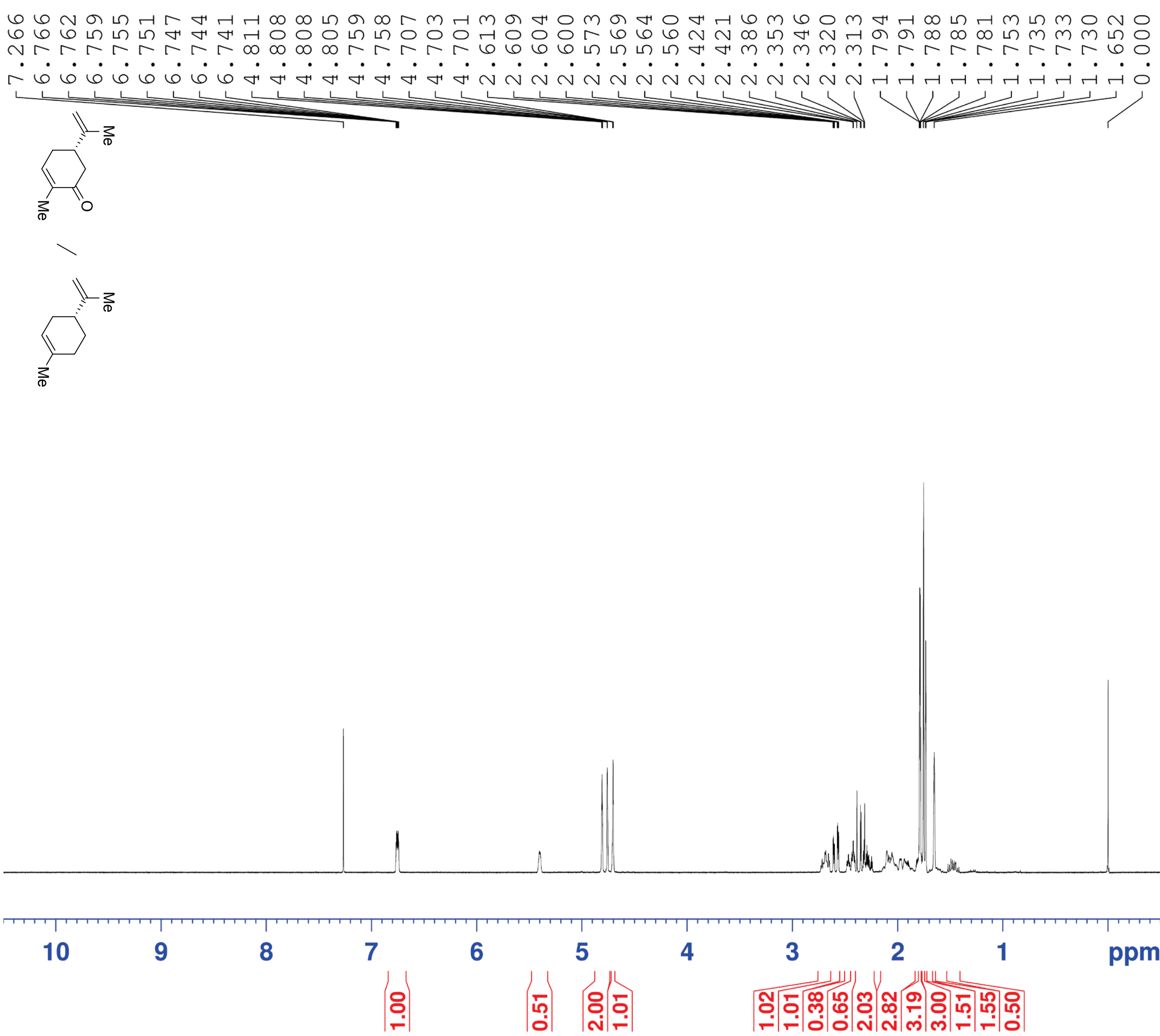


Spectrum S-17: ^{1}H NMR spectrum from Table 3.



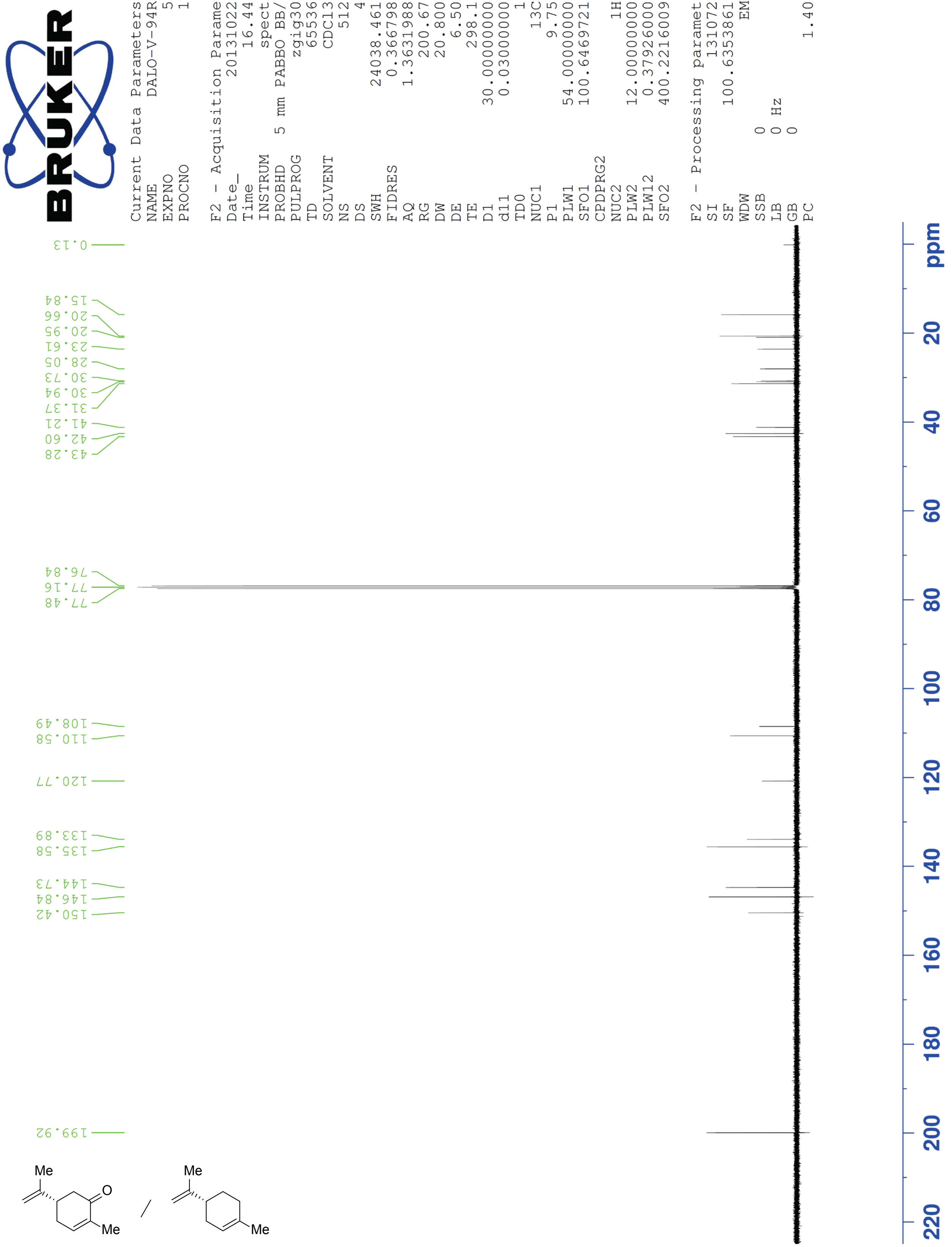
```
Current Data Parameters
NAME          DALO-V-91R
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131021
Time               20.09
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG           zgig30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1           30.00000000 sec
d11           0.03000000 sec
TD0                    1
NUC1                 13C
P1                  9.75 usec
PLW1         54.00000000 W
SFO1         100.6469721 MHz
CPDPRG2
NUC2                  1H
PLW2         12.00000000 W
PLW12         0.37926000 W
SFO2         400.2216009 MHz

F2 - Processing parameters
SI                131072
SF           100.6353857 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.40
```

Spectrum S-18: ^{13}C NMR spectrum from Table 3.



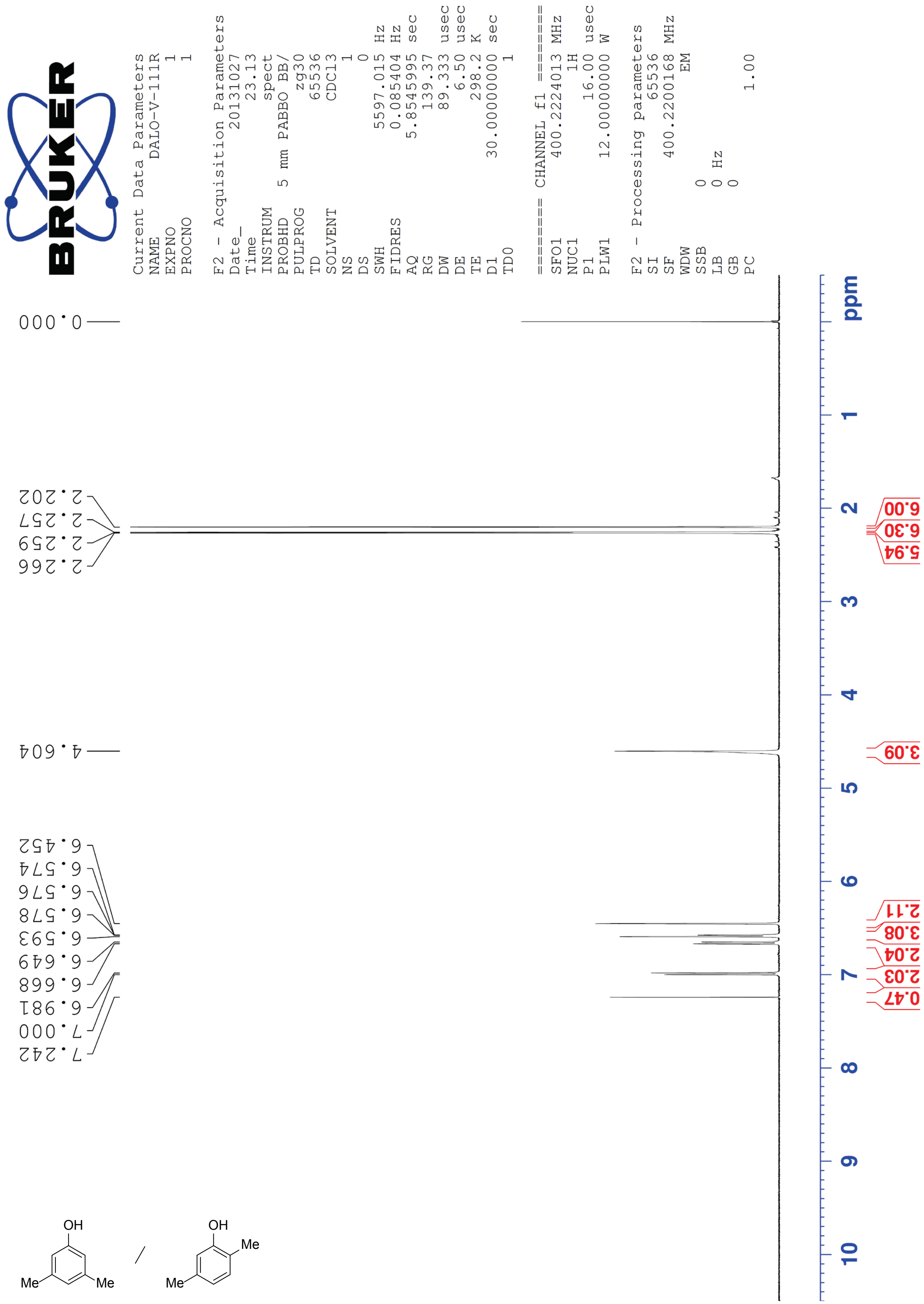
```
Current Data Parameters
NAME          DALO-V-94R
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131022
Time               11.06
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     1
DS                     0
SWH             5597.015 Hz
FIDRES          0.085404 Hz
AQ             5.8545995 sec
RG                100.36
DW                89.333 usec
DE                  6.50 usec
TE                 298.1 K
D1           30.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.2224013 MHz
NUC1                  1H
P1                 16.00 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.2200072 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```

Spectrum S-19: ^{1}H NMR spectrum from Table 3.



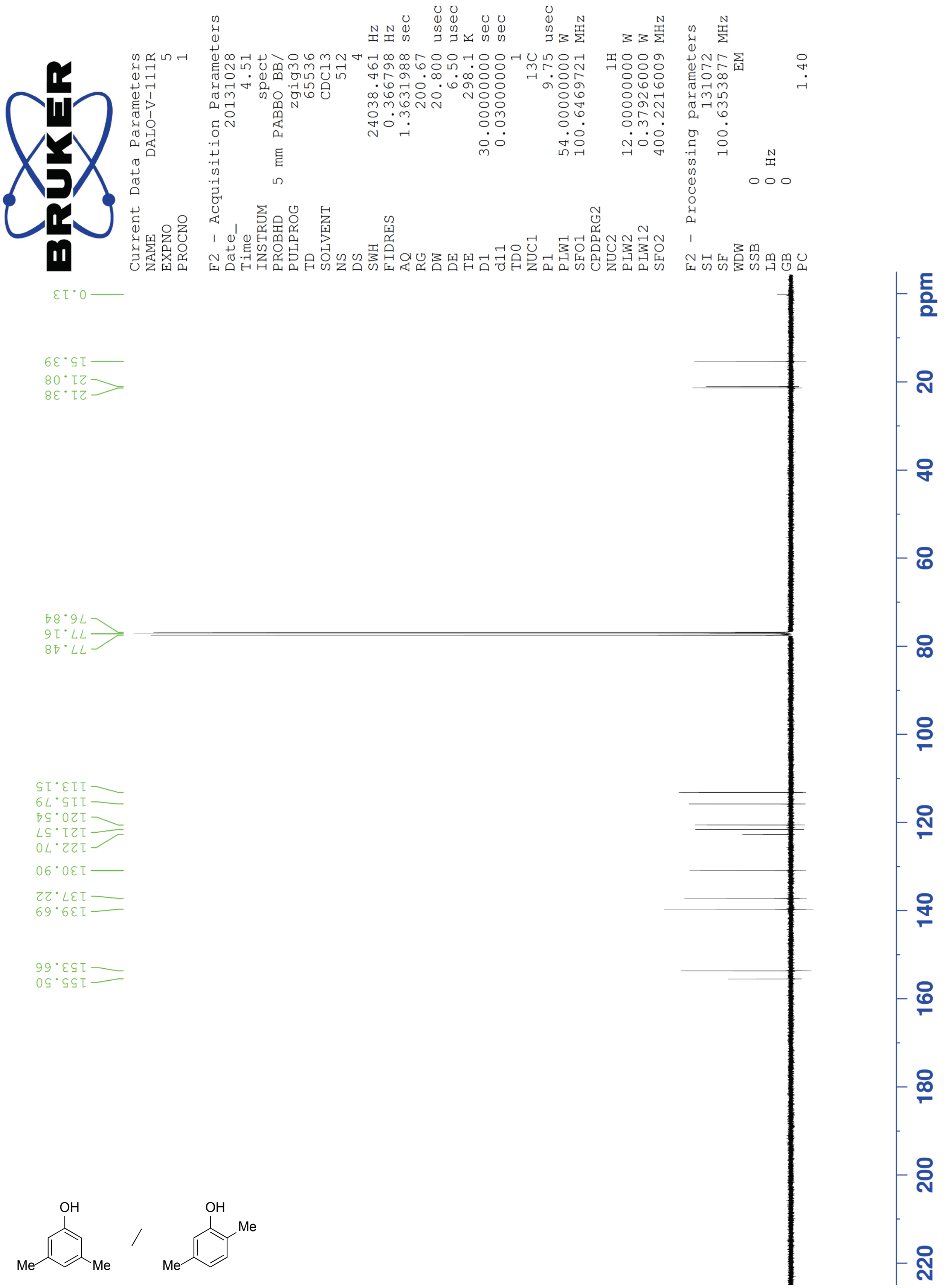
```
Current Data Parameters
NAME          DALO-V-94R
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20131022
Time               16.44
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1           30.00000000 sec
d11           0.03000000 sec
TD0                    1
NUC1                 13C
P1                  9.75 usec
PLW1         54.00000000 W
SFO1         100.6469721 MHz
CPDPRG2
NUC2                  1H
PLW2         12.00000000 W
PLW12         0.37926000 W
SFO2         400.2216009 MHz

F2 - Processing parameters
SI                131072
SF           100.6353861 MHz
WDW                   EM
SSB      0
LB       0 Hz
GB       0
PC                  1.40
```

Spectrum S-20: ^{13}C NMR spectrum from Table 3.



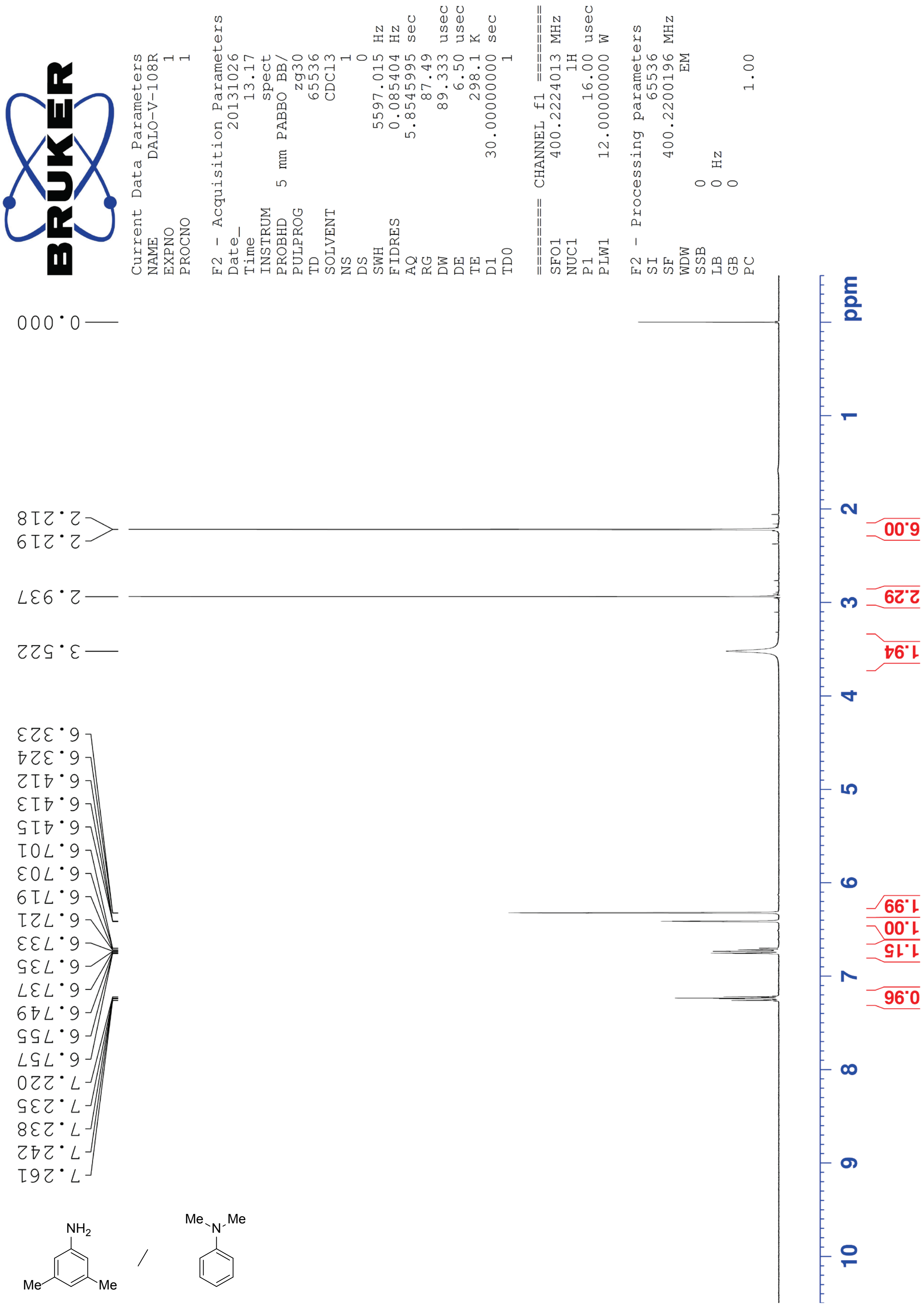
```
Current Data Parameters
NAME          DALO-V-111R
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131027
Time                23.13
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      1
DS                      0
SWH              5597.015 Hz
FIDRES           0.085404 Hz
AQ              5.8545995 sec
RG                 139.37
DW                 89.333 usec
DE                   6.50 usec
TE                  298.2 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2224013 MHz
NUC1                   1H
P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.2200168 MHz
WDW                    EM
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

Spectrum S-21: ^{1}H NMR spectrum from Table 3.

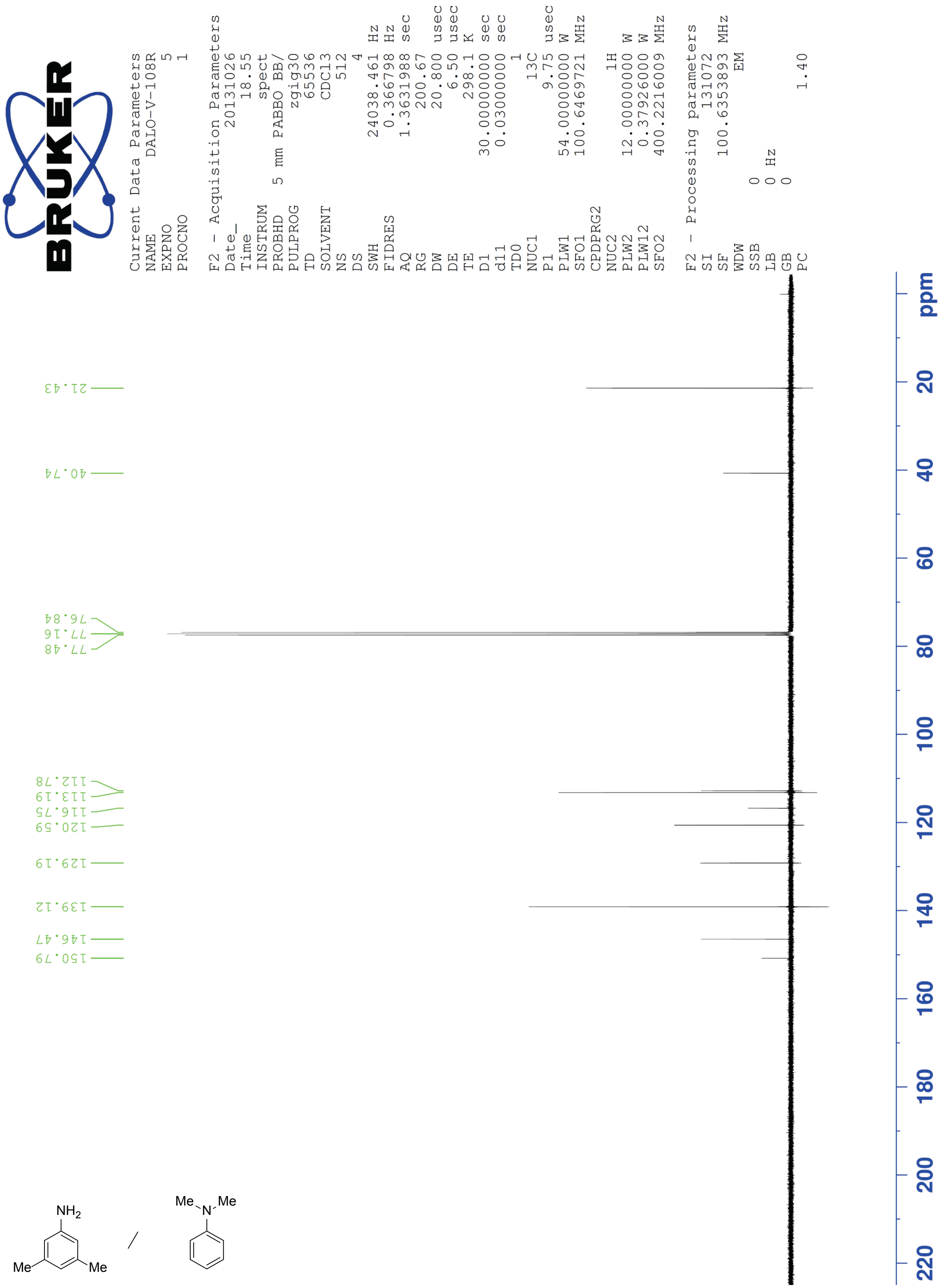


```
Current Data Parameters
NAME           DALO-V-111R
EXPNO                    5
PROCNO                   1

F2 - Acquisition Parameters
Date_             20131028
Time                  4.51
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgig30
TD                   65536
SOLVENT              CDCl3
NS                     512
DS                       4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ               1.3631988 sec
RG                  200.67
DW                  20.800 usec
DE                    6.50 usec
TE                   298.1 K
D1             30.00000000 sec
d11             0.03000000 sec
TD0                      1
NUC1                   13C
P1                    9.75 usec
PLW1           54.00000000 W
SFO1           100.6469721 MHz
CPDPRG2
NUC2                    1H
PLW2           12.00000000 W
PLW12           0.37926000 W
SFO2           400.2216009 MHz

F2 - Processing parameters
SI                  131072
SF             100.6353877 MHz
WDW                     EM
SSB      0
LB       0 Hz
GB       0
PC                    1.40
```

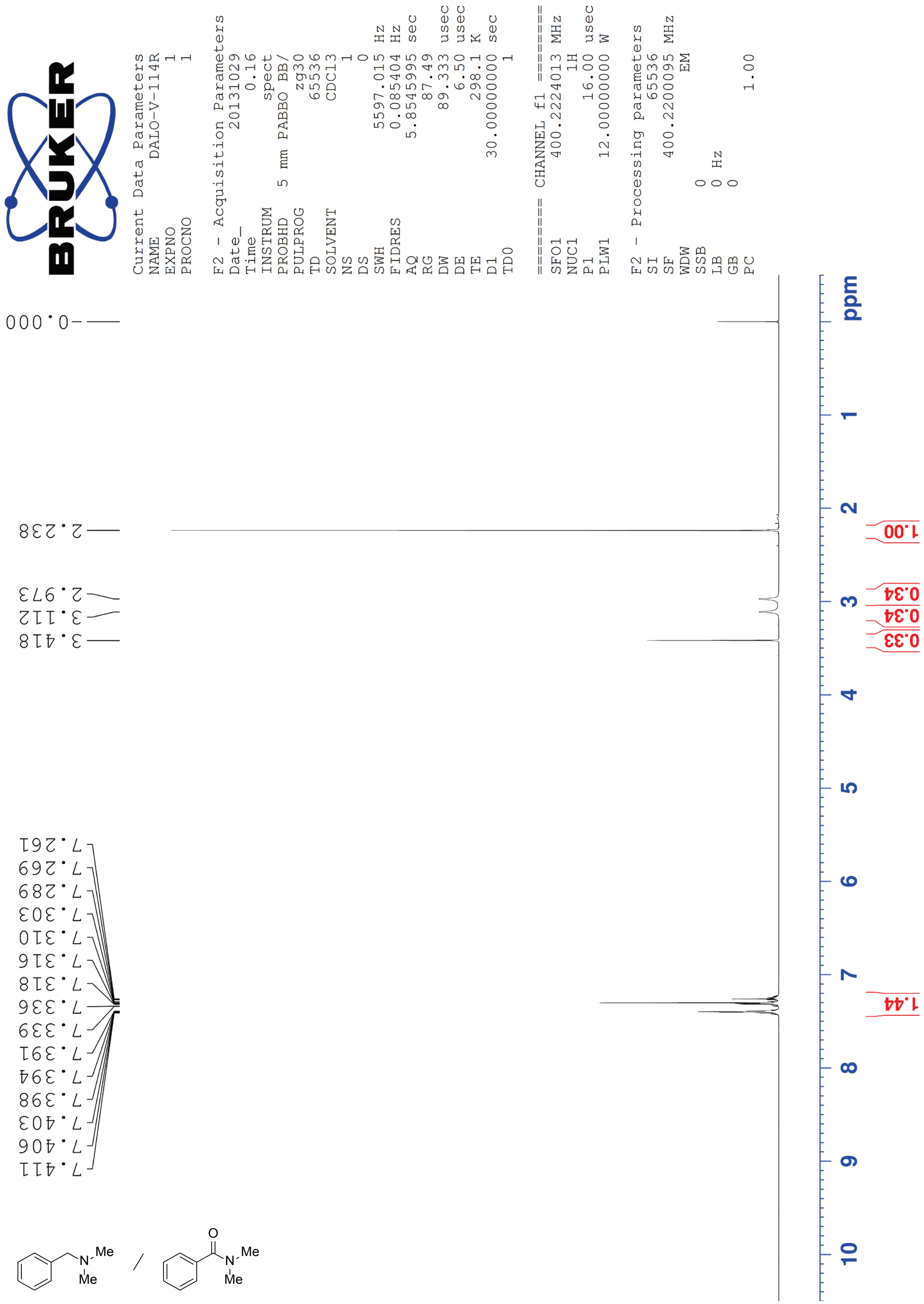
Spectrum S-22: ^{13}C NMR spectrum from Table 3.



Spectrum S-23: ^{1}H NMR spectrum from Table 3.

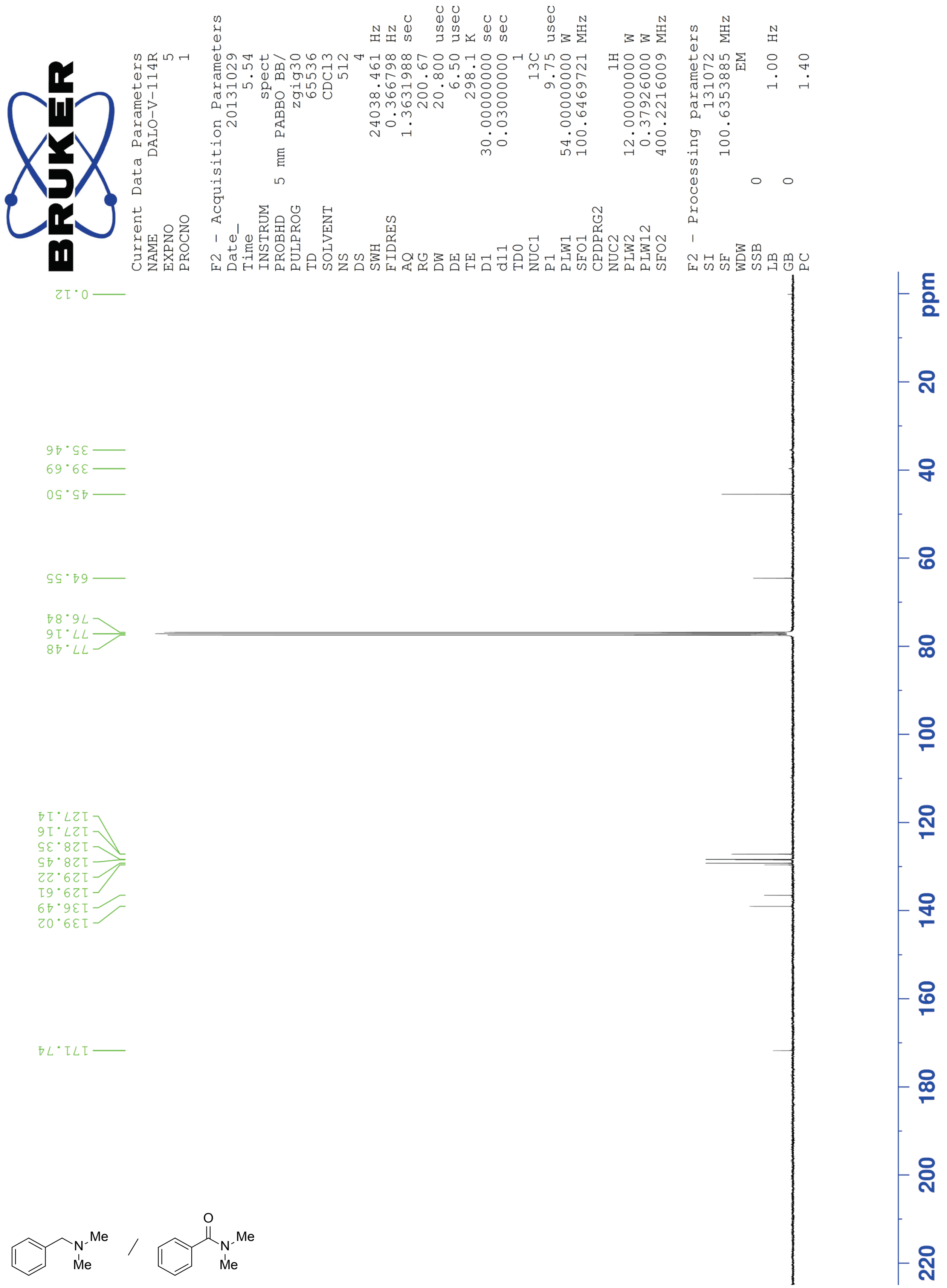


Spectrum S-24: ^{13}C NMR spectrum from Table 3.



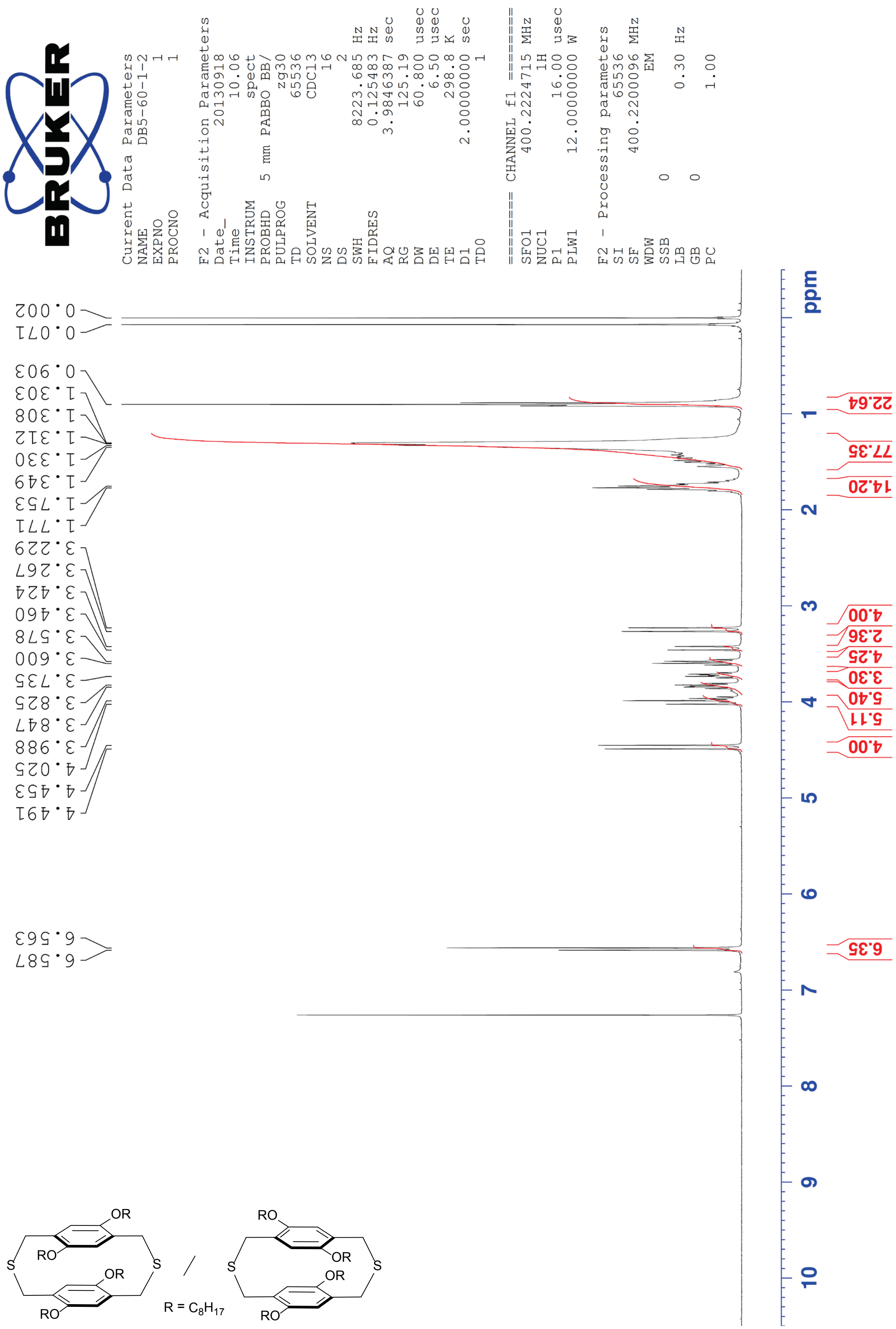
```
Current Data Parameters
NAME          DALO-V-114R
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131029
Time                 0.16
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      1
DS                      0
SWH              5597.015 Hz
FIDRES           0.085404 Hz
AQ              5.8545995 sec
RG                  87.49
DW                 89.333 usec
DE                   6.50 usec
TE                  298.1 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2224013 MHz
NUC1                   1H
P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.2200095 MHz
WDW                    EM
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

Spectrum S-25: ^{1}H NMR spectrum from Table 3.

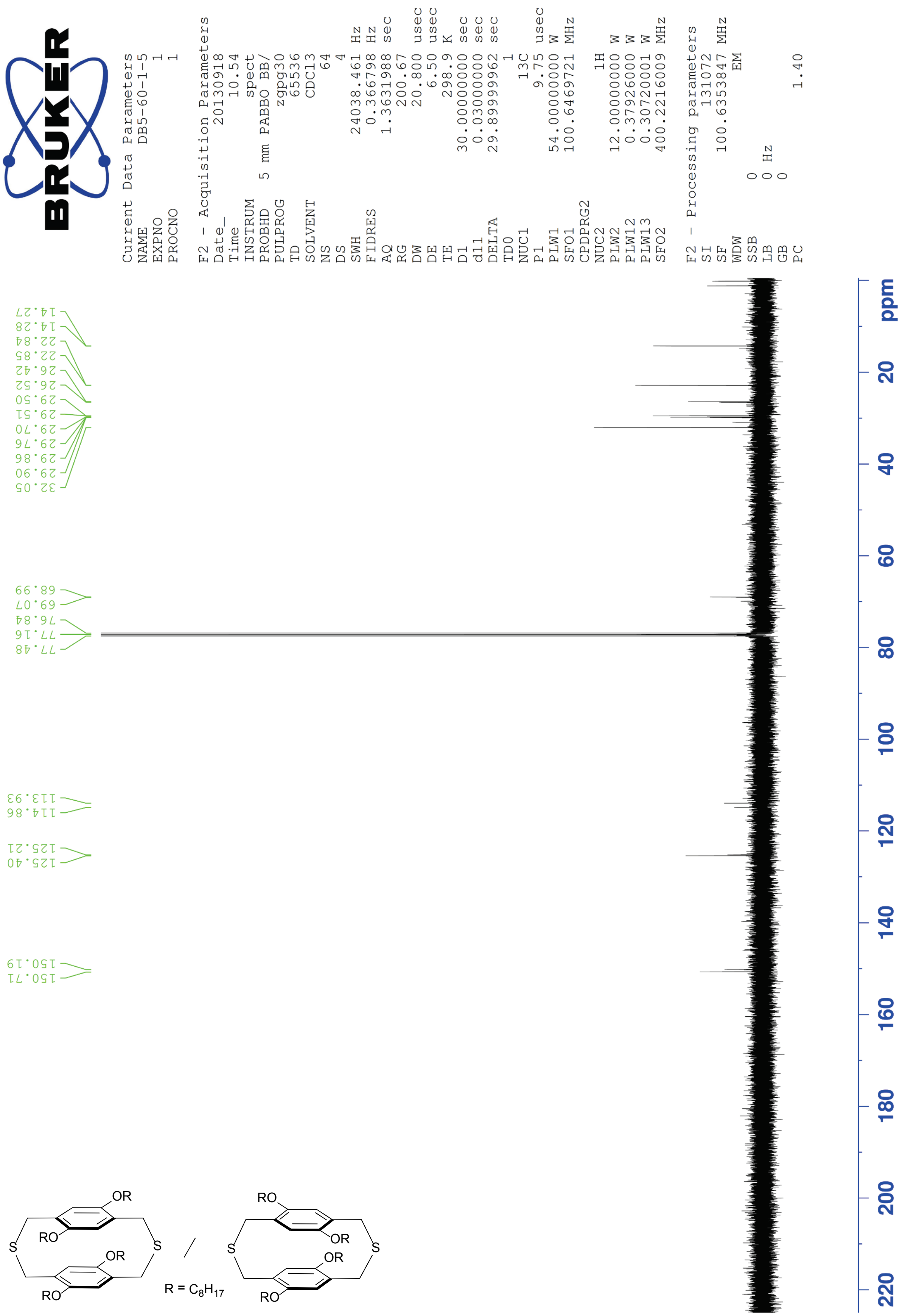


```
Current Data Parameters
NAME          DALO-V-114R
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131029
Time                 5.54
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1           30.00000000 sec
d11           0.03000000 sec
TD0                    1
NUC1                 13C
P1                  9.75 usec
PLW1         54.00000000 W
SFO1         100.6469721 MHz
CPDPRG2
NUC2                  1H
PLW2         12.00000000 W
PLW12         0.37926000 W
SFO2         400.2216009 MHz

F2 - Processing parameters
SI                131072
SF           100.6353885 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

Spectrum S-26: ^{13}C NMR spectrum from Table 3.

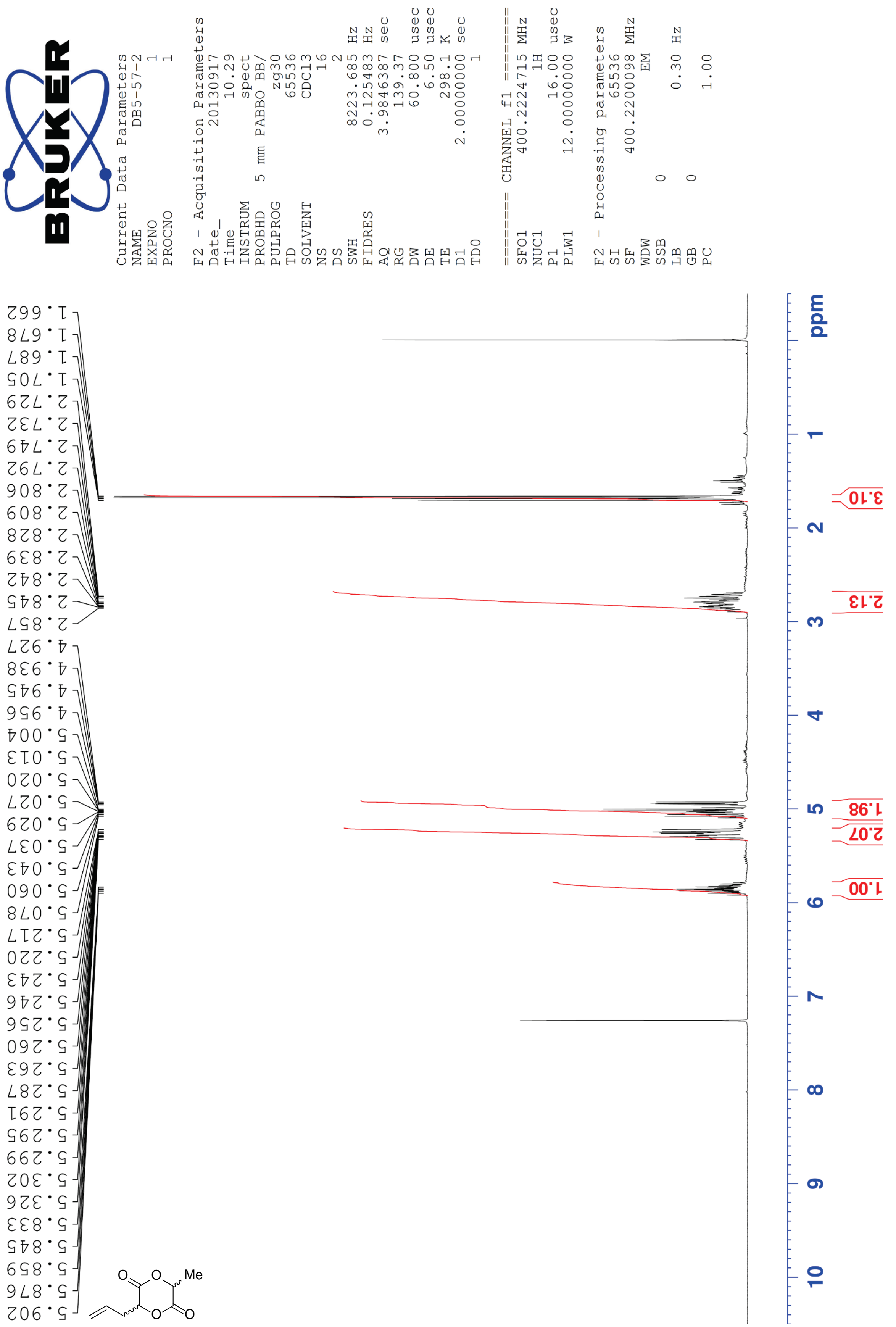

```
Current Data Parameters
NAME          DB5-60-1-2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130918
Time               10.06
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                125.19
DW                60.800 usec
DE                  6.50 usec
TE                 298.8 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.2224715 MHz
NUC1                  1H
P1                 16.00 usec
PLW1         12.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.2200096 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

Spectrum S-27: ^{1}H NMR spectrum from Table 4.



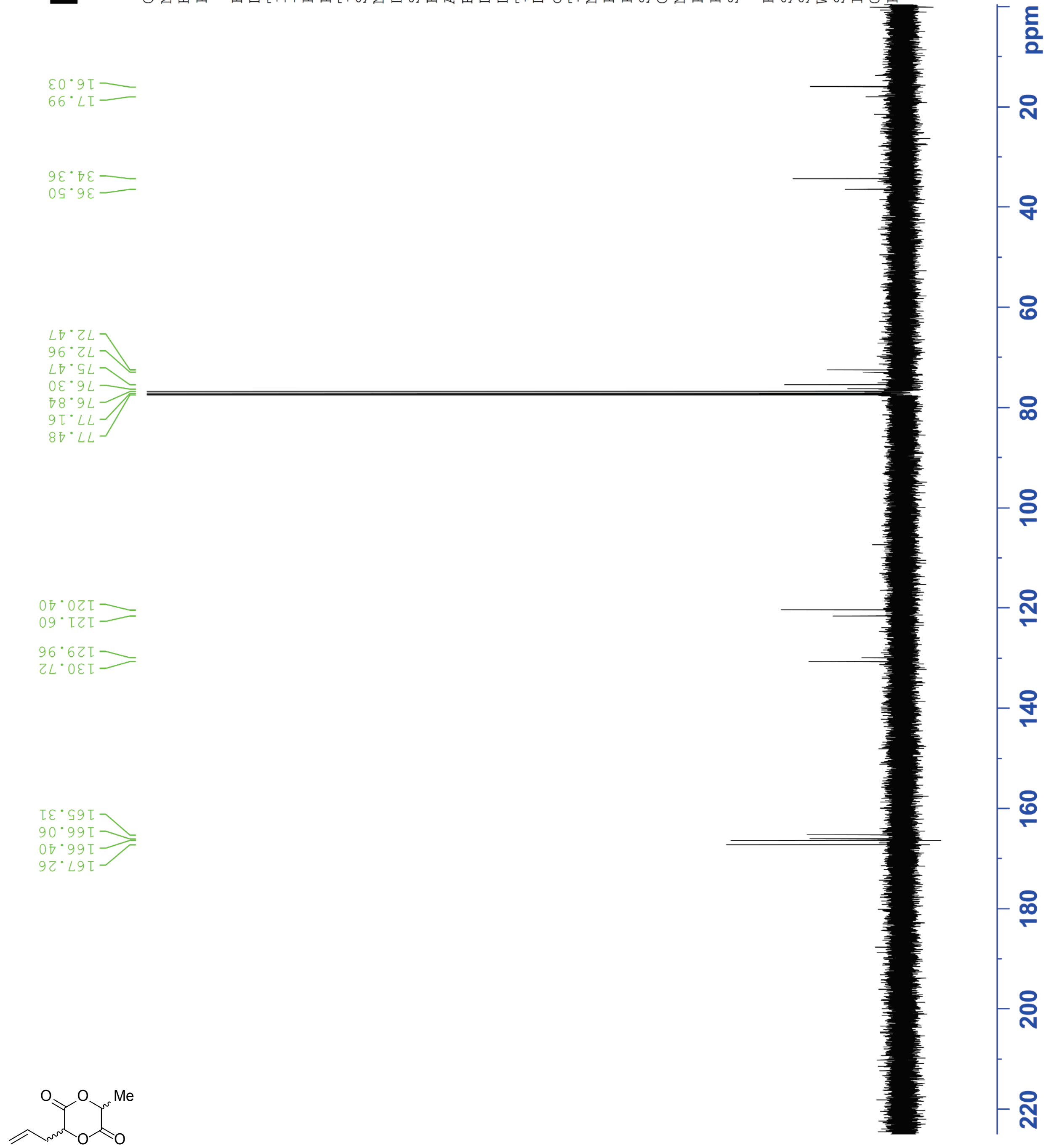
```
Current Data Parameters
NAME         DB5-60-1-5
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130918
Time              10.54
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               200.67
DW               20.800 usec
DE                 6.50 usec
TE                298.9 K
D1          30.00000000 sec
d11          0.03000000 sec
DELTA       29.89999962 sec
TD0                   1
NUC1                13C
P1                 9.75 usec
PLW1        54.00000000 W
SFO1        100.6469721 MHz
CPDPRG2
NUC2                 1H
PLW2        12.00000000 W
PLW12        0.37926000 W
PLW13        0.30720001 W
SFO2        400.2216009 MHz

F2 - Processing parameters
SI               131072
SF          100.6353847 MHz
WDW                  EM
SSB      0
LB       0 Hz
GB       0
PC                 1.40
```

Spectrum S-28: ^{13}C NMR spectrum from Table 4.

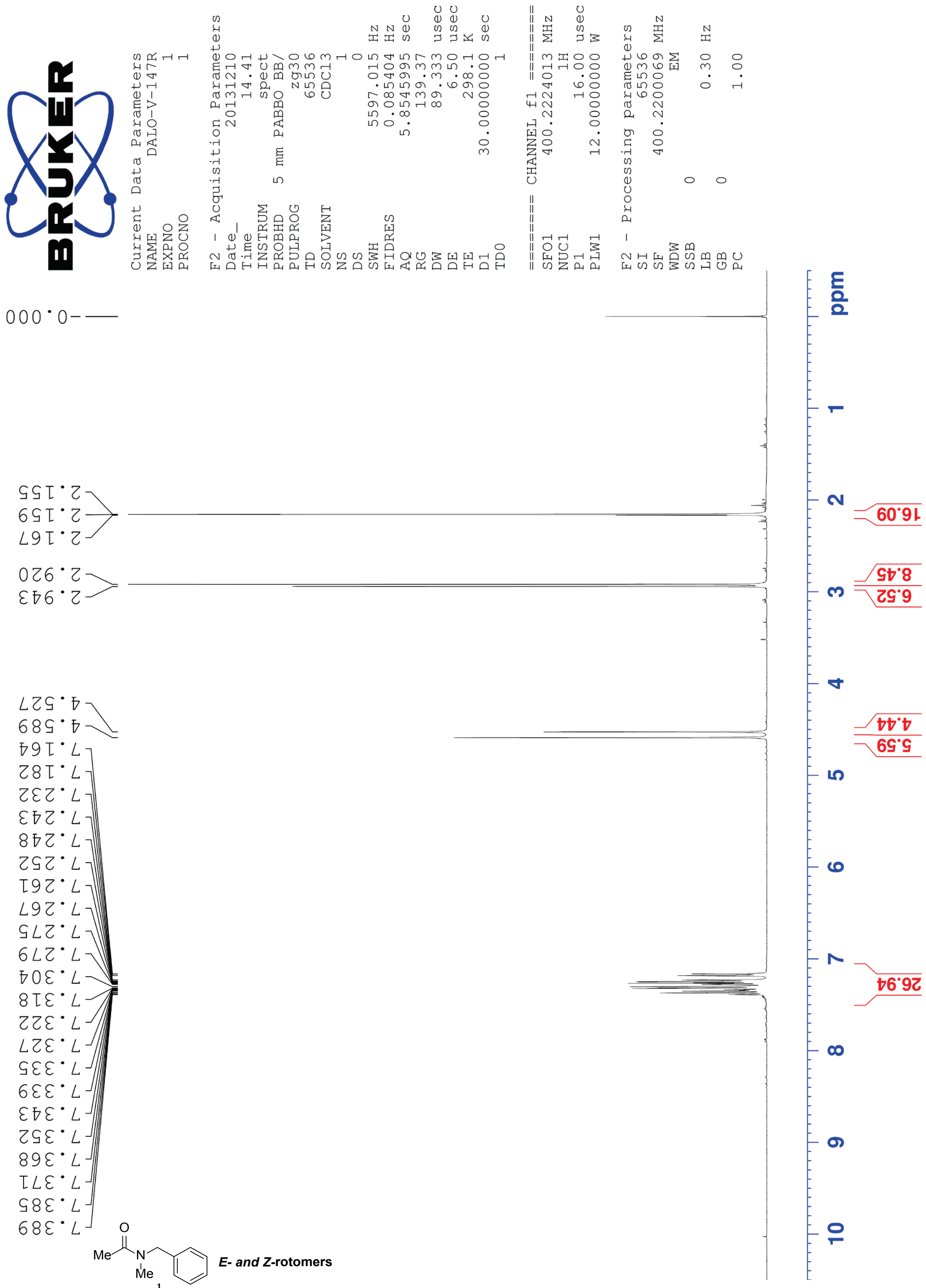


Spectrum S-29: ^{1}H NMR spectrum from Table 4.

```
Current Data Parameters
NAME        DB5-55-3
EXPNO              1
PROCNO             1

F2 - Acquisition Parameters
Date_       20130915
Time           17.28
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG       zgig30
TD             65536
SOLVENT        CDCl3
NS               128
DS                 4
SWH        24038.461 Hz
FIDRES      0.366798 Hz
AQ         1.3631988 sec
RG            200.67
DW            20.800 usec
DE              6.50 usec
TE             298.1 K
D1       30.00000000 sec
d11       0.03000000 sec
TD0                1
NUC1             13C
P1              9.75 usec
PLW1     54.00000000 W
SFO1     100.6469721 MHz
CPDPRG2
NUC2              1H
PLW2     12.00000000 W
PLW12     0.37926000 W
SFO2     400.2216009 MHz

F2 - Processing parameters
SI            131072
SF       100.6353867 MHz
WDW               EM
SSB      0
LB       0 Hz
GB       0
PC              1.40
```

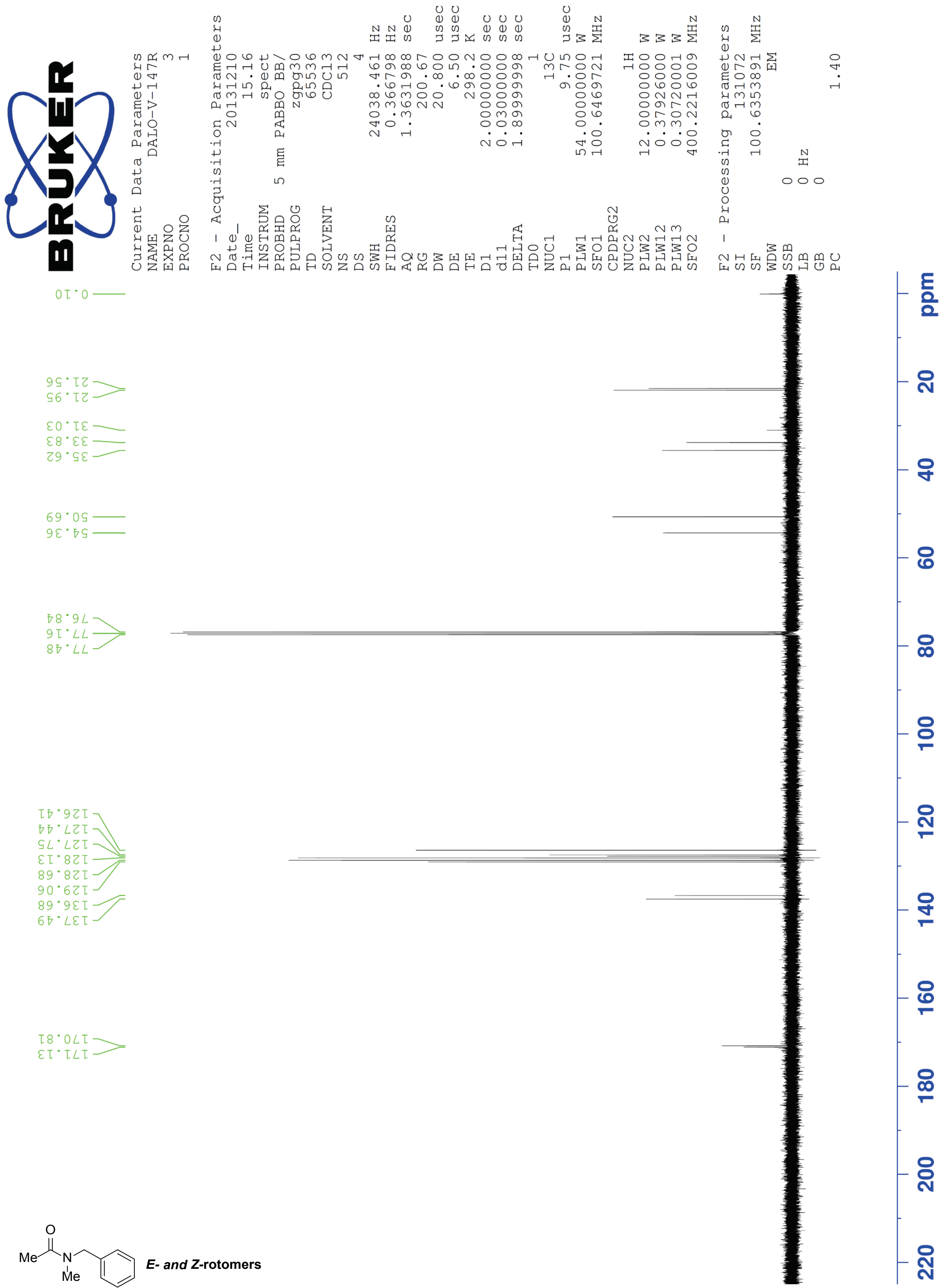


Spectrum S-30: ^{13}C NMR spectrum from Table 4.

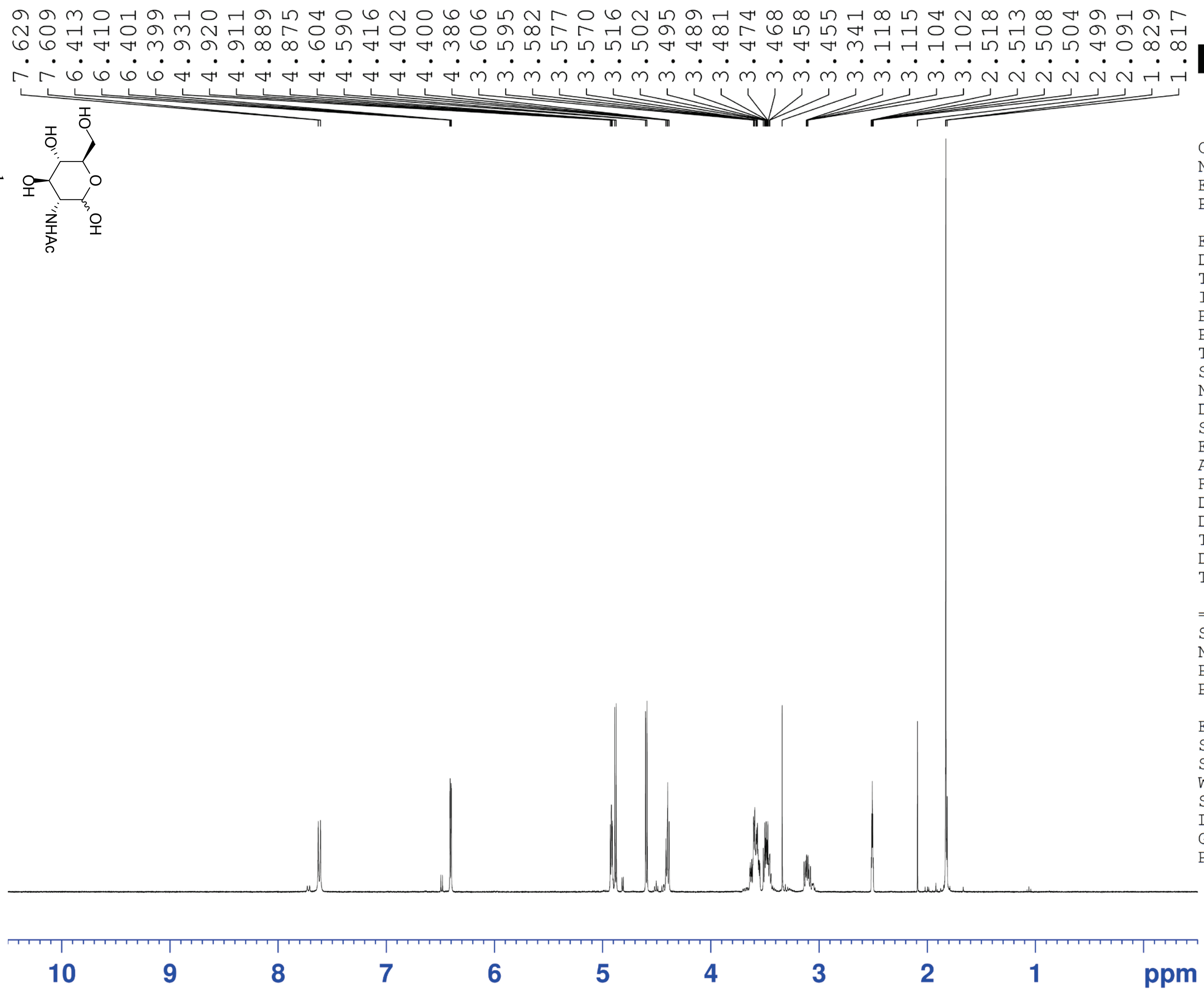


```
Current Data Parameters
NAME          DALO-V-147R
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131210
Time                14.41
INSTRUM             spect
PROBHD     5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      1
DS                      0
SWH              5597.015 Hz
FIDRES           0.085404 Hz
AQ              5.8545995 sec
RG                 139.37
DW                 89.333 usec
DE                   6.50 usec
TE                  298.1 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2224013 MHz
NUC1                   1H
P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.2200069 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

Spectrum S-31: ^{1}H NMR spectrum from Table 4.

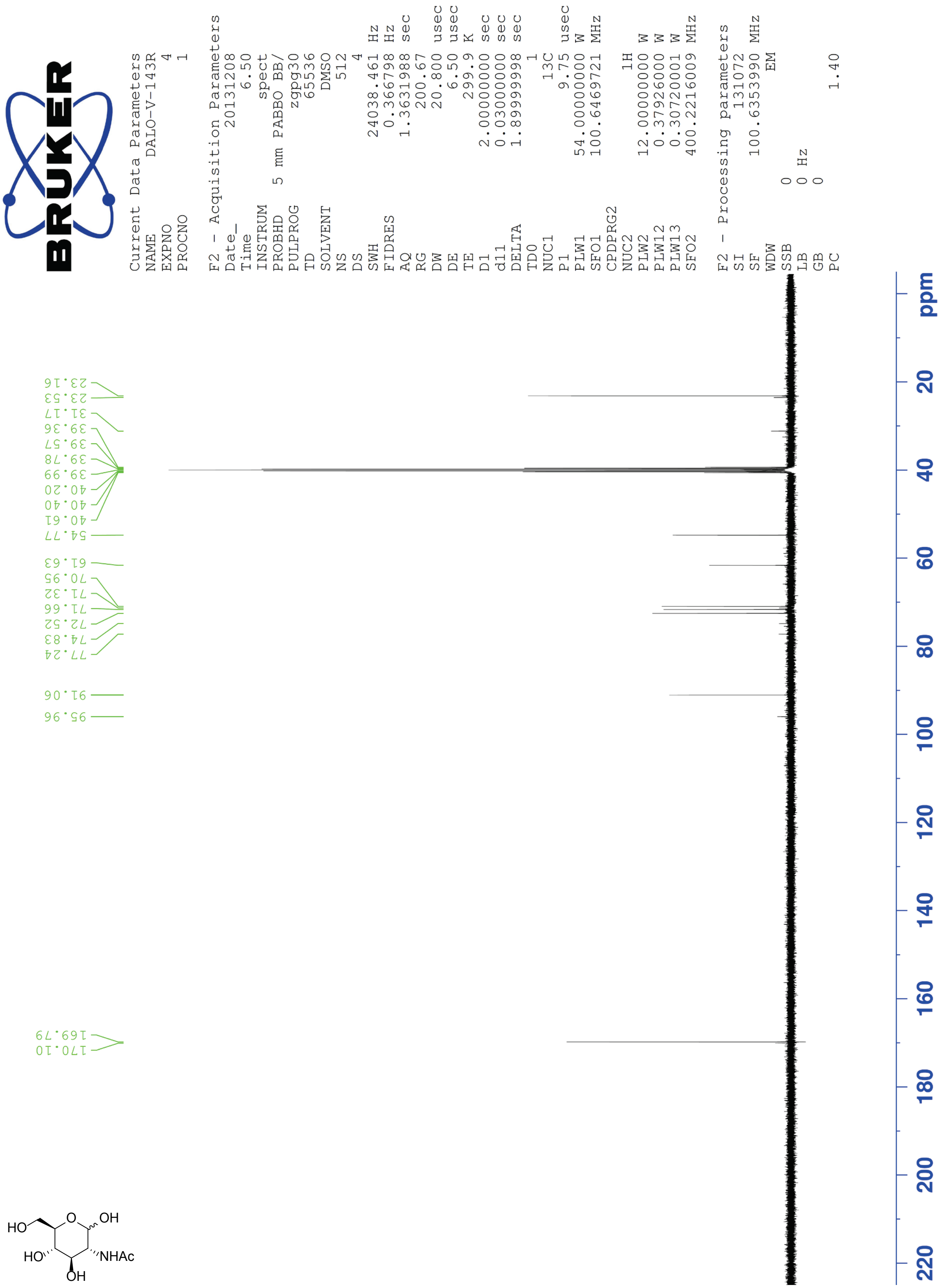


Spectrum S-32: ^{13}C NMR spectrum from Table 4.



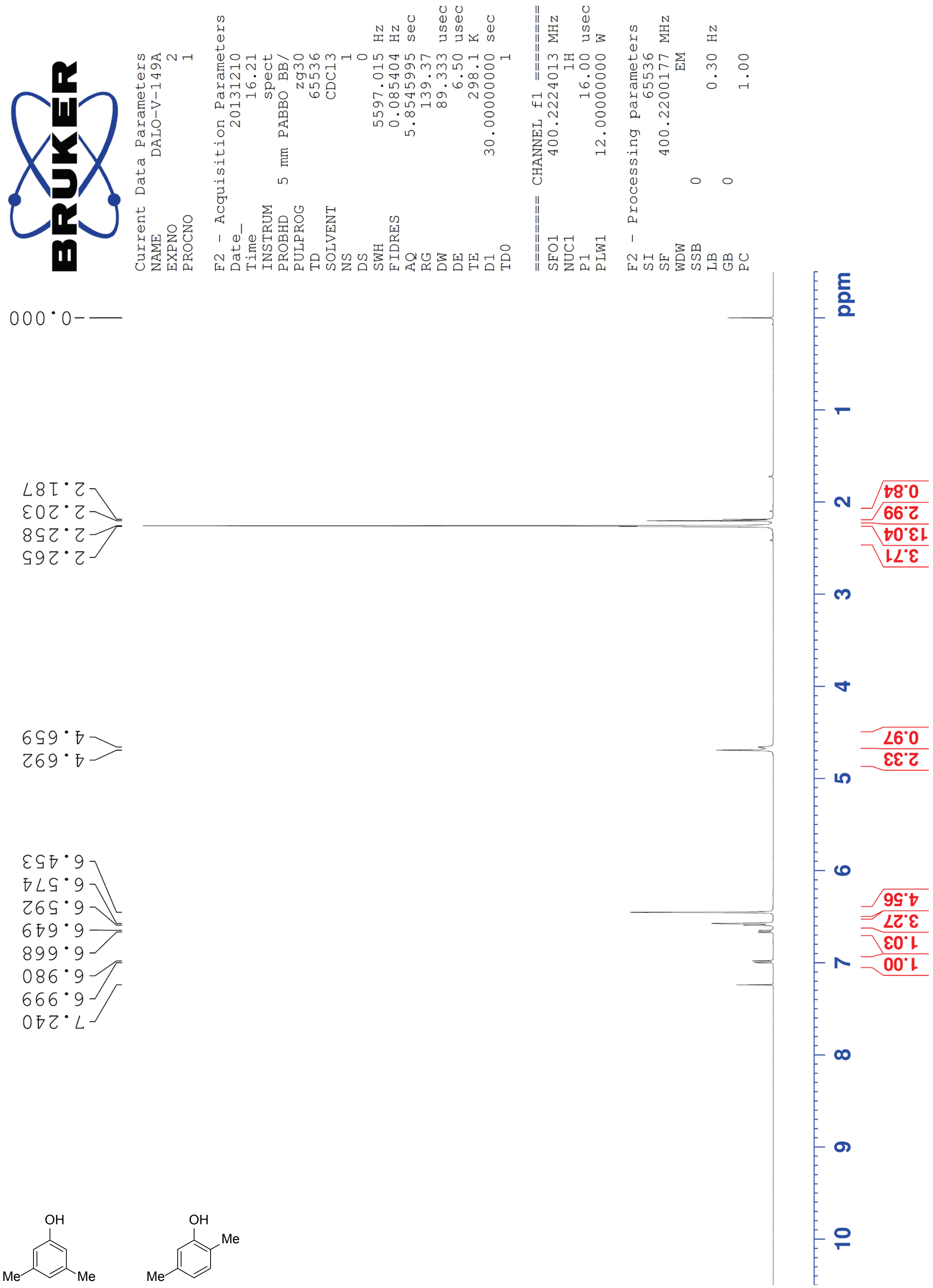
```
Current Data Parameters
NAME          DALO-V-143R
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131208
Time                 5.45
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                      1
DS                      0
SWH              5597.015 Hz
FIDRES           0.085404 Hz
AQ              5.8545995 sec
RG                 100.36
DW                 89.333 usec
DE                   6.50 usec
TE                  298.9 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2224013 MHz
NUC1                   1H
P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.2200000 MHz
WDW                    EM
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```

Spectrum S-33: ^{1}H NMR spectrum from Table 4.



```
Current Data Parameters
NAME       DALO-V-143R
EXPNO                4
PROCNO               1

F2 - Acquisition Parameters
Date_         20131208
Time              6.50
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG        zgpg30
TD              65536
SOLVENT          DMSO
NS                512
DS                  4
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ          1.3631988 sec
RG             200.67
DW             20.800 usec
DE               6.50 usec
TE              299.9 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0                 1
NUC1              13C
P1               9.75 usec
PLW1      54.00000000 W
SFO1      100.6469721 MHz
CPDPRG2
NUC2               1H
PLW2      12.00000000 W
PLW12      0.37926000 W
PLW13      0.30720001 W
SFO2      400.2216009 MHz

F2 - Processing parameters
SI             131072
SF        100.6353990 MHz
WDW                EM
SSB                 0
LB                  0 Hz
GB                  0
PC               1.40
```

Spectrum S-34: ^{13}C NMR spectrum from Table 4.



```
Current Data Parameters
NAME          DALO-V-149A
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131210
Time                16.21
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      1
DS                      0
SWH              5597.015 Hz
FIDRES           0.085404 Hz
AQ              5.8545995 sec
RG                 139.37
DW                 89.333 usec
DE                   6.50 usec
TE                  298.1 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          400.2224013 MHz
NUC1                   1H
P1                  16.00 usec
PLW1          12.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.2200177 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
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Spectrum S-35: ^{1}H NMR spectrum from Table 5.

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Current Data Parameters
NAME          DALO-V-149A
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                    1
NUC1                 13C
P1                  9.75 usec
PLW1         54.00000000 W
SFO1         100.6469721 MHz
CPDPRG2
NUC2                  1H
PLW2         12.00000000 W
PLW12         0.37926000 W
PLW13         0.30720001 W
SFO2         400.2216009 MHz

F2 - Processing parameters
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SSB      0
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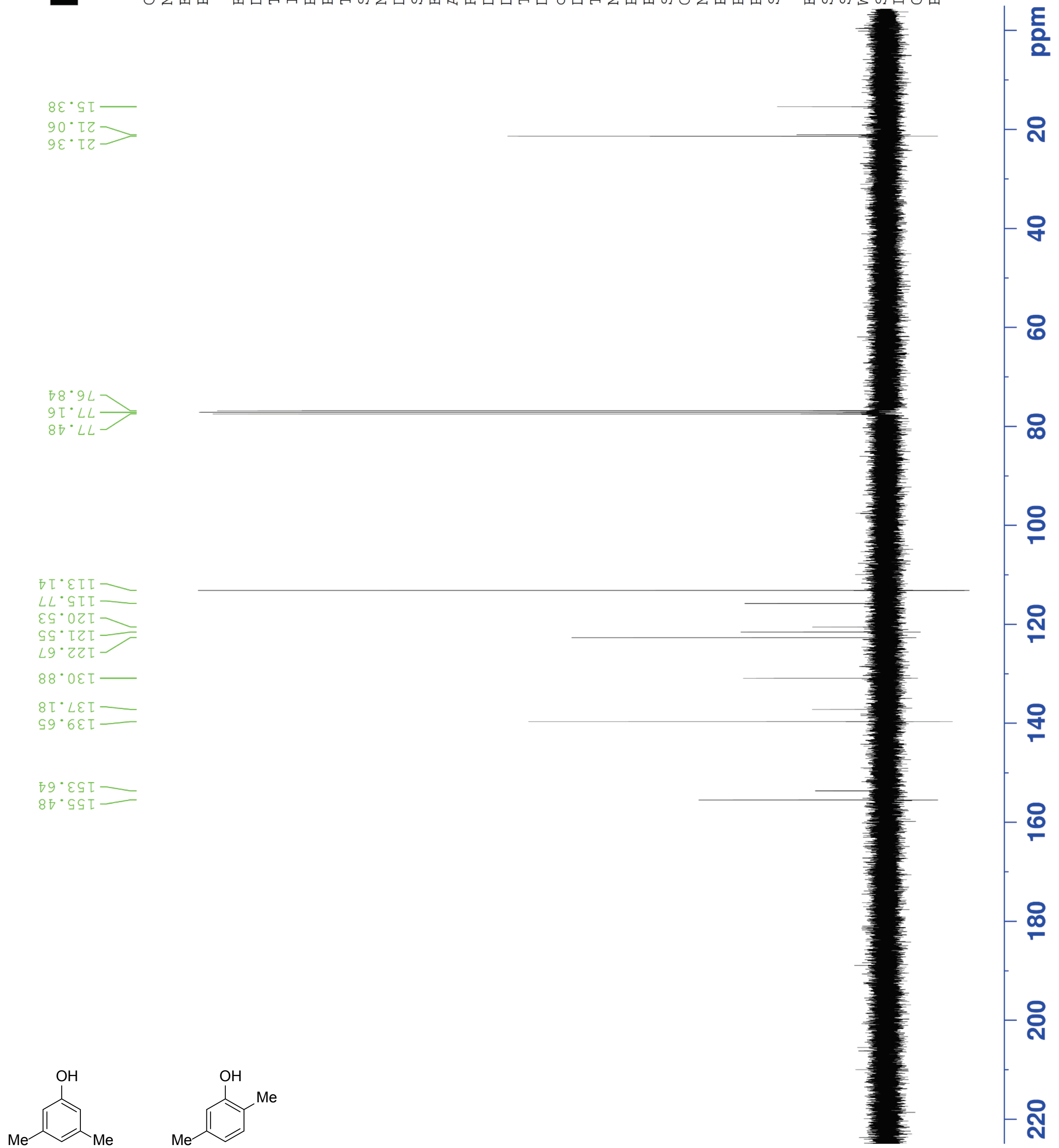
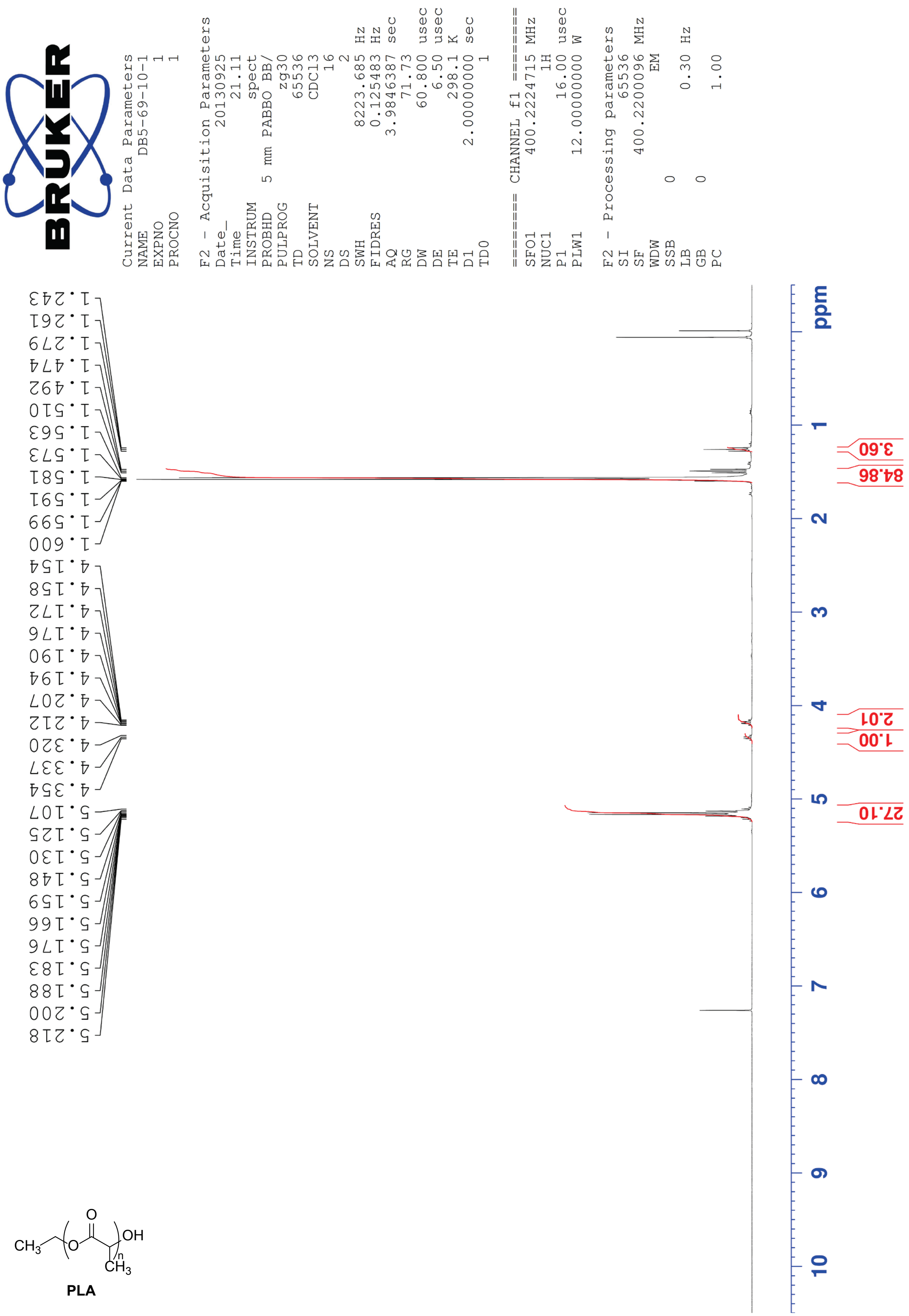


Spectrum S-36: ^{13}C NMR spectrum from Table 5.



Spectrum S-37: ^{1}H NMR spectrum from Table 6.

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Current Data Parameters
NAME          DB5-69-10-2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
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Time                21.42
INSTRUM             spect
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PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    512
DS                      4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ              1.3631988 sec
RG                 200.67
DW                 20.800 usec
DE                   6.50 usec
TE                  298.1 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1
NUC1                  13C
P1                   9.75 usec
PLW1          54.00000000 W
SFO1          100.6469721 MHz
CPDPRG2
NUC2                   1H
PLW2          12.00000000 W
PLW12          0.37926000 W
PLW13          0.30720001 W
SFO2          400.2216009 MHz

F2 - Processing parameters
SI                 131072
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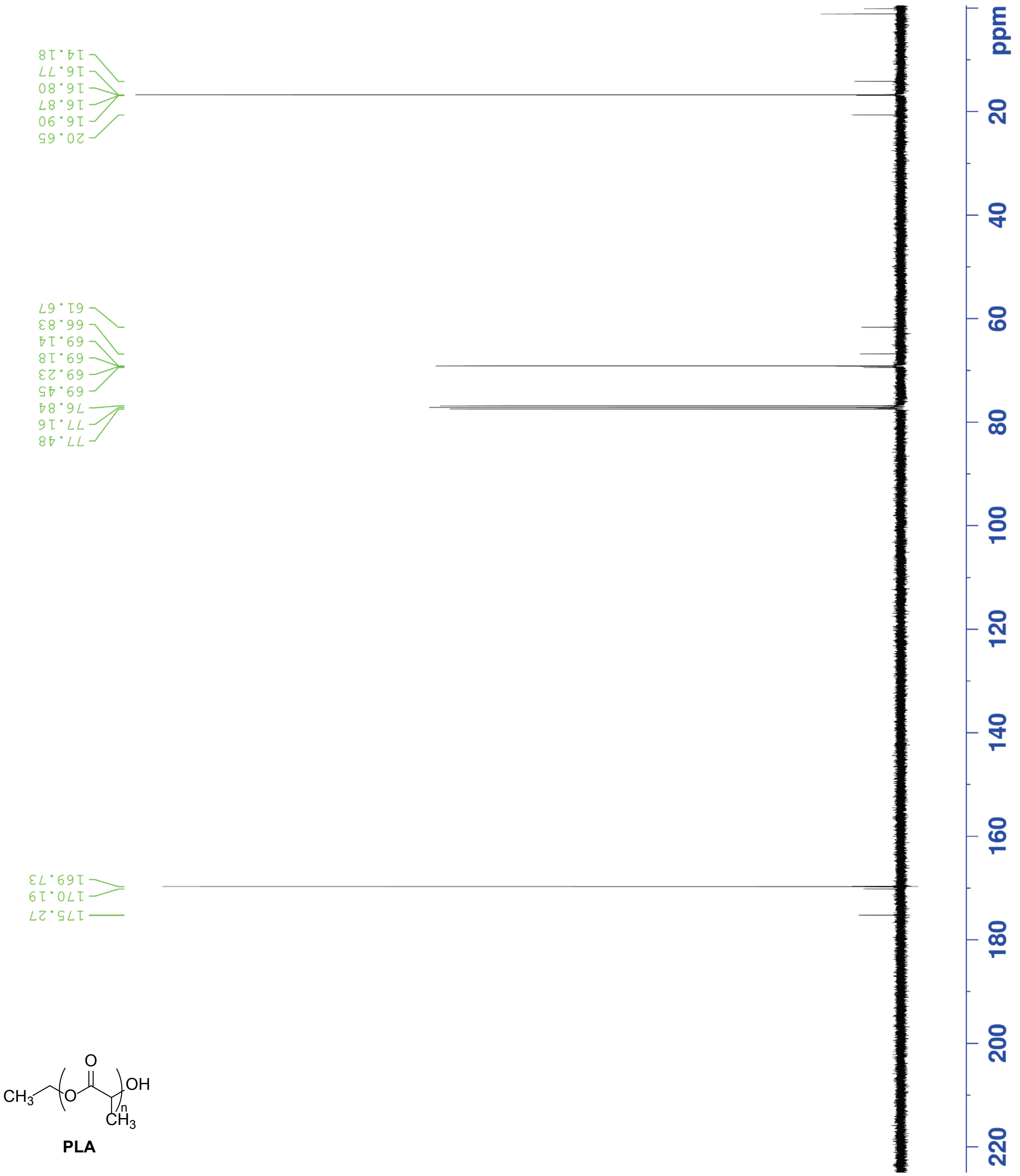
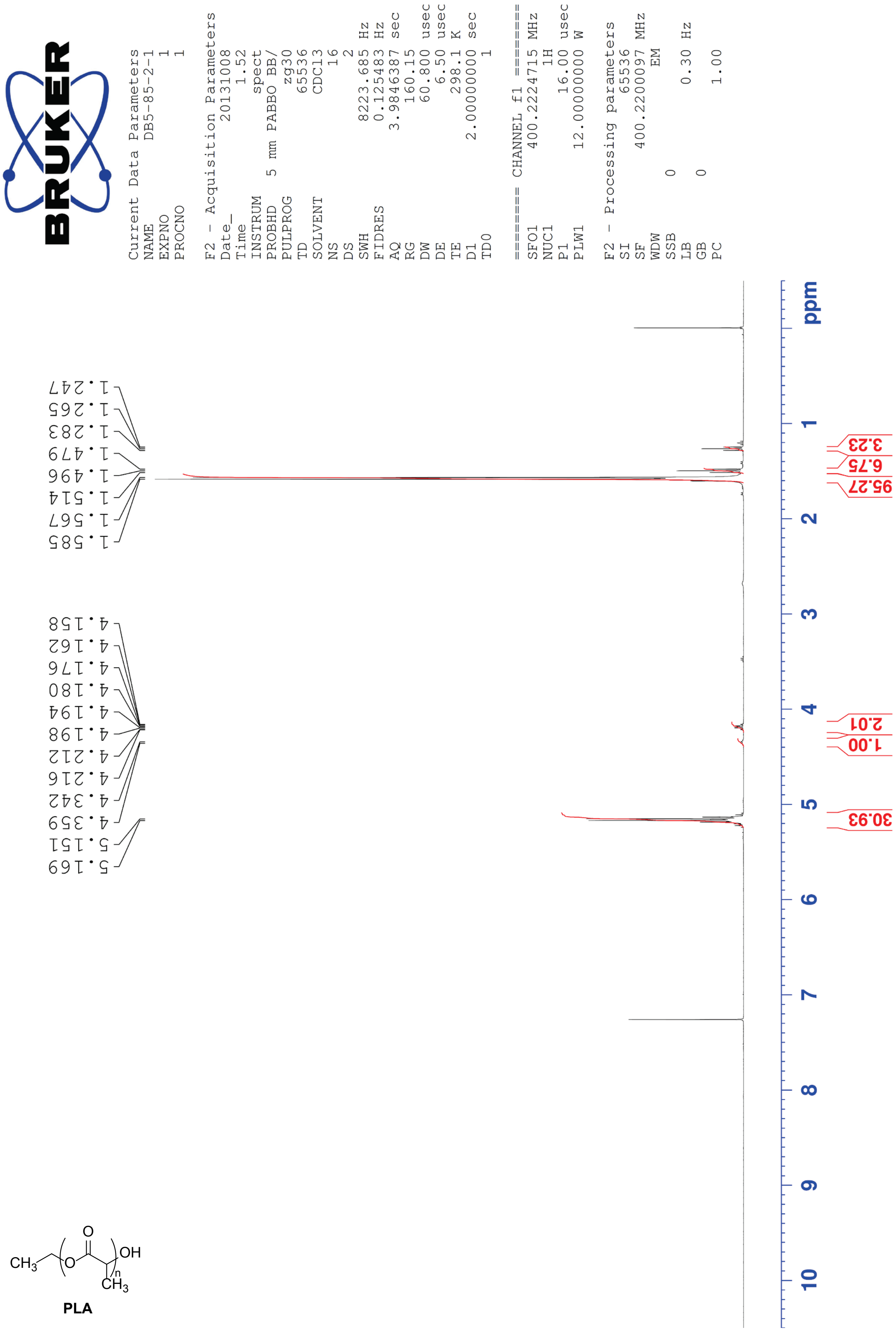


PLA

Spectrum S-38: ^{13}C NMR spectrum from Table 6.



Spectrum S-39: ^{1}H NMR spectrum from Table 6.

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Current Data Parameters
NAME          DB5-85-2-2
EXPNO                  1
PROCNO                 1

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Time                2.23
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               200.67
DW               20.800 usec
DE                 6.50 usec
TE                298.2 K
D1           2.00000000 sec
d11          0.03000000 sec
DELTA        1.89999998 sec
TD0                   1
NUC1                13C
P1                 9.75 usec
PLW1        54.00000000 W
SFO1       100.6469721 MHz
CPDPRG2
NUC2                 1H
PLW2        12.00000000 W
PLW12        0.37926000 W
PLW13        0.30720001 W
SFO2       400.2216009 MHz

F2 - Processing parameters
SI               131072
SF          100.6353855 MHz
WDW                  EM
SSB      0
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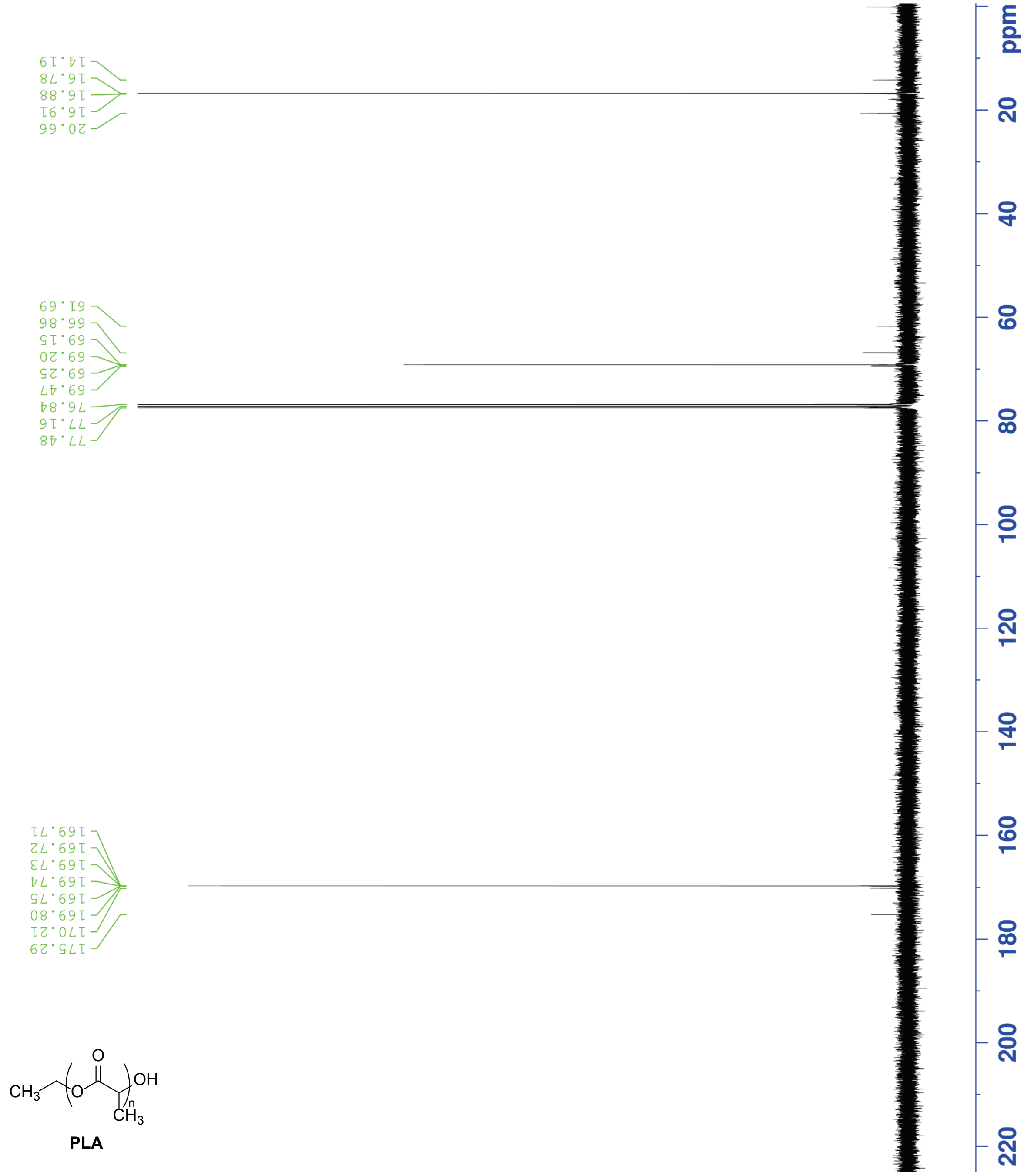
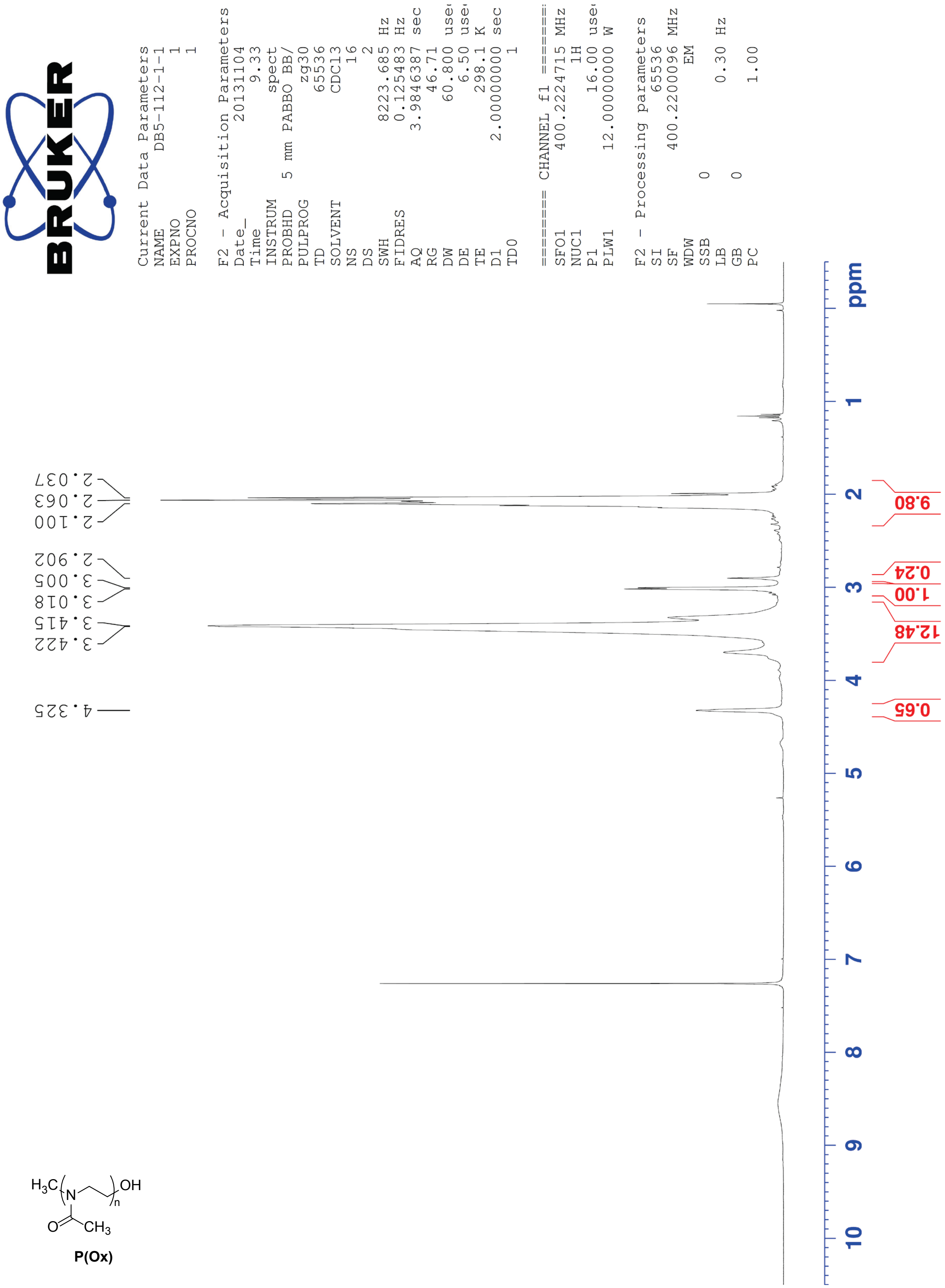
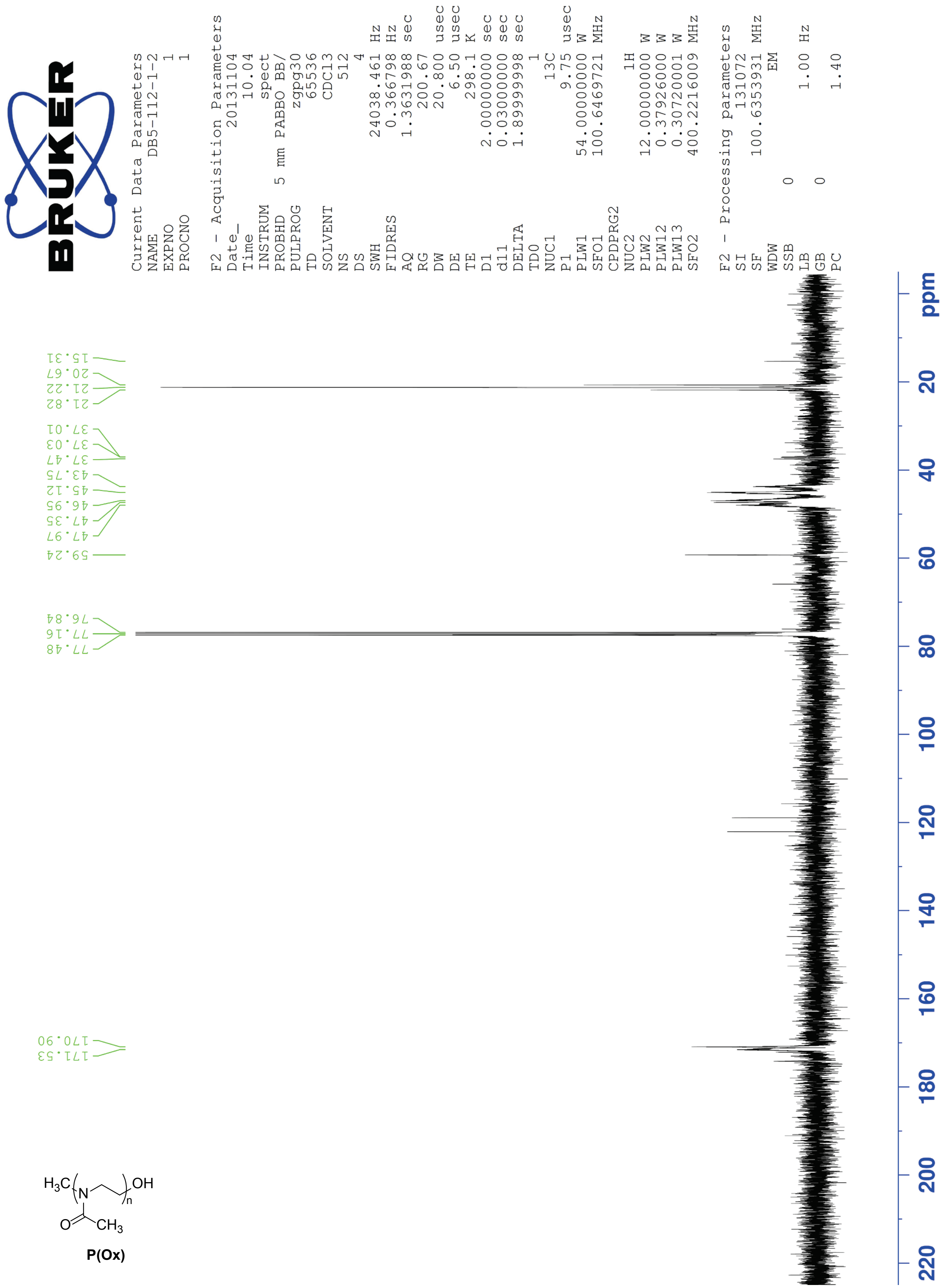


PLA

Spectrum S-40: ^{13}C NMR spectrum from Table 6.



Spectrum S-41: ^{1}H NMR spectrum of 10-mer from Table 6.



```
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EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
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Time            10.04
INSTRUM         spect
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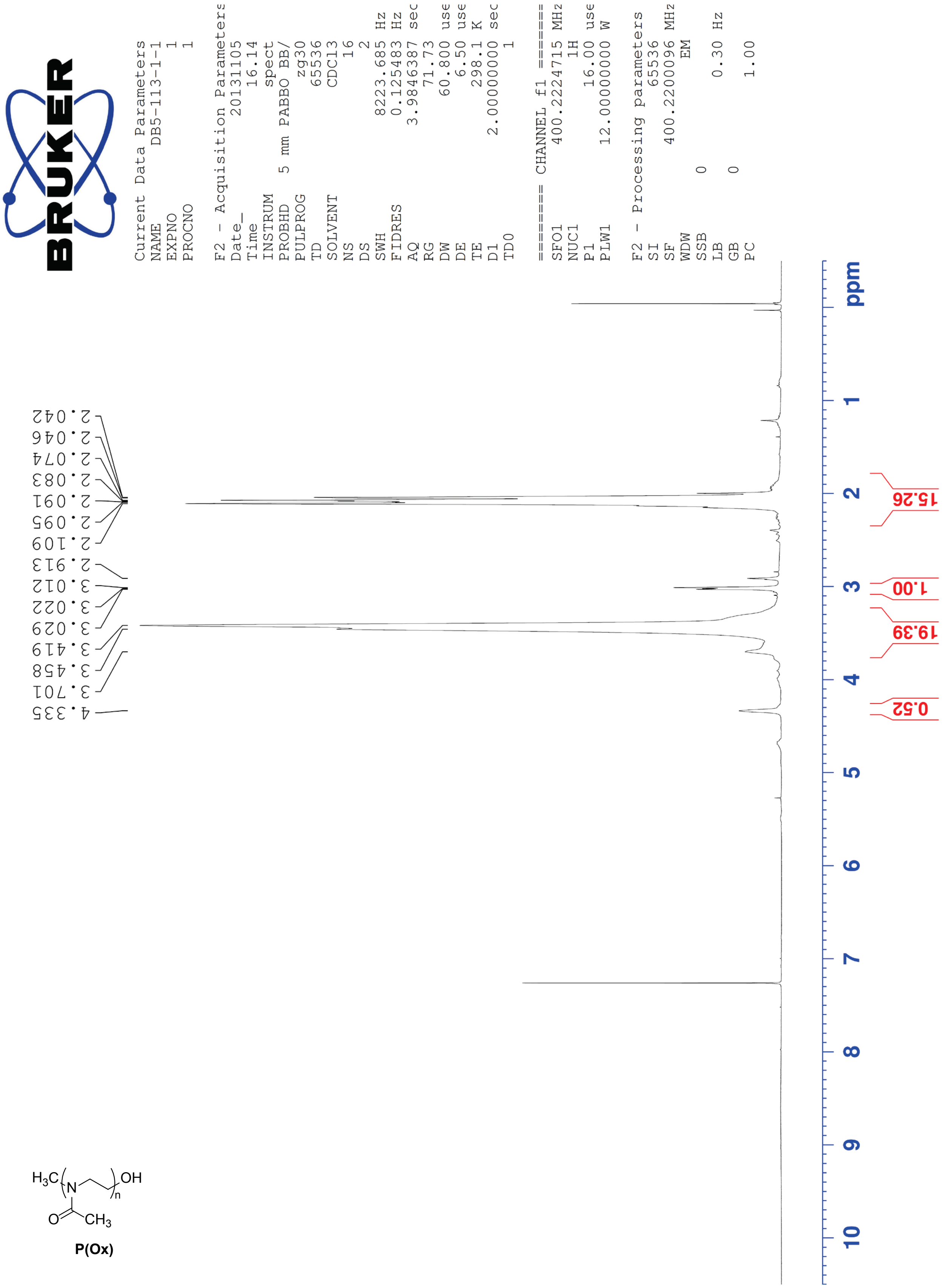
PULPROG       zgpg30
TD              65536
SOLVENT         CDCl3
NS                512
DS                  4
SWH         24038.461 Hz
FIDRES       0.366798 Hz
AQ          1.3631988 sec
RG             200.67
DW             20.800 usec
DE               6.50 usec
TE              298.1 K
D1         2.00000000 sec
d11        0.03000000 sec
DELTA      1.89999998 sec
TD0                 1
NUC1              13C
P1               9.75 usec
PLW1      54.00000000 W
SFO1      100.6469721 MHz
CPDPRG2
NUC2               1H
PLW2      12.00000000 W
PLW12      0.37926000 W
PLW13      0.30720001 W
SFO2      400.2216009 MHz

F2 - Processing parameters
SI             131072
SF        100.6353931 MHz
WDW                EM
SSB      0
LB               1.00 Hz
GB       0
PC               1.40
```

Spectrum S-42: ^{13}C NMR spectrum of 10-mer from Table 6.



```
Current Data Parameters
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EXPNO               1
PROCNO              1

F2 - Acquisition Parameters
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Time            16.14
INSTRUM         spect
PROBHD   5 mm PABBO BB/
PULPROG          zg30
TD              65536
SOLVENT         CDCl3
NS                 16
DS                  2
SWH          8223.685 Hz
FIDRES       0.125483 Hz
AQ          3.9846387 sec
RG              71.73
DW             60.800 use
DE               6.50 use
TE              298.1 K
D1         2.00000000 sec
TD0                 1

======== CHANNEL f1 ========
SFO1      400.2224715 MHz
NUC1               1H
P1              16.00 use
PLW1      12.00000000 W

F2 - Processing parameters
SI              65536
SF        400.2200096 MHz
WDW                EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
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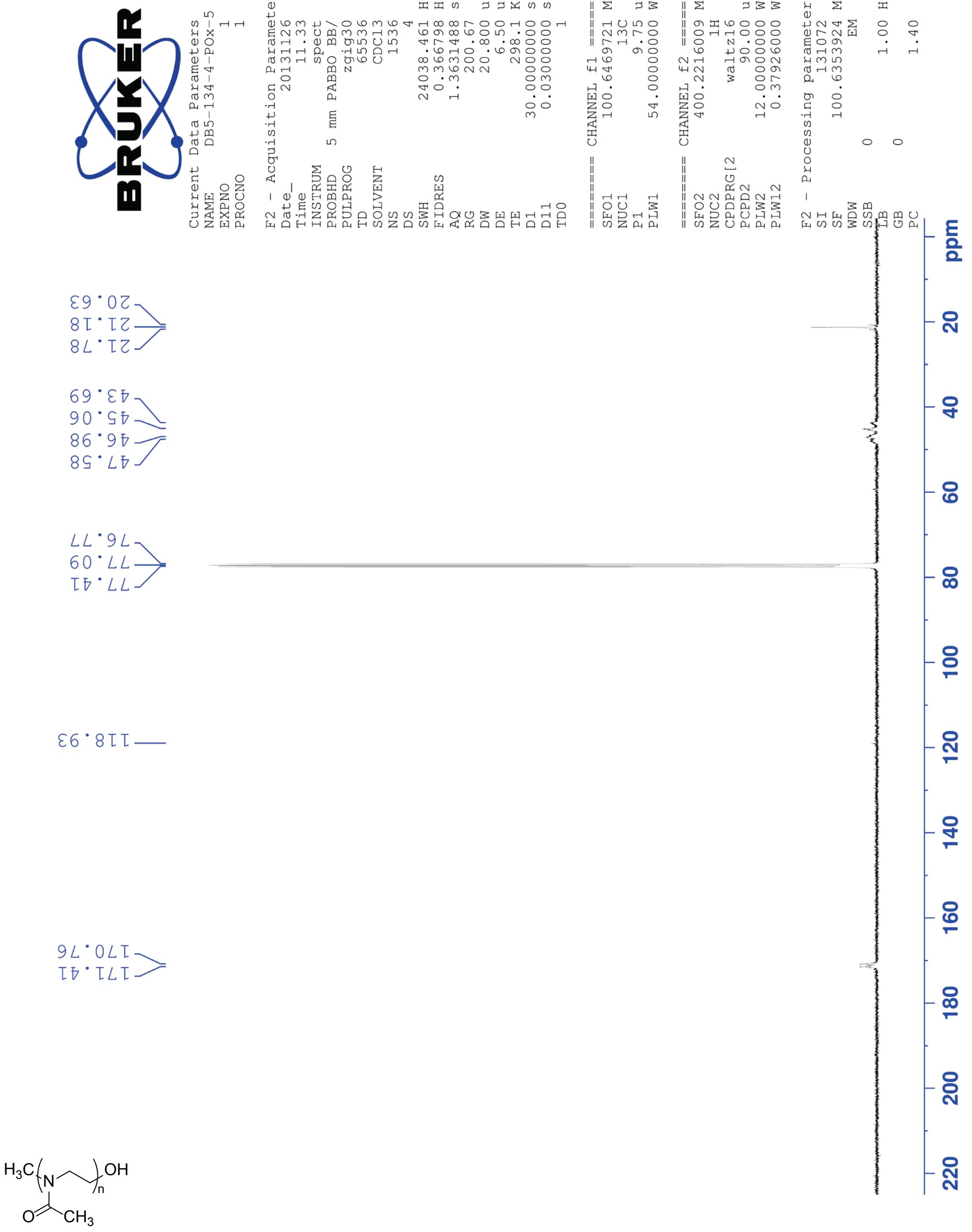
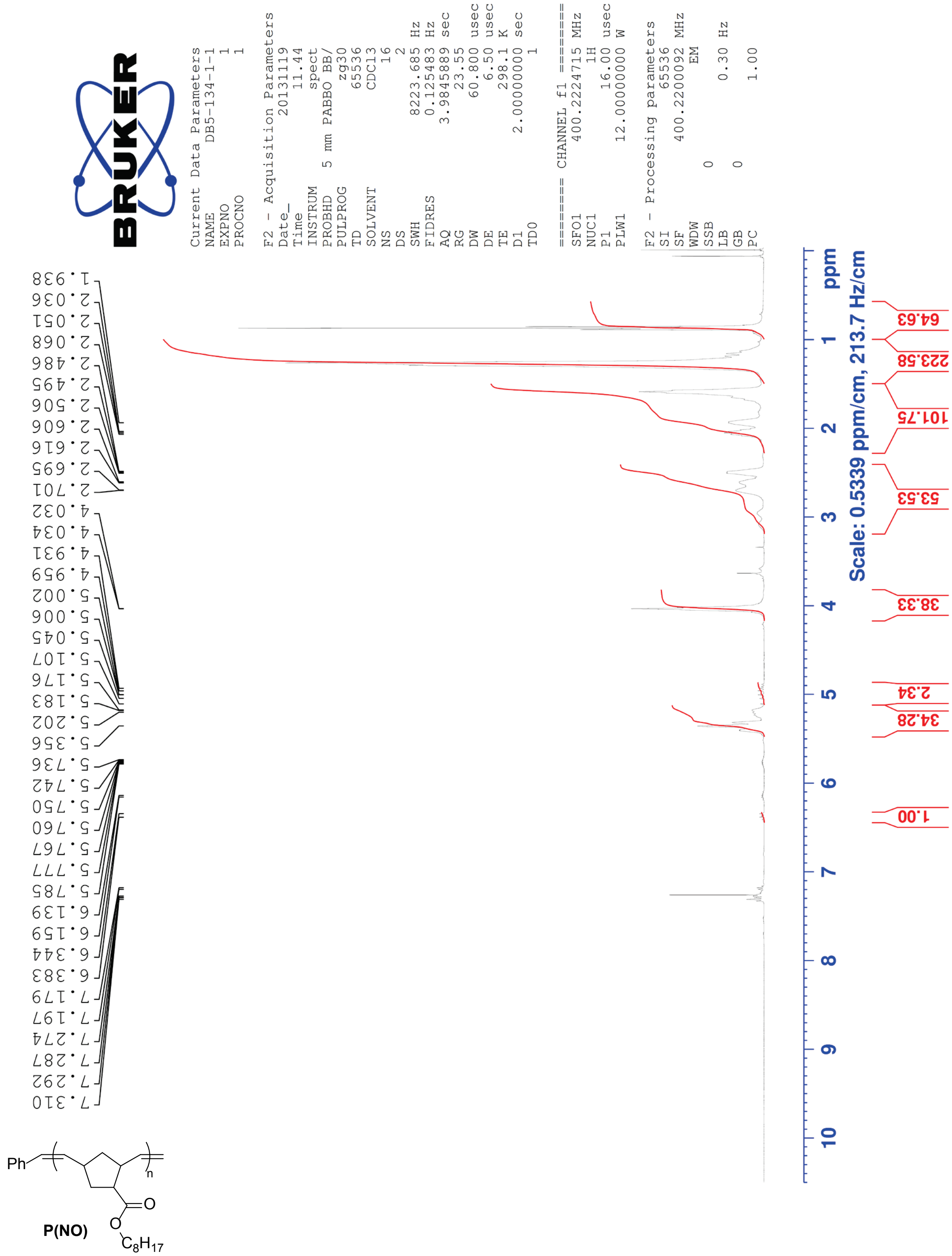
Spectrum S-43: ^{1}H NMR spectrum of 15-mer from Table 6.



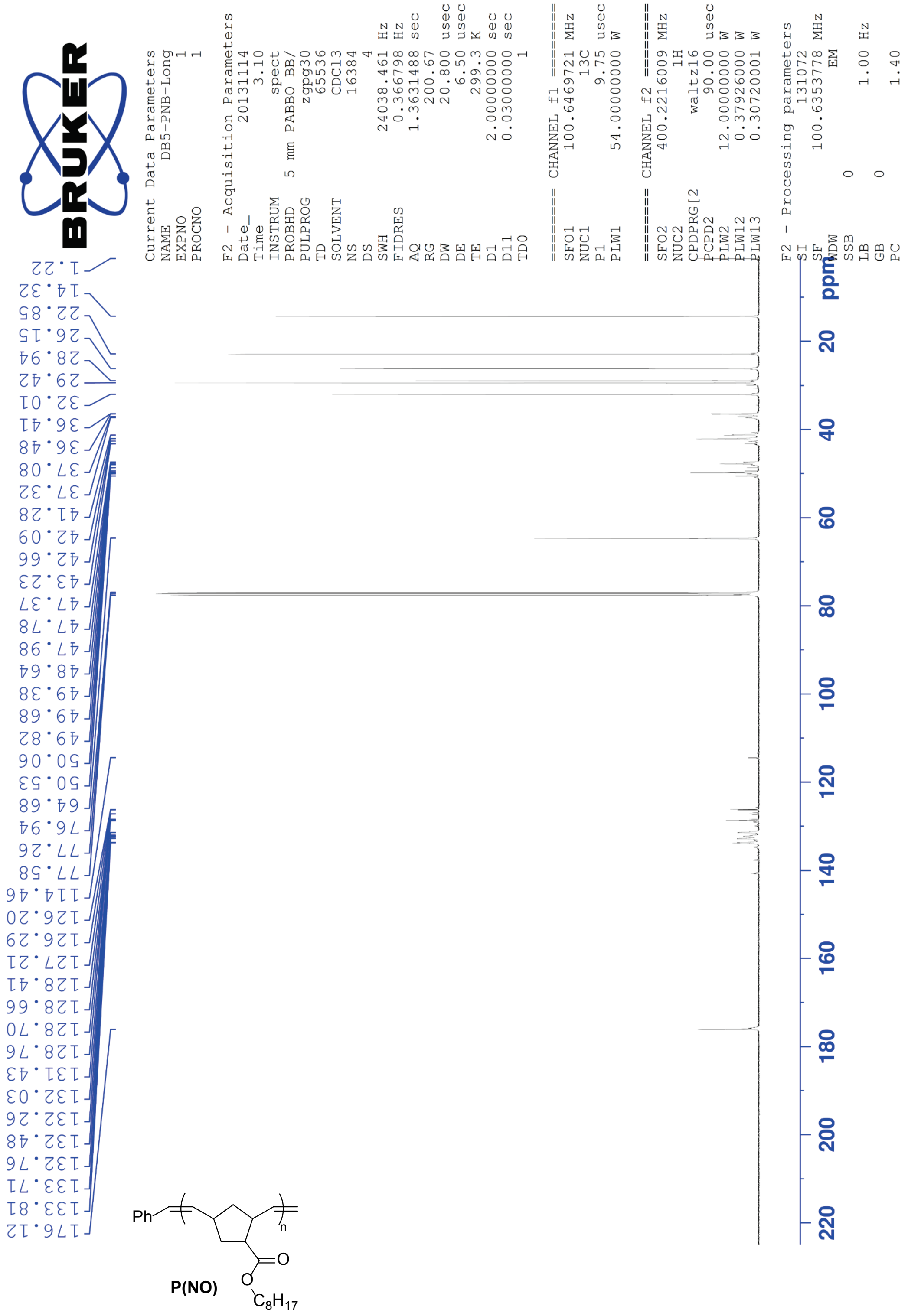
P(Ox)

Spectrum S-44: ^{13}C NMR spectrum of 15-mer from Table 6.



P(NO)

Spectrum S-45: ^{1}H NMR spectrum from Table 6.



Spectrum S-46: ^{13}C NMR spectrum from Table 6.

Tables of Deconvolution Data:

General: ^{13}C NMR spectra of polymers were acquired using BBD acquisition with D1 = 2 sec and at least 512 scans (in cases of complex polymer structures, 8192 scans are recommended).

Table SI-1. Deconvolution results for the ^{13}C NMR spectrum* of 2 from Scheme 1.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
148.0	0.60	Major Diastereomer
147.7	0.40	Minor Diastereomer
128.3	4.61	Both Diastereomers
126.64	1.23	Minor Diastereomer
126.58	0.92	Minor Diastereomer
125.0	1.86	Minor Diastereomer
124.9	2.45	Major Diastereomer
74.6	0.79	Minor Diastereomer
74.5	0.97	Major Diastereomer
38.2	1.30	Major Diastereomer
38.1	1.02	Minor Diastereomer
31.4	0.85	Minor Diastereomer
30.6	1.05	Major Diastereomer

*BBD, 64 scans, D1 = 2 sec

Table SI-2. Deconvolution results for the ^{13}C NMR spectrum* of fenchone:camphor (39.2 mol% fenchone) sample from Table 2.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
Not Found	N/A	Fenchone
219.9	0.81	Camphor
57.9	1.00	Camphor
54.3	0.77	Fenchone
47.5	0.61	Fenchone
46.9	0.88	Camphor
45.5	1.85	Fenchone
43.5	3.07	Camphor
43.2	2.89	Camphor
41.8	1.80	Fenchone
32.0	1.96	Fenchone
30.1	2.99	Camphor
27.2	3.12	Camphor
25.1	2.10	Fenchone
23.5	1.59	Fenchone
21.8	1.97	Fenchone
19.9	2.86	Camphor
19.3	2.88	Camphor
14.8	1.69	Fenchone
9.4	2.42	Camphor

*IGD, 16 scans, D1 = 2 sec. See Spectrum S-9 for deconvoluted ^{13}C NMR spectrum.

Table SI-3. Deconvolution results for the ^{13}C NMR spectrum* of Nerol:Geraniol mixture from Table 3.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
140.1	1.57	Nerol
139.9	1.01	Geraniol
132.6	1.65	Nerol
131.9	0.98	Geraniol
124.6	1.36	Nerol
124.02	0.86	Geraniol
123.95	1.51	Nerol
123.5	0.92	Geraniol
59.5	0.85	Geraniol
59.1	1.47	Nerol
39.7	0.89	Geraniol
32.1	1.44	Nerol
26.7	1.48	Nerol
26.5	0.87	Geraniol
25.81	1.05	Geraniol
25.79	1.43	Nerol
23.6	1.53	Nerol
17.82	1.09	Geraniol
17.79	1.53	Nerol
16.4	1.00	Geraniol

*IGD, 512 scans, D1 = 30 sec

Table SI-4. Deconvolution results for the ^{13}C NMR spectrum* of 1,8-Cineole:L-Menthol mixture from Table 3.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
73.8	1.66	Cineole
71.7	1.03	Menthol
69.9	1.89	Cineole
50.3	0.99	Menthol
45.2	0.97	Menthol
34.7	0.98	Menthol
33.1	1.60	Cineole
31.8	1.03	Menthol
31.6	3.14	Cineole
29.0	2.94	Cineole
27.7	1.44	Cineole
26.0	0.93	Menthol
23.3	0.95	Menthol
23.0	3.18	Cineole
22.4	0.94	Menthol
21.2	1.00	Menthol
16.3	1.00	Menthol

*IGD, 512 scans, D1 = 30 sec

Table SI-5. Deconvolution results for the ^{13}C NMR spectrum* of L-(-)-Carvone:(+)-Limonene mixture from Table 3.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
199.9	0.97	Carvone
150.4	0.57	Limonene
146.8	1.02	Carvone
144.7	0.92	Carvone
135.6	1.04	Carvone
133.9	0.61	Limonene
120.8	0.44	Limonene
110.6	0.94	Carvone
108.5	0.54	Limonene
43.3	0.89	Carvone
42.6	0.95	Carvone
41.2	0.53	Limonene
31.4	0.91	Carvone
30.9	0.53	Limonene
30.7	0.46	Limonene
28.1	0.49	Limonene
23.6	0.51	Limonene
21.0	0.52	Limonene
20.7	1.03	Carvone
15.8	1.00	Carvone

*IGD, 512 scans, D1 = 30 sec

Table SI-6. Deconvolution results for the ^{13}C NMR spectrum* of 3,5-dimethylphenol:2,5-dimethylphenol mixture from Table 3.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
155.5	0.58	3,5-dimethylphenol
153.7	1.09	2,5-dimethylphenol
139.7	1.25	3,5-dimethylphenol
137.2	1.05	2,5-dimethylphenol
130.9	1.01	2,5-dimethylphenol
122.7	0.52	3,5-dimethylphenol
121.6	0.99	2,5-dimethylphenol
120.5	0.98	2,5-dimethylphenol
115.8	1.00	2,5-dimethylphenol
113.2	1.14	3,5-dimethylphenol
21.4	1.02	3,5-dimethylphenol
21.1	0.90	2,5-dimethylphenol
15.4	1.00	2,5-dimethylphenol

*IGD, 512 scans, D1 = 30 sec

Table SI-7. Deconvolution results for the ^{13}C NMR spectrum* of 3,5-dimethylaniline:N,N-dimethylaniline mixture from Table 3.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
150.8	0.18	N,N-dimethylaniline
146.5	0.58	3,5-dimethylaniline
139.1	1.29	3,5-dimethylaniline
129.2	0.46	N,N-dimethylaniline
120.6	0.61	3,5-dimethylaniline
116.8	0.24	N,N-dimethylaniline
113.2	1.23	3,5-dimethylaniline
112.8	0.47	N,N-dimethylaniline
40.7	0.41	N,N-dimethylaniline
21.4	1.00	3,5-dimethylaniline

*IGD, 512 scans, D1 = 30 sec

Table SI-8. Deconvolution results for the ^{13}C NMR spectrum* of N,N-dimethylbenzylamine:N,N-dimethylbenzamide from Table 3.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
171.7	1.38	N,N-dimethylbenzamide
139.0	1.13	N,N-dimethylbenzylamine
136.5	1.76	N,N-dimethylbenzamide
129.6	1.70	N,N-dimethylbenzamide
129.2	2.33	N,N-dimethylbenzylamine
128.4	3.37	N,N-dimethylbenzamide
128.3	2.24	N,N-dimethylbenzylamine
127.2	3.58	N,N-dimethylbenzamide
1271	1.15	N,N-dimethylbenzylamine
64.5	1.10	N,N-dimethylbenzylamine
45.5	2.00	N,N-dimethylbenzylamine
39.7	2.23	N,N-dimethylbenzamide
35.5	1.89	N,N-dimethylbenzamide

*IGD, 512 scans, D1 = 30 sec

Table SI-9. Deconvolution results for the ^{13}C NMR spectrum* of 5,8,14,17-tetraoctyloxy-2,11-dithia[3.3]paracyclophane and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
150.7	1.25	C_{ar}
150.2	0.73	C_{ar}
125.4	1.59	C_{ar}
125.2	0.92	C_{ar}
114.8	1.05	C_{ar}
113.9	1.93	C_{ar}
69.1	1.00	CH_2
69.0	1.89	CH_2
26.5	1.51	CH_2
26.4	2.20	CH_2
22.8	1.36	CH_2
22.8	2.50	CH_2
14.3	1.50	CH_3
14.3	2.55	CH_3

*BBD, 512 scans, D1 = 30 sec.

Table SI-10. Deconvolution results for the ^{13}C NMR spectrum* of allyl lactide from Table 4.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
167.2	0.49	C=O
166.4	0.60	C=O
166.1	0.12	C=O
165.3	0.31	C=O
130.7	1.54	C(alkene)
130.0	0.76	C(alkene)
121.6	0.76	C(alkene)
120.4	1.80	C(alkene)
76.3	1.01	CH
75.5	1.83	CH
73.0	0.86	CH
72.5	1.81	CH
36.5	0.98	CH_2
34.4	1.85	CH_2
18.0	1.00	CH_3
16.1	1.96	CH_3

*BBD, 512 scans, D1 = 2 sec.

Table SI-11. Deconvolution results for the ^{13}C NMR spectrum* of the peptoid model from Table 4.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
171.0	0.35	Unassigned
170.7	0.47	Unassigned
137.4	0.60	Rotomer A
136.6	0.49	Rotomer B
129.0	1.81	Unassigned
128.6	2.31	Unassigned
128.0	2.24	Unassigned
127.7	0.93	Unassigned
127.3	1.17	Unassigned
126.3	1.74	Unassigned
54.3	0.90	Rotomer B
50.6	1.12	Rotomer A
35.5	0.75	Rotomer A
33.7	0.68	Rotomer B
21.9	1.00	Rotomer A
21.5	0.75	Rotomer B

*BBD, 512 scans, D1 = 2 sec

Table SI-12. Deconvolution results for the ^{13}C NMR spectrum* of N-acyl-D-glucosamine from Table 4.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
170.1	0.06	Minor Anomer
169.8	0.80	Major Anomer
96.0	0.10	Minor Anomer
91.1	1.05	Major Anomer
77.2	0.07	Minor Anomer
74.8	0.11	Minor Anomer
72.5	1.08	Major Anomer
71.7	1.09	Major Anomer
71.3	0.07	Minor Anomer
71.0	1.10	Major Anomer
61.6	1.10	Major Anomer
57.7	N/A	Minor Anomer
54.8	1.08	Major Anomer
31.2	0.06	Minor Anomer
23.5	0.10	Minor Anomer
23.2	1.00	Major Anomer

*BBD, 512 scans, D1 = 2 sec

Table SI-13. Deconvolution results for the ^{13}C NMR spectrum* of the 3,5-dimethylphenol:2,5-dimethylphenol mixture (with addition of O_2) from Table 5.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
155.5	0.86	3,5-dimethylphenol
153.6	0.34	2,5-dimethylphenol
139.7	1.72	3,5-dimethylphenol
137.2	0.43	2,5-dimethylphenol
130.9	0.69	2,5-dimethylphenol
122.7	1.69	3,5-dimethylphenol
121.6	0.71	2,5-dimethylphenol
120.5	0.42	2,5-dimethylphenol
115.8	0.73	2,5-dimethylphenol
113.1	3.71	3,5-dimethylphenol
21.4	2.00	3,5-dimethylphenol
21.1	0.43	2,5-dimethylphenol
15.4	0.55	2,5-dimethylphenol

*BBD, 64 scans, D1 = 2 sec

Table SI-14. Deconvolution results for the ^{13}C NMR spectrum of Poly(lactic acid) (P(LA)) from Table 6.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
20.7	1.09	CH_3 backbone
16.9	1.11	CH_3 backbone
16.9-16.8	25.01	CH_3 backbone
14.18	1.00	CH_3 end-group

*For backbone integration, the four signals were added. These data suggest DP = 27.1.

Table SI-15. Deconvolution results for the ^{13}C NMR spectrum* of poly(4-methyl-oxazoline) P(Ox) from Table 6.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
37.4	0.70	CH_3 backbone
37.1	0.30	CH_3 backbone
21.8	9.68	CH_3 end-group
21.2		CH_3 end-group
20.1		CH_3 end-group

*BBD, 512 scans, D1 = 30 sec. For backbone integration, the three signals were added. These data suggest DP = 9.7.

Table SI-16. Deconvolution results for the ^{13}C NMR spectrum* of poly(4-methyl-oxazoline) P(Ox) from Table 6.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
37.5	0.80	CH_3 backbone
37.1	0.20	CH_3 backbone
21.8	17.68	CH_3 end-group
21.3		CH_3 end-group
20.7		CH_3 end-group

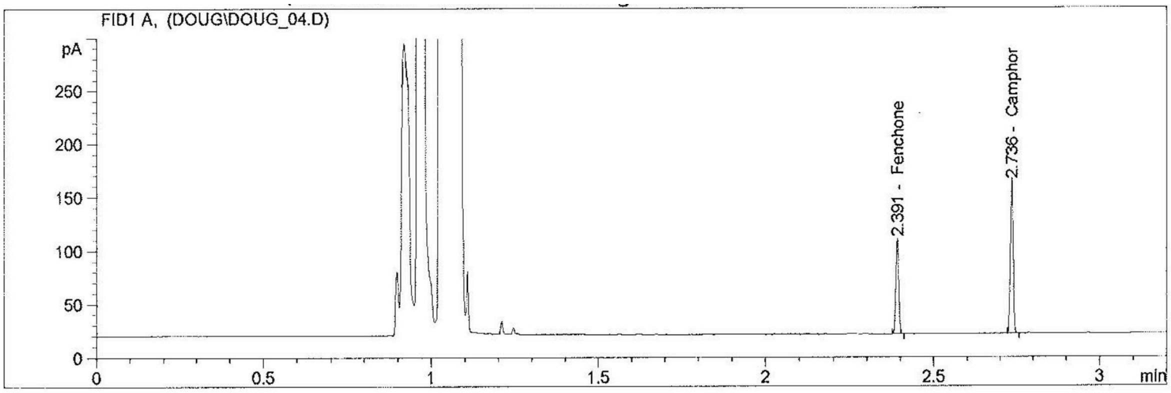
*BBD, 512 scans, D1 = 30 sec. For backbone integration, the three signals were added. These data suggest DP = 17.7.

Table SI-17. Deconvolution results for the ^{13}C NMR spectrum of Poly(norbornene octanoate) P(NO) from Table 6.

Peak chemical shift (δ ppm)	Peak Integral	Peak Assignment
142.0	0.35	CH backbone
140.6	0.87	CH backbone
137.6-137.5	0.67	CH backbone
133.9-132.1	35.23	CH backbone
114.5-113.3	2	CH_2 end-group

*For backbone integration, the four signals were added and then divided by two, because there are 2 backbone carbons to account for. These data suggest DP = 18.6.

<u>GC, HPLC, MALDI, IR, HRMS Data</u>:



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Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime  Type   Width     Area      Area    Name
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----|-------|------|-------|----------|--------|---------------------
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   2   2.736 BP      0.0104   88.63033 62.12039 Camphor

Totals :                     142.67510
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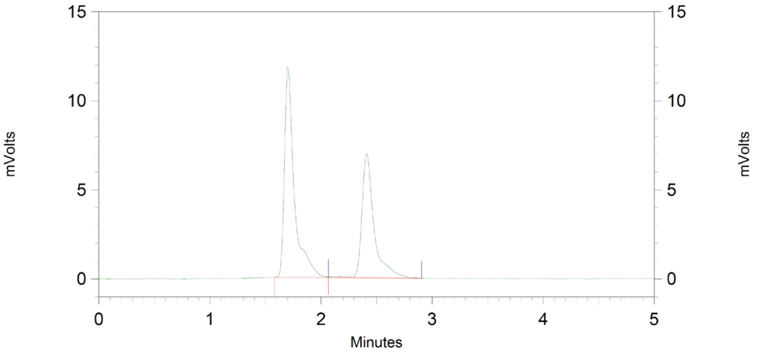
Figure S-1: GC Data of camphor:fenchone (mol % fenchone = 39.2%) from Figure 1.

Area % Report

Data File: C:\Documents and Settings\User\Desktop\Data\DALO\DALO20131205-007-BE10.dat
Method: C:\Documents and Settings\User\Desktop\DALO_Dorothee-30min--0.1%---Fast.met
Acquired: 12/5/2013 5:53:01 PM
Printed: 12/18/2013 5:32:39 PM



UV Detector
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
1.702	72671	57.58	11792	62.84
2.412	53536	42.42	6972	37.16

Totals				
	126207	100.00	18764	100.00

Figure S-2: HPLC of 5,8,14,17-tetraoctyloxy-2,11-dithia[3.3]paracyclophane and 6,9,14,17-tetraoctyloxy-2,11-dithia-[3.3]paracyclophane

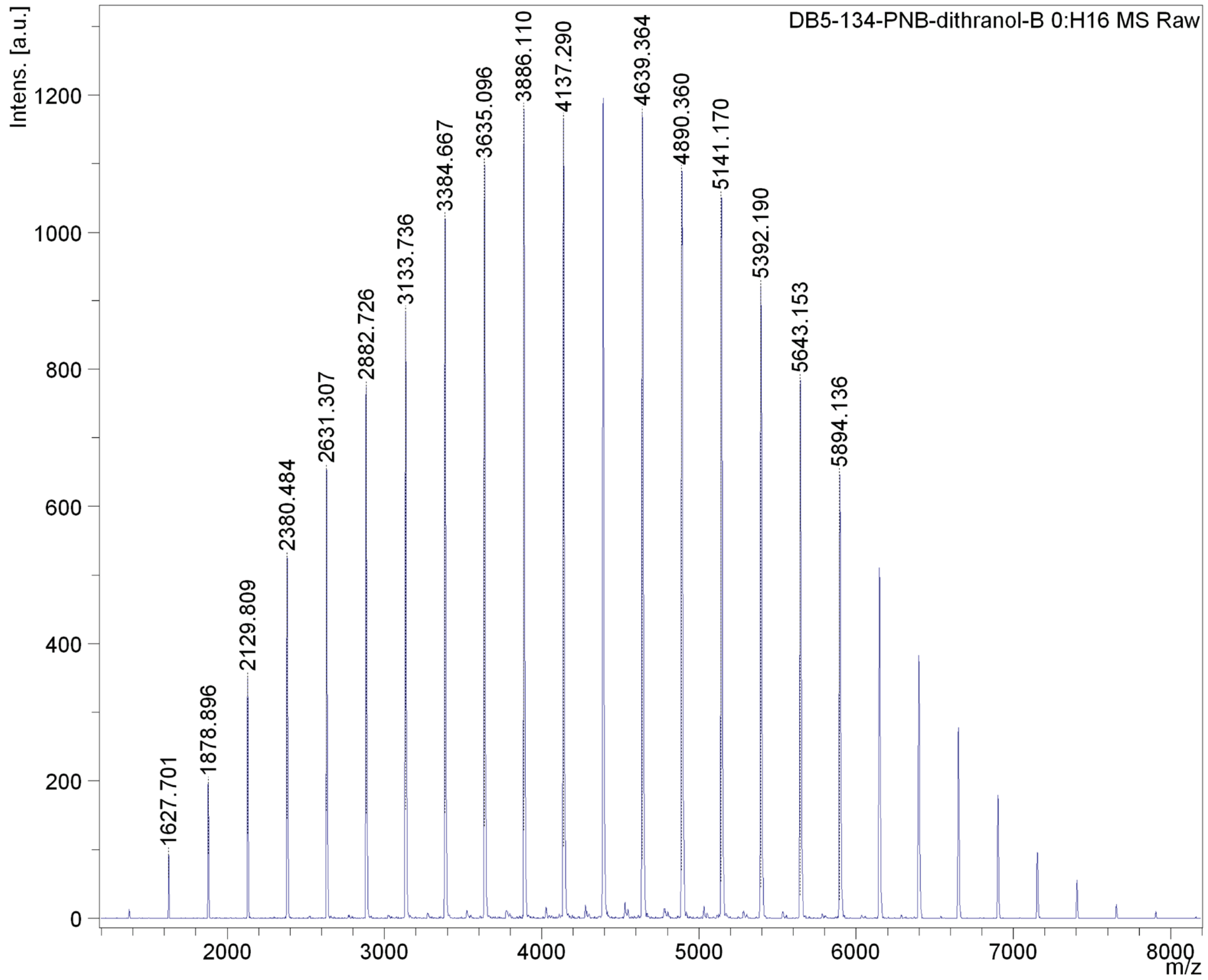


Figure S-3: MALDI-ToF spectrum of poly(norbornene octanoate) (P(NO))

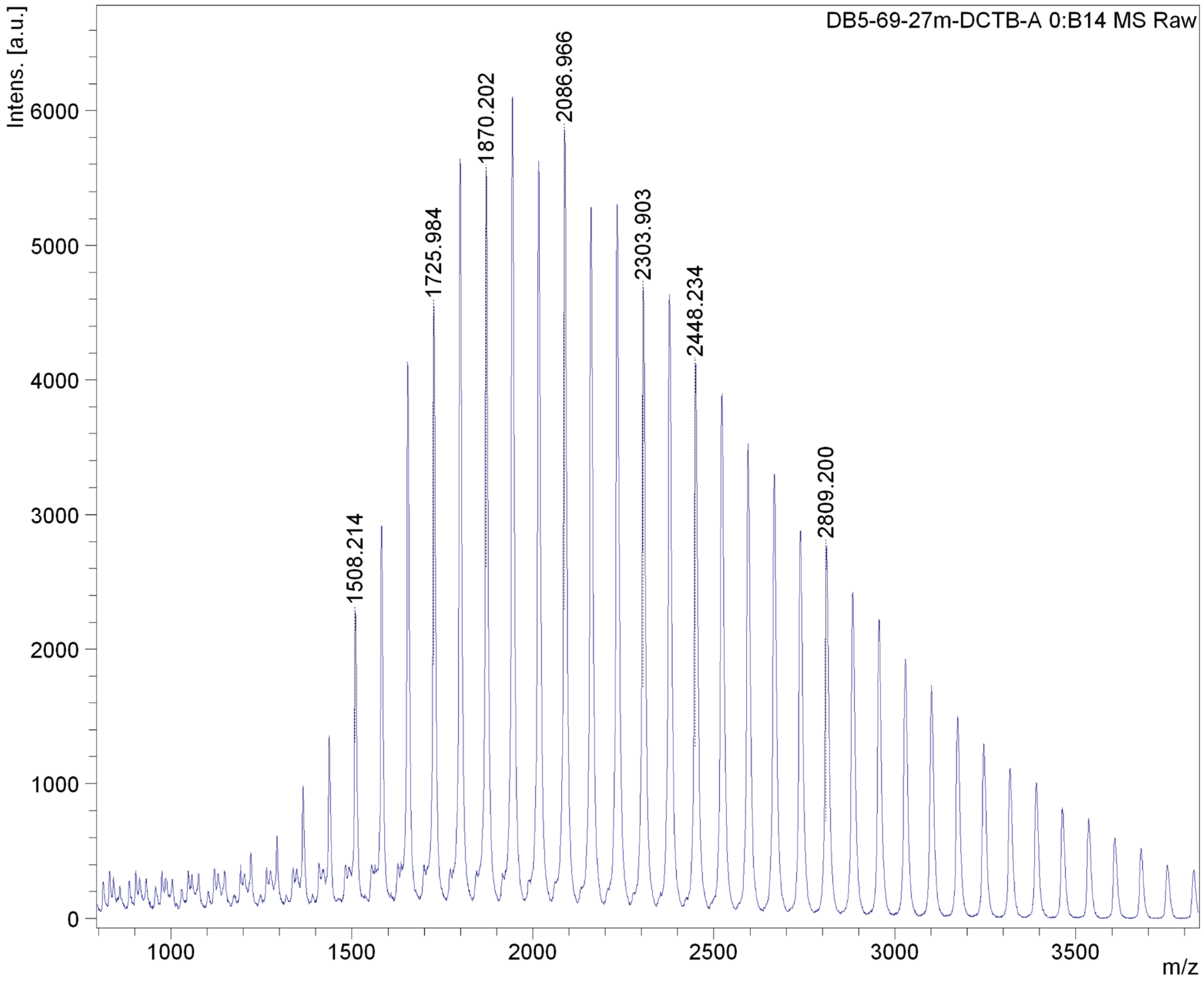


Figure S-4: MALDI-ToF spectrum of poly(lactic acid) 1 (PLA1)

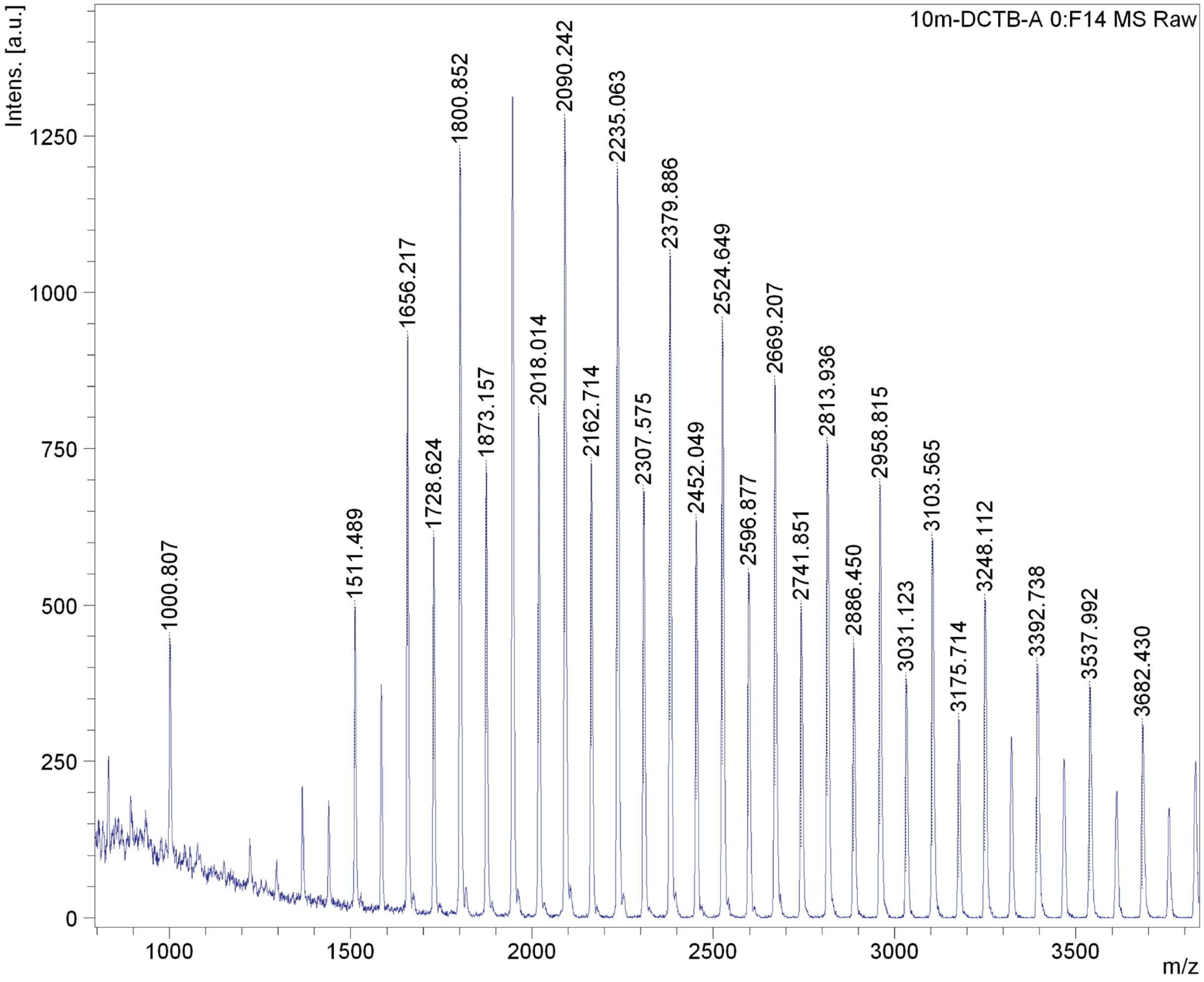


Figure S-5: MALDI-ToF spectrum of poly(lactic acid) 2 (PLA2)

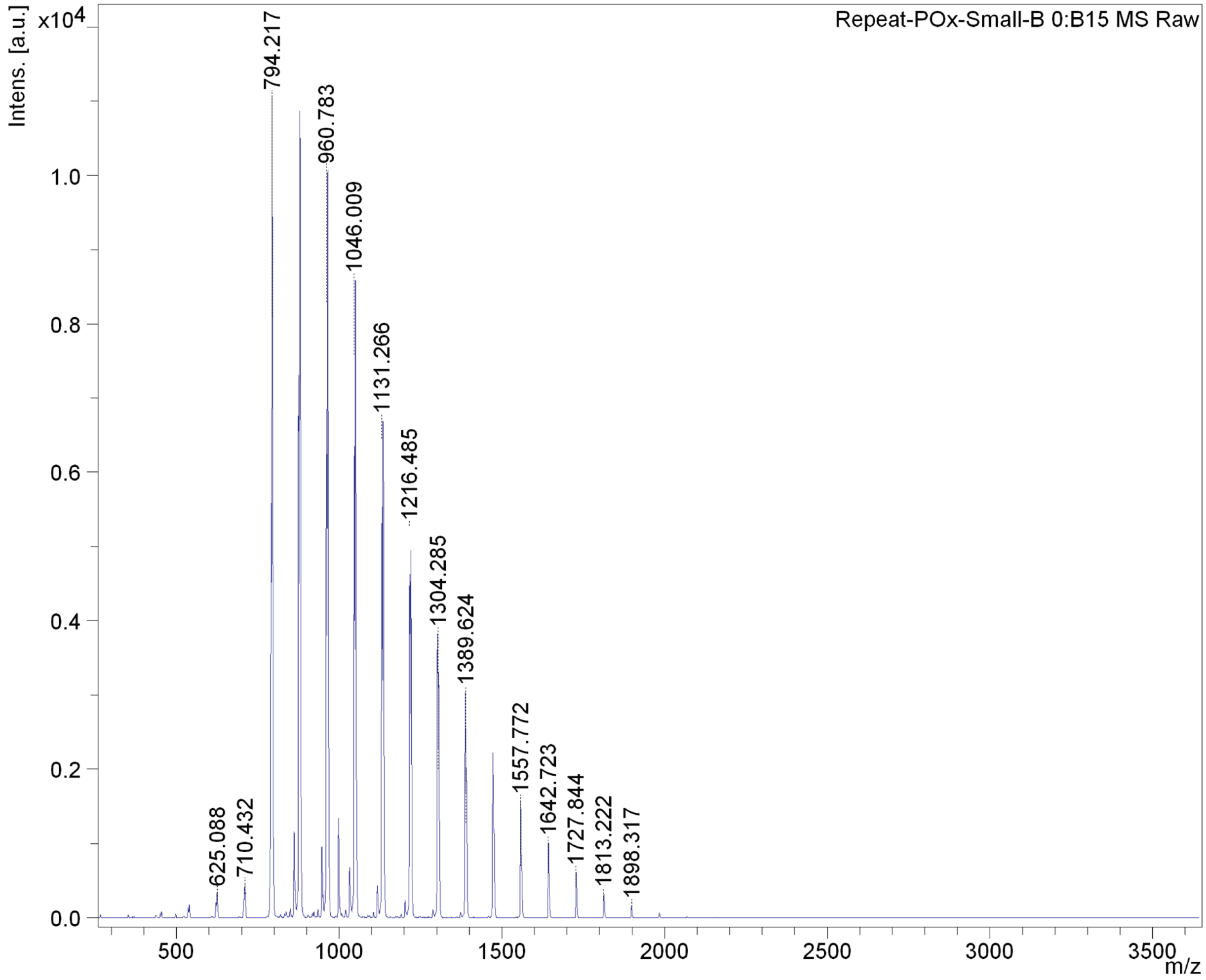


Figure S-6: MALDI-ToF spectrum of poly(2-methyloxazoline) 1 (P(Ox)1)

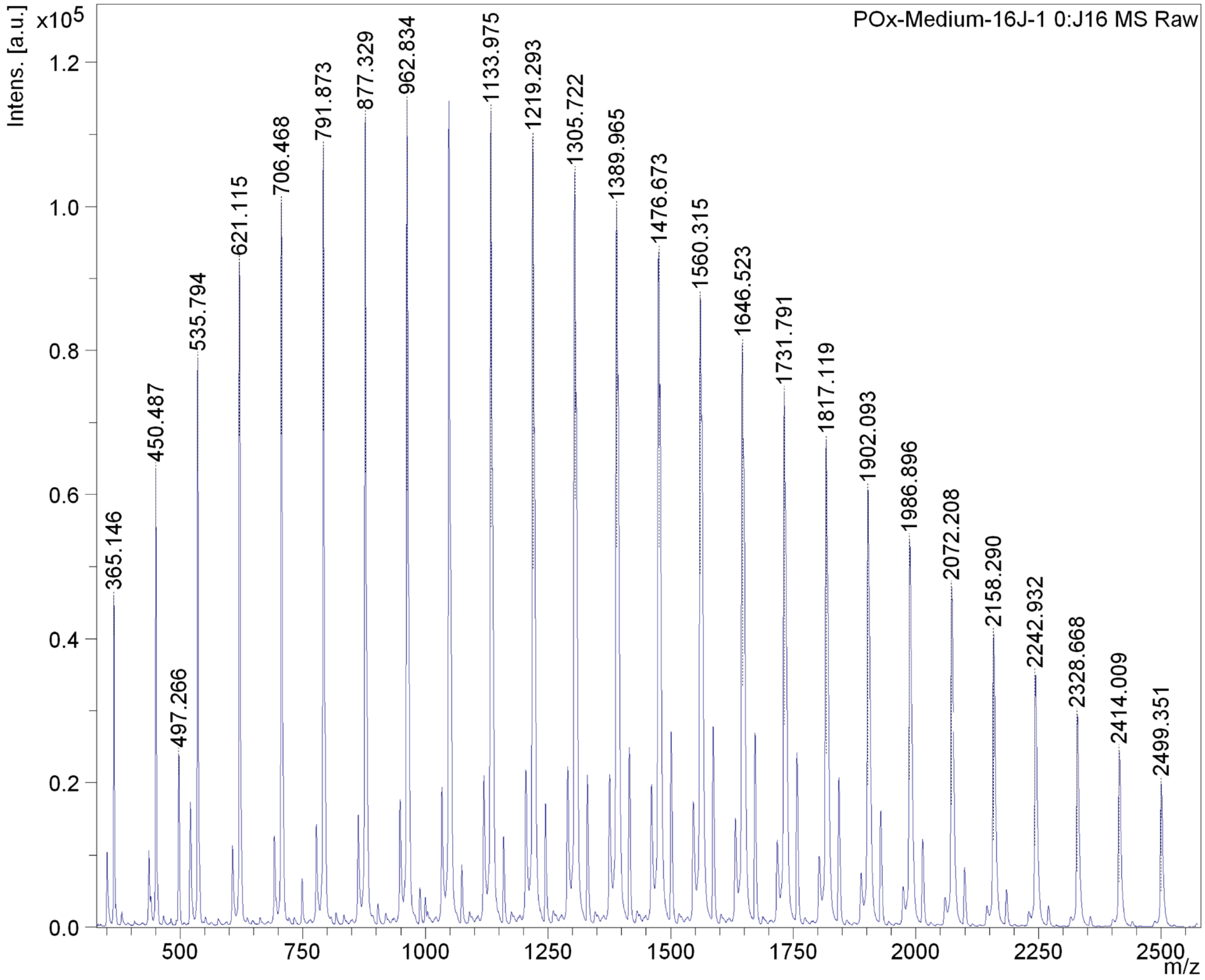


Figure S-7: MALDI-ToF spectrum of poly(2-methyloxazoline) 2 (P(Ox)2)

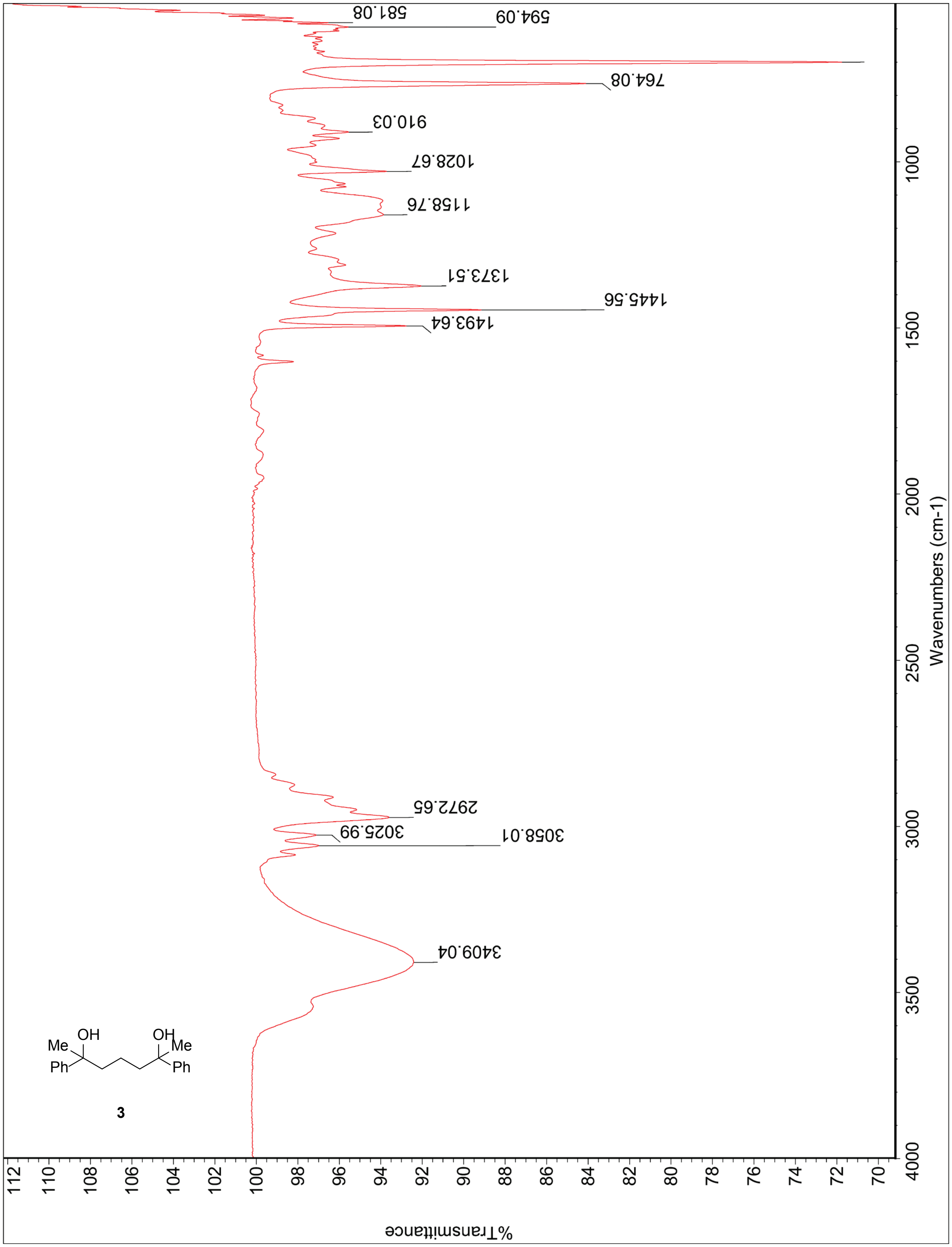


Figure S-8: IR spectrum of **3**.

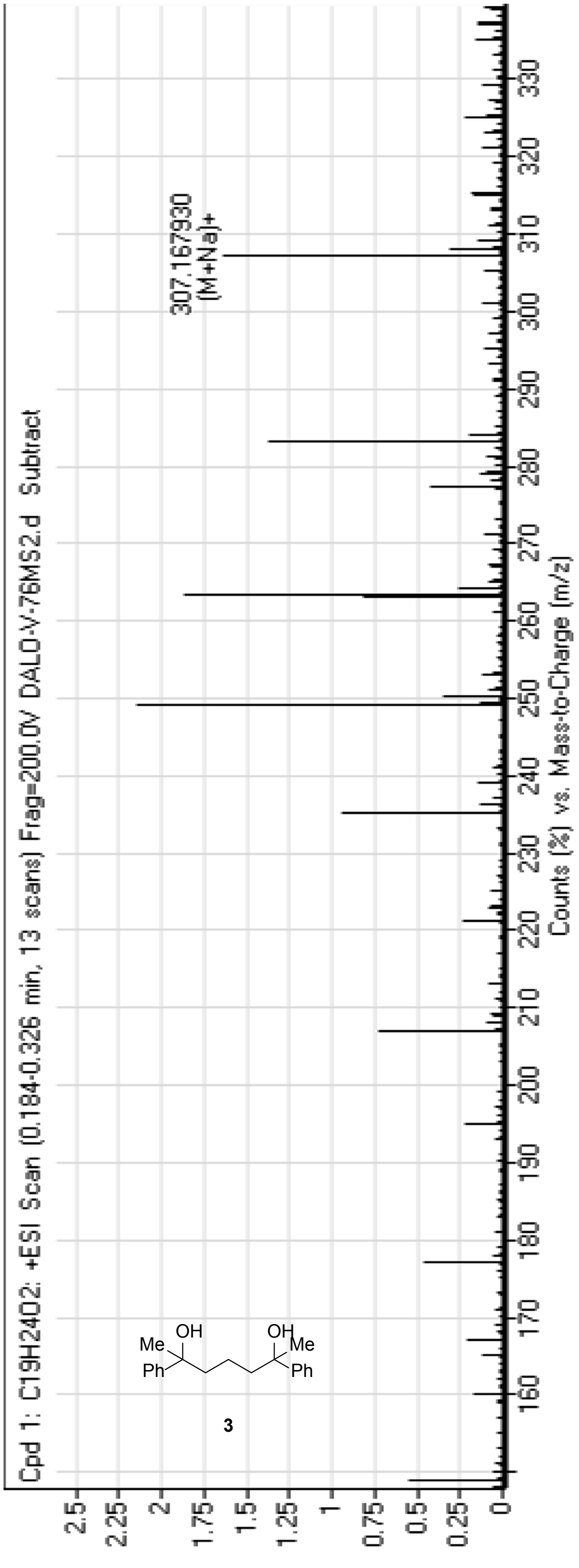


Figure S-9: HRMS of **3**.