

## Supplementary Material

### Four-directional synthesis of adamantane derivatives

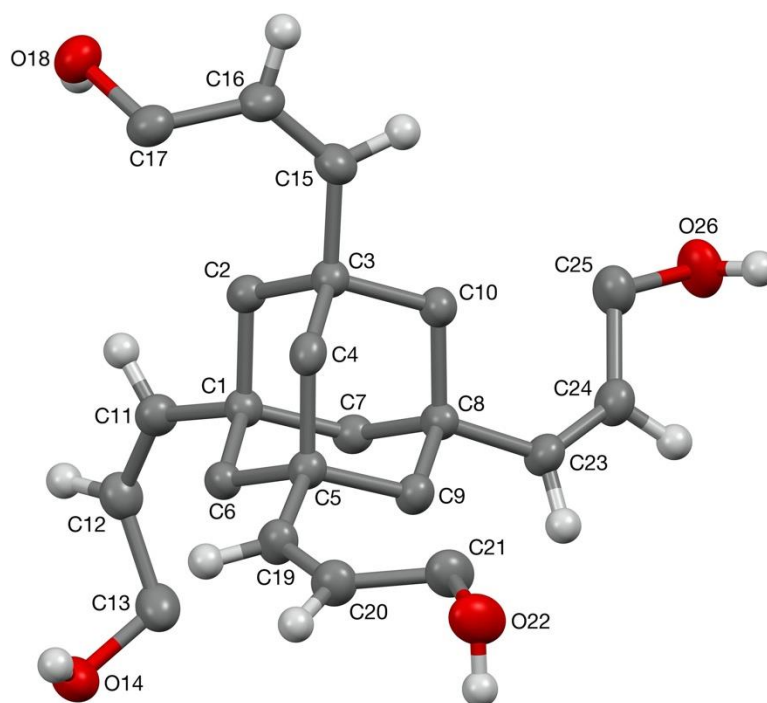
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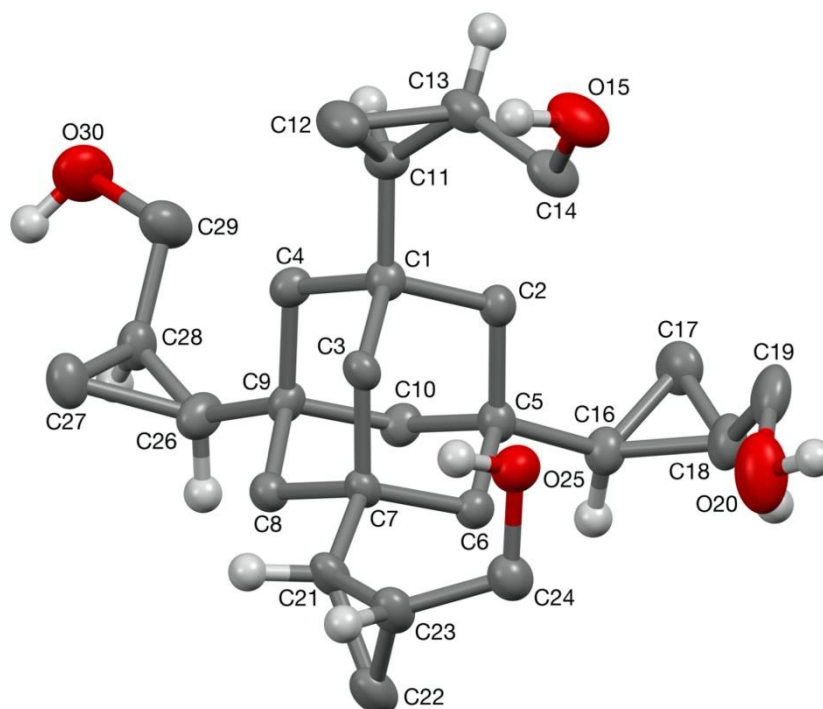
Appendix 1: X-ray Crystal Structure Determination of Tetra-(Z)-allylic Alcohol **21**

**Figure 3.** The crystal structure of tetra-(Z)-allylic alcohol **21** (50% probability ellipsoids).

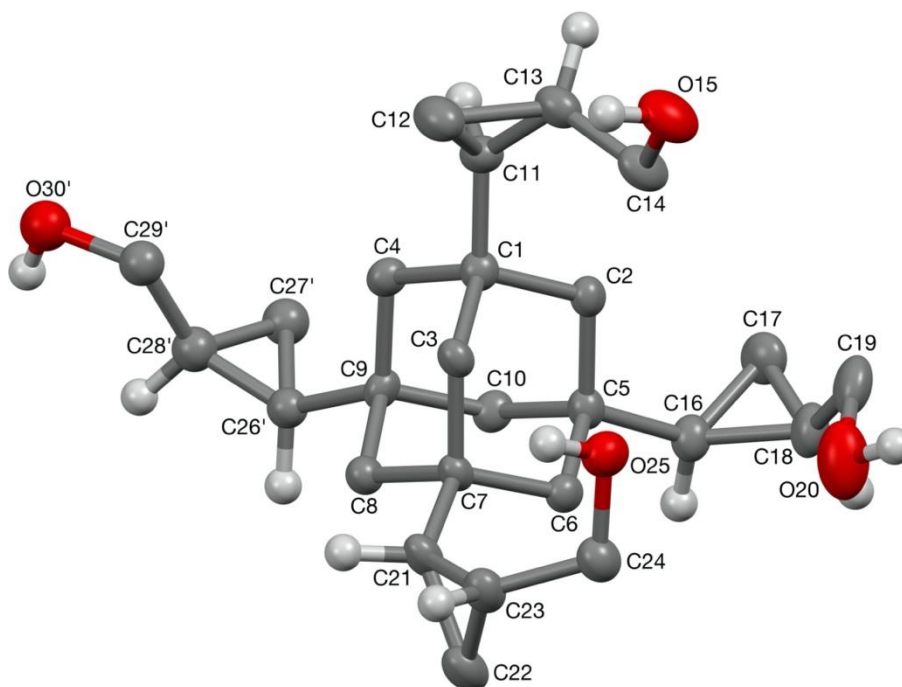
*Crystal data for tetra-(Z)-allylic alcohol 21:*  $C_{22}H_{32}O_4$ ,  $M = 360.47$ , monoclinic,  $P2_1$  (no. 4),  $a = 7.2942(7)$ ,  $b = 11.5286(12)$ ,  $c = 11.5044(10)$  Å,  $\beta = 92.841(8)^\circ$ ,  $V = 966.24(16)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.239$  g cm<sup>-3</sup>,  $\mu(\text{Cu-K}\alpha) = 0.665$  mm<sup>-1</sup>,  $T = 173$  K, colorless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 3465 independent measured reflections ( $R_{\text{int}} = 0.0378$ ),  $F^2$  refinement,<sup>51,52</sup>  $R_1(\text{obs}) = 0.0334$ ,  $wR_2(\text{all}) = 0.0826$ , 2910 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ], completeness to  $\theta_{\text{full}}(67.7^\circ) = 99.7\%$ ], 252 parameters. The absolute structure of **21** could not be unambiguously determined [Flack parameter  $x^+ = -0.01(17)$ ]. CCDC 1982520.

The hydrogen atoms of the O14-, O18-, O22- and O26-based OH groups in the structure of tetra-(Z)-allylic alcohol **21** were all located from  $\Delta F$  maps and refined freely subject to O–H distance constraints of 0.90 Å.

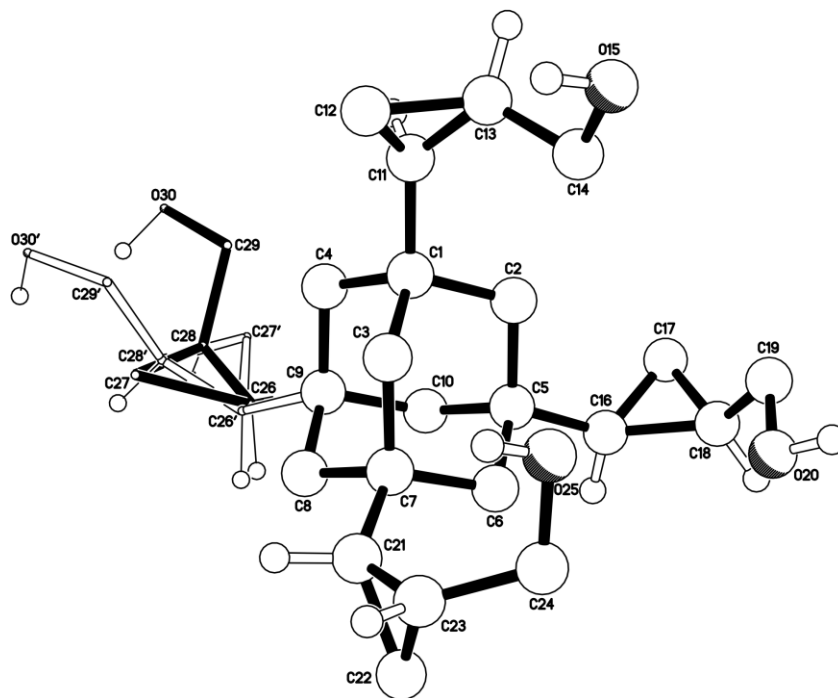
Appendix 2: X-ray Crystal Structure Determination of Tetra-syn-Cyclopropyl Alcohol **35**



**Figure 4.** The crystal structure of tetra-*syn*-cyclopropyl alcohol **35** showing the major (*ca.* 64%) occupancy orientation of the C9-bound cyclopropyl alcohol moiety, isomer A (25% probability ellipsoids).



**Figure 5.** The crystal structure of tetra-*syn*-cyclopropyl alcohol **35** showing the minor (*ca.* 36%) occupancy orientation of the C9-bound cyclopropyl alcohol moiety, isomer B (25% probability ellipsoids).



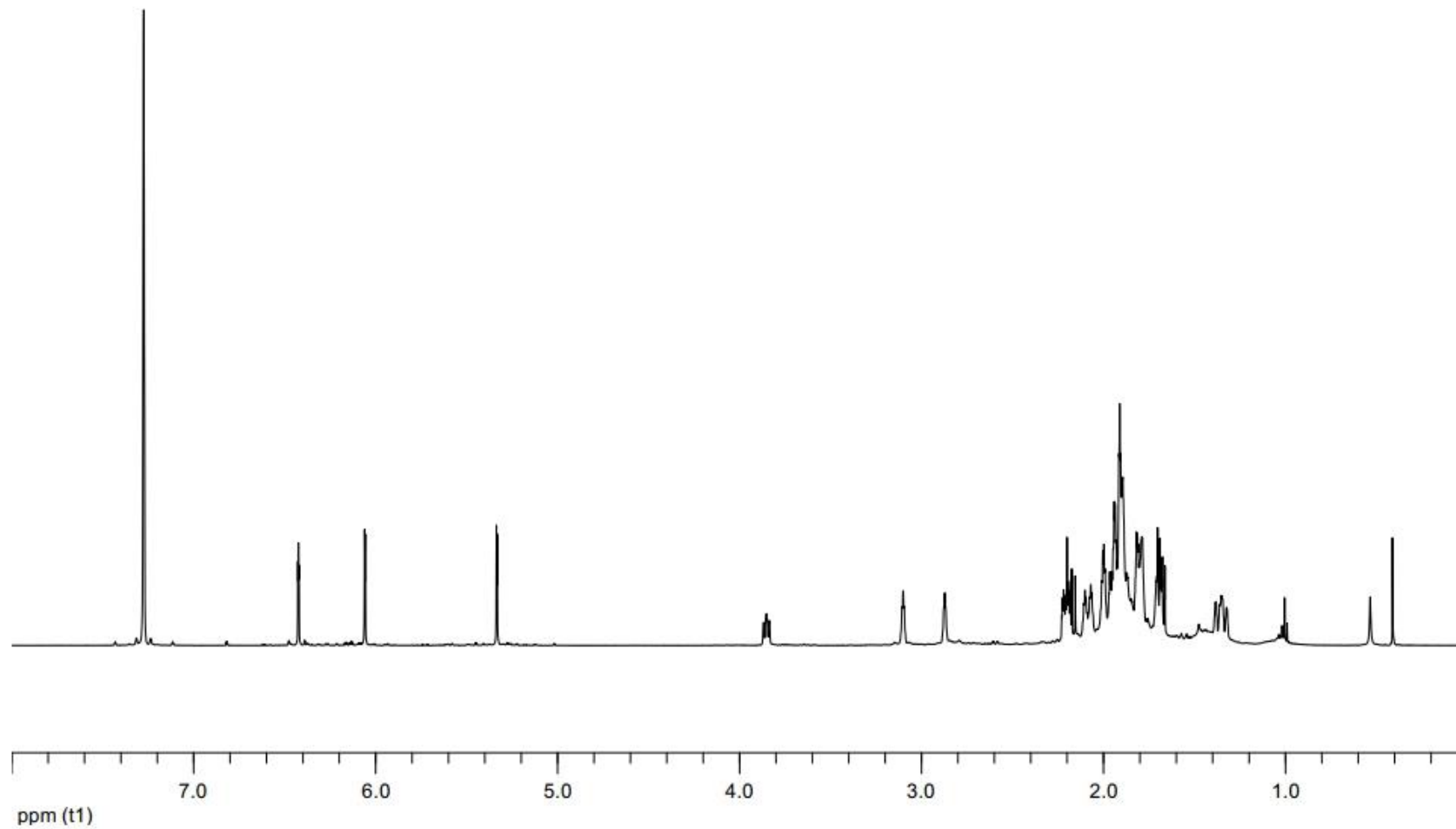
**Figure 6.** The crystal structure of tetra-*syn*-cyclopropyl alcohol **35** showing an overlay of both the major and minor occupancy orientations of the C9-bound cyclopropyl alcohol moiety. The major (*ca.* 64%) occupancy orientation (isomer A) has been drawn with dark bonds, whilst the minor (*ca.* 36%) occupancy orientation (isomer B) has been drawn with open bonds.

*Crystal data for tetra-syn-cyclopropyl alcohol 35:* C<sub>26</sub>H<sub>40</sub>O<sub>4</sub>, *M* = 416.58, monoclinic, *C*2 (no. 5), *a* = 22.471(3), *b* = 10.5857(11), *c* = 9.5321(12) Å,  $\beta$  = 96.404(11)°, *V* = 2253.3(5) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.228 g cm<sup>-3</sup>,  $\mu$ (Mo-K $\alpha$ ) = 0.081 mm<sup>-1</sup>, *T* = 173 K, colorless plates, Oxford Diffraction Xcalibur 3 diffractometer; 6184 independent measured reflections (*R*<sub>int</sub> = 0.0833), *F*<sup>2</sup> refinement,<sup>51,52</sup> *R*<sub>1</sub>(obs) = 0.0905, *wR*<sub>2</sub>(all) = 0.2903, 2785 independent observed absorption-corrected reflections [ $|F_o| > 4\sigma(|F_o|)$ ], completeness to  $\theta_{full}(25.2^\circ)$  = 99.4%, 294 parameters. The absolute structure of tetra-*syn*-cyclopropyl alcohol **35** could not be determined from the diffraction data [Fleck parameter *x*<sup>+</sup> = 10.0(10)] and so was set by internal reference based on the known stereo-chemistries of the four cyclopropyl alcohol groups. CCDC 1982521.

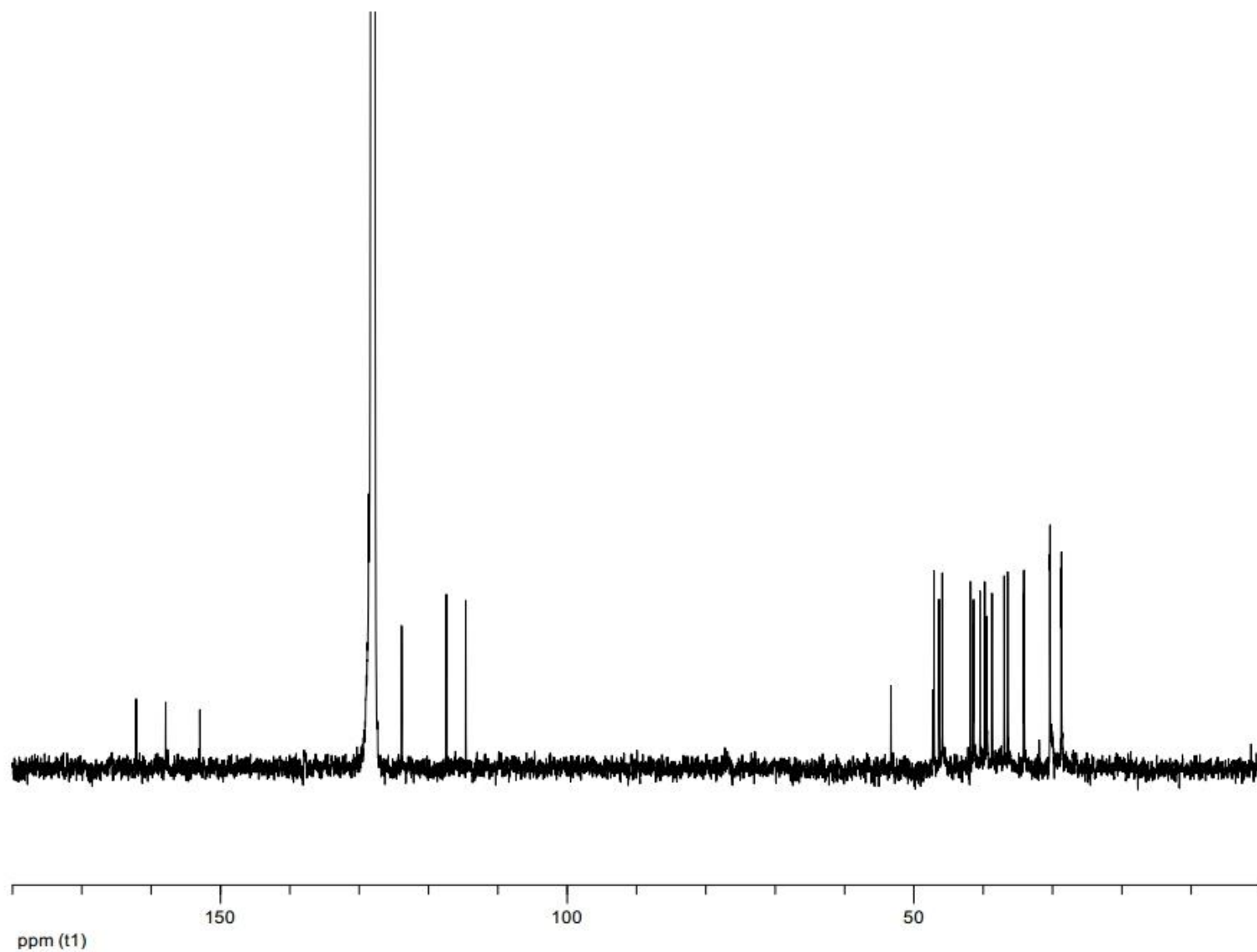
The C26-based cyclopropyl sidearm in the structure of tetra-*syn*-cyclopropyl alcohol **35** was found to be disordered. Two orientations were identified of *ca.* 64 and 36% occupancy (corresponding to inverted stereo-chemistries at C26 and C28), their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The hydrogen atoms of the O15-, O20-, O25- and O30/O30'-based OH groups could not be reliably located from  $\Delta F$  maps, and adding them in idealized positions with free rotation about the C–O vector to find the best fit with the observed electron density (the SHELX HFIX/AFIX 147 command) gave positions that clashed with adjacent molecules. So, they were added in somewhat arbitrary positions that should be treated with caution.

## References

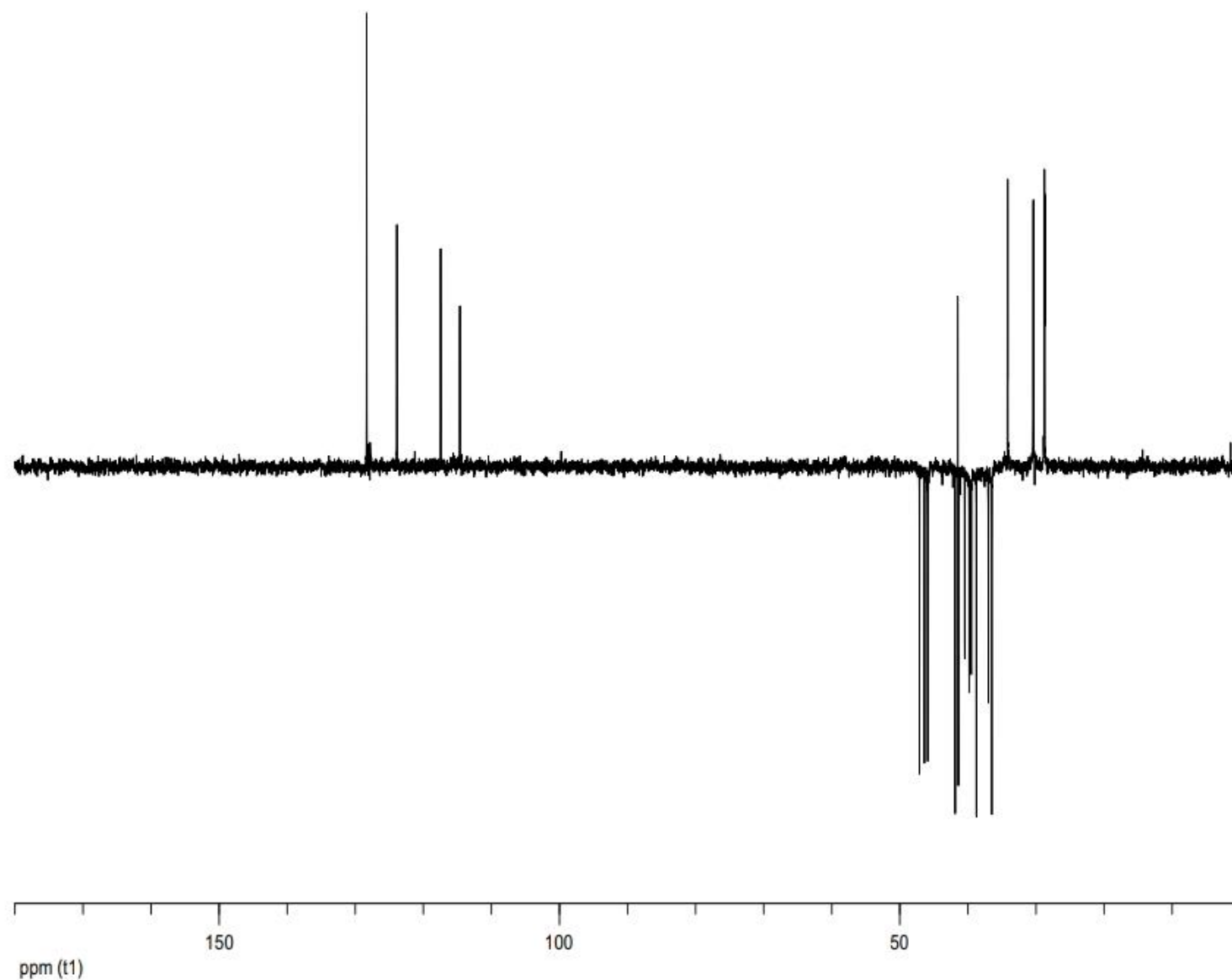
- 51 SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.
- 52 SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

Appendix 3:  $^1\text{H}$  and  $^{13}\text{C}$  spectra of dimer **63**.

$^1\text{H}$  NMR of dimer **63** in  $\text{C}_6\text{D}_6$  (500 MHz).

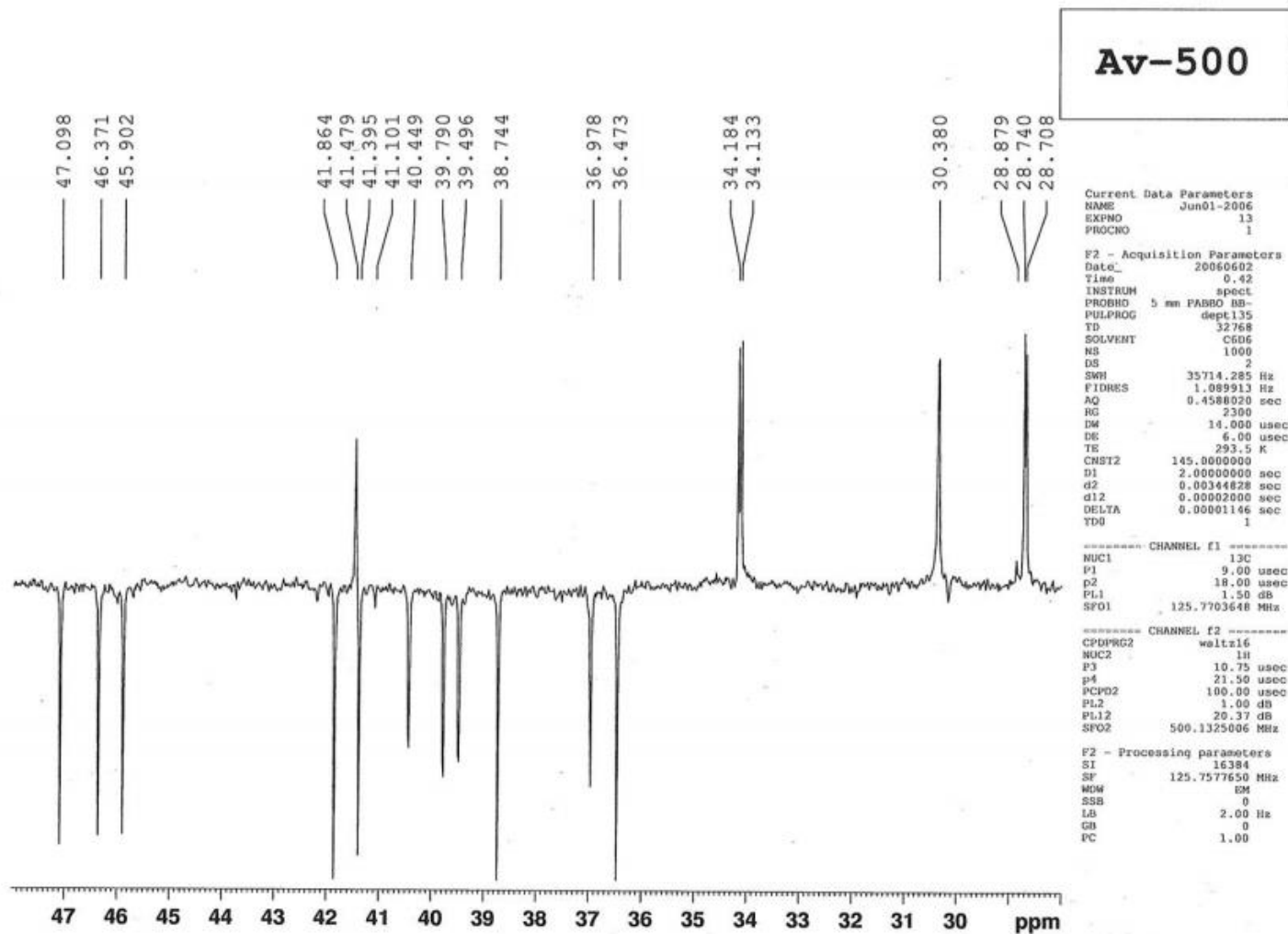


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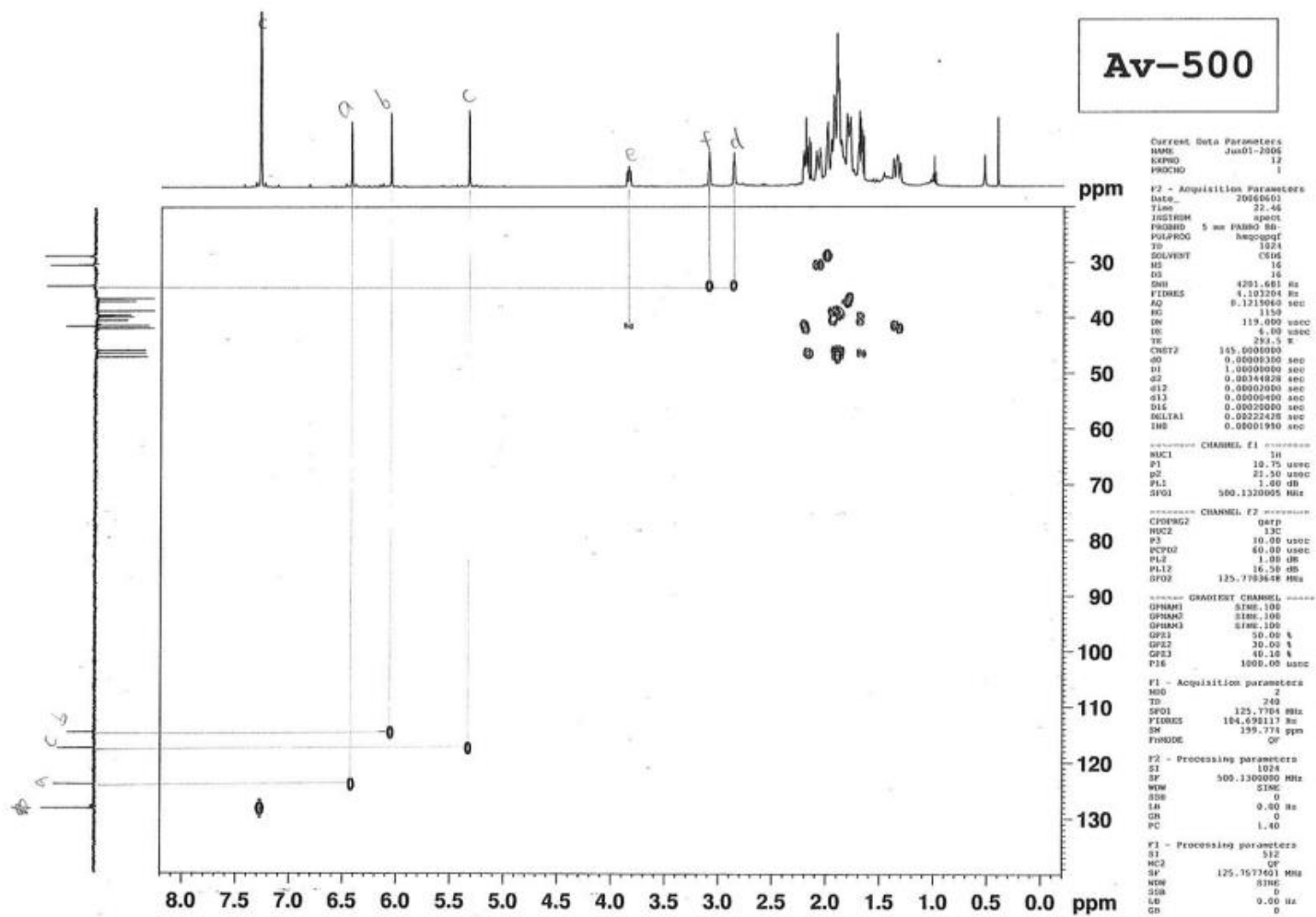


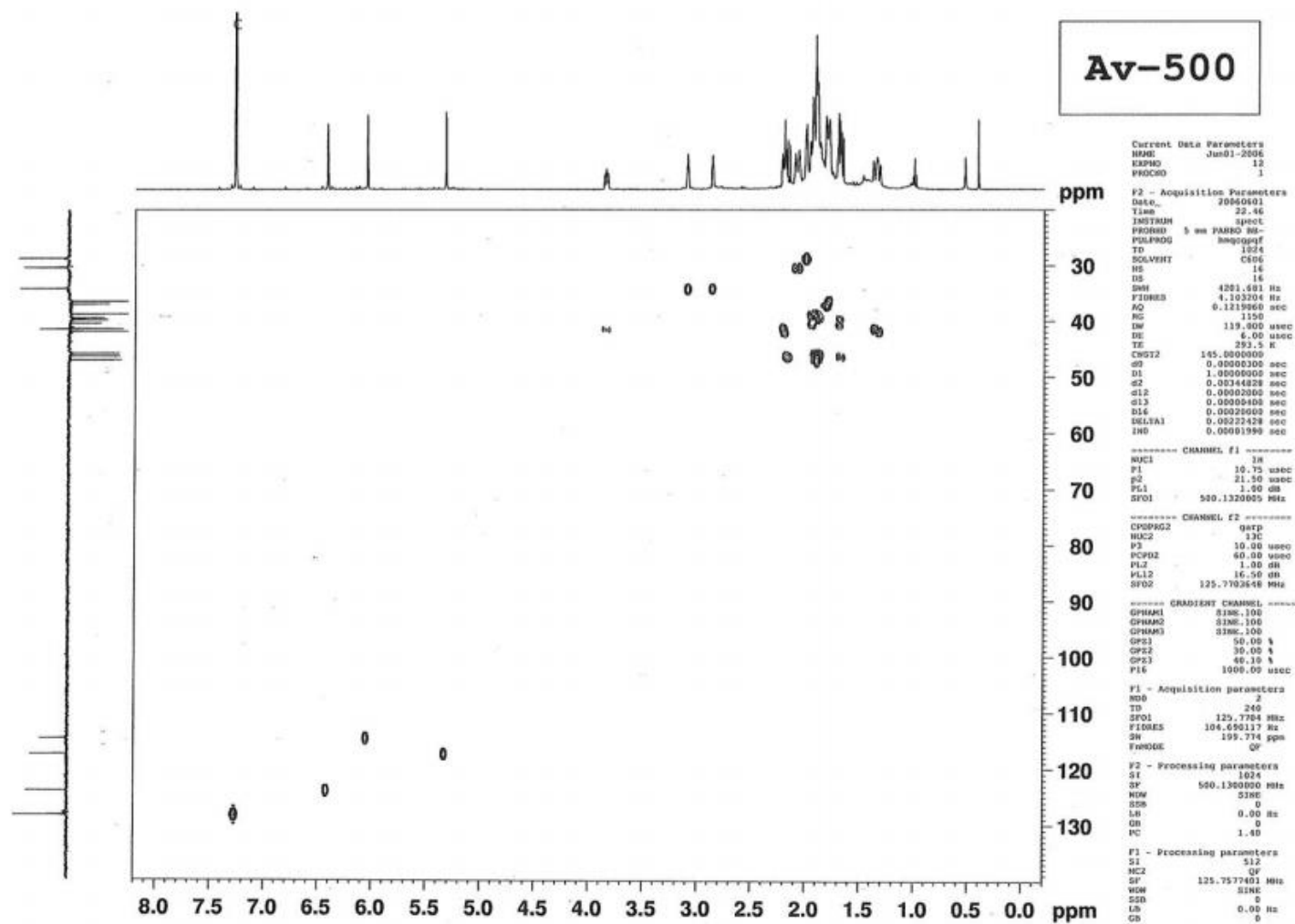
<sup>13</sup>C DEPT of dimer **63** in C<sub>6</sub>D<sub>6</sub> (125 MHz).

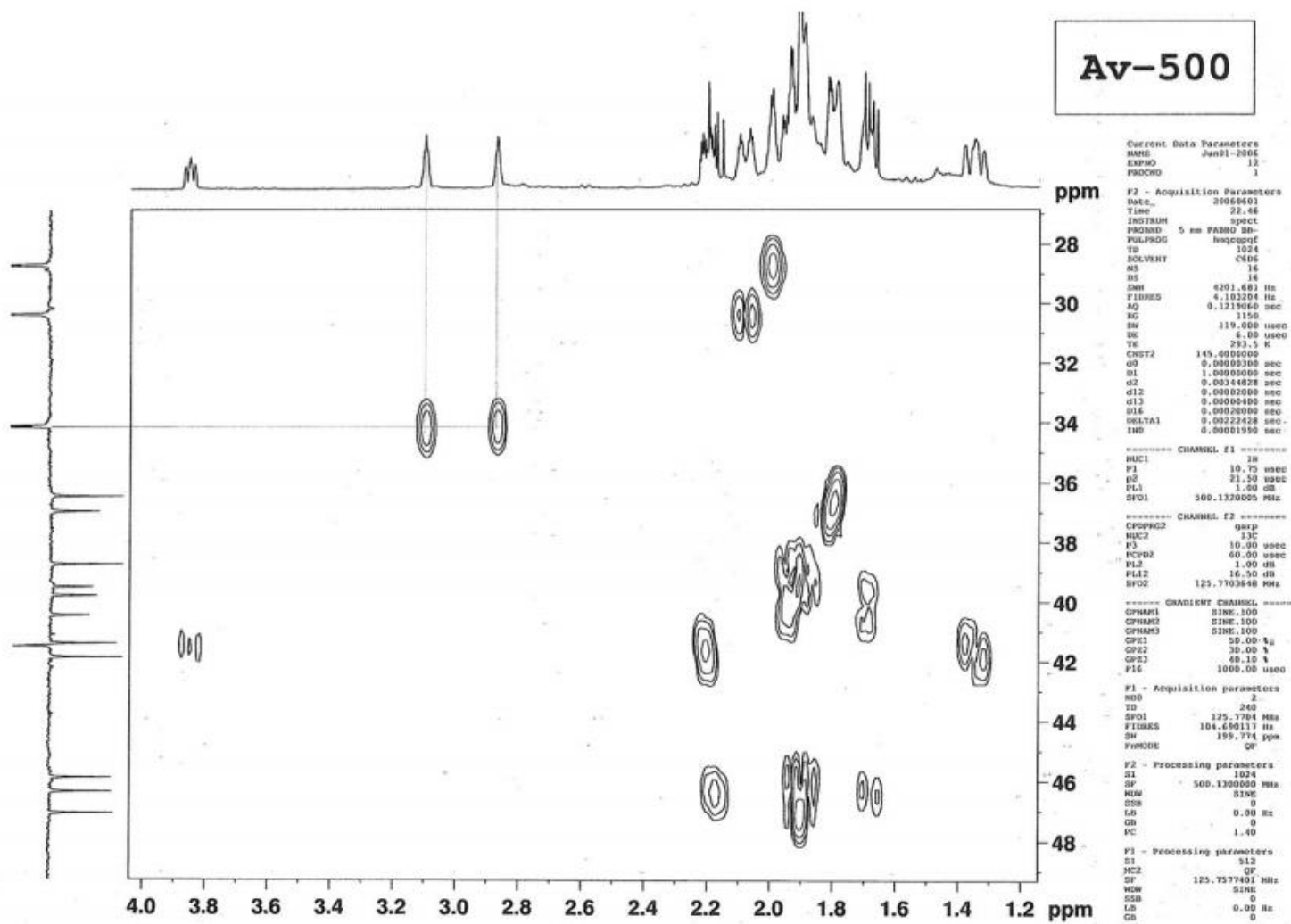


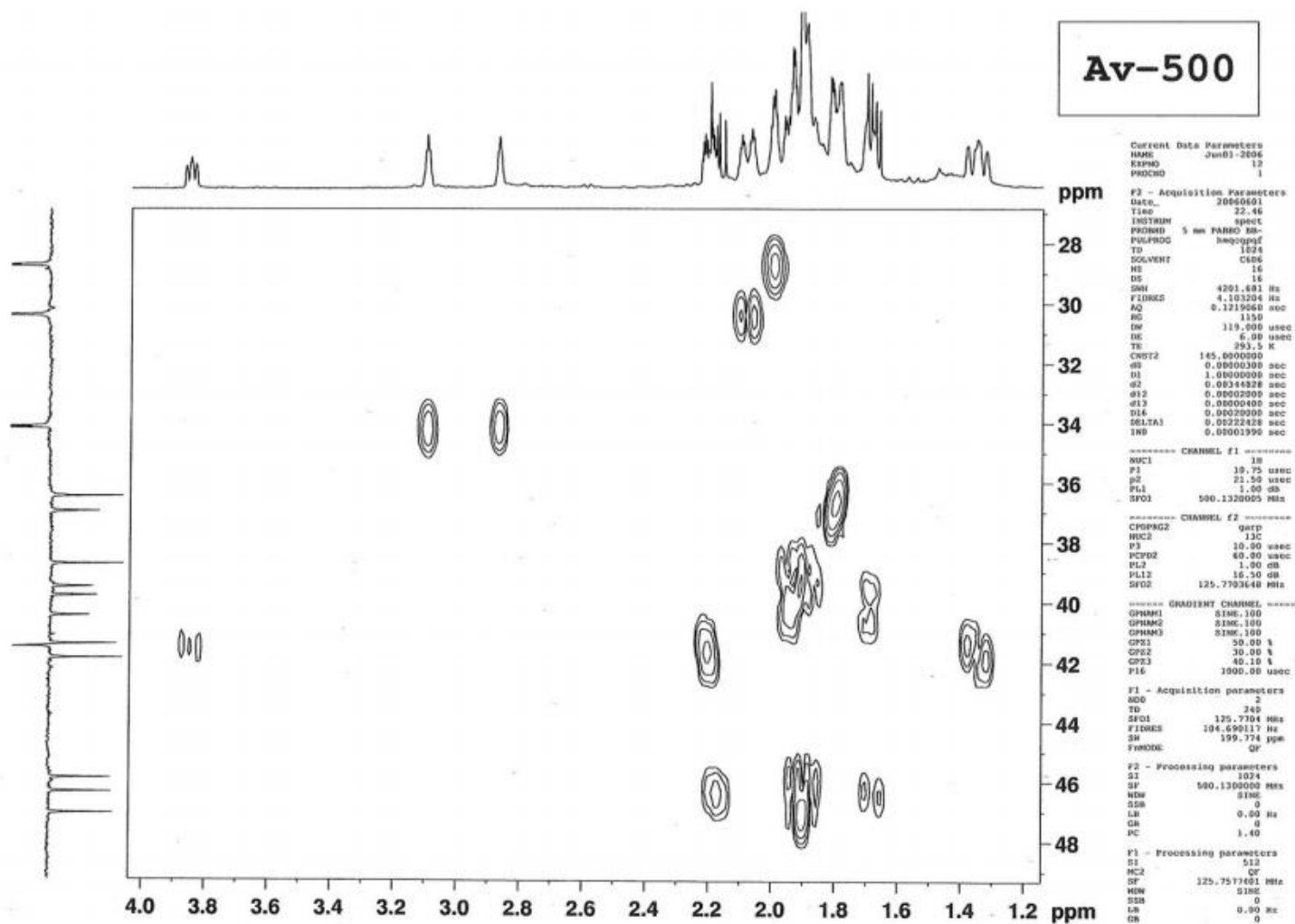


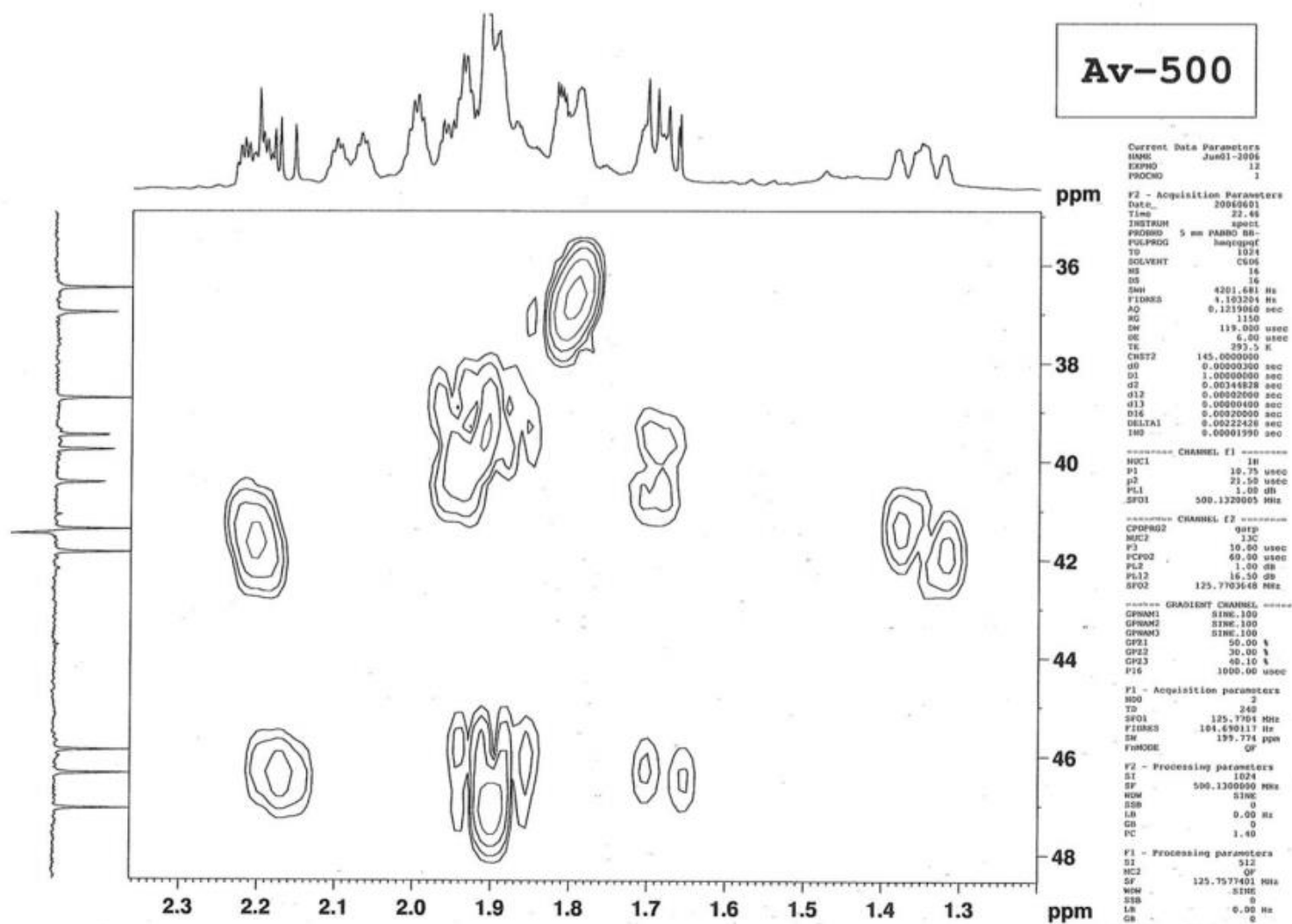
<sup>13</sup>C DEPT of dimer **63** in C<sub>6</sub>D<sub>6</sub> (125 MHz).

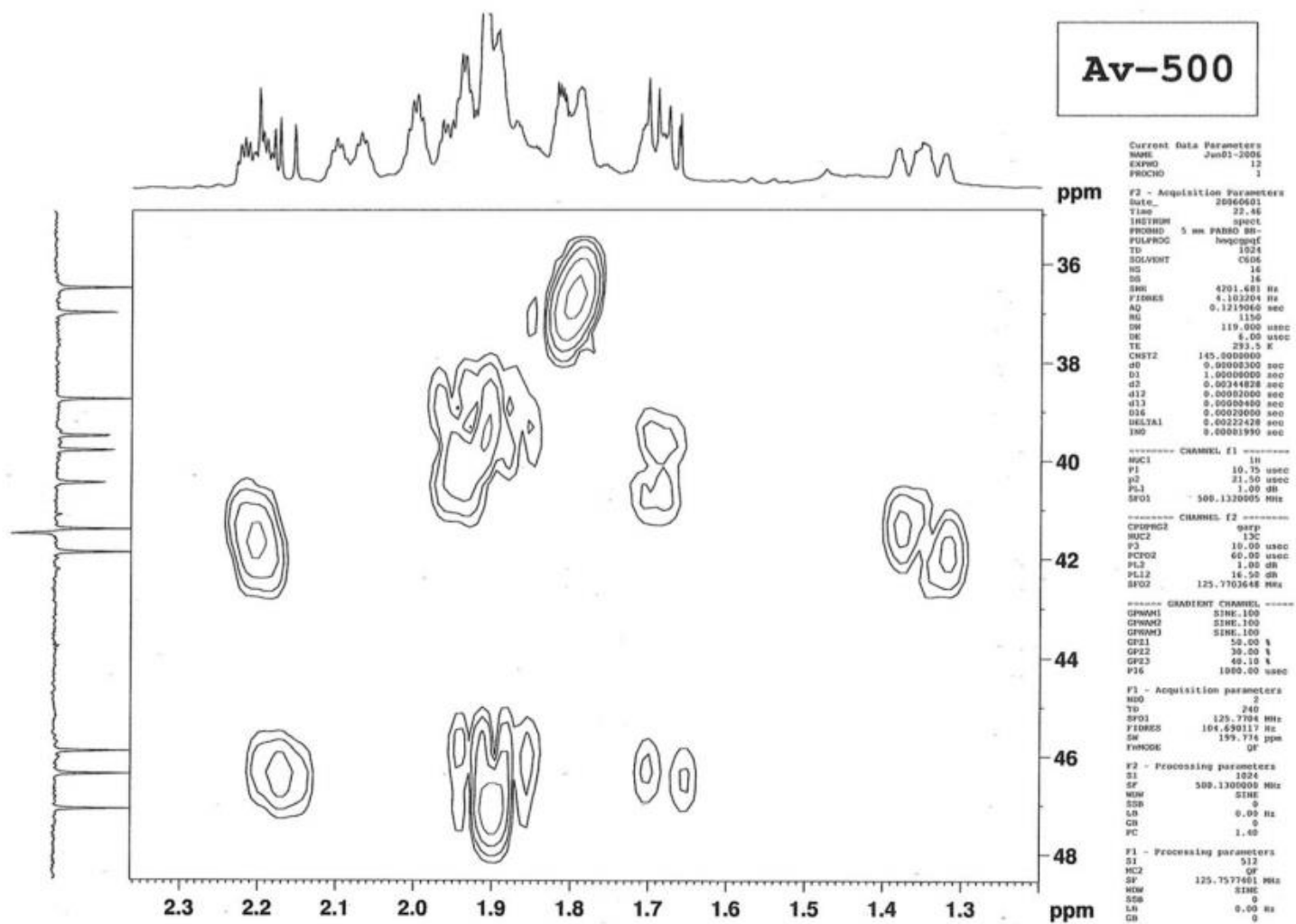
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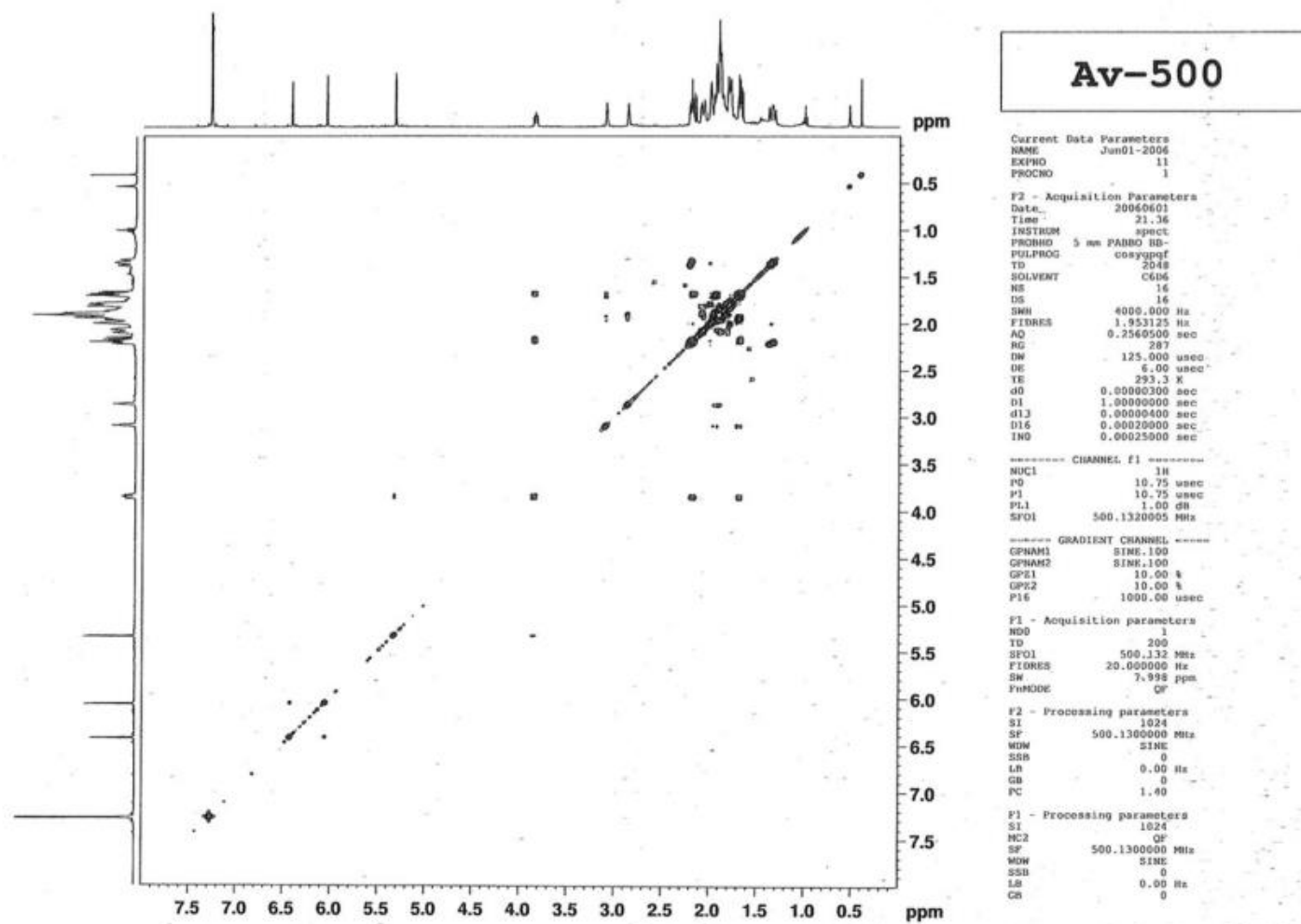
 $^1\text{H}$  and  $^{13}\text{C}$  correlation spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

 $^1\text{H}$  and  $^{13}\text{C}$  correlation spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

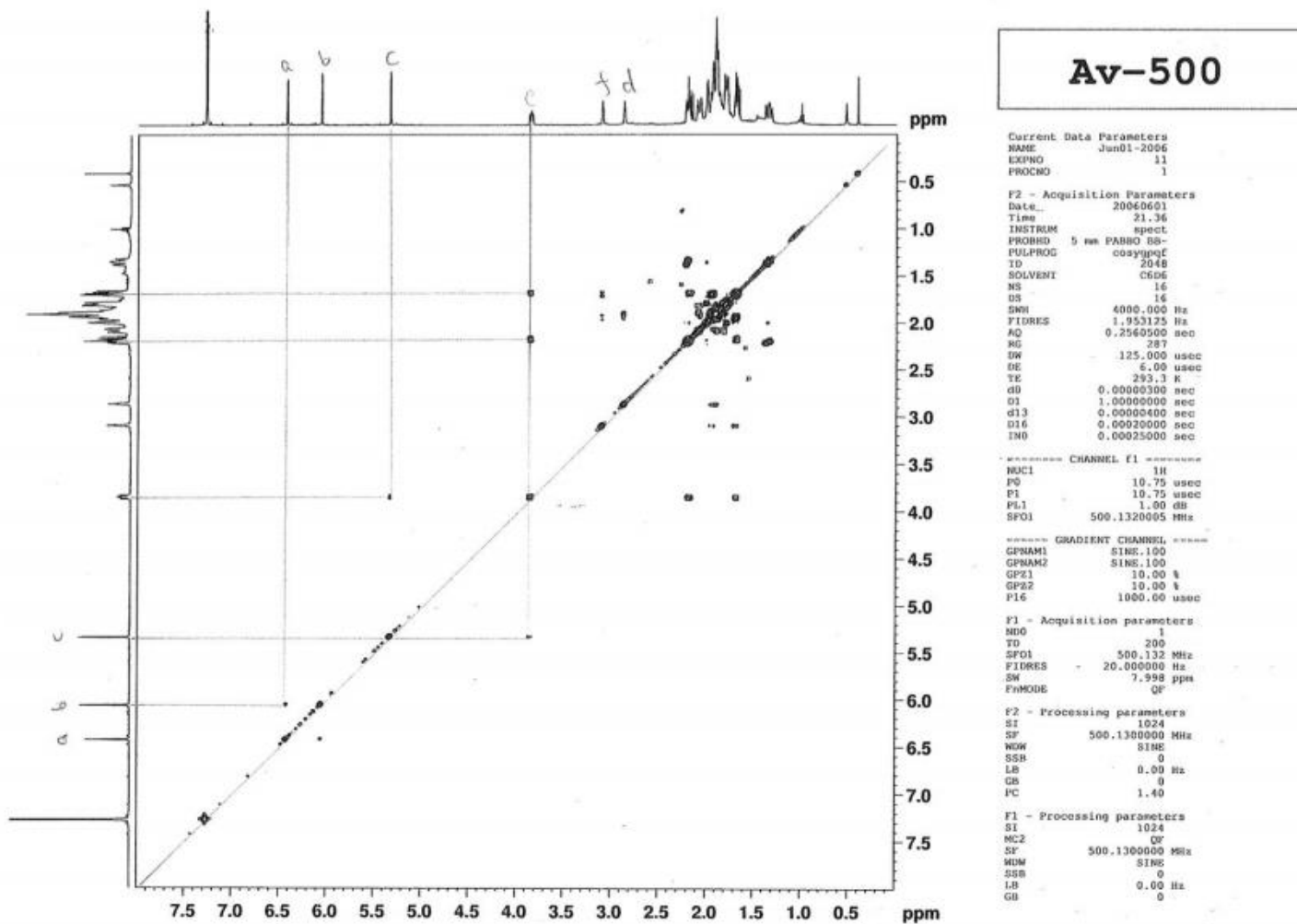
 $^1\text{H}$  and  $^{13}\text{C}$  correlation spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

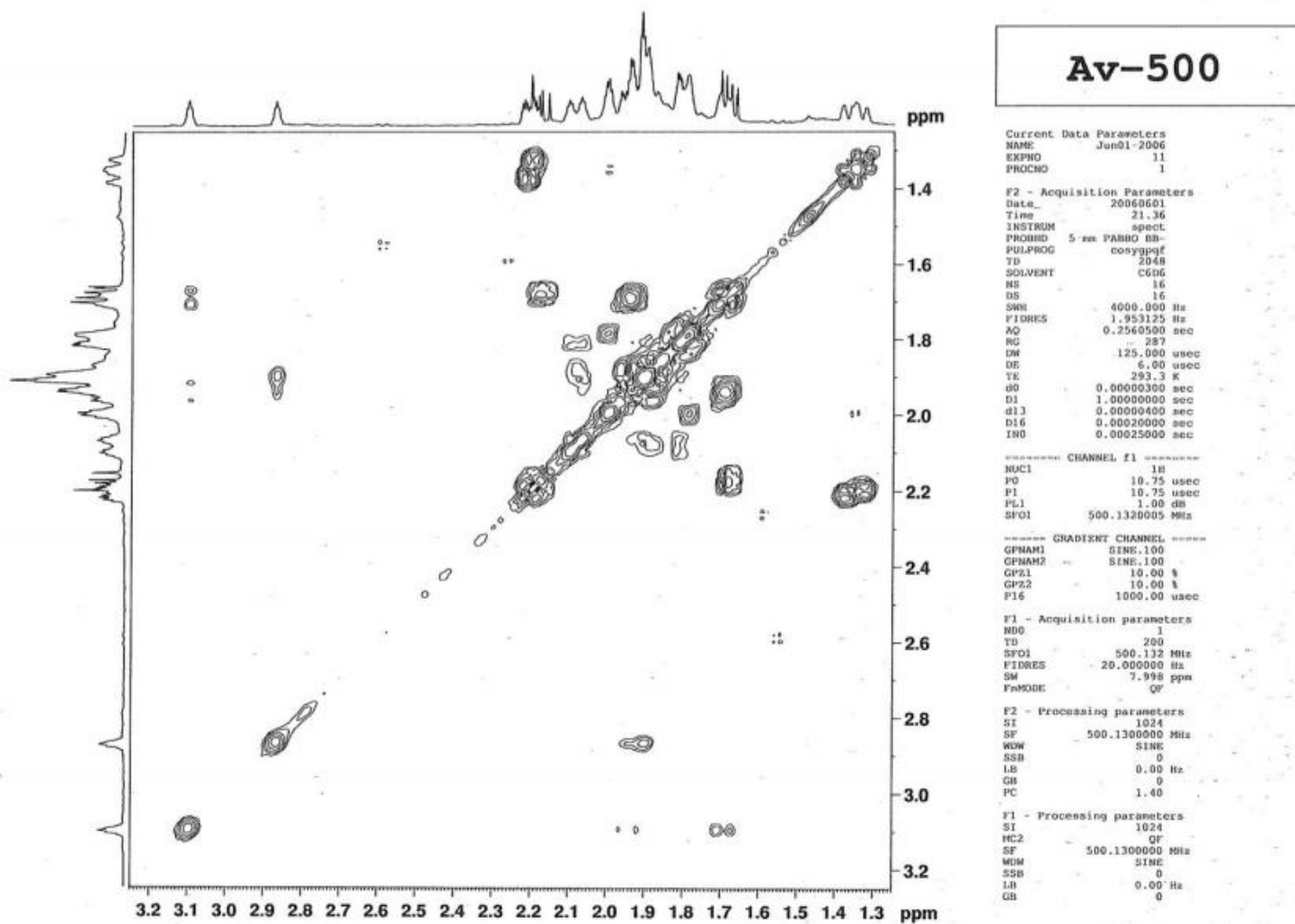
 $^1\text{H}$  and  $^{13}\text{C}$  correlation spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

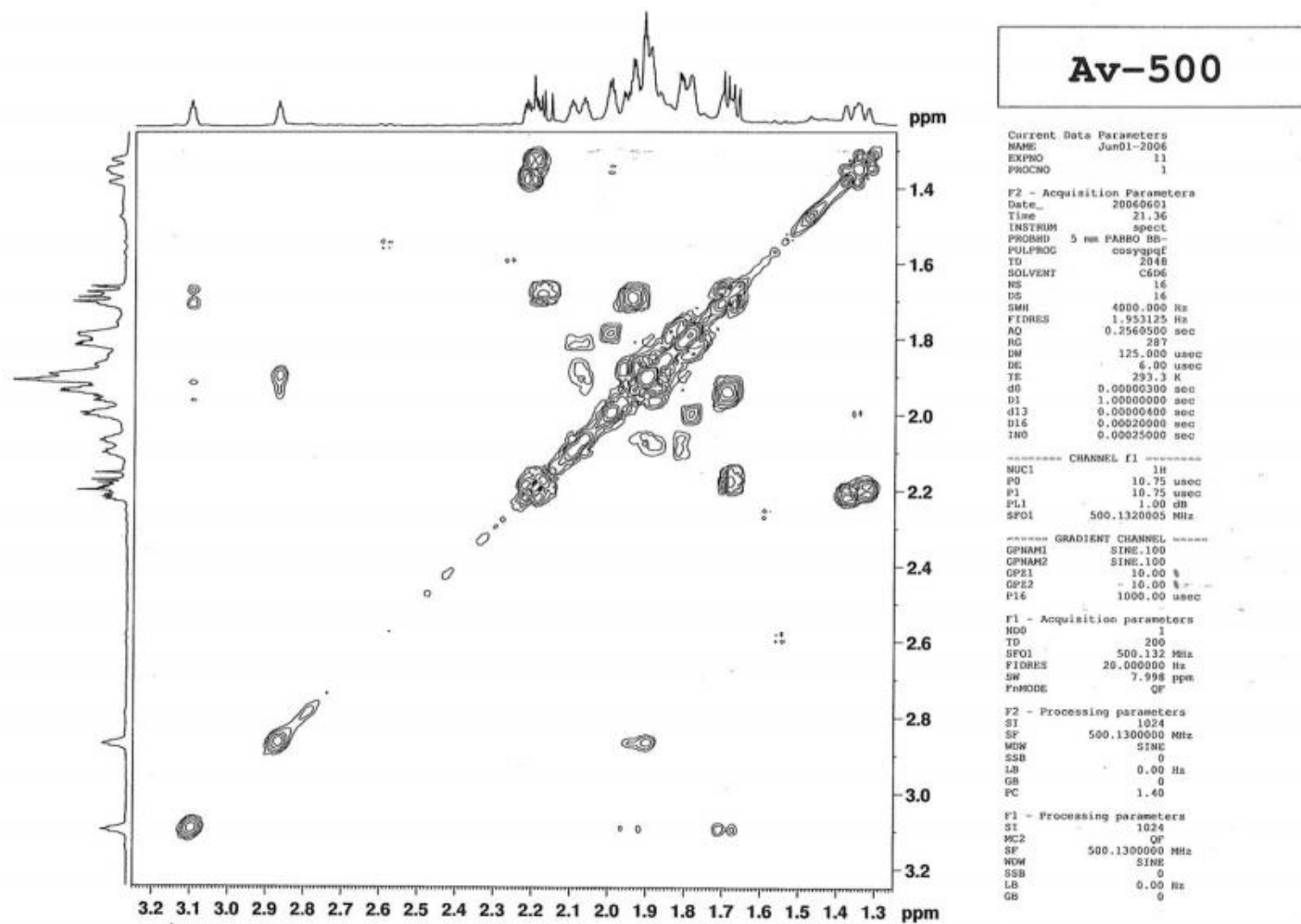
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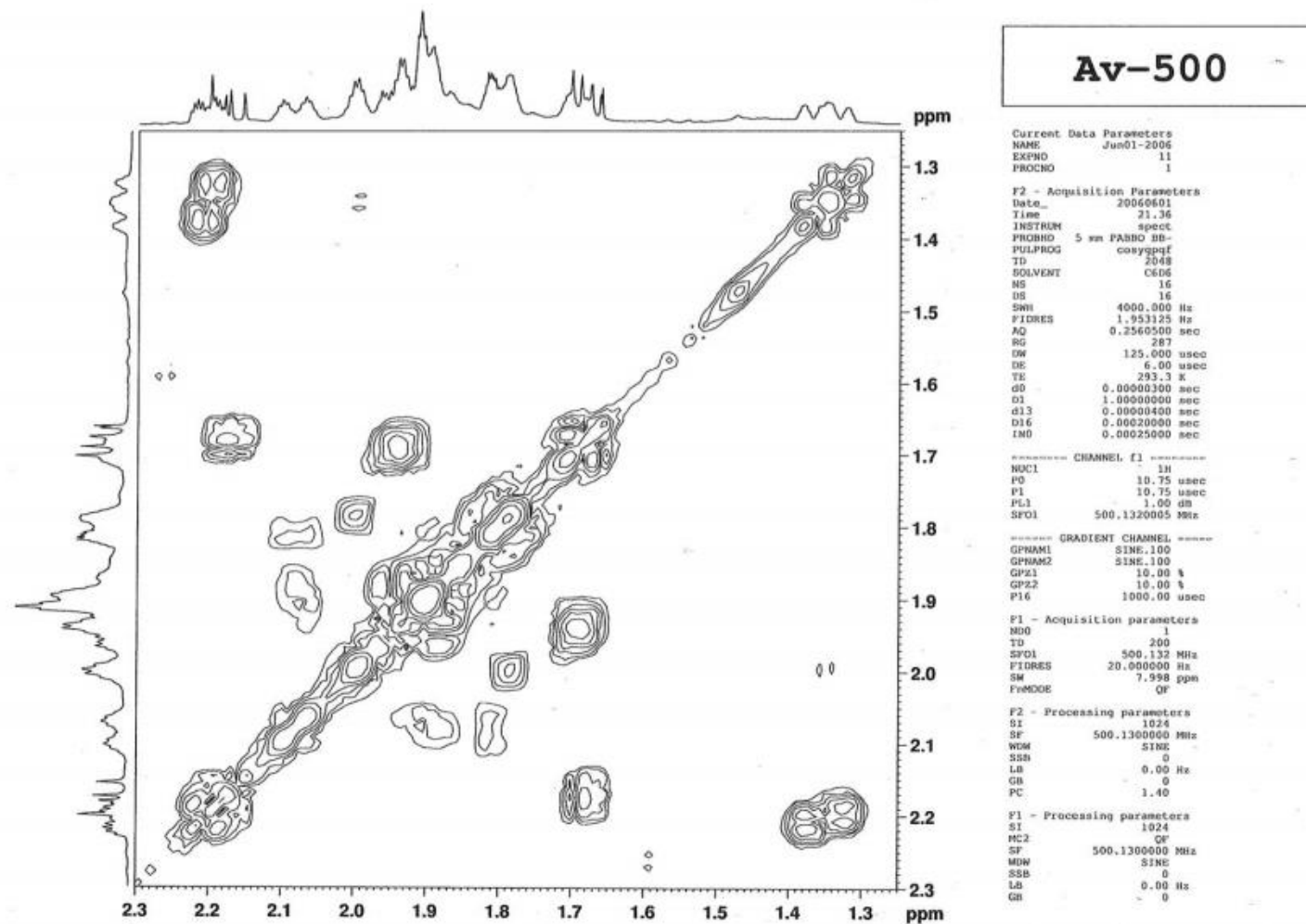
<sup>1</sup>H COSY spectrum of dimer **63** in C<sub>6</sub>D<sub>6</sub>.

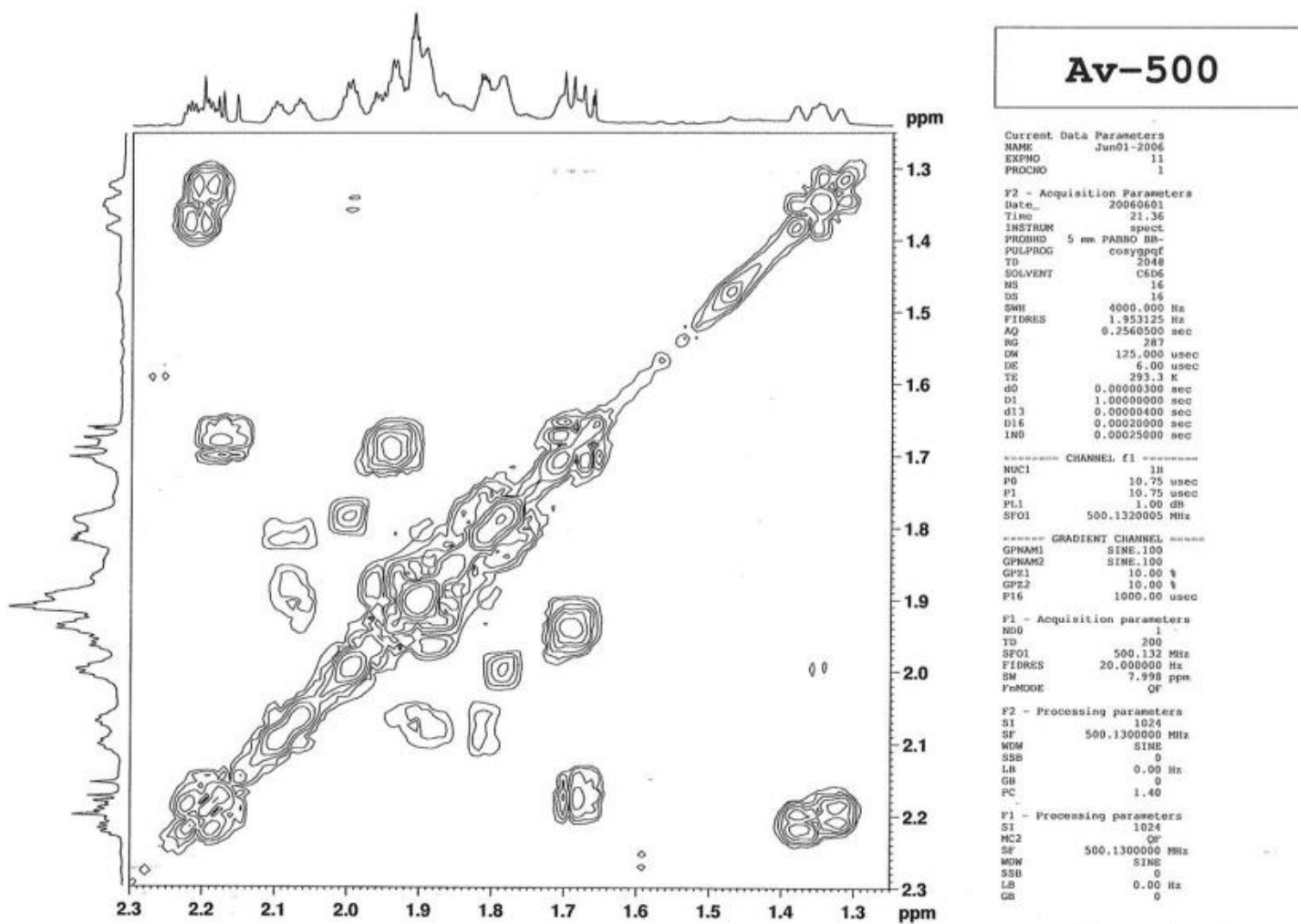


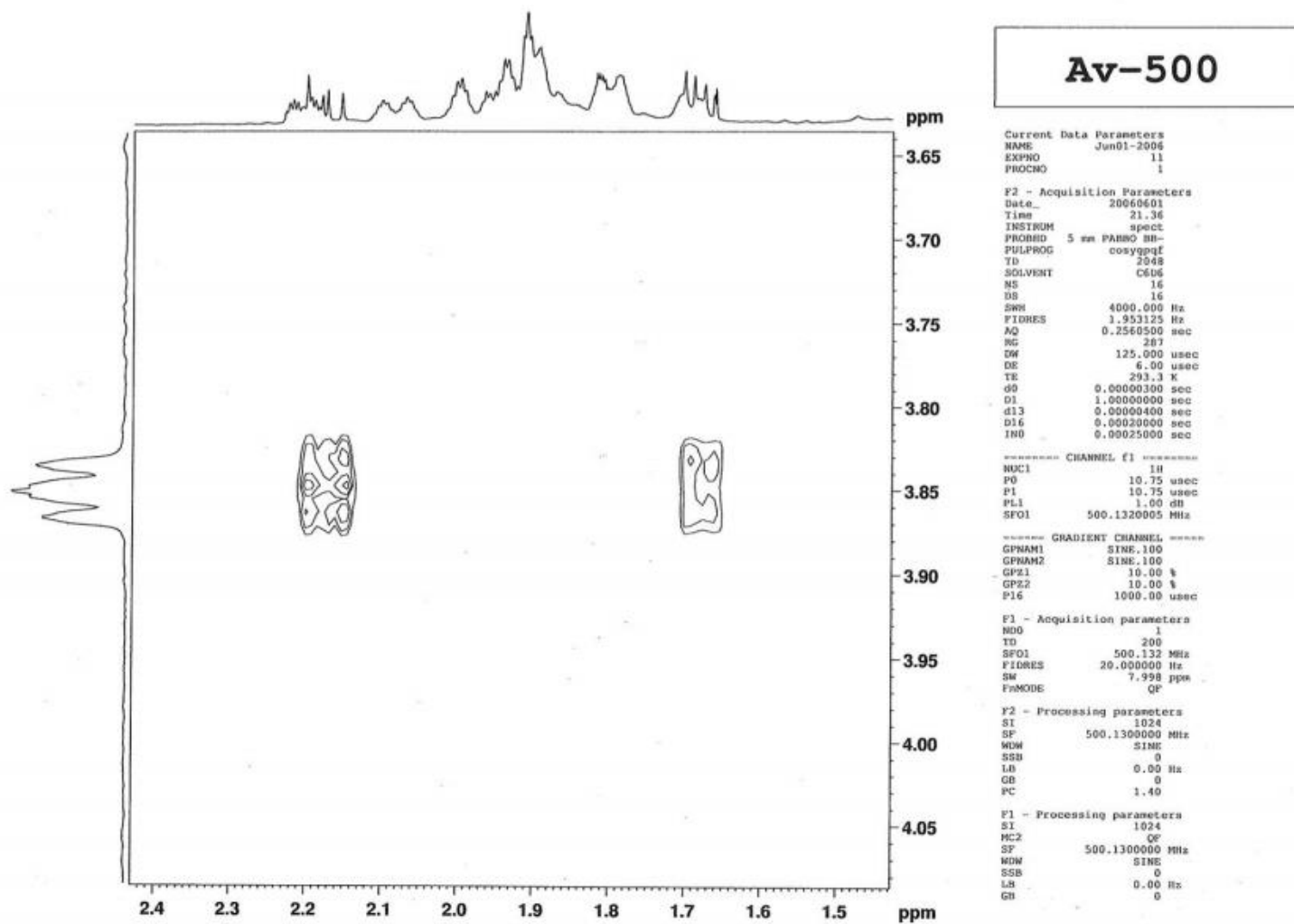
 $^1\text{H}$  COSY spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

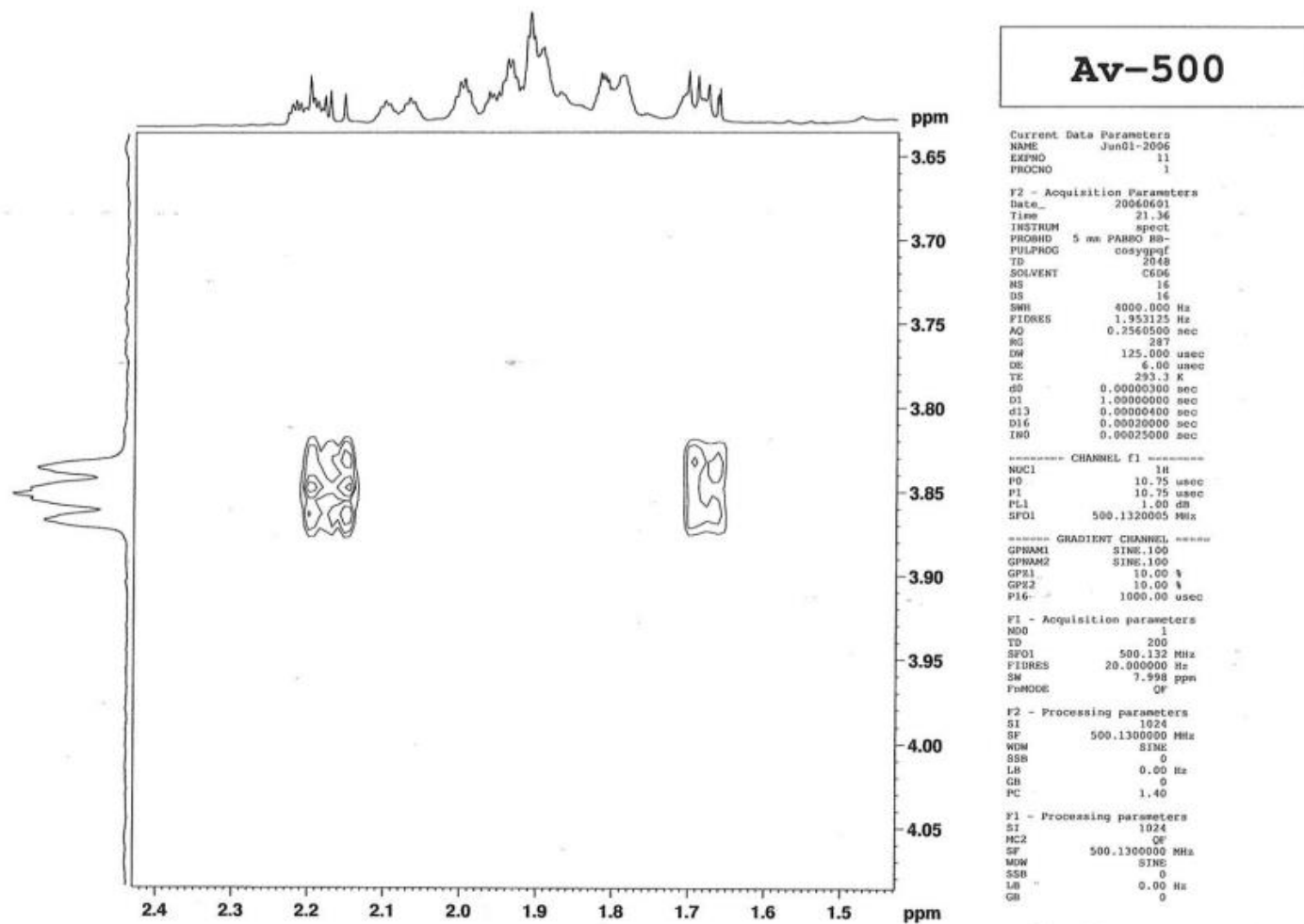
 $^1\text{H}$  COSY spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

 $^1\text{H}$  COSY spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

<sup>1</sup>H COSY spectrum of dimer **63** in C<sub>6</sub>D<sub>6</sub>.

<sup>1</sup>H COSY spectrum of dimer **63** in C<sub>6</sub>D<sub>6</sub>.

<sup>1</sup>H COSY spectrum of dimer **63** in C<sub>6</sub>D<sub>6</sub>.

 $^1\text{H}$  COSY spectrum of dimer **63** in  $\text{C}_6\text{D}_6$ .

**checkCIF (basic structural check) running**

Checking for embedded fcf data in CIF ...  
 Found embedded fcf data in CIF. Extracting fcf data from uploaded CIF, please wait . . . . .

**checkCIF/PLATON (basic structural check)**

Structure factors have been supplied for datablock(s) 21, 35

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No syntax errors found. [CIF dictionary](#)  
 Please wait while processing .... [Interpreting this report](#)

[Structure factor report](#)

**Datablock: 21**

Bond precision: C-C = 0.0040 Å Wavelength=1.54248  
 Cell: a=7.2942(7) b=11.5286(12) c=11.5044(10)  
 alpha=90 beta=92.841(8) gamma=90  
 Temperature: 173 K

	Calculated	Reported
Volume	966.24(16)	966.24(16)
Space group	P 21	P 21
Hall group	P 2yb	P 2yb
Moiety formula	C22 H32 O4	C22 H32 O4
Sum formula	C22 H32 O4	C22 H32 O4
Mr	360.48	360.47
Dx, g cm <sup>-3</sup>	1.239	1.239
Z	2	2
Mu (mm <sup>-1</sup> )	0.665	0.665
F000	392.0	392.0
F000'	393.15	
h, k, lmax	8, 14, 14	8, 13, 13
Nref	3709 [ 1952]	3465
Tmin, Tmax	0.946, 0.967	0.880, 0.969
Tmin'	0.858	

Correction method= # Reported T Limits: Tmin=0.880 Tmax=0.969  
 AbsCorr = ANALYTICAL  
 Data completeness= 1.78/0.93 Theta(max)= 70.874  
 R(reflections)= 0.0334( 2910) wR2(reflections)= 0.0826( 3465)  
 S = 0.981 Npar= 252

The following ALERTS were generated. Each ALERT has the format  
**test-name\_ALERT\_alert-type\_alert-level**.  
 Click on the hyperlinks for more details of the test.

**Alert level C**

[RADNW01\\_ALERT\\_1\\_C](#) The radiation wavelength lies outside the expected range for the supplied radiation type. Expected range 1.54175-1.54180  
 Wavelength given = 1.54248

[PLAT222\\_ALERT\\_3\\_C](#) NonSolvent Resd 1 H Uiso(max)/Uiso(min) Range 4.1 Ratio  
[PLAT911\\_ALERT\\_3\\_C](#) Missing FCF Refl Between Thmin & STh/L= 0.600 6 Report  
[PLAT915\\_ALERT\\_3\\_C](#) No Flack x Check Done: Low Friedel Pair Coverage 88 %  
[PLAT978\\_ALERT\\_2\\_C](#) Number C-C Bonds with Positive Residual Density. 0 Info

**Alert level G**

[PLAT002\\_ALERT\\_2\\_G](#) Number of Distance or Angle Restraints on AtSite 8 Note



PLAT172\_ALERT\_4\_G The CIF-Embedded .res File Contains DFIX Records 1 Report  
 PLAT860\_ALERT\_3\_G Number of Least-Squares Restraints ..... 5 Note  
 PLAT883\_ALERT\_1\_G No Info/Value for \_atom\_sites\_solution\_primary . Please Do !  
 PLAT912\_ALERT\_4\_G Missing # of FCF Reflections Above STh/L= 0.600 20 Note  
 PLAT961\_ALERT\_5\_G Dataset Contains no Negative Intensities ..... Please Check

0 **ALERT level A** = Most likely a serious problem - resolve or explain  
 0 **ALERT level B** = A potentially serious problem, consider carefully  
 5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight  
 6 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data  
 2 ALERT type 2 Indicator that the structure model may be wrong or deficient  
 4 ALERT type 3 Indicator that the structure quality may be low  
 2 ALERT type 4 Improvement, methodology, query or suggestion  
 1 ALERT type 5 Informative message, check

## Datablock: 35

Bond precision: C-C = 0.0076 Å Wavelength=0.71073  
 Cell: a=22.471(3) b=10.5857(11) c=9.5321(12)  
 alpha=90 beta=96.404(11) gamma=90

Temperature: 173 K

	Calculated	Reported
Volume	2253.3(5)	2253.3(5)
Space group	C 2	C 2
Hall group	C 2y	C 2y
Moiety formula	C26 H40 O4	C26 H40 O4
Sum formula	C26 H40 O4	C26 H40 O4
Mr	416.58	416.58
Dx, g cm <sup>-3</sup>	1.228	1.228
Z	4	4
Mu (mm <sup>-1</sup> )	0.081	0.081
F000	912.0	912.0
F000'	912.41	
h, k, lmax	34, 16, 14	34, 15, 13
Nref	8399[ 4395]	6184
Tmin, Tmax	0.987, 0.996	0.987, 0.996
Tmin'	0.984	

Correction method= # Reported T Limits: Tmin=0.987 Tmax=0.996

AbsCorr = ANALYTICAL

Data completeness= 1.41/0.74 Theta(max)= 32.843

R(reflections)= 0.0905( 2785) wR2(reflections)= 0.2903( 6184)

S = 1.003 Npar= 294

The following ALERTS were generated. Each ALERT has the format

**test-name\_ALERT\_alert-type\_alert-level.**

Click on the hyperlinks for more details of the test.

### Alert level B

PLAT910\_ALERT\_3\_B Missing # of FCF Reflection(s) Below Theta(Min). 13 Note

### Alert level C

STRVA01\_ALERT\_2\_C Chirality of atom sites is inverted?

From the CIF: \_refine\_ls\_abs\_structure\_Flack 10.000

From the CIF: \_refine\_ls\_abs\_structure\_Flack\_su 1.000

PLAT026\_ALERT\_3\_C Ratio Observed / Unique Reflections (too) Low .. 45% Check

PLAT084\_ALERT\_3\_C High wR2 Value (i.e. > 0.25) ..... 0.29 Report

PLAT241\_ALERT\_2\_C High MainMol Ueq as Compared to Neighbors of C12 Check

PLAT340\_ALERT\_3\_C Low Bond Precision on C-C Bonds ..... 0.00763 Ang.

PLAT906\_ALERT\_3\_C Large K Value in the Analysis of Variance ..... 3.764 Check

PLAT907\_ALERT\_2\_C Flack x > 0.5, Structure Needs to be Inverted? . 10.00 Check

PLAT915\_ALERT\_3\_C No Flack x Check Done: Low Friedel Pair Coverage 53 %

### Alert level G

PLAT002\_ALERT\_2\_G Number of Distance or Angle Restraints on AtSite 11 Note

PLAT003\_ALERT\_2\_G Number of Uiso or Uij Restrained non-H Atoms ... 10 Report

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PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 5 Report
PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High . 1.000 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero . 10.000 Note
PLAT066_ALERT_1_G Predicted and Reported Tmin&Tmax Range Identical ? Check
PLAT072_ALERT_2_G SHELXL First Parameter in WGHT Unusually Large 0.12 Report
PLAT111_ALERT_2_G ADDSYM Detects New (Pseudo) Centre of Symmetry . 84 %Fit
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New Space Group C2/m Check
PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records 1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 5 Report
PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1 ) 17% Note
PLAT410_ALERT_2_G Short Intra H...H Contact H4B ..H29A . 2.12 Ang.
x,y,z = 1_555 Check
PLAT417_ALERT_2_G Short Inter D-H...H-D H25 ..H30 . 2.05 Ang.
-1/2+x,1/2+y,z = 3_455 Check
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group # 24 Check
PLAT791_ALERT_4_G Model has Chirality at C11 (Chiral SPGR) S Verify
And 9 other PLAT791 Alerts
Less ...

PLAT791_ALERT_4_G Model has Chirality at C13 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C16 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C18 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C21 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C23 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C26 (Chiral SPGR) S Verify
PLAT791_ALERT_4_G Model has Chirality at C28 (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C26' (Chiral SPGR) R Verify
PLAT791_ALERT_4_G Model has Chirality at C28' (Chiral SPGR) S Verify

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 40 Note
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary . Please Do !
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 259 Note
PLAT916_ALERT_2_G Hooft y and Flack x Parameter Values Differ by . 7.70 Check
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 1 Info
PLAT992_ALERT_5_G Repd & Actual _reflns_number_gt Values Differ by 1 Check

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17 ALERT type 4 Improvement, methodology, query or suggestion  
2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special\_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

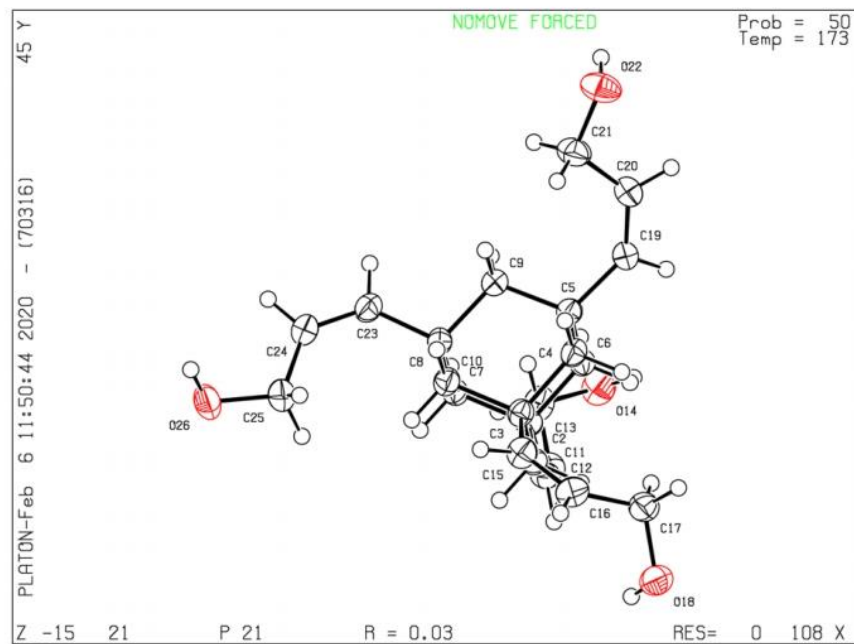
#### Publication of your CIF in IUCr journals

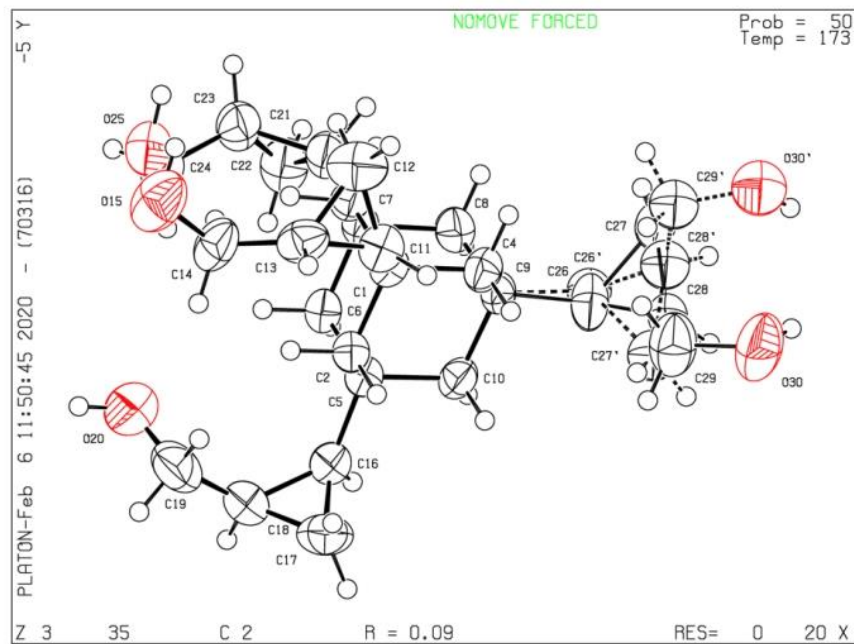
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

#### Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 22/12/2019; check.def file version of 13/12/2019

**Datablock 21** - ellipsoid plot**Datablock 35** - ellipsoid plot



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