

Supporting Information for publication

An Efficient Synthesis of Dihydro- and Tetrahydropyran via Oxonium-Ene Cyclization Reaction

S. Bondalapati, U. C. Reddy, Pipas Saha and Anil K. Saikia*

Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati 781039, India

asaikia@iitg.ernet.in

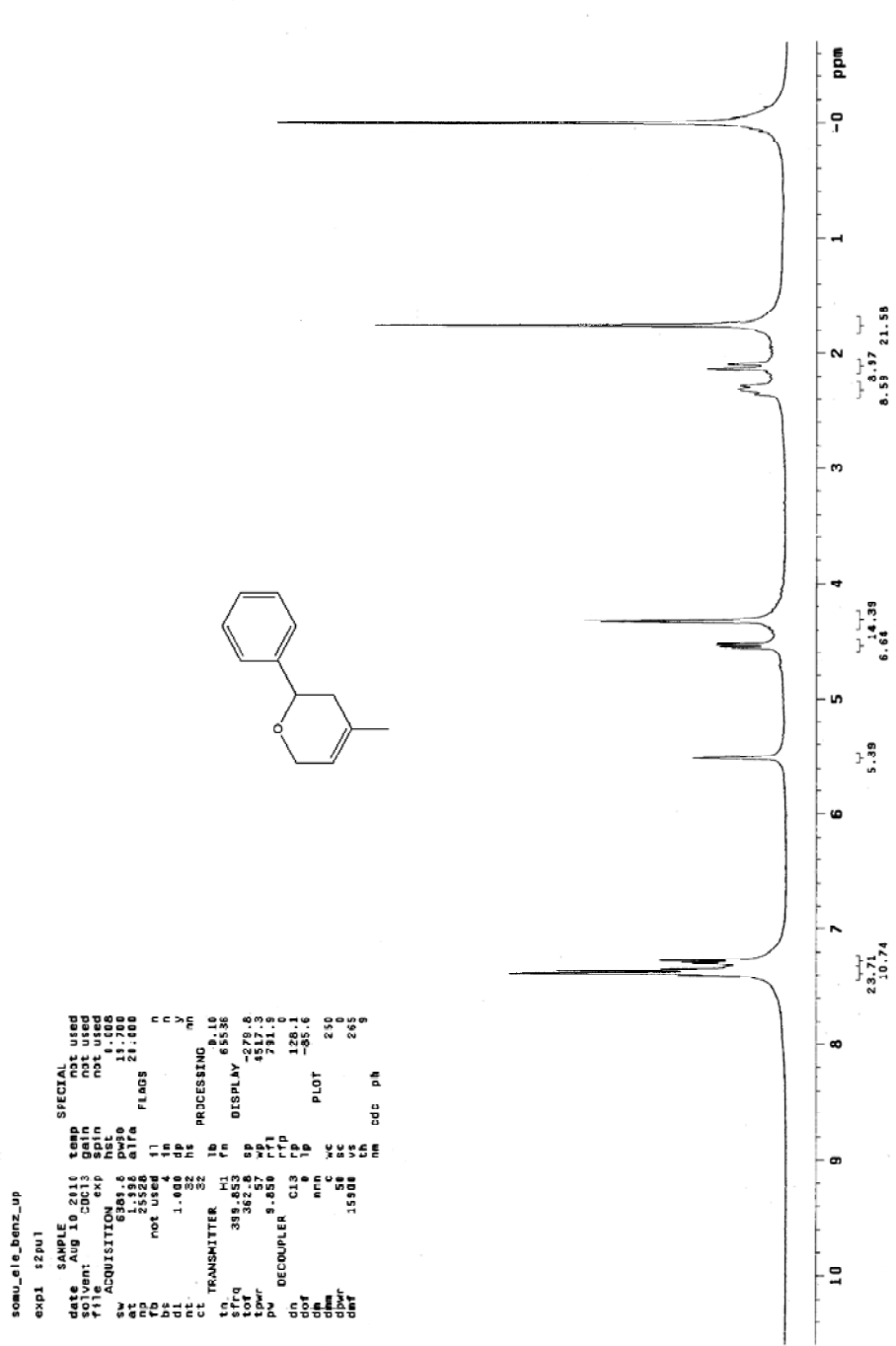
Supplementary information: General Experimental Section, ^1H NMR data **8a**, ^1H and ^{13}C NMR spectra of all compounds, Crystal structure & Crystallographic data of **6e**, **10** and **17j**.

General Experimental Section

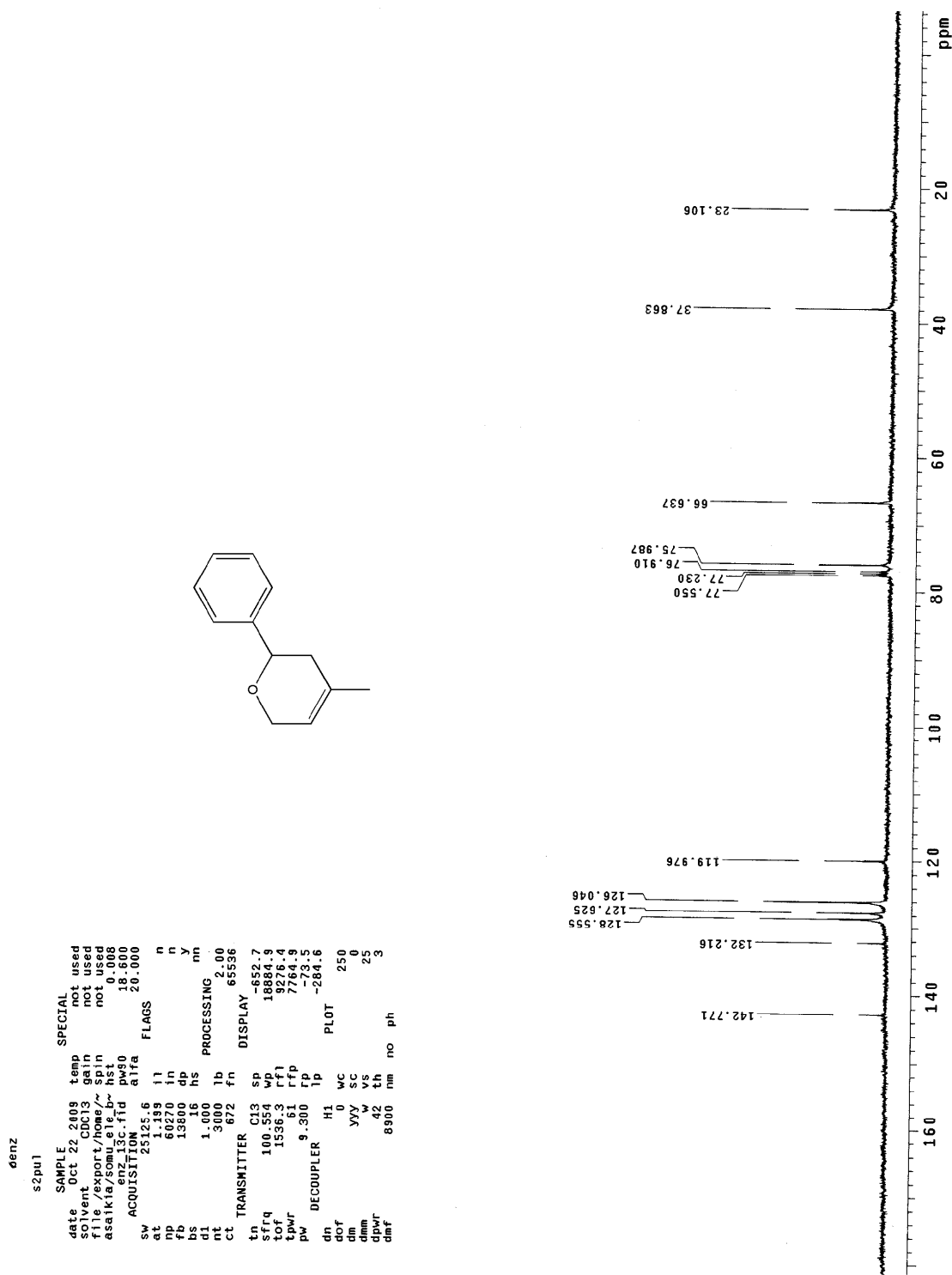
Melting points are uncorrected. ^1H NMR spectra were recorded in CDCl_3 on Varian AS 400 (400 MHz) spectrometer using TMS as internal standard. ^{13}C and ^{19}F NMR spectra were obtained on Varian AS 400 operating at 100 MHz and 376 MHz, respectively. IR spectra were recorded on Nicolet Impact 410 FT-IR spectrometer. Mass spectra were recorded using Waters LC-MS/MS system (Q-TOF–Premier). HRMS (ESCI-TOF) were calibrated with sodium formate solution and leucine enkephalin (SIGMA) was used as an external standard. Elemental analysis was performed on Perkin Elmer 2400 Series II CHNS analyser.

^1H NMR of 8a: ^1H NMR (400 MHz, CDCl_3): δ 2.20-2.25 (m, 1 H), 2.28-2.36 (m, 1 H), 2.40-2.48 (m, 2 H), 3.56 (dt, $J = 12.4$ and 1.8 Hz, 1 H), 4.24 (dd, $J = 10.4$ and 5.2 Hz, 1 H), 4.29 (dd, $J = 11.2$ and 2.4 Hz, 1 H), 4.78-4.82 (m, 2 H), 7.22-7.29 (m, 2 H, ArH), 7.34-7.40 (m, 3 H, ArH).

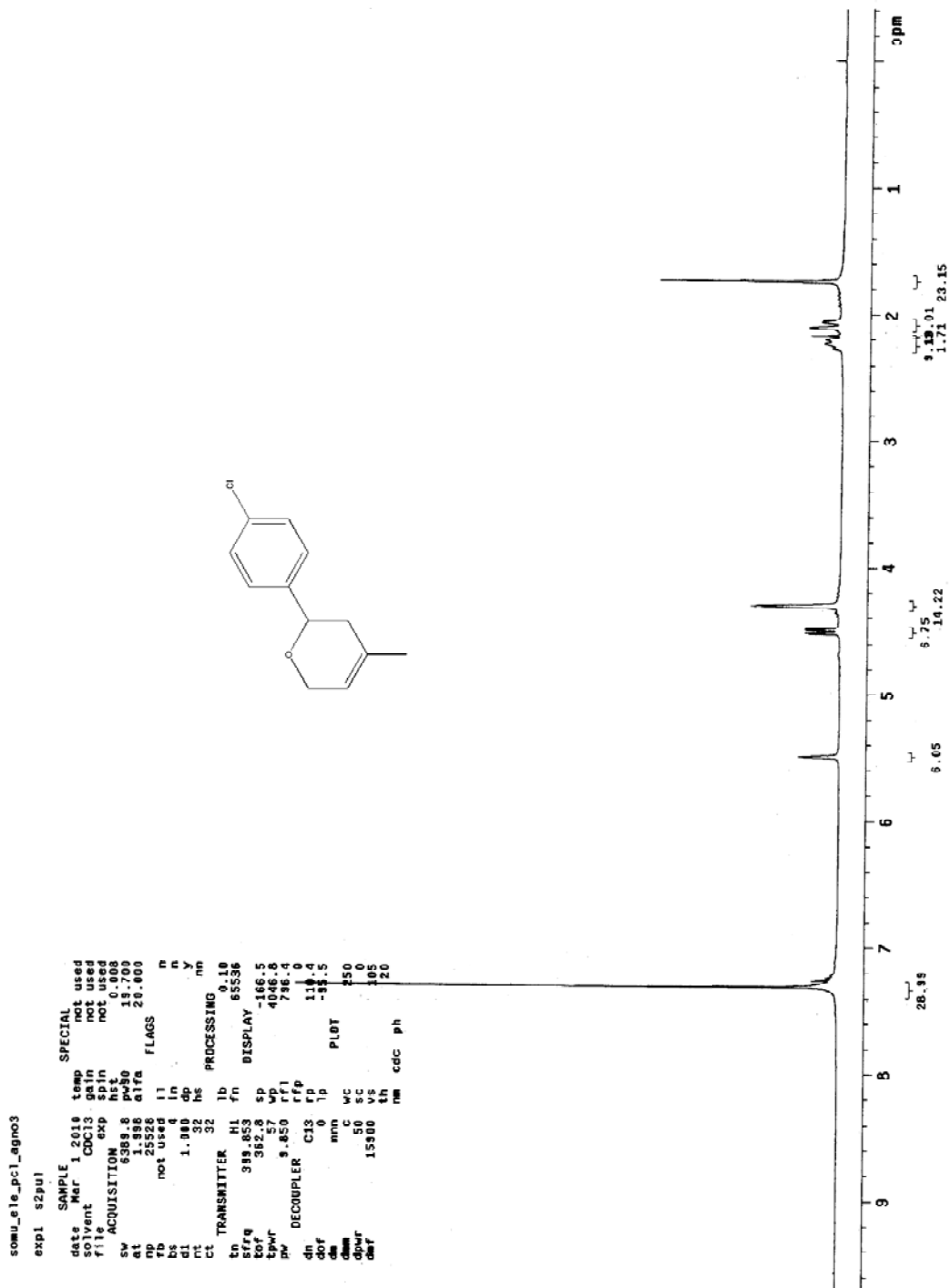
¹H NMR of **6a**



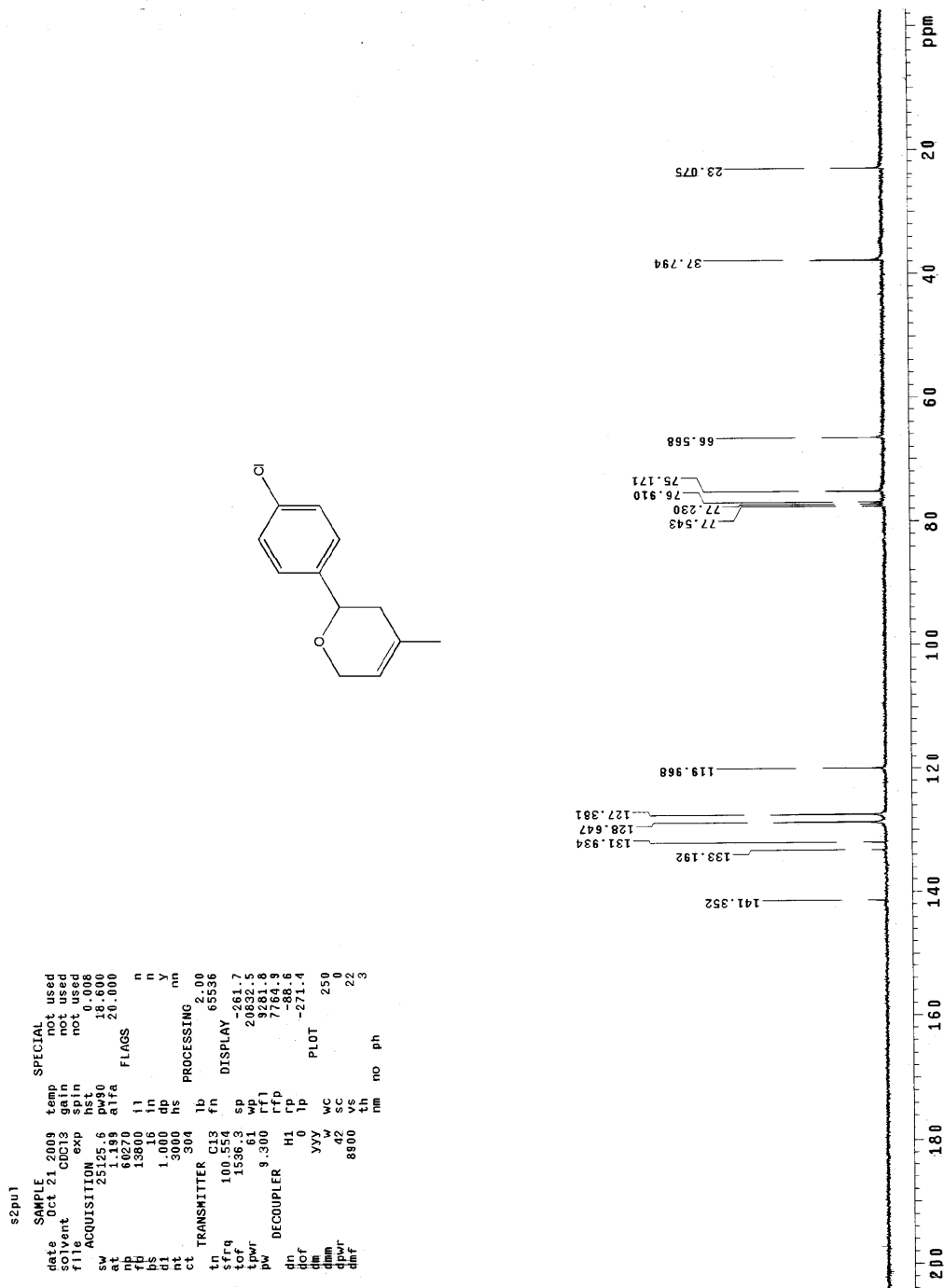
^{13}C NMR of **6a**



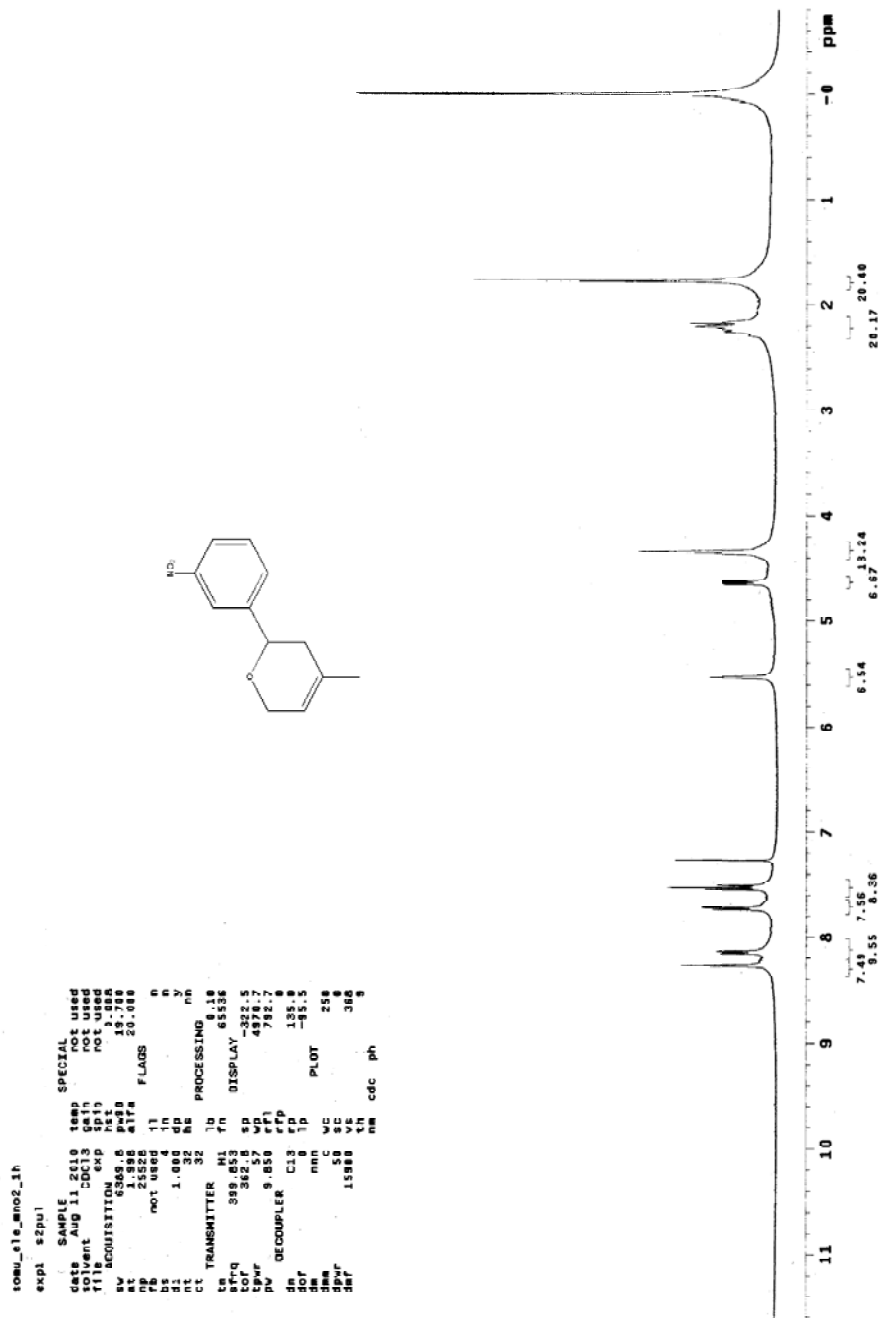
¹H NMR of **6b**



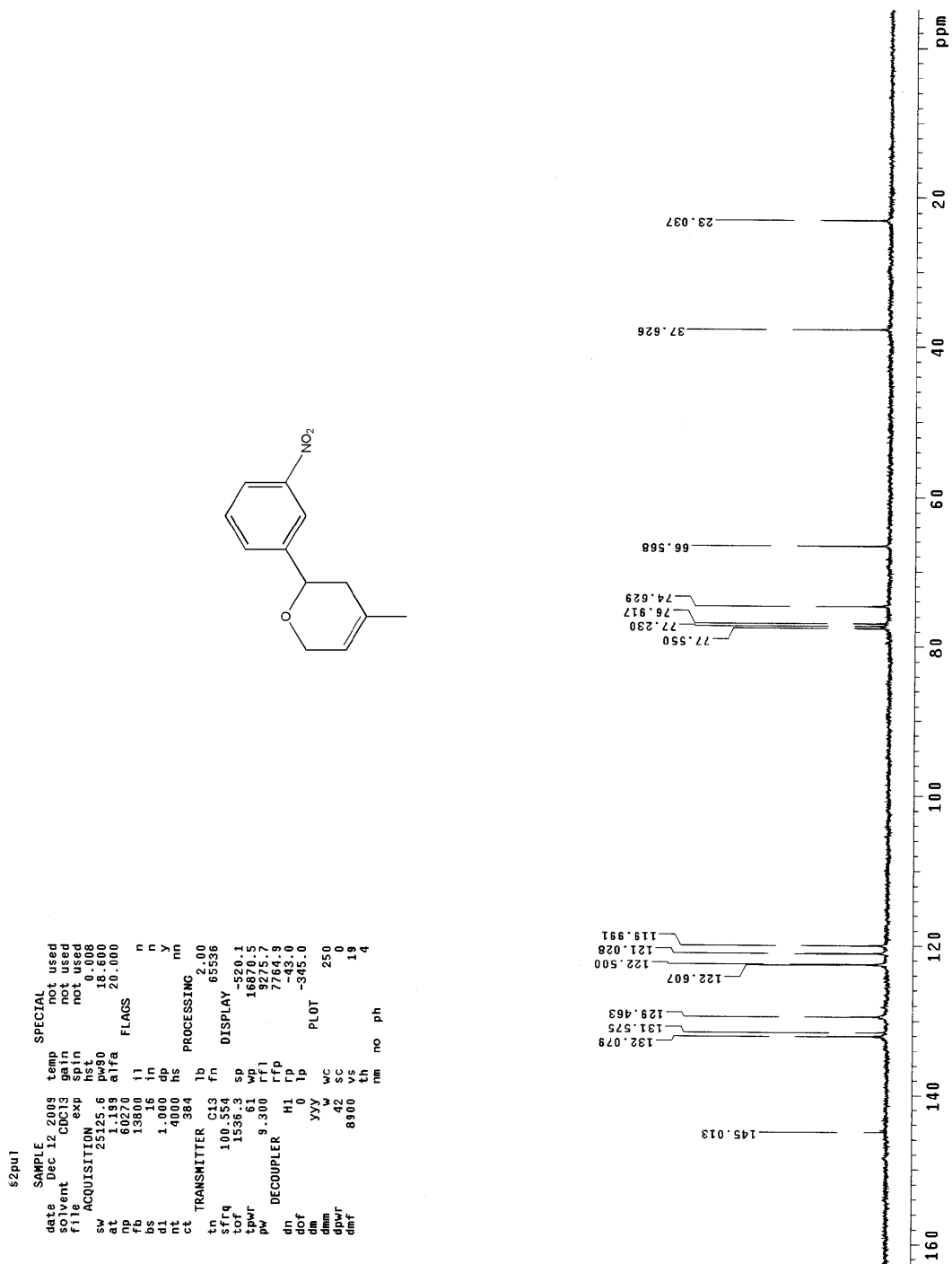
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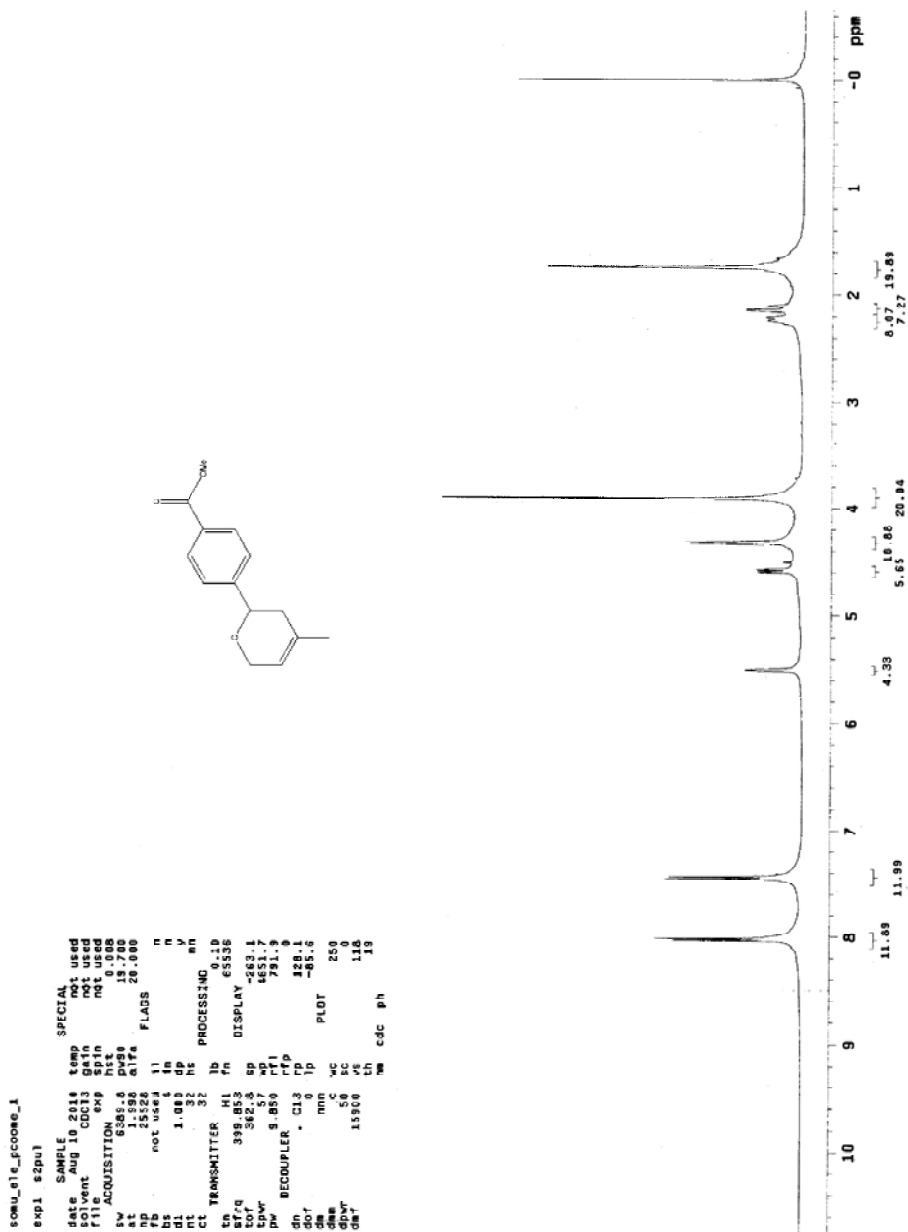
¹H NMR of 6c



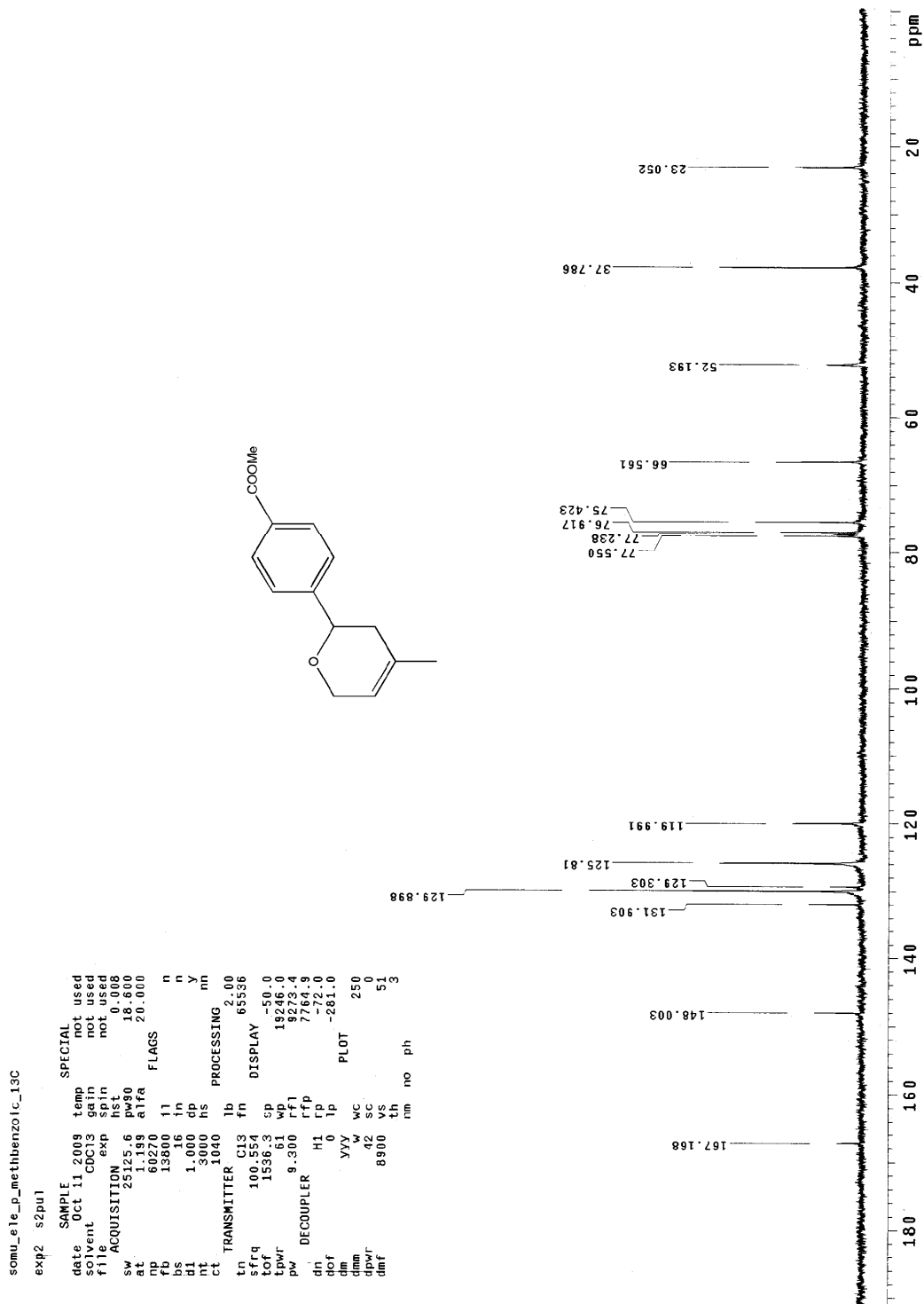
¹³C NMR of 6c



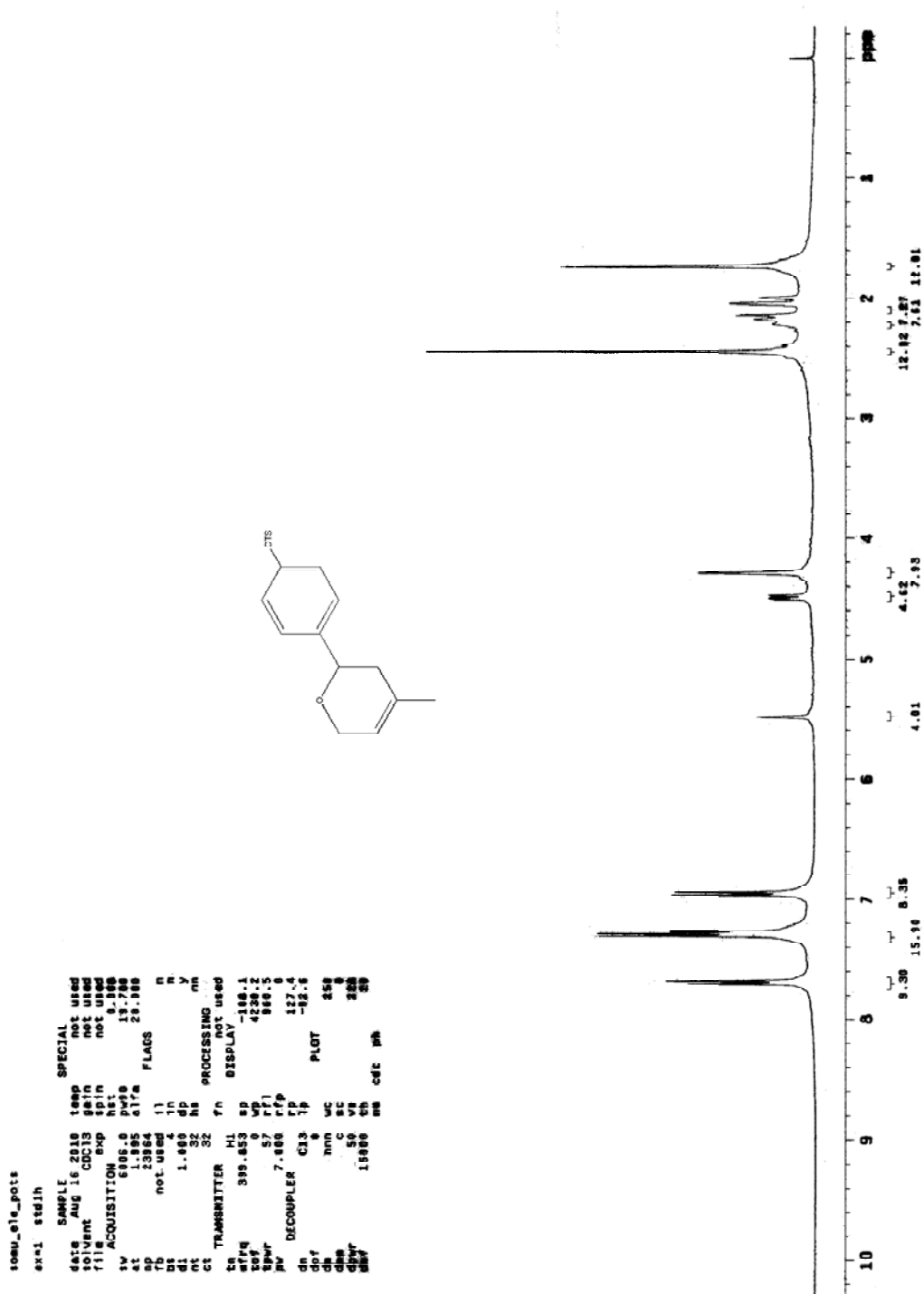
¹H NMR of 6d



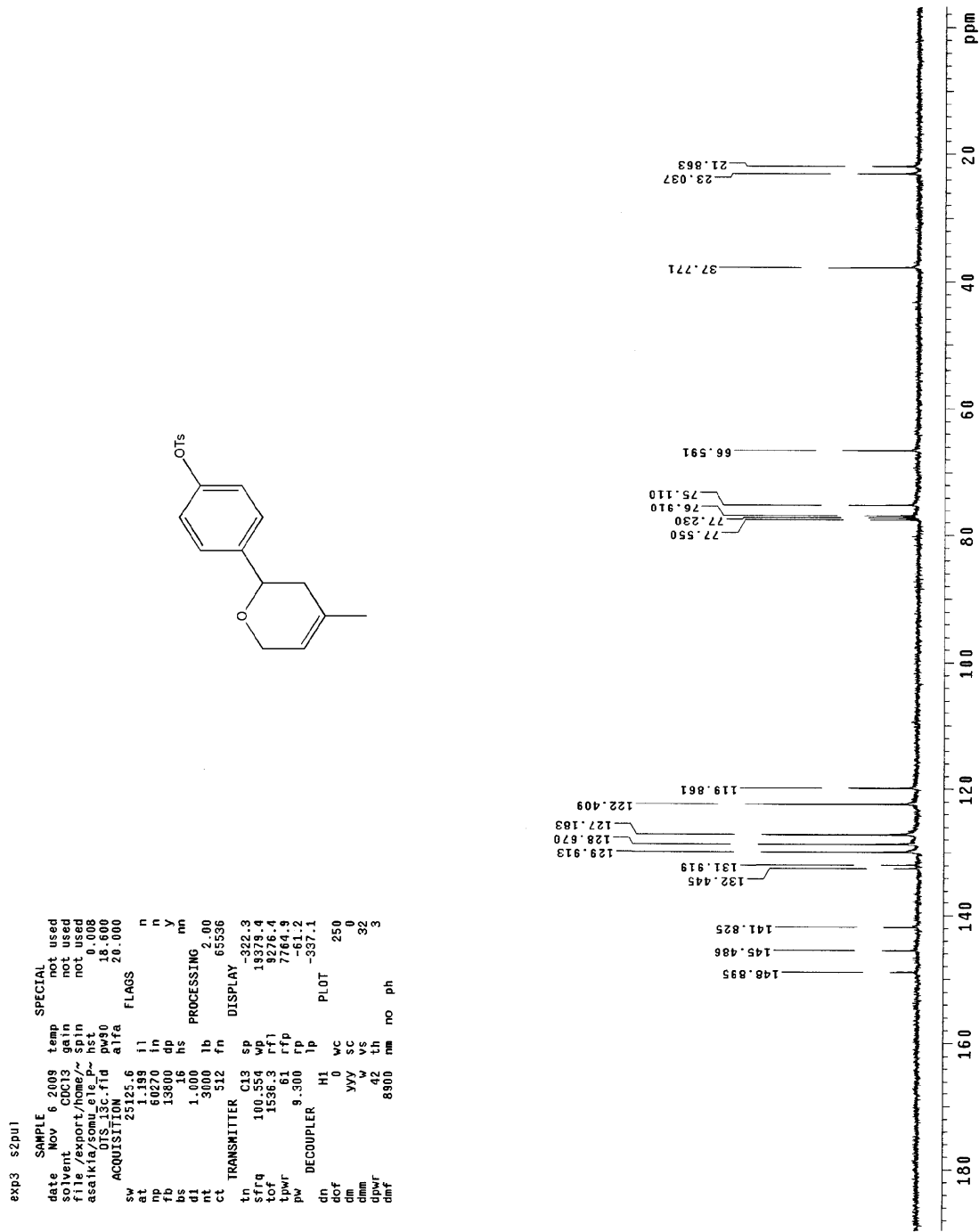
¹³C NMR of **6d**



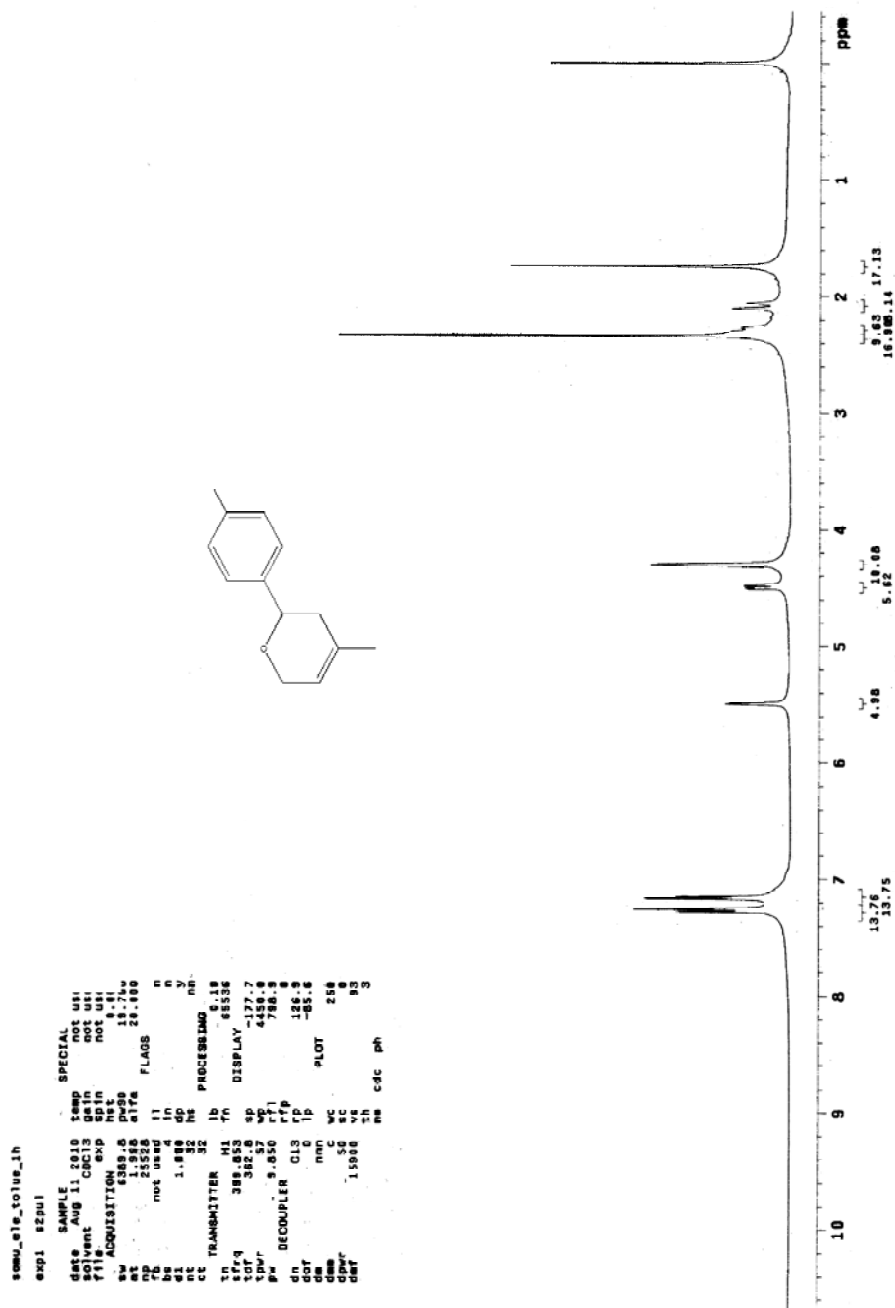
¹H NMR of 6e



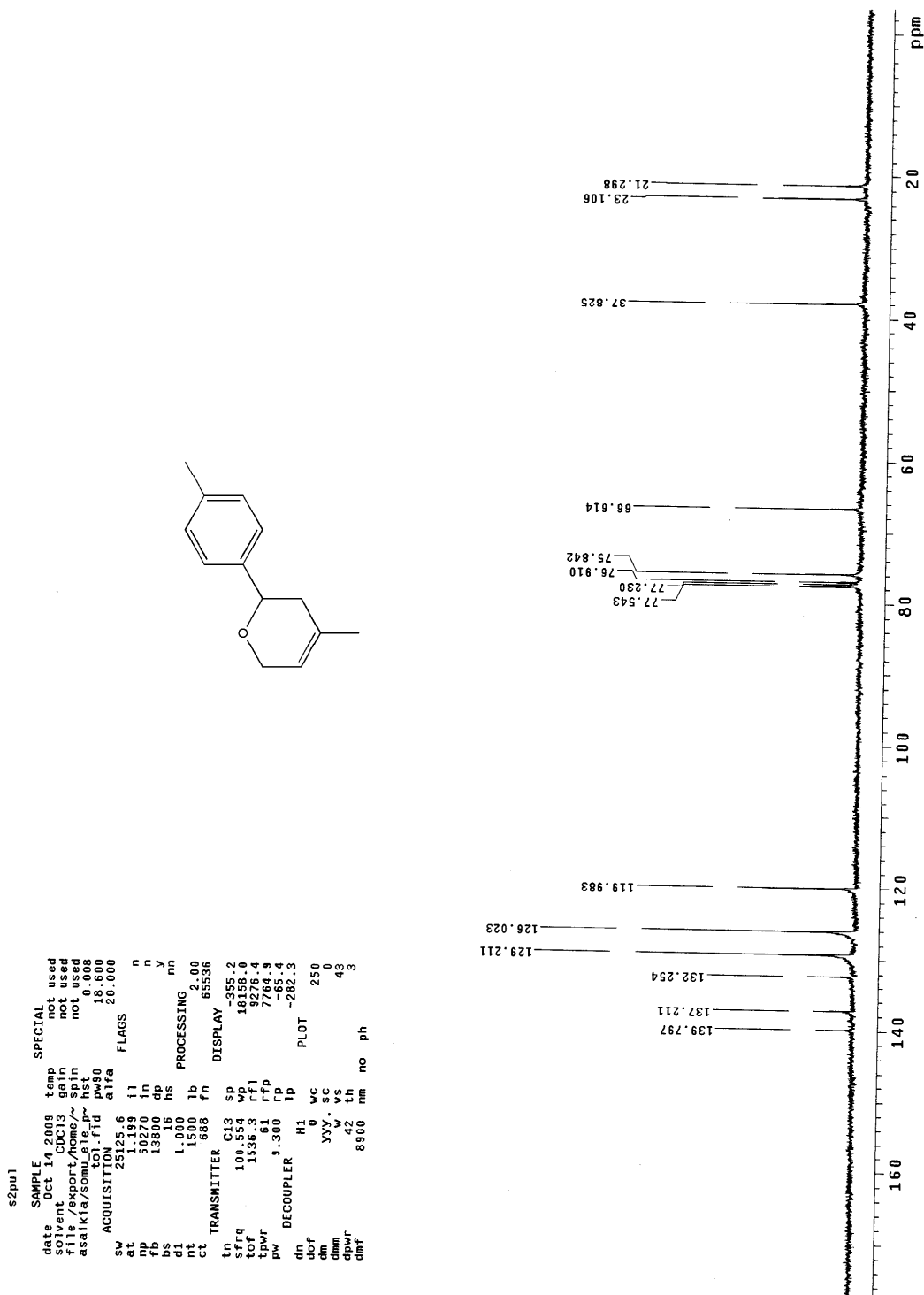
¹³C NMR of **6e**



¹H NMR of **6f**



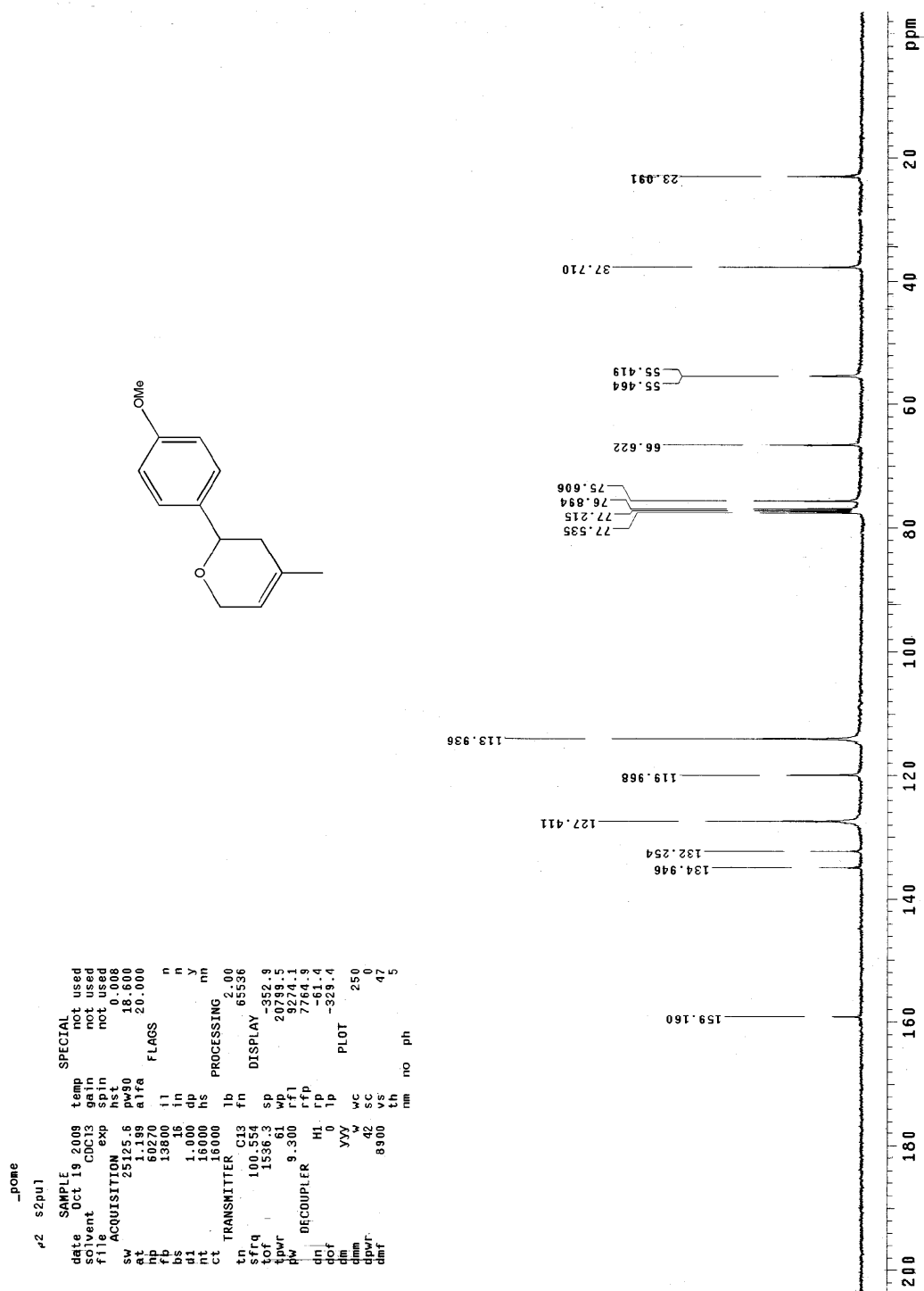
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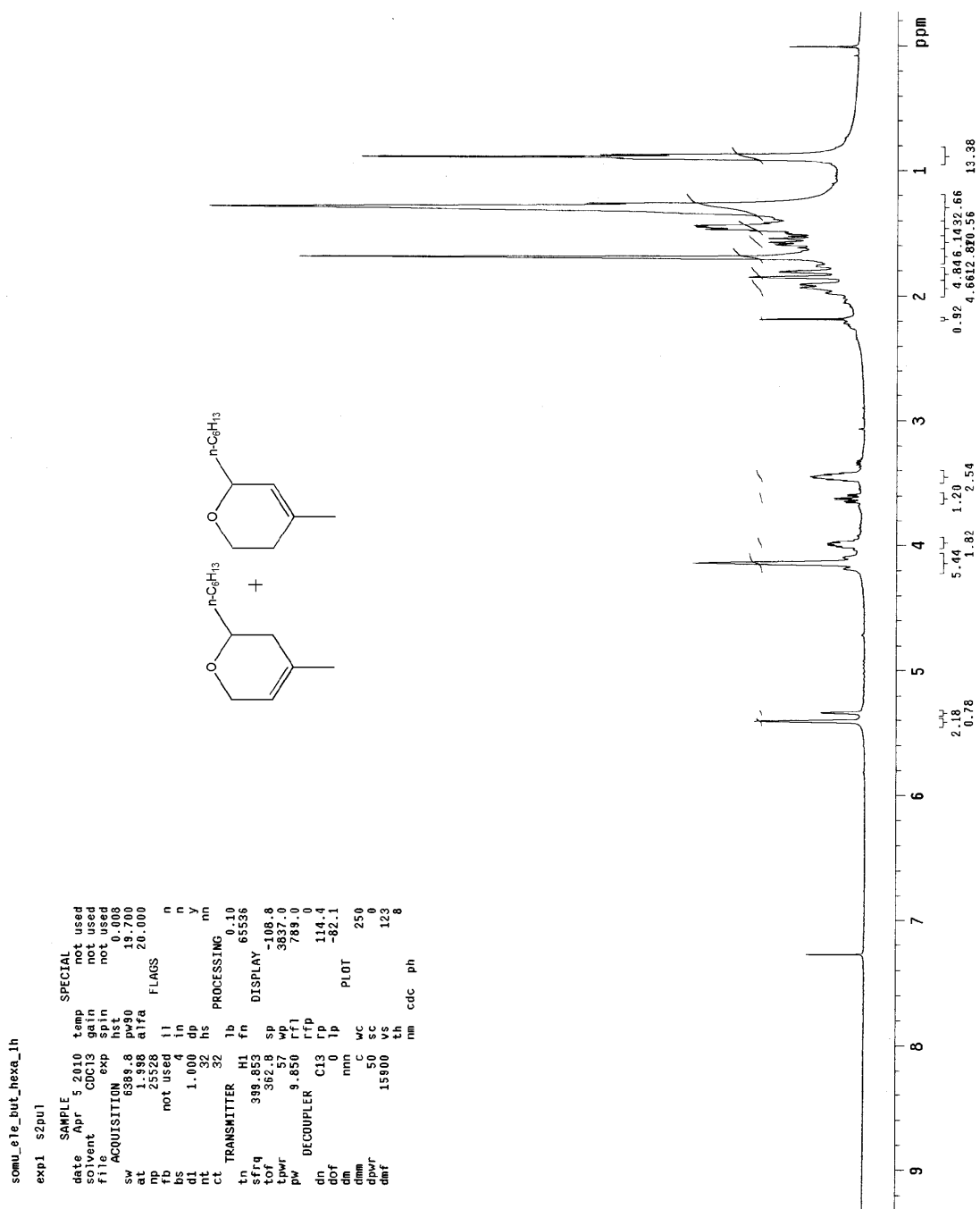
¹H NMR of 6g



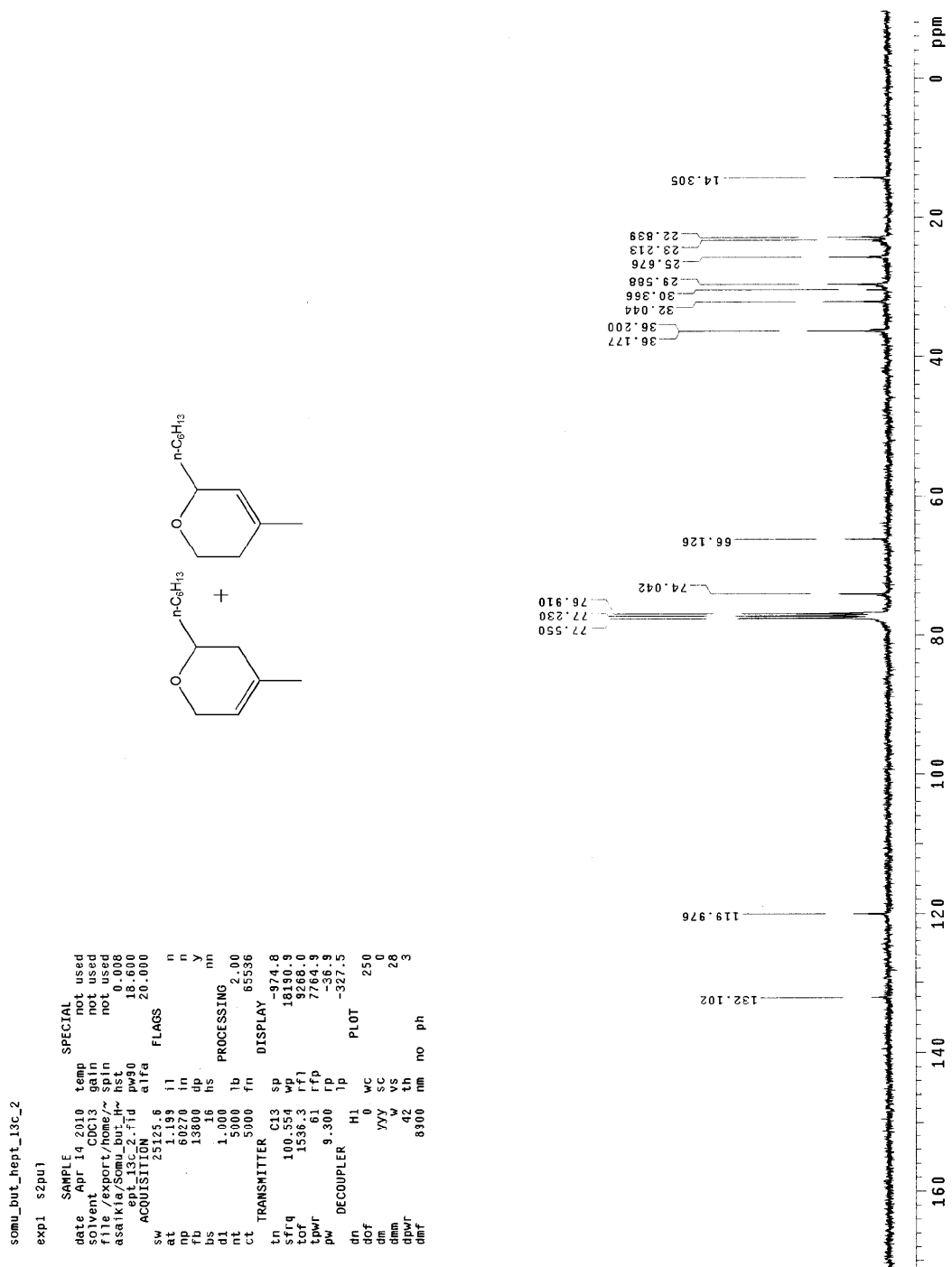
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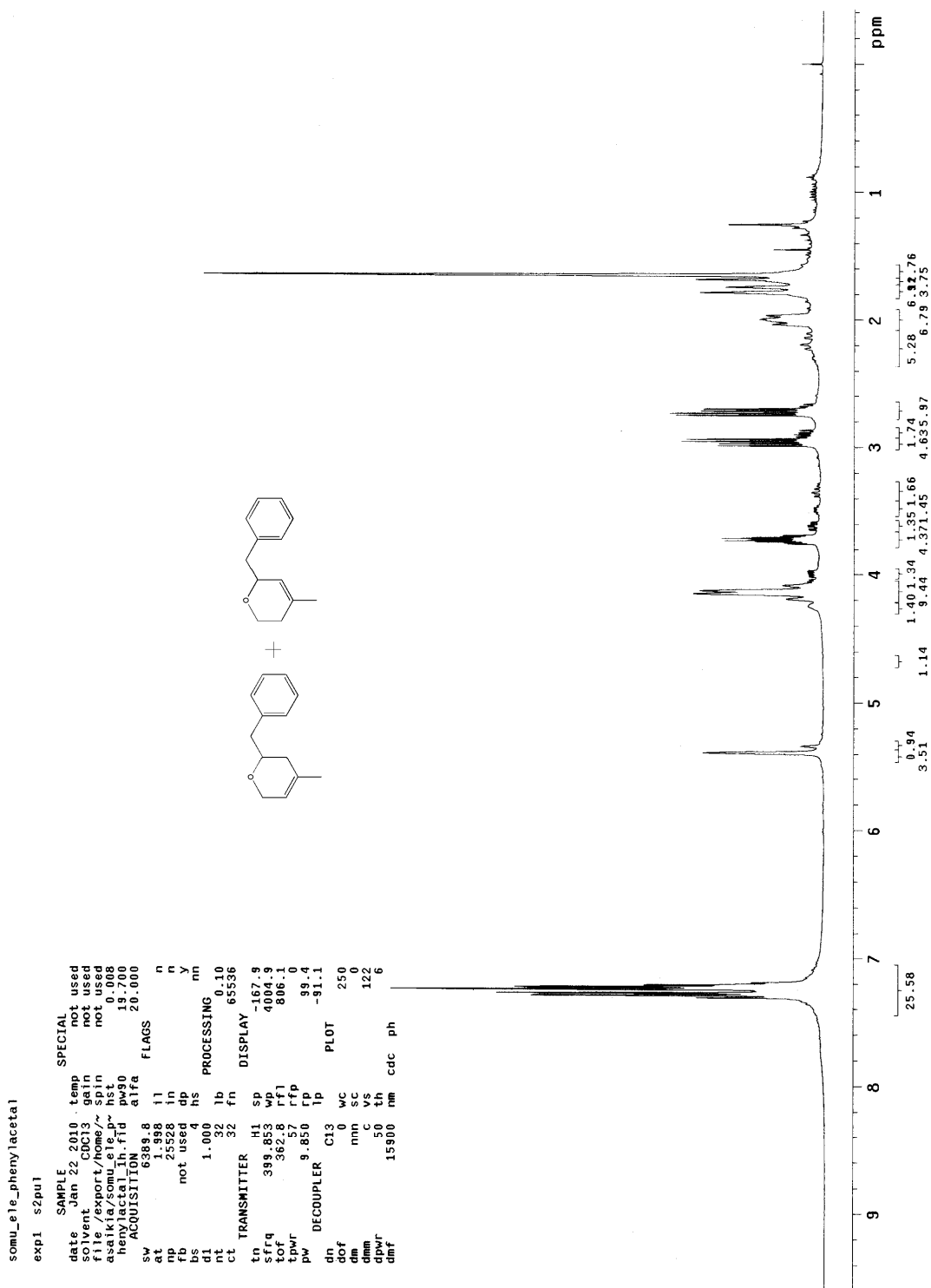
¹H NMR of **6h** & **7h**



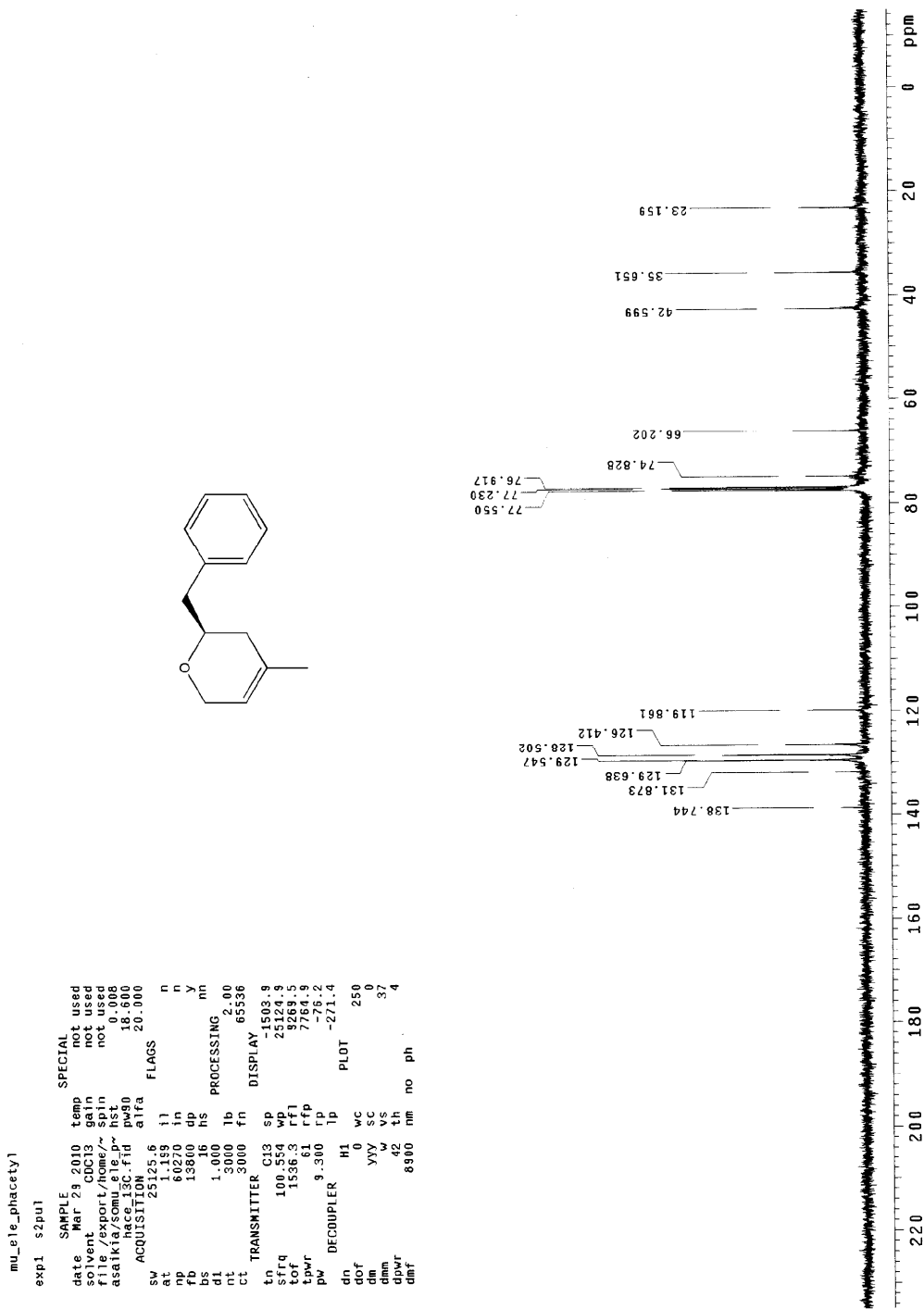
^{13}C NMR of **6h** & **7h**



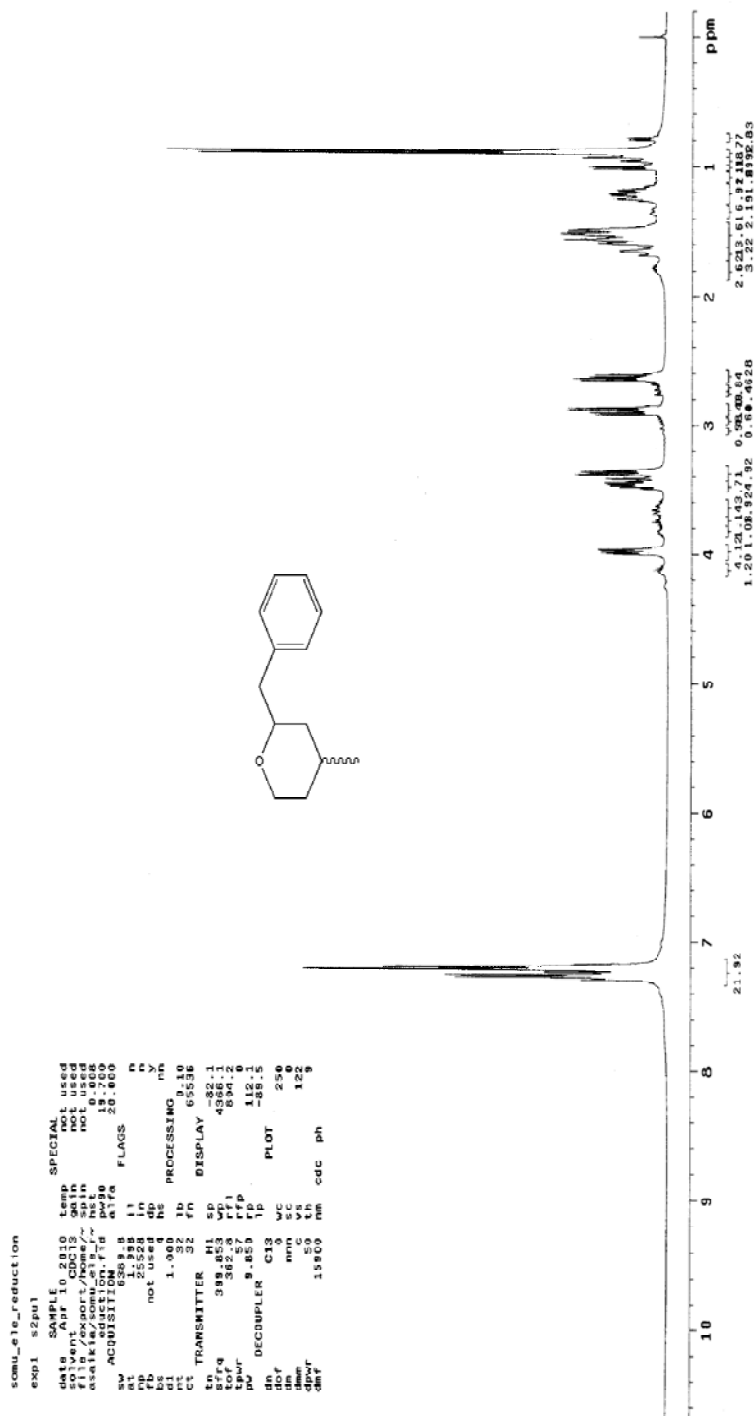
¹H NMR of **6i** & **7i**



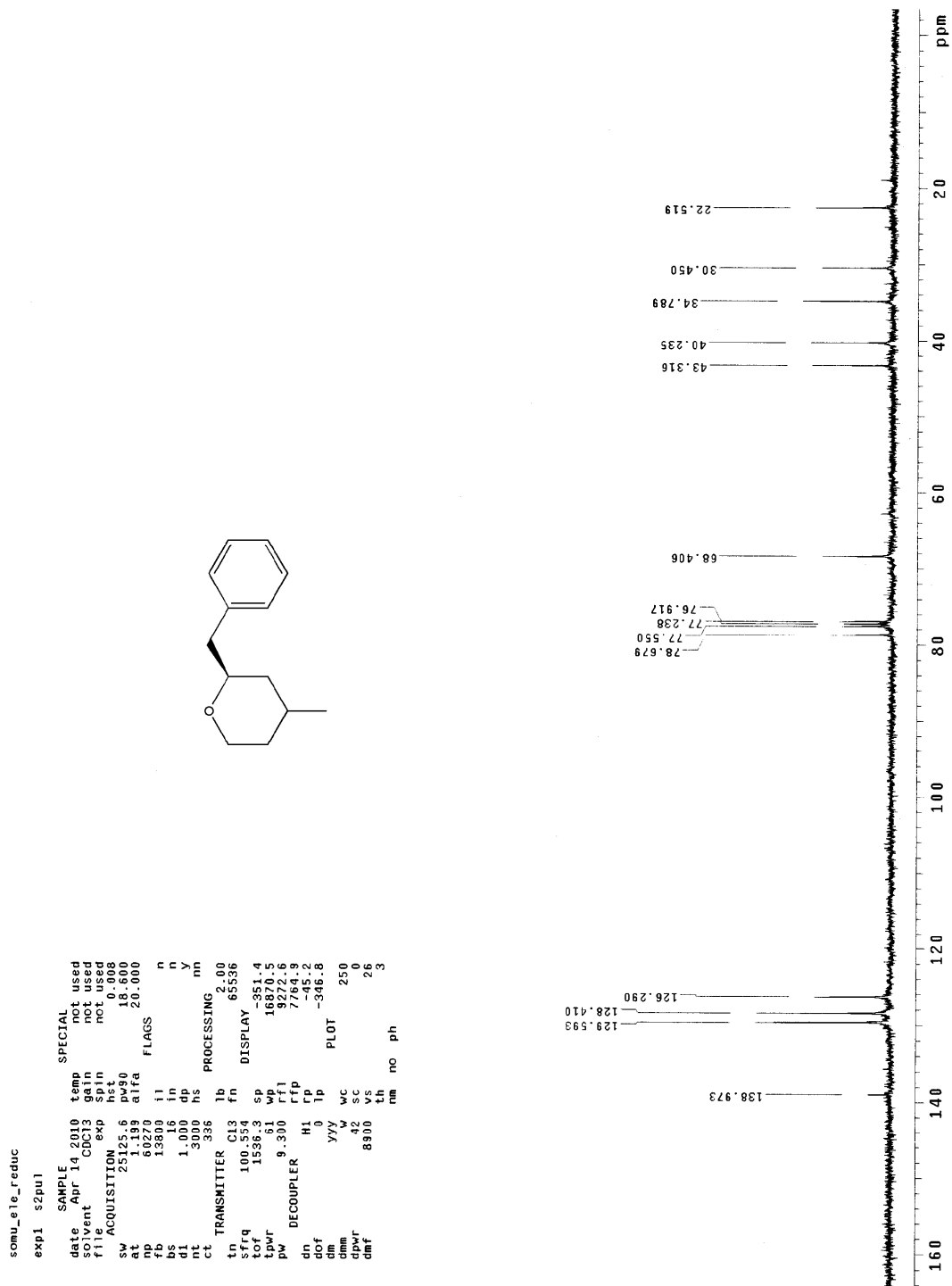
¹³C NMR of **6i**



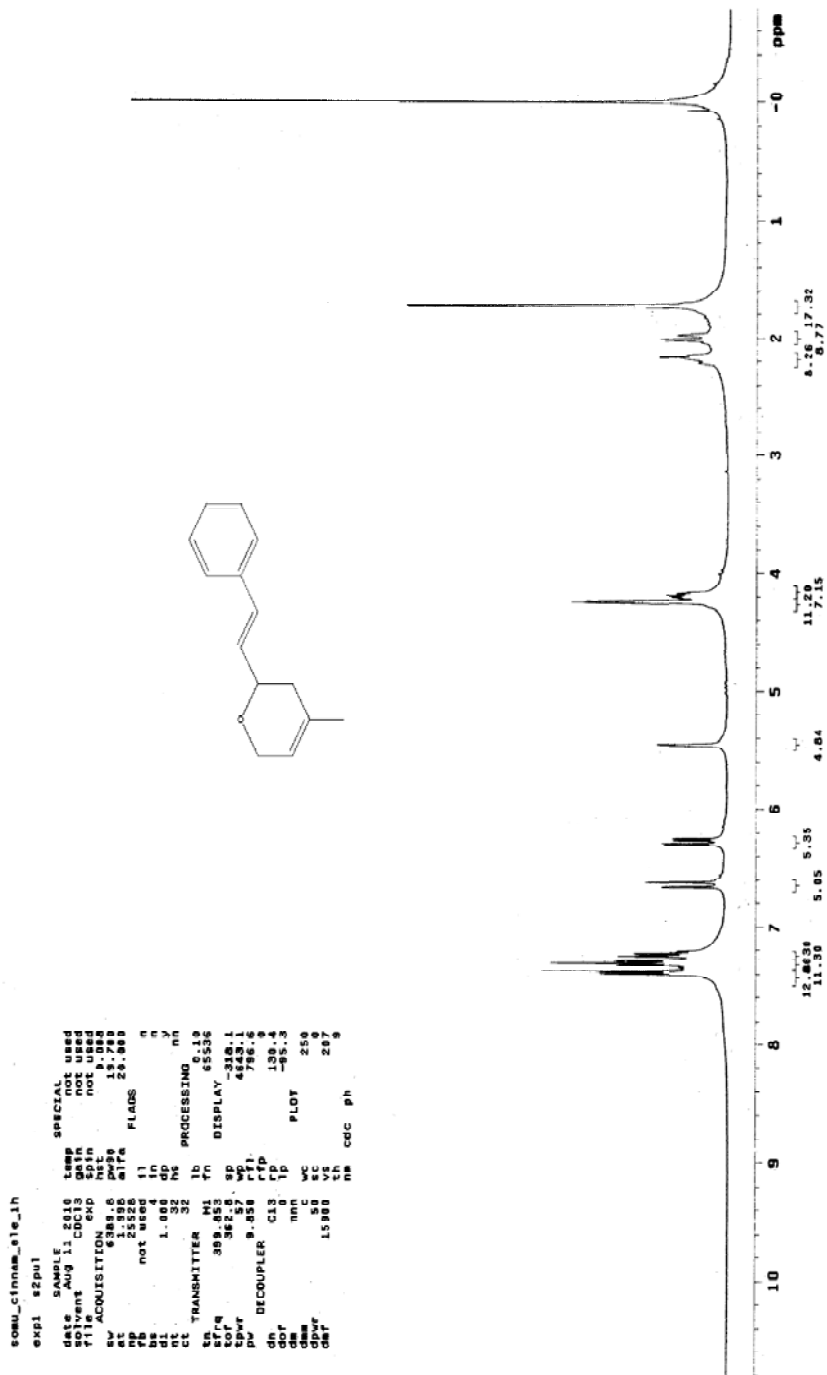
Hydrogenation product of **6i** & **7i**



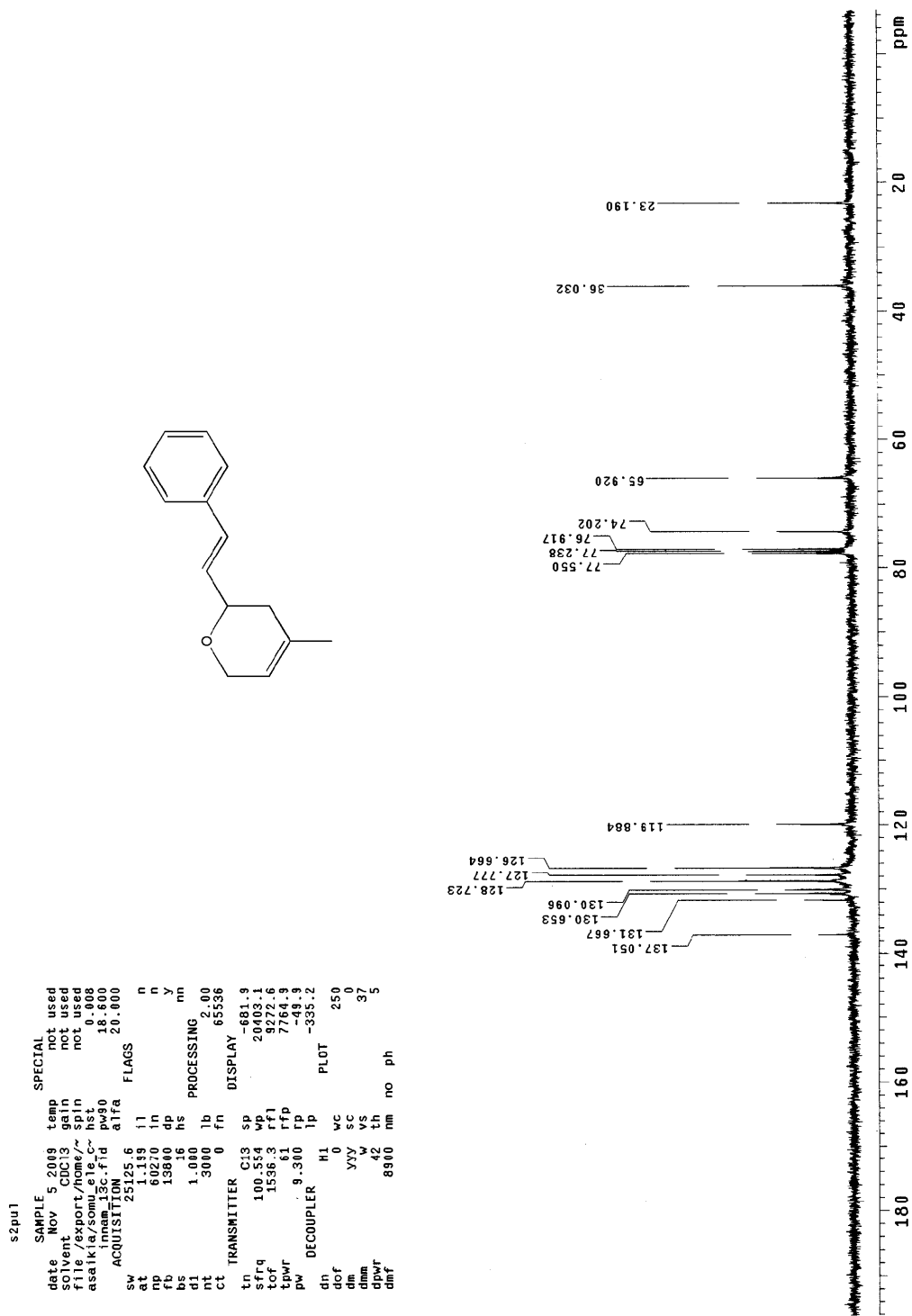
^{13}C NMR of hydrogenation product of **6i** & **7i** (Major product)



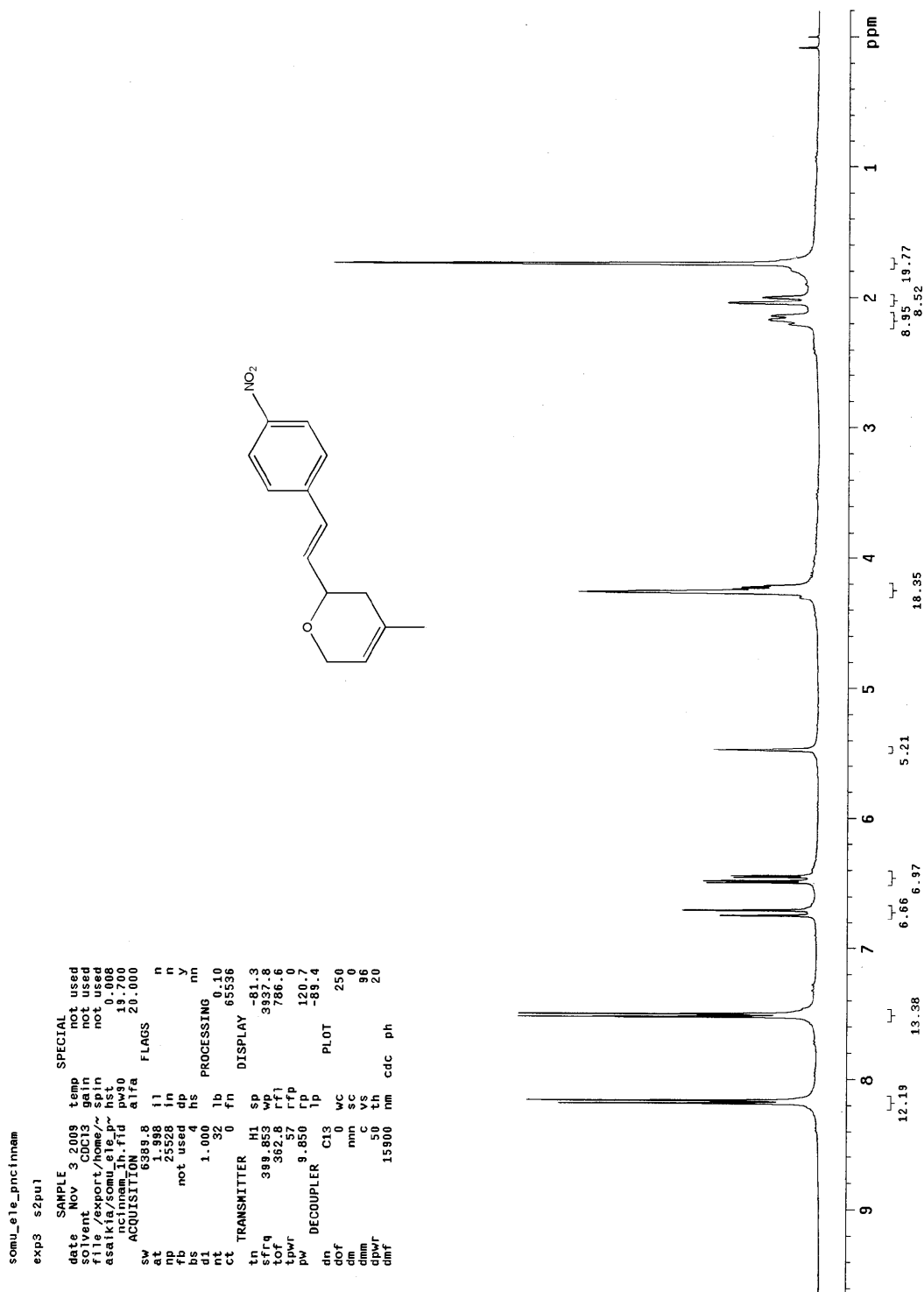
¹H NMR of 6j



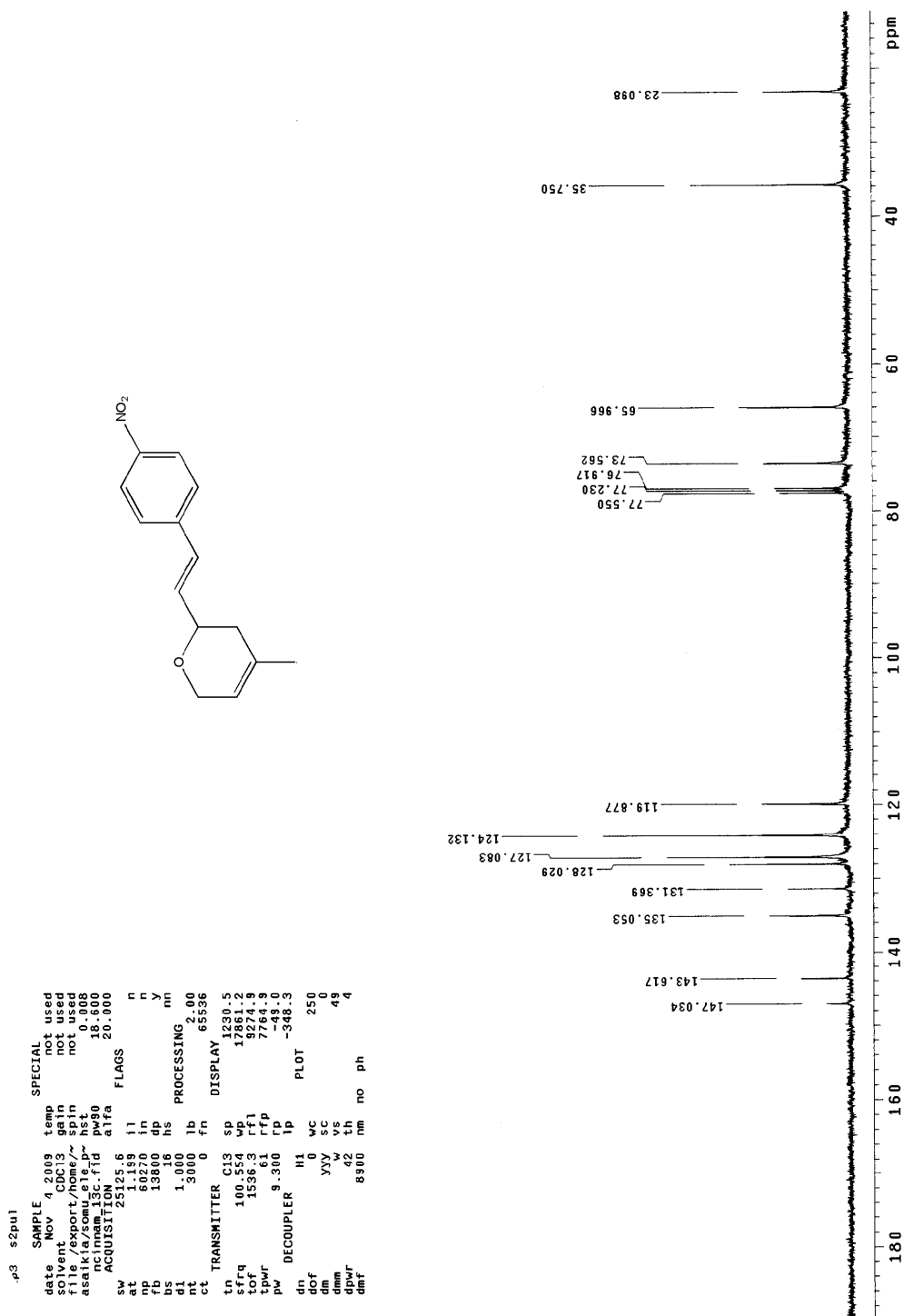
¹³C NMR of 6j



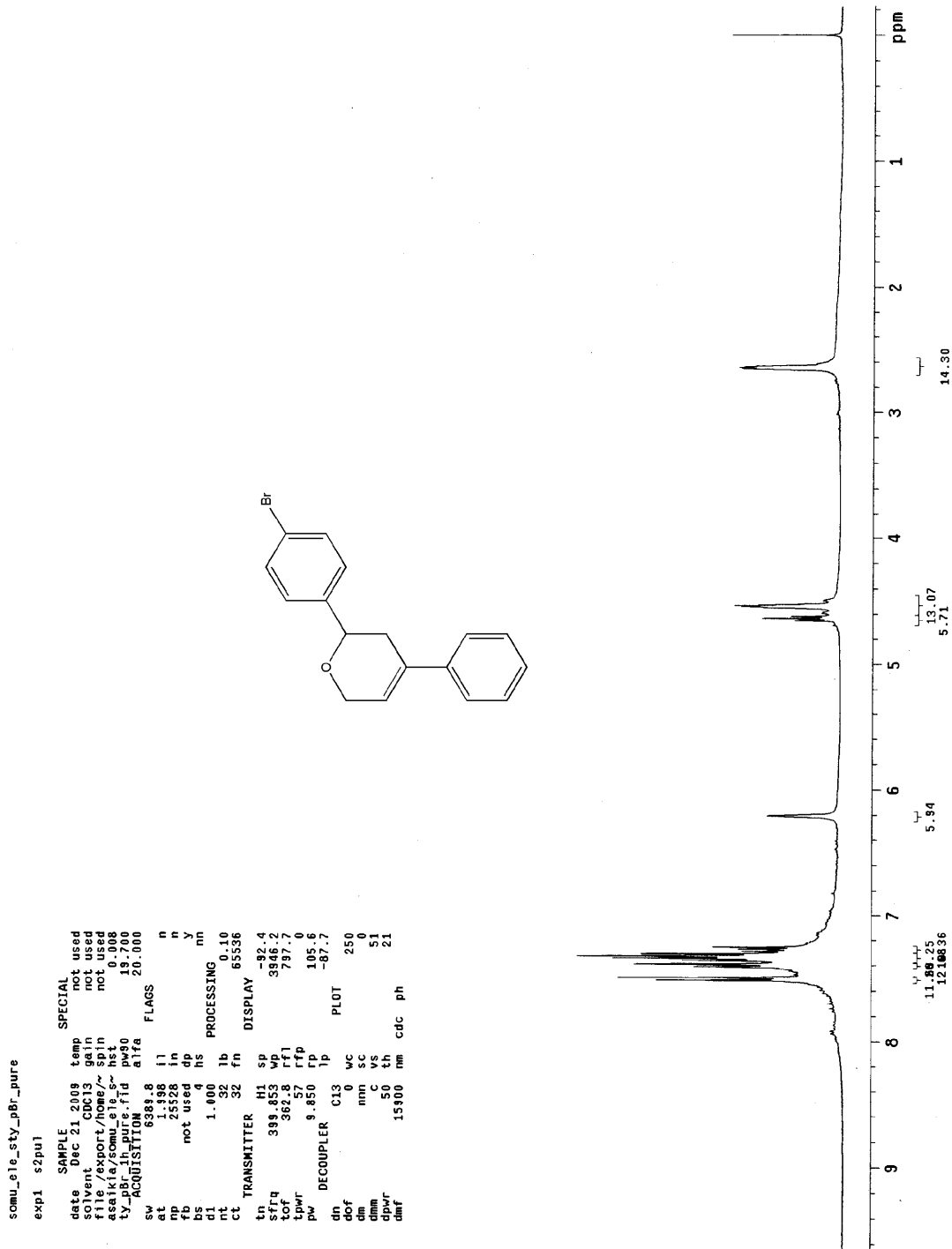
¹H NMR of 6k



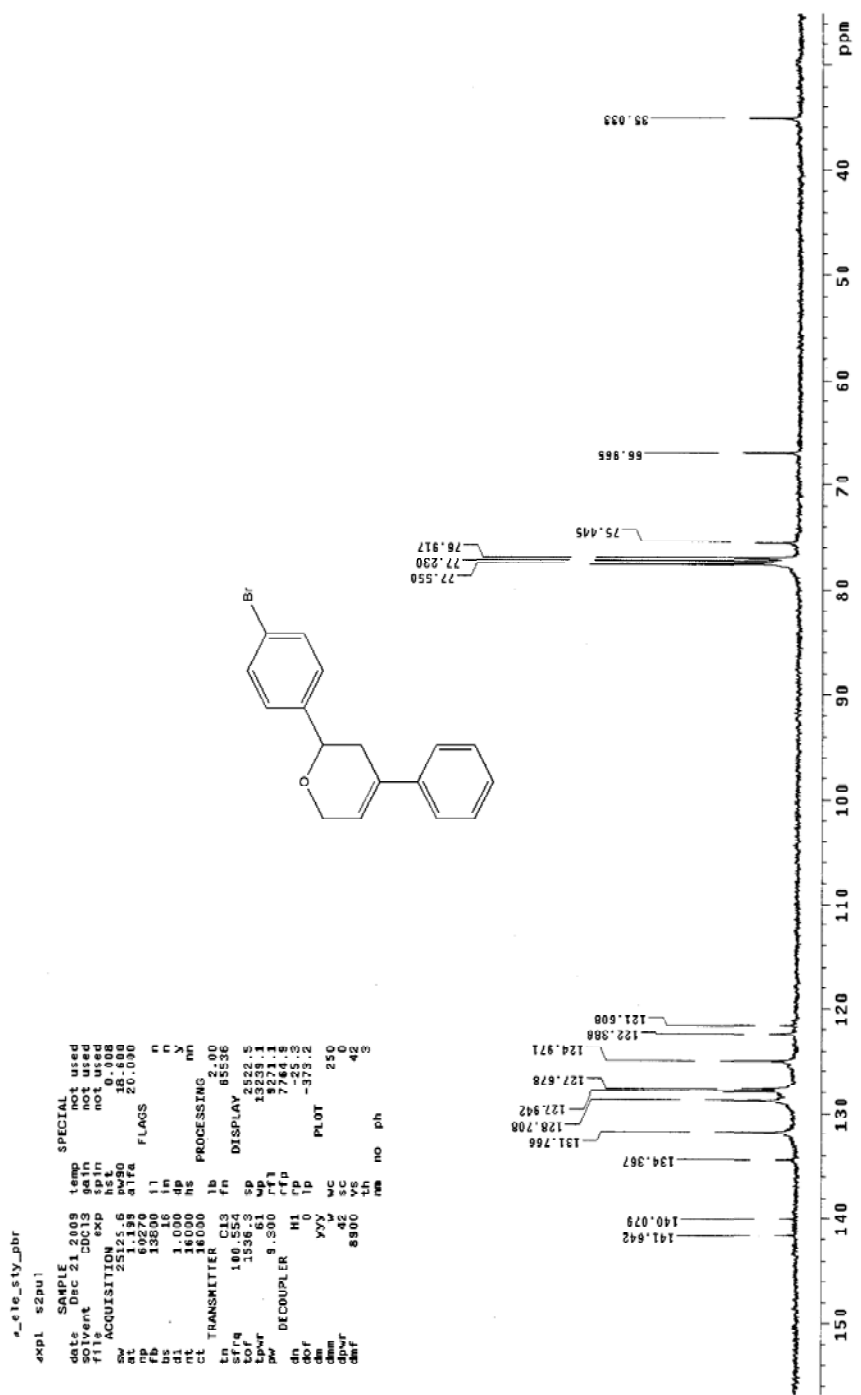
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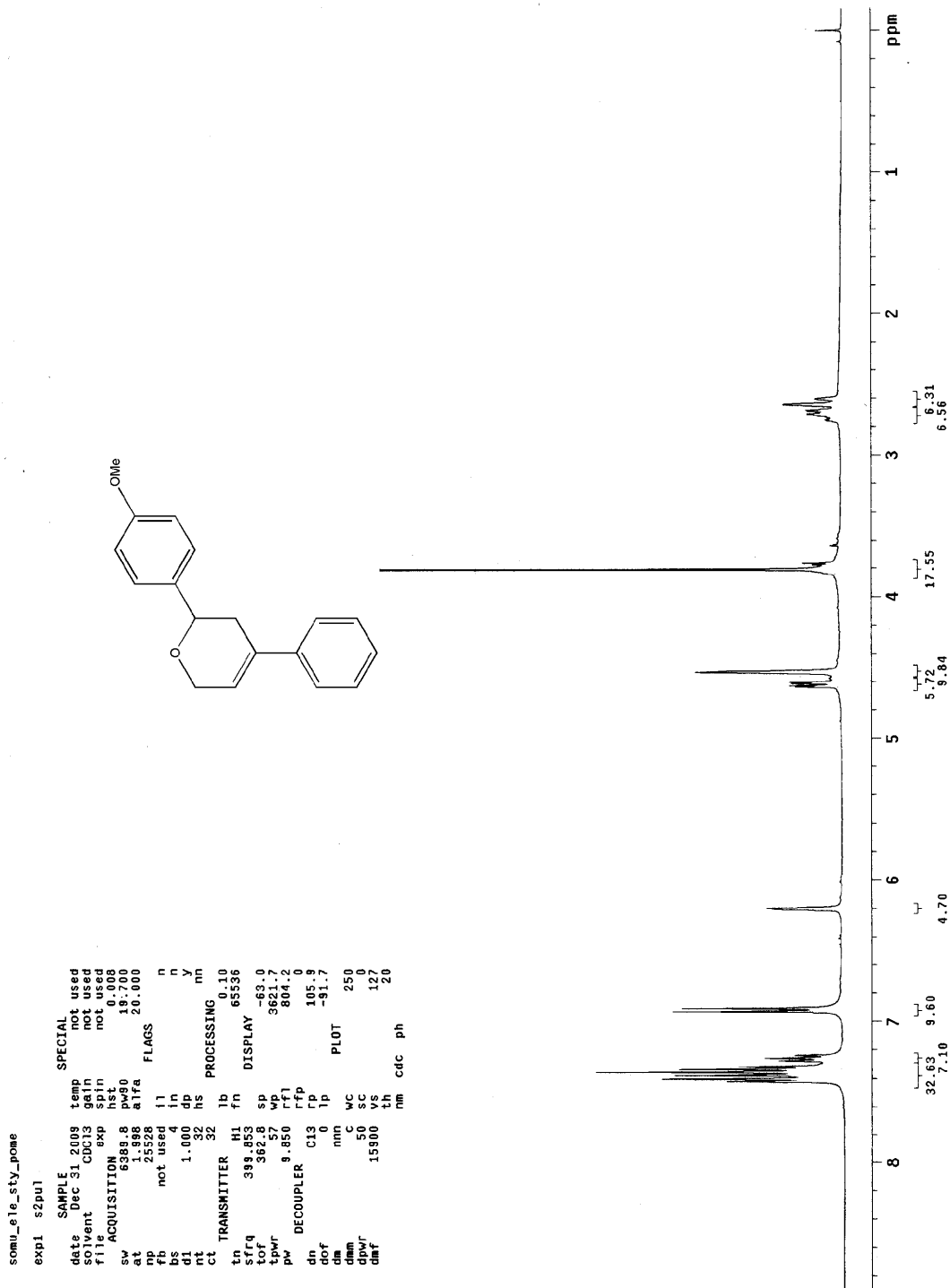
¹H NMR of **6l**



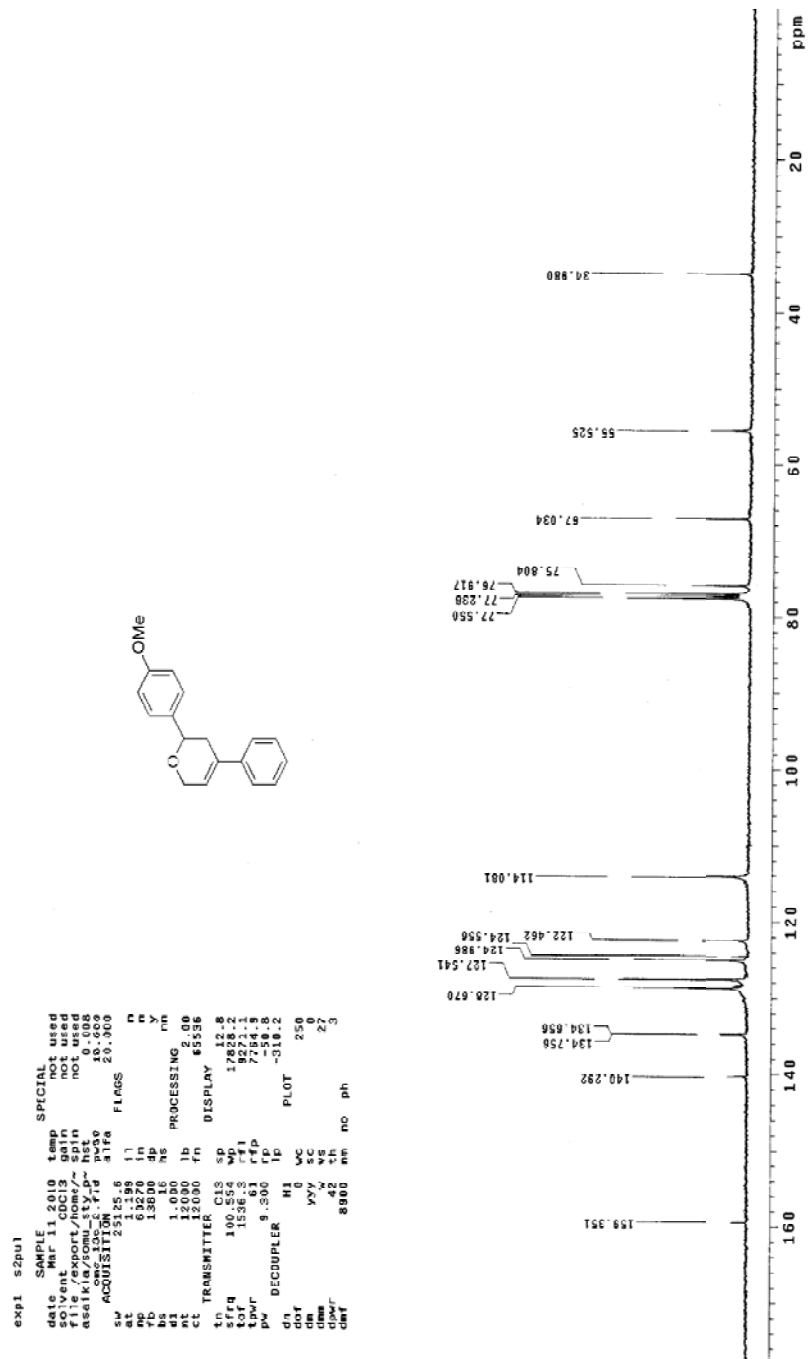
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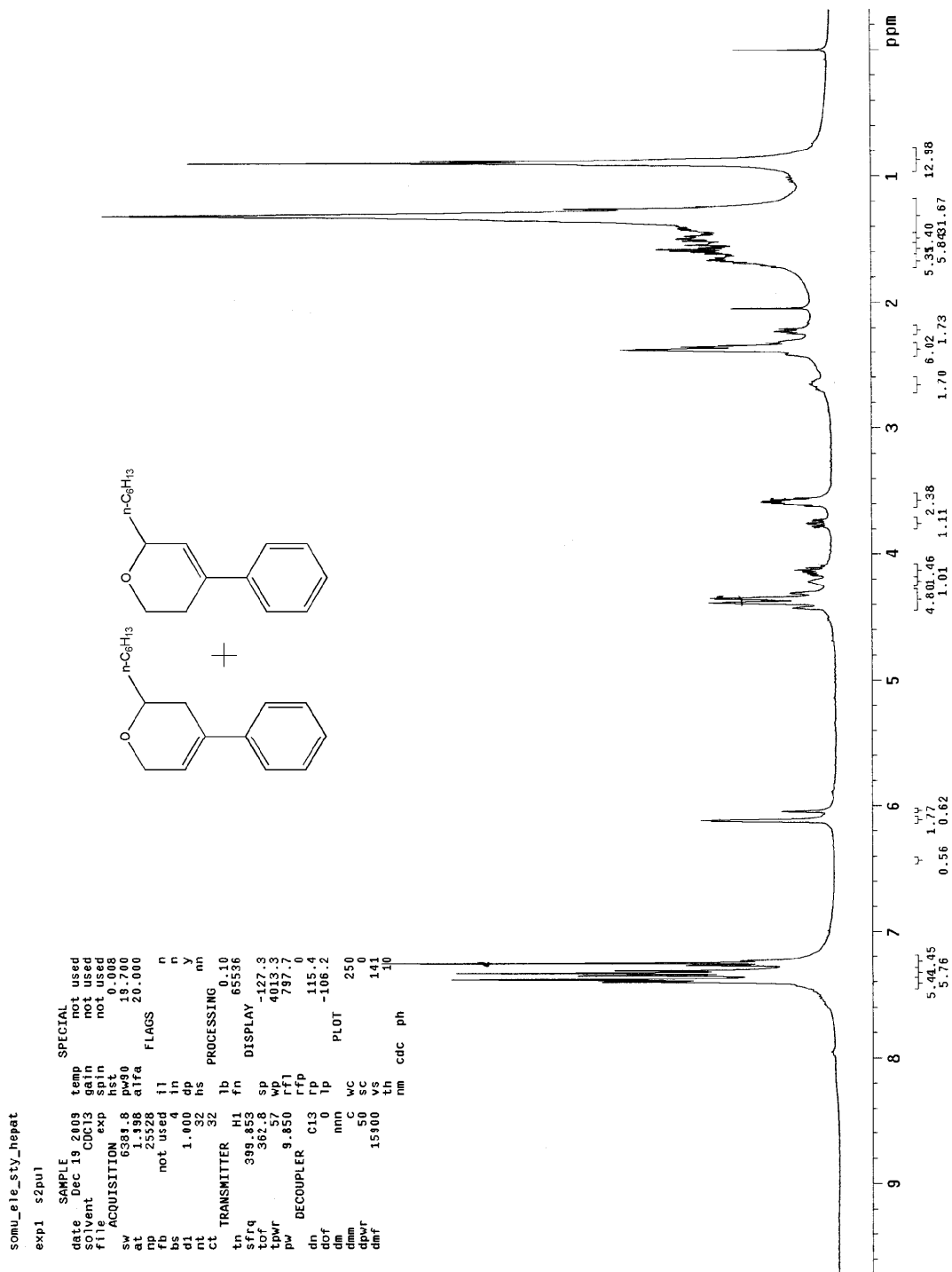
¹H NMR of 6m



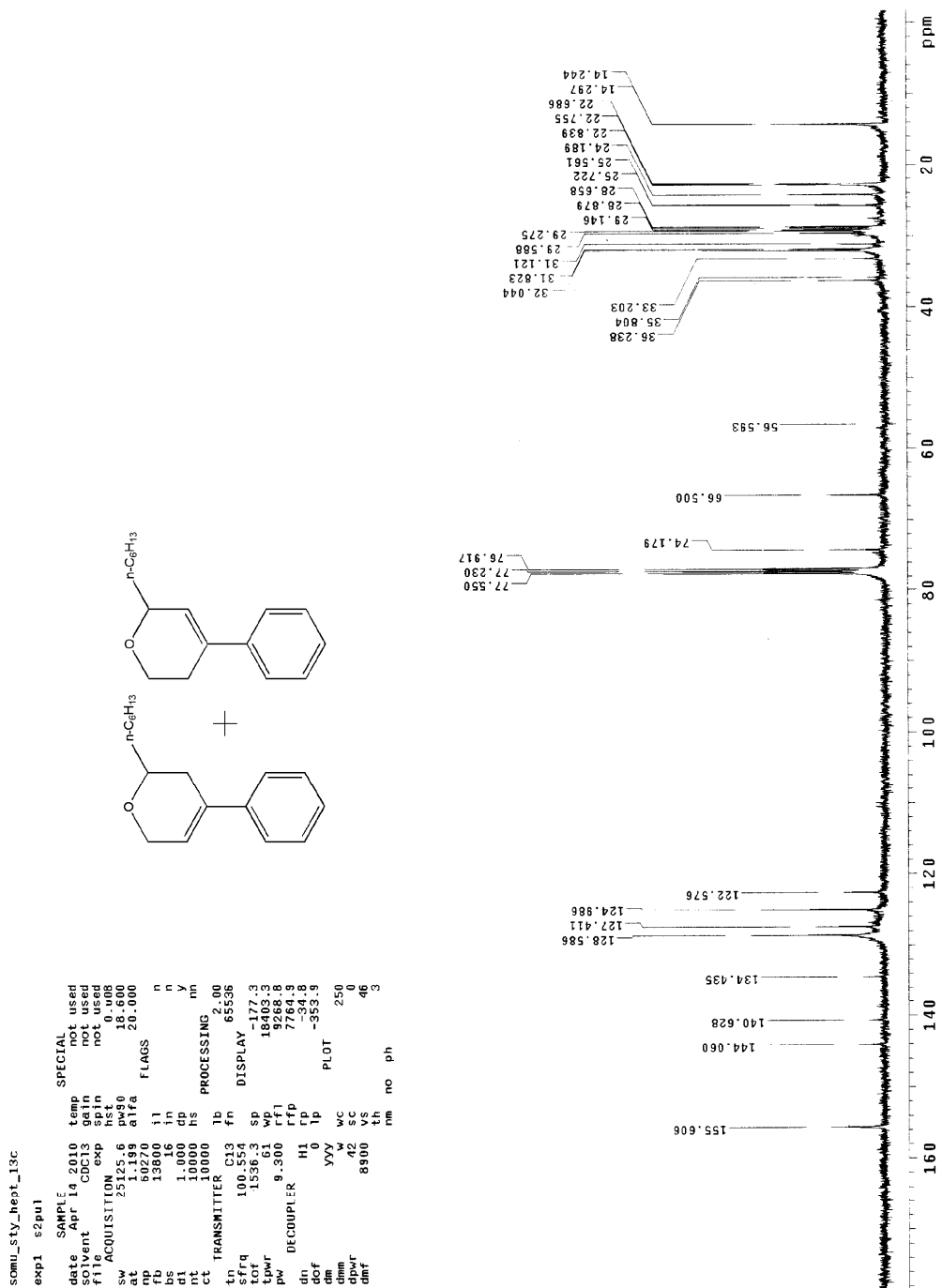
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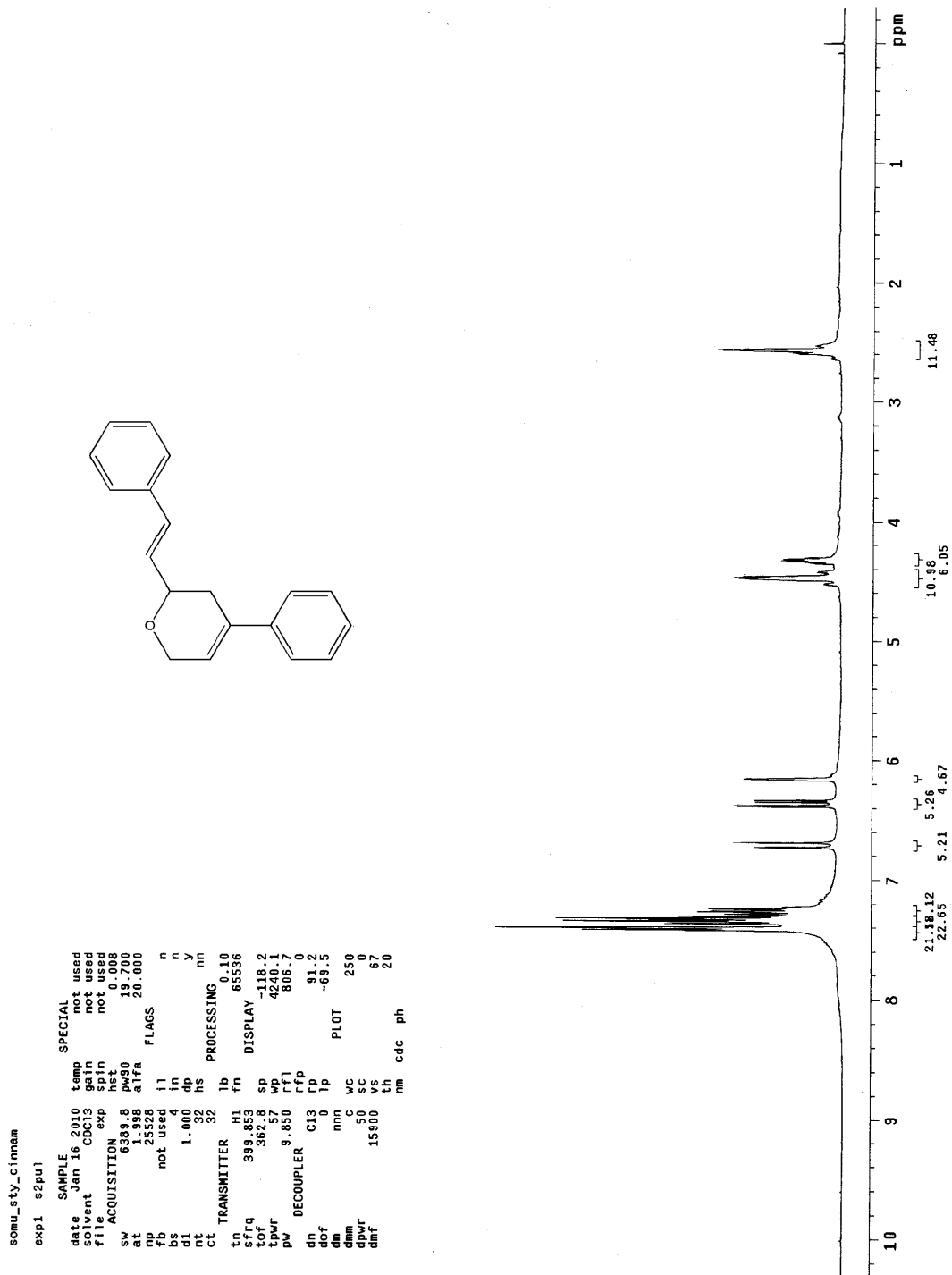
¹H NMR of 6n & 7n



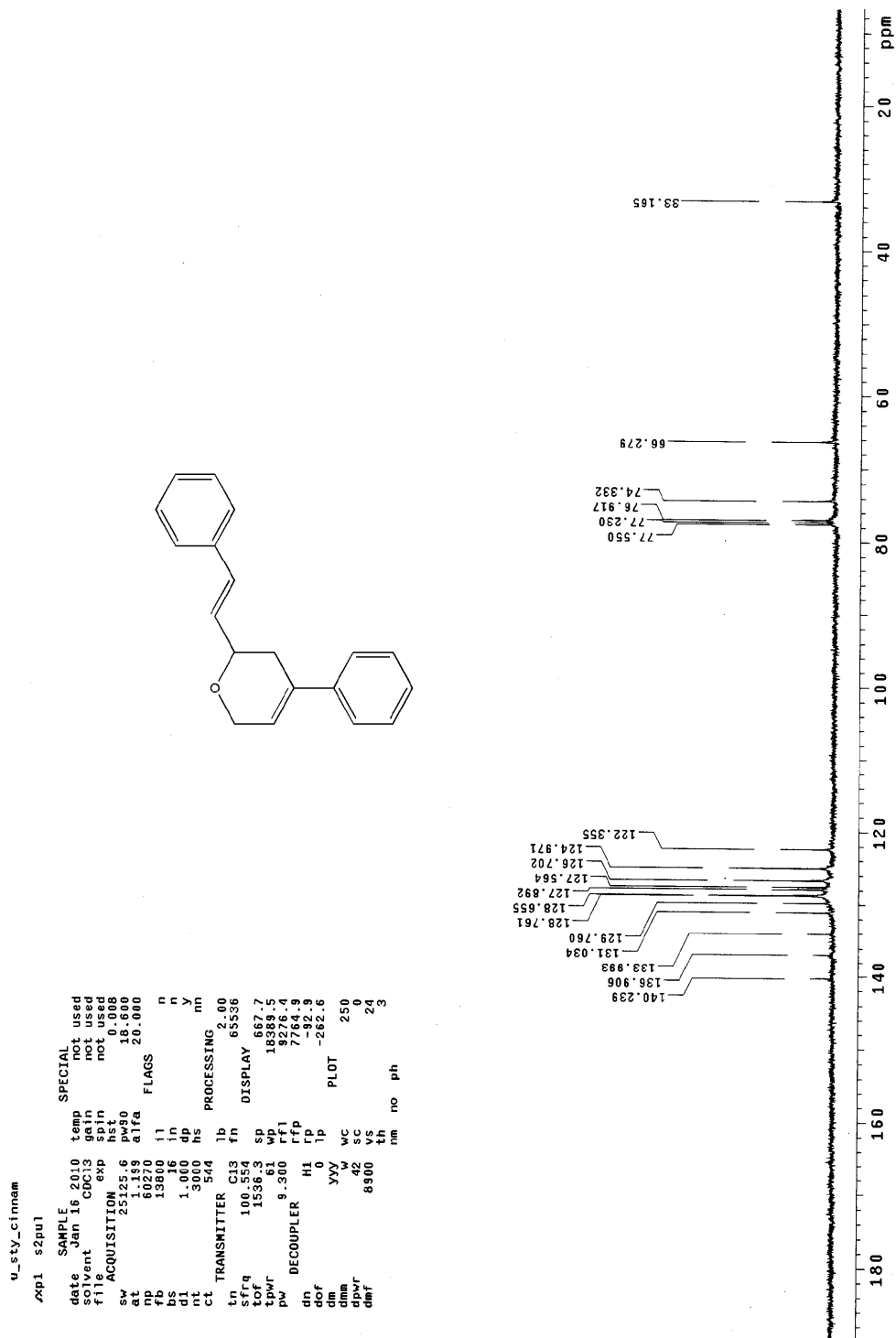
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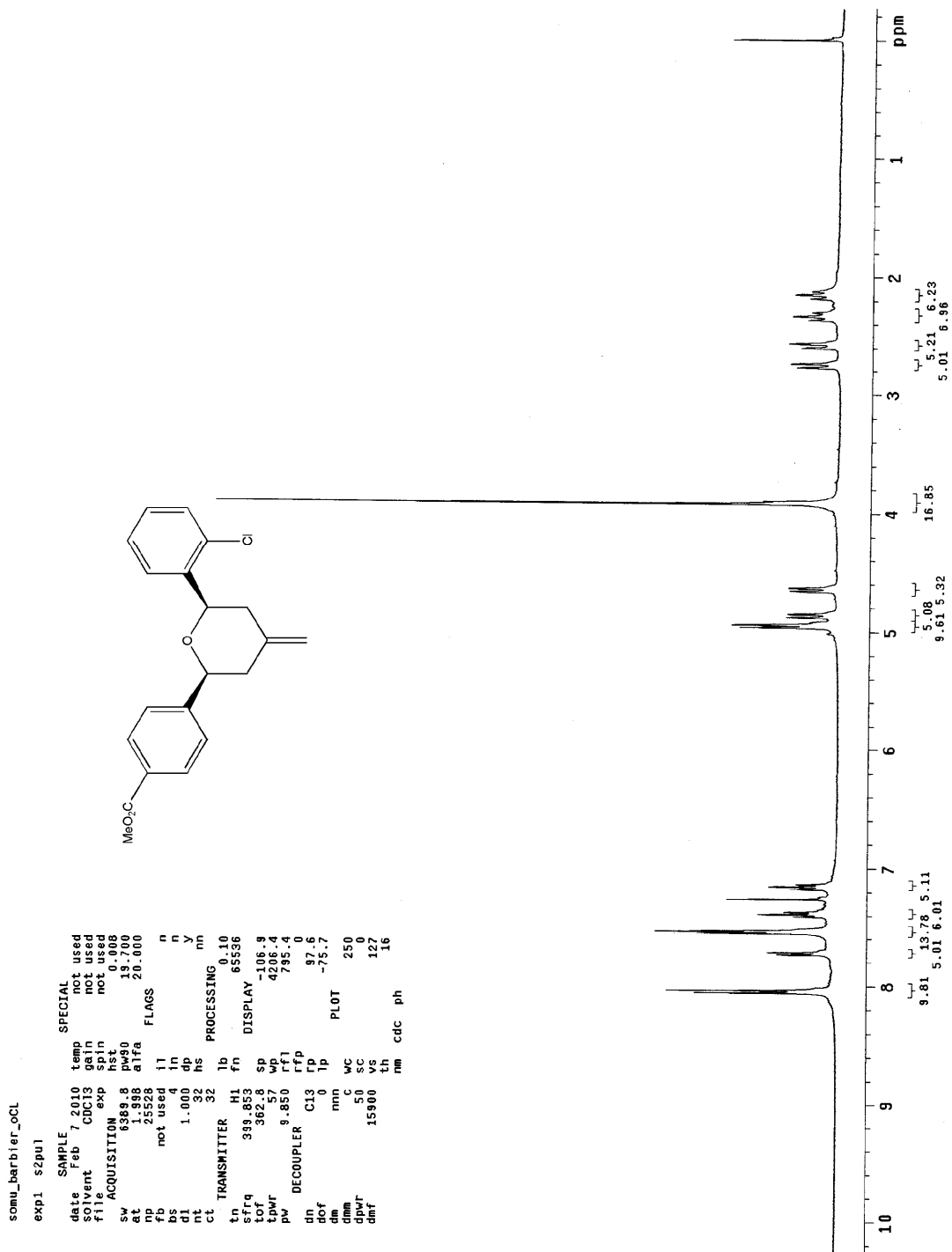
¹H NMR of **60**



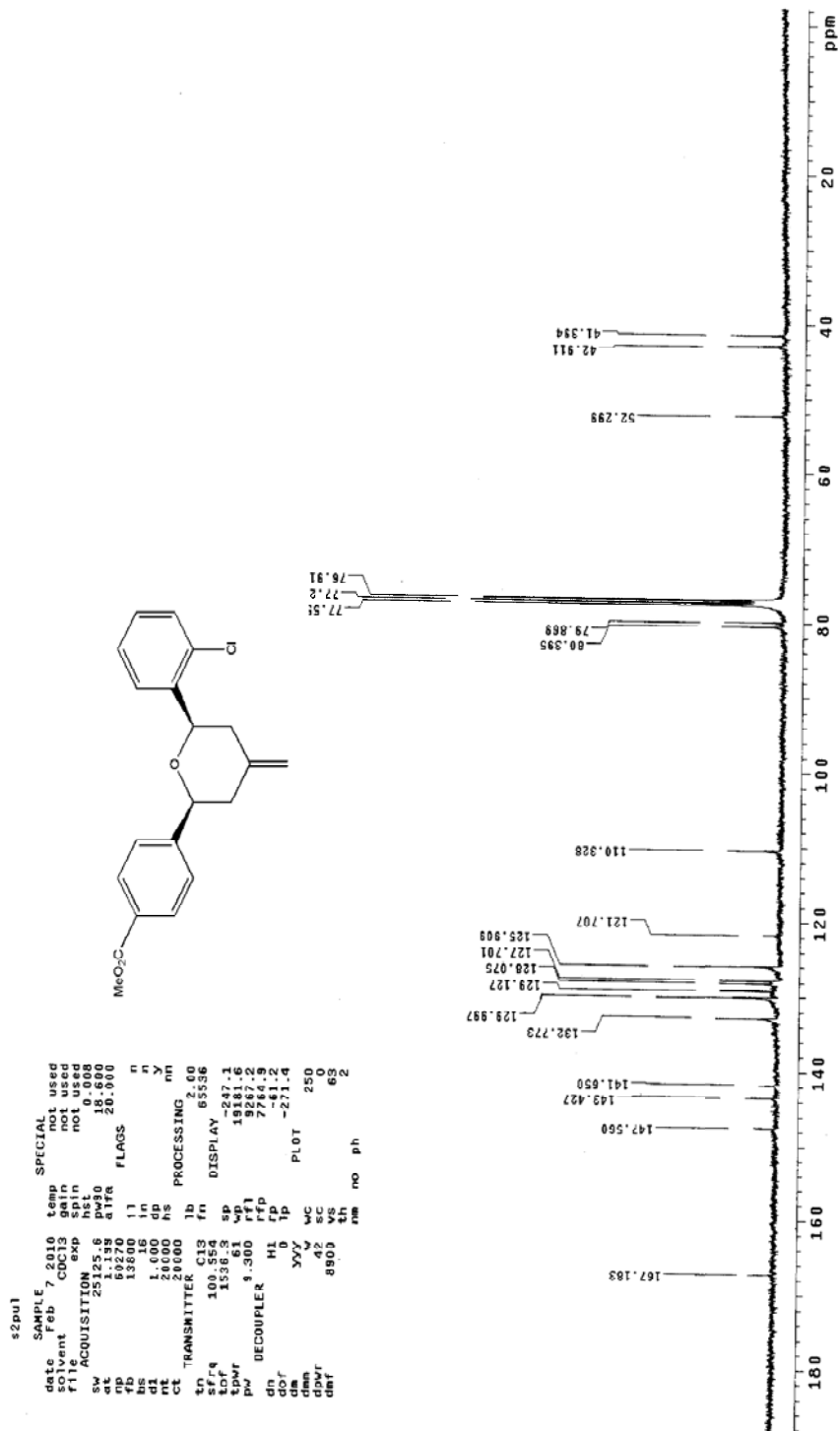
¹³C NMR of 60



¹H NMR of **8p**



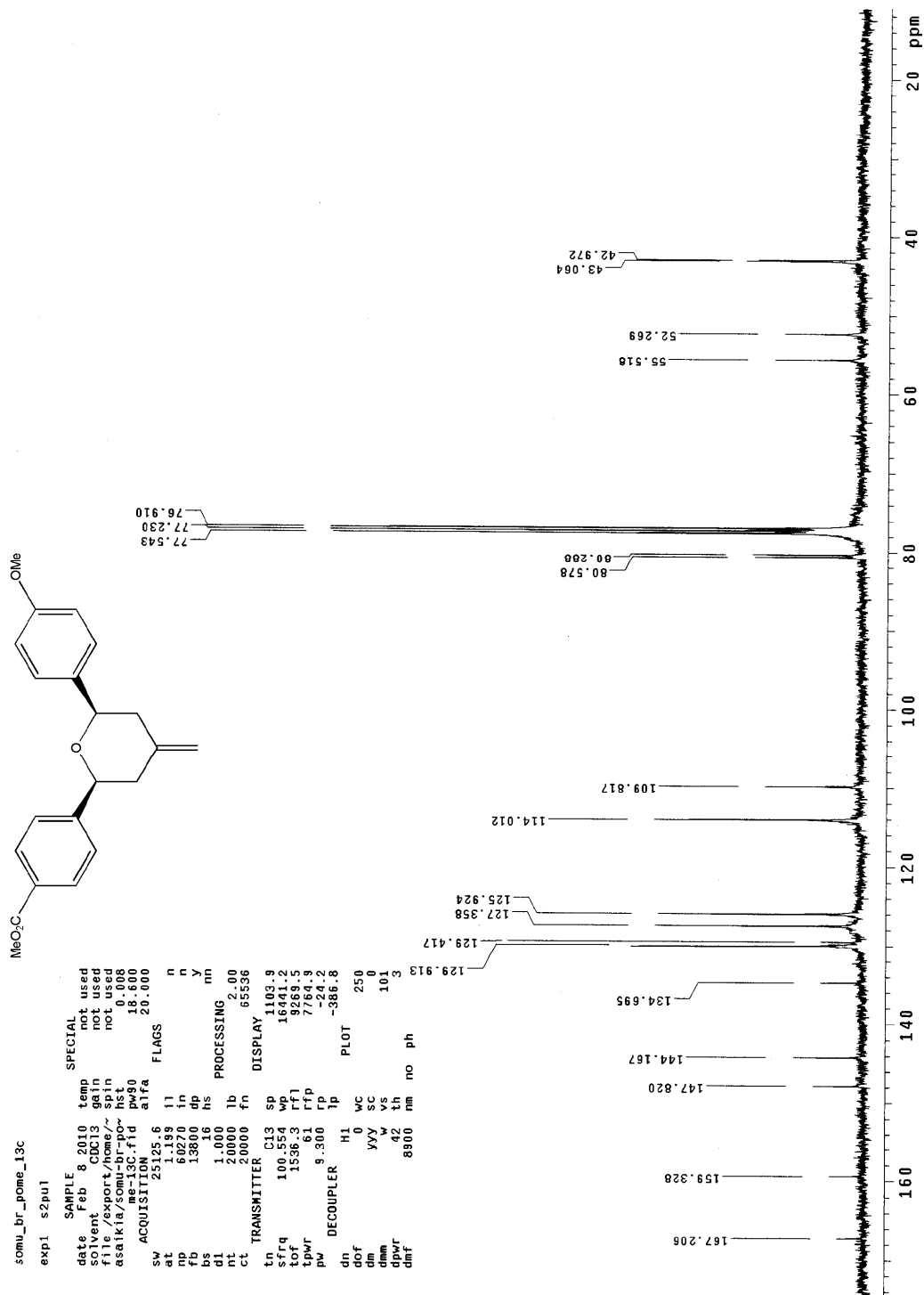
¹³C NMR of **8p**



¹H NMR of 8q

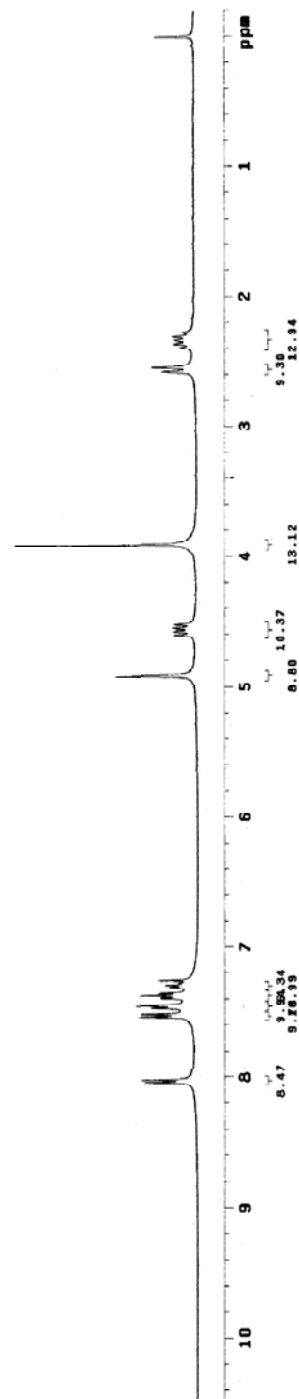
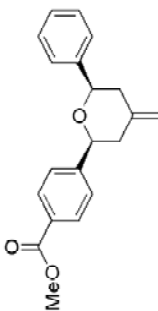


¹³C NMR of **8q**

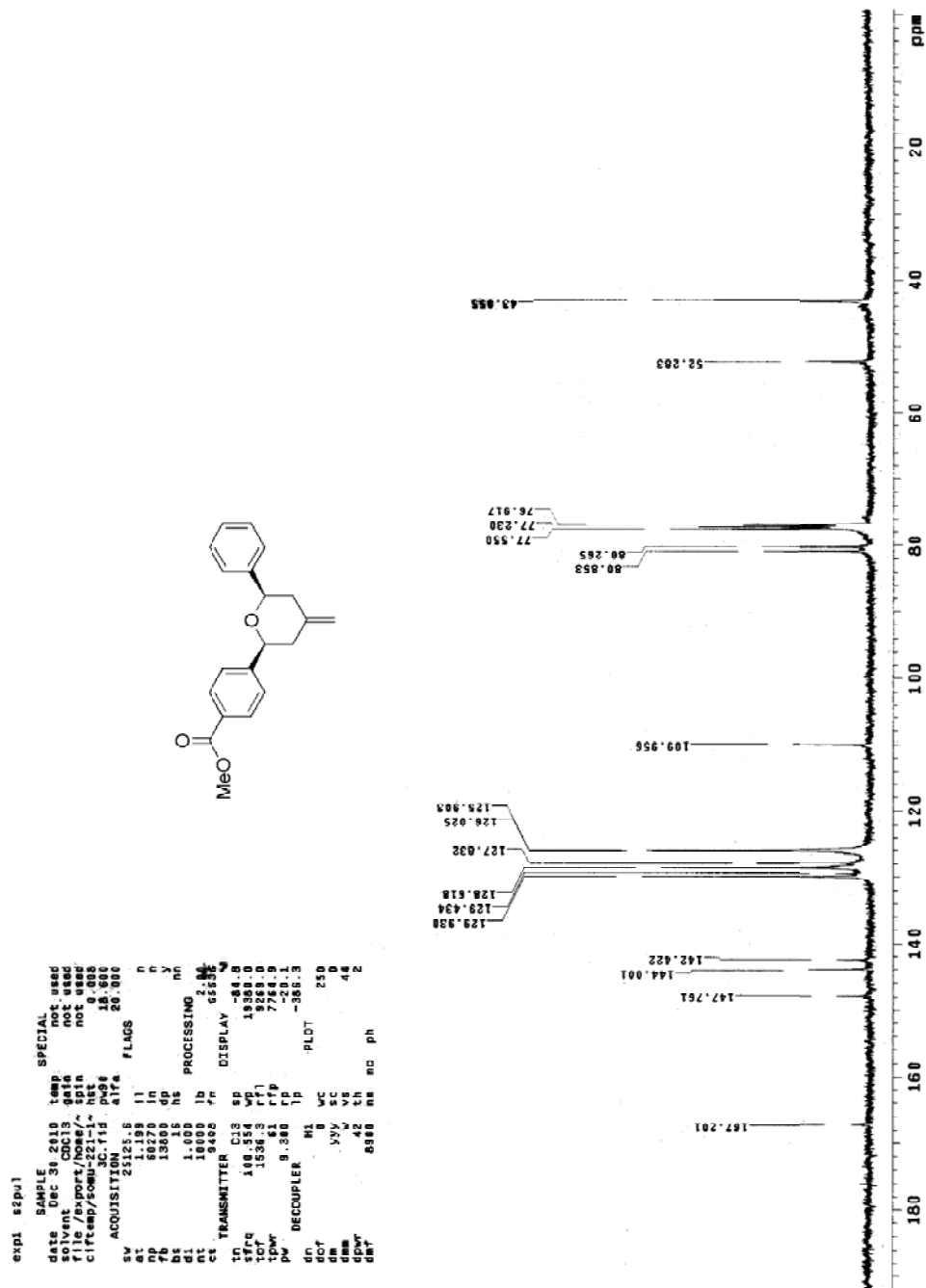


^1H NMR of 8r

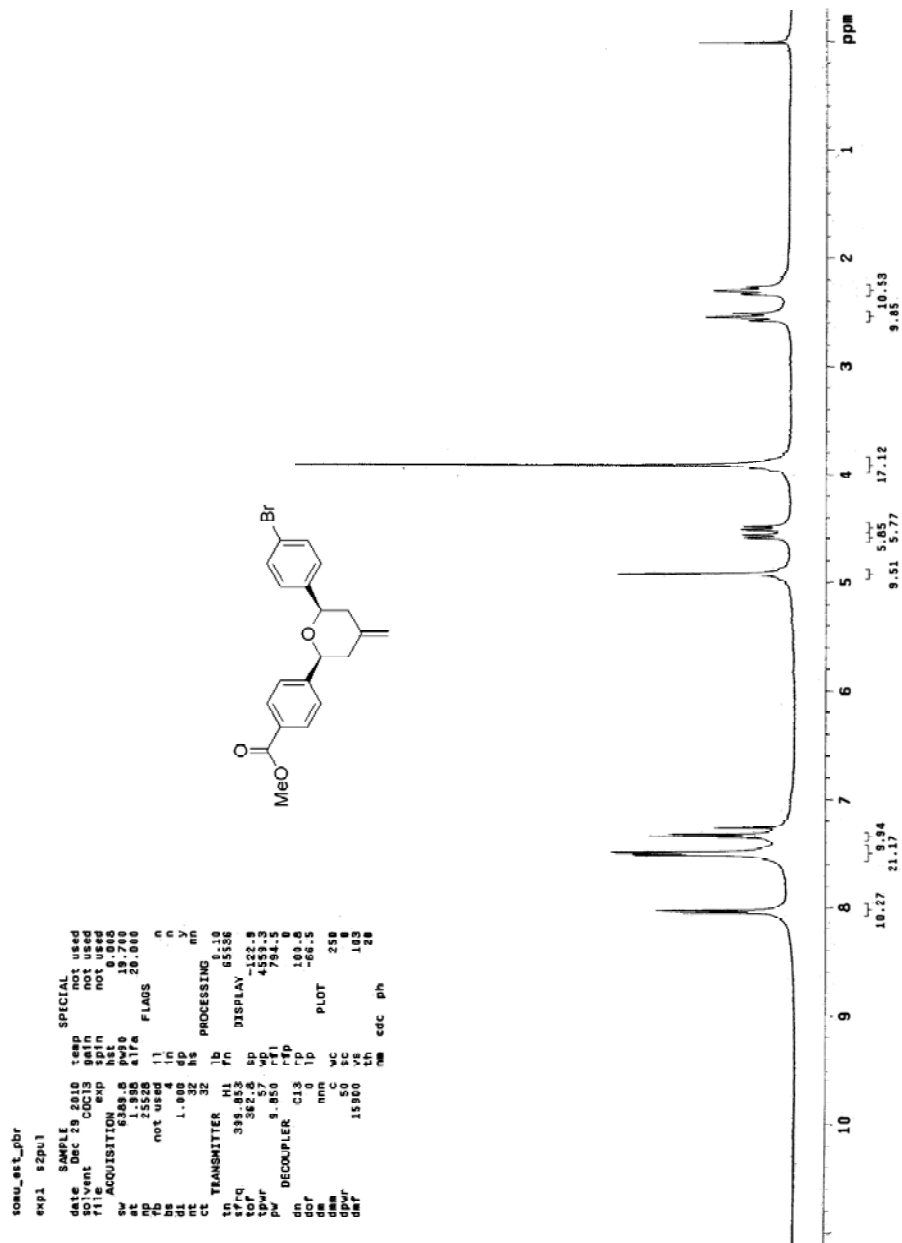
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expt  szdu1  
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solvent   Oct 13      gain      not used  
fl1       not used  
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sw        6389.8      pvs0     19.760  
nt        21528      n1       26.563  
wb        not used   fl       FLABS  
bt        1.004      in       n  
nt        1.38       nt       n  
ct        32        n1  
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IN TRANSMITTER  HI  lb  9.18  
rfq           398.653  rn  DISPLAY  6538  
tof           312.0   sp  
tpr           8.57   wf  422.8  
pw            8.859  rfp  793.8  
dc           c13  fp  151.7  
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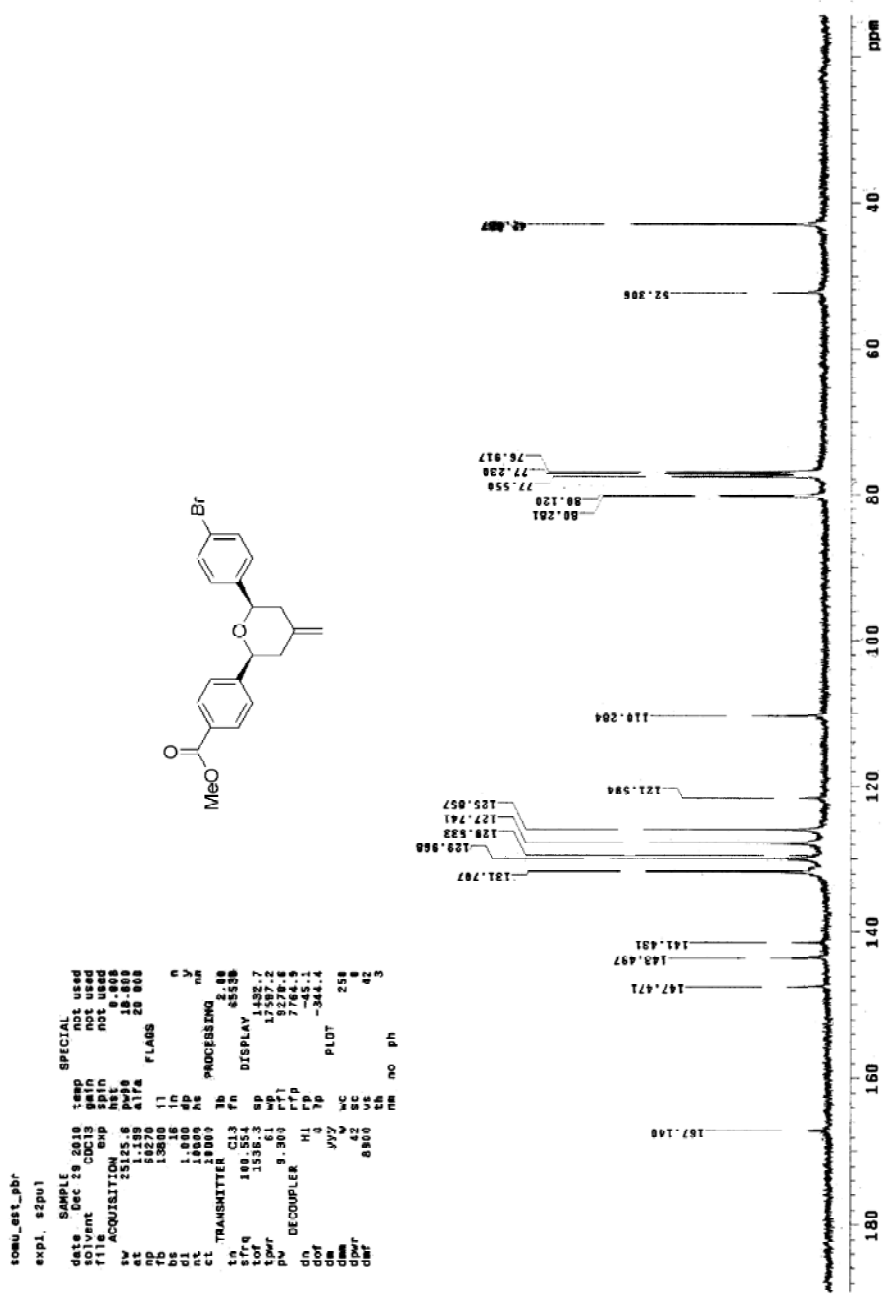
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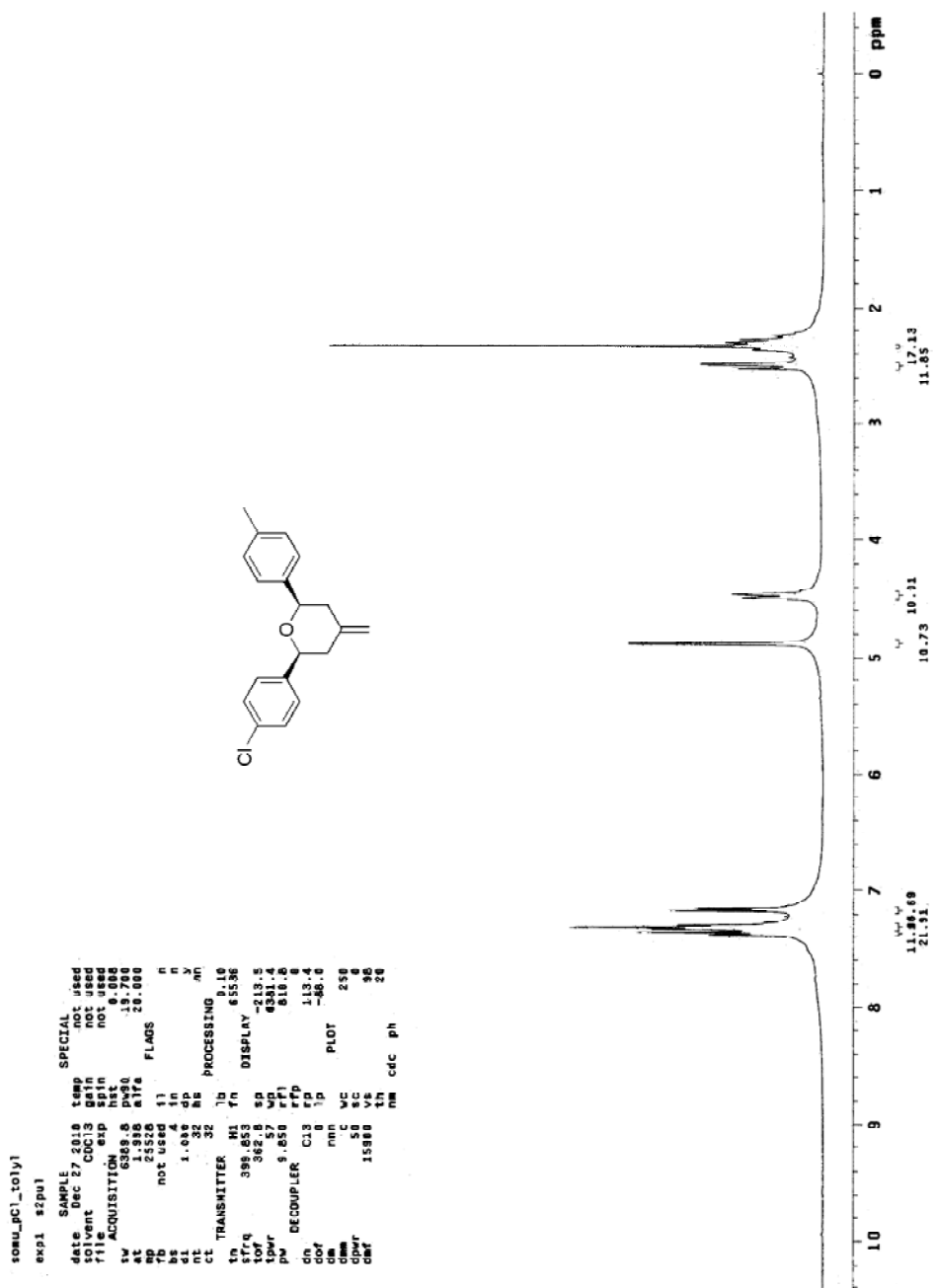
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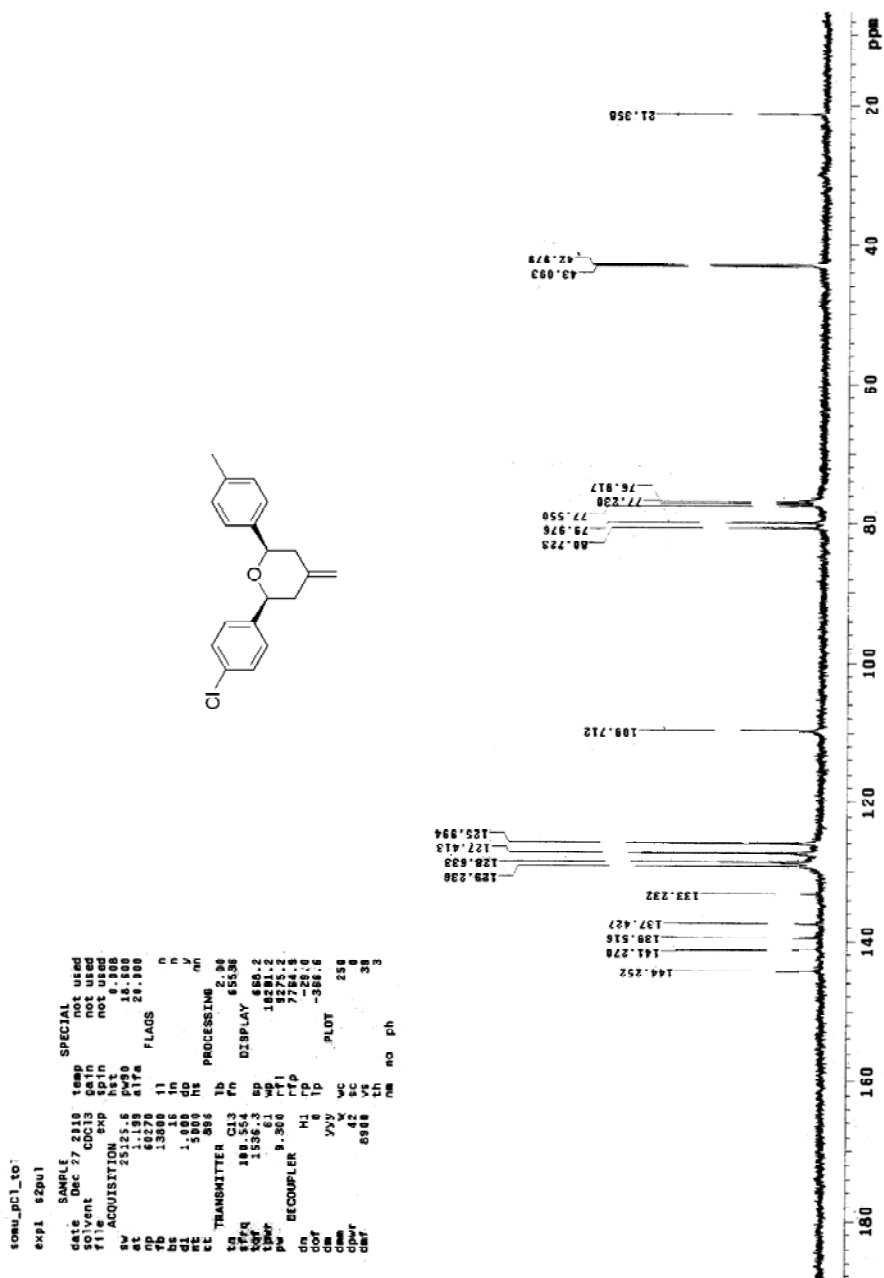
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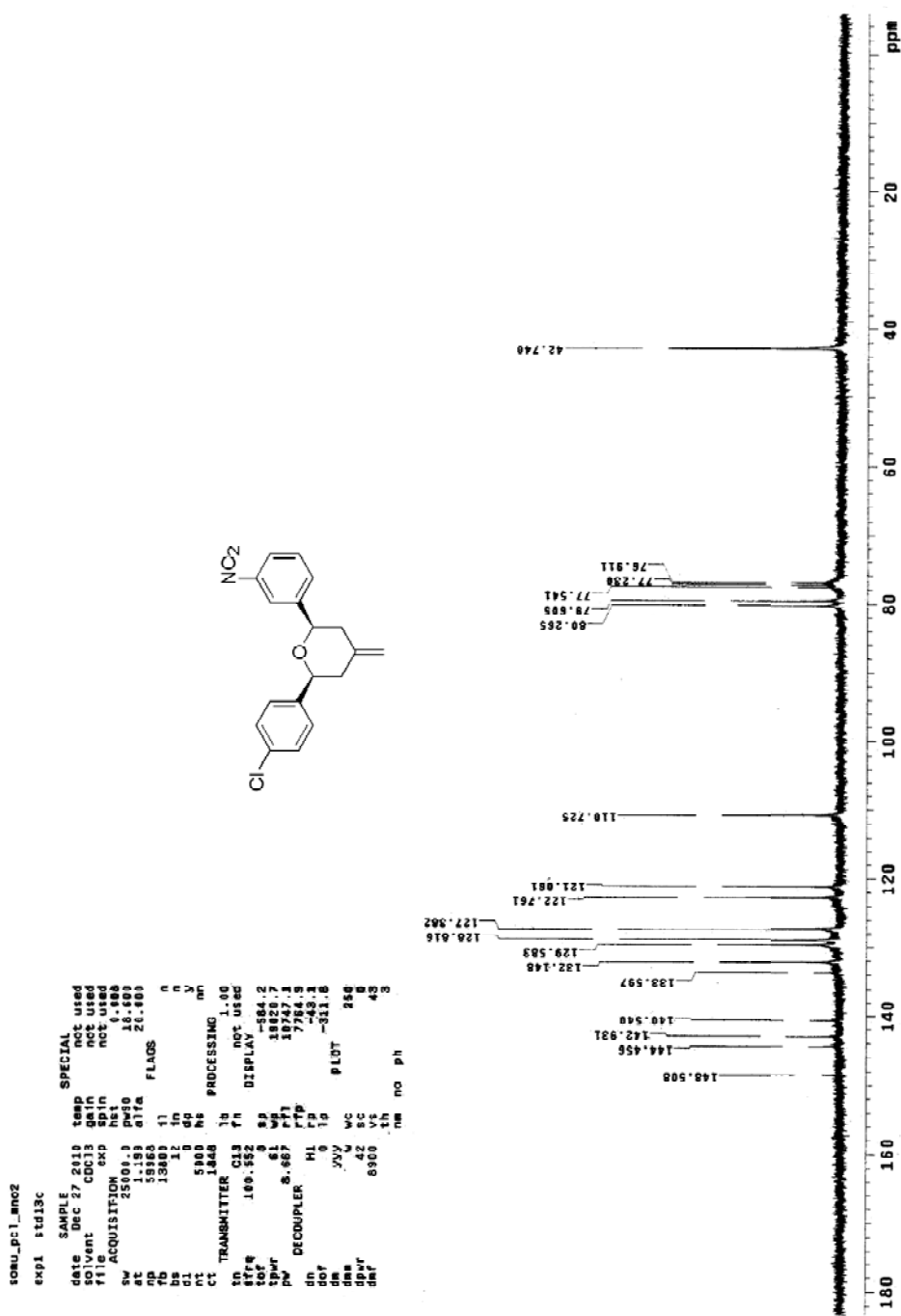
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¹³C NMR of 8t



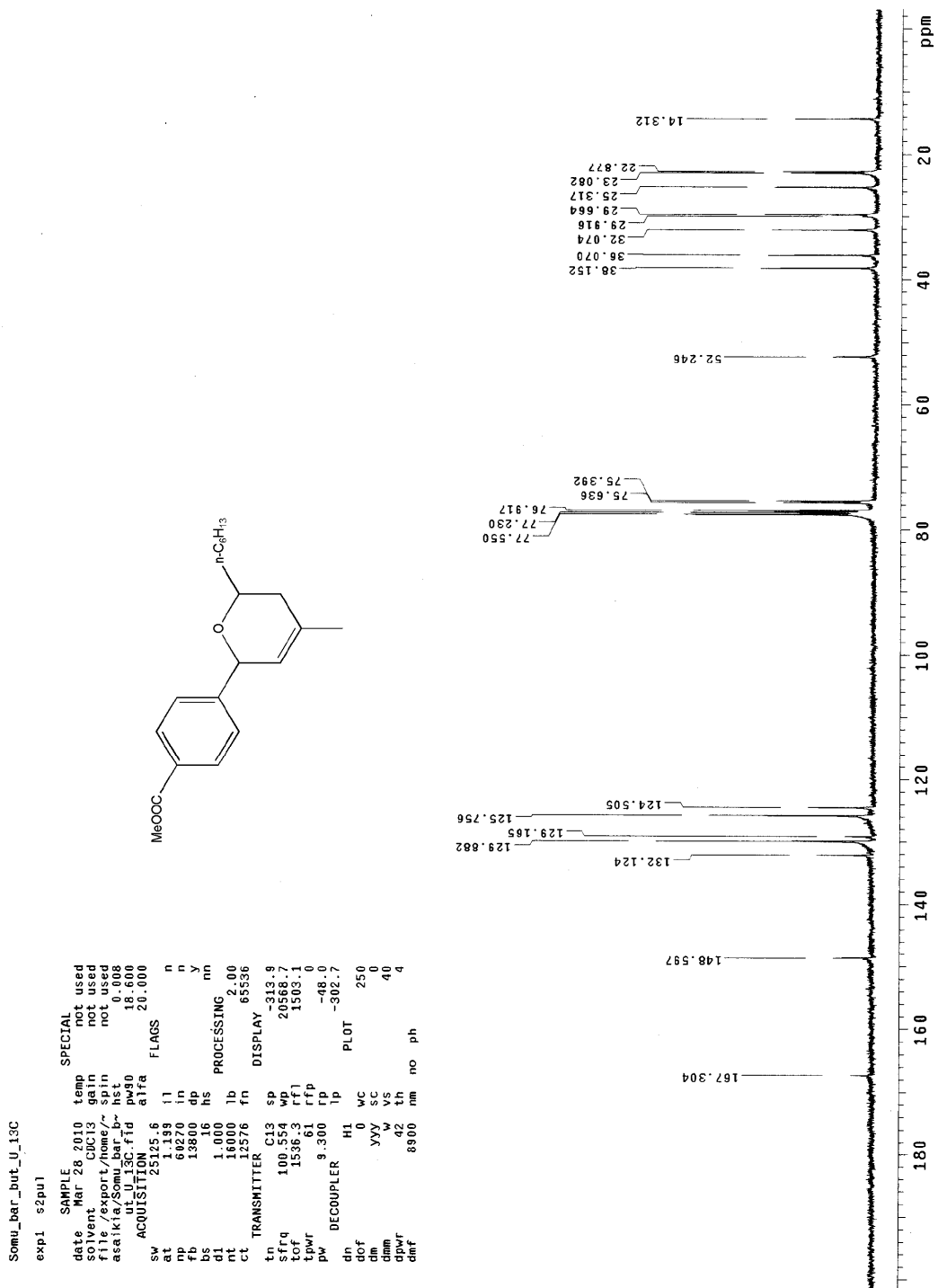
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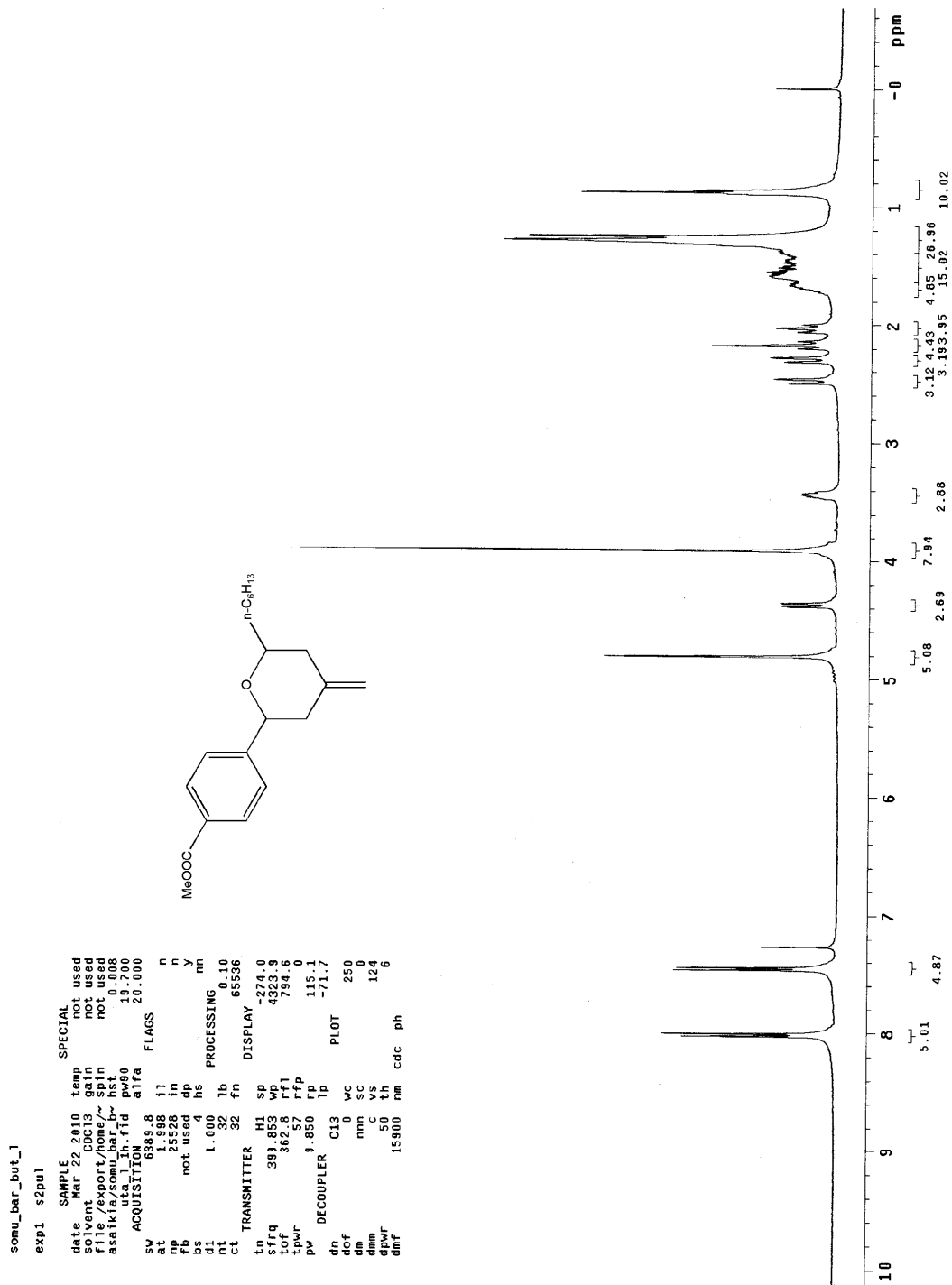
¹H NMR of 6v



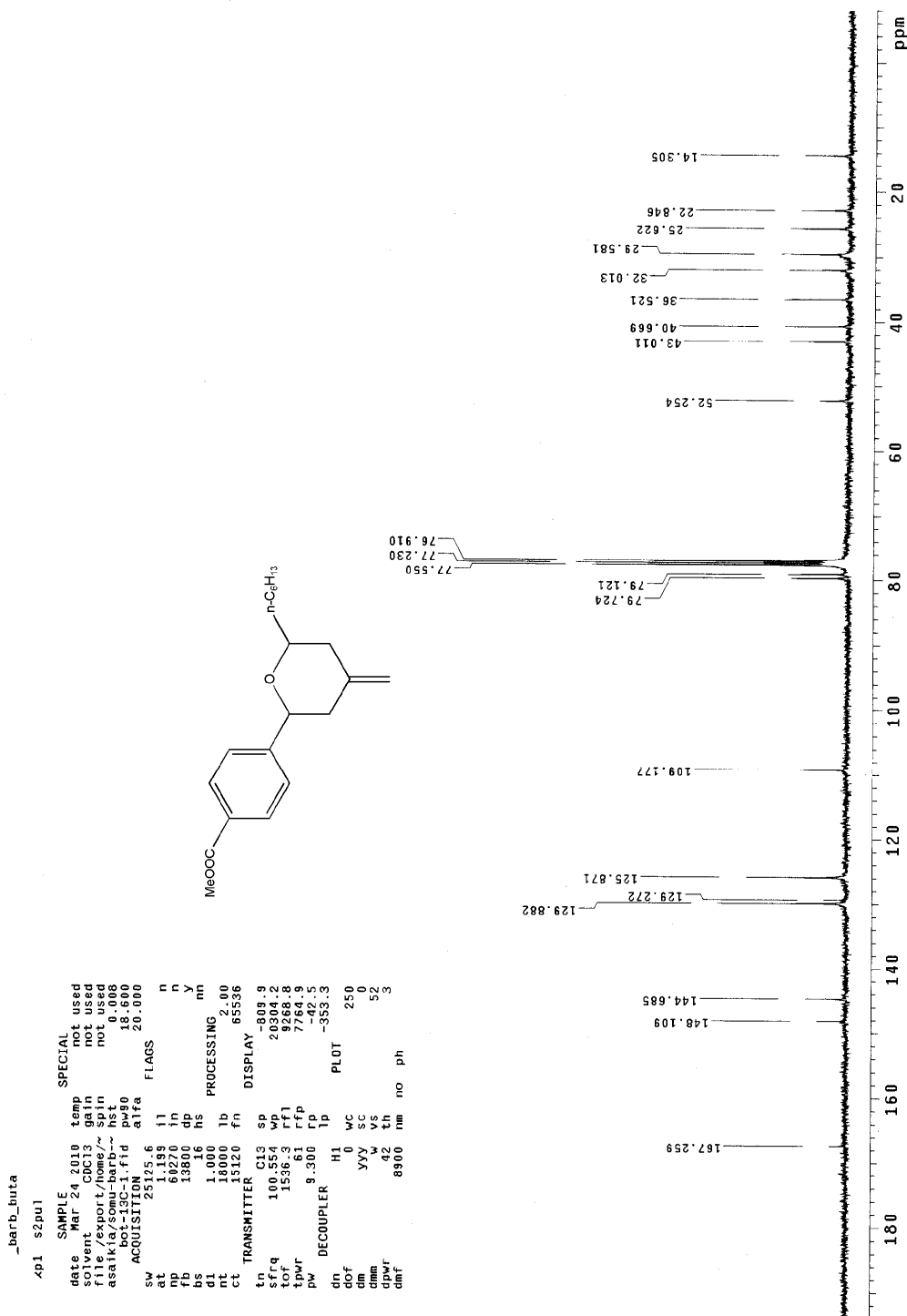
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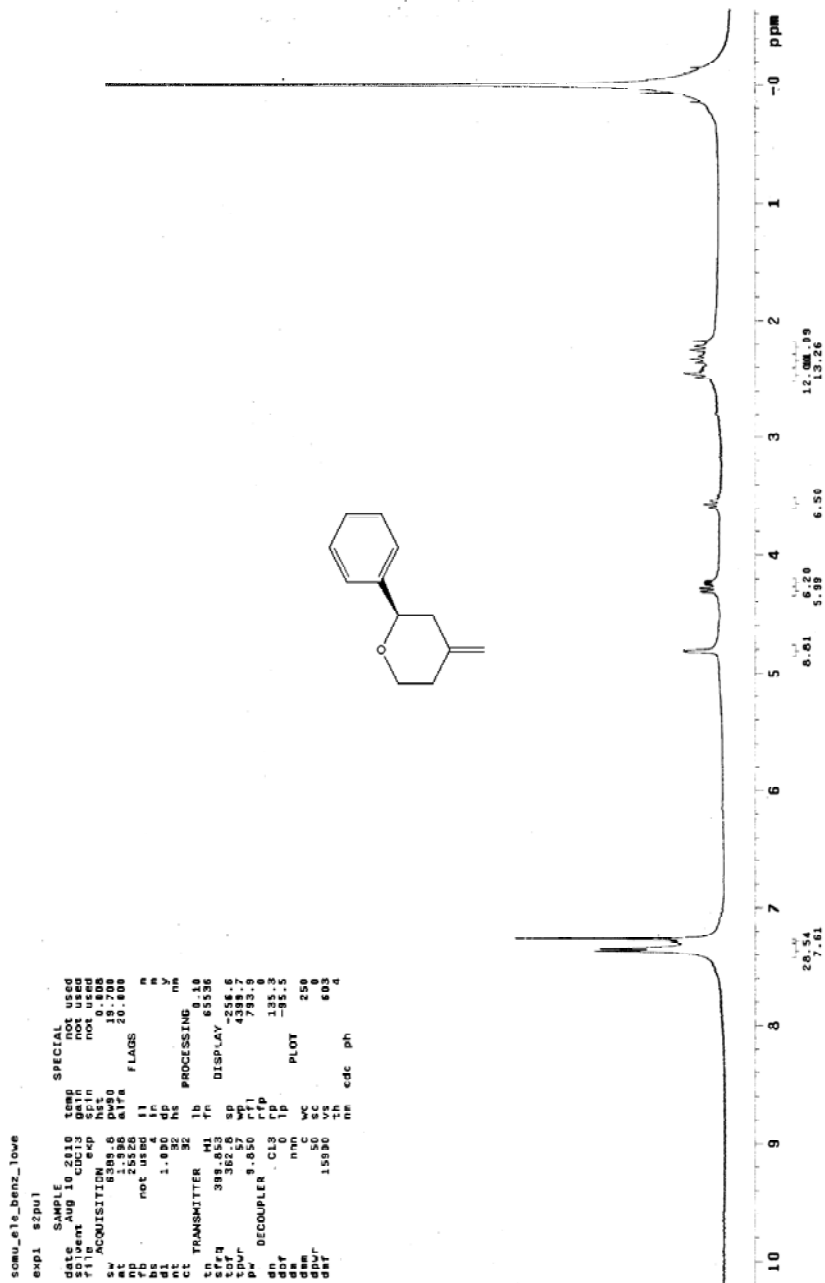
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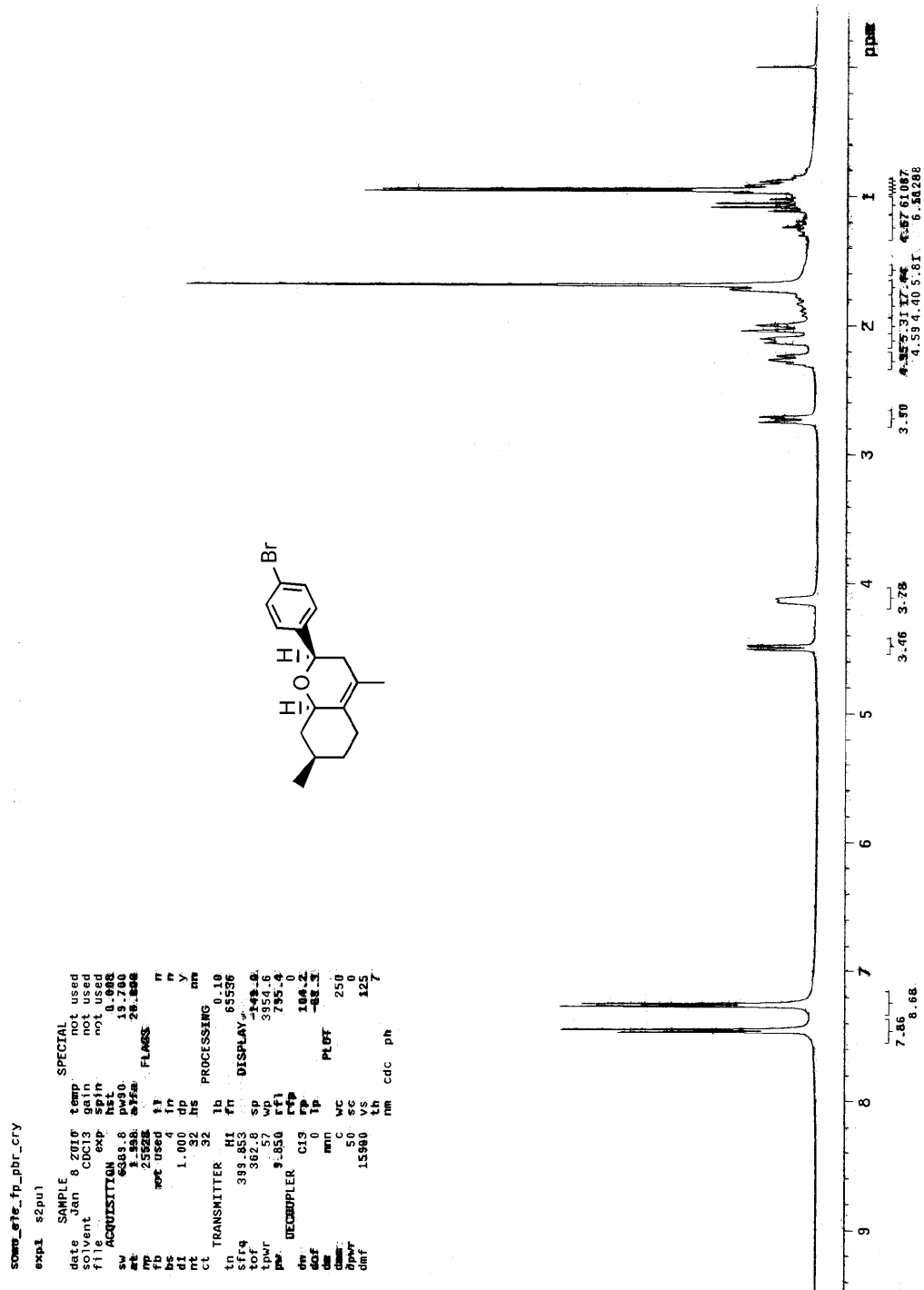
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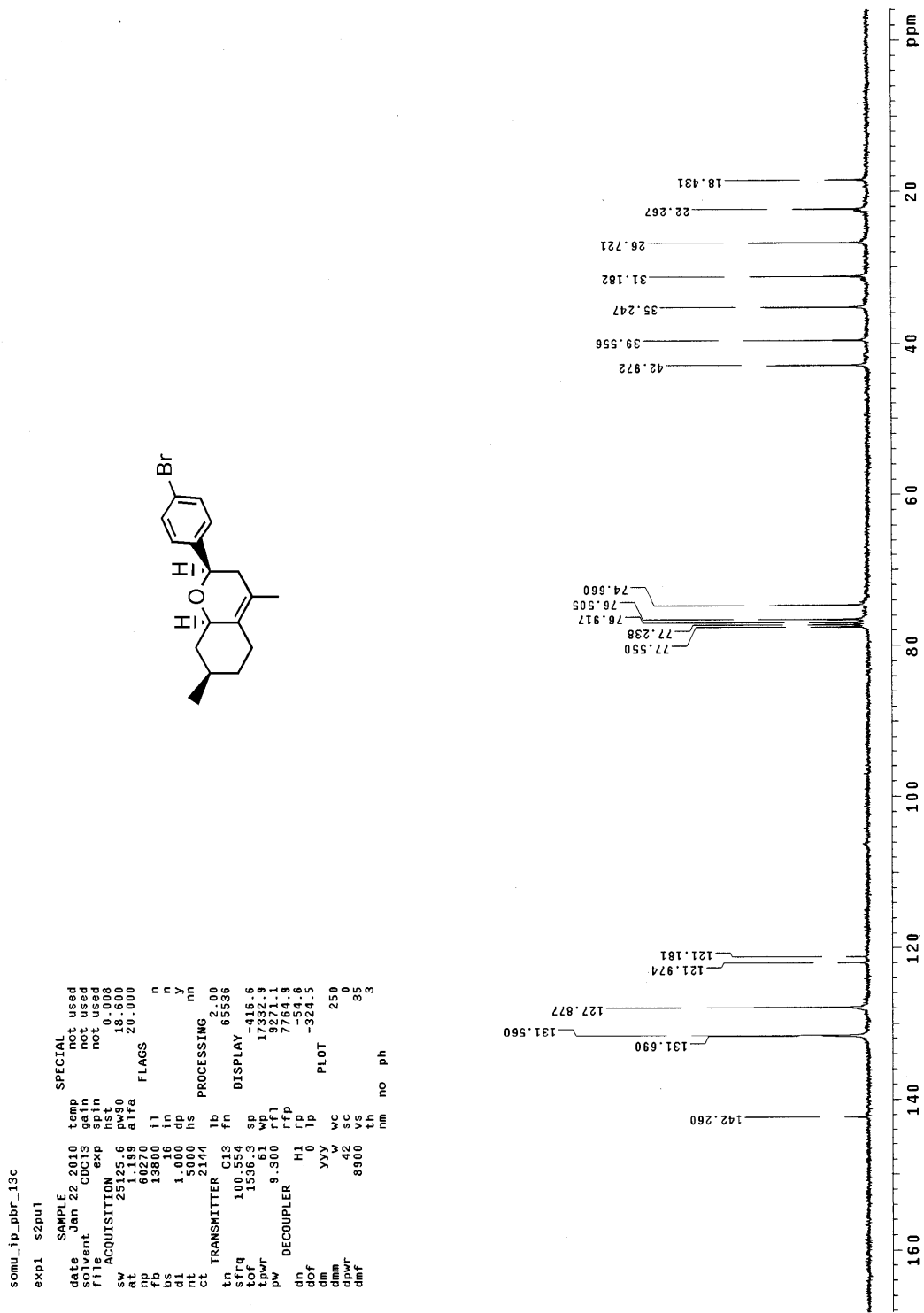
^1H NMR of **8a**



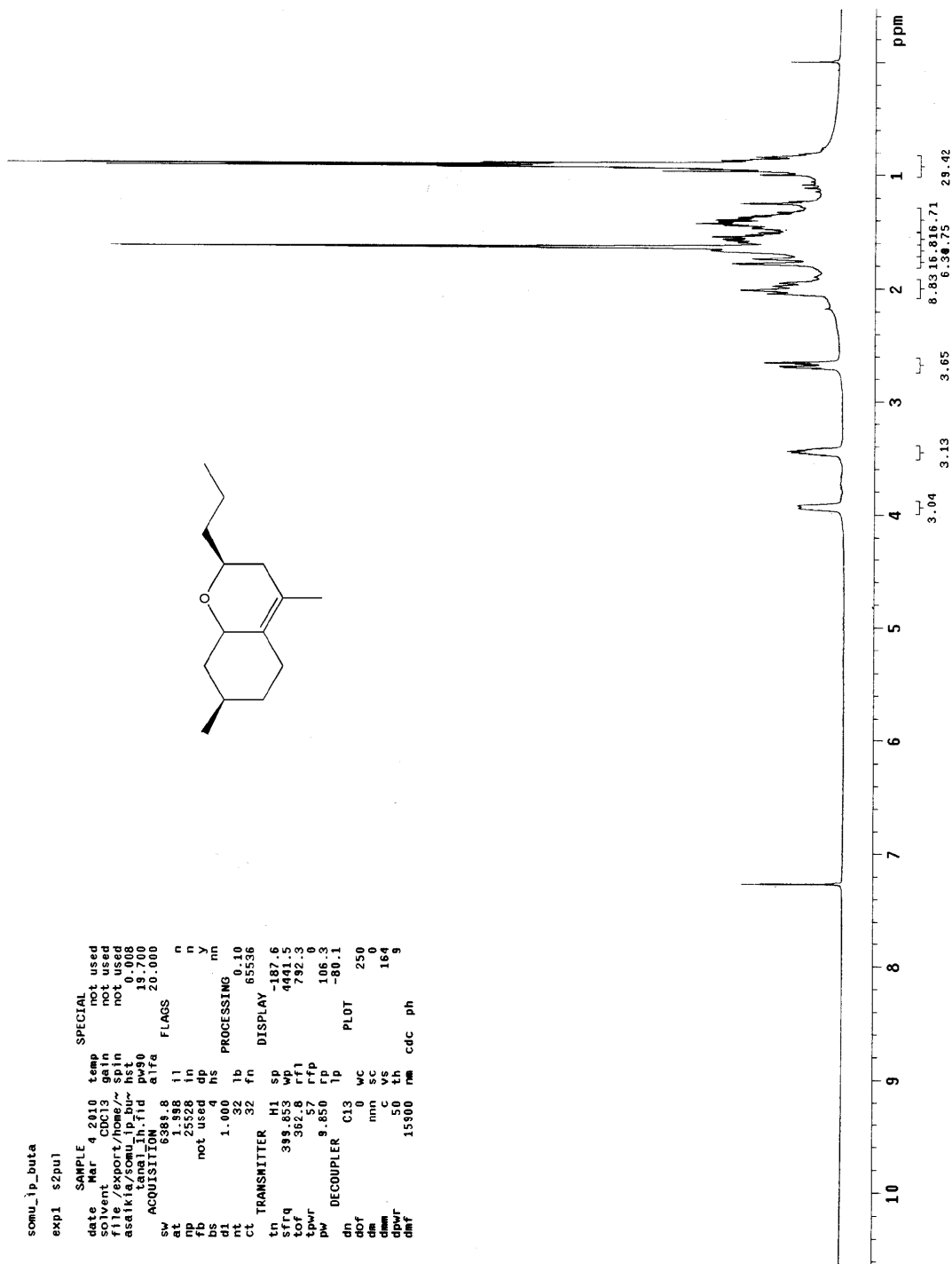
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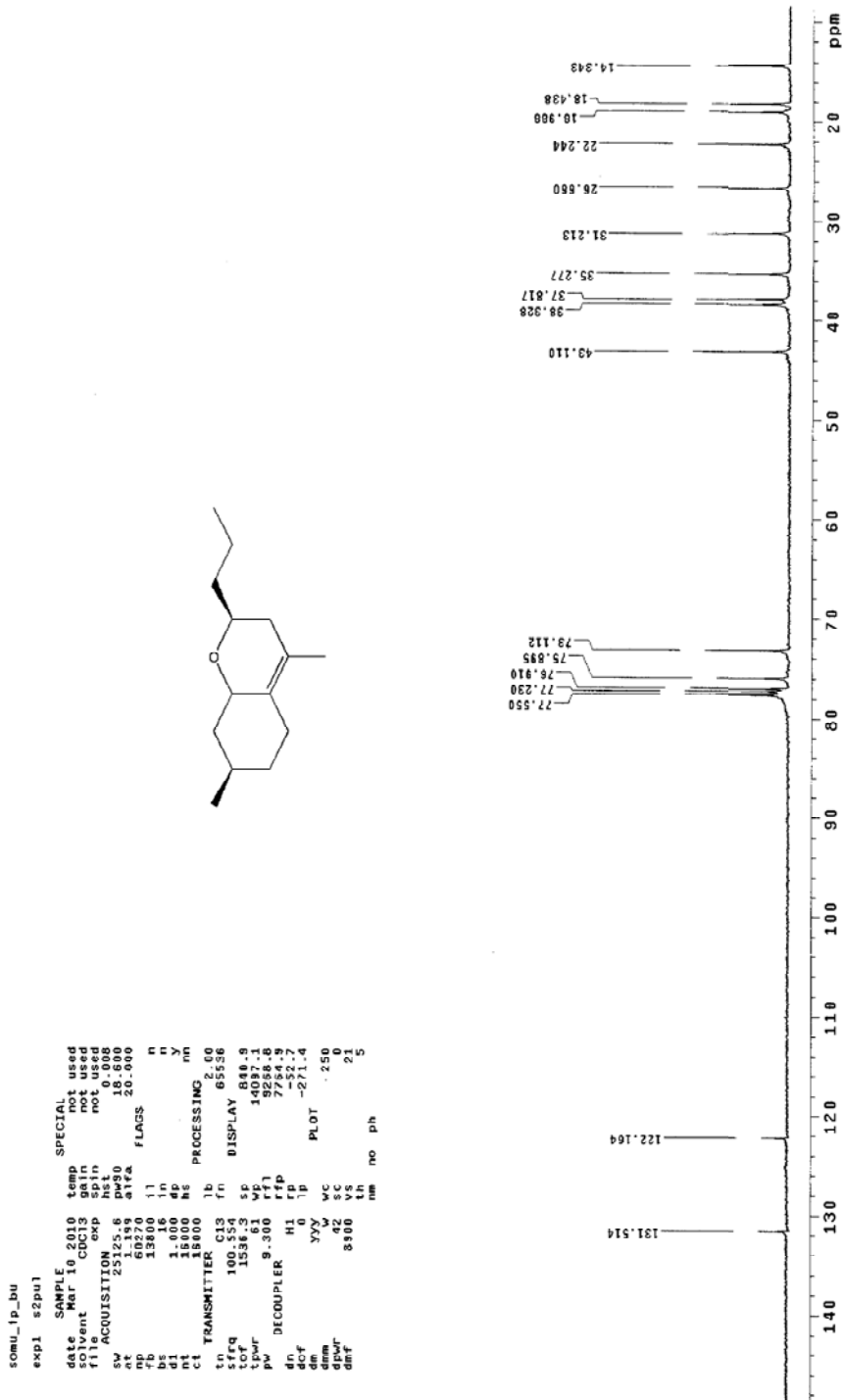
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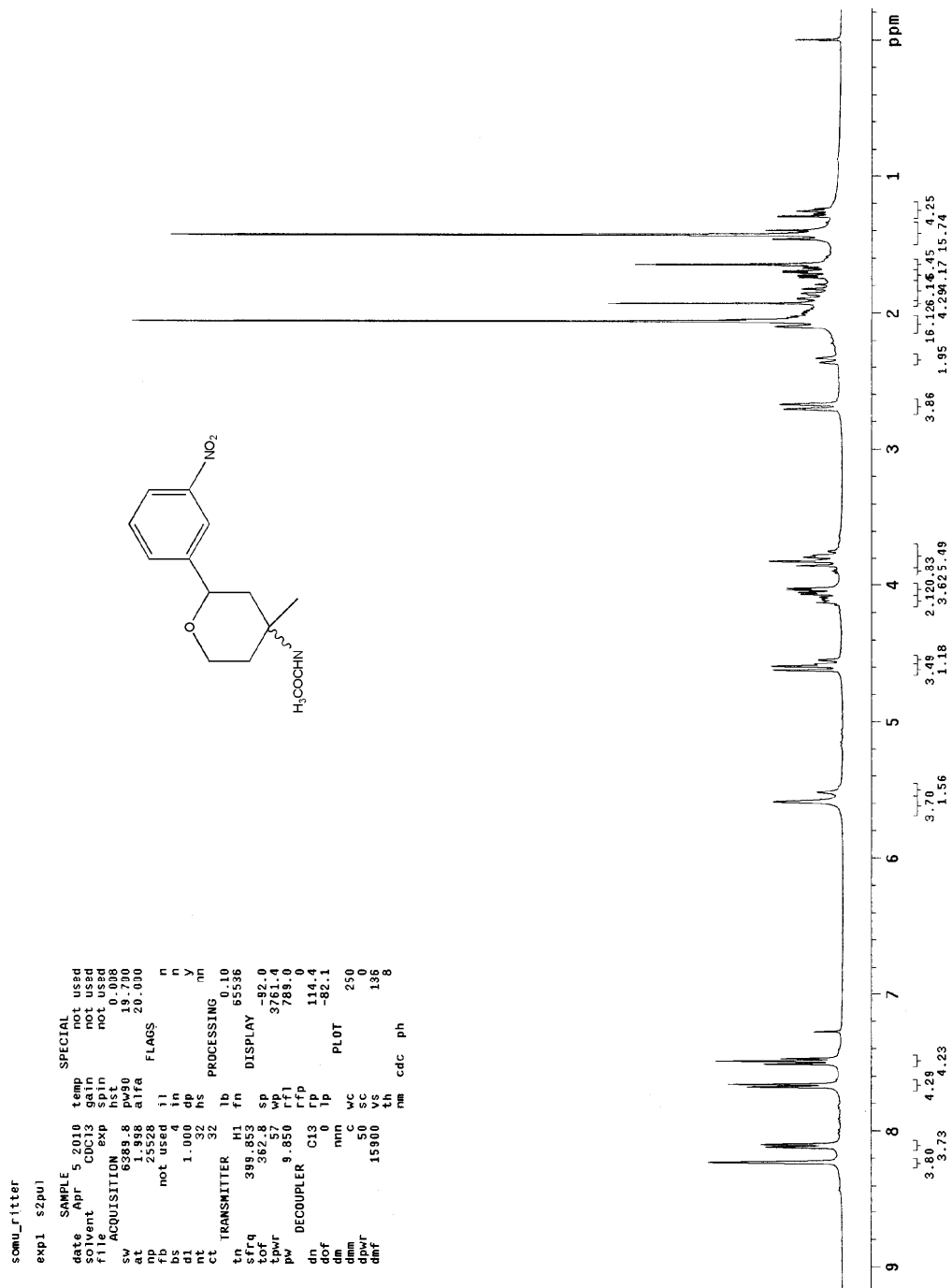
¹H NMR of 11



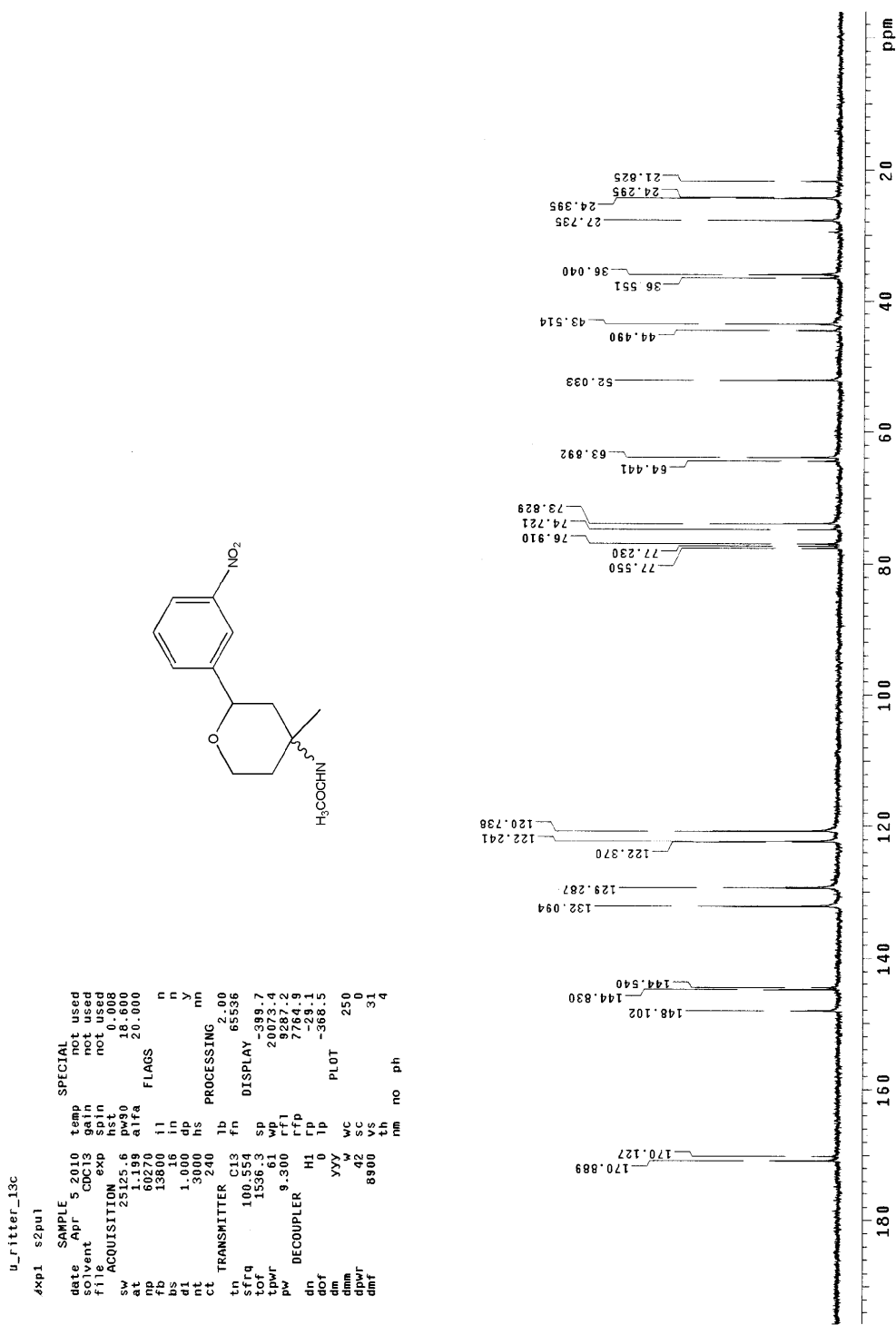
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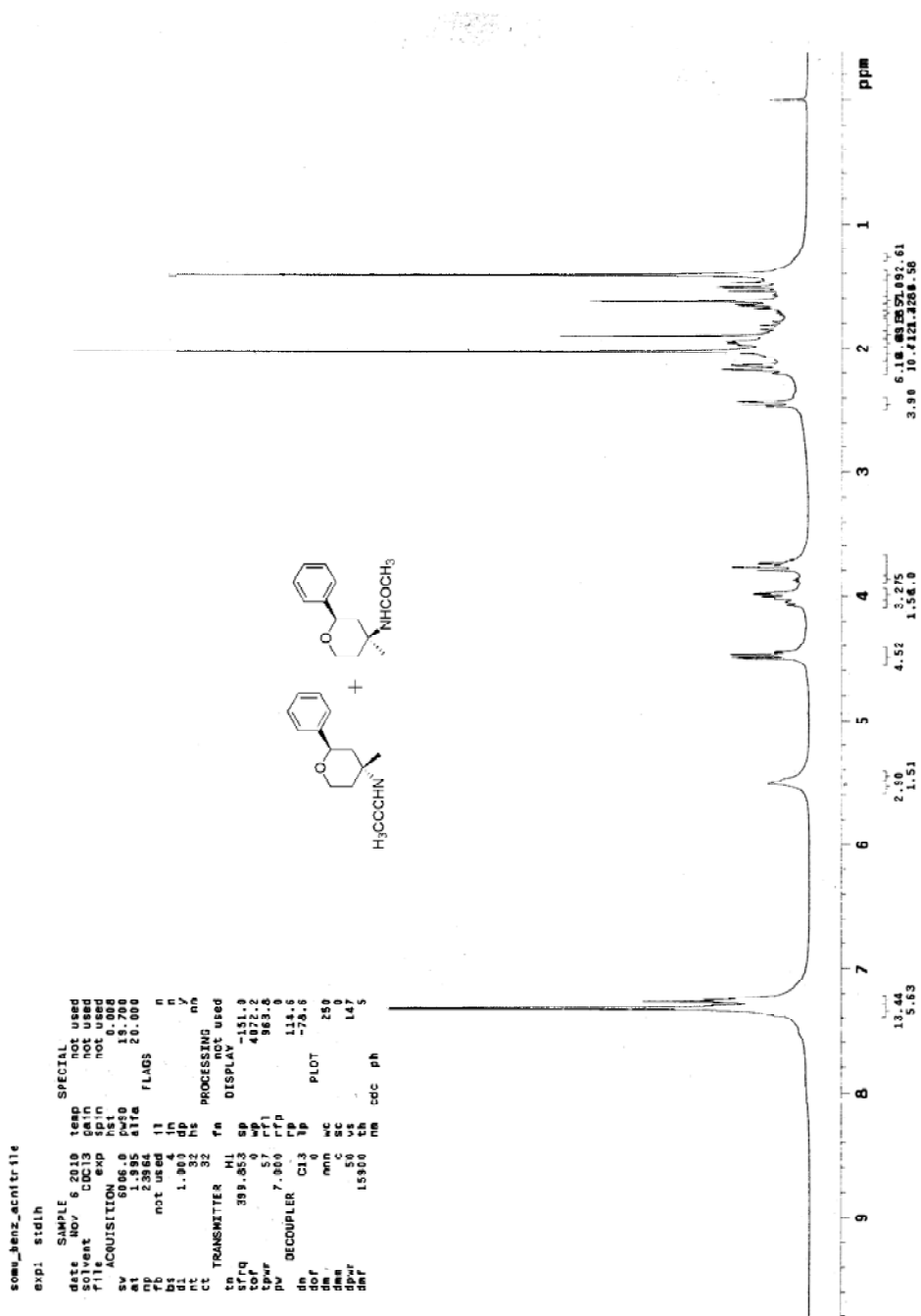
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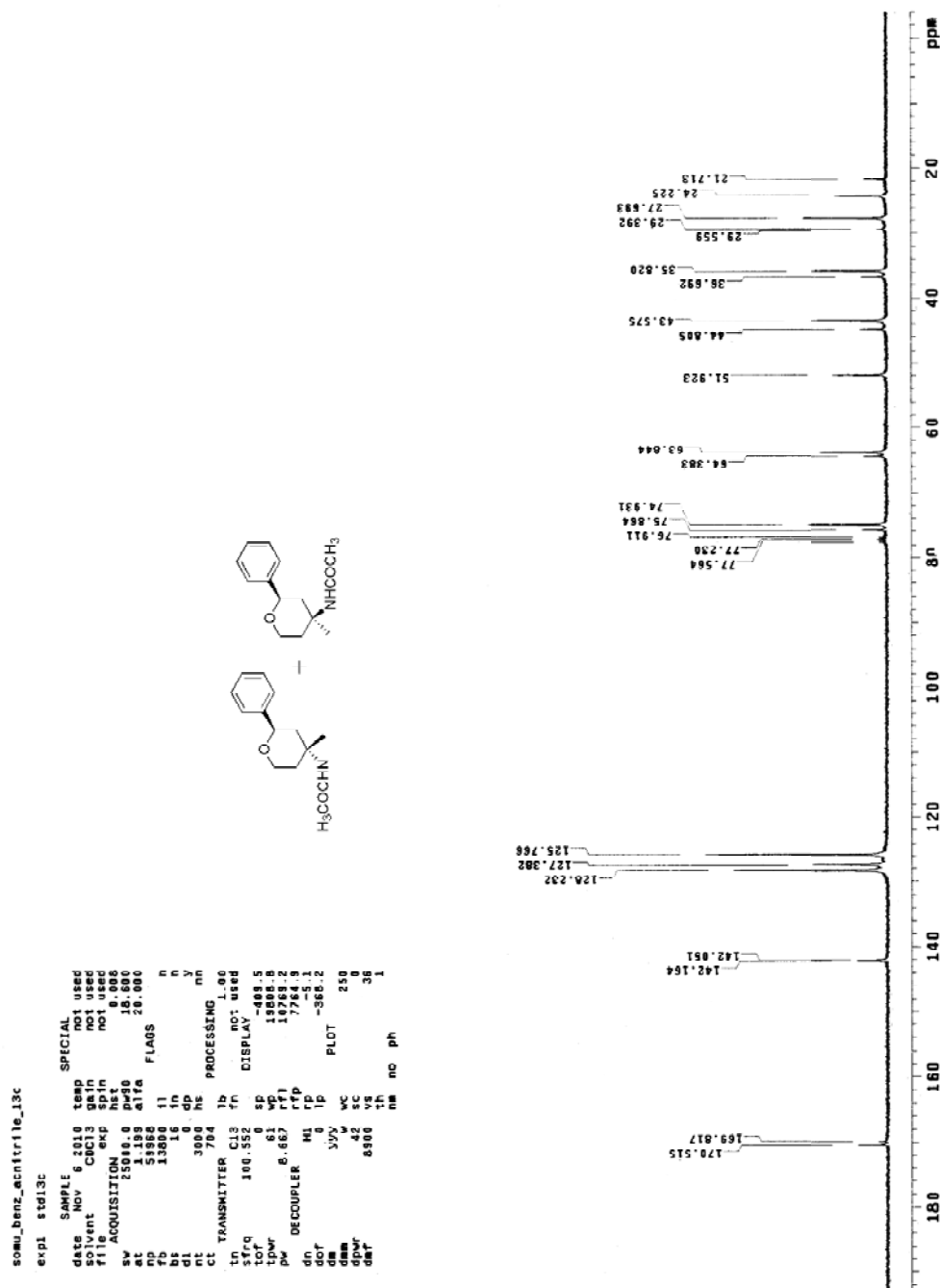
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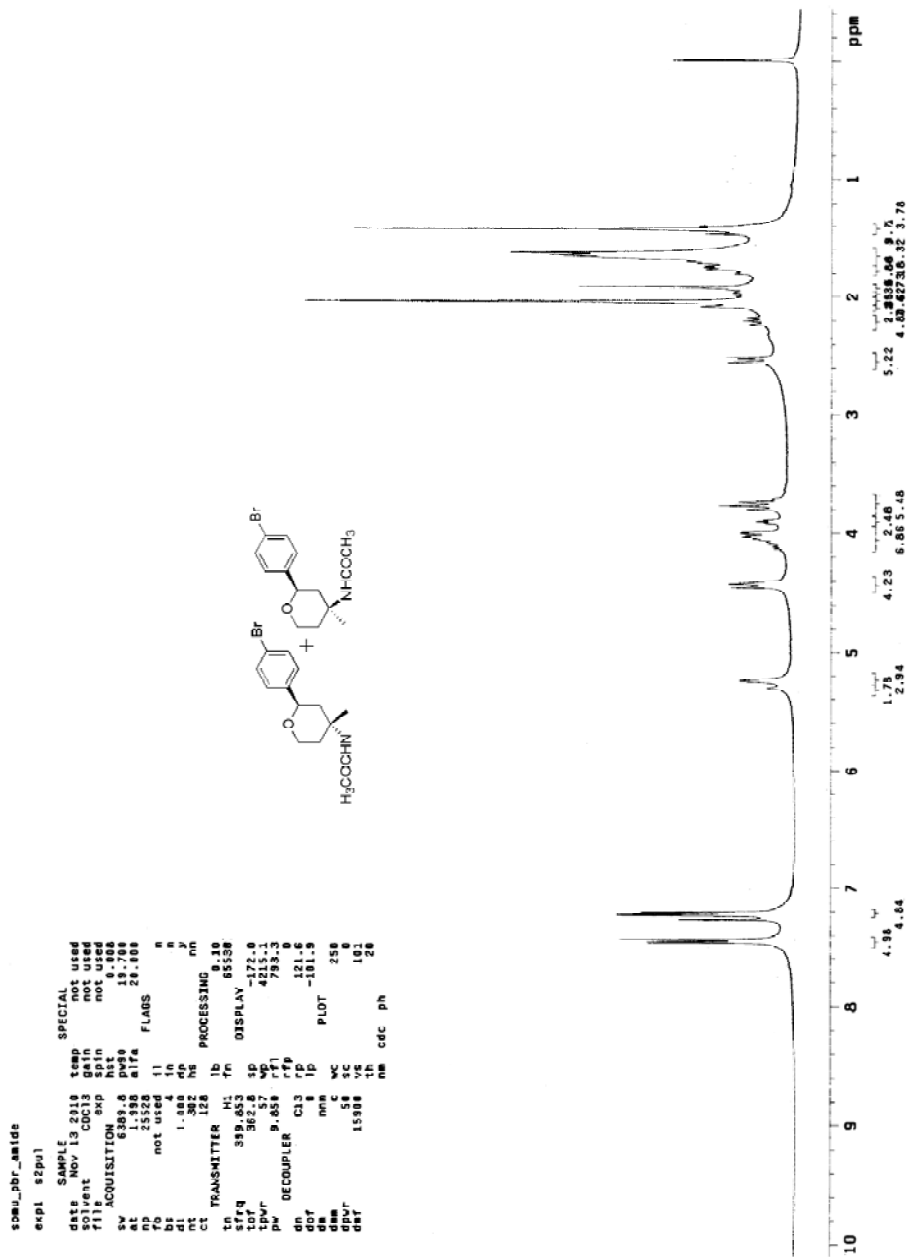
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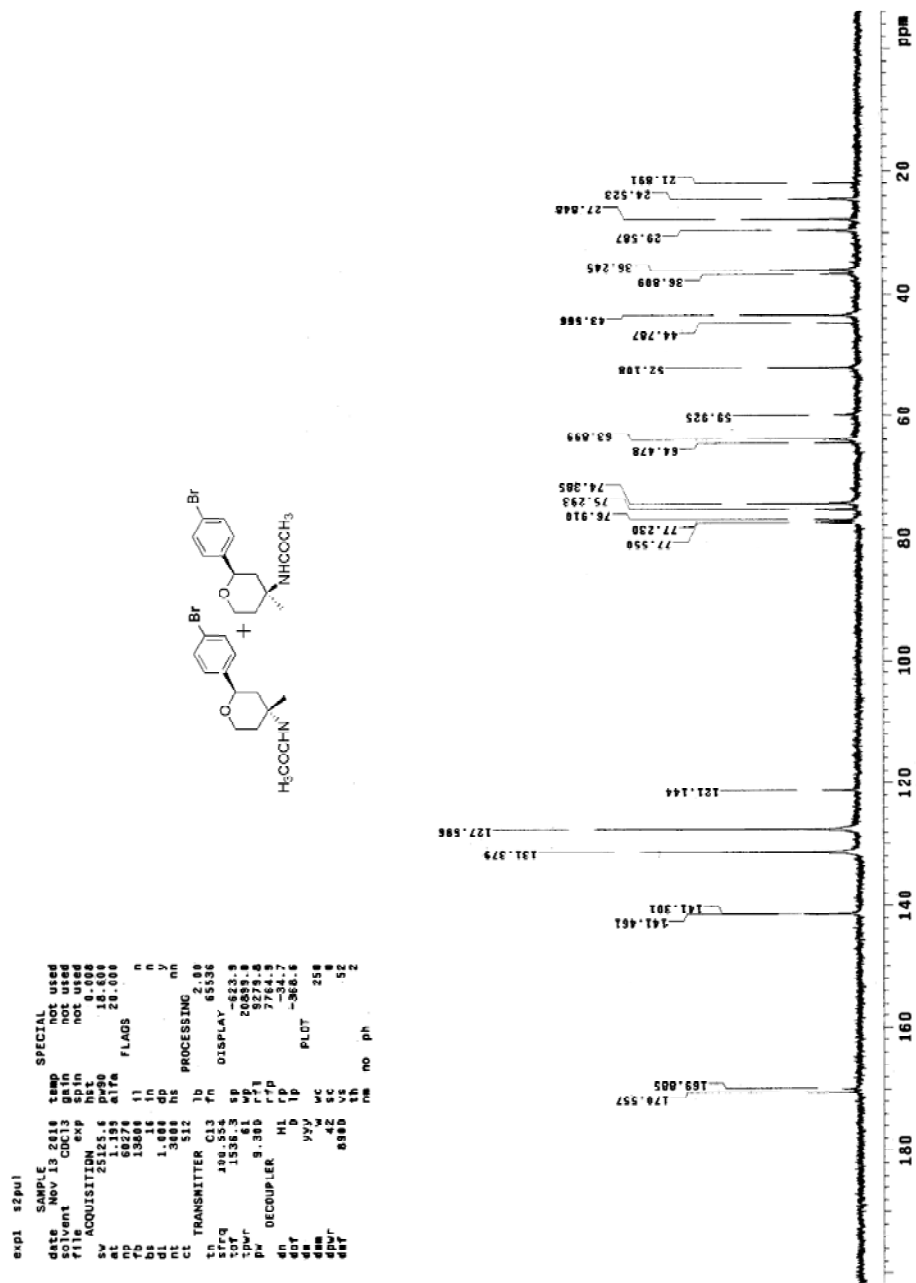
^{13}C NMR of **17b/18b**



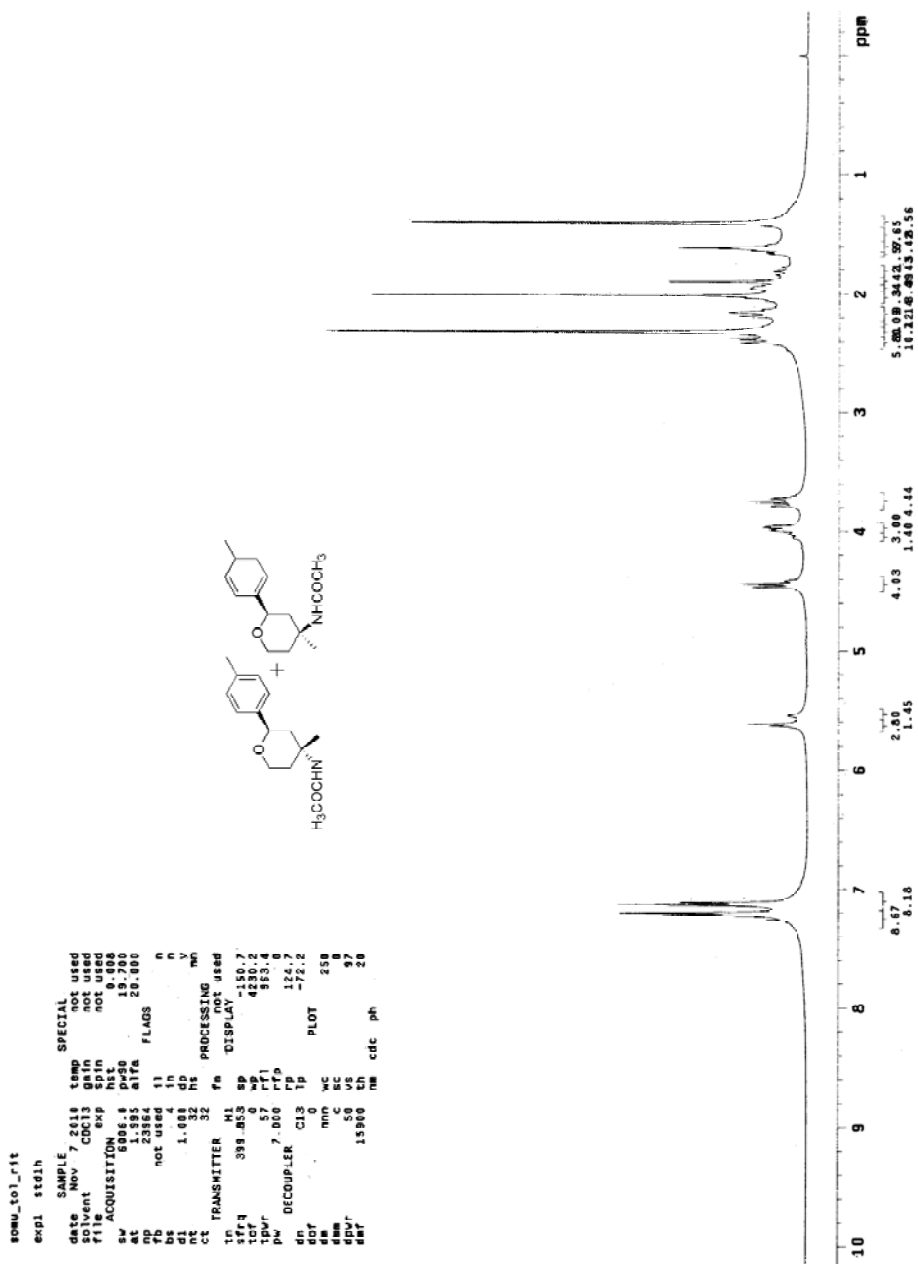
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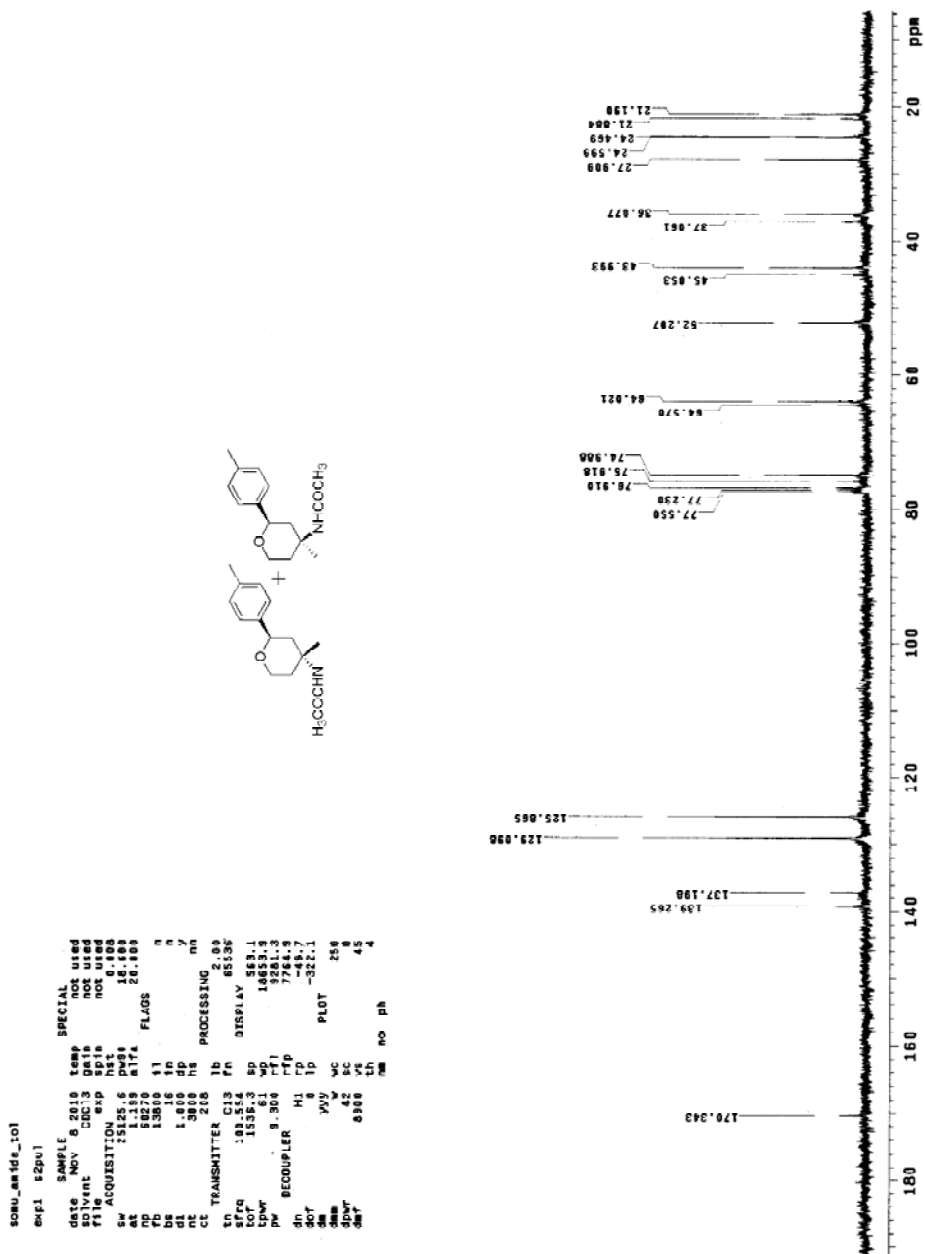
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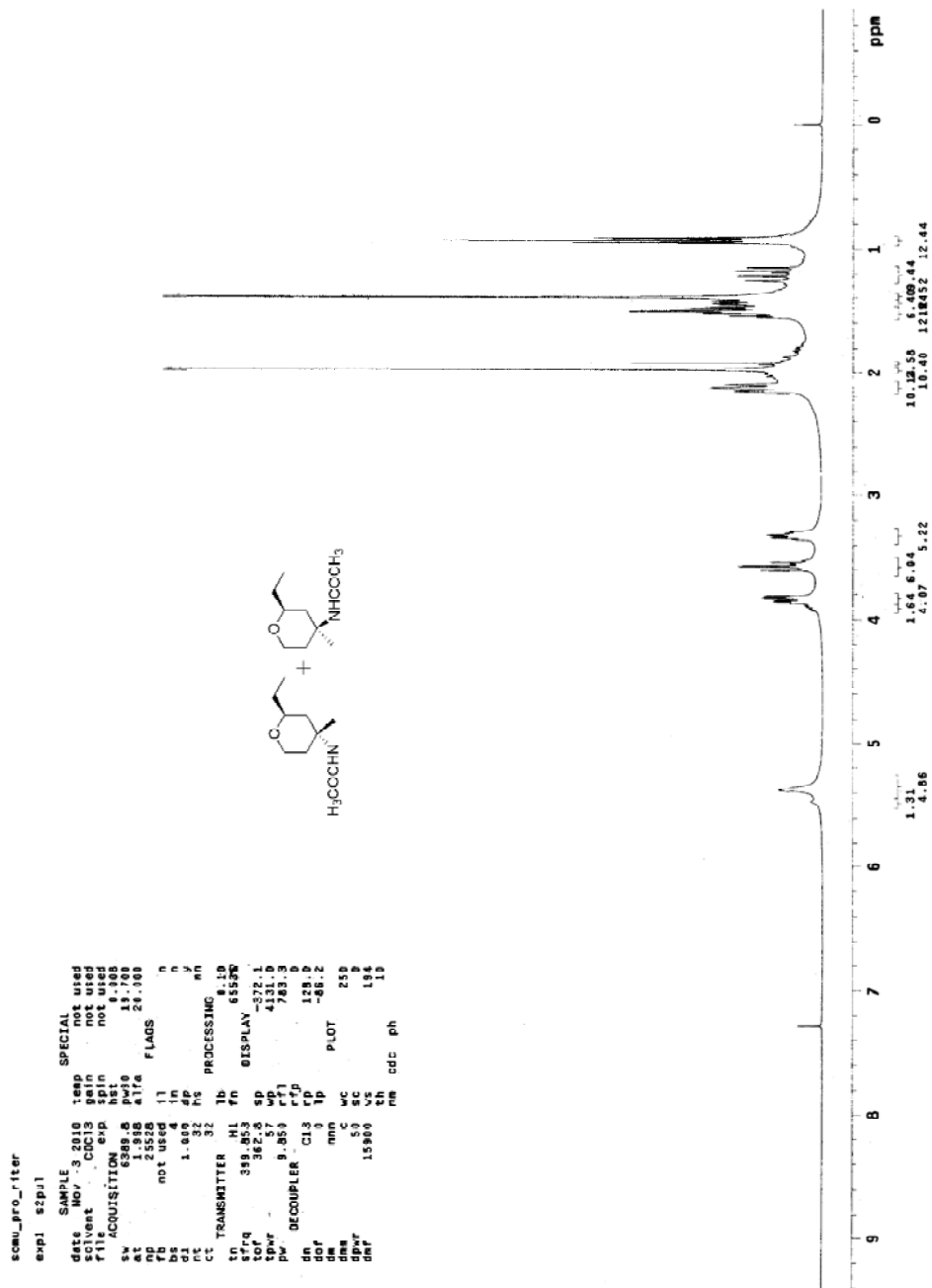
^1H NMR of **17d/18d**



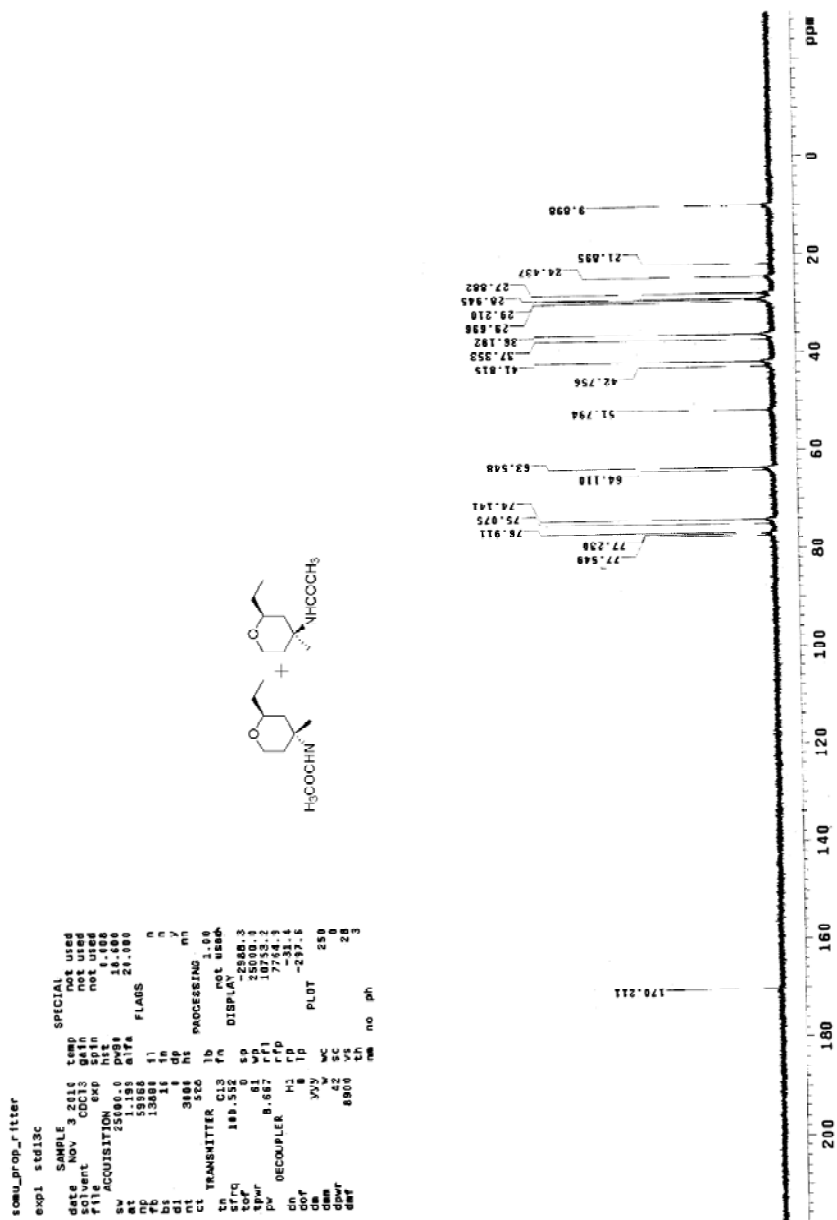
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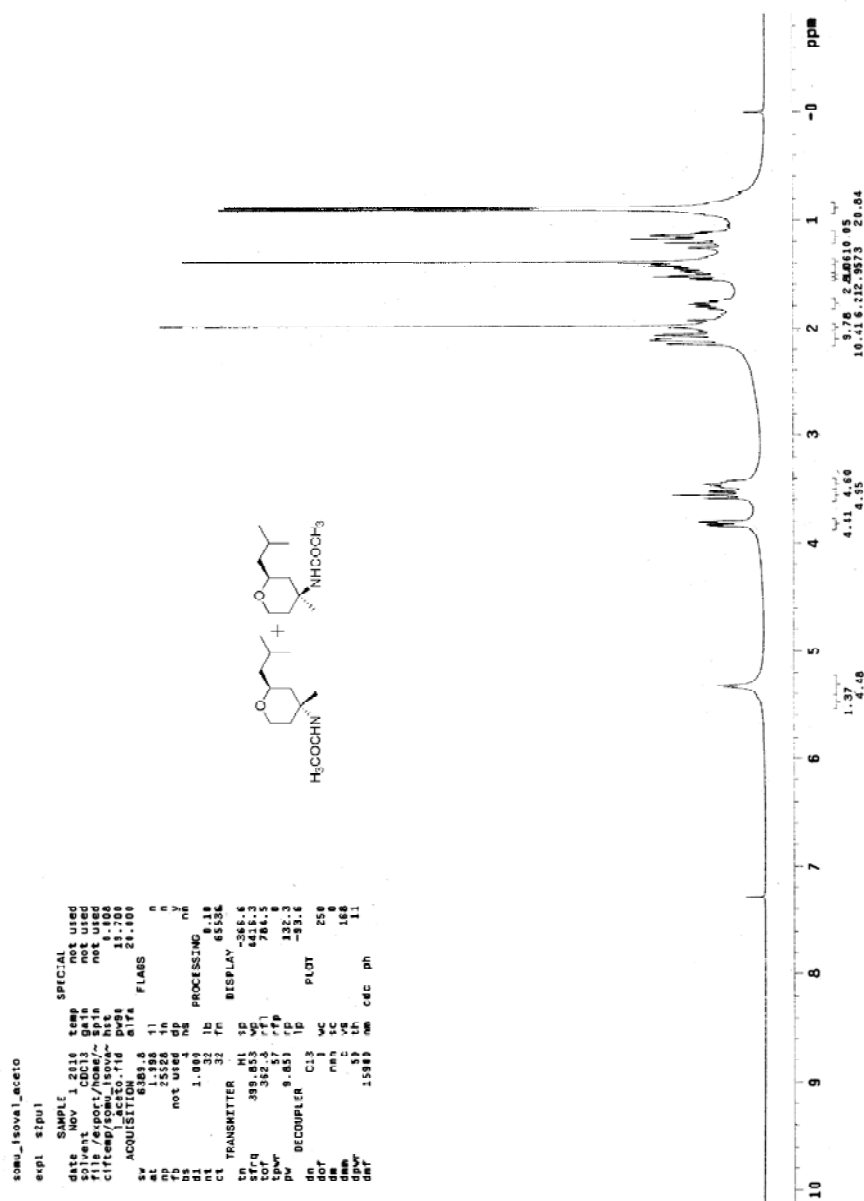
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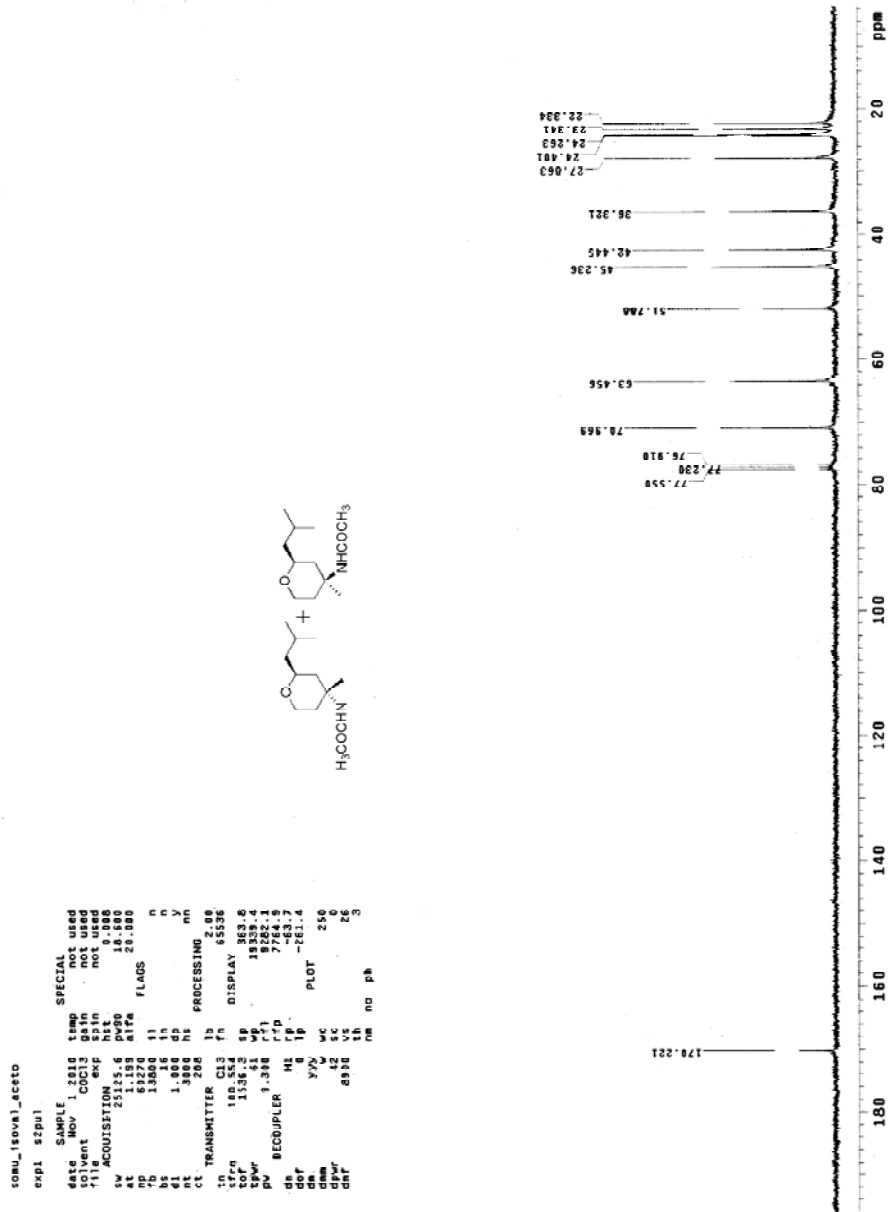
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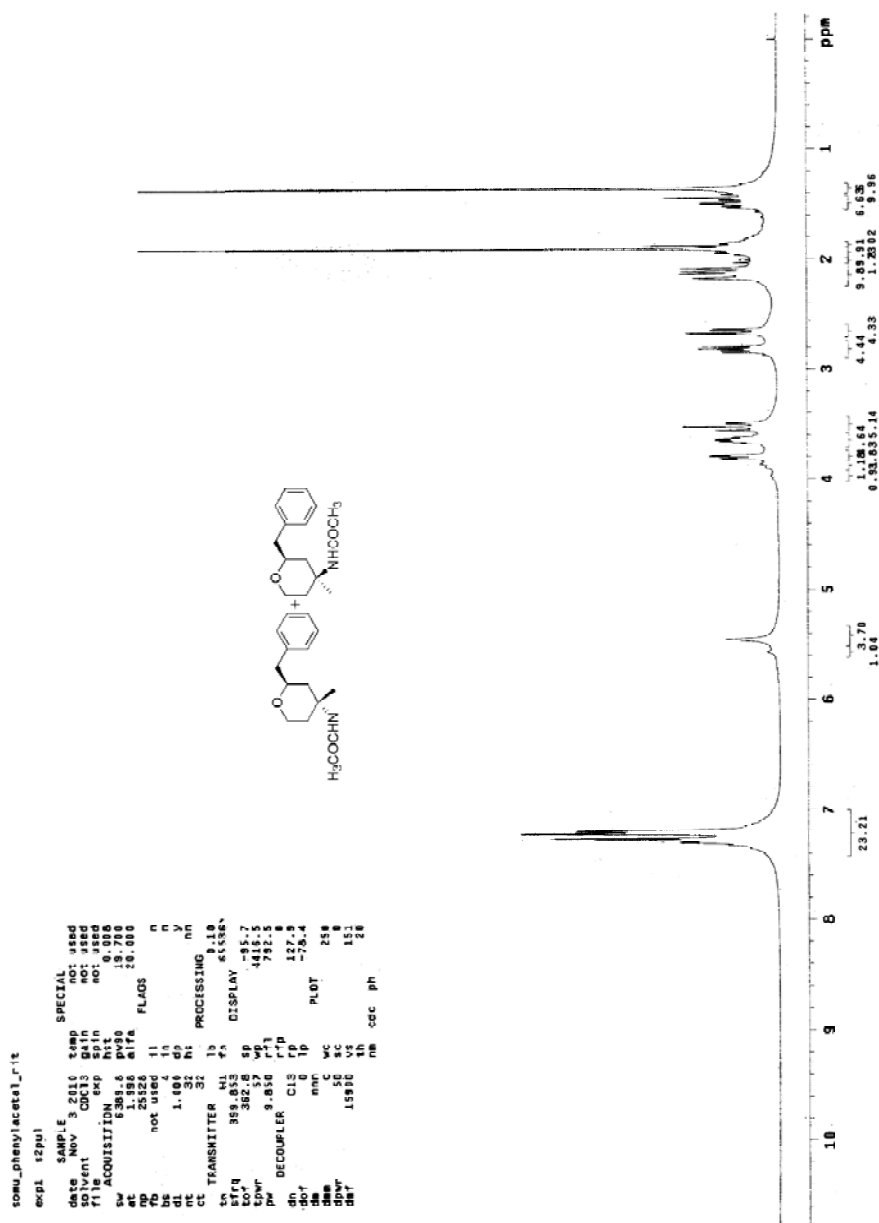
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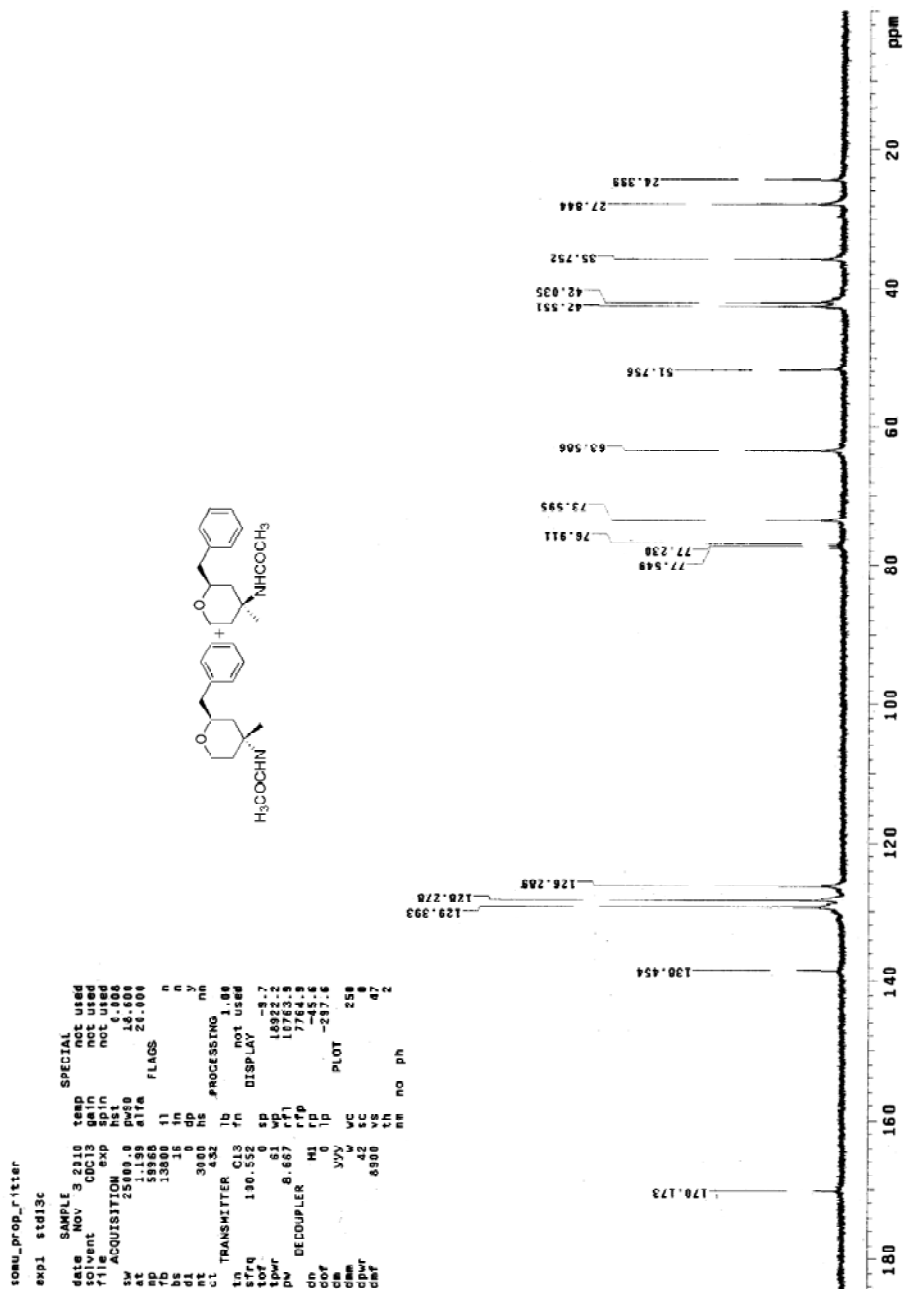
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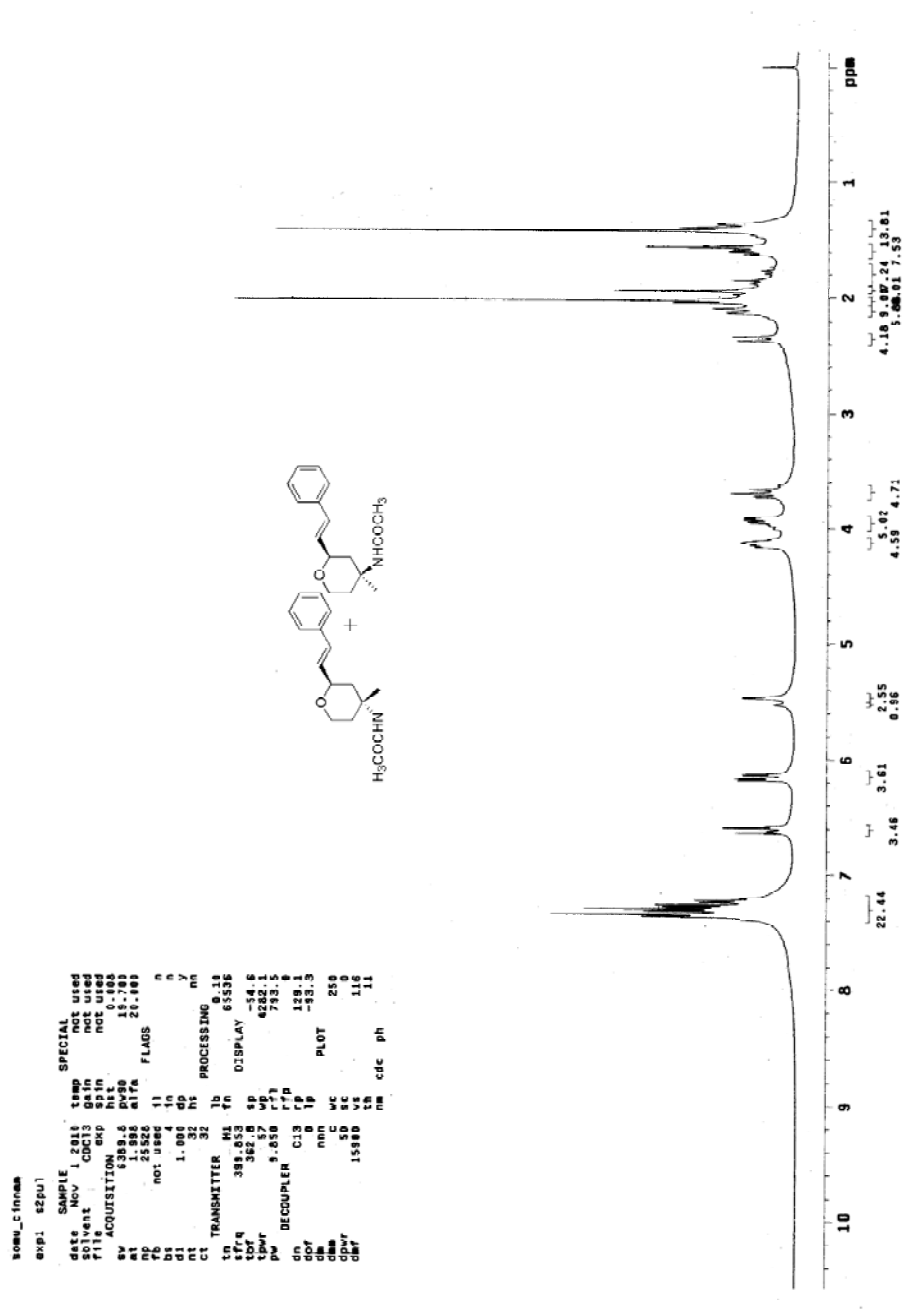
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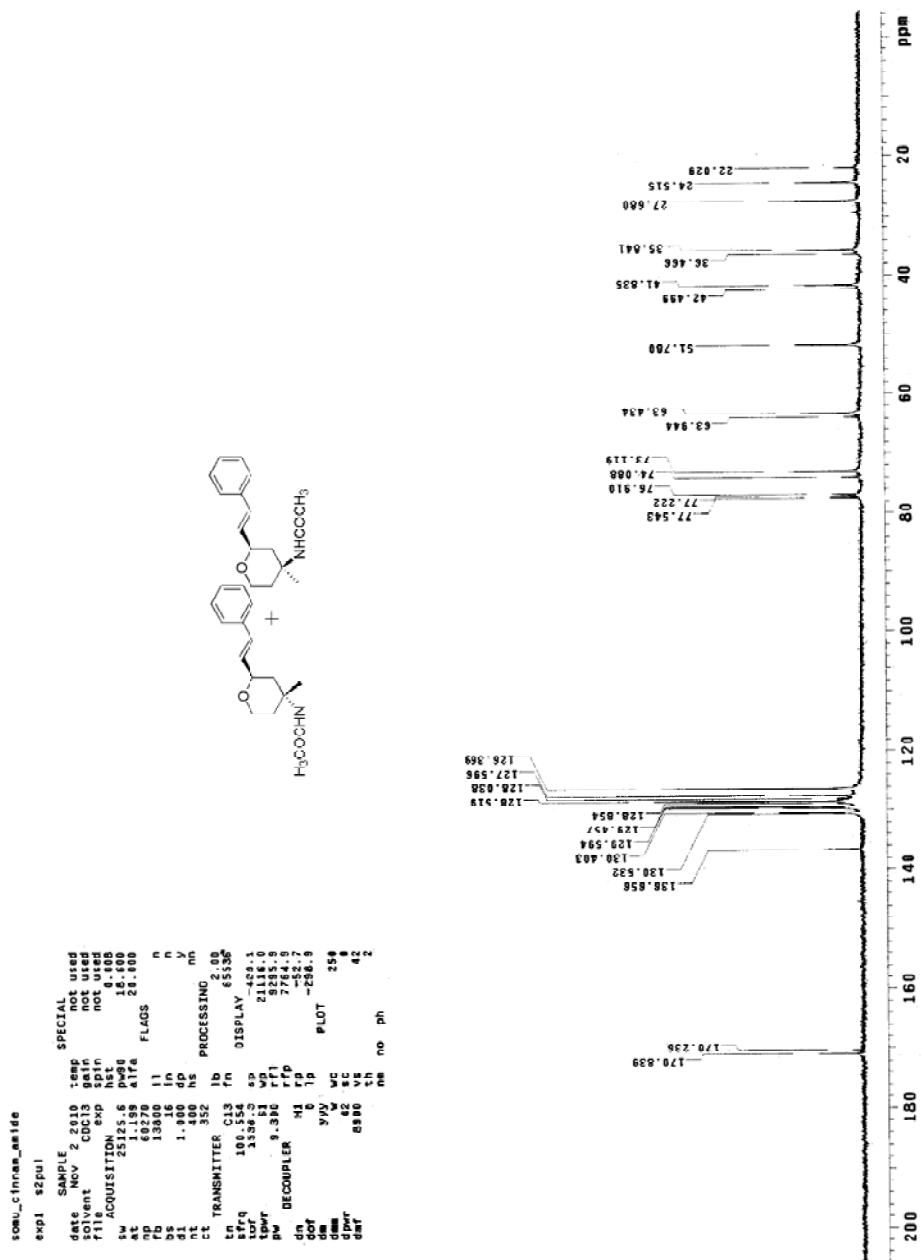
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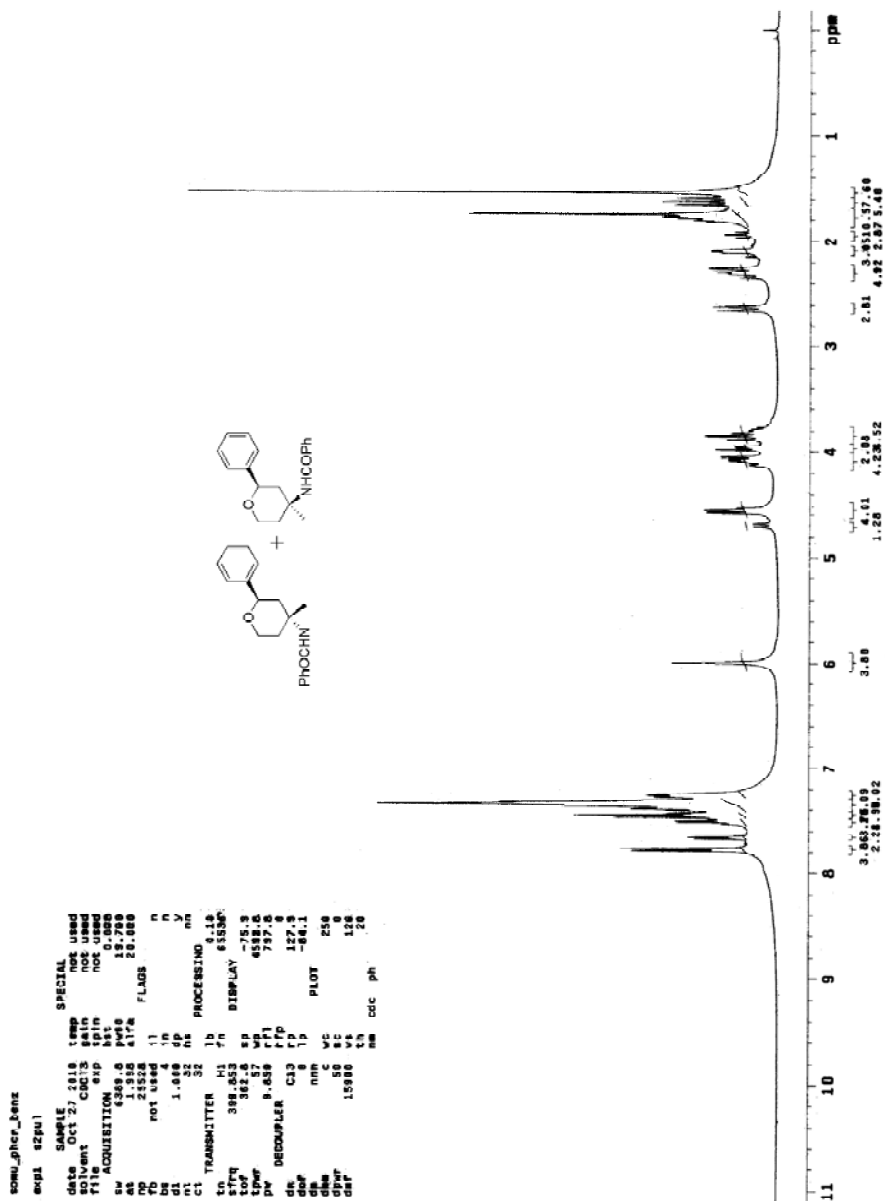
^1H NMR of 17h/18h



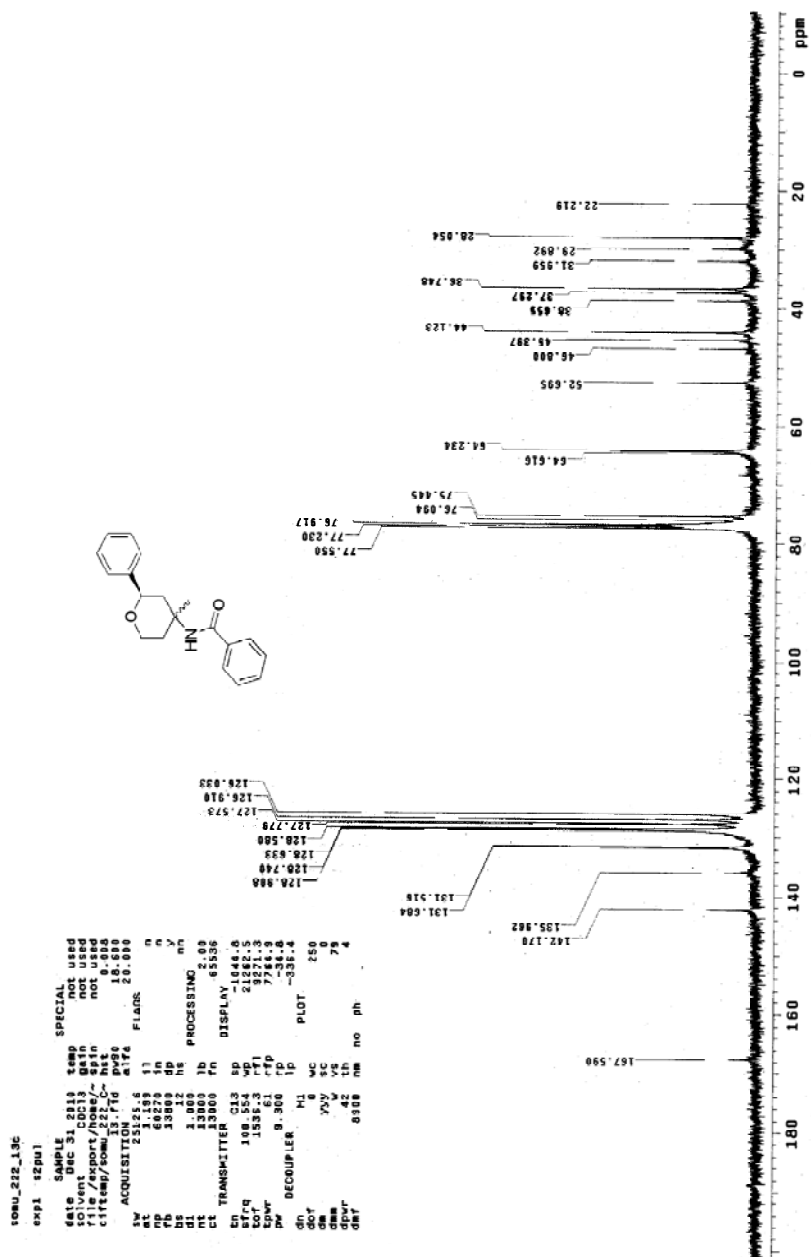
¹³C NMR of 17h/18h



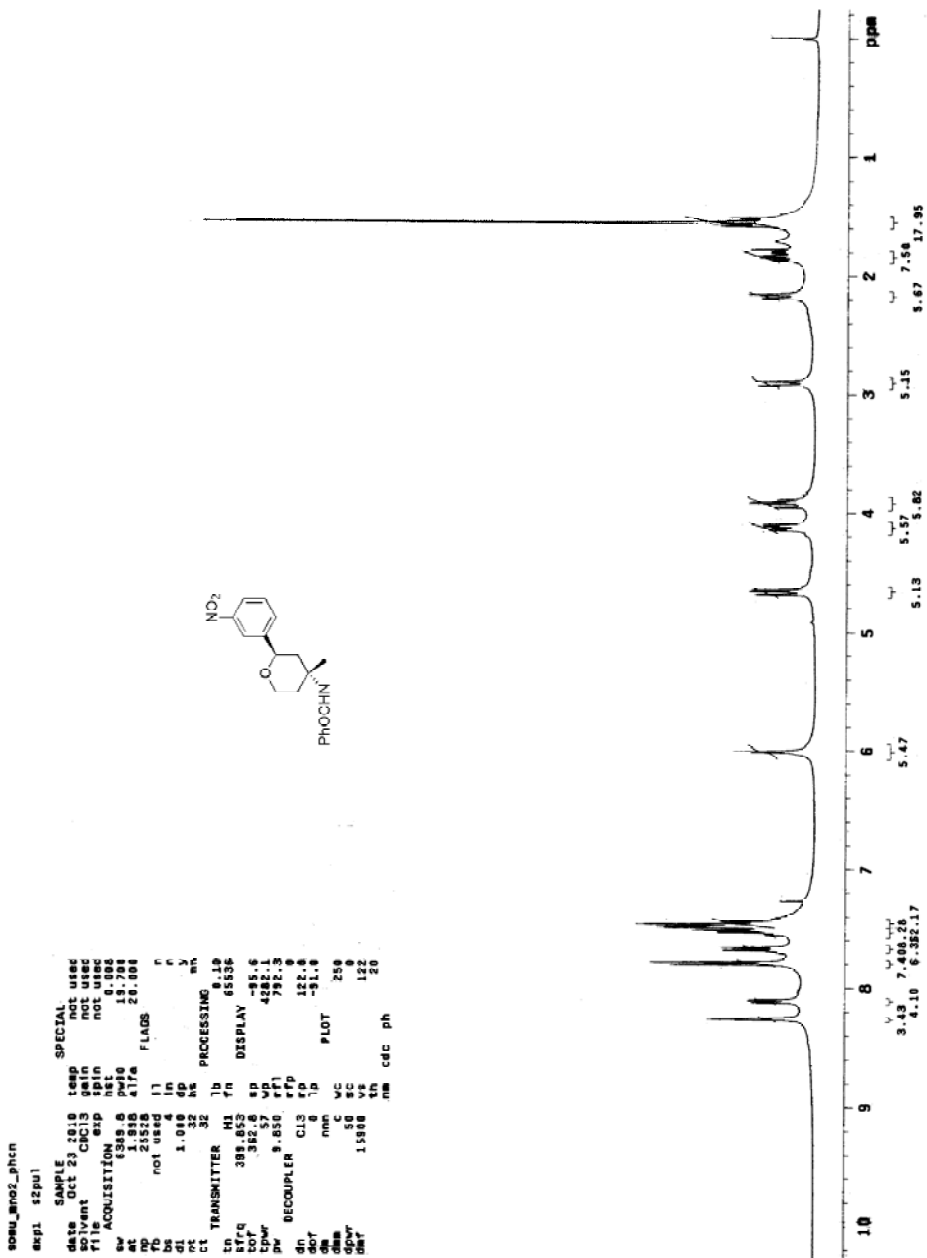
¹H NMR of **17i/18i**



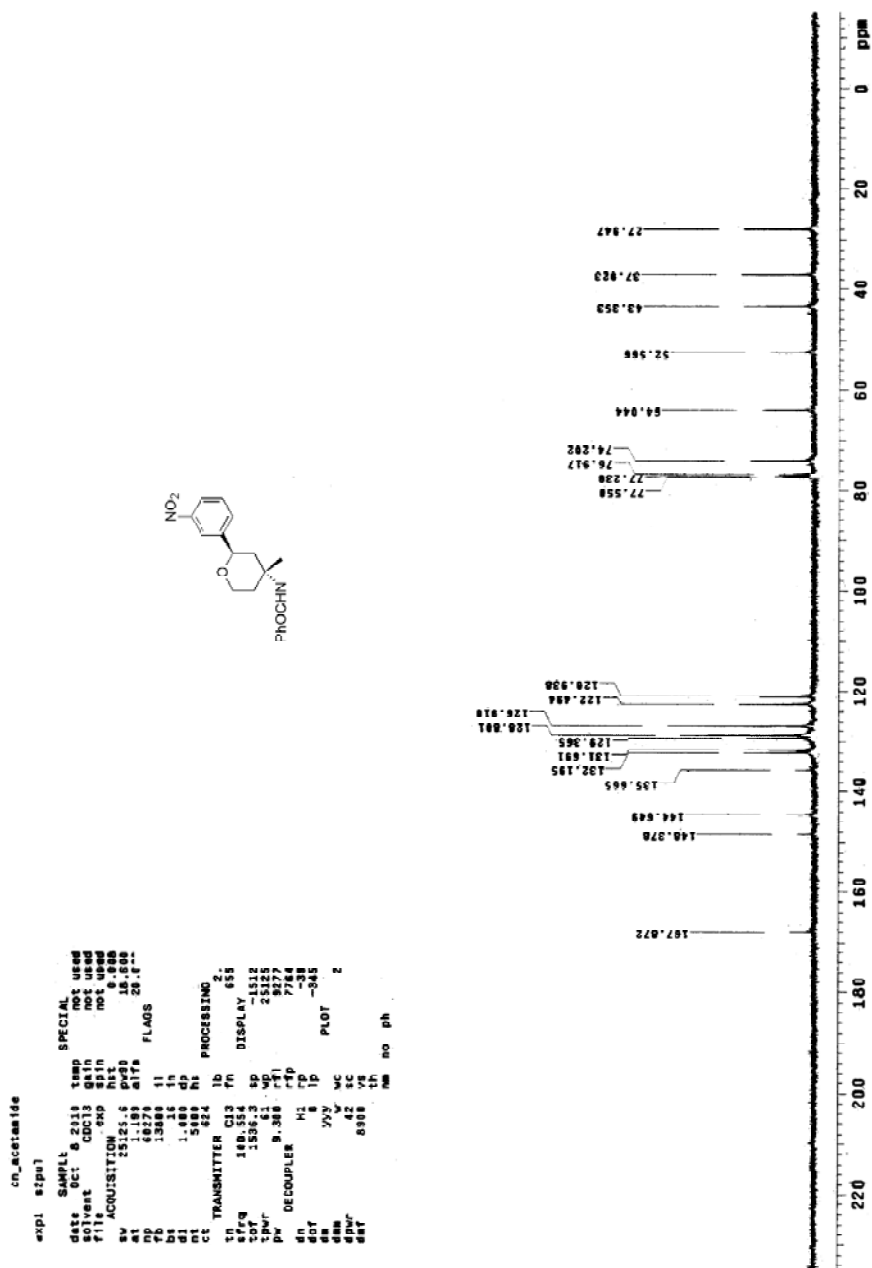
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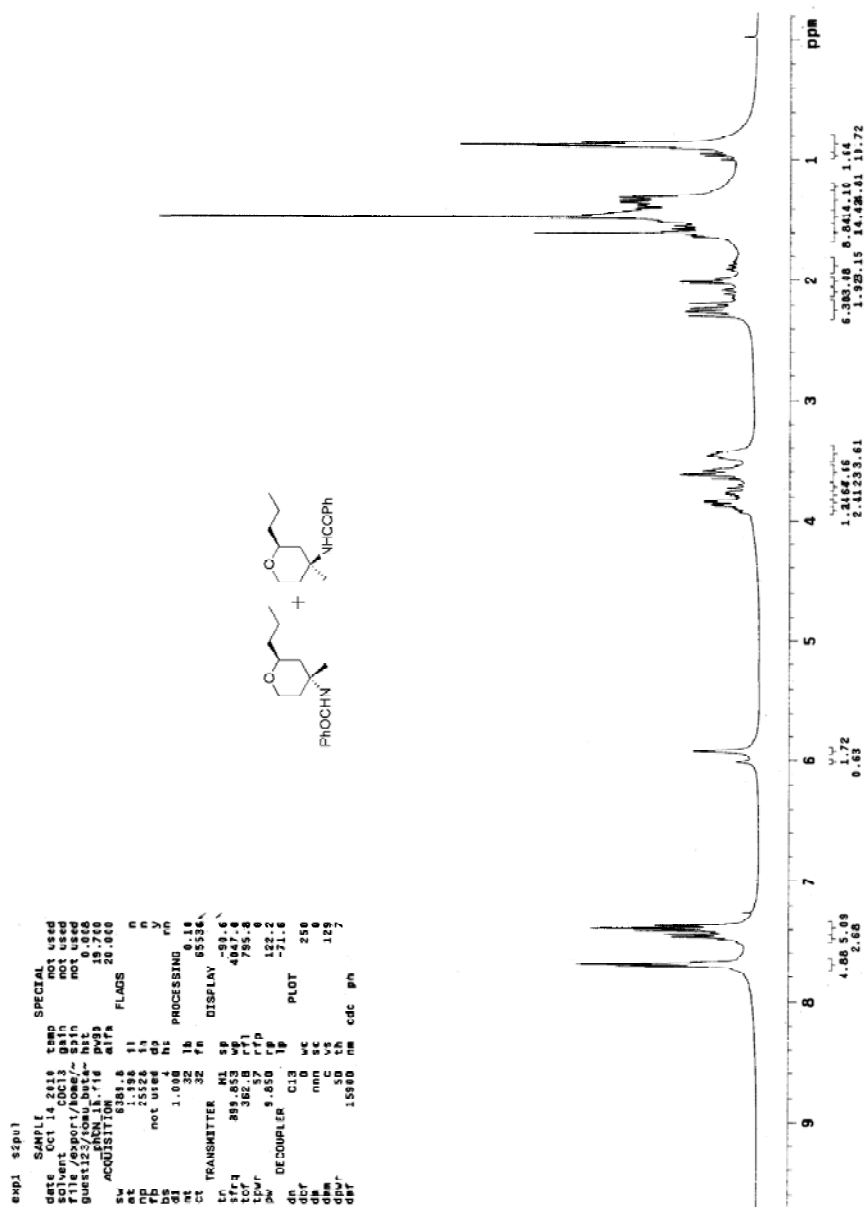
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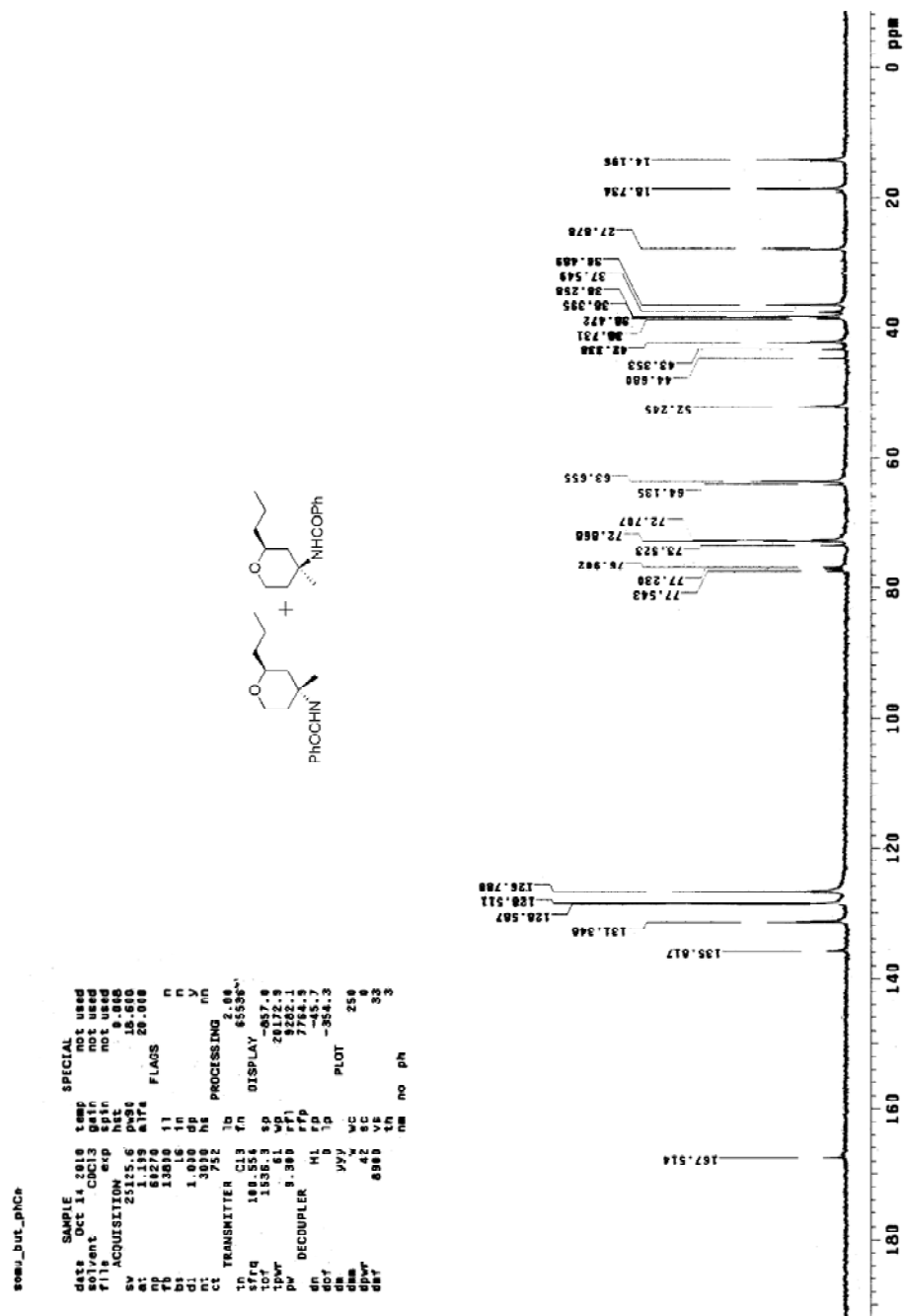
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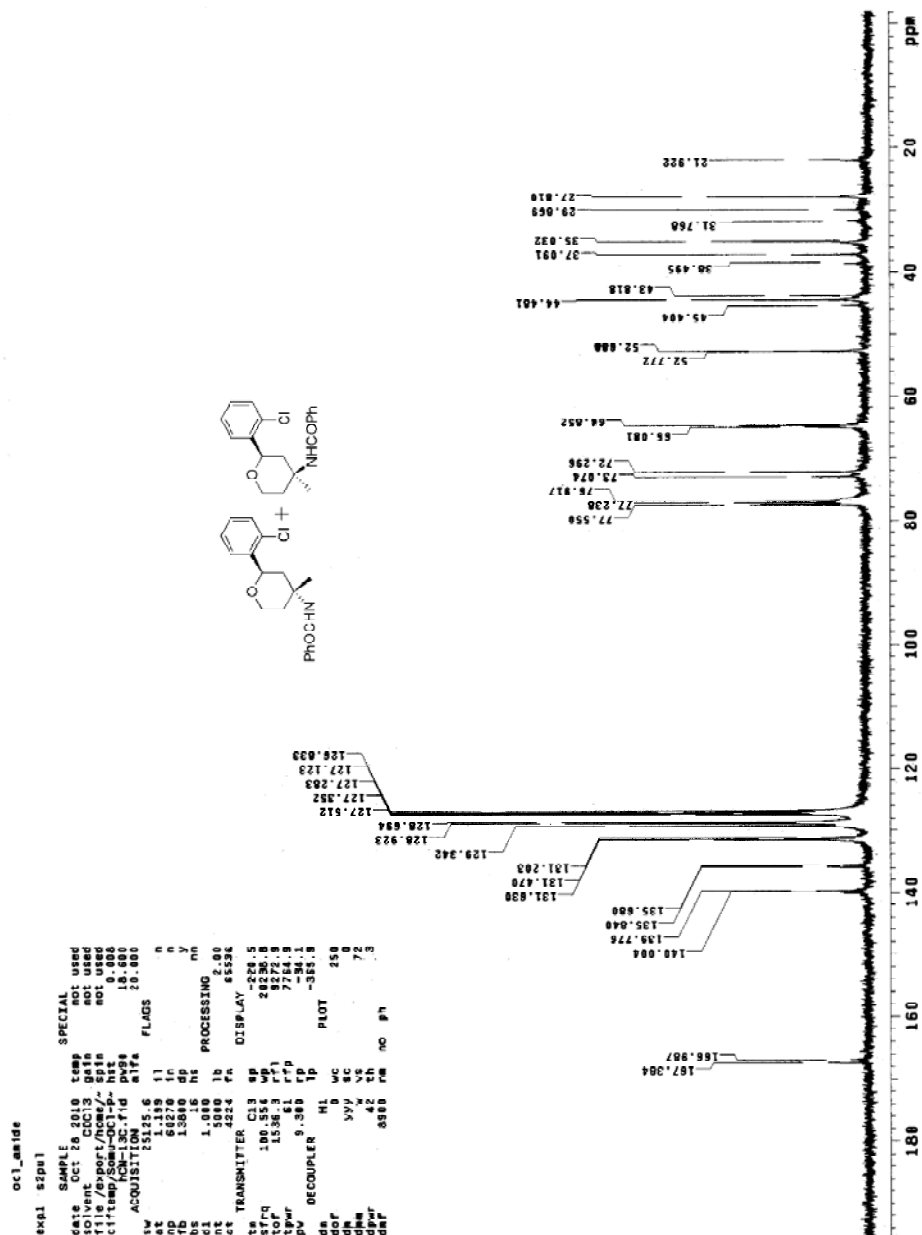
¹H NMR of 17k/18k



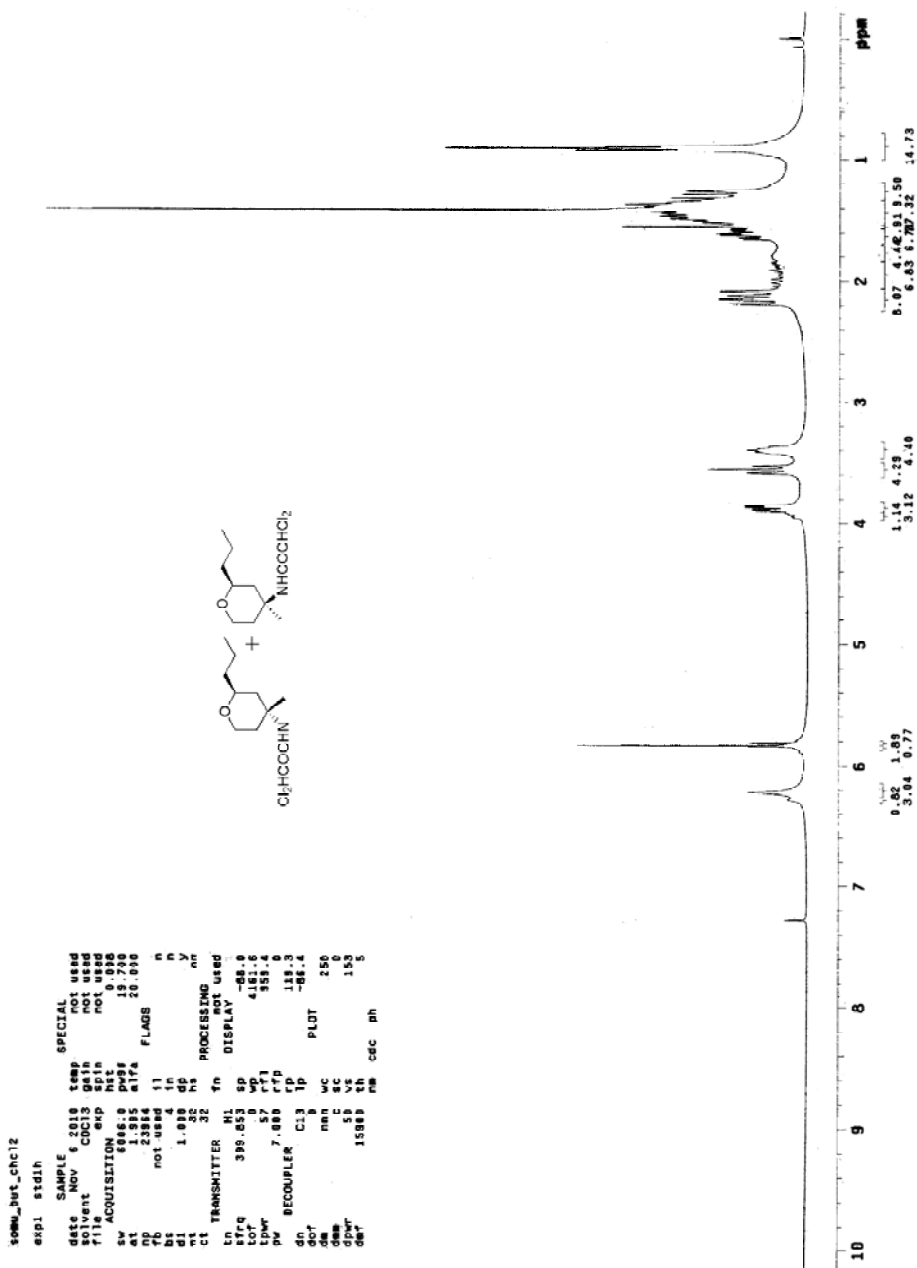
¹³C NMR of 17k/18k



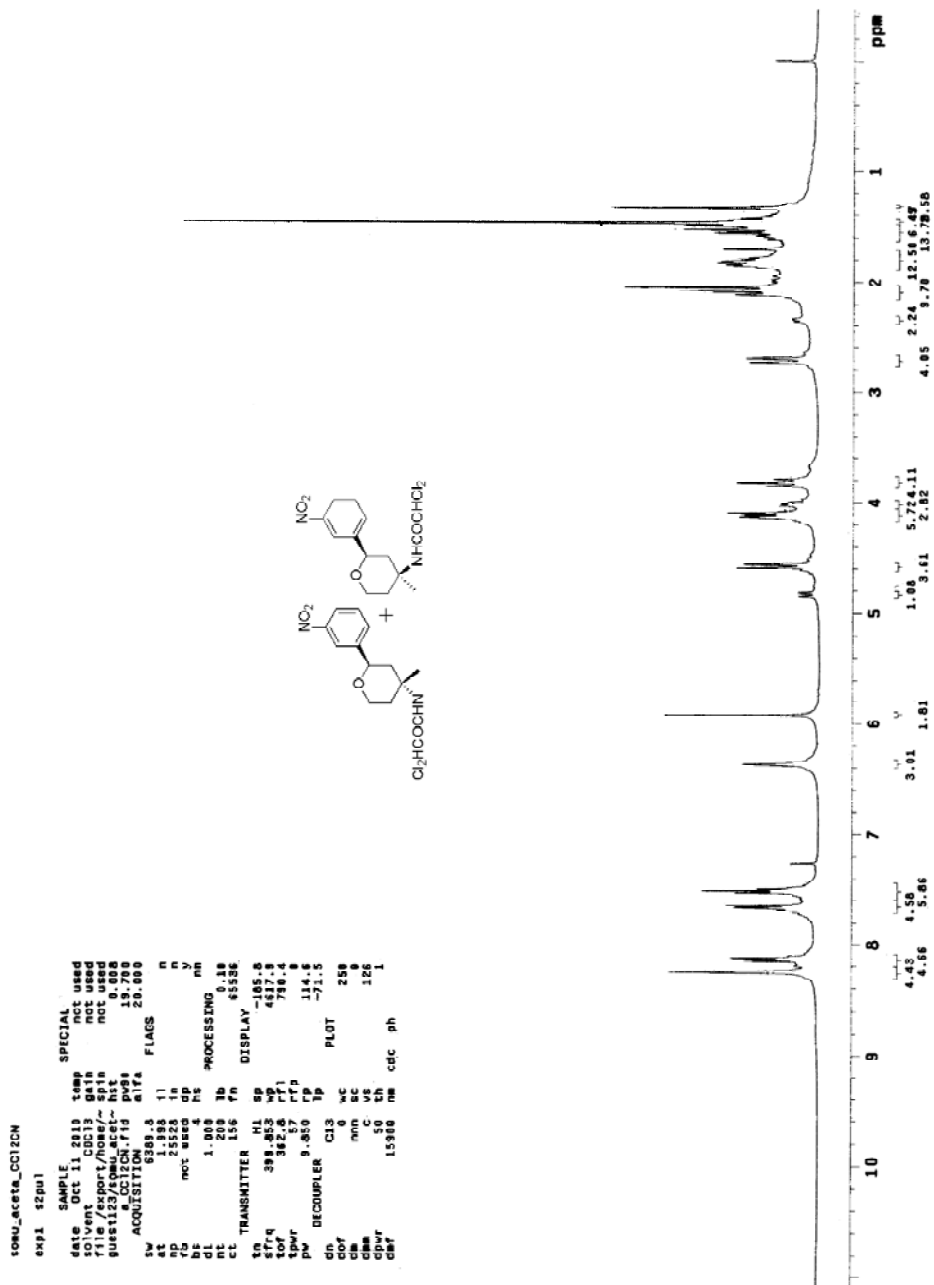
¹³C NMR of 17/18I



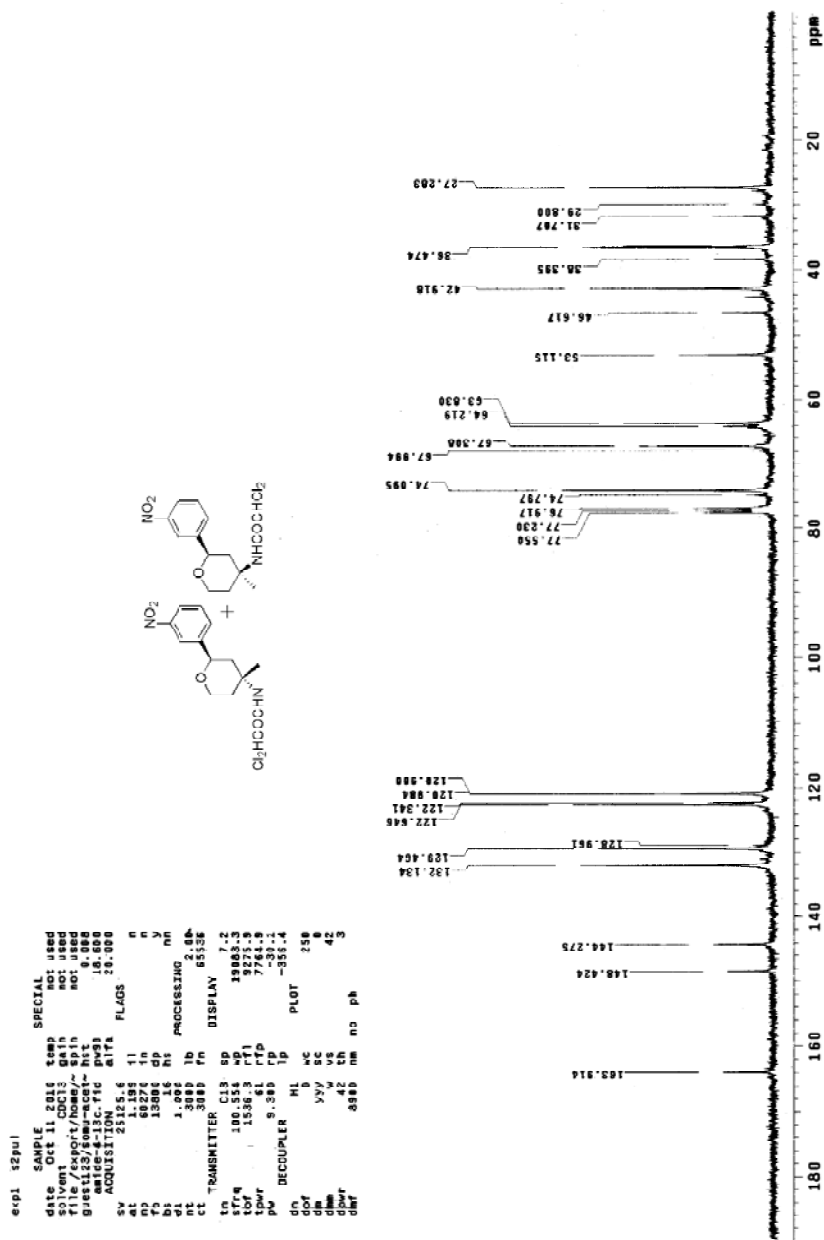
¹H NMR of 17m/18m



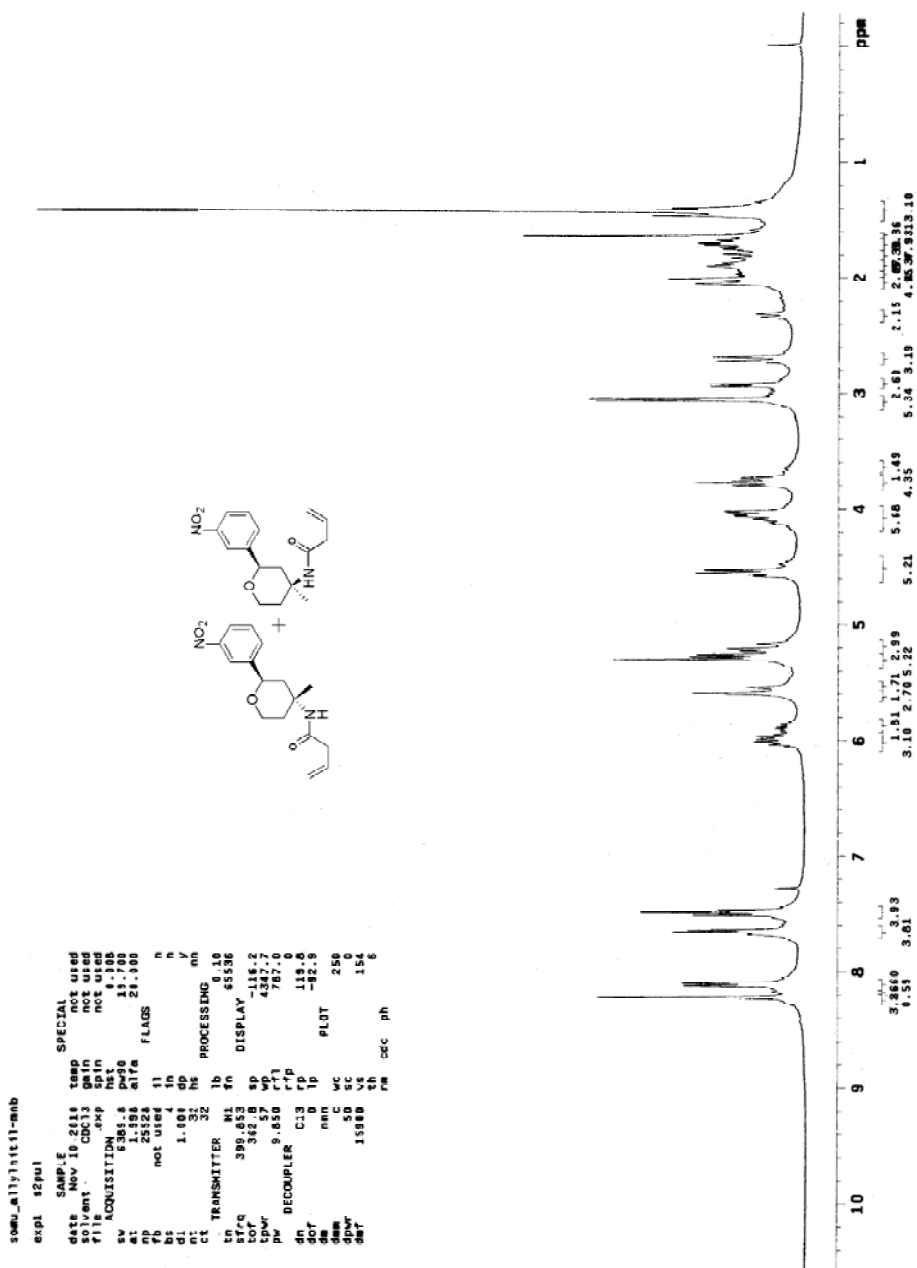
¹H NMR of 17n/18n



¹³C NMR of 17n/18n

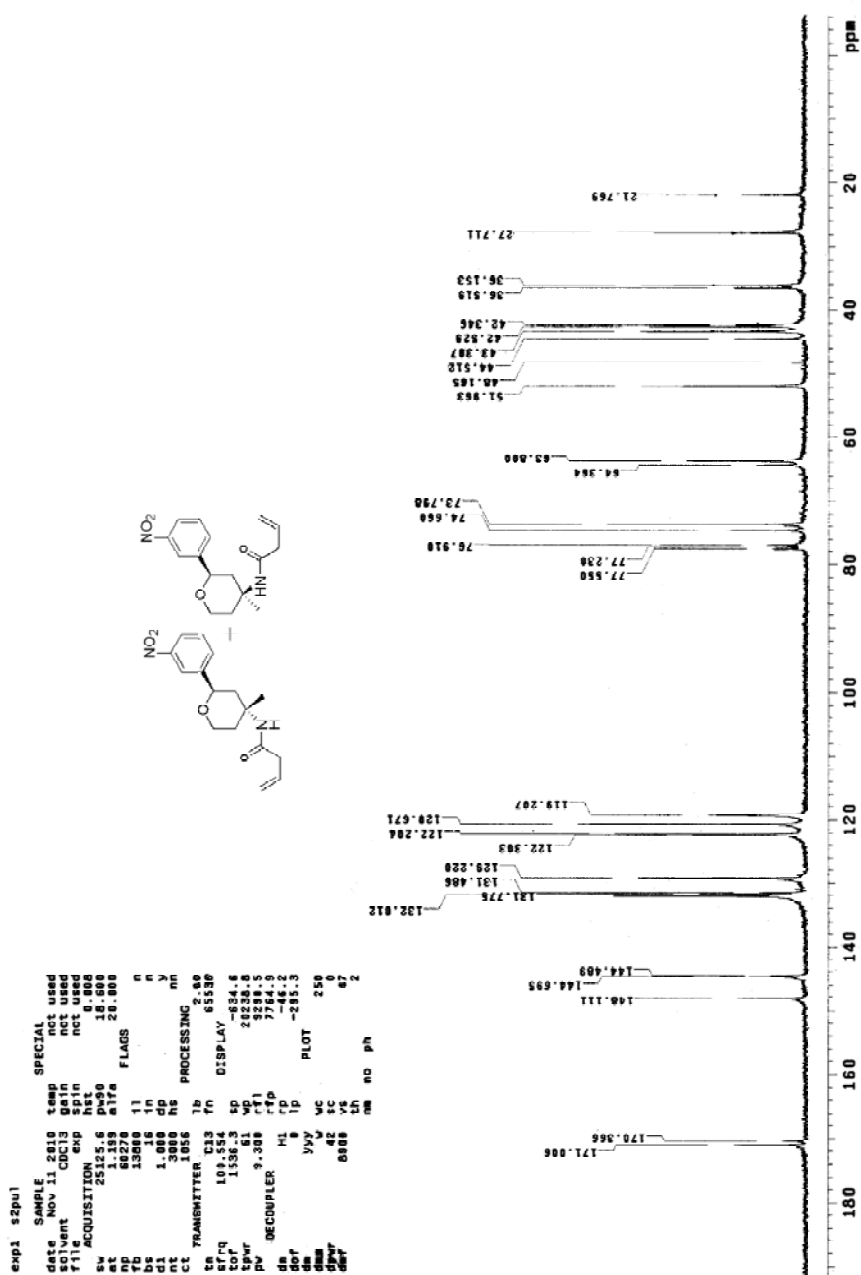


¹H NMR of 17o/18o



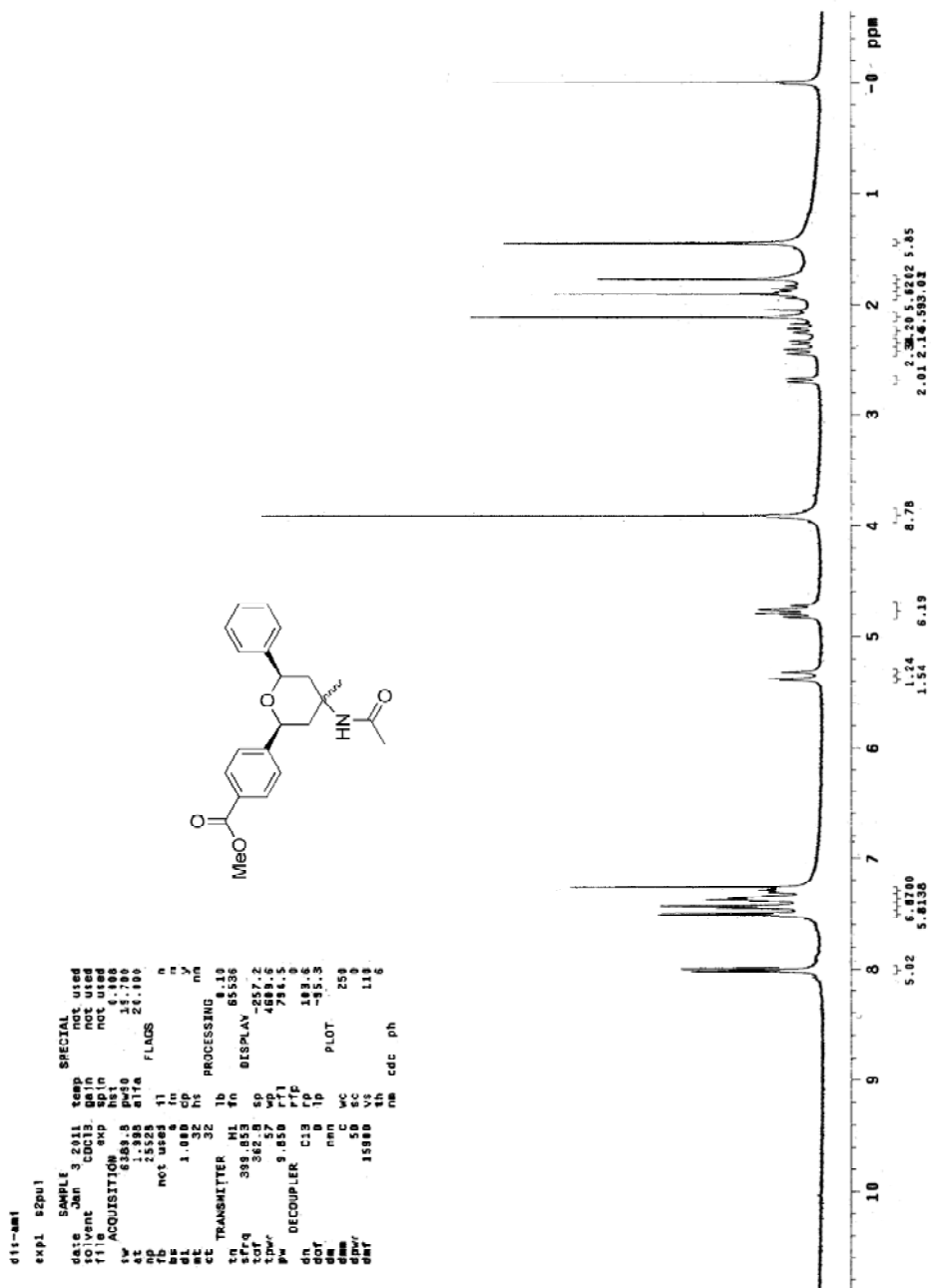
S-83

¹³C NMR of 17o/18o



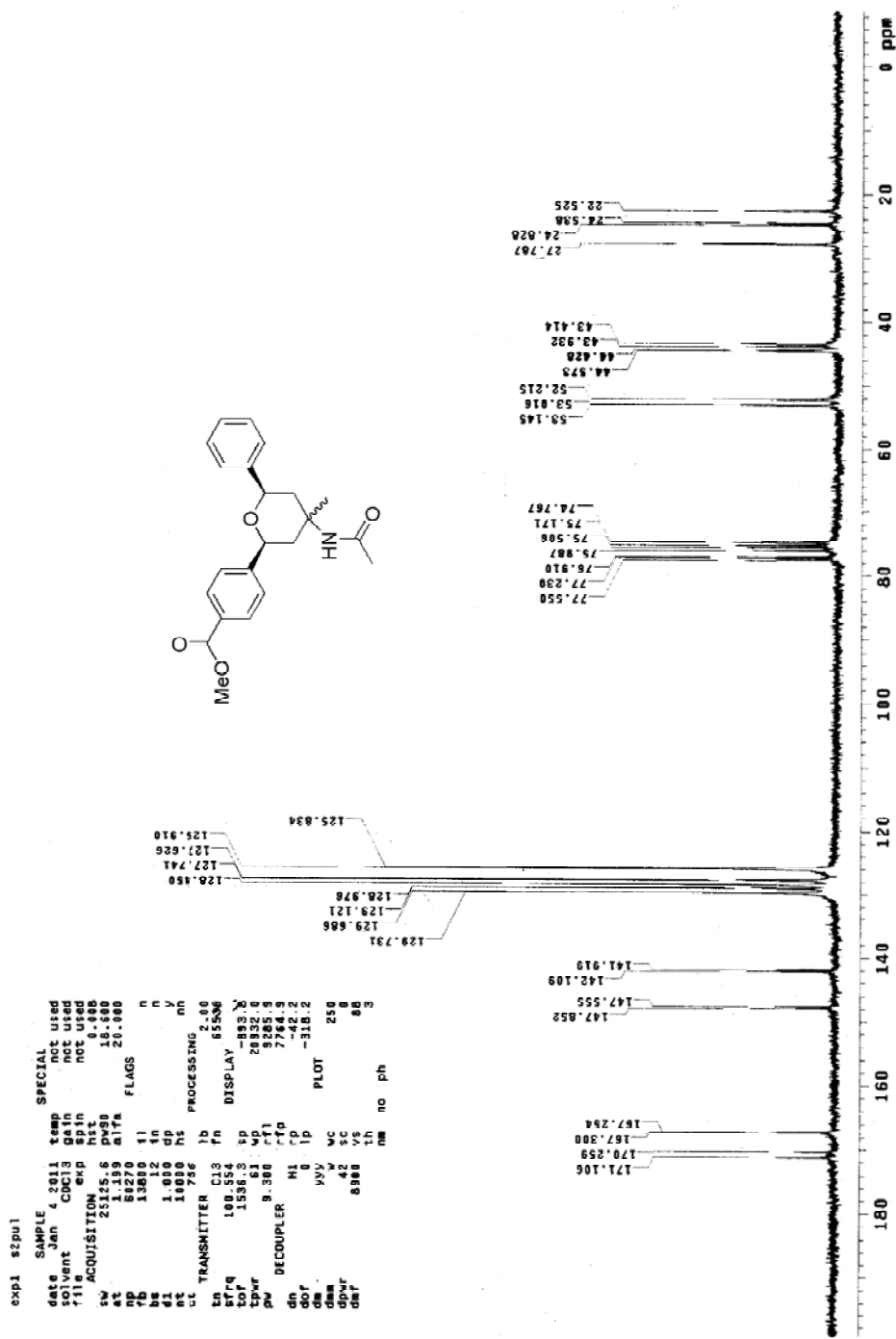
S-84

¹H NMR of 17p/18p



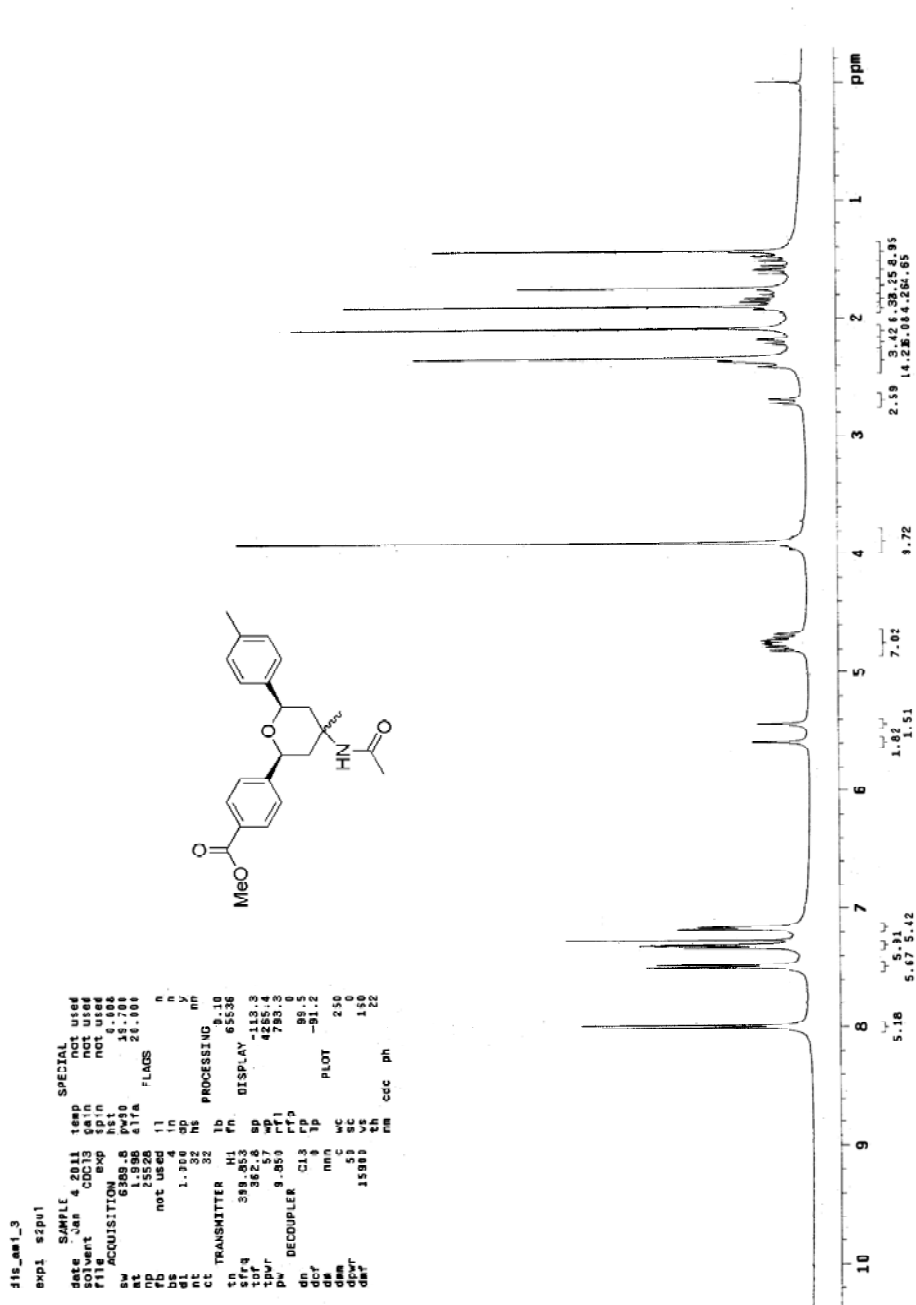
S-85

¹³C NMR of 17p/18p

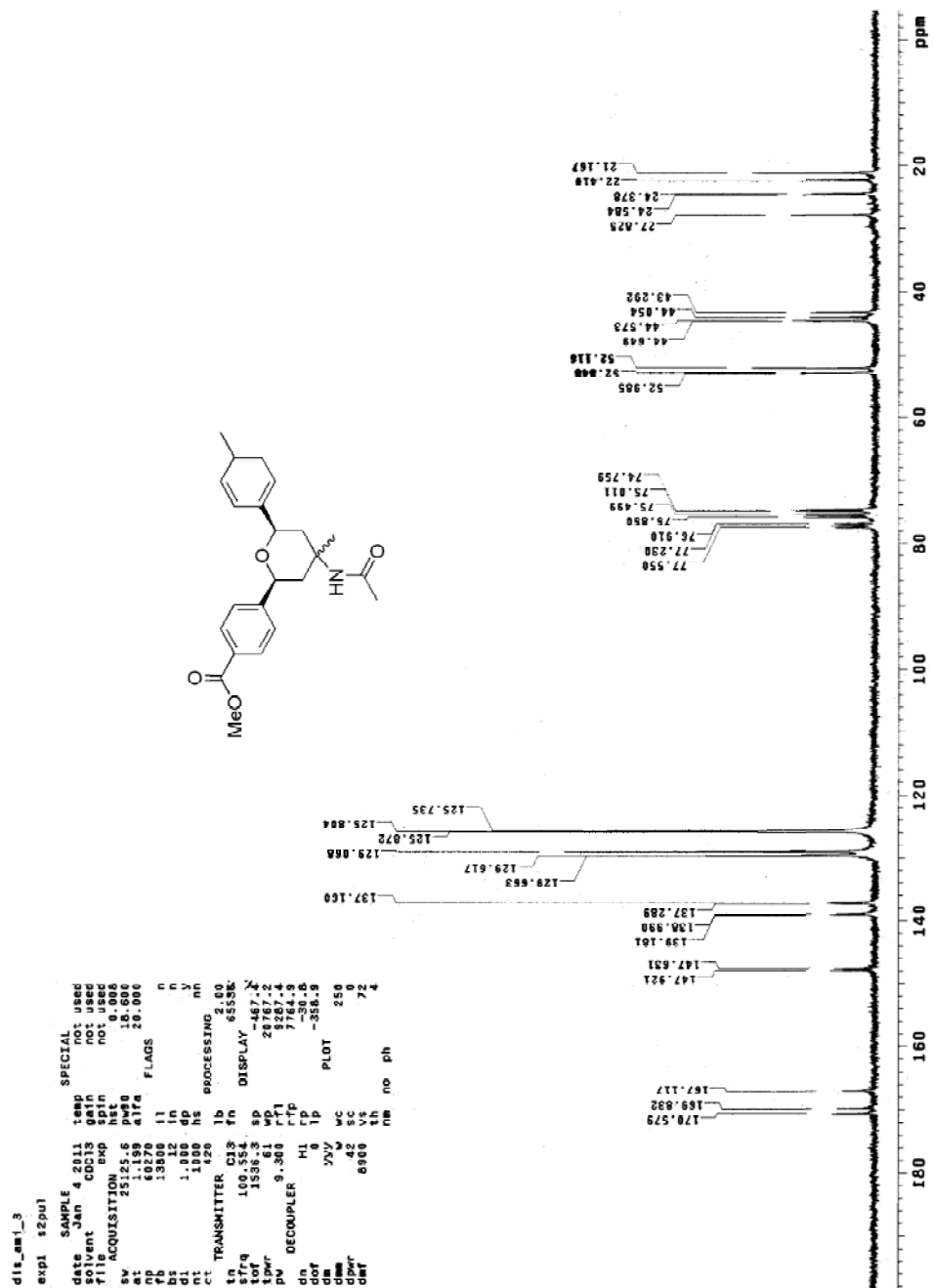


S-86

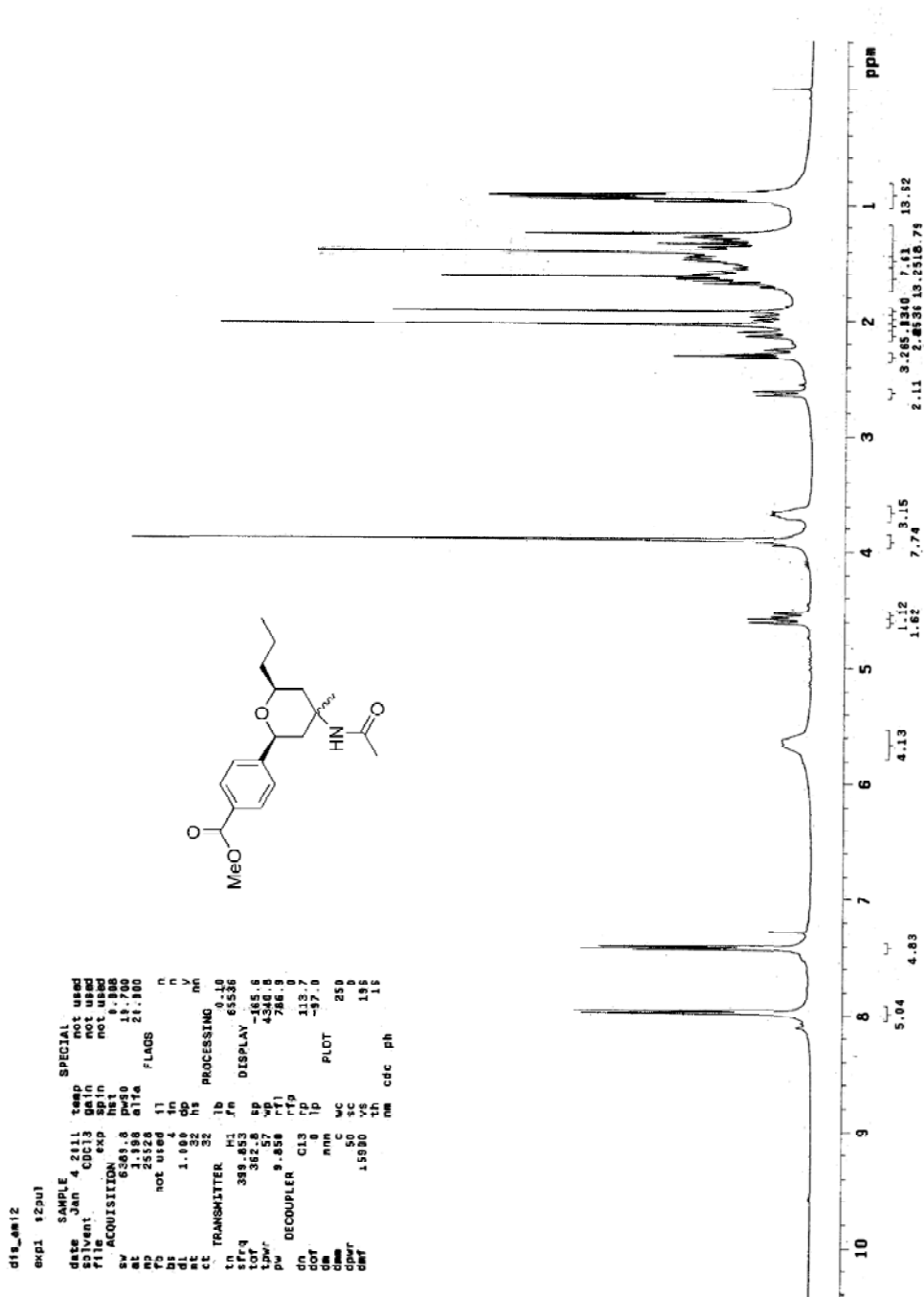
¹H NMR of 17q/18q



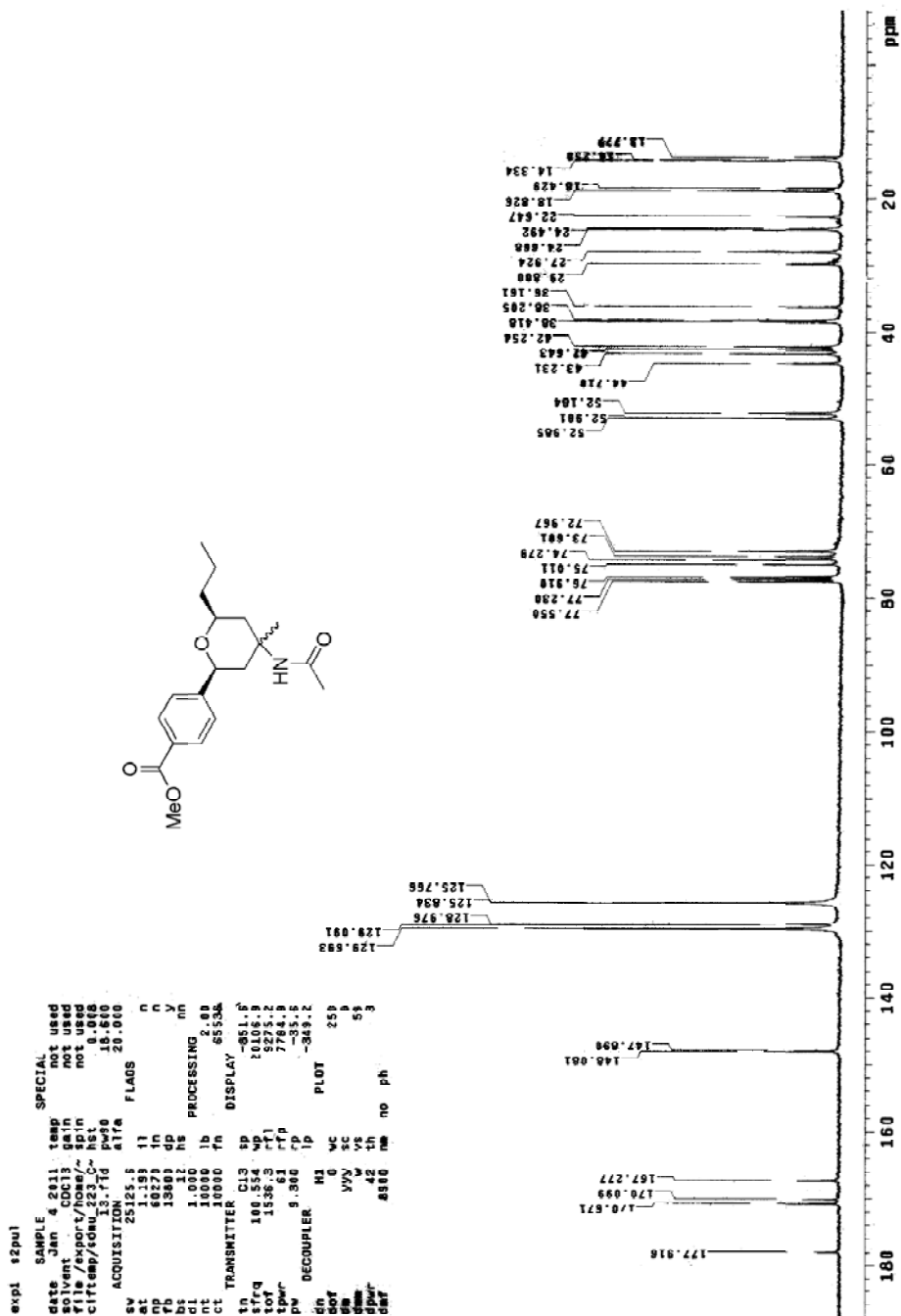
¹³C NMR of 17q/18q



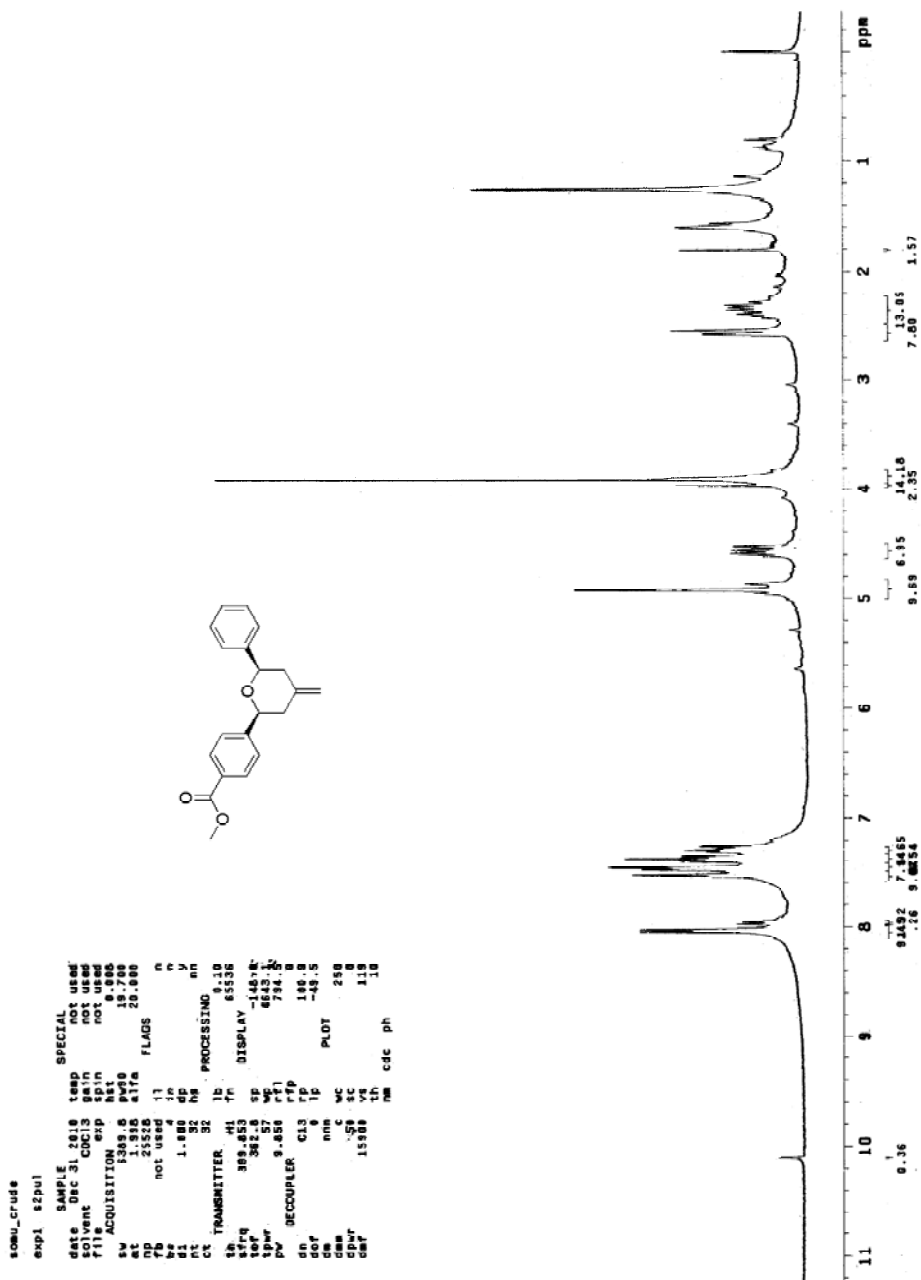
¹H NMR of 17r/18r



¹³C NMR of 17r/18r

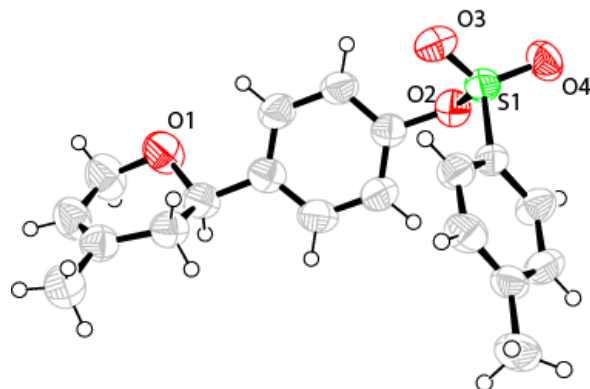


Crude ^1H NMR of **8r**



Crystallographic data

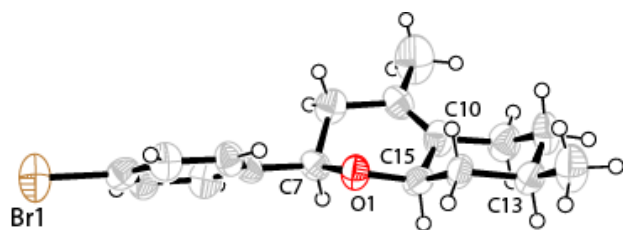
Figure 1: ORTEP Diagram of “Toluene 4-sulfonic acid 4-(4-Methyl-2,3-dihydro-2*H*-pyran-2-yl) phenyl ester” **6e**



The crystal parameters of compound **6e**

	6e- CCDC 765896
Formula	C19 H20 O4 S
Formula weight	344.41
<i>T</i> /K	296(2)
Crystal system	Triclinic
Space group	P (1)
<i>a</i> /Å	9.8247(5)
<i>b</i> /Å	11.1954(6)
<i>c</i> /Å	16.1562(9)
α /°	101.883(3)
β /°	95.733(3)
γ /°	91.650(3)
<i>V</i> /Å ³	1728.04(16)
<i>Z</i>	4
Abs. Coeff./mm ⁻¹	0.207
Abs. Correction	Multi-Scan
GOF on <i>F</i> ²	1.007
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>RI</i> = 0.0514 <i>wR2</i> = 0.1409
<i>R</i> indices [all data]	<i>RI</i> = 0.0798 <i>wR2</i> = 0.1578

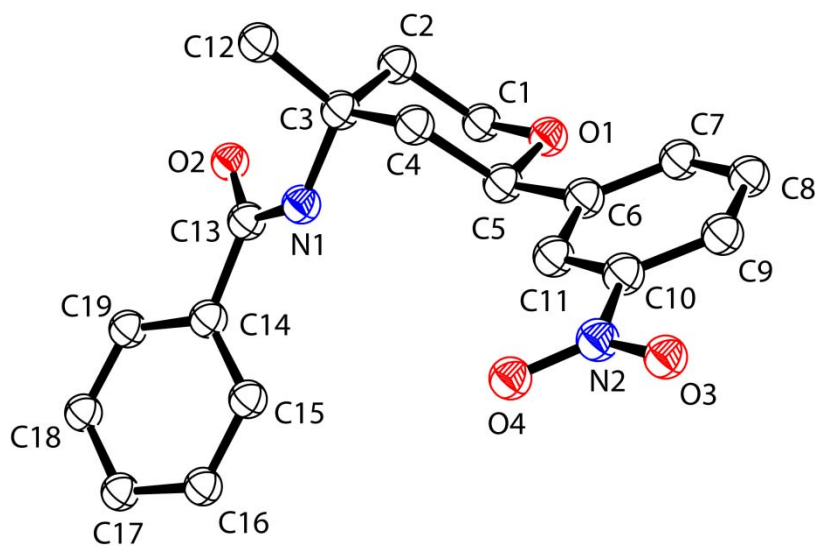
Figure 2: ORTEP Diagram of “2-(4-Bromophenyl)-4,7-dimethyl-3,5,6,7,8,8a-hexahydro-2,4-chromene” **10**



The crystal parameters of compound 10

	10- CCDC 765895
Formula	C ₁₇ H ₂₁ Br O
Formula weight	321.24
<i>T</i> /K	296(2)
Crystal system	Monoclinic
Space group	P2 (1)
<i>a</i> /Å	4.7575 (2)
<i>b</i> /Å	9.8672 (4)
<i>c</i> /Å	16.6178 (6)
α /°	90.00
β /°	92.210 (2)
γ /°	90.00
<i>V</i> /Å ³	779.51 (5)
<i>Z</i>	2
Abs. Coeff./mm ⁻¹	2.628
Abs. Correction	Multi-Scan
GOF on <i>F</i> ²	1.077
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>RI</i> = 0.0525 <i>wR2</i> = 0.1308
<i>R</i> indices [all data]	<i>RI</i> = 0.0605 <i>wR2</i> = 0.1449

Figure 3: ORTEP Diagram of *N*-[4-Methyl-2-(3-nitrophenyl)-tetrahydropyran-4-yl]-benzamide 17j



The crystal parameters of compound 17j

	17j- CCDC 800377
Formula	C ₁₉ H ₂₀ N ₂ O ₄
Formula weight	340.37
<i>T</i> /K	296(2)
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> /Å	11.6207(12)
<i>b</i> /Å	19.274(2)
<i>c</i> /Å	16.3163(15)
α /°	90.00
β /°	100.451(7)
γ /°	90.00
<i>V</i> /Å ³	3593.8(6)
<i>Z</i>	8
Abs. Coeff./mm ⁻¹	0.089
Abs. Correction	Multi-Scan
GOF on <i>F</i> ²	1.003
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0522 <i>wR</i> 2 = 0.1180
<i>R</i> indices [all data]	<i>R</i> 1 = 0.0988 <i>wR</i> 2 = 0.1411