

**Nucleophilic Ring-opening of *meso*-Substituted 5-Oxaporphyrin**

**by Oxygen, Nitrogen, Sulfur, and Carbon Nucleophiles**

Kazuhisa Kakeya, Masakatsu Aozasa, Tadashi Mizutani,\* Yutaka Hitomi and Masahito Kodera

Department of Molecular Chemistry and Biochemistry, Faculty of Science and Engineering, and Center for

Nanoscience Research, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

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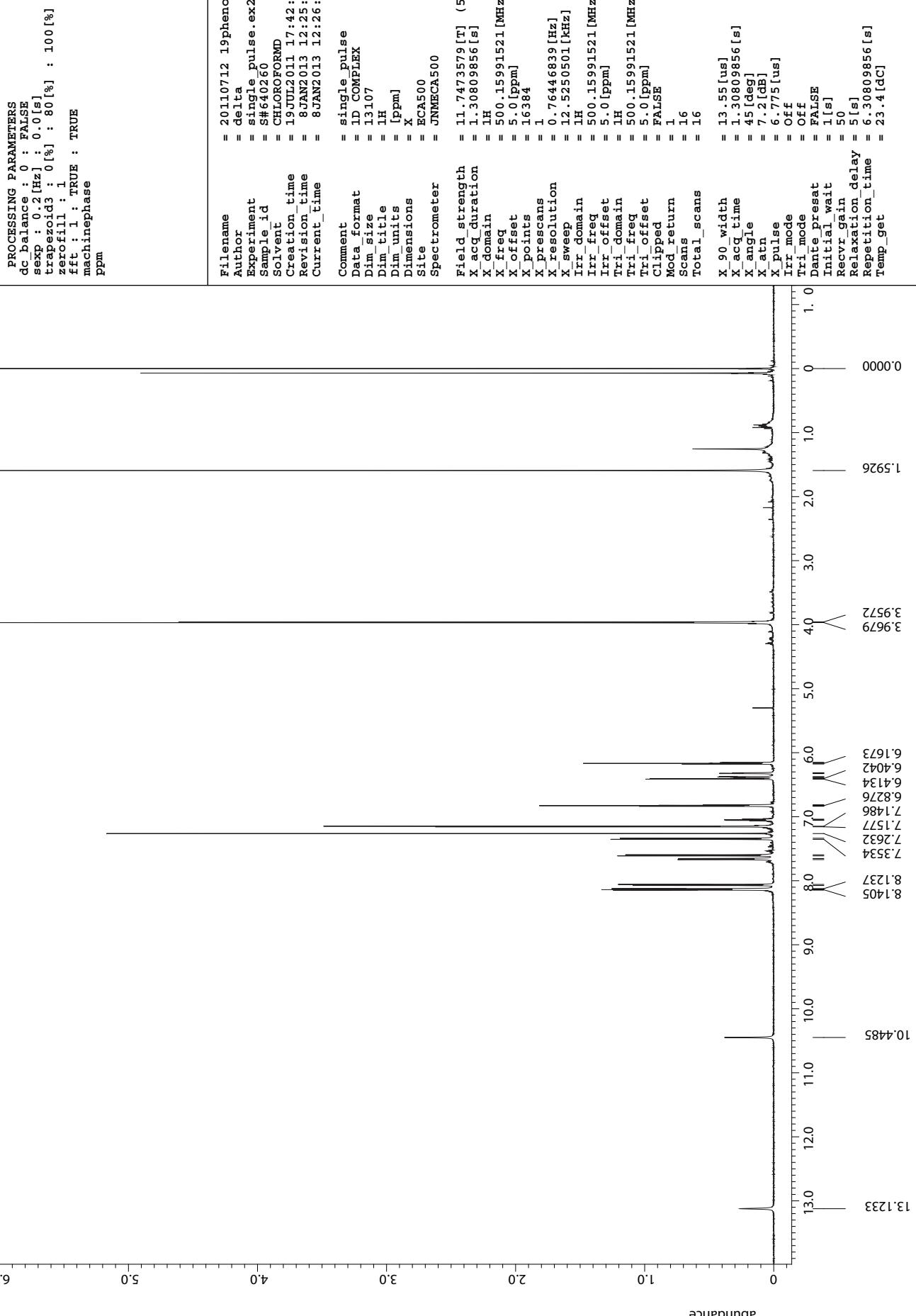


Figure S1.  $^1\text{H}$  NMR of 4.

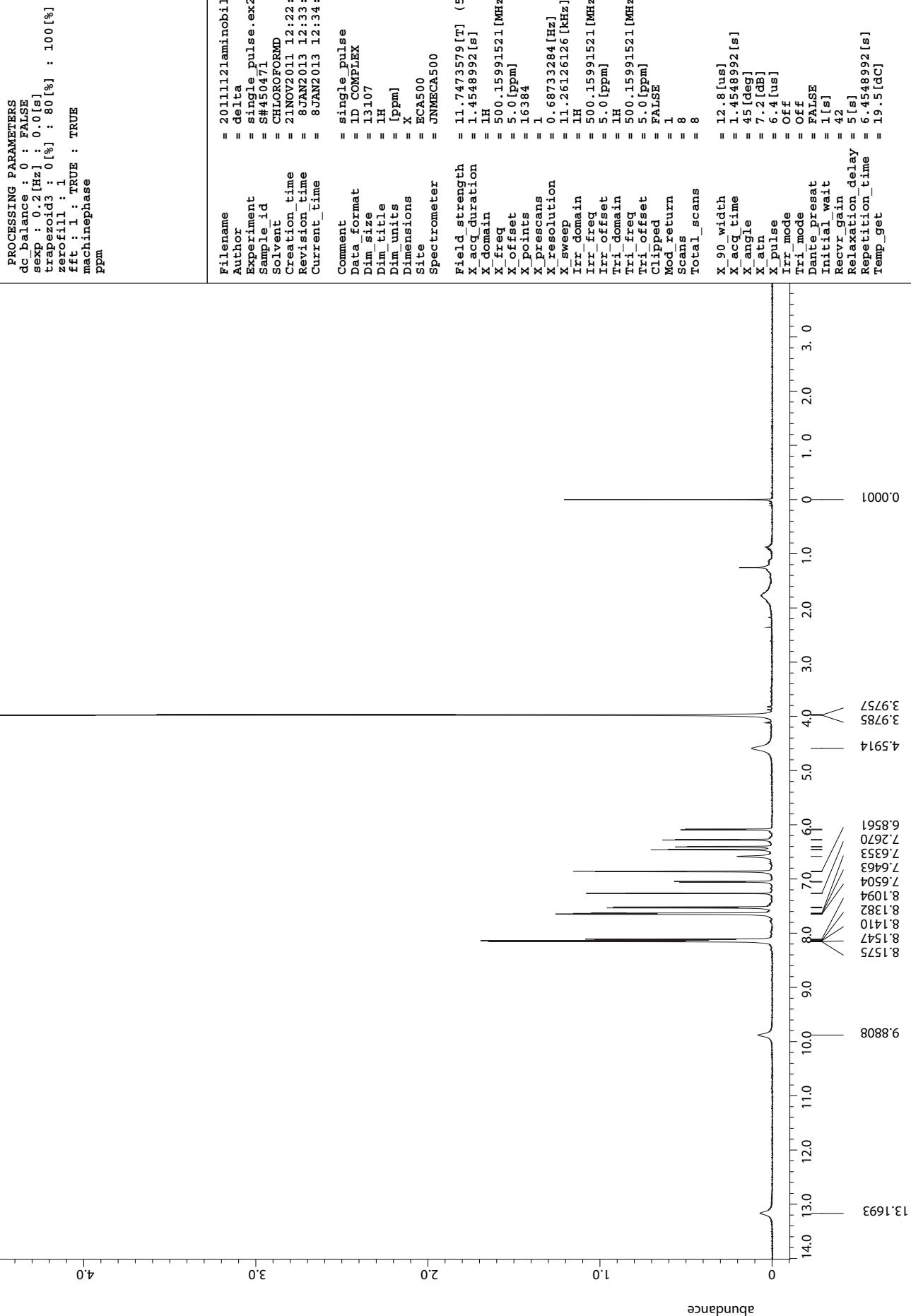


Figure S2.  $^1\text{H}$  NMR of 5.



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ppm

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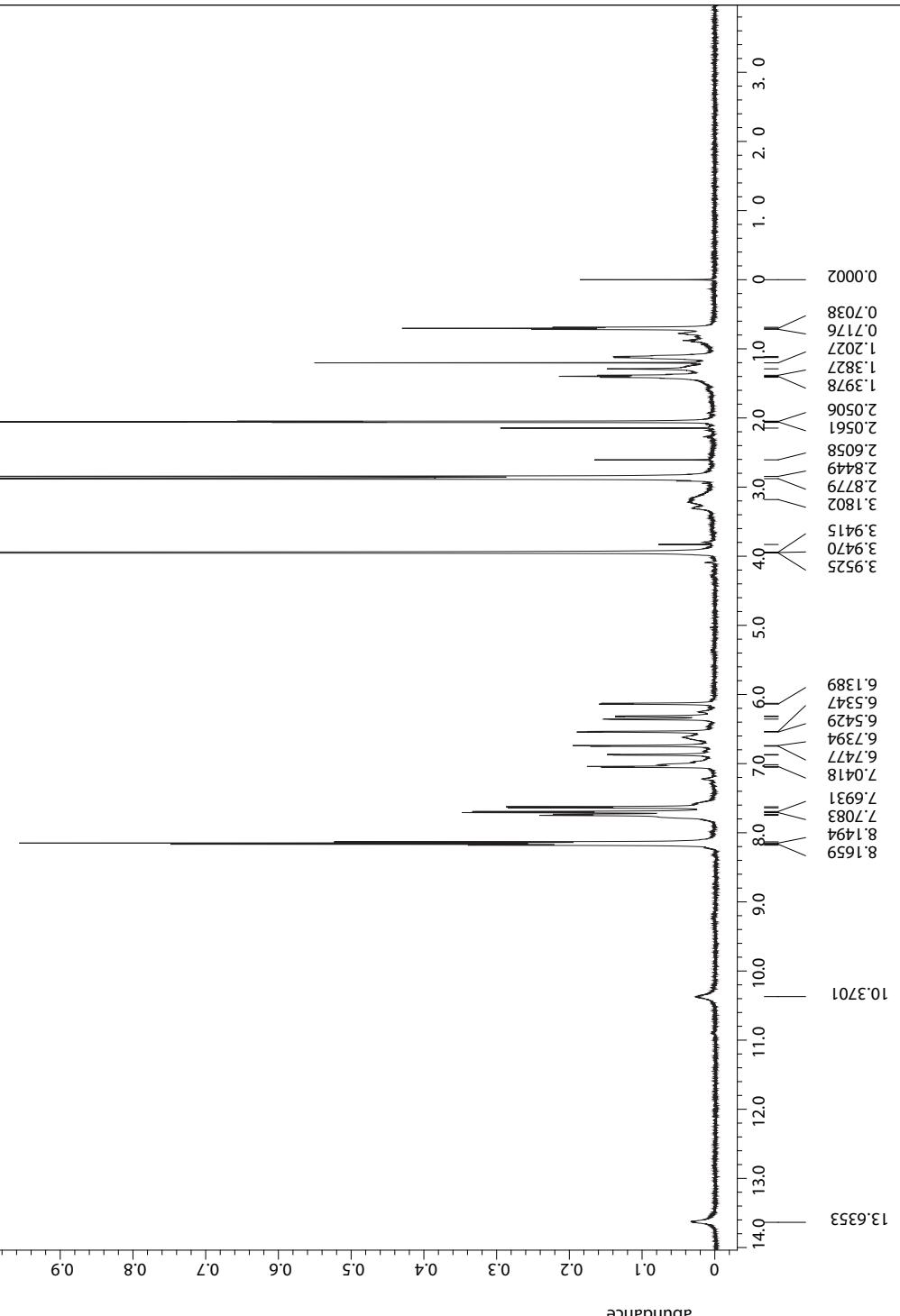


Figure S3.  $^1\text{H}$  NMR of **6**.

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field_strength = 11.7473579 [T] (500 [MHz])
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x_offset = 5.0 [ppm]
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x_sweep = 11.26126126 [kHz]
irr_domain = 1H
irr_freq = 500.15991521 [MHz]
irr_offset = 5.0 [ppm]
tri_domain = 1H
tri_freq = 500.15991521 [MHz]
tri_offset = 5.0 [ppm]
clipped = FALSE
mod_return = 1
scans = 8
total_scans = 8

x_90_width = 6.34 [us]
x_acq_time = 1.4548992 [s]
x_angle = 45 [deg]
x_atn = 6.5 [dB]
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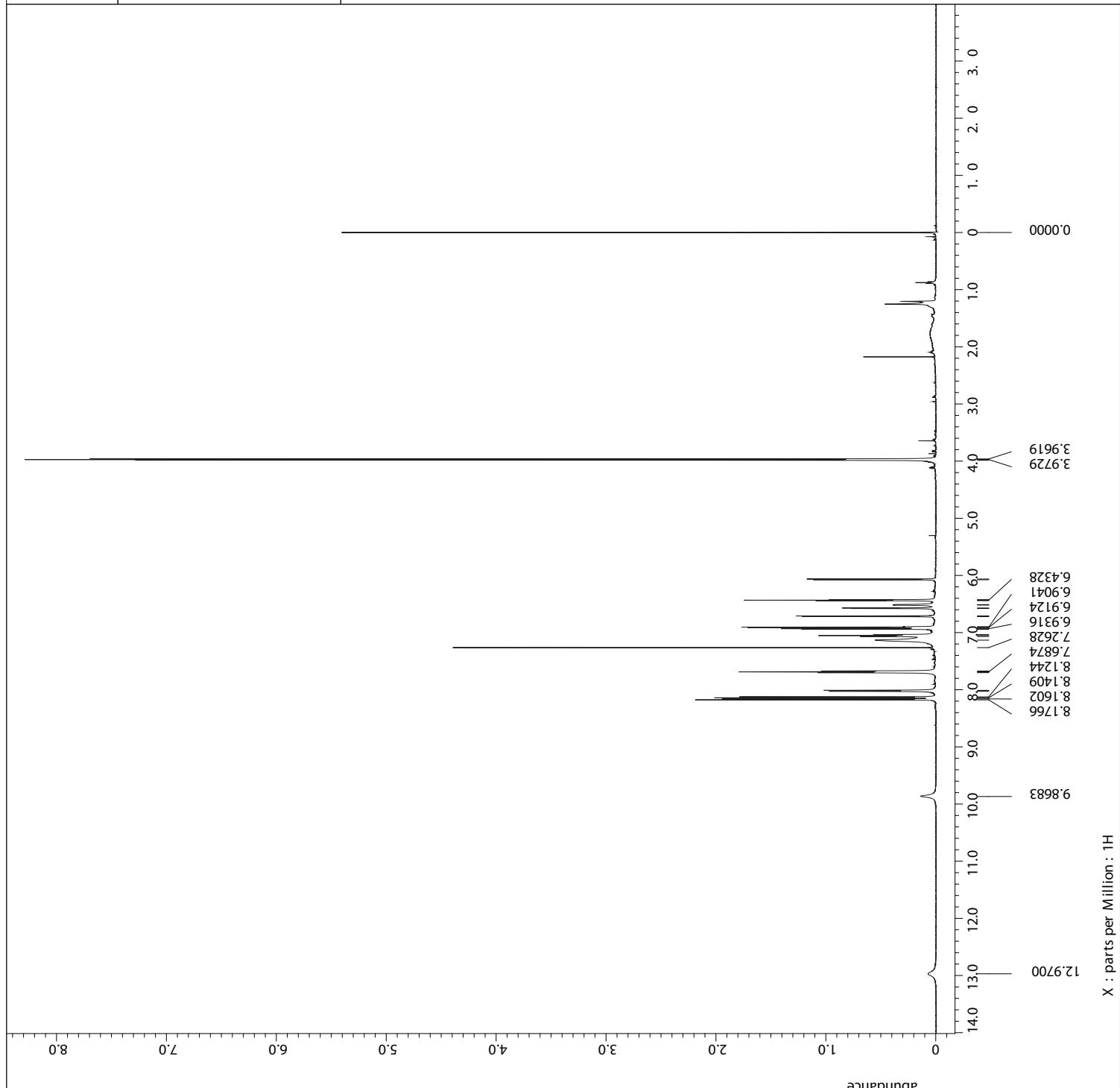


Figure S4.  $^1\text{H}$  NMR of 7.

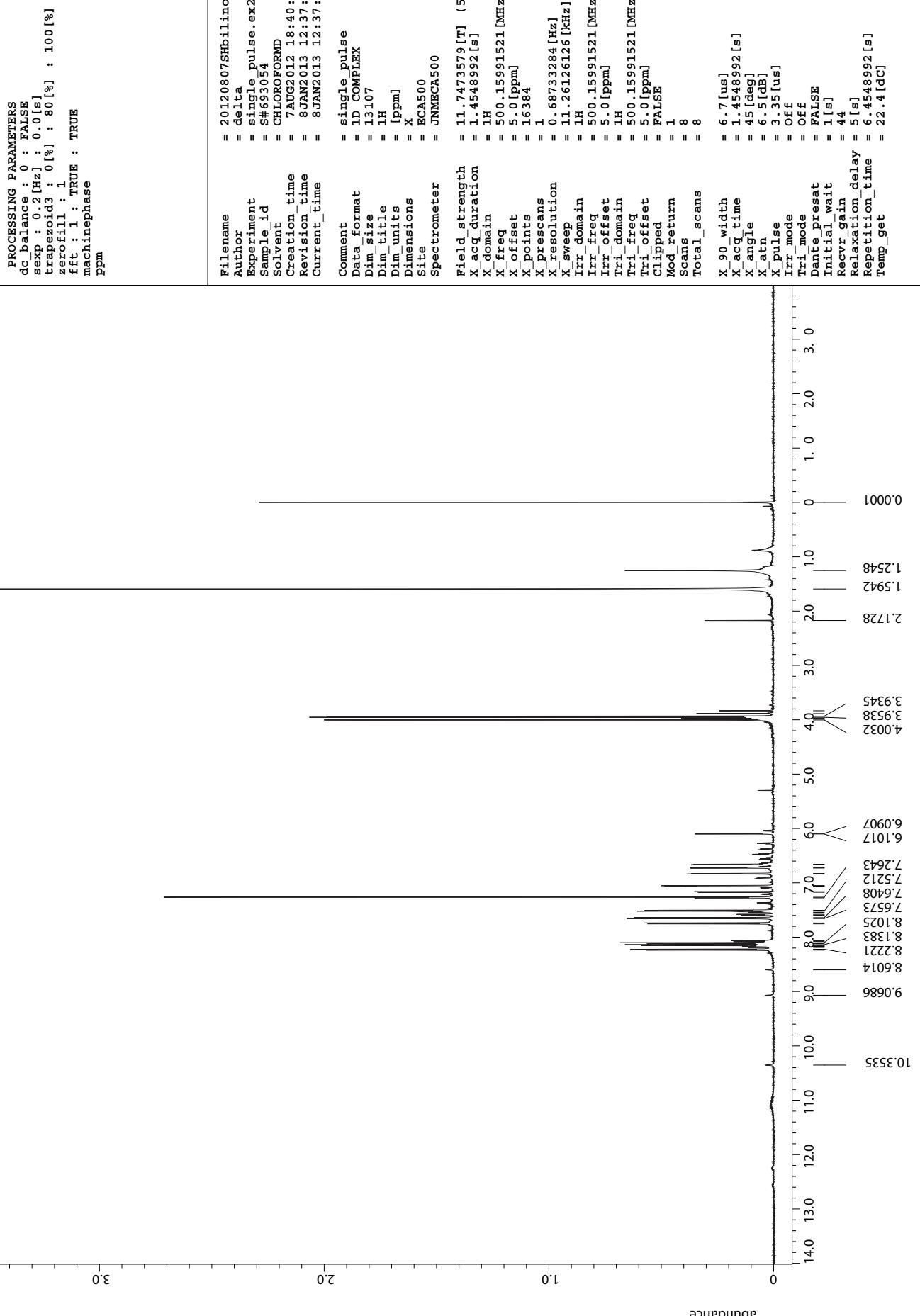


Figure S5.  $^1\text{H}$  NMR of **8**.

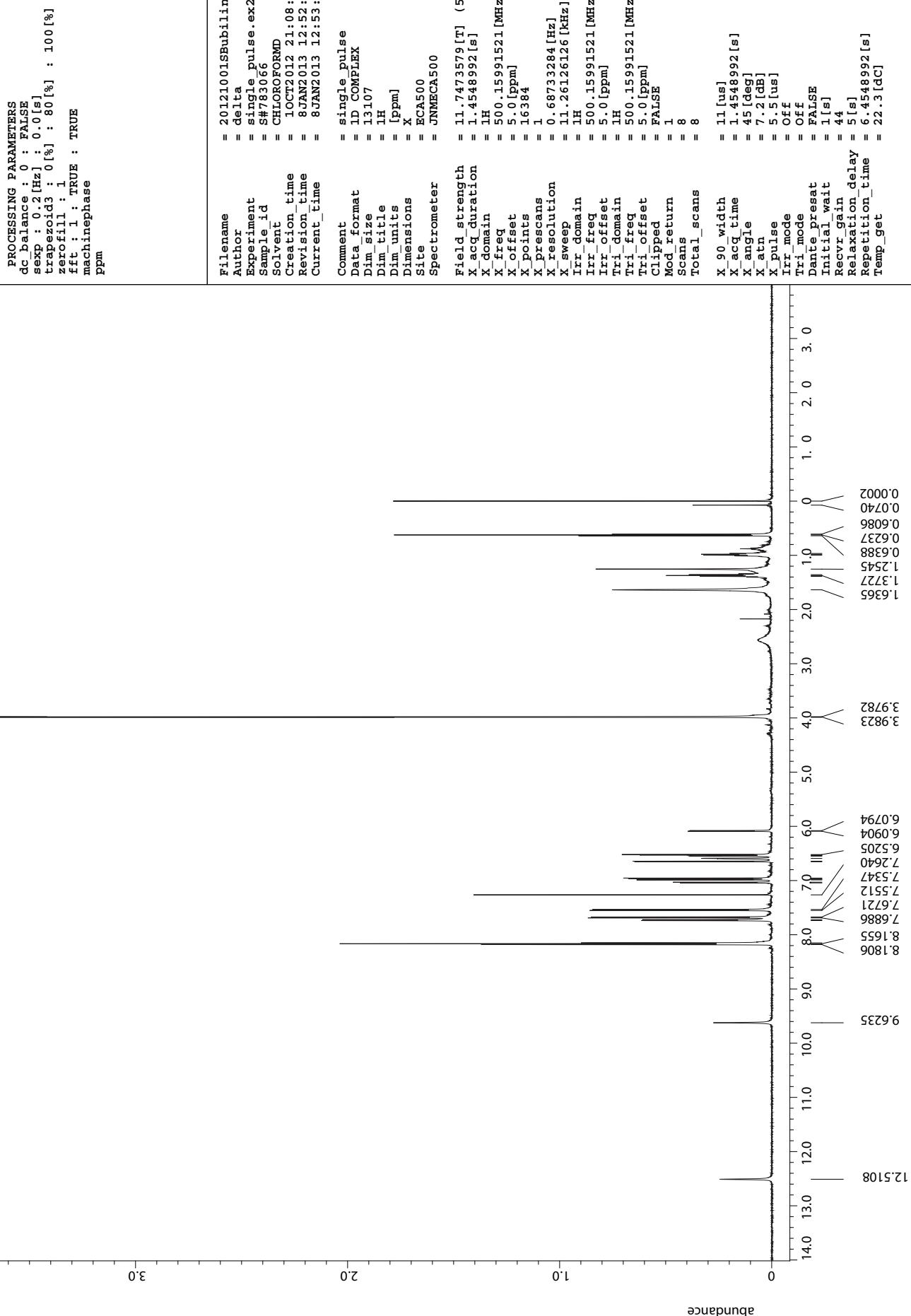


Figure S6.  $^1\text{H}$  NMR of **9**.

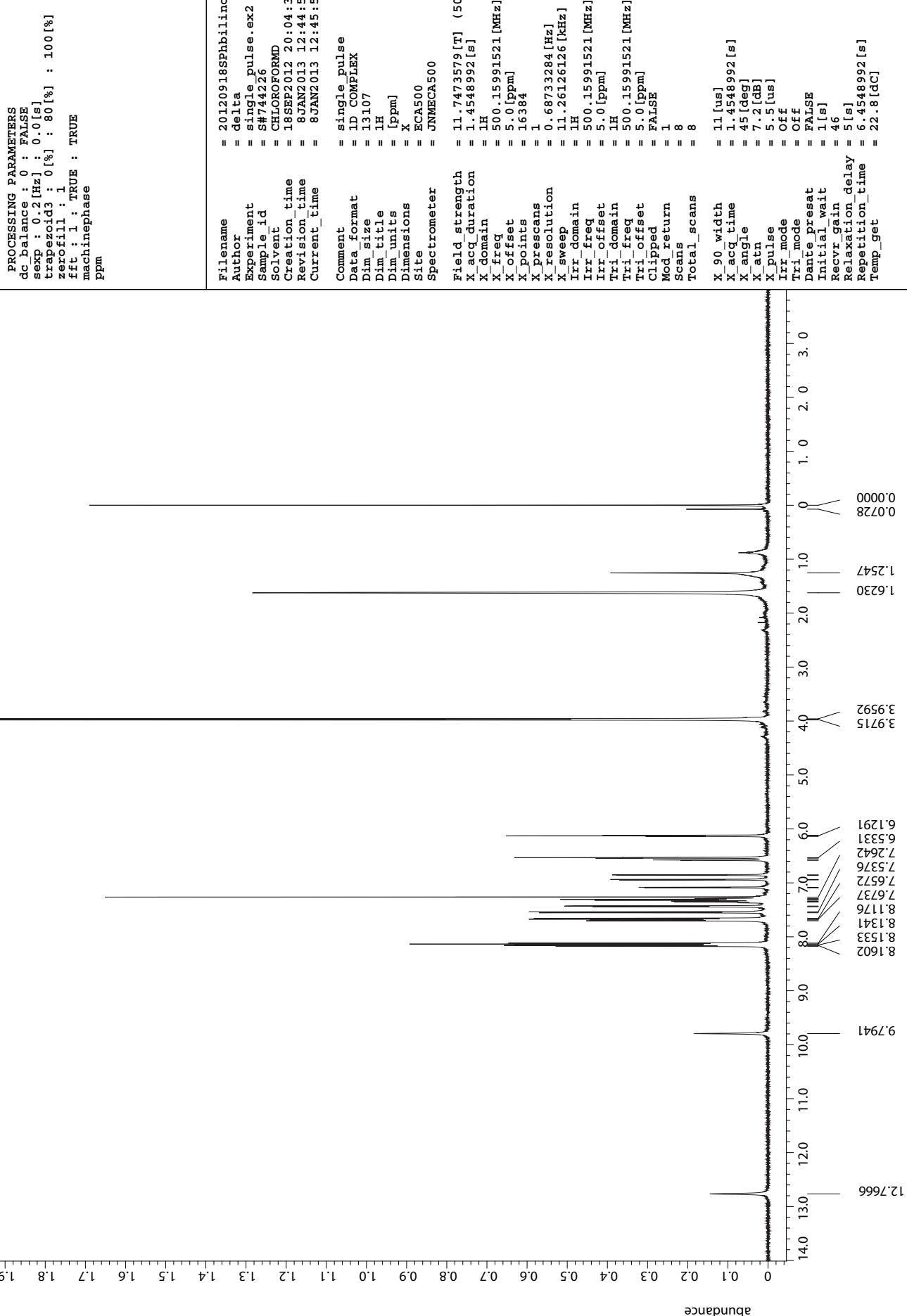


Figure S7.  $^1\text{H}$  NMR of **10**.

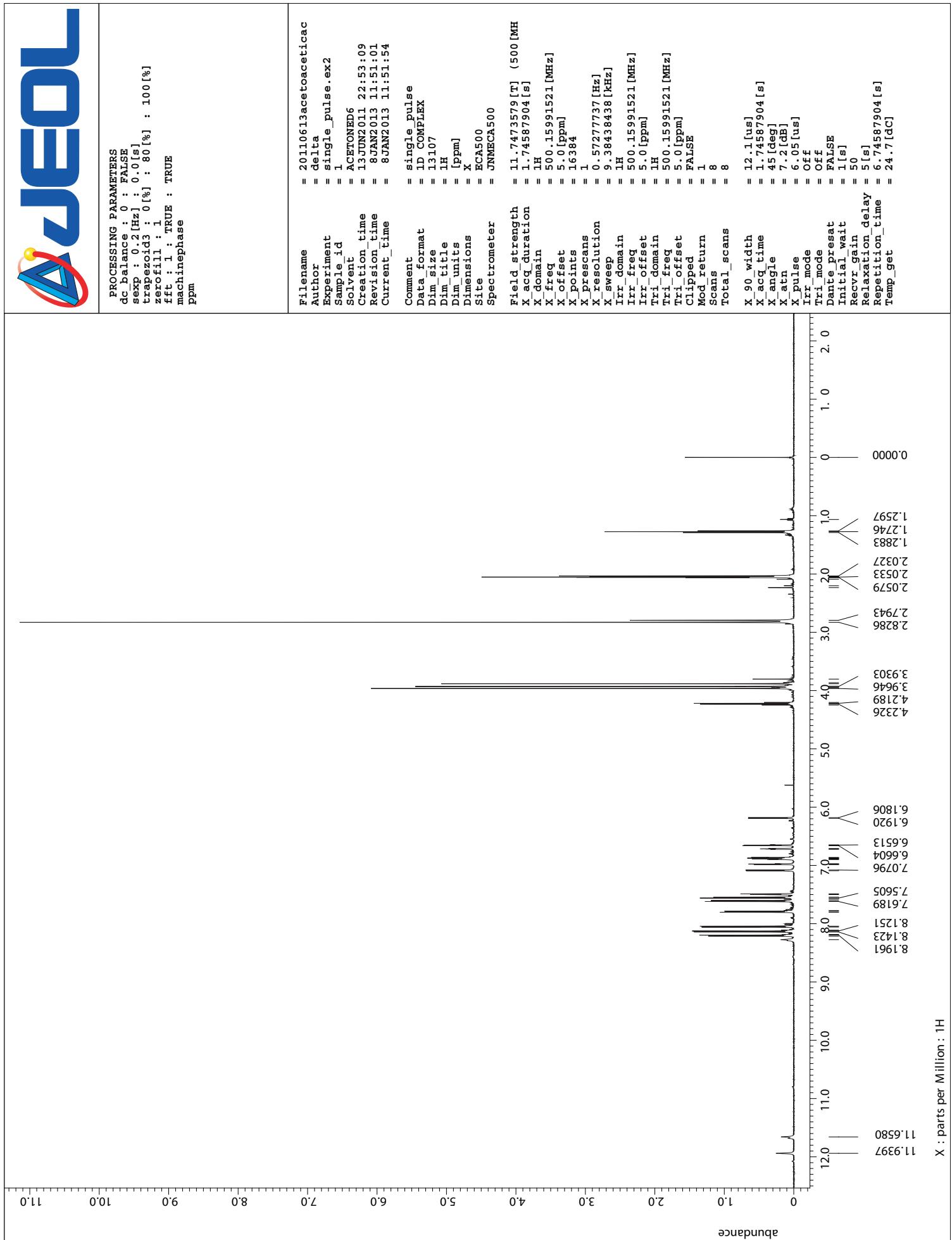


Figure S8.  $^1\text{H}$  NMR of 11.

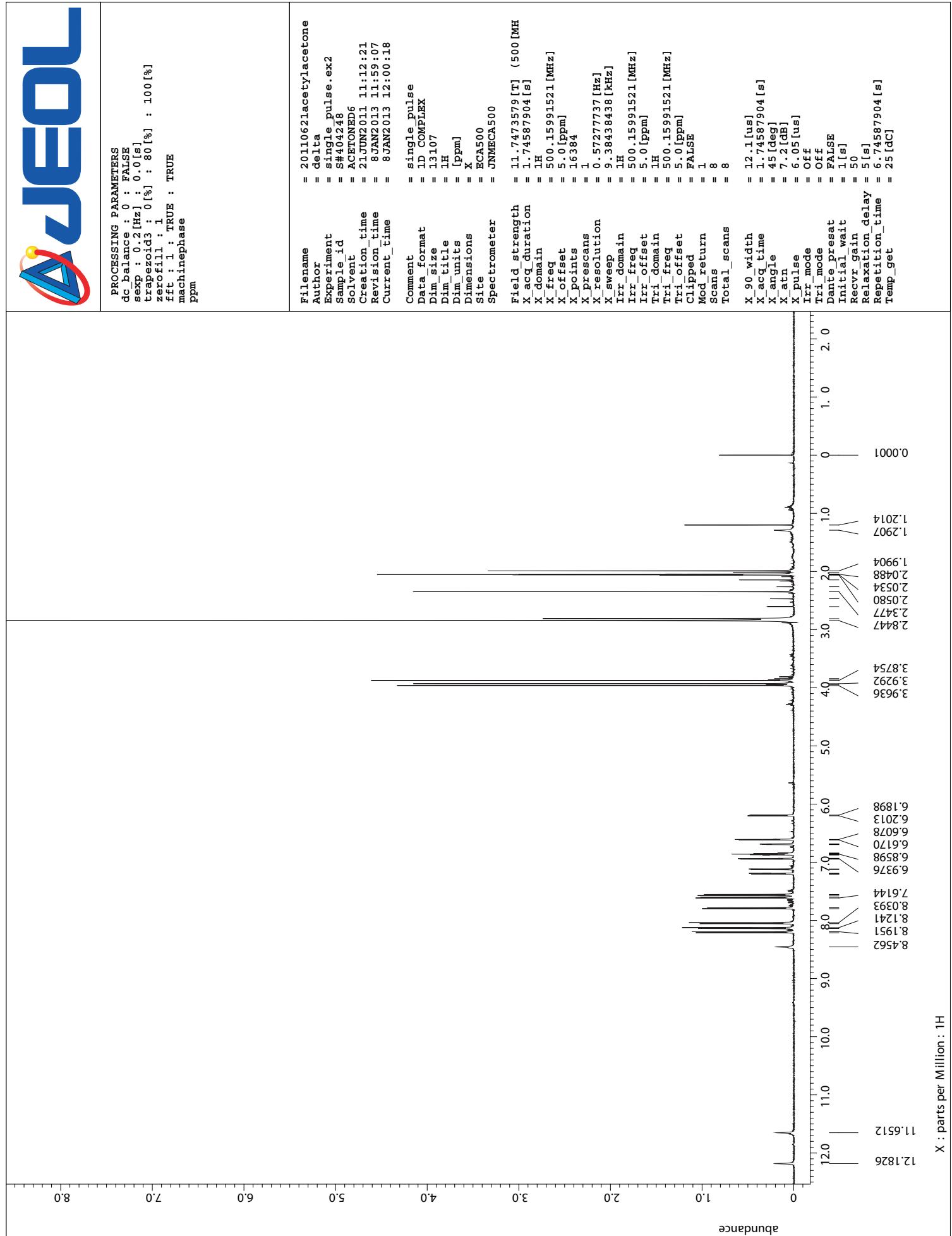


Figure S9.  $^1\text{H}$  NMR of **12**.

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PROCESSING PARAMETERS
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fft : 1 : TRUE : TRUE
machinemphase
ppm

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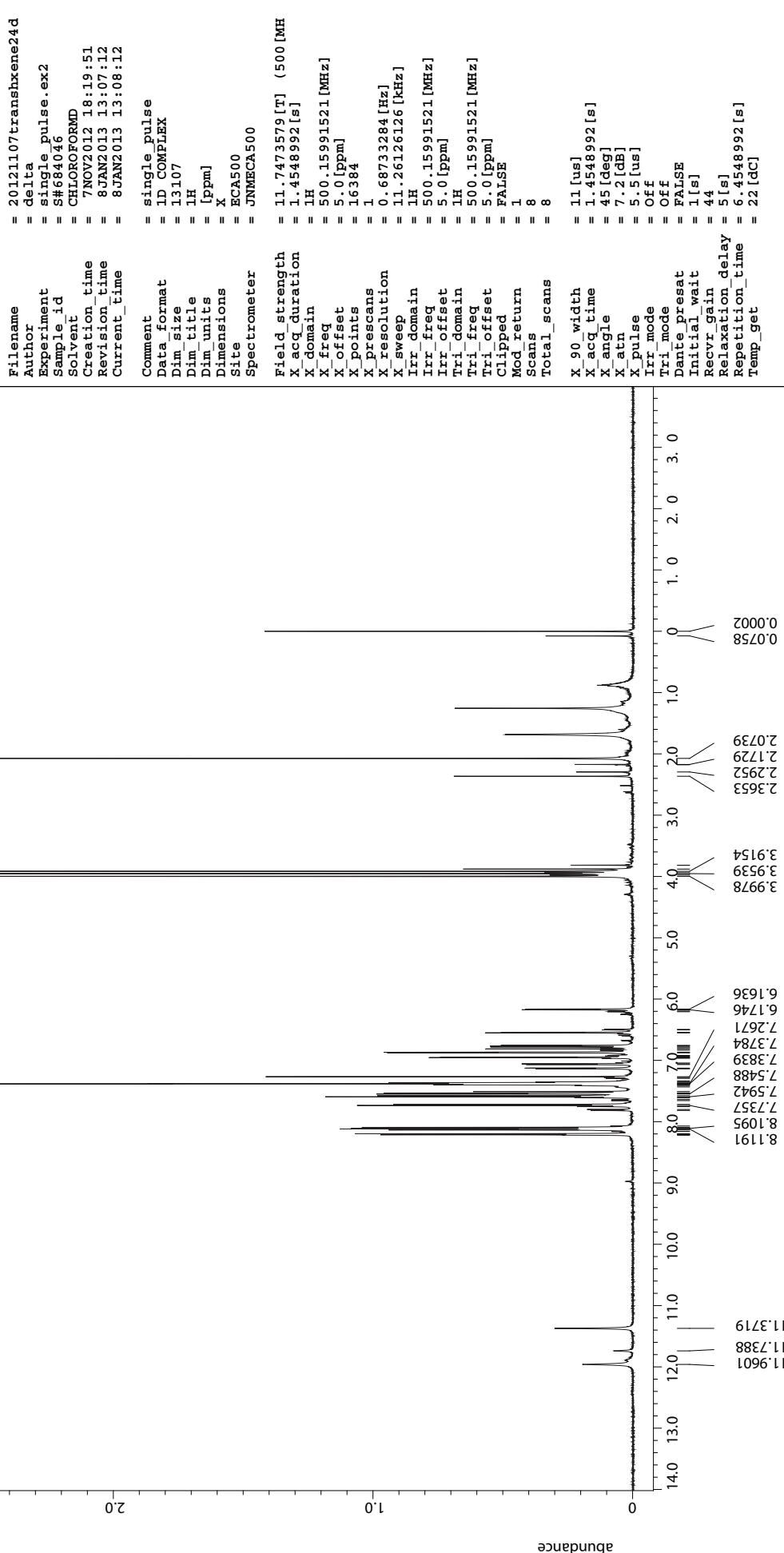


Figure S10.  $^1\text{H}$  NMR of **13**.

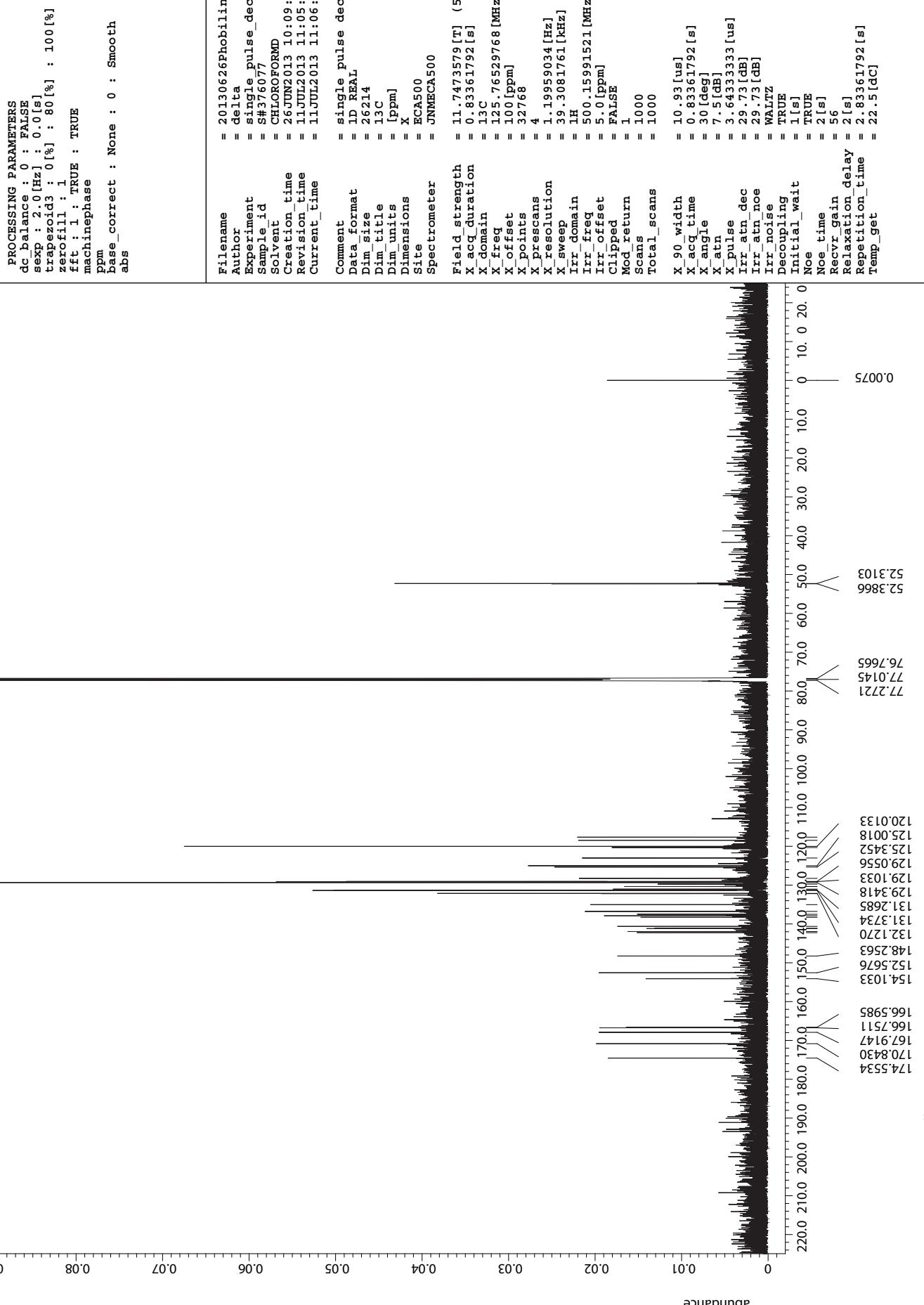


Figure S11.  $^{13}\text{C}$  NMR of **4**.

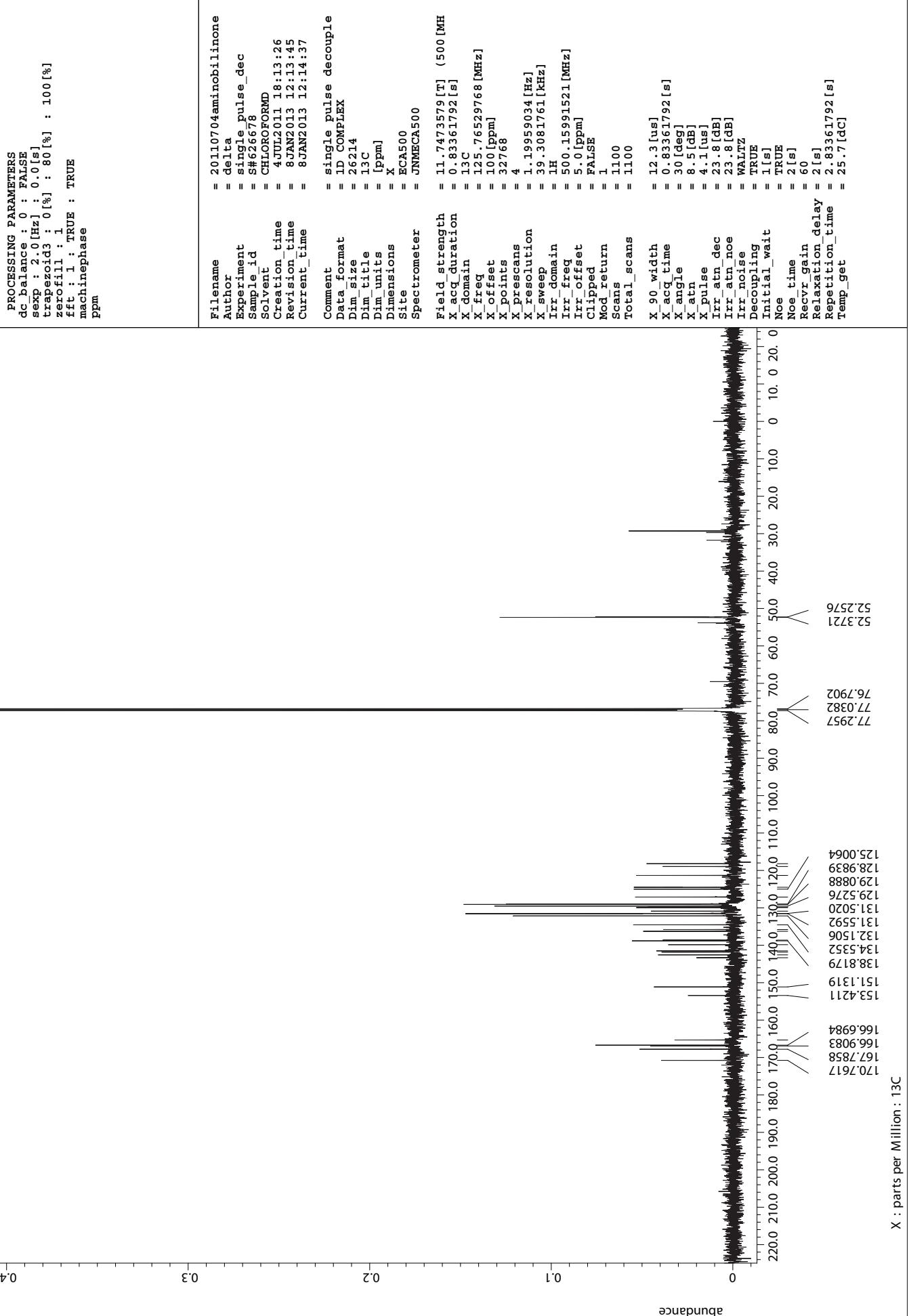


Figure S12.  $^{13}\text{C}$  NMR of **5**.

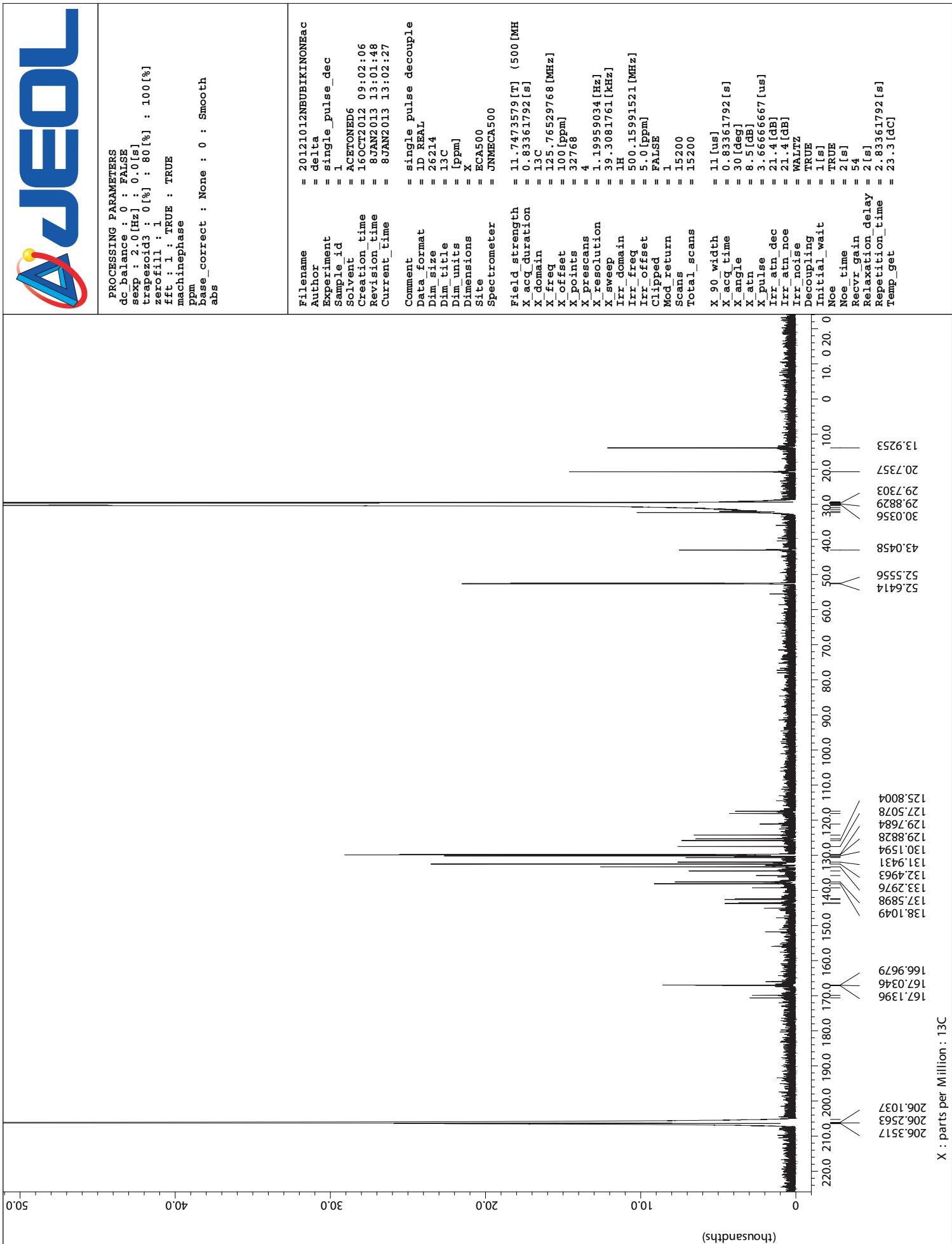


Figure S13.  $^{13}\text{C}$  NMR of **6**.

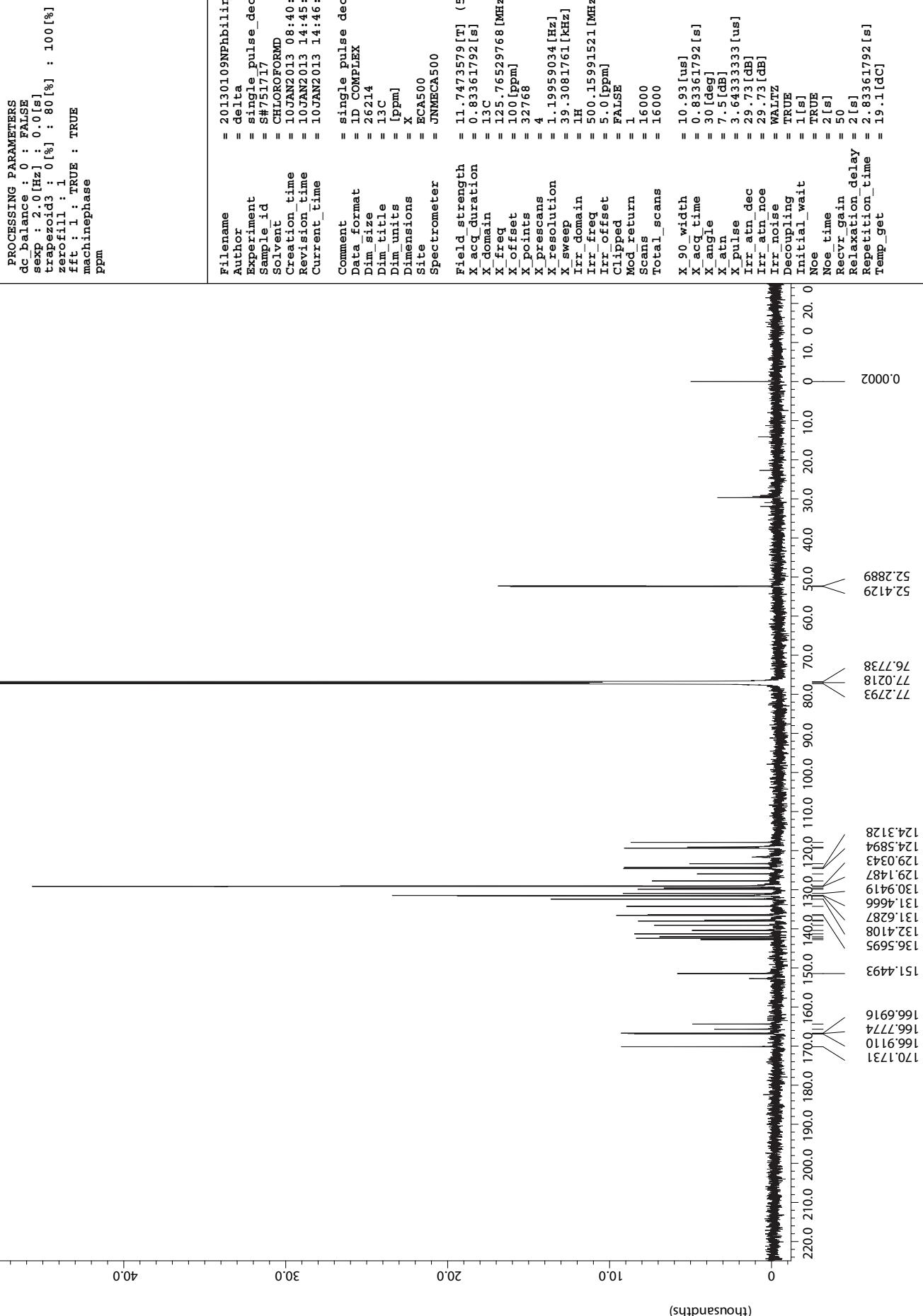
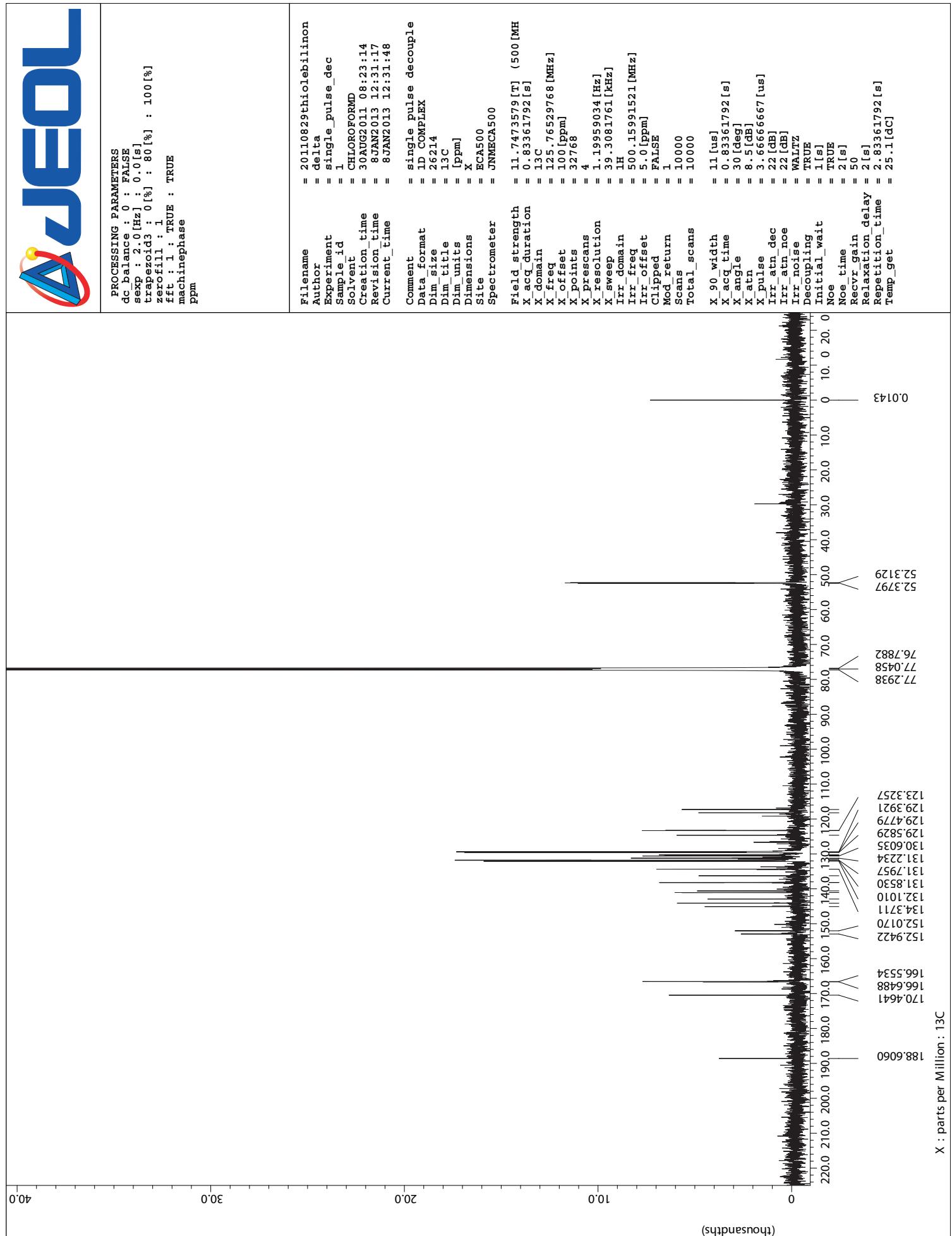


Figure S14.  $^1\text{H}$  NMR of 7.



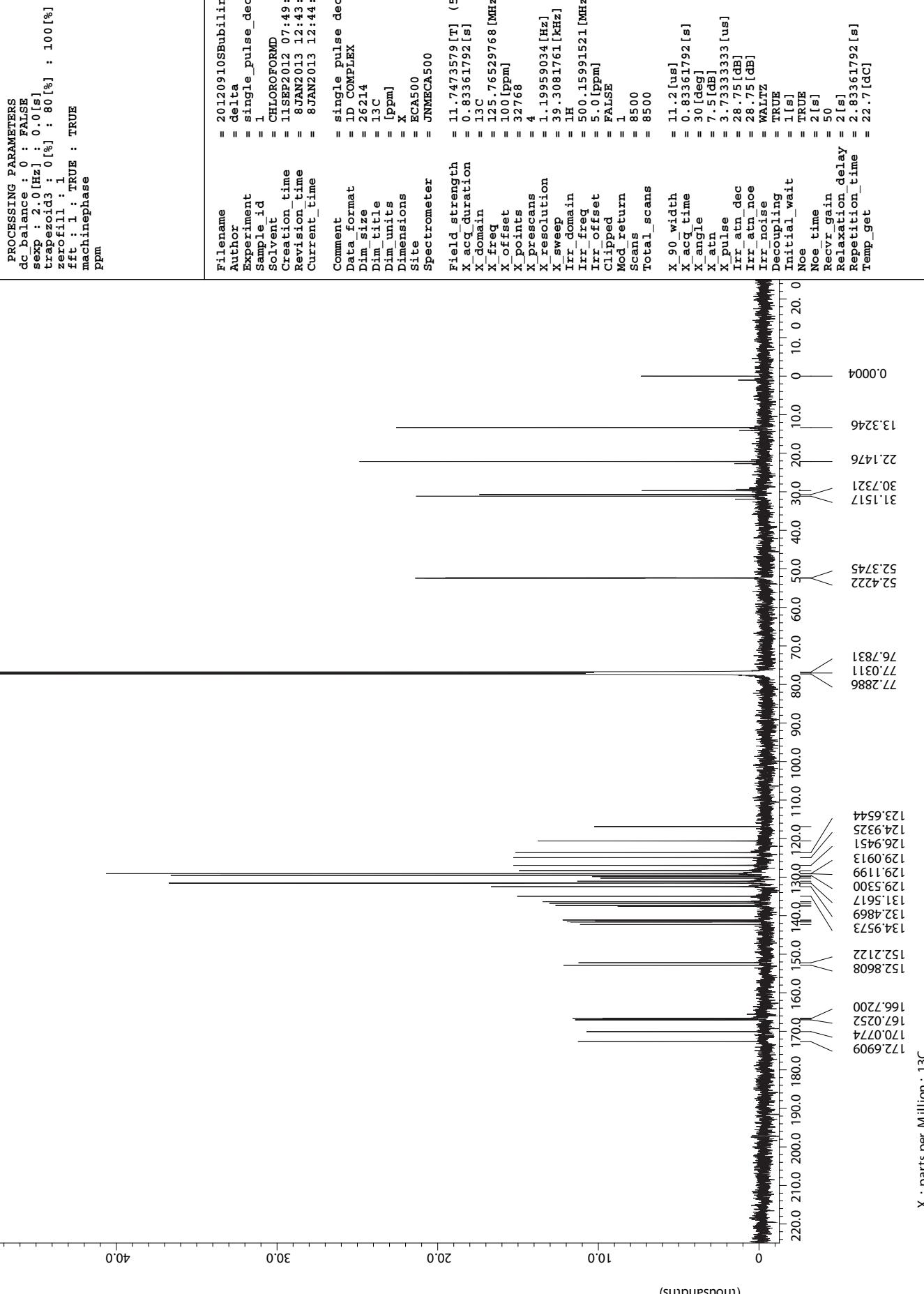


Figure S16.  $^{13}\text{C}$  NMR of **9**.

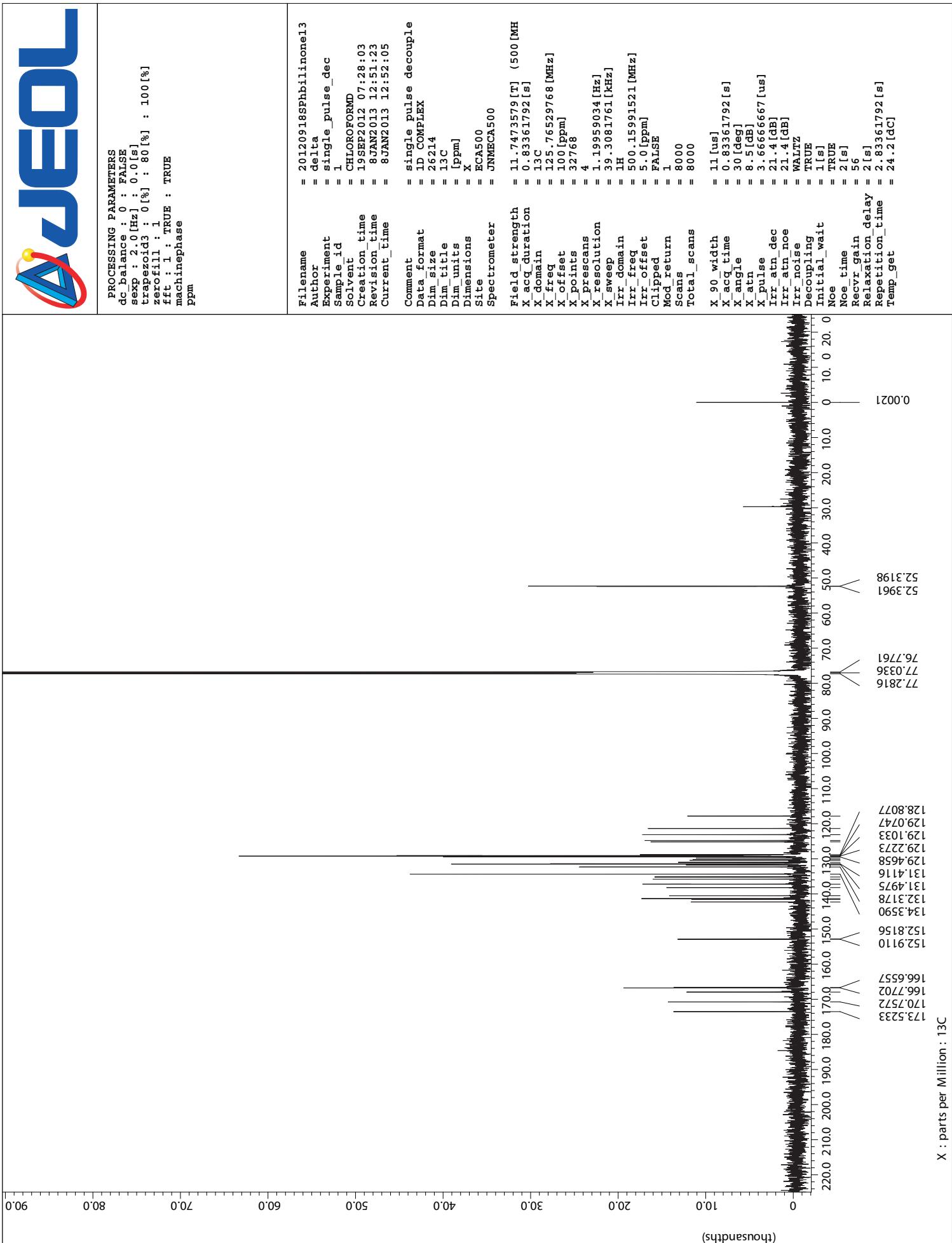


Figure S17.  $^{13}\text{C}$  NMR of **10**.

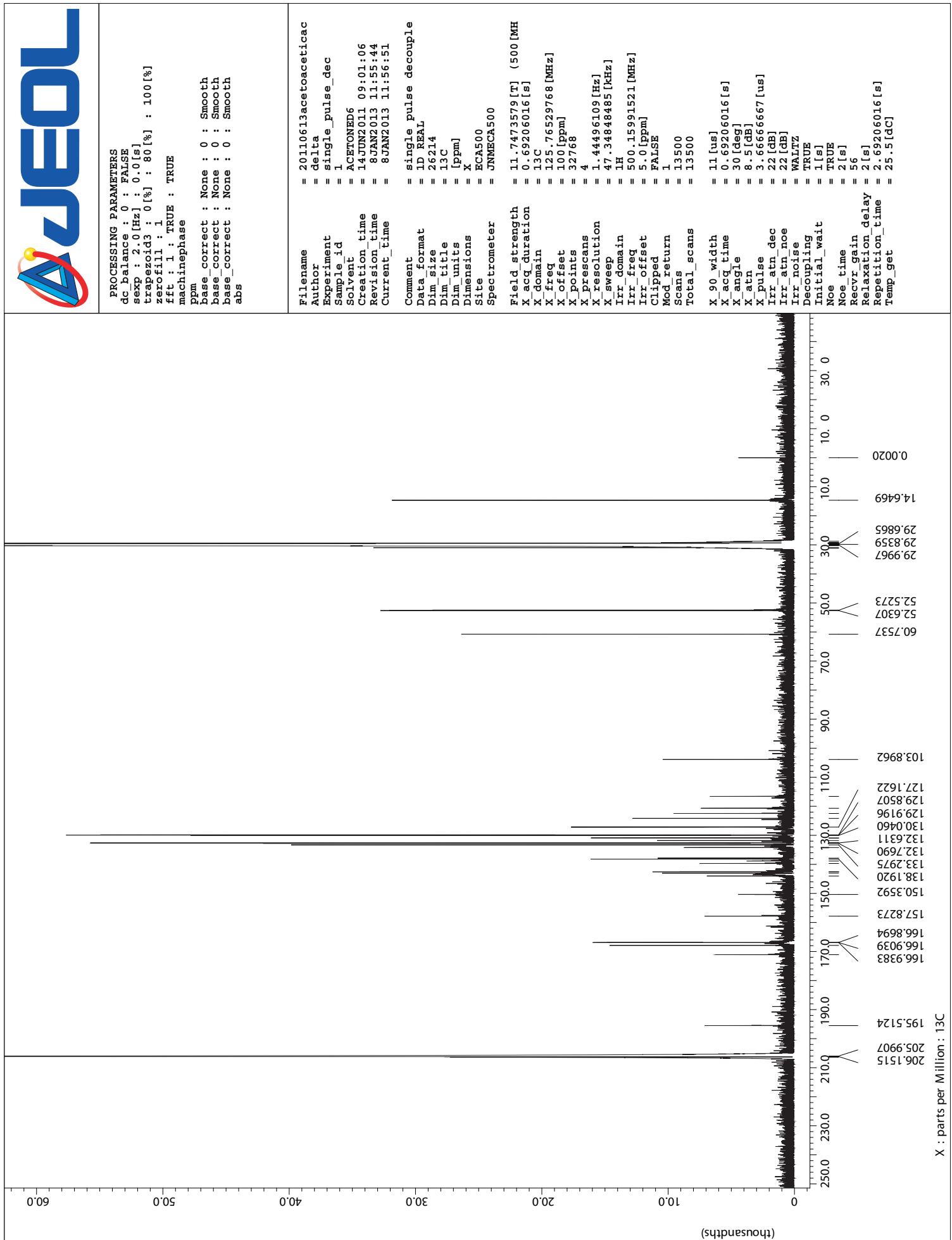


Figure S18.  $^{13}\text{C}$  NMR of 11.

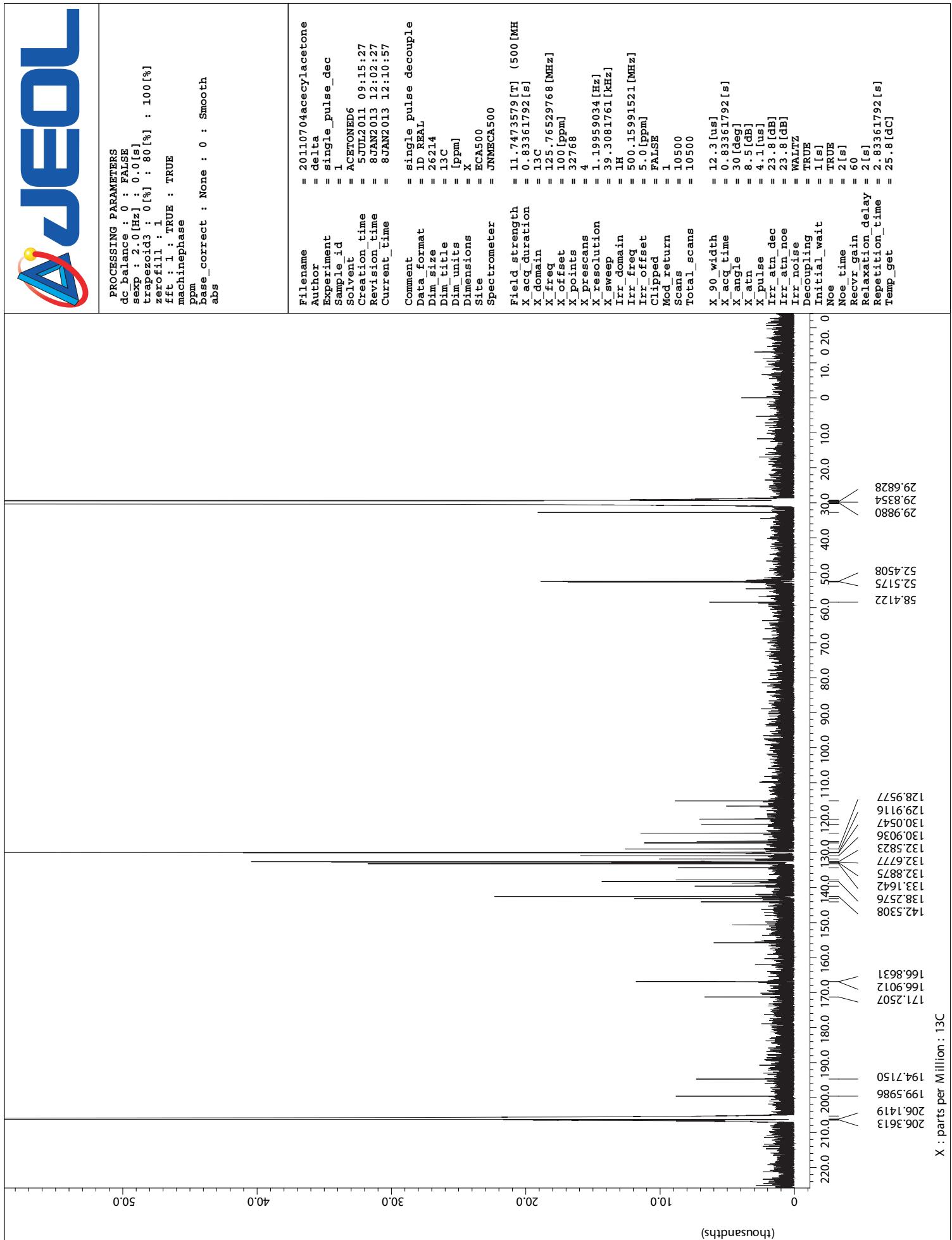


Figure S19.  $^{13}\text{C}$  NMR of **12**.

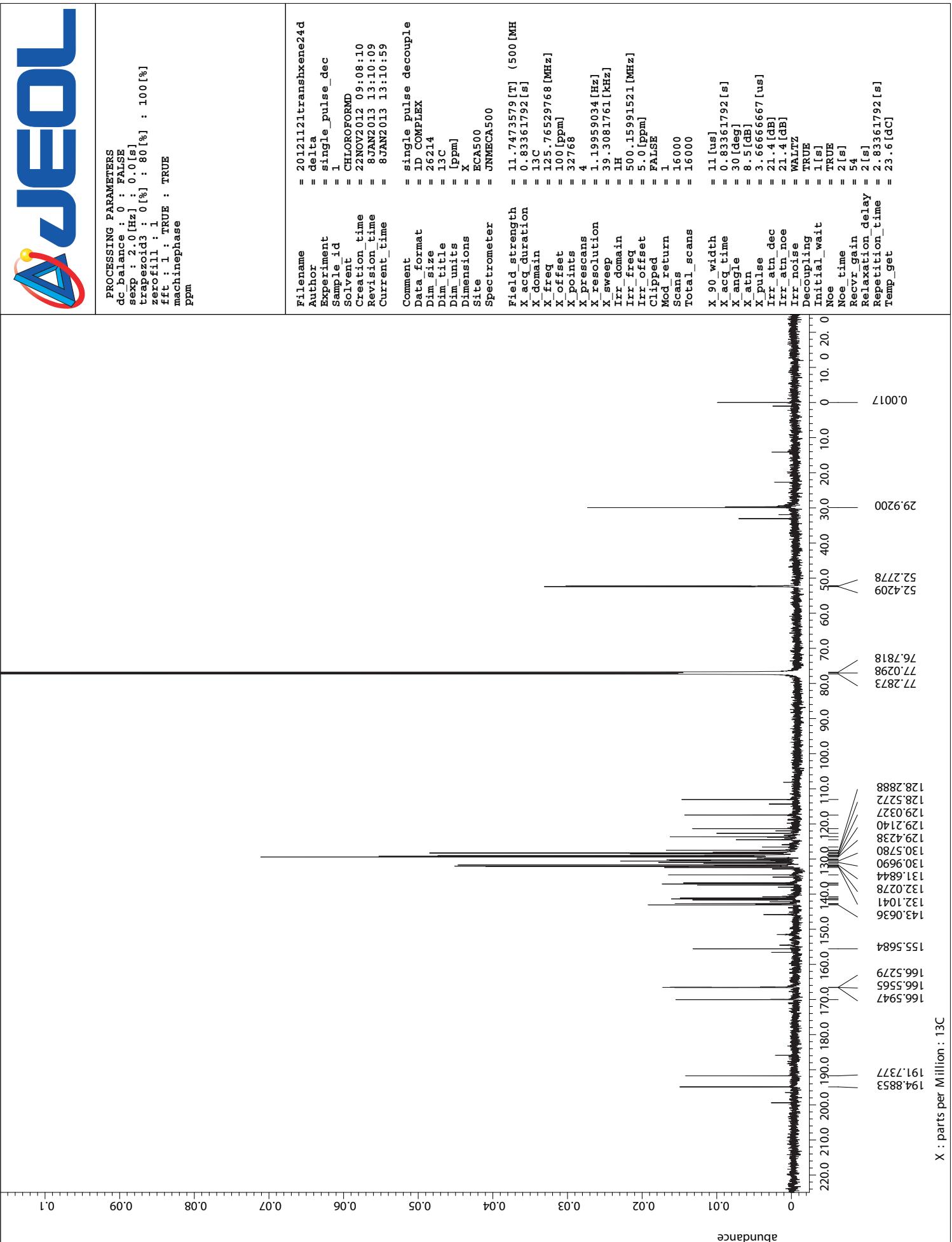
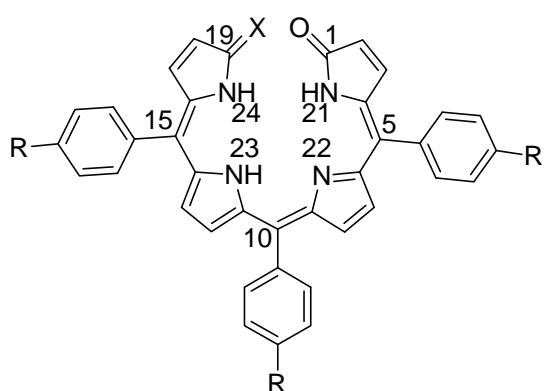
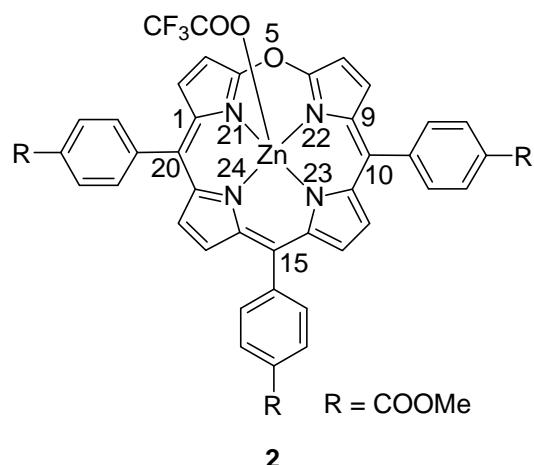


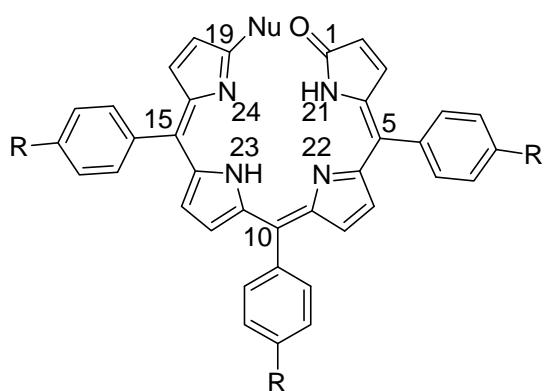
Figure S20.  $^{13}\text{C}$  NMR of **13**.



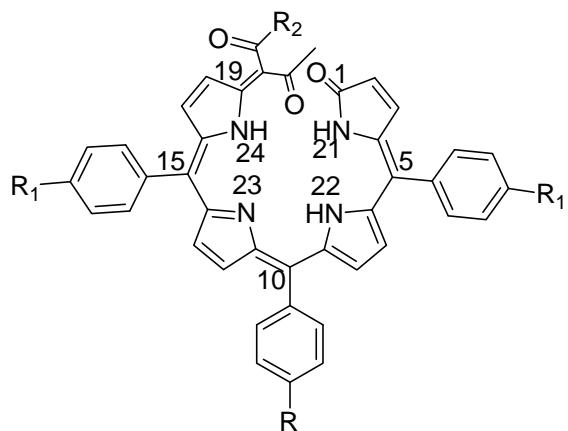
**1:** R = COOMe, X = O  
**8:** R = COOMe, X = S



**2**



**3:** R = COOMe, Nu = OMe  
**4:** R = COOMe, Nu = OPh  
**5:** R = COOMe, Nu = NH<sub>2</sub>  
**6:** R = COOMe, Nu = NHBu  
**7:** R = COOMe, Nu = NHPH  
**9:** R = COOMe, Nu = SBu  
**10:** R = COOMe, Nu = SPh



**11:** R<sub>1</sub> = COOMe, R<sub>2</sub> = OEt  
**12:** R<sub>1</sub> = COOMe, R<sub>2</sub> = Me  
**13:** R<sub>1</sub> = COOMe, R<sub>2</sub> = CH=CHPh

Scheme S1. Numbering scheme of **1-13**.

Table S1. Crystallographic data for **3**.

formula	C <sub>47</sub> H <sub>40</sub> N <sub>4</sub> O <sub>8</sub>	V, Å <sup>3</sup>	1996.62(8)
formula wt.	788.83	Z	2
color and habit	blue plate	T, K	123(2)
crystal system	triclinic	d <sub>calcd</sub> , mg cm <sup>-3</sup>	1.312
space group	P-1	radiation, (λ Å)	Cu K <sub>α</sub> (1.54187)
a, Å	7.6123(2)	μ, mm <sup>-1</sup>	0.739
b, Å	12.0814(3)	range of transmission factors	0.6655 to 0.9640
c, Å	22.5696(5)	R <sub>1</sub> <sup>a</sup>	0.0560
α deg	83.4051(13)	wR <sub>2</sub> <sup>b</sup>	0.1482
β, deg	83.9689(12)	GOF	1.093
γ, deg	76.2855(12)		

*a* R<sub>1</sub> = Σ||F<sub>o</sub>| - |F<sub>c</sub>|| / Σ|F<sub>o</sub>|. *b* wR<sub>2</sub> = [Σ[w(F<sub>o</sub><sup>2</sup> - F<sub>c</sub><sup>2</sup>)<sup>2</sup>] / Σ[w(F<sub>o</sub><sup>2</sup>)<sup>2</sup>]]<sup>1/2</sup>

Table S2. Selected bond distances (Å) of **3**.

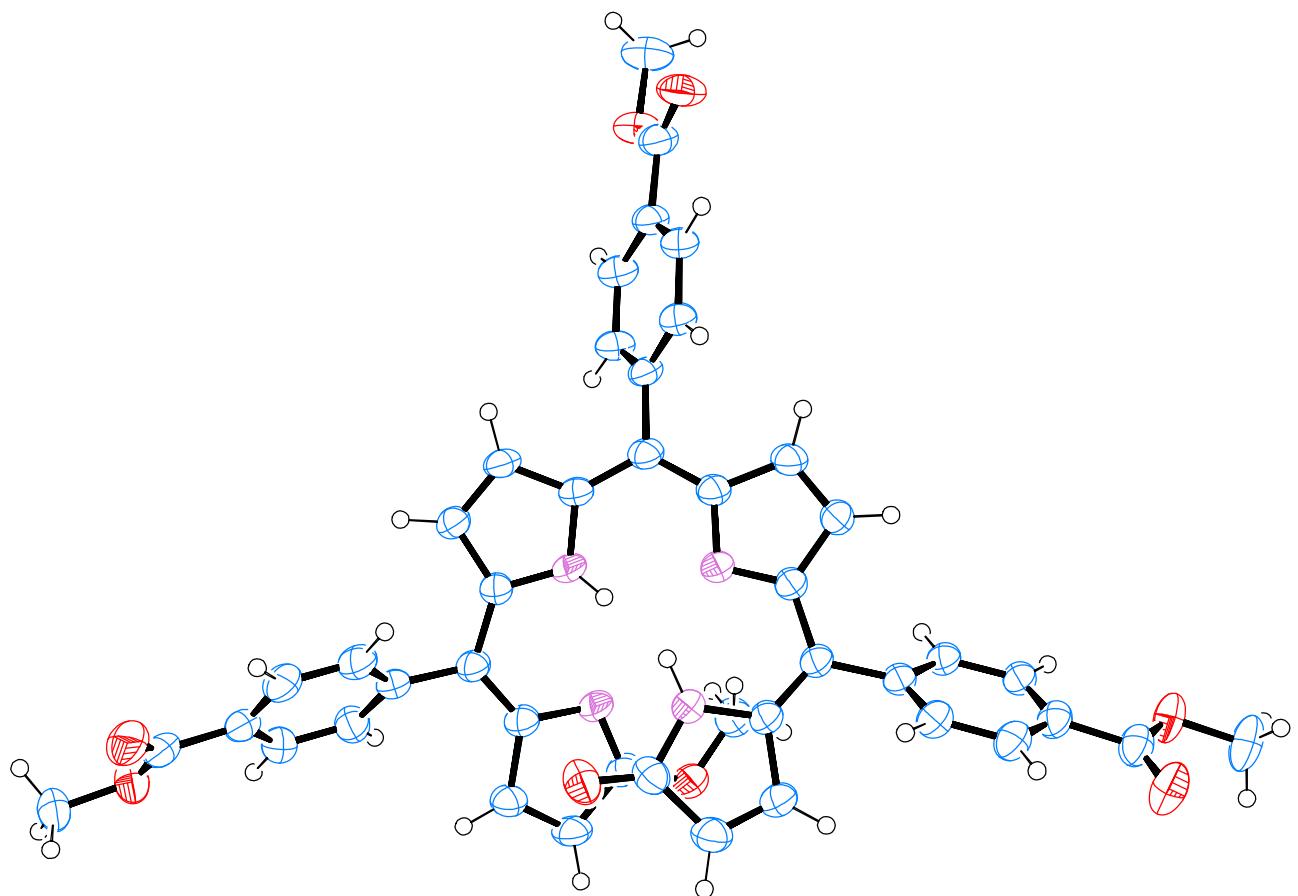
O(1)-C(1)	1.222(3)	C(5)-C(6)	1.462(3)
O(2)-C(19)	1.327(3)	C(6)-C(7)	1.442(3)
C(1)-N(1)	1.384(3)	C(7)-C(8)	1.349(3)
C(4)-N(1)	1.385(3)	C(8)-C(9)	1.446(3)
C(6)-N(2)	1.336(3)	C(9)-C(10)	1.391(3)
C(9)-N(2)	1.392(3)	C(10)-C(11)	1.425(3)
C(11)-N(3)	1.370(3)	C(11)-C(12)	1.412(3)
C(14)-N(3)	1.357(3)	C(12)-C(13)	1.371(3)
C(16)-N(4)	1.419(3)	C(13)-C(14)	1.408(3)
C(19)-N(4)	1.304(3)	C(14)-C(15)	1.447(3)
C(1)-C(2)	1.471(3)	C(15)-C(16)	1.373(3)
C(2)-C(3)	1.337(3)	C(16)-C(17)	1.462(3)
C(3)-C(4)	1.457(3)	C(17)-C(18)	1.340(3)
C(4)-C(5)	1.370(3)	C(18)-C(19)	1.456(3)

Table S3. Selected bond angles (degree) of **3**.

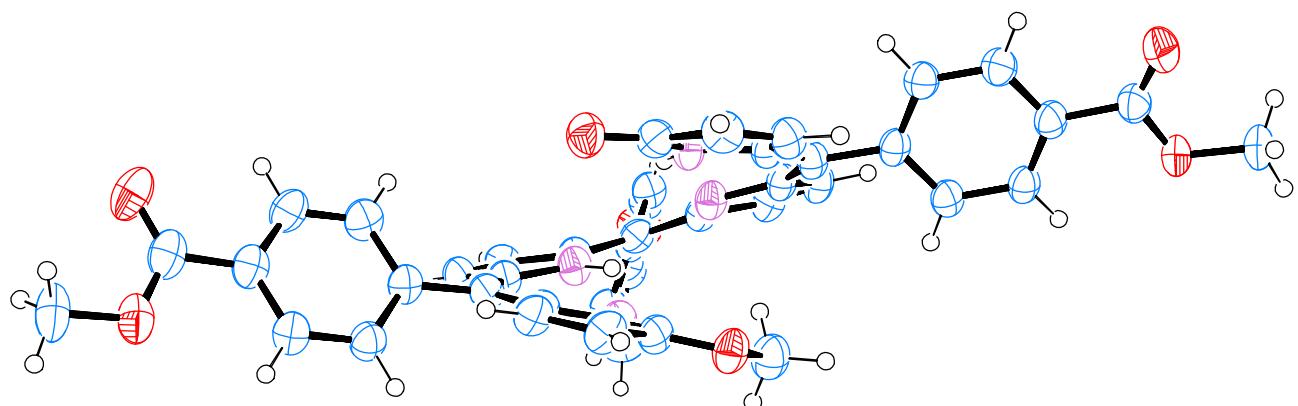
O(1)-C(1)-N(1)	125.0(2)	C(10)-C(9)-N(2)	122.5(2)	C(15)-C(16)-C(17)	128.4(2)
O(1)-C(1)-C(2)	130.1(2)	C(10)-C(9)-C(8)	128.7(2)	N(4)-C(16)-C(17)	109.00(18)
N(1)-C(1)-C(2)	104.9(2)	N(2)-C(9)-C(8)	108.69(19)	C(18)-C(17)-C(16)	106.8(2)
C(3)-C(2)-C(1)	108.8(2)	C(9)-C(10)-C(11)	123.4(2)	C(17)-C(18)-C(19)	105.8(2)
C(2)-C(3)-C(4)	109.3(2)	N(3)-C(11)-C(12)	105.76(19)	N(4)-C(19)-O(2)	125.1(2)
C(5)-C(4)-N(1)	125.2(2)	N(3)-C(11)-C(10)	124.2(2)	N(4)-C(19)-C(18)	113.6(2)
C(5)-C(4)-C(3)	129.5(2)	C(12)-C(11)-C(10)	129.9(2)	O(2)-C(19)-C(18)	121.3(2)
N(1)-C(4)-C(3)	105.2(2)	C(13)-C(12)-C(11)	108.4(2)	C(1)-N(1)-C(4)	111.8(2)
C(4)-C(5)-C(6)	121.4(2)	C(12)-C(13)-C(14)	108.0(2)	C(6)-N(2)-C(9)	106.65(18)
N(2)-C(6)-C(7)	110.9(2)	N(3)-C(14)-C(13)	106.6(2)	C(14)-N(3)-C(11)	111.3(2)
N(2)-C(6)-C(5)	121.5(2)	N(3)-C(14)-C(15)	122.7(2)	C(19)-N(4)-C(16)	104.78(19)
C(7)-C(6)-C(5)	127.5(2)	C(13)-C(14)-C(15)	130.7(2)	C(19)-O(2)-C(20)	116.60(19)
C(8)-C(7)-C(6)	106.7(2)	C(16)-C(15)-C(14)	122.4(2)		
C(7)-C(8)-C(9)	107.0(2)	C(15)-C(16)-N(4)	122.6(2)		

Table S4. Selected dihedral angles (degree) of **3**.

O(1)-C(1)-C(2)-C(3)	180.9(2)	C(7)-C(8)-C(9)-C(10)	182.8(7)	C(14)-C(15)-C(16)-C(17)	172.8(5)
C(1)-C(2)-C(3)-C(4)	359.7(3)	C(8)-C(9)-C(10)-C(11)	170.9(6)	C(15)-C(16)-C(17)-C(18)	180.9(1)
C(2)-C(3)-C(4)-C(5)	182.1(1)	C(9)-C(10)-C(11)-C(12)	163.2(8)	C(5)-C(6)-C(37)-C(42)	132.5(4)
C(3)-C(4)-C(5)-C(6)	170.0(6)	C(10)-C(11)-C(12)-C(13)	185.0(5)	C(9)-C(10)-C(29)-C(34)	125.7(3)
C(4)-C(5)-C(6)-C(7)	169.4(6)	C(11)-C(12)-C(13)-C(14)	359.1(8)	C(14)-C(15)-C(21)-C(26)	130.2(9)
C(5)-C(6)-C(7)-C(8)	182.5(2)	C(12)-C(13)-C(14)-C(15)	179.3(9)		
C(6)-C(7)-C(8)-C(9)	359.6(8)	C(13)-C(14)-C(15)-C(16)	166.1(6)		



Top view



Side view

Figure S21. ORTEP view of **3**.

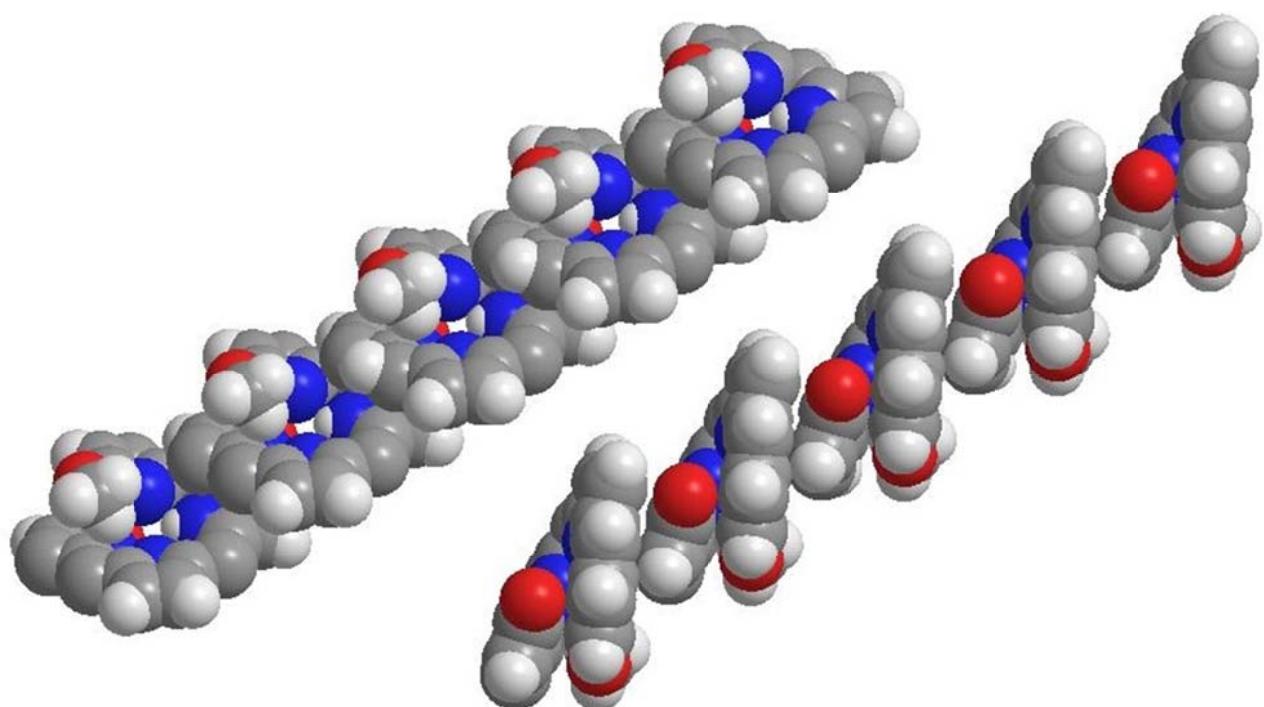
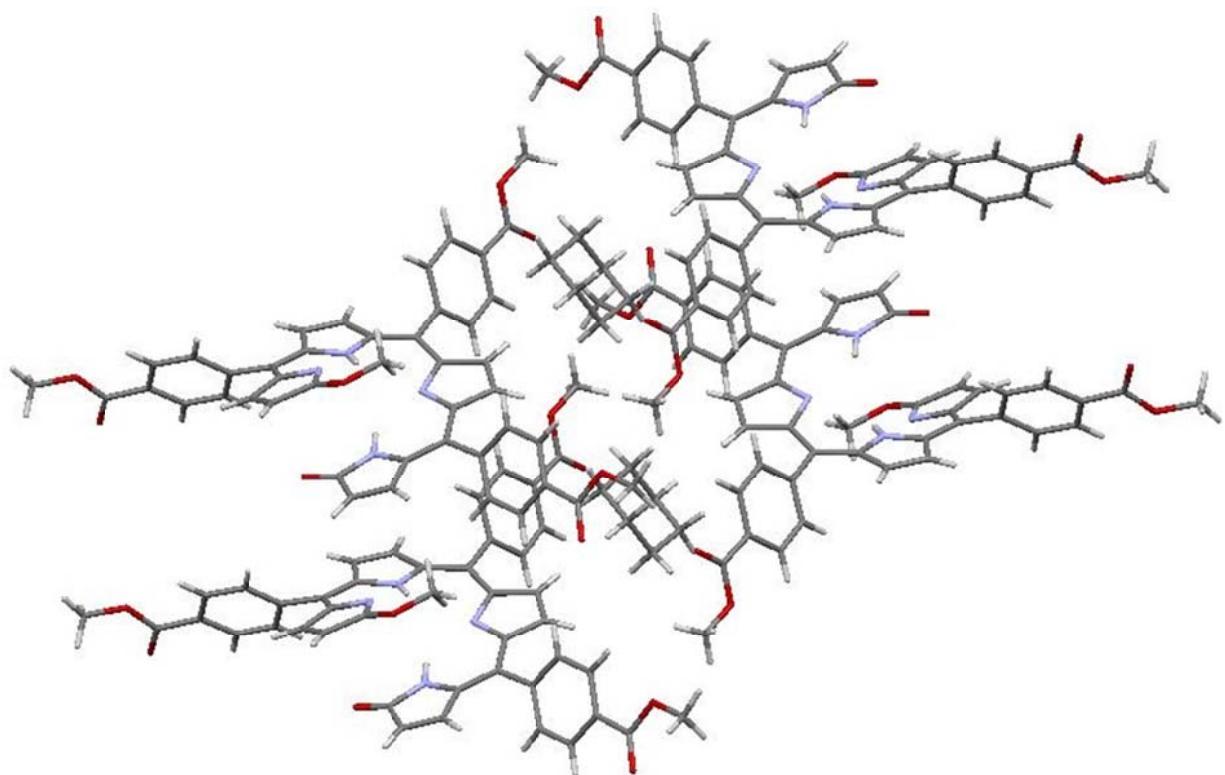
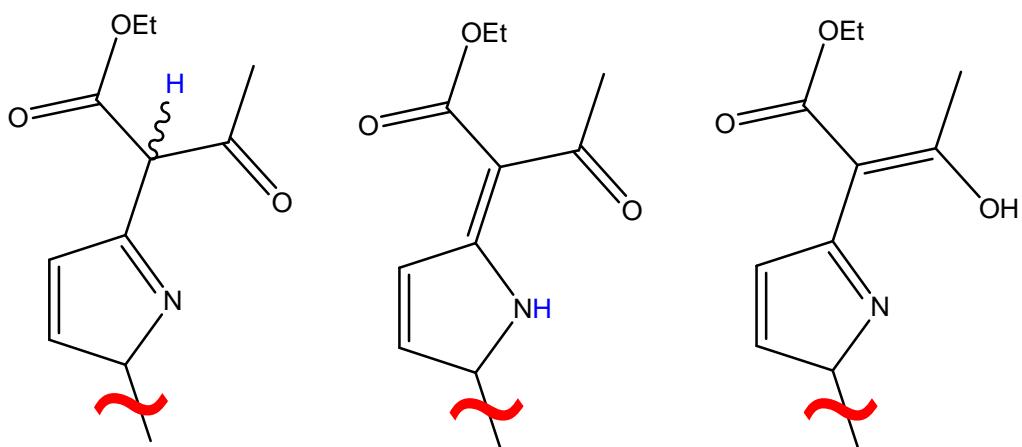
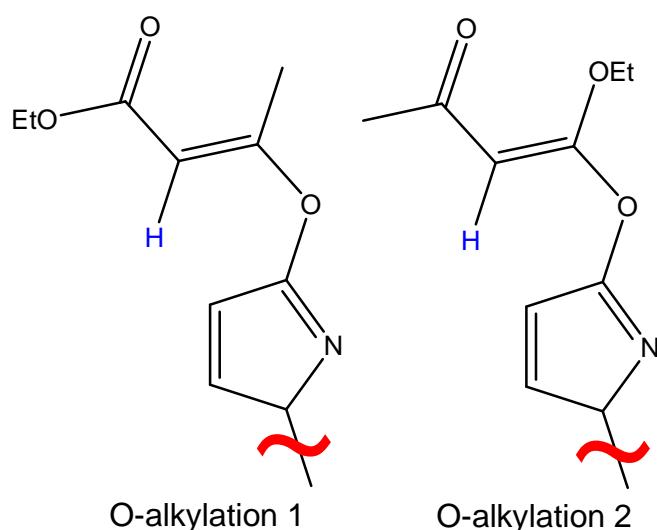


Figure S22. (Top) Cell packing of **3** along the *a*-axis. (Bottom) Structure of spiral column made up of helical molecules. The phenyl groups are omitted for clarity.



C-alkylation  
*(RS)-* $\beta$ -diketo      C-alkylation  
 $\beta$ -diketo NH      C-alkylation  
enol



Scheme S2. Tautomeric structures of enolate appended bilinone **11**. Only D-ring is shown.

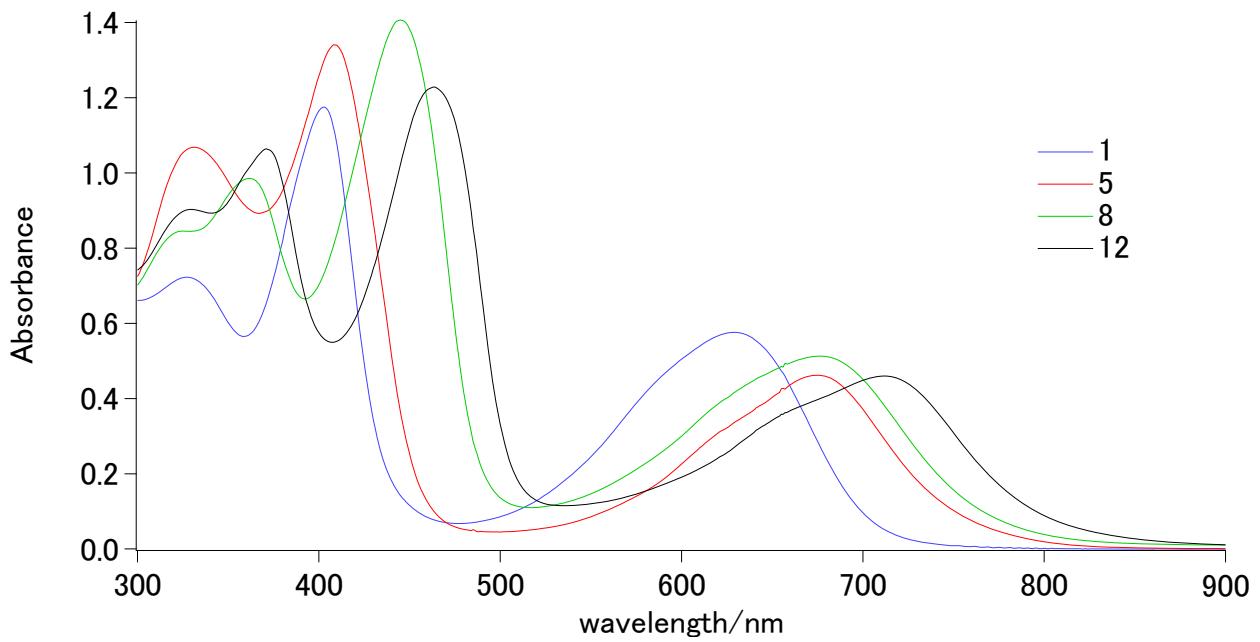


Figure S23. UV-vis spectra of  $3 \times 10^{-5}$  M of **1**, **5**, **8** and **12** in  $\text{CHCl}_3$  at 25 °C.

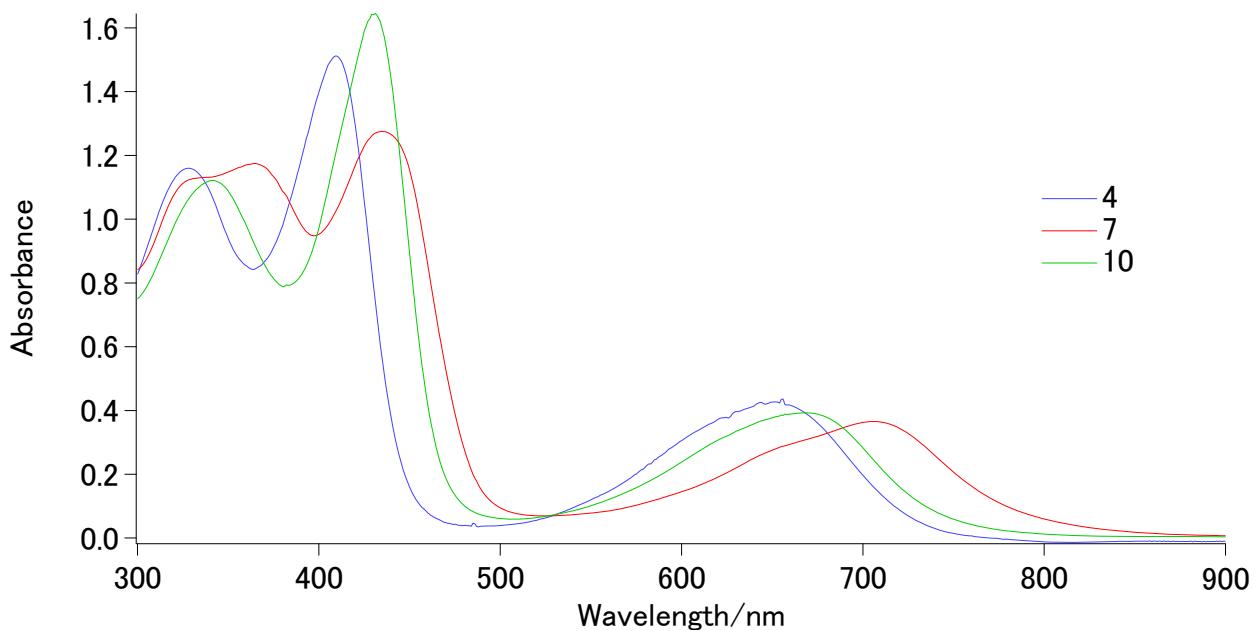


Figure S24. UV-vis spectra of  $3 \times 10^{-5}$  M of **4**, **7** and **10** in  $\text{CHCl}_3$  at 25 °C.