

## Supplementary Materials

### Preparation of Solid Solution and Crystal-Glass Composite Consisting of Stable Phenoxyl Radical and Its Phenol Analogue

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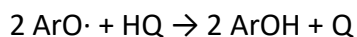
*Email: [nhayashi@sci.u-toyama.ac.jp](mailto:nhayashi@sci.u-toyama.ac.jp)*

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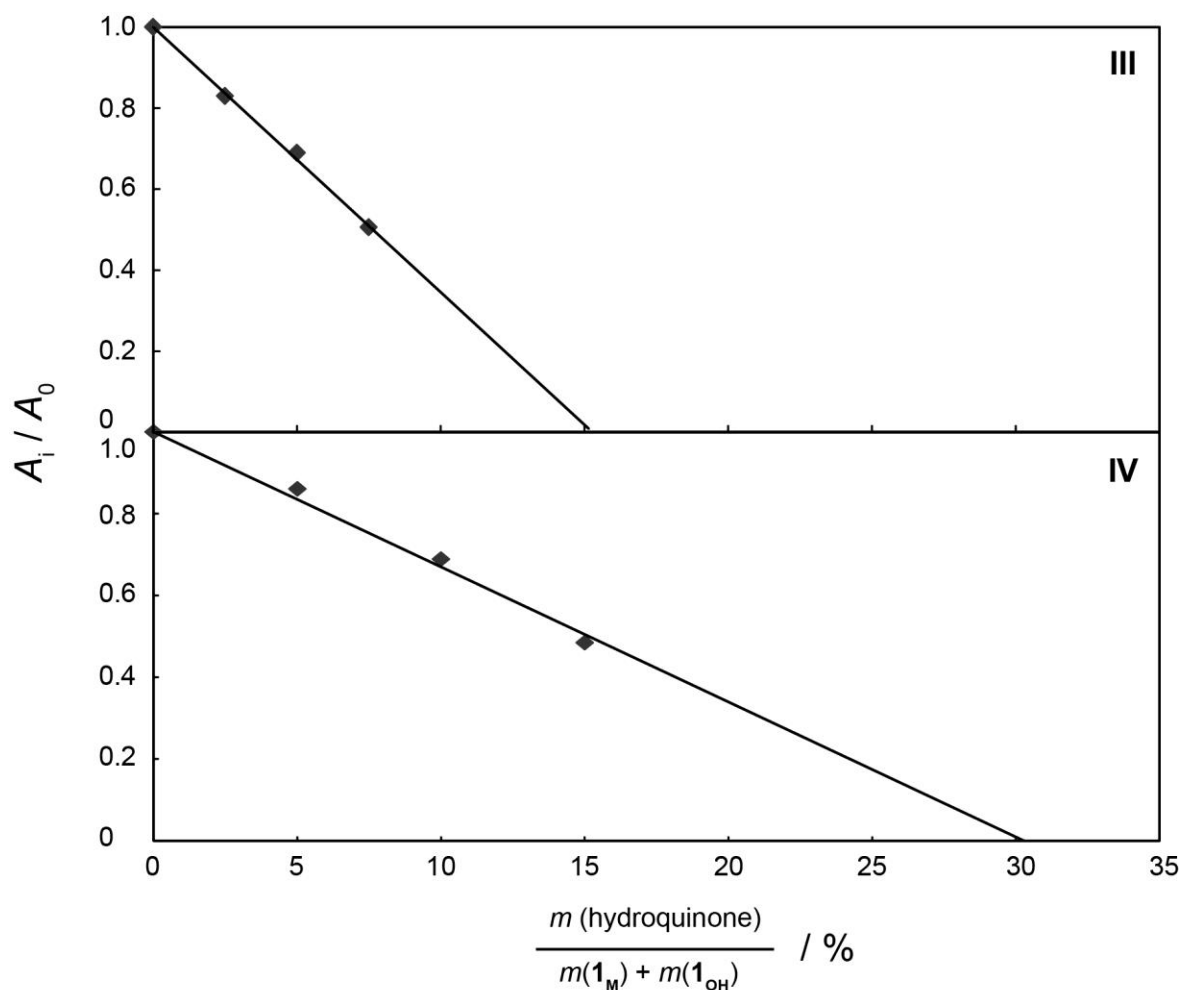
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**Titration experiment of III and IV**

It is known that the phenoxyl and hydroquinone (HQ) react to yield the corresponding phenol and quinone (Q) as follows:



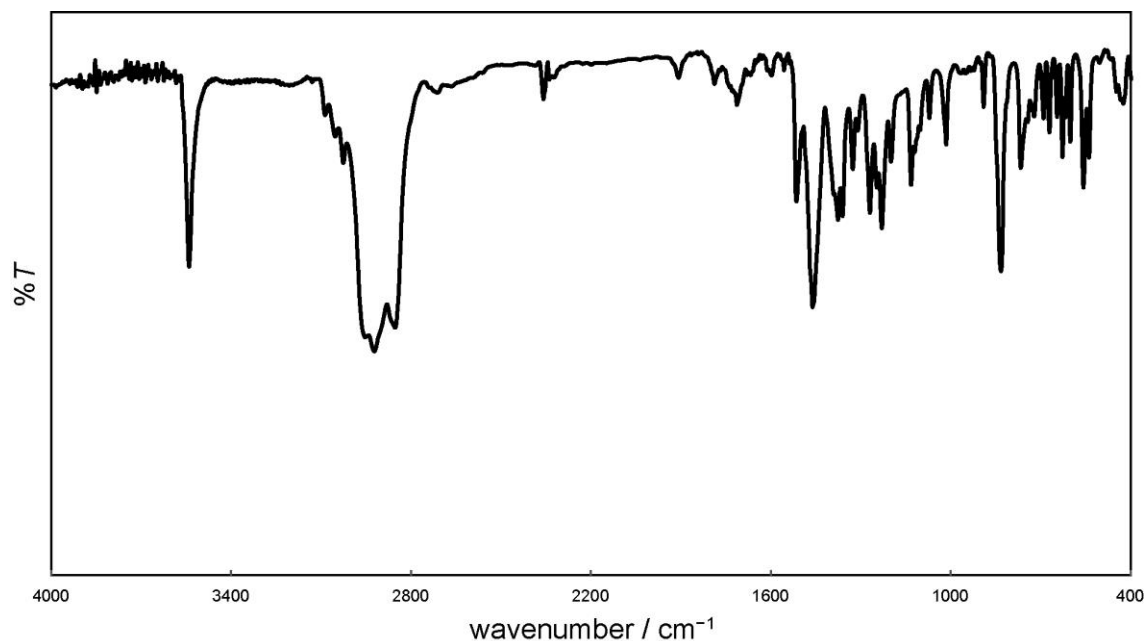
Since the deep color of the phenoxyl disappears along this reaction, it can be used to estimate the amount of phenoxyl by titration experiment.<sup>[18]</sup> The change in color, however, was found to be unclear in the present study. Thus, the following modified experiment was conducted instead. First, **III** (2.4 mg) was dissolved in distilled acetone (50 mL). 5 mL of this solution was pipetted and diluted with the same amount distilled acetone. The UV/Vis spectrum was measured to estimate the absorbance at 752 nm of the dilute solution (which was defined to be  $A_0$ ). Next, other three 5 mL of the original solutions were pipetted, and each solution was mixed with of 1.2, 2.4, and 3.6  $\mu\text{M}$  solutions of hydroquinone in acetone (5 mL), respectively. The absorbances at 752 nm of the resultant mixed solutions were also measured, which were  $A_1$ ,  $A_2$ , and  $A_3$ , respectively. A graph representing of the molar ratio of hydroquinone to the sum of  $\mathbf{1_M}$  and  $\mathbf{1_{OH}}$  on the x axis and  $A_i/A_0$  ( $i = 1-3$ ) on the y axis was generated, then extrapolated to meet the x axis. The line cut the x axis at 15% (Figure S1). Since one mole of hydroquinone reacts two moles of  $\mathbf{1_M}$  as aforementioned, this indicates that the stoichiometric ratio of  $\mathbf{1_{OH}}$  to  $\mathbf{1_M}$  in **III** should be 0.70 : 0.30. In a similar way, the stoichiometric ratio of  $\mathbf{1_{OH}}$  to  $\mathbf{1_M}$  in **IV** was estimated to be 0.40 : 0.60.



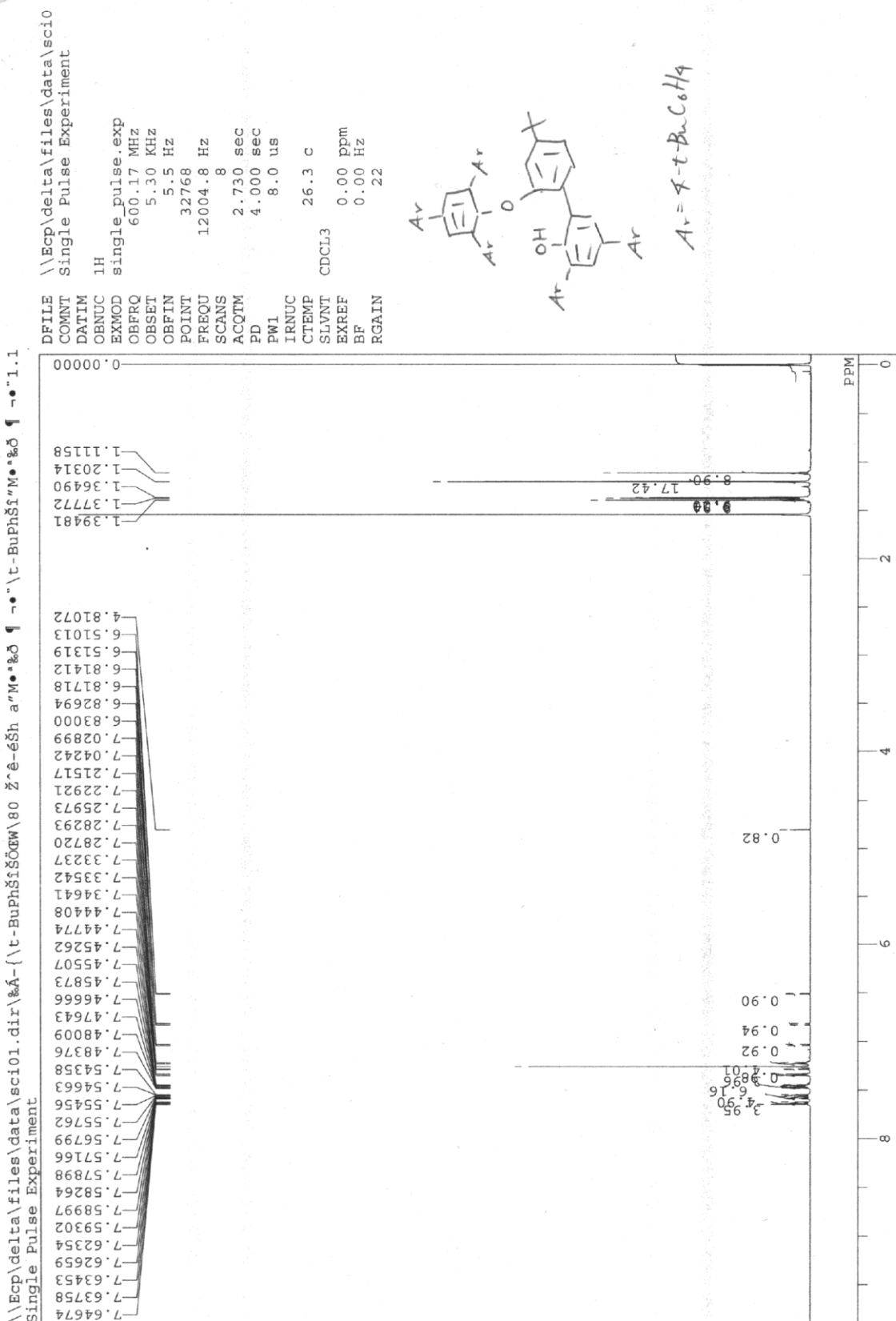
**Figure S1.** Titration of **III** and **IV** using hydroquinone.

**Solvolysis of  $1_M$  in acetone**

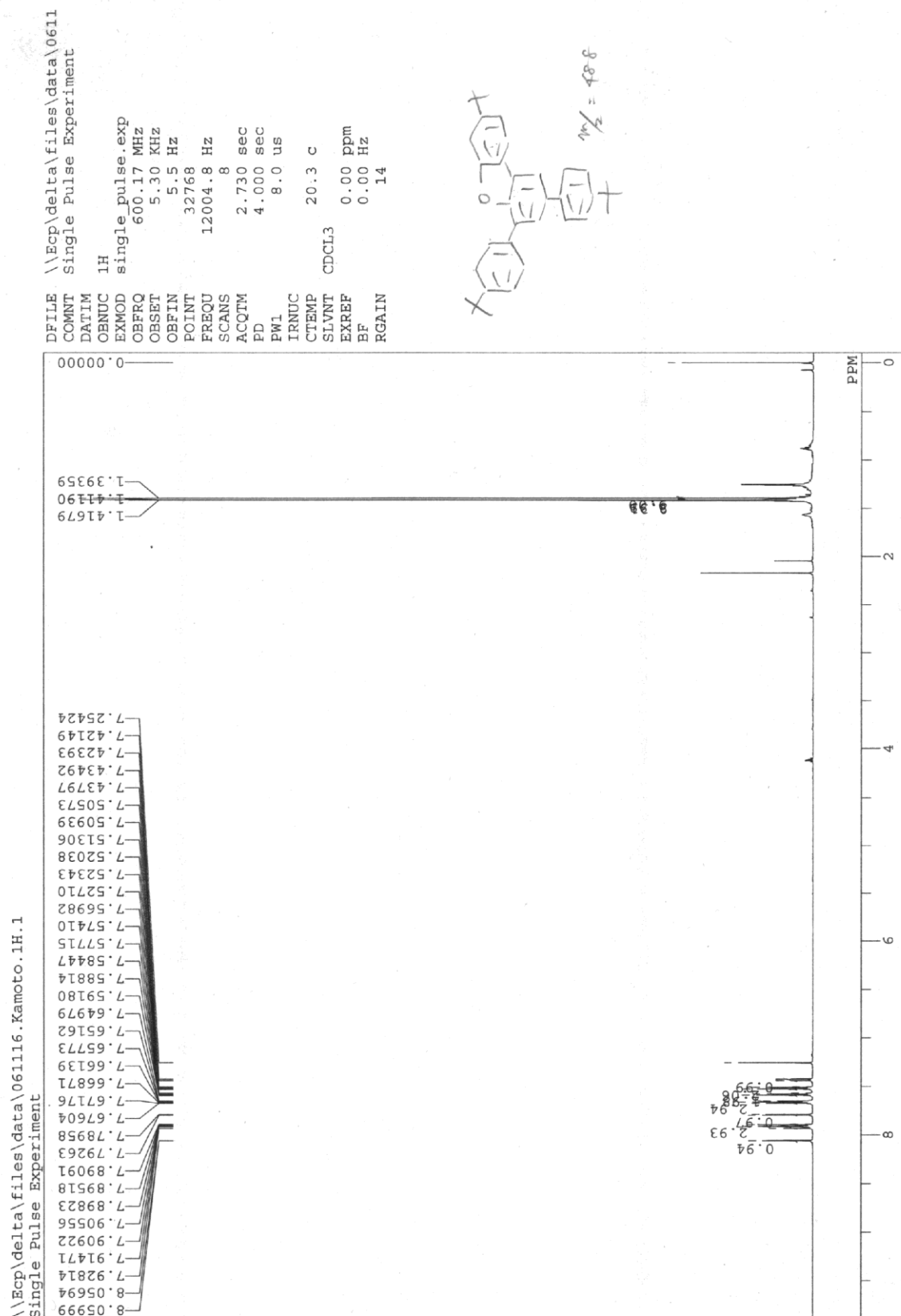
0.80 mg of  $1_M$  (as I) was dissolved in distilled acetone (50 mL). UV/Vis spectrum of this solution was measured to estimate the absorbance at 752 nm ( $A_{\text{before}}$ ). After standing 1 h, the absorbance at 752 nm ( $A_{\text{after}}$ ) was again measured, the ratio of ( $A_{\text{after}} / A_{\text{before}}$ ) being 0.97.



**Figure S2.** IR spectrum of II (Nujol mull).



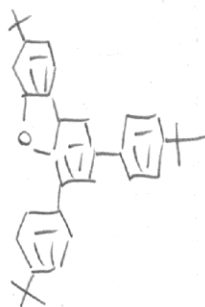
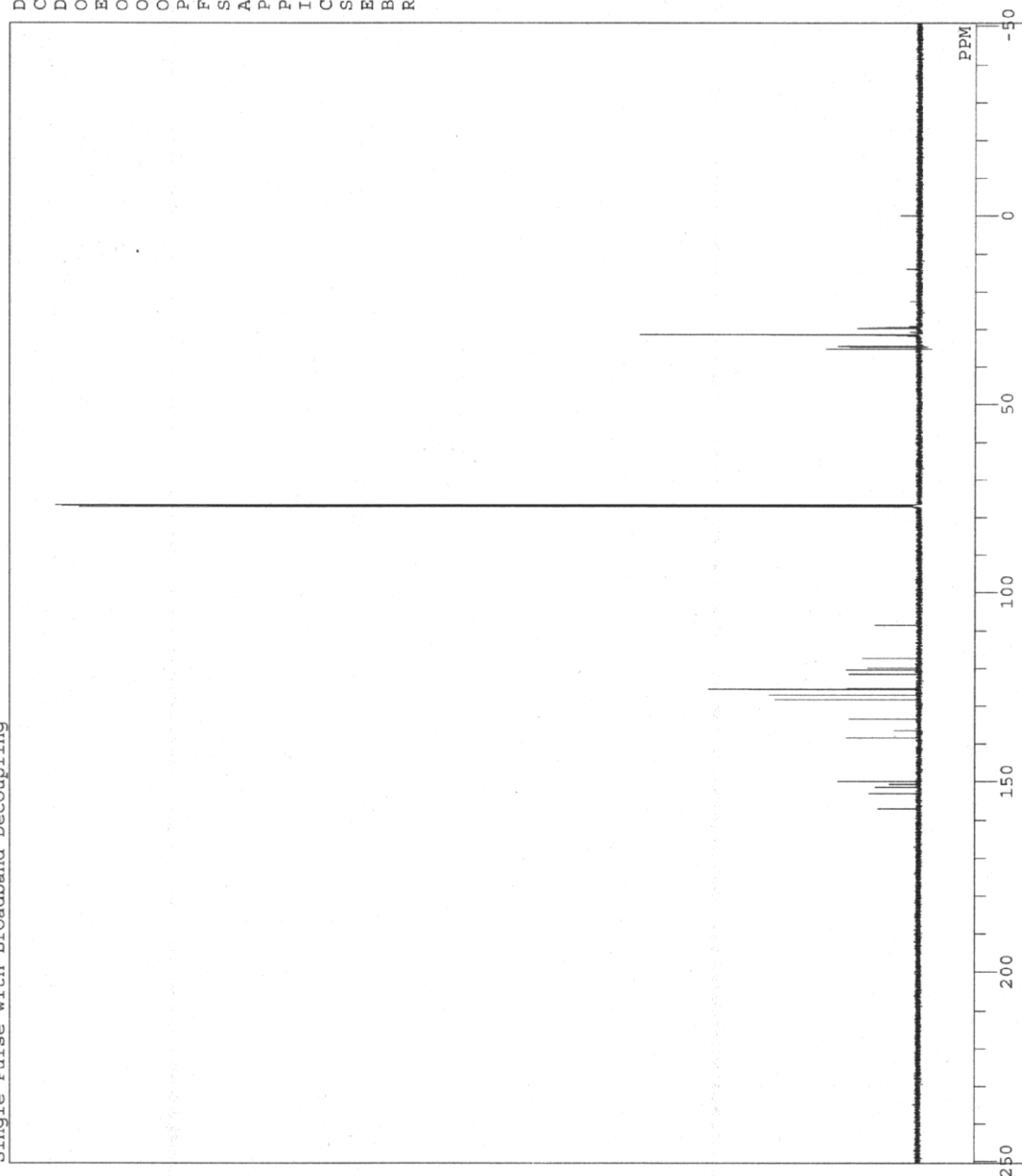
**Figure S3.**  $^1\text{H}$  NMR of **2**.

Figure S4. <sup>1</sup>H NMR of 3.

(a)

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Single Pulse with Broadband Decoupling

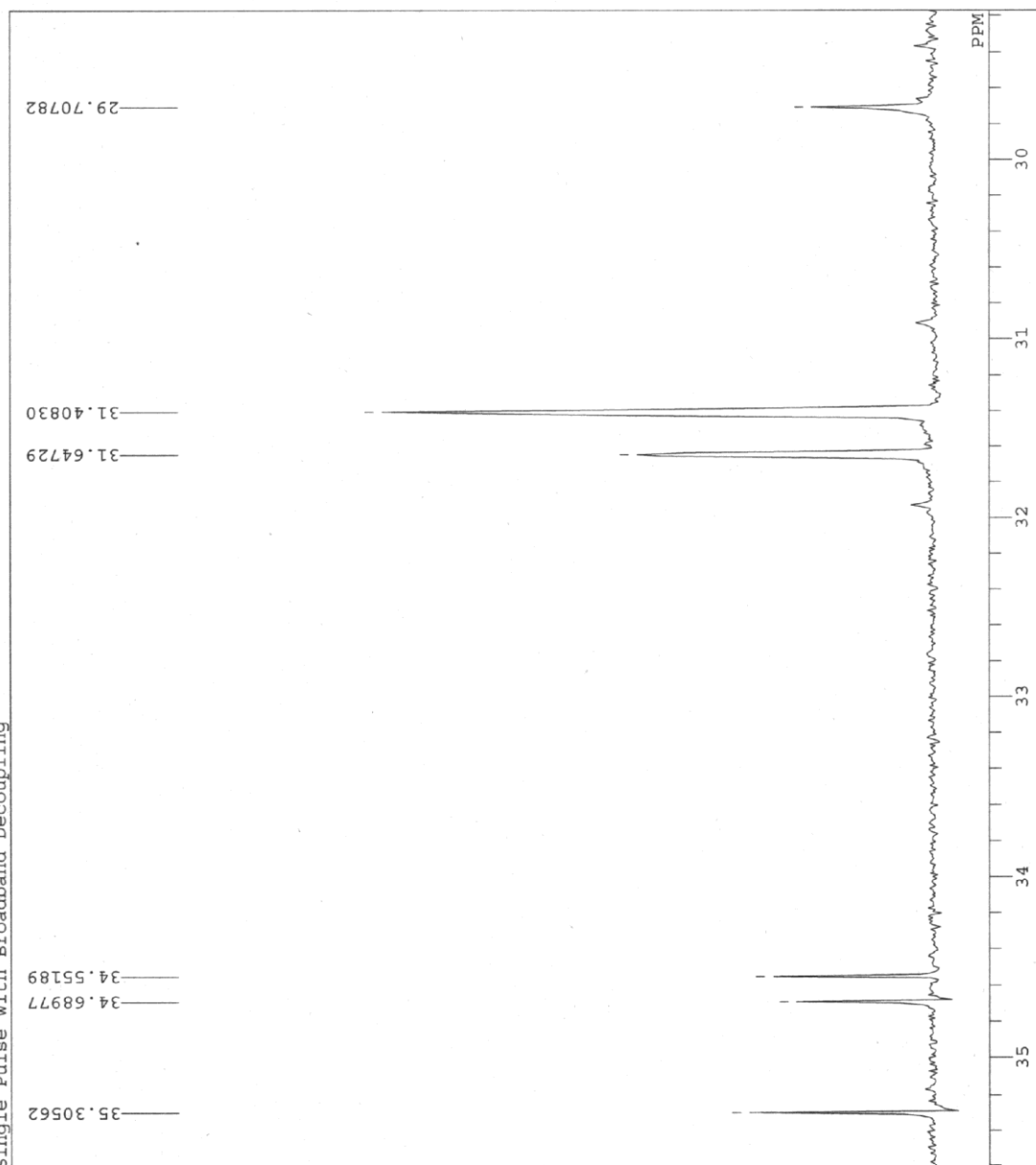
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OBNUC 13C  
EXMOD single pulse dec  
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OBSET 8.52 KHz  
OBFIN 1.7 Hz  
POINT 32768  
FREQU 45454.5 Hz  
SCANS 16907  
ACQTM 0.721 sec  
PD 1.000 sec  
PW1 4.0 us  
IRNUC 23.7 c  
CTEMP CDCL3  
SLVNT 0.00 ppm  
EXREF 0.00 Hz  
BF 26  
RGAIN

<sup>13</sup>C NMR

**Figure S5.** <sup>13</sup>C NMR of **3**. (a) Overall view. (b)–(e) Enlarged views. Note that two signals overlap at  $\delta \sim 108.8$  ppm in (c). Indeed, two signals appeared in this region when the broadening factor (BF) was changed to  $-1.0$  ppm as shown in (d).

(b)

D:\%A-{061116 X V j\T-BuphŠiŠÖW\180 Ž'ê-ěŠh a"M•&š ¶ -•'\061116.Kamoto.13C.1  
Single Pulse with Broadband Decoupling



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D:\&A-{{061116 X V j}\t-BuPh
Single Pulse with Broadband

13C
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EXMOD      150.92 MHz
OBFREQ     8.52 KHz
OBSSET     1.7 Hz
OBFIN      32768
POINT      45454.5 Hz
FREQU      16907
SCANS      0.721 sec
ACQTM      1.000 sec
PD         4.0 us
PWL
IRNUC
CTEMP      23.7 C
SLVNT      CDCL3
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BF         0.00 Hz
RGAIN      26

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**Figure S5 (contd).**

(c)

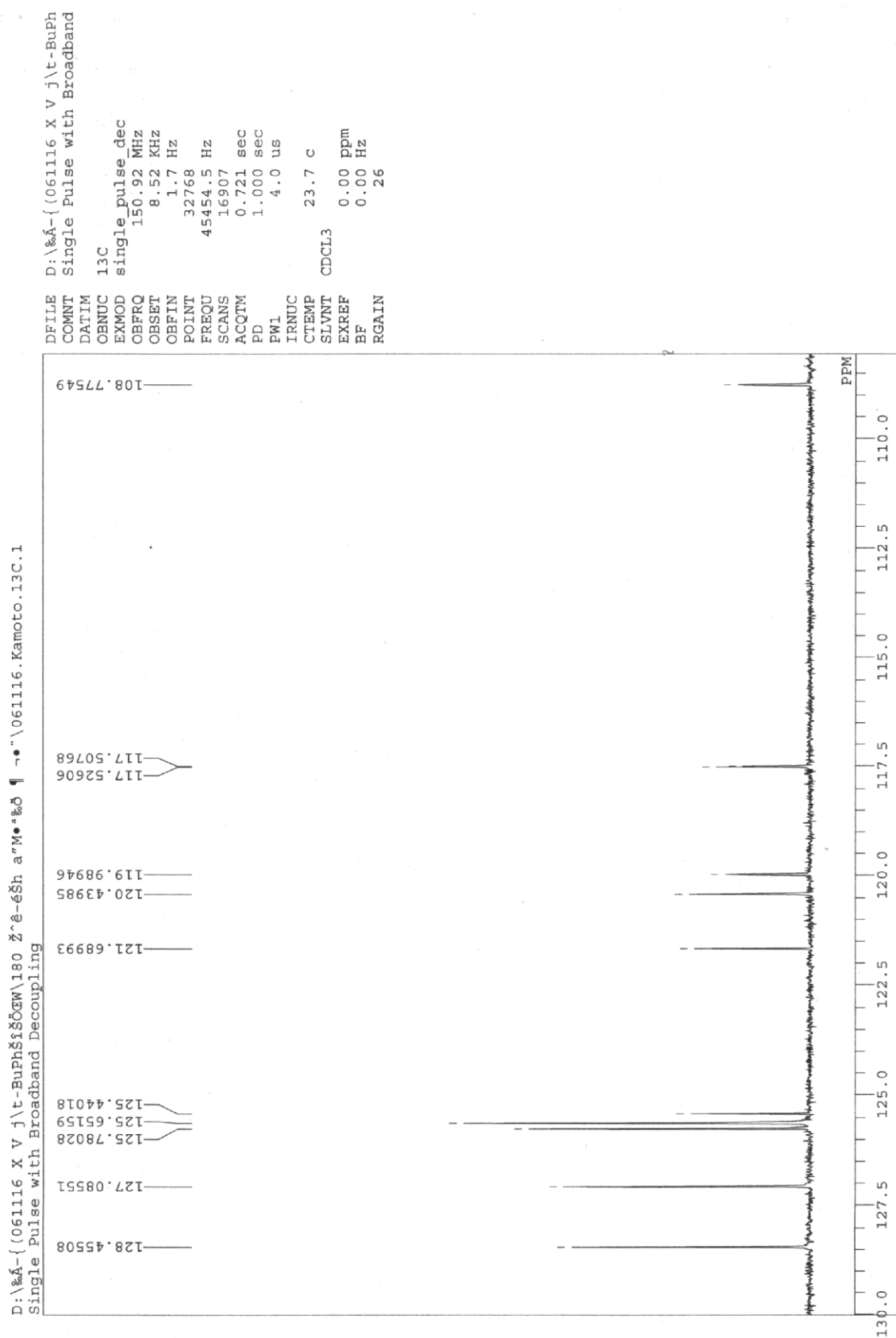
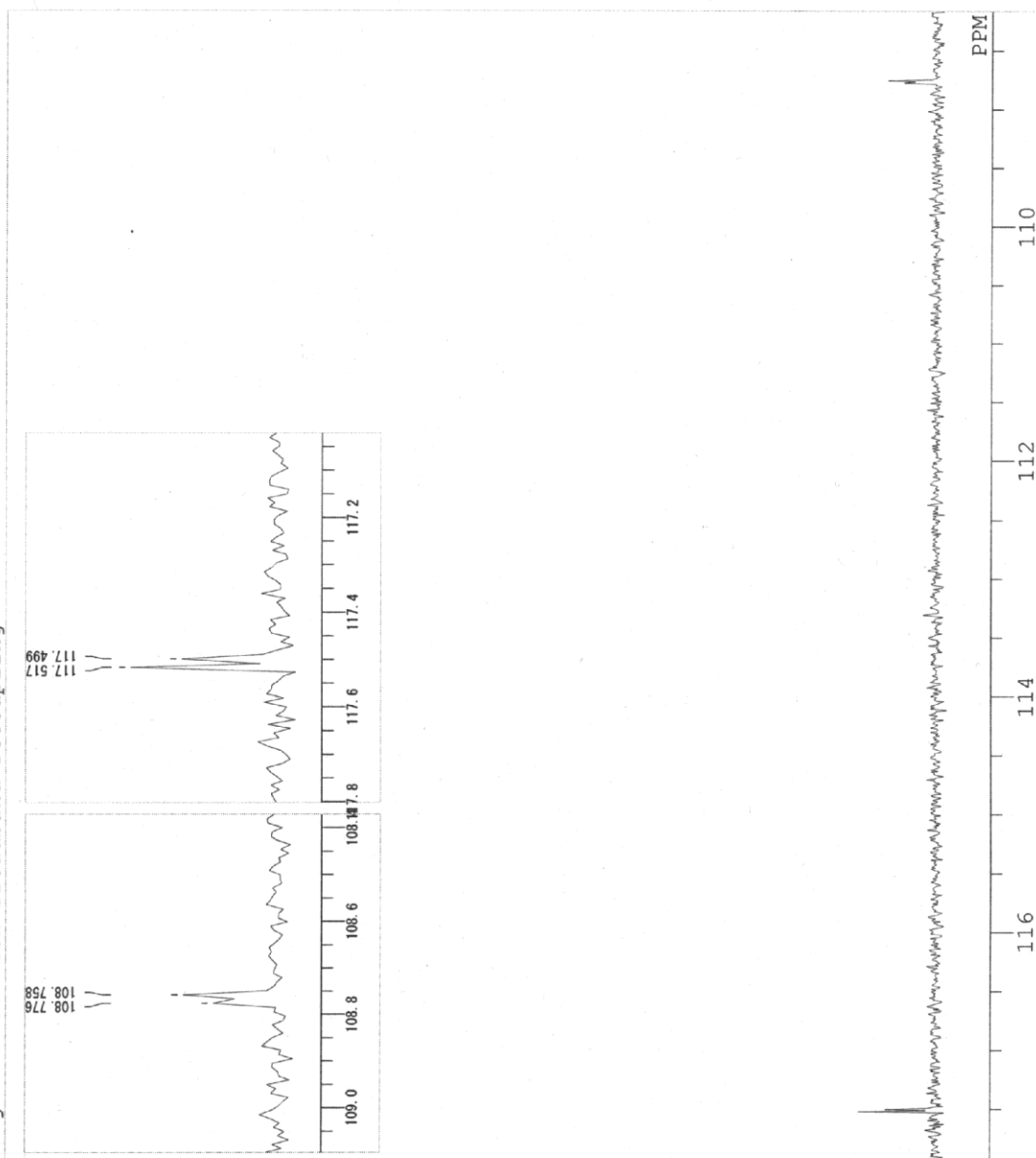


Figure S5 (contd).



(d)

C:\Documents and Settings\H-L,P\fffxNfgfbfv\061116.Kamoto.13C.1  
Single Pulse with Broadband Decoupling



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OBFRQ 8.52 KHz  
OBSET 1.7 Hz  
OBFIN 32768  
POINT 45454.5 Hz  
FREQU 16907  
SCANS 0.721 sec  
ACQTM 1.000 sec  
PD 4.0 us  
PWL 23.7 c  
IRNUC CDCL3  
CTEMP 77.00 ppm  
SLVNT -1.00 Hz  
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BF  
RGAIN

Figure S5 (contd).

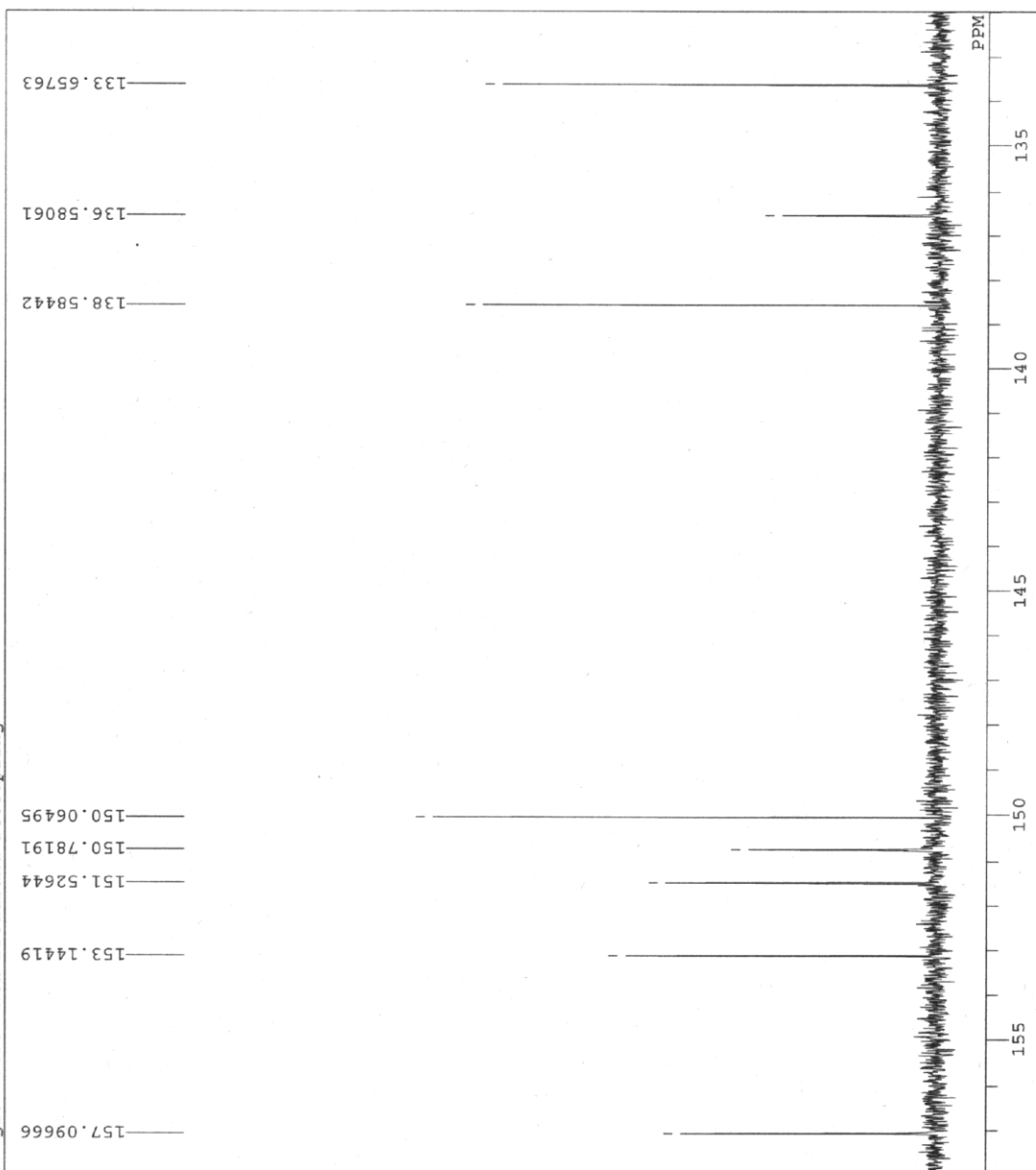
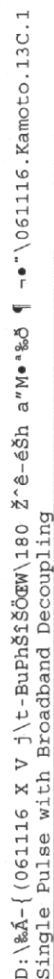
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D:\&A-{\061116 X V j\t-Buph
Single Pulse with Broadband

DFILE
COMINT
DATIM
OBNUC
EXMOD
OBFREQ
OBSRT
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PWL
IRNUC
CTEMP
SLVNT
EXREF
BF
GAIN

13C
single_pulse_dec
150.92 MHz
8.52 KHz
1.7 Hz
32768
45454.5 Hz
16907
0.721 sec
1.000 sec
4.0 us
23.7 C
0.00 ppm
0.00 Hz
26

```



**Figure S5 (contd).**