Supplementary Materials

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

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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:

2 ArO· + HQ → 2 ArOH + Q

Since the deep color of the phenoxyl disappears along this reaction, it can be used to estimate the amount of phenoxyl by titration experiment.[18] 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). 5mL 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 5mL of the original solutions were pipetted, and each solution was mixed with of 1.2, 2.4, and 3.6 μM 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 of $\mathbf{1_{OH}}$ to $\mathbf{1_M}$ in **IV** was estimated to be 0.40 : 0.60.

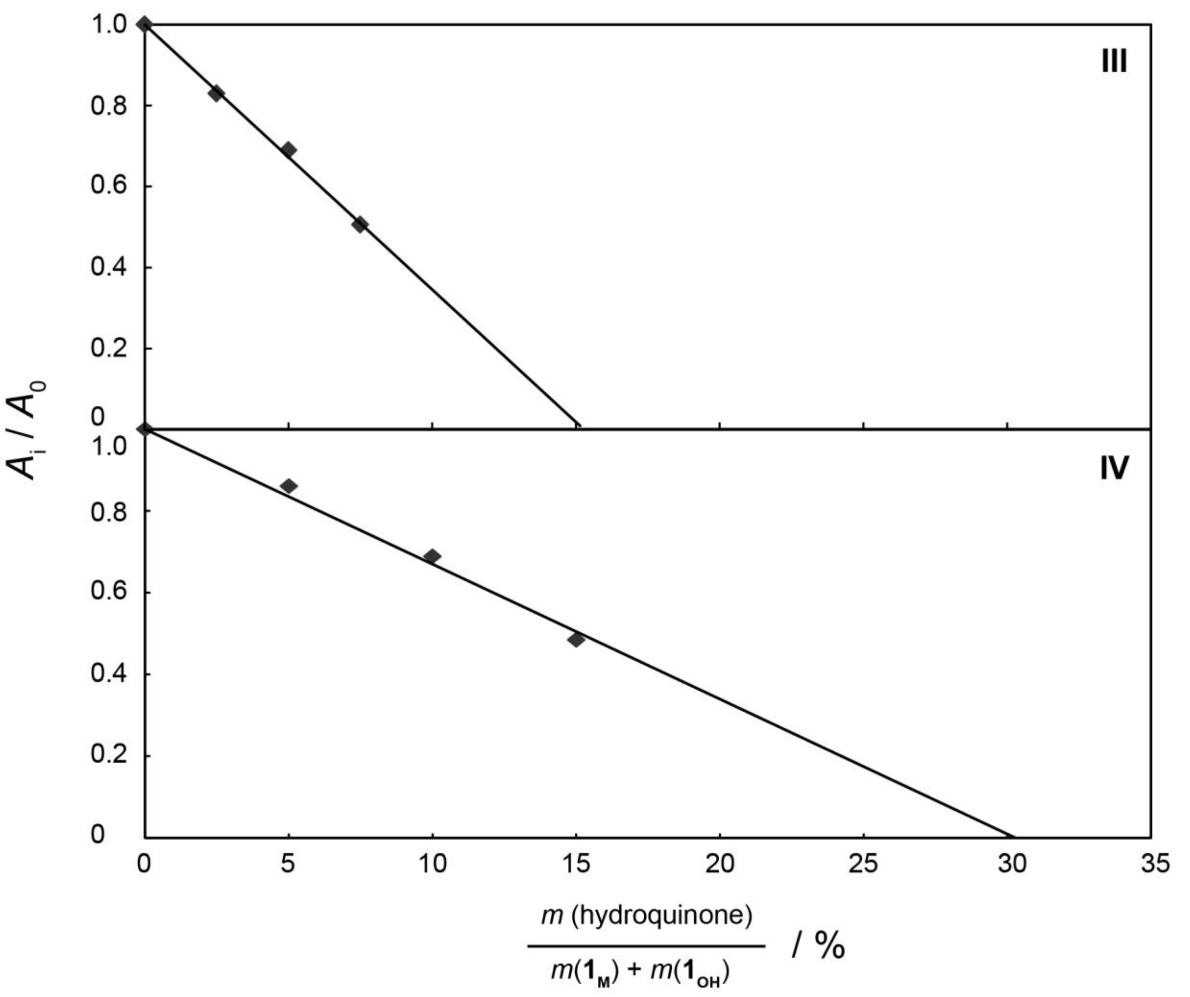

Figure S1. Titration of **III** and **IV** using hydroquinone.

Solvolysis of 1_M in acetone

0.80 mg of $\mathbf{1_M}$ (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_{before}). After standing 1 h, the absorbance at 752 nm (A_{after}) was again measured, the ratio of (A_{after} / A_{before}) being 0.97.

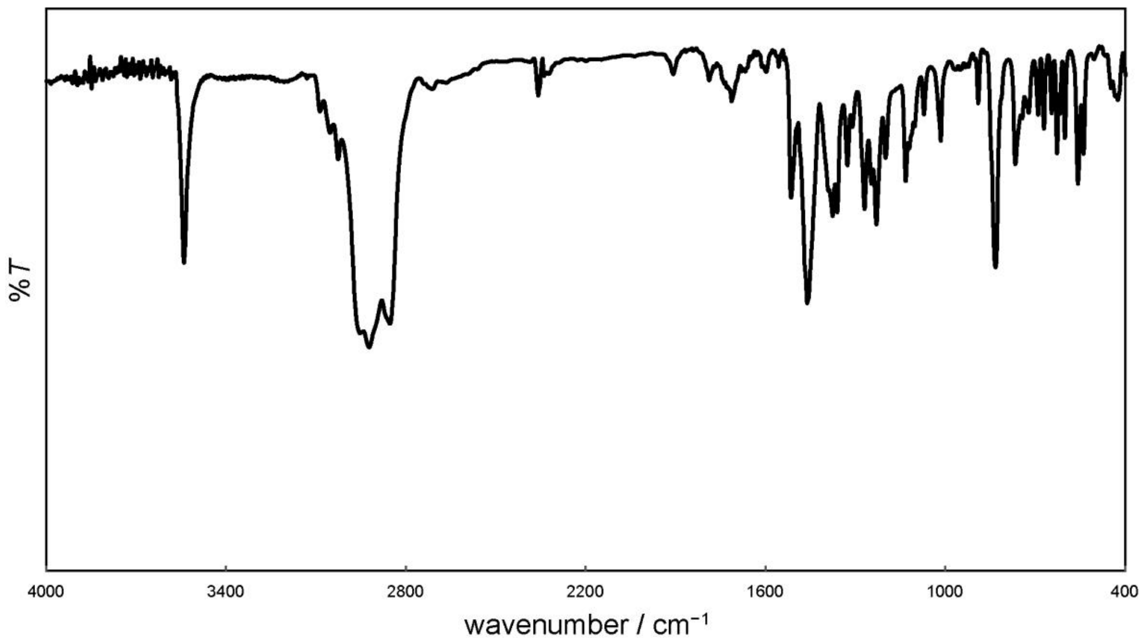

Figure S2. IR spectrum of **II** (Nujol mull).

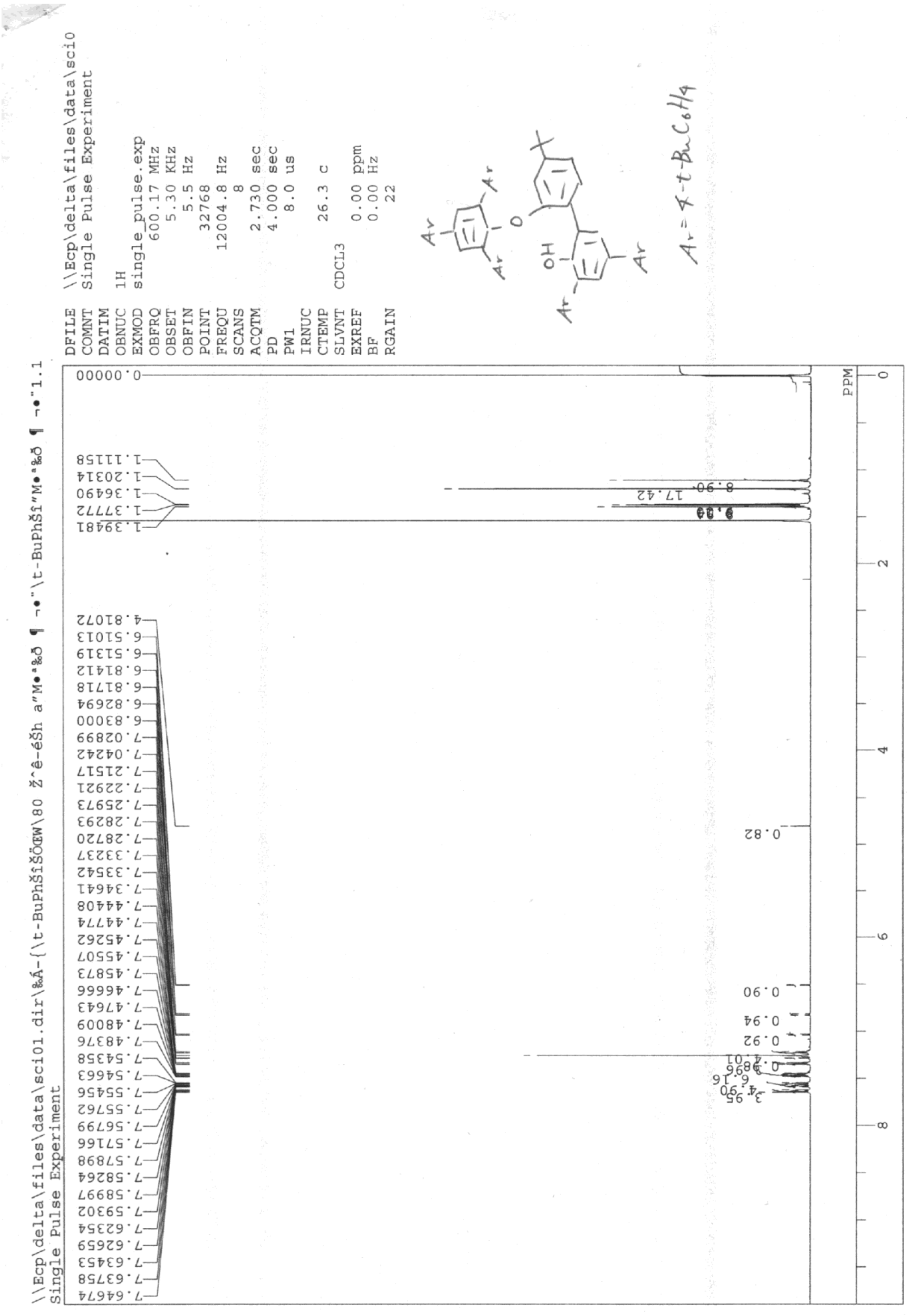

Figure S3. ^{1}H NMR of **2**.

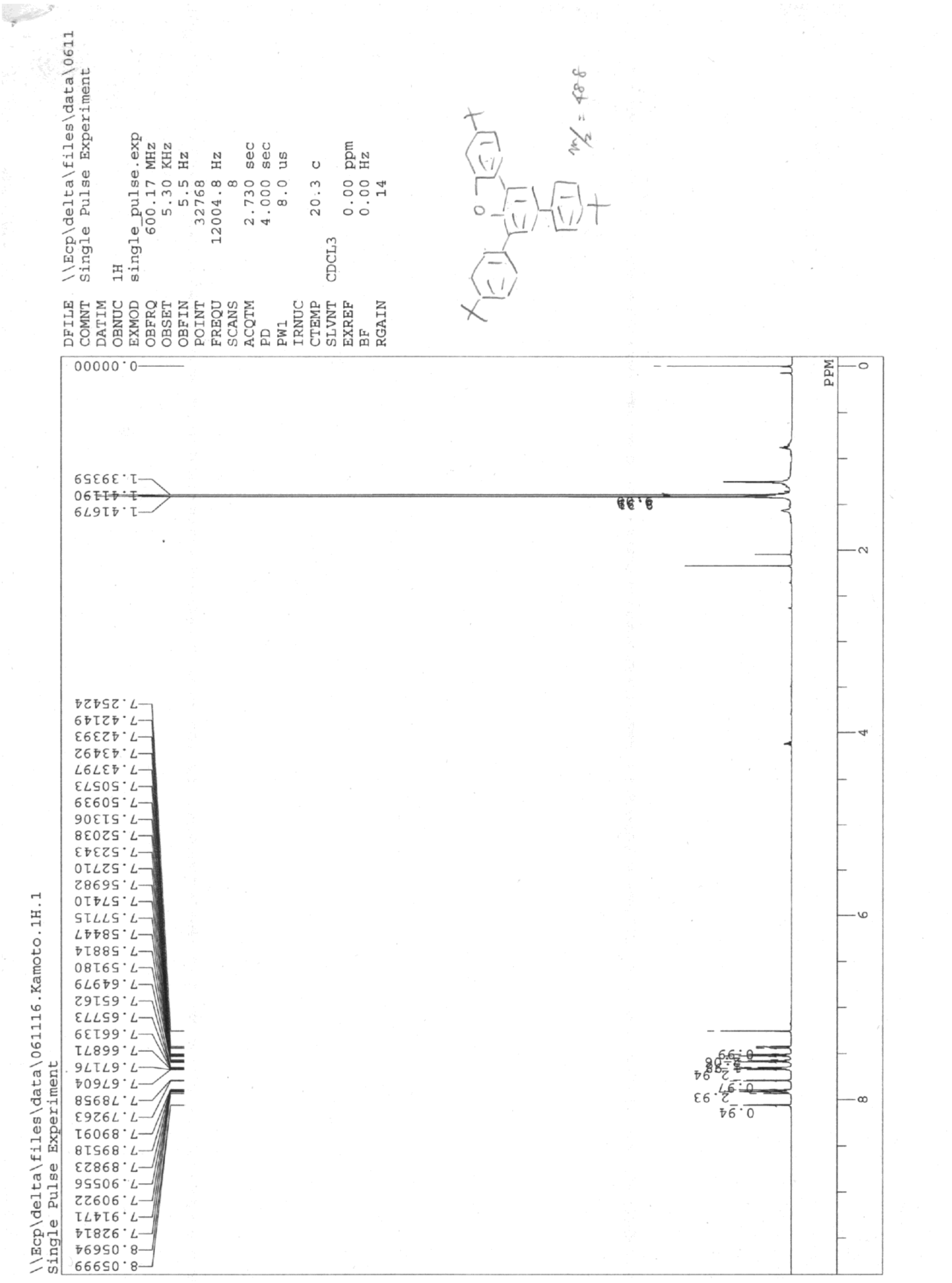

Figure S4. ^{1}H NMR of **3**.

(a)

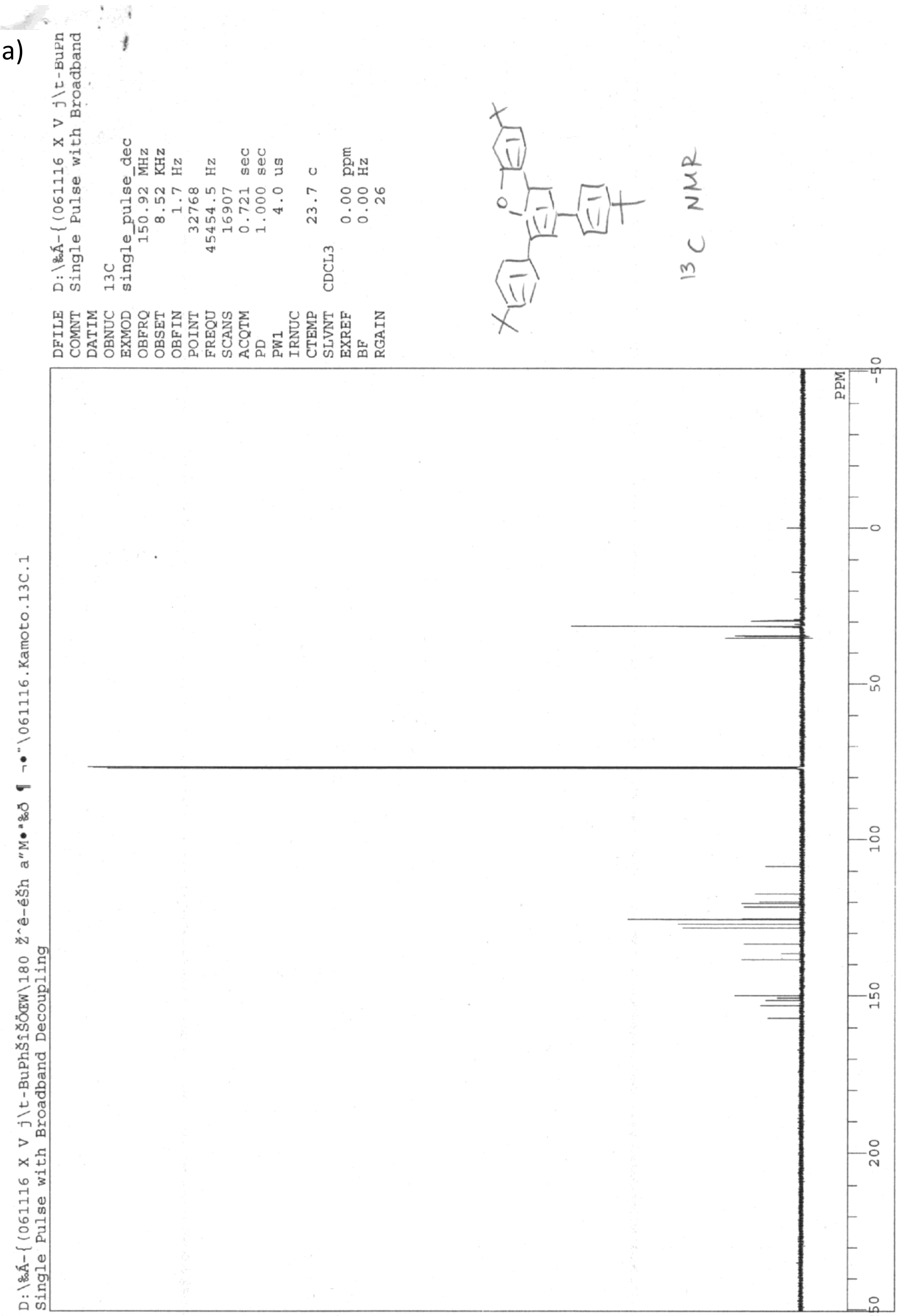

Figure S5. ^{13}C NMR of **3**. (a) Overall view. (b)–(e) Enlarged views. Note that two signals overlap at δ ~ 108.8 ppm in (c). Indeed, two signals appeared in this region when the broadening factor (BF) was changed to –1.0 ppm as shown in (d).

(b)

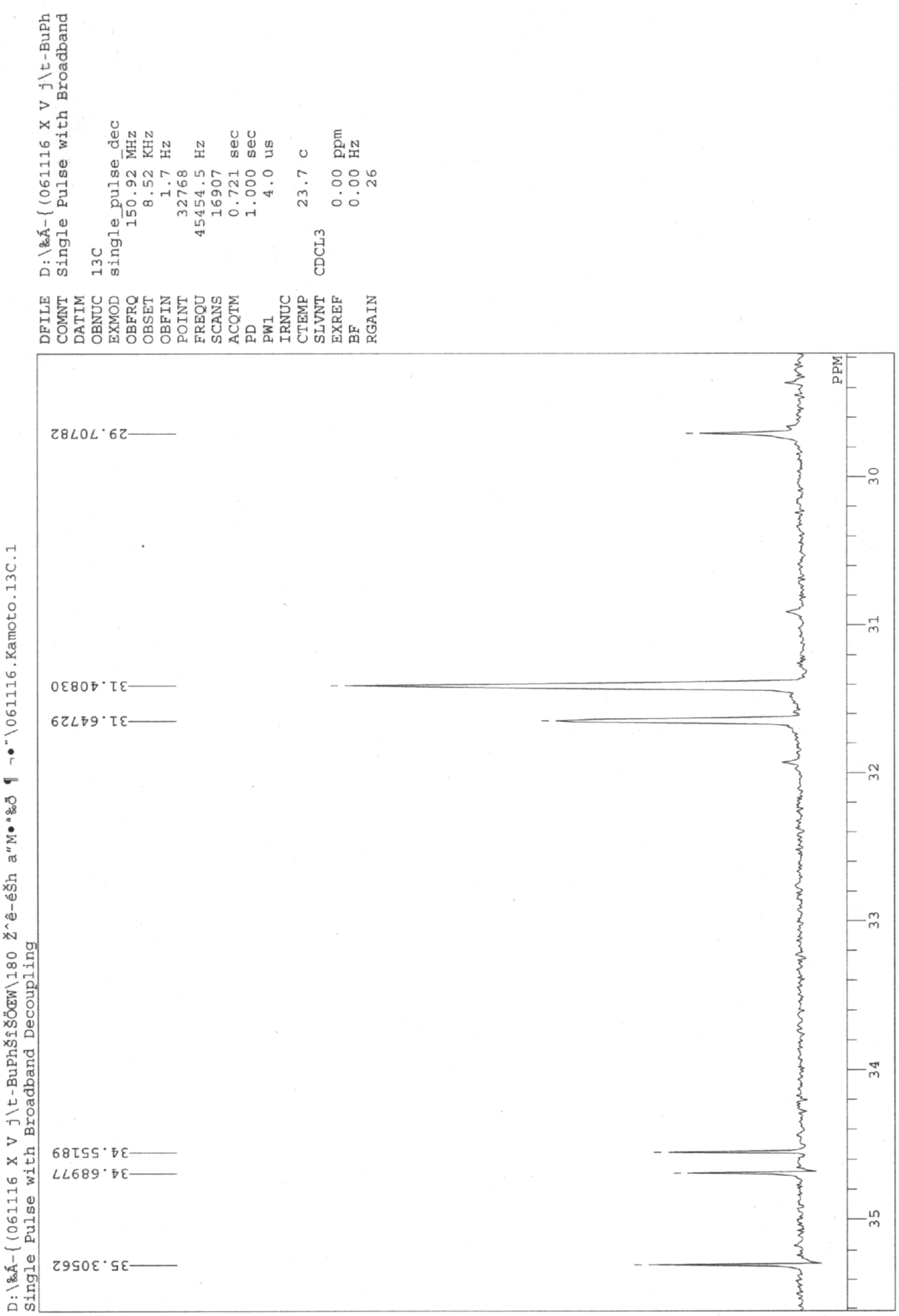

Figure S5 (contd).

(c)

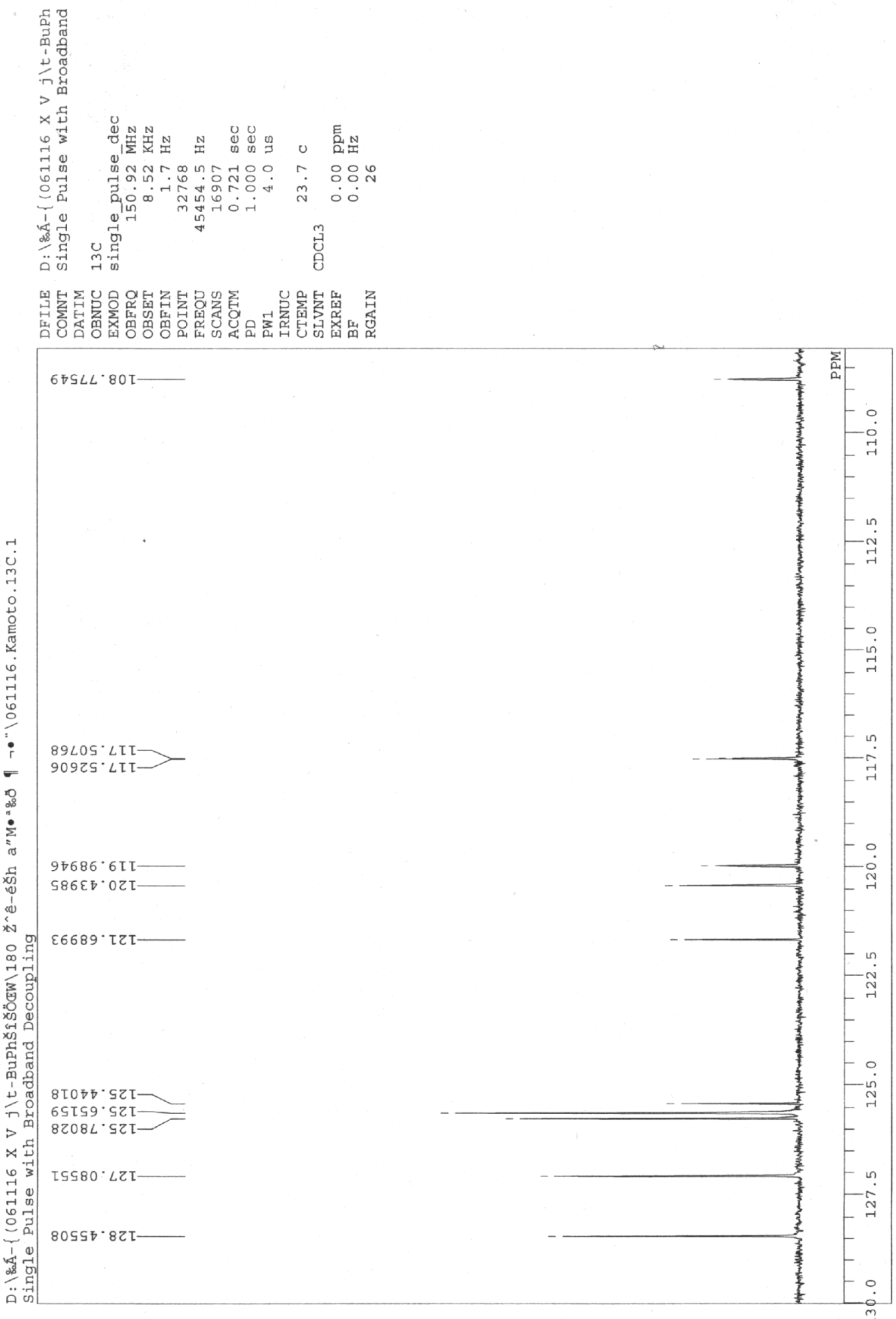

Figure S5 (contd).

(d)

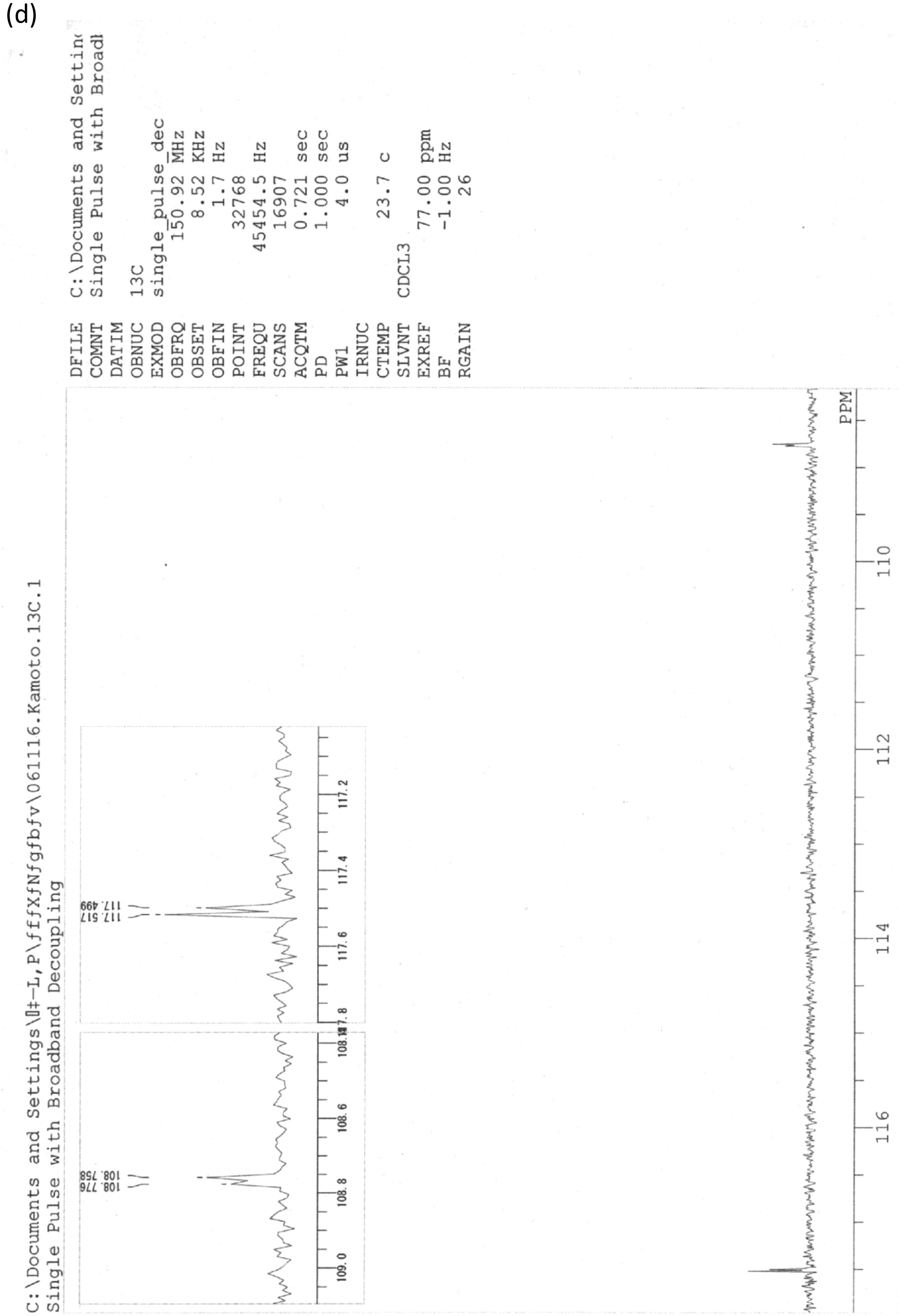

Figure S5 (contd).

(e)

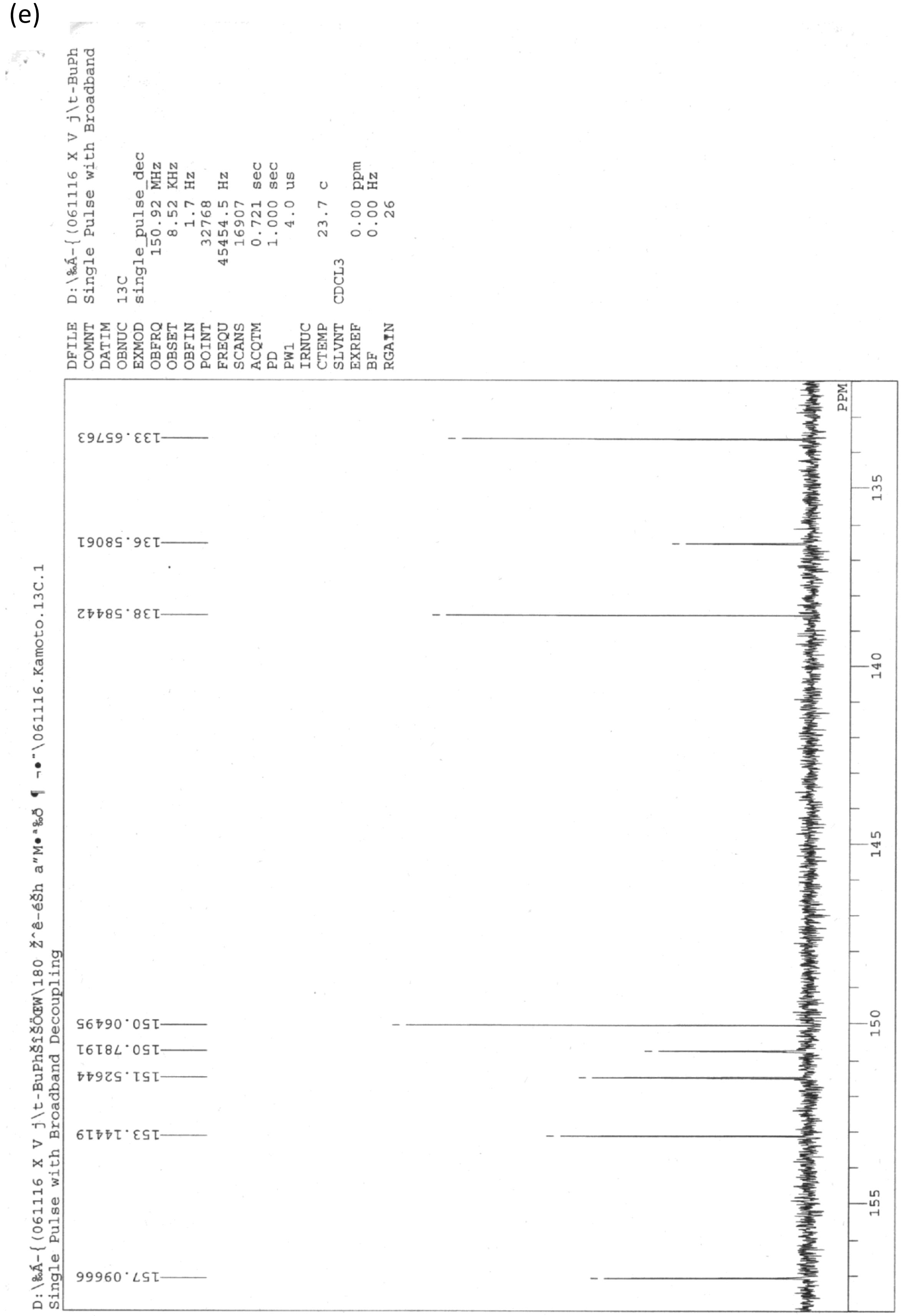

Figure S5 (contd).

