

# Palladium-Catalyzed Synthesis of 9-Fluorenylidenes through Aryne Annulation

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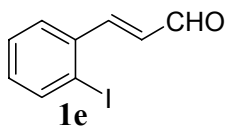
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## Supporting Information

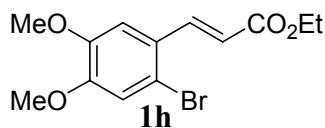
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**General.** The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. Thin layer chromatography was performed using 60 mesh silica gel plates, and visualization was effected with short wavelength UV light (254 nm). All melting points are uncorrected. All high resolution mass spectra were recorded using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted.

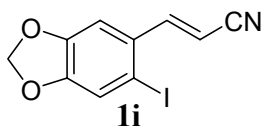
**General procedure for the synthesis of the starting *ortho*-halostyrenes by a Wittig reaction.** To a solution of triphenylphosphoranylidene (4.5 mmol) in 30 ml of  $\text{CH}_2\text{Cl}_2$  was added dropwise a solution of the aldehyde (3.0 mmol) in 6 ml of  $\text{CH}_2\text{Cl}_2$  at 0 °C under an inert argon atmosphere. The resulting mixture was stirred at 25 °C until completion of the reaction, which was monitored by TLC. The solvent was then evaporated under reduced pressure. The solid residue was dissolved in 15 ml of hexanes and the mixture was stirred at 25 °C for 30 min. The  $\text{Ph}_3\text{PO}$  was filtered off and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ EtOAc as the eluent to afford the desired product.



**(*E*)-3-(2-Iodophenyl)propenal (1e).** This compound was obtained as a yellow solid: mp 79-80 °C (lit.<sup>1</sup> 78-79 °C);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.56-6.62 (m, 1H), 7.07-7.11 (m, 1H), 7.39 (t,  $J$  = 7.6 Hz, 1H), 7.60 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 7.71 (d,  $J$  = 15.7 Hz, 1H), 7.92 (dd,  $J$  = 7.9, 0.9 Hz, 1H), 9.76 (d,  $J$  = 7.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.0, 127.7, 128.8, 130.8, 132.2, 136.9, 140.3, 155.4, 193.4.



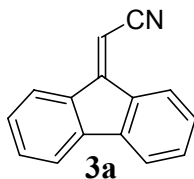
**(E)-Ethyl 3-(2-bromo-4,5-dimethoxyphenyl)propenoate (1h).** This compound was obtained as a white solid: mp 112-114 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.34 (t,  $J = 7.2$  Hz, 3H), 3.89 (s, 6H), 4.27 (q,  $J = 7.1$  Hz, 2H), 6.28 (d,  $J = 15.8$  Hz, 1H), 7.04 (d,  $J = 13.7$  Hz, 2H), 7.96 (d,  $J = 15.9$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.3, 56.0, 56.2, 60.5, 109.0, 115.4, 117.1, 118.5, 126.2, 142.6, 148.5, 151.2, 166.5; HRMS  $m/z$  314.01596 (calcd  $\text{C}_{13}\text{H}_{15}\text{BrO}_4$ , 314.01537).



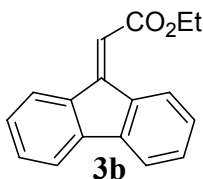
**3-(6-Iodobenzo[1,3]dioxol-5-yl)acrylonitrile (1i).** This compound was obtained as a white solid: mp 104-106 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.35 (d,  $J = 11.8$  Hz, 1H), 5.97 (s, 2H), 7.18 (d,  $J = 11.9$  Hz, 1H), 7.26 (s, 1H), 7.48 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  91.0, 96.4, 97.1, 102.5, 105.8, 108.6, 116.8, 119.2, 152.2, 153.5; HRMS  $m/z$  298.94482 (calcd  $\text{C}_{10}\text{H}_6\text{INO}_2$ , 298.94433).

**General procedure for the palladium-catalyzed annulation of arynes by *ortho*-halostyrenes and *ortho*-haloallylicbenzenes.** To 0.3 mmol of the aryl halide was added the *o*-silylaryl triflate (1.5 equiv),  $\text{Pd}(\text{dba})_2$  (10 mol %), dppm (20 mol %) and 1:1  $\text{CH}_3\text{CN}/\text{PhCH}_3$  (5 ml).  $\text{CsF}$  (3.0 equiv) was then added and the vial was sealed with a screw cap. The reaction mixture was then stirred at 110 °C for 24 h. After the reaction was complete, the resulting solution was washed with brine (25 mL) and extracted with EtOAc

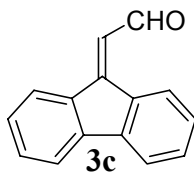
(25 mL). The combined EtOAc fractions were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ EtOAc as the eluent to afford the desired product.



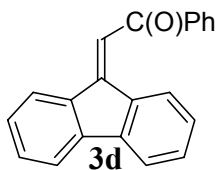
**2-(9H-Fluoren-9-ylidene)acetonitrile (3a).** This compound was obtained as a yellow solid: mp 109-111 °C (lit.<sup>2</sup> 109-110 °C); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 88.6, 120.3, 120.4, 121.7, 125.5, 128.0, 128.5, 131.9, 132; HRMS m/z 203.07381 (calcd C<sub>15</sub>H<sub>9</sub>N, 203.07350). The <sup>1</sup>H NMR spectrum matches the literature data.<sup>2</sup>



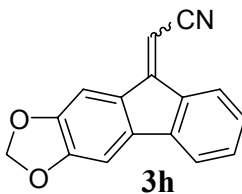
**Ethyl 2-(9H-fluoren-9-ylidene)acetate (3b).** This compound was obtained as a yellow solid: mp 75-76 °C; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.5, 60.9, 114.1, 119.7, 119.9, 121.4, 127.6, 128.2, 129.3, 130.7, 131.0, 135.3, 139.0, 140.9, 142.6, 148.4, 166.5. The <sup>1</sup>H NMR spectrum matches the literature data.<sup>3</sup>



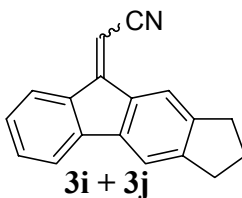
**2-(9H-Fluoren-9-ylidene)acetaldehyde (3c).** This compound was obtained as a yellow solid: mp 115-117 °C (lit.<sup>4</sup> 115.6-116.3 °C). The <sup>1</sup>H and <sup>13</sup>C NMR spectra match the literature data.<sup>3</sup>



**2-(9H-Fluoren-9-ylidene)-1-phenylethanone (3d).** This compound was obtained as a yellow solid: mp 130-132 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.19-7.24 (m, 1H), 7.29 (dt,  $J$  = 7.5, 0.8 Hz, 1H), 7.34-7.42 (m, 2H), 7.48-7.52 (m, 2H), 7.58-7.63 (m, 4H), 7.76 (d,  $J$  = 7.6 Hz, 1H), 8.09-8.11 (m, 2H), 8.33 (d,  $J$  = 7.8 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  119.6, 119.8, 120.0, 121.2, 127.6, 127.7, 128.1, 128.94, 128.98, 130.6, 130.9, 133.5, 135.5, 138.4, 138.9, 141.0, 142.4, 146.2, 192.6 ; HRMS  $m/z$  282.10477 (calcd  $\text{C}_{21}\text{H}_{14}\text{O}$ , 282.10447).

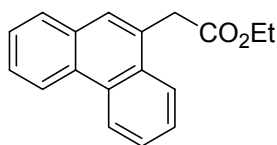


**(1,3-Dioxacyclopenta[b]fluoren-9-ylidene)acetonitrile (3h).** This compound was obtained as a pale yellow solid: mp 193-195 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.17 (s, 2H), 7.24-7.25 (m, 1H, merged  $\text{CDCl}_3$  peak shows extra proton), 7.67-7.73 (m, 2H), 8.00 (s, 1H), 8.10 (s, 1H), 8.25-8.27 (m, 1H), 8.47-8.50 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  101.2, 102.2, 106.4, 107.5, 118.4, 123.0, 126.2, 126.5, 127.5, 127.9, 128.8, 129.2, 129.9, 134.7, 148.5, 150.9; HRMS  $m/z$  247.0633 (calcd  $\text{C}_{16}\text{H}_9\text{NO}_2$ , 247.0633).



**(2,3-Dihydro-1H-cyclopenta[b]fluoren-9-ylidene)acetonitriles (3i + 3j).** These compounds were obtained as a yellow oil as a 11:1 mixture:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$

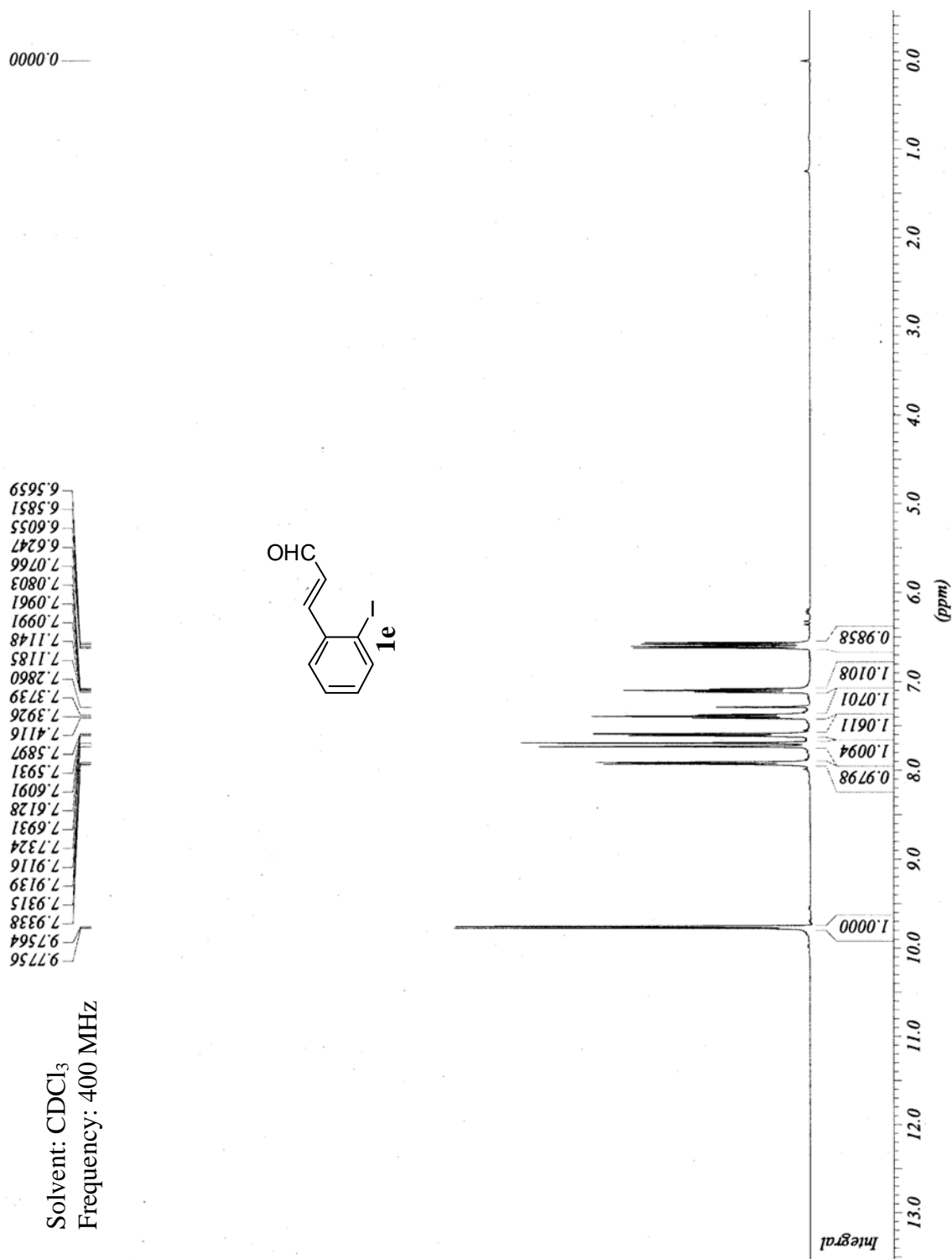
2.08-2.24 (m, 6H), 2.88-3.04 (m, 11H), 3.13-3.18 (m, 1H), 7.09-7.29 (m, 4H), 7.38-7.42 (m, 6H), 7.50-7.89 (m, 5H), 8.10-8.64 (m, 3H);  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  25.7, 32.8, 32.9, 33.2, 33.3, 87.1, 87.2, 116.4, 117.7, 117.9, 119.7, 119.8, 121.51, 121.53, 125.3, 127.3, 127.8, 131.6, 131.7, 133.7, 135.2, 135.4, 137.0, 139.6, 140.9, 141.1, 142.3, 144.6, 145.0, 149.15, 149.18, 153.80, 153.84; HRMS  $m/z$  243.10514 (calcd  $\text{C}_{18}\text{H}_{13}\text{N}$ , 243.10480).

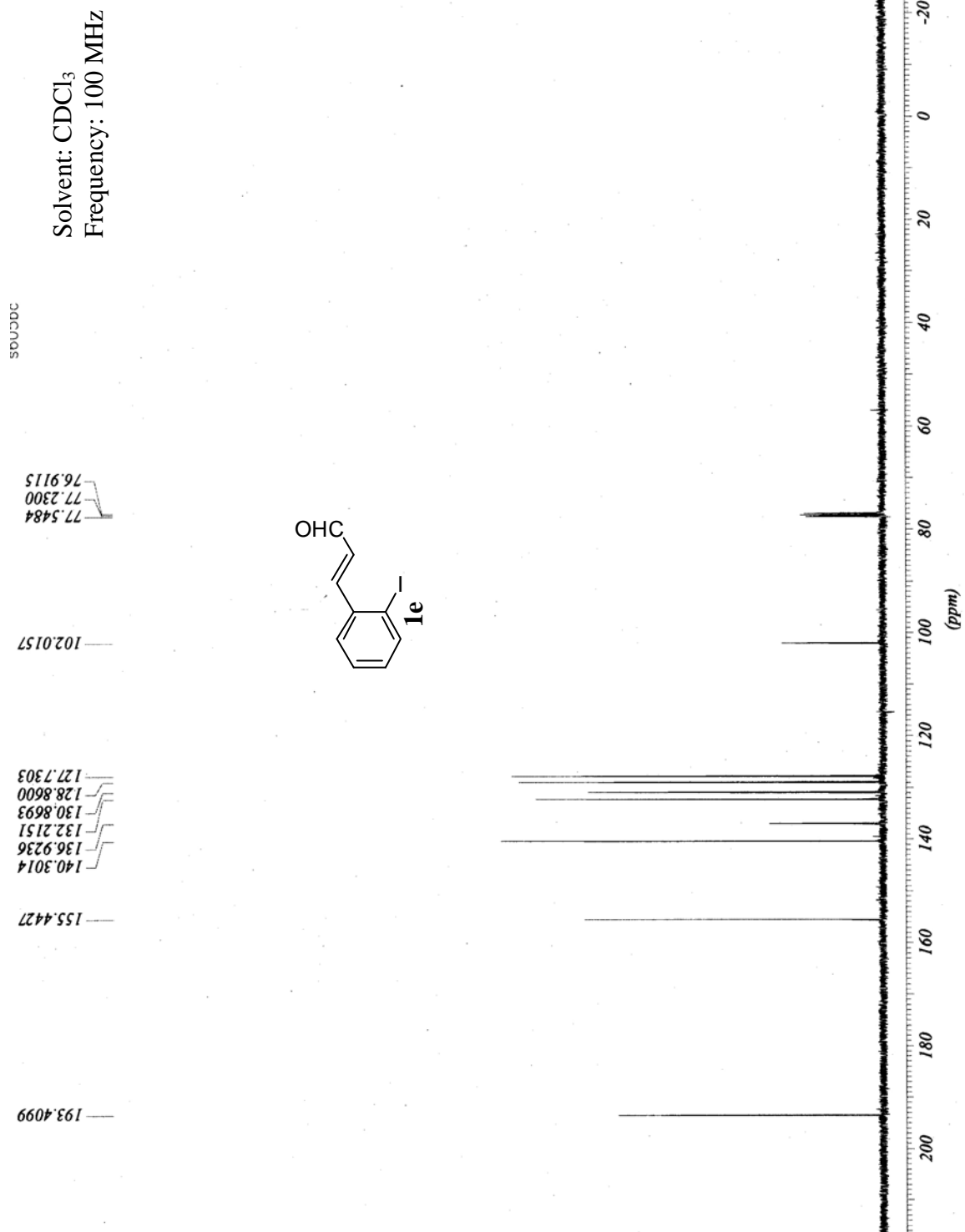


**Ethyl phenanthren-9-yl-acetate.** This compound was obtained as a yellow solid: mp 55-57 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.21 (t,  $J$  = 7.1 Hz, 3H), 4.10 (s, 2H), 4.16 (q,  $J$  = 7.1 Hz, 2H), 7.56-7.68 (m, 5H), 7.85 (d,  $J$  = 7.5 Hz, 1H), 8.02-8.04 (m, 1H), 8.66 (d,  $J$  = 8.1 Hz, 1H), 8.72-8.74 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.4, 40.0, 61.2, 122.6, 123.3, 124.6, 126.6, 126.8, 126.9, 127.0, 128.5, 129.0, 129.3, 130.3, 130.8, 131.2, 131.7, 171.7; HRMS  $m/z$  264.11547 (calcd  $\text{C}_{18}\text{H}_{16}\text{O}_2$ , 264.11503).

## References

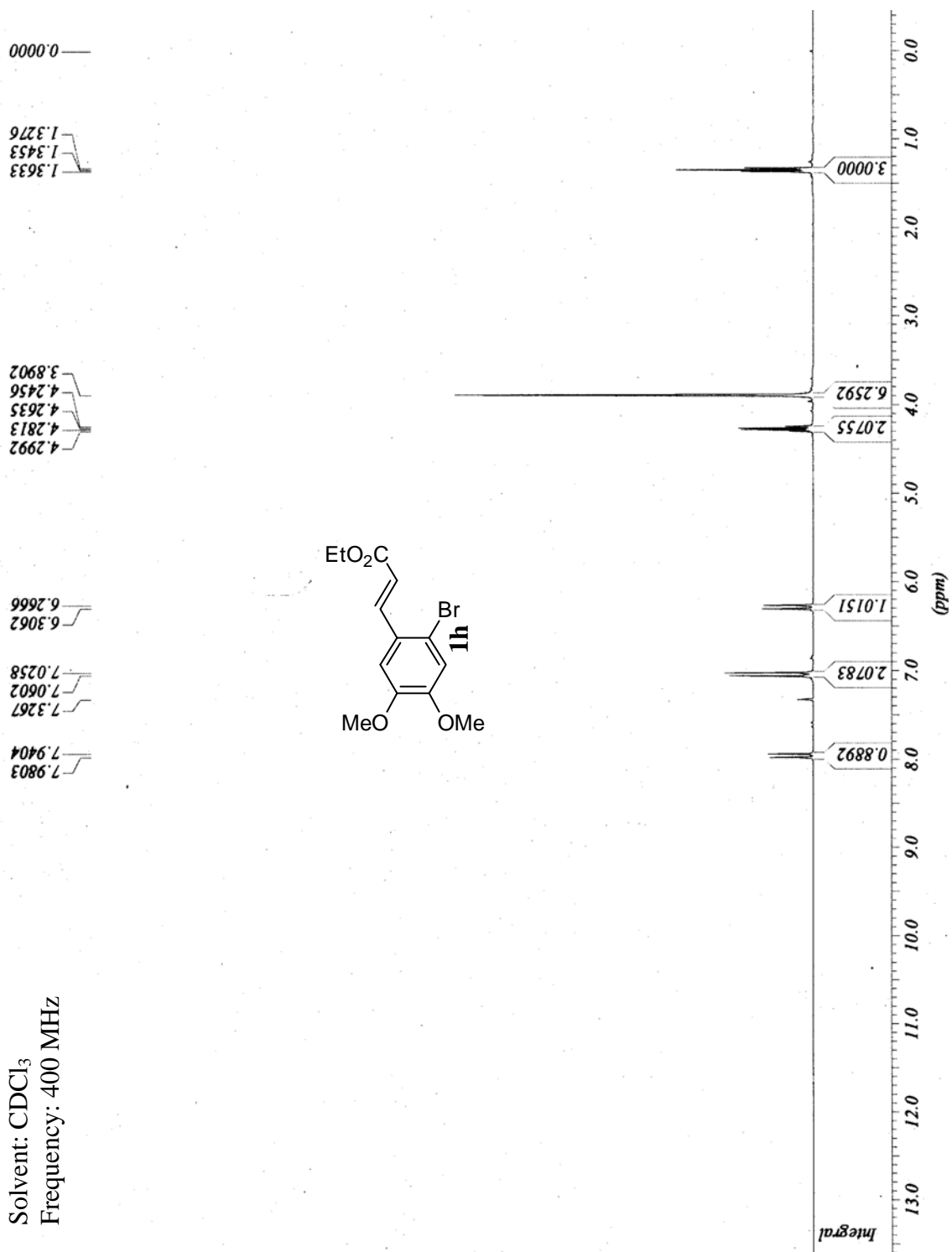
1. Rapson, W. S.; Shuttleworth, R. G. *J. Chem. Soc.* **1941**, 487.
2. Dibbiase, S. A.; Lipisko, B. A.; Haag, A.; Wolak, R. A.; Gokel, G. W. *J. Org. Chem.* **1979**, *44*, 4640.
3. Hayashi, T.; Ishigedani, M. *Tetrahedron* **2001**, *57*, 2589.
4. Ye, J.; Ge, J.; Chen, X.; Zhao, Z.; Lu, P. *Tetrahedron* **2007**, *63*, 11040.

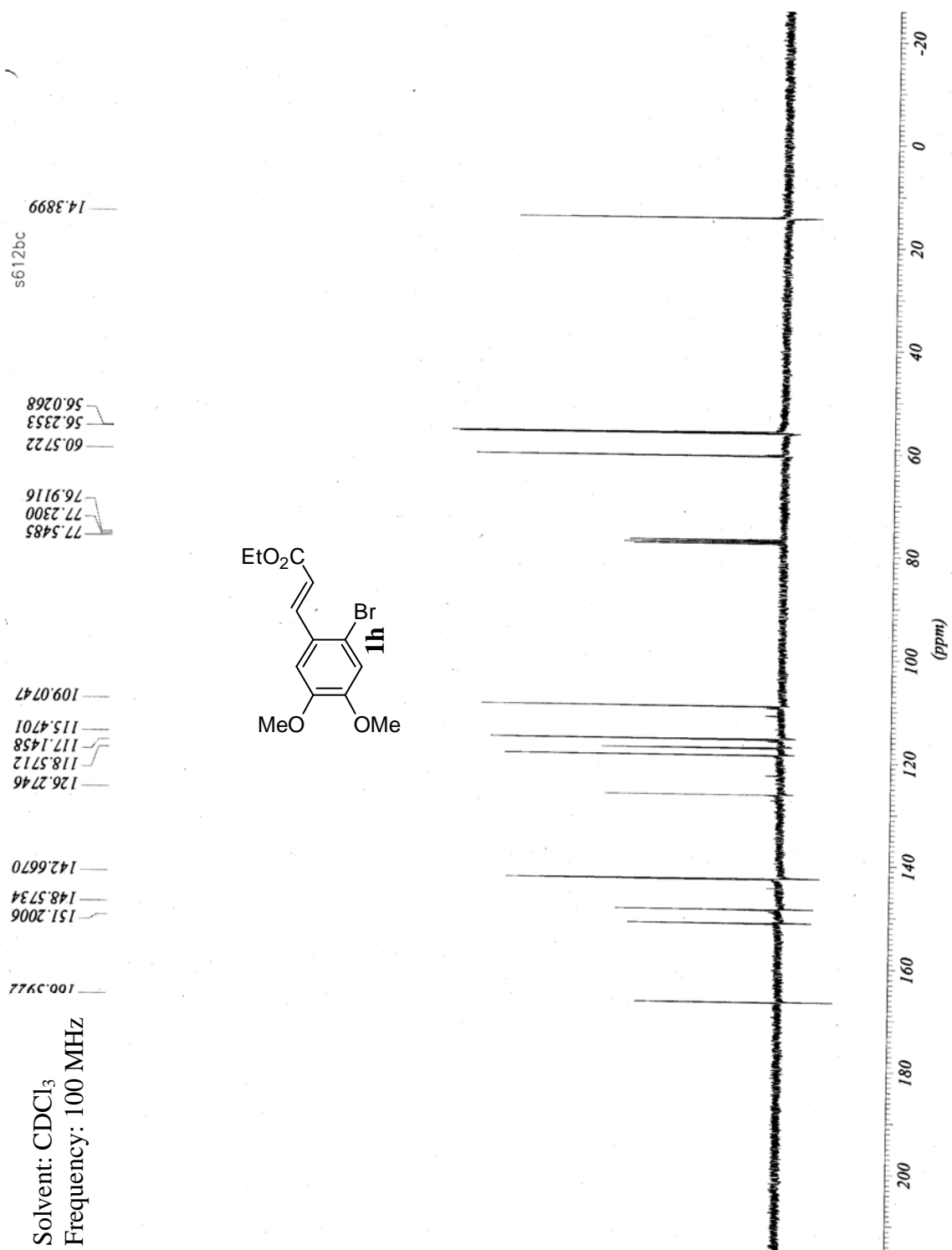


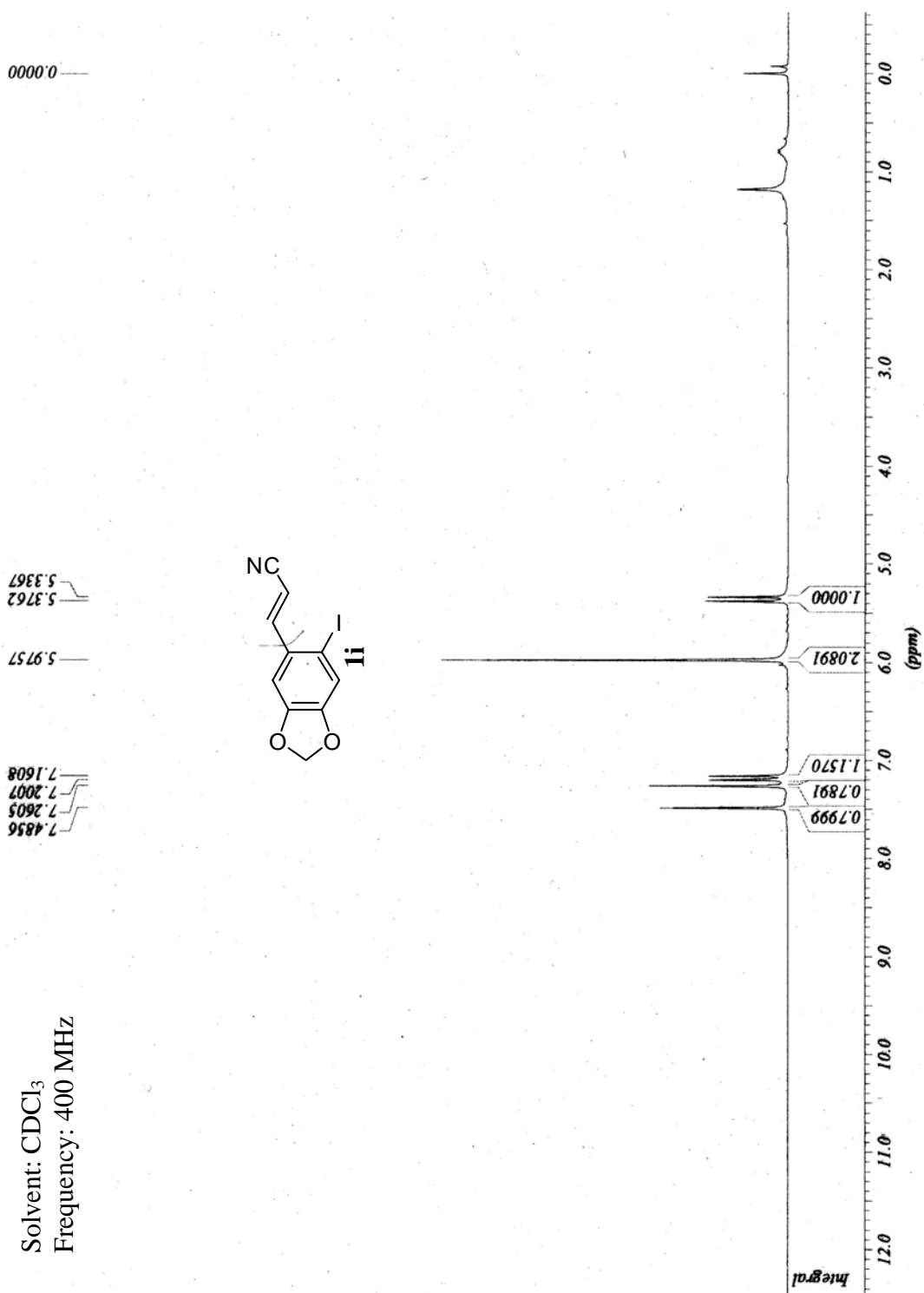


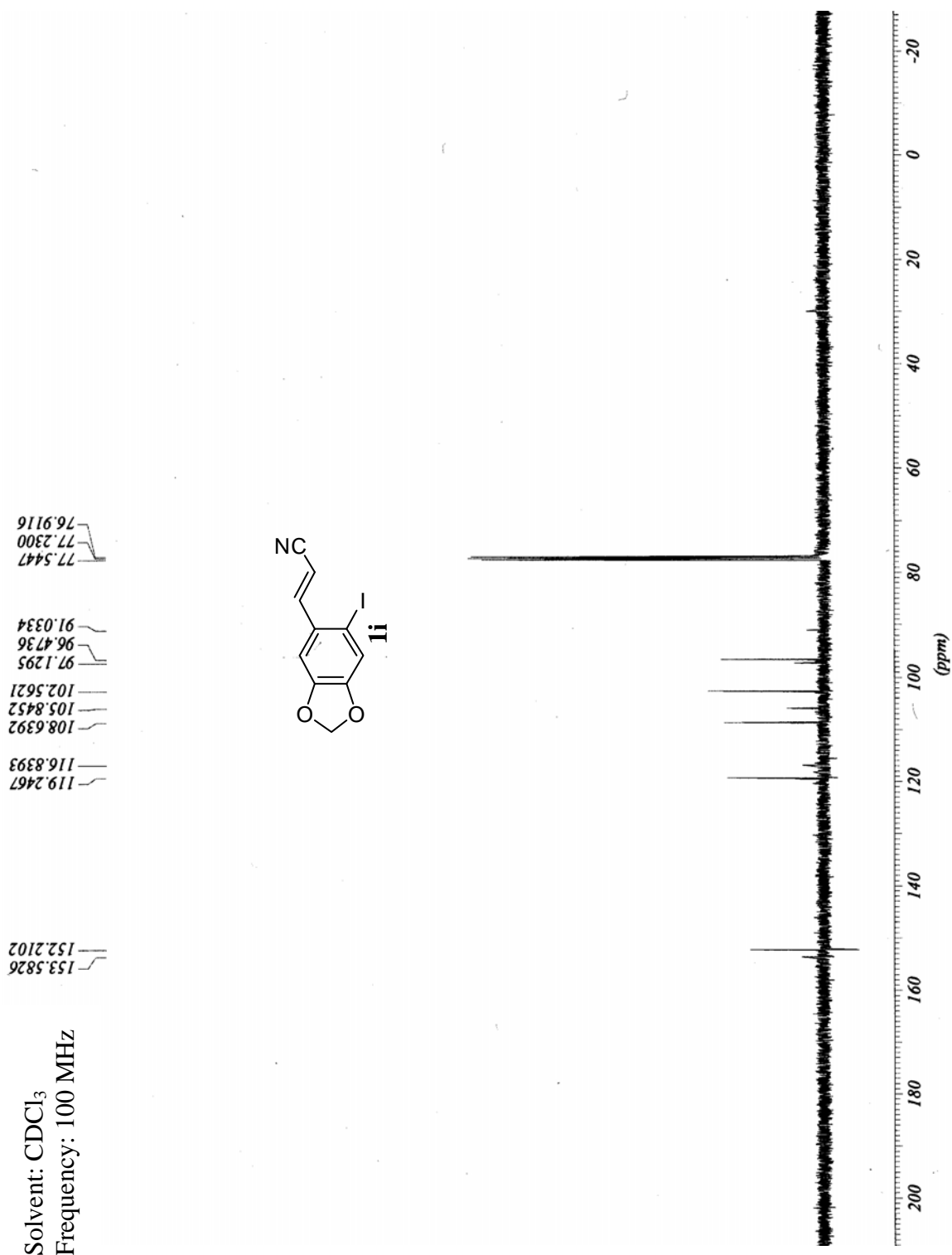


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Frequency: 400 MHz







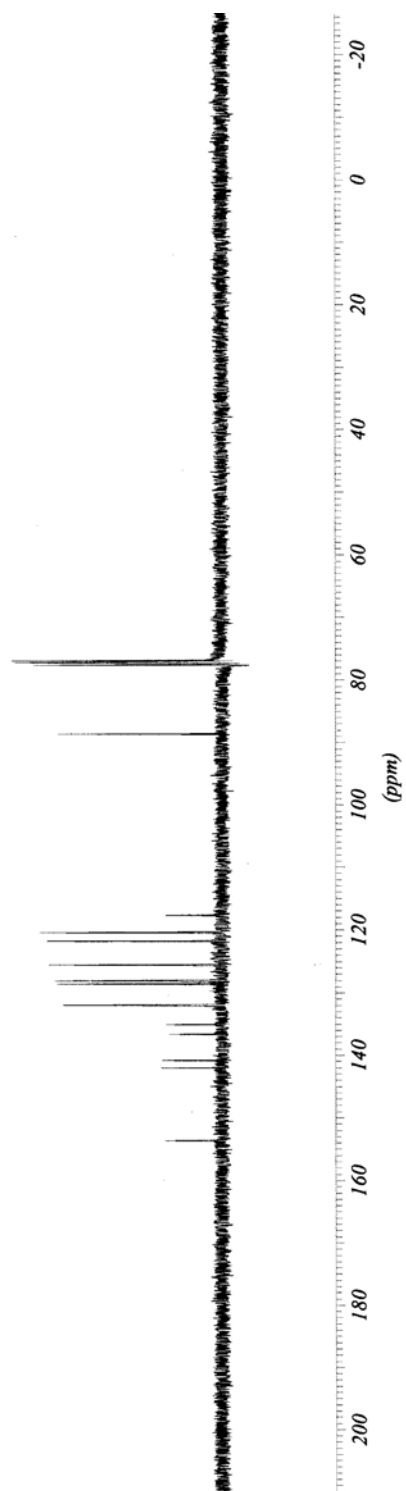
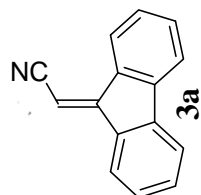


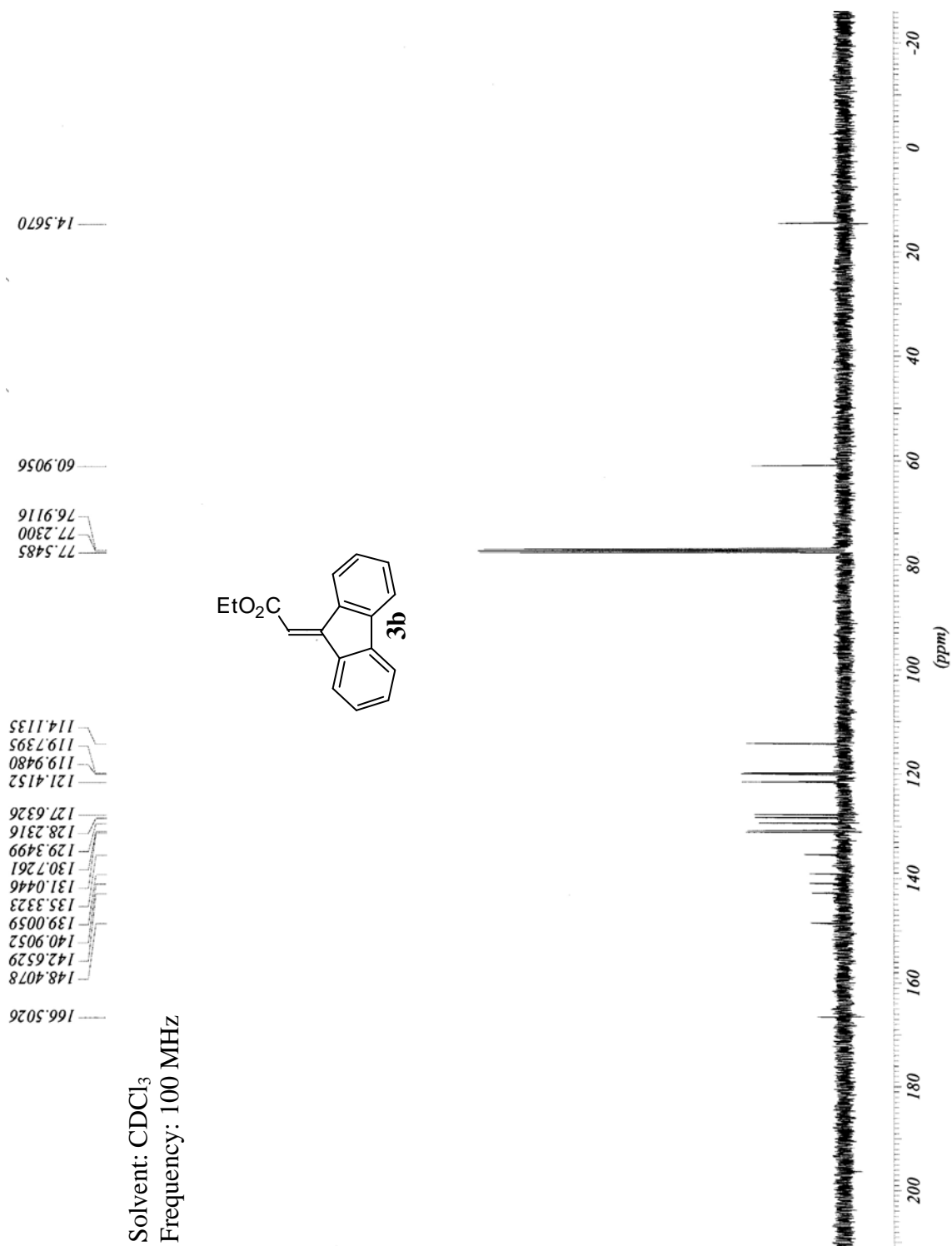
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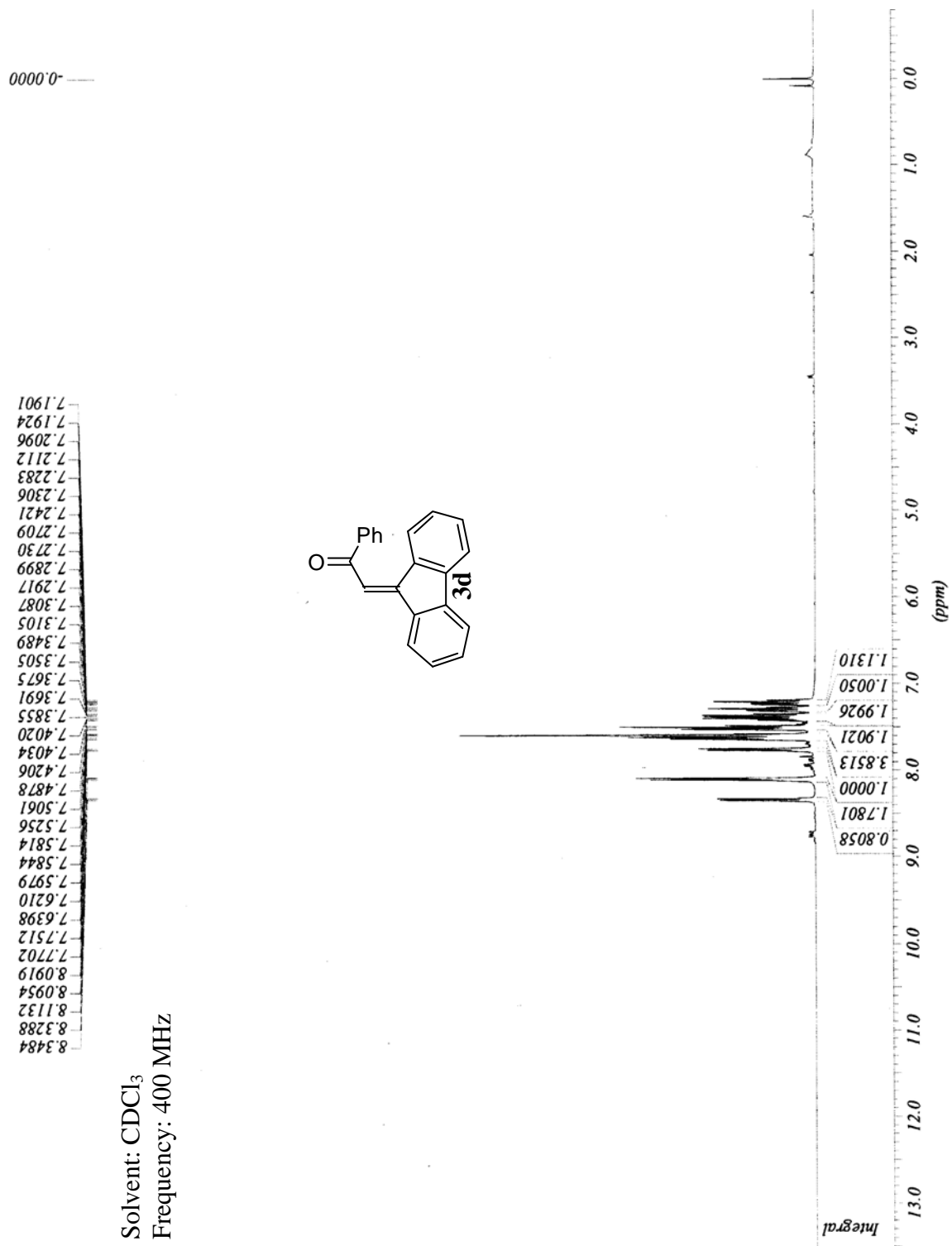
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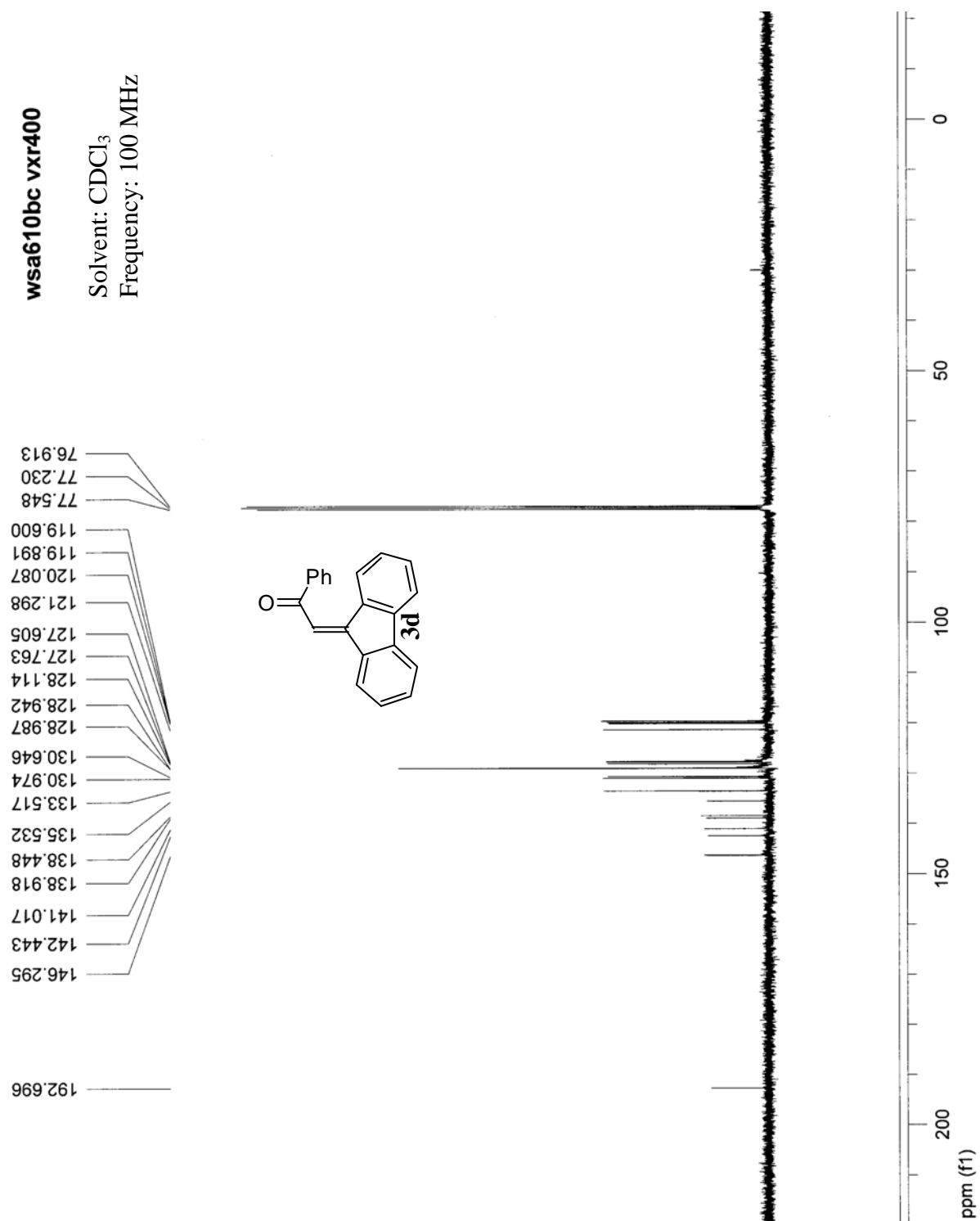
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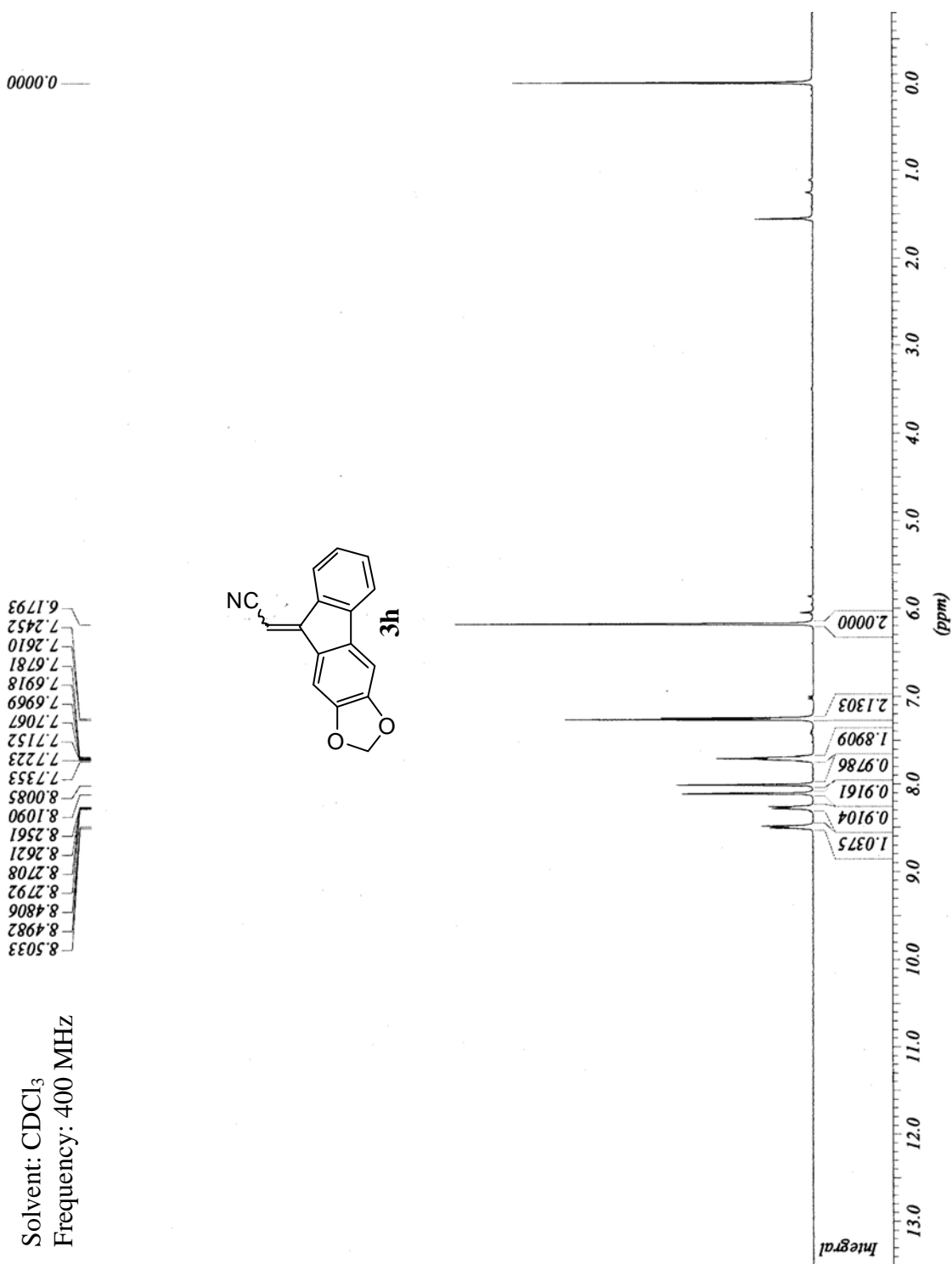


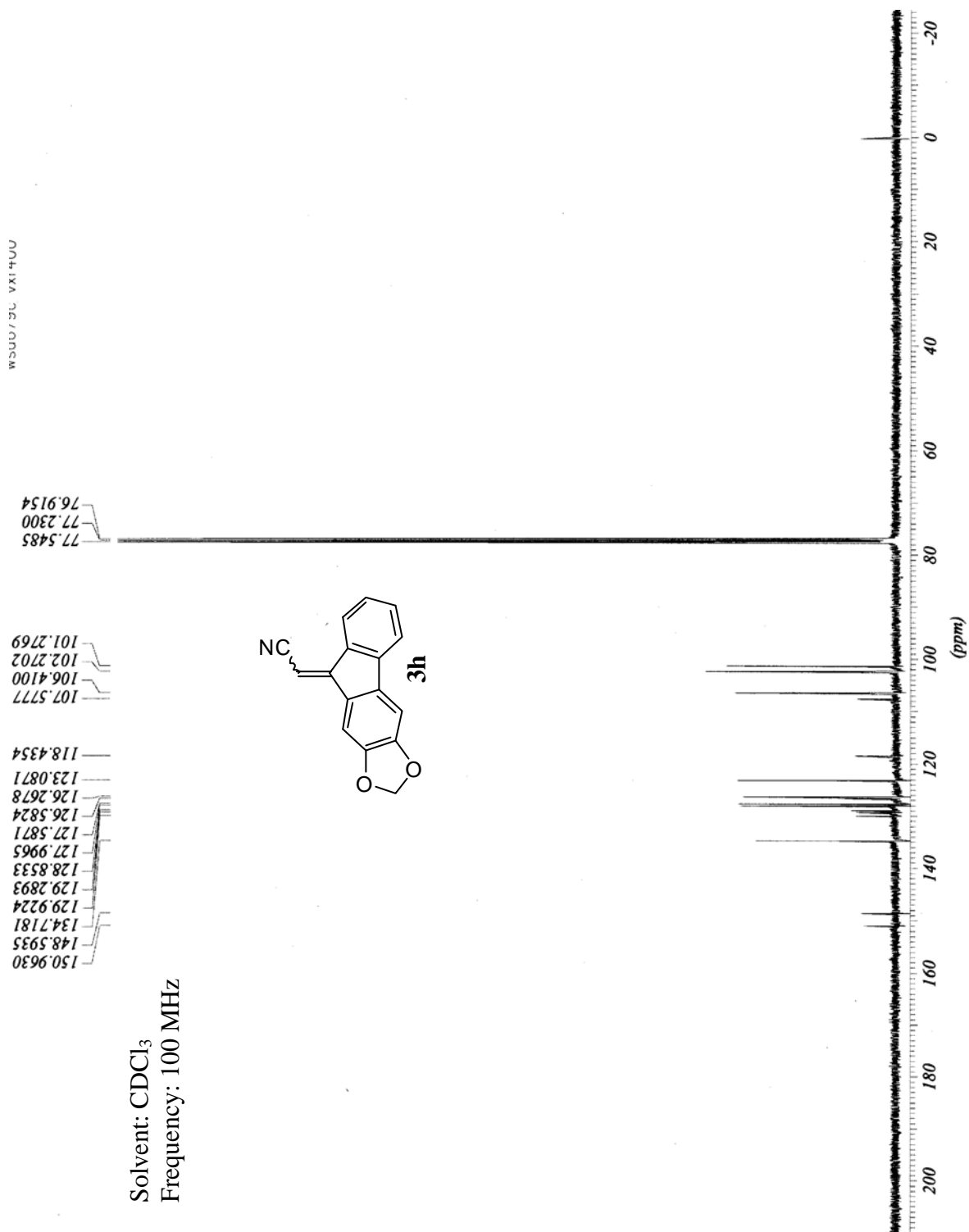


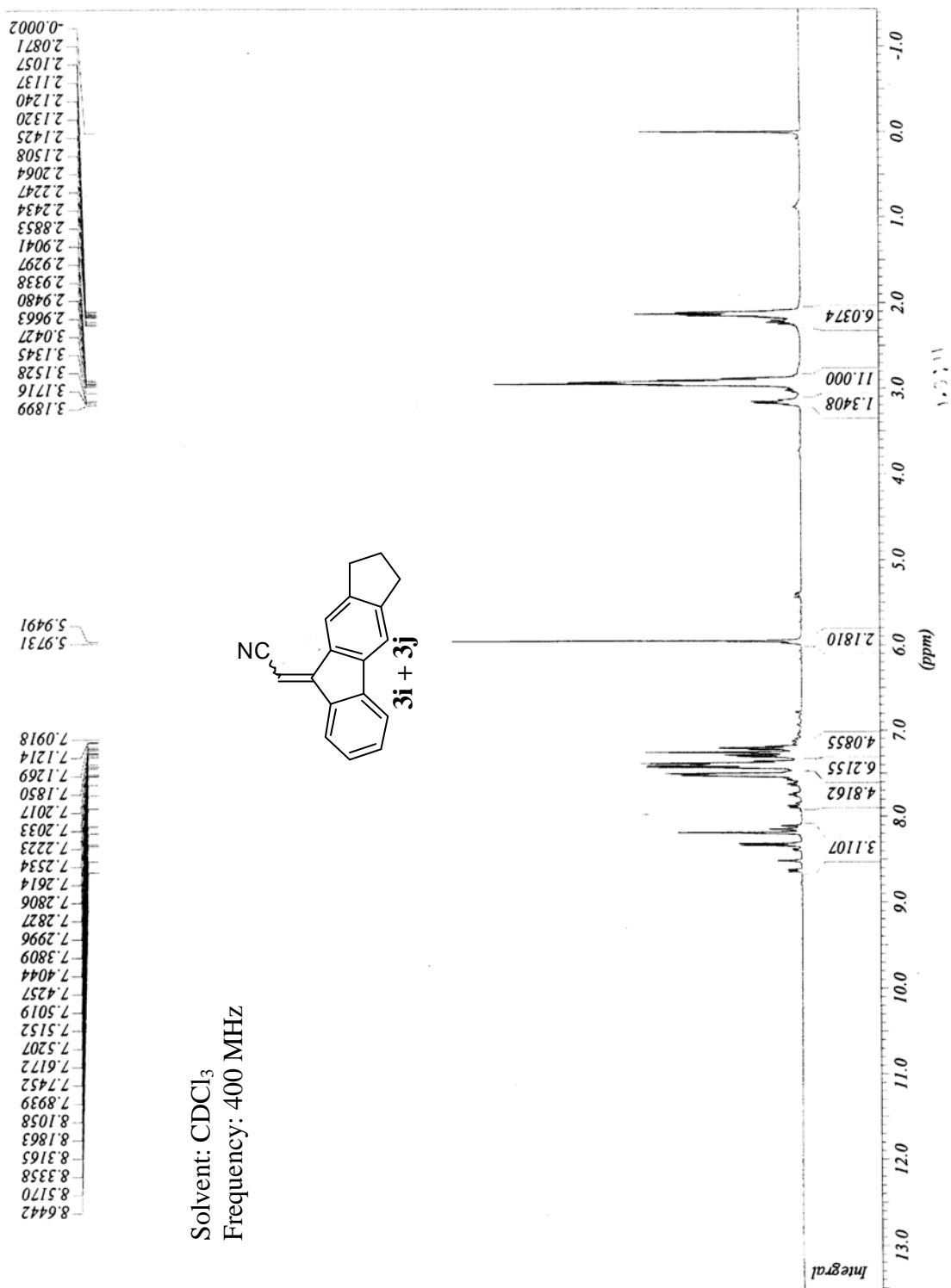


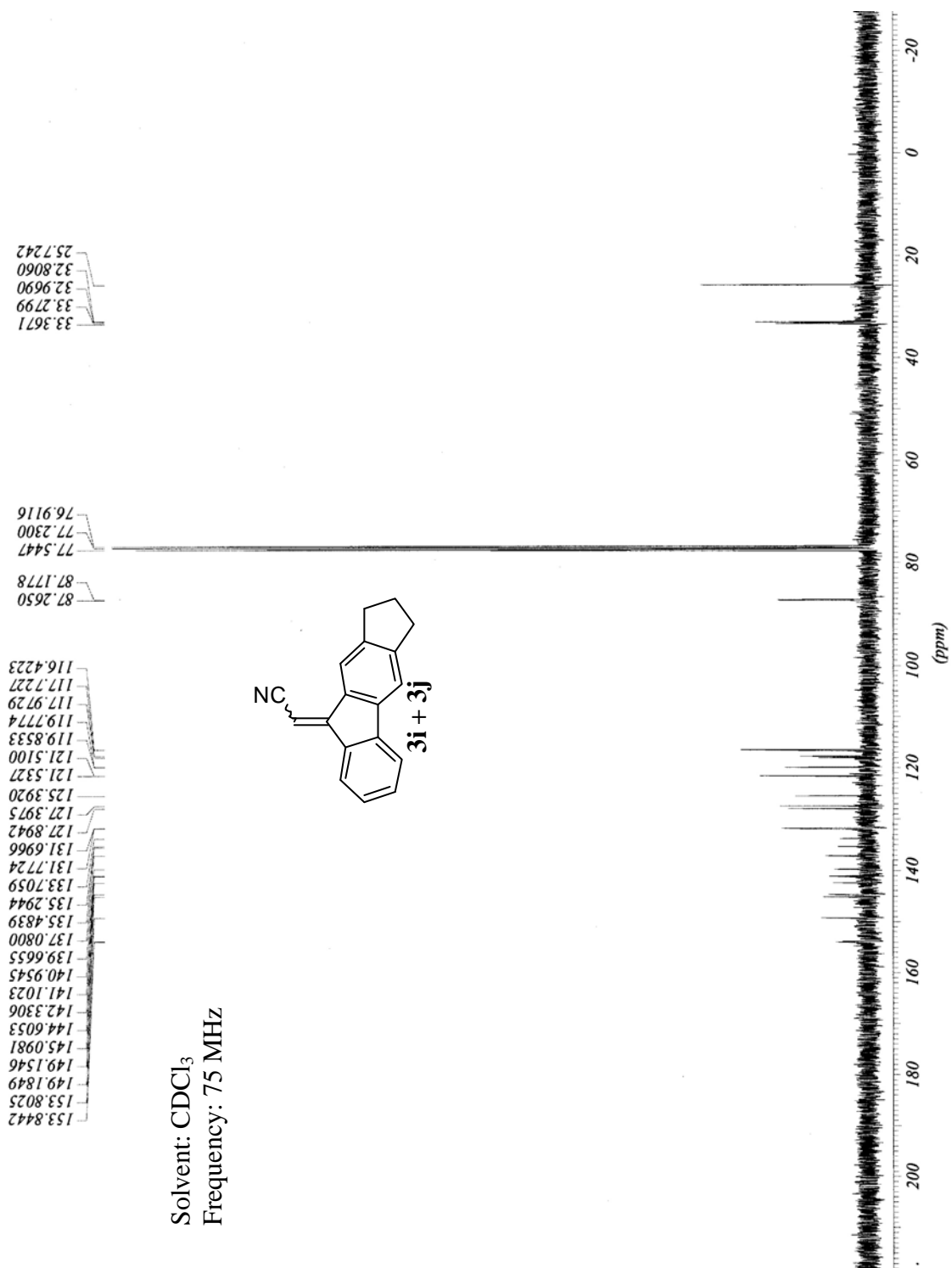


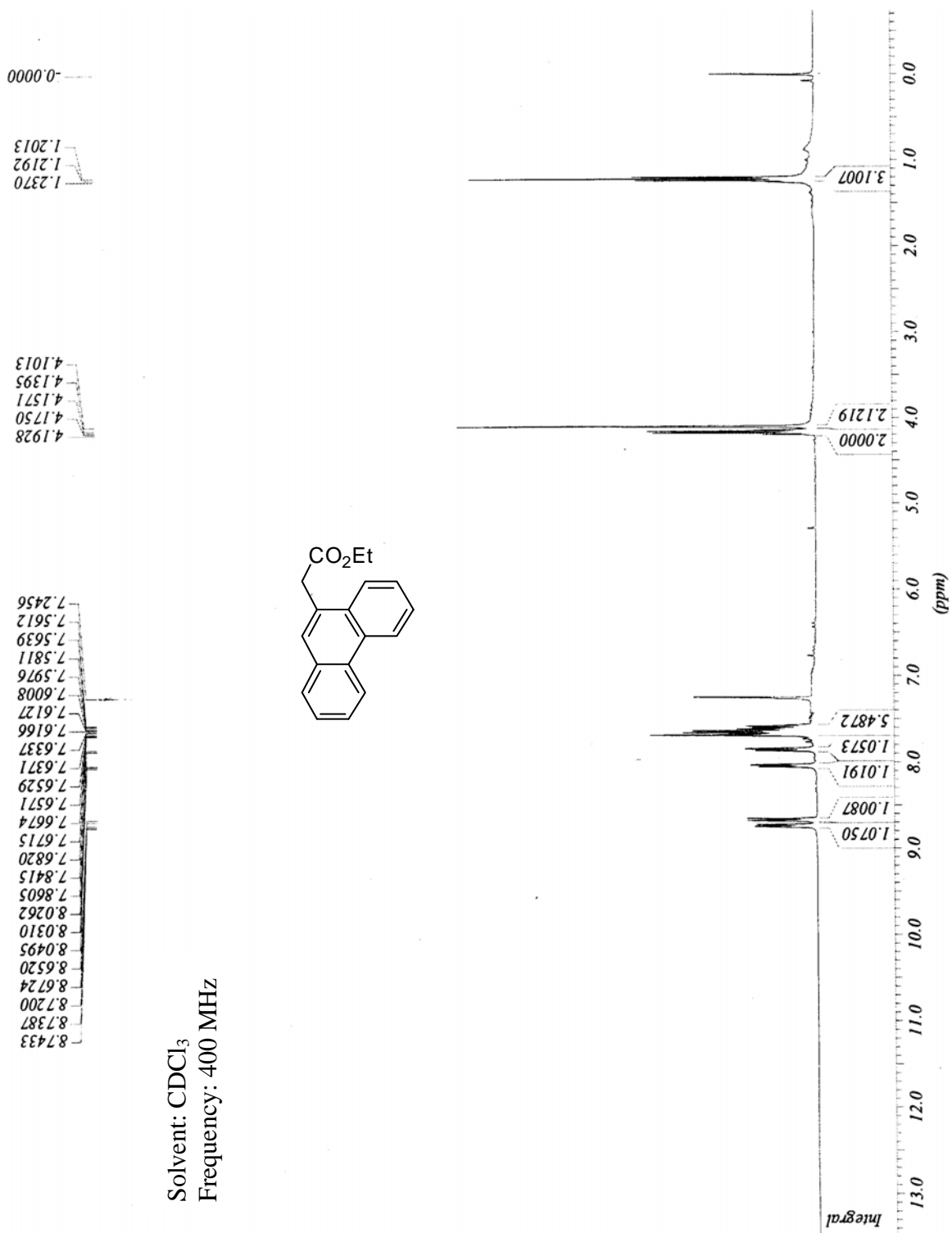












**wsa686c vxr400**

Solvent: CDCl<sub>3</sub>  
Frequency: 100 MHz

