

Supplementary Information

Synthesis of α -Keto Esters by the Rhodium-Catalysed Reaction of Cyanoformate with Arylboronic Acids

Hiroshi Shimizu and Masahiro Murakami*

Department of Synthetic Chemistry and Biological Chemistry, Kyoto University,
Katsura, Kyoto 615-8510, Japan

General. ^1H - and ^{13}C -NMR spectra were recorded on a Varian Gemini 2000 (^1H at 300 MHz and ^{13}C at 75 MHz) spectrometer using CHCl_3 (^1H , $\delta = 7.26$) and CDCl_3 (^{13}C , $\delta = 77.16$) as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A spectrometer. Preparative thin-layer chromatography was performed with silica gel 60 PF_{254} (Merck).

Materials. 1,4-Dioxane was freshly distilled from sodium benzophenone ketyl. $[\text{Rh}(\text{OH})(\text{cod})_2]_2$ was prepared according to the reported procedure.¹ Boric acid and all arylboronic acids were purchased from commercial sources and used without further purification. Ethyl cyanoformate was purchased from TCI and used after distillation. Phenylboroxine were prepared from the commercially available phenylboronic acids by azeotropic removal of water from its toluene solution and purified by washing the crude boroxines repeatedly with hexane.²

General procedure for rhodium-catalysed reaction of cyanoformate with arylboronic acids

A mixture of arylboronic acid **2** (0.6 mmol, 1.2 equiv), H_3BO_3 (1.0 mmol, 2.0 equiv), $[\text{Rh}(\text{OH})(\text{cod})]_2$ (0.0125 mmol, 2.5 mol%) and ethyl cyanoformate (**1**, 0.5 mmol, 1.0 equiv) in 1,4-dioxane (1 ml) was stirred for 30 min at room temperature and then at 60 °C for 3 h under an Ar atmosphere. Then the reaction mixture was cooled and diluted with AcOEt (10 ml) and citric acid (10% aq. 5 ml). The organic layer was separated and the aqueous layer was extracted with AcOEt (5 ml x 3). The combined extracts were washed with water and brine, and dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative thin-layer chromatography (hexane:AcOEt) to give the product **3**, which were characterized by ^1H and ^{13}C NMR spectra.

Ethyl benzoylformate (3a)³

According to general procedure, **3a** (73.7 mg, 83%) was prepared from **1** (49.5mg, 0.5 mmol) and **2a** (73.2 mg, 0.6 mmol). : ^1H NMR: $\delta = 1.43$ (t, $J = 7.2$ Hz, 3H), 4.46 (q, $J = 7.2$ Hz, 2H), 7.49-7.55 (m, 2H), 7.63-7.69 (m, 1H), 8.00-8.03 (m, 2H); ^{13}C NMR: $\delta = 14.2, 62.4, 128.9, 130.0, 132.4, 135.0, 163.8, 186.4$

¹ R. Uson, L. A. Oro and J. A. Cabeza, *Inorg. Synth.*, 1985, **23**, 129.

² F.-X. Chen, A. Kina and T. Hayashi, *Org. Lett.*, 2006, **8**, 341.

³ T. Sakakura, H. Yamashita, T. Kobayashi, T. Hayashi and M. Tanaka, *J. Org. Chem.*, 1987, **52**, 5733

Ethyl 4-methoxybenzoylformate (3b)⁴

According to general procedure, **3b** (83.6 mg, 80%) was prepared from **1** (49.5mg, 0.5 mmol) and **2b** (91.2 mg, 0.6 mmol). : ¹H NMR: δ = 1.42 (t, *J* = 7.2 Hz, 3H), 3.90 (s, 3H), 4.43 (q, *J* = 7.2 Hz, 2H), 6.96-6.99 (m, 2H), 7.99-8.02 (m, 2H); ¹³C NMR: δ = 14.2, 55.7, 62.3, 114.3, 125.5, 132.6, 164.2, 165.0, 184.9

Ethyl 3-methoxybenzoylformate (3c)⁵

According to general procedure, **3c** (77.5 mg, 74%) was prepared from **1** (49.5mg, 0.5 mmol) and **2c** (91.2 mg, 0.6 mmol). : ¹H NMR: δ = 1.43 (t, *J* = 7.2 Hz, 3H), 3.87 (s, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.20 (ddd, *J*=0.9Hz, 2.7Hz, 8.1Hz, 1H), 7.42 (t, *J*=8.1Hz, 1H), 7.51-7.59 (m, 2H); ¹³C NMR: δ = 14.2, 55.6, 62.5, 113.3, 121.9, 123.2, 130.0, 133.7, 160.0, 163.9, 186.4

Ethyl 2-methoxybenzoylformate (3d)⁶

According to general procedure, **3d** (90.1 mg, 87%) was prepared from **1** (49.5mg, 0.5 mmol) and **2d** (91.2 mg, 0.6 mmol). : ¹H NMR: δ = 1.40 (t, *J* = 7.2 Hz, 3H), 3.87 (s, 3H), 4.49 (q, *J* = 7.2 Hz, 2H), 6.99 (d, *J*=6.6Hz, 1H), 7.04-7.11 (m, 1H), 7.55-7.63 (m, 1H), 7.88 (dd, *J*=1.8Hz, 7.8Hz, 1H); ¹³C NMR: δ = 14.2, 56.1, 61.9, 112.1, 121.3, 122.7, 130.7, 136.4, 160.3, 165.3, 186.6

Ethyl 4-bromobenzoylformate (3e)⁴

According to general procedure, **3e** (105.2 mg, 82%) was prepared from **1** (49.5mg, 0.5 mmol) and **2e** (120.5 mg, 0.6 mmol). : ¹H NMR: δ = 1.43 (t, *J* = 6.9 Hz, 3H), 4.45 (q, *J* = 6.9 Hz, 2H), 7.64-7.68 (m, 2H), 7.88-7.92 (m, 2H); ¹³C NMR: δ = 14.2, 62.7, 130.6, 131.3, 131.5, 132.3, 163.2, 185.1

Ethyl 4-fluorobenzoylformate (3f)⁴

According to general procedure, **3f** (71.3 mg, 73%) was prepared from **1** (49.5mg, 0.5 mmol) and **2f** (84.0 mg, 0.6 mmol). : ¹H NMR: δ = 1.43 (t, *J* = 7.2 Hz, 3H), 4.45 (q, *J* = 7.2 Hz, 2H), 7.15-7.23 (m, 2H), 8.05-8.15 (m, 2H); ¹³C NMR: δ = 14.2, 62.6, 116.3 (d, *J*_{C-F}=22.1Hz), 129.0 (d, *J*_{C-F}=3.5Hz), 133.0 (d, *J*_{C-F}=9.3Hz), 163.4, 166.8 (d, *J*_{C-F}=257.5Hz), 184.6

Ethyl 3-chlorobenzoylformate (3g)⁷

According to general procedure, **3g** (85.8 mg, 81%) was prepared from **1** (49.5mg, 0.5 mmol) and **2g** (93.8 mg, 0.6 mmol). : ¹H NMR: δ = 1.43 (t, *J* = 7.2 Hz, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 7.47 (t, *J*=7.8 Hz, 1H), 7.60-7.65 (m, 1H), 7.89-7.94 (m, 1H), 8.00-8.03 (m, 1H); ¹³C NMR: δ = 14.2, 62.8, 128.3, 129.9, 130.3, 134.1, 134.9, 135.3, 163.0, 184.9

Ethyl 2-chlorobenzoylformate (3h)⁸

According to general procedure, **3h** (48.6 mg, 46%) was prepared from **1** (49.5mg, 0.5 mmol) and **2h** (93.8 mg, 0.6 mmol). : ¹H NMR: δ = 1.41 (t, *J* = 6.9 Hz, 3H), 4.43 (q, *J* = 6.9 Hz, 2H), 7.37-7.45

4 S. Hu and D. C. Neckers, *J. Org. Chem.*, 1996, **61**, 6407

5 N. Thasana, V. Prachyawarakom, S. Tontoolarug and S. Ruchirawat, *Tetrahedron Lett.*, 2003, **44**, 1019

6 R. S. Mali, S. G. Tilve, *Synth. Commun.*, 1990, **20**, 1781

7 J-F. Carpentier and A. Mortreux, *Tetrahedron: Asymmetry*, 1997, **18**, 1083

8 Y. Sun, X. Wan, J. Wang, Q. Meng, H. Zhang, L. Jiang and Z. Zhang, *Org. Lett.*, 2005, **7**, 5425

(m, 2H), 7.50-7.57 (m, 1H), 7.77 (dd, $J=1.8\text{Hz}$, 7.8Hz , 1H); ^{13}C NMR: $\delta = 14.0, 63.0, 127.4, 130.6, 131.7, 133.4, 133.9, 134.4, 163.2, 186.7$

Ethyl 2-methylbenzoylformate (3i)⁹

According to general procedure, **3i** (79.7 mg, 83%) was prepared from **1** (49.5mg, 0.5 mmol) and **2i** (81.2 mg, 0.6 mmol). : ^1H NMR: $\delta = 1.42$ (t, $J = 7.2$ Hz, 3H), 2.61 (s, 3H), 4.43 (q, $J = 7.2$ Hz, 2H), 7.32 (t, $J=7.5\text{Hz}$, 2H), 7.45-7.53 (m, 1H), 7.69 (d, $J=7.5\text{Hz}$, 1H); ^{13}C NMR: $\delta = 14.2, 21.6, 62.3, 126.0, 131.2, 132.3, 132.4, 133.7, 141.3, 164.7, 188.8$

Ethyl 2-phenylbenzoylformate (3j)

According to general procedure, **3j** (63.5 mg, 50%) was prepared from **1** (49.5mg, 0.5 mmol) and **2j** (118.8 mg, 0.6 mmol). : ^1H NMR: $\delta = 1.04$ (t, $J = 6.9$ Hz, 3H), 3.72 (q, $J = 6.9$ Hz, 2H), 7.29-7.38 (m, 2H), 7.38-7.54 (m, 5H), 7.65 (dt, $J=1.5\text{Hz}$, 7.5Hz , 1H), 7.82 (dd, $J=1.2\text{Hz}$, 7.8Hz , 1H); ^{13}C NMR: $\delta = 13.7, 62.2, 127.7, 128.3, 128.8, 129.6, 130.2, 130.4, 132.9, 134.5, 139.4, 143.1, 162.6, 189.7$; HRMS (FAB+): Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_3$, M^+ 254.0943. Found m/z 254.0945.

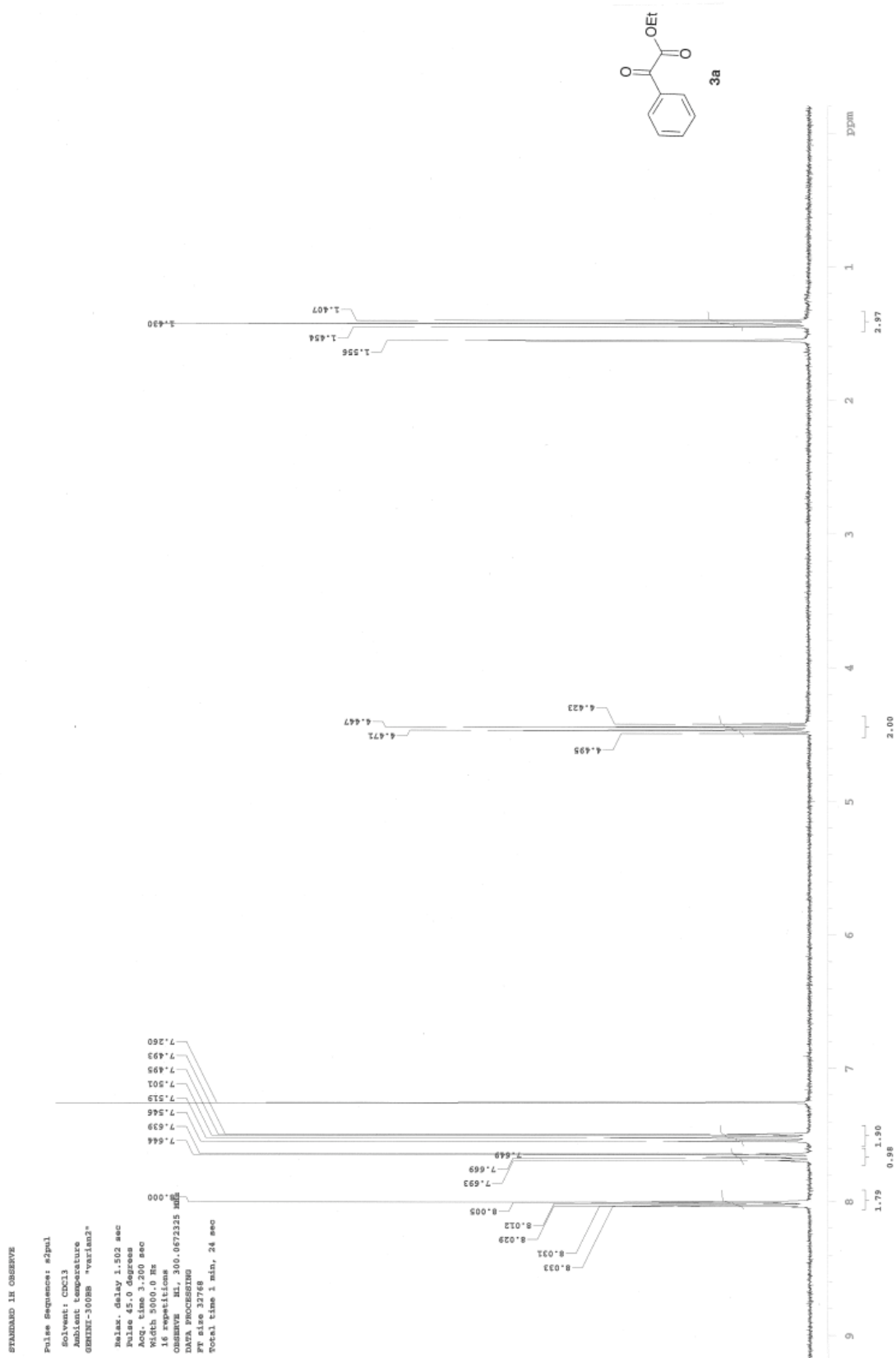
Ethyl 4-methoxycarbonylbenzoylformate (3k)

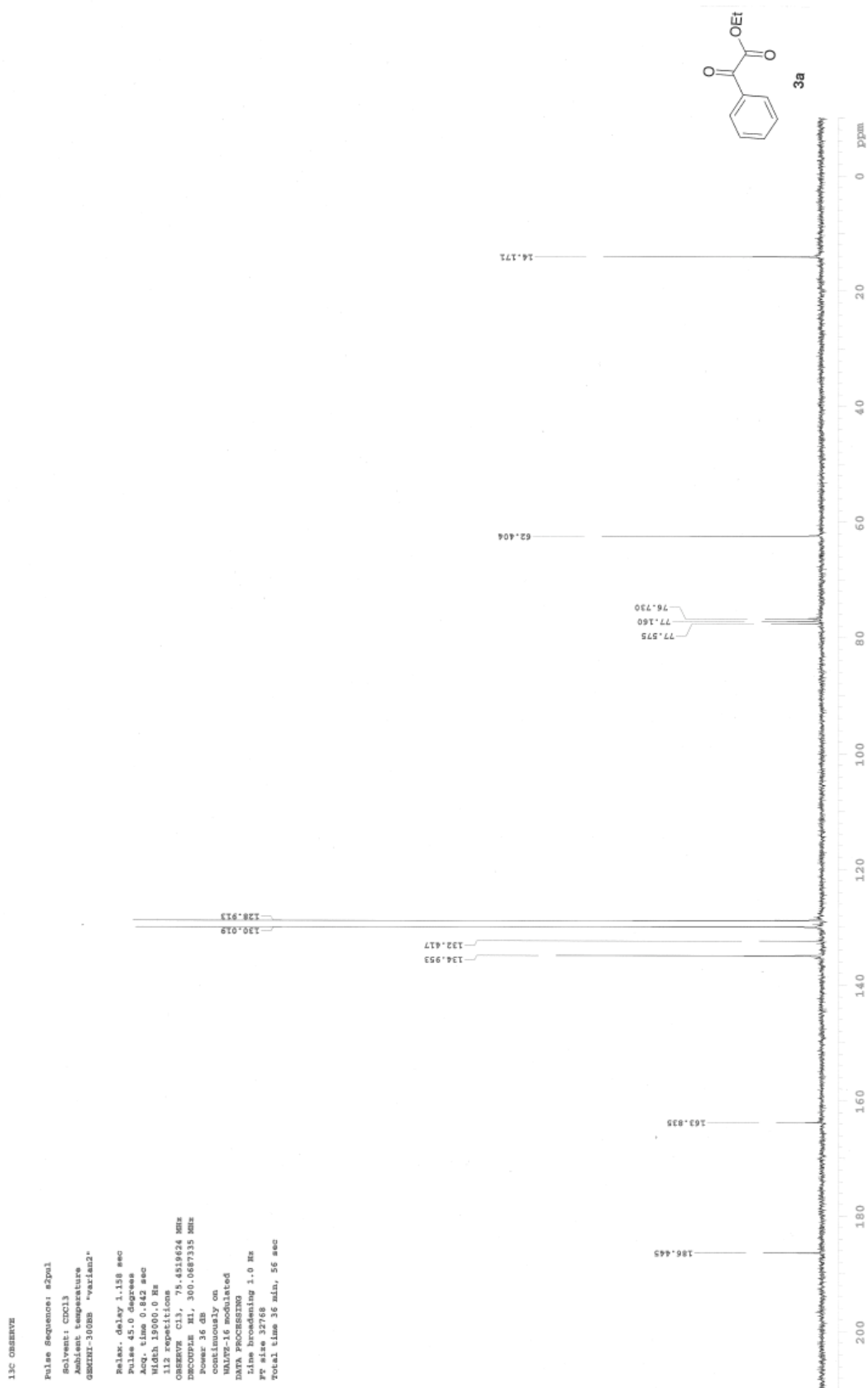
According to general procedure, **3k** (68.6 mg, 58%) was prepared from **1** (49.5mg, 0.5 mmol) and **2k** (108.0 mg, 0.6 mmol). : ^1H NMR: $\delta = 1.44$ (t, $J = 7.2$ Hz, 3H), 3.97 (s, 3H), 4.47 (q, $J = 7.2$ Hz, 2H), 8.06-8.12 (m, 2H), 8.14-8.20 (m, 2H); ^{13}C NMR: $\delta = 14.3, 52.8, 62.8, 130.05, 130.10, 135.4, 135.7, 163.2, 166.0, 185.7$; HRMS (FAB+): Calcd for $\text{C}_{12}\text{H}_{13}\text{O}_5$, $(\text{M}+\text{H})^+$ 237.0763. Found m/z 237.0770.

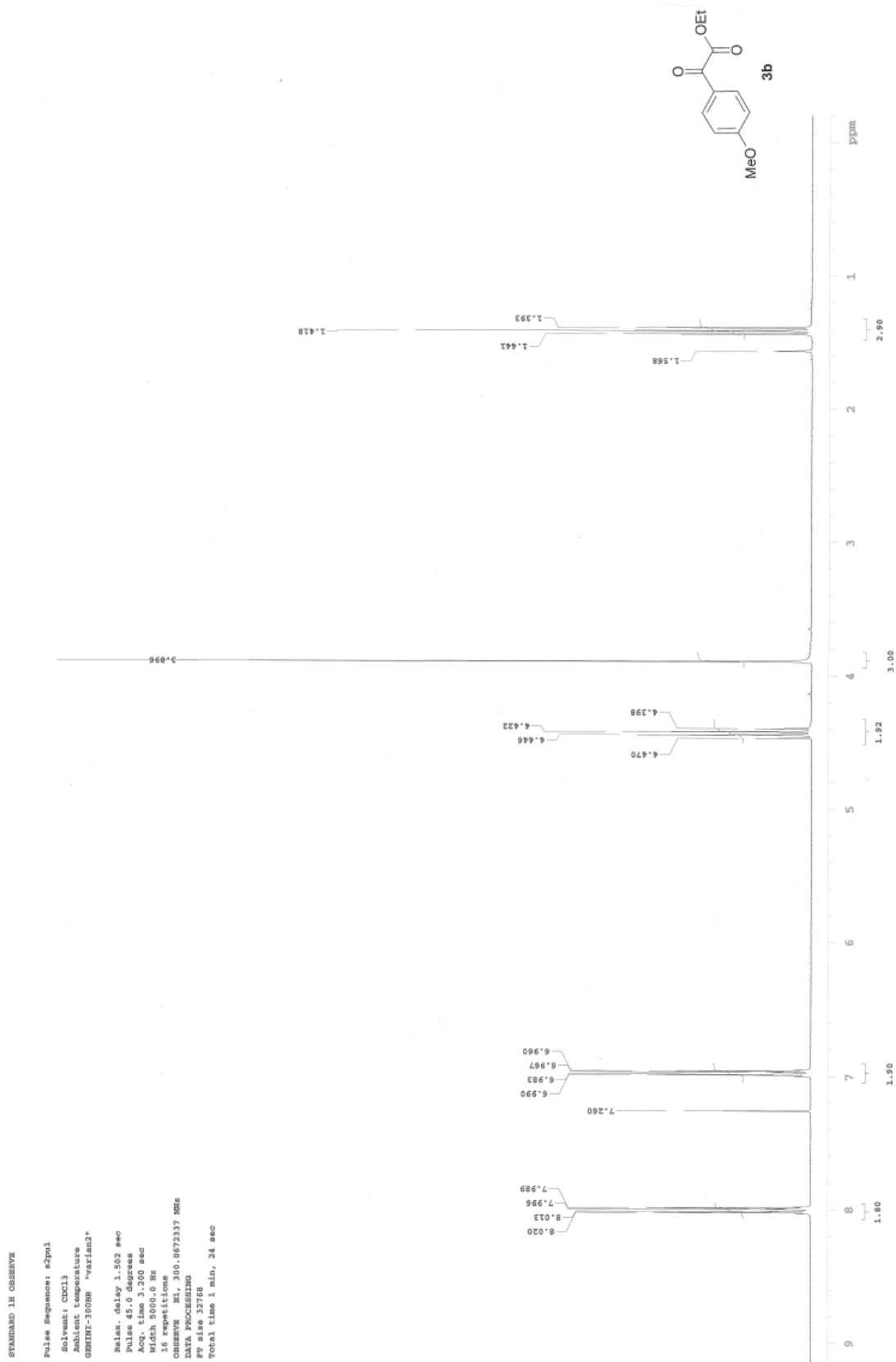
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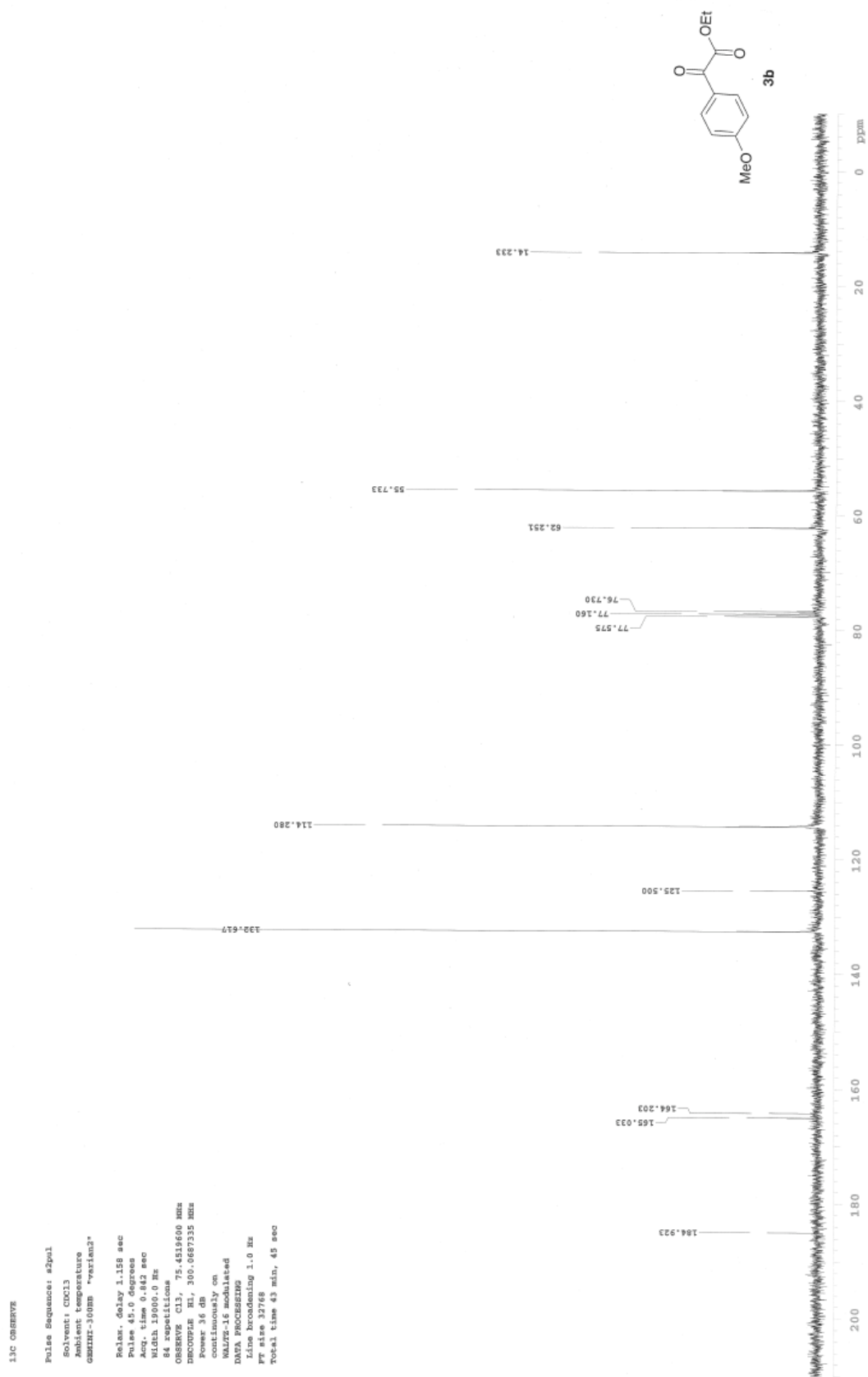
According to general procedure, **3l** (51.7 mg, 50%) was prepared from **1** (49.5mg, 0.5 mmol) and **2l** (90.0 mg, 0.6 mmol). : ^1H NMR: $\delta = 1.45$ (t, $J = 6.9$ Hz, 3H), 4.49 (q, $J = 6.9$ Hz, 2H), 7.72 (t, $J=7.8$ Hz, 1H), 8.19 (dt, $J=1.5\text{Hz}$, 7.8Hz , 1H), 8.32 (dt, $J=1.5\text{Hz}$, 7.8Hz , 1H), 8.53 (t, $J=1.5\text{Hz}$, 1H), 10.10 (s, 1H); ^{13}C NMR: $\delta = 14.2, 62.9, 129.9, 131.7, 133.5, 134.8, 135.4, 136.8, 162.9, 185.0, 191.0$; HRMS (FAB+): Calcd for $\text{C}_{11}\text{H}_{11}\text{O}_4$, $(\text{M}+\text{H})^+$ 207.0657. Found m/z 207.0668.

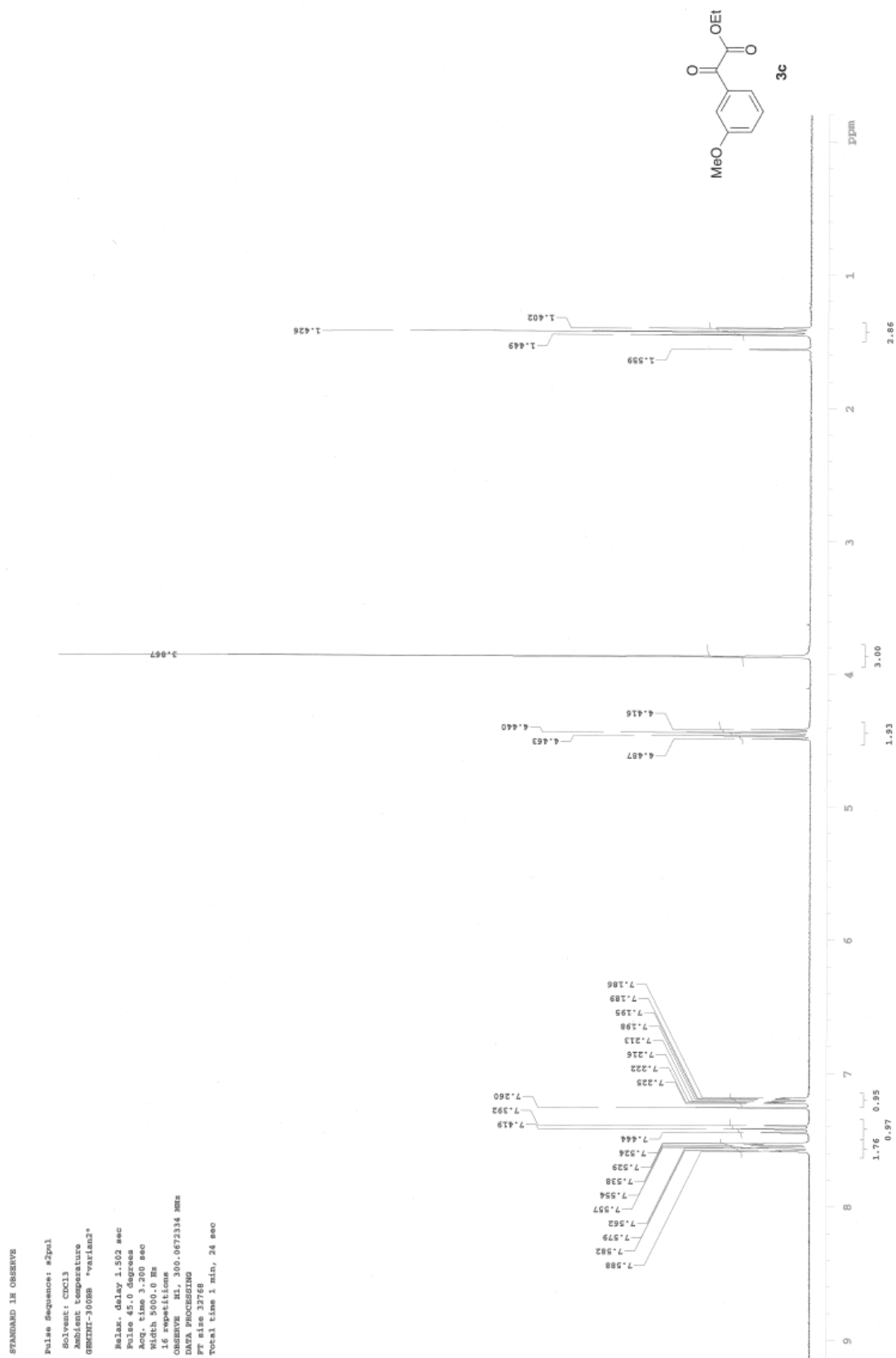
⁹L. J. In, *J. Korean. Chem. Soc.*, 2004, **48**, 103

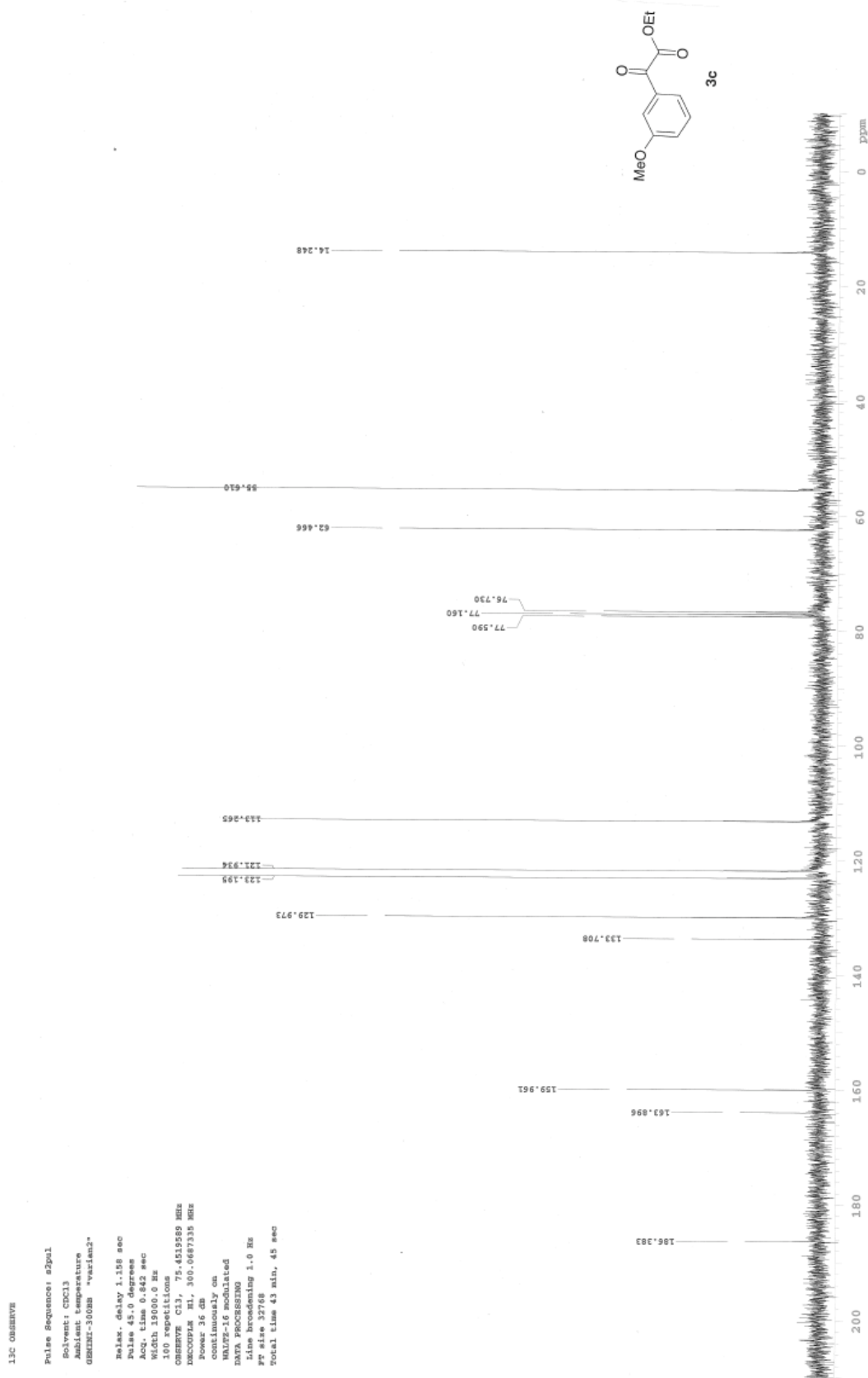


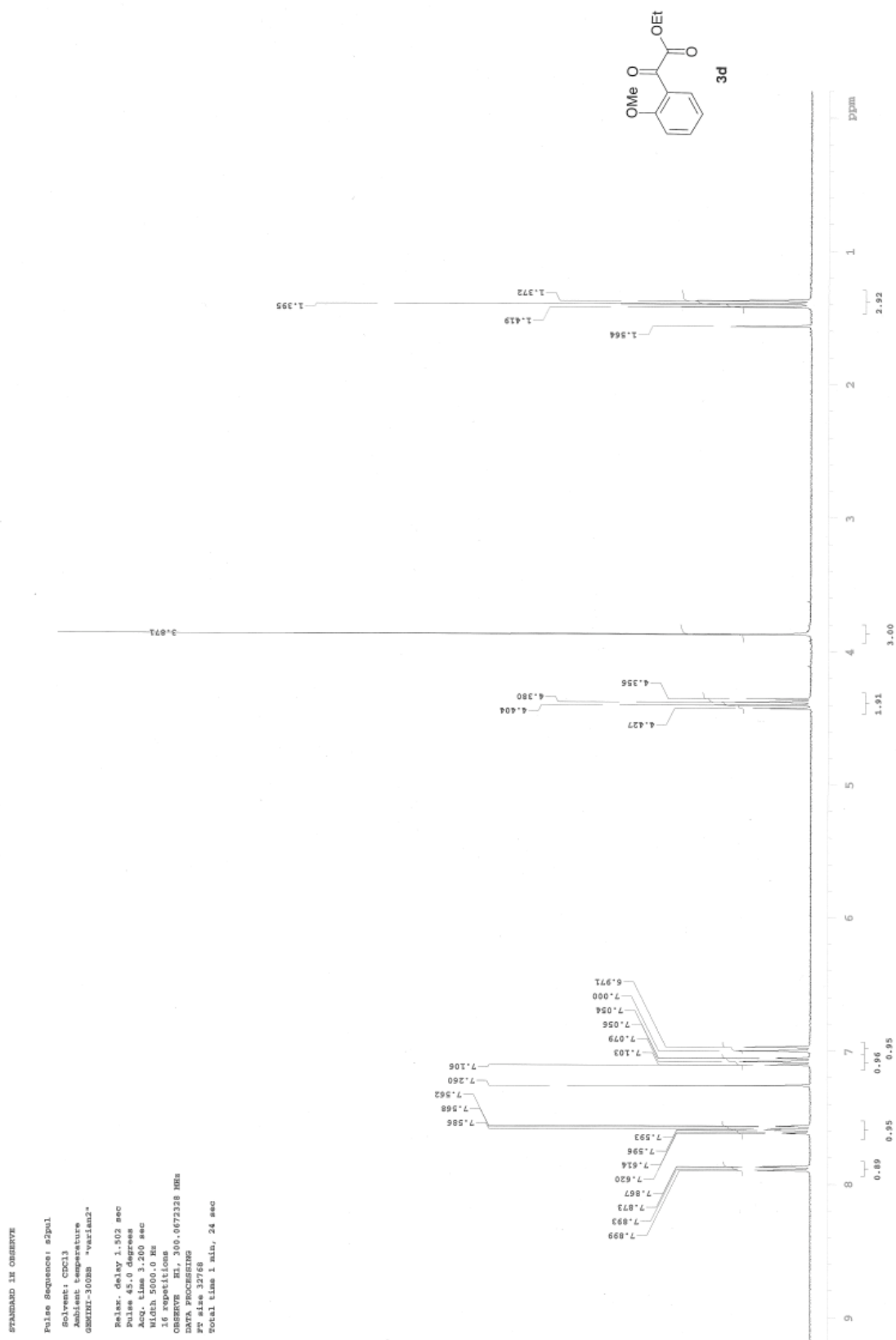


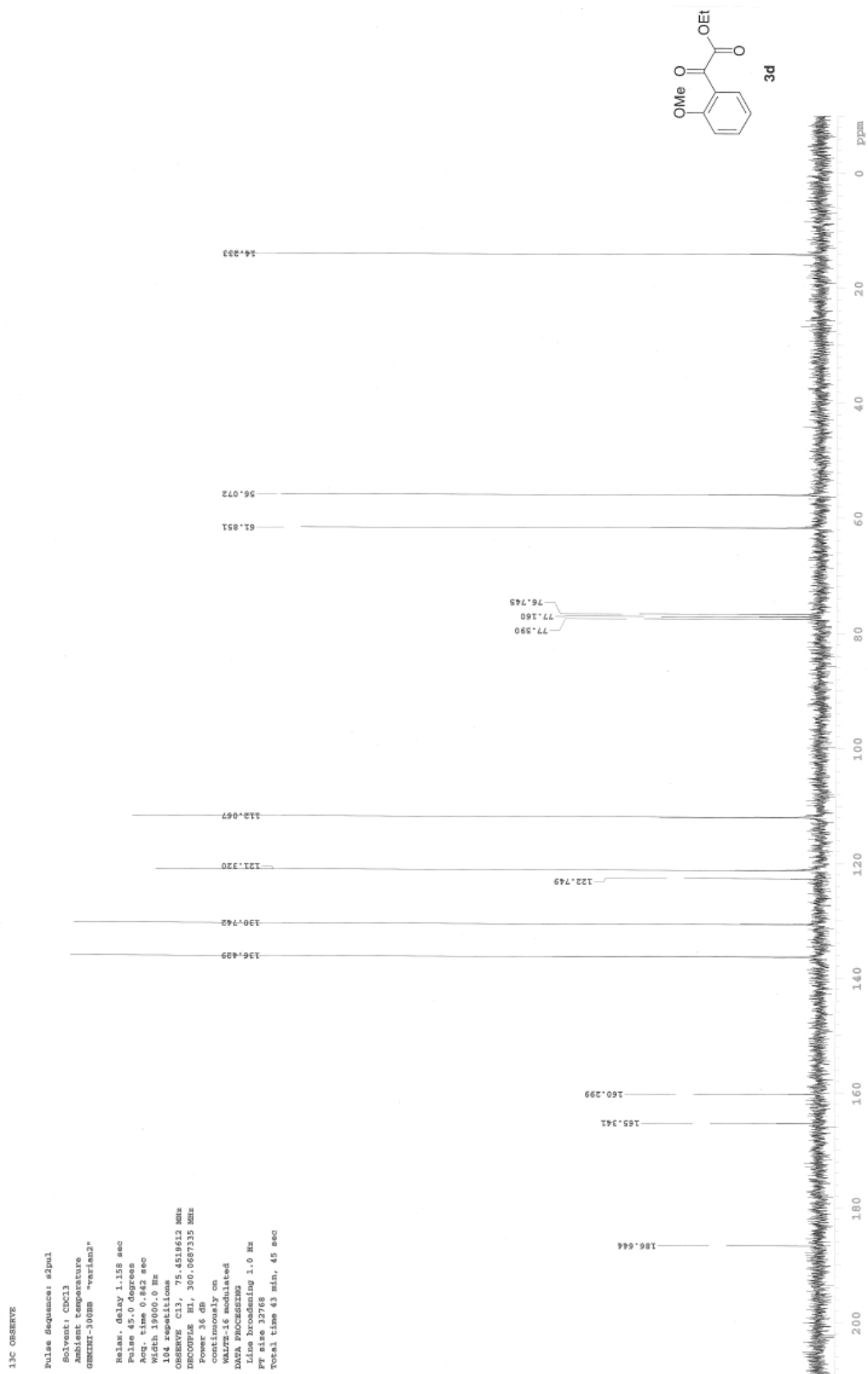


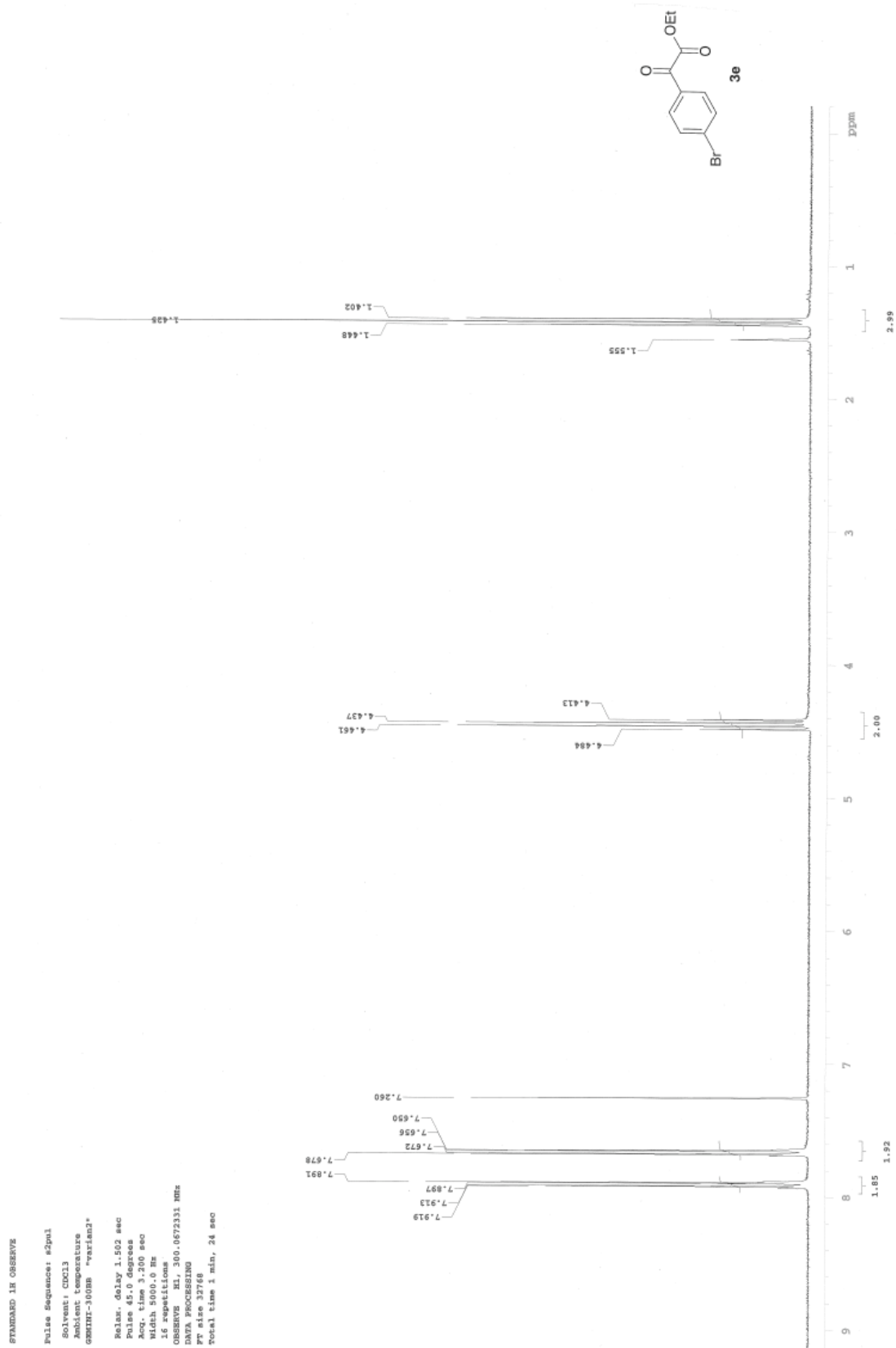


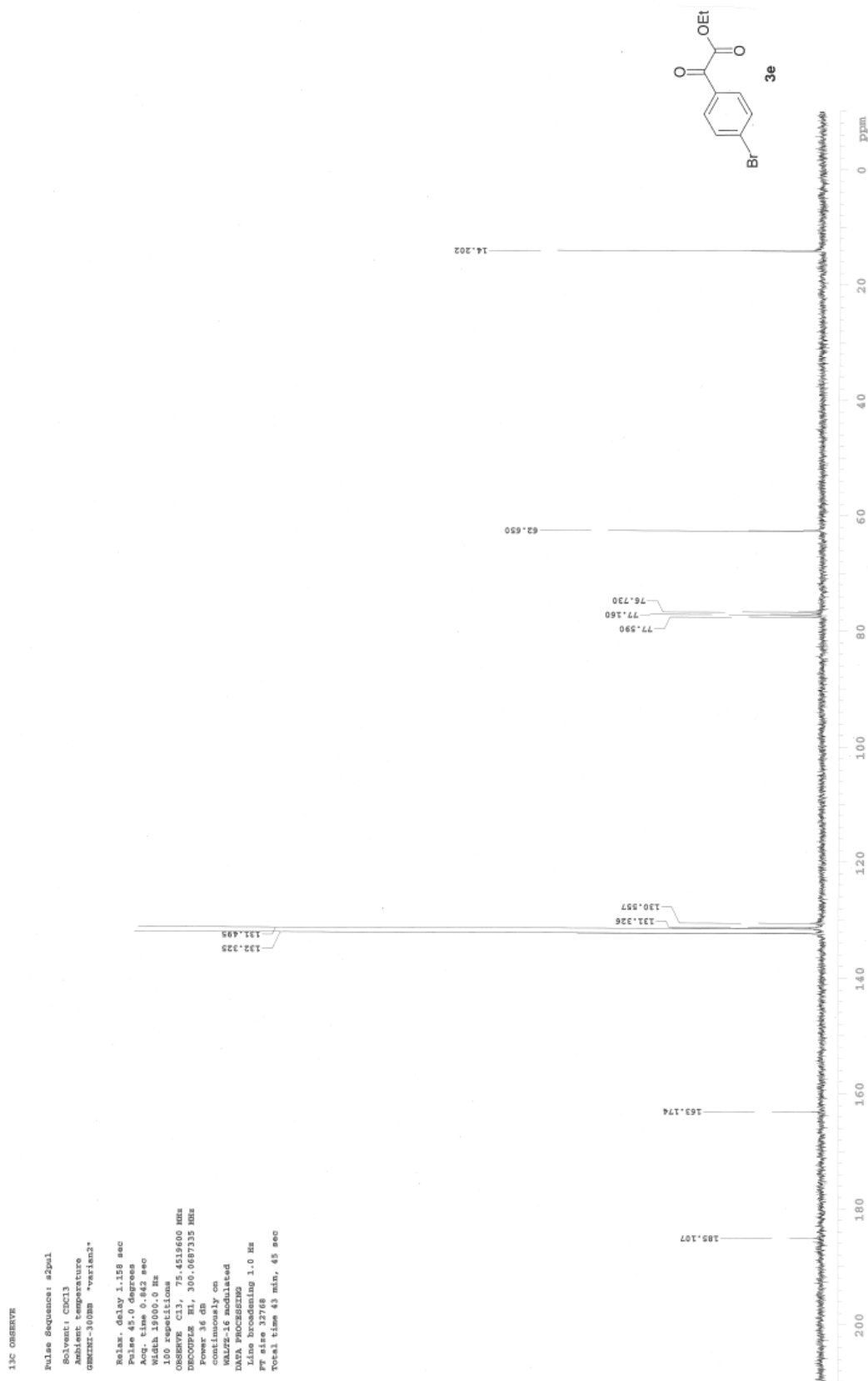


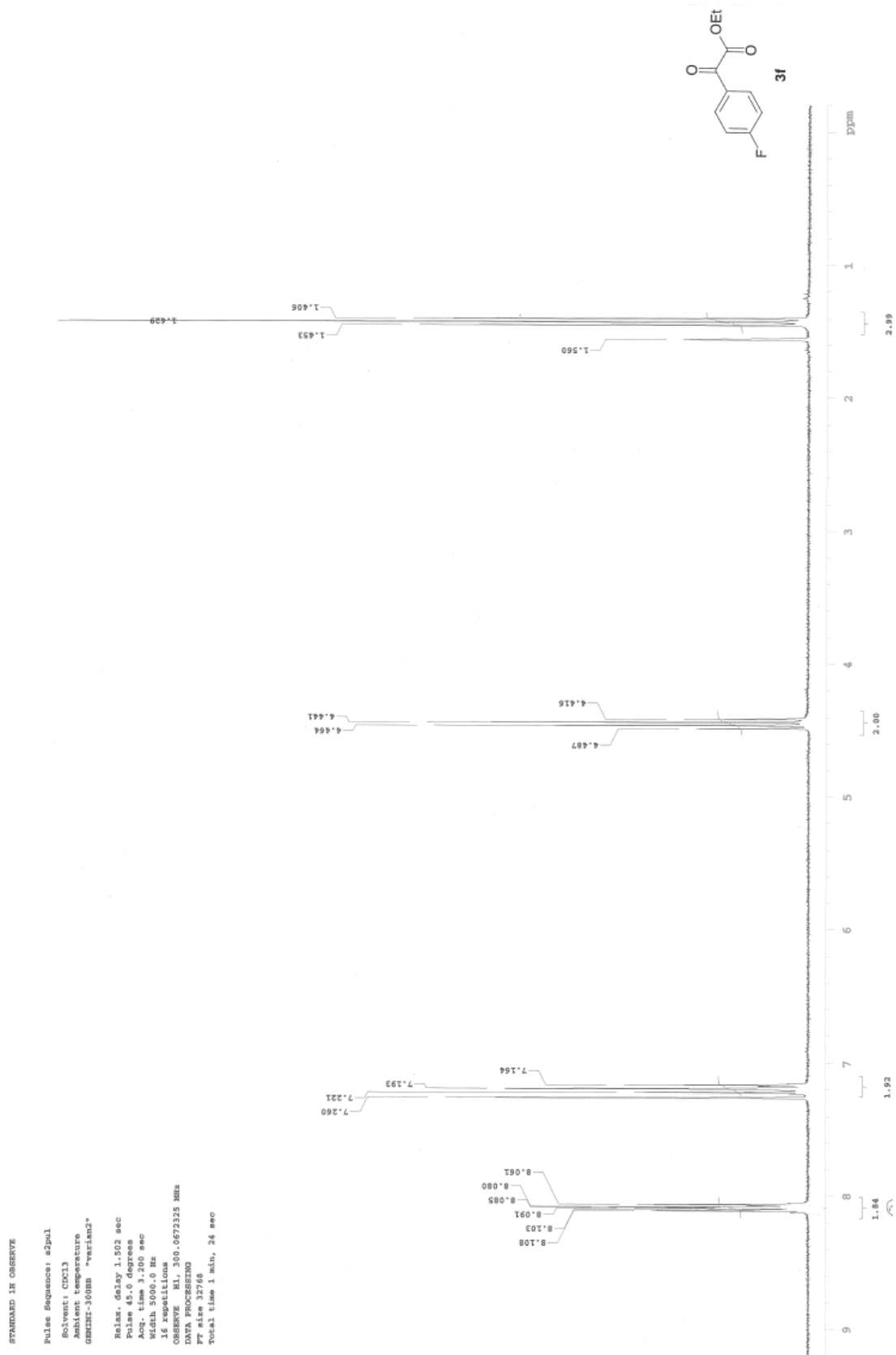


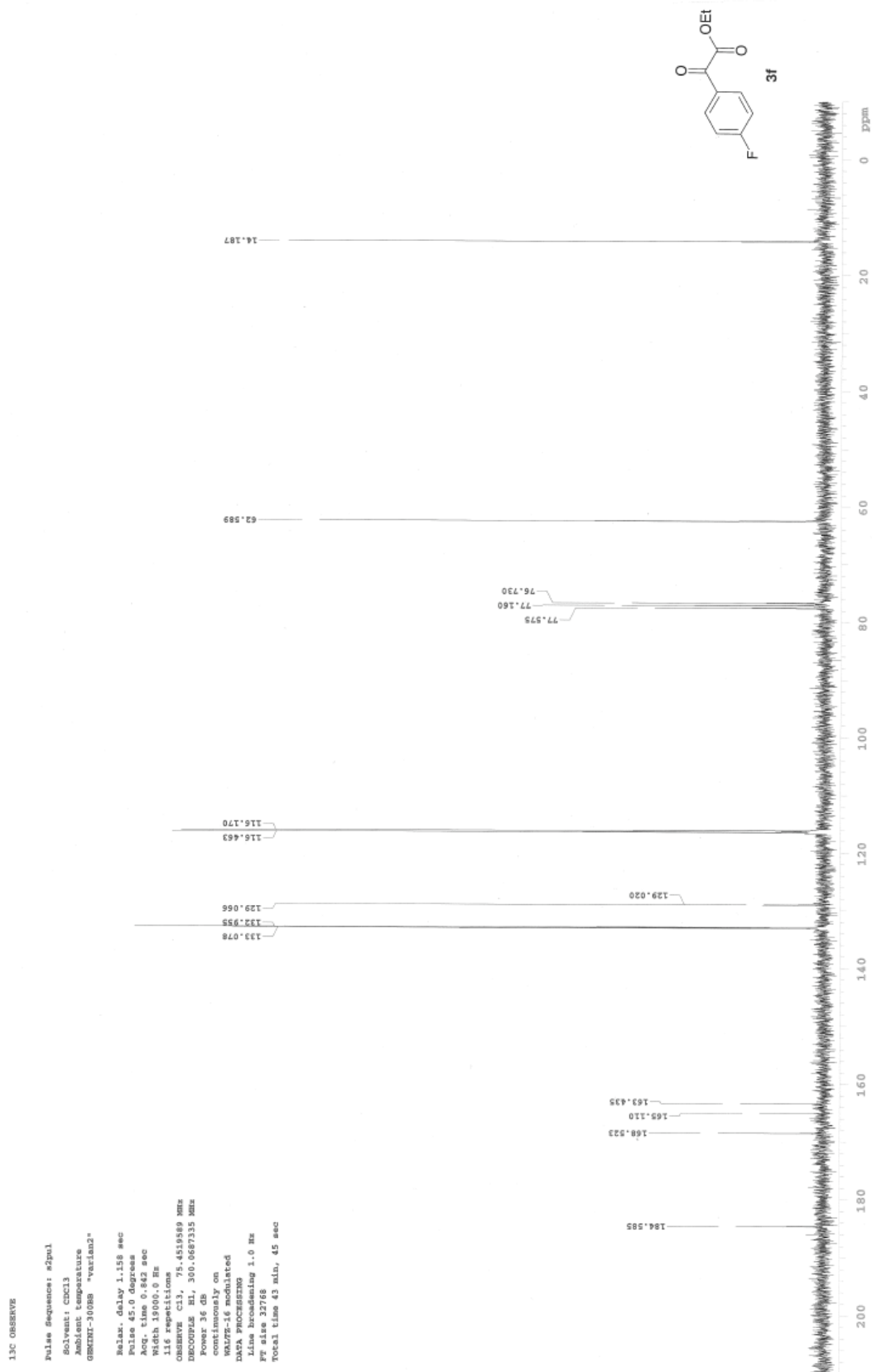


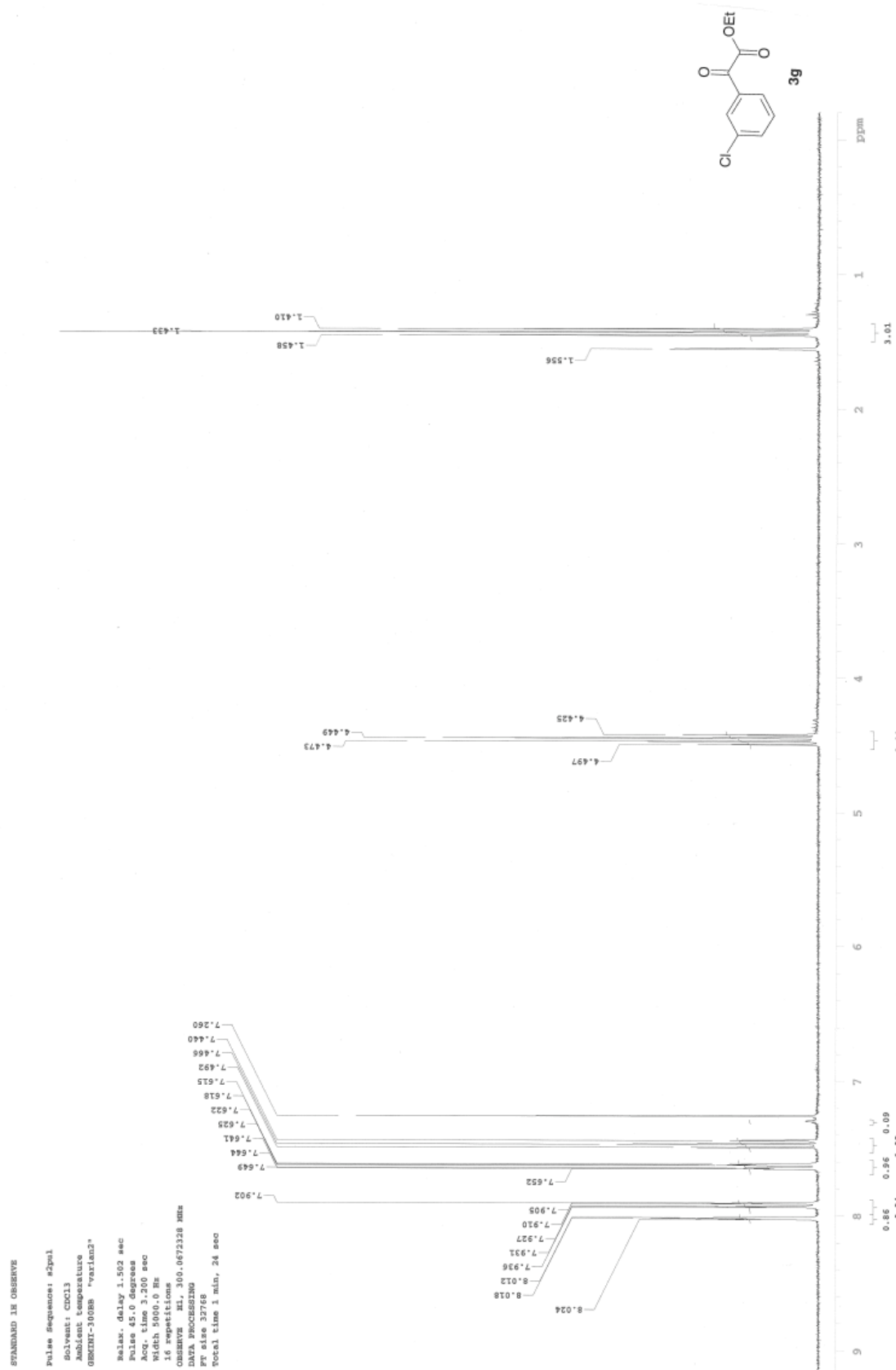


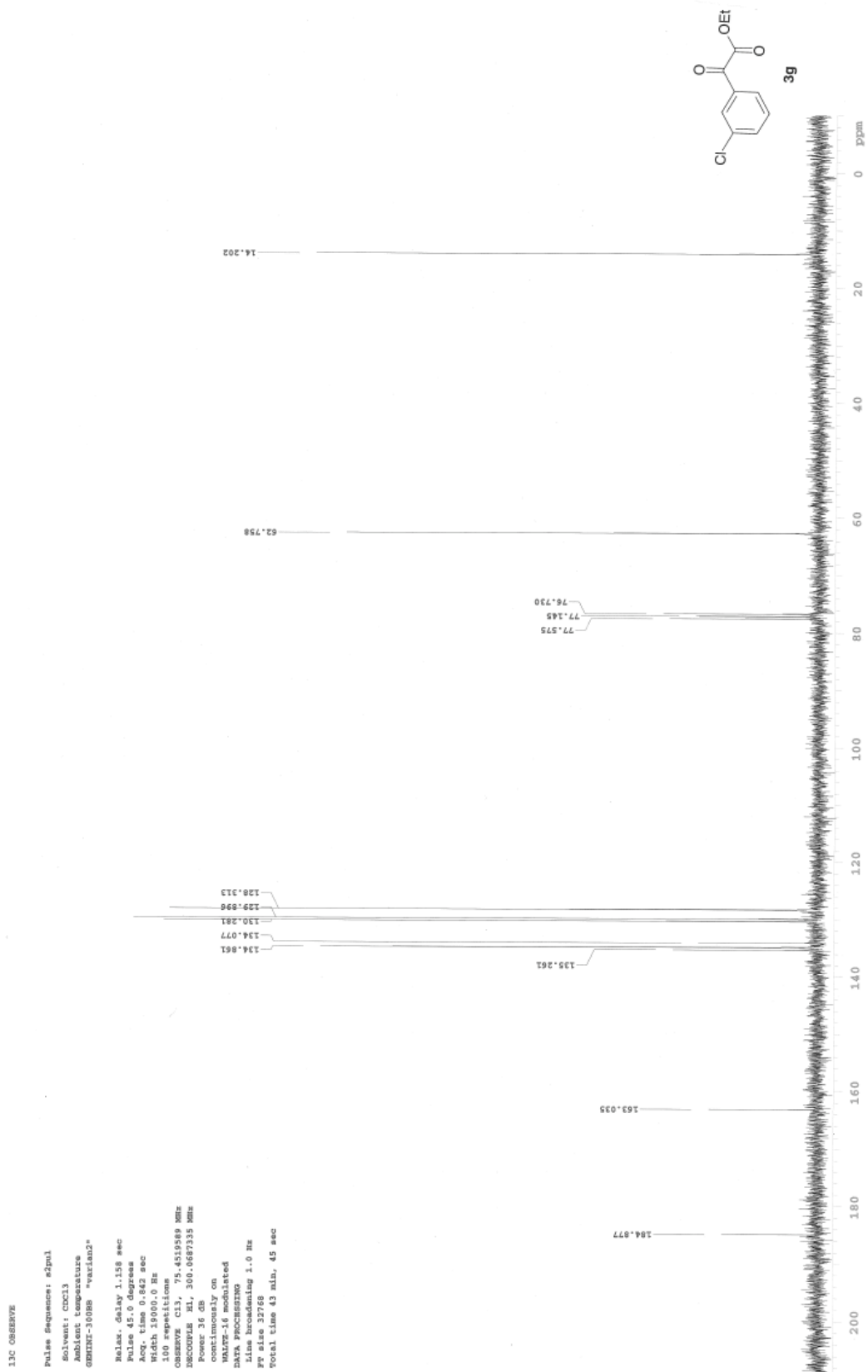


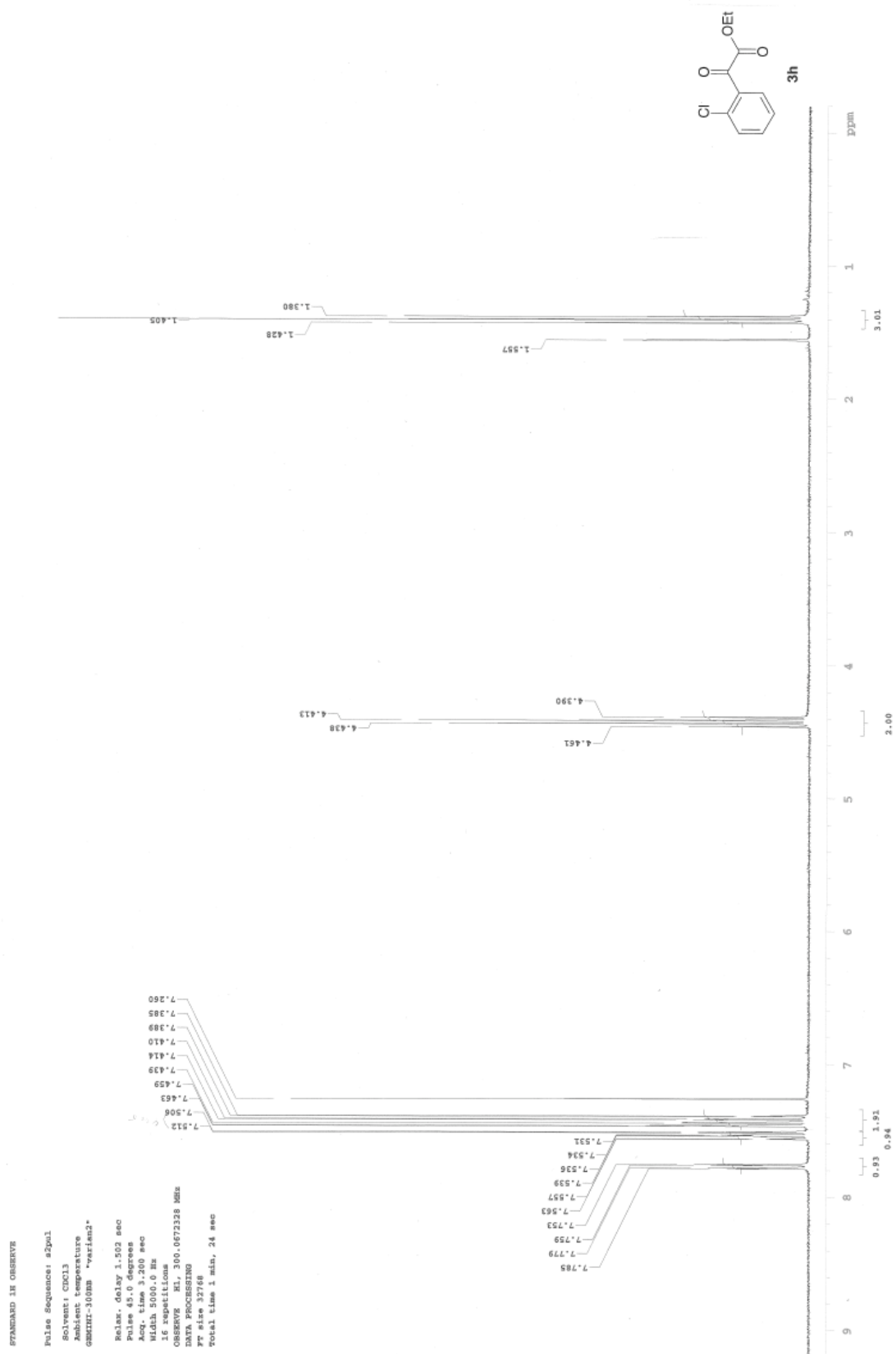


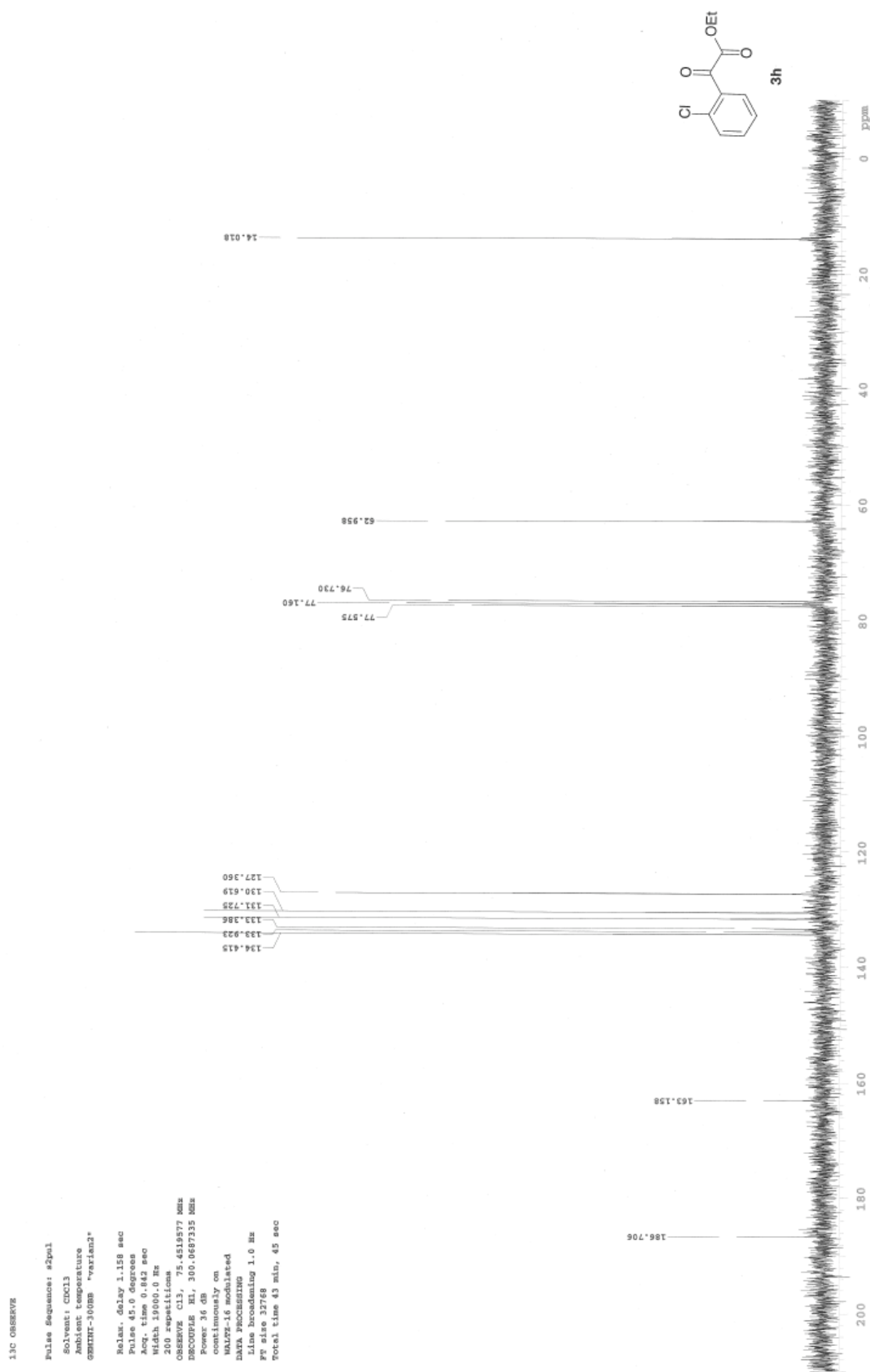


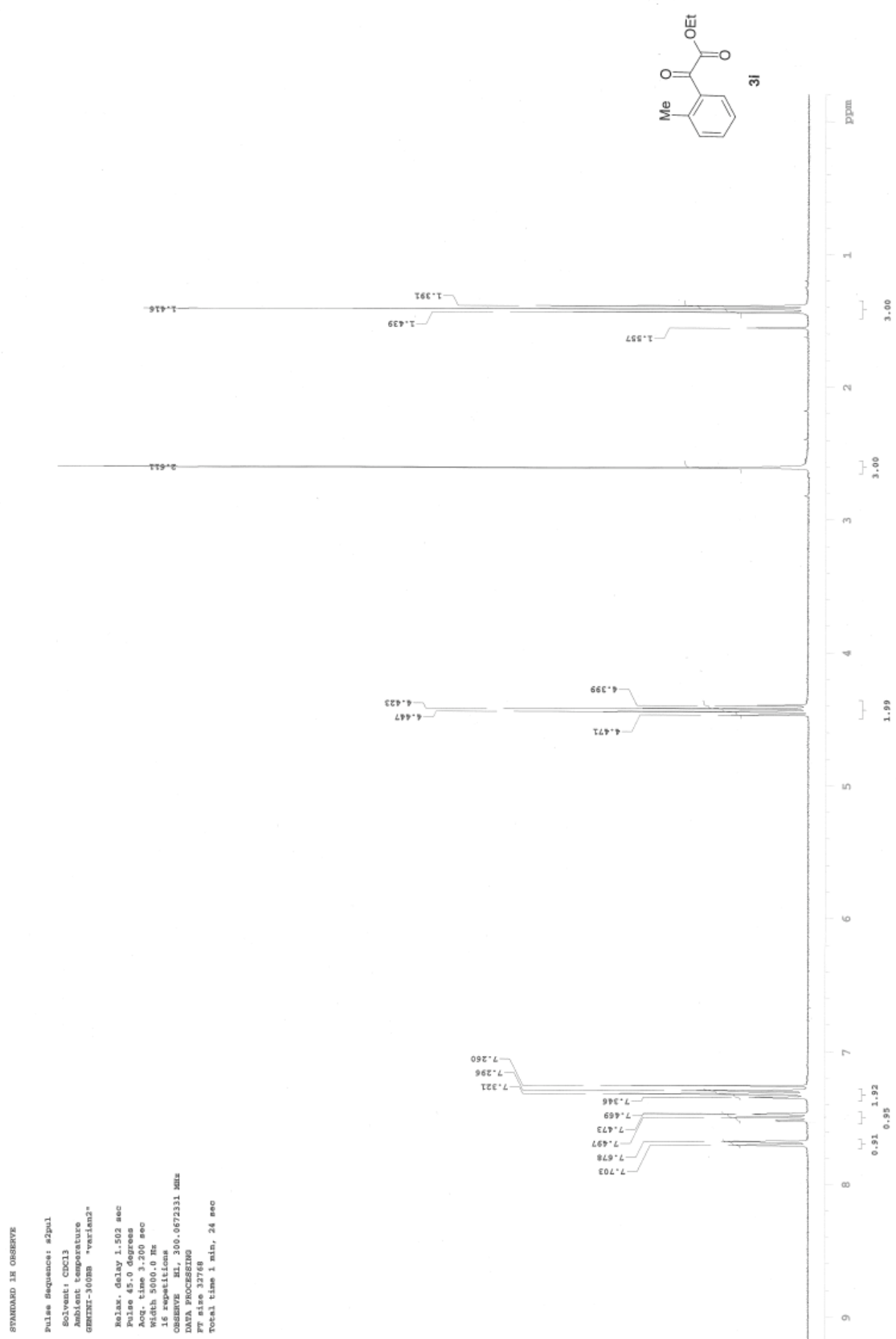


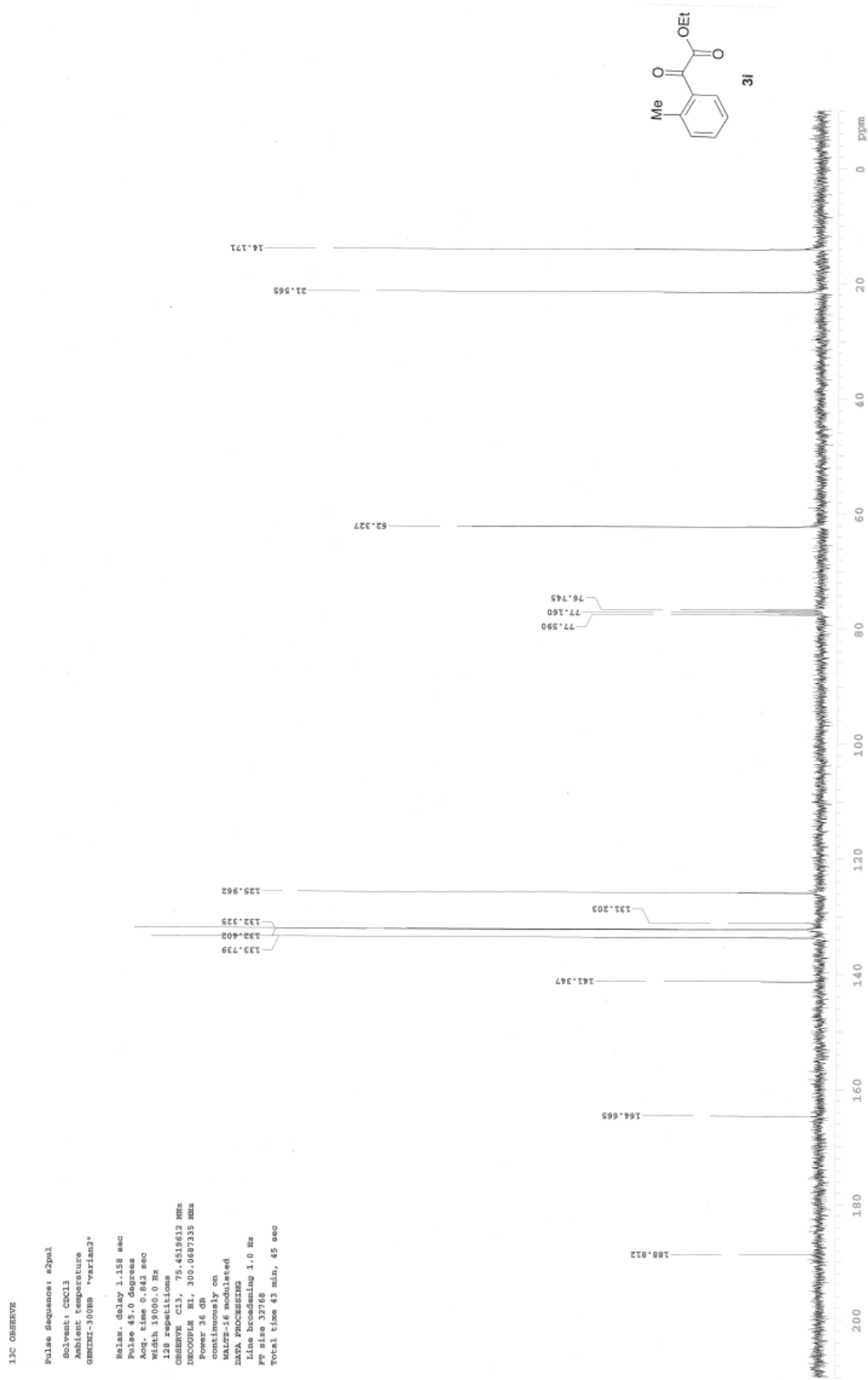


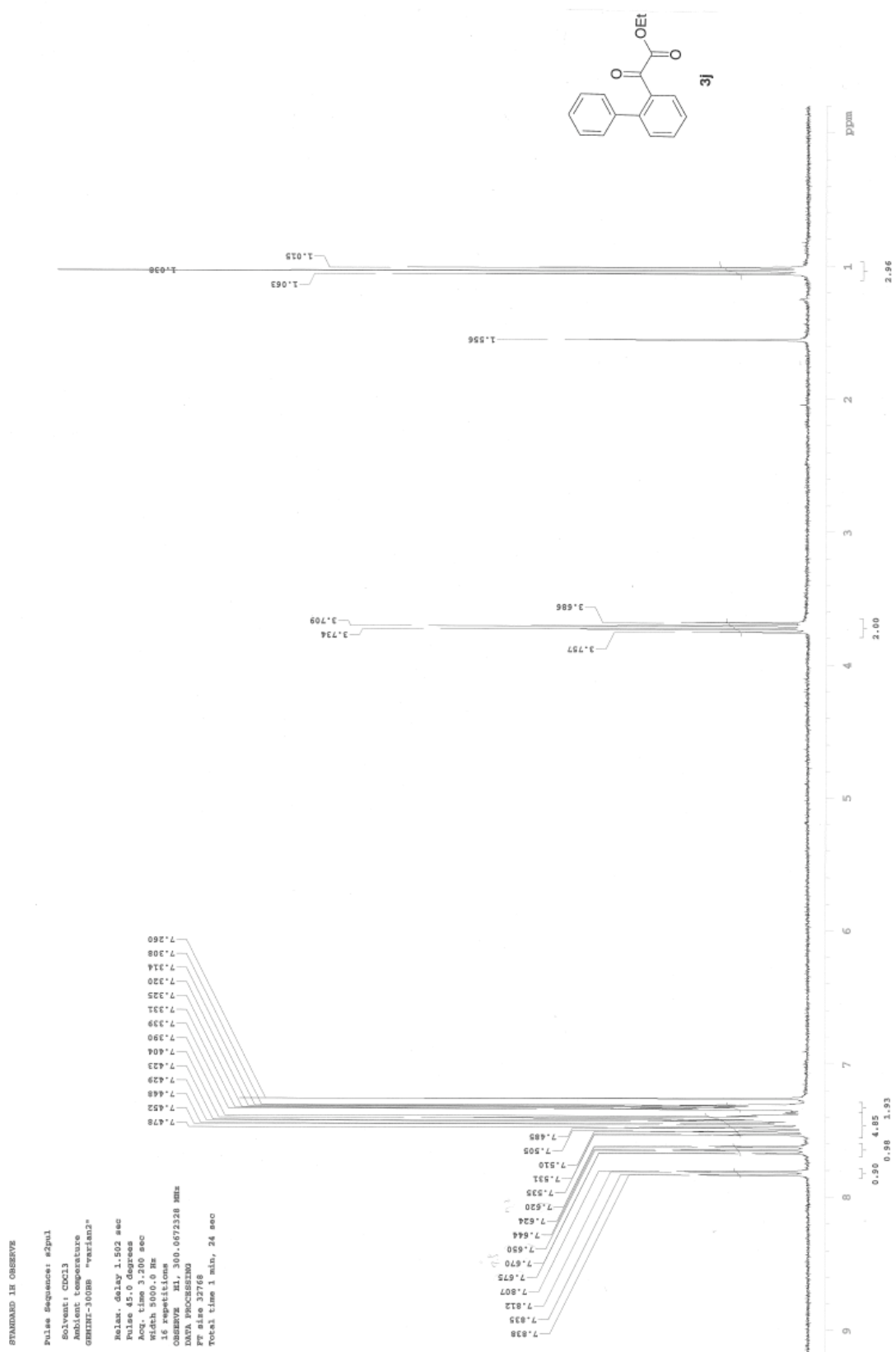












13C OBSERVE

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Solvent: CDCl3

Acquisition Date: 20070818

Chemical Shift Reference: TMS

Temperature: 300.2 K

Relaxation Delay: 1.156 sec

Relaxation Delay: 45.000 sec

Acq. Time: 0.842 sec

Width: 19000.0 Hz

104 repetitions

OBSERVE C13, 75.4519600 MHz

DECOUPLE H1, 300.0687335 MHz

Power: 36 dB

continuously on

WALTZ-16 modulated

DATA PROCESSING

Line broadening: 1.0 Hz

FF size: 32768

Total time: 45 min, 45 sec

