

## Supporting Information

### A Chelation-Assisted Transformation : Synthesis of Maleimides by the Rh-Catalyzed Carbonylation of Internal Alkynes with Pyridin-2-yl-methylamine

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**Materials.** Unless otherwise noted, all reagents were obtained commercial suppliers and used as received. Cyclododecyne was prepared by the method of Brandsma with minor modification. (L. Brandsma; H. D. Verkruissse, *Synthesis of Acetylenes, Allenes and Cumulenes*; Elisevier, Amsterdam **1981**, Vol 8, pp119.).

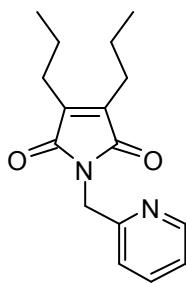
4-Dipropyl-1-(pyridin-2-yl-methyl)pyrrolidine-2,5-dione was prepared by the method of Katsuki et al. with minor modification. (*Tetrahedron* **1999**, *55*, 9439-9454.)

**Typical Procedure for Carbonylation of Alkynes with Pyridin-2-yl-methylamine (2).** Rh<sub>4</sub>(CO)<sub>12</sub> (15 mg, 0.02 mmol), P(OEt)<sub>3</sub> (13 mg, 0.08 mmol), pyridin-2-yl-methylamine (**2**, 108 mg, 1.00 mmol), 4-octyne (220 mg, 2.00 mmol) and toluene (1 mL) were placed in a 50-mL stainless steel autoclave under N<sub>2</sub>. The system was flushed with 10 atm of carbon monoxide three times. Finally, it was pressurized to 3 atm. The autoclave was heated in an oil bath at 100 °C for 20 h, followed by cooling to rt. Then CO was released. The contents were transferred to a round-bottom flask with EtOAc, and the volatiles were removed in vacuo. The residue was subjected to flash column

chromatography on silica-gel (eluent; Hexane/EtOAc = 9/1→0/1) to give 3,4-dipropyl-1-(pyridin-2-ylmethyl)-pyrrole-2,5-dione (**3a**) (188 mg, 69% yield based on **2**) as a pale yellow oil and 2-propyl-hex-2-enoic acid (pyridin-2-yl-methyl)amide (**4**) (29 mg, 12% yield).

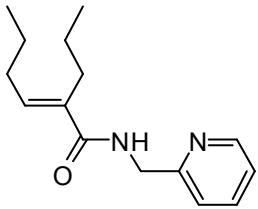
**Procedure for Scheme 3.** Rh<sub>4</sub>(CO)<sub>12</sub> (15.0 mg, 0.02 mmol), benzylamine (108 mg, 1.00 mmol), 4-octyne (220 mg, 2.00 mmol) and toluene (1 mL) were placed in a 50-mL stainless steel autoclave under N<sub>2</sub>. The system was flushed with 10 atm of carbon monoxide three times. Finally, it was pressurized to 3 atm. The autoclave was heated in an oil bath at 100 °C for 20 h, followed by cooling to rt. Then CO was released. The contents were transferred to a round-bottom flask with EtOAc and the volatiles were removed in vacuo. The residue was subjected to flash column chromatography on silica-gel (eluent; Hexane/EtOAc = 9/1→2/1) to give 2-propyl-hex-2-enoic acid (benzyl)amide (**5**) (94.5 mg, 39%) and *N,N'*-dibenzyl-2,3-dipropylsuccinamide (**6**) (38 mg, 20%) as a colorless oil.

### 3,4-Dipropyl-1-(pyridin-2-yl-methyl)-1H-pyrrole-2,5-dione (**3a**)



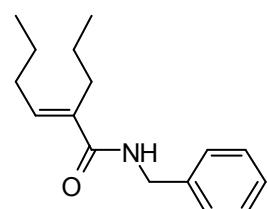
pale yellow oil. *Rf* = 0.48 (hexane/EtOAc = 1/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.97 (t, *J* = 7.3 Hz, 6H), 1.60 (m, *J* = 7.3 Hz, 4H), 2.40 (t, *J* = 7.6 Hz, 4H), 4.81 (s, 2H), 7.13-7.18 (c, 2H), 7.63 (dt, *J* = 1.9, 7.8 Hz, 1H), 8.52 (dd, *J* = 1.6, 5.9 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 14.21, 22.04, 25.84, 42.89, 121.18, 122.25, 136.65, 141.18, 149.24, 155.64, 171.65. IR (neat): 1768 w, 1708 s, 1594 m, 1430 s, 1402 s, 1355 w, 1110 m, 754 m. MS, m/z (relative intensity, %): 272 (M<sup>+</sup>, 18), 258 (7), 257 (39), 244 (19), 243 (100), 215 (13), 107 (10), 93 (39), 92 (63), 81 (15), 80 (8), 79 (22). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C; 70.56, H; 7.40, N; 10.29, O; 11.75. Found: C; 70.28, H; 7.38, N; 10.15.

### 2-Propyl-hex-2-enoic acid (pyridin-2-yl-methyl)amide (**4**)



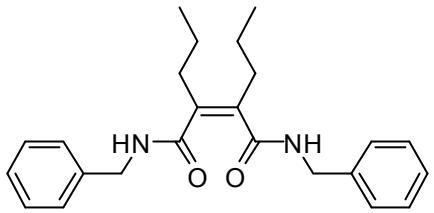
pale yellow oil. *Rf* = 0.11 (hexane/EtOAc = 1/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.90-0.97 (c, 6H), 1.53-1.38 (c, 4H), 2.09-2.18 (c, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 4.63 (d, *J* = 4.8 Hz, 2H), 6.32 (t, *J* = 7.3 Hz, 1H), 7.06 (s, 1H), 7.21-7.32 (c, 2H), 8.55 (d, *J* = 4.3 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 13.98, 14.07, 22.34, 22.36, 29.15, 30.24, 44.58, 122.99, 122.11, 135.45, 136.14, 136.58, 148.73, 156.53, 169.40. IR (neat): 1770 w, 1706 s, 1592 w, 1430 m, 1402 m, 1355 w, 1126 w, 919 w, 757 m, 696 w.. MS, m/z (relative intensity, %): 246 (M<sup>+</sup>, 8), 217 (11), 138 (17), 123 (43), 109 (21), 108 (10), 107 (100), 95 (12), 93 (25), 92 (42), 82 (10), 81 (21), 80 (11), 79 (15) 69 (30). Exact Mass Calcd for C<sub>15</sub>H<sub>22</sub>N<sub>2</sub>O: 246.1732. Found: 246.1723.

### 2-Propyl-hex-2-enoic acid (benzyl)amide (**5**)



colorless oil. *Rf* = 0.50 (hexane/EtOAc = 1/1). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 0.92 (t, *J* = 7.3 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H) 1.36-1.50 (c, 4H), 2.11 (q, *J* = 7.8 Hz, 2H), 2.31 (t, *J* = 7.8 Hz, 2H), 4.51 (d, *J* = 5.4 Hz, 2H), 5.99 (s, 1H), 6.19 (t, *J* = 7.6 Hz), 7.27-7.37 (c, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 13.94, 14.01, 22.29, 22.31, 29.20, 30.17, 43.72, 127.43, 127.76, 128.69, 135.10, 136.77, 138.56, 169.69. IR (neat): 1743 w, 1656 s, 1621 s, 1531 s, 1457 m, 1311 m, 1234 m, 1168 w, 1078 w, 908 w, 728 m, 698 m. MS, m/z (relative intensity, %): 245 (M<sup>+</sup>, 4), 216 (23), 202 (57), 117 (6), 106 (7), 92 (8), 91 (100), 79 (100), 77 (6), 69 (41). Exact Mass Calcd for C<sub>16</sub>H<sub>23</sub>NO: 245.1780. Found: 245.1789.

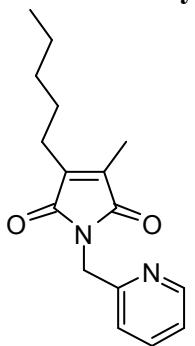
**N,N'-Dibenzyl-2,3-dipropylsuccinamide (6)**



colorless oil.  $R_f = 0.34$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.92 (t,  $J= 7.0$  Hz, 6H), 1.42 (m,  $J= 7.3$  Hz, 4H), 2.29 (c, 4H), 4.19 (d,  $J= 5.7$  Hz, 1H), 6.33-6.38 (c, 1H), 7.19-1.32 (c, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.13, 21.55, 31.58, 43.50, 127.39, 127.79, 128.59, 137.60, 170.19. IR (neat): 3282 s, 1752 w, 1629 s, 1529 s, 1455 m, 1425 m, 1363 m, 1295 m, 1241 m, 1114 w, 1081 w,

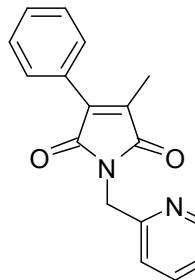
1006 w, 730 m, 698 m. MS, m/z (relative intensity, %): 272 (8), 271 (40), 243 (7), 242 (23), 214 (10), 165 (8), 164 (32), 106 (10), 104 (8), 92 (9), 91 (100), 81 (15), 79 (16), 77 (15). Exact Mass Calcd for  $\text{C}_{24}\text{H}_{30}\text{N}_2\text{O}_2$ : 378.2307. Found: 379.2393.

**4-Methyl-3-pentyl-1-(pyridin-2-yl-methyl)-1H-pyrrole-2,5-dione (3b)**



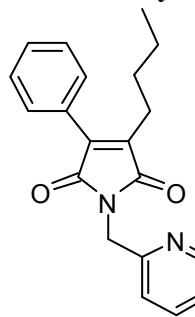
pale yellow oil.  $R_f = 0.57$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.89 (t,  $J= 6.8$  Hz, 3H), 1.31-1.34 (c, 4H), 1.55 (m,  $J= 7.3$  Hz, 2H), 2.01 (s, 3H), 2.41 (t,  $J= 7.3$  Hz, 2H), 4.81 (s, 2H), 7.13-7.19 (c, 2H), 7.62 (dt,  $J= 1.6, 7.56$  Hz, 1H), 8.53 (d,  $J= 4.3$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 8.91, 14.04, 22.42, 23.81, 27.90, 31.70, 42.94, 121.23, 122.23, 136.51, 137.16, 141.41, 149.38, 155.60, 171.58, 171.86. IR (neat): 1770 w, 1708 s, 1594 w, 1432 m, 1402 m, 914 w, 736 m. MS, m/z (relative intensity, %): 272 ( $M^+$ , 19), 257 (30), 244 (12), 243 (68), 230 (19), 229 (78), 217 (11), 216 (63), 215 (41), 107 (13), 95 (16), 93 (63), 92 (100), 81 (26), 80 (13), 79 (25), 67 (19), 65 (29), 53 (43). Exact Mass Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ : 272.1525. Found: 272.1527.

**4-Methyl-3-phenyl-1-(pyridin-2-yl-methyl)-1H-pyrrole-2,5-dione (3c)**



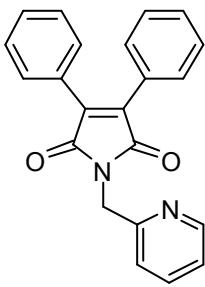
pale yellow oil.  $R_f = 0.31$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.25 (s, 3H), 4.91 (s, 2H), 7.15-7.20 (Ar, 1H), 7.28-7.59 (Ar, 1H), 7.42-7.51 (Ar, 3H), 7.59-7.65 (Ar, 3H), 8.55 (d,  $J= 4.9$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 10.10, 43.11, 121.54, 122.44, 128.53, 128.97, 129.53, 129.59, 136.72, 137.27, 149.53, 155.49, 170.77, 171.69. IR (neat): 1770 m, 1706 s, 1573 m, 1477 w, 1432 s, 1402 s, 1355 m, 1155 w, 1126 w, 997 w, 917 m, 759 s, 734 s, 696 m. MS, m/z (relative intensity, %): 278 ( $M^+$ , 56), 234 (5), 219 (14), 145 (17), 134 (15), 117 (16), 116 (100), 115 (77), 93 (6), 92 (8), 91 (8), 89 (9), 79 (14), 65 (11), 63 (7), 56 (10). Exact Mass Calcd for  $\text{C}_{17}\text{H}_{14}\text{N}_2\text{O}_2$ : 278.3053. Found: 278.1059.

**4-Butyl-3-phenyl-1-(pyridin-2-ylmethyl)-1H-pyrrole-2,5-dione (3d)**



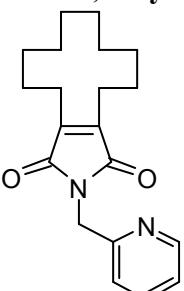
pale yellow oil.  $R_f = 0.40$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.91 (t,  $J= 7.3$  Hz, 3H), 1.62 (c, 2H), 1.39 (c, 2H), 2.64 (t,  $J= 7.6$  Hz, 2H), 4.90 (s, 2H), 7.16-7.65 (Ar, 7H), 8.55 (ddd,  $J= 1.1, 1.6, 4.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 13.69, 22.89, 24.17, 30.63, 43.12, 121.47, 122.42, 128.54, 128.95, 129.36, 129.53, 136.31, 137.35, 141.21, 149.52, 155.56, 170.88, 171.52. IR (neat): 1770 w, 1706 s, 1592 w, 1430 m, 1402 m, 1355 w, 1126 w, 919 w, 757 m, 696 w. MS, m/z (relative intensity, %): 320 ( $M^+$ , 36), 319 (51), 305 (14), 292 (13), 291 (53), 278 (47), 143 (13), 129 (27), 128 (21), 116 (17), 115 (94), 107 (11), 93 (100), 92 (69), 91 (11), 89 (12), 79 (16), 65 (23). Exact Mass Calcd for  $\text{C}_{15}\text{H}_{21}\text{NO}_2$ : 320.1525. Found: 320.1521.

**3,4-Diphenyl-1-(pyridin-2-ylmethyl)-1H-pyrrole-2,5-dione (3e)**



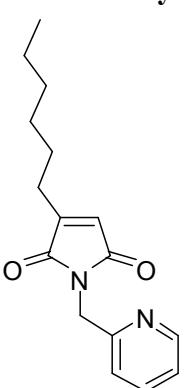
yellow solid.  $R_f = 0.34$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 4.98 (s, 2H), 7.15-7.21 (c, 2H), 7.29-7.40 (c, 6H), 7.49-7.53 (c, 4H), 7.67 (dt,  $J = 1.6, 7.6$  Hz, 1H), 8.57 (d,  $J = 4.9$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 43.35, 121.68, 122.49, 128.49, 128.58, 129.84, 129.92, 136.28, 136.77, 149.52, 155.39, 170.48. IR (neat): 1762 w, 1702 s, 1592 w, 1477 w, 1432 s, 1402 m, 1355 w, 1321 w, 1145 w, 1095 w, 792 w, 755 m, 692 m. MS, m/z (relative intensity, %): 340 ( $M^+$ , 84), 339 (30), 296 (14), 219 (10), 207 (15), 179 (27), 178 (100), 177 (10), 176 (18), 152 (14), 151 (8), 103 (14), 93 (14), 92 (35), 70 (21). Exact Mass Calcd for  $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_2$ : 340.1212. Found: 340.1219.

**3,4-Cyclododecanyl-1-(pyridin-2-ylmethyl)-1H-pyrrole-2,5-dione (3f)**



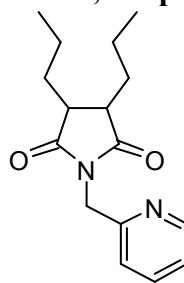
pale yellow oil.  $R_f = 0.48$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 1.30-1.40 (c, 12H), 1.70-1.80 (c, 4H), 2.46 (t,  $J = 6.8$  Hz, 4H), 4.80 (s, 2H), 7.13-7.18 (c, 2H), 7.63 (dt,  $J = 1.6, 7.8$  Hz, 1H), 8.52 (d,  $J = 4.1$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 21.52, 22.29, 24.43, 25.20, 25.99, 42.86, 121.19, 122.22, 136.54, 141.55, 149.36, 155.66, 171.61. IR (neat): 1768 w, 1706 s, 1594 m, 1471 m, 1432 s, 1400 s, 1355 m, 1114 w, 993 w, 912 m, 732 s. MS, m/z (relative intensity, %): 326 ( $M^+$ , 21), 311 (5), 297 (6), 285 (14), 283 (15), 271 (6), 270 (9), 269 (33), 257 (10), 256 (10), 255 (27), 243 (14), 242 (19), 241 (13), 229 (17), 228 (7), 217 (7), 216 (30), 215 (55), 203 (9), 107 (15), 94 (7), 93 (62), 92 (100), 91 (10), 79 (25). Exact Mass Calcd for  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_2$ : 326.1994. Found: 326.1998.

**3-Hexyl-1-(pyridin-2-ylmethyl)-1H-pyrrole-2,5-dione (3g)**

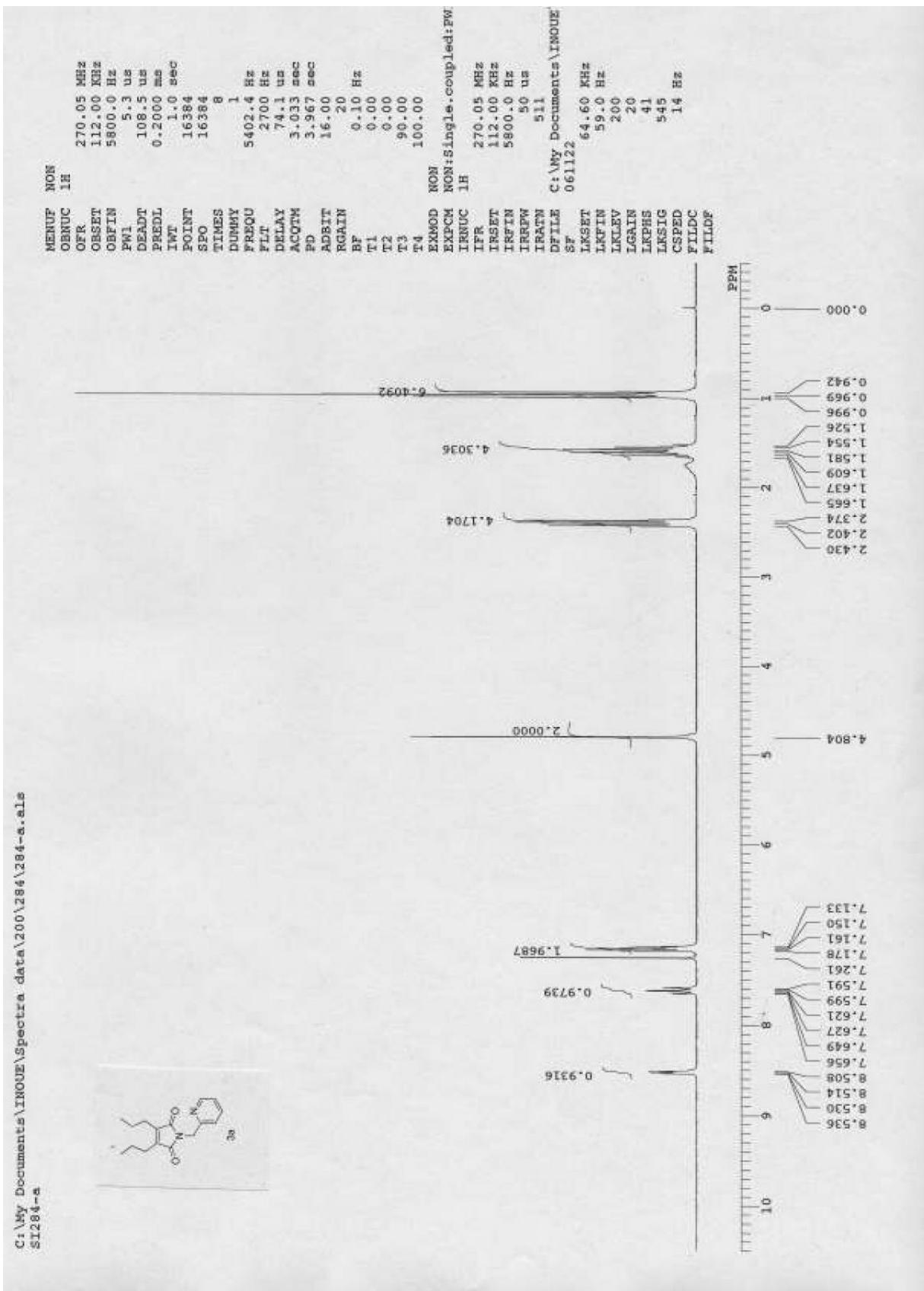


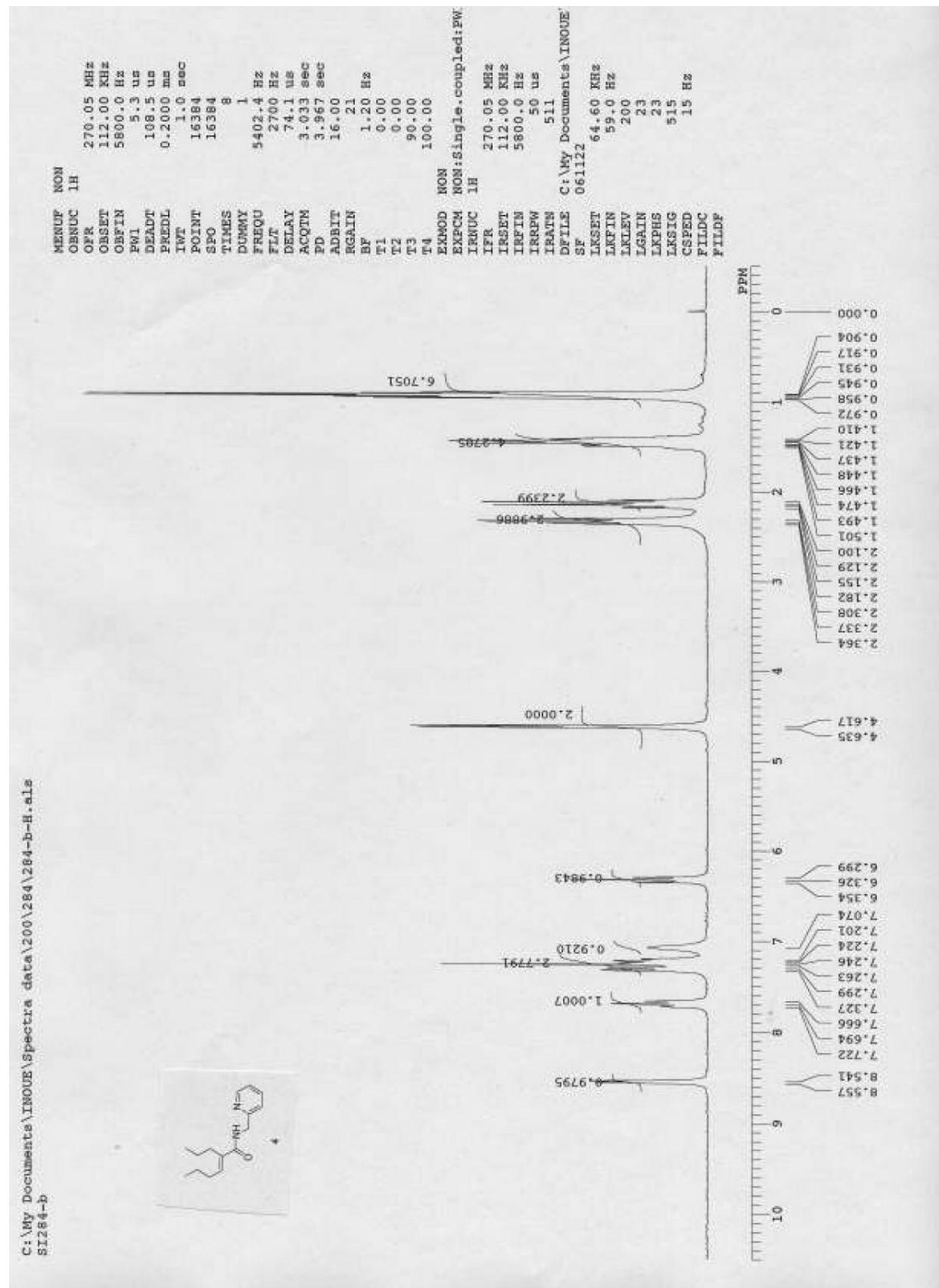
pale yellow oil.  $R_f = 0.48$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.89 (t,  $J = 6.8$  Hz, 6H), 1.27-1.41 (c, 6H), 1.40-1.67 (c, 2H), 2.46 (dt,  $J = 1.6, 7.8$  Hz, 2H), 4.82 (s, 2H), 6.35 (t,  $J = 2.1$  Hz), 7.13-7.21 (c, 2H), 7.63 (dt,  $J = 1.9, 7.6$  Hz, 1H), 8.53 (d,  $J = 3.8$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.13, 22.57, 25.54, 27.05, 28.92, 31.48, 42.85, 121.28, 122.33, 126.31, 136.54, 149.44, 150.44, 155.30, 170.61, 171.29. IR (neat): 1774 m, 1712 s, 1633 w, 1592 m, 1432 m, 1402 m, 1357 m, 1322 w, 1133 w, 1085 w, 914 m, 734 m. MS, m/z (relative intensity, %): 273 ( $M^+ + 1$ , 20), 272 ( $M^+$ , 100), 229 (22), 216 (13), 215 (19), 107 (38), 106 (16), 96 (20), 95 (18), 93 (37), 92 (52), 82 (27), 81 (34), 79 (40). Exact Mass Calcd for  $\text{C}_{16}\text{H}_{20}\text{N}_2\text{O}_2$ : 272.1525. Found: 272.1527.

**3,4-Dipropyl-1-(pyridin-2-yl-methyl)-1-pyrrolidine-2,5-dione (7)**

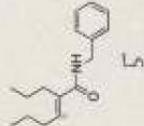


colorless oil.  $R_f = 0.45$  (hexane/EtOAc = 1/1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 0.89-0.99 (c, 6H), 1.41-1.76 (c, 8H), 2.89-2.93 (c, 2H), 4.78 (s, 2H), 7.13-7.22 (c, 2H), 7.62 (dt,  $J = 1.6, 7.6$  Hz, 1H), 8.52 (d,  $J = 4.1$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 14.21, 22.04, 25.84, 42.89, 121.18, 122.25, 136.65, 141.18, 149.24, 155.64, 171.65. IR (neat): 1706 s, 1596 w, 1423 w, 1398 w, 1342 w, 1180 w, 1060 w, 759 w. MS, m/z (relative intensity, %): 245 (18), 232 (22), 231 (19), 203 (43), 190 (100), 189 (84), 107 (26), 106 (11), 93 (38), 92 (76), 79 (26), 70 (13), 69 (20), 67 (14), 65 (27). Exact Mass Calcd for  $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_2$ : 274.1681. Found: 274.1682.





C:\WINMM98\COMMON\DESMBTR.ABS  
S1198-B



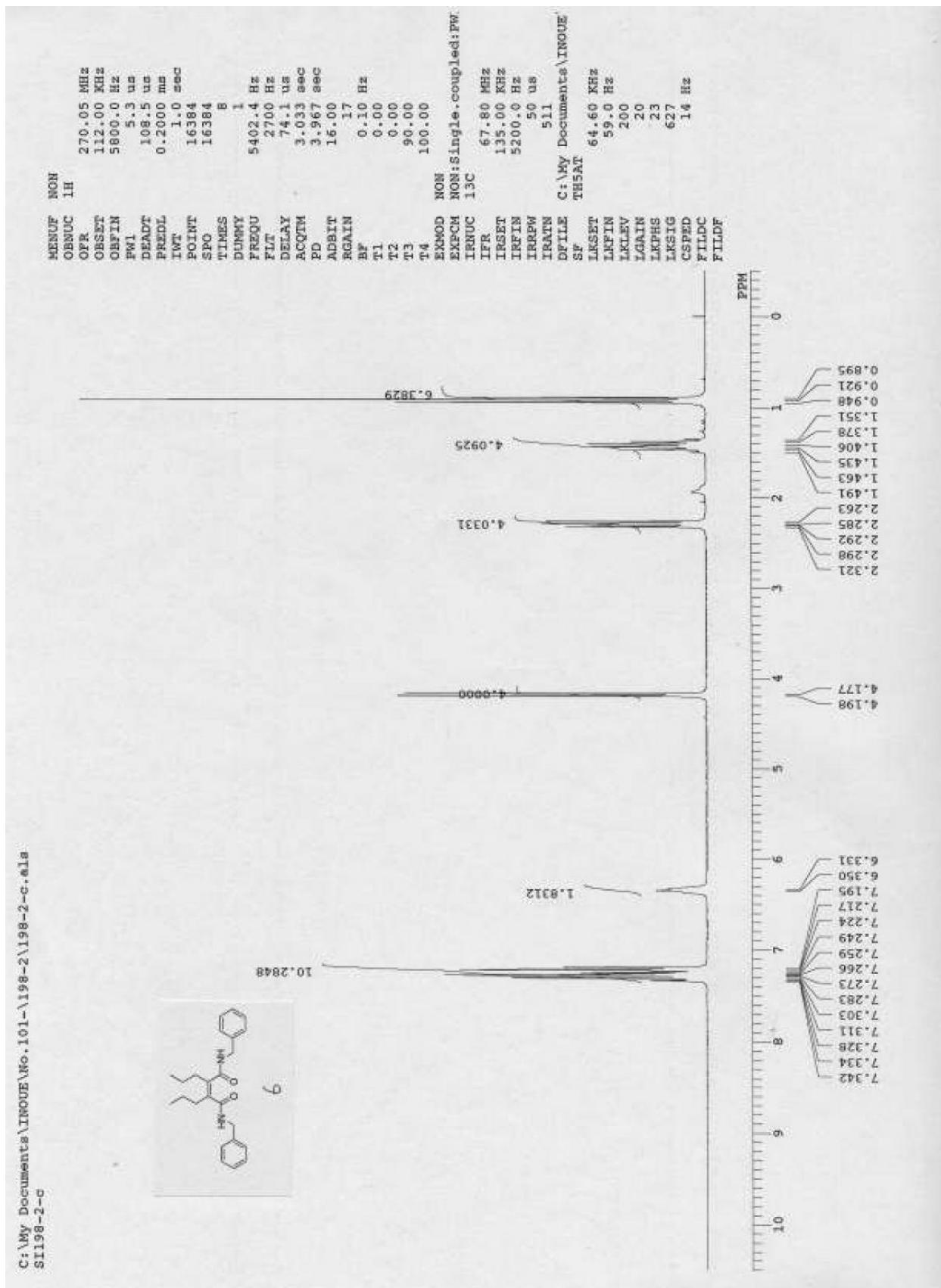
5

Chemical structure of compound 5:

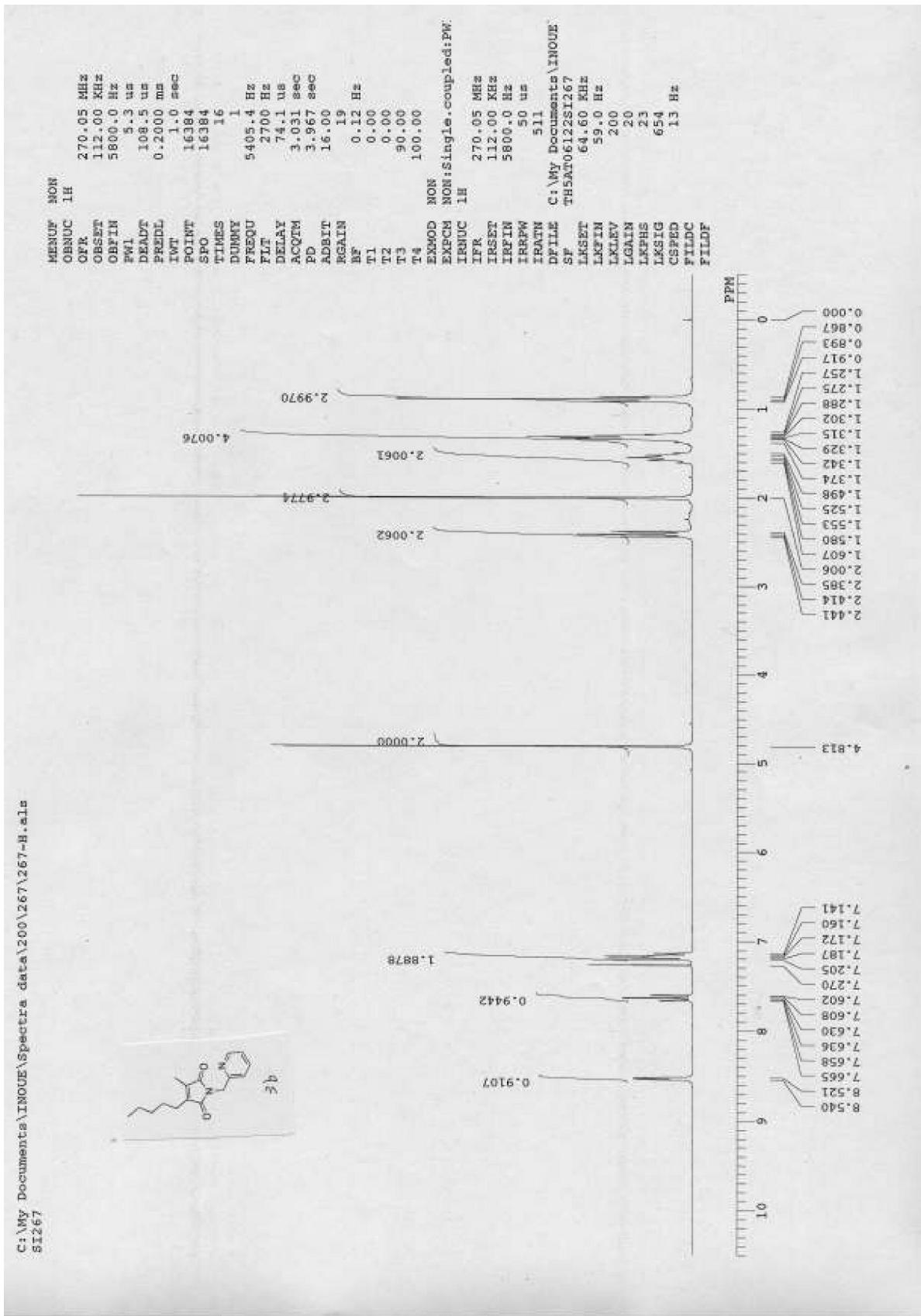
CC(C)C(=O)c1ccccc1N(C)C

NMR parameters:

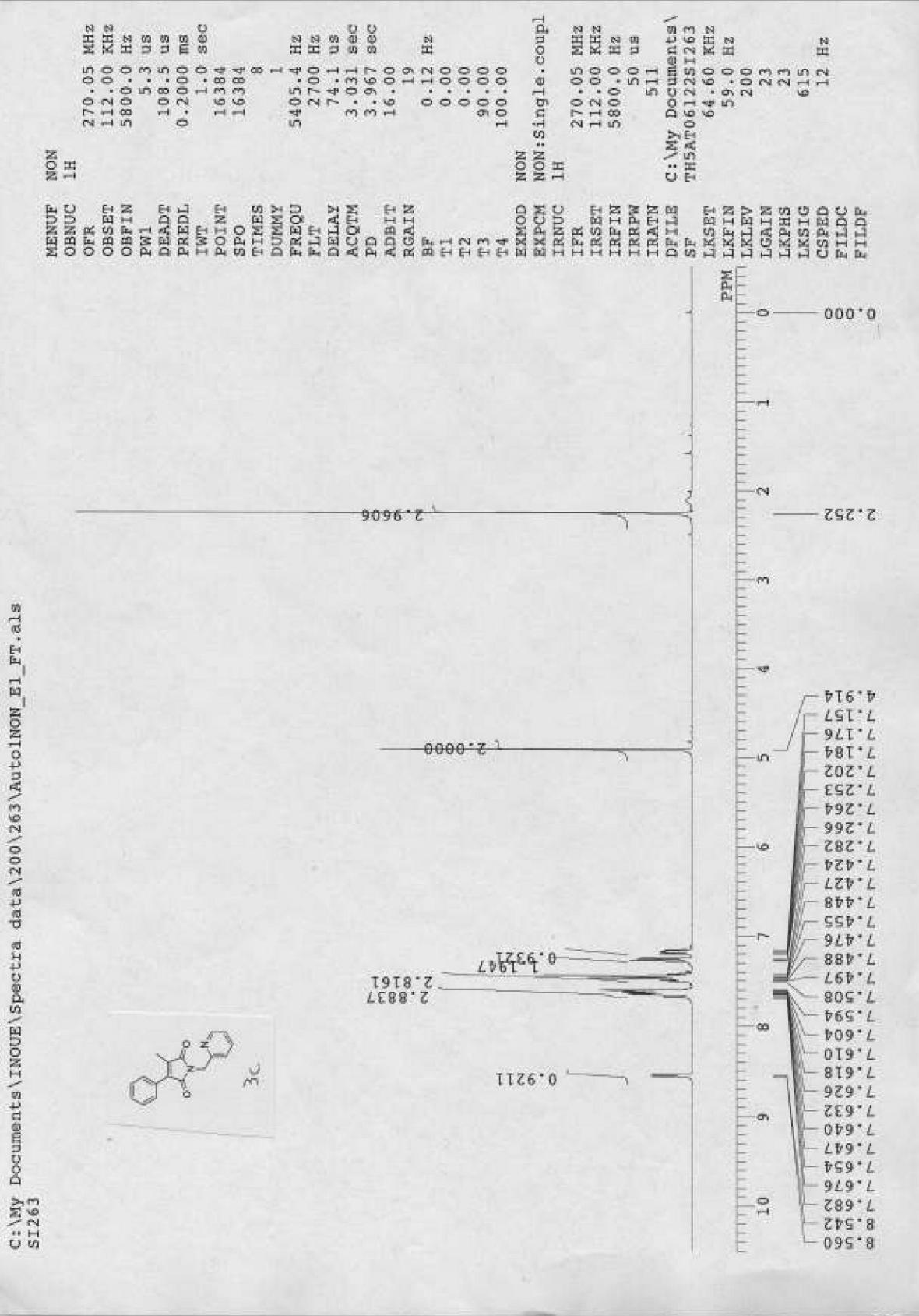
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OBPTN	5800.0 Hz
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IWT	1.0 sec
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SPO	16384
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FLT	2700 Hz
DELAY	74.1 us
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PD	3.967 sec
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T3	90.00
T4	100.00
EXMOD	NON
EXPCH	NON:Single-coupled,TW
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IFR	270.05 MHz
IRSET	112.00 kHz
IRP IN	5800.0 Hz
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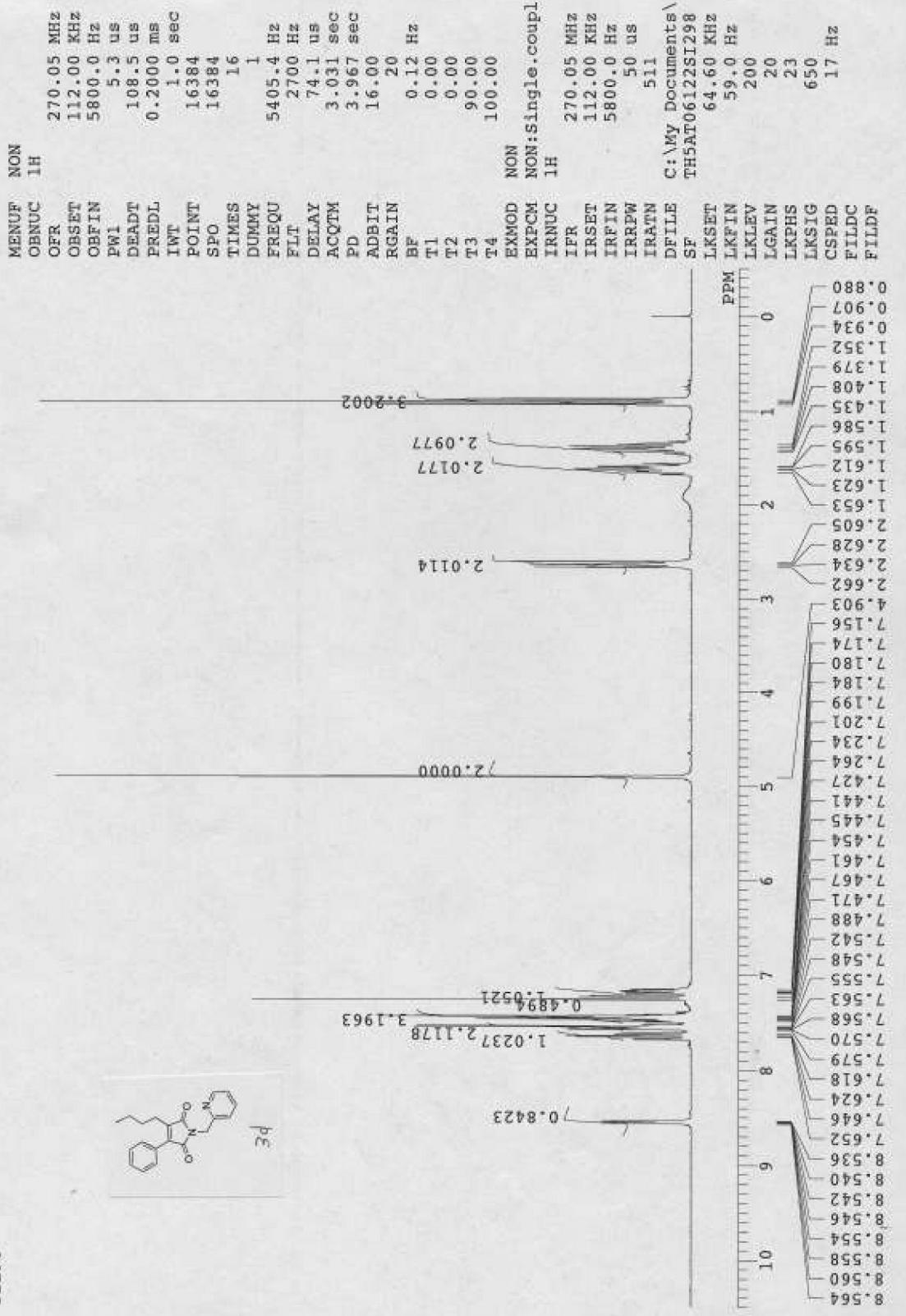


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S1267

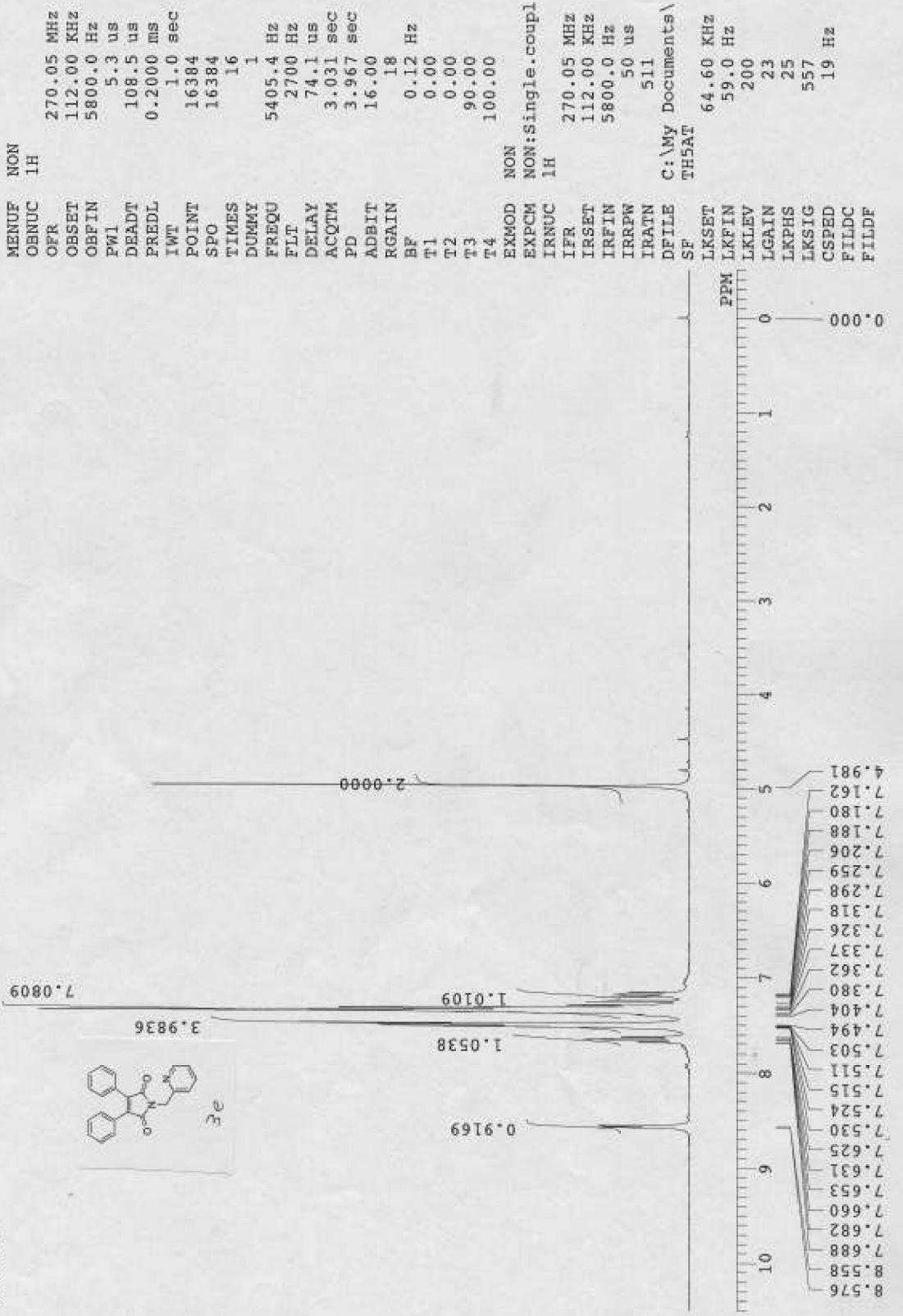


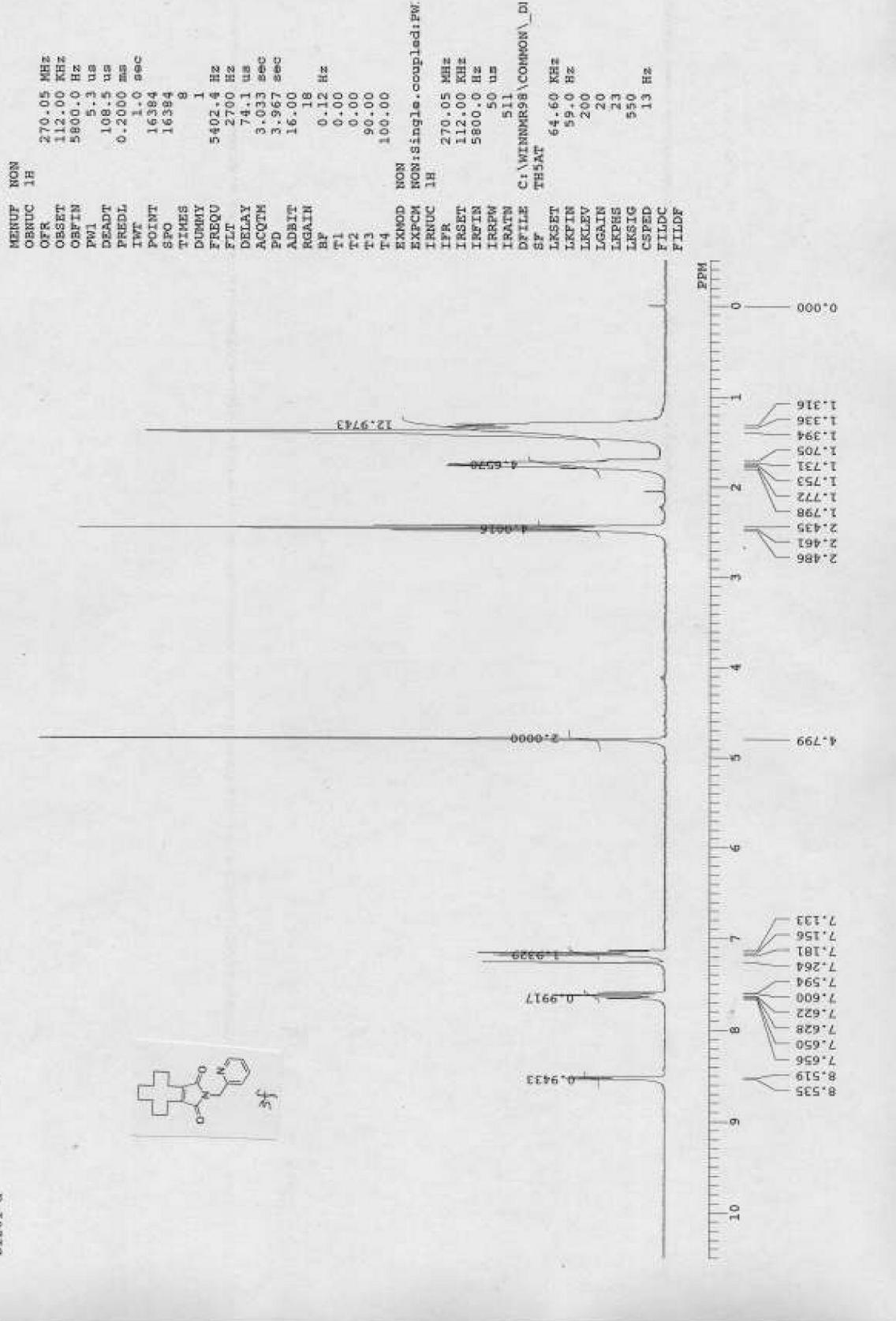
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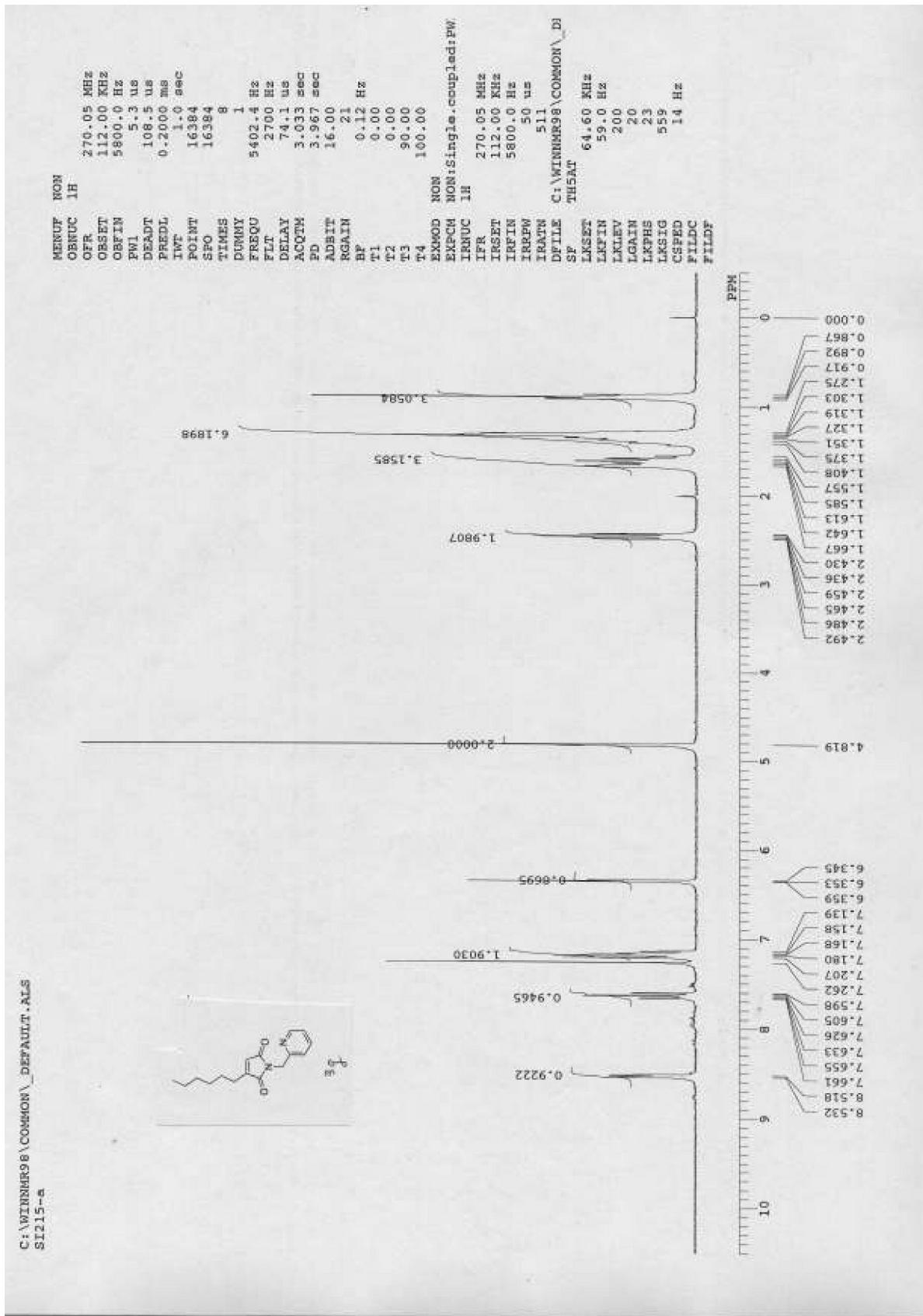


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