

# I-Catalyzed Methyl-Oxygen Bond Cleavage in 2-Methoxyfurans. An Efficient Synthesis of Butenolides

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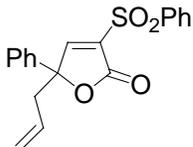
[masm@mail.sioc.ac.cn](mailto:masm@mail.sioc.ac.cn)

## Supporting Information

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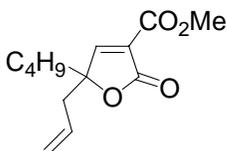
Analytical data for compounds <b>3</b>	S2
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**(1) 3-(Benzenesulfonyl)-5-phenyl-5-allyl-2(5H)-furanone (3ba):**



The reaction of **1b** (152 mg, 0.5 mmol), **2a** (168 mg, 1.0 mmol), NaI (8 mg, 0.05 mmol), and Na<sub>2</sub>CO<sub>3</sub> (6 mg, 0.05 mmol) in 2 mL of dry THF afforded **3ba** (78 mg, 46%): solid, mp 102.5-104 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.80-7.92 (m, 2 H), 7.55-7.70 (m, 1 H), 7.25-7.55 (m, 7 H), 5.90 (s, 1 H), 5.45-5.65 (m, 1 H), 5.09-5.24 (m, 2 H), 3.06 (dd, *J* = 13.5, 6.3 Hz, 1 H), 2.95 (dd, *J* = 13.5, 7.8 Hz, 1 H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 169.9, 156.7, 134.8, 134.3, 130.9, 130.4, 129.0, 128.9, 128.8, 126.6, 125.3, 121.6, 97.0, 77.7, 34.8; MS *m/z* 199 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>, 100); IR (neat) 1803, 1643, 1313 cm<sup>-1</sup>. Anal. calcd for C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>S: C 67.04; H 4.74. Found: C 67.00; H 4.62.

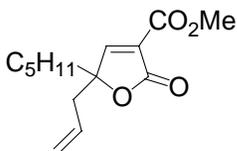
**(2) 3-(Methoxycarbonyl)-5-butyl-5-allyl-2(5H)-furanone (3ca):**



The reaction of **1c** (105 mg, 0.5 mmol), **2a** (102 mg, 0.6 mmol), and NaI (8 mg, 0.05 mmol) in 2 mL of dry THF afforded **3ca** (87 mg, 73%): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 5.53-5.70 (m, 1 H), 5.08-5.20 (m, 2 H), 5.15 (s, 1 H), 3.73 (s, 3 H), 2.78 (dd, *J* = 13.8, 6.9 Hz, 1 H), 2.67 (dd, *J* = 13.8, 7.5 Hz, 1 H), 2.31 (t, *J* = 8.2 Hz, 2 H), 1.45-1.60 (m, 2 H), 1.27-1.41 (m, 2 H), 0.90 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 174.2, 168.4, 157.9, 130.8, 120.2, 103.1, 59.5, 53.1, 38.2, 27.6, 27.5, 21.9, 13.6; MS *m/z* 238 (M<sup>+</sup>, 7.08), 197 (100); IR (neat) 1804, 1745, 1677, 1241 cm<sup>-1</sup>. Anal. calcd for C<sub>13</sub>H<sub>18</sub>O<sub>4</sub>: C 65.53; H

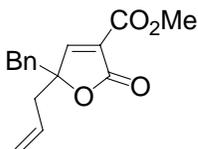
7.61. Found: C 65.52; H 7.63.

**(3) 3-(Methoxycarbonyl)-5-pentyl-5-allyl-2(5H)-furanone (3da):**



The reaction of **1d** (114 mg, 0.5 mmol), **2a** (102 mg, 0.6 mmol), and NaI (8 mg, 0.05 mmol) in 2 mL of dry THF afforded **3da** (84 mg, 71%): liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  5.53-5.70 (m, 1 H), 5.08-5.21 (m, 2 H), 5.15 (s, 1 H), 3.73 (s, 3 H), 2.79 (dd,  $J = 13.8, 6.6$  Hz, 1 H), 2.67 (dd,  $J = 13.8, 7.5$  Hz, 1 H), 2.31 (t,  $J = 7.2$  Hz, 2 H), 1.45-1.62 (m, 2 H), 1.23-1.37 (m, 4 H), 0.88 (t,  $J = 6.9$  Hz, 3 H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 168.4, 157.9, 130.8, 120.3, 103.2, 59.5, 53.1, 38.2, 30.9, 27.9, 25.2, 22.2, 13.9; MS  $m/z$  252 ( $\text{M}^+$ , 2.84), 43 (100); IR (neat) 1804, 1746, 1677, 1240  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_4$ : C 66.65; H 7.99. Found: C 66.75; H 8.02.

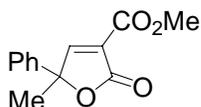
**(4) 3-(Methoxycarbonyl)-5-benzyl-5-allyl-2(5H)-furanone (3ea):**



The reaction of **1e** (63 mg, 0.25 mmol), **2a** (56 mg, 0.33 mmol), and NaI (5 mg, 0.033 mmol) in 2 mL of dry THF afforded **3ea** (48 mg, 71%): liquid;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20-7.38 (m, 5 H), 5.50-5.70 (m, 1 H), 5.10-5.22 (m, 2 H), 5.13 (s, 1 H), 3.73 (s, 3 H), 3.64 (s, 2 H), 2.78 (dd,  $J = 13.8, 6.9$  Hz, 1 H), 2.69 (dd,  $J = 13.8, 7.5$  Hz, 1 H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  173.8, 168.1, 156.5, 134.4, 130.56, 128.9, 128.6, 127.1, 120.4,

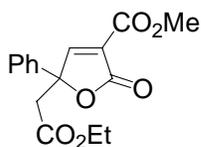
104.7, 59.5, 53.2, 38.2, 34.5; MS  $m/z$  272 ( $M^+$ , 11.75), 91 (100); IR (neat) 1804, 1744, 1677, 1242  $\text{cm}^{-1}$ . HRMS calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4\text{Na}^+$ : 295.09408. Found: 295.09560.

**(5) 3-(Methoxycarbonyl)-5-phenyl-5-methyl-2(5H)-furanone (3ab):**<sup>1</sup>



The reaction of **1a** (116 mg, 0.5 mmol), **2b** (213 mg, 1.5 mmol), and NaI (8 mg, 0.05 mmol) in 2 mL of dry THF in a sealed tube afforded **3ab** (92 mg, 79%): solid, mp 45-47 °C (petroleum ether/ether); <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50-7.58 (m, 2 H), 7.29-7.35 (m, 3 H), 5.76 (s, 1 H), 3.65 (s, 3 H), 1.58 (s, 3 H); <sup>13</sup>C NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  174.8, 168.8, 153.9, 130.2, 128.7, 127.4, 125.0, 104.2, 55.5, 53.3, 20.3; MS  $m/z$  232 ( $M^+$ , 10.91), 173 (100); IR (neat) 1809, 1747, 1650, 1244  $\text{cm}^{-1}$ . Anal. calcd for  $\text{C}_{13}\text{H}_{12}\text{O}_4$ : C 67.23; H 5.21. Found: C 67.44; H 5.15.

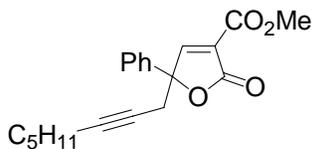
**(6) 3-(Methoxycarbonyl)-5-phenyl-5-(ethoxycarbonylmethyl)-2(5H)-furanone (3ac):**<sup>2</sup>



The reaction of **1a** (115 mg, 0.5 mmol), **2c** (128 mg, 0.6 mmol), and NaI (8 mg, 0.05 mmol) in 2 mL of dry THF afforded **3ac** (124 mg, 82%): solid, mp 62-65 °C (petroleum ether/ethyl acetate); <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58-7.72 (m, 2 H), 7.37-7.48 (m, 3 H), 5.99 (s, 1 H), 4.05-4.21 (m, 2 H), 3.78 (s, 3 H), 3.30 (d,  $J = 17.1$  Hz, 1 H), 3.02 (d,  $J = 17.1$  Hz, 1 H), 1.21 (t,  $J = 6.9$  Hz, 3 H); <sup>13</sup>C NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  173.0, 169.0, 167.3, 155.3, 130.3, 128.7, 127.3, 125.1, 101.8, 61.2, 57.2, 53.6, 38.4, 13.9; MS  $m/z$  304

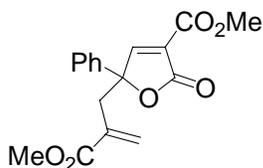
(M<sup>+</sup>, 9.62), 105 (100); IR (KBr) 1808, 1740, 1651, 1234 cm<sup>-1</sup>.

**(7) 3-(Methoxycarbonyl)-5-phenyl-5-(2'-octynyl)-2(5H)-furanone (3ad):**



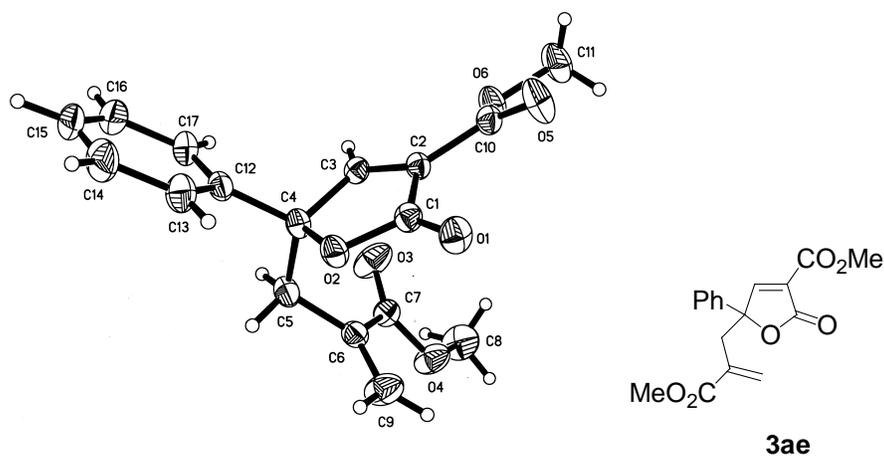
The reaction of **1a** (116 mg, 0.5 mmol), **2d** (140 mg, 0.6 mmol), and NaI (7 mg, 0.05 mmol) in 2 mL of dry THF afforded **3ad** (134 mg, 82%): liquid; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.62-7.70 (m, 2 H), 7.37-7.47 (m, 3 H), 5.87 (s, 1 H), 3.77 (s, 3 H), 2.97-3.02 (m, 2 H), 1.97-2.07 (m, 2 H), 1.02-1.38 (m, 6 H), 0.75 (t, *J* = 6.9 Hz, 3 H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 173.0, 167.5, 154.9, 130.2, 128.7, 127.5, 125.1, 102.0, 84.3, 72.8, 60.0, 53.4, 30.7, 28.2, 24.9, 22.0, 18.4, 13.8; MS *m/z* 327 (M<sup>+</sup>+1, 1.31), 217 (100); IR (neat) 1810, 1747, 1652, 1241 cm<sup>-1</sup>. Anal. calcd for C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>: C 73.60; H 6.79. Found: C 73.67; H 6.86.

**(8) 3-(Methoxycarbonyl)-5-phenyl-5-(2'-methoxycarbonyl-2'-propenyl)-2(5H)-furanone (3ae):**



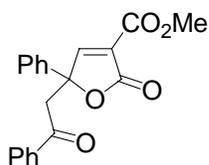
The reaction of **1a** (116 mg, 0.5 mmol), **2e** (224 mg, 1.0 mmol), and NaI (8 mg, 0.05 mmol) in 2 mL of dry THF afforded **3ae** (132 mg, 84%): solid, mp 81-83 °C (petroleum ether/ether); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.35 (s, 1 H), 7.30-7.50 (m, 5 H), 6.37 (s, 1 H), 5.83 (s, 1 H), 3.84 (s, 3 H), 3.73 (s, 3 H), 3.36 (d, *J* = 13.9 Hz, 1 H), 3.01 (d, *J* = 13.9 Hz, 1

H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ 167.0, 166.3, 164.7, 160.1, 137.1, 132.3, 132.0, 128.9, 128.7, 124.9, 123.4, 87.2, 52.4, 52.1, 41.4; MS  $m/z$  285 ( $\text{M}^+ - \text{CH}_3\text{O}$ , 3.67), 217 ( $\text{M}^+ - \text{C}_5\text{H}_7\text{O}_2$ , 100); IR (KBr) 1791, 1778, 1720, 1630, 1259  $\text{cm}^{-1}$ . HRMS calcd for  $\text{C}_{17}\text{H}_{17}\text{O}_6$  ( $\text{M}^+ + 1$ ): 317.10197. Found: 317.10460.



**Figure 1:** ORTEP representation of **3ae**

**(9) 3-(Methoxycarbonyl)-5-phenyl-5-(benzoylmethyl)-2(5H)-furanone (3af):**



The reaction of **1a** (59 mg, 0.25 mmol), **2f** (76 mg, 0.3 mmol), and NaI (4 mg, 0.025 mmol) in 2 mL of dry THF afforded **3af** (80 mg, 94%) (eluent: petroleum ether/ether/methanol = 10:1:0.15): solid, mp 148-151 $^{\circ}$  (petroleum ether/ethyl acetate);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.1$  Hz, 2 H), 7.35-7.70 (m, 8 H), 6.09 (s, 1 H), 4.22 (d,  $J = 18.3$  Hz, 1 H), 3.78 (s, 3 H), 3.55 (d,  $J = 18.3$  Hz, 1 H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$ 195.1, 173.7, 167.7, 155.0, 135.6, 133.8, 130.2, 128.7, 128.7, 128.1, 127.6, 125.2, 102.7, 57.1, 53.6, 43.4; MS  $m/z$  336 ( $\text{M}^+$ , 2.42), 105 (100); IR (KBr) 1801, 1746, 1679, 1236  $\text{cm}^{-1}$ .

Anal. calcd for C<sub>20</sub>H<sub>16</sub>O<sub>5</sub>: C 71.42; H 4.79. Found: C 71.35; H 4.73.

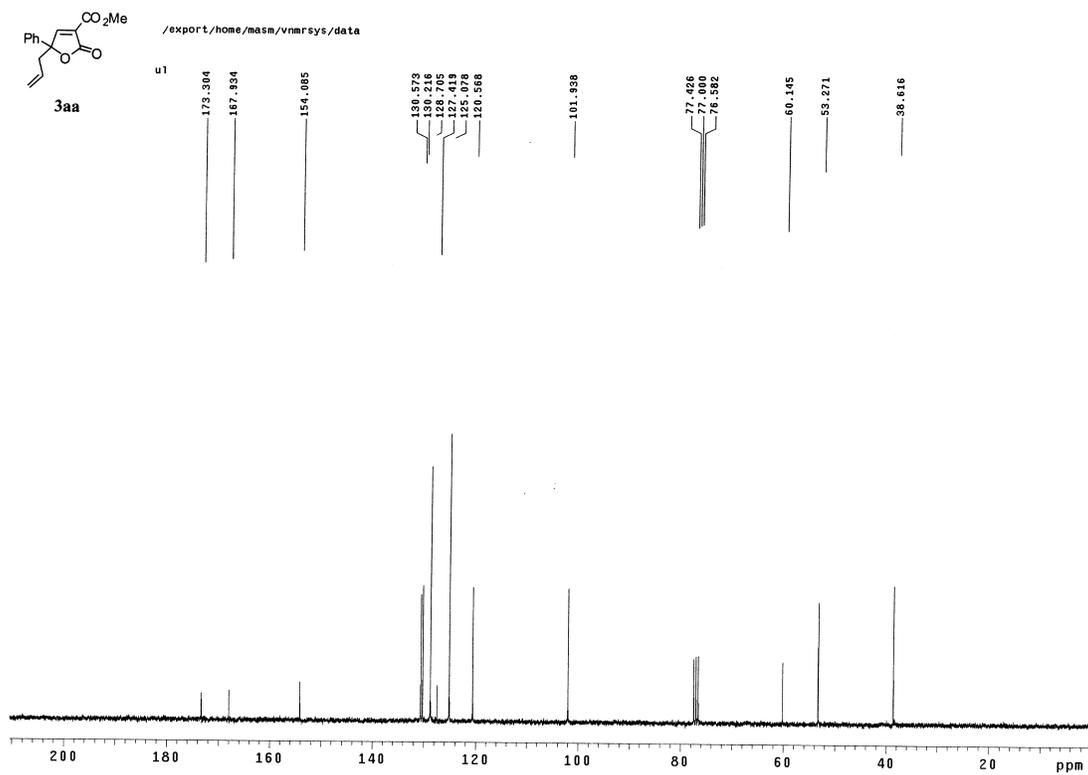
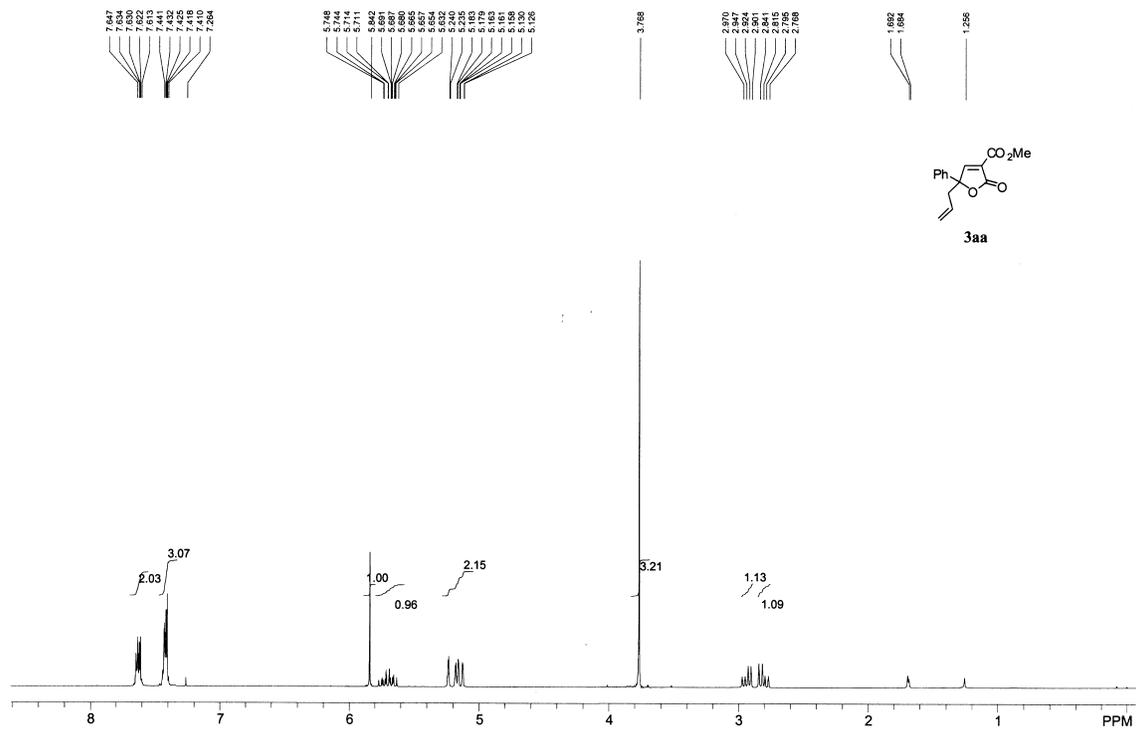
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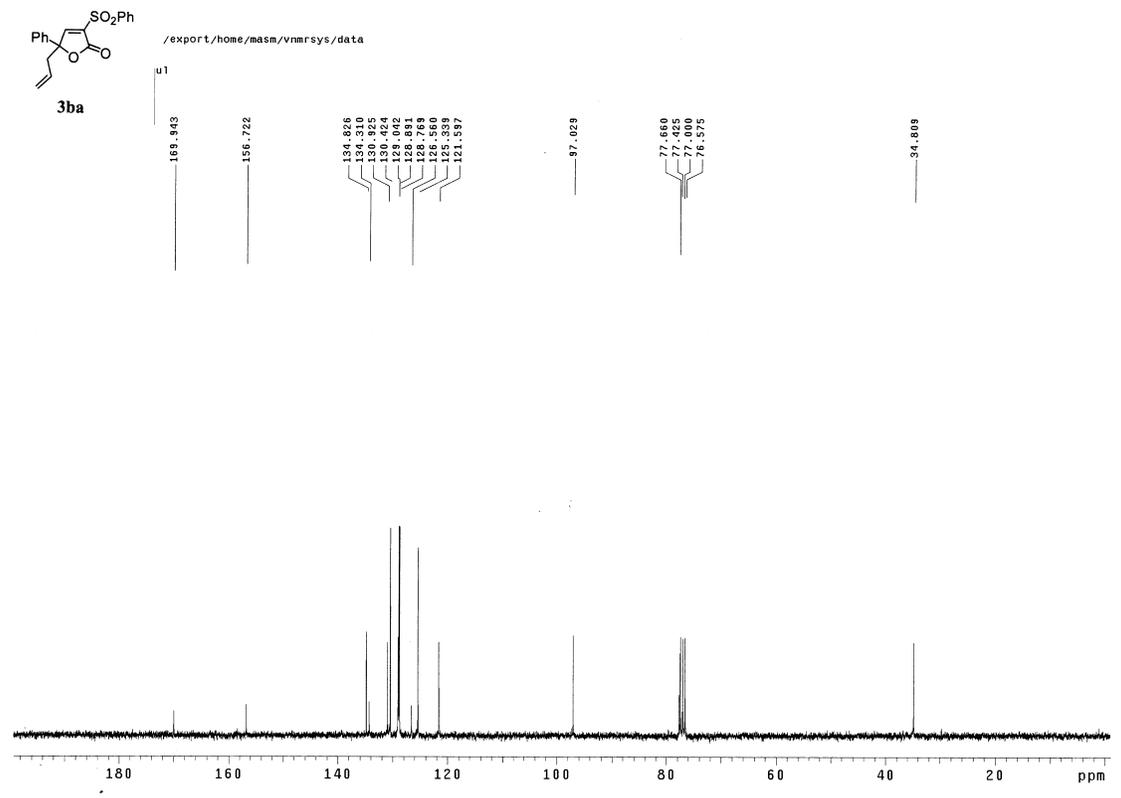
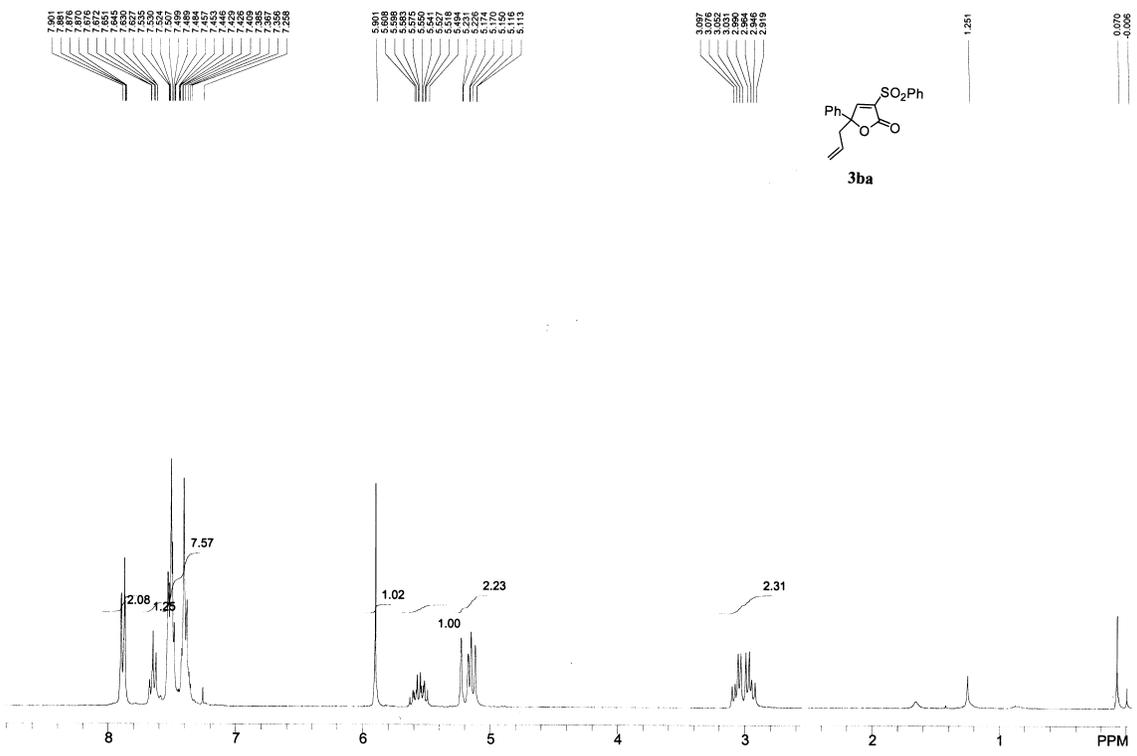
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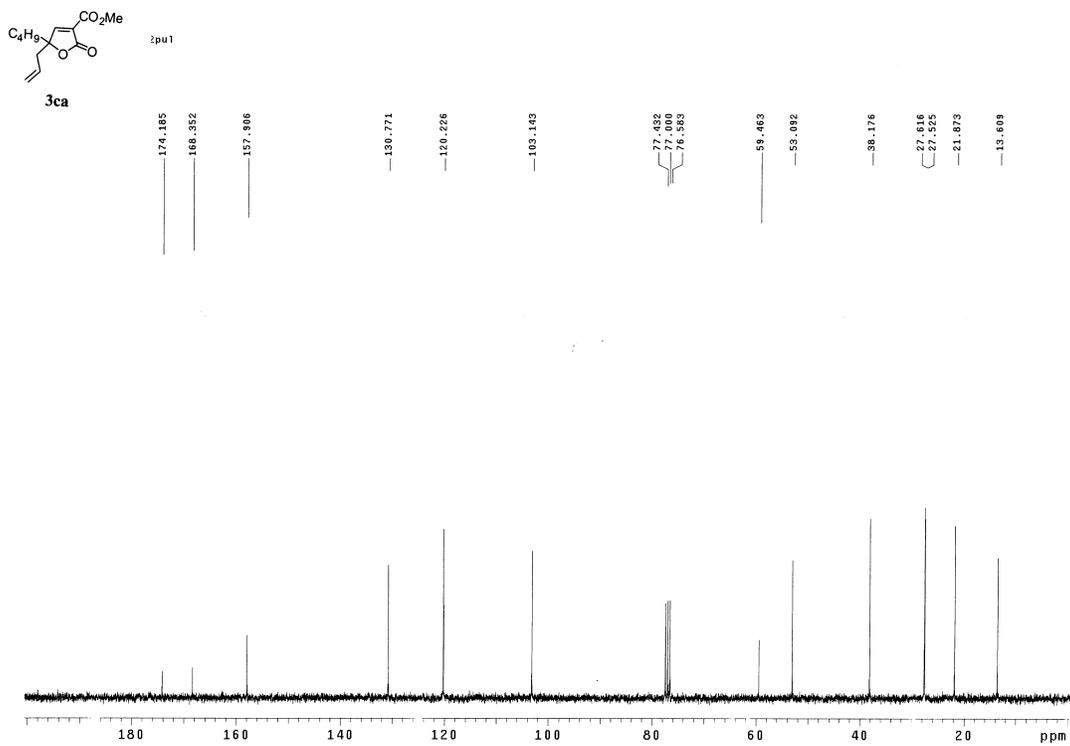
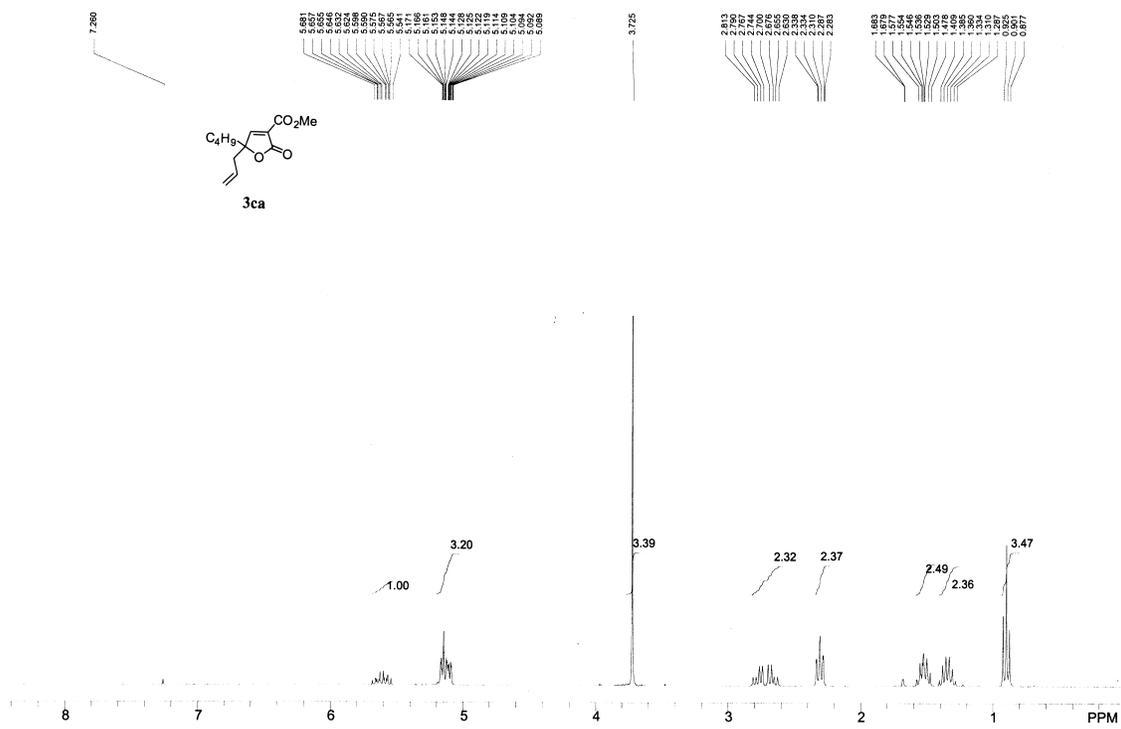
*Belg.* **1978**, *87*, 215.

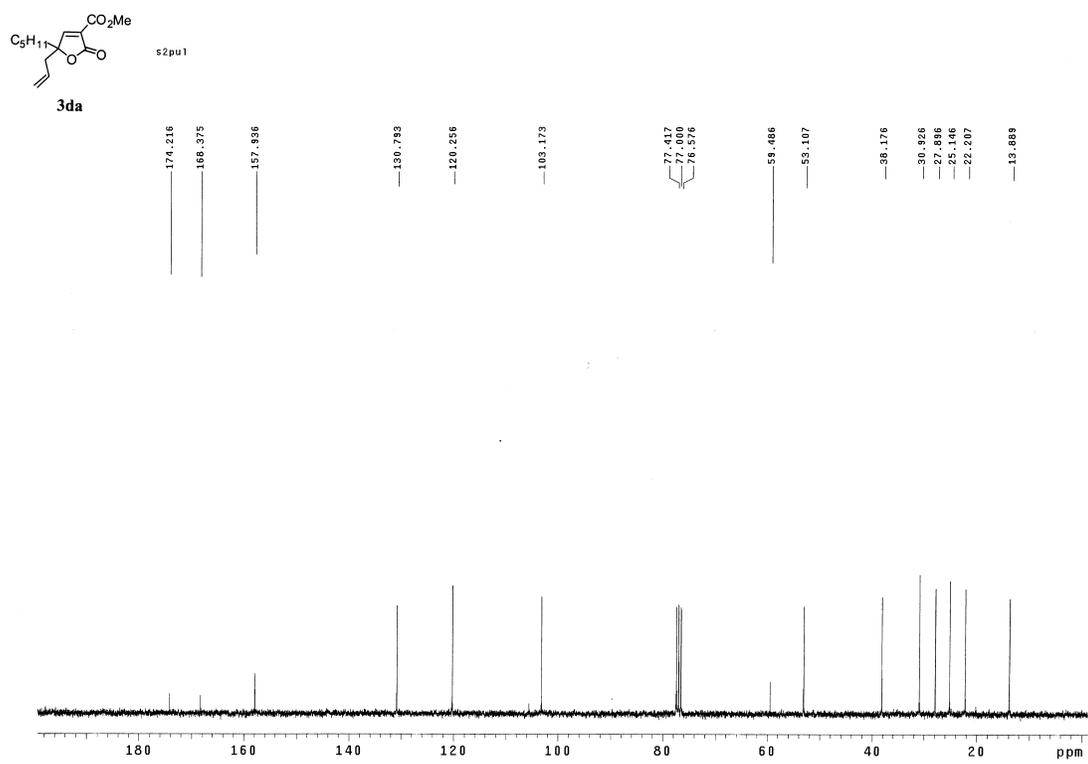
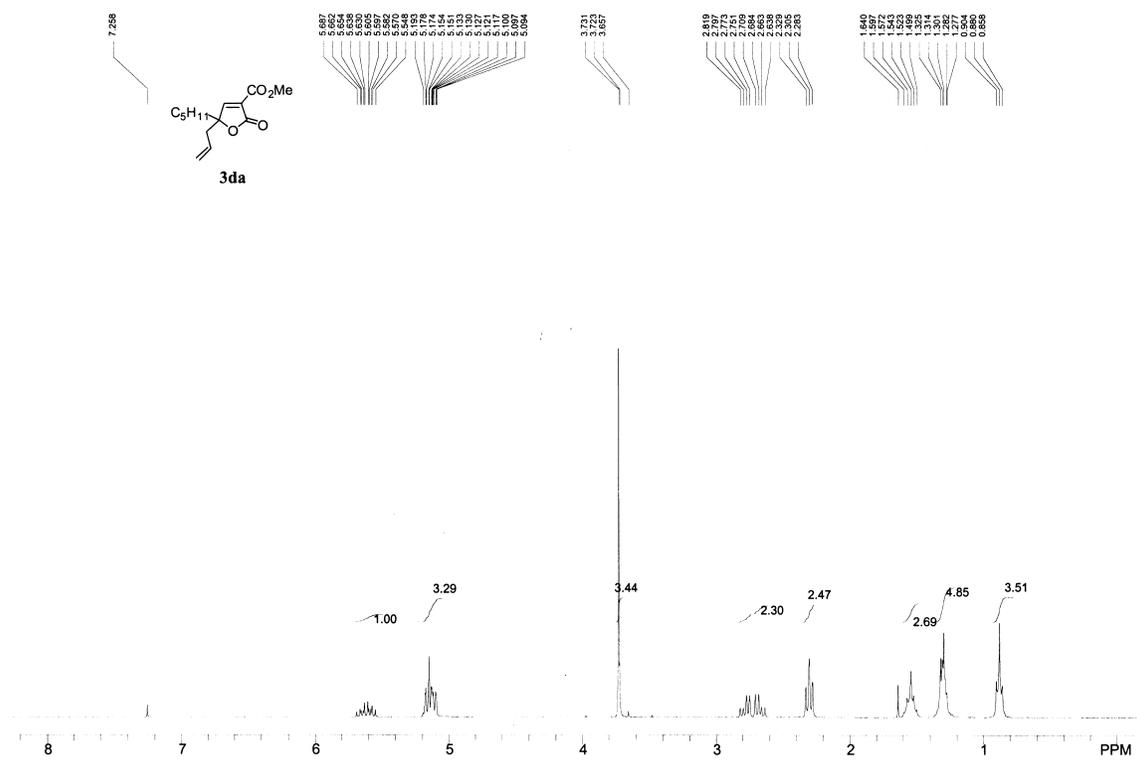
(2) Iesce, M. R.; Graziano, M. L.; Cermola, F.; Cimminiello, G.; Scarpati, R. *Gazz. Chim.*

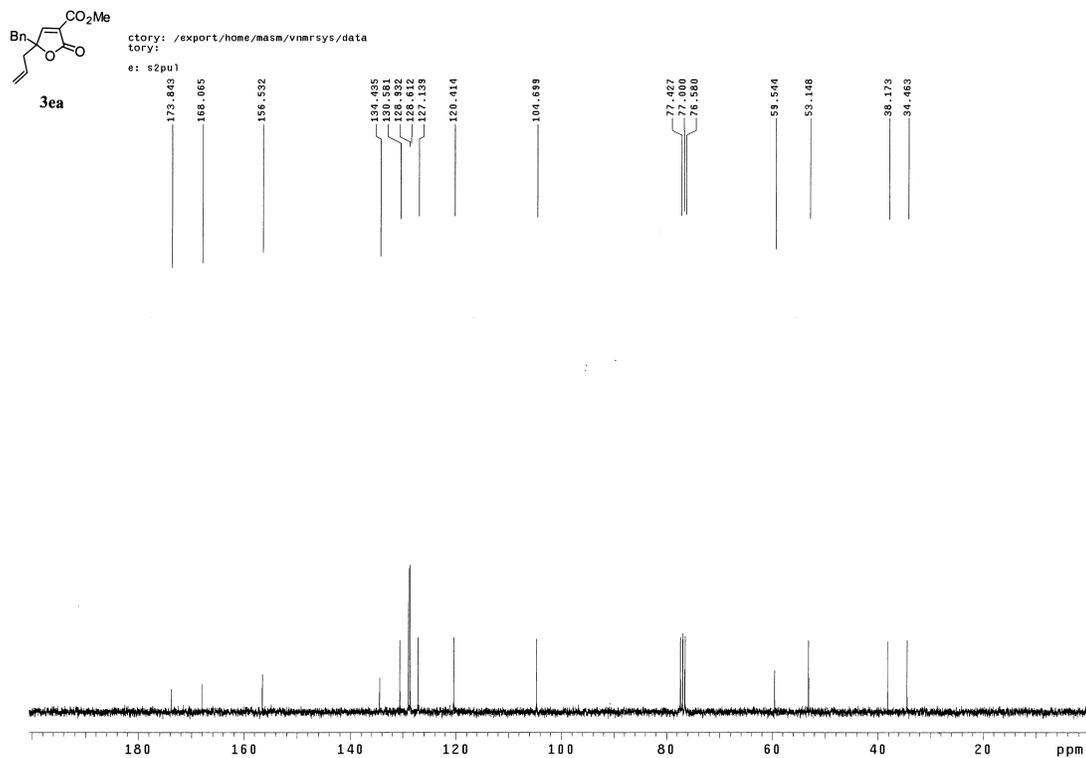
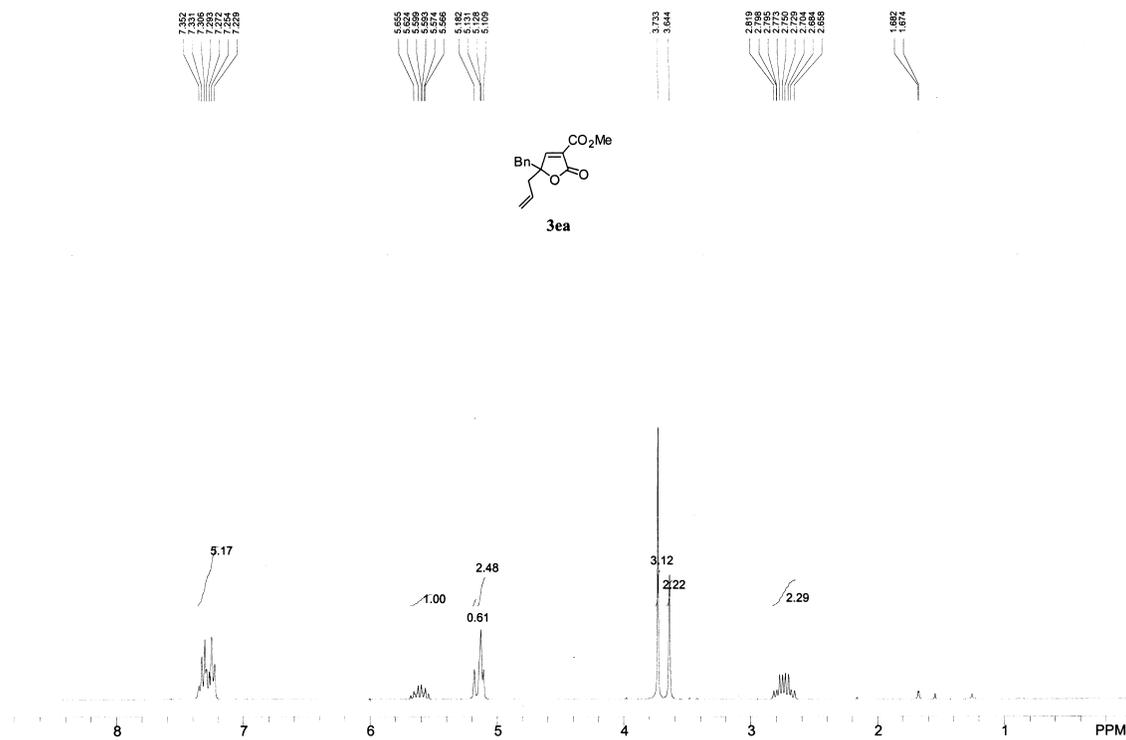
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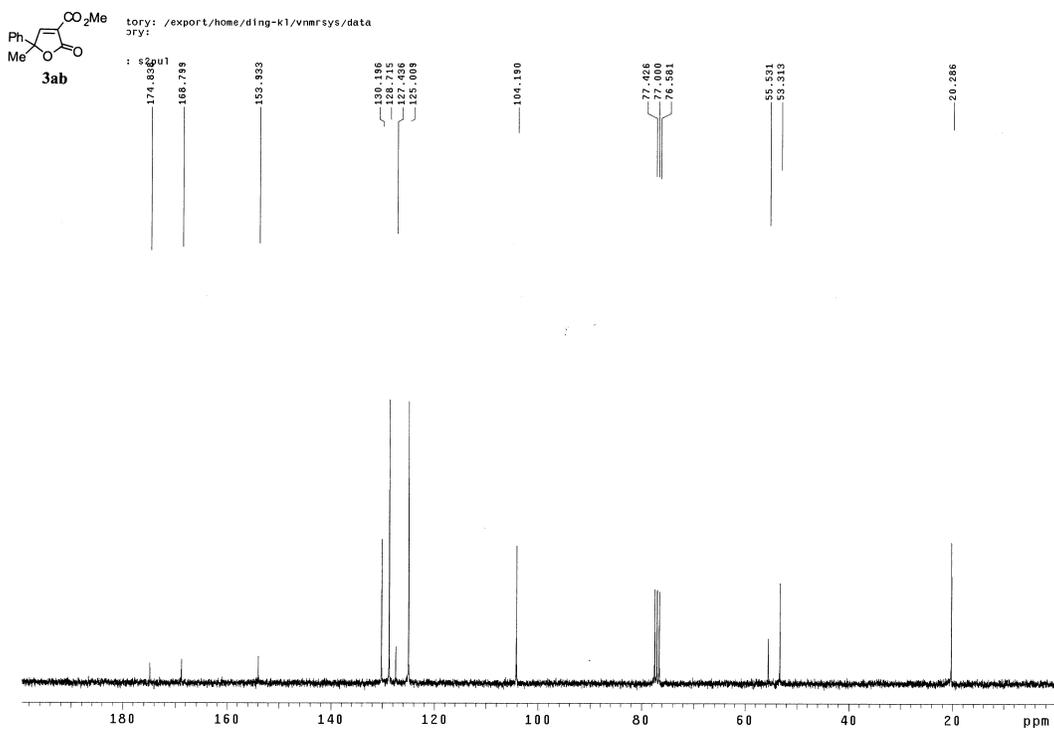
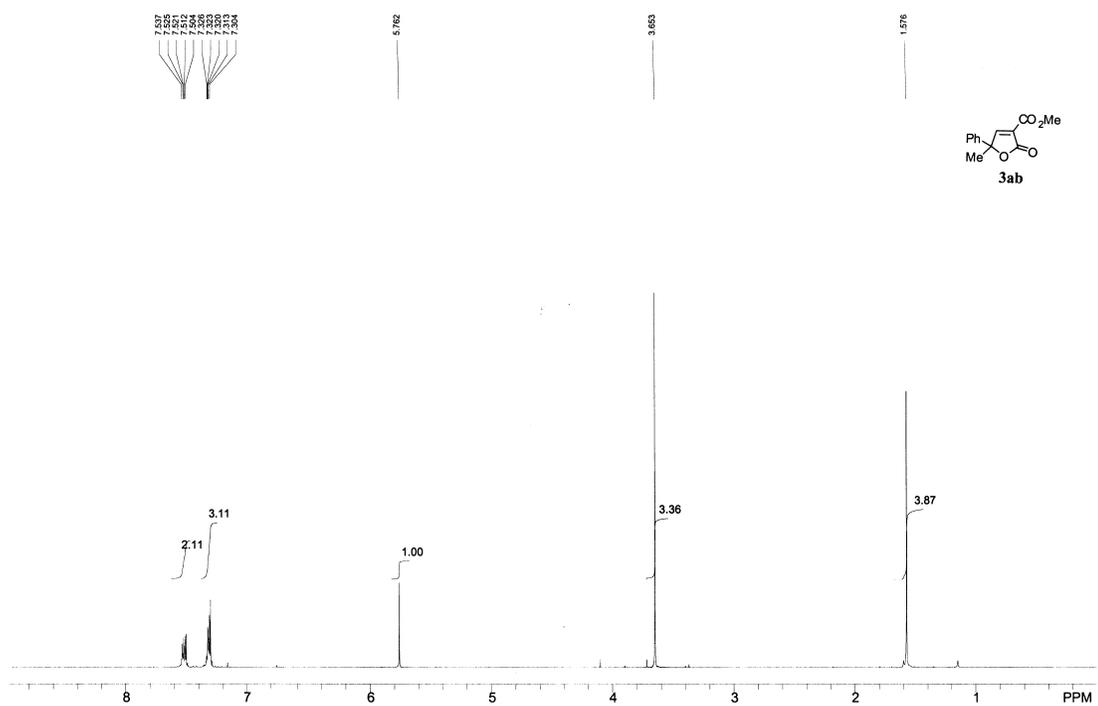


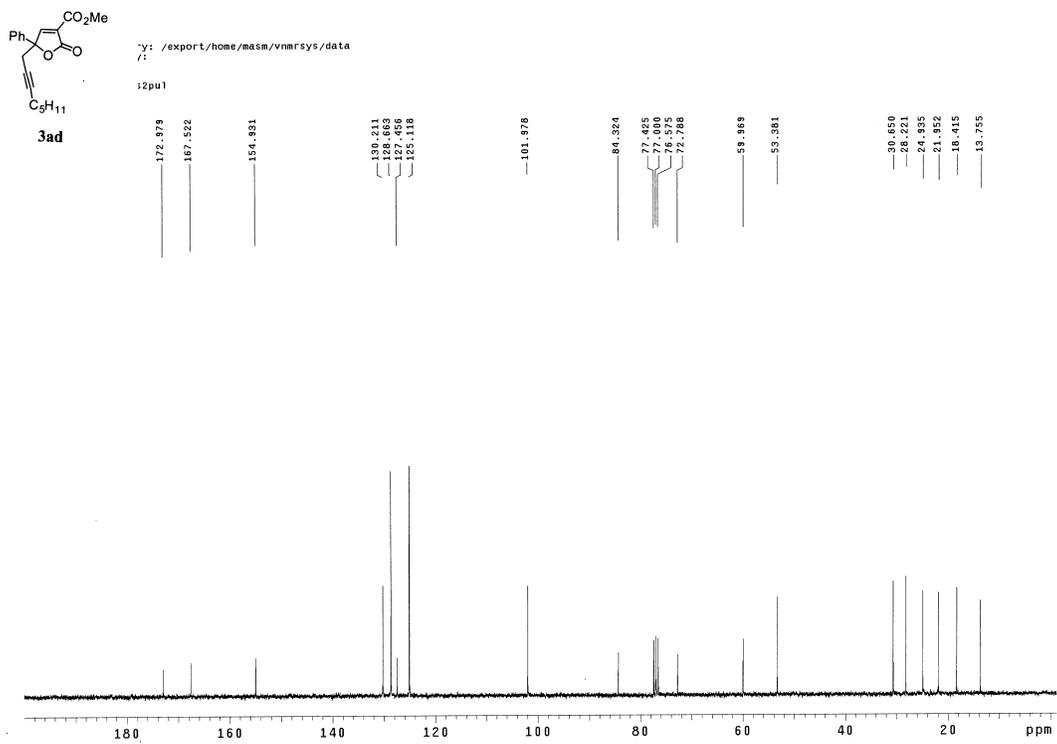
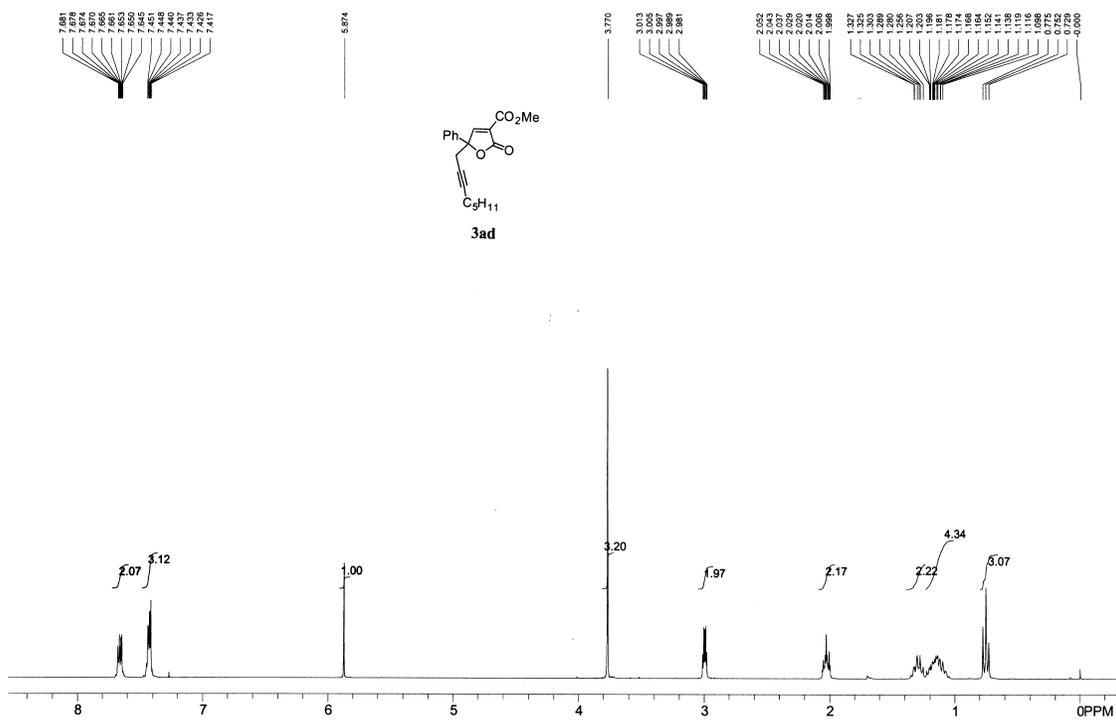


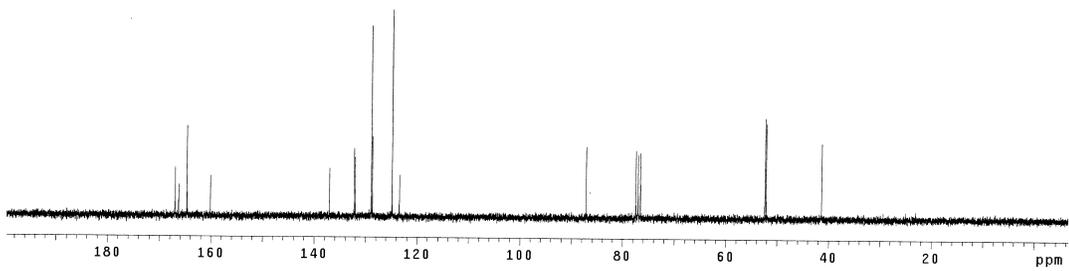
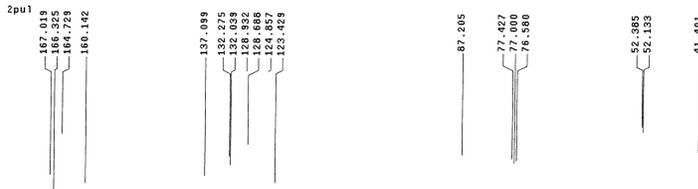
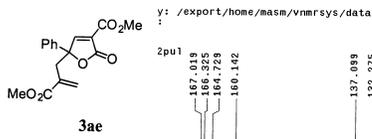
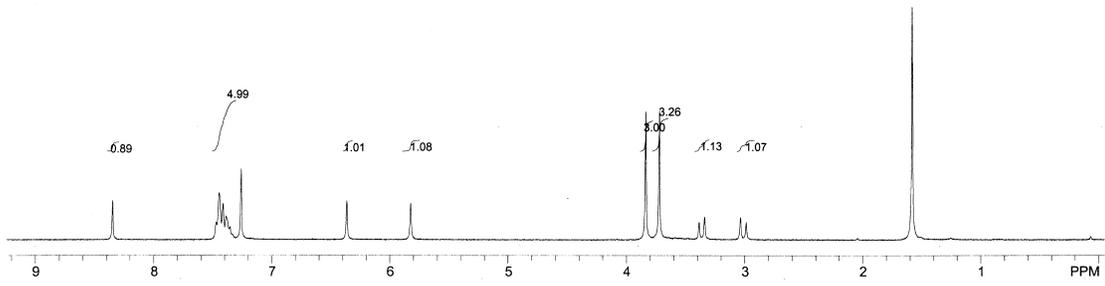
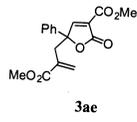
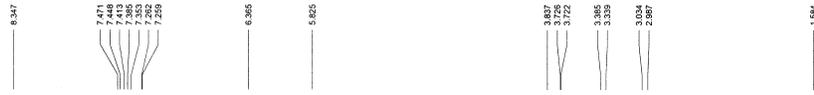


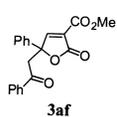
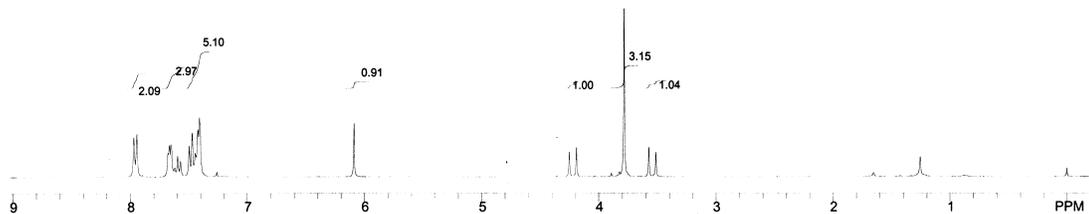
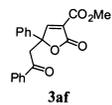
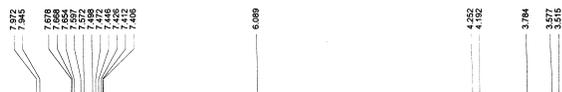












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