

## Supporting Information

# Pd-Catalyzed Cyclization Reaction: A Convenient Domino Process for Synthesis of $\alpha$ -Carbonyl Furans Derivatives

Hua Cao<sup>a,b</sup>, Huan-Feng Jiang,<sup>b\*</sup> Hua-Wen Huang,<sup>b</sup> Jin-Wu Zhao<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Guangdong Pharmaceutical University, Guangzhou 510006, P.R. of China

<sup>b</sup> School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P.R. of China

*[jianghf@scut.edu.cn](mailto:jianghf@scut.edu.cn)*

### Experimental Section

#### General method

General. All reactions were performed at the room temperature under air atmosphere in a round bottom flask equipped with magnetic stir bar. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer and referenced to 7.26 ppm and 77.0 ppm for chloroform solvent respectively with TMS as internal standard. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. Mass spectra were recorded on a Shimadzu GCMS-QP5050A at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). Elemental analysis was performed on a Vario EL elemental analyzer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals.

**General procedure for the synthesis of 3-methyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde (4aa).**

cyclohexane-1,3-dione (**1a** 0.5 mmol), but-2-yn-1-ol (**2a** 0.6 mmol), and Iron(III) p-toluenesulfonate in DCE were refluxed to form intermediate product 3a for 12 hours at 80 °C. And then the solution was evaporated to dryness under reduced pressure. Subsequently, PdCl<sub>2</sub>/CuI, Bu<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> and DMF were added. After completion of the reaction (monitored by TLC), the solution was evaporated to dryness under reduced pressure and then water (8 mL) was added. The aqueous solution was extracted with diethyl ether (3×8 mL) and the combined extract was dried with anhydrous MgSO<sub>4</sub>. The solvent was removed and the crude product was separated by column chromatography to give a pure sample of **4aa**.

**3-methyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde(4aa)**

IR (KBr) 2950, 2849, 1772, 1673, 1565; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.76 (s, 1H), 2.95 (t, *J*=6.0 Hz, 2H), 2.58 (s, 3H), 2.52-2.57 (m, 2H), 2.18-2.24 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 195.0, 177.3, 171.0, 148.3, 122.1, 115.2, 38.5, 24.0, 22.2, 9.65; MS (EI) *m/z* (%): 178, 150, 122, 93, 77, 65. C<sub>10</sub>H<sub>10</sub>O<sub>3</sub>: Calcd. C, 67.41; H, 5.66; Found: C, 67.03; H, 5.69.

**4-oxo-3-phenyl-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde(4ab)**

IR (KBr) 2936, 2821, 1769, 1672; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.50 (s, 1H), 7.51-7.54 (m, 2H), 7.44-7.47 (m, 3H), 3.03 (t, *J*=6.4 Hz, 2H), 2.57 (t, *J*=6.4 Hz, 2H), 2.21-2.28 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 193.2, 177.9, 171.2, 147.8, 137.2, 130.4, 129.5, 128.2, 127.9, 120.3, 38.7, 24.0, 21.8; MS (EI) *m/z* (%): 240, 212, 184, 156, 127, 77, 51. C<sub>15</sub>H<sub>12</sub>O<sub>3</sub>: Calcd. C, 74.99; H, 5.03; Found: C, 74.47; H, 5.00.

**3,6,6-trimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde(4ba)**

IR (KBr) 2942, 2845, 1773, 1669; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.75 (s, 1H), 2.80 (s, 2H), 2.58 (s, 3H), 2.41 (s, 2H), 1.16 (s, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 194.0, 177.3, 169.9, 149.0, 121.2, 115.2, 53.08, 38.1, 35.0, 28.6, 9.43; MS (EI) *m/z* (%): 206, 191, 150, 122, 93, 77, 65. C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>: Calcd. C, 69.88; H, 6.84; Found: C, 69.41; H, 6.89.

**6,6-dimethyl-4-oxo-3-phenyl-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde(4bb)**

IR (KBr) 3089, 2928, 2836, 1782, 1665; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 9.52 (s, 1H),

7.54-7.57(m, 2H), 7.46-7.48(m, 3H), 2.91 (s, 2H), 2.47 (s, 3H), 1.20 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  192.8, 177.9, 170.5, 148.1, 137.1, 130.4, 129.6, 128.2, 127.8, 119.2, 53.07, 37.8, 34.7, 28.4; MS (EI)  $m/z$  (%):268, 240, 212, 184, 156, 127, 115, 77, 55.  $\text{C}_{17}\text{H}_{16}\text{O}_3$ : Calcd. C, 76.10; H, 6.01; Found: C, 75.47; H, 5.98.

**3-methyl-4-oxo-6-phenyl-4,5,6,7-tetrahydrobenzofuran-2-carbaldehyde(4ca)**

IR (KBr) 3093, 2943, 2845, 1780, 1662;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  9.78 (s, 1H), 7.28-7.39 (m, 5H), 3.54-3.62 (m, 1H), 3.08-3.28 (m, 2H), 2.80-2.82 (d,  $J=7.2$  Hz, 2H), 2.61 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  194.5, 177.6, 171.4, 148.5, 136.4, 130.5, 129.7, 128.3, 128.0, 122.9, 47.5, 38.8, 32.0, 9.51; MS (EI)  $m/z$  (%):254, 240, 207, 165, 150, 122, 93, 77, 65.  $\text{C}_{16}\text{H}_{14}\text{O}_3$ : Calcd. C, 75.57; H, 5.55; Found: C, 76.06; H, 5.50.

**4-benzoyl-3-methyl-5-phenylfuran-2-carbaldehyde (4da)<sup>1</sup>**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  9.86 (s, 1H), 7.79–7.81 (m, 2H), 7.23-7.55 (m, 8H), 2.31 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  192.0, 177.7, 156.8, 147.4, 136.8, 133.9, 132.4, 130.1, 129.6, 128.7, 128.6, 128.3, 127.5, 127.1, 123.8, 9.37;

**4-benzoyl-3,5-diphenylfuran-2-carbaldehyde (4db)<sup>1</sup>**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  9.61 (s, 1H), 7.69–7.77 (m, 4H), 7.26-7.45 (m, 11H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  191.9, 177.4, 156.2, 146.5, 140.1, 136.6, 133.9, 130.4, 129.6, 129.4, 129.2, 128.7, 128.6, 127.9, 127.4, 122.8;

**4-benzoyl-3-(4-methoxyphenyl)-5-phenylfuran-2-carbaldehyde (3dd)<sup>1</sup>**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  9.61 (s, 1H), 7.26–7.78 (m, 14H), 3.73 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  192.1, 177.3, 160.4, 156.0, 146.5, 139.7, 136.8, 133.9, 131.0, 130.3, 129.7, 128.7, 128.6, 128.1, 127.4, 122.9, 120.8, 114.2, 55.2;

**4-benzoyl-3-(4-nitrophenyl)-5-phenylfuran-2-carbaldehyde (4de)<sup>1</sup>**

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 Hz)  $\delta$  9.66 (s, 1H), 7.65–7.98 (m, 6H), 7.29–7.49 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 Hz)  $\delta$  191.2, 177.1, 156.8, 146.5, 136.3, 134.3, 132.4, 132.2, 132.1, 130.7, 130.3, 129.6, 128.9, 128.8, 128.6, 127.5, 127.1, 122.6;

**Ethyl 5-formyl-4-methyl-2-phenylfuran-3-carboxylate (4ea)**<sup>1</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  9.81 (s, 1H), 7.81–7.83 (m, 2H), 7.41–7.43 (m, 3H), 4.27 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz)  $\delta$  177.7, 163.1, 160.8, 147.4, 135.2, 130.5, 128.9, 128.6, 128.1, 116.6, 60.9, 13.9, 10.1;

**Ethyl 5-formyl-2,4-diphenylfuran-3-carboxylate (4eb)**<sup>1</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  9.47 (s, 1H), 7.93–7.95 (m, 2H), 7.44 (s, 8H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz)  $\delta$  177.4, 163.1, 159.3, 146.9, 140.1, 130.8, 129.8, 129.1, 128.5, 128.4, 128.2, 116.4, 61.2, 13.5;

**Ethyl 5-formyl-4-(4-methoxyphenyl)-2-phenylfuran-3-carboxylate (4ed)**<sup>1</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  9.50 (s, 1H), 7.91–7.93 (m, 2H), 7.39–7.48 (m, 5H), 6.98–7.00 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 1.05 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz)  $\delta$  177.5, 163.4, 160.5, 147.0, 139.8, 131.5, 131.2, 130.7, 130.3, 128.8, 128.5, 128.4, 121.2, 113.8, 61.2, 55.3, 13.6;

**Ethyl 5-formyl-4-(4-nitrophenyl)-2-phenylfuran-3-carboxylate (4ee)**<sup>1</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  9.52 (s, 1H), 7.93–7.95 (m, 2H), 7.75–7.77 (m, 2H), 7.48–7.60 (m, 5H), 4.11 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz)  $\delta$  176.4, 161.9, 159.7, 146.4, 136.3, 133.9, 131.4, 130.6, 130.2, 128.3, 128.0, 127.5, 117.7, 115.6, 112.5, 60.9, 13.1;

**Ethyl 5-formyl-2-phenyl-4-(thiophen-2-yl)furan-3-carboxylate (4ef)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  9.67 (s, 1H), 7.86–7.89 (m, 2H), 7.12–7.50 (m, 6H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 Hz)  $\delta$  177.2, 163.1, 158.9, 147.9, 135.3, 133.5, 130.8, 130.2, 128.5, 128.4, 128.3, 127.4, 126.9, 125.8, 116.5, 61.5, 13.6;

**Ethyl 5-formyl-2-phenyl-4-m-tolylfuran-3-carboxylate (4eg)**<sup>1</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  9.50 (s, 1H), 7.94–7.97 (m, 2H), 7.27–7.48 (m, 7H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100

Hz)  $\delta$  176.9, 162.7, 158.6, 146.5, 139.7, 137.4, 130.2, 130.0, 129.3, 128.6, 128.2, 128.1, 128.0, 127.9, 127.7, 126.6, 116.1, 60.7, 20.8, 13.0;

**2-methyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5a)<sup>2</sup>**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  7.26-7.37 (m, 5H), 2.87 (t, 2H, *J* = 6.4 Hz), 2.46-2.49 (m, 2H), 2.30 (s, 3H), 2.12-2.19 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): 194.3, 165.9, 148.9, 130.1, 131.9, 128.1, 127.3, 120.0, 119.4, 38.9, 23.9, 22.7, 12.2.

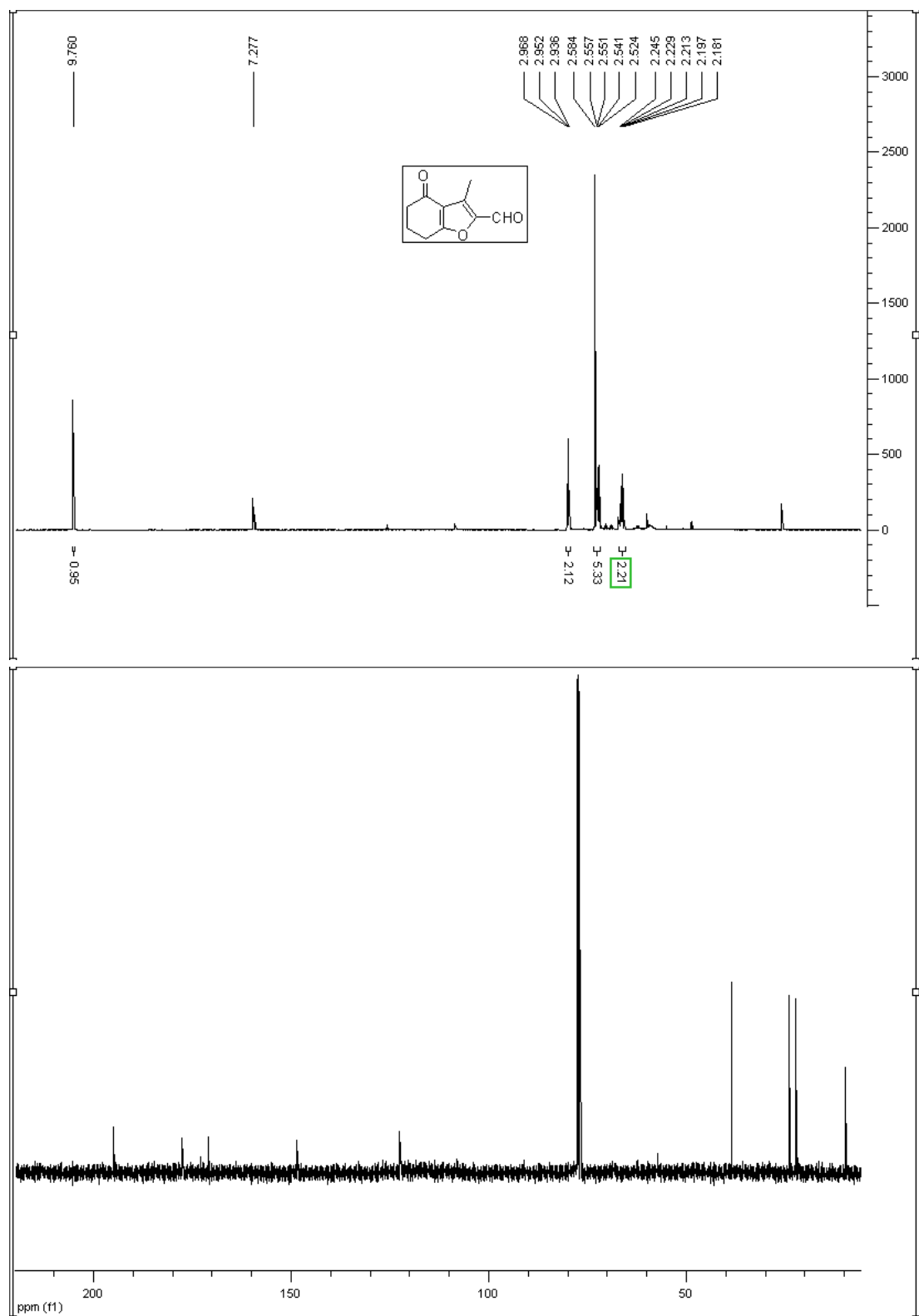
**2,6,6-trimethyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (5b)<sup>2</sup>**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 Hz)  $\delta$  7.26-7.42 (m, 5H) 2.75 (s, 2H), 2.38 (s, 2H), 2.33 (s, 3H), 1.17 (s, 6H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>)  $\delta$  193.1, 164.5, 148.7, 131.3, 129.4, 127.5, 126.7, 118.7, 118.1, 52.7, 37.3, 34.6, 28.2, 11.7.

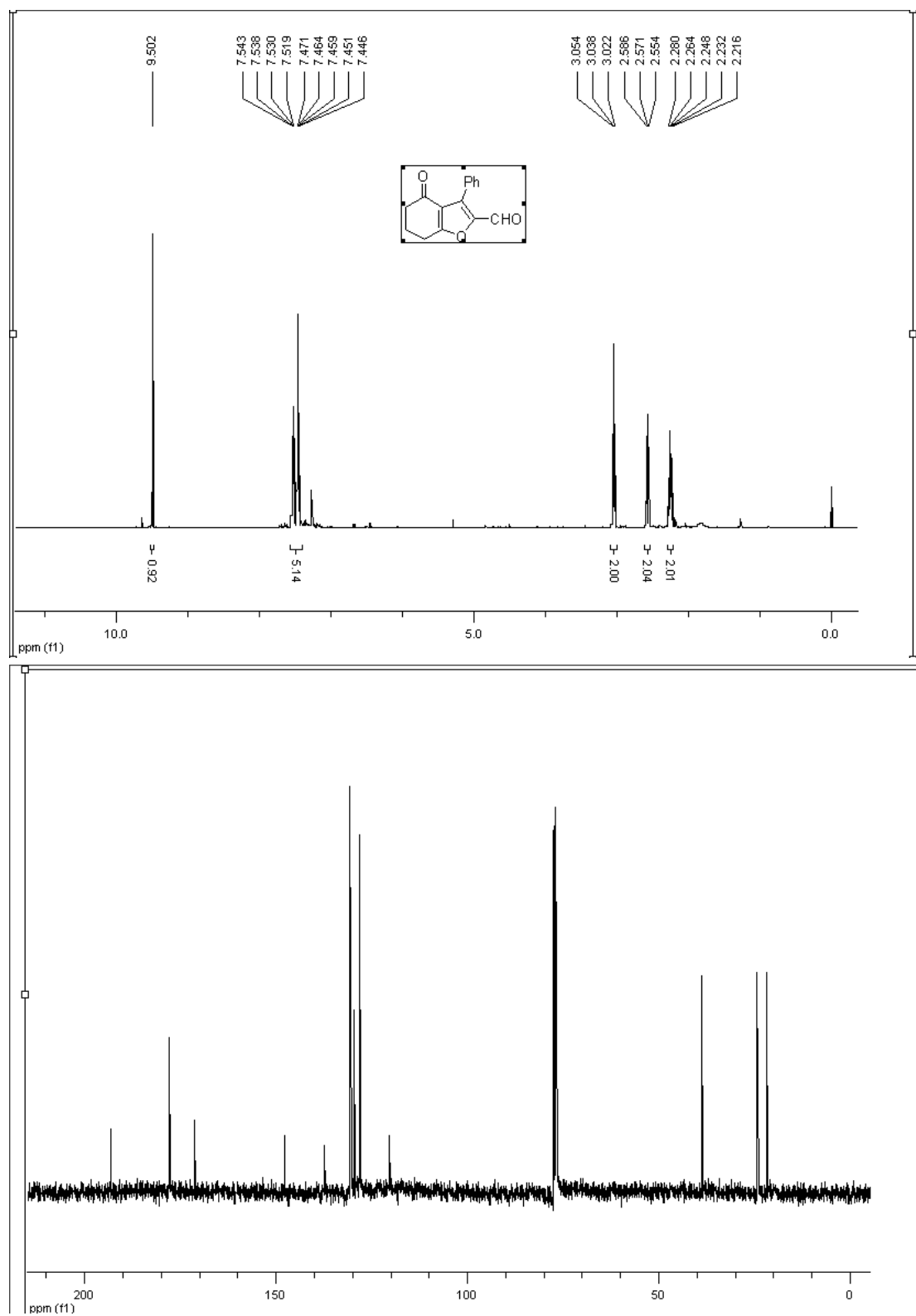
Reference

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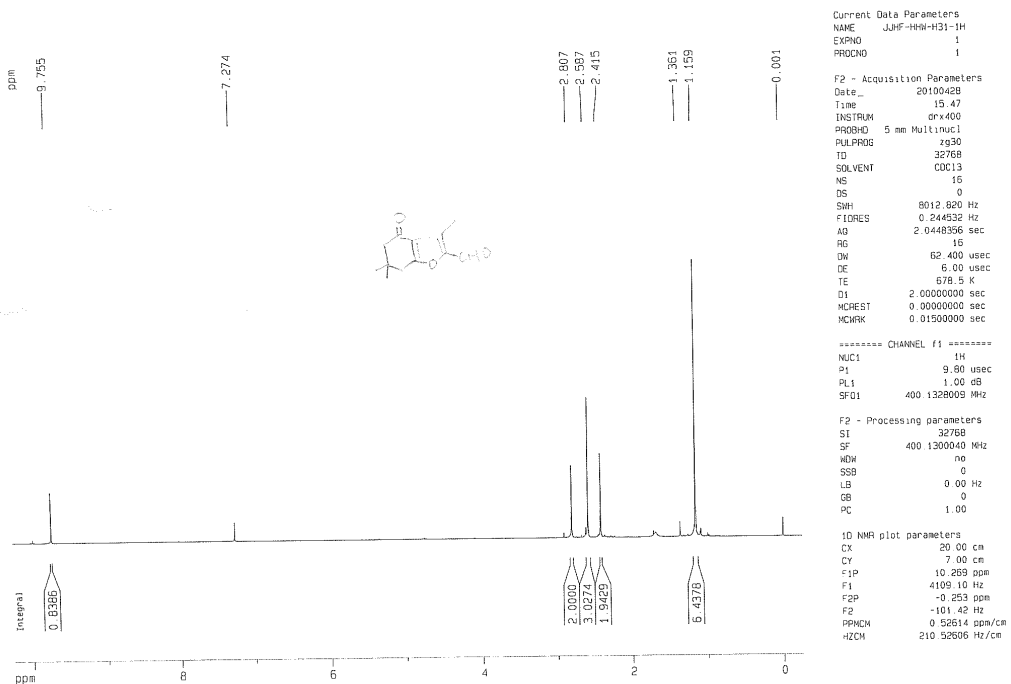
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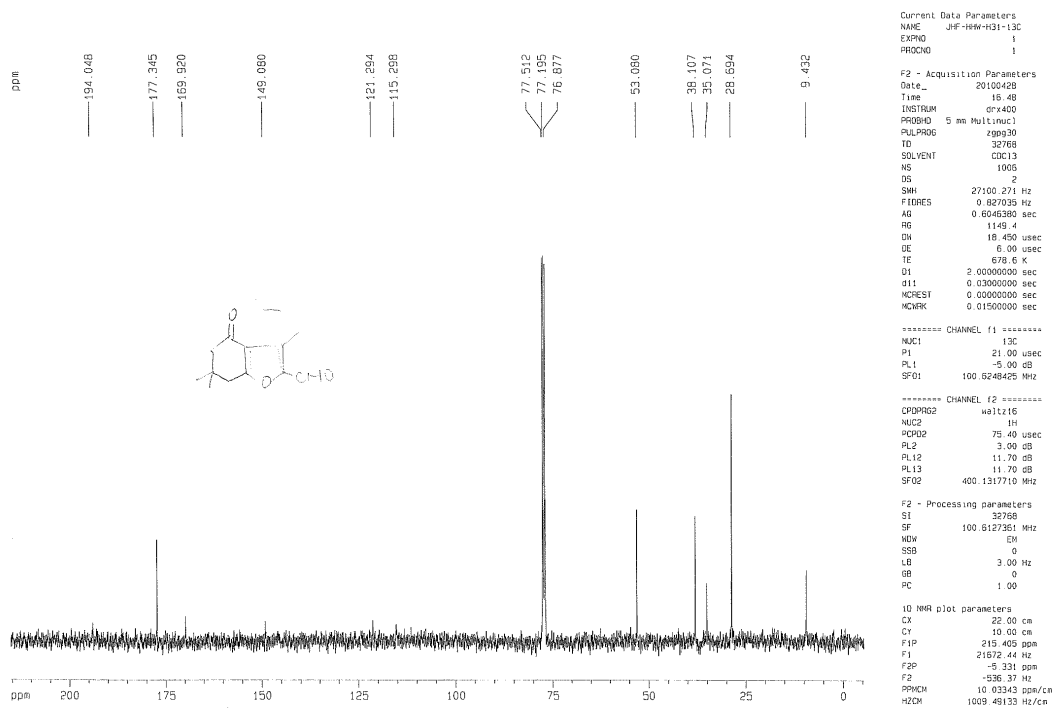
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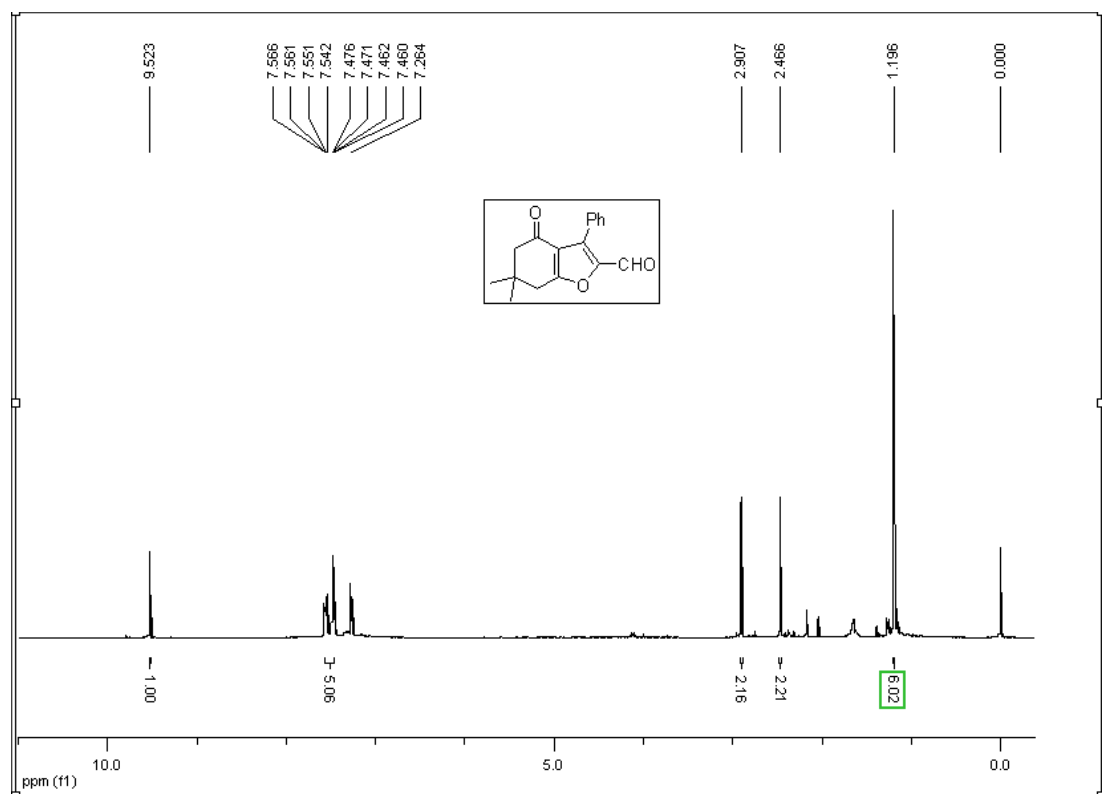
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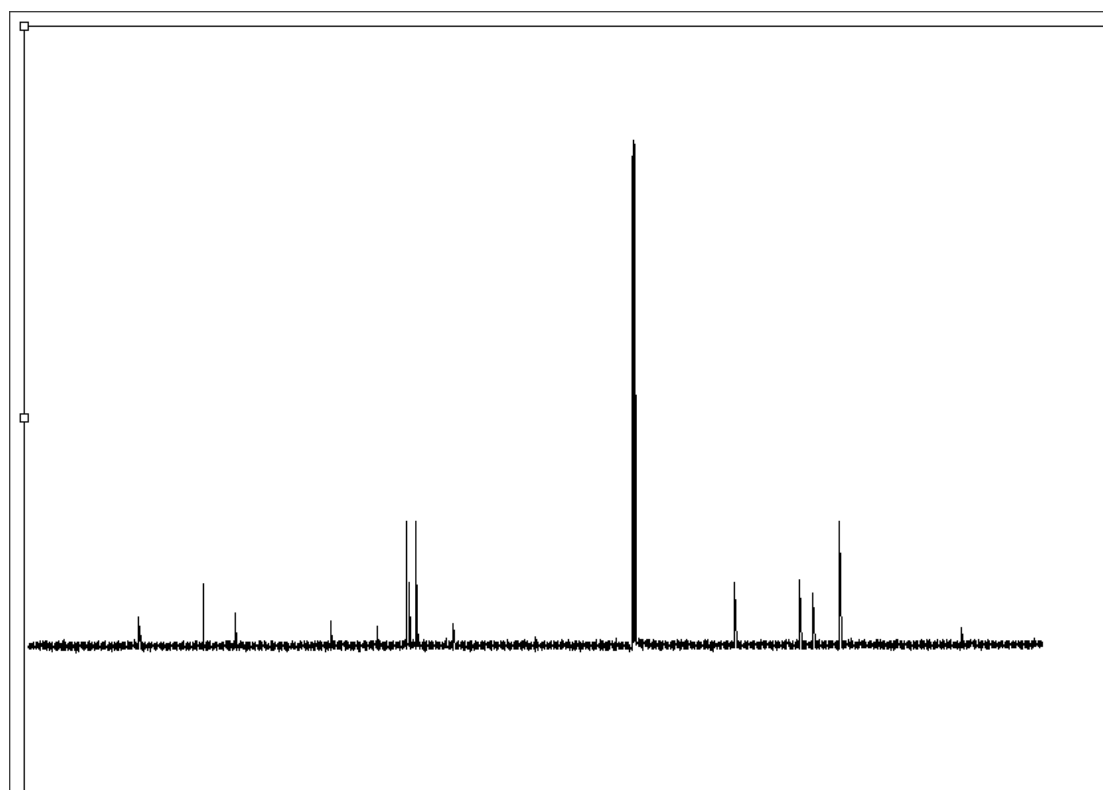






4bb





4ca

