

## Supporting information for the paper:

Expanding the scope of In-promoted allylation reaction: 4-(bromomethyl)-1,3-dioxol-2-one as a synthetic equivalent of a 3-arylhydroxyacetone enolate

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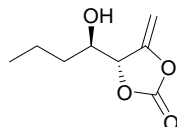
### General experimental:

IR spectra were recorded on a Nicolet 6700 FT instrument, and are expressed in  $\text{cm}^{-1}$ . NMR spectra were recorded on a Varian Gemini 200 ( $^1\text{H}$  NMR at 200 MHz,  $^{13}\text{C}$  NMR at 50 MHz, for samples in deuterated chloroform), and on Bruker Avance III 500 ( $^1\text{H}$  NMR at 500 MHz,  $^{13}\text{C}$  NMR at 125 MHz). Chemical shifts are expressed in ppm ( $\delta$ ) using tetramethylsilane as internal standard, coupling constants ( $J$ ) are in Hz. Reactions induced by microwave irradiation were performed in a Biotage Initiator 2.5. microwave reactor. All chromatographic separations<sup>i</sup> were performed on Silica, 10-18, 60A, ICN Biomedicals. Standard techniques were used for the purification of reagents and solvents.<sup>ii</sup> Mass spectra were obtained on Agilent technologies 6210 TOF LC/MS instrument (LC: series 1200). Microanalyses were performed at the Vario EL III instrument CHNOS Elementar Analyzer, Elementar Analysensysteme GmbH, Hanau-Germany. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

### Preparation of starting enol carbonates

Enol carbonates **2a-d** were prepared according literature procedures.<sup>iii</sup>

#### 4-(1-Hydroxybutyl)-5-methylene-1,3-dioxolan-2-one **2e**

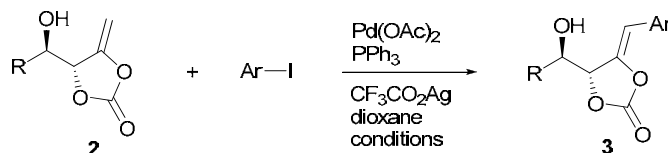


Butyraldehyde (27 mg, 33 $\mu\text{L}$ , 0.37 mmol) was added to a mixture of 4-(bromomethyl)-1,3-dioxol-2-one **1** (100 mg, 0.56 mmol), indium (64 mg, 0.56 mmol), THF (1 mL) and water (2 mL), and the reaction mixture was stirred at rt. The reaction was monitored by TLC (eluent: 20% EtOAc in petroleum-ether) and it was complete after 15 min. The reaction mixture was diluted with dichloromethane (10 mL) and water (10 mL), the aqueous layer was extracted with dichloromethane (2 x 10 mL), combined organic extracts were dried over anhydrous  $\text{MgSO}_4$ , filtered, concentrated under reduced pressure and the crude product was purified by dry-flash chromatography ( $\text{SiO}_2$ ; eluent: 20% EtOAc in petroleum-ether). 4-(1-Hydroxybutyl)-5-methylene-1,3-dioxolan-2-one was obtained as viscous oil (51 mg, 89 %)

Physical data for **2e**: FT-IR (film,  $\text{cm}^{-1}$ ): 3475, 2963, 2938, 2875, 1830, 1690, 1152, 1059.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz): 5.07-5.02 (m, 1H), 4.97 (dd,  $J_1 = 3.9$  Hz,  $J_2 = 2.3$  Hz, 1H), 4.50 (dd,  $J_1 = 3.9$  Hz,  $J_2 = 1.7$  Hz, 1H), 3.92-3.79 (m, 1H), 2.62 (d,  $J = 3.4$  Hz, 1H), 1.59-1.34 (m, 4H), 0.97 (t,  $J = 7.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz): 152.4, 149.8,

89.0, 82.1, 71.6, 32.9, 18.6, 13.7. HRMS (ESI): calcd. for  $[C_8H_{12}O_4 + NH_4^+]$ : 190.1074, found for  $[M+NH_4]^+$ : 190.1073.

### Experimental procedures for the Heck reactions



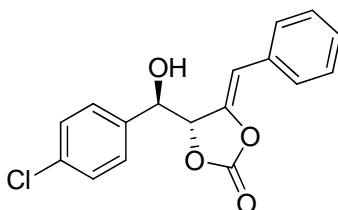
#### General procedure for the Heck reaction under thermal conditions

To a solution of enol carbonate **2** (0.1 mmol) in dioxane (1 mL) were added aryl iodide (0.15 mmol), silver trifluoroacetate (0.15 mmol), palladium acetate (0.02 mmol) and triphenylphosphine (0.02 mmol) under an argon atmosphere. The reaction mixture was vigorously stirred and heated to 95 °C, while the progress of the reaction was monitored by TLC (SiO<sub>2</sub> plates, eluent: 30% EtOAc in benzene). Upon completion, the reaction mixture was partitioned between water and EtOAc, the water layer was extracted with EtOAc and the combined organic extract was dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated under reduced pressure. Purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether) afforded the title compound **3**.

#### General procedure for the Heck reaction under microwave conditions

A solution of enol carbonate **2** (1.0 mmol) in dioxane (1.5 mL) is put in a microwave tube, equipped with a magnetic stirring bar and a septum. To this solution were added (in the following order): aryl iodide (0.12 mmol), silver trifluoroacetate (0.12 mmol), palladium acetate (7.5 μmol) and triphenylphosphine (7.5 μmol), under an argon atmosphere. A tube with the reaction mixture was transferred into a microwave reactor (Biotage Initiator 2.5) and irradiated with a 160 W, over 30 min. An additional amount of palladium acetate (7.5 μmol) and triphenylphosphine (7.5 μmol) was added and irradiation was continued for additional 20 min, when the reaction was complete. Work-up as for the thermally induced reaction afforded compound **3**.

#### 4-Benzylidene-5-((4-chlorophenyl)-hydroxymethyl)-1,3-dioxolan-2-one **3a**



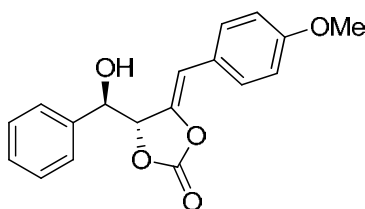
According to the general procedure for the Heck reaction under thermal conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (23.5 mg, 0.098 mmol), iodobenzene (30.0 mg, 17 μL, 0.15 mmol), silver trifluoroacetate

(33.2 mg, 0.15 mmol), palladium acetate (4.4 mg, 0.02 mmol) and triphenylphosphine (5.1 mg, 0.02 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 18.0 mg (58%) of the title compound **3a** was obtained as white crystals.

According to the general procedure for the Heck reaction under thermal conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (23.5 mg, 0.098 mmol), iodobenzene (30.0 mg, 17 μL, 0.15 mmol), silver trifluoroacetate (33.2 mg, 0.15 mmol), palladium acetate (4.4 mg, 0.02 mmol) and triphenylphosphine (5.1 mg, 0.02 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 18.9 mg (61%) of the title compound **3a** was obtained as white crystals.

Physical data for **3a**: mp 115-117 °C; FT-IR (film, cm<sup>-1</sup>): 3475, 3029, 1832, 1705, 1494, 1370, 1232, 1129, 1086, 1054, 762, 697. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.40-7.24 (m, 9H), 5.32 (dd, *J*<sub>1</sub> = 3.7 Hz, *J*<sub>2</sub> = 1.8 Hz, 1H), 5.13 (d, *J* = 3.7 Hz, 1H), 5.09 (d, *J* = 1.5 Hz, 1H), 2.86 (bs, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 152.1 (C), 140.6 (C), 134.9 (C), 134.8 (C), 131.9 (C), 128.9 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 127.9 (CH), 106.0 (CH), 82.6 (CH), 73.7 (CH). HRMS (ESI): calcd. for [C<sub>17</sub>H<sub>13</sub>ClO<sub>4</sub> + NH<sub>4</sub><sup>+</sup>]: 334.0841, found for [M+NH<sub>4</sub>]<sup>+</sup>: 334.0839.

#### 4-(Hydroxy(phenyl)methyl)-5-(4-methoxybenzylidene)-1,3-dioxolan-2-one **3b**



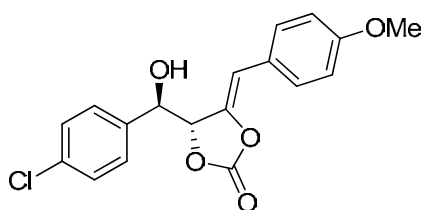
According to the general procedure for the Heck reaction under thermal conditions, starting from 4-(hydroxy(phenyl)methyl)-5-methylene-1,3-dioxolan-2-one **2b** (20.0 mg, 0.097 mmol), 4-iodoanisole (31.8 mg, 0.15 mmol), silver trifluoroacetate (32.2 mg, 0.15 mmol), palladium acetate (4.4 mg, 0.019 mmol) and triphenylphosphine (5.0 mg, 0.019 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 30% EtOAc in petroleum-ether), 15.4 mg (51%) of the title compound **3b** was obtained as a yellow oil.

According to the general procedure for the Heck reaction under microwaves conditions, starting from 4-(hydroxy(phenyl)methyl)-5-methylene-1,3-dioxolan-2-one **2b** (15.0 mg, 0.073 mmol), 4-iodoanisole (24.0 mg, 0.12 mmol), silver trifluoroacetate (24.2 mg, 0.12 mmol), palladium acetate (3.3 mg, 0.015 mmol) and triphenylphosphine (4.0 mg, 0.015

mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 30% EtOAc in petroleum-ether), 11.2 mg (49%) of the title compound **3b** was obtained as a yellow oil.

Physical data for **3b**: FT-IR (film, cm<sup>-1</sup>): 3447, 2932, 1823, 1512, 1251, 1183, 1051, 762, 703, 623. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.40 (s, 5H), 7.34 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.35 (dd, *J*<sub>1</sub> = 3.5 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 5.15 (bs, 1H), 5.01 (d, *J* = 1.5 Hz, 1H), 3.80 (s, 3H), 2.62 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 159.1 (C), 152.3 (C), 139.1 (C), 136.5 (C), 130.0 (CH), 128.9 (CH), 128.7 (CH), 126.6 (CH), 124.8 (C), 114.0 (CH), 105.5 (CH), 82.8 (CH), 74.3 (CH), 55.3 (CH<sub>3</sub>). HRMS (ESI): calcd. for [C<sub>18</sub>H<sub>16</sub>O<sub>5</sub> + NH<sub>4</sub><sup>+</sup>]: 330.1336, found for [M+NH<sub>4</sub>]<sup>+</sup>: 330.1341.

#### 4-((4-Chlorophenyl)(hydroxy)methyl)-5-(4-methoxybenzylidene)-1,3-dioxolan-2-one **3c**



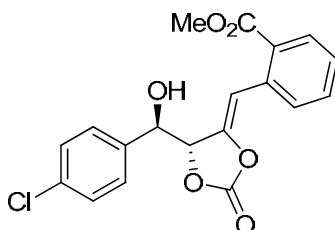
According to the general procedure for the Heck reaction under thermal conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (40.0 mg, 0.17 mmol), 4-iodoanisole (56.0 mg, 0.25 mmol), silver trifluoroacetate (56.0 mg, 0.25 mmol), palladium acetate (7.6 mg, 0.034 mmol) and triphenylphosphine (9.0 mg, 0.034 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 29.0 mg (55%) of the title compound **3c** was obtained as a yellow oil.

According to the general procedure for the Heck reaction under microwave conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (40.0 mg, 0.17 mmol), 4-iodoanisole (56.0 mg, 0.25 mmol), silver trifluoroacetate (56.0 mg, 0.25 mmol), palladium acetate (7.6 mg, 0.034 mmol) and triphenylphosphine (9.0 mg, 0.034 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 26.0 mg (50%) of the title compound **3c** was obtained as a yellow oil.

Physical data for **3c**: FT-IR (film, cm<sup>-1</sup>): 3467, 2932, 1820, 1702, 1512, 1252, 1129, 1080, 857, 764, 739. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.41-7.34 (m, 6H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.31 (dd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 5.11 (bs, 1H), 5.08 (d, *J* = 1.5 Hz, 1H), 3.81 (s, 3H), 2.60 (d, *J* = 4.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 159.0 (C), 152.1 (C), 138.9 (C), 135.0 (C), 134.9 (C), 130.1 (CH), 128.9 (CH), 128.0 (CH), 124.6 (C), 114.1 (CH), 105.7 (CH), 82.5 (CH), 73.9 (CH), 55.3 (CH<sub>3</sub>). HRMS (ESI): calcd. for [C<sub>18</sub>H<sub>15</sub>ClO<sub>5</sub>

+ NH<sub>4</sub><sup>+</sup>]: 364.0946, found for [M+NH<sub>4</sub>]<sup>+</sup>: 364.0945. Microanal: calcd. for C<sub>18</sub>H<sub>15</sub>ClO<sub>5</sub>: C 62.33, H 4.33; found: C 62.01, H 4.42.

*Methyl 2-((4-chlorophenyl)(hydroxy)methyl)-2-oxo-1,3-dioxolan-4-ylidene)methyl)benzoate 3d*

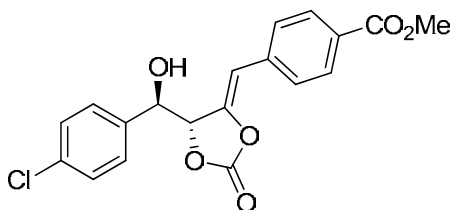


According to the general procedure for the Heck reaction under thermal conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (40.0 mg, 0.17 mmol), methyl 2-iodobenzoate (65.0 mg, 0.25 mmol), silver trifluoroacetate (56.3 mg, 0.25 mmol), palladium acetate (8.0 mg, 0.034 mmol) and triphenylphosphine (8.8 mg, 0.034 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 31.2 mg (50%) of the title compound **3d** was obtained as a yellow oil.

According to the general procedure for the Heck reaction under microwave conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (10.0 mg, 0.042 mmol), methyl 2-iodobenzoate (16.3 mg, 0.063 mmol), silver trifluoroacetate (14.1 mg, 0.63 mmol), palladium acetate (2.0 mg, 0.0084 mmol) and triphenylphosphine (2.2 mg, 0.0084 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 6.3 mg (40%) of the title compound **3d** was obtained as a yellow oil.

Physical data for **3d**: FT-IR (film, cm<sup>-1</sup>): 3479, 2953, 1835, 1720, 1491, 1299, 1269, 1126, 1085, 980, 762. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.96 (dd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.6 Hz, 1H), 7.66 (dd, *J*<sub>1</sub> = 7.8 Hz, *J*<sub>2</sub> = 1.6 Hz, 1H), 7.55 (td, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.6 Hz, 1H), 7.45-7.35 (m, 5H), 6.23 (d, *J* = 1.5 Hz, 1H), 5.36 (dd, *J*<sub>1</sub> = 4.3 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 5.04 (d, *J* = 4.3 Hz, 1H), 3.88 (s, 3H), 3.44 (bs, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): 167.6 (C), 151.7 (C), 142.2 (C), 135.3 (C), 134.7 (C), 133.0 (C), 132.5 (CH), 130.7 (CH), 130.4 (CH), 128.9 (CH), 128.3 (C), 128.1 (CH), 127.7 (CH), 104.0 (CH), 82.5 (CH), 74.2 (CH), 52.4 (CH<sub>3</sub>). HRMS (ESI): calcd. for [C<sub>19</sub>H<sub>15</sub>ClO<sub>6</sub> + NH<sub>4</sub>]<sup>+</sup>: 392.0895, found for [M+NH<sub>4</sub>]<sup>+</sup>: 392.0894.

*Methyl 4-((4-chlorophenyl)(hydroxy)methyl)-2-oxo-1,3-dioxolan-4-ylidene)methyl)benzoate 3e*

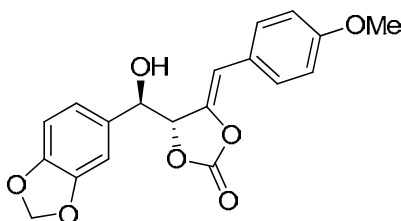


According to the general procedure for the Heck reaction under thermal conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (10.0 mg, 0.042 mmol), methyl 4-iodobenzoate (16.0 mg, 0.06 mmol), silver trifluoroacetate (13.3 mg, 0.06 mmol), palladium acetate (2.0 mg, 0.008 mmol) and triphenylphosphine (2.2 mg, 0.008 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 9.6 mg (61%) of the title compound **3e** as yellowish crystals.

According to the general procedure for the Heck reaction under microwave conditions, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2a** (10.0 mg, 0.042 mmol), methyl 4-iodobenzoate (16.0 mg, 0.06 mmol), silver trifluoroacetate (13.3 mg, 0.06 mmol), palladium acetate (2.0 mg, 0.008 mmol) and triphenylphosphine (2.2 mg, 0.008 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 7.2 mg (46%) of the title compound **3e** as yellowish crystals.

Physical data for **3e**: mp 163-164 °C; FT-IR (KBr, cm<sup>-1</sup>): 3481, 2955, 2928, 1835, 1722, 1438, 1288, 1188, 1116, 1087, 767. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 7.97 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.41-7.37 (m, 4H), 5.35 (dd, *J*<sub>1</sub> = 3.9 Hz, *J*<sub>2</sub> = 1.6 Hz, 1 H), 5.18 (bs, 1H), 5.12 (d, *J* = 1.6 Hz, 1H), 3.91 (s, 3H), 2.93 (d, *J* = 3.9 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz): 166.7 (C), 142.6 (C), 136.4 (C), 135.2 (C), 134.8 (C), 129.9 (CH), 129.1 (C), 129.0 (CH), 128.5 (CH), 127.9 (CH), 127.5 (C), 105.1 (CH), 82.6 (CH), 73.6 (CH), 52.2 (CH<sub>3</sub>). HRMS (ESI): calcd for [C<sub>19</sub>H<sub>15</sub>ClO<sub>6</sub> + NH<sub>4</sub><sup>+</sup>]: 392.0557, found for [M+NH<sub>4</sub>]<sup>+</sup>: 392.0907.

*4-(Benzo[d][1,3]dioxol-5-yl)(hydroxy)methyl)-5-(4-methoxybenzylidene)-1,3-dioxolan-2-one 3f*

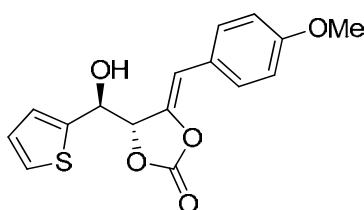


According to the general procedure for the Heck reaction under thermal conditions, starting from 4-(benzo[d][1,3]dioxol-5-yl(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2c** (40.0 mg, 0.16 mmol), 4-iodoanisole (57.0 mg, 0.24 mmol), silver trifluoroacetate (53.0 mg, 0.24 mmol), palladium acetate (7.0 mg, 0.032 mmol) and triphenylphosphine (8.4 mg, 0.032 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 30.0 mg (53%) of the title compound **3f** was obtained as a yellow oil.

According to the general procedure for the Heck reaction under microwave conditions, starting from 4-(benzo[d][1,3]dioxol-5-yl(hydroxy)methyl)-5-methylene-1,3-dioxolan-2-one **2c** (40.0 mg, 0.16 mmol), 4-iodoanisole (57.0 mg, 0.24 mmol), silver trifluoroacetate (53.0 mg, 0.24 mmol), palladium acetate (7.0 mg, 0.032 mmol) and triphenylphosphine (8.4 mg, 0.032 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 23.0 mg (40%) of the title compound **3f** was obtained as a yellow oil.

Physical data for **3f**: FT-IR (film, cm<sup>-1</sup>): 3500, 2927, 1827, 1513, 1255, 1130, 1042. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.38 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 1.8 Hz, 1H), 6.86 (s, 1H), 6.84 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 5.98 (s, 2H), 5.28 (dd, *J*<sub>1</sub> = 4.0 Hz, *J*<sub>2</sub> = 1.9 Hz, 1H), 5.19 (d, *J* = 1.9 Hz, 1H), 4.99 (bs, 1H), 3.80 (s, 3H), 2.74 (d, *J* = 3.5 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 159.1 (C), 152.3 (C), 148.0 (C), 147.9 (C), 139.4 (C), 130.5 (C), 130.0 (CH), 124.8 (C), 120.3 (CH), 114.0 (CH), 108.3 (CH), 107.0 (CH), 105.4 (CH), 101.3 (CH<sub>2</sub>), 82.8 (CH), 74.2 (CH), 55.3 (CH<sub>3</sub>). HRMS (ESI): calcd. for [C<sub>19</sub>H<sub>16</sub>O<sub>7</sub> + NH<sub>4</sub><sup>+</sup>]: 374.1234, found for [M+NH<sub>4</sub>]<sup>+</sup>: 374.1238.

#### 4-(Hydroxy(thiophen-2-yl)methyl)-5-(4-methoxybenzylidene)-1,3-dioxolan-2-one **3g**



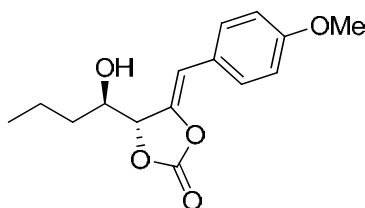
According to the general procedure for the Heck reaction under thermal conditions, starting from 4-(hydroxy(thiophen-2-yl)methyl)-5-methylene-1,3-dioxolan-2-one **2d** (27.5 mg, 0.13 mmol), 4-iodoanisole (42.6 mg, 0.2 mmol), silver trifluoroacetate (43.1 mg, 0.2 mmol), palladium acetate (5.8 mg, 0.026 mmol) and triphenylphosphine (6.8 mg, 0.026 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 30.0 mg (53%) of the title compound **3g** was obtained as a yellow oil.



According to the general procedure for the Heck reaction under microwave conditions, starting from 4-(hydroxy(thiophen-2-yl)methyl)-5-methylene-1,3-dioxolan-2-one **2d** (30.4 mg, 0.14 mmol), 4-iodoanisole (46.0 mg, 0.21 mmol), silver trifluoroacetate (46.0 mg, 0.21 mmol), palladium acetate (6.3 mg, 0.028 mmol) and triphenylphosphine (7.3 mg, 0.028 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 21.0 mg (47%) of the title compound **3g** was obtained as a yellow oil.

Physical data for **3g**: FT-IR (film, cm<sup>-1</sup>): 3463, 2960, 1830, 1705, 1609, 1515, 1254, 1187, 1130, 1085, 858, 712. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.38 (d, *J* = 9.0 Hz, 2H), 7.34 (dd, *J*<sub>1</sub> = 5.0 Hz, *J*<sub>2</sub> = 1.5 Hz, 1H), 7.09-7.08 (m, 1H), 7.04 (dd, *J*<sub>1</sub> = 5.0 Hz, *J*<sub>2</sub> = 4.5 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H), 5.39 (dd, *J*<sub>1</sub> = 3.7 Hz, *J*<sub>2</sub> = 1.7 Hz, 1H), 5.28 (d, *J* = 3.7 Hz, 1H), 5.26 (d, *J* = 1.7 Hz, 1H), 3.79 (s, 3H), 3.12 (bs, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): 159.1 (C), 152.2 (C), 139.8 (C), 130.1 (CH), 128.3 (C), 127.2 (CH), 126.1 (CH), 125.5 (CH), 124.7 (C), 114.0 (CH), 105.5 (CH), 82.5 (CH), 71.4 (CH), 55.3 (CH<sub>3</sub>). HRMS (ESI): calcd. for [C<sub>16</sub>H<sub>14</sub>SO<sub>5</sub> + NH<sub>4</sub><sup>+</sup>]: 336.0900, found for [M+NH<sub>4</sub>]<sup>+</sup>: 336.0900.

#### 4-(1-Hydroxybutyl)-5-(4-methoxybenzylidene)-1,3-dioxolan-2-one **3h**



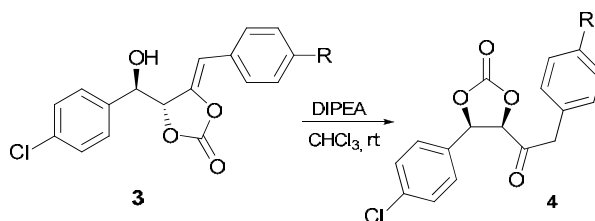
According to the general procedure for the Heck reaction under thermal conditions, starting from 4-(1-hydroxybutyl)-5-methylene-1,3-dioxolan-2-one **2e** (30 mg, 0.19 mmol), 4-iodoanisole (66.0 mg, 0.29 mmol), silver trifluoroacetate (66.3 mg, 0.30 mmol), palladium acetate (8.5 mg, 0.038 mmol) and triphenylphosphine (10.0 mg, 0.038 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 20.0 mg (38 %) of the title compound **3h** was obtained as a yellow oil.

According to the general procedure for the Heck reaction under microwave conditions, starting from 4-(1-hydroxybutyl)-5-methylene-1,3-dioxolan-2-one **2e** (56.0 mg, 0.54 mmol), 4-iodoanisole (118.0 mg, 0.54 mmol), silver trifluoroacetate (119.0 mg, 0.54 mmol), palladium acetate (16.1 mg, 0.072 mmol) and triphenylphosphine (18.8 mg, 0.072 mmol), after purification by dry-flash chromatography (SiO<sub>2</sub>; eluent: 20% EtOAc in petroleum-ether), 39.4 mg (40%) of the title compound **3h** was obtained as a yellow oil.

Physical data for **3h**: FT-IR (film, cm<sup>-1</sup>): 3491, 2963, 2365, 1828, 1706, 1611, 1516, 1254, 1188, 1266, 1053. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): 7.49 (d, *J* = 8.8 Hz, 2H), 6.89 (d,

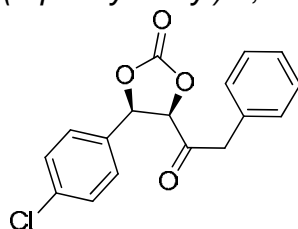
$J = 8.8$  Hz, 2H), 5.61 (d,  $J = 1.8$  Hz, 1H), 5.12 (dd,  $J_1 = 4.0$  Hz,  $J_2 = 1.8$  Hz, 1H), 3.89-3.84 (m, 1H), 3.82 (s, 3H), 2.12 (d,  $J = 7.0$  Hz, 1H), 1.61-1.58 (m, 3H), 1.44-1.42 (m, 1H), 0.98 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz): 159.1 (C), 152.3 (C), 140.4 (C), 130.1 (CH), 124.8 (C), 114.1 (CH), 104.8 (CH), 82.7 (CH), 72.5 (CH), 55.3 ( $\text{CH}_3$ ), 33.3 ( $\text{CH}_2$ ), 18.7 ( $\text{CH}_2$ ), 13.8 ( $\text{CH}_3$ ). HRMS (ESI): calcd. for  $[\text{C}_{15}\text{H}_{18}\text{O}_5 + \text{NH}_4^+]$ : 296.1492, found for  $[\text{M} + \text{NH}_4]^+$ : 296.1489.

### General procedure for the isomerization of carbonates **3a-c**:



A solution of carbonate **3** (0.08 mmol) and DIPEA (0.04 mmol) in chloroform (1.0 mL) was stirred at rt for 1 h. The solvent was removed under reduced pressure and the crude product was purified by dry-flash chromatography ( $\text{SiO}_2$ ; eluent: 20% EtOAc in petroleum-ether), to give the compound **4**.

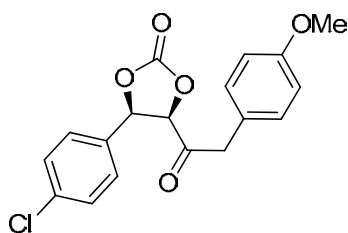
#### *cis*-4-(4-Chlorophenyl)-5-(2-phenylacetyl)-1,3-dioxolan-2-one **4a**



According to the general procedure for the isomerization of carbonates, starting from 4-benzylidene-5-((4-chlorophenyl)-hydroxymethyl)-1,3-dioxolan-2-one **3a** (24.0 mg, 0.08 mmol) and DIPEA (2.2 mg, 3.0  $\mu\text{L}$ , 0.04 mmol), after purification by dry-flash chromatography ( $\text{SiO}_2$ ; eluent: 20% EtOAc in petroleum-ether), 21.6 mg (80%) of the title compound **4a** was obtained as white crystals.

Physical data for **4a** 142-143  $^\circ\text{C}$ ; FT-IR (KBr,  $\text{cm}^{-1}$ ): 3064, 2934, 1808, 1733, 1600, 1494, 1335, 1174, 1154, 1057.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.38 (d,  $J = 8.4$  Hz, 2H), 7.26 - 7.22 (m, 3H), 7.16 (d,  $J = 8.4$  Hz, 2H), 6.74 - 6.69 (m, 2H), 5.90 (d,  $J = 8.7$  Hz, 1H), 5.34 (d,  $J = 8.7$  Hz, 1H), 3.54 (d,  $J = 16.9$  Hz, 1H), 3.29 (d,  $J = 16.9$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 201.0 (C), 153.3 (C), 136.2 (C), 130.5 (C), 130.4 (C), 129.5 (CH), 129.4 (CH), 128.7 (CH), 127.7 (CH), 127.6 (CH), 81.7 (CH), 78.8 (CH), 47.2 ( $\text{CH}_2$ ). HRMS (ESI): calcd. for  $[\text{C}_{17}\text{H}_{13}\text{ClO}_4 + \text{NH}_4^+]$ : 334.0502, found for  $[\text{M} + \text{NH}_4]^+$ : 334.0831.

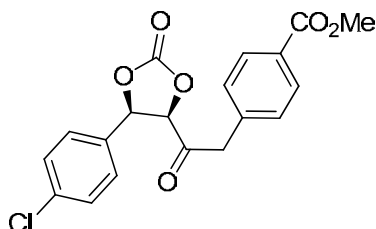
*cis*-4-(4-Chlorophenyl)-5-(2-(4-methoxyphenyl)acetyl)-1,3-dioxolan-2-one **4b**



According to the general procedure for the isomerization of carbonates, starting from 4-((4-chlorophenyl)(hydroxy)methyl)-5-(4-methoxybenzylidene)-1,3-dioxolan-2-one **3c** (13.8 mg, 0.04 mmol) and DIPEA (2.2 mg, 3.0  $\mu$ L, 0.04 mmol), after purification by dry-flash chromatography ( $\text{SiO}_2$ ; eluent: 30% EtOAc in petroleum-ether), 10.8 mg (78%) of the title compound **4b** was obtained as white crystals.

Physical data for **4b** 121-123  $^\circ\text{C}$ ; FT-IR (KBr,  $\text{cm}^{-1}$ ): 2930, 2832, 1819, 1728, 1515, 1331, 1249, 1173, 1063, 841, 755.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.36 (d,  $J = 8.3$  Hz, 2H), 7.15 (d,  $J = 8.3$  Hz, 2H), 6.77 (d,  $J = 8.5$  Hz, 2H), 6.64 (d,  $J = 8.5$  Hz, 2H), 5.88 (d,  $J = 8.8$  Hz, 1H), 5.32 (d,  $J = 8.8$  Hz, 1H), 3.77 (s, 3H), 3.47 (d,  $J = 17.0$  Hz, 1H), 3.25 (d,  $J = 17.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 201.2 (C), 159.0 (C), 153.3 (C), 136.1 (C), 130.5 (CH), 129.3 (CH), 127.7 (CH), 127.5 (C), 122.3 (C), 114.2 (CH), 81.7 (CH), 78.8 (CH), 55.2 ( $\text{CH}_3$ ), 46.4 ( $\text{CH}_2$ ). HRMS (ESI): calcd. for  $[\text{C}_{18}\text{H}_{15}\text{ClO}_5 + \text{NH}_4^+]$ : 364.0946, found for  $[\text{M} + \text{NH}_4]^+$ : 364.0933.

*cis*-Methyl 4-((4-chlorophenyl)-2-oxo-1,3-dioxolan-4-yl)-2-oxoethyl)benzoate **4c**



According to the general procedure for the isomerization of carbonates, starting from methyl 4-((4-chlorophenyl)(hydroxy)methyl)-2-oxo-1,3-dioxolan-4-ylidene)methyl) benzoate **3e** (6.0 mg, 0.016 mmol) and DIPEA (1.0 mg, 1.4  $\mu$ L, 0.008 mmol), after purification by dry-flash chromatography ( $\text{SiO}_2$ ; eluent: 30% EtOAc in petroleum-ether), 4.1 mg (68%) of the title compound **4c** was obtained as viscous oil.

Physical data for **4c**: FT-IR (KBr,  $\text{cm}^{-1}$ ): 3094, 2953, 1810, 1717, 1612, 1282, 1165, 1060, 766.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.90 (d,  $J = 8.4$  Hz, 2H), 7.39 (d,  $J = 8.4$  Hz, 2H), 7.18 (d,  $J = 8.8$  Hz, 2H), 6.74 (d,  $J = 8.6$  Hz, 2H), 5.94 (d,  $J = 8.8$  Hz, 1H), 5.35 (d,  $J = 8.8$  Hz, 1H), 3.90 (s, 3H), 3.48 (d,  $J = 17.1$  Hz, 1H), 3.37 (d,  $J = 17.1$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 200.6 (C), 166.7 (C), 153.2 (C), 136.4 (C), 135.7 (C), 130.4 (C), 129.9 (CH),

129.5 (CH), 129.4 (CH), 128.5 (C), 127.7 (CH), 81.9 (CH), 78.6 (CH), 52.1 (CH<sub>2</sub>), 47.0 (CH<sub>3</sub>). HRMS (ESI): calcd. for [C<sub>19</sub>H<sub>15</sub>ClO<sub>6</sub> + NH<sub>4</sub><sup>+</sup>]: 392.0557, found for [M+NH<sub>4</sub>]<sup>+</sup>: 392.0892.

## References

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<sup>i</sup> For description of the technique of dry-flash chromatography, see: a) Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25; b) *Vogel's Textbook of Practical Organic Chemistry*, Longman Scientific & Technical, 5<sup>th</sup> edition, London, 1989, p. 220; c) A recent account which includes some improvements of the separation technique: Pedersen, D. S.; Rosenbohm, C. *Synthesis* **2001**, 2431.

<sup>ii</sup> Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3<sup>rd</sup> edition, Pergamon Press, **1988**.

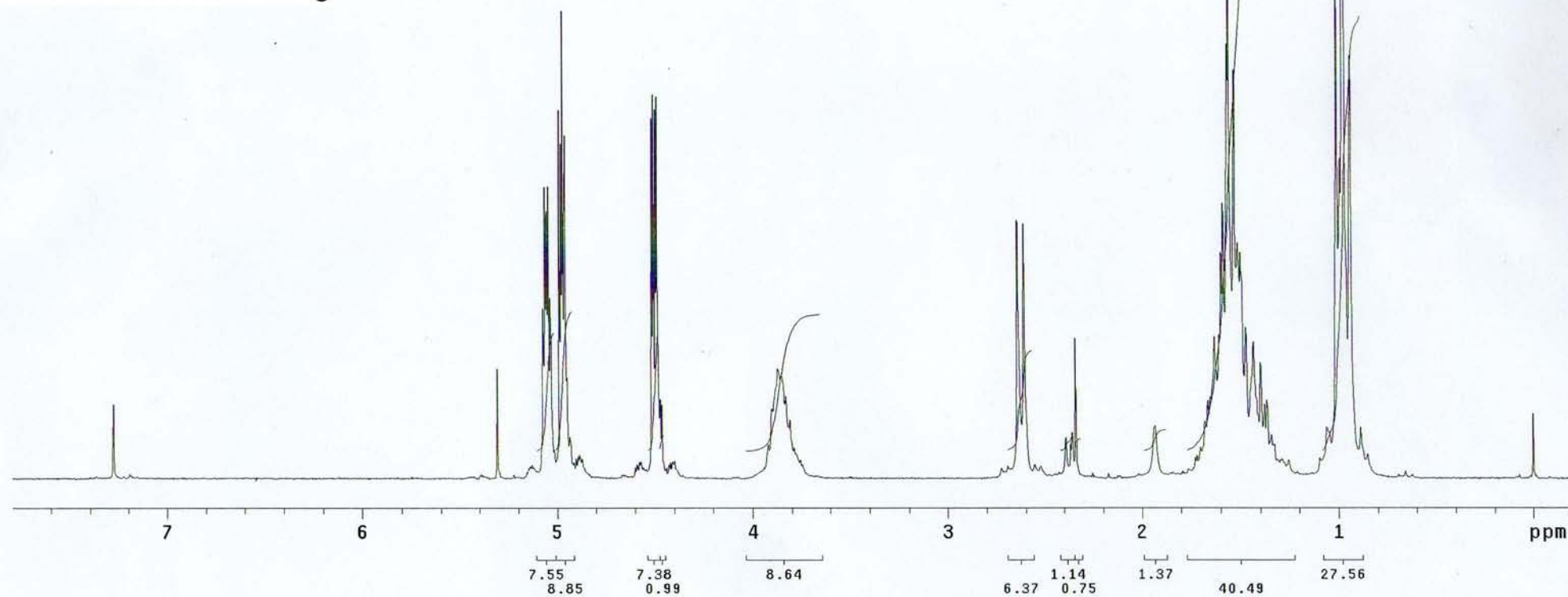
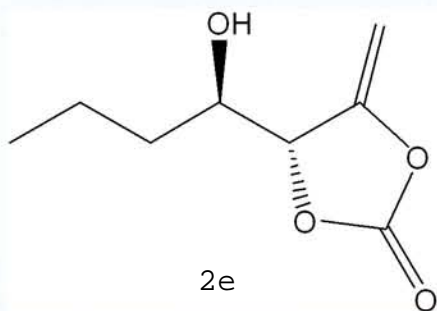
<sup>iii</sup> Bigovic, M., Maslak, V., Tokic-Vujosevic, Z., Saicic, R. N. *Org. Lett.* **2011**, *13*, 4720.

VM-MB-7-24A

Solvent: cdc13  
Ambient temperature  
GEMINI-200 "nmr"

PULSE SEQUENCE

Relax. delay arrayed  
1st pulse arrayed  
2nd pulse 90.0 degrees  
Acq. time 1.391 sec  
Width 4600.0 Hz  
Arrayed repetitions  
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DATA PROCESSING  
FT size 16384  
Total time 1 minute

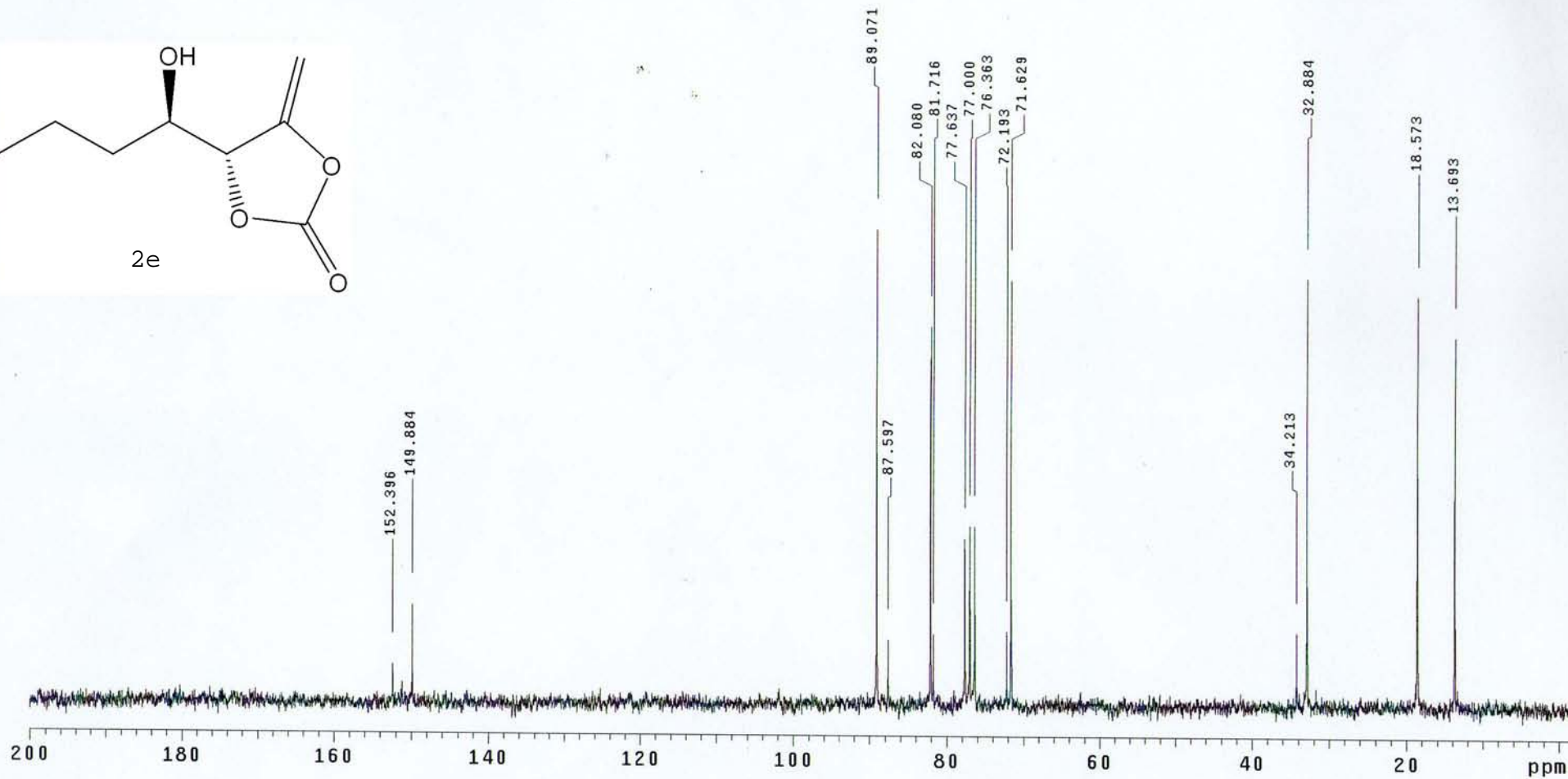
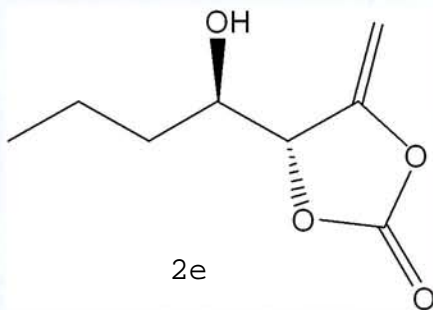


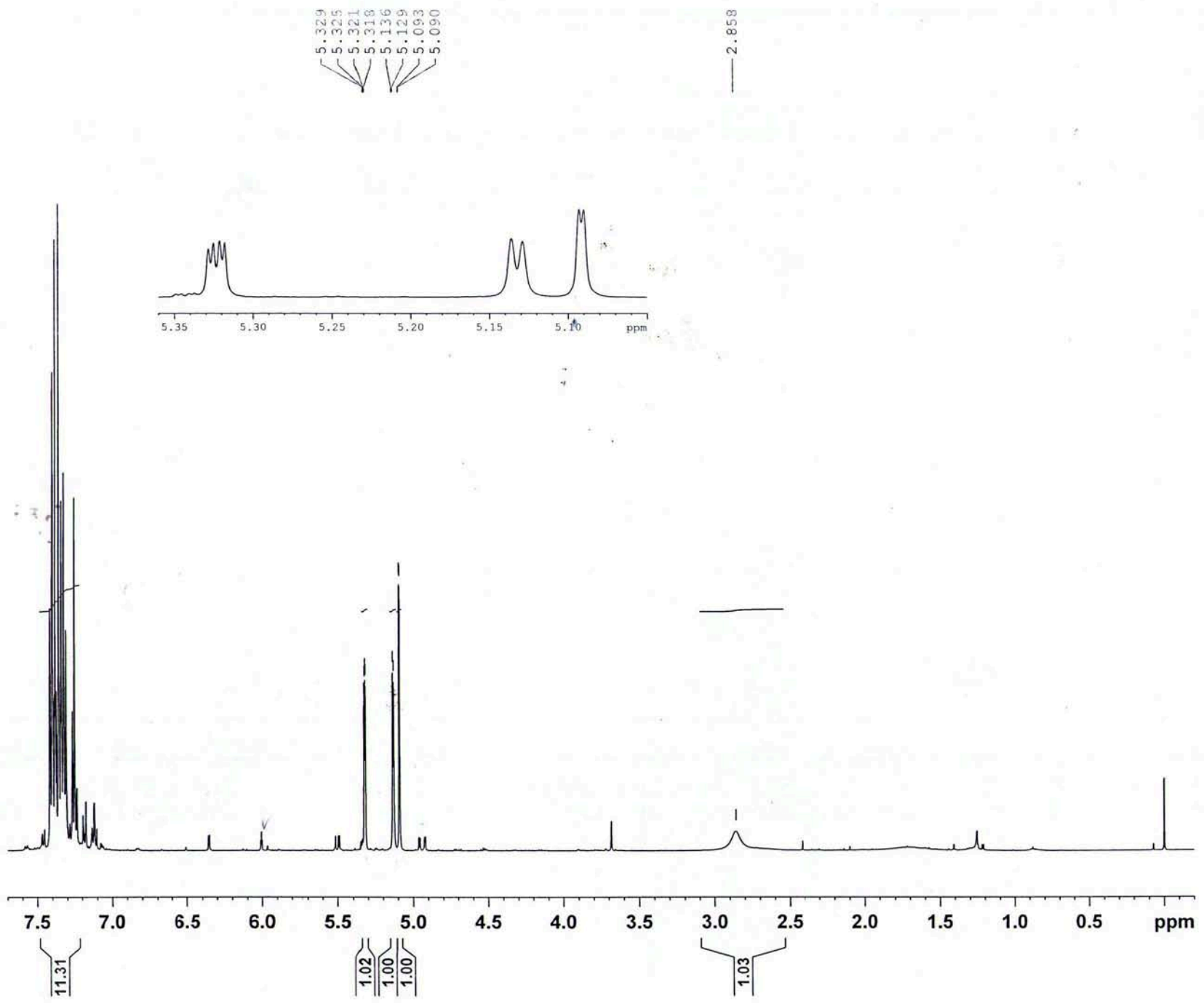
VM-MB-7-24 A

Solvent: cdc13  
Ambient temperature  
GEMINI-200 "nmr"

PULSE SEQUENCE

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2nd pulse 81.8 degrees  
Acq. time 1.067 sec  
Width 15000.0 Hz  
Arrayed repetitions  
OBSERVE C13, 50.2827800 MHz  
DECOUPLE H1, 199.9712807 MHz  
Power 0 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 32768  
Total time 36 minutes





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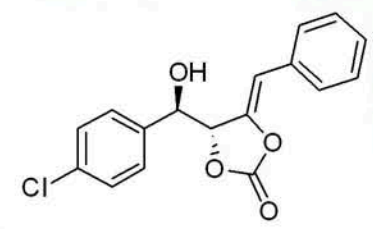
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PROCNO 1
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TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 4743.833 Hz
FIDRES 0.144770 Hz
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RG 203
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TD0 1

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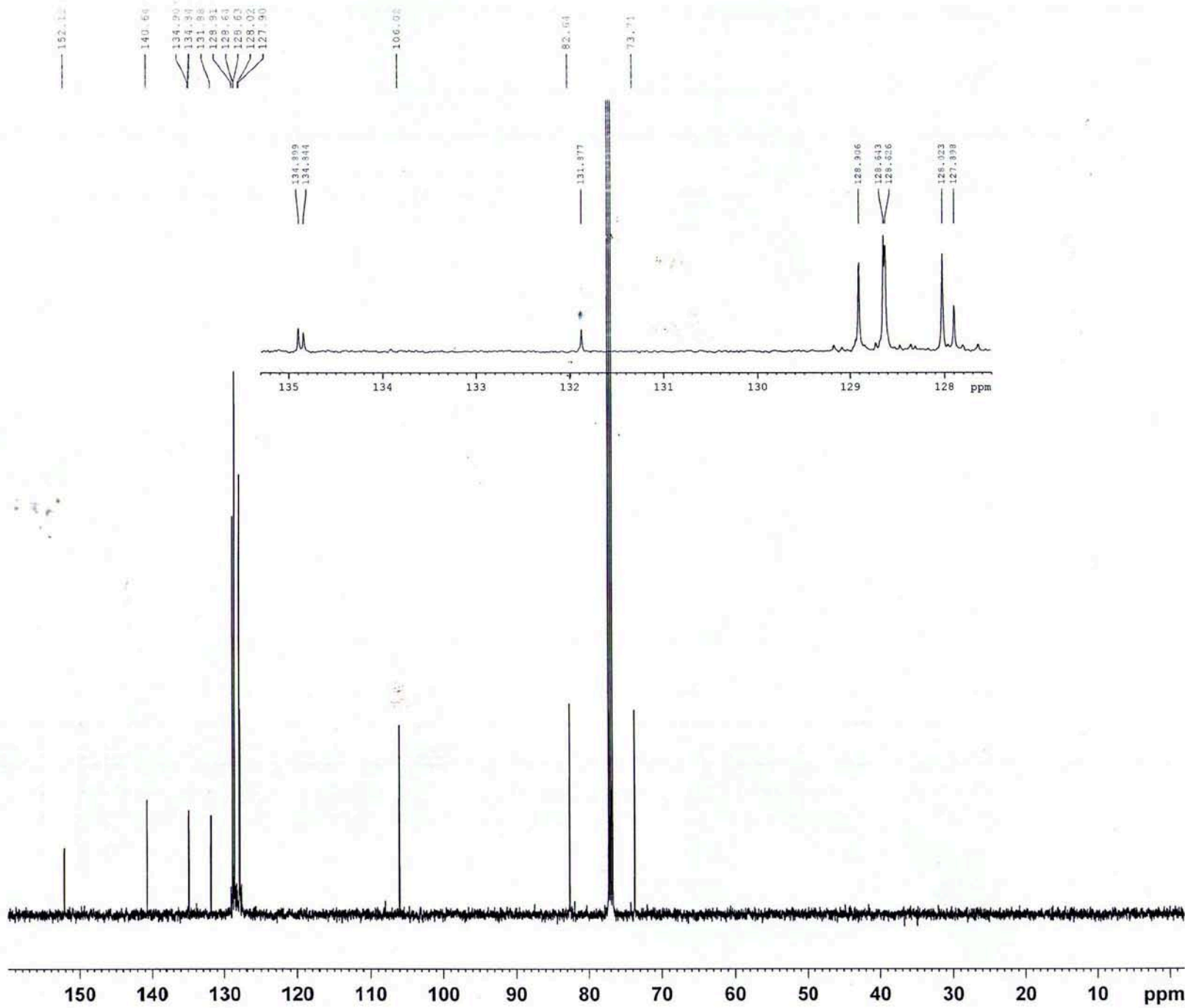
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PL1 0.00 dB
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SI 32768
SF 500.2600177 MHz
WDW EM
SSB 0
LB 0.20 Hz
GB 0
PC 1.00

```



3a



```

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EXPNO          2
PROCNO         1
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Time           16.32
INSTRUM        spect
PROBHD         5 mm BBO BB-1H
PULPROG        zgpg30
TD             32768
SOLVENT        CDCl3
NS             332
DS             4
SWH            29761.904 Hz
FIDRES         0.908261 Hz
AQ             0.5505524 sec
RG            1030
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D1            2.00000000 sec
D11           0.03000000 sec
TD0           1

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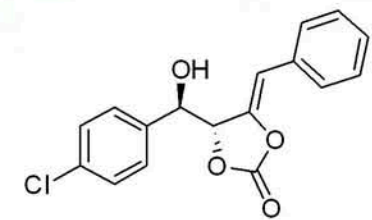
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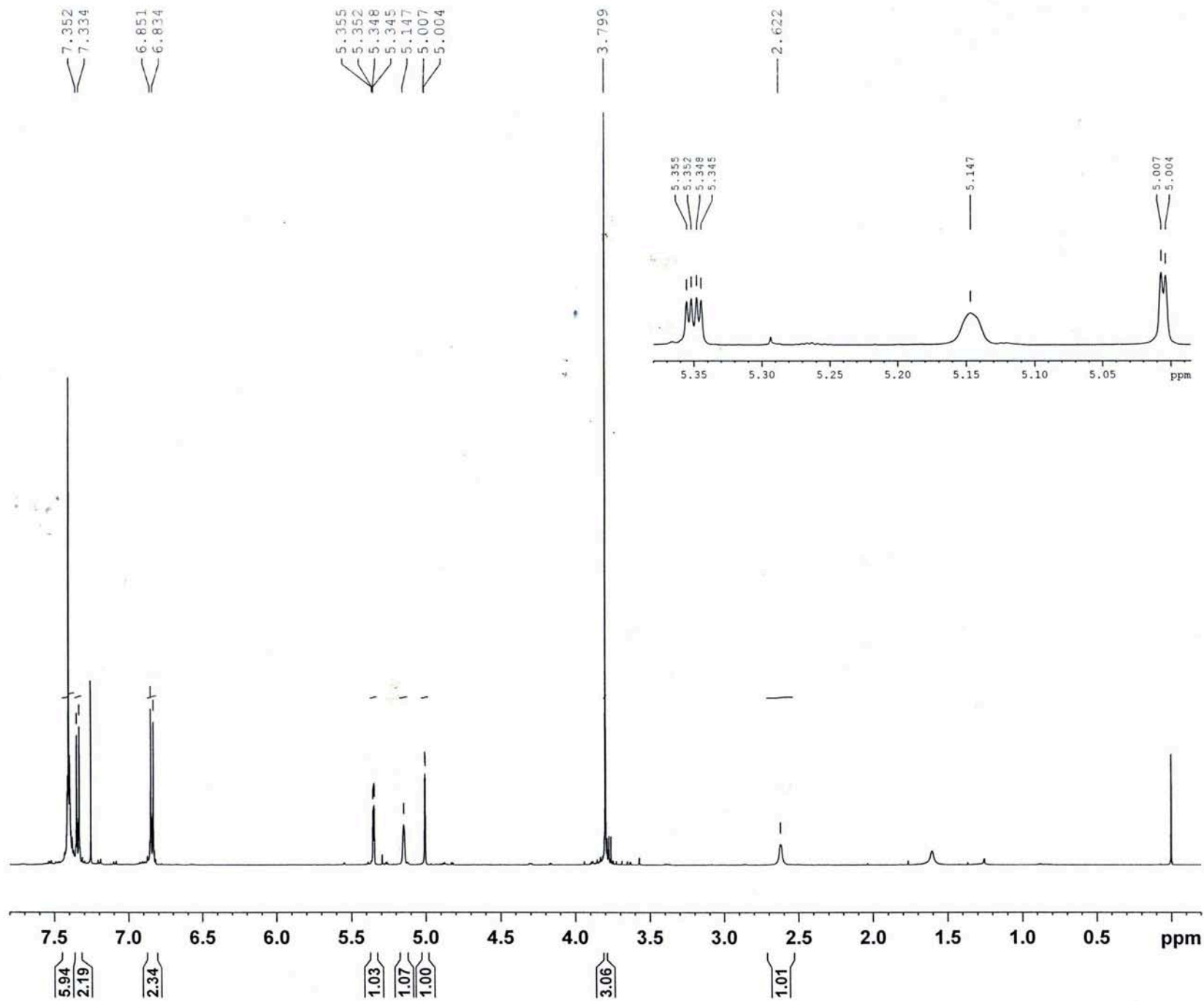
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NUC2           1H
PCPD2         80.00 usec
PL2           1.20 dB
PL12          18.40 dB
PL13          18.40 dB
PL2W          20.76952171 W
PL12W         0.39575511 W
PL13W         0.39575511 W
SFO2          500.2620155 MHz
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SSB           0
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GB            0
PC            1.40

```



3a





```

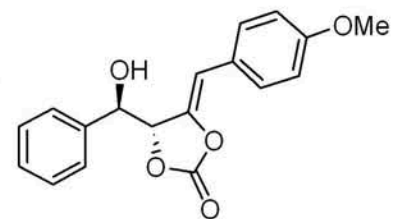
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PROCNO        1
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TD            32768
SOLVENT       CDC13
NS            16
DS            0
SWH           4770.992 Hz
FIDRES        0.145599 Hz
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RG            256
DW            104.800 usec
DE            6.50 usec
TE            298.0 K
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TD0           1

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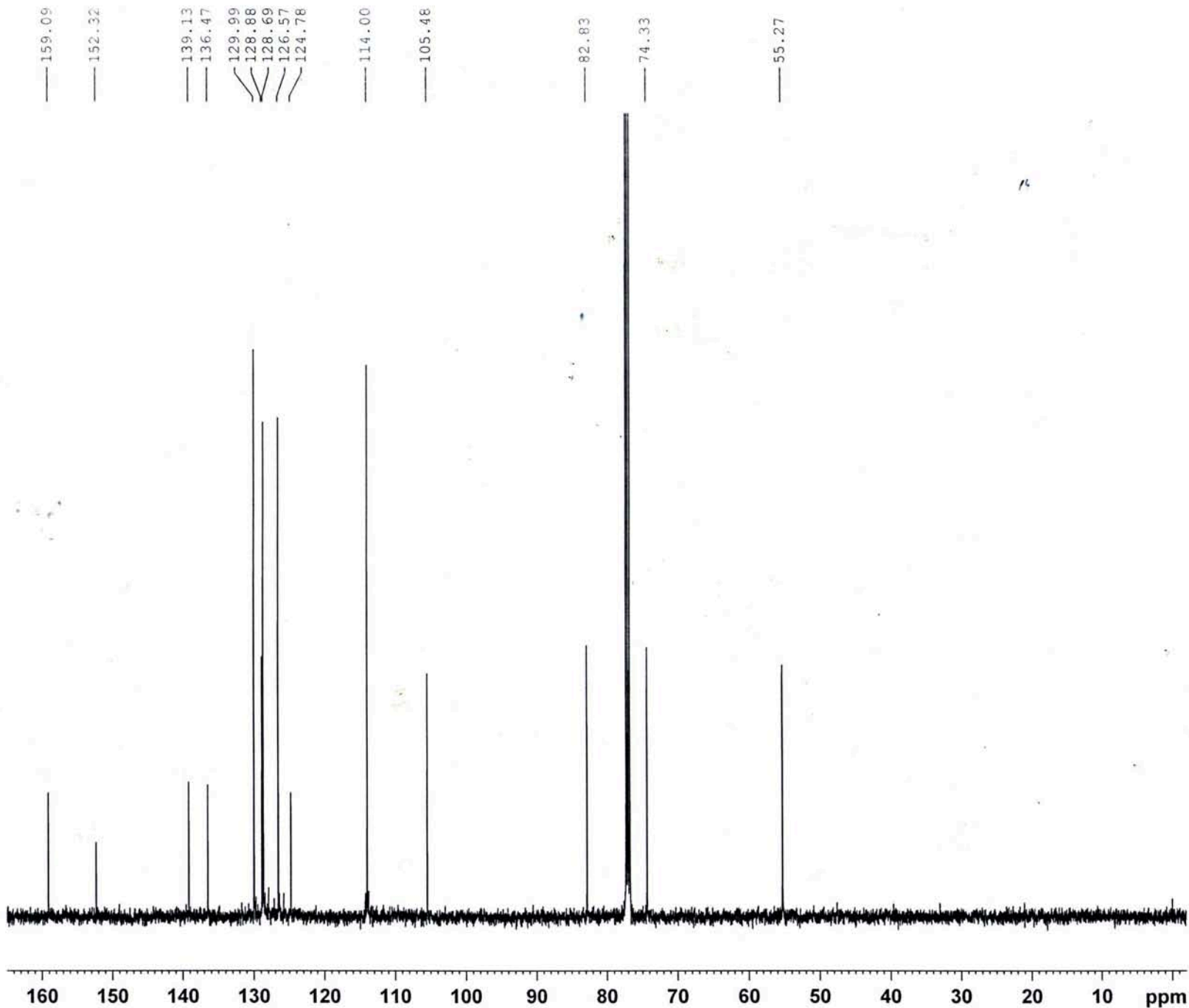
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SF01          500.2621162 MHz
SI            32768
SF            500.2600163 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00

```



3b



```

NAME           MB-266
EXPNO          2
PROCNO        1
Date_         20120629
Time_         12.02
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zgpg30
TD            32768
SOLVENT       CDC13
NS            647
DS            4
SWH           29761.904 Hz
FIDRES        0.908261 Hz
AQ            0.5505524 sec
RG            1030
DW            16.800 usec
DE            6.50 usec
TE            298.0 K
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D11           0.03000000 sec
TDO           1

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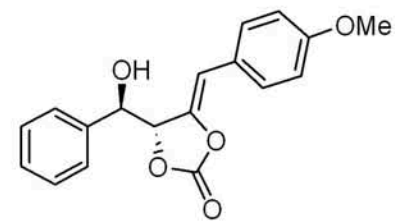
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SFO1           125.8043140 MHz

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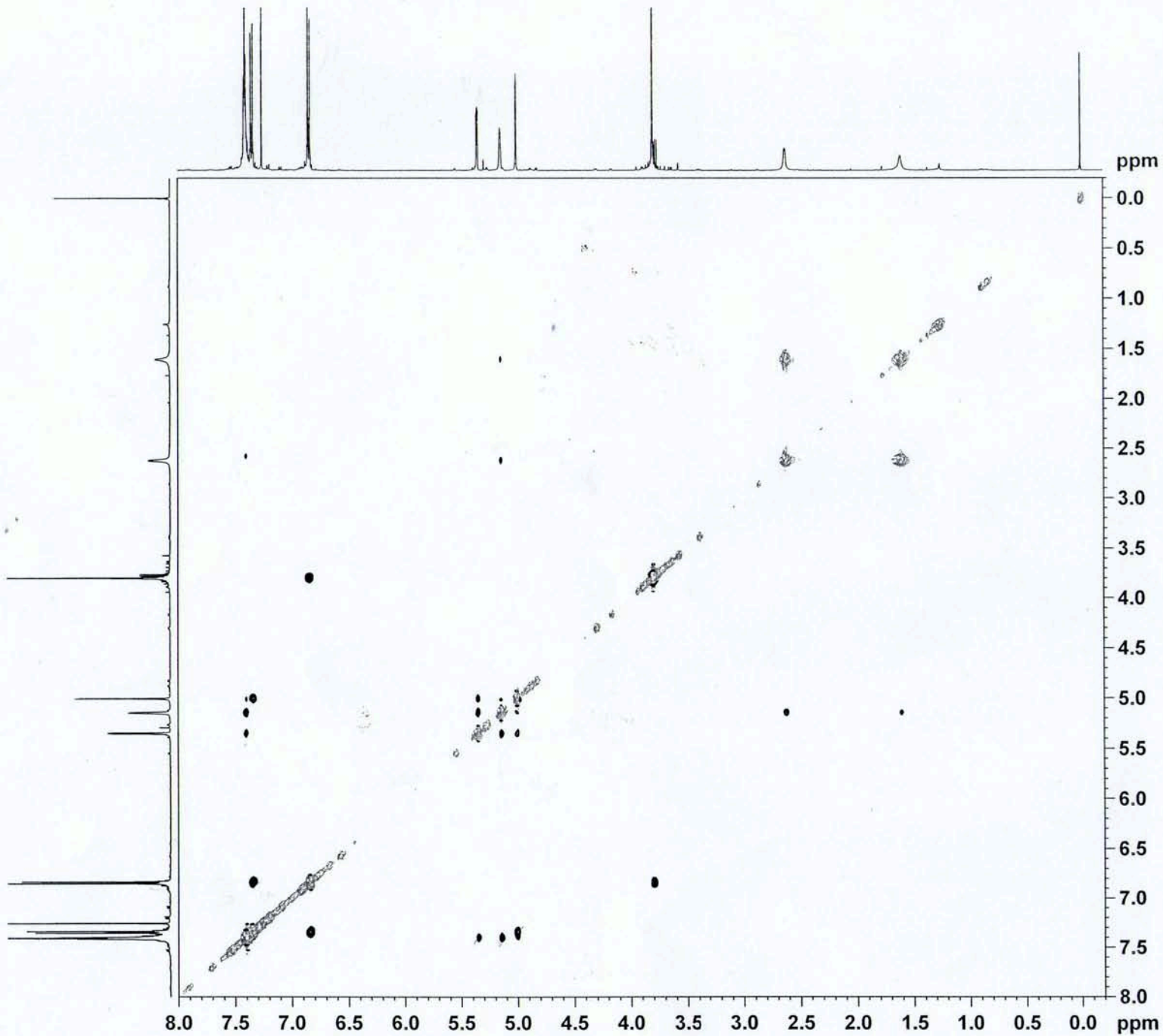
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PL12          18.40 dB
PL13          18.40 dB
PL2W          20.76952171 W
PL12W         0.39575511 W
PL13W         0.39575511 W
SFO2          500.2621161 MHz
SI            32768
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SSB           0
LB            1.50 Hz
GB            0
PC            1.40

```



3b



```

NAME           MB-266
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PROCNO         1
Date_          20120629
Time           13.34
INSTRUM       spect
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PULPROG       noesygpph
TD             1024
SOLVENT       CDCl3
NS             8
DS             16
SWH           4770.992 Hz
FIDRES        4.659172 Hz
AQ            0.1073652 sec
RG            256
DW            104.800 usec
DE             6.50 usec
TE            298.0 K
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D16           0.00020000 sec
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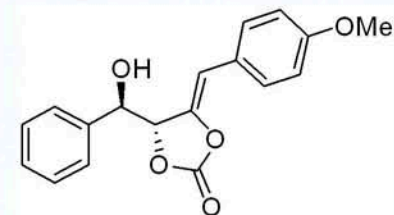
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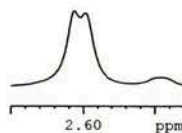
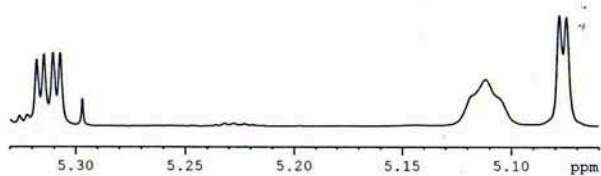
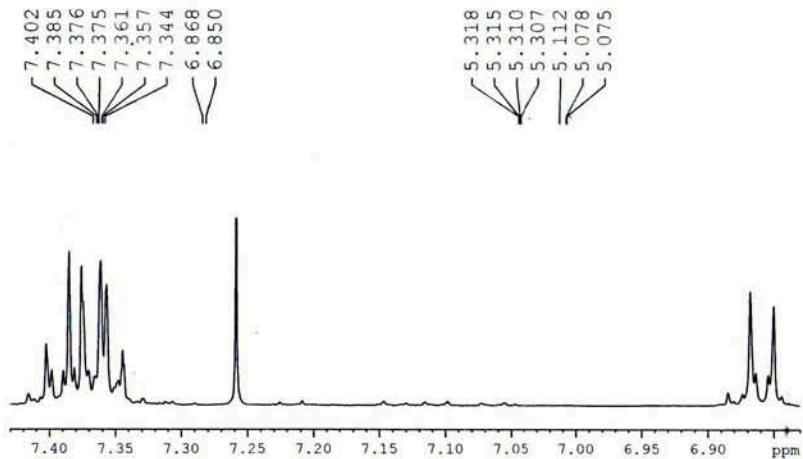
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TD             160
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SW             9.537 ppm
FnMODE         States-TPPI
SI             512
SF             500.2600134 MHz
WDW            QSINE
SSB            2
LB             0.00 Hz
GB             0
PC             1.00
SI             512
MC2            States-TPPI
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WDW            QSINE
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GB             0

```



3b

S19

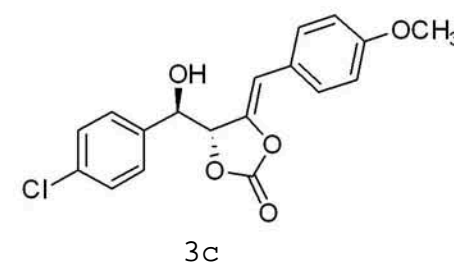
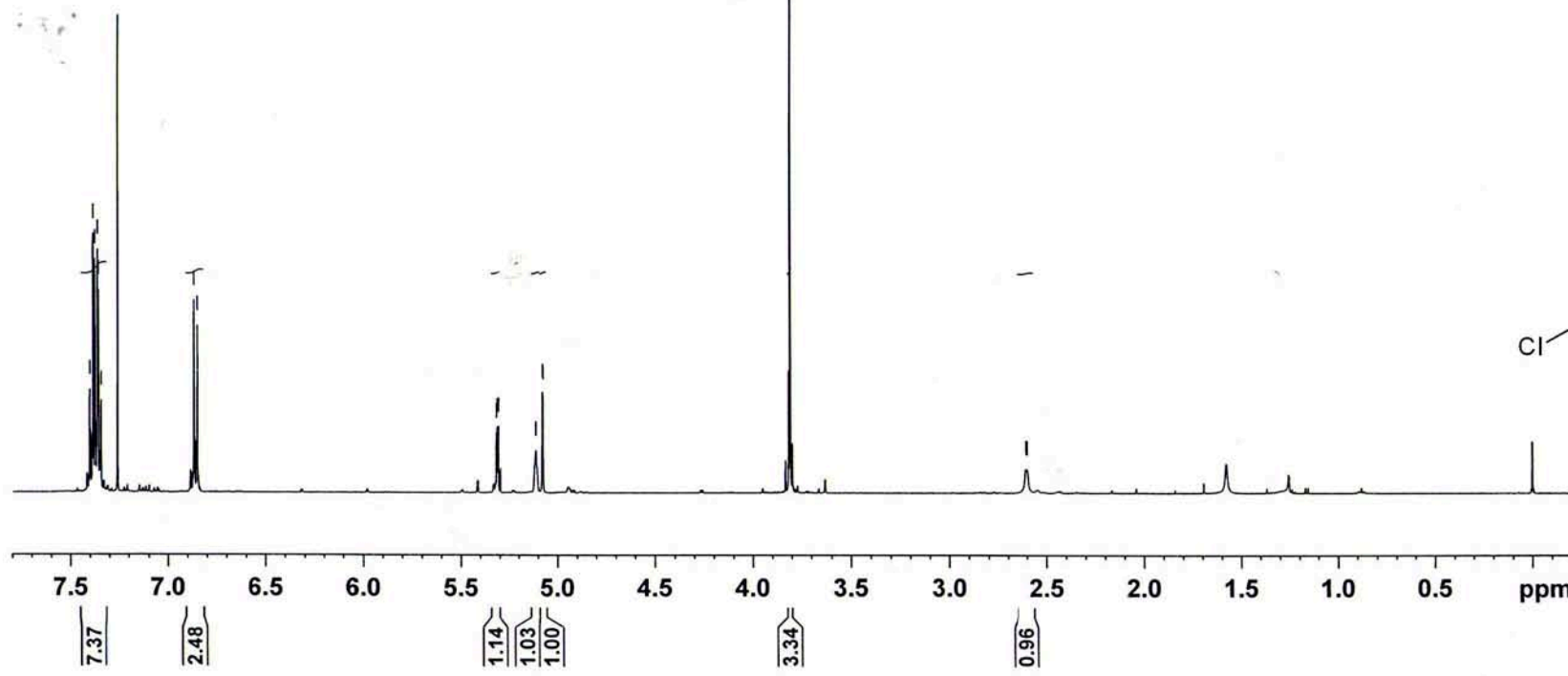


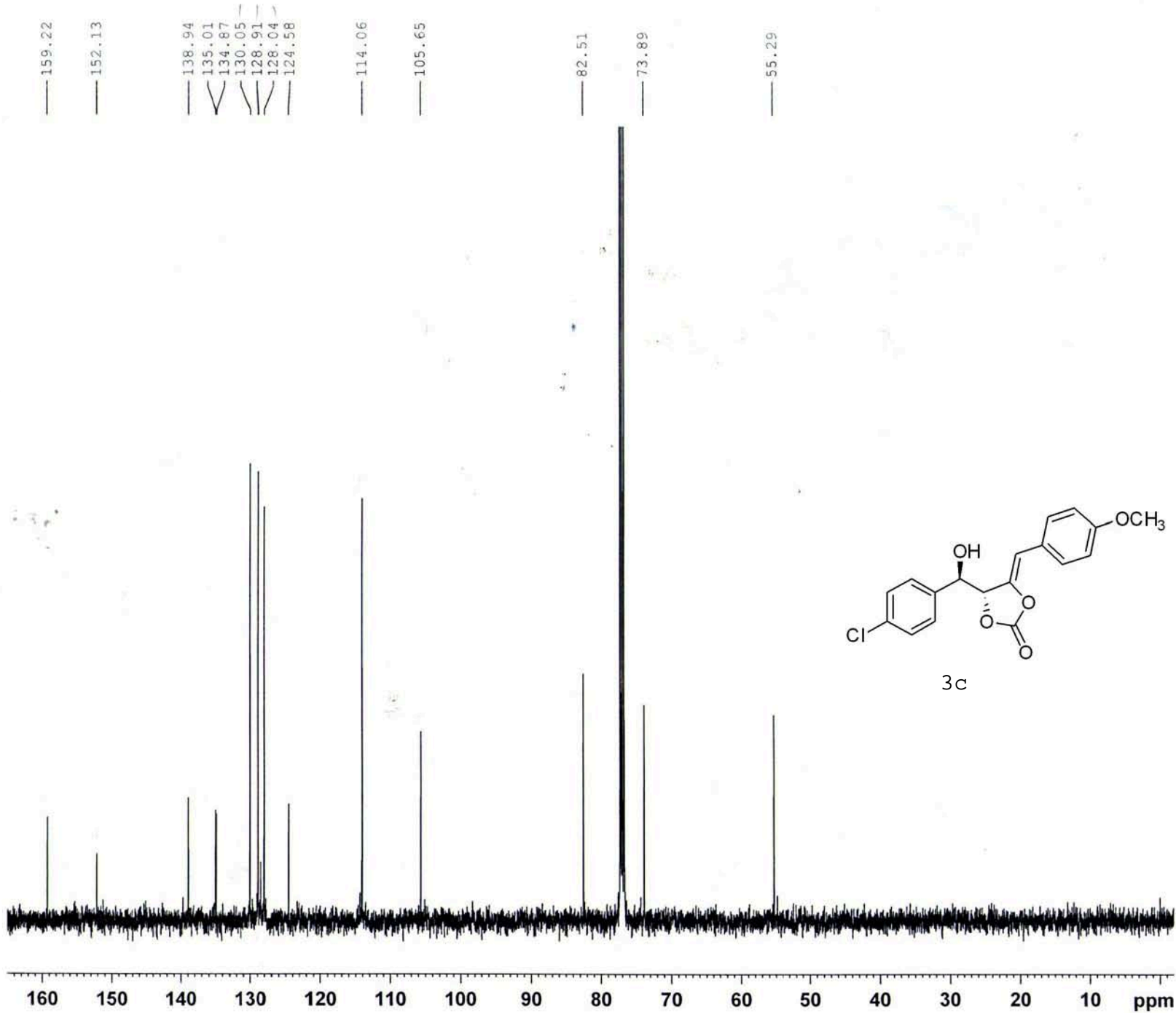
```

NAME          MB-263
EXPNO         1
PROCNO        1
Date_         20120625
Time          10.59
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDC13
NS            16
DS            0
SWH           5013.369 Hz
FIDRES        0.152996 Hz
AQ            3.2681119 sec
RG            322
DW            99.733 usec
DE            6.50 usec
TE            298.0 K
D1            2.0000000 sec
TDO           1
  
```

```

===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
PL1           0.00 dB
PL1W          27.37956238 W
SFO1          500.2617630 MHz
SI            32768
SF            500.2600152 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00
  
```





```

NAME           MB-263
EXPNO          2
PROCNO         1
Date_          20120625
Time_          11.14
INSTRUM        spect
PROBHD         5 mm BBO BB-1H
PULPROG        zgpg30
TD             32768
SOLVENT        CDC13
NS             682
DS             4
SWH            29761.904 Hz
FIDRES         0.908261 Hz
AQ             0.5505524 sec
RG             912
DW             16.800 usec
DE             6.50 usec
TE             298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0            1

```

```

===== CHANNEL f1 =====
NUC1           13C
PL1            11.50 usec
PL1            3.00 dB
PL1W           32.22848892 W
SFO1           125.8043140 MHz

```

```

===== CHANNEL f2 =====
CPDPRG2        waltz16
NUC2           1H
PCPD2          80.00 usec
PL2            1.20 dB
PL12           18.40 dB
PL13           18.40 dB
PL2W           20.76952171 W
PL12W          0.39575511 W
PL13W          0.39575511 W
SFO2           500.2617629 MHz
SI             32768
SF             125.7904805 MHz
WDW            EM
SSB            0
LB             1.50 Hz
GB             0
PC             1.40

```

```

NAME          MB-263-1
EXPNO         2
PROCNO        1
Date_         20120628
Time          11.13
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       noesygpph
TD            1024
SOLVENT       CDCl3
NS            8
DS            16
SWH           4629.629 Hz
FIDRES        4.521122 Hz
AQ            0.1106420 sec
RG            322
DW            108.000 usec
DE            6.50 usec
TE            298.0 K
D0            0.00009610 sec
D1            2.00000000 sec
D8            0.80000001 sec
D16           0.00020000 sec
INO           0.00021600 sec

```

```

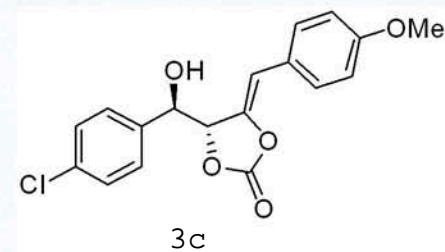
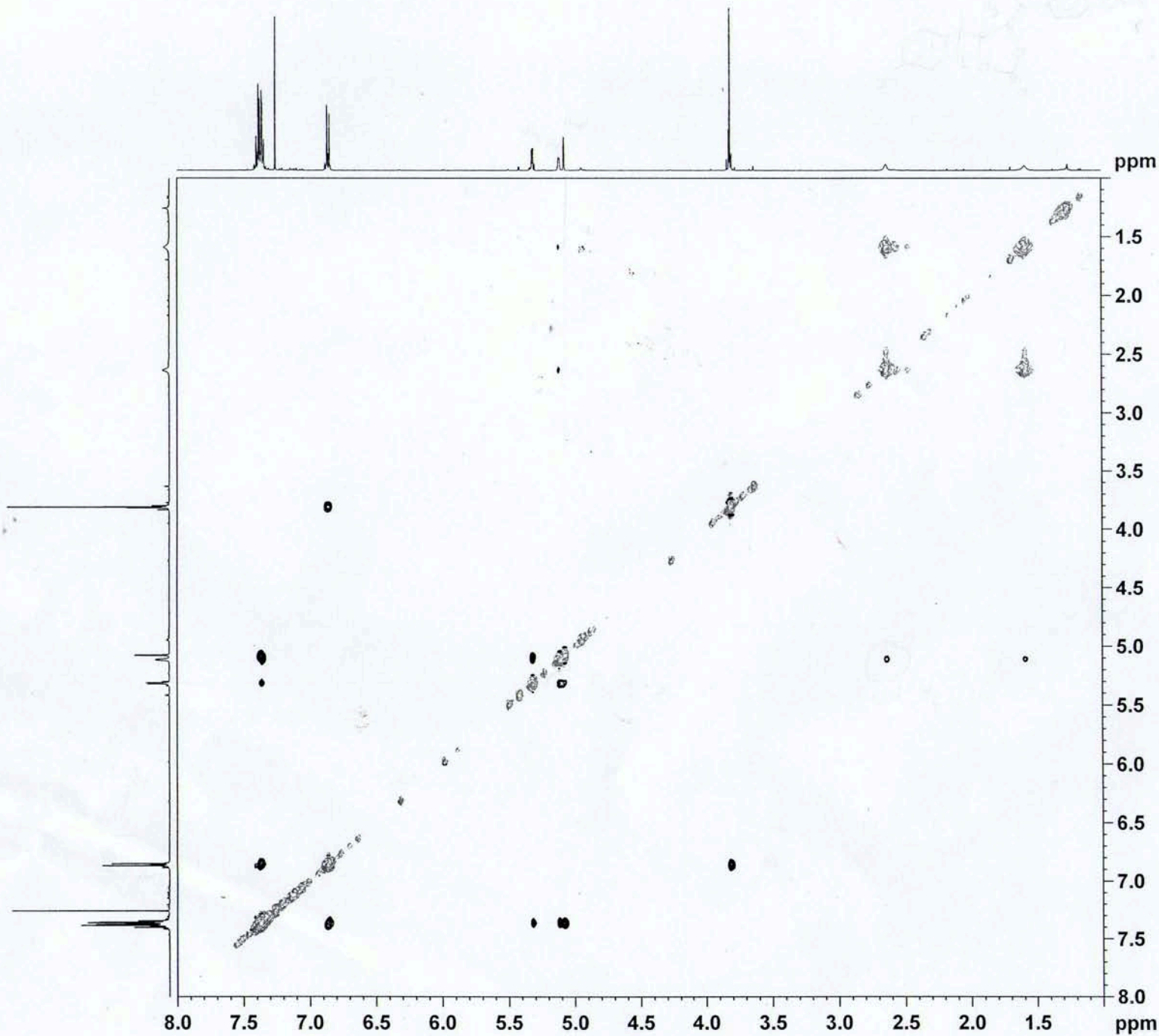
===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
P2            18.70 usec
PL1           0.00 dB
PL1W          27.37956238 W
SFO1          500.2619510 MHz

```

```

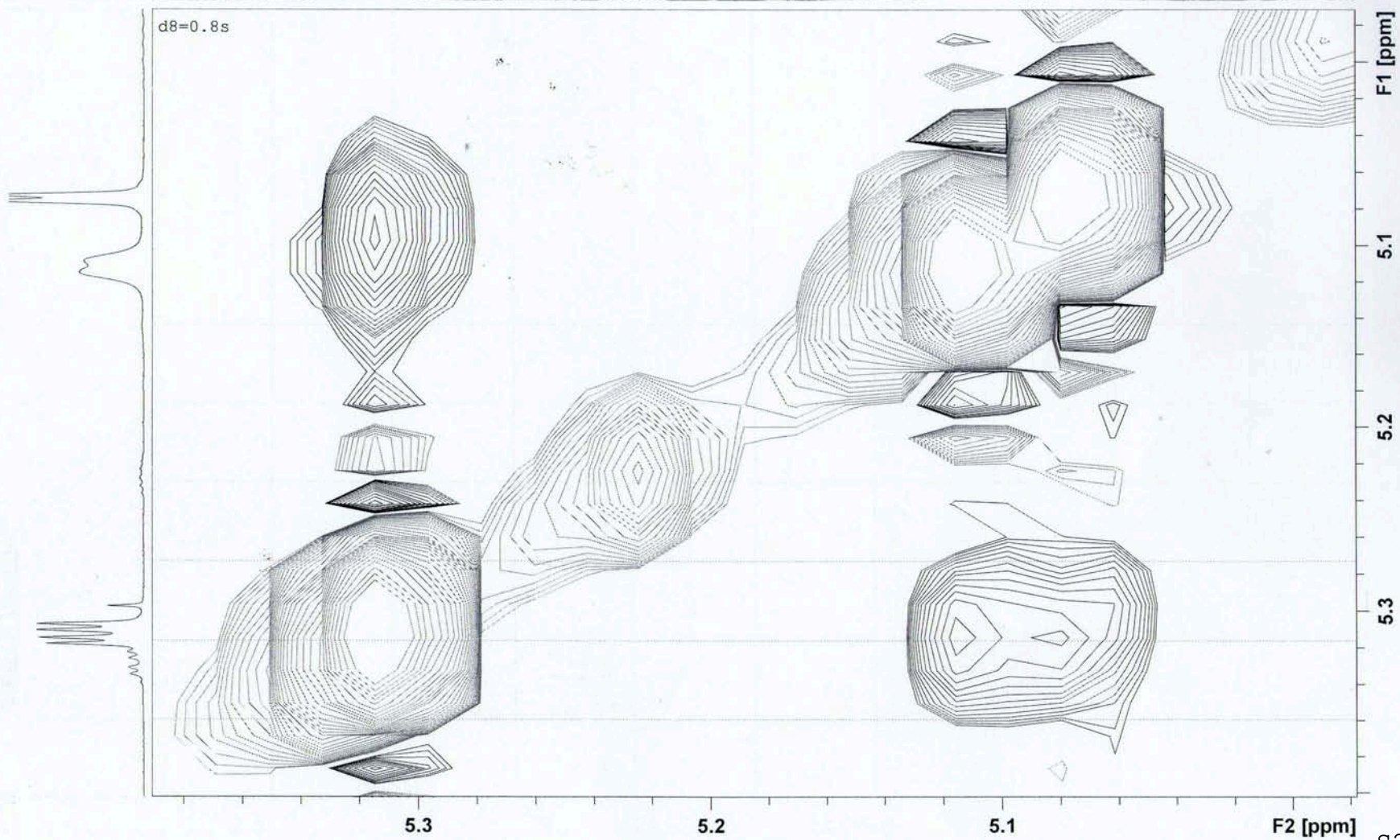
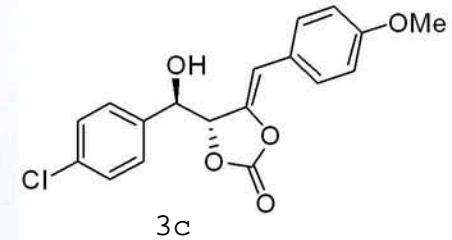
===== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPZ1          40.00 %
P16           1000.00 usec
NDO           1
TD            164
SFO1          500.262 MHz
FIDRES        28.229416 Hz
SW            9.254 ppm
FnMODE        States-TPPI
SI            512
SF            500.2600112 MHz
WDW           QSINE
SSB           2
LB            0.00 Hz
GB            0
PC            1.00
SI            512
MC2           States-TPPI
SF            500.2600115 MHz
WDW           QSINE
SSB           2
LB            0.00 Hz
GB            0

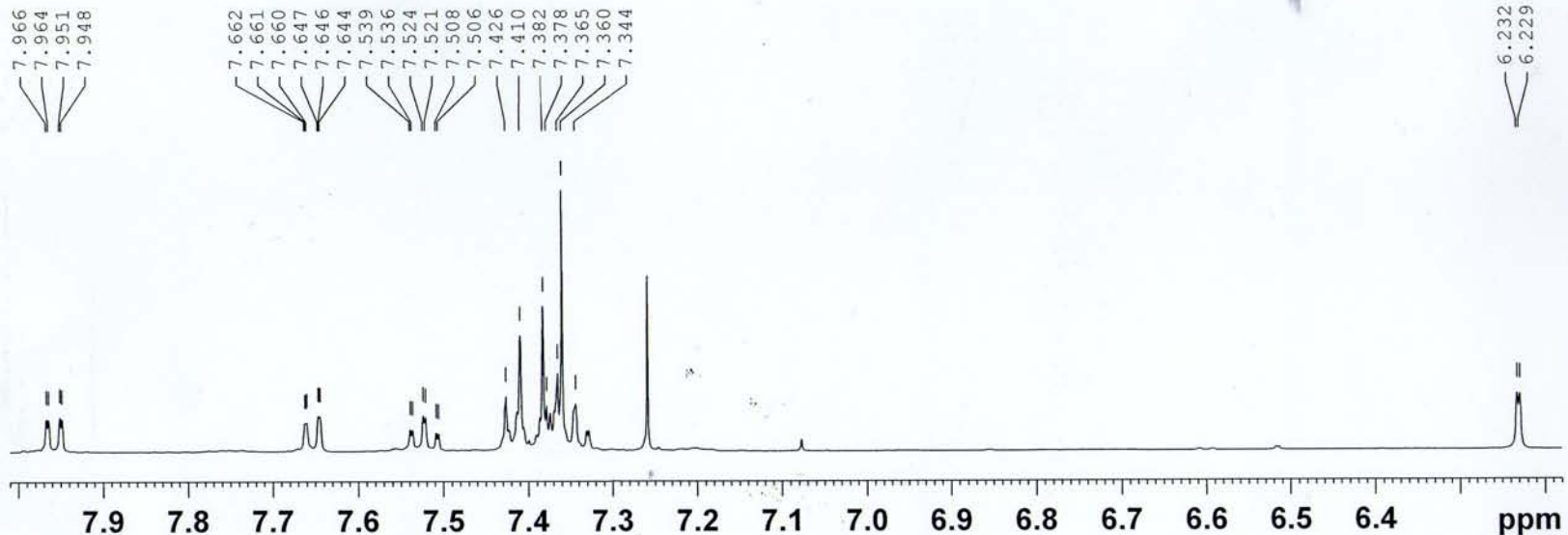
```



S22

MB-263-1 2 1 C:\Bruker\TOPSPIN guest



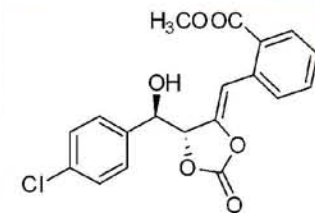
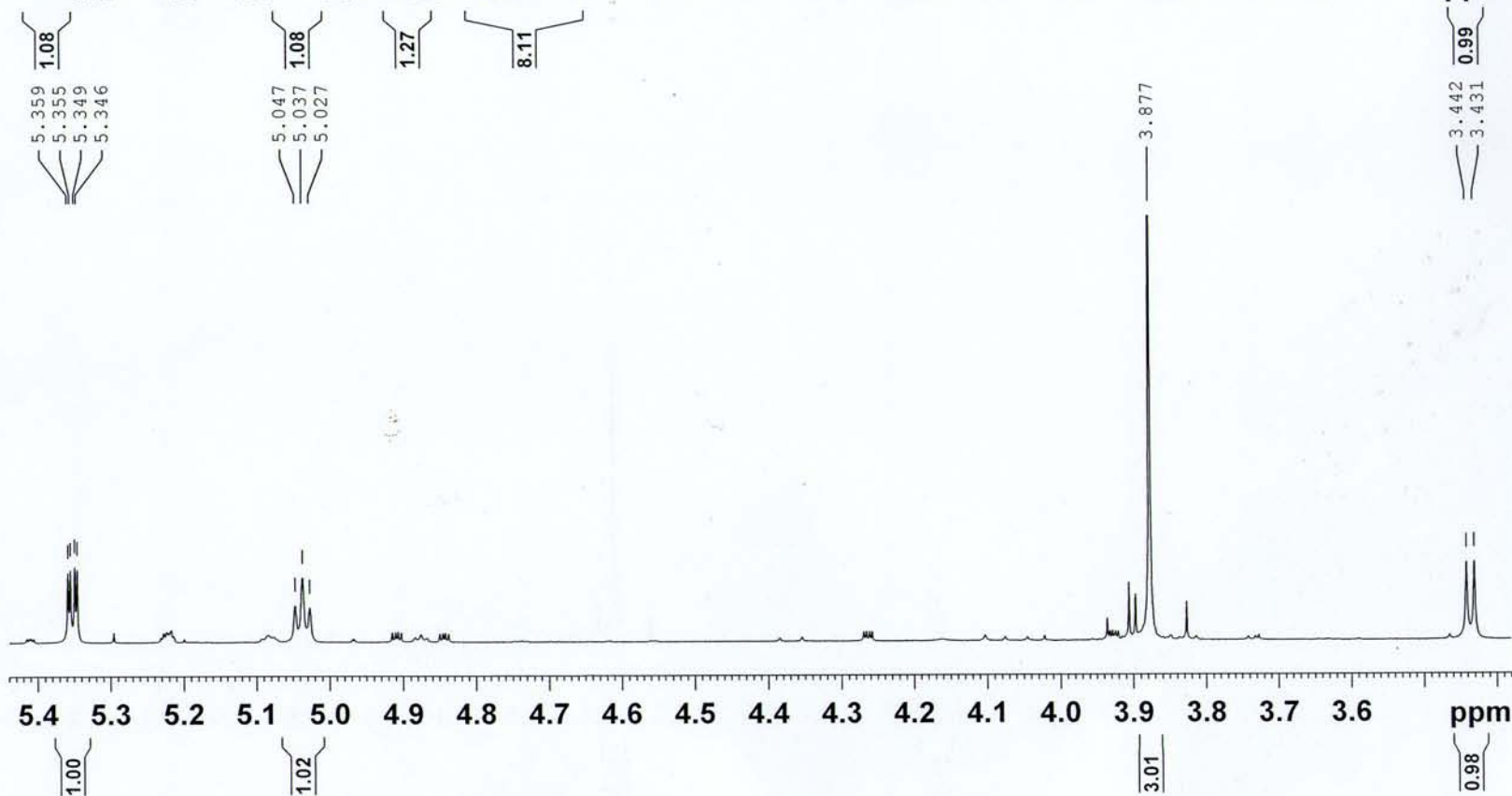


Current Data Parameters  
 NAME MB-315-2  
 EXPNO 1  
 PROCNO 1

F2 - Acquisition Parameters  
 Date\_ 20121010  
 Time\_ 11.52  
 INSTRUM spect  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 0  
 SWH 4870.130 Hz  
 FIDRES 0.148625 Hz  
 AQ 3.3642313 sec  
 RG 181  
 DW 102.667 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 TD0 1

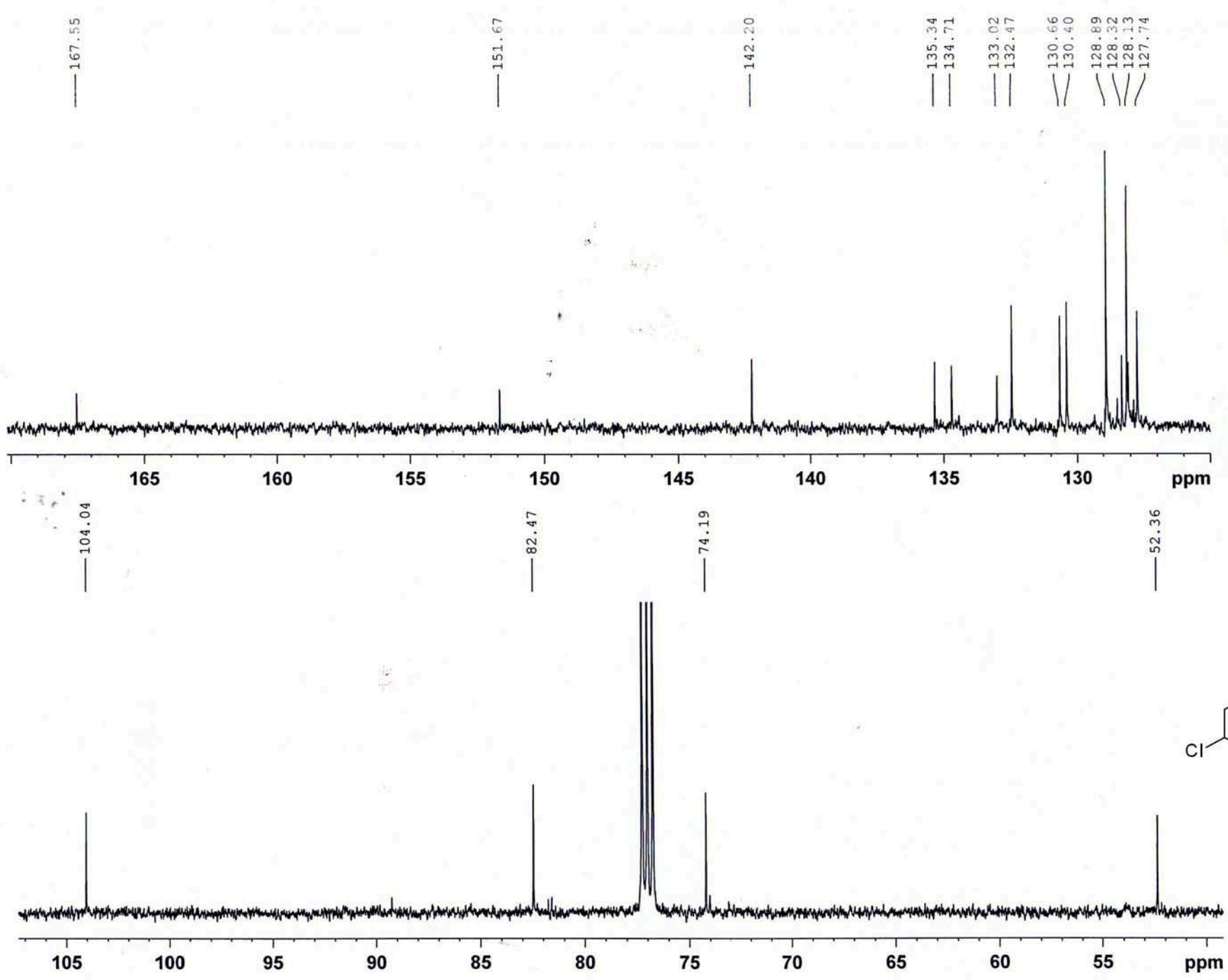
===== CHANNEL f1 =====  
 NUC1 1H  
 P1 9.35 usec  
 PL1 0.00 dB  
 PL1W 27.37956238 W  
 SFO1 500.2620828 MHz

F2 - Processing parameters:  
 SI 32768  
 SF 500.2600154 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00



3d





```

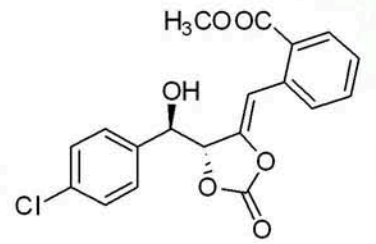
NAME      MB-315-2
EXPNO    2
PROCNO   1
Date_    20121010
Time     12.06
INSTRUM  spect
PROBHD   5 mm BBO BB-1H
PULPROG  zgpg30
TD       32768
SOLVENT  CDCl3
NS       517
DS       4
SWH      29761.904 Hz
FIDRES   0.908261 Hz
AQ       0.5505524 sec
RG       1030
DW       16.800 usec
DE       6.50 usec
TE       298.0 K
D1       2.00000000 sec
D11      0.03000000 sec
TDO      1
  
```

```

===== CHANNEL f1 =====
NUC1     13C
P1       11.50 usec
PL1      3.00 dB
PL1W     32.22848892 W
SFO1     125.8043140 MHz
  
```

```

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCPD2    80.00 usec
PL2      1.20 dB
PL12     18.40 dB
PL13     18.40 dB
PL12W    20.76952171 W
PL12W    0.39575511 W
PL13W    0.39575511 W
SFO2     500.2620826 MHz
SI       32768
SF       125.7904814 MHz
WDW      EM
SSB      0
LB       1.50 Hz
GB       0
PC       1.40
  
```



3d

MB-336

Solvent: cdcl3  
Ambient temperature  
File: hmb336  
GEMINI-200 "nmr"

PULSE SEQUENCE

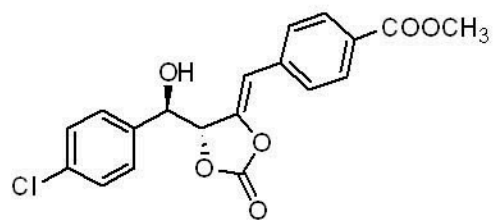
Relax. delay arrayed  
1st pulse arrayed  
2nd pulse 90.0 degrees  
Acq. time 1.440 sec  
Width 4600.0 Hz  
Arrayed repetitions

OBSERVE H1, 199.9710956 MHz

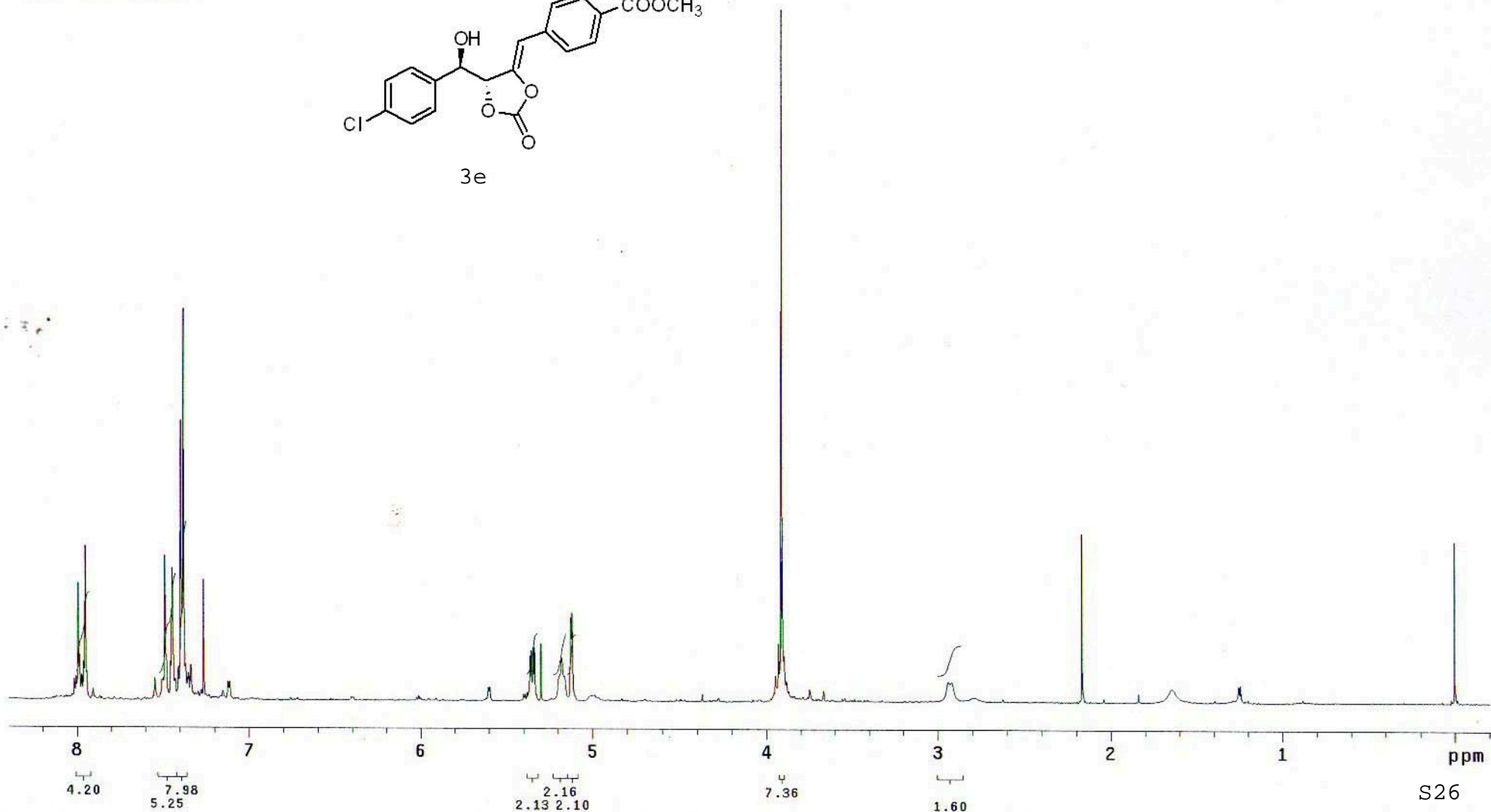
DATA PROCESSING

FT size 16384

Total time 5 minutes



3e

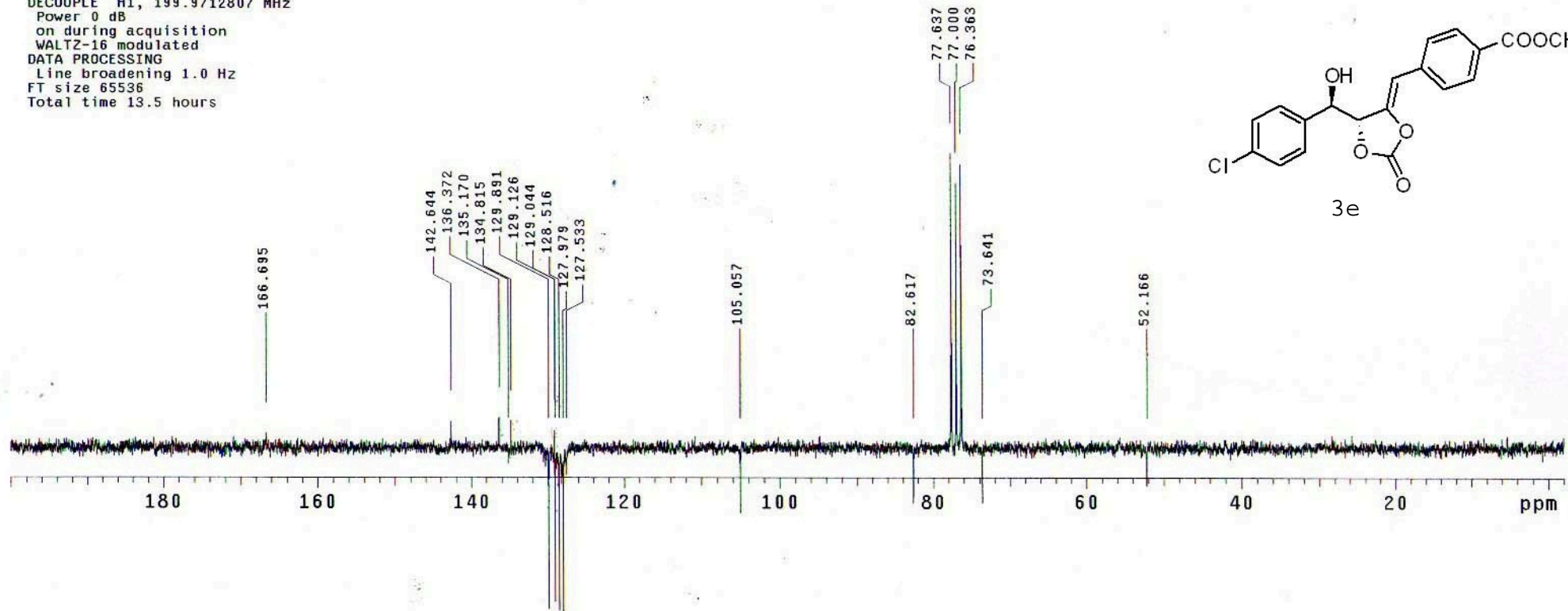


S26

MB-336-2

Solvent: cdcl3  
Ambient temperature  
GEMINI-200 "nmr"

PULSE SEQUENCE: apt  
Relax. delay arrayed  
1st pulse arrayed  
2nd pulse 122.7 degrees  
Acq. time 2.000 sec  
Width 15000.0 Hz  
Arrayed repetitions  
OBSERVE C13, 50.2827780 MHz  
DECOUPLE H1, 199.9712807 MHz  
Power 0 dB  
on during acquisition  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 65536  
Total time 13.5 hours



```

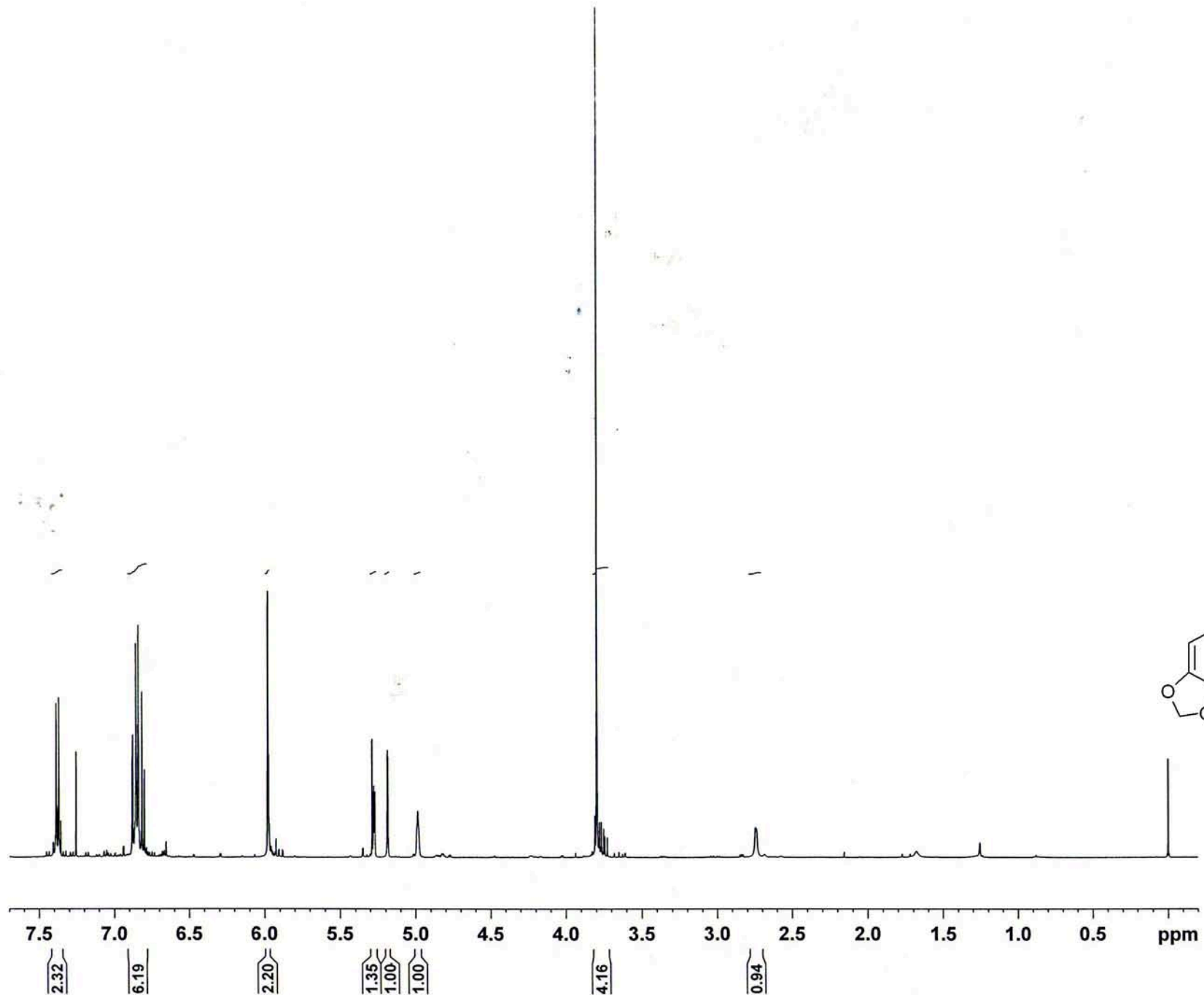
NAME          MB-307-2
EXPNO         1
PROCNO        1
Date_         20120924
Time_         11.00
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            0
SWH           4652.605 Hz
FIDRES        0.141986 Hz
AQ            3.5215178 sec
RG            101
DW            107.467 usec
DE            6.50 usec
TE            298.0 K
D1            2.00000000 sec
TD0           1

```

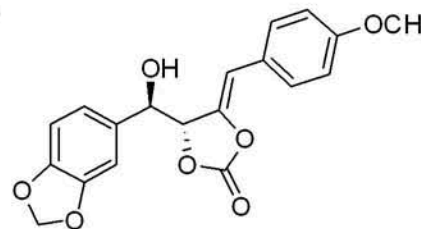
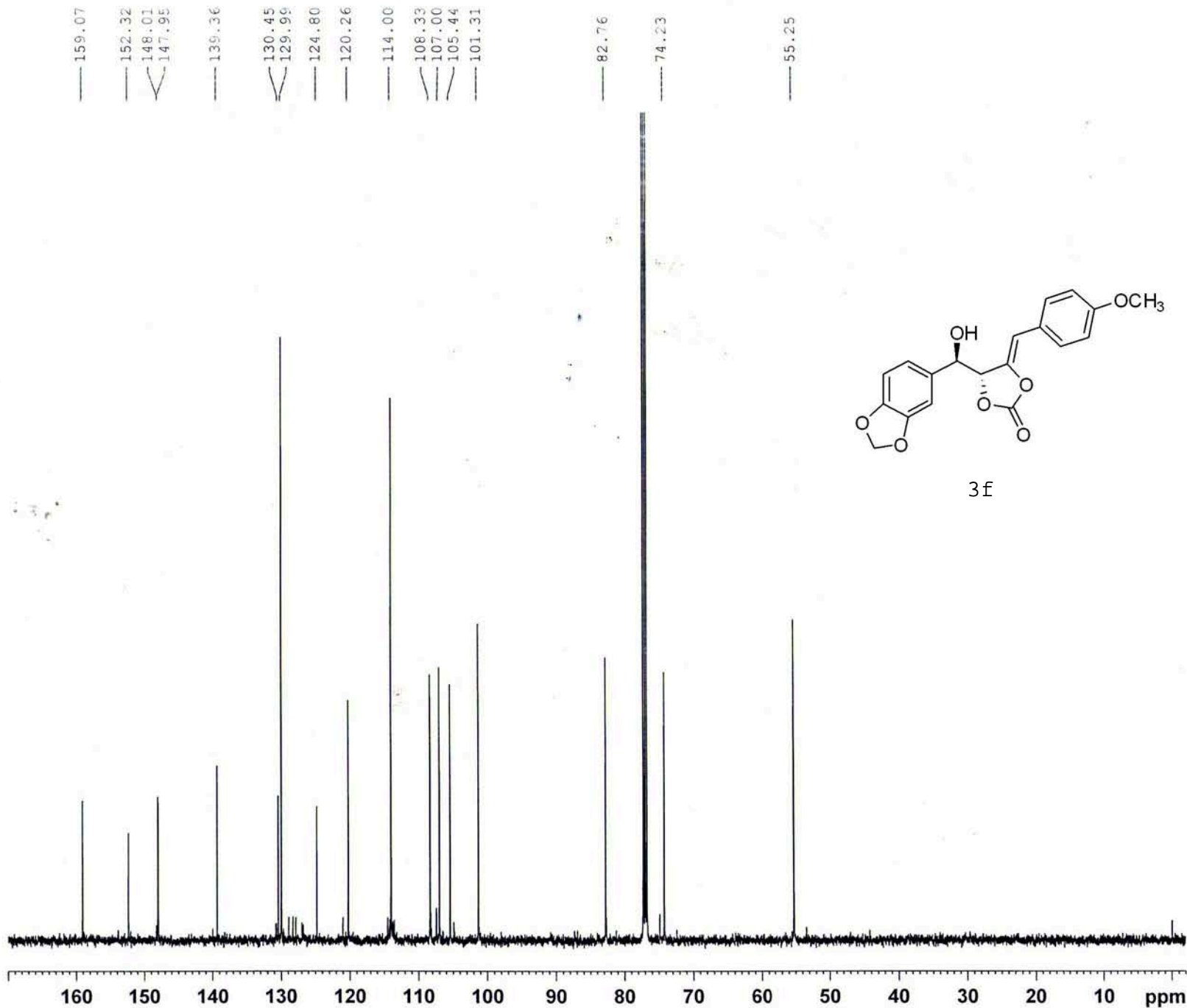
```

===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
PL1           0.00 dB
PL1W         27.37956238 W
SFO1         500.2620531 MHz
SI            32768
SF            500.2600169 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00

```



3f



3f

```

NAME          MB-307-2
EXPNO         2
PROCNO        1
Date_         20120924
Time          11.20
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
NS            512
DS            4
SWH           29761.904 Hz
FIDRES        0.908261 Hz
AQ            0.5505524 sec
RG            912
DW            16.800 usec
DE            6.50 usec
TE            298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1
  
```

```

===== CHANNEL f1 =====
NUC1          13C
P1            11.50 usec
PL1           3.00 dB
PL1W          32.22848892 W
SFO1          125.8043140 MHz
  
```

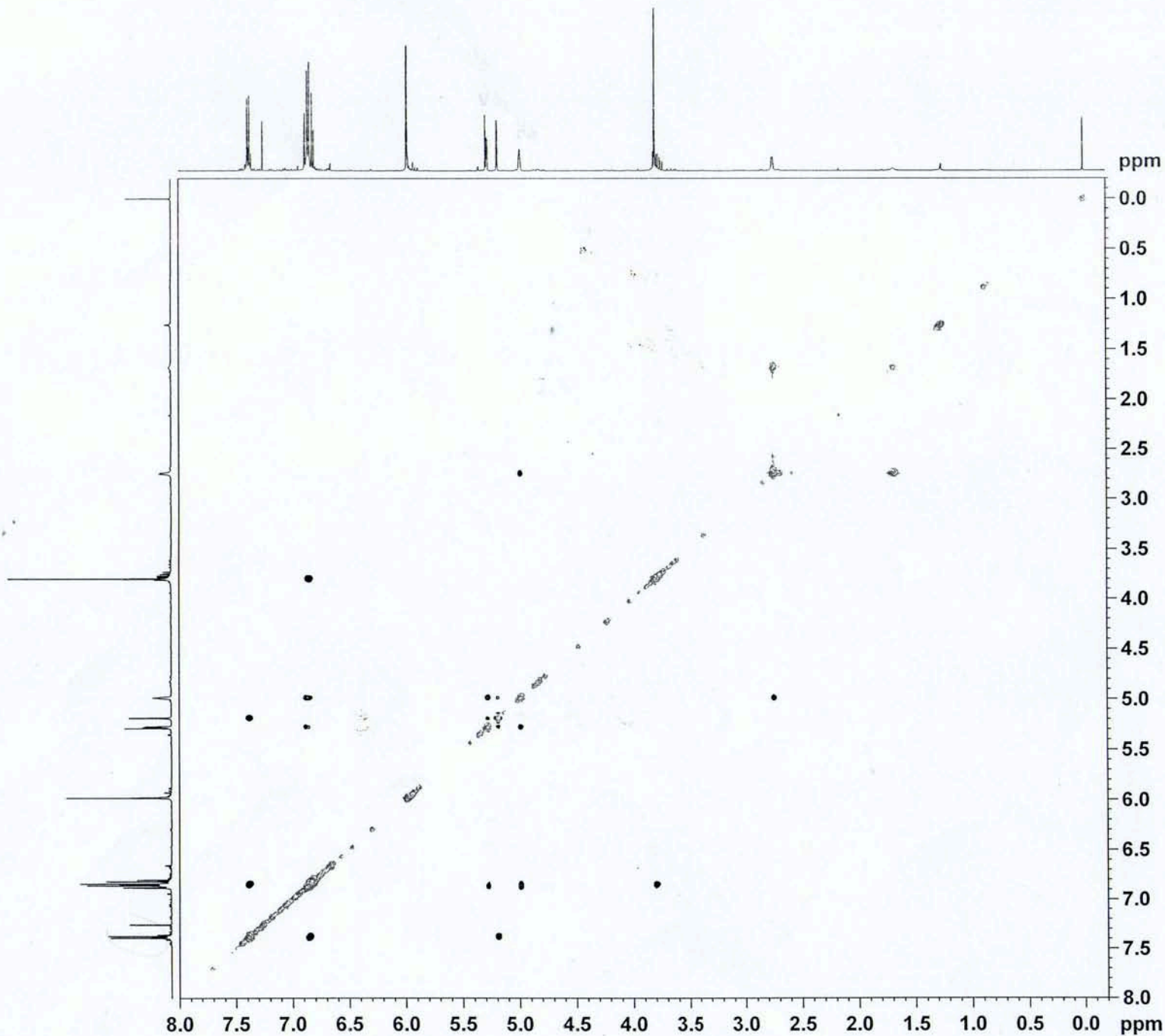
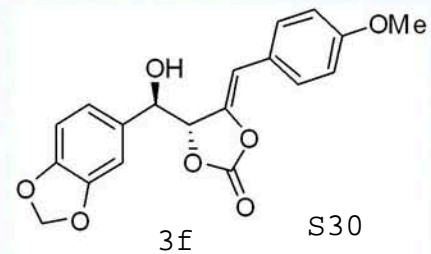
```

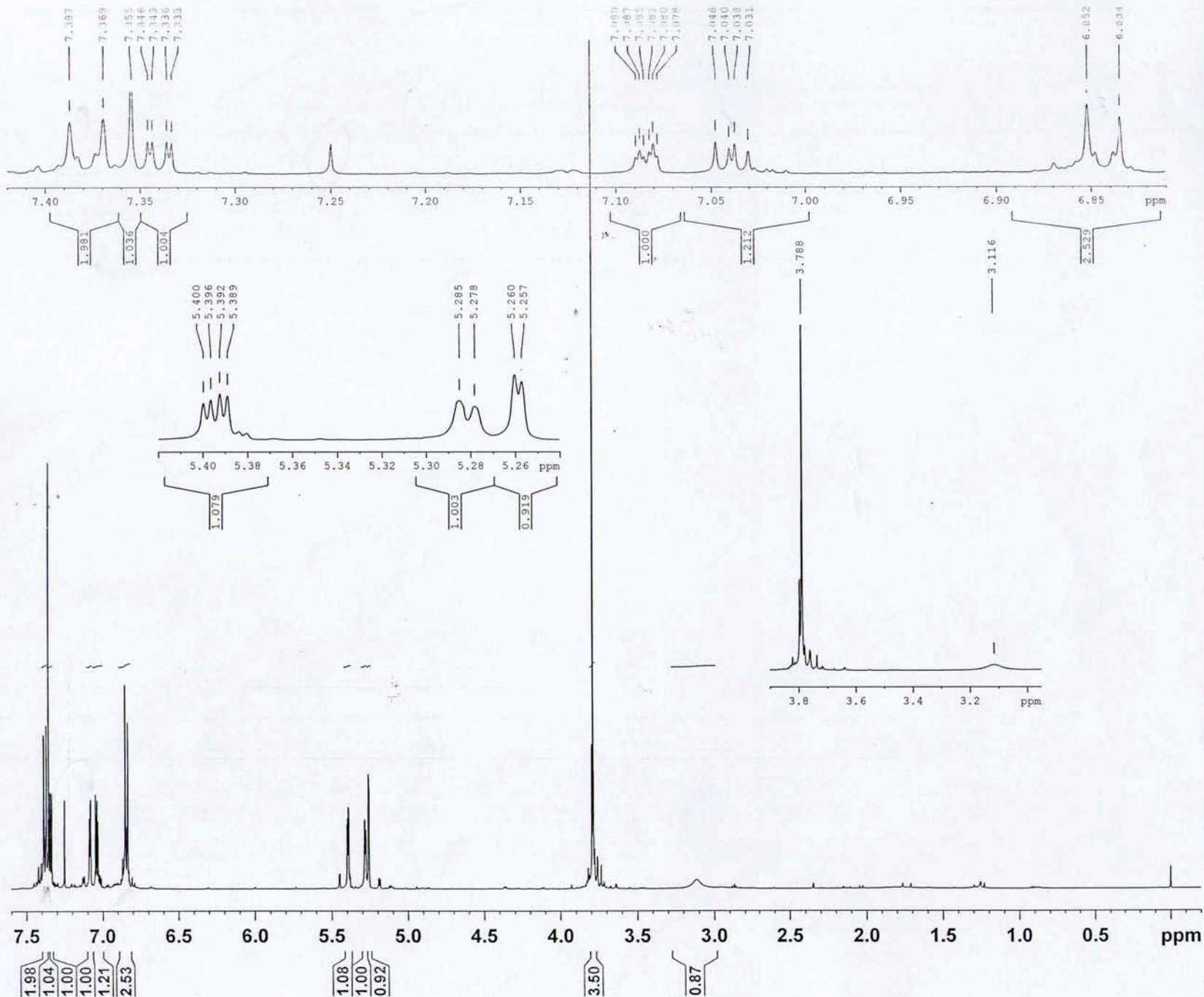
===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           1.20 dB
PL12          18.40 dB
PL13          18.40 dB
PL2W          20.76952171 W
PL12W         0.39575511 W
PL13W         0.39575511 W
SFO2          500.2620531 MHz
SI            32768
SF            125.7904847 MHz
WDW           EM
SSB           0
LB            1.50 Hz
GB            0
PC            1.40
  
```

NAME MB-307-2  
 EXPNO 4  
 PROCNO 1  
 Date\_ 20120924  
 Time\_ 11.52  
 INSTRUM spect  
 PROBHD 5 mm BBO BB-1H  
 PULPROG noesygpph  
 TD 1024  
 SOLVENT CDCl3  
 NS 4  
 DS 16  
 SWH 4652.605 Hz  
 FIDRES 4.543560 Hz  
 AQ 0.1100959 sec  
 RG 101  
 DW 107.467 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D0 0.00009556 sec  
 D1 2.00000000 sec  
 D8 1.00000000 sec  
 D16 0.00020000 sec  
 IN0 0.00021495 sec

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 9.35 usec  
 P2 18.70 usec  
 PL1 0.00 dB  
 PL1W 27.37956238 W  
 SFO1 500.2620531 MHz

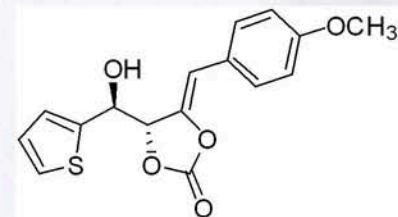
===== GRADIENT CHANNEL =====  
 GPNAM1 SINE.100  
 GPZ1 40.00 %  
 P16 1000.00 usec  
 NDO 1  
 TD 256  
 SFO1 500.2621 MHz  
 FIDRES 18.174170 Hz  
 SW 9.300 ppm  
 FmMODE States-TPPI  
 SI 512  
 SF 500.2600130 MHz  
 WDW QSINE  
 SSB 2  
 LB 0.00 Hz  
 GB 0  
 PC 1.00  
 SI 512  
 MC2 States-TPPI  
 SF 500.2600131 MHz  
 WDW QSINE  
 SSB 2  
 LB 0.00 Hz  
 GB 0



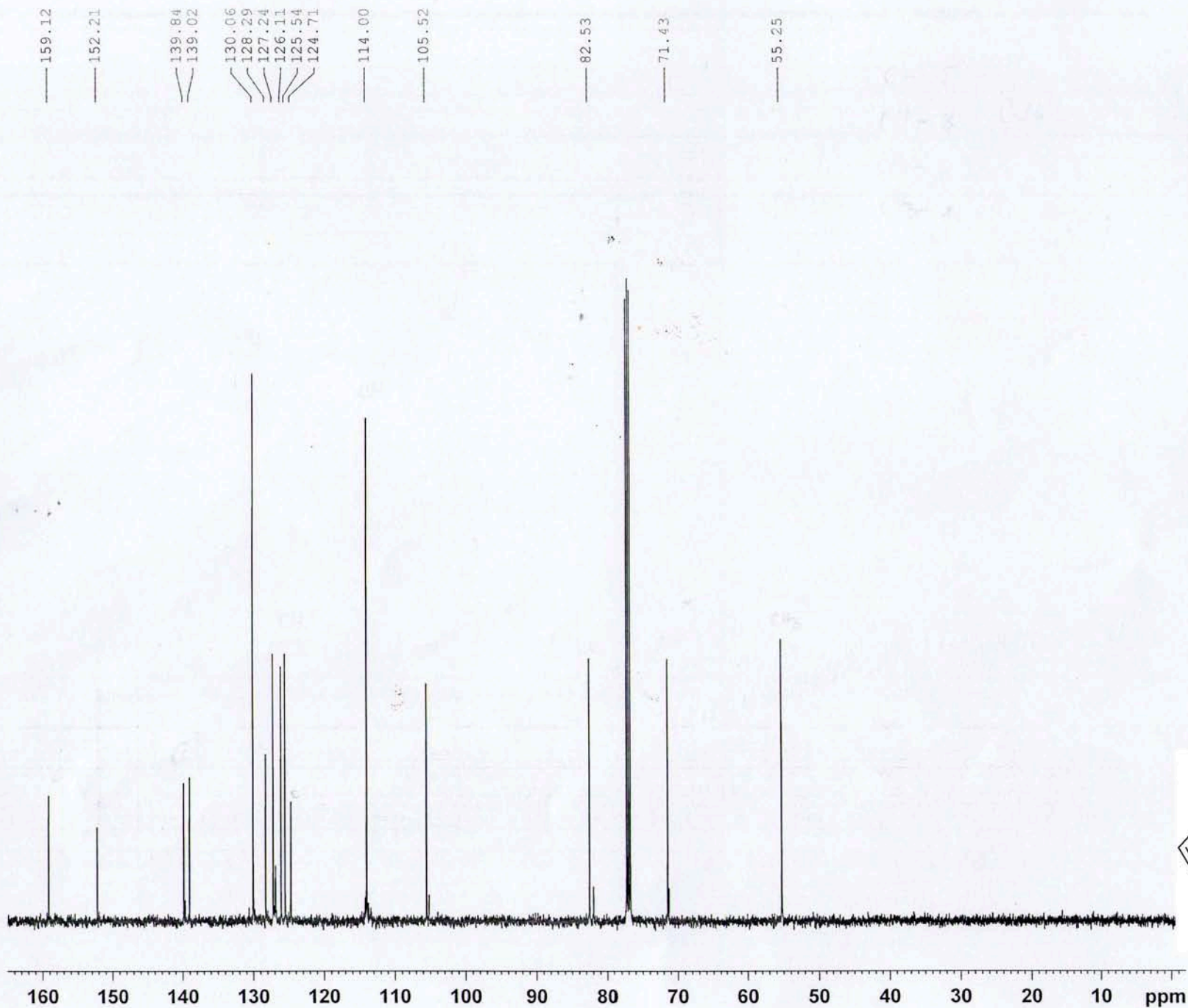


NAME MB-322  
 EXPNO 1  
 PROCNO 1  
 Date\_ 20121010  
 Time\_ 15.33  
 INSTRUM spect  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 0  
 SWH 4746.835 Hz  
 FIDRES 0.144862 Hz  
 AQ 3.4516127 sec  
 RG 101  
 DW 105.333 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 9.35 usec  
 PL1 0.00 dB  
 PL1W 27.37956238 W  
 SFO1 500.2621415 MHz  
 SI 32768  
 SF 500.2600196 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00



3g



```

NAME MB-322
EXPNO 2
PROCNO 1
Date_ 20121010
Time_ 15.40
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 271
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 0.5505524 sec
RG 1030
DW 16.800 usec
DE 6.50 usec
TE 298.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

```

```

===== CHANNEL f1 =====
NUC1 13C
P1 11.50 usec
PL1 3.00 dB
PL1W 32.22848892 W
SFO1 125.8043140 MHz

```

```

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.20 dB
PL12 18.40 dB
PL13 18.40 dB
PL2W 20.76952171 W
PL12W 0.39575511 W
PL13W 0.39575511 W
SFO2 500.2621416 MHz
SI 32768
SF 125.7904860 MHz
WDW EM
SSB 0
LB 1.50 Hz
GB 0
PC 1.40

```

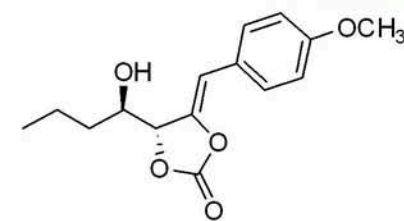
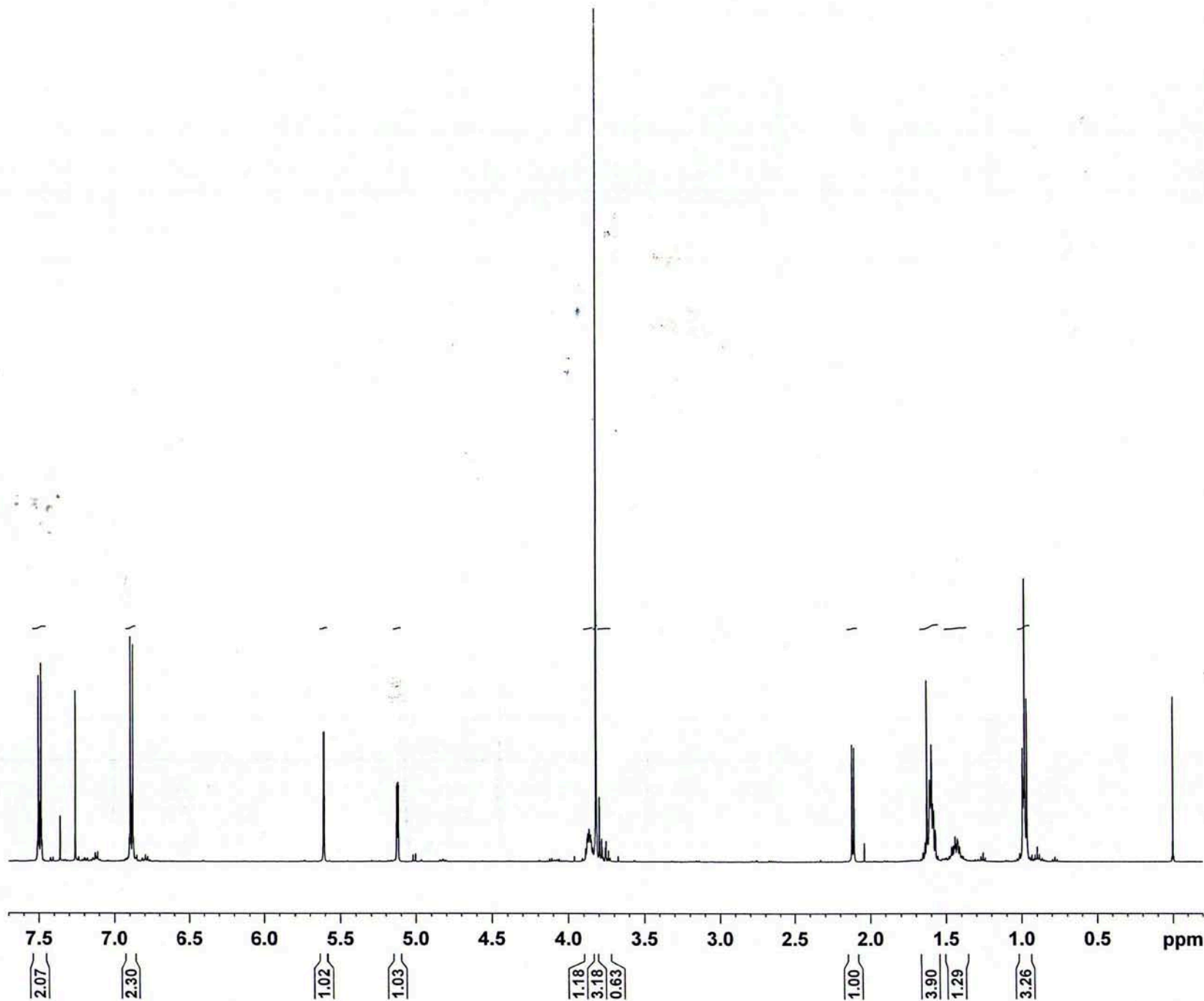


S32

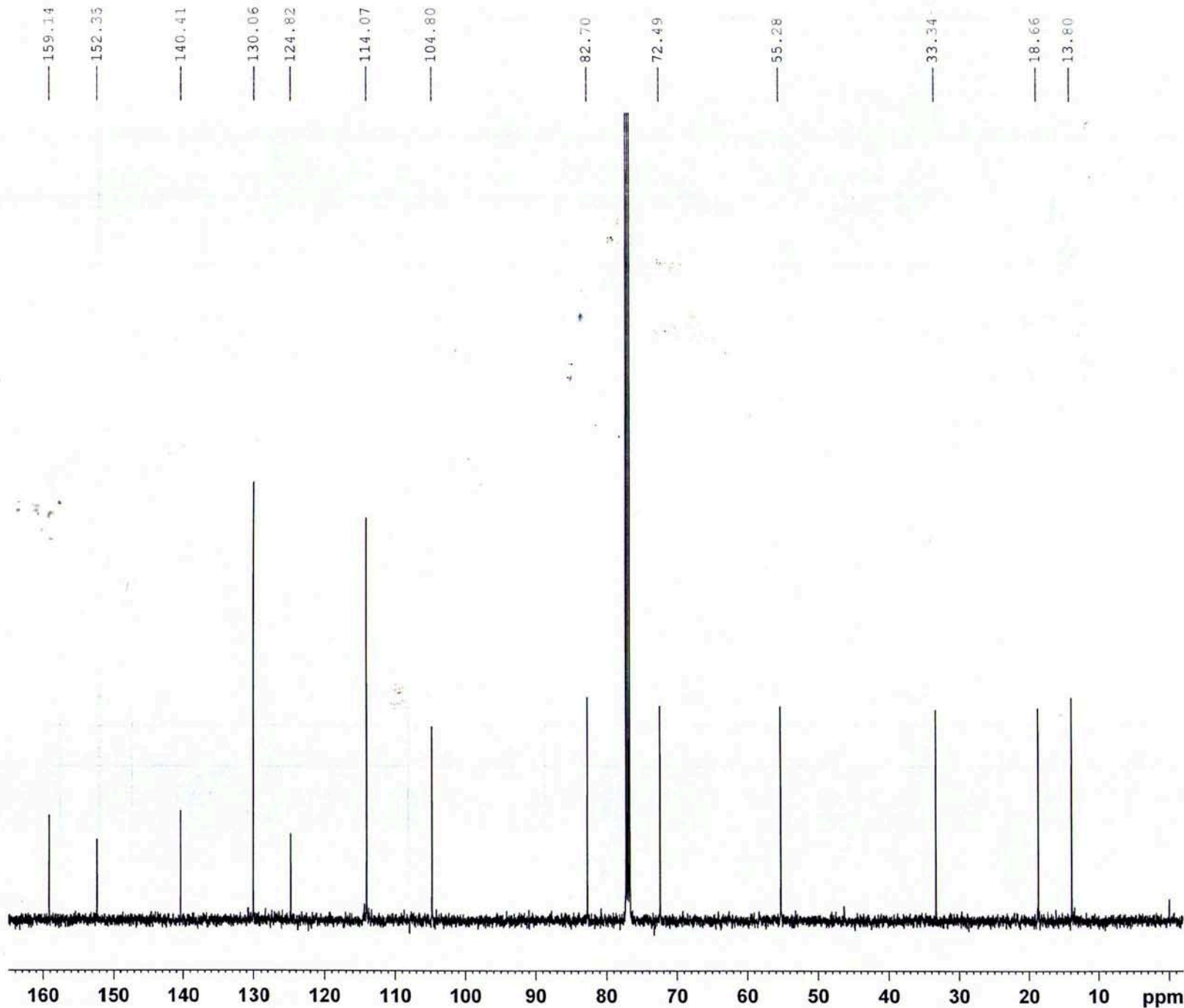


NAME MB-317-1  
 EXPNO 1  
 PROCNO 1  
 Date\_ 20121010  
 Time 10.51  
 INSTRUM spect  
 PROBHD 5 mm BBO BB-1H  
 PULPROG zg30  
 TD 32768  
 SOLVENT CDCl3  
 NS 16  
 DS 0  
 SWH 4826.255 Hz  
 FIDRES 0.147286 Hz  
 AQ 3.3948147 sec  
 RG 181  
 DW 103.600 usec  
 DE 6.50 usec  
 TE 298.0 K  
 D1 2.00000000 sec  
 TD0 1

===== CHANNEL f1 =====  
 NUC1 1H  
 P1 9.35 usec  
 PL1 0.00 dB  
 PL1W 27.37956238 W  
 SFO1 500.2621043 MHz  
 SI 32768  
 SF 500.2600145 MHz  
 WDW EM  
 SSB 0  
 LB 0.20 Hz  
 GB 0  
 PC 1.00



3h



```

NAME          MB-317-1
EXPNO         2
PROCNO        1
Date_         20121010
Time          10.56
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       zgpg30
TD            32768
SOLVENT       CDCl3
NS            259
DS            4
SWH           29761.904 Hz
FIDRES        0.908261 Hz
AQ            0.5505524 sec
RG            1030
DW            16.800 usec
DE            6.50 usec
TE            298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1

```

```

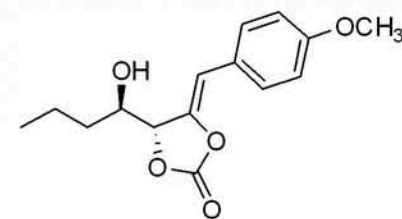
===== CHANNEL f1 =====
NUC1          13C
P1            11.50 usec
PL1           3.00 dB
PL1W          32.22848892 W
SFO1          125.8043140 MHz

```

```

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           1.20 dB
PL12          18.40 dB
PL13          18.40 dB
PL2W          20.76952171 W
PL12W         0.39575511 W
PL13W         0.39575511 W
SFO2          500.2621041 MHz
SI            32768
SF            125.7904826 MHz
WDW           EM
SSB           0
LB            1.50 Hz
GB            0
PC            1.40

```



3h

S34

MB-SS-351

Solvent: cdc13  
Ambient temperature  
File: hmbss351  
GEMINI-200 "nmr"

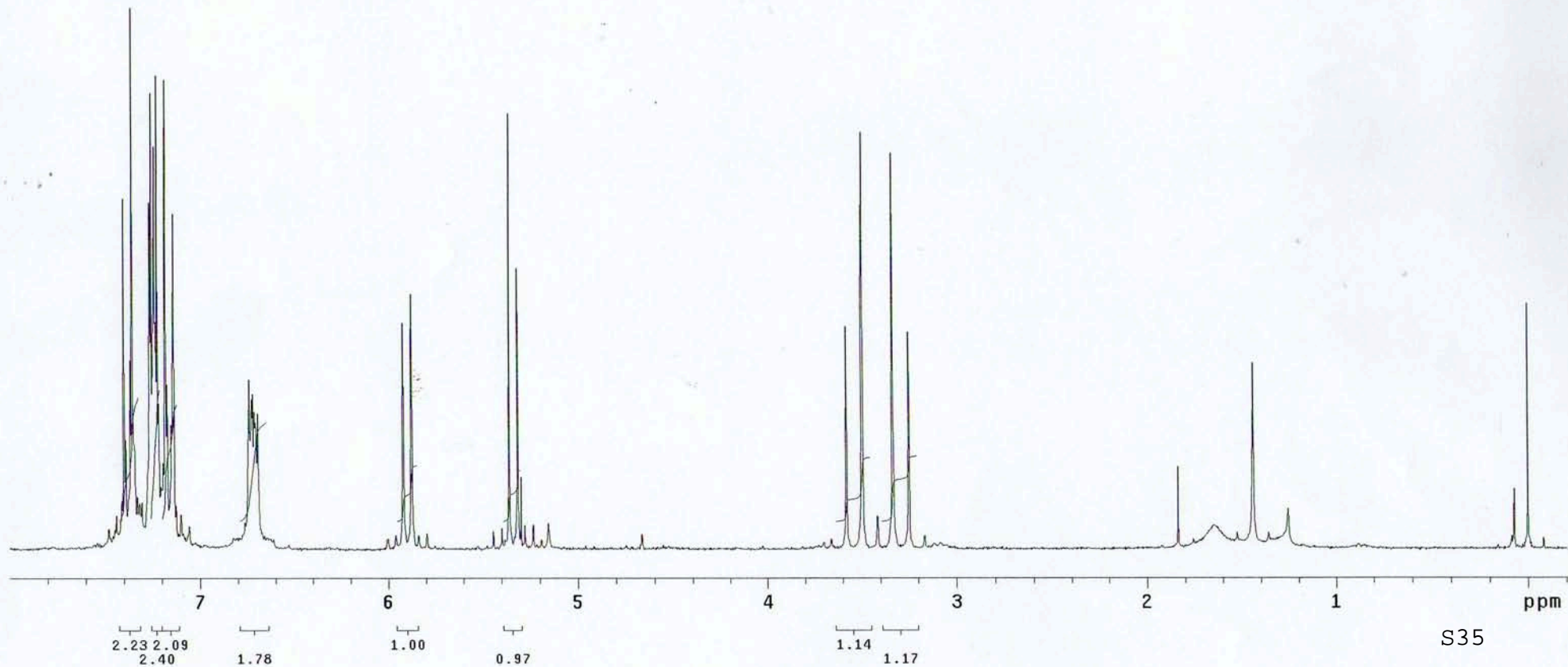
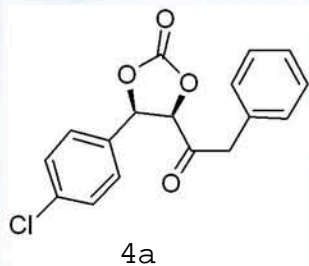
PULSE SEQUENCE

Relax. delay arrayed  
1st pulse arrayed  
2nd pulse 90.0 degrees  
Acq. time 1.437 sec  
Width 4600.0 Hz

Arrayed repetitions  
OBSERVE H1, 199.9710962 MHz

DATA PROCESSING  
FT size 16384

Total time 2 minutes

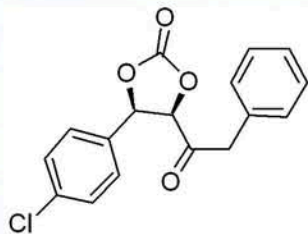


MB-SS-351

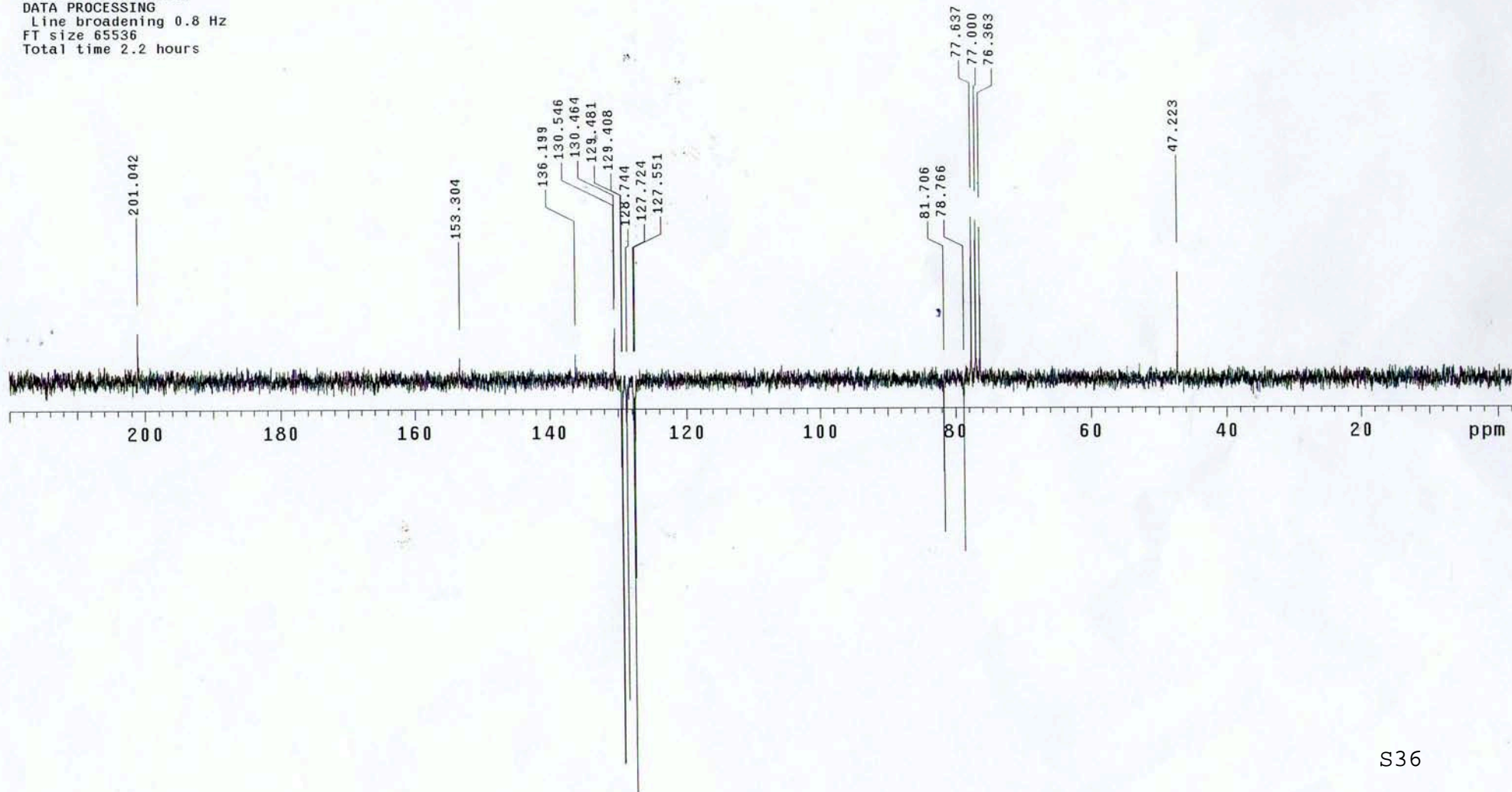
Solvent: cdc13  
Ambient temperature  
GEMINI-200 "nmr"

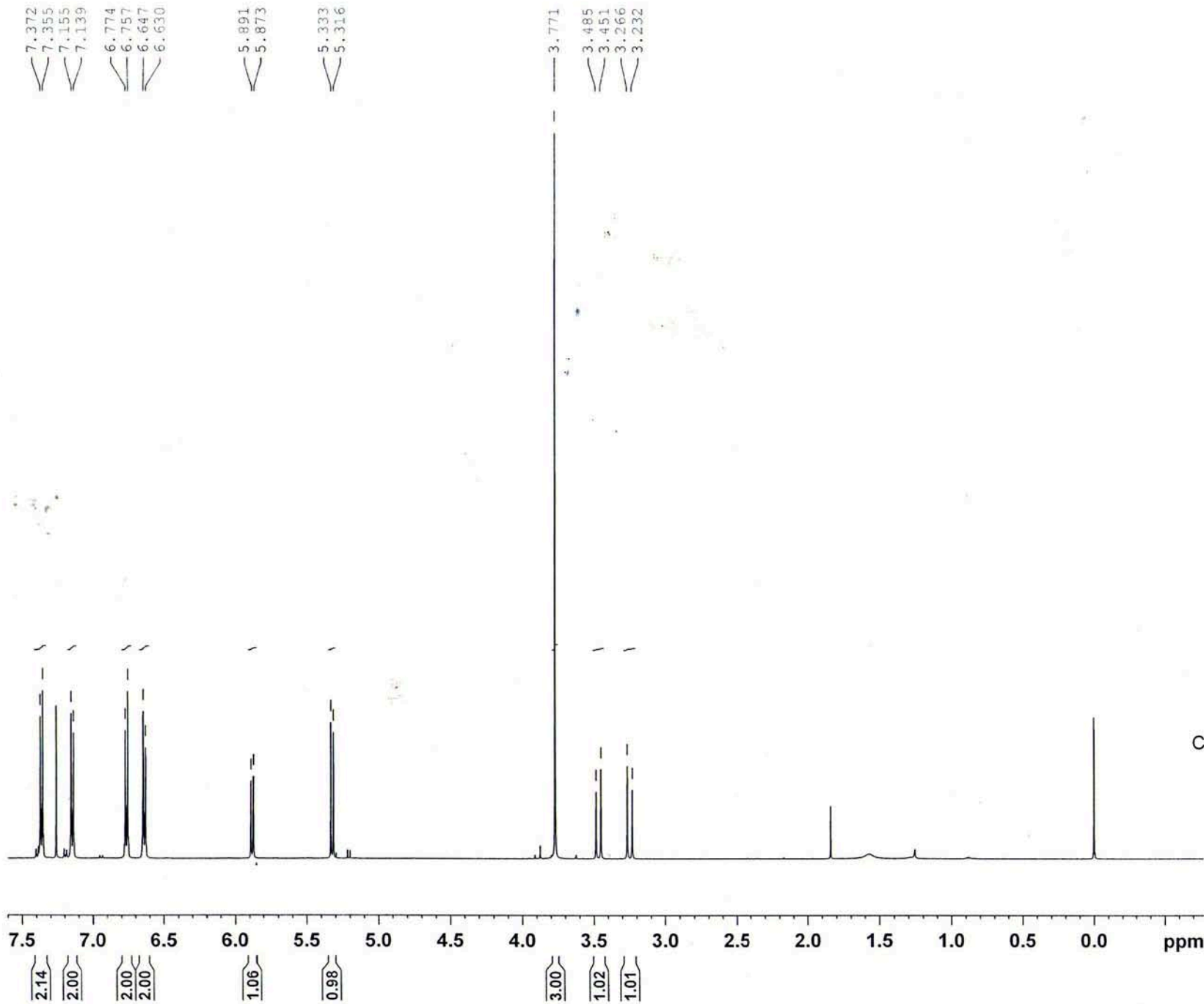
PULSE SEQUENCE: apt  
Relax. delay arrayed  
1st pulse arrayed  
2nd pulse 122.7 degrees  
Acq. time 2.000 sec  
Width 15000.0 Hz  
Arrayed repetitions

OBSERVE C13, 50.2827785 MHz  
DECOUPLE H1, 199.9712807 MHz  
Power 0 dB  
on during acquisition  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.8 Hz  
FT size 65536  
Total time 2.2 hours



4a





```

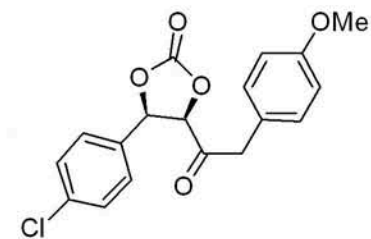
NAME          MB-289
EXPNO         1
PROCNO       1
Date_        20120817
Time         14.16
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zg30
TD           32768
SOLVENT      CDC13
NS           16
DS           0
SWH          4629.629 Hz
FIDRES       0.141285 Hz
AQ           3.5389941 sec
RG           256
DW           108.000 usec
DE           6.50 usec
TE           298.0 K
D1           2.00000000 sec
TD0          1

```

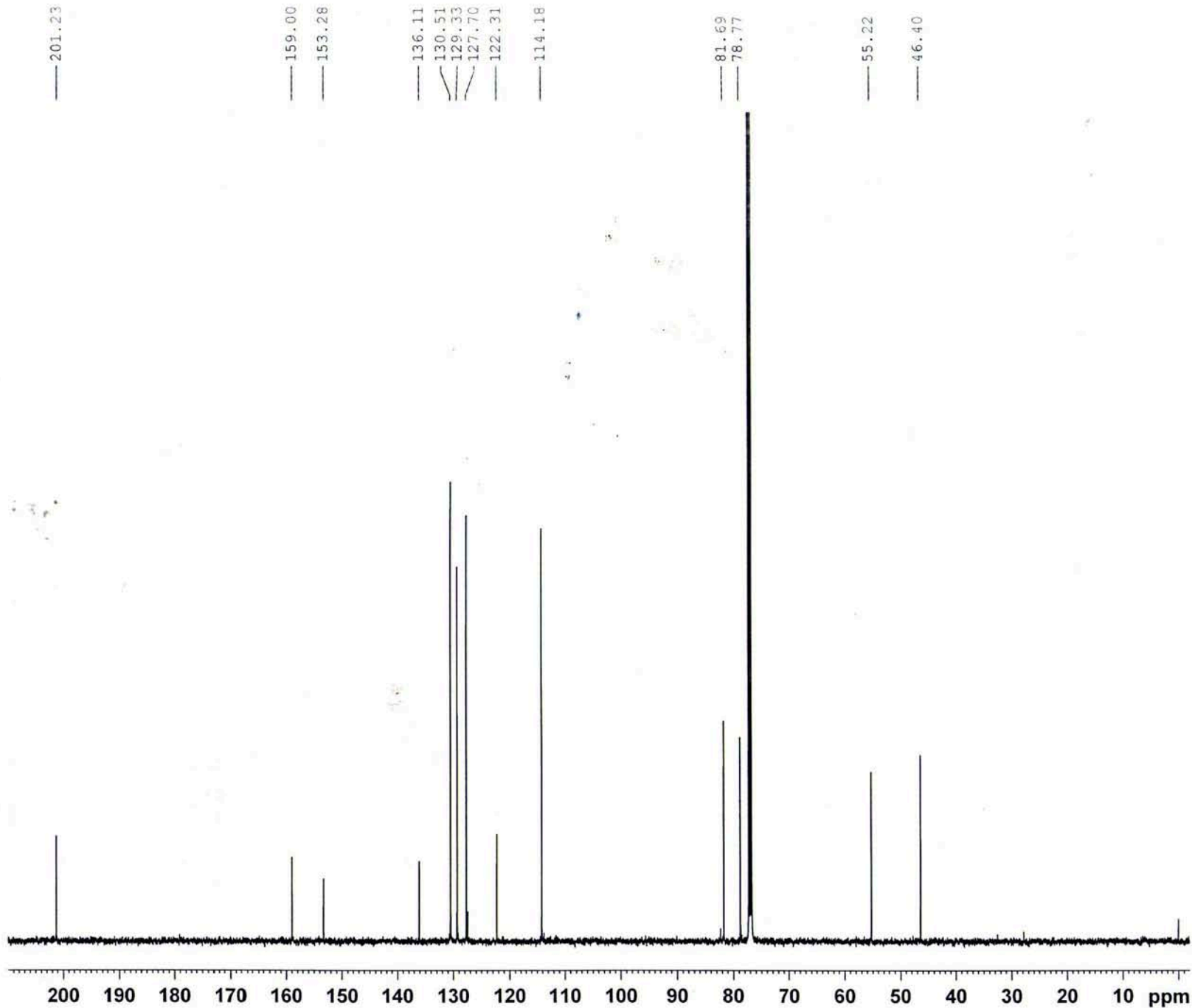
```

===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
PL1           0.00 dB
PL1W         27.37956238 W
SFO1         500.2619427 MHz
SI            32768
SF           500.2600148 MHz
WDW           EM
SSB           0
LB            0.20 Hz
GB            0
PC            1.00

```



4b



```

NAME          MB-289
EXPNO         2
PROCNO       1
Date_        20120817
Time_        14.21
INSTRUM      spect
PROBHD       5 mm BBO BB-1H
PULPROG      zgpg30
TD           32768
SOLVENT      CDCl3
NS           1651
DS           4
SWH          29761.904 Hz
FIDRES       0.908261 Hz
AQ           0.5505524 sec
RG           1030
DW           16.800 usec
DE           6.50 usec
TE           298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0          1

```

```

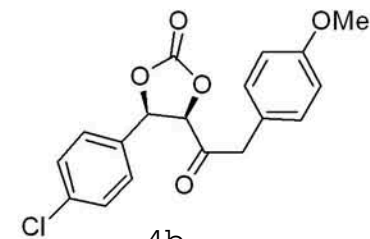
===== CHANNEL f1 =====
NUC1          13C
P1            11.50 usec
PL1           3.00 dB
PL1W          32.22848892 W
SFO1          125.8043140 MHz

```

```

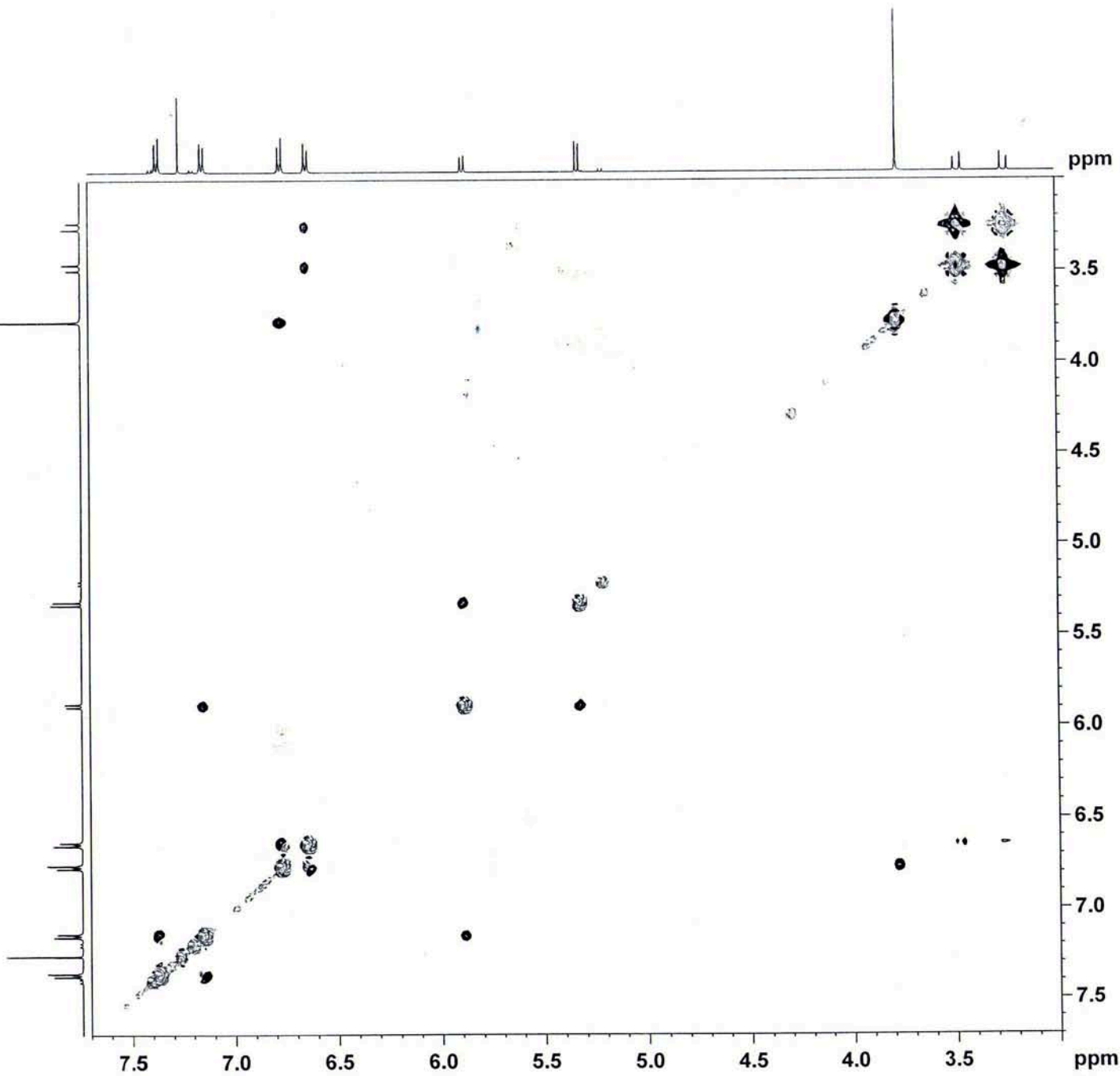
===== CHANNEL f2 =====
CPDPRG2      waltz16
NUC2          1H
PCPD2        80.00 usec
PL2           1.20 dB
PL12         18.40 dB
PL13         18.40 dB
PL2W          20.76952171 W
PL12W         0.39575511 W
PL13W         0.39575511 W
SFO2          500.2619425 MHz
SI            32768
SF            125.7904814 MHz
WDW           EM
SSB           0
LB            1.50 Hz
GB            0
PC            1.40

```



4b

S38



```

NAME          MB-286-3
EXPNO         4
PROCNO        1
Date_         20120814
Time          13.48
INSTRUM       spect
PROBHD        5 mm BBO BB-1H
PULPROG       noesygpph
TD            1024
SOLVENT       CDCl3
NS            8
DS            16
SWH           4629.629 Hz
FIDRES        4.521122 Hz
AQ            0.1106420 sec
RG            287
DW            108.000 usec
DE            6.50 usec
TE            298.0 K
DO            0.00009610 sec
D1            2.00000000 sec
D8            1.00000000 sec
D16           0.00020000 sec
IN0           0.00021600 sec

```

```

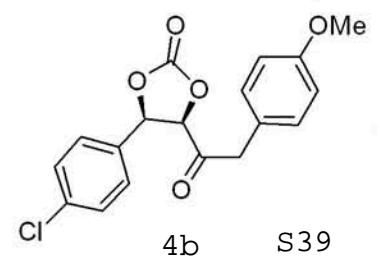
===== CHANNEL f1 =====
NUC1          1H
P1            9.35 usec
P2            18.70 usec
PL1           0.00 dB
PL1W          27.37956238 W
SFO1          500.2620786 MHz

```

```

===== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPZ1          40.00 %
P16           1000.00 usec
ND0           1
TD            256
SFO1          500.2621 MHz
FIDRES        18.084475 Hz
SW            9.254 ppm
FnMODE        States-TPPI
SI            512
SF            500.2600091 MHz
WDW           QSINE
SSB           2
LB            0.00 Hz
GB            0
PC            1.00
SI            512
MC2           States-TPPI
SF            500.2600097 MHz
WDW           QSINE
SSB           2
LB            0.00 Hz
GB            0

```



MB-SS-355

Solvent: cdc13  
Ambient temperature  
GEMINI-200 "nmr"

PULSE SEQUENCE

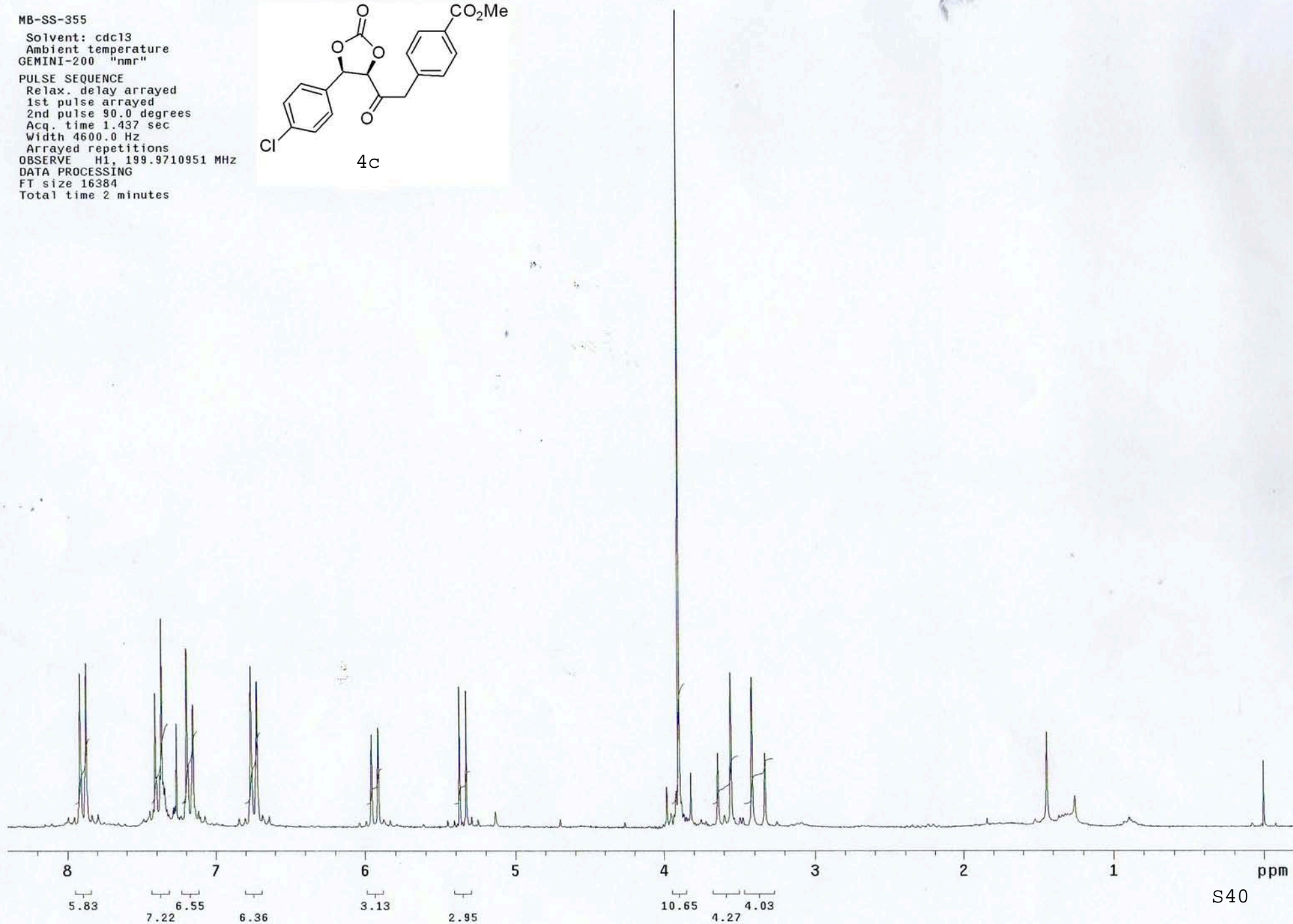
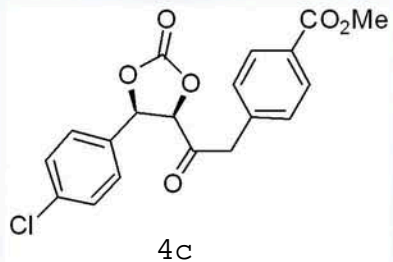
Relax. delay arrayed  
1st pulse arrayed  
2nd pulse 90.0 degrees  
Acq. time 1.437 sec  
Width 4600.0 Hz  
Arrayed repetitions

OBSERVE H1, 199.9710951 MHz

DATA PROCESSING

FT size 16384

Total time 2 minutes





cmbss355  
MB-SS-355

—200.56

—166.31

—153.18

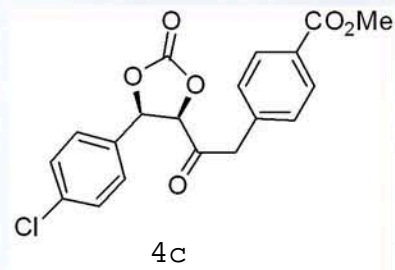
136.34  
135.71  
130.39  
129.86  
129.54  
129.48  
128.45  
127.65

—81.90

—78.63

—52.15

—46.96



cmbss355  
MB-SS-355

—130.39

—129.86

—129.54

—129.48

—128.45

—127.65

