

### **Supporting Information**

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Organocatalytic highly enantioselective conjugate addition of aldehydes to alkylidene malonates

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### **Supporting Information**

General methods: Chemicals and solvents were either purchased puriss p. A. from commercial suppliers or purified by standards techniques. Catalyst 7 was synthesized according to litterature procedures. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (25 g), Ce(SO<sub>4</sub>)<sub>2</sub>. H<sub>2</sub>O (10 g), conc. H<sub>2</sub>SO<sub>4</sub> (60 mL) and H<sub>2</sub>O (940 mL) followed by heating or by treatment with a solution of p-anisaldehyde (23 mL), conc. H<sub>2</sub>SO<sub>4</sub> (35 mL), acetic acid (10 mL) and ethanol (900mL) followed by heating. Flash chromatography was performed using silica gel Merck 60 (particle size 0.040-0.063 mm), <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Varian AS 400 or 300. Chemical shifts are given in δ relative to tetramethylsilane (TMS), the coupling constants J are given in Hz. The spectra were recorded in CDCl<sub>3</sub> as solvent at room temperature, TMS served as internal standard ( $\delta$  = 0 ppm) for <sup>1</sup>H NMR and CDCl<sub>3</sub> was used as internal standard ( $\delta = 77.16$  ppm) for <sup>13</sup>C NMR. GC was carried out using a Varian 3800 GC instrument. Chiral GC-column used: CP-Chiralsil-Dex CB 25m x 0.32 mm. HPLC was carried out using a Waters 2690 Millenium with photodiode array detector. Optical rotations were recorded on a Perkin

<sup>1.</sup> a) M. Marigo, T. C. Wabnitz, D. Fielenbach, K. A. Jørgensen, *Angew. Chem. Int. Ed.* **2005**, *44*, 794. b) M. Marigo, D. Fielenbach, A. Braunton, A. Kjaersgaard, K. A. Jørgensen, *Angew. Chem. Int. Ed.* **2005**, *44*, 3703. c) J. Franzén, M. Marigo, D. Fielenbach, T. C. Wabnitz, A. Kjaersgaard, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 18296. d) Y. Hayashi, H. Gotoh, T. Hayashi, M. Shoji, *Angew. Chem. Int. Ed.* **2005**, *44*, 4212. e) M. Marigo, J. Franzén, T. B. Poulsen, W. Zhuang, K. A. Jørgensen, *J. Am. Chem. Soc.* **2005**, *127*, 6964. g) H. Sundén, I. Ibrahem, A. Córdova, *Tetrahedron Lett.* **2006**, 47, 99. h) I. Ibrahem, A. Córdova, *Chem. Commun.* **2006**, 1760.

Elemer 241 Polarimeter (d = 589 nm, 1 dm cell). High-resolution mass (ESI) were obtained with a Bruker MicrOTOF spectrometer.

# General procedure for the catalyst screen for the conjugate addition of propionaldehyde to dimethyl 2-(4-nitrobenzylidene)malonate:

To a stirred solution of the catalyst (20 mol %) in solvent (0.5 mL) was added propional dehyde (15 mg, 0.25 mmol) and dimethyl 2-(4-nitrobenzylidene) malonate (32.5 mg, 0.125 mmol) at the temperature given in Table 1. The reaction was vigorously stirred and monitored by TLC analysis for the time shown in Table 1. Next, the reaction mixture was directly loaded on the silica gel column and the residue was purified by silica gel chromatography (pentane: ethyl acetate = 4:1) to give product 3a.

## General procedure for chiral amine 7-catalyzed conjugate addition of unmodified aldehydes to different alkylidine malonates:

To a stirred solution of the catalyst **10** (20 mol %) in CHCl<sub>3</sub> (0.5 mL) at -20 °C or CH<sub>3</sub>CN (0.5 mL) at + 4 °C was added aldehyde **1** (0.25 mmol) and alkylidene malonate (0.125 mmol). The reaction was vigorously stirred for the time shown in Table 2 and monitored by TLC analysis. Next, the reaction mixture was directly loaded on the silica gel column and the residue was purified by silica gel chromatography (pentane: ethyl acetate = 8:1-4:1) to give product **3**.

**Dimethyl 2-((1***R***,2***R***)-2-methyl-1-(4-nitrophenyl)-3-oxopropyl)malonate 3a**:  $[\alpha]_D^{25} = -13.2$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.62 (d, J = 1.6 Hz, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 4.13 (dd, J = 6.8, 10.0 Hz, 1H), 4.00 (d, J = 10.0 Hz, 1H), 3.76 (s, 3H), 3.50 (s, 3H), 2.90-2.86 (m, 1H), 0.96 (d, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.9, 168.2, 167.6, 147.4, 145.3, 130.1, 123.8, 54.8, 53.3, 52.9, 48.7, 44.6, 11.2; The enantiomeric excess was determined by HPLC with an OJ column.

(*iso*-hexane: *i*-PrOH = 90:10,  $\lambda$  =250 nm), 0.5 mL/min;  $t_R$  = major enantiomer 120.4 min, minor enantiomer 162.0 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>15</sub>H<sub>17</sub>NO<sub>7</sub>) requires m/z 346.0897, found 346.0885.

**Dimethyl 2-((1R,2R)-2-formyl-1-(4-nitrophenyl)butyl)malonate 3g**:  $[\alpha]_D^{25} = +15.9$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.58 (d, J = 2.8 Hz, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.40 (d, J = 8.8 Hz, 2H), 4.02-3.97 (m, 1H), 3.93 (d, J = 9.6 Hz, 1H), 3.72 (s, 3H), 3.47 (s, 3H), 2.74-2.68 (m, 1H), 1.44-1.38 (m, 2H), 0.81 (d, J = 7.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.7, 168.3, 167.6, 147.4, 145.8, 130.1, 123.8, 56.0, 55.3, 53.2, 52.8, 44.2, 20.3, 11.5; The enantiomeric excess was determined by HPLC with an OJ column. (n-hexane: i-PrOH = 90:10,  $\lambda$  =210 nm), 0.5 mL/min;  $t_R$  = minor enantiomer 43.3 min, major enantiomer 63.2 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>16</sub>H<sub>19</sub>NO<sub>7</sub>) requires m/z 360.1054, found 360.1036.

Dimethyl 2-((1R,2R)-2-benzyl-1-(4-nitrophenyl)-3-oxopropyl)malonate 3h:  $[α]_D^{25} = -16.3$  (c = 1.0, CHCl<sub>3</sub>);  $^1$ H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.59 (d, J = 2.4 Hz, 1H), 8.19 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.26-7.18 (m, 3H), 7.02-7.00 (m, 2H), 4.12 (dd, J = 7.2, 10.0 Hz, 1H), 4.03 (d, J = 10.0 Hz, 1H), 3.74 (s, 3H), 3.49 (s, 3H), 3.22-3.16 (m, 1H), 2.78-2.67 (m, 2H);  $^{13}$ C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.2, 168.2, 167.5, 147.5, 145.4, 137.6, 130.1, 128.91, 128.88, 127.0, 123.9, 55.7, 54.7, 53.2, 52.9, 44.5, 33.4; The enantiomeric excess was determined by HPLC with an Ad column. (n-hexane: i-PrOH = 85:15, λ =210 nm), 0.5 mL/min;  $t_R$  = minor enantiomer 50.3 min, major enantiomer 86.9 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>21</sub>H<sub>21</sub>NO<sub>7</sub>) requires m/z 422.1210, found 422.1226.

Dimethyl 2-((1R,2R)-2-formyl-1-(4-nitrophenyl)pent-4-enyl)malonate 3i:  $[\alpha]_D^{25} = + 17.1 \ (c = 1.0, \text{CHCl}_3); ^1\text{H NMR (400 MHz, CDCl}_3) δ 9.60 \ (d, J = 2.4 \text{ Hz, 1H}), 8.16 \ (d, J = 8.8 \text{ Hz, 2H}), 7.41 \ (d, J = 8.8 \text{ Hz, 2H}), 5.66-5.55 \ (m, 1H), 5.04 \ (dd, J = 1.6, 10.4 \text{ Hz, 1H}), 4.95 \ (dd, J = 1.6, 17.2 \text{ Hz, 1H}), 4.07-3.99 \ (m, 2H), 3.72 \ (s, 3H), 3.46 \ (s, 3H), 2.96-2.90 \ (m, 1H), 2.18-2.16 \ (m, 2H); <math>^{13}\text{C NMR (100 MHz, CDCl}_3) δ 202.2, 168.3, 167.6, 147.5, 145.4, 133.5, 130.2, 123.8, 118.6, 54.9, 53.5, 53.2, 52.8, 44.0, 31.4; The enantiomeric excess was determined by HPLC with an Ad column. ($ *n*-hexane:*i* $-PrOH = 90:10, λ = 210 nm), 0.5 mL/min; <math>t_R = \text{minor enantiomer } 42.5 \text{ min, major enantiomer} 74.3 \text{ min. HRMS (ESI): calcd. for } [\text{M+Na}]^+(\text{C}_{17}\text{H}_{19}\text{NO}_7}) \text{ requires m/z } 372.1054, \text{ found } 372.1055.$ 

Dimethyl 2-((1R,2R)-2-methyl-3-oxo-1-phenylpropyl)malonate 3f:  $[\alpha]_D^{25}$  = -13.2 (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.62 (d, J = 2.0 Hz, 1H), 7.28-7.27 (m, 2H), 7.24-7.22 (m, 1H), 7.16-7.14 (m, 2H), 4.00-3.95 (m, 2H), 3.75 (s, 3H), 3.43 (s, 3H), 2.80-2.73 (m, 1H), 0.95 (d, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.1, 168.8, 167.9, 137.3, 128.9, 128.6, 127.7, 55.5, 53.1, 52.6, 49.4, 45.2, 11.0; The enantiomeric excess was determined by HPLC with an Ad column. (n-hexane: i-PrOH = 90:10,  $\lambda$  =210 nm), 0.5 mL/min;  $t_R$  = major enantiomer 21.0 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>15</sub>H<sub>18</sub>O<sub>5</sub>) requires m/z 301.1046, found 301.1047.

**Dimethyl 2-((1R,2R)-1-(4-chlorophenyl)-2-methyl-3-oxopropyl)malonate 3c**:  $[α]_D^{25} =$  -6.5 (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.59 (d, J = 1.6 Hz, 1H), 7.27-7.25 (m, 2H), 7.11-7.09 (m, 2H), 3.98 (dd, J = 6.8, 10.8 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.47 (s, 3H), 2.77 (ddd, J = 1.6, 6.8, 6.8 Hz, 1H), 0.94 (d, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.6, 168.5, 167.8, 135.9, 133.6, 130.4, 128.8, 55.2, 53.1, 52.7, 49.1, 44.4, 11.0; The enantiomeric excess was determined by HPLC with an Ad column. (n-hexane: i-PrOH = 97:3,  $\lambda$  =250 nm), 0.3 mL/min;  $t_R$  = minor enantiomer 60.4 min, major enantiomer 98.1 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>15</sub>H<sub>17</sub>ClO<sub>5</sub>) requires m/z 335.0657, found 335.0645.

**Dimethyl 2-((1R,2R)-1-(4-bromophenyl)-2-methyl-3-oxopropyl)malonate 3d**:  $[α]_D^{25}$  = - 3.8 (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.59 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 3.97 (dd, J = 6.4, 10.8 Hz, 1H), 3.92 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.48 (s, 3H), 2.79-2.75 (m, 1H), 0.94 (d, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.6, 168.5, 167.8, 136.4, 131.8, 130.7, 121.7, 55.1, 53.1, 52.7, 49.0, 44.5, 11.0; The enantiomeric excess was determined by HPLC with an Ad column. (n-hexane: i-PrOH = 90:10, λ =225 nm), 0.3 mL/min; t<sub>R</sub> = minor enantiomer 34.2 min, major enantiomer 52.6 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>15</sub>H<sub>17</sub>BrO<sub>5</sub>) requires m/z 379.0152, found 379.0134.

**Dimethyl 2-((1R,2R)-2-methyl-1-(3-nitrophenyl)-3-oxopropyl)malonate 3b**:  $[\alpha]_D^{25}$  = + 11.2 (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.63 (d, J = 1.6 Hz, 1H), 8.13-8.10 (m, 1H), 8.07-8.06 (m, 1H), 7.58-7.56 (m, 1H), 7.50-7.46 (m, 1H), 4.12 (dd, J = 6.8, 10.0 Hz, 1H), 4.01 (d, J = 10.0 Hz, 1H), 3.75 (s, 3H), 3.50 (s, 3H), 2.93-2.89 (m, 1H),

0.97 (d, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  201.9, 168.2, 167.6, 148.3, 139.8, 135.7, 129.6, 123.7, 122.8, 54.8, 53.2, 52.8, 48.6, 44.4, 11.3; The enantiomeric excess was determined by HPLC with an Ad column. (*n*-hexane: *i*-PrOH = 95:5,  $\lambda$  =210 nm), 0.5 mL/min;  $t_R$  = minor enantiomer 44.8 min, major enantiomer 54.5 min. HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>15</sub>H<sub>17</sub>NO<sub>7</sub>) requires m/z 346.0897, found 346.0896.

**Dimethyl 2-((2***R***,3***R***)-2-methyl-1-oxohexan-3-yl)malonate 3j**:  $[α]_D^{25} = -19.1$  (c = 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.70 (d, J = 1.6 Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.48 (d, J = 8.4 Hz, 1H), 2.91-2.85 (m, 1H), 2.51 (ddd, J = 3.2, 7.2, 14.4 Hz, 1H), 1.33-1.25 (m, 2H), 1.21-1.15 (m, 2H), 1.03 (d, J = 7.2 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 203.8, 169.2, 169.1, 54.8, 52.8, 52.7, 48.0, 37.6, 31.3, 21.2, 14.3, 8.4; HRMS (ESI): calcd. for [M+Na]<sup>+</sup>(C<sub>12</sub>H<sub>20</sub>O<sub>5</sub>) requires m/z 267.1203, found 267.1201. The enantiomeric excess was determined by chiral phase GC analysis of the corresponding lactone **8** derived by reduction of product **3j**:

# Synthesis of (3*R*,4*R*,5*R*)-Methyl 5-methyl-2-oxo-4-propyl-tetrahydro-2H-pyran-3-carboxylate 8:

Chiral malonate **3j** (59 mg, .24 mmol, 1.0 equiv.) was dissolved in 1 mL THF. The solution was cooled to 0 °C and 263 µL concentrated AcOH and 22 mg (0.36 mmol, 1.5 equiv.) NaCNBH<sub>3</sub> (95%) were subsequently added. The reaction mixture was warmed up to rt overnight. Next, brine (1 mL) was added and the pH was adjusted to 7 with saturated NaHCO<sub>3</sub> solution. The aqueous layer was extracted 3 times with 10 mL Et<sub>2</sub>O and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents under reduced pressure, the crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). Silica (256 mg) was

added and the mixture was stirred slowly for 4 d. After filtration the solvent was removed under reduced pressure and the crude product was subjected to silica gel column chromatography (pentane: ethyl acetate = 4:1) to give lactone **8** (41 mg, 80%) as a colorless oil.

(3R,4R,5R)-Methyl 5-methyl-2-oxo-4-propyl-tetrahydro-2H-pyran-3-carboxylate 8f:  $[\alpha]_D^{25} = +11.3 \ (c=1.0, \text{CHCl}_3); \ ^1\text{H NMR} \ (400 \text{ MHz}, \text{CDCl}_3) \ \delta \ 4.21 \ (dd, \textit{J}=4.0, 11.2 \text{ Hz}, 1\text{H}), 3.96 \ (dd, \textit{J}=8.4, 11.2 \text{ Hz}, 1\text{H}), 3.78 \ (s, 3\text{H}), 3.32 \ (d, \textit{J}=8.0 \text{ Hz}, 1\text{H}), 2.09-2.03 \ (m, 1\text{H}), 1.84-1.77 \ (m, 1\text{H}), 1.43-1.26 \ (m, 4\text{H}), 1.04 \ (d, \textit{J}=6.8 \text{ Hz}, 3\text{H}), 0.91 \ (d, \textit{J}=7.2 \text{ Hz}, 3\text{H}); \ ^{13}\text{C NMR} \ (100 \text{ MHz}, \text{CDCl}_3) \ \delta \ 169.7, 168.7, 72.7, 53.0, 52.6, 41.2, 36.2, 32.9, 18.9, 16.6, 14.2; The enantiomeric excess was determined on a Chromasil CP-Chirasil-Dex CB-column. Temperature program: 70 °C, hold 10 min, 70 °C to 90 °C, rate 5 °C/min, hold 10 min, 90 °C to 130 °C, rate 1 °C/min, hold 15 min, 130 °C to 200 °C, rate 20 °C/min, hold 5 min; <math>t_R$  = major enantiomer 65.7 min, minor enantiomer 66.6 min. HRMS (ESI): calcd. for [M+Na]^+(C<sub>11</sub>H<sub>18</sub>O<sub>4</sub>) requires m/z 237.1097, found 237.1102.

The relative configuration was confirmed with H-HCOSEY and NOESY experiment (Fig.1). From <sup>1</sup>H NMR, we know that the chemical shift of Ha is 3.32 ppm. From H-HCOSEY, the proton with chemical shift 2.09-2.03 ppm has strong interaction with Ha. Aslo, the proton with chemical shift 1.84-1.77 ppm interacts with methyl group d. So Hb has chemical shift 2.09-2.03 ppm and Hc has chimcal shift 1.84-1.77 ppm. From NOESY, we could not see any interaction between Ha, Hb and Hc, which suggests that the relative stereochemistry is 3,4-*trans* and 4,5-*trans*.

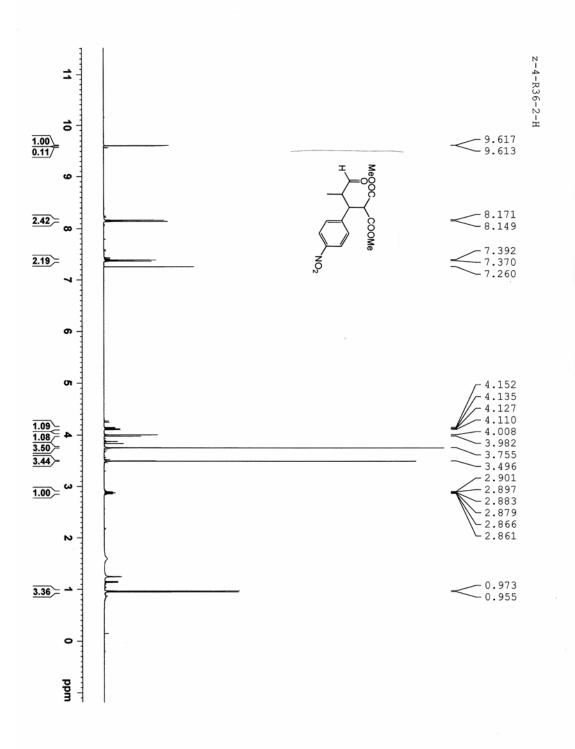
Fig.1

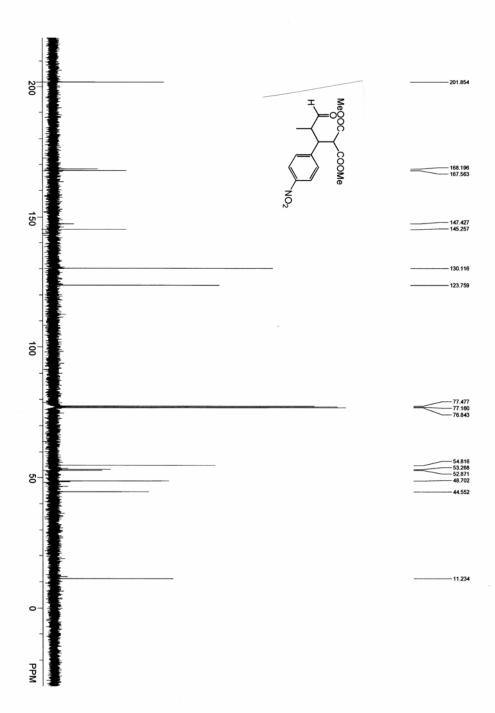
**(3R,4R,5R)-methyl 5-methyl-4-(4-nitrophenyl)-2-oxo-tetrahydro-2H-pyran-3-carboxylate**:  $[\alpha]_D^{25} = -47.0 \text{ (c} = 1.0, \text{CHCl}_3); ^1\text{H NMR } (400 \text{ MHz, CDCl}_3) \delta 8.24-8.21 \text{ (m, 2H), 7.39-7.35 (m, 2H), 4.48 (dd, <math>J = 4.8, 11.2 \text{ Hz, 1H), 4.14 (t, } J = 11.2 \text{ Hz, 1H), 3.69 (d, } J = 11.2 \text{ Hz, 1H), 3.63 (s, 3H), 3.30 (t, <math>J = 11.2 \text{ Hz, 1H}), 2.37-2.29 \text{ (m, 1H), 0.83 (d, } J = 6.4 \text{ Hz, 3H); } ^{13}\text{C NMR } (100 \text{ MHz, CDCl}_3) \delta 168.2, 166.1, 147.7, 147.1, 128.7, 124.5, 74.3, 54.8, 53.1, 48.7, 34.0, 14.7; The enantiomeric excess was determined by HPLC with an ODH column. ($ *n*-hexane:*i* $-PrOH = 93:7, λ =205 nm), 0.5 mL/min; <math>t_R = 1.4 \text{ minor enantiomer } 69.0 \text{ min, major enantiomer } 93.6 \text{ min. HRMS } (ESI): calcd. for <math>1.4 \text{ MH}_1 + 1.4 \text{ NO}_6 + 1.4 \text{ NO}_6$ 

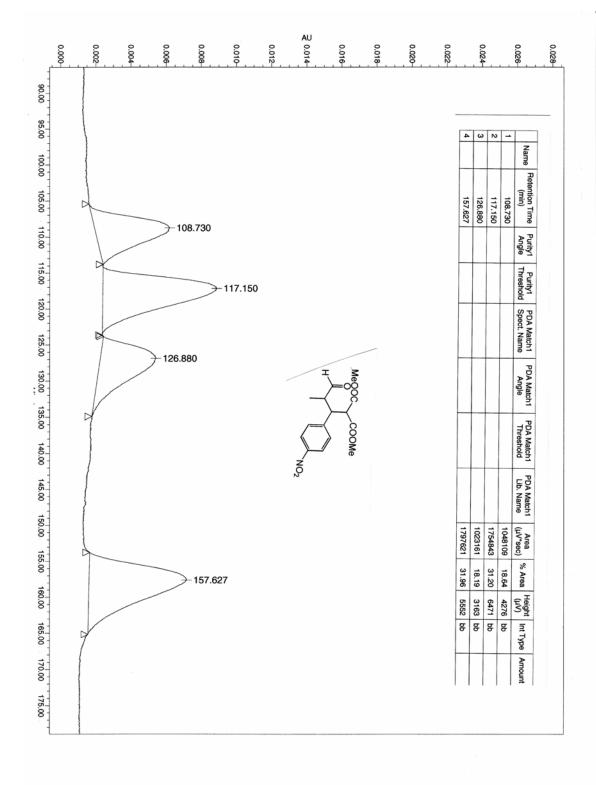
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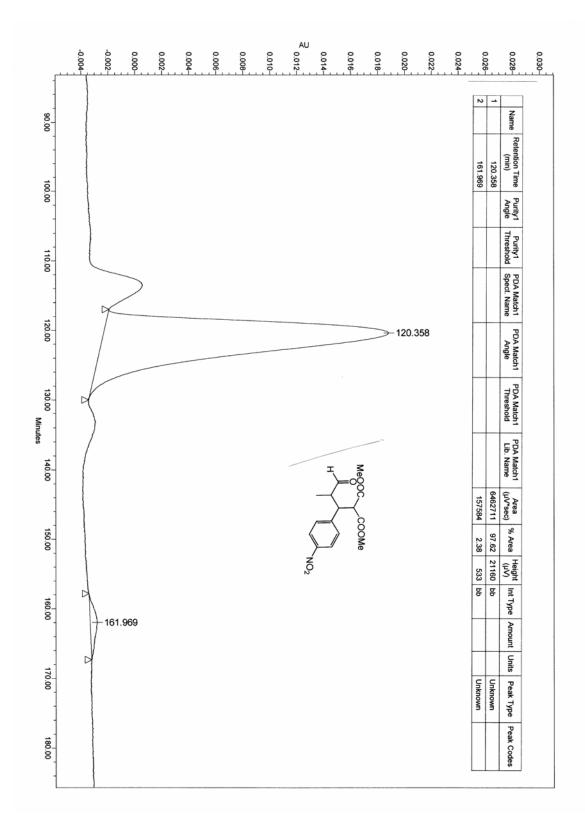
To a stirred solution of aldehyde **3h** (56 mg, 0.14 mmol) in *t*-BuOH/H<sub>2</sub>O (8/1, 1.8 mL) were added KH<sub>2</sub>PO<sub>4</sub> (38 mg, 0.28 mmol), 2-methyl-2-butene (78 mg, 1.12 mmol) and NaClO<sub>2</sub> (51 mg, 0.56 mmol). After stirring the mixture overnight, the resulting yellow solution turned colorless. The solvent was removed under reduced pressure and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with H<sub>2</sub>O, brine, dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed and the residue was purified by silica gel chromatography (pentane: ethyl acetate = 1:1) to give the corresponding acid **9** (49 mg, 85% yield). The acid **9** was recrystallized once (CH<sub>2</sub>Cl<sub>2</sub>:pentane mixtures) prior to X-ray analysis.

(2R,3R)-2-Benzyl-5-methoxy-4-(methoxycarbonyl)-3-(4-nitrophenyl)-5oxopentanoic acid:  $[\alpha]_D^{25} = +3.6$  (c = 0.5, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, J = 8.0 Hz, 2H), 7.49 (dd, J = 2.0, 7.2 Hz, 2H), 7.38-7.36 (m, 1H), 7.23-7.15 (m, 2H), 7.04-7.02 (m, 2H), 4.07-4.06 (m, 1H), 4.01 (d, J = 8.0 Hz, 1H), 3.69 (s, 3H), 3.53 (s, 3H), 3.33-3.28 (m, 1H), 2.71 (dd, J = 6.4, 13.6 Hz, 1H), 2.62 (dd, J = 4.0, 13.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  168.2. 168.1, 167.6, 147.6, 138.1, 130.3, 129.4, 129.0, 128.7, 127.0, 123.9, 55.0, 53.2, 52.9, 46.8, 35.4, 29.9; HRMS(ESI) the exact mass calculated for [M+Na]<sup>+</sup> (C<sub>21</sub>H<sub>21</sub>O<sub>8</sub>N) requires m/z 438.1159, found m/z 438.1164.

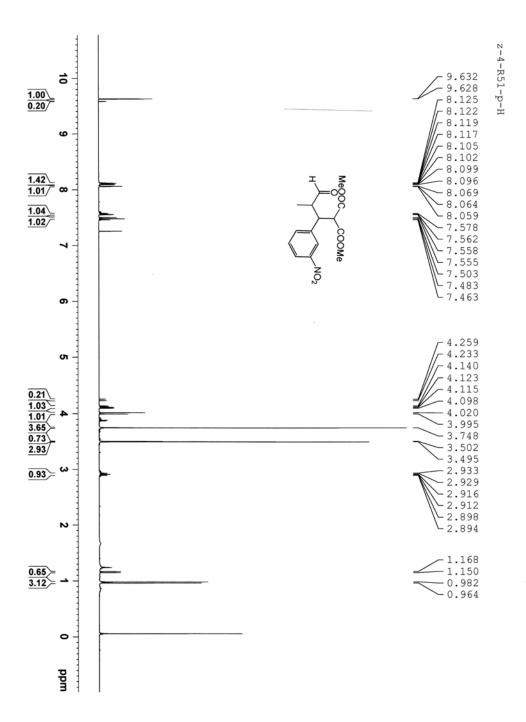


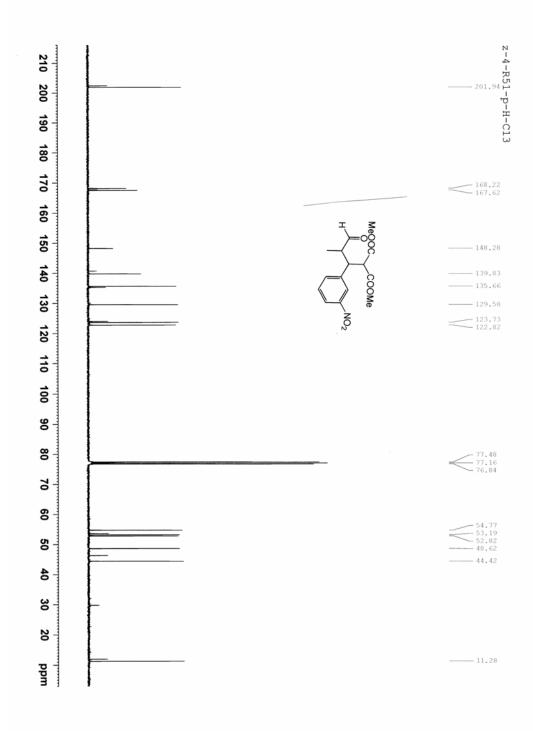


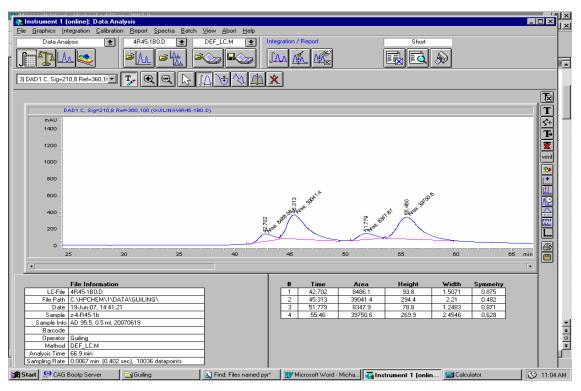


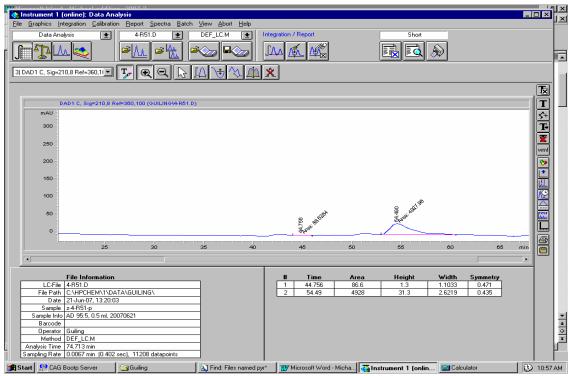


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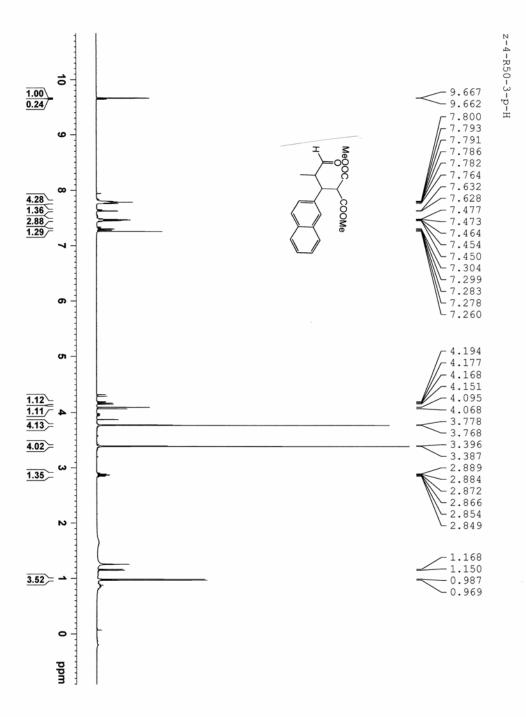
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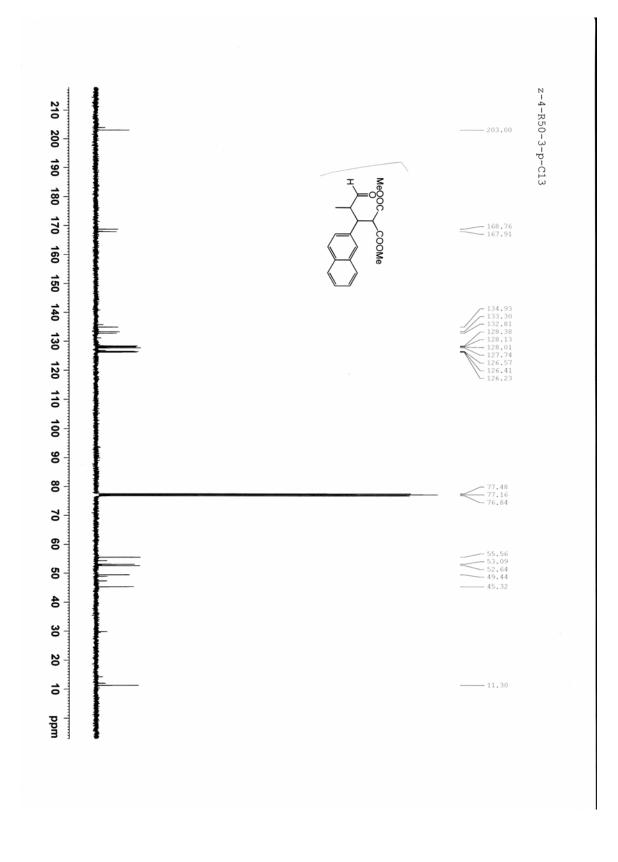
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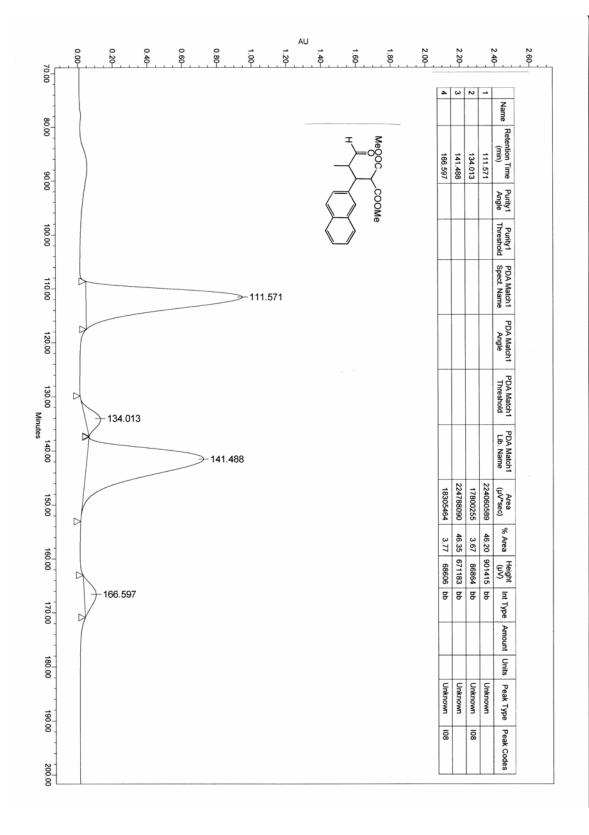
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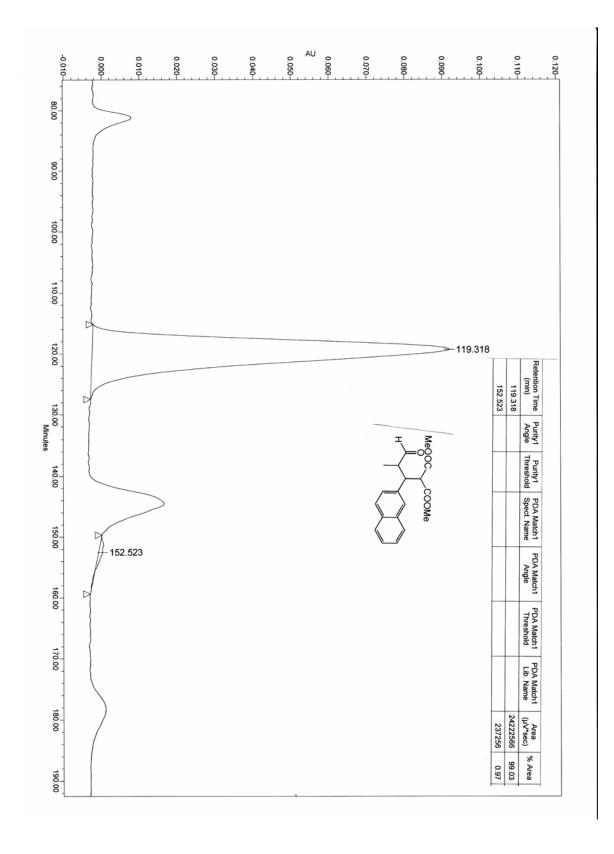
Bruker Daltonics DataAnalysis 3.4

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200

250

350

300

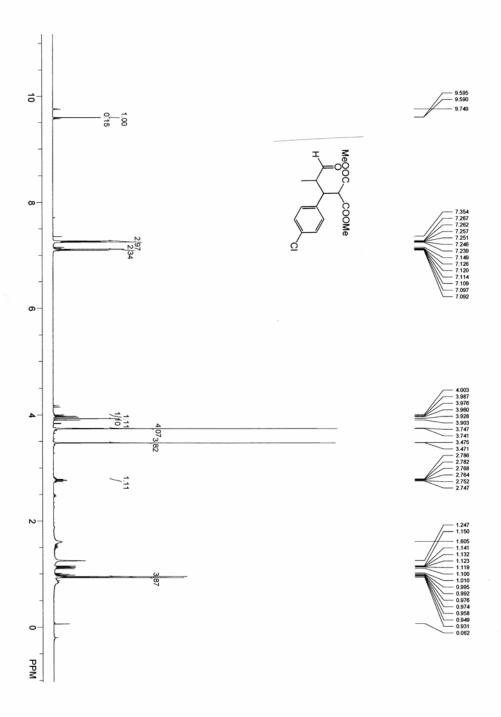
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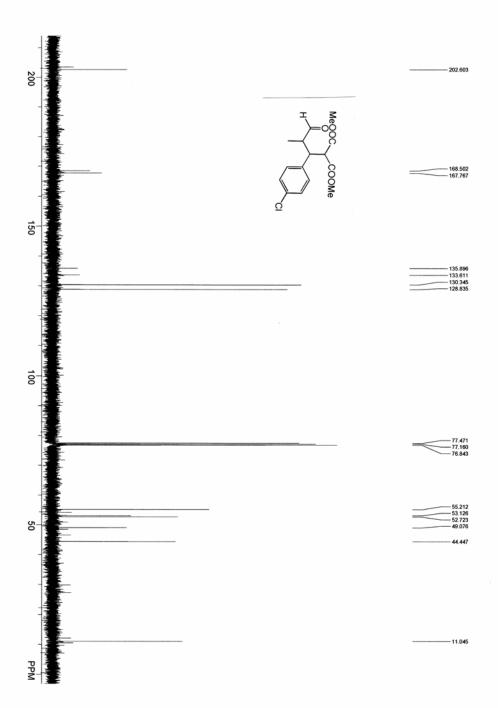
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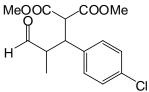
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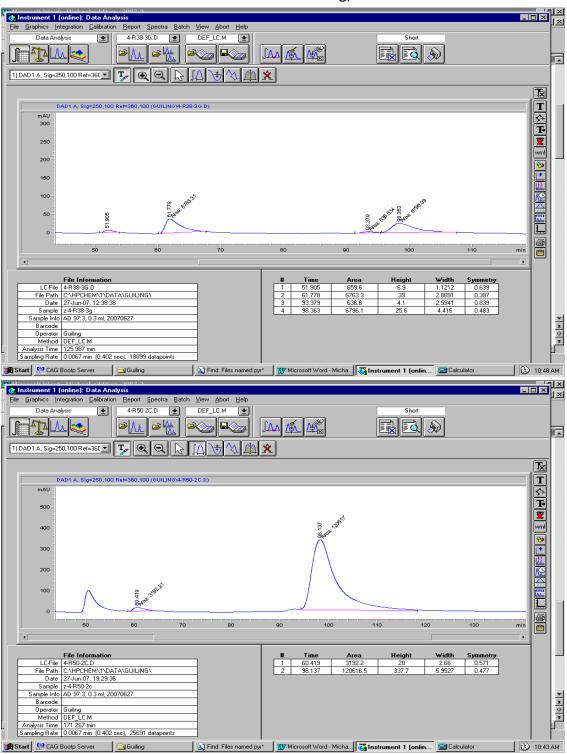
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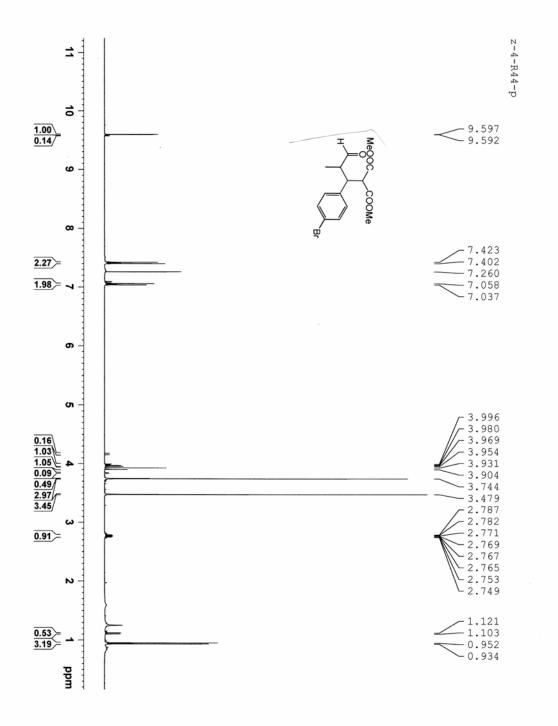


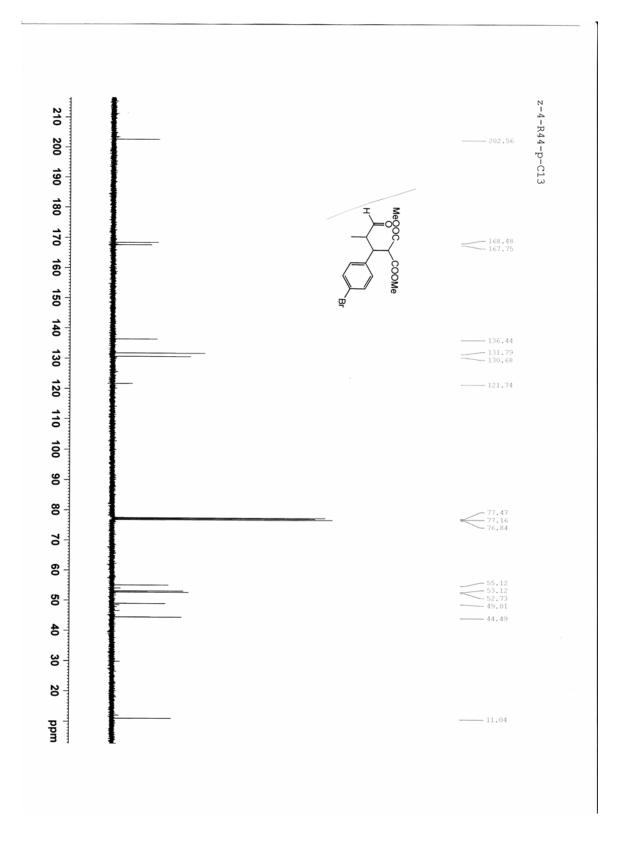


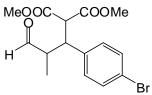


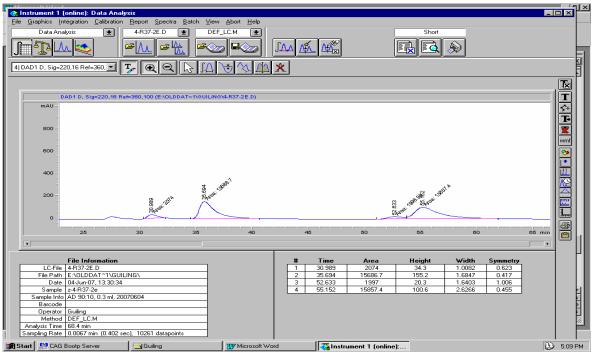


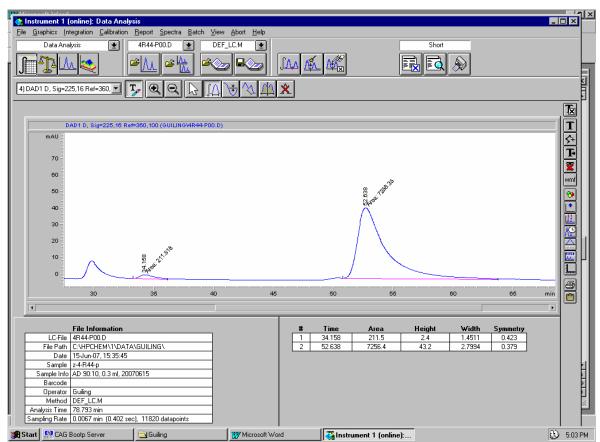
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373.0905

376.1712 376

2000

378

380.0186

383.0133

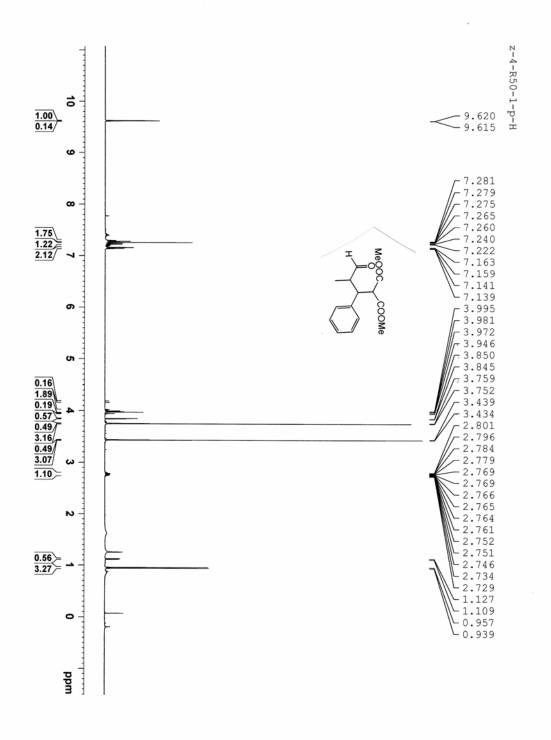
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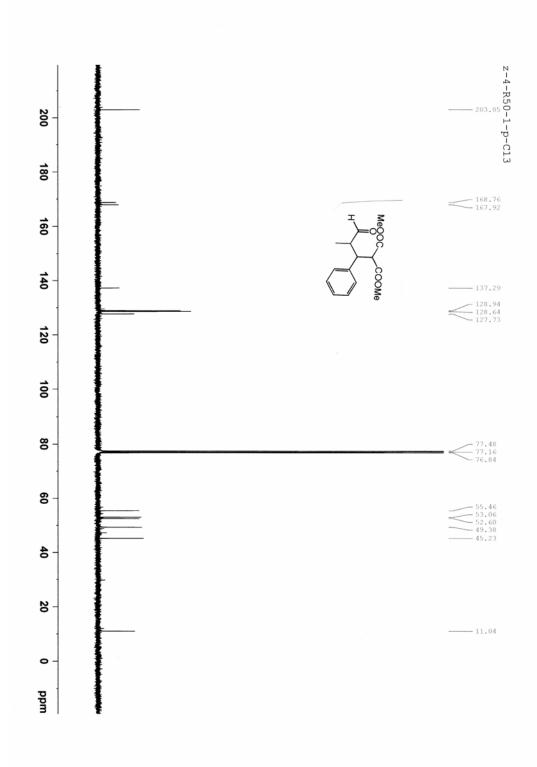
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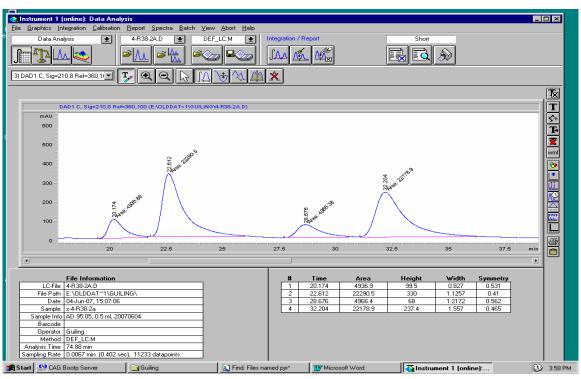
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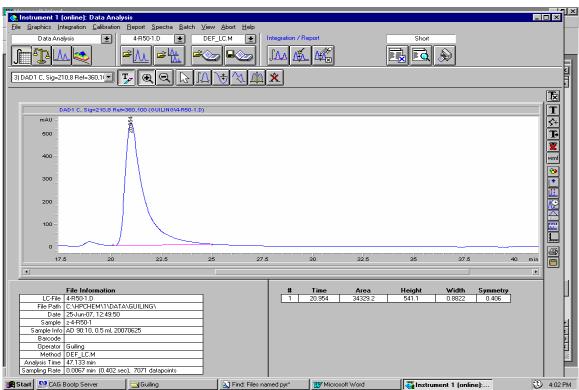
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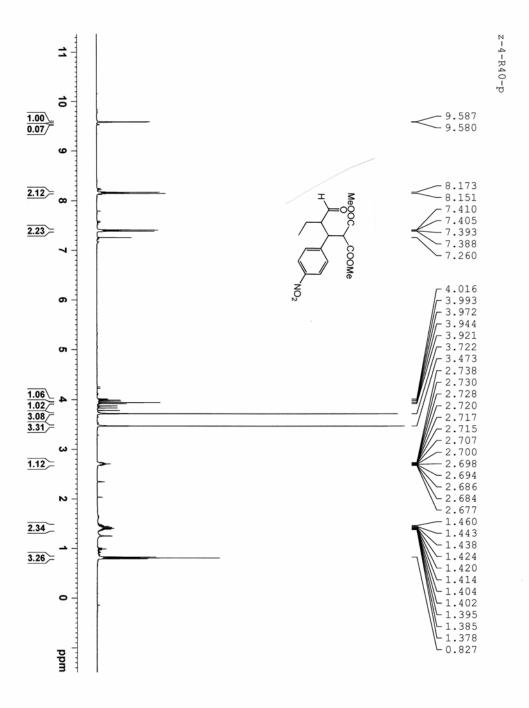
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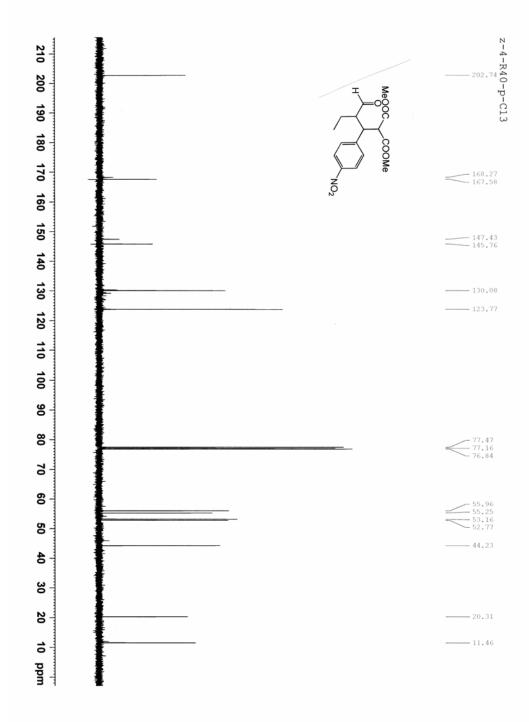
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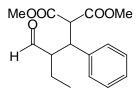
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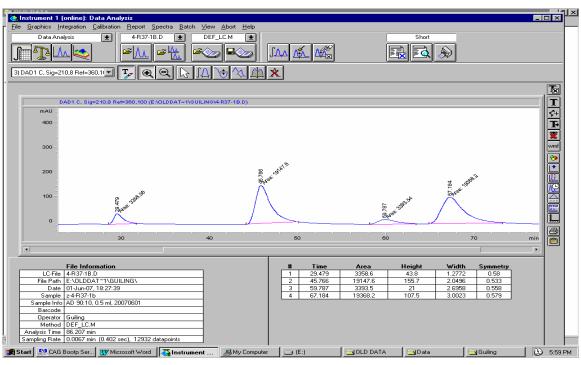
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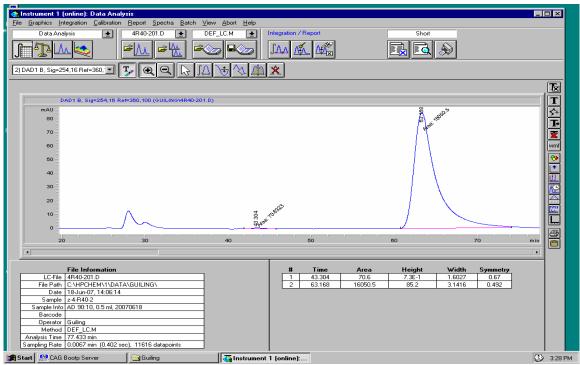
Bruker Daltonics DataAnalysis 3.4











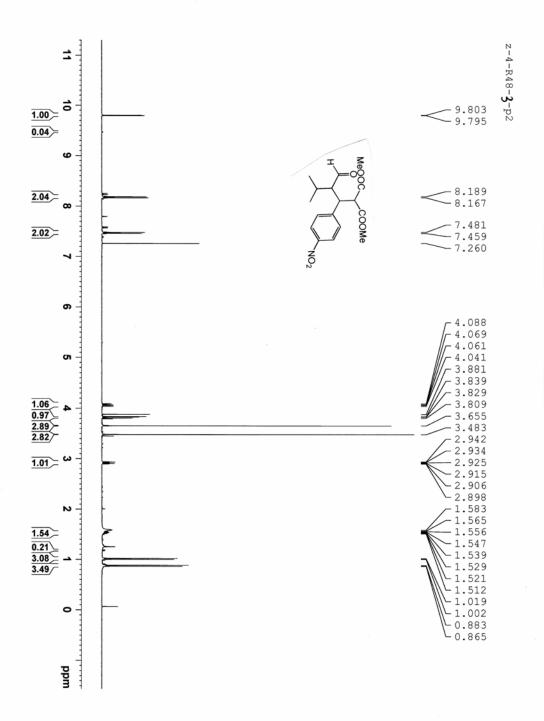
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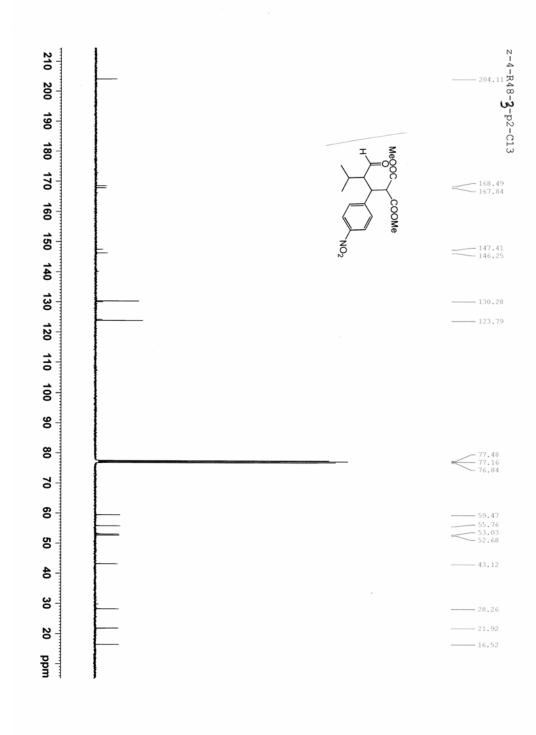
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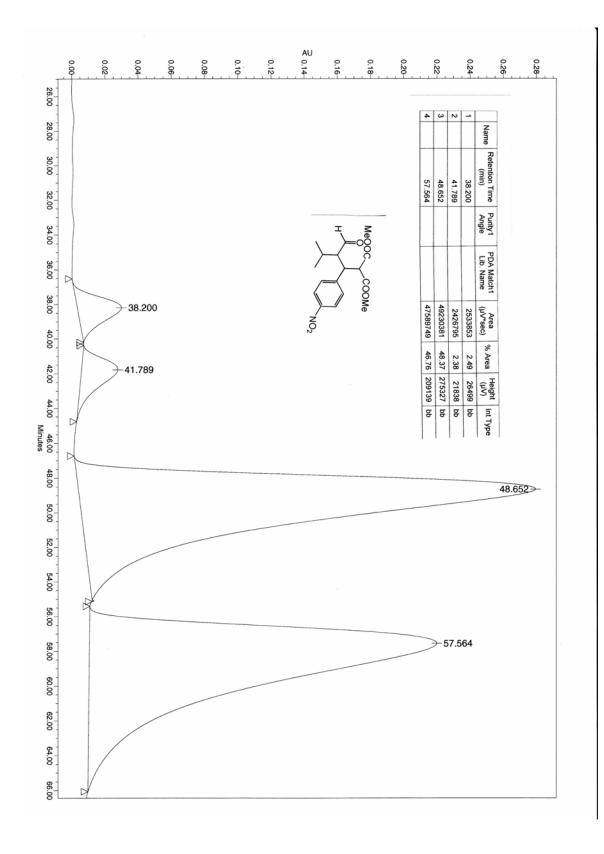
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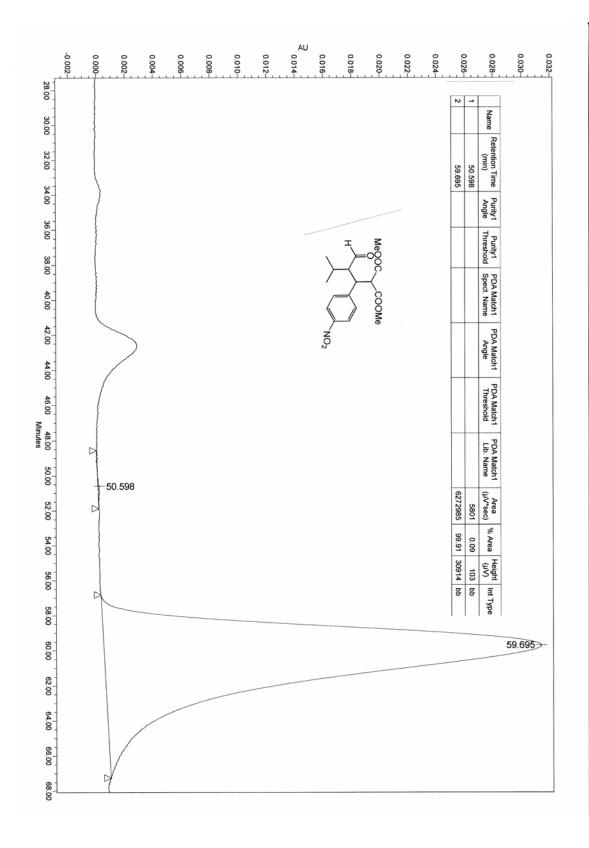
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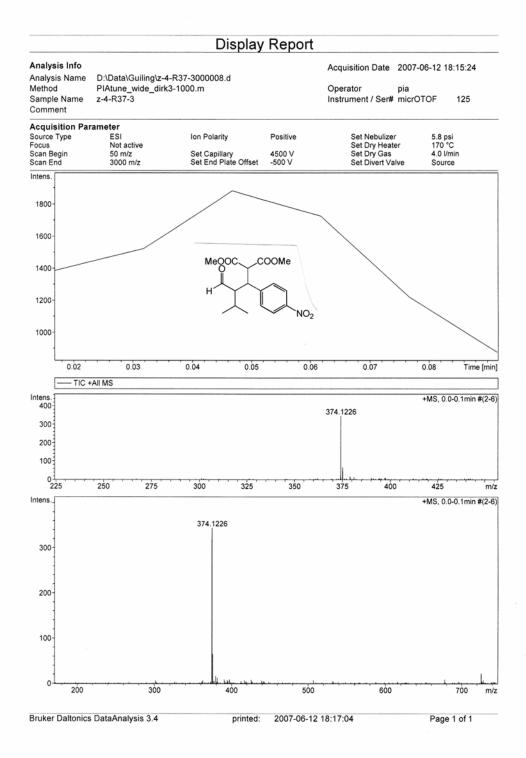
Bruker Daltonics DataAnalysis 3.4

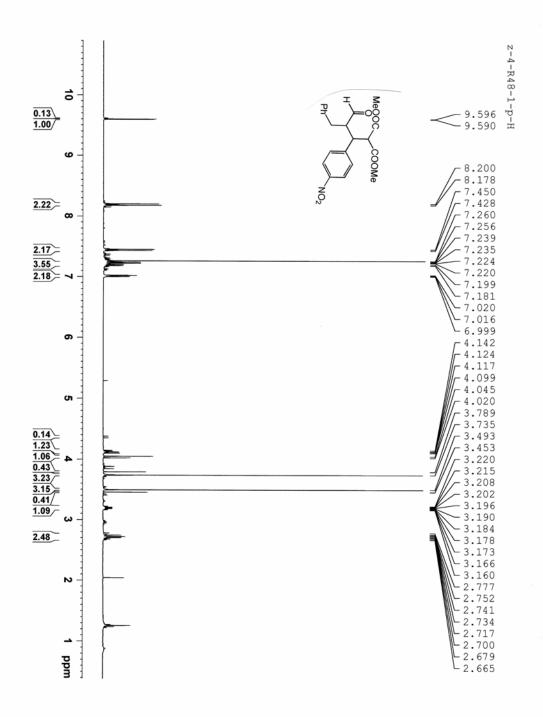


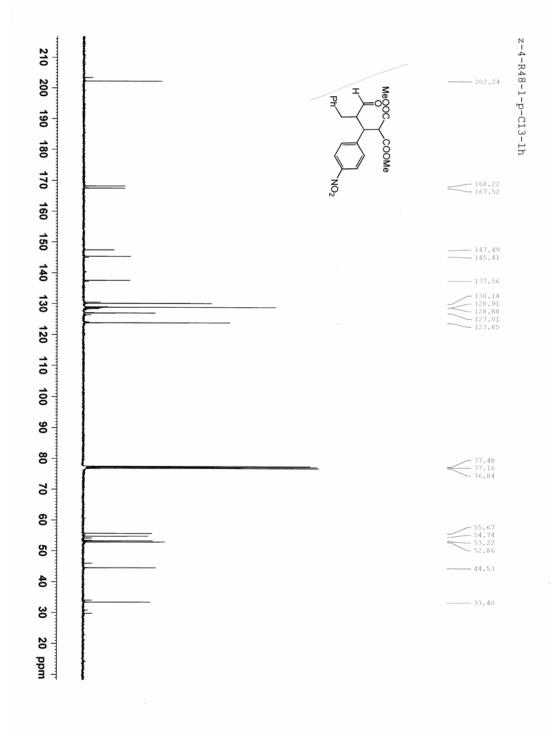


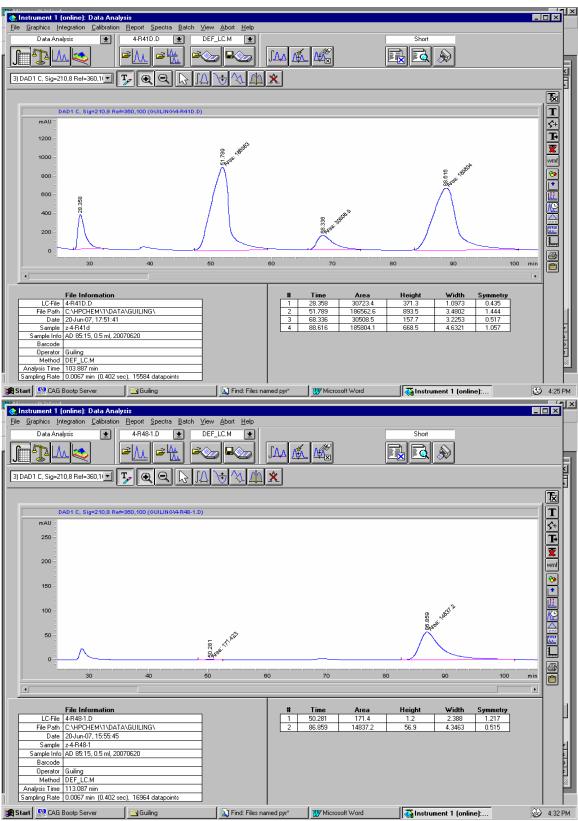




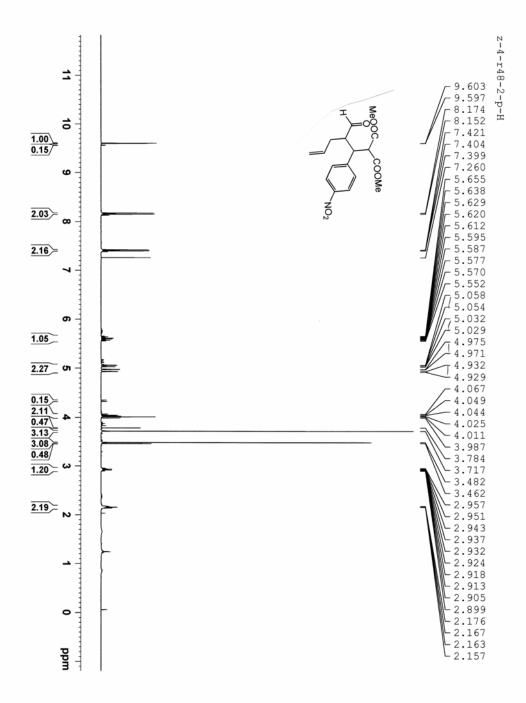


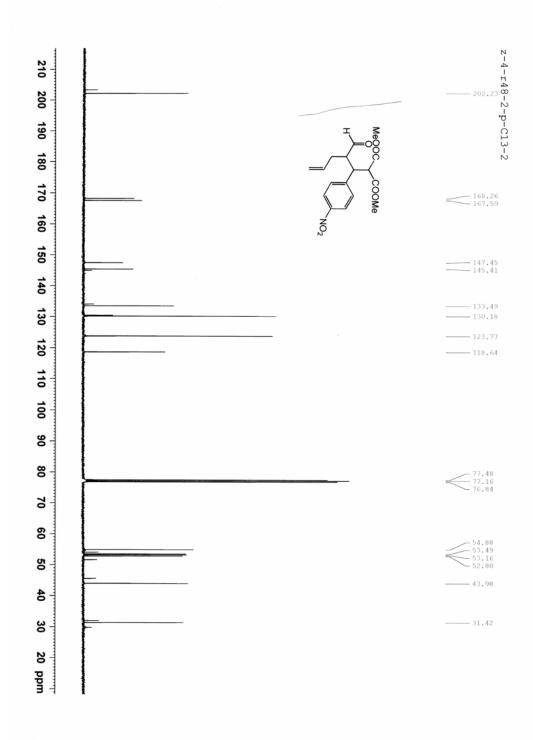


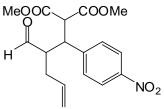


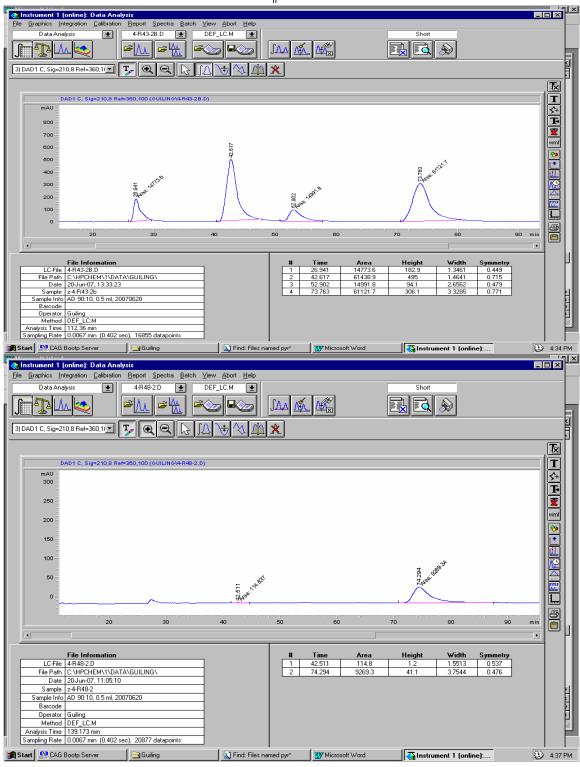


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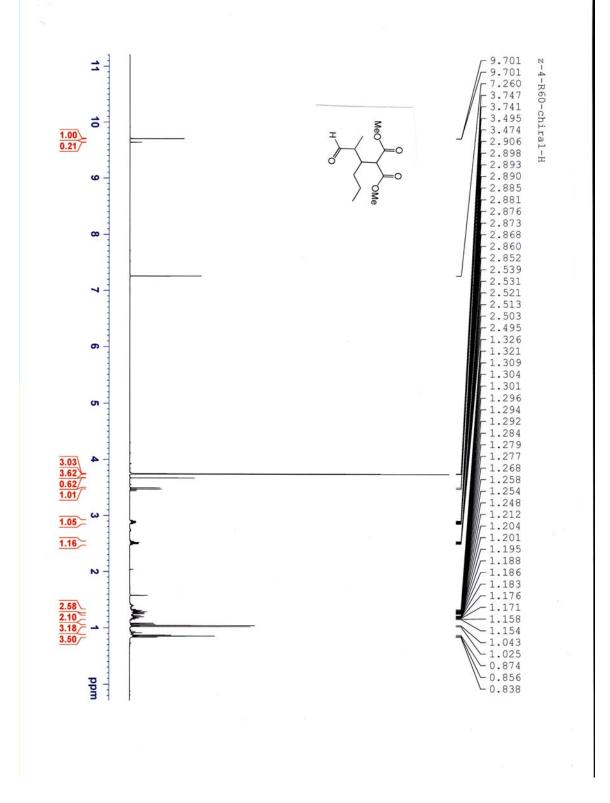
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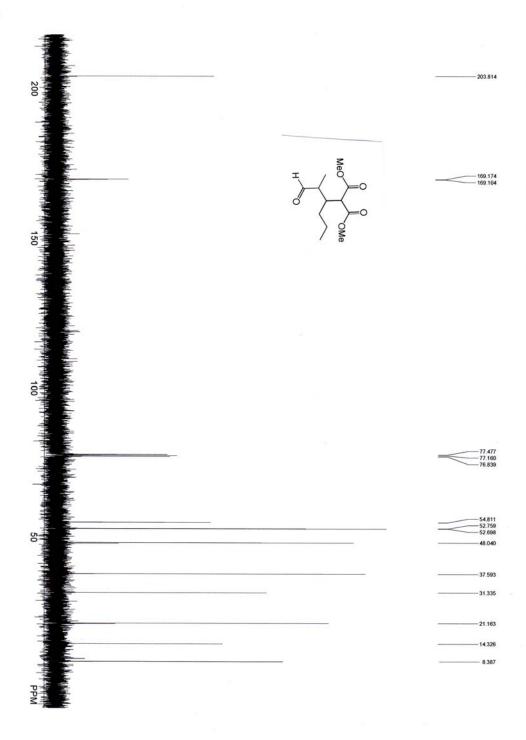
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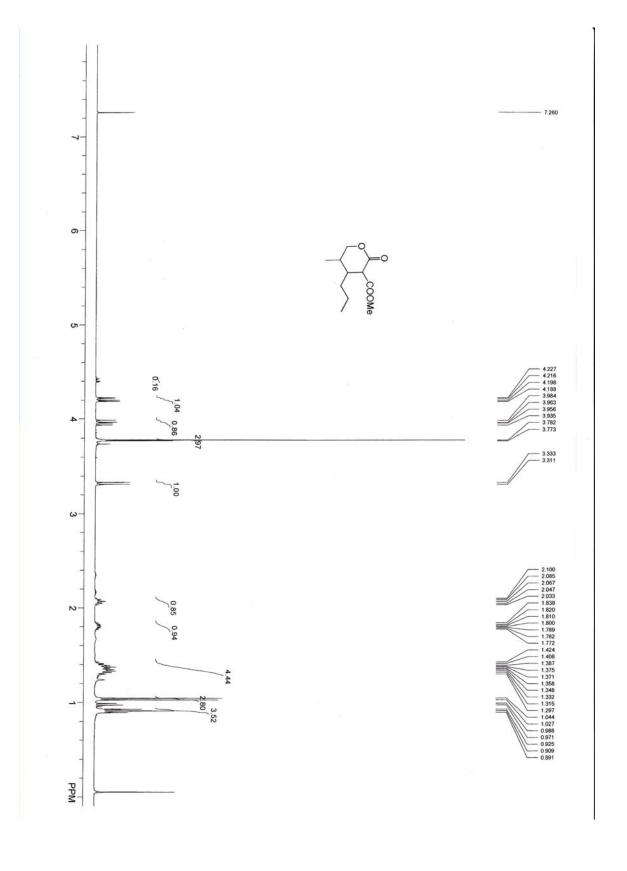
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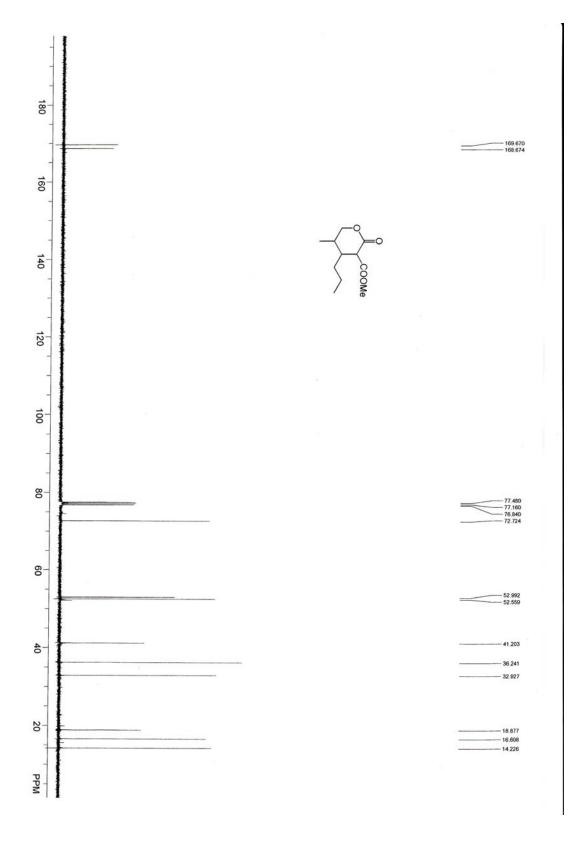
Bruker Daltonics DataAnalysis 3.4





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Title

: c:\star\gui-ling\z-4-r54-rac-l.run Run File  $\label{eq:method_file} \mbox{Method File: } c:\star\gui-\ling\z-4-r54-\rac-l-\front.mth$ 

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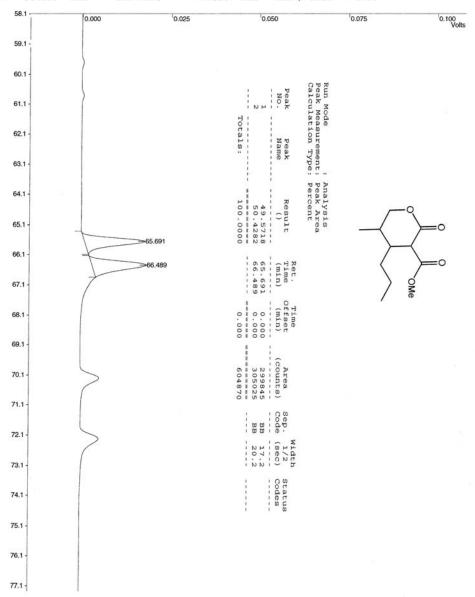
Workstation: ORGAN-GC-DELL1ÿ□HÚ"â□ Bus Address : 44

Sample Rate : 10.00 Hz

Instrument : gc2 (right) Channel : Front = FID Run Time : 87.410 min

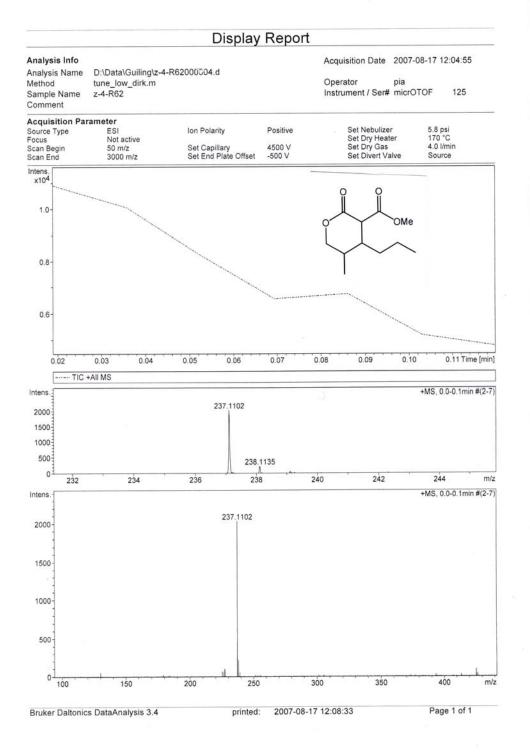
\*\* GC Workstation Multi Instrument Version 6.41 \*\* 00195-2088-D6B-20A1 \*\*

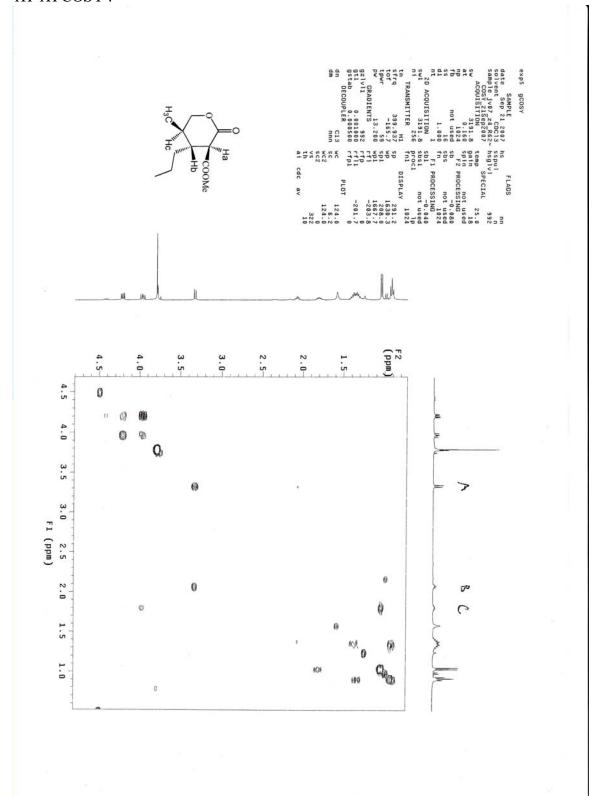
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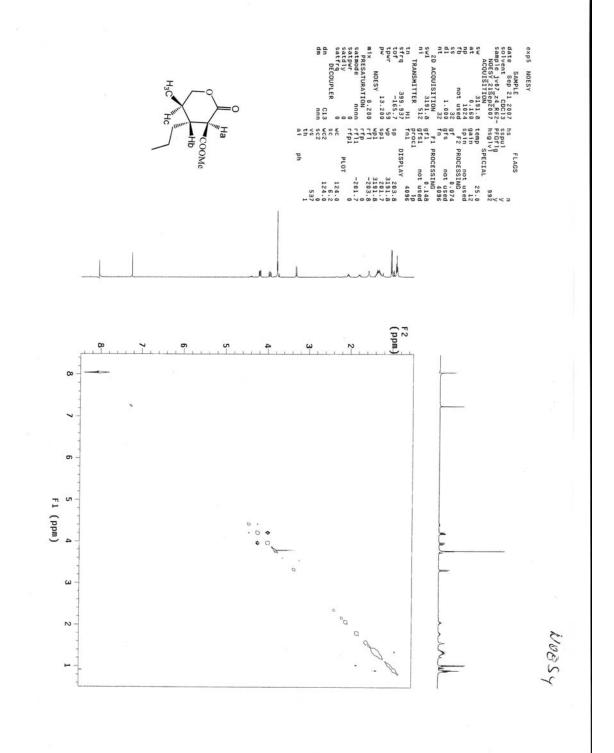


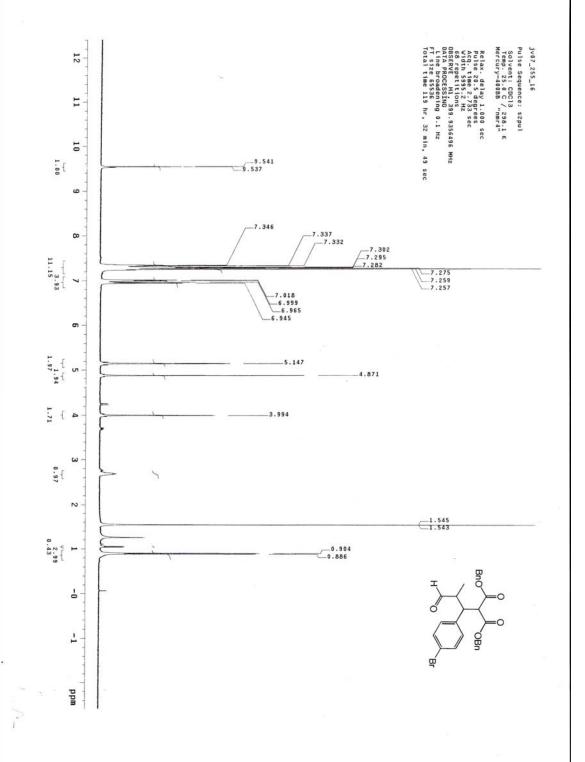
File : c:\star\gui-ling\z-4-r62-chiral.run
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nel : Front = FID : 87.410 min Run Time C Workstation Multi Instrument Version 6.41 \*\* 00195-2088-D6B-20A1 \*\* Attenuation = 192 Zero Offset = 5%End Time = 75.160 min Min / Tick = 1.001.30 cm/min Attenuation = 192 t Speed = t Time = 58.580 min 30 58.6 -10 mVolts 59.6 Run Mode : Peak Measurement: Calculation Type: No. 60.6 61.6 62.6 97.6793 2.3207 100.0000 63.6 64.6 Time (min) 65.6 66.577 66.6 67.6 68.6 69.6 70.6 71.6 72.6 73.6

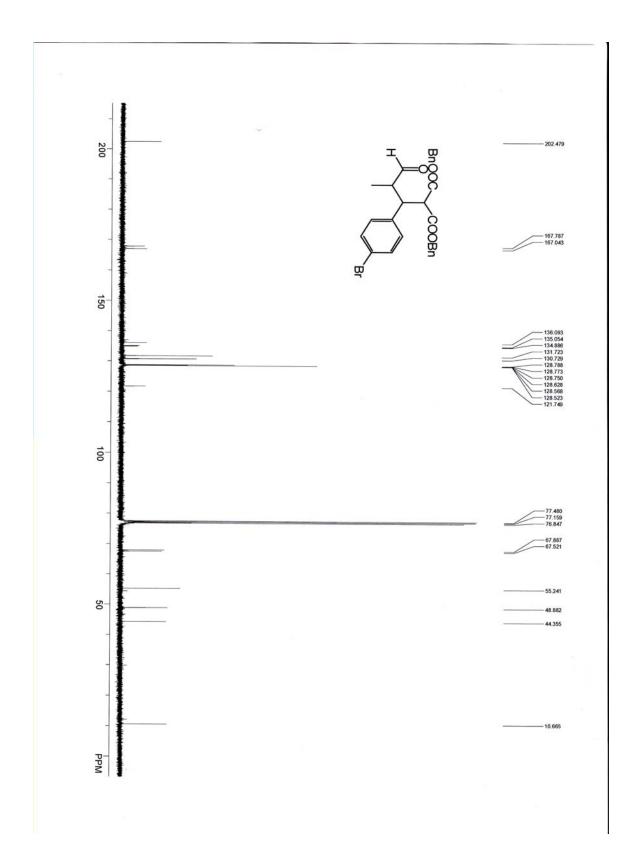
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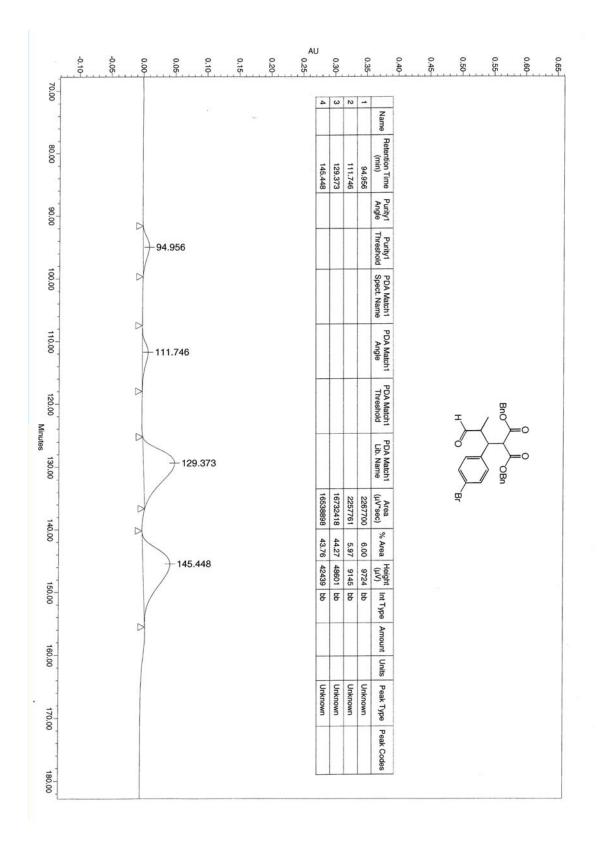


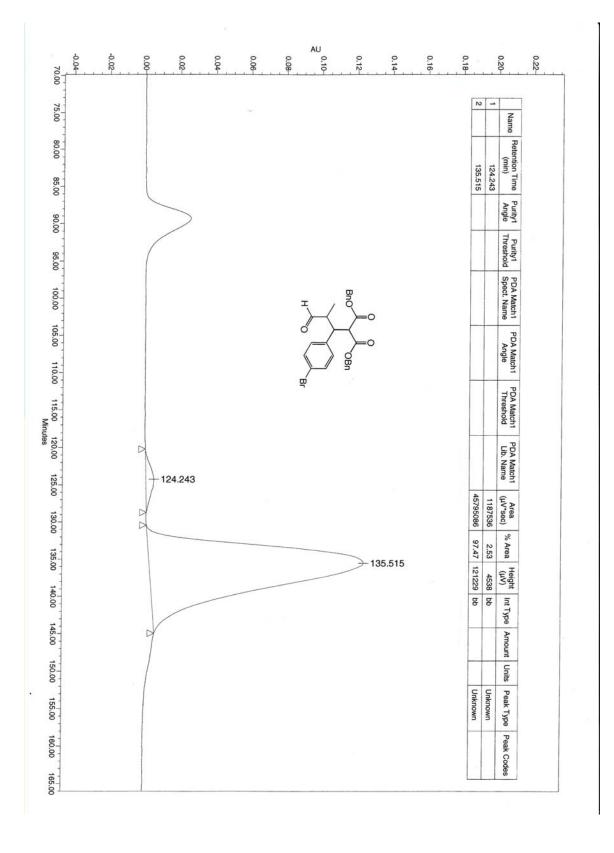


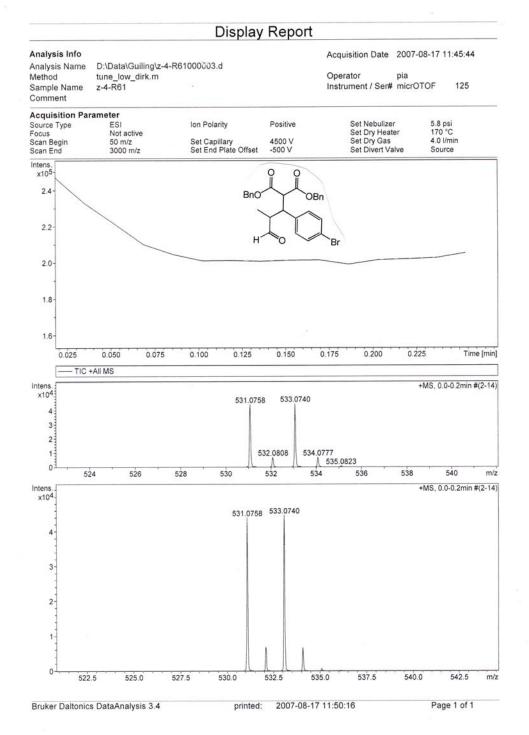


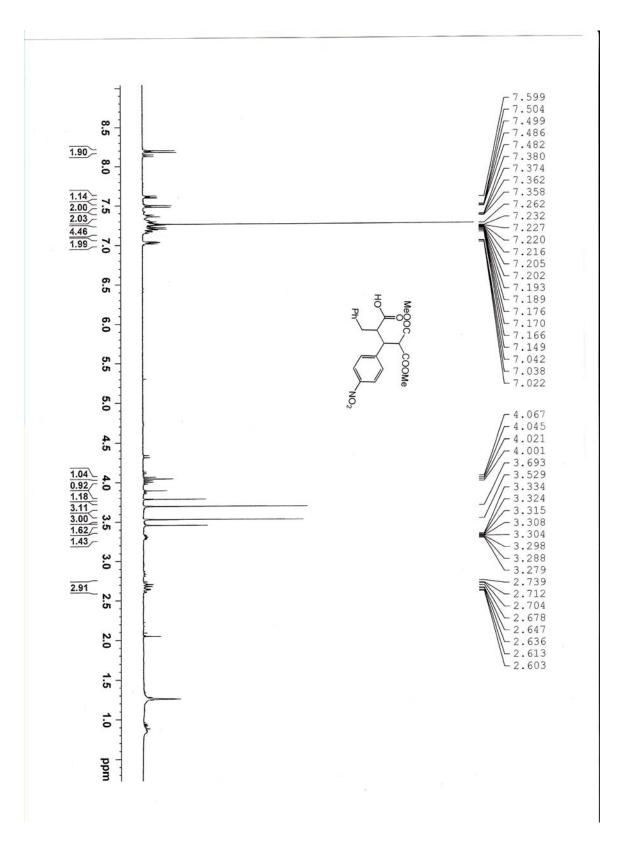


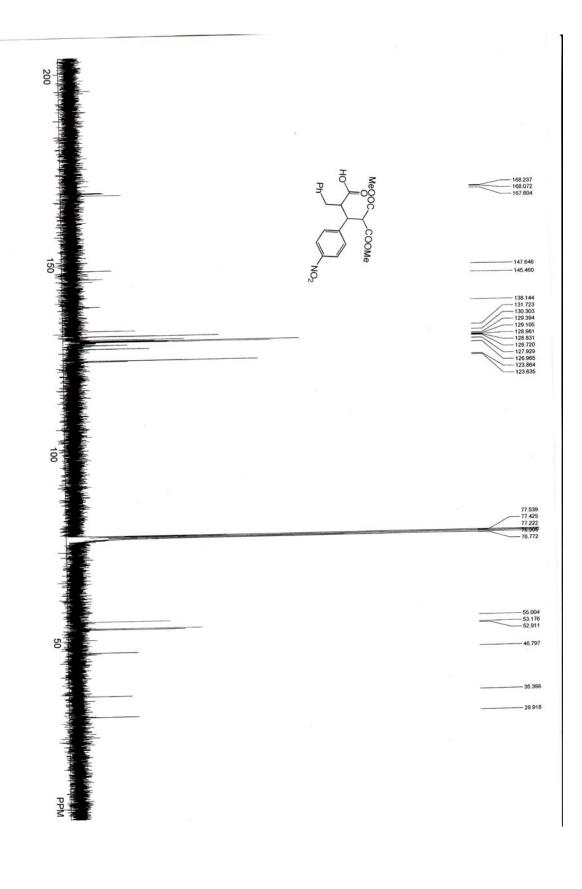


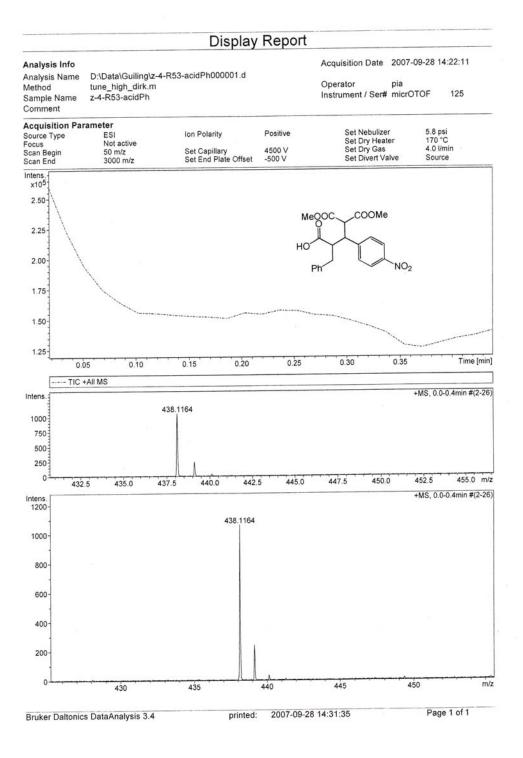


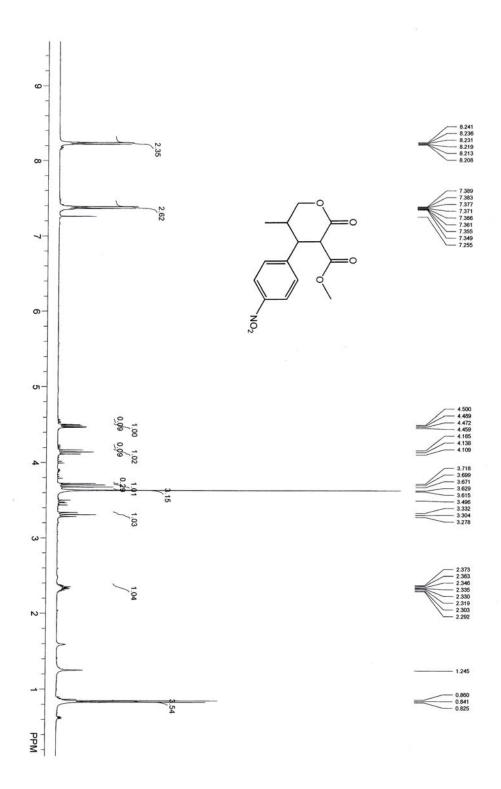


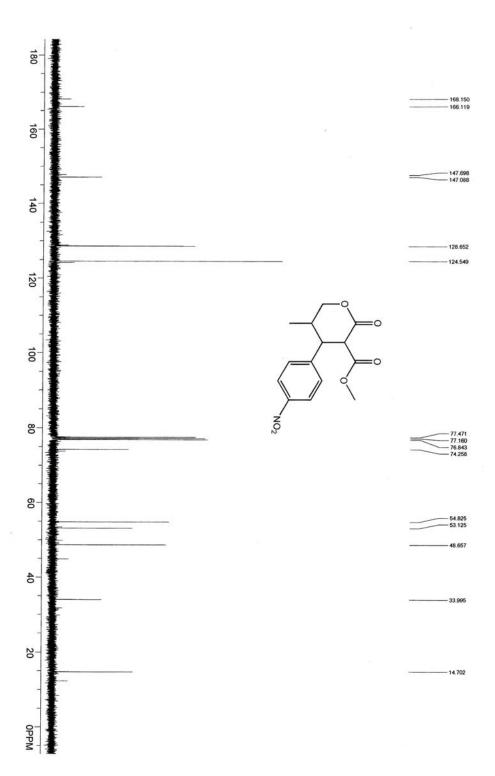


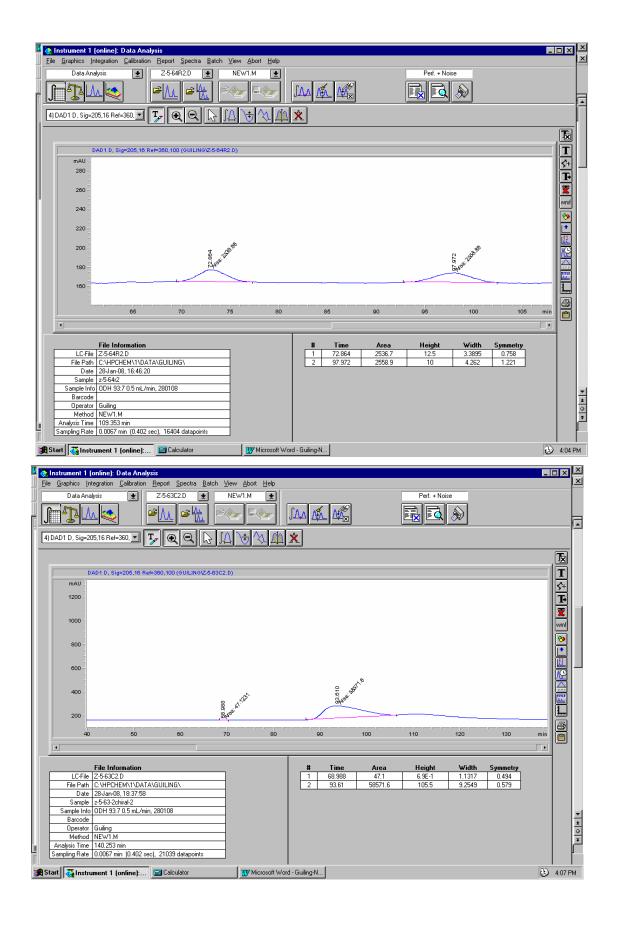












# Display Report Analysis Info Acquisition Date 1/28/2008 3:48:33 PM D:\Data\Guiling\z-5-63-2000003.d tune\_wide\_dirk.m z-5-63-2 28.01.2008 Analysis Name Method Operator pia Instrument / Ser# micrOTOF 125 Sample Name Comment Acquisition Parameter Source Type ESI Focus Not a Scan Begin 50 m Scan End 3000 Set Nebulizer Set Dry Heater Set Dry Gas Set Divert Valve 5.8 psi 160 °C 4.0 l/min Positive Ion Polarity Not active 50 m/z 3000 m/z 4500 V -500 V Set Capillary Set End Plate Offset Source Intens. x10<sup>5</sup> 1.5-1.0-0.5 0.0 Time [min] 0.02 0.04 0.06 0.08 0.10 0.12 ---- TIC +All MS +MS, 0.0-0.1min #(2-8) Intens. 316.0788 400 300 200 100 500 550 450 400 200 250 300 350 +MS, 0.0-0.1min #(2-8) Intens. 600 316.0788 400 200 450 500 550 m/z 300 400 200 250