

## Supporting information

### Asymmetric Oxidative Lewis Base Catalysis – Unifying Iminium and Enamine Organocatalysis with Oxidations

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**General:** Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Solvents for extraction and chromatography were technical grade and distilled prior to use. Solvents used in reaction were reagent grade and distilled from the indicated drying agents: CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub> (CaH<sub>2</sub>). MnO<sub>2</sub> was dried in a glassware oven at 120 °C for two days. Amine catalysts 2-(bis(3,5-bis(trifluoromethyl)phenyl)(trimethylsilyloxy)methyl)pyrrolidine and 2-(diphenyl(trimethylsilyloxy)methyl)pyrrolidine and NHC-catalyst were prepared as described in the literature.<sup>1, 2</sup> For thin-layer chromatography (TLC), silica gel coated aluminium plates (Merck, silica gel 60 F254) were used and chromatograms were visualised by irradiation with UV light at 254 nm and Cerium Molybdate stain. Column chromatography was performed using Merck silica gel 60 (particle size 0.040-0.063 mm). Solvents mixtures are understood as volume/volume. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR were recorded on a Bruker AV 300 or AM 250 XP spectrometers in CDCl<sub>3</sub>. Data are reported in the following order: chemical shift ( $\delta$ ) in ppm; multiplicities (bs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants ( $J$ ) are in Hertz (Hz). MS-EI (70 eV) were recorded on a GC-MS Shimadzu QP2010 machine (column: Equity®-5, length × I.D. 30 m × 0.25 mm, df 0.25 m, lot # 28089-U, Supelco). IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported in terms of frequency of absorption (cm<sup>-1</sup>). The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (Daicel Co. CHIRALCEL OD-H, AD-H and AS-H; eluent: hexane / 2-propanol), by comparing the samples with the corresponding racemic mixtures. Optical rotations were measured on a Perkin Elmer 241 polarimeter.

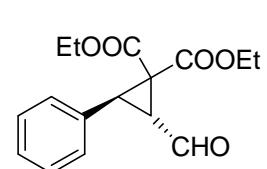
**General procedure A. Cyclopropanation of allylic alcohols.** To a vial containing the reaction solvent (1.0 ml) and triethyl amine (0.7 equiv., 0.14 mmol) were subsequently added allylic alcohol (1.0 equiv., 0.2 mmol), MnO<sub>2</sub> (10.0 equiv., 2.0 mmol) and diethyl bromomalonate (1.3 equiv., 0.26 mmol). When the appropriate temperature was reached TMS-prolinol catalyst (0.2 equiv., 0.04 mmol) was added and the reaction was left to stir for 18h. The reaction mixture was directly purified by column chromatography on silica gel (hexane:ethyl acetate) to afford the chiral cyclopropane derivative.

**General procedure B. Malonate addition to allylic alcohols.** To a vial containing ethanol (1.0 ml) were subsequently added allylic alcohol (1.0 equiv., 0.2 mmol), MnO<sub>2</sub> (10 equiv., 2.0 mmol), dimethyl malonate (1.3 equiv., 0.26 mmol) and TMS-prolinol catalyst (0.2 equiv., 0.04 mmol) and left to stir for 3 days. The reaction mixture was directly purified by column chromatography on silica gel (hexane:ethyl acetate) to afford the chiral aldehyde derivative.

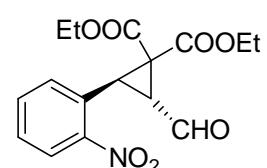
**Procedure C. Oxidative esterification of formyl cyclopropanes.** To a 0.2 M solution of cyclopropane in ethanol were subsequently added MnO<sub>2</sub> (15.0 equiv.), NHC-carbene (0.3 equiv.) and DBU (0.3 equiv.). The reaction was stirred at room temperature until full conversion could be established by crude <sup>1</sup>H NMR (21h). The reaction mixture was directly purified by column chromatography on silica gel (hexane:ethyl acetate) to afford the desired ester.

**Procedure D. Oxidation of the malo-aldehydes to the carboxylic esters.** Representative procedure: (*R*)-dimethyl 2-(3-oxo-1-phenylpropyl)malonate was diluted with 2.0 ml *t*-BuOH and 2.0 ml 1 M NaH<sub>2</sub>PO<sub>4</sub> (aq.). 2.0 ml 1 M KMnO<sub>4</sub> were added successively. After 5 min of vigorous stirring 5.0 ml saturated NaHSO<sub>3</sub> was added and the pH was adjusted to roughly 3 with 1 M HCl. The resulting mixture was extracted 3 times with 10 mL EtOAc, the combined organic layers were washed with 10 ml of water and 10 ml of brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. The organic layer was concentrated in vacuum and the residual acid was dissolved in 2.0 ml toluene and 3.0 ml MeOH. TMSCHN<sub>2</sub> (2.0 M in n-hexane) was added dropwise until the yellow colour persisted. The solution was stirred for an additional 10 min and quenched with a drop of concentrated AcOH. The solvents were evaporated under vacuum. The crude product was subjected to silica gel chromatography (hexane: ethyl acetate) to give the desired product.

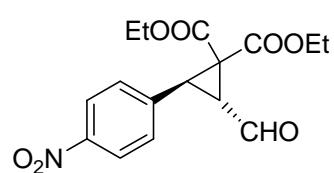
**(2*R*,3*S*)-Diethyl 2-formyl-3-phenylcyclopropane-1,1-dicarboxylate**

  
was synthesized using general procedure A.  
 $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.46 (d, 1H,  $J$  = 4.8 Hz), 7.31-7.22 (m, 5H), 4.35-4.22 (m, 2H), 3.93 (dq, 2H,  $J$  = 1.2, 7.2 Hz), 3.83 (d, 1H,  $J$  = 7.4 Hz), 3.37 (dd, 1H,  $J$  = 4.7, 7.5 Hz), 1.30 (t, 3H,  $J$  = 7.1 Hz), 0.93 (t, 3H,  $J$  = 7.1 Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.0, 166.0, 164.6, 132.3, 128.6, 128.4, 128.0, 62.4, 62.0, 44.7, 38.2, 35.3, 14.0, 13.7. MS-EI: m/z (%) = 291.2 (0.1), 290.2 (0.1), 262.1 (12) 261.1 (53), 245.0 (2), 233.1 (6), 217.1 (9), 216.1 (30), 188.1 (8), 187.1 (43), 173.1 (9), 171.1 (18), 170.1 (47), 160.1 (7), 159.1 (12), 145.1 (12), 131.1 (14), 116.1 (36), 115.1 (100), 105.1 (19), 91.1 (20), 77.1 (12). IR (NaCl):  $\tilde{\nu}$  = 2983, 2742, 1730, 1448, 1369, 1288, 1217, 1184, 1144, 1019, 862, 749, 698.  $[\alpha]_D^{RT} = -49.3$  ( $c$  = 1 in  $\text{CHCl}_3$ ). HPLC conditions: AS-H column, n-hexane/2-propanol=85/15, flow rate=0.6  $\text{mL}\cdot\text{min}^{-1}$ ,  $\lambda$ =210 nm; major enantiomer  $t_R$ =10.8 min and minor enantiomer:  $t_R$ =12.4 min.

**(2*R*,3*S*)-Diethyl 2-Formyl-3-(2-nitrophenyl)-cyclopropane-1,1-dicarboxylate**

  
was synthesized using general procedure A.  
 $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.52 (d, 1H,  $J$  = 4.7 Hz), 8.06 (dd, 1H,  $J$  = 1.3, 8.0 Hz), 7.59 (td, 1H,  $J$ =1.4, 7.5 Hz), 7.49 (t, 1H,  $J$  = 7.6 Hz), 7.36 (d, 1H,  $J$  = 7.6 Hz), 4.42-4.20 (m, 3H), 4.00-3.83 (m, 2H), 3.22 (dd, 1H,  $J$  = 4.7, 7.8 Hz), 1.31 (t, 3H,  $J$  = 7.1 Hz), 0.99 (t, 3H,  $J$  = 7.1 Hz).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 195.6, 165.5, 164.7, 149.7, 133.3, 131.2, 129.3, 128.4, 125.0, 62.6, 62.4, 43.5, 38.8, 33.9, 14.0, 13.6. MS-EI: m/z (%) = 336.1 (0.8), 306.1 (3), 290.1 (4), 272.1 (2), 261.1 (11), 244.0 (19), 216.0 (35), 215.0 (37), 201.1 (11), 200.0 (22), 288.0 (34), 172.1 (46), 170.1 (32), 160.1 (29), 155.1 (22), 144.1 (46), 135.1 (81), 116.1 (54), 115.1 (52), 104.1 (43), 92.1 (65), 91.1 (100), 79.0 (73), 77.1 (71). IR (NaCl):  $\tilde{\nu}$  = 2984, 2744, 1730, 1611, 1577, 1530, 1349, 1289, 1217, 1187, 1146, 1018, 855, 790, 740, 702.  $[\alpha]_D^{RT} = +30.1$  ( $c$  = 1 in  $\text{CHCl}_3$ ). HPLC conditions: AS-H column, n-hexane/2-propanol=65/35, flow rate=0.6  $\text{mL}\cdot\text{min}^{-1}$ , converted to the corresponding enone with  $\text{Ph}_3\text{P}=\text{CHCOPh}$ ,  $\lambda$ =220 nm): major enantiomer  $t_R$ =16.6 min and minor enantiomer  $t_R$ =29.6 min.

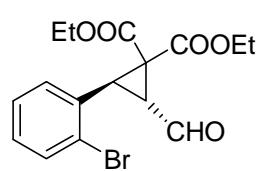
**(2*R*,3*S*)-Diethyl 2-formyl-3-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate**



was synthesized using general procedure A.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.53 (d, 1H, J = 4.1 Hz), 8.17 (d, 1H, J = 8.8 Hz), 7.43 (d, 2H, J = 8.9 Hz), 4.36-4.24 (m, 2H), 4.04-3.91 (m, 2H), 3.84 (d, 1H, J = 7.5 Hz), 3.43 (dd, 1H, J = 4.1 Hz, 7.5 Hz), 1.31 (t, 3H, J = 7.1 Hz), 1.01 (t, 3H, J = 7.1 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 194.9, 165.3, 164.2, 147.6, 139.8, 129.6, 123.5, 62.7, 62.4, 45.0, 39.0, 34.54, 14.00, 13.8. MS-EI: m/z (%) = 336.1 (0.9), 307.1 (18), 106.1 (67), 2901. (4), 278.1 (29), 262.1 (23), 261.1 (100), 250.0 (12), 232.0 (79), 218.1 (20), 216.1 (20), 205.0 (32), 190.1 (16), 170.1 (15), 159.1 (20), 143.1 (20), 131.1 (31), 115.1 (91), 102.1 (28), 89.1 (16), 77.0 (19). IR (NaCl):  $\tilde{\nu}$  = 2984, 2859, 2744, 2456, 1723, 1603, 1523, 1465, 1445, 1391, 1369, 1349, 1297, 1220, 1185, 1015, 855, 757, 695. [α]<sub>D</sub><sup>RT</sup> = -38.4 (c = 1 in CHCl<sub>3</sub>). HPLC conditions: AS-H column, n-hexane/2-propanol=60/40, flow rate=0.6 mL·min<sup>-1</sup>, λ=210 nm; minor enantiomer t<sub>R</sub>=19.2 min and major enantiomer t<sub>R</sub>=23.7 min.

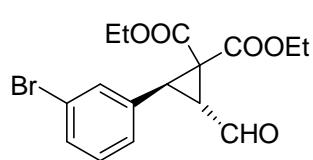
**(2*R*,3*S*)-Diethyl 2-Formyl-3-(2-bromo)-cyclopropane-1,1-dicarboxylate**



was synthesized using general procedure A.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.47 (d, 1H, J=4.7 Hz), 7.56 (dd, 1H, J = 1.3, 7.9 Hz), 7.25 (td, 1H, J = 1.3, 7.5 Hz), 7.18-7.11 (m, 2H), 4.37-4.24 (m, 2H), 3.96 (q, 2H, J = 7.1 Hz), 3.85 (d, 1H, J = 7.7 Hz), 3.36 (dd, 1H, J = 4.7, 7.7 Hz), 1.31 (t, 3H, J = 7.1 Hz), 0.96 (t, 3H, J = 7.1 Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 195.7, 165.6, 164.6, 132.8, 132.3, 129.7, 129.5, 128.1, 126.0, 62.4, 62.0, 44.1, 38.7, 36.3, 14.0, 13.6. MS-EI: m/z (%) = 370.9 (1.0), 368.9 (0.9), 341.0 (85), 339.0 (83), 325.0 (4), 323.0 (5), 313.0 (14), 311.0 (14), 296.0 (38), 294.0 (39), 267.0 (41), 265.0 (43), 215.1 (100), 185.0 (17), 183.0 (17), 159.1 (54), 131.1 (31), 115.1 (87), 102.1 (19). IR (NaCl):  $\tilde{\nu}$  = 2982, 2742, 1731, 1369, 1290, 1217, 1186, 1144, 1027, 862, 753. [α]<sub>D</sub><sup>RT</sup> = -36.9 (c = 1 in CHCl<sub>3</sub>). HPLC conditions: AS-H column, n-hexane/2-propanol=98/2, flow rate=0.6 mL·min<sup>-1</sup>, converted to the corresponding enone with Ph<sub>3</sub>P=CHCOPh, λ=220 nm; minor enantiomer t<sub>R</sub>=48.8 min and major enantiomer t<sub>R</sub>=54.5 min.

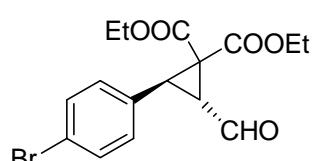
**(2*R*,3*S*)-Diethyl 2-(3-bromophenyl)-3-formylcyclopropane-1,1-dicarboxylate**



was synthesized using general procedure A.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.47 (d, 1H, J = 4.5 Hz), 7.41 (m, 2H), 7.17 (m, 2H), 4.36-4.21 (m, 2H), 3.98 (q, 2H, J = 7.1 Hz), 3.78 (d, 1H, J = 7.3 Hz), 3.35 (dd, 1H, J = 4.5 Hz, 7.5 Hz), 1.30 (t, 3H, J = 7.1 Hz), 1.00 (t, 3H, J = 7.1 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 195.5, 165.67, 164.4, 134.6, 131.8, 131.2, 129.9, 127.2, 122.4, 62.6, 61.2, 44.7, 38.0, 34.5, 14.0, 13.8. MS-EI: m/z (%) = 371.0 (0.4), 369.0 (0.3), 341.0 (57), 339.0 (56), 313.0 (11), 311.0 (11), 296.0 (39), 294.0 (39), 267.0 (42), 265.0 (43), 251.0 (13), 250.0 (13), 215.1 (11), 195.0 (20), 193.0 (10), 172.1 (20), 159.2 (22), 143.1 (32), 15.1 (100), 102.1 (17). IR (NaCl):  $\tilde{\nu}$  = 2982, 2741, 1733, 1597, 1567, 1370, 1292, 1218, 1185, 1023, 864, 758, 691. [α]<sub>D</sub><sup>RT</sup> = -34.3 (c = 1 in CHCl<sub>3</sub>). HPLC conditions: OD-H column, n-hexane/2-propanol=90/10, flow rate=0.6 mL·min<sup>-1</sup>, λ=210 nm; major enantiomer t<sub>R</sub>=14.3 min and minor enantiomer t<sub>R</sub>=24.1 min.

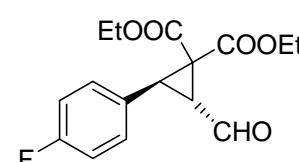
**(2*R*,3*S*)-Diethyl 2-(4-bromophenyl)-3-formylcyclopropane-1,1-dicarboxylate**



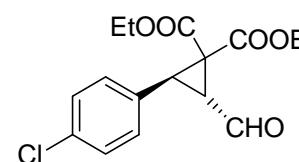
was synthesized using general procedure A.

<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 9.46 (d, 1H, J = 4.5 Hz), 7.42 (d, 2H, J = 8.5 Hz), 7.12 (d, 2H, J = 8.2 Hz), 4.36-4.20 (m, 2H), 4.03-3.89 (m, 2H), 3.74 (d, 1H, J = 7.5 Hz), 3.33 (dd, 1H, J = 4.5, 7.5 Hz), 1.29 (t, 3H, J = 7.1 Hz), 0.99 (t, 3H, J = 7.1 Hz). <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ=195.6, 165.7, 164.4, 131.5, 131.3, 130.2, 122.1, 62.5, 62.2, 44.7, 38.0, 34.6, 14.0, 13.8. MS-EI: m/z (%) = 371.0 (1.0), 369.0 (1), 341.0 (100), 339.0 (100), 313.0 (13), 311.0 (13), 296.0 (55), 294.0 (55), 267.0 (65), 265.0 (66), 250.0 (30), 248.0 (30), 215.1 (36), 195.0 (20), 193.0 (18), 172.1 (20), 170.0 (20), 159.1 (35), 143.1 (40), 131.1 (25), 115.1 (73), 102.1 (16). IR (NaCl):  $\tilde{\nu}$  = 2982, 2742, 1731, 1492, 1392, 1369, 1289, 1217, 1182, 1011, 838, 757. [α]<sub>D</sub><sup>RT</sup> = -46.0 (c = 1 in CHCl<sub>3</sub>). HPLC conditions: AS-H column, n-hexane/2-propanol=95/5, flow rate=0.6 mL·min<sup>-1</sup>, converted to the corresponding enone with Ph<sub>3</sub>P=CHOPh, λ=220 nm; minor enantiomer t<sub>R</sub>=32.7 min and major enantiomer t<sub>R</sub>=36.9 min and.

**(2*R*,3*S*)-Diethyl 2-(4-fluorophenyl)-3-formylcyclopropane-1,1-dicarboxylate**

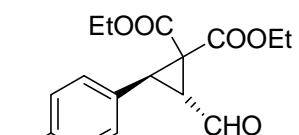
  
was synthesized using general procedure A.  
<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 9.46 (d, 1H, J = 4.6 Hz), 7.26-7.18 (m, 2H), 7.04-6.93 (m, 2H), 4.36-4.20 (m, 2H), 4.02-3.88 (m, 2H), 3.78 (d, 1H, J = 7.1 Hz), 3.34 (dd, 1H, J = 4.6, 7.5 Hz), 1.30 (t, 3H, J = 7.5 Hz), 0.98 (t, 3H, J = 7.1 Hz). <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ = 195.6, 165.8, 164.5, 161.5 (d, J<sub>CF</sub> = 247.3 Hz), 130.3 (d, J<sub>CF</sub> = 8.3 Hz), 128.0 (d, J = 3.3 Hz), 115.4 (d, J = 21.7 Hz), 62.5, 62.1, 44.7, 38.3, 34.5, 14.00, 13.8. <sup>19</sup>F NMR (282 MHz, CDCl<sub>3</sub>): δ = -113.78 (m). MS-EI: m/z (%) = 309.2 (0.2), 308.2 (0.1), 280.2 (11), 279.2 (57), 263.1 (2), 251.1 (8), 235.1 (10), 234.1 (40), 217.0 (3), 205.1 (53), 188.1 (48), 177.1 (15), 163.1 (10), 162.1 (11), 149.1 (10), 133.1 (100), 123.1 (27), 109.1 (20). IR (NaCl):  $\tilde{\nu}$  = 2984, 2743, 1731, 1606, 1515, 1370, 1290, 1220, 1016, 850, 841, 788. [α]<sub>D</sub><sup>RT</sup> = -47.7 (c=1 in CHCl<sub>3</sub>). HPLC conditions: AS-H column, n-hexane/2-propanol=90/10, flow rate=0.6 mL·min<sup>-1</sup>, λ=210 nm; major enantiomer t<sub>R</sub>=15.6 min and minor enantiomer: t<sub>R</sub>=16.9 min.

**(2*R*,3*S*)-Diethyl 2-Formyl-3-(4-chloro-phenyl)-cyclopropane-1,1-dicarboxylate**

  
was synthesized using general procedure A.  
<sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 9.47 (d, 1H, J = 4.5 Hz), 7.28 (d, 2H, J = 8.4 Hz), 7.18 (d, 2H, J = 8.5 Hz), 4.37-4.20 (m, 2H), 4.04-3.89 (m, 2H), 3.77 (d, 1H, J = 7.5 Hz), 3.34 (dd, 1H, J = 4.5, 7.5 Hz), 1.30 (t, 3H, J = 7.1 Hz), 1.00 (t, 3H, J = 7.1 Hz). <sup>13</sup>C NMR (62.9 MHz, CDCl<sub>3</sub>): δ = 195.7, 165.8, 164.4, 134.0, 130.8, 129.9, 128.6, 62.6, 62.2, 44.7, 38.1, 34.6, 14.0, 13.8. MS-EI: m/z (%) = 325.0 (0.9), 297.1 (39), 295.1 (100), 279.0 (5), 267.0 (16), 252.0 (23), 250.0 (62), 223.0 (30), 221.0 (83), 204.0 (73), 193.0 (18), 179.0 (12), 178.0 (13), 151.0 (20), 149.0 (53), 139.0 (25), 115.1 (68). IR (NaCl):  $\tilde{\nu}$  = 2983, 2742, 1731, 1496, 1369, 1290, 1218, 1183, 1093, 1015, 839, 757. [α]<sub>D</sub><sup>RT</sup> = -48.4 (c = 1 in CHCl<sub>3</sub>). HPLC conditions: AS-H column, n-hexane/2-propanol=98/2, flow rate=0.6 mL·min<sup>-1</sup>, converted to the corresponding enone with Ph<sub>3</sub>P=CHCOPh, λ=220 nm; minor enantiomer t<sub>R</sub>=53.2 min and major enantiomer t<sub>R</sub>=63.4 min.

**(2*R*,3*S*)-Diethyl 2-Formyl-3-*p*-tolyl-cyclopropane-1,1-dicarboxylate**

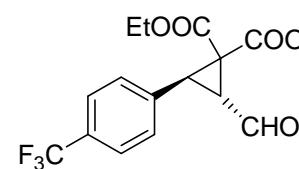
was synthesized using general procedure A.



$^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.44 (d, 1H,  $J$  = 4.8 Hz), 7.15-7.06 (m, 4H), 4.36-4.20 (m, 2H), 4.01-3.87 (m, 2H), 3.78 (d, 1H,  $J$  = 7.5 Hz), 3.34 (dd, 1H,  $J$  = 4.8, 7.5 Hz), 2.30 (s, 3H), 1.30 (t, 3H,  $J$  = 7.1 Hz), 0.97 (t, 3H,  $J$  = 7.1 Hz).  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.2, 166.1, 164.6, 137.7, 129.1, 129.0, 128.4, 62.4, 61.9, 44.7, 38.3, 35.1, 21.1, 14.0, 13.7. MS-EI: m/z (%) = 305.1 (0.5), 304.1 (0.4), 276.1 (21), 275.1 (78), 259.1 (5), 247.1 (4), 230.1 (47), 213.1 (4), 201.1 (64), 185.0 (26), 184.0 (100), 173.1 (12), 1581. (10), 145.1 (10), 129.1 (56), 128.1 (33), 119.1 (21), 115.1 (20), 105.1 (12), 91.1 (12). IR (NaCl)  $\tilde{\nu}$  = 2981, 2740, 1731, 1519, 1465, 1446, 1391, 1369, 1288, 1218, 1179, 1145, 1020, 863, 836, 809, 771, 560.  $[\alpha]_D^{RT} = -48.7$  ( $c$  = 1 in  $\text{CHCl}_3$ ). HPLC conditions: AS-H column, n-hexane/2-propanol=98/2, flow rate=0.6  $\text{mL}\cdot\text{min}^{-1}$ , converted to the corresponding enone with  $\text{Ph}_3\text{P}=\text{CHCOPh}$ ,  $\lambda$ =254 nm; minor enantiomer  $t_R$ =39.8 min and major enantiomer  $t_R$ =47.1 min.

**(2*R*,3*S*)-Diethyl 2-Formyl-3-(4-trifluoromethyl-phenyl)-cyclo-propane-1,1-dicarboxylate**

was synthesized using general procedure A.



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.50 (d, 1H,  $J$  = 4.4 Hz), 7.56 (d, 2H,  $J$  = 8.2 Hz), 7.37 (d, 2H,  $J$  = 8.2 Hz), 4.36-4.22 (m, 2H), 4.02-3.89 (m, 2H), 3.84 (d, 1H,  $J$  = 7.5 Hz), 3.41 (dd, 1H,  $J$  = 4.4, 7.5 Hz), 1.30 (t, 3H,  $J$  = 7.1 Hz), 0.96 (t, 3H,  $J$  = 7.1 Hz).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 195.3, 165.6, 164.4, 136.5 (m), 130.3 (q,  $^2J_{\text{CF}} = 32.7$  Hz), 129.0, 125.4 (q,  $^3J_{\text{CF}} = 3.8$  Hz), 123.9 (q,  $^1J_{\text{CF}} = 272.1$  Hz), 62.6, 62.2, 44.8, 37.9, 34.7, 14.0, 13.7.  $^{19}\text{F}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  [ppm] = -62.75 (s). MS-EI: m/z (%) = 359.1 (3), 339.1 (5), 330.1 (34), 329.1 (100), 313.1 (8), 301.1 (24), 285.1 (25), 284.1 (89), 273.0 (7), 255.0 (100), 238.0 (50), 228.0 (29), 213.1 (16), 183.1 (44), 173.0 (22), 159.1 (15), 133.1 (20), 115.1 (55). IR (NaCl):  $\tilde{\nu}$  = 2985, 2743, 1731, 1620, 1370, 1327, 1299, 1220, 1168, 1127, 1068, 1018, 855, 759.  $[\alpha]_D^{RT} = -37.6$  ( $c$  = 1 in  $\text{CHCl}_3$ ). HPLC conditions: AS-H column, n-hexane/2-propanol=95/5, flow rate 0.6  $\text{mL}\cdot\text{min}^{-1}$ , converted to the corresponding enone with  $\text{Ph}_3\text{P}=\text{CHCOPh}$ ,  $\lambda$ =220 nm); minor enantiomer  $t_R$ =22.6 min and major enantiomer  $t_R$ =27.7.

**(R)-dimethyl 2-(3-oxo-1-phenylpropyl)malonate 6a**

Was synthesized using general procedure B (72h).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.60 (t, 1H,  $J$  = 1.9 Hz), 7.28-7.22 (m, 5H), 4.07-4.00 (m, 1H), 3.76 (d, 1H,  $J$  = 10.6 Hz) 3.75 (s, 3H), 3.50 (s, 3H), 2.95-2.91 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 199.9, 168.4, 167.8, 139.8, 128.8, 128.0, 127.6, 57.3, 52.7, 52.4, 47.2, 39.6; IR (NaCl):  $\tilde{\nu}$  = 3032, 2955, 1731, 1455, 1435, 1258, 1200, 1241, 1156, 701  $\text{cm}^{-1}$ ; MS-EI:  $m/z$ (%): 265 (0.4)  $[\text{M}+\text{H}]^+$ , 264 (0.1)  $[\text{M}]^{+\bullet}$ , 236 (8), 187 (3), 173 (11), 144 (13), 133 (25), 132 (100), 131 (33), 117 (15), 115 (24), 104 (38), 105 (40), 13 (24), 100 (16), 91 (13), 78 (12), 77 (21), 59 (15);  $[\alpha]_D^{\text{RT}} = -6.5$  ( $c$  = 1.0 in  $\text{CHCl}_3$ ); HPLC conditions: AD-H column, n-hexane/2-propanol = 90/10, flow rate = 1.0  $\text{mL min}^{-1}$ , converted to the corresponding methyl ester according to procedure D  $\lambda$  = 254 nm. major enantiomer  $t_R$  = 12.9 min and minor enantiomer:  $t_R$  = 15.3 min.

**(R)-dimethyl 2-(1-(4-nitrophenyl)-3-oxopropyl)malonate 6b**

Was synthesized using general procedure B (65h).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.62 (t, 1H,  $J$  = 0.9 Hz), 8.15 (d, 1H,  $J$  = 8.8 Hz), 7.44 (d, 1H,  $J$  = 8.8 Hz), 4.13 (dt, 1H,  $J$  = 5.1, 9.0 Hz), 3.78 (d, 1H,  $J$  = 9.4 Hz) 3.75 (s, 3H), 3.54 (s, 3H), 3.11-2.94 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 198.4, 167.8, 164.4, 147.6, 147.2, 129.2, 123.8, 56.3, 52.9, 52.7, 46.9, 38.8; IR (NaCl):  $\tilde{\nu}$  = 3032, 2955, 1731, 1496, 1455, 1435, 1258, 1200, 1156, 701  $\text{cm}^{-1}$ ; MS-EI:  $m/z$ (%): 310 (0.1)  $[\text{M}+\text{H}]^+$ , 132 (100), 115 (13), 101 (12), 100 (22), 77 (11), 59 (12);  $[\alpha]_D^{\text{RT}} = -21.2$  ( $c$  = 1.0 in  $\text{CHCl}_3$ ); HPLC conditions: AD-H column, n-hexane/2-propanol = 80/20, flow rate = 1.0  $\text{mL min}^{-1}$ , converted to the corresponding methyl ester according to procedure D,  $\lambda$  = 254 nm. major enantiomer  $t_R$  = 18.3 min and minor enantiomer:  $t_R$  = 30.4 min.

**(R)-dimethyl 2-(1-(2-nitrophenyl)-3-oxopropyl)malonate 6c**

Was synthesized using general procedure B (65h).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 9.67 (t, 1H,  $J$  = 1.5 Hz), 7.80 (dd, 1H,  $J$  = 1.3, 8.0 Hz), 7.55 (m, 1H) 7.41 (m, 2H) 4.58 (dt, 1H,  $J$  = 5.4, 8.6 Hz), 3.97 (d, 1H,  $J$  = 8.9 Hz) 3.73 (s, 3H), 3.58 (s, 3H), 3.15-2.97 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 199.2, 168.0, 164.5, 134.6, 132.9, 129.0, 128.3, 124.8, 56.0, 52.8, 52.8, 46.6, 33.2; IR (NaCl):  $\tilde{\nu}$  = 3473, 2995, 2848, 1734, 1528, 1435, 1355, 1251, 1160  $\text{cm}^{-1}$ ; MS-EI:  $m/z$ (%): 309 (1.1)  $[\text{M}]^{+\bullet}$ , 293 (18), 261 (23), 219 (51), 177 (15), 162 (16), 161 (100), 146 (10), 135 (12), 134 (38), 132 (16), 131 (13), 130 (23), 120 (11), 118 (13), 116 (12), 115 (22), 105 (11), 104 (19), 103 (16), 92 (11), 91 (18), 89 (10), 77 (22), 59 (48);  $[\alpha]_D^{\text{RT}} = +83.1$  ( $c$

= 1.0 in CHCl<sub>3</sub>); HPLC conditions: AD-H column, n-hexane/2-propanol=80/20, flow rate=1.0 mL min<sup>-1</sup>, converted to the corresponding methyl ester according to procedure D, λ=254 nm. major enantiomer t<sub>R</sub>=13.5 min and minor enantiomer: t<sub>R</sub>=23.3 min.

**(R)-dimethyl 2-(3-oxo-1-p-tolylpropyl)malonate 6d**

Was synthesized using general procedure B (72h). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.58 (t, 1H, J = 1.9 Hz), 7.13-7.07 (m, 4H), 4.20-3.94 (m, 1H), 3.73 (s, 3H), 3.72 (d, 1H, J = 8.9 Hz), 3.51 (s, 3H), 2.96-2.80 (m, 2H), 2.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 200.1, 168.4, 167.9, 137.2, 136.6, 129.5, 127.8, 57.4, 52.7, 52.4, 47.3, 39.2, 21.0; IR (NaCl):  $\tilde{\nu}$ =3441, 3026, 2954, 1734, 1514, 1435, 1436, 1195, 1156, 820 cm<sup>-1</sup>; MS-EI: m/z(%):278 (0.8) [M]<sup>+</sup>, 187 (12), 158 (11), 147 (26), 132 (26), 131 (20), 129 (10), 119 (49), 118 (100), 117 (25), 115 (20), 91 (27), 59 (12); [α]<sub>D</sub><sup>RT</sup> = -10.2 (c = 1.0 in CHCl<sub>3</sub>); HPLC conditions: AD-H column, n-hexane/2-propanol=90/10, flow rate=0.6 mL min<sup>-1</sup>, converted to the corresponding methyl ester according to procedure D, λ=220 nm. major enantiomer t<sub>R</sub>=12.2 min and minor enantiomer: t<sub>R</sub>=15.1 min.

**(R)-dimethyl 2-(1-(4-bromophenyl)-3-oxopropyl)malonate 6e**

Was synthesized using general procedure B (69h). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.59 (t, 1H, J = 1.7 Hz), 7.41 (d, 2H, J = 8.5 Hz ) 7.12 (d, 2H, J = 8.4 Hz ), 4.03-3.95 (m, 1H), 3.73 (s, 3H), 3.71 (d, 1H, J = 9.6 Hz), 3.53 (s, 3H), 3.51 (s, 3H), 3.00-2.83 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 199.3, 168.1, 167.6, 138.9, 131.8, 129.8, 121.5, 56.9, 52.8, 52.5, 47.1, 38.8; IR (NaCl):  $\tilde{\nu}$ =3006, 2954, 1731, 1489, 1436, 1257, 1200, 1157, 1011 cm<sup>-1</sup>; MS-EI: m/z(%): 344 (0.2) [M]<sup>+</sup>, 342 (0.3) [M]<sup>+</sup>, 254 (4), 253 (6), 211 (8), 184 (9), 184 (9), 132 (100), 131 (13), 116 (13), 115 (15), 104 (27), 103 (19), 102 (16), 101 (9), 100 (12), 77 (11), 59 (16); [α]<sub>D</sub><sup>RT</sup> = -2.7 (c = 0.7 in CHCl<sub>3</sub>); HPLC conditions: AD-H column, n-hexane/2-propanol=90/10, flow rate=1.0 mL min<sup>-1</sup>, converted to the corresponding methyl ester according to procedure D, λ=220 nm. major enantiomer t<sub>R</sub>=15.6 min and minor enantiomer: t<sub>R</sub>=20.9 min.

**(R)-dimethyl 2-(1-(2,4-dimethylphenyl)-3-oxopropyl)malonate 6f**

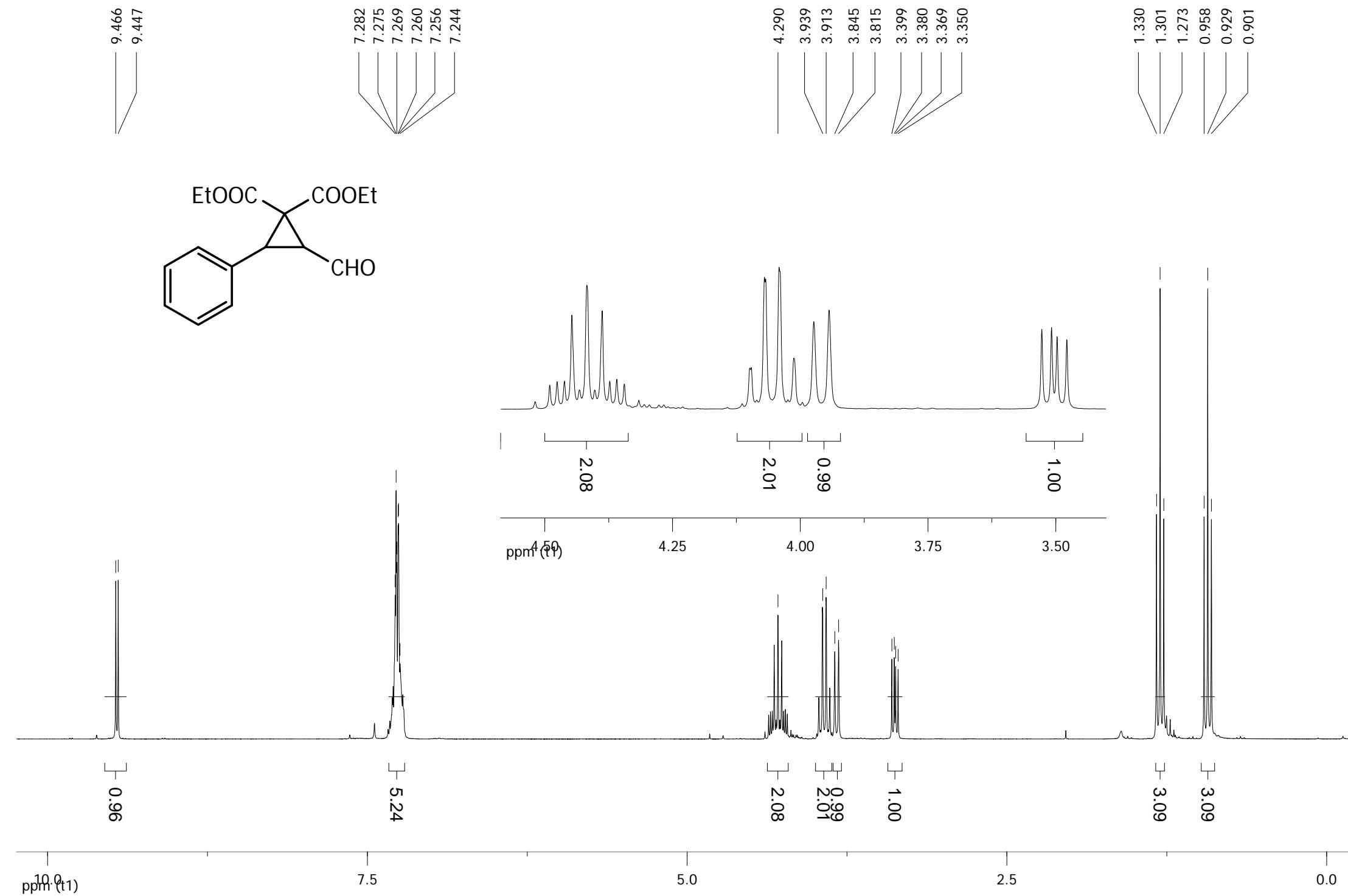
Was synthesized using general procedure B (69h). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 9.55 (t, 1H, J = 1.8 Hz), 7.01-6.93 (m, 3H), 4.29-4.21 (m, 1H), 3.75 (d, 1H, J = 2.8 Hz), 3.74 (s, 3H), 3.49 (s, 3H), 3.51 (s, 3H), 2.95-2.80 (m, 2H), 2.41 (s, 3H), 2.25 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 200.0, 168.6, 167.9, 136.6, 136.2, 135.1, 131.6, 127.1, 126.2, 56.9, 52.6, 52.3,

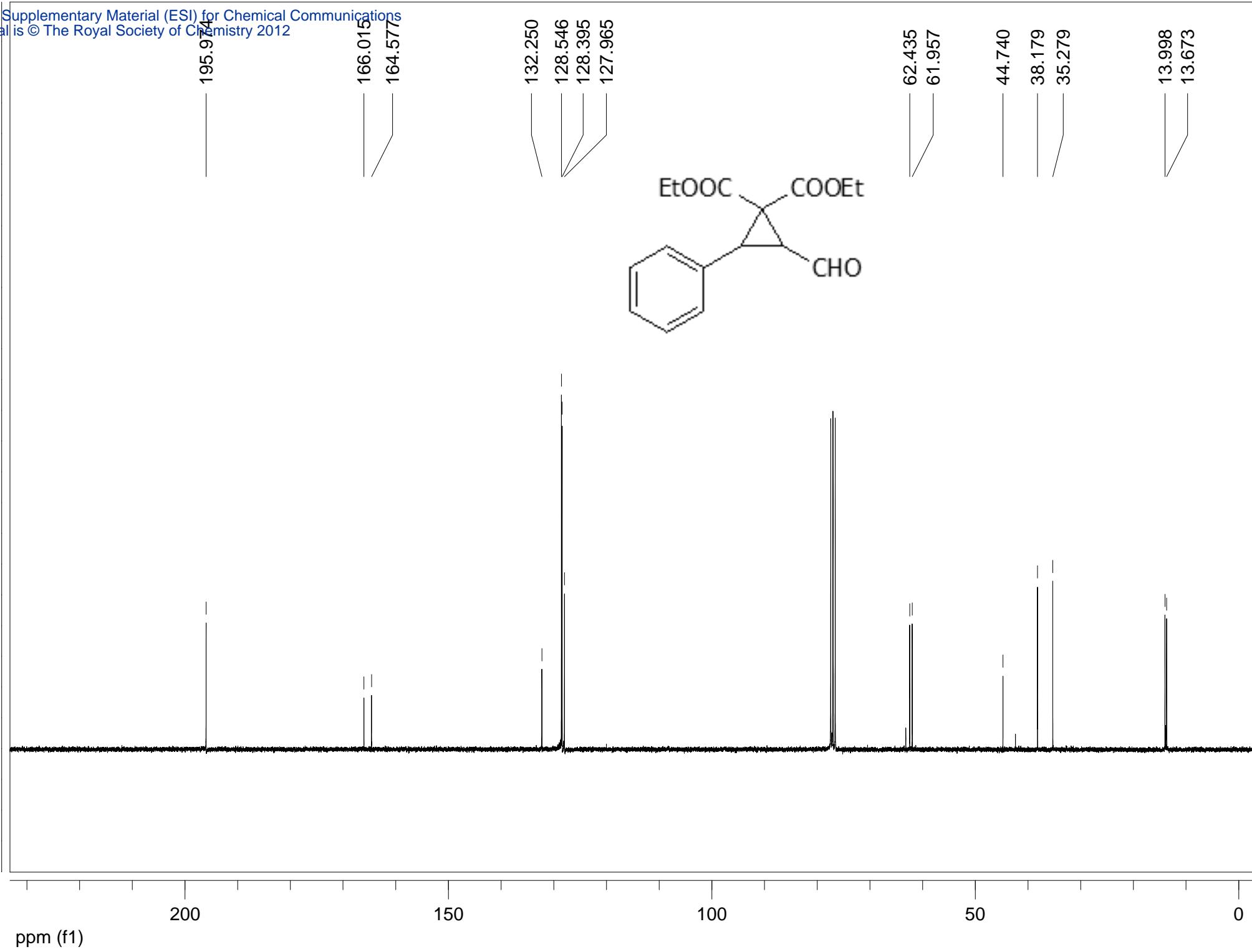
47.9, 34.1, 20.9, 19.6; IR (NaCl):  $\tilde{\nu}$  = 3475, 3012, 2954, 2925, 1731, 1434, 1281, 1258, 1157, 1026, 756 cm<sup>-1</sup>; MS-EI: *m/z*(%): 292 (1.3) [M]<sup>+</sup>, 161 (13), 149 (11), 145 (22), 143 (15), 142 (51), 133 (70), 132 (100), 131 (18), 130 (13), 129 (16), 128 (10), 117 (22), 116 (10), 115 (20), 105 (16), 91 (23), 59 (13);  $[\alpha]_D^{RT} = -6.6$  (*c* = 1.0 in CHCl<sub>3</sub>); HPLC conditions: AD-H column, n-hexane/2-propanol = 90/10, flow rate = 0.6 mL min<sup>-1</sup>, converted to the corresponding methyl ester according to procedure D,  $\lambda$  = 220 nm. major enantiomer *t<sub>R</sub>* = 13.3 min and minor enantiomer: *t<sub>R</sub>* = 14.4 min.

**(2R,3S)-triethyl 3-phenylcyclopropane-1,1,2-tricarboxylate 8a**

Was synthesized using general procedure C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.27 (m, 5H), 4.35-4.13 (m, 4H) 3.93 (dq, 2H, *J* = 0.8, 7.2 Hz), 3.64 (d, 1H, *J* = 7.5 Hz), 3.23 (d, 1H, *J* = 7.5 Hz), 1.30 (t, 1H, *J* = 7.4 Hz), 1.30 (t, 1H, *J* = 7.4 Hz), 0.94 (t, 1H, *J* = 7.1 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 169.0, 165.9, 165.3, 133.1, 128.7, 128.2, 127.6, 62.0, 61.8, 61.5, 44.3, 35.7, 31.0, 14.2, 14.0, 13.7; IR (NaCl):  $\tilde{\nu}$  = 3469, 3030, 2954, 1737, 1437, 1282, 1252, 1142, 755, 698 cm<sup>-1</sup>; MS-EI: *m/z*(%): 334 (6) [M]<sup>+</sup>, 233 (37), 202 (22), 173 (25), 171 (15), 107 (36), 145 (22), 131 (13), 129 (15), 116 (17), 115 (100), 114 (11), 103 (10), 91 (12), 99 (10), 77 (11), 59 (20);  $[\alpha]_D^{RT} = -84.5$  (*c* = 1.0 in CHCl<sub>3</sub>); HPLC conditions: AD-H column, n-hexane/2-propanol = 90/10, flow rate = 1.0 mL min<sup>-1</sup>,  $\lambda$  = 220 nm. major enantiomer *t<sub>R</sub>* = 7.9 min and minor enantiomer: *t<sub>R</sub>* = 12.0 min (95% ee).

1. Marigo, M.; Wabnitz, T. C.; Fielenbach, D.; Jorgensen, K. A. *Angew. Chem., Int. Ed. Engl.* **2005**, 44, 794.
2. Mirzaei, Y. R.; Twamley, B.; Shreeve, J. n. M. *J. Org. Chem.* **2002**, 67, 9340.
3. Brandau, S.; Landa, A.; Franzen, J.; Marigo, M.; Jorgensen, K. A. *Angew. Chem., Int. Ed. Engl.* **2006**, 45, 4305.



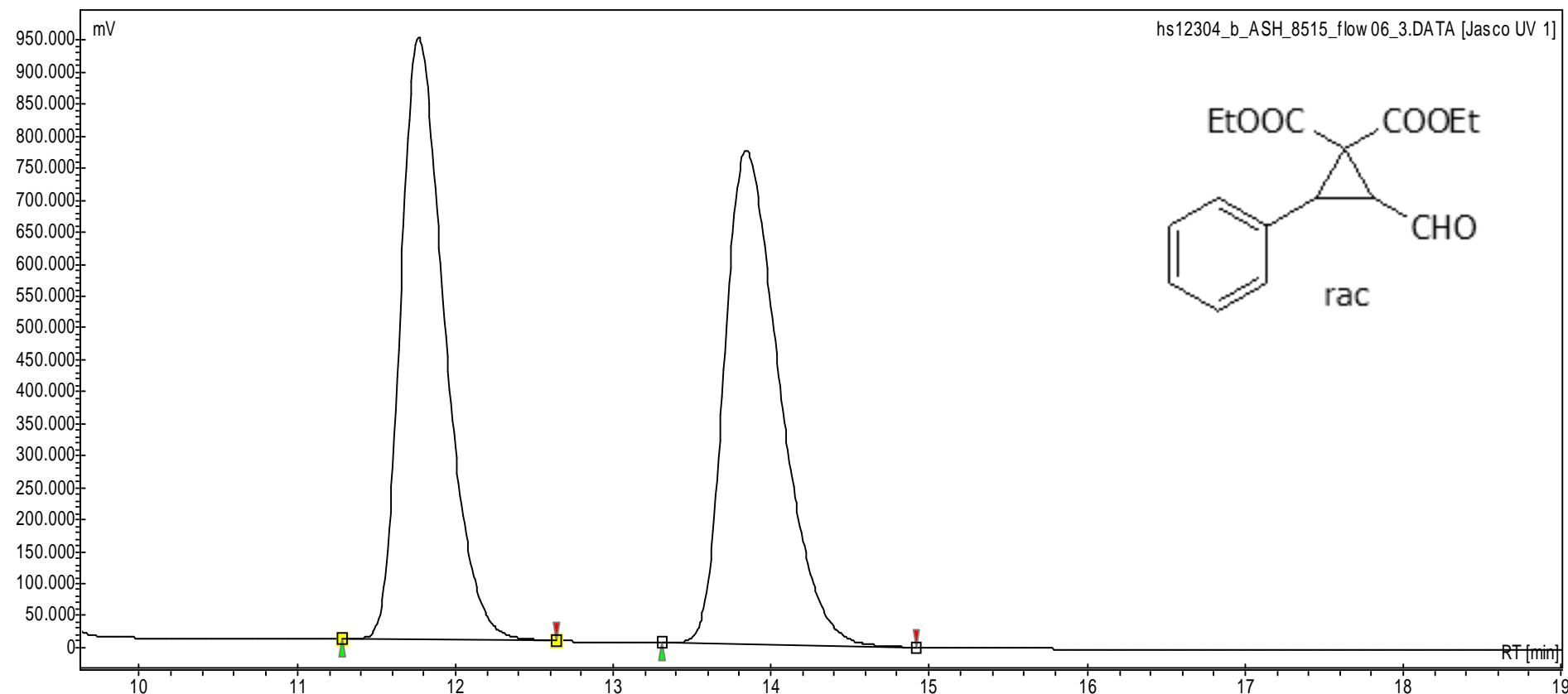


## Chromatogram : hs12304\_b\_ASH\_8515\_flow06\_3

Method: HPLC2\_ASH\_8515\_flow06\_acq40\_210nm

Data file: hs12304\_b\_ASH\_8515\_flow06\_3.DATA

Date: 30.04.2008 14:59:07



hs12304\_b\_ASH\_8515\_flow06\_3.DATA [Jasco UV 1]

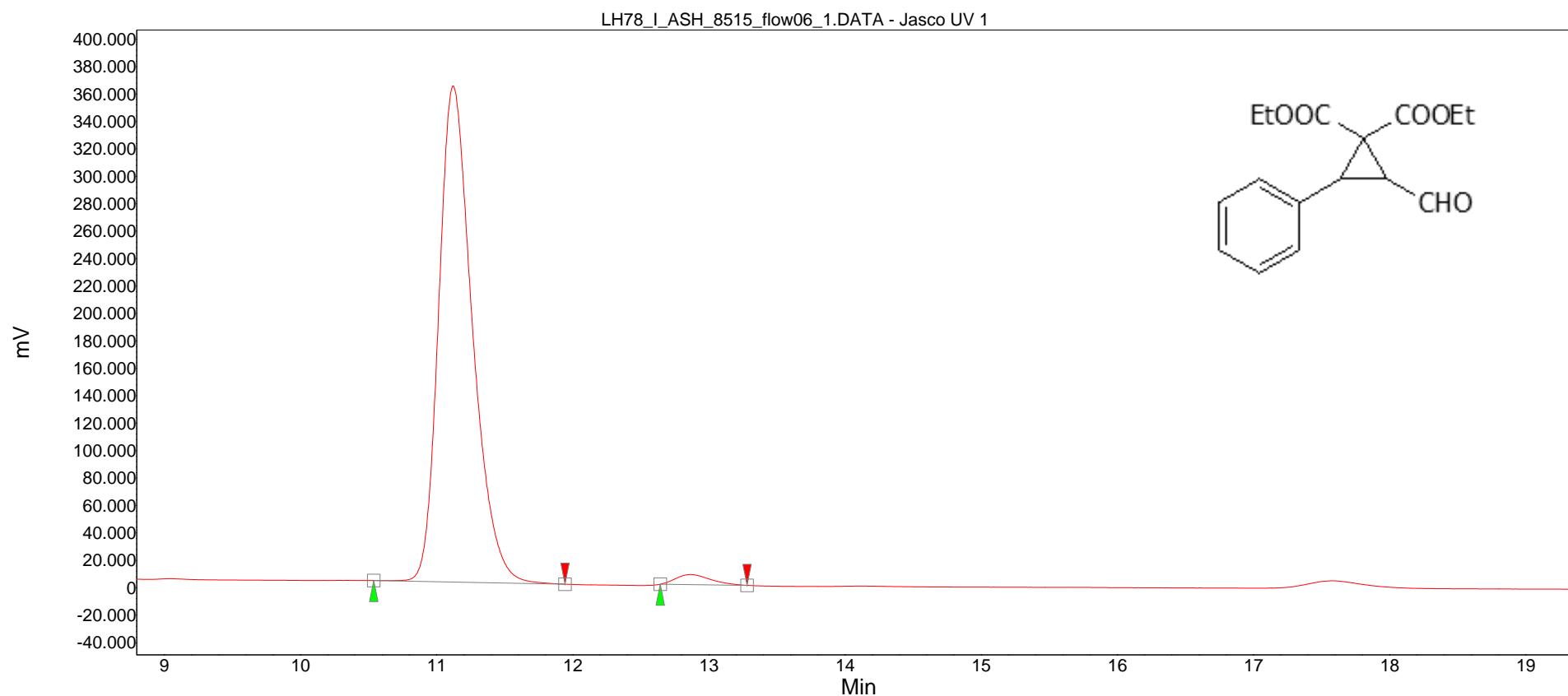
Index	Start	Time	End	Area %
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1	11,281	11,767	12,645	49,331
2	13,306	13,842	14,917	50,669
Total				100,000

## Chromatogram : LH78\_I\_ASH\_8515\_flow06\_1

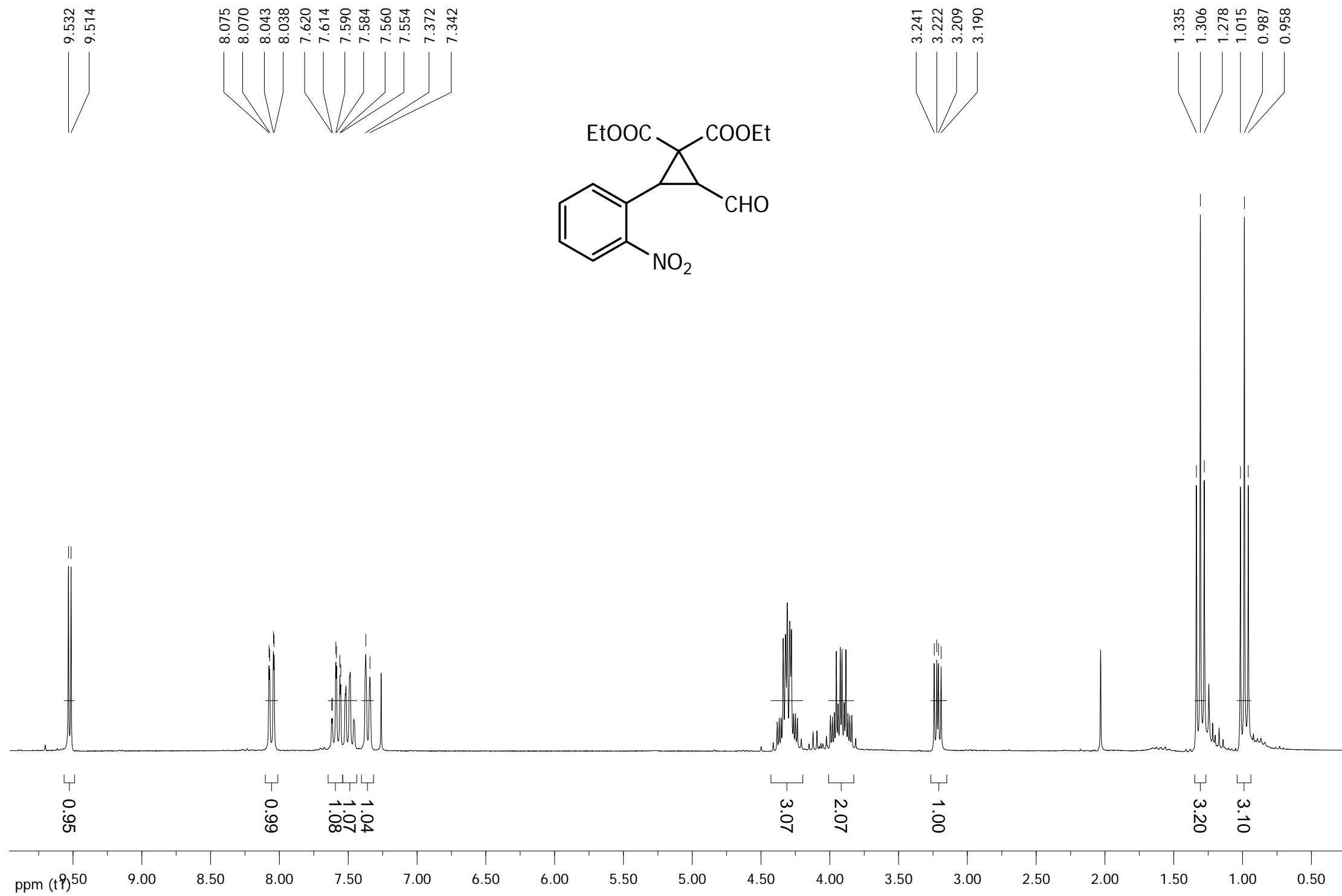
Method: HPLC2\_ASH\_8515\_flow06\_acq40\_210nm

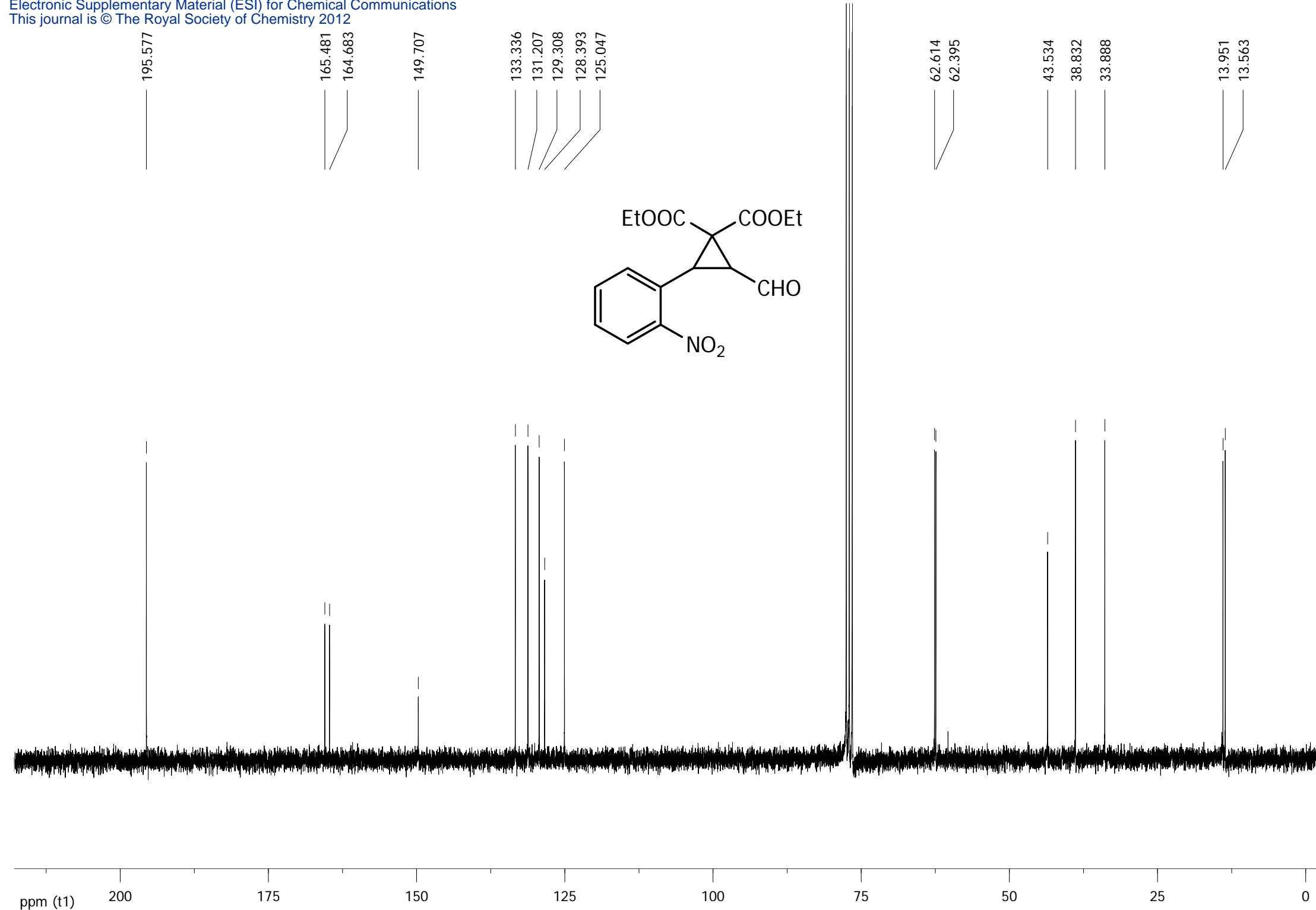
Data file: LH78\_I\_ASH\_8515\_flow06\_1.DATA

Date: 12.05.2008 16:42:17



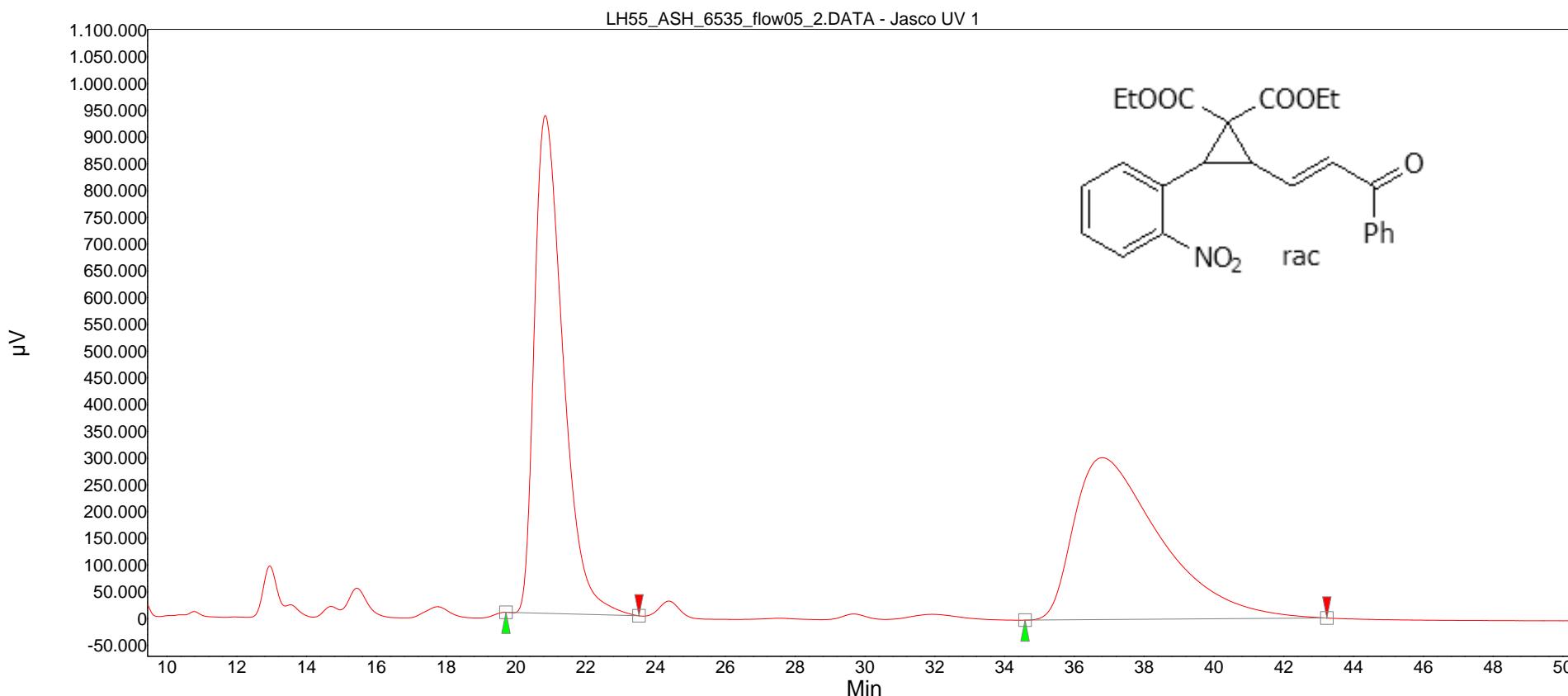
Index	Start Time [Min]	End Time [Min]	Area [%]
1	10,537	11,117	97,954
2	12,642	12,867	2,046
Total			100,000





## Chromatogram : LH55\_ASH\_6535\_flow05\_2

Method: HPLC1\_ASH\_6535\_flow05\_acq\_90  
Data file: LH55\_ASH\_6535\_flow05\_2.DATA  
Date: 25.03.2008 13:02:34



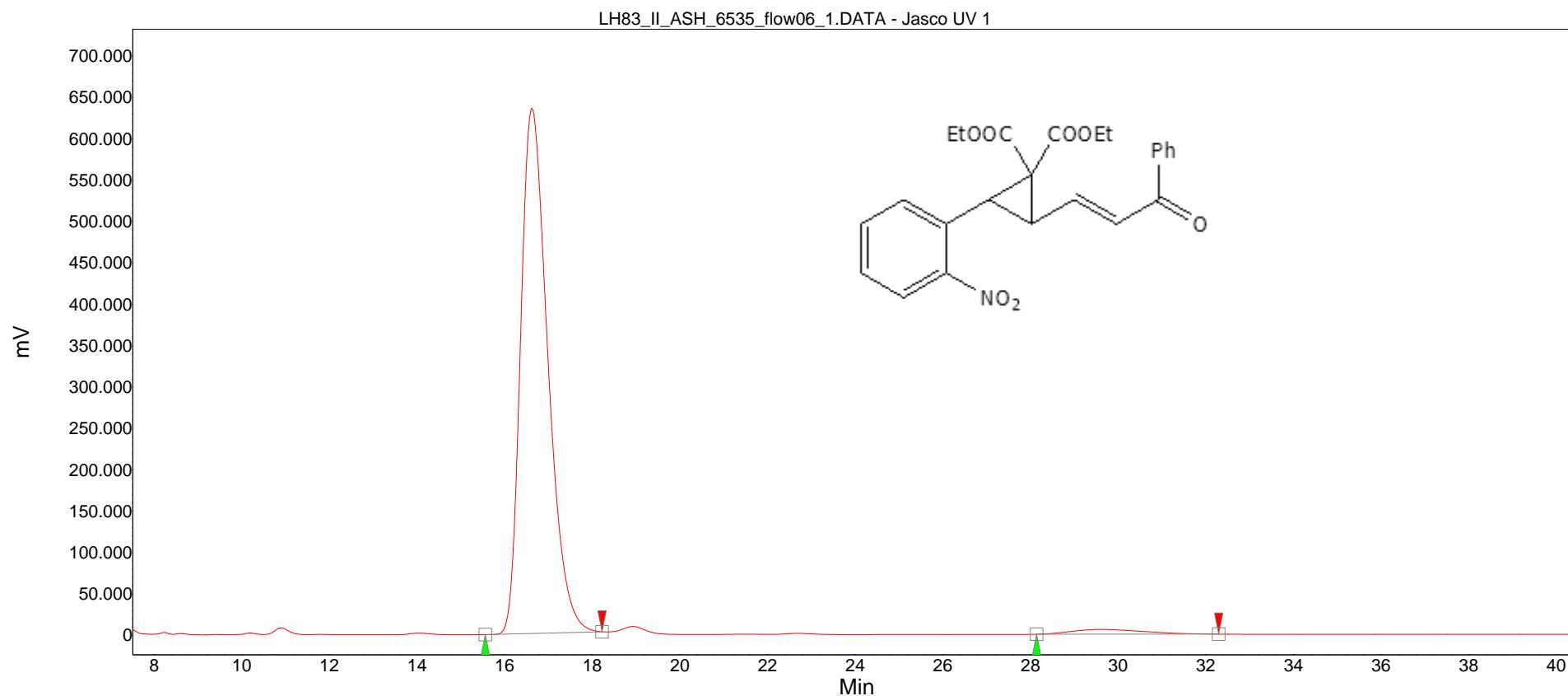
Index	Start Time [Min]	Time [Min]	End Time [Min]	Area %
1	19,711	20,842	23,523	50,489
2	34,587	36,808	43,233	49,511
Total				100,000

## Chromatogram : LH83\_II\_ASH\_6535\_flow06\_1

Method: HPLC2\_ASH\_6535\_flow06\_acq60

Data file: LH83\_II\_ASH\_6535\_flow06\_1.DATA

Date: 15.05.2008 20:55:03

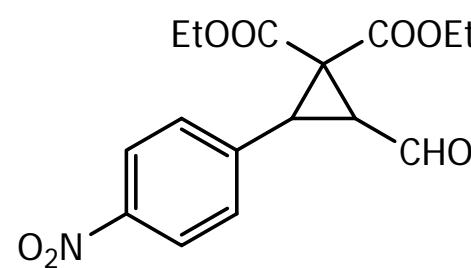


Index	Start [Min]	Time [Min]	End [Min]	Area %
1	15,558	16,625	18,223	97,660
2	28,140	29,625	32,293	2,340
Total				100,000

9.540  
9.526

8.177  
8.148

7.444  
7.416



3.855  
3.830  
3.455  
3.442  
3.430  
3.417

1.324  
1.300  
1.276  
1.025  
1.001  
0.978

-0.96

-2.02

-2.11

-2.19

-0.98

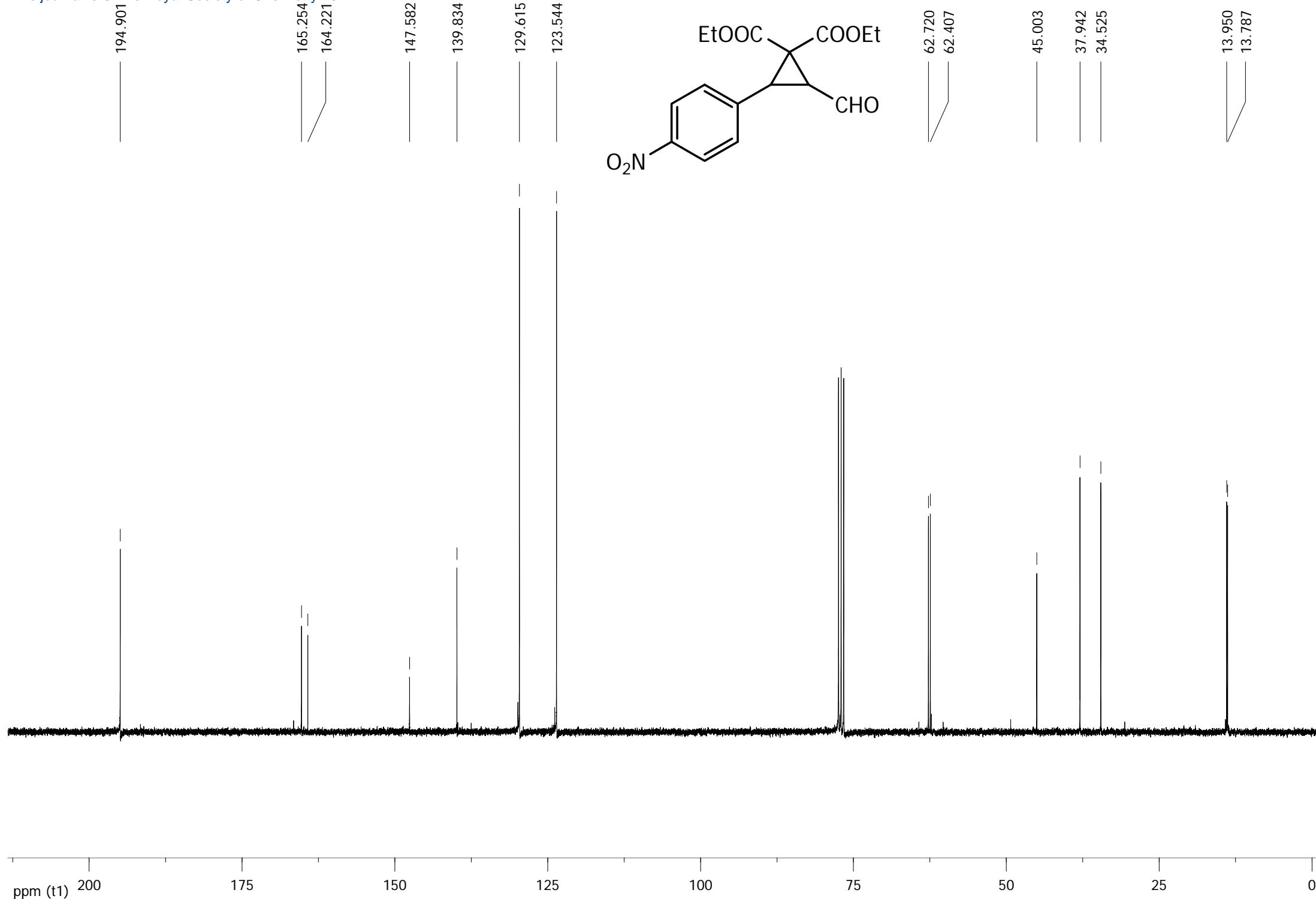
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0.0

ppm

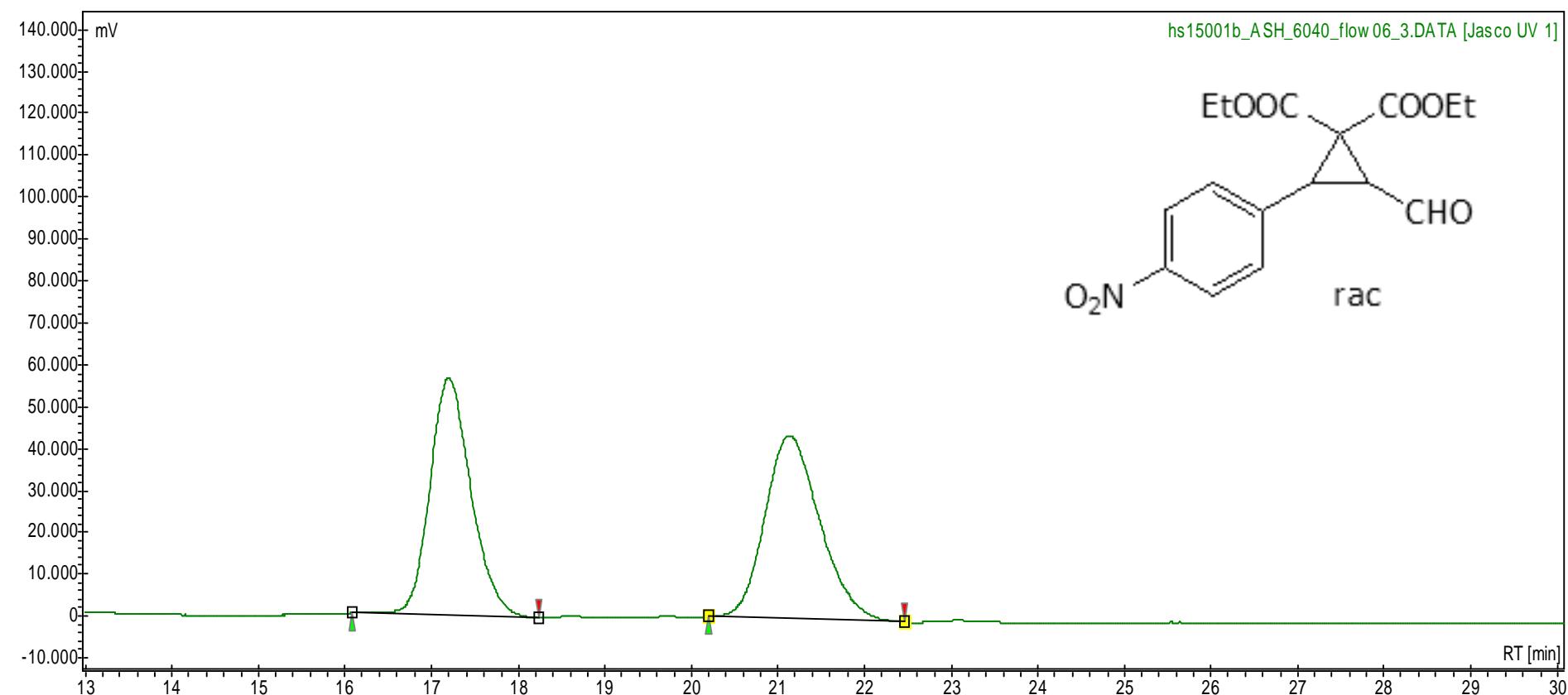


## Chromatogram : hs15001b\_ASH\_6040\_flow06\_3

Method: HPLC2\_ASH\_6040\_flow06\_acq45\_210nm

Data file: hs15001b\_ASH\_6040\_flow06\_3.DATA

Date: 30.04.2008 16:57:00



hs15001b\_ASH\_6040\_flow06\_3.DATA [Jasco UV 1]

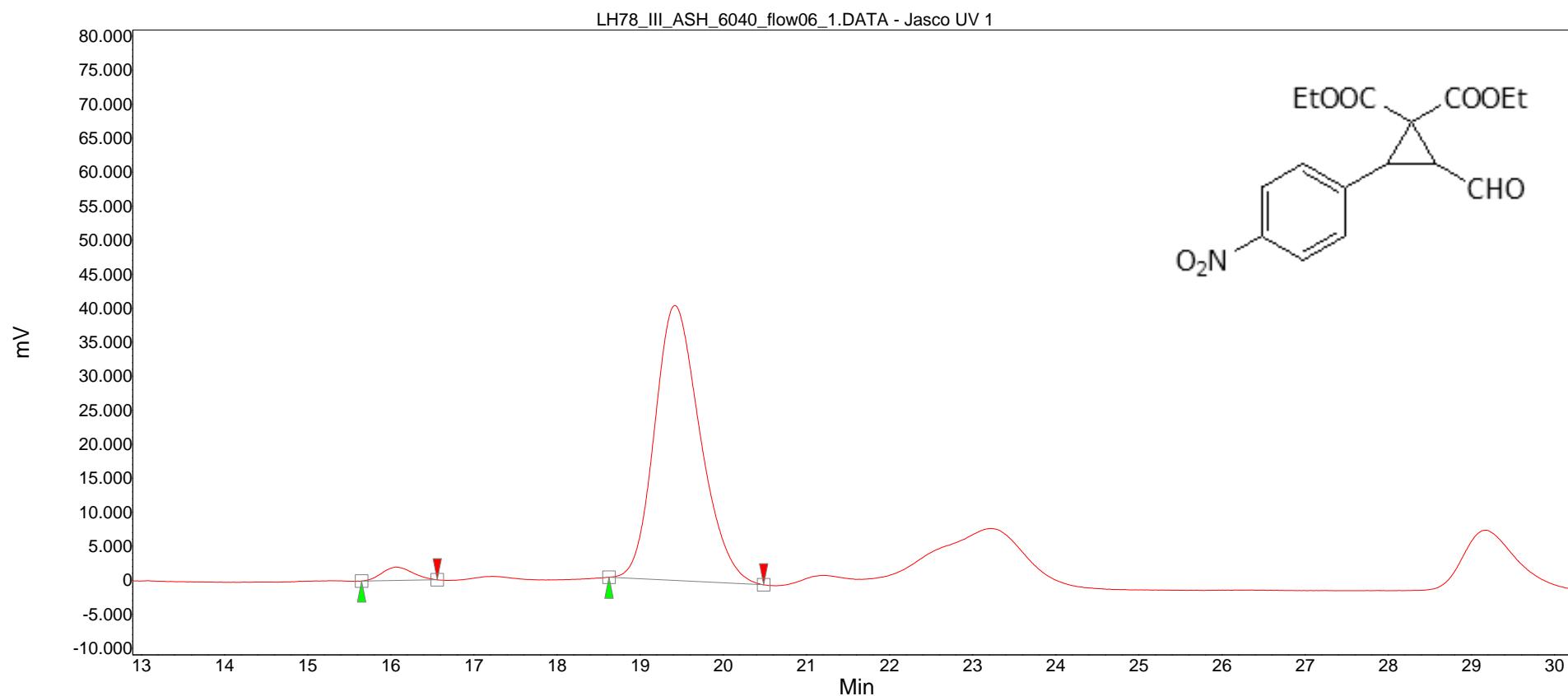
Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	16,074	17,192	18,230	49,173
1	20,199	21,133	22,465	50,827
Total				100,000

## Chromatogram : LH78\_III\_ASH\_6040\_flow06\_1

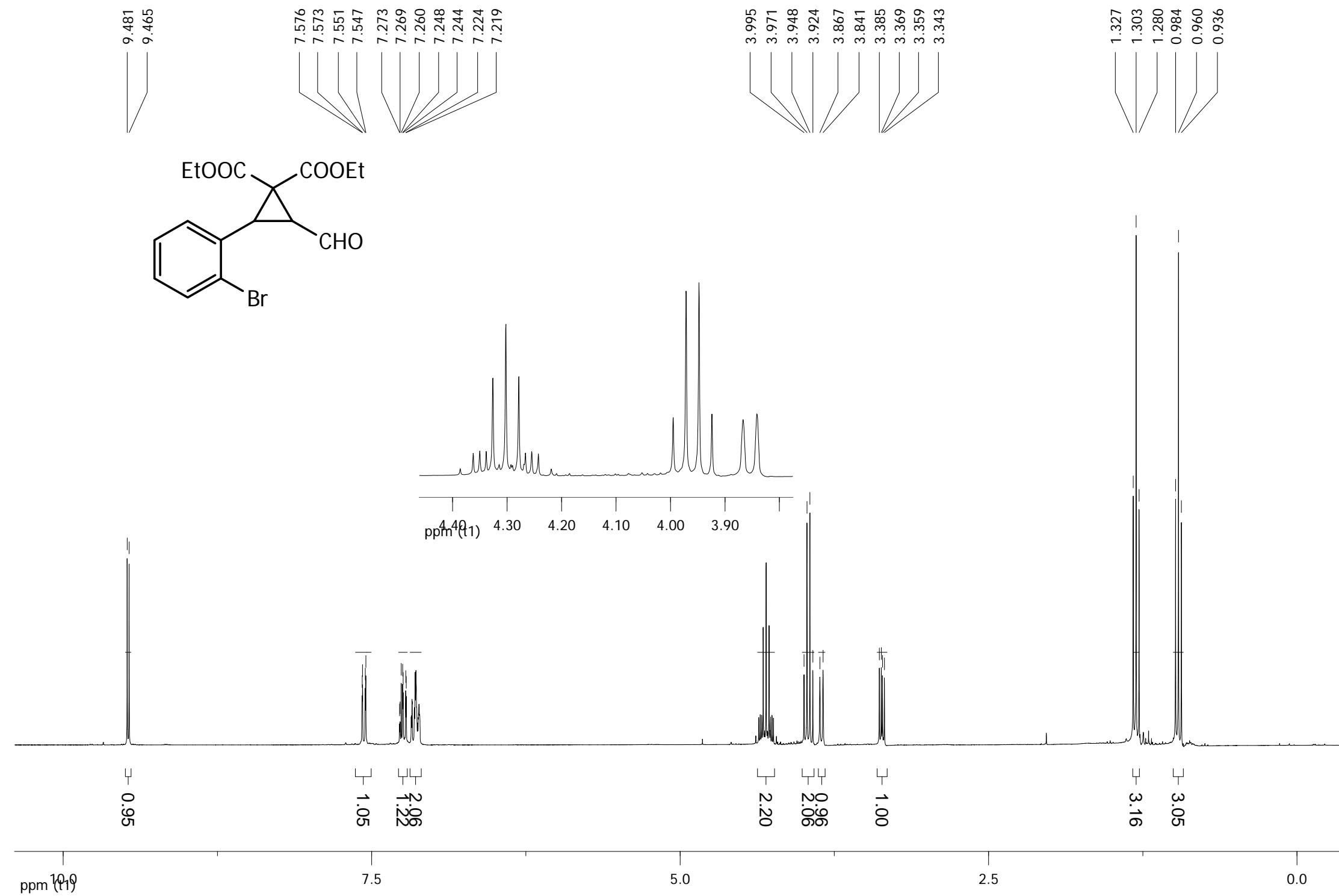
Method: HPLC2\_ASH\_6040\_flow06\_acq45\_210nm

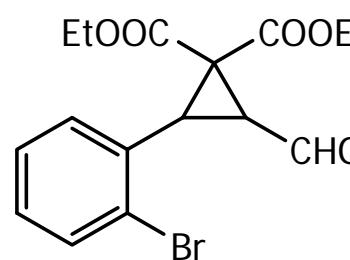
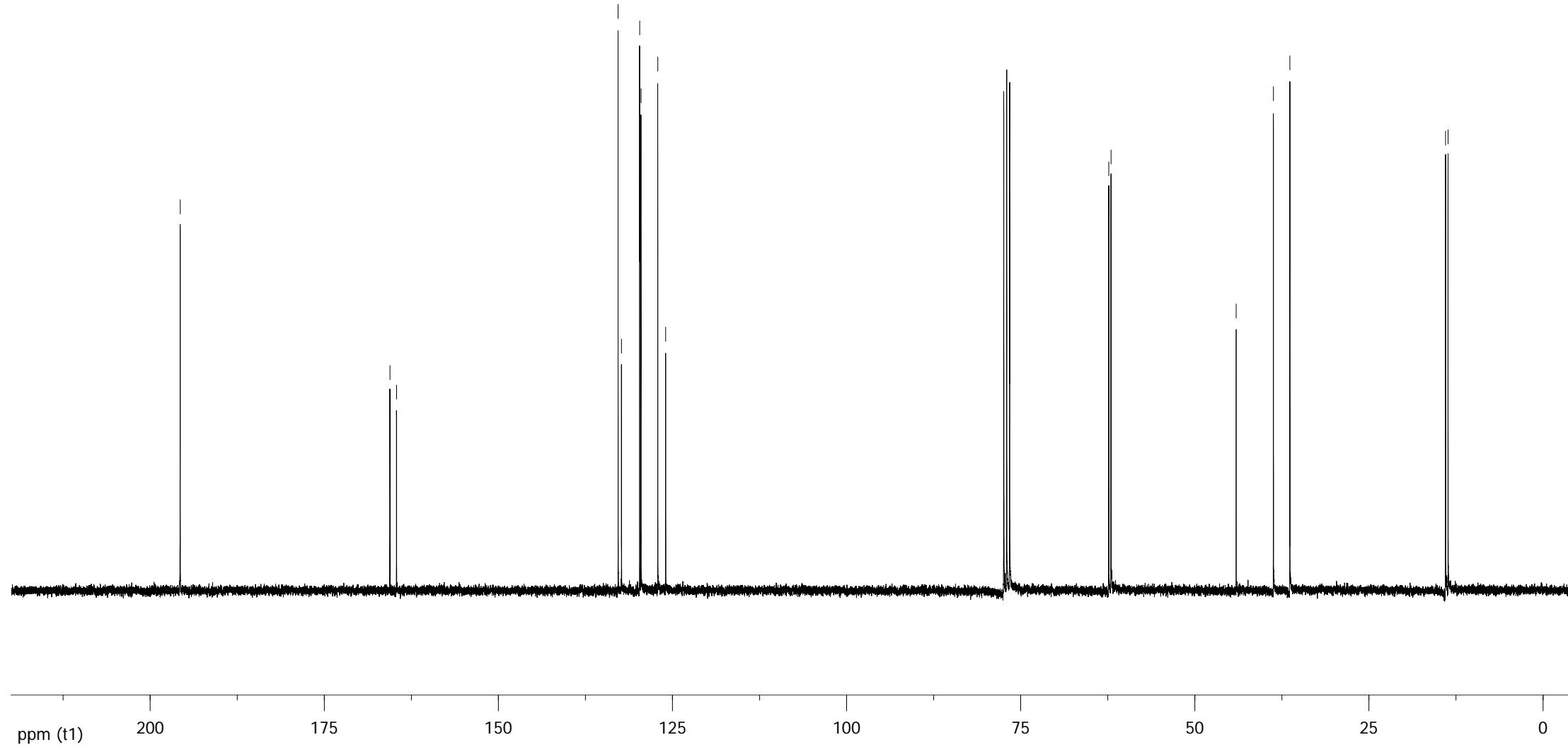
Data file: LH78\_III\_ASH\_6040\_flow06\_1.DATA

Date: 12.05.2008 19:32:42



Index	Start [Min]	Time [Min]	End [Min]	Area %
1	15,649	16,067	16,558	3,132
2	18,625	19,417	20,484	96,868
Total				100,000



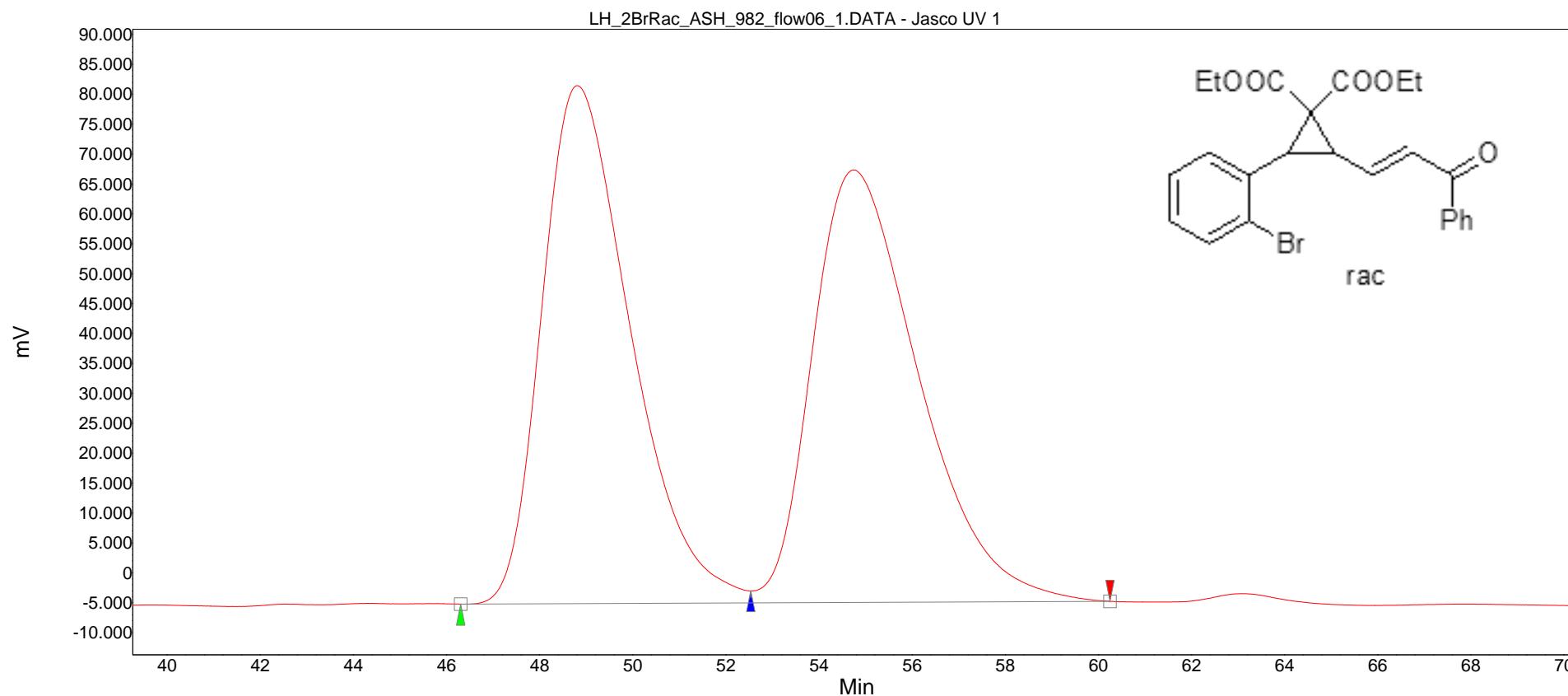


## Chromatogram : LH\_2BrRac\_ASH\_982\_flow06\_1

Method: HPLC2\_ASH\_982\_flow06\_acq90

Data file: LH\_2BrRac\_ASH\_982\_flow06\_1.DATA

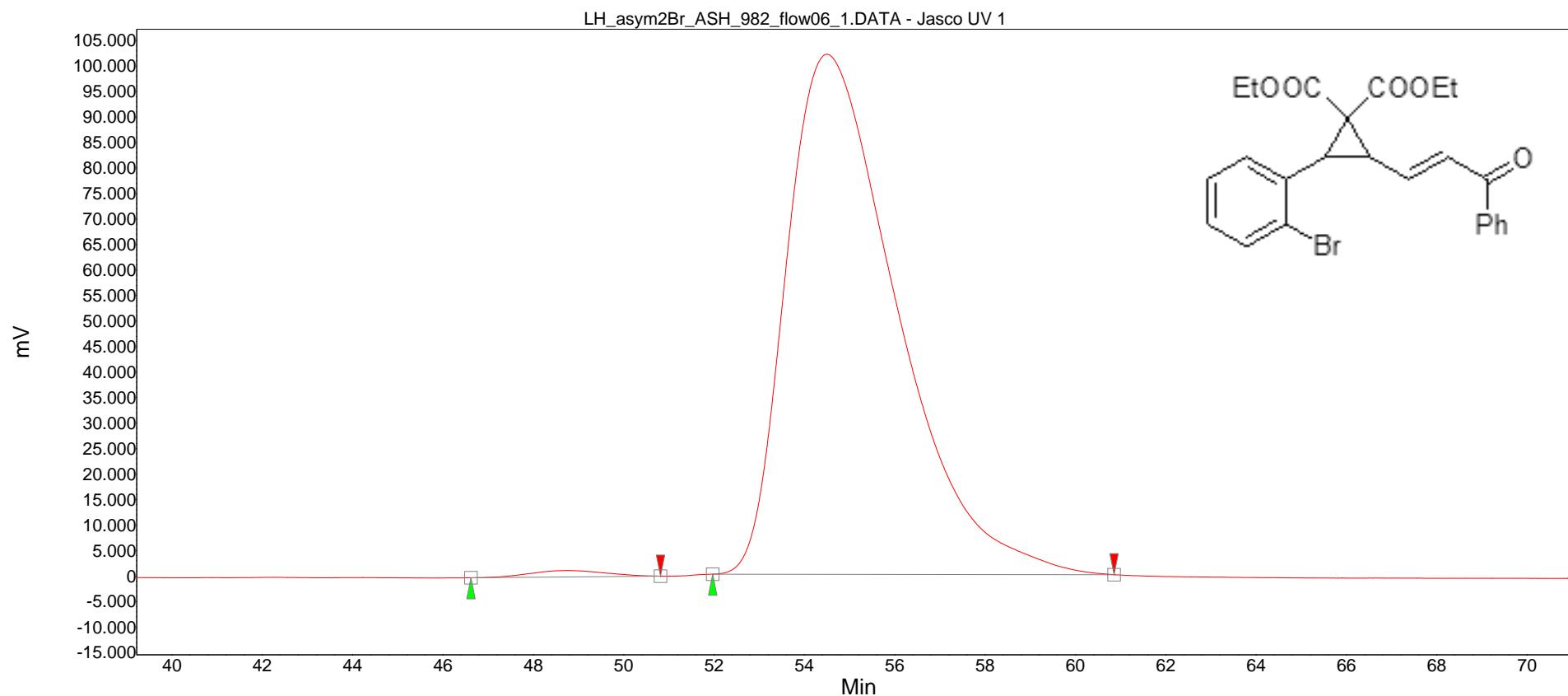
Date: 21.05.2008 23:31:19



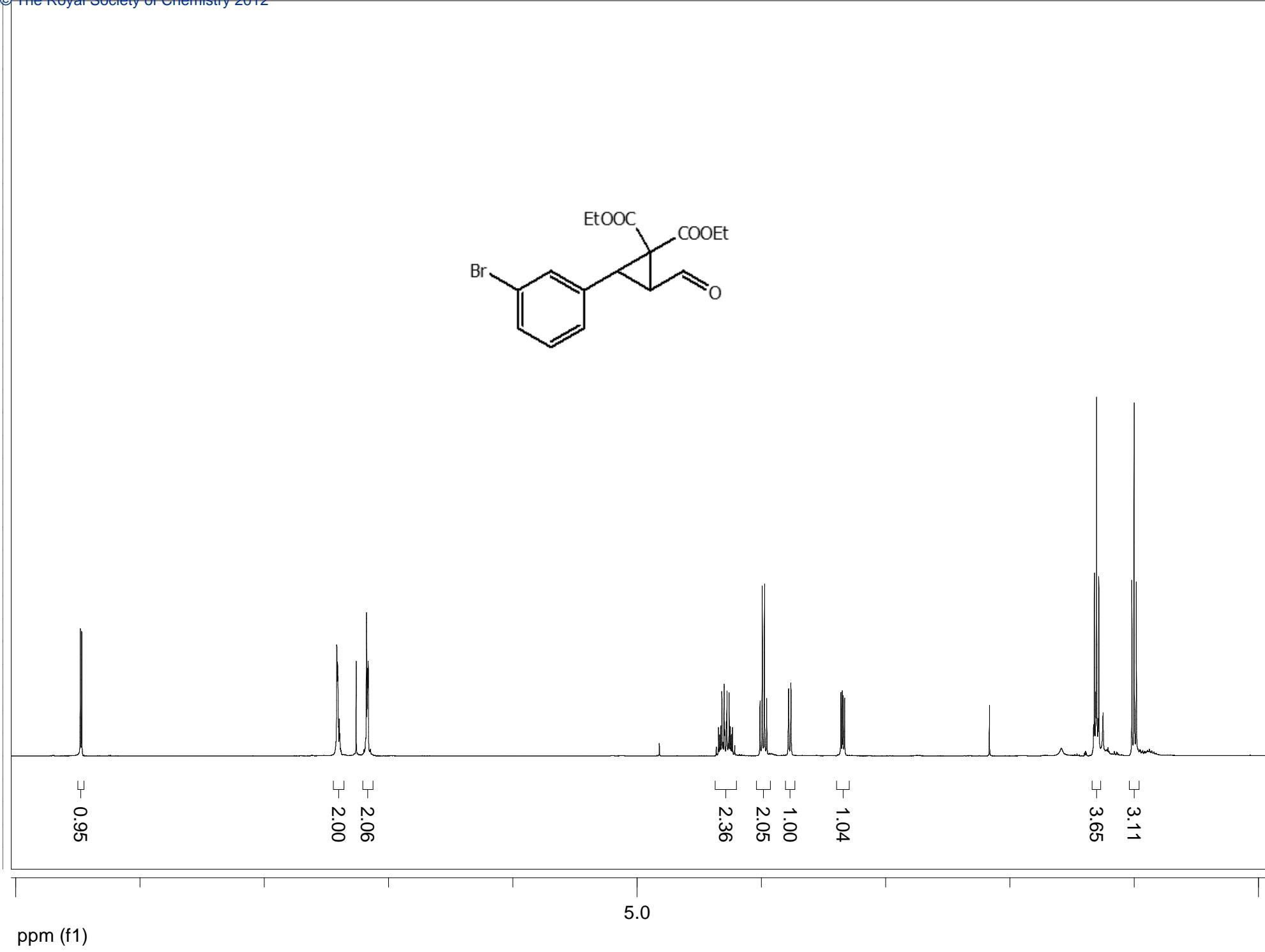
Index	Start [Min]	Time [Min]	End [Min]	Area %
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Total				100,000

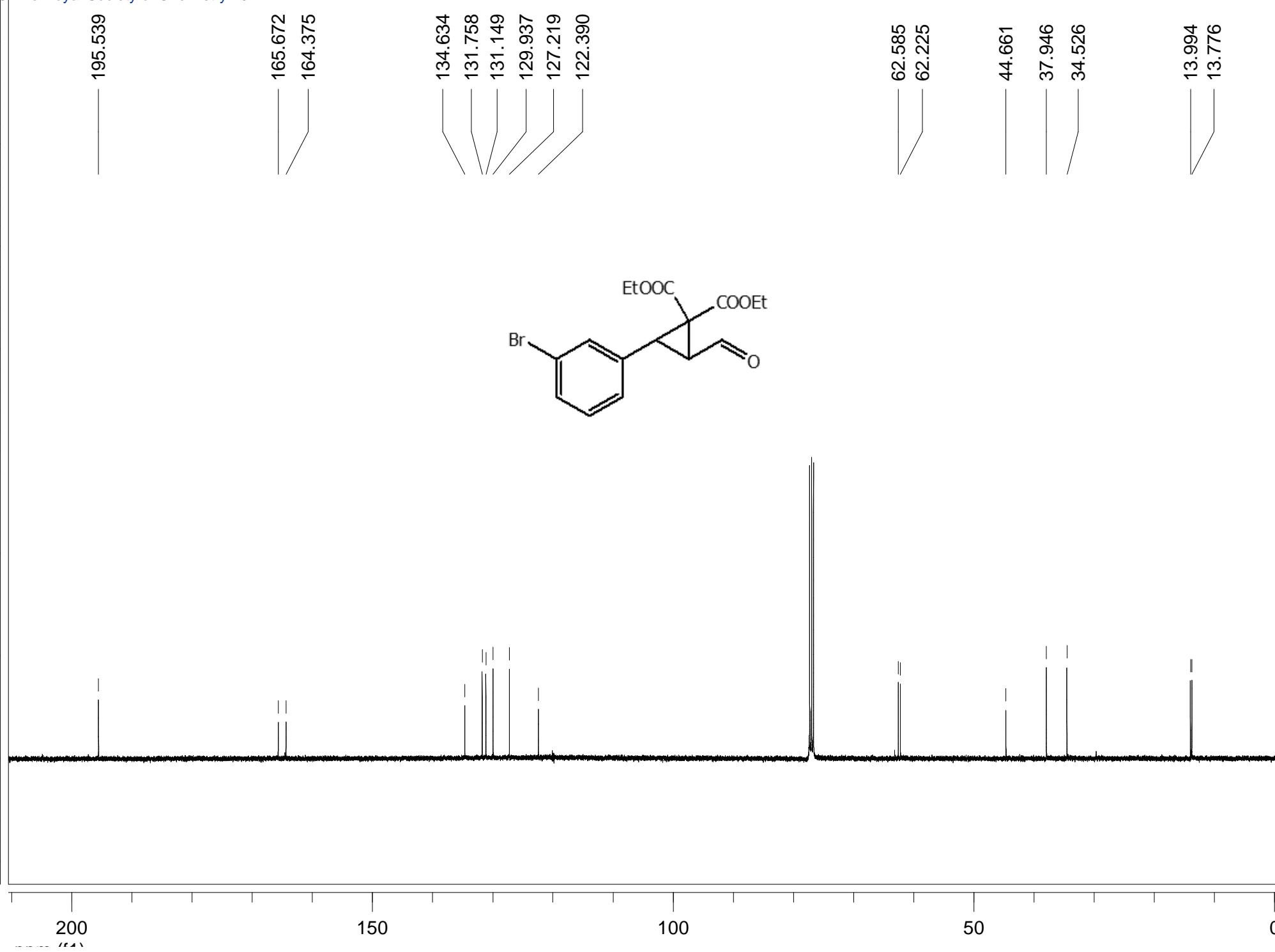
## Chromatogram : LH\_asym2Br\_ASH\_982\_flow06\_1

Method: HPLC2\_ASH\_982\_flow06\_acq90  
Data file: LH\_asym2Br\_ASH\_982\_flow06\_1.DATA  
Date: 22.05.2008 01:03:59



Index	Start [Min]	Time [Min]	End [Min]	Area [%]
1	46,619	48,750	50,814	0,830
2	51,970	54,500	60,856	99,170
Total				100,000



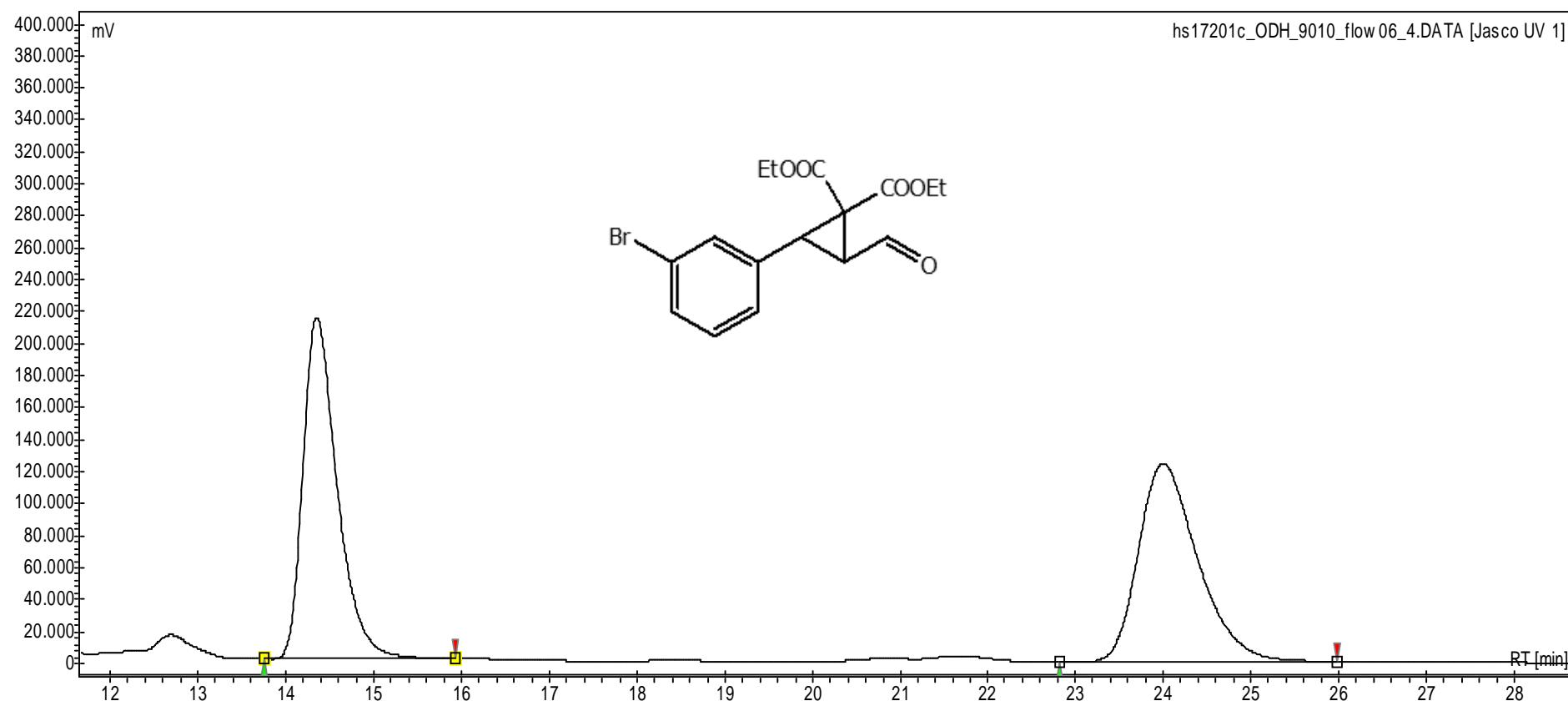


## Chromatogram : hs17201c\_ODH\_9010\_flow06\_4

Method: HPLC2\_ODH\_9010\_flow06\_acq60\_210nm

Data file: hs17201c\_ODH\_9010\_flow06\_4.DATA

Date: 01.05.2008 22:38:11



hs17201c\_ODH\_9010\_flow06\_4.DATA [Jasco UV 1]

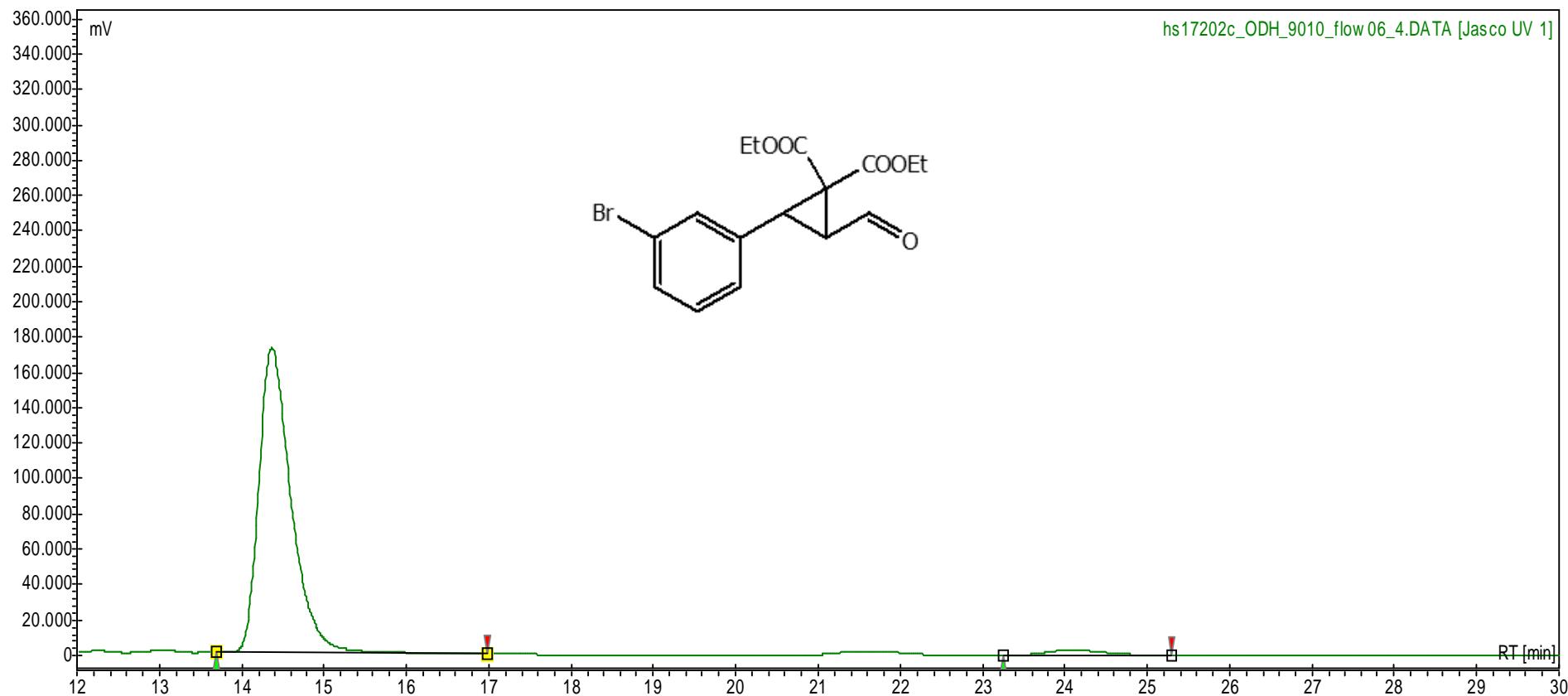
Index	Start [Min]	Time [Min]	End [Min]	Area %
1	13,760	14,350	15,930	49,618
2	22,810	23,992	25,971	50,382
Total				100,000

## Chromatogram : hs17202c\_ODH\_9010\_flow06\_4

Method: HPLC2\_ODH\_9010\_flow06\_acq60\_210nm

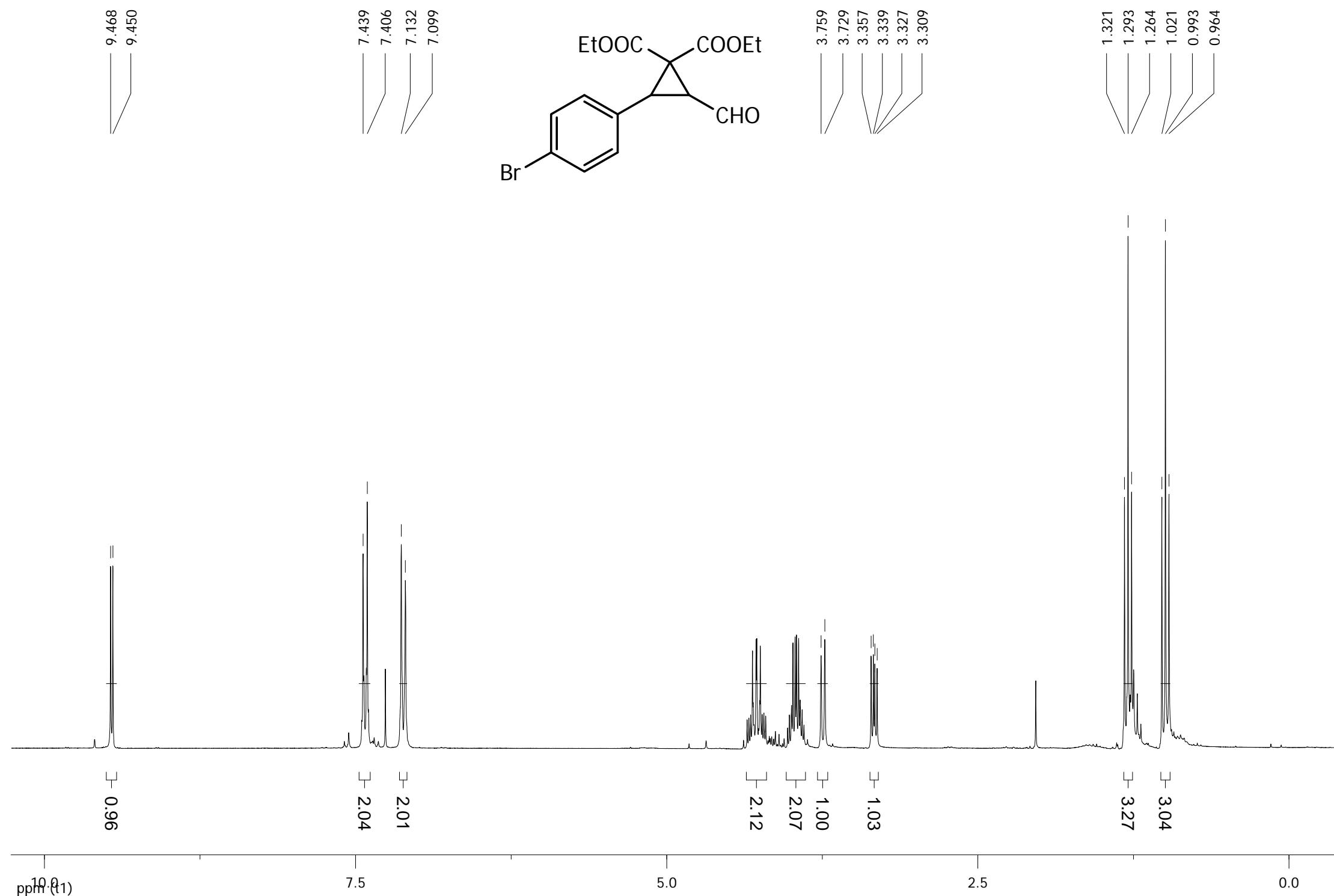
Data file: hs17202c\_ODH\_9010\_flow06\_4.DATA

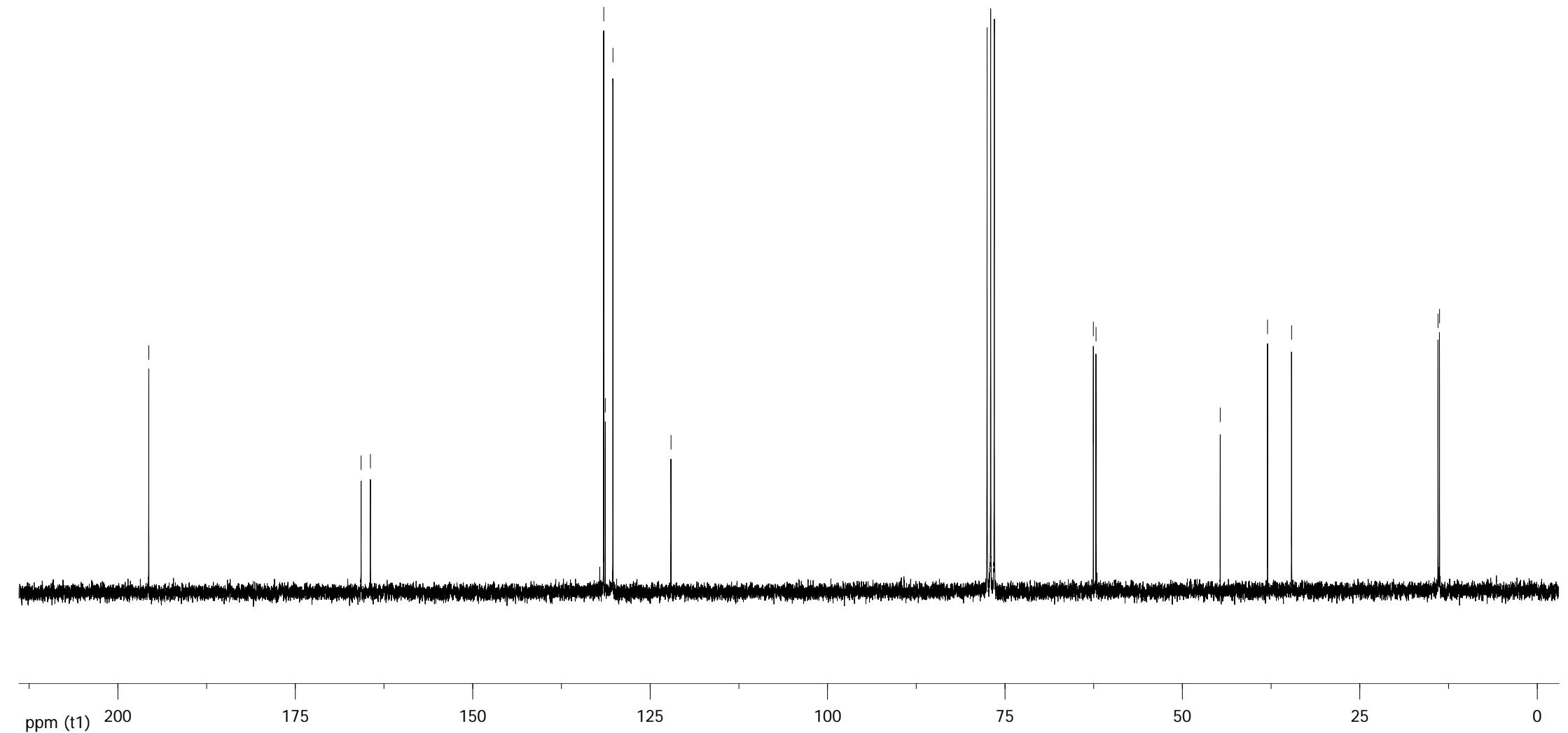
Date: 01.05.2008 23:40:49



hs17202c\_ODH\_9010\_flow06\_4.DATA [Jasco UV 1]

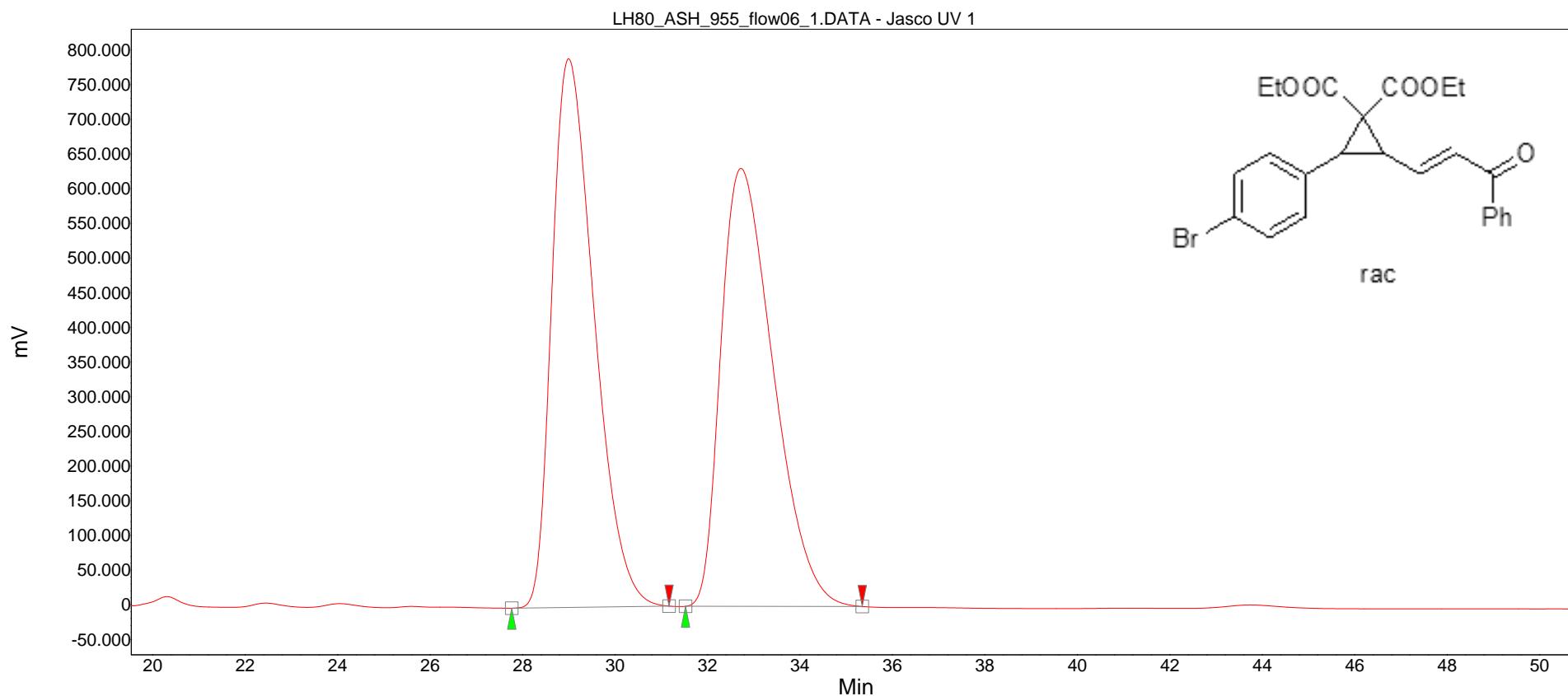
Index	Start [Min]	Time [Min]	End [Min]	Area %
1	13,698	14,367	16,983	96,861
2	23,244	24,075	25,289	3,139
Total				100,000





## Chromatogram : LH80\_ASH\_955\_flow06\_1

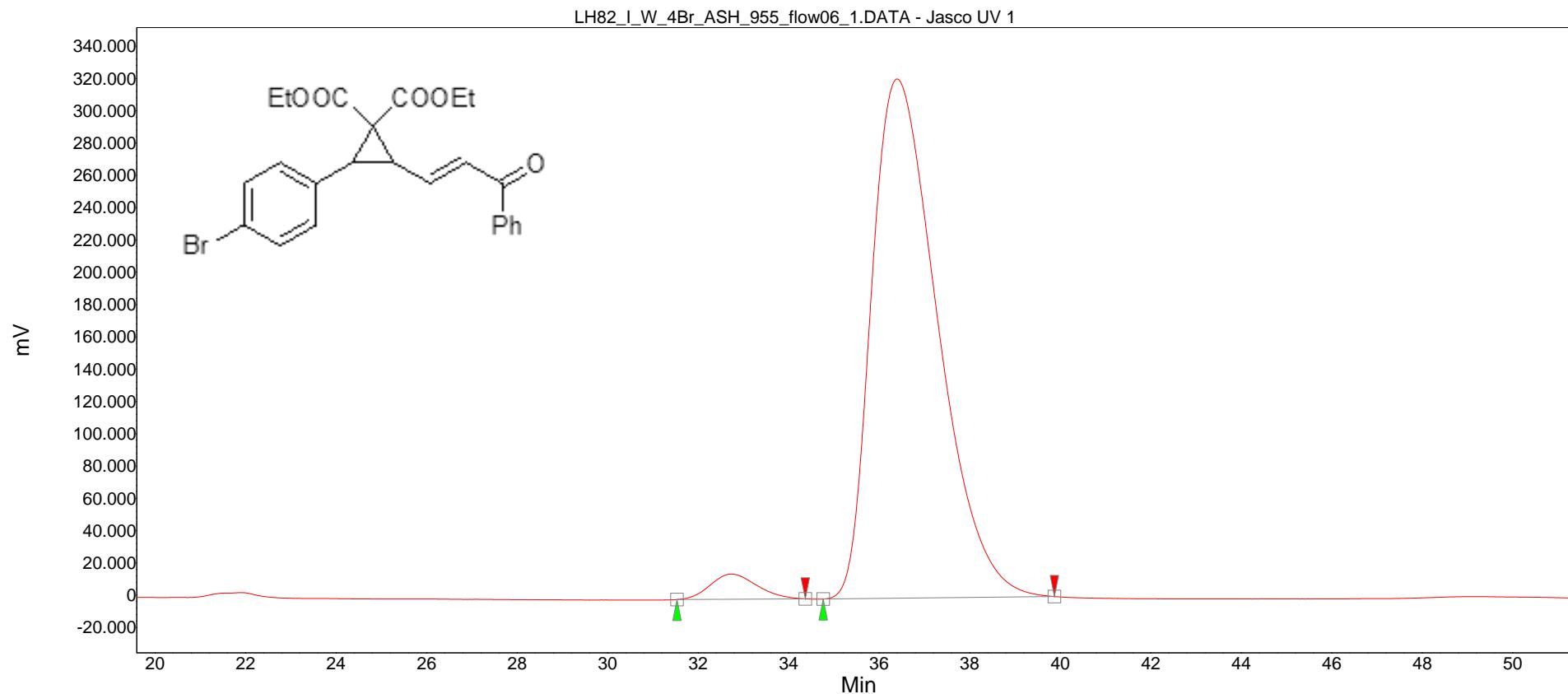
Method: HPLC2\_ASH\_955\_flow06\_acq60  
Data file: LH80\_ASH\_955\_flow06\_1.DATA  
Date: 13.05.2008 19:10:44



Index	Start Time [Min]	End Time [Min]	Area [%]
1	27,764	28,992	50,210
2	31,523	32,725	49,790
Total			100,000

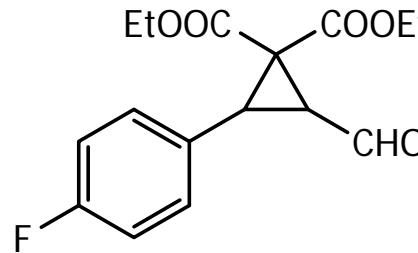
## Chromatogram : LH82\_I\_W\_4Br\_ASH\_955\_flow06\_1

Method: HPLC2\_ASH\_955\_flow06\_acq60  
Data file: LH82\_I\_W\_4Br\_ASH\_955\_flow06\_1.DATA  
Date: 19.05.2008 19:58:54



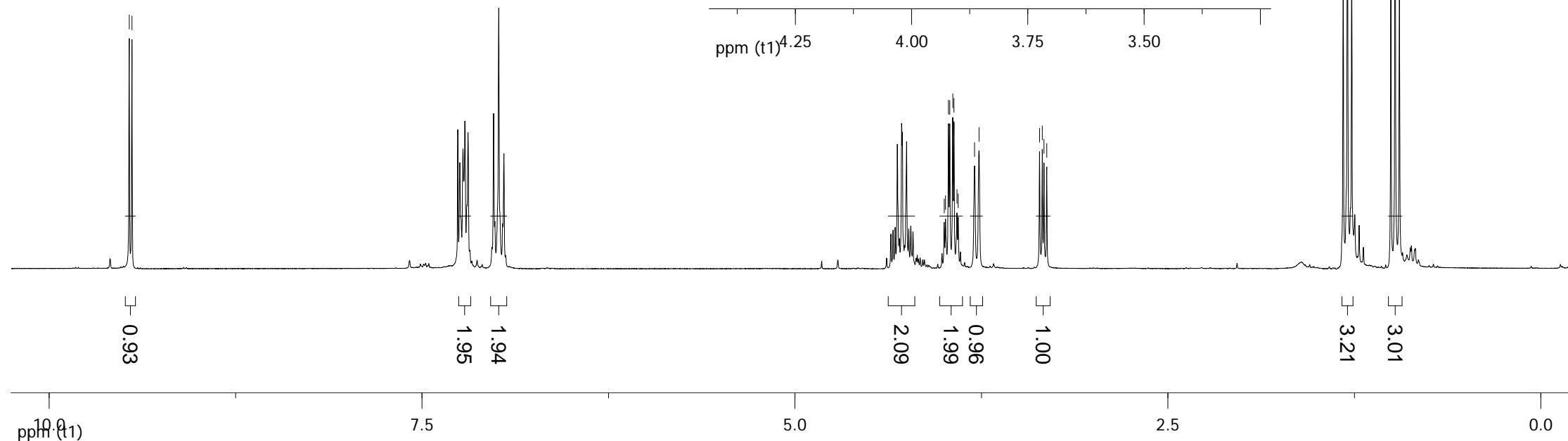
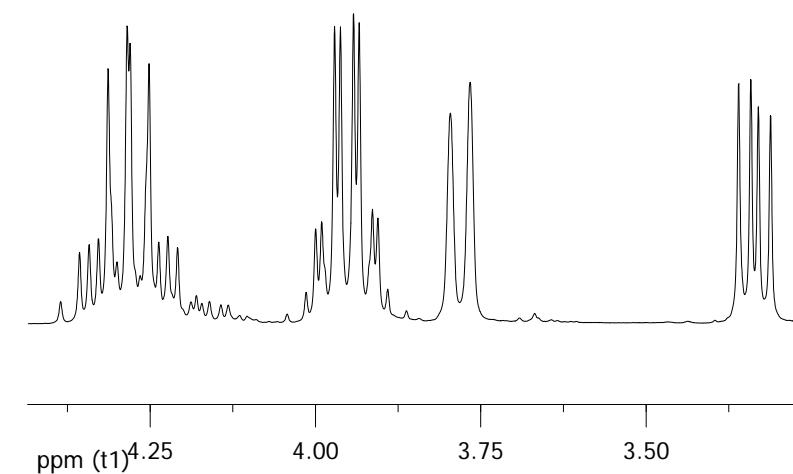
Index	Start Time [Min]	End Time [Min]	Area [%]
1	31,530	32,733	3,290
2	34,761	36,392	96,710
Total			100,000

9.463  
9.444



3.999  
3.990  
3.971  
3.962  
3.942  
3.934  
3.914  
3.905  
3.796  
3.766  
3.360  
3.341  
3.330  
3.312

1.324  
1.296  
1.267  
1.005  
0.976  
0.948

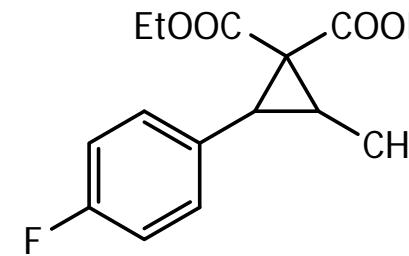


195.697

165.836  
164.493  
164.057  
160.780

130.331  
130.221  
128.055  
128.012

115.529  
115.241



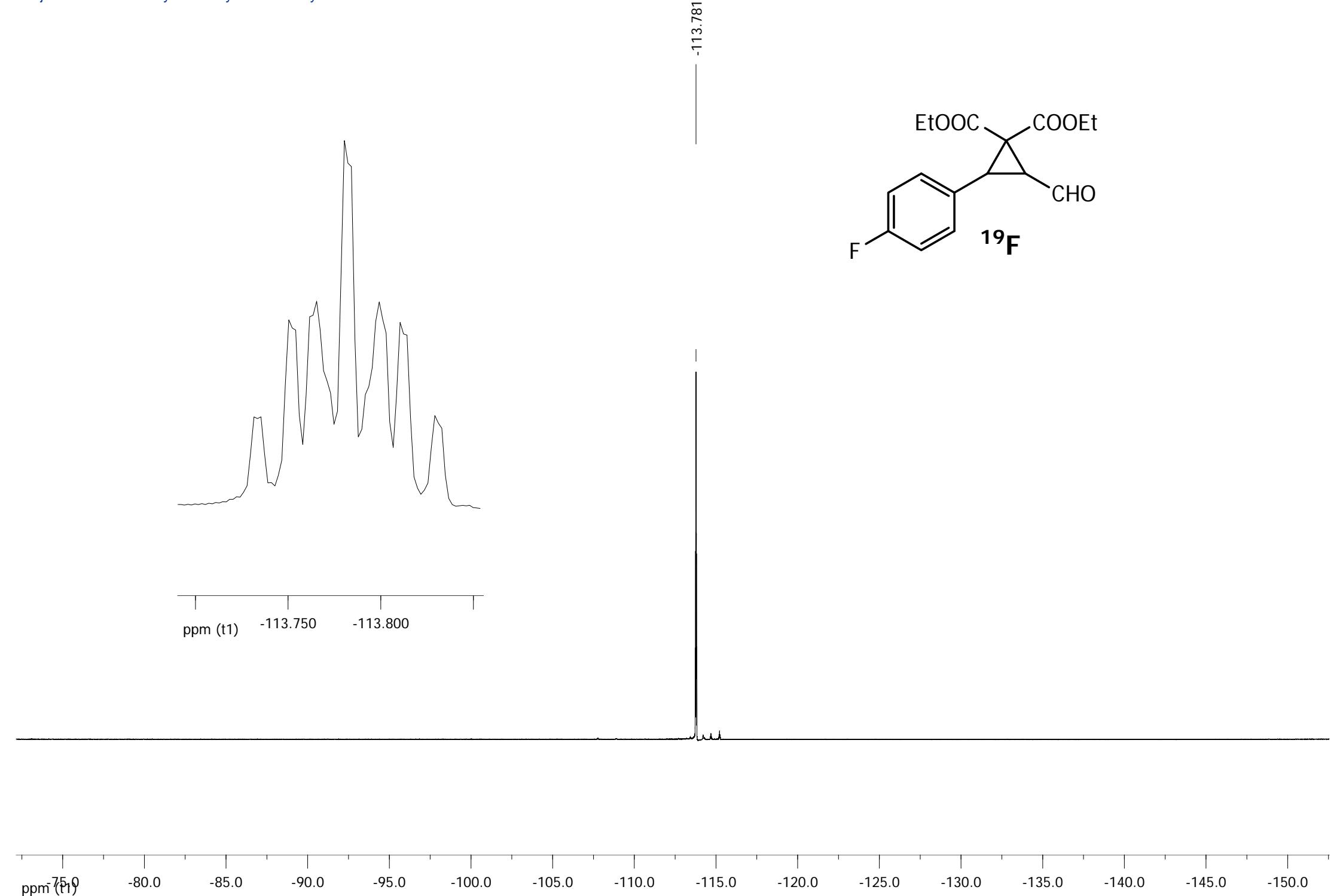
62.484  
62.069

44.708

38.248

34.493

13.979  
13.745

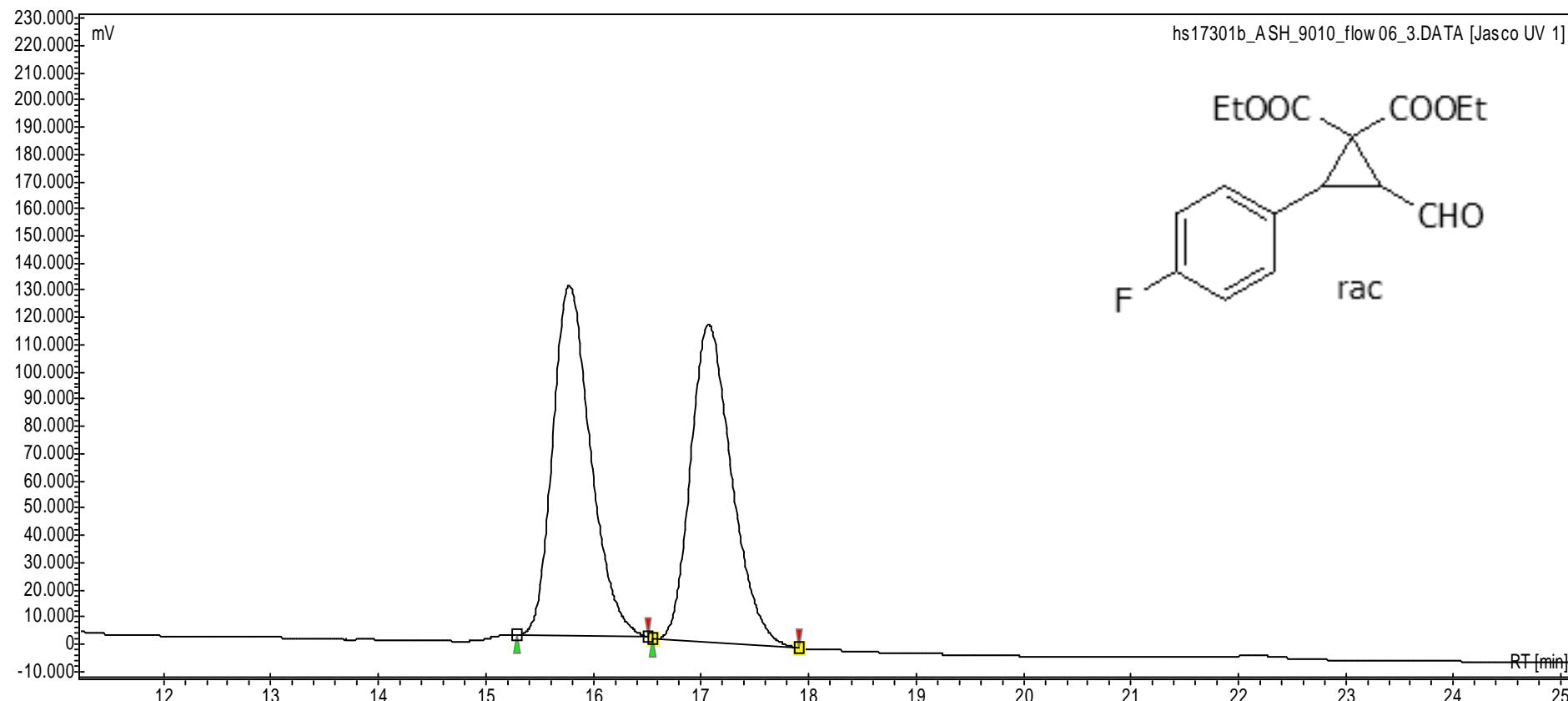


## Chromatogram : hs17301b\_ASH\_9010\_flow06\_3

Method: HPLC2\_ASH\_9010\_flow06\_acq60\_210nm

Data file: hs17301b\_ASH\_9010\_flow06\_3.DATA

Date: 30.04.2008 18:50:57



hs17301b\_ASH\_9010\_flow06\_3.DATA [Jasco UV 1]

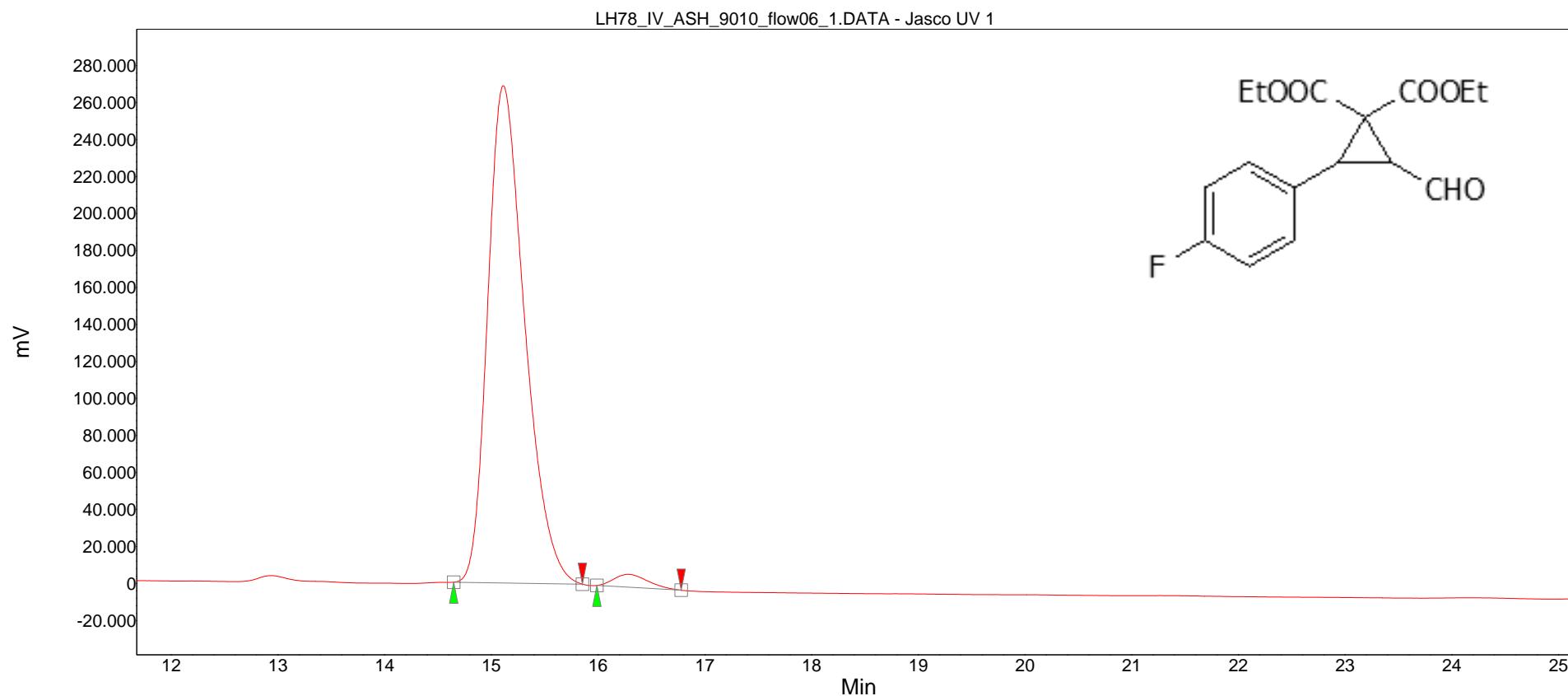
Index	Start Time	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
2	15,291	15,775	16,504	50,443
1	16,550	17,075	17,913	49,557
Total				100,000

## Chromatogram : LH78\_IV\_ASH\_9010\_flow06\_1

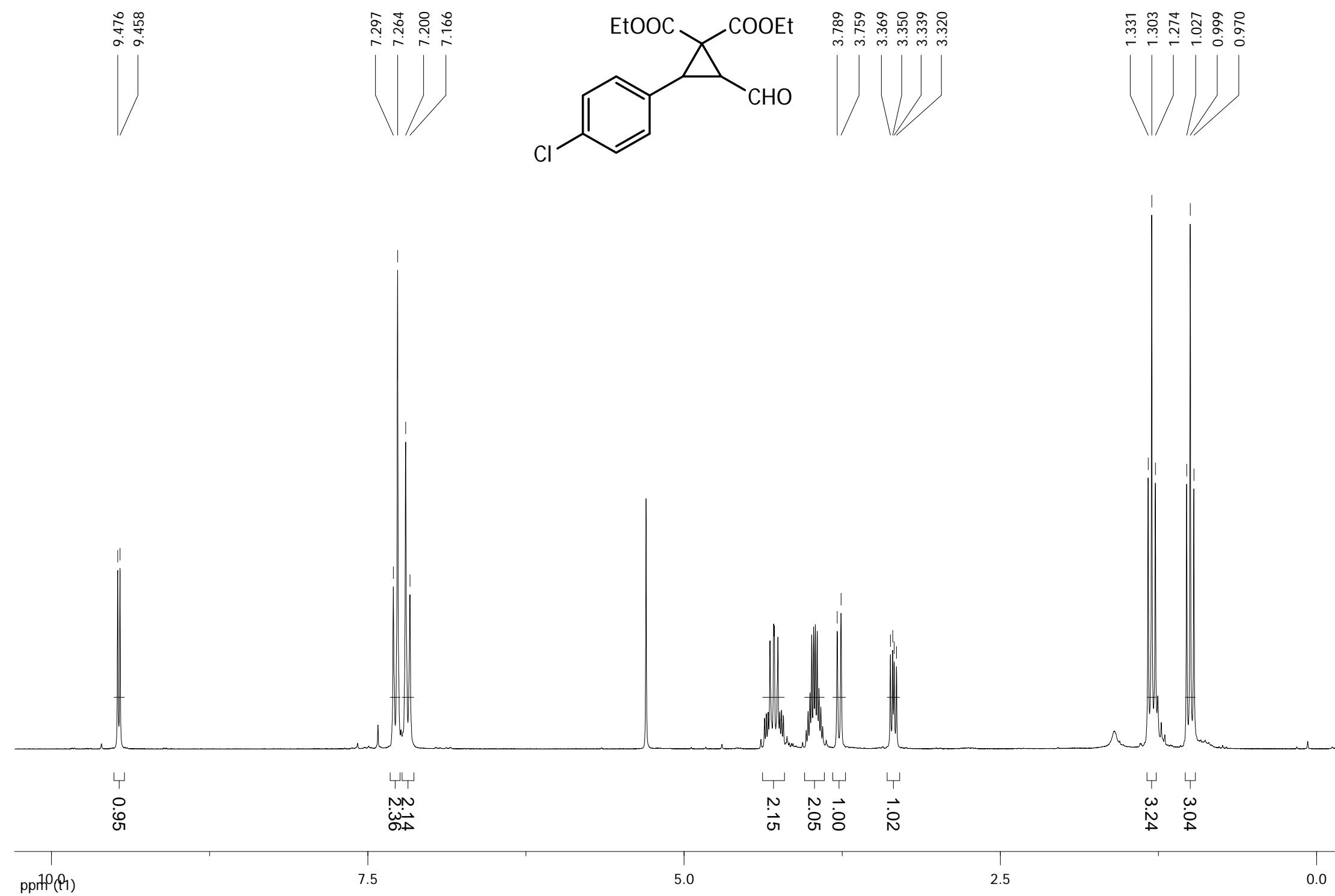
Method: HPLC2\_ASH\_9010\_flow06\_acq60\_210nm

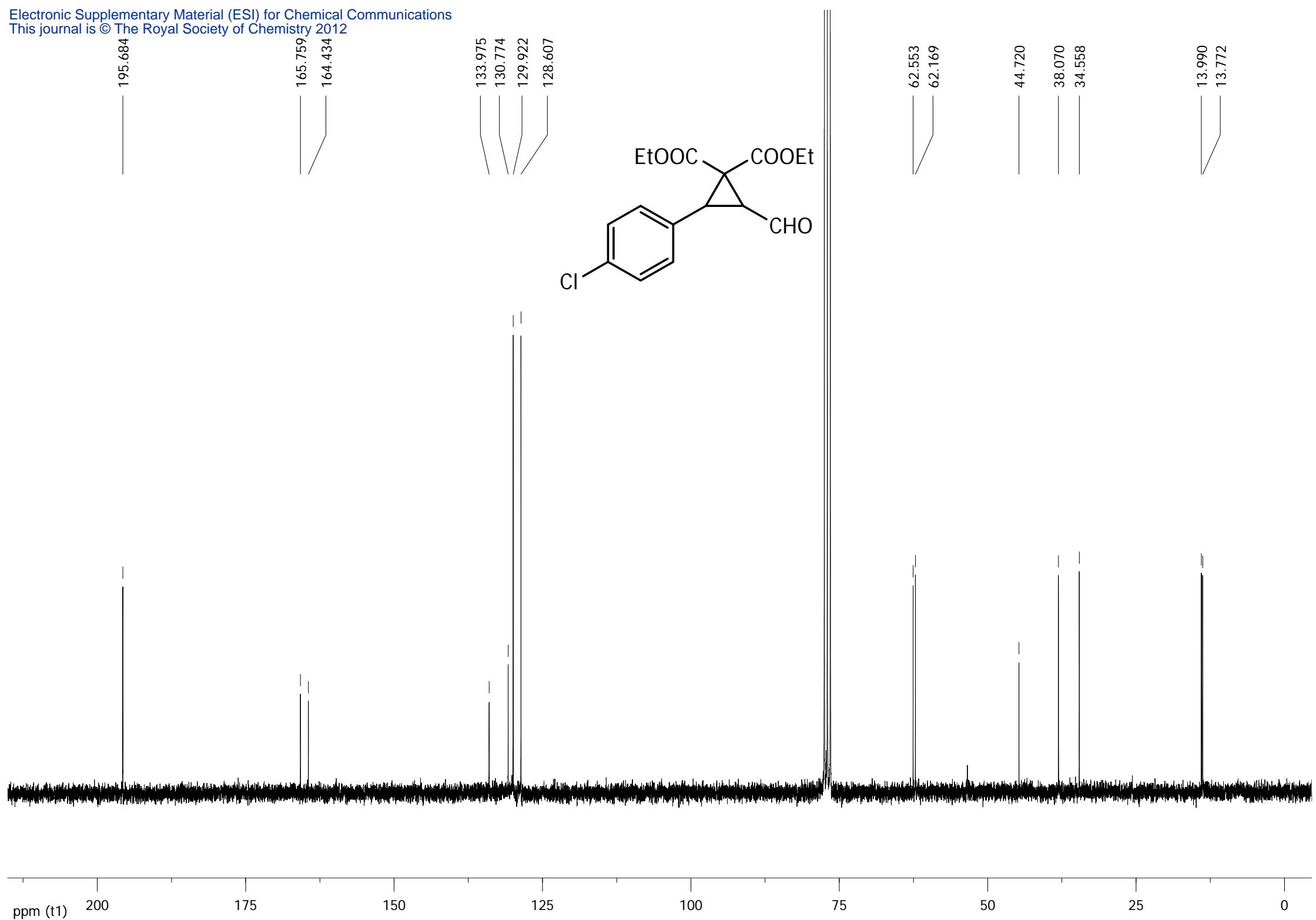
Data file: LH78\_IV\_ASH\_9010\_flow06\_1.DATA

Date: 12.05.2008 17:57:28



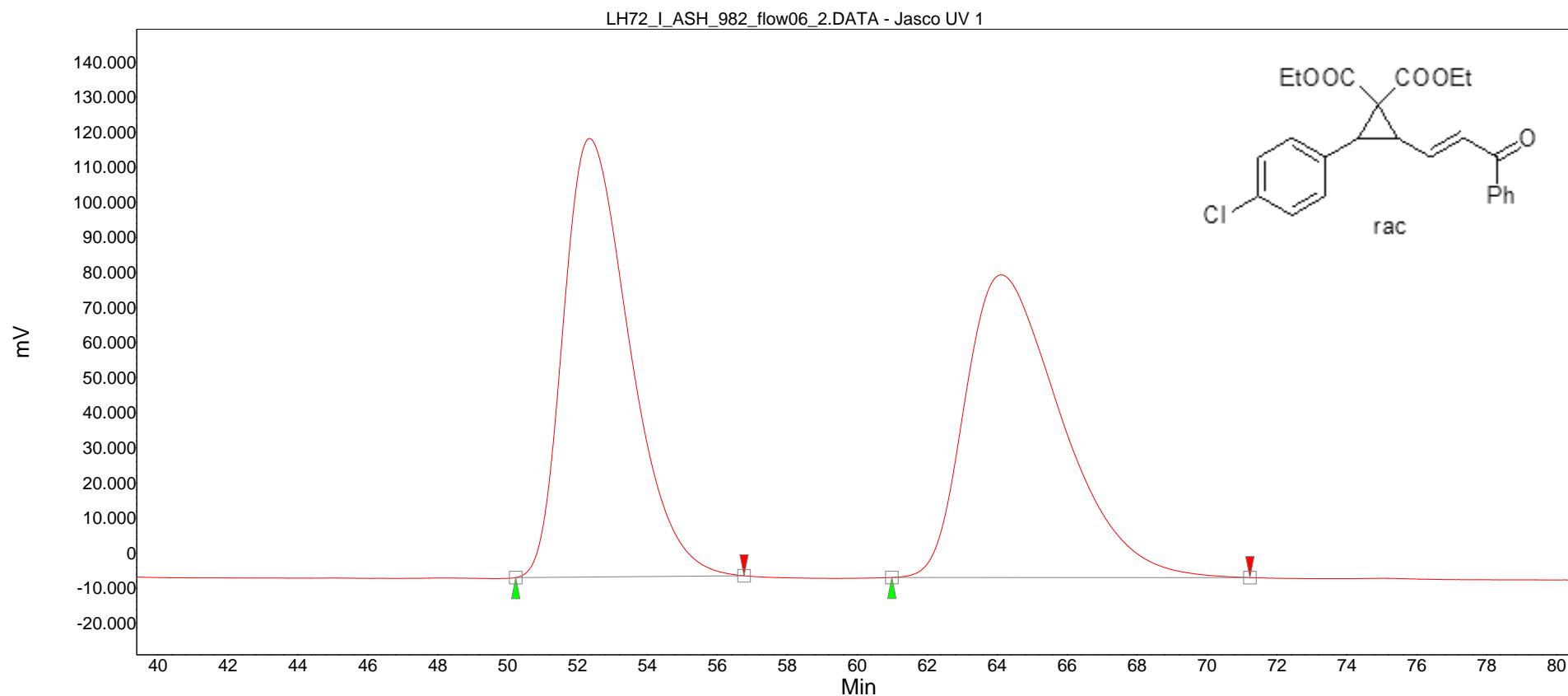
Index	Start [Min]	Time [Min]	End [Min]	Area [%]
1	14,646	15,108	15,853	97,680
2	15,988	16,292	16,778	2,320
Total				100,000





## Chromatogram : LH72\_I\_ASH\_982\_flow06\_2

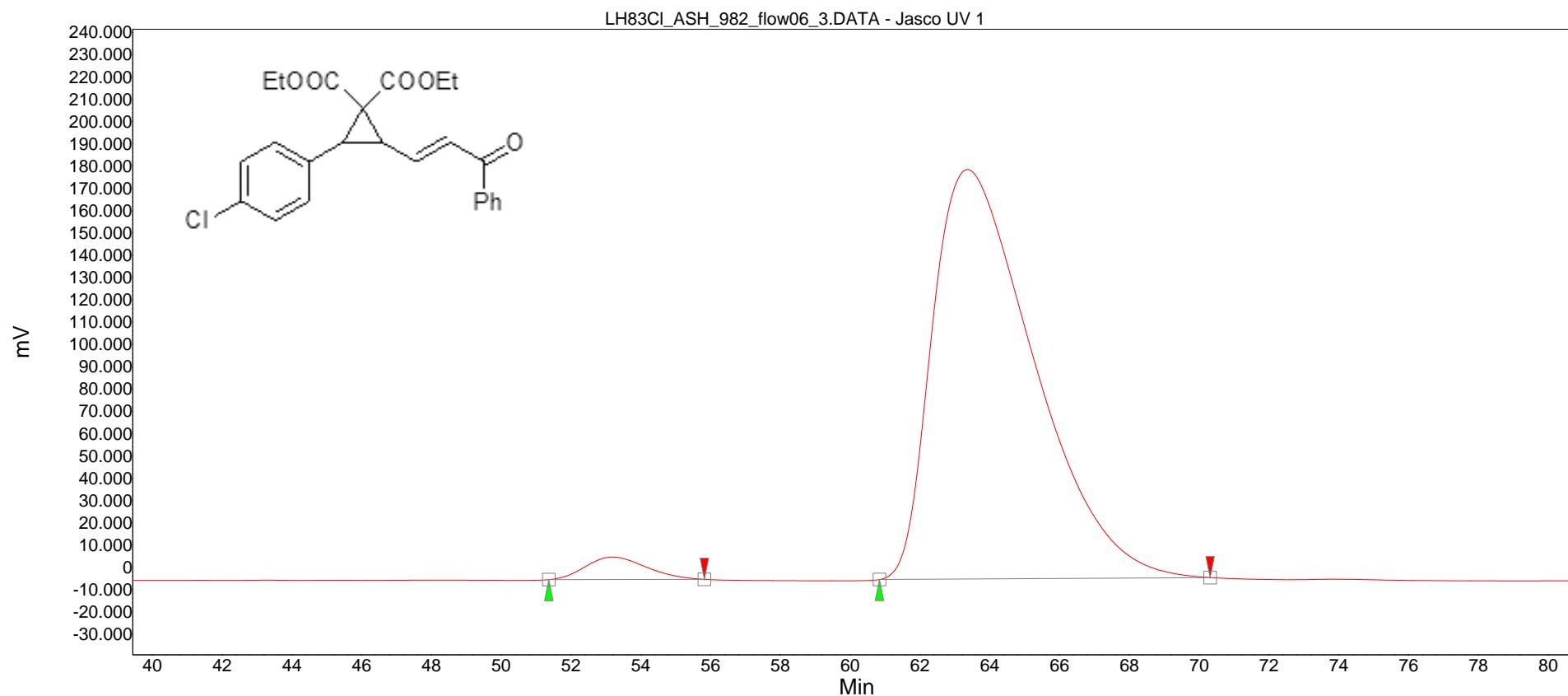
Method: HPLC2\_ASH\_982\_flow06\_acq90  
Data file: LH72\_I\_ASH\_982\_flow06\_2.DATA  
Date: 25.04.2008 19:35:36



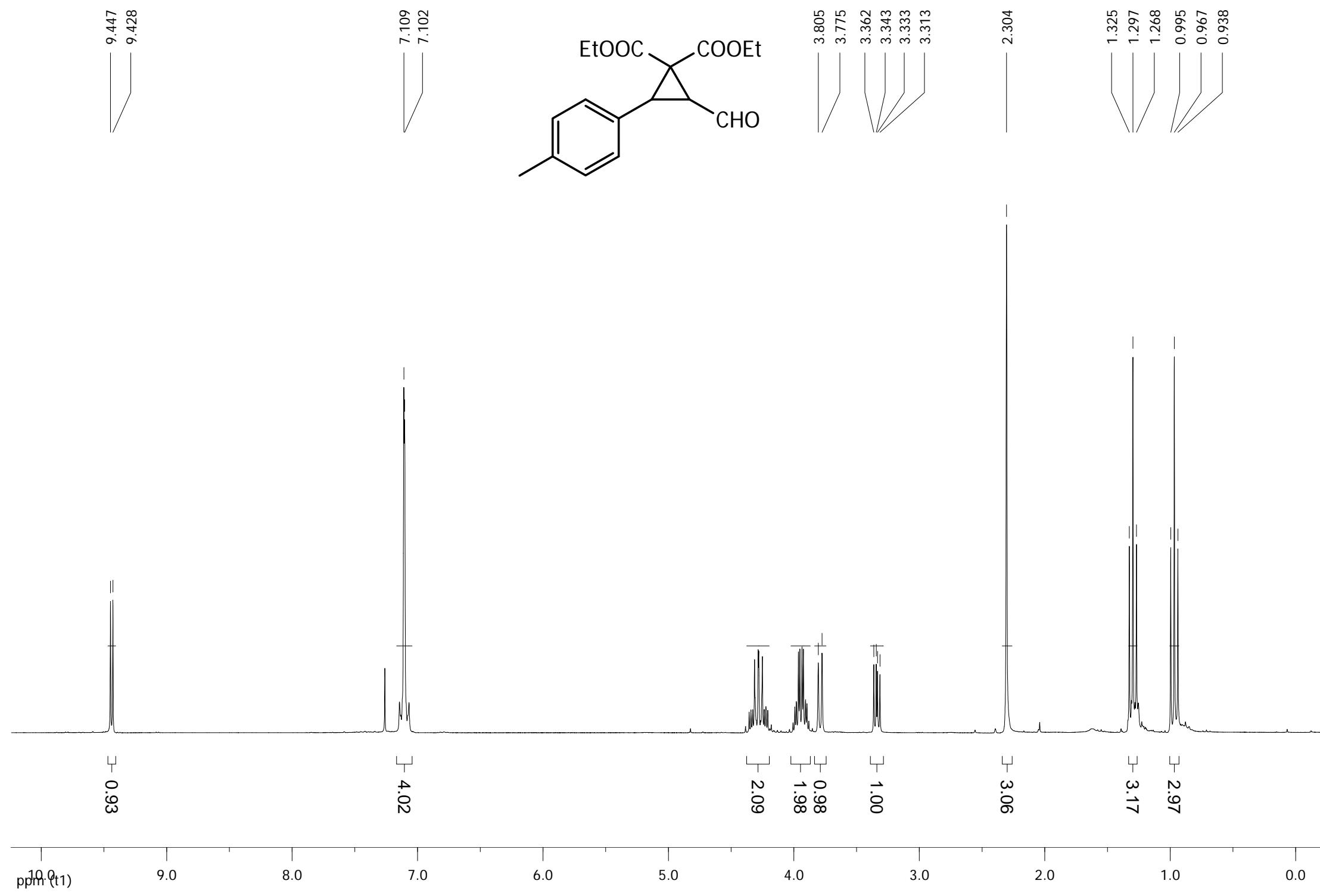
Index	Start Time [Min]	End Time [Min]	Area [%]
1	50,232	52,342	49,914
2	60,985	64,108	50,086
Total			100,000

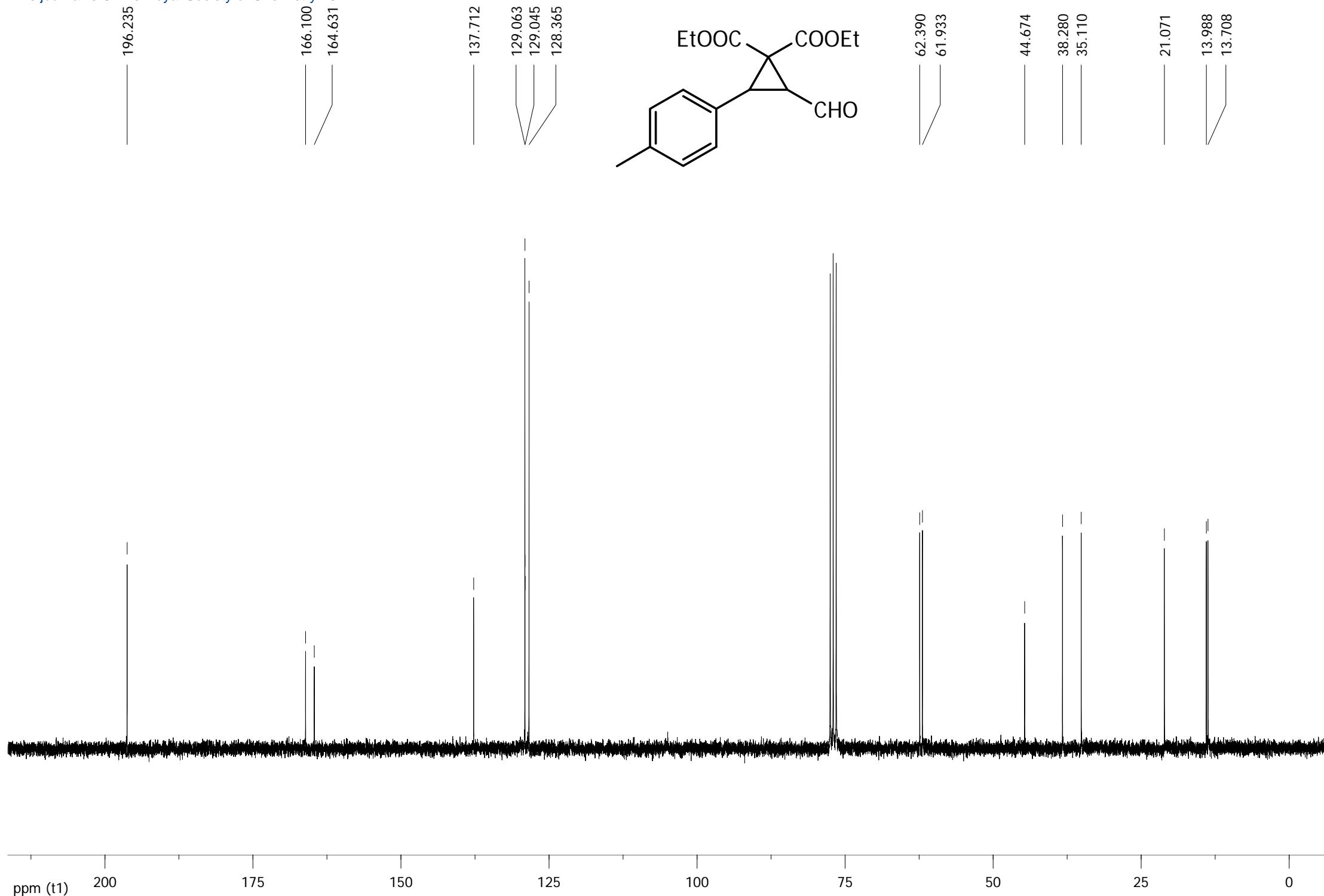
## Chromatogram : LH83Cl\_ASH\_982\_flow06\_3

Method: HPLC2\_ASH\_982\_flow06\_acq90  
Data file: LH83Cl\_ASH\_982\_flow06\_3.DATA  
Date: 21.05.2008 02:34:38



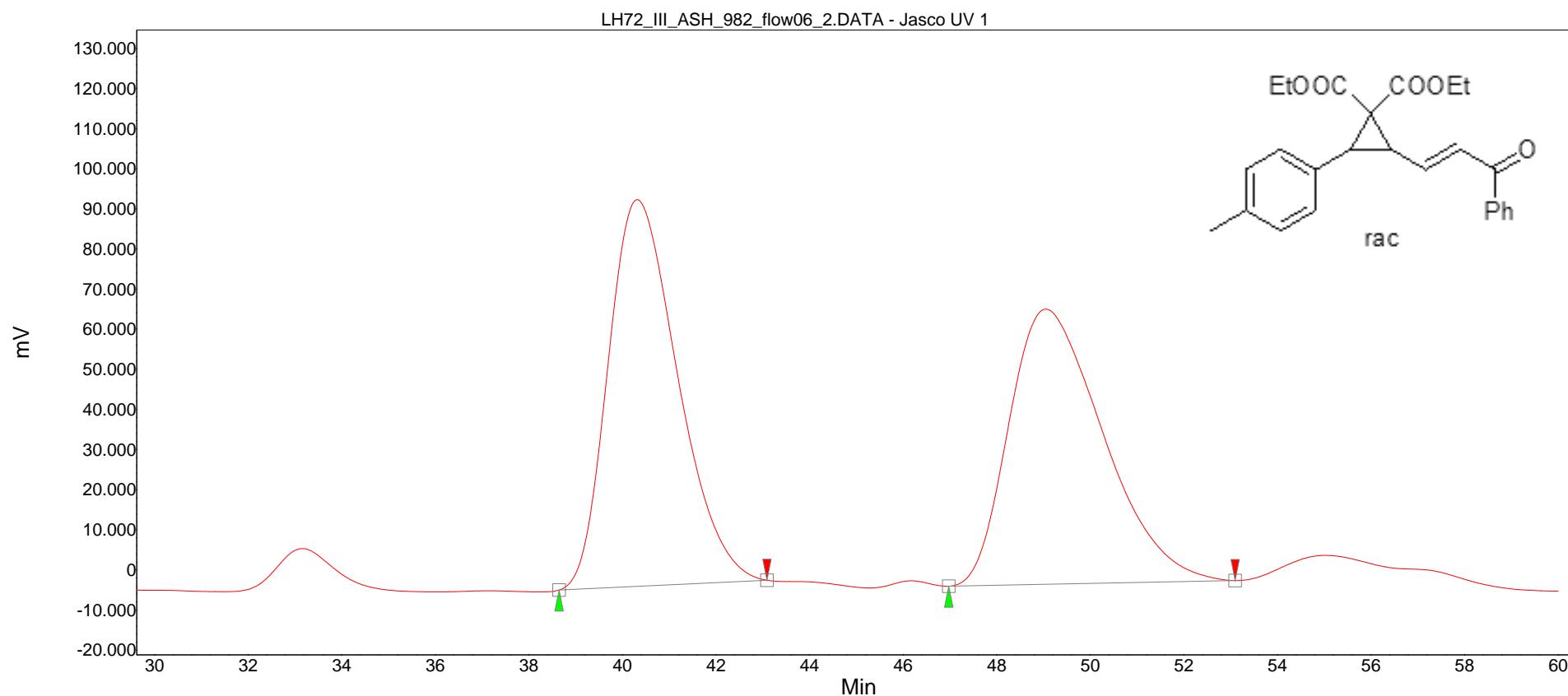
Index	Start [Min]	Time [Min]	End [Min]	Area [%]
1	51,361	53,183	55,820	3,159
2	60,836	63,358	70,312	96,841
Total				100,000





## Chromatogram : LH72\_III\_ASH\_982\_flow06\_2

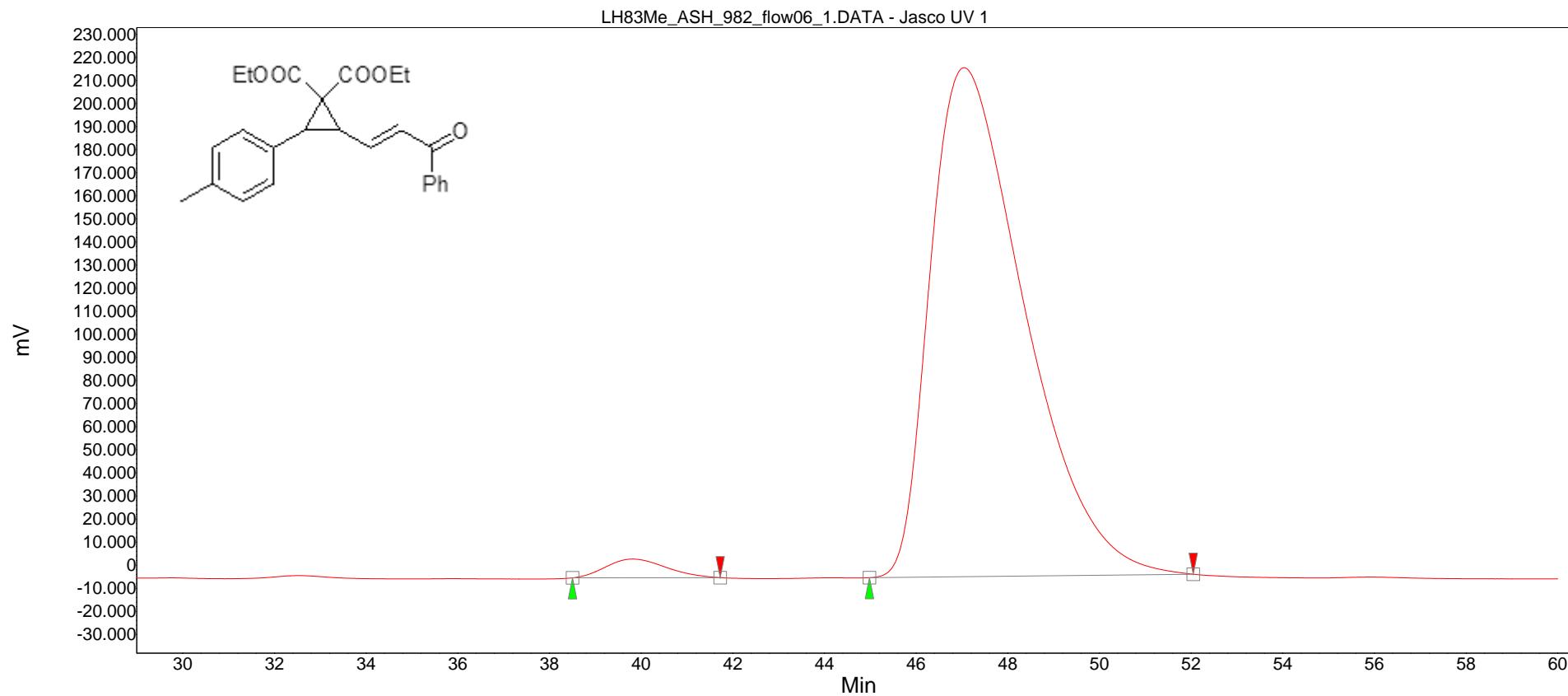
Method: HPLC2\_ASH\_982\_flow06\_acq60  
Data file: LH72\_III\_ASH\_982\_flow06\_2.DATA  
Date: 30.04.2008 23:36:36



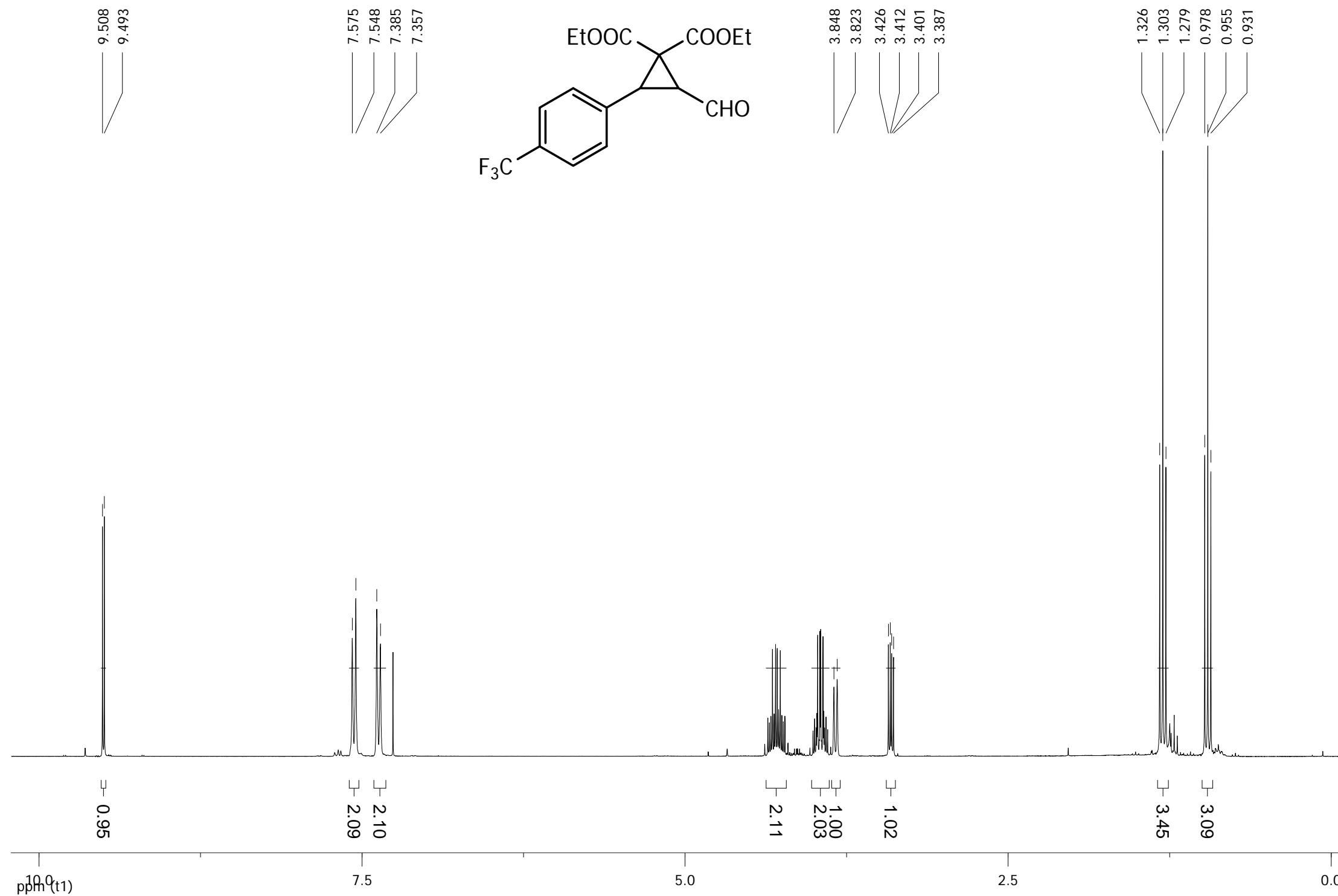
Index	Start [Min]	Time [Min]	End [Min]	Area [%]
2	38,646	40,317	43,089	50,956
1	46,973	49,042	53,094	49,044
Total				100,000

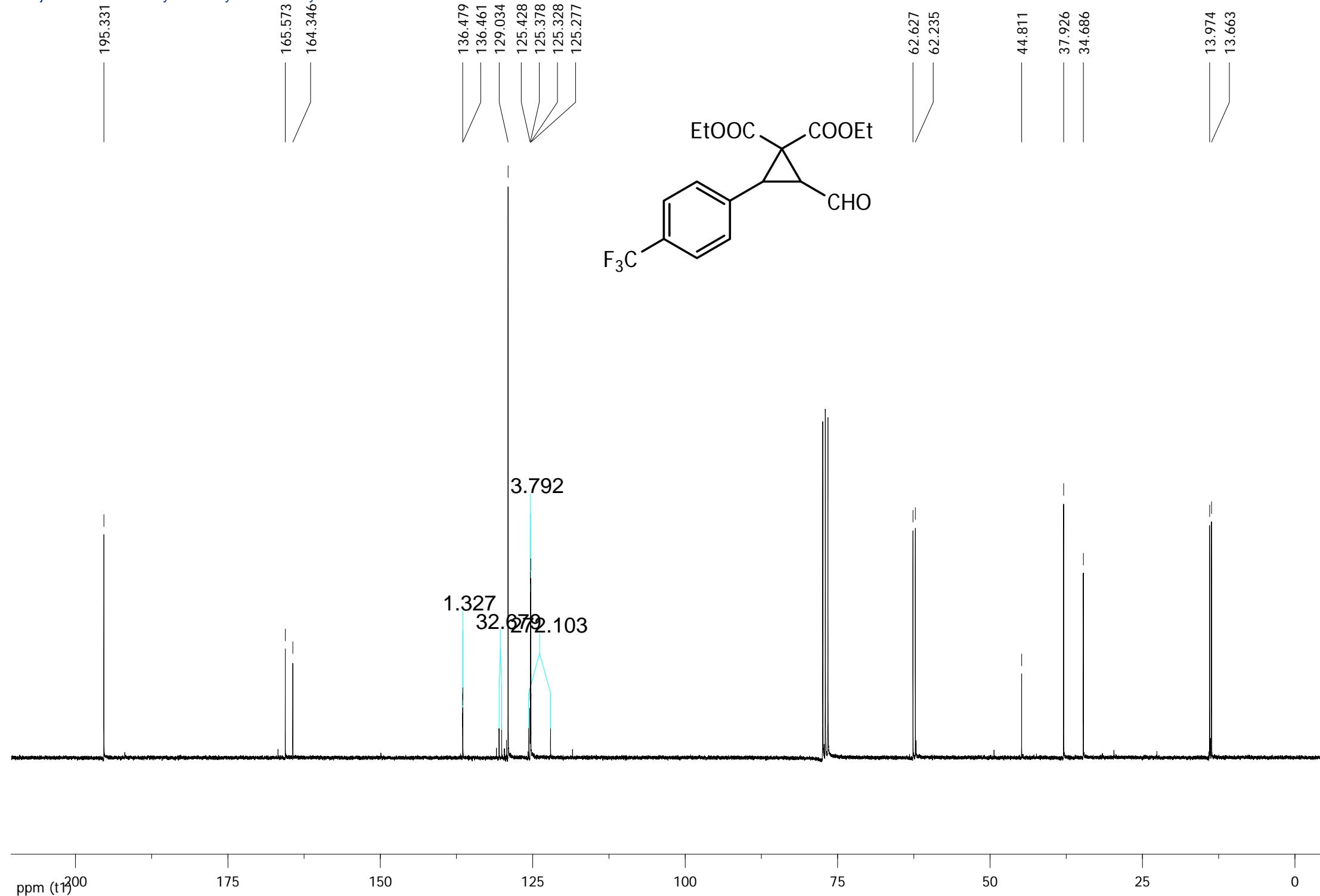
## Chromatogram : LH83Me\_ASH\_982\_flow06\_1

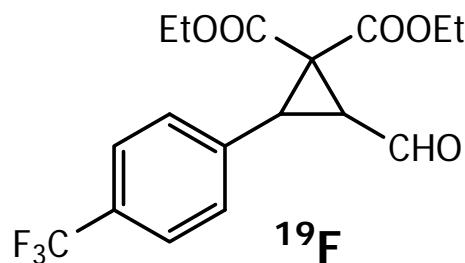
Method: HPLC2\_ASH\_982\_flow06\_acq60  
Data file: LH83Me\_ASH\_982\_flow06\_1.DATA  
Date: 19.05.2008 22:36:48



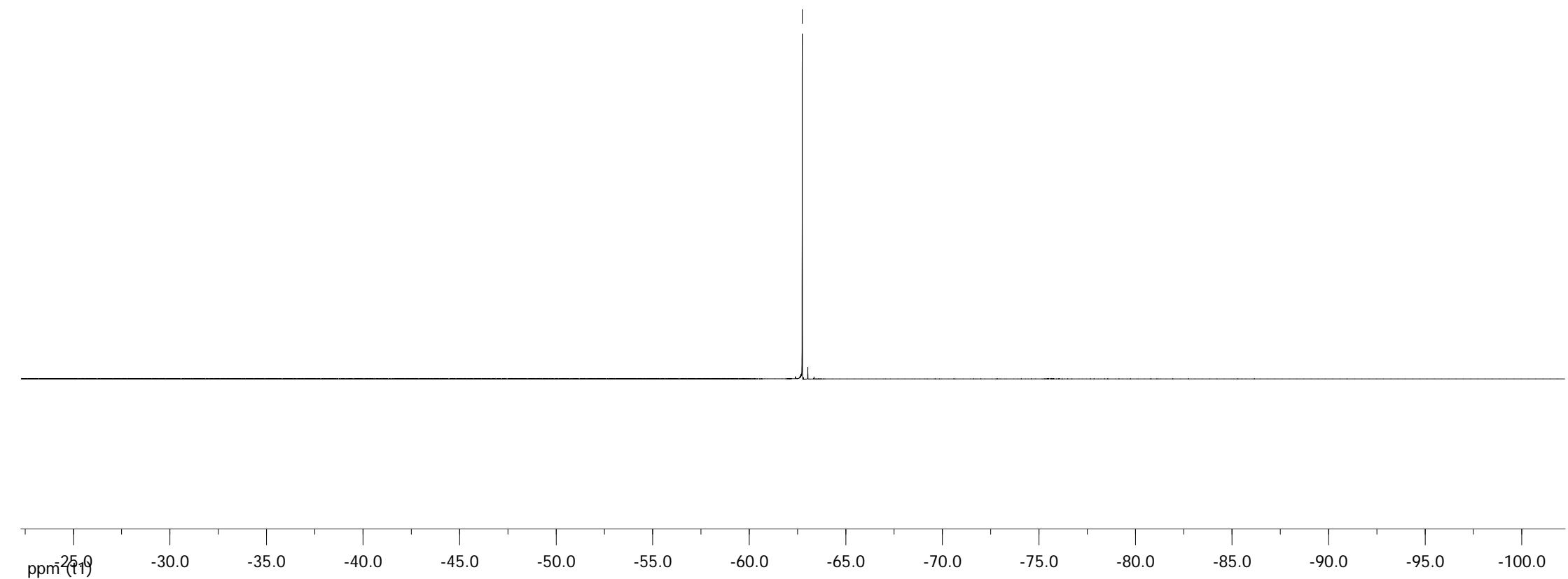
Index	Start Time [Min]	End Time [Min]	Area [%]
1	38,501	39,808	41,725
2	44,981	47,042	52,046
Total			100,000





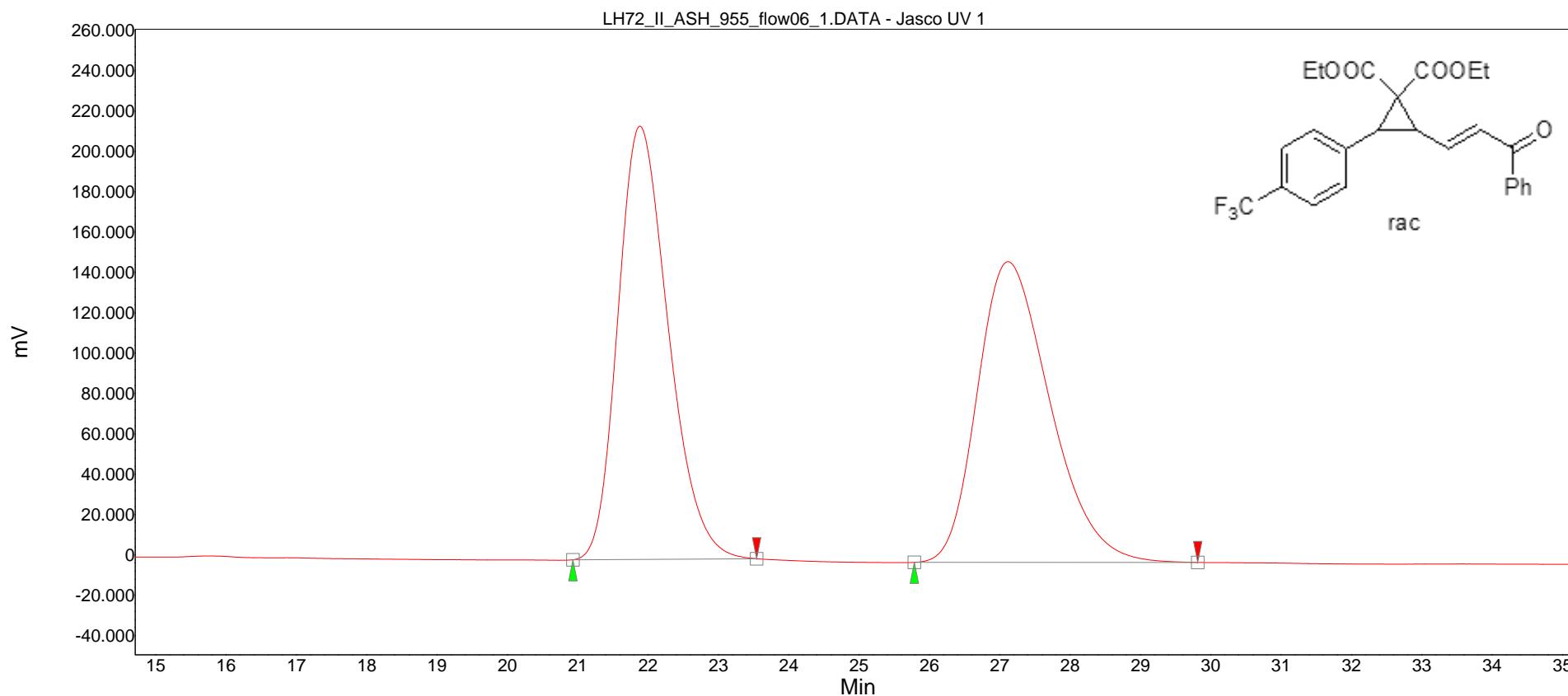


-62.746



## Chromatogram : LH72\_II\_ASH\_955\_flow06\_1

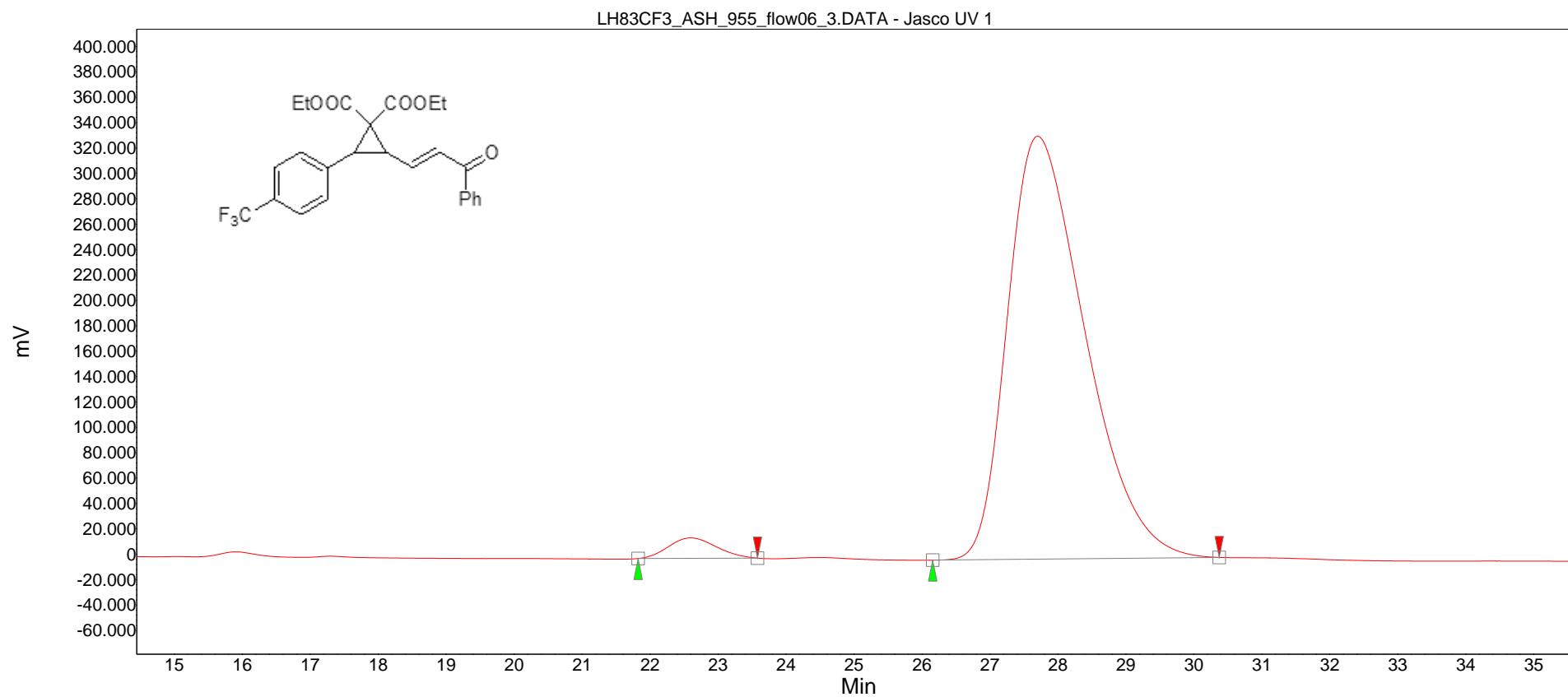
Method: HPLC2\_ASH\_955\_flow06\_acq60  
Data file: LH72\_II\_ASH\_955\_flow06\_1.DATA  
Date: 25.04.2008 16:57:43



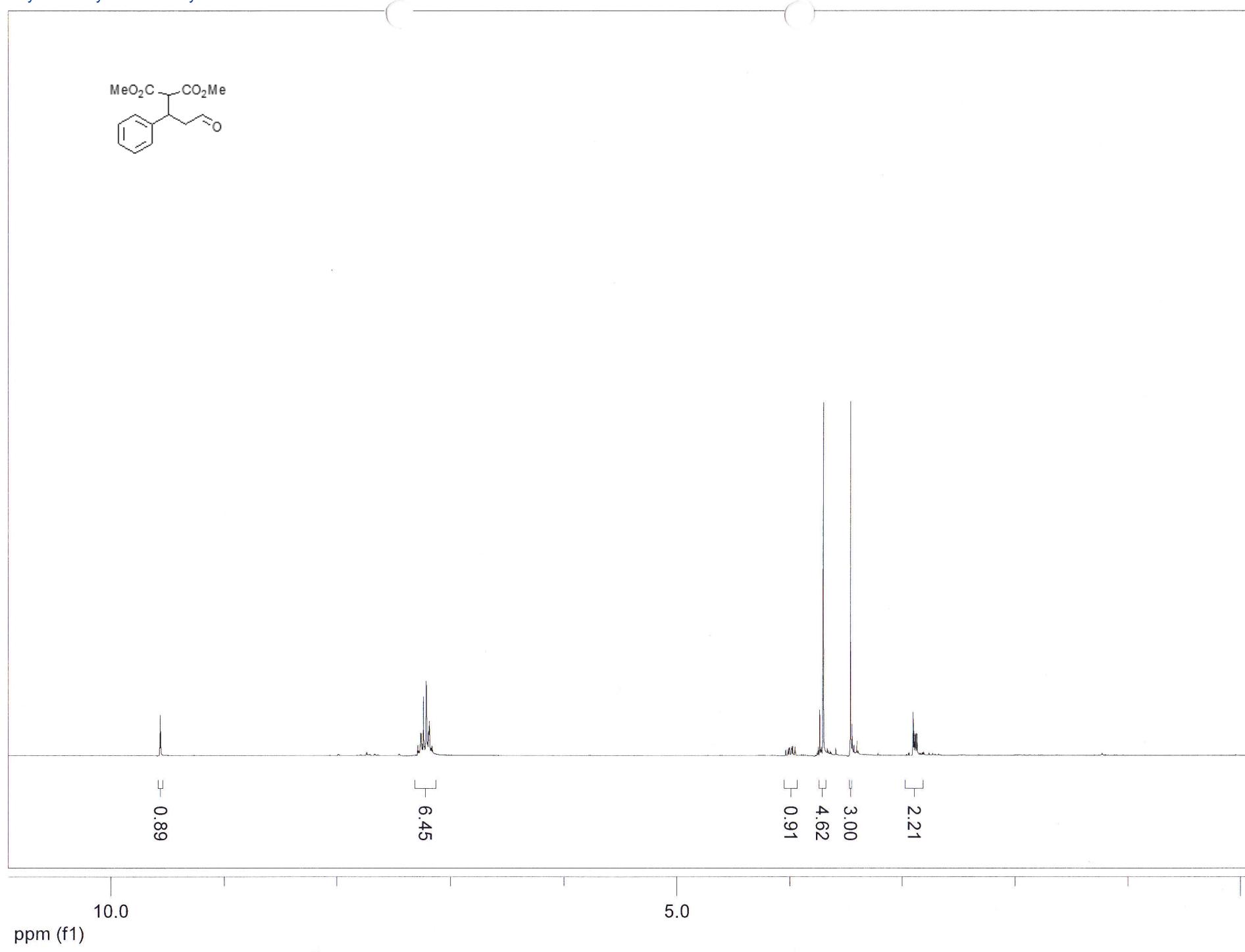
Index	Start Time [Min]	End Time [Min]	Area [%]
2	20,931	21,883	50,013
1	25,785	27,117	49,987
Total			100,000

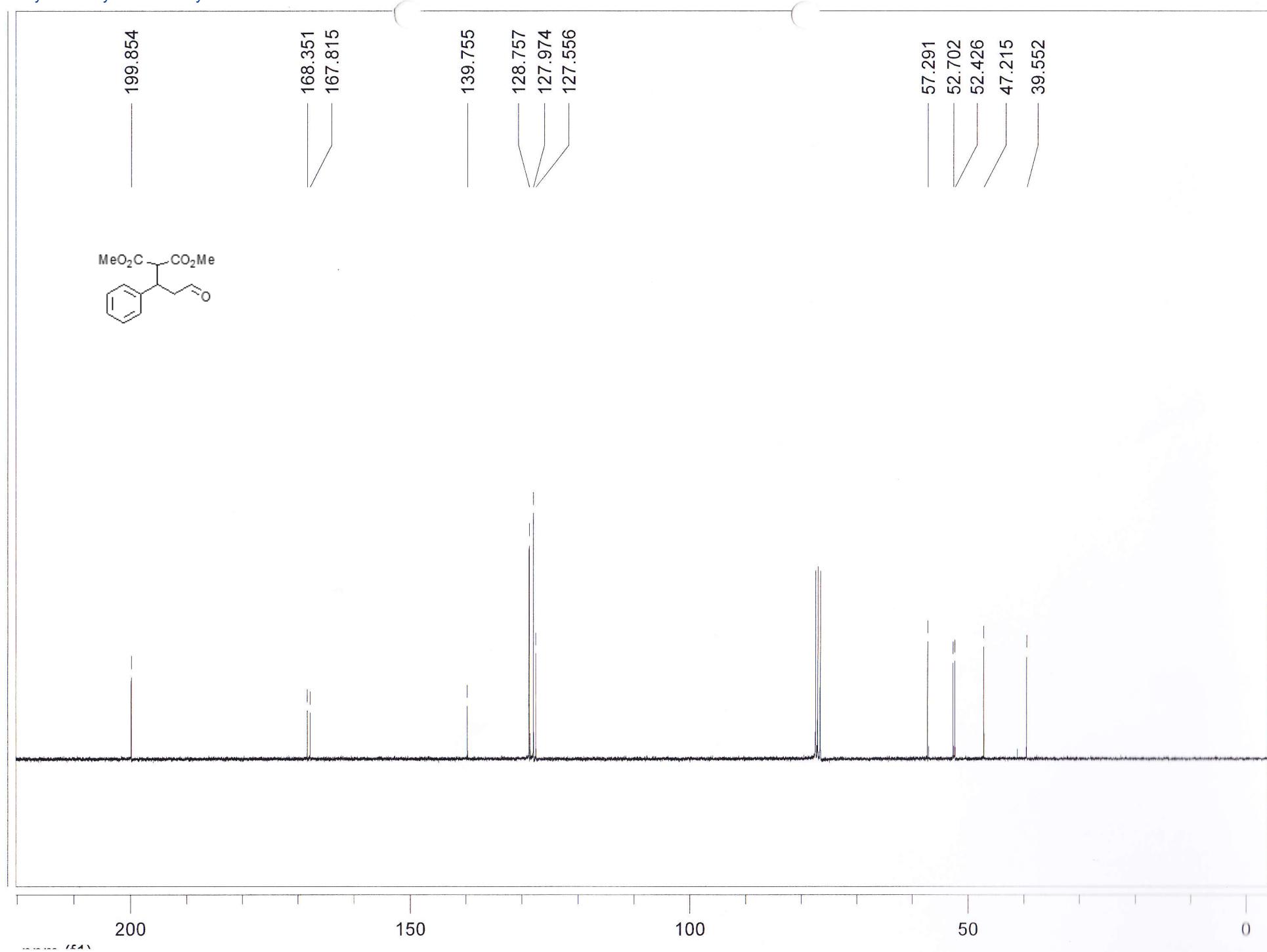
## Chromatogram : LH83CF3\_ASH\_955\_flow06\_3

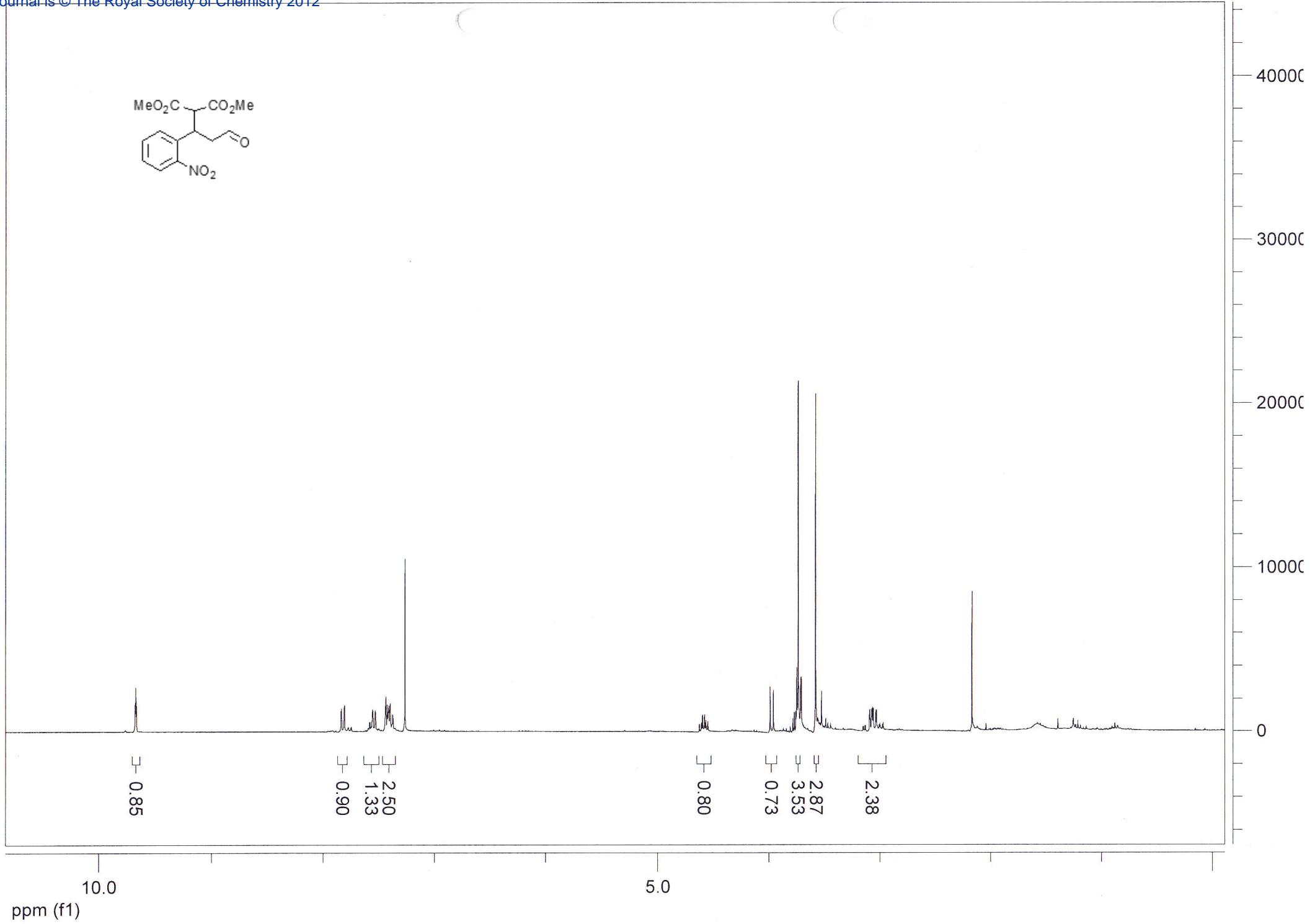
Method: HPLC2\_ASH\_955\_flow06\_acq60  
Data file: LH83CF3\_ASH\_955\_flow06\_3.DATA  
Date: 21.05.2008 00:59:25

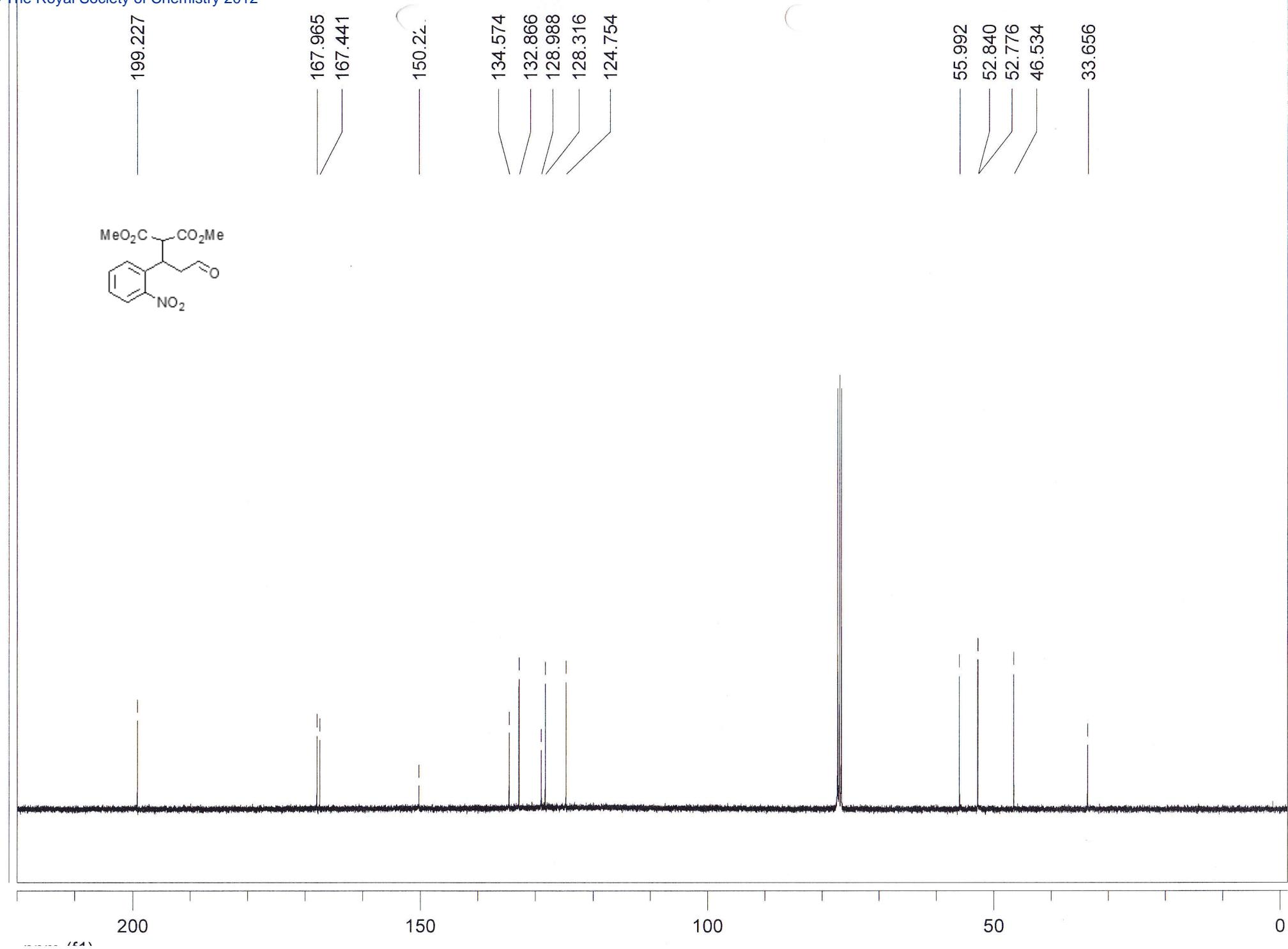


Index	Start Time [Min]	End Time [Min]	Area [%]
2	21,823	22,592	23,579 2,883
1	26,157	27,700	30,372 97,117
Total			100,000





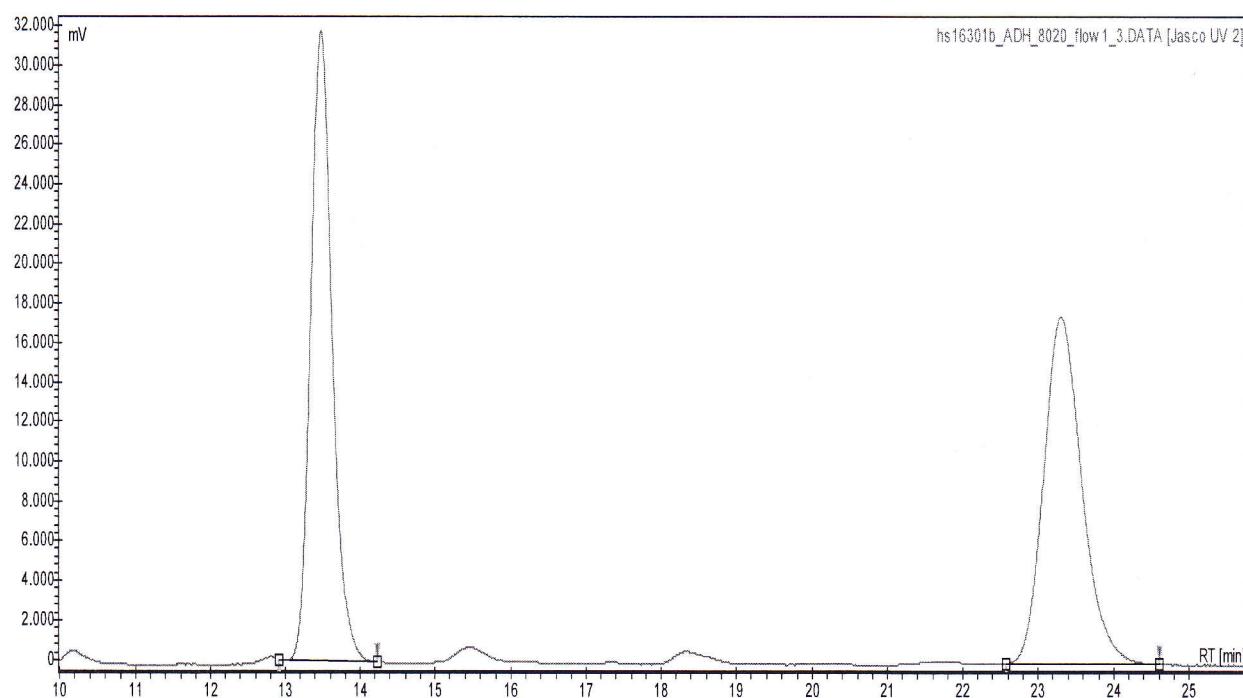




# Chromatogram : hs16301b\_ADH\_8020\_flow1\_3\_channel2

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_8020\_flow1\_acq30  
User : USER1

Acquired : 01.05.2008 12:23:29  
Processed : 02.05.2008 10:35:27  
Printed : 02.05.2008 10:35:49



## Peak results :

hs16301b_ADH_8020_flow1_3.DATA [Jasco UV 2]				
Index	Start Time	End Time	Area	%
	[Min]	[Min]	[Min]	[%]
1	12,924	13,475	14,225	50,204
2	22,562	23,308	24,607	49,796
Total				100,000

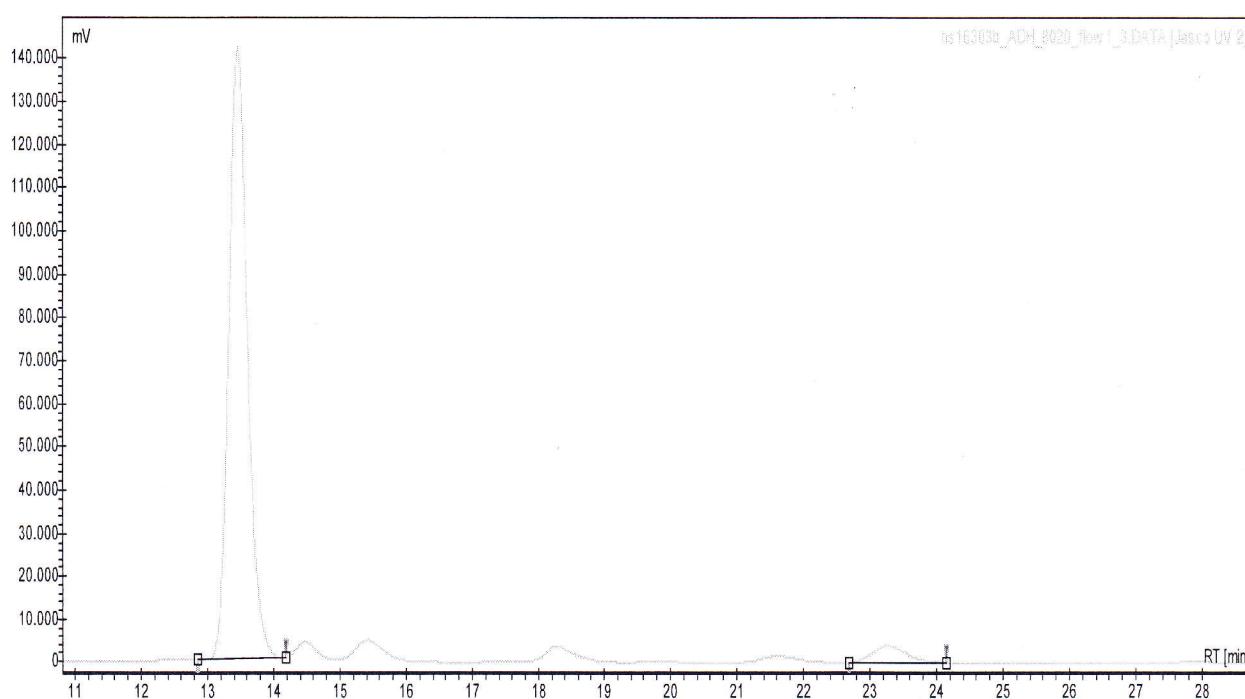
## Group results :

hs16301b_ADH_8020_flow1_3.DATA [Jasco UV 2]					
Index	Name	Area	Quantity	RF	Resp.
		[mV.Min]	[% Area]		
Total		0,0	0,00		0,00

# Chromatogram : hs16303b\_ADH\_8020\_flow1\_3\_channel2

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_8020\_flow1\_acq30  
User : USER1

Acquired : 01.05.2008 12:56:08  
Processed : 02.05.2008 10:37:07  
Printed : 02.05.2008 10:38:03

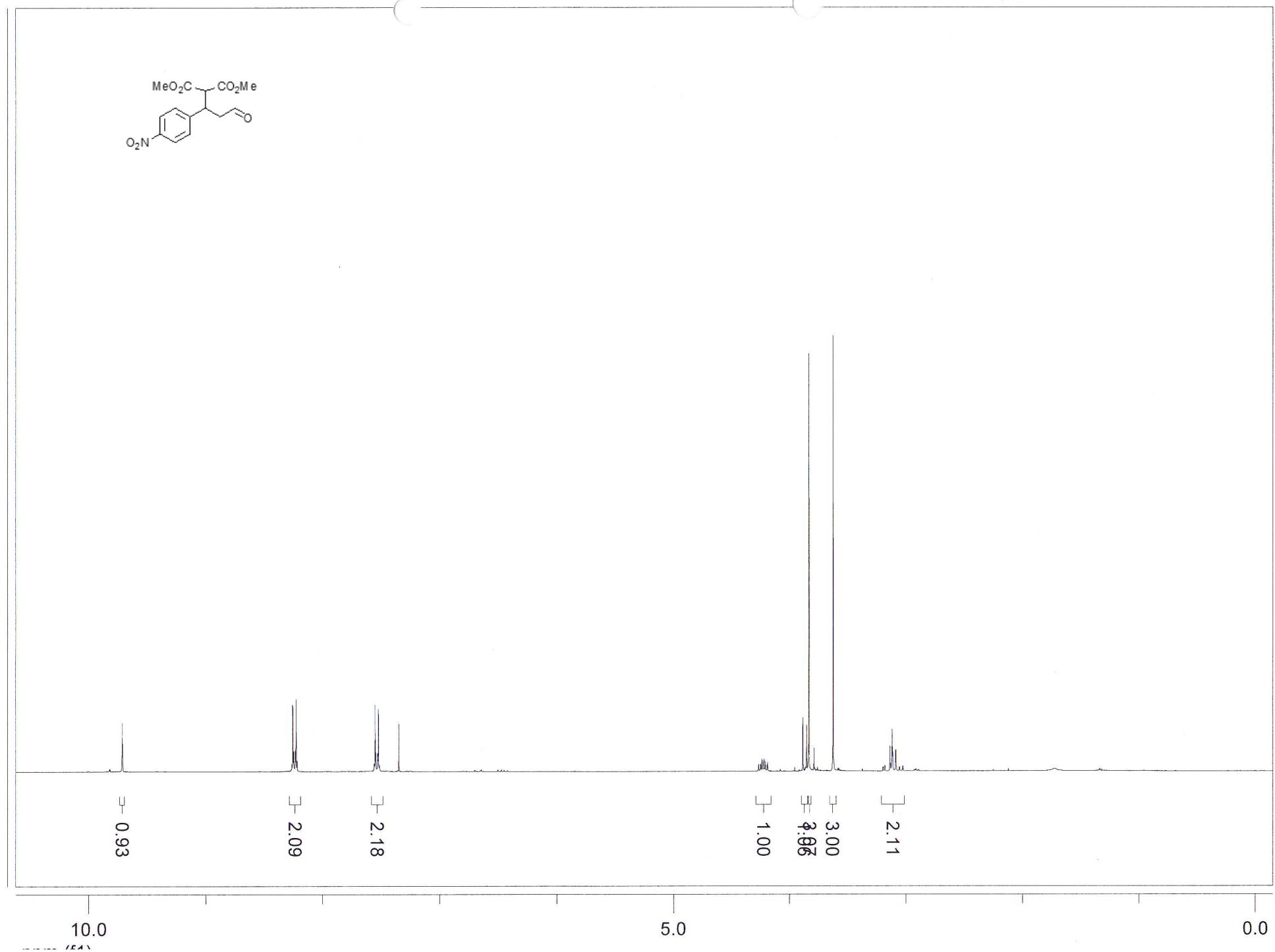


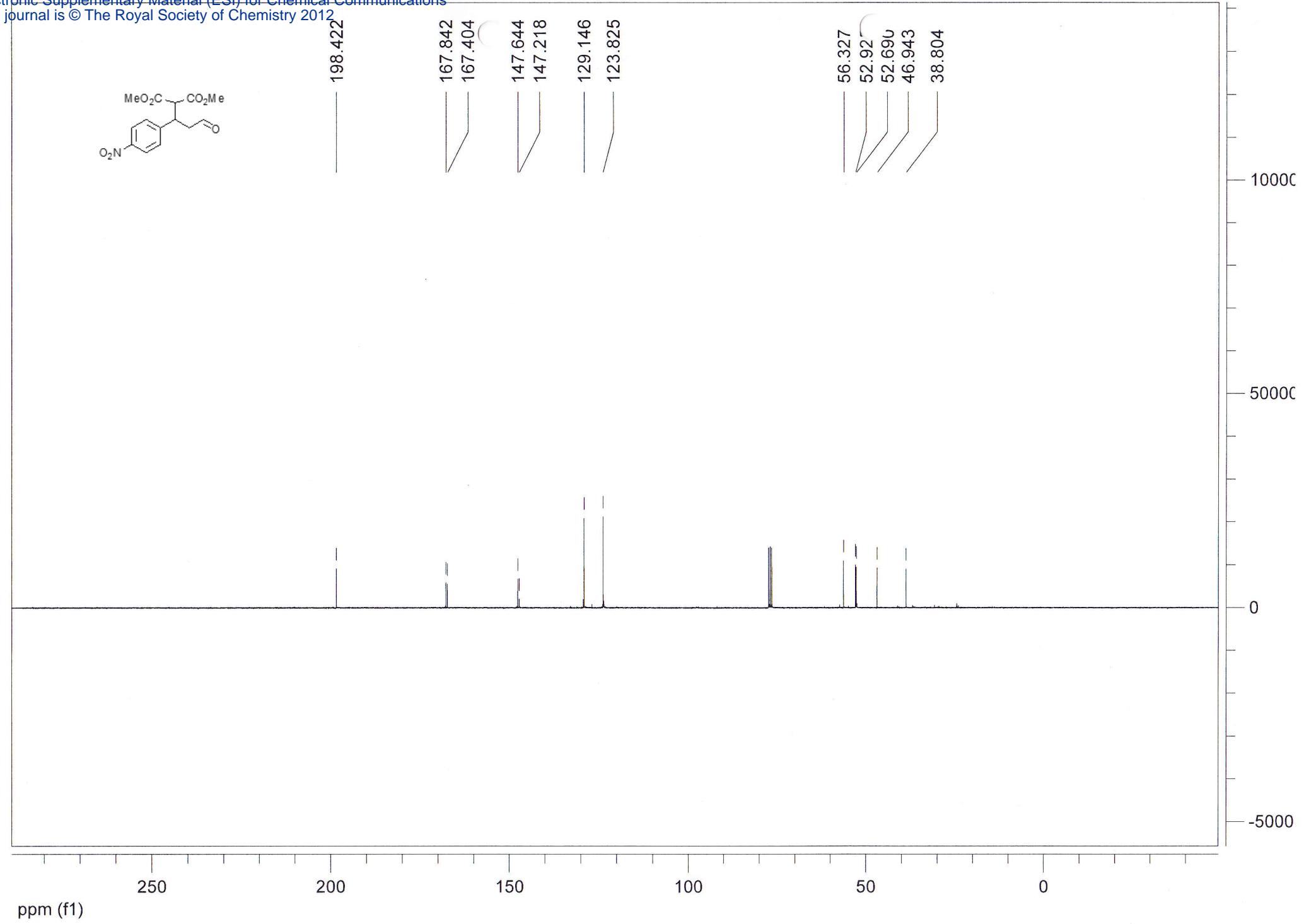
## Peak results :

hs16303b_ADH_8020_flow1_3.DATA [Jasco UV 2]				
Index	Start Time	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	12,862	13,467	14,194	95,443
2	22,686	23,267	24,143	4,557
Total				100,000

## Group results :

hs16303b_ADH_8020_flow1_3.DATA [Jasco UV 2]					
Index	Name	Area	Quantity	RF	Resp.
		[mV.Min]	[% Area]		
Total		0,0	0,00		0,00

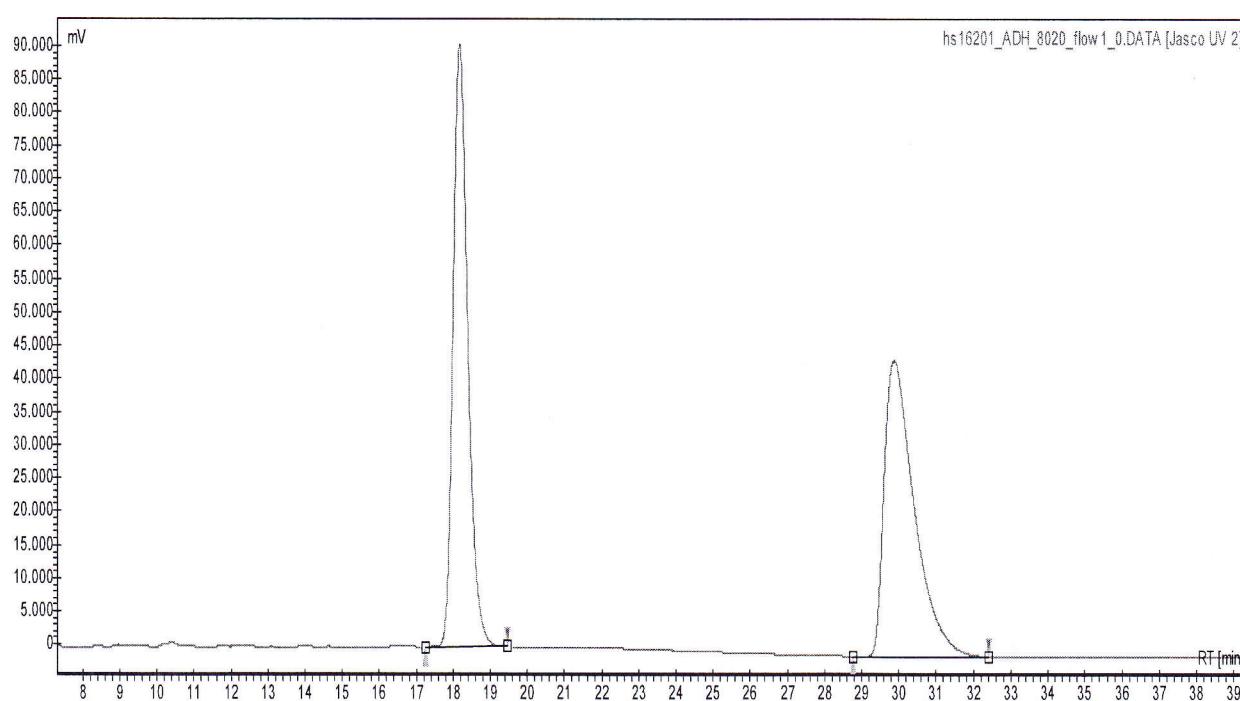




# Chromatogram : hs16201\_ADH\_8020\_flow1\_0\_channel2

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_8020\_flow1\_acq60  
User : USER1

Acquired : 10.04.2008 15:43:37  
Processed : 02.05.2008 10:31:38  
Printed : 02.05.2008 10:34:21



## Peak results :

hs16201\_ADH\_8020\_flow1\_0.DATA [Jasco UV 2]

Index	Start Time	End Time	Area %
	[Min]	[Min]	[%]
1	17,231	18,175	19,463
2	28,760	29,875	32,417
Total			100,000

## Group results :

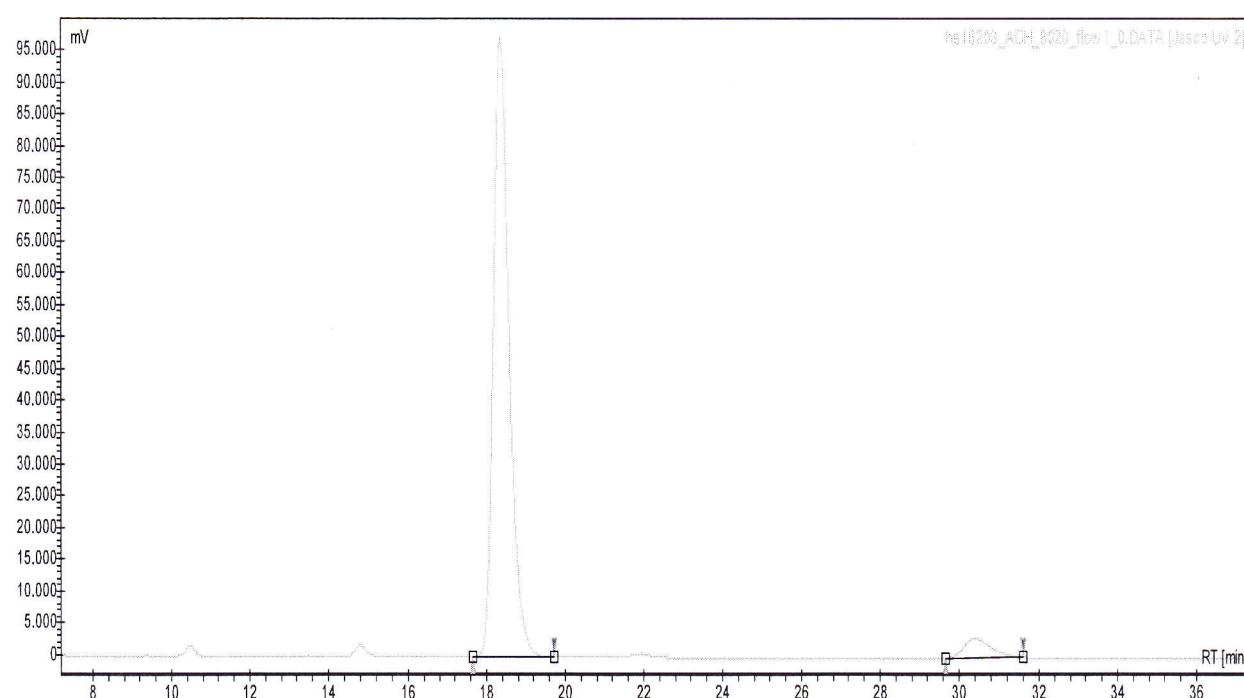
hs16201\_ADH\_8020\_flow1\_0.DATA [Jasco UV 2]

Index	Name	Area	Quantity	RF	Resp.
		[mV.Min]	[% Area]		
Total		0,0	0,00		0,00

# Chromatogram : hs16203\_ADH\_8020\_flow1\_0\_channel2

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_8020\_flow1\_acq60  
User : USER1

Acquired : 21.04.2008 23:58:28  
Processed : 02.05.2008 10:32:22  
Printed : 02.05.2008 10:33:16



## Peak results :

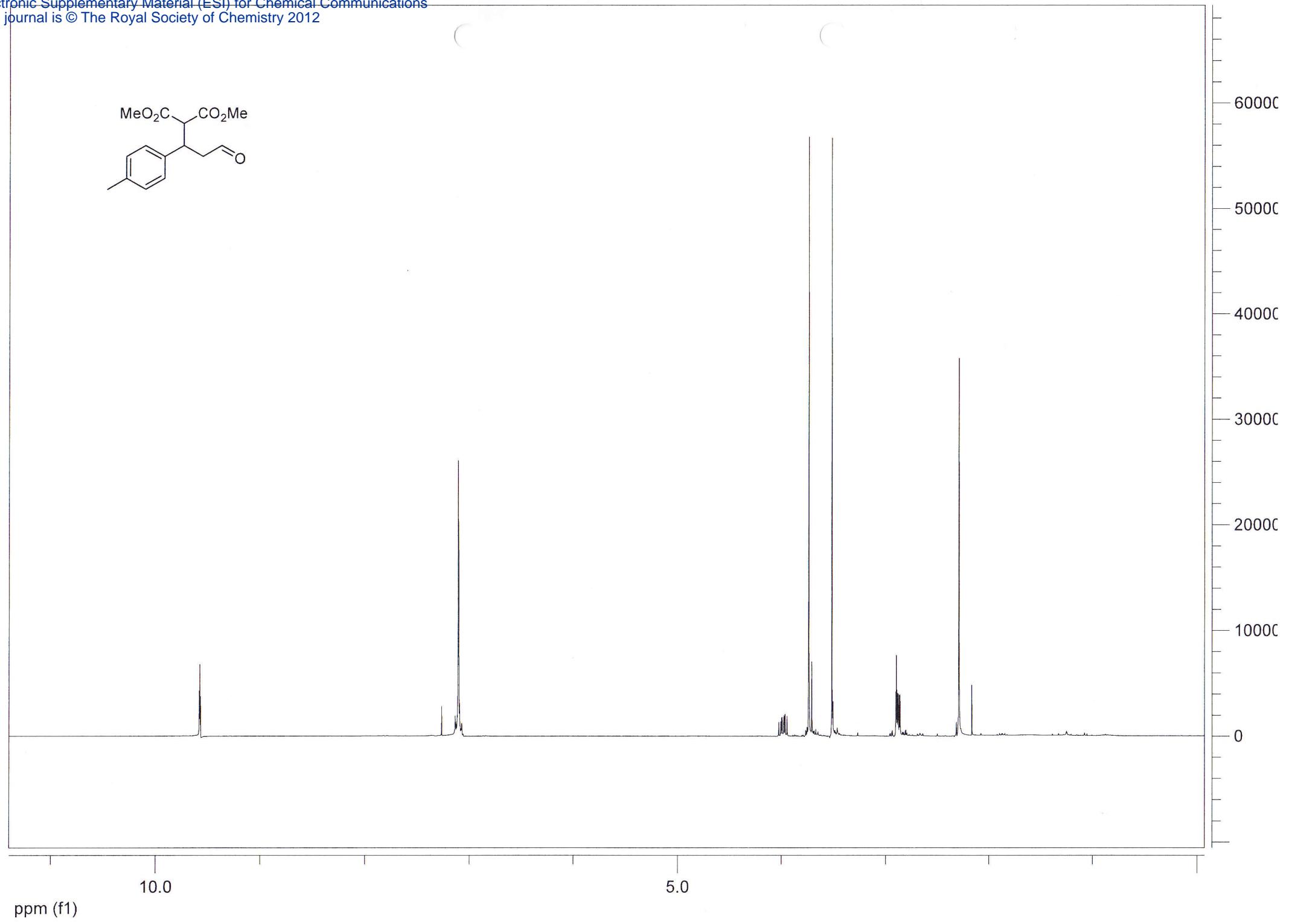
hs16203\_ADH\_8020\_flow1\_0.DATA [Jasco UV 2]

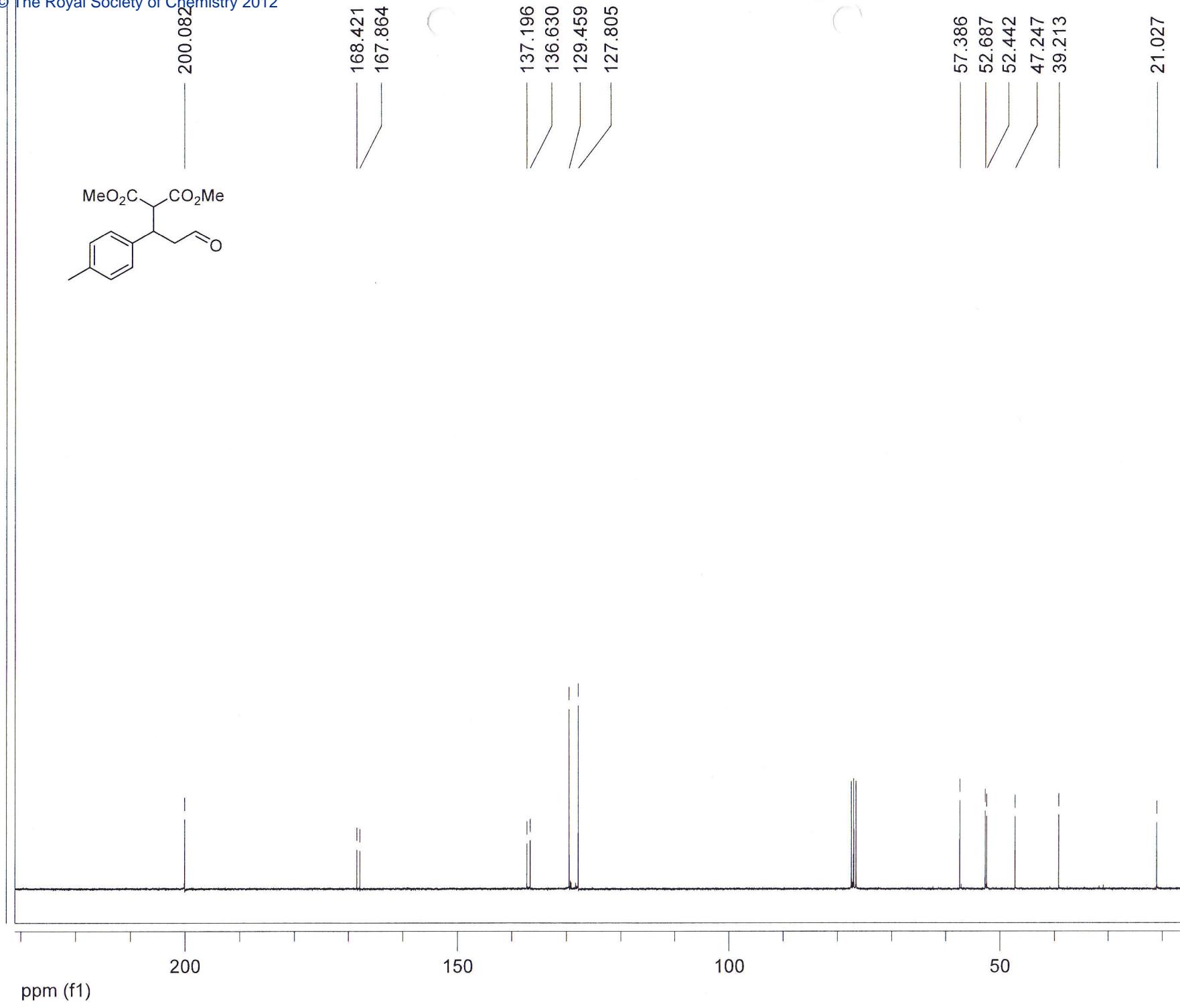
Index	Start [Min]	Time [Min]	End [Min]	Area %
1	17,665	18,367	19,711	94,972
2	29,628	30,400	31,612	5,028
Total				100,000

## Group results :

hs16203\_ADH\_8020\_flow1\_0.DATA [Jasco UV 2]

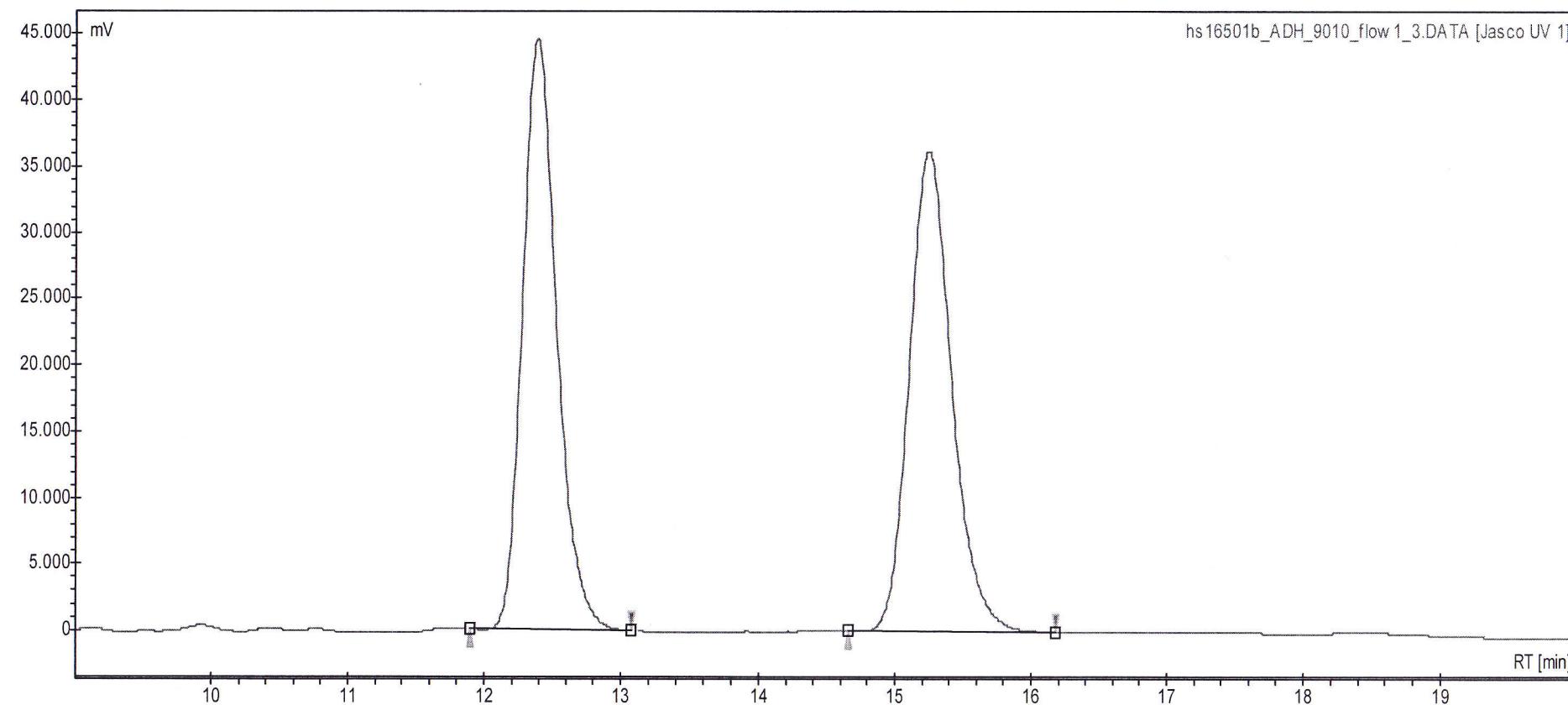
Index	Name	Area [mV.Min]	Quantity [% Area]	RF	Resp.
Total		0,0	0,00		0,00





## Chromatogram : hs16501b\_ADH\_9010\_flow1\_3

Method:HPLC2\_ADH\_9010\_flow1\_acq30  
Data file: hs16501b\_ADH\_9010\_flow1\_3.DATA  
Date: 01.05.2008 14:01:25



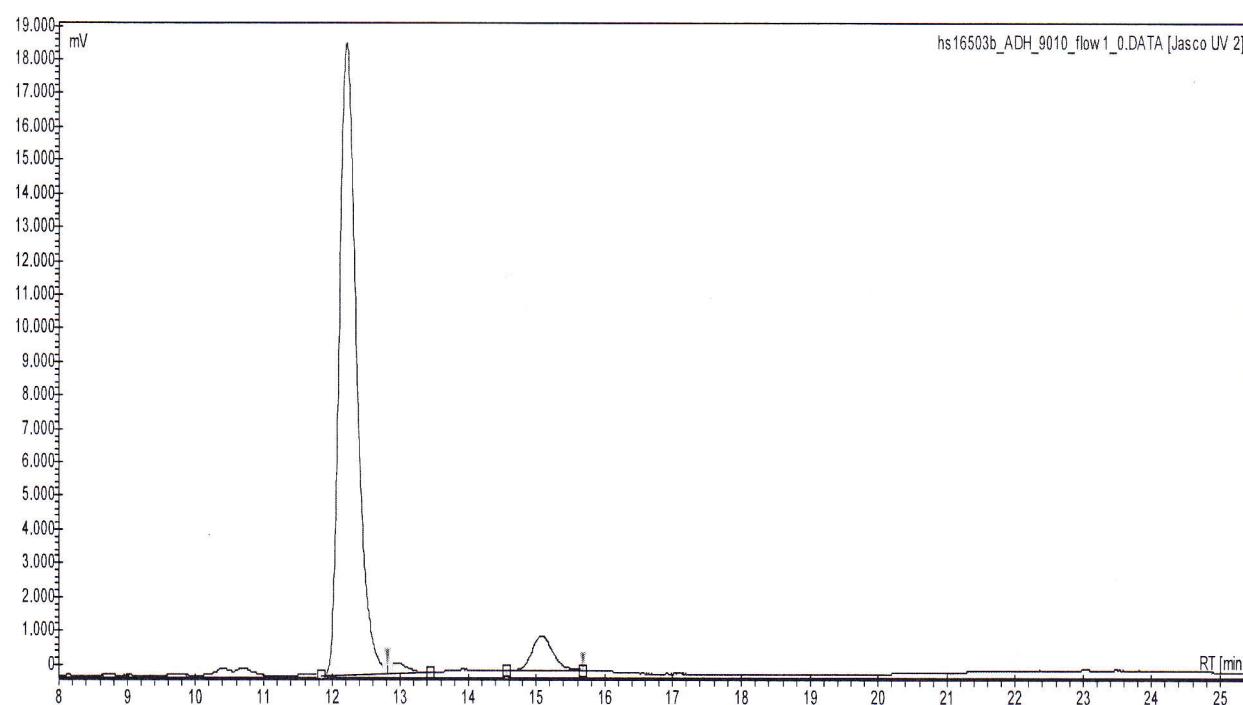
hs16501b\_ADH\_9010\_flow1\_3.DATA [Jasco UV 1]

Index	Start	Time	End	Area %
	[Min]	[Min]	[Min]	[%]
1	11,901	12,383	13,079	49,864
2	14,659	15,250	16,178	50,136
Total				100,000

# Chromatogram : hs16503b\_ADH\_9010\_flow1\_0\_channel2

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_9010\_flow1\_acq60  
User : USER1

Acquired : 22.04.2008 23:34:30  
Processed : 02.05.2008 10:45:18  
Printed : 02.05.2008 10:49:04



## Peak results :

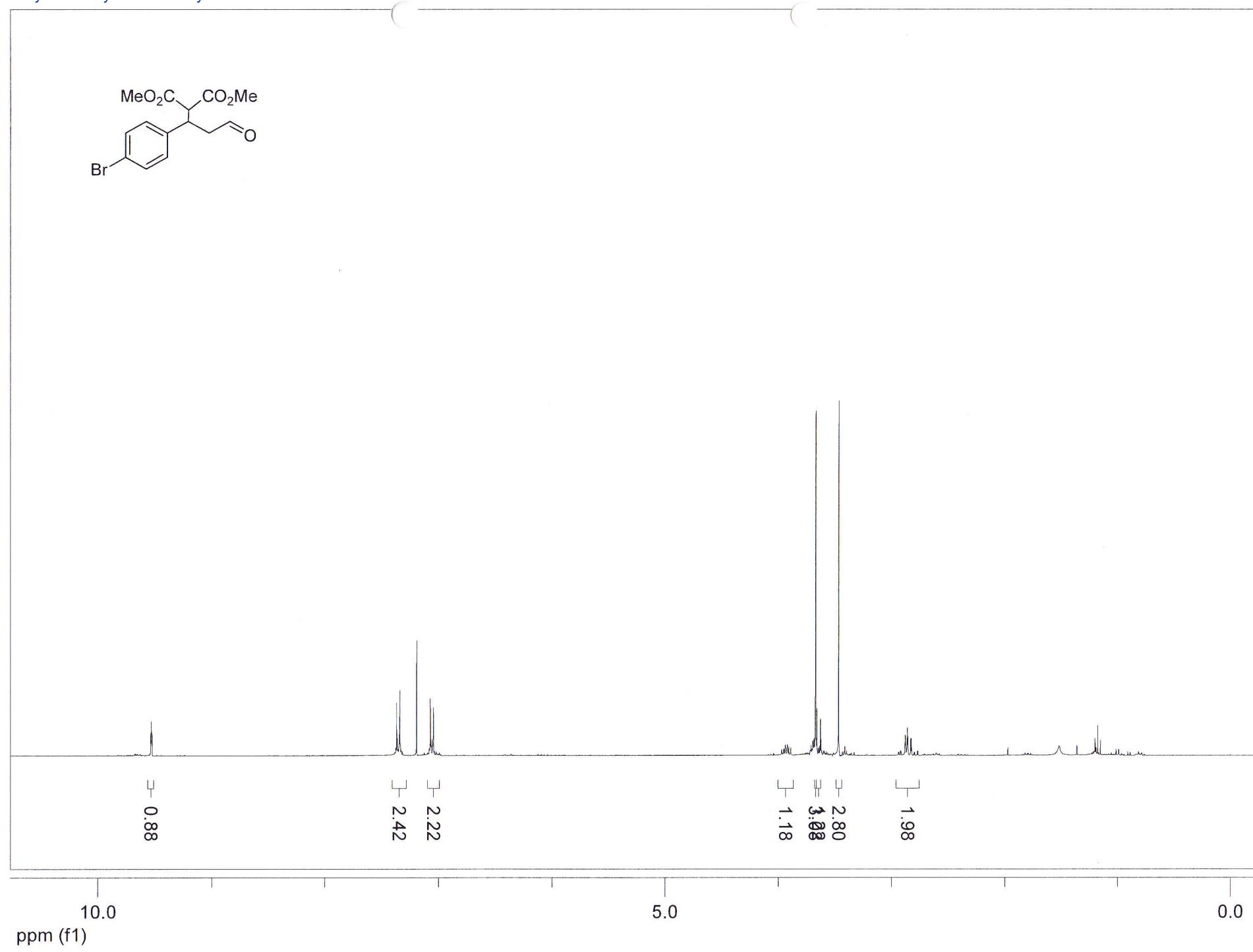
hs16503b\_ADH\_9010\_flow1\_0.DATA [Jasco UV 2]

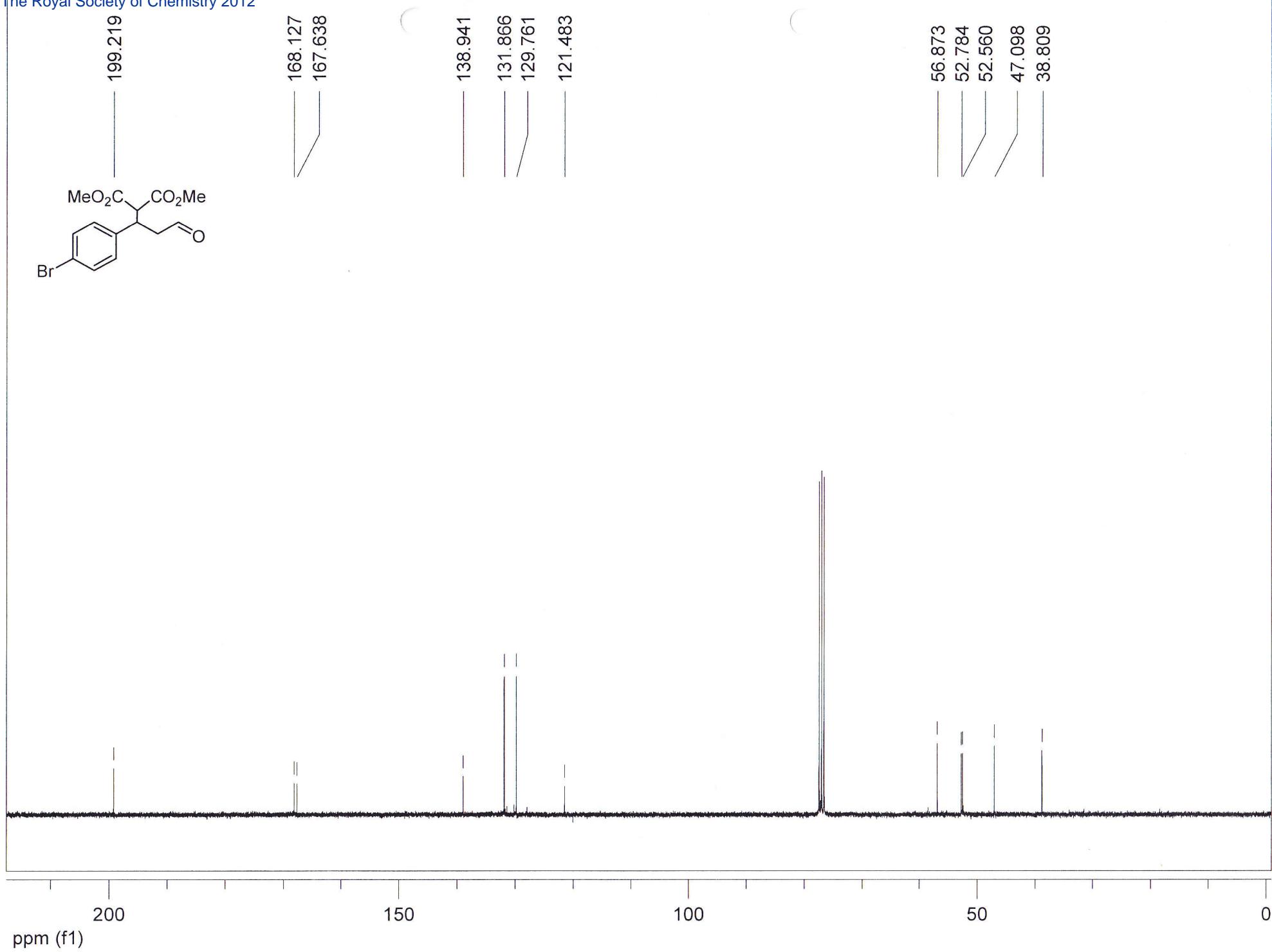
Index	Start [Min]	Time [Min]	End [Min]	Area %
1	11,848	12,217	12,816	93,717
2	14,571	15,075	15,686	6,283
Total				100,000

## Group results :

hs16503b\_ADH\_9010\_flow1\_0.DATA [Jasco UV 2]

Index	Name	Area [mV.Min]	Quantity [% Area]	RF	Resp.
Total		0,0	0,00		0,00

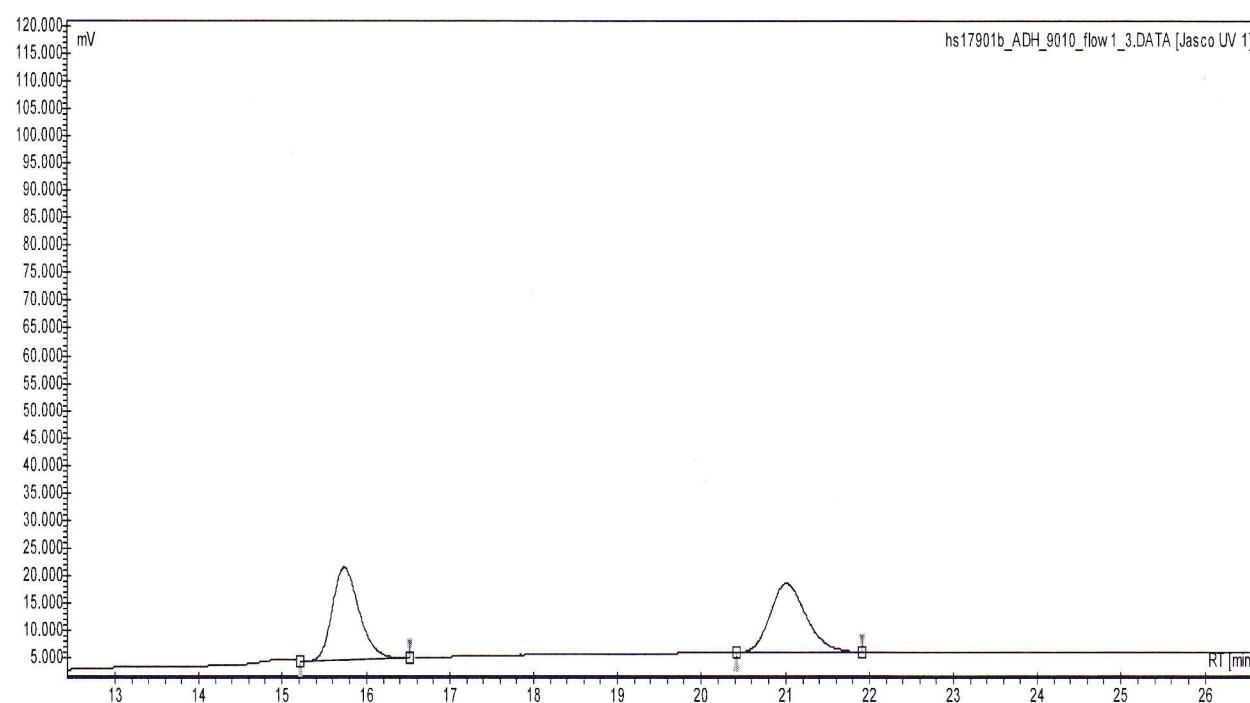




# Chromatogram : hs17901b\_ADH\_9010\_flow1\_3\_channel1

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_9010\_flow1\_acq30  
User : USER1

Acquired : 01.05.2008 16:31:58  
Processed : 02.05.2008 10:59:29  
Printed : 02.05.2008 11:04:05



## Peak results :

hs17901b_ADH_9010_flow1_3.DATA [Jasco UV 1]				
Index	Start Time [Min]	Time [Min]	End [Min]	Area % [%]
1	15,217	15,733	16,519	49,845
2	20,424	21,017	21,911	50,155
Total				100,000

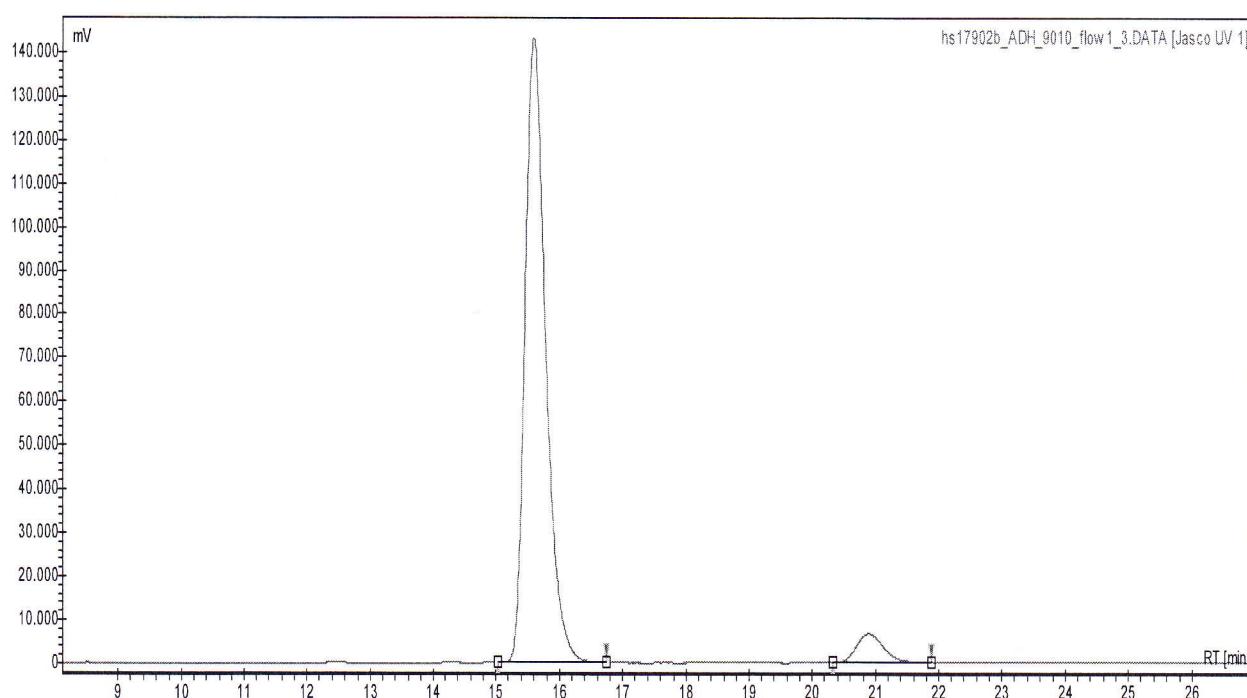
## Group results :

hs17901b_ADH_9010_flow1_3.DATA [Jasco UV 1]					
Index	Name	Area [mV.Min]	Quantity [% Area]	RF	Resp.
Total		0,0	0,00		0,00

# Chromatogram : hs17902b\_ADH\_9010\_flow1\_3\_channel1

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_9010\_flow1\_acq30  
User : USER1

Acquired : 01.05.2008 17:04:36  
Processed : 02.05.2008 11:00:28  
Printed : 02.05.2008 11:01:11



## Peak results :

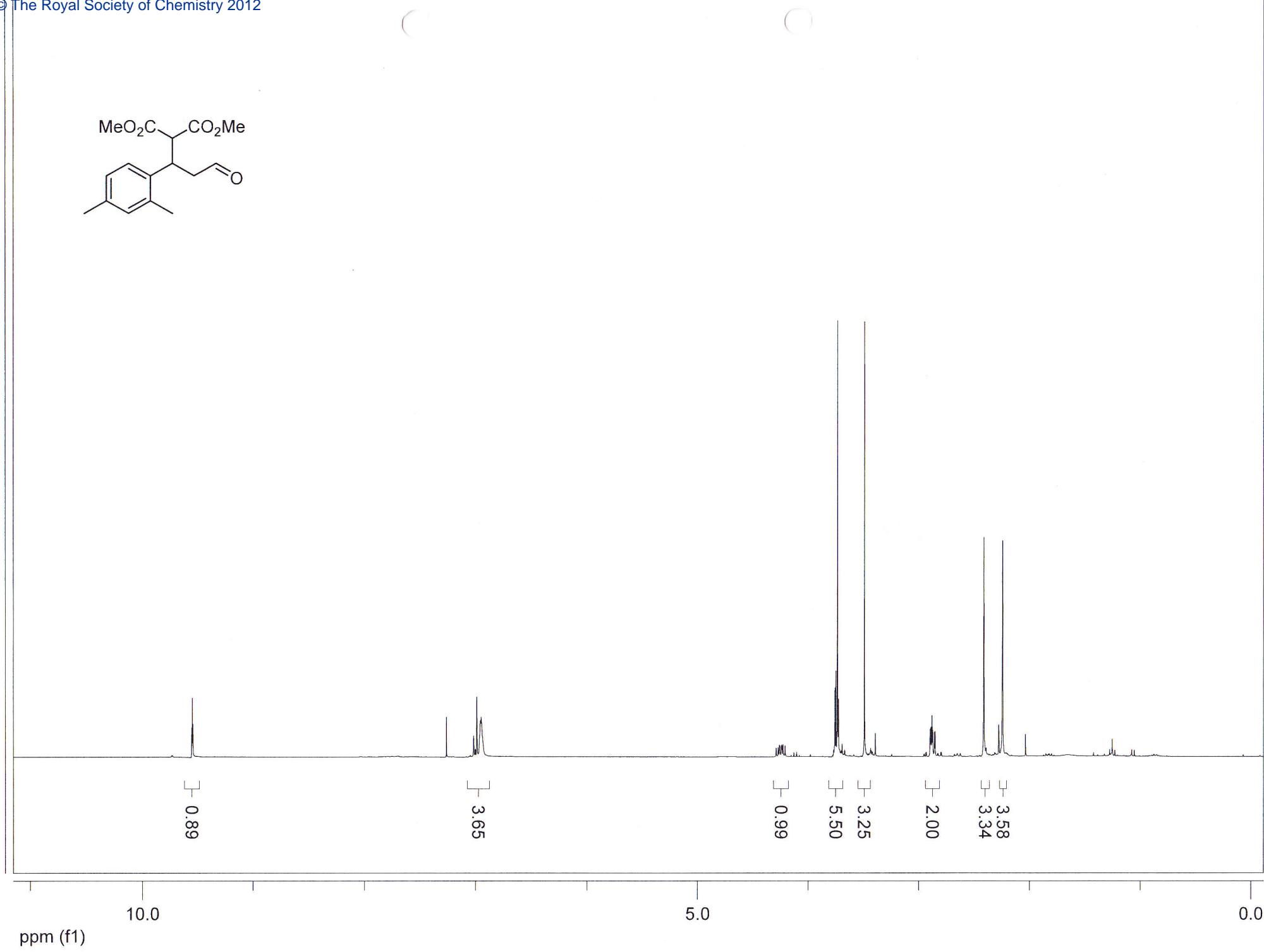
hs17902b\_ADH\_9010\_flow1\_3.DATA [Jasco UV 1]

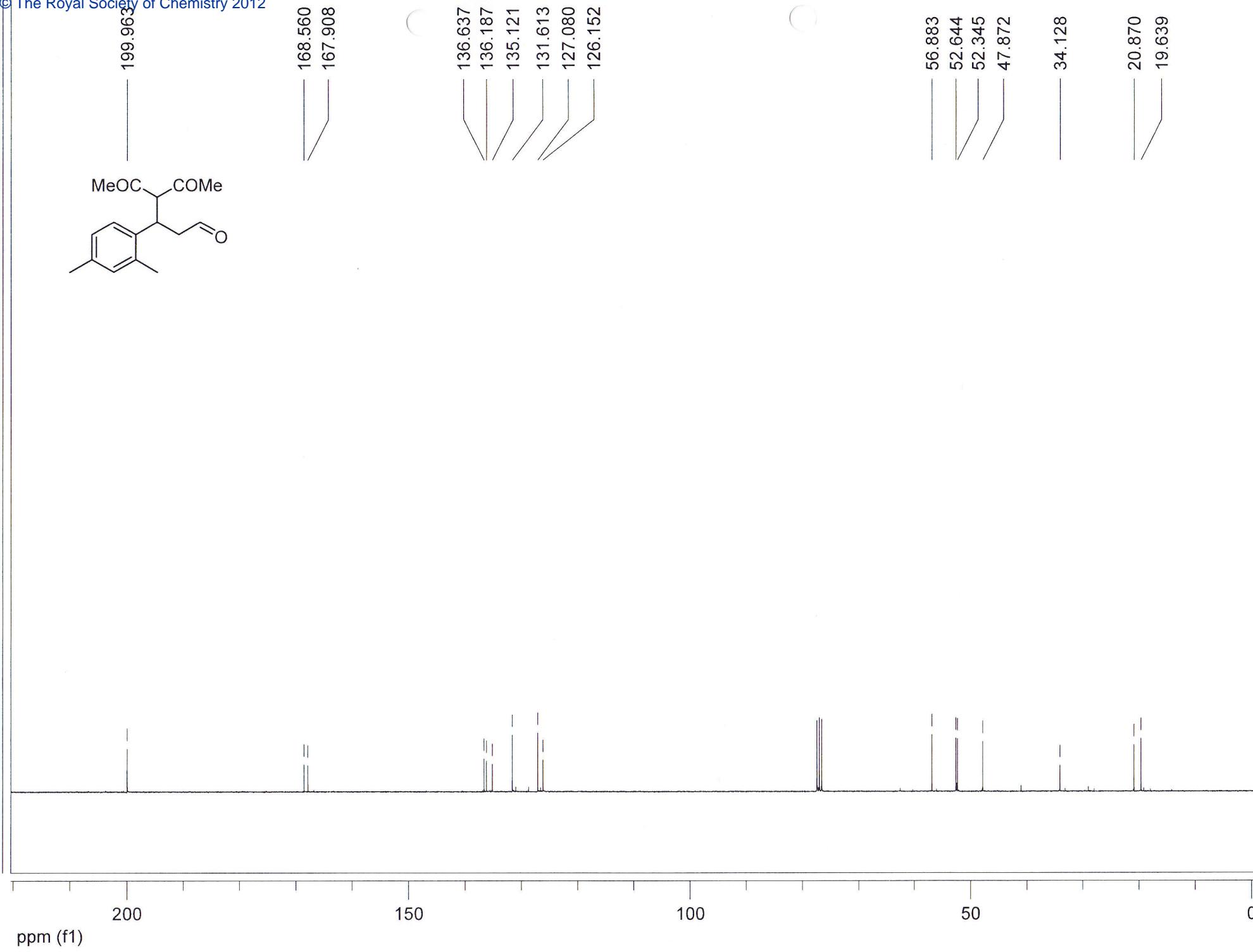
Index	Start Time	End Time	Area %
	[Min]	[Min]	[%]
1	15,031	15,592	16,736
2	20,331	20,900	21,880
Total			100,000

## Group results :

hs17902b\_ADH\_9010\_flow1\_3.DATA [Jasco UV 1]

Index	Name	Area	Quantity	RF	Resp.
		[mV.Min]	[% Area]		
Total		0,0	0,00		0,00

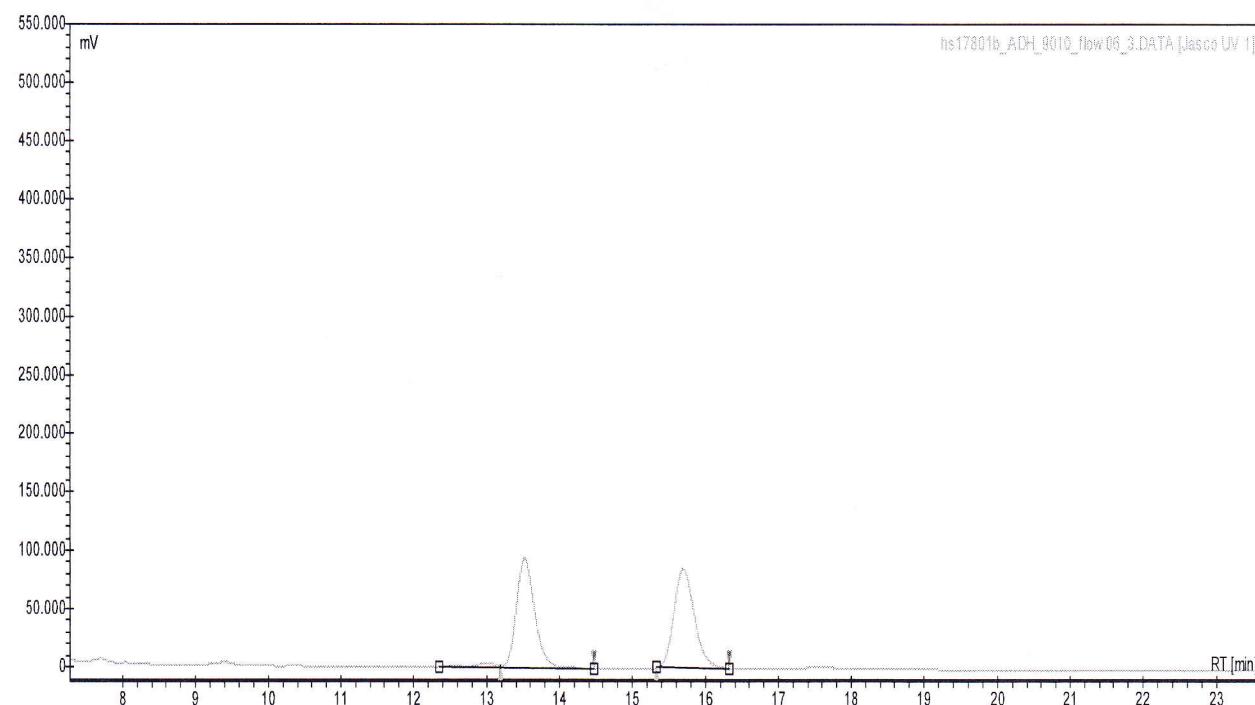




# Chromatogram : hs17801b\_ADH\_9010\_flow06\_3\_channel1

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_9010\_flow06\_acq40  
User : USER1

Acquired : 01.05.2008 15:06:42  
Processed : 02.05.2008 10:55:32  
Printed : 02.05.2008 10:56:24



## Peak results :

hs17801b\_ADH\_9010\_flow06\_3.DATA [Jasco UV 1]

Index	Start [Min]	Time [Min]	End [Min]	Area %
2	13,191	13,525	14,470	49,591
1	15,331	15,700	16,322	50,409
Total				100,000

## Group results :

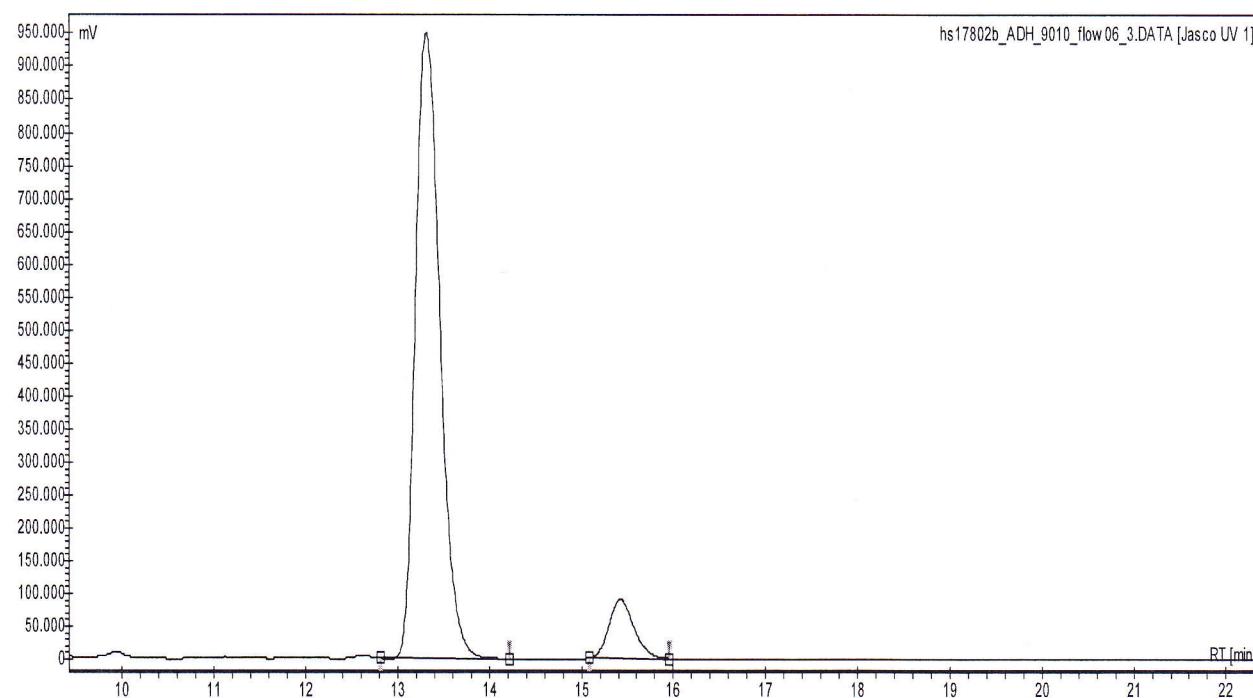
hs17801b\_ADH\_9010\_flow06\_3.DATA [Jasco UV 1]

Index	Name	Area [mV.Min]	Quantity [% Area]	RF	Resp.
Total		0,0	0,00		0,00

# Chromatogram : hs17802b\_ADH\_9010\_flow06\_3\_channel1

System : Jasco HPLC 2  
Method : HPLC2\_ADH\_9010\_flow06\_acq40  
User : USER1

Acquired : 01.05.2008 15:49:21  
Processed : 02.05.2008 10:57:05  
Printed : 02.05.2008 10:57:54



## Peak results :

hs17802b\_ADH\_9010\_flow06\_3.DATA [Jasco UV 1]

Index	Start [Min]	Time [Min]	End [Min]	Area %
1	12,810	13,308	14,215	91,351
2	15,083	15,425	15,950	8,649
Total				100,000

## Group results :

hs17802b\_ADH\_9010\_flow06\_3.DATA [Jasco UV 1]

Index	Name	Area [mV.Min]	Quantity [% Area]	RF	Resp.
Total		0.0	0.00		0.00