

## Supporting Information for:

### Rhodium-Catalysed Enantioselective Synthesis of 4-arylchroman-2-ones

Joseph C. Allen, Gabriele Kociok-Köhn and Christopher G. Frost\*

*Department of Chemistry, University of Bath, Bath, BA2 7AY, UK*

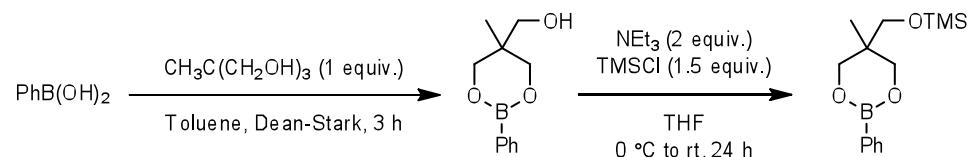
*c.g.frost@bath.ac.uk*

**General information:** IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer, using NaCl discs.  $^1\text{H}$  NMR spectra were obtained on a Bruker Avance 300 spectrometer operating at 300 MHz, unless otherwise noted, with tetramethylsilane as an internal standard.  $J$  values are given in Hz.  $^{13}\text{C}$  NMR spectra were obtained on a Bruker Advance 300 spectrometer operating at 75 MHz, unless otherwise noted. Microwave reactions were performed in a CEM Discover model 045704 system. All dry solvents were freshly distilled under nitrogen prior to use. Tetrahydrofuran was distilled over alumina column. 1,4-Dioxane was distilled under reduced pressure over 4 $\text{\AA}$  molecular sieves. MeOH was distilled over 4 $\text{\AA}$  molecular sieves. Petroleum ether refers to that fraction obtained between 40–60°C. All other reagents were obtained from commercial suppliers and used as received. All glassware used under anhydrous conditions was dried in an oven and allowed to cool under nitrogen prior to use. All reactions were carried out under argon unless otherwise stated. Flash chromatography was conducted under medium pressure, using matrix 60 silica.

CCDC 836829 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

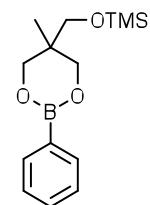
Alkylidene Meldrum's acid derivatives were prepared by literature procedures.<sup>1</sup>

**General Procedure for Synthesis of Trimethyl((5-methyl-2-(aryl)-1,3,2-dioxaborinan-5-yl)methoxy)silanes**



Aryl boronic acid (16 mmol), was added to a stirring suspension of 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol) in toluene (25 mL) distilled under Dean-Stark apparatus. The mixture was then concentrated *in vacuo*. Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalent) was added dropwise to a stirring mixture of (2-Aryl-5-methyl-1,3,2-dioxaborinan-5-yl)methanol (8 mmol, 1 equivalent), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) in *anhydrous* THF (50 mL), under an inert atmosphere at 0 °C for 1 hour. The mixture was allowed to warm to room temperature and stirred for a further 18 hours, quenched with water, extracted with EtOAc. Organics were washed with brine, dried with  $\text{MgSO}_4$  and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography.

**Trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (7)**



Phenylboronic acid (1.95 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol), Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), (triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) was reacted under standard protocol to give the desired product as an off-white solid; (4.28 g, 96% yield);  $R_f$  0.55 (9:1, petrol : EtOAc);

**IR** (solid,  $\text{cm}^{-1}$ )  $\nu$  2957, 1601, 1493, 1480, 1440, 1412, 1366, 1345, 1306, 1262, 1247, 1203, 1177, 1123, 1079, 1023, 875, 837, 781, 758, 747, 720, 698, 669, 638;

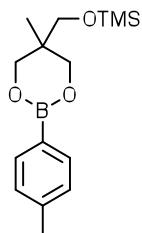
**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.82 (2H, d,  $J$  = 7.9 Hz, ArH), 7.47-7.34 (3H, m, ArH), 4.04 (2H, d,  $J$  = 11.0 Hz,  $\text{CH}_2$ ), 3.79 (2H, d,  $J$  = 11.0 Hz,  $\text{CH}_2$ ), 3.53 (2H, s,  $\text{CH}_2$ ), 0.98 (3H, s,  $\text{CH}_3$ ), 0.12 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );

**$^{11}\text{B-NMR}$**  (95 MHz,  $\text{CDCl}_3$ ) 30.0;

**$^{13}\text{C-NMR}$**  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  133.8, 130.6, 127.5, 68.1, 64.6, 36.9, 17.7, -0.7;

**HRMS (ESI):** calcd for  $\text{C}_{14}\text{H}_{24}\text{BO}_3\text{Si} [\text{M}+\text{H}]^+$  :  $m/z$  279.1588, found 279.1593.

**Trimethyl((5-methyl-2-(*p*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (7b)**



*p*-tolylboronic acid (2.18 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol), Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) and THF (50 mL) was reacted under standard protocol to give the desired product as an off-white solid (4.43 g, 95% yield);  $R_f$  0.60 (9:1, petrol : EtOAc);

**IR** (solid,  $\text{cm}^{-1}$ )  $\nu$  2955, 2904, 2161, 1610, 1478, 1417, 1367, 1347, 1314, 1243, 1208, 1179, 1125, 1072, 1020, 874, 838, 817, 747, 723, 663, 625;

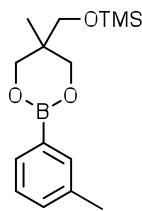
**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.70 (2H, d,  $J$  = 8.0 Hz, ArH), 7.08 (2H, d,  $J$  = 8.0 Hz, ArH), 4.01 (2H, d,  $J$  = 11.0 Hz,  $\text{CH}_2$ ), 3.72 (2H, d,  $J$  = 11.0 Hz,  $\text{CH}_2$ ), 3.51 (2H, s,  $\text{CH}_2$ ), 2.37 (3H, s,  $\text{CH}_3$ ), 0.95 (3H, s,  $\text{CH}_3$ ), 0.11 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );

**$^{11}\text{B-NMR}$**  (95 MHz,  $\text{CDCl}_3$ ) 30.0;

**$^{13}\text{C-NMR}$**  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 136.1, 128.5, 68.1, 64.7, 37.7, 21.8, 17.8, -0.5;

**HRMS** (ESI): calcd for  $\text{C}_{15}\text{H}_{26}\text{BO}_3\text{Si}$  [M+H] $^+$  :  $m/z$  293.1744, found 293.1725.

**Trimethyl((5-methyl-2-(*m*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (7c)**



*m*-tolylboronic acid (2.18 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol), Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) and THF (50 mL) was reacted under standard protocol to give the desired product as an off-white solid; (4.67 g, 96% yield);  $R_f$  0.63 (9:1, petrol : EtOAc);

**IR** (solid,  $\text{cm}^{-1}$ )  $\nu$  2957, 2150, 1580, 1481, 1422, 1342, 1317, 1245, 1211, 1123, 1085, 1017, 985, 875, 838, 793, 748, 706, 669, 651;

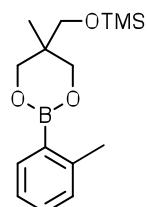
**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.63-7.53 (2H, m, ArH), 7.25-7.12 (2H, m, ArH), 3.99 (2H, d,  $J$  = 10.9 Hz,  $\text{CH}_2$ ), 3.74 (2H, d,  $J$  = 10.9 Hz,  $\text{CH}_2$ ), 3.47 (2H, s,  $\text{CH}_2$ ), 2.33 (3H, s,  $\text{ArCH}_3$ ), 0.91 (3H, s,  $\text{CH}_3$ ), 0.07 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );

**<sup>11</sup>B-NMR** (95 MHz, CDCl<sub>3</sub>) 30.0;

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 137.6, 135.2, 132.1, 131.6, 128.2, 68.8, 65.2, 37.6, 22.1, 18.4, 0.0;

**HRMS** (ESI): calcd for C<sub>15</sub>H<sub>26</sub>BO<sub>3</sub>Si [M+H]<sup>+</sup> : m/z 293.1744, found 293.1751.

**Trimethyl((5-methyl-2-(*o*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (7d)**



*o*-tolylboronic acid (2.18 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol), Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) and THF (50 mL) was reacted under standard protocol to give the desired product as an off-white solid; (4.25 g, 91% yield); R<sub>f</sub> 0.63 (9:1, petrol : EtOAc);

**IR** (solid, cm<sup>-1</sup>) ν 2955, 2899, 2155, 1596, 1478, 1436, 1411, 1308, 1263, 1250, 1238, 1174, 1130, 1077, 872, 836, 661, 747, 728, 711, 661;

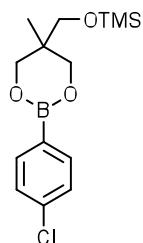
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.73 (1H, d, J = 7.5 Hz), 7.28 (1H, td, J = 7.5, 1.8 Hz, ArH), 4.02 (2H, d, J = 11.0 Hz, CH<sub>2</sub>), 3.78 (2H, d, J = 11.0 Hz, CH<sub>2</sub>), 3.51 (2H, s, CH<sub>2</sub>), 2.51 (3H, s, ArCH<sub>3</sub>), 0.93 (3H, s, CH<sub>3</sub>), 0.11 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>);

**<sup>11</sup>B-NMR** (95 MHz, CDCl<sub>3</sub>) 30.2;

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 144.7, 135.6, 130.7, 130.6, 125.3, 68.7, 65.2, 37.3, 23.1, 18.4, 0.0;

**HRMS** (ESI): calcd for C<sub>15</sub>H<sub>25</sub>BNaO<sub>3</sub>Si [M+Na]<sup>+</sup> : m/z 315.1564, found 315.1558.

**((2-(4-Chlorophenyl)-5-methyl-1,3,2-dioxaborinan-5-yl)methoxy)trimethylsilane (7e)**



4-Chlorophenylboronic acid (2.50 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol), Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) and THF (50 mL) was reacted under standard protocol to give the desired product as an off-white solid; (4.89 g, 98% yield);  $R_f$  0.50 (9:1, petrol : EtOAc);

**IR** (film,  $\text{cm}^{-1}$ )  $\nu$  2956, 2905, 2153, 2044, 1589, 1560, 1480, 1420, 1369, 1343, 1313, 1243, 1202, 1124, 1089, 1014, 984, 938, 878, 836, 827, 740, 724, 695, 656, 636;

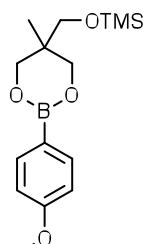
**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.71 (2H, d,  $J$  = 8.4 Hz, ArH), 7.32 (2H, d,  $J$  = 8.4 Hz, ArH), 4.01 (2H, d,  $J$  = 11.0 Hz,  $\text{CH}_2$ ), 3.76 (2H, d,  $J$  = 11.0 Hz,  $\text{CH}_2$ ), 3.49 (2H, s,  $\text{CH}_2$ ), 0.94 (3H, s,  $\text{CH}_3$ ), 0.10 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );

**$^{11}\text{B-NMR}$**  (95 MHz,  $\text{CDCl}_3$ ) 29.7;

**$^{13}\text{C-NMR}$**  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  137.6, 136.0, 128.5, 68.0, 65.3, 37.6, 18.4, 0.0;

**HRMS** (ESI): calcd for  $\text{C}_{14}\text{H}_{23}\text{BClO}_3\text{Si} [\text{M}+\text{H}]^+$  :  $m/z$  313.1198, found 313.1204.

**((2-(4-Methoxyphenyl)-5-methyl-1,3,2-dioxaborinan-5-yl)methoxy)trimethylsilane (7f)**



4-methoxyboronic acid (2.43 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol), Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) and THF (50 mL) was reacted under standard protocol to give the desired product as an off-white solid; (4.63 g, 94% yield);  $R_f$  0.45 (9:1, petrol : EtOAc);

**IR** (solid,  $\text{cm}^{-1}$ )  $\nu$  3312, 2957, 2903, 2027, 1602, 1567, 1512, 1477, 1416, 1400, 1311, 1295, 1237, 1172, 1122, 1104, 1035, 1025, 874, 835, 794, 778, 706, 664, 645, 634 626, 612;

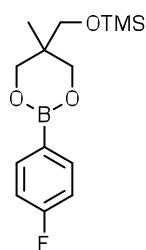
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.75 (2H, d, J = 8.7 Hz, ArH), 6.90 (2H, d, J = 8.7 Hz, ArH), 4.01 (2H, d, J = 10.9 Hz, CH<sub>2</sub>), 3.83 (3H, s, CH<sub>3</sub>), 3.76 (2H, d, J = 10.9 Hz, CH<sub>2</sub>), 3.51 (2H, s, CH<sub>2</sub>), 0.93 (3H, s, CH<sub>3</sub>), 0.14 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>);

**<sup>11</sup>B-NMR** (95 MHz, CDCl<sub>3</sub>) 29.8;

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 161.7, 135.5, 113.1, 68.0, 64.5, 55.0, 36.9, 17.7, -0.7;

**HRMS** (ESI): calcd for C<sub>15</sub>H<sub>26</sub>BO<sub>4</sub>Si [M+H]<sup>+</sup> : m/z 309.1693, found 309.1690.

**((2-(4-Fluorophenyl)-5-methyl-1,3,2-dioxaborinan-5-yl)methoxy)trimethylsilane (7g)**



4-fluoroboronic acid (2.23 g, 16 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1.92 g, 16 mmol) Chlorotrimethylsilane (2.03 mL 16 mmol, 2 equivalents), triethylamine (1.67 mL, 12 mmol, 1.5 equivalents) and THF (50 mL) was reacted under standard protocol to give the desired product as an off-white solid; (4.61 g, 97% yield); R<sub>f</sub> 0.70 (9:1, petrol : EtOAc);

**IR** (solid, cm<sup>-1</sup>) ν 2959, 2905, 2877, 1599, 1480, 1439, 1412, 1347, 1312, 1295, 1247, 1203, 1078, 875, 835;

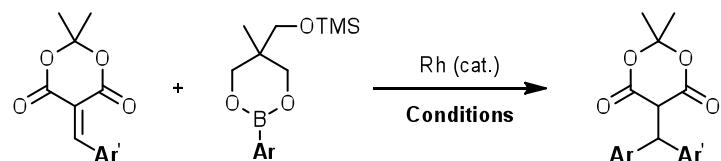
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.92-7.74 (2H, m, ArH), 7.07-6.98 (2H, m, ArH), 4.00 (2H, d, J = 11.0 Hz, CH<sub>2</sub>), 3.76 (2H, d, J = 11.0 Hz, CH<sub>2</sub>), 3.50 (2H, s, CH<sub>2</sub>), 0.93 (3H, s, CH<sub>3</sub>), 0.11 (9H, s, Si(CH<sub>3</sub>)<sub>3</sub>);

**<sup>11</sup>B-NMR** (95 MHz, CDCl<sub>3</sub>) 29.6;

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 165.0 (d, <sup>1</sup>J<sub>CF</sub> = 249 Hz,), 136.2 (d, <sup>3</sup>J<sub>C-F</sub> = 8 Hz), 114.7 (d, <sup>2</sup>J<sub>C-F</sub> = 20 Hz), 68.2, 37.1, 17.8, -0.6;

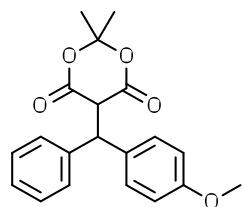
**HRMS** (ESI): calcd for C<sub>14</sub>H<sub>22</sub>BFNaO<sub>3</sub>Si [M+Na]<sup>+</sup> : m/z 319.1313, found 319.1319.

**General Procedure for the Rhodium-Catalysed 1,4-Addition of Trimethyl((5-methyl-2-(aryl)-1,3,2-dioxaborinan-5-yl)methoxy)silanes to Monoalkylidene Derivatives of Meldrum's Acid.**



To an oven dried carousel tube was charged chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%) and (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%) and *anhydrous* 1,4-dioxane (2 mL) under an atmosphere of argon. The resulting solution was stirred at room temperature for 10 minutes before the addition of potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), trimethyl((5-methyl-2-(aryl)-1,3,2-dioxaborinan-5-yl)methoxy)silanes (0.5 mmol, 2 equivalent) and monoalkylidene derivative of Meldrum's acid (0.25 mmol, 1 equivalent). The reaction mixture was heated to 65 °C for 24 hours. The reaction mixture was cooled, quenched with saturated ammonium chloride solution (10 mL), extracted with dichloromethane (3 x 10 mL), dried over MgSO<sub>4</sub> and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography.

**5-((4-Methoxyphenyl)(phenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (9)**



Cyclooctadiene rhodium (I) chloride dimer (1.5 mg, 0.0062 mmol, 2.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (139 mg, 0.5 mmol, 2 equivalent) and 5-(2-(methoxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (66 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid; (54 mg, 64% yield); **mp** (EtOAc/petrol) 131-133 °C;

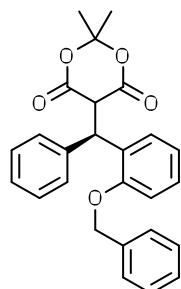
**IR** (film, cm<sup>-1</sup>) 2703, 1756 (C=O), 1710 (C=O), 1567, 1491, 1403, 1386, 1321, 1213, 1255, 1200, 1143;

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.36-7.20 (5H, m, ArH), 7.24 (2H, d, J = 8.6 Hz, ArH), 6.84 (2H, d, J = 8.6 Hz, ArH), 5.35 (1H, d, J = 2.7 Hz, CH), 4.35 (1H, d, J = 2.7 Hz, CH), 3.79 (3H, s, OCH<sub>3</sub>), 1.74 (3H, s, CCH<sub>3</sub>) 1.52 (3H, s, CCH<sub>3</sub>);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 165.0, 164.7, 158.7, 140.4, 132.0, 120.5, 129.0, 128.4, 127.9, 113.8, 105.1, 55.2, 51.3, 48.6, 28.3, 27.7;

**HRMS** (ESI): calcd for C<sub>20</sub>H<sub>20</sub>NaO<sub>5</sub> [M+Na]<sup>+</sup> : *m/z* 363.1208, found 363.1214.

**(R)-5-((2-(benzyloxy)phenyl)(phenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (10)**



Chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (139 mg, 0.5 mmol, 2 equivalent) and 5-(2-(benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid; (70 mg, 68% yield);

**mp** (EtOAc/petrol) 142–144 °C (decomposes);

**R<sub>f</sub>** 0.15 (9:1, petrol : EtOAc);

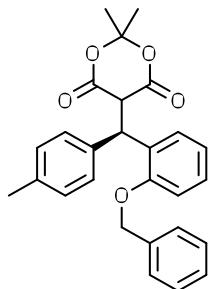
**IR** (film, cm<sup>-1</sup>) ν 3033, 2513, 2160, 2008, 1782 (C=O), 1746 (C=O), 1599, 1489, 1451, 1289, 1239, 1205, 1108, 1076, 1055, 1011, 899, 836, 750, 734, 697, 634;

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.29–7.15 (9H, m, ArH), 7.11 (1H, td, *J* = 7.8, 1.5 Hz, ArH), 6.97 (2H, dd, *J* = 7.7, 1.0 Hz, ArH), 6.84 (1H, dd, *J* = 8.3, 1.0 Hz, ArH), 6.79 (1H, dd, *J* = 7.5, 1.0 Hz, ArH), 5.43 (1H, d, *J* = 3.8 Hz, CH), 5.04 (2H, s, OCH<sub>2</sub>), 4.49 (1H, d, *J* = 3.8 Hz, CH), 1.51 (3H, s, CCH<sub>3</sub>) 1.47 (3H, s, CCH<sub>3</sub>);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 164.9, 155.4, 139.7, 139.6, 136.8, 131.1, 129.5, 129.4, 128.7, 128.6, 128.1, 127.2, 127.1, 120.9, 111.5, 104.7, 70.1, 49.6, 44.3, 28.3, 27.2;

**HRMS** (ESI): calcd for C<sub>26</sub>H<sub>25</sub>O<sub>5</sub> [M+H]<sup>+</sup> : *m/z* 417.1702, found 417.1710.

**(R)-5-((2-(benzyloxy)phenyl)(*p*-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (11)**



Chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), trimethyl((5-methyl-2-(*p*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (146 mg, 0.5 mmol, 2 equivalent) and 5-(2-benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid; (93 mg, 87% yield);

**mp** (EtOAc/petrol) 149–151 °C (decomposes);

**R<sub>f</sub>** 0.13 (9:1, petrol : EtOAc);

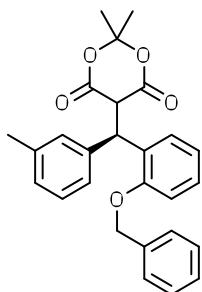
**IR** (film, cm<sup>-1</sup>) ν 3466, 2881, 1741 (C=O), 1590, 1479, 1452, 1422, 1408, 1384, 1342, 1310, 1289, 1254, 1253, 1199, 1114, 1088, 1014, 910, 825, 806, 725, 657;

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.38–7.18 (8H, m, ArH), 7.14 (2H, app. d, *J* = 8.1 Hz, ArH), 7.08 (2H, dd, *J* = 7.7, 1.1 Hz, ArH), 6.93 (2H, dd, *J* = 8.3, 1.0 Hz, ArH), 6.88 (1H, dd, *J* = 7.5, 1.0 Hz, ArH), 5.47 (1H, d, *J* = 3.8 Hz, CH), 5.15 (2H, s, OCH<sub>2</sub>), 4.58 (1H, d, *J* = 3.8 Hz, CH), 2.34 (3H, s, ArCH<sub>3</sub>), 1.61 (3H, s, CCH<sub>3</sub>) 1.55 (3H, s, CCH<sub>3</sub>);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 165.0, 164.9, 155.6, 136.8, 136.7, 136.5, 131.1, 129.6, 129.3, 128.7, 128.0, 127.9, 127.2, 120.9, 111.4, 104.6, 70.0, 49.6, 44.1, 28.2, 27.0, 21.1;

**HRMS** (ESI): calcd for C<sub>27</sub>H<sub>27</sub>O<sub>5</sub> [M+H]<sup>+</sup> : *m/z* 431.1859, found 431.1857.

**(R)-5-((2-(benzyloxy)phenyl)(m-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (12)**



Chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), trimethyl((5-methyl-2-(*m*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (146 mg, 0.5 mmol, 2 equivalent) and 5-(2-(benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid; (78 mg, 73% yield);

$R_f$  0.15 (9:1, petrol : EtOAc);

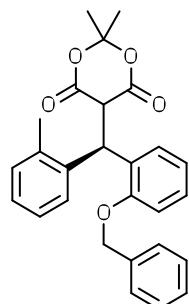
**IR** (film,  $\text{cm}^{-1}$ )  $\nu$  2971, 1774 (C=O), 1729 (C=O), 1635, 1544, 1461, 1383, 1187, 1062, 902, 892, 764, 628;

**<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.45-7.29 (5H, m, ArH), 7.25-7.17 (2H, m, ArH), 7.13 (2H, d,  $J$  = 8.8 Hz, ArH), 7.07 (1H, d,  $J$  = 7.6 Hz, ArH), 6.93 (1H, d,  $J$  = 7.4 Hz, ArH), 6.89 (1H, d,  $J$  = 7.5 Hz, ArH), 5.49 (1H, d,  $J$  = 3.8 Hz, CH), 5.15 (2H, s,  $\text{ArCH}_2$ ), 4.58 (1H, d,  $J$  = 3.8 Hz, CH), 2.33 (3H, s,  $\text{ArCH}_3$ ), 1.61 (3H, s,  $\text{CCH}_3$ ) 1.57 (3H, s,  $\text{CCH}_3$ );

**<sup>13</sup>C-NMR** (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 164.9, 155.5, 139.6, 138.2, 136.8, 131.1, 130.3, 129.6, 128.7, 128.5, 128.1, 128.0, 127.2, 126.3, 120.9, 111.5, 104.6, 70.1, 49.5, 44.5, 28.2, 27.1, 21.6;

**HRMS** (ESI): calcd for  $\text{C}_{27}\text{H}_{27}\text{O}_5$   $[\text{M}+\text{H}]^+$  :  $m/z$  431.1859, found 431.1854.

**(R)-5-((2-(benzyloxy)phenyl)(o-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (13)**



Chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), trimethyl((5-methyl-2-(*o*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (146 mg, 0.5 mmol, 2 equivalent) and 5-(2-(benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid. (41 mg, 38% yield);

$R_f$  0.15 (9:1, petrol : EtOAc);

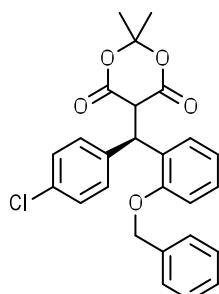
**IR** (film,  $\text{cm}^{-1}$ )  $\nu$ , 3046, 2971, 1794 (C=O), 1748 (C=O), 1650, 1594, 1437, 1386, 1154, 1062, 902, 769, 607;

**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.44-7.27 (5H, m, ArH), 7.24-7.14 (4H, m, ArH), 6.92 (1H, d,  $J$  = 7.9 Hz, ArH), 6.86-6.76 (2H, m, ArH), 5.64 (1H, d,  $J$  = 3.9 Hz, CH), 5.19 (2H, dd,  $J$  = 14.4, 12.3 Hz,  $\text{ArCH}_2$ ), 4.54 (1H, d,  $J$  = 3.9 Hz, CH), 2.17 (3H, s,  $\text{ArCH}_3$ ), 1.64 (3H, s,  $\text{CCH}_3$ ) 1.57 (3H, s,  $\text{CCH}_3$ );

**$^{13}\text{C-NMR}$**  (75.5 MHz,  $\text{CDCl}_3$ ) 165.5, 164.9, 155.4, 138.3, 137.2, 136.8, 130.9, 128.8, 128.5, 128.1, 128.0, 127.6, 127.1, 126.4, 120.9, 111.3, 104.6, 69.9, 48.9, 40.7, 28.2, 27.0, 19.8;

**HRMS** (ESI): calcd for  $\text{C}_{27}\text{H}_{26}\text{NaO}_5$  [ $\text{M}+\text{Na}]^+$  :  $m/z$  453.1678, found 453.1689.

**(R)-5-((2-(benzyloxy)phenyl)(4-chlorophenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (14)**



Chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), ((2-(4-chlorophenyl)-5-methyl-1,3,2-dioxaborinan-5-yl)methoxy)trimethylsilane (156 mg, 0.5 mmol, 2 equivalent) and 5-(2-(benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid. (104 mg, 93% yield);

**R<sub>f</sub>** 0.15 (9:1, petrol : EtOAc);

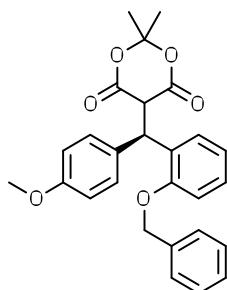
**IR** (film, cm<sup>-1</sup>) 3069, 2159, 2008, 1785 (C=O), 1744 (C=O), 1599, 1485, 1396, 1385, 1351, 1329, 1291, 1233, 1203, 1176, 1088, 1060, 989, 902, 828, 741, 772, 635, 612;

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.30-7.19 (5H, m, ArH), 7.18-7.08 (5H, m, ArH), 6.98 (1H, d, *J* = 7.8 Hz, ArH), 6.87-6.77 (2H, m, ArH), 5.38 (1H, d, *J* = 3.8 Hz, CH), 5.01 (2H, s, OCH<sub>2</sub>), 4.36 (1H, d, *J* = 3.6 Hz, CH), 1.53 (3H, s, CCH<sub>3</sub>) 1.47 (3H, s, CCH<sub>3</sub>);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 165.4, 165.3, 156.2, 139.0, 137.3, 133.6, 131.5, 131.3, 129.5, 129.4, 129.3, 129.0, 128.8, 127.9, 121.7, 112.3, 105.4, 70.8, 50.3, 44.21, 28.9, 27.5;

**HRMS** (ESI): calcd for C<sub>26</sub>H<sub>24</sub>ClO<sub>5</sub> [M+H]<sup>+</sup> : *m/z* 451.1391, found 451.1398.

**(R)-5-((2-(benzyloxy)phenyl)(4-methoxyphenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (15)**



Chlorobis(ethylene)rhodium (I) dimer (2.4 mg, 0.0062 mmol, 2.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (3.6 mg, 0.0138 mmol, 5.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), ((2-(4-methoxyphenyl)-5-methyl-1,3,2-dioxaborinan-5-yl)methoxy)trimethylsilane (154 mg, 0.5 mmol, 2 equivalent) and 5-(2-(benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid; (97 mg, 88% yield);

$R_f$  0.09 (9:1, petrol : EtOAc);

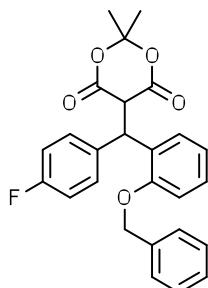
**IR** (film,  $\text{cm}^{-1}$ )  $\nu$  3109, 2121, 2037, 1789 (C=O), 1742 (C=O), 1608, 1412, 1376, 1343, 1383, 1291, 1251, 1177, 1062;

**<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.38-7.31 (5H, m, ArH), 7.26 (2H, d,  $J$  = 8.7 Hz, ArH), 7.19 (1H, dd,  $J$  = 7.7 Hz, 1.5 Hz, ArH), 7.11 (1H, d,  $J$  = 7.7, 1.0 Hz, ArH), 6.96-6.90 (2H, m, ArH), 6.86 (2H, d,  $J$  = 8.7 Hz, ArH), 5.47 (1H, d,  $J$  = 3.7 Hz, CH), 5.15 (2H, s,  $\text{OCH}_2$ ), 4.60 (1H, d,  $J$  = 3.7 Hz, CH), 3.80 (3H, s,  $\text{OCH}_3$ ), 1.60 (3H, s,  $\text{CCH}_3$ ) 1.56 (3H, s,  $\text{CCH}_3$ );

**<sup>13</sup>C-NMR** (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  165.0, 164.9, 158.6, 155.4, 136.8, 131.6, 131.1, 130.6, 129.7, 128.7, 128.1, 128.0, 127.2, 120.9, 114.0, 104.6, 70.0, 55.2, 49.8, 43.8, 28.2, 27.1;

**HRMS** (ESI): calcd for  $\text{C}_{27}\text{H}_{26}\text{NaO}_6$  [ $\text{M}+\text{Na}$ ]<sup>+</sup> :  $m/z$  469.1627, found 469.1604.

**5-((2-(BenzylOxy)phenyl)(4-fluorophenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (16)**



Cyclooctadiene rhodium (I) chloride dimer (3.0 mg, 0.0062 mmol, 2.5 mol%), 1,4-dioxane (2 mL), potassium hydroxide (14 mg, 0.25 mmol, 1 equivalent), ((2-(4-fluorophenyl)-5-methyl-1,3,2-

dioxaborinan-5-yl)methoxy)trimethylsilane (148 mg, 0.5 mmol, 2 equivalent) and 5-(2-(benzyloxy)benzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (85 mg, 0.25 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as an off-white solid; (58 mg, 90% yield);  $R_f$  0.18 (9:1, petrol : EtOAc);

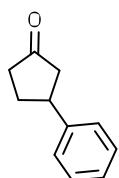
**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.41-7.17 (8H, m, ArH), 7.09 (1H, dd,  $J$  = 7.7, 1.1 Hz, ArH), 7.05-6.88 (4H, m, ArH), 5.50 (1H, d,  $J$  = 3.7 Hz, CH), 5.13 (2H, s,  $\text{OCH}_2$ ), 4.57 (1H, d,  $J$  = 3.7 Hz, CH), 1.62 (3H, s,  $\text{CCH}_3$ ) 1.57 (3H, s,  $\text{CCH}_3$ );

**$^{13}\text{C-NMR}$**  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  164.8, 164.7, 155.5, 136.7, 135.4, 135.3, 131.1 (d,  $^3J_{\text{CF}}$  = 8 Hz), 131.7, 129.1, 128.7, 128.2, 128.1, 127.2, 121.0, 115.4 (d,  $^2J_{\text{CF}}$  = 21 Hz), 111.6, 104.7, 70.1, 49.7, 43.5, 28.2, 26.9;

**$^{19}\text{F-NMR}$**  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -115.5 (m);

**HRMS (ESI)**: calcd for  $\text{C}_{26}\text{H}_{24}\text{F}_1\text{O}_5$  [ $\text{M}+\text{H}]^+$  :  $m/z$  435.1607, found 435.1613.

### 3-Phenylcyclopentanone (17)<sup>2</sup>

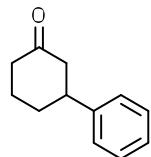


Chlorobis(ethylene)rhodium (I) dimer (3 mg, 0.0074 mmol, 1.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (4.4 mg, 0.0170 mmol, 3.3 mol%), 1,4-dioxane (2 mL), potassium hydroxide (28 mg, 0.5 mmol, 1 equivalent), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (278 mg, 1 mmol, 2 equivalent) and cyclopent-2-enone (41 mg, 0.5 mmol, 1 equiv) was reacted under standard protocol to give the desired product as a yellow oil; (74 mg, 93% yield).

**$^1\text{H-NMR}$**  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.37-7.28 (2H, m, ArH), 7.27-7.20 (3H, m, ArH), 3.49-3.33 (1H, m, CH), 2.66 (1H, dd,  $J$  = 18.3, 7.7 Hz, CH), 2.52-2.37 (2H, m,  $\text{CH}_2$ ), 2.36-2.21 (2H, m,  $\text{CH}_2$ ), 2.07-1.87 (1H, m, CH);

**$^{13}\text{C-NMR}$**  (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  218.5, 143.1, 128.7, 126.8, 45.8, 42.3, 38.9, 31.2; Data were in accordance with previous results in the literature.<sup>2</sup>

**3-phenylcyclohexanone (18 )<sup>3</sup>**

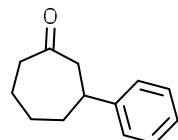


Chlorobis(ethylene)rhodium (I) dimer (3 mg, 0.0074 mmol, 1.5 mol%), (1*R*,4*R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (4.4 mg, 0.0170 mmol, 3.3 mol%), 1,4-dioxane (2 mL), potassium hydroxide (28 mg, 0.5 mmol, 1 equivalent), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (153 mg, 1 mmol, 1.1 equivalents) and cyclohex-2-enone (48 mg, 0.5 mmol, 1 equivalent) was reacted under standard protocol to give the desired product as a yellow oil; (83 mg, 99% yield);

**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.37–7.31 (2H, m, ArH), 7.28–7.21 (3H, m, ArH), 3.08–2.99 (1H, m, CH), 2.60–2.30 (4H, m), 2.21–2.09 (2H m), 1.89–1.70 (2H, m);

**<sup>13</sup>C NMR** (75 MHz)  $\delta$  210.6, 146.9, 128.4, 126.4, 126.3, 48.7, 40.3, 36.2, 22.3; Data were in accordance with previous results in the literature.<sup>3</sup>

**3-Phenylcycloheptanone (19 )<sup>4</sup>**



Chlorobis(ethylene)rhodium (I) dimer (3 mg, 0.0074 mmol, 1.5 mol%), (1*Z*,5*Z*)-cycloocta-1,5-diene (4 mg, 0.0340 mmol, 6.6 mol%), 1,4-dioxane (2 mL), potassium hydroxide (28 mg, 0.5 mmol, 1 equivalent), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (278 mg, 1 mmol, 2 equivalent) and cyclohept-2-enone (55 mg, 0.5 mmol, 1 equiv) was reacted under standard protocol to give the desired product as a yellow oil; (90 mg, 96% yield).

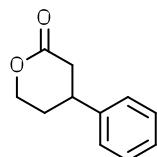
**IR** (film,  $\text{cm}^{-1}$ )  $\nu$  3027, 2924, 2857, 2159, 1696, 1600, 1494, 1445, 1345, 1313, 1345 1252, 1206, 1156, 1071, 1029, 934, 869, 643, 750, 699;

**<sup>1</sup>H-NMR** (300 MHz,  $\text{CDCl}_3$ ),  $\delta$  7.31–7.25 (2H, m, ArH), 7.34–7.15 (3H, m, ArH), 3.00–2.84 (2H, m,  $\text{CH}_2$ ), 2.76–2.40 (3H, m) 2.14–1.94 (3H, m), 1.84–1.63 (2H, m,  $\text{CH}_2$ ), 1.60–1.39 (2H, m,  $\text{CH}_2$ );

**<sup>13</sup>C-NMR** (75.5 MHz,  $\text{CDCl}_3$ )  $\delta$  213.6, 146.9, 129.6, 128.7, 126.5, 51.3, 44.0, 42.8, 39.3, 29.3, 24.2;

**HRMS (ESI)**: calcd for  $\text{C}_{13}\text{H}_{16}\text{NaO} [\text{M}+\text{Na}]^+$  :  $m/z$  211.1099, found 211.1094; Data were in accordance with previous results in the literature.<sup>4</sup>

**4-phenyltetrahydro-2H-pyran-2-one (20 )<sup>3</sup>**



Chlorobis(ethylene)rhodium (I) dimer (3 mg, 0.0074 mmol, 1.5 mol%), (*1R,4R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene (4.4 mg, 0.0170 mmol, 3.3 mol%), 1,4-dioxane (2 mL), potassium hydroxide (28 mg, 0.5 mmol, 1 equivalent), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (278 mg, 1 mmol, 2 equivalent) and 5,6-dihydro-2H-pyran-2-one (49 mg, 0.5 mmol, 1 equiv) was reacted under standard protocol to give the desired product as a yellow oil; (84 mg, 99% yield);

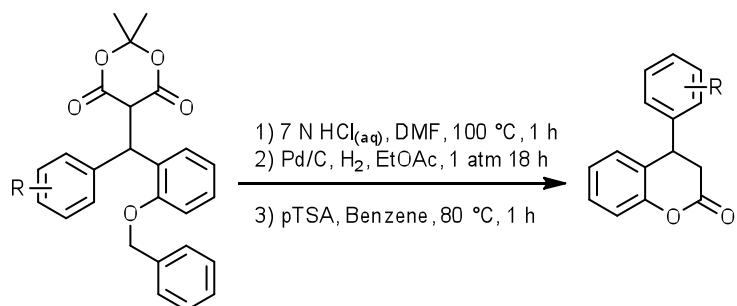
**IR** (film, cm<sup>-1</sup>)  $\nu$  3419, 3922, 2160, 2017, 1721, 1602, 1495, 1453, 1402, 1374, 1256, 1222, 1154, 1107, 1072, 951, 756, 699, 662;

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>),  $\delta$  7.41 (2H, m, ArH), 7.31-7.16 (3H, m, ArH), 4.51 (1H, ddd, *J* = 11.4, 4.9, 4.0 Hz, CH), 4.39 (1H, ddd, *J* = 11.4, 10.2, 4.0 Hz, CH), 3.34-3.16 (1H, m, CH), 2.94 (1H, ddd, *J* = 17.6, 6.0, 1.2 Hz, CH), 2.64 (1H, dd, *J* = 17.6, 10.2 Hz, CH) 2.87-2.84 (1H, m, CH), 2.12-1.97 (1H, m, CH);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  170.6, 142.8, 129.0, 127.3, 126.5, 68.6, 37.5, 37.4, 30.3;

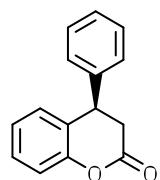
**HRMS** (ESI): calcd for C<sub>11</sub>H<sub>13</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> : *m/z* 177.0915, found 177.0956; Data were in accordance with previous results in the literature.<sup>3</sup>

### Stereochemical correlation: Synthesis of Aryl-3,4-dihydrocoumarin



5-((2-(benzyloxy)phenyl)(Aryl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg) was slowly added to a stirring mixture of dimethylformaldehyde (0.7 mL) and 7 M HCl<sub>(aq)</sub> (0.3 mL). The mixture was stirred at 100 °C for 1 hour. The reaction mixture was allowed to cool, diluted with water (10 mL) and extracted with Et<sub>2</sub>O (3 x 10 mL), dried over MgSO<sub>4</sub>, concentrated *in vacuo*. The resulting crude residue was diluted with ethyl acetate (10 mL). 10% palladium on carbon (5 mg) was added and hydrogen gas bubbled through the solution. The reaction was left for 18 hours. The reaction mixture was passed through a pad of celite and concentrated *in vacuo*. The resulting crude residue was diluted with benzene (1 mL) and *p*-toluenesulfonic acid (2 mg) was added. The reaction mixture was refluxed for 2 hours, concentrated *in vacuo* and the resulting residue was purified by flash column chromatography.

#### (R)-4-(phenyl)-3,4-dihydrocoumarin (21)<sup>5</sup>



5-((2-(Benzyl)phenyl)(phenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg, 0.048 mmol) was reacted under standard protocol to give the desired product as an off-white solid; (5.8 mg, 54% yield);

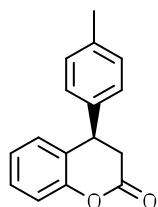
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.39-7.25 (4H, m, ArH), 7.20-7.12 (2H, m, ArH), 7.09 (1H, td, *J* = 7.4, 1.2 Hz, ArH), 6.98 (2H, d, *J* = 7.2 Hz, ArH), 4.35 (1H, app.t, *J* = 6.7 Hz, CH), 3.10 (1H, dd, *J* = 15.8, 6.7 Hz, CH), 3.02 (1H, dd, *J* = 15.8, 7.7 Hz, CH);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 167.6, 151.8, 140.3, 129.2, 128.8, 128.4, 127.7, 125.8, 124.7, 117.2, 40.7, 37.0, 29.7;

**HRMS (ESI):** calcd for C<sub>15</sub>H<sub>12</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> : *m/z* 247.0735, found 247.0736;

**HPLC** Diacel Chiralcel OD-H, hexane/propan-2-ol (95 : 5), 6.5 : 93.5 er, 0.5 mL min<sup>-1</sup>, t<sub>R</sub> = 26.23 (Minor) and 27.77 min (Major); Data were in accordance with previous results in the literature.<sup>5</sup>

**(R)-4-(*p*-tolyl)chroman-2-one (22)<sup>5</sup>**



5-((2-(Benzyl)oxy)phenyl)(*p*-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg, 0.046 mmol) was reacted under standard protocol to give the desired product as an off-white solid; (8.2 mg, 75% yield);

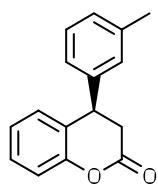
**IR** (film, cm<sup>-1</sup>)  $\nu$  3462, 2926, 2161, 2026, 1769 (C=O), 1483, 1454, 1421, 1382, 1343, 1311, 1280, 1255, 1280, 1233, 1213, 1161, 1051, 1015, 958, 916, 886, 825, 756, 740, 725, 697, 639; **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>),  $\delta$  7.29 (1H, td, *J* = 8.3, 1.3 Hz, ArH), 7.16 (2H, d, *J* = 8.4 Hz ArH), 7.11 (1H, dd, *J* = 3.7, 1.3 Hz ArH), 7.06 (1H, dd, *J* = 7.2, 1.3 Hz, ArH), 7.04 (2H, d, *J* = 8.4 Hz, ArH), 6.98 (1H, br.d, *J* = 7.2 Hz, ArH), 4.31 (1H, app.t, *J* = 7.0 Hz, CH), 3.07 (1H, dd, *J* = 15.8, 6.1 Hz, CH), 2.99 (1H, dd, *J* = 15.8, 7.8 Hz, CH), 2.34 (3H, s, ArCH<sub>3</sub>);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  167.8, 151.7, 137.4, 137.3, 129.8, 128.7, 128.3, 127.5, 126.1, 124.6, 117.1, 40.3, 37.1, 21.0;

**HRMS** (ESI): calcd for C<sub>16</sub>H<sub>14</sub>NaO<sub>2</sub> [M+Na]<sup>+</sup> : *m/z* 261.0892, found 261.0893;

**HPLC** Diacel Chiralcel OD-H, hexane/propan-2-ol (95:5), 6.5 : 93.5 er, 0.8 mL min<sup>-1</sup>, t<sub>R</sub> = 14.84 (Minor) and 15.45 min (Major); Data were in accordance with previous results in the literature.<sup>5</sup>

**(R)-4-(*m*-tolyl)chroman-2-one (23)<sup>5</sup>**



5-((2-(Benzyl)oxy)phenyl)(*m*-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg, 0.046 mmol) was reacted under standard protocol to give the desired product as an off-white solid; (6.6 mg, 60% yield);

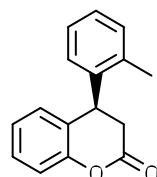
**IR** (film, cm<sup>-1</sup>) 2980, 2923, 2513, 2157, 2030, 1976, 1768 (C=O), 1607, 1586, 1485, 1454, 1279, 1213, 1175, 1161, 1132, 1108, 1032, 967, 919, 884, 752, 731, 701, 675;

**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>),  $\delta$  7.30 (1H, td, *J* = 8.1, 1.4 Hz, ArH), 7.24 (1H, t, *J* = 7.6 Hz, ArH), 7.17-7.03 (3H, m, ArH), 7.02-6.91 (3H, m, ArH), 4.31 (1H, app.t, *J* = 6.9 Hz, CH), 3.08 (1H, dd, *J* = 15.9, 6.2 Hz, CH), 3.01 (1H, dd, *J* = 15.9, 7.8 Hz, CH);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  167.7, 151.7, 140.3, 138.9, 129.0, 128.8, 128.5, 128.4, 128.3, 125.9, 124.6, 117.1, 40.7, 37.0, 21.5;

**HRMS** (ESI): calcd for  $C_{16}H_{14}NaO_2 [M+Na]^+$  :  $m/z$  261.0892, found 261.0878; **HPLC** Diacel Chiralcel OD-H, hexane/propan-2-ol (95:5), 3.5 : 96.5 er, 0.8 mL min<sup>-1</sup>,  $t_R$  = 13.04 (Minor) and 13.81 min (Major); Data were in accordance with previous results in the literature.<sup>5</sup>

**(R)-4-(o-tolyl)chroman-2-one (24)**



5-((2-(Benzylxy)phenyl)(o-tolyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg, 0.046 mmol) was reacted under standard protocol to give the desired product as an off-white solid; (5.7 mg, 52% yield);

**mp** (EtOAc/petrol) 154-156 °C;

**IR** (film, cm<sup>-1</sup>)  $\nu$  2980, 2925, 1768 (C=O), 1607, 1586, 1485, 1453, 1417, 1380, 1344, 1279, 1212, 1175, 1161, 1131, 1031, 919, 869, 886, 792, 751, 700;

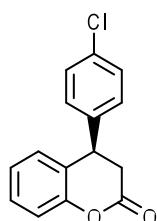
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>),  $\delta$  7.34-7.27 (1H, m, ArH), 7.26-7.23 (2H, m, ArH), 7.20 (1H, dd,  $J$  = 7.0, 1.8 Hz, ArH), 7.15 (1H, dd,  $J$  = 6.4, 1.6 Hz, ArH), 7.06 (1H, td,  $J$  = 7.5, 1.2 Hz, ArH), 6.91 (1H, dd,  $J$  = 7.1, 1.8 Hz, ArH), 6.84 (1H, br.d,  $J$  = 7.6 Hz, ArH), 4.60 (1H, dd,  $J$  = 8.8, 6.1 Hz, CH), 3.04 (1H, dd,  $J$  = 15.6, 6.1 Hz, CH), 2.96 (1H, dd,  $J$  = 15.6, 8.8 Hz, CH), 2.41 (3H, s, ArCH<sub>3</sub>);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>)  $\delta$  167.9, 152.1, 138.0, 136.0, 128.7, 128.0, 127.6, 127.0, 126.9, 125.9, 124.8, 117.1, 36.5, 36.0, 29.7, 19.6;

**HRMS** (ESI): calcd for  $C_{16}H_{13}O_2 [M-H]^-$  :  $m/z$  237.0916, found 237.0903;

**HPLC** Diacel Chiralcel OD-H, hexane/propan-2-ol (95:5), 72 : 28 er, 0.8 mL min<sup>-1</sup>,  $t_R$  = 15.38 (Major) and 16.89 min (Minor).

**(R)-4-(4-chlorophenyl)chroman-2-one (25)**



5-((2-(Benzylxy)phenyl)(4-chlorophenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg, 0.044 mmol) was reacted under standard protocol to give the desired product as an off-white solid; (6.8 mg, 61% yield);

**mp** (EtOAc/petrol) 124-127 °C (lit. (methanol) 115-117 °C<sup>6</sup>);

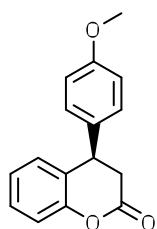
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.41-7.28 (3H, m, ArH), 7.21-7.05 (4H, m, ArH), 6.97 (1H, br.d, J = 7.5 Hz, ArH), 4.33 (1H, app.t, J = 6.8 Hz, CH), 3.08 (1H, dd, J = 15.8, 6.0 Hz, CH), 2.98 (1H, dd, J = 15.8, 7.7 Hz, CH);

**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 167.2, 151.7, 138.8, 133.6, 129.4, 129.1, 129.0, 128.2, 125.2, 124.8, 117.3, 40.2, 37.0;

**HRMS** (ESI): calcd for C<sub>15</sub>H<sub>11</sub>ClNaO<sub>2</sub> [M+Na]<sup>+</sup> : *m/z* 281.0345, found 281.0342;

**HPLC** Diacel Chiralcel OB-H, hexane/propan-2-ol (90:10), 1.5 : 98.5 er, 1.0 mL min<sup>-1</sup>, t<sub>R</sub> = 19.20 (Minor) and 25.33 min (Minor).

**(R)-4-(4-methoxyphenyl)-3,4-dihydrocoumarin (26)<sup>7</sup>**



5-((2-(Benzylxy)phenyl)(4-methoxyphenyl)methyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (20 mg, 0.045 mmol) was reacted under standard protocol to give the desired product as an off-white solid; (5.1 mg, 45% yield);

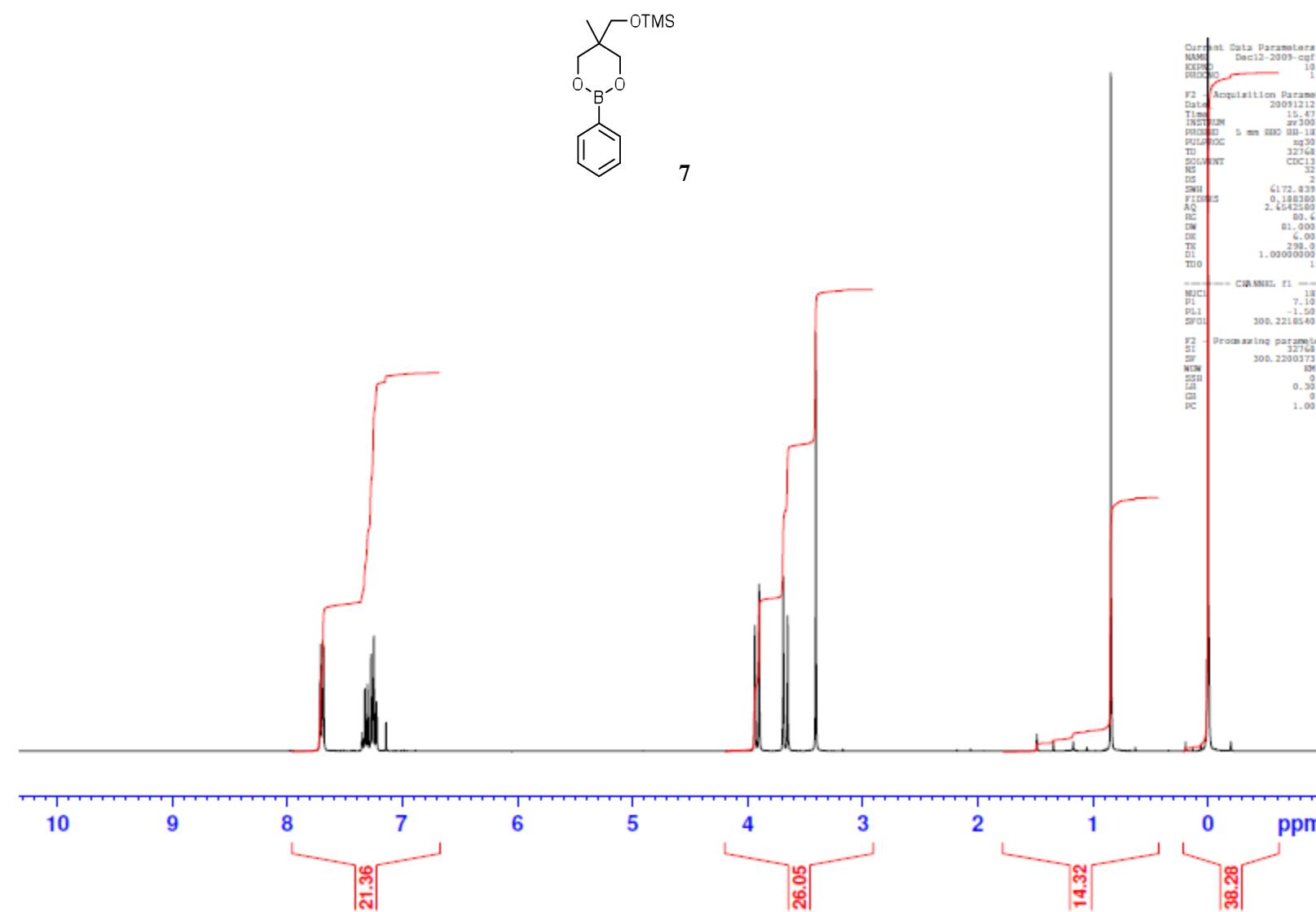
**mp** (EtOAc/petrol) 130-133 °C (lit. (CH<sub>2</sub>Cl<sub>2</sub>/petrol) 137-139 °C<sup>18</sup>);

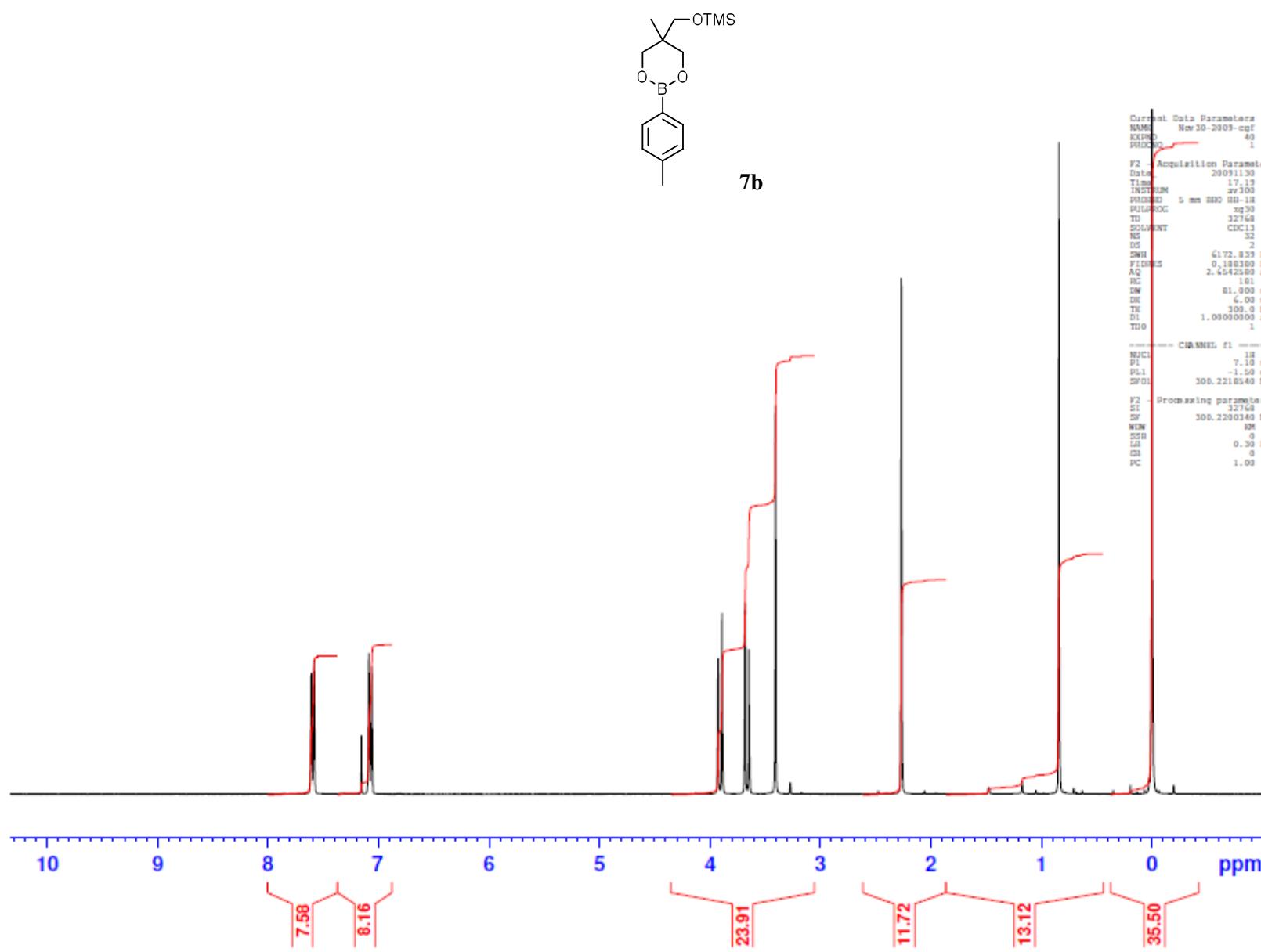
**<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>), δ 7.29 (1H, tdd, J = 7.9, 1.6, 0.3 Hz, ArH), 7.14-7.06 (4H, m, ArH), 6.98 (1H, br.d, J = 7.4 Hz, ArH), 6.87 (2H, app d, J = 8.8 Hz, ArH), 4.30 (1H, t, J = 6.9 Hz, CH), 3.79 (3H, s, OCH<sub>3</sub>), 3.06 (1H, dd, J = 15.8, 6.0 Hz, CH), 2.98 (1H, dd, J = 15.8, 7.9 Hz, CH);

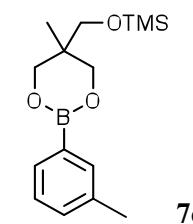
**<sup>13</sup>C-NMR** (75.5 MHz, CDCl<sub>3</sub>) δ 167.8, 159.0, 151.7, 132.2, 128.7, 128.6, 128.3, 126.2, 124.6, 117.1, 114.5, 55.3, 39.9, 37.2;

**HRMS (ESI):** calcd for  $C_{16}H_{13}NO_4 [M-H]^-$  :  $m/z$  253.0865, found 253.0858;

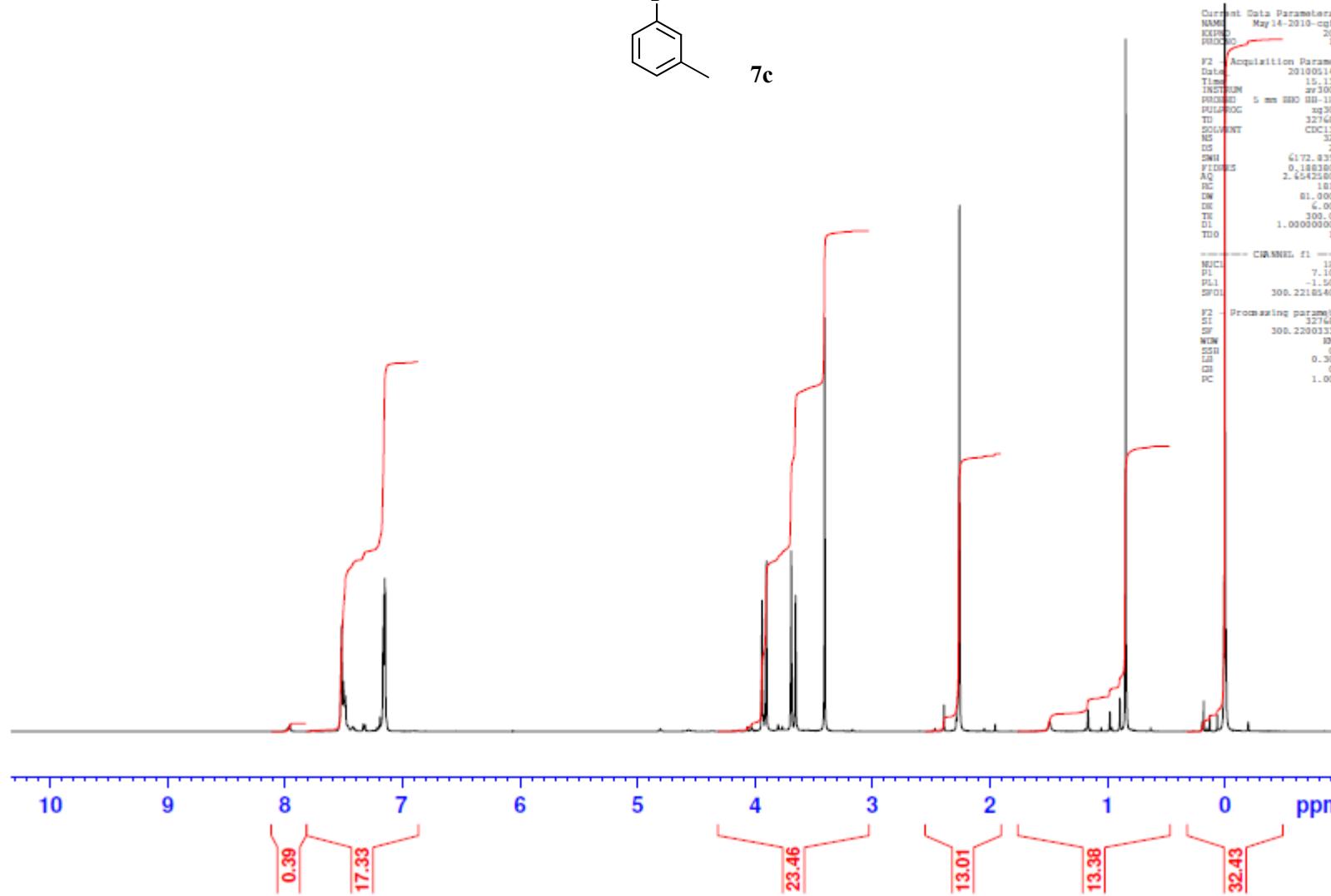
**HPLC** Diacel Chiralcel OJ, hexane/propan-2-ol (95:5), 89 : 11 er, 0.5 mL min<sup>-1</sup>,  $t_R$  = 35.90 (Major) and 38.49 min (Minor). Data were in accordance with previous results in the literature.<sup>7</sup>

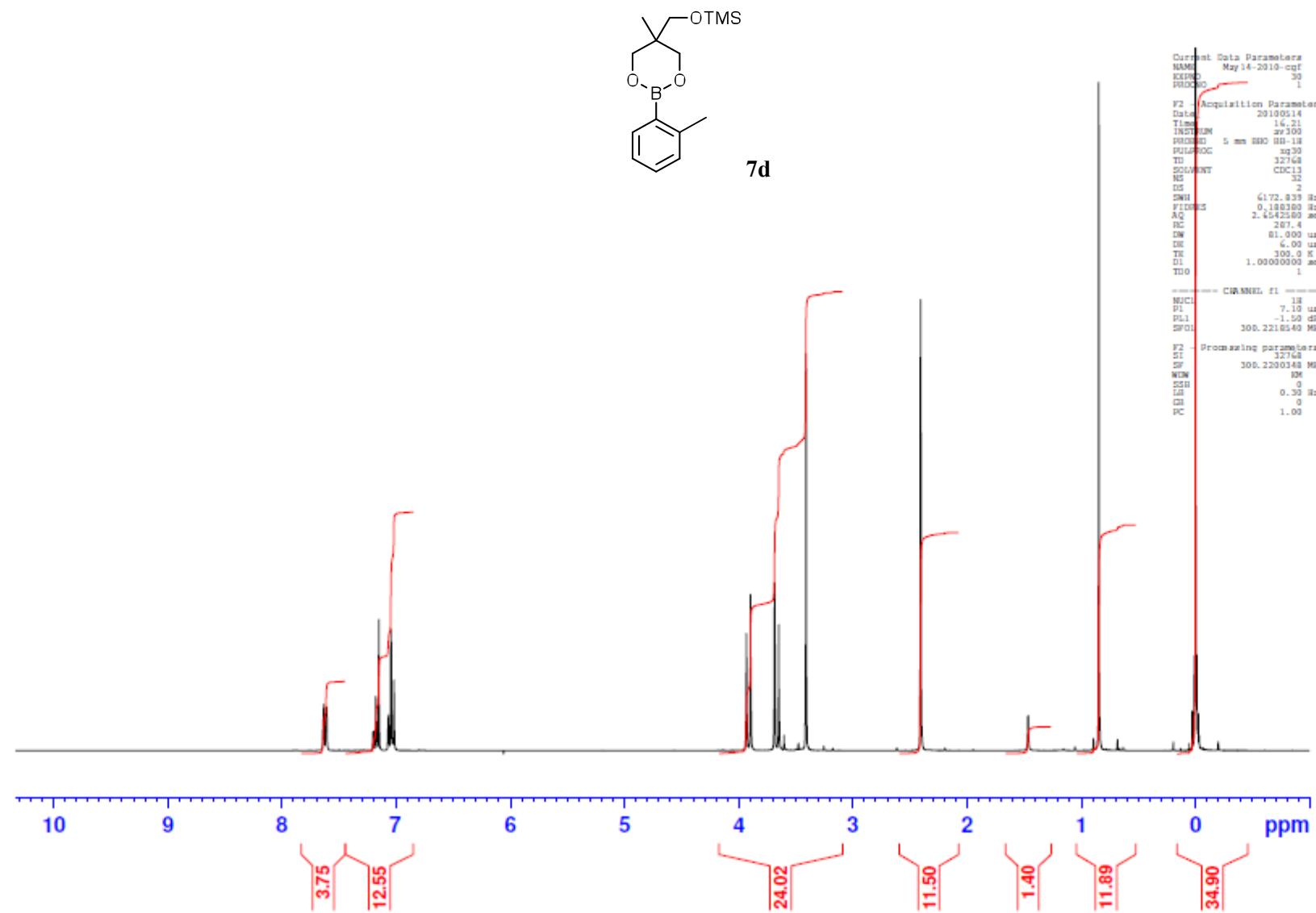


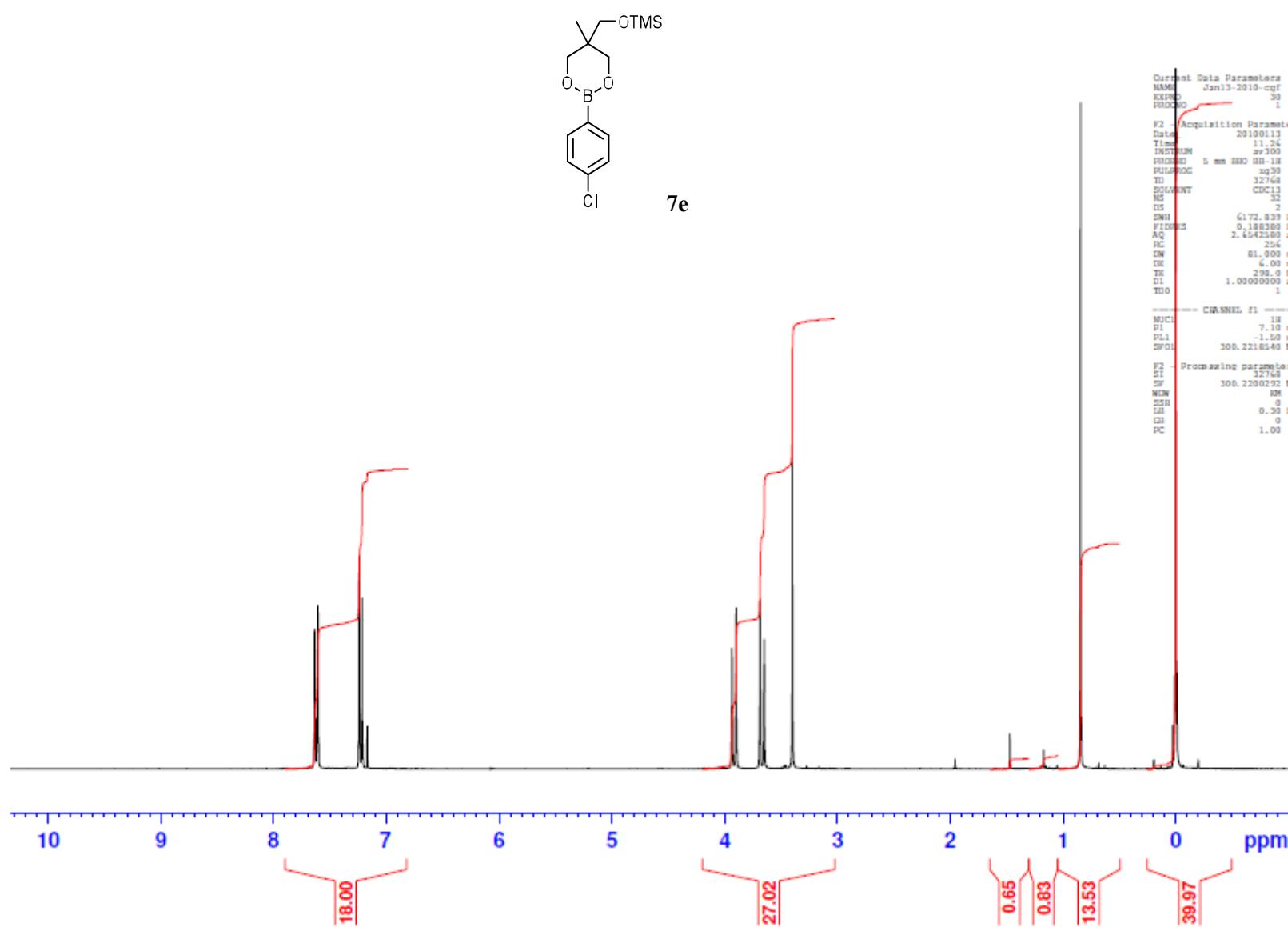


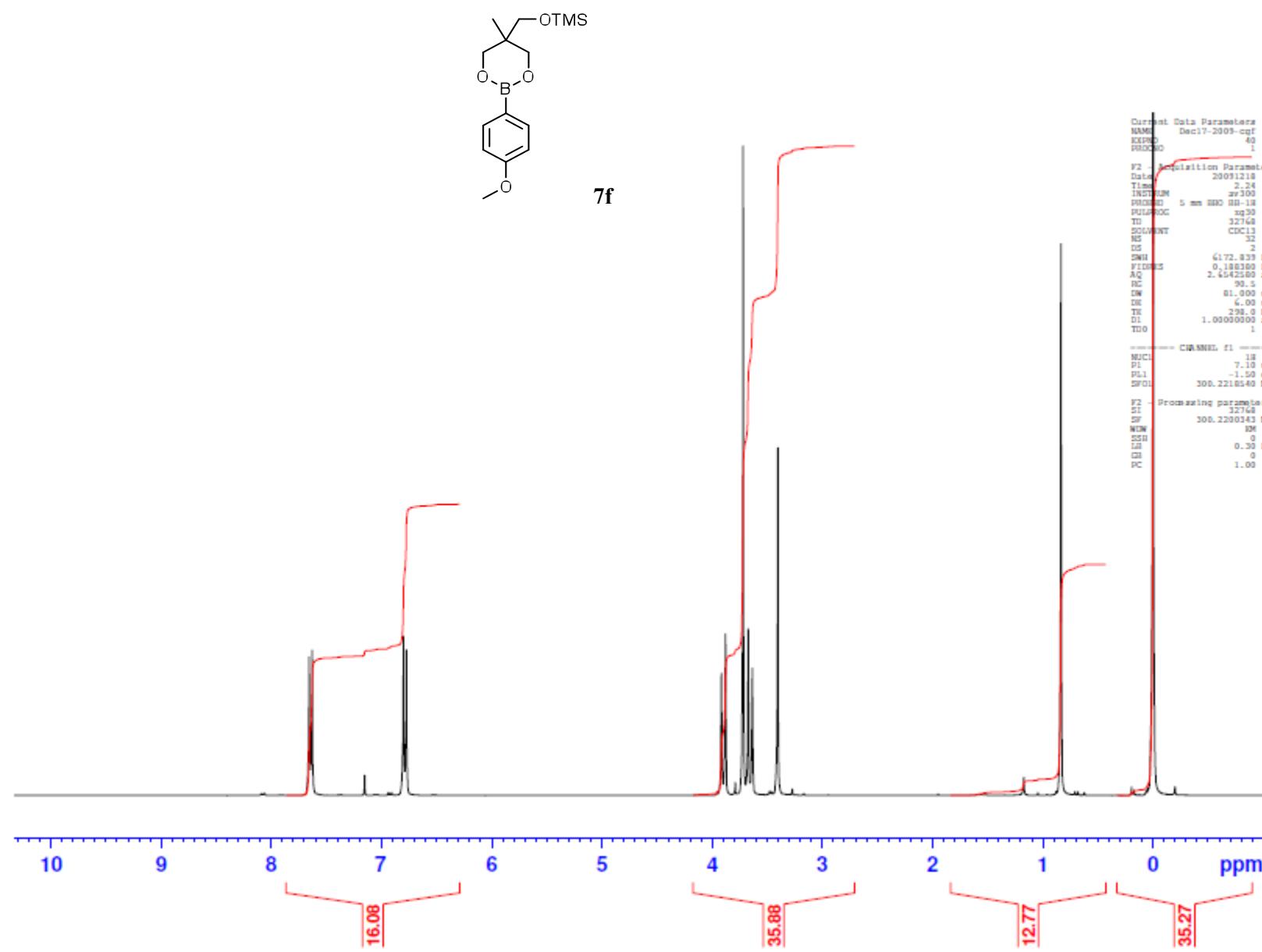


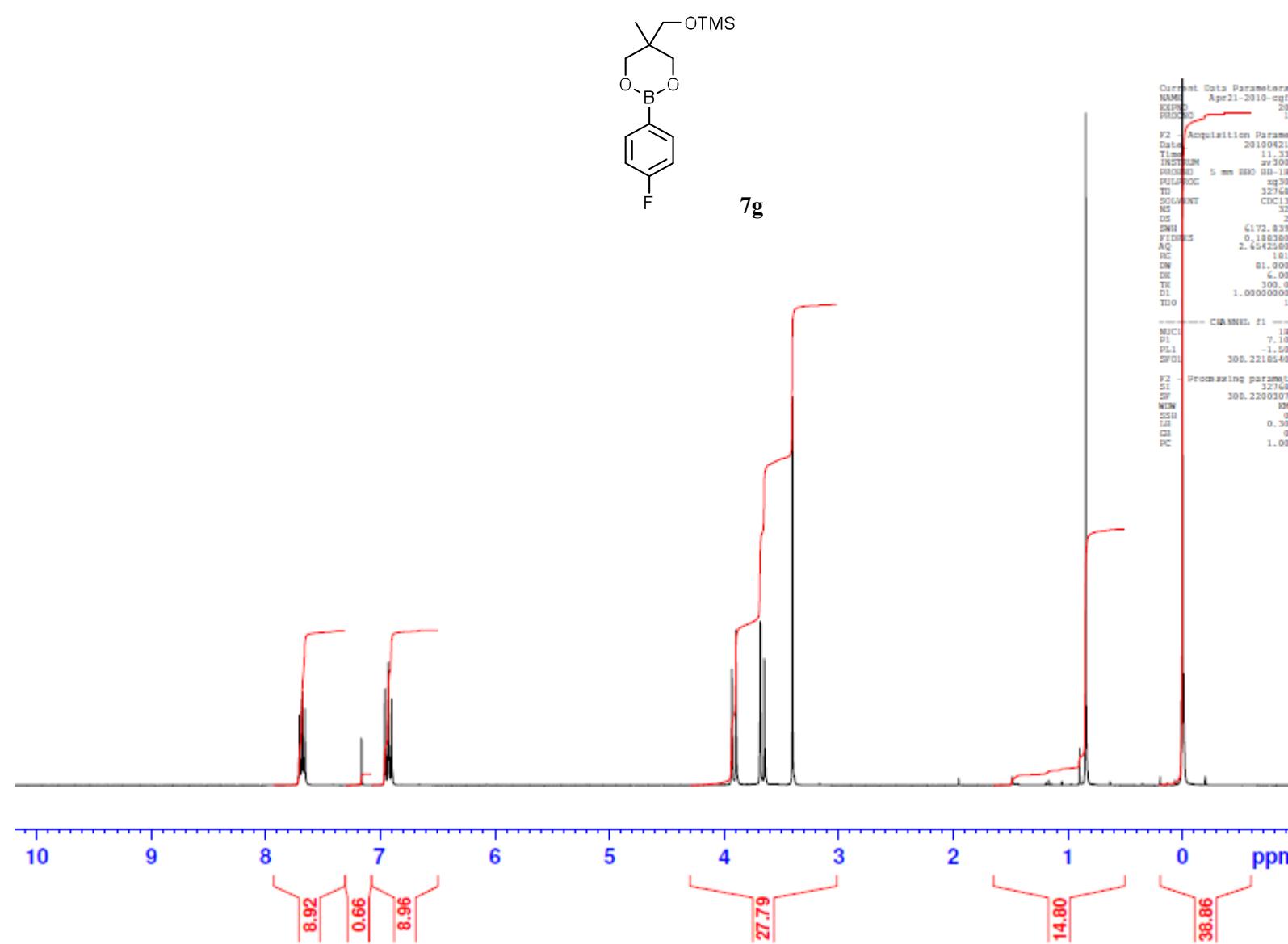
7c

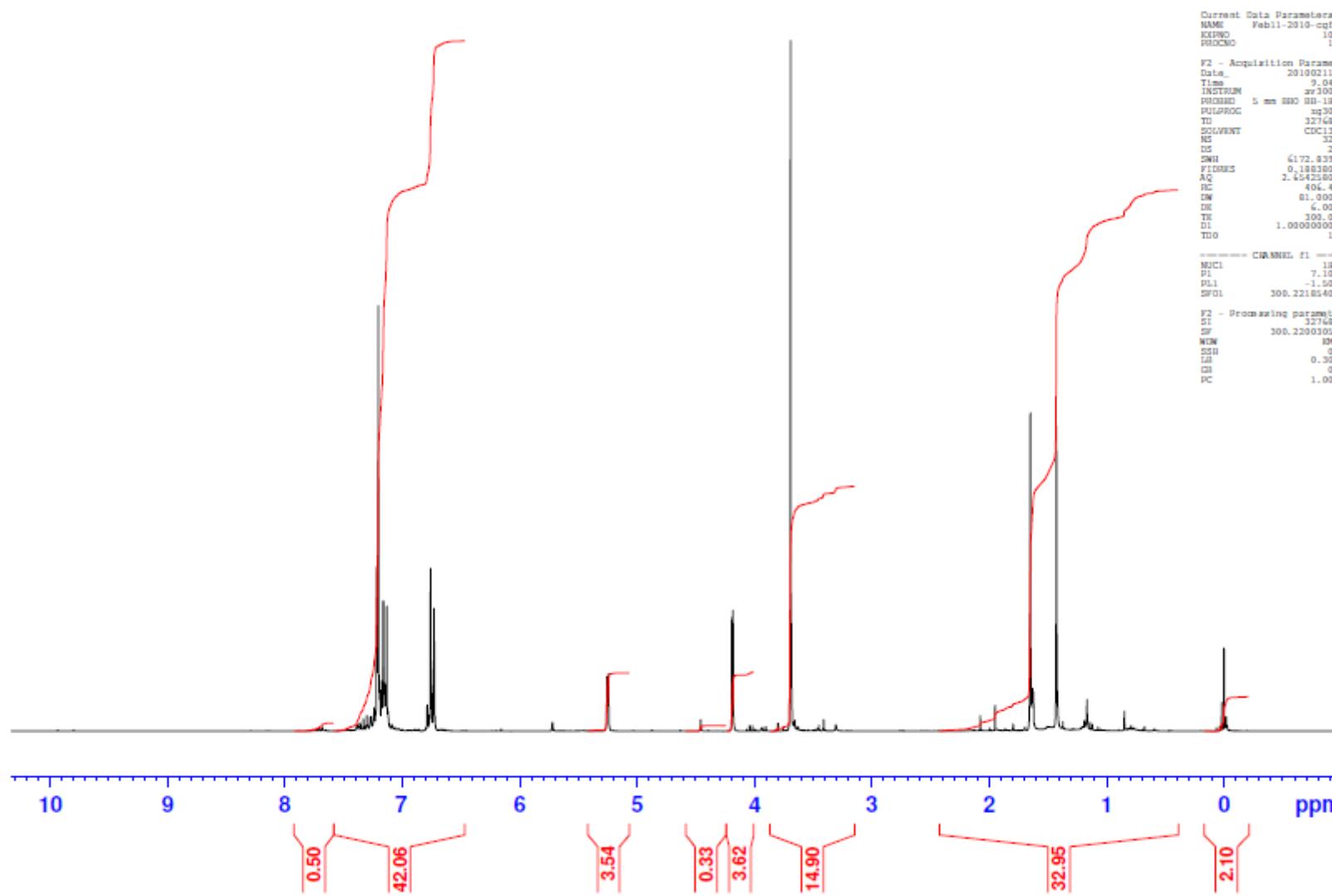
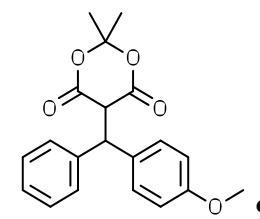


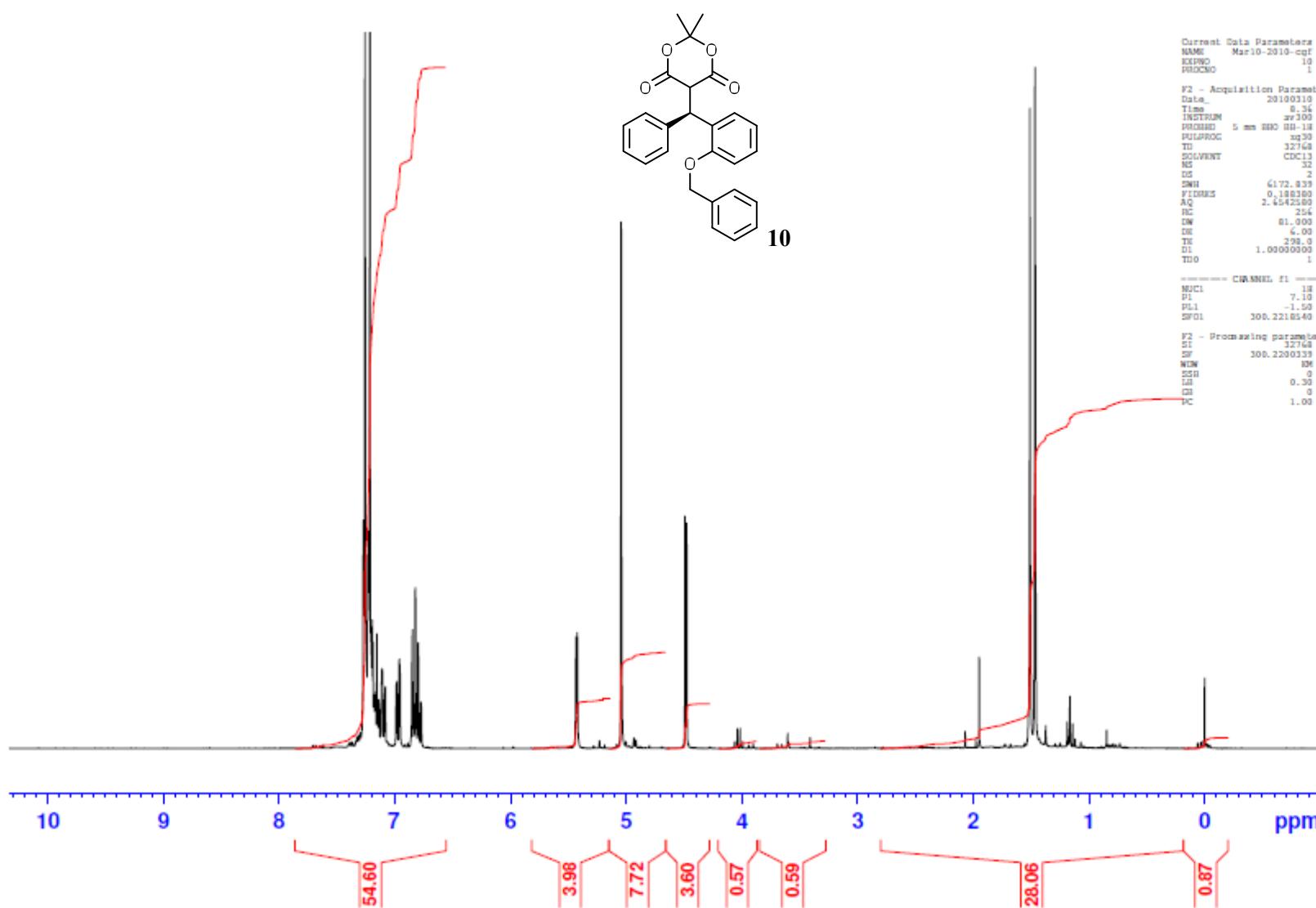


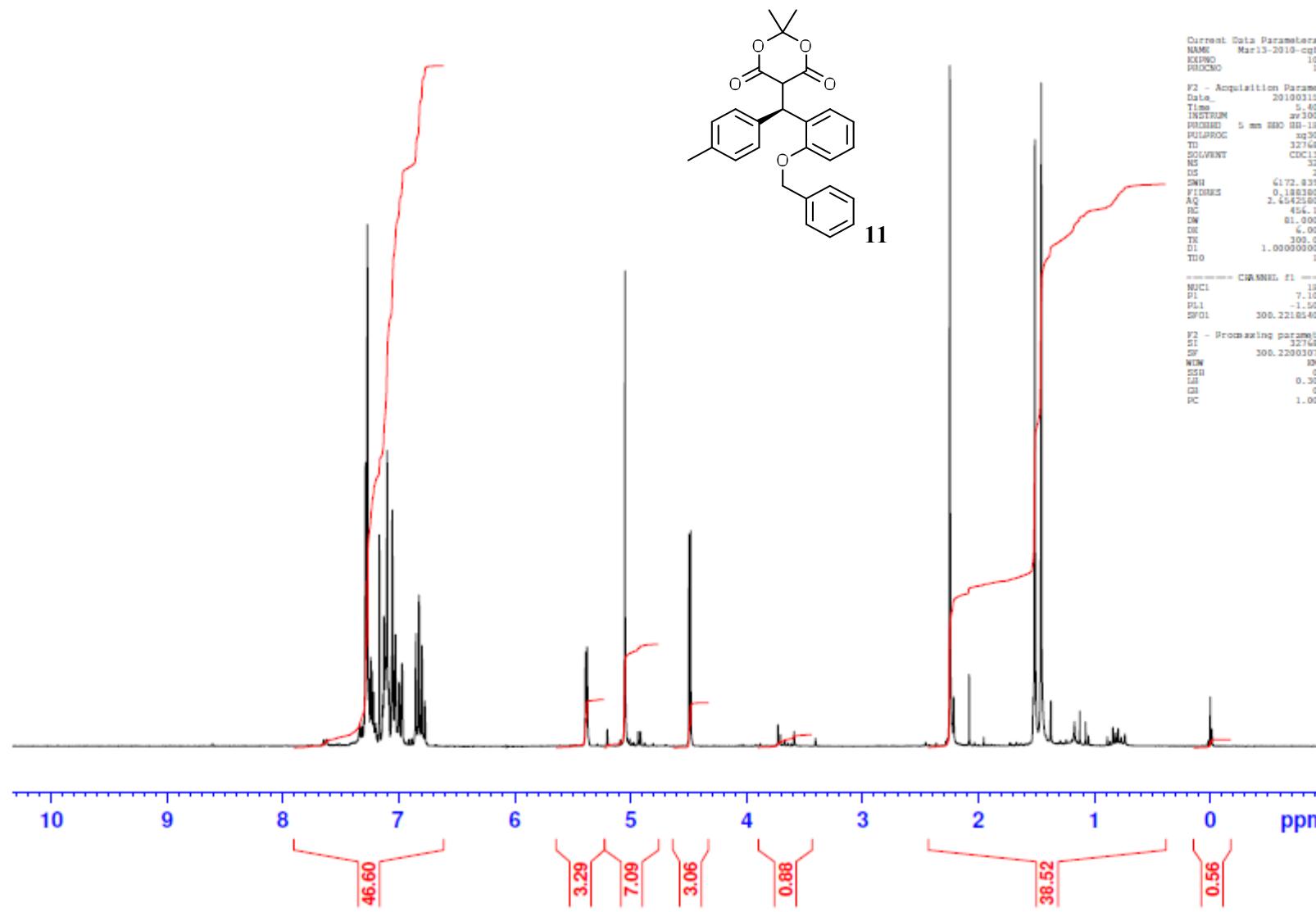


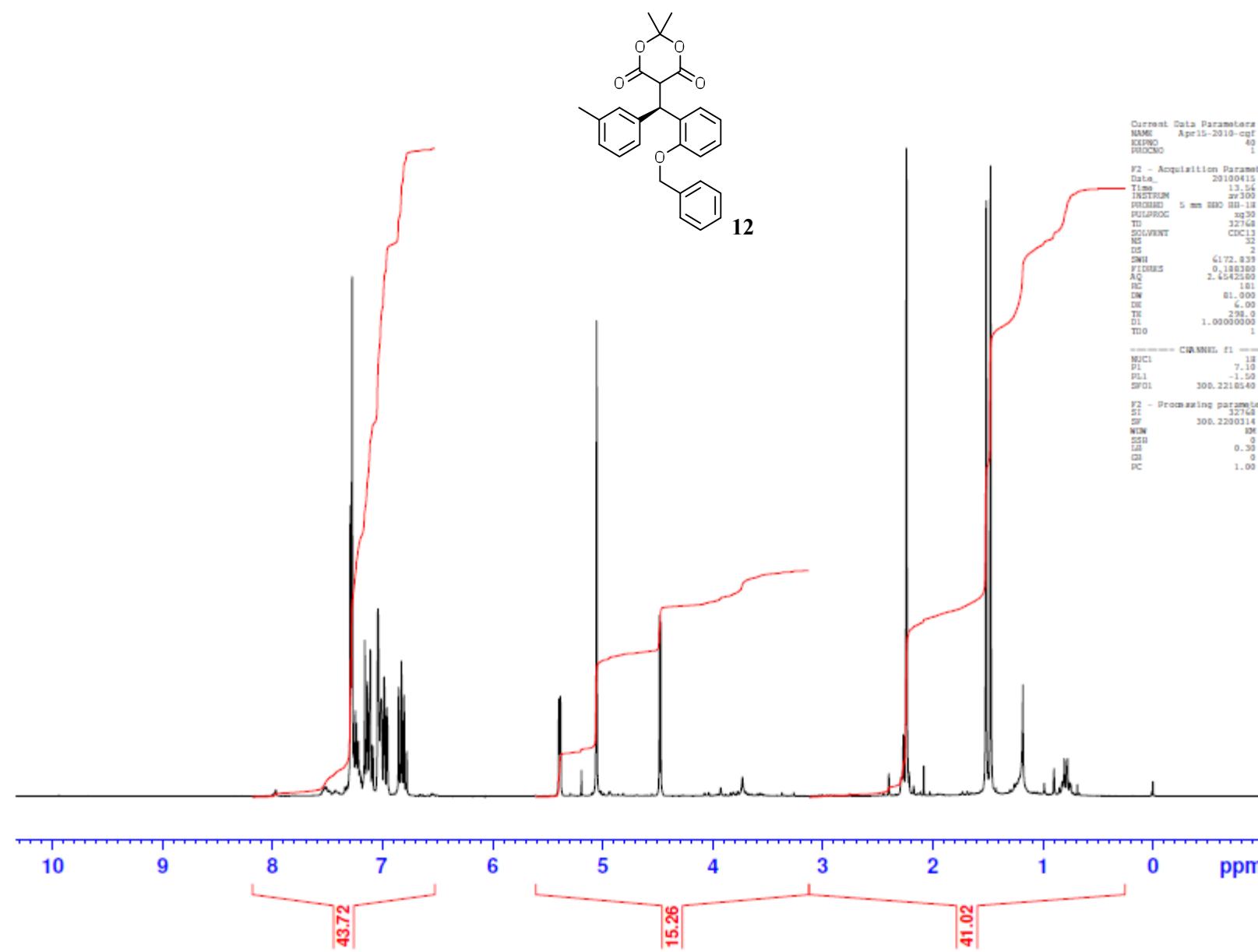


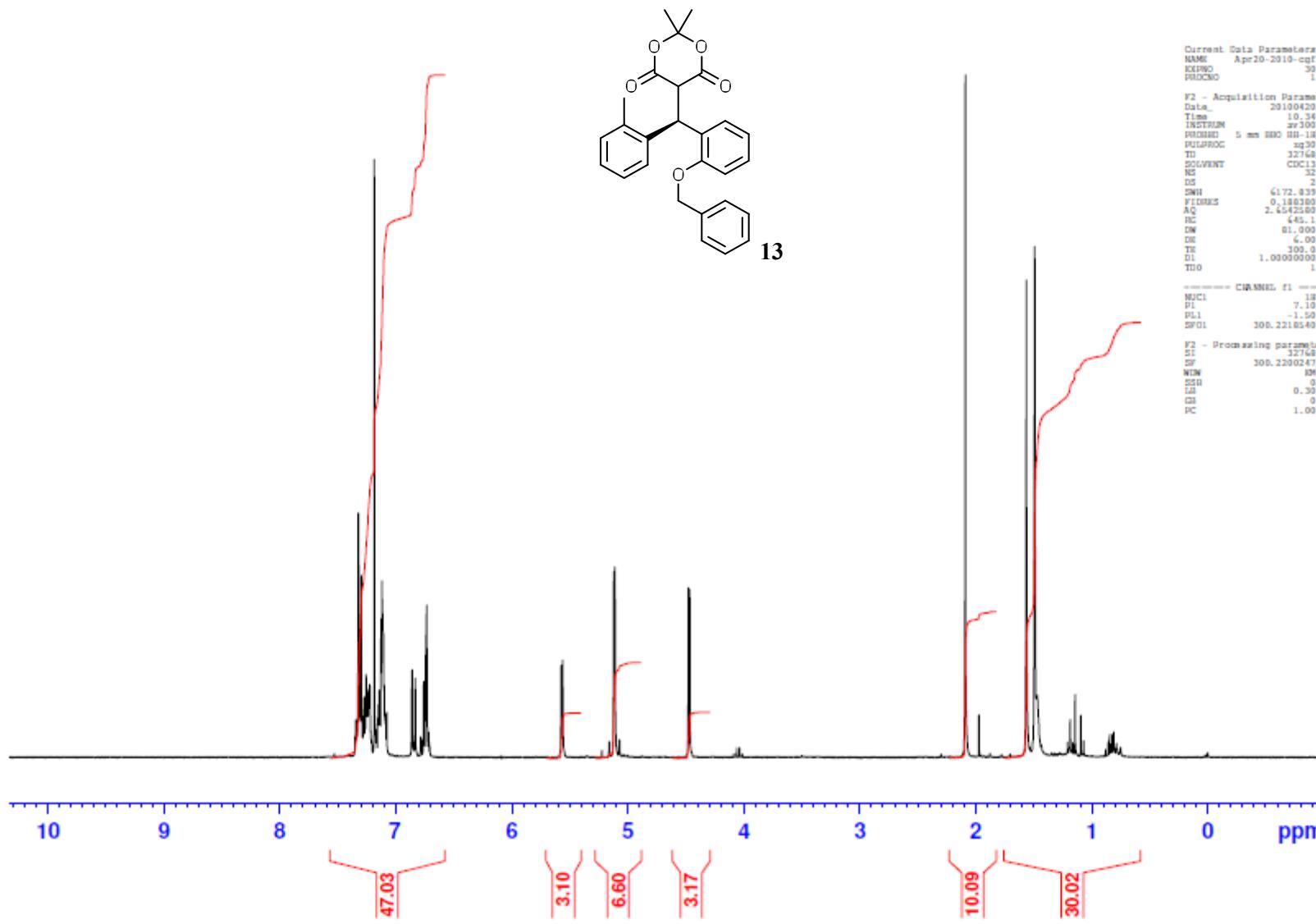


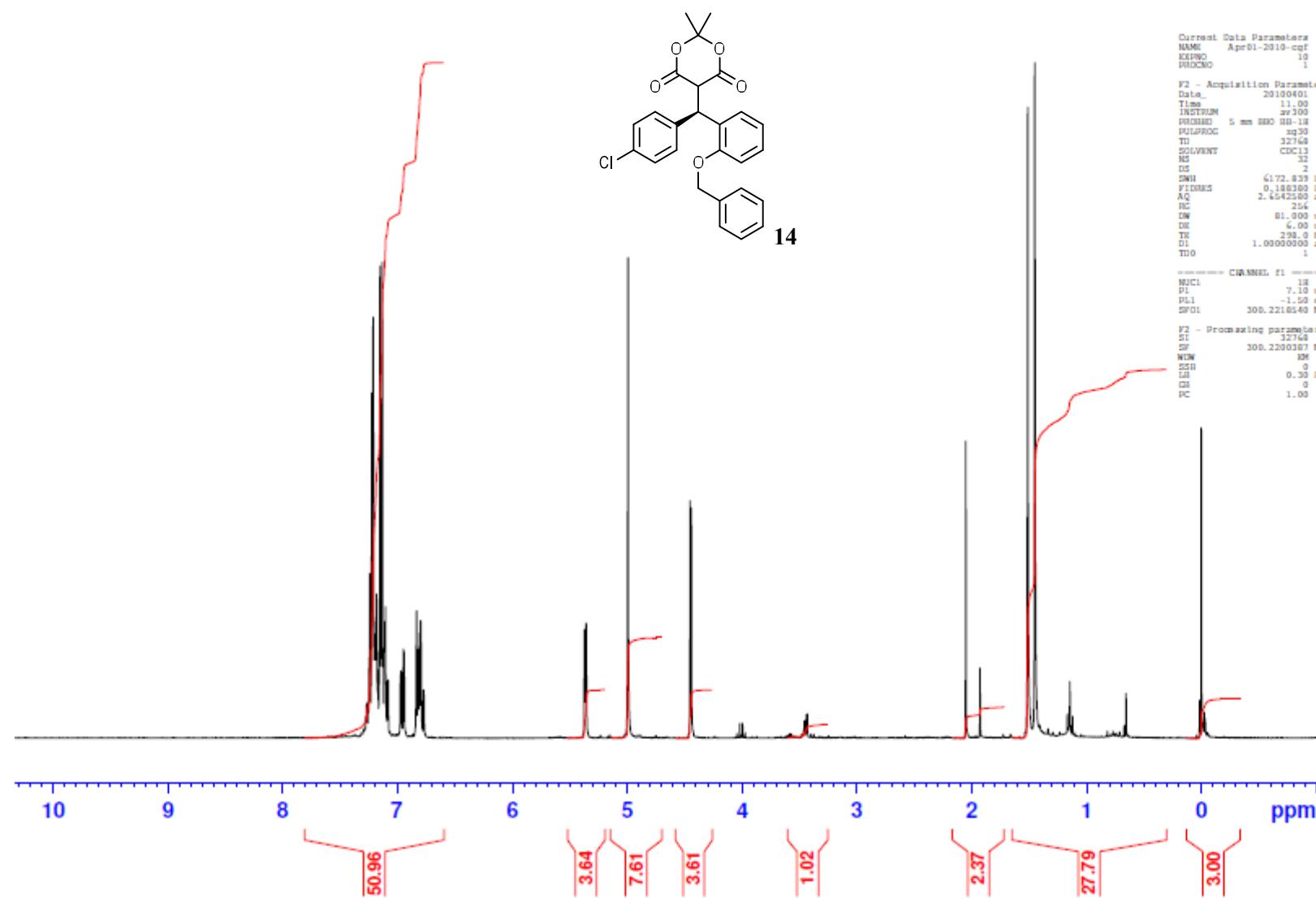


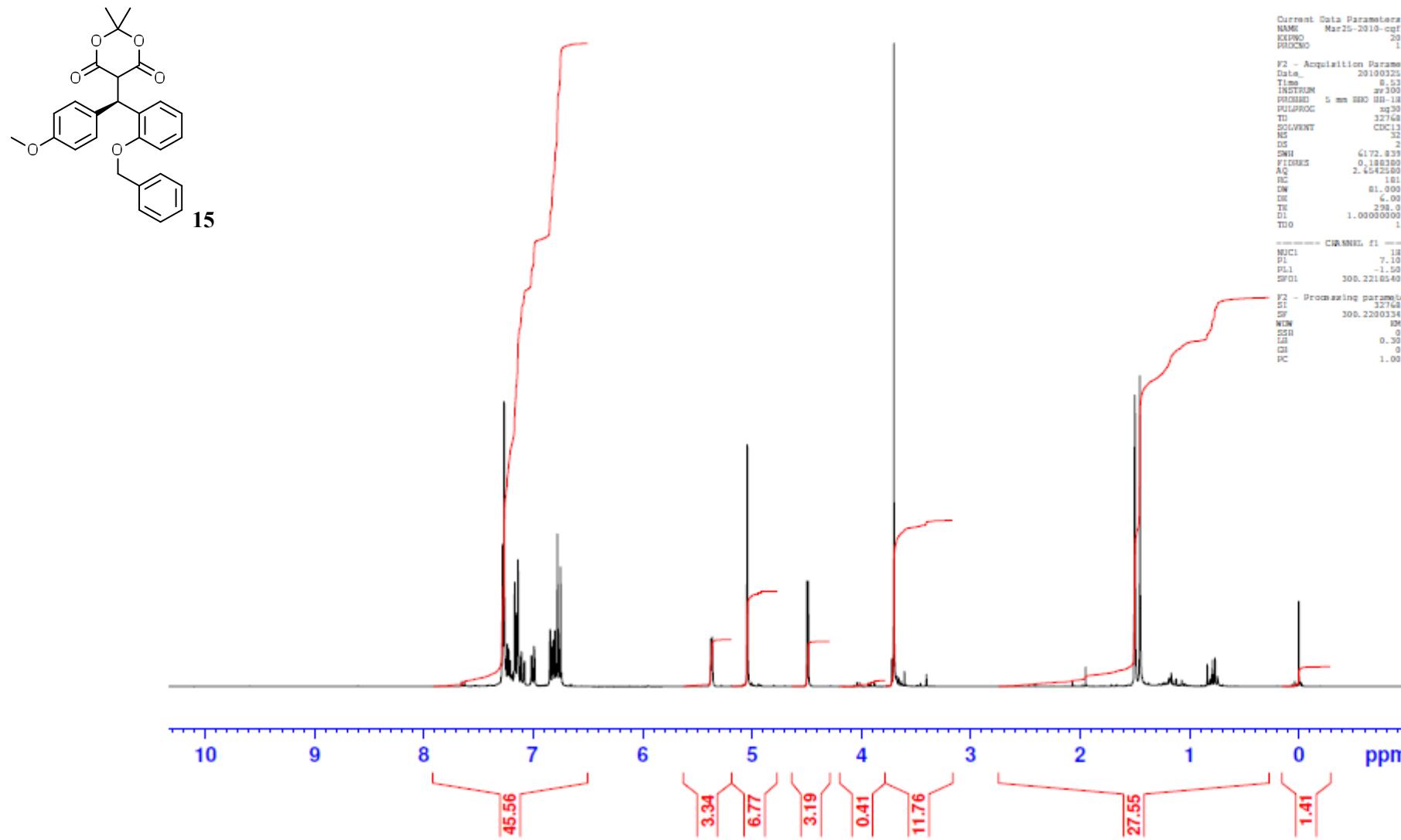


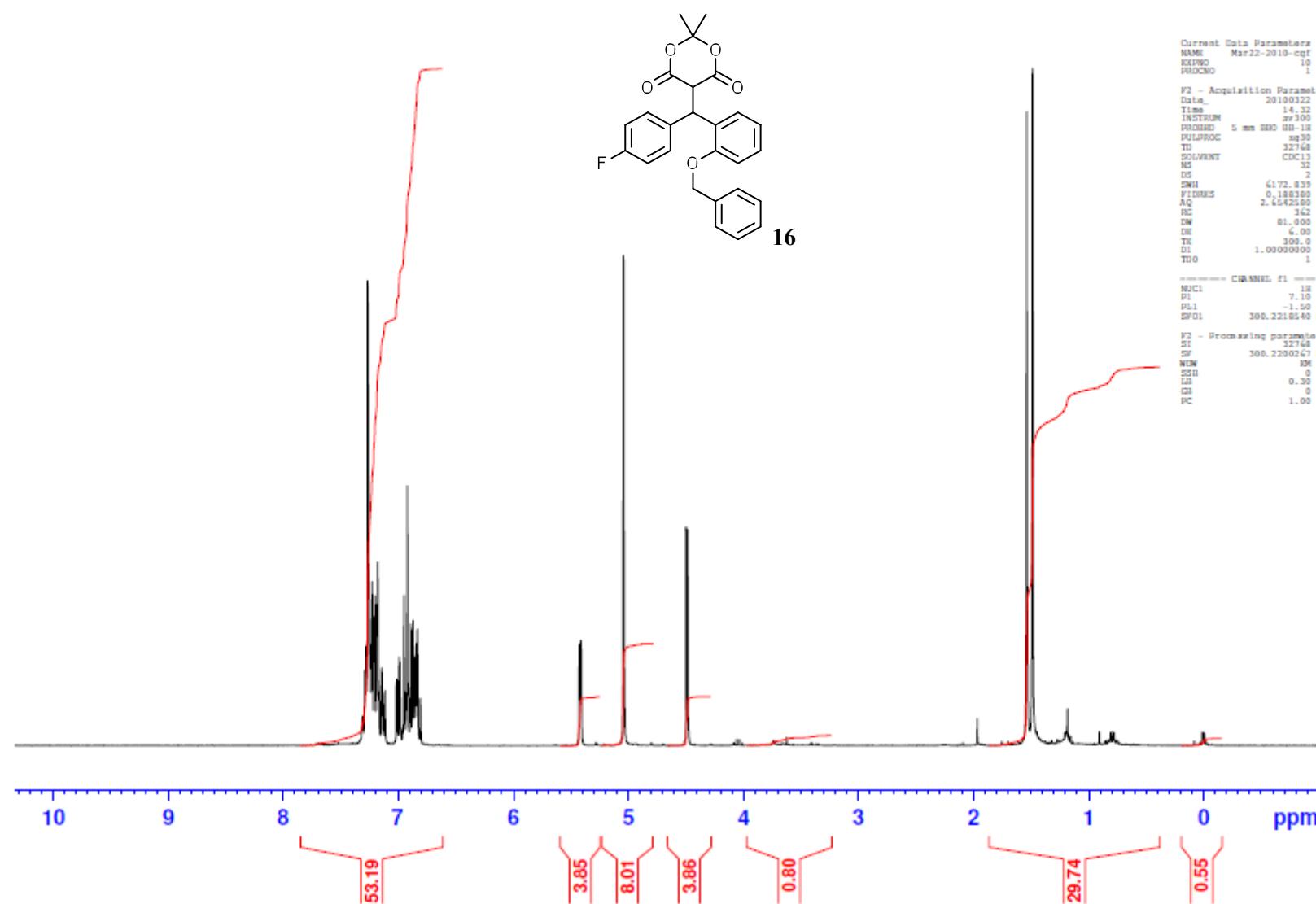


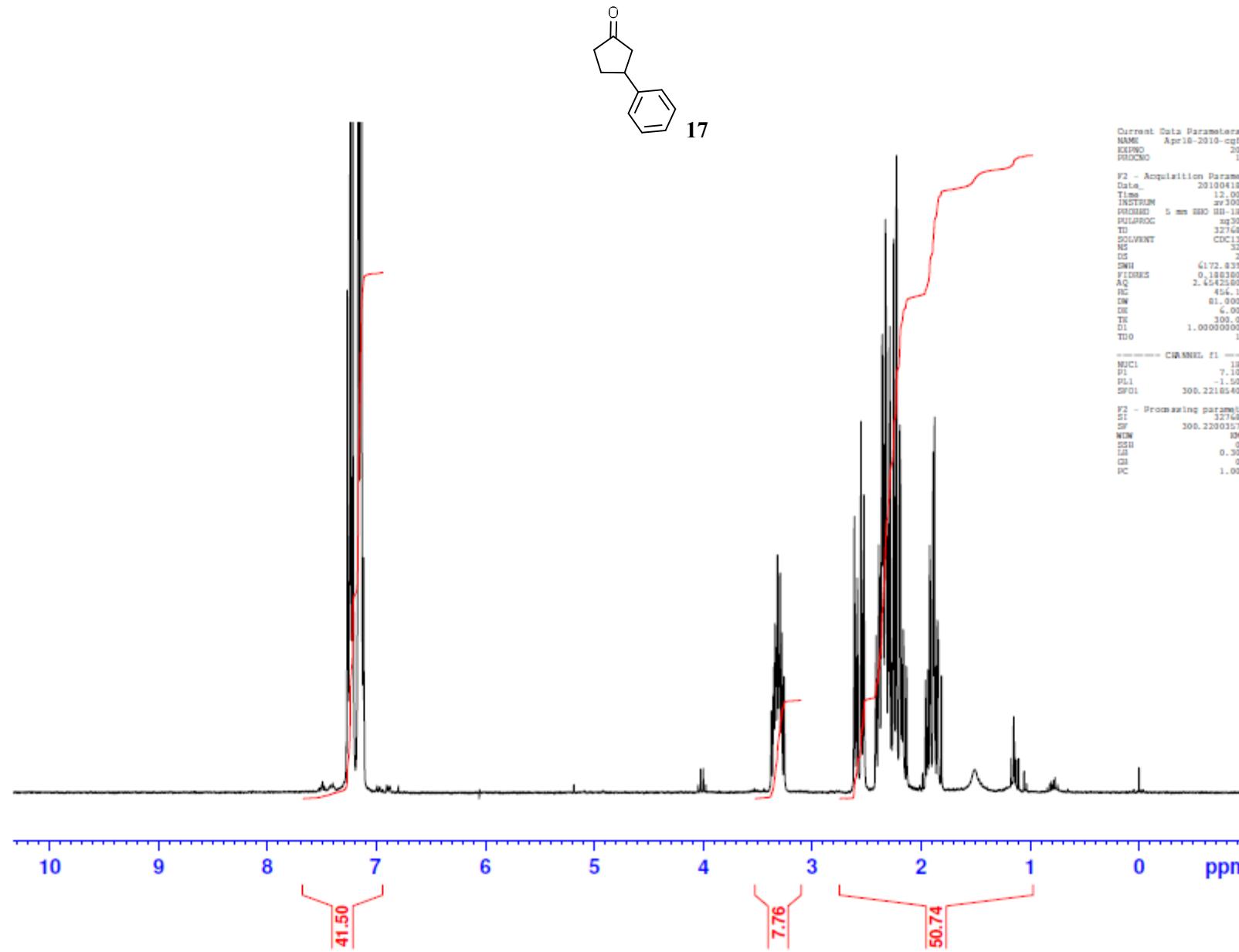


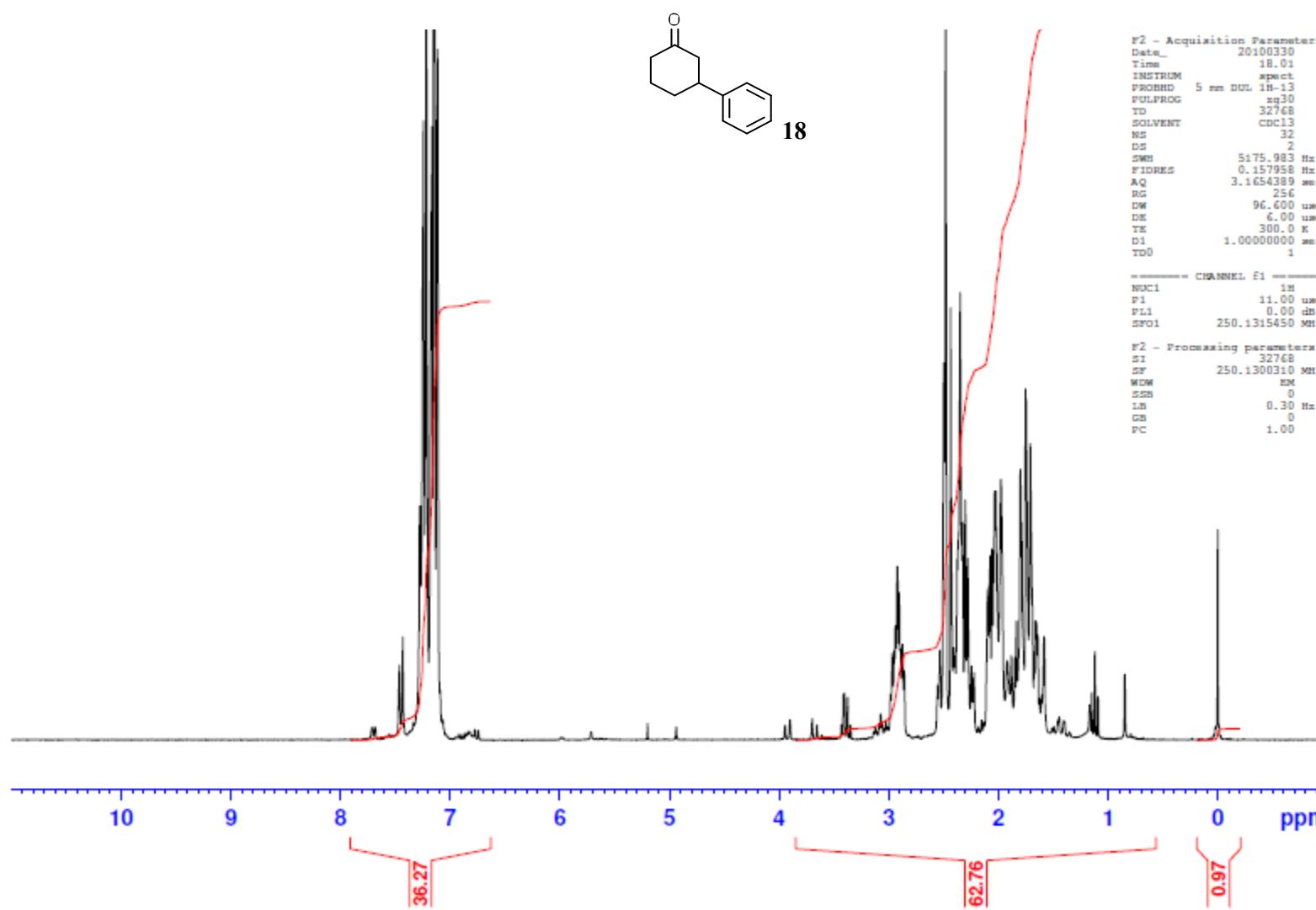


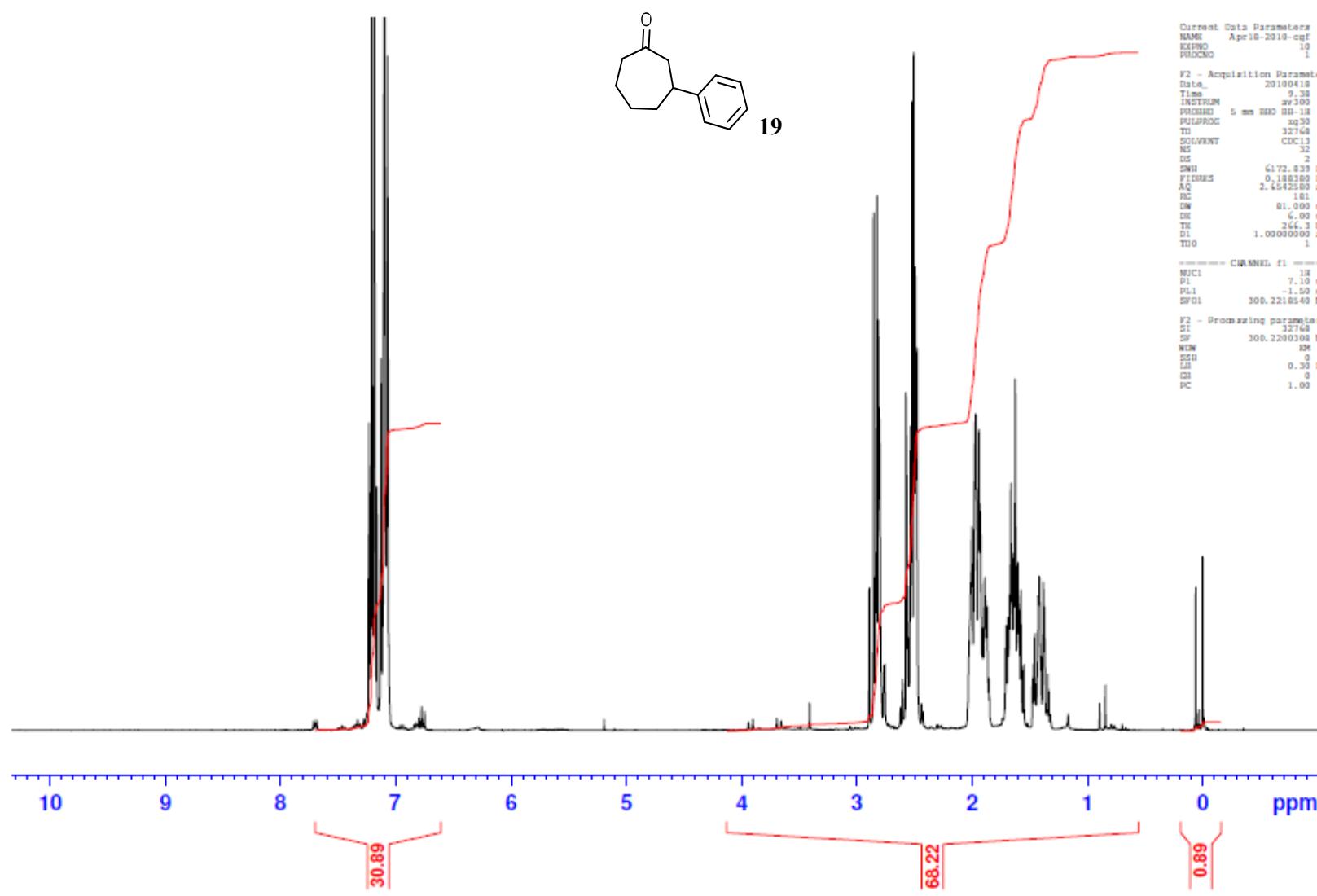


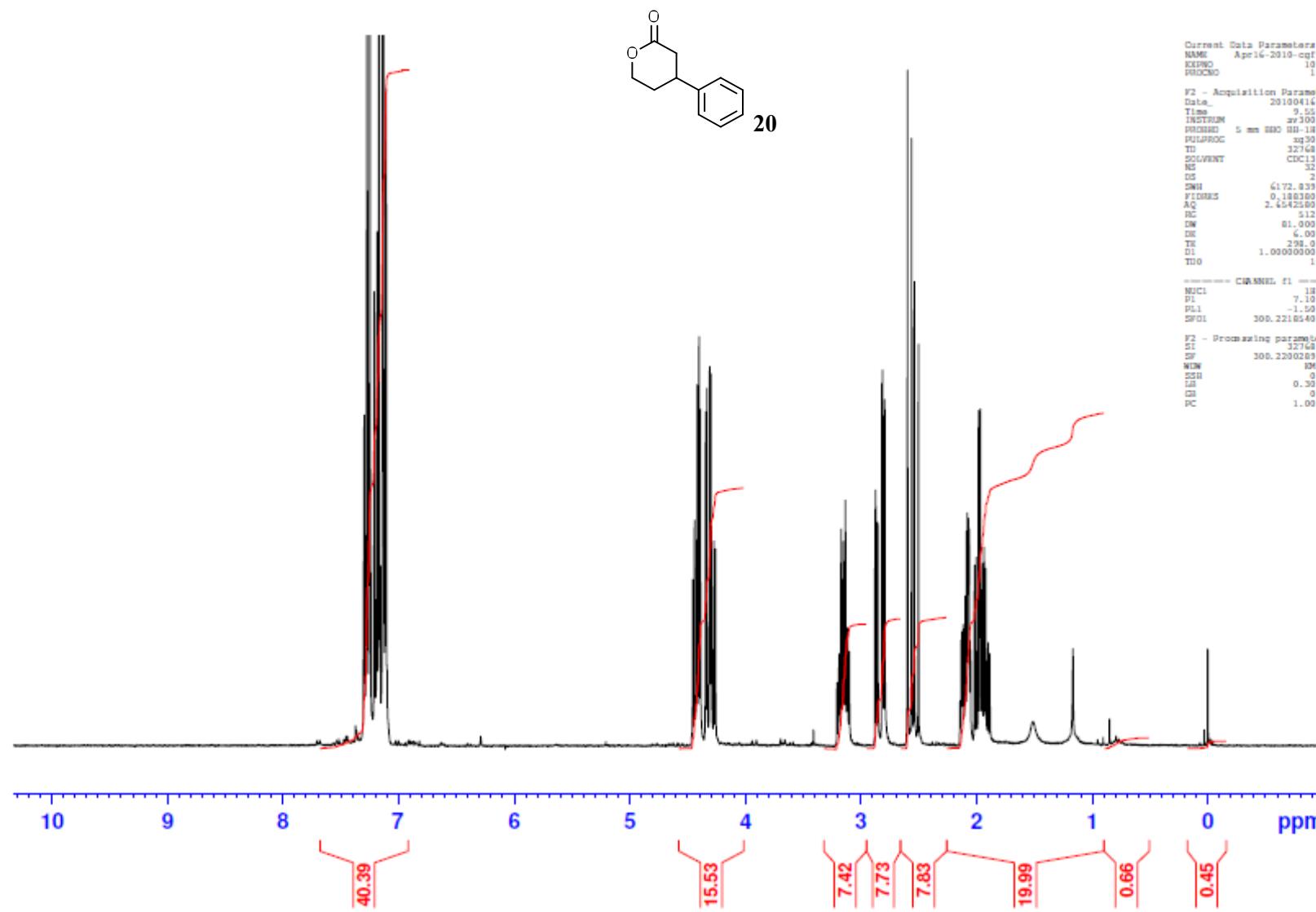


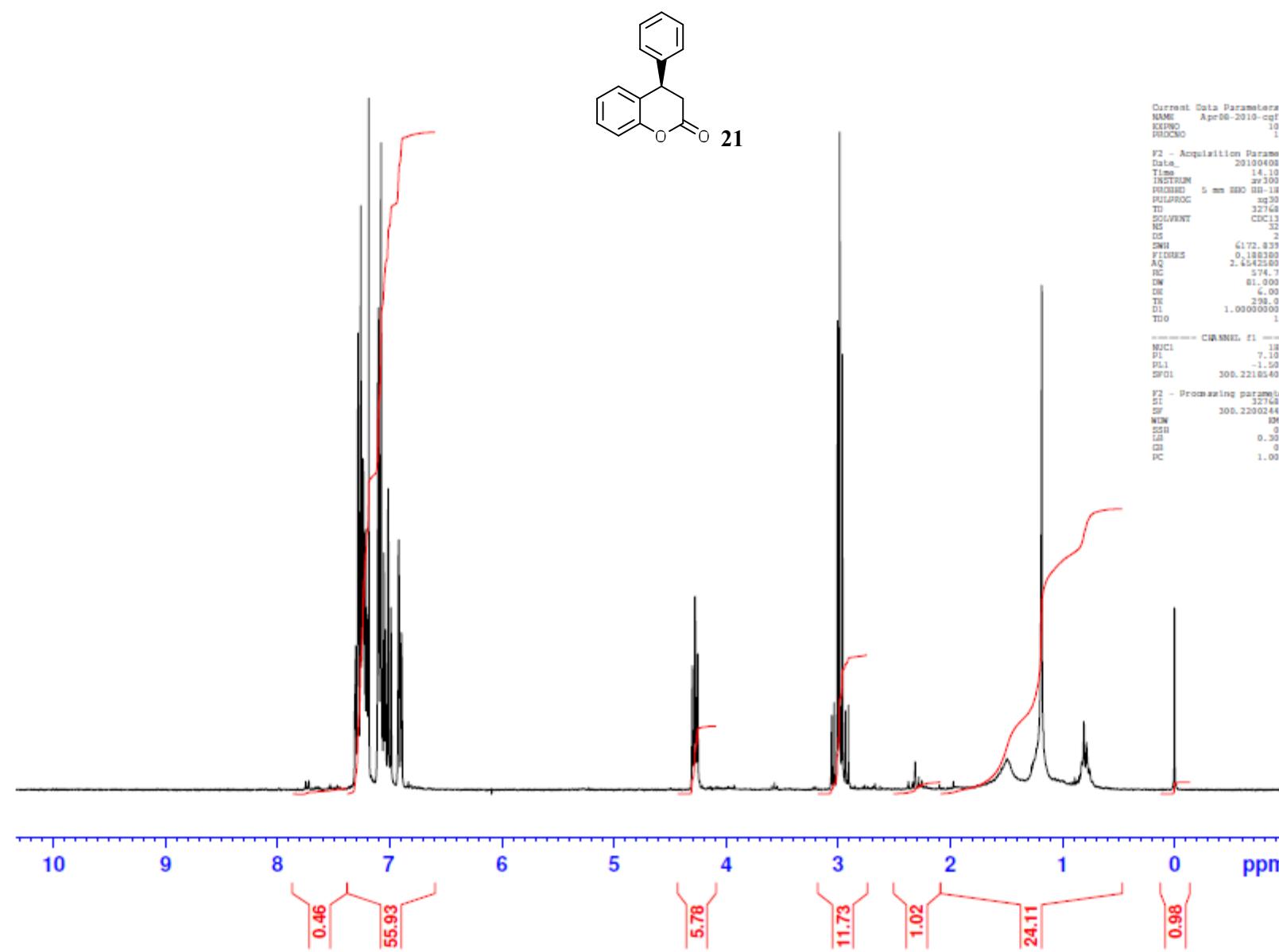


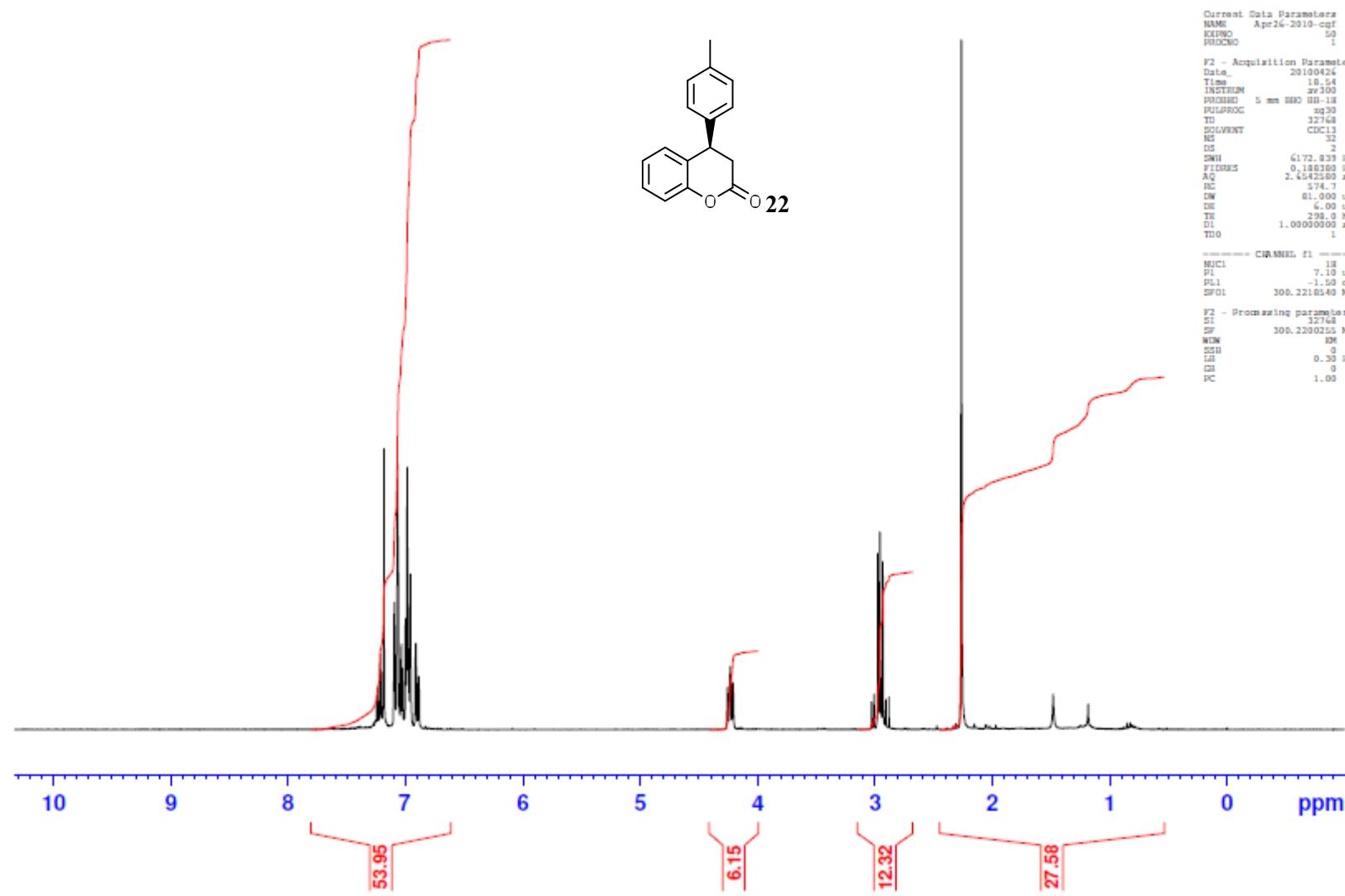


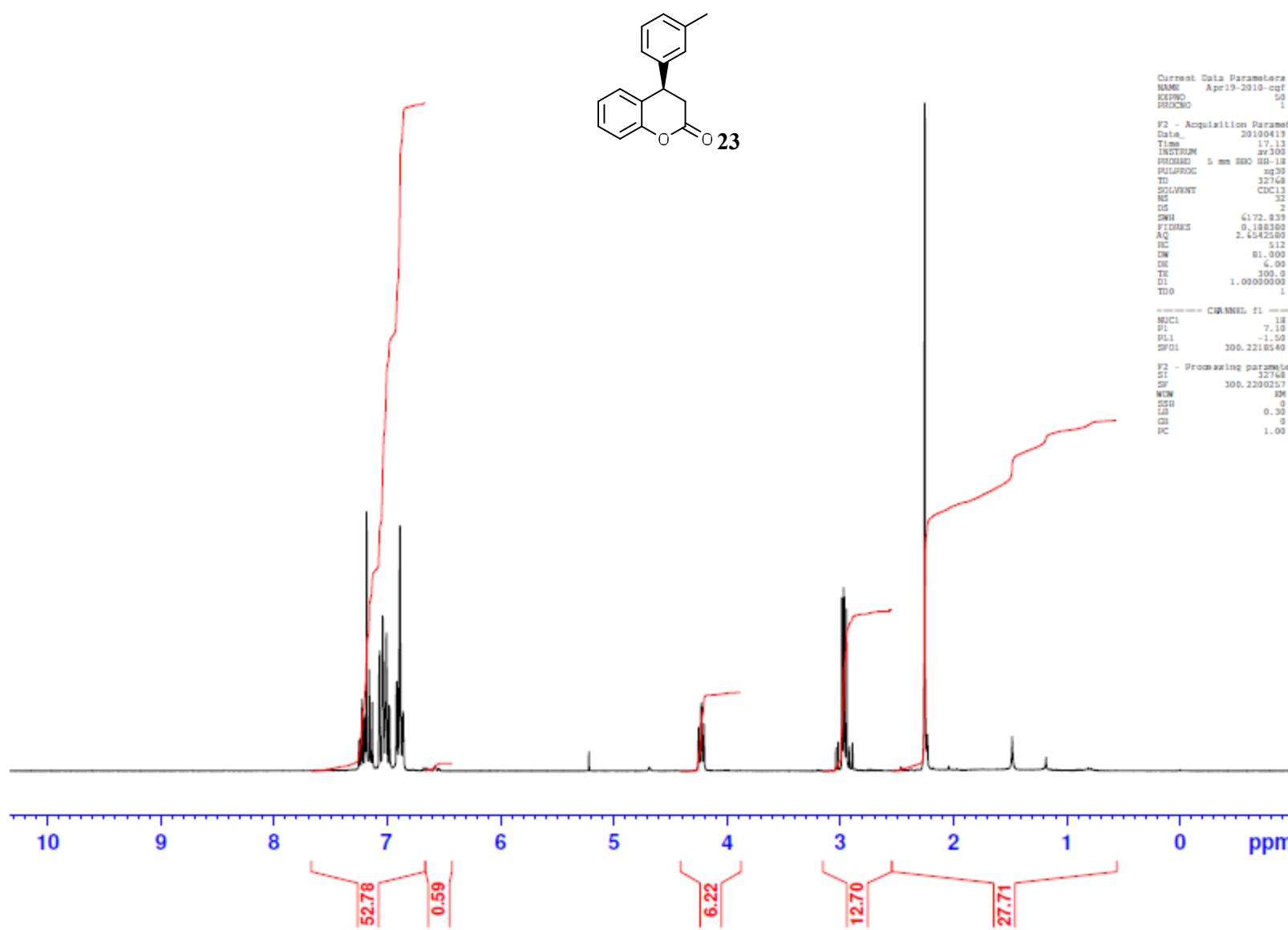


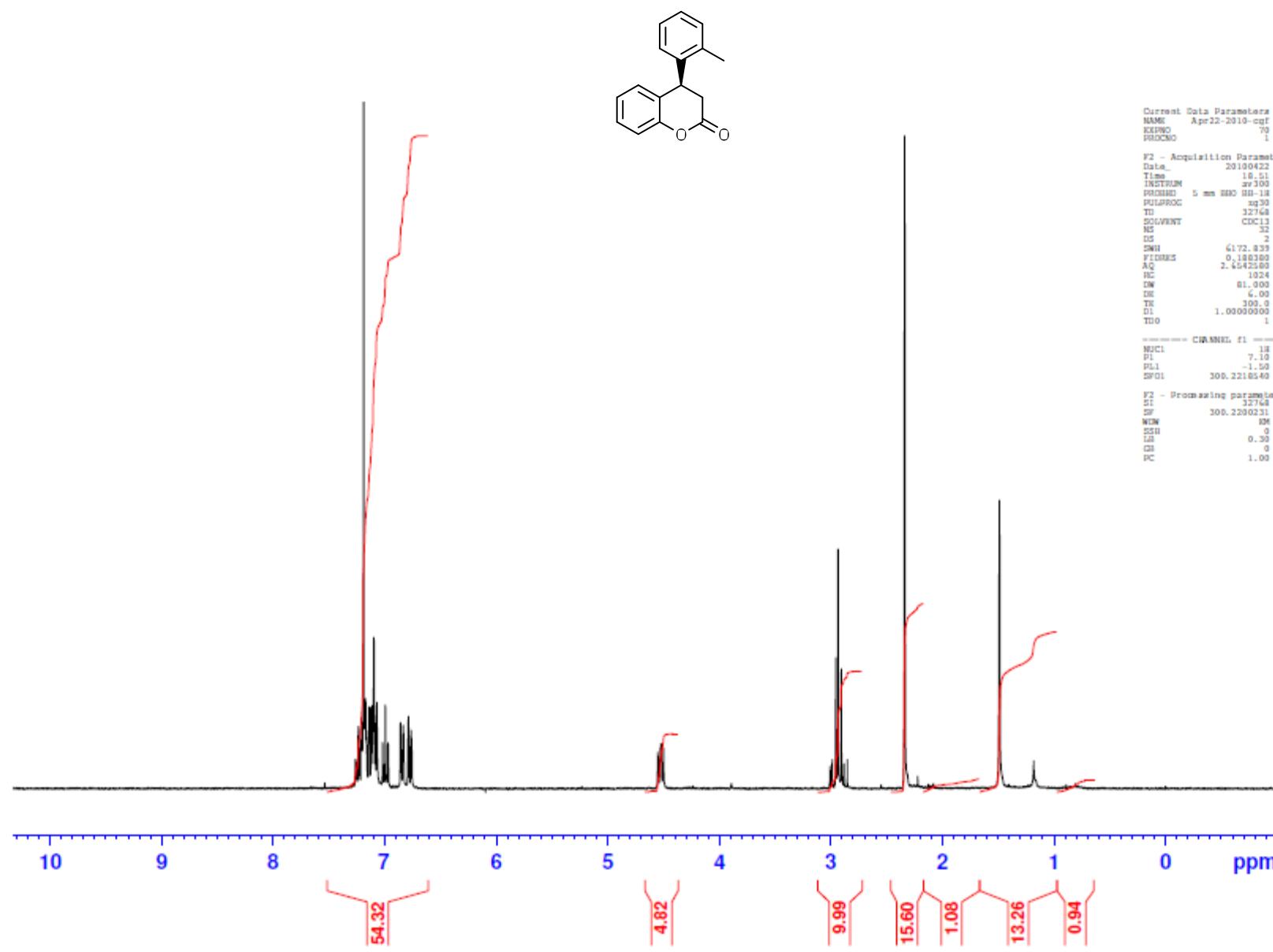


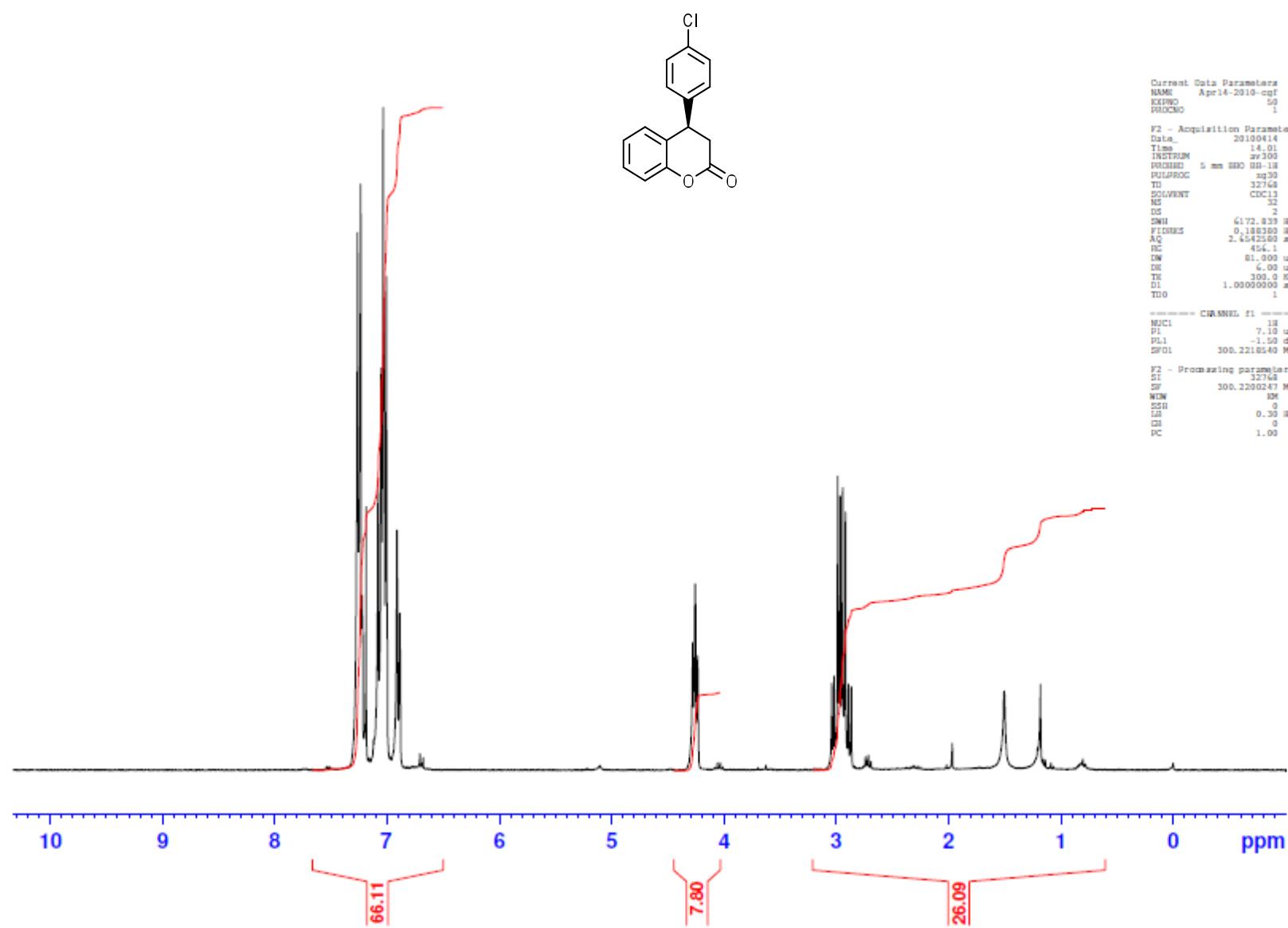


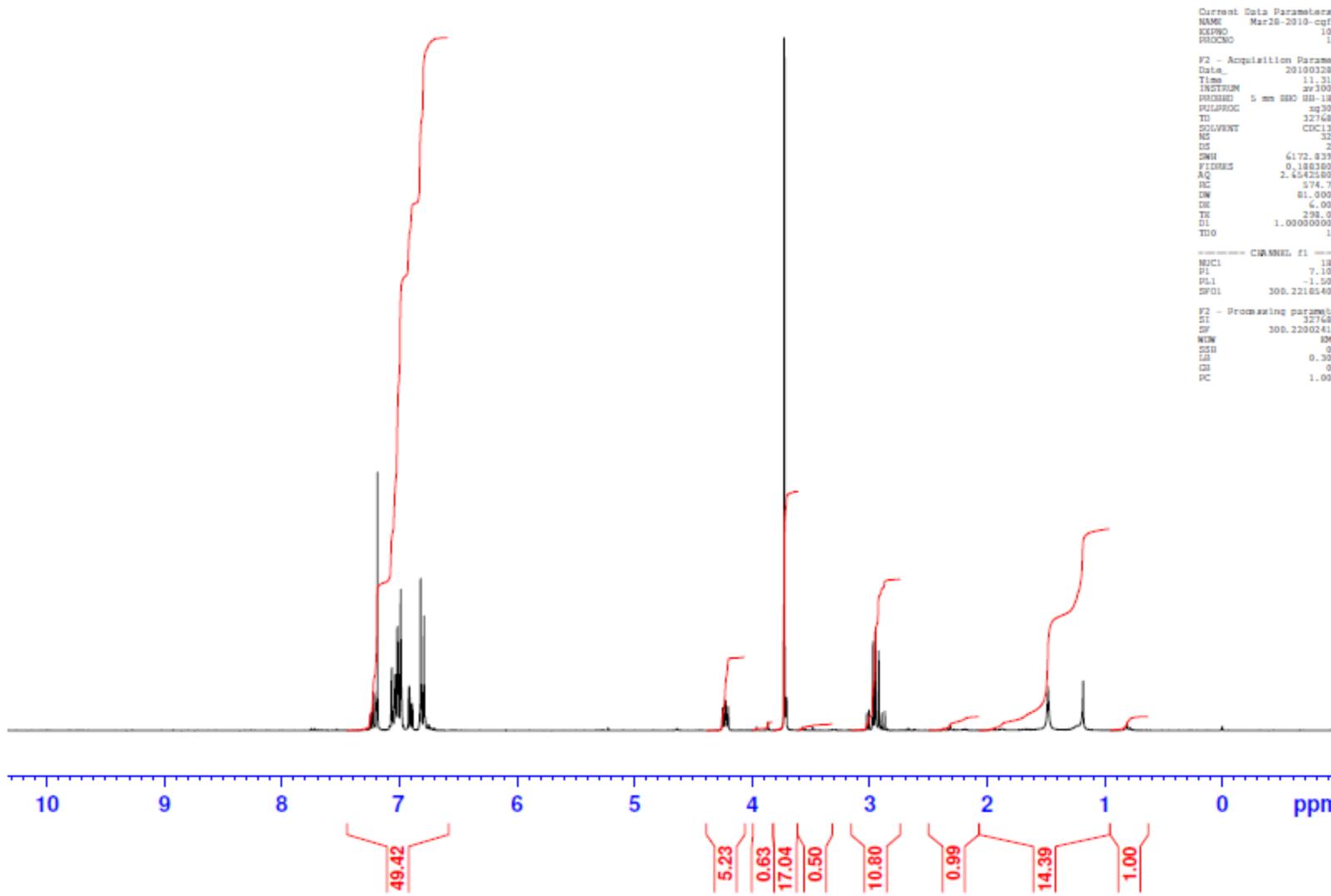
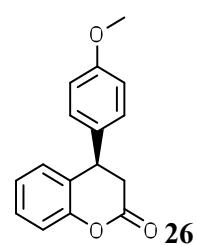


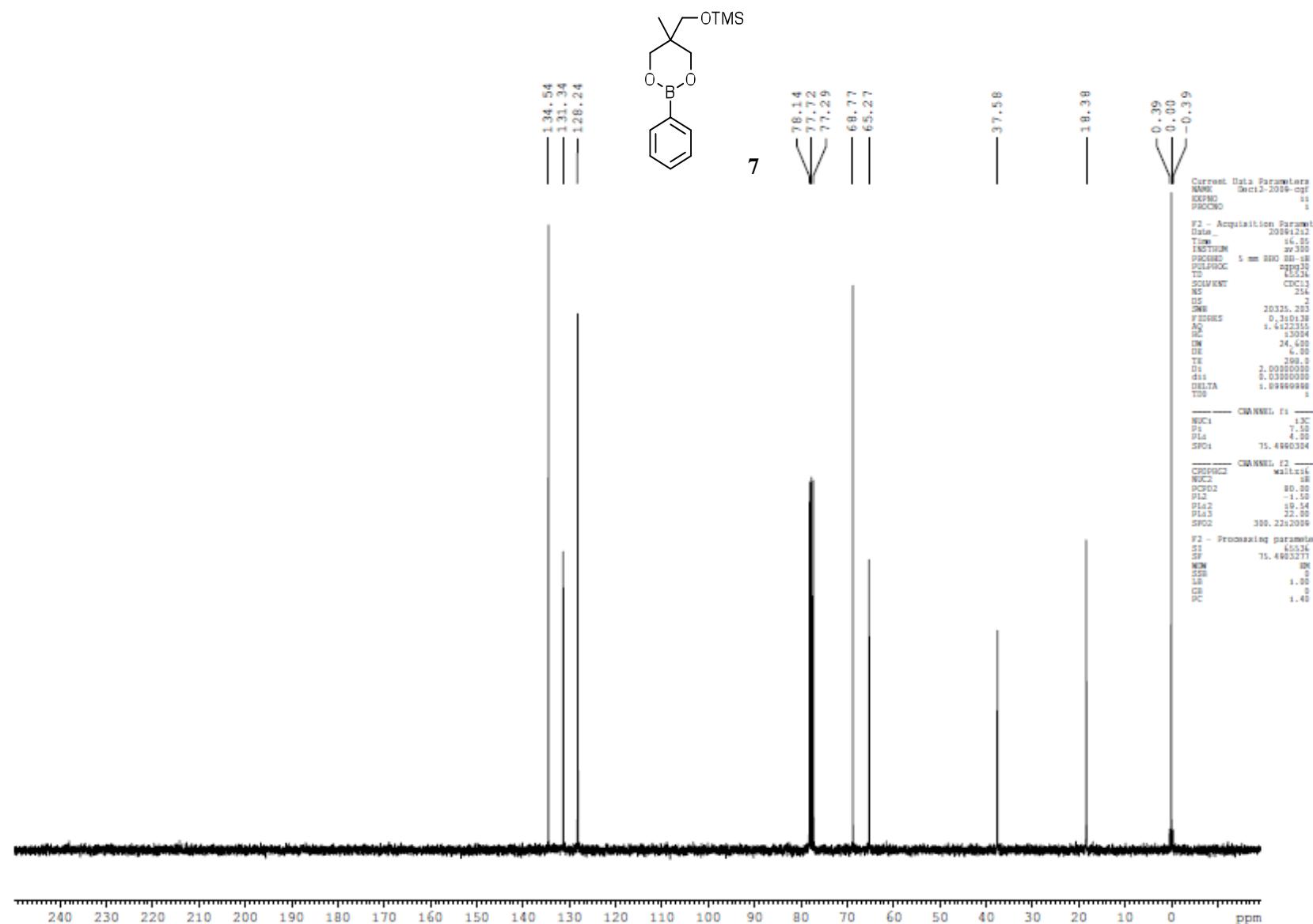


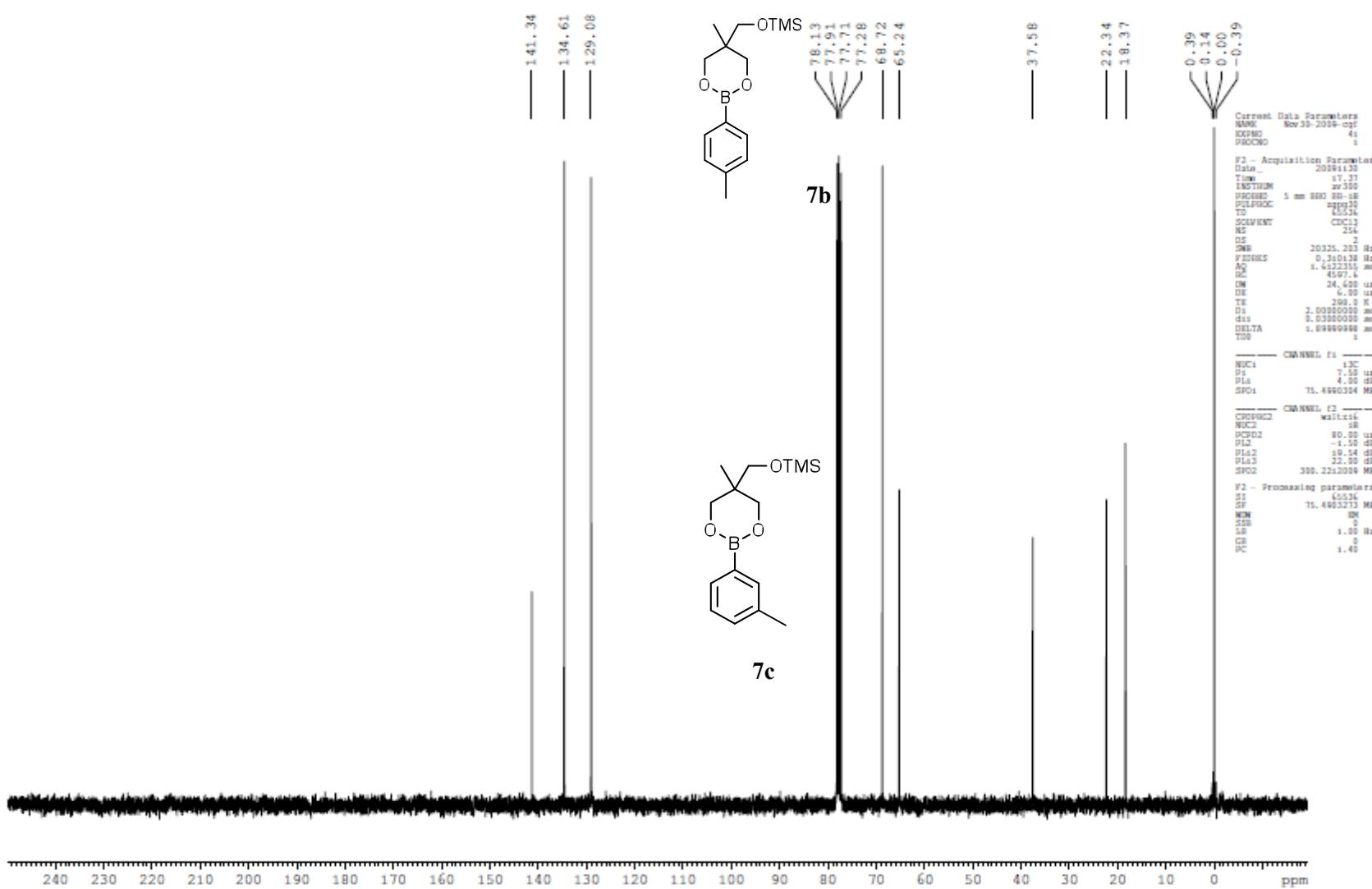


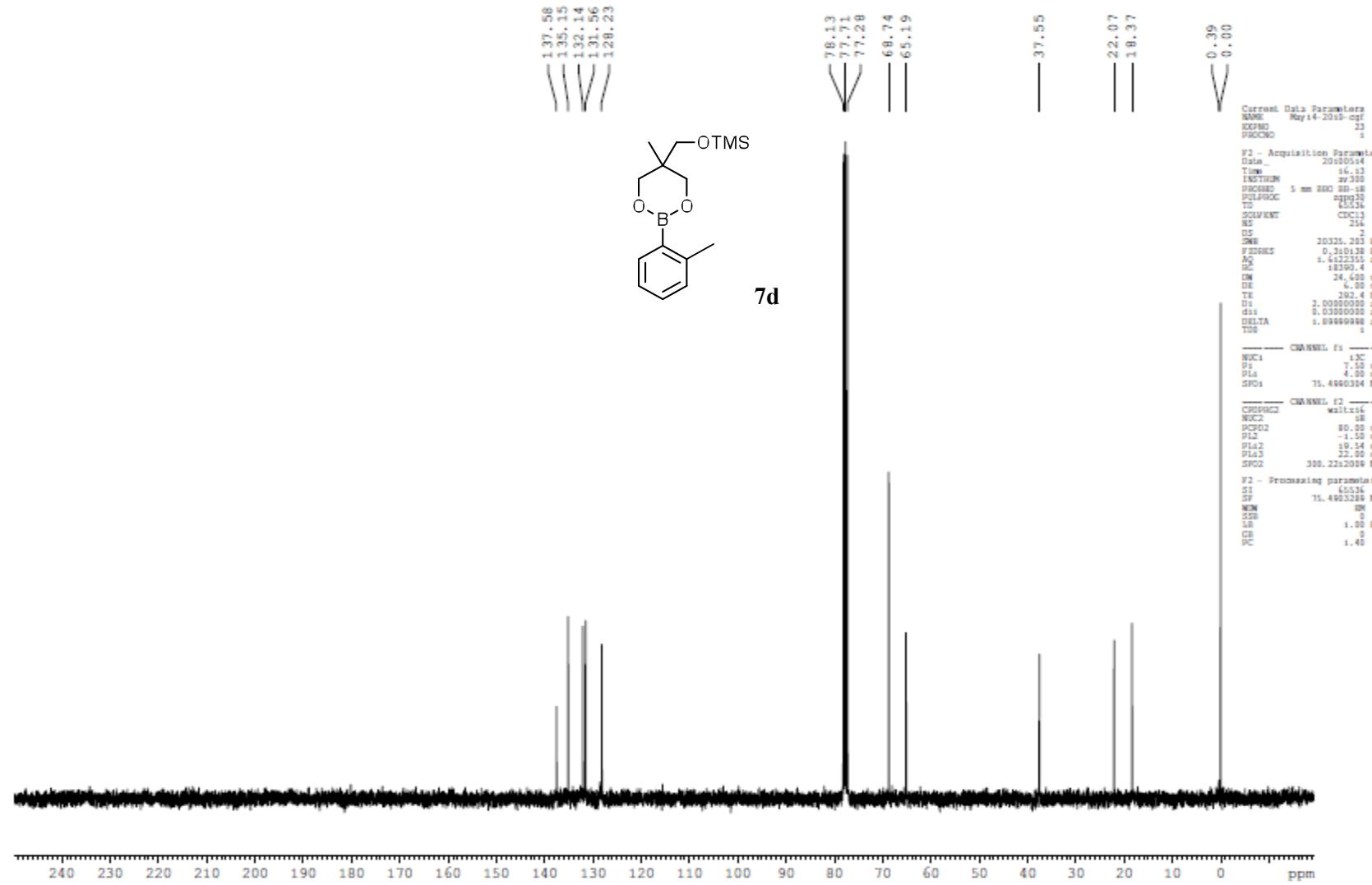


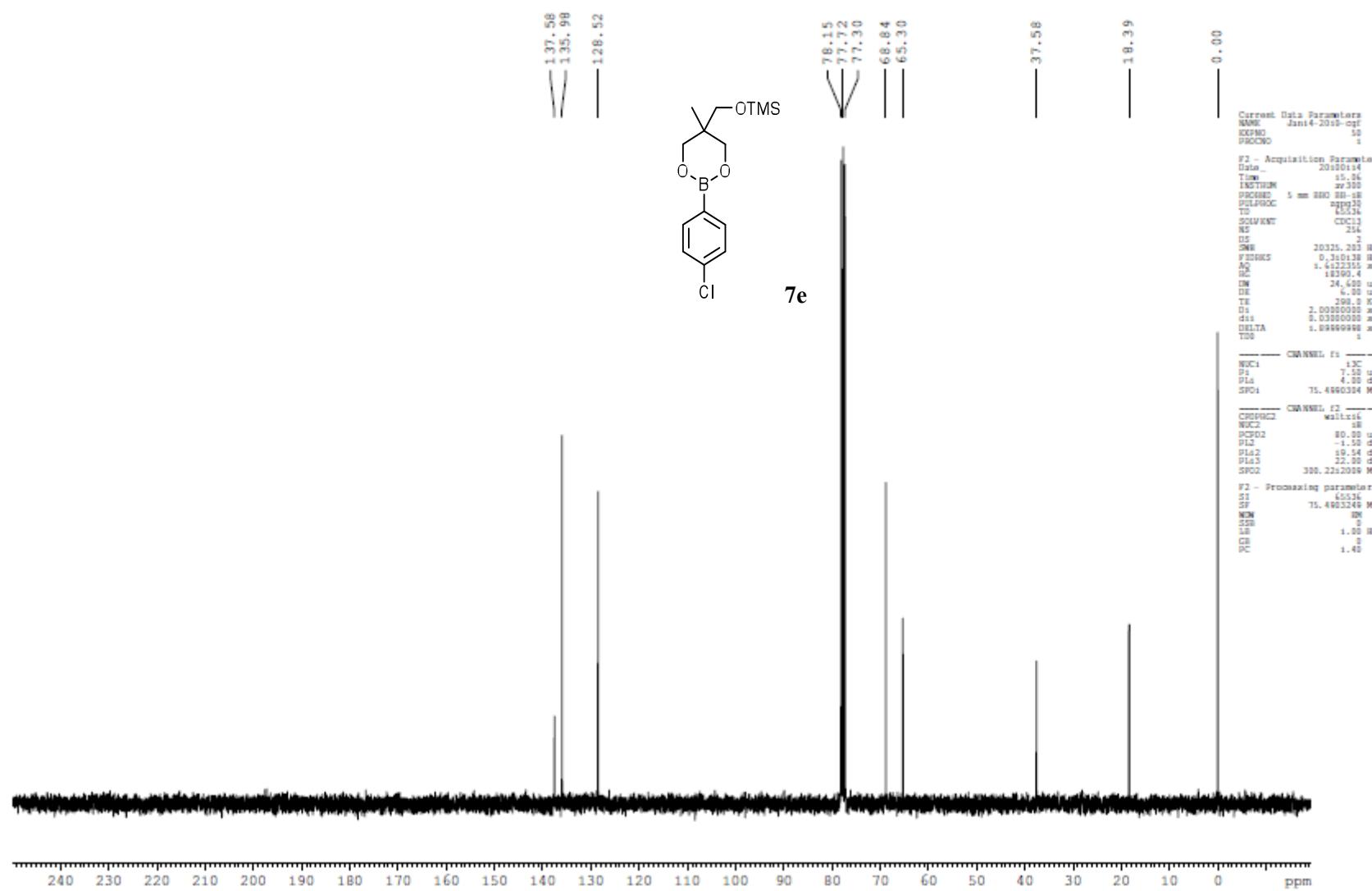


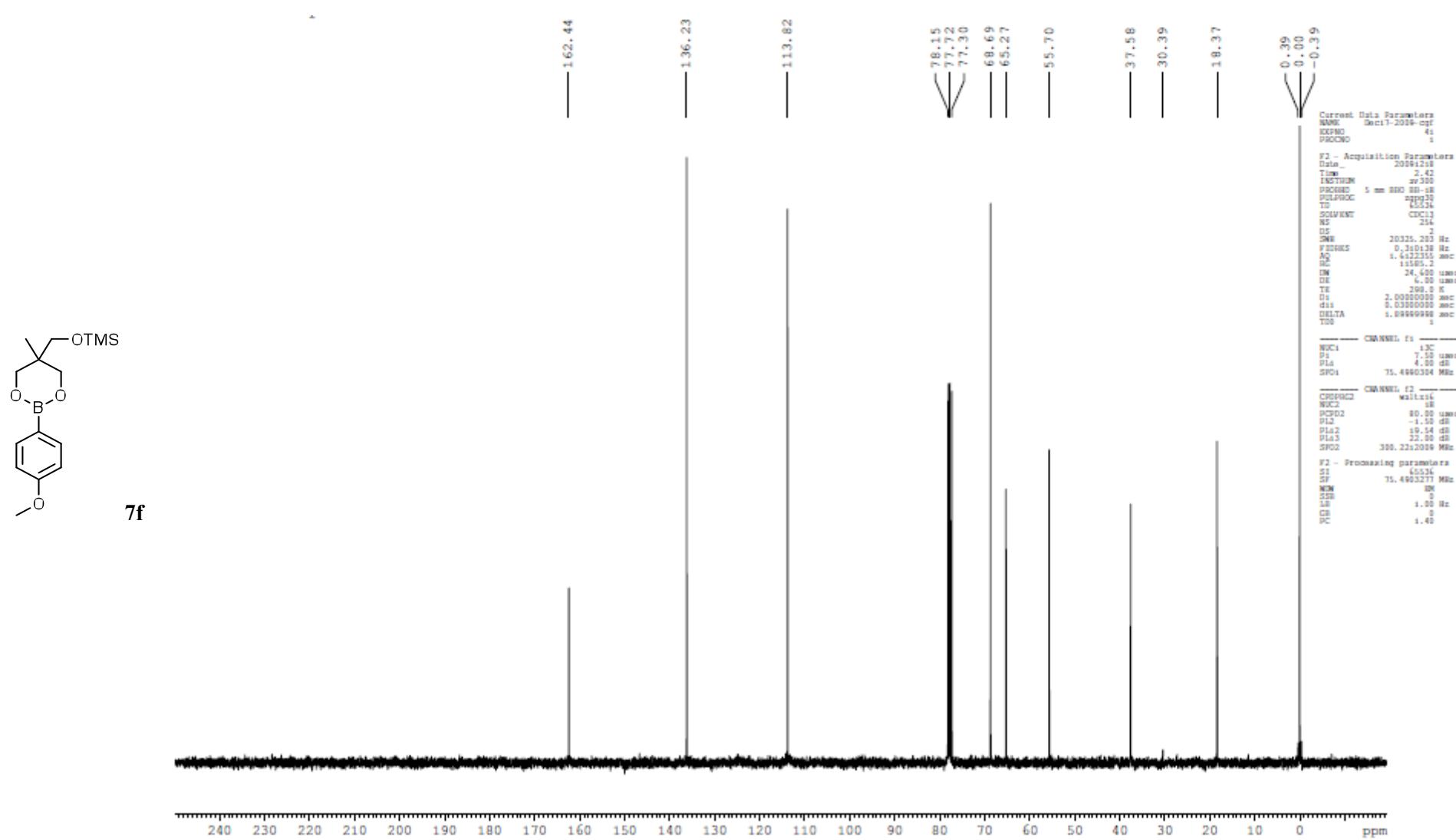


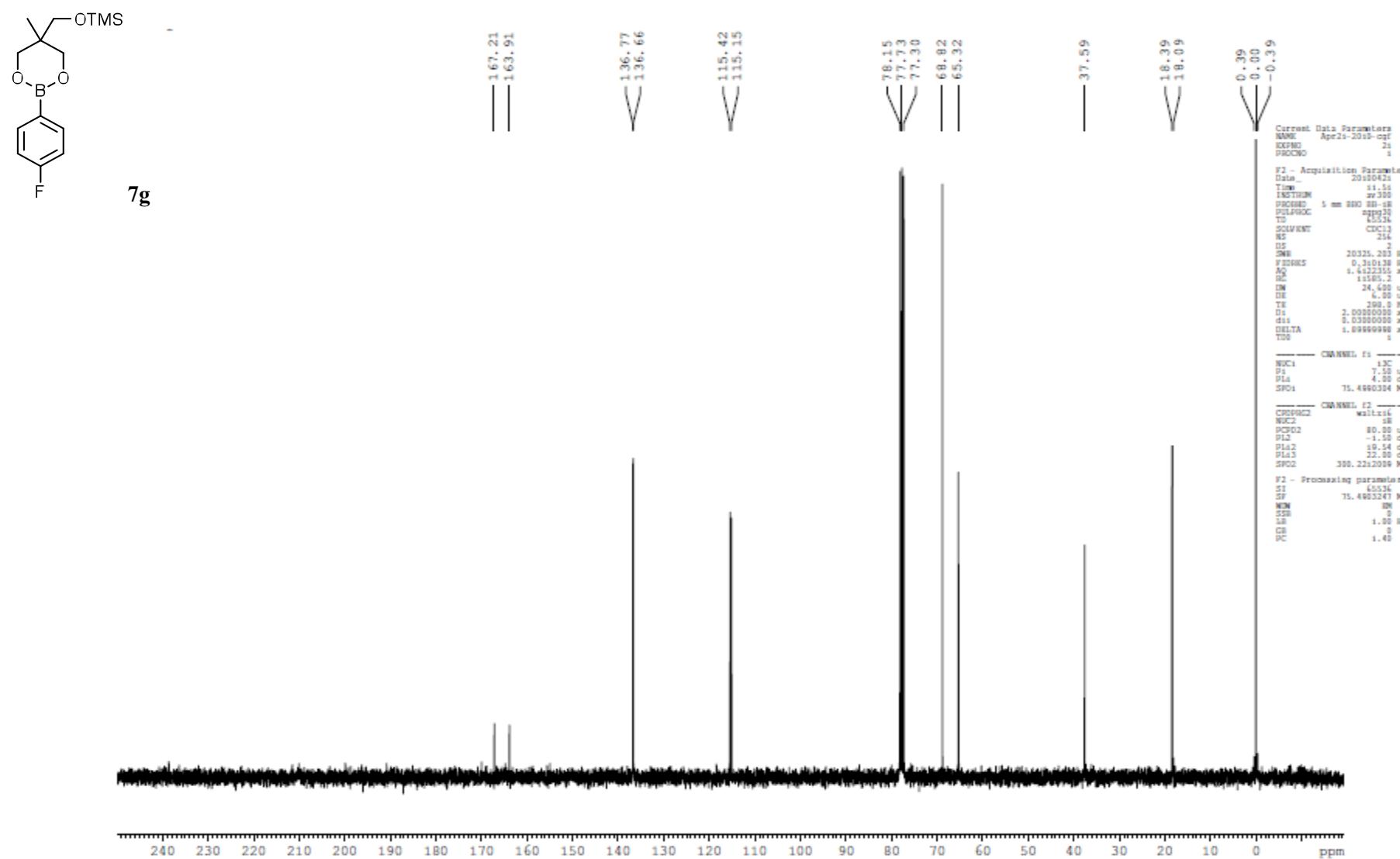


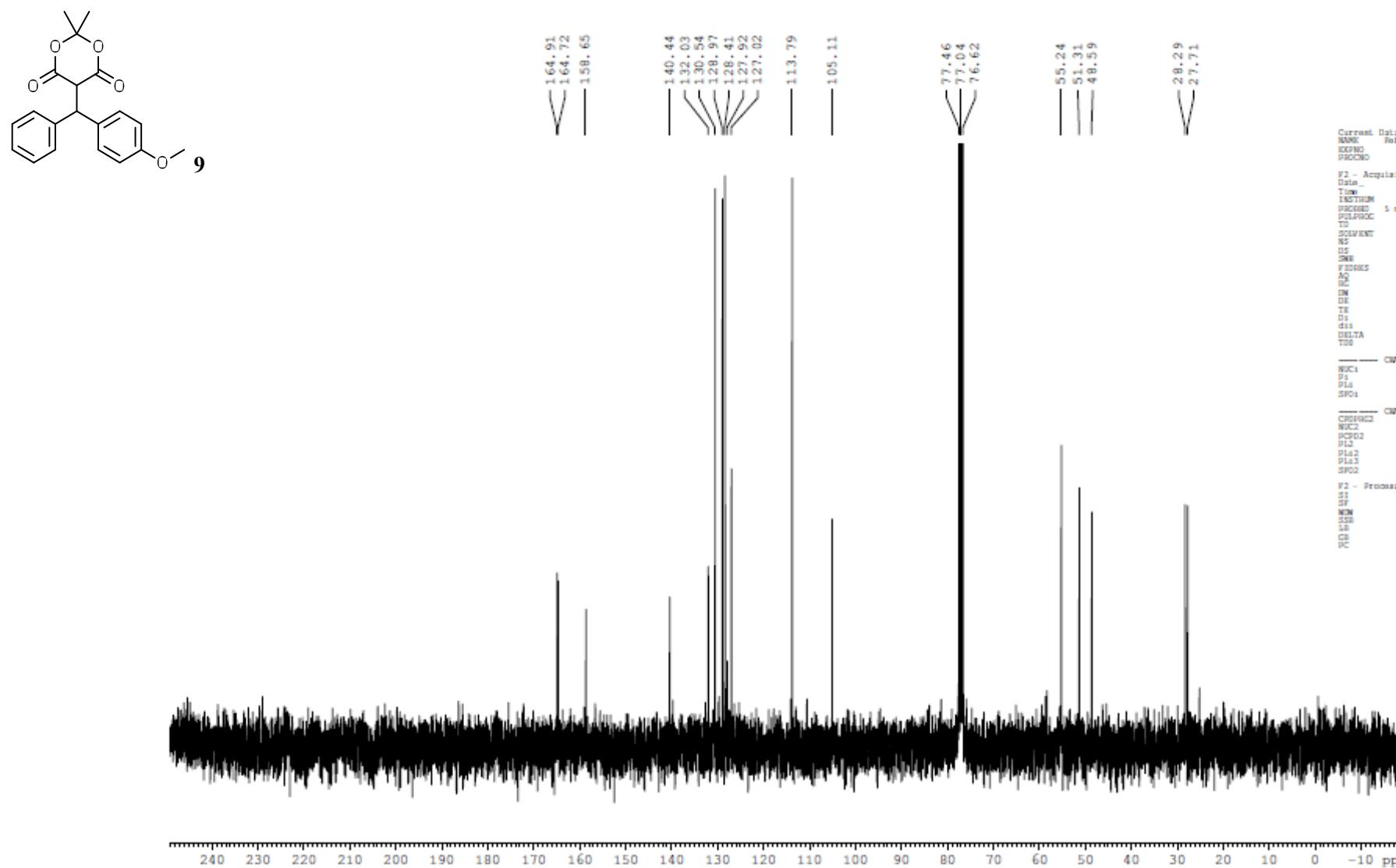


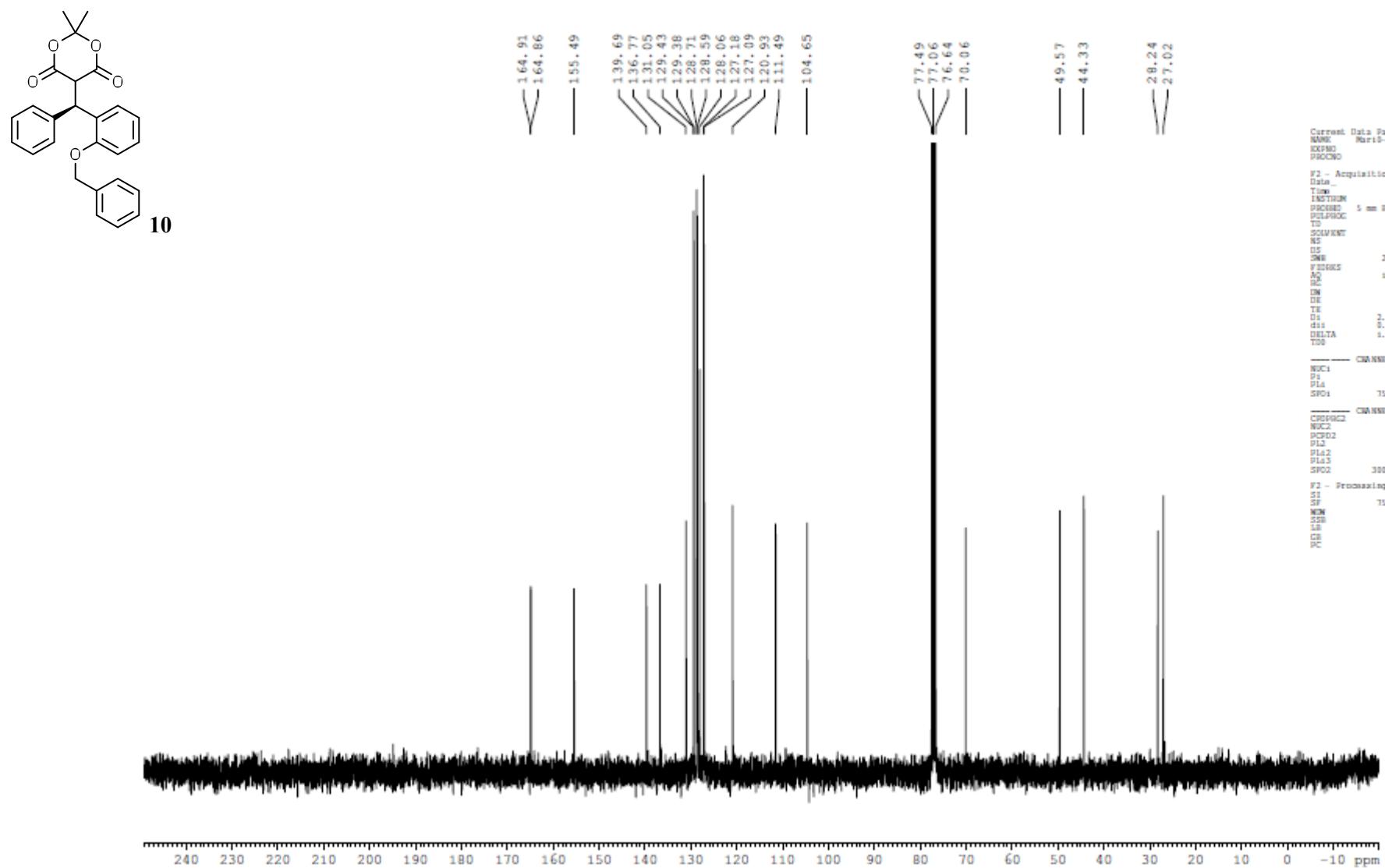


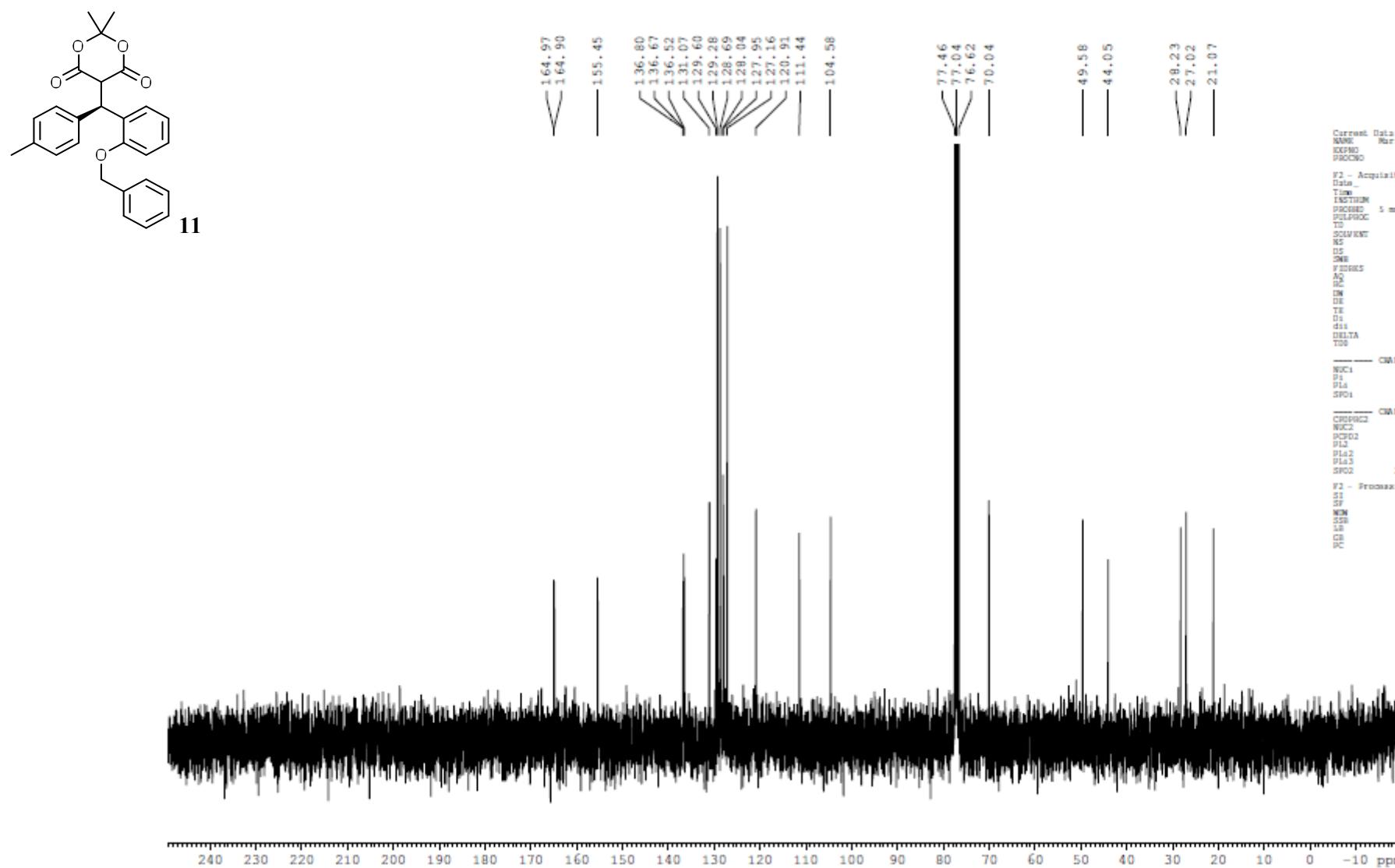


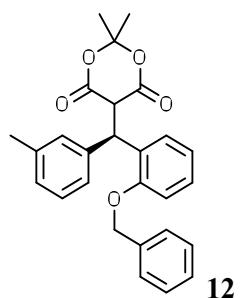




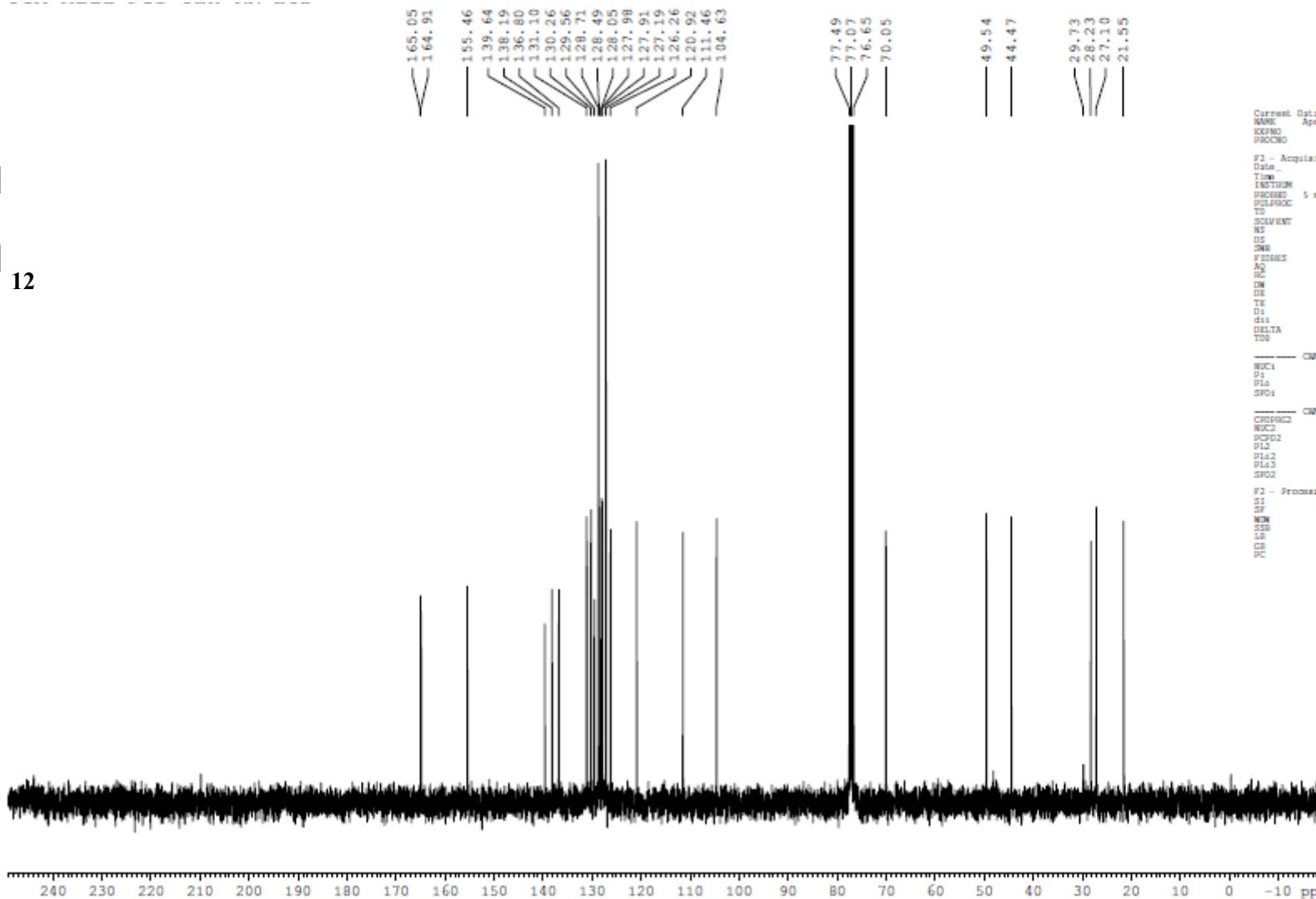








12



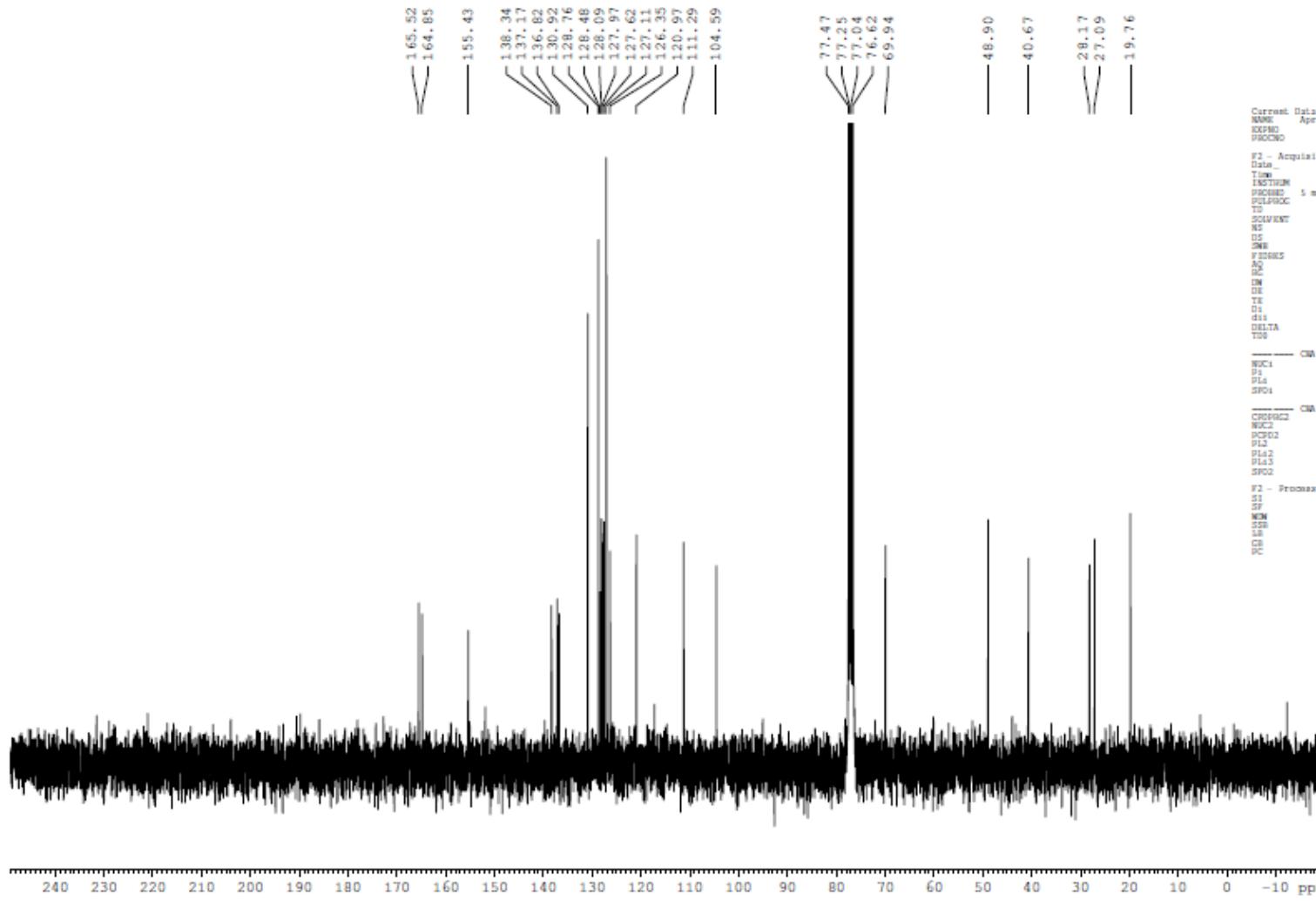
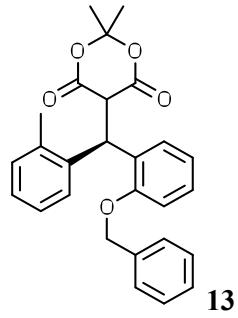
Current Data Parameters  
NAME April5-2010-cpf  
EXPNO 41  
PROCNO 1

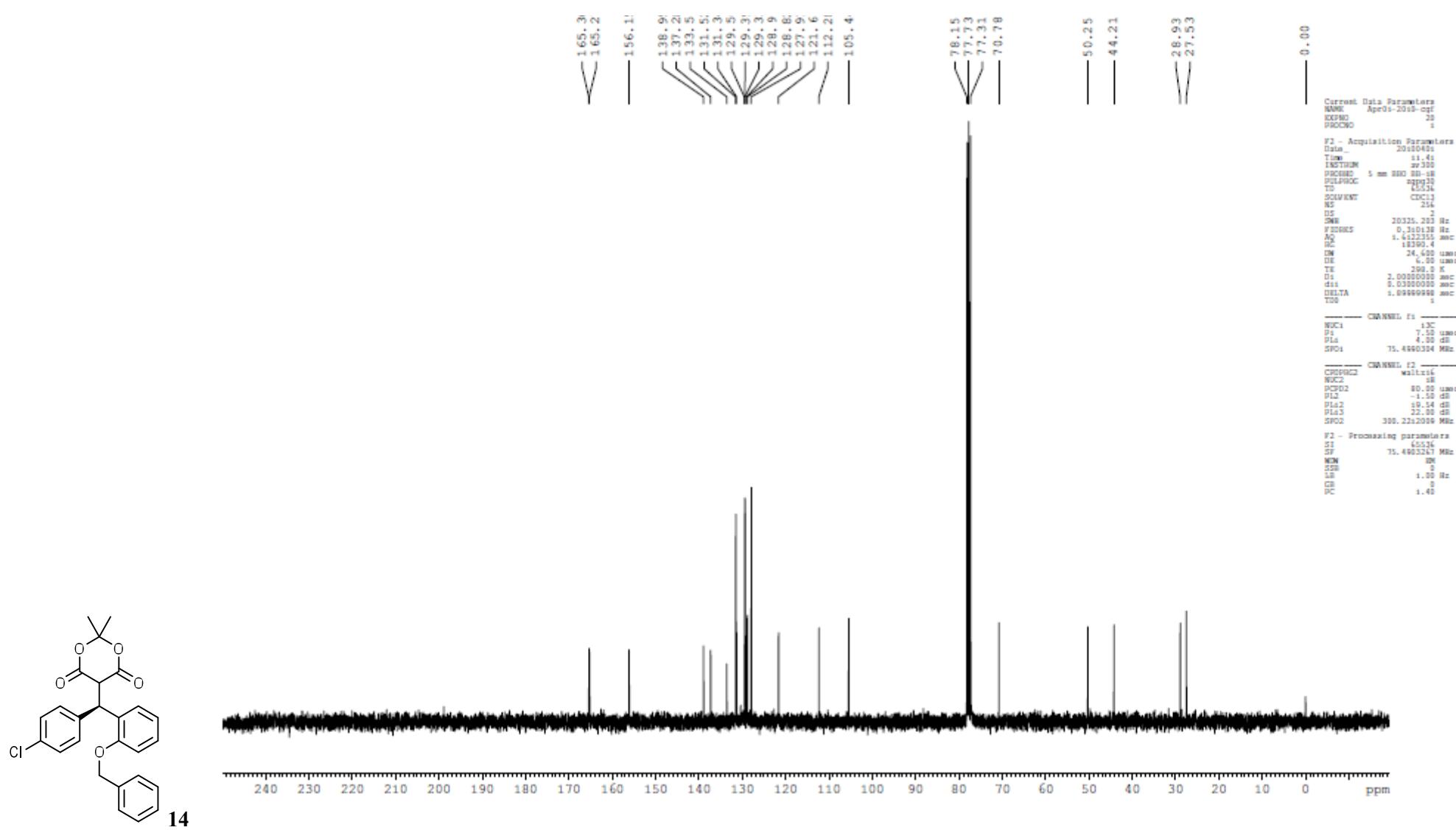
F2 - Acquisition Parameters  
Date\_ 20100415  
Time 14.34  
TE[ms] 20.00  
DPPMDS 5 mm H2O 3H-1H  
PULPROG zgpp32  
TD 32768  
SOLVENT CDCl3  
R2 256  
DS 2  
SW0 20325.203 Hz  
FIDRES 0.310138 Hz  
AQ 1.432000 sec  
RG 14384  
DM 24.400 usec  
DE 6.00 usec  
TR 298.0 K  
D1 3.000000 sec  
d1s 0.3330000 sec  
DELTA 1.0000000 sec  
TDD 1

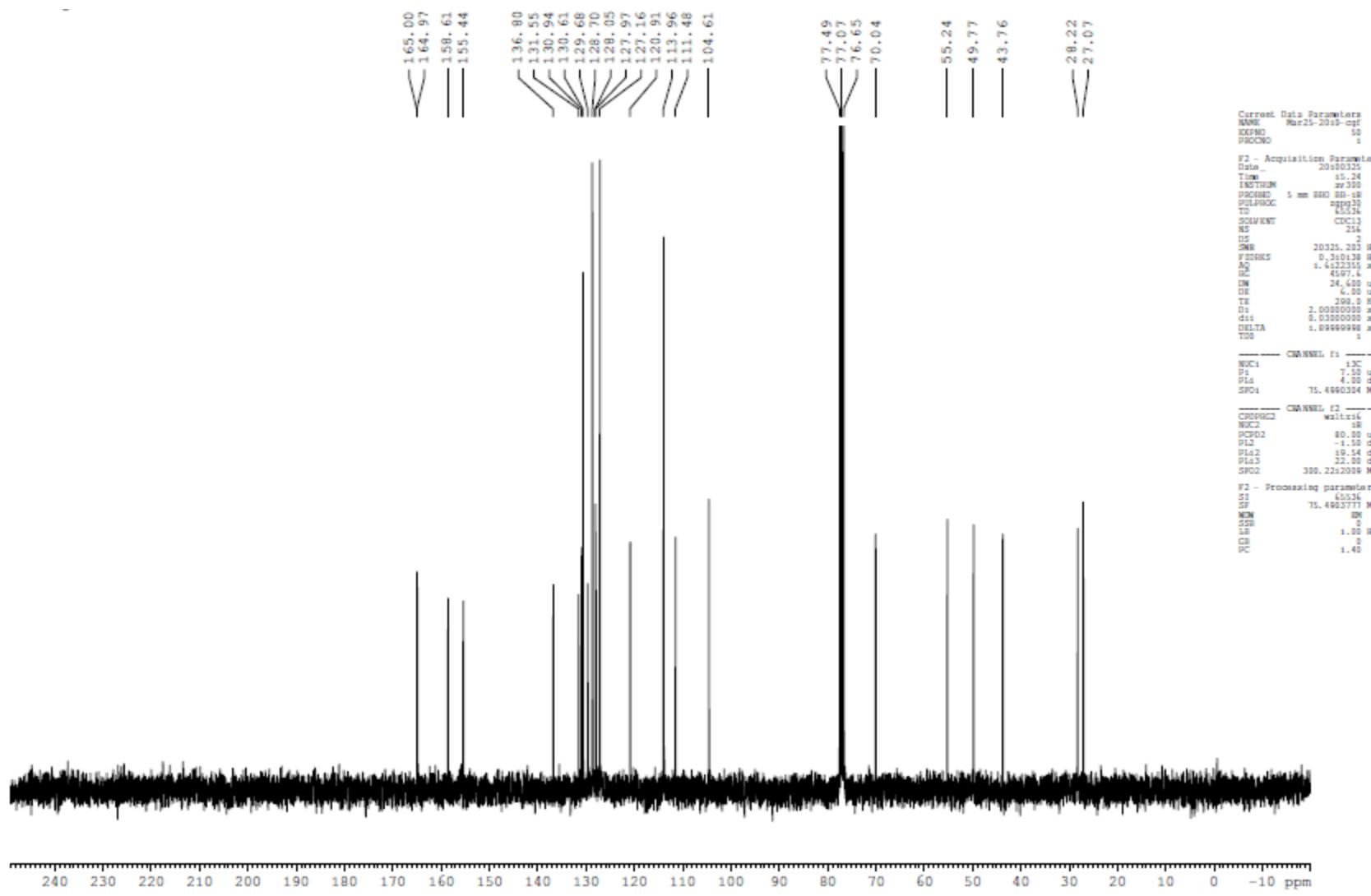
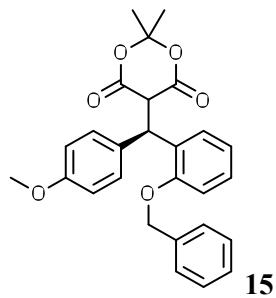
CHANNEL f1  
NUC1 <sup>13</sup>C  
P1 7.50 usec  
PL1 4.00 dB  
SW1 75.490334 MHz

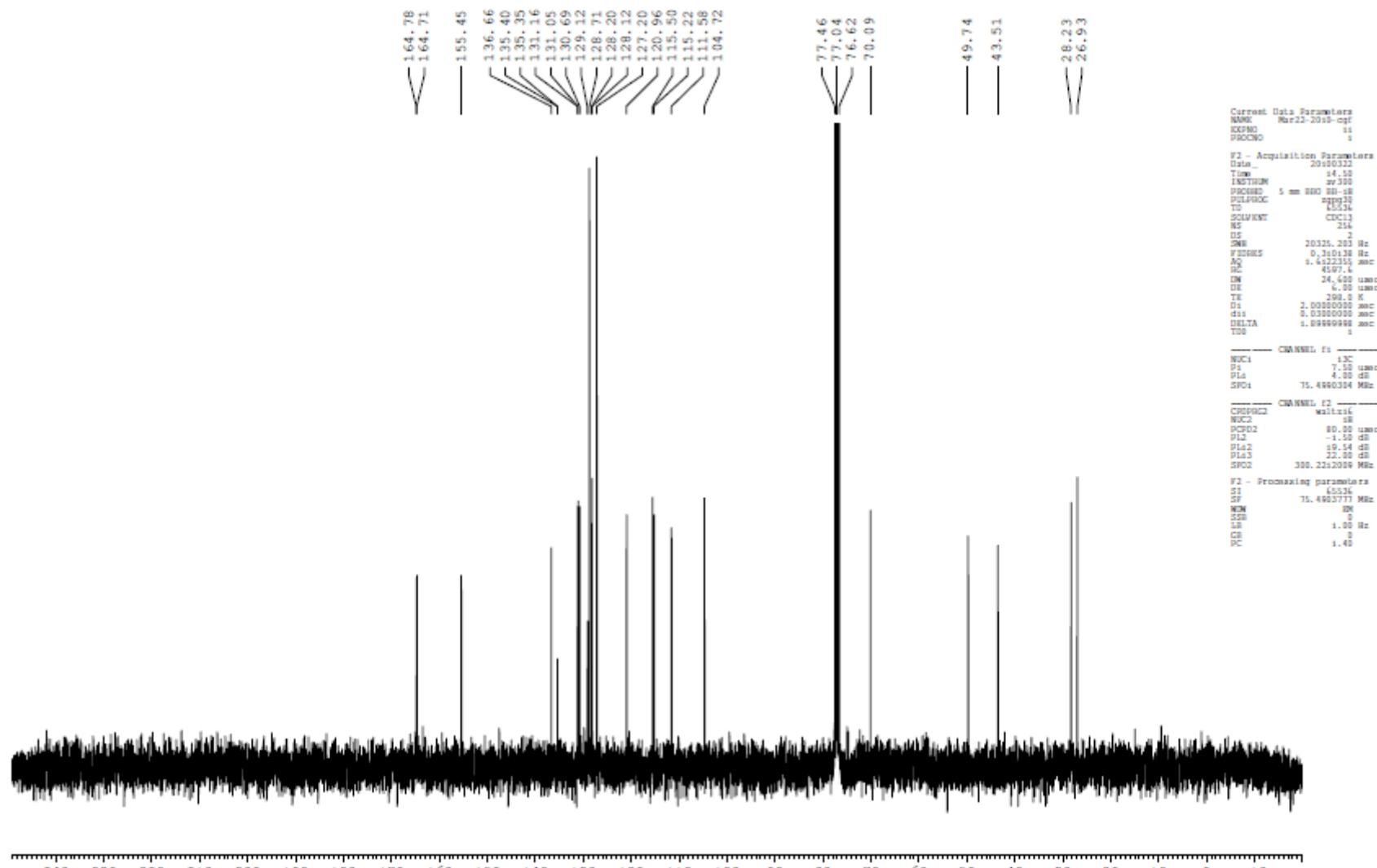
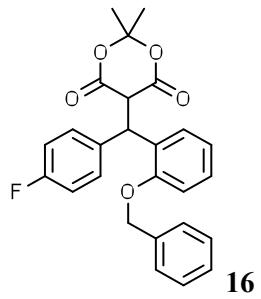
CHANNEL f2  
CRDPHC2 waltz16  
NUC2 <sup>1</sup>H  
PCP02 80.00 usec  
PL2 -1.50 dB  
PL3 19.54 dB  
PL4 22.00 dB  
SW2 300.2212039 MHz

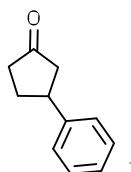
F2 - Processing parameters  
SI 455537  
SF 75.4903347 MHz  
RM 1  
SSB 0  
LB 1.00 sec  
PB 1.40



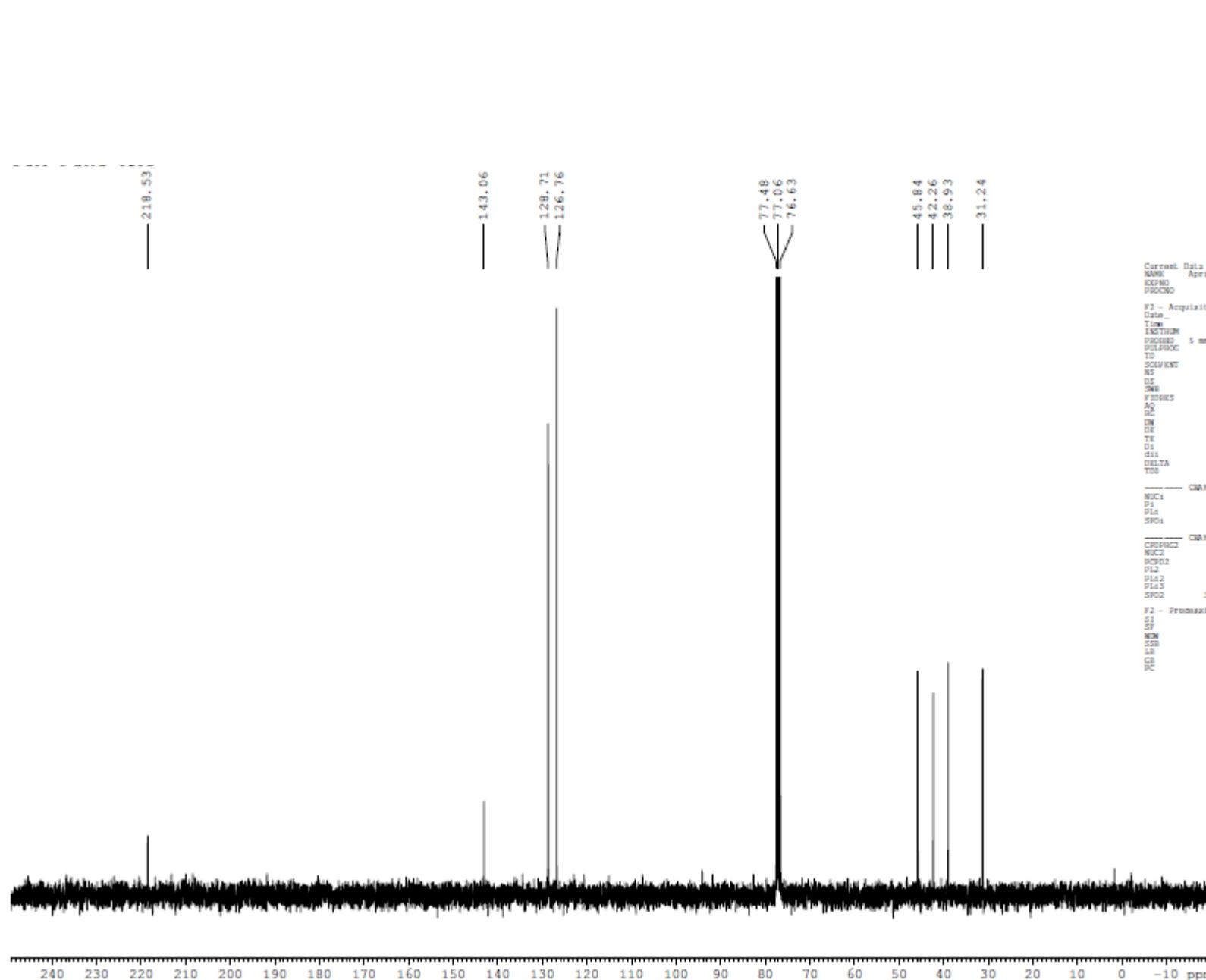


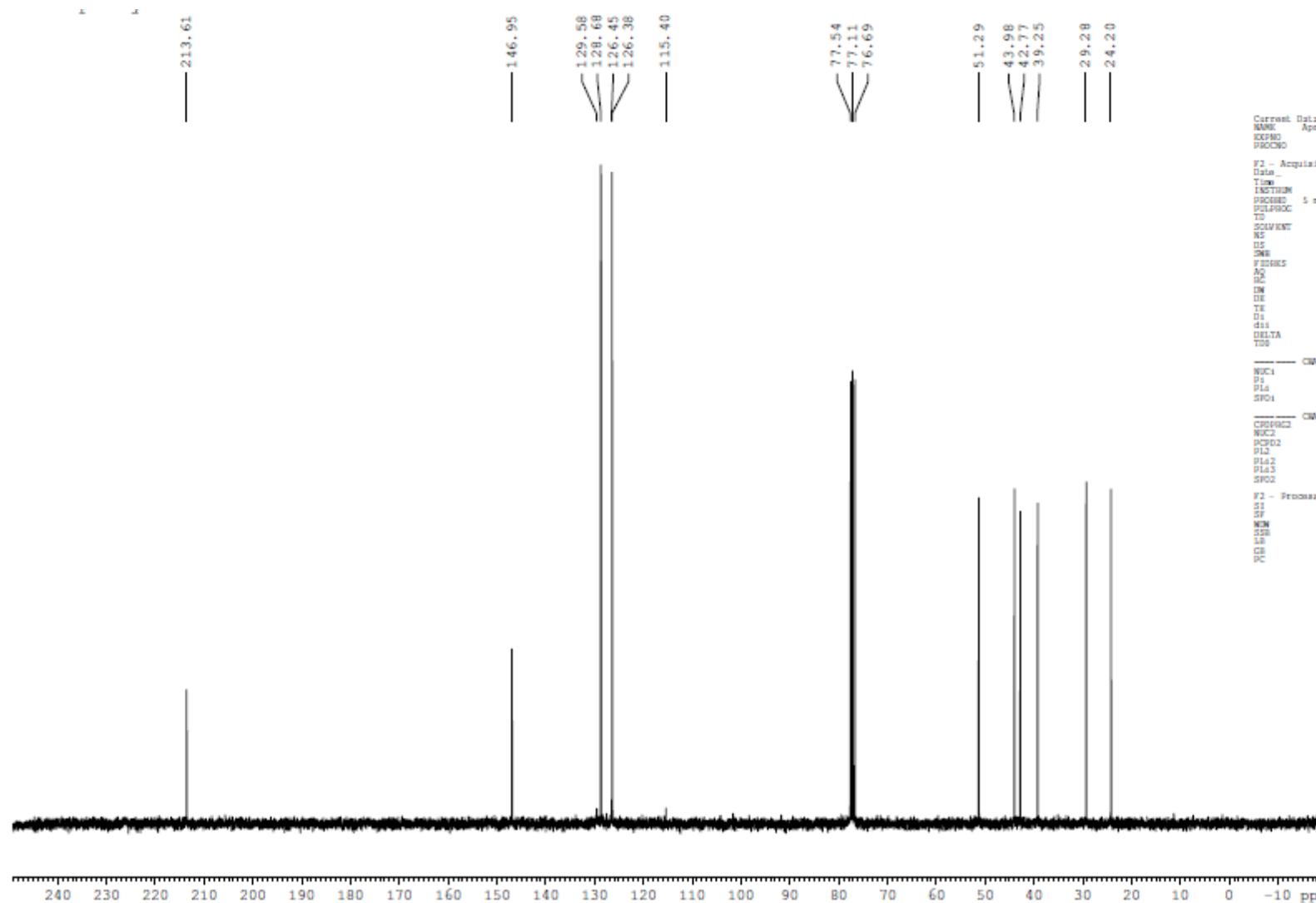
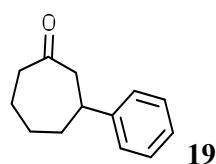


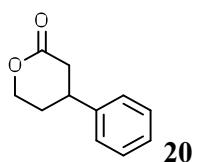
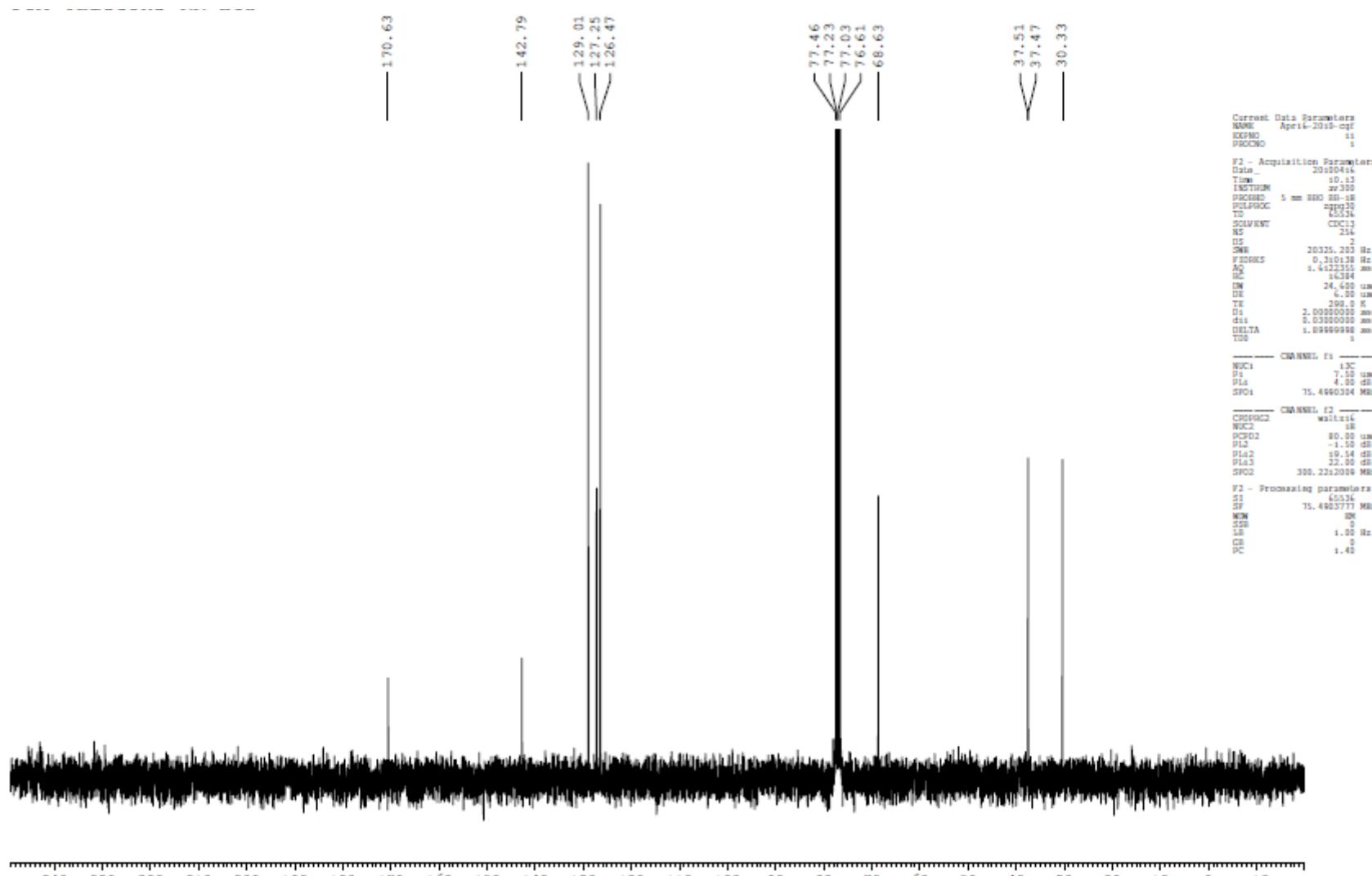


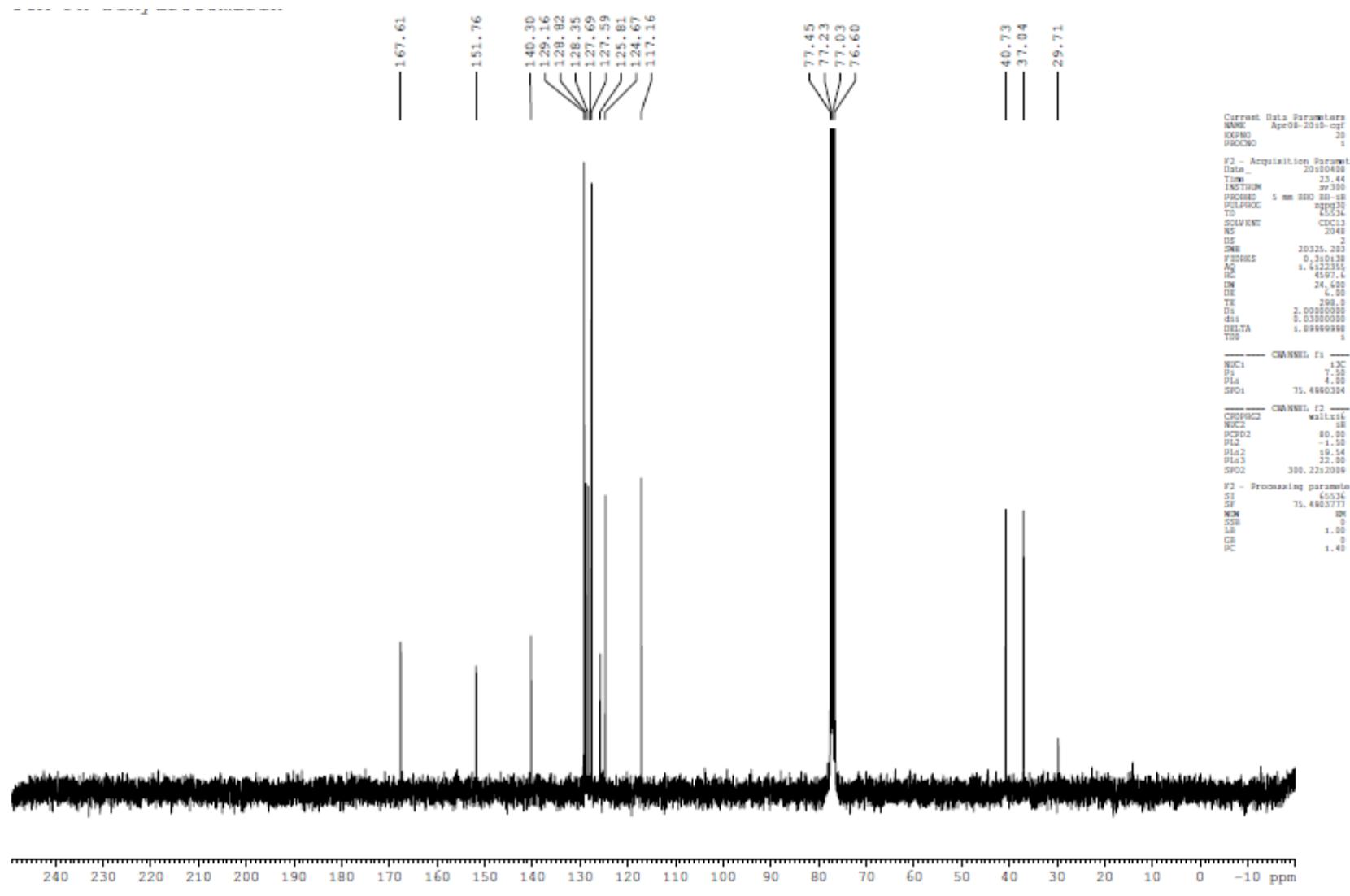
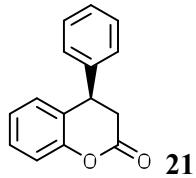


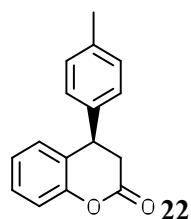
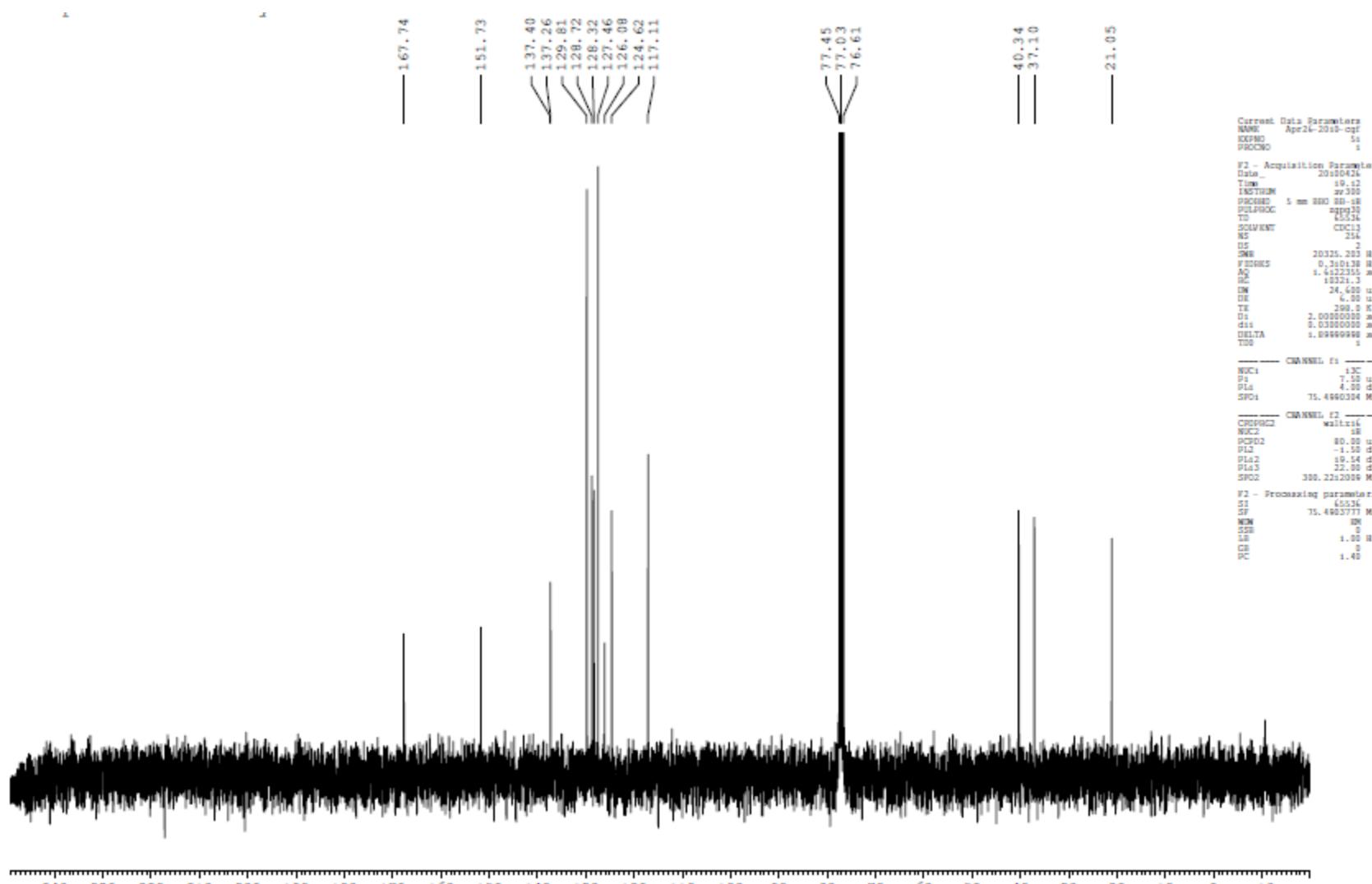
17

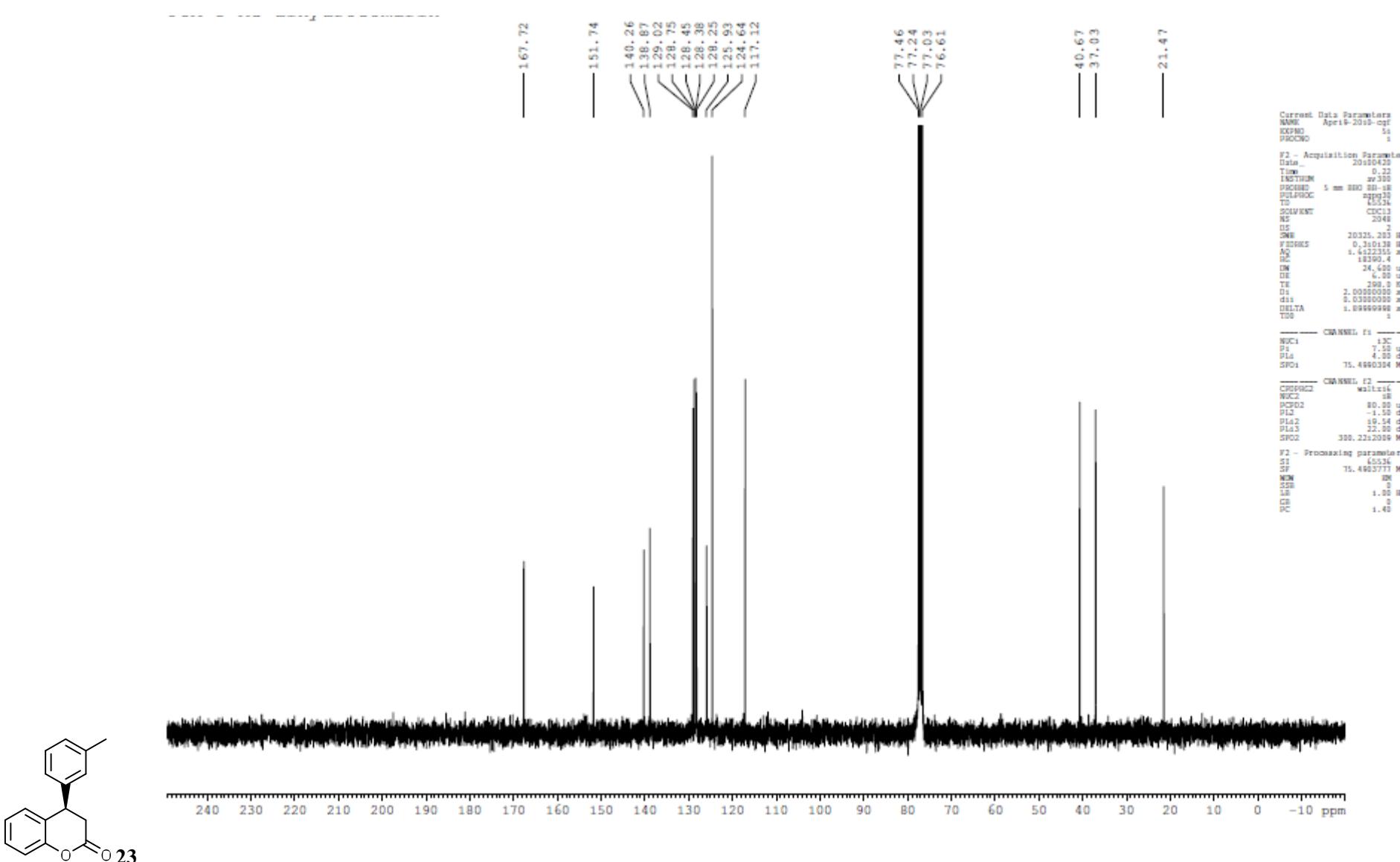


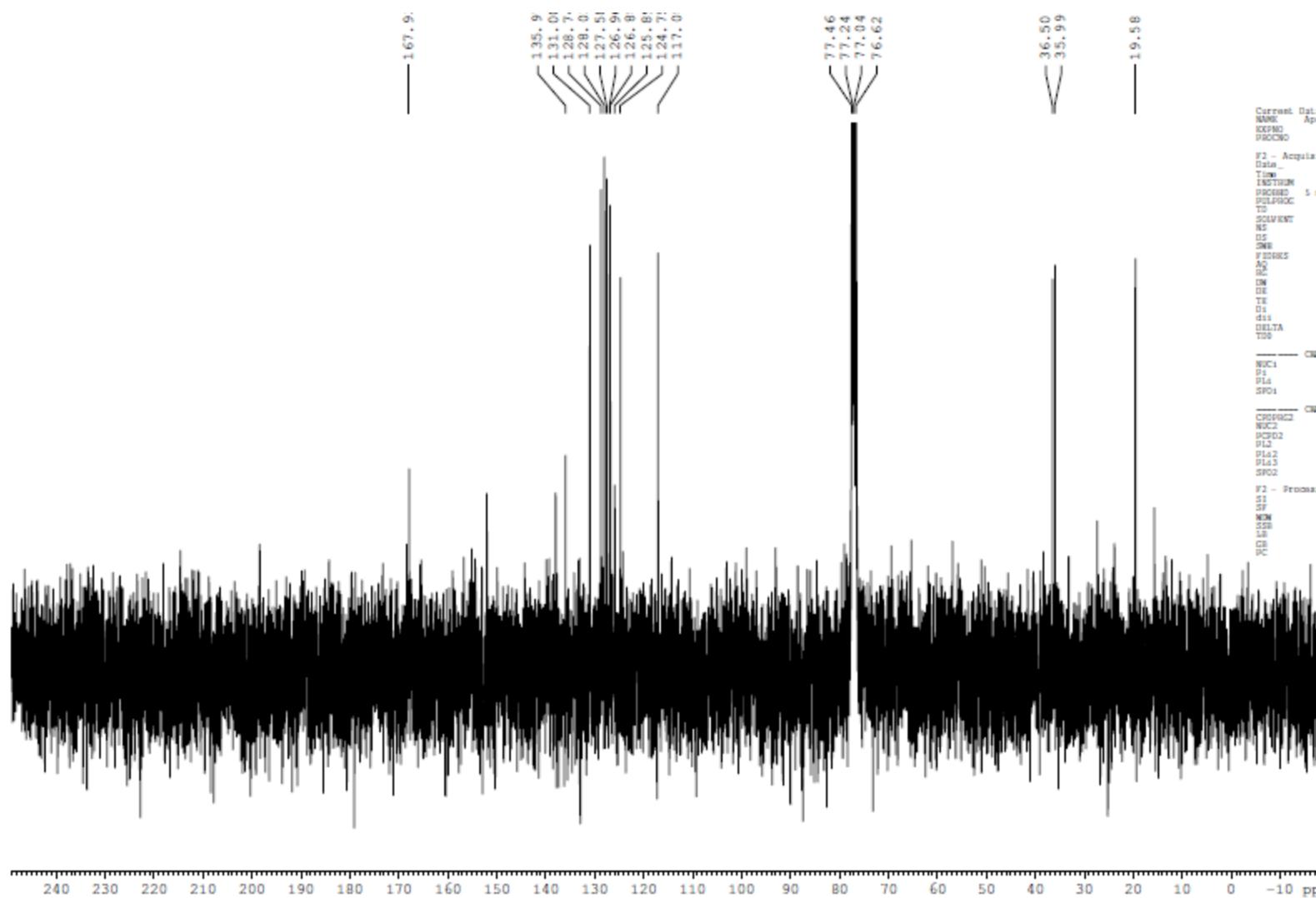
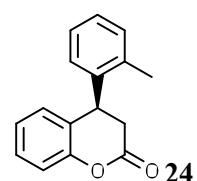


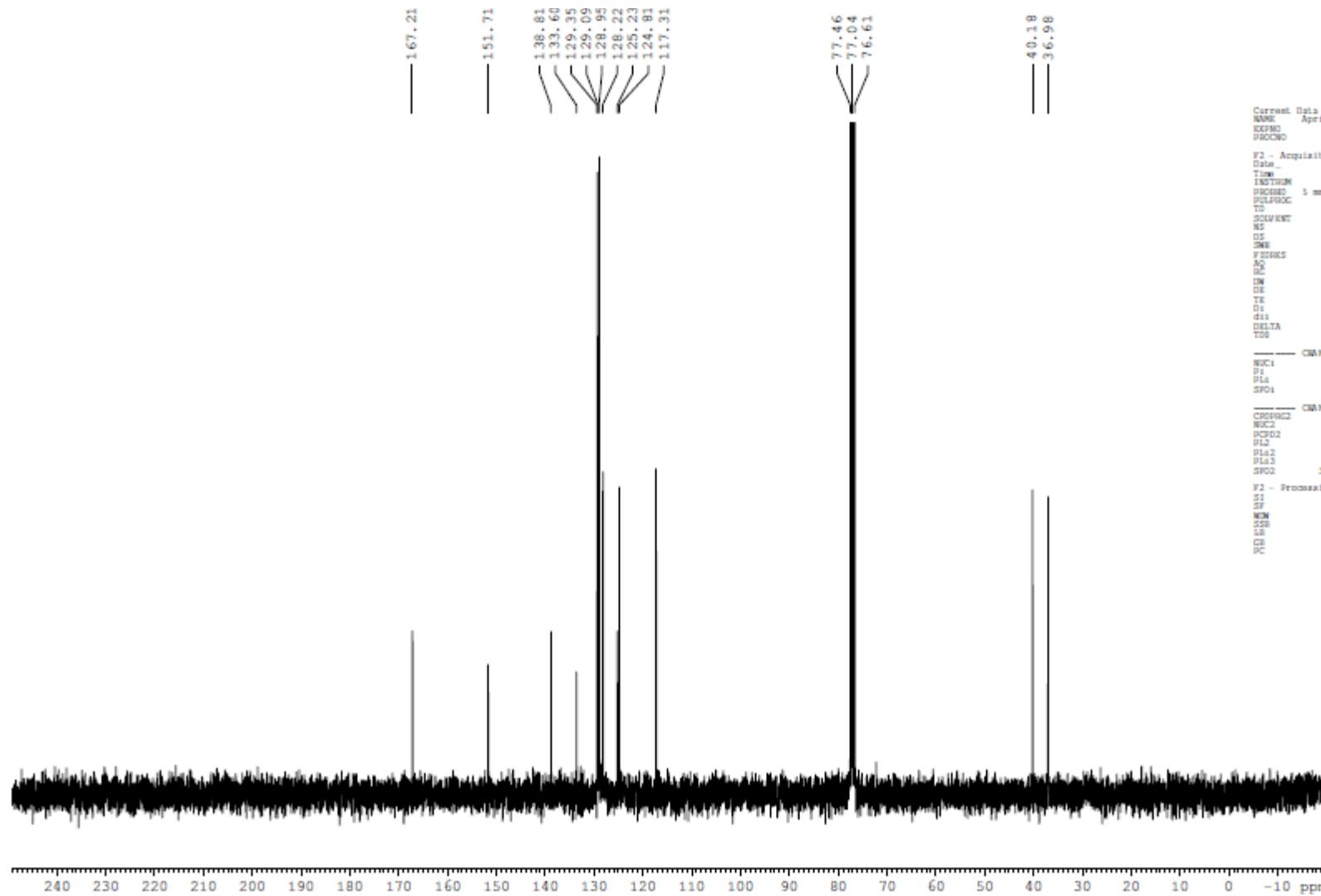
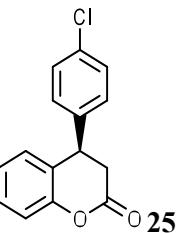


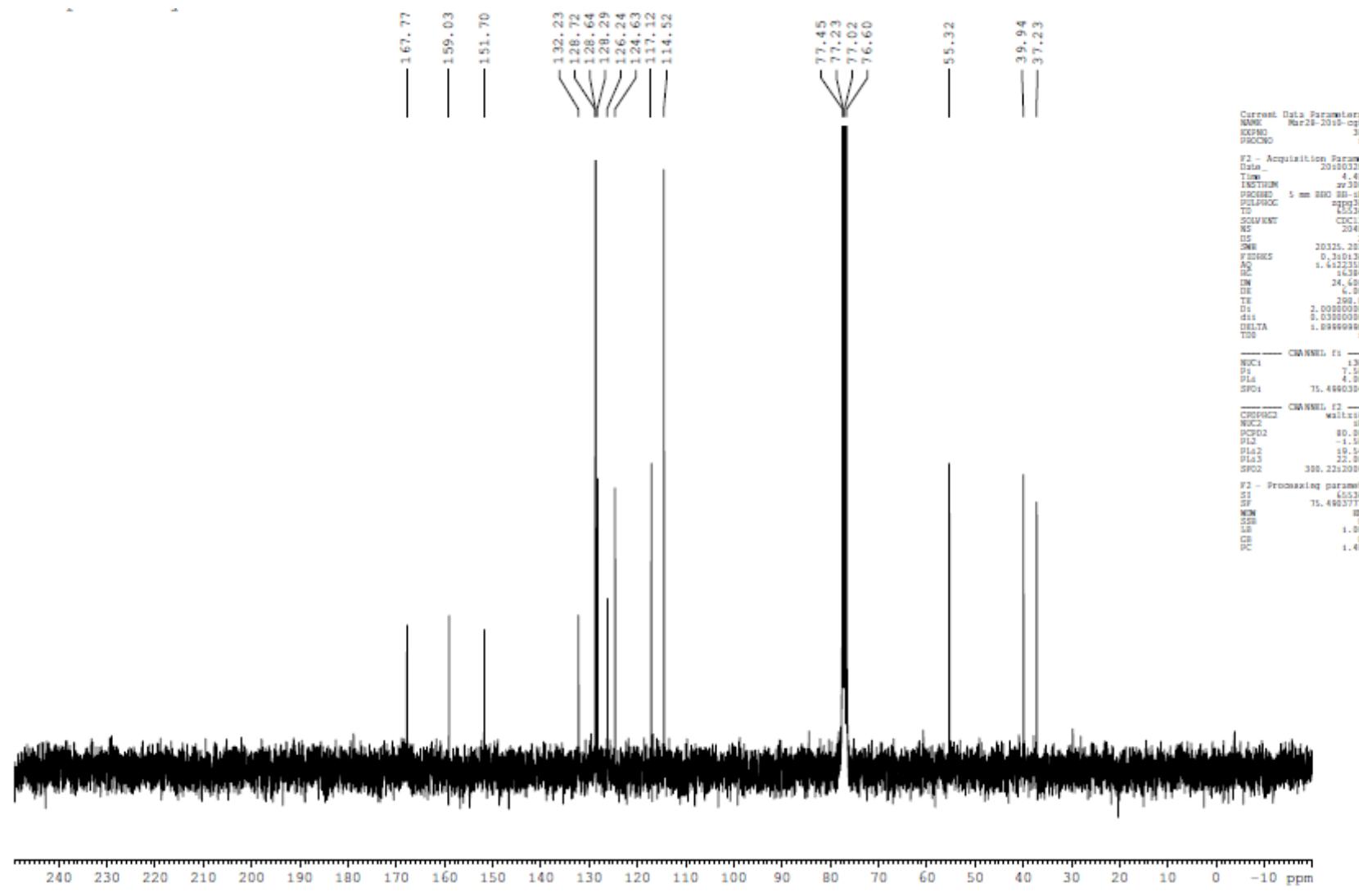
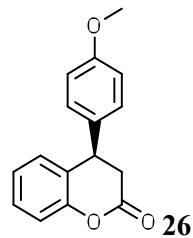












**References:**

1. Frost, C. G.; Penrose, S. D.; Gleave, R., *Synthesis* **2009**, 627-635.
2. Shintani, R.; Ichikawa, Y.; Takatsu, K.; Chen, F. X.; Hayashi, T., *J. Org. Chem.* **2009**, 74, 869-873.
3. Bűrgi, J.; Mariz, R.; Gatti, M.; Drinkel, E.; Luan, X.; Blumentritt, S.; Linden, A.; Dorta, R., *Angew. Chem. Int. Ed.* **2009**, 48, 2768-2771.
4. Jana, R.; Tunge, J. A., *Org. Lett.* **2009**, 11, 971-974.
5. Chen, G.; Tokunaga, N.; Hayashi, T., *Org. Lett.* **2005**, 7, 2285-2288.
6. Buu-Hoi, N. P.; Bihan, H. L.; Binon, F.; Maleyran, P., *J. Org. Chem.* **1952**, 17, 1122-1127.
7. Aoki, S.; Amamoto, C.; Oyamada, J.; Kitamura, T., *Tetrahedron* **2005**, 61, 9291-9297.