

**Diastereoselective and Enantioselective Mukaiyama Aldol Reactions of  
 $\alpha$ -Ketoesters using Hydrogen Bond Catalysis**

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## General Information

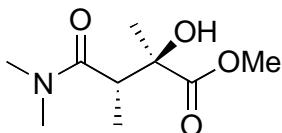
Unless otherwise noted, all solvents were degassed by purging with argon and dried over activated alumina. All reactions were performed under argon with either flame or oven dried glassware. *N,N*-disopropylethylamine was distilled over CaH<sub>2</sub>. Pyruvates were purchased from Aldrich and were purified by bulb-to-bulb distillation before use. *N,O*-ketene acetals were synthesized by the known procedure<sup>1</sup> and purified by distillation. Melting points were measured on a Thomas Hoover melting point apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on Bruker DRX-400 or 500 MHz spectrometers. Proton chemical shifts are internally referenced to the residual solvent proton resonance (CHCl<sub>3</sub> δ 7.26). Carbon chemical shifts are internally referenced to the deuterated solvent signal (CDCl<sub>3</sub> δ 77.00). Infrared spectra were obtained on a Nicolet 20 SXB FT-IR spectrometer. High resolution mass spectra were recorded at the Mass Spectroscopy Facility at Ohio State University. Optical rotations were recorded using a Jasco DIP-1000 instrument. Analytical thin layer chromatography (tlc) was run on Whatman 0.25 mm K6F silica gel 60 Å plates and visualized with the aid of UV light, KMnO<sub>4</sub> stain or PMA stain. Flash chromatography was run using silica gel (60 Å, 230-400 mesh) obtained from Silicycle and used as received. High pressure liquid chromatography was performed on an Agilent 1100 system using Chiralcel OD-H, AD-H and AD columns and a 210 nm UV detector. Gas chromatography was performed on an Agilent 6850 system using a Cyclosilb chiral column.

<sup>1</sup> V. B. Gondi, K. Hagihara and V. H. Rawal, *Angew. Chem., Int Ed.*, 2009, **48**, 776-779

### General Procedure for Enantioselective Aldol Reactions

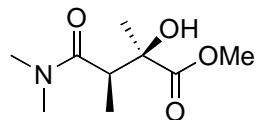
To a solution of (*4S-trans*)-2,2-dimethyl- $\alpha,\alpha,\alpha',\alpha'$ -tetra(1-naphthyl)-1,3-dioxolane-4,5-dimethanol (**4**) (20 mg, 0.031 mmol, 0.2 equiv) in 0.5 mL of toluene at -78 °C were added sequentially the pyruvate (0.153 mmol), and the *N,O*-ketene acetal (0.23 mmol) dropwise. The reaction mixture was then stirred at the indicated temperature for the required time shown in Table 2. The reaction was quenched by adding 5-25% aq HF in CH<sub>3</sub>CN (0.25 - 0.5 mL) at the same temperature, stirred at room temperature for 3-4 h (followed the reaction by TLC), then neutralized with a saturated aqueous solution of NaHCO<sub>3</sub>. The aqueous layer was extracted with Et<sub>2</sub>O or CH<sub>2</sub>Cl<sub>2</sub> (2 × 3mL). The organic layers were combined, dried over MgSO<sub>4</sub>, and concentrated *in vacuo*. The crude residue was purified by flash column chromatography (EtOAc: Hexanes, 1:1 to 1:4) to afford the products.

### Characterization Data for Aldol Products



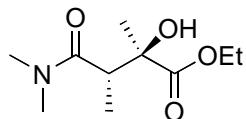
#### (2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (**3a**)

colorless oily liquid; R<sub>f</sub>=0.24 (50% EtOAc/Hex); IR (neat/CHCl<sub>3</sub>, cm<sup>-1</sup>) 3373.2, 2988, 1751, 1622, 1264; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.58 (s, 1H), 3.70 (s, 3H), 3.16 (q, *J* = 7.3, 14.5 Hz, 1H), 3.06 (s, 1H), 2.90 (s, 1H), 1.32 (s, 3H), 1.20 (d, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.42, 177.34, 76.03, 52.40, 40.62, 37.33, 35.32, 22.99, 11.67; HRMS: Exact mass of C<sub>9</sub>H<sub>17</sub>NO<sub>4</sub>Na<sup>+</sup> = 226.10498u, Observed mass: 226.10516u; HPLC: OD-H, 5% iPrOH/Hexanes, 1 mL/min, 11.1 min (minor), 12.0 min (major), ee = 85%.



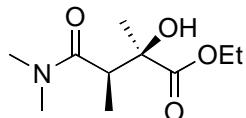
#### (2*R*,3*R*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (**3a'**)

colorless oily liquid; R<sub>f</sub>=0.18 (50% EtOAc/Hex); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.40 (s, 1H), 3.80 (s, 3H), 3.18 (q, *J* = 7.1, 14.2 Hz, 1H), 3.10 (s, 1H), 2.98 (s, 1H), 1.43 (s, 3H), 1.18 (d, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.68, 175.00, 76.61, 52.51, 41.98, 37.57, 35.47, 26.17, 13.27; HPLC: OD-H, 5% iPrOH/Hexanes, 1 mL/min, 11.2 min (major), 15.9 min (minor), ee = 60%.



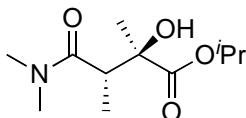
**(2*R*,3*S*)-Ethyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3b)**

colorless oily liquid;  $R_f$ =0.27 (50% EtOAc/Hex); IR (neat/CHCl<sub>3</sub>, cm<sup>-1</sup>) 3381, 2983, 2939, 1748, 1623, 1418, 1257; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.48 (s, 1H), 4.20-4.00 (m, 2H), 3.14 (q,  $J$  = 7.1, 14.2 Hz, 1H), 3.05 (s, 3H), 2.88 (s, 3H), 1.30 (s, 3H), 1.23-1.179 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.35, 176.69, 75.77, 40.57, 37.32, 35.23, 22.86, 14.04, 10.69; HPLC: OD-H, 5% iPrOH/Hexanes, 1 mL/min, 13.1 min (major), 18.4 min (minor); ee = 79%.



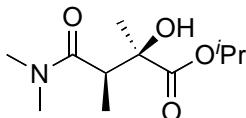
**(2*R*,3*R*)-Ethyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3b')**

colorless oily liquid;  $R_f$ =0.21 (50% EtOAc/Hex); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.52 (s, 1H), 4.19 (m, 2H), 3.20 (q,  $J$  = 7.3 Hz, 1H), 3.10 (s, 3H), 2.93 (s, 3H), 1.36 (s, 3H), 1.28 (t,  $J$  = 2.2 Hz, 3H), 1.25 (t,  $J$  = 7.3 Hz, 3H); HPLC: AD-H, 5% iPrOH/Hexanes, 1 mL/min, 13.1 min (major), 18.4 min (minor), ee = 69%.



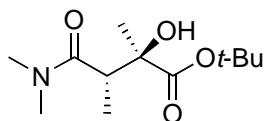
**(2*R*,3*S*)-Propyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3c)**

colorless oil;  $R_f$ =0.33 (50% EtOAc/Hex); IR (neat/CHCl<sub>3</sub>, cm<sup>-1</sup>) 3392, 2981, 1717, 1623, 1506, 1375; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.35 (bs, 1H), 5.01 (m, 1H), 3.16 (q,  $J$  = 7.3, 14.6 Hz, 1H), 3.08 (s, 3H), 2.91 (s, 3H), 1.32 (s, 3H), 1.22 (m, 3H), 1.22 (m, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.33, 176.06, 75.60, 68.34, 40.64, 37.30, 35.23, 22.81, 21.62, 21.50; HRMS: Exact mass of C11H21NO4Na<sup>+</sup> = 254.13628u, Observed mass: 254.13599u; ; HPLC: OD-H, 5% iPrOH/Hexanes, 1 mL/min, 11.2 min (major), 15.9 min (minor), ee = 89%.



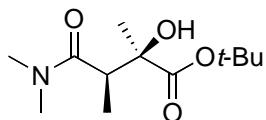
**(2*R*,3*R*)-Propyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3c')**

colorless oily liquid;  $R_f=0.27$  (50% EtOAc/Hex);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.12 (m, 1H), 3.18 (q,  $J = 7.1, 14.2$  Hz, 1H), 3.10 (s, 3H), 2.98 (s, 3H), 1.41 (s, 3H), 1.30 (m, 6H), 1.19 (d, 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.70, 174.01, 76.18, 69.04, 41.99, 37.62, 35.49, 26.07, 21.77, 21.67, 13.23; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 13.3 min (major), 15.1 min (minor).



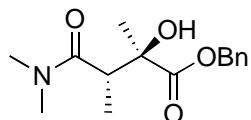
**(2*R*,3*S*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3d)**

white solid;  $R_f=0.34$  (50% EtOAc/Hex); IR (neat/ $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ) 3390, 2982, 1733, 1635;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.10 (q,  $J = 7.2, 14.5$  Hz, 1H), 3.07 (s, 3H), 1.42 (s, 9H), 1.25 (s, 3H), 1.20 (d,  $J = 7.2$  Hz 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.22, 175.65, 80.99, 75.75, 40.84, 37.31, 35.21, 27.82, 22.78, 10.84; HRMS: Exact mass of  $\text{C}_{12}\text{H}_{23}\text{NO}_4\text{Na}^+ = 268.15193\text{u}$ , Observed mass: 268.15211u; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 6.2 min (minor), 6.9 min (major), ee = 93%.



**(2*R*,3*R*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3d')**

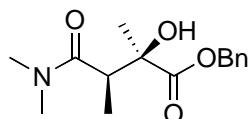
colorless oily liquid;  $R_f=0.30$  (50% EtOAc/Hex);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.16 (q,  $J = 7.1, 14.2$  Hz, 1H), 3.09 (s, 3H), 2.98 (s, 3H), 1.52 (s, 9H), 1.39 (s, 3H), 1.21 (d,  $J = 7.1$  Hz 3H);



**(2*R*,3*S*)-Benzyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3e)**

white solid;  $R_f=0.30$  (50% EtOAc/Hex); IR (neat/ $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ) 3364, 2940, 1749, 1506, 1419;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (m, 5H), 5.29 (s, 1H), 5.26 (d,  $J = 12.2$ , 1H), 5.07 (d,  $J = 12.2$ , 1H), 3.13 (q,  $J = 7.2, 14.5$  Hz, 1H), 2.89 (s, 3H), 2.77 (s, 3H), 1.35 (s, 3H), 1.21 (d,  $J = 7.2$  Hz 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.06, 176.30, 135.76, 128.43, 128.27, 128.18, 75.80, 66.72, 40.58, 37.07, 35.16, 22.90, 10.73; Exact mass of  $\text{C}_{15}\text{H}_{21}\text{NO}_4\text{Na}^+ = 302.13628\text{u}$  Observed mass: 302.13641u; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 24.6 min (major), 31.0

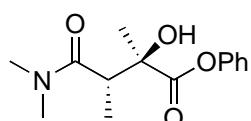
min (minor), ee = 78%.



**(2*R*,3*S*)-Benzyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3e')**

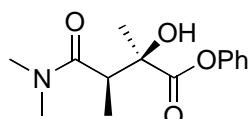
colorless oily liquid; Rf=0.26 (50% EtOAc/Hex); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35 (m, 5H), 5.25 (m, 2H), 3.17

(q, J = 7.1, 14.2 Hz, 1H), 3.08 (s, 3H), 2.97 (s, 3H), 1.43 (s, 3H), 1.14 (d, J = 7.1 Hz 3H);



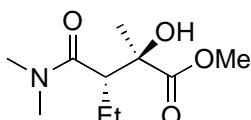
**(2*R*,3*S*)-Phenyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (3f)**

White solid. Rf=0.40 (50% EtOAc/Hex); IR (neat/CHCl<sub>3</sub>, cm<sup>-1</sup>) 3409, 2997, 2939, 1769, 1597; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (t, J = 7.6, 3H), 7.21 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 7.6 Hz, 2H), 5.73 (s, 3H), 3.27 (q, J = 7.3, 14.6 Hz, 1H), 3.07 (s, 3H), 2.94 (s, 3H), 1.51 (s, 3H), 1.29 (d, J = 7.3 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.34, 175.77, 150.88, 129.41, 125.88, 121.35, 76.14, 41.06, 37.39, 35.40, 22.93, 10.76; HRMS: Exact mass of C<sub>14</sub>H<sub>19</sub>NO<sub>4</sub>Na<sup>+</sup> = 288.12063u, Observed mass: 288.12079u; HPLC: OD-H, 5% iPrOH/Hexanes, 1 mL/min, 14.0 min (minor), 16.6 min (major), ee = 60%.



**(2*S*,3*R*)-Phenyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylbutanoate (3f')**

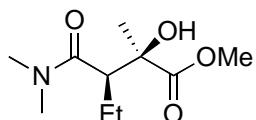
White solid. Rf=0.35 (50% EtOAc/Hex); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 (t, J = 7.9, 3H), 7.25 (t, J = 5.5 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 5.38 (s, 1H), 3.30 (q, J = 7.1, 14.2 Hz, 1H), 3.14 (s, 3H), 3.02 (s, 3H), 1.61 (s, 3H), 1.35 (d, J = 7.1 Hz, 3H);



**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylpentanoate (6a)**

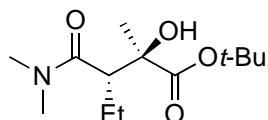
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 5.62 (s, 1H), 3.68 (s, 1H), 3.08 (m, 1H), 3.07 (s, 3H), 2.93 (s, 3H), 1.81-

1.74 (m, 2H), 1.37 (s, 3H), 0.93 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.08, 176.60, 76.49, 52.40, 46.70, 37.87, 35.46, 23.40, 20.11, 11.92; HRMS: Exact mass of  $\text{C}_{10}\text{H}_{19}\text{NO}_4\text{Na}^+ = 240.12063\text{u}$ , Observed mass: 240.12024u; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 9.4 min (minor), 10.6 min (major), ee = 78%.



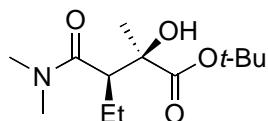
**(2*R*,3*R*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylpentanoate (6a')**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.23 (s, 1H), 3.79 (s, 1H), 3.20-3.16 (m, 1H), 3.15 (s, 3H), 3.03 (s, 3H), 1.97-1.89 (m, 1H), 1.50-1.43 (m, 1H), 1.38 (s, 3H), 0.86 (t,  $J = 7.5$  Hz, 3H).



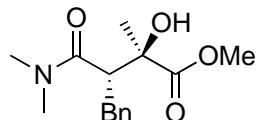
**(2*R*,3*S*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylpentanoate (6b)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.26 (s, 1H), 3.09 (s, 3H), 3.04 (dd,  $J = 5.8, 8.9$  Hz, 1H), 1.80-1.74 (m, 2H), 1.42 (s, 9H), 1.34 (s, 3H), 0.93 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.29, 175.55, 81.16, 76.12, 46.96, 37.92, 35.31, 27.79, 23.19, 20.33, 12.00; HPLC: 5% *iPrOH*/Hexanes, 1 mL/min, 5.8 min (minor), 7.2 min (minor), ee = 84%.



**(2*R*,3*R*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylpentanoate (6b')**

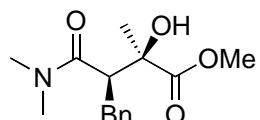
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.86 (s, 1H), 3.14 (m, 1H), 3.13 (s, 3H), 3.02 (s, 3H), 1.95 (m, 1H), 1.51 (m, 1H), 1.51 (s, 9H), 1.34 (s, 3H), 0.87 (t,  $J = 7.46$  Hz, 3H);



**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methyl-4-phenylbutanoate (6c)**

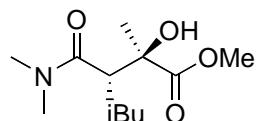
IR (neat,  $\text{cm}^{-1}$ ) 3362.1, 2948.4, 1751.4, 1724.9, 1618.5, 1495.0, 1418.0, 1287.8, 1179.0, 703.6;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.18 (m, 5H), 3.72 (s, 3H), 3.38 (dd,  $J = 4.3, 11.31$  Hz, 1H), 3.08-2.99 (m, 2H), 2.74 (s, 3H), 2.33 (s,

3H), 1.54 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.70, 175.60, 138.58, 129.04, 128.32, 126.62, 76.31, 52.40, 48.01, 36.83, 35.08, 33.08, 33.46, 23.43; HRMS: Exact Mass of  $\text{C}_{15}\text{H}_{21}\text{NO}_4\text{Na}^+$  = 302.13628u Observed mass: 302.13542u; HPLC: Chiral Cel OJ column, 5% *iPrOH*/Hexanes, 1 mL/min, 18.88 min (major), 22.69 min (minor), ee = 88%.



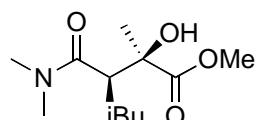
**(2*R*,3*R*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methyl-4-phenylbutanoate (6c')**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) 7.29-7.16 (m, 5H), 5.62 (s, 1H), 3.48 (dd,  $J$  = 3.54, 11.53 Hz, 1H), 3.15 (dd,  $J$  = 11.8, 12.9 Hz, 1H), 2.84 (s, 3H), 2.75 (dd,  $J$  = 3.49, 12.9 Hz, 1H), 2.41 (s, 3H), 1.45 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.80, 174.43, 138.67, 128.95, 128.38, 126.66, 76.66, 52.70, 49.62, 37.23, 35.83, 35.28, 26.45.



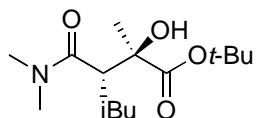
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2,5-dimethylhexanoate (6d)**

White solid.  $R_f$  = 0.38 (50% EtOAc/Hex); IR (neat,  $\text{cm}^{-1}$ ) 3383, 2955, 2870, 1751, 1619, 1417;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.36 (s, 1H), 3.62 (s, 3H), 3.1 (dd,  $J$  = 2.26, 10.45 Hz, 1H), 3.02 (s, 3H), 2.85 (s, 3H), 1.70 (m, 1H), 1.37 (m, 2H), 1.31 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.96, 176.73, 76.60, 43.77, 43.67, 37.90, 36.58, 35.59, 25.89, 23.89, 23.40, 22.30; HRMS: Exact Mass of  $\text{C}_{12}\text{H}_{23}\text{NO}_4\text{Na}^+$  = 268.15193u Observed mass: 268.15107u; HPLC: AD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 10.16 min (major), 13.89 min (minor), ee = 90%.



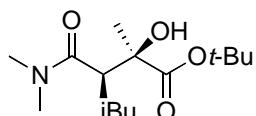
**(2*R*,3*R*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2,5-dimethylhexanoate (6d')**

White solid.  $R_f$  = 0.33 (50% EtOAc/Hex);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.01 (s, 1H), 3.78 (s, 3H), 3.29 (dd,  $J$  = 3.05, 10.88 Hz, 1H), 3.14 (s, 3H), 3.00 (s, 3H), 1.94 (ddd,  $J$  = 3.88, 10.92, 13.89 Hz, 1H), 1.35 (s, 3H), 1.32 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.33, 174.82, 52.56, 45.27, 38.67, 38.10, 35.65, 26.20, 26.09, 23.62, 22.10;



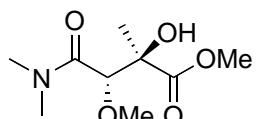
**(2*R*,3*S*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2,5-dimethylhexanoate (6e)**

White solid.  $R_f=0.60$  (50% EtOAc/Hex); IR (neat,  $\text{cm}^{-1}$ ) 3395, 2957, 2870, 1744, 1621, 1397;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.06 (m, 1H), 3.05 (s, 3H), 2.87 (s, 3H), 1.72 (m, 1H), 1.38 (m, 2H), 1.38 (s, 9H), 1.29 (s, 3H), 0.88 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.32, 175.38, 81.17, 76.14, 43.74, 37.84, 36.76, 35.33, 27.66, 25.77, 23.78, 23.11, 22.23; HRMS: Exact Mass of  $\text{C}_{15}\text{H}_{29}\text{NO}_4\text{Na}^+$  = 310.19888u Observed mass: 310.19816u ; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 4.7 min (minor), 6.0 min (major), ee = 93%.



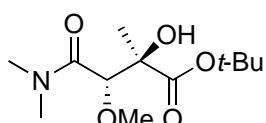
**(2*R*,3*R*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2,5-dimethylhexanoate (6e')**

White solid.  $R_f=0.50$  (50% EtOAc/Hex);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.69 (s, 1H), 3.24 (m, 1H), 3.11 (s, 3H), 2.97 (s, 3H), 1.98 (m, 1H), 1.48 (s, 9H), 1.30 (s, 3H), 1.13 (m, 1H);



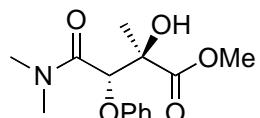
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-3-methoxy-2-methylpropanoate (6f)**

White solid.  $R_f=0.13$  (50% EtOAc/Hex); IR (neat,  $\text{cm}^{-1}$ ) 3388, 2927, 1727, 1657, 1257;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.09 (s, 1H), 4.49 (s, 1H), 3.73 (s, 3H), 3.47 (s, 3H), 3.17 (s, 3H), 2.97 (s, 3H), 2.97 (s, 3H), 1.47 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.64, 170.61, 78.59, 77.31, 57.31, 52.61, 37.17, 35.79, 22.20; HRMS: Exact Mass of  $\text{C}_9\text{H}_{17}\text{NO}_5\text{Na}^+$  = 242.09989u, Observed mass: 242.09978u ; HPLC: AD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 15.84 min (minor), 17.12 min (major), ee = 89%.



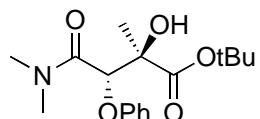
**(2*R*,3*S*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-3-methoxy-2-methylpropanoate (6g)**

White solid.  $R_f=0.31$  (50% EtOAc/Hex); IR (neat,  $\text{cm}^{-1}$ ) 3403.5, 2979.5, 2829, 1744, 1639, 1368;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.77 (s, 1H), 4.35 (s, 1H), 3.40 (s, 3H), 3.11 (s, 3H), 2.91 (s, 3H), 1.389 (s, 9H), 1.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.98, 170.42, 81.79, 78.96, 77.31, 57.39, 37.10, 35.65, 27.66, 21.95; HRMS: Exact Mass of  $\text{C}_{12}\text{H}_{23}\text{NO}_5\text{Na}^+$  = 284.14684u Observed mass: 284.14621u ; HPLC: AD-H, 3% *iPrOH*/Hexanes, 1 mL/min, 35 °C, 11.39 min (major), 20.18 min (minor), ee = 93%.



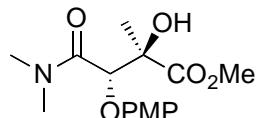
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methyl-3-phenoxypropanoate (6h)**

Colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\tau^m$  7.32-7.28 (m, 2H), 7.02-6.97 (m, 3H), 5.23 (s, 1H), 4.73 (s, 1H), 3.83 (s, 3H), 2.97 (s, 3H), 2.91 (s, 3H), 1.53 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.35, 169.37, 157.71, 129.82, 122.33, 115.40, 79.37, 53.07, 46.61, 37.33, 36.55, 22.64; HPLC: OJ-H, 5% *iPrOH*/Hexanes, 1 mL/min, 21.40 min (major), 24.07 min (minor), ee = 97%.



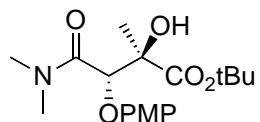
**(2*R*,3*S*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methyl-3-phenoxypropanoate (6i)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.26 (m, 2H), 7.02-6.94 (m, 3H), 5.11 (s, 1H), 4.44 (s, 1H), 3.00 (s, 3H), 2.89 (s, 3H), 1.50 (s, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.81, 169.16, 157.74, 129.75, 122.09, 115.29, 83.03, 80.64, 76.65, 37.26, 36.63, 27.85, 22.63; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 5.28 min (minor), 5.63 min (major), ee = 95%.



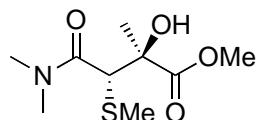
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-3-(4-methoxyphenoxy)-2-hydroxy-2-methylpropanoate (6j)**

White solid.  $R_f = 0.17$  (50% EtOAc/Hex);  $[\alpha]^{25}_D -75.3^\circ$  ( $c = 0.96$ ,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 3380, 2951, 1741, 1636, 1456, 1401, 1218;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.93 (d,  $J = 9.1$  Hz, 2H), 6.82 (d,  $J = 9.1$  Hz, 2H), 5.10 (s, 1H), 4.94 (s, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.93 (s, 3H), 2.91 (s, 3H), 1.56 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.59, 170.06, 155.30, 151.97, 117.44, 115.05, 79.90, 77.18, 55.89, 53.21, 37.21, 36.65, 22.93; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 14.1 min (major), 16.090 min (minor), ee = 89%.



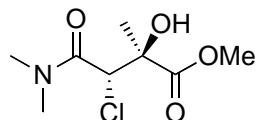
**(2*R*,3*S*)-*tert*-Butyl 3-(dimethylcarbamoyl)-3-(4-methoxyphenoxy)-2-hydroxy-2-methylpropanoate (6k)**

White solid.  $R_f = 0.45$  (50% EtOAc/Hex);  $[\alpha]^{25}_D -30.1^\circ$  ( $c = 1.14$ ,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 3397, 2979, 2936, 1734, 1638, 1510, 1457, 1395, 1369, 1226;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (d,  $J = 9.1$  Hz, 2H), 6.82 (d,  $J = 9.1$  Hz, 2H), 5.00 (s, 1H), 4.61 (s, 1H), 3.77 (s, 3H), 2.96 (s, 3H), 2.96 (s, 3H), 2.90 (s, 3H), 1.53 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  174.14, 169.90, 155.17, 152.10, 117.26, 115.05, 83.14, 81.09, 77.02, 55.94, 37.60, 36.77, 28.15, 22.93; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 7.3 min (minor), 8.3 min (major), ee = 95%.



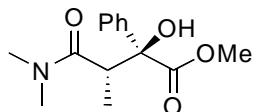
**(2*S*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methyl-3-(methylthio)propanoate (6l)**

White solid.  $R_f = 0.38$  (50% EtOAc/Hex);  $[\alpha]^{25}_D -43.4^\circ$  ( $c = 1.15$ ,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 3396, 2988, 2929, 1750, 1723, 1626, 1497, 1440, 1399;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.57 (s, 1H), 3.84 (s, 1H), 3.73 (s, 3H), 3.16 (s, 3H), 2.97 (s, 3H), 2.17 (s, 3H), 1.51 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.11, 171.97, 78.67, 52.92, 48.30, 37.89, 35.89, 23.92, 14.29; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 8.5 min (minor), 10.3 min (major), ee = 91%.



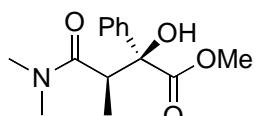
**(2*S*,3*S*)-Methyl 3-(dimethylcarbamoyl)-3-chloro-2-hydroxy-2-methylpropanoate (6m)**

White solid.  $R_f = 0.45$  (50% EtOAc/Hex);  $[\alpha]^{25}_D -34.8^\circ$  ( $c = 1.00$ ,  $\text{CHCl}_3$ ); IR (neat,  $\text{cm}^{-1}$ ) 3446, 2957, 1760, 1718, 1644, 1278;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.56, (s, 1H), 4.83 (s, 1H), 3.77 (s, 3H), 3.16 (s, 3H), 2.98 (s, 3H), 1.51 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.63, 170.21, 76.37, 56.87, 53.20, 37.89, 36.15, 23.46; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 10.0 min (minor), 11.0 min (major), ee = 88%.



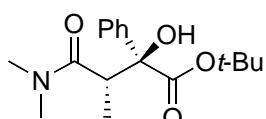
**(2S,3S)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylbutanoate (13a)**

White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.36$  Hz, 2H), 7.37 (t,  $J = 7.1$ , 2H), 7.30 (m, 1H), 6.53 (s, 1H), 3.68 (s, 3H), 3.58 (q,  $J = 7.3$ , 14.5 Hz, 1Hz), 3.18 (s, 3H), 2.99 (s, 3H), 0.92 (d,  $J = 7.30$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.70, 175.66, 138.73, 128.36, 127.83, 125.02, 80.27, 52.79, 42.57, 37.48, 35.53, 10.85; HRMS: Exact mass of  $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{Na}^+ = 288.120629\text{u}$ , Observed mass: 288.120893u Difference = <+1.0 ppm; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 8.6 min (minor), 9.7 min (major), ee = 76%.



**(2S,3R)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylbutanoate (13a')**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (m, 2H), 7.34-7.24 (m, 3H), 6.45 (s, 1H), 3.90 (q,  $J = 6.9$ , 13.8 Hz, 1H), 3.74 (s, 3H), 2.97 (s, 3H), 2.69 (s, 3H), 1.34 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  175.48, 172.50, 141.52, 128.16, 127.76, 125.03, 80.31, 52.71, 41.65, 37.26, 35.11, 13.27; HPLC: OD-H, 5% *iPrOH*/Hexanes, 1 mL/min, 11.4 min (minor), 12.3 min (major), ee = 71%.

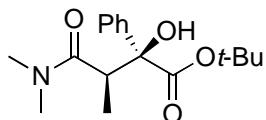


**(2S,3S)-tert-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylbutanoate (13b)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.3$  Hz, 2H), 7.34-7.24 (m, 3H), 6.10 (s, 1H), 3.48 (q,  $J = 7.28$ , 1H), 3.13 (s, 3H), 2.96 (s, 3H), 1.36 (s, 9H), 0.89 (d,  $J = 7.28$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  177.72, 173.78, 139.39, 128.28, 127.64, 125.29, 81.66, 80.30, 42.88, 37.55, 29.81, 27.88, 11.09; HRMS: Exact mass of  $\text{C}_{17}\text{H}_{25}\text{NO}_4\text{Na}^+ =$

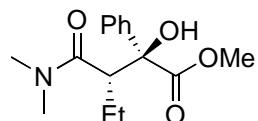
330.167579u, Observed mass: 330.167458u Difference = <-1.0 ppm;

HPLC: AD-H, 5% *i*PrOH/Hexanes, 1 mL/min, 10.1 min (major), 13.6 min (minor), ee = 73%.



**(2*S*,3*R*)-*tert*-Butyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylbutanoate (13b')**

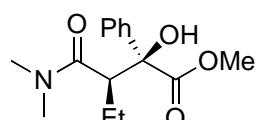
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, 2H), 7.29-7.20 (m, 3H), 6.18 (s, 1H), 3.81 (q, *J* = 6.9 Hz, 1H), 2.93 (s, 3H), 2.66 (s, 3H), 1.39 (s, 9H), 1.31 (d, *J* = 6.9 Hz, 3H); HPLC: AD-H, 5% *i*PrOH/Hexanes, 1 mL/min, 14.7 min (major), 19.6 min (major), ee = 86%.



**(2*S*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylpentanoate (13c)**

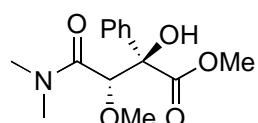
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60-7.58 (m, 2H), 7.38-7.27 (m, 3H), 6.66 (s, 1H), 3.64 (s, 3H), 3.51 (dd, *J* = 4.3, 10.1 Hz, 1H), 3.25 (s, 3H), 3.02 (s, 3H), 1.71-1.58 (m, 1H), 1.31-1.19 (m, 1H), 0.73 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.17, 175.55, 139.14, 128.38, 127.85, 125.03, 80.62, 52.81, 48.23, 38.10, 35.69, 20.49, 11.73; HRMS: Exact mass of C<sub>15</sub>H<sub>21</sub>NO<sub>4</sub>Na<sup>+</sup> = 302.13628u, Observed mass: 302.13640u;

HPLC: OD-H, 5% *i*PrOH/Hexanes, 1 mL/min, 7.6 min (minor), 11 min (major), ee = 69-71%.



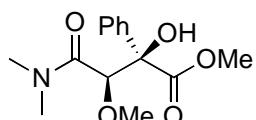
**(2*S*,3*R*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-phenylpentanoate (13c')**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61-7.59 (m, 2H), 7.32-7.24 (m, 3H), 6.35 (s, 1H), 3.78 (dd, *J* = 3.5, 10.9 Hz, 1H), 3.74 (s, 3H), 2.84 (s, 3H), 2.64 (s, 3H), 2.11-1.98 (m, 1H), 1.75-1.63 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 175.20, 175.04, 77.65, 77.33, 76.52, 52.62, 48.67, 38.17, 35.58, 26.39, 22.53, 11.94;



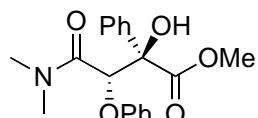
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-3-methoxy-2-phenylpropanoate (13d)**

White solid.  $R_f=0.32$  (50% EtOAc/Hex); IR (neat,  $\text{cm}^{-1}$ ) 3335, 2951, 1752, 1632, 1435, 1260;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68 (d,  $J = 1.42$  Hz, 2H), 7.36 (t,  $J = 7.8$  Hz, 2H), 7.29 (m, 1H), 6.04 (s, 1H), 4.91 (s, 1H), 3.67 (s, 3H), 3.15 (s, 3H), 3.10 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.99, 171.10, 137.50, 128.29, 128.10, 125.24, 80.46, 79.98, 58.32, 52.72, 37.29, 35.72; HRMS: Exact Mass of  $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{Na}^+ = 304.11554\text{u}$  Observed mass: 304.11491u; HPLC: 5% *iPrOH*/Hexanes, 1 mL/min, 13.8 min (minor), 19.2 min (major), ee = 83%.



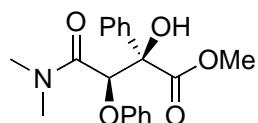
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-3-methoxy-2-phenylpropanoate (13d')**

White solid.  $R_f=0.28$  (50% EtOAc/Hex);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (m, 2H), 7.31 (m, 3H), 5.83 (s, 3H), 4.99 (s, 1H), 3.80 (s, 3H), 3.40 (s, 3H), 2.72 (s, 3H), 2.71 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  172.05, 169.70, 137.48, 128.55, 128.29, 125.33, 80.68, 78.38, 77.33, 57.97, 53.08, 37.09, 35.56; HPLC: 5% *iPrOH*/Hexanes, 1 mL/min, 26.2 min (minor), 32.2 min (major), ee = 88%.



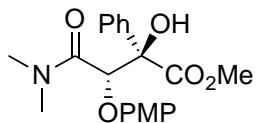
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-3-phenoxy-2-phenylpropanoate (13e)**

ee = 86%. This and the corresponding diastereomer were obtained as mixture. Could not separate by column chromatography. ( $\text{dr} = 9:1$ ).



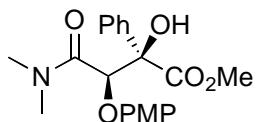
**(2*R*,3*R*)-Methyl 3-(dimethylcarbamoyl)-2-hydroxy-3-phenoxy-2-phenylpropanoate (13e')**

ee = 92%. This and the corresponding diastereomer were obtained as mixture. Could not separate by column chromatography.



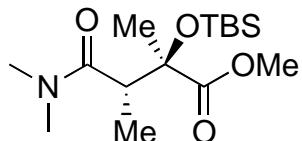
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-3-(4-methoxyphenoxy)-2-hydroxy-2-phenylpropanoate (13f)**

White solid.  $R_f$ =0.38 (50% EtOAc/Hex);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68-7.64 (m, 2H), 7.38-7.32 (m, 2H), 6.62 (d,  $J$  = 9.1 Hz, 2H), 6.47 (d,  $J$  = 9.1 Hz, 2H), 6.32 (s, 1H), 5.40 (s, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 2.97 (s, 3H), 2.88 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.07, 171.05, 155.37, 151.82, 137.71, 128.47, 128.36, 125.83, 118.84, 114.49, 80.77, 80.41, 55.65, 53.15, 37.67, 36.24; HPLC: OD-H, 5% *i*PrOH/Hexanes, 1 mL/min, 16.0 min (minor), 16.8 min (major), ee = 88%.



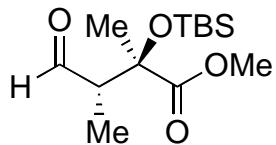
**(2*R*,3*S*)-Methyl 3-(dimethylcarbamoyl)-3-(4-methoxyphenoxy)-2-hydroxy-2-phenylpropanoate (13f')**

ee = 87% .



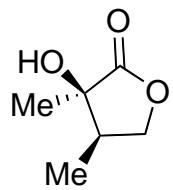
**TBS ether of (2*R*,3*S*)-methyl 3-(dimethylcarbamoyl)-2-hydroxy-2-methylbutanoate (7)**

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.56 (s, 3H), 3.32 (q,  $J$  = 7, 14 Hz, 1H), 3.15 (s, 3H), 2.92 (s, 3H), 1.51 (s, 3H), 1.05 (d,  $J$  = 7 Hz, 3H), 0.84 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H); dr = 15:1.



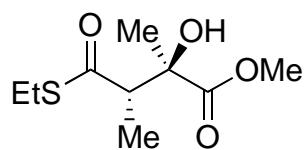
**TBS ether of (2*R*,3*S*)-methyl 3-formyl-2-hydroxy-2-methylbutanoate (8)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.68 (s, 1H), 3.73 (s, 3H), 2.70 (q,  $J$  = 7 Hz, 14 Hz, 1H), 1.44 (s, 3H), 1.09 (d,  $J$  = 7 Hz, 3H), 0.87 (s, 9H), 0.09 (d,  $J$  = 8 Hz, 6H); dr = 15:1.

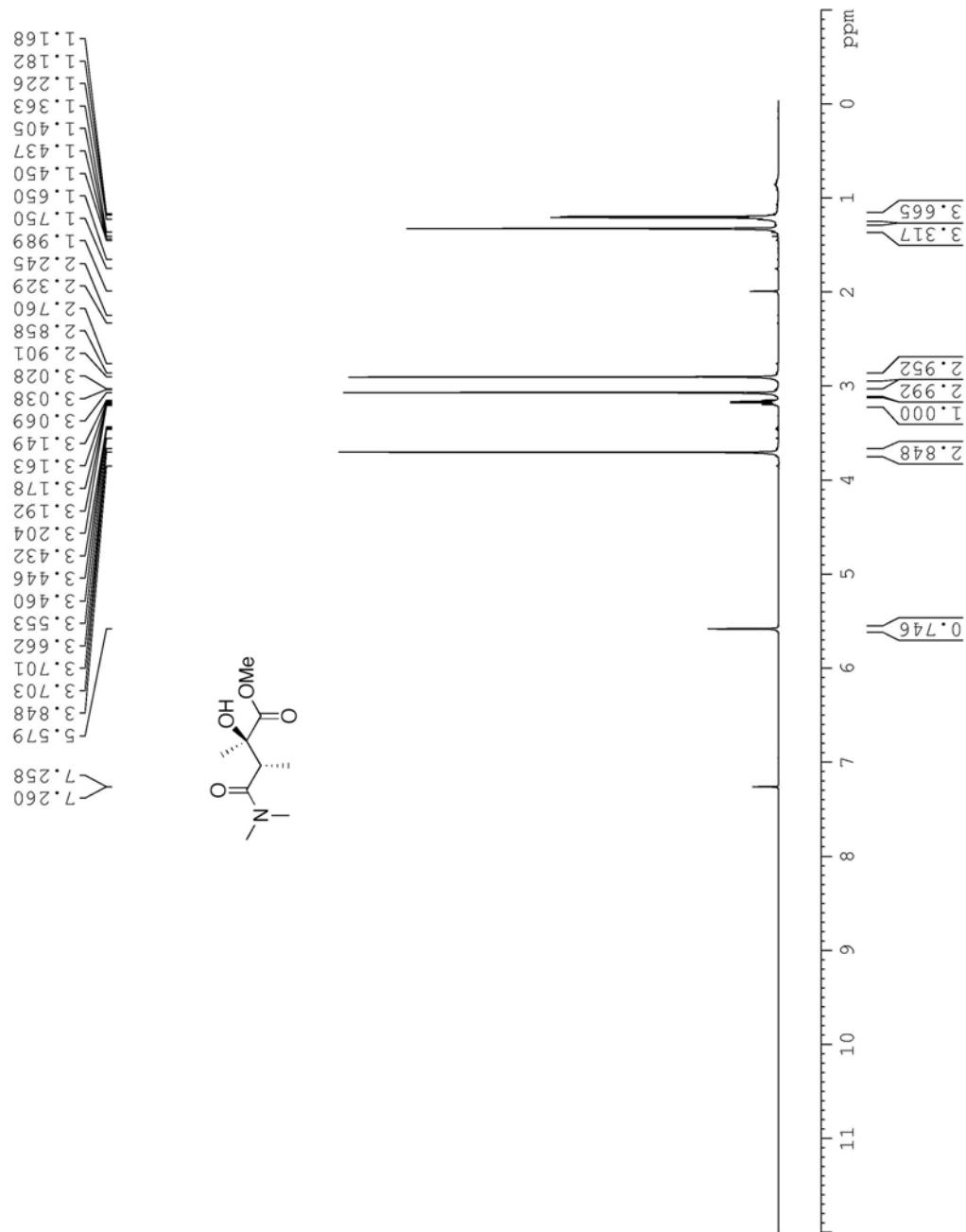


**(3*R*,4*R*)-Dihydro-3-hydroxy-3,4-dimethylfuran-2(3*H*)-one (10)**

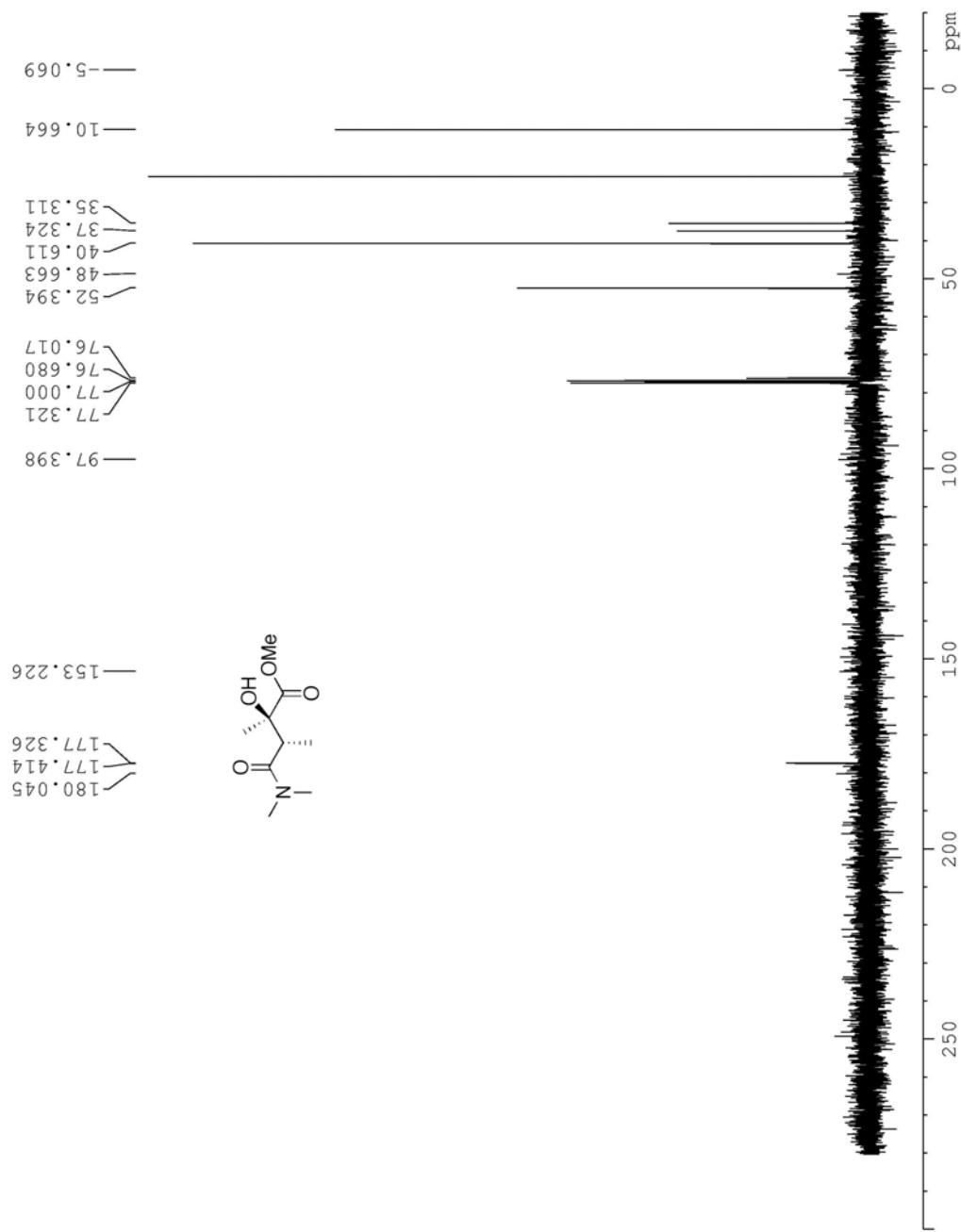
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.34-4.31 (m, 1H), 4.00-3.97 (m, 1H), 2.37-2.28 (m, 2H), 1.45 (s, 3H), 1.1 (d,  $J = 2.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  179.06, 73.45, 72.17, 40.86, 22.97, 10.57.



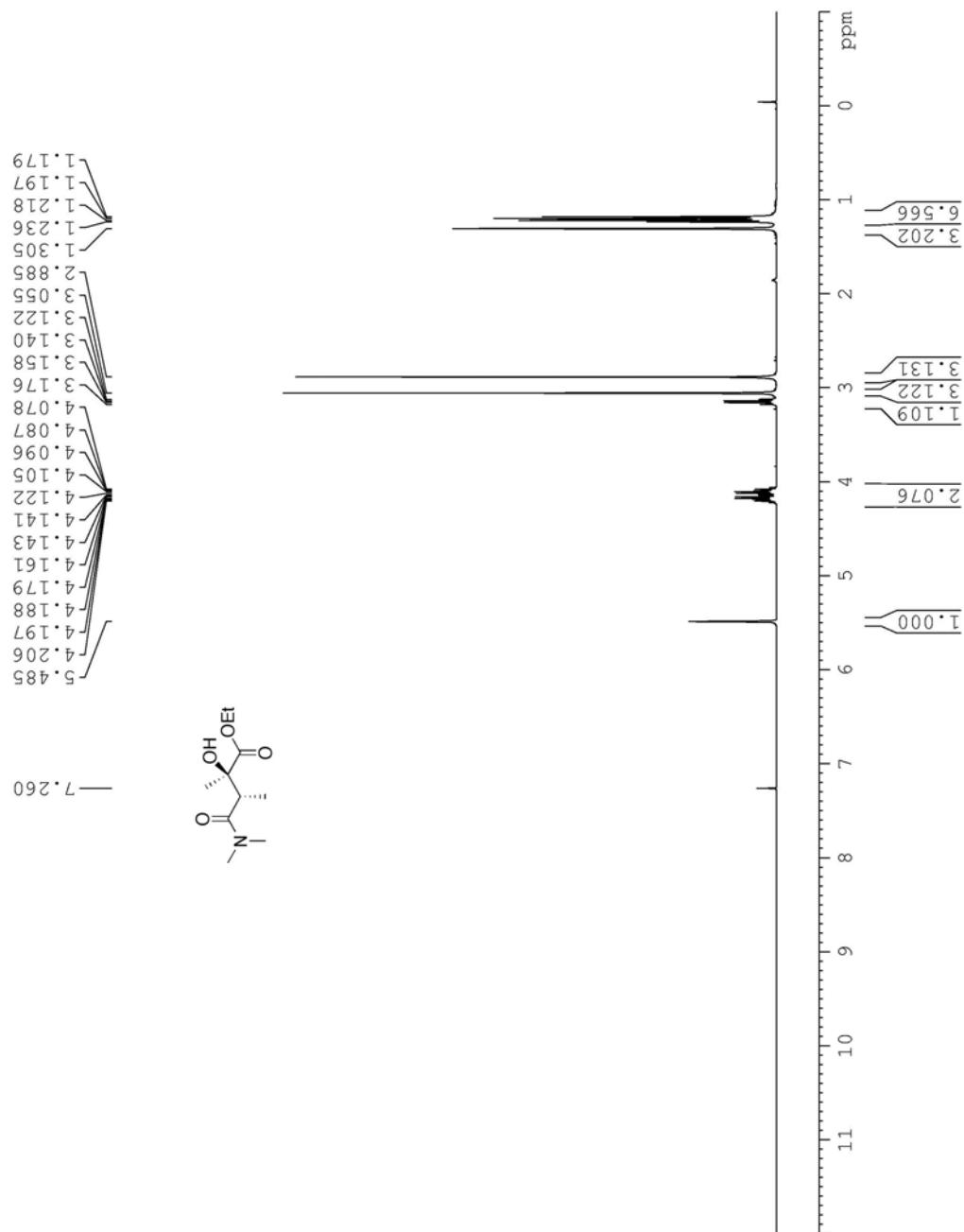
**Spectral data**



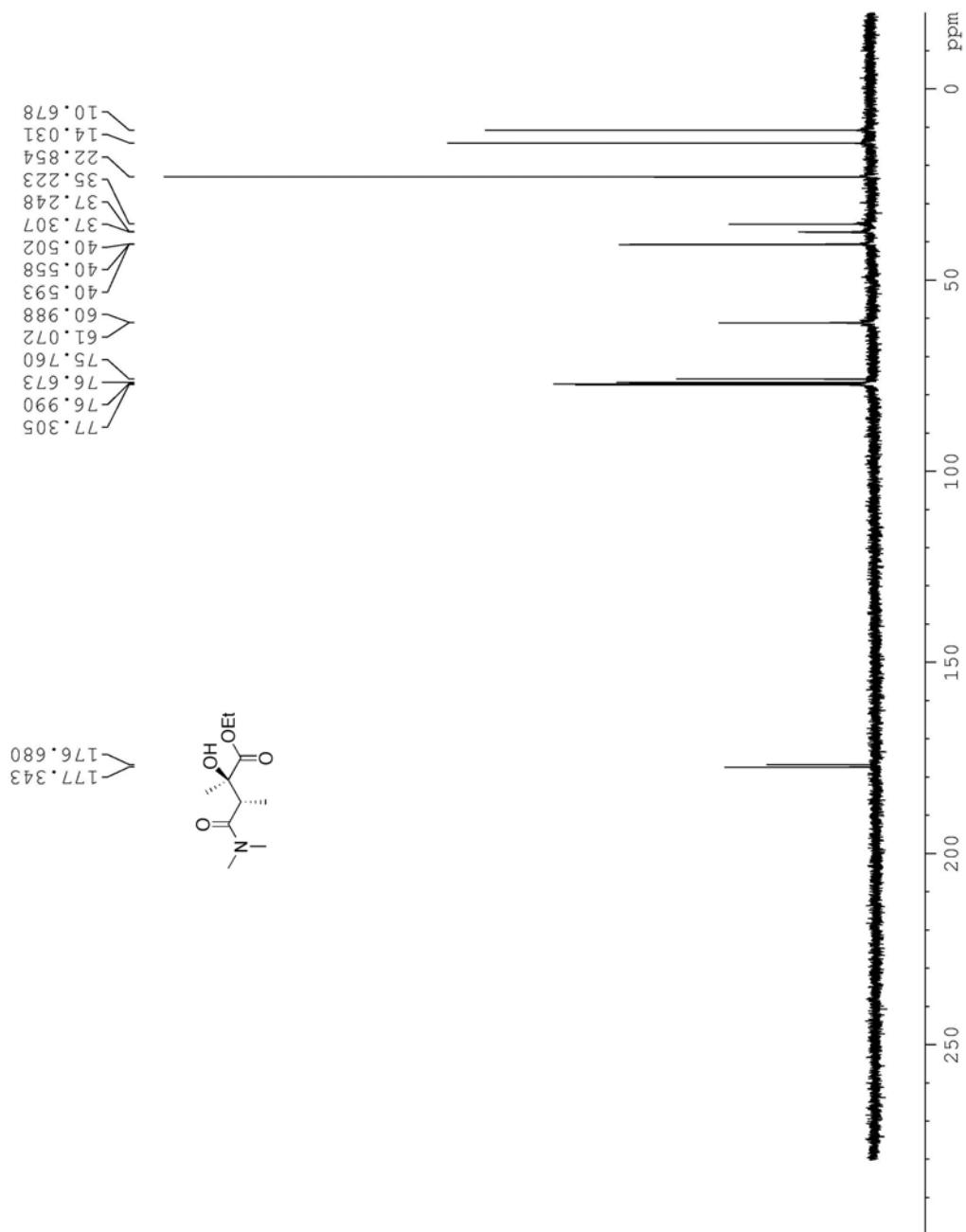
**<sup>1</sup>H NMR spectrum of 3a ( $\text{CDCl}_3$ , 298 K)**



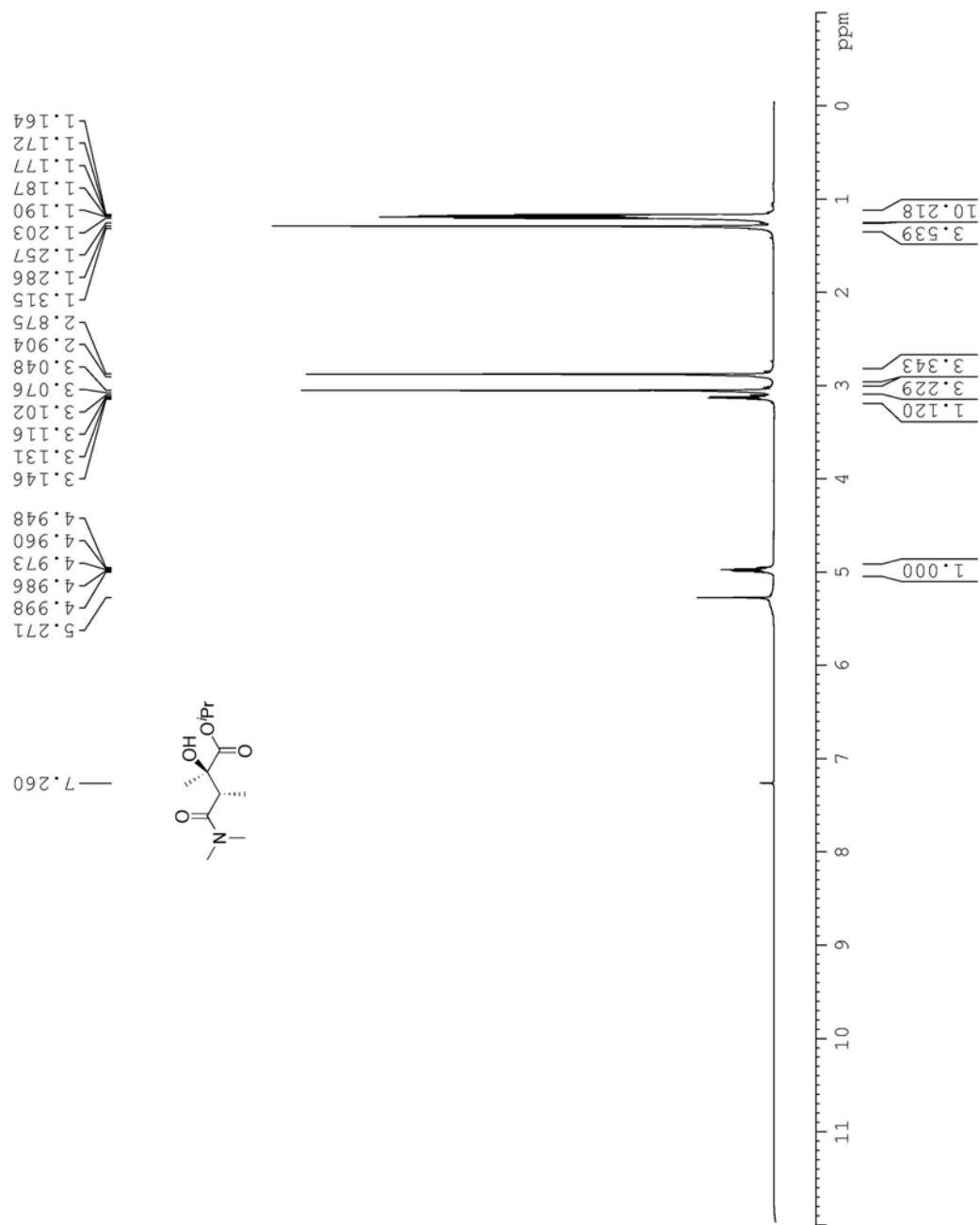
$^{13}\text{C}$  NMR spectrum of 3a ( $\text{CDCl}_3$ , 298 K)



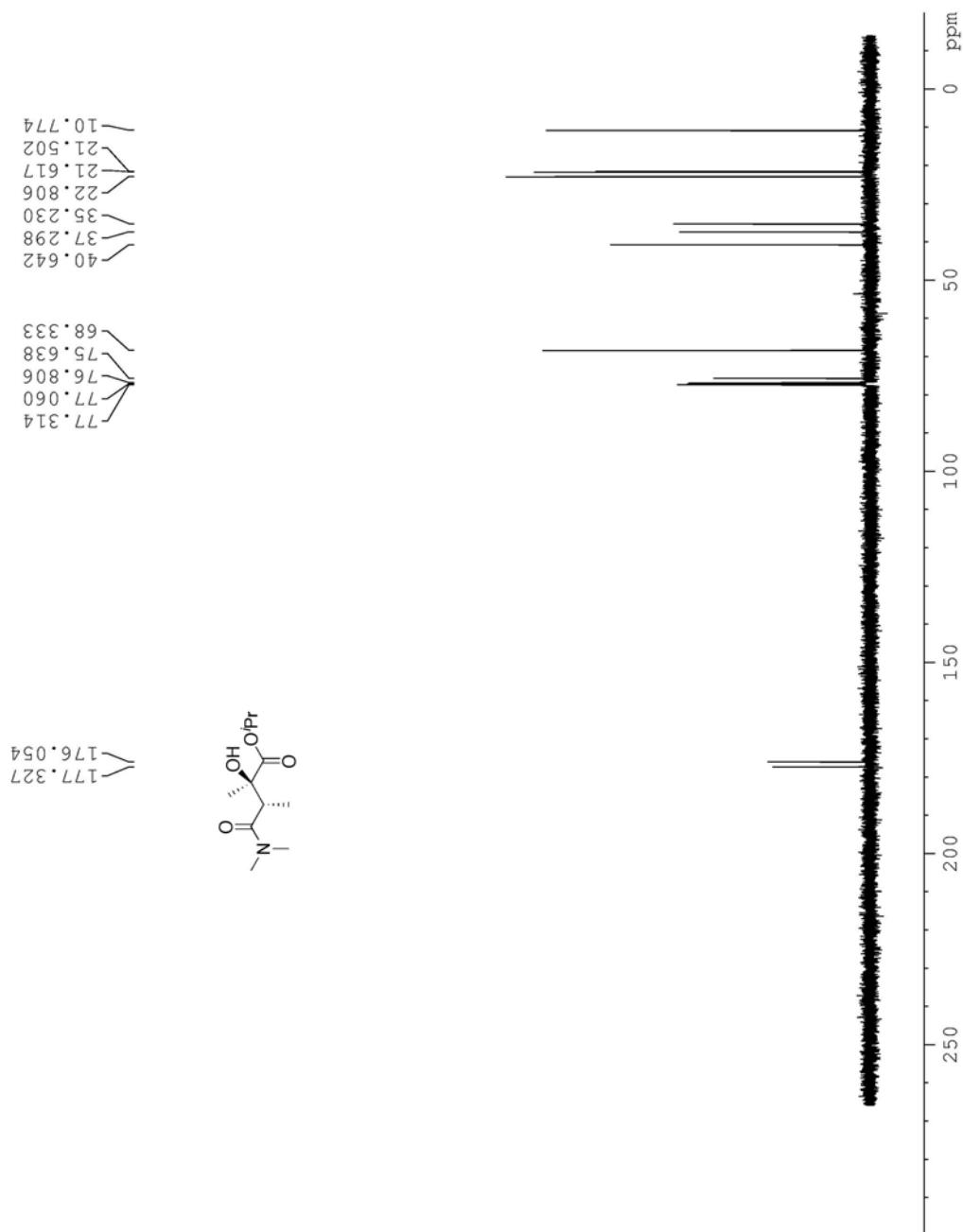
$^1\text{H}$  NMR spectrum of 3b ( $\text{CDCl}_3$ , 298 K)



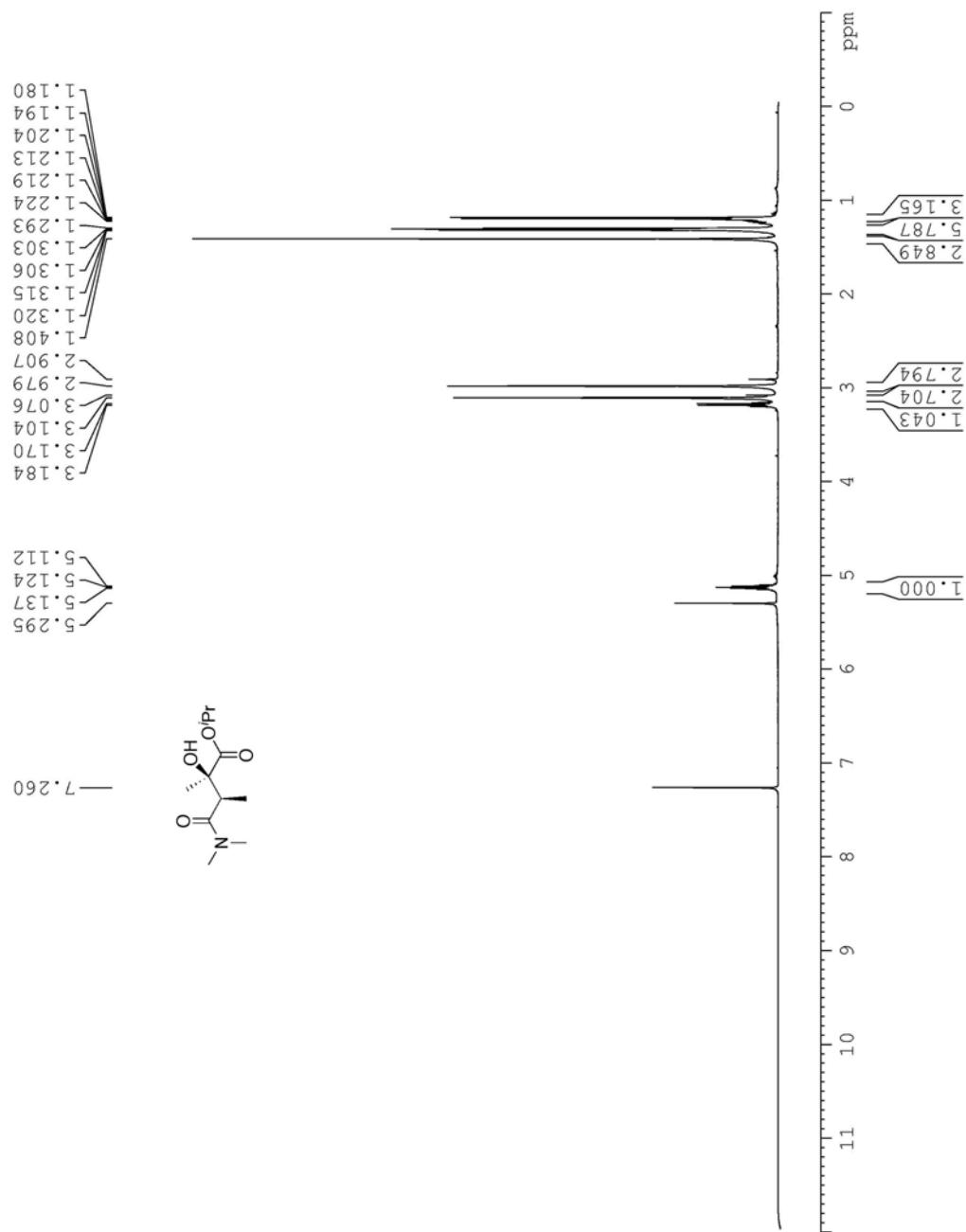
$^{13}\text{C}$  NMR spectrum of 3b ( $\text{CDCl}_3$ , 298 K)



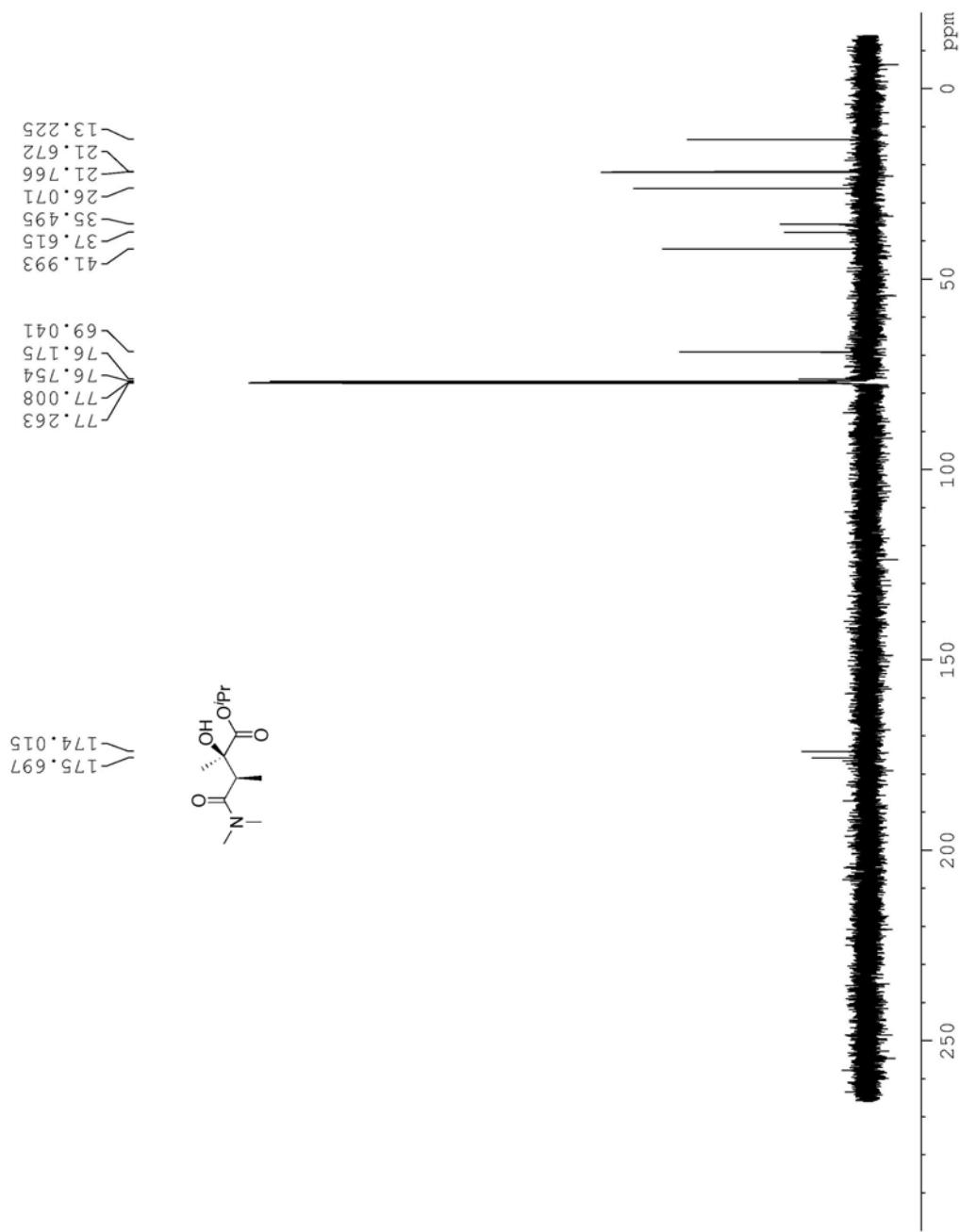
$^1\text{H}$  NMR spectrum of **3c** ( $\text{CDCl}_3$ , 298 K)



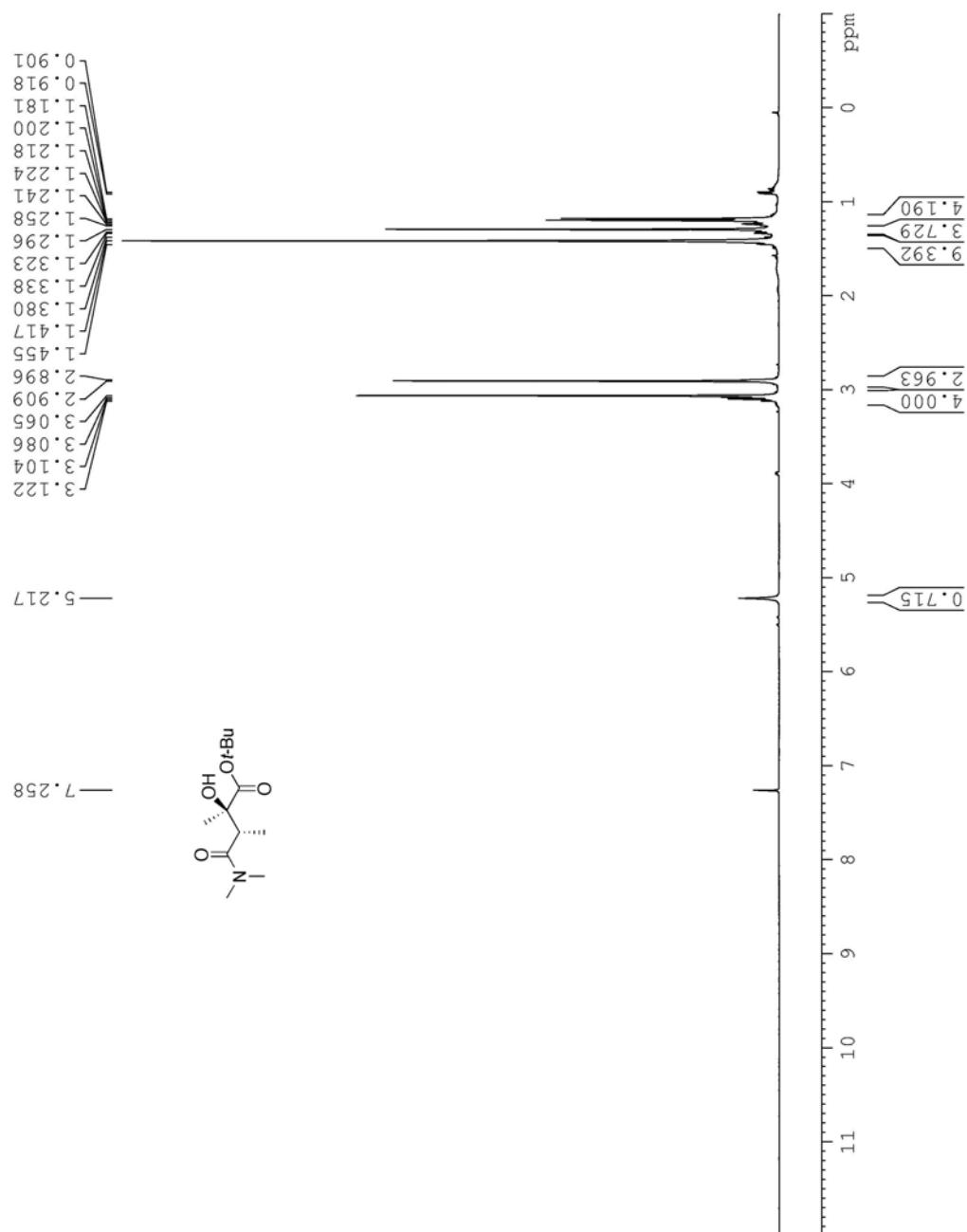
$^{13}\text{C}$  NMR spectra of 3c ( $\text{CDCl}_3$ , 298 K)



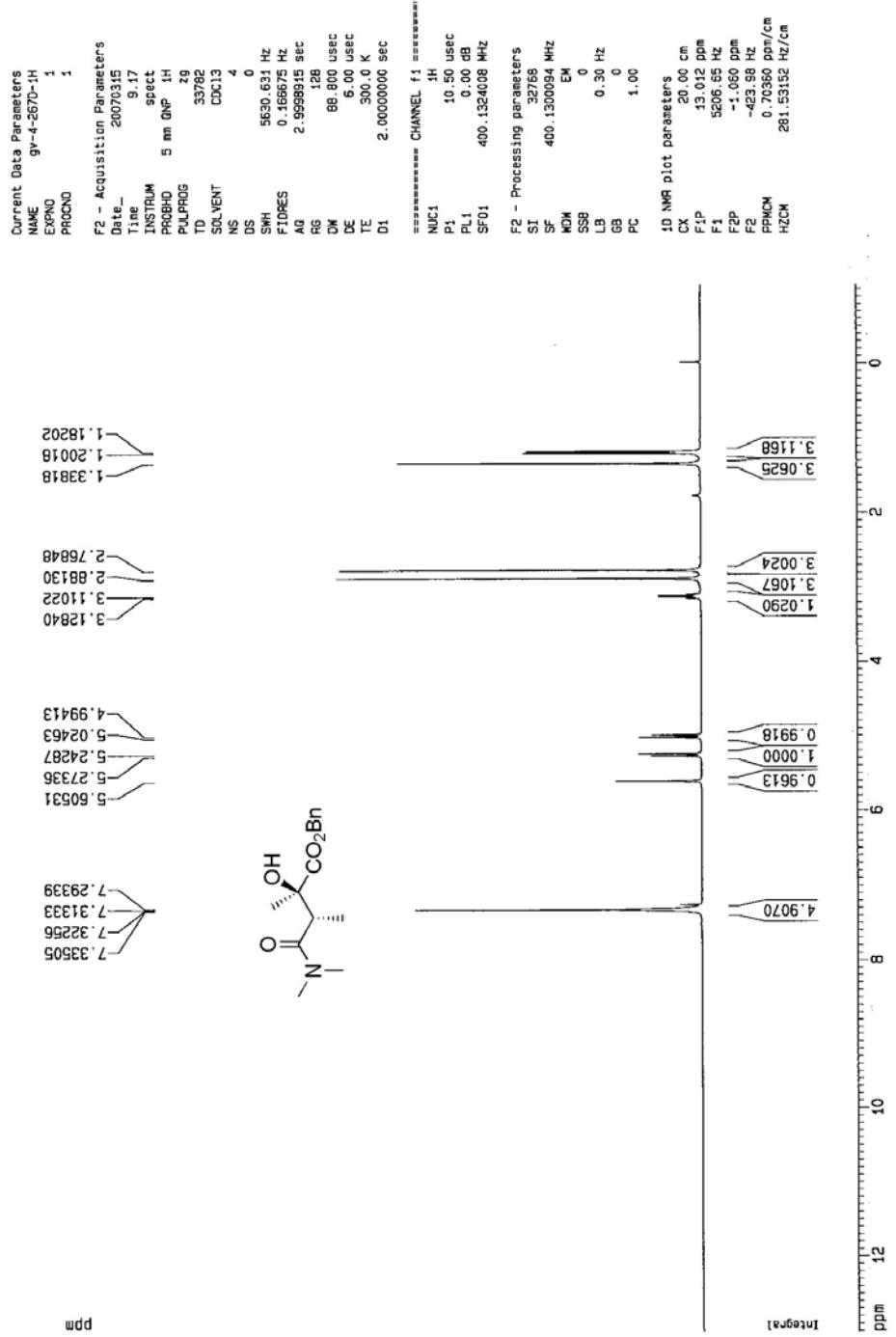
<sup>1</sup>H NMR spectrum of 3c' (CDCl<sub>3</sub>, 298 K)



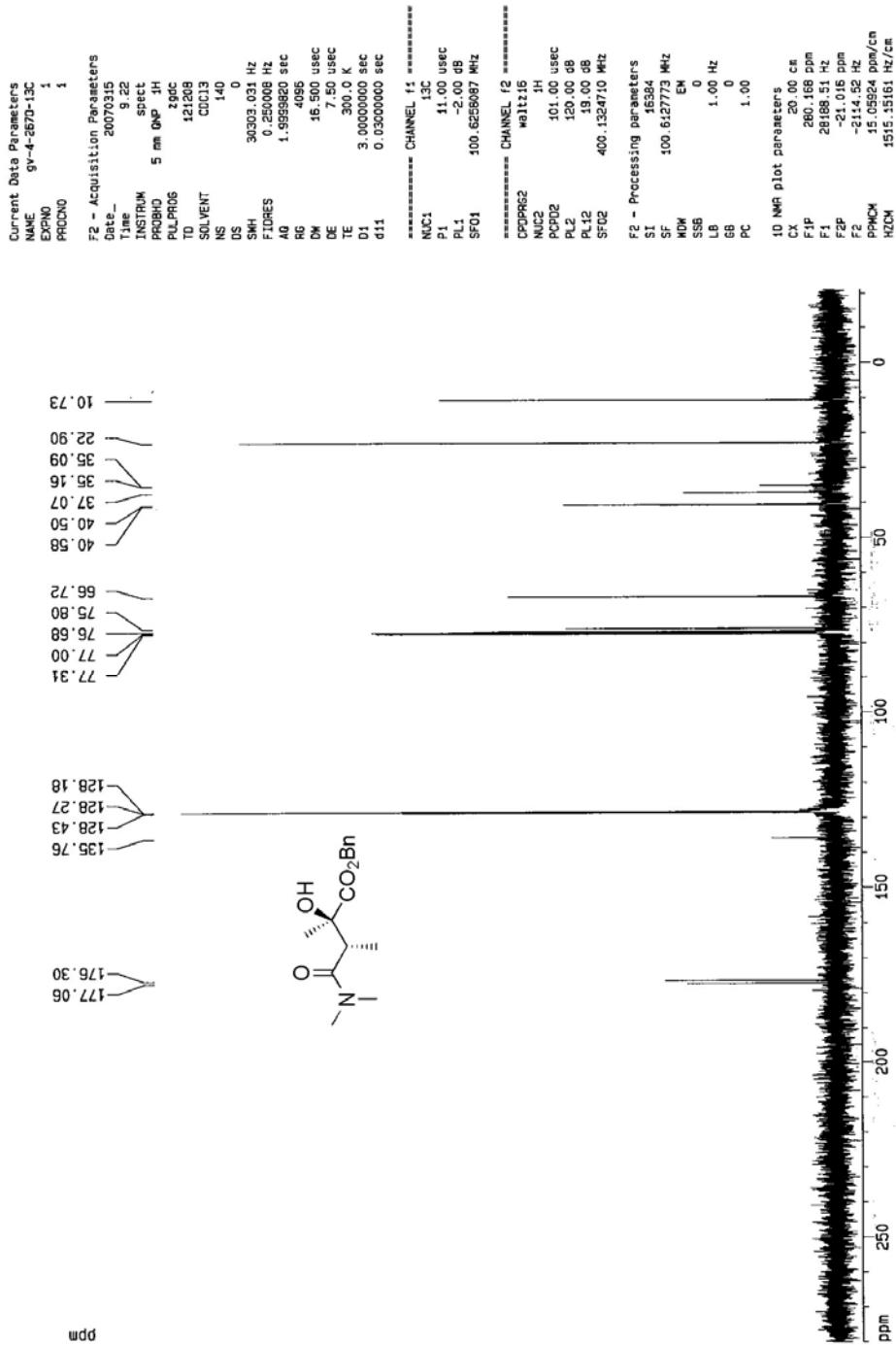
<sup>13</sup>C NMR spectrum of 3c' (CDCl<sub>3</sub>, 298 K)



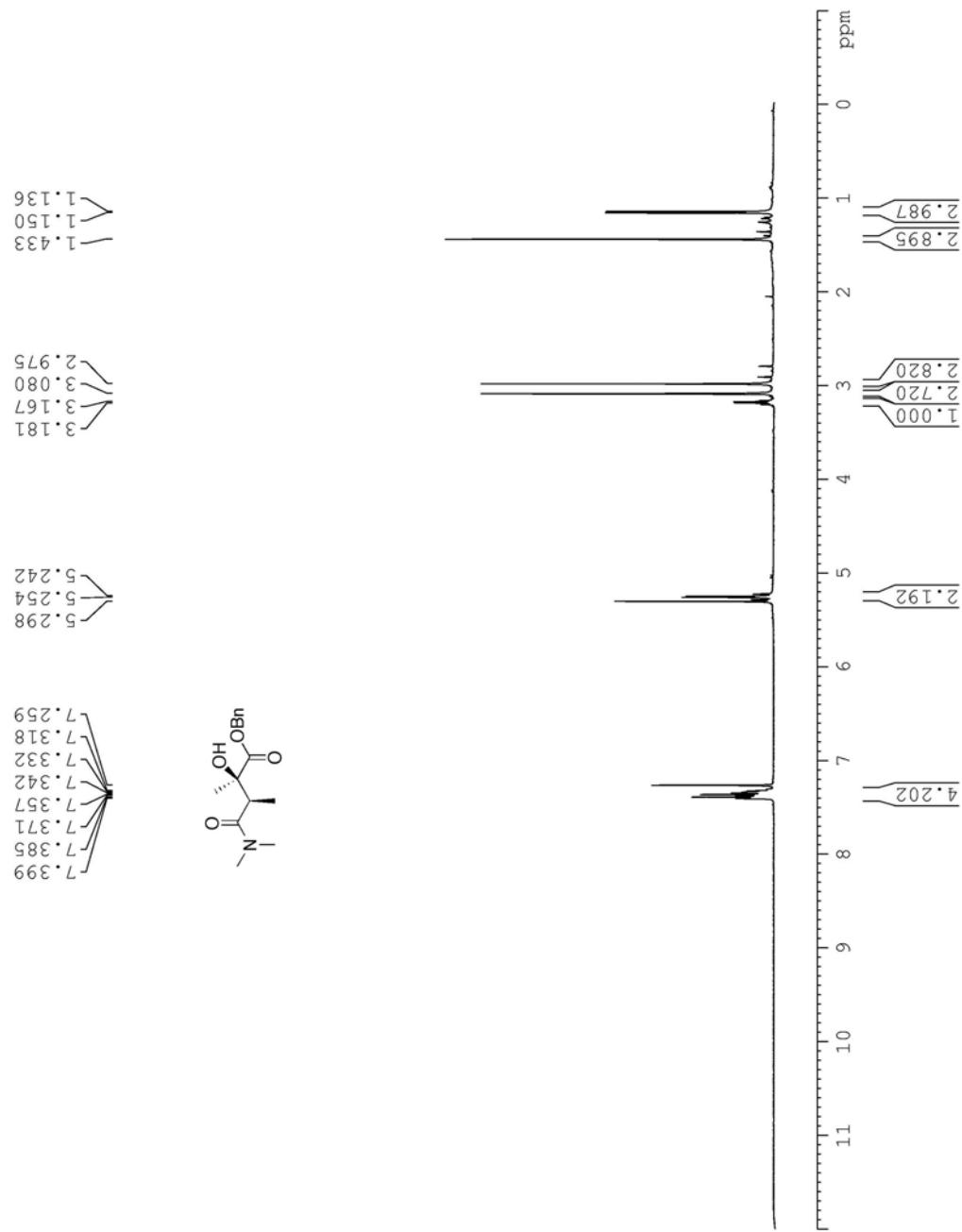
<sup>1</sup>H NMR spectra of 3d ( $\text{CDCl}_3$ , 298 K)



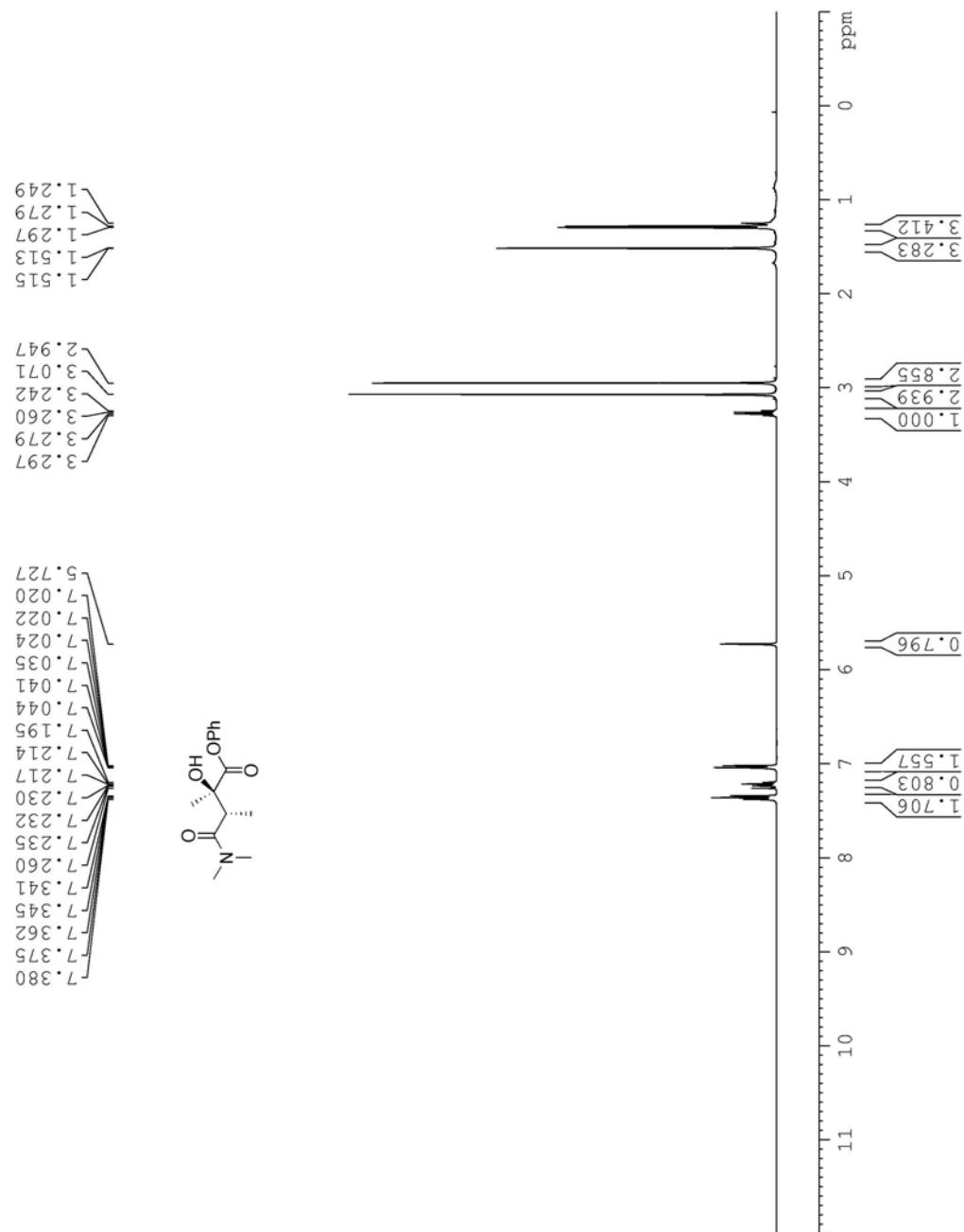
**<sup>1</sup>H NMR spectrum of 3e (CDCl<sub>3</sub>, 298 K)**



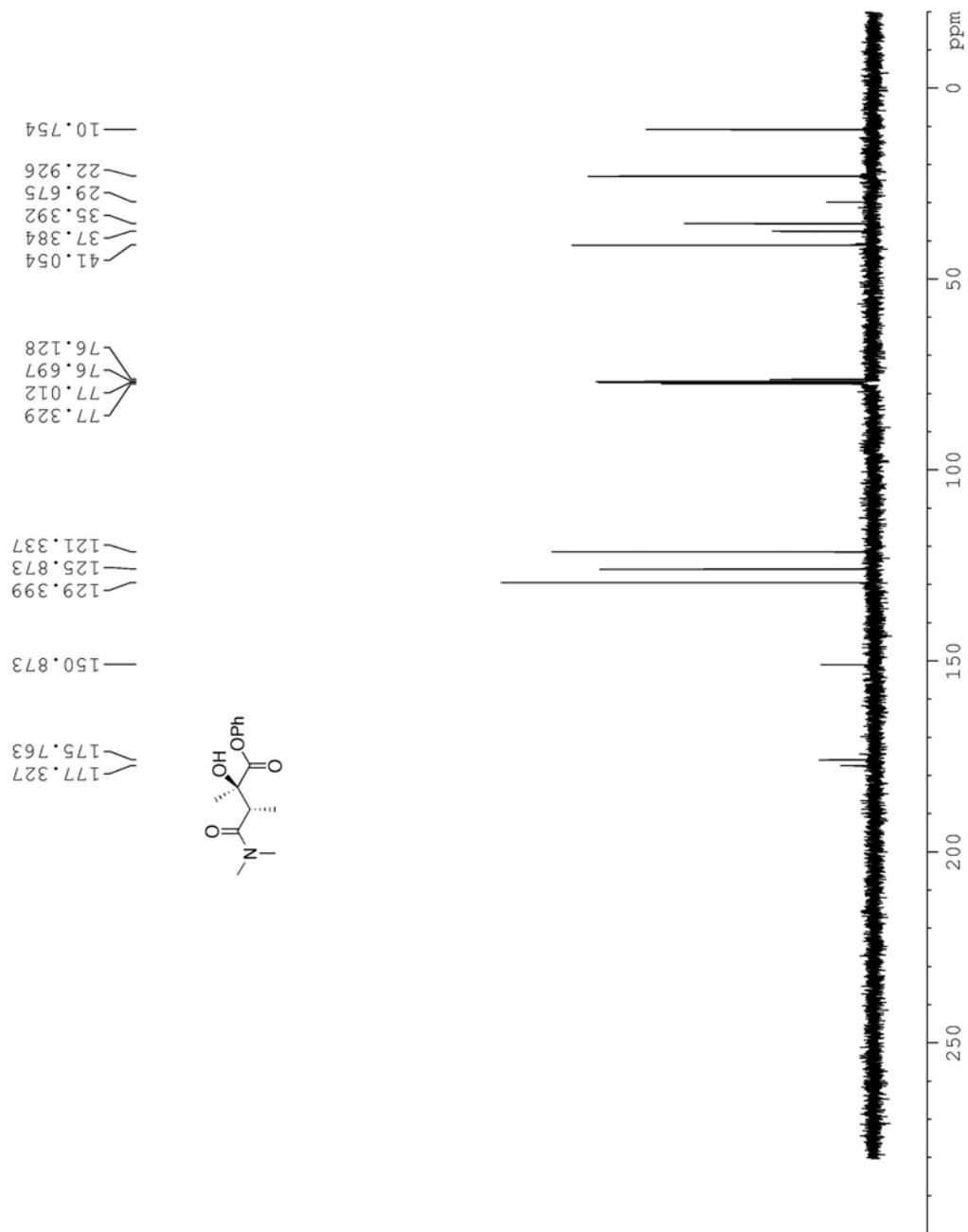
**<sup>13</sup>C NMR spectrum of 3e (CDCl<sub>3</sub>, 298 K)**



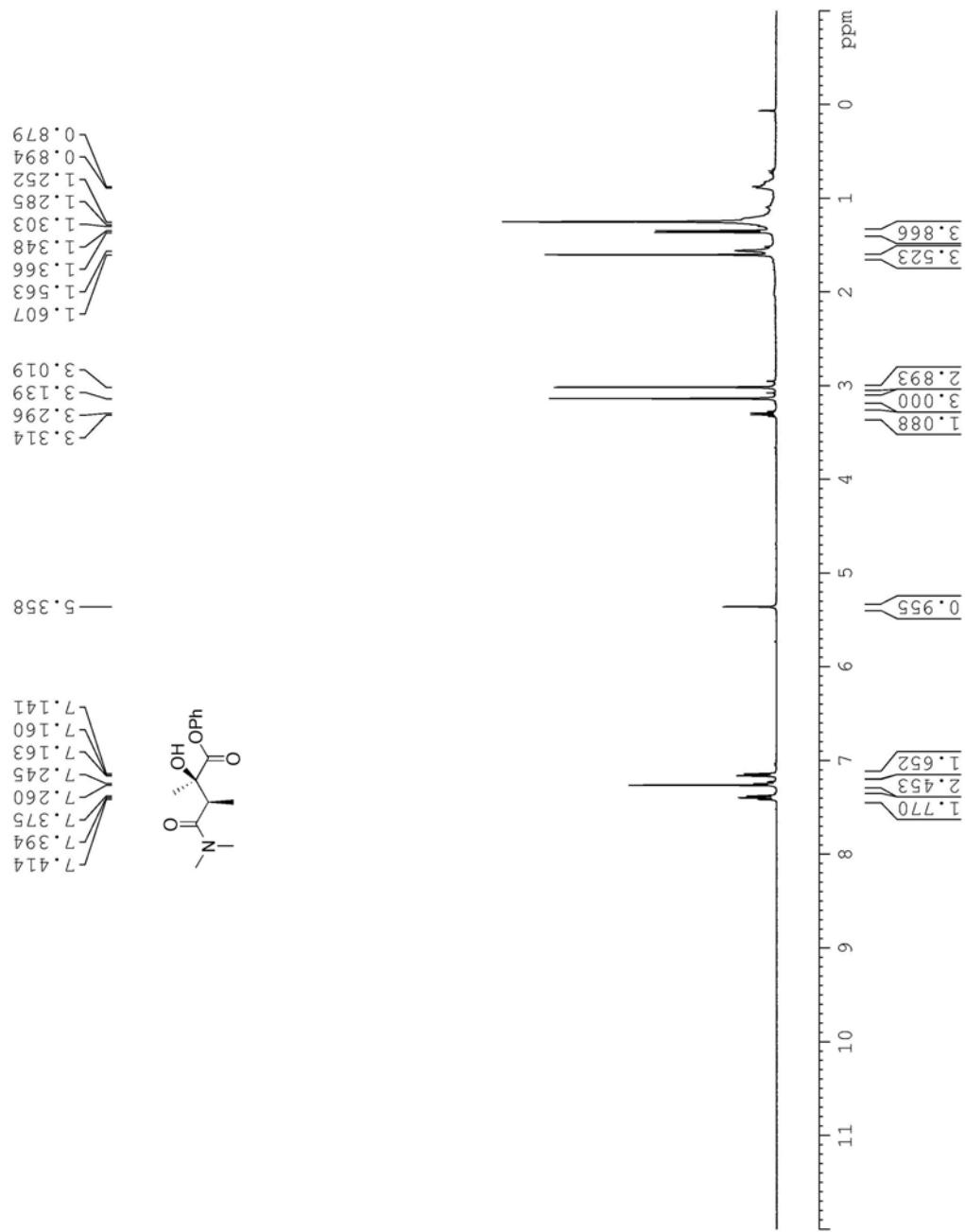
$^1\text{H}$  NMR spectrum of  $3\text{e}'$  ( $\text{CDCl}_3$ , 298 K)



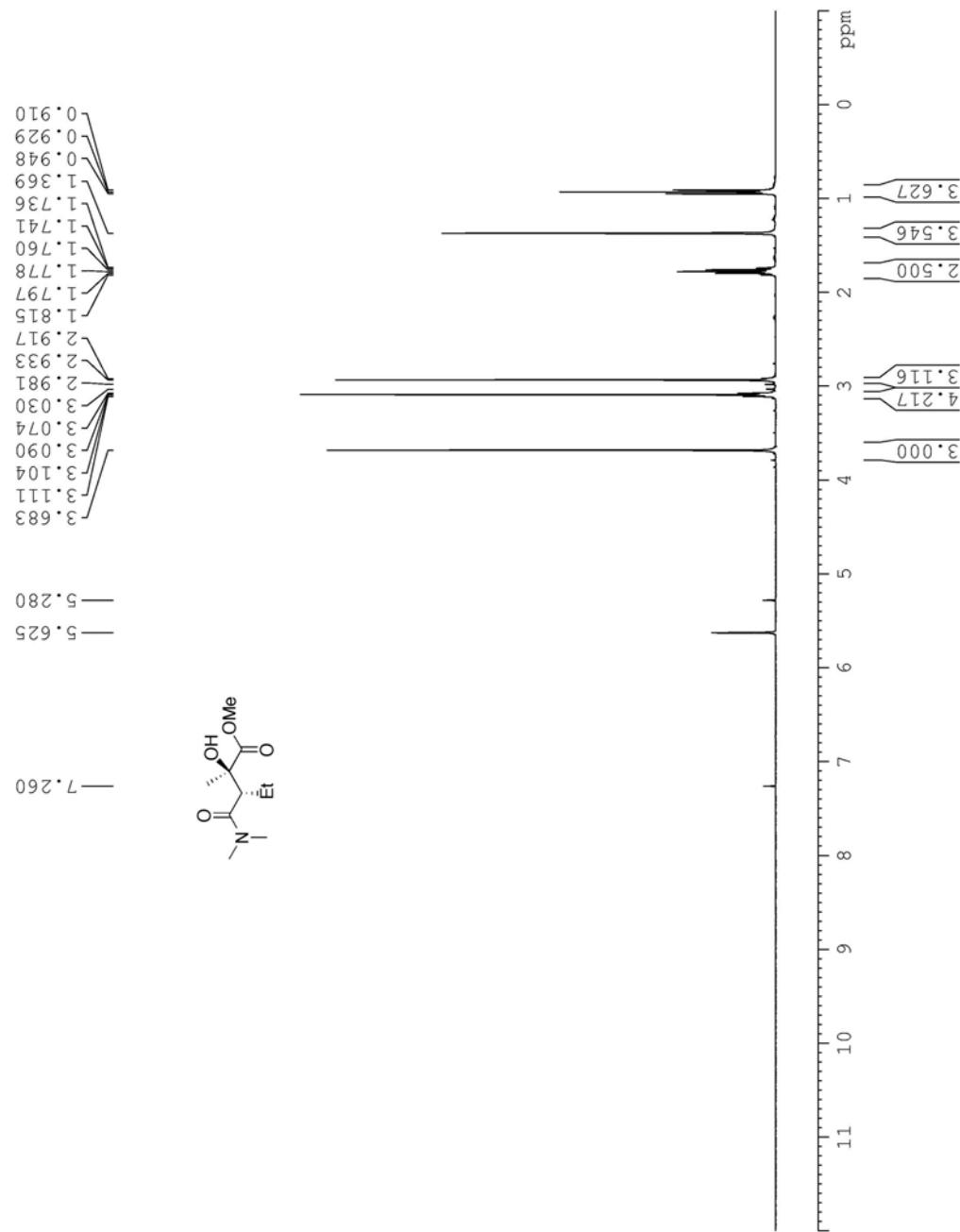
$^1\text{H}$  NMR spectrum of **3f** ( $\text{CDCl}_3$ , 298 K)



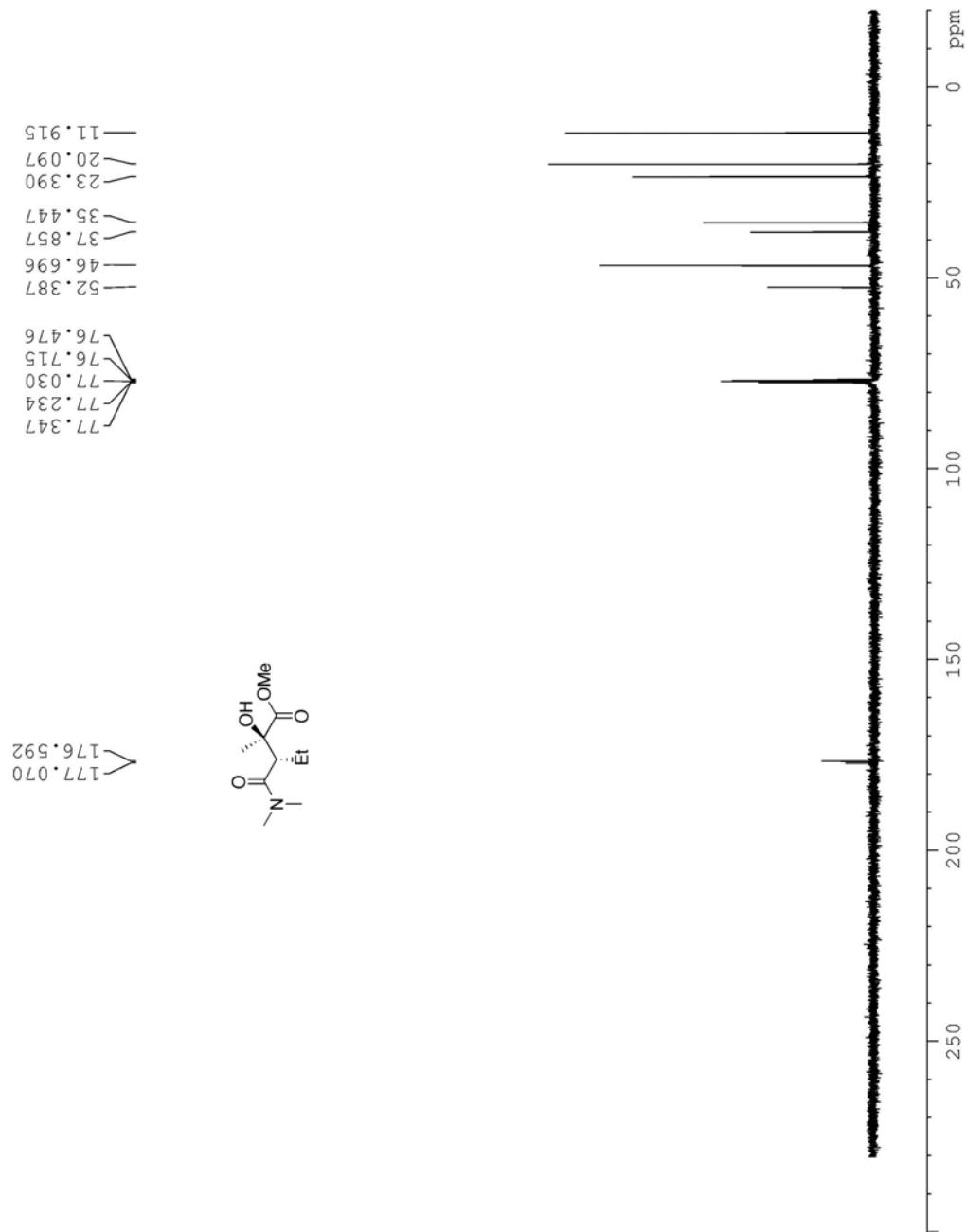
**$^{13}\text{C}$  NMR spectrum of **3f** ( $\text{CDCl}_3$ , 298 K)**



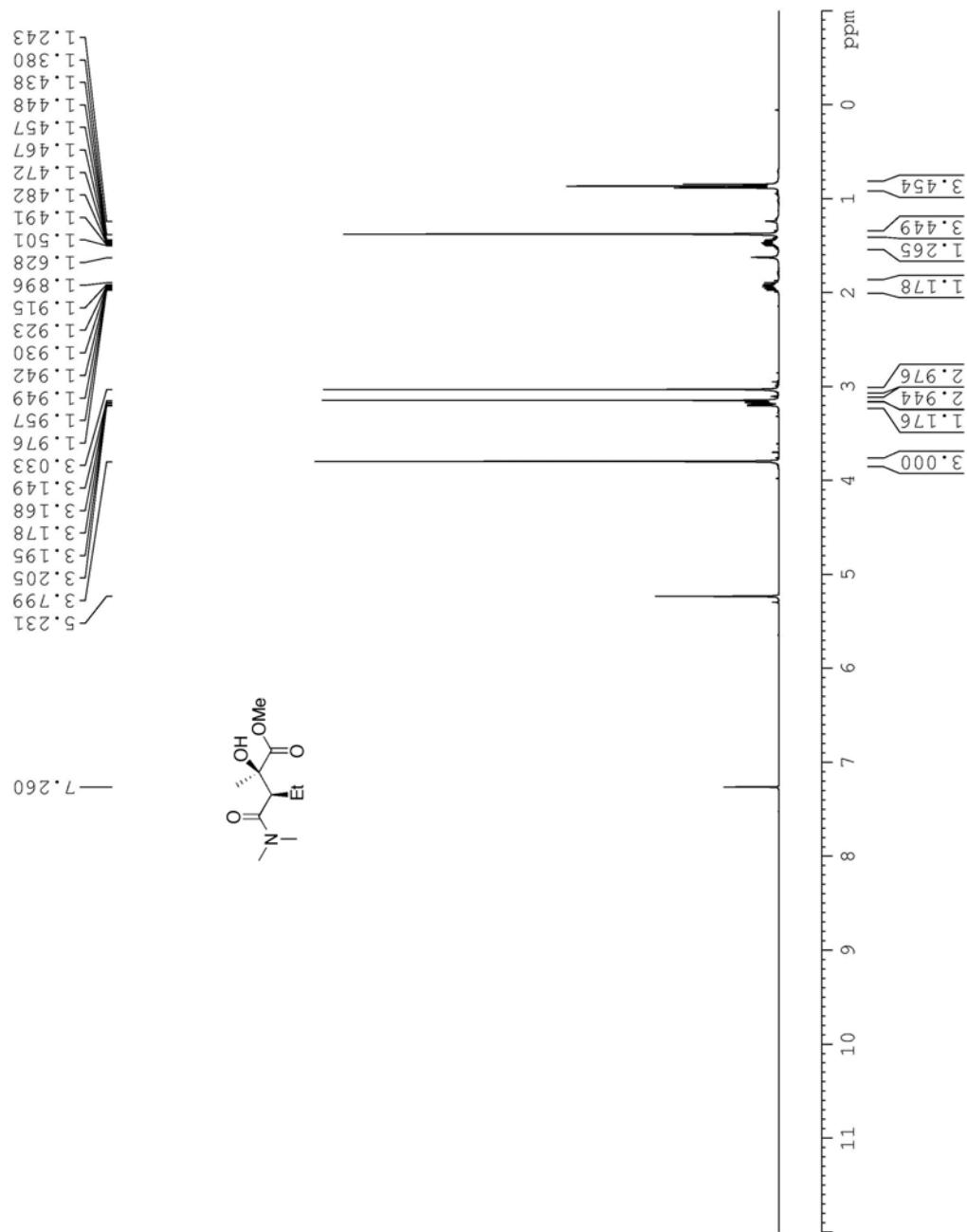
<sup>1</sup>H NMR spectra of **3f'** ( $\text{CDCl}_3$ , 298 K)



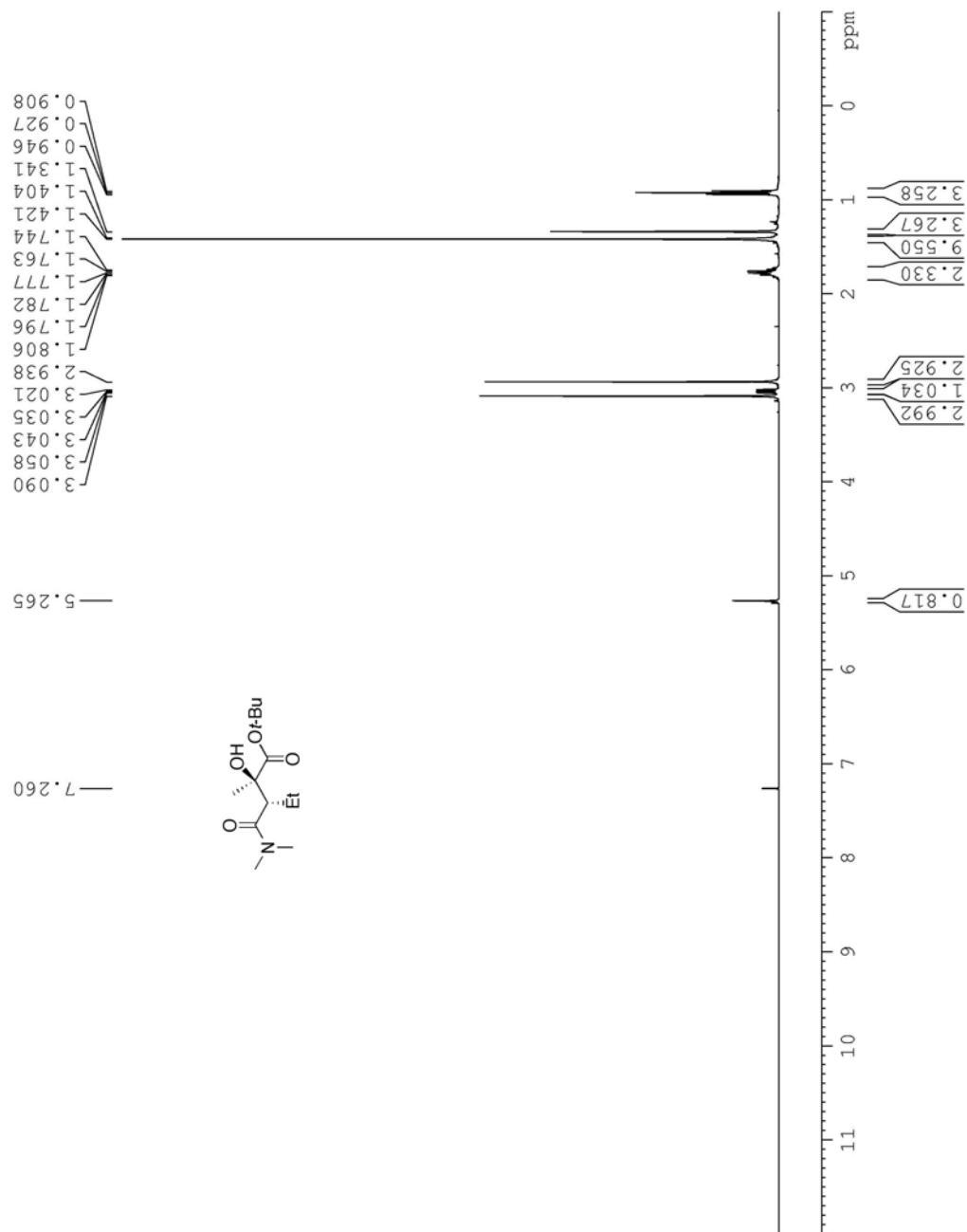
<sup>1</sup>H NMR spectrum of 6a ( $\text{CDCl}_3$ , 298 K)



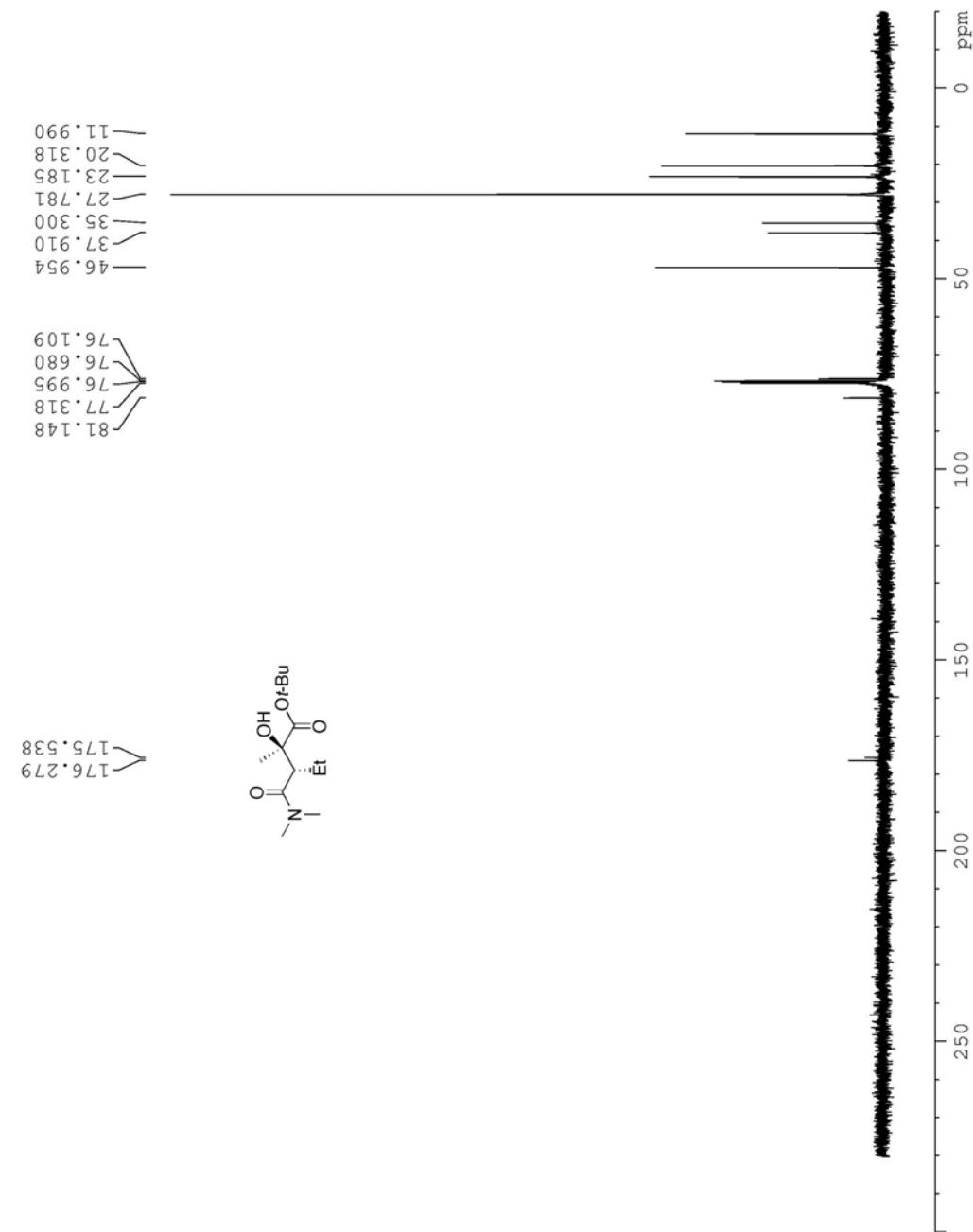
$^{13}\text{C}$  NMR spectrum of 6a ( $\text{CDCl}_3$ , 298 K)



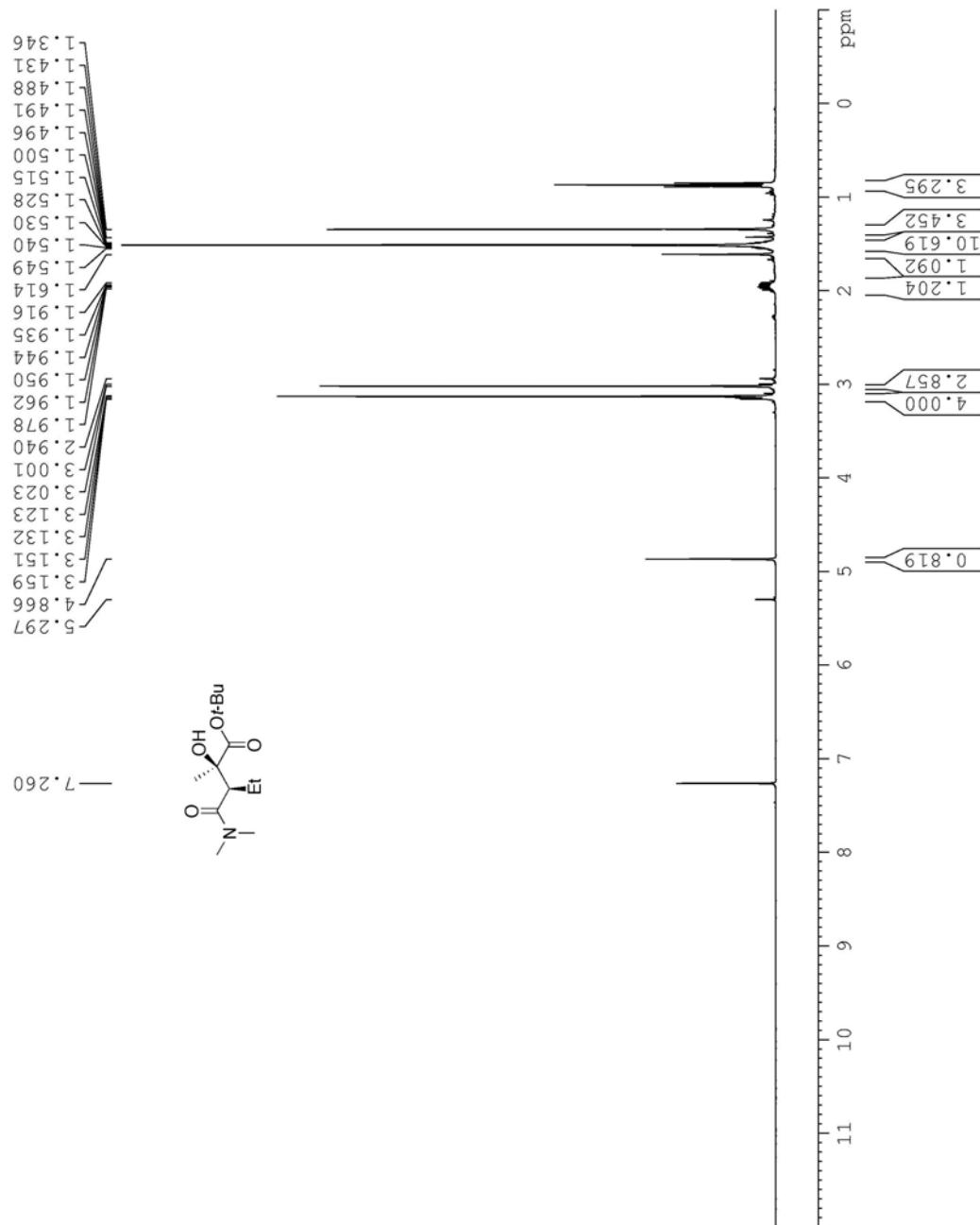
**<sup>1</sup>H NMR spectrum of 6a' (CDCl<sub>3</sub>, 298 K)**



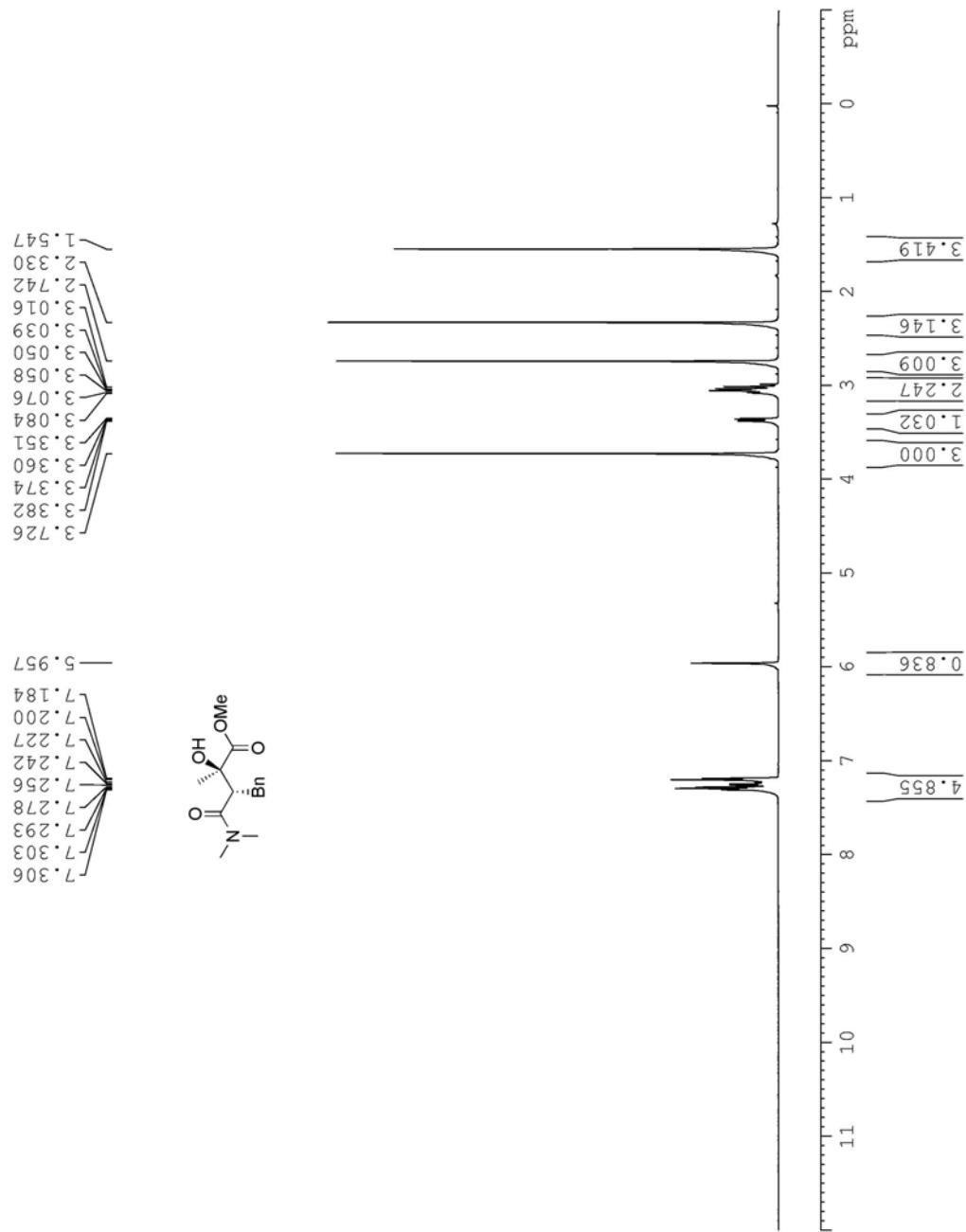
<sup>1</sup>H NMR spectrum of 6b ( $\text{CDCl}_3$ , 298 K)



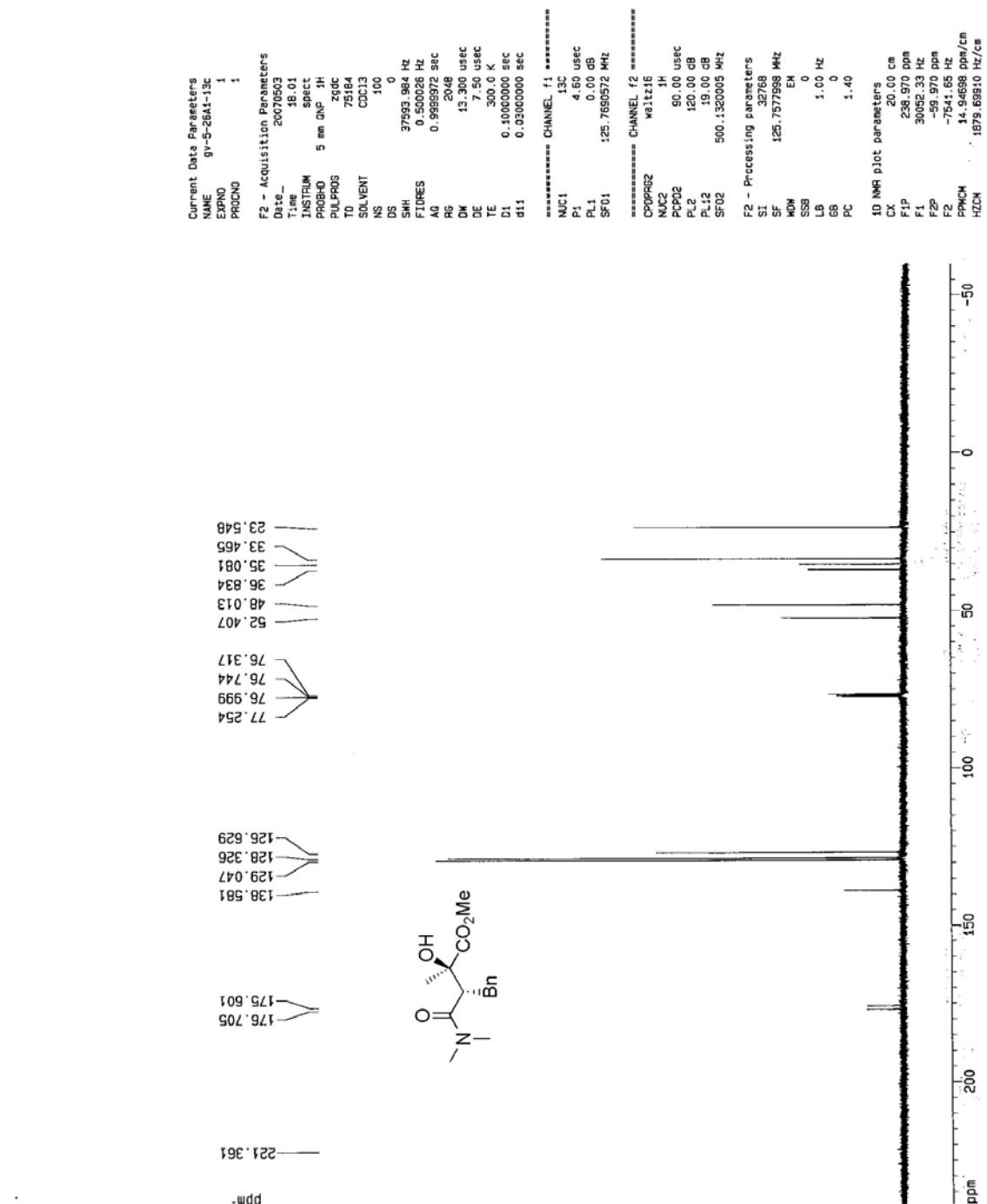
$^{13}\text{C}$  NMR spectrum of **6b** ( $\text{CDCl}_3$ , 298 K)



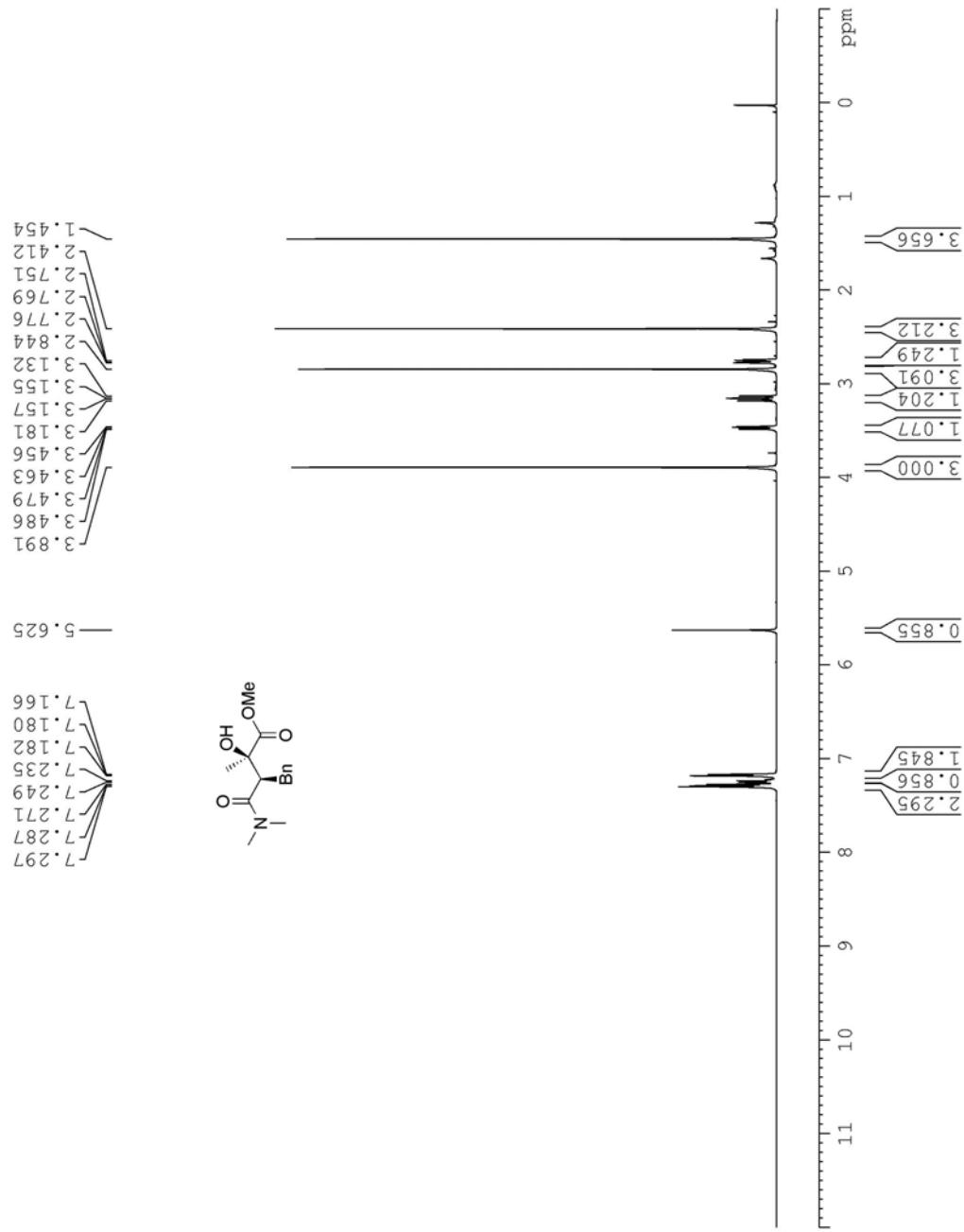
<sup>1</sup>H NMR spectrum of 6b' (CDCl<sub>3</sub>, 298 K)



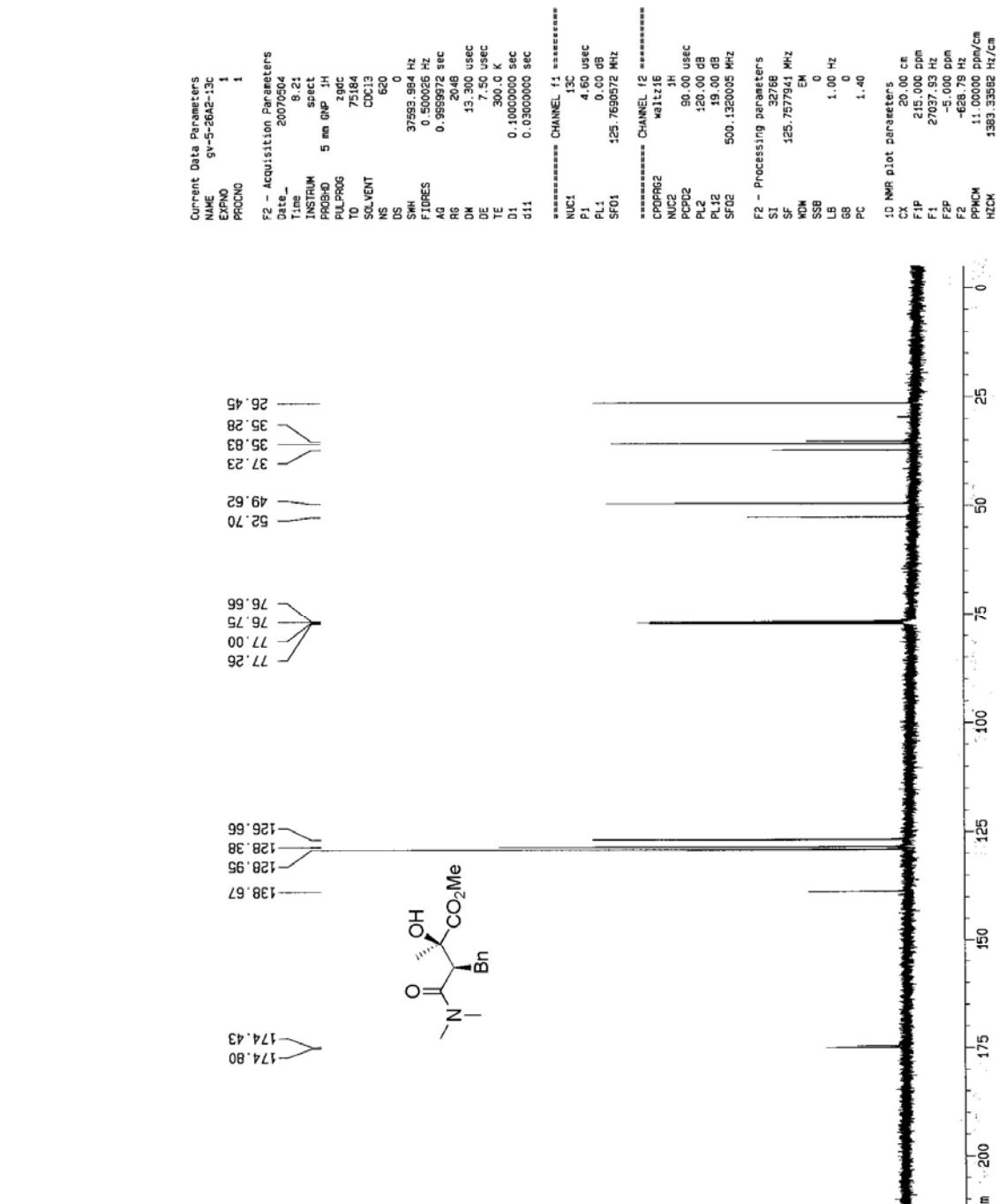
<sup>1</sup>H NMR spectrum of 6c ( $\text{CDCl}_3$ , 298 K)



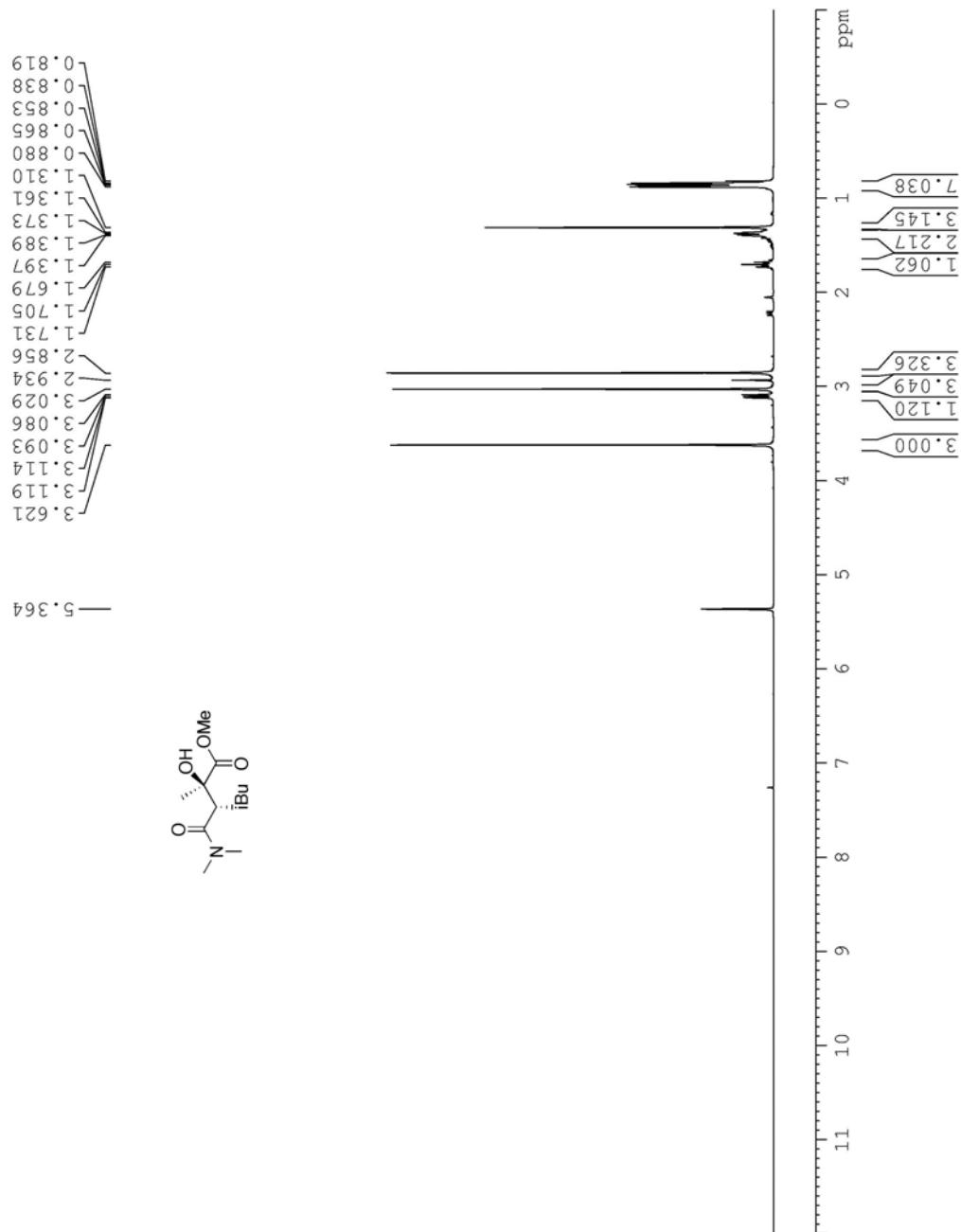
**<sup>13</sup>C NMR spectrum of 6c (CDCl<sub>3</sub>, 298 K)**



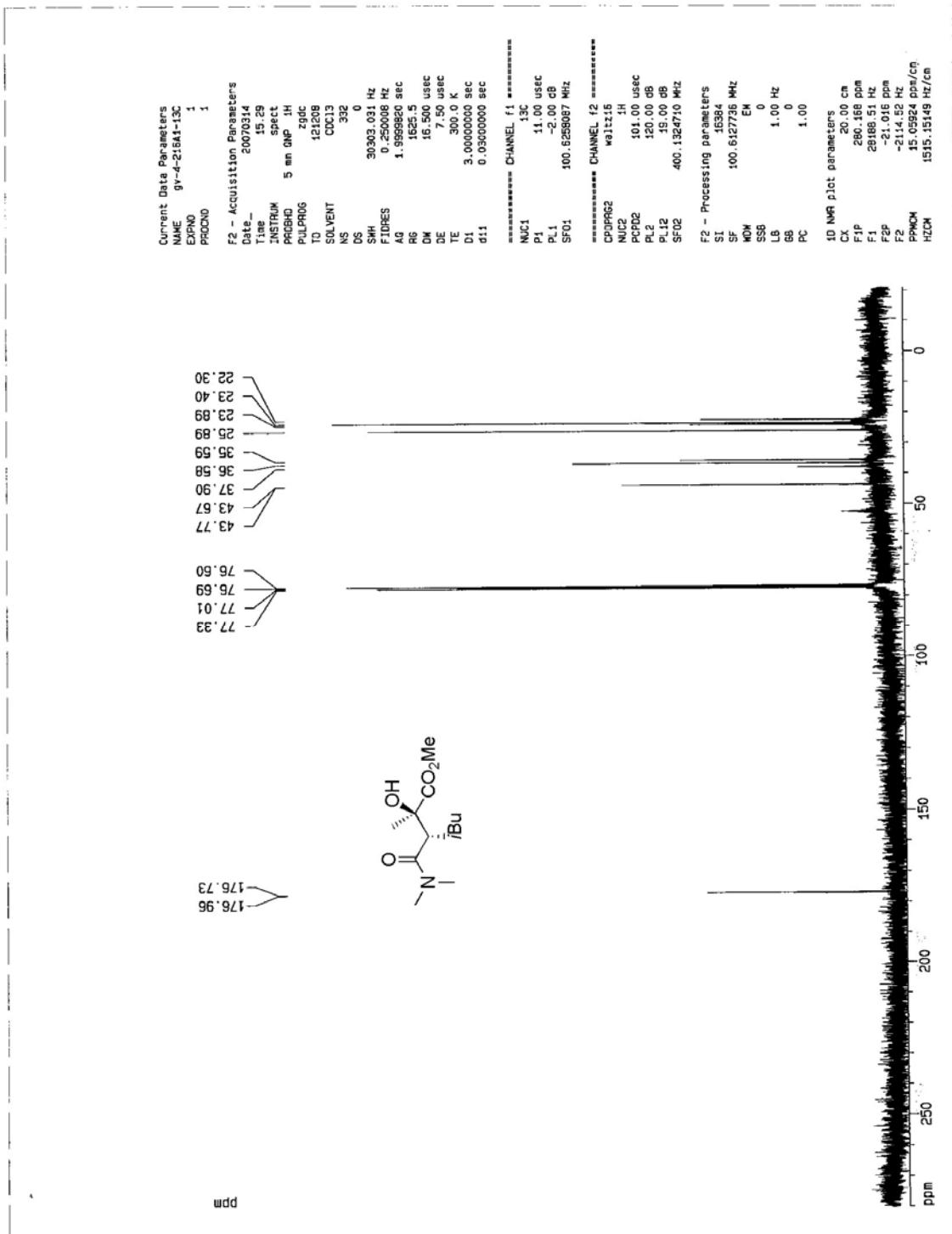
$^1\text{H}$  NMR spectrum of  $6\text{c}'$  ( $\text{CDCl}_3$ , 298 K)



**<sup>13</sup>C NMR spectrum of 6c' (CDCl<sub>3</sub>, 298 K)**



<sup>1</sup>H NMR spectrum of 6d ( $\text{CDCl}_3$ , 298 K)



<sup>13</sup>C NMR spectrum of 6d (CDCl<sub>3</sub>, 298 K)

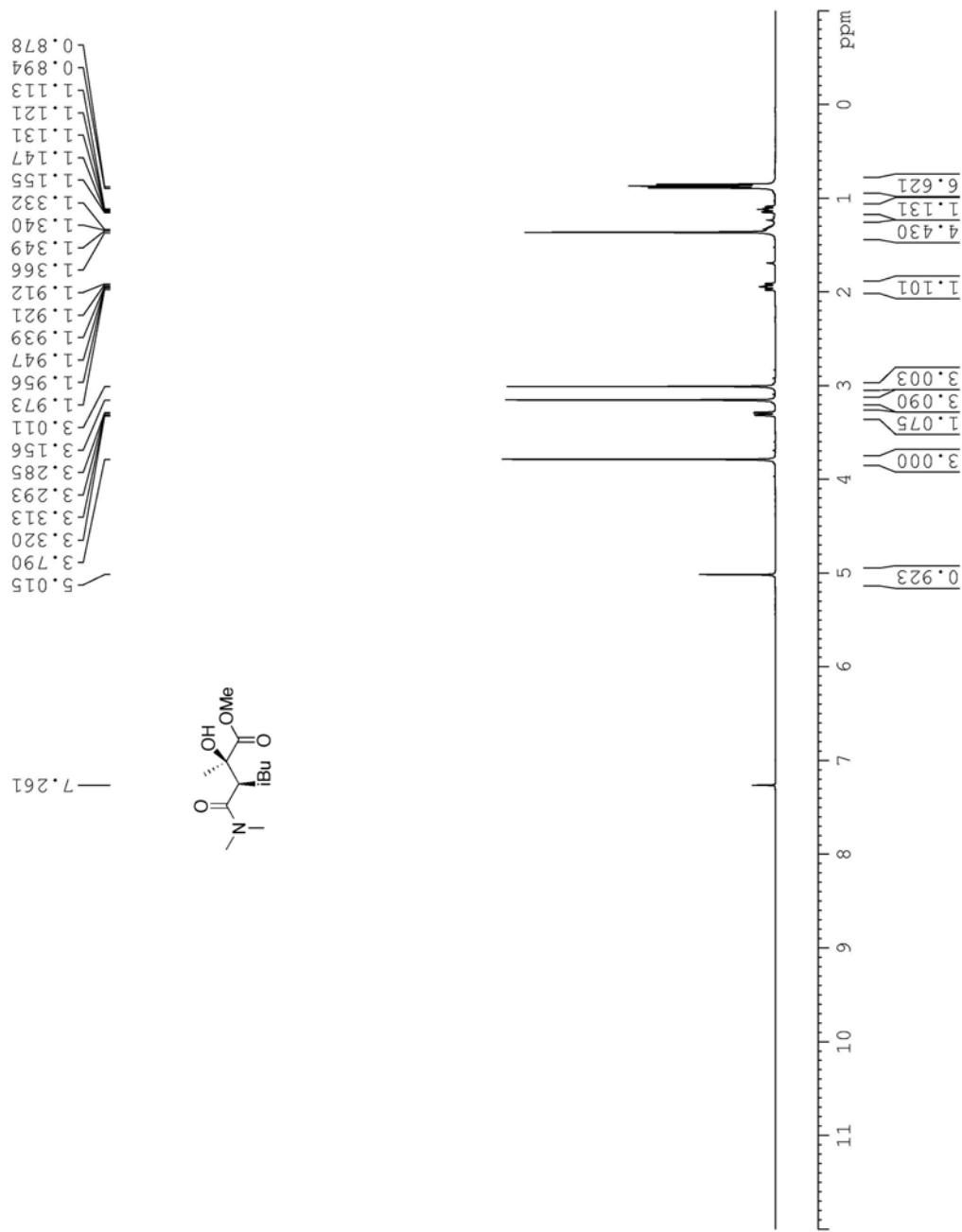
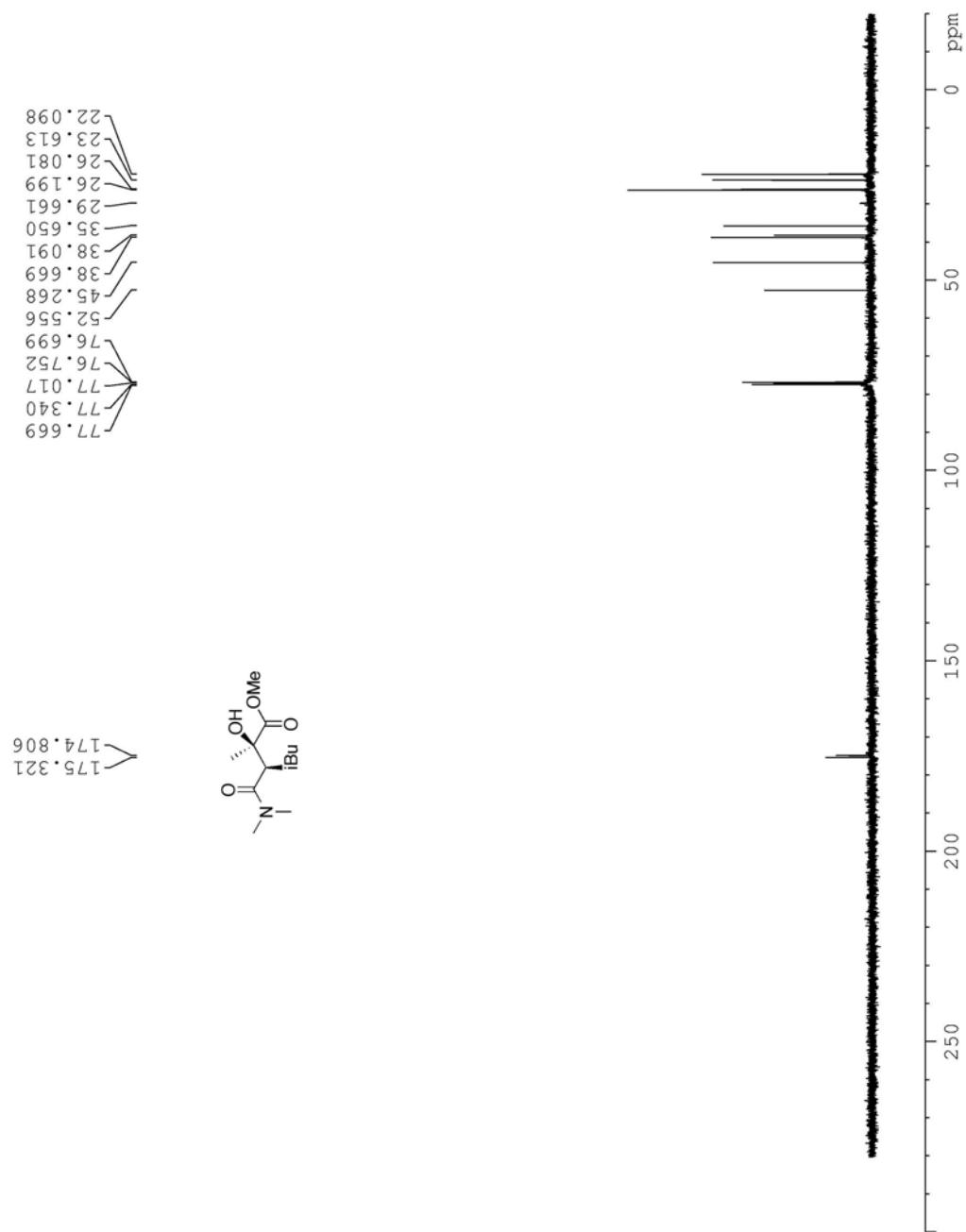
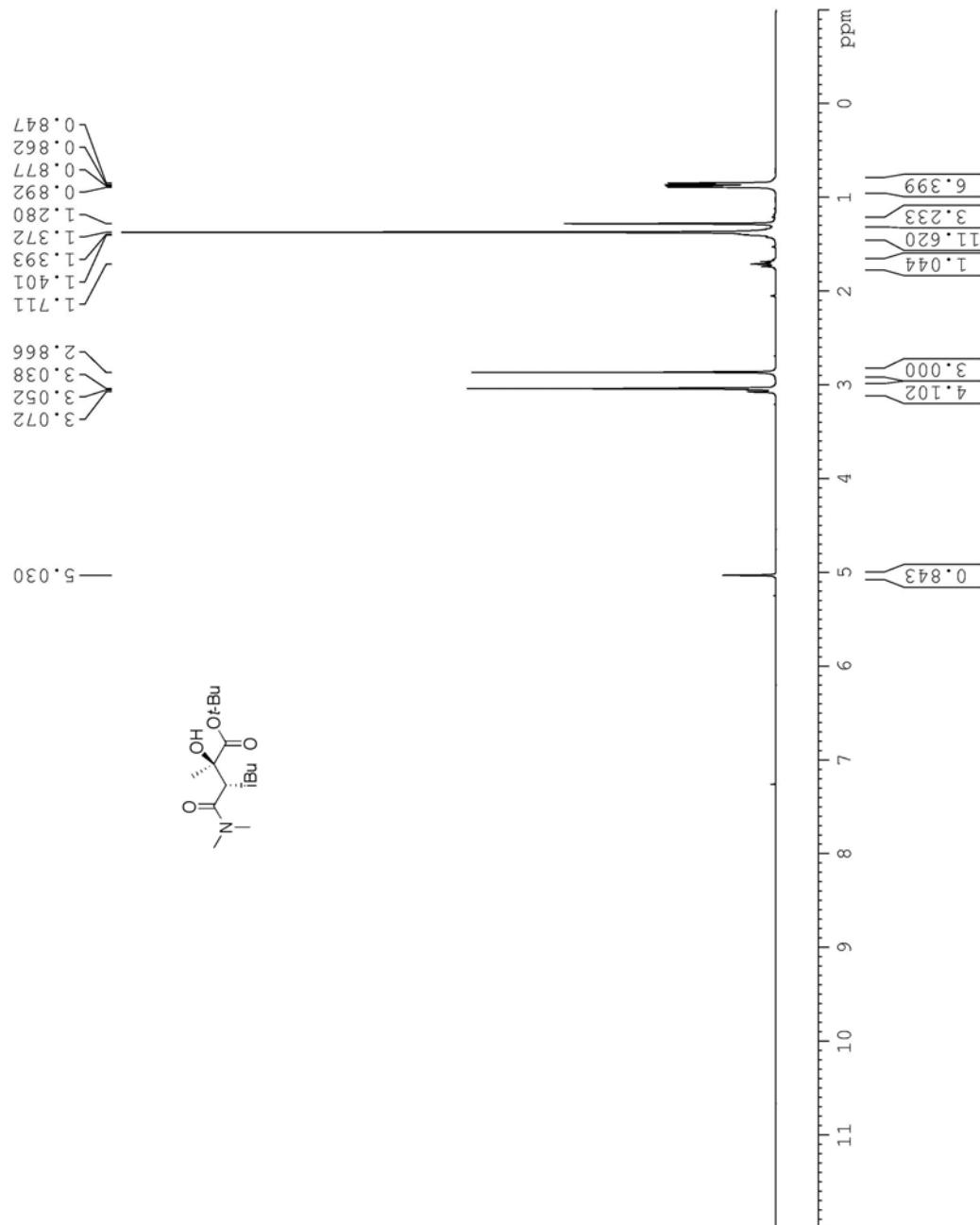


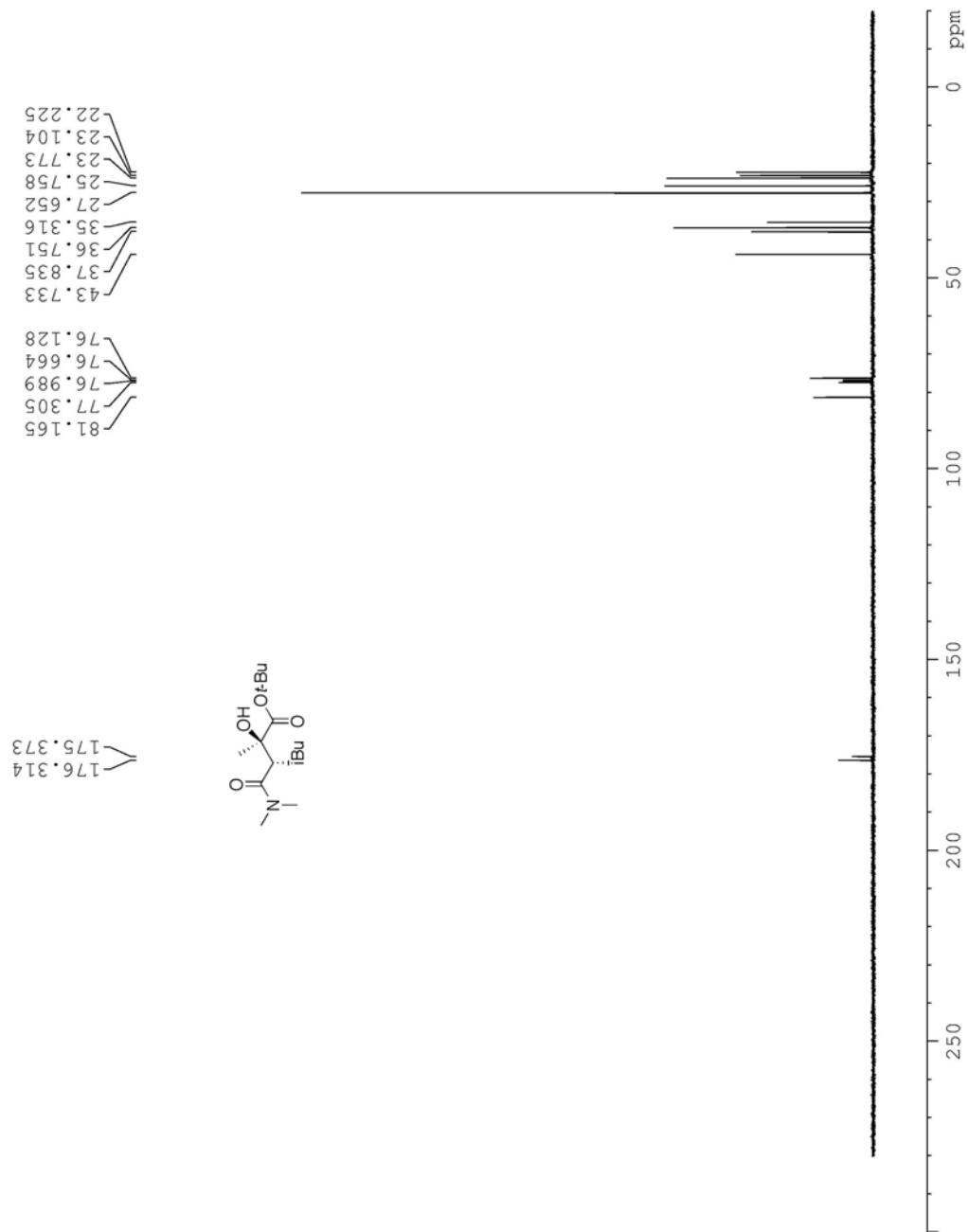
Figure 130.  $^1\text{H}$  NMR spectrum of  $6\text{d}'$  ( $\text{CDCl}_3$ , 298 K)



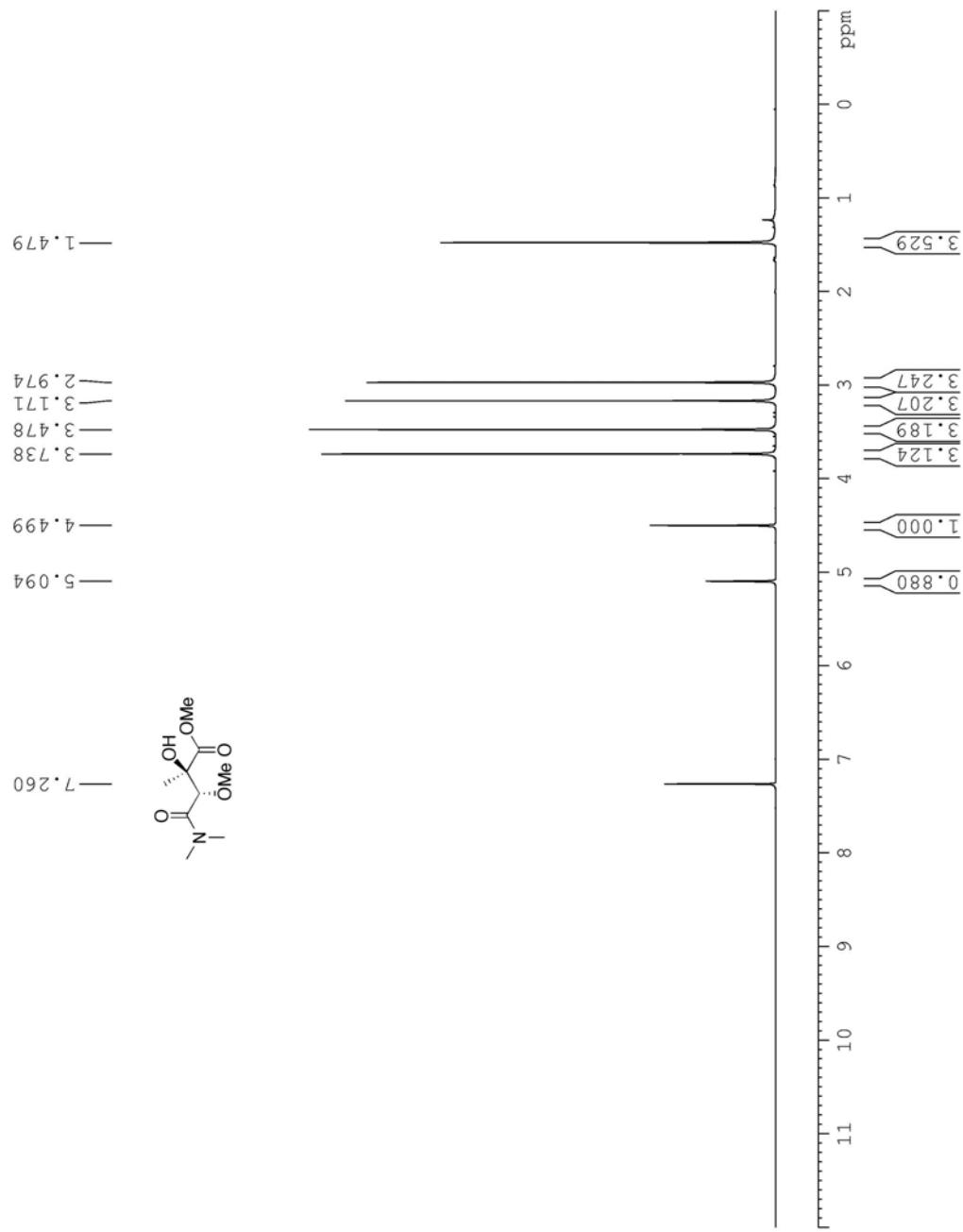
$^{13}\text{C}$  NMR spectrum of  $6\text{d}'$  ( $\text{CDCl}_3$ , 298 K)



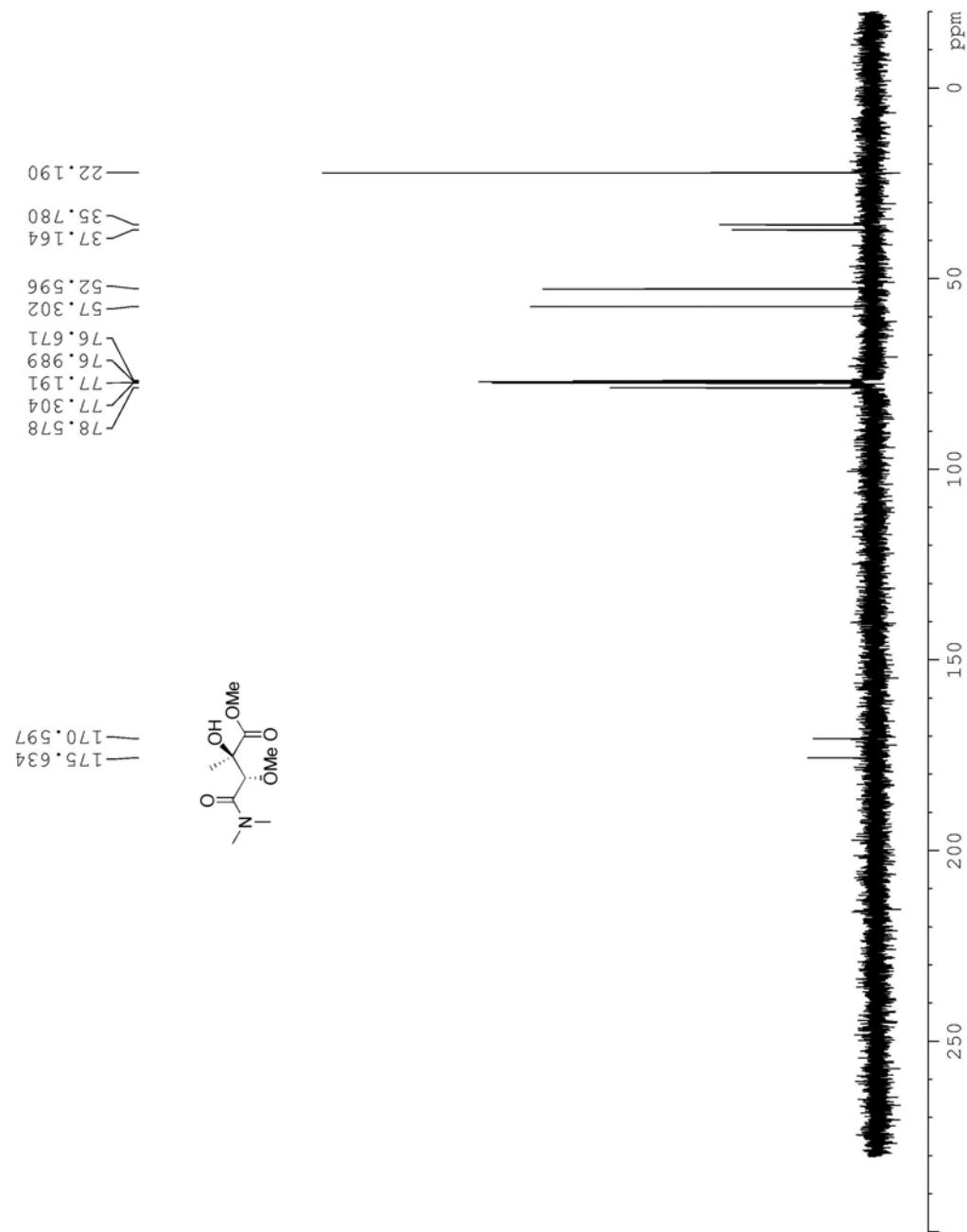
$^1\text{H}$  NMR spectrum of **6e** ( $\text{CDCl}_3$ , 298 K)



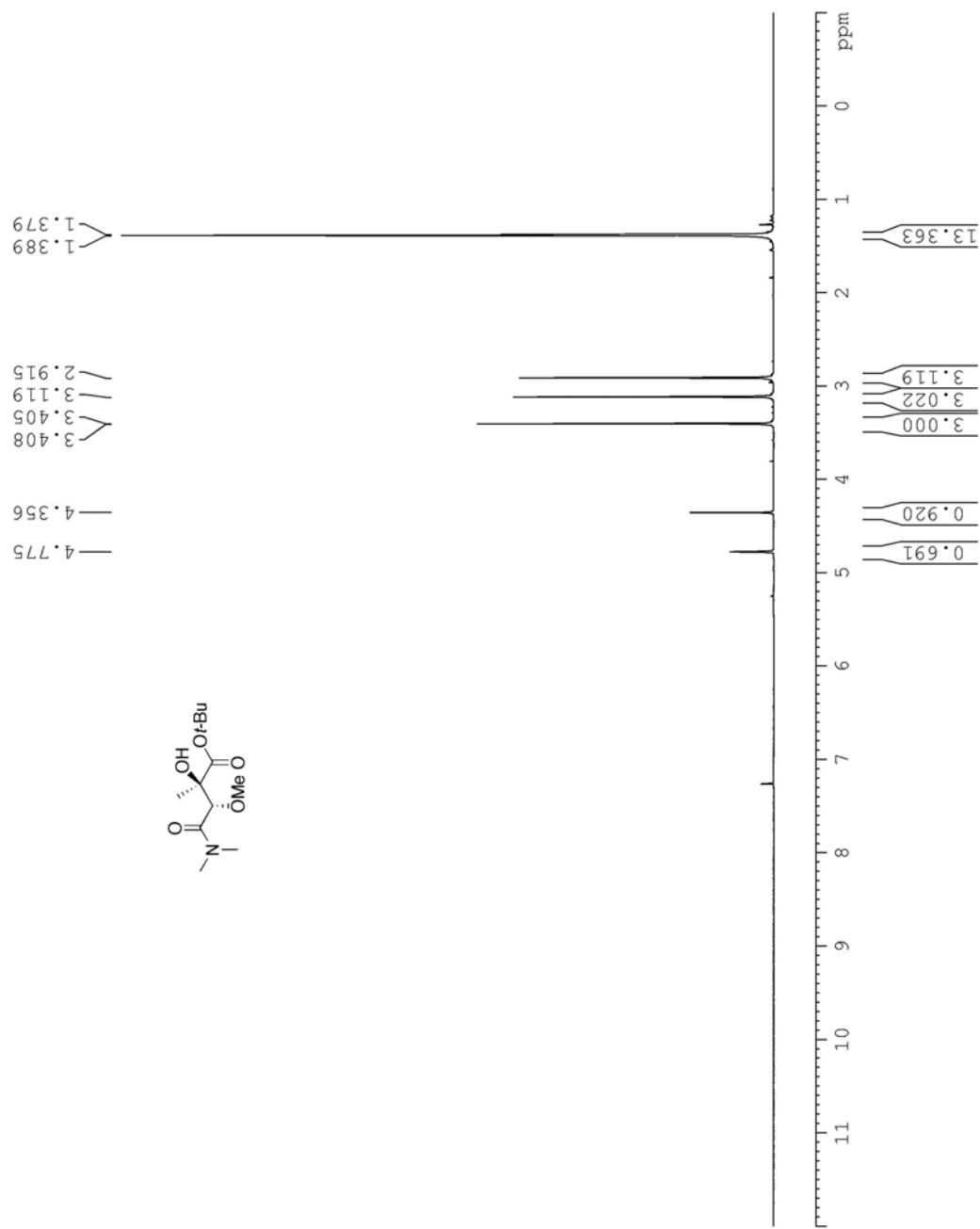
$^{13}\text{C}$  NMR spectrum of 6e ( $\text{CDCl}_3$ , 298 K)



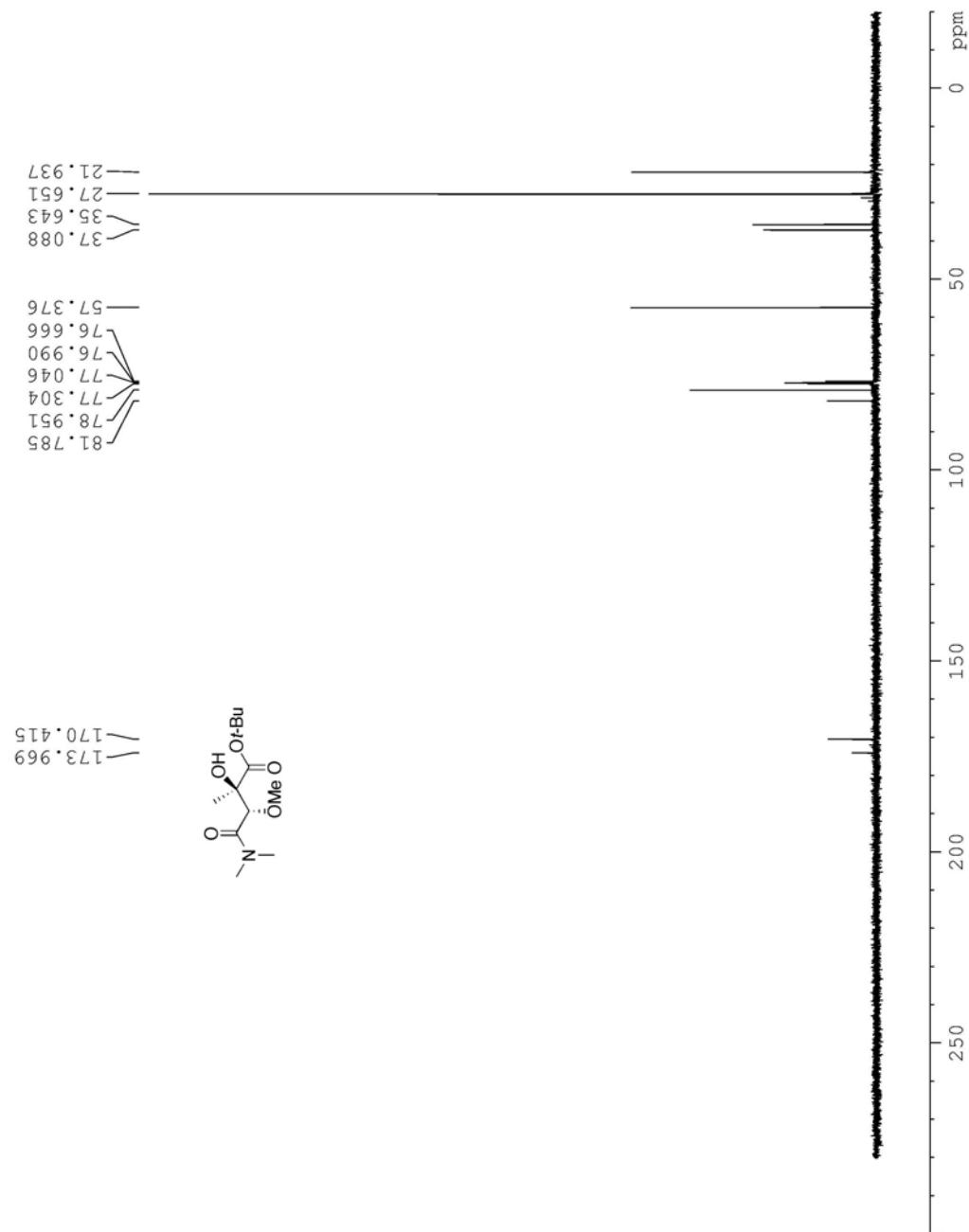
<sup>1</sup>H NMR spectrum of 6f ( $\text{CDCl}_3$ , 298 K)



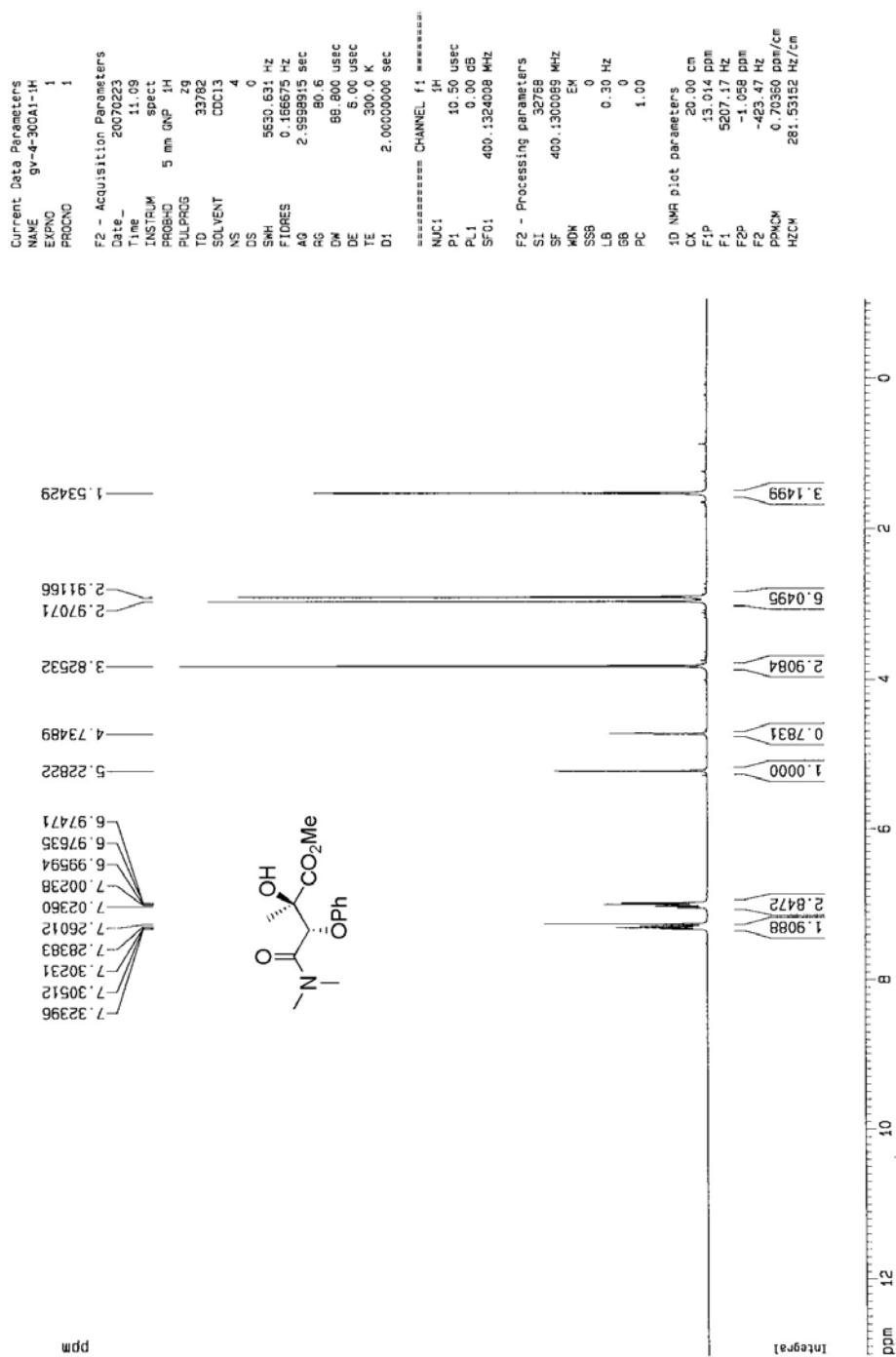
$^{13}\text{C}$  NMR spectrum of **6f** ( $\text{CDCl}_3$ , 298 K)



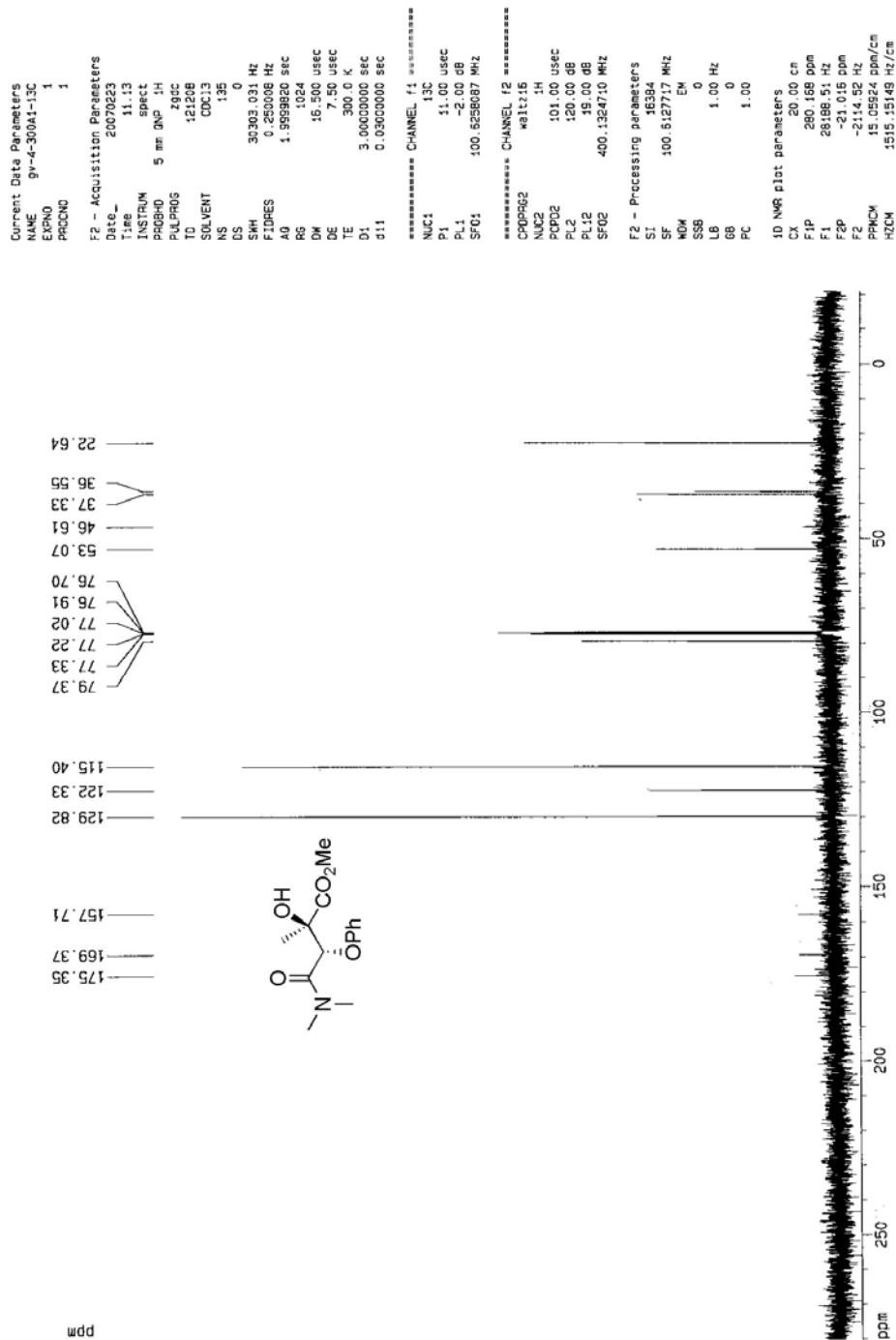
<sup>1</sup>H NMR spectrum of 6g ( $\text{CDCl}_3$ , 298 K)



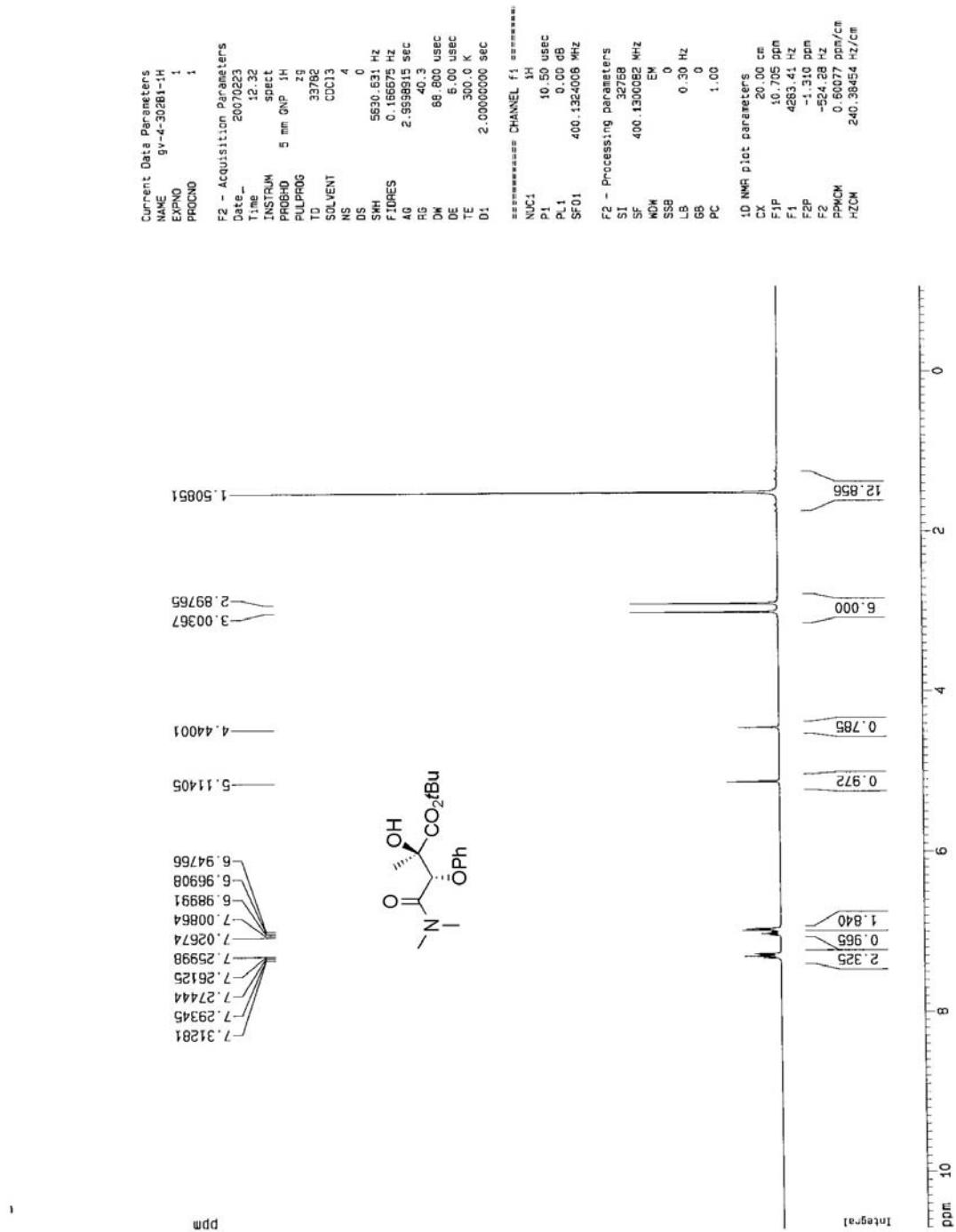
$^{13}\text{C}$  NMR spectrum of **6g** ( $\text{CDCl}_3$ , 298 K)



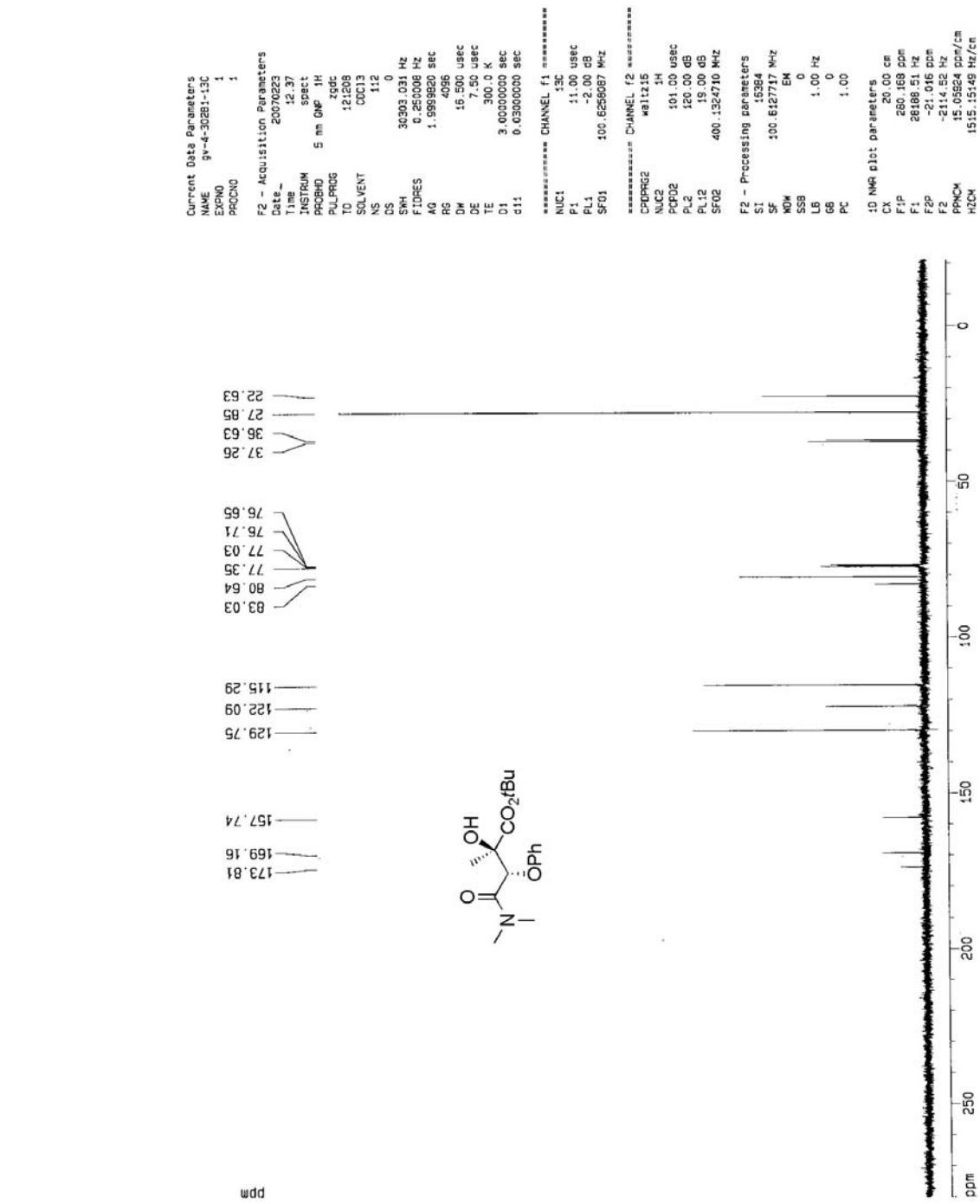
**<sup>1</sup>H NMR spectrum of 6h (CDCl<sub>3</sub>, 298 K)**



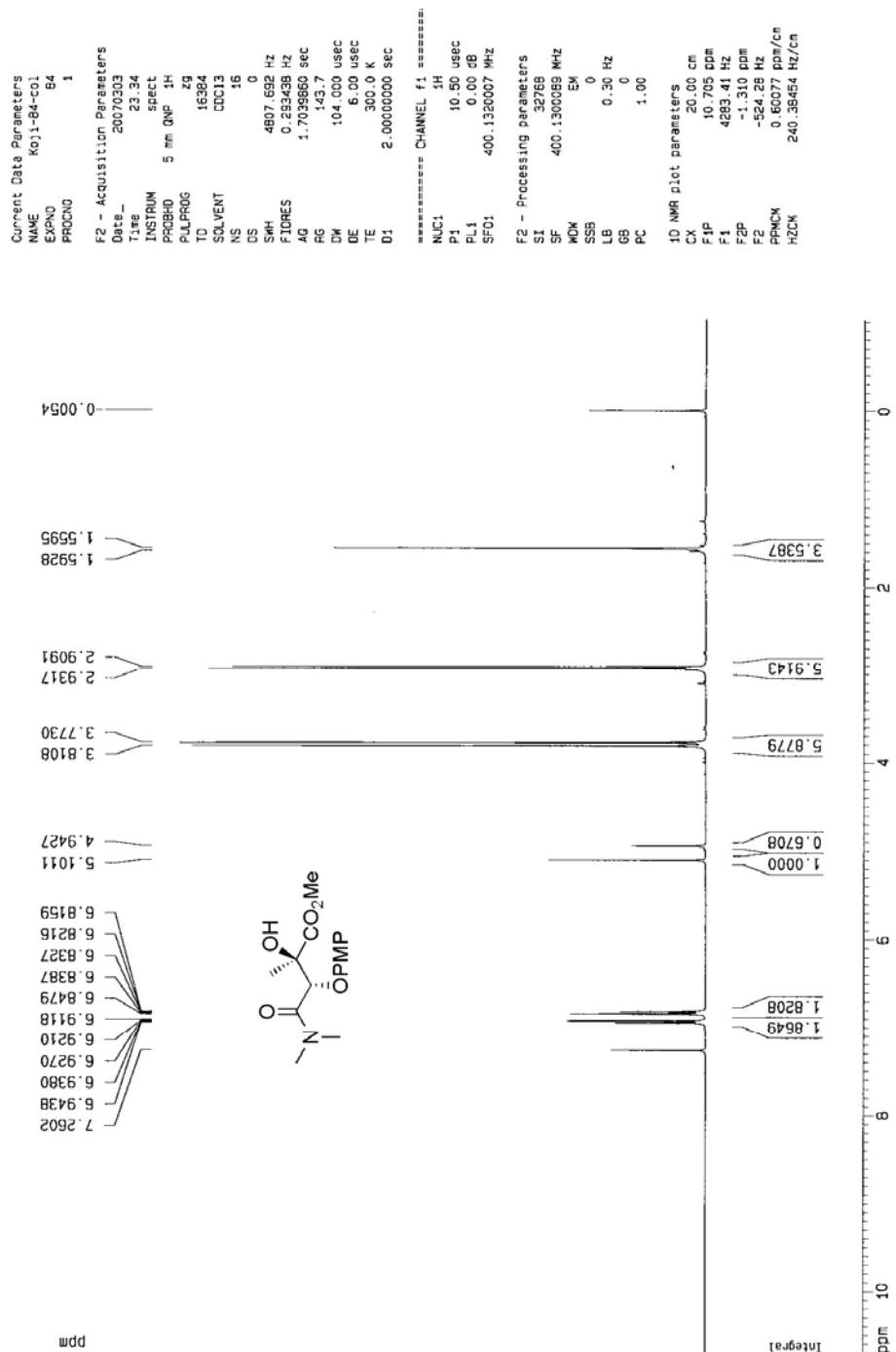
<sup>13</sup>C NMR spectrum of 6h (CDCl<sub>3</sub>, 298 K)

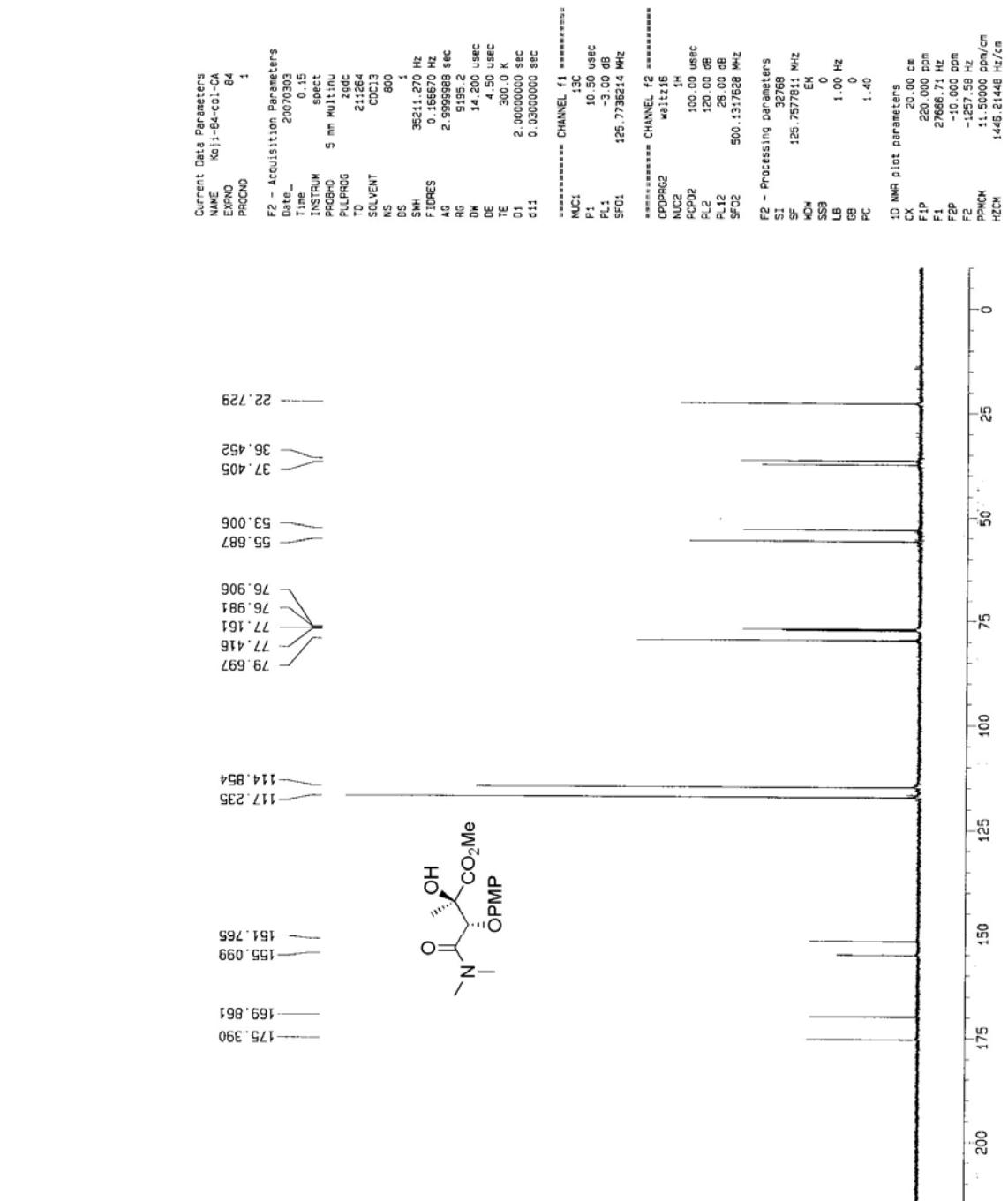


<sup>1</sup>H NMR spectrum of 6i (CDCl<sub>3</sub>, 298 K)

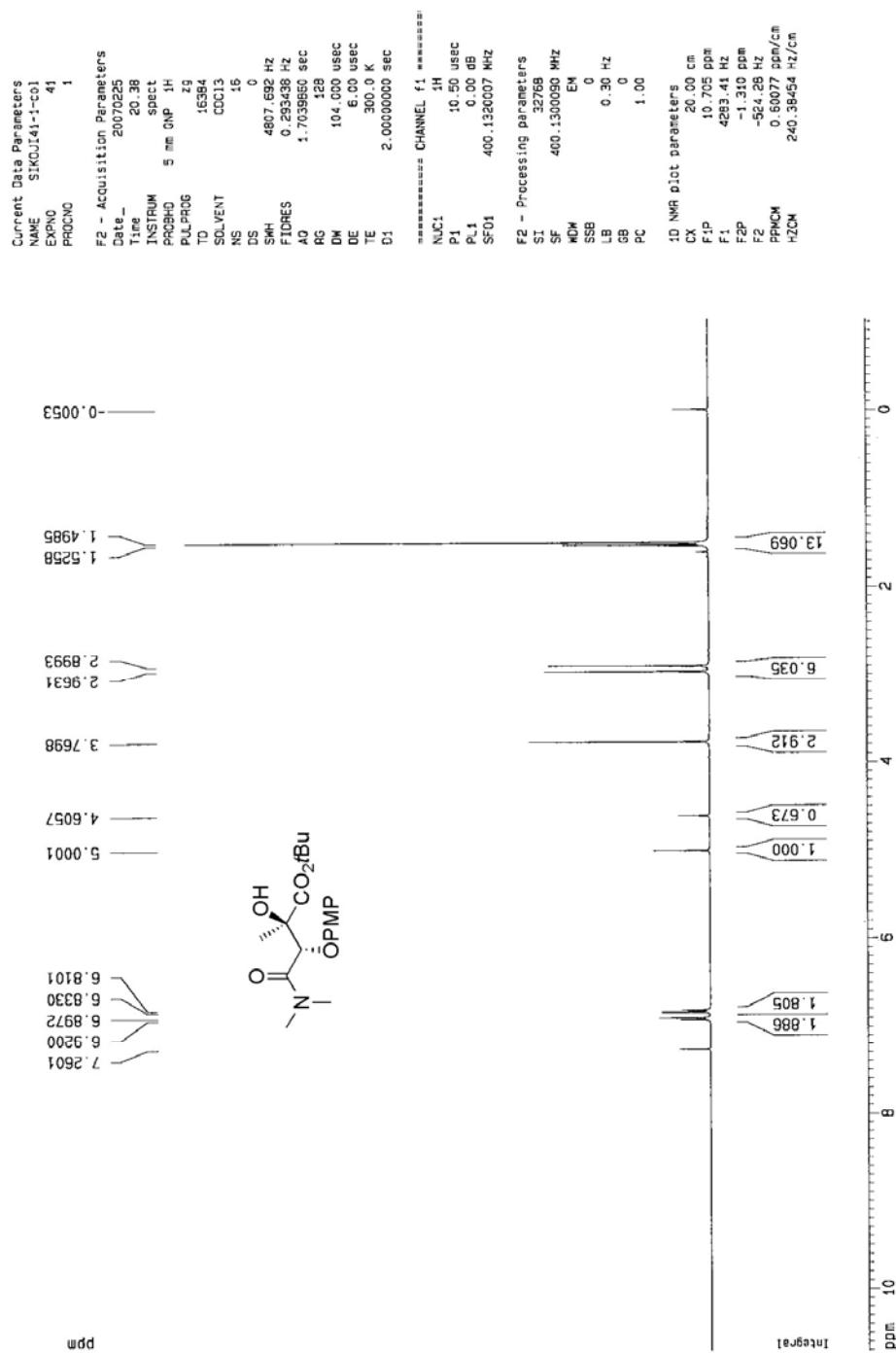


**<sup>13</sup>C NMR spectrum of 6i (CDCl<sub>3</sub>, 298 K)**

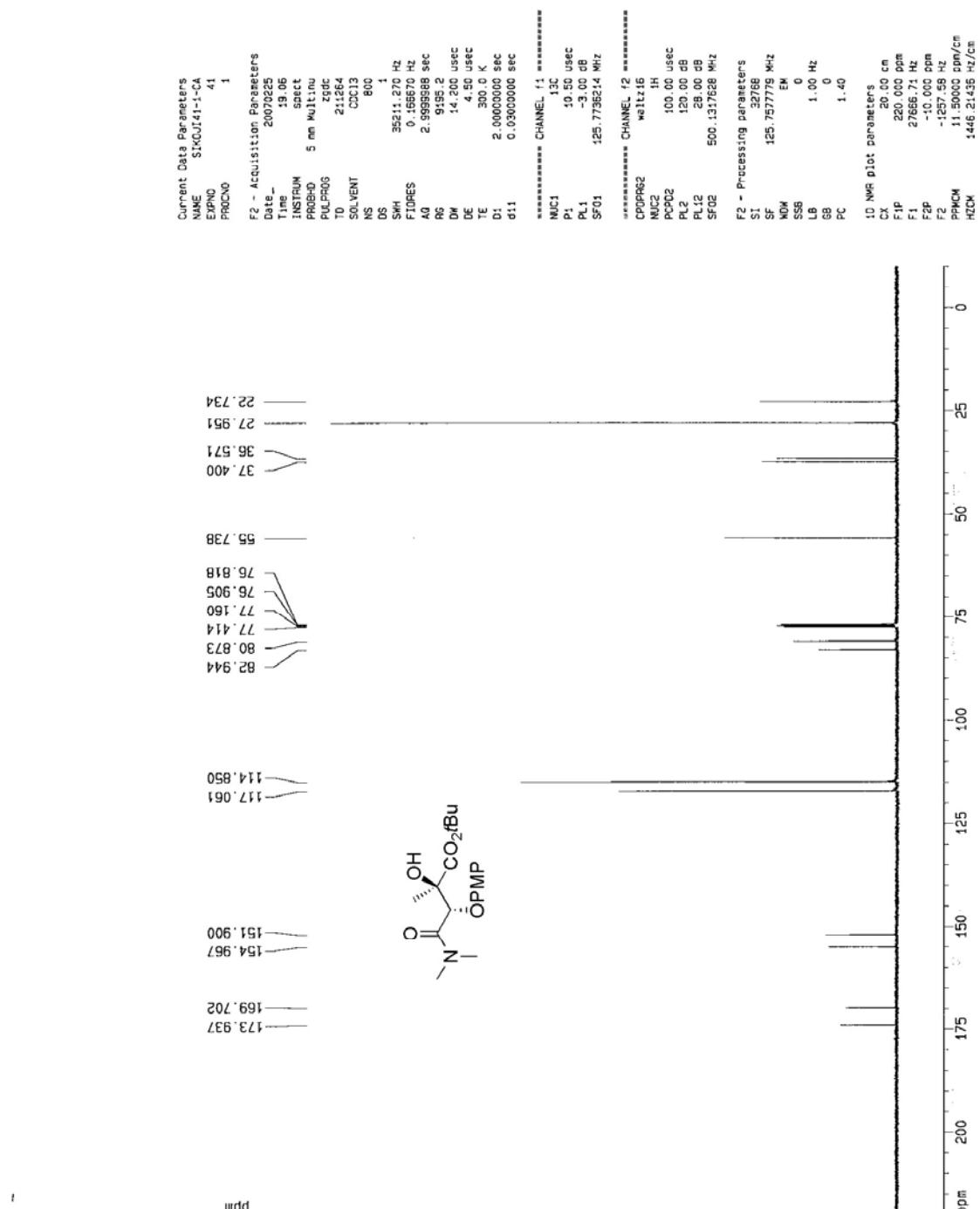




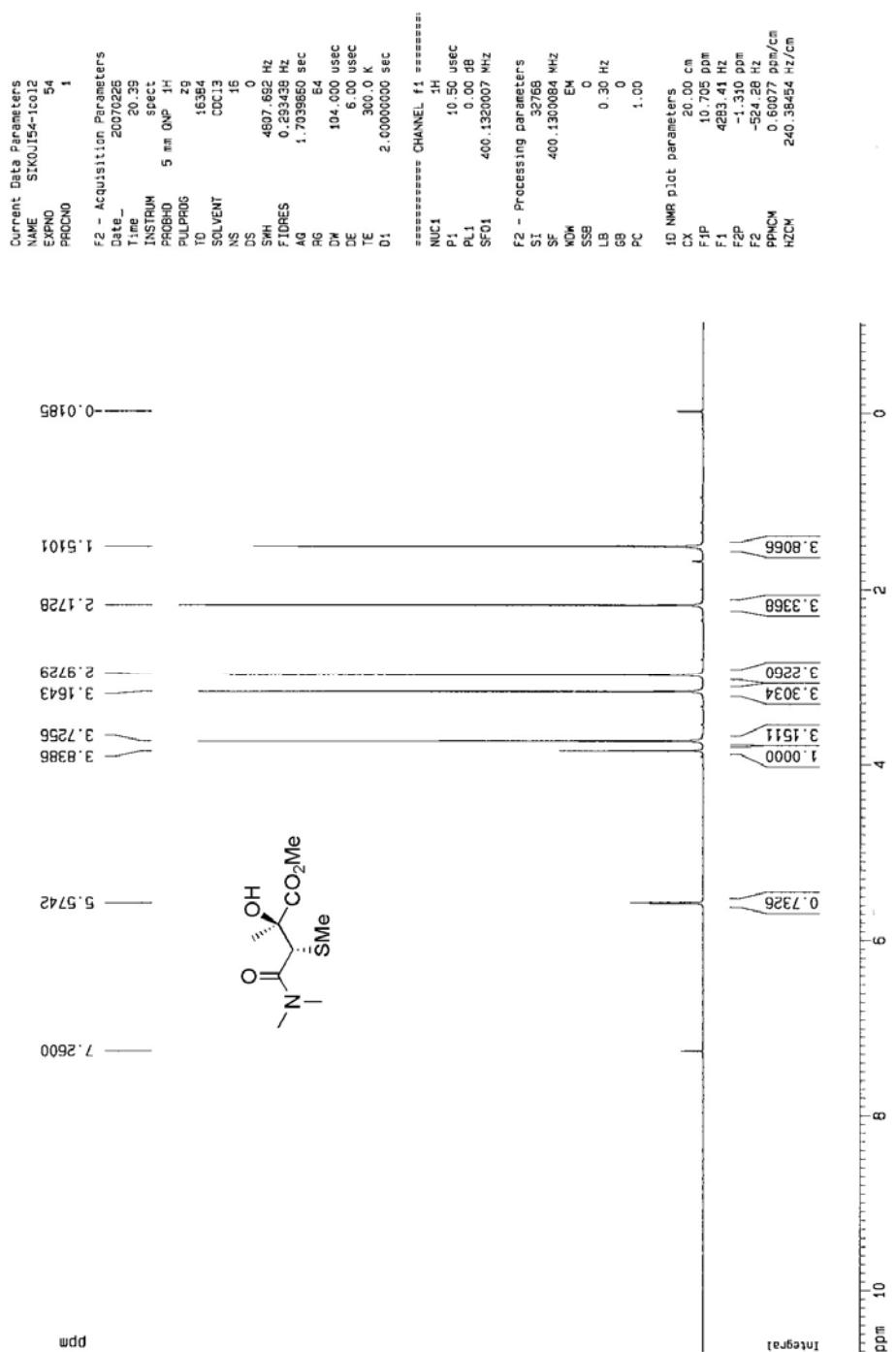
<sup>13</sup>C NMR spectrum of 6j (CDCl<sub>3</sub>, 298 K)



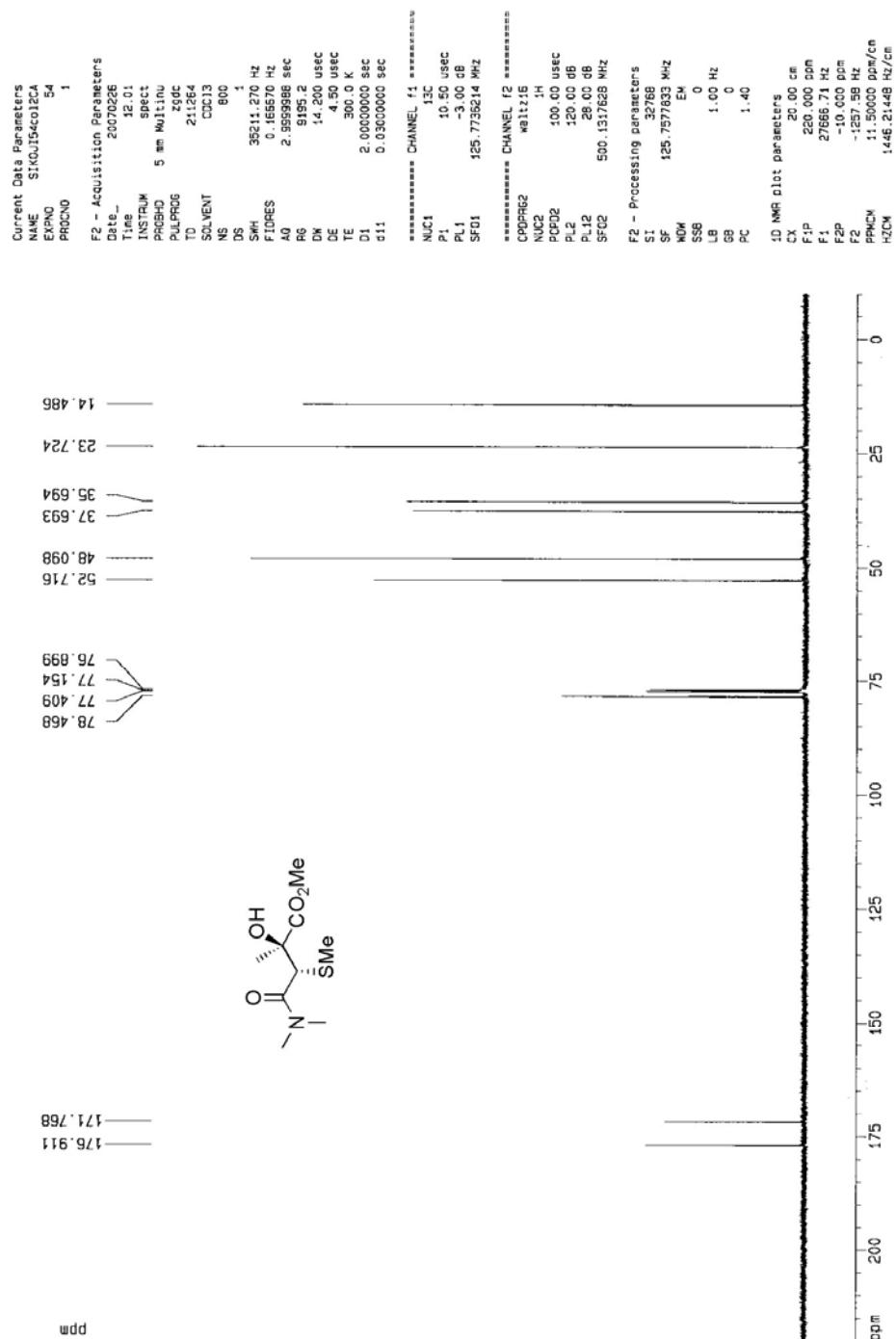
<sup>1</sup>H NMR spectrum of 6k (CDCl<sub>3</sub>, 298 K)



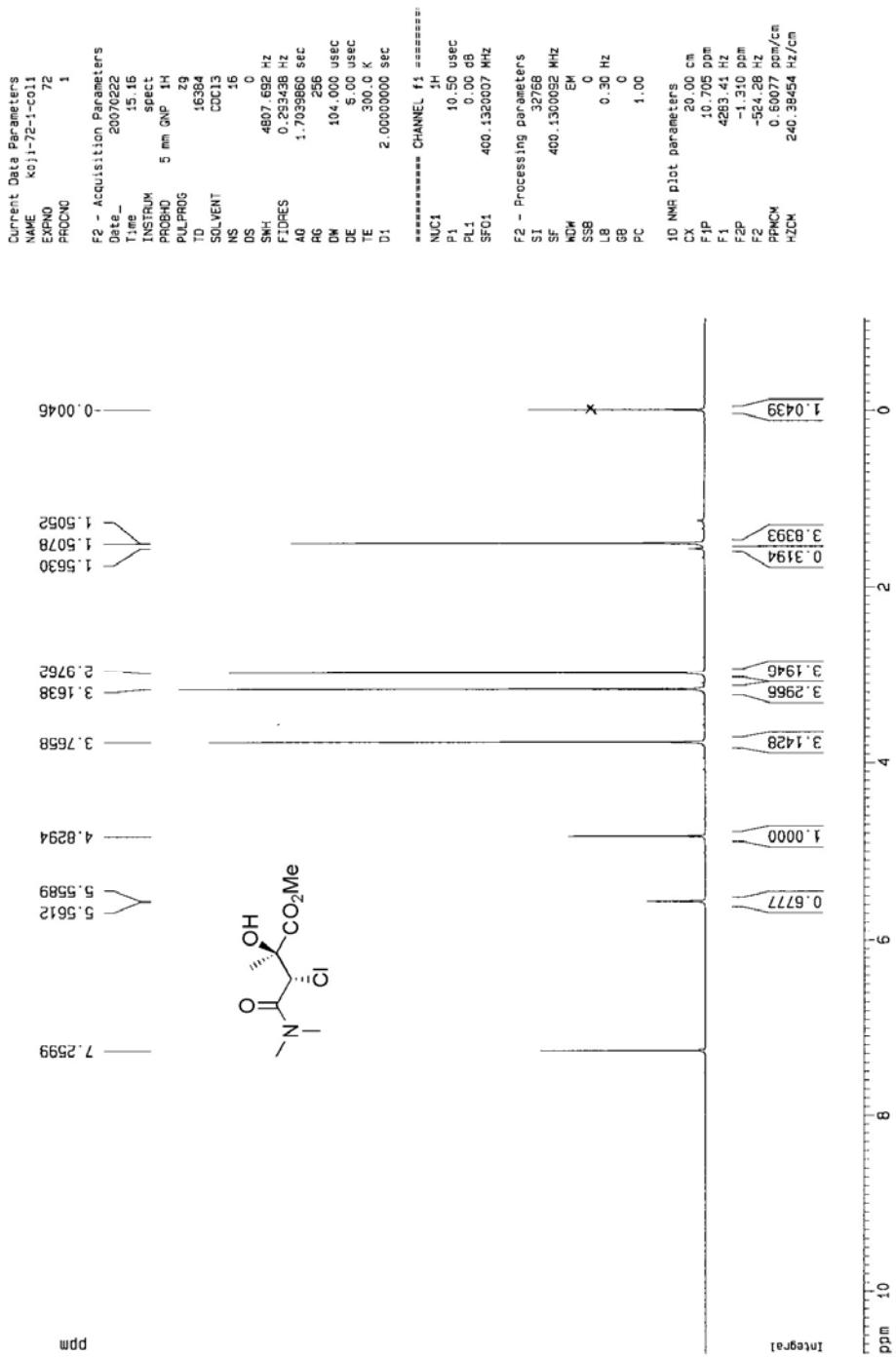
**<sup>13</sup>C NMR spectrum of 6k (CDCl<sub>3</sub>, 298 K)**



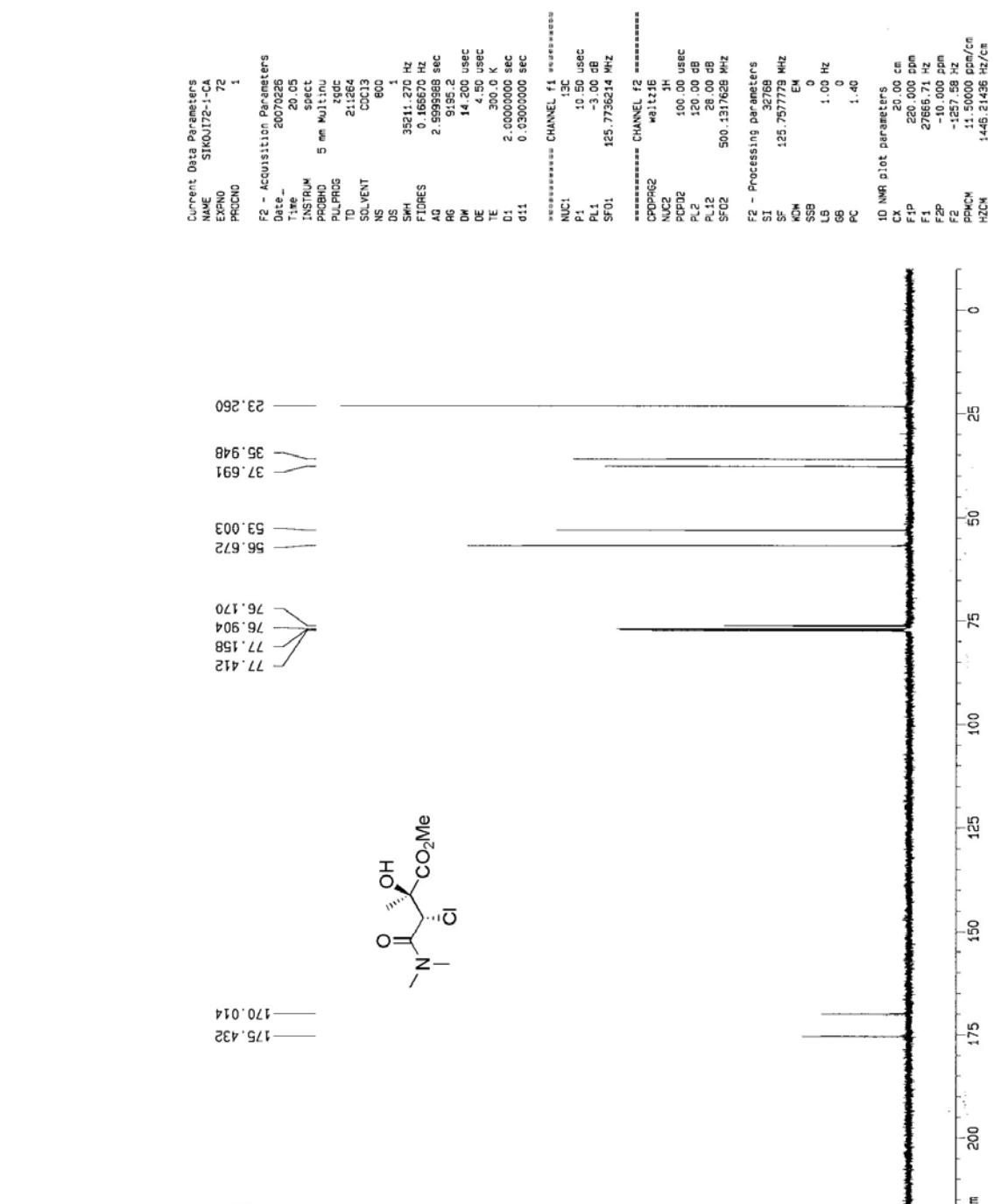
<sup>1</sup>H NMR spectrum of 6l (CDCl<sub>3</sub>, 298 K)



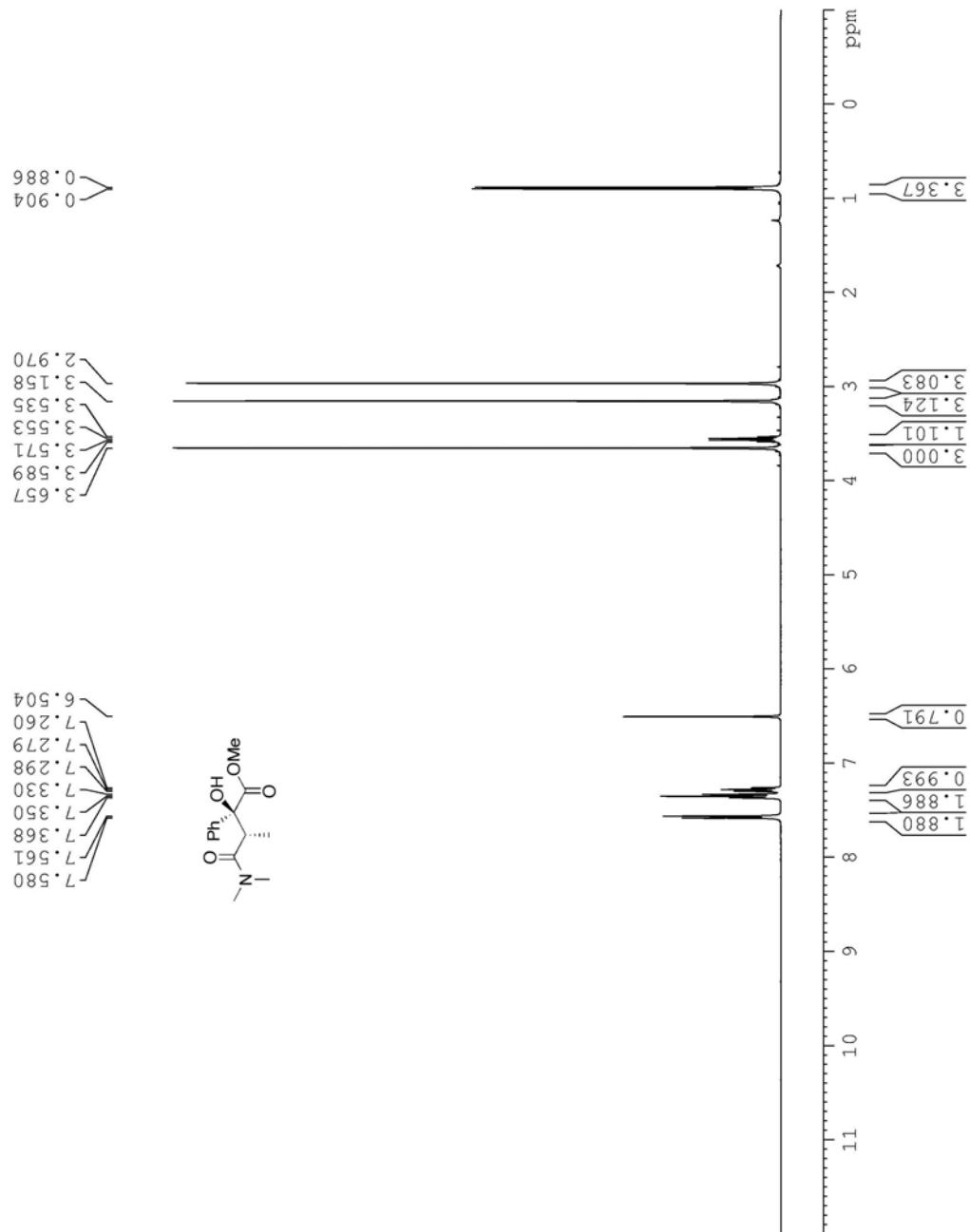
<sup>13</sup>C NMR spectrum of 6l (CDCl<sub>3</sub>, 298 K)



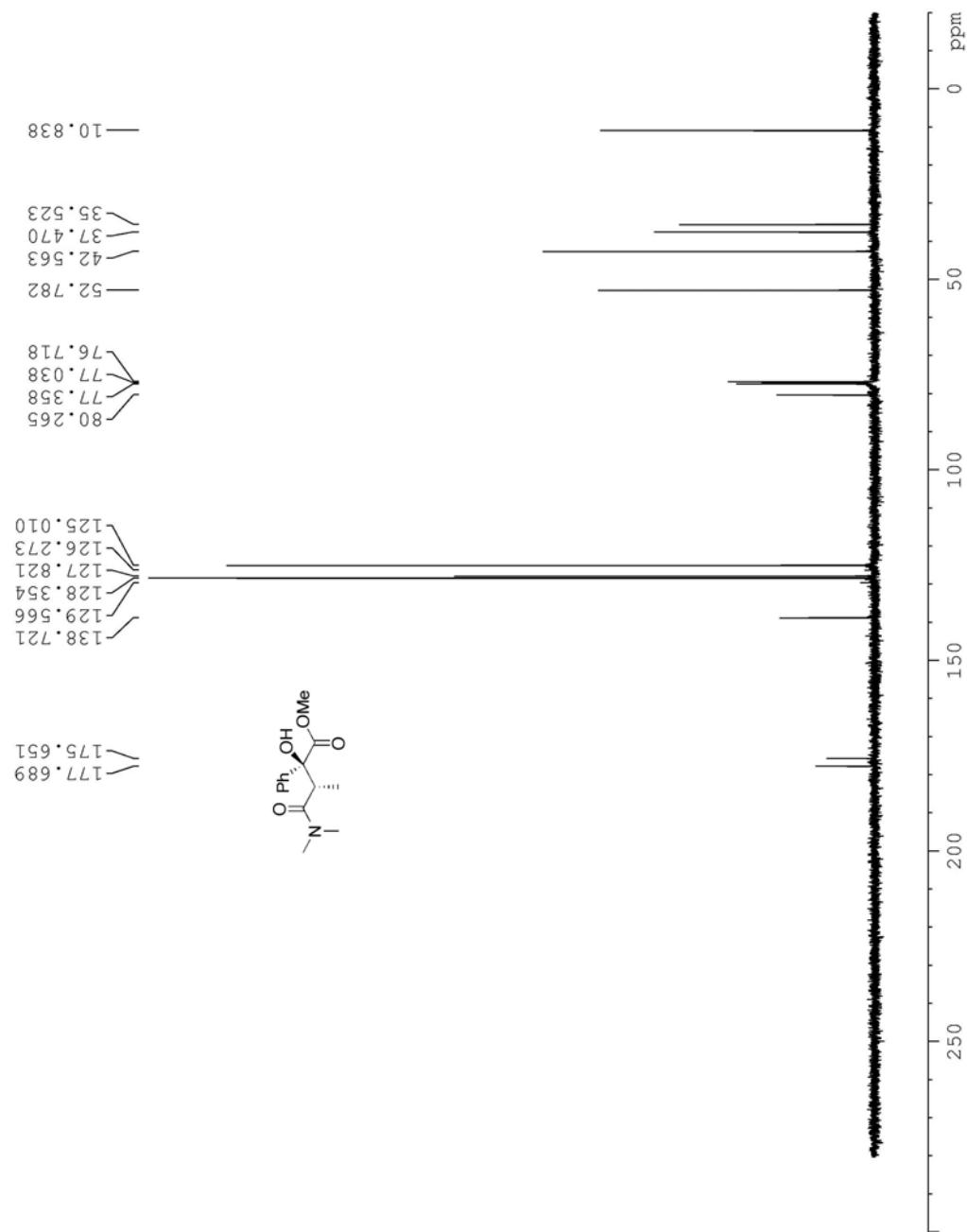
<sup>1</sup>H NMR spectrum of 6m (CDCl<sub>3</sub>, 298 K)



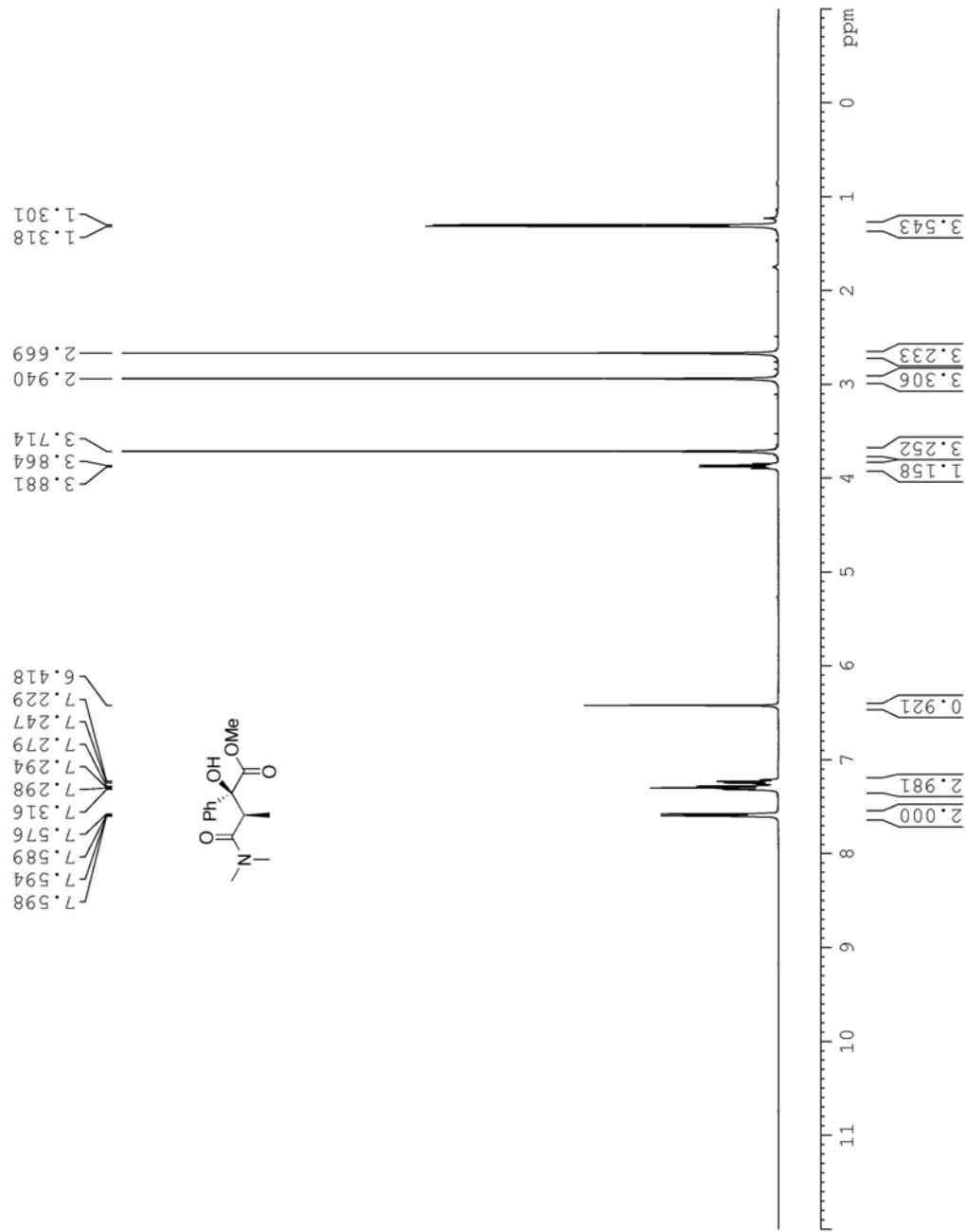
**<sup>13</sup>C NMR spectrum of 6m (CDCl<sub>3</sub>, 298 K)**



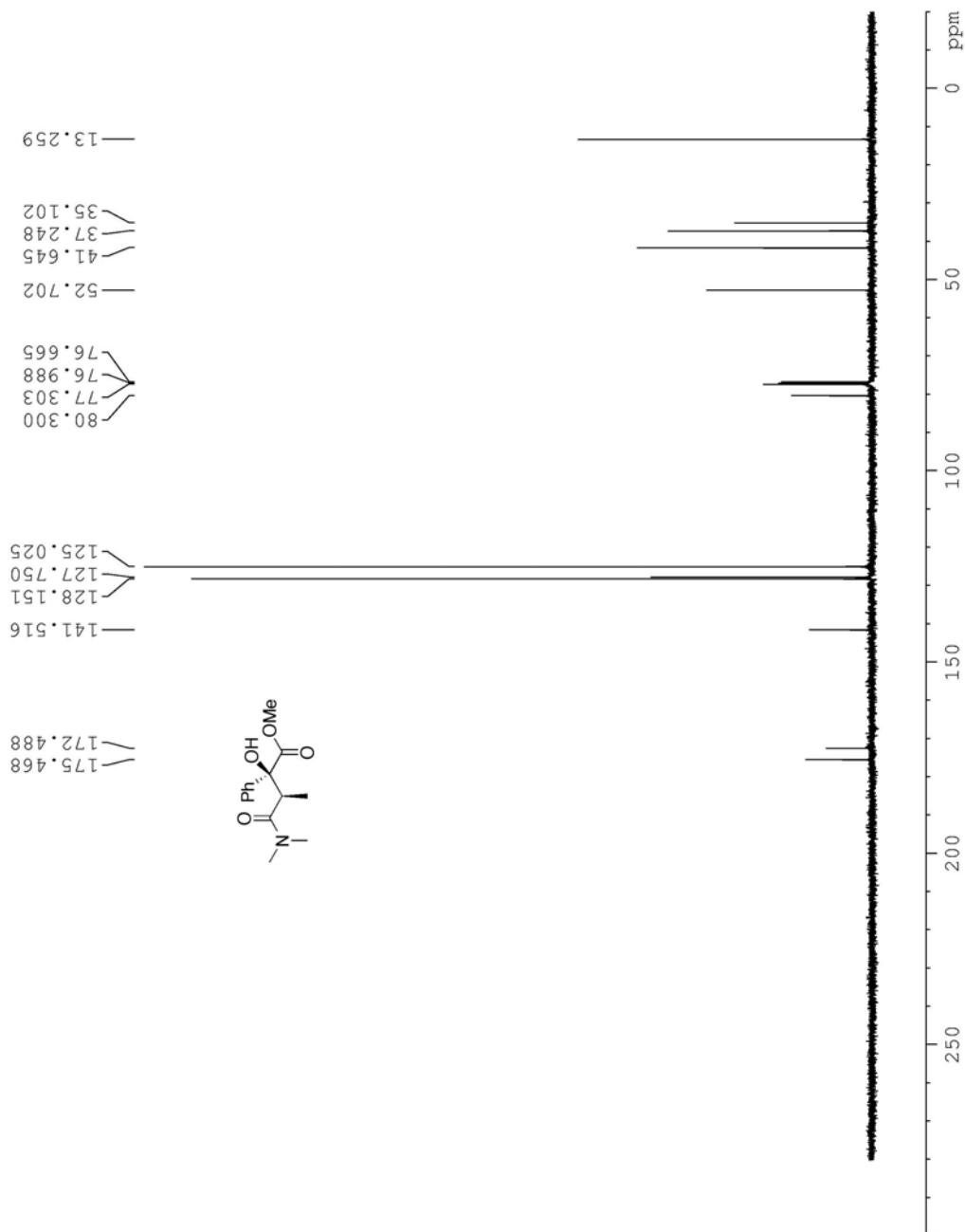
<sup>1</sup>H NMR spectrum of 13a ( $\text{CDCl}_3$ , 298 K)



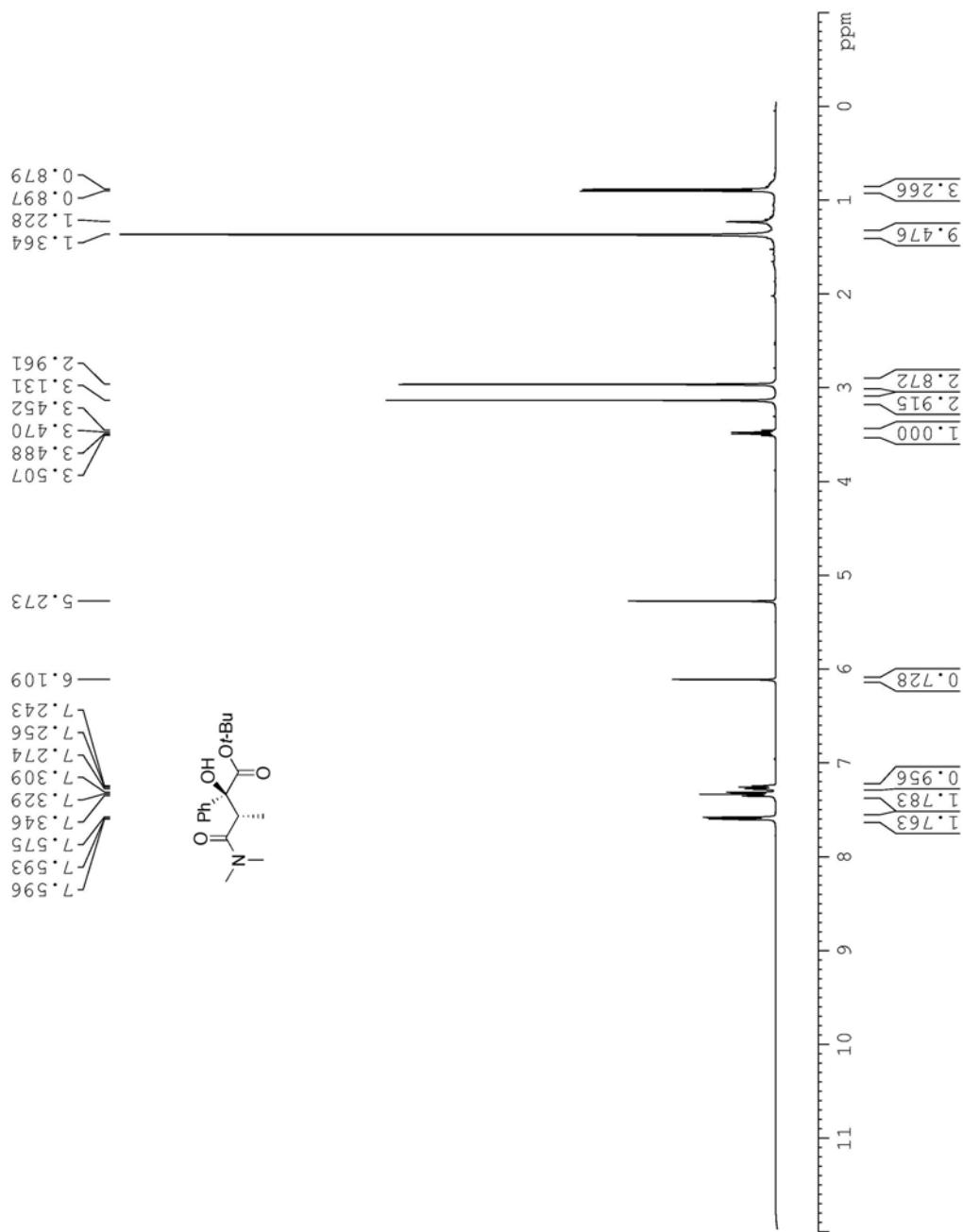
$^{13}\text{C}$  NMR spectrum of 13a ( $\text{CDCl}_3$ , 298 K)



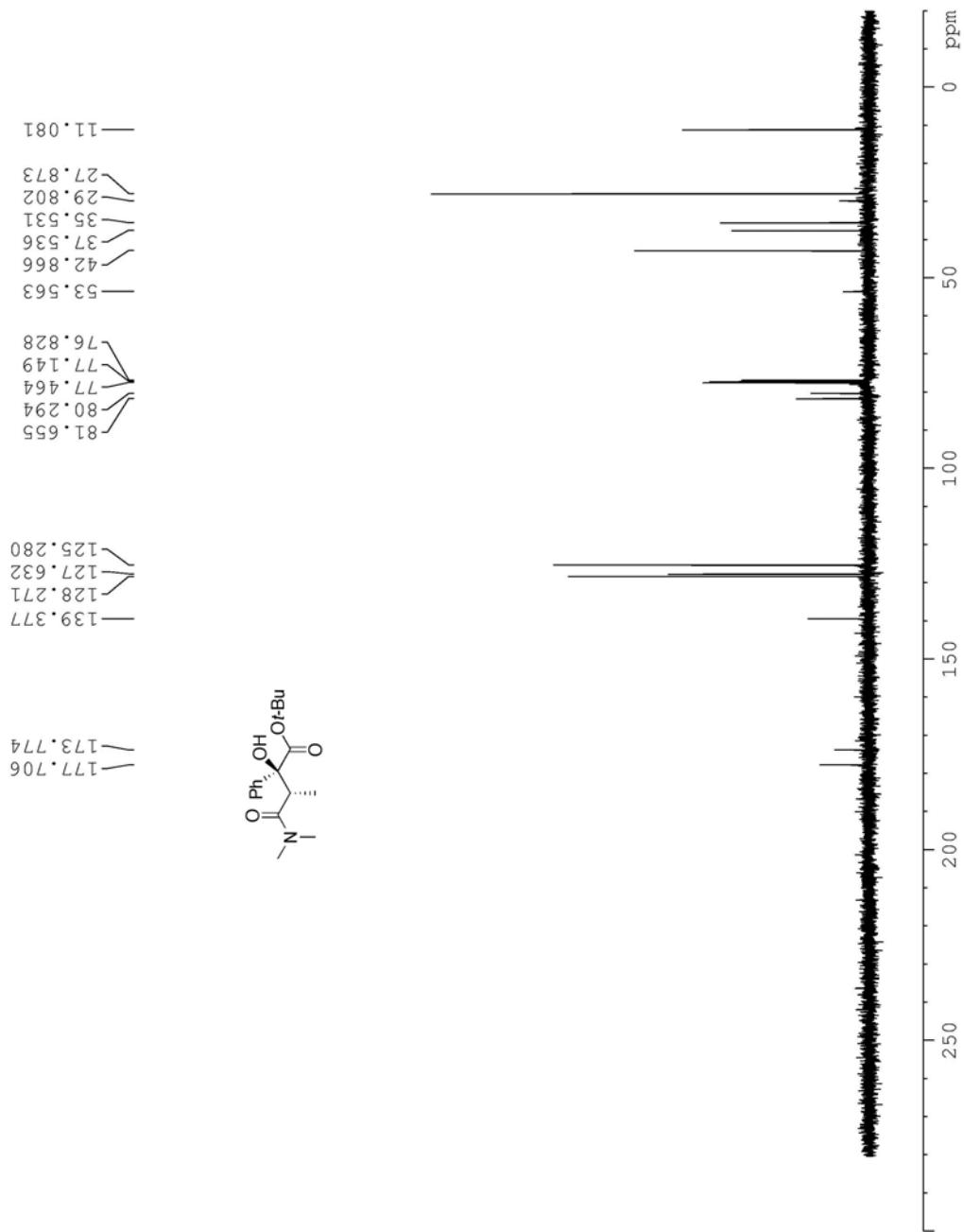
<sup>1</sup>H NMR spectrum of 13a' ( $\text{CDCl}_3$ , 298 K)



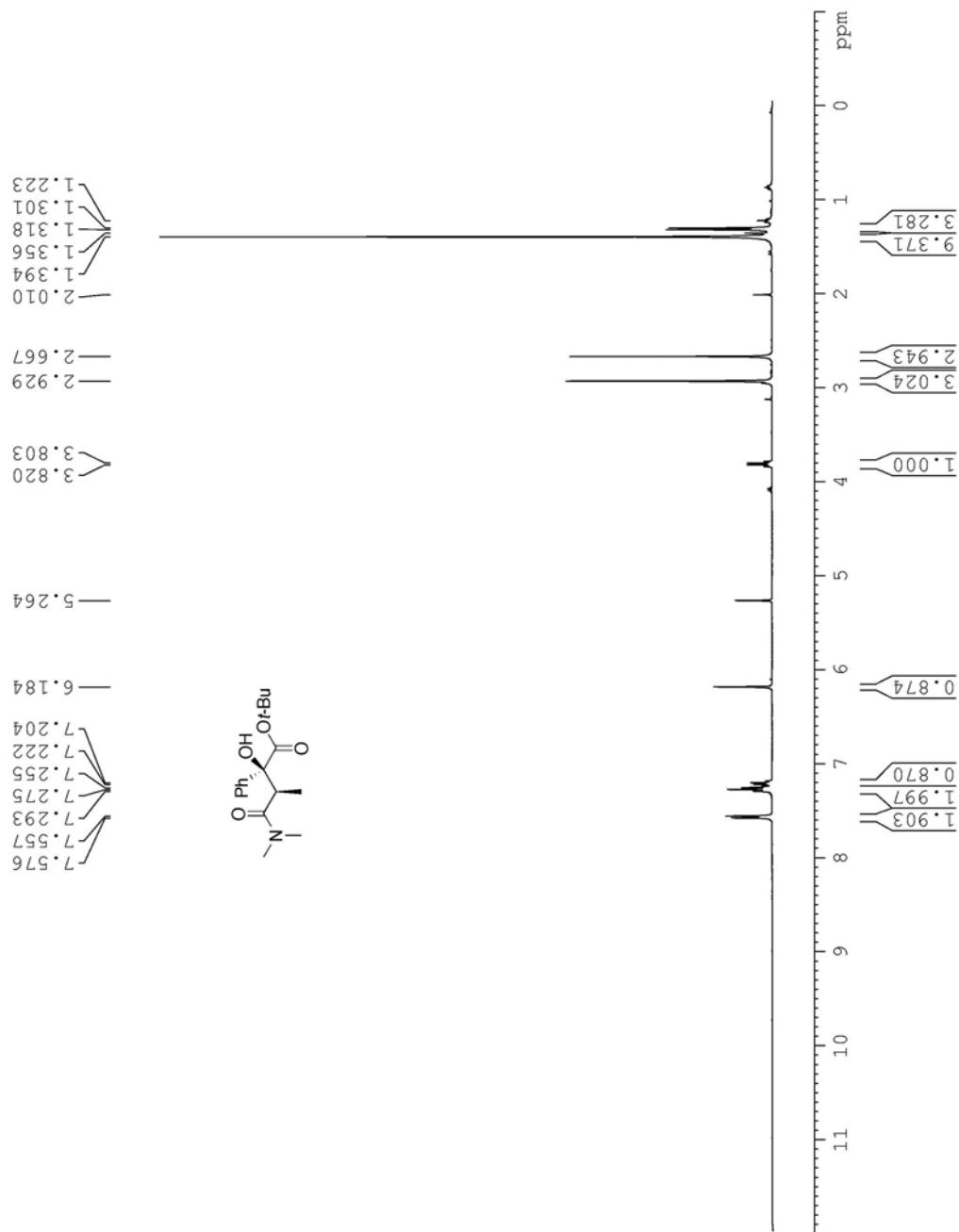
$^{13}\text{C}$  NMR spectrum of  $13\text{a}'$  ( $\text{CDCl}_3$ , 298 K)



<sup>1</sup>H NMR spectrum of 13b ( $\text{CDCl}_3$ , 298 K)

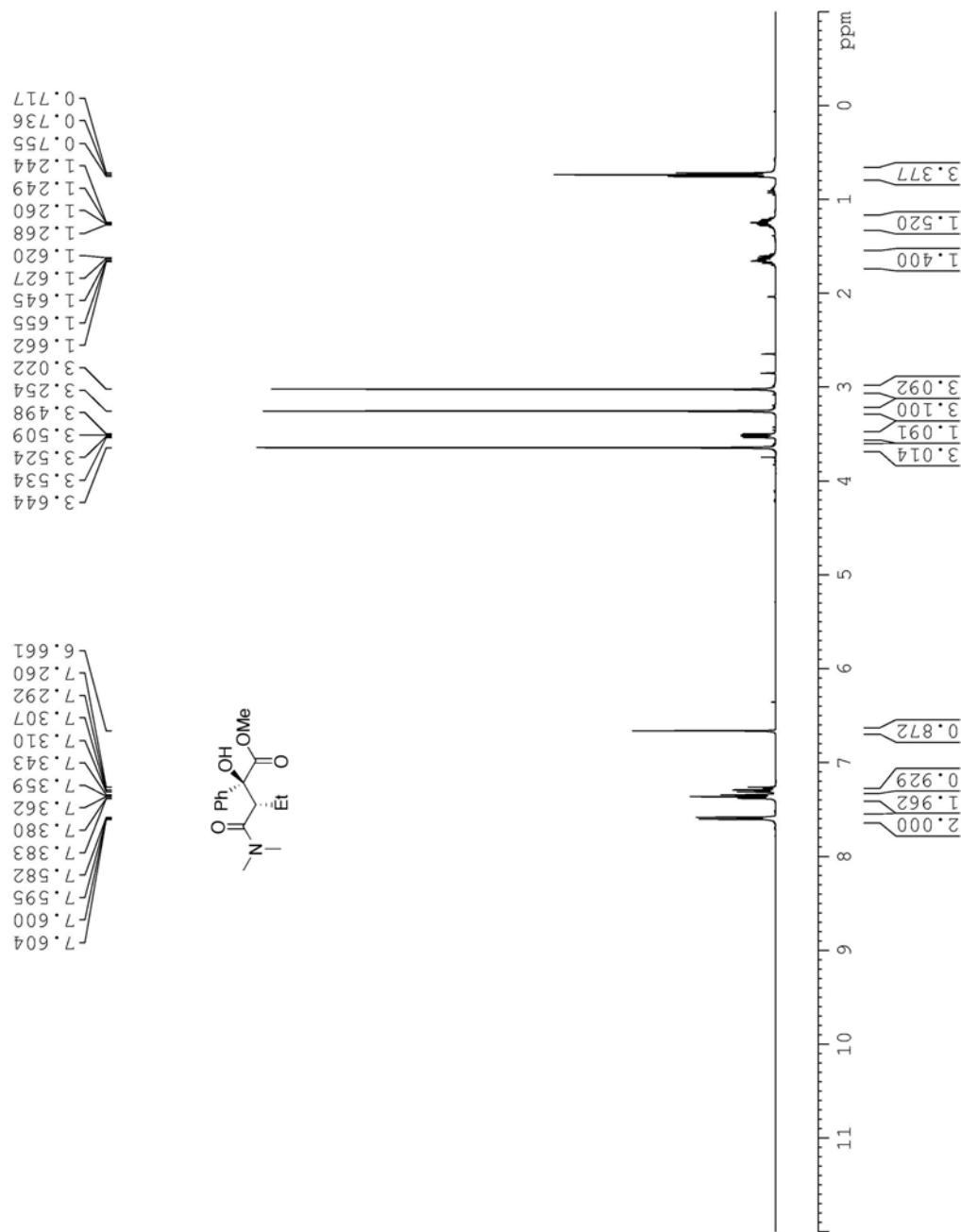


$^{13}\text{C}$  NMR spectrum of 13b ( $\text{CDCl}_3$ , 298 K)

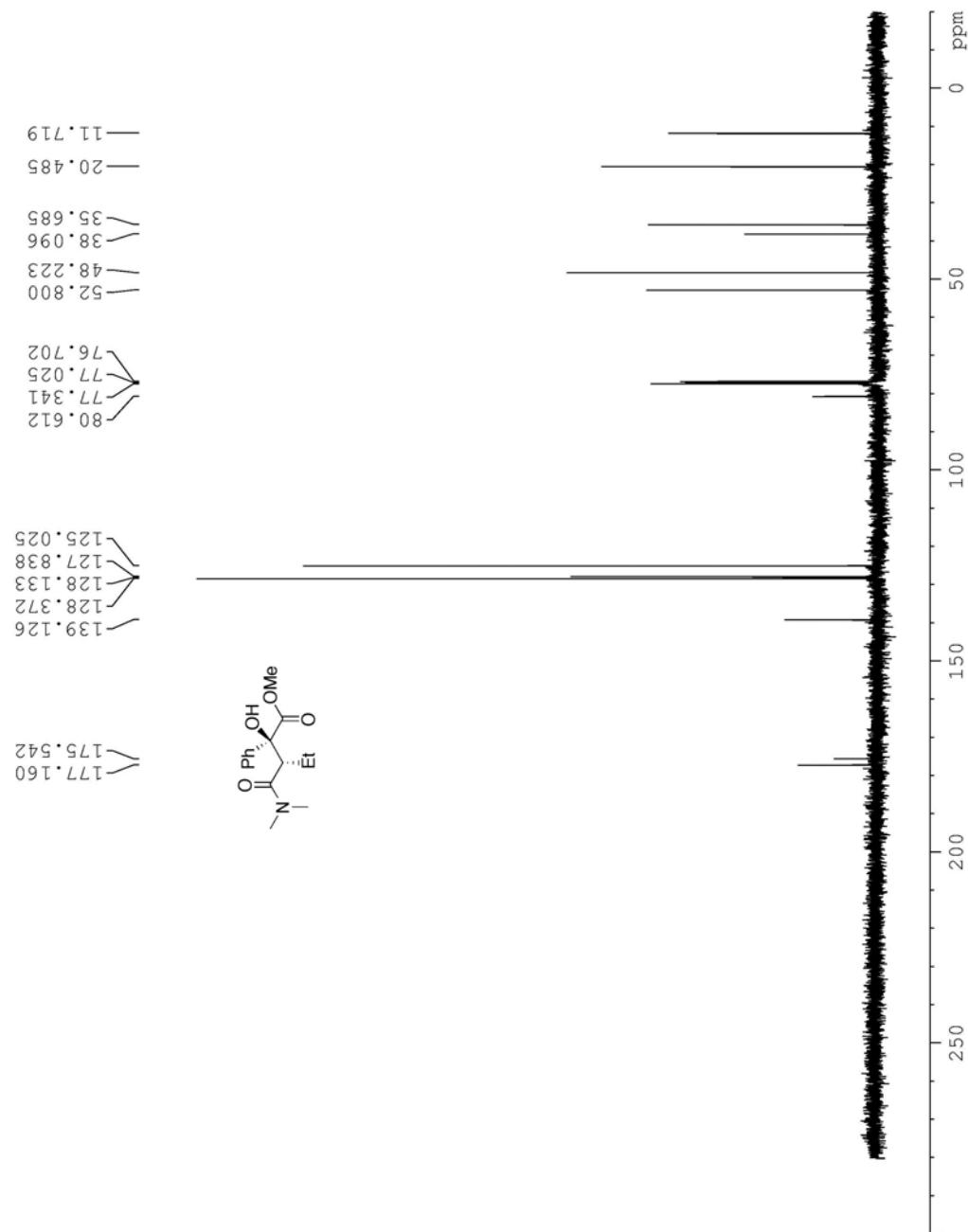


**<sup>1</sup>H NMR spectrum of 13b' (CDCl<sub>3</sub>, 298 K)**

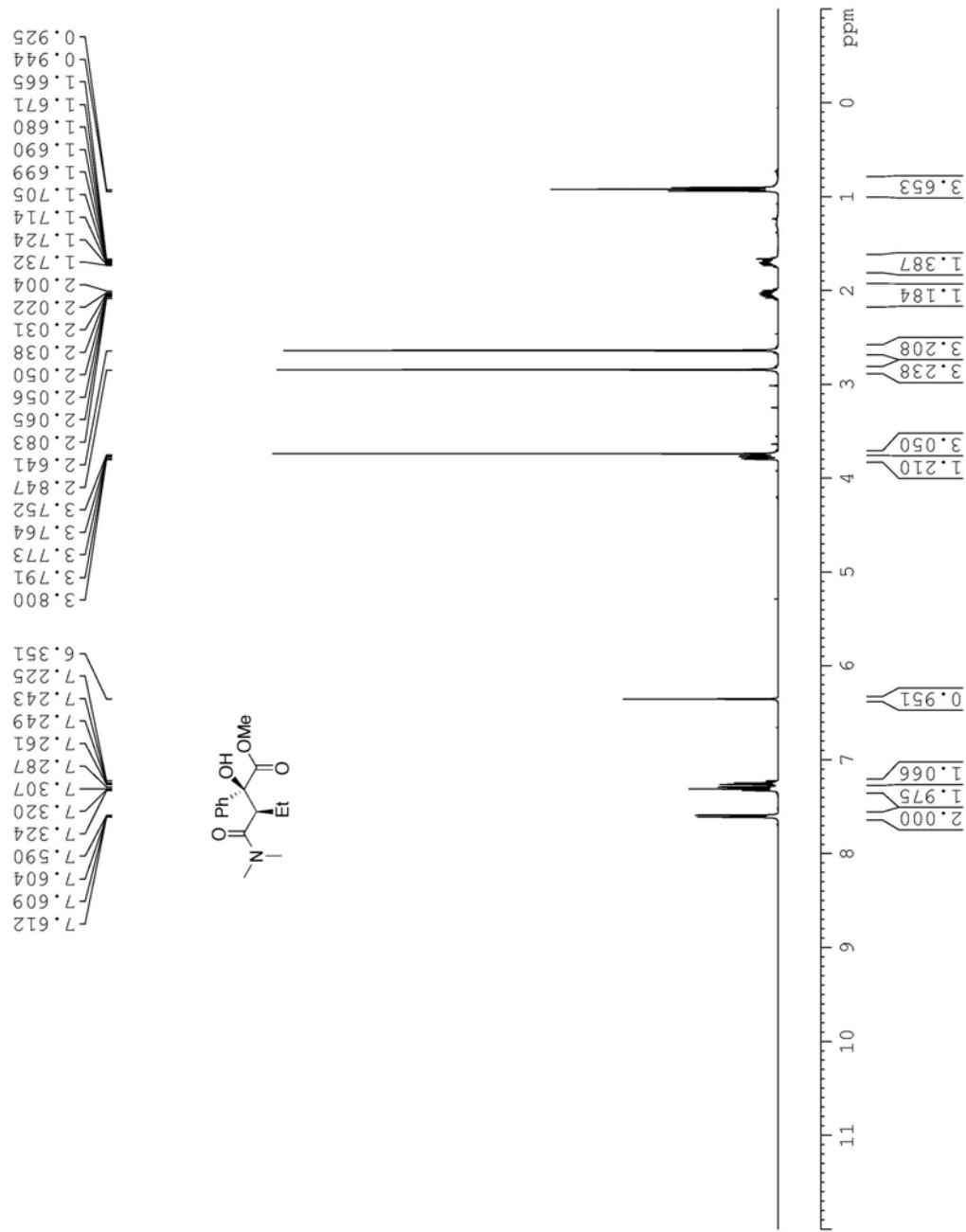




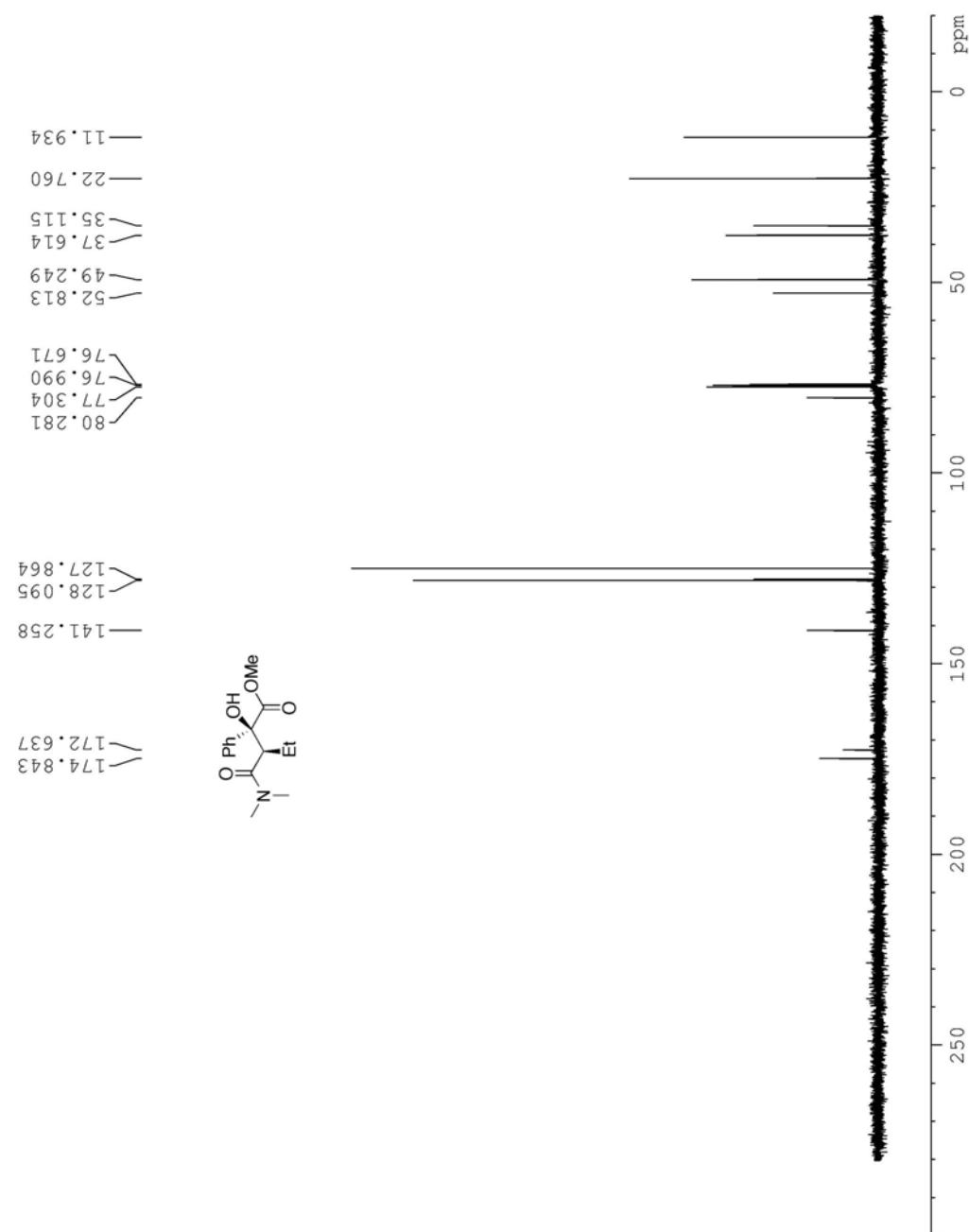
<sup>1</sup>H NMR spectrum of 13c ( $\text{CDCl}_3$ , 298 K)



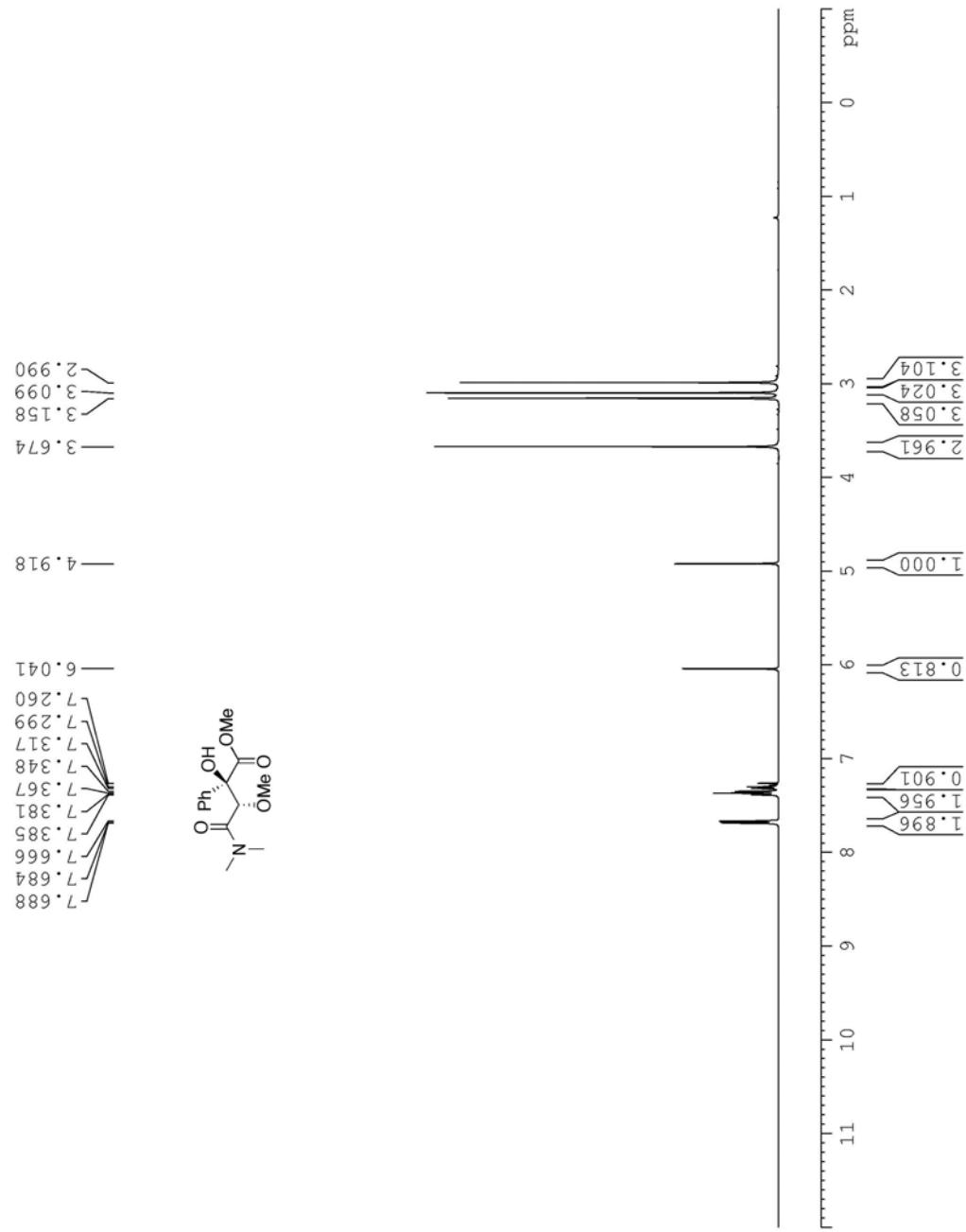
$^{13}\text{C}$  NMR spectrum of 13c ( $\text{CDCl}_3$ , 298 K)



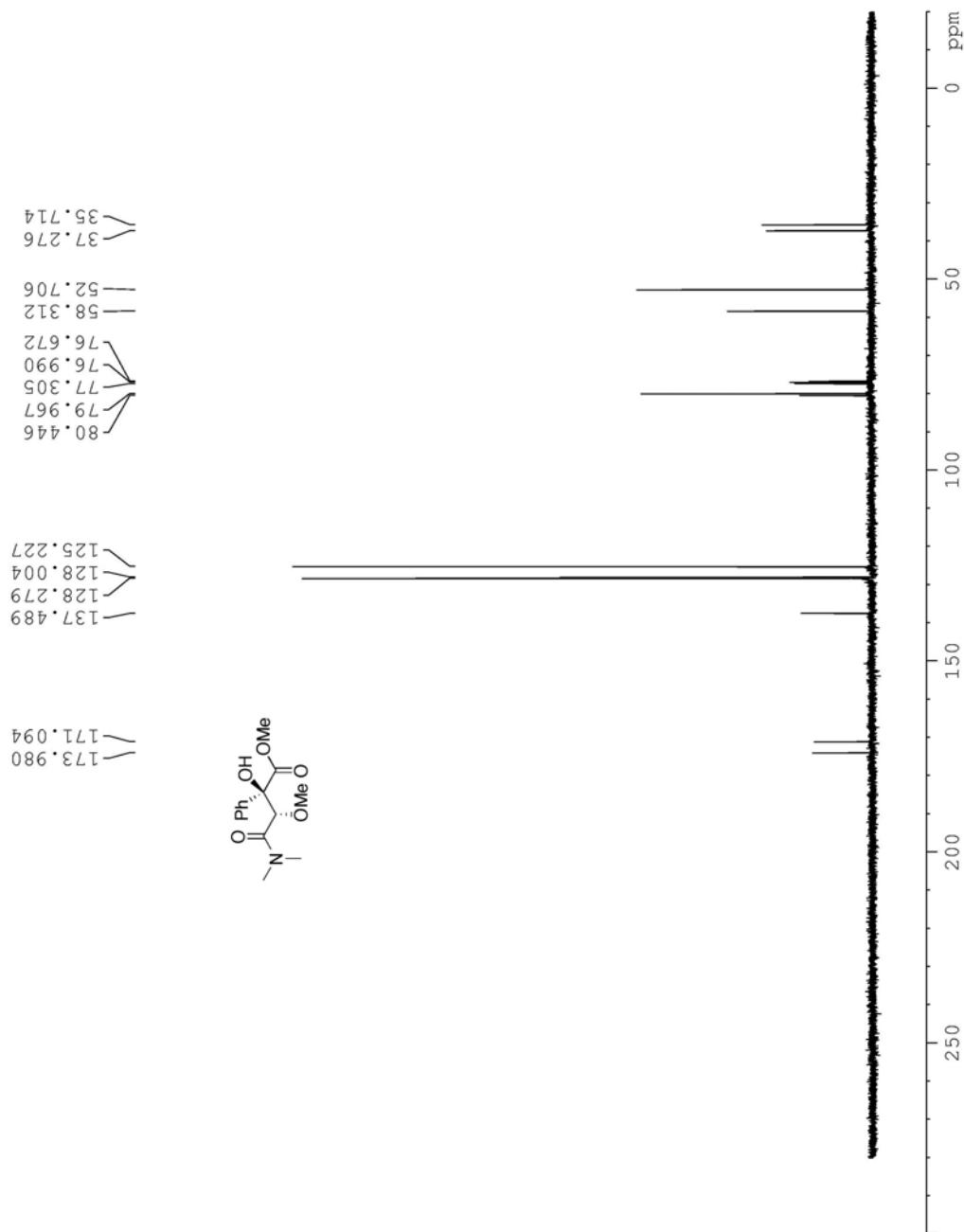
<sup>1</sup>H NMR spectrum of 13c' ( $\text{CDCl}_3$ , 298 K)



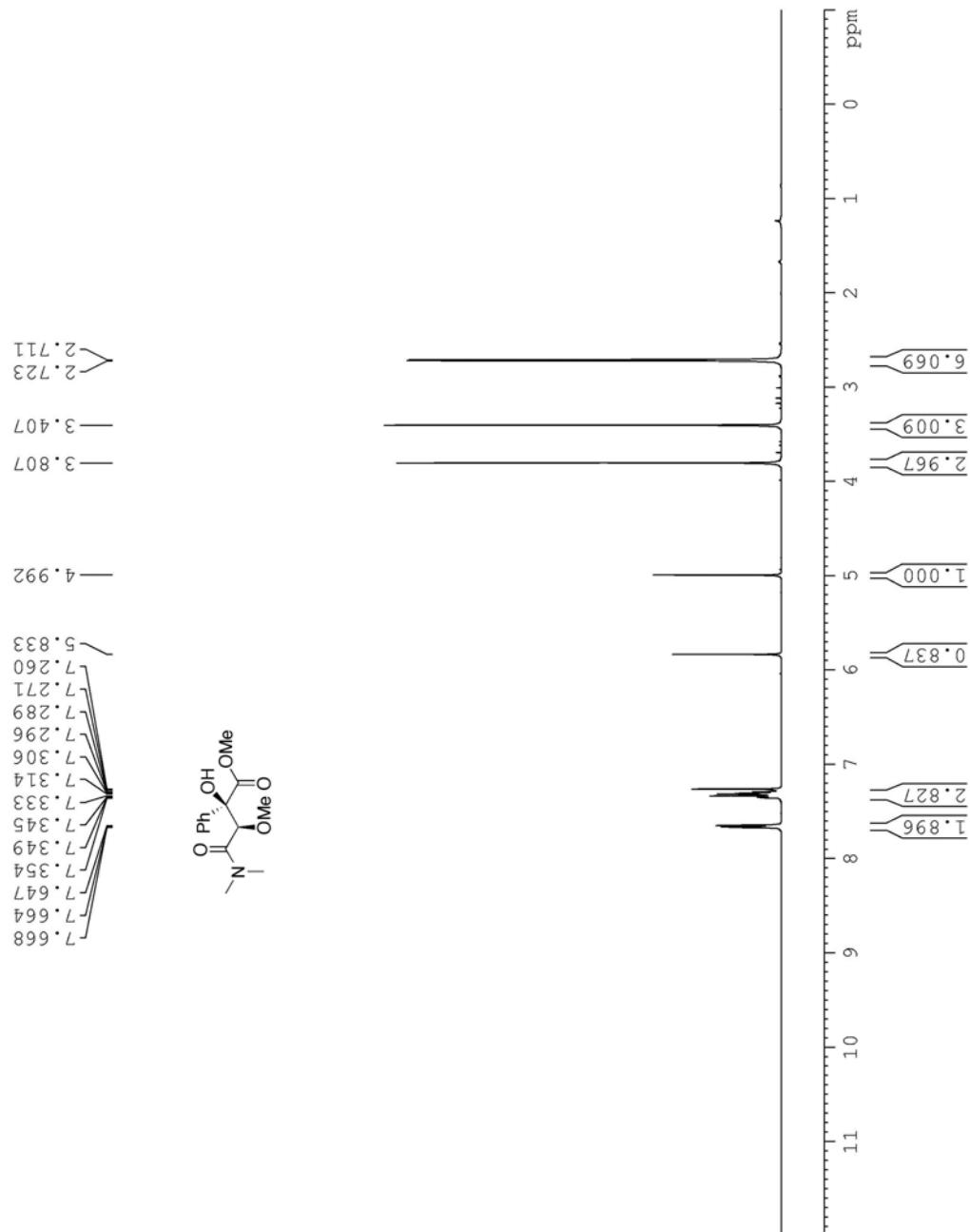
<sup>1</sup>H NMR spectrum of 13c' ( $\text{CDCl}_3$ , 298 K)



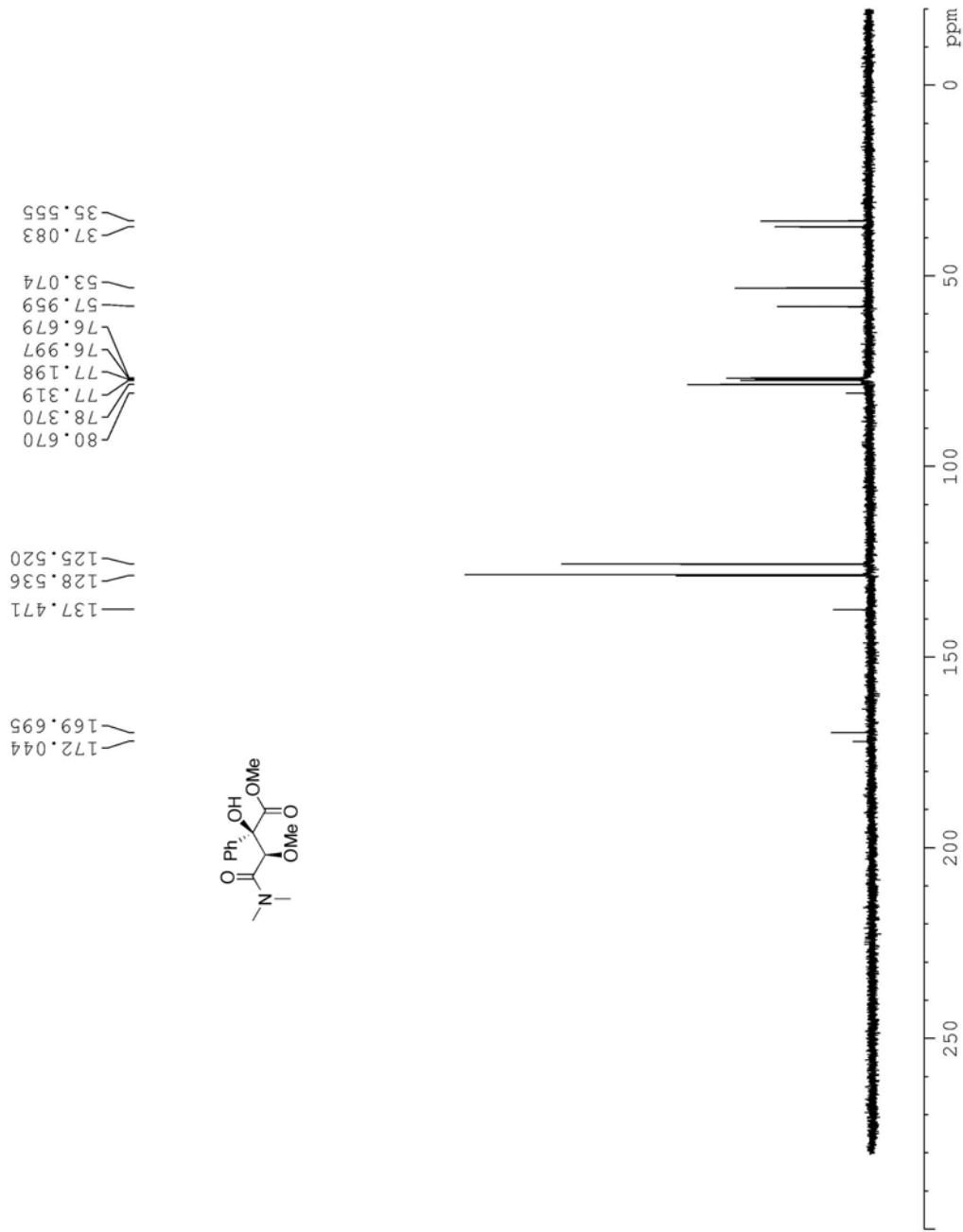
<sup>1</sup>H NMR spectrum of 13d ( $\text{CDCl}_3$ , 298 K)



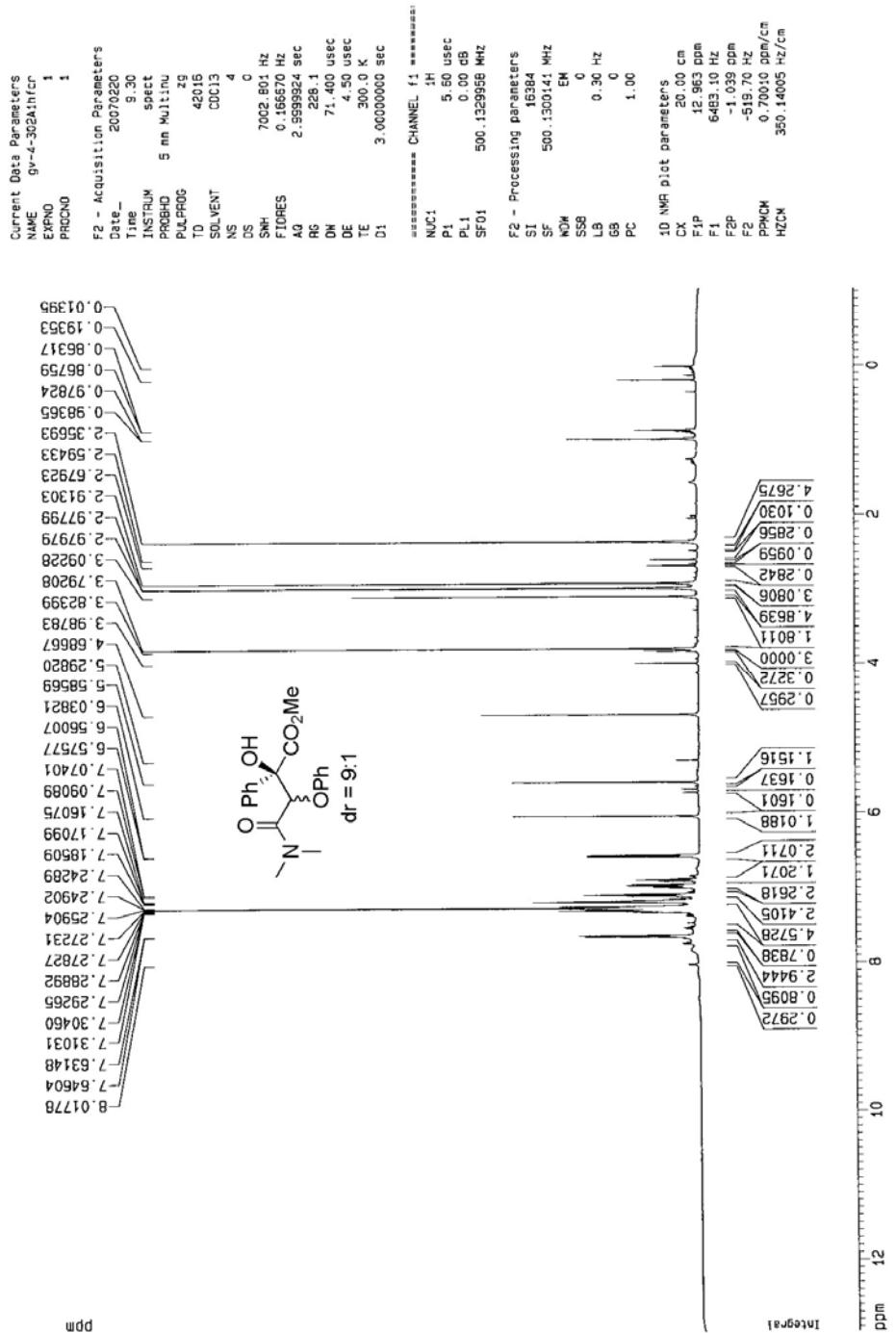
$^{13}\text{C}$  NMR spectrum of 13d ( $\text{CDCl}_3$ , 298 K)



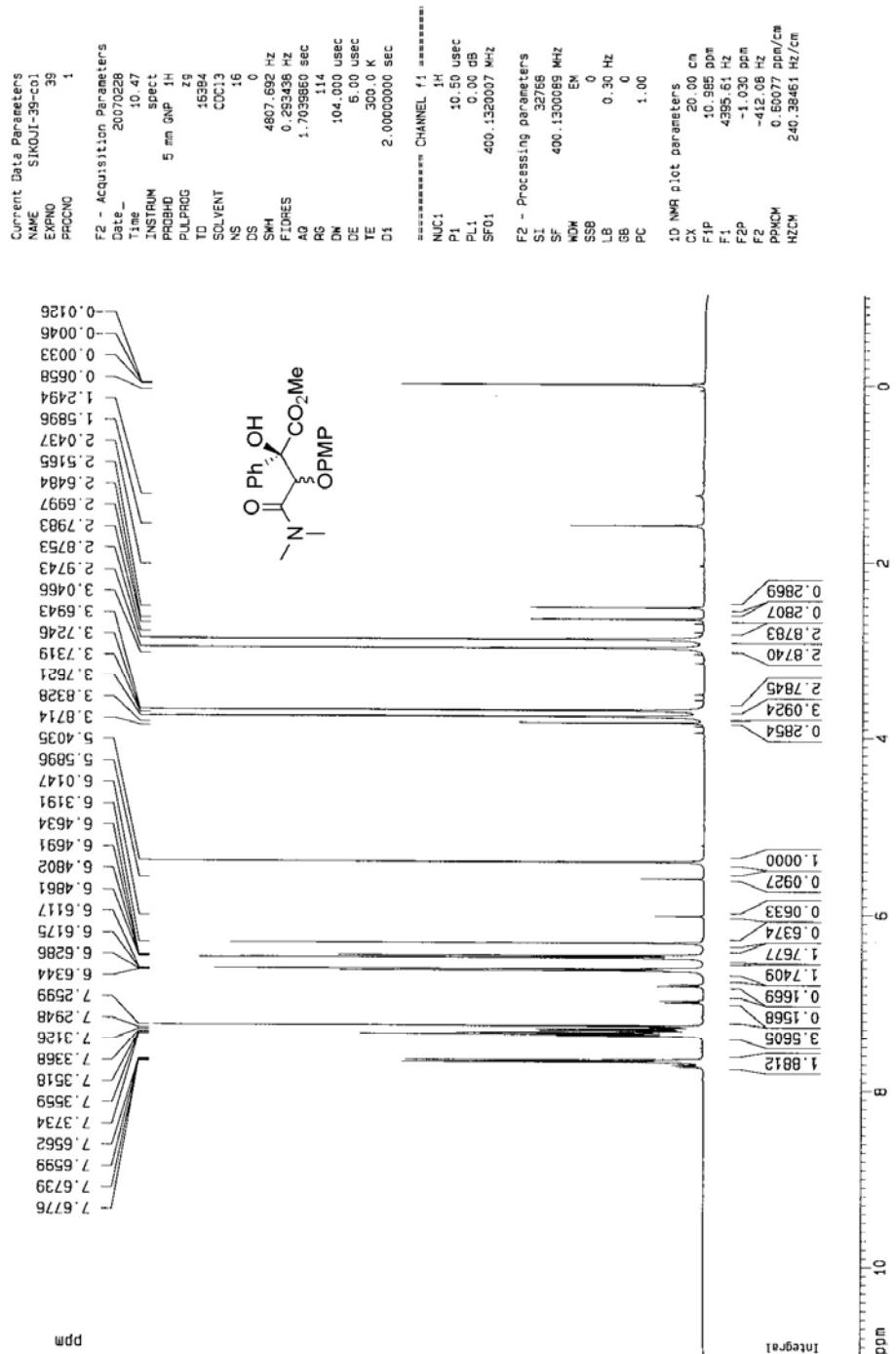
$^1\text{H}$  NMR spectrum of  $7\text{d}'$  ( $\text{CDCl}_3$ , 298 K)



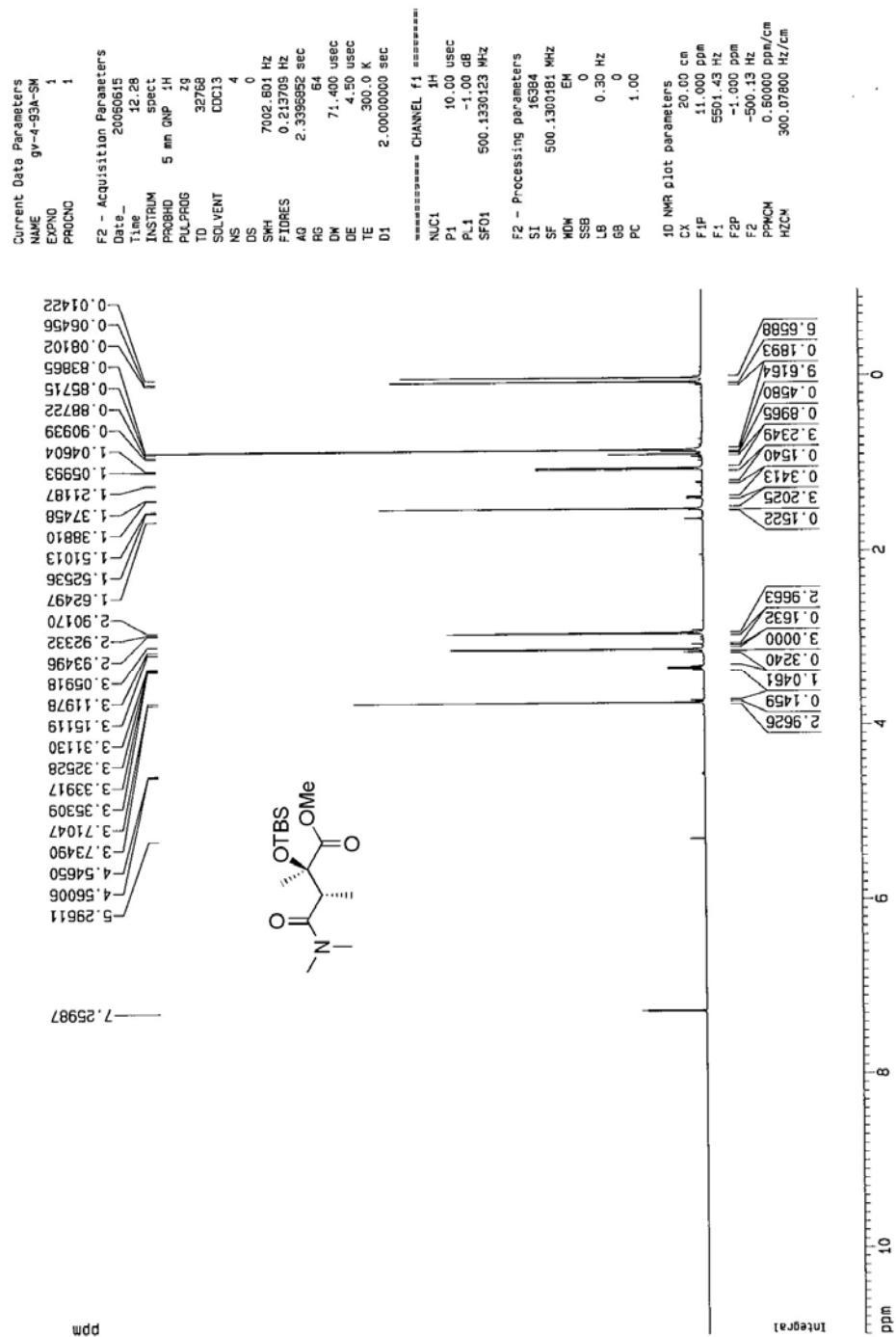
$^{13}\text{C}$  NMR spectrum of  $13\text{d}'$  ( $\text{CDCl}_3$ , 298 K)



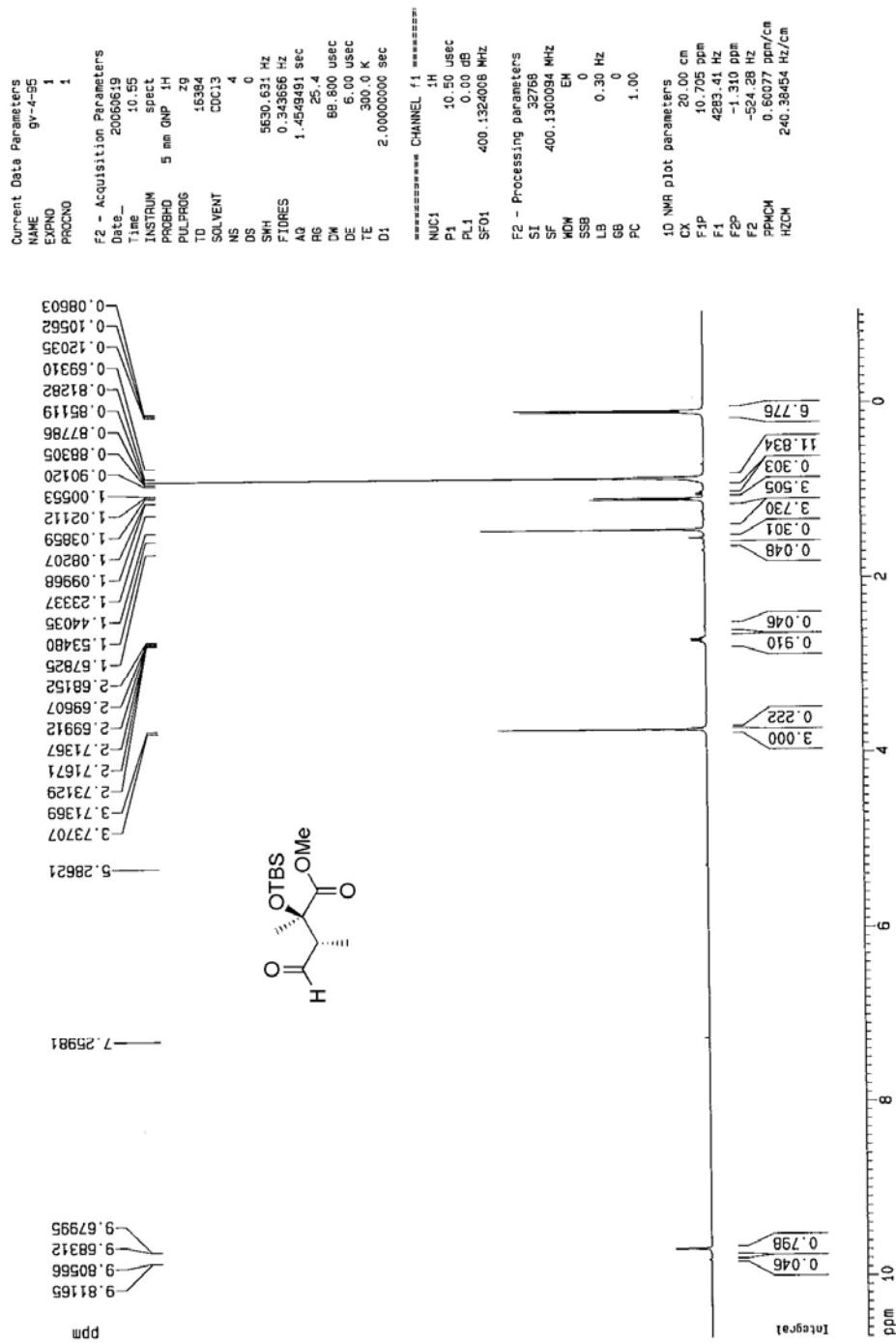
<sup>1</sup>H NMR spectrum of 13e + 13e' (CDCl<sub>3</sub>, 298 K)



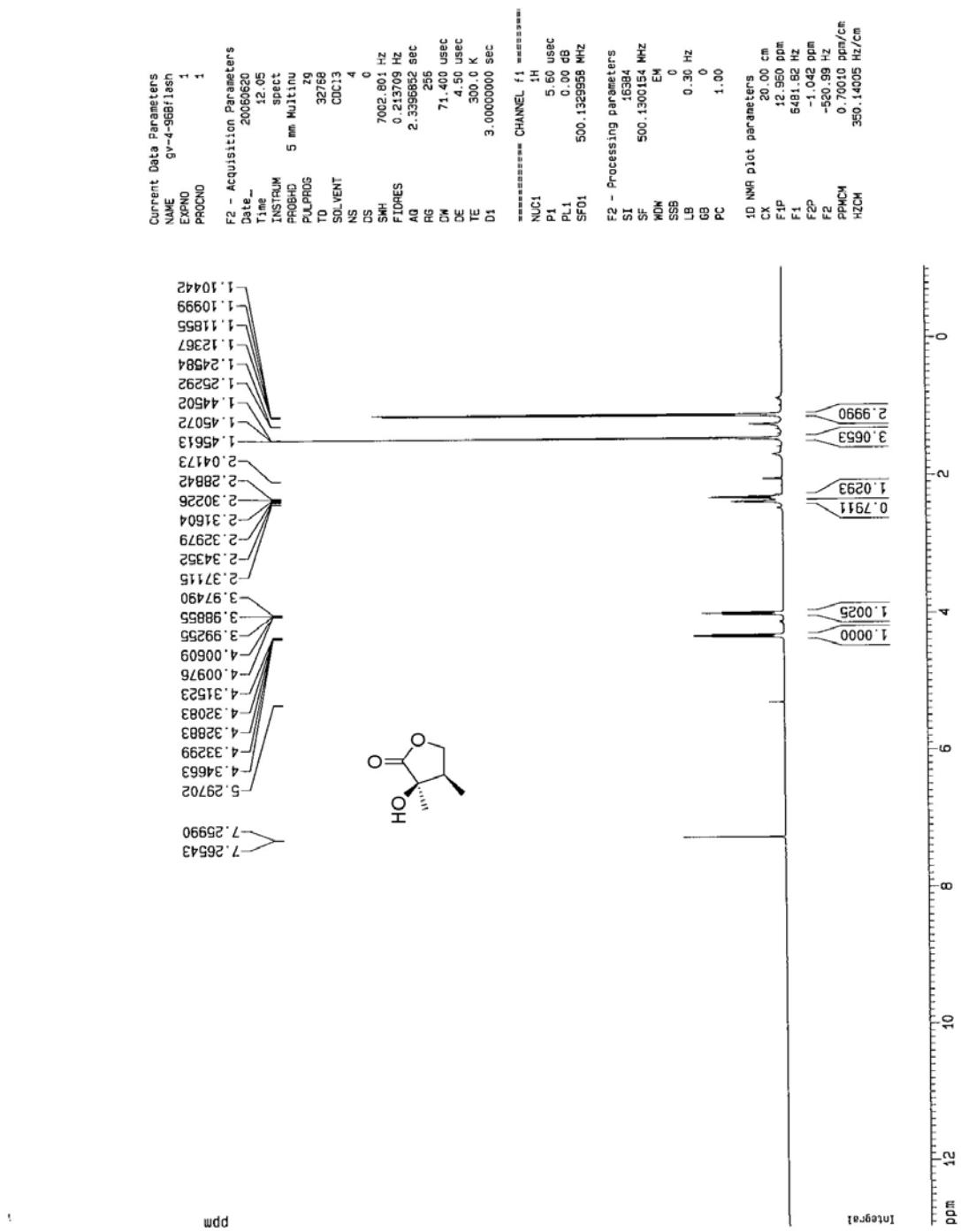
<sup>1</sup>H NMR spectrum of 13f+13f' (CDCl<sub>3</sub>, 298 K)



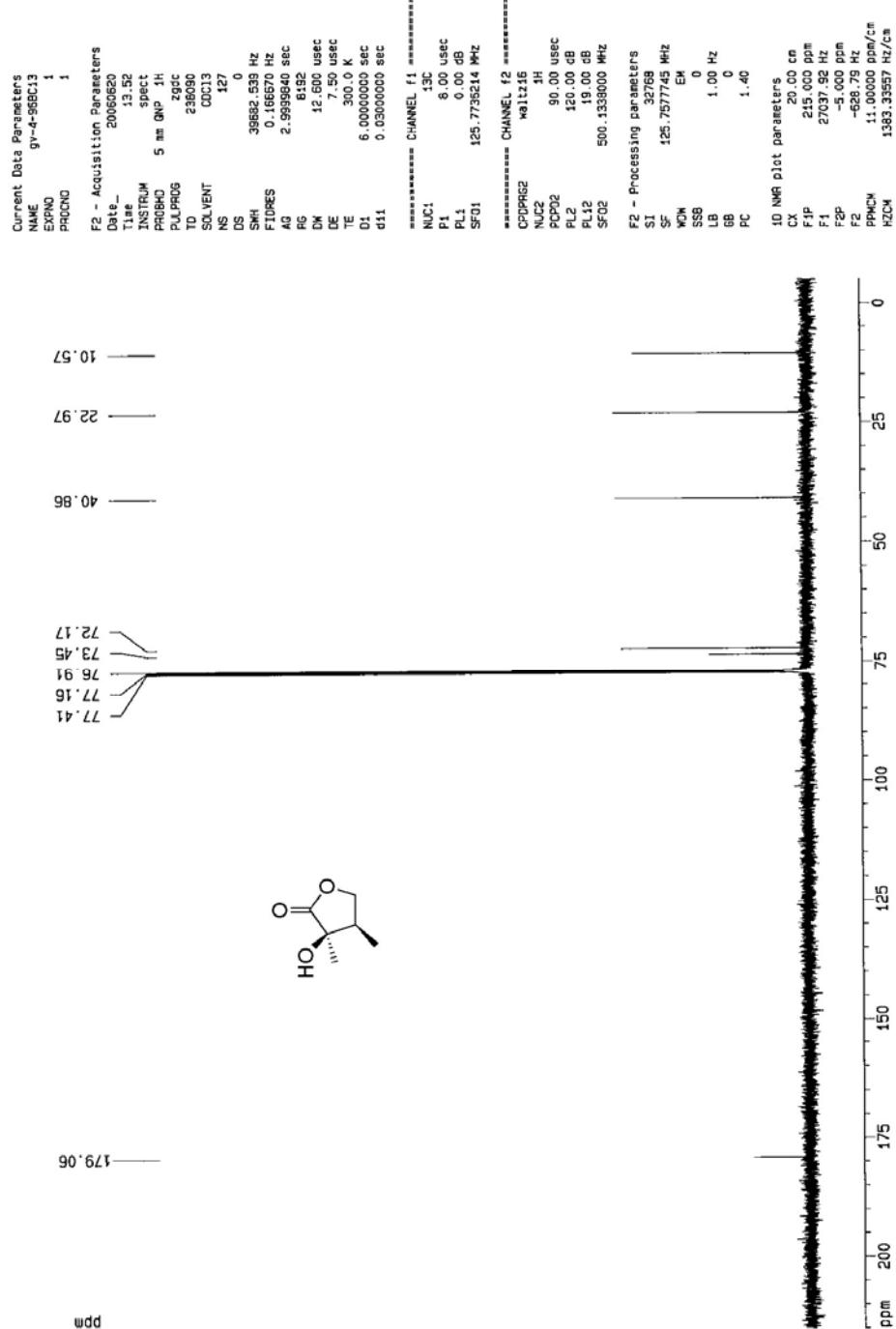
<sup>1</sup>H NMR spectrum of 7 (CDCl<sub>3</sub>, 298 K)



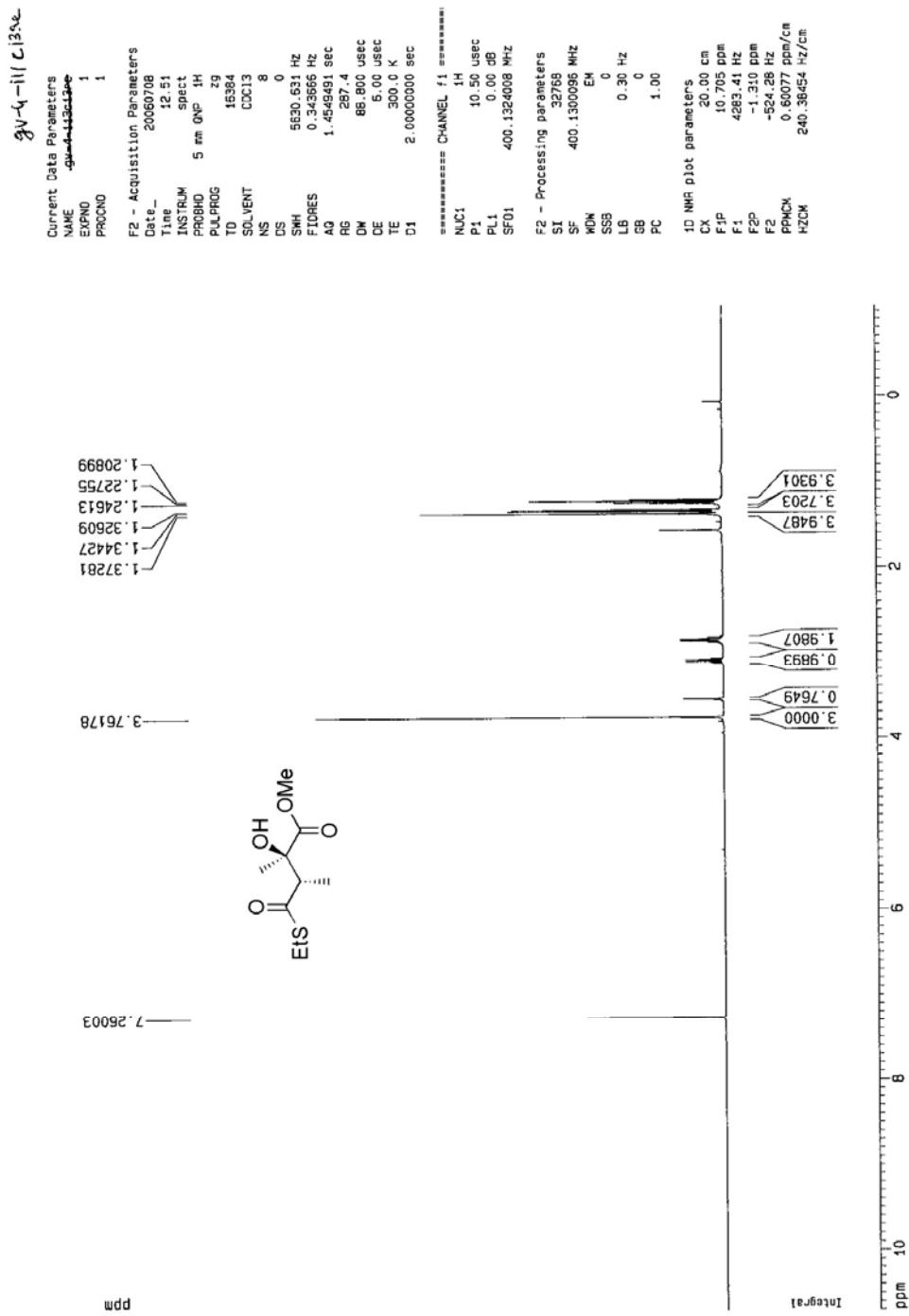
<sup>1</sup>H NMR spectrum of 9 (CDCl<sub>3</sub>, 298 K)



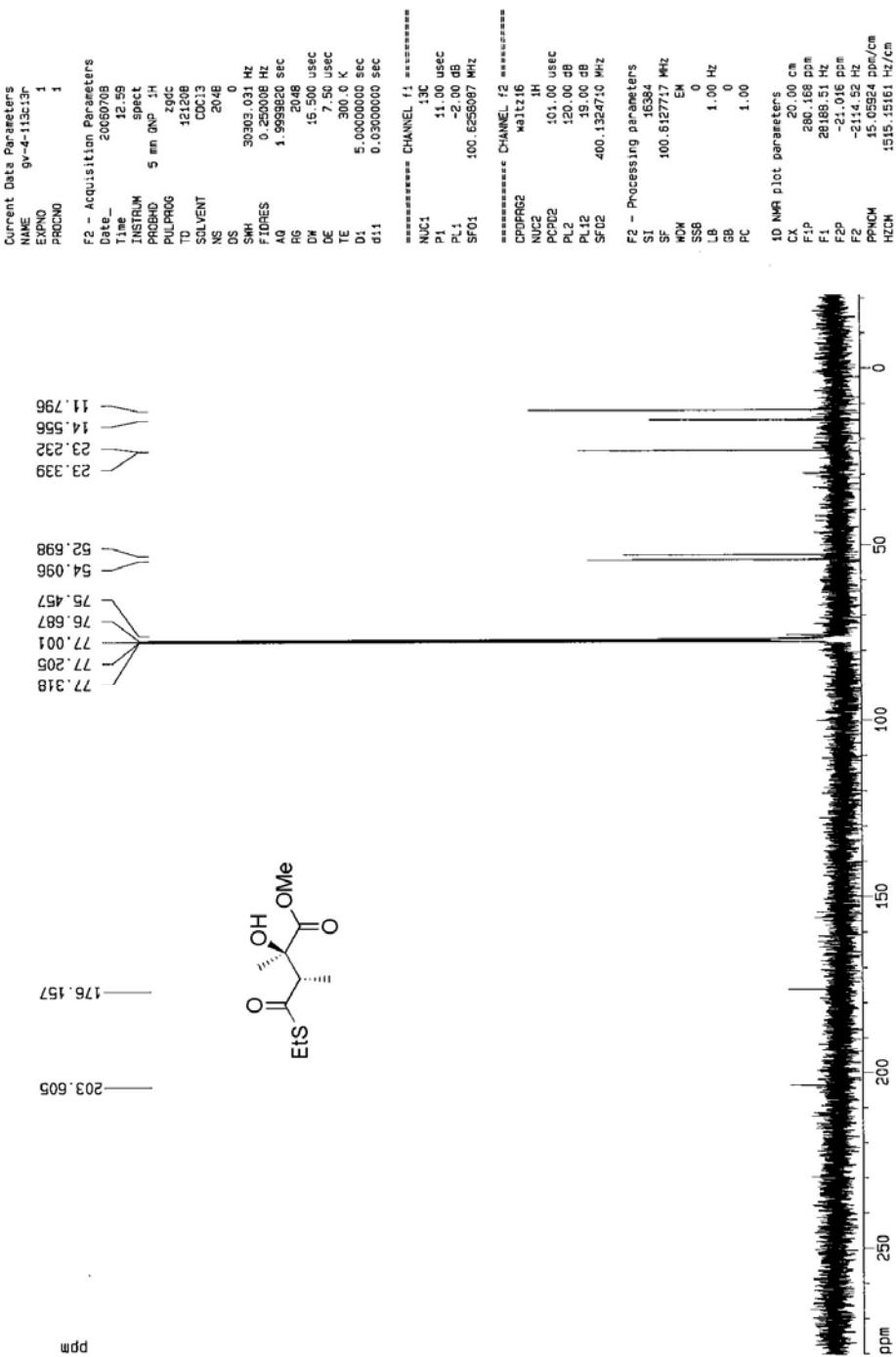
<sup>1</sup>H NMR spectrum of 10 (CDCl<sub>3</sub>, 298 K)



<sup>13</sup>C NMR spectrum of 10 (CDCl<sub>3</sub>, 298 K)



<sup>1</sup>H NMR spectrum of 12 (CDCl<sub>3</sub>, 298 K)( Absolute Config. Determination)



<sup>13</sup>C NMR spectrum of 12 (CDCl<sub>3</sub>, 298 K) ( Absolute Config. Determination)