

**Supporting Information**  
**for**  
**Switching the reaction pathways of electrochemically**  
**generated  $\beta$ -haloalkoxysulfonium ions – synthesis of**  
**halohydrins and epoxides**

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**Experimental and analytical data**

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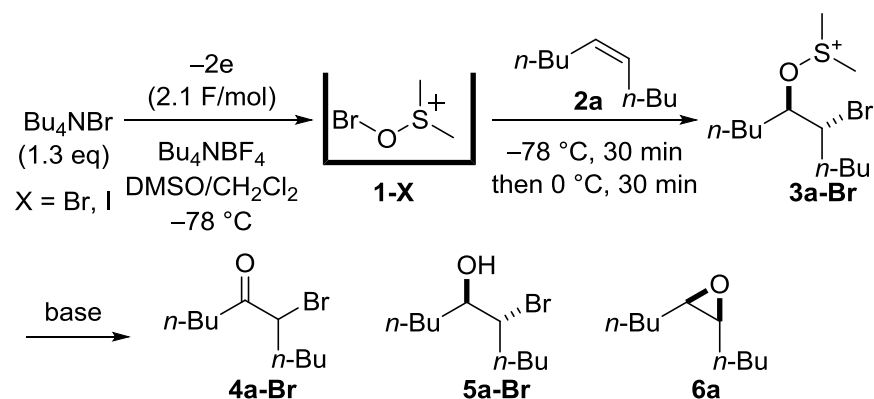
## 1. General

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  using a Varian MERCURY plus-400 ( $^1\text{H}$  400 MHz,  $^{13}\text{C}$  100 MHz) spectrometer, or a JEOL ECA-600P spectrometer ( $^1\text{H}$  600 MHz,  $^{13}\text{C}$  150 MHz) with tetramethylsilane as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL EXACTIVE (ESI and APCI) mass spectrometer, and JEOL JMS-SX102A mass spectrometer (EI). GC analysis was performed on a SHIMADZU GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column (column, CBP1; 0.22 mm x 25 m). Merck precoated silica gel F254 plates (thickness 0.25 mm) were used for thin layer chromatography (TLC) analysis. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40–100  $\mu\text{m}$ ) unless otherwise noted. All reactions were carried out under argon atmosphere unless otherwise noted. The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon GF-20-P21E, ca. 160 mg for 0.25 mmol scale, dried at 300  $^\circ\text{C}/1$  mmHg for 3 h before use) and a platinum plate cathode (10 mm x 10 mm).  $\text{Bu}_4\text{NBF}_4$  was purchased from TCI and dried at 25  $^\circ\text{C}/1$  mmHg for 12 h. Dichloromethane was washed with water, distilled from  $\text{P}_2\text{O}_5$ , redistilled from dry  $\text{K}_2\text{CO}_3$  to remove trace amounts of acid, and stored over molecular sieves 4  $\text{\AA}$ . Dimethyl sulfoxide (DMSO) and triethylamine were dried over molecular sieves 4  $\text{\AA}$  before use. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification.

## 2. Reaction of 3a-X (X = Br, I) with bases

Generation of 1-Br and 1-I was conducted in a similar manner to a procedure from reference<sup>1</sup>.

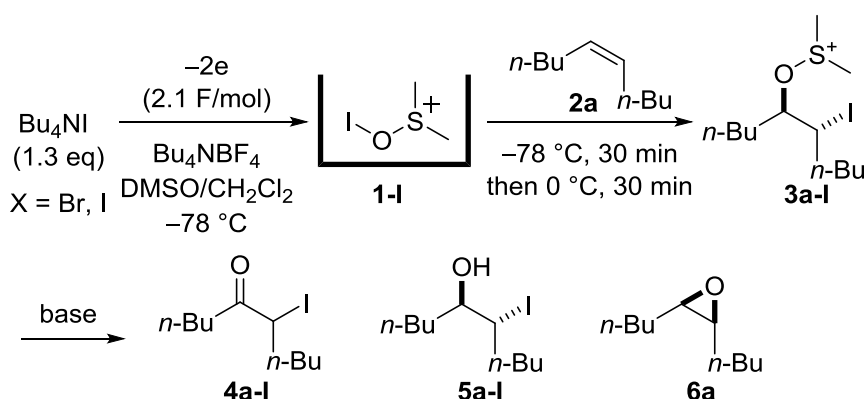
### Typical procedure for generation of 1-Br and 3a-Br and reaction of 3a-Br with bases



In the anodic chamber were placed  $\text{Bu}_4\text{NBr}$  (80.7 mg, 0.251 mmol),  $\text{Bu}_4\text{NBF}_4$  (100 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$  (9 mL). In the cathodic chamber were placed TfOH (60  $\mu\text{L}$ , 0.68 mmol) and 0.3 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$  (10 mL). The constant current electrolysis (8.0 mA) was carried out at  $-78$   $^\circ\text{C}$  with magnetic stirring until  $2.1 \text{ F mol}^{-1}$  of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (2a) (27.7 mg, 0.197 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and to the cathodic chamber 0.5 mL of  $\text{CH}_2\text{Cl}_2$  was added at  $-78$   $^\circ\text{C}$ . The solution was stirred for 30 min at  $-78$   $^\circ\text{C}$  then stirring was stirred continued for 30 min at  $0$   $^\circ\text{C}$ .  $\text{Et}_3\text{N}$  (100  $\mu\text{L}$ ) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25  $^\circ\text{C}$  and stirred for 1 h. The solution in the anodic

chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove  $\text{Bu}_4\text{NBF}_4$  by using hexane/EtOAc (1:1) as an eluent. The GC analysis using hexadecane as an internal standard indicated that 6-bromodecan-5-one (**4a-Br**) was obtained in 83% yield (38.6 mg, 0.164 mmol). The  $^1\text{H}$  NMR data was reported previously<sup>1</sup>. Addition of NaOH (2.5 M in  $\text{H}_2\text{O}$ , 0.16 mL) instead of  $\text{Et}_3\text{N}$  gave (*5R*\*,*6R*\*)-6-bromodecan-5-ol (**5a-Br**) in 89% yield (0.174 mmol). TLC  $R_f$  0.19 (hexane/EtOAc 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.2$  Hz, 6 H), 1.25–1.61 (m, 10 H), 1.84 (d,  $J = 8.0$  Hz, 1 H), 1.86–2.00 (m, 2 H), 3.20–3.57 (m, 1 H), 4.07 (ddd,  $J = 3.2, 5.2, 8.4$  Hz, 1 H); The  $^1\text{H}$  NMR spectrum is in agreement with that of an authentic sample synthesized using NBS according to the literature<sup>2</sup> (*vide infra*). Addition of NaOMe (5.0 M in MeOH, 0.2 mL) instead of  $\text{Et}_3\text{N}$  gave (*5R*\*,*6S*\*)-5,6-epoxydecane (**6a**) in 95% yield (0.187 mmol). TLC  $R_f$  0.83 (hexane/EtOAc 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.93 (t,  $J = 7.2$  Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for  $\text{C}_{10}\text{H}_{21}\text{O}$  ( $\text{M}+\text{H}^+$ ): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the  $^1\text{H}$  NMR spectrum with that in the literature<sup>3</sup>.

#### Typical procedure for the generation of **1-I** and **3a-I** and reaction of **3a-I** with bases



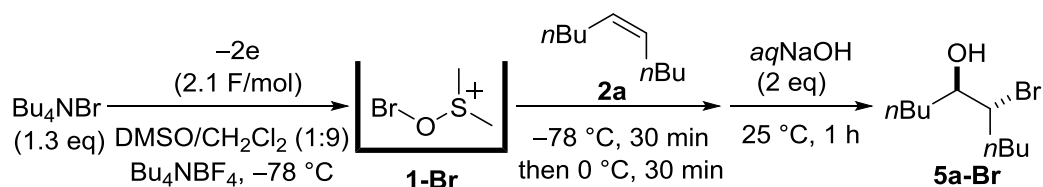
In the anodic chamber were placed  $\text{Bu}_4\text{NI}$  (91.6 mg, 0.248 mmol),  $\text{Bu}_4\text{NBF}_4$  (102 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$  (9 mL). In the cathodic chamber were placed TfOH (60  $\mu\text{L}$ , 0.68 mmol) and 0.3 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$  (10 mL). The constant current electrolysis (8.0 mA) was carried out at  $-78^\circ\text{C}$  with magnetic stirring until  $2.1 \text{ F mol}^{-1}$  of electricity was consumed. To the anodic chamber was added a solution of (*Z*)-5-decene (**2a**) (28.7 mg, 0.205 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and to the cathodic chamber was added 0.5 mL of  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . The solution was stirred for 30 min at  $-78^\circ\text{C}$  then stirring was continued for 30 min at  $0^\circ\text{C}$ .  $\text{Et}_3\text{N}$  (100  $\mu\text{L}$ ) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to  $25^\circ\text{C}$  and stirred for 1 h. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove  $\text{Bu}_4\text{NBF}_4$  by using hexane/EtOAc (1:1 v/v) as an eluent. The GC analysis using hexadecane as an internal standard indicated that 6-iododecan-5-one (**4a-I**) was obtained in 85% yield (49.2 mg, 0.174 mmol). The  $^1\text{H}$  NMR data was reported previously<sup>1</sup>. Addition of NaOH (2.5 M in  $\text{H}_2\text{O}$ , 0.16 mL) instead of  $\text{Et}_3\text{N}$  gave (*5R*\*,*6R*\*)-6-iododecan-5-ol (**5a-I**) in 84% yield (0.169 mmol). TLC  $R_f$  0.19 (hexane/EtOAc 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.2$  Hz, 6 H), 1.25–1.61 (m, 10 H), 1.84 (d,

$J = 8.0$  Hz, 1 H), 1.86–2.00 (m, 2 H), 3.20–3.57 (m, 1 H), 4.07 (ddd,  $J = 3.2, 5.2, 8.4$  Hz, 1 H); The  $^1\text{H}$  NMR spectrum is in agreement with that of an authentic sample synthesized using  $\text{I}_2$  and  $\text{H}_2\text{O}_2$  according to the literature<sup>4</sup> (*vide infra*). Addition of NaOMe (5.0 M in MeOH, 0.2 mL) instead of  $\text{Et}_3\text{N}$  gave ( $5R^*,6S^*$ )-5,6-epoxydecane (**6a**) in 96% yield (0.191 mmol). TLC  $R_f$  0.83 (hexane/EtOAc 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.93 (t,  $J = 7.2$  Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for  $\text{C}_{10}\text{H}_{21}\text{O}$  ( $\text{M}+\text{H}^+$ ): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the  $^1\text{H}$  NMR spectrum with that in the literature<sup>3</sup>.

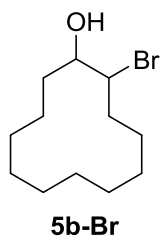
### 3. Synthesis of halohydrins

Generation of **1-Br** and **1-I** was conducted in a similar manner to a procedure from ref. 1.

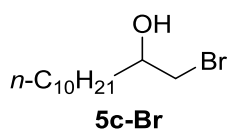
#### Typical procedure for generation of **1-Br** and synthesis of bromohydrins



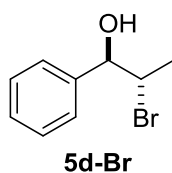
In the anodic chamber were placed  $\text{Bu}_4\text{NBr}$  (81.0 mg, 0.252 mmol),  $\text{Bu}_4\text{NBF}_4$  (101 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$  (9 mL). In the cathodic chamber were placed TfOH (60  $\mu\text{L}$ , 0.68 mmol) and 0.3 M  $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$  (10 mL). The constant current electrolysis (8.0 mA) was carried out at  $-78^\circ\text{C}$  with magnetic stirring until  $2.1 \text{ F mol}^{-1}$  of electricity was consumed. To the anodic chamber was added a solution of (*Z*)-5-decene (**2a**) (27.0 mg, 0.193 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and to the cathodic chamber 0.5 mL of  $\text{CH}_2\text{Cl}_2$  was added at  $-78^\circ\text{C}$ . The solution was stirred for 30 min at  $-78^\circ\text{C}$  then stirring was continued for 30 min at  $0^\circ\text{C}$ . NaOH (2.5 M in  $\text{H}_2\text{O}$ , 0.16 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to  $25^\circ\text{C}$  and was stirred for 1 h. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove  $\text{Bu}_4\text{NBF}_4$  by using hexane/EtOAc (1:1) as an eluent. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (hexane/EtOAc 20:1) to obtain ( $5R^*,6R^*$ )-6-bromodecan-5-ol (**5a-Br**) in 87% yield (40.0 mg, 0.169 mmol). TLC  $R_f$  0.19 (hexane/EtOAc 20:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.2$  Hz, 6 H), 1.25–1.61 (m, 10 H), 1.84 (d,  $J = 8.0$  Hz, 1 H), 1.86–2.00 (m, 2 H), 3.20–3.57 (m, 1 H), 4.07 (ddd,  $J = 3.2, 5.2, 8.4$  Hz, 1 H); The  $^1\text{H}$  NMR spectrum is in agreement with that of an authentic sample synthesized using NBS according to the literature<sup>2</sup> (*vide infra*).



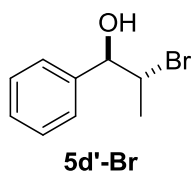
**2-Bromocyclododecan-1-ol (5b-Br).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NBr}$  (82 mg, 0.25 mmol), subsequent addition of the solution of cyclododecene (**2b**) ( $Z/E = 72:28$ , 31.6 mg, 0.190 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 20:1) gave the title compound as mixture of the diastereomers (37.3 mg, 0.142 mmol, 74%, *trans:cis* = 79:21). TLC  $R_f$  0.42 and 0.48 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.24–1.82 (m, 18 H), 1.85–1.96 (m, 1 H), 2.01–2.16 (m, 2 H), 2.23 (d,  $J = 5.2 \text{ Hz}$ , 1 H), 3.80 (td,  $J = 5.2, 12.0 \text{ Hz}$ , *trans* 1 H), 3.90 (br, *cis* 1 H), 4.32–4.41 (m, 1 H); The  $^1\text{H NMR}$  spectrum is in agreement with that in the literature<sup>5</sup>.



**1-Bromododecan-2-ol (5c-Br).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NBr}$  (81 mg, 0.25 mmol), subsequent addition of the solution of 1-dodecene (**2c**) (32.5 mg, 0.193 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 50:1) gave the title compound (29.3 mg, 0.110 mmol, 57%). TLC  $R_f$  0.48 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 6.8 \text{ Hz}$ , 3 H), 1.23–1.61 (m, 20 H), 2.10–2.14 (m, 1 H), 3.39 (dd,  $J = 7.2, 10.4 \text{ Hz}$ , 1 H), 3.55 (dd,  $J = 2.8, 10.4 \text{ Hz}$ , 1 H), 3.74–3.82 (m, 1 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 25.6, 29.3, 29.47, 29.48, 29.54, 29.6, 31.9, 35.1, 40.7, 71.1; HRMS (EI) calcd for  $\text{C}_{12}\text{H}_{24}\text{OBr}$  ( $M-H^+$ ): 263.1016, found: 263.1013. The  $^1\text{H NMR}$  spectrum is in agreement with that in the literature<sup>6</sup>.

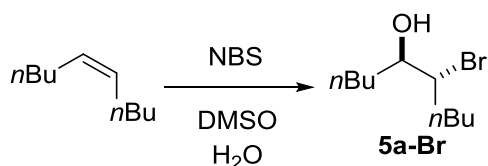


**(1R\*,2S\*)-2-Bromo-1-phenyl-1-propanol (5d-Br).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NBr}$  (81.2 mg, 0.252 mmol), subsequent addition of the solution of (*E*)- $\beta$ -methylstyrene (**(E)-2d**) (22.8 mg, 0.193 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 20:1) gave the title compound (30.2 mg, 0.140 mmol, 73%). TLC  $R_f$  0.33 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.54 (d,  $J = 6.8 \text{ Hz}$ , 3 H), 2.51 (m, 1 H), 4.43 (dq,  $J = 3.6, 6.8 \text{ Hz}$ , 1 H), 5.01 (t,  $J = 3.6 \text{ Hz}$ , 1 H), 7.27–7.40 (m, 5 H). The  $^1\text{H NMR}$  spectrum is in agreement with that in the literature<sup>1</sup>.



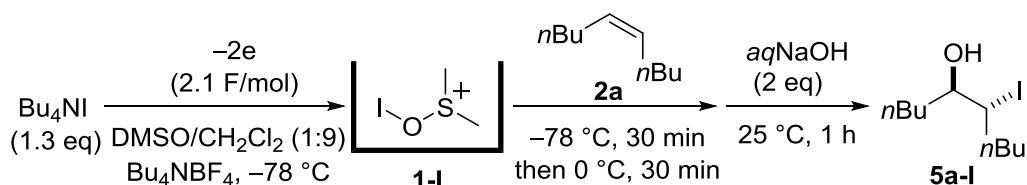
**(1R\*,2R\*)-2-Bromo-1-phenyl-1-propanol (5d'-Br).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NBr}$  (81.9 mg, 0.254 mmol), subsequent addition of the solution of (*Z*)- $\beta$ -methylstyrene (**(Z)-2d**) (23.5 mg, 0.199 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 20:1) gave the title compound (32.2 mg, 0.150 mmol, 75%). TLC  $R_f$  0.38 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.57 (d,  $J = 6.8 \text{ Hz}$ , 3 H), 2.77 (m, 1 H), 4.34 (dq,  $J = 6.8, 7.6 \text{ Hz}$ , 1 H), 4.62 (dd,  $J = 3.6, 7.6 \text{ Hz}$ , 1 H), 7.30–7.40 (m, 5 H). The  $^1\text{H NMR}$  spectrum is in agreement with that in the literature<sup>1</sup>.

### Synthesis of (5*R*\*,6*R*\*)-6-bromodecan-5-ol (**5a-Br**)

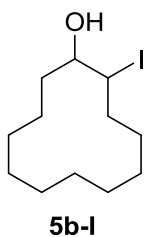


To a round-bottom flask were added NBS (640 mg, 3.59 mmol), (*Z*)-5-decene (417 mg, 2.97 mmol), DMSO (10 mL), and H<sub>2</sub>O (0.1 mL) and the mixture was stirred for 4 h. After the addition of NBS (600 mg, 3.37 mmol), the mixture was stirred at room temperature for 1 d. The solution was diluted with EtOAc (30 mL), washed with sat aq NaHCO<sub>3</sub> (10 mL x 2), H<sub>2</sub>O (10 mL x 2), and brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent under reduced pressure, the crude product was purified by flash chromatography (hexane/EtOAc 100:0 to 20:1) to obtain (5*R*\*,6*R*\*)-6-bromodecan-5-ol (**5a-Br**) in 60% yield (420 mg, 1.77 mmol). TLC *R<sub>f</sub>* 0.19 (hexane/EtOAc 20:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.92 (t, *J* = 7.2 Hz, 6 H), 1.25–1.61 (m, 10 H), 1.84 (d, *J* = 8.0 Hz, 1 H), 1.86–2.00 (m, 2 H), 3.20–3.57 (m, 1 H), 4.07 (ddd, *J* = 3.2, 5.2, 8.4 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 13.9, 14.0, 22.1, 22.6, 27.8, 30.0, 35.48, 35.52, 65.5, 73.8; HRMS (EI) calcd for C<sub>10</sub>H<sub>20</sub>OBr (M–H<sup>+</sup>): 235.0703, found: 235.0702.

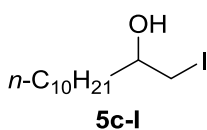
### Typical procedure for the generation of **1-I** and the synthesis of iodohydrins



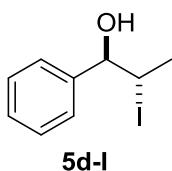
In the anodic chamber were placed Bu<sub>4</sub>NI (93 mg, 0.25 mmol), Bu<sub>4</sub>NBF<sub>4</sub> (980 mg, 3.0 mmol), DMSO (1 mL), and CH<sub>2</sub>Cl<sub>2</sub> (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The constant current electrolysis (8.0 mA) was carried out at –78 °C with magnetic stirring until 2.1 F mol<sup>–1</sup> of electricity was consumed. To the anodic chamber was added a solution of (*Z*)-5-decene (**2a**) (27.0 mg, 0.193 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and to the cathodic chamber was added 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> at –78 °C. The solution was stirred for 30 min at –78 °C then stirring was continued for 30 min at 0 °C. NaOH (2.5 M in H<sub>2</sub>O, 0.16 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 1 h. The solution in the anodic chamber was collected and the solvent was removed under reduced pressure. The residue was filtered through a short column (2 x 4 cm) of silica gel to remove Bu<sub>4</sub>NBF<sub>4</sub> by using hexane/EtOAc (1:1 v/v) as an eluent. The GC analysis using hexadecane as an internal standard indicated that (5*R*\*,6*R*\*)-6-iododecan-5-ol (**5a-I**) was obtained in 84% yield (0.169 mmol). TLC *R<sub>f</sub>* 0.56 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.92 (t, *J* = 7.2 Hz, 6 H), 1.25–1.46 (m, 6 H), 1.47–1.60 (m, 4 H), 1.62 (d, *J* = 8.4 Hz, 1 H), 1.78–1.88 (m, 1 H), 1.98–2.09 (m, 1 H), 2.85–2.90 (m, 1 H), 4.19 (ddd, *J* = 2.8, 4.8, 9.2 Hz, 1 H); The <sup>1</sup>H NMR spectrum is in agreement with that of an authentic sample synthesized using I<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> according to the literature<sup>4</sup> (*vide infra*).



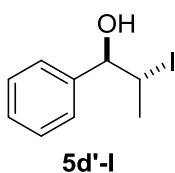
**2-Iodocyclododecan-1-ol (5b-I).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NI (90.8mg, 0.246 mmol), subsequent addition of the solution of cyclododecene (**2b**) (*Z/E* = 72:28, 31.4 mg, 0.189 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 20:1) gave the title compound (55.0 mg, 0.177 mmol, 94%, *trans:cis* = 71:29). TLC R<sub>f</sub> 0.42 and 0.50 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.20–1.80 (m, 18 H), 1.91–2.08 (m, 3 H), 3.39 (m, *trans* 1 H), 4.51 (dt, *J* = 6.0, 6.0 Hz, 1 H); The <sup>1</sup>H NMR spectrum is in agreement with that of an authentic sample synthesized using I<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> according to the literature<sup>4</sup> (*vide infra*).



**1-Iodododecan-2-ol (5c-I).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NI (93 mg, 0.25 mmol), subsequent addition of the solution of 1-dodecene (**2c**) (33.9 mg, 0.201 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 10:1) gave the title compound (33.0 mg, 0.106 mmol, 53%). TLC R<sub>f</sub> 0.26 (hexane/EtOAc 10:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.10–1.50 (m, 16 H), 1.52–1.58 (m, 2 H), 1.98 (d, *J* = 5.2 Hz, 1 H), 3.23 (dd, *J* = 6.8, 10.0 Hz, 1 H), 3.40 (dd, *J* = 3.6, 10.4 Hz, 1 H), 3.45–3.60 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 16.9, 22.7, 25.6, 29.3, 29.43, 29.47, 29.53, 29.6, 31.9, 36.6, 71.0; HRMS (EI) calcd for C<sub>12</sub>H<sub>25</sub>OBr (M<sup>+</sup>): 312.0951, found: 312.0958. The <sup>1</sup>H NMR spectrum is in agreement with that in the literature<sup>7</sup>.



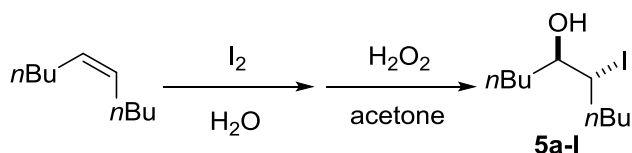
**(1R\*,2S\*)-2-Iodo-1-phenyl-1-propanol (5d-I).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NI (87.4 mg, 0.236 mmol), subsequent addition of the solution of (*E*)-β-methylstyrene (**(E)-2d'**) (21.8 mg, 0.185 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 100:0 to 50:1) gave the title compound (16.9 mg, 0.064 mmol, 35%). TLC R<sub>f</sub> 0.35 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.74 (d, *J* = 6.8 Hz, 3 H), 2.37 (s, 1 H), 4.52 (dq, *J* = 3.6, 7.2 Hz, 1 H), 4.96 (t, *J* = 3.6 Hz, 1 H), 7.29–7.40 (m, 5 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.2, 35.9, 78.5, 126.4, 128.0, 128.4, 139.7; HRMS (EI) calcd for C<sub>9</sub>H<sub>11</sub>OI (M<sup>+</sup>): 261.9855, found: 261.9860. Stereochemistry was determined by comparison of the <sup>1</sup>H NMR spectrum with that in the literature<sup>8</sup>.



**(1R\*,2R\*)-2-Iodo-1-phenyl-1-propanol (5d'-I).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NI (93.1 mg, 0.252 mmol), subsequent addition of the solution of (*Z*)-β-methylstyrene (**(Z)-2d**) (22.4 mg, 0.190 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and the treatment with NaOH followed by flash chromatography (hexane/EtOAc 10:1) gave the title compound (27.0 mg, 0.098 mmol, 51%). TLC R<sub>f</sub> 0.13 (hexane/EtOAc 10:1);

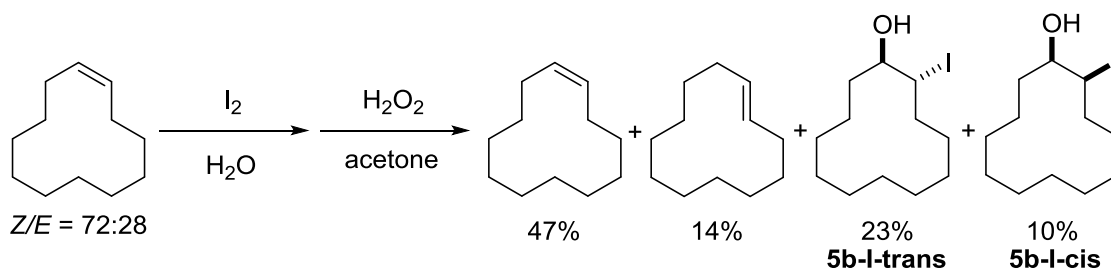
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.81 (d,  $J = 6.8$  Hz, 3 H), 2.51 (d,  $J = 4.0$  Hz, 1 H), 4.39–4.47 (m, 2 H), 7.31–7.41 (m, 5 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  25.4, 39.1, 79.6, 126.3, 128.4, 128.6, 139.9; HRMS (EI) calcd for  $\text{C}_9\text{H}_{11}\text{OI}$  ( $\text{M}^+$ ): 261.9855, found: 261.9856. Stereochemistry was determined by comparison of the  $^1\text{H}$  NMR spectrum with that in the literature<sup>8</sup>.

### Synthesis of (5*R*\*,6*R*\*)-6-iododecan-5-ol (5a-I)



To a round-bottom flask were added iodine (1.07 g, 4.22 mmol), (*Z*)-5-decene (271 mg, 1.94 mmol),  $\text{H}_2\text{O}$  (10 mL) and stirred for 30 min. Then acetone (10 mL),  $\text{H}_2\text{O}_2$  (31% in  $\text{H}_2\text{O}$ , 400  $\mu\text{L}$ , 3.64 mmol) were added and the mixture was stirred at room temperature for 3 d. Afterwards, the solution was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL x 3), dried over  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (hexane/EtOAc 100:0 to 20:1) to obtain (5*R*\*,6*R*\*)-6-iododecan-5-ol (**5a-I**) in 91% yield (500 mg, 1.76 mmol). TLC  $R_f$  0.56 (hexane/EtOAc 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.2$  Hz, 6 H), 1.25–1.46 (m, 6 H), 1.47–1.60 (m, 4 H), 1.62 (d,  $J = 8.4$  Hz, 1 H), 1.78–1.88 (m, 1 H), 1.98–2.09 (m, 1 H), 2.85–2.90 (m, 1 H), 4.19 (ddd,  $J = 2.8, 4.8, 9.2$  Hz, 1 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.9, 14.0, 22.0, 22.6, 27.7, 32.0, 37.4, 37.7, 50.5, 74.1; HRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{21}\text{OICl}$  ( $\text{M}+\text{Cl}^-$ ): 319.0331, found: 319.0331.

### Synthesis of 2-iodocyclododecan-1-ol (5b-I)



To a round-bottom flask were added iodine (550 mg, 2.16 mmol), cyclododecene ( $Z/E = 72:28$ , 174 mg, 1.05 mmol), and  $\text{H}_2\text{O}$  (5 mL). The mixture was stirred for 30 min at room temperature. After the addition of acetone (5 mL) and  $\text{H}_2\text{O}_2$  (31% in  $\text{H}_2\text{O}$ , 200  $\mu\text{L}$ , 1.82 mmol), the mixture was stirred at room temperature for 3 d. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  (20 mL x 3), dried over  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure. NMR analysis of the crude product indicated that (*Z*)- and (*E*)-cyclododecenes were recovered in 47%, 14% yield, respectively and that (1*S*\*,2*S*\*)-2-iodocyclododecan-1-ol and (1*S*\*,2*R*\*)-2-iodocyclododecan-1-ol were obtained in 23%, and 10% yield, respectively. (1*S*\*,2*S*\*)-2-Iodocyclododecan-1-ol and (1*S*\*,2*R*\*)-2-iodocyclododecan-1-ol were isolated by column chromatography.

(1*R*\*,2*R*\*)-2-Iodocyclododecan-1-ol (*trans*-5b-I): TLC  $R_f$  0.57 (hexane/EtOAc 5:1);  $^1\text{H}$  NMR (400 MHz,



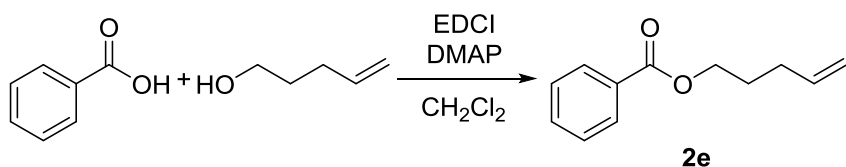
CDCl<sub>3</sub>)  $\delta$  1.20–1.80 (m, 18 H), 1.88 (d,  $J = 6.4$  Hz, 1 H), 1.91–2.01 (m, 1 H), 2.08–2.18 (m, 1 H), 3.39 (m, 1 H), 4.52 (dt,  $J = 6.0, 6.0$  Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  20.9, 23.0, 23.3, 23.4, 23.8, 23.9, 24.0, 24.4, 32.1, 34.9, 47.3, 70.8; HRMS (ESI) calcd for C<sub>12</sub>H<sub>23</sub>IONa<sup>+</sup> (M+Na<sup>+</sup>): 333.0686, found: 333.0685.

**(1*R*\*,2*S*\*)-2-iodocyclododecan-1-ol (cis-5b-I)**: TLC R<sub>f</sub> 0.45 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 50 °C)  $\delta$  1.25–1.56 (m, 17 H), 1.71–1.80 (m, 1 H), 1.88 (s, br, 1 H), 2.02 (dt,  $J = 7.2, 7.2$  Hz, 2 H), 3.59 (s, br, 1 H), 4.50 (t,  $J = 7.2$  Hz, 1 H); <sup>13</sup>C NMR (150 MHz, pyridine-d<sub>5</sub>, 100 °C)  $\delta$  22.8, 22.9, 24.91, 24.98, 25.01, 25.4, 25.9, 32.5, 33.8, 45.5, 73.5; HRMS (ESI) calcd for C<sub>12</sub>H<sub>23</sub>OICl<sup>-</sup> (M+Cl<sup>-</sup>): 345.0488, found: 345.0490.

#### 4. Synthesis of epoxides

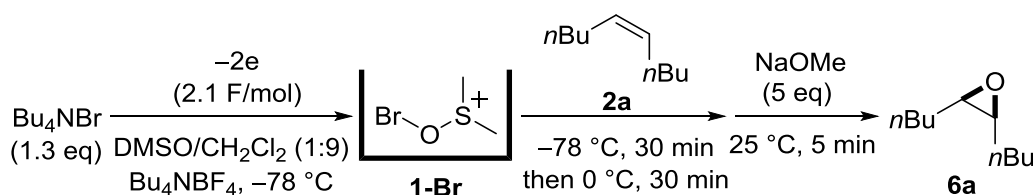
Generation of **1-Br** and **1-I** was conducted in a similar manner to a procedure from ref. <sup>1</sup>.

##### Preparation of 4-pentenyl benzoate



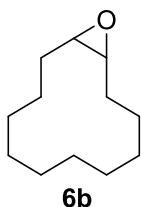
To a round-bottom flask were added 4-pentenol (430 mg, 5.0 mmol), benzoic acid (630 mg, 5.2 mmol), EDCI (1.15 g, 6.0 mmol), DMAP (120 mg, 0.98 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (15 mL). The mixture was stirred at room temperature for 2 d. After the addition of water, the solution was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL x 3). The solvent was removed under reduced pressure, and the residue was purified through a short column (2 x 4 cm) of silica gel by using hexane/EtOAc (1:1) as an eluent. After removal of the solvent under reduced pressure, the crude product was further purified by flash chromatography (hexane/EtOAc 20:1) to obtain 4-pentenyl benzoate (**2e**) in 96% yield (910 mg, 4.78 mmol). TLC R<sub>f</sub> 0.59 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.88 (tt,  $J = 6.4, 7.6$  Hz, 2 H), 2.23 (td,  $J = 6.8, 8.0$  Hz, 2 H), 4.34 (t,  $J = 6.4$  Hz, 2 H), 5.02 (dd,  $J = 2.0, 10.0$  Hz, 1 H), 5.08 (dd,  $J = 2.0, 16.8$  Hz, 1 H), 5.86 (tdd,  $J = 6.4, 10.4, 17.2$  Hz, 1 H), 7.44 (t,  $J = 7.2$  Hz, 2 H), 7.56 (t,  $J = 7.6$  Hz, 1 H), 8.05 (d,  $J = 7.6$  Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  27.9, 30.2, 64.3, 115.4, 128.3, 129.5, 130.4, 132.8, 137.5, 166.6; HRMS (EI) calcd for C<sub>12</sub>H<sub>14</sub>O<sub>2</sub>Ma (M+Na<sup>+</sup>): 213.0886, found: 213.0883. The <sup>1</sup>H NMR spectrum is in agreement with that in the literature<sup>9</sup>.

##### Typical procedure for the generation of **1-Br** and the synthesis of epoxides

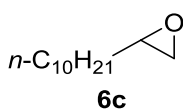


In the anodic chamber were placed Bu<sub>4</sub>NBr (80.6 mg, 0.250 mmol), Bu<sub>4</sub>NBF<sub>4</sub> (97 mg, 0.29 mmol), DMSO (1 mL), and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (9 mL). In the cathodic chamber were placed TfOH (60  $\mu$ L,

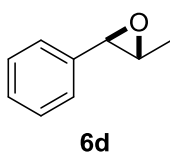
0.68 mmol) and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The constant current electrolysis (8.0 mA) was carried out at -78 °C with magnetic stirring until 2.1 F mol<sup>-1</sup> of electricity was consumed. To the anodic chamber was added a solution of (*Z*)-5-decene (**2a**) (27.7 mg, 0.197 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and to the cathodic chamber 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added at -78 °C. The solution was stirred for 30 min at -78 °C then stirring was continued for 30 min at 0 °C. NaOMe (5.0 M in MeOH, 0.2 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 5 min. The solution in the anodic chamber was filtered through a short column (2 x 4 cm) of silica gel to remove Bu<sub>4</sub>NBF<sub>4</sub> by using Et<sub>2</sub>O as an eluent. The GC analysis using hexadecane as an internal standard indicated that (5*R*\*,6*S*\*)-5,6-epoxydecane (**6a**) was obtained in 95% yield (0.187 mmol). TLC R<sub>f</sub> 0.83 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.93 (t, *J* = 7.2 Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for C<sub>10</sub>H<sub>21</sub>O (M+H<sup>+</sup>): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the <sup>1</sup>H NMR spectrum with that in the literature<sup>3</sup>.



**1,2-Epoxydodecane (6b).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NBr (81.7 mg, 0.254 mmol), subsequent addition of the solution of cyclododecene (**2b**) (*Z/E* = 72:28, 32.7 mg, 0.196 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and treatment with NaOMe followed by flash chromatography (hexane) gave the title compound (22.3 mg, 0.134 mmol, 68%, *cis:trans* = 74:26). TLC R<sub>f</sub> 0.54 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.20–1.61 (m, 20 H), 1.70–1.87 (m, *cis* 2 H), 2.15–2.23 (m, *trans* 2 H), 2.71 (m, *trans* 2 H), 2.90 (td, *J* = 1.6, 10.0 Hz, *cis* 2 H). The <sup>1</sup>H NMR spectrum is in agreement with the literature<sup>10</sup>.

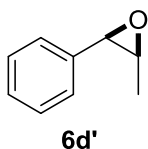


**1,2-Epoxydodecane (6c).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NBr (80.5 mg, 0.250 mmol), subsequent addition of the solution of 1-dodecene (**2c**) (31.8 mg, 0.189 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and treatment with NaOMe gave the title compound (0.138 mmol, 73%). The yield was determined by GC analysis using hexadecane as internal standard. TLC R<sub>f</sub> 0.63 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.88 (t, *J* = 6.8 Hz, 3 H), 1.20–1.38 (m, 14 H), 1.40–1.56 (m, 4 H), 2.46 (dd, *J* = 2.8, 4.8 Hz, 1 H), 2.75 (dd, *J* = 3.6, 4.0 Hz, 1 H), 2.88–2.94 (m, 1 H). The <sup>1</sup>H NMR spectrum is in agreement with the literature<sup>11</sup>.

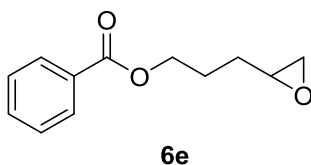


**(1*R*\*,2*R*\*)-1-Phenyl-1,2-epoxypropane (6d).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NBr (82.4 mg, 0.256 mmol), subsequent addition of the solution of (*E*)-β-methylstyrene (**(E)-2d**) (22.9 mg, 0.194 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane) gave

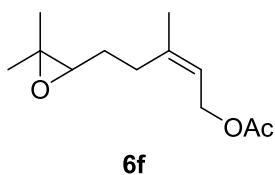
the title compound (13.7 mg, 0.102 mmol, 53%). TLC  $R_f$  0.58 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46 (d,  $J = 5.2$  Hz, 3 H), 3.04 (dq,  $J = 2.0, 5.2$  Hz, 1 H), 3.58 (d,  $J = 1.6$  Hz, 2 H), 7.24–7.39 (m, 5 H). The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>13</sup>.



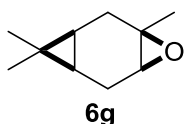
**(1*R*\*,2*S*\*)-1-Phenyl-1,2-epoxypropane (6d')**. Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of  $\text{Bu}_4\text{NBr}$  (81.7 mg, 0.254 mmol), subsequent addition of the solution of (*Z*)- $\beta$ -methylstyrene ((*Z*)-**2d**) (22.9 mg, 0.194 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane) gave the title compound (15.7 mg, 0.117 mmol, 60%). TLC  $R_f$  0.56 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09 (d,  $J = 5.6$  Hz, 3 H), 3.34 (dq,  $J = 4.4, 5.2$  Hz, 1 H), 4.07 (d,  $J = 4.4$  Hz, 1 H) 7.26–7.40 (m, 5 H). The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>13</sup>.



**4,5-Epoxy-pentenyl benzoate (6e)**. Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of  $\text{Bu}_4\text{NBr}$  (81.6 mg, 0.253 mmol), subsequent addition of the solution of 4-pentenyl benzoate (**2f**) (37.2 mg, 0.196 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane/EtOAc 100:0 to 20:1) gave the title compound (21.0 mg, 0.102 mmol, 52%). TLC  $R_f$  0.29 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.62–1.82 (m, 2 H), 1.88–2.04 (m, 2 H), 2.52 (dd,  $J = 2.8, 5.2$  Hz, 1 H), 2.78 (dd,  $J = 4.0, 5.2$  Hz, 1 H), 2.98–3.02 (m, 1 H), 4.38 (dt,  $J = 2.4, 6.4$  Hz, 2 H), 7.44 (t,  $J = 8.0$  Hz, 2 H), 7.56 (t,  $J = 7.6$  Hz, 1 H), 8.04 (d,  $J = 8.4$  Hz, 2 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  25.3, 29.1, 47.0, 51.7, 64.4, 128.3, 129.5, 130.2, 132.9, 166.5; HRMS (ESI) calcd for  $\text{C}_7\text{H}_7\text{O}_2$  ( $\text{M}-\text{H}^+$ ): 207.1016, found: 207.1012. The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>14</sup>.

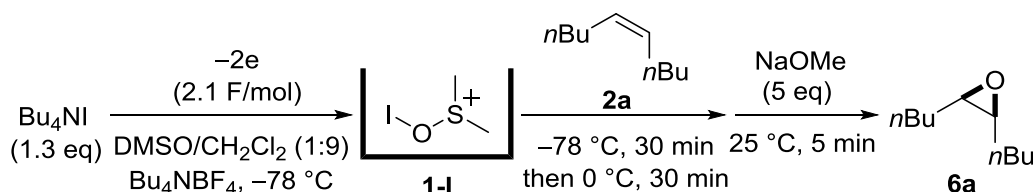


**6,7-Epoxyneryl acetate (6f)**. Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of  $\text{Bu}_4\text{NBr}$  (80.7 mg, 0.251 mmol), subsequent addition of the solution of neryl acetate (**2f**) (357.3 mg, 0.190 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane/EtOAc 100:0 to 50:1) gave the title compound (19.7 mg, 0.093 mmol, 49%). TLC  $R_f$  0.30 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.27 (s, 3 H), 1.31 (s, 3 H), 1.56–1.71 (m, 2 H), 1.79 (s, 3 H), 2.05 (s, 3 H) 2.23–2.29 (m, 2 H), 2.71 (t,  $J = 6.0$  Hz, 1 H), 4.59 (d,  $J = 7.6$  Hz, 2 H), 5.41 (t,  $J = 7.2$  Hz, 1 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  18.7, 21.0, 23.4, 24.8, 27.5, 28.8, 58.4, 60.8, 63.7, 119.7, 141.7, 171.0; HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{20}\text{O}_3\text{Na}$  ( $\text{M}+\text{Na}^+$ ): 235.1305, found: 235,1299. The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>15</sup>.

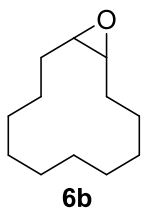


**(1S,3R,4S,6R)-3,4-Epoxycarane (6g).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NBr (80.4 mg, 0.250 mmol), subsequent addition of the solution of (+)-3-carene (**2g**) (26.1 mg, 0.192 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane) gave the title compound. (20.1 mg, 0.132 mmol, 69%). TLC R<sub>f</sub> 0.50 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.52 (dt, *J* = 2.0, 9.2 Hz, 1 H), 0.57 (dt, *J* = 2.0, 9.2 Hz, 1 H), 0.92 (s, 3 H), 0.96 (s, 3 H), 1.30 (s, 3 H), 1.78 (d, *J* = 15.6 Hz, 2 H), 2.06 (dd, *J* = 9.2, 16.4 Hz, 1 H) 2.28 (ddd, *J* = 5.6, 9.2, 16.4 Hz, 1 H) 2.88 (d, 5.6 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.7, 17.3, 17.5, 18.3, 19.4, 23.9, 24.7, 29.1, 55.9, 58.2; HRMS (ESI) calcd for C<sub>10</sub>H<sub>17</sub>O (M+H<sup>+</sup>): 153.1274, found: 153.1270. Stereochemistry was determined by comparison of the <sup>1</sup>H NMR spectrum with that in the literature<sup>16</sup>.

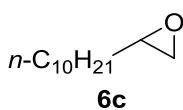
#### Typical procedure for the generation of 1-I and the synthesis of epoxides



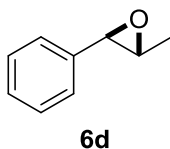
In the anodic chamber were placed Bu<sub>4</sub>NI (91.7 mg, 0.248 mmol), Bu<sub>4</sub>NBF<sub>4</sub> (102 mg, 0.3 mmol), DMSO (1 mL), and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (9 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The constant current electrolysis (8.0 mA) was carried out at -78 °C with magnetic stirring until 2.1 F mol<sup>-1</sup> of electricity was consumed. To the anodic chamber was added a solution of (Z)-5-decene (**2a**) (27.9 mg, 0.199 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and to the cathodic chamber 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added at -78 °C. The solution was stirred for 30 min at -78 °C then stirring was continued for 30 min at 0 °C. NaOMe (5.0 M in MeOH, 0.2 mL) was added to both the anodic and the cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 5 min. The solution in the anodic chamber was filtered through a short column (2 x 4 cm) of silica gel to remove Bu<sub>4</sub>NBF<sub>4</sub> by using Et<sub>2</sub>O as an eluent. The GC analysis using hexadecane as an internal standard indicated that (5*R*\*,6*S*\*)-5,6-epoxydecane (**6a**) was obtained in 96% yield (0.191 mmol). TLC R<sub>f</sub> 0.83 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.93 (t, *J* = 7.2 Hz, 6 H), 1.37–1.55 (m, 12 H), 2.88–2.94 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.0, 22.6, 27.5, 28.3, 57.2; HRMS (APCI) calcd for C<sub>10</sub>H<sub>21</sub>O (M+H<sup>+</sup>): 157.1587, found: 157.1587. Stereochemistry was determined by comparison of the <sup>1</sup>H NMR spectrum with that in the literature<sup>3</sup>.



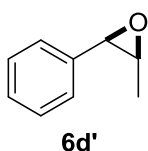
**1,2-Epoxycyclododecane (6b).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NI}$  (92.5 mg, 0.250 mmol), subsequent addition of the solution of cyclododecene (**2b**) ( $Z/E = 72:28$ , 33.3 mg, 0.200 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe followed by flash chromatography (hexane/EtOAc 50:1) gave the title compound (32.6 mg, 0.179 mmol, 89%, *cis:trans* = 74:26). TLC  $R_f$  0.54 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.20–1.61 (m, 20 H), 1.70–1.87 (m, *cis* 2 H), 2.15–2.23 (m, *trans* 2 H), 2.71 (m, *trans* 2 H), 2.90 (td,  $J = 1.6, 10.0 \text{ Hz}$ , *cis* 2 H). The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>10</sup>.



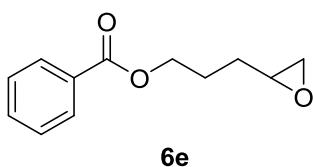
**1,2-Epoxydodecane (6c).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NI}$  (91.5 mg, 0.248 mmol), subsequent addition of the solution of 1-dodecene (**2c**) (31.8 mg, 0.189 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe gave the title compound (0.162 mmol, 86%, The yield was determined by GC analysis using hexadecane as internal standard. TLC  $R_f$  0.63 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 6.8 \text{ Hz}$ , 3 H), 1.20–1.38 (m, 14 H), 1.40–1.56 (m, 4 H), 2.46 (dd,  $J = 2.8, 4.8 \text{ Hz}$ , 1 H), 2.75 (dd,  $J = 3.6, 4.0 \text{ Hz}$ , 1 H), 2.88–2.94 (m, 1 H). The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>11</sup>.



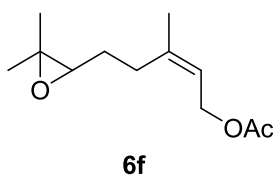
**(1*R*\*,2*R*\*)-1-Phenyl-1,2-epoxypropane (6d).** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NI}$  (148 mg, 0.401 mmol), subsequent addition of the solution of (*E*)- $\beta$ -methylstyrene (**(E)-2d**) (22.8 mg, 0.193 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane) gave the title compound (10.0 mg, 0.074 mmol, 38%). TLC  $R_f$  0.58 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46 (d,  $J = 5.2 \text{ Hz}$ , 3 H), 3.04 (dq,  $J = 2.0, 5.2 \text{ Hz}$ , 1 H), 3.58 (d,  $J = 1.6 \text{ Hz}$ , 2 H), 7.24–7.39 (m, 5 H); The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>13</sup>.



**(1*R*\*,2*S*\*)-1-Phenyl-1,2-epoxypropane (6d').** Electrochemical oxidation ( $2.1 \text{ F mol}^{-1}$ ) of  $\text{Bu}_4\text{NI}$  (149 mg, 0.403 mmol), subsequent addition of the solution of (*Z*)- $\beta$ -methylstyrene (**(Z)-2d**) (23.6 mg, 0.200 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>9</sup> (hexane) gave the title compound (134 mg, 0.134 mmol, 67%). TLC  $R_f$  0.56 (hexane/EtOAc 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.09 (d,  $J = 5.6 \text{ Hz}$ , 3 H), 3.34 (dq,  $J = 4.4, 5.2 \text{ Hz}$ , 1 H), 4.07 (d,  $J = 4.4 \text{ Hz}$ , 1 H), 7.26–7.40 (m, 5 H). The  $^1\text{H NMR}$  spectrum is in agreement with the literature<sup>13</sup>.



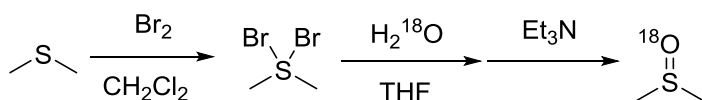
**4,5-Epoxy-pentenyl benzoate (6e).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NI (91.0 mg, 0.246 mmol), subsequent addition of the solution of 4-pentenyl benzoate (**2f**) (39.0 mg, 0.205 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane/EtOAc 100:0 to 20:1) gave the title compound (24.0 mg, 0.116 mmol, 57%). TLC R<sub>f</sub> 0.29 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.62–1.82 (m, 2 H), 1.88–2.04 (m, 2 H), 2.52 (dd, *J* = 2.8, 5.2 Hz, 1 H), 2.78 (dd, *J* = 4.0, 5.2 Hz, 1 H), 2.98–3.02 (m, 1 H), 4.38 (dt, *J* = 2.4, 6.4 Hz, 2 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.56 (t, *J* = 7.6 Hz, 1 H), 8.04 (d, *J* = 8.4 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 25.3, 29.1, 47.0, 51.7, 64.4, 128.3, 129.5, 130.2, 132.9, 166.5; HRMS (ESI) calcd for C<sub>7</sub>H<sub>7</sub>O<sub>2</sub> (M+H<sup>+</sup>): 207.1016, found: 207.1012. The <sup>1</sup>H NMR spectrum is in agreement with the literature<sup>14</sup>.



**6,7-Epoxy-neryl acetate (6f).** Electrochemical oxidation (2.1 F mol<sup>-1</sup>) of Bu<sub>4</sub>NI (92.8 mg, 0.251 mmol), subsequent addition of the solution of neryl acetate (**2f**) (35.6 mg, 0.182 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and treatment with NaOMe followed by flash chromatography<sup>12</sup> (hexane/EtOAc 100:0 to 20:1) gave the title compound (18.2 mg, 0.086 mmol, 47%). TLC R<sub>f</sub> 0.30 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.27 (s, 3 H), 1.31 (s, 3 H), 1.56–1.71 (m, 2 H), 1.79 (s, 3 H), 2.05 (s, 3 H) 2.23–2.29 (m, 2 H), 2.71 (t, *J* = 6.0 Hz, 1 H), 4.59 (d, *J* = 7.6 Hz, 2 H), 5.41 (t, *J* = 7.2 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 18.7, 21.0, 23.4, 24.8, 27.5, 28.8, 58.4, 60.8, 63.7, 119.7, 141.7, 171.0; HRMS (ESI) calcd for C<sub>12</sub>H<sub>20</sub>O<sub>3</sub>Na (M+Na<sup>+</sup>): 235.1305, found: 235,1299. The <sup>1</sup>H NMR spectrum is in agreement with the literature<sup>15</sup>.

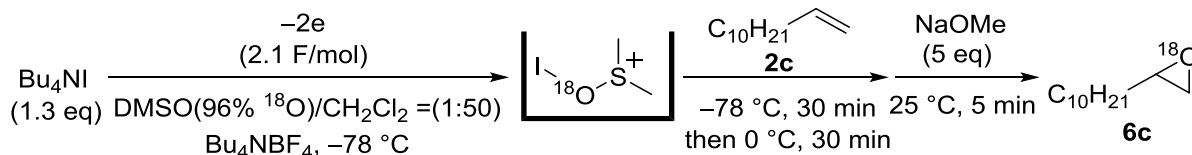
## 5. Synthesis of <sup>18</sup>O-labelled epoxide

### Synthesis of <sup>18</sup>O-labelled DMSO<sup>17</sup>



To a round-bottom flask were added dimethylsulfide (2.6 mL, 33 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Bromine (1.8 mL, 33 mmol) was added dropwise to the solution at 0 °C over a period of 30 min. The mixture was stirred at 0 °C for 30 min to precipitate a yellow solid material. The liquid phase was removed by syringe and the solid material washed with dry CH<sub>2</sub>Cl<sub>2</sub> under an Ar atmosphere. THF (10 mL) was added, followed by the dropwise addition of H<sub>2</sub><sup>18</sup>O (242 mg, 12.1 mmol) at 0 °C over a period of 5 min. After stirring at 0 °C for 1 h, Et<sub>3</sub>N (6.4 mL) was added to the mixture. The precipitate of triethylamine hydrobromide was separated by filtration and was washed twice with CH<sub>2</sub>Cl<sub>2</sub>. The combined yellow filtrate and washings were evaporated under reduced pressure to remove the solvents. The residue was purified by flash chromatography (hexane/EtOAc 1:1 to 0:100 to EtOAc/MeOH 10:1). After Kugelrohr distillation (20 mmHg, 80 °C), <sup>18</sup>O-labelled DMSO was obtained in 34% yield (332 mg, 4.14 mmol). TLC R<sub>f</sub> 0.05 (EtOAc); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.62 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 40.5; HRMS (ESI) calcd for C<sub>4</sub>H<sub>12</sub><sup>18</sup>O<sub>2</sub>S (2M+H<sup>+</sup>): 161.0436, found: 161.0433.

### Synthesis of <sup>18</sup>O-labelled epoxide **6c**



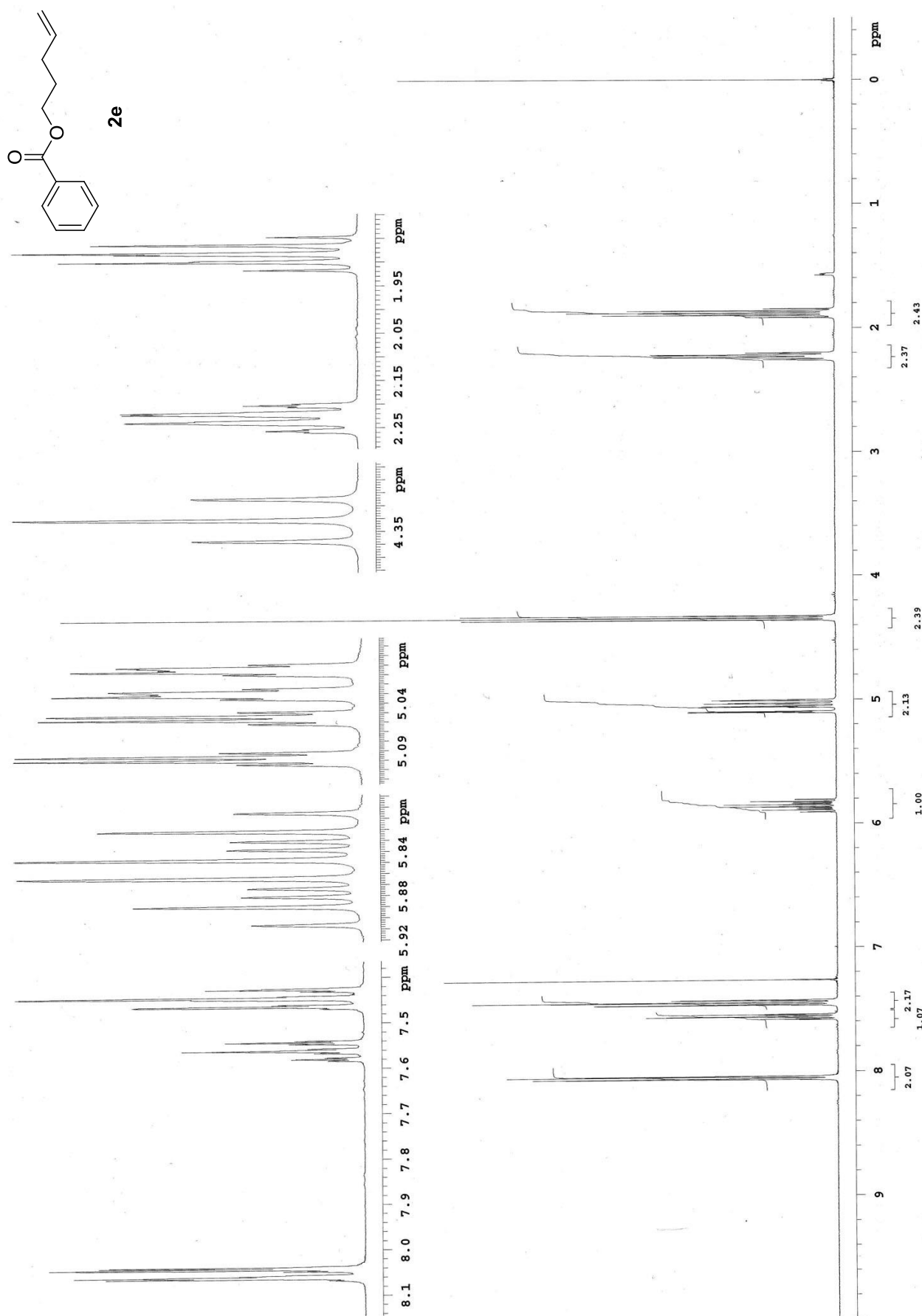
In the anodic chamber were placed Bu<sub>4</sub>NI (91.8 mg, 0.248 mmol), DMSO (96% <sup>18</sup>O, 0.2 mL), and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (10 mL). In the cathodic chamber were placed TfOH (60 μL, 0.68 mmol) and 0.3 M Bu<sub>4</sub>NBF<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The constant current electrolysis (8.0 mA) was carried out at -78 °C with magnetic stirring until 2.1 F mol<sup>-1</sup> of electricity was consumed. To the anodic chamber was added a solution of 1-dodecene (**2c**) (32.5 mg, 0.193 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), and to the cathodic chamber was added 0.5 mL of CH<sub>2</sub>Cl<sub>2</sub> at -78 °C. The solution was stirred for 30 min at -78 °C then stirring was continued for 30 min at 0 °C. NaOMe (5.0 M in MeOH, 0.2 mL) was added to both the anodic and cathodic chambers, and the resulting mixture was warmed to 25 °C and stirred for 5 min. The solution in the anodic chamber was filtered through a short column (2 x 4 cm) of silica gel to remove Bu<sub>4</sub>NBF<sub>4</sub> by using Et<sub>2</sub>O as an eluent. After removal of the solvent under reduced pressure the crude product was purified by flash chromatography<sup>9</sup> (hexane) to obtain <sup>18</sup>O-labelled 1,2-epoxydodecane (**6c**) in 81% yield (29.0 mg, 0.155 mmol). TLC R<sub>f</sub> 0.67 (hexane/EtOAc 5:1); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.88 (t, *J* = 6.8 Hz, 6 H), 1.22–1.56 (m, 18 H), 2.46 (dd, *J* = 2.8, 5.2 Hz, 1 H), 2.74 (dd, *J* = 4.0, 5.2 Hz, 1 H), 2.88–2.93 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 22.7, 26.0, 29.3, 29.4, 29.54, 29.57, 31.9, 32.5, 47.1, 52.4; HRMS (APCI) calcd for C<sub>12</sub>H<sub>25</sub><sup>18</sup>O (M+H<sup>+</sup>): 187.1942, found: 187.1940.

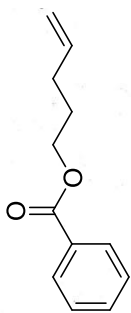
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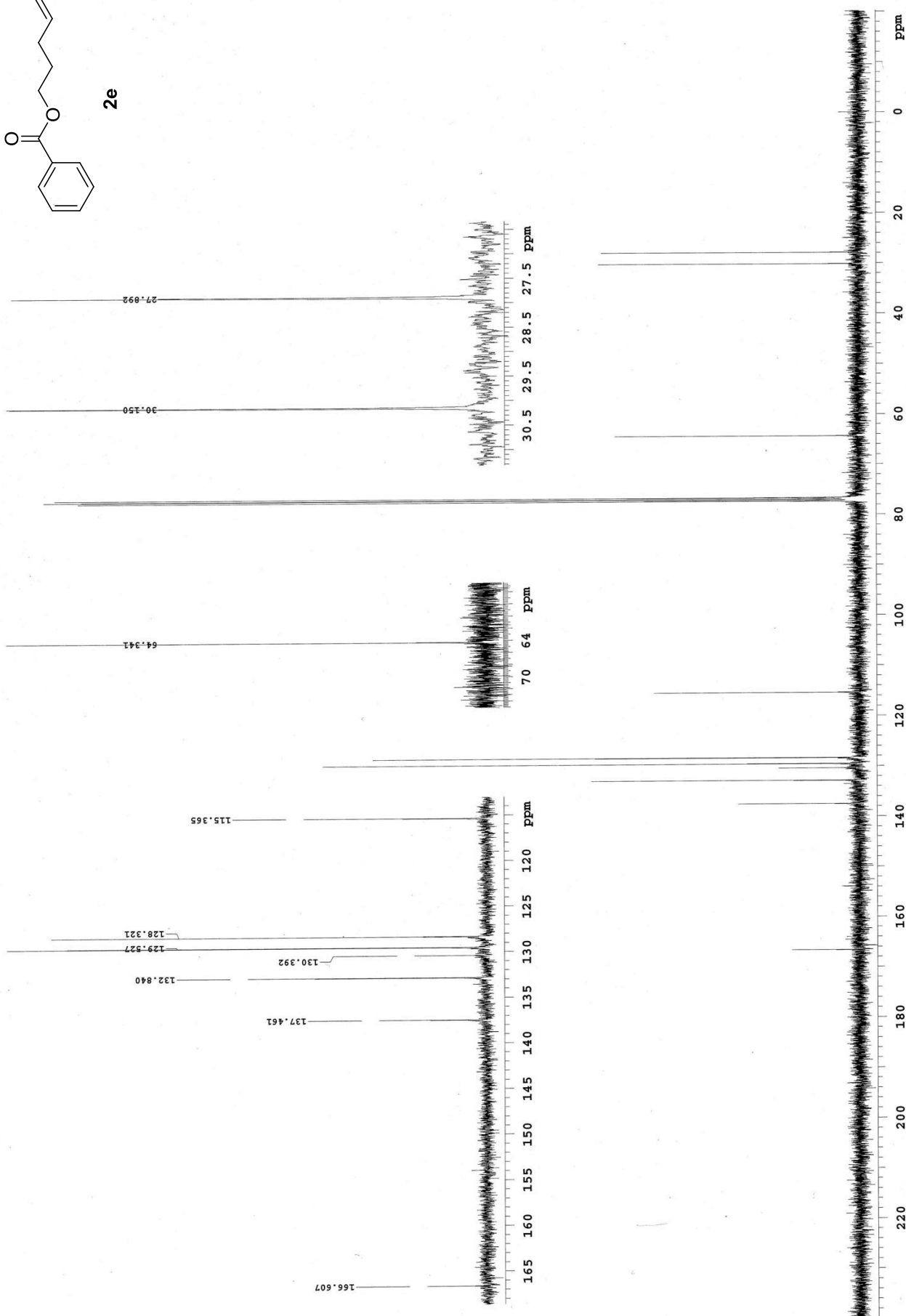


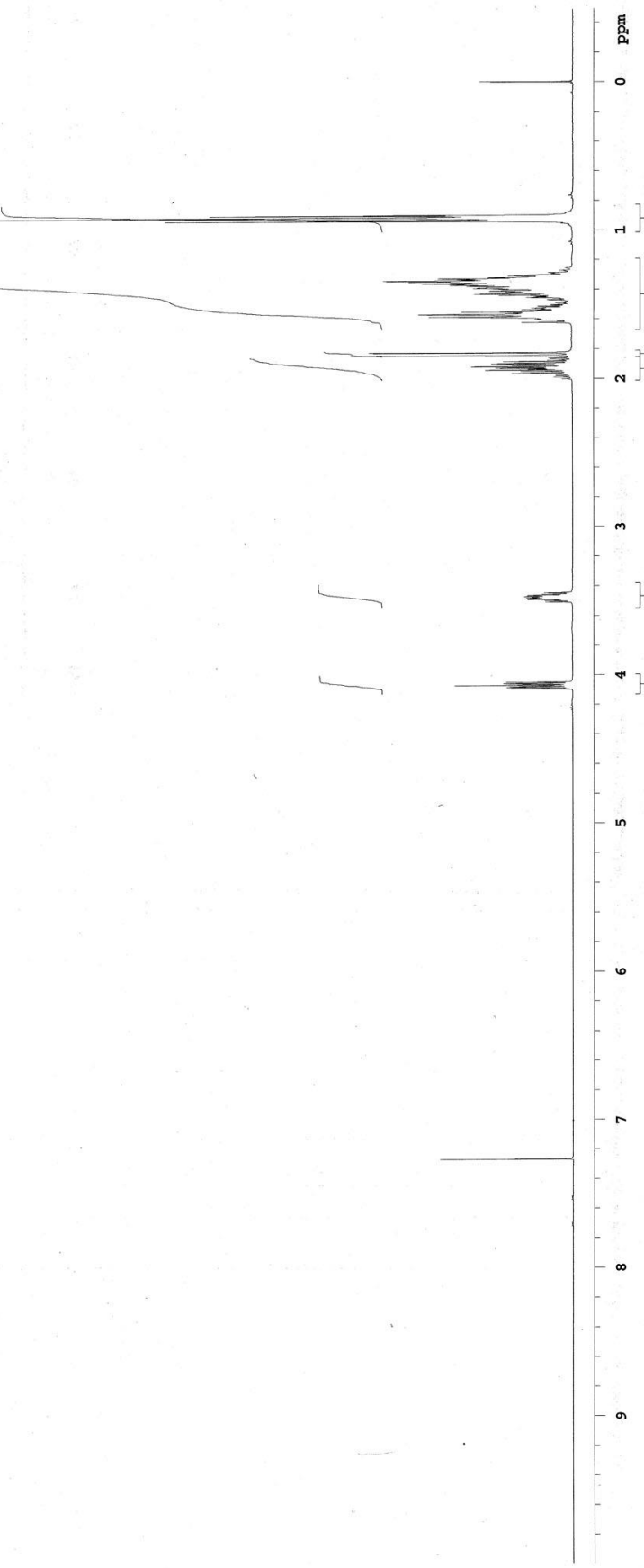
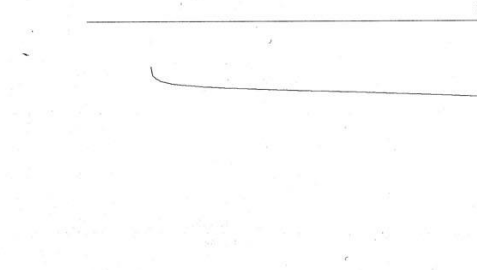
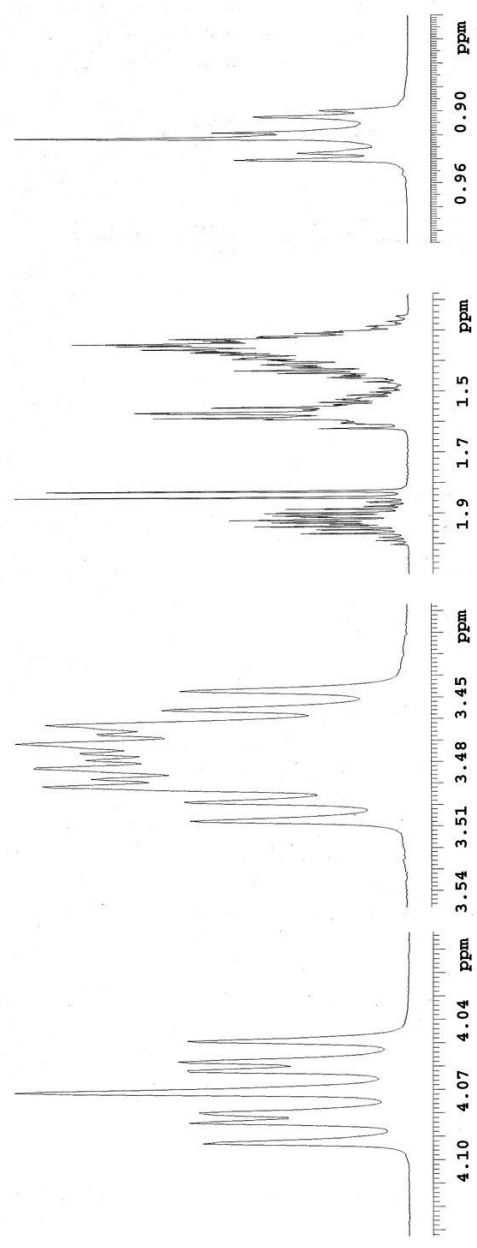
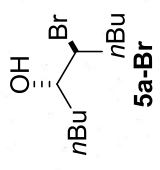
## 7. NMR spectra

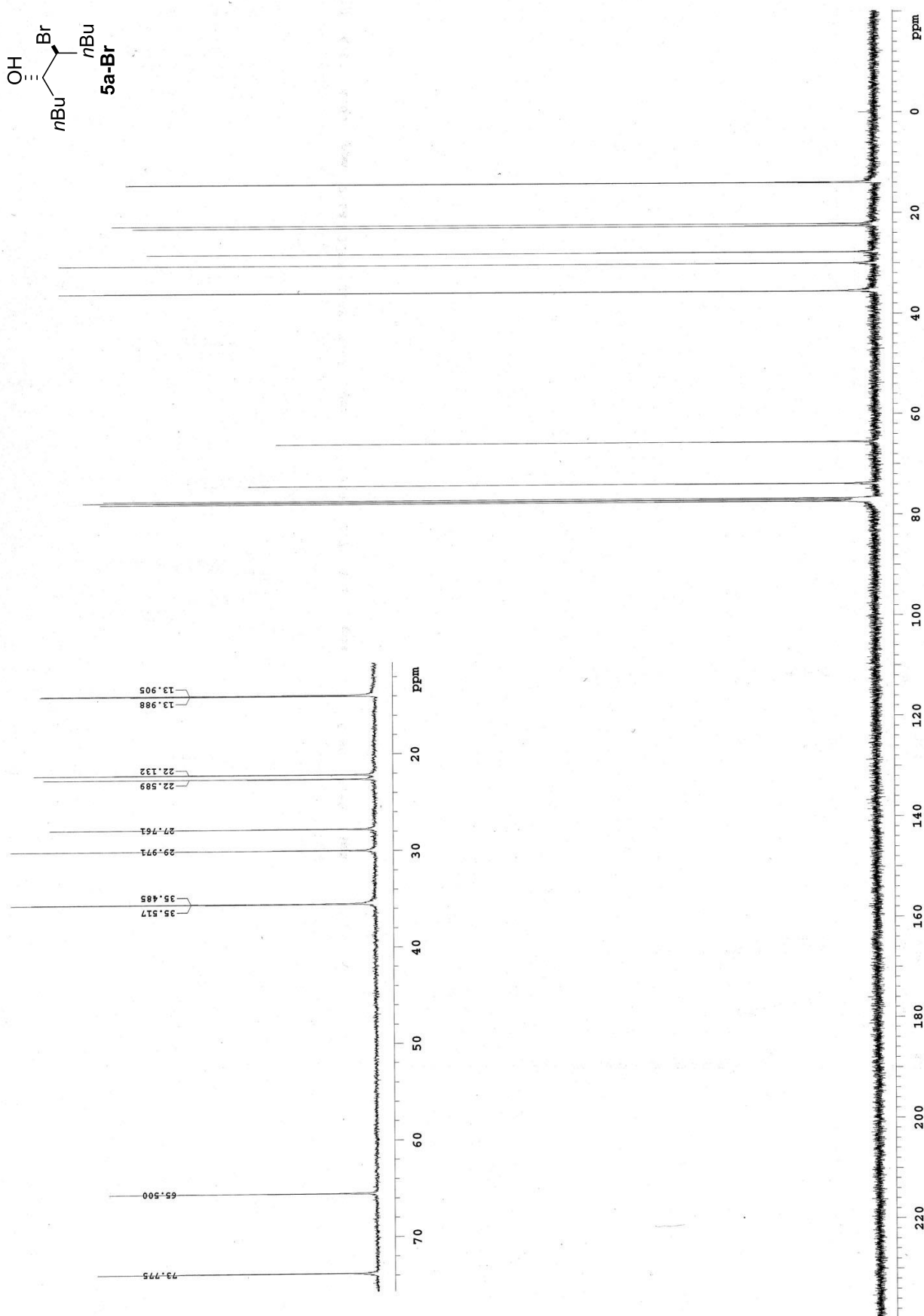
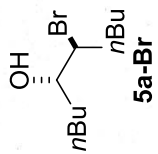


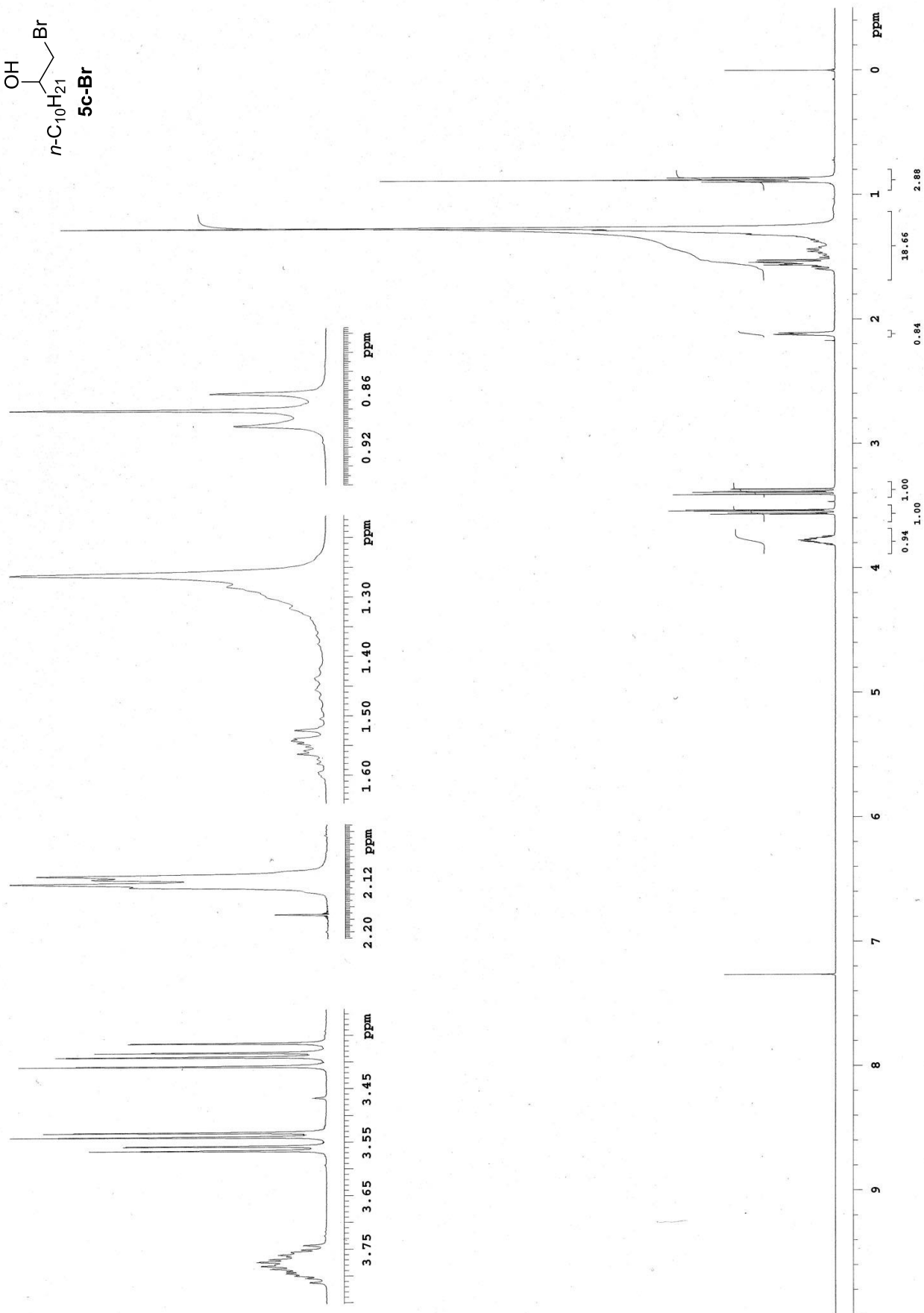
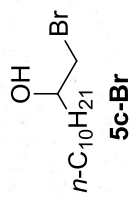


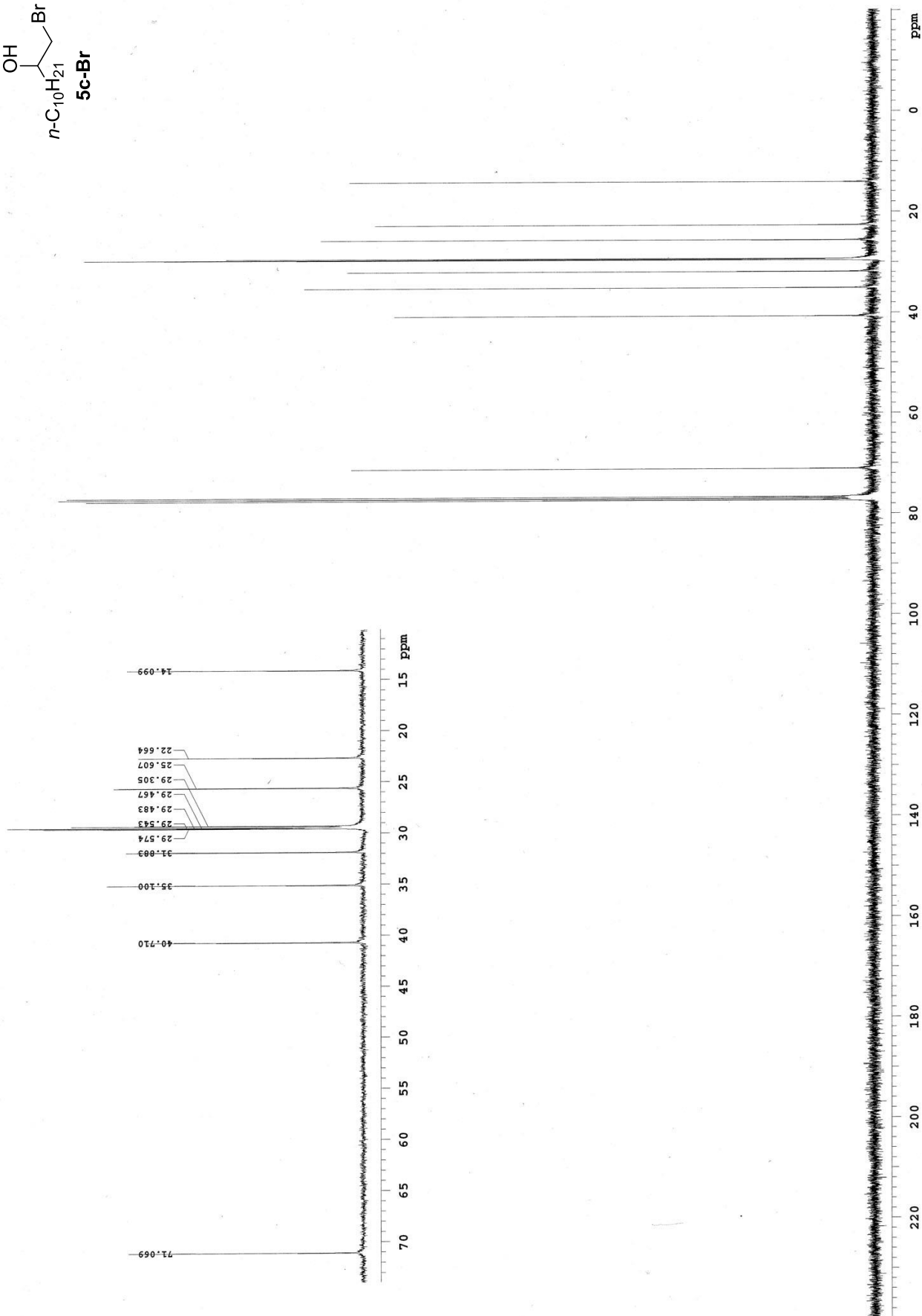
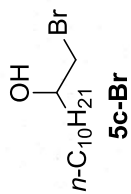
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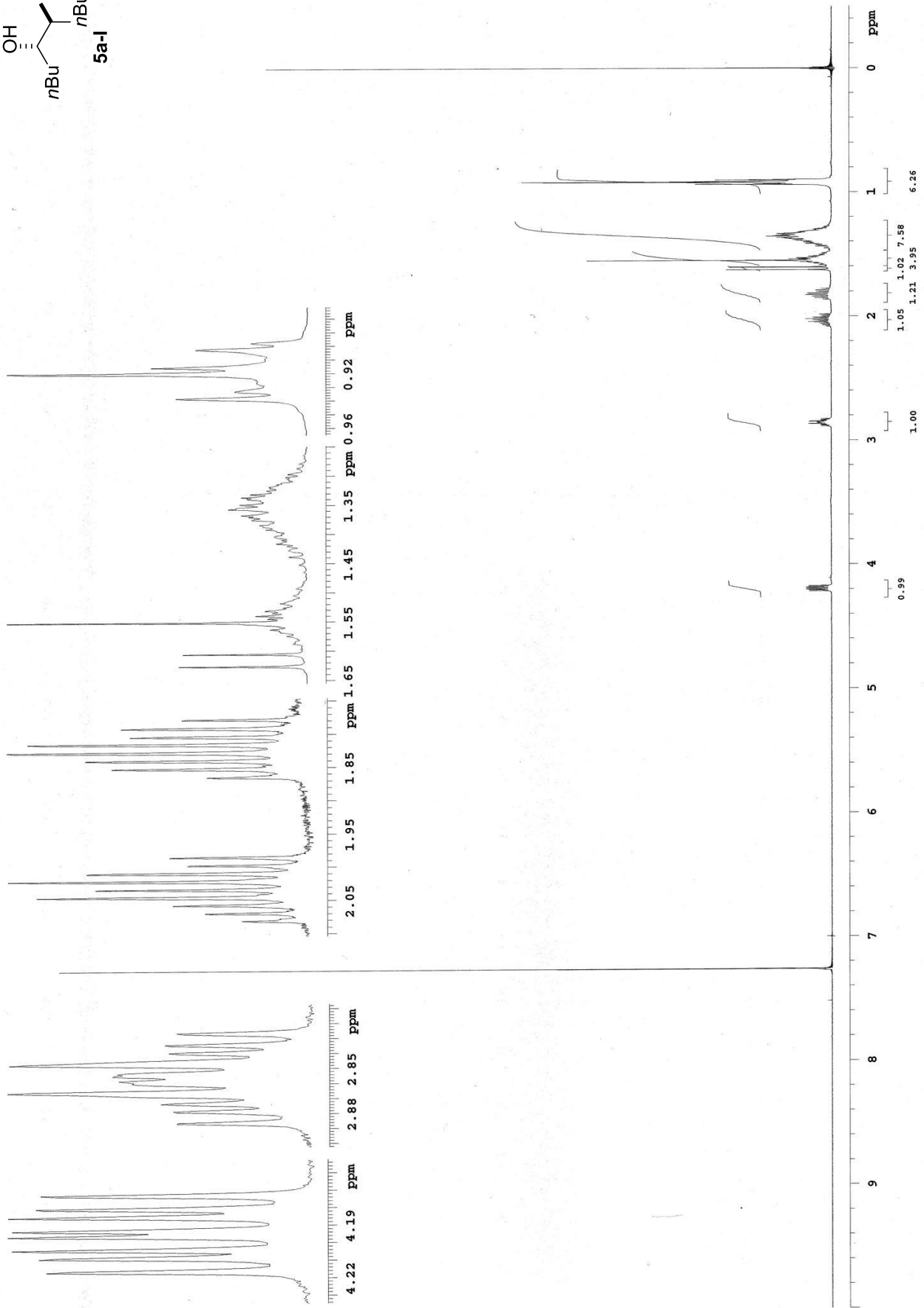
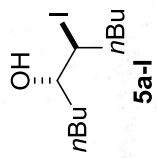


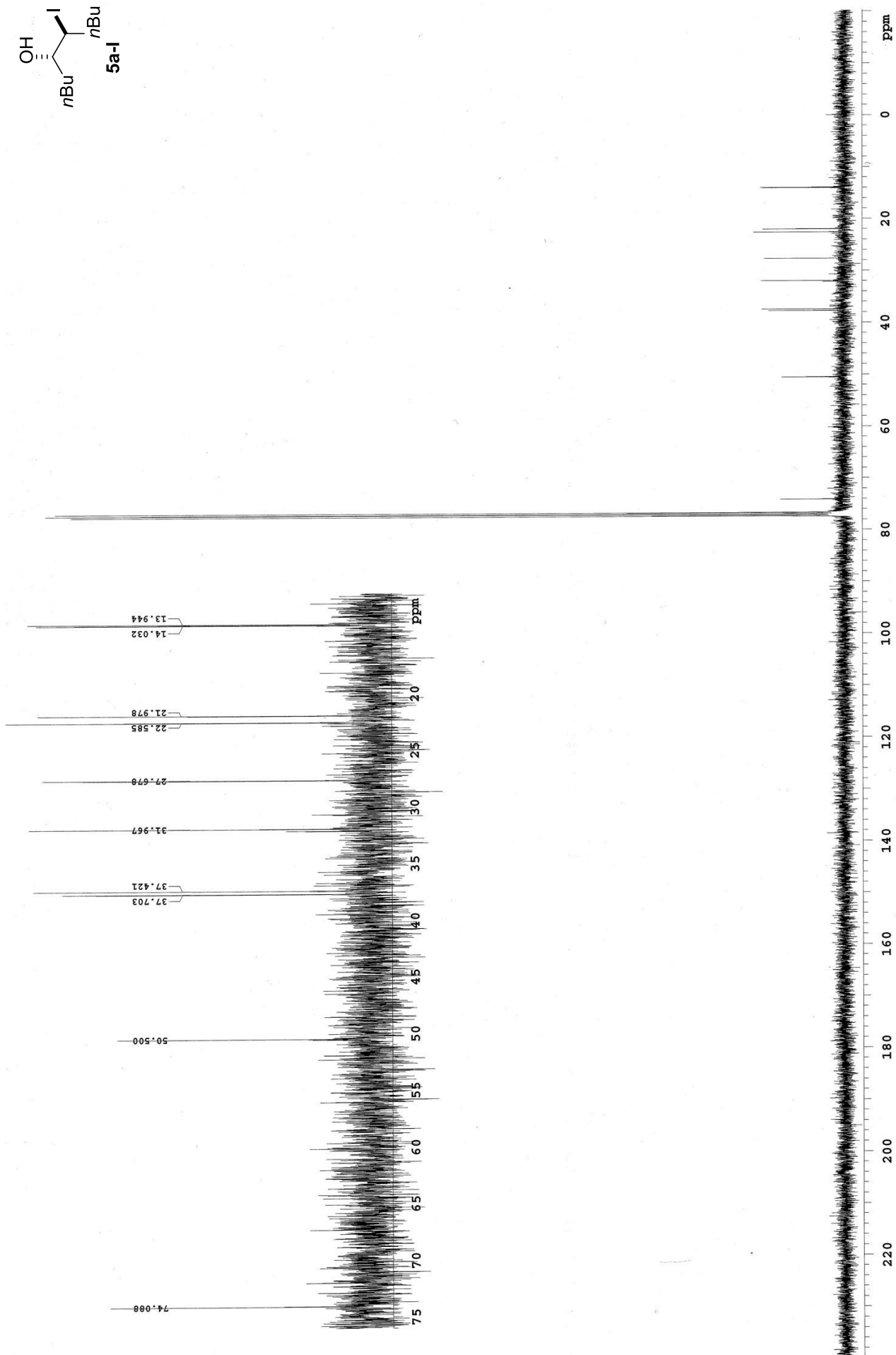
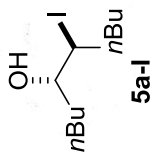




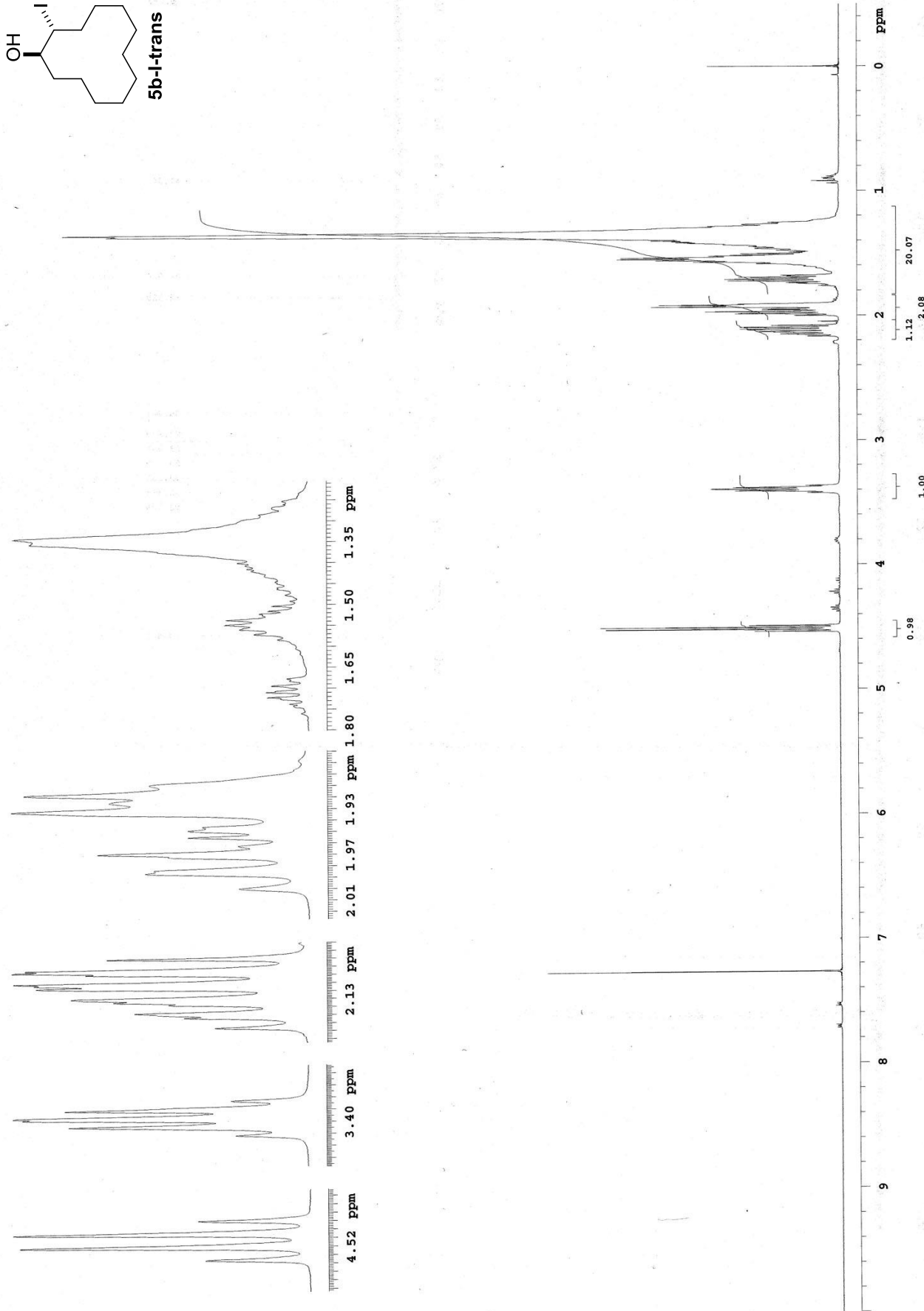
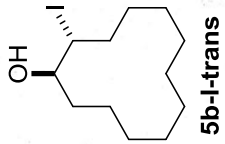


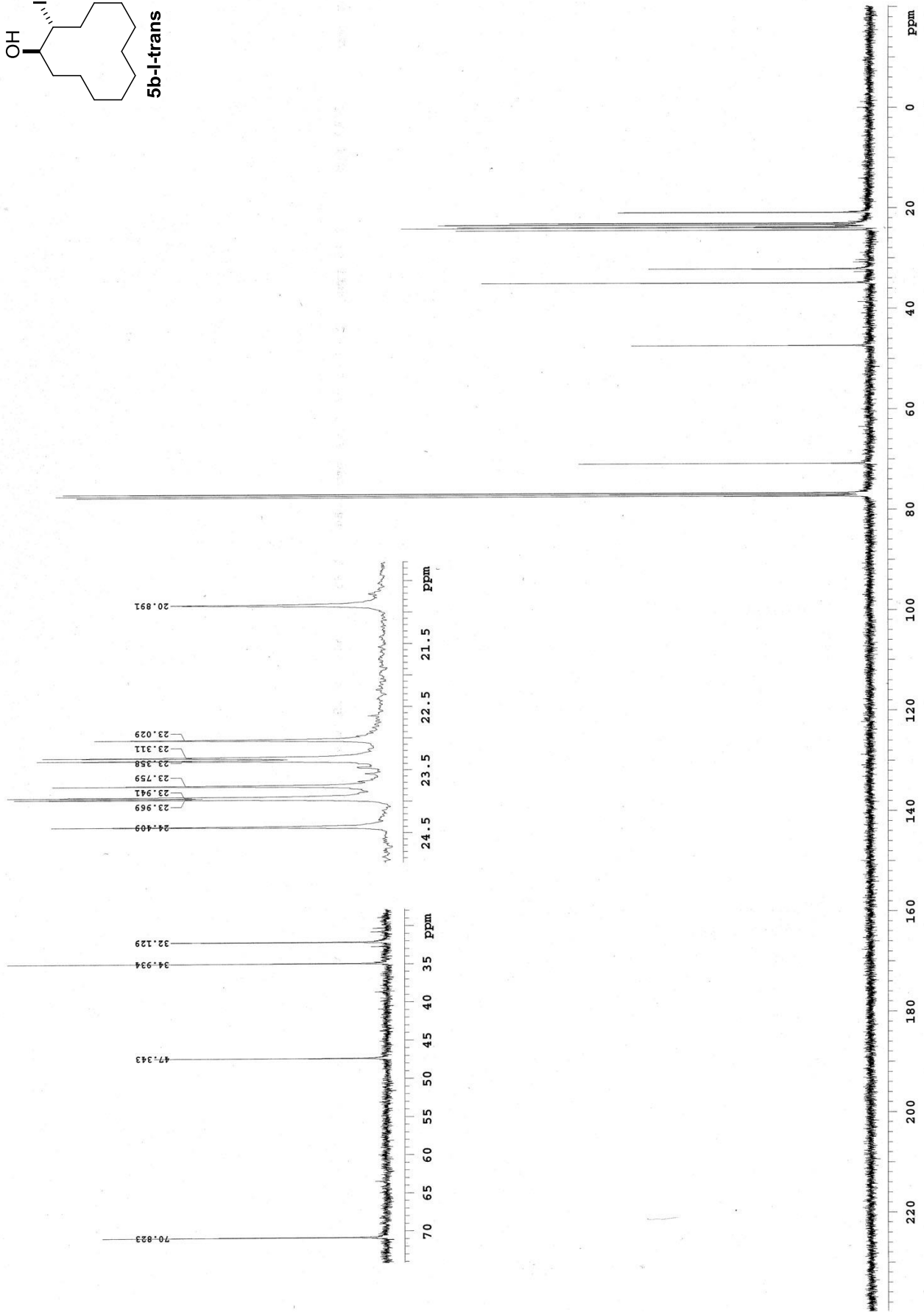
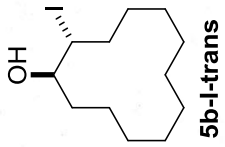


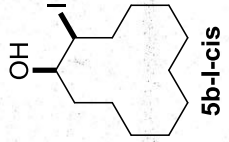




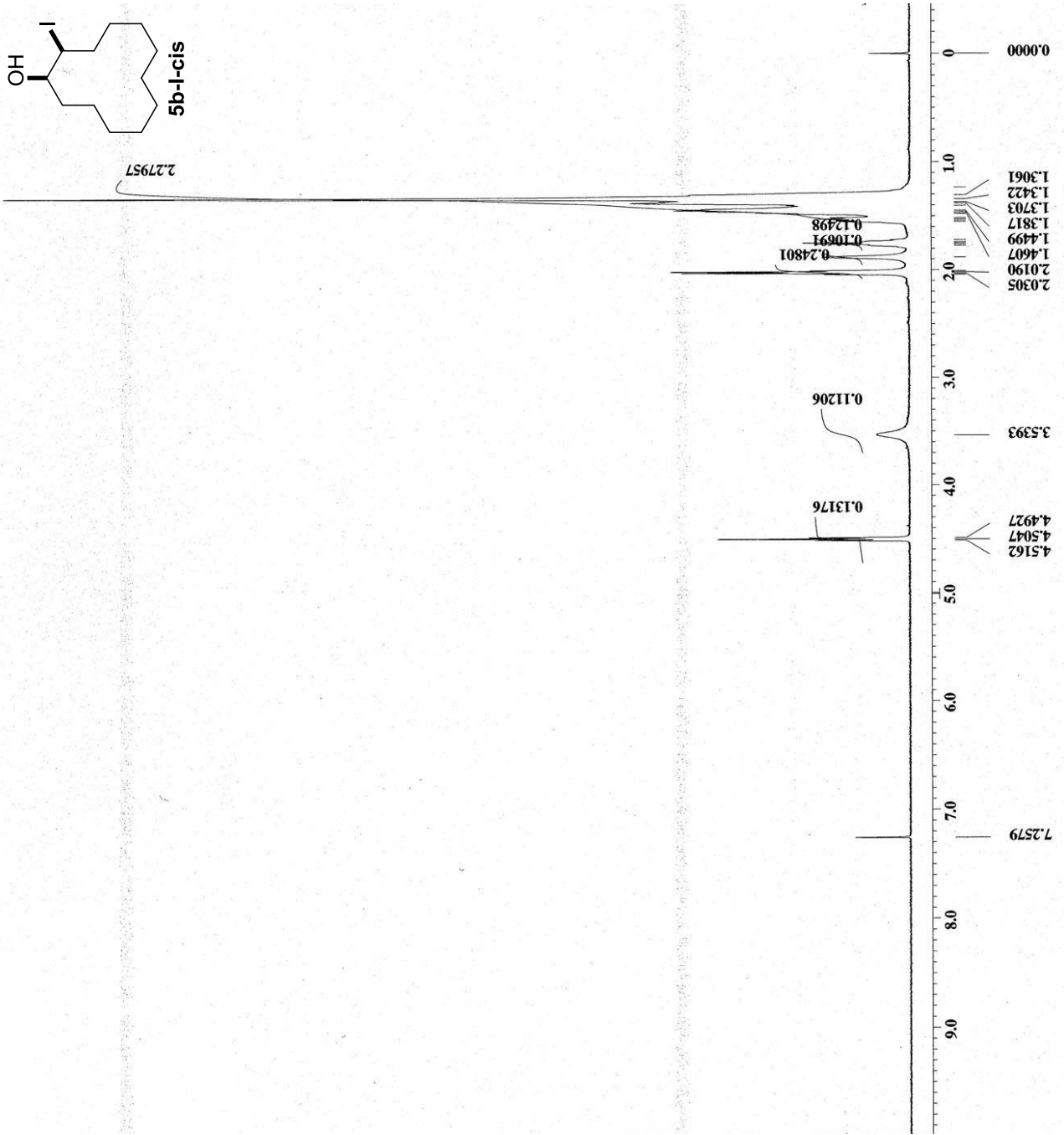


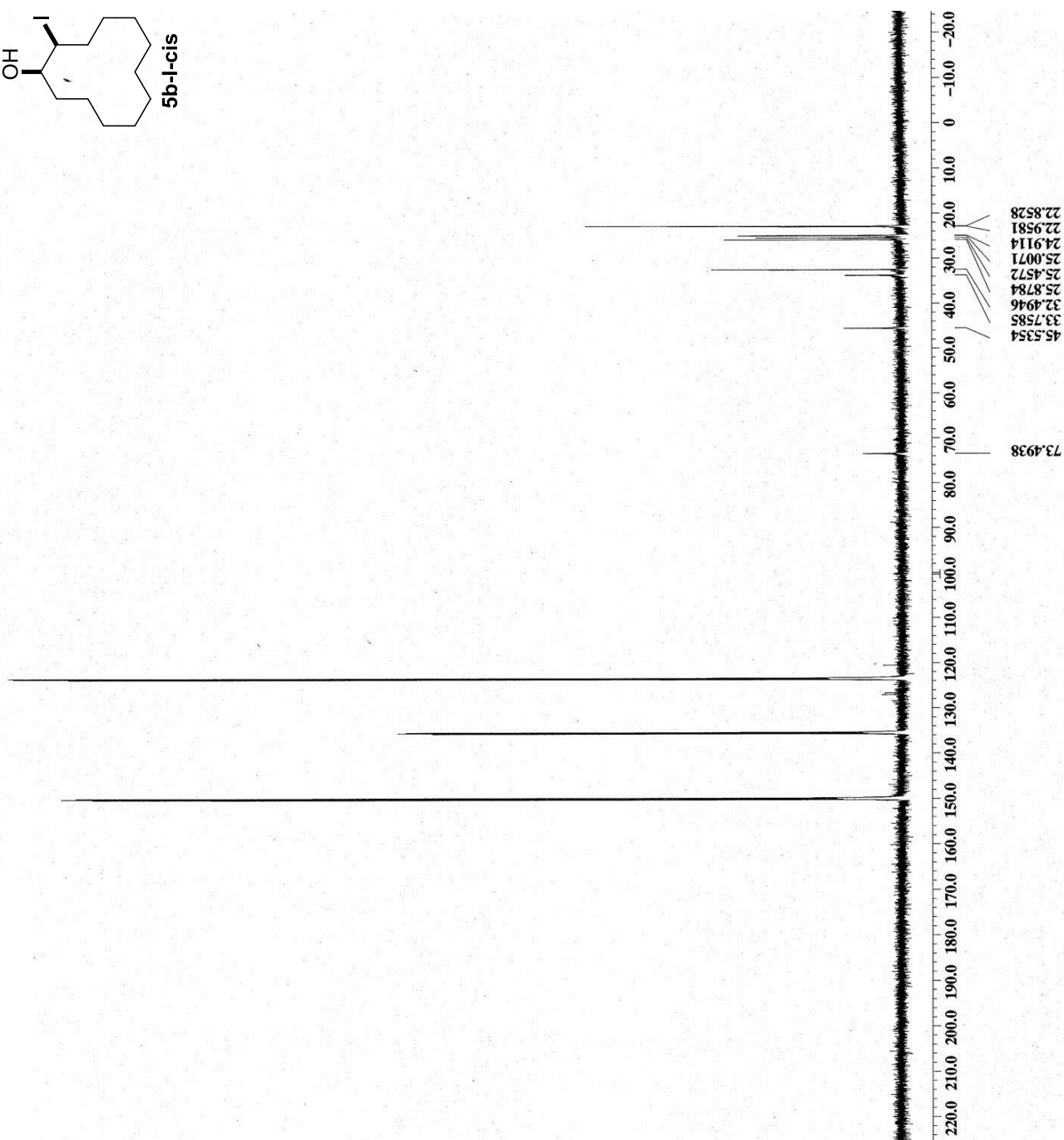
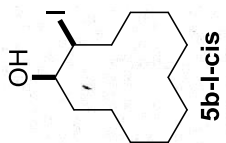


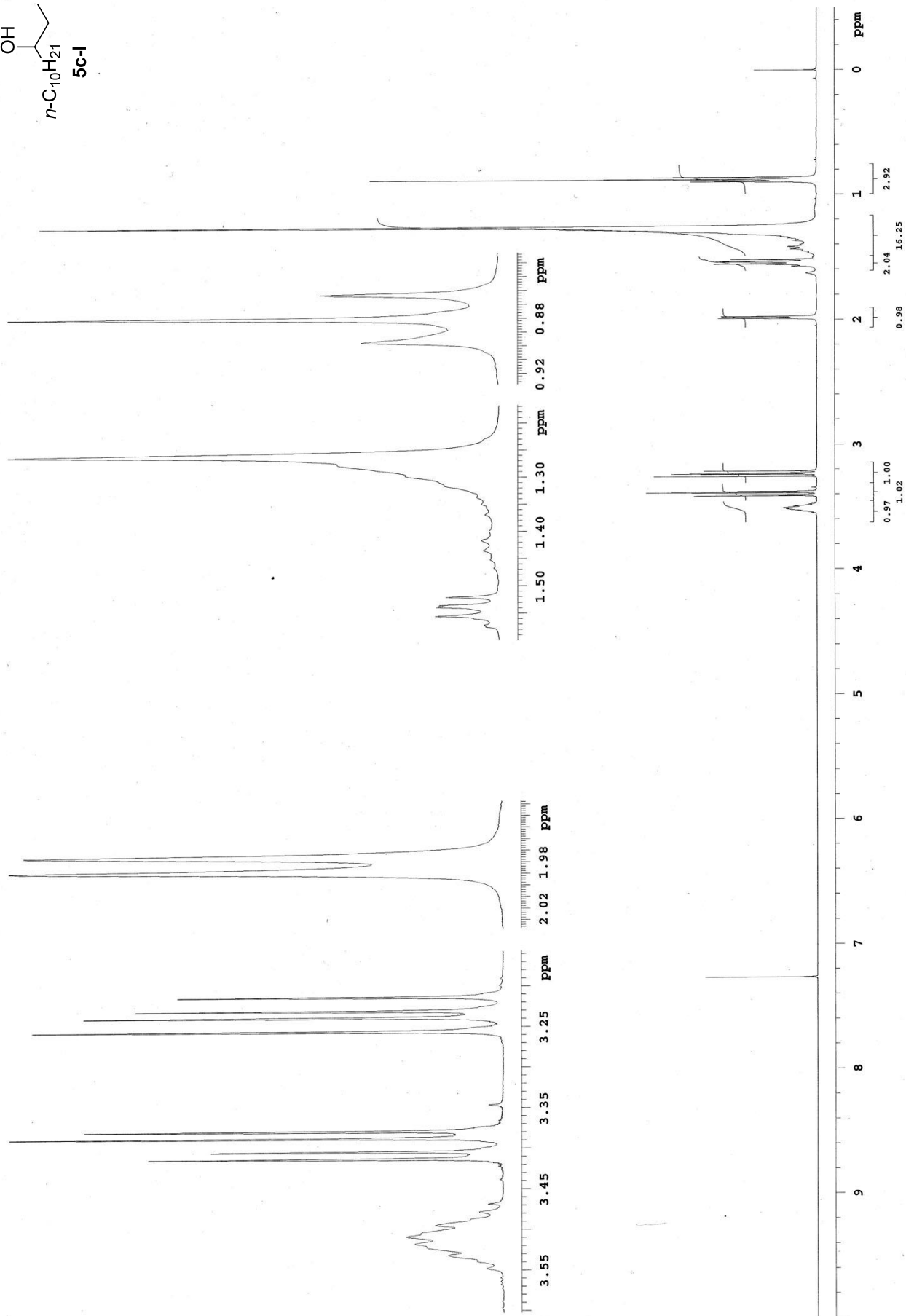
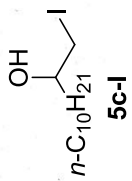


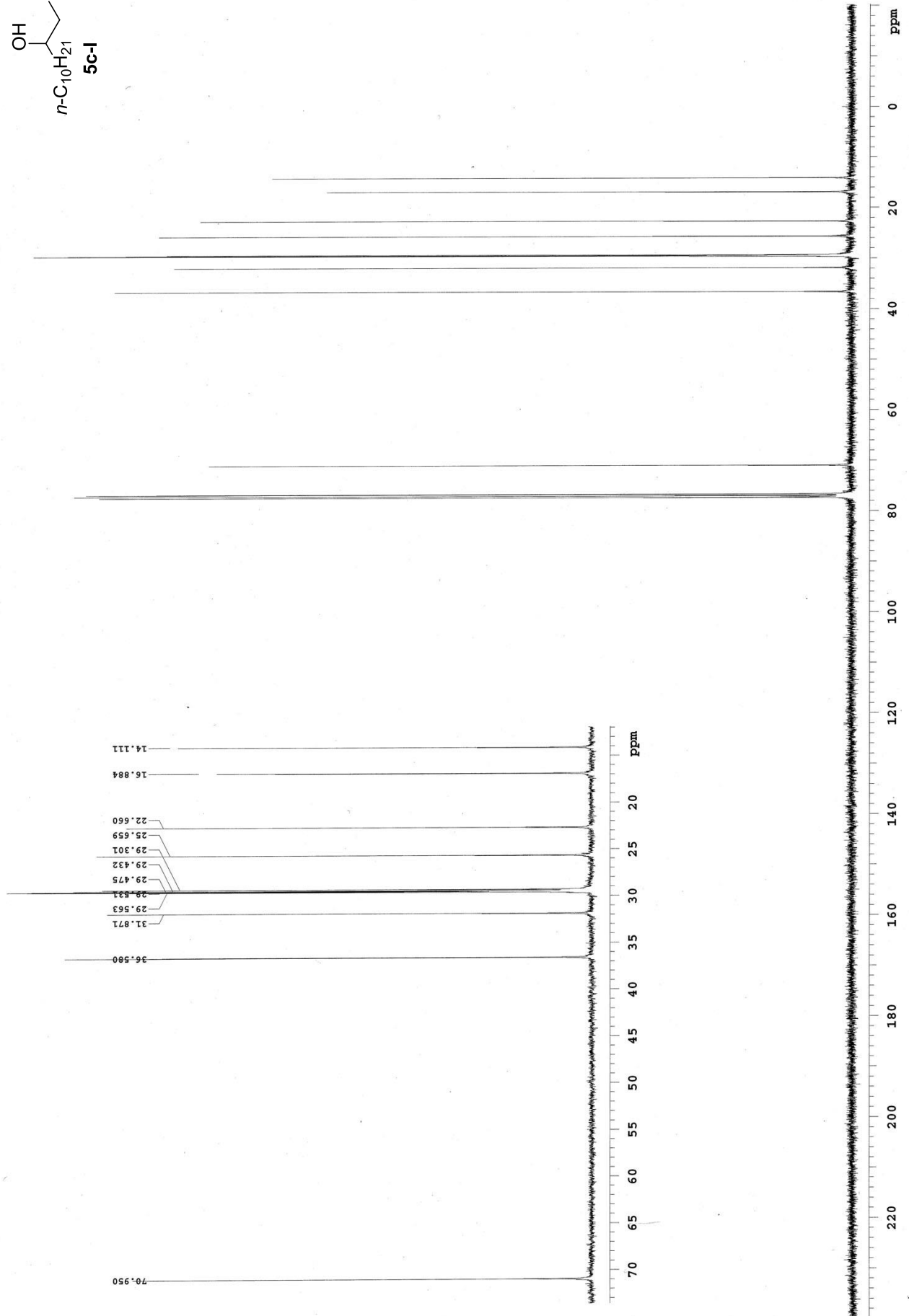
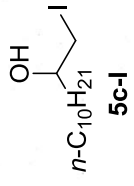


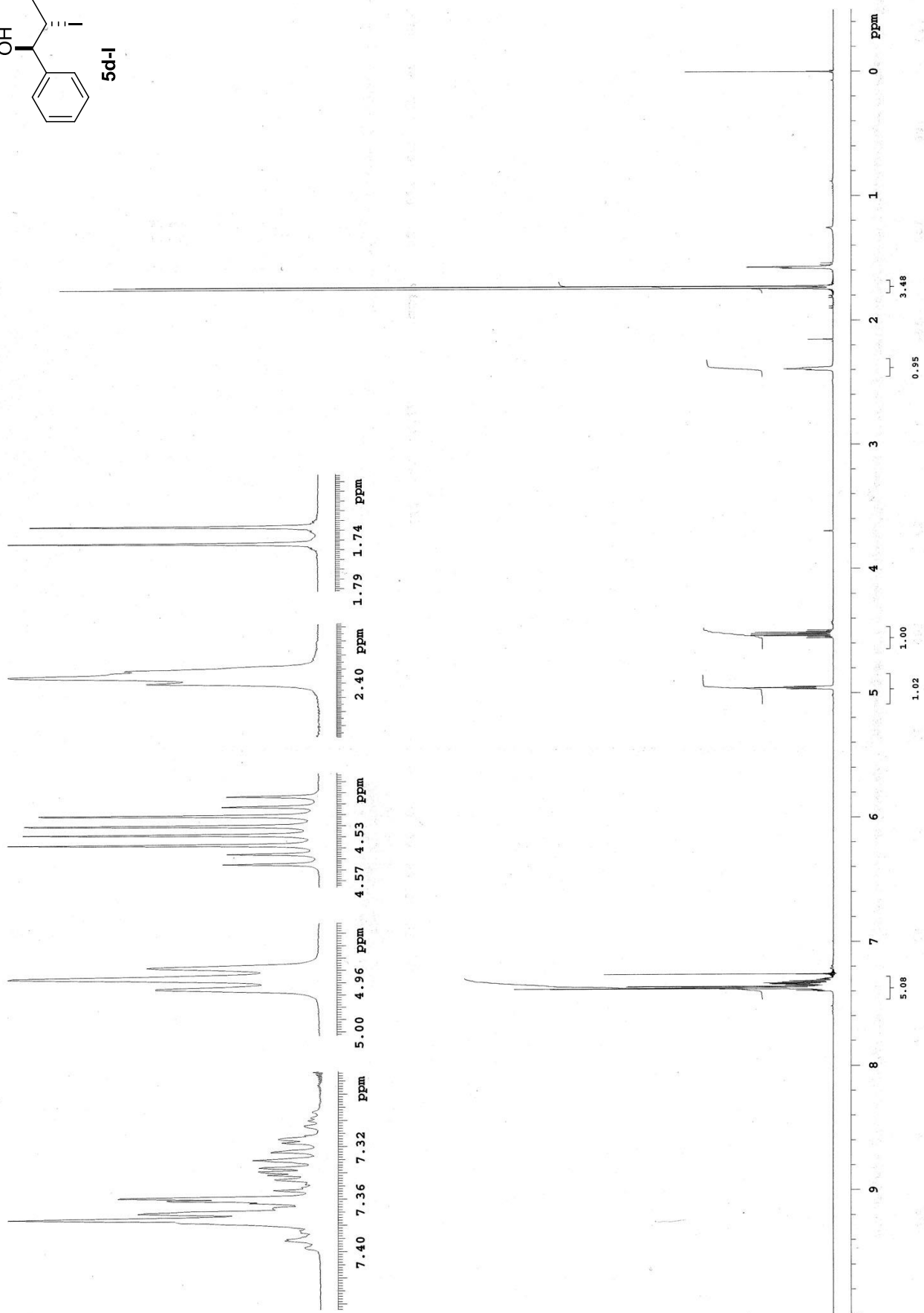
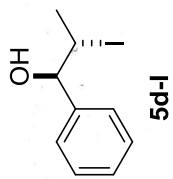
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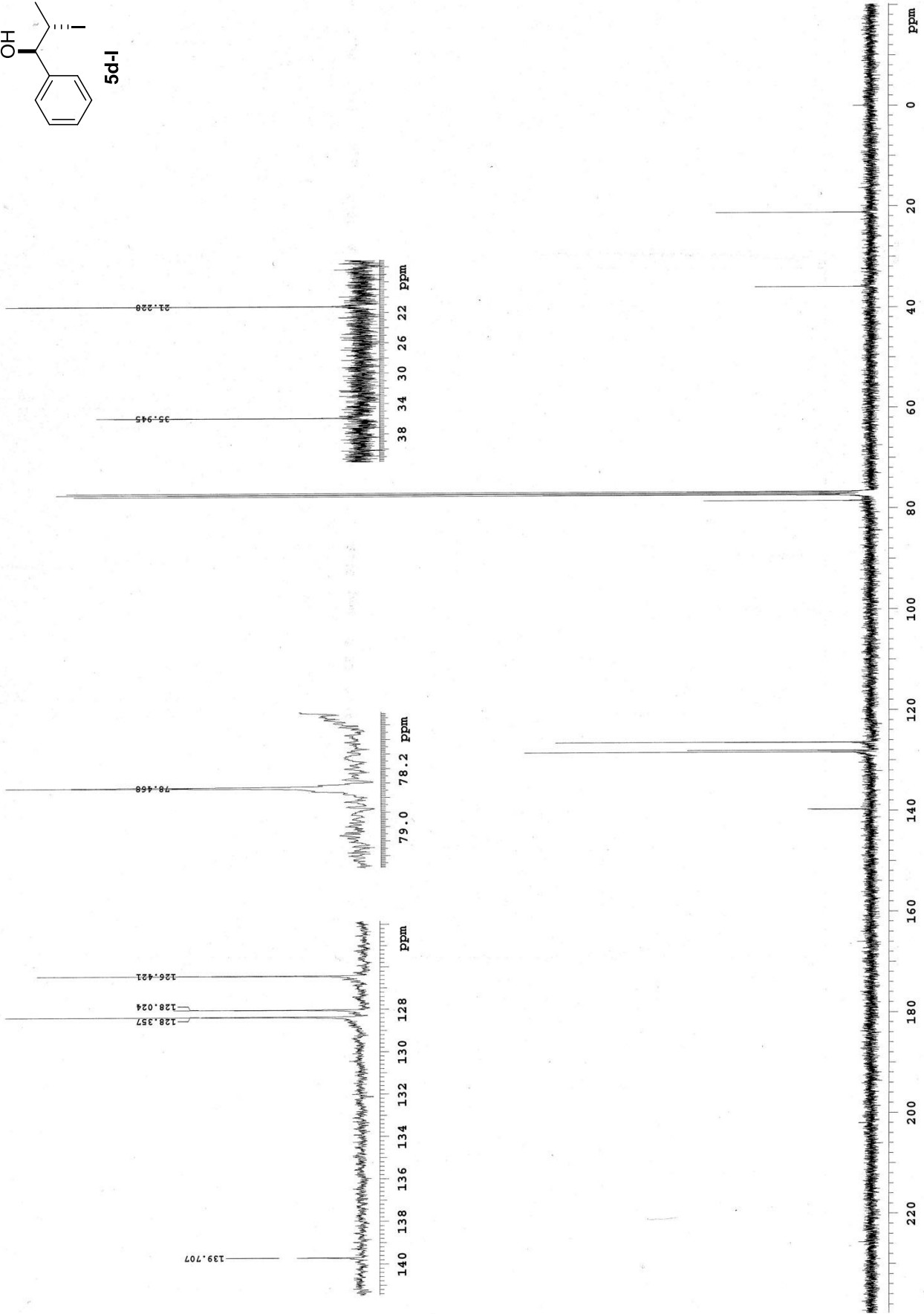
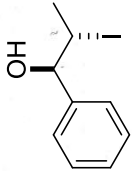




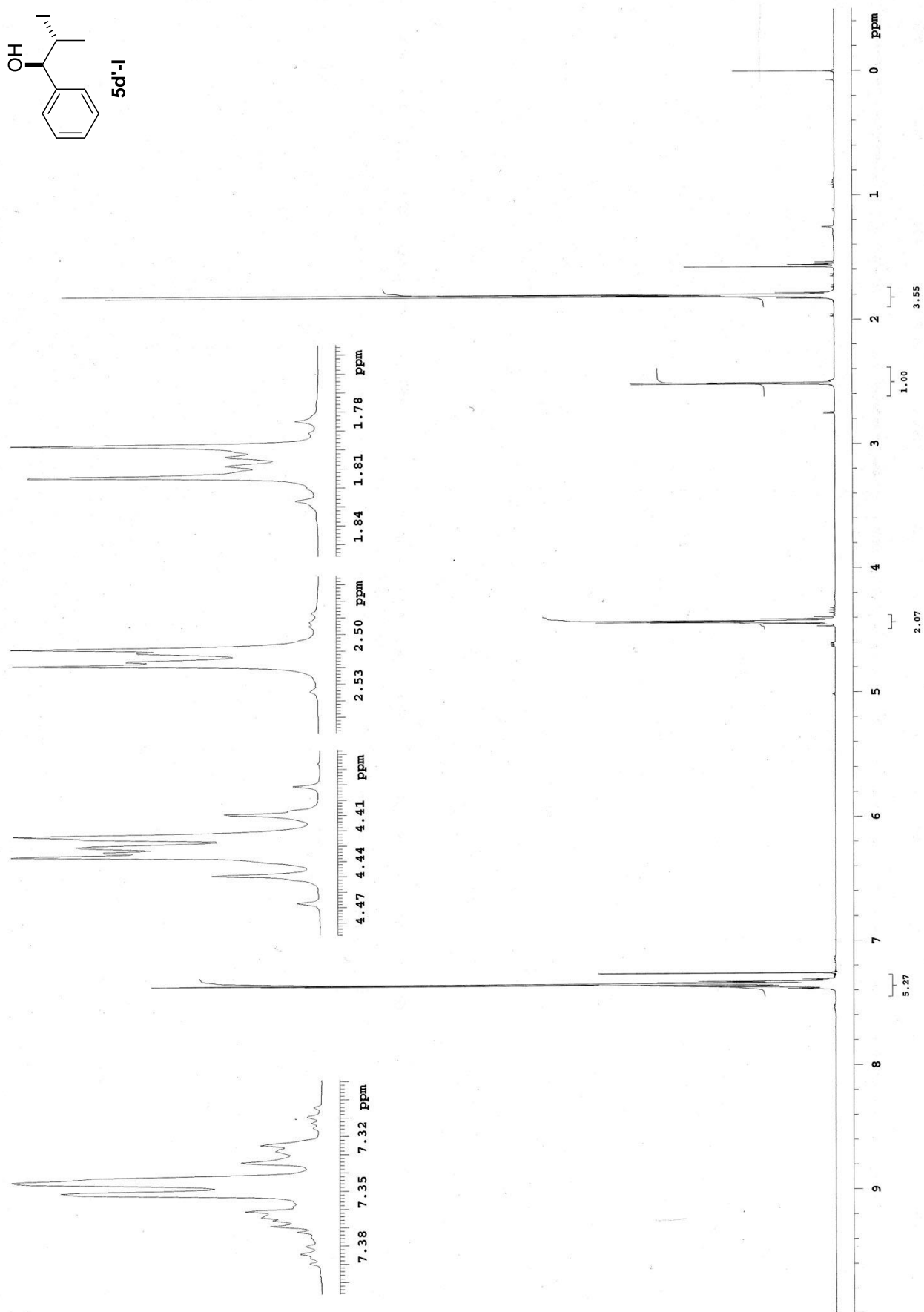
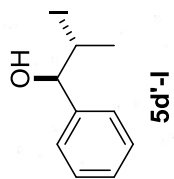


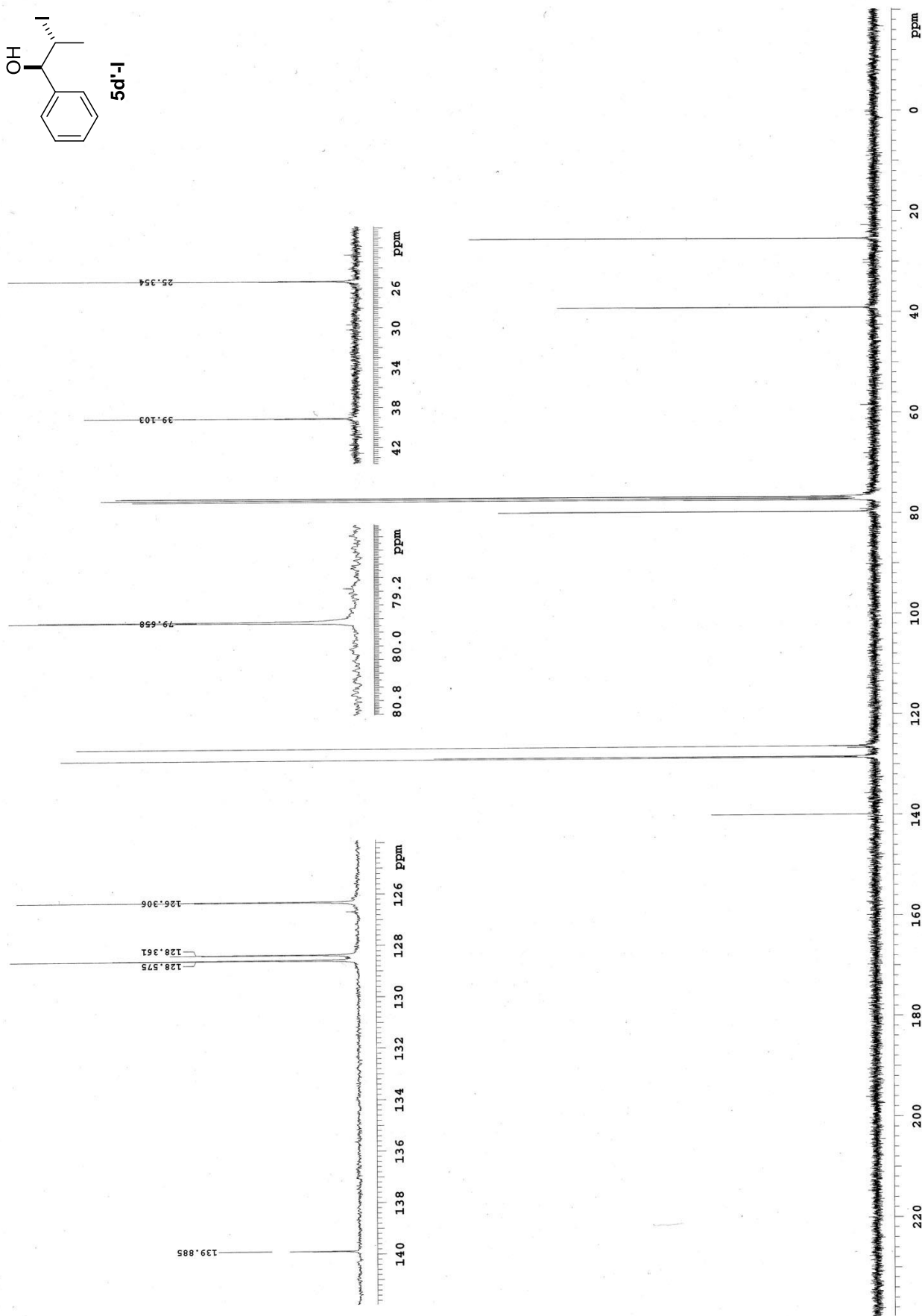
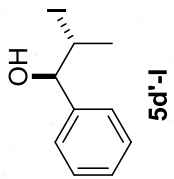


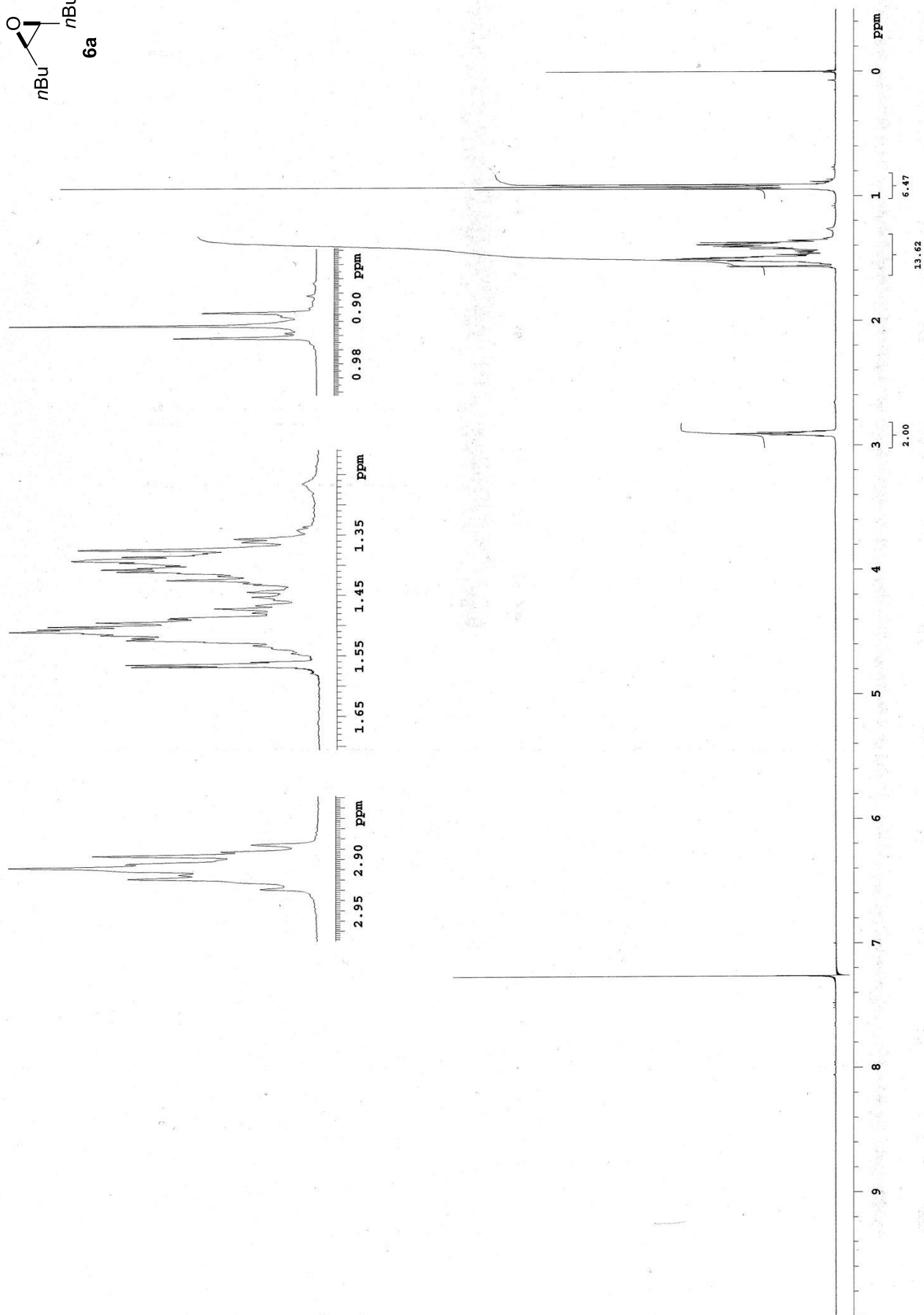
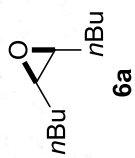


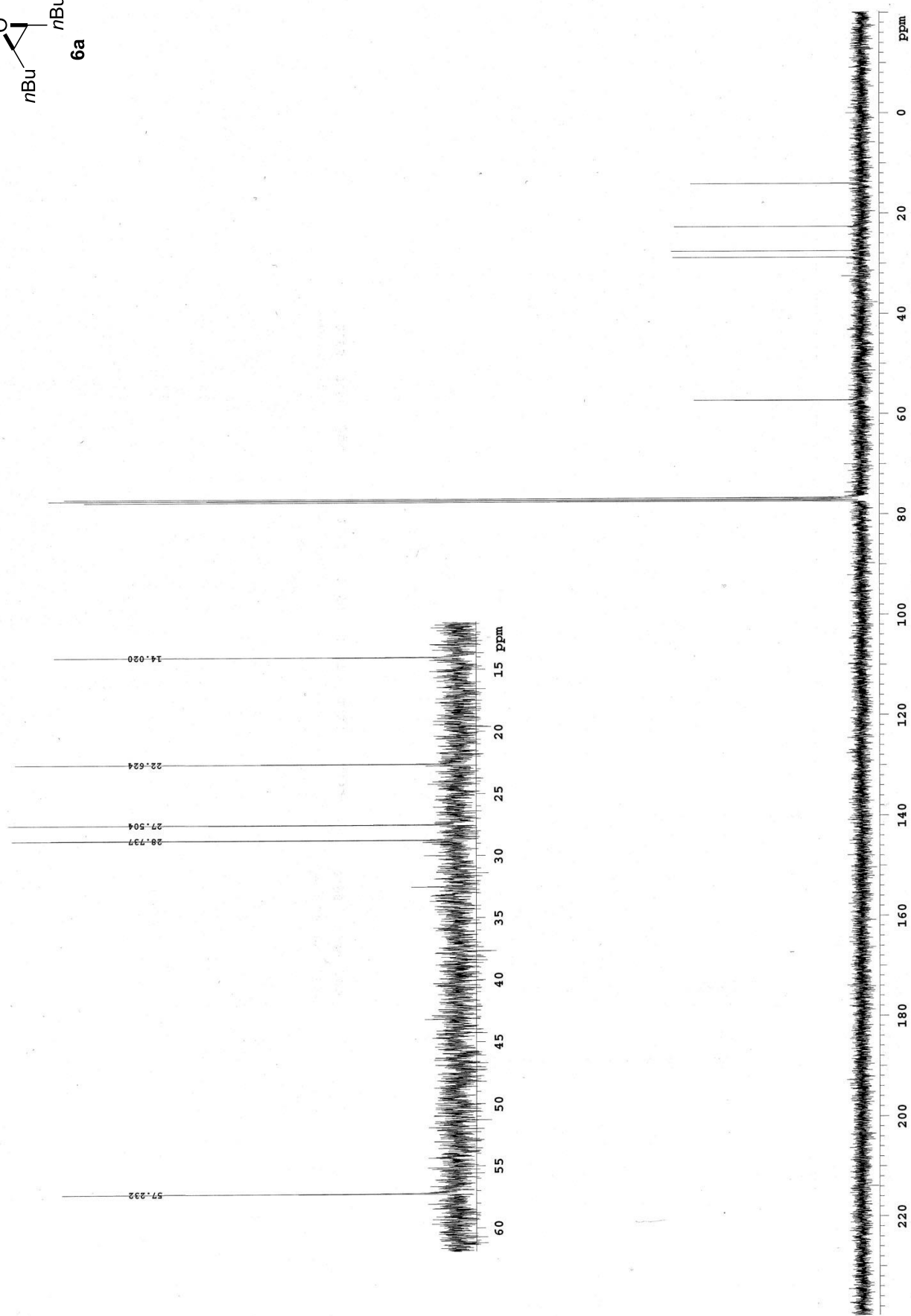
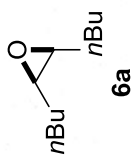


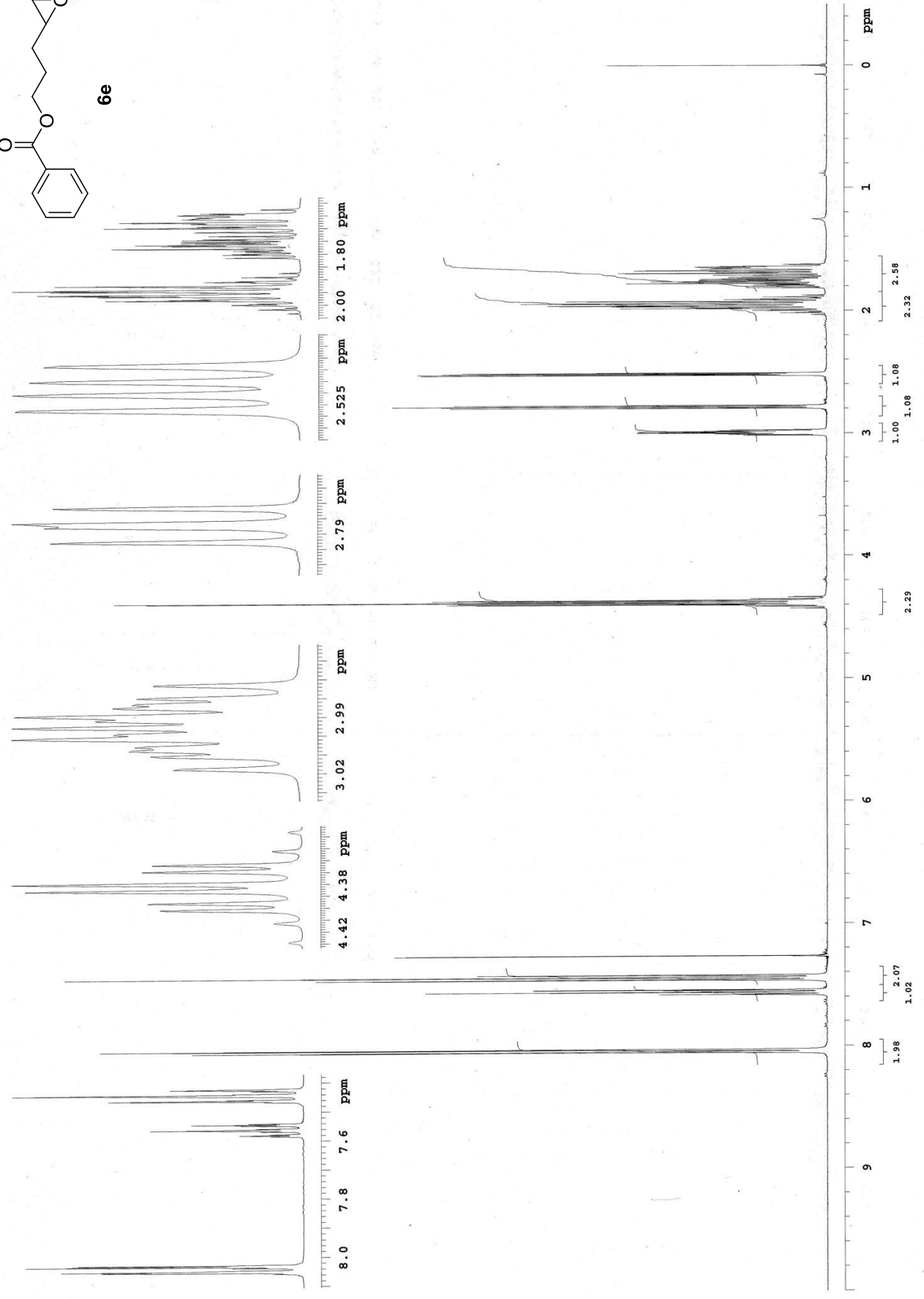
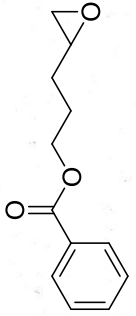


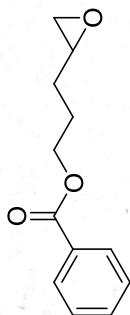




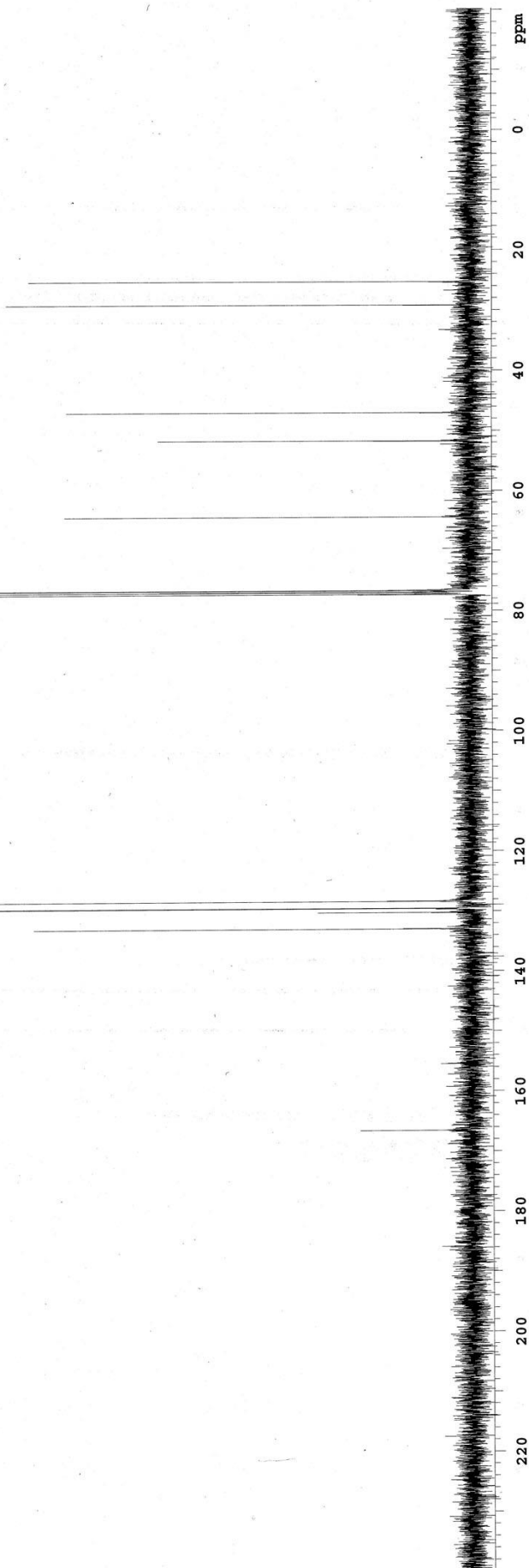
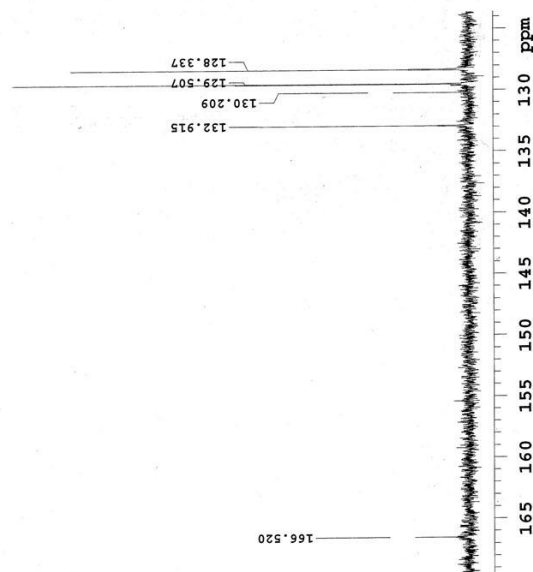
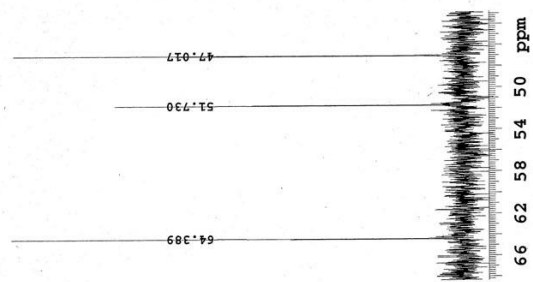
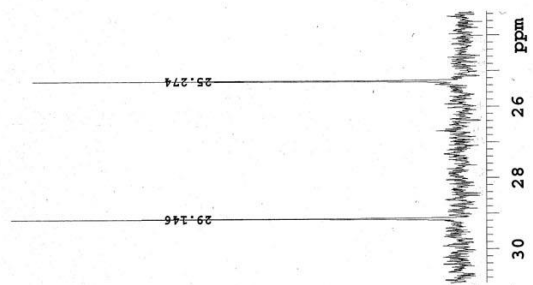


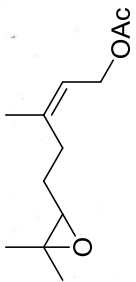




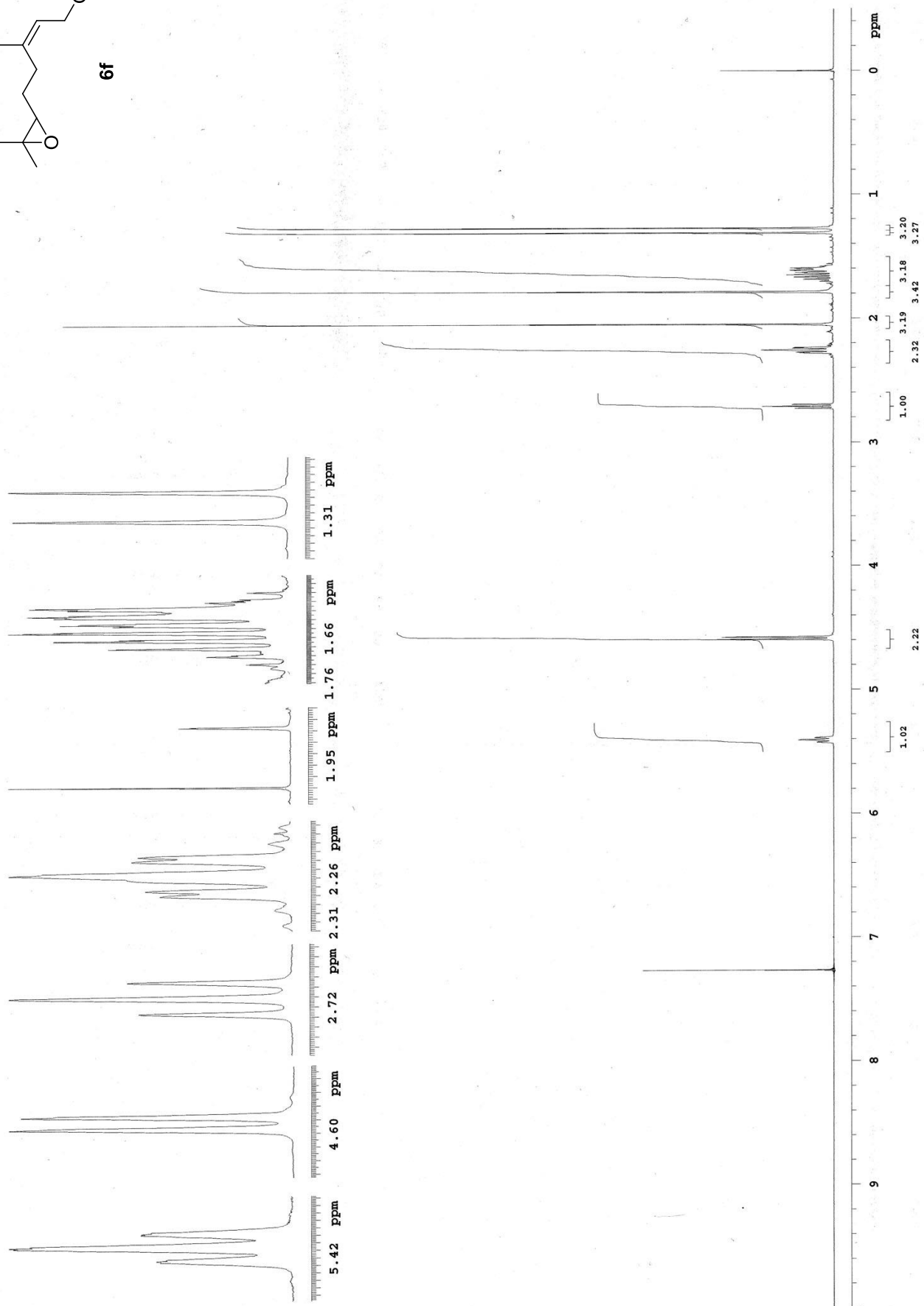


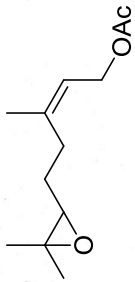
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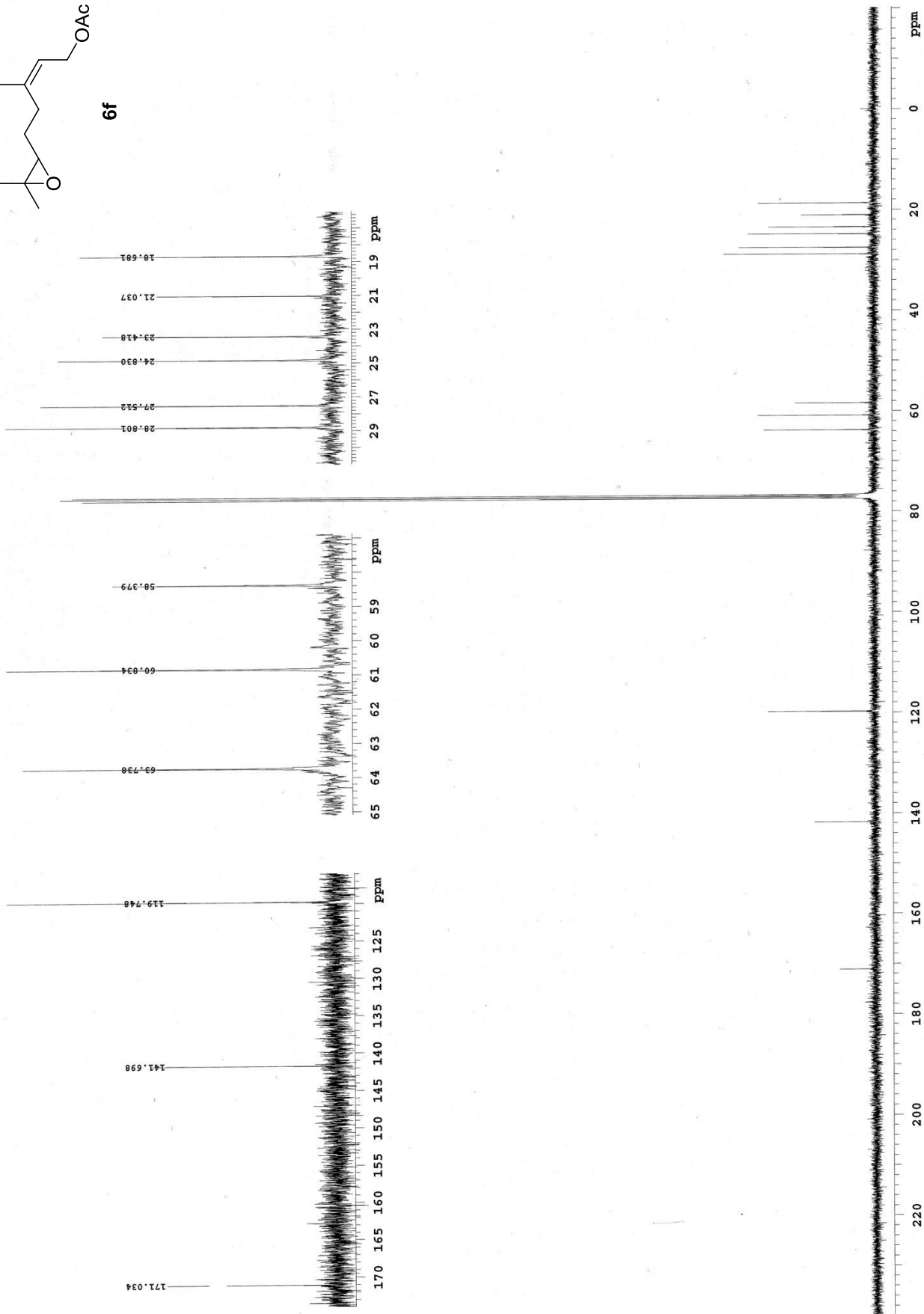


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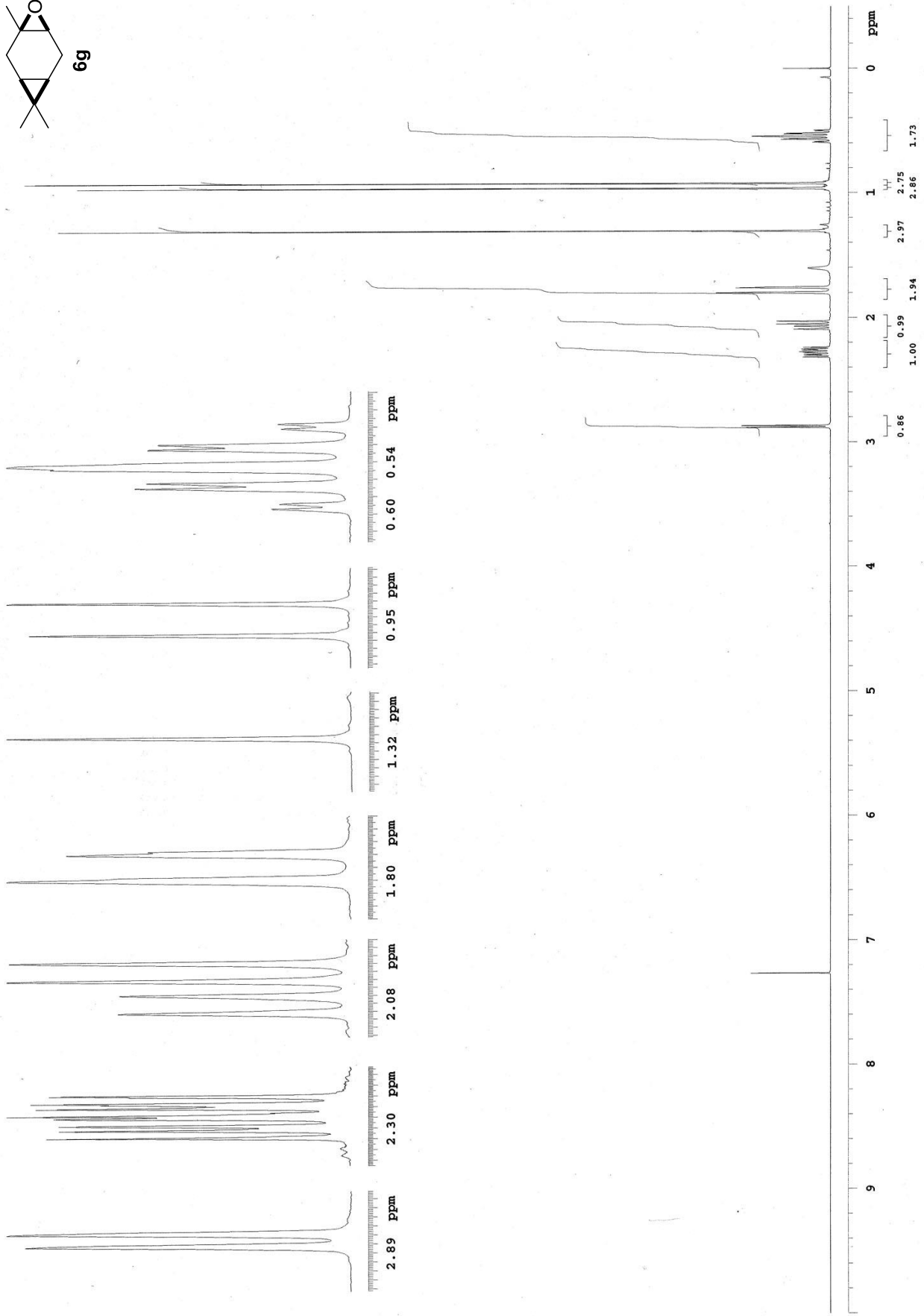
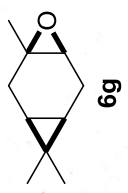


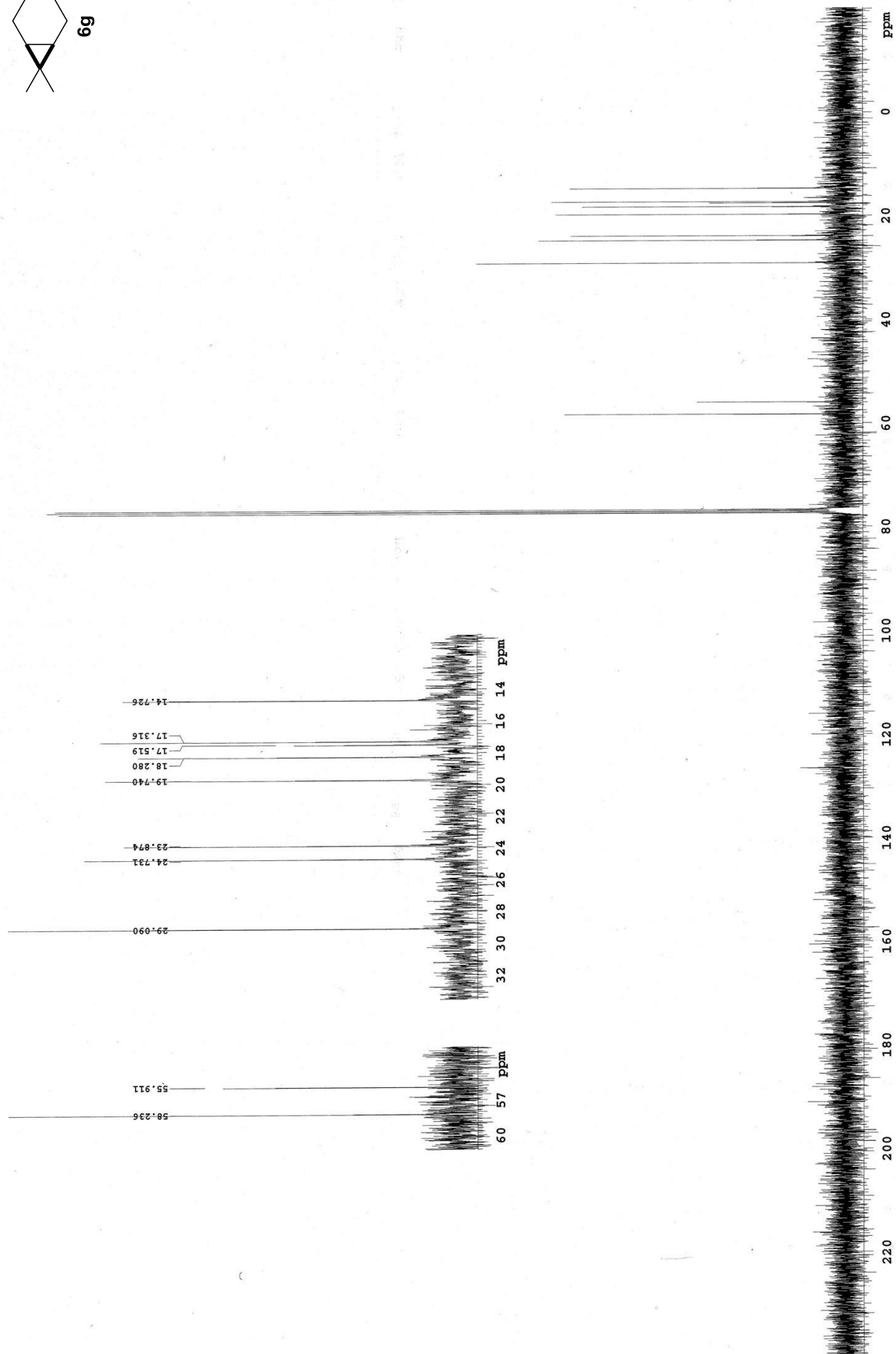
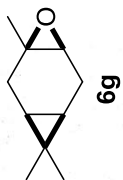


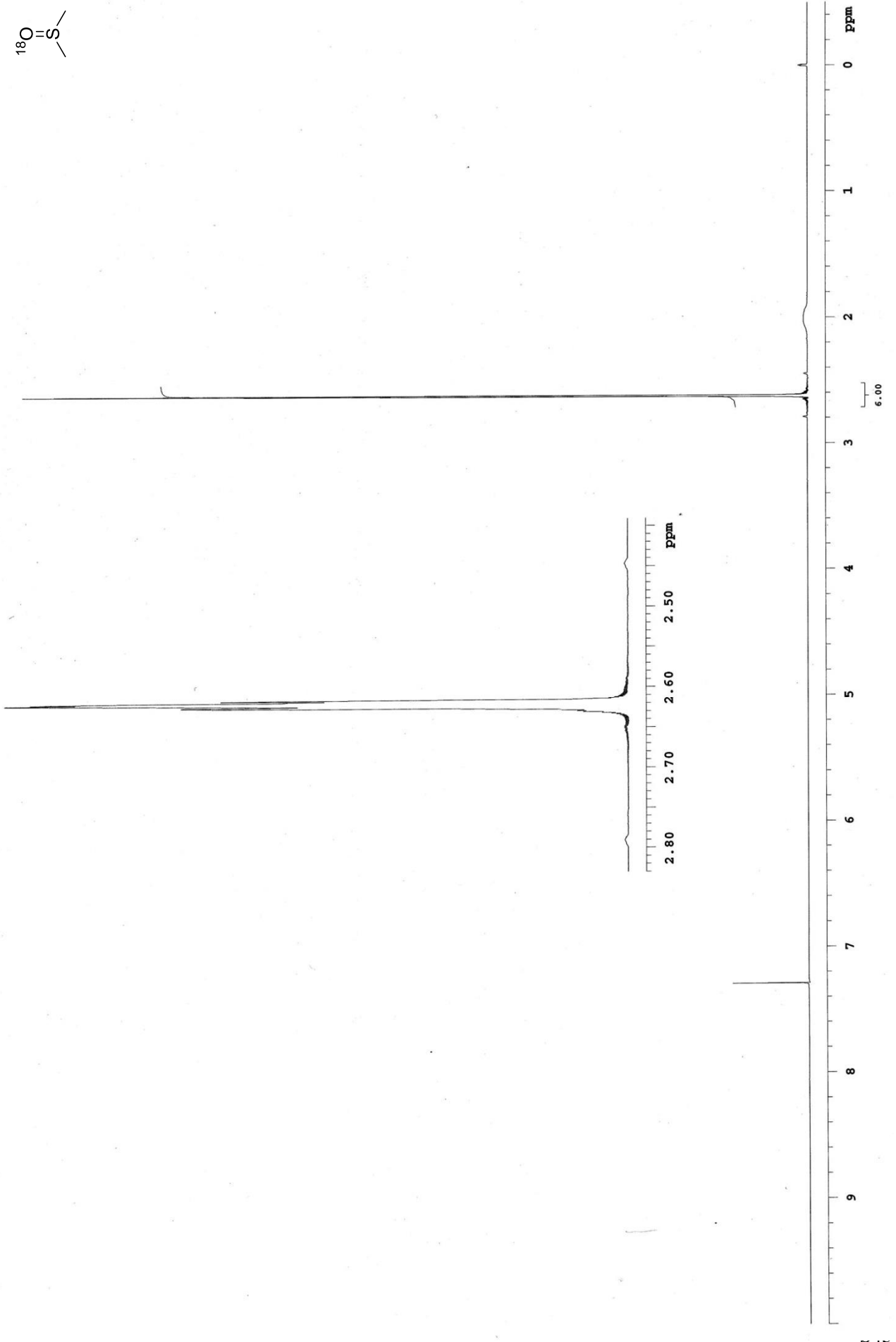
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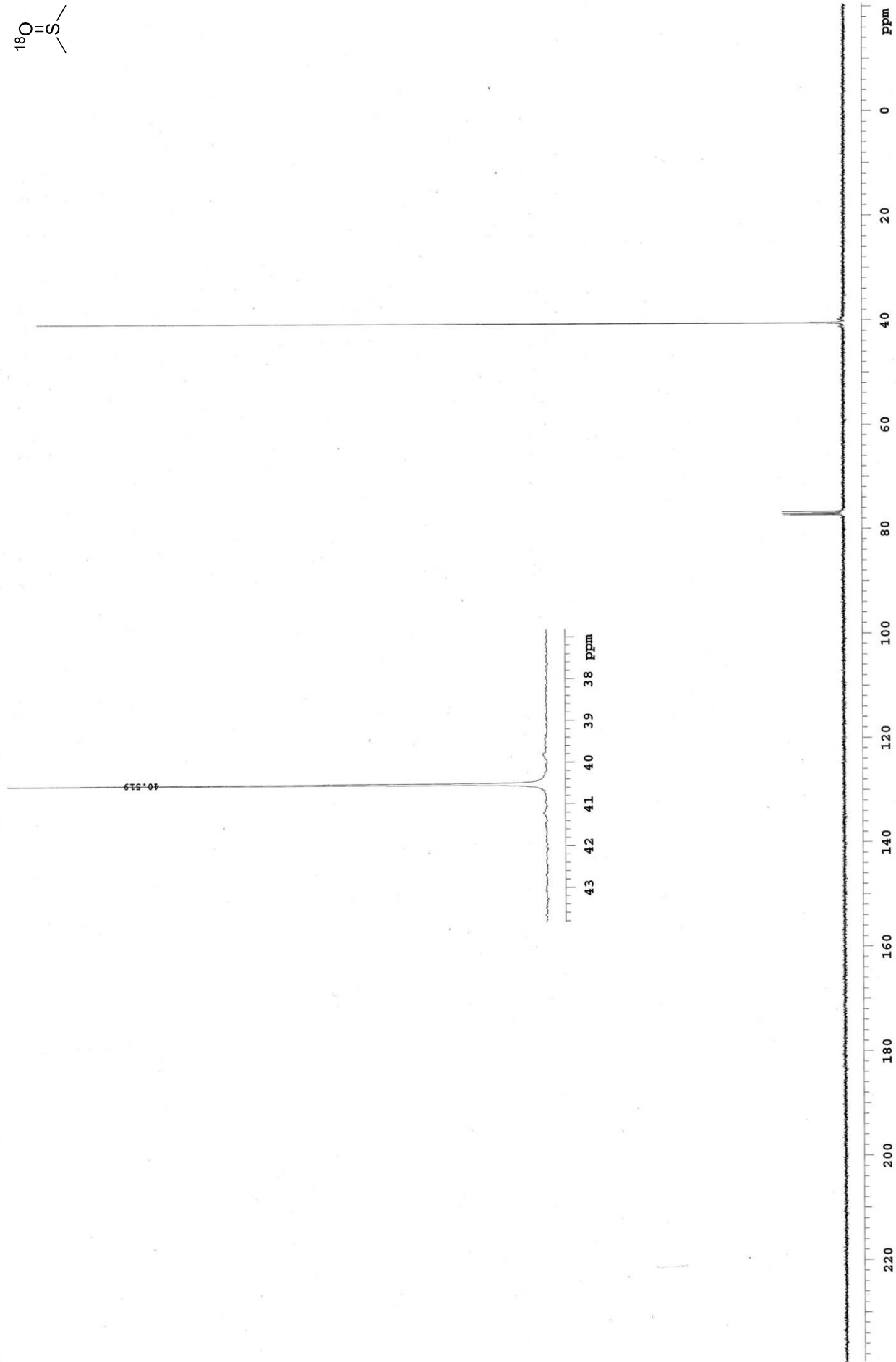


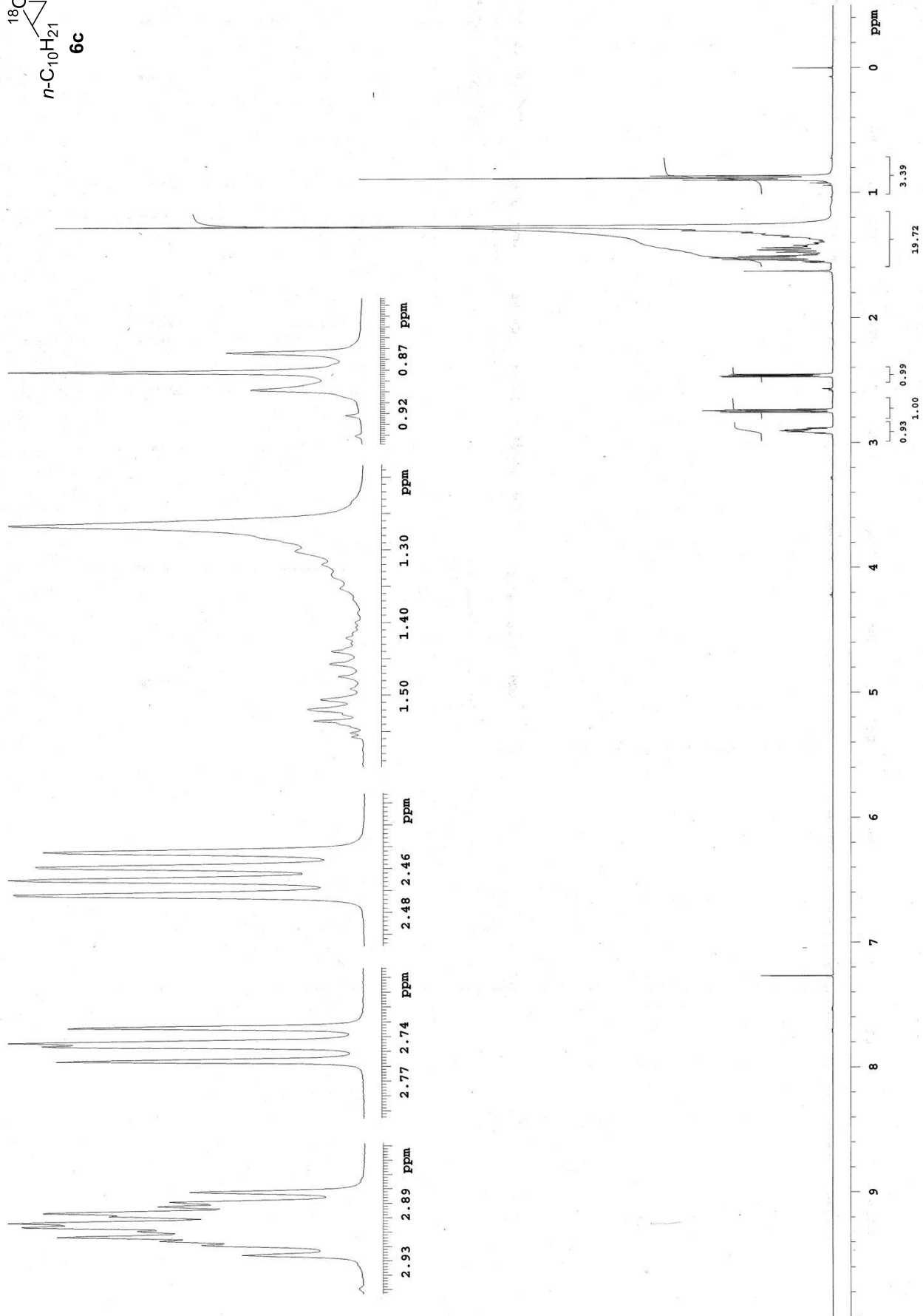
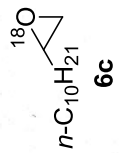


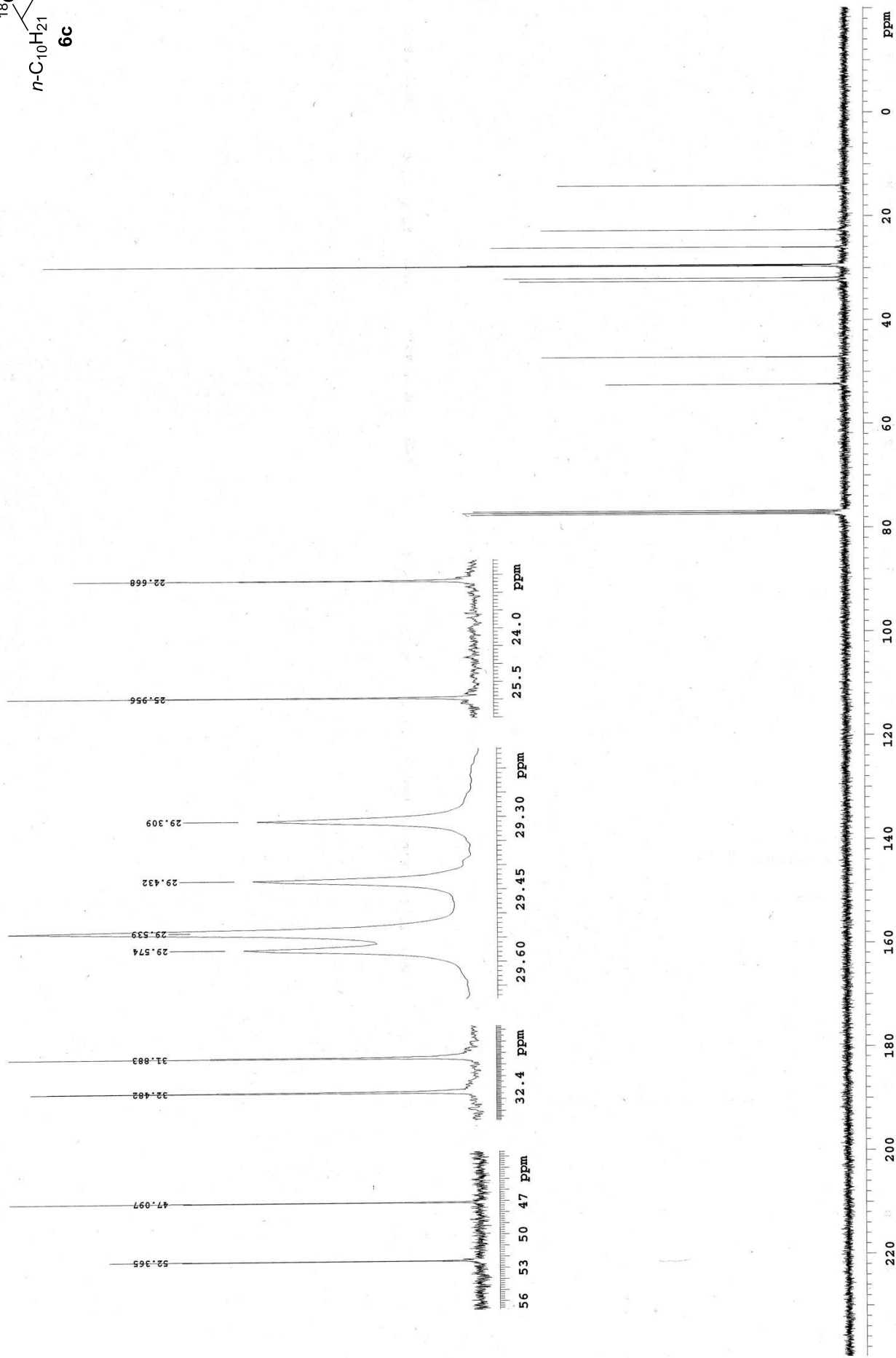
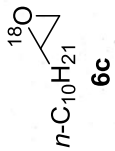






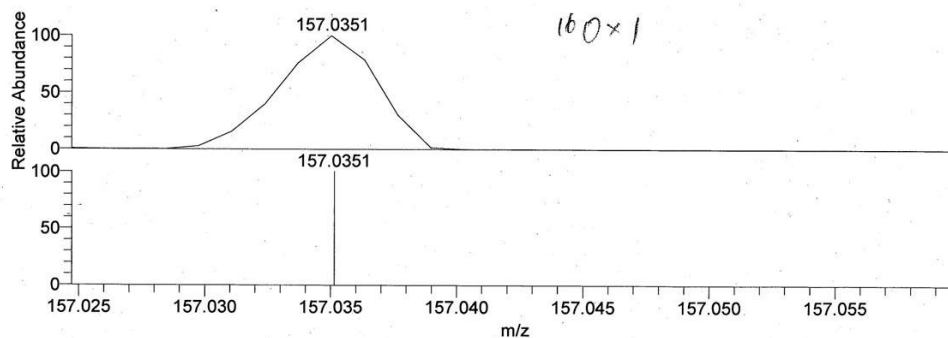
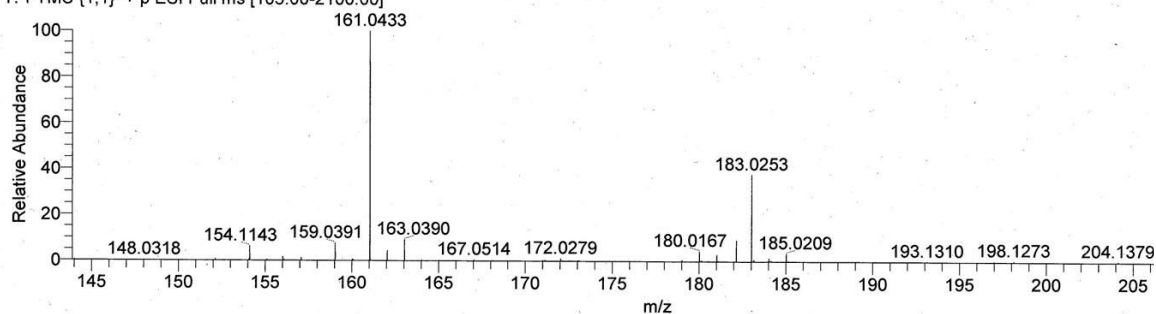






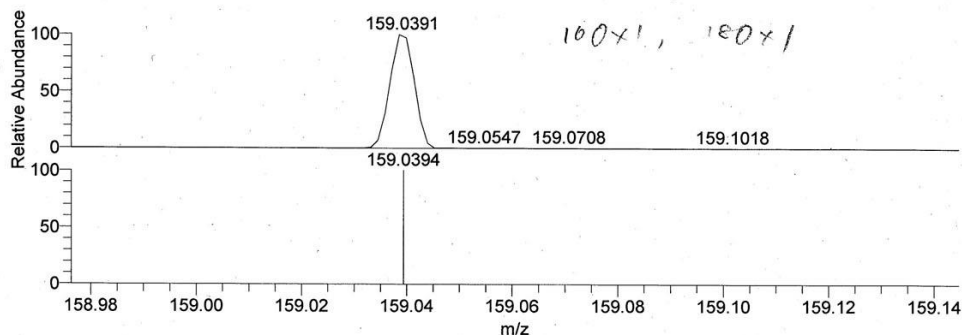
## 8. Mass spectra of <sup>18</sup>O-labelled DMSO and 6c

RH-7-97p\_141112115204 #23-41 RT: 0.22-0.38 AV: 10 NL: 8.00E6  
T: FTMS {1,1} + p ESI Full ms [105.00-2100.00]



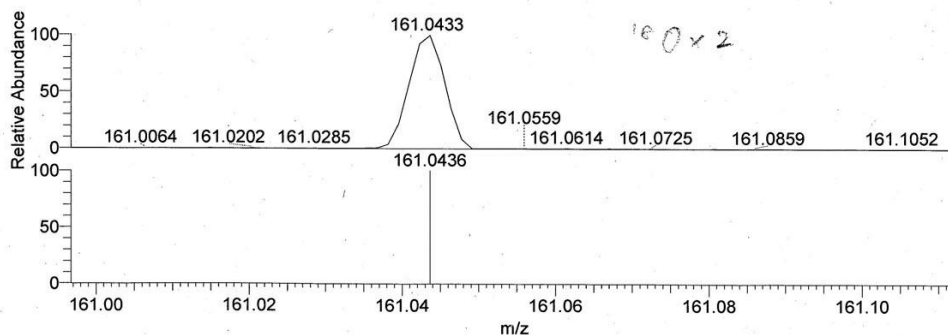
NL:  
1.19E4  
RH-7-97p\_14111211:  
RT: 0.22-0.38 AV: 10  
{1,1} + p ESI Full ms  
[105.00-2100.00]

NL:  
8.58E5  
C<sub>4</sub>H<sub>13</sub>O<sub>2</sub>S<sub>2</sub>:  
C<sub>4</sub>H<sub>13</sub>O<sub>2</sub>S<sub>2</sub>:  
pa Chrg 1



NL:  
6.12E5  
RH-7-97p\_14111211:  
RT: 0.22-0.38 AV: 10  
{1,1} + p ESI Full ms  
[105.00-2100.00]

NL:  
8.60E5  
C<sub>4</sub>H<sub>13</sub>O<sub>1</sub><sup>18</sup>O<sub>1</sub>S<sub>2</sub>:  
C<sub>4</sub>H<sub>13</sub>O<sub>1</sub><sup>18</sup>O<sub>1</sub>S<sub>2</sub>:  
pa Chrg 1



NL:  
8.00E6  
RH-7-97p\_14111211:  
RT: 0.22-0.38 AV: 10  
{1,1} + p ESI Full ms  
[105.00-2100.00]

NL:  
8.62E5  
C<sub>4</sub>H<sub>13</sub><sup>18</sup>O<sub>2</sub>S<sub>2</sub>:  
C<sub>4</sub>H<sub>13</sub><sup>18</sup>O<sub>2</sub>S<sub>2</sub>:  
pa Chrg 1

RH-7-99\_141118162118 #12-23 RT: 0.22-0.40 AV: 6 NL: 1.40E7  
 T: FTMS {1,1} + p APCI corona Full ms [105.00-2100.00]

