

– Supporting Information: Part A –

**Asymmetric Total Synthesis and Structure Confirmation of  
(+)-(3*E*)-Isolaurefucin Methyl Ether**

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**Part A (S1- S18)**

Experimental Procedures and Product Characterization

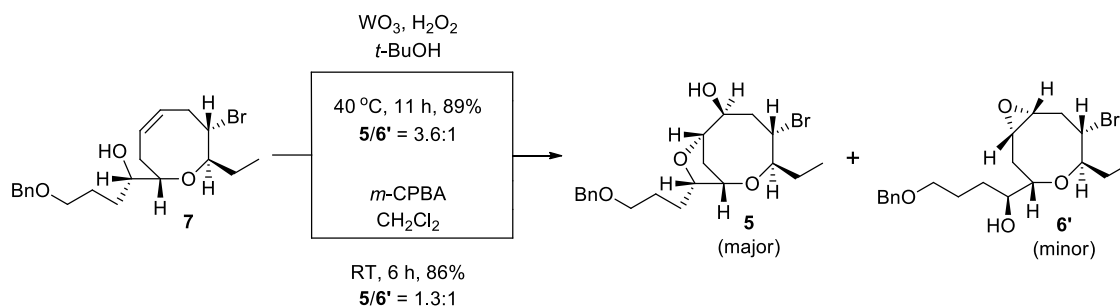
<b>General:</b>	<b>S2</b>
<b>Intramolecular Epoxide Opening Route &amp; Completion of Synthesis:</b>	<b>S3 ~ S8</b>
<b>Organoselenium-mediated Alkoxyetherification Route:</b>	<b>S9 ~ S14</b>
<b>Epoxidation of Protected Oxocenes:</b>	<b>S15 ~ S18</b>
<b>References:</b>	<b>S18</b>

## General

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) NMR spectra were obtained on a Bruker AV 400 (400/100 MHz), Bruker AMX 500 (500/125 MHz), or Jeol JNM-ECA600 (600/150 MHz) spectrometer. Chemical shifts are reported in ppm units with  $\text{Me}_4\text{Si}$  or  $\text{CHCl}_3$  as the internal standard. All reactions were routinely carried out under an inert atmosphere of dry nitrogen or argon. Reactions were checked by thin layer chromatography (Kieselgel 60 F254, Merck). Spots were detected by viewing under a UV light, and by colorizing with charring after immersion in a *p*-anisaldehyde solution or phosphomolybdic acid solution. In aqueous work-up, all organic solutions were dried over anhydrous sodium sulfate and filtered prior to rotary evaporation at water pump pressure. The crude compounds were purified by column chromatography on a silica gel (Kieselgel 60, 70-230 mesh, Merck). Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. All solvents were purified and dried by standard techniques just before use. THF and  $\text{Et}_2\text{O}$  were freshly distilled from sodium and benzophenone. Methylene chloride and toluene were purified by refluxing with  $\text{CaH}_2$ . Hexanes and ethyl acetate were purified by simple distillation.

## Intramolecular Epoxide Opening Route & Completion of Synthesis: S3 ~ S8

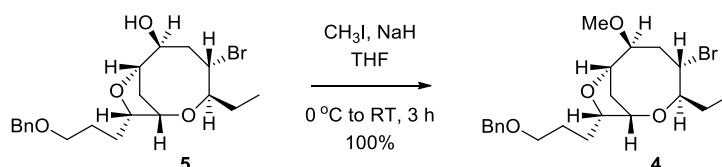
### Preparation of $\alpha,\alpha'$ -*trans*-Hydroxy Ether **5** and $\alpha,\alpha'$ -*trans*- $\alpha$ -Epoxide **6'**



**[WO<sub>3</sub>]** To a solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (19.3 mg, 0.049 mmol) in  $t\text{-BuOH}$  (0.49 mL, 0.1 M) were added tungsten(VI) oxide (1.13 mg, nano powder <100 nm, 0.004 mmol) and hydrogen peroxide (0.06 mL, 50 wt. % in  $\text{H}_2\text{O}$ , 0.971 mmol) at room temperature under Ar. After being stirred at  $40^\circ\text{C}$  (oil bath temperature) for 11 h, the reaction mixture was filtered through a short pad of Celite<sup>TM</sup>. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, hexanes/EtOAc, 4/1) to afford  $\alpha,\alpha'$ -*trans*-hydroxy ether **5** and  $\alpha,\alpha'$ -*trans*- $\alpha$ -epoxide **6'** (17.9 mg, 89% total yield,  $5/6' = 3.6:1$  by  $^1\text{H}$  NMR analysis): **For  $\alpha,\alpha'$ -*trans*-hydroxy ether **5****;  $R_f$  0.18 (hexanes/EtOAc, 2/1); colorless oil;  $[\alpha]_D^{20} = -4.6^\circ$  ( $c$  0.31,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.36 (m, 5 H), 4.58 (dd,  $J = 9.6, 9.6$  Hz, 1 H), 4.51 (s, 2 H), 4.12 (dd,  $J = 3.9, 9.7$  Hz, 1 H), 3.97 (d,  $J = 1.9$  Hz, 2 H), 3.87 (ddd,  $J = 2.5, 11.6, 11.6$  Hz, 1 H), 3.70 (ddd,  $J = 1.5, 6.9, 6.9$  Hz, 1 H), 3.51 (dd,  $J = 6.6, 6.6$  Hz, 2 H), 3.03 (ddd,  $J = 1.4, 9.7, 15.2$  Hz, 1 H), 2.30 (dd,  $J = 5.2, 15.2$  Hz, 1 H), 2.26 (d,  $J = 15.4$  Hz, 1 H), 1.92-1.98 (m, 2 H), 1.65-1.86 (m, 5H), 1.56 (s, 1 H), 1.04 (dd,  $J = 7.3, 7.3$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 128.3, 127.6, 127.5, 84.5, 83.2, 78.4, 72.8, 70.5, 70.4, 70.1, 52.0, 38.7, 33.2, 26.4, 25.6, 23.1, 11.8; IR (neat) 3420, 2934, 1456, 1364, 1181, 1150, 1065, 914, 739, 698  $\text{cm}^{-1}$ ; HRMS (FAB) found 413.1312 [calcd for  $\text{C}_{20}\text{H}_{30}\text{BrO}_4$  ( $\text{M}+\text{H}$ )<sup>+</sup> 413.1327]; **For  $\alpha,\alpha'$ -*trans*- $\alpha$ -epoxide **6'****;  $R_f$  0.30 (hexanes/EtOAc, 2/1); colorless oil;  $[\alpha]_D^{24} = -13.6^\circ$  ( $c$  0.74,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.37 (m, 5 H), 4.52 (dd,  $J = 3.5$  Hz, 2 H), 3.97 (ddd,  $J = 2.1, 9.7, 12.0$  Hz, 1 H), 3.86 (ddd,  $J = 3.0, 3.0, 9.5$  Hz, 1 H), 3.64-3.68 (m, 2 H), 3.53 (dd,  $J = 6.1, 6.1$  Hz, 2 H), 2.98-3.09 (m, 3 H), 2.72 (brs, 1 H), 2.14-2.17 (m, 1 H), 2.09-2.12 (m, 1 H), 1.86-1.92 (m, 1 H), 1.72-1.85 (m, 3 H), 1.60-1.66 (m, 1 H), 1.46-1.53 (m, 2 H), 0.96 (dd,  $J = 7.5, 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 128.4, 127.8, 79.1, 77.0, 73.1, 70.8, 70.0, 55.2, 53.4, 47.5, 40.7, 30.5, 28.21, 28.18, 25.5, 5.9; IR (neat) 3444, 2937, 1462, 1362, 1255, 1172, 1074, 1008, 903, 802, 740, 698  $\text{cm}^{-1}$ ; HRMS (FAB) found 413.1315 [calcd for  $\text{C}_{20}\text{H}_{30}\text{BrO}_4$  ( $\text{M}+\text{H}$ )<sup>+</sup> 413.1327].

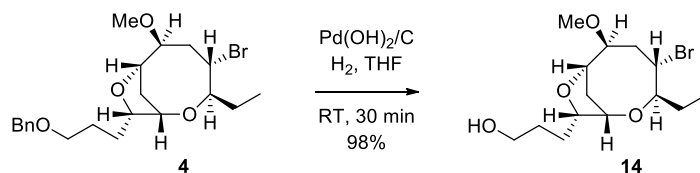
[*m*-CPBA] To a solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (15.5 mg, 0.034 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (4.0 mL, 0.01 M) was added 3-chloroperoxybenzoic acid (26.2 mg,  $\leq$  77% purity, 0.117 mmol) at room temperature under Ar. After being stirred at the same temperature for 6 h, the reaction mixture was quenched with 1N NaOH (5 mL) solution and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 20 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 10/1 to 3/1) to afford  $\alpha,\alpha'$ -*trans*-hydroxy ether **5** and  $\alpha,\alpha'$ -*trans*- $\alpha$ -epoxide **6'** (13.8 mg, 86% total yield, **5/6'** = 1.3:1 by <sup>1</sup>H NMR analysis).

#### Preparation of $\alpha,\alpha'$ -*trans*-Methoxy Ether **4**



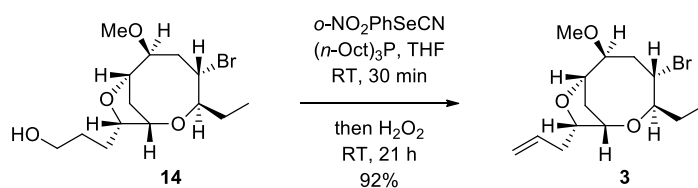
To a cooled (0 °C) solution of  $\alpha,\alpha'$ -*trans*-hydroxy ether **5** (10.1 mg, 0.024 mmol) in anhydrous THF (0.49 mL, 0.05 M) was added sodium hydride (14.7 mg, 60% dispersion in mineral oil, 0.367 mmol) under N<sub>2</sub>. After the resulting mixture was stirred at the same temperature for 30 min, methyl iodide (104 mg, 0.733 mmol) was added. The reaction mixture was warmed to room temperature while stirring for 2.5 h. The reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl solution (2 mL) and diluted with EtOAc (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 20/1) to afford  $\alpha,\alpha'$ -*trans*-methoxy ether **4** (10.4 mg, 100%) as a colorless oil: R<sub>f</sub> 0.31 (hexanes/EtOAc, 5/1); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +7.5° (*c* 0.31, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.36 (m, 5 H), 4.51 (s, 2 H), 4.44 (dd, *J* = 9.3, 9.3 Hz, 1 H), 4.17 (dd, *J* = 4.0, 9.6 Hz, 1 H), 3.95 (brs, 1 H), 3.86 (ddd, *J* = 2.5, 11.6, 11.6 Hz, 1 H), 3.68 (ddd, *J* = 1.5, 6.8, 6.8 Hz, 1 H), 3.51 (dd, *J* = 6.6, 6.6 Hz, 2 H), 3.40-3.44 (m, 4 H), 2.91 (ddd, *J* = 1.1, 9.3, 15.4 Hz, 1 H), 2.46 (dd, *J* = 5.4, 15.4 Hz, 1 H), 2.17 (d, *J* = 15.4 Hz, 1 H), 1.88-1.99 (m, 2 H), 1.74-1.86 (m, 2 H), 1.63-1.73 (m, 3 H), 1.03 (dd, *J* = 7.3, 7.3 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 128.3, 127.6, 127.5, 84.4, 83.1, 79.6, 76.7, 72.9, 70.4, 70.2, 57.0, 52.1, 33.6, 33.5, 26.5, 25.5, 23.2, 11.8; IR (neat) 2934, 1457, 1364, 1306, 1204, 1153, 1099, 1065, 978, 953, 916, 737, 698 cm<sup>-1</sup>; HRMS (FAB) found 427.1497 [calcd for C<sub>21</sub>H<sub>32</sub>O<sub>4</sub>Br (M+H)<sup>+</sup> 427.1484].

### Preparation of $\alpha,\alpha'$ -*trans*-Primary Alcohol **14**



To a solution of  $\alpha,\alpha'$ -*trans*-methoxy ether **4** (24.9 mg, 0.058 mmol) in anhydrous THF (5.8 mL, 0.01 M) was added palladium hydroxide on carbon (12.3 mg, 20 wt. % loading dry basis, 0.017 mmol) at room temperature under H<sub>2</sub>. After being stirred at room temperature for 30 min, the reaction mixture was filtered through a short pad of Celite<sup>TM</sup>. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, hexanes/EtOAc, 2/1) to afford  $\alpha,\alpha'$ -*trans*-primary alcohol **14** (19.3 mg, 98%) as a colorless oil: *R*<sub>f</sub> 0.10 (hexanes/EtOAc, 2/1); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +2.0° (*c* 0.85, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.44 (dd, *J* = 9.4, 9.4 Hz, 1 H), 4.19 (dd, *J* = 4.0, 9.7 Hz, 1 H), 3.98 (brs, 1 H), 3.87 (ddd, *J* = 2.6, 11.6, 11.6 Hz, 1 H), 3.62-3.72 (m, 3 H), 3.40-3.43 (m, 4 H), 2.90 (ddd, *J* = 1.3, 9.3, 15.5 Hz, 1 H), 2.47 (dd, *J* = 5.4, 15.4 Hz, 1 H), 2.22 (brs, 1 H), 2.19 (d, *J* = 15.5 Hz, 1 H), 1.90-1.99 (m, 2 H), 1.76-1.87 (m, 2 H), 1.61-1.79 (m, 3 H), 1.04 (dd, *J* = 7.3, 7.3 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  84.6, 83.3, 79.5, 76.8, 70.8, 62.9, 57.0, 51.8, 33.54, 33.51, 29.6, 25.7, 23.2, 11.8; IR (neat) 3398, 2933, 1458, 1380, 1241, 1151, 1123, 1063, 950, 916, 879, 855, 664 cm<sup>-1</sup>; HRMS (FAB) found 337.1024 [calcd for C<sub>14</sub>H<sub>26</sub>BrO<sub>4</sub> (M+H)<sup>+</sup> 337.1014].

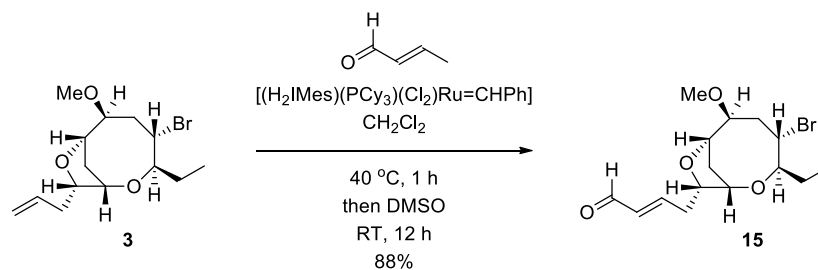
### Preparation of $\alpha,\alpha'$ -*trans*-Terminal Alkene **3**



To a solution of  $\alpha,\alpha'$ -*trans*-primary alcohol **14** (13.4 mg, 0.040 mmol) in anhydrous THF (3.97 mL, 0.01 M) were added *o*-nitrophenylselenocyanide (27.1 mg, 0.119 mmol) and tri-*n*-octylphosphine (0.118 mL, tech. 90%, 0.238 mmol) at room temperature under Ar. After being stirred at the same temperature for 30 min, hydrogen peroxide (0.25 mL, 30 wt. % in H<sub>2</sub>O) was added dropwise. The resulting mixture was stirred at room temperature for 21 h, dimethyl sulfide (0.25 mL) was added at 0 °C. The resulting mixture was allowed to stand at room temperature for 2 h, concentrated under reduced pressure, and diluted with EtOAc (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with

EtOAc (2 x 15 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 100/1) to afford  $\alpha,\alpha'$ -*trans*-terminal alkene **3** (11.7 mg, 92%) as colorless oil: *R<sub>f</sub>* 0.48 (hexanes/EtOAc, 4/1); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +15.2° (*c* 0.96, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  5.81 (dddd, *J* = 7.1, 7.1, 10.1, 14.2 Hz, 1 H), 5.15 (dd, *J* = 1.4, 17.2 Hz, 1 H), 5.06 (d, *J* = 10.2 Hz, 1 H), 4.45 (dd, *J* = 9.4, 9.4 Hz, 1 H), 4.19 (dd, *J* = 4.0, 9.7 Hz, 1 H), 3.96 (brs, 1 H), 3.88 (ddd, *J* = 2.4, 11.6, 11.6 Hz, 1 H), 3.71 (ddd, *J* = 1.4, 7.1, 7.1 Hz, 1 H), 3.44 (dd, *J* = 4.4, 4.4 Hz, 1 H), 3.40 (s, 3 H), 2.93 (dd, *J* = 9.3, 15.4 Hz, 1 H), 2.41-2.56 (m, 3 H), 2.18 (d, *J* = 15.4 Hz, 1 H), 1.90-1.99 (m, 2 H), 1.67 (dddd, *J* = 7.1, 7.1, 7.1, 14.2, 18.5 Hz, 1 H), 1.04 (dd, *J* = 7.4, 7.4 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  134.8, 117.1, 83.9, 83.2, 79.5, 76.9, 70.1, 57.0, 52.0, 33.6, 33.4, 33.4, 23.1, 11.7; IR (neat) 2967, 2934, 1643, 1460, 1381, 1153, 1101, 1065, 985, 917 cm<sup>-1</sup>; HRMS (FAB) found 319.0911 [calcd for C<sub>14</sub>H<sub>24</sub>BrO<sub>3</sub> (M+H)<sup>+</sup> 319.0909].

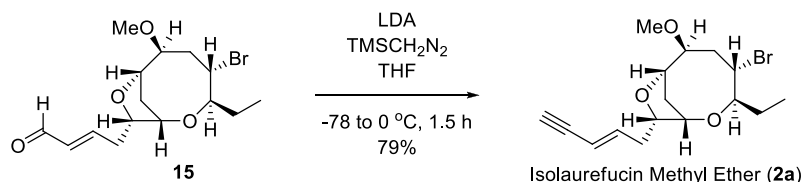
### Preparation of $\alpha,\alpha'$ -*trans*- $\alpha,\beta$ -*trans*-Enal **15**



To a solution of  $\alpha,\alpha'$ -*trans*-terminal alkene **3** (13.3 mg, 0.042 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.42 mL, 0.10 M) were added crotonaldehyde (0.034 mL, 0.417 mmol) and Grubbs 2<sup>nd</sup> catalyst (10.6 mg, 0.012 mmol) at room temperature under N<sub>2</sub>. The reaction mixture was gently refluxed at 40 °C (oil bath temperature) for 1 h. Dimethyl sulfoxide (0.1 mL) was added to the solution, and it was stirred open to the air for 12 h. The resulting mixture was concentrated *in vacuo* and the residue was purified by column chromatography (silica gel, hexanes/EtOAc, 4/1) to afford  $\alpha,\alpha'$ -*trans*- $\alpha,\beta$ -*trans*-enal **15** (12.8 mg, 88%) as a colorless oil: *R<sub>f</sub>* 0.12 (hexanes/EtOAc, 4/1); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -1.3° (*c* 0.79, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.52 (d, *J* = 7.8 Hz, 1 H), 6.87 (ddd, *J* = 7.1, 7.1, 15.6 Hz, 1 H), 6.22 (dd, *J* = 7.9, 15.7 Hz, 1 H), 4.44 (dd, *J* = 9.4, 9.4 Hz, 1 H), 4.21 (dd, *J* = 4.0, 9.7 Hz, 1 H), 3.99 (brs, 1 H), 3.88 (ddd, *J* = 2.5, 11.6, 11.6 Hz, 1 H), 3.82 (ddd, *J* = 1.6, 7.6, 7.6 Hz, 1 H), 3.41-3.44 (m, 4 H), 2.70-2.89 (m, 3 H), 2.49 (dd, *J* = 5.3, 15.5 Hz, 1 H), 2.23 (d, *J* = 15.5 Hz, 1 H), 1.90-2.04 (m, 2 H), 1.61-1.74 (m, 1 H), 1.03 (dd, *J* = 7.3, 7.3 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  193.9, 154.7, 134.6, 83.4, 82.4, 79.3, 77.2, 70.5, 57.0, 51.5,

33.6, 33.3, 32.6, 23.1, 11.8; IR (neat) 2966, 2933, 1691, 1460, 1381, 1306, 1151, 1124, 1099, 1065, 977, 917, 878, 768, 734  $\text{cm}^{-1}$ ; HRMS (FAB) found 347.0866 [calcd for  $\text{C}_{15}\text{H}_{24}\text{BrO}_4$  ( $\text{M}+\text{H}$ )<sup>+</sup> 347.0858].

### Preparation of (+)-(3E)-Isolaurefucin Methyl Ether (2a)



To a cooled ( $-78\text{ }^{\circ}\text{C}$ ) solution of LDA (0.74 mL, 0.5 M solution in THF, 0.369 mmol) was added dropwise trimethylsilyldiazomethane (0.18 mL, 2.0 M solution in Et<sub>2</sub>O, 0.369 mmol) under Ar. After being stirred at the same temperature for 30 min, *trans*- $\alpha,\beta$ -unsaturated aldehyde **15** (12.8 mg, 0.037 mmol) in THF (0.74 mL, 0.05 M) was dropwise added at  $-78\text{ }^{\circ}\text{C}$ . After the reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 1 h, and then at  $0\text{ }^{\circ}\text{C}$  for 30 min, the reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (1 mL). The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O (2 x 5 mL). The organic layers were washed with saturated brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 80/1) to afford (+)-(3E)-isolaurefucin methyl ether (**2a**) (10.0 mg, 79%) as colorless oil:  $R_f$  0.39 (hexanes/EtOAc, 4/1);  $[\alpha]_D^{25} = +9.5^{\circ}$  ( $c$  1.04,  $\text{CHCl}_3$ ) {lit.<sup>1</sup>  $[\alpha]_D = +12.0^{\circ}$  ( $c$  0.30,  $\text{CHCl}_3$ )}; <sup>1</sup>H NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.22 (ddd,  $J = 7.5, 7.5, 15.5$  Hz, 1 H), 5.59 (dd,  $J = 1.8, 16.0$  Hz, 1 H), 4.43 (dd,  $J = 9.4, 9.4$  Hz, 1 H), 4.19 (dd,  $J = 4.0, 9.7$  Hz, 1 H), 3.96 (brs, 1 H), 3.87 (ddd,  $J = 2.5, 11.6, 11.6$  Hz, 1 H), 3.70 (ddd,  $J = 1.6, 7.2, 7.2$  Hz, 1 H), 3.42 (dd,  $J = 4.3, 4.3$  Hz, 1 H), 3.40 (s, 3 H), 2.89 (ddd,  $J = 1.2, 9.3, 15.4$  Hz, 1 H), 2.80 (d,  $J = 2.1$  Hz, 1 H), 2.56-2.62 (m, 1 H), 2.45-2.52 (m, 2 H), 2.18 (d,  $J = 15.4$  Hz, 1 H), 1.90-1.98 (m, 2 H), 1.61-1.71 (m, 1 H), 1.04 (dd,  $J = 7.3, 7.3$  Hz, 3 H); <sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  142.3, 111.1, 83.3, 83.2, 82.2, 79.4, 77.3, 76.3, 70.1, 57.0, 51.8, 33.6, 33.4, 32.7, 23.1, 11.8; IR (neat) 3291, 2966, 2934, 1731, 1460, 1381, 1306, 1204, 1152, 1099, 1065, 955, 918, 879, 767  $\text{cm}^{-1}$ ; HRMS (FAB) found 343.0909 [calcd for  $\text{C}_{16}\text{H}_{24}\text{BrO}_3$  ( $\text{M}+\text{H}$ )<sup>+</sup> 343.0898].

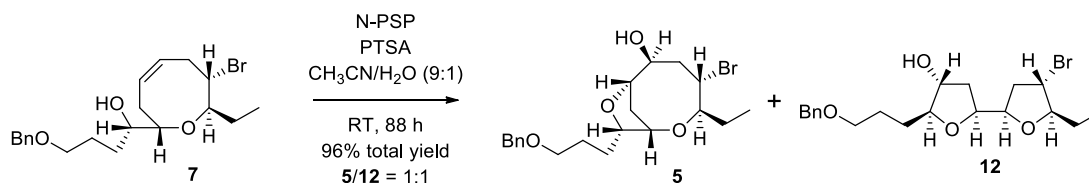
**Table 1.** Comparative <sup>13</sup>C NMR data for (+)-(3E)-Isolaurefucin Methyl Ether (**2a**)

Carbon No.	Natural (Bowden) <sup>1</sup> 135 MHz, $\text{CDCl}_3$	$\Delta\delta$ Nat. – Syn.	Synthetic (Kim) 125 MHz, $\text{CDCl}_3$
1	76.4 (d)	0.1	76.3

<b>2</b>	82.8 (s)	0.6	82.2
<b>3</b>	111.3 (d)	0.2	111.1
<b>4</b>	141.2 (d)	-1.1	142.3
<b>5</b>	32.5 (t)	-0.2	32.7
<b>6</b>	83.3 (d)	0.1	83.2
<b>7</b>	70.0 (d)	-0.1	70.1
<b>8</b>	33.2 (t)	-0.2	33.4
<b>9</b>	76.4 (d)	-0.4	77.0
<b>10</b>	79.4 (d)	0	79.4
<b>11</b>	33.6 (t)	0	33.6
<b>12</b>	51.8 (d)	0	51.8
<b>13</b>	83.2 (d)	-0.1	83.3
<b>14</b>	23.1 (t)	0	23.1
<b>15</b>	11.8 (q)	0	11.8
<b>OMe</b>	57.0 (q)	0	57.0

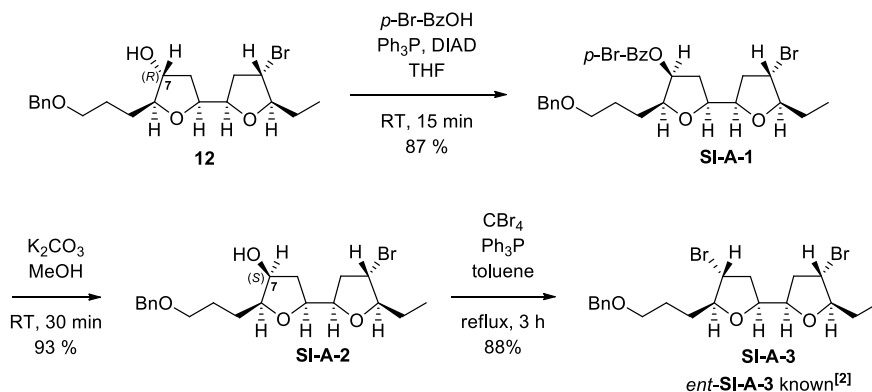
## Organoselenium-mediated Alkoxyetherification Route: S9 ~ S14

### Preparation of $\alpha,\alpha'$ -*trans*-Hydroxy Ether **5** and bis-Tetrahydrofuranyl Alcohol **12**



To a solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (48.0 mg, 0.121 mmol) in CH<sub>3</sub>CN/H<sub>2</sub>O (9:1, total 24 mL, 0.005 M) were successively added *N*-phenylselenophthalimide (110.0 mg, 0.363 mmol) and *p*-toluenesulfonic acid (4.6 mg, 0.024 mmol) at room temperature. After the reaction mixture was stirred at the same temperature for 40 h, additional *N*-phenylselenophthalimide (110 mg, 0.363 mmol) and *p*-toluenesulfonic acid (4.6 mg, 0.024 mmol) were added and stirred for 48 h. The reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl (20 mL) and diluted with EtOAc (30 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 30 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 2/1) to afford  $\alpha,\alpha'$ -*trans*-hydroxy ether **5** and bis-tetrahydrofuranyl alcohol **12** (48.0 mg, 96% total yield, **5/12** = 1:1 by <sup>1</sup>H NMR analysis): **For bis-tetrahydrofuranyl alcohol 12**; R<sub>f</sub> 0.23 (CH<sub>2</sub>Cl<sub>2</sub>/MeOAc, 5/1); colorless oil; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +0.03° (*c* 0.90, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.26-7.36 (m, 5 H), 4.50 (s, 2 H), 4.04-4.12 (m, 3 H), 4.00 (ddd, *J* = 5.3, 5.3, 7.2 Hz, 1 H), 3.95 (ddd, *J* = 5.1, 5.1, 6.9 Hz, 1 H), 3.75 (ddd, *J* = 3.4, 6.5, 7.3 Hz, 1 H), 3.48-3.54 (m, 2 H), 2.25-2.36 (m, 2 H), 1.86-1.97 (m, 3 H), 1.46-1.80 (m, 5 H), 0.98 (dd, *J* = 7.5, 7.5 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.3, 128.4, 127.7, 127.6, 88.6, 86.5, 79.8, 79.3, 75.8, 73.0, 70.2, 49.1, 38.7, 37.4, 31.0, 26.7, 26.1, 10.0; IR (neat) 3424, 2929, 1069 cm<sup>-1</sup>; HRMS (FAB) found 413.1319 [calcd for C<sub>20</sub>H<sub>30</sub>O<sub>4</sub>Br (M+H)<sup>+</sup> 413.1327].

### SI-A-Scheme 1: Structure Determination of bis-Tetrahydrofuranyl Alcohol **12**



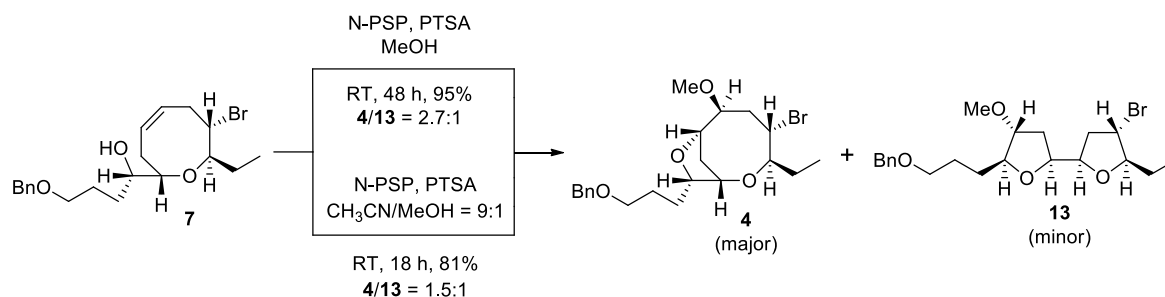
**[Conversion 12 to SI-A-1]** To a solution of bis-tetrahydrofuranyl alcohol **12** (16.0 mg, 0.038 mmol) in THF (3.8 mL, 0.01 M) was successively added triphenylphosphine (50.0 mg 0.038 mmol), 4-bromobenzoic acid (39.0 mg, 0.193 mmol) and diisopropyl azodicarboxylate (0.046 mL, 0.232 mmol) at room temperature under Ar. After being stirred at the same temperature for 15 min, the reaction mixture was quenched with H<sub>2</sub>O (10 mL) and diluted with EtOAc (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed successively H<sub>2</sub>O with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 15/1 to 6/1) to afford bis-THF PBB ester **SI-A-1** (20.0 mg, 87%) as a colorless oil:  $R_f$  0.60 (hexanes/EtOAc, 3/1);  $[\alpha]_D^{25} = +22.9^\circ$  ( $c$  1.07, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.88 (d,  $J = 8.5$  Hz, 2 H), 7.56 (d,  $J = 8.5$  Hz, 2 H), 7.25-7.31 (m, 5 H), 5.46-5.48 (m, 1 H), 4.42-4.47 (m, 2 H), 4.19 (ddd,  $J = 6.7, 6.7, 6.7$  Hz, 1 H), 3.97-4.01 (m, 2 H), 3.93 (ddd,  $J = 5.9, 5.9, 8.4$  Hz, 1 H), 3.85-3.88 (m, 1 H), 3.43-3.50 (m, 2 H), 2.53 (ddd,  $J = 6.7, 8.3, 14.8$  Hz, 1 H), 2.39-2.44 (m, 1 H), 2.30-2.35 (m, 1 H), 1.96 (ddd,  $J = 1.3, 6.0, 14.7$  Hz, 1 H), 1.73-1.82 (m, 3 H), 1.59-1.69 (m, 2 H), 1.44-1.52 (m, 1 H), 0.94 (dd,  $J = 7.4, 7.4$  Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  165.2, 138.5, 131.8, 131.1, 128.9, 128.3, 127.53, 127.49, 88.6, 82.0, 79.6, 79.1, 75.3, 72.8, 69.9, 49.1, 38.8, 36.0, 26.6, 26.5, 25.9, 9.9; IR (neat) 2936, 2873, 1720, 1270, 1103, 756 cm<sup>-1</sup>; HRMS (FAB) found 595.0707 [calcd for C<sub>27</sub>H<sub>33</sub>O<sub>5</sub>Br<sub>2</sub> (M+H)<sup>+</sup> 595.0695].

**[Conversion SI-A-1 to SI-A-2]** To a solution of bis-THF PBB ester **SI-A-1** (14.0 mg, 0.023 mmol) in MeOH (0.47 mL, 0.05 M) was added potassium carbonate (10.0 mg, 0.070 mmol) at room temperature. After being stirred at the same temperature for 30 min, the reaction mixture was quenched by saturated aqueous NH<sub>4</sub>Cl (5 mL) and diluted with EtOAc (10 mL) and H<sub>2</sub>O (3 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed successively with H<sub>2</sub>O and saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in*

*vacuo*. The residue was purified by column chromatography (silica gel; hexanes/EtOAc, 20/1) to give (7*S*)-bis-tetrahydrofuranyl alcohol **SI-A-2** (9.0 mg, 93%) as a colorless oil:  $R_f$  0.21 (hexanes/EtOAc, 3/1);  $[\alpha]_D^{25} = +21.9^\circ$  ( $c$  0.64,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25-7.35 (m, 5 H), 4.50 (s, 2 H), 4.39-4.42 (m, 1 H), 4.08-4.15 (m, 2 H), 4.01 (ddd,  $J = 2.3, 5.1, 10.6$  Hz, 1 H), 3.92 (ddd,  $J = 4.8, 4.8, 8.1$  Hz, 1 H), 3.61-3.64 (m, 1 H), 3.51-3.55 (m, 2 H), 3.39 (d,  $J = 10.7$  Hz, 1 H, OH), 2.21-2.29 (m, 2 H), 2.09 (ddd,  $J = 8.5, 8.5, 14.1$  Hz, 1 H), 1.67-1.81 (m, 6 H), 1.54-1.62 (m, 1 H), 1.01 (dd,  $J = 7.5, 7.5$  Hz, 3 H);  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 128.3, 127.6, 127.5, 89.0, 84.0, 79.0, 78.0, 72.9, 71.2, 70.3, 48.0, 38.8, 34.9, 26.4, 25.5, 10.2; HRMS (FAB) found 413.1332 [calcd for  $\text{C}_{20}\text{H}_{30}\text{O}_4\text{Br}$  ( $\text{M}+\text{H}$ ) $^+$  413.1327].

**[Conversion SI-A-2 to SI-A-3]** To a solution of (7*S*)-bis-tetrahydrofuranyl alcohol **SI-A-2** (7.0 mg, 0.017 mmol) in anhydrous toluene (0.7 mL, 0.025 M) were added triphenylphosphine (22.0 mg, 0.084 mmol) and carbon tetrabromide (28.0 mg, 0.084 mmol) at room temperature under  $\text{N}_2$ . After being stirred at 90 °C (oil bath temperature) for 3 h, the reaction mixture was quenched by addition of  $\text{H}_2\text{O}$  (2 mL) and diluted with EtOAc (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed successively with  $\text{H}_2\text{O}$  and saturated brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel; hexanes/EtOAc, 30/1 to 5/1) to afford bis-tetrahydrofuranyl bromide **SI-A-3** (7.0 mg, 88%) as a colorless oil:  $R_f$  0.52 (hexanes/EtOAc, 10/1);  $[\alpha]_D^{25} = -8.6^\circ$  ( $c$  0.50,  $\text{CH}_2\text{Cl}_2$ ) [lit.<sup>2</sup>  $[\alpha]_D^{25} = +9.5^\circ$  ( $c$  1.15,  $\text{CH}_2\text{Cl}_2$ ) for *ent*-**SI-A-3**]. The spectral data were in accordance with those of the enantiomer.<sup>[2]</sup>

### Preparation of $\alpha,\alpha'$ -*trans*-Methoxy Ether **4** and bis-Tetrahydrofuranyl Methyl Ether **13**

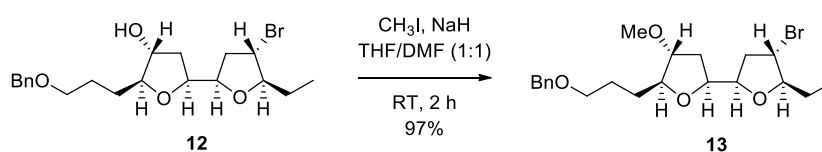


**[MeOH only]** To a solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (48.0 mg, 0.121 mmol) in anhydrous MeOH (24 mL, 0.005 M) were added *N*-phenylselenophthalimide (110.0 mg, 0.363 mmol) and *p*-toluenesulfonic acid (4.6 mg, 0.024 mmol) at room temperature under Ar. After being stirred at the same temperature for 48 h, the reaction was quenched with saturated aqueous  $\text{NaHCO}_3$  (20 mL) and

diluted with EtOAc (30 mL) and H<sub>2</sub>O (10 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 15/1 to 5/1) to afford  $\alpha,\alpha'$ -*trans*-methoxy ether **4** and bis-tetrahydrofuranyl methyl ether **13** (49.0 mg, 95% total yield, **4/13** = 2.7:1 by <sup>1</sup>H NMR analysis): **For bis-tetrahydrofuranyl methyl ether 13**; R<sub>f</sub> 0.31 (hexanes/EtOAc, 5/1); colorless oil; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = -4.7° (*c* 0.14, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.36 (m, 5 H), 4.50 (s, 2 H), 4.09 (ddd, *J* = 7.0, 7.0, 7.0 Hz, 1 H), 3.94-4.02 (m, 3 H), 3.84 (ddd, *J* = 3.1, 5.8, 8.0 Hz, 1 H), 3.58 (ddd, *J* = 2.3, 2.3, 5.5 Hz, 1 H), 3.46-3.54 (m, 2 H), 3.30 (s, 3 H), 2.27-2.37 (m, 2 H), 2.03 (ddd, *J* = 2.1, 5.8, 13.3 Hz, 1 H), 1.71-1.79 (m, 2 H), 1.59-1.69 (m, 3 H), 1.47-1.59 (m, 2 H), 0.98 (dd, *J* = 7.5, 7.5 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 128.3, 127.6, 127.5, 88.6, 85.3, 83.9, 79.9, 79.7, 72.9, 70.1, 56.8, 49.2, 38.9, 34.4, 31.2, 29.7, 26.7, 26.2, 10.0; IR (neat) 2928, 2876, 1454, 1073, 736, 698 cm<sup>-1</sup>; HRMS (FAB) found 427.1482 [calcd for C<sub>21</sub>H<sub>32</sub>O<sub>4</sub>Br (M+H)<sup>+</sup> 427.1484].

**[CH<sub>3</sub>CN/MeOH (9:1)]** To a solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (8.0 mg, 0.020 mmol) in anhydrous CH<sub>3</sub>CN/MeOH (9:1, total 4.0 mL, 0.005 M) were added *N*-phenylselenophthalimide (18.0 mg, 0.060 mmol) and *p*-toluenesulfonic acid (0.7 mg, 0.004 mmol) at room temperature under Ar. After being stirred at the same temperature for 18 h, the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> (10 mL) and diluted with EtOAc (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 15/1 to 5/1) to afford  $\alpha,\alpha'$ -*trans*-methoxy ether **4** and bis-THF methyl ether **13** (7.0 mg, 81% total yield, **4/13** = 1.5:1 by <sup>1</sup>H NMR analysis).

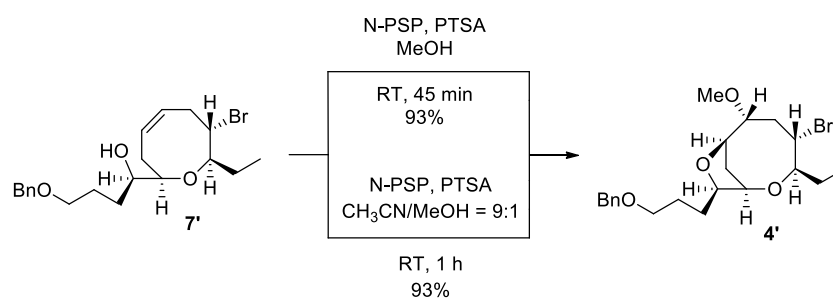
### SI-A-Scheme 2: Structure Determination of bis-Tetrahydrofuranyl Methyl Ether **13**



To a solution of bis-tetrahydrofuranyl alcohol **12** (2.0 mg, 0.0048 mmol) in anhydrous THF/DMF (1:1, total 0.24 mL, 0.02 M) were added sodium hydride (3.0 mg, 60% dispersion in mineral oil, 0.072 mmol) and methyl iodide (20.0 mg, 0.145 mmol) at room temperature under N<sub>2</sub>. After being stirred at the same

temperature for 2 h, the reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (3 mL) and diluted with EtOAc (10 mL) and  $\text{H}_2\text{O}$  (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with saturated brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ EtOAc, 30/1 to 5/1) to afford bis-tetrahydrofuranyl methyl ether **13** (2.0 mg, 97%).

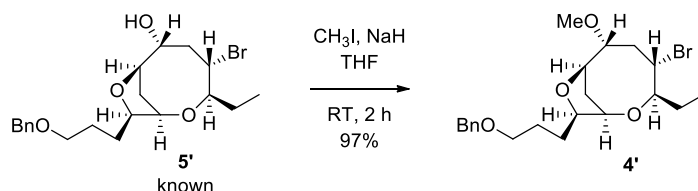
### Preparation of $\alpha,\alpha'$ -*cis*-Methoxy Ether **4'**



**[MeOH only]** To a solution of  $\alpha,\alpha'$ -*cis*- $\gamma,\delta$ -unsaturated oxocene alcohol **7'** (7.0 mg, 0.017 mmol) in anhydrous MeOH (3.5 mL, 0.005 M) were added *N*-phenylselenophthalimide (16.0 mg, 0.053 mmol) and *p*-toluenesulfonic acid (0.7 mg, 0.0035 mmol) at room temperature under Ar. After being stirred at the same temperature for 45 min, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  (10 mL), and diluted with EtOAc (10 mL) and  $\text{H}_2\text{O}$  (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with saturated brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 20/1 to 5/1) to afford  $\alpha,\alpha'$ -*cis*-methoxy ether **4** (7.0 mg, 93%) as a colorless oil:  $R_f$  0.36 (hexanes/EtOAc, 5/1);  $[\alpha]_D^{25} = -48.5^\circ$  ( $c$  0.50,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.36 (m, 5 H), 4.51 (s, 2 H), 4.15 (dd,  $J = 3.5, 7.7$  Hz, 1 H), 3.99 (brs, 1 H), 3.72-3.80 (m, 2 H), 3.50-3.53 (m, 2 H), 3.43-3.47 (m, 1 H), 3.38 (s, 3 H), 3.34 (dd,  $J = 3.5, 10.0$  Hz, 1 H), 2.47 (d,  $J = 14.1$  Hz, 1 H), 2.31 (dd,  $J = 4.8, 14.9$  Hz, 1 H), 2.09-2.17 (m, 2 H), 1.86 (ddd,  $J = 2.0, 7.8, 14.1$  Hz, 1 H), 1.64-1.77 (m, 4 H), 1.44-1.53 (m, 1 H), 0.95 (dd,  $J = 7.3, 7.3$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.6, 128.3, 127.6, 127.5, 88.1, 83.2, 82.5, 80.3, 77.1, 72.8, 70.4, 57.0, 52.9, 41.7, 33.8, 28.1, 26.5, 26.4, 9.6; IR (neat) 2933, 1465, 1455, 1098, 1066, 698  $\text{cm}^{-1}$ ; HRMS (FAB) found 427.1471 [calcd for  $\text{C}_{21}\text{H}_{32}\text{O}_4\text{Br}$  ( $\text{M}+\text{H}$ ) $^+$  427.1484].

[CH<sub>3</sub>CN/MeOH (9:1)] To a solution of  $\alpha,\alpha'$ -*cis*- $\gamma,\delta$ -unsaturated oxocene alcohol **7'** (5.0 mg, 0.012 mmol) in anhydrous CH<sub>3</sub>CN/MeOH (9:1, total 2.5 mL, 0.005 M) were added *N*-phenylselenophthalimide (12.0 mg, 0.037 mmol) and *p*-toluenesulfonic acid (0.5 mg, 0.0025 mmol) at room temperature under Ar. After being stirred at the same temperature for 1 h, the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> (10 mL), and diluted with EtOAc (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 20/1 to 5/1) to afford  $\alpha,\alpha'$ -*cis*-methoxy ether **4'** (5.0 mg, 93%).

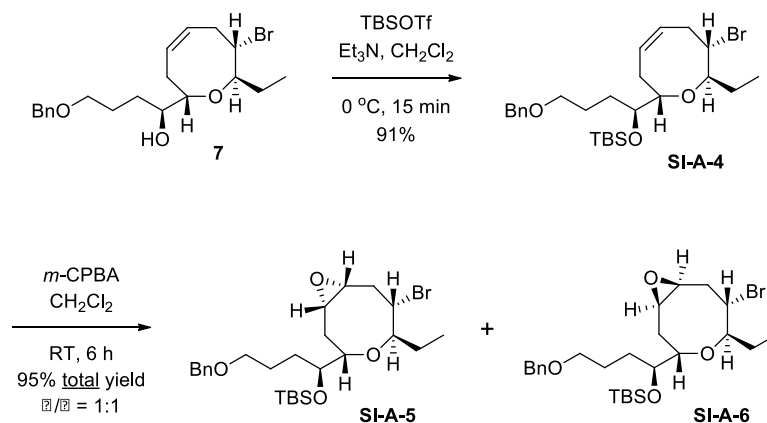
**SI-A-Scheme 3:** Structure Determination of  $\alpha,\alpha'$ -*cis*-Methoxy Ether **4'**



To a solution of known<sup>3</sup>  $\alpha,\alpha'$ -*cis*-hydroxy ether **5'** (4.0 mg, 0.0096 mmol) in anhydrous THF (0.2 mL, 0.05 M) were added sodium hydride (1.2 mg, 60% dispersion in mineral oil, 0.029 mmol) and methyl iodide (3.0 mg, 0.019 mmol) at room temperature under N<sub>2</sub>. After being stirred at the same temperature for 2 h, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl (3 mL), and diluted with EtOAc (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 30/1 to 5/1) to afford  $\alpha,\alpha'$ -*cis*-methoxy ether **4'** (4.0 mg, 97%).

## Epoxidation of Protected Oxocenes: S15 ~ S18

### Preparation of TBS-Protected Oxocene SI-A-4 and TBS-Protected- $\alpha$ - and $\beta$ -Epoxide SI-A-5 and SI-A-6

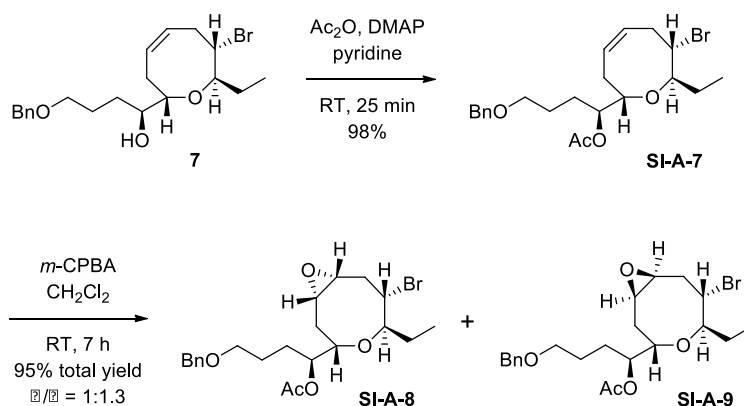


**[Conversion 7 to SI-A-4]** To a cooled (0 °C) solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (30.0 mg, 0.075 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (1.5 mL, 0.05 M) were added triethylamine (0.02 mL, 0.151 mmol) and trimethylsilyl trifluoromethanesulfonate (0.04 mL, 0.151 mmol). After being stirred at the same temperature for 15 min, the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> (5 mL), and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 20 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 40/1) to afford TBS-protected oxocene **SI-A-4** (35.0 mg, 91%) as a colorless oil: *R*<sub>f</sub> 0.51 (hexanes/EtOAc, 15/1); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +34.4° (*c* 1.10, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.37 (m, 5 H), 5.77-5.81 (m, 1 H), 5.66-5.71 (m, 1 H), 4.50 (s, 2 H), 4.09 (ddd, *J* = 3.1, 6.2, 9.5 Hz, 1 H), 3.96 (ddd, *J* = 2.8, 7.7, 10.2 Hz, 1 H), 3.88 (m, 1 H), 3.62 (ddd, *J* = 3.0, 7.0, 7.0 Hz, 1 H), 3.47 (dd, *J* = 6.5, 6.5 Hz, 2 H), 3.00-3.07 (m, 1 H), 2.65 (ddd, *J* = 7.7, 7.7, 15.3 Hz, 1 H), 2.52 (ddd, *J* = 6.0, 11.2, 16.8 Hz, 1 H), 2.15-2.19 (m, 1 H), 1.98-2.03 (m, 1 H), 1.74-1.82 (m, 1 H), 1.57-1.69 (m, 2 H), 1.44-1.49 (m, 1 H), 0.96 (dd, *J* = 7.4, 7.4 Hz, 3 H), 0.90 (s, 9 H), 0.60 (d, *J* = 3.3 Hz, 6 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 130.2, 128.3, 127.54, 127.46, 126.6, 77.7, 76.1, 75.8, 72.8, 70.4, 56.0, 35.4, 29.7, 29.5, 26.7, 26.5, 25.8, 18.0, 8.9, -4.4, -4.6; IR (neat) 2953, 2856, 1456, 1362, 1254, 1104, 1074, 836, 774 cm<sup>-1</sup>; HRMS (FAB) found 511.2234 [calcd for C<sub>26</sub>H<sub>44</sub>O<sub>3</sub>BrSi (M+H)<sup>+</sup> 511.2243].

**[*m*-CPBA Epoxidation]** To a solution of TBS-protected oxocene **SI-A-4** (14.0 mg, 0.027 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (2.7 mL, 0.01 M) was added 3-chloroperoxybenzoic acid (18.4 mg,  $\leq$  77% purity, 0.082 mmol) at room temperature under Ar. After being stirred at the same temperature for 6 h, the

reaction mixture was quenched with 1N NaOH (5 mL), and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 20 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 30/1 to 15/1) to afford TBS-protected  $\alpha$ -epoxide **SI-A-5** and  $\beta$ -epoxide **SI-A-6** (13.7 mg, 95% total yield,  $\alpha/\beta$  = 1:1 by <sup>1</sup>H NMR analysis): **For TBS-protected- $\alpha$ -epoxide SI-A-5**; R<sub>f</sub> 0.35 (hexanes/EtOAc, 15/1); colorless oil; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +2.7° (*c* 0.78, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.36 (m, 5 H), 4.50 (s, 2 H), 4.35 (dd, *J* = 3.4, 3.4, 9.8 Hz, 1 H), 3.89 (ddd, *J* = 2.0, 10.0, 12.2 Hz, 1 H), 3.75-3.78 (m, 1 H), 3.56-3.58 (m, 1 H), 3.45-3.52 (m, 2 H), 3.06-3.10 (m, 2 H), 2.98-3.02 (m, 1 H), 2.06-2.10 (m, 1 H), 1.86-1.96 (m, 5 H), 1.57-1.66 (m, 3 H), 0.92 (dd, *J* = 7.4, 7.4 Hz, 3 H), 0.90 (s, 9 H), 0.06 (d, *J* = 9.5 Hz, 6 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  138.5, 128.3, 127.5, 78.3, 74.1, 72.8, 70.2, 55.7, 53.6, 47.9, 41.1, 31.3, 29.9, 27.3, 26.4, 25.8, 17.9, 5.7, -4.3, -4.9; IR (neat) 2953, 2857, 1461, 1255, 1074, 1010, 836, 775 cm<sup>-1</sup>; HRMS (FAB) found 527.2198 [calcd for C<sub>26</sub>H<sub>44</sub>O<sub>4</sub>BrSi (M+H)<sup>+</sup> 527.2192]; **For TBS-protected- $\beta$ -epoxide SI-A-6**; R<sub>f</sub> 0.45 (hexanes/EtOAc, 4/1); colorless oil; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +36.2° (*c* 0.84, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.36 (m, 5 H), 4.96 (s, 2 H), 3.92 (ddd, *J* = 2.7, 4.5, 10.0 Hz, 1 H), 3.83 (ddd, *J* = 3.2, 3.2, 8.7 Hz, 1 H), 3.74-3.79 (m, 1 H), 3.58 (ddd, *J* = 3.7, 3.7, 7.6 Hz, 1 H), 3.47 (dd, *J* = 6.2, 6.2 Hz, 2 H), 3.20-3.26 (m, 2 H), 2.77 (ddd, *J* = 4.9, 4.9, 19.3 Hz, 1 H), 2.17-2.32 (m, 3 H), 2.00-2.10 (m, 1 H), 1.63-1.80 (m, 2 H), 1.43-1.63 (m, 2 H), 1.32-1.40 (m, 1 H), 0.97 (dd, *J* = 7.4, 7.4 Hz, 3 H), 0.89 (s, 9 H), 0.05 (d, *J* = 3.6 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 128.3, 127.6, 127.5, 76.8, 74.8, 73.0, 72.8, 70.4, 54.0, 53.9, 53.1, 34.0, 28.6, 27.6, 26.4, 26.2, 25.9, 18.1, 10.6, -4.4, -4.5; IR (neat) 2955, 2931, 2856, 1454, 1362, 1254, 1105, 1065, 835, 775 cm<sup>-1</sup>; HRMS (FAB) found 527.2176 [calcd for C<sub>26</sub>H<sub>44</sub>O<sub>4</sub>BrSi (M+H)<sup>+</sup> 527.2192].

**Preparation of Ac-Protected Oxocene SI-A-7 and Ac-Protected- $\alpha$ - and  $\beta$ -Epoxide SI-A-8 and SI-A-9**



**[Conversion 7 to SI-A-7]** To a solution of  $\alpha,\alpha'$ -*trans*- $\gamma,\delta$ -unsaturated oxocene alcohol **7** (40.6 mg, 0.204 mmol) in anhydrous pyridine (0.2 mL, 0.5 M) were added acetic anhydride (0.02 mL, 0.204 mmol) and 4-(dimethylamino)pyridine (6.2 mg, 0.051 mmol) at room temperature under Ar. After being stirred at the same temperature for 25 min, the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> (5 mL), and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 20 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 10/1 to 5/1) to afford Ac-protected oxocene **SI-A-7** (44.0 mg, 98%) as a colorless oil: *R<sub>f</sub>* 0.50 (hexanes/EtOAc, 4/1); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +25.1° (*c* 0.96, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.27-7.36 (m, 5 H), 5.70-5.77 (m, 2 H), 4.94 (ddd, *J* = 4.5, 4.5, 8.5 Hz, 1 H), 4.49 (s, 2 H), 4.01-4.09 (m, 2 H), 3.87-3.89 (m, 1 H), 3.48 (dd, *J* = 6.3, 6.3 Hz, 2 H), 3.02-3.07 (m, 1 H), 2.58-2.64 (m, 1 H), 2.25-2.38 (m, 2 H), 1.83-1.90 (m, 1 H), 1.67-1.81 (m, 3 H), 1.61-1.67 (m, 2 H), 0.97 (dd, *J* = 7.4, 7.4 Hz, 3 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  170.7, 138.5, 128.8, 128.4, 127.61, 127.55, 127.3, 77.1, 75.5, 75.3, 72.9, 69.8, 55.8, 34.6, 30.4, 27.6, 26.4, 25.7, 21.1, 8.8; IR (neat) 2938, 2858, 1737, 1454, 1370, 1239, 1103 cm<sup>-1</sup>; HRMS (FAB) found 439.1476 [calcd for C<sub>22</sub>H<sub>32</sub>O<sub>4</sub>Br (M+H)<sup>+</sup> 439.1484].

**[*m*-CPBA Epoxidation]** To a solution of Ac-protected oxocene **SI-A-7** (15.3 mg, 0.034 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (3.5 mL, 0.01 M) was added 3-chloroperoxybenzoic acid (23.4 mg,  $\leq$  77% purity, 0.104 mmol) at room temperature Ar. After being stirred at the same temperature for 7 h, the reaction mixture was quenched with 1N NaOH (5 mL), and diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and H<sub>2</sub>O (5 mL). The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 x 20 mL). The organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/EtOAc, 30/1 to 15/1) to afford TBS-

protected  $\alpha$ -epoxide **SI-A-8** and  $\beta$ -epoxide **SI-A-9** (15.0 mg, 95% total yield,  $\alpha/\beta = 1:1.3$  by  $^1\text{H}$  NMR analysis). **For Ac-protected- $\alpha$ -epoxide SI-A-8**;  $R_f$  0.30 (hexanes/EtOAc, 4/1); colorless oil;  $[\alpha]_D^{24} = -21.0^\circ$  ( $c$  0.60,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.36 (m, 5 H), 4.91-4.95 (m, 1 H), 4.47-4.52 (m, 2 H), 3.91-3.97 (m, 2 H), 3.85 (ddd,  $J = 2.8, 2.8, 9.4$  Hz, 1 H), 3.48 (dd,  $J = 6.2, 6.2$  Hz, 2 H), 2.98-3.09 (m, 3 H), 2.05-2.16 (m, 3 H), 1.83-1.92 (m, 1 H), 1.76-1.83 (m, 1 H), 1.59-1.73 (m, 4 H), 1.49-1.58 (m, 1 H), 0.93 (dd,  $J = 7.4, 7.4$  Hz, 3 H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 138.4, 128.4, 127.6, 77.8, 75.0, 74.8, 72.9, 69.6, 55.0, 53.3, 47.5, 40.7, 28.8, 28.2, 27.7, 25.3, 21.1, 5.9; IR (neat) 2965, 1737, 1461, 1370, 1239, 1102, 698  $\text{cm}^{-1}$ ; HRMS (FAB) found 477.1247 [calcd for  $\text{C}_{22}\text{H}_{31}\text{O}_5\text{BrNa}$  ( $\text{M}+\text{Na}$ ) $^+$  477.1253]; **For Ac-protected- $\beta$ -epoxide SI-A-9**;  $R_f$  0.30 (hexanes/EtOAc, 4/1); colorless oil;  $[\alpha]_D^{24} = +32.5^\circ$  ( $c$  0.95,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27-7.36 (m, 5 H), 4.86-4.91 (m, 1 H), 4.49 (s, 2 H), 3.91-3.96 (m, 2 H), 3.74-3.79 (m, 1 H), 3.47 (dd,  $J = 6.3, 6.3$  Hz, 2 H), 3.25 (ddd,  $J = 5.1, 5.1, 7.5$  Hz, 1 H), 3.15 (ddd,  $J = 3.8, 3.8, 3.8$  Hz, 1 H), 2.76 (ddd,  $J = 5.0, 5.0, 15.5$  Hz, 1 H), 2.21-2.29 (m, 2 H), 2.08-2.16 (m, 1 H), 1.96-2.05 (m, 2 H), 1.66-1.82 (m, 2 H), 1.48-1.66 (m, 3 H), 0.99 (dd,  $J = 7.3, 7.3$  Hz, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 138.4, 128.4, 127.60, 127.55, 76.9, 75.7, 72.9, 71.6, 69.7, 53.9, 53.3, 52.3, 33.8, 29.6, 27.2, 26.0, 25.8, 21.0, 9.9; IR (neat) 2935, 2874, 1736, 1454, 1370, 1240, 1104, 1063, 739, 699  $\text{cm}^{-1}$ ; HRMS (FAB) found 455.1443 [calcd for  $\text{C}_{22}\text{H}_{32}\text{O}_5\text{Br}$  ( $\text{M}+\text{H}$ ) $^+$  455.1433].

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– Supporting Information: Part B –

**Asymmetric Total Synthesis and Structure Confirmation of  
(+)-(3*E*)-Isolaurefucin Methyl Ether**

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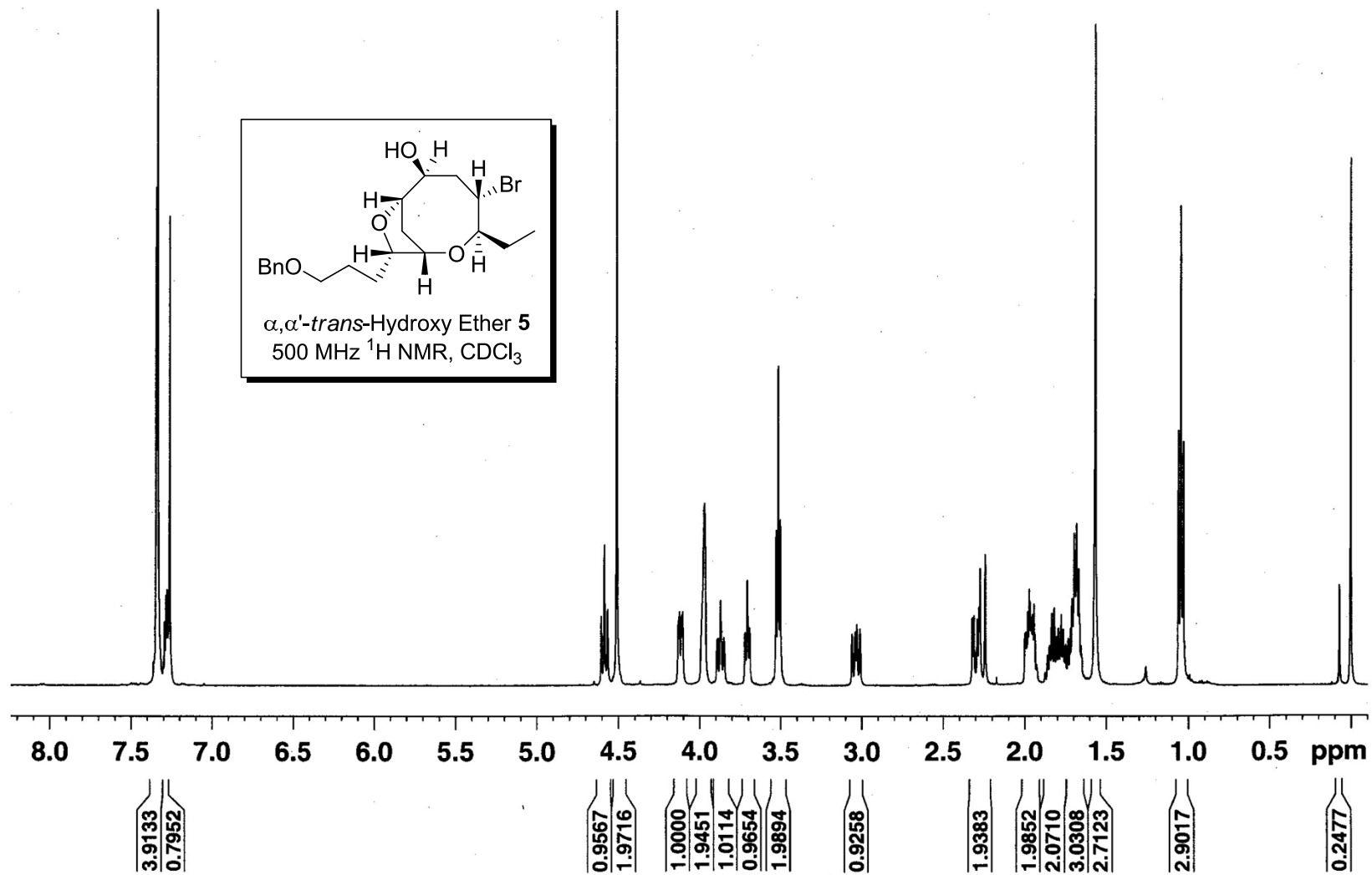
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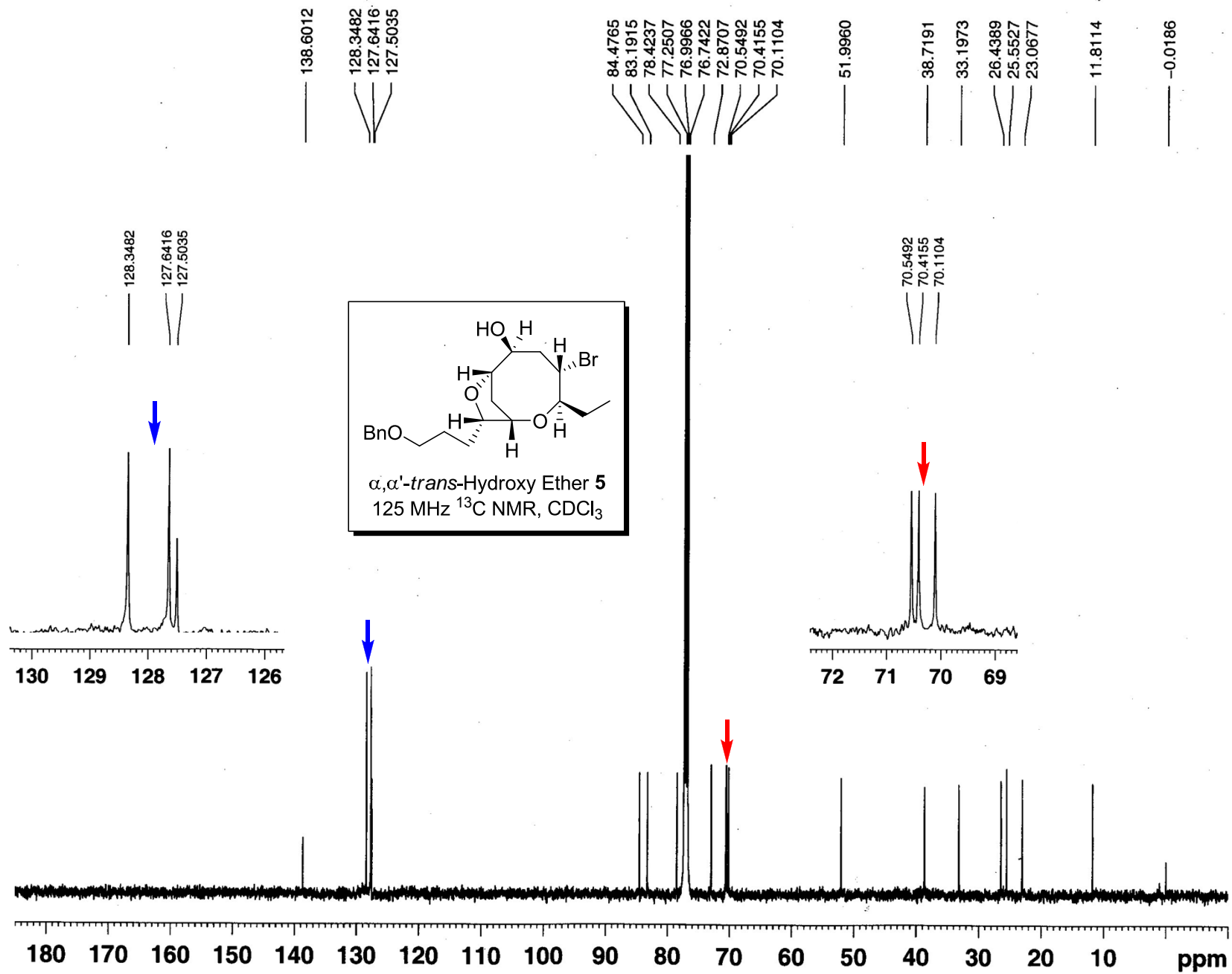
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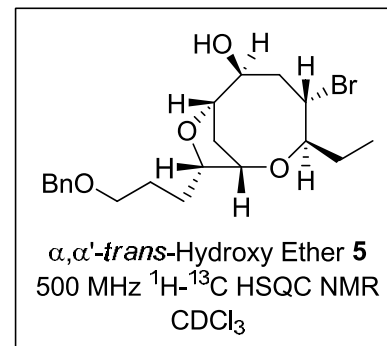
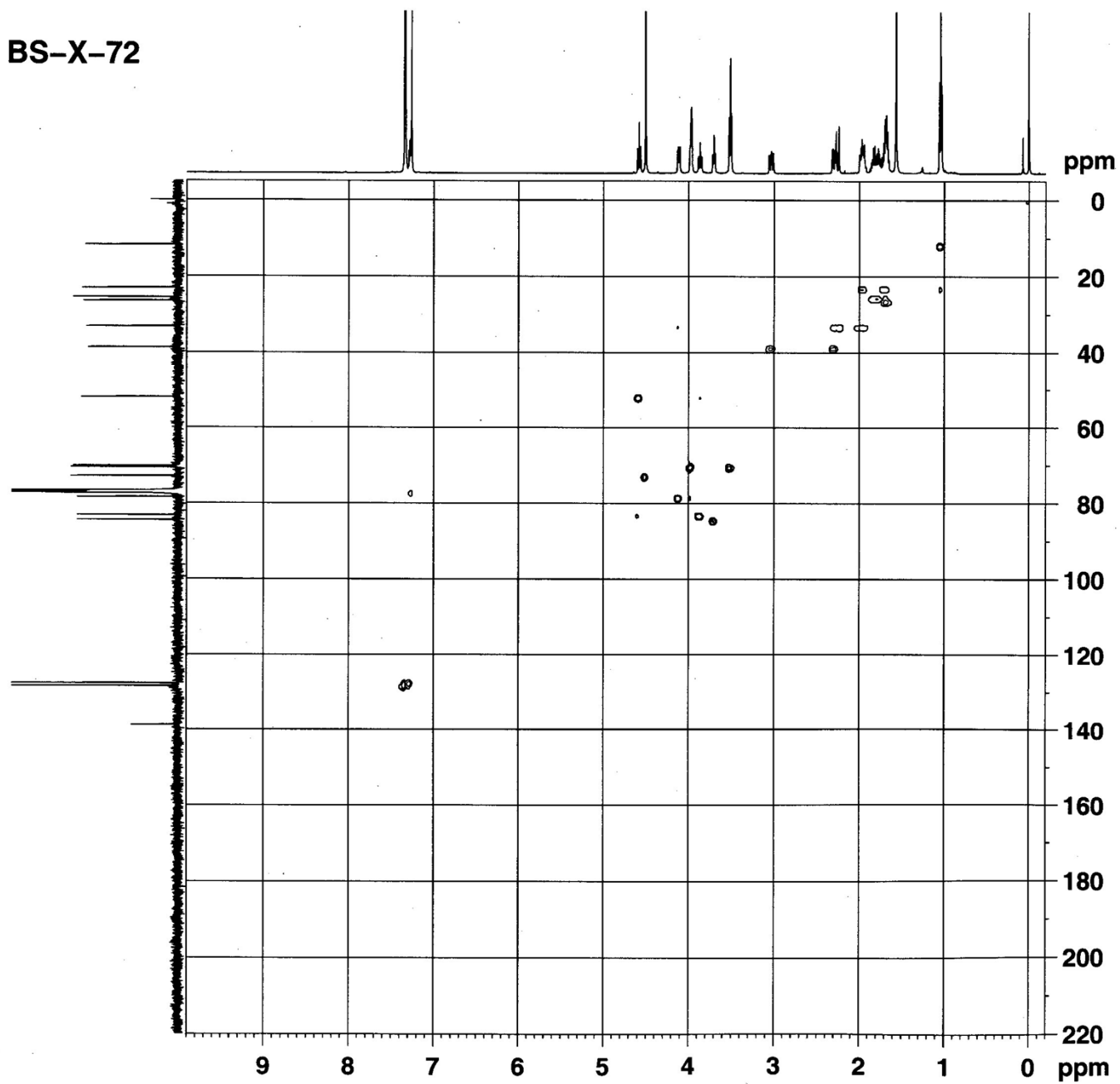
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# Intramolecular Epoxide Opening Route

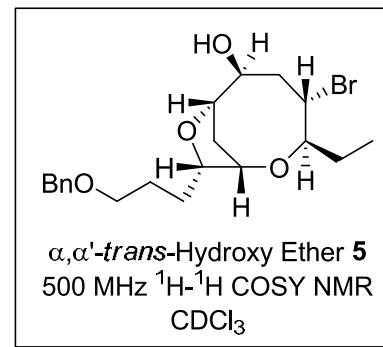
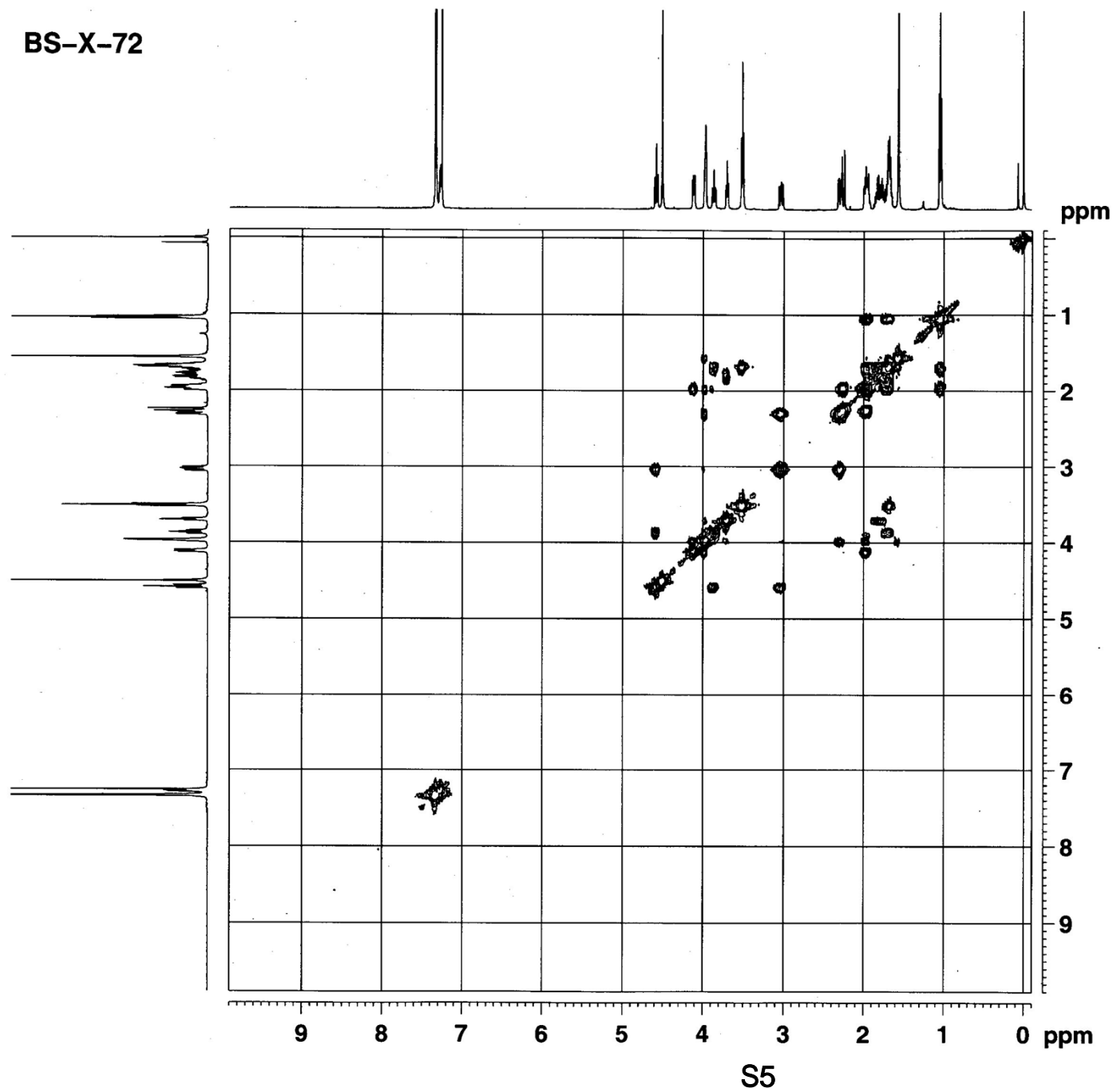




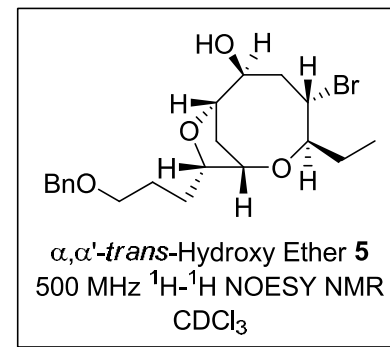
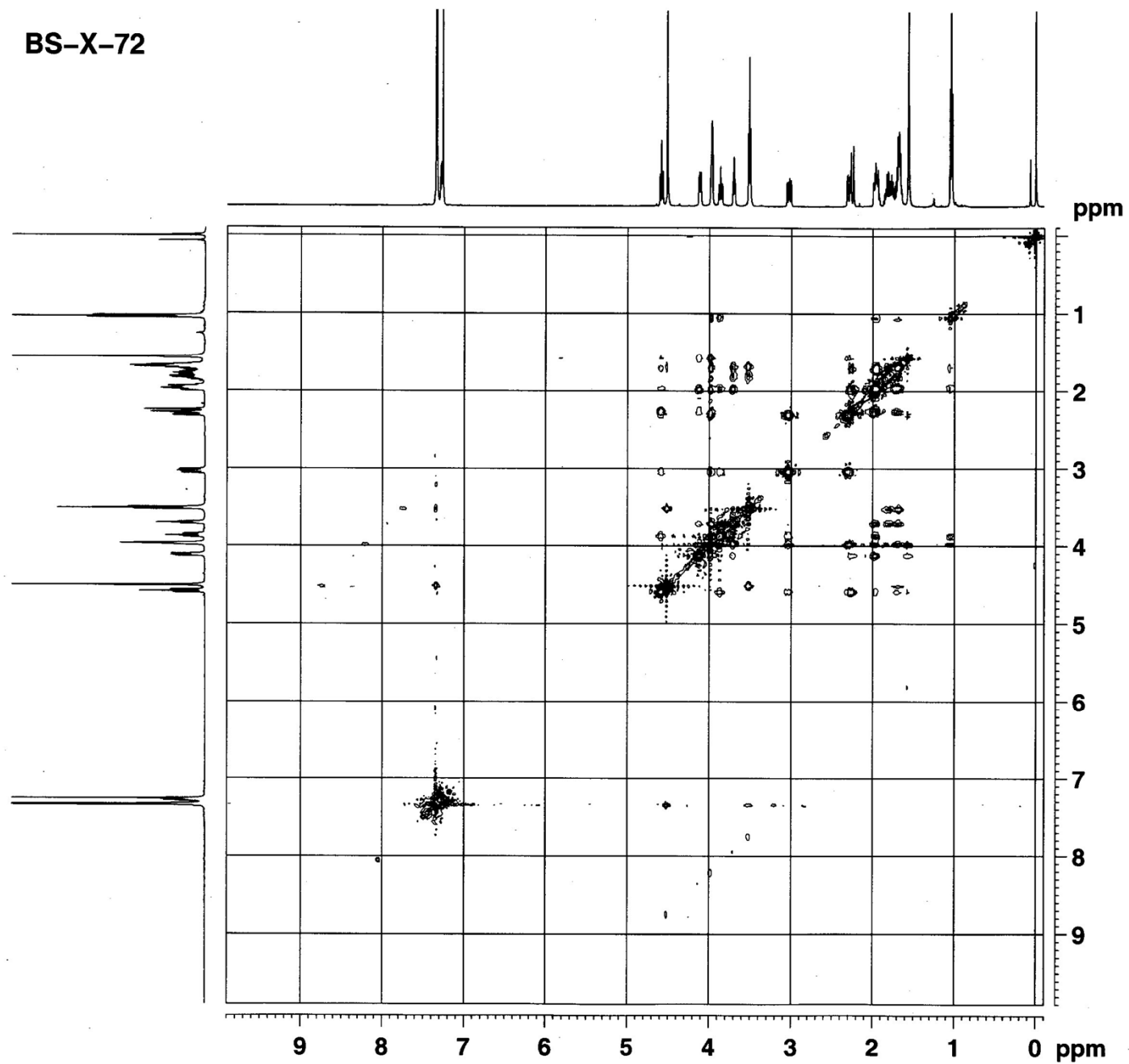
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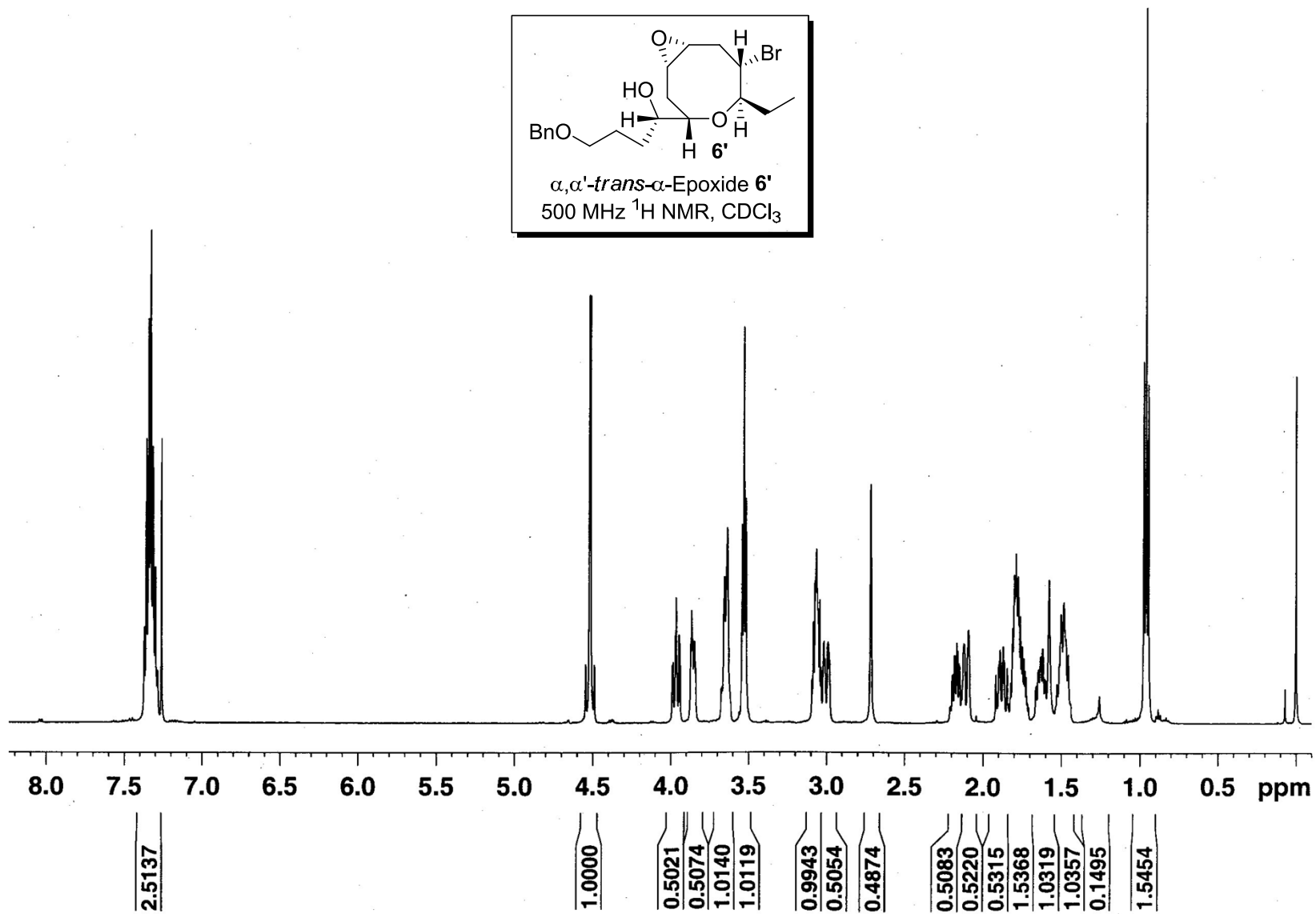
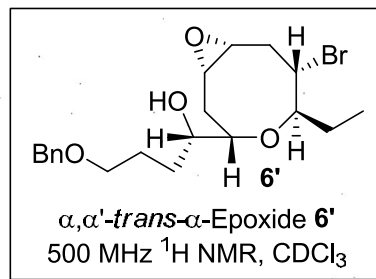


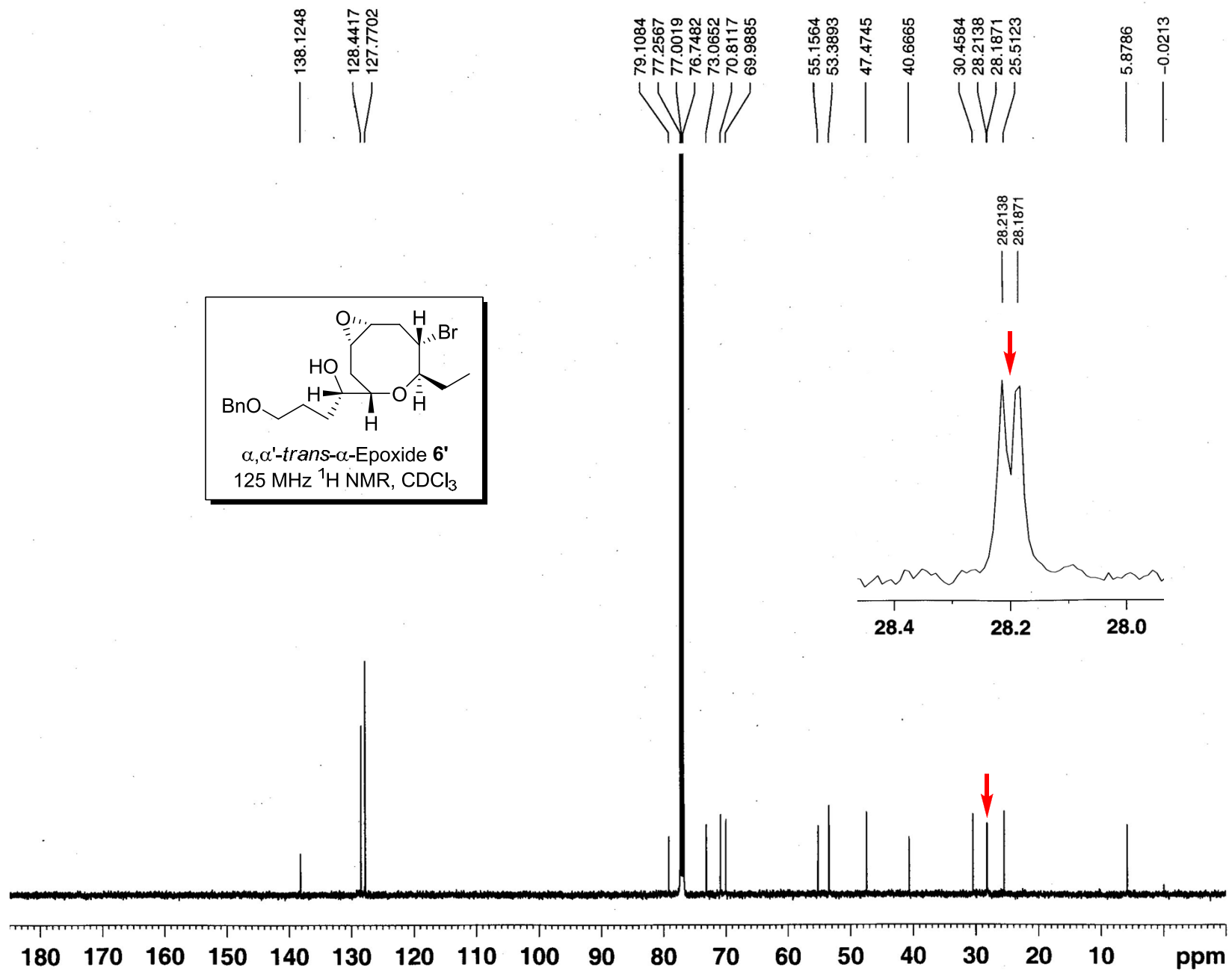
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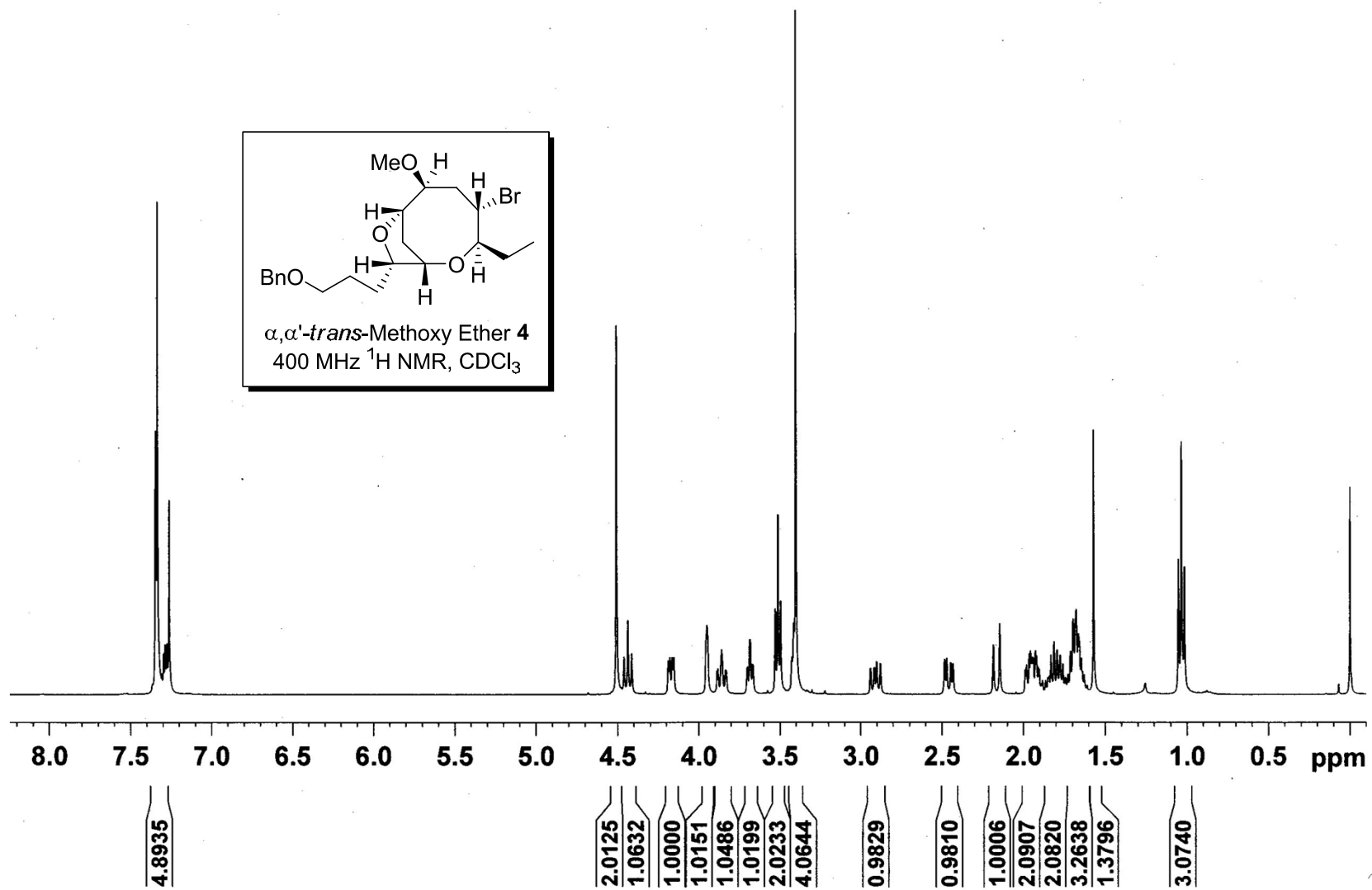


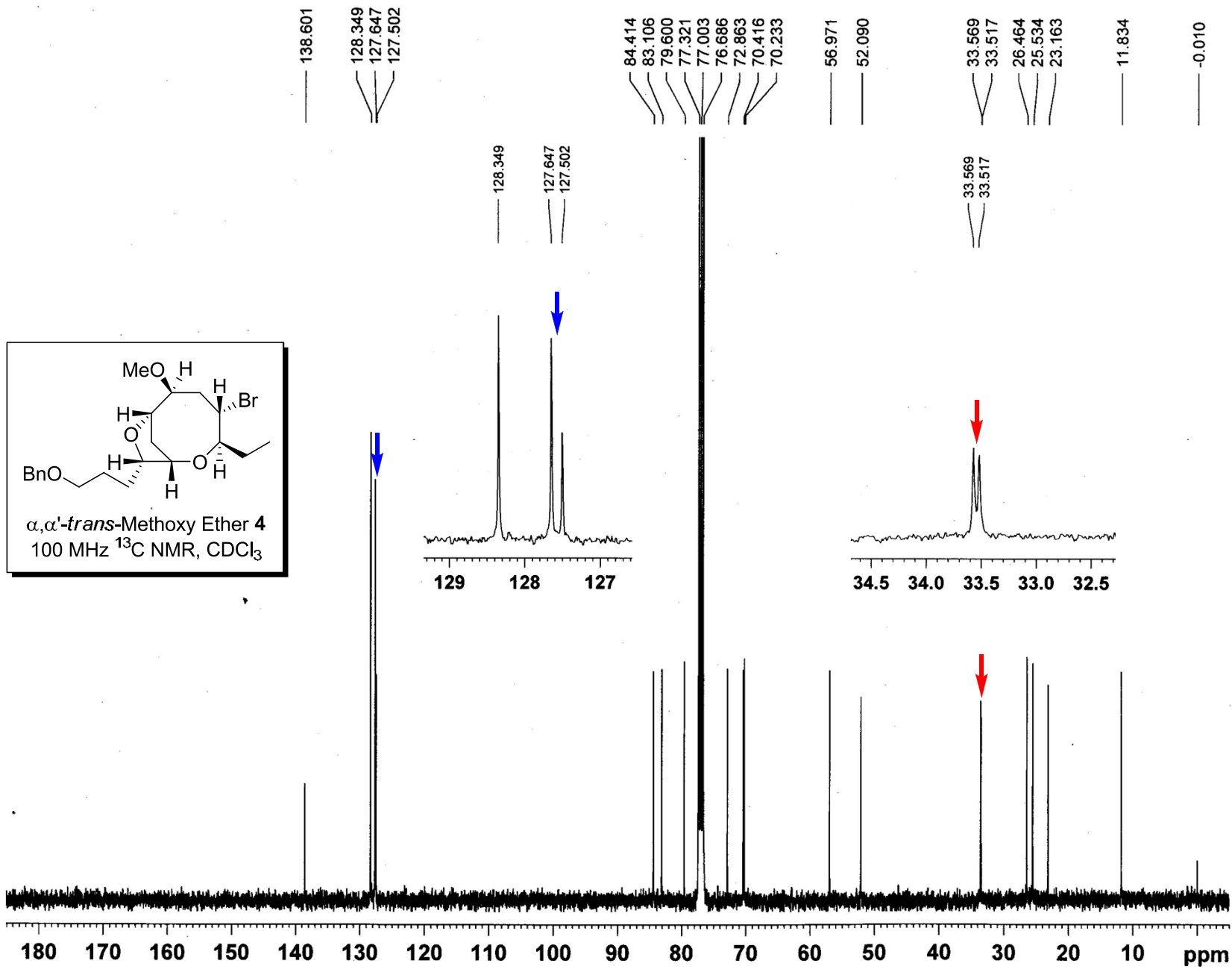
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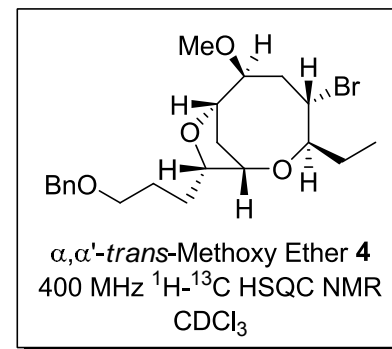
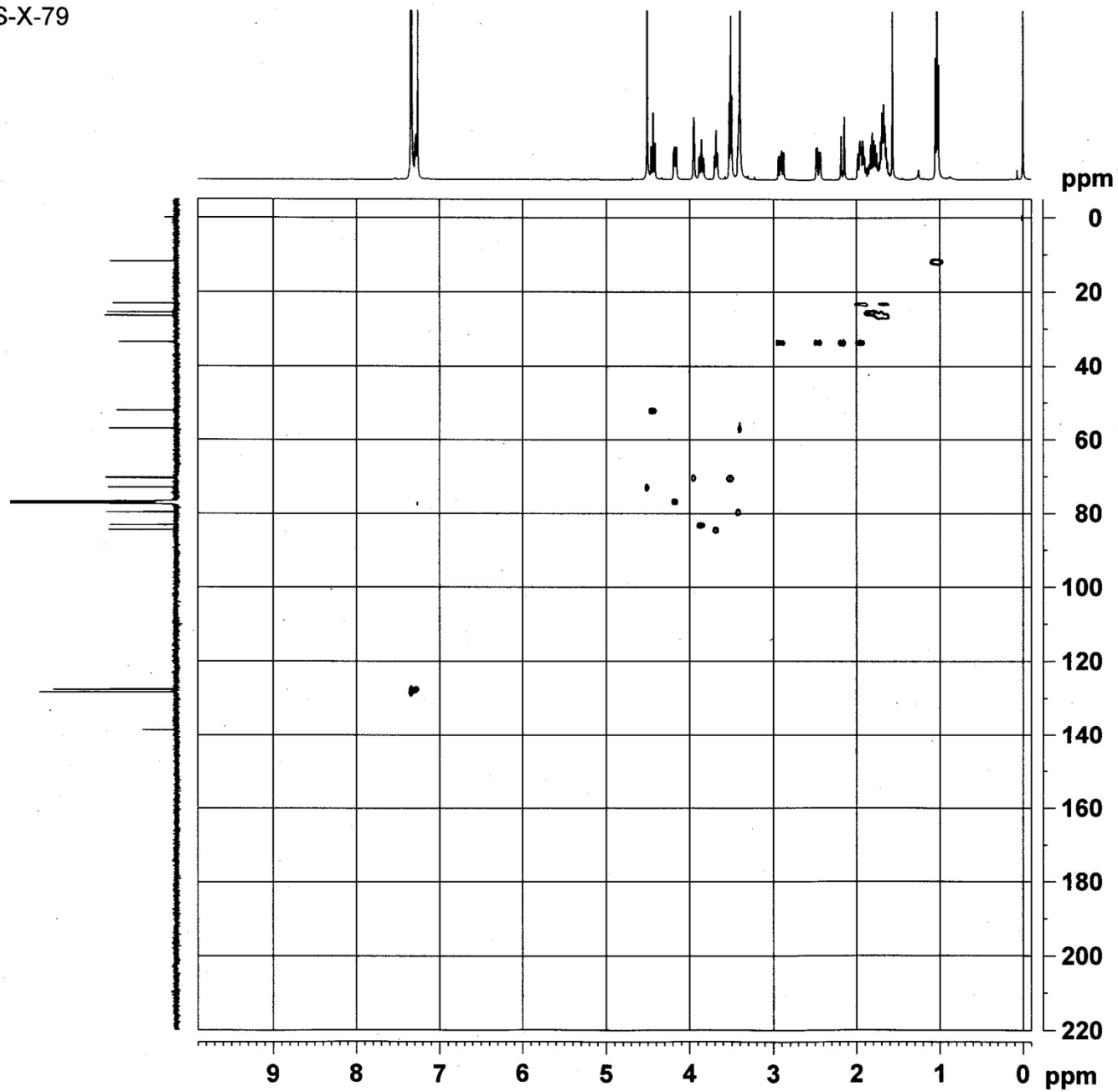






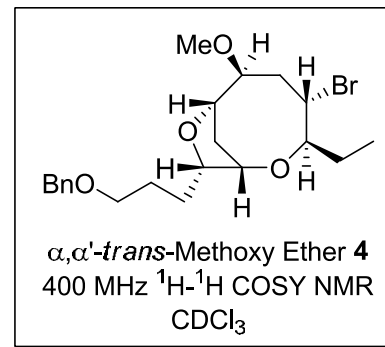
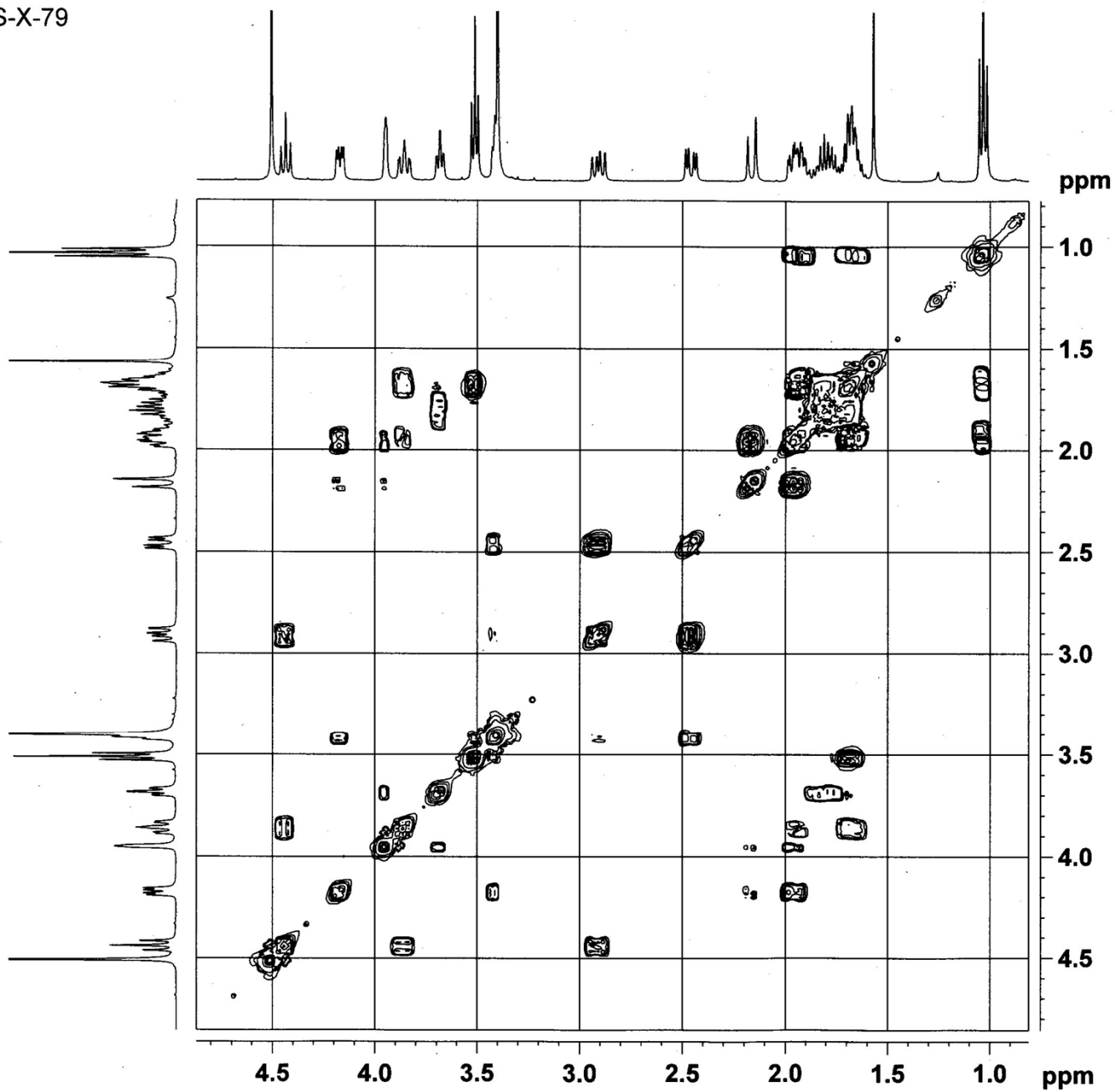


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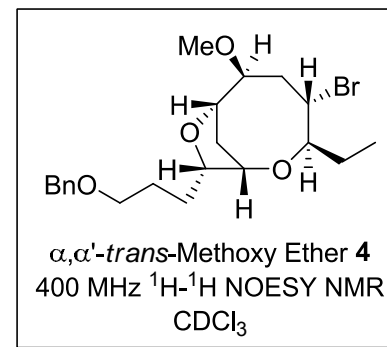
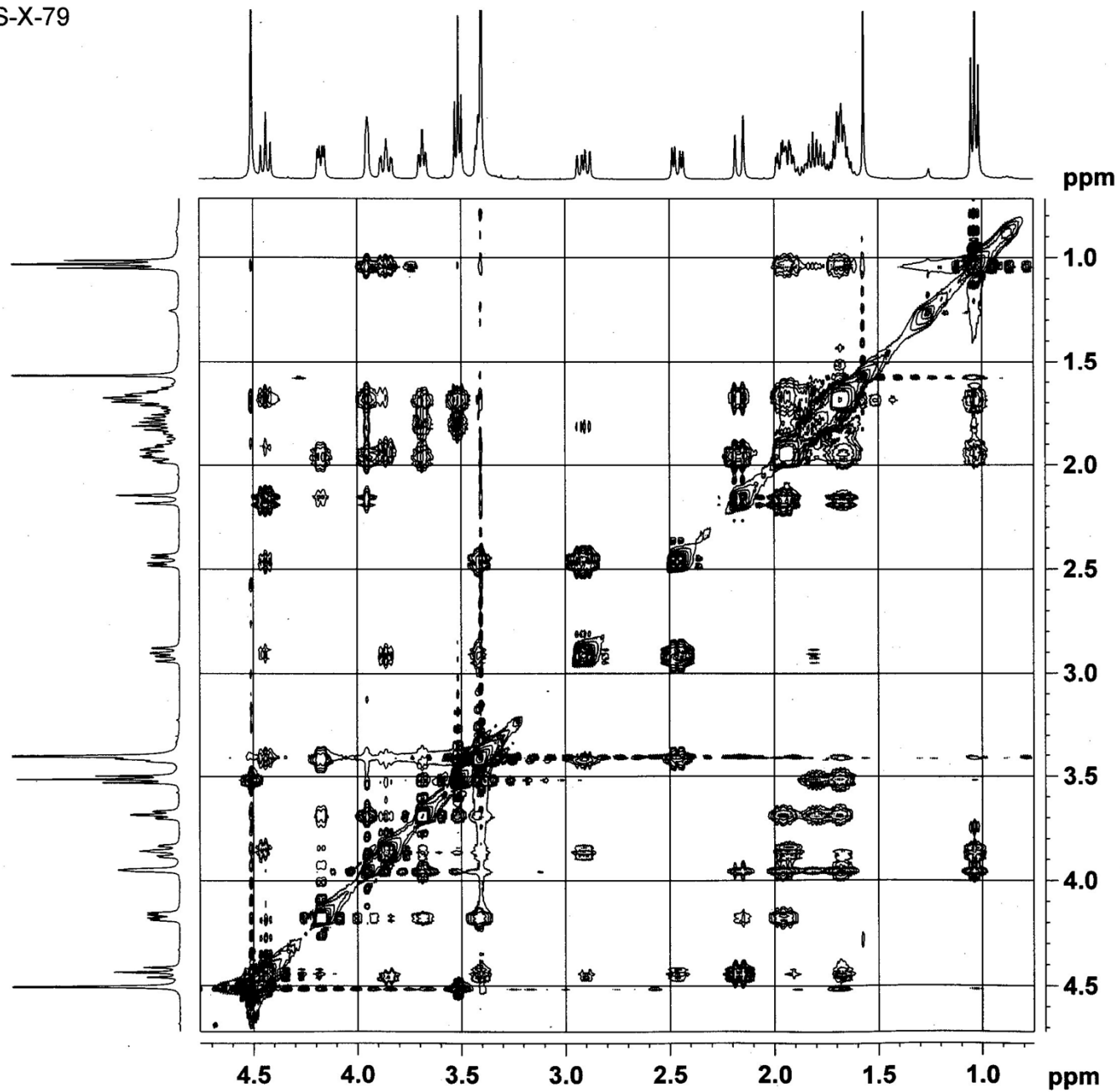
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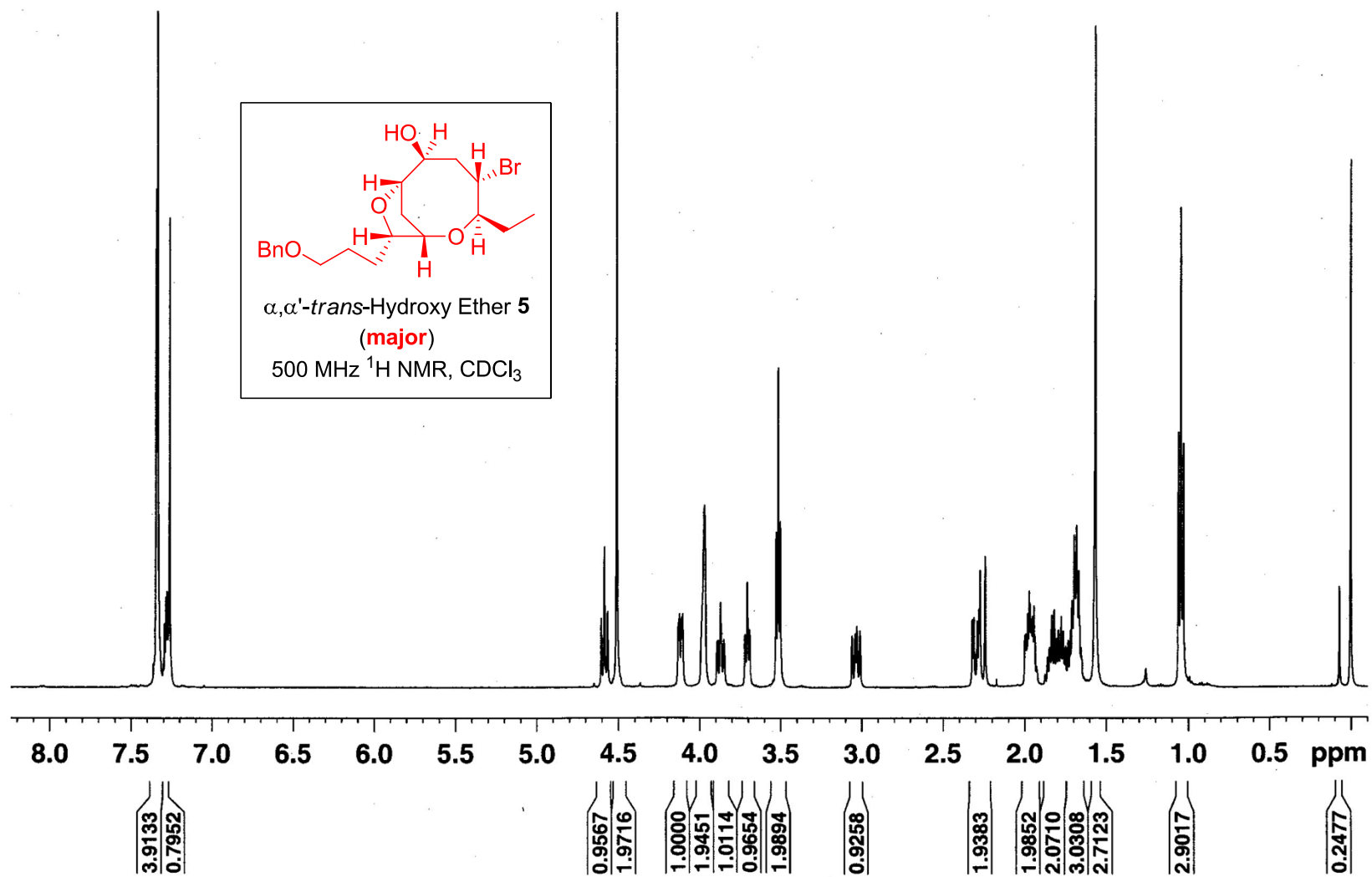
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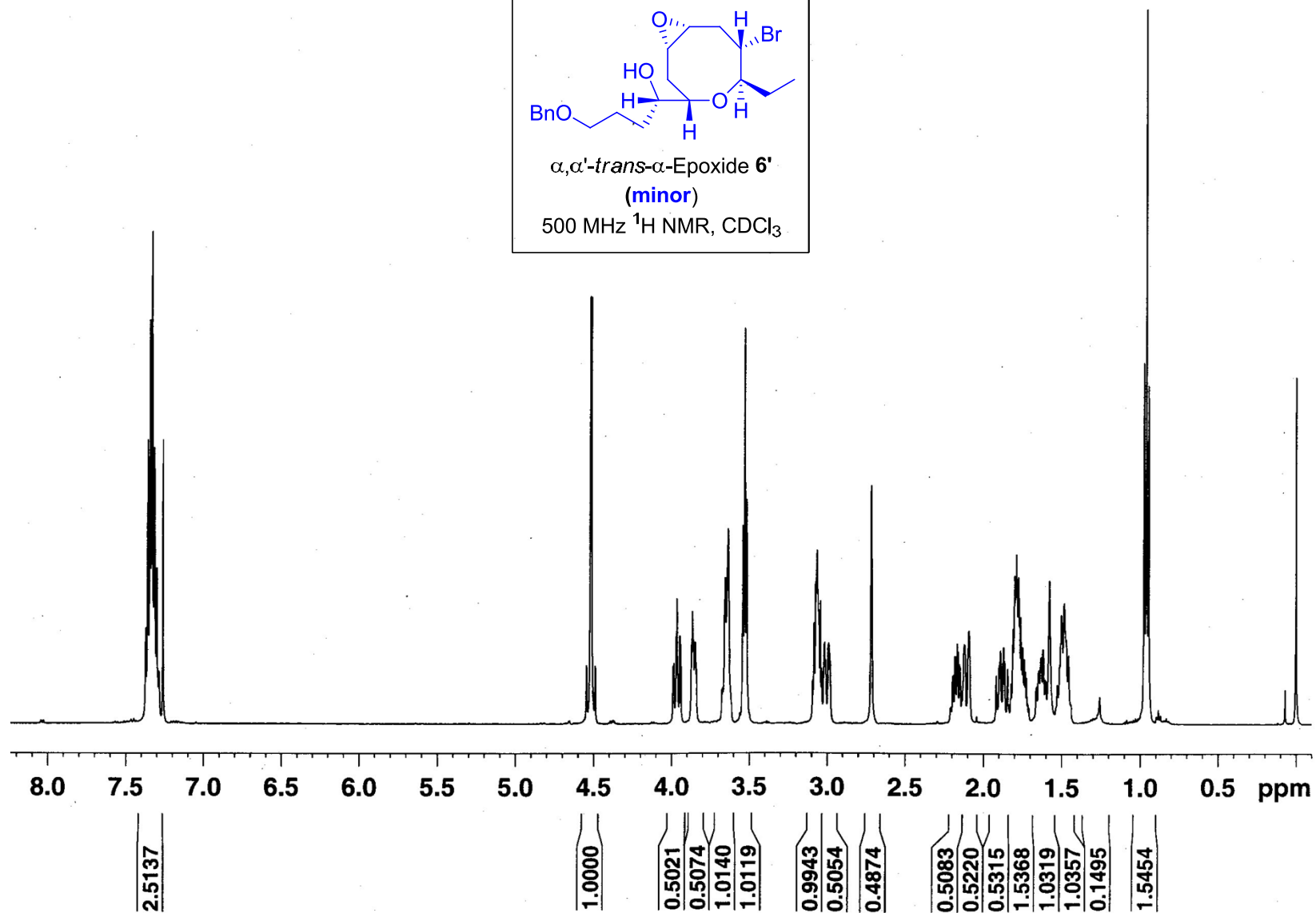
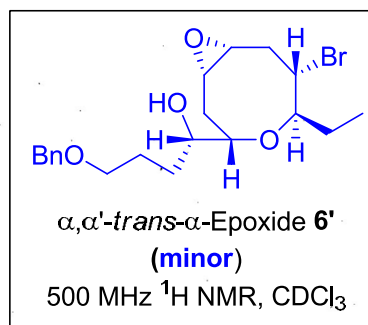
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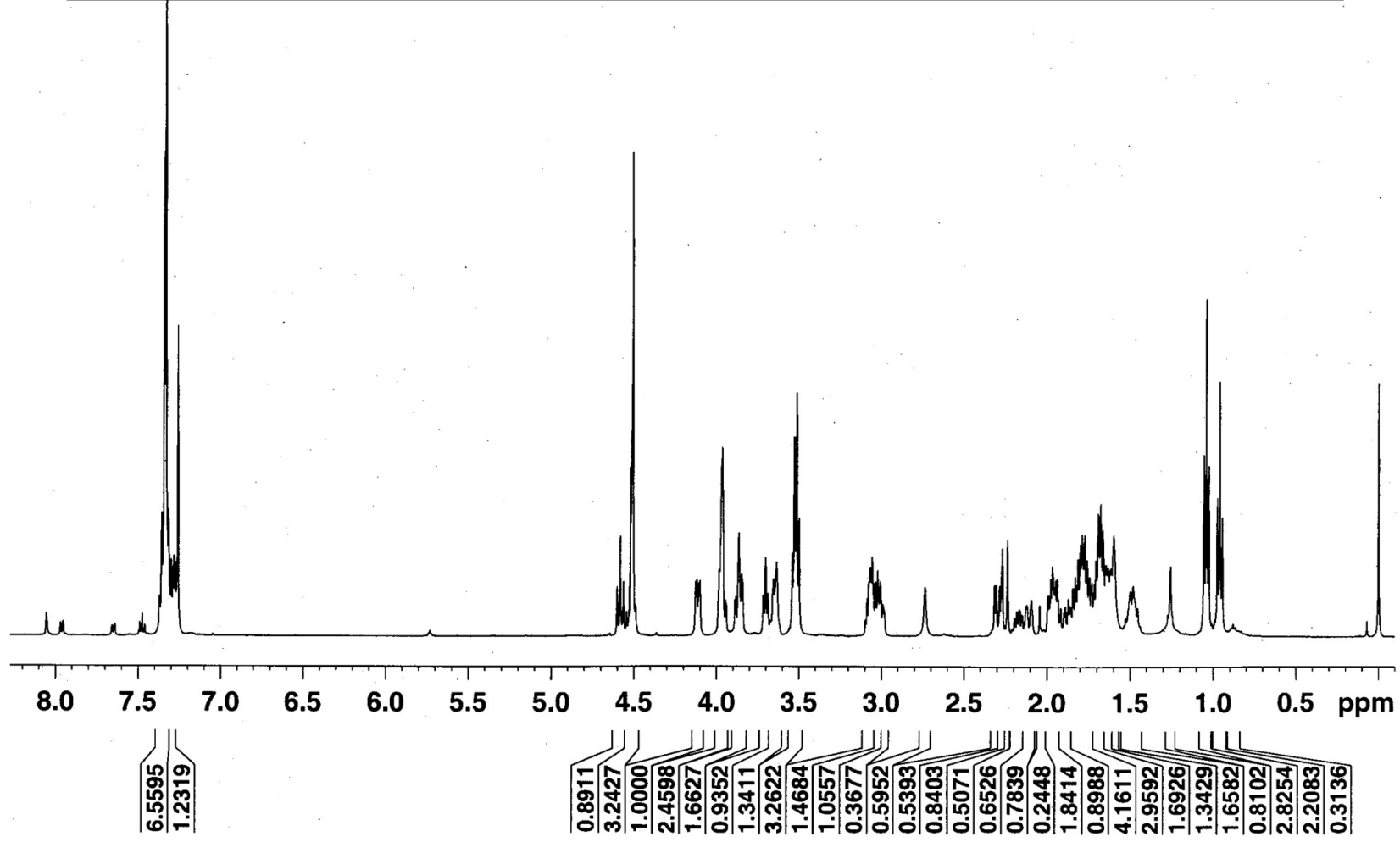
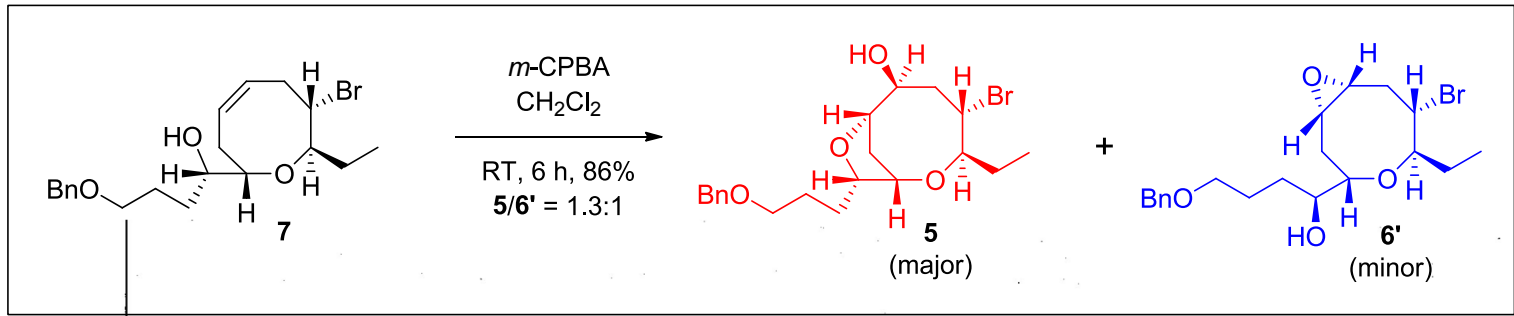


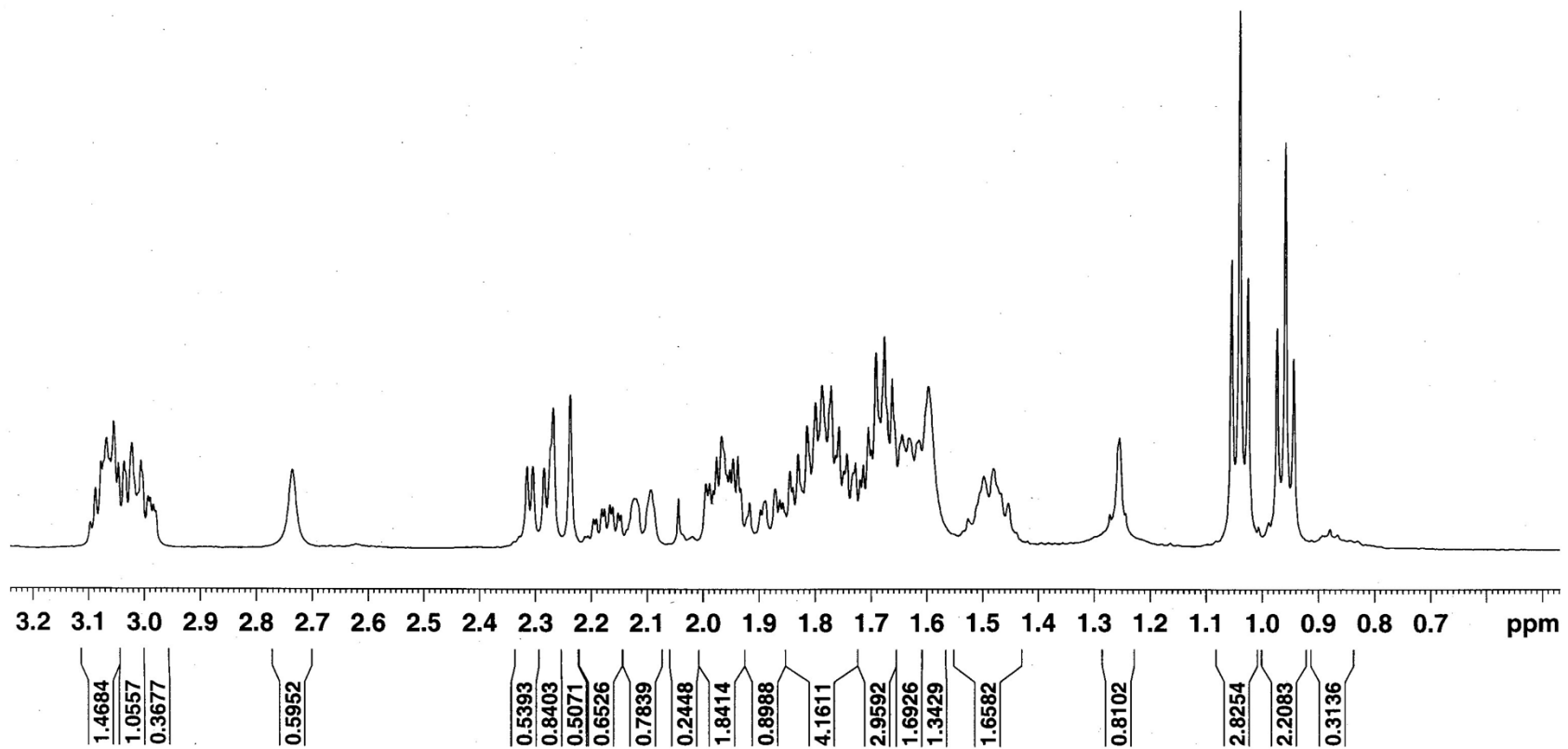
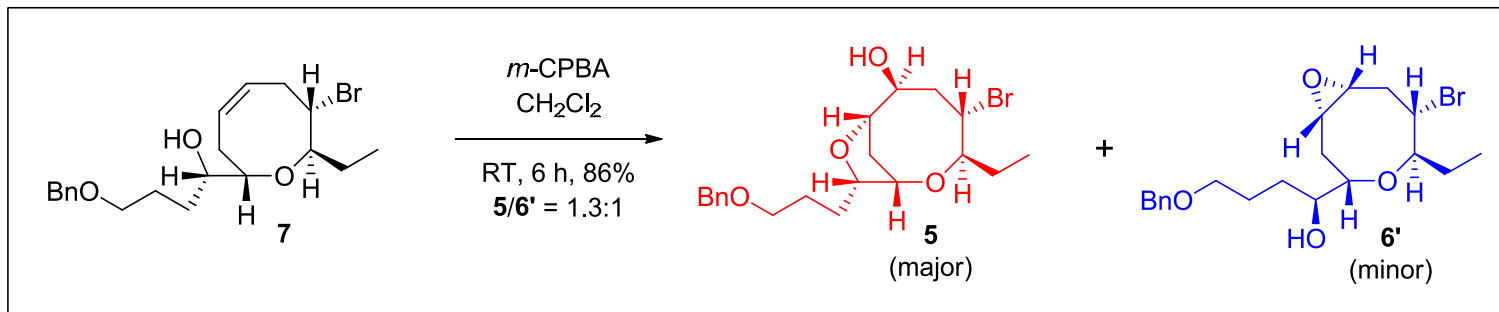
S13

# Stereoselectivity in Epoxidation of 7

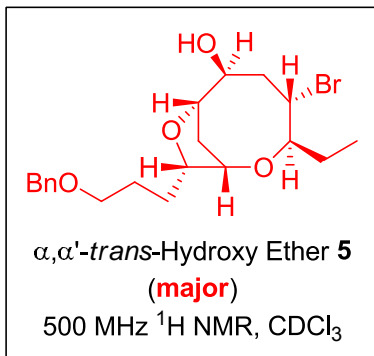




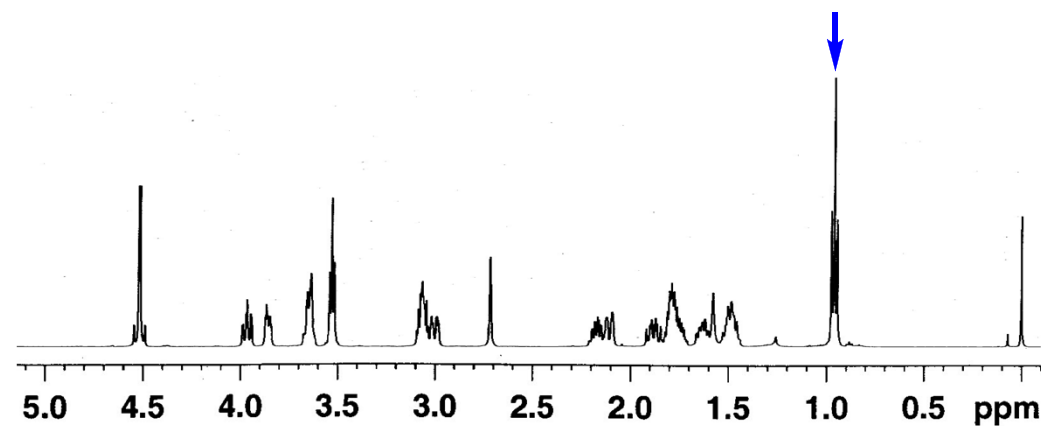
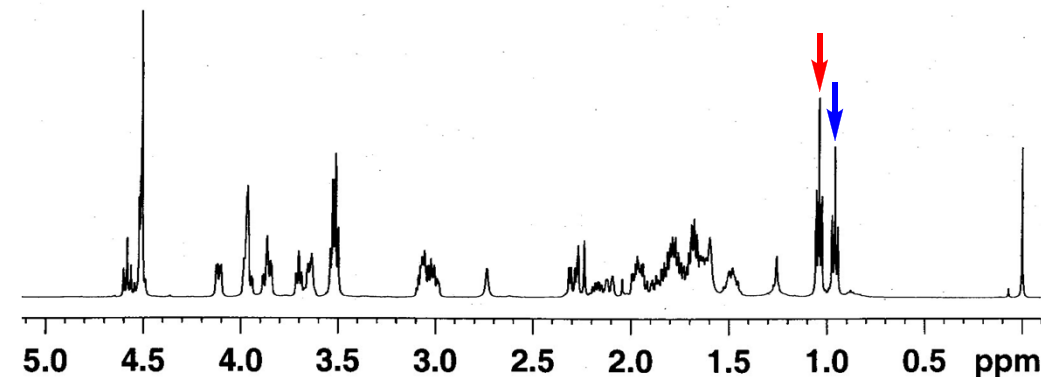
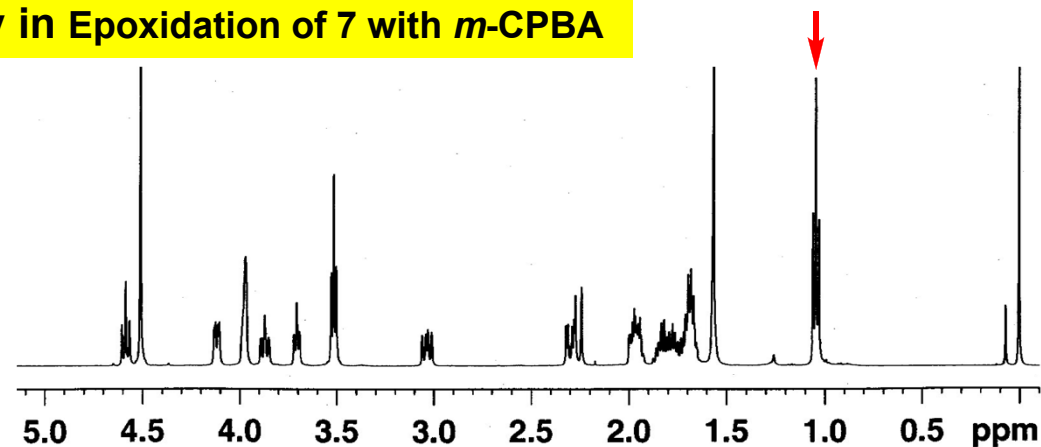
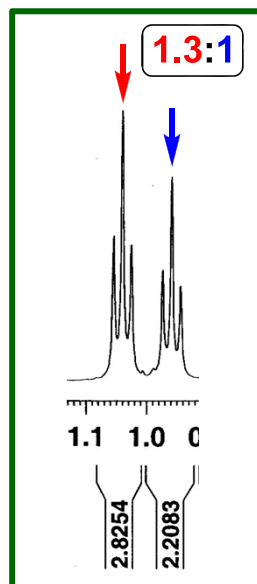
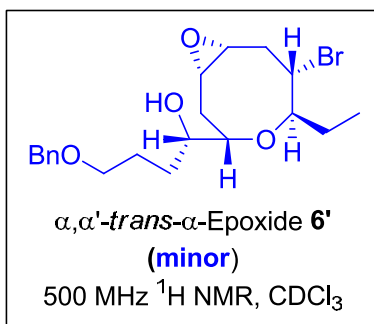


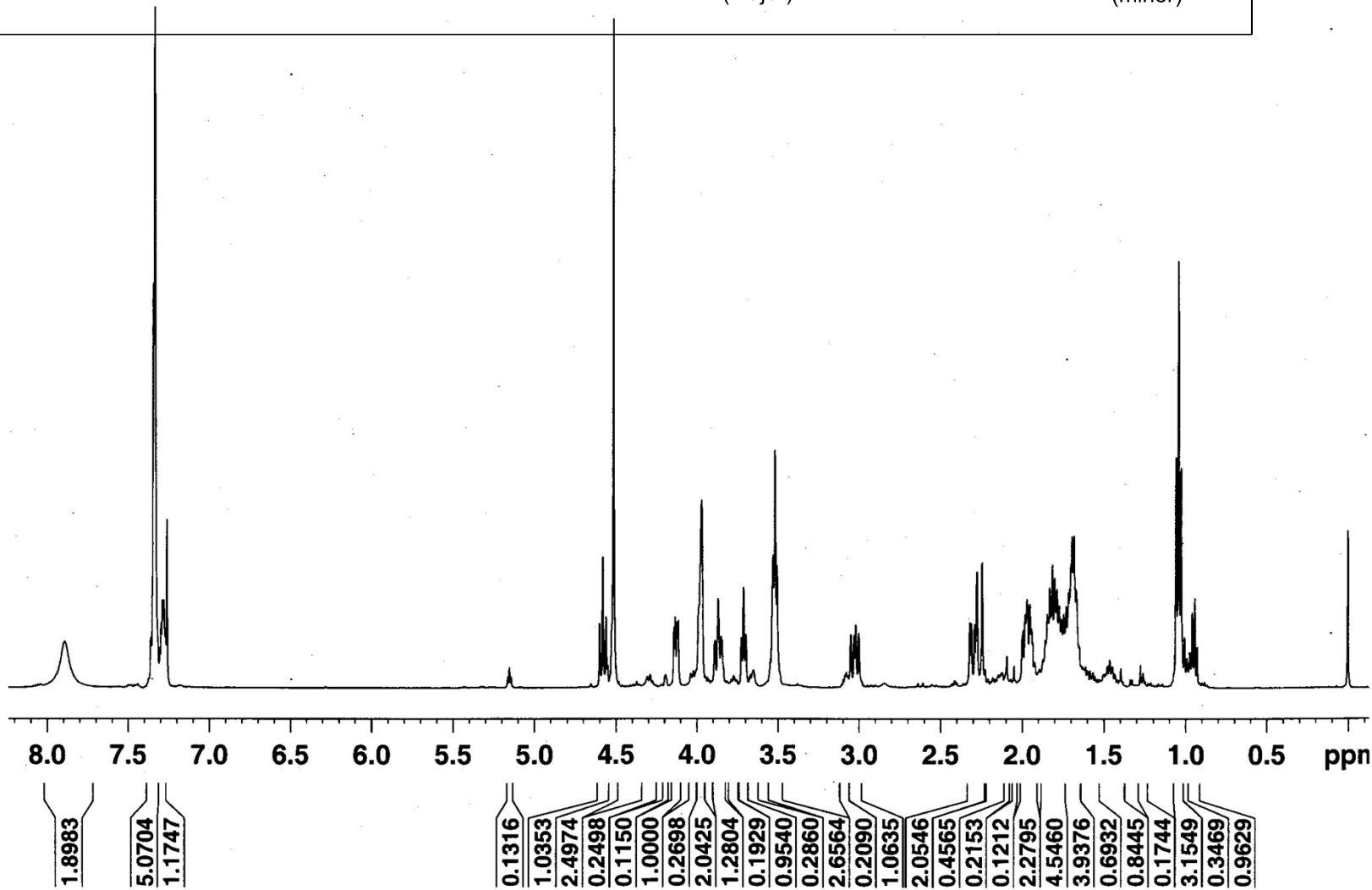
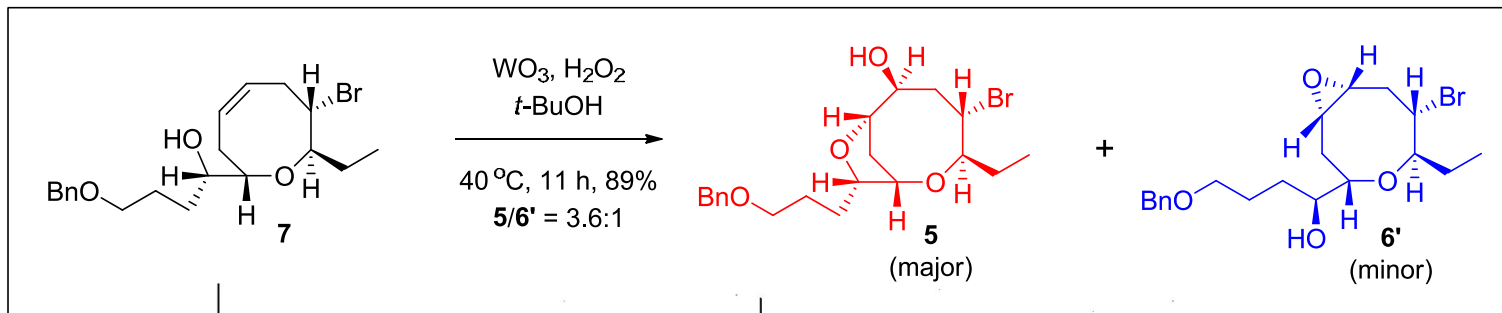


## Steroselectivity in Epoxidation of 7 with *m*-CPBA

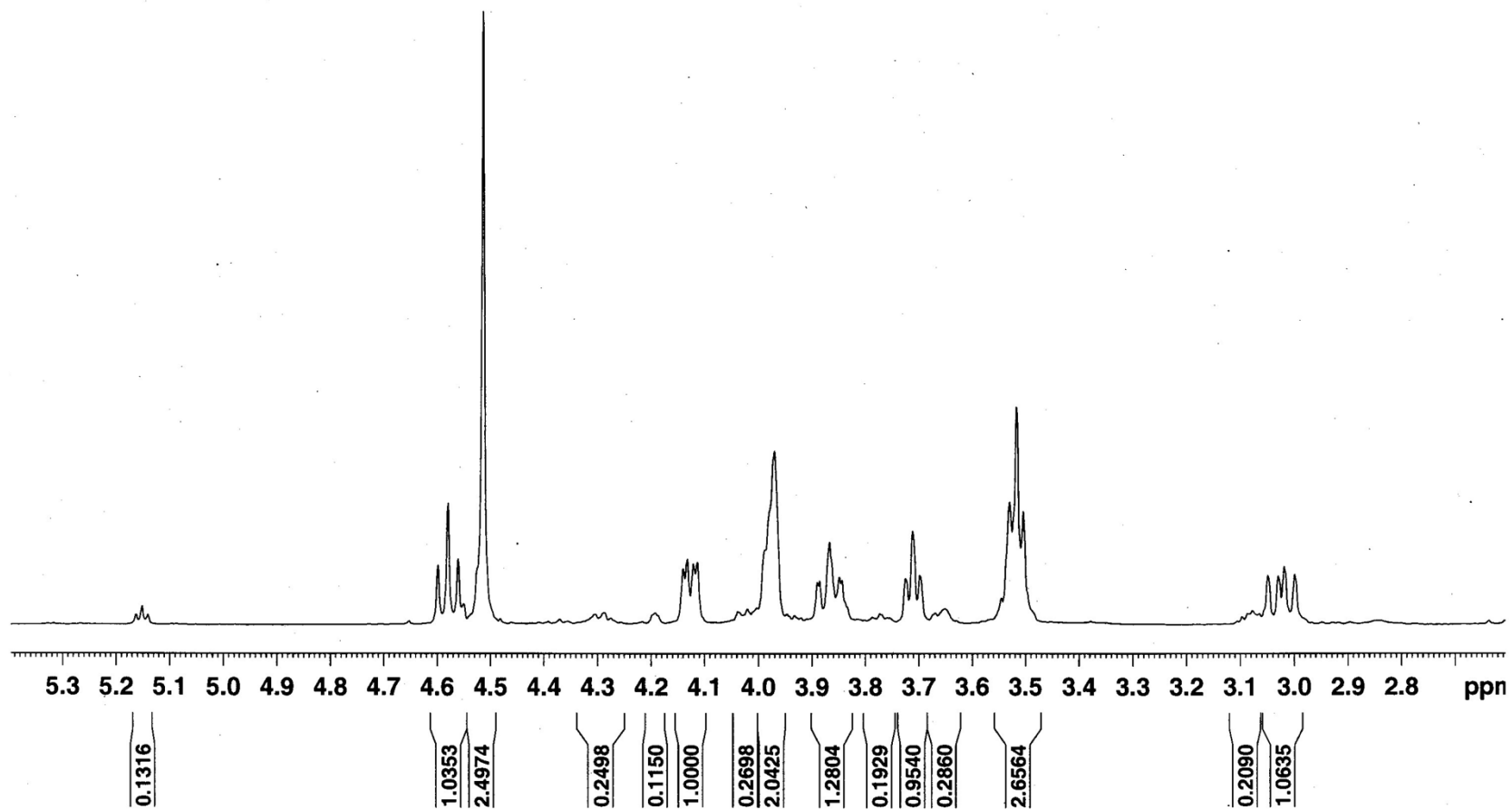
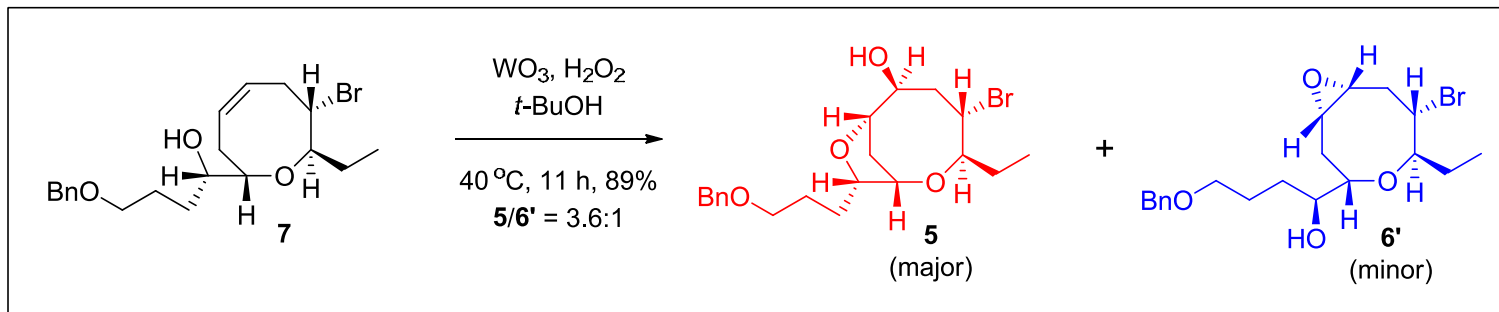


*m*-CPBA  
 $\text{CH}_2\text{Cl}_2$   
RT, 6 h, 86%  
(**mixture**)  
500MHz  $^1\text{H}$  NMR

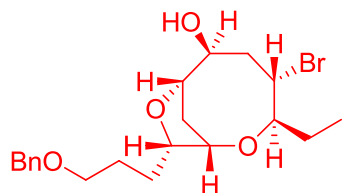




S19

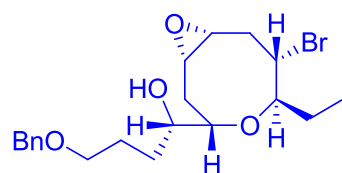


## Stereoselectivity in Epoxidation of 7 with $\text{WO}_3/\text{H}_2\text{O}_2$

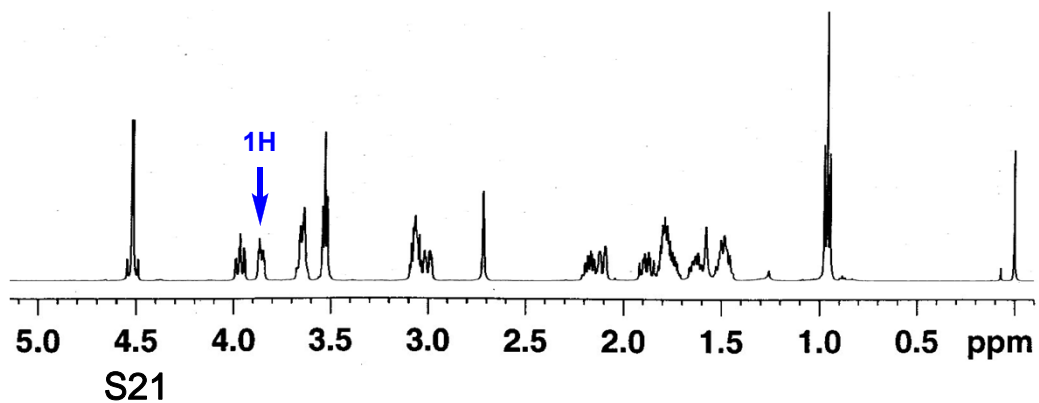
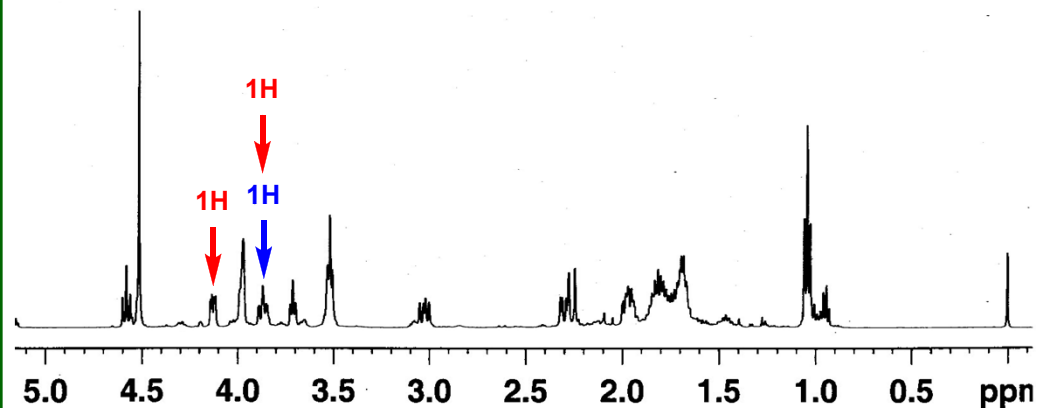
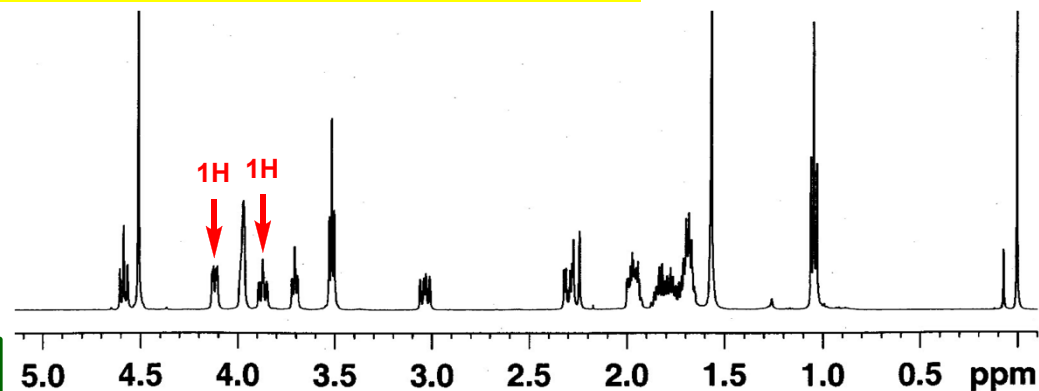
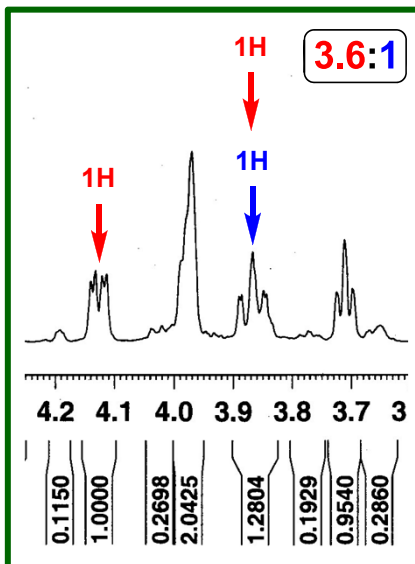


$\alpha, \alpha'$ -*trans*-Hydroxy Ether **5**  
(**major**)  
500 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

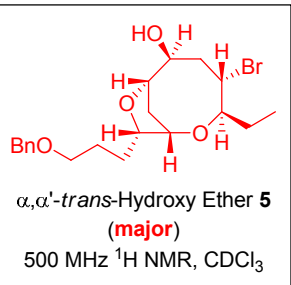
$\text{WO}_3, \text{H}_2\text{O}_2$   
*t*-BuOH  
40  $^\circ\text{C}$ , 11 h, 89%  
(**mixture**)  
500MHz  $^1\text{H}$  NMR



$\alpha, \alpha'$ -*trans*- $\alpha$ -Epoxide **6'**  
(**minor**)  
500 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

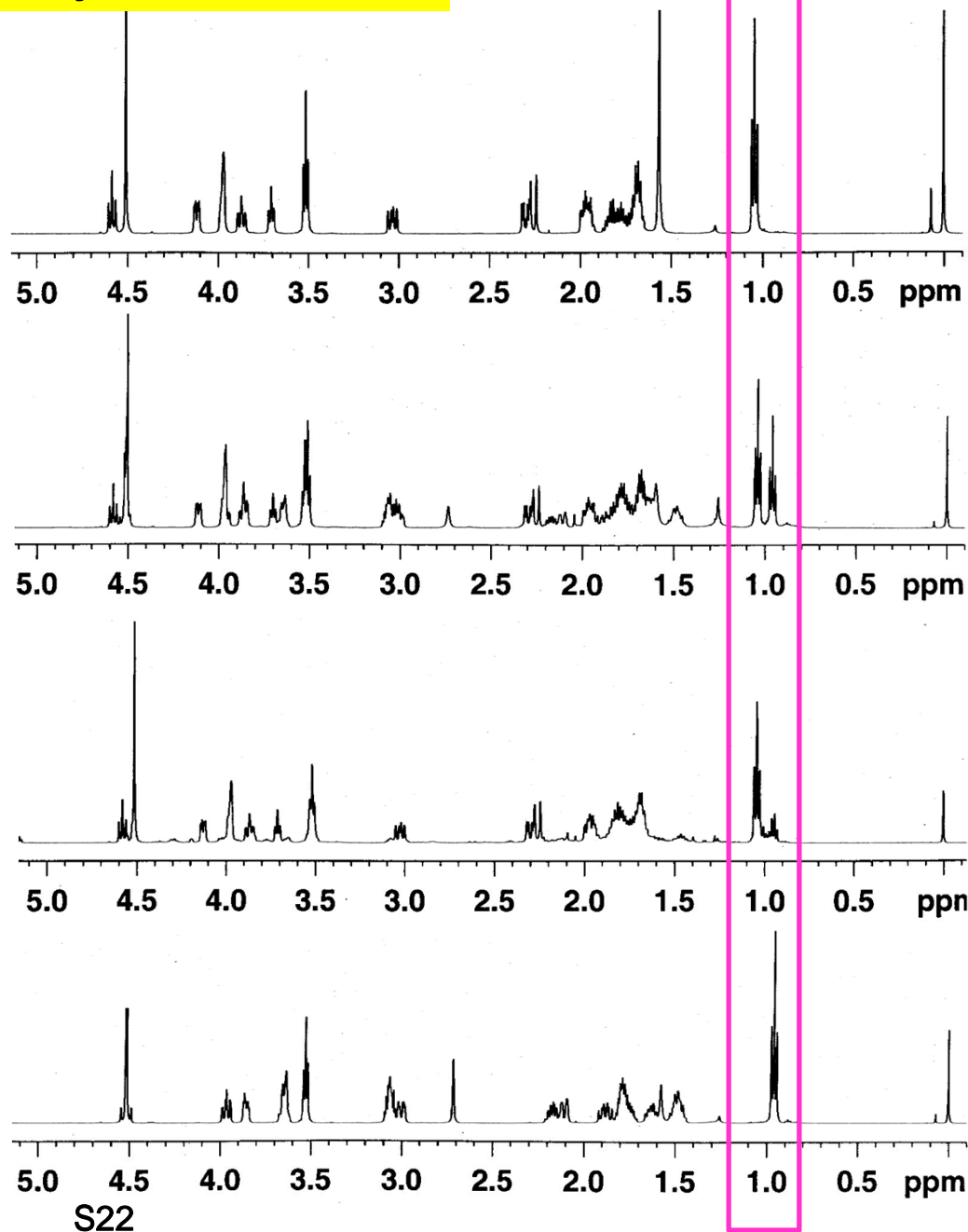
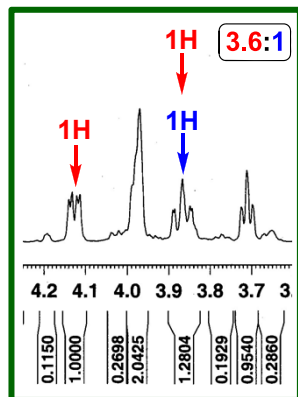
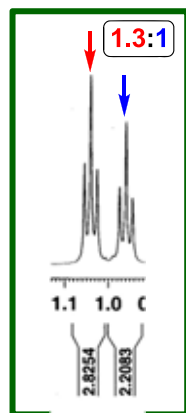
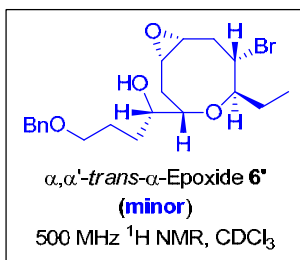


## Stereoselectivity in Epoxidation of 7



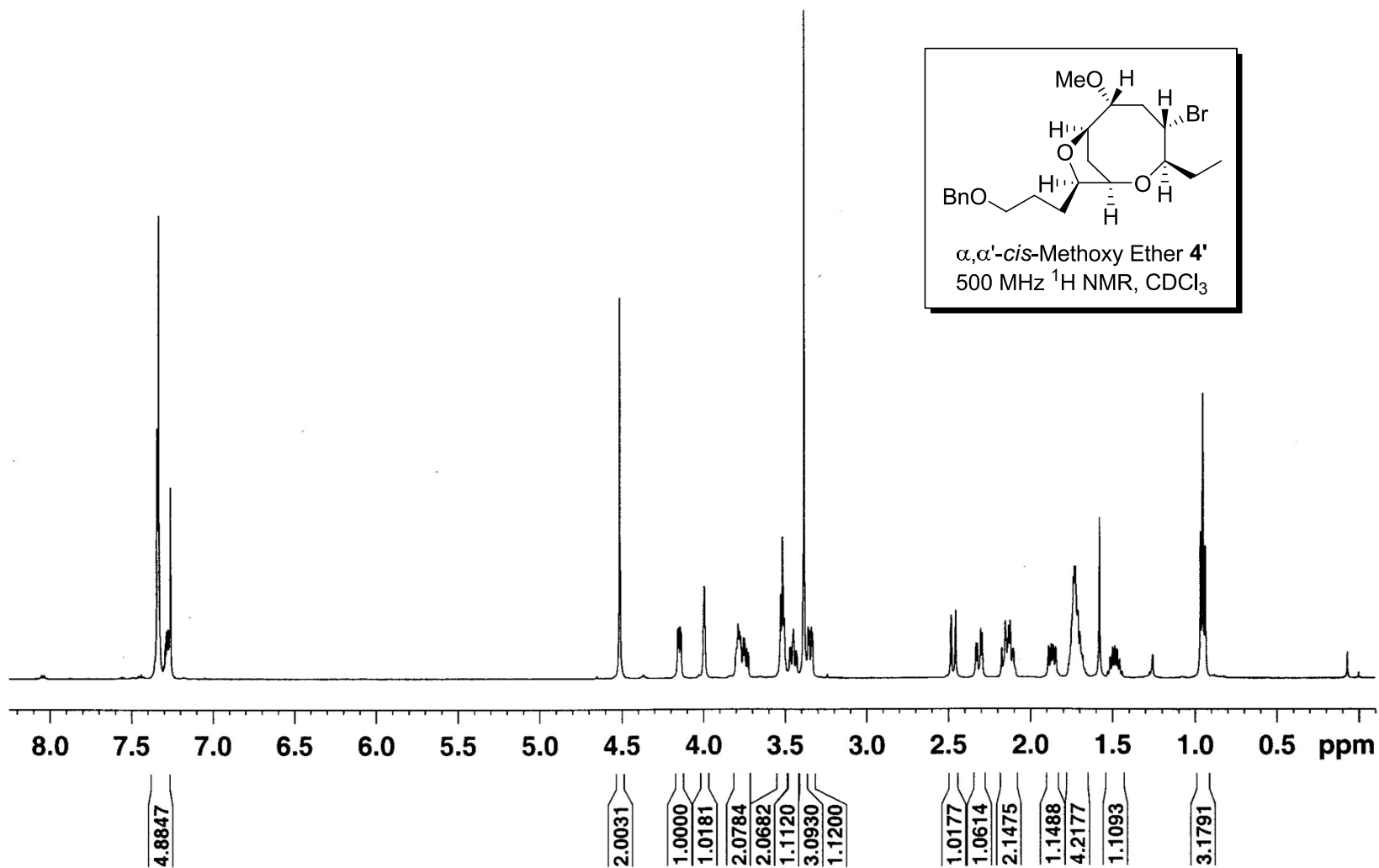
*m*-CPBA  
 $\text{CH}_2\text{Cl}_2$   
RT, 6 h, 86%  
(**mixture**)  
500MHz  $^1\text{H}$  NMR

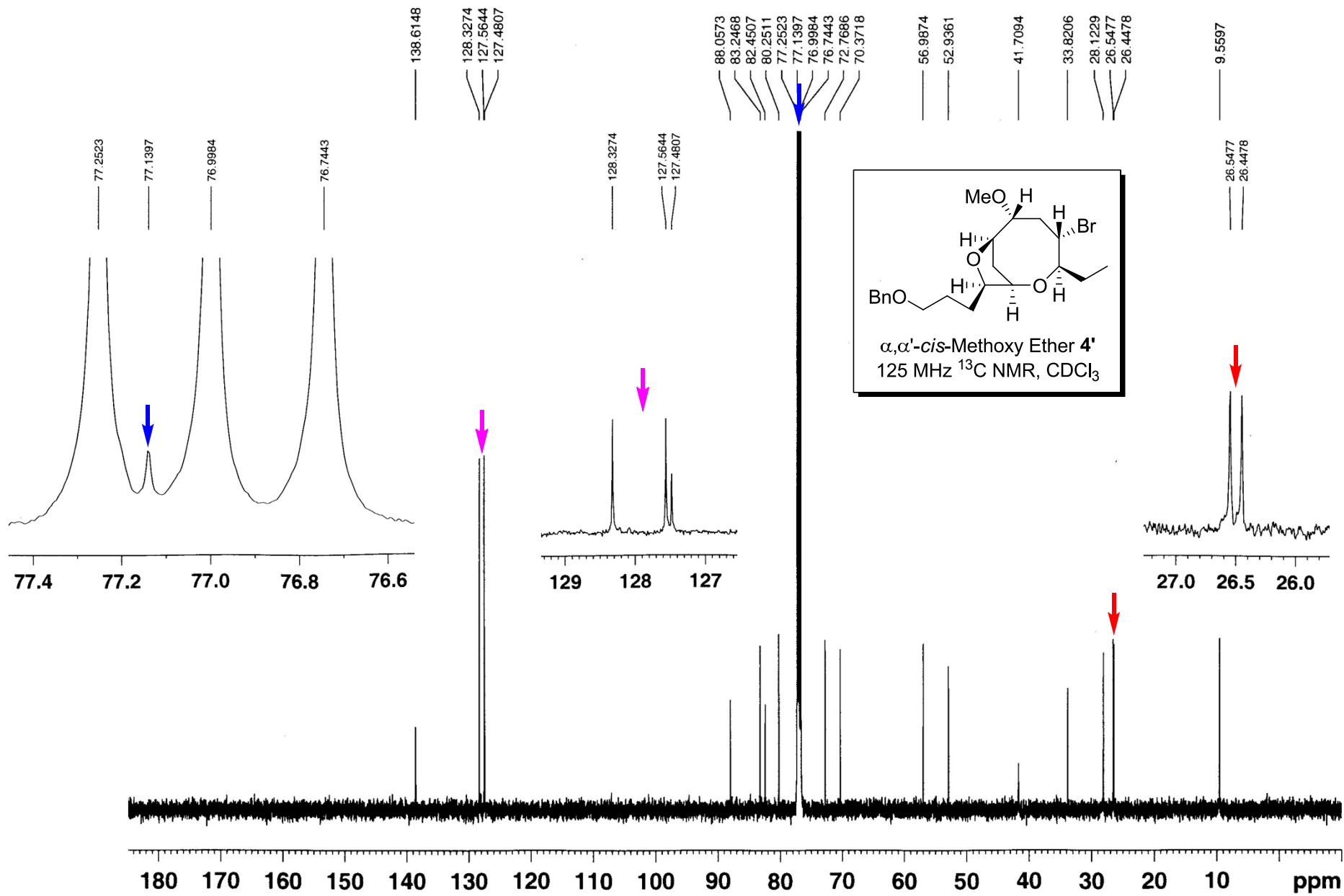
$\text{WO}_3, \text{H}_2\text{O}_2$   
*t*-BuOH  
40 °C, 11 h, 89%  
(**mixture**)  
500MHz  $^1\text{H}$  NMR



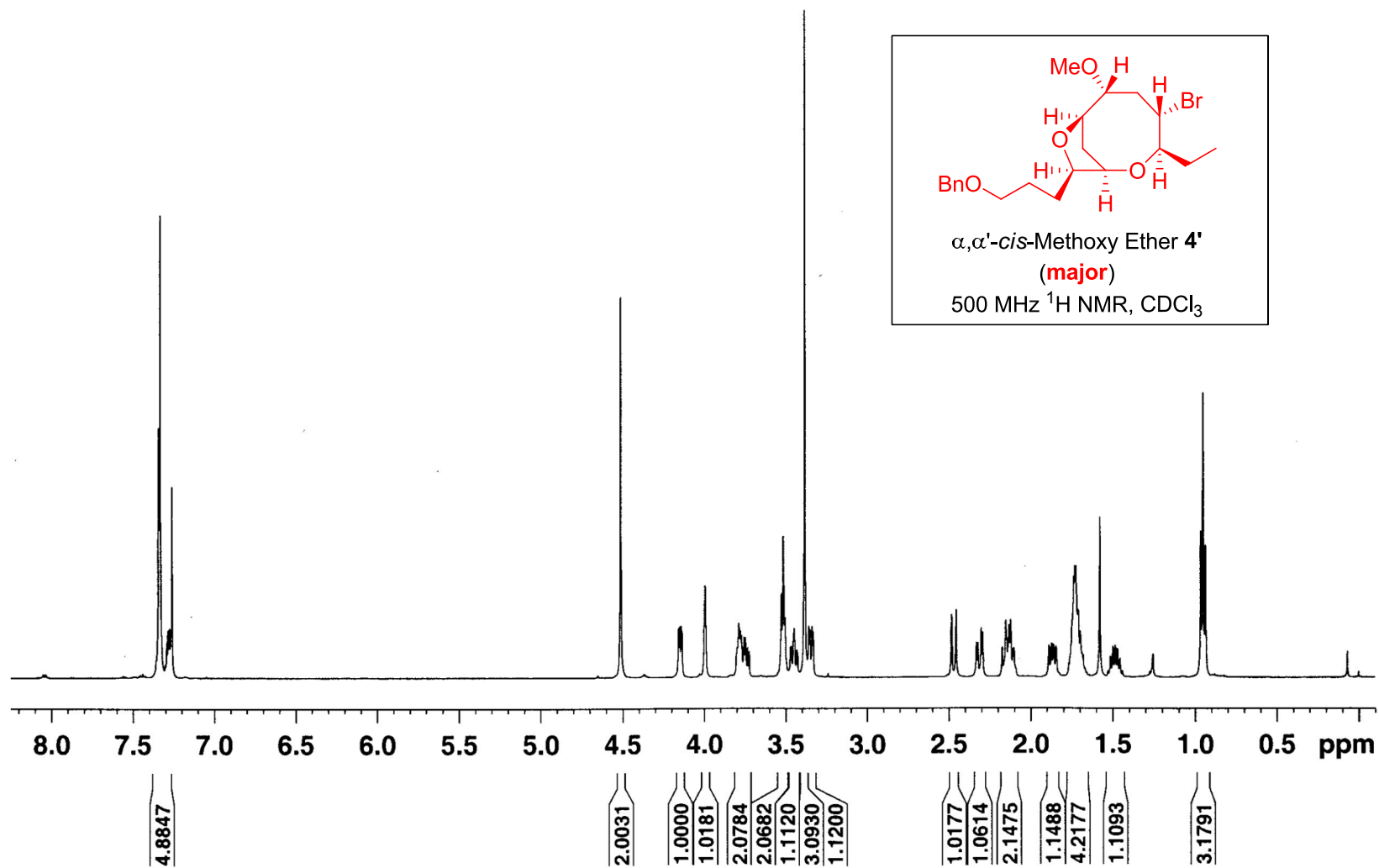
# Organoselenium-Mediated Alkoxyetherification Route

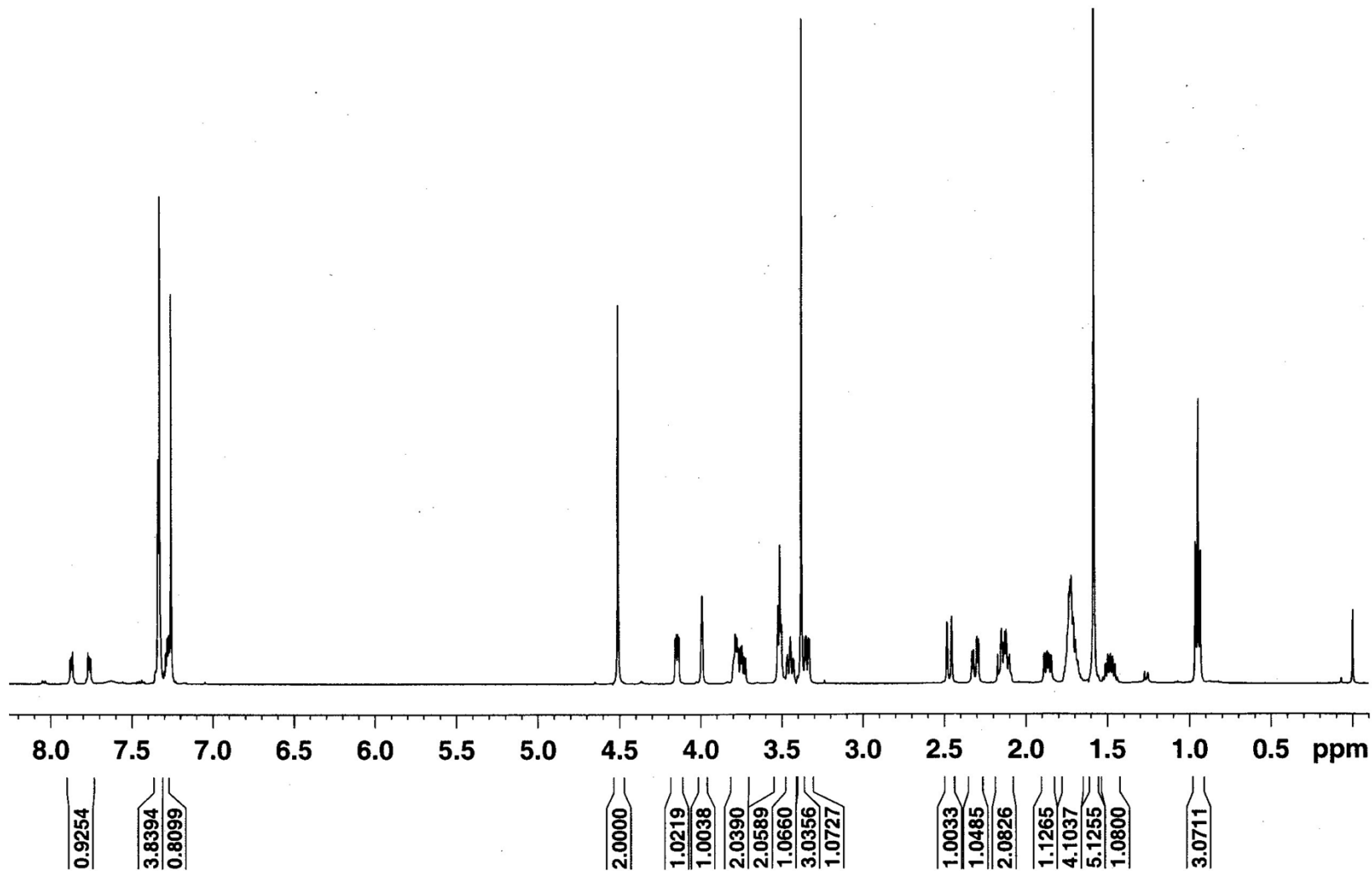
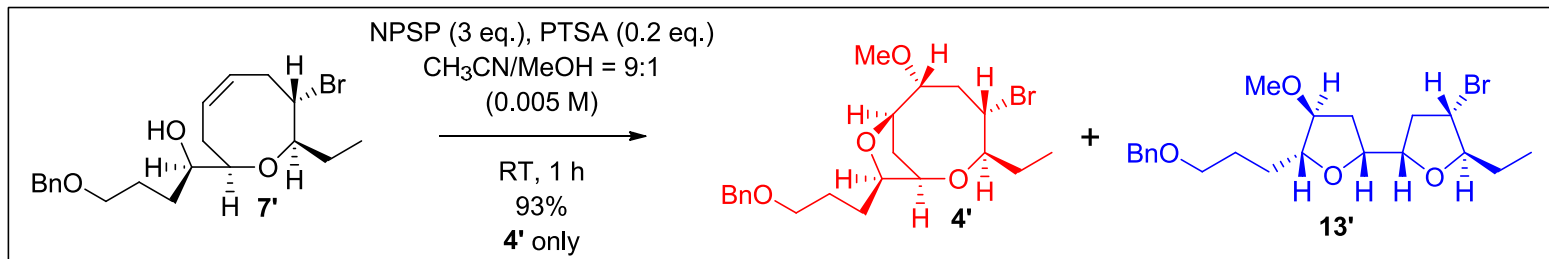
## Laurefucin series ( $\alpha,\alpha'$ -cis)

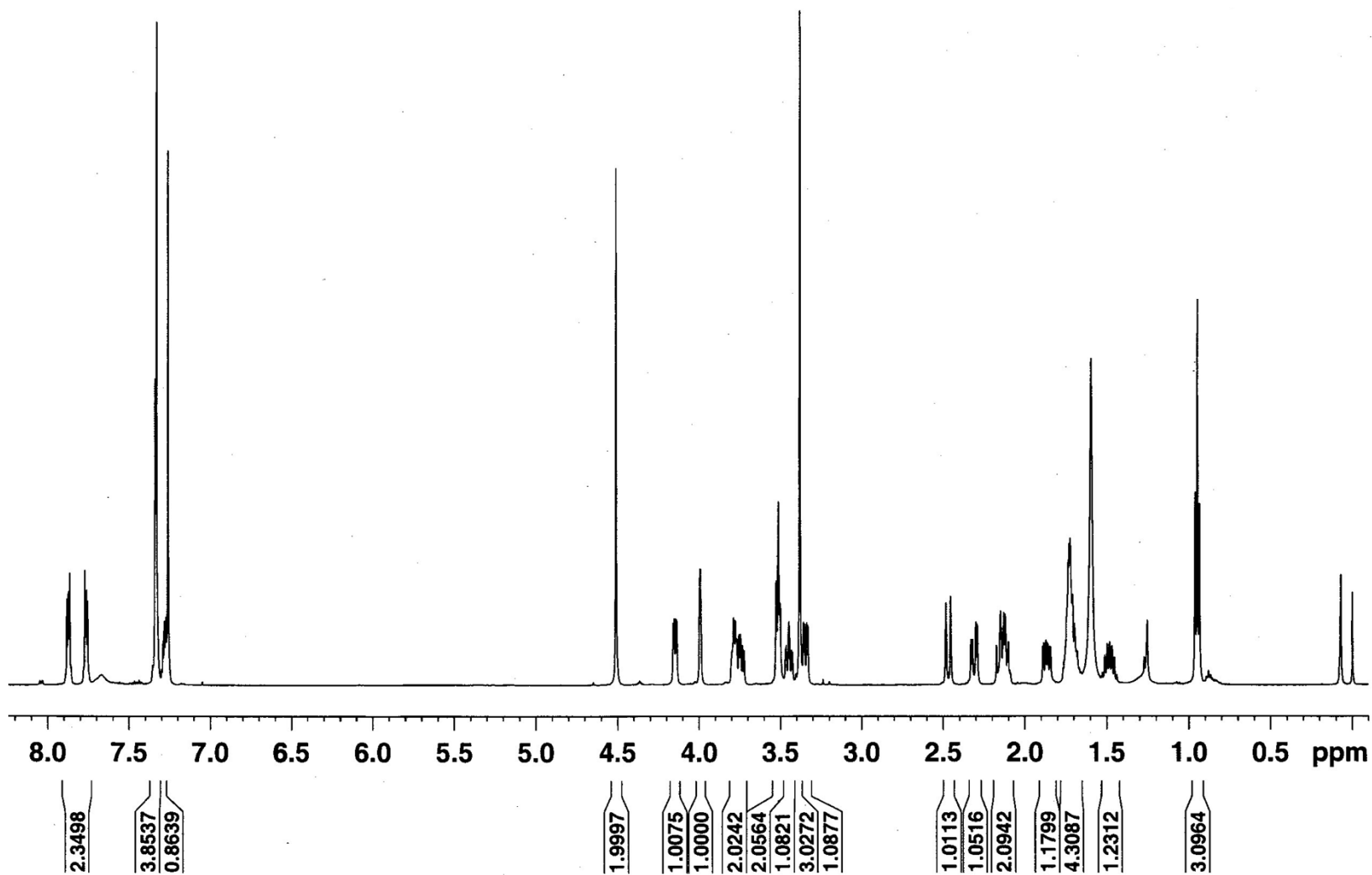
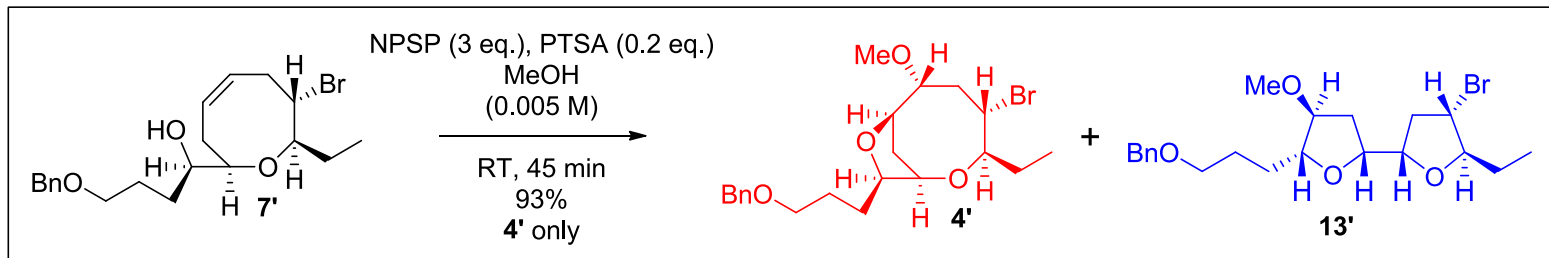


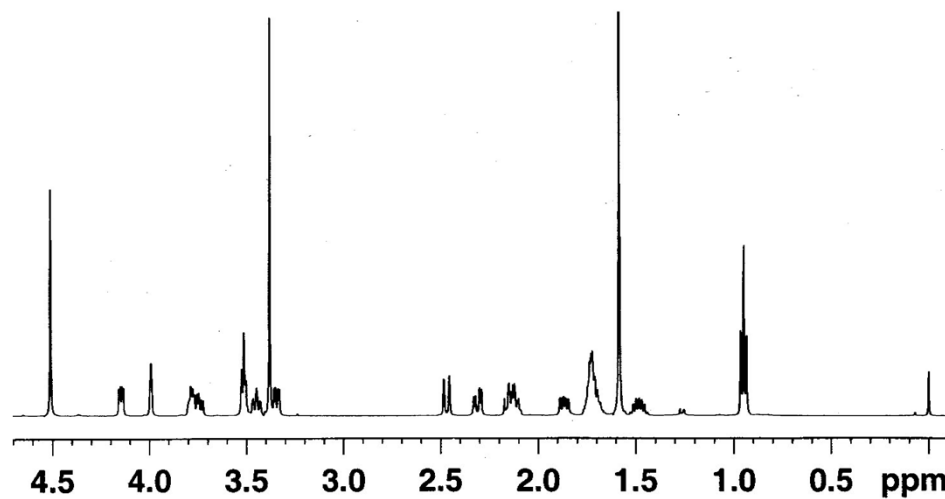
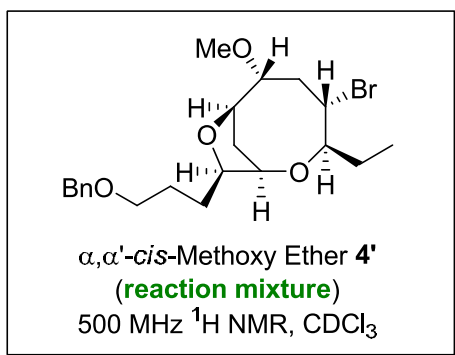
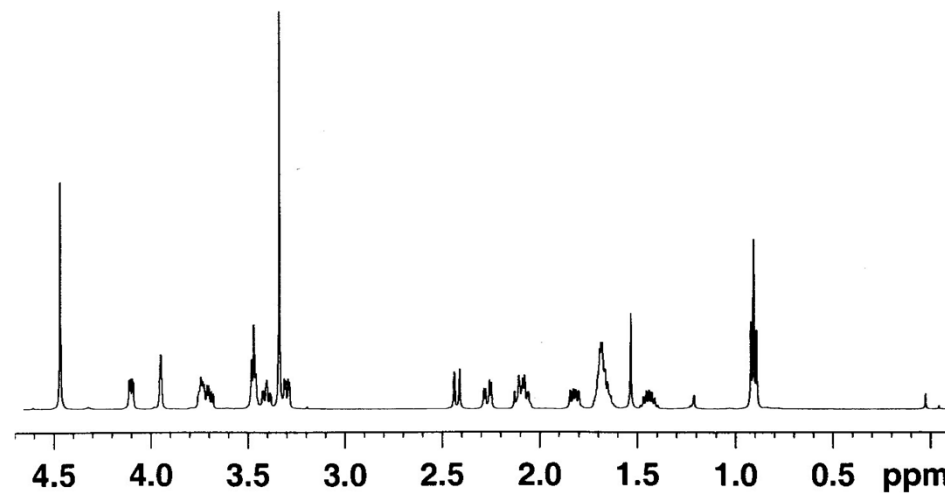
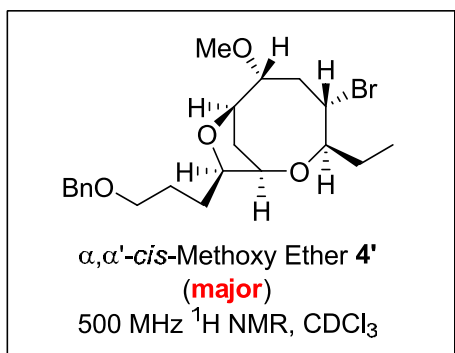
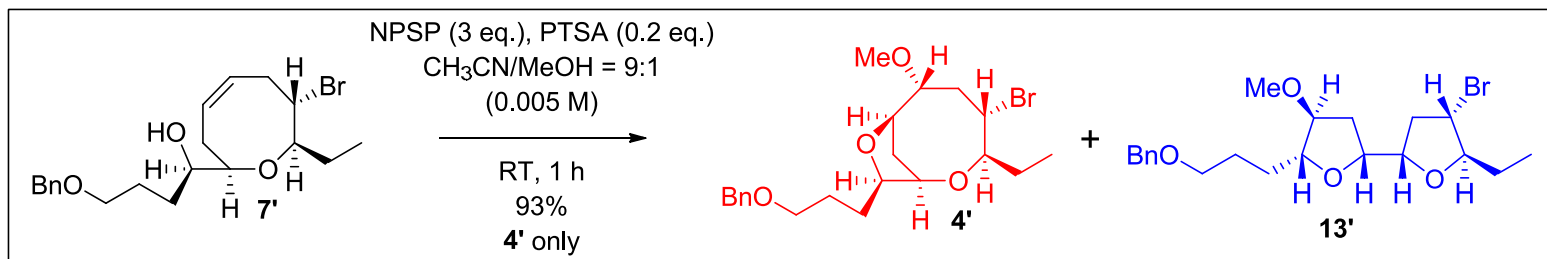


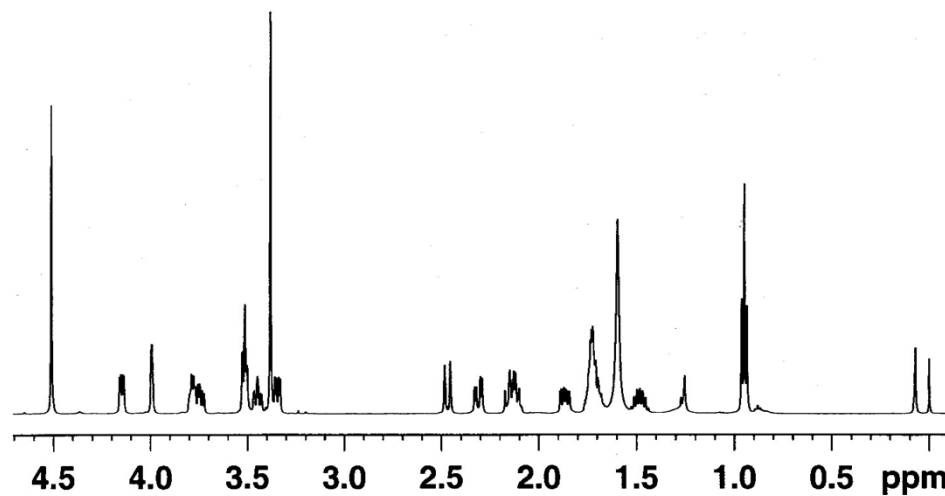
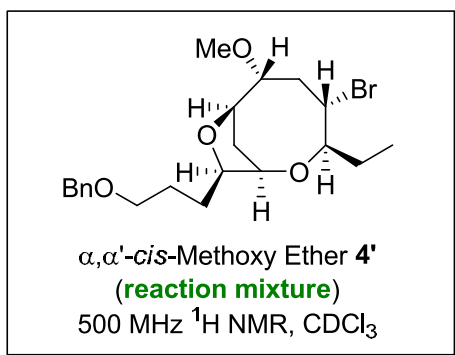
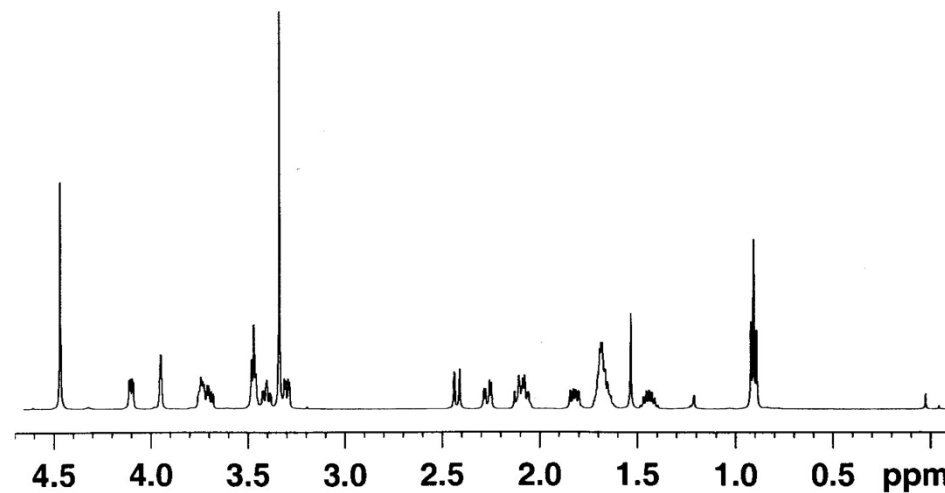
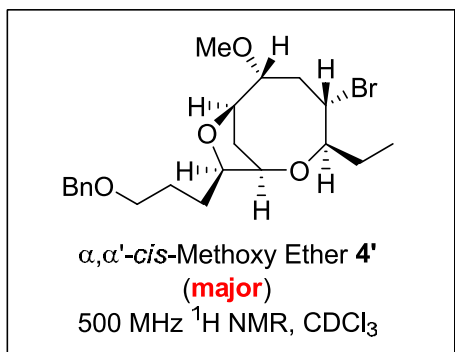
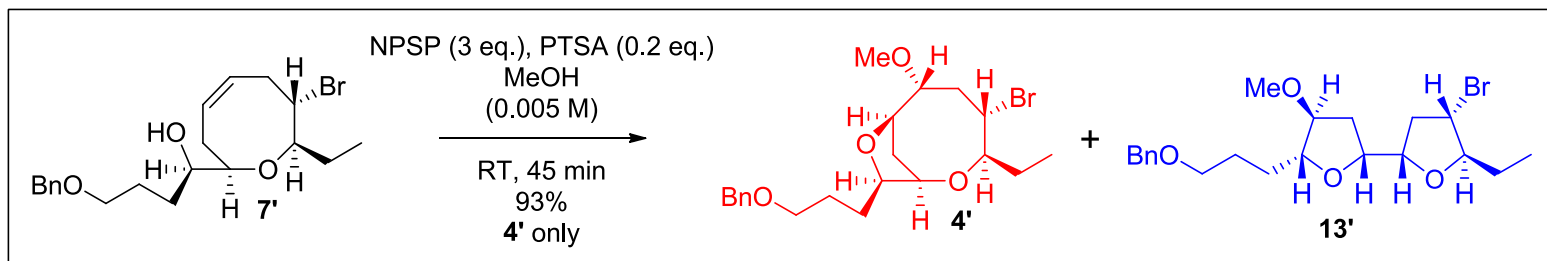
S24



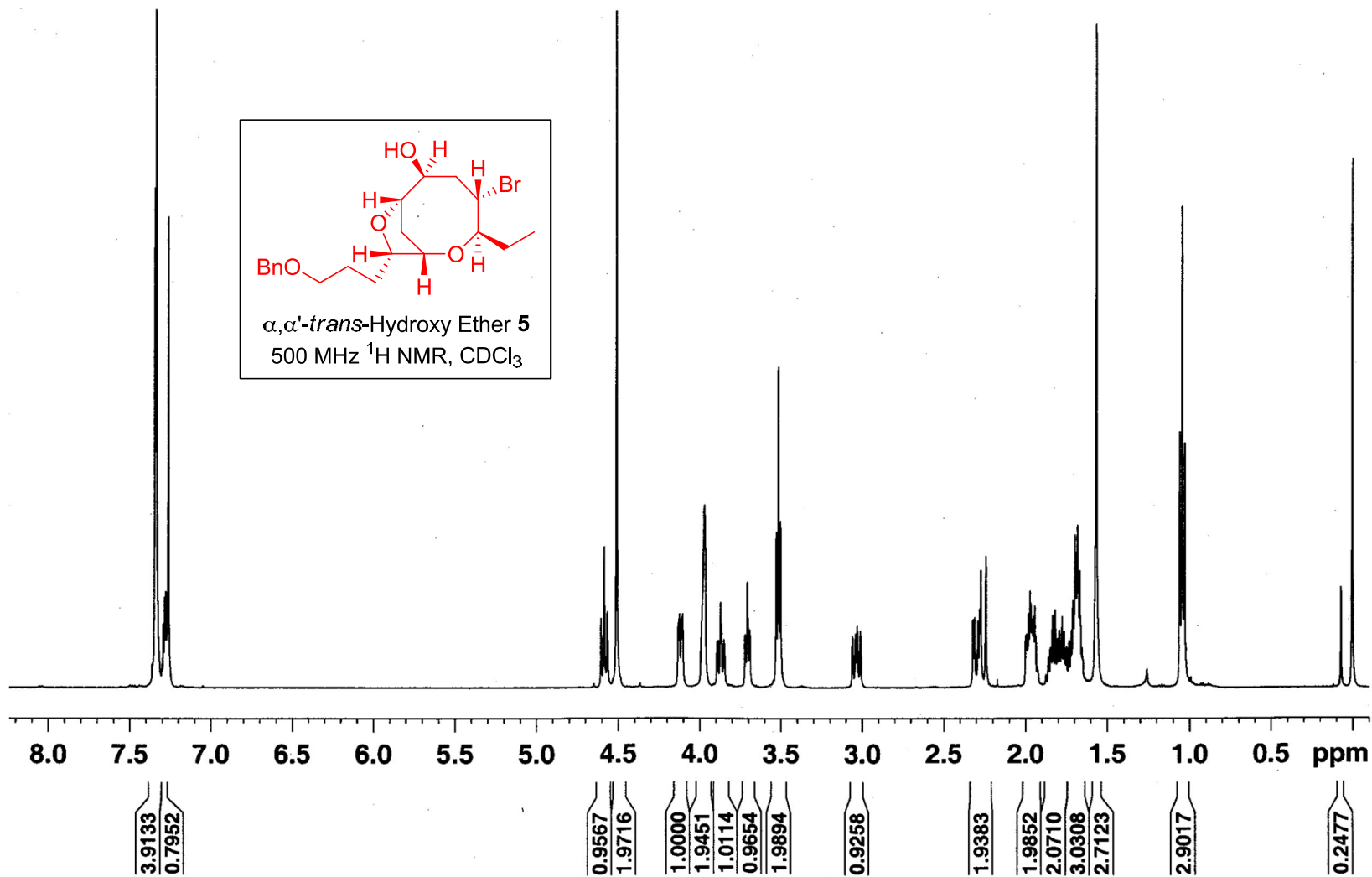


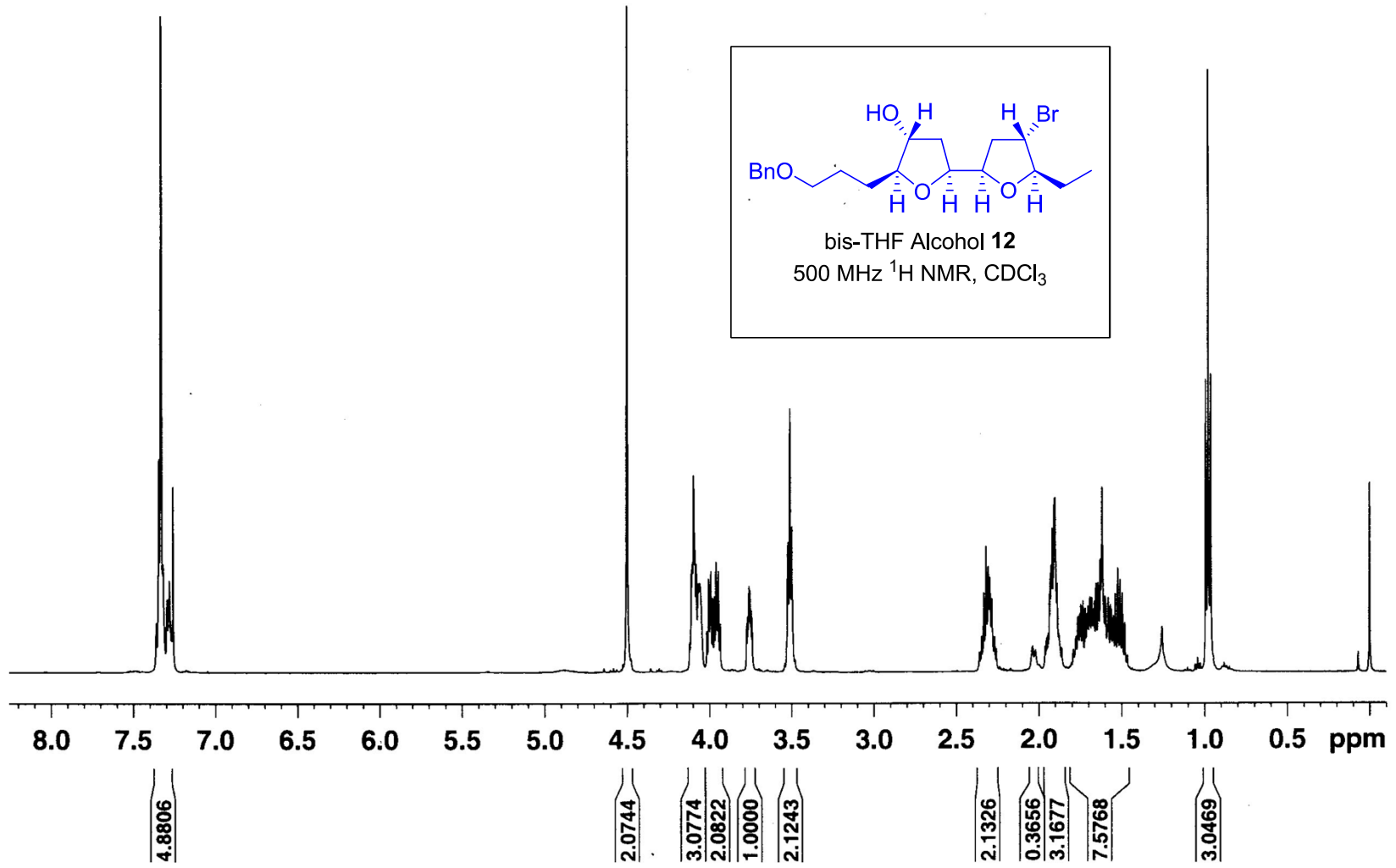
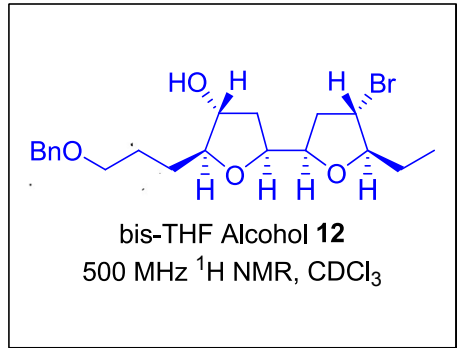


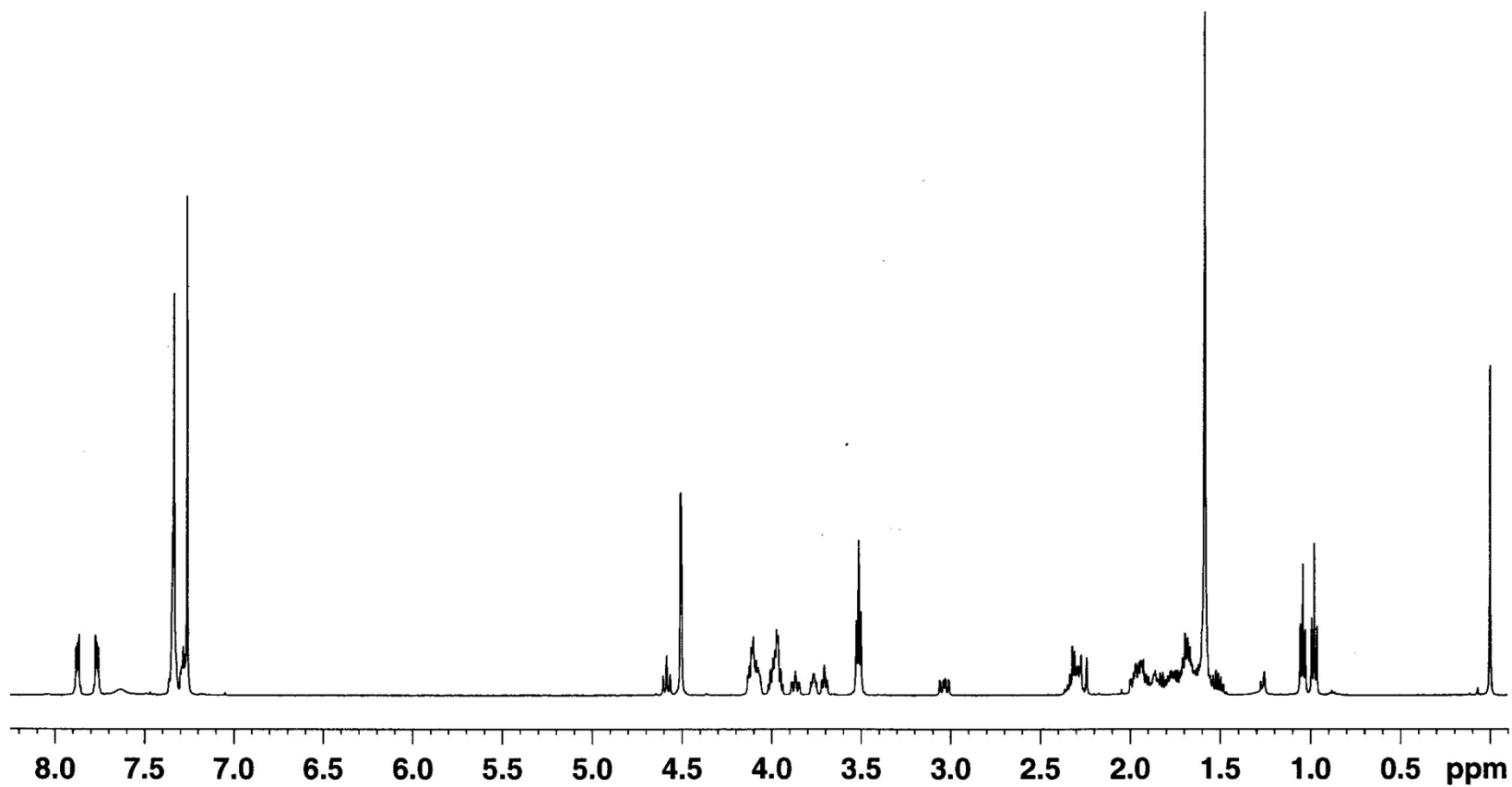
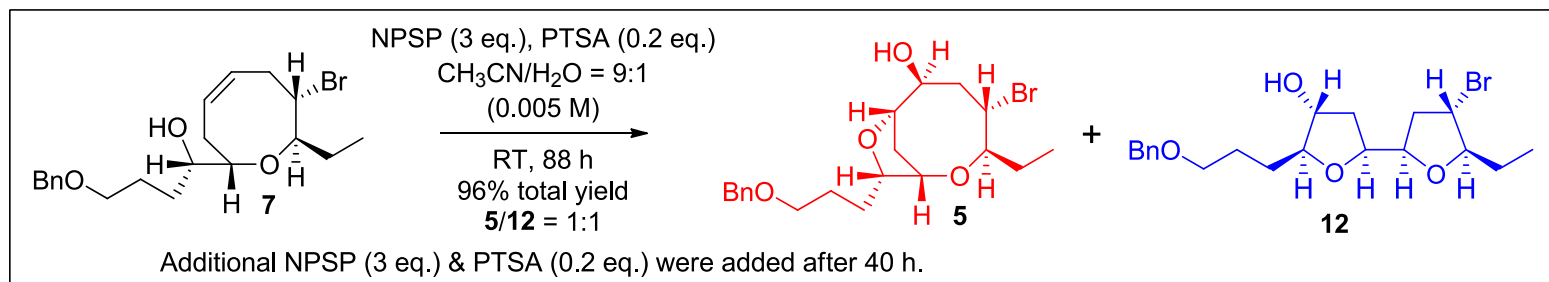


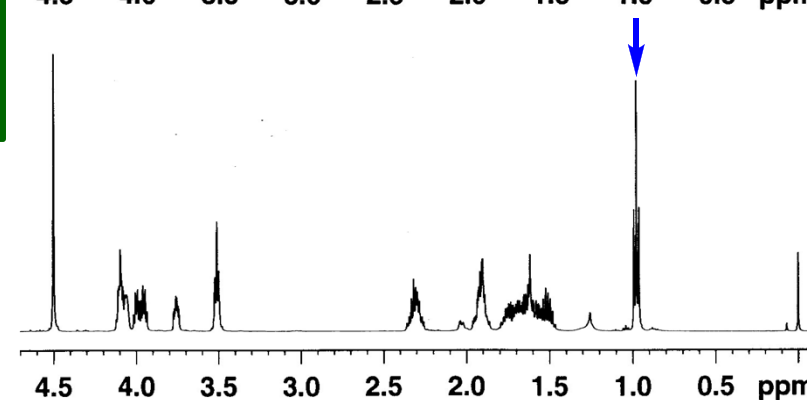
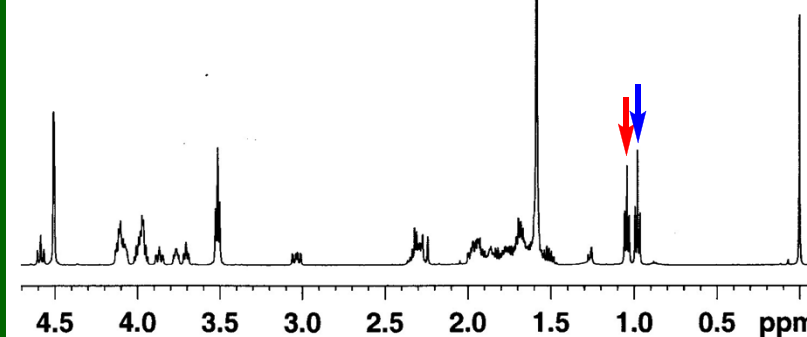
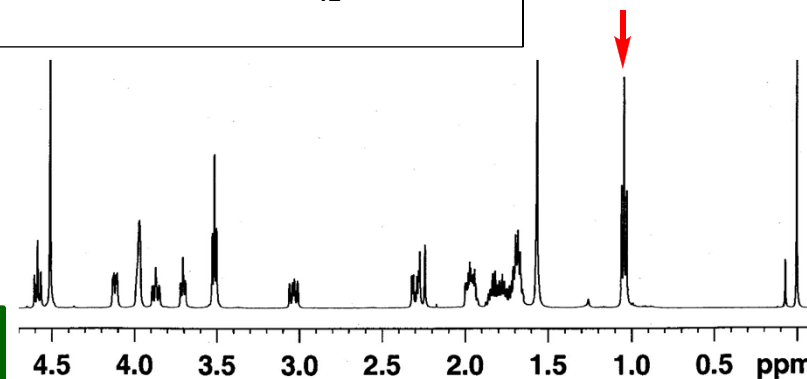
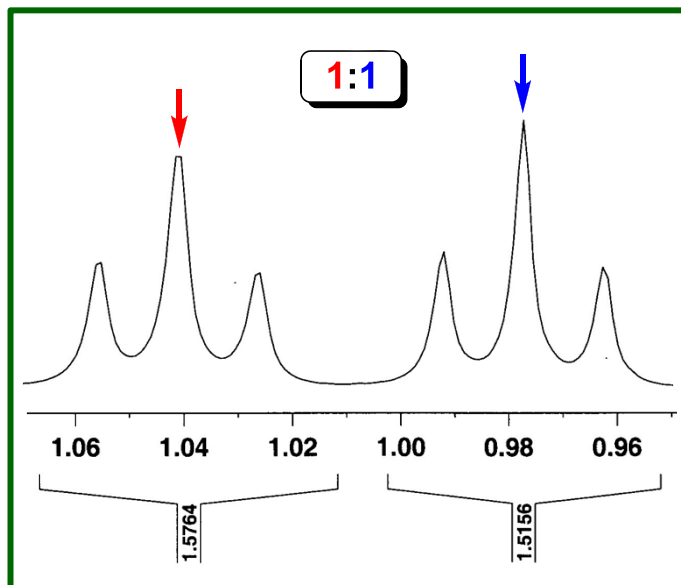
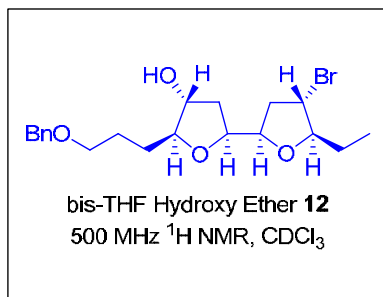
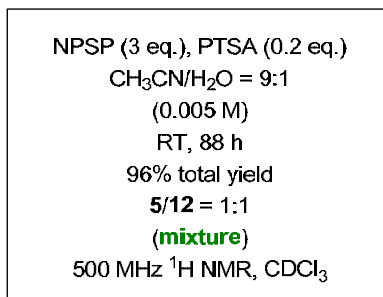
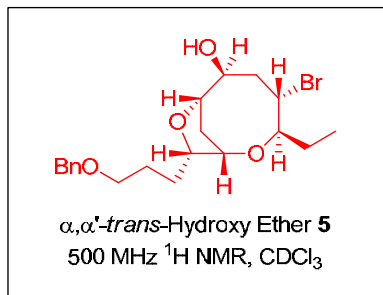
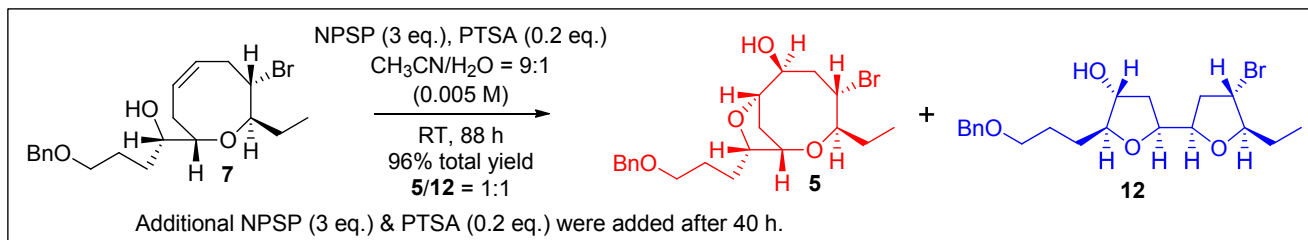


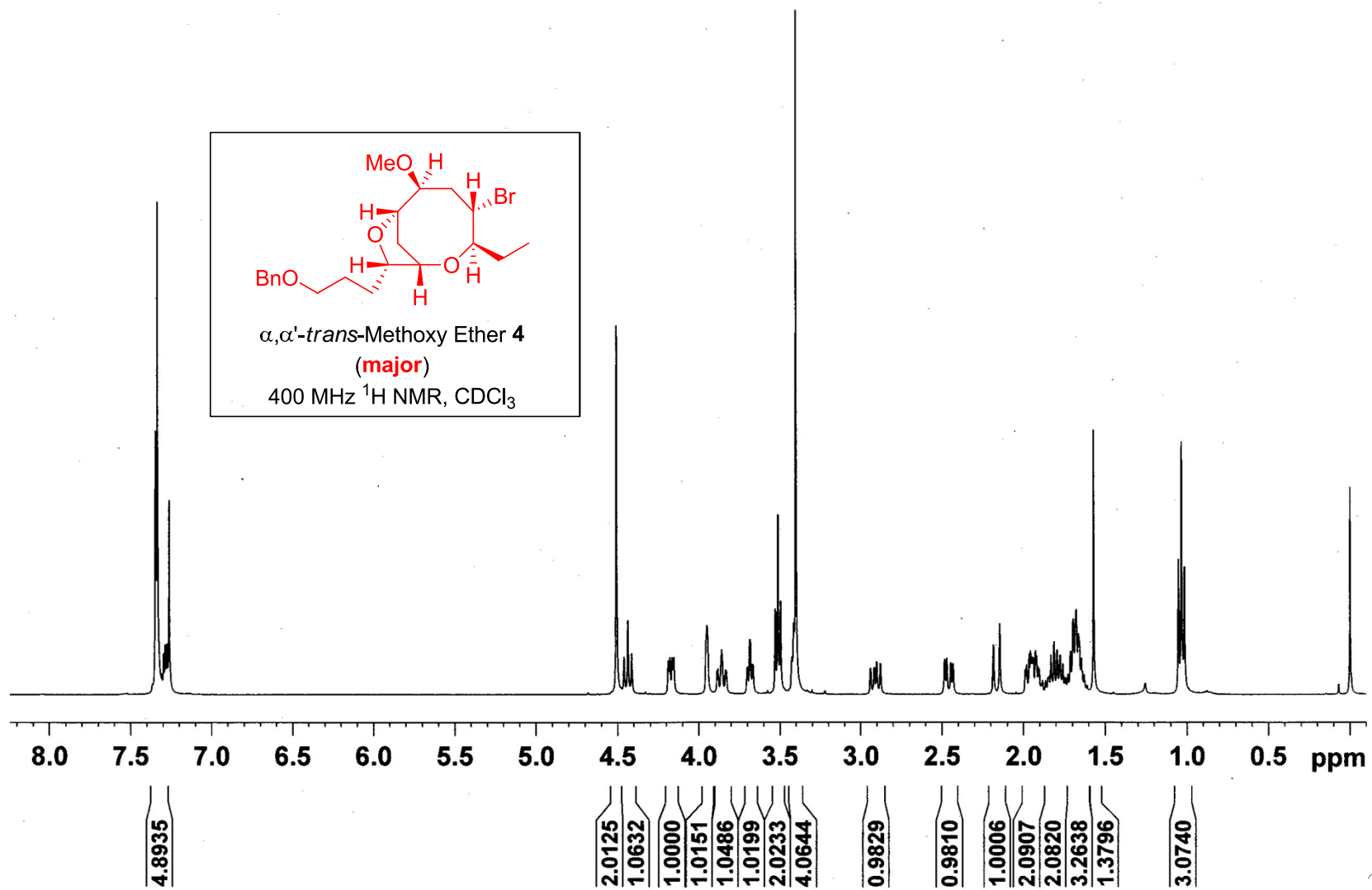
Isolaurefucin series ( $\alpha,\alpha'$ -trans)

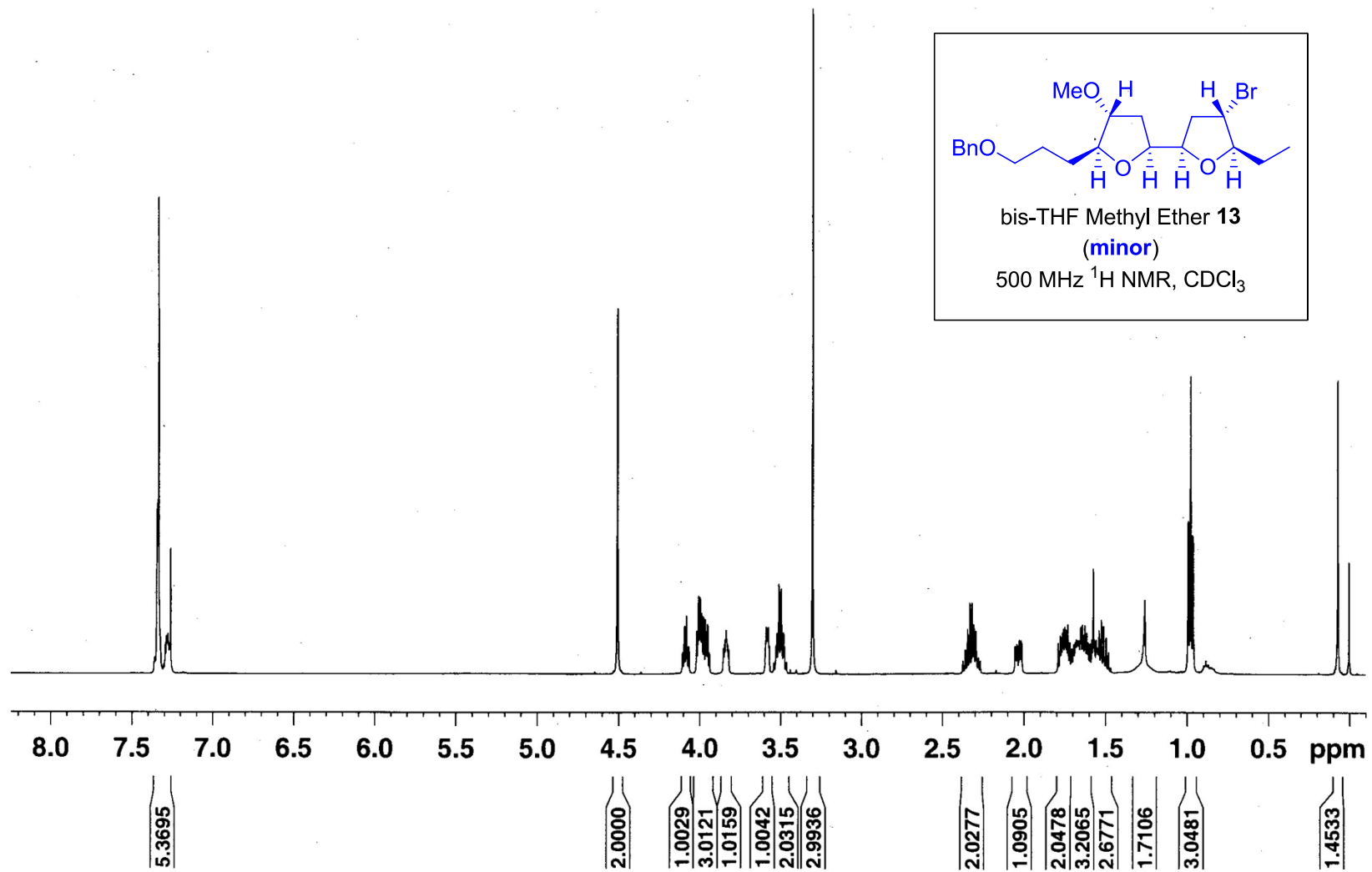


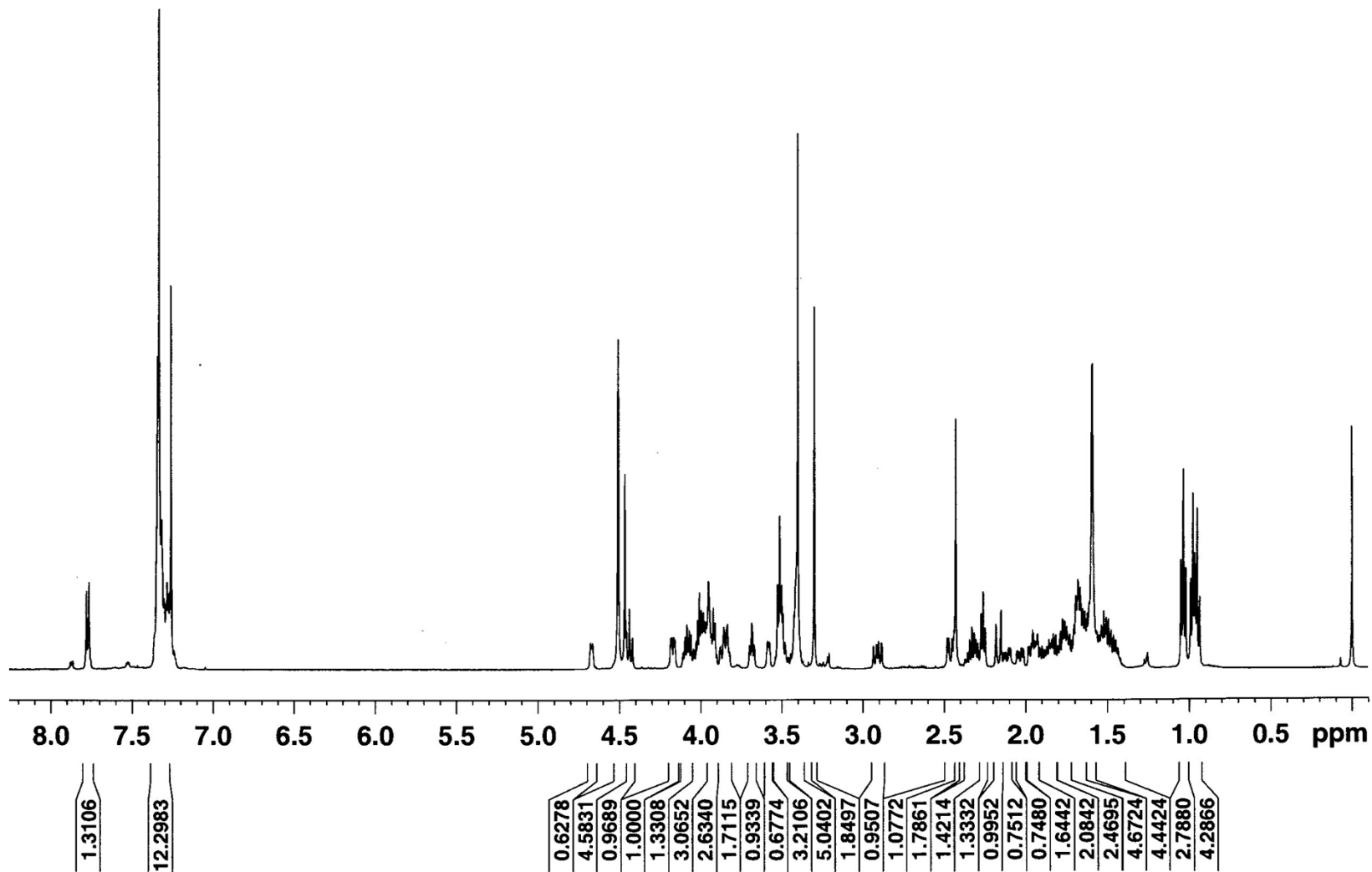
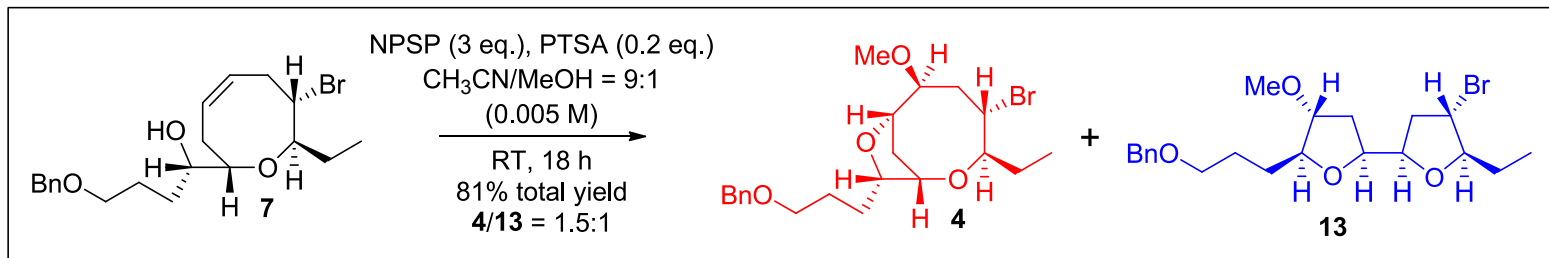


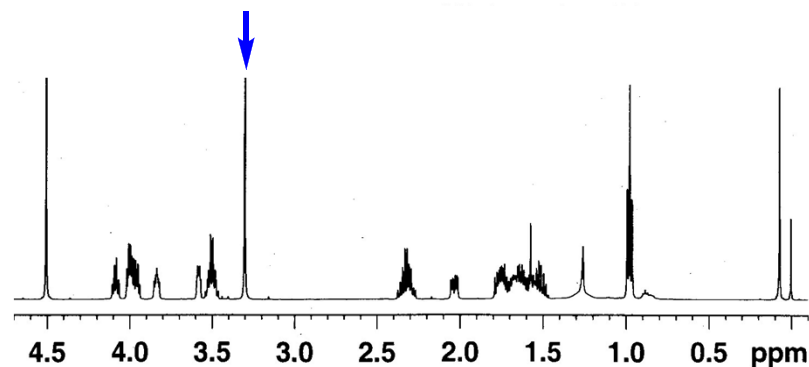
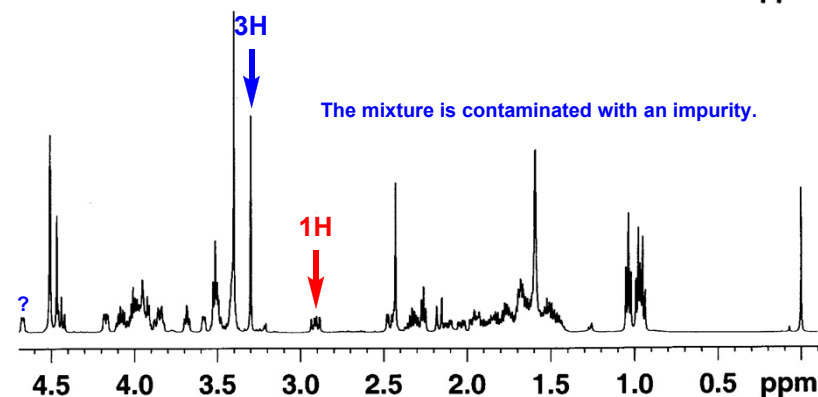
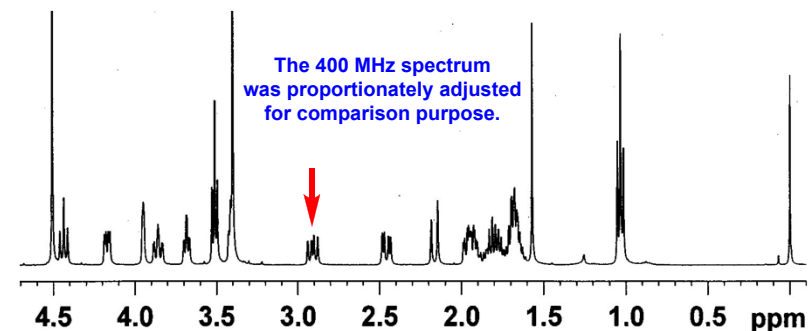
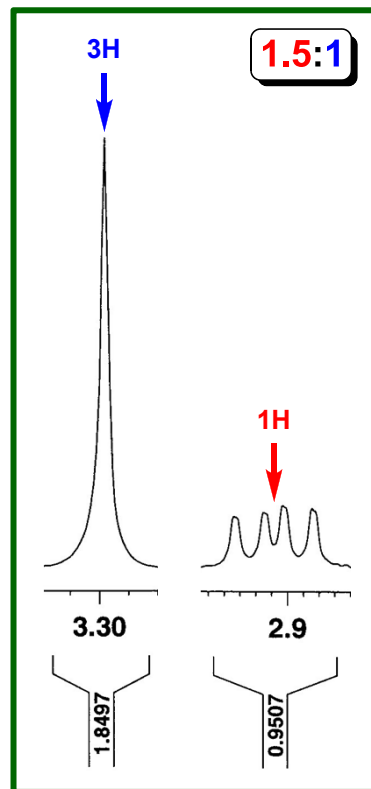
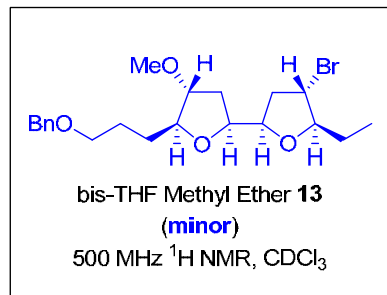
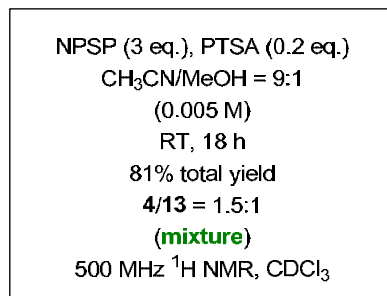
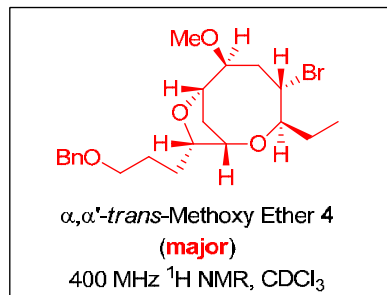
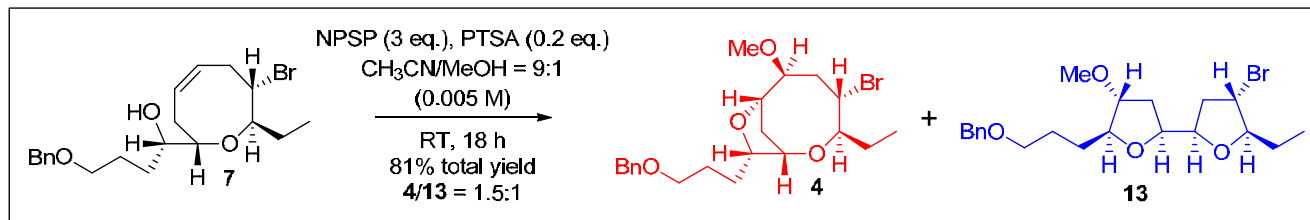




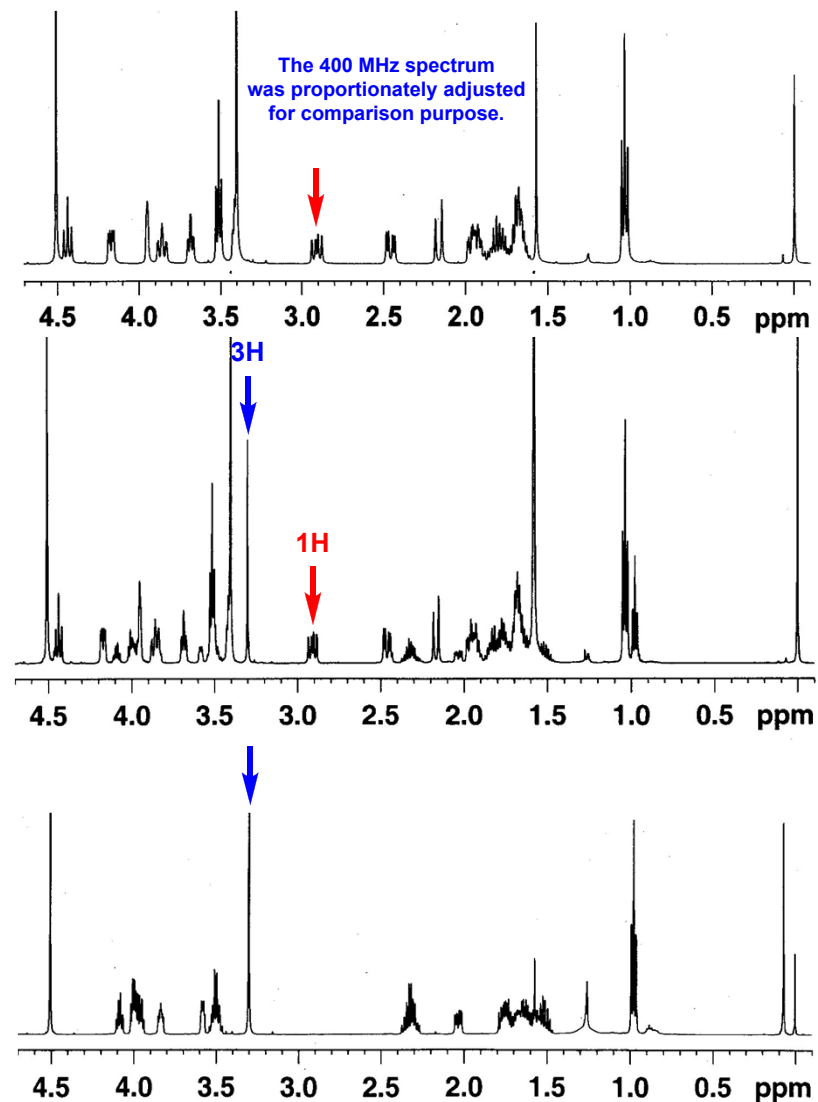
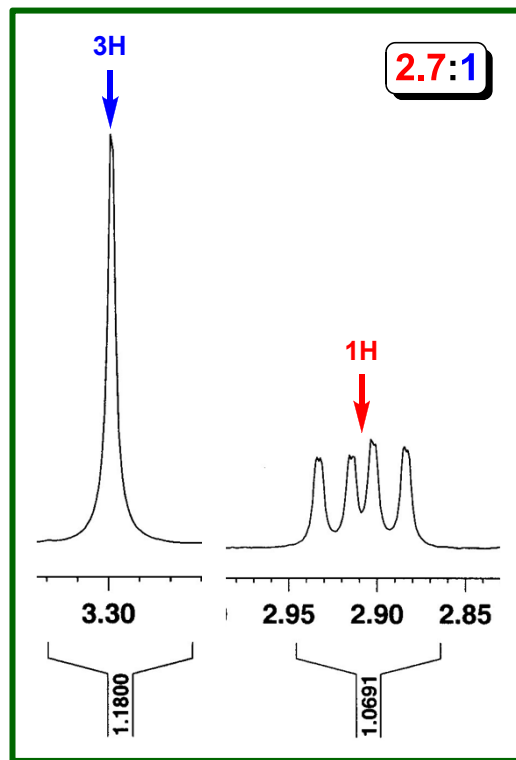
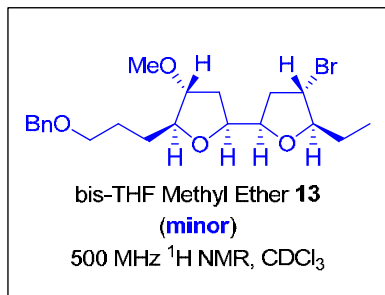
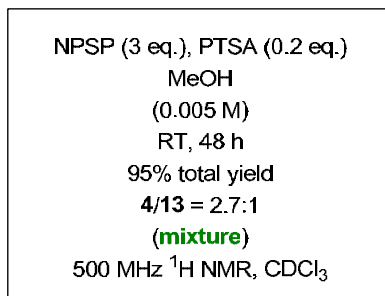
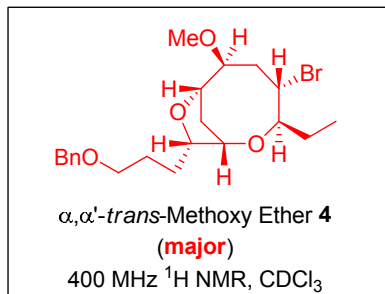
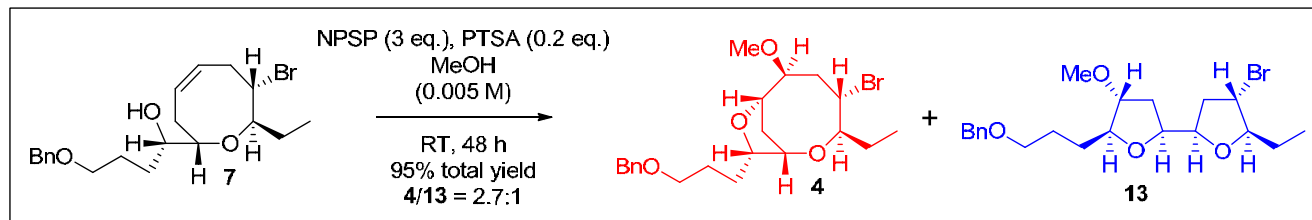






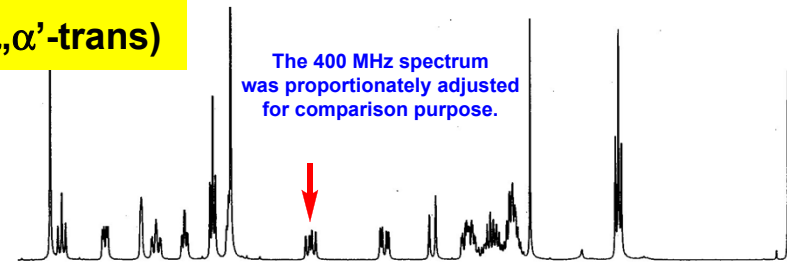
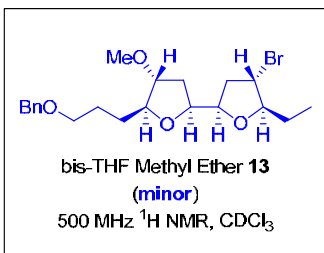
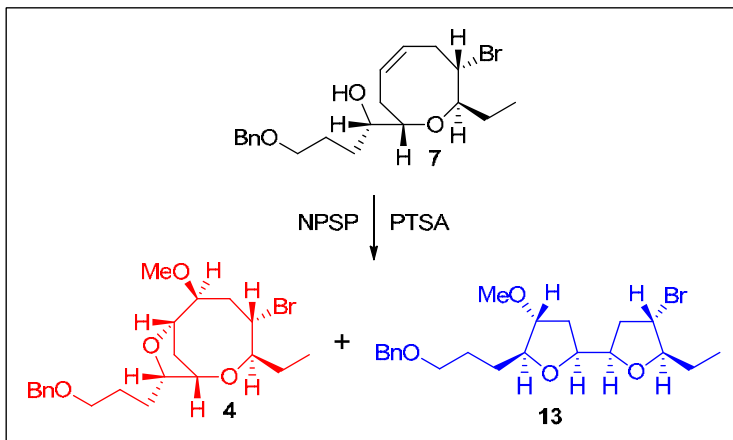
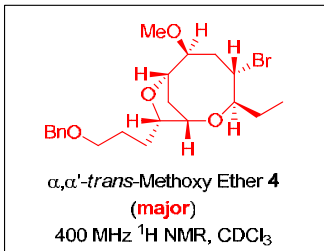




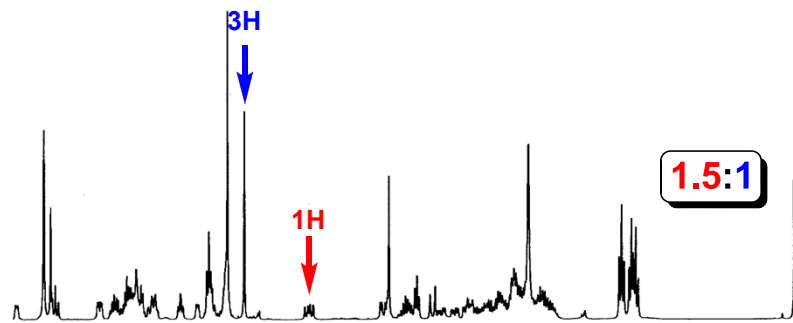


# Summary of Stereoselectivity in Organoselenium-Mediated Alkoxyetherification

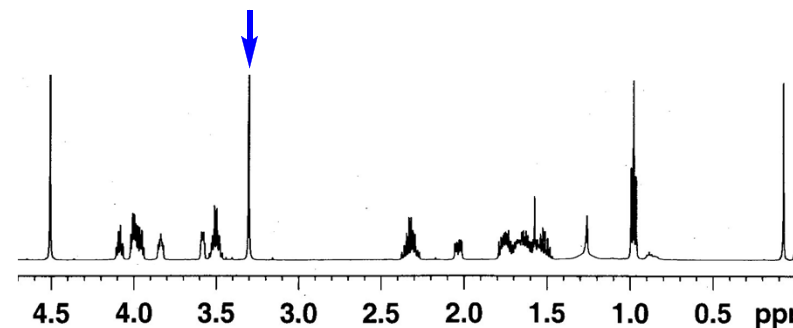
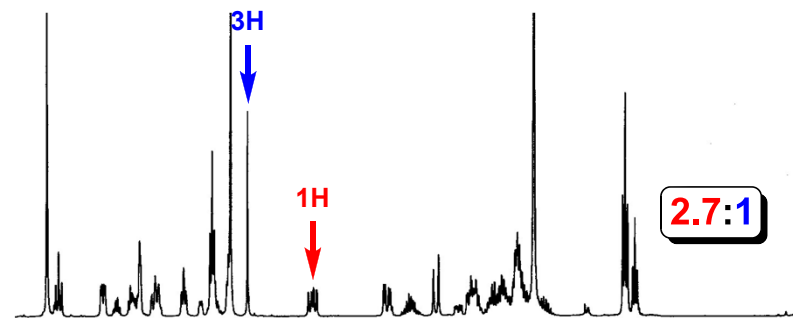
## Isolaurefucin series ( $\alpha, \alpha'$ -trans)



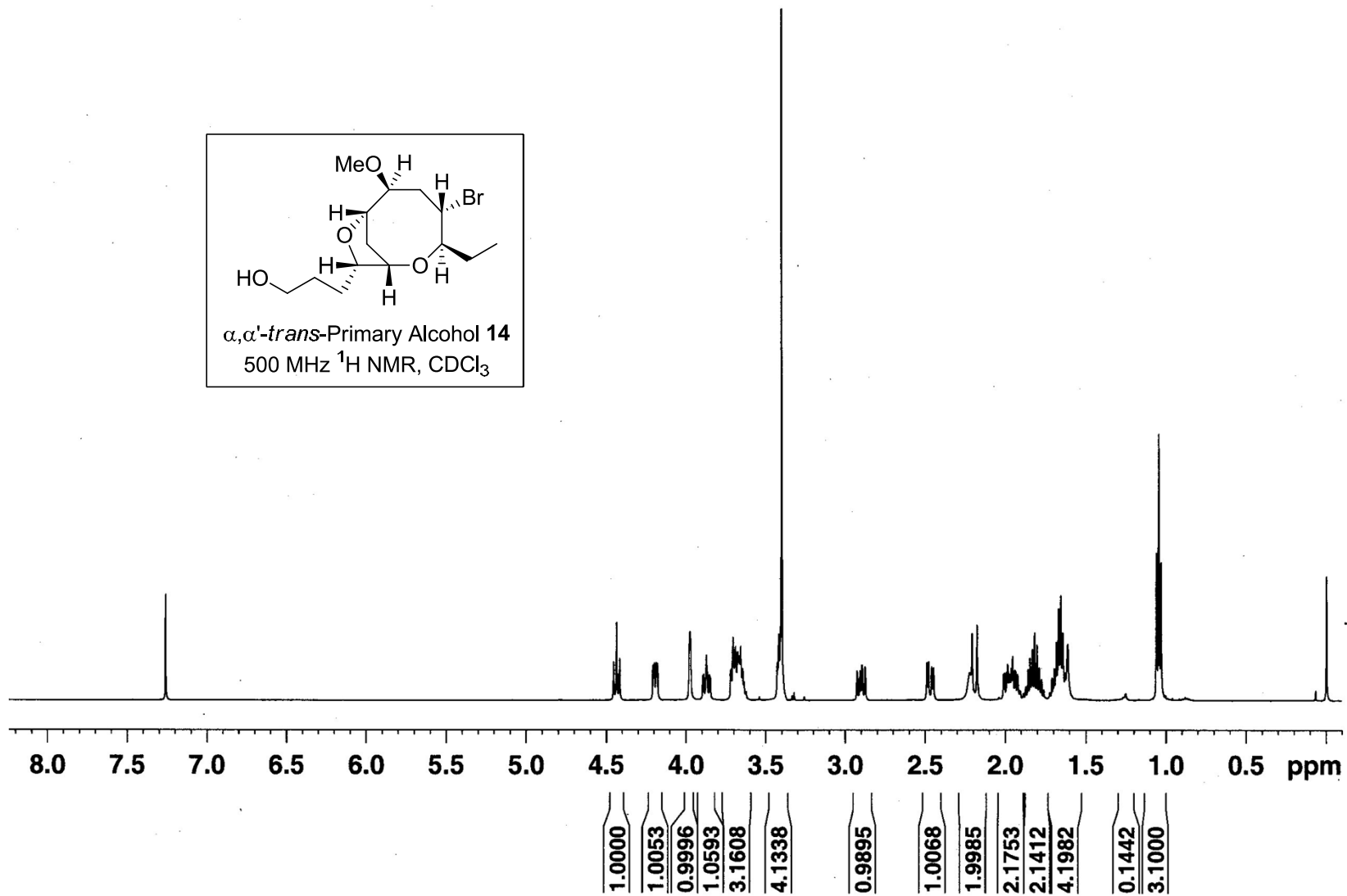
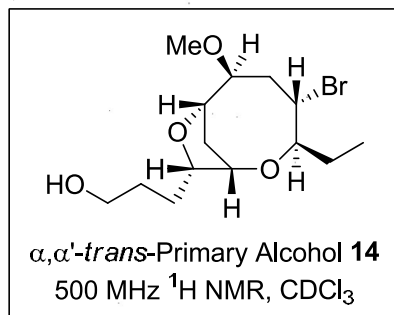
$\text{CH}_3\text{CN}/\text{MeOH}$   
(9:1)

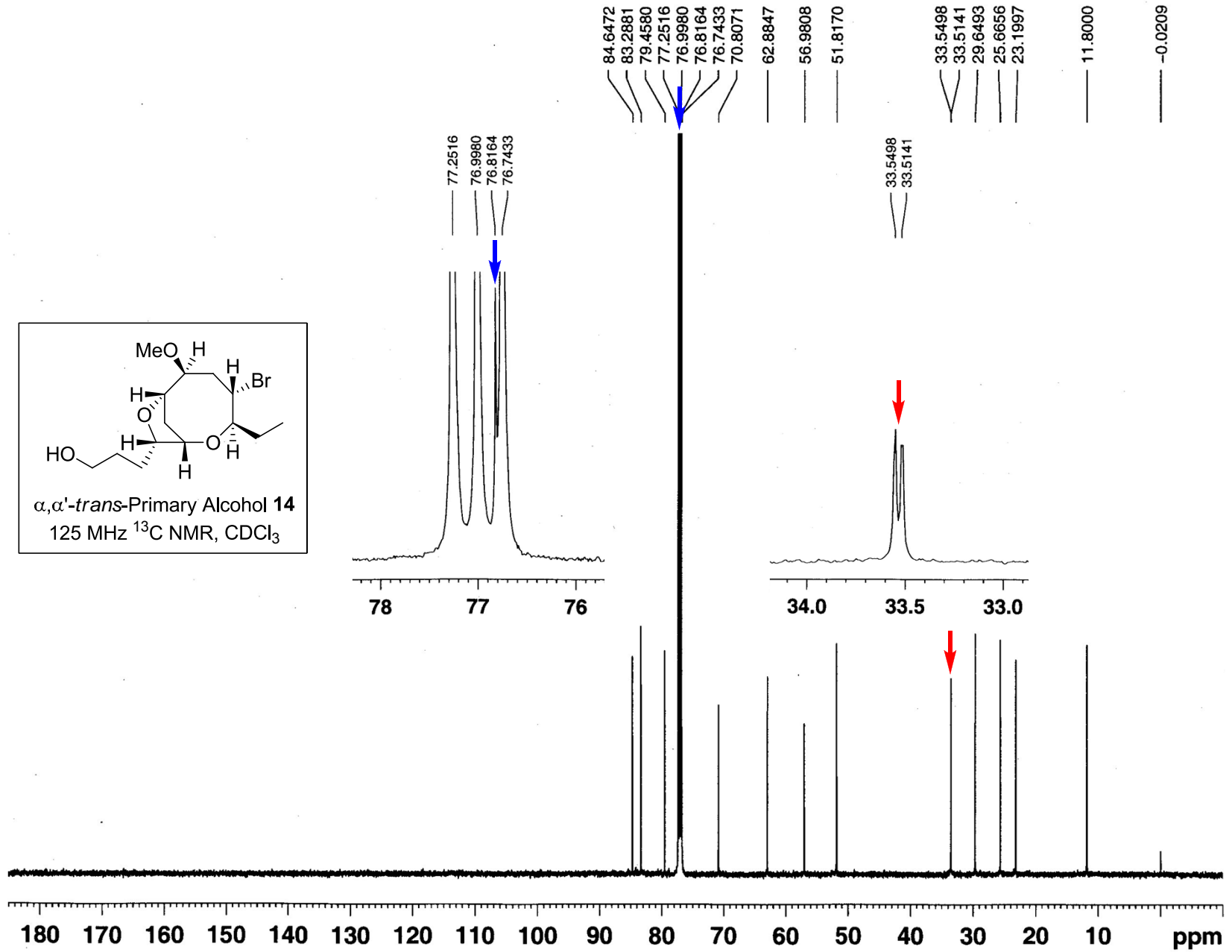
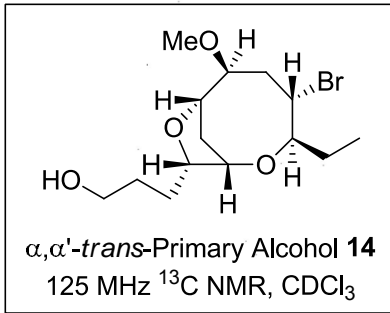


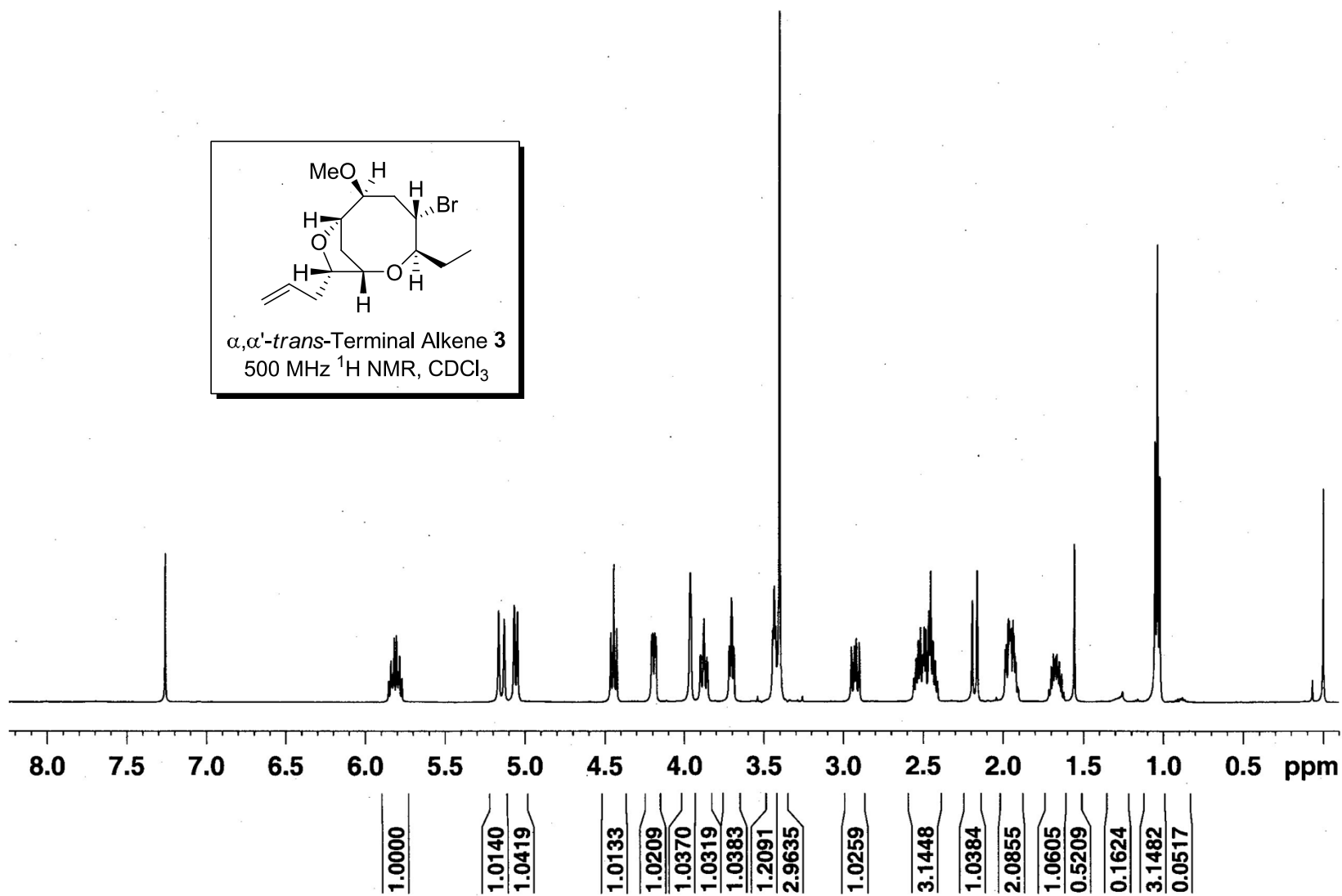
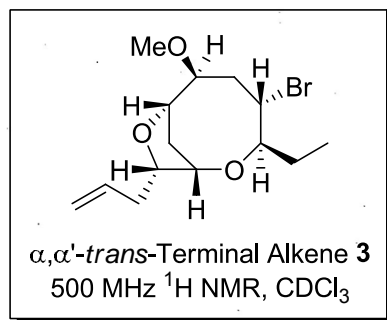
MeOH

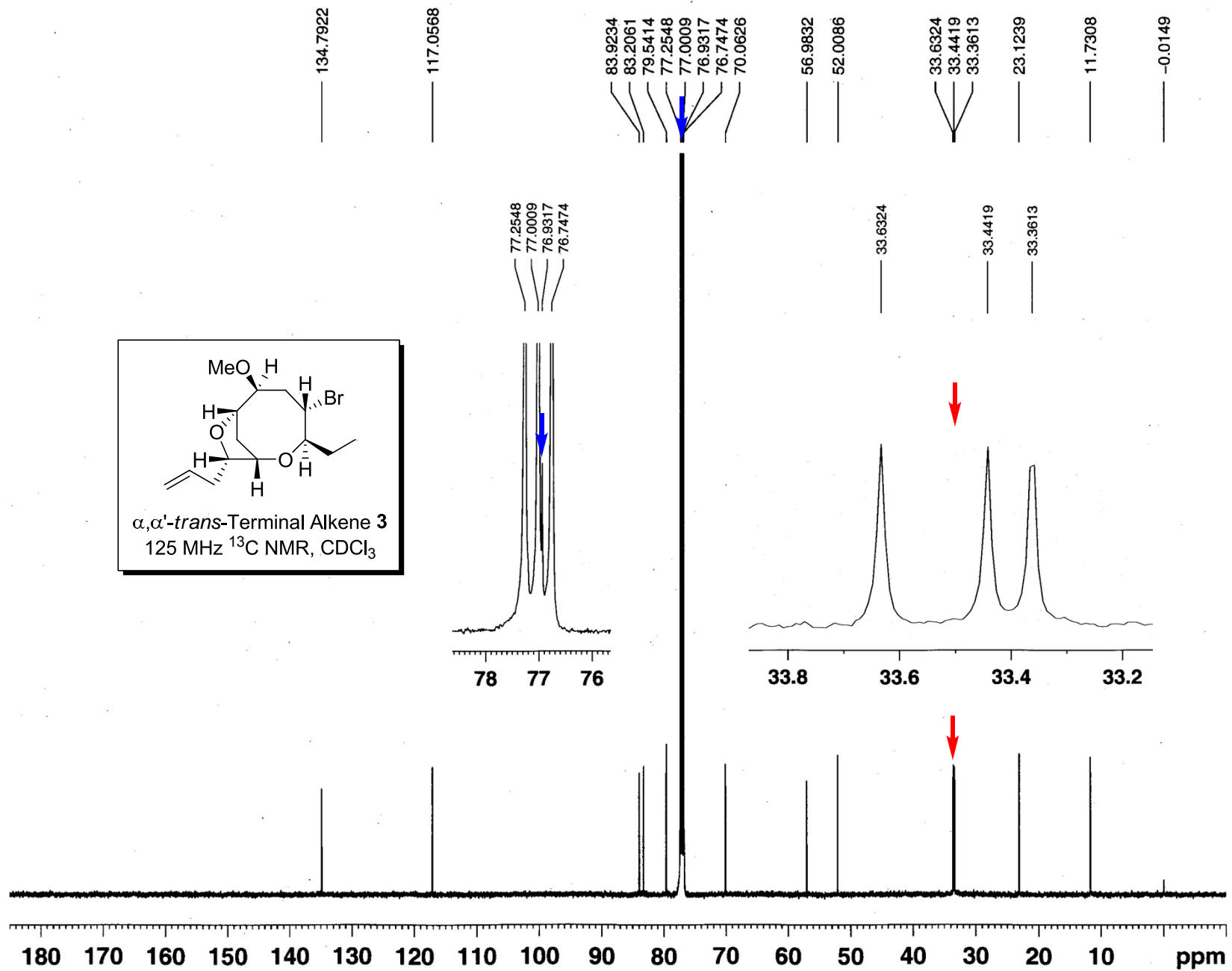


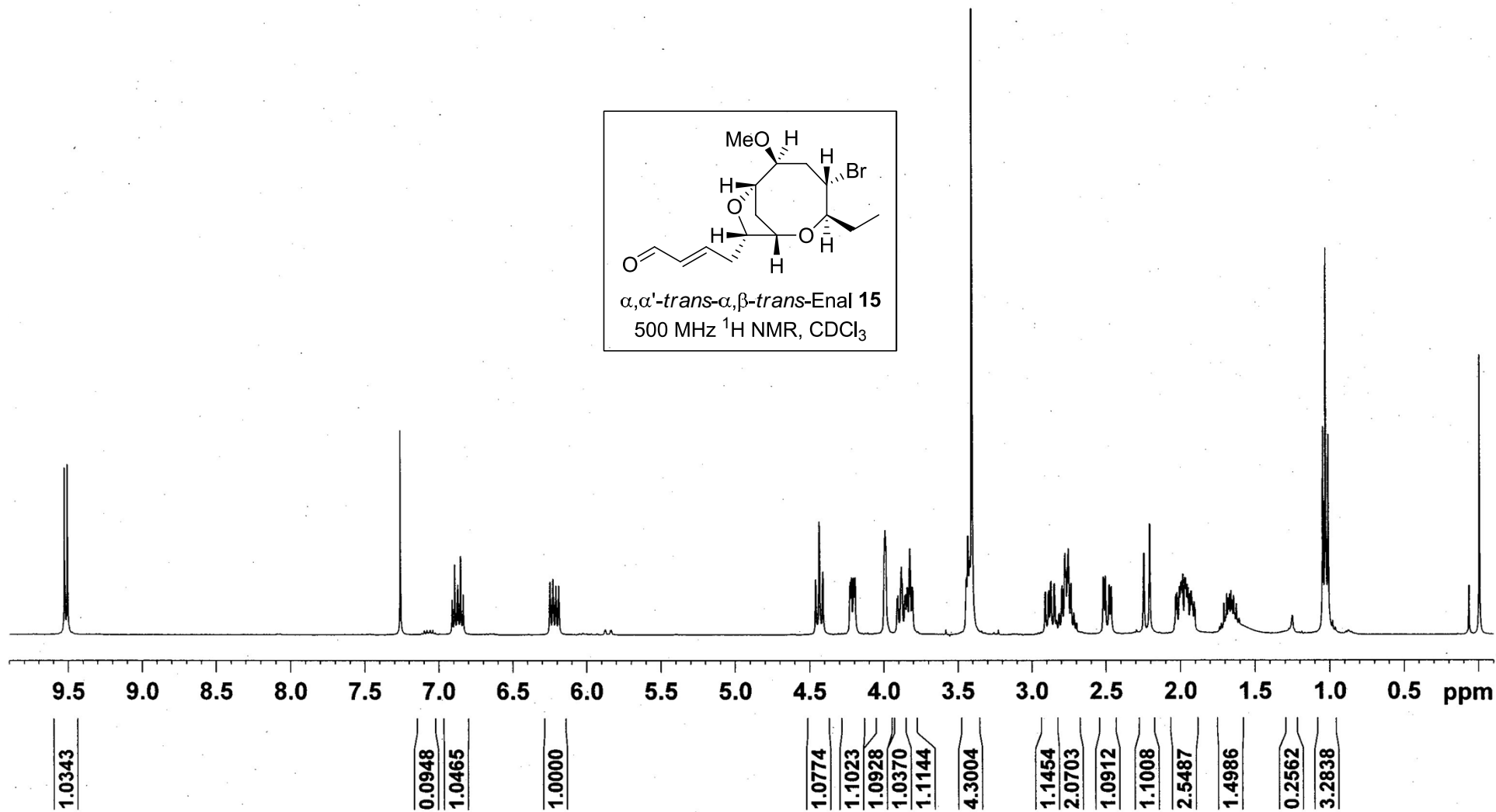
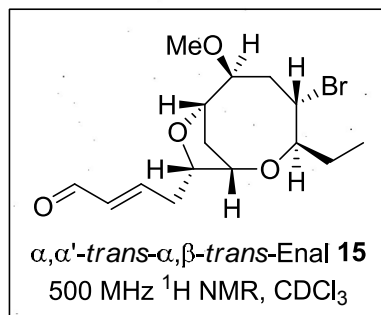
# Completion of the Synthesis

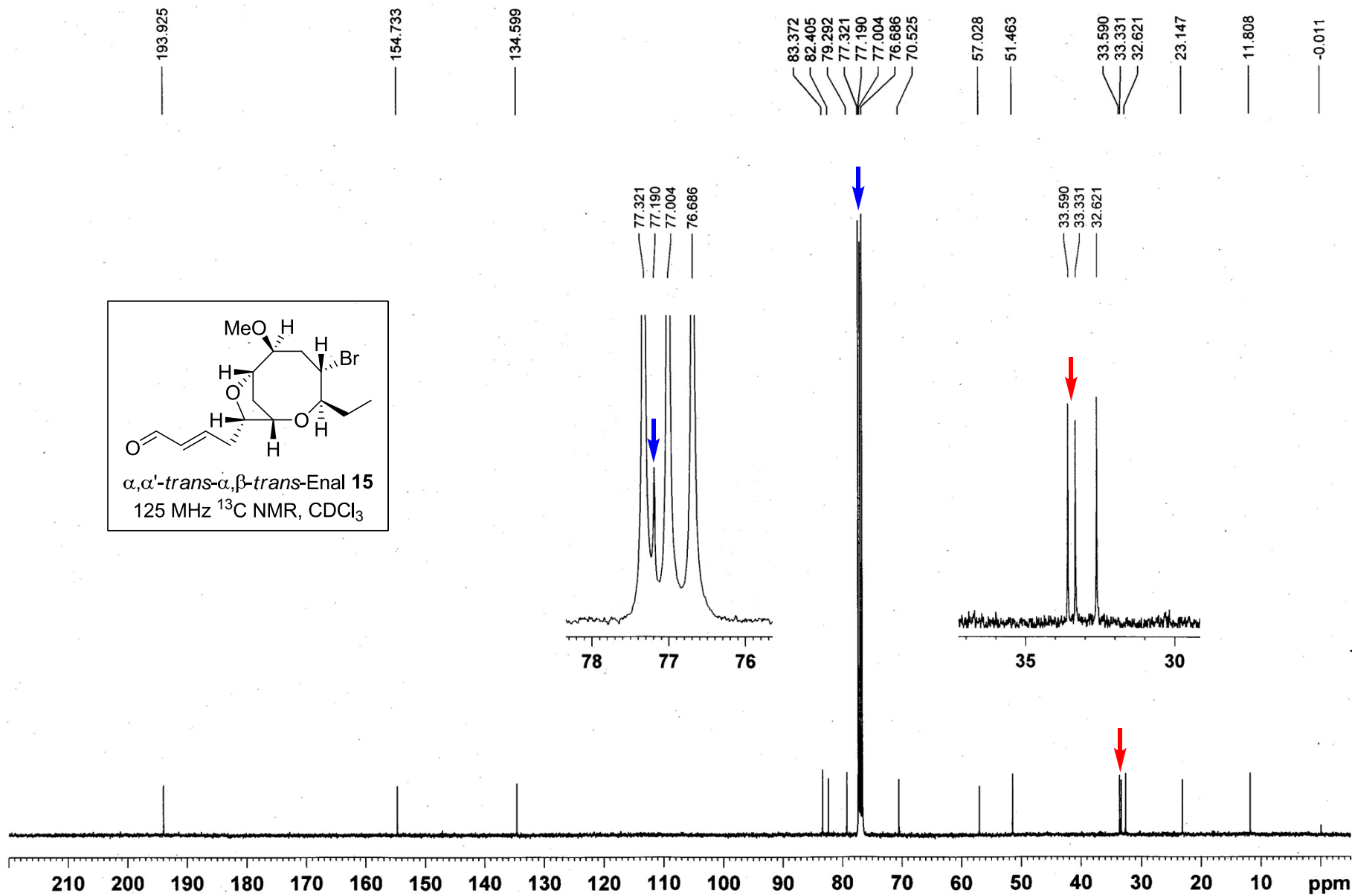


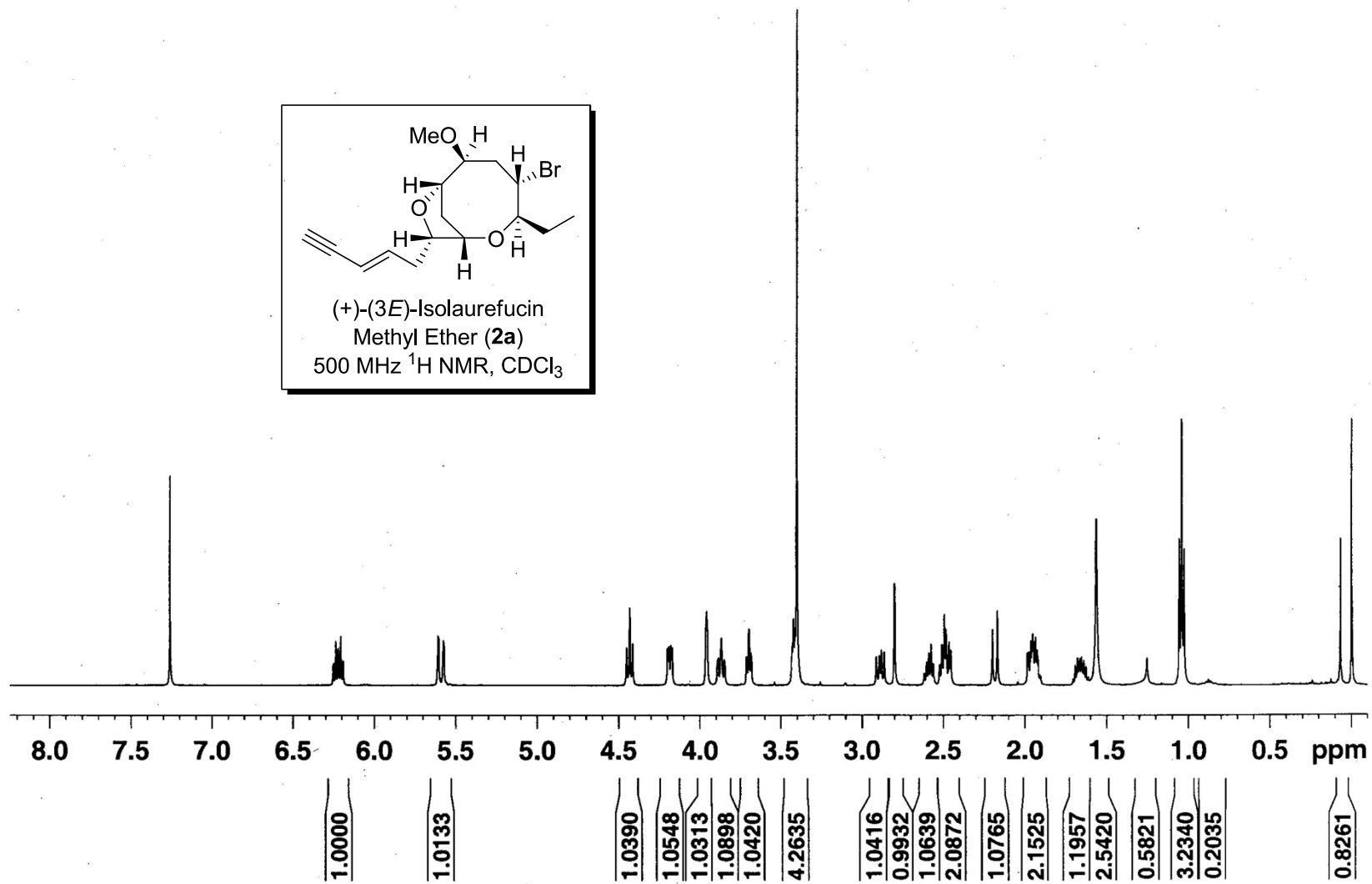
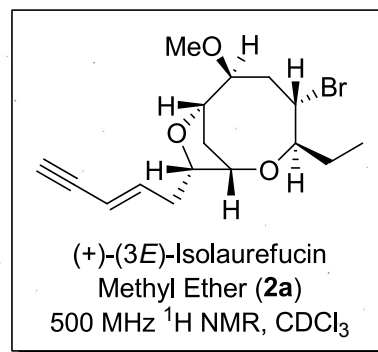






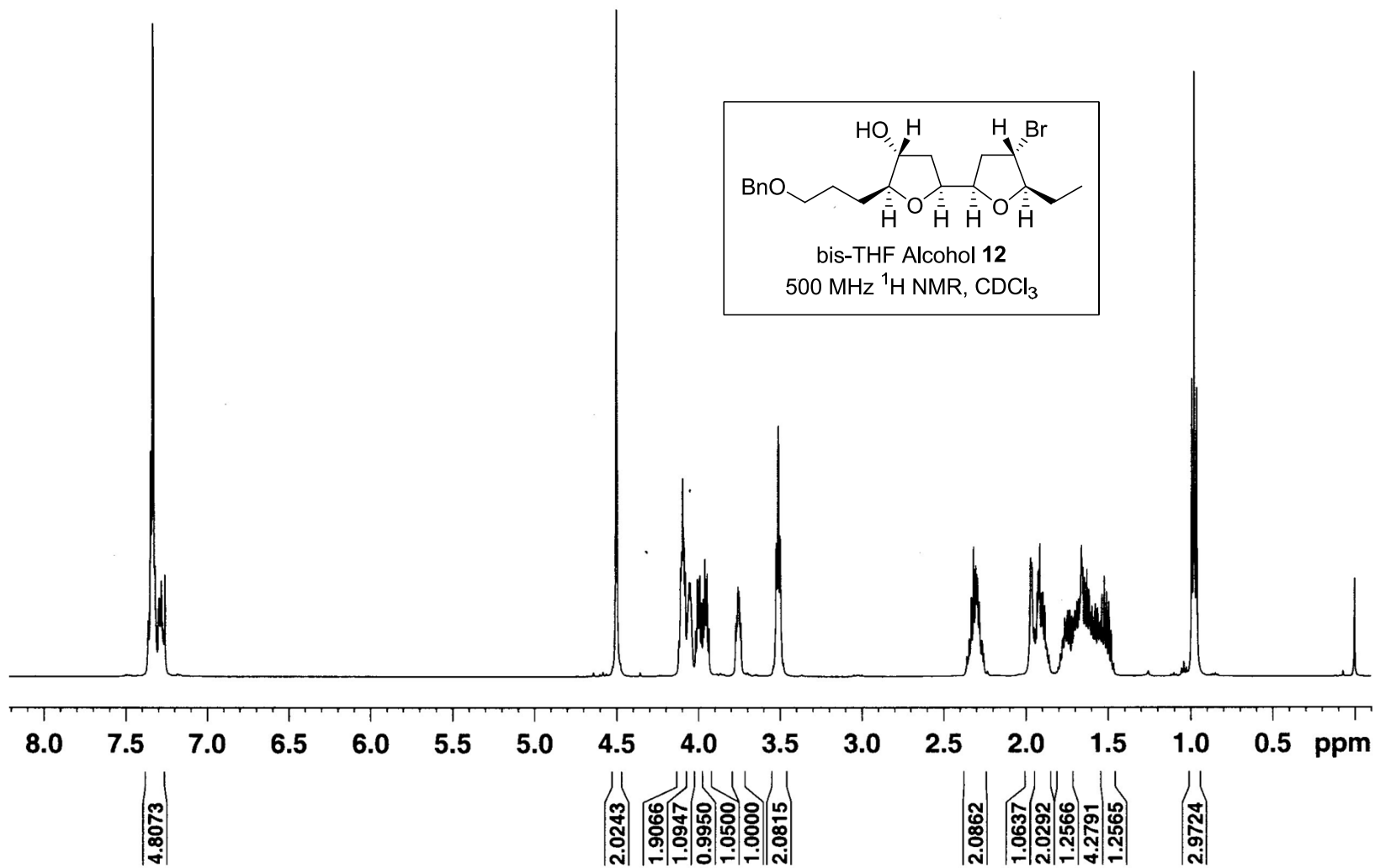


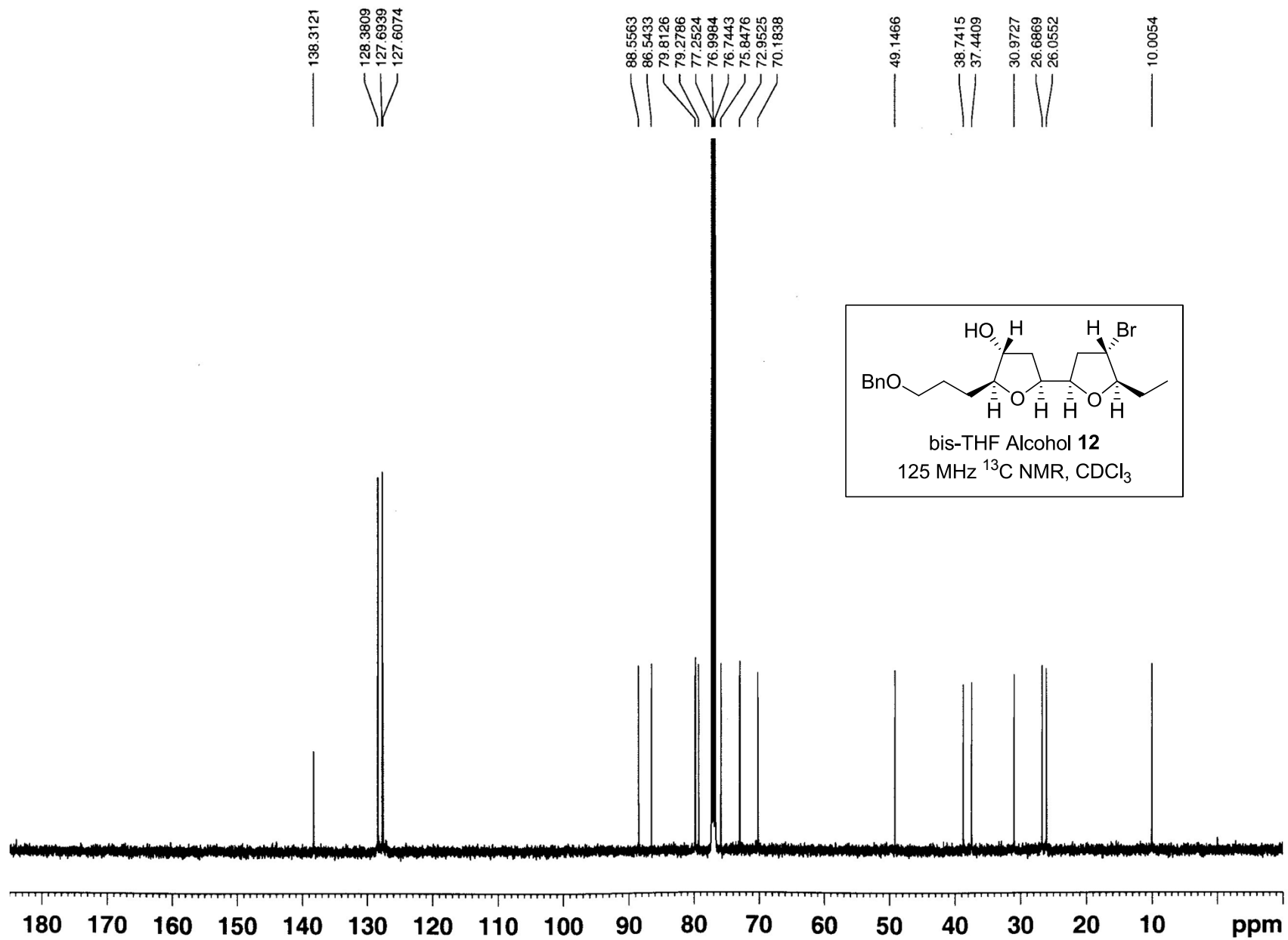




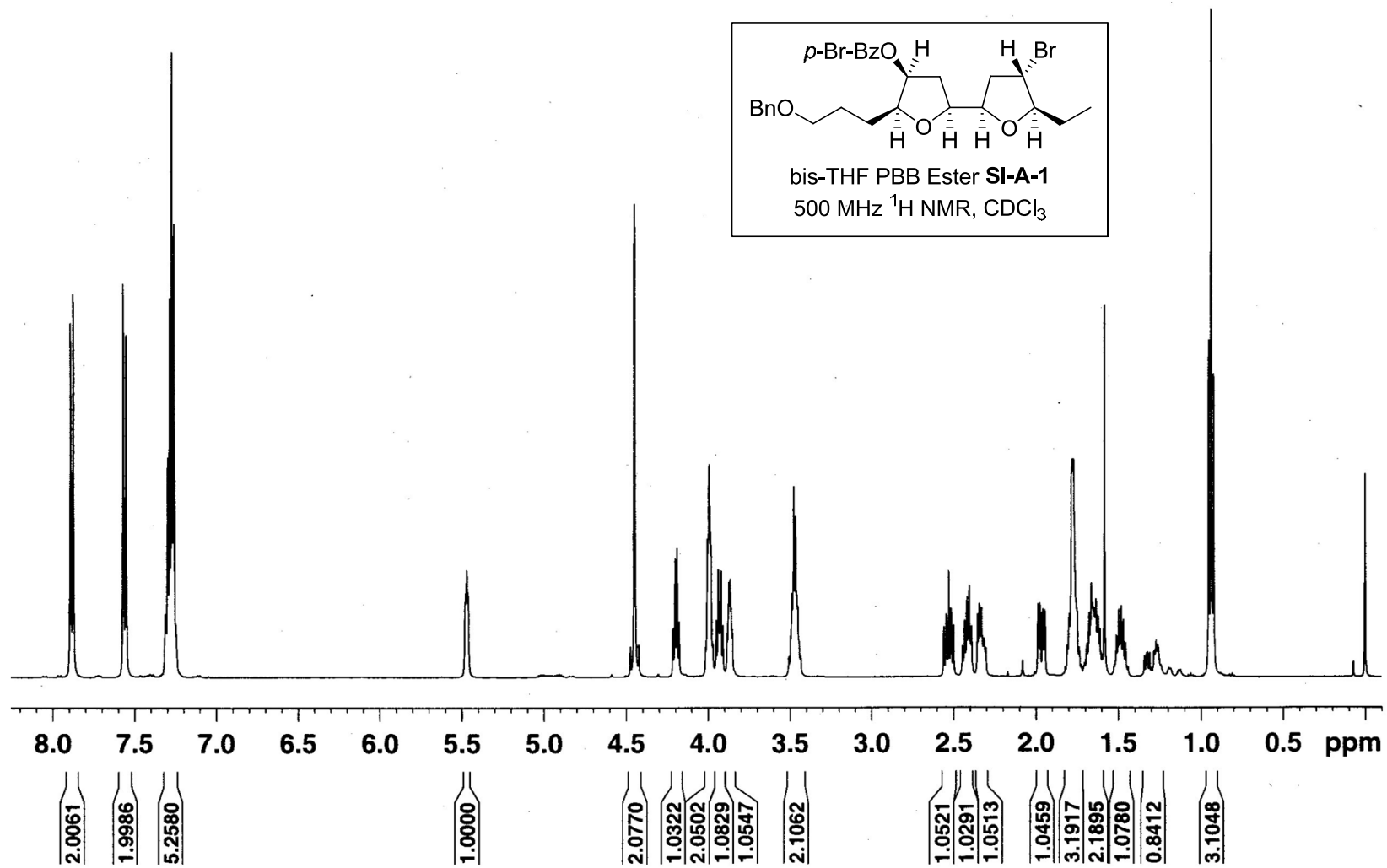
# Structure Determination of bis-Tetrahydrofuranyl Alcohol 12

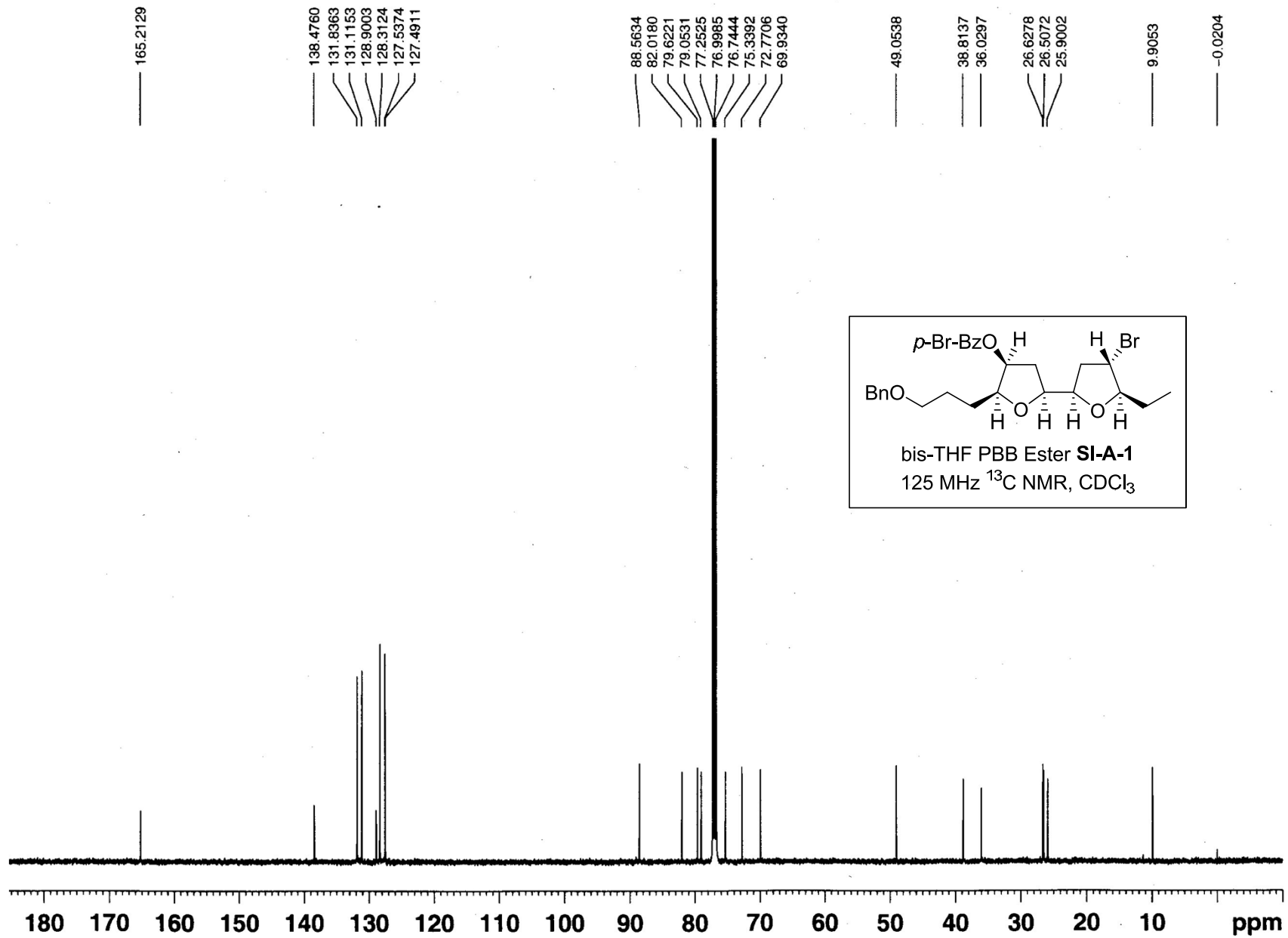
## Isolaurefucin series ( $\alpha,\alpha'$ -trans)



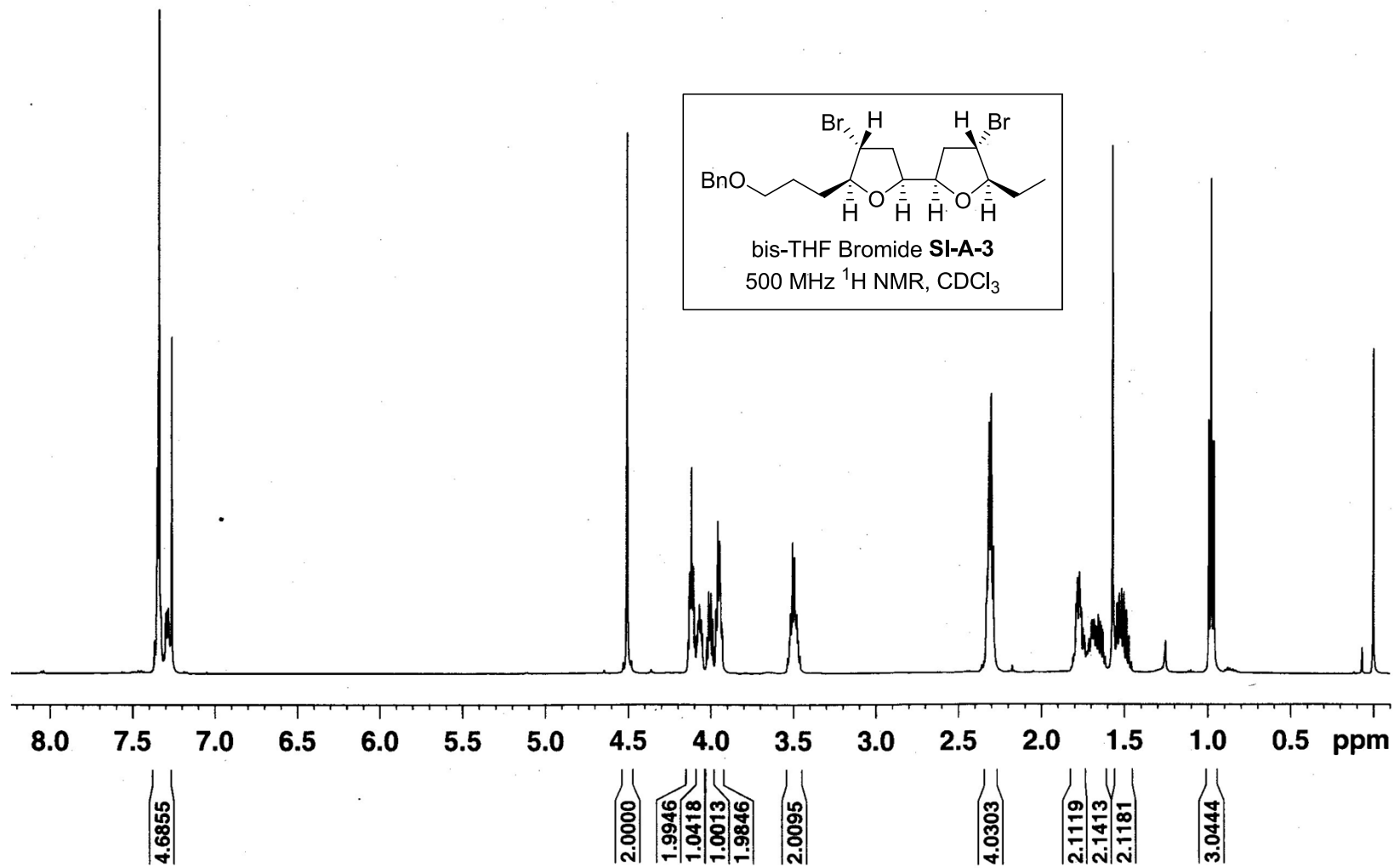


S49

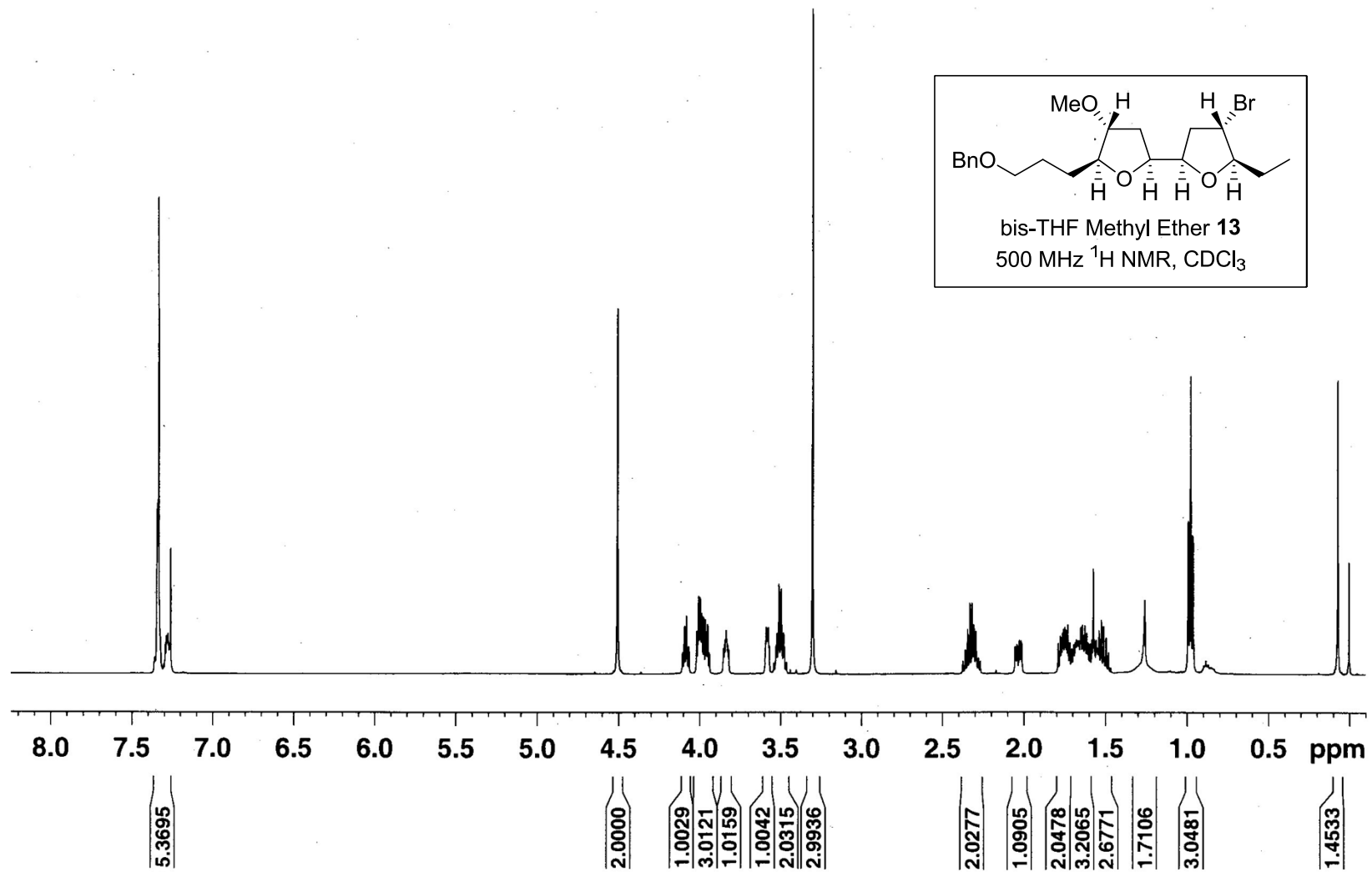


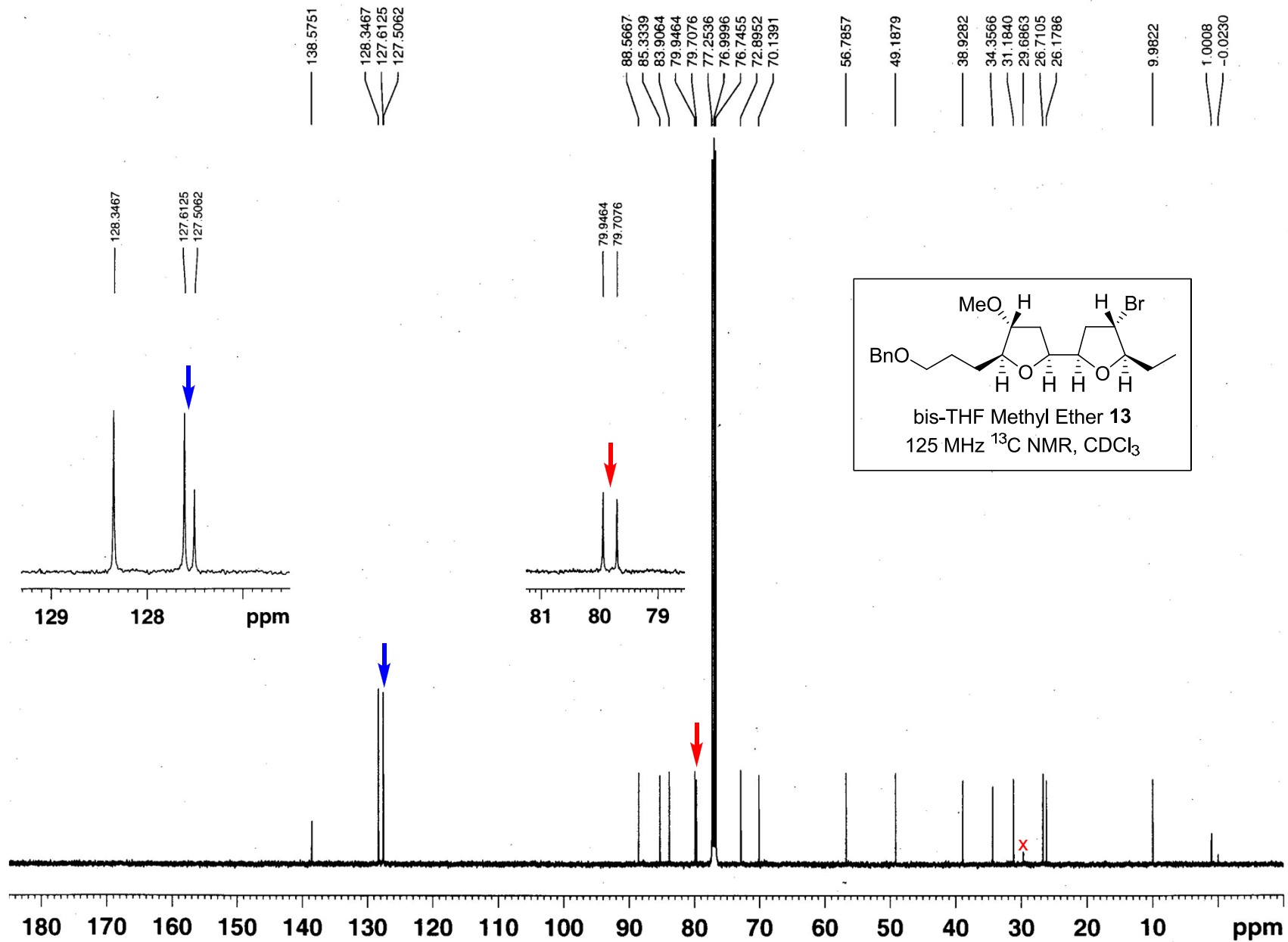


S51



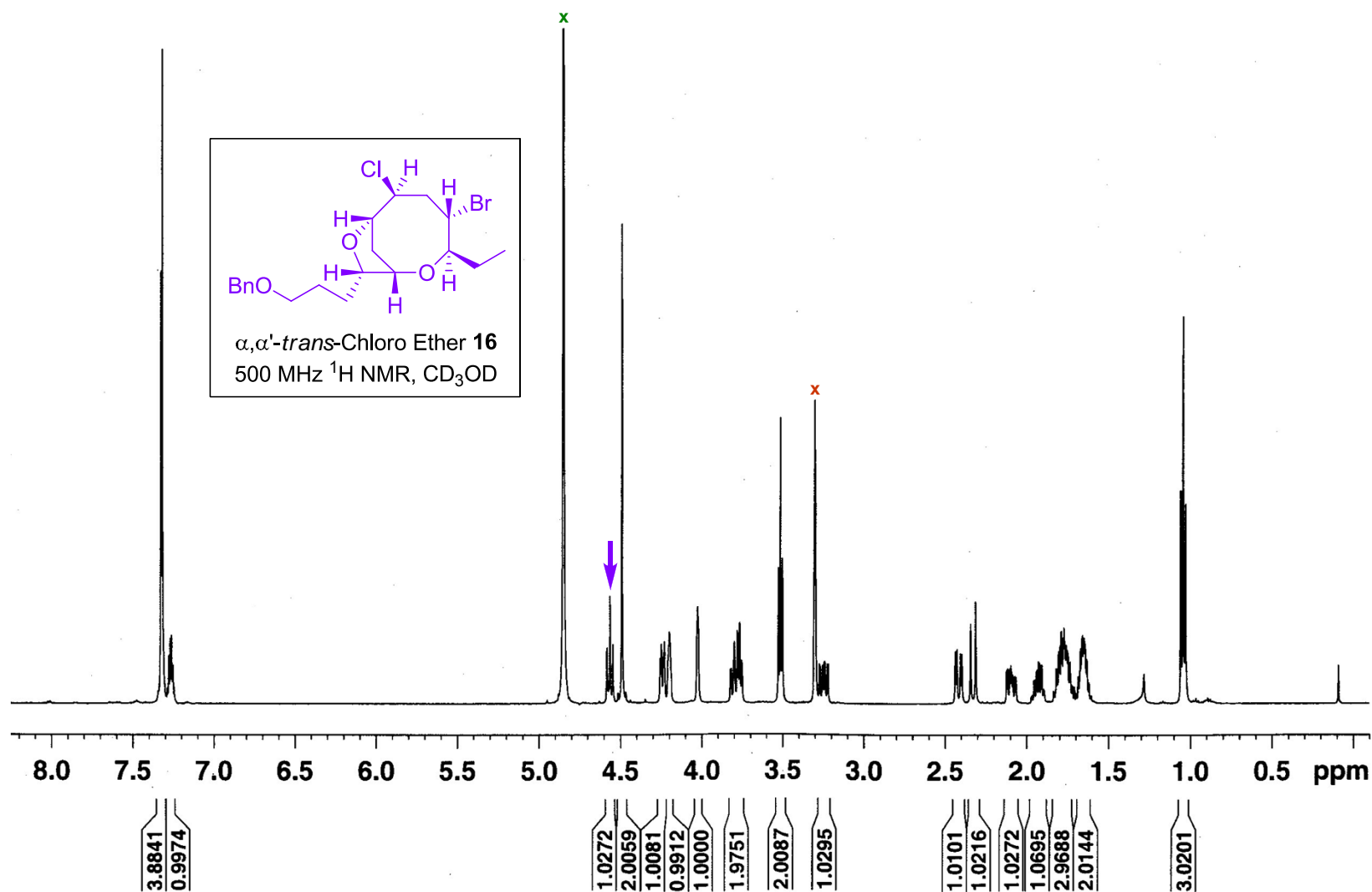




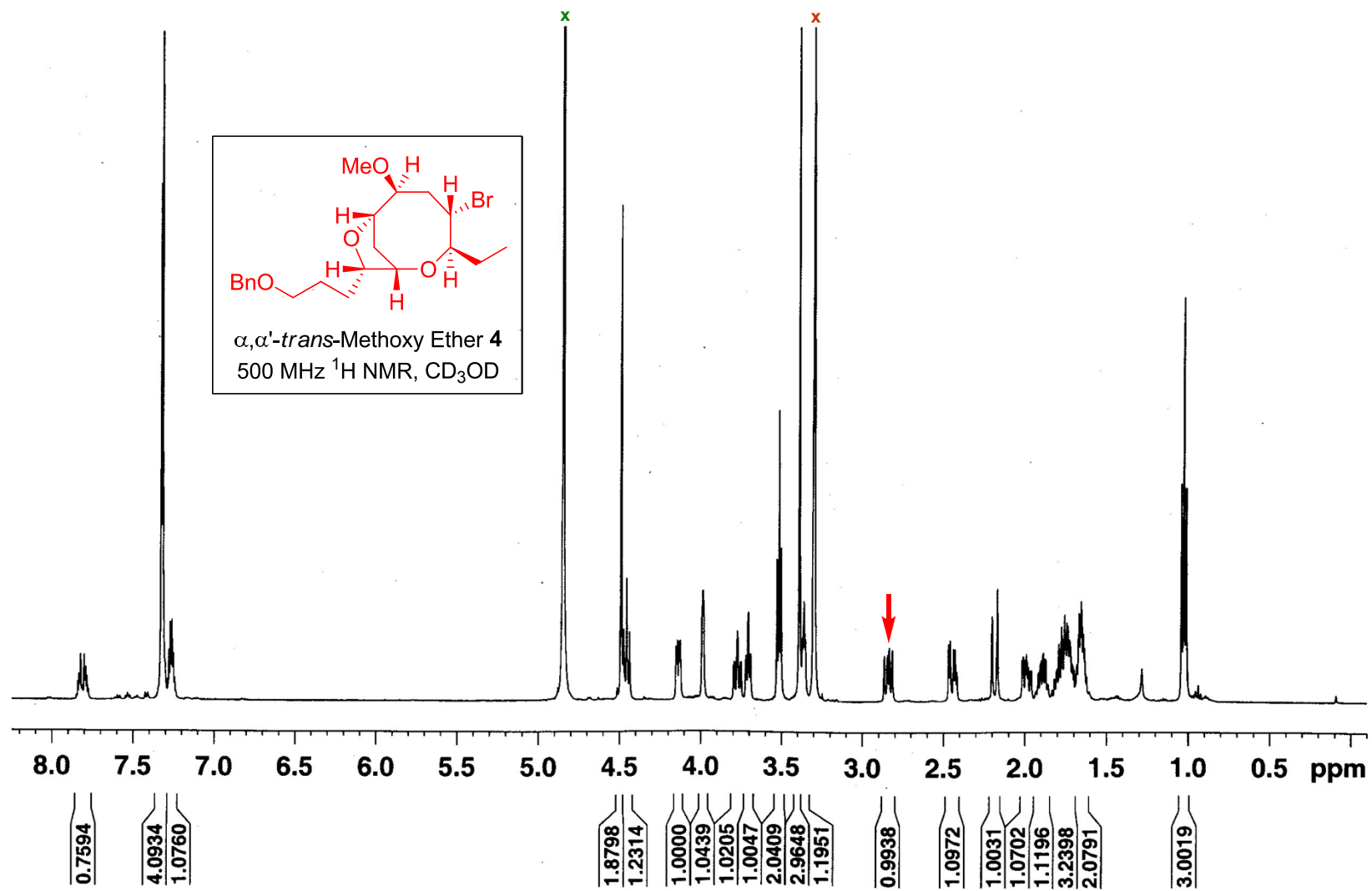


# Artifact Issue

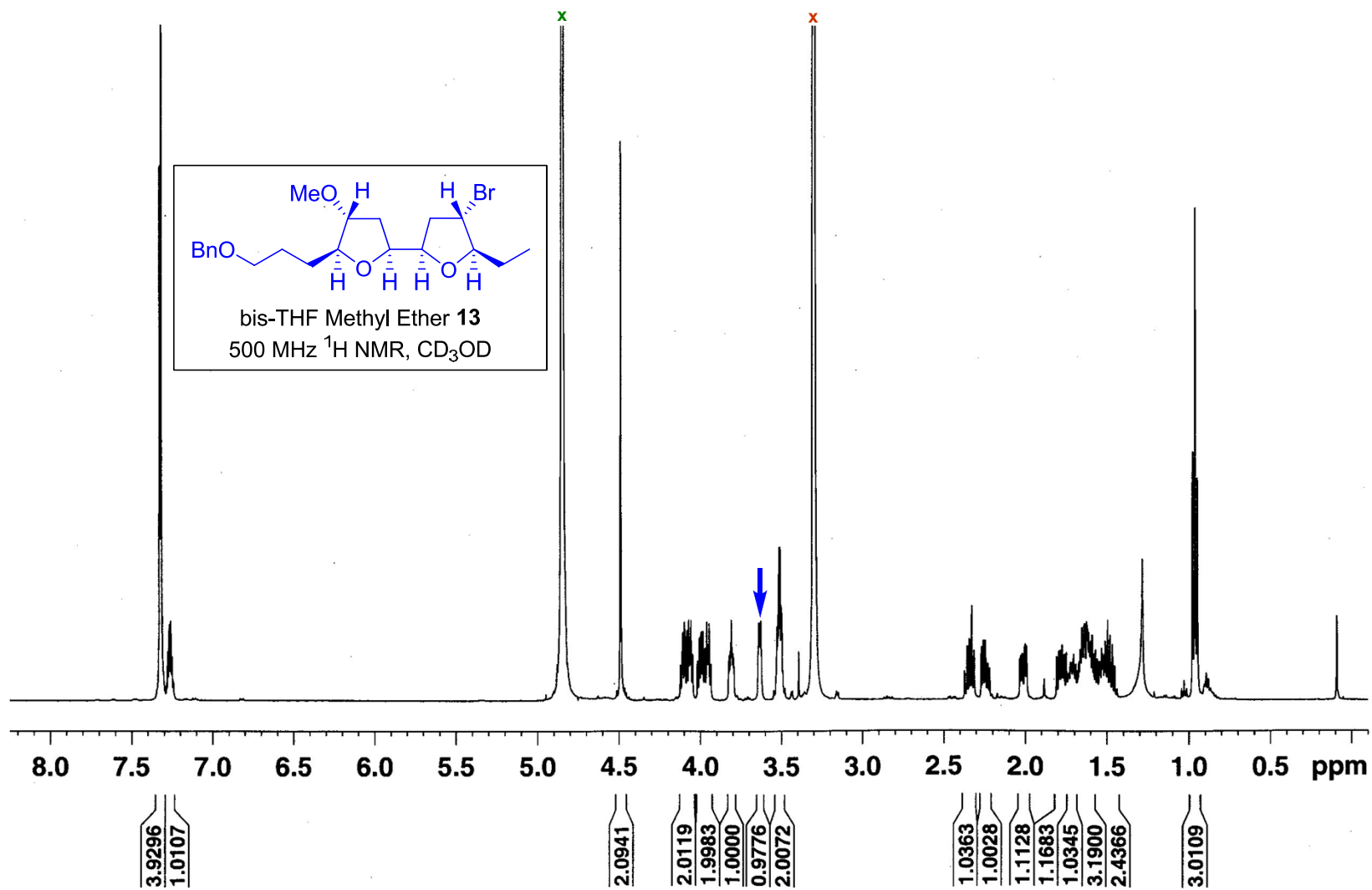
## Isolaurefucin series ( $\alpha,\alpha'$ -trans)



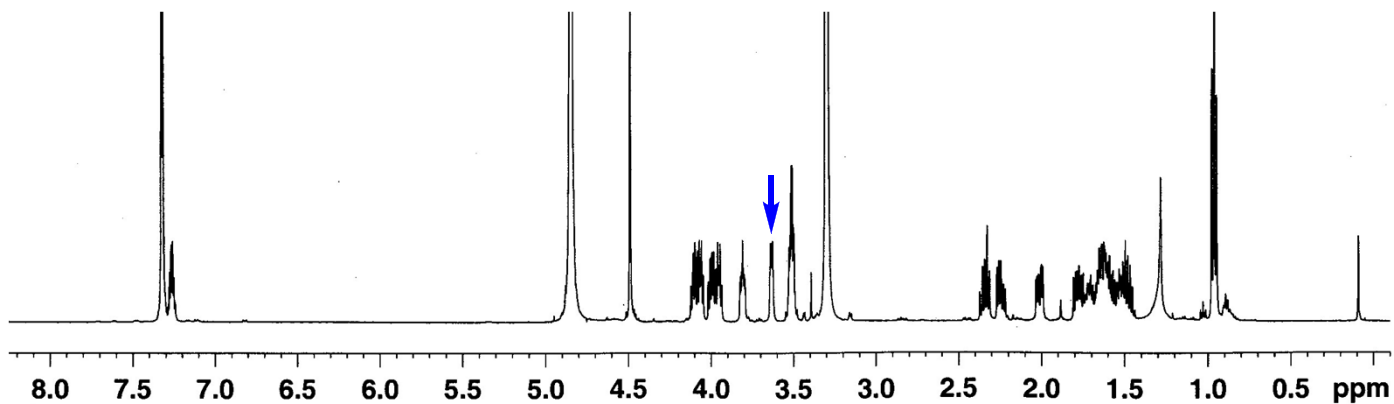
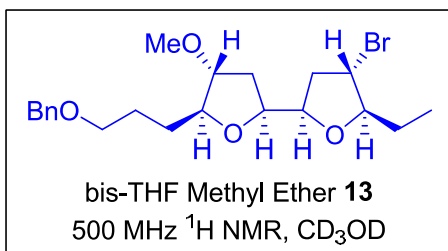
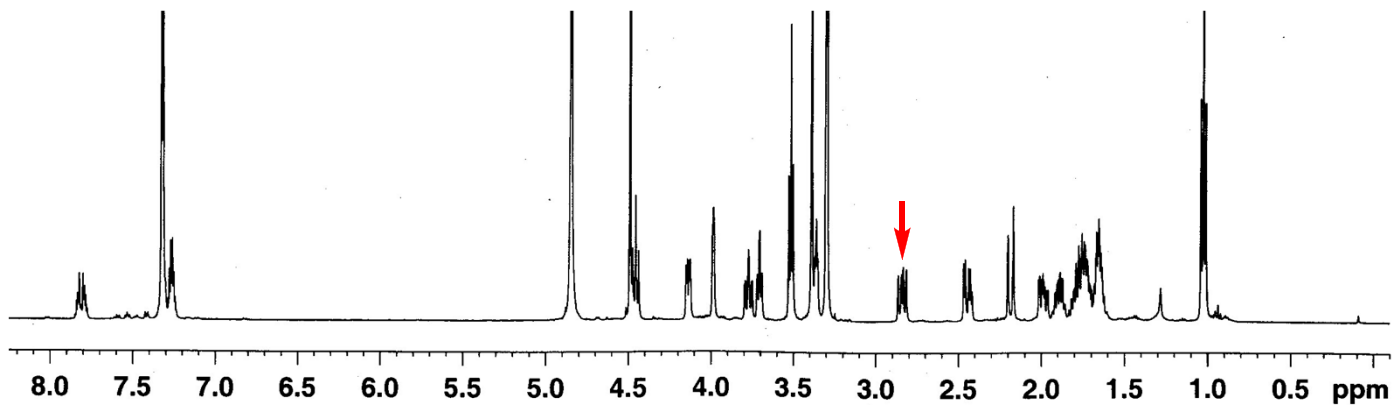
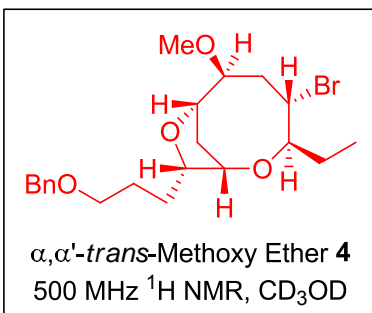
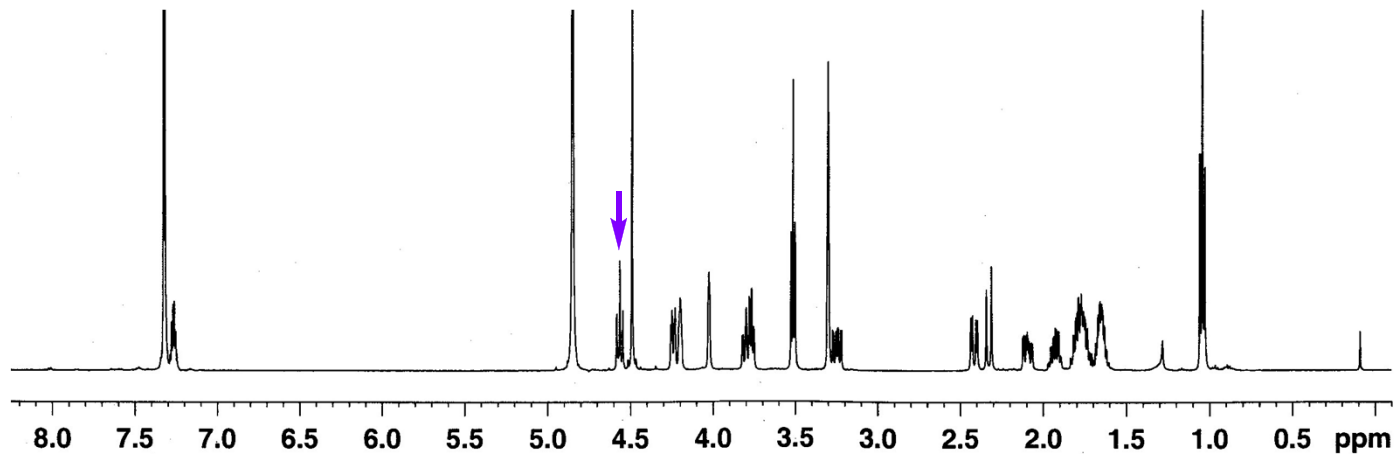
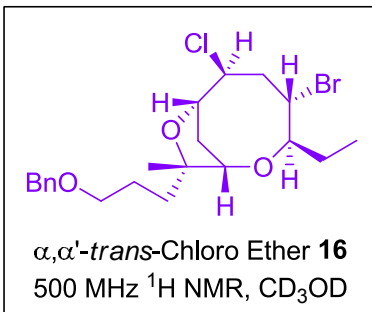
X:  $\text{CD}_3\text{OH}$   
X:  $\text{CHD}_2\text{OD}$



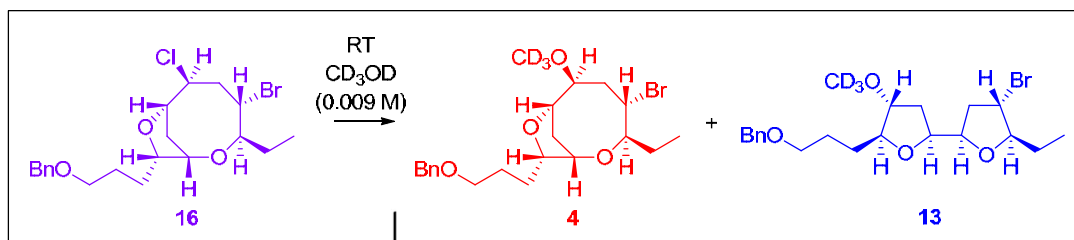
X:  $\text{CD}_3\text{OH}$   
X:  $\text{CHD}_2\text{OD}$



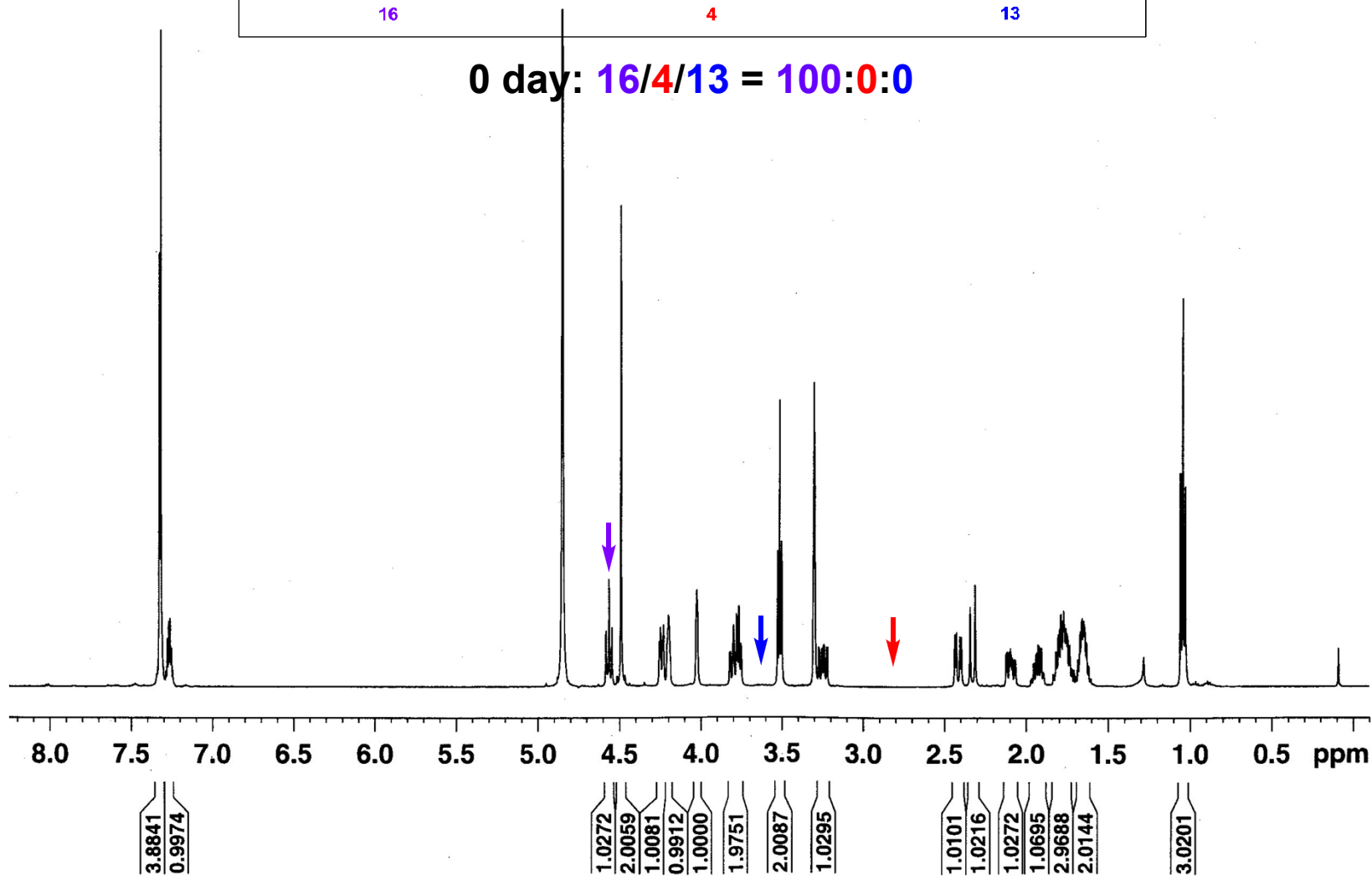
X: CD<sub>3</sub>OH  
X: CHD<sub>2</sub>OD



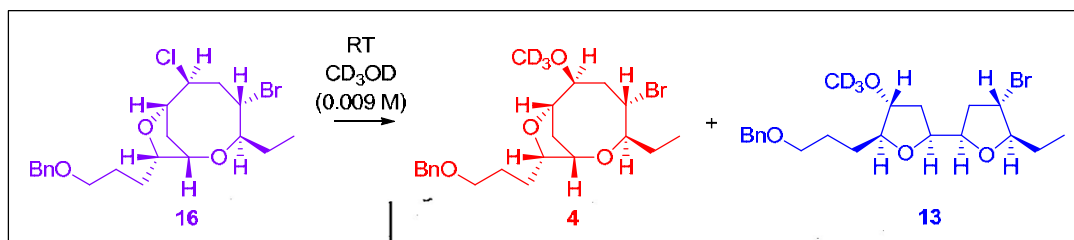
# NMR Experiment on Methanolysis of $\alpha,\alpha'$ -*trans*-Chloro Ether 16



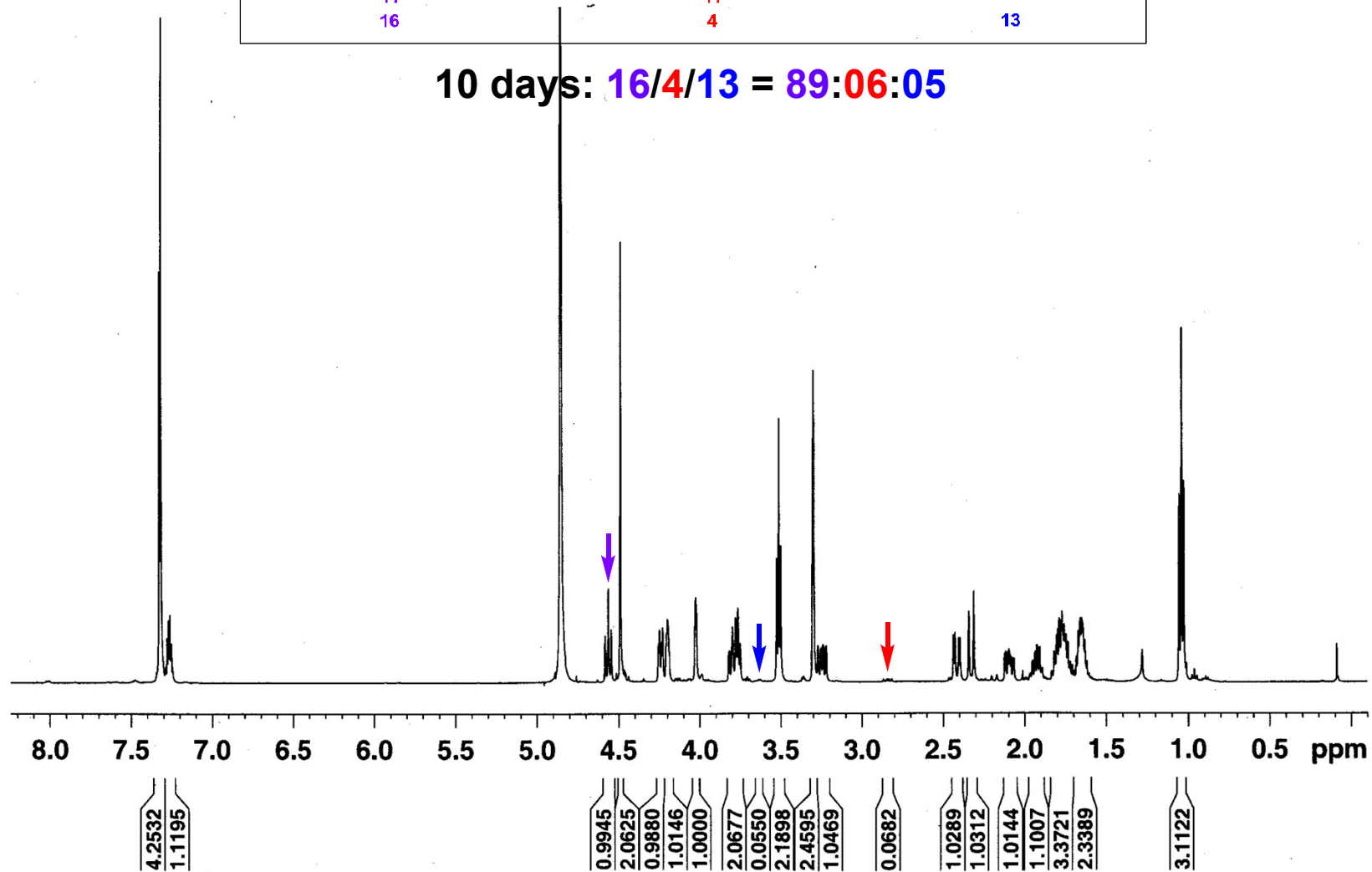
0 day: 16/4/13 = 100:0:0



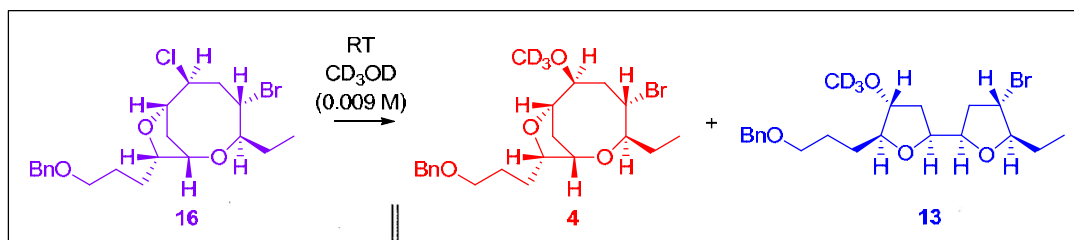
S60



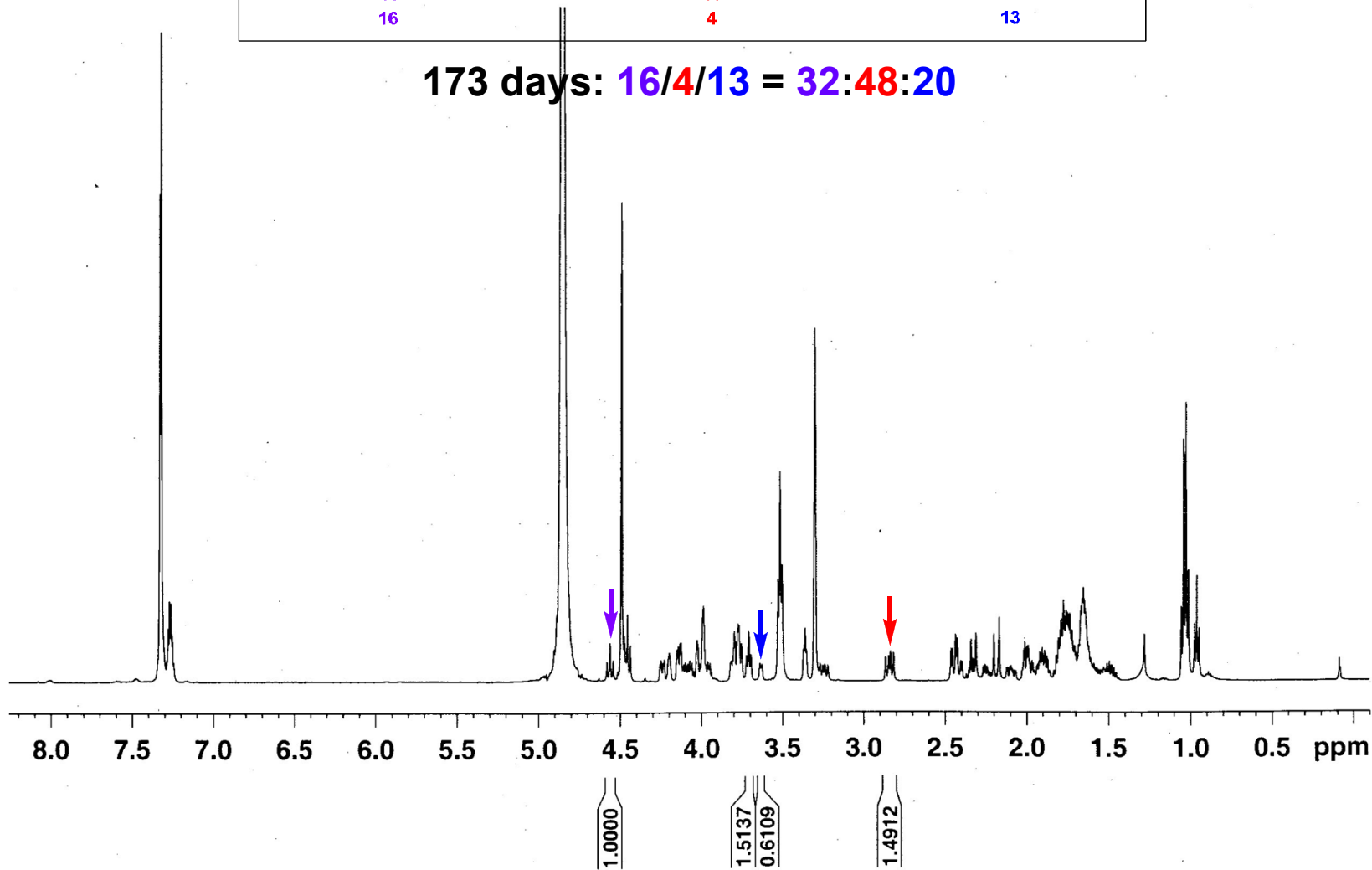
10 days: 16/4/13 = 89:06:05





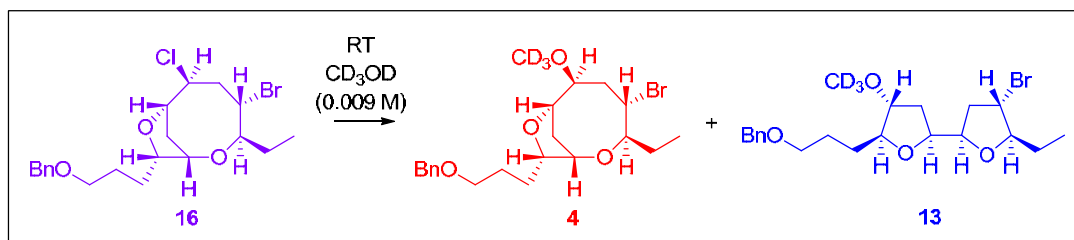


173 days: 16/4/13 = 32:48:20



S63

# Summary of NMR Experiment on Methanolysis of $\alpha,\alpha'$ -*trans*-Chloro Ether 16

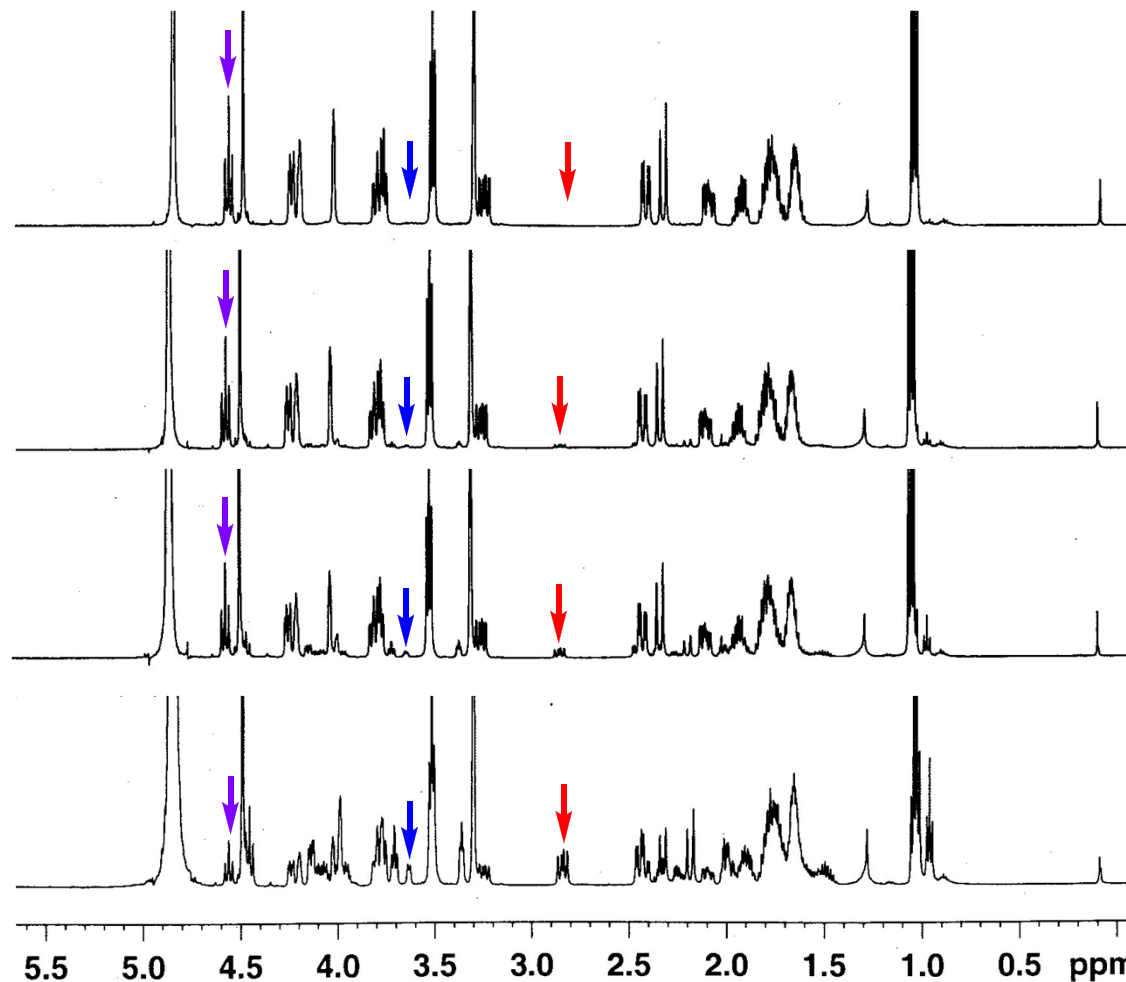


0 day: **16/4/13** = **100:0:0**

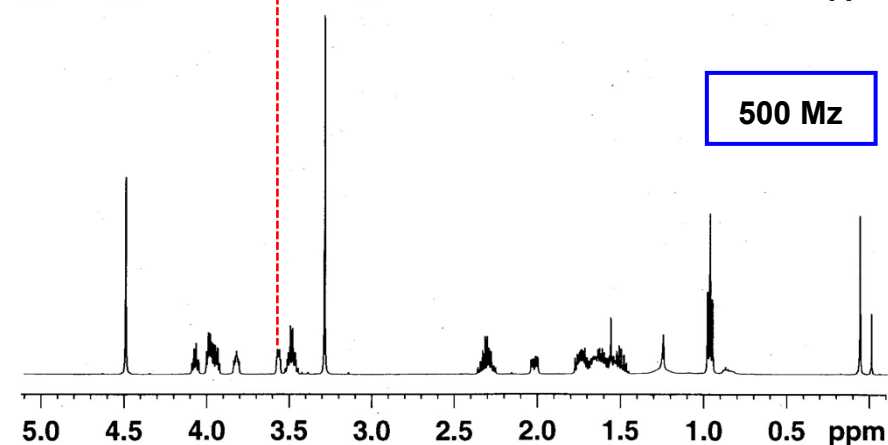
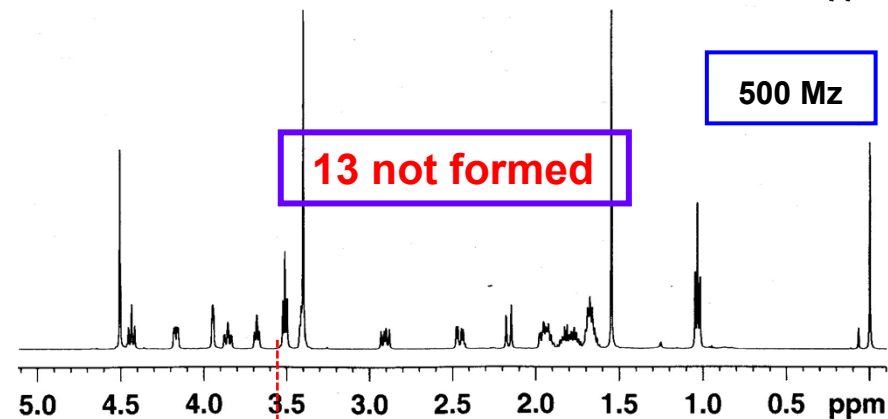
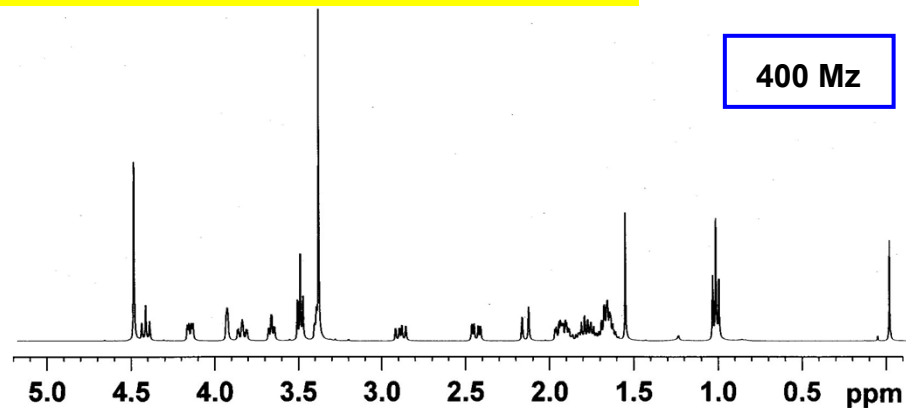
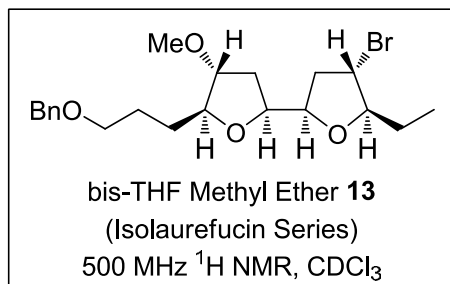
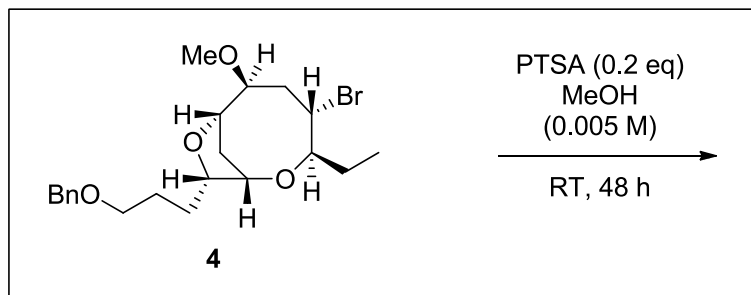
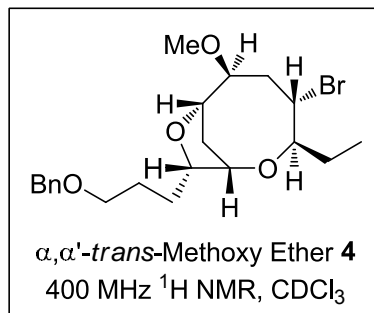
10 days: **16/4/13** = **89:06:05**

26 days: **16/4/13** = **74:17:09**

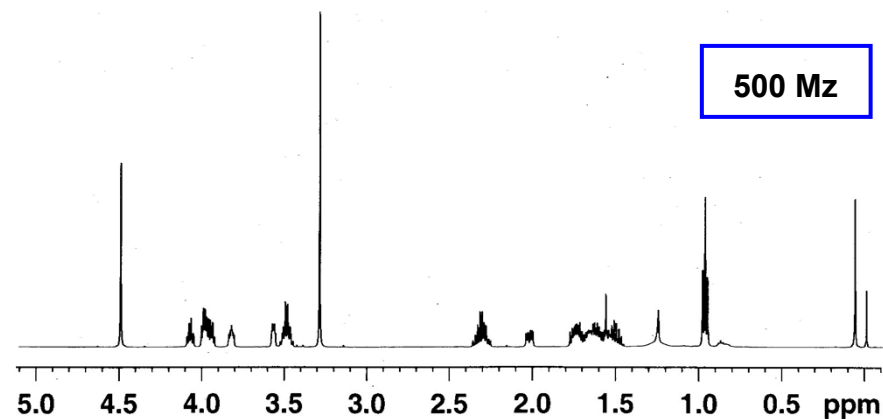
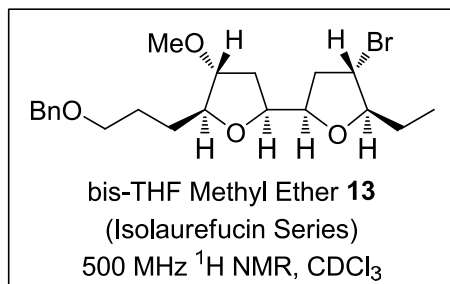
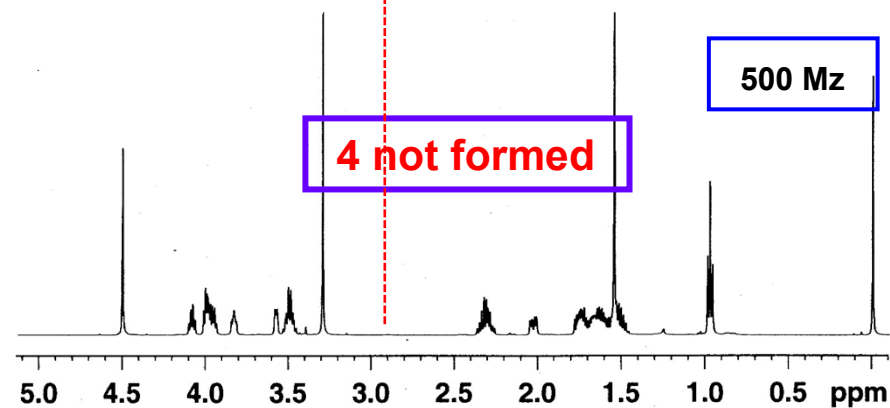
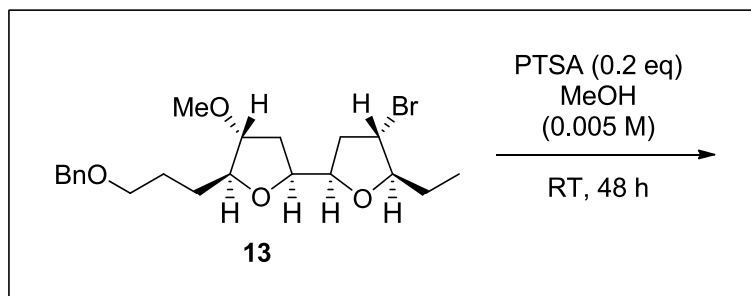
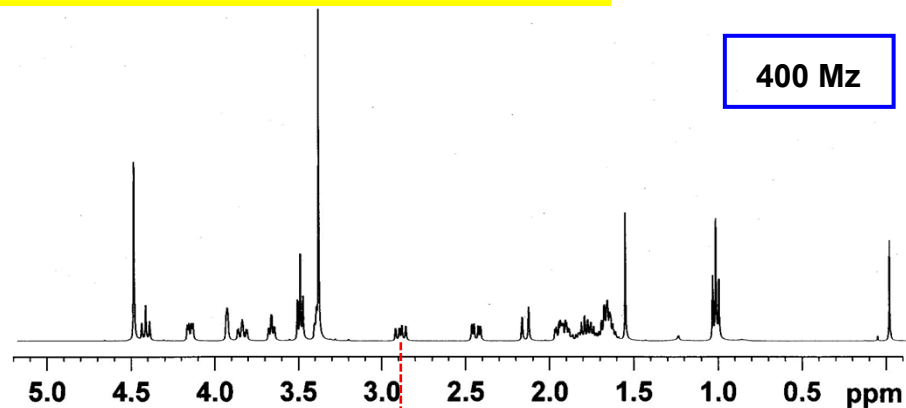
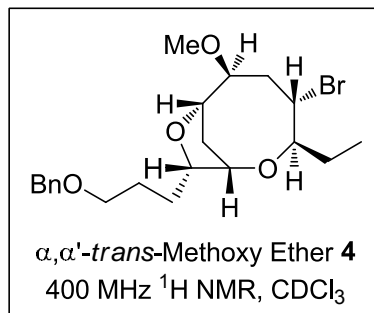
173 days: **16/4/13** = **32:48:20**



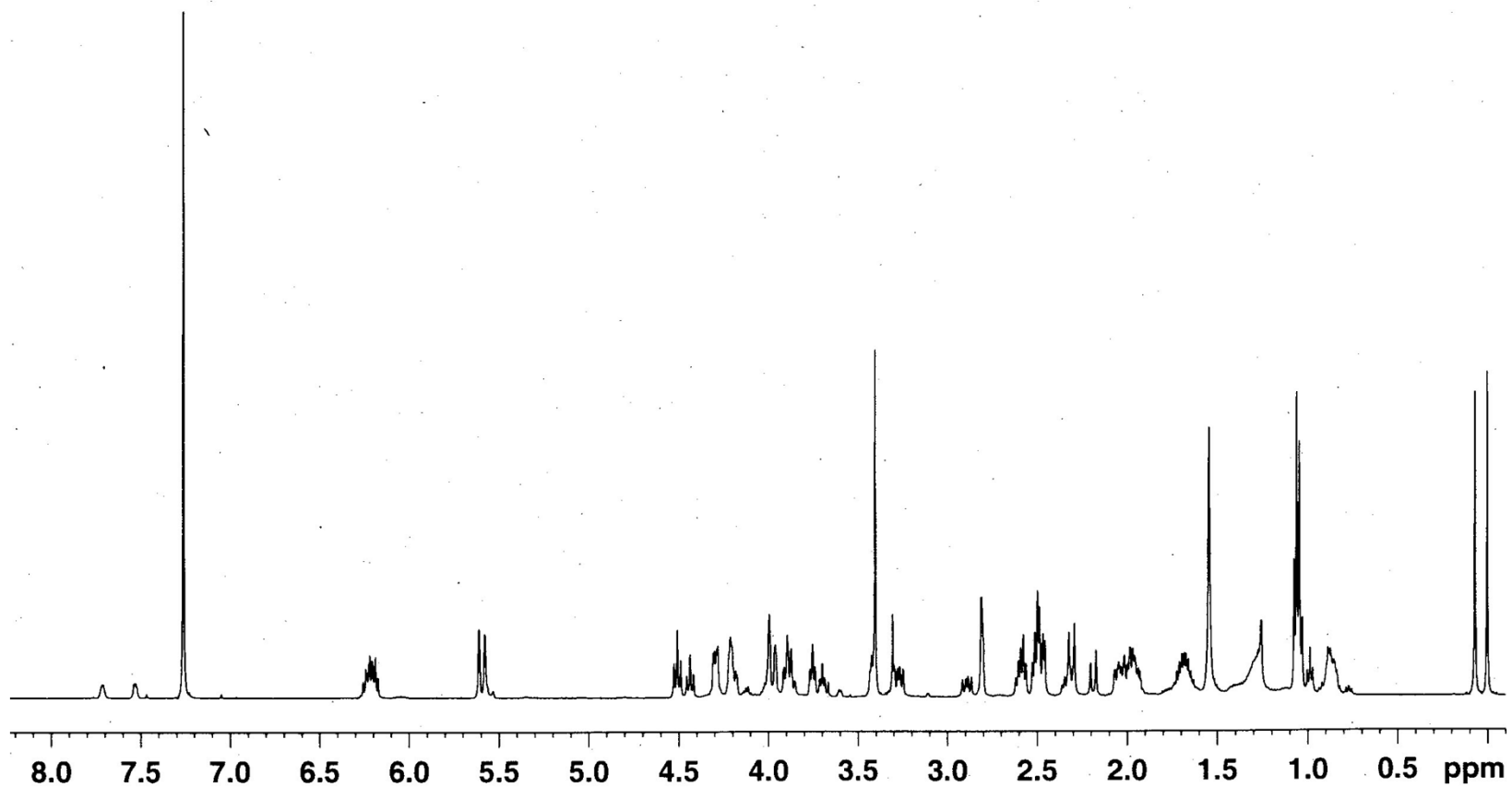
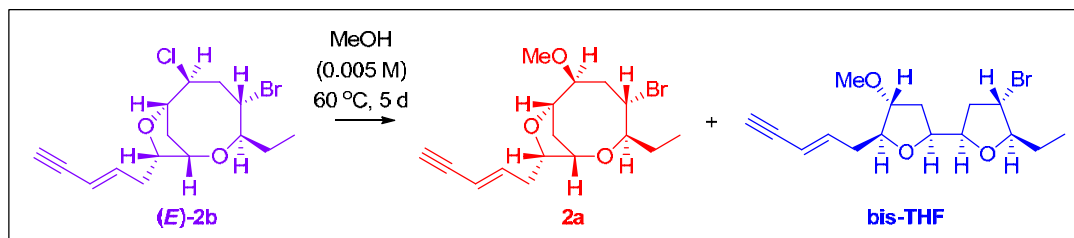
# Re-subjection of $\alpha,\alpha'$ -*trans*-Methoxy Ether 4 to PTSA in MeOH

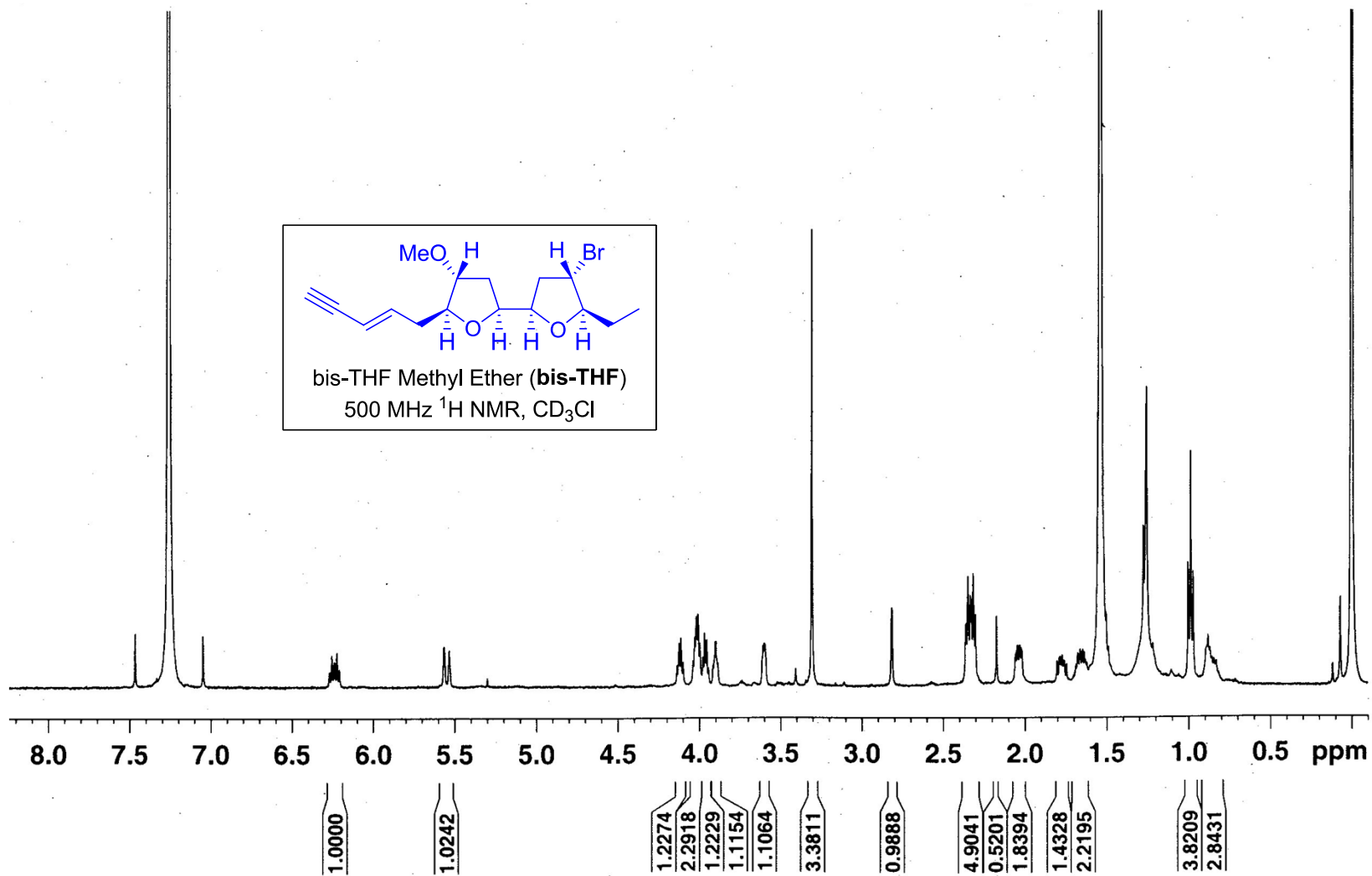


# Re-subjection of bis-THF Methyl Ether 13 to PTSA in MeOH

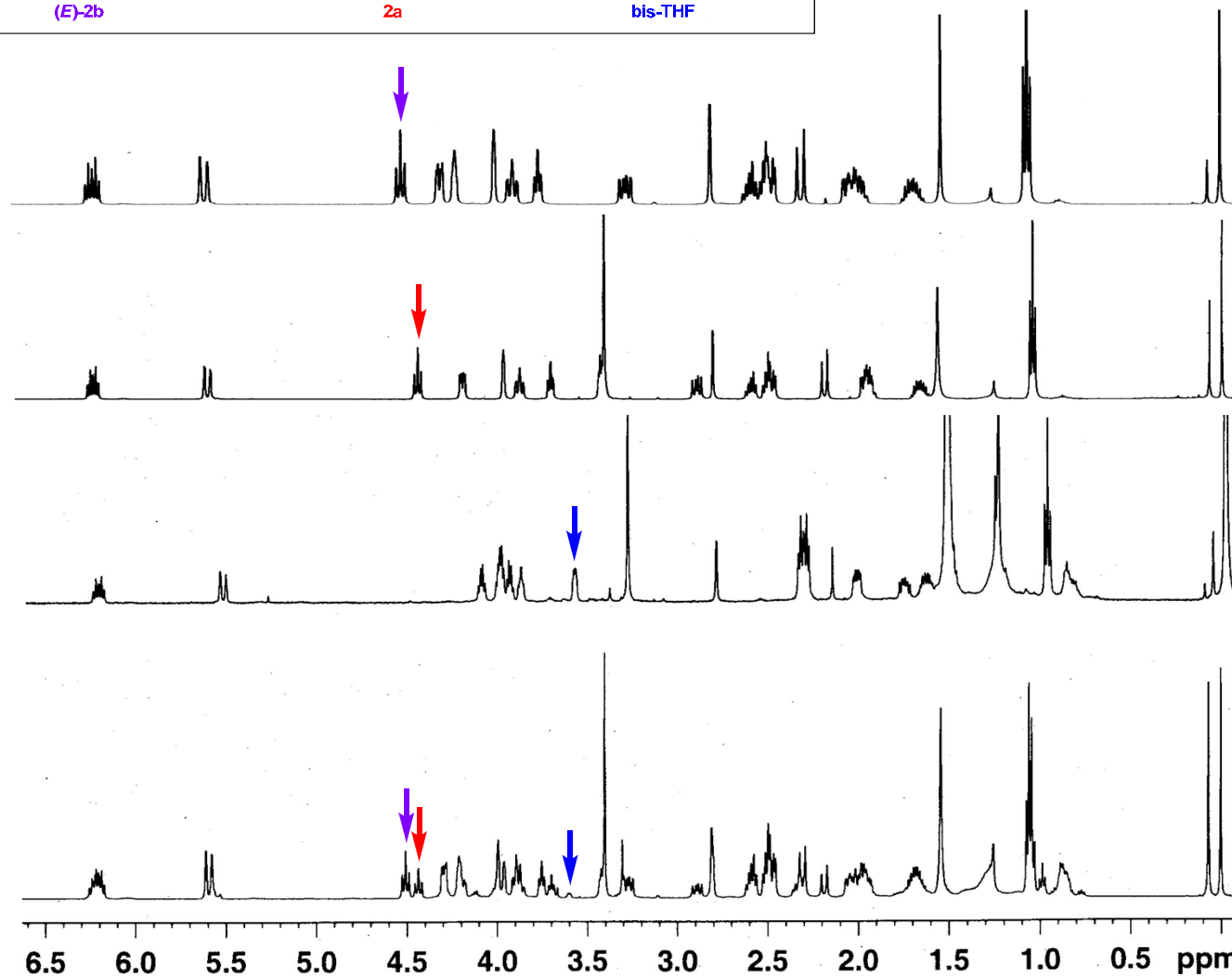
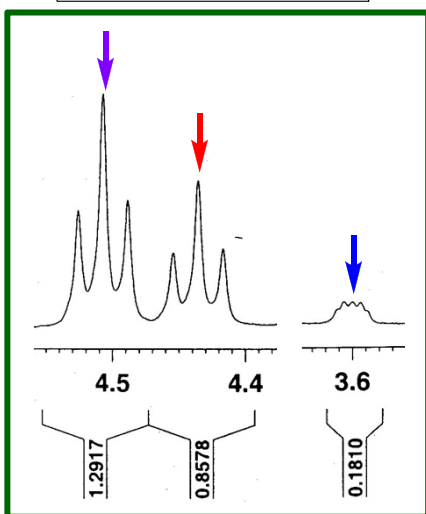
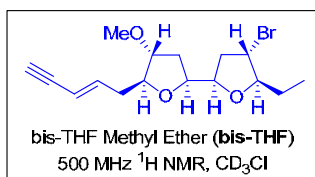
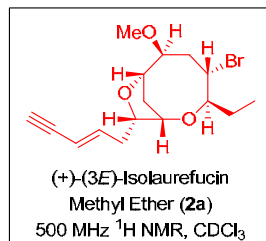
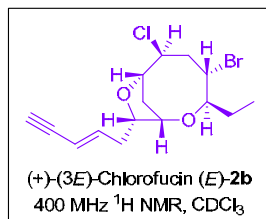
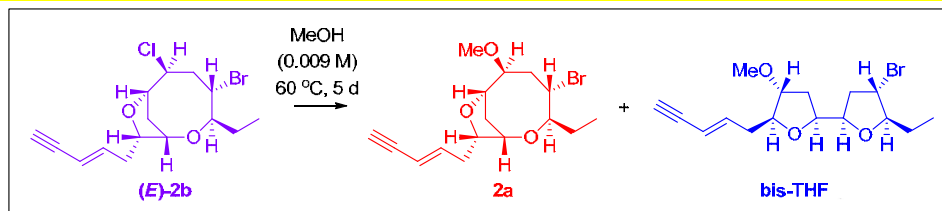


# Methanolysis of (+)-(3*E*)-Chlorofucin (*E*-2b





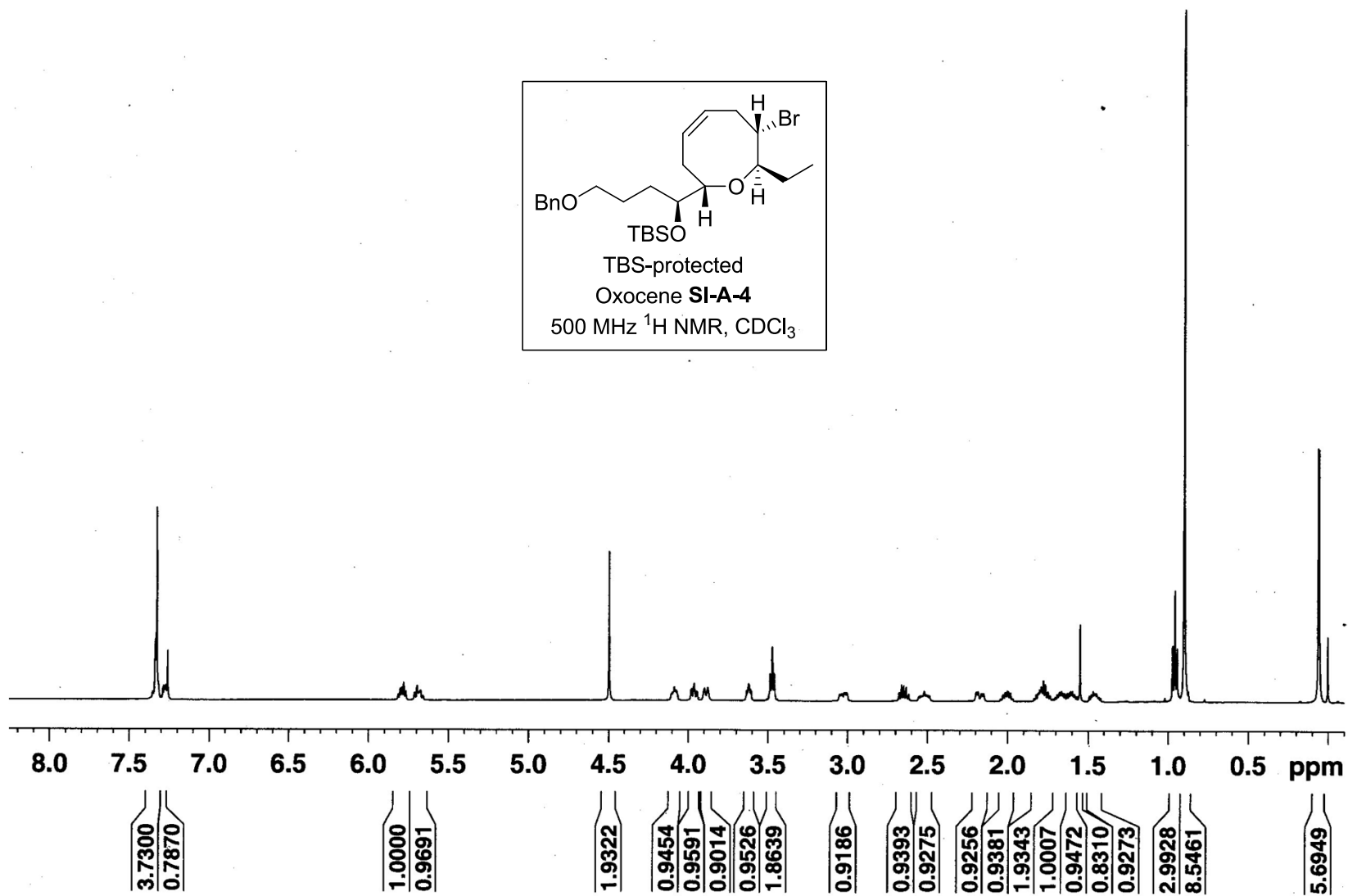
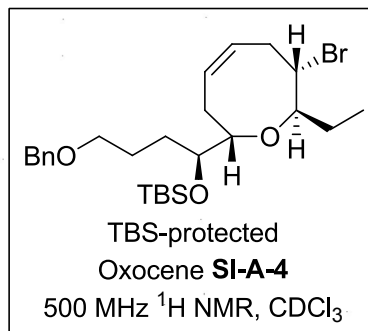
# Methanolysis of $\alpha,\alpha'$ -*trans*-Chloro Ether (+)-(3*E*)-Chlorofucin (*E*-2b

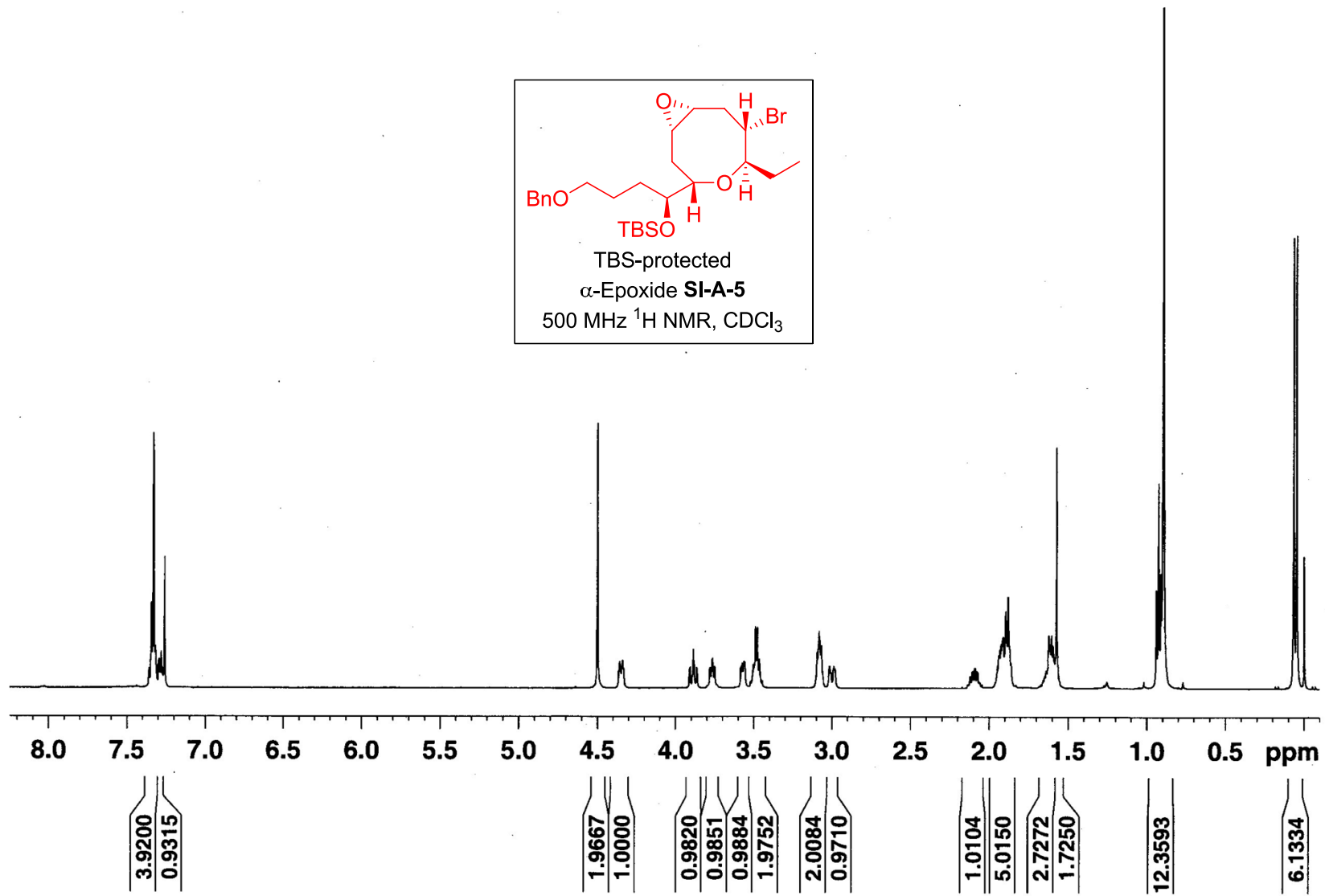
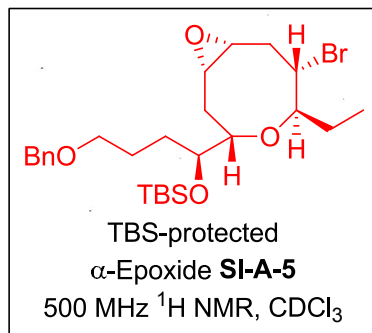


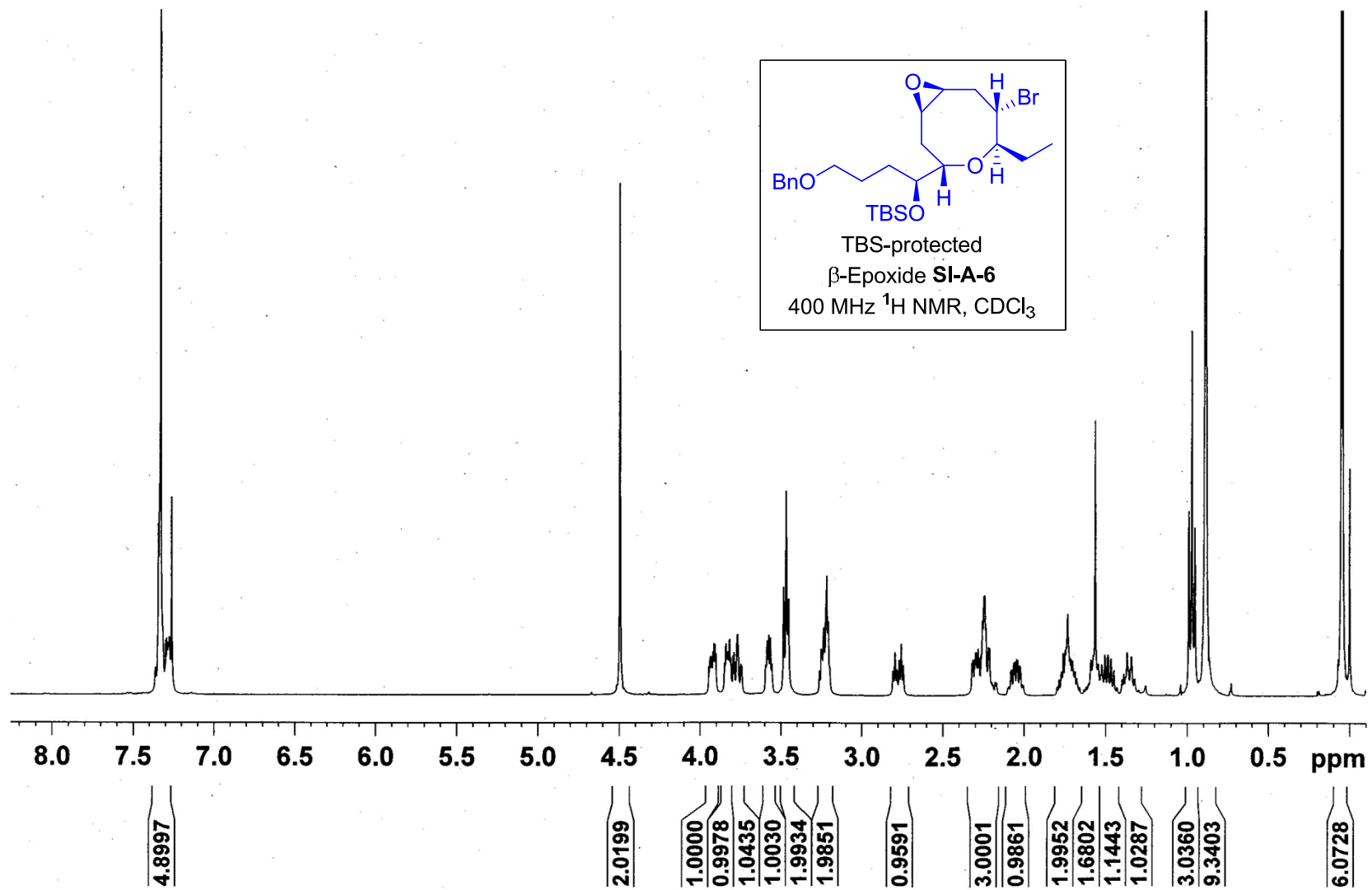
S69

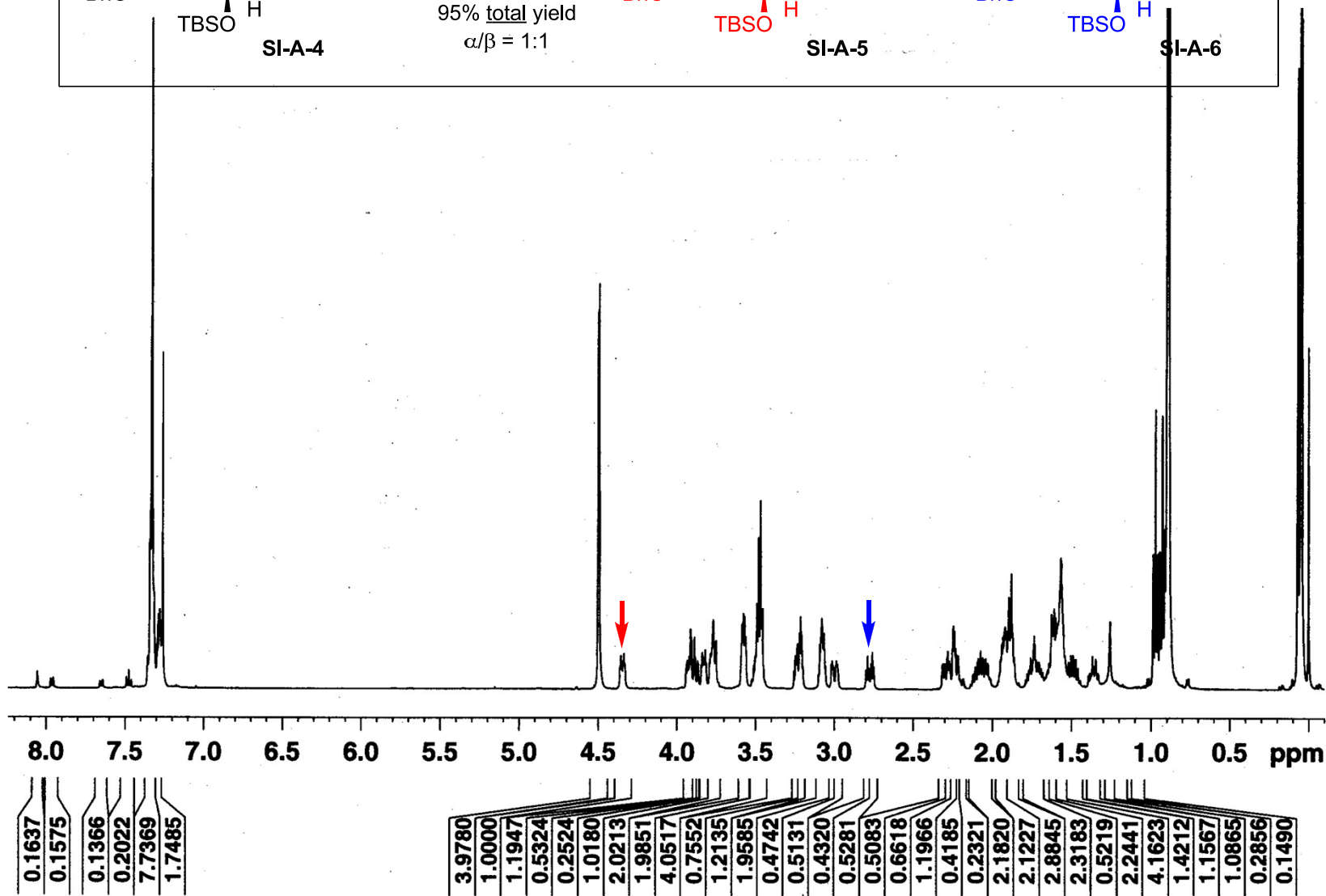
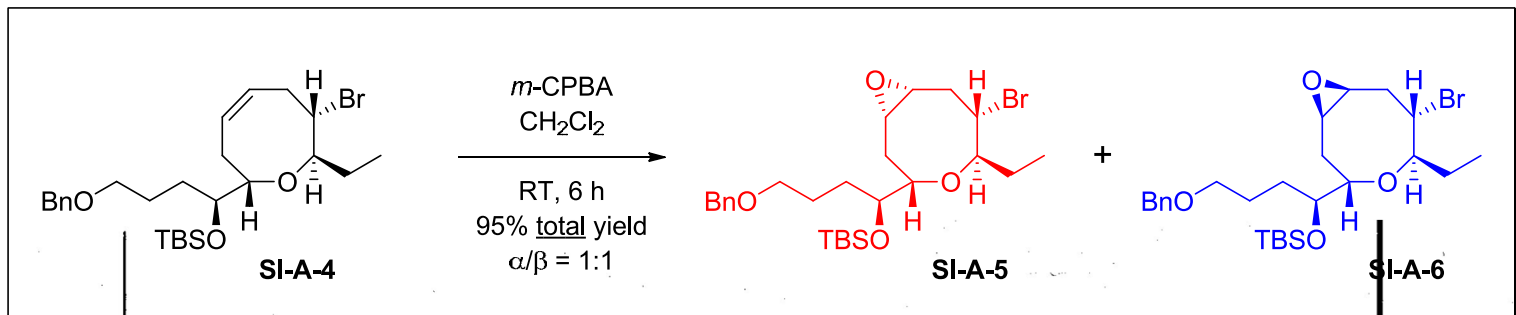
5 days: (*E*-2b/2a/bis-THF = 55:37:08

# Stereoselectivities in Epoxidation of Protected Oxocene Alcohols



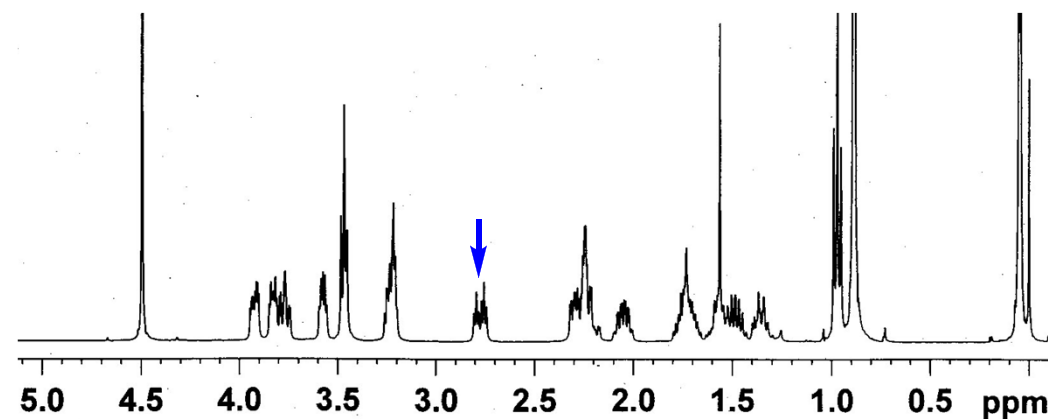
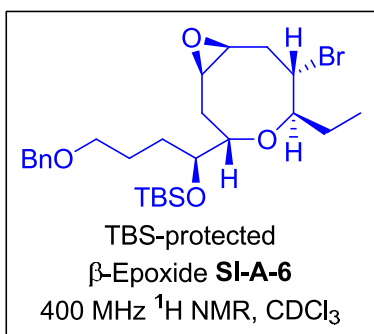
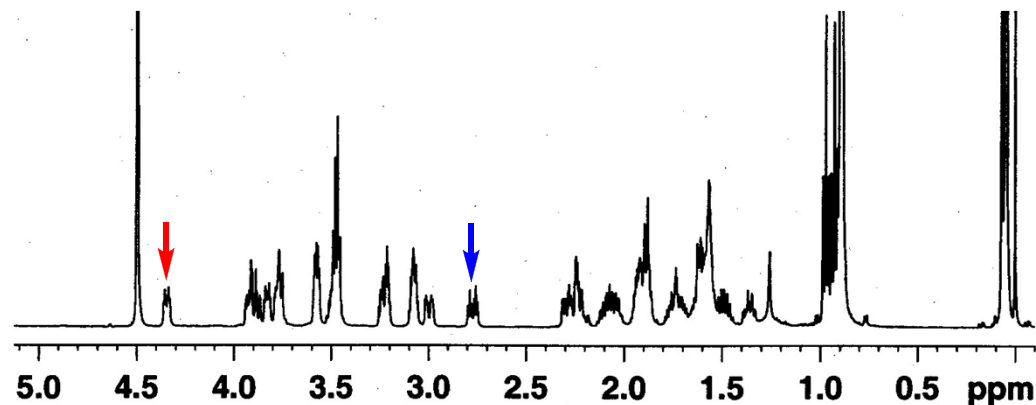
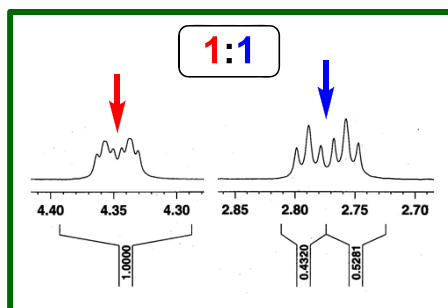
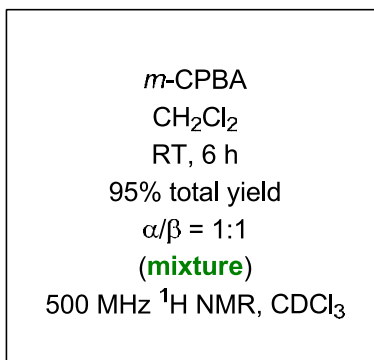
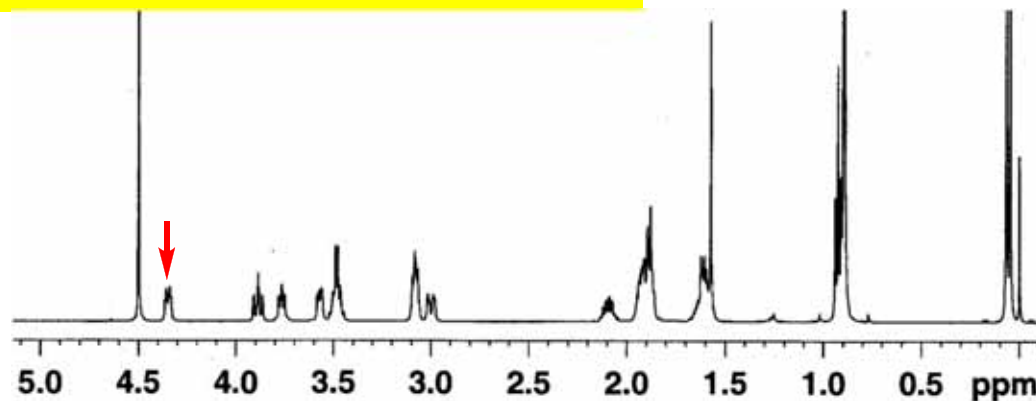
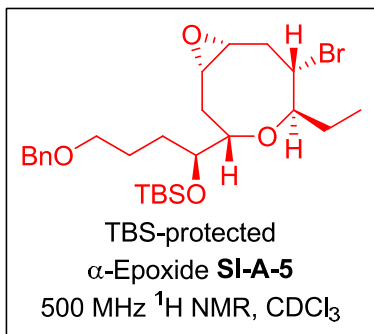


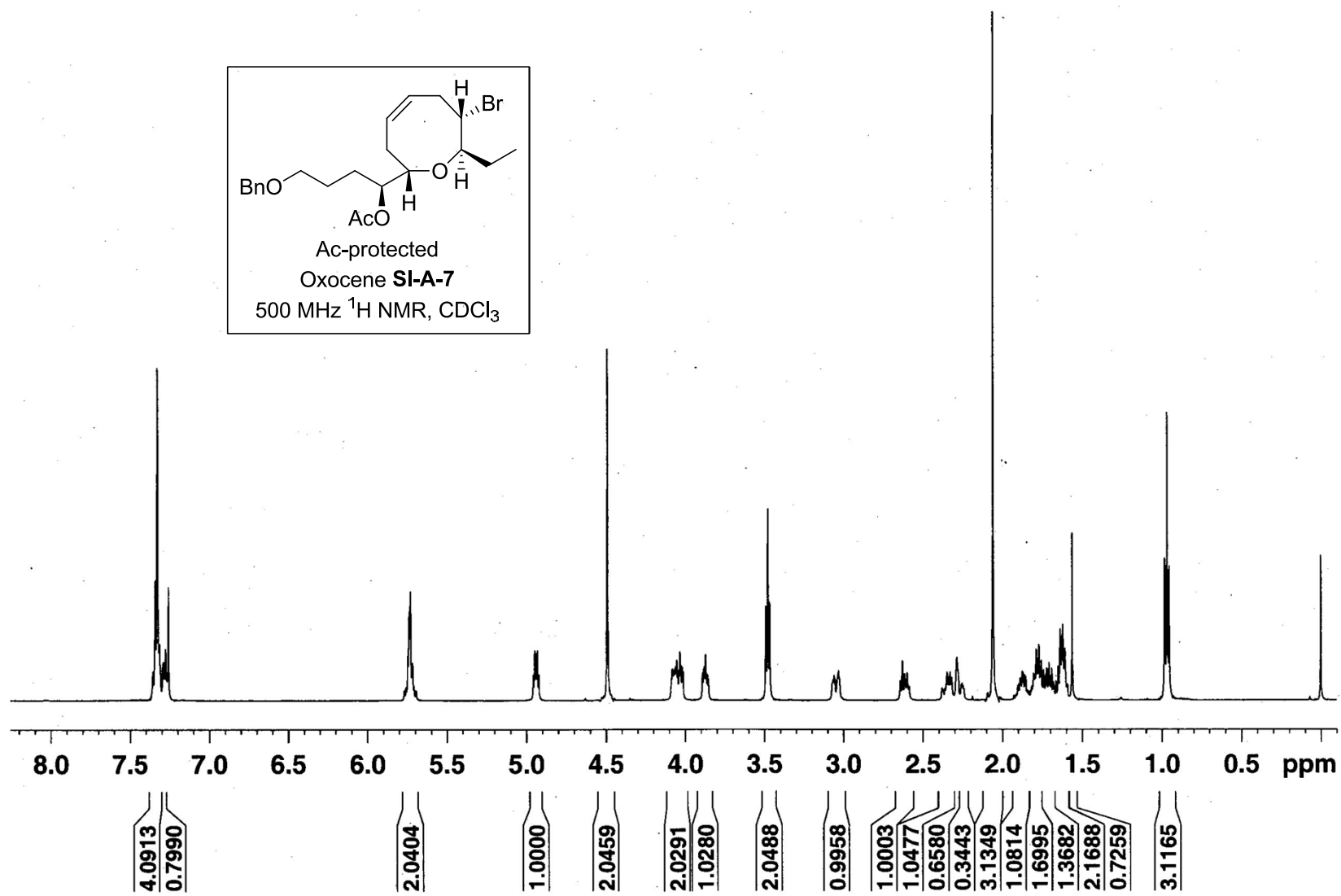
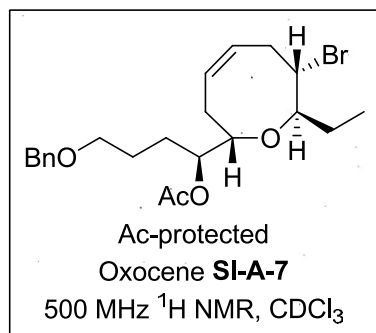


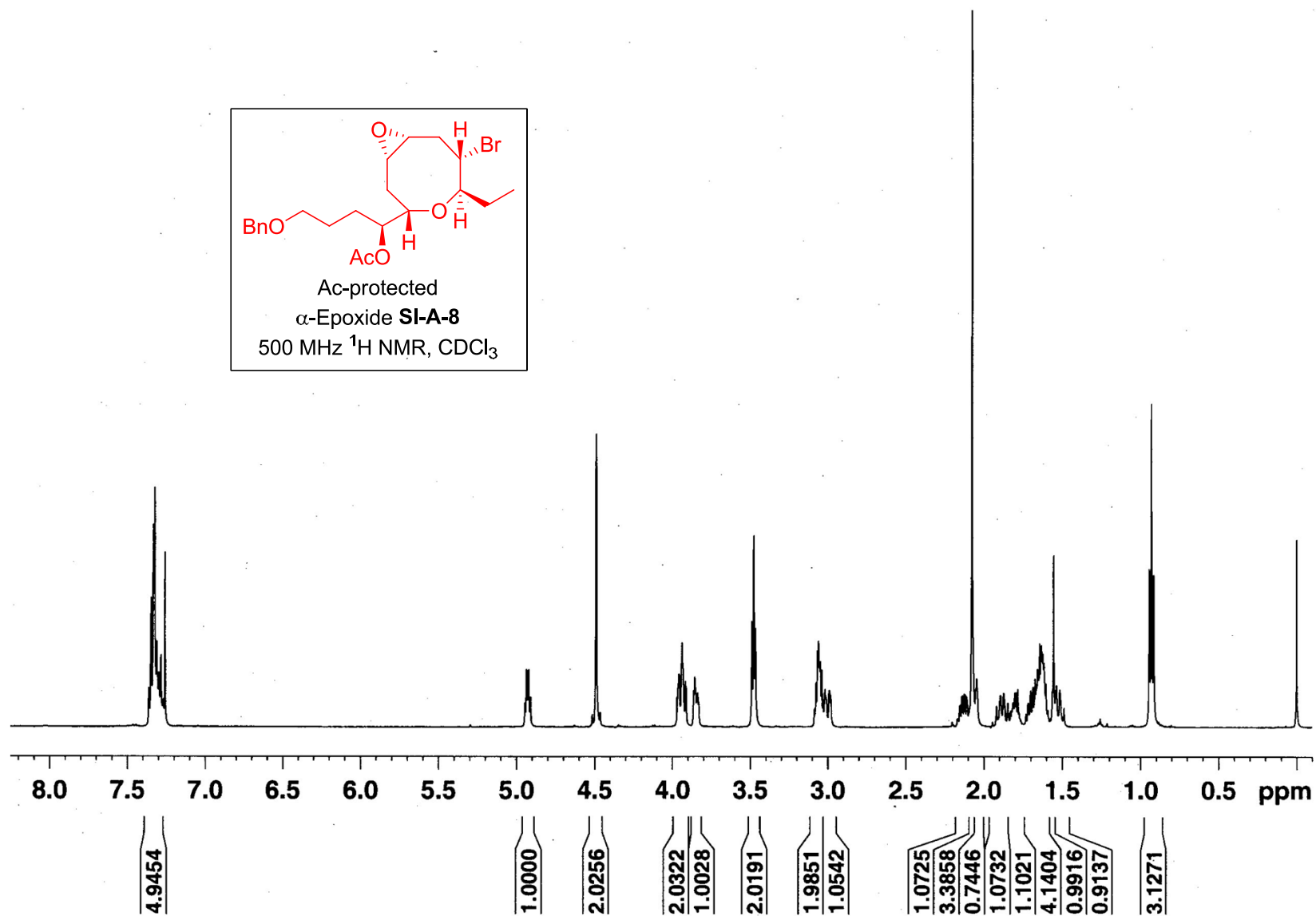
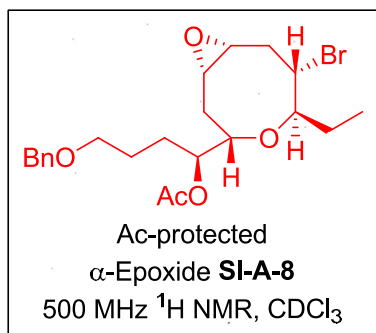


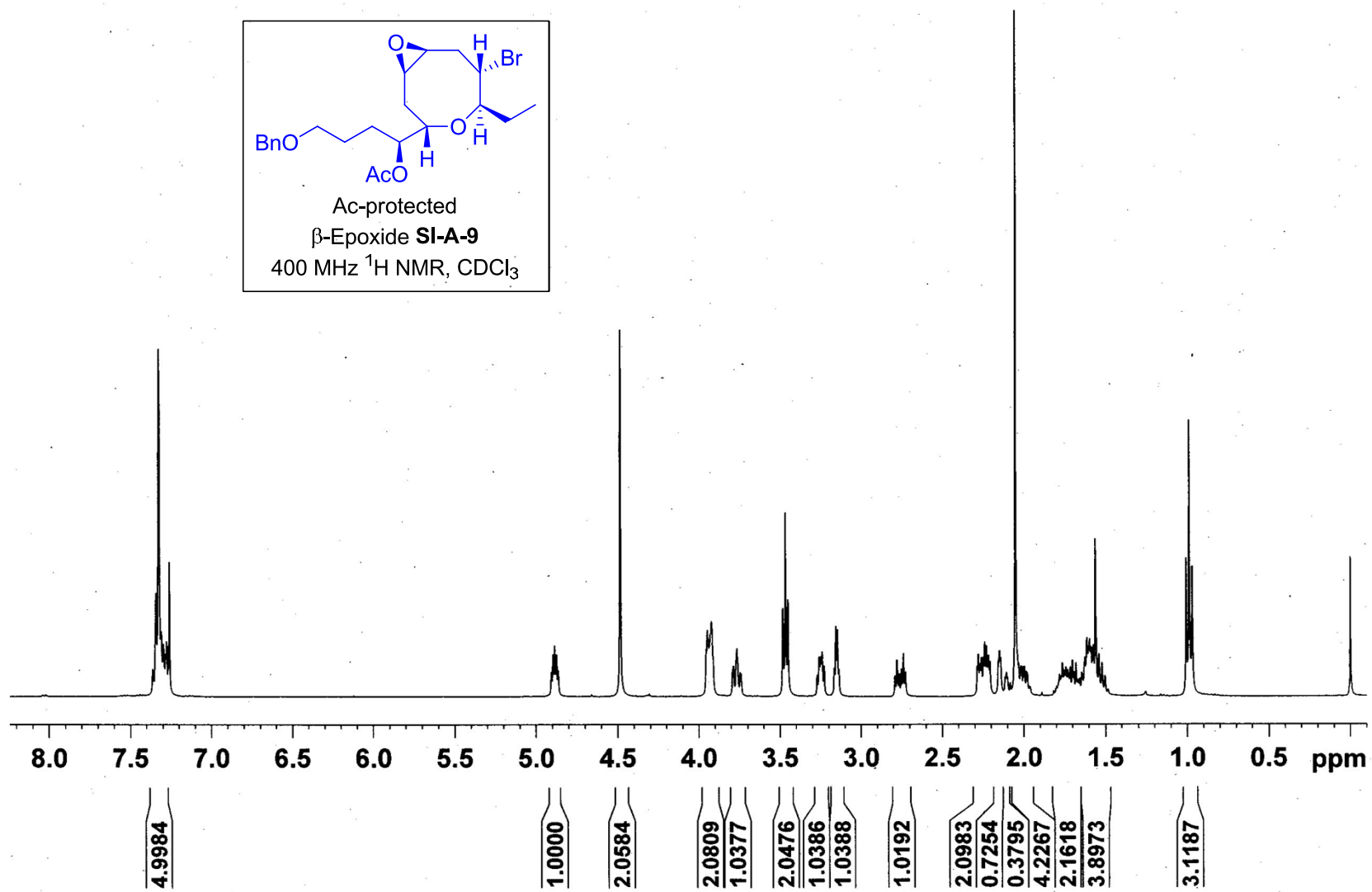
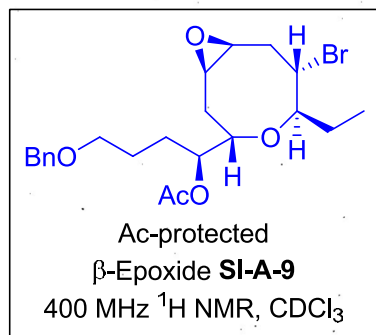
S73

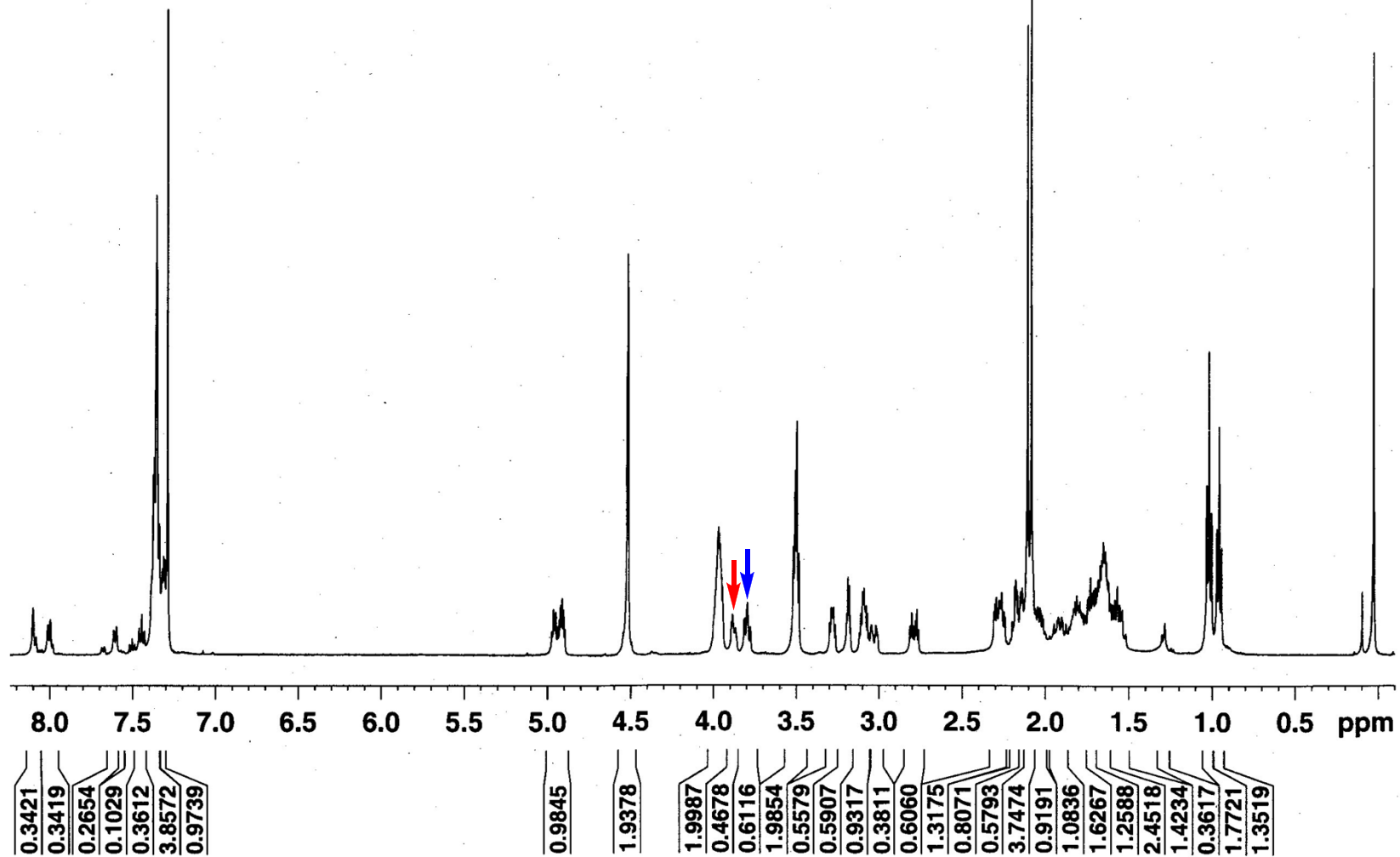
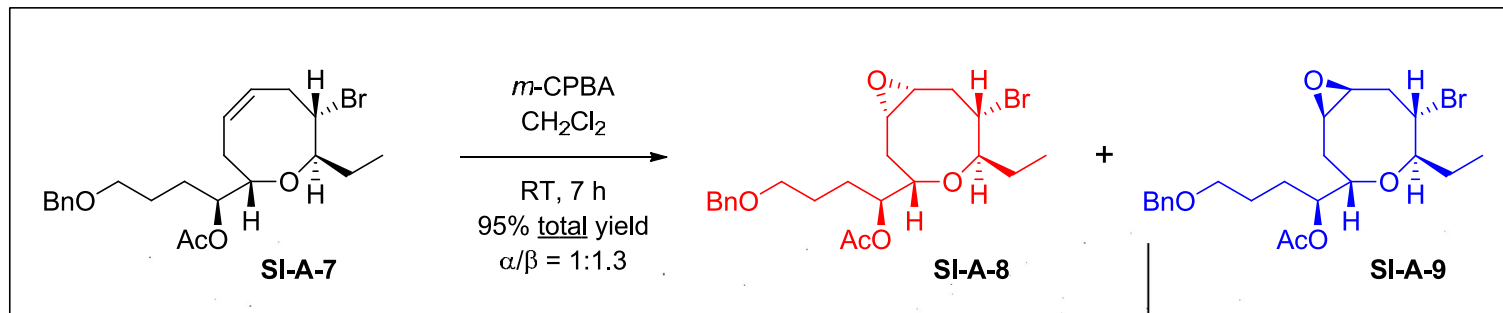
# Stereoselectivity in Epoxidation of SI-A-4 with *m*-CPBA



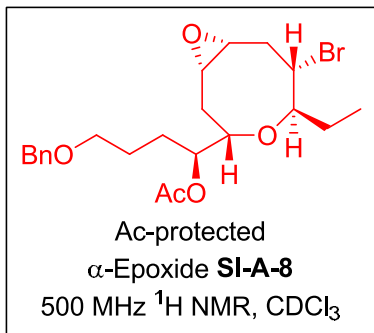








# Stereoselectivity in Epoxidation of SI-A-7 with *m*-CPBA



*m*-CPBA  
 $\text{CH}_2\text{Cl}_2$   
RT, 7 h  
95% total yield  
 $\alpha/\beta = 1:1.3$   
(mixture)  
500 MHz  $^1\text{H}$  NMR,  $\text{CDCl}_3$

