

–**Electronic Supplementary Information (ESI)**–

**Stereoselective total synthesis of (3*Z*)- and (3*E*)-elatenynes**

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# – Electronic Supplementary Information –

## Part A (S1 ~ S29)

### Experimental Procedures and Product Characterizations

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## General & Note: S3

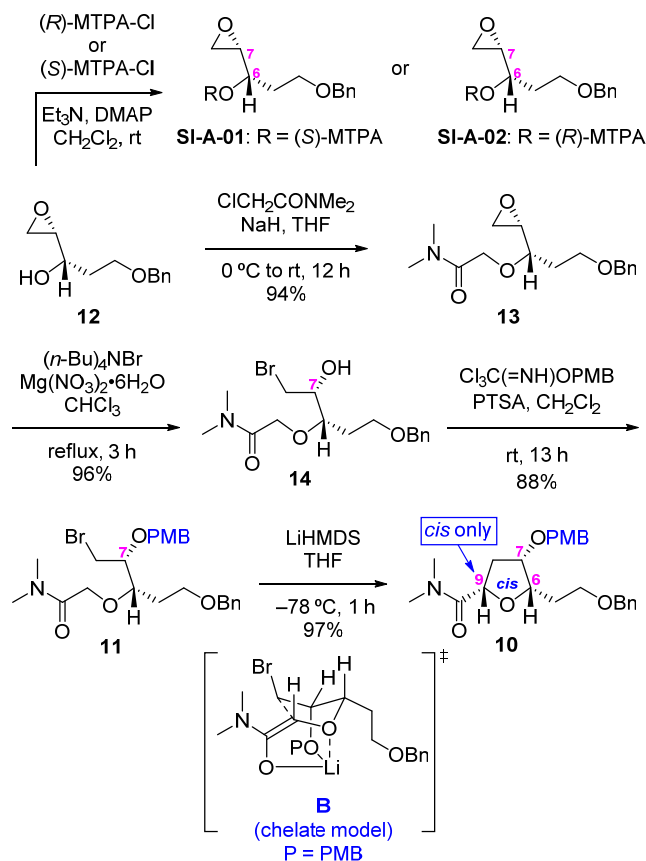
### General

Proton ( $^1\text{H}$ ) and carbon ( $^{13}\text{C}$ ) NMR spectra were obtained on Varian Mercury 400 and ECZ600R. Chemical shifts are reported in ppm units with  $\text{Me}_4\text{Si}$  or  $\text{CHCl}_3$  as the internal standard. Structural assignments were made with additional information from gCOSY, gHSQC, gHMQC, and gHMBC experiments. Specific rotation was obtained on a Jasco P-2000 (light source, WI 589 nm). High resolution mass spectra (HRMS) were recorded using electronionization (EI) and fast atom bombardment (FAB). All reactions were routinely carried out under an inert atmosphere of dry nitrogen. All reactions that required heating were carried out using oil bath. 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 dipping in *p*-anisaldehyde solution in a mixture of acetic acid, sulfuric acid, and methanol. In aqueous work-up, all organic solutions were dried over anhydrous sodium sulfate and filtered prior to rotary evaporation. The crude compounds were purified by column chromatography on a silica gel (Kieselgel 60, 70-230 mesh, Merck and Kieselgel 60, 63-200 mesh, Merck). Unless otherwise noted, materials and all solvents were obtained from commercial suppliers and were used without purification. Toluene and methylene chloride were dried with 4Å molecular sieve.

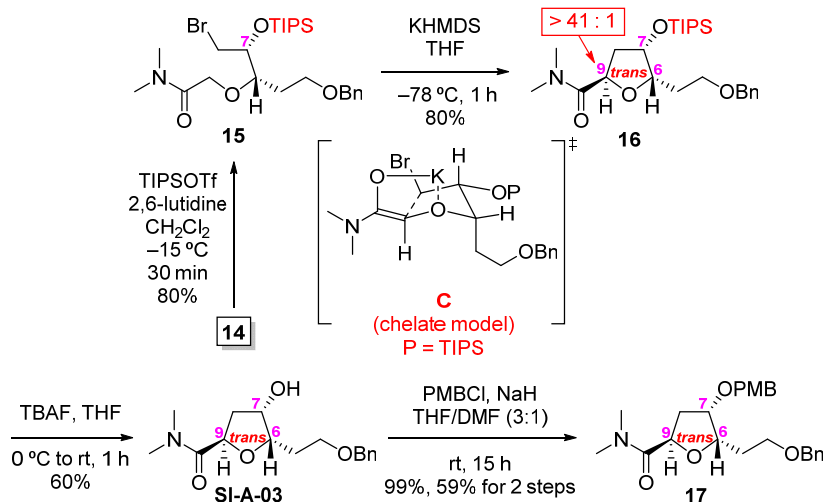
**Note:** The present Supporting Information A includes modified versions of the experimental procedures that have been already described in the literature in case the experimental procedures were improved in terms of reaction conditions, yields, selectivity, and so on, or where additional spectroscopic data are available.

## Construction of Key 7-Hydroxy-6, 7-*threo*-6,9-*cis*-THF 10: S4 ~ S10

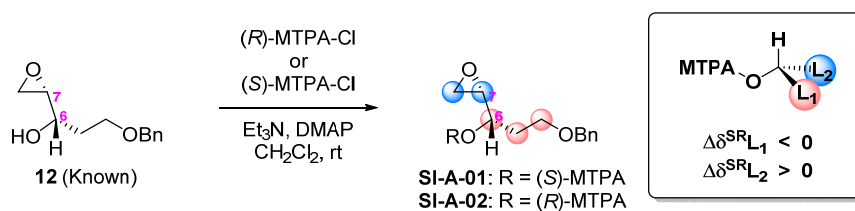
### Scheme ESI-01. Stereoselective Synthesis of Key 6,7-*cis*-6,9-*cis*-THF 10 via IAEA



Scheme 2b. Preparation of 6,7-*cis*-6,9-*trans*-THF 17 for comparison

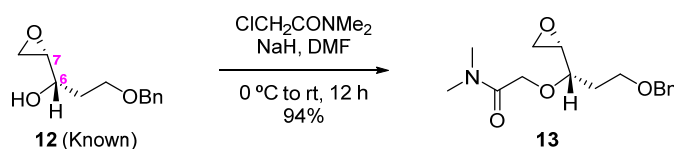


## Determination of *ee* Value and Confirmation of C(6) Absolute Stereochemistry of Secondary Alcohol **12**<sup>1</sup>



To a solution of secondary epoxy alcohol **12** in  $\text{CH}_2\text{Cl}_2$  were successively added (*R*)- or (*S*)- $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetyl chloride (5.0 eq),  $\text{Et}_3\text{N}$  (6.0 eq), and DMAP (0.4 eq) at room temperature. After stirring for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$ , diluted with  $\text{Et}_2\text{O}$ . The layers were separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combine layers were washed with 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/(ethyl acetate, 6 : 1) to afford the crude (*S*)-MTPA ester **SI-A-01** or (*R*)-MTPA ester **SI-A-02** as a colorless oil: [**For (*S*)-Mosher Derivative SI-A-01**]  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56–7.55 (m, 2 H), 7.42–7.37 (m, 3 H), 7.36–7.33 (m, 2 H), 7.32–7.28 (m, 3 H), 5.06 (q,  $J = 6.8$  Hz, 1 H), 4.42 (AB,  $J_{\text{AB}} = 11.8$  Hz,  $\Delta\nu_{\text{AB}} = 24.4$  Hz, 2 H), 3.59 (s, 3 H), 3.46 (dt,  $J = 9.4, 5.7$  Hz, 1 H), 3.38 (dt,  $J = 9.6, 6.4$  Hz, 1 H), 3.17 (ddd,  $J = 7.0, 4.1, 2.5$  Hz, 1 H), 2.85 (dd,  $J = 4.8, 4.1$  Hz, 1 H), 2.68 (dd,  $J = 4.9, 2.6$  Hz, 1 H), 1.99 (q,  $J = 6.3$  Hz, 2 H) [**For (*R*)-Mosher Derivative SI-A-02**]  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56–7.55 (m, 2 H), 7.42–7.37 (m, 3 H), 7.36–7.34 (m, 2 H), 7.32–7.28 (m, 3 H), 5.13 (q,  $J = 6.6$  Hz, 1 H), 4.48 (AB,  $J_{\text{AB}} = 11.8$  Hz,  $\Delta\nu_{\text{AB}} = 15.3$  Hz, 2 H), 3.59–3.55 (m, 1 H), 3.52–3.49 (m, 1 H), 3.51 (s, 3 H), 3.12 (ddd,  $J = 6.6, 4.1, 2.6$  Hz, 1 H), 2.76 (t,  $J = 4.5$  Hz, 1 H), 2.58 (dd,  $J = 4.9, 2.6$  Hz, 1 H), 2.06 (q,  $J = 6.1$  Hz, 2 H).

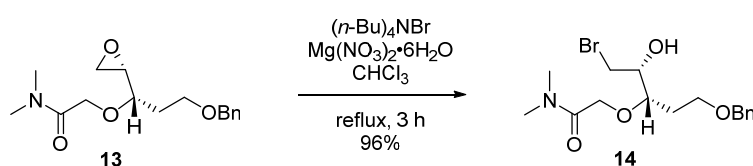
## Preparation of Epoxy Amide **13**



To a cooled ( $0\text{ }^\circ\text{C}$ ) solution of known epoxy alcohol **12** (6.04 g, 28.99 mmol) in DMF (290 mL, 0.1 M) was added 2-chloro-*N,N*-dimethylacetamide (3.58 mL, 34.79 mmol) and sodium hydride (2.32 g, 60% dispersion in mineral oil, 57.98 mmol). After being stirred for 12 h at

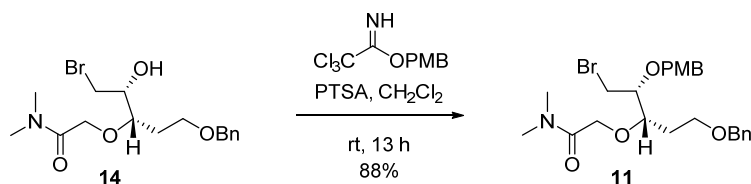
room temperature, the reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and diluted with  $\text{EtOAc}$ . The layers were separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with saturated brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 1 : 2) to afford the epoxy amide **13** (10.12 g, 94%) as a colorless oil:  $[\alpha]^{24}_{\text{D}} = +0.027$  (*c* 0.95,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.26 (m, 5 H), 4.52–4.47 (m, 2 H), 4.33 (AB,  $J_{\text{AB}} = 13.9$  Hz,  $\Delta\nu_{\text{AB}} = 94.69$  Hz, 2 H), 3.69–3.62 (m, 2 H), 3.23 (td,  $J = 7.8, 4.9$  Hz, 1 H), 3.05 (ddd,  $J = 7.3, 4.2, 2.7$  Hz, 1 H), 2.96 (s, 3 H), 2.95 (s, 3 H), 2.74–2.73 (m, 1 H), 2.46 (dd,  $J = 4.8, 2.7$  Hz, 1 H), 2.00 (ddt,  $J = 13.9, 8.1, 5.7$  Hz, 1 H), 1.92–1.86 (m, 1 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  168.7, 137.9, 128.0, 127.3, 127.2, 79.0, 72.7, 68.2, 66.0, 54.4, 42.9, 36.0, 35.2, 32.4; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{16}\text{H}_{23}\text{NO}_4$  293.1627; Found 293.1624.

#### Preparation of Bromohydrin Amide **14**



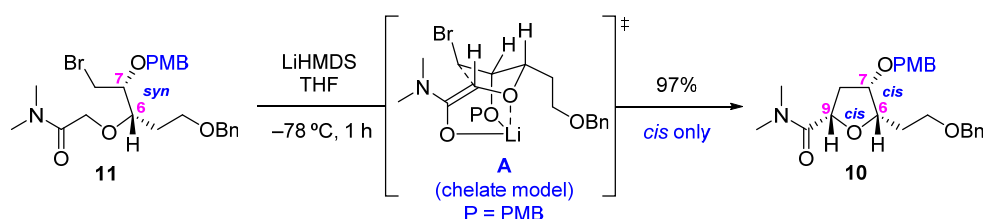
To a solution of epoxy amide **13** (8.50 g, 28.97 mmol) in  $\text{CHCl}_3$  (116 mL, 0.25 M) was added tetrabutylammonium bromide (14.01 g, 43.46 mmol) and magnesium nitrate hexahydrate (5.20 g, 20.28 mmol) in portions. After being stirred for 3 h at 80 °C, the reaction mixture was quenched with saturated aqueous  $\text{H}_2\text{O}$  and diluted with  $\text{Et}_2\text{O}$ . 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/ethyl acetate, 1 : 5) to afford the bromohydrin amide **14** (10.42 g, 96%) as a colorless oil:  $[\alpha]^{23}_{\text{D}} = -0.60$  (*c* 0.95,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.32 (m, 4 H), 7.30–7.27 (m, 1 H), 6.15 (d,  $J = 1.4$  Hz, 1 H), 4.52 (AB,  $J_{\text{AB}} = 11.8$  Hz,  $\Delta\nu_{\text{AB}} = 59.35$  Hz, 2 H), 4.26 (AB,  $J_{\text{AB}} = 15.7$  Hz,  $\Delta\nu_{\text{AB}} = 121.75$  Hz, 2 H), 3.81 (tt,  $J = 6.7, 3.2$  Hz, 1 H), 3.68 (ddd,  $J = 9.7, 8.4, 4.5$  Hz, 1 H), 3.65–3.61 (m, 3 H), 3.45 (ddd,  $J = 10.9, 4.1, 1.0$  Hz, 1 H), 2.94 (s, 3 H), 2.77 (s, 3 H), 2.00–1.95 (m, 1 H), 1.74–1.68 (m, 1 H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 138.1, 128.4, 127.7, 82.6, 72.9, 72.6, 68.6, 65.8, 35.73, 35.70, 31.2; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{16}\text{H}_{24}\text{BrNO}_4$  373.0889; Found 373.0884.

## Preparation of PMB-Protected Bromo Amide **11**



To a solution of bromohydrin amide **14** (10.45 g, 27.92 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (280 mL, 0.1 M) was added *p*-methoxybenzyl-2,2,2-trichloroacetimidate (29.00 g, 139.61 mmol) and PTSA (1.06 g, 5.58 mmol) in portions at the room temperature. The resulting mixture was stirred for 13 h at the same temperature, the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> and diluted with CH<sub>2</sub>Cl<sub>2</sub>. 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, ether/ethyl acetate, 2 : 1) to afford the PMB-protected bromo amide **11** (12.14 g, 88%) as a colorless oil:  $[\alpha]_D^{24} = +0.47$  (*c* 0.99, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35–7.28 (m, 4 H), 7.27–7.25 (m, 3 H), 6.85–6.82 (m, 2 H), 4.58 (AB, *J*<sub>AB</sub> = 11.2 Hz, Δ*v*<sub>AB</sub> = 46.87 Hz, 2 H), 4.46 (s, 2 H), 4.20 (d, *J* = 5.0 Hz, 2 H), 3.82–3.75 (m, 2 H), 3.78 (s, 3 H), 3.66 (dd, *J* = 10.6, 4.3 Hz, 1 H), 3.59–3.48 (m, 2 H), 3.42 (dd, *J* = 10.6, 6.0 Hz, 1 H), 2.90 (s, 3 H), 2.86 (s, 3 H), 1.99–1.91 (m, 1 H), 1.82–1.74 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.6, 158.9, 130.0, 129.6, 129.5, 128.0, 127.3, 127.2, 113.4, 79.6, 77.6, 72.7, 72.5, 69.5, 66.3, 55.1, 36.1, 35.3, 32.0, 29.9; HRMS (EI-magnetic sector) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>32</sub>BrNO<sub>5</sub> 493.1464; Found 493.1462.

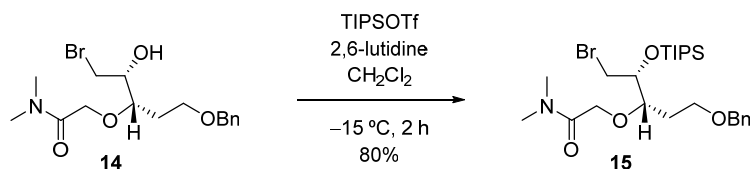
## Preparation of 7-OPMB-6,7-*cis*-6,9-*cis*-THF **10**



To a cooled (–78 °C) solution of 7-OPMB-6,7-*syn*- $\omega$ -bromo amide **11** (1.57 g, 3.18 mmol) in THF (635 mL, 0.005 M) was dropwise added LiHMDS (9.53 mL, 1.0 M solution in THF, 9.53 mmol). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc. 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, ether/ethyl acetate, 4 : 1) to afford 7-OPMB-6,7-*cis*-6,9-*cis*-THF **10** (1.27 g, 97%, *cis* only, see page S39 & S57) as a colorless oil:  $[\alpha]_D^{24} = -0.19$  (*c* 0.97, CHCl<sub>3</sub>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34–7.30 (m, 4 H), 7.28–7.26 (m, 1 H), 7.23–7.21 (m, 2 H), 6.86–6.83 (m, 2 H), 4.51–4.47 (m, 3 H), 4.43 (AB, *J*<sub>AB</sub> = 11.6 Hz, Δ*v*<sub>AB</sub> = 162.9 Hz, 2 H), 3.97–3.94 (m, 2 H), 3.79 (s, 3 H), 3.62–3.55 (m, 2 H), 3.09 (s, 3 H), 2.94 (s, 3 H), 2.70 (ddd, *J* = 13.5, 6.6, 2.7 Hz, 1 H), 2.23–2.17 (m, 1 H), 2.07–1.97 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.5, 158.8, 138.3, 130.1, 129.1, 128.1, 127.4, 127.3, 113.5, 80.1, 77.5, 75.8, 72.8, 70.1, 67.3, 55.2, 37.1, 36.1, 33.8, 29.2; HRMS (EI-magnetic sector) *m/z*: [M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>NO<sub>5</sub> 413.2202; Found 413.2205.

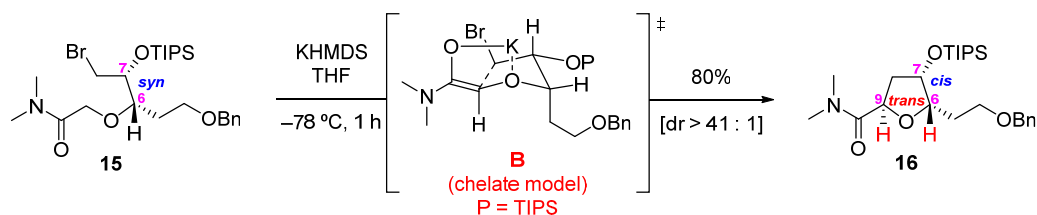
### Preparation of TIPS-Protected Bromo Amide **15**



To a cooled (−15 °C) solution of bromohydrin amide **14** (1.42 g, 3.80 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (38 mL, 0.1 M) was added 2,6-lutidine (2.65 mL, 22.77 mmol) and triisopropylsilyl trifluoromethanesulfonate (TIPSOTf, 2.02 mL, 11.40 mmol). The resulting mixture was stirred for 2 h at the same temperature, the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub> and diluted with EtOAc. 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, ether/ethyl acetate, 3 : 1) to afford the TIPS-protected bromo amide **15** (1.60 g, 80%) as a colorless oil:  $[\alpha]_D^{24} = -18.2$  (*c* 0.88, CHCl<sub>3</sub>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34–7.31 (m, 4 H), 7.29–7.25 (m, 1 H), 4.52–4.48 (m, 2 H), 4.23 (dt, *J* = 7.4, 4.2 Hz, 1 H), 4.22–4.17 (m, 2 H), 3.73 (ddd, *J* = 9.3, 4.3, 3.1 Hz, 1 H), 3.68 (dd, *J* = 10.4, 4.0 Hz, 1 H), 3.62 (dd, *J* = 7.4, 5.4 Hz, 2 H), 3.35 (dd, *J* = 10.4, 6.4 Hz, 1 H), 2.94 (s, 3 H), 2.91 (s, 3 H), 2.07 (dtd, *J* = 14.5, 7.4, 3.1 Hz, 1 H), 1.73 (ddt, *J* = 14.7, 9.4, 5.4 Hz, 1 H), 1.13–1.05 (m, 21 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 169.0, 138.5, 128.3, 127.6, 127.5, 79.8, 73.5, 72.9, 70.2, 66.9, 36.4, 35.4, 34.6, 29.3, 18.1, 12.7; HRMS (EI-magnetic sector) *m/z*: [M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>44</sub>BrNO<sub>4</sub>Si 529.2223; Found 529.2225.

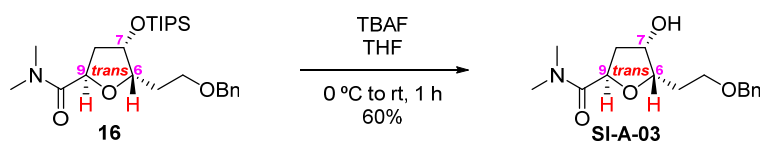


## Preparation of 7-OTIPS-6,7-*cis*-6,9-*trans*-THF **16**



To a cooled ( $-78\text{ }^{\circ}\text{C}$ ) solution of TIPS-protected bromo amide **15** (52.4 mg, 0.0988 mmol) in THF (20 mL, 0.005 M) was dropwise added KHMDS (0.42 mL, 0.7 M solution in toluene, 0.30 mmol). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc. 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, ether/ethyl acetate, 1 : 2) to afford 7-OTIPS-6,7-*cis*-6,9-*trans*-THF **16** (35.6 mg, 80%, *trans:cis* > 41 : 1, see page S48) as a colorless oil:  $[\alpha]_D^{23} = -12.8$  ( $c$  0.89,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.32 (m, 4 H), 7.28–7.26 (m, 1 H), 4.81 (t,  $J = 7.4$  Hz, 1 H), 4.51 (s, 2 H), 4.50–4.48 (m, 1 H), 4.08 (ddd,  $J = 7.8, 5.4, 3.9$  Hz, 1 H), 3.65–3.58 (m, 2 H), 3.08 (s, 3 H), 2.95 (s, 3 H), 2.56 (ddd,  $J = 13.0, 7.7, 5.2$  Hz, 1 H), 2.05 (ddd,  $J = 13.1, 7.1, 2.6$  Hz, 1 H), 1.96–1.91 (m, 2 H), 1.08–1.04 (m, 21 H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 138.6, 128.3, 127.6, 127.4, 80.5, 74.1, 73.7, 73.0, 67.9, 38.5, 37.0, 35.8, 29.9, 18.09, 18.05, 12.4; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{25}\text{H}_{43}\text{NO}_4\text{Si}$  449.2961; Found 449.2961.

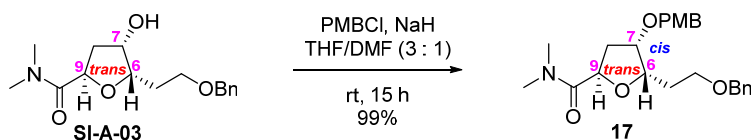
## Preparation of Alcohol SI-A-03



To a cooled ( $0\text{ }^{\circ}\text{C}$ ) solution of 7-OTIPS-6,7-*threo*-6,9-*trans*-THF **16** (0.36 g, 0.79 mmol) in anhydrous THF (8 mL, 0.1 M) was added tetrabutylammonium fluoride (TBAF, 0.79 mL, 0.79 mmol). After being stirred for 1 h at the room temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and diluted with Et<sub>2</sub>O. The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O. 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, ethyl acetate only) to afford alcohol **SI-A-03** (0.14 g, 60%) as a colorless oil:  $[\alpha]^{23}_D = -21.4$  ( $c$  0.31,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37–7.34 (m, 2 H), 7.32–7.29 (m, 3 H), 4.92 (dd,  $J = 8.4, 7.1$  Hz, 1 H), 4.53 (AB,  $J_{AB} = 11.7$  Hz,  $\Delta\nu_{AB} = 13.4$  Hz, 2 H), 4.35 (dt,  $J = 5.4, 2.7$  Hz, 1 H), 4.04 (ddd,  $J = 9.8, 5.1, 3.0$  Hz, 1 H), 3.67 (ddd,  $J = 9.5, 4.7, 3.4$  Hz, 1 H), 3.49 (ddd,  $J = 10.6, 9.4, 2.5$  Hz, 1 H), 3.25 (t,  $J = 2.1$  Hz, 1 H), 3.08 (s, 3 H), 2.95 (s, 3 H), 2.50 (dddd,  $J = 13.7, 8.4, 5.1, 1.6$  Hz, 1 H), 2.19–2.15 (m, 1 H), 2.12–2.06 (m, 1 H), 2.05–2.00 (m, 1 H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  171.6, 137.3, 128.6, 128.0, 127.8, 83.5, 73.8, 73.7, 72.6, 66.9, 37.2, 36.9, 35.8, 29.3; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{16}\text{H}_{23}\text{NO}_4$  293.1627; Found 293.1624.

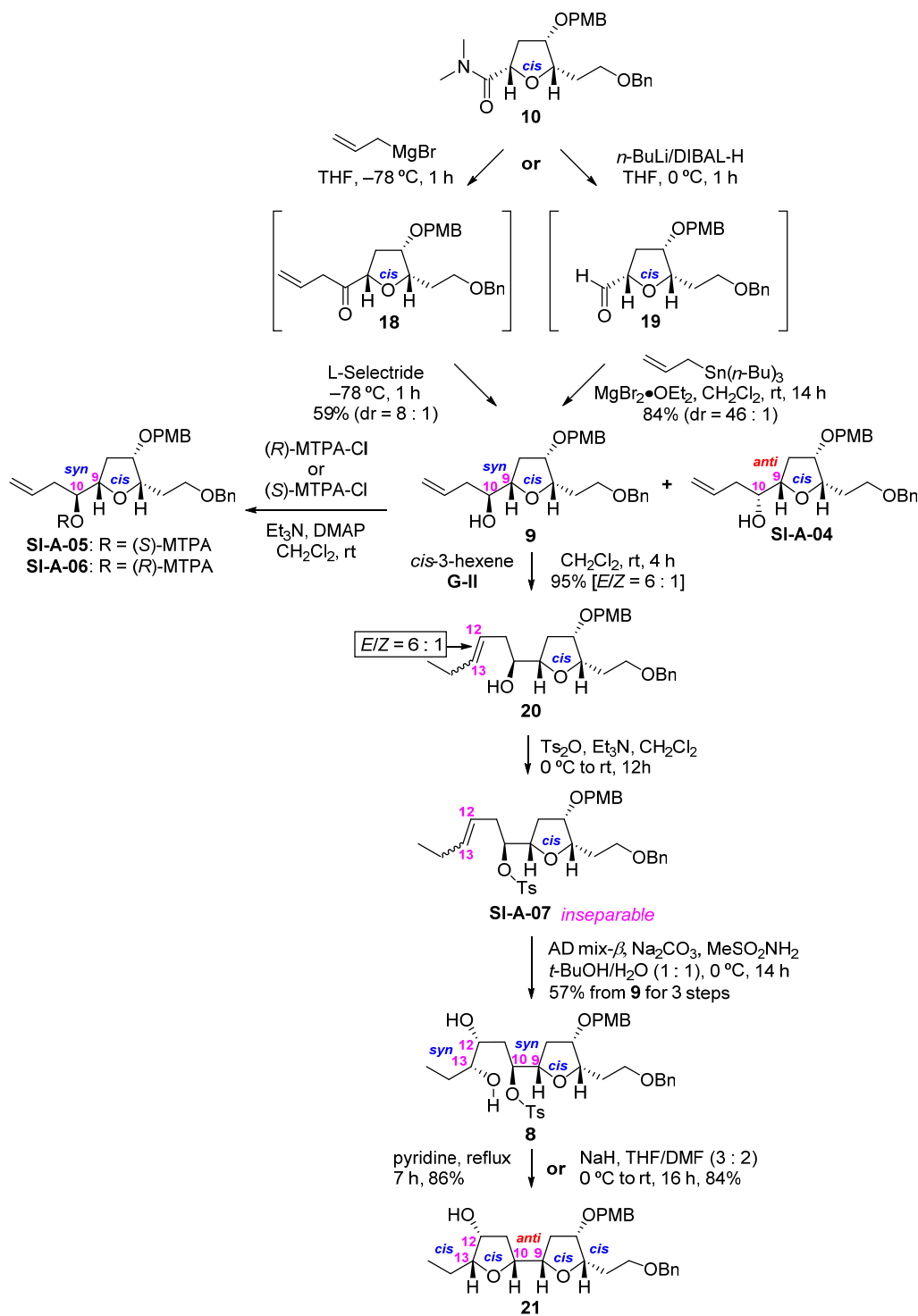
### Preparation of 7-OPMB-6,7-*cis*-6,9-*trans*-THF **17**



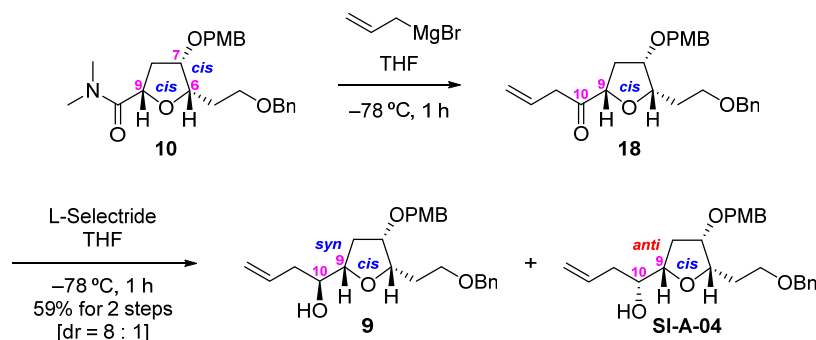
To a solution of alcohol **SI-A-03** (0.13 g, 0.45 mmol) in THF/DMF (3 : 1, 4.4 mL, 0.3 M) was added *p*-methoxybenzyl chloride (0.26 mL, 1.80 mmol) and sodium hydride (63 mg, 60% dispersion of mineral oil, 1.575 mmol) in portions at the room temperature. The resulting mixture was stirred for 15 h at the same temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and diluted with  $\text{CH}_2\text{Cl}_2$ . 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/ethyl acetate, 3 : 1) to afford the 7-OPMB-6,7-*cis*-6,9-*trans*-THF **17** (0.184 g, 99%) as a colorless oil:  $[\alpha]^{23}_D = -13.6$  ( $c$  0.90,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.30 (m, 4 H), 7.28–7.26 (m, 1 H), 7.24–7.21 (m, 2 H), 6.87–6.85 (m, 2 H), 4.82 (t,  $J = 7.6$  Hz, 1 H), 4.48 (AB,  $J_{AB} = 12.0$  Hz,  $\Delta\nu_{AB} = 11.2$  Hz, 2 H), 4.44 (AB,  $J_{AB} = 11.6$  Hz,  $\Delta\nu_{AB} = 104.7$  Hz, 2 H), 4.09 (ddd,  $J = 7.8, 5.7, 3.6$  Hz, 1 H), 4.03–4.02 (m, 1 H), 3.80 (s, 3 H), 3.56 (td,  $J = 6.7, 2.4$  Hz, 2 H), 3.08 (s, 3 H), 2.95 (s, 3 H), 2.49 (ddd,  $J = 13.1, 7.9, 5.0$  Hz, 1 H), 2.20 (ddd,  $J = 13.3, 7.3, 1.5$  Hz, 1 H), 2.06–1.98 (m, 2 H);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 159.2, 138.5, 130.2, 129.2, 128.3, 127.6, 127.5, 113.7, 80.0, 79.1, 74.1, 72.9, 71.0, 67.7, 55.2, 37.0, 35.8, 34.3, 29.4; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{24}\text{H}_{31}\text{NO}_5$  413.2202; Found 413.2202.

## Construction of 7,12-Dihydroxy Adjacent Bis-THF 21

### Scheme ESI-02. Construction of 7,12-Dihydroxy Adjacent Bis-THF 21

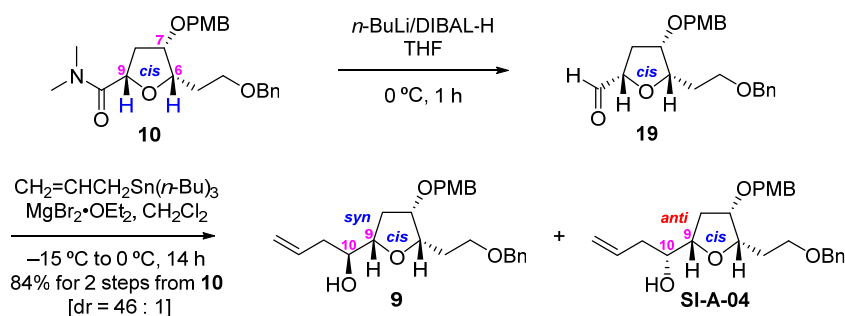


## Preparation of (10S)-Alcohol SI-A-04 by Direct Ketone Synthesis/L-Selectride Sequence



**[Direct Ketone Synthesis]**<sup>3</sup> To a cooled (-78 °C) solution of 7-OPMB-6,7-*cis*-6,9-*cis*-THF **10** (438.1 mg, 1.06 mmol) in anhydrous THF (20 mL, 0.1 M) was dropwise added allylmagnesium chloride (1.06 mL, 2.0 M solution in THF, 2.12 mmol). After being stirred at the same temperature for 1 h, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl, and diluted with Et<sub>2</sub>O. The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O. The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to afford the crude ketone **18** as a colorless oil. **[L-Selectride Reduction]** To a cooled (-78 °C) solution of the above crude ketone **18** in THF (20 mL) was added lithium *tri*-*sec*-butylborohydride (L-Selectride, 3.2 mL, 1.0 M in THF, 3.2 mmol). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with MeOH, and H<sub>2</sub>O<sub>2</sub> (5.0 mL, 1.0 M in H<sub>2</sub>O, 5.0 mmol) and NaOH (5 mL, 2.0 M in H<sub>2</sub>O, 10.0 mmol) were added. The resulting mixture was vigorously stirred for 12 h at room temperature and diluted with Et<sub>2</sub>O. The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O. 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/ethyl acetate, 10 : 1) to afford (10*S*)-9,10-*syn* homoallylic alcohol **9** (259.6 mg, 59%, dr = 8 : 1, [see page S59](#)) as a colorless oil.

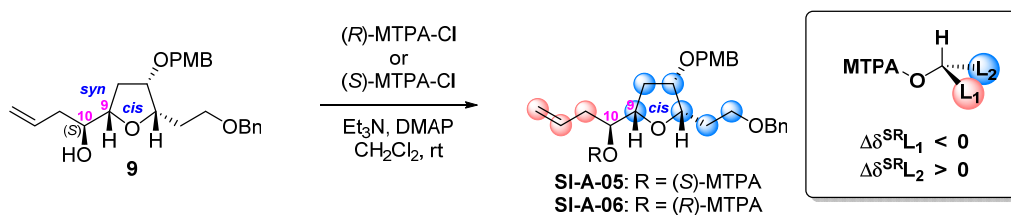
## Preparation of (10*S*)-9,10-*syn* Homoallylic Alcohol **9** by a Sequential Ate Complex/Keck Allylation



**[Ate Complex Reduction] Ate Complex Generation:** To a cooled ( $-78\text{ }^\circ\text{C}$ ) solution of  $n\text{-BuLi}$  (1.0 mL, 1.6 M in hexane) in THF (13.3 mL) was added DIBAL-H (1.7 mL, 1.0 M in toluene) and stirred for 30 min at the same temperature. To a cooled ( $0\text{ }^\circ\text{C}$ ) solution of 7-OPMB-6,7-*cis*-6,9-*cis*-THF **10** (96.7 mg, 0.23 mmol) in dry THF (23.4 mL, 0.01 M) were added dropwise ate complex solution (4.67 mL, 0.47 mmol). After being stirred at the same temperature for 1 h, the reaction mixture was quenched with MeOH and diluted with Et<sub>2</sub>O and saturated aqueous NH<sub>4</sub>Cl. The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O. The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to afford the crude aldehyde **19**, which was immediately employed to the next step without further purification. **[Keck Allylation]**<sup>2</sup> To a cooled ( $-15\text{ }^\circ\text{C}$ ) solution of the above crude aldehyde **19** in dry CH<sub>2</sub>Cl<sub>2</sub> (4.7 mL, 0.05 M) was added MgBr<sub>2</sub>·OEt<sub>2</sub> (0.30 g, 1.17 mmol). The resulting mixture was stirred for 10 min, and then allyltributyltin (0.29 mL, 0.94 mmol) was added dropwise. After being stirred for 14 h at  $0\text{ }^\circ\text{C}$ , the reaction mixture was quenched with saturated aqueous NaHCO<sub>3</sub>, and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The layers were separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The residue was filtrated by column chromatography (silica gel, hexanes/ethyl acetate/dichloromethane, 4 : 1 : 1) to afford (10*S*)-9,10-*syn* homoallylic alcohol **9** (81.1 mg, 84%, dr = 46 : 1, [see page S61](#)) as colorless oils: **[For 9]**  $[\alpha]^{24}_{\text{D}} = -0.15$  ( $c$  0.93, CHCl<sub>3</sub>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.35–7.31 (m, 4 H), 7.29–7.27 (m, 1 H), 7.22–7.19 (m, 2 H), 6.86–6.84 (m, 2 H), 5.88 (ddt,  $J = 17.2, 10.2, 7.0$  Hz, 1 H), 5.13–5.05 (m, 2 H), 4.49 (AB,  $J_{\text{AB}} = 12.0$  Hz,  $\Delta\nu_{\text{AB}} = 15.73$  Hz, 2 H), 4.38 (AB,  $J_{\text{AB}} = 11.5$  Hz,  $\Delta\nu_{\text{AB}} = 148.63$  Hz, 2 H), 3.95–3.92 (m, 1 H), 3.93–3.90 (m, 2 H), 3.80 (s, 3 H), 3.61–3.54 (m, 3 H), 3.00 (d,  $J = 5.1$  Hz, 1 H),

2.29 (tq,  $J = 7.2, 1.4$  Hz, 2 H), 2.14 (ddd,  $J = 14.0, 8.8, 5.4$  Hz, 1 H), 2.06–1.95 (m, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 138.5, 135.3, 129.8, 129.4, 128.3, 127.7, 127.5, 116.9, 113.8, 79.7, 79.4, 78.6, 73.2, 72.9, 70.6, 67.6, 55.3, 38.6, 33.9, 29.4; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{25}\text{H}_{32}\text{O}_5$  412.2250; Found 412.2242. **[For SI-A-04]**  $[\alpha]^{24}_{\text{D}} = +26.6$  ( $c$  0.77,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.30 (m, 4 H), 7.29–7.27 (m, 1 H), 7.22–7.20 (m, 2 H), 6.87–6.84 (m, 2 H), 5.85 (ddt,  $J = 17.2, 10.2, 7.0$  Hz, 1 H), 5.13–5.07 (m, 2 H), 4.48 (AB,  $J_{\text{AB}} = 12.0$  Hz,  $\Delta\nu_{\text{AB}} = 21.82$  Hz, 2 H), 4.40 (AB,  $J_{\text{AB}} = 11.5$  Hz,  $\Delta\nu_{\text{AB}} = 177.83$  Hz, 2 H), 3.98 (ddd,  $J = 8.5, 5.3, 2.8$  Hz, 1 H), 3.90–3.84 (m, 3 H), 3.80 (s, 3 H), 3.60–3.54 (m, 2 H), 2.82 (d,  $J = 1.7$  Hz, 1 H), 2.27–2.22 (m, 1 H), 2.19–2.14 (m, 2 H), 2.04 (ddt,  $J = 13.8, 7.9, 5.8$  Hz, 1 H), 2.01–1.94 (m, 2 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.2, 138.5, 134.7, 129.9, 129.4, 128.3, 127.7, 127.5, 117.2, 113.8, 80.0, 79.6, 78.2, 73.0, 71.3, 70.4, 67.7, 55.3, 38.1, 30.2, 29.3; HRMS (FAB-magnetic sector)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{25}\text{H}_{33}\text{O}_5$  413.2328; Found 413.2328.

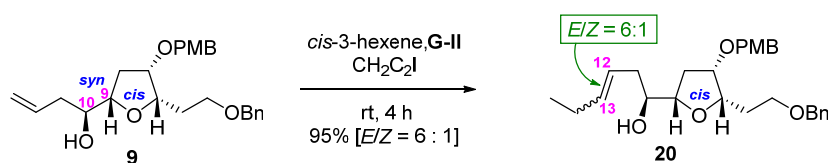
### Confirmation of C(10) Absolute Stereochemistry in Secondary Alcohol **9**



To a solution of (10*S*)-alcohol **9** in  $\text{CH}_2\text{Cl}_2$  were successively added (*R*)- or (*S*)- $\alpha$ -methoxy- $\alpha$ -trifluoromethylphenylacetyl chloride (5.0 eq),  $\text{Et}_3\text{N}$  (6.0 eq), and DMAP (0.4 eq) at room temperature. After stirring for 40 min at the same temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$ , diluted with  $\text{Et}_2\text{O}$ . The layers were separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combine layers were washed with 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/ethyl acetate, 10:1) to afford the crude (*S*)-MTPA ester **SI-A-05** or (*R*)-MTPA ester **SI-A-06** as a colorless oil: **[For (*S*)-Mosher Derivative SI-A-05]**  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63–7.61 (m, 2 H), 7.37–7.35 (m, 3 H), 7.34–7.27 (m, 5 H), 7.23–7.21 (m, 2 H), 6.88–6.86 (m, 2 H), 5.64–5.57 (m, 1 H), 5.31 (td,  $J = 7.8, 3.7$  Hz, 1 H), 4.97 (s, 1 H), 4.95 (d,  $J = 6.3$  Hz, 1 H), 4.47–4.42 (m, 2 H), 4.40 (AB,  $J_{\text{AB}} = 11.7$  Hz,  $\Delta\nu_{\text{AB}} = 85.1$  Hz, 2 H), 3.99–3.96 (m, 3 H), 3.80 (s, 3 H), 3.58 (s, 3 H), 3.54 (t,  $J = 6.4$  Hz, 2 H), 2.42–2.38 (m, 1 H), 2.22 (dt,  $J = 15.2, 7.8$  Hz, 1 H), 2.18–2.13 (m, 1 H), 1.98 (q,  $J = 6.8$  Hz, 2 H),

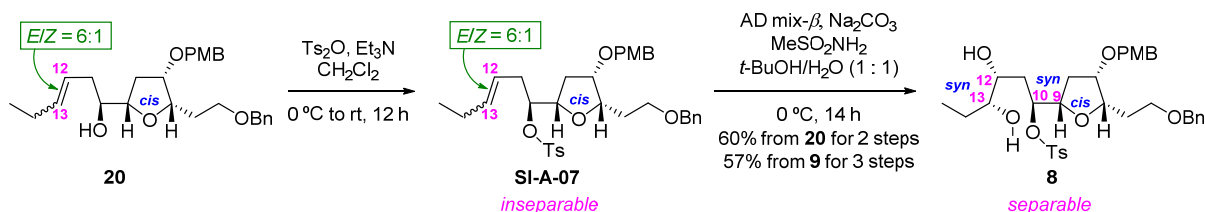
1.83–1.79 (m, 1 H); HRMS (FAB-magnetic sector)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{35}H_{40}F_3O_7$  629.2726; Found 629.2719. [**For (R)-Mosher Derivative SI-A-06**]  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.59–7.58 (m, 2 H), 7.37–7.36 (m, 3 H), 7.34–7.27 (m, 5 H), 7.20–7.17 (m, 2 H), 6.87–6.84 (m, 2 H), 5.81–5.74 (m, 1 H), 5.32 (ddd,  $J = 8.1, 6.9, 3.9$  Hz, 1 H), 5.12–5.08 (m, 2 H), 4.46–4.42 (m, 2 H), 4.34 (AB,  $J_{AB} = 11.6$  Hz,  $\Delta\nu_{AB} = 89.9$  Hz, 2 H), 3.96–3.90 (m, 3 H), 3.80 (s, 3 H), 3.51 (s, 3 H), 3.53–3.50 (m, 2 H), 2.52–2.48 (m, 1 H), 2.33 (dt,  $J = 15.5, 8.1$  Hz, 1 H), 2.04 (ddd,  $J = 13.6, 7.8, 5.9$  Hz, 1 H), 1.96–1.86 (m, 2 H), 1.74 (ddd,  $J = 13.5, 7.0, 3.4$  Hz, 1 H); HRMS (FAB-magnetic sector)  $m/z$ :  $[M+H]^+$  Calcd for  $C_{35}H_{40}F_3O_7$  629.2726; Found 629.2722.

### Preparation of Alkene 20



To a solution of (10*S*)-alcohol **9** (670.8 mg, 1.626 mmol) in dry  $CH_2Cl_2$  (16.3 mL, 0.1 M) were added *cis*-3-hexene (2.01 mL, 16.3 mmol) and second-generation Grubb's catalyst  $[(H_2IMes)(Cy_3P)Cl_2Ru=CHPh, \mathbf{G-II}, 138.0$  mg, 0.163 mmol]<sup>4</sup> at room temperature. After being stirred for 4 h at the same temperature, the reaction mixture was quenched with dimethyl sulfoxide (0.5 mL), stirred for 15 h, and concentrated *in vacuo*. Purification of the residue by column chromatography (silica gel, hexanes/ethyl acetate, 5 : 1) to afford the inseparable mixture of alkene **20** (680.5 mg, 95% yield,  $E/Z = 6 : 1$ , see page S69) as a colorless oil; [**For (12*E*)-20**]  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.35–7.31 (m, 4 H), 7.29–7.26 (m, 1 H), 7.22–7.19 (m, 2 H), 6.87–6.84 (m, 2 H), 5.58–5.53 (m, 1 H), 5.50–5.45 (m, 1 H), 4.53–4.47 (m, 3 H), 4.27 (d,  $J = 11.4$  Hz, 1 H), 3.94–3.90 (m, 3 H), 3.80 (s, 3 H), 3.62–3.55 (m, 2 H), 3.53–3.48 (m, 1 H), 3.51 (tt,  $J = 6.4, 4.6$  Hz, 1 H), 2.94 (d,  $J = 5.0$  Hz, 1 H), 2.22 (tq,  $J = 6.5, 1.1$  Hz, 2 H), 2.13 (ddd,  $J = 13.9, 8.7, 5.5$  Hz, 1 H), 2.10–1.96 (m, 4 H), 0.97 (t,  $J = 7.5$  Hz, 3 H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  159.2, 138.5, 134.7, 129.9, 129.3, 128.3, 127.6, 127.5, 125.2, 113.8, 79.7, 79.4, 78.6, 73.7, 72.9, 70.6, 67.7, 55.3, 37.3, 34.0, 29.5, 25.6, 13.7; HRMS (EI-magnetic sector)  $m/z$ :  $[M]^+$  Calcd for  $C_{27}H_{36}O_5$  440.2563; Found 440.2558.

## Preparation of Diol 8

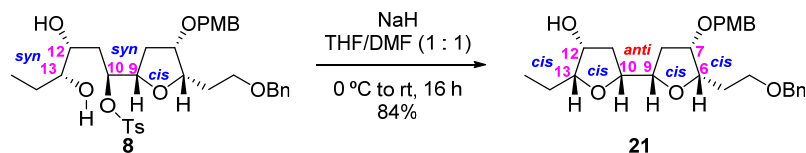


**[Tosylation]** To a cooled ( $0^\circ\text{C}$ ) solution of inseparable mixture of (*E*)/(*Z*)-hex-3-enol **20** (680.5 mg, 1.55 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (20 mL, 0.077 M) was added triethylamine (2.15 mL, 15.5 mmol) and *p*-toluenesulfonyl anhydride ( $\text{Ts}_2\text{O}$ , 210.8 mg, 4.63 mmol). After being stirred for 12 h at room temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and diluted with  $\text{H}_2\text{O}$ . The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . 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/ethyl acetate, 6 : 1) to afford the *inseparable mixture* of tosylate **SI-A-07** (878.4 mg, 96%) as a colorless oil: **[For (12*E*)-Tosylate SI-A-07]**  $[\alpha]_D^{25} = -0.70$  (*c* 0.79,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78–7.76 (m, 2 H), 7.35–7.30 (m, 4 H), 7.29–7.26 (m, 1 H), 7.24–7.22 (m, 2 H), 7.20–7.18 (m, 2 H), 6.88–6.85 (m, 2 H), 5.46 (dtt,  $J = 15.3, 6.3, 1.3$  Hz, 1 H), 5.21 (dddt,  $J = 15.7, 8.1, 6.7, 1.6$  Hz, 1 H), 4.61–4.58 (m, 1 H), 4.46 (AB,  $J_{\text{AB}} = 11.9$  Hz,  $\Delta\nu_{\text{AB}} = 16.57$  Hz, 2 H), 4.34 (AB,  $J_{\text{AB}} = 11.6$  Hz,  $\Delta\nu_{\text{AB}} = 116.40$  Hz, 2 H), 4.02 (dt,  $J = 8.2, 6.4$  Hz, 1 H), 3.89 (ddd,  $J = 6.0, 4.5, 2.9$  Hz, 1 H), 3.84 (dt,  $J = 8.4, 4.7$  Hz, 1 H), 3.81 (s, 3 H), 3.49–3.43 (m, 2 H), 2.54–2.49 (m, 1 H), 2.39 (s, 3 H), 2.25–2.20 (m, 1 H), 2.08 (ddd,  $J = 13.9, 8.2, 6.0$  Hz, 1 H), 1.95–1.87 (m, 3 H), 1.85–1.82 (m, 1 H), 1.81–1.75 (m, 1 H), 0.91 (t,  $J = 7.4$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 144.1, 138.6, 136.1, 134.3, 130.2, 129.4, 129.0, 128.3, 128.0, 127.6, 127.5, 122.6, 113.7, 83.8, 79.3, 78.3, 76.9, 72.9, 70.6, 67.5, 55.2, 34.1, 33.0, 29.4, 25.5, 21.5, 13.5; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{34}\text{H}_{42}\text{O}_7\text{S}$  594.2651; Found 594.2654. **[Sharpless Asymmetric Dihydroxylation]** To a cooled ( $0^\circ\text{C}$ ) solution of inseparable mixture of tosylate **SI-A-07** (530.7 mg, 0.892 mmol) in *tert*-butanol/ $\text{H}_2\text{O}$  (1 : 1, 10.0 mL, 0.089 M) was added methanesulfonamide (349.2 mg, 3.671 mmol),  $\text{K}_2\text{CO}_3$  (634.3 mg, 4.589 mmol). The reaction mixture was stirred for 30 min at same temperature and AD-mix  $\beta$  (2.12 g, 1.22 mmol) was added. After being stirred at the same temperature for 14 h, the reaction mixture was quenched with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ , and diluted with  $\text{Et}_2\text{O}$ . The layers were separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ .



The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo*. The residue was filtered through a short column of silica gel (hexanes/ethyl acetate, 1 : 1) to afford the pure diol **8** (337.4 mg, 60% for two steps) as a colorless oil:  $[\alpha]^{25}_D = +1.31$  (*c* 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.79–7.77 (m, 2 H), 7.35–7.27 (m, 5 H), 7.26–7.25 (m, 2 H), 7.20–7.18 (m, 2 H), 6.87–6.85 (m, 2 H), 4.86 (dt, *J* = 6.6, 4.5 Hz, 1 H), 4.45 (AB, *J*<sub>AB</sub> = 12.0 Hz, Δ*v*<sub>AB</sub> = 16.70 Hz, 2 H), 4.34 (AB, *J*<sub>AB</sub> = 11.4 Hz, Δ*v*<sub>AB</sub> = 118.84 Hz, 2 H), 4.09 (ddd, *J* = 8.3, 6.8, 4.6 Hz, 1 H), 3.90 (ddd, *J* = 6.0, 4.4, 2.8 Hz, 1 H), 3.87 (dt, *J* = 8.7, 4.5 Hz, 1 H), 3.80 (s, 3 H), 3.63 (ddd, *J* = 9.1, 4.7, 3.3 Hz, 1 H), 3.49–3.45 (m, 2 H), 3.17 (dt, *J* = 8.7, 4.5 Hz, 1 H), 2.40 (s, 3 H), 2.11 (ddd, *J* = 14.1, 8.3, 6.0 Hz, 1 H), 2.05 (ddd, *J* = 14.9, 6.7, 3.3 Hz, 1 H), 1.98 (ddd, *J* = 13.9, 6.8, 2.8 Hz, 1 H), 1.92–1.82 (m, 2 H), 1.74 (ddd, *J* = 14.9, 9.1, 4.5 Hz, 1 H), 1.45–1.38 (m, 1 H), 1.39–1.31 (m, 1 H), 0.89 (t, *J* = 7.4 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 159.0, 144.5, 138.4, 133.9, 130.0, 129.5, 129.0, 128.2, 127.7, 127.5, 127.4, 113.6, 80.6, 79.6, 78.0, 77.3, 75.3, 72.8, 70.4, 69.6, 67.3, 55.1, 35.5, 33.0, 29.1, 26.1, 21.4, 9.9; HRMS (FAB-magnetic sector) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>45</sub>O<sub>9</sub>S 629.2784; Found 629.2787.

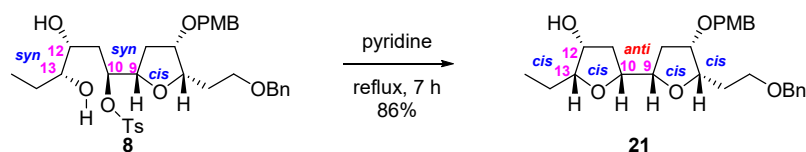
### Preparation of Adjacent Bis-THF **21**



To a cooled (0 °C) solution of diol **8** (51.1 mg, 0.0813 mmol) in THF/DMF (1 : 1, 8.13 mL, 0.01 M) was added sodium hydride (16.26 mg, 0.406 mmol). After being stirred for 16 h at room temperature, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and diluted with Et<sub>2</sub>O. The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O. 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/ethyl acetate, 2 : 1) to afford the adjacent bis-THF **21** (31.2 mg, 84%) as a colorless oil:  $[\alpha]^{24}_D = +18.1$  (*c* 1.00, CHCl<sub>3</sub>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.34–7.29 (m, 4 H), 7.28–7.25 (m, 1 H), 7.21–7.18 (m, 2 H), 6.87–6.85 (m, 2 H), 4.50–4.43 (m, 3 H), 4.25 (d, *J* = 11.7 Hz, 1 H), 4.18–4.13 (m, 2 H), 3.99–3.96 (m, 2 H), 3.90 (ddd, *J* = 6.1, 4.0, 1.7 Hz, 1 H), 3.83 (d, *J* = 11.1 Hz, 1 H), 3.80 (s, 3 H), 3.58–3.52 (m, 3 H), 2.28 (dd, *J* = 14.0, 2.6 Hz, 1 H), 2.19

(ddd,  $J = 13.9, 8.9, 6.4$  Hz, 1 H), 2.16–2.08 (m, 2 H), 2.06–2.01 (m, 1 H), 1.78–1.66 (m, 2 H), 1.61 (ddd,  $J = 14.1, 7.0, 1.7$  Hz, 1 H), 0.97 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 138.5, 130.1, 129.0, 128.3, 127.7, 127.5, 113.8, 86.2, 80.5, 79.3, 78.6, 78.2, 72.9, 70.7, 70.4, 67.4, 55.3, 34.5, 33.6, 28.9, 21.9, 10.5; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{27}\text{H}_{36}\text{O}_6$  456.2512; Found 456.2510.

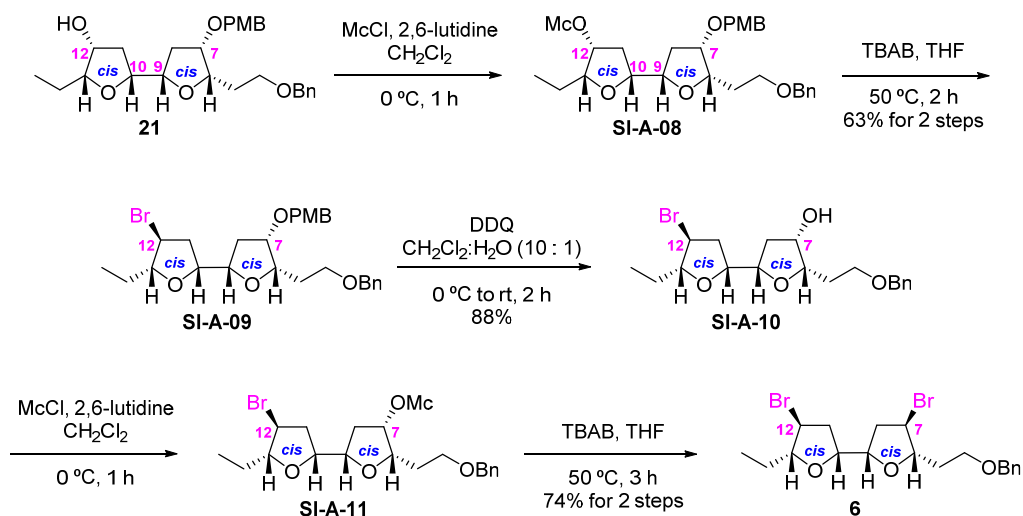
### Preparation of Adjacent Bis-THF 21<sup>5</sup>



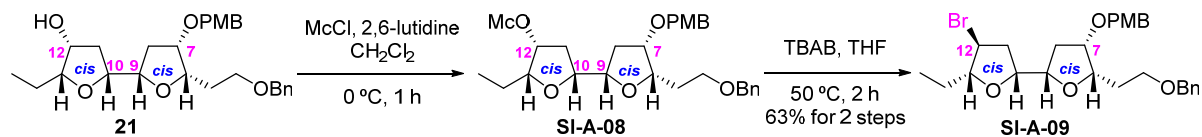
Diol **8** (178.4 mg, 0.284 mmol) was dissolved in pyridine (28 mL, 0.01 M), and the resulting solution was refluxed for 7 h. The reaction mixture was cooled to room temperature, concentrated *in vacuo*, and diluted with  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$ . The layers were separated, and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . 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/ethyl acetate, 3 : 1) to afford the adjacent bis-THF **21** (110.9 mg, 86%) as a colorless oil.

### Construction of 7,12-Dibromo Adjacent bis-THF 6: S18 ~ S23

#### Scheme ESI-03. Synthesis of 7,12-Dibromo-Adjacent Bis-THF 6 in Step-By-Step Manner



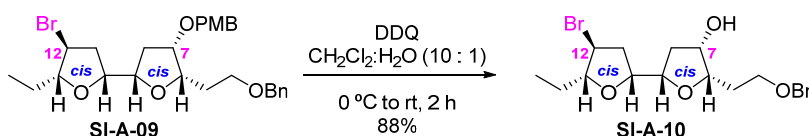
## Preparation of 12-Bromo-Adjacent bis-THF SI-A-09



**[Chloromethanesulfonylation]** To a cooled ( $0\text{ }^\circ\text{C}$ ) solution of 12-hydroxy-adjacent bis-THF **21** (272.9 mg, 0.598 mmol) in  $\text{CH}_2\text{Cl}_2$  (6 mL, 0.1 M) were dropwise added 2,6-lutidine (1.11 mL, 9.56 mmol) and chloromethanesulfonyl chloride ( $\text{McCl}$ , 0.434 mL, 4.78 mmol). The resulting mixture was stirred for 1 h at the same temperature, quenched with saturated aqueous  $\text{NaHCO}_3$ , and diluted with  $\text{CH}_2\text{Cl}_2$ . The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with  $\text{H}_2\text{O}$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The residue was filtered through a short pad of silica gel (hexanes/ethyl acetate, 4 : 1) to afford the crude chloromethanesulfonate **SI-A-08** (296.0 mg, 92%) as a brown oil:  $[\alpha]^{24}_{\text{D}} = +15.4$  ( $c$  1.00,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.31 (m, 4 H), 7.29–7.27 (m, 1 H), 7.22–7.20 (m, 2 H), 6.87–6.84 (m, 2 H), 5.23 (ddd,  $J = 6.0, 3.3, 1.4$  Hz, 1 H), 4.56 (s, 2 H), 4.49 (AB,  $J_{\text{AB}} = 11.9$  Hz,  $\Delta\nu_{\text{AB}} = 21.76$  Hz, 2 H), 4.39 (AB,  $J_{\text{AB}} = 11.5$  Hz,  $\Delta\nu_{\text{AB}} = 138.66$  Hz, 2 H), 3.94–3.87 (m, 4 H), 3.80 (s, 3 H), 3.67 (ddd,  $J = 7.2, 6.1, 3.3$  Hz, 1 H), 3.59–3.56 (m, 2 H), 2.49–2.44 (m, 1 H), 2.35 (ddd,  $J = 15.2, 5.0, 1.4$  Hz, 1 H), 2.20 (ddd,  $J = 13.4, 7.5, 5.7$  Hz, 1 H), 2.05 (ddd,  $J = 13.7, 4.8, 1.9$  Hz, 1 H), 2.01–1.98 (m, 2 H), 1.79–1.71 (m, 2 H), 1.03 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 138.6, 130.3, 129.1, 128.3, 127.6, 127.5, 113.7, 85.6, 83.7, 79.9, 79.7, 79.3, 78.7, 72.8, 70.4, 67.6, 55.2, 54.2, 36.4, 34.7, 29.6, 22.2, 10.5. **[ $\text{S}_{\text{N}}2$  Displacement]** To a solution of the above crude chloromethanesulfonate **SI-A-08** in THF (30 mL, 0.018 M) was added tetrabutylammonium bromide (TBAB, 1.78 g, 5.54 mmol). After being stirred at  $50\text{ }^\circ\text{C}$  for 2 h, the reaction mixture was cooled to room temperature, quenched with  $\text{H}_2\text{O}$ , and diluted with  $\text{Et}_2\text{O}$ . The layers were separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 5 : 1 to 4 : 1) to afford 12-bromo-adjacent bis-THF **SI-A-09** (198.5 mg, 69% yield for two steps) as a colorless oil:  $[\alpha]^{25}_{\text{D}} = +29.8$  ( $c$  1.00,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.31 (m, 4 H), 7.29–7.26 (m, 1 H), 7.22–7.20 (m, 2 H), 6.87–6.85 (m, 2 H), 4.48 (AB,  $J_{\text{AB}} = 12.0$  Hz,  $\Delta\nu_{\text{AB}} = 22.48$  Hz, 2 H), 4.38 (AB,  $J_{\text{AB}} = 11.6$  Hz,  $\Delta\nu_{\text{AB}} = 142.39$  Hz, 2 H), 4.15 (q,  $J$

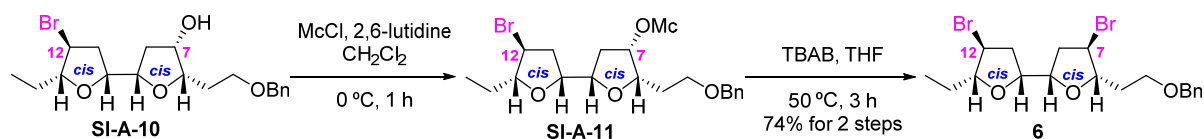
= 6.8 Hz, 1 H), 4.00–3.94 (m, 2 H), 3.93–3.88 (m, 2 H), 3.85 (dt,  $J = 8.2, 6.0$  Hz, 1 H), 3.80 (s, 3 H), 3.57 (t,  $J = 6.5$  Hz, 2 H), 2.48 (dt,  $J = 13.7, 6.9$  Hz, 1 H), 2.28 (ddd,  $J = 13.7, 7.0, 5.2$  Hz, 1 H), 2.17 (ddd,  $J = 14.0, 8.2, 5.9$  Hz, 1 H), 2.04–1.96 (m, 2 H), 1.93 (ddd,  $J = 13.8, 6.1, 2.3$  Hz, 1 H), 1.69–1.62 (m, 1 H), 1.51 (dp,  $J = 14.5, 7.3$  Hz, 1 H), 0.98 (t,  $J = 7.4$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 138.6, 130.3, 129.1, 128.3, 127.6, 127.4, 113.7, 88.4, 80.2, 79.7, 79.1, 78.5, 72.8, 70.4, 67.6, 55.2, 49.3, 38.5, 34.6, 29.5, 26.5, 10.0; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{27}\text{H}_{35}\text{BrO}_5$  518.1668; Found 518.1669.

### Preparation of 7-Hydroxyl- 12-Bromo-Adjacent Bis-THF **SI-A-10**



To a cooled (0 °C) solution of 12-bromo-adjacent bis-THF **SI-A-09** (283.8 mg, 0.546 mmol) in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (10 : 1, 11 mL, 0.05 M) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 186.6 mg, 0.820 mmol). After being stirred for 2 h at the room temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and diluted with  $\text{CH}_2\text{Cl}_2$ . The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . 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/ethyl acetate, 4 : 1) to afford 7-hydroxyl-12-bromo-adjacent bis-THF **SI-A-10** (196.2 mg, 88%) as a colorless oil:  $[\alpha]_D^{24} = +23.2$  ( $c$  1.00,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.31 (m, 4 H), 7.29–7.26 (m, 1 H), 4.52 (s, 2 H), 4.35 (ddd,  $J = 8.4, 6.9, 3.0$  Hz, 1 H), 4.09–4.04 (m, 3 H), 3.93 (ddd,  $J = 7.8, 5.8, 4.8$  Hz, 1 H), 3.80 (dt,  $J = 6.9, 3.4$  Hz, 1 H), 3.64 (dt,  $J = 9.5, 5.3$  Hz, 1 H), 3.59 (ddd,  $J = 9.5, 8.5, 4.5$  Hz, 1 H), 3.45 (d,  $J = 8.5$  Hz, 1 H), 2.29–2.19 (m, 3 H), 2.09–2.03 (m, 1 H), 2.01–2.96 (m, 1 H), 1.79 (ddd,  $J = 14.0, 4.0, 1.1$  Hz, 1 H), 1.70 (dddd,  $J = 15.0, 12.6, 6.9, 5.1$  Hz, 1 H), 1.60–1.53 (m, 1 H), 1.01 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 128.4, 127.66, 127.64, 88.8, 81.9, 79.2, 78.2, 73.1, 71.6, 67.4, 48.4, 38.6, 35.4, 29.2, 26.4, 10.1; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{19}\text{H}_{27}\text{BrO}_4$  398.1093; Found 398.1094.

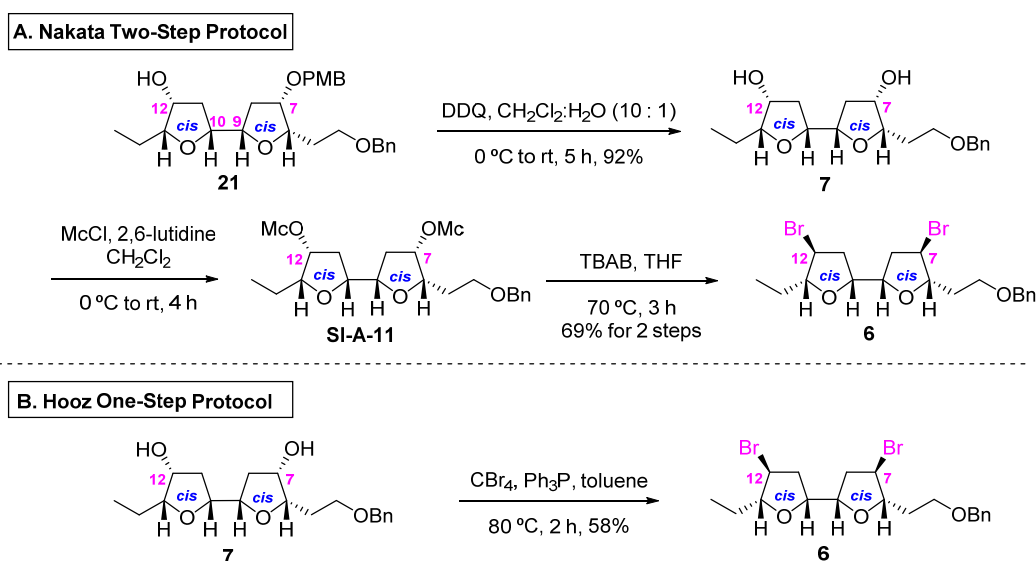
## Preparation of 7,12-Dibromo-Adjacent Bis-THF **6**



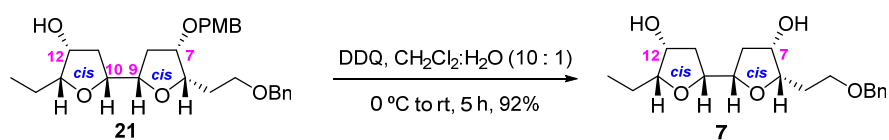
**[Chloromethanesulfonylation]** To a cooled ( $0\text{ }^\circ\text{C}$ ) solution of 7-hydroxy-12-bromo-adjacent bis-THF **SI-A-10** (196.2 mg, 0.491 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL, 0.1 M) were dropwise added 2,6-lutidine (0.916 mL, 7.86 mmol) and chloromethanesulfonyl chloride ( $\text{McCl}$ , 0.357 mL, 3.93 mmol). The resulting mixture was stirred for 1 h at the same temperature, quenched with saturated aqueous  $\text{NaHCO}_3$ , and diluted with  $\text{CH}_2\text{Cl}_2$ . The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with  $\text{H}_2\text{O}$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The residue was filtered through a short pad of silica gel (hexanes/ethyl acetate, 4 : 1) to afford the crude chloromethanesulfonate **SI-A-11** (237.9 mg, 95%) as a brown oil:  $[\alpha]_{\text{D}}^{24} = +14.9$  ( $c$  1.00,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.28 (m, 5 H), 5.22 (ddd,  $J = 6.2, 3.3, 1.2$  Hz, 1 H), 4.54 (AB,  $J_{\text{AB}} = 12.7$  Hz,  $\Delta\nu_{\text{AB}} = 23.66$  Hz, 2 H), 4.50 (AB,  $J_{\text{AB}} = 11.8$  Hz,  $\Delta\nu_{\text{AB}} = 12.44$  Hz, 2 H), 4.16 (td,  $J = 6.9, 5.6$  Hz, 1 H), 4.01 (dt,  $J = 7.3, 5.4$  Hz, 1 H), 3.99–3.95 (m, 2 H), 3.88 (dt,  $J = 8.6, 5.8$  Hz, 1 H), 3.66–3.59 (m, 2 H), 2.53 (ddd,  $J = 15.0, 8.6, 6.2$  Hz, 1 H), 2.40 (dt,  $J = 14.3, 7.2$  Hz, 1 H), 2.33 (ddd,  $J = 13.8, 6.9, 5.1$  Hz, 1 H), 2.23 (ddd,  $J = 15.3, 5.9, 1.2$  Hz, 1 H), 2.10–2.04 (m, 1 H), 1.99 (ddt,  $J = 14.3, 7.9, 4.9$  Hz, 1 H), 1.69–1.62 (m, 1 H), 1.52 (td,  $J = 14.4, 7.4$  Hz, 1 H), 0.98 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  138.3, 128.5, 127.9, 127.8, 88.7, 85.8, 79.6, 79.5, 78.9, 73.2, 67.0, 54.2, 49.0, 38.7, 36.8, 29.3, 26.7, 10.0. **[S<sub>N</sub>2 Displacement]** To a solution of the chloromethanesulfonate **SI-A-11** (117.5 mg, 0.246 mmol) in THF (14 mL, 0.018 M) was added tetrabutylammonium bromide (TBAB, 0.79 g, 2.46 mmol). After being stirred at  $50\text{ }^\circ\text{C}$  for 3 h, the reaction mixture was cooled to room temperature, quenched with  $\text{H}_2\text{O}$ , and diluted with  $\text{Et}_2\text{O}$ . The layers were separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 15 : 1 to 10 : 1) to afford 7,12-dibromo-adjacent bis-THF **6** (88.9 mg, 74% for two steps) as a colorless oil:  $[\alpha]_{\text{D}}^{25} = -12.6$  ( $c$  1.00,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37–7.33 (m, 4 H), 7.30–7.27 (m, 1 H), 4.52 (AB,  $J_{\text{AB}} = 11.9$  Hz,  $\Delta\nu_{\text{AB}} = 11.38$  Hz, 2 H), 4.22 (dt,  $J = 7.7, 5.0$  Hz, 1 H), 4.15–4.09 (m, 3 H), 4.00 (dt,

$J = 7.4, 5.2$  Hz, 1 H), 3.96–3.93 (m, 1 H), 3.64–3.56 (m, 2 H), 2.33–2.26 (m, 4 H), 1.97 (dddd,  $J = 14.0, 7.7, 6.3, 4.8$  Hz, 1 H), 1.77 (ddt,  $J = 13.6, 7.8, 5.7$  Hz, 1 H), 1.65 (dtd,  $J = 14.9, 7.4, 5.0$  Hz, 1 H), 1.50 (dp,  $J = 14.6, 7.4$  Hz, 1 H), 0.97 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  138.4, 128.4, 127.8, 127.7, 88.8, 85.1, 79.6, 79.4, 73.2, 66.8, 49.6, 48.9, 39.1, 38.7, 34.0, 26.8, 10.1; HRMS (EI-magnetic sector)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{19}\text{H}_{26}\text{Br}_2\text{O}_3$  460.0249; Found 460.0243.

### Scheme ESI-04. Synthesis of 7,12-Dibromo-Adjacent Bis-THF **6** in Double Bromination



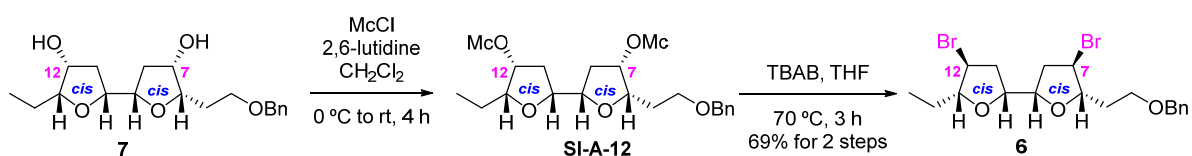
### Preparation of 7,12-Dihydroxy-Adjacent Bis-THF Diol **7**



To a cooled (0 °C) solution of 12-dihydroxy-adjacent bis-THF **21** (110.8 mg, 0.243 mmol) in  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  (10 : 1, 11 mL, 0.022 M) was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 208.8 mg, 0.972 mmol). After being stirred for 5 h at the same temperature, the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and diluted with  $\text{CH}_2\text{Cl}_2$ . The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . 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/ethyl acetate, 2 : 1) to afford 7,12-dihydroxy-adjacent bis-THF **7** (75.1 mg, 92%) as a colorless oil:  $[\alpha]_D^{24} = +23.2$  ( $c$  1.00,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.33 (m, 2 H), 7.31–7.28 (m, 3 H),

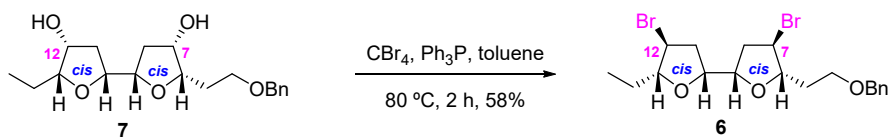
4.51 (AB,  $J_{AB} = 11.7$  Hz,  $\Delta\nu_{AB} = 14.46$  Hz, 2 H), 4.23 (dtd,  $J = 7.0, 3.5, 1.4$  Hz, 1 H), 4.17–4.12 (m, 2 H), 4.02 (ddt,  $J = 10.1, 4.2, 2.0$  Hz, 1 H), 3.80 (ddd,  $J = 9.4, 5.1, 3.3$  Hz, 1 H), 3.67 (ddd,  $J = 9.4, 4.9, 3.7$  Hz, 1 H), 3.56–3.51 (m, 2 H), 3.46 (d,  $J = 10.2$  Hz, 1 H), 3.37 (d,  $J = 3.7$  Hz, 1 H), 2.32 (dddd,  $J = 14.0, 9.2, 6.8, 0.8$  Hz, 1 H), 2.23–2.14 (m, 3 H), 2.02 (dtd,  $J = 14.5, 4.9, 2.5$  Hz, 1 H), 1.75–1.67 (m, 2 H), 1.63 (ddd,  $J = 14.1, 6.6, 1.5$  Hz, 1 H), 0.97 (t,  $J = 7.5$  Hz, 3 H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  137.5, 128.5, 127.9, 127.8, 86.0, 83.4, 79.1, 78.7, 73.6, 71.7, 70.9, 67.1, 36.2, 34.3, 28.6, 21.8, 10.5; HRMS (FAB-magnetic sector)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{29}\text{O}_5$  337.2015; Found 337.2017.

### Preparation of 7,12-Dibromo-Adjacent Bis-THF **6** by Modified Nakata Two-Step Protocol.



**[Chloromethanesulfonylation]** To a cooled ( $0\text{ }^\circ\text{C}$ ) solution of 7,12-dihydroxy-adjacent bis-THF **7** (42.5 mg, 0.126 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL, 0.025 M) were dropwise added 2,6-lutidine (0.294 mL, 2.52 mmol) and chloromethanesulfonyl chloride (McCl, 0.069 mL, 0.738 mmol). The resulting mixture was stirred for 4 h at room temperature, quenched with saturated aqueous  $\text{NaHCO}_3$ , and diluted with  $\text{CH}_2\text{Cl}_2$ . The layers were separated, and the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with  $\text{H}_2\text{O}$  and brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The residue was filtered through a short pad of silica gel (hexanes/ethyl acetate, 10 : 1) to afford the crude bis-chloromethanesulfonate **SI-A-12** as a brown oil, which was immediately employed to the next step without further purification. **[ $\text{S}_{\text{N}}2$  Displacement]** To a solution of the above crude bis-chloromethanesulfonate **SI-A-12** in THF (15 mL) was added tetrabutylammonium bromide (TBAB, 407.3 mg, 1.26 mmol). After being stirred at  $70\text{ }^\circ\text{C}$  for 3 h, the reaction mixture was cooled to room temperature, quenched with  $\text{H}_2\text{O}$ , and diluted with  $\text{Et}_2\text{O}$ . The layers were separated and the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 40 : 1 to 10 : 1) to afford 7,12-dibromo-adjacent bis-THF **6** (40.3 mg, 69% yield for two steps) as a colorless oil.

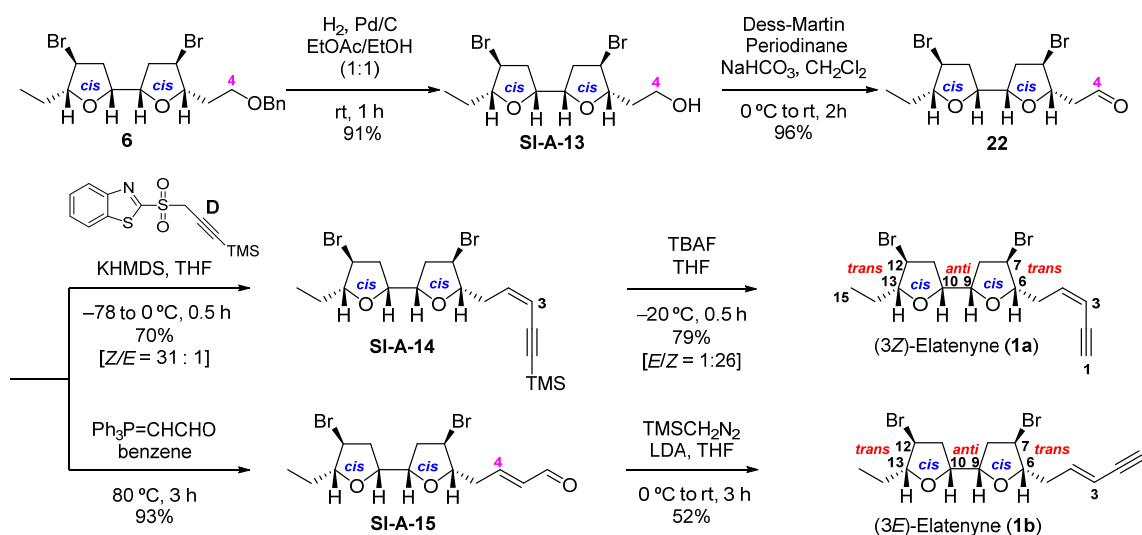
## Preparation of 7,12-Dibromo-Adjacent Bis-THF **6** by Hooz One-Step Protocol.



To a solution of 7,12-dihydroxy-adjacent bis-THF **7** (30.3 mg, 0.0901 mmol) in dry toluene (3.60 mL, 0.025 M) were added  $\text{CBr}_4$  (14.6 mg, 0.0440 mmol) and  $\text{Ph}_3\text{P}$  (116 mg, 0.442 mmol) at room temperature. After being stirred at  $80^\circ\text{C}$  for 2 h, the reaction mixture was cooled to rt, quenched with saturated aqueous  $\text{NaHCO}_3$ , and diluted with  $\text{Et}_2\text{O}$ . The layers were separated, the aqueous layer was extracted with  $\text{Et}_2\text{O}$ . 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/ethyl acetate, 20 : 1) to afford 7,12-dibromo-adjacent bis-THF **6** (24.2 mg, 58%).

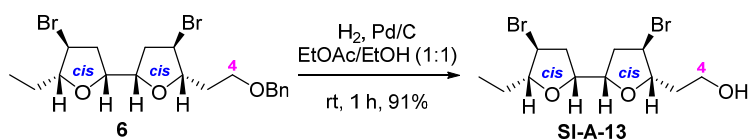
## Completion of Total Synthesis of (3*Z*)- and (3*E*)-Elatenyne: S25 ~ S29

### Scheme ESI-05. Completion of Total Synthesis of **1a** and **1b**.



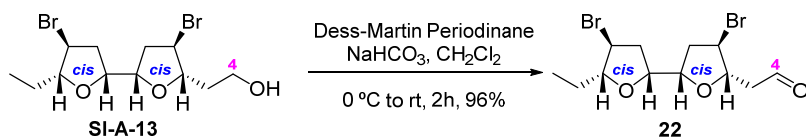


## Preparation of Primary Alcohol SI-A-13



To a solution of 7,12-dibromo-adjacent bis-THF **6** (88.9 mg, 0.192 mmol) in EtOH/EtOAc (1 : 1, 20 mL, 0.01 M) was added palladium on carbon (Pd/C, 88.0 mg, 0.827 mmol) under H<sub>2</sub> gas. After being stirred for 1 h at the room temperature, the reaction mixture was filtered through a pad of celite and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 5 : 1) to afford primary alcohol **SI-A-13** (65.2 mg, 91%) as a colorless oil:  $[\alpha]_D^{25} = -2.63$  (*c* 0.99, CHCl<sub>3</sub>); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  4.21–4.15 (m, 3 H), 4.04–3.99 (m, 2 H), 3.95 (dt, *J* = 7.4, 5.1 Hz, 1 H), 3.82–3.77 (m, 2 H), 2.39 (ddd, *J* = 13.8, 7.6, 6.4 Hz, 1 H), 2.33–2.27 (m, 3 H), 2.25–2.22 (m, 1 H), 2.03–1.98 (m, 1 H), 1.76–1.70 (m, 1 H), 1.66 (dq, *J* = 15.0, 7.5, 5.0 Hz, 1 H), 1.54–1.47 (m, 1 H), 0.98 (t, *J* = 7.4 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  88.8, 86.4, 79.8, 79.1, 60.5, 48.7, 48.6, 38.9, 38.1, 35.2, 26.8, 10.1; HRMS (FAB-magnetic sector) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>21</sub>Br<sub>2</sub>O<sub>3</sub> 370.9857; Found 370.9854.

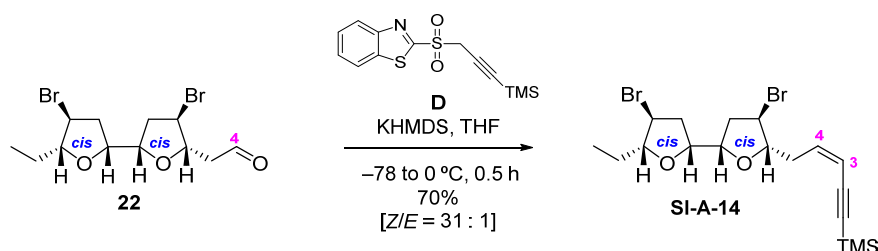
## Preparation of Aldehyde 22



To a cooled (0 °C) solution of primary alcohol **SI-A-13** (13.6 mg, 0.0366 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2.2 mL, 0.017 M) was added NaHCO<sub>3</sub> (4.60 mg, 0.0548 mmol) and Dess-Martin periodinane (46.5 mg, 0.110 mmol). After being stirred for 2 h at the room temperature, the reaction mixture was quenched with hexane and filtered through a pad of column washing with EtOAc. The residue was concentrated *in vacuo* and purified by column chromatography (silica gel, hexanes/ethyl acetate, 4 : 1) to afford aldehyde **22** (13.0 mg, 96%) as a yellow oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.78 (dd, *J* = 2.3, 1.6 Hz, 1 H), 4.47 (ddd, *J* = 8.1, 6.5, 4.1 Hz, 1 H), 4.19–4.13 (m, 2 H), 4.03–3.97 (m, 2 H), 3.93 (dt, *J* = 7.5, 5.0 Hz, 1 H), 2.79 (ddd, *J* = 16.5, 4.1, 1.6 Hz, 1 H), 2.64 (ddd, *J* = 16.5, 8.2, 2.3 Hz, 1 H), 2.43 (ddd, *J* = 13.8, 7.7, 6.1 Hz, 1 H), 2.36–2.27 (m, 2 H), 2.25–2.21 (m, 1 H), 1.66 (dq, *J* = 13.8, 7.5, 5.0 Hz, 1 H), 1.49 (dt, *J* = 13.9, 7.4 Hz, 1 H), 0.98 (t, *J* = 7.4 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  199.4, 88.8, 81.94, 81.89,

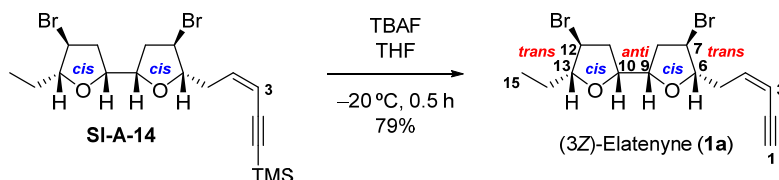
79.9, 79.0, 48.6, 47.6, 38.9, 37.9, 26.7, 10.0.

### Preparation of TMS-(3Z)-Enyne SI-A-14



To a cooled ( $-78$  °C) solution of aldehyde **22** (14.1 mg, 0.0381 mmol) and sulfone **D** (117.9 mg, 0.381 mmol) in anhydrous THF (9 mL, 0.0042 M) was dropwise added KHMDS (0.61 mL, 0.5 M solution in toluene, 0.30 mmol). After being stirred for 30 min at  $0$  °C, the reaction mixture was quenched with  $H_2O$  and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated brine, dried over anhydrous  $Na_2SO_4$ , filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ether/ethyl acetate, 50 : 1) to afford TMS-(3Z)-enyne **SI-A-14** (12.4 mg, 70%,  $Z/E = 31 : 1$ , see page S101) as a colorless oil:  $[\alpha]_D^{24} = +2.1$  ( $c$  0.81,  $CHCl_3$ );  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  5.99 (dt,  $J = 10.9, 7.5$  Hz, 1 H), 5.64–5.62 (m, 1 H), 4.22 (q,  $J = 5.7$  Hz, 1 H), 4.18–4.13 (m, 2 H), 4.08 (q,  $J = 5.5$  Hz, 1 H), 4.00 (dt,  $J = 7.5, 5.2$  Hz, 1 H), 3.95 (q,  $J = 5.7$  Hz, 1 H), 2.67 (dt,  $J = 13.7, 6.7$  Hz, 1 H), 2.56 (dt,  $J = 14.2, 6.8$  Hz, 1 H), 2.34–2.31 (m, 4 H), 1.70–1.63 (m, 1 H), 1.54–1.47 (m, 1 H), 0.98 (t,  $J = 7.4$  Hz, 3 H), 0.21 (s, 9 H);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  139.0, 112.3, 101.3, 99.9, 88.7, 86.6, 79.7, 79.2, 48.8, 48.5, 38.9, 38.7, 34.4, 26.7, 10.0,  $-0.04$ ; HRMS (EI-magnetic sector)  $m/z$ :  $[M]^+$  Calcd for  $C_{18}H_{28}Br_2O_2Si$  462.0225; Found 462.0219.

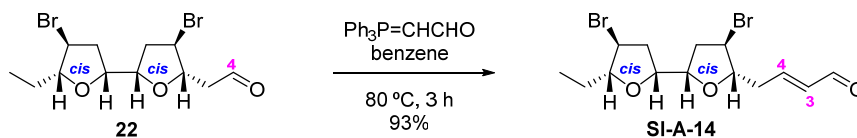
### Preparation of (3Z)-Elatenyne (1a)



To a cooled ( $-20$  °C) solution of TMS-(3Z)-enyne **SI-A-14** (9.8 mg, 0.0211 mmol) in THF (4.2 mL, 0.005 M) was dropwise added tetrabutylammonium fluoride (0.0593 mL, 0.211 mmol). After being stirred for 30 min at the same temperature, the reaction mixture was quenched with

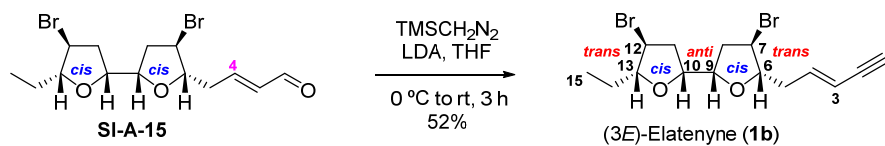
saturated aqueous NH<sub>4</sub>Cl and diluted with Et<sub>2</sub>O. The layers were separated, and the aqueous layer was extracted with Et<sub>2</sub>O. The combined organic layers were washed with saturated brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, diethyl ether/ethyl acetate, 50 : 1) to afford (3*Z*)-elatenyne (**1a**) (6.5 mg, 79%) as a colorless oil:  $[\alpha]_D^{24} = -1.66$  (*c* 0.18, CH<sub>2</sub>Cl<sub>2</sub>),  $[\alpha]_D^{23} = -1.90$  (*c* 0.62, CHCl<sub>3</sub>); {lit. nat.<sup>6a</sup>  $[\alpha]_D^{25} = +16.8$  (*c* 1.4, CH<sub>2</sub>Cl<sub>2</sub>)}, {nat.<sup>6b</sup>  $[\alpha]_D^{25} = -10.0$  (*c* 0.0498, CH<sub>2</sub>Cl<sub>2</sub>)}, {syn.<sup>6c</sup>  $[\alpha]_D^{25} = -4.00$  (*c* 0.25, CHCl<sub>3</sub>),  $[\alpha]_D^{25} = -1.6$  (*c* 0.25, CH<sub>2</sub>Cl<sub>2</sub>)}, {syn.<sup>6c</sup> **For ent-1a**;  $[\alpha]_D^{25} = +0.85$  (*c* 0.714, CHCl<sub>3</sub>),  $[\alpha]_D^{25} = +0.80$  (*c* 0.714, CH<sub>2</sub>Cl<sub>2</sub>)}; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.06 (ddt, *J* = 10.9, 8.6, 1.0 Hz, 1 H), 5.60 (ddt, *J* = 10.9, 2.6, 1.4 Hz, 1 H), 4.22 (q, *J* = 5.7 Hz, 1 H), 4.18–4.13 (m, 2 H), 4.06 (dt, *J* = 6.9, 5.1 Hz, 1 H), 4.01 (dt, *J* = 7.4, 5.1 Hz, 1 H), 3.97 (dd, *J* = 6.5, 5.5 Hz, 1 H), 3.13 (dd, *J* = 2.3, 0.9 Hz, 1 H), 2.70–2.65 (m, 1 H), 2.60–2.56 (m, 1 H), 2.35–2.30 (m, 4 H), 1.70–1.63 (m, 1 H), 1.53–1.47 (m, 1 H), 0.98 (t, *J* = 7.4 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  139.8, 111.1, 88.7, 86.4, 82.4, 79.93, 79.76, 79.2, 48.9, 48.5, 38.9, 38.7, 34.5, 26.7, 10.0; HRMS (EI-magnetic sector) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub> 389.9830; Found 389.9825.

### Preparation of (3*E*)-Enal SI-A-15



To a solution of aldehyde **23** (13.0 mg, 0.0351 mmol) in dry benzene (0.351 mL, 0.1 M) was added (triphenylphosphoranylidene)acetaldehyde (64.15 mg, 0.211 mmol) at 80 °C. After being stirred at the same temperature for 3 h, the reaction mixture was cooled to rt, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 10 : 1) to afford (3*E*)-enal **SI-A-15** (12.9 mg, 93%) as a yellow oil; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  9.53 (d, *J* = 7.8 Hz, 1 H), 6.85 (dt, *J* = 15.7, 7.0 Hz, 1 H), 6.21 (ddt, *J* = 15.7, 7.8, 1.5 Hz, 1 H), 4.19–4.14 (m, 3 H), 4.02 (dt, *J* = 7.5, 5.2 Hz, 1 H), 3.96–3.91 (m, 2 H), 2.74 (dddd, *J* = 15.2, 6.7, 4.4, 1.5 Hz, 1 H), 2.55 (dtd, *J* = 15.0, 7.3, 1.4 Hz, 1 H), 2.41 (ddd, *J* = 13.7, 7.8, 6.1 Hz, 1 H), 2.35–2.28 (m, 2 H), 2.23 (dt, *J* = 13.8, 7.5 Hz, 1 H), 1.65 (dtd, *J* = 14.9, 7.5, 5.0 Hz, 1 H), 1.53–1.45 (m, 1 H), 0.97 (t, *J* = 7.4 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  193.6, 152.5, 135.2, 88.8, 85.1, 79.7, 79.0, 48.6, 47.4, 39.0, 38.0, 36.1, 26.7, 10.0.

## Preparation of (3E)-Elatenyne (1b)



To a cooled ( $-78\text{ }^{\circ}\text{C}$ ) solution of LDA (1.33 mL, 0.66 mmol) in THF (1.33 mL, 0.05 M) was added dropwise TMSCH<sub>2</sub>N<sub>2</sub> (0.37 mL, 1.8 M in hexane, 0.66 mmol) under N<sub>2</sub> atmosphere. After the mixture was stirred at the same temperature for 30 min, (3E)-enal **SI-A-15** (26.3 mg, 0.0664 mmol) in THF (1 mL) was dropwise added at the same temperature. After being stirred for 3 h at 0 °C, the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc. 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/ethyl acetate, 50 : 1) to afford (3E)-elatenyne (**1b**) (13.6 mg, 52%) as a colorless oil:  $[\alpha]^{24}_{\text{D}} = -28.3$  (*c* 0.66, CHCl<sub>3</sub>);  $[\alpha]^{24}_{\text{D}} = -22.3$  (*c* 0.25, CH<sub>2</sub>Cl<sub>2</sub>); {lit. syn.<sup>6d</sup>  $[\alpha]^{25}_{\text{D}} = -33.0$  (*c* 0.09, CH<sub>2</sub>Cl<sub>2</sub>)}, {For *ent*-**1b**, lit. syn.<sup>6d</sup>  $[\alpha]^{25}_{\text{D}} = +29.5$  (*c* 0.35, CH<sub>2</sub>Cl<sub>2</sub>)}; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  6.23 (dt, *J* = 15.9, 7.2 Hz, 1 H), 5.57 (dq, *J* = 16.0, 1.8 Hz, 1 H), 4.15–4.10 (m, 3 H), 4.01 (dt, *J* = 7.4, 5.2 Hz, 1 H), 3.94 (dq, *J* = 7.4, 5.2 Hz, 2 H), 2.83 (d, *J* = 2.2 Hz, 1 H), 2.48 (dddd, *J* = 14.0, 6.9, 4.9, 1.6 Hz, 1 H), 2.37–2.25 (m, 5 H), 1.66 (dtd, *J* = 14.9, 7.5, 5.0 Hz, 1 H), 1.50 (dp, *J* = 14.7, 7.4 Hz, 1 H), 0.99 (t, *J* = 7.4 Hz, 3 H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  140.6, 111.9, 88.7, 85.9, 81.8, 79.6, 79.1, 76.7, 48.7, 47.8, 38.9, 38.4, 36.5, 26.7, 10.0; HRMS (EI-magnetic sector) *m/z*: [M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub> 389.9830; Found 389.9834.

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– **Electronic Supplementary Information: Part B** –

**Stereoselective total synthesis of (3*Z*)- and (3*E*)-elatenynes**

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Hyoungsu Kim,<sup>\*a</sup> and Deukjoon Kim<sup>b</sup>

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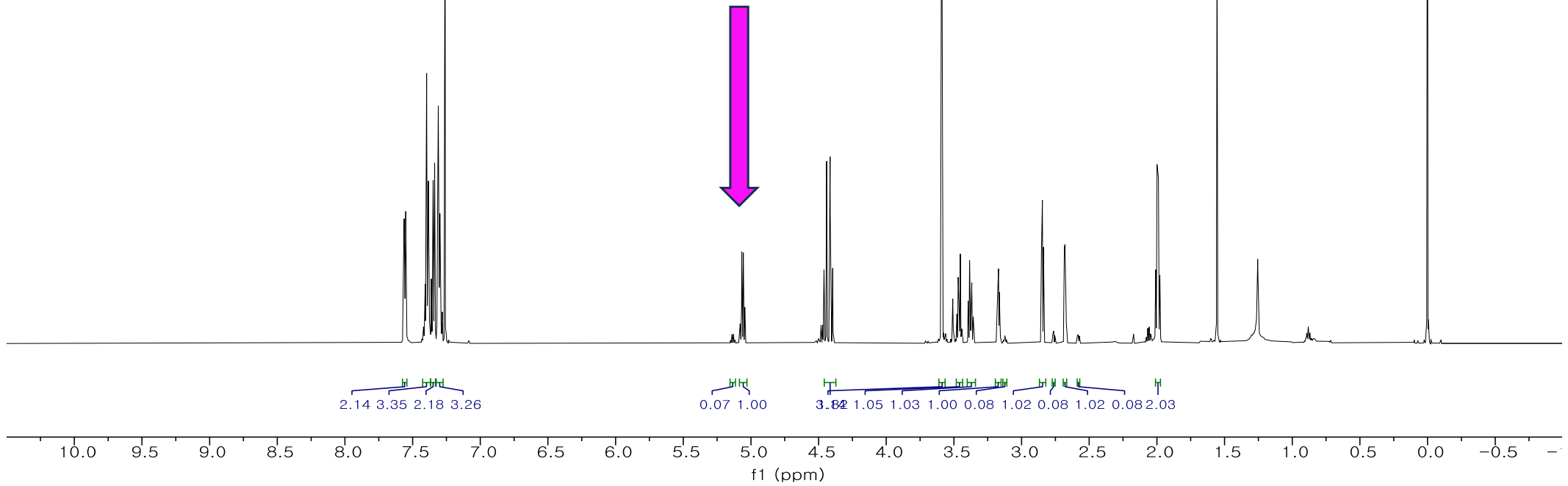
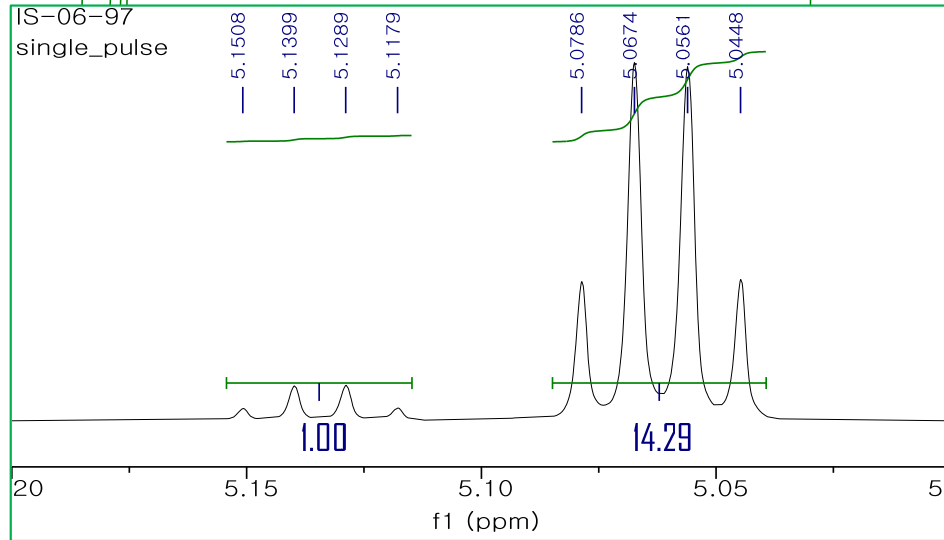
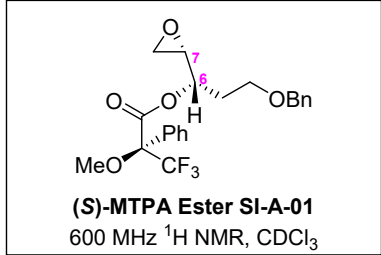
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<sup>‡</sup>These authors contributed equally to this work.

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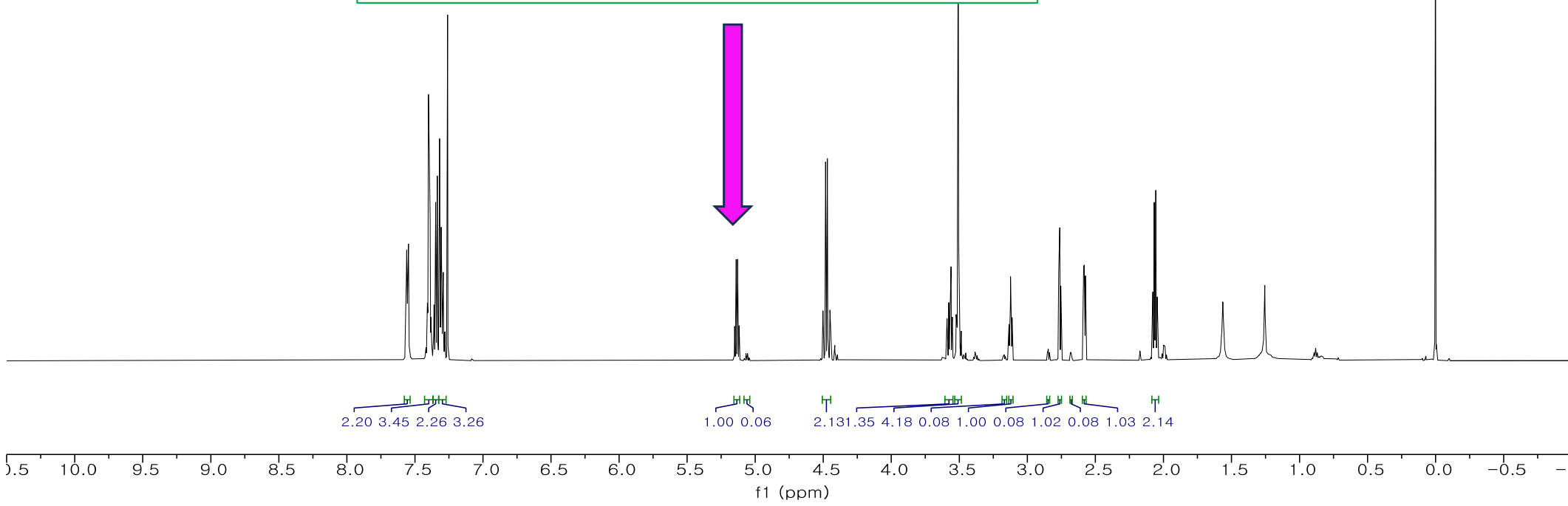
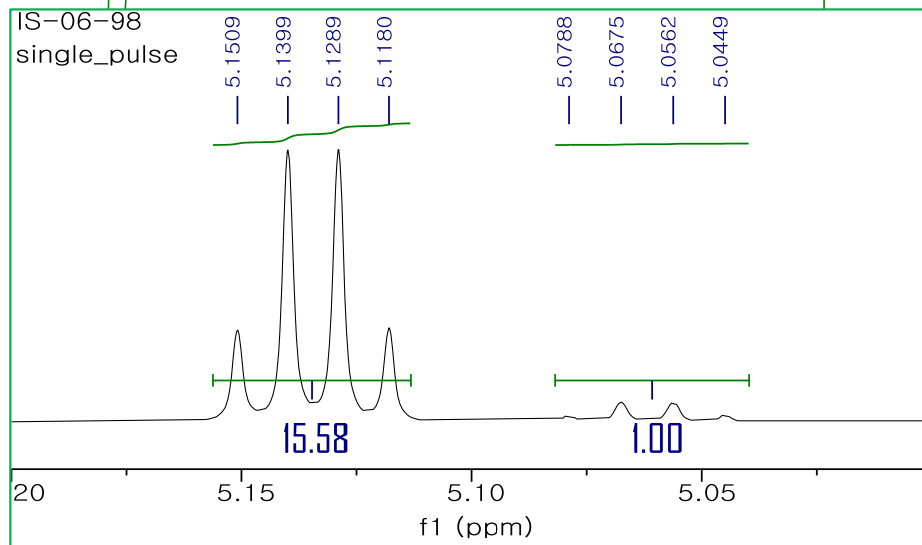
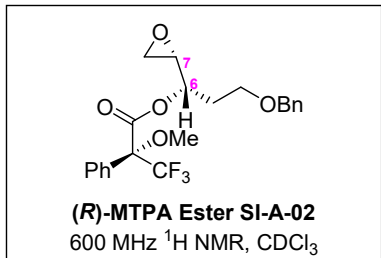
**Part B (S30 ~ S113)**  
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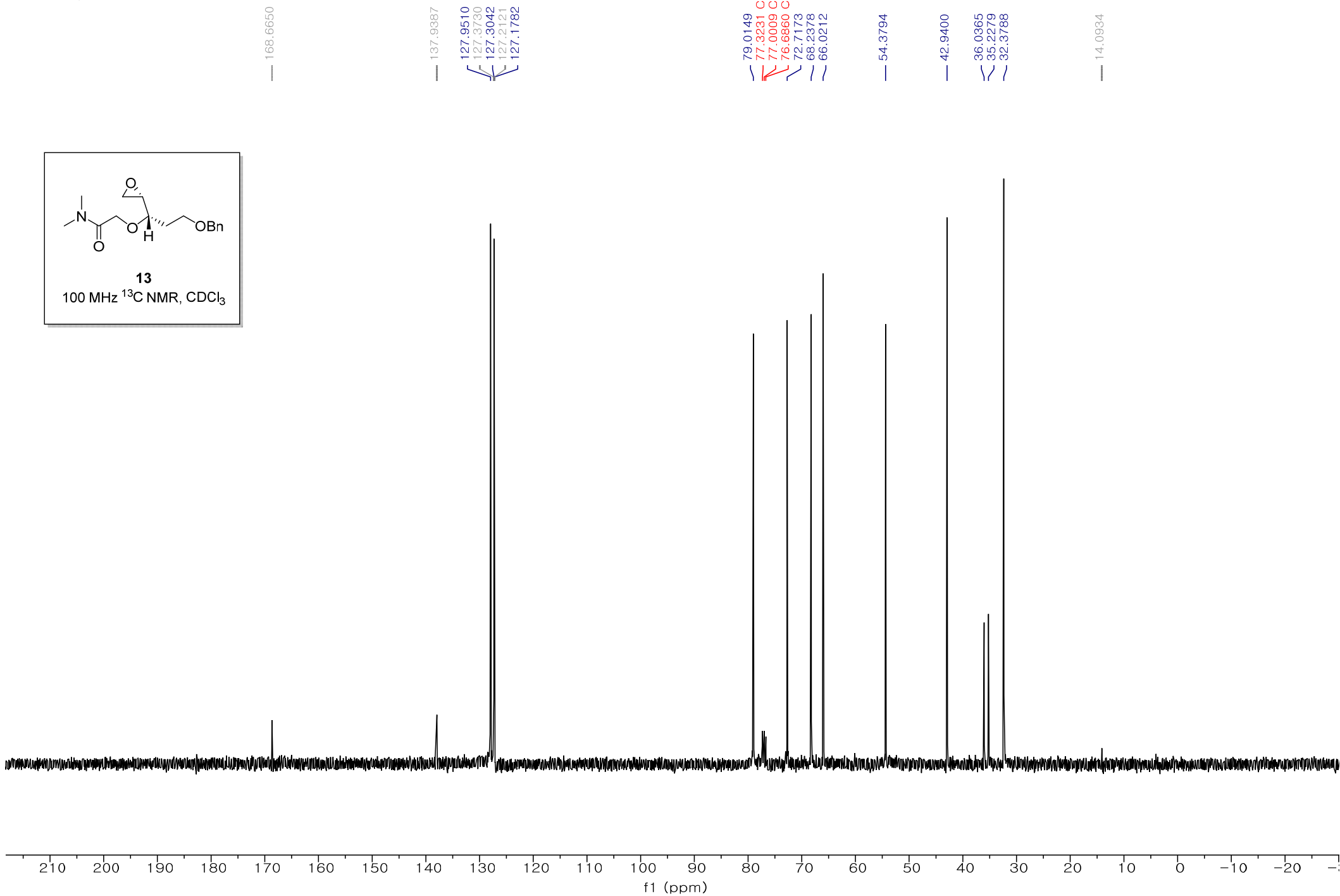
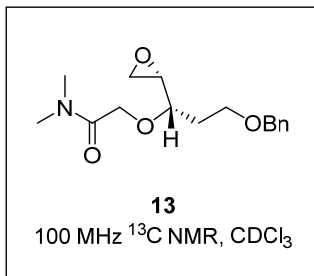
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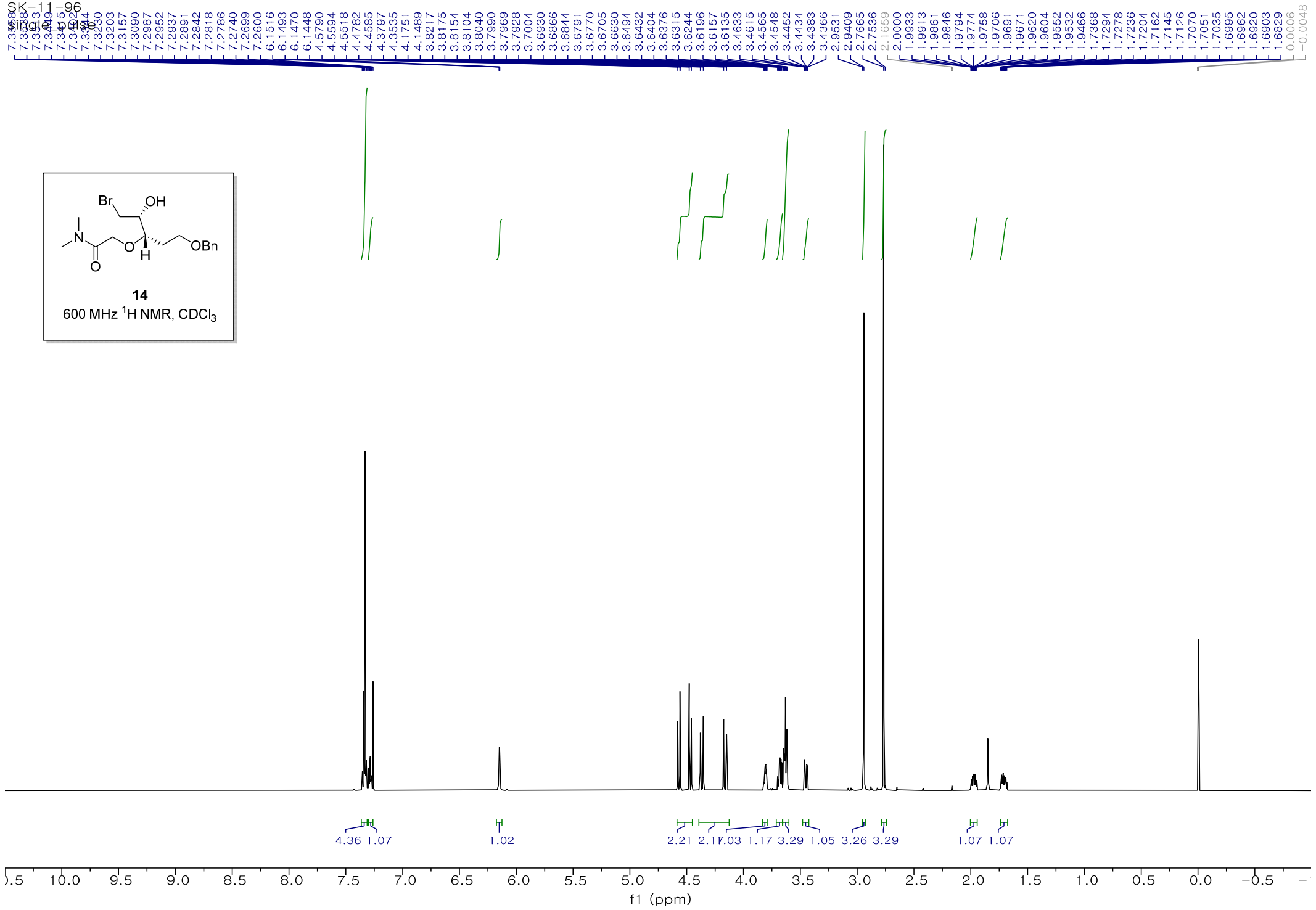
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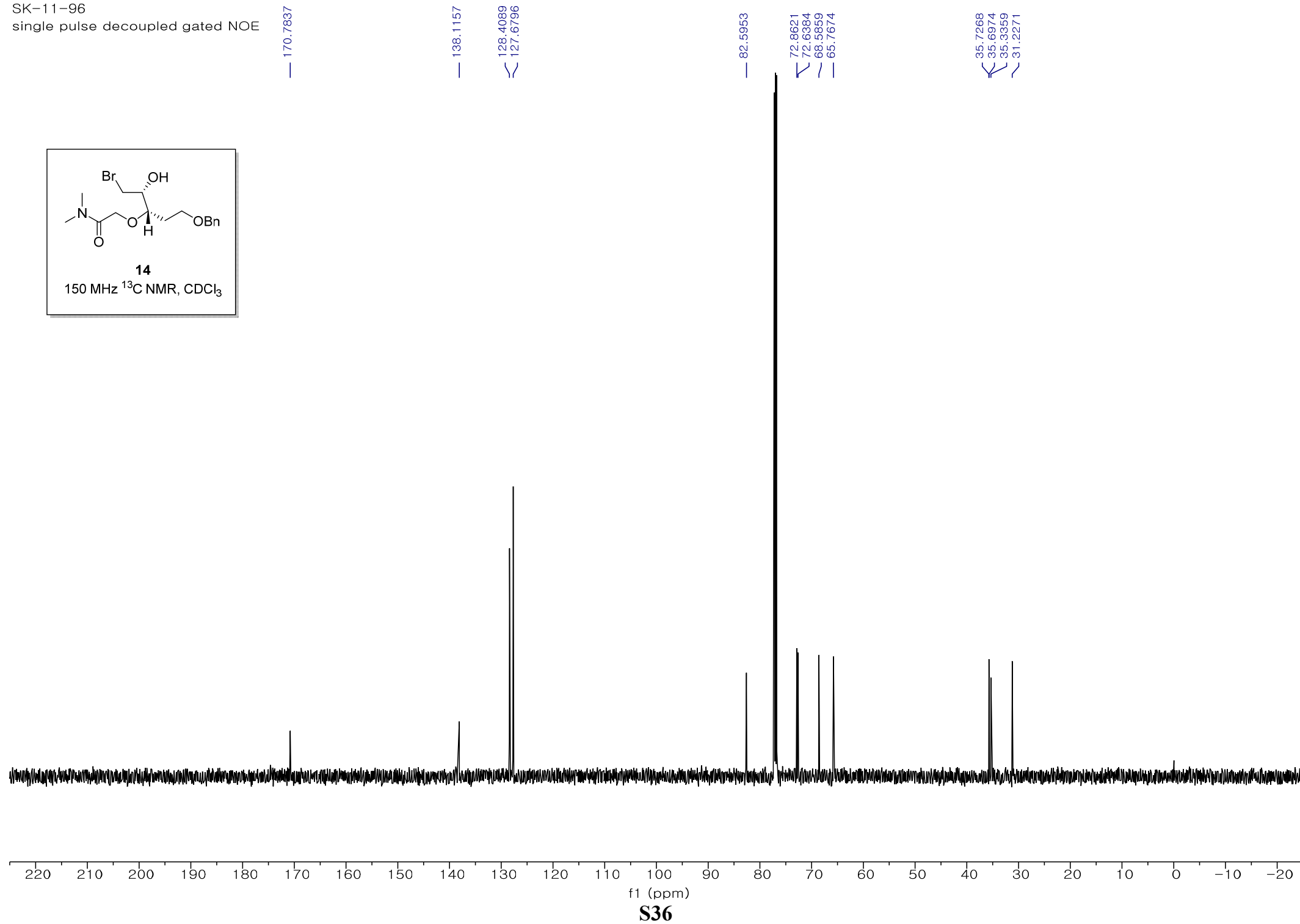
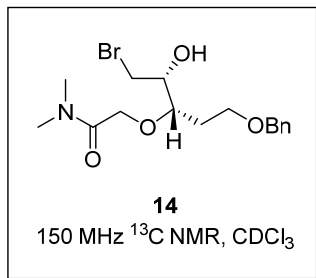








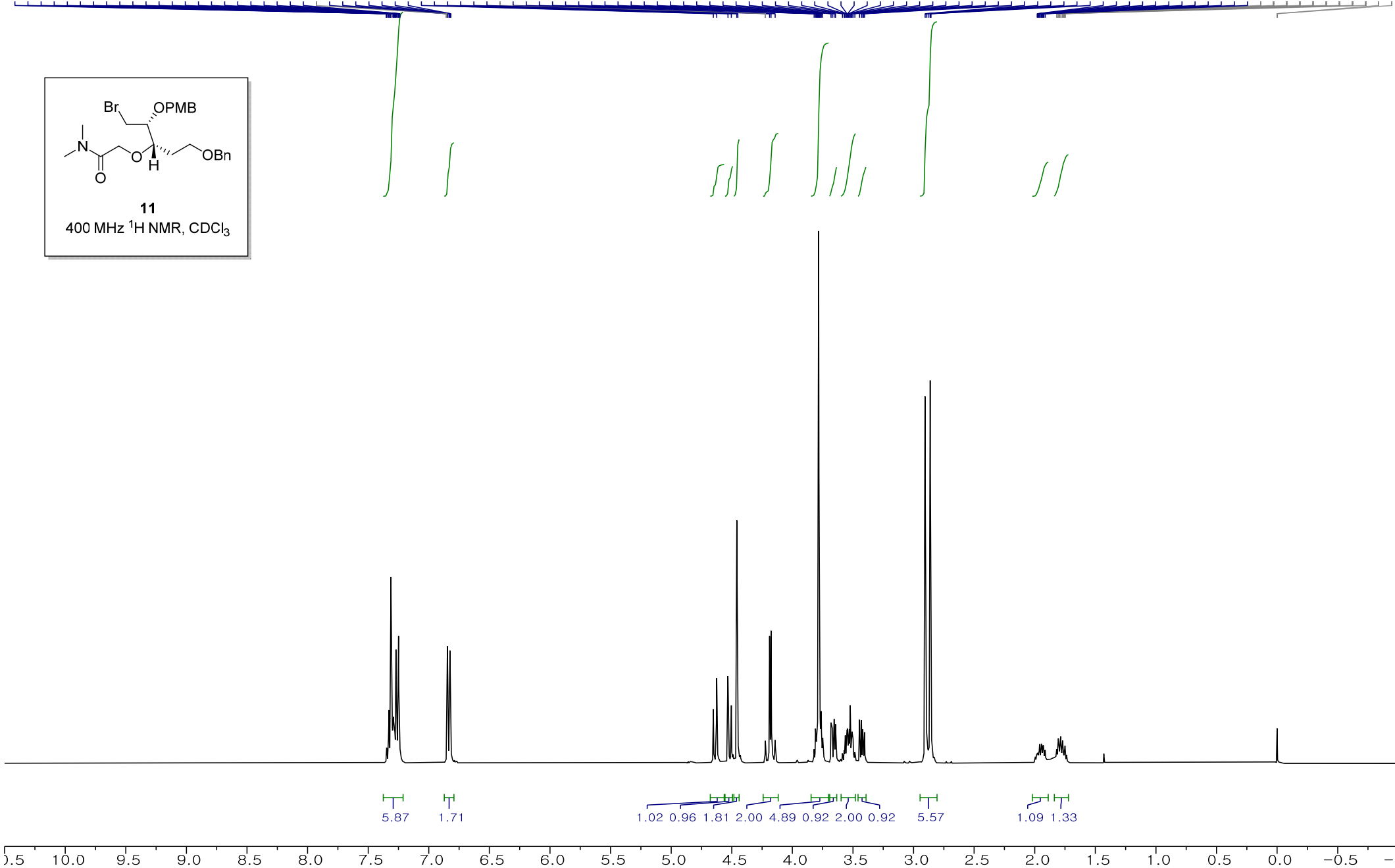
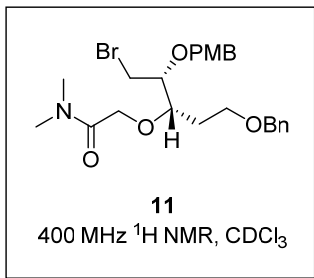
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Is-5-63-product

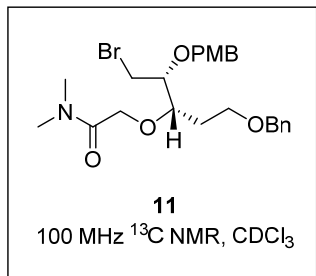
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f1 (ppm)

S37

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Is-5-63-product



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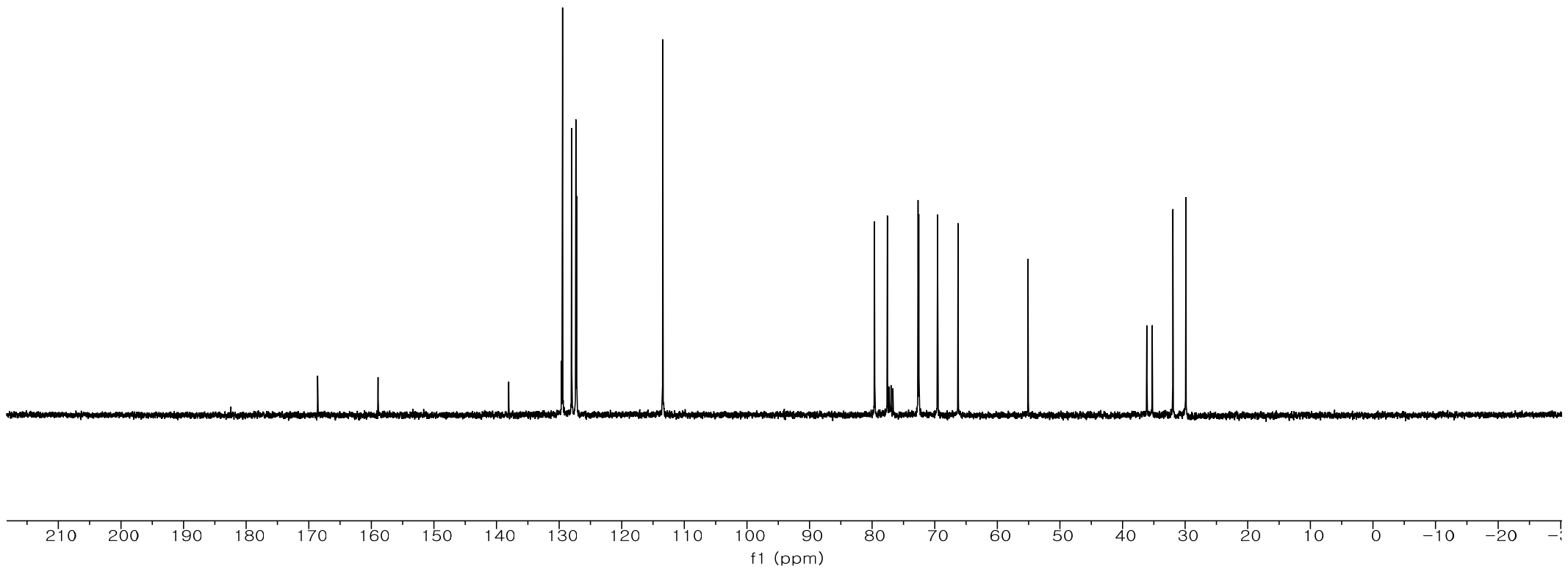
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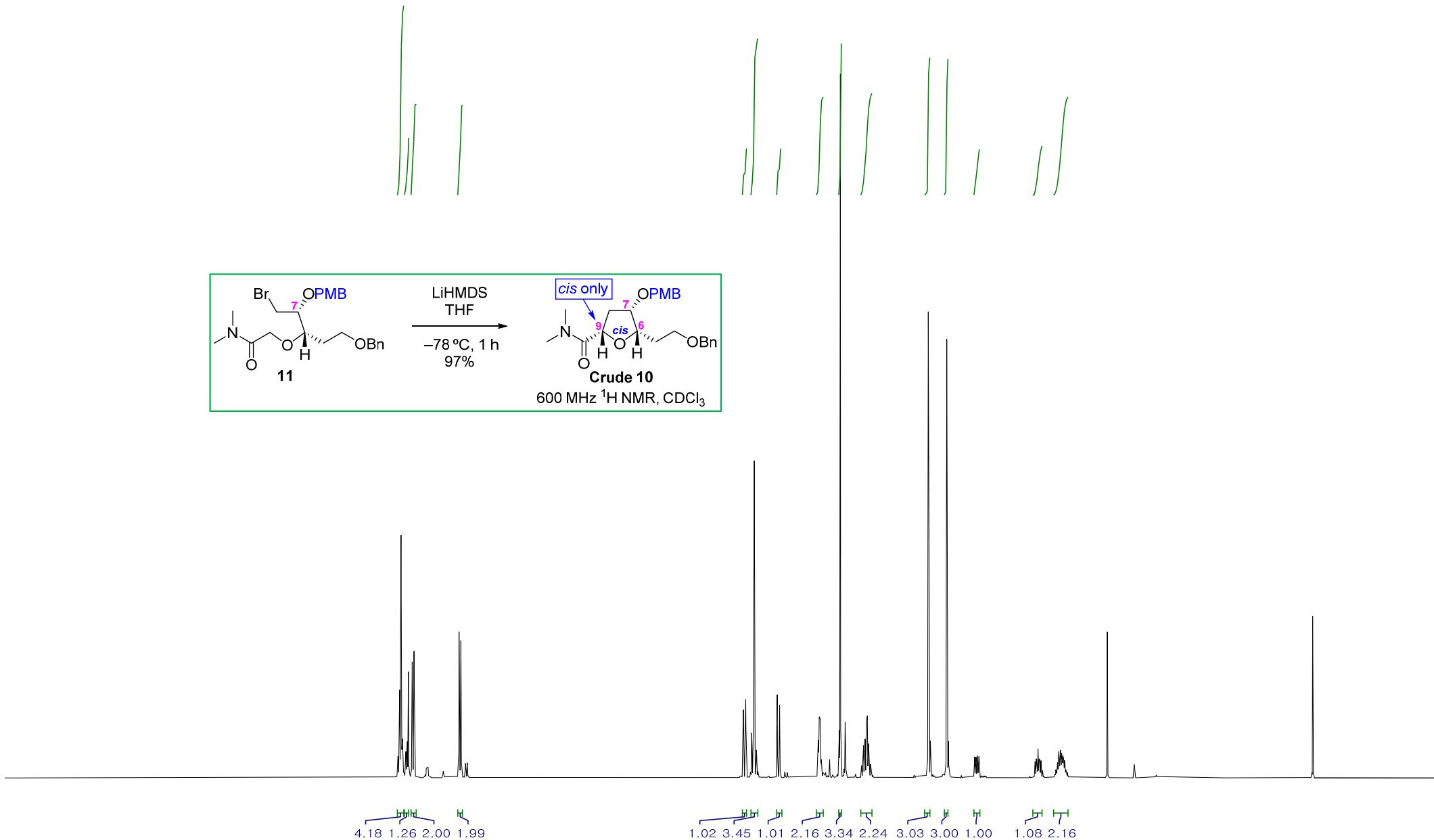
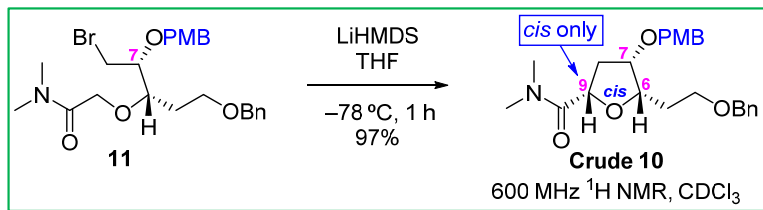
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S38

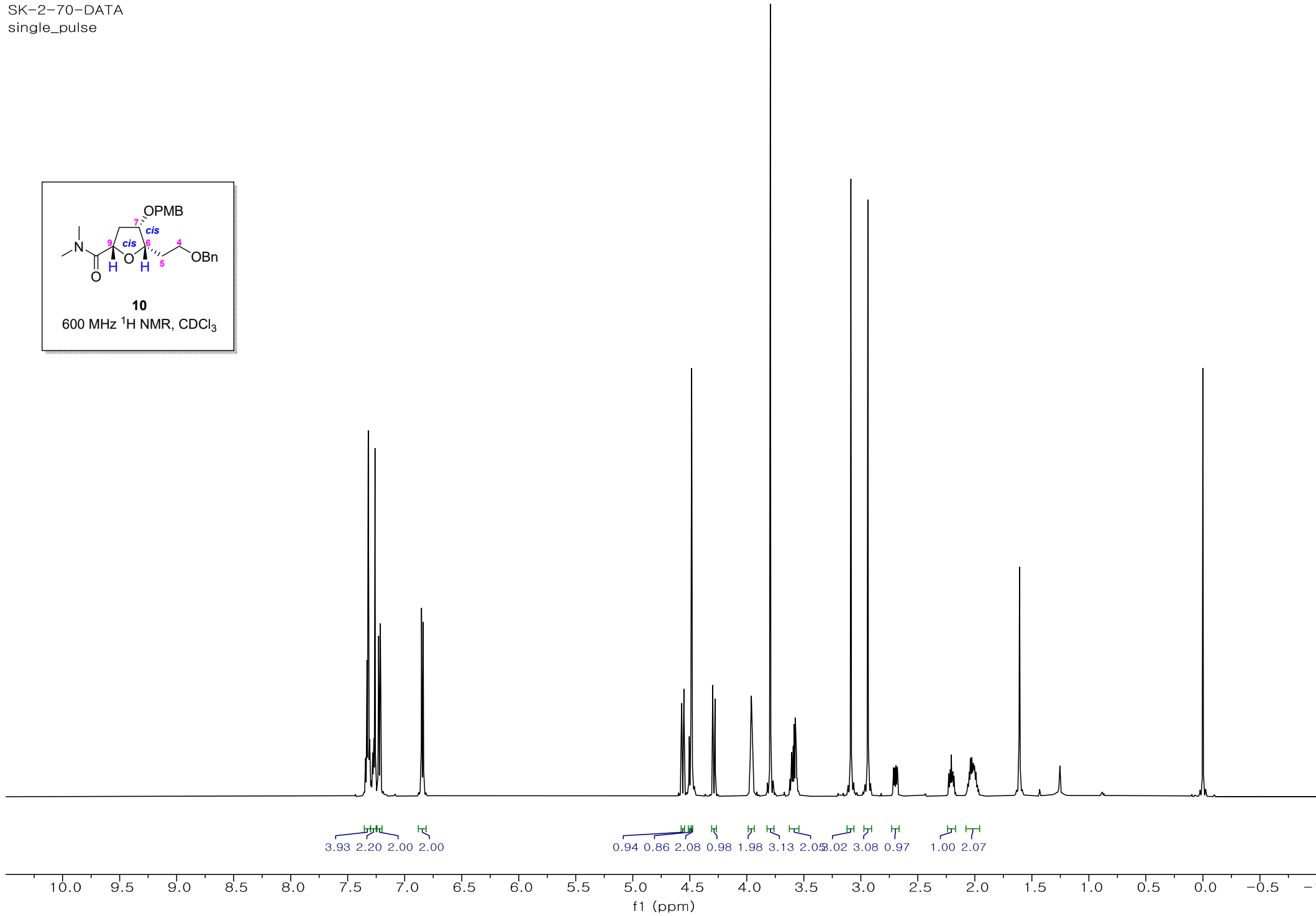
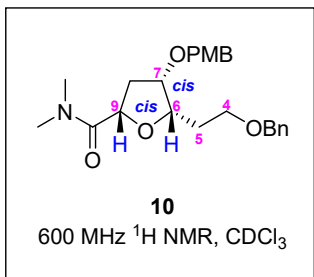
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f1 (ppm)

S39





— 169.5391

— 158.7560

— 138.3350

130.1037

129.0933

128.0893

127.3961

127.2663

— 113.4678

80.0908

77.5232

75.8219

72.7903

70.0694

67.3449

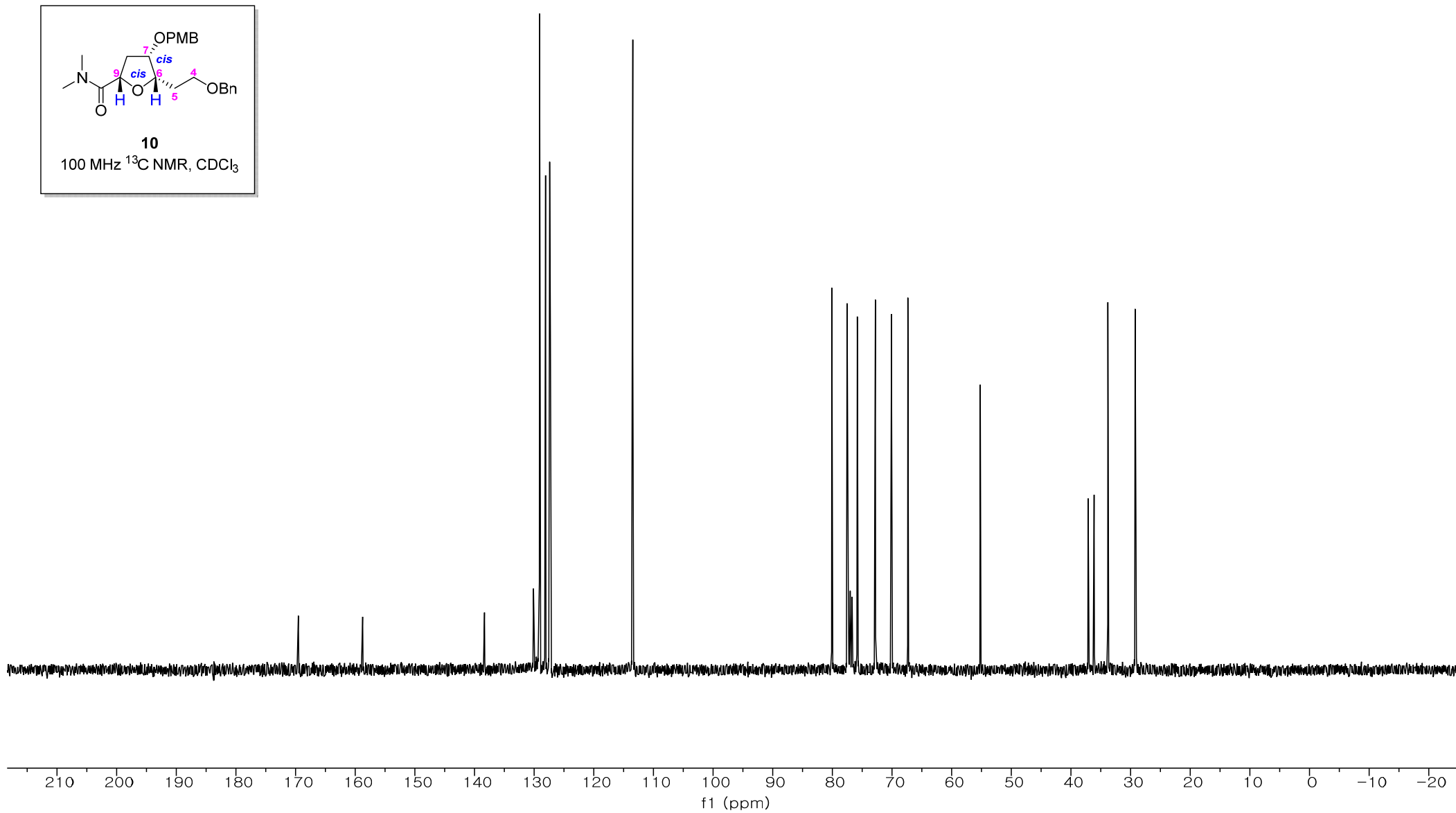
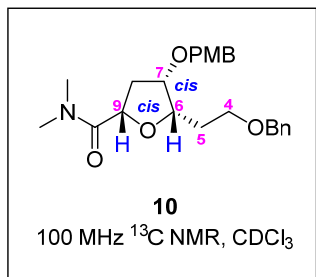
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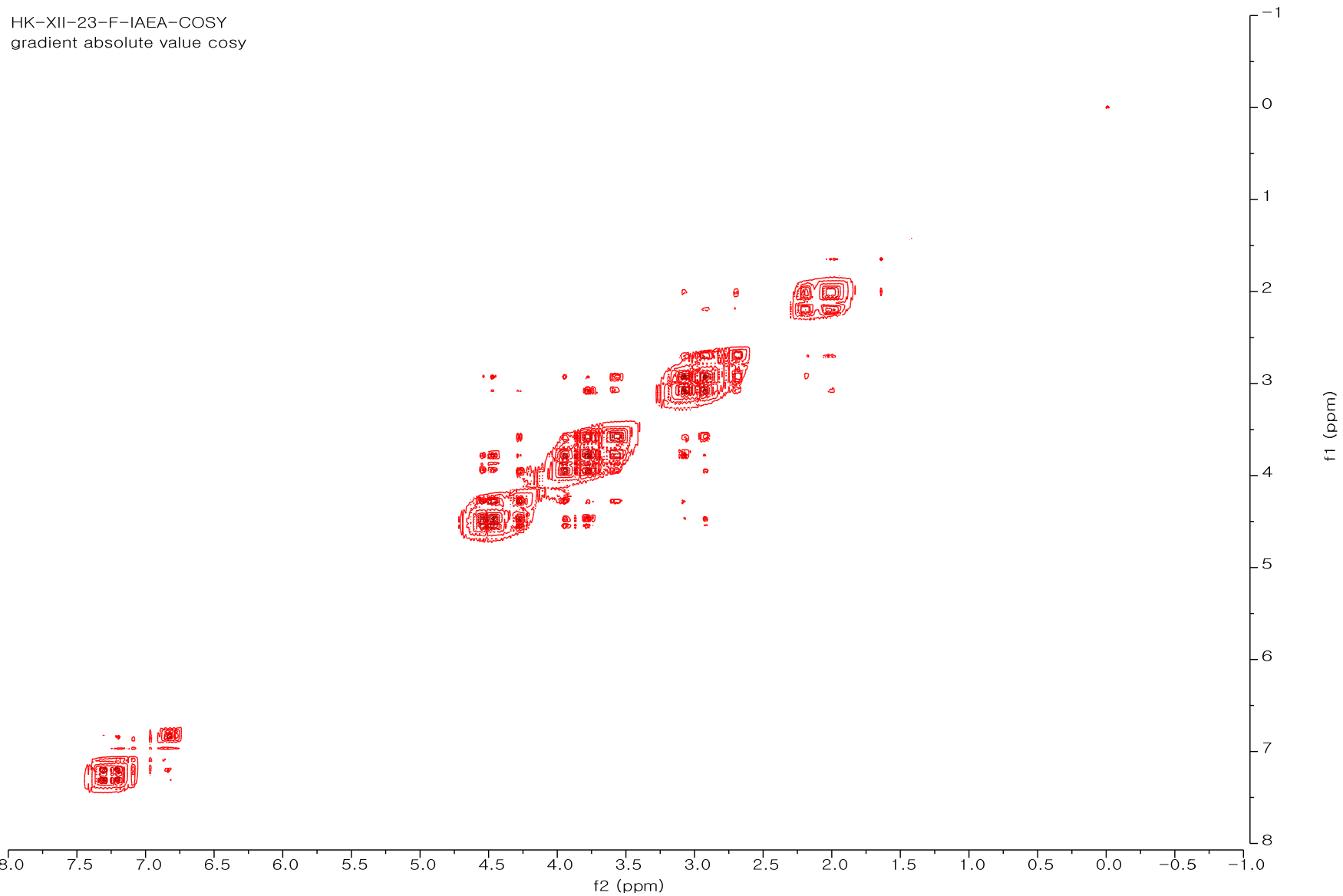
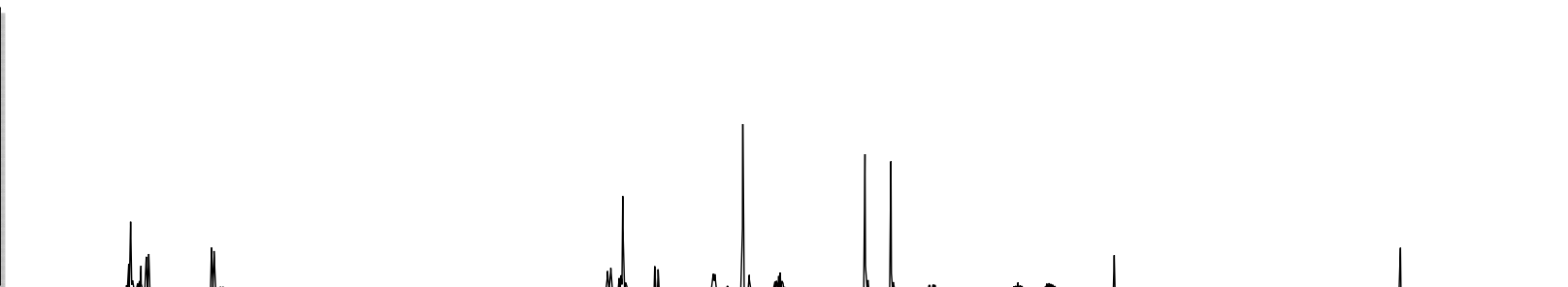
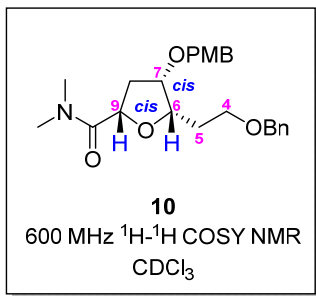
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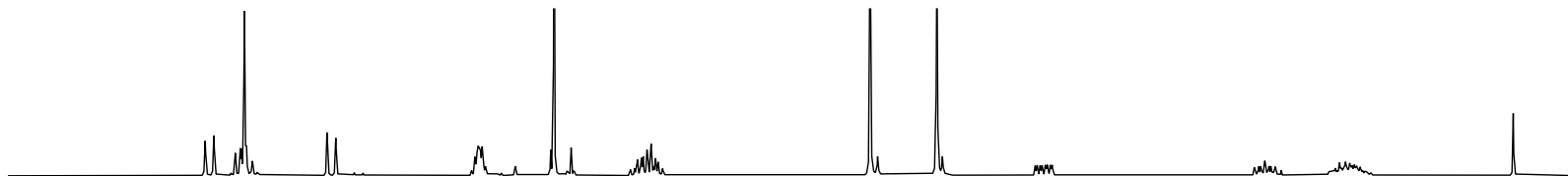
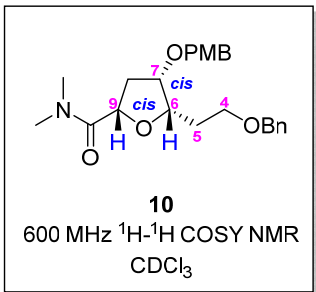
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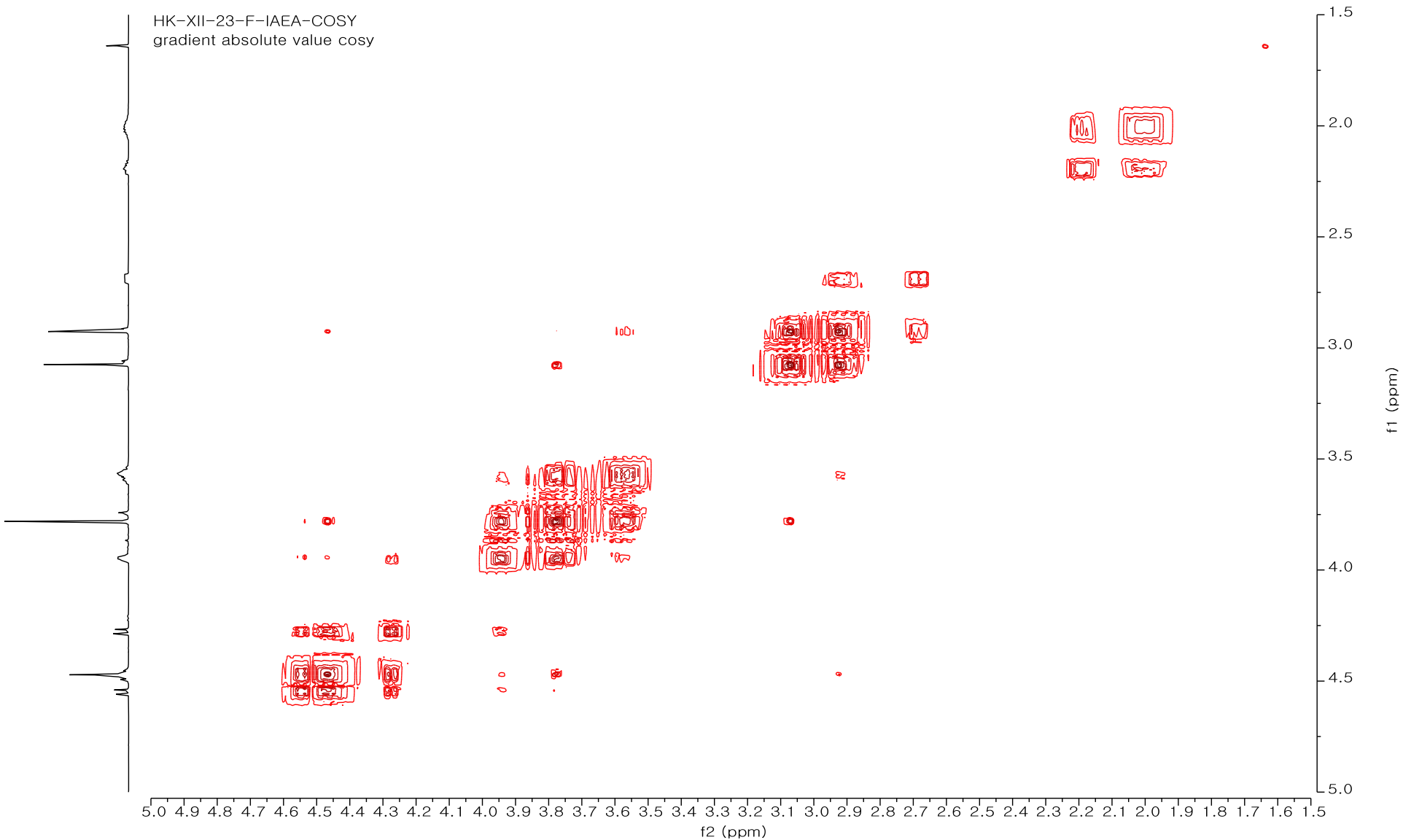
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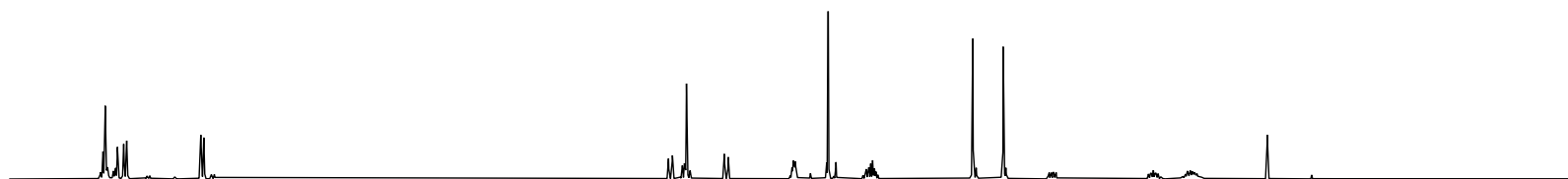
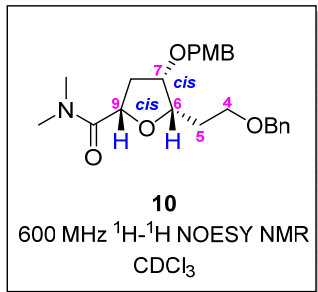




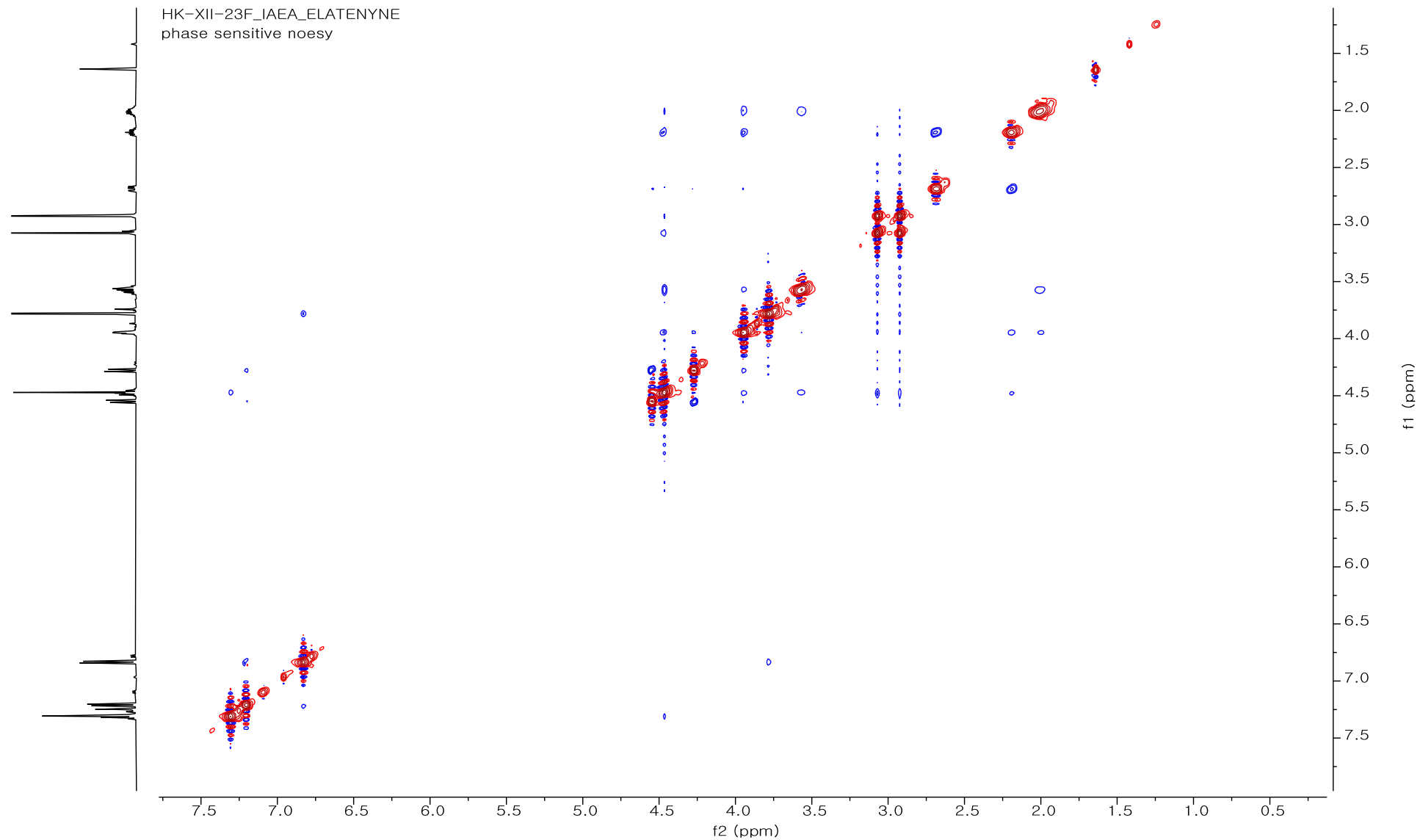


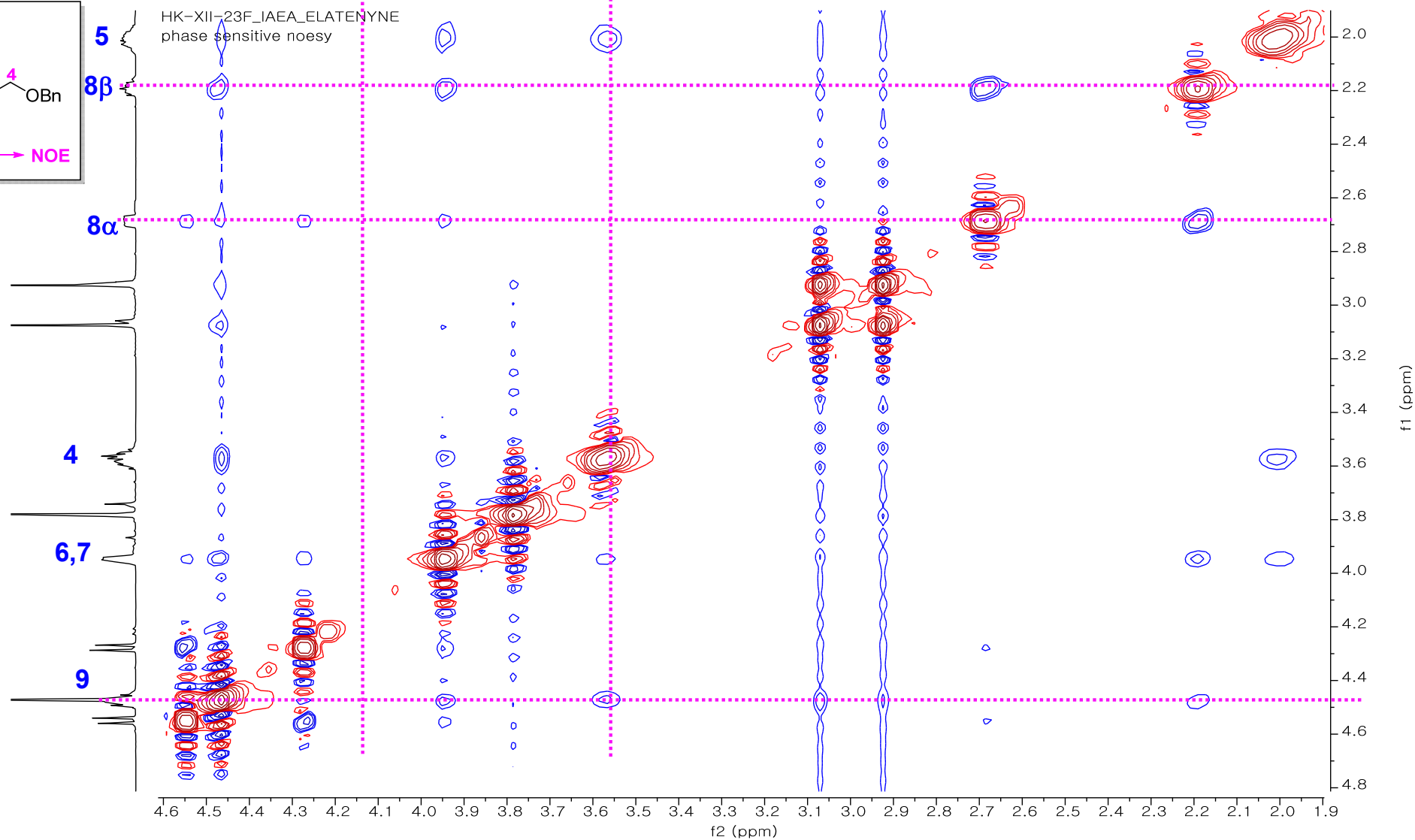
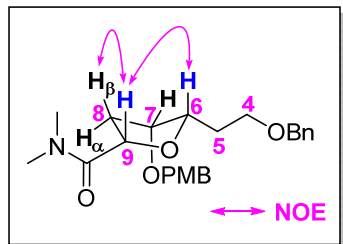
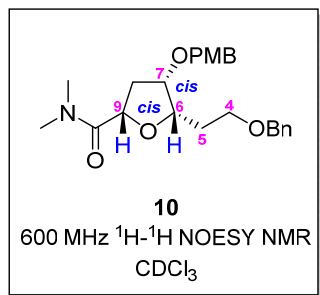
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HK-XII-23F\_IAEA\_ELATENYNE  
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SK-11-118  
single pulse decoupled gated NOE

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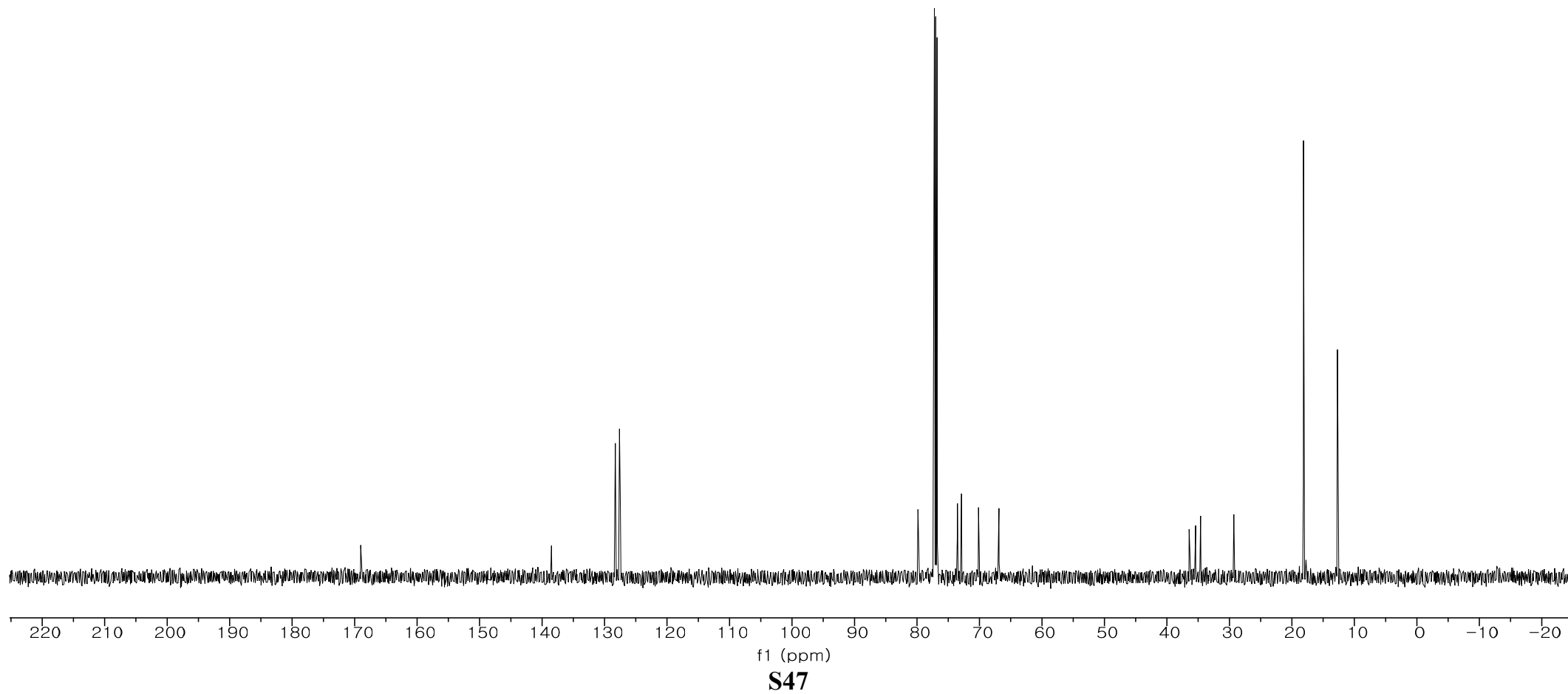
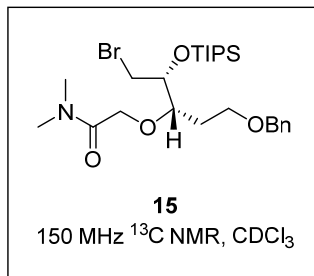
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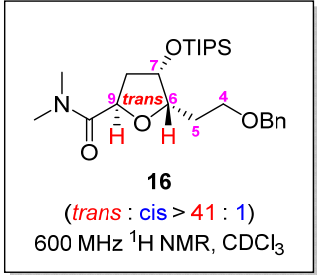
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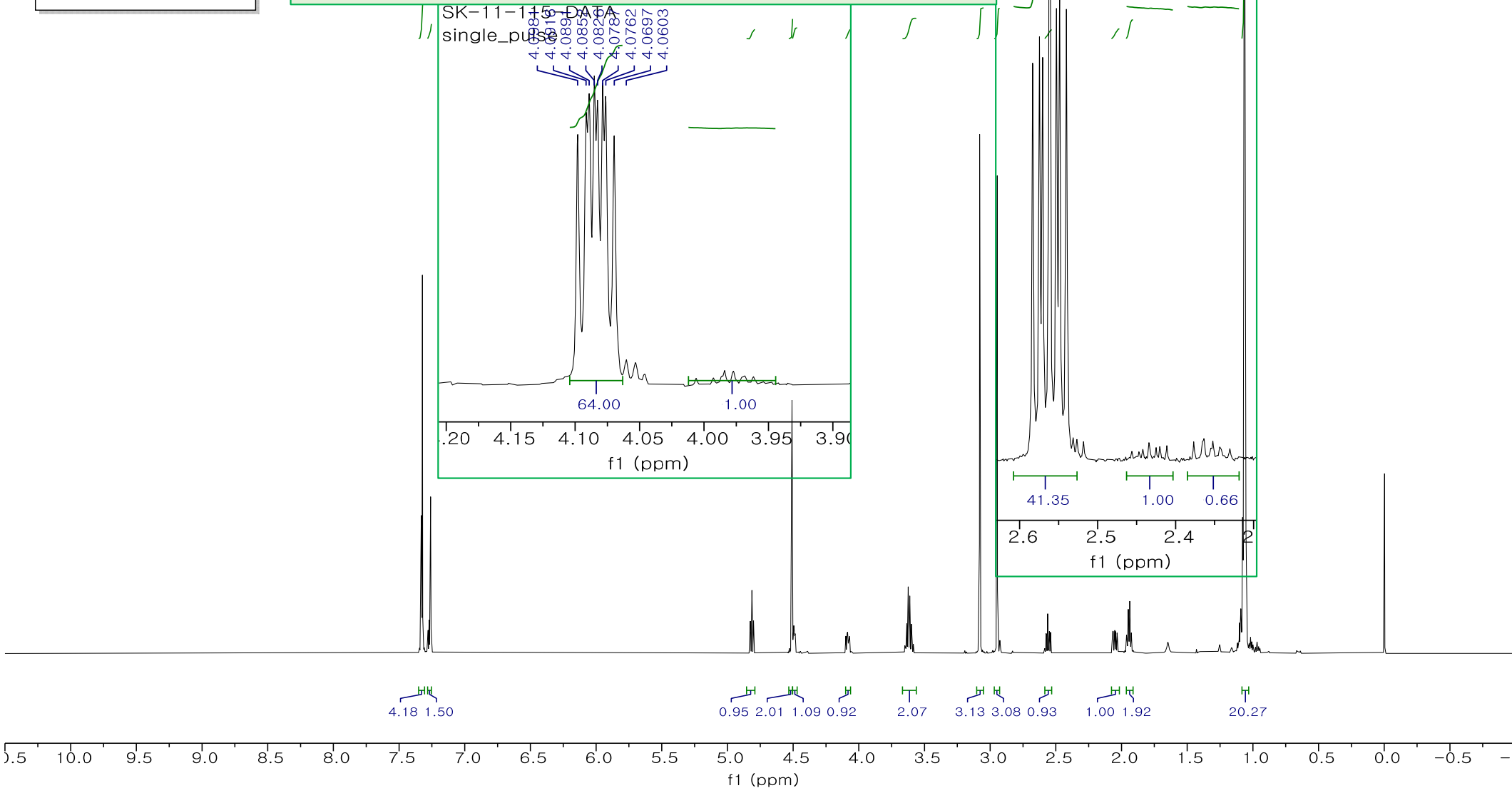
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 1.644  
 1.168  
 1.032  
 0.983  
 0.949  
 1.0931  
 1.0913  
 1.0876  
 1.0791  
 1.0722  
 1.0658  
 1.0633  
 1.0569  
 1.0551  
 1.0532  
 1.0499  
 1.0451  
 1.0368  
 1.0277  
 1.0180  
 1.0158  
 1.0081  
 1.0002  
 0.9799  
 0.9679  
 0.9606  
 0.9559  
 0.9467  
 -0.0021

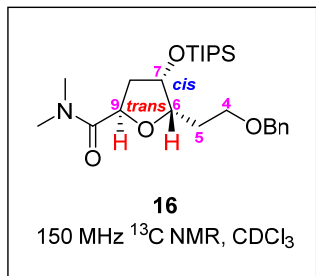


The diastereoselectivity (*trans*:*cis*) was determined to be greater than 41:1, on the assumption that the minor peak corresponds to the *cis* isomer.





SK-11-115  
single pulse decoupled gated NOE



— 171.1628

— 138.6130

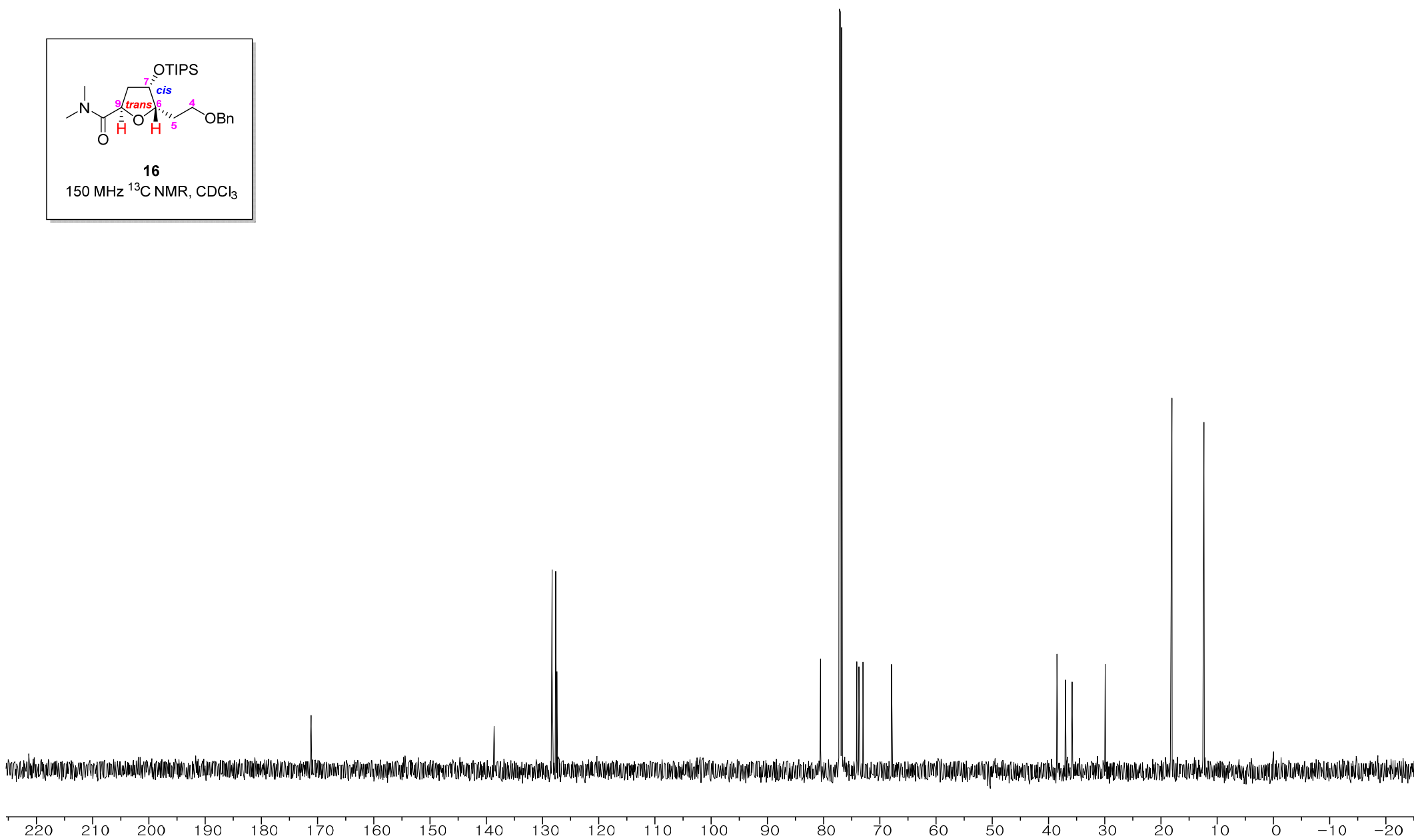
128.2912  
127.6381  
127.4316

— 80.5391

74.1006  
73.7271  
72.9876  
— 67.9328

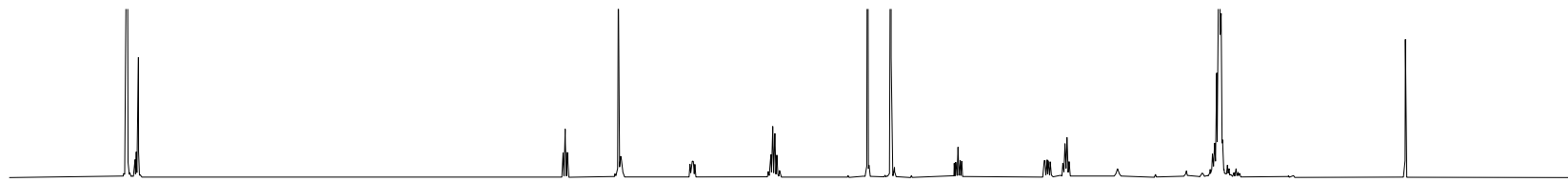
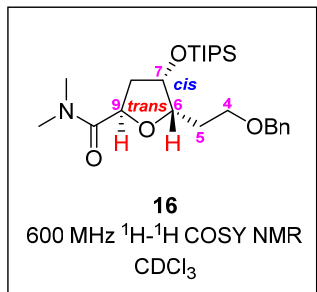
38.4881  
36.9946  
35.8063  
— 29.9137

18.0912  
18.0540  
— 12.3512

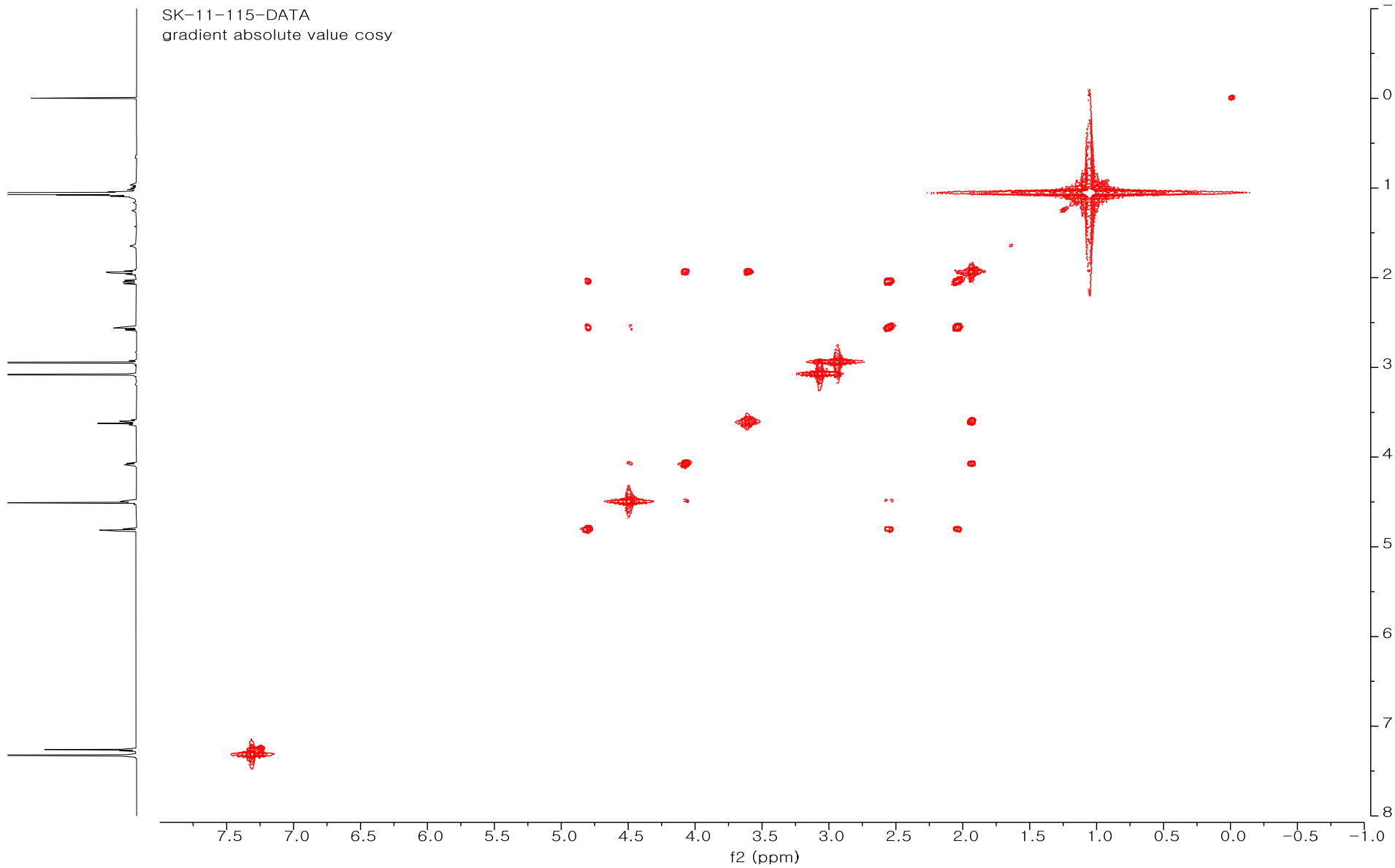


f1 (ppm)

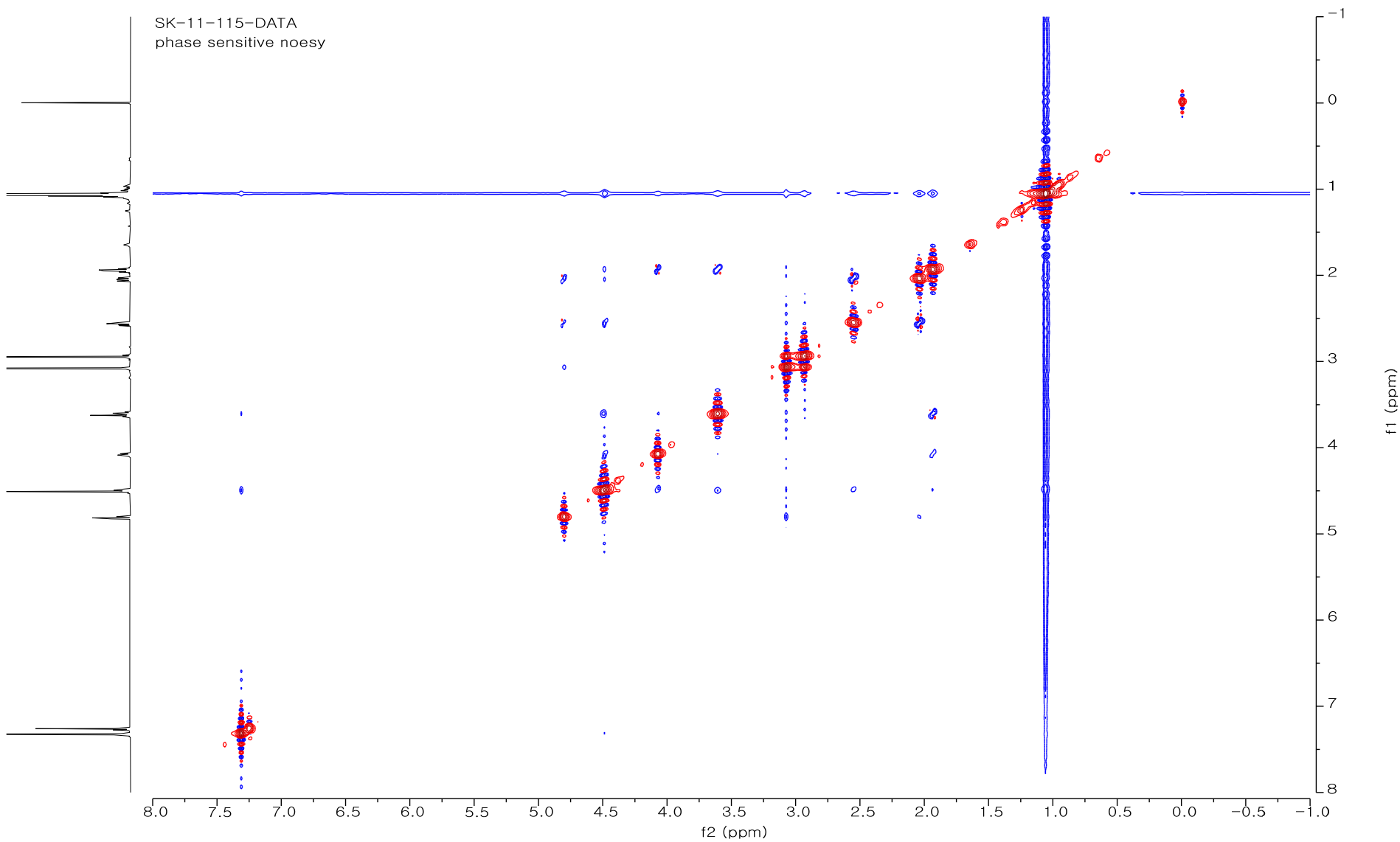
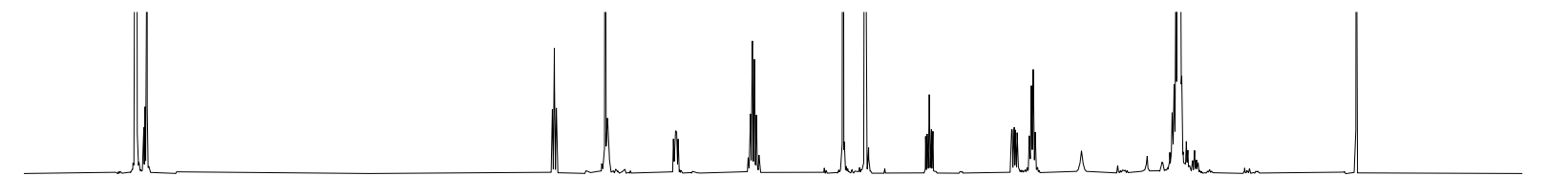
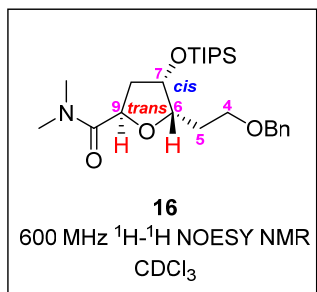
**S49**

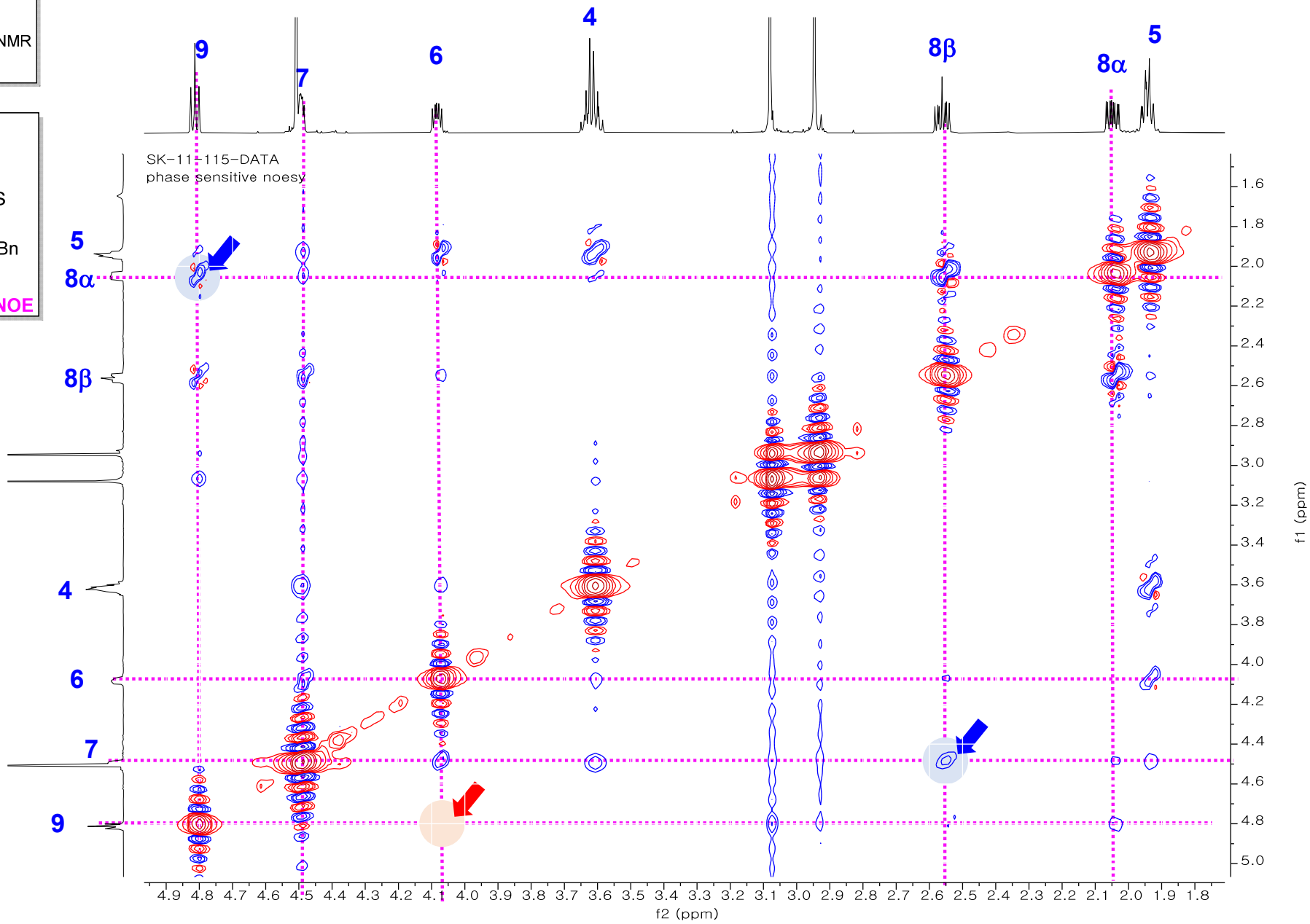
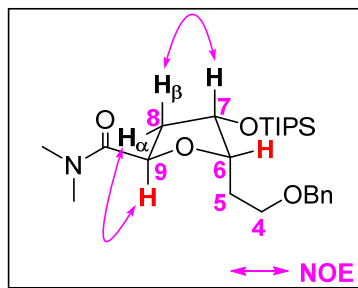
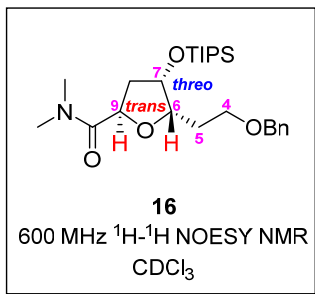


SK-11-115-DATA  
gradient absolute value cosy

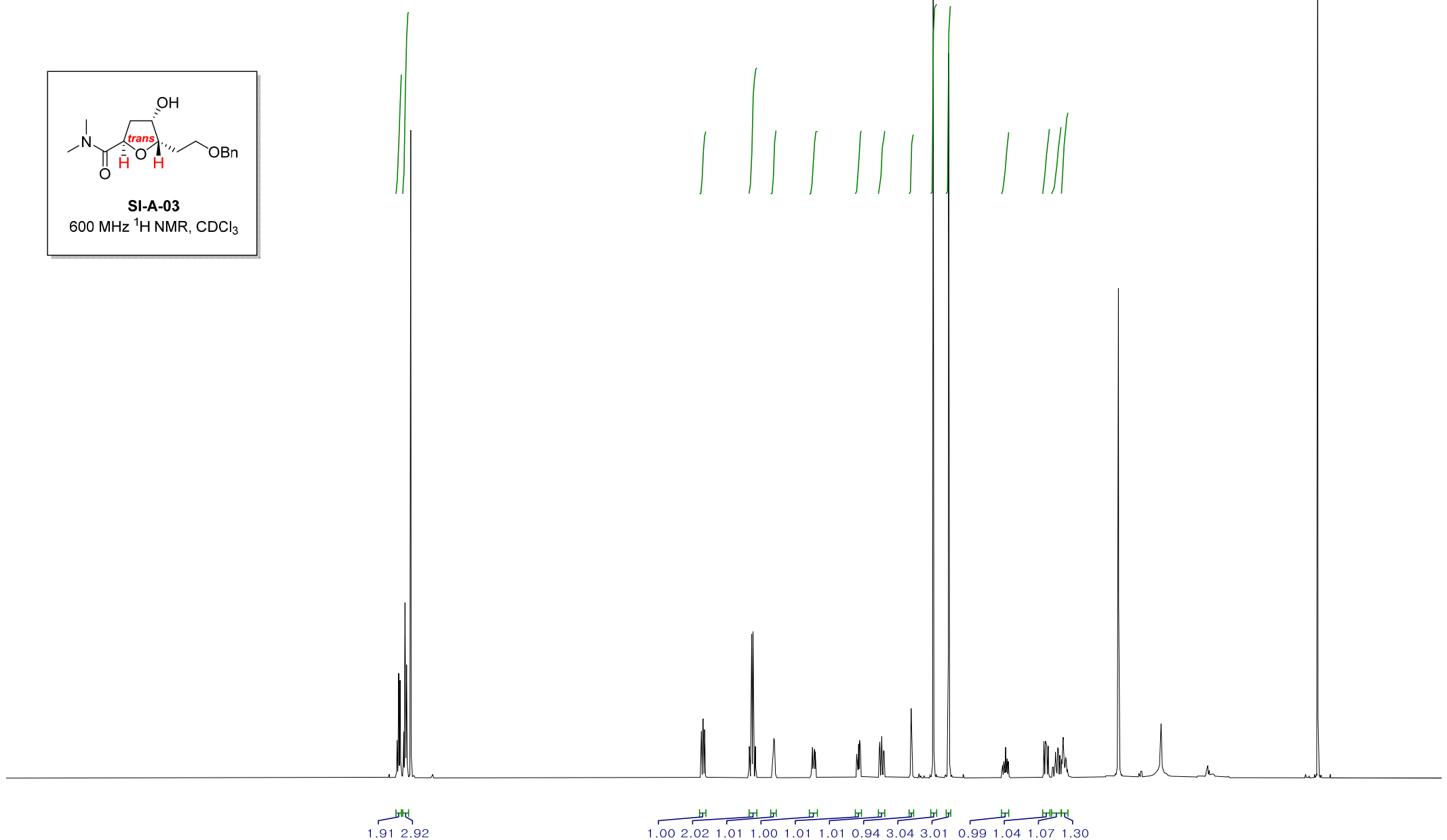
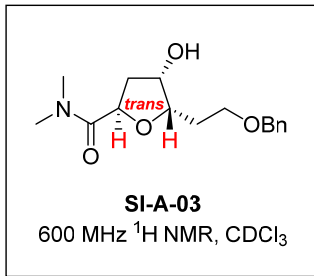


S50





7.31300  
7.30841  
7.30591  
7.3005  
7.3021  
7.3027  
7.3027  
7.3044  
7.3044  
7.3470  
7.3453  
7.3438  
7.3418  
7.3174  
7.3152  
7.3062  
7.3030  
7.2960  
7.2927  
7.2583  
7.2571  
7.2558  
4.9325  
4.9207  
4.9185  
4.5489  
4.5294  
4.5192  
4.4997  
4.3614  
4.3569  
4.3523  
4.3477  
4.3432  
4.0513  
4.0463  
4.0429  
4.0378  
4.0350  
4.0300  
4.0265  
4.0215  
3.6800  
3.6834  
3.6812  
3.6756  
3.6733  
3.6677  
3.6654  
3.6598  
3.5079  
3.5038  
3.4922  
3.4902  
3.4880  
3.4861  
3.4745  
3.4703  
3.2563  
3.2529  
3.2493  
3.0765  
3.0736  
3.0722  
3.0707  
2.9530  
2.9490  
2.9473  
2.9473  
2.4983  
2.4957  
2.4845  
2.1913  
2.1902  
2.1889  
2.1793  
2.1782  
2.1771  
2.1686  
2.1676  
2.1664  
2.1568  
2.1545  
2.0969  
2.0912  
2.0804  
2.0789  
2.0748  
2.0733  
2.0628  
2.0571  
2.0480  
2.0441  
2.0400  
2.0357  
2.0318  
2.0276  
2.0155  
1.5858  
1.2518  
1.2507  
0.0027  
-0.0028  
-0.0057  
-0.0069  
-0.0084

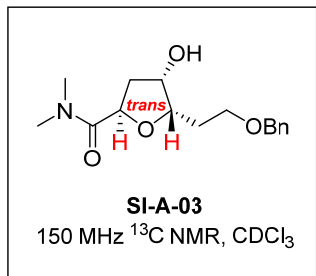


7.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -

f1 (ppm)

S53

SK-11-119-DATA-1  
single pulse decoupled gated NOE



— 171.5832

— 137.3176

128.5978  
128.0130  
127.7931

— 83.4790

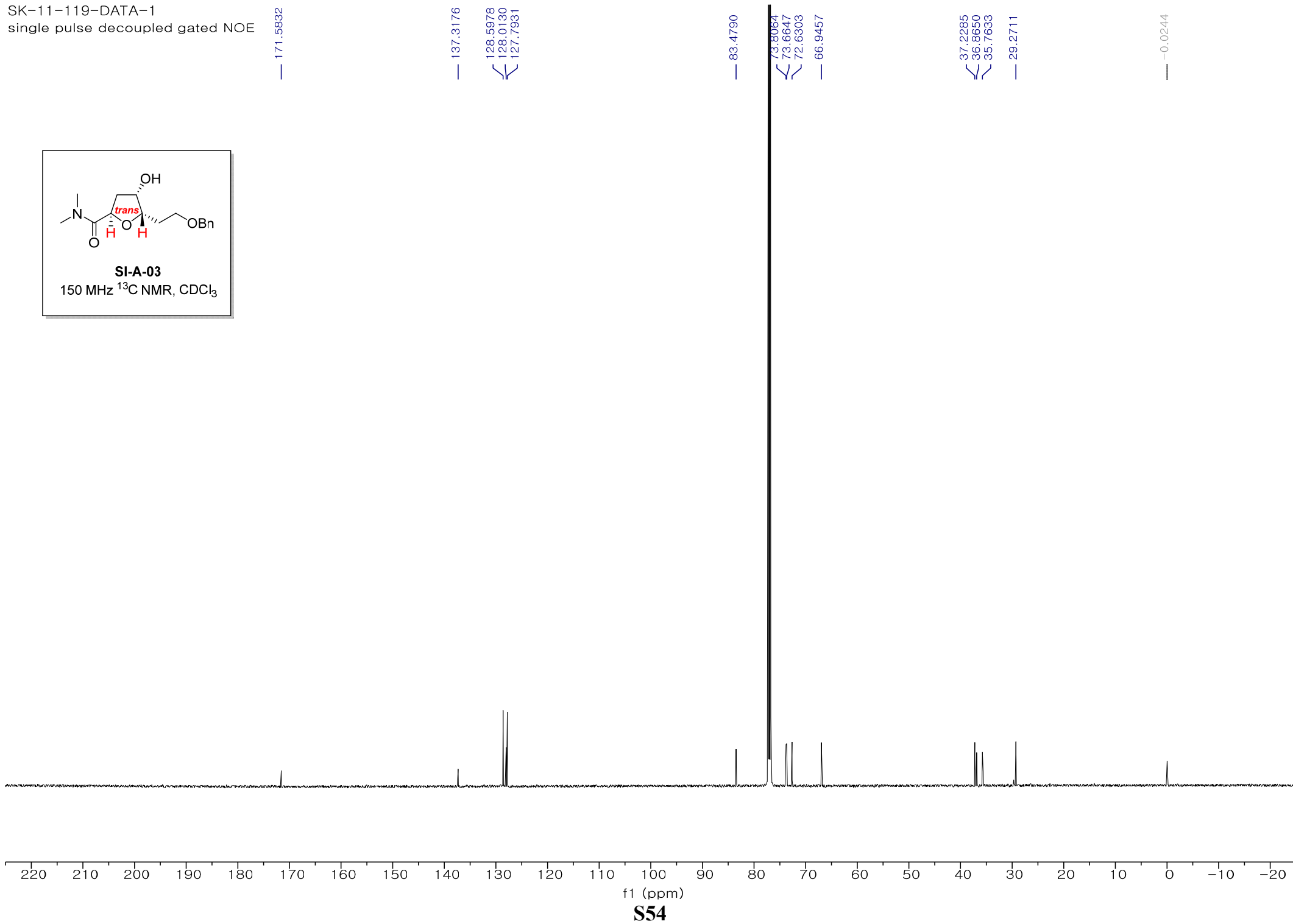
73.8064  
73.6647  
72.6303

— 66.9457

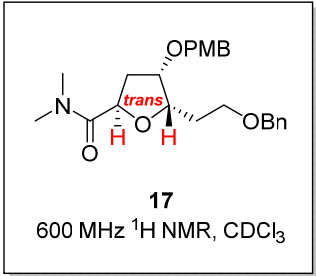
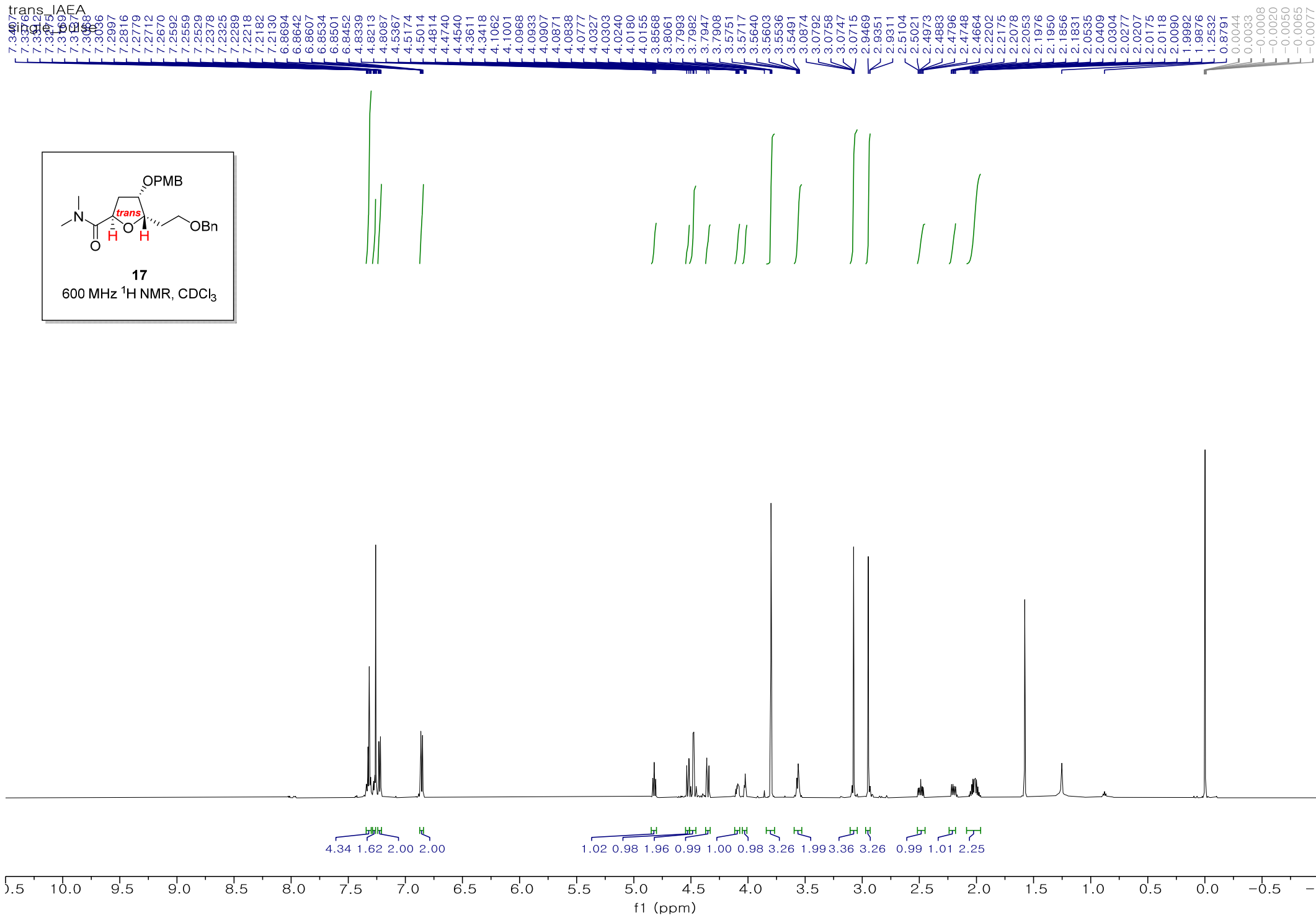
37.2285  
36.8650  
35.7633

— 29.2711

— -0.0244



f1 (ppm)  
**S54**



Elatenyne\_IAEA-trans-2  
single pulse decoupled gated NOE

— 171.0887

— 159.1733

— 138.5051

130.2417

129.2292

128.3051

127.6261

127.4630

— 113.7478

80.0301

79.1151

74.0752

72.9350

70.9522

67.7162

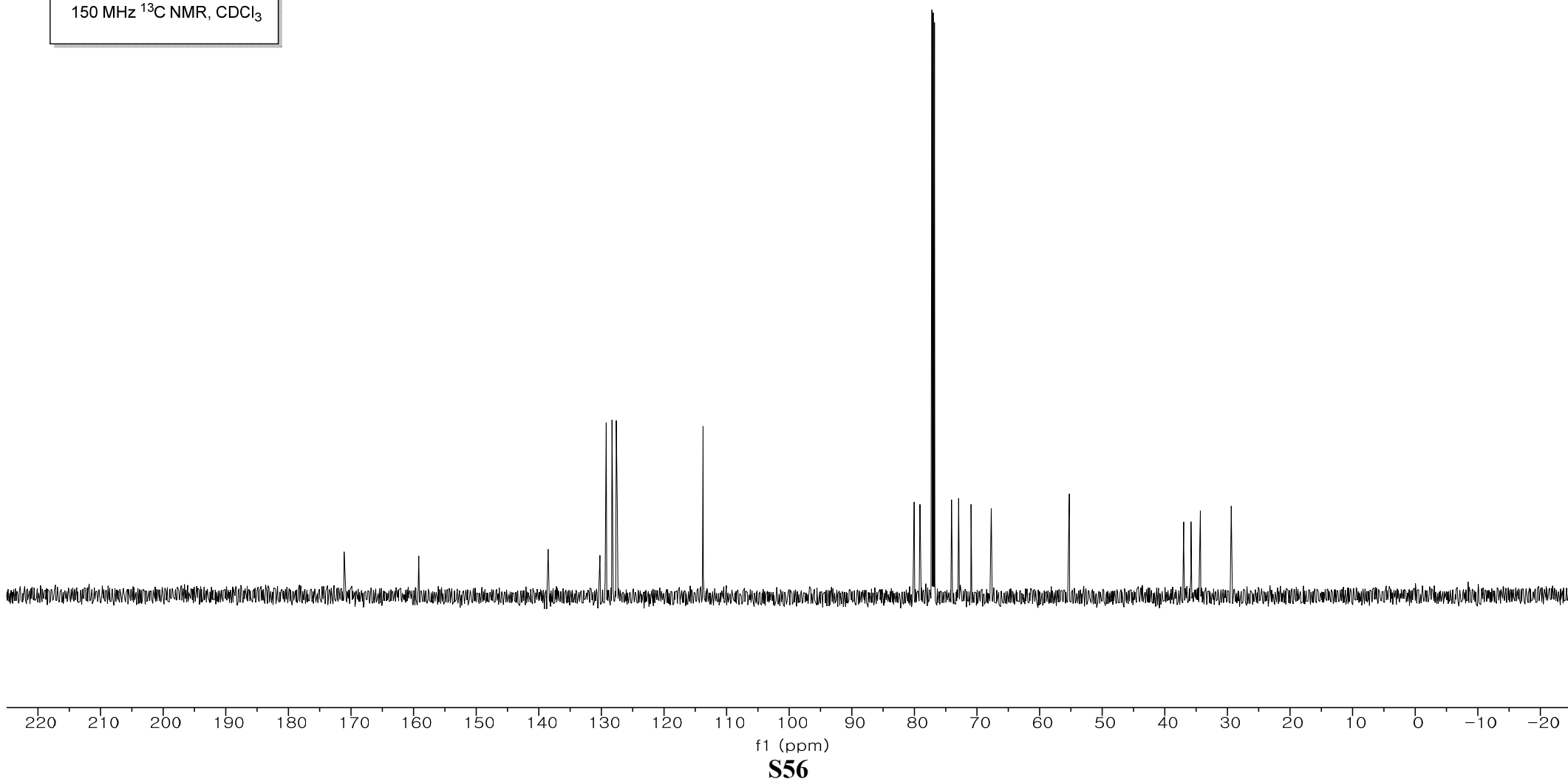
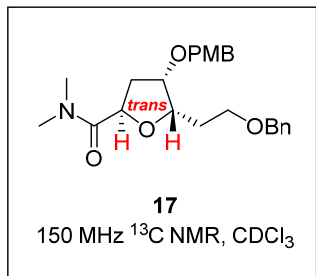
— 55.2440

36.9760

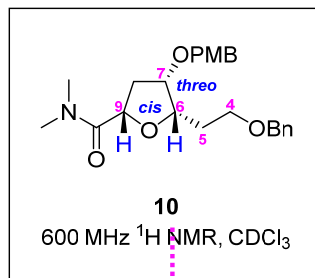
35.8057

34.3126

— 29.3880

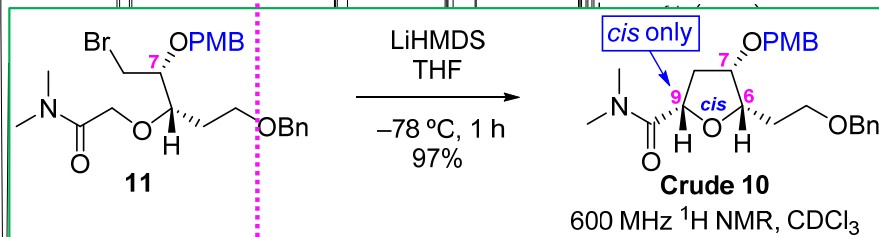
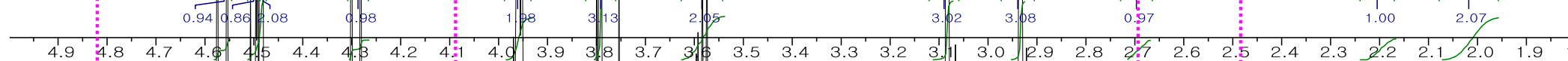




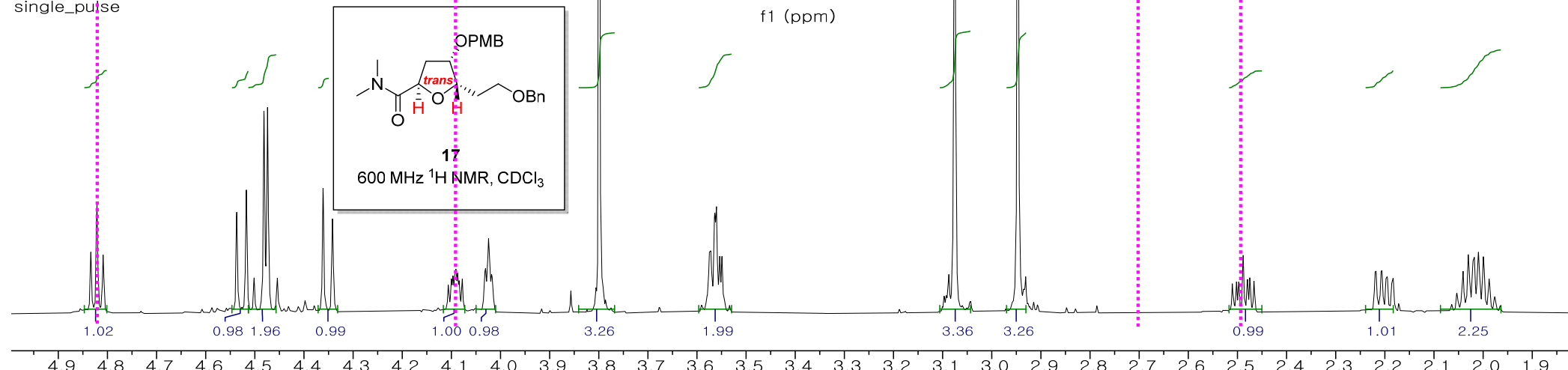
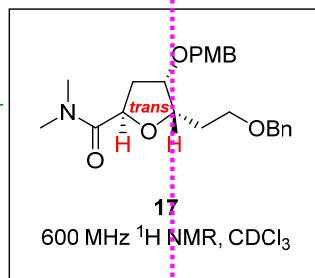


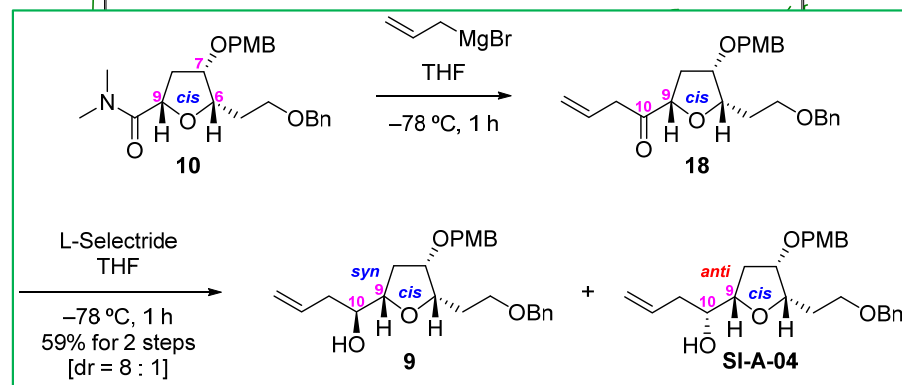
In comparison the spectra of the crude **10** with that of the authentic *trans* isomer **17**, no peaks corresponding to the **17** were found, so the selectivity was determined as *cis only*.

HK-XII-23F\_IAEA\_ELATENYNE  
single\_pulse

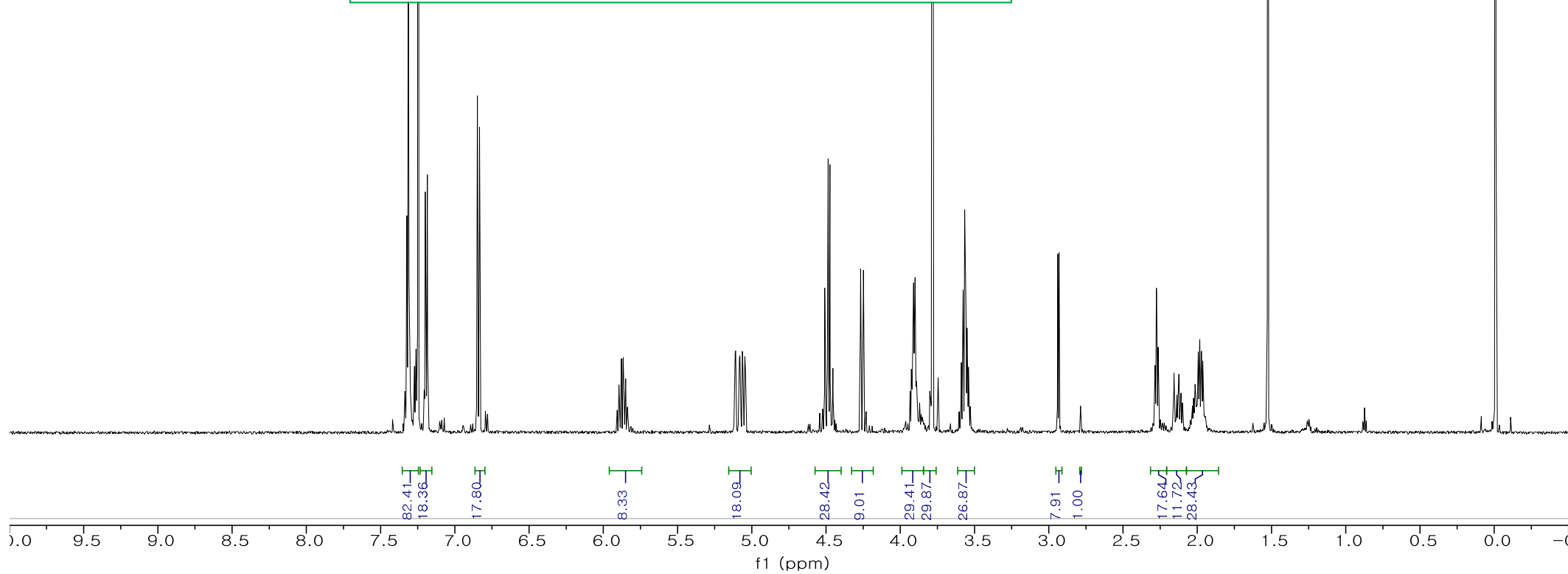


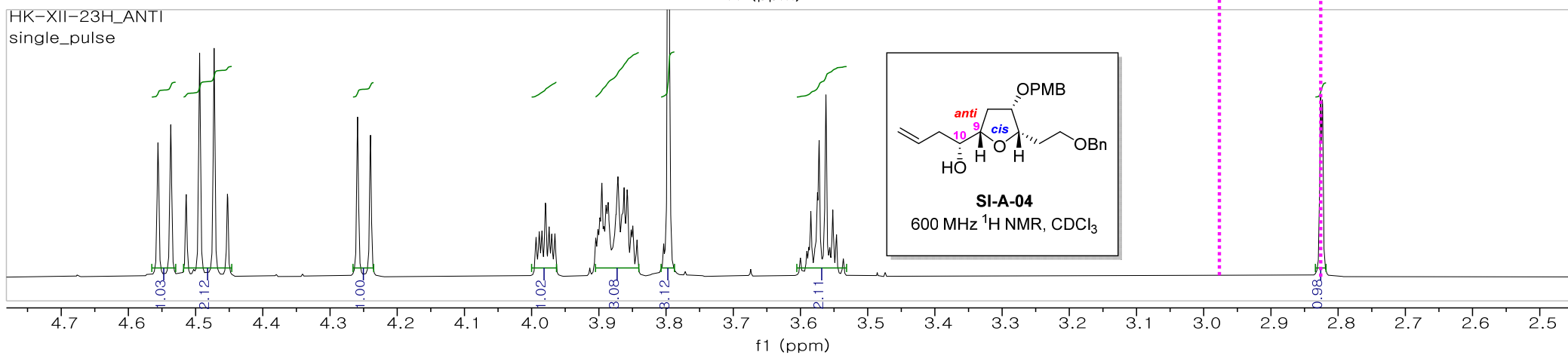
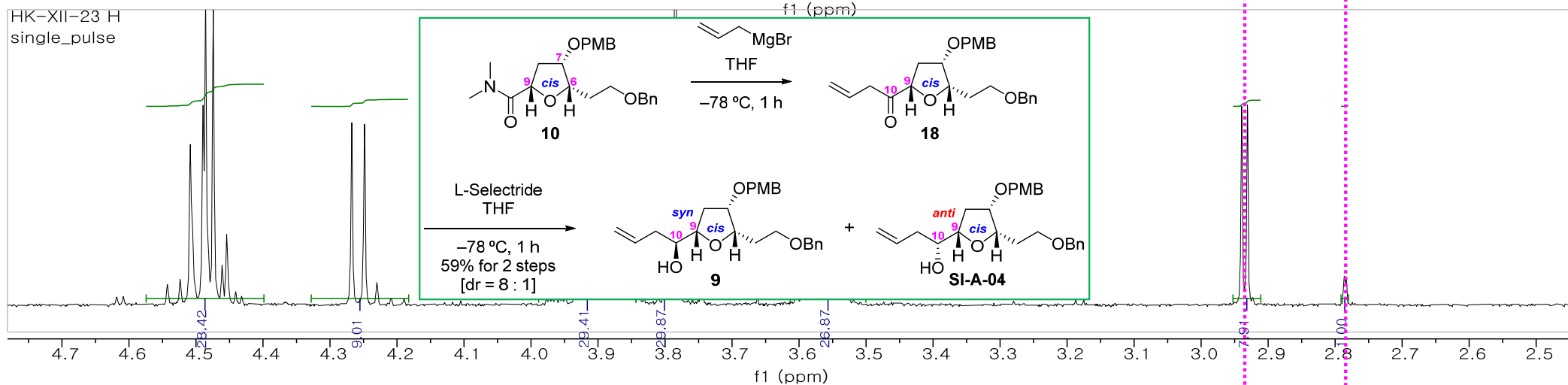
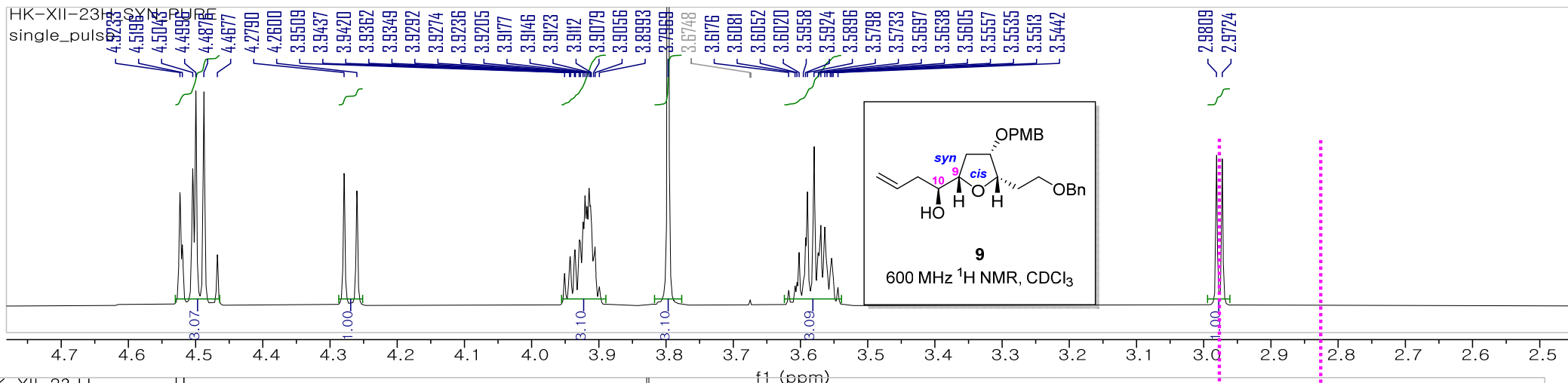
trans\_IAEA  
single\_pulse

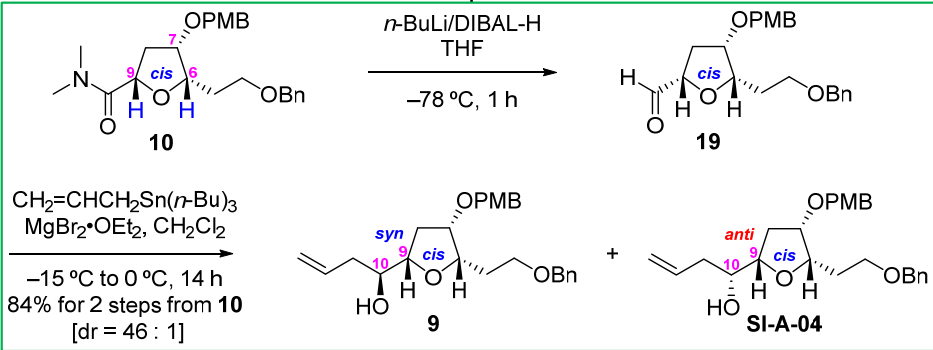
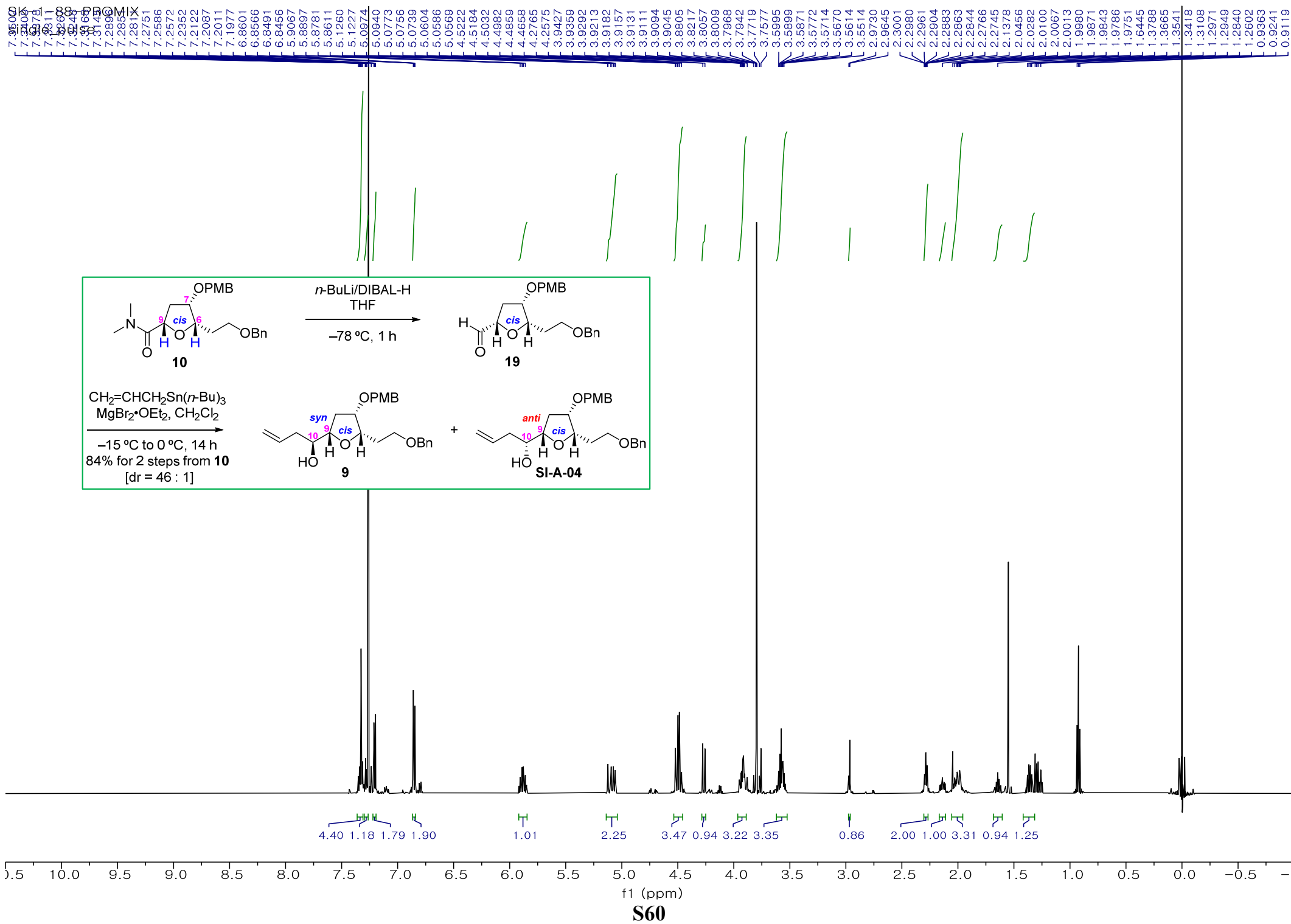




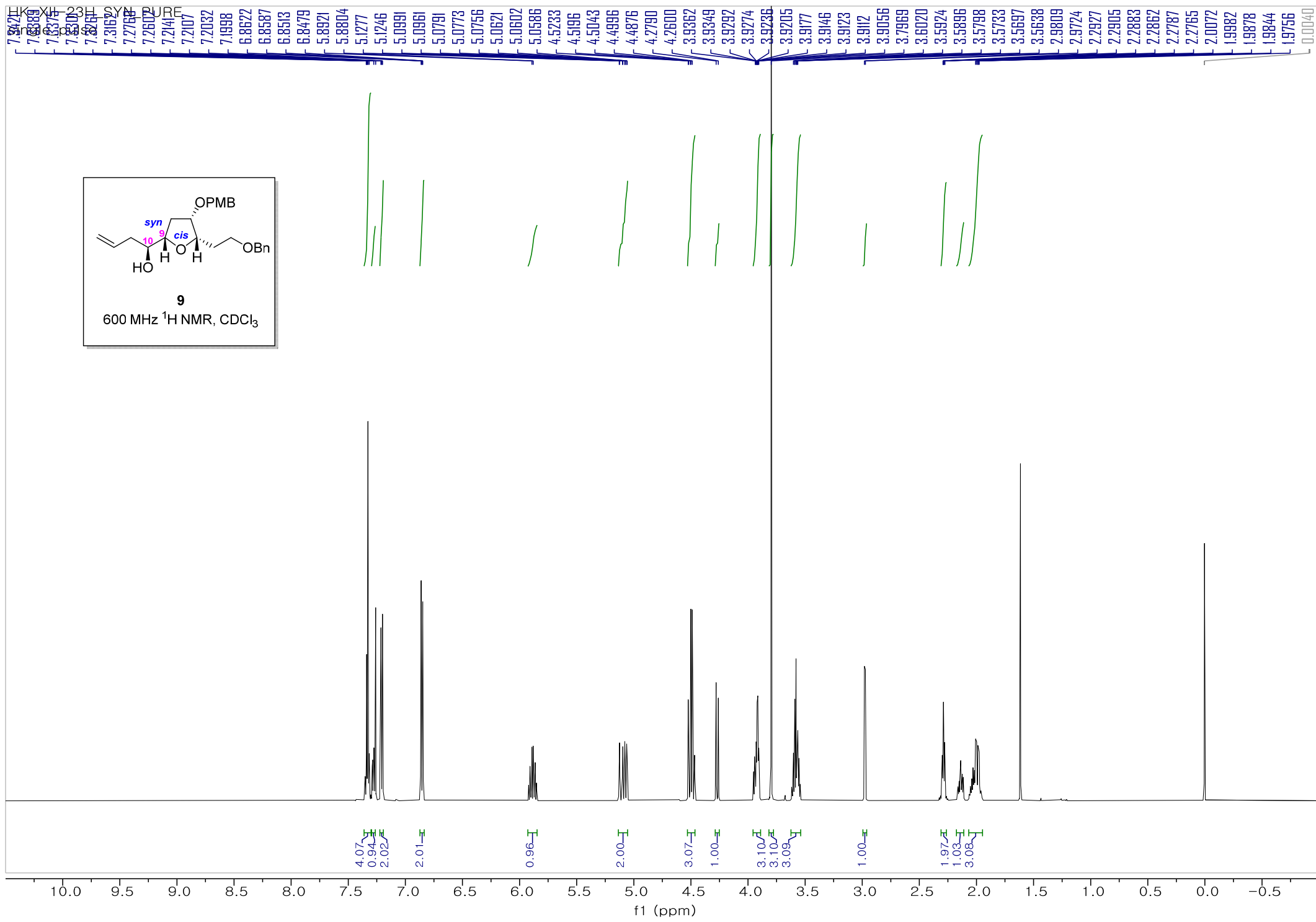
1. [ ] [ ] [ ]



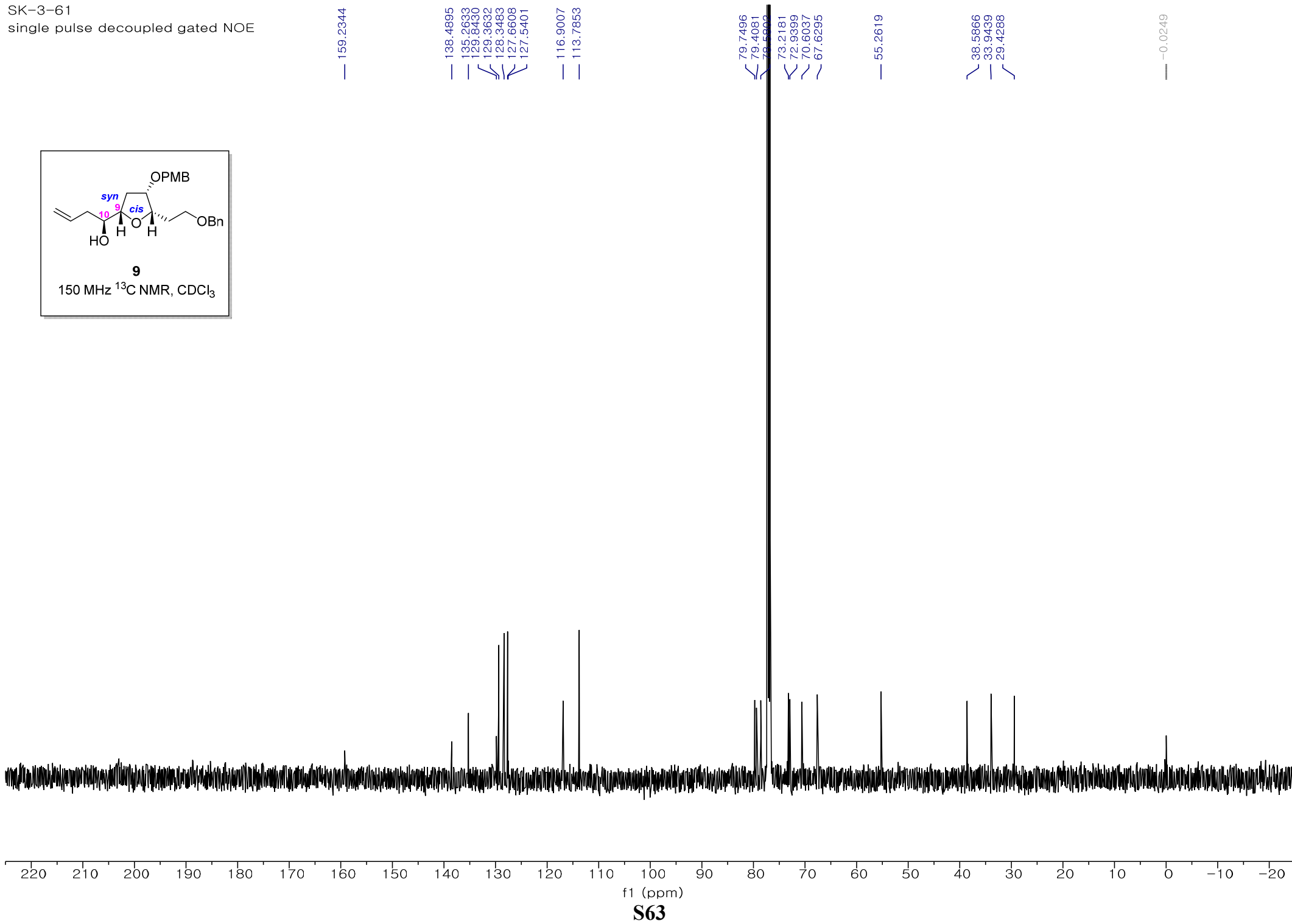
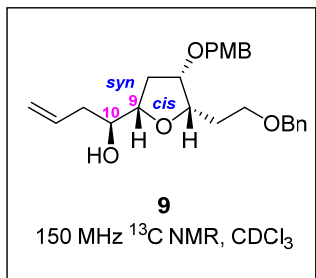






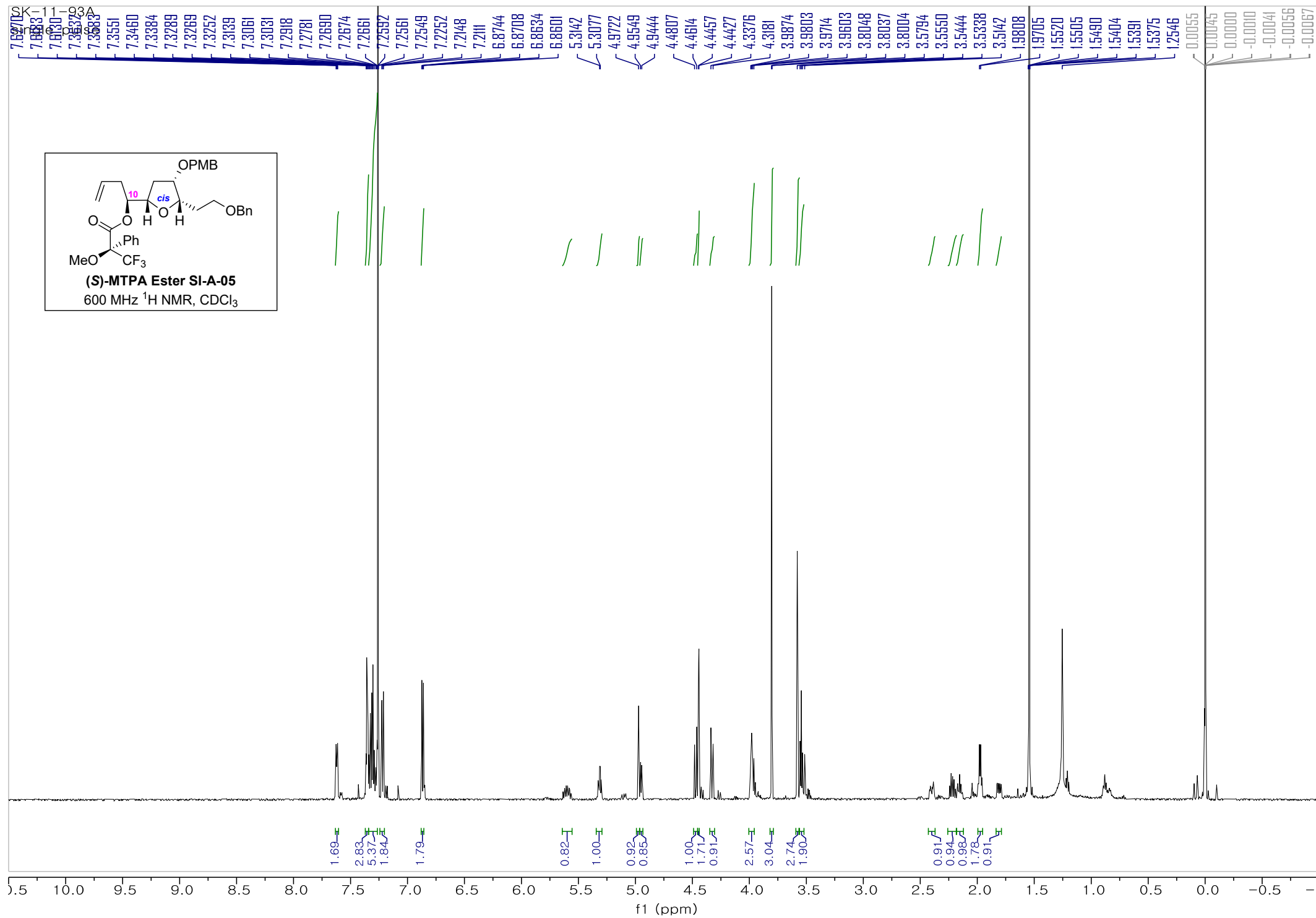


SK-3-61  
single pulse decoupled gated NOE



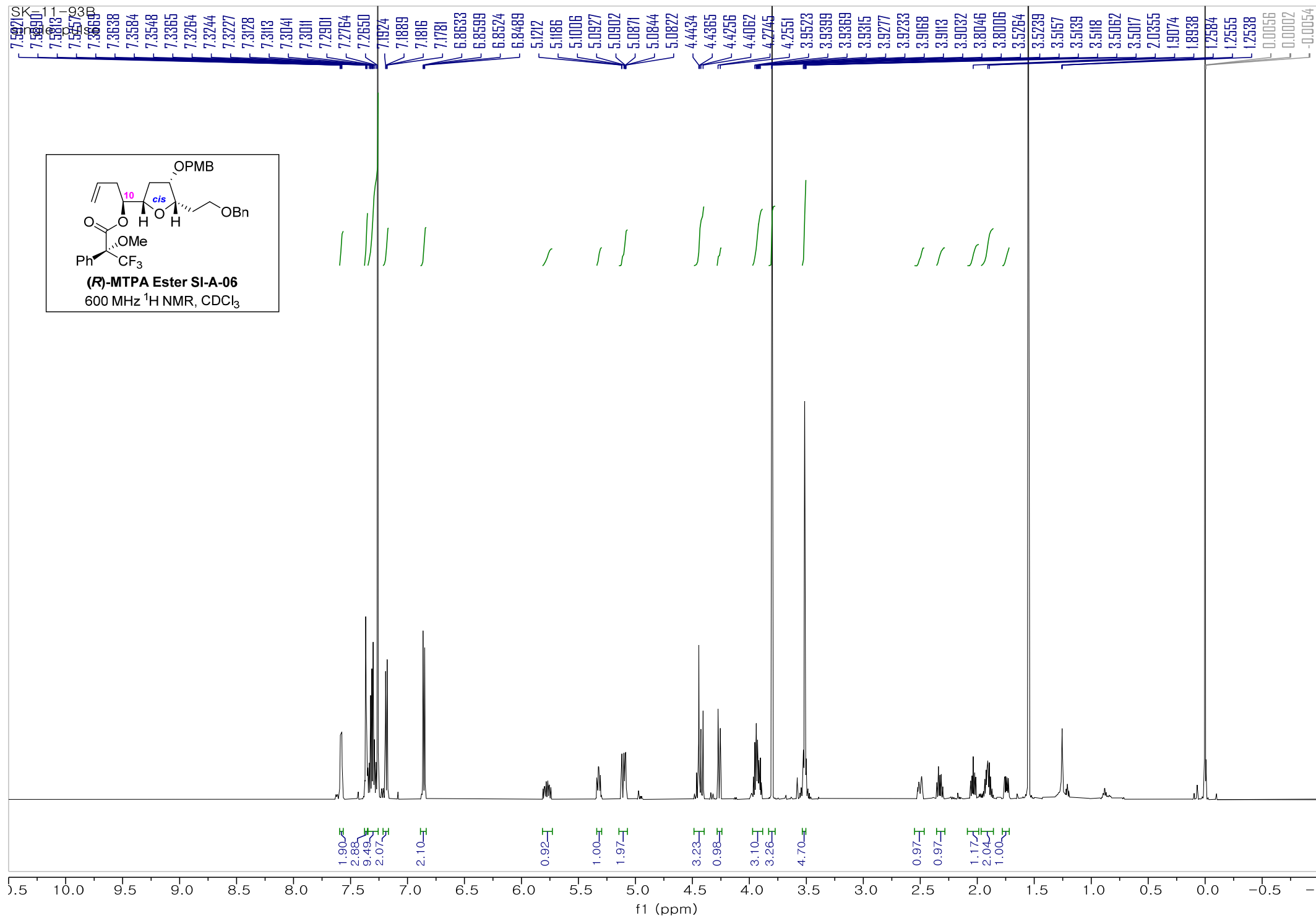






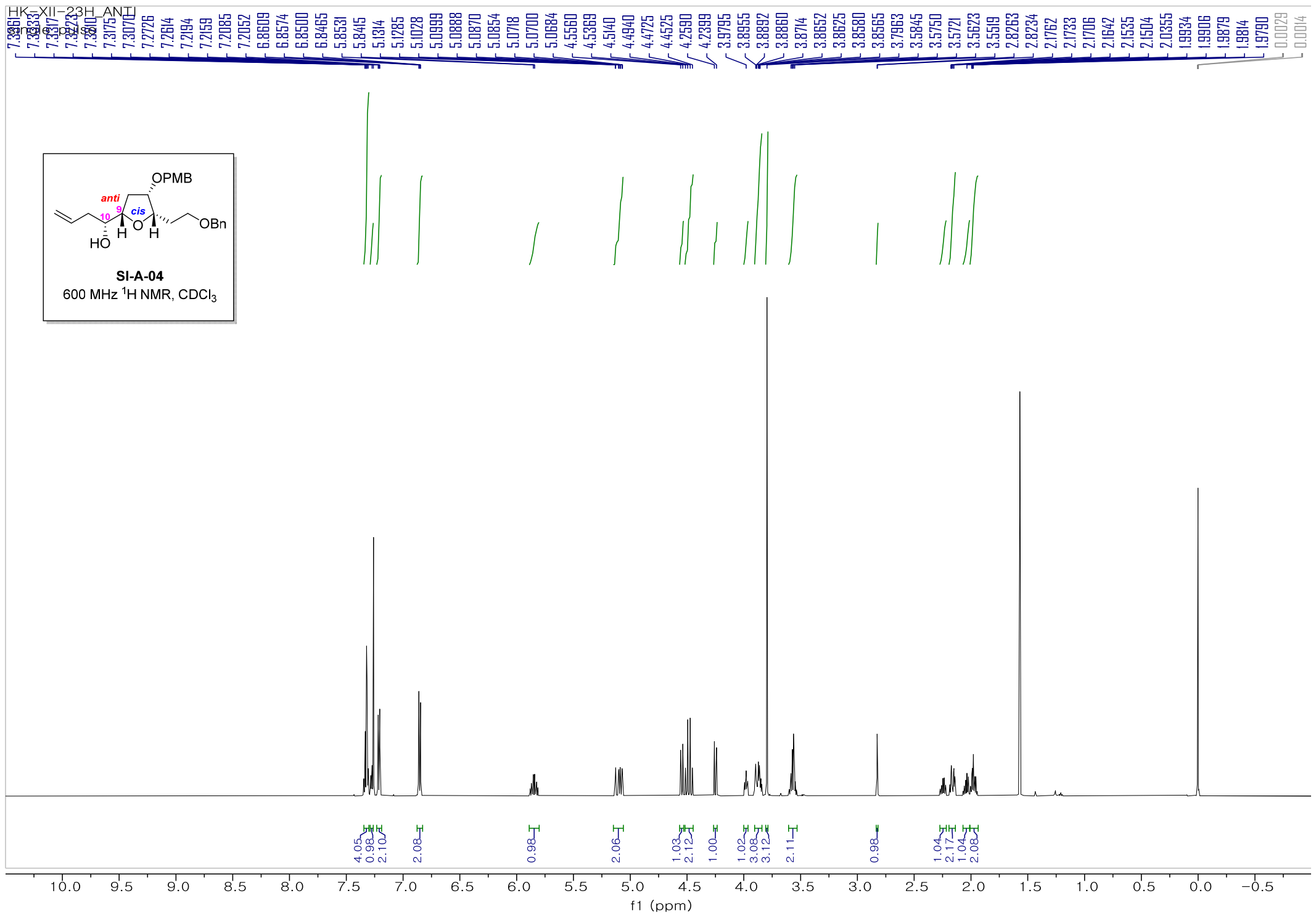
f1 (ppm)

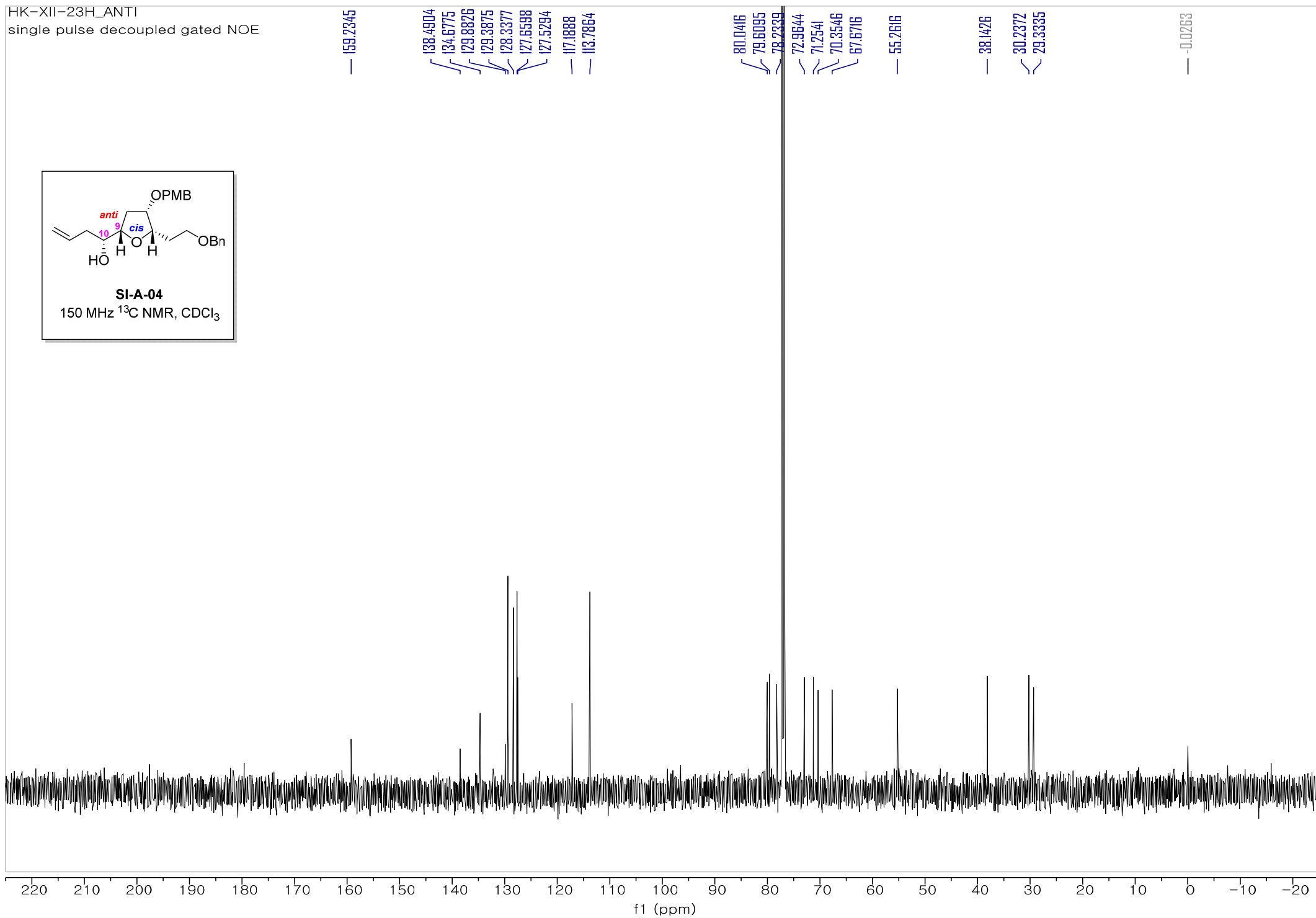
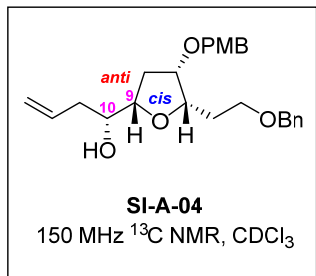
S65



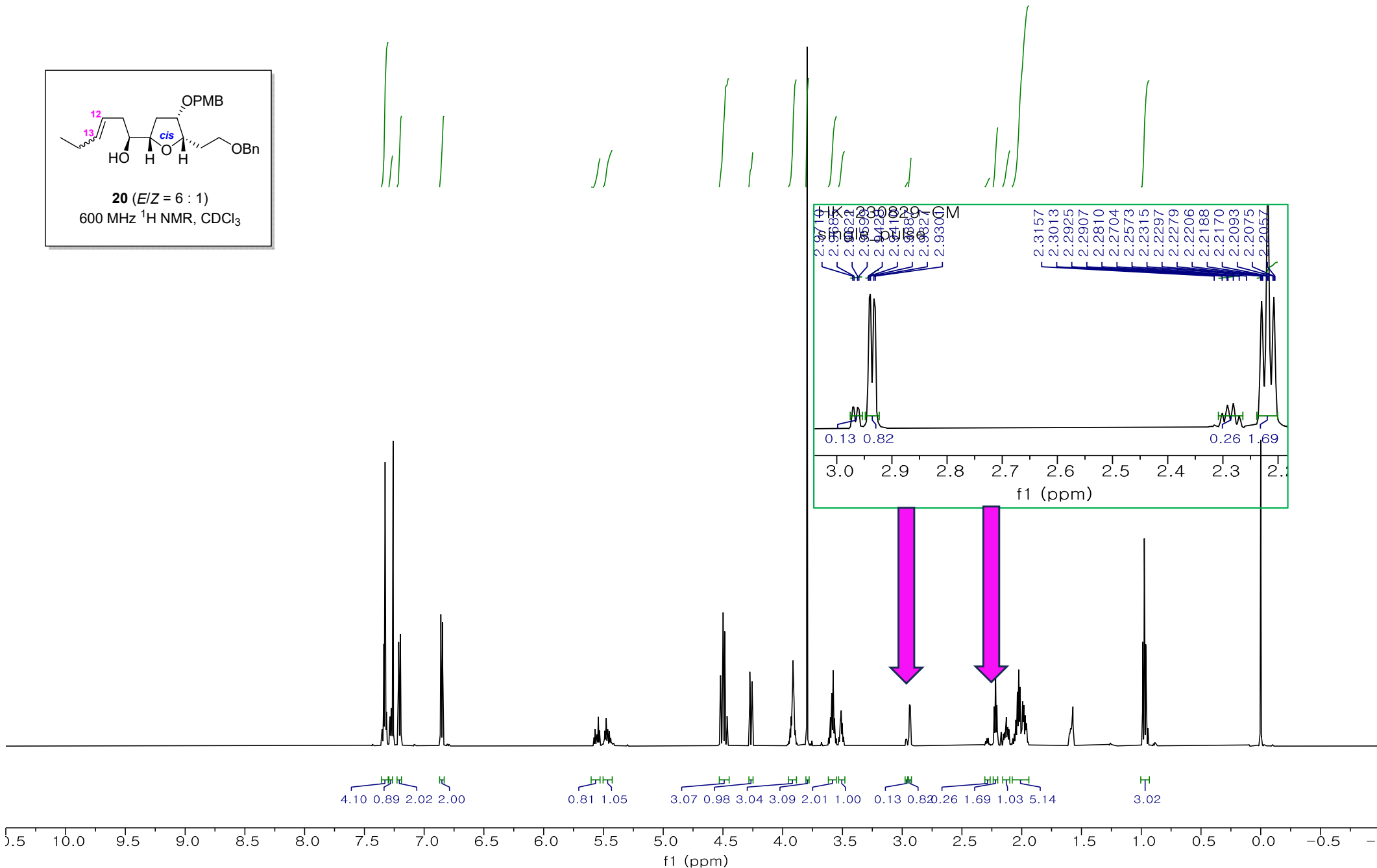
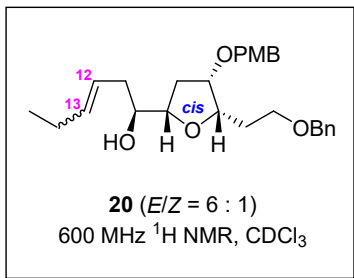
f1 (ppm)

S66

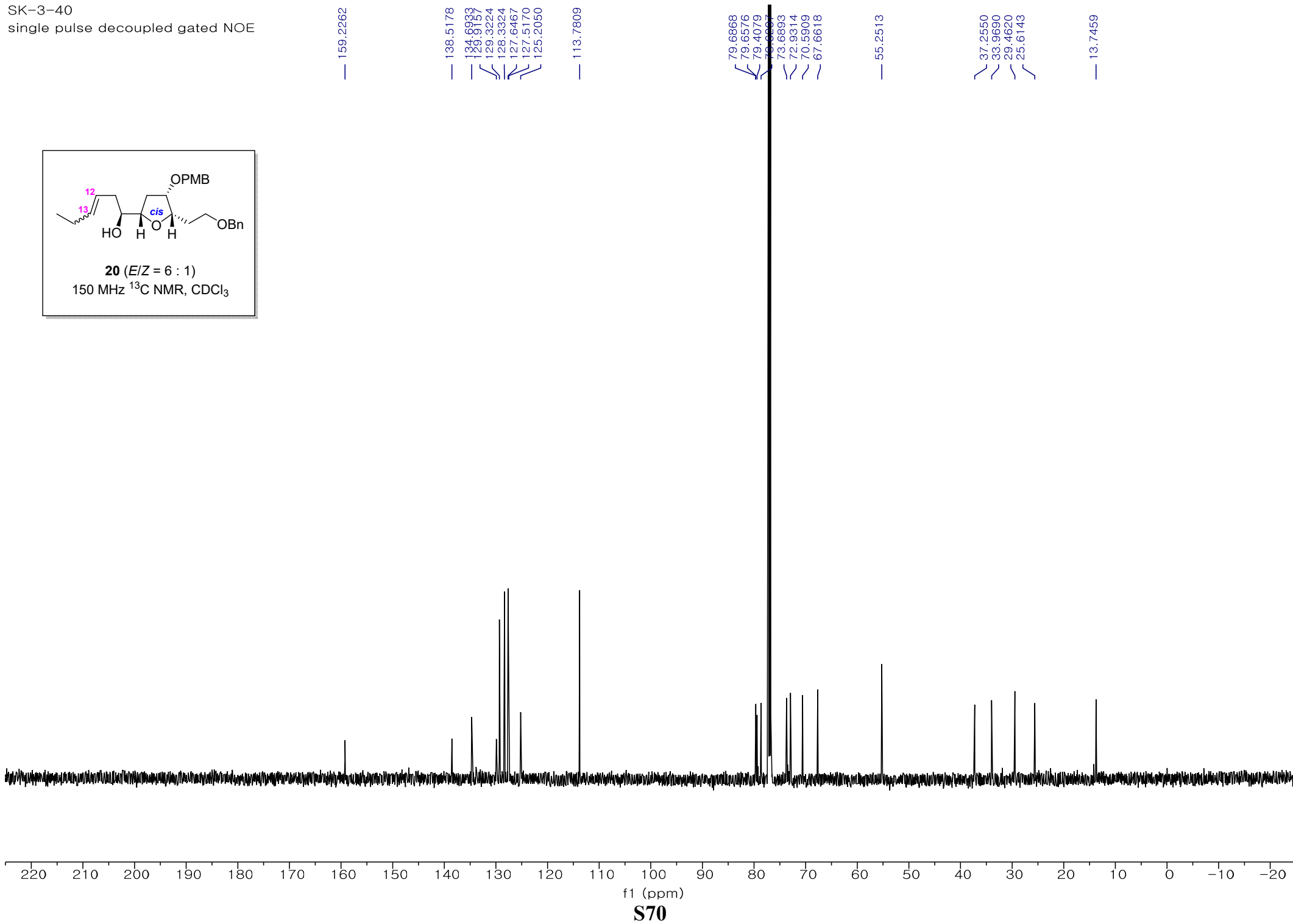
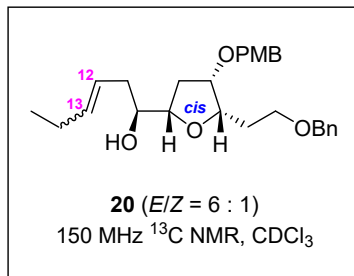


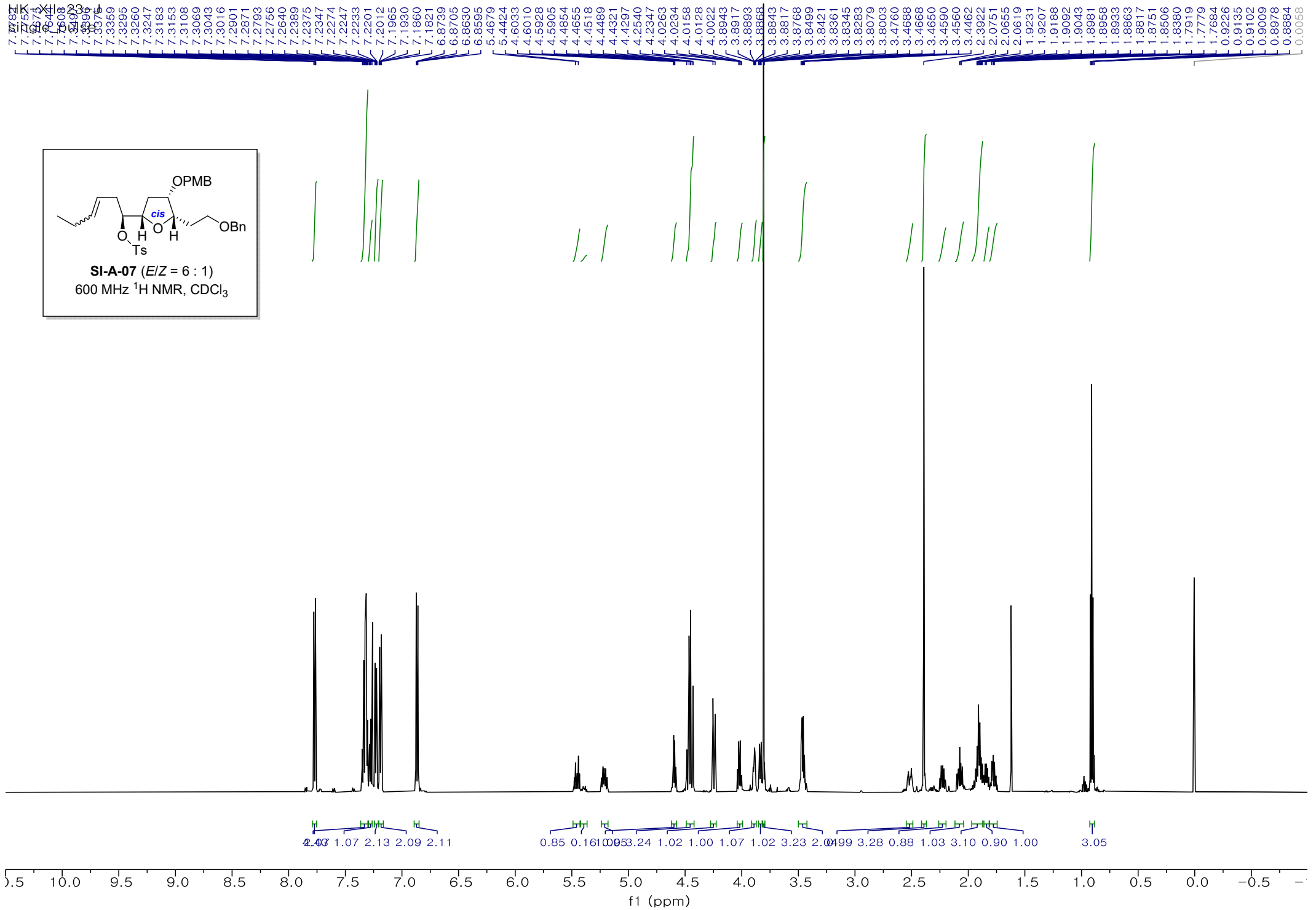


7.3071  
7.3044  
7.3016  
7.2986  
7.2956  
7.2926  
7.2894  
7.2866  
7.2798  
7.2749  
7.2645  
7.2128  
7.2018  
7.1987  
6.8603  
6.8592  
6.8564  
6.8491  
6.8456  
5.5434  
5.5418  
5.4772  
5.4755  
4.5195  
4.5012  
4.4983  
4.4848  
4.4648  
4.2744  
4.2554  
3.9293  
3.9235  
3.9208  
3.9147  
3.9090  
3.9020  
3.7963  
3.6005  
3.5938  
3.5911  
3.5881  
3.5780  
3.5677  
3.5212  
3.5188  
3.5176  
3.5105  
3.5032  
3.5020  
3.4995  
2.9428  
2.9410  
2.9387  
2.9327  
2.9301  
2.9301  
2.2315  
2.2297  
2.2279  
2.2206  
2.2188  
2.2170  
2.2093  
2.2075  
2.2057  
2.2057  
2.1294  
2.1153  
2.0505  
2.0490  
2.0466  
2.0397  
2.0379  
2.0361  
2.0342  
2.0261  
2.0239  
2.0218  
2.0134  
2.0028  
2.0011  
1.9942  
1.9914  
1.9828  
1.9786  
1.9717  
1.9690  
1.9631  
1.9597  
1.5792  
1.5753  
0.9875  
0.9861  
0.9750  
0.9736  
0.9693  
0.9679  
0.9625  
0.9611  
0.9568  
0.9554  
0.0034  
0.0017  
0.0004



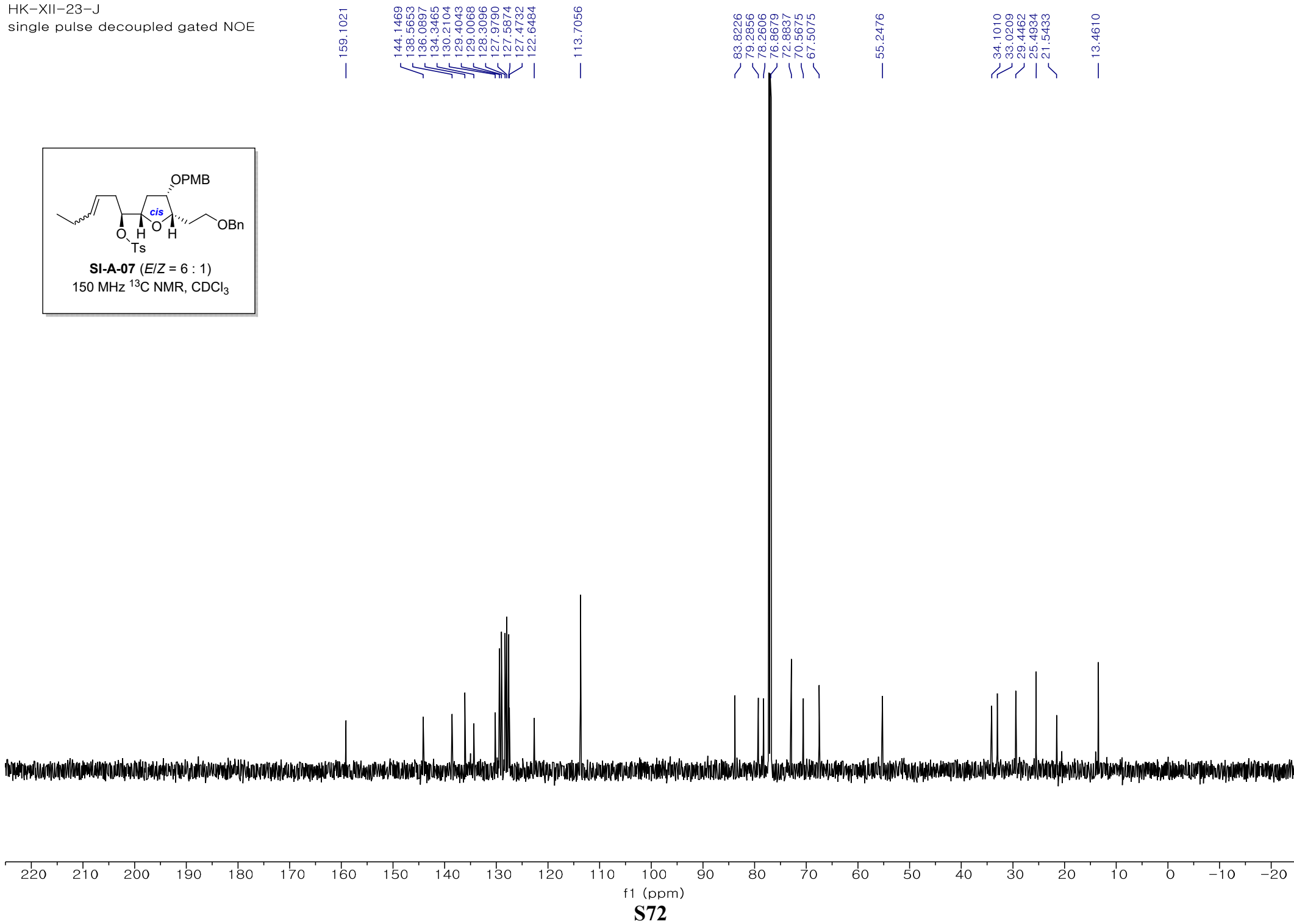
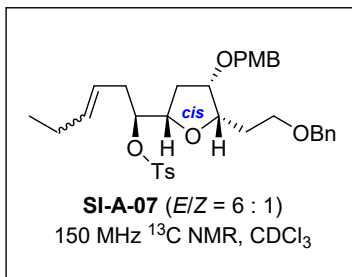
SK-3-40  
single pulse decoupled gated NOE





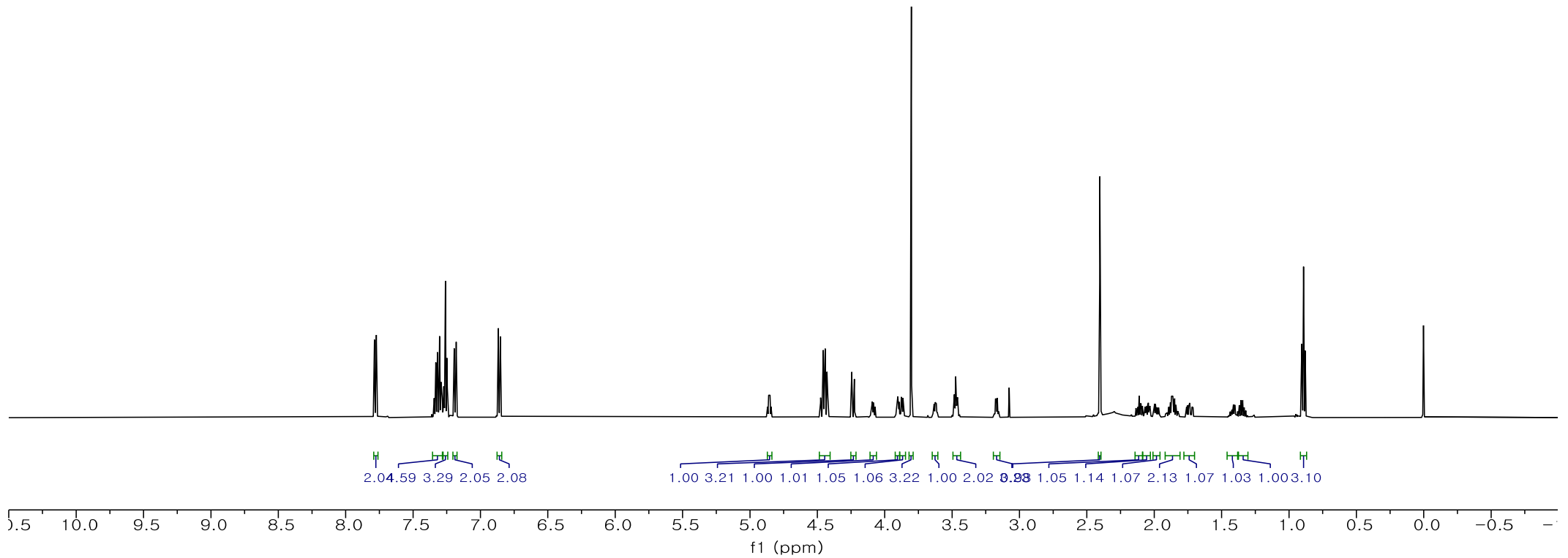
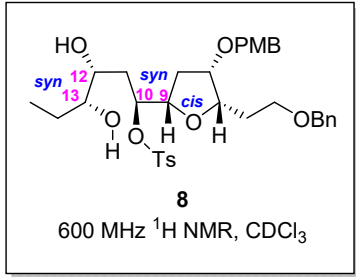
S71

HK-XII-23-J  
single pulse decoupled gated NOE



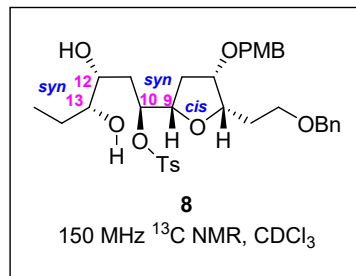


7.7051  
7.7039  
7.7027  
7.7016  
7.3411  
7.3399  
7.3387  
7.3292  
7.3226  
7.3188  
7.3062  
7.3033  
7.2992  
7.2946  
7.2919  
7.2867  
7.2840  
7.2763  
7.2725  
7.2620  
7.2478  
7.1946  
7.1911  
7.1838  
7.1803  
6.8668  
6.8634  
6.8559  
6.8525  
4.8619  
4.8585  
4.8543  
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3.8025  
3.6342  
3.6320  
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3.6246  
3.6192  
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3.4810  
3.4741  
3.4719  
3.4688  
3.4638  
3.4594  
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3.1640  
3.0767  
2.4034  
2.1117  
2.1020  
2.0982  
2.0882  
2.0485  
2.0433  
2.0375  
2.0023  
1.9976  
1.9909  
1.9862  
1.8838  
1.8803  
1.8719  
1.8487  
1.8389  
1.7523  
1.7371  
1.7350  
1.4126  
1.4054  
1.4001  
1.3692  
1.3571  
1.3556  
1.3434  
0.9045  
0.8921  
0.8797  
0.0021



**S73**

HK-230902-1C  
single pulse decoupled gated NOE



159.0302

144.4705  
138.3598  
133.8630  
130.0062  
129.5315  
128.9810  
128.1962  
127.7405  
127.4817  
127.4433  
127.3866

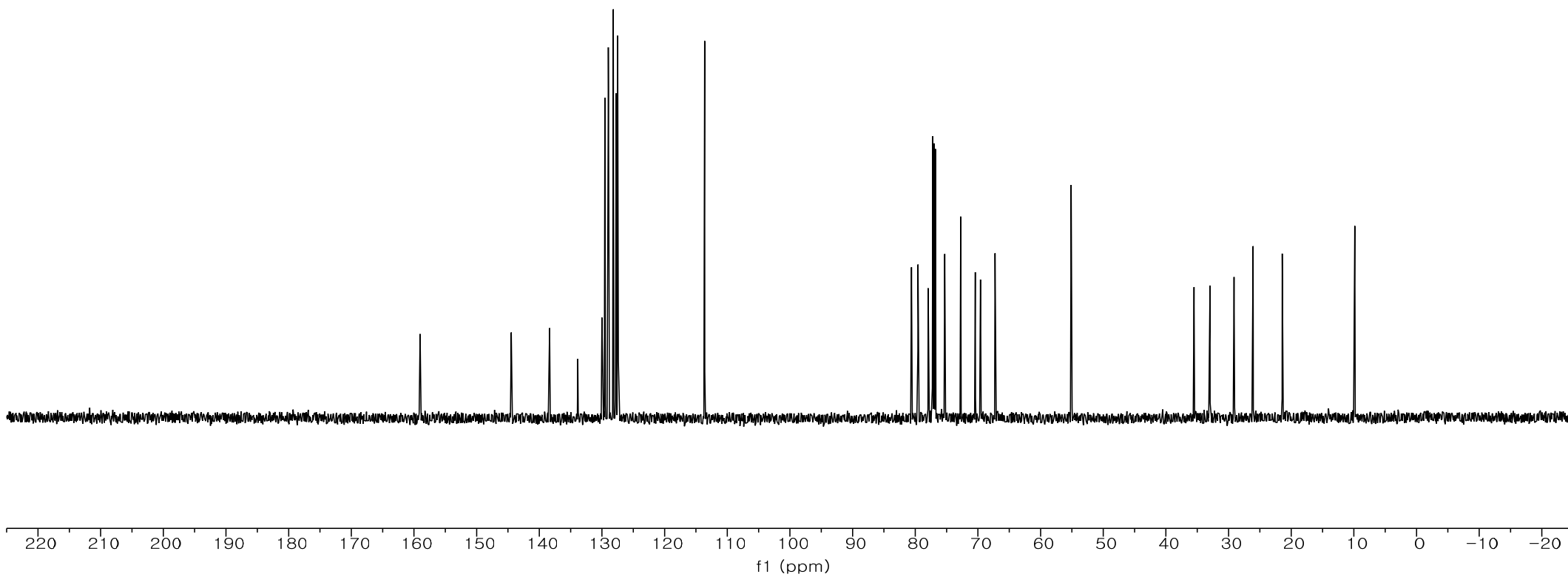
113.6124

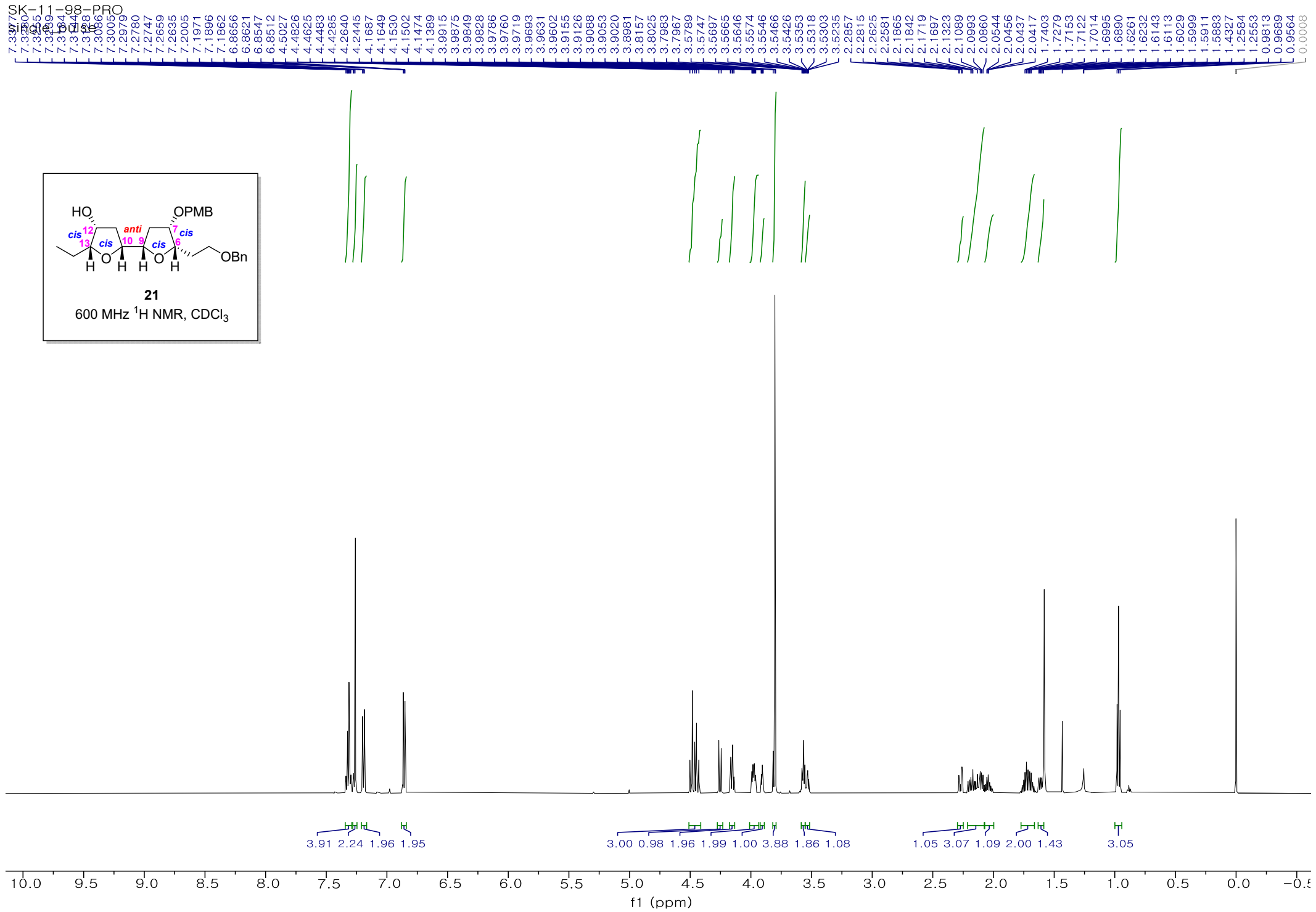
80.6101  
79.5723  
77.9403  
77.2632  
75.2991  
72.7518  
70.4198  
69.5861  
67.2627

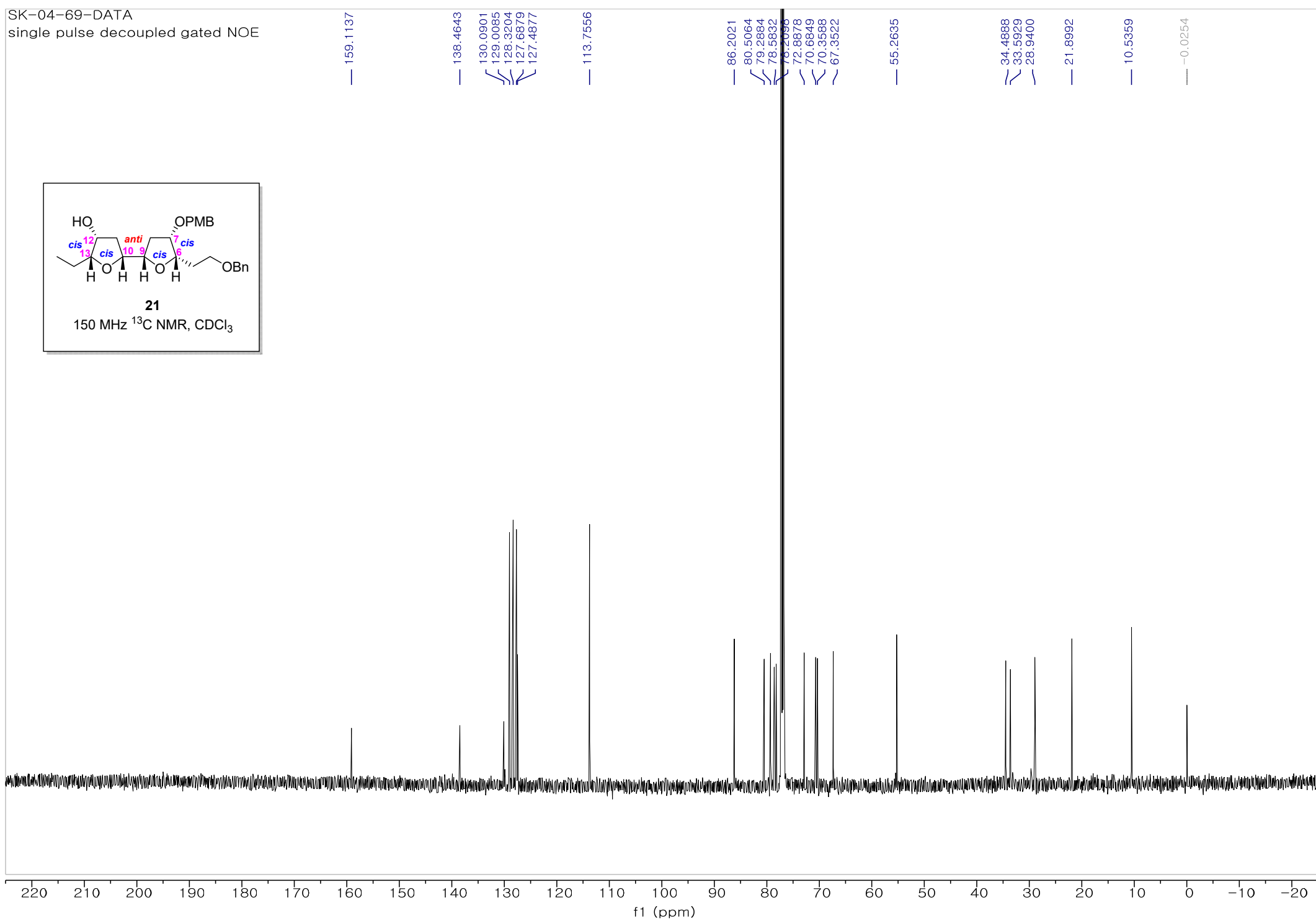
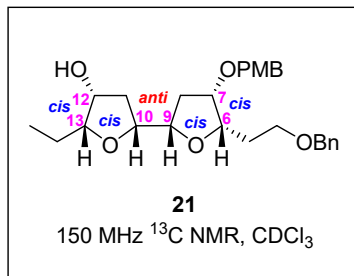
55.1145

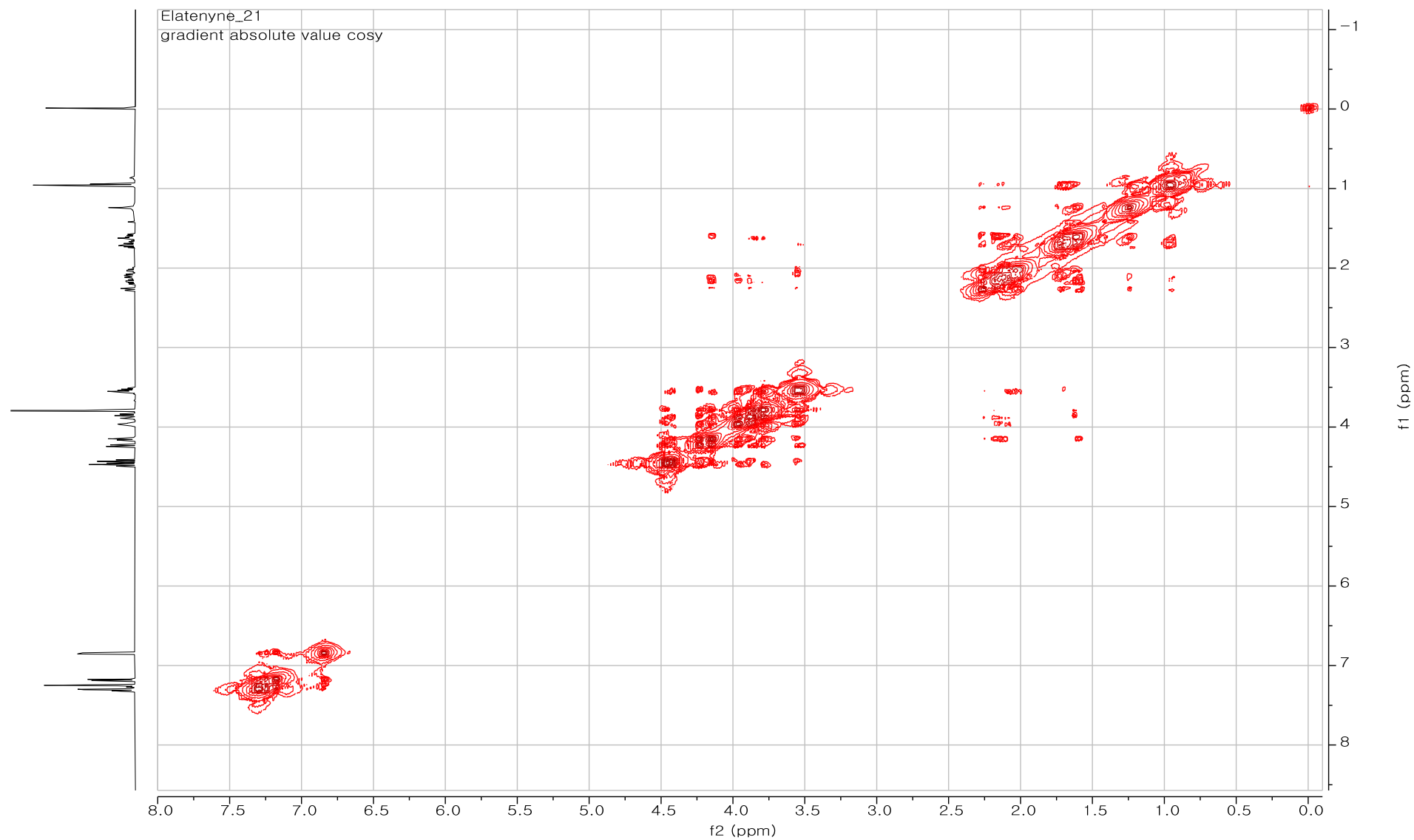
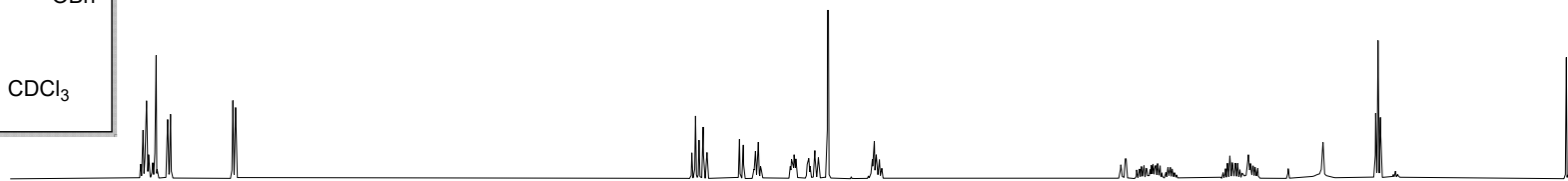
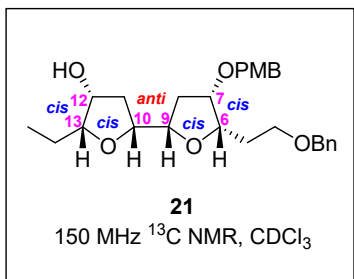
35.5102  
32.9679  
29.1255  
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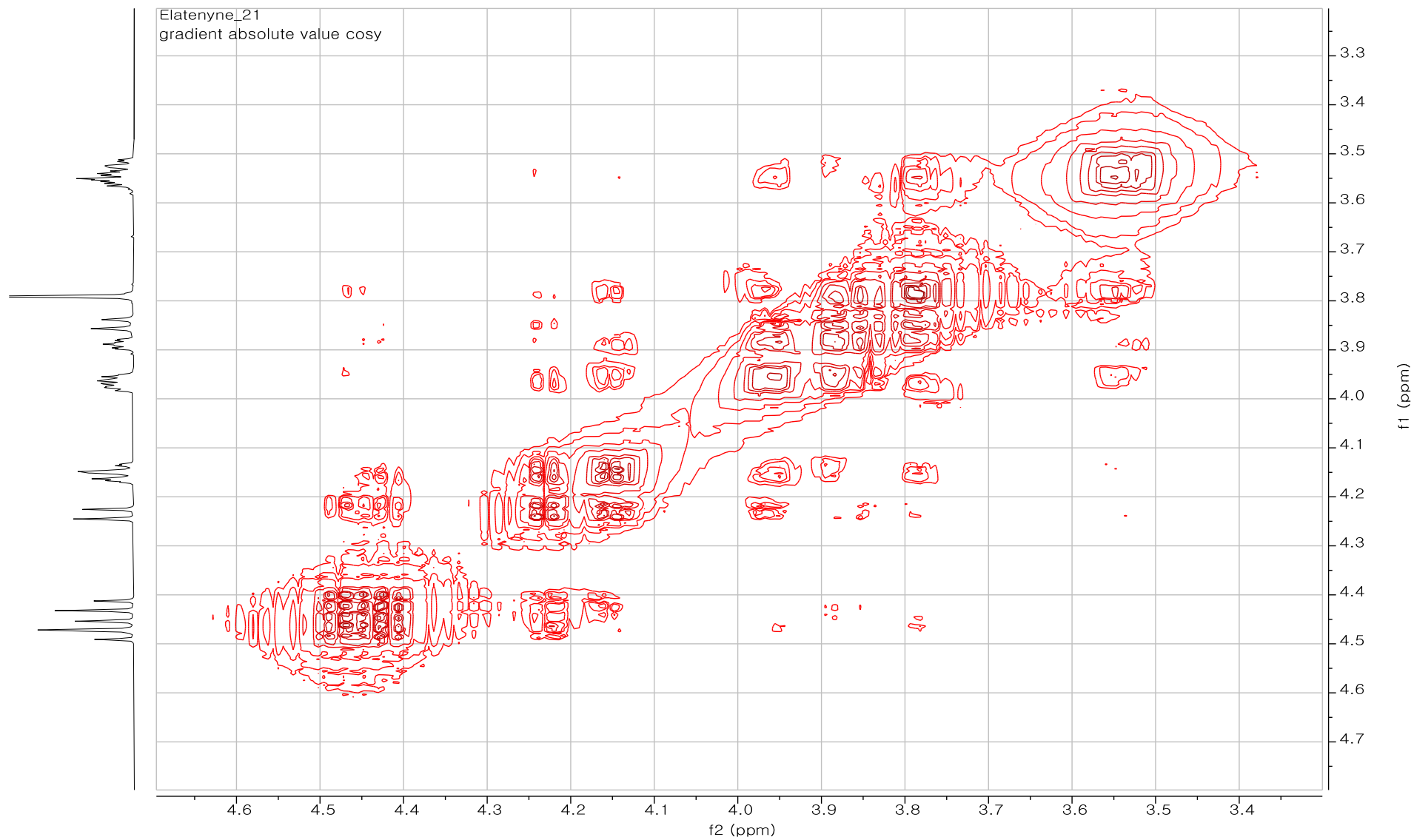
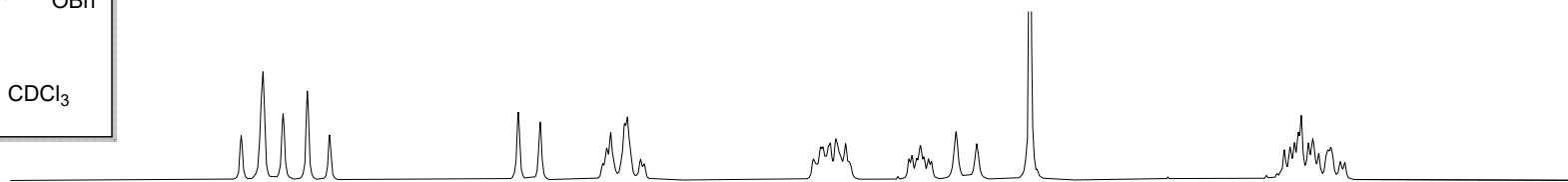
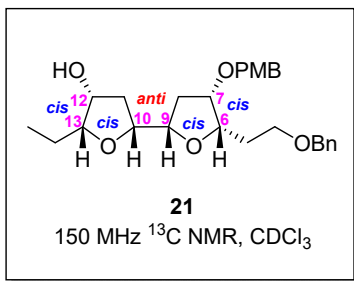
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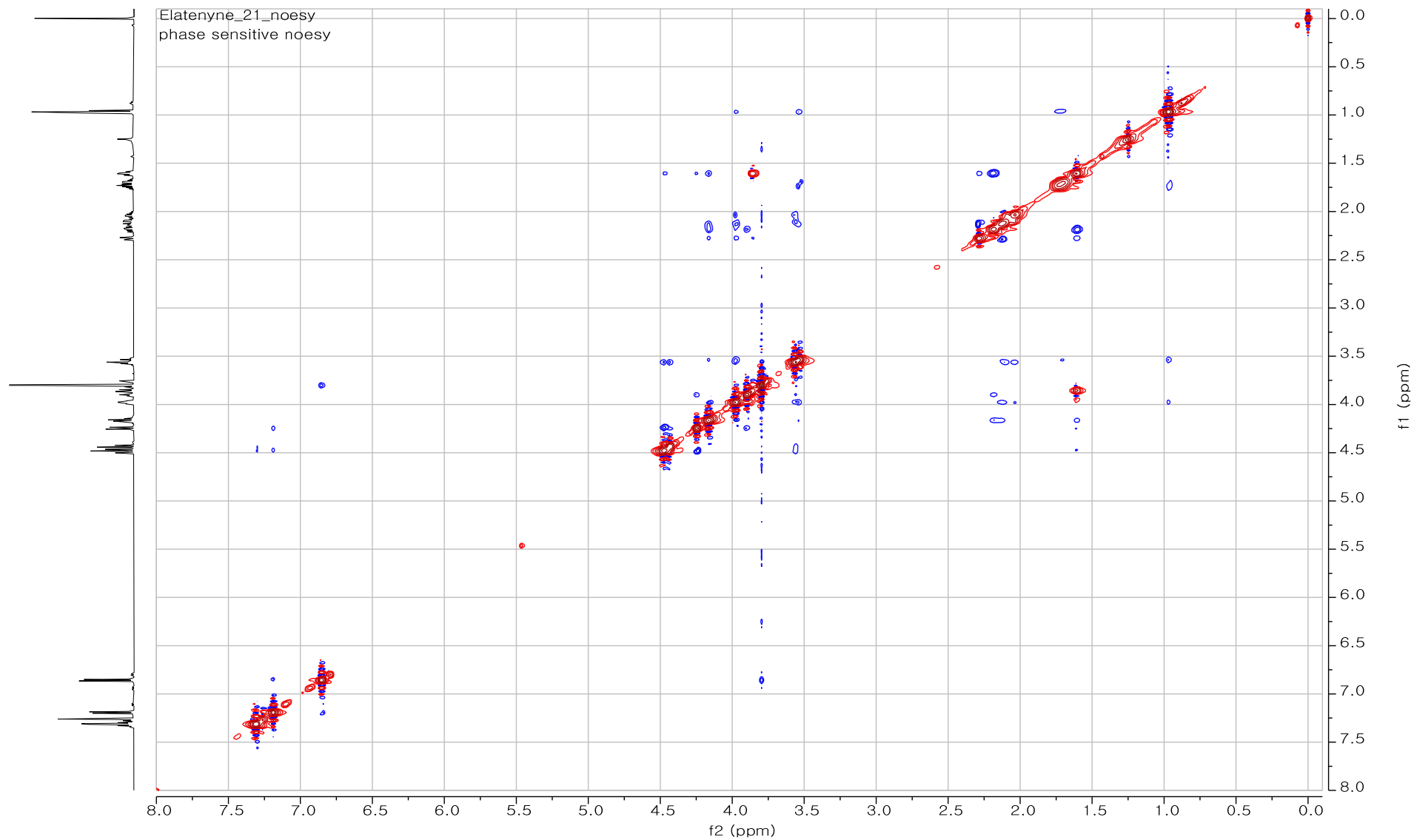
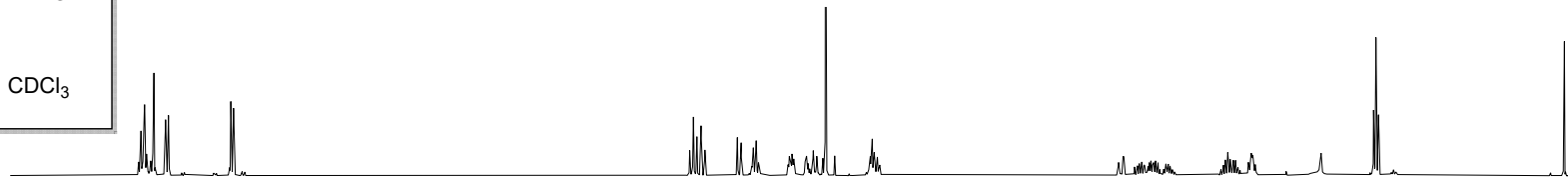
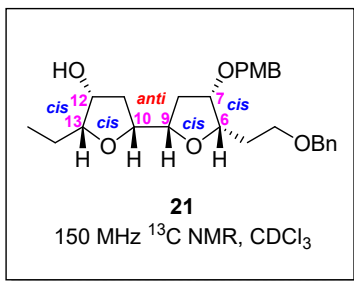


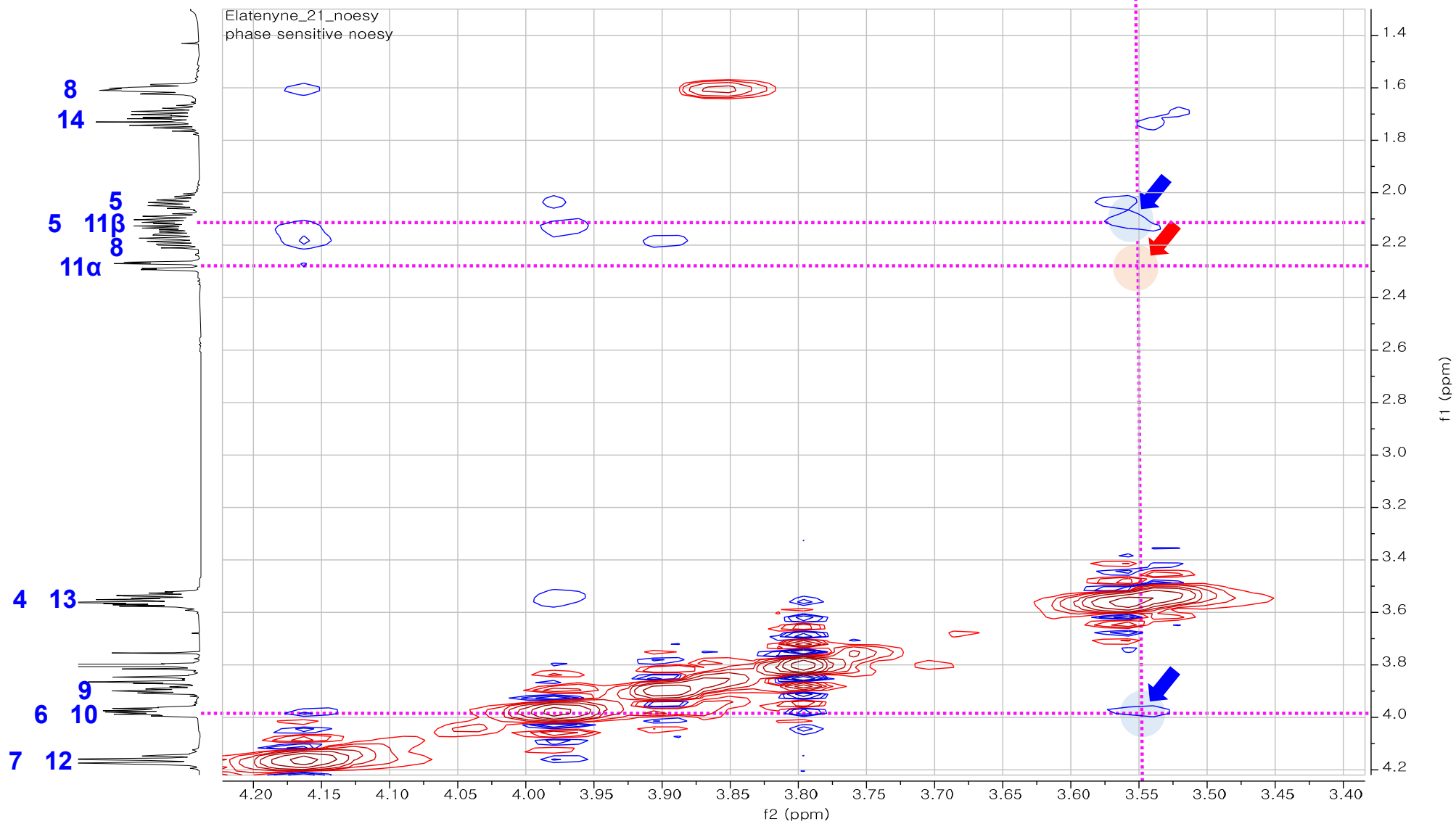
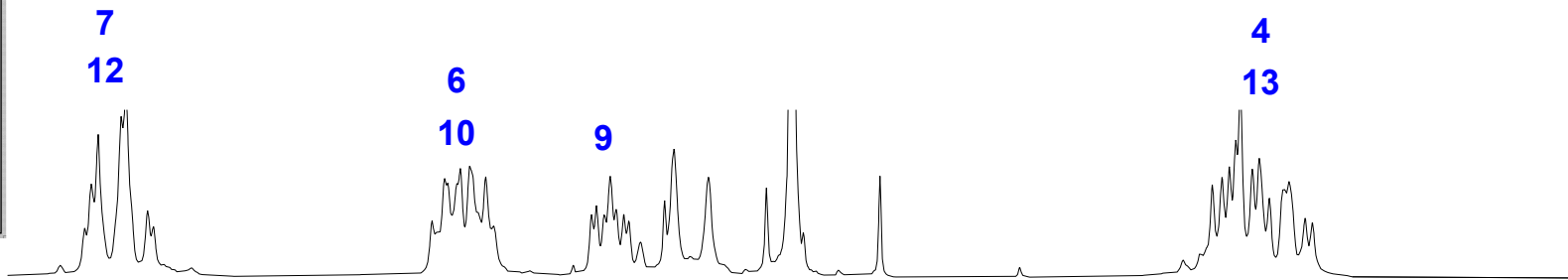
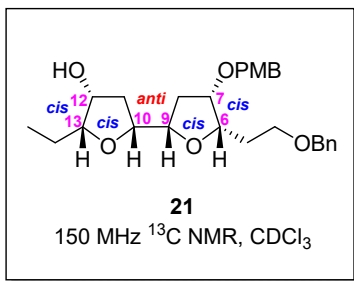






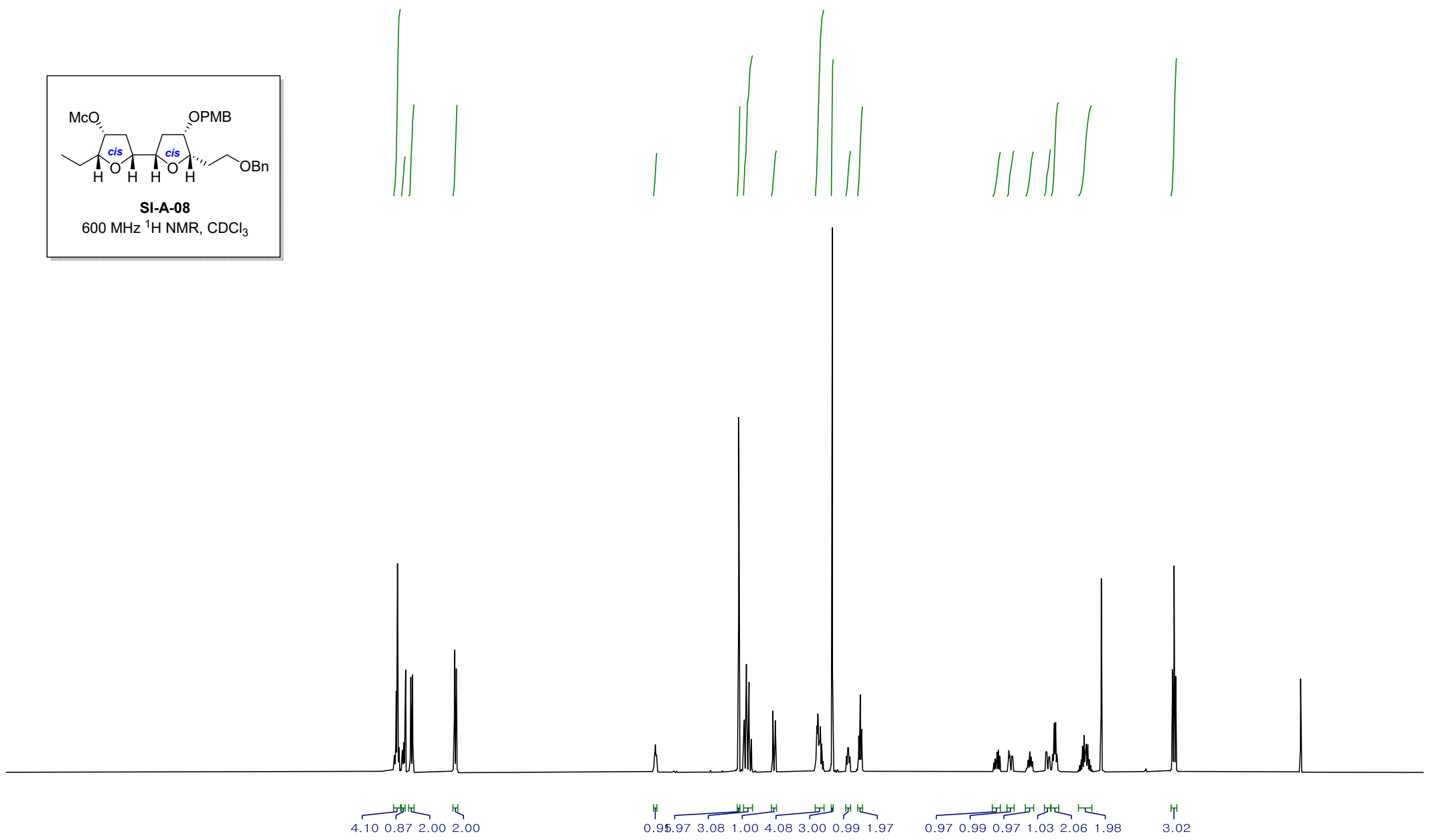
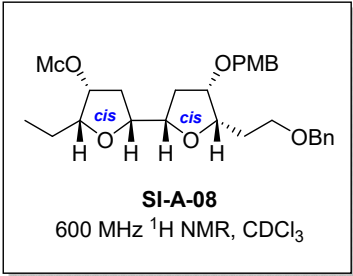








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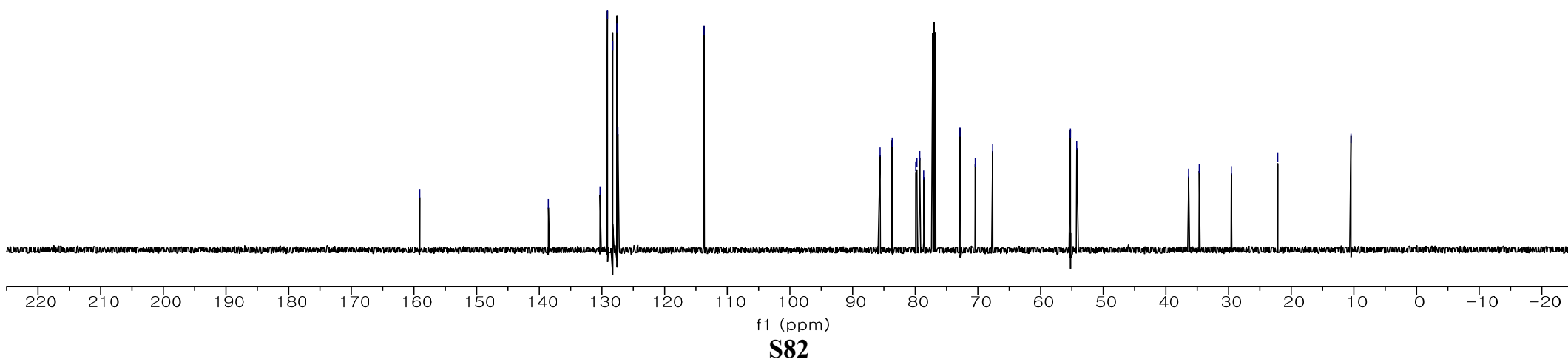
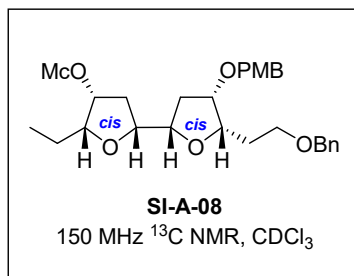


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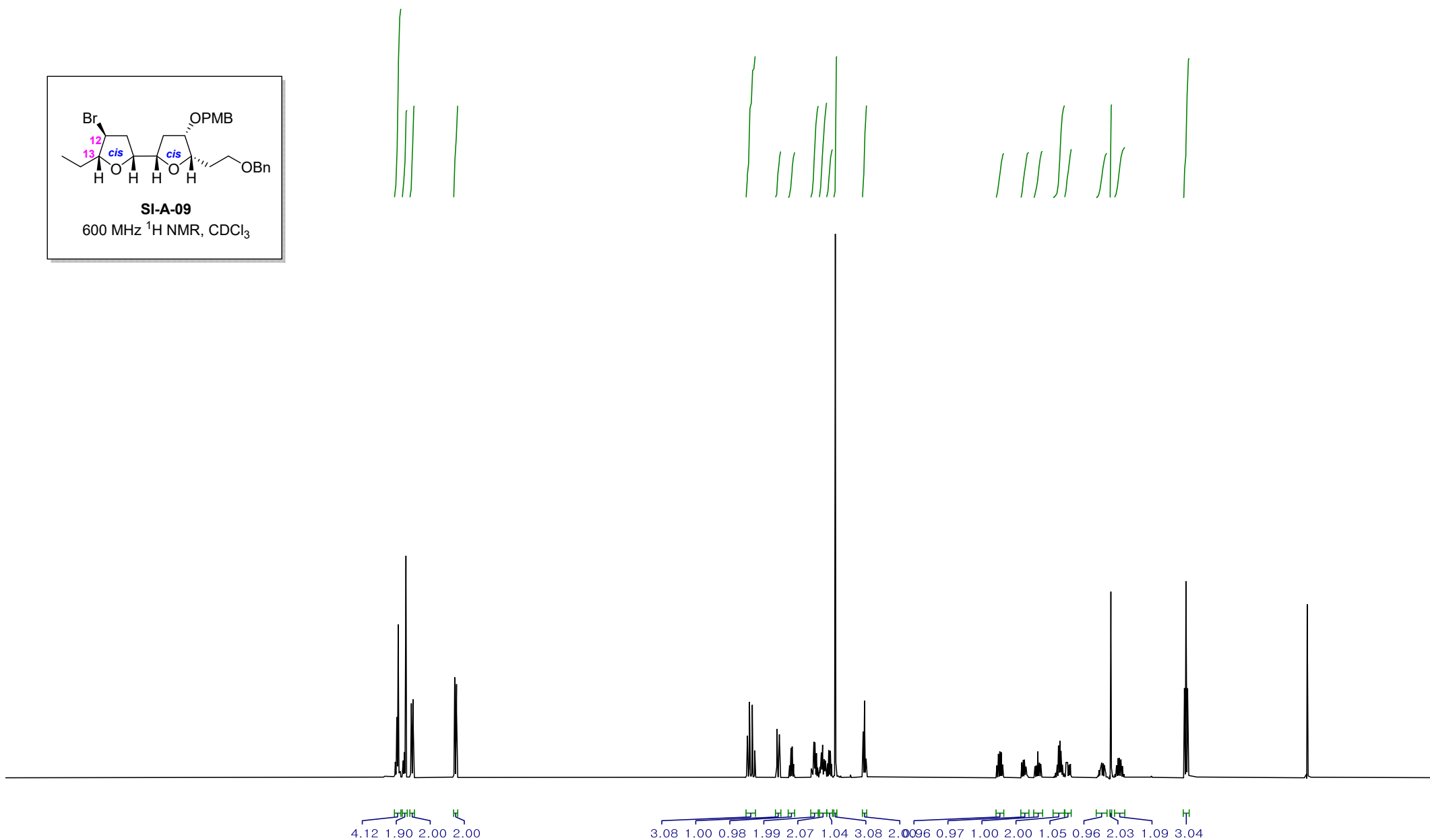
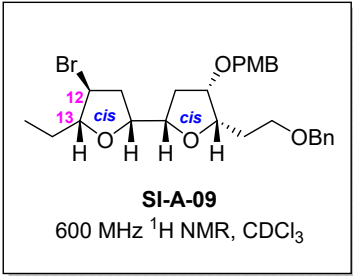
f1 (ppm)

**S81**

SK-2-4-C  
single pulse decoupled gated NOE

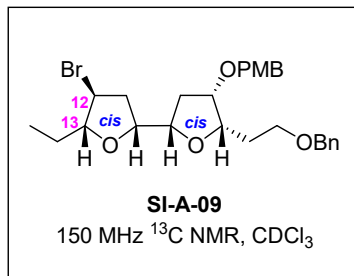


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f1 (ppm)  
**S83**

SK-2-14-C  
single pulse decoupled gated NOE



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— 138.5597

130.2630

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127.4394

— 113.7116

— 88.3697

80.2163

79.6905

79.0677

78.4707

72.8379

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55.1901

— 49.3082

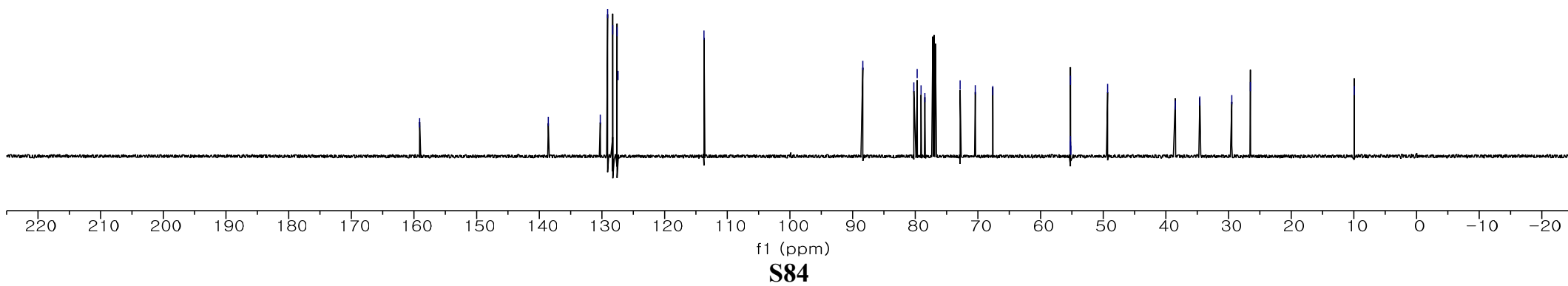
— 38.4877

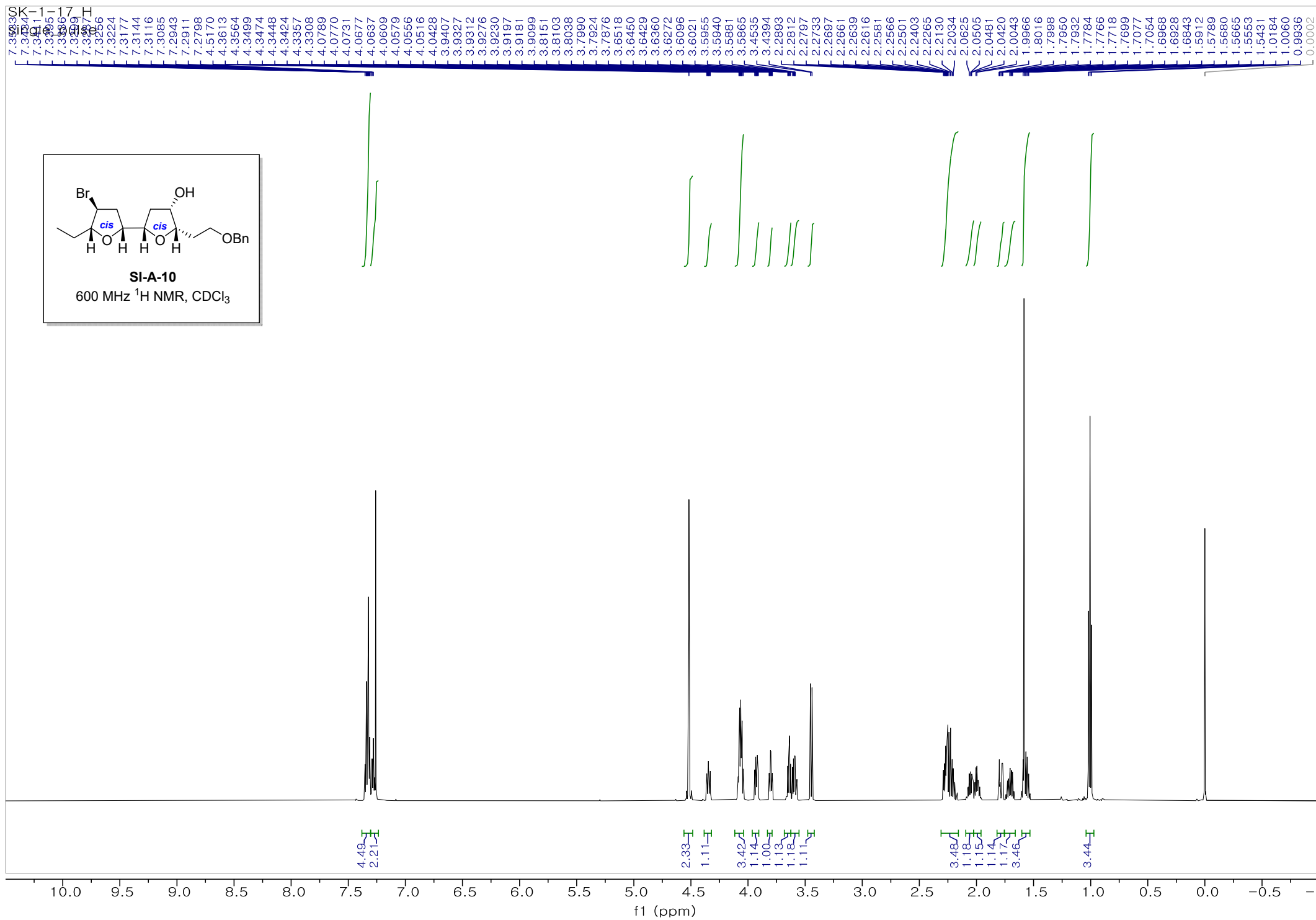
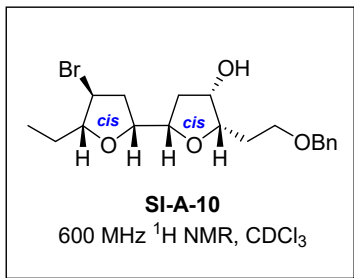
— 34.5898

— 29.4906

— 26.5140

— 9.9512

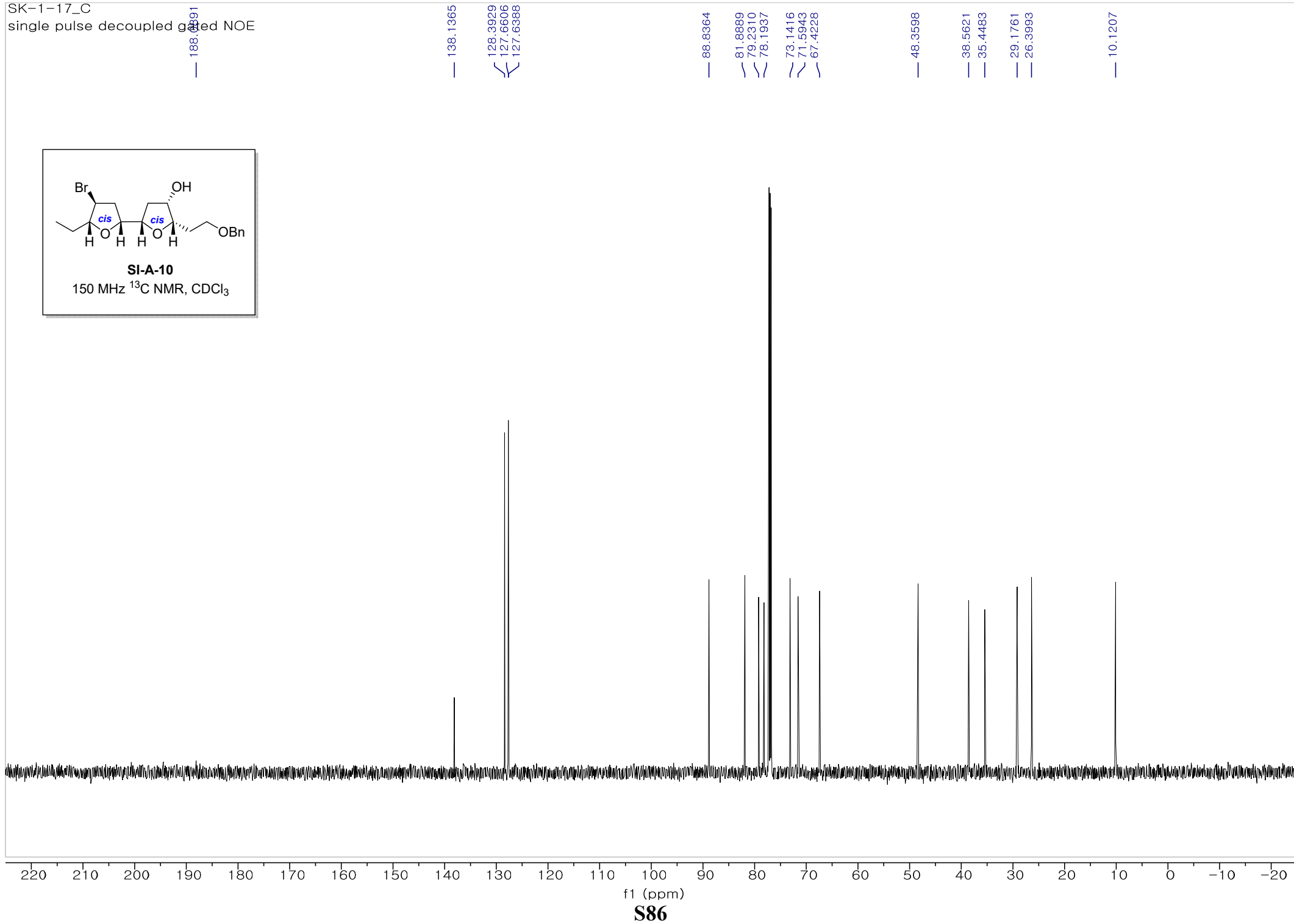
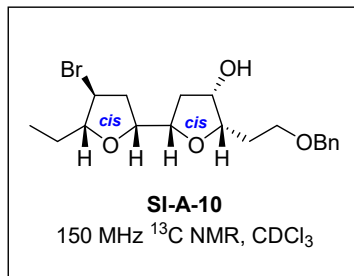




f1 (ppm)

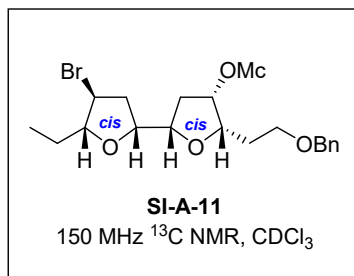
S85

SK-1-17\_C  
single pulse decoupled gated NOE



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SK-2-18\_C  
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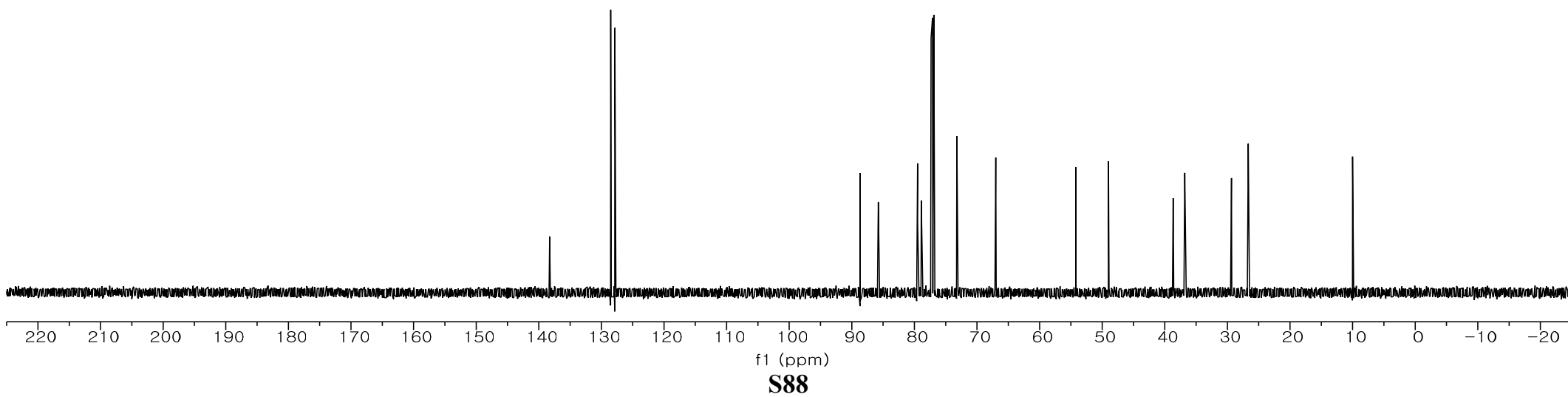
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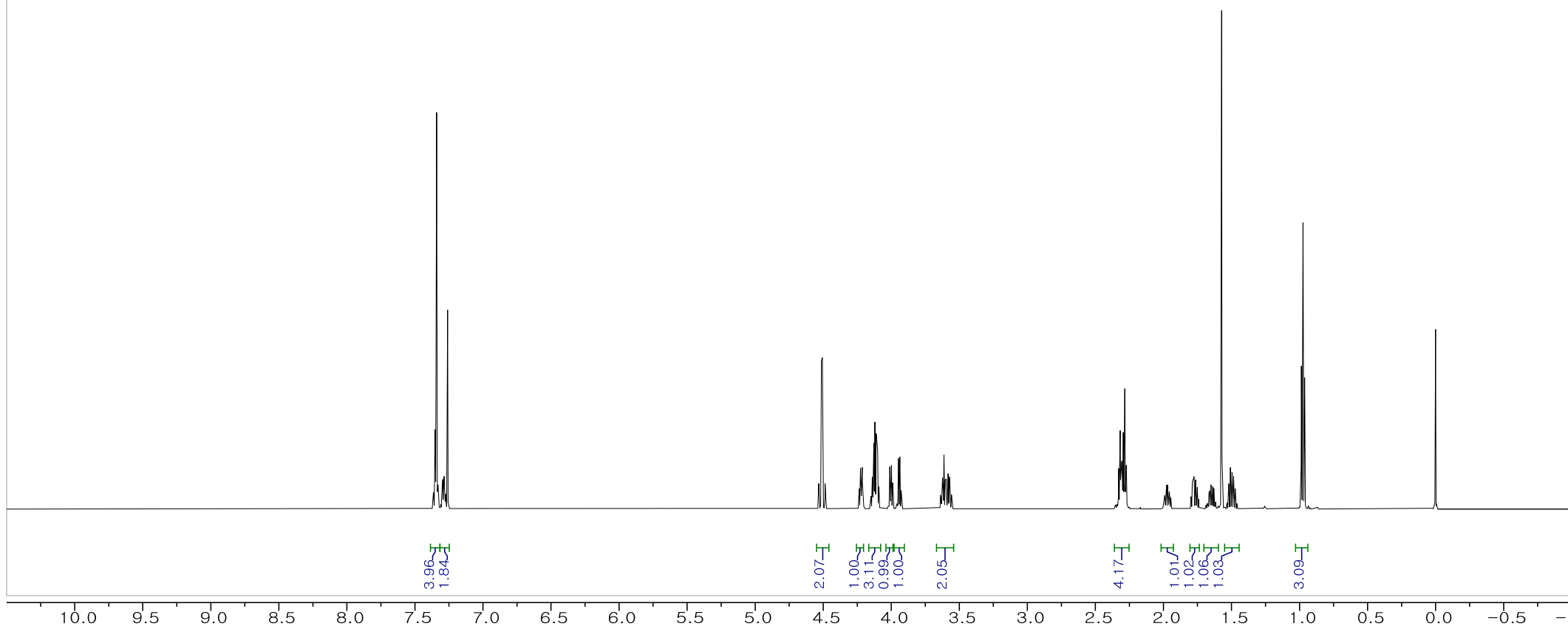
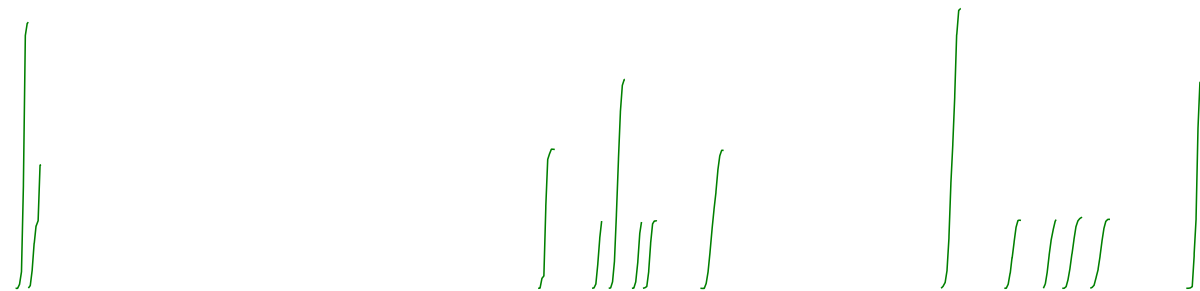
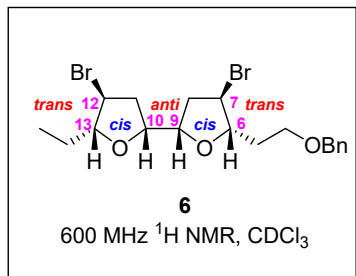
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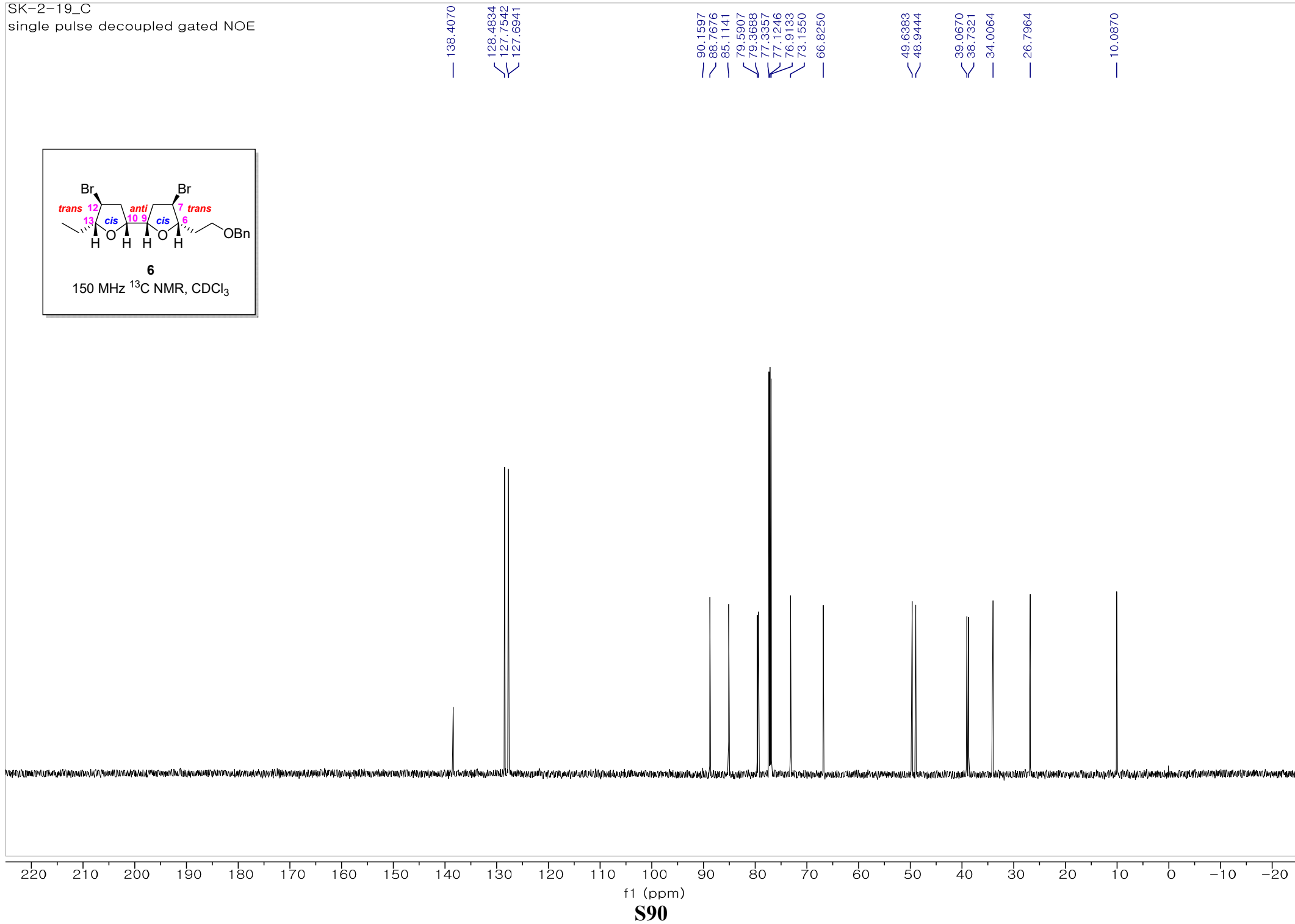
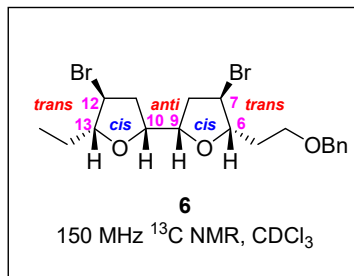
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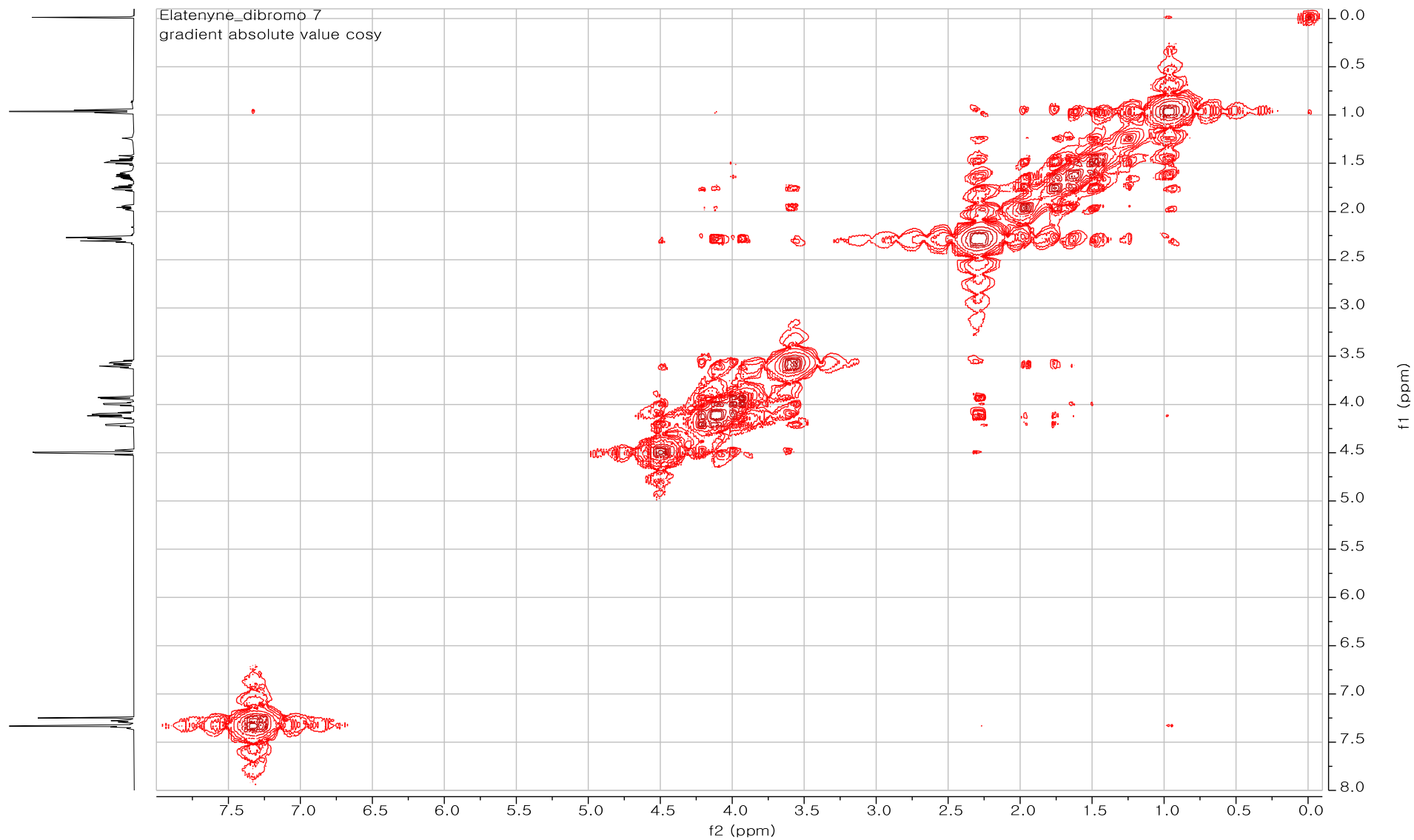
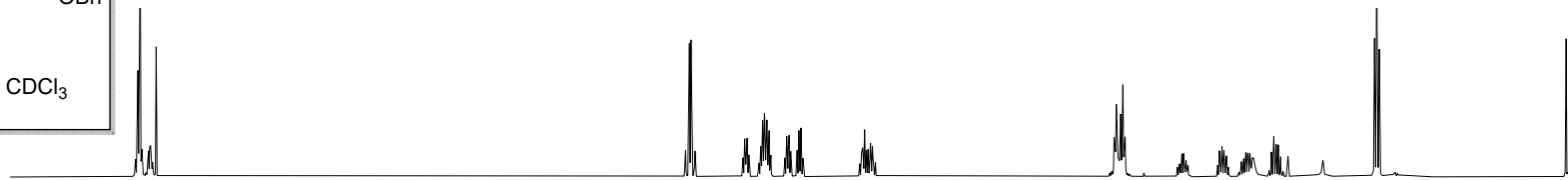
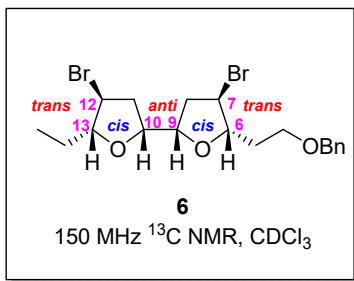


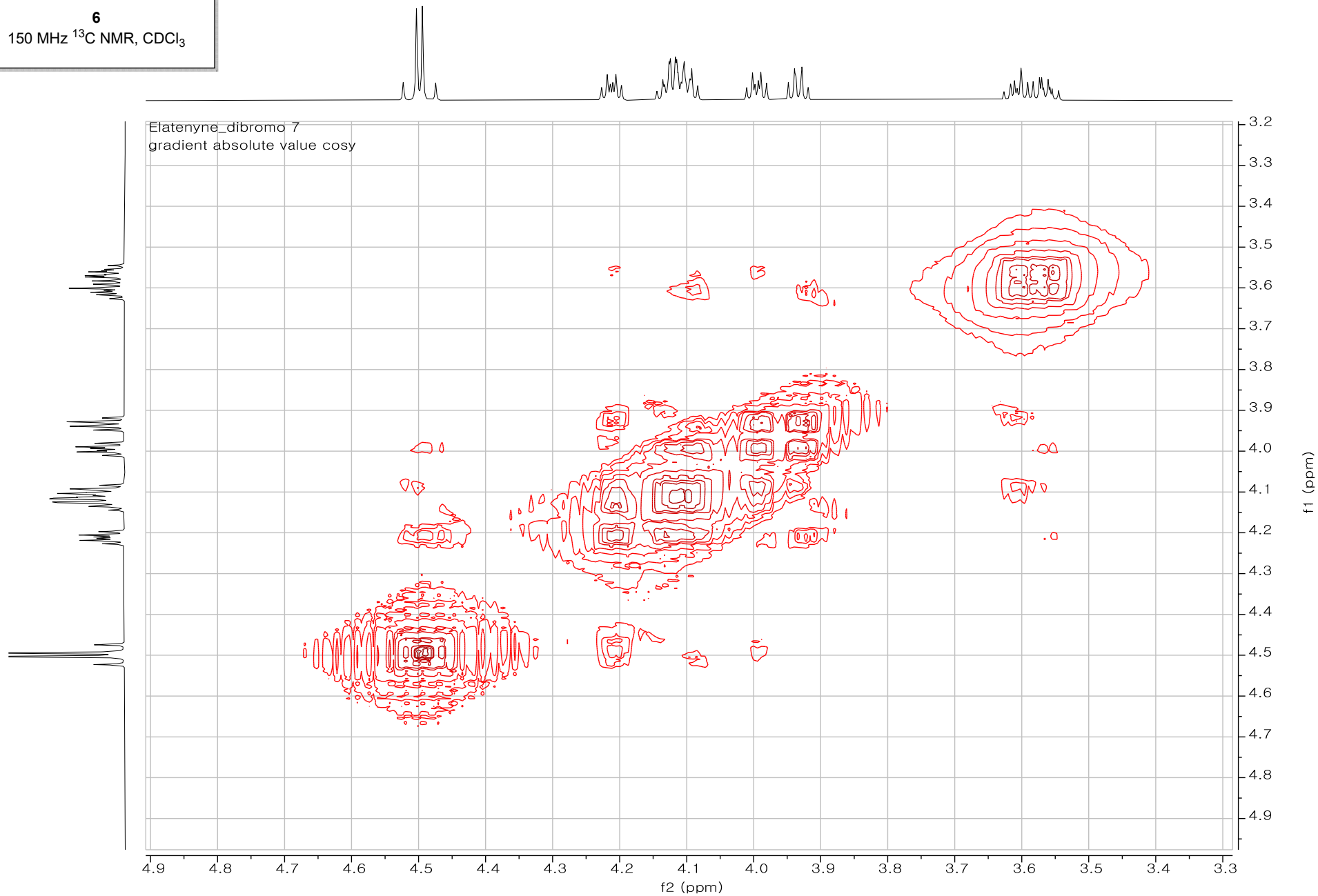
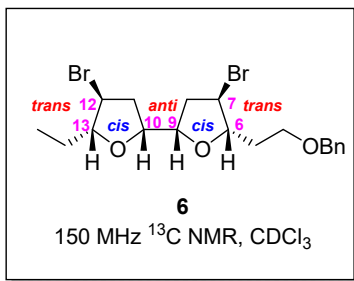
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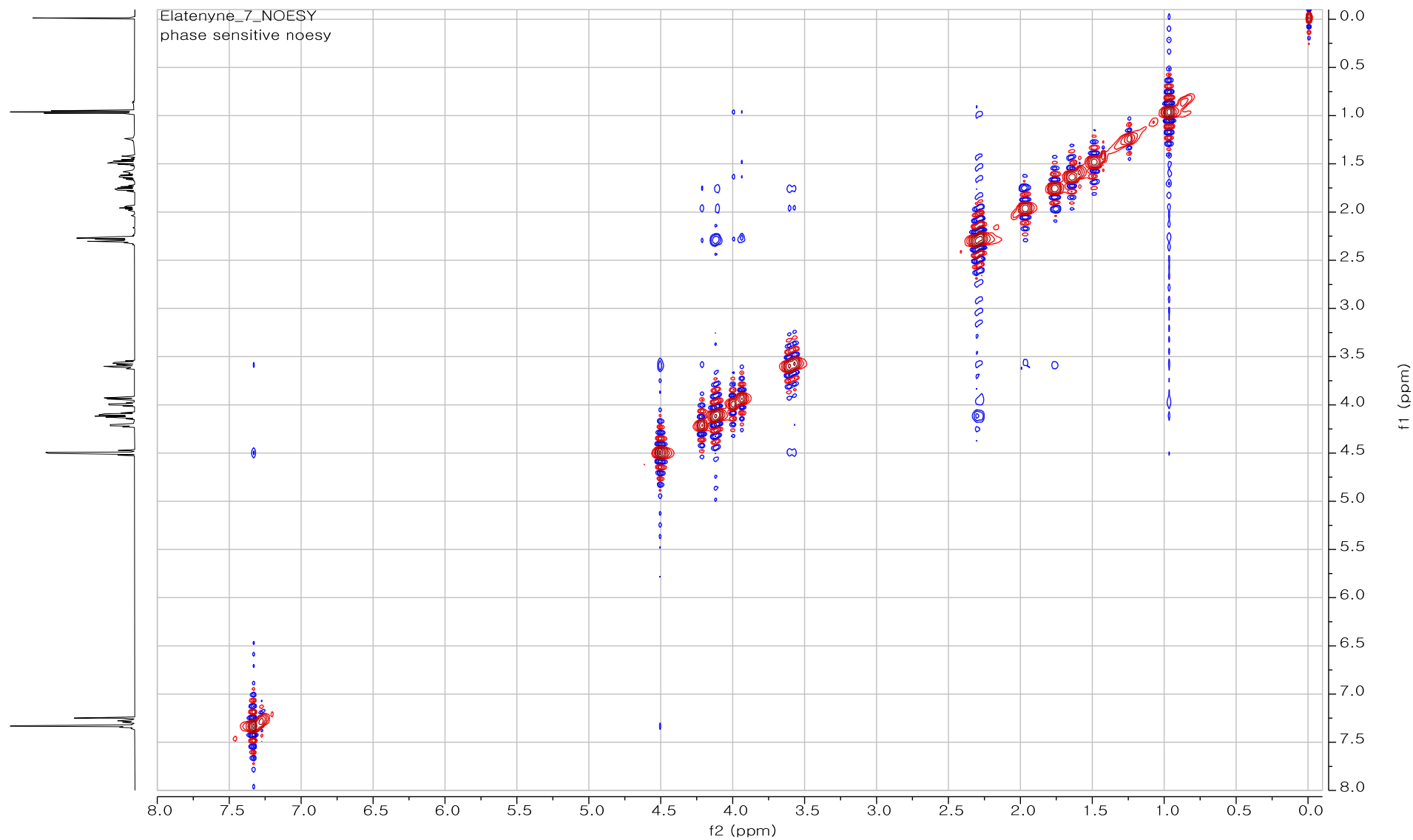
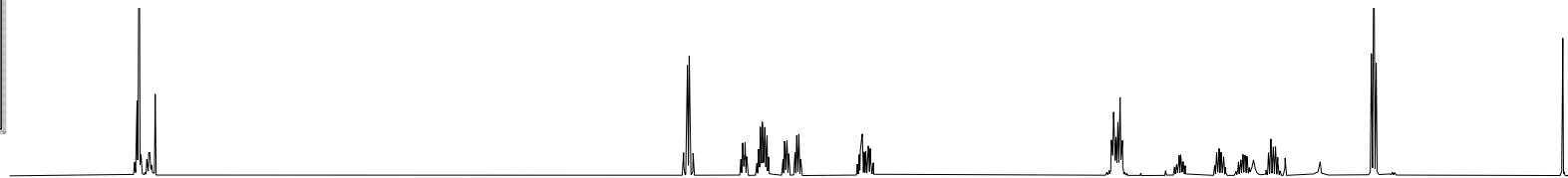
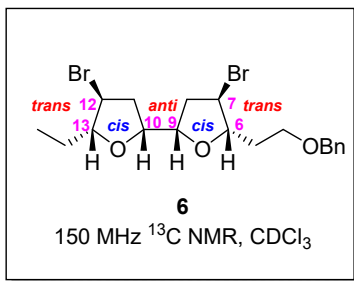
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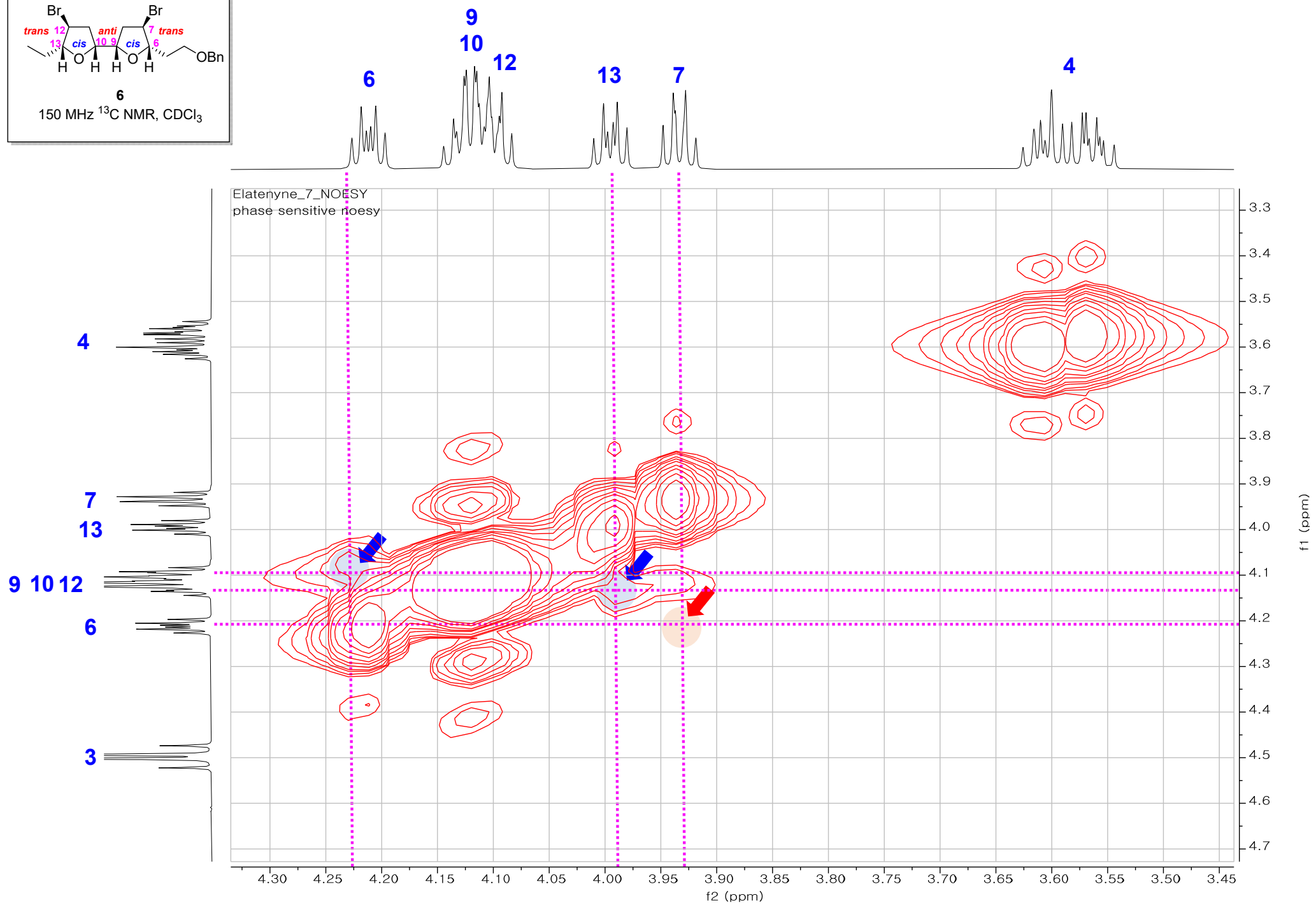
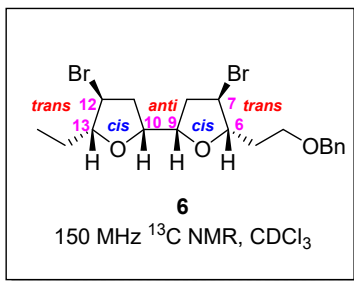
single pulse decoupled gated NOE

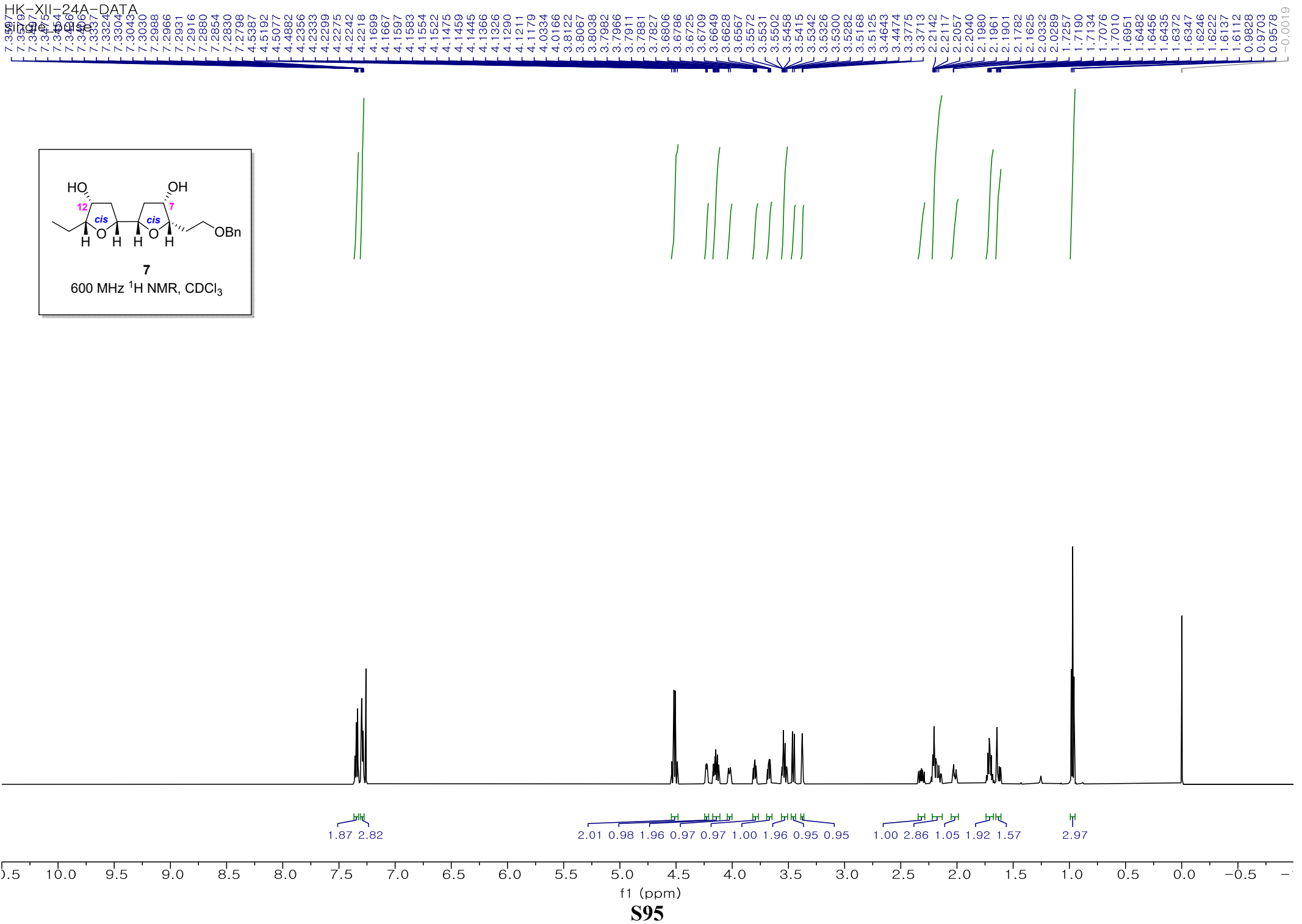
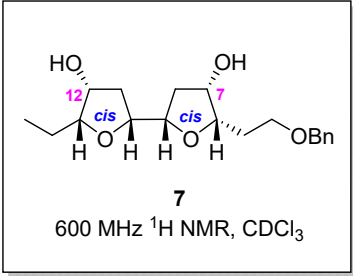




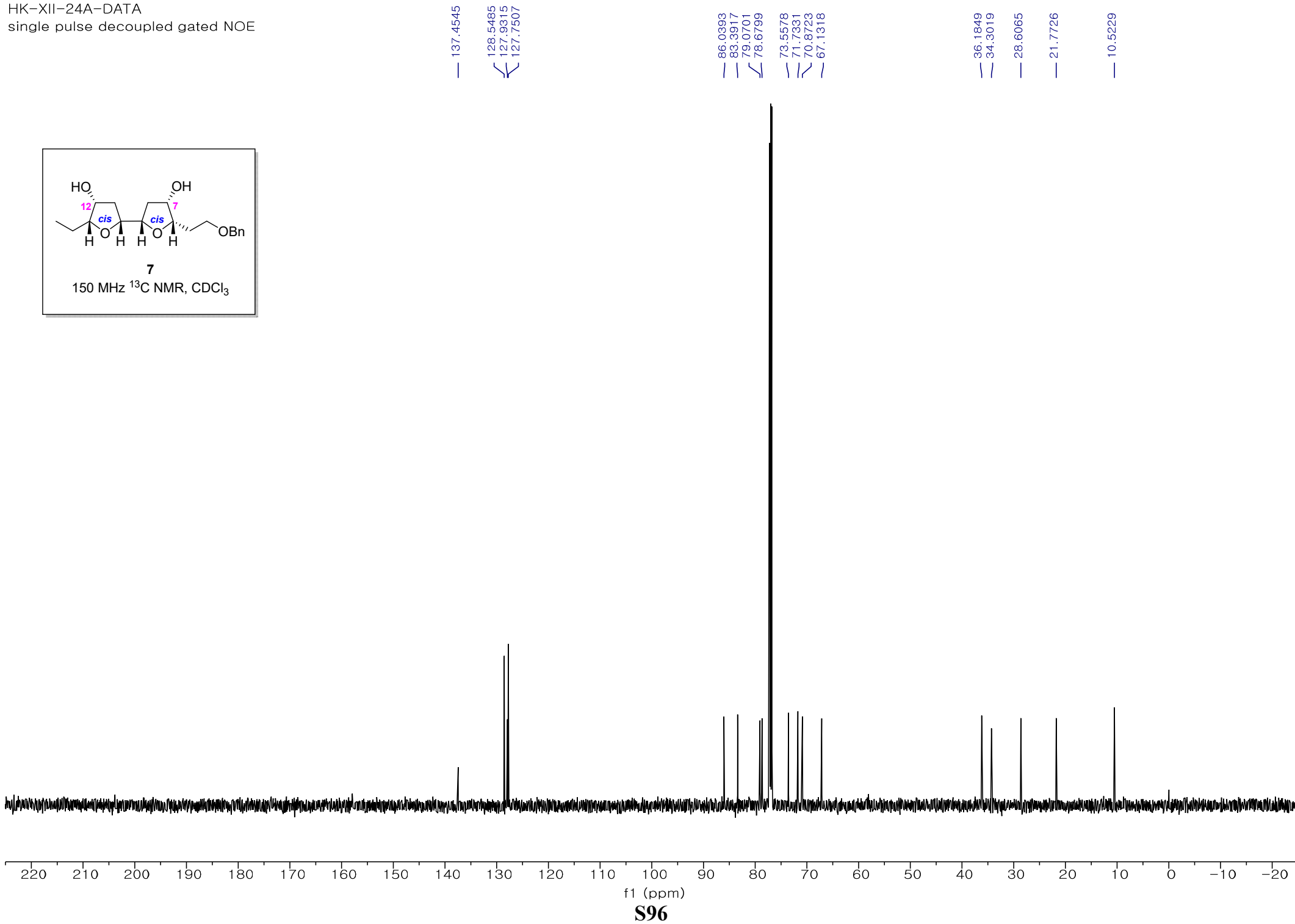
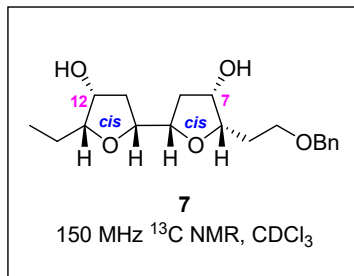








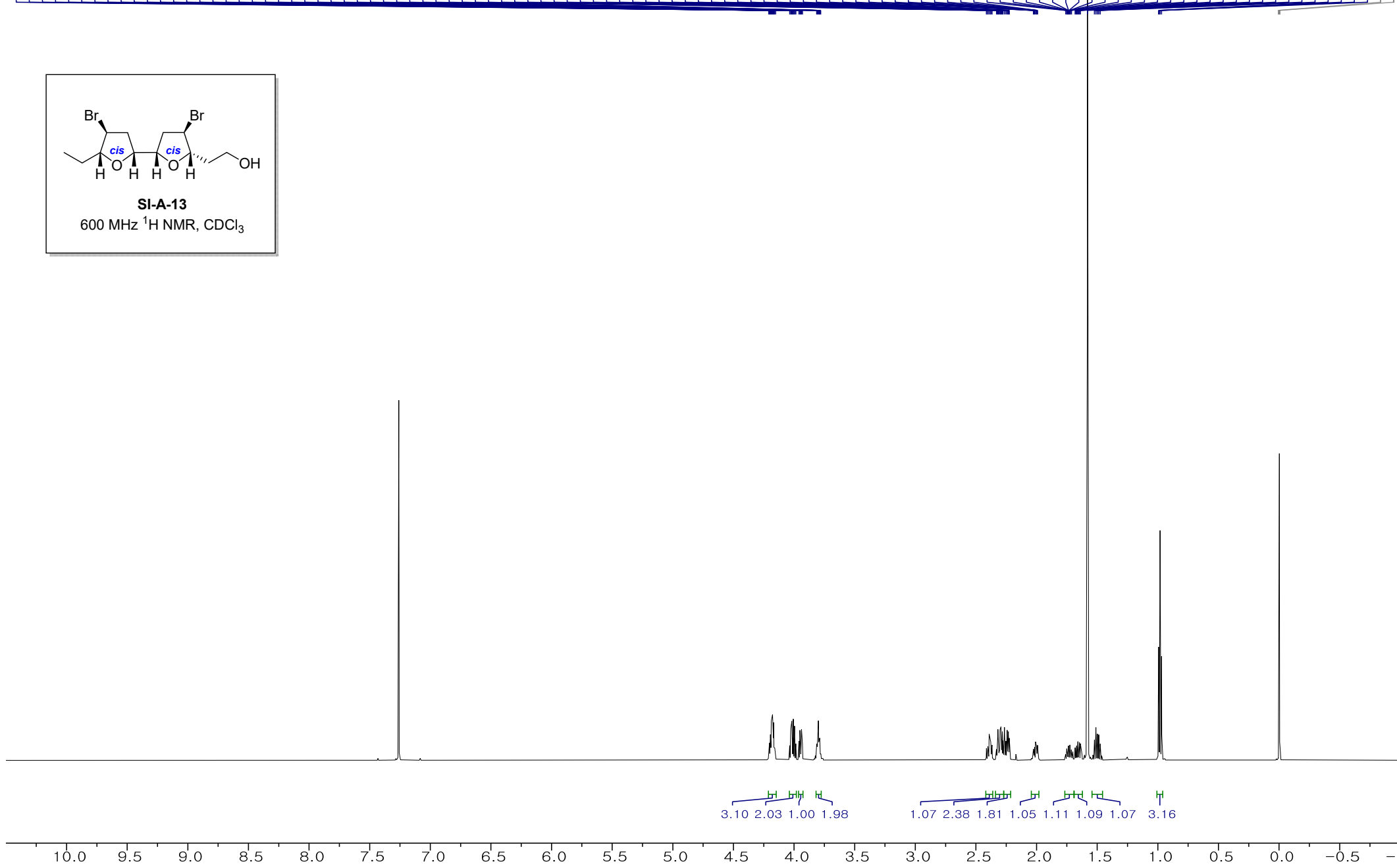
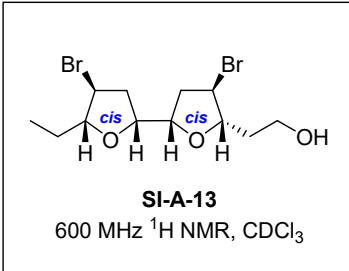
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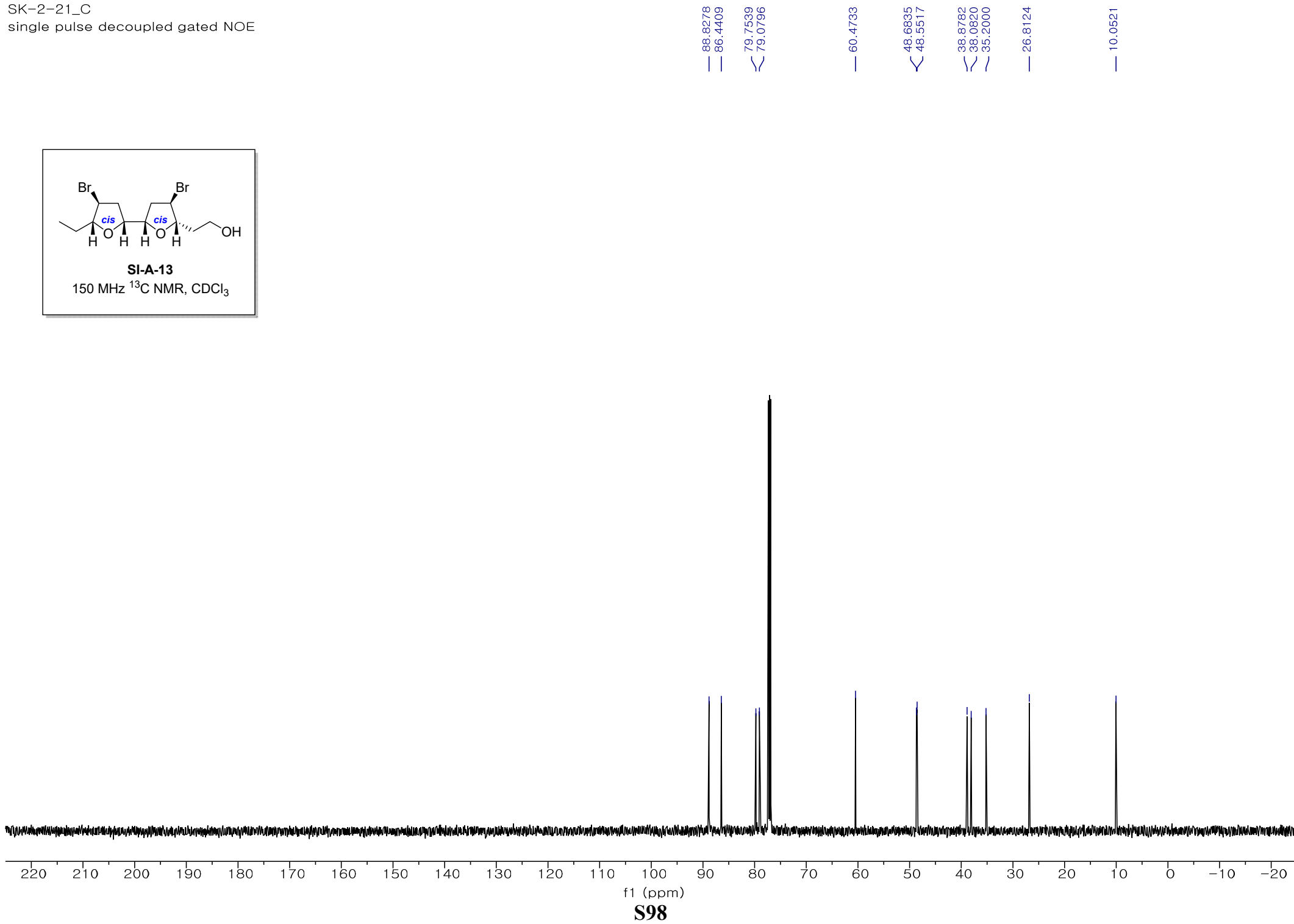
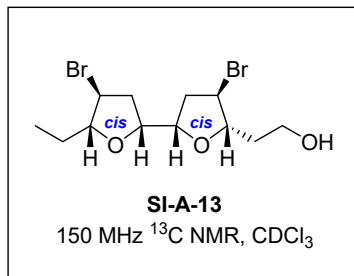
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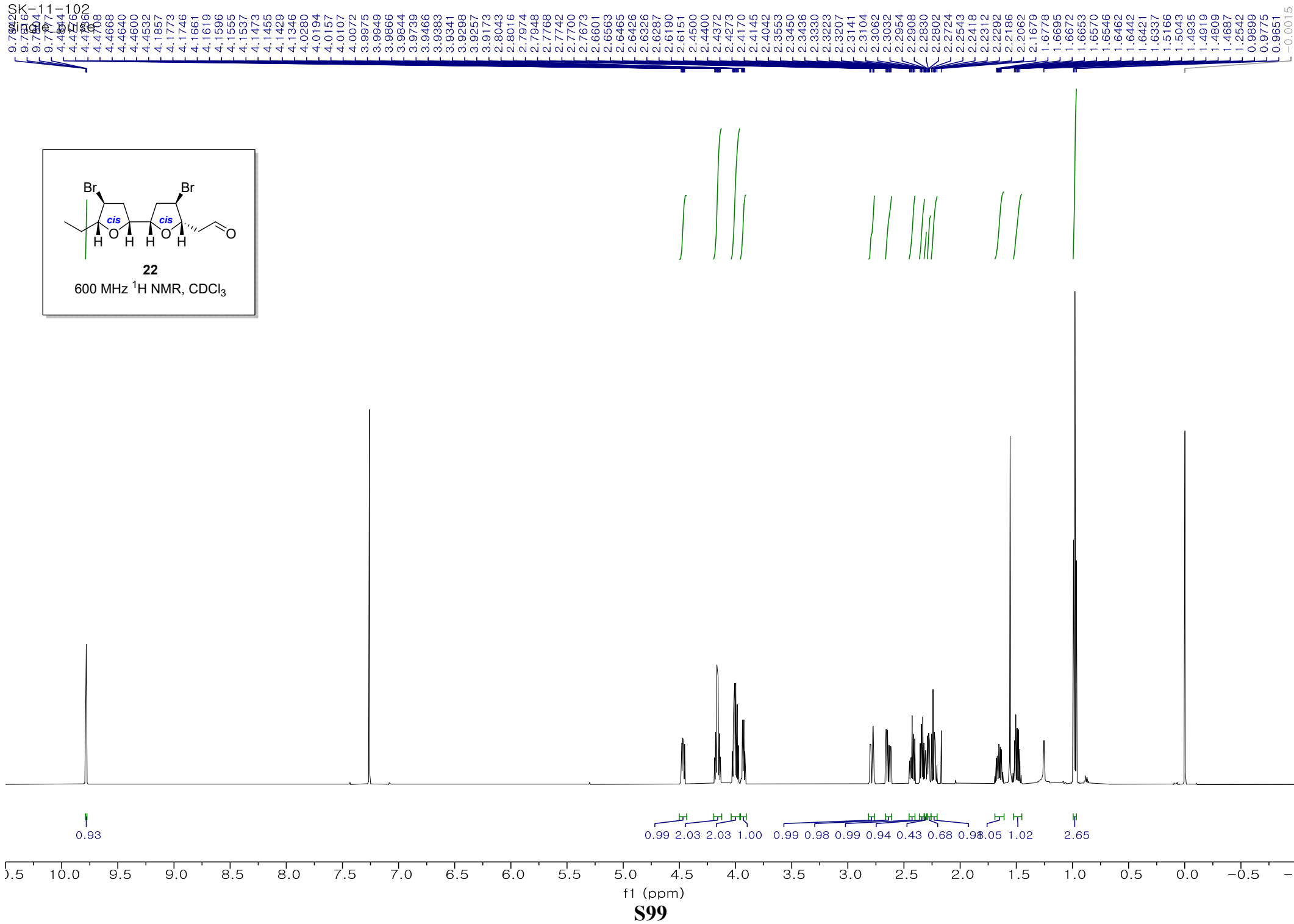
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1.7210  
1.7126  
1.6820  
1.6736  
1.6696  
1.6611  
1.6589  
1.6504  
1.6464  
1.6380  
1.5796  
1.5227  
1.5103  
1.4982  
1.4871  
1.4748  
0.9939  
0.9893  
0.9815  
0.9690  
0.0027  
-0.0028



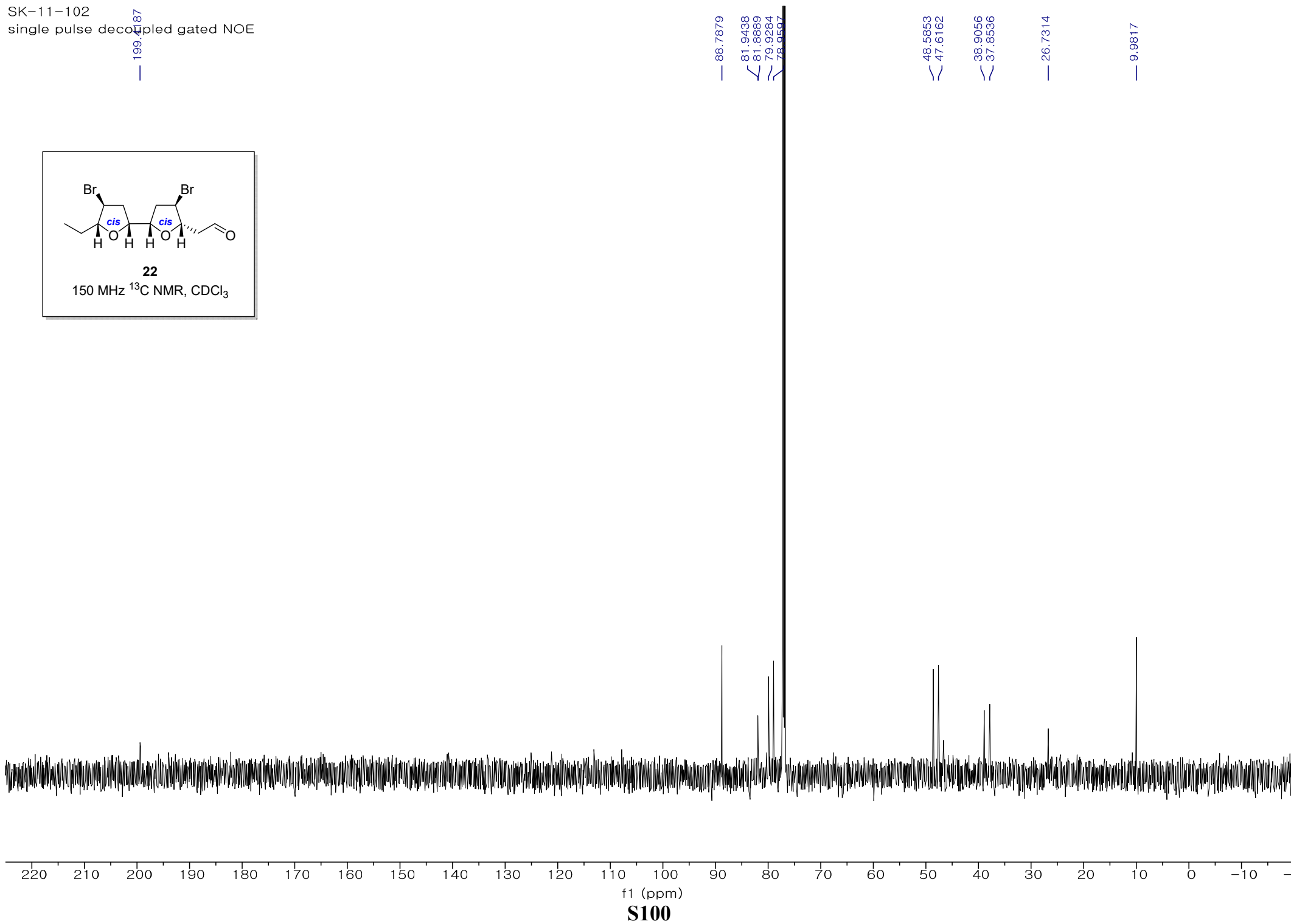
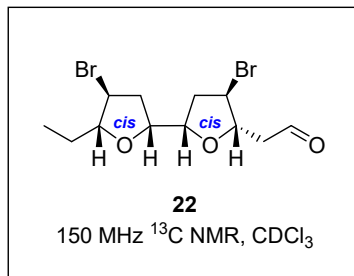
f1 (ppm)  
**S97**

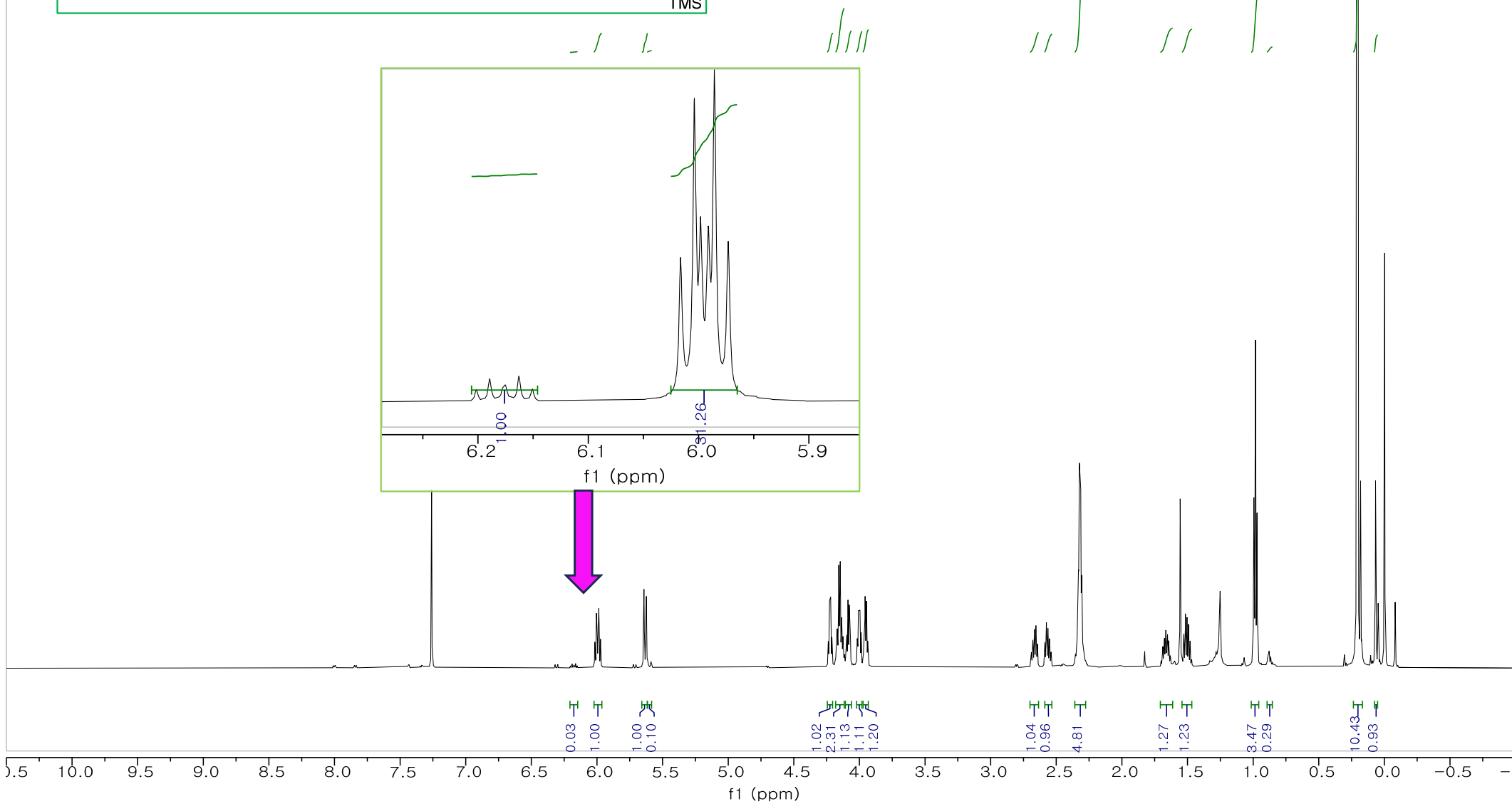
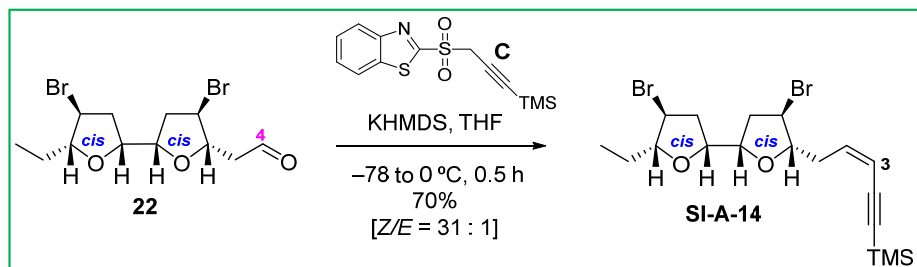
SK-2-21\_C  
single pulse decoupled gated NOE

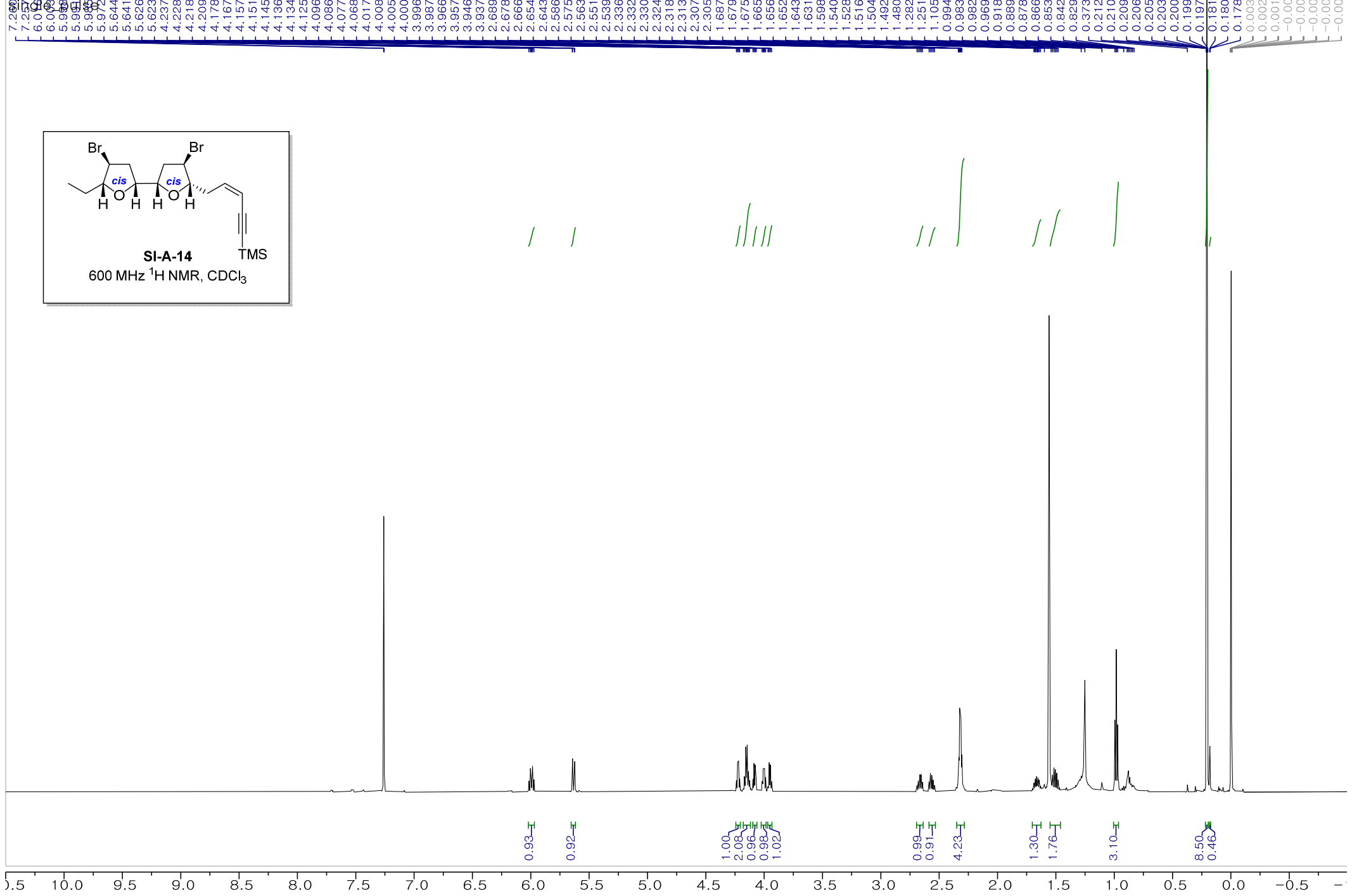
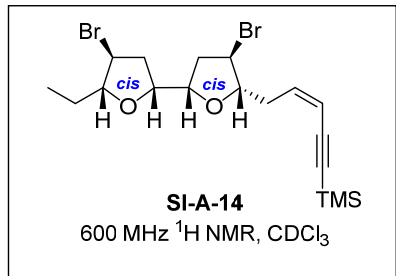


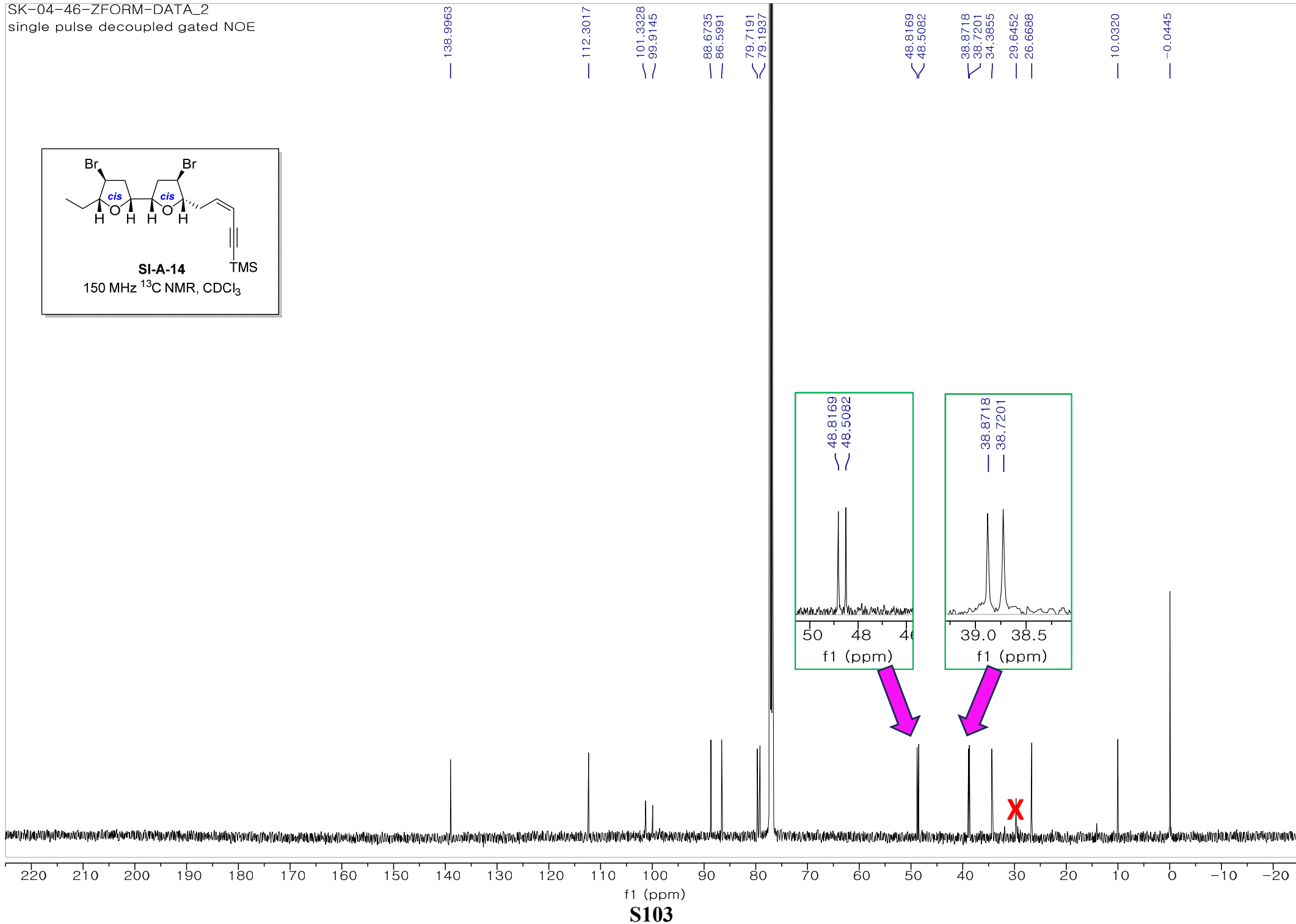
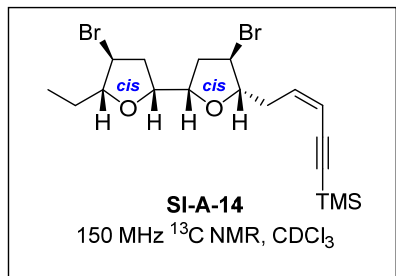


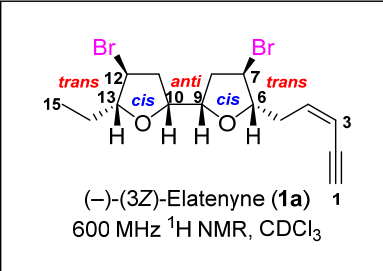
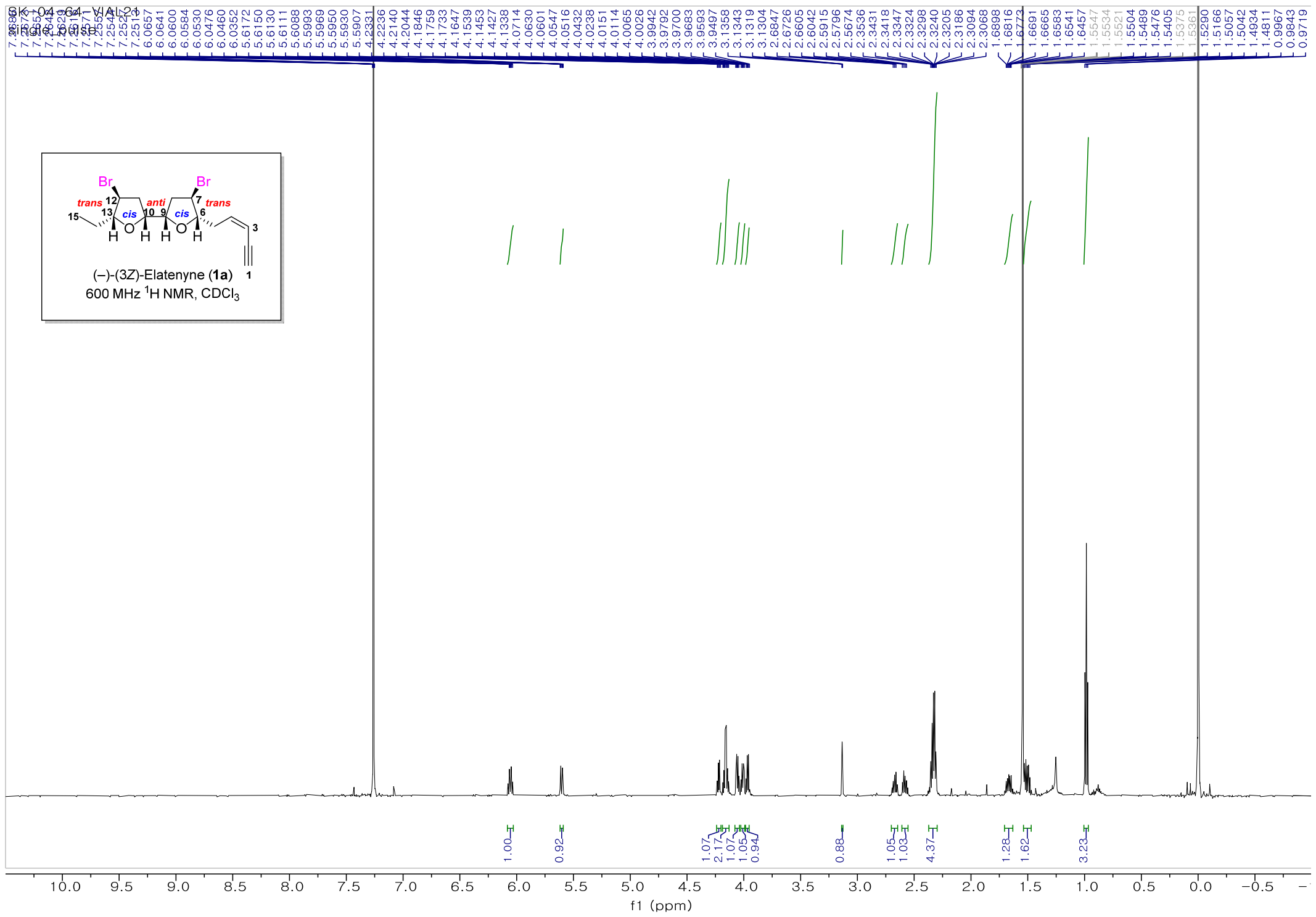
SK-11-102  
single pulse decoupled gated NOE



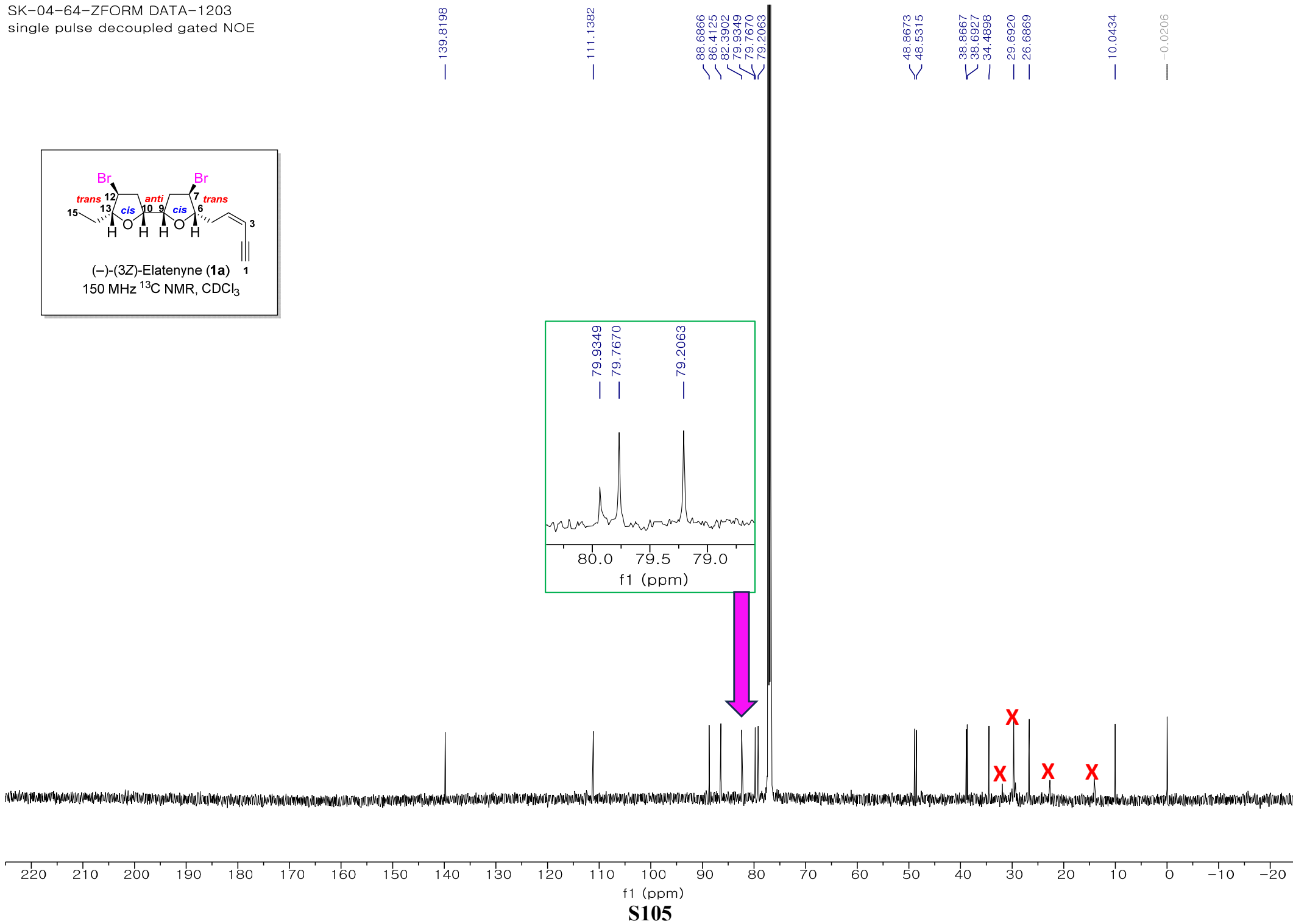
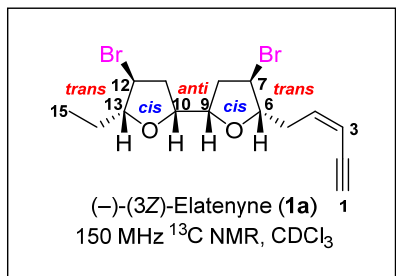




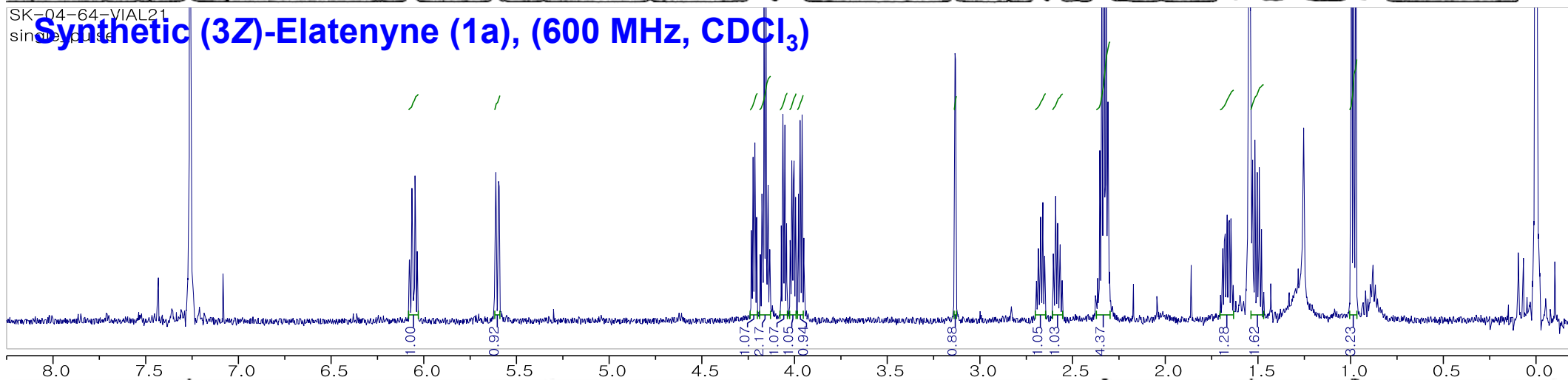
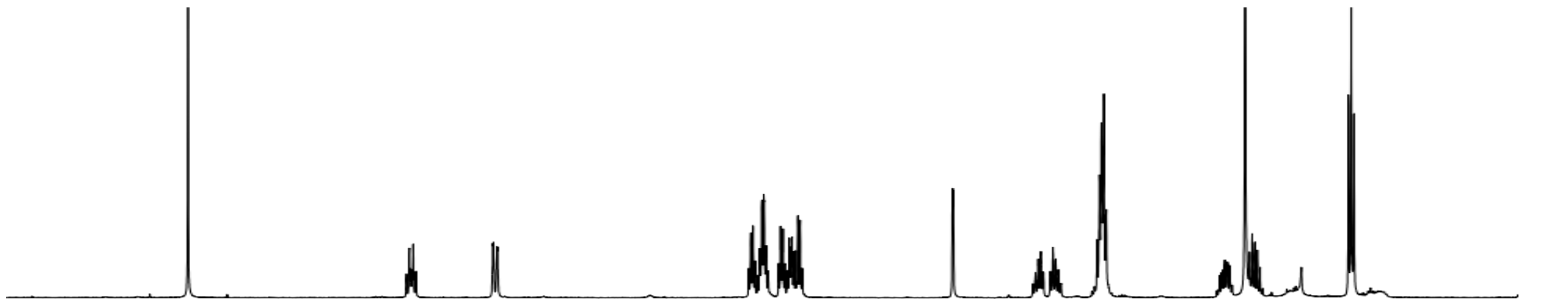




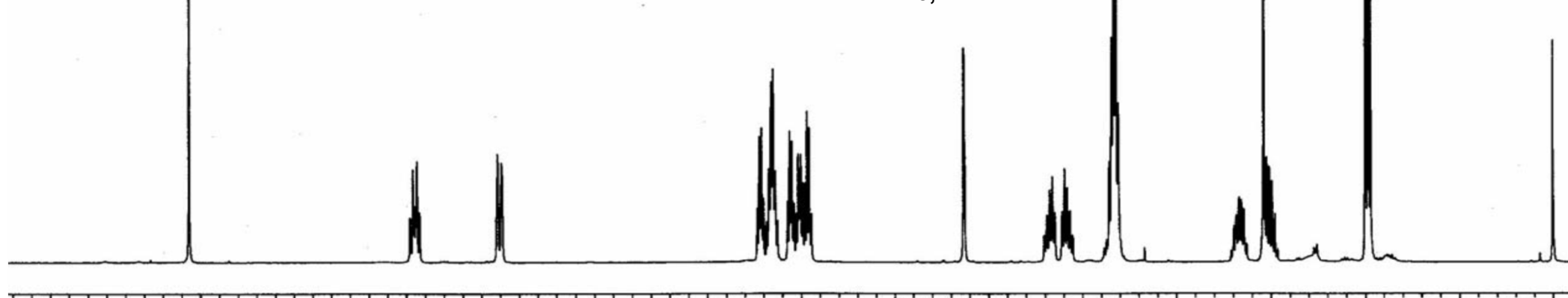




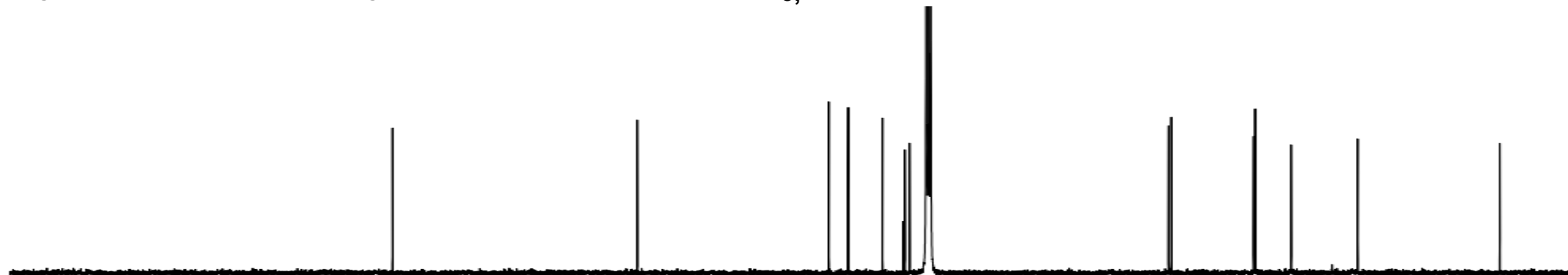
Synthetic (3Z)-Elatenyne (**1a**), (500 MHz, CDCl<sub>3</sub>, *J. Am. Chem. Soc.*, 2012, 134, 11781–11790)



Synthetic *ent*-(3Z)-Elatenyne (*ent*-**1a**), (500 MHz, CDCl<sub>3</sub>, *J. Am. Chem. Soc.*, 2012, 134, 11781–11790)

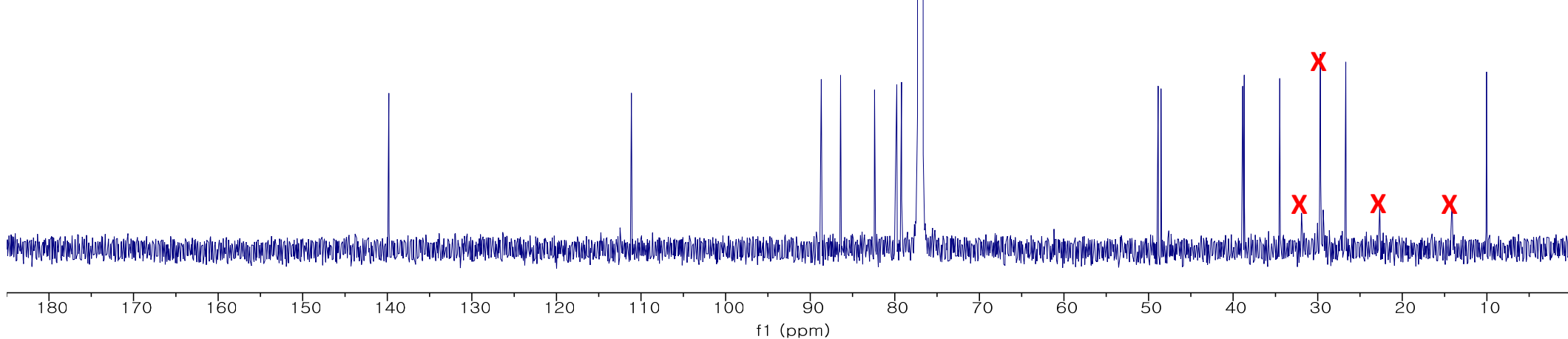


**Synthetic (3Z)-Elatenyne (1a), (125 MHz, CDCl<sub>3</sub>, *J. Am. Chem. Soc.*, 2012, 134, 11781–11790)**

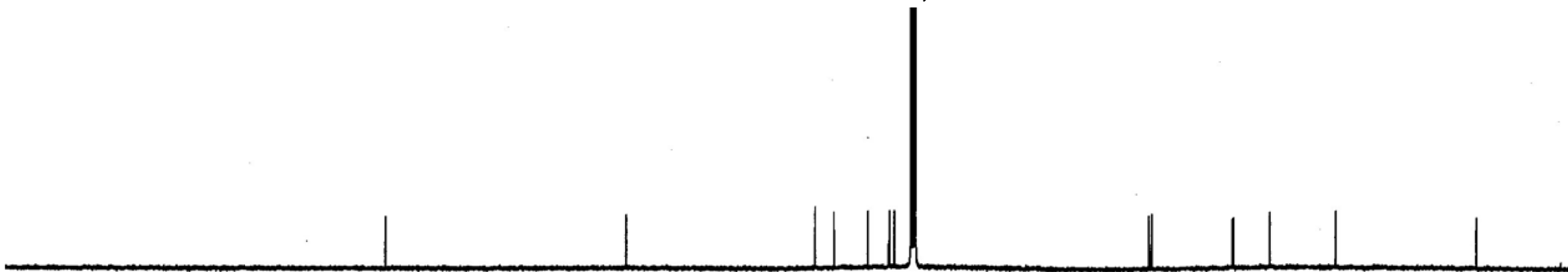


SK-04-64-ZFORM DATA-1203  
single pulse decoupled gated NOE

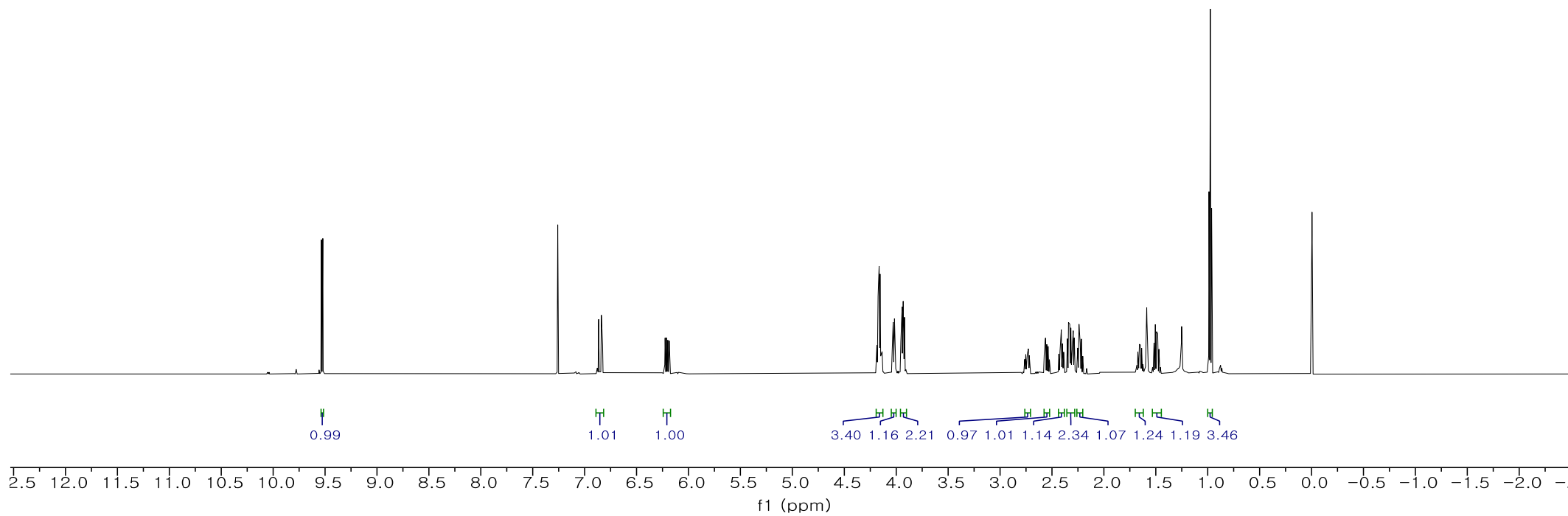
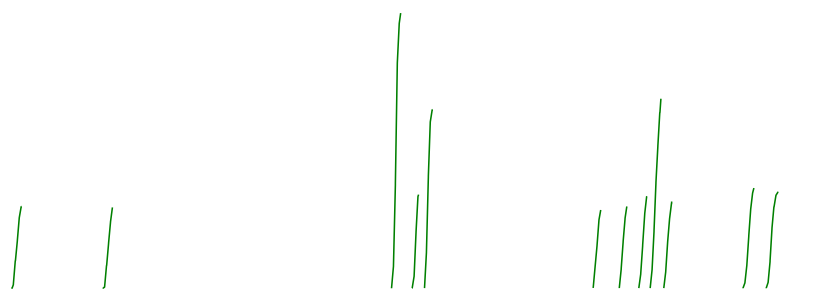
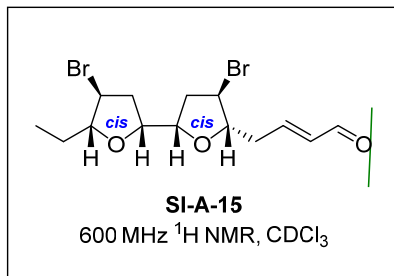
**Kim's Synthetic (3Z)-Elatenyne (1a), (150 MHz, CDCl<sub>3</sub>)**



**Synthetic *ent*-(3Z)-Elatenyne (*ent*-1a), (125 MHz, CDCl<sub>3</sub>, *J. Am. Chem. Soc.*, 2012, 134, 11781–11790)**

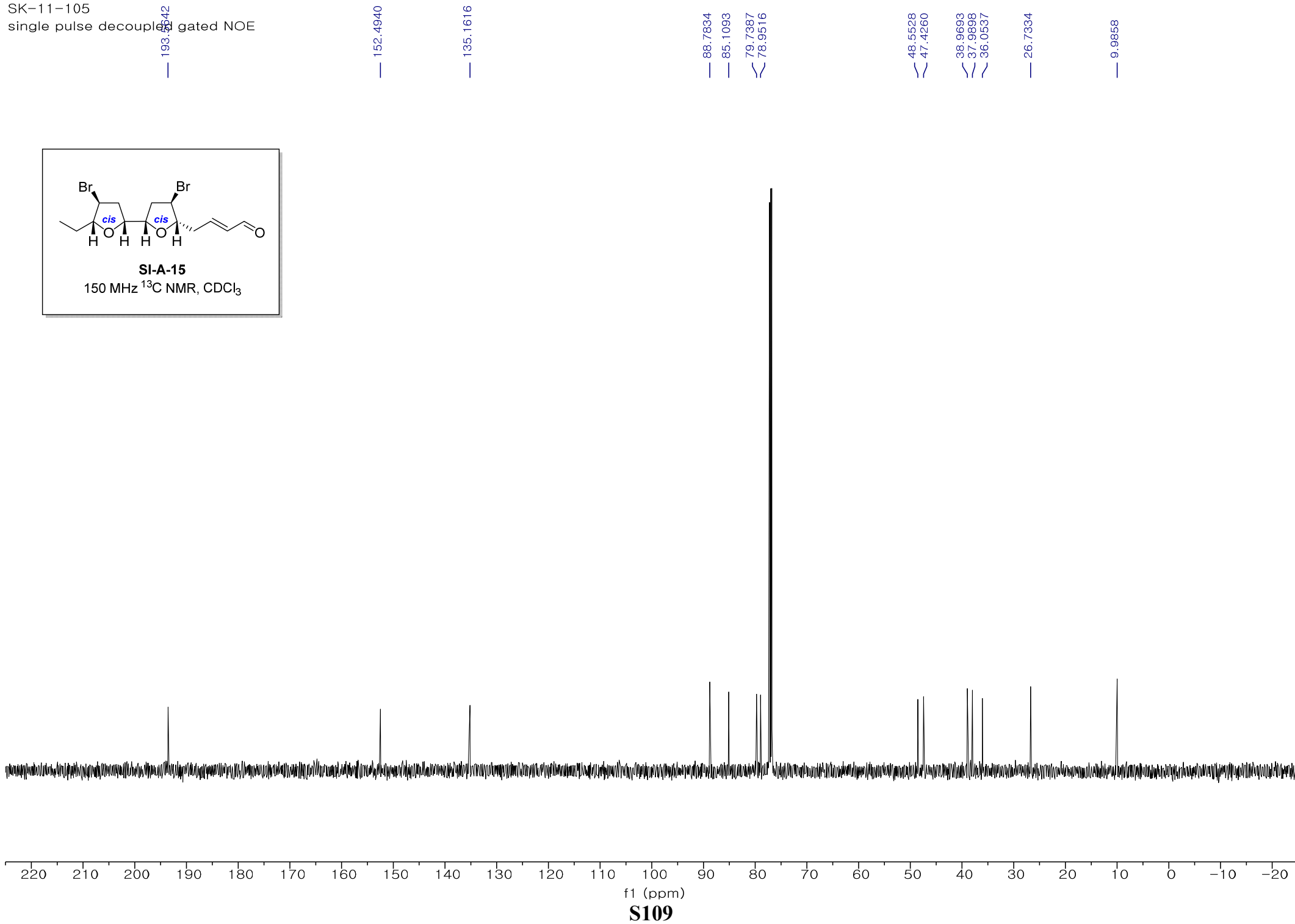
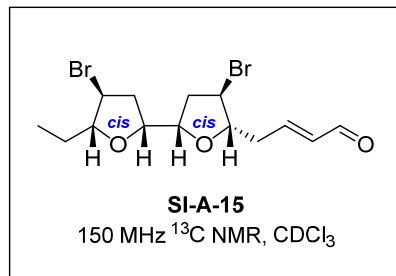


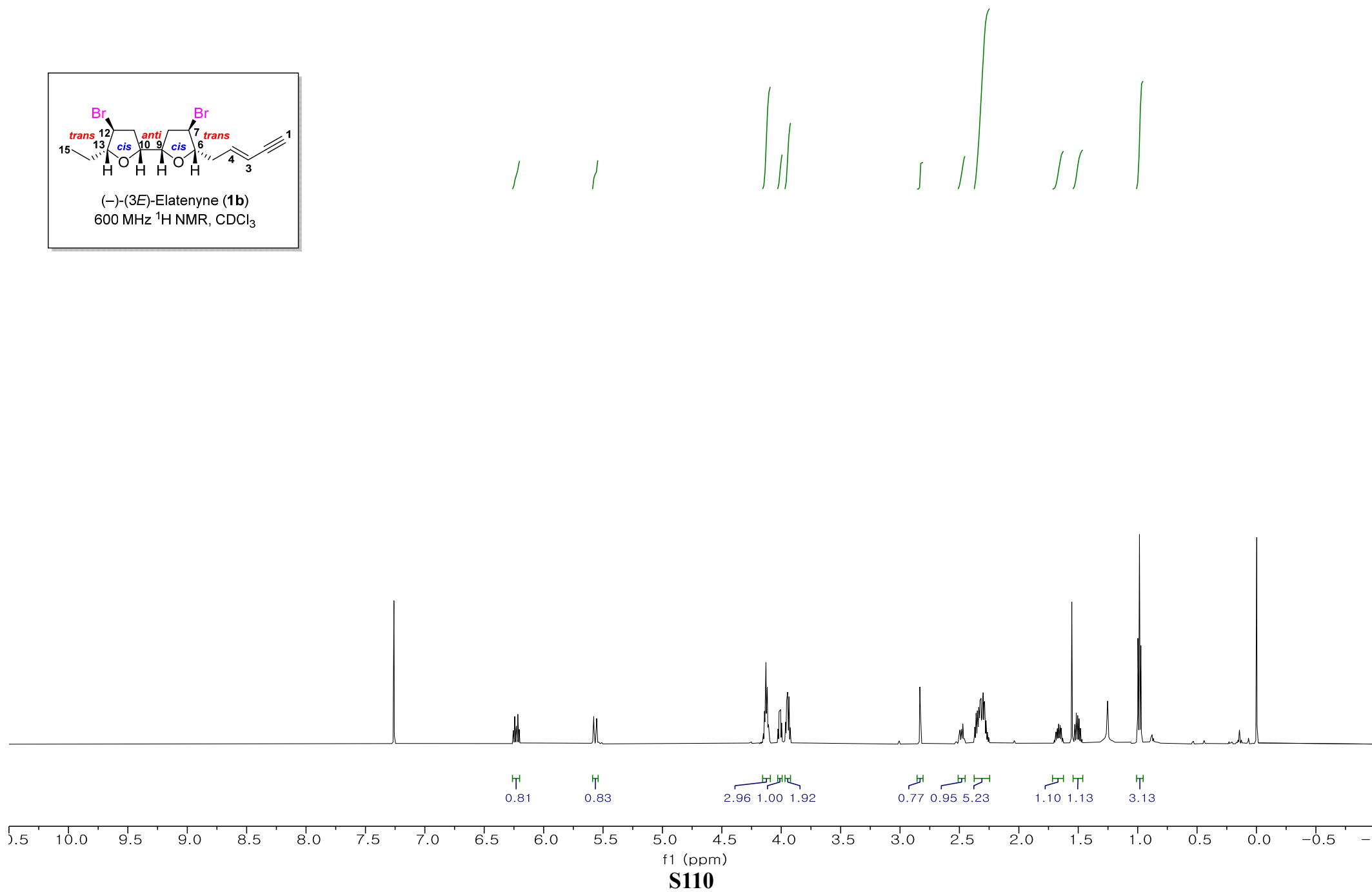
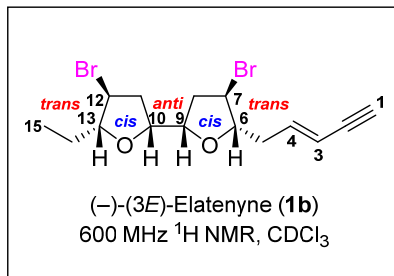
SK-11-105  
single\_pulse

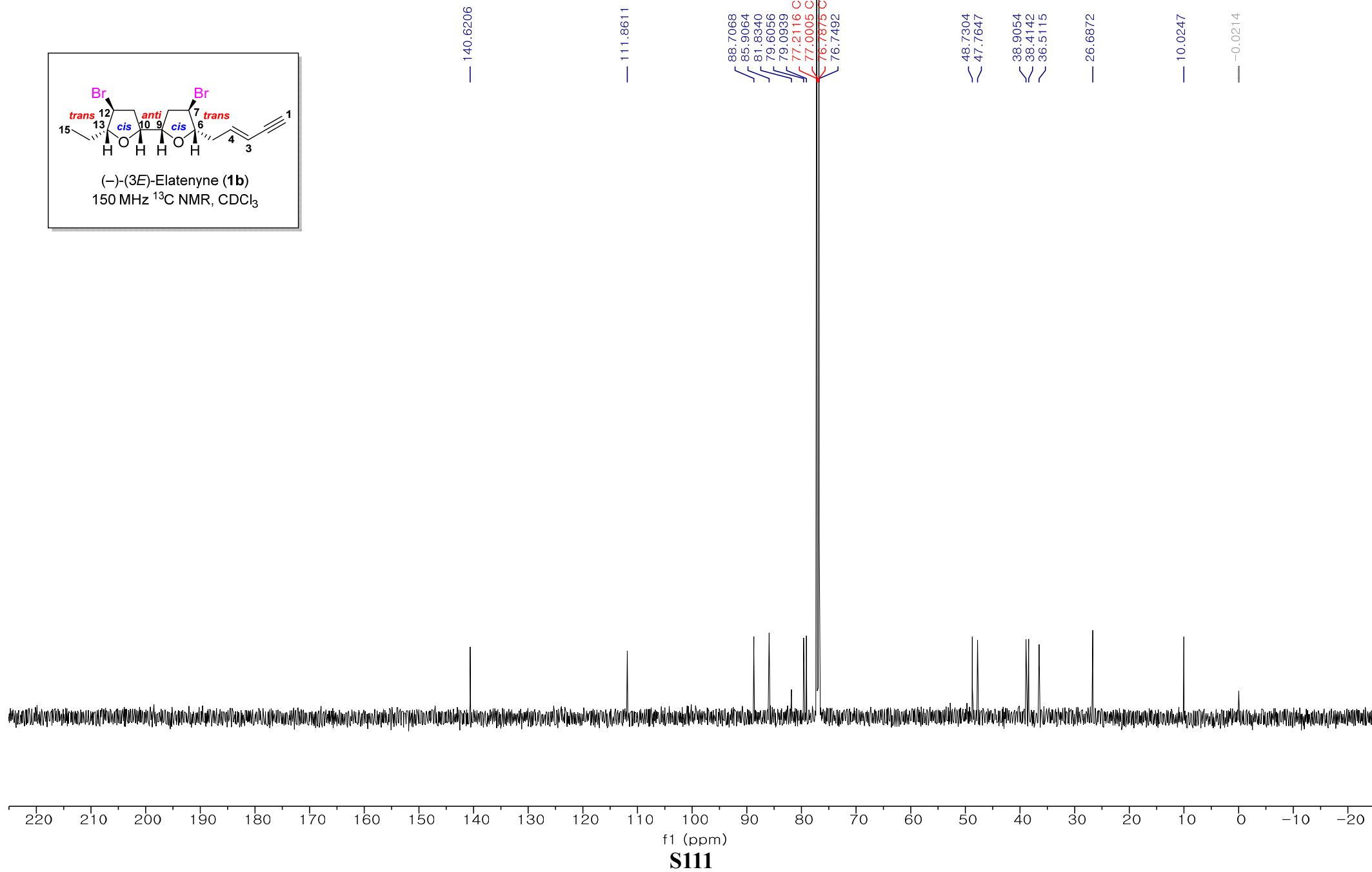
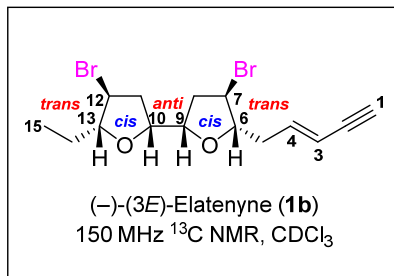


S108

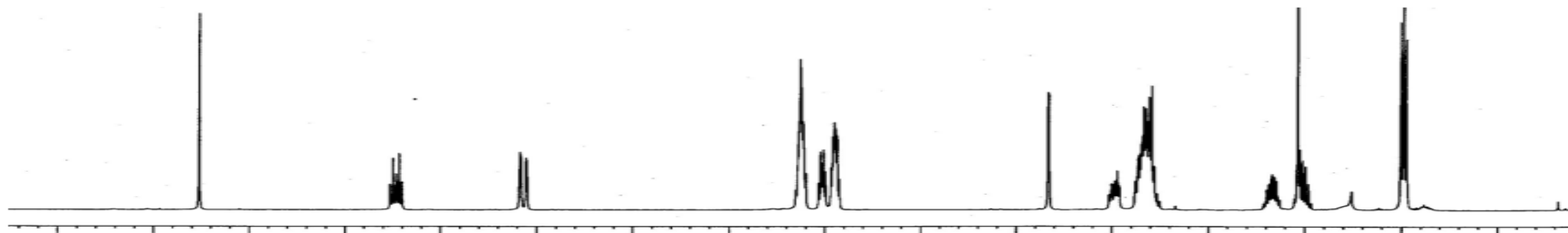
SK-11-105  
single pulse decoupled gated NOE





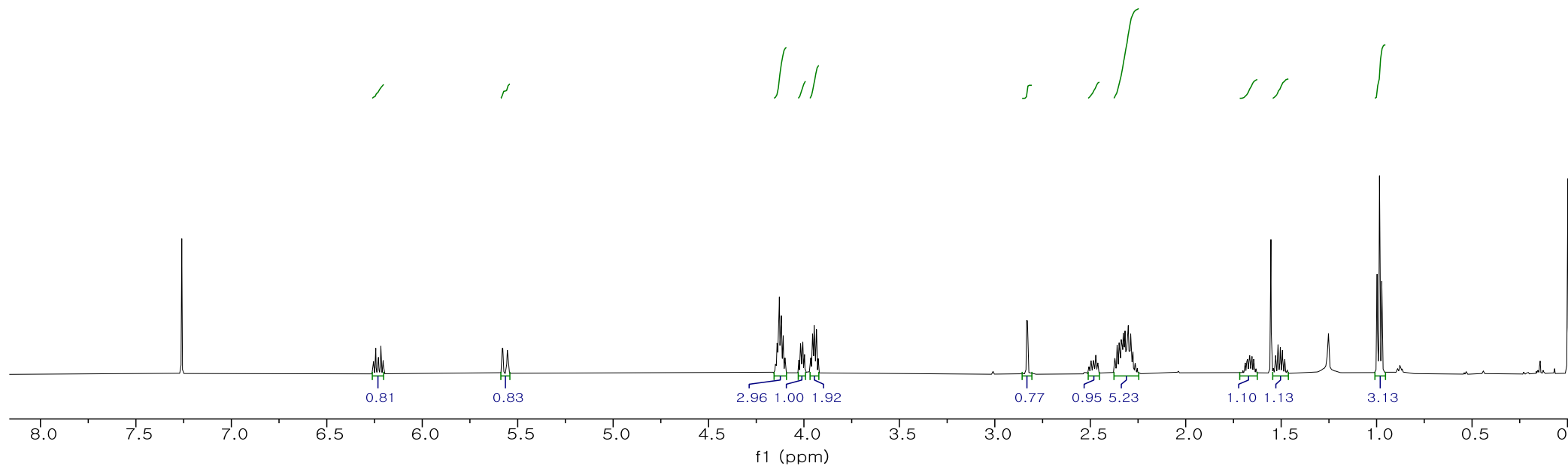


Synthetic *ent*-(*E*)-Elatenyne (*ent*-1b), (500 MHz, CDCl<sub>3</sub>, *J. Am. Chem. Soc.*, 2012, 134, 11781–11790)



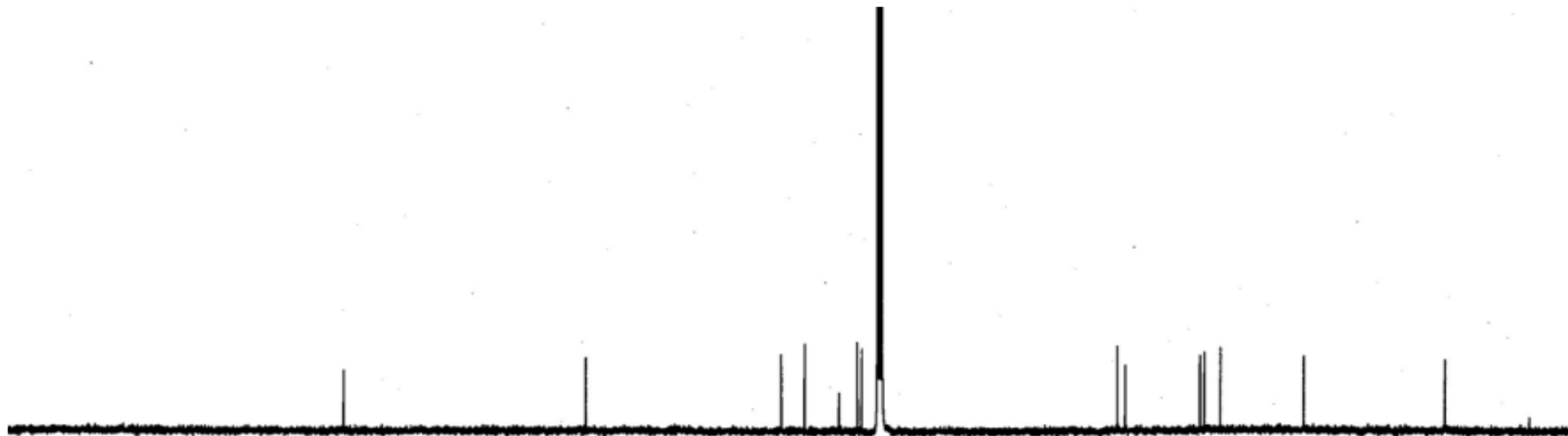
Kim's Synthetic (*3E*)-Elatenyne (1b), (600 MHz, CDCl<sub>3</sub>)

SK-11-106  
single\_pulse



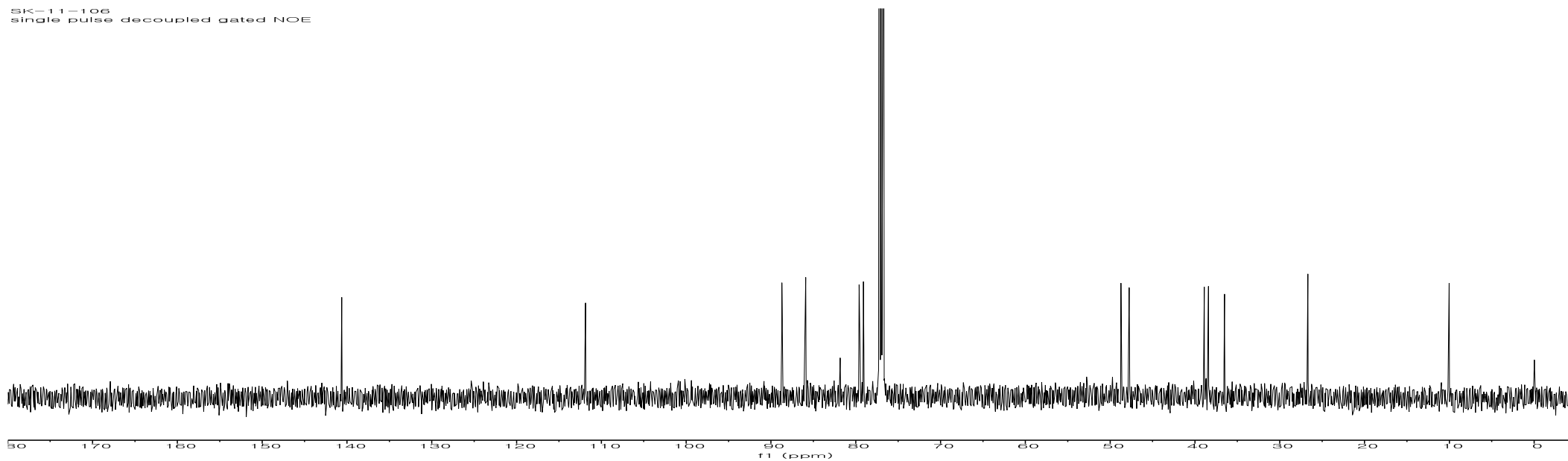


Synthetic *ent*-(*E*)-Elatenyne (*ent*-1b), (500 MHz, CDCl<sub>3</sub>, *J. Am. Chem. Soc.*, 2012, 134, 11781–11790)



Kim's Synthetic (*3E*)-Elatenyne (1b), (600 MHz, CDCl<sub>3</sub>)

SK-11-106  
single pulse decoupled gated NOE



– **Electronic Supplementary Information: Part C** –

**Stereoselective total synthesis of (3*Z*)- and (3*E*)-elatenynes**

Soo Yeon Kwak,<sup>a‡</sup> Iljin Shin,<sup>a‡</sup> Hongjun Jang,<sup>a</sup> Youngjik Park,<sup>a</sup> Seongju Lim,<sup>a</sup> Dongjoo Lee,<sup>a</sup>  
Hyoungsu Kim,<sup>\*a</sup> and Deukjoon Kim<sup>b</sup>

<sup>a</sup>College of Pharmacy and Research Institute of Pharmaceutical Science and Technology (RIPST), Ajou University, Suwon 16499, Korea

<sup>b</sup>The Research Institute of Pharmaceutical Sciences, College of Pharmacy, Seoul National University, Seoul 08826, Korea

<sup>‡</sup>These authors contributed equally to this work.

\* E-mail: [hkimajou@ajou.ac.kr](mailto:hkimajou@ajou.ac.kr)

**Part C (S114 ~ S140)**  
**Copies of HRMS Spectra**

**Copies of Original Reports for HRMS.....S115 ~ S116**

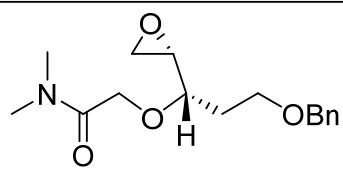
**Copies of Original HRMS Spectra.....S117 ~ S140**

## Copies of Original Reports for HRMS

Compound	Mode	Formula	m/z	Calculated	Observed	Page
<b>13</b>	EI	C <sub>16</sub> H <sub>23</sub> NO <sub>4</sub>	[M] <sup>+</sup>	293.1627	293.1624	S117
<b>14</b>	EI	C <sub>16</sub> H <sub>24</sub> BrNO <sub>4</sub>	[M] <sup>+</sup>	373.0889	373.0884	S118
<b>11</b>	EI	C <sub>24</sub> H <sub>32</sub> BrNO <sub>5</sub>	[M] <sup>+</sup>	493.1464	493.1462	S119
<b>10</b>	EI	C <sub>24</sub> H <sub>31</sub> NO <sub>5</sub>	[M] <sup>+</sup>	413.2202	413.2205	S120
<b>15</b>	EI	C <sub>25</sub> H <sub>44</sub> BrNO <sub>4</sub> Si	[M] <sup>+</sup>	529.2223	529.2225	S121
<b>16</b>	EI	C <sub>25</sub> H <sub>43</sub> NO <sub>4</sub> Si	[M] <sup>+</sup>	449.2961	449.2961	S122
<b>SI-A-03</b>	EI	C <sub>16</sub> H <sub>23</sub> NO <sub>4</sub>	[M] <sup>+</sup>	293.1627	293.1624	S123
<b>17</b>	EI	C <sub>24</sub> H <sub>31</sub> NO <sub>5</sub>	[M] <sup>+</sup>	413.2202	413.2202	S124
<b>9</b>	EI	C <sub>25</sub> H <sub>32</sub> O <sub>5</sub>	[M] <sup>+</sup>	412.2250	412.2242	S125
<b>SI-A-04</b>	FAB	C <sub>25</sub> H <sub>33</sub> O <sub>5</sub>	[M+H] <sup>+</sup>	413.2328	413.2328	S126
<b>(S)-MTPA-SI-A-05</b>	FAB	C <sub>35</sub> H <sub>40</sub> F <sub>3</sub> O <sub>7</sub>	[M+H] <sup>+</sup>	629.2726	629.2719	S127
<b>(R)-MTPA-SI-A-06</b>	FAB	C <sub>35</sub> H <sub>40</sub> F <sub>3</sub> O <sub>7</sub>	[M+H] <sup>+</sup>	629.2726	629.2722	S128
<b>20</b>	EI	C <sub>27</sub> H <sub>36</sub> O <sub>5</sub>	[M] <sup>+</sup>	440.2563	440.2558	S129
<b>SI-A-07</b>	EI	C <sub>34</sub> H <sub>42</sub> O <sub>7</sub> S	[M] <sup>+</sup>	594.2651	594.2654	S130
<b>8</b>	FAB	C <sub>34</sub> H <sub>45</sub> O <sub>9</sub> S	[M+H] <sup>+</sup>	629.2784	629.2787	S131
<b>21</b>	EI	C <sub>27</sub> H <sub>36</sub> O <sub>6</sub>	[M] <sup>+</sup>	456.2512	456.2510	S132
<b>SI-A-09</b>	EI	C <sub>27</sub> H <sub>35</sub> BrO <sub>5</sub>	[M] <sup>+</sup>	518.1668	518.1669	S133
<b>SI-A-10</b>	EI	C <sub>19</sub> H <sub>27</sub> BrO <sub>4</sub>	[M] <sup>+</sup>	398.1093	398.1094	S134
<b>6</b>	EI	C <sub>19</sub> H <sub>26</sub> Br <sub>2</sub> O <sub>3</sub>	[M] <sup>+</sup>	460.0249	460.0243	S135
<b>7</b>	FAB	C <sub>19</sub> H <sub>29</sub> O <sub>5</sub>	[M+H] <sup>+</sup>	337.2015	337.2017	S136
<b>SI-A-13</b>	FAB	C <sub>12</sub> H <sub>21</sub> Br <sub>2</sub> O <sub>3</sub>	[M+H] <sup>+</sup>	370.9857	370.9854	S137

## Copies of Original Reports for HRMS

Compound	Mode	Formula	m/z	Calculated	Observed	Page
<b>SI-A-14</b>	EI	C <sub>18</sub> H <sub>28</sub> Br <sub>2</sub> O <sub>2</sub> Si	[M] <sup>+</sup>	462.0225	462.0219	S138
<b>(3Z)-Elatenyne (1a)</b>	EI	C <sub>15</sub> H <sub>20</sub> Br <sub>2</sub> O <sub>2</sub>	[M] <sup>+</sup>	389.9830	389.9825	S139
<b>(3E)-Elatenyne (1a)</b>	EI	C <sub>15</sub> H <sub>20</sub> Br <sub>2</sub> O <sub>2</sub>	[M] <sup>+</sup>	389.9830	389.9834	S140



13

Chemical Formula: C<sub>16</sub>H<sub>23</sub>NO<sub>4</sub>

Exact Mass: 293.1627

[M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>4</sub> 293.1627

[ Elemental Composition ]

Data : 1-SK-01-001

Date : 10-Oct-2023 15:52

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 1.77 min

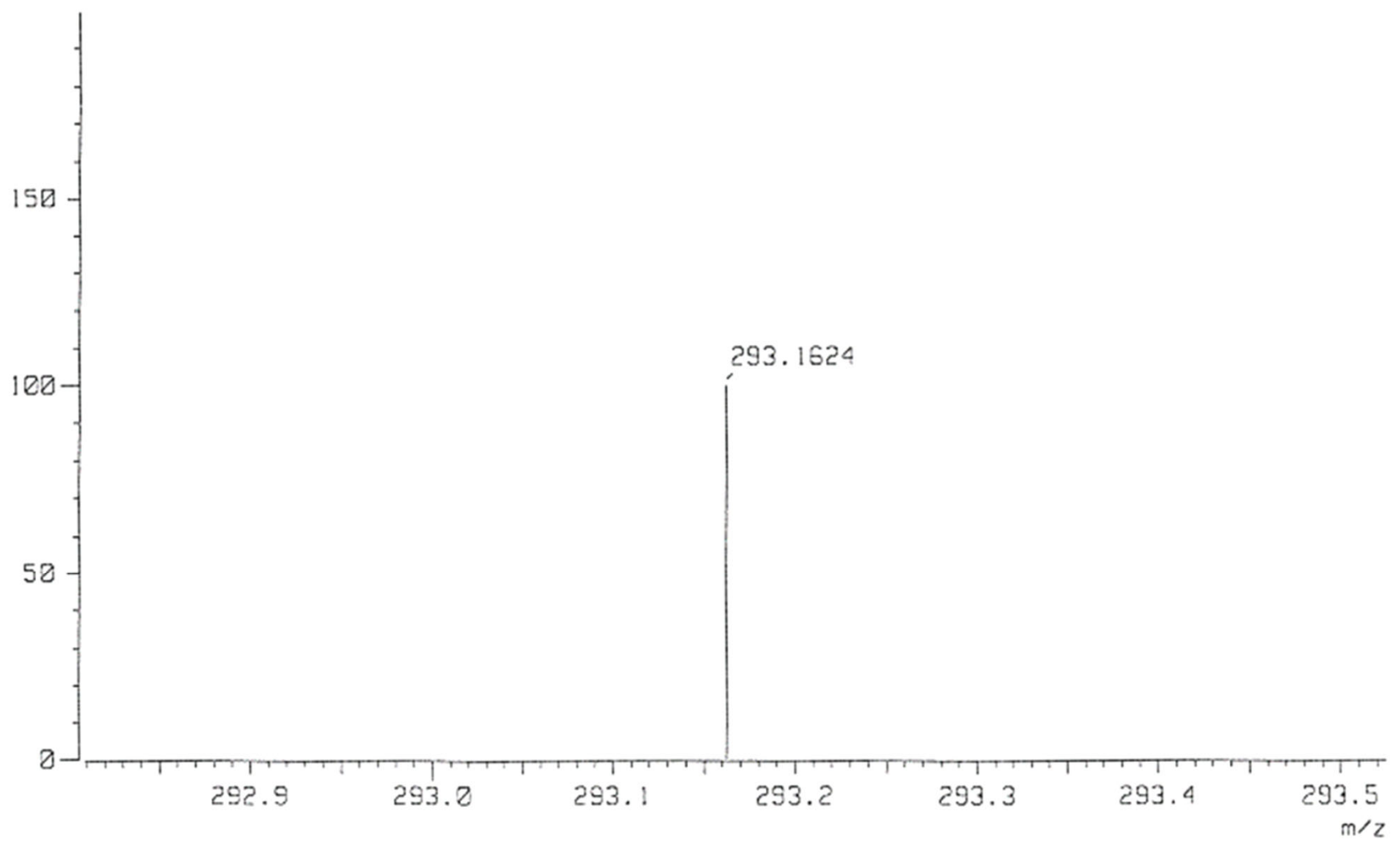
Scan#: 54+58

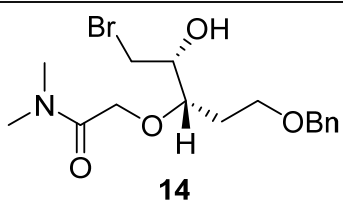
Elements : C 18/0, H 25/0, O 4/0, N 2/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
293.1624	100.0	-1.1 / -0.3	6.0	C 16 H 23 O 4 N





**14**

Chemical Formula: C<sub>16</sub>H<sub>24</sub>BrNO<sub>4</sub>

Exact Mass: 373.0889

**[M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>24</sub>BrNO<sub>4</sub> 373.0889**

[ Elemental Composition ]

Data : 2-SK-02-001

Date : 10-Oct-2023 16:03

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 1.75 min

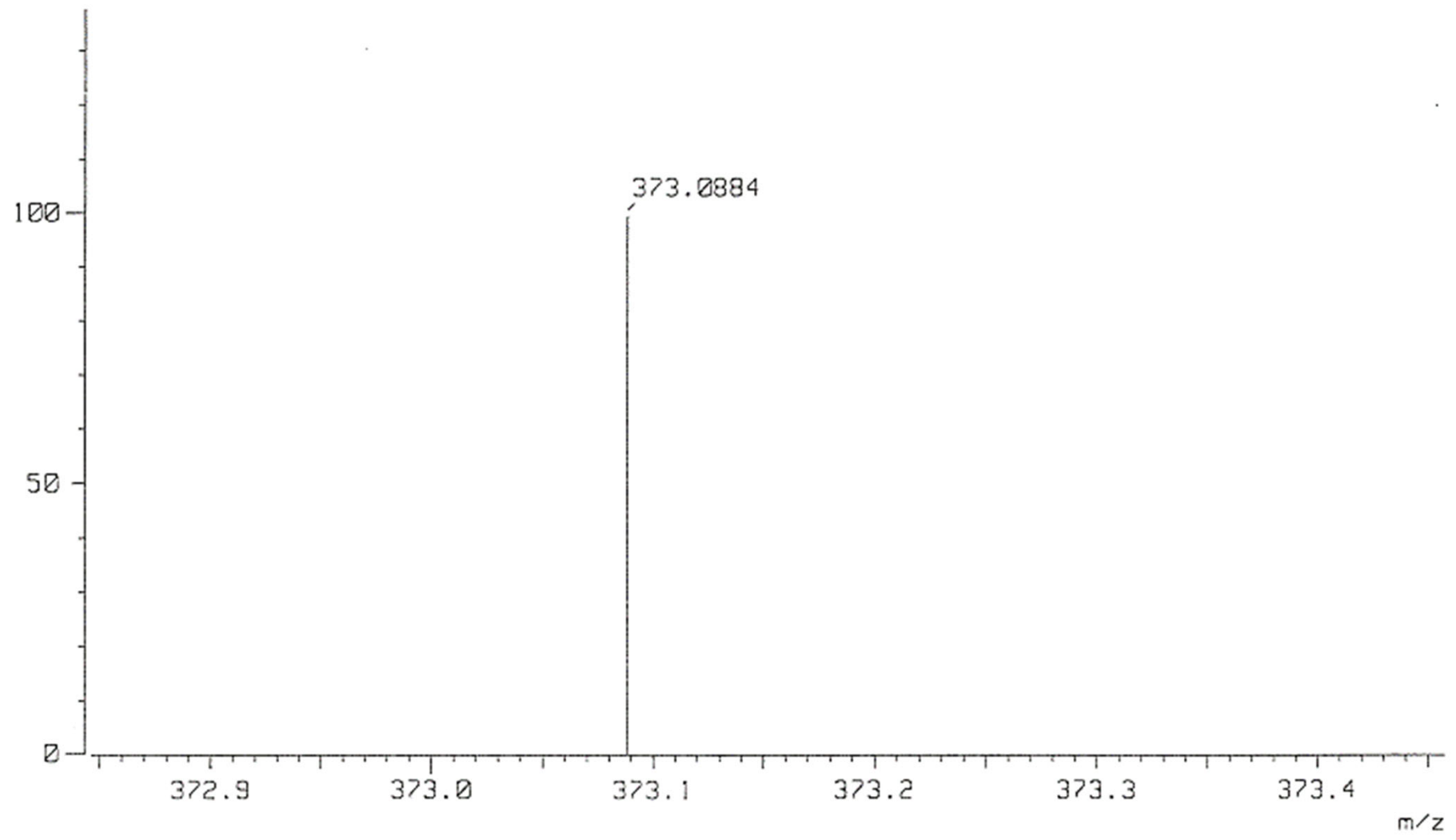
Scan#: (53,54)+62+66+70

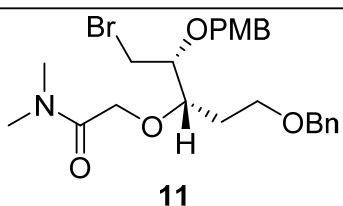
Elements : C 18/0, H 25/0, O 4/0, N 2/0, Br 1/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
373.0884	99.4	-1.2 / -0.5	5.0	C 16 H 24 O 4 N Br





Chemical Formula: C<sub>24</sub>H<sub>32</sub>BrNO<sub>5</sub>

Exact Mass: 493.1464

**[M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>32</sub>BrNO<sub>5</sub> 493.1464**

[ Elemental Composition ]

Data : 3-SK-03-010

Date : 10-Oct-2023 16:17

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 2.57 min

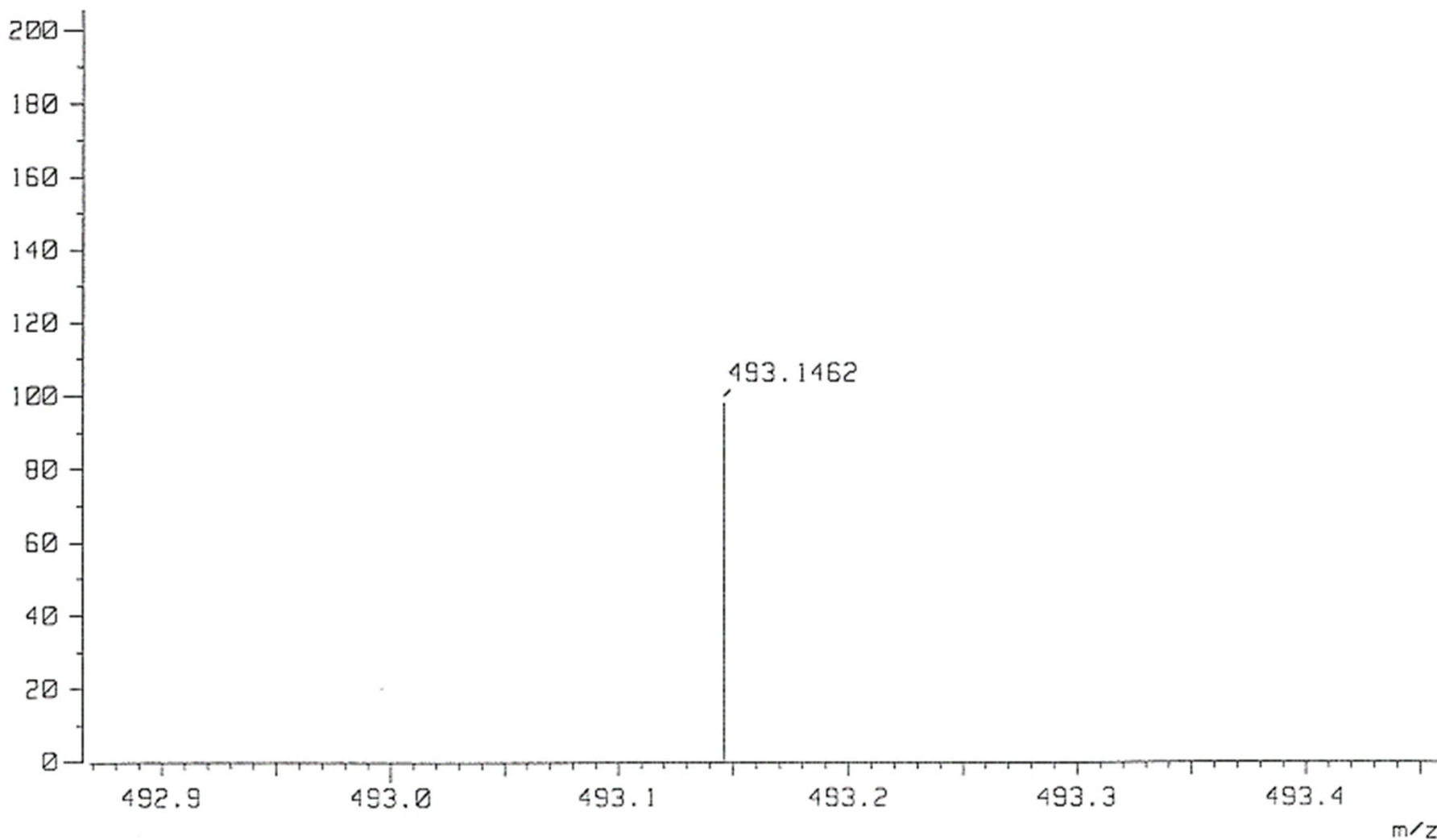
Scan#: 78

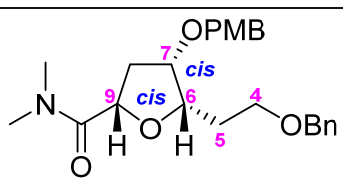
Elements : C 25/0, H 35/0, O 5/0, N 2/0, Br 1/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
493.1462	98.1	-0.4 / -0.2	9.0	C 24 H 32 O 5 N Br





**10**

Chemical Formula: C<sub>24</sub>H<sub>31</sub>NO<sub>5</sub>

Exact Mass: 413.2202

**[M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>NO<sub>5</sub> 413.2202**

[ Elemental Composition ]

Data : 4-SK-04-012

Date : 10-Oct-2023 16:23

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 1.87 min

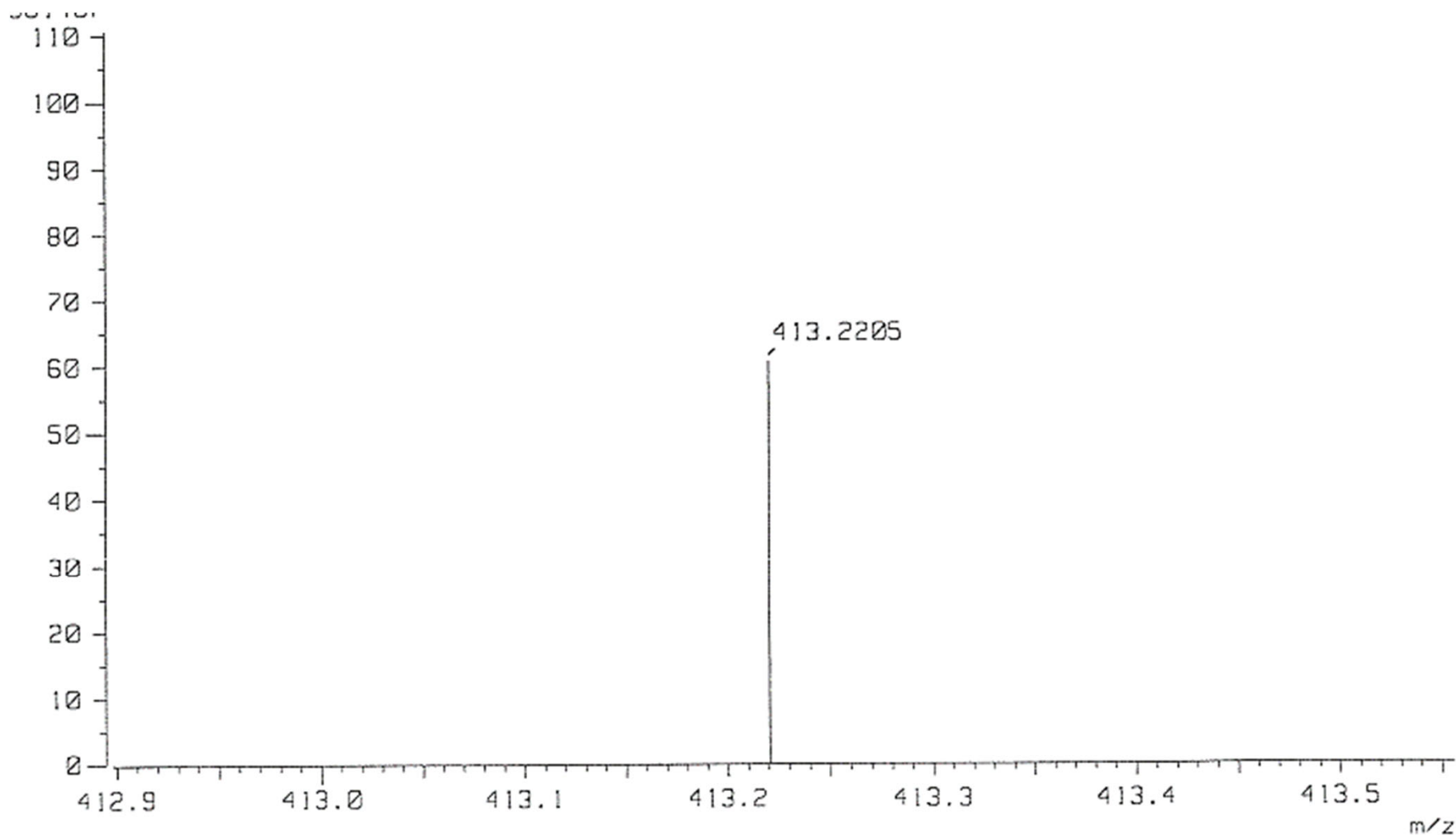
Scan#: (56,58)+62+65

Elements : C 25/0, H 32/0, O 6/0, N 2/0

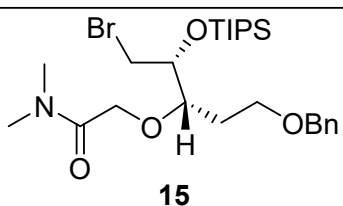
Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
413.2205	60.7	+0.6 / +0.2	10.0 C 24 H 31 O 5 N







Chemical Formula: C<sub>25</sub>H<sub>44</sub>BrNO<sub>4</sub>Si

Exact Mass: 529.2223

**[M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>44</sub>BrNO<sub>4</sub>Si 529.2223**

[ Elemental Composition ]

Data : 5-SK-05-016

Date : 10-Oct-2023 16:32

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 0.54 min

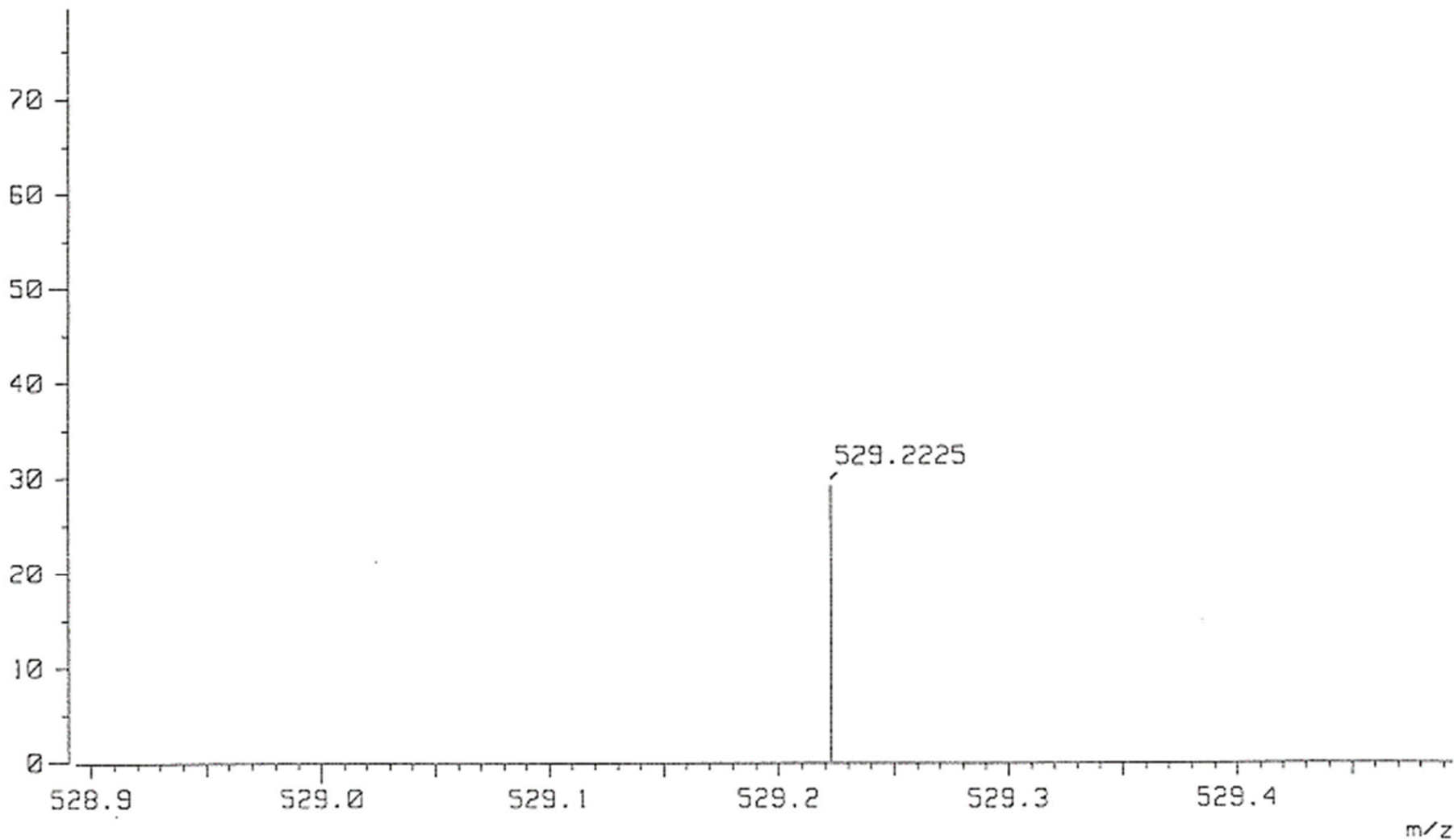
Scan#: 17+19

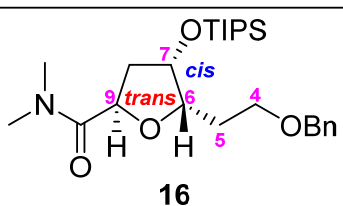
Elements : C 26/0, H 45/0, O 5/0, N 2/0, Br 1/0, Si 1/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
529.2225	29.2	+0.4 / +0.2	5.0	C 25 H 44 O 4 N Br Si





Chemical Formula: C<sub>25</sub>H<sub>43</sub>NO<sub>4</sub>Si

Exact Mass: 449.2961

**[M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>43</sub>NO<sub>4</sub>Si 449.2961**

[ Elemental Composition ]

Data : 6-SK-06-018

Date : 10-Oct-2023 16:36

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 1.44 min

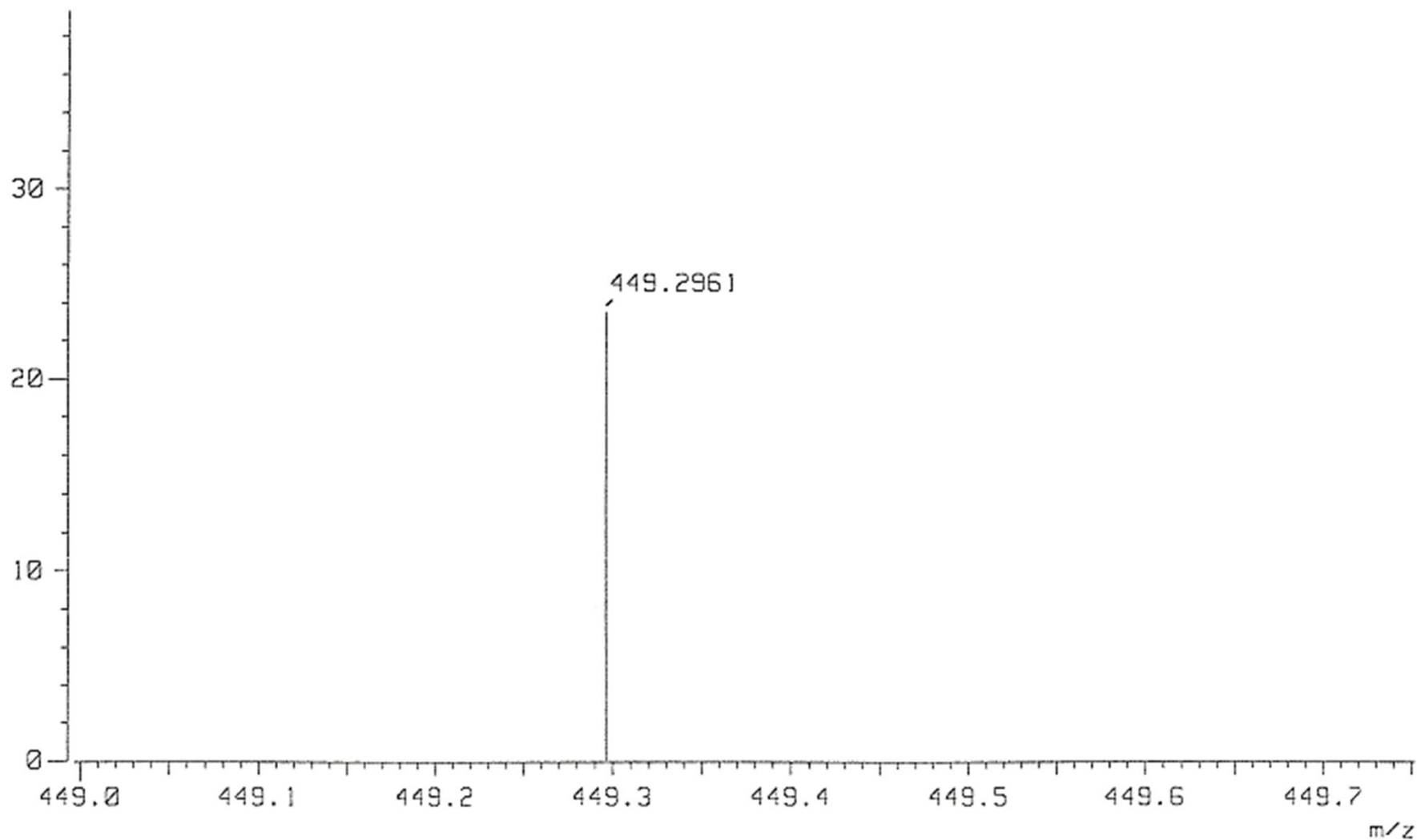
Scan#: 44+44+46+47

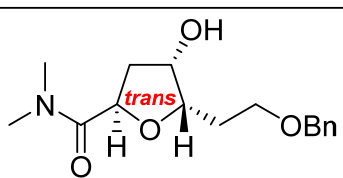
Elements : C 27/0, H 45/0, O 4/0, N 2/0, Si 1/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
449.2961	23.5	-0.1 / +0.0	6.0	C 25 H 43 O 4 N Si





**SI-A-03**

Chemical Formula: C<sub>16</sub>H<sub>23</sub>NO<sub>4</sub>

Exact Mass: 293.1627

**[M]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>23</sub>NO<sub>4</sub> 293.1627**

[ Elemental Composition ]

Data : 7-SK-07-003

Date : 10-Oct-2023 15:57

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 2.52 min

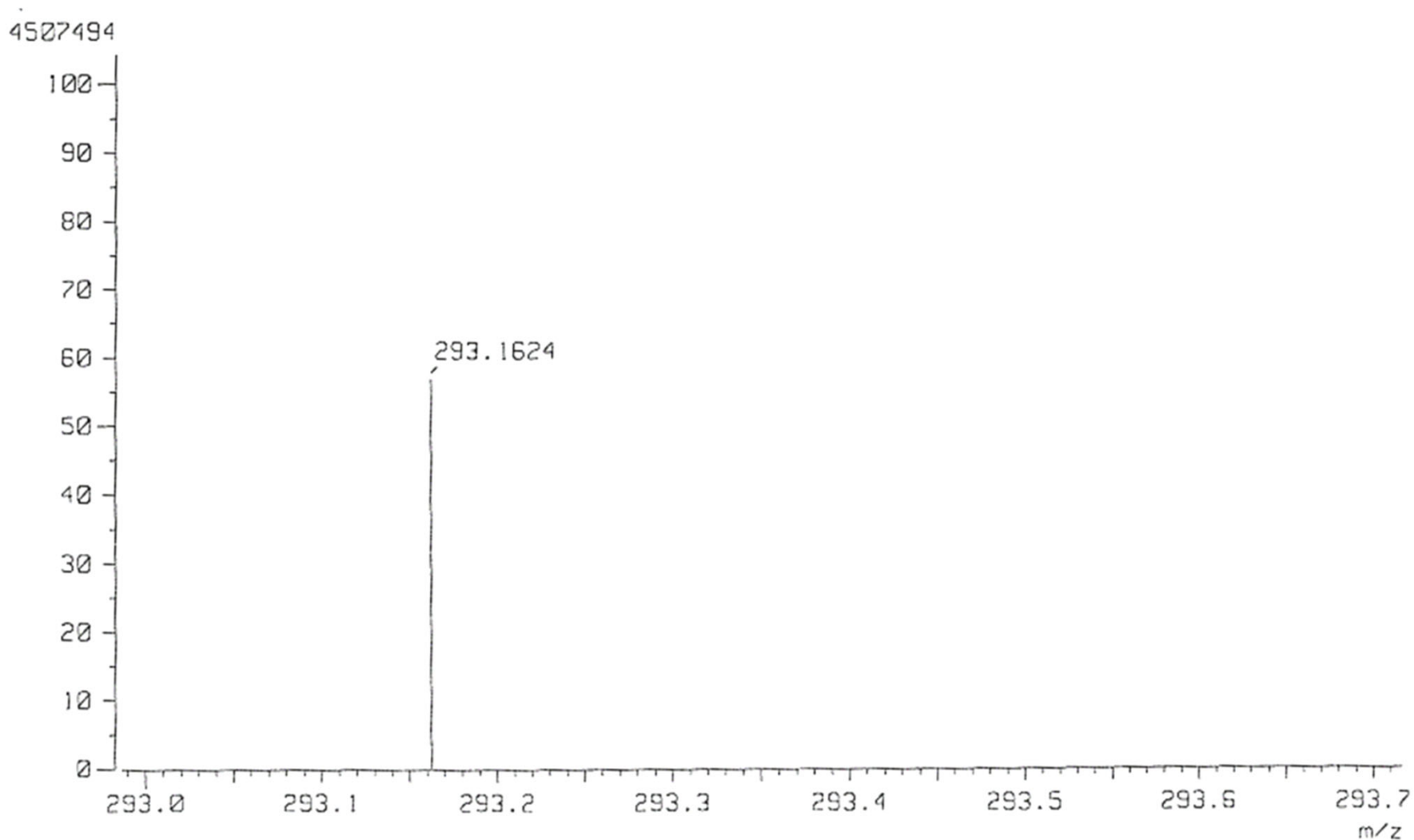
Scan#: (75,78)+68+64+70+71+72+74

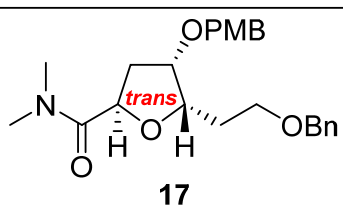
Elements : C 20/0, H 25/0, O 4/0, N 2/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
293.1624	56.9	-1.2 / -0.4	6.0 C 16 H 23 O 4 N





17

Chemical Formula: C<sub>24</sub>H<sub>31</sub>NO<sub>5</sub>

Exact Mass: 413.2202

[M]<sup>+</sup> Calcd for C<sub>24</sub>H<sub>31</sub>NO<sub>5</sub> 413.2202

[ Elemental Composition ]

Data : 8-SK-08-014

Date : 10-Oct-2023 16:28

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 1.60 min

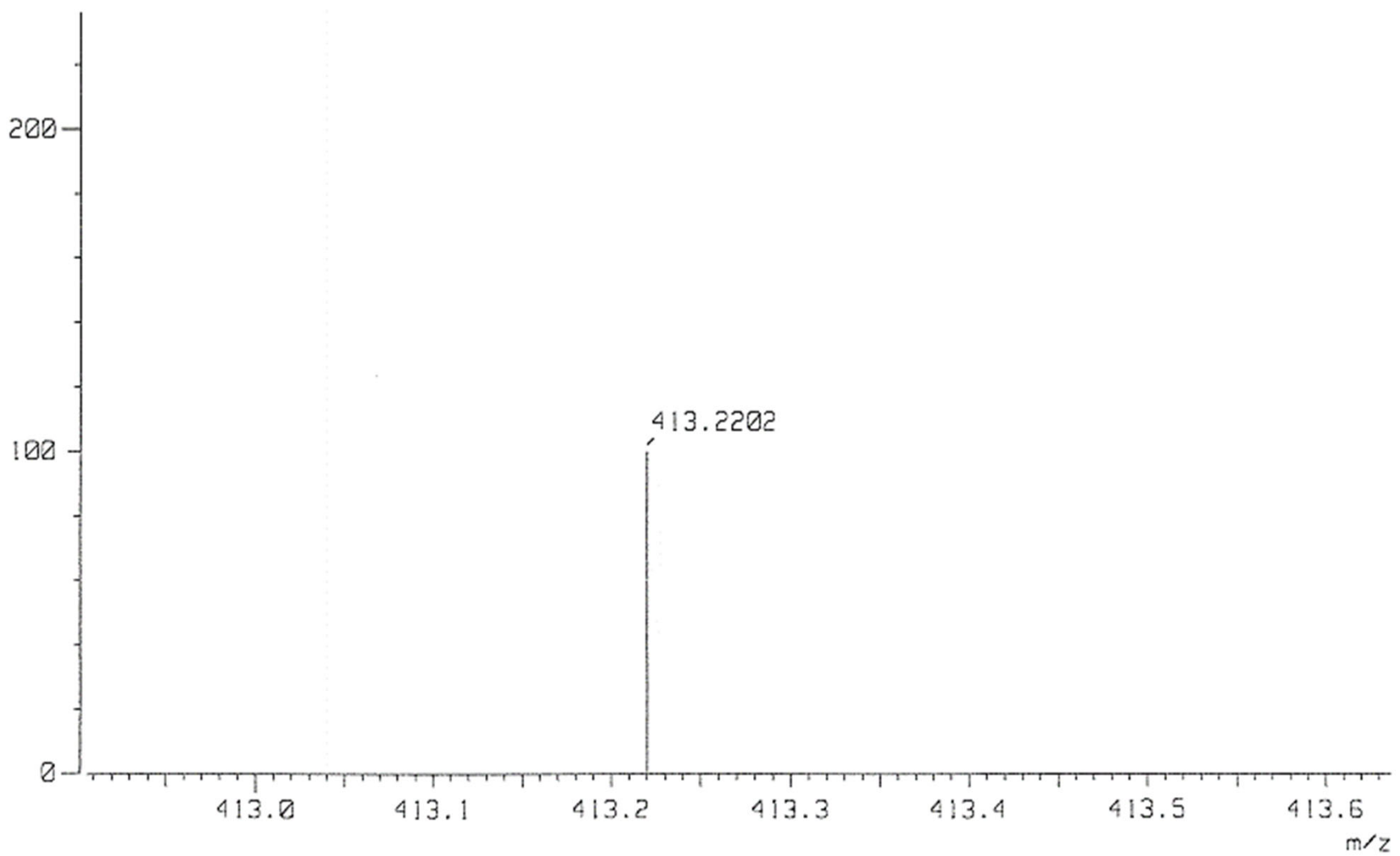
Scan#: 49+51+49

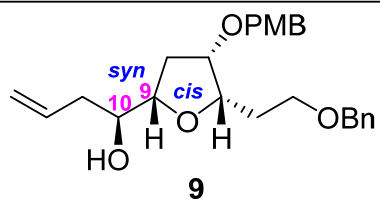
Elements : C 25/0, H 33/0, O 5/0, N 2/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
413.2202	100.0	+0.0 / +0.0	10.0	C 24 H 31 O 5 N





9

Chemical Formula: C<sub>25</sub>H<sub>32</sub>O<sub>5</sub>

Exact Mass: 412.2250

[M]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>32</sub>NO<sub>5</sub> 412.2228

[ Elemental Composition ]

Data : SK-24-013

Date : 20-Dec-2019 16:20

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

Ion Mode : EI+

RT : 1.17 min

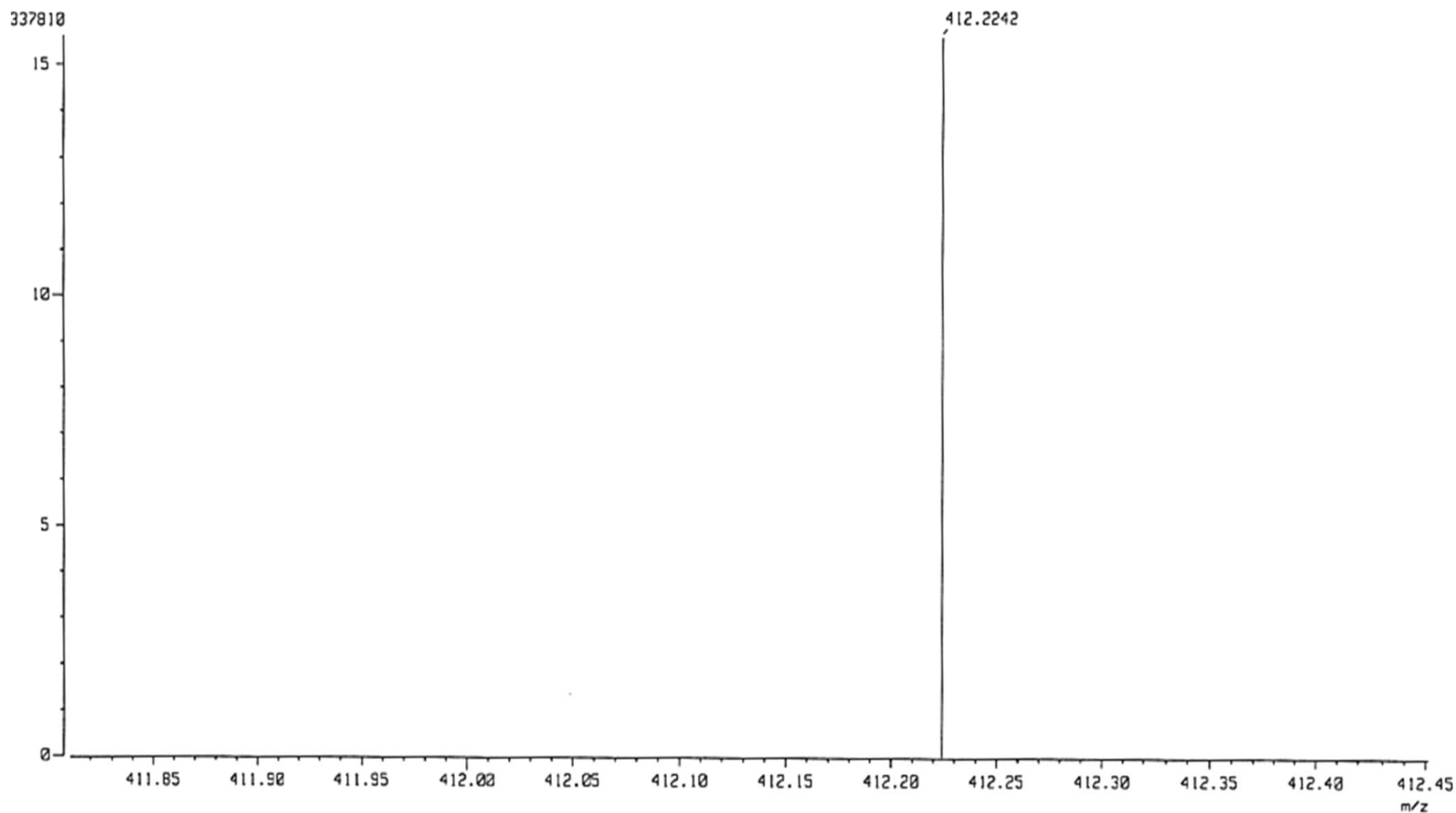
Scan#: 36+32

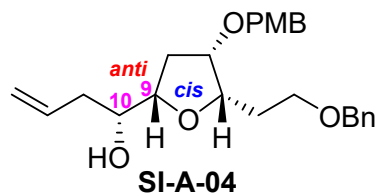
Elements : C 25/0, H 45/0, O 6/0

Mass Tolerance : 10mmu

Unsaturation (U.S.) : -1.0 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
412.2242	23.7	-2.0 / -0.8	10.0 C 25 H 32 O 5





Chemical Formula: C<sub>25</sub>H<sub>32</sub>O<sub>5</sub>

Exact Mass: 412.2250

**[M+H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>33</sub>NO<sub>5</sub> 413.2328**

[ Elemental Composition ]

Data : FAB-SK-11-011

Date : 11-Oct-2023 14:55

Sample:

Note : SM Lab Research Center (Jeol JMS-700)

Inlet : Reserv.

Ion Mode : FAB+

RT : 1.04 min

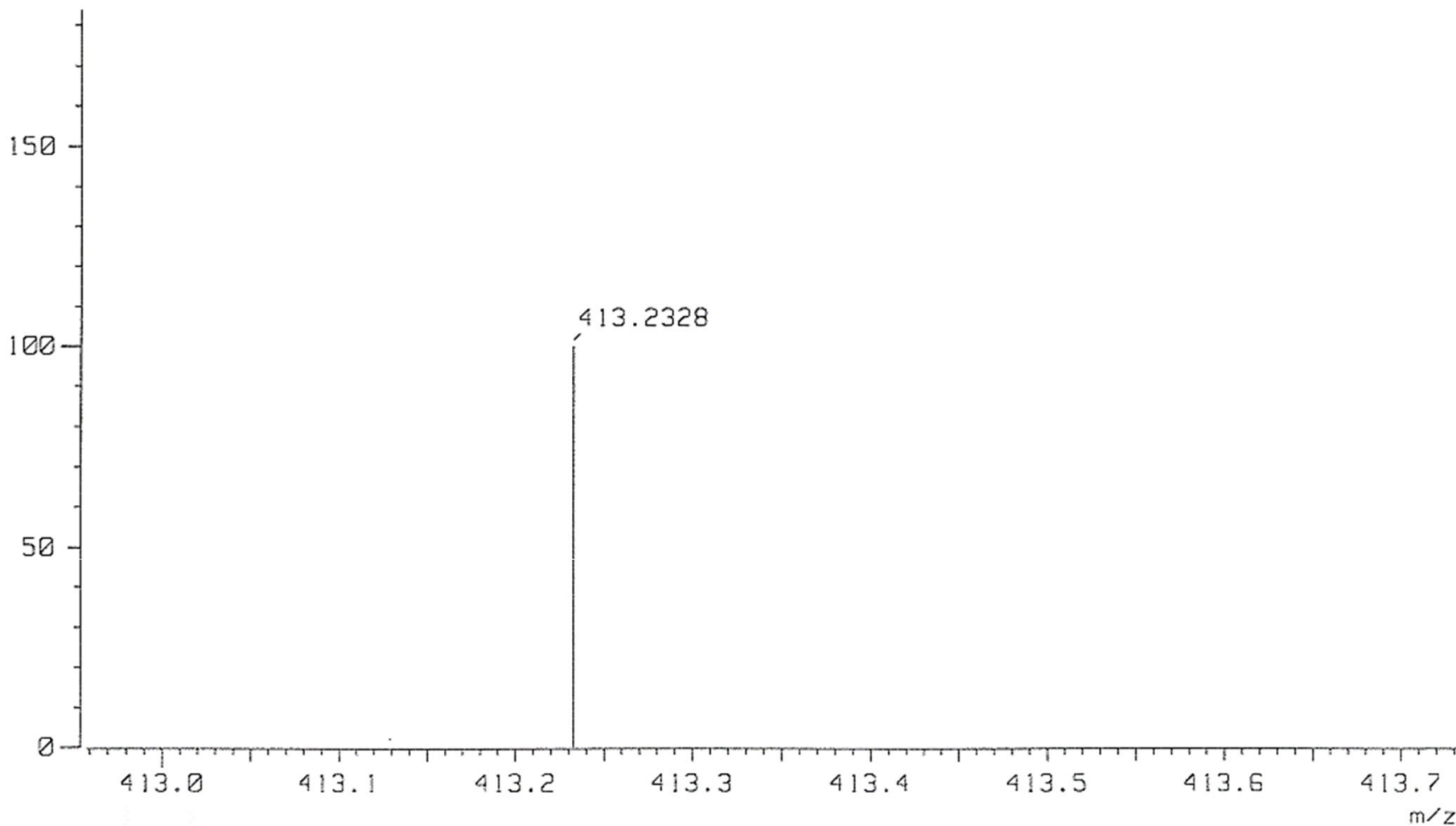
Scan#: 32+18+8

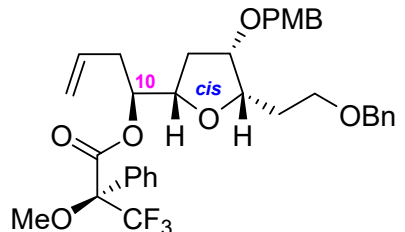
Elements : C 27/0, H 37/0, O 7/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 80.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
413.2328	100.0	+0.0 / +0.0	9.5	C 25 H 33 O 5





**SI-A-(S)-MTPA-05**

Chemical Formula: C<sub>35</sub>H<sub>39</sub>F<sub>3</sub>O<sub>7</sub>

Exact Mass: 628.2648

**[M+H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>40</sub>F<sub>3</sub>O<sub>7</sub> 629.2726**

[ Elemental Composition ]

Data : FAB-SK-09-003

Date : 11-Oct-2023 12:20

Sample:

Note : SM Lab Research Center (Jeol JMS-700)

Inlet : Reserv.

Ion Mode : FAB+

RT : 0.44 min

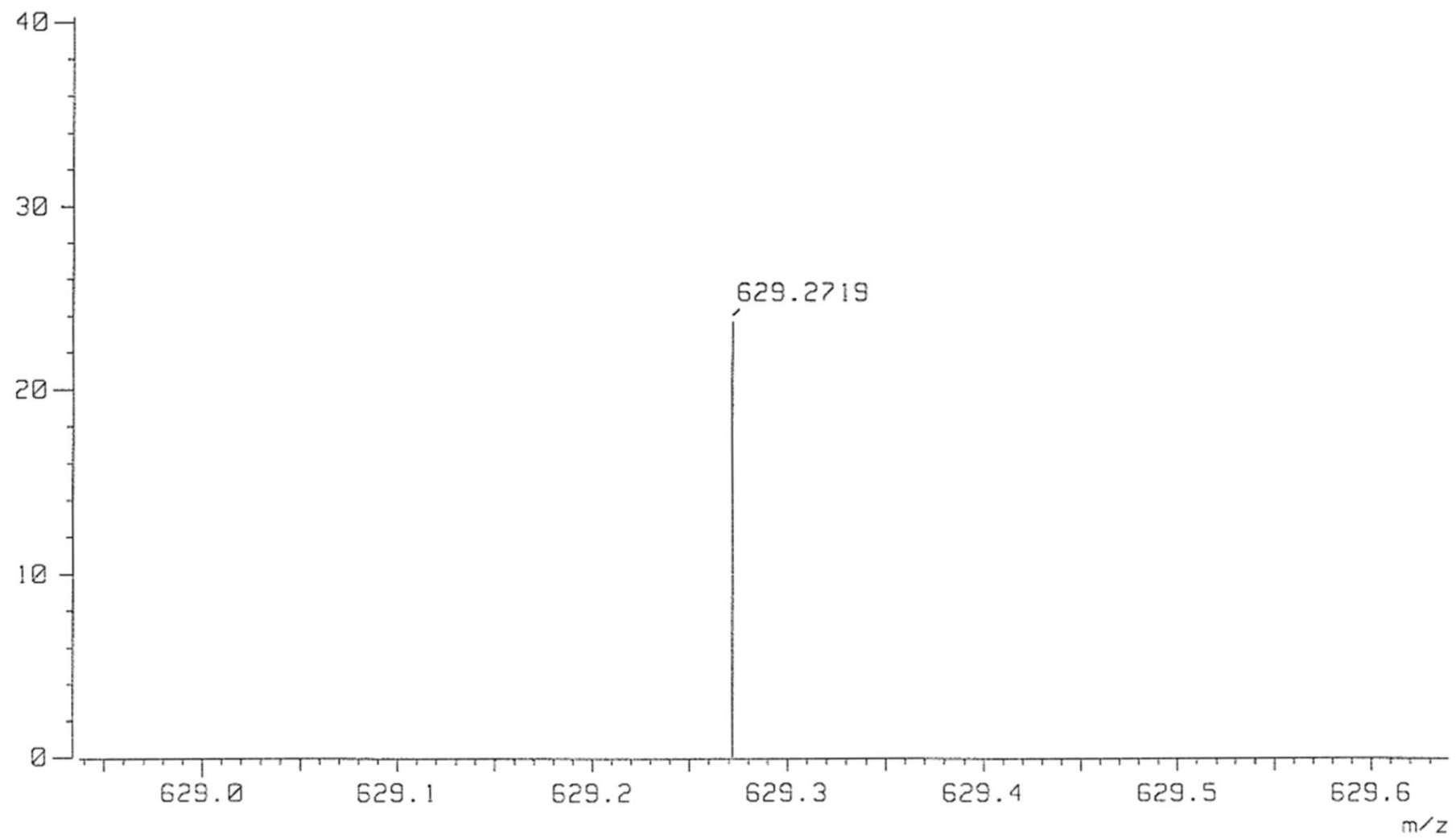
Scan#: (11,17)+24+18+18

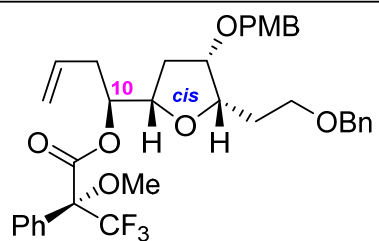
Elements : C 37/0, H 44/0, O 7/0, F 3/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 80.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
629.2719	23.7	-1.1 / -0.7	14.5	C 35 H 40 O 7 F 3





**SI-A-(R)-MTPA-06**

Chemical Formula: C<sub>35</sub>H<sub>39</sub>F<sub>3</sub>O<sub>7</sub>

Exact Mass: 628.2648

**[M+H]<sup>+</sup> Calcd for C<sub>35</sub>H<sub>40</sub>F<sub>3</sub>O<sub>7</sub> 629.2726**

[ Elemental Composition ]

Data : FAB-SK-10-005

Date : 11-Oct-2023 12:49

Sample:

Note : SM Lab Research Center (Jeol JMS-700)

Inlet : Reserv.

Ion Mode : FAB+

RT : 5.40 min

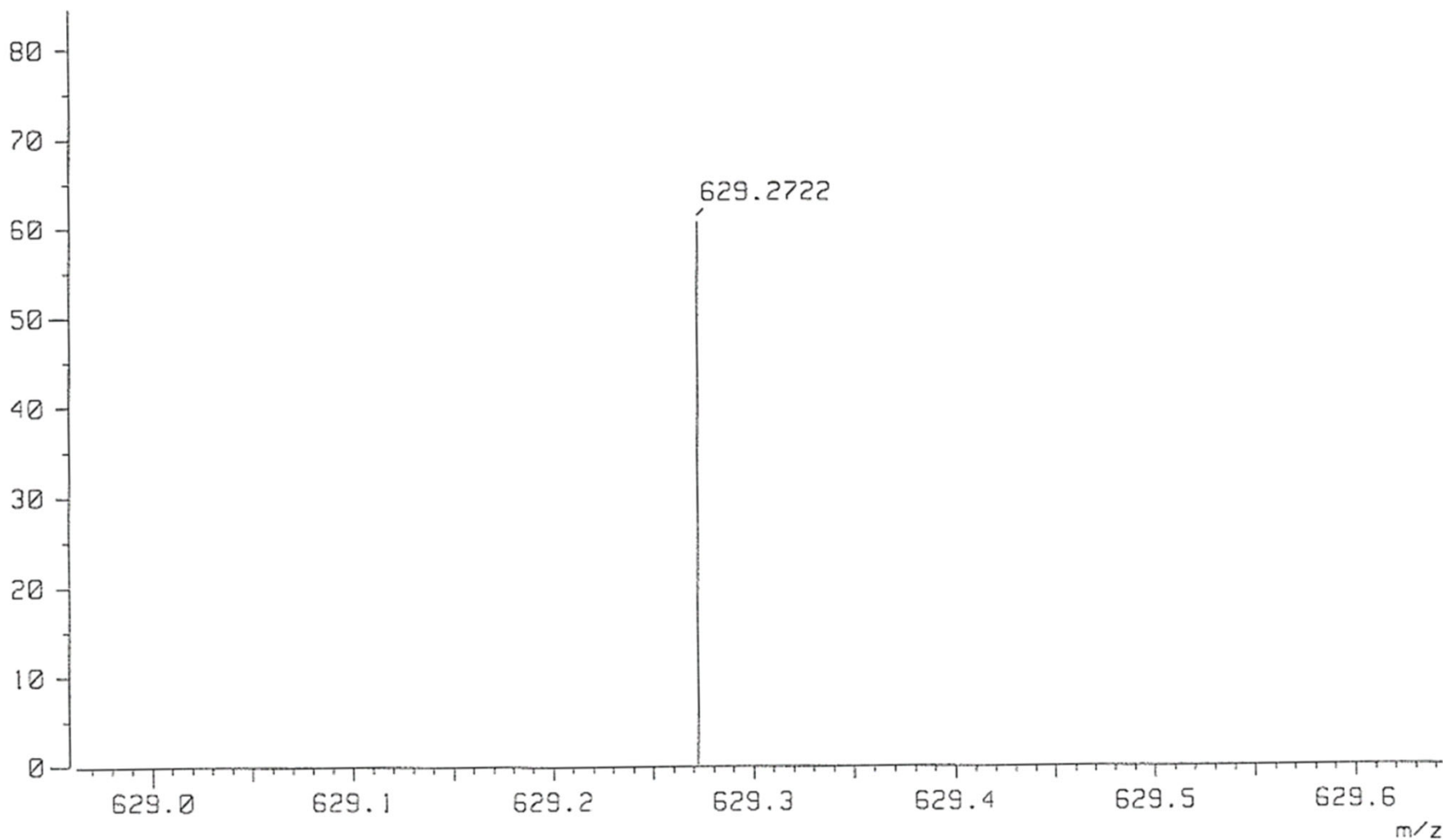
Scan#: 163+85

Elements : C 37/0, H 44/0, O 7/0, F 3/0

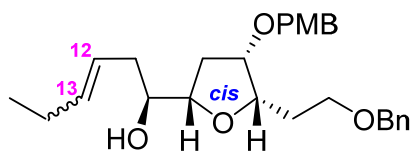
Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 80.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
629.2722	60.8	-0.6 / -0.4	14.5 C 35 H 40 O 7 F 3







**20**

Chemical Formula: C<sub>27</sub>H<sub>36</sub>O<sub>5</sub>

Exact Mass: 440.2563

**[M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>36</sub>O<sub>5</sub> 440.2563**

[ Elemental Composition ]

Data : SK-25-017

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

RT : 0.97 min

Elements : C 30/0, H 45/0, O 6/0

Mass Tolerance : 10mmu

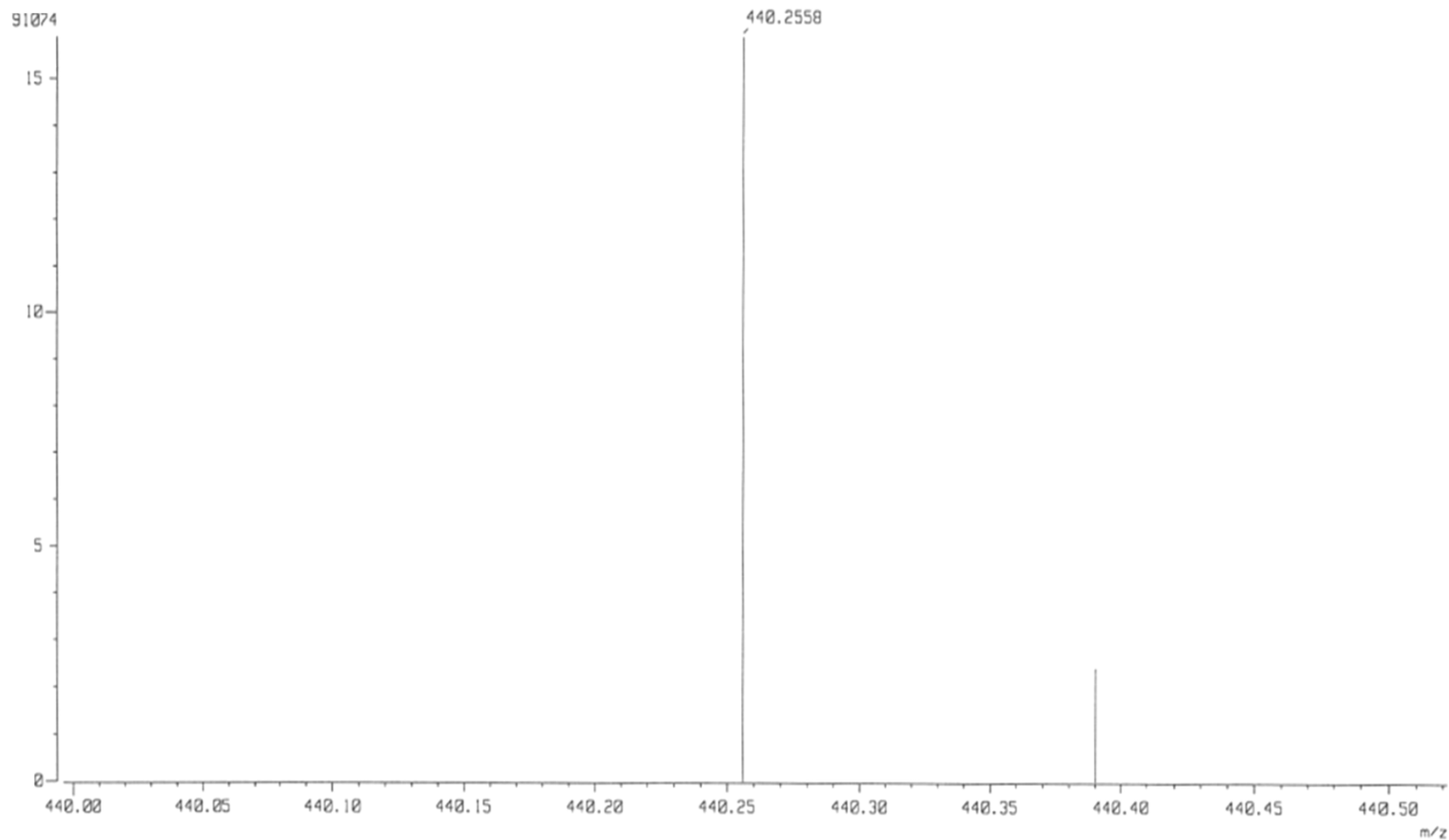
Unsaturation (U.S.) : -1.0 - 50.0

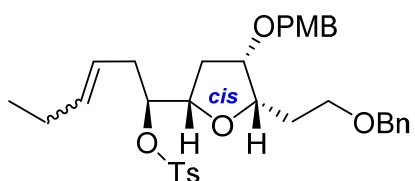
Date : 20-Dec-2019 16:52

Ion Mode : EI+

Scan#: 30+30+31+30

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
440.2558	19.2	-1.1 / -0.5	10.0	C 27 H 36 O 5





**SI-A-07**

Chemical Formula: C<sub>34</sub>H<sub>42</sub>O<sub>7</sub>S

Exact Mass: 594.2651

**[M]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>42</sub>O<sub>7</sub>S 594.2651**

[ Elemental Composition ]

Data : SK-26-019

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

RT : 1.94 min

Elements : C 35/0, H 45/0, O 7/0, S 1/0

Mass Tolerance : 10mmu

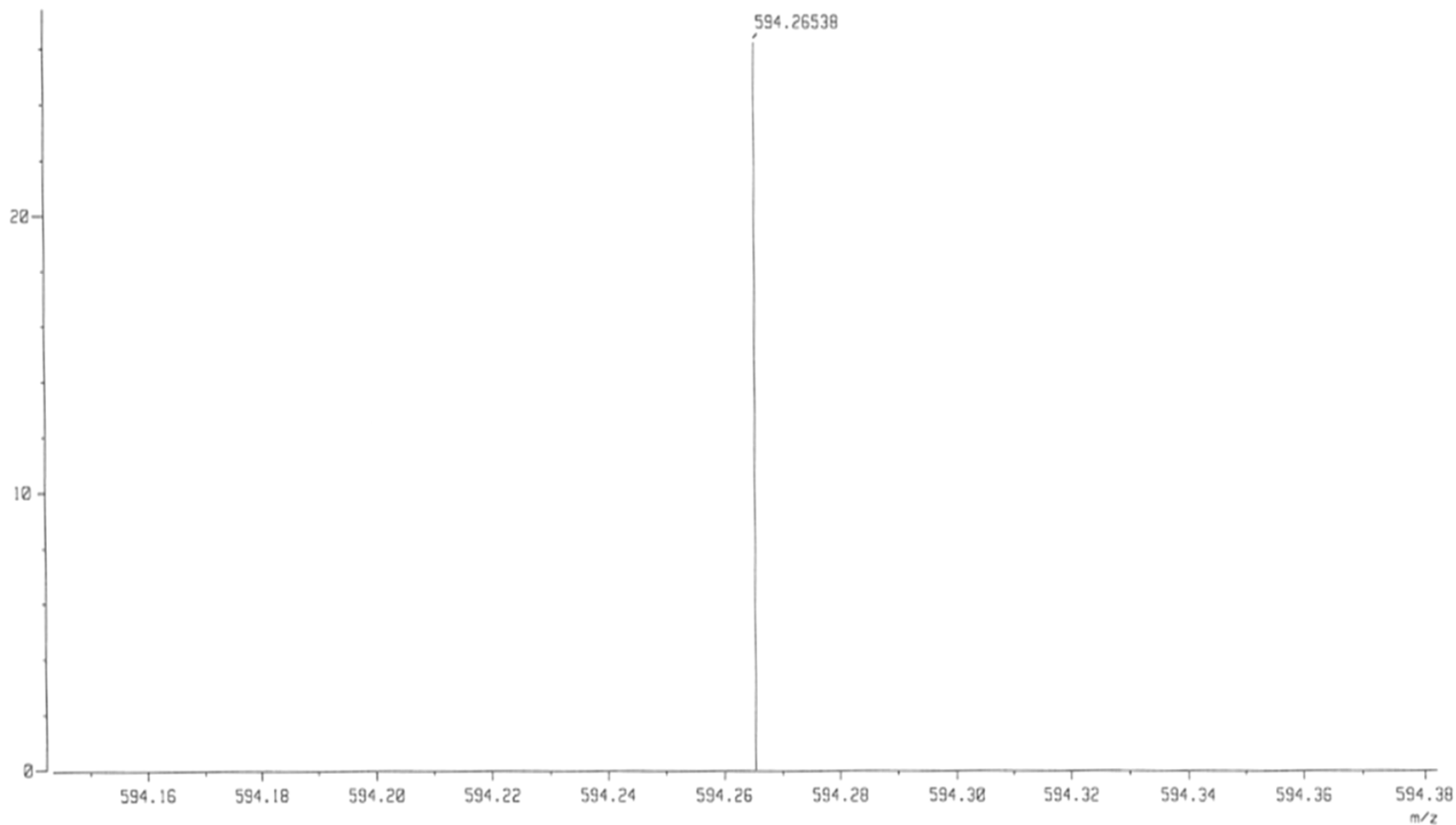
Unsaturation (U.S.) : -1.0 - 50.0

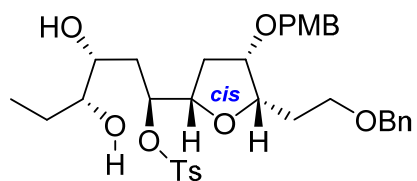
Date : 20-Dec-2019 17:14

Ion Mode : EI+

Scan#: 59+58+58+57+59+59+58

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
594.2654	26.2	+0.4 / +0.3	15.0	C 34 H 42 O 7 S





8

Chemical Formula: C<sub>34</sub>H<sub>44</sub>O<sub>9</sub>S

Exact Mass: 628.2706

**[M+H]<sup>+</sup> Calcd for C<sub>34</sub>H<sub>45</sub>O<sub>9</sub>S 629.2784**

[ Elemental Composition ]

Data : FAB-SK-12-007

Date : 11-Oct-2023 12:55

Sample:

Note : SM Lab Research Center (Jeol JMS-700)

Inlet : Reserv.

Ion Mode : FAB+

RT : 1.27 min

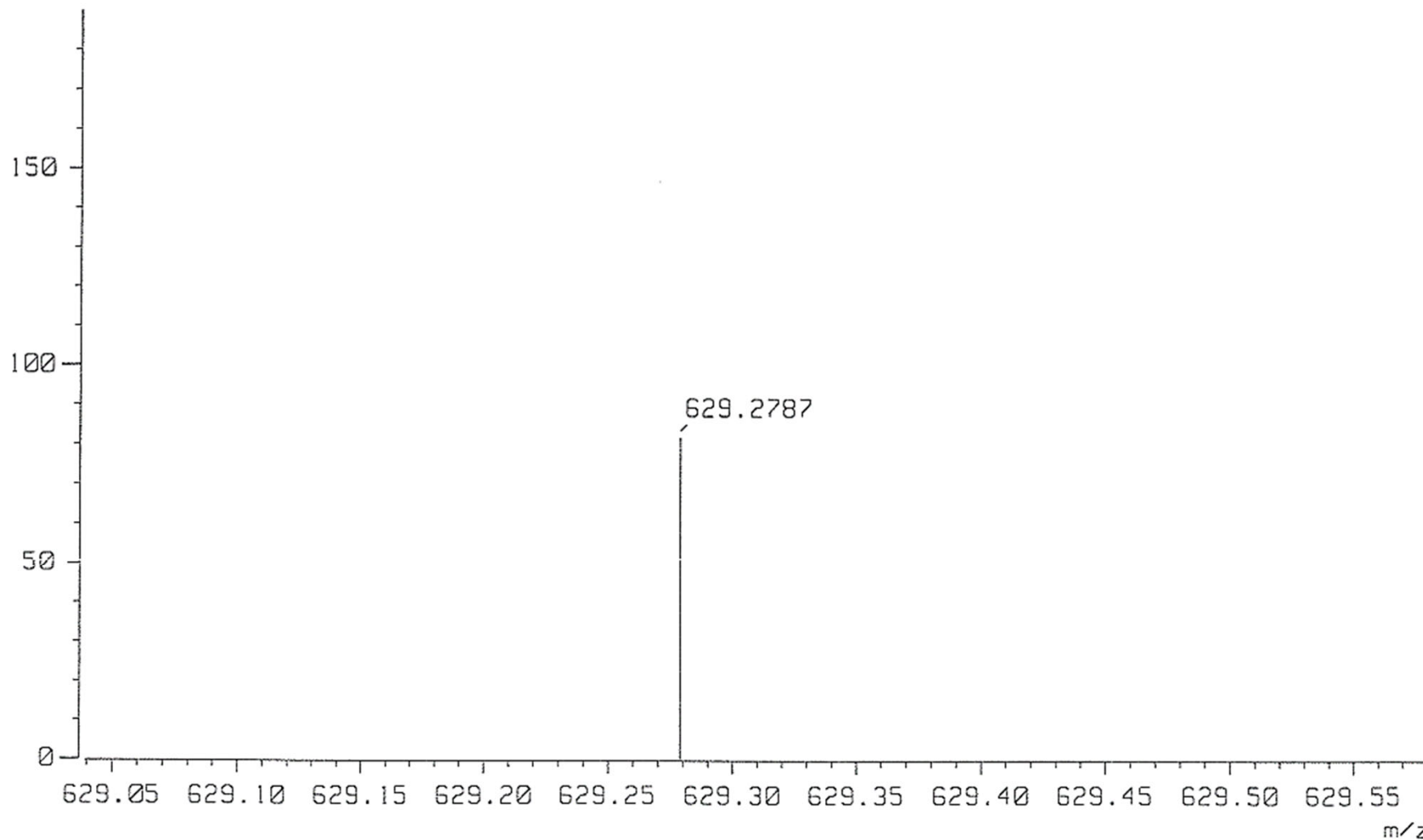
Scan#: 39

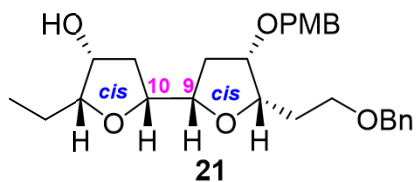
Elements : C 36/0, H 46/0, O 9/0, S 1/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 80.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
629.2787	81.9	+0.5 / +0.3	13.5	C 34 H 45 O 9 S





Chemical Formula: C<sub>27</sub>H<sub>36</sub>O<sub>6</sub>

Exact Mass: 456.2512

**[M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>36</sub>O<sub>6</sub> 456.2512**

[ Elemental Composition ]

Data : SK-1-001

Date : 20-Dec-2019 14:03

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

Ion Mode : EI+

RT : 1.10 min

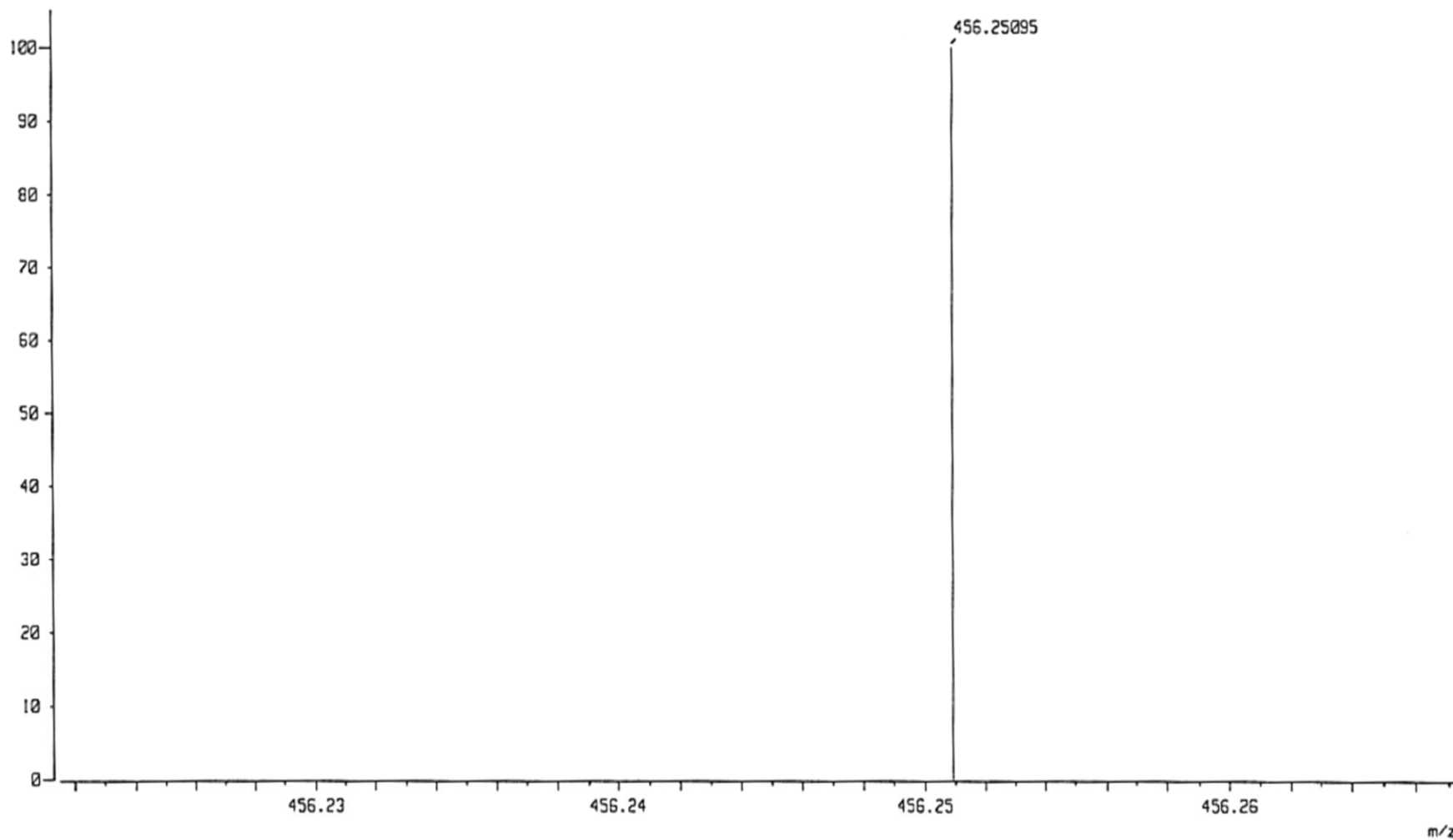
Scan#: 34+38+39

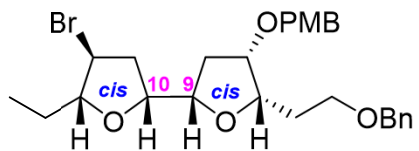
Elements : C 27/0, H 50/0, O 7/0

Mass Tolerance : 10mmu

Unsaturation (U.S.) : -1.0 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
456.2509	100.0	-0.5 / -0.2	10.0 C 27 H 36 O 6





SI-A-09

Chemical Formula: C<sub>27</sub>H<sub>35</sub>BrO<sub>5</sub>

Exact Mass: 518.1668

[M]<sup>+</sup> Calcd for C<sub>27</sub>H<sub>35</sub>BrO<sub>5</sub> 518.1668

[ Elemental Composition ]

Data : SK-2-002

Date : 20-Dec-2019 14:06

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

Ion Mode : EI+

RT : 0.74 min

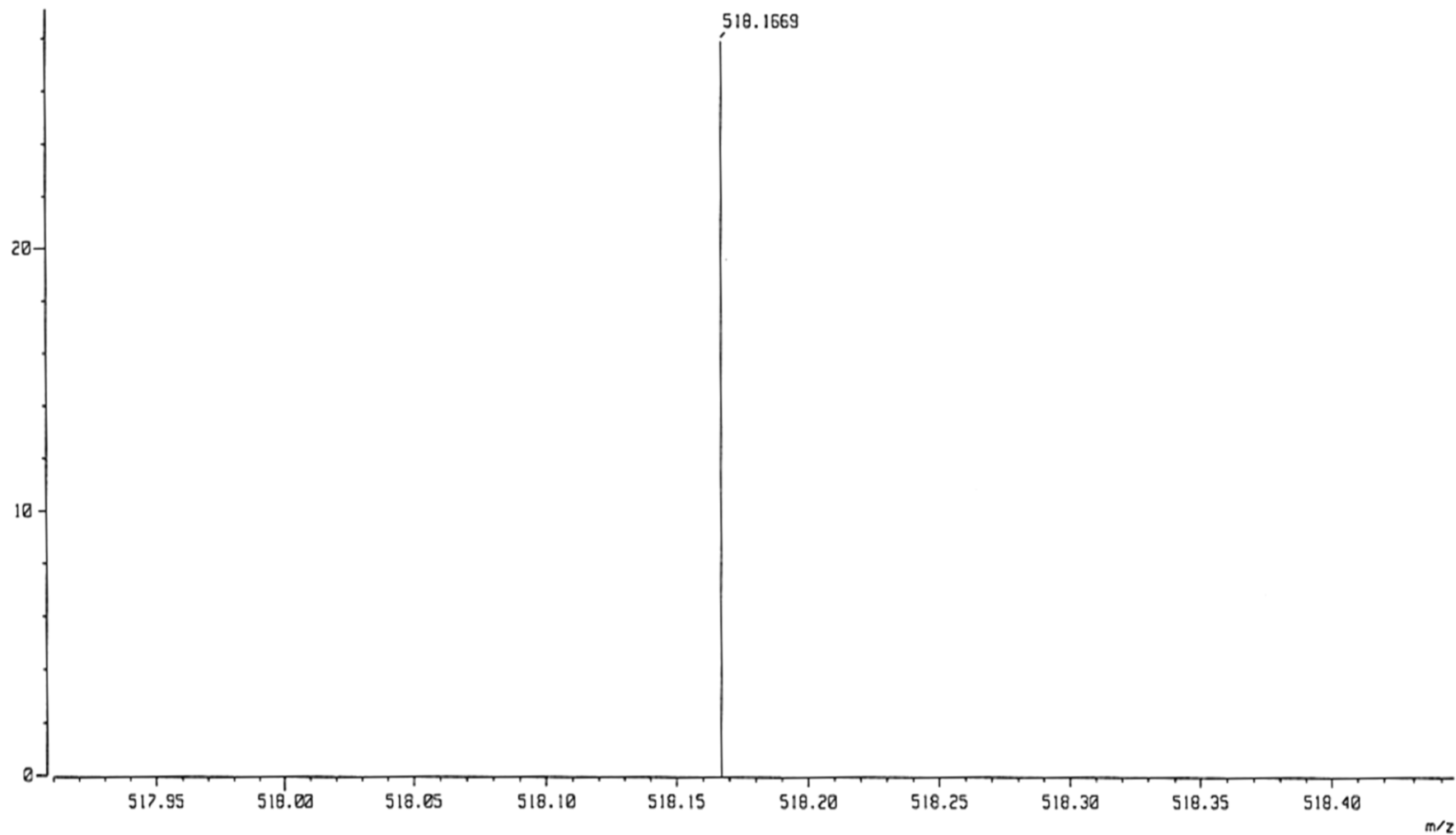
Scan#: 23

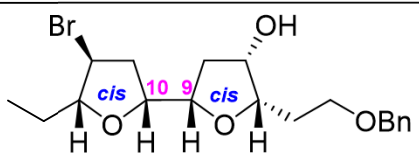
Elements : C 28/0, H 50/0, Br 1/0, O 7/0

Mass Tolerance : 10mmu

Unsaturation (U.S.) : -1.0 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
518.1669	27.9	+0.3 / +0.1	10.0	C 27 H 35 Br O 5





SI-A-10

Chemical Formula: C<sub>19</sub>H<sub>27</sub>BrO<sub>4</sub>

Exact Mass: 398.1093

[M]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>27</sub>BrO<sub>4</sub> 398.1093

[ Elemental Composition ]

Data : SK-3-003

Date : 20-Dec-2019 14:10

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

Ion Mode : EI+

RT : 0.74 min

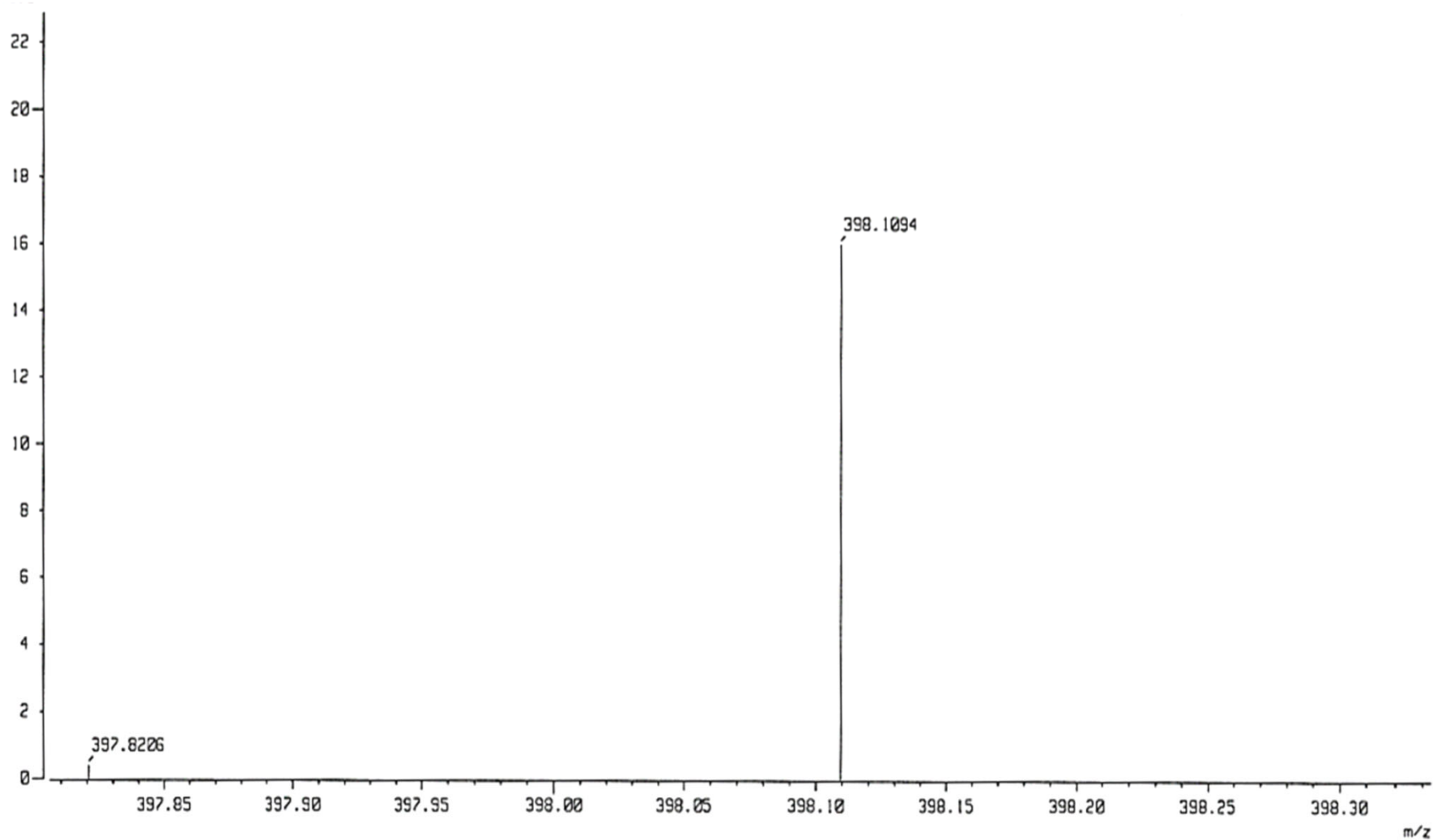
Scan#: 23

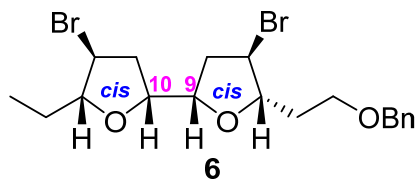
Elements : C 20/0, H 30/0, Br 1/0, O 7/0

Mass Tolerance : 10mmu

Unsaturation (U.S.) : -1.0 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
398.1094	16.0	+0.3 / +0.1	6.0 C 19 H 27 Br O 4





Chemical Formula:  $C_{19}H_{26}Br_2O_3$

Exact Mass: 460.0249

$[M]^+$  Calcd for  $C_{19}H_{26}Br_2O_3$  460.0249

[ Elemental Composition ]

Data : SK-4-004

Date : 20-Dec-2019 14:13

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

Ion Mode : EI+

RT : 0.90 min

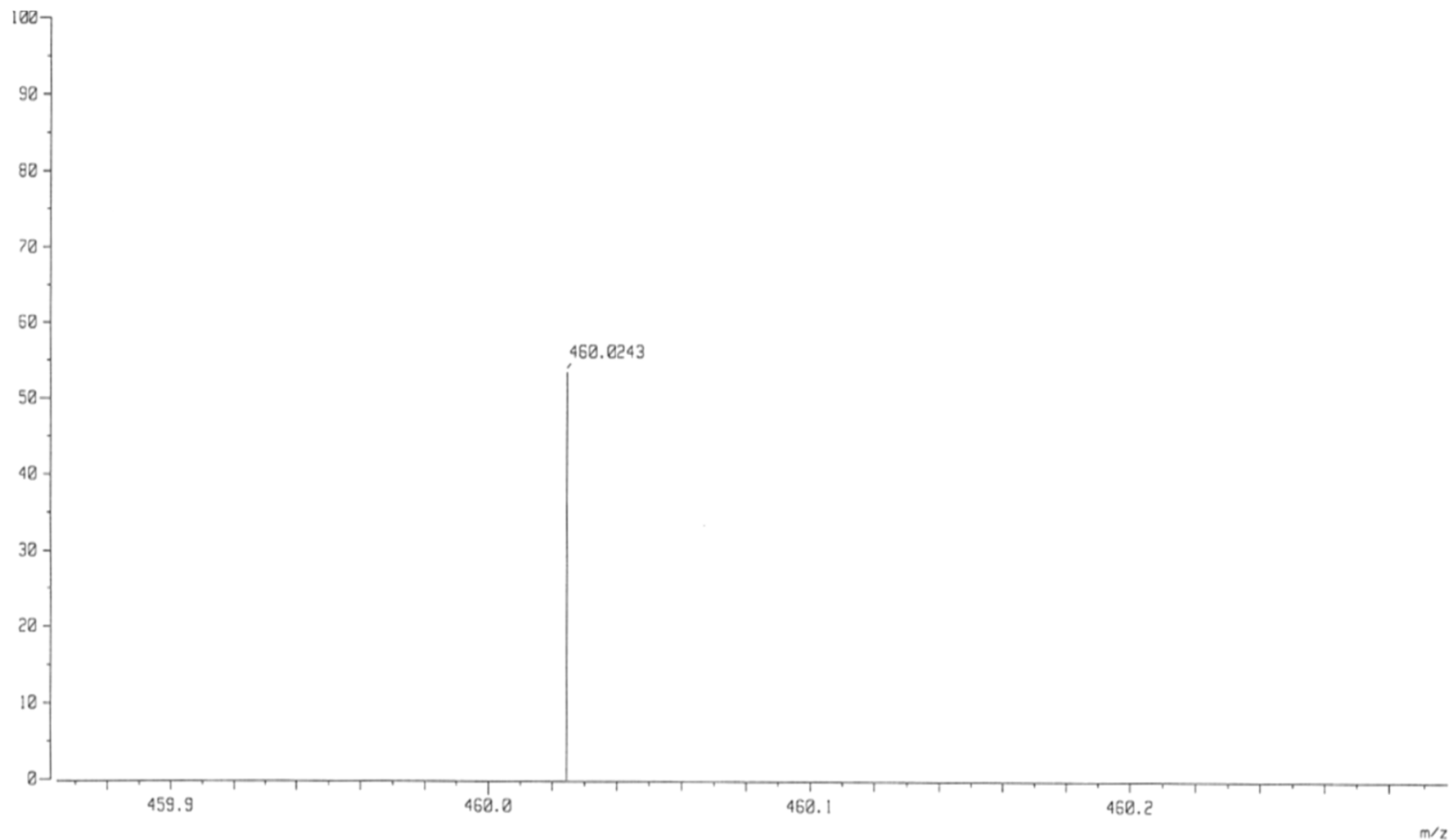
Scan#: 28+32

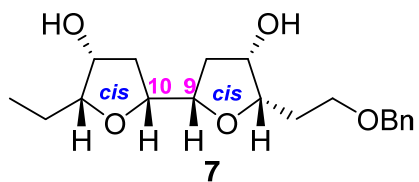
Elements : C 20/0, H 30/0, Br 2/0, O 7/0

Mass Tolerance : 10mmu

Unsaturation (U.S.) : -1.0 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
460.0243	53.5	-1.2 / -0.5	6.0	C 19 H 26 Br 2 O 3





Chemical Formula: C<sub>19</sub>H<sub>28</sub>O<sub>5</sub>

Exact Mass: 336.1937

**[M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>29</sub>O<sub>5</sub> 337.2015**

[ Elemental Composition ]

Data : FAB-SK-13-013

Sample:

Note : SM Lab Research Center (Jeol JMS-700)

Inlet : Reserv.

RT : 3.34 min

Elements : C 27/0, H 37/0, O 7/0

Mass Tolerance : 5mmu

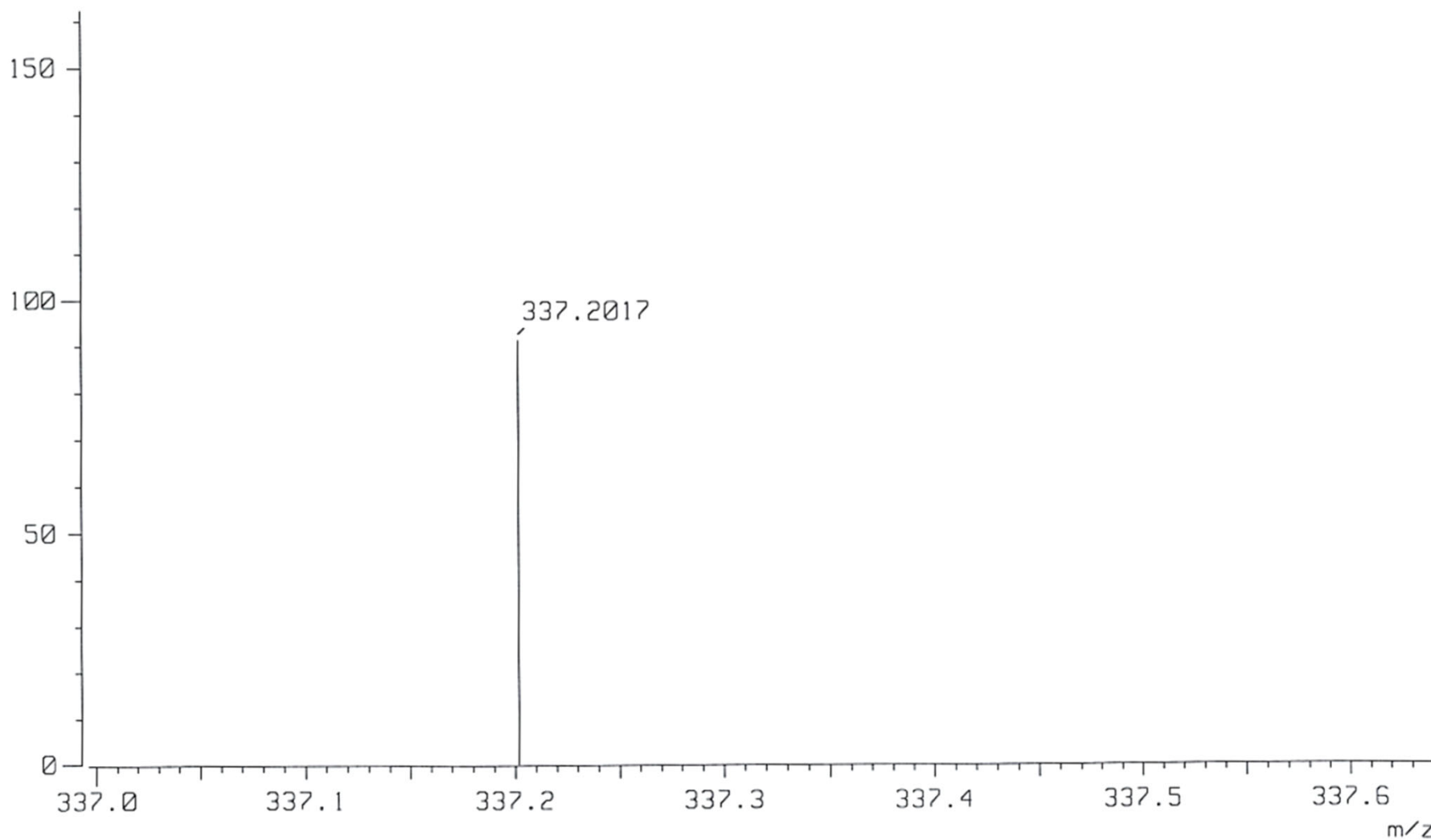
Unsaturation (U.S.) : -0.5 - 80.0

Date : 11-Oct-2023 15:05

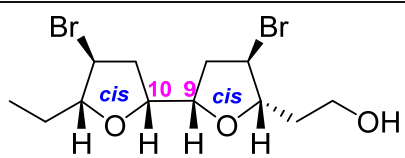
Ion Mode : FAB+

Scan#: 101

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
337.2017	91.3	+0.7 / +0.2	5.5 C 19 H 29 O 5







**SI-A-13**

Chemical Formula:  $C_{12}H_{20}Br_2O_3$

Exact Mass: 369.9779

$[M+H]^+$  Calcd for  $C_{12}H_{21}Br_2O_3$  370.9857

[ Elemental Composition ]

Data : FAB-SK-14-015

Date : 11-Oct-2023 15:15

Sample:

Note : SM Lab Research Center (Jeol JMS-700)

Inlet : Reserv.

Ion Mode : FAB+

RT : 1.47 min

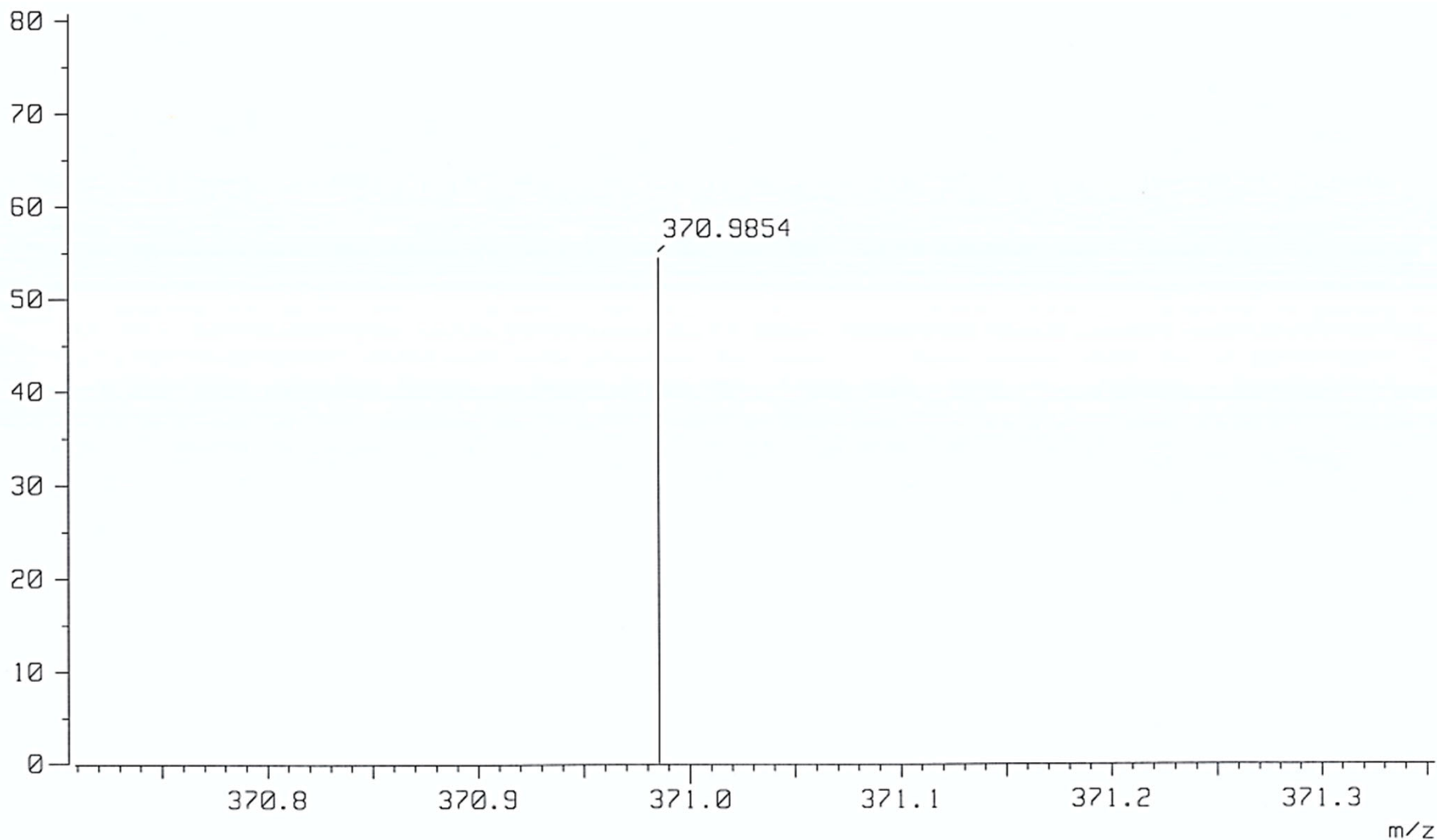
Scan#: (44,46)

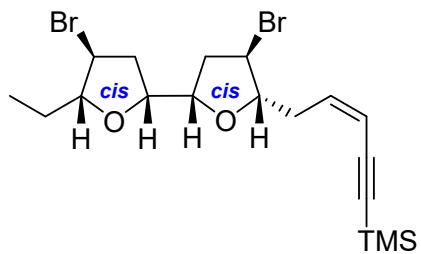
Elements : C 15/0, H 22/0, O 3/0, Br 2/0

Mass Tolerance : 5mmu

Unsaturation (U.S.) : -0.5 - 80.0

Observed m/z	Int%	Err [ppm / mmu]	U.S. Composition
370.9854	54.4	-1.0 / -0.4	1.5 C 12 H 21 O 3 Br 2





**TMS-(3Z)-Enyne SI-A-14**

Chemical Formula:  $C_{18}H_{28}Br_2O_2Si$

Exact Mass: 462.0225

$[M]^+$  Calcd for  $C_{18}H_{28}Br_2O_2Si$  462.0225

[ Elemental Composition ]

Data : SK-6-006

Date : 20-Dec-2019 14:34

Sample: Ajou-Univ.

Note : SM Lab Research institute for Analysis

Inlet : Reserv.

Ion Mode : EI+

RT : 0.80 min

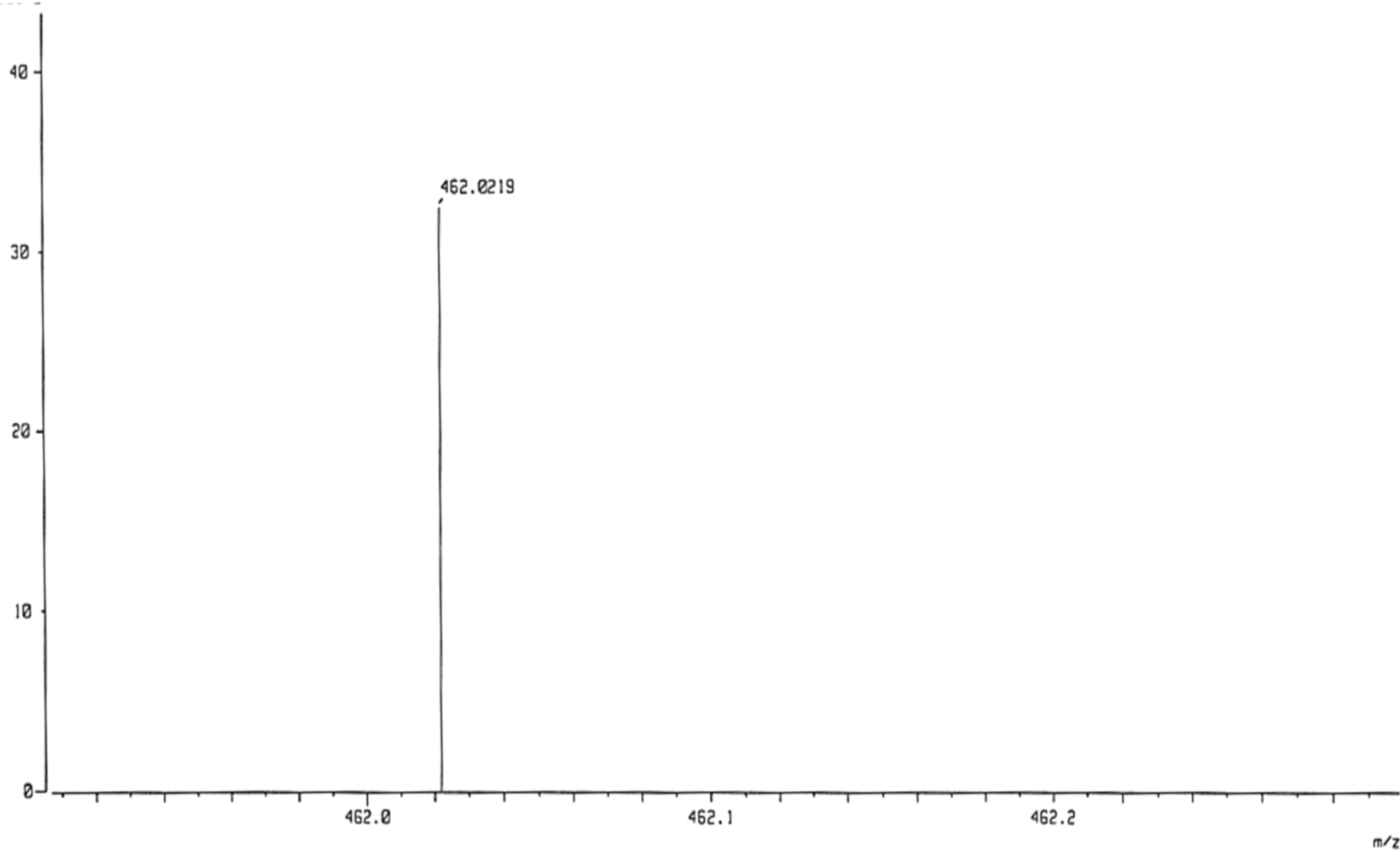
Scan#: 25

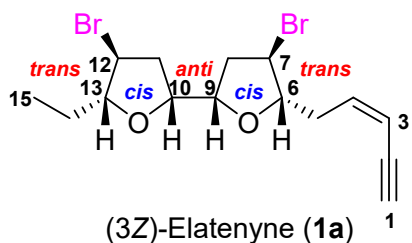
Elements : C 20/0, H 30/0, Br 2/0, O 2/0, Si 2/0

Mass Tolerance : 10mmu

Unsaturation (U.S.) : -1.0 - 50.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
462.0219	32.5	-1.3 / -0.6	5.0	C 18 H 28 Br 2 O 2 Si





Chemical Formula: C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub>

Exact Mass: 389.9830

**[M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub> 389.9830**

[ Elemental Composition ]

Data : 16-SK-16-031

Date : 10-Oct-2023 17:10

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 0.94 min

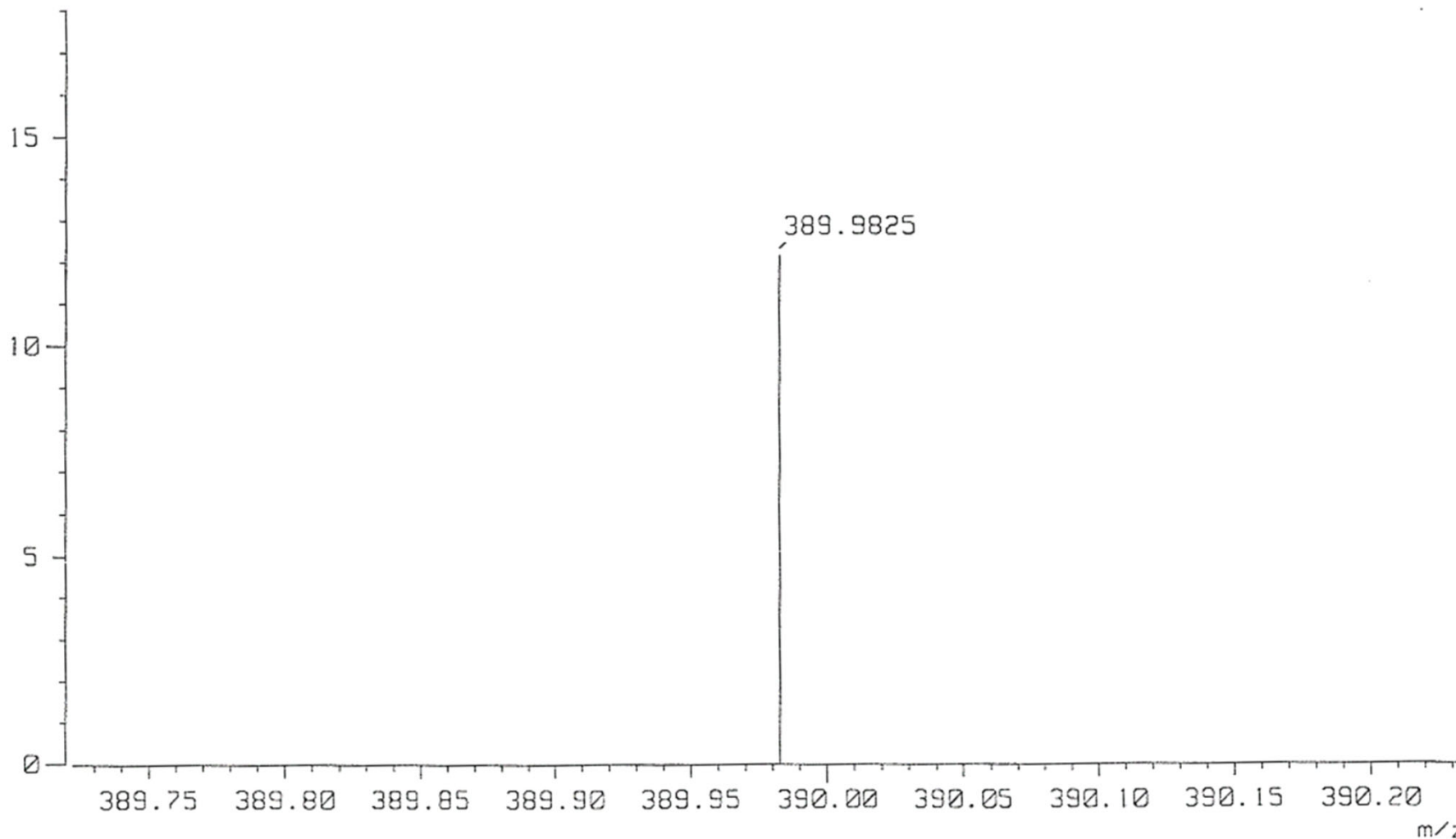
Scan#: 29

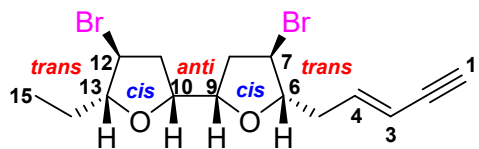
Elements : C 16/0, H 22/0, O 2/0, Br 2/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
389.9825	12.2	-1.2 / -0.5	5.0	C 15 H 20 O 2 Br 2





(3E)-Elatenyne (**1b**)

Chemical Formula: C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub>

Exact Mass: 389.9830

**[M]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>2</sub> 389.9830**

[ Elemental Composition ]

Data : 15-SK-15-029

Date : 10-Oct-2023 17:06

Sample:

Note : SMLab Mass analysis (Jeol HRMS JMS-700D)

Inlet : Direct

Ion Mode : EI+

RT : 1.27 min

Scan#: 39

Elements : C 16/0, H 22/0, O 2/0, Br 2/0

Mass Tolerance : 3mmu

Unsaturation (U.S.) : -0.5 - 70.0

Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
389.9834	9.5	+0.9 / +0.4	5.0	C 15 H 20 O 2 Br 2

