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–Electronic Supplementary Information (ESI)–

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

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Part A (S1 ~ S29)

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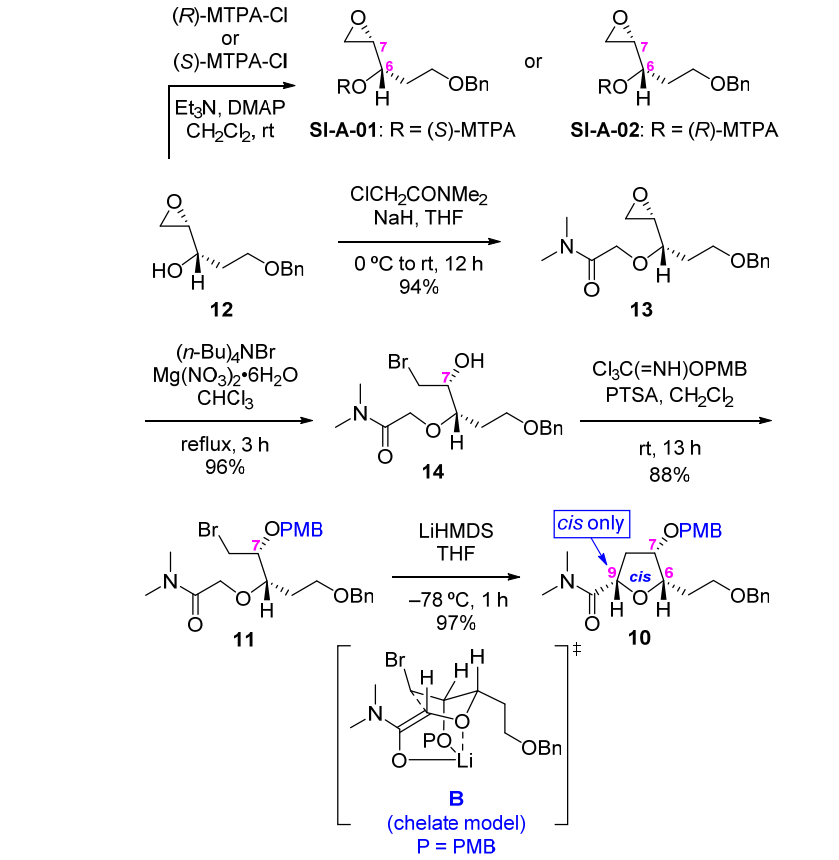
General

Proton (^{1}H) and carbon (^{13}C) NMR spectra were obtained on Varian Mercury 400 and ECZ600R. Chemical shifts are reported in ppm units with Me_4Si or $CHCl_3$ 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.

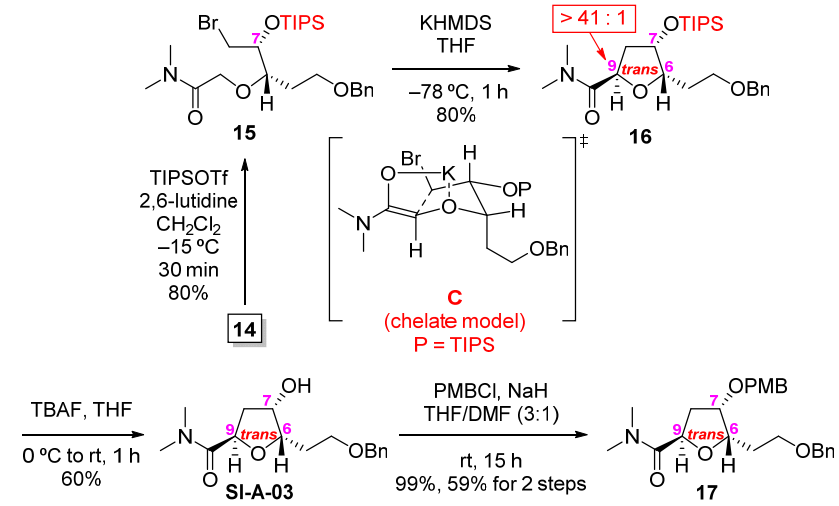
Note: The present Supporting Information A includes modified versions of the experimental procedures that have been already described in the literature in case the experimental procedures were improved in terms of reaction conditions, yields, selectivity, and so on, or where additional spectroscopic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

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

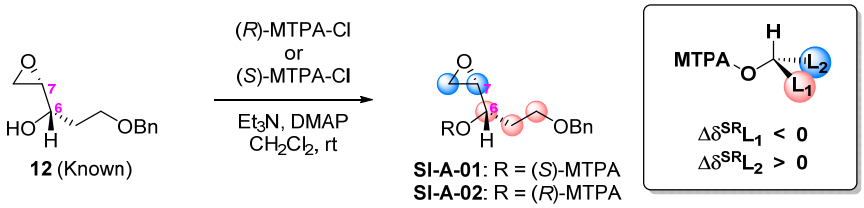
Scheme ESI-01. Stereoselective Synthesis of Key 6,7-*cis*-6,9-*cis*-THF 10 via IAEA



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

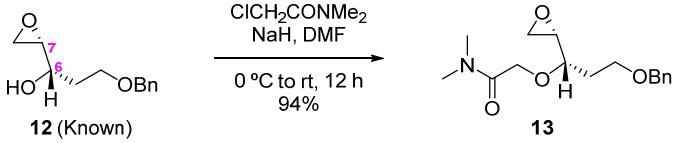


Determination of *ee* Value and Confirmation of C(6) Absolute Stereochemistry of Secondary Alcohol 12[1]



To a solution of secondary epoxy alcohol **12** in CH_2Cl_2 were successively added (*R*)- or (*S*)-*α*-methoxy-*α*-trifluoromethylphenylacetyl chloride (5.0 eq), Et_3N (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 $NaHCO_3$, diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combine layers were washed with brine, dried over anhydrous Na_2SO_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}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 11.8 Hz, $\Delta\nu_{AB}$ = 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}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 11.8 Hz, $\Delta\nu_{AB}$ = 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).

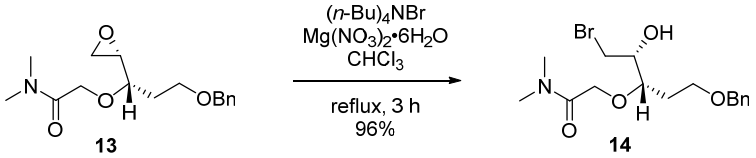
Preparation of Epoxy Amide 13



To a cooled (0 °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

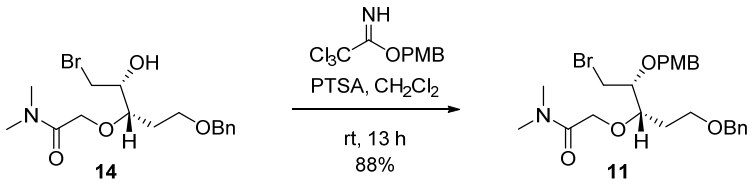
room temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, hexanes/ethyl acetate, 1 : 2) to afford the epoxy amide **13** (10.12 g, 94%) as a colorless oil: $[\alpha]^{24}_D$ = +0.027 (*c* 0.95, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5 H), 4.52–4.47 (m, 2 H), 4.33 (AB, J_{AB} = 13.9 Hz, $\Delta\nu_{AB}$ = 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}C NMR (100 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{16}H_{23}NO_4$ 293.1627; Found 293.1624.

Preparation of Bromohydrin Amide 14



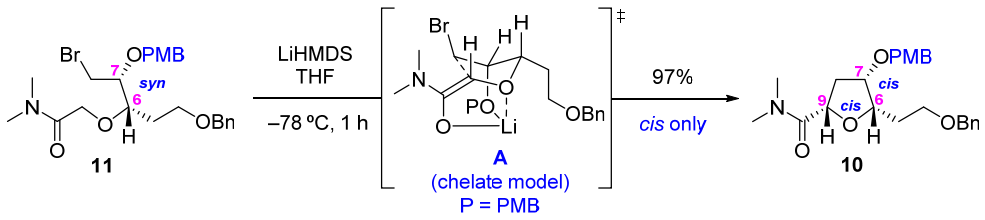
To a solution of epoxy amide **13** (8.50 g, 28.97 mmol) in $CHCl_3$ (116 mL, 0.25 M) was added tetrabutylammonium bromide (14.01 g, 43.46 mmol) and magnesium nitrate hexahydrate (5.20 g, 20.28 mmol) in portions. After being stirred for 3 h at 80 °C, the reaction mixture was quenched with saturated aqueous H_2O and diluted with Et_2O. 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, hexanes/ethyl acetate, 1 : 5) to afford the bromohydrin amide **14** (10.42 g, 96%) as a colorless oil: $[\alpha]^{23}_D$ = –0.60 (*c* 0.95, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 11.8 Hz, $\Delta\nu_{AB}$ = 59.35 Hz, 2 H), 4.26 (AB, J_{AB} = 15.7 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{16}H_{24}BrNO_4$ 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_2Cl_2 (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 $NaHCO_3$ and diluted with CH_2Cl_2. 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, 2 : 1) to afford the PMB-protected bromo amide **11** (12.14 g, 88%) as a colorless oil: $[\alpha]^{24}_D = +0.47$ (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) 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_{AB} = 11.2 Hz, $\Delta\nu_{AB}$ = 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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*: $[M]^+$ Calcd for $C_{24}H_{32}BrNO_5$ 493.1464; Found 493.1462.

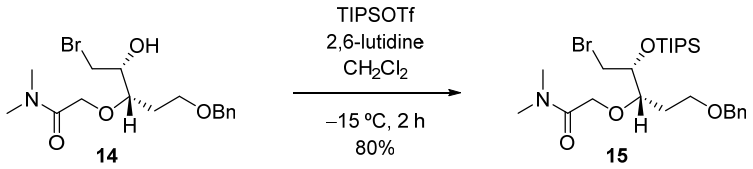
Preparation of 7-OPMB-6,7-*cis*-6,9-*cis*-THF 10



To a cooled (–78 °C) solution of 7-OPMB-6,7-*syn*-*ω*-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_4Cl and diluted with EtOAc. The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with

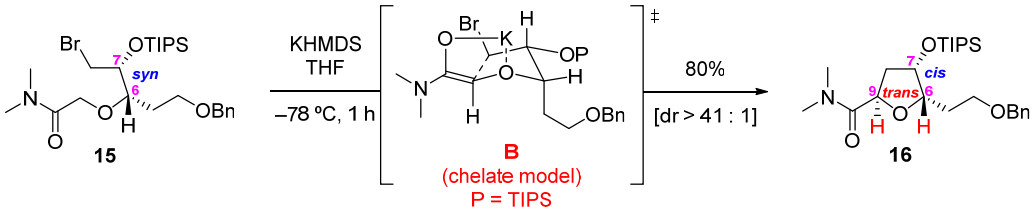
saturated brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, ether/ethyl acetate, 4 : 1) to afford 7-OPMB-6,7-*cis*-6,9-*cis*-THF **10** (1.27 g, 97%, *cis* only, see page S39 & S57) as a colorless oil: $[\alpha]^{24}_D = -0.19$ (*c* 0.97, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 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_{AB} = 11.6 Hz, $\Delta\nu_{AB}$ = 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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*: $[M]^+$ Calcd for $C_{24}H_{31}NO_5$ 413.2202; Found 413.2205.

Preparation of TIPS-Protected Bromo Amide 15



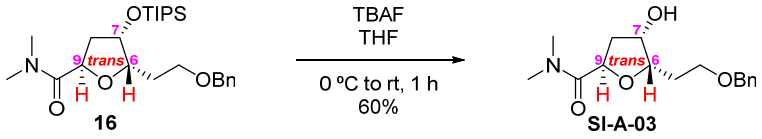
To a cooled (–15 °C) solution of bromohydrin amide **14** (1.42 g, 3.80 mmol) in CH_2Cl_2 (38 mL, 0.1 M) was added 2,6-lutidine (2.65 mL, 22.77 mmol) and triisopropylsilyl trifluoromethansulfonate (TIPSOTf, 2.02 mL, 11.40 mmol). The resulting mixture was stirred for 2 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and diluted 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, 3 : 1) to afford the TIPS-protected bromo amide **15** (1.60 g, 80%) as a colorless oil: $[\alpha]^{24}_D = -18.2$ (*c* 0.88, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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*: $[M]^+$ Calcd for $C_{25}H_{44}BrNO_4Si$ 529.2223; Found 529.2225.

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



To a cooled (–78 ºC) 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 NH_4Cl 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, 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: $[\alpha]^{23}_D = -12.8$ (*c* 0.89, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{25}H_{43}NO_4Si$ 449.2961; Found 449.2961.

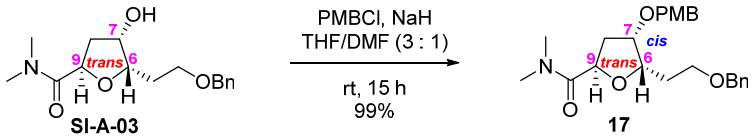
Preparation of Alcohol SI-A-03



To a cooled (0 ºC) 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 $NaHCO_3$ and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. 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, 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, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{16}H_{23}NO_4$ 293.1627; Found 293.1624.

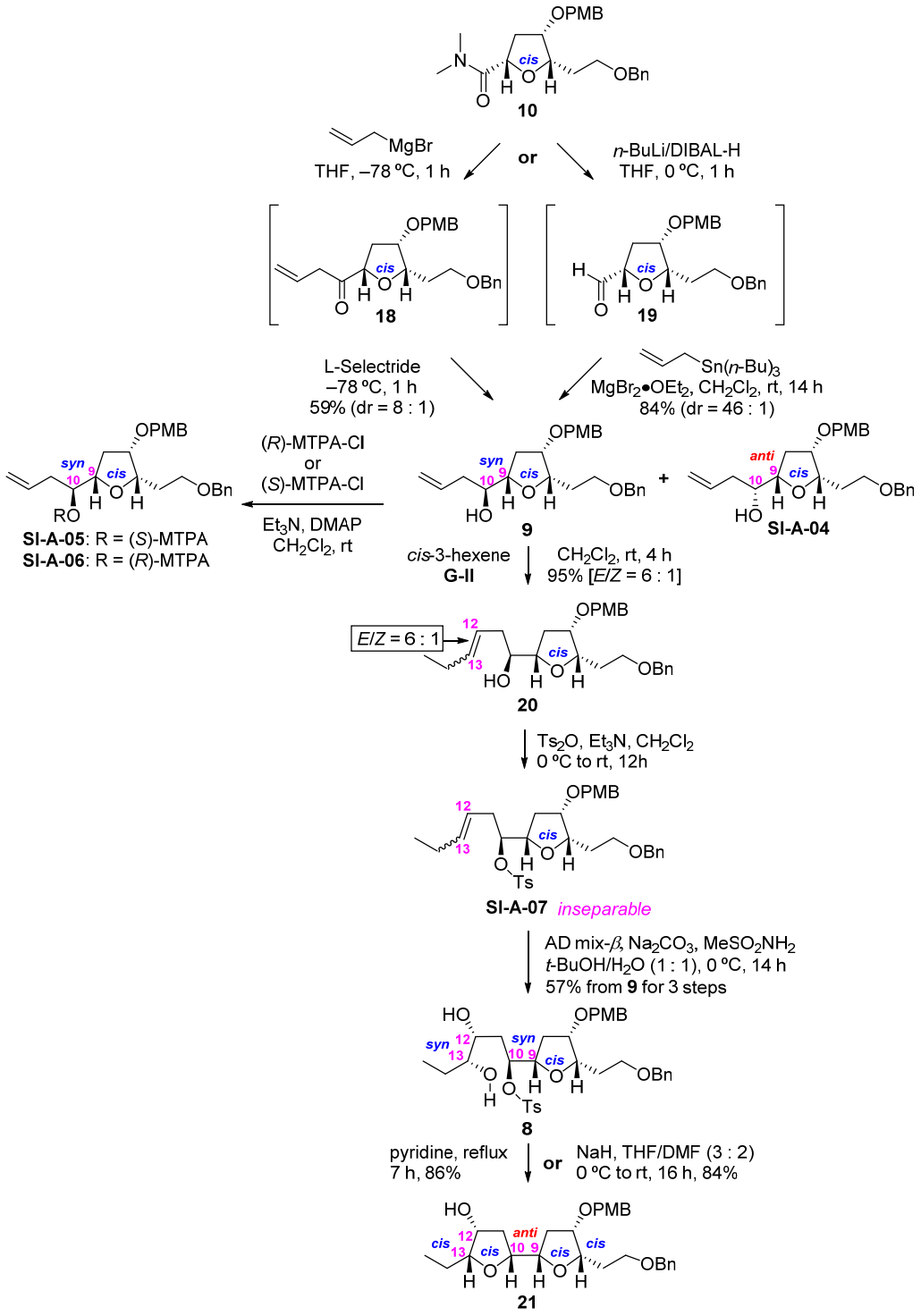
Preparation of 7-OPMB-6,7-*cis*-6,9-*trans*-THF 17



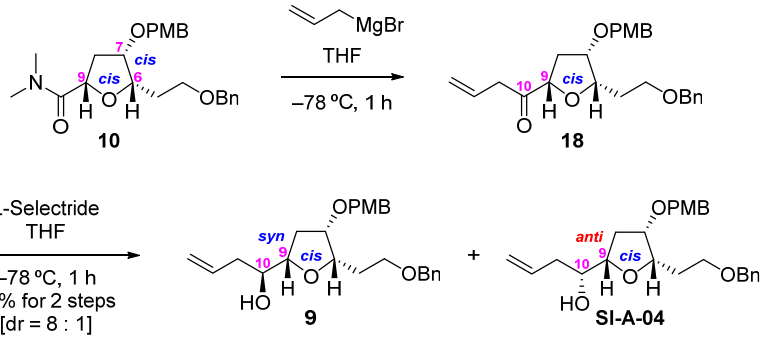
To a solution of alcohol **SI-A-03** (0.13 g, 0.45 mmol) in THF/DMF (3 : 1, 4.4 mL, 0.3 M) was added *p*-methoxybenzyl chloride (0.26 mL, 1.80 mmol) and sodium hydride (63 mg, 60% dispersion of mineral oil, 1.575 mmol) in portions at the room temperature. The resulting mixture was stirred for 15 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and diluted with CH_2Cl_2. 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, 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, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{24}H_{31}NO_5$ 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

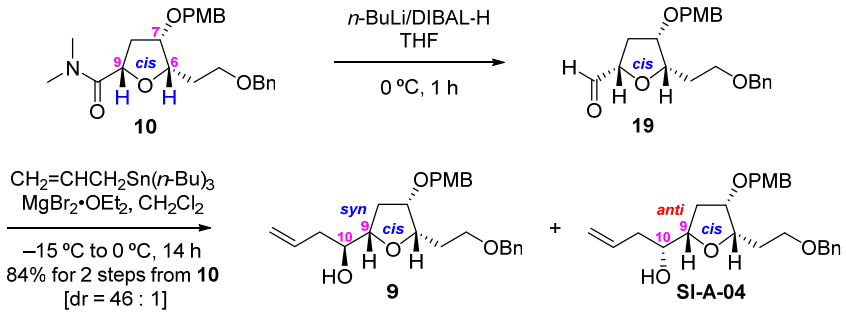


Preparation of (10*S*)-Alcohol SI-A-04 by Direct Ketone Synthesis/L-Selectride Sequence



[Direct Ketone Synthesis][3] 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_4Cl, and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, 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_2O_2 (5.0 mL, 1.0 M in H_2O, 5.0 mmol) and NaOH (5 mL, 2.0 M in H_2O, 10.0 mmol) were added. The resulting mixture was vigorously stirred for 12 h at room temperature and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. 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, 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.

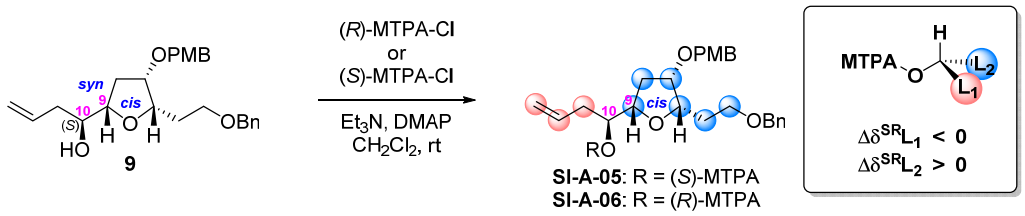
Preparation of (10*S*)-9,10-*syn* Homoallylic Alcohol 9 by a Sequential Ate Complex/Keck Allylation



[Ate Complex Reduction] Ate Complex Generation: To a cooled (–78 °C) solution of *n*-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 °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_2O and saturated aqueous NH_4Cl. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to afford the crude aldehyde **19**, which was immediately employed to the next step without further purification. **[Keck Allylation]**[2] To a cooled (–15 °C) solution of the above crude aldehyde **19** in dry CH_2Cl_2 (4.7 mL, 0.05 M) was added $MgBr_2$•OEt_2 (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 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, 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]** $[\alpha]^{24}_D = -0.15$ (*c* 0.93, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 15.73 Hz, 2 H), 4.38 (AB, J_{AB} = 11.5 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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: $[M]^+$ Calcd for $C_{25}H_{32}O_5$ 412.2250; Found 412.2242. **[For SI-A-04]** $[\alpha]^{24}_D$ = +26.6 (*c* 0.77, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 21.82 Hz, 2 H), 4.40 (AB, J_{AB} = 11.5 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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: $[M+H]^+$ Calcd for $C_{25}H_{33}O_5$ 413.2328; Found 413.2328.

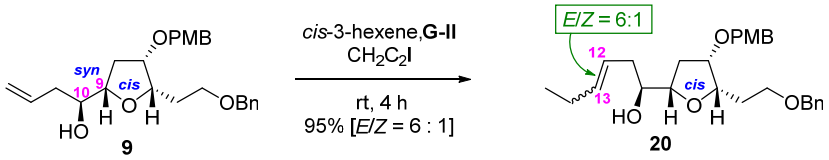
Confirmation of C(10) Absolute Stereochemistry in Secondary Alcohol 9



To a solution of (10*S*)-alcohol **9** in CH_2Cl_2 were successively added (*R*)- or (*S*)-α-methoxy-α-trifluoromethylphenylacetyl chloride (5.0 eq), Et_3N (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 $NaHCO_3$, diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combine layers were washed with brine, dried over anhydrous Na_2SO_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}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 11.7 Hz, $\Delta\nu_{AB}$ = 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),

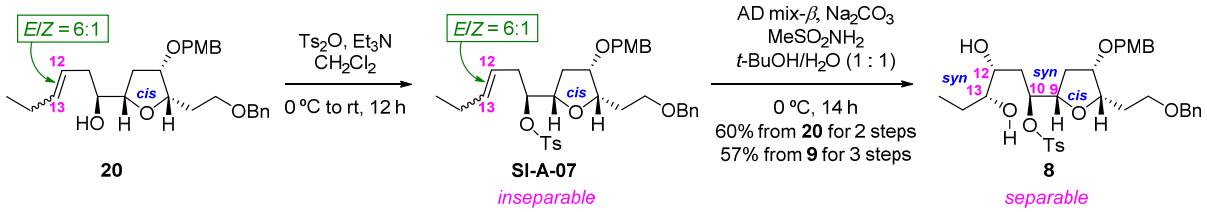
1.83–1.79 (m, 1 H); HRMS (FAB-magnetic sector) *m*/*z*: $[M+H]^+$ Calcd for $C_{35}H_{40}F_3O_7$ 629.2726; Found 629.2719. **[For (*R*)-Mosher Derivative SI-A-06]** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59–7.58 (m, 2 H), 7.37–7.36 (m, 3 H), 7.34–7.27 (m, 5 H), 7.20–7.17 (m, 2 H), 6.87–6.84 (m, 2 H), 5.81–5.74 (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, **G-II**, 138.0 mg, 0.163 mmol][4] 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]** ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

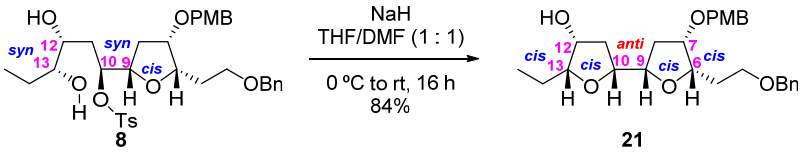
Preparation of Diol 8



[Tosylation]To a cooled (0 °C) solution of inseparable mixture of (*E*)/(*Z*)-hex-3-enol **20** (680.5 mg, 1.55 mmol) in dry CH_2Cl_2 (20 mL, 0.077 M) was added triethylamine (2.15 mL, 15.5 mmol) and *p*-toluenesulfonyl anhydride (Ts_2O, 210.8 mg, 4.63 mmol). After being stirred for 12 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and diluted with H_2O. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. 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, 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]** $[\alpha]^{25}_D = -0.70$ (*c* 0.79, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 11.9 Hz, $\Delta\nu_{AB}$ = 16.57 Hz, 2 H), 4.34 (AB, J_{AB} = 11.6 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{34}H_{42}O_7S$ 594.2651; Found 594.2654. **[Sharpless Asymmetric Dihydroxylation]** To a cooled (0 °C) solution of inseparable mixture of tosylate **SI-A-07** (530.7 mg, 0.892 mmol) in *tert*-butanol/H_2O (1 : 1, 10.0 mL, 0.089 M) was added methanesulfonamide (349.2 mg, 3.671 mmol), K_2CO_3 (634.3 mg, 4.589 mmol). The reaction mixture was stirred for 30 min at same temperature and AD-mix β (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 $Na_2S_2O_3$, and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O.

The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, 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: $[\alpha]^{25} = +1.31$ (*c* 1.00, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 16.70 Hz, 2 H), 4.34 (AB, J_{AB} = 11.4 Hz, $\Delta\nu_{AB}$ = 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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*: $[M+H]^+$ Calcd for $C_{34}H_{45}O_9S$ 629.2784; Found 629.2787.

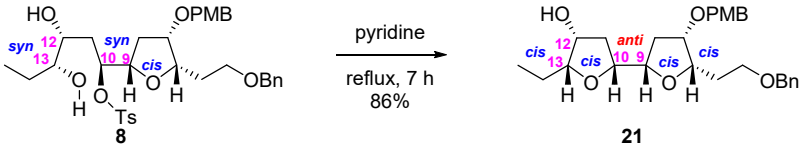
Preparation of Adjacent Bis-THF 21



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_4Cl and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. 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, 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, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{27}H_{36}O_6$ 456.2512; Found 456.2510.

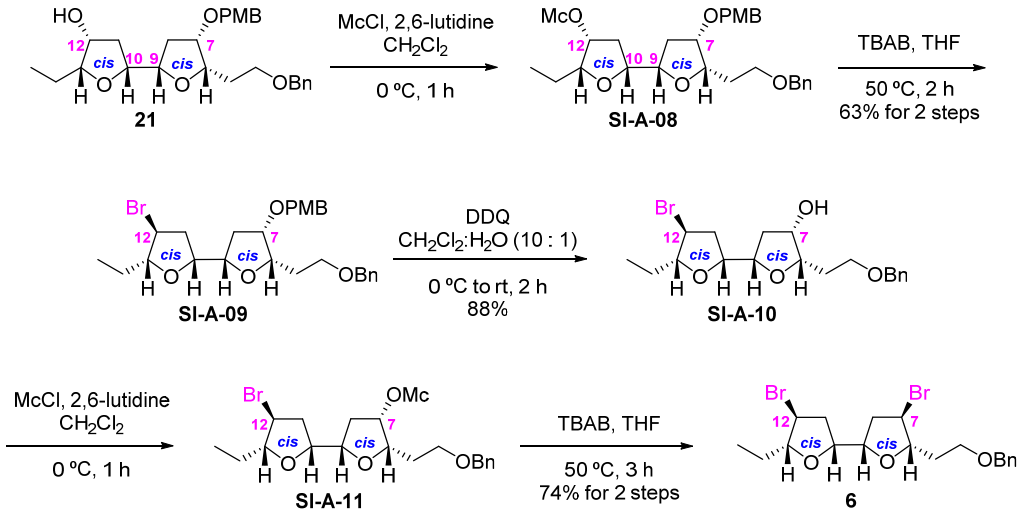
Preparation of Adjacent Bis-THF 21[5]



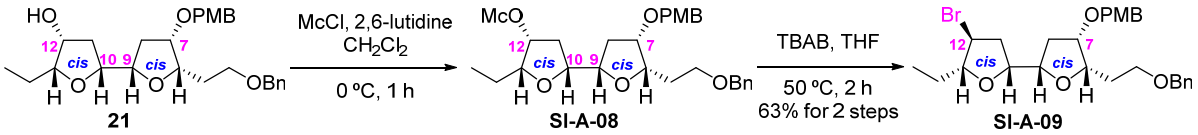
Diol **8** (178.4 mg, 0.284 mmol) was dissolved in pyridine (28 mL, 0.01 M), and the resulting solution was refluxed for 7 h. The reaction mixture was cooled to room temperature, concentrated *in vacuo*, and diluted with Et_2O and H_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. 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, 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



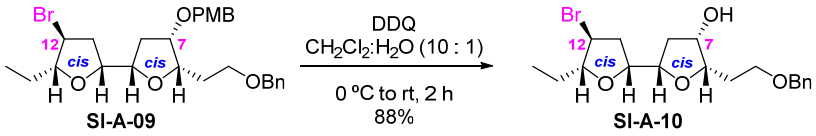
Preparation of 12-Bromo-Adjacent bis-THF SI-A-09



[Chloromethanesulfonylation] To a cooled (0 °C) solution of 12-hydroxy-adjacent bis-THF **21** (272.9 mg, 0.598 mmol) in CH_2Cl_2 (6 mL, 0.1 M) were dropwise added 2,6-lutidine (1.11 mL, 9.56 mmol) and chloromethanesulfonyl chloride (McCl, 0.434 mL, 4.78 mmol). The resulting mixture was stirred for 1 h at the same temperature, quenched with saturated aqueous $NaHCO_3$, and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_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: $[\alpha]^{24}_D$ = +15.4 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 11.9 Hz, $\Delta\nu_{AB}$ = 21.76 Hz, 2 H), 4.39 (AB, J_{AB} = 11.5 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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. **[S_N2 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 °C for 2 h, the reaction mixture was cooled to room temperature, quenched with H_2O, and diluted with Et_2O. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_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: $[\alpha]^{25}_D$ = +29.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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_{AB} = 12.0 Hz, $\Delta\nu_{AB}$ = 22.48 Hz, 2 H), 4.38 (AB, J_{AB} = 11.6 Hz, $\Delta\nu_{AB}$ = 142.39 Hz, 2 H), 4.15 (q, *J*

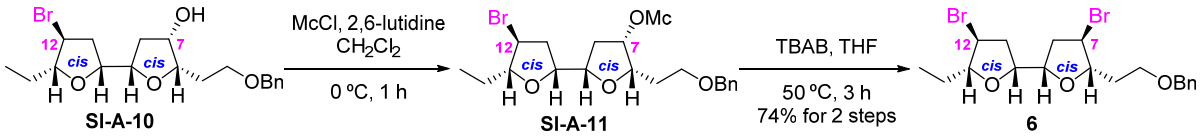
= 6.8 Hz, 1 H), 4.00–3.94 (m, 2 H), 3.93–3.88 (m, 2 H), 3.85 (dt, *J* = 8.2, 6.0 Hz, 1 H), 3.80 (s, 3 H), 3.57 (t, *J* = 6.5 Hz, 2 H), 2.48 (dt, *J* = 13.7, 6.9 Hz, 1 H), 2.28 (ddd, *J* = 13.7, 7.0, 5.2 Hz, 1 H), 2.17 (ddd, *J* = 14.0, 8.2, 5.9 Hz, 1 H), 2.04–1.96 (m, 2 H), 1.93 (ddd, *J* = 13.8, 6.1, 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{27}H_{35}BrO_5$ 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 CH_2Cl_2/H_2O (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 $NaHCO_3$ and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. 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, 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: $[\alpha]^{24}_D$ = +23.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{19}H_{27}BrO_4$ 398.1093; Found 398.1094.

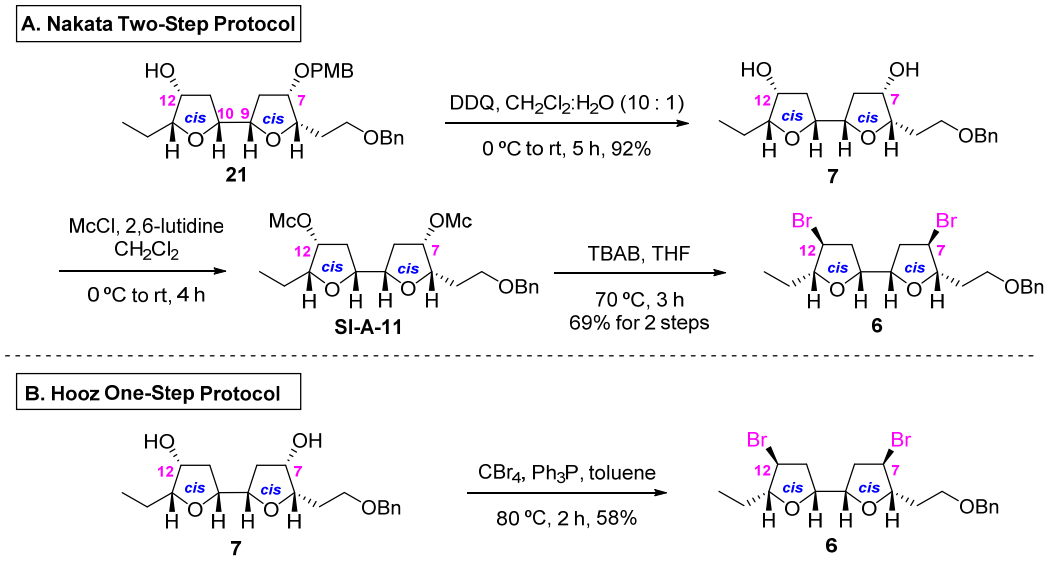
Preparation of 7,12-Dibromo-Adjacent Bis-THF 6



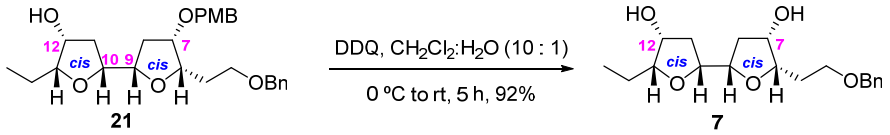
[Chloromethanesulfonylation] To a cooled (0 °C) solution of 7-hydroxyl-12-bromo-adjacent bis-THF **SI-A-10** (196.2 mg, 0.491 mmol) in CH_2Cl_2 (5 mL, 0.1 M) were dropwise added 2,6-lutidine (0.916 mL, 7.86 mmol) and chloromethanesulfonyl chloride (McCl, 0.357 mL, 3.93 mmol). The resulting mixture was stirred for 1 h at the same temperature, quenched with saturated aqueous $NaHCO_3$, and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_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: $[\alpha]^{24}_D$ = +14.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.28 (m, 5 H), 5.22 (ddd, *J* = 6.2, 3.3, 1.2 Hz, 1 H), 4.54 (AB, J_{AB} = 12.7 Hz, $\Delta\nu_{AB}$ = 23.66 Hz, 2 H), 4.50 (AB, J_{AB} = 11.8 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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_N2 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 °C for 3 h, the reaction mixture was cooled to room temperature, quenched with H_2O, and diluted with Et_2O. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_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: $[\alpha]^{25}_D$ = –12.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.33 (m, 4 H), 7.30–7.27 (m, 1 H), 4.52 (AB, J_{AB} = 11.9 Hz, $\Delta\nu_{AB}$ = 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}C NMR (150 MHz, $CDCl_3$) δ 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: $[M]^+$ Calcd for $C_{19}H_{26}Br_2O_3$ 460.0249; Found 460.0243.

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



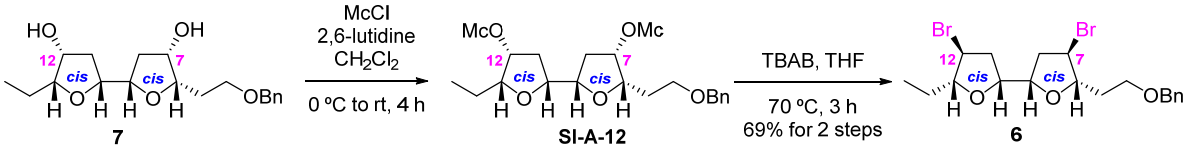
Preparation of 7,12-Dihydroxy-Adjacent Bis-THF Diol 7



To a cooled (0 °C) solution of 12-dihydroxy-adjacent bis-THF **21** (110.8 mg, 0.243 mmol) in CH_2Cl_2/H_2O (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 $NaHCO_3$ and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. 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, hexanes/ethyl acetate, 2 : 1) to afford 7,12-dihydroxy-adjacent bis-THF **7** (75.1 mg, 92%) as a colorless oil: $[\alpha]^{24}_D$ = +23.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.33 (m, 2 H), 7.31–7.28 (m, 3 H),

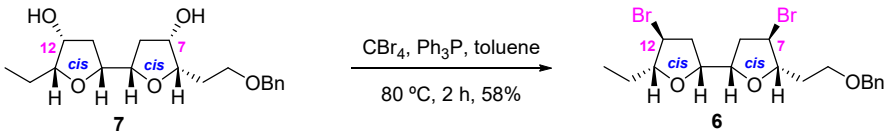
4.51 (AB, J_{AB} = 11.7 Hz, $\Delta\nu_{AB}$ = 14.46 Hz, 2 H), 4.23 (dtd, J = 7.0, 3.5, 1.4 Hz, 1 H), 4.17–4.12 (m, 2 H), 4.02 (ddt, J = 10.1, 4.2, 2.0 Hz, 1 H), 3.80 (ddd, J = 9.4, 5.1, 3.3 Hz, 1 H), 3.67 (ddd, J = 9.4, 4.9, 3.7 Hz, 1 H), 3.56–3.51 (m, 2 H), 3.46 (d, J = 10.2 Hz, 1 H), 3.37 (d, J = 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}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M+H]^+$ Calcd for $C_{19}H_{29}O_5$ 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 °C) solution of 7,12-dihydroxy-adjacent bis-THF **7** (42.5 mg, 0.126 mmol) in CH_2Cl_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 $NaHCO_3$, and diluted with CH_2Cl_2. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_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. **[S_N2 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 °C for 3 h, the reaction mixture was cooled to room temperature, quenched with H_2O, and diluted with Et_2O. The layers were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_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.

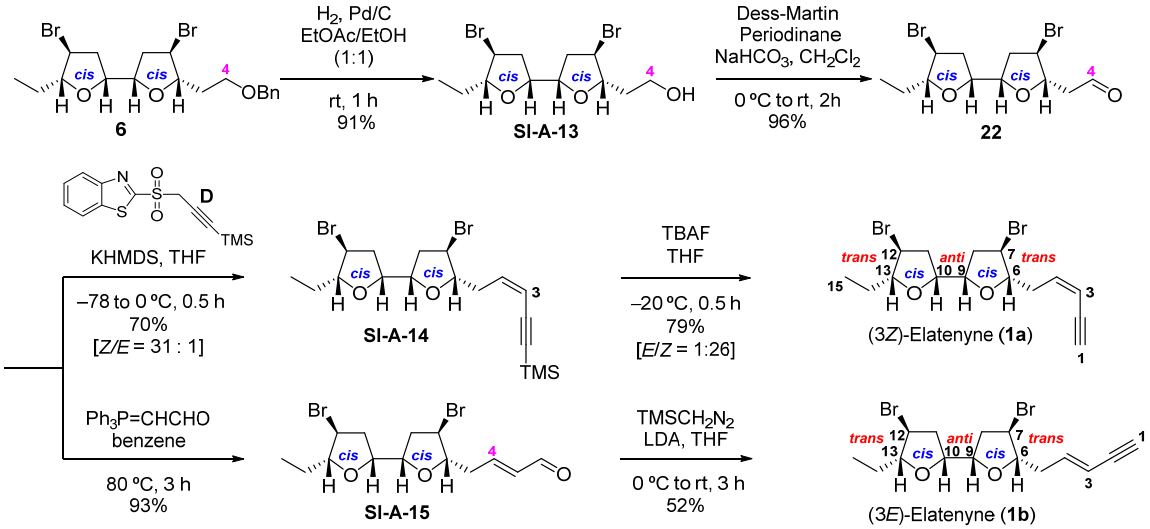
Preparation of 7,12-Dibromo-Adjacent Bis-THF 6 by Hooz One-Step Protocol.



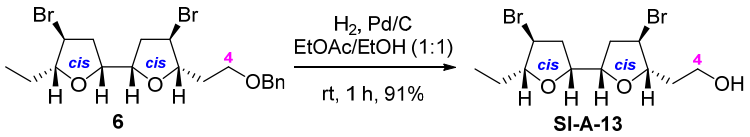
To a solution of 7,12-dihydroxy-adjacent bis-THF **7** (30.3 mg, 0.0901 mmol) in dry toluene (3.60 mL, 0.025 M) were added CBr_4 (14.6 mg, 0.0440 mmol) and Ph_3P (116 mg, 0.442 mmol) at room temperature. After being stirred at 80 °C for 2 h, the reaction mixture was cooled to rt, quenched with saturated aqueous $NaHCO_3$, and diluted with Et_2O. The layers were separated, the aqueous layer was extracted with Et_2O. 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, 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*)-Elatenynes: S25 ~ S29

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

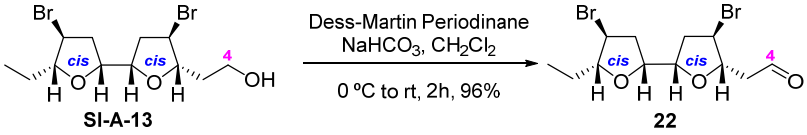


Preparation of Primary Alcohol SI-A-13



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_2 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: $[\alpha]^{25}_D = -2.63$ (*c* 0.99, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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 (dqd, *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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M+H]^+$ Calcd for $C_{12}H_{21}Br_2O_3$ 370.9857; Found 370.9854.

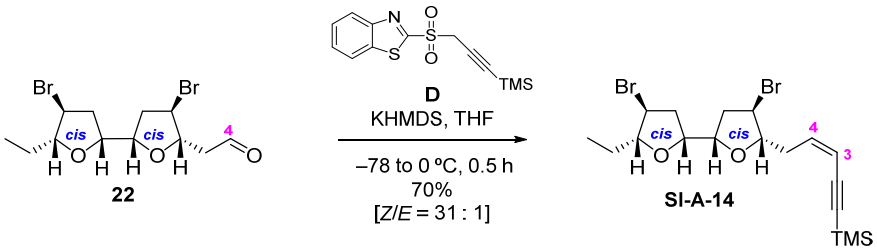
Preparation of Aldehyde 22



To a cooled (0 °C) solution of primary alcohol **SI-A-13** (13.6 mg, 0.0366 mmol) in CH_2Cl_2 (2.2 mL, 0.017 M) was added $NaHCO_3$ (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; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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 (dqd, *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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 199.4, 88.8, 81.94, 81.89,

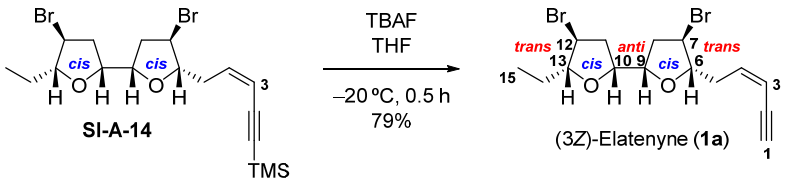
79.9, 79.0, 48.6, 47.6, 38.9, 37.9, 26.7, 10.0.

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



To a cooled (–78 ºC) 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 ºC, 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-(3*Z*)-enyne **SI-A-14** (12.4 mg, 70%, *Z*/*E* = 31 : 1, see page S101) as a colorless oil: $[\alpha]^{24}_D$ = +2.1 (*c* 0.81, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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.

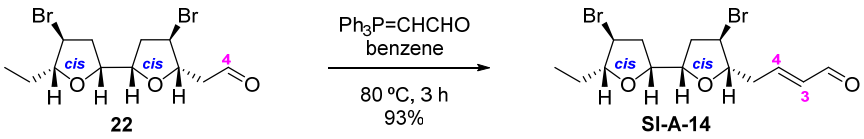
Preparation of (3*Z*)-Elatenyne (1a)



To a cooled (–20 ºC) solution of TMS-(3*Z*)-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

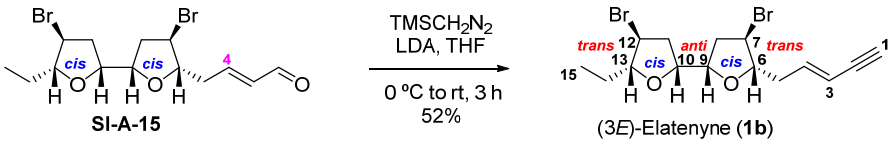
saturated aqueous NH_4Cl and diluted with Et_2O. The layers were separated, and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, diethyl ether/ethyl acetate, 50 : 1) to afford (3*Z*)-elatenyne (**1a**) (6.5 mg, 79%) as a colorless oil: $[\alpha]^{24}_D = -1.66$ (*c* 0.18, CH_2Cl_2), $[\alpha]^{23}_D = -1.90$ (*c* 0.62, $CHCl_3$); {lit. nat.[6a] $[\alpha]^{25}_D = +16.8$ (c 1.4, CH_2Cl_2)}, {nat.[6b] $[\alpha]^{25}_D = -10.0$ (*c* 0.0498, CH_2Cl_2)}, {syn.[6c] $[\alpha]^{25}_D = -4.00$ (*c* 0.25, $CHCl_3$), $[\alpha]^{25}_D = -1.6$ (*c* 0.25, CH_2Cl_2)}, {syn.[6c] **For *ent*-1a**; $[\alpha]^{25}_D = +0.85$ (*c* 0.714, $CHCl_3$), $[\alpha]^{25}_D = +0.80$ (*c* 0.714, CH_2Cl_2)}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{15}H_{20}Br_2O_2$ 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; ^{1}H NMR (600 MHz, $CDCl_3$) δ 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 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 (3*E*)-Elatenyne (1b)



To a cooled (–78 °C) solution of LDA (1.33 mL, 0.66 mmol) in THF (1.33 mL, 0.05 M) was added dropwise $TMSCH_2N_2$ (0.37 mL, 1.8 M in hexane, 0.66 mmol) under N_2 atmosphere. After the mixture was stirred at the same temperature for 30 min, (3*E*)–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_4Cl 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, hexanes/ethyl acetate, 50 : 1) to afford (3*E*)-elatenyne (**1b**) (13.6 mg, 52%) as a colorless oil: $[\alpha]^{24}_D = -28.3$ (*c* 0.66, $CHCl_3$); $[\alpha]^{24}_D = -22.3$ (*c* 0.25, CH_2Cl_2); {lit. syn.[6d] $[\alpha]^{25}_D = -33.0$ (*c* 0.09, CH_2Cl_2)}, {**For *ent*-1b**, lit. syn.[6d] $[\alpha]^{25}_D = +29.5$ (*c* 0.35, CH_2Cl_2)}; ^1H NMR (600 MHz, $CDCl_3$) δ 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 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*: $[M]^+$ Calcd for $C_{15}H_{20}Br_2O_2$ 389.9830; Found 389.9834.

References: S29

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– Electronic Supplementary Information: Part B –

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

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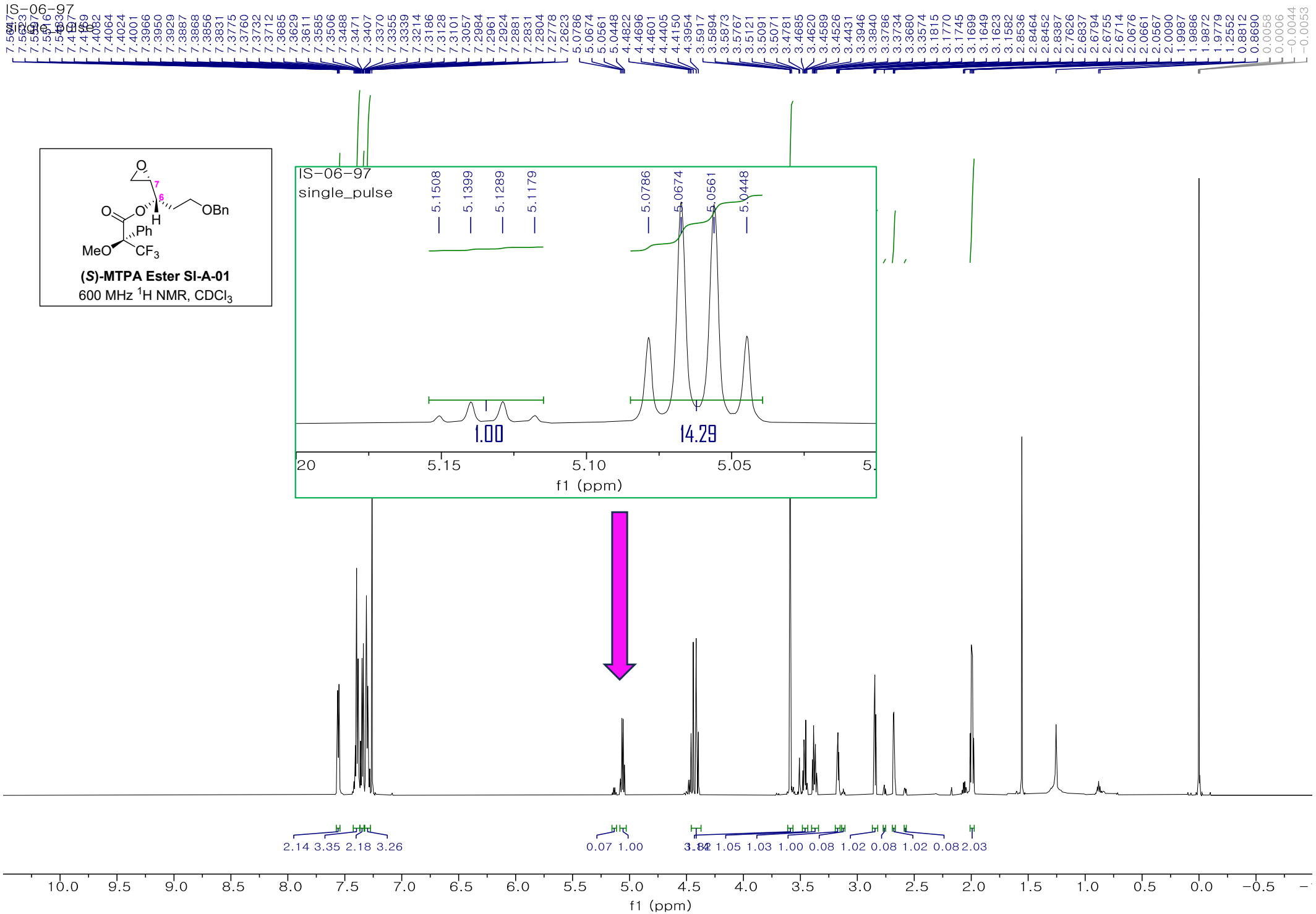
Part B (S30 ~ S113)
Copies of ^{1}H, ^{13}C NMR, and Other NMR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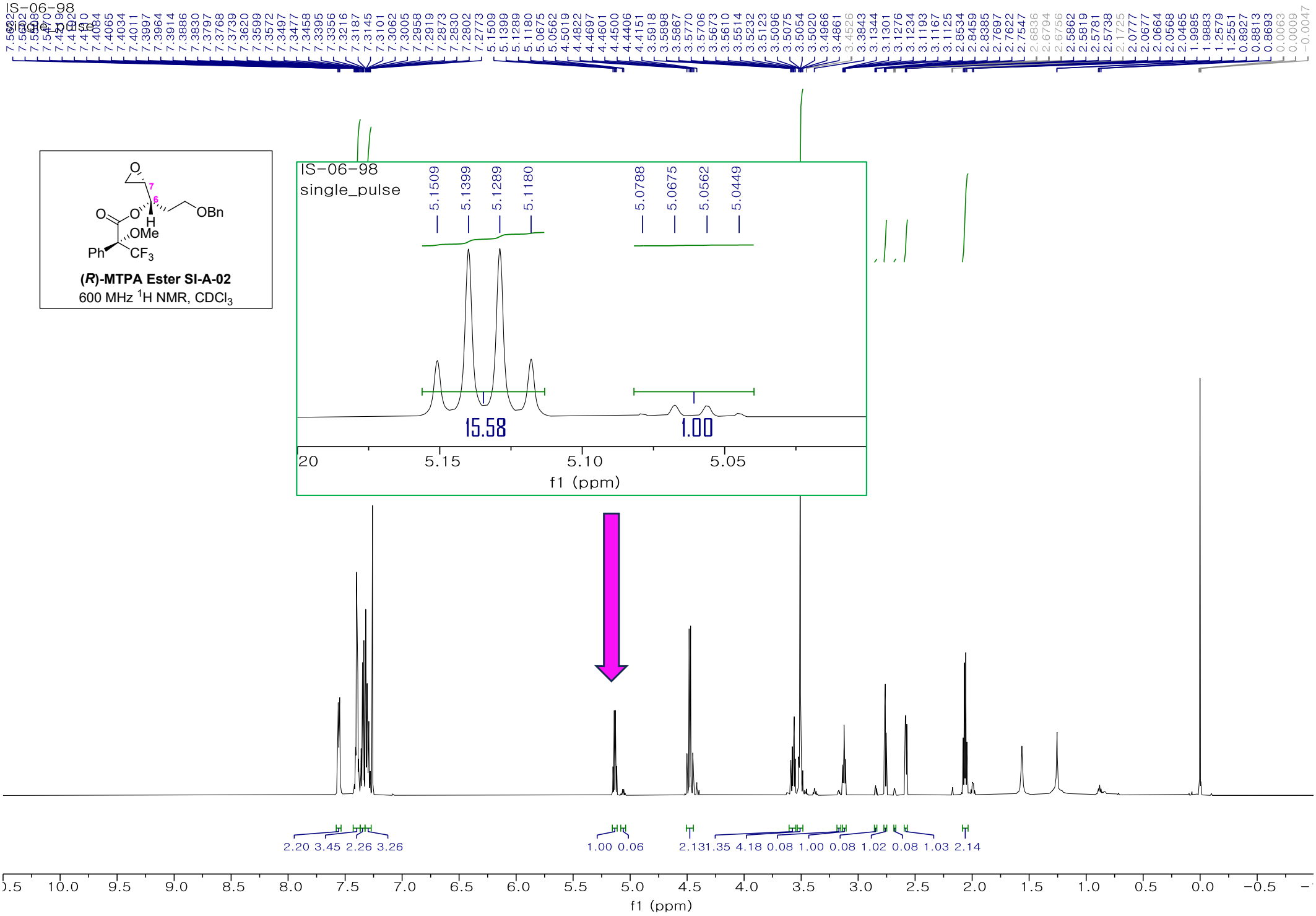
OBn
Ph
MeO
CF3
5.1508
5.1399
5.1289
5.1179
5.0786
5.0674
5.0561
5.0448
1.00
14.29
f1 (ppm)
2.14 3.35 2.18 3.26
0.07 1.00
1.05 1.03 1.00 0.08 1.02 0.08 1.02 0.08 2.03
f1 (ppm)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OBn
OMe
Ph
CF3
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5.0788
5.0675
5.0562
5.0449
15.58
1.00
f1 (ppm)
2.20 3.45 2.26 3.26
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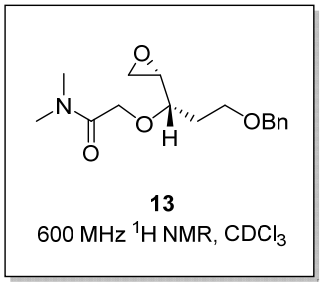
2.13 1.35 4.18 0.08 1.00 0.08 1.02 0.08 1.03 2.14
f1 (ppm)

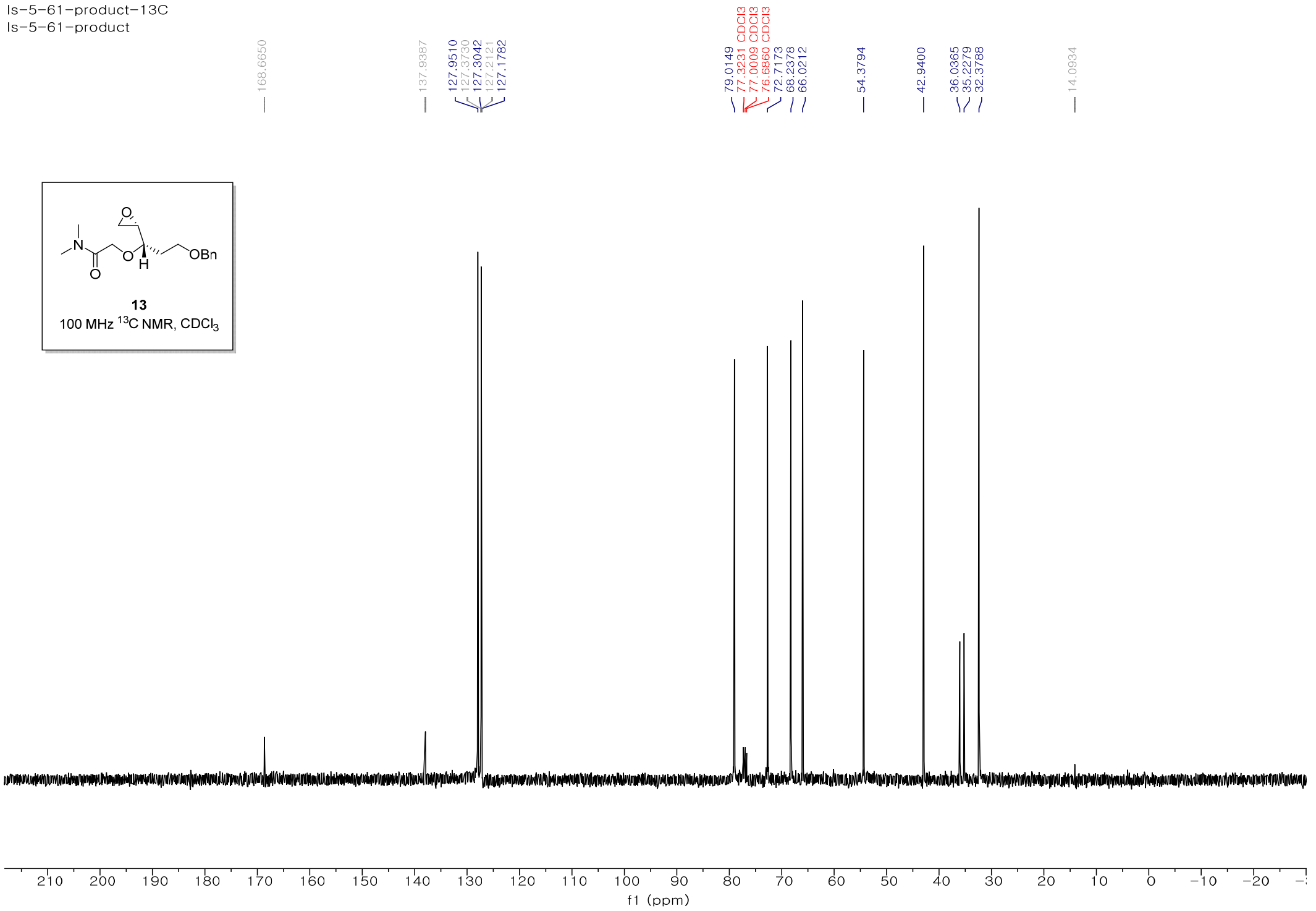
SK-11-97

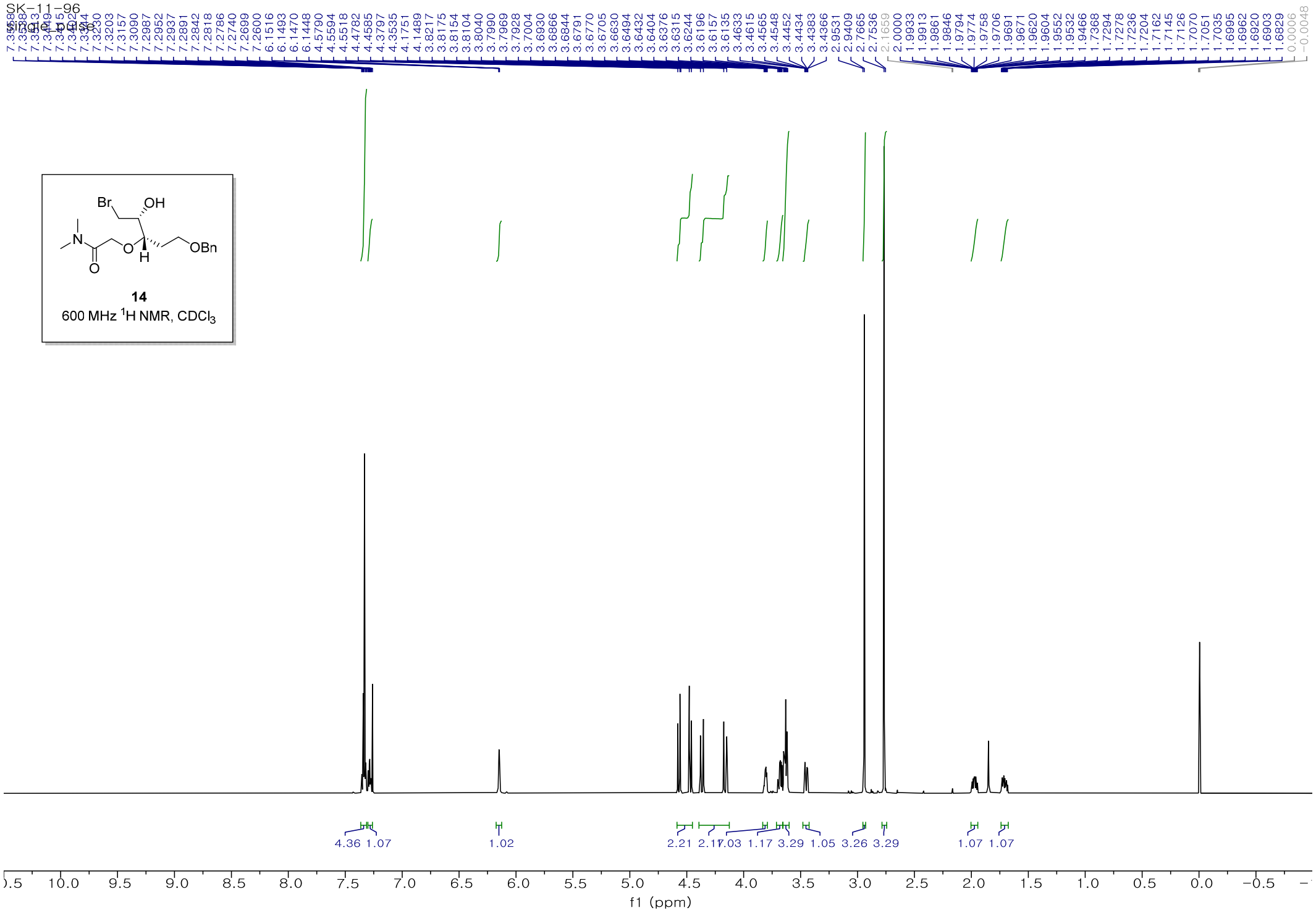


13

600 MHz ^{1}H NMR, $CDCl_3$

ls-5-61-product-13C
ls-5-61-product




SK-11-96
single pulse
Br
OH
N
O
O
H
OBn
14
600 MHz ^{1}H NMR, $CDCl_3$
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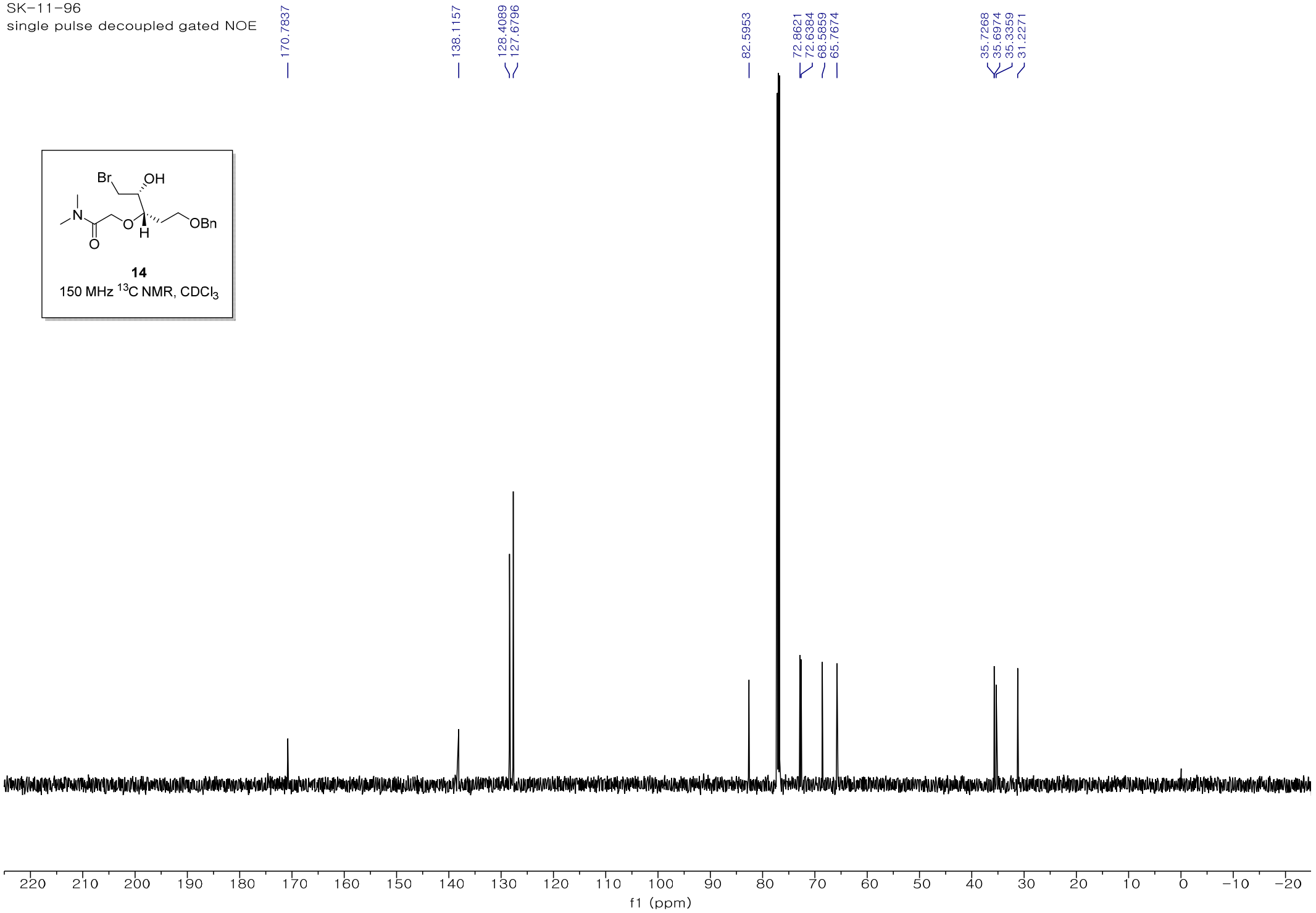
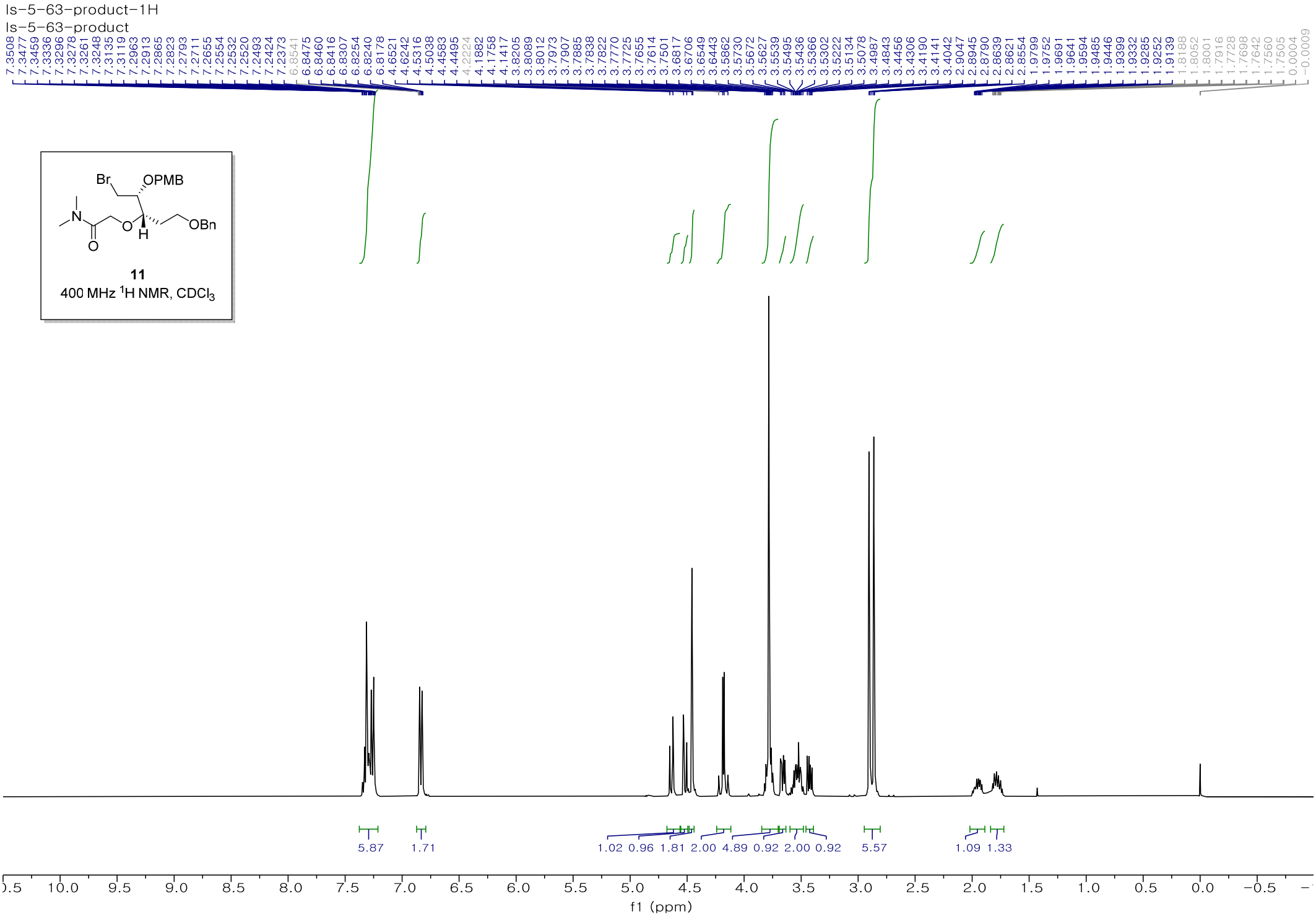
1.02
2.21 2.17 7.03 1.17 3.29 1.05 3.26 3.29
1.07 1.07
f1 (ppm)

SK-11-96
single pulse decoupled gated NOE

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Br
OPMB
N
O
O
H
OBn
11
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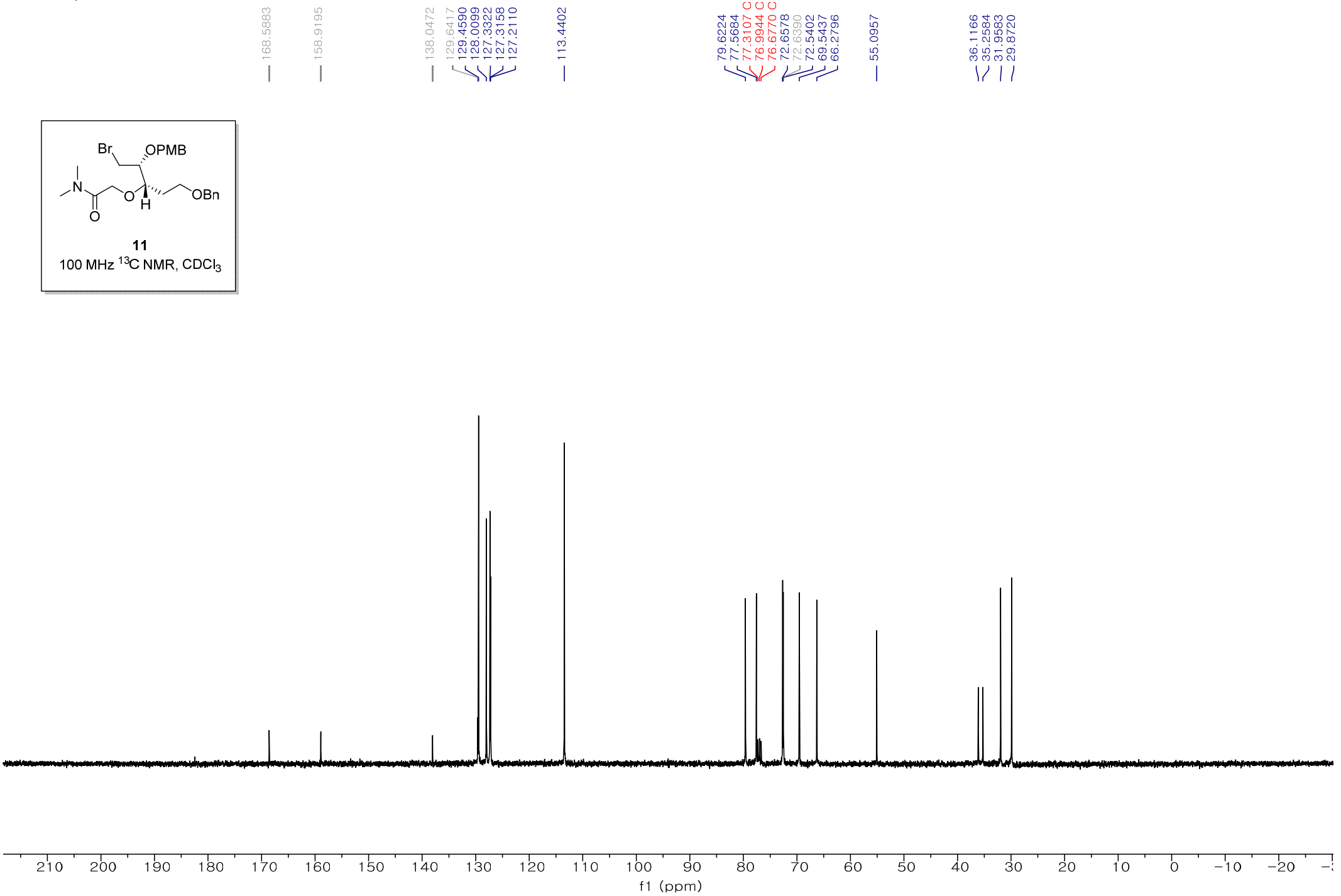
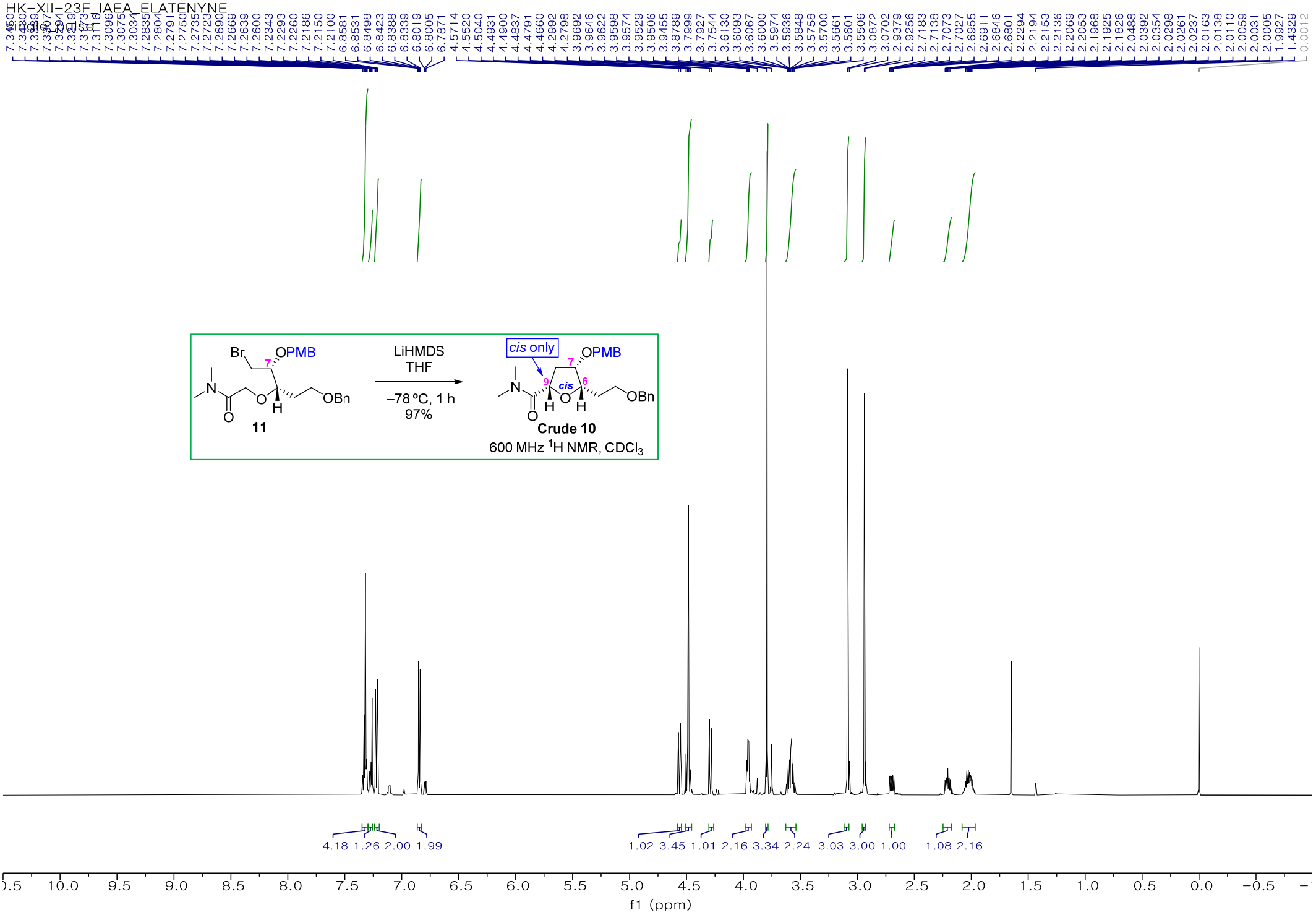
1.71
1.02 0.96 1.81 2.00 4.89 0.92 2.00 0.92
5.57
1.09 1.33
f1 (ppm)

IS-5-63-porduct-13C
Is-5-63-product

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Edge_cause
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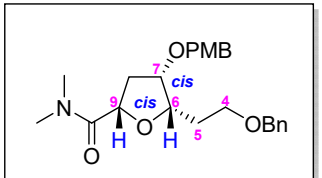
OPMB
7
N
O
H
OBn
11
LiHMDS
THF
–78 °C, 1 h
97%
cis only
OPMB
7
9
6
cis
Crude 10
600 MHz 1H NMR, CDCl3
4.18 1.26 2.00 1.99
1.02 3.45 1.01 2.16 3.34 2.24 3.03 3.00 1.00 1.08 2.16
f1 (ppm)

SK-2-70-DATA
single_pulse



10
600 MHz ^{1}H NMR, $CDCl_3$

IS-5-104-1-THF-13C
Is-5-104-1-THF

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138.3350
130.1037
129.0933
128.0893
127.3961
127.2663
113.4678
80.0908
77.5232
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72.7903
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37.1134
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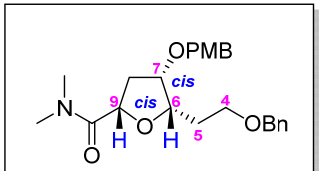
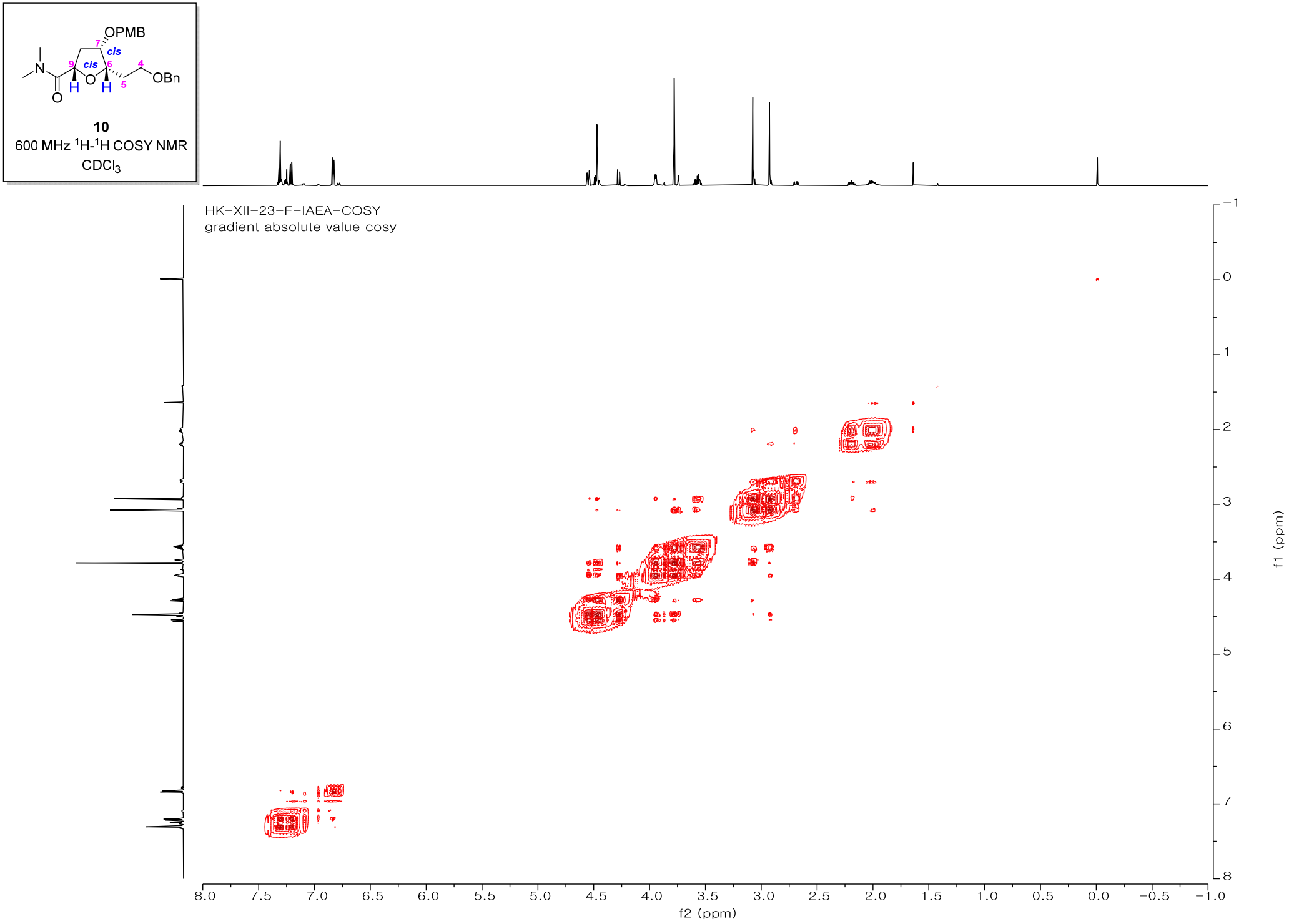
29.2328



10
100 MHz ^{13}C NMR, $CDCl_3$


OPMB
7
cis
9
cis
6
4
N
O
H
O
H
5
OBn
O
10
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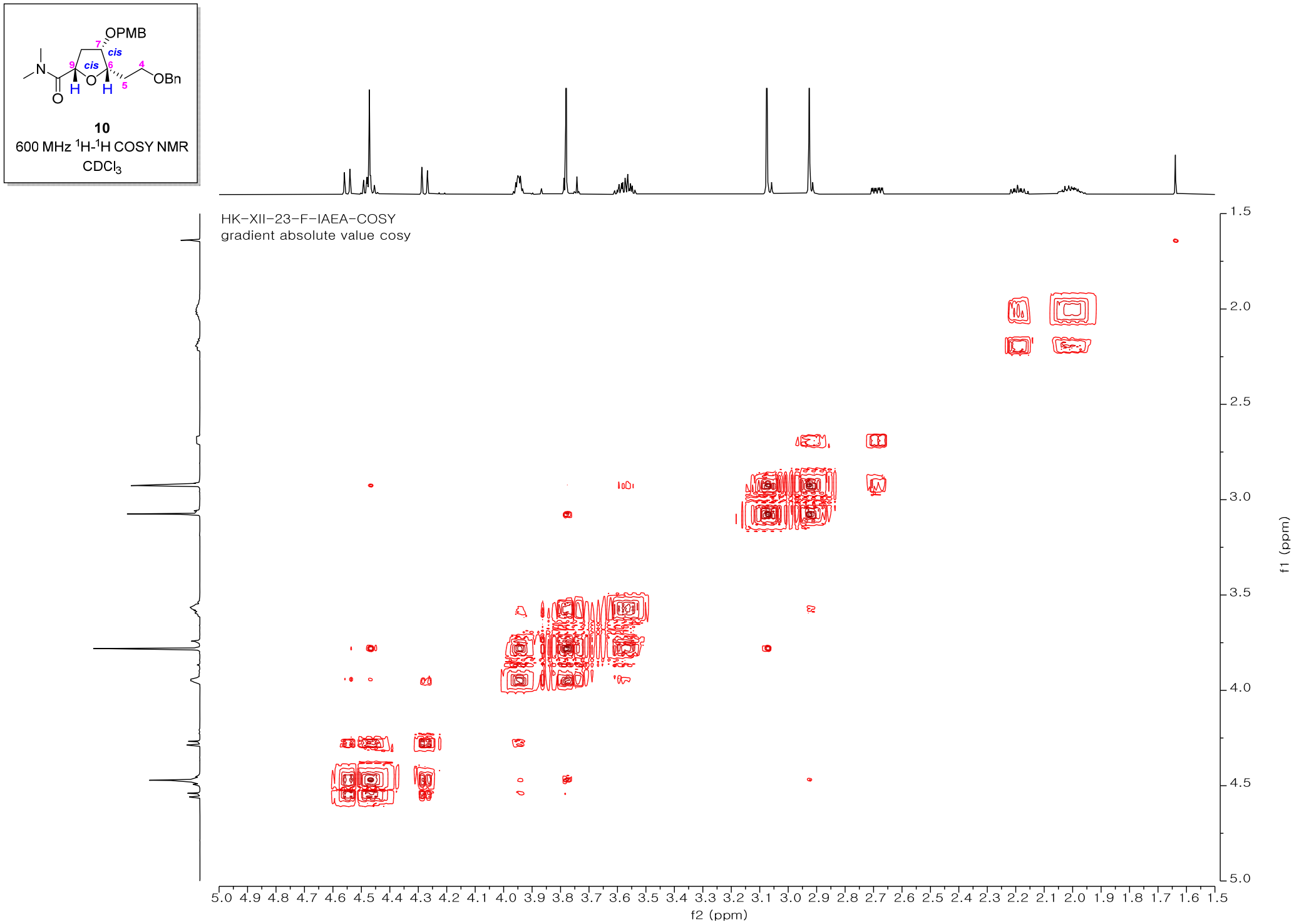
gradient absolute value cosy
f2 (ppm)
f1 (ppm)


OPMB
7
cis
9
cis
6
4
N
O
H
O
H
5
OBn
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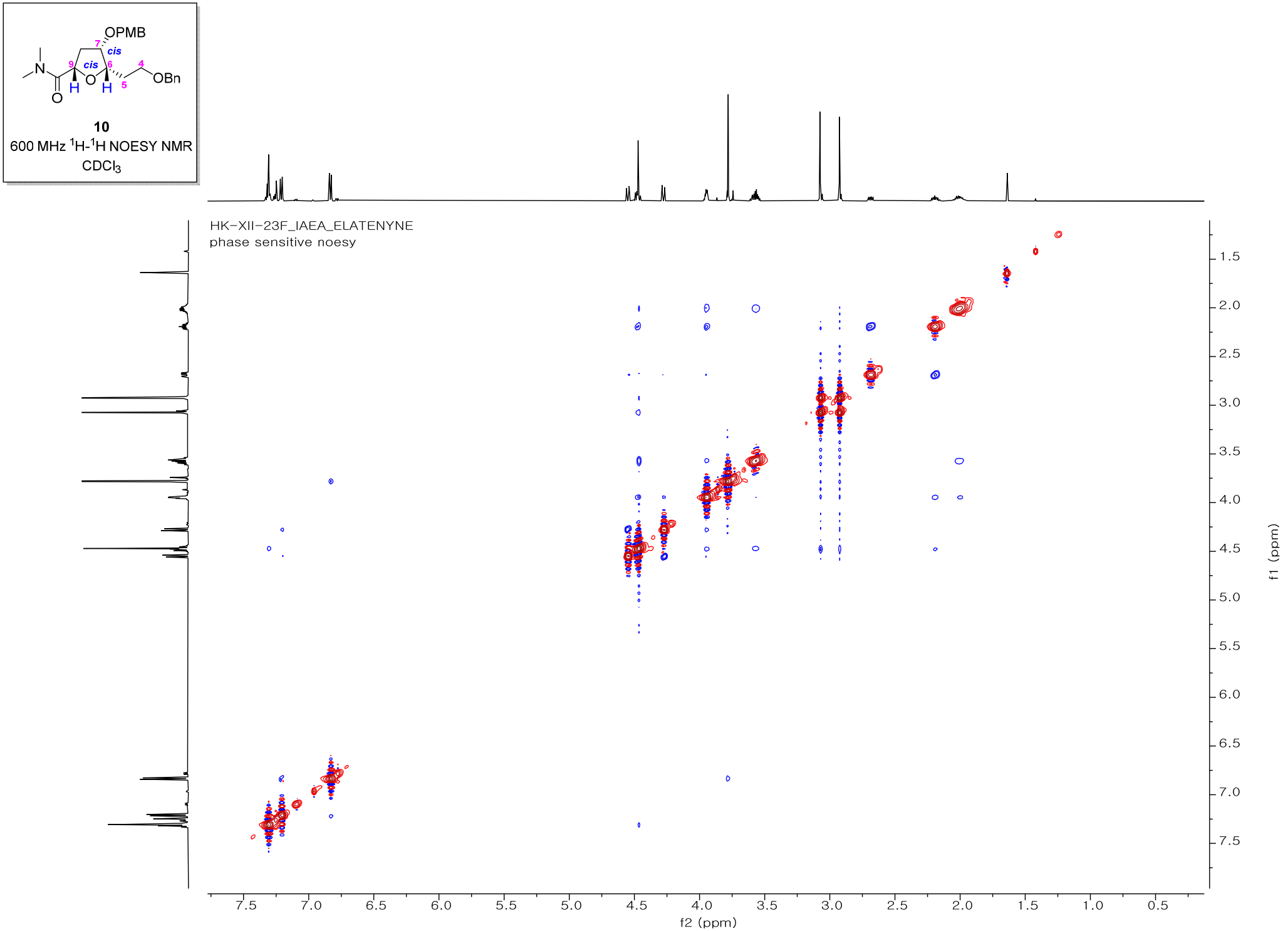
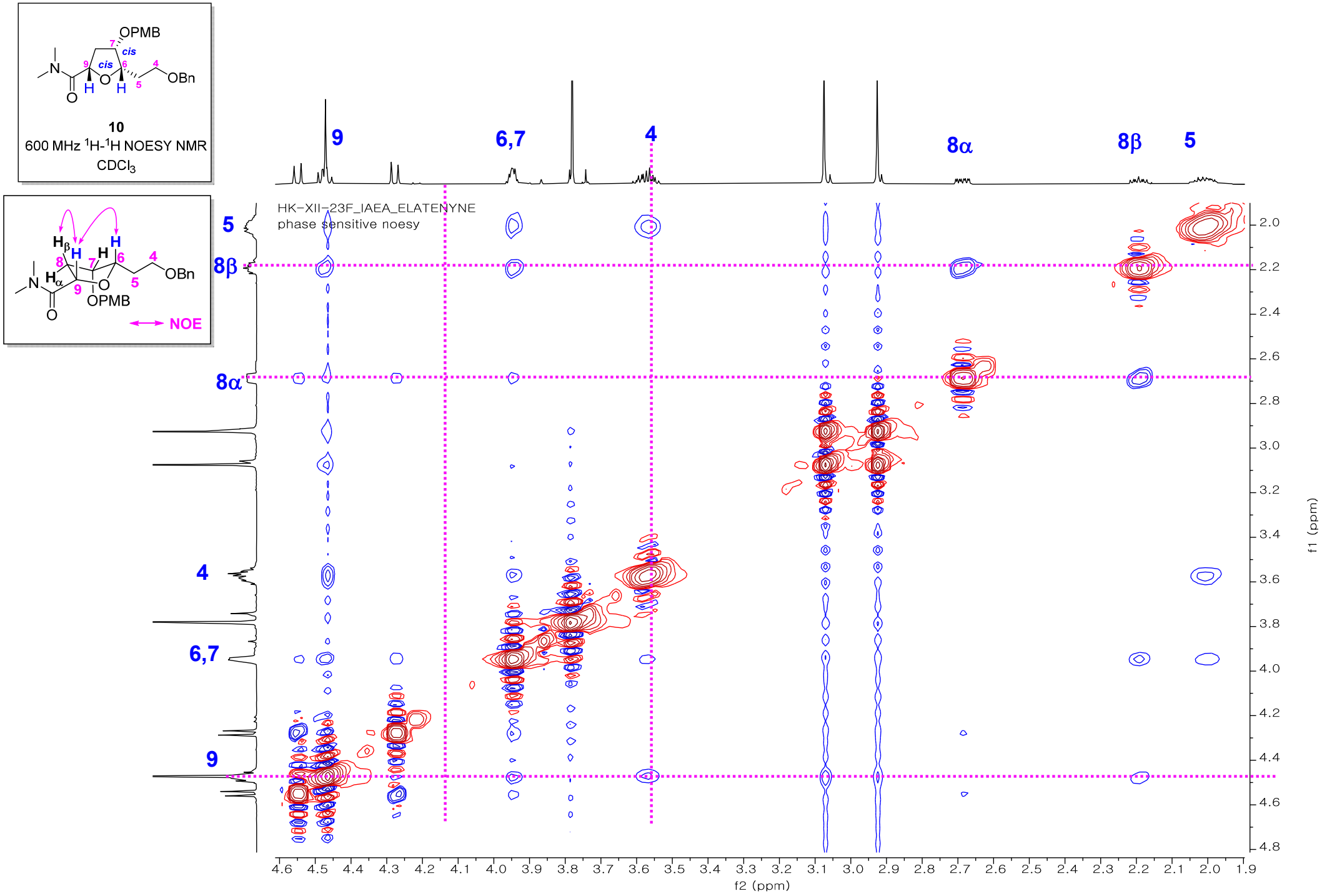
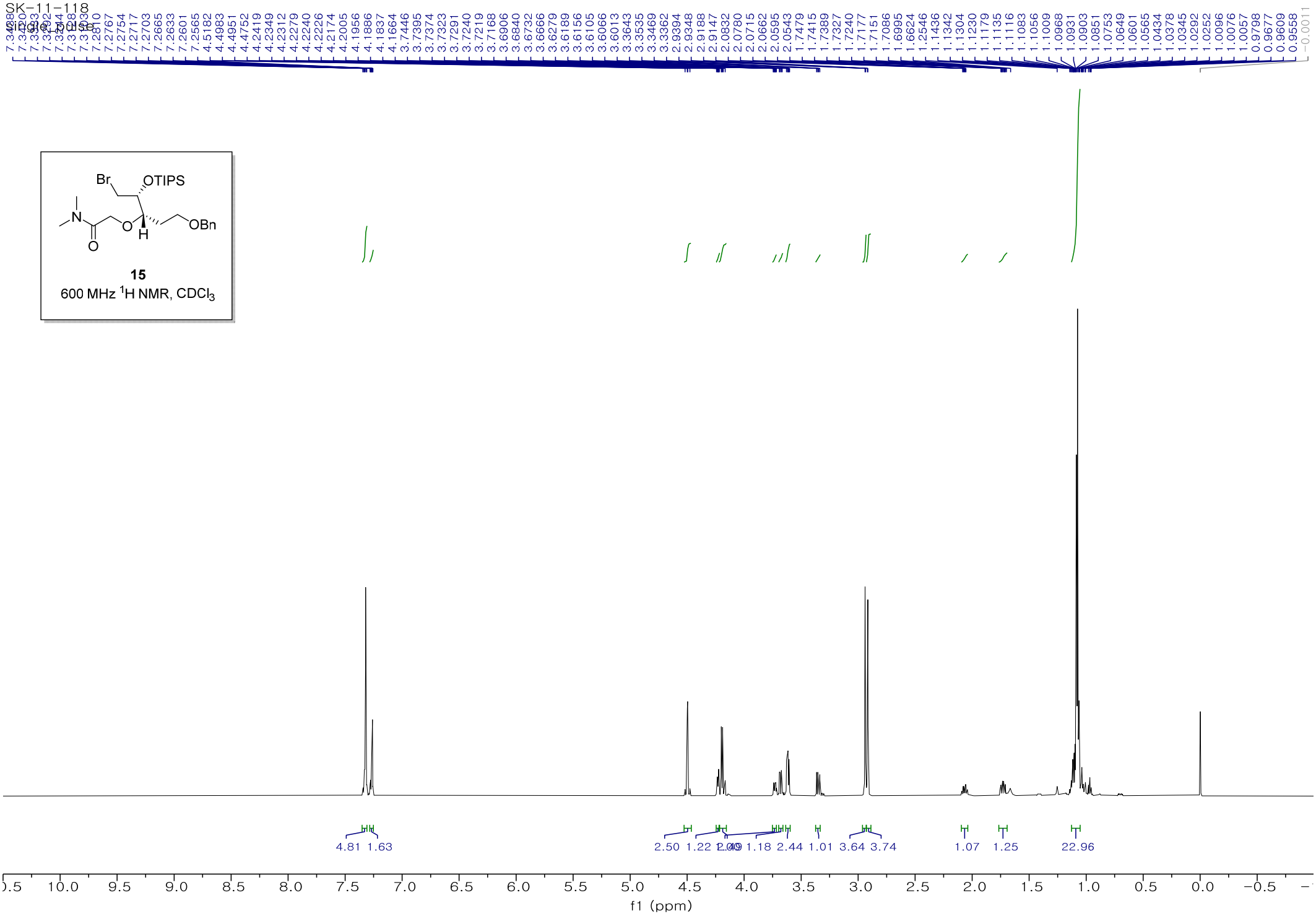
CDCl3
HK-XII-23-F-IAEA-COSY
gradient absolute value cosy
f1 (ppm)
f2 (ppm)

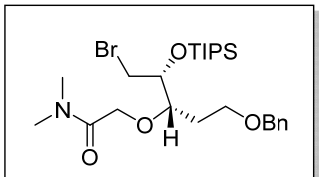

OPMB
7
cis
9
cis
6
4
N
H
O
H
5
OBn
O
10
600 MHz ^{1}H-^{1}H NOESY NMR
$CDCl_3$
HK-XII-23F_IAEA_ELATENYNE
phase sensitive noesy
f2 (ppm)
f1 (ppm)


OPMB
cis
cis
OBn
10
600 MHz ^{1}H-^{1}H NOESY NMR
$CDCl_3$
NOE
HK-XII-23F_IAEA_ELATENYNE
phase sensitive noesy
9
6,7
4
8α
8β
5
f2 (ppm)
f1 (ppm)

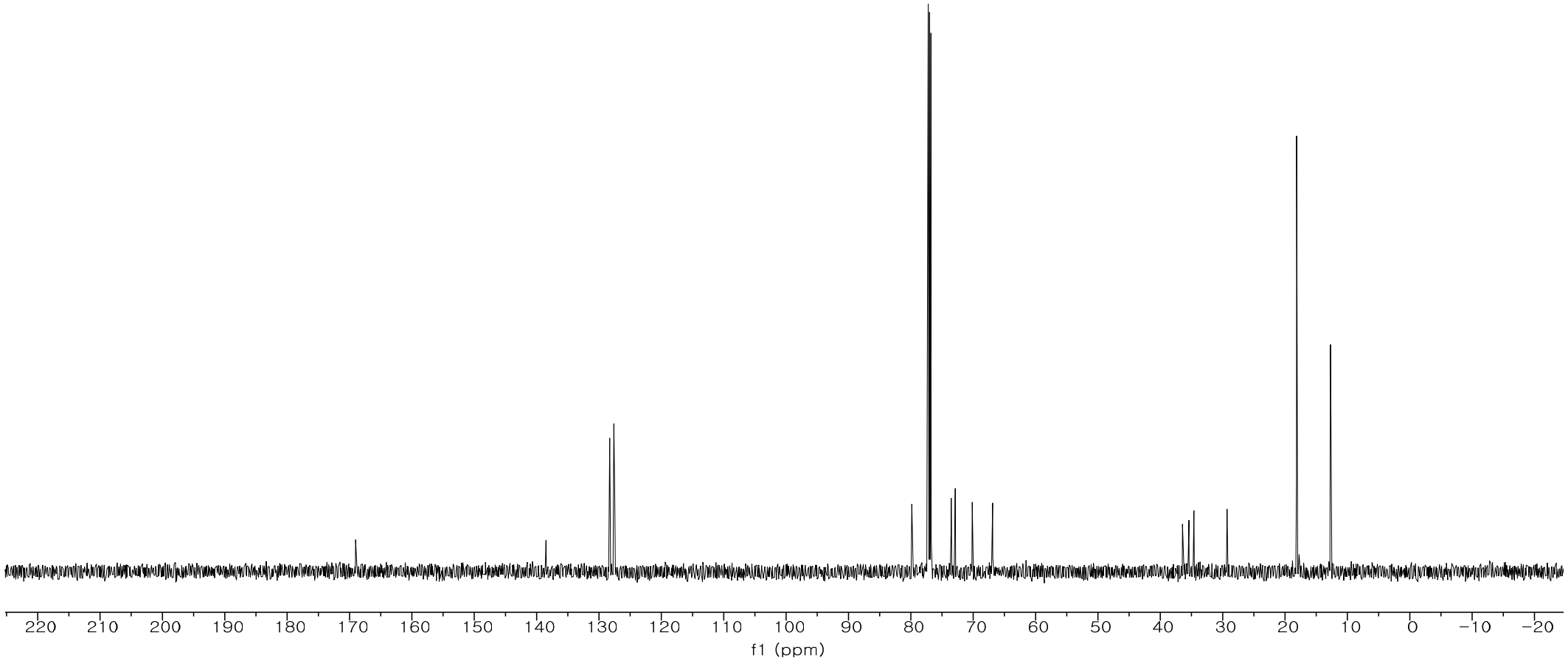

SK-11-118
single pulse
Br
OTIPS
N
O
O
H
OBn
15
600 MHz ^{1}H NMR, $CDCl_3$
4.81 1.63
2.50 1.22 1.18 2.44 1.01 3.64 3.74
1.07 1.25 22.96
f1 (ppm)

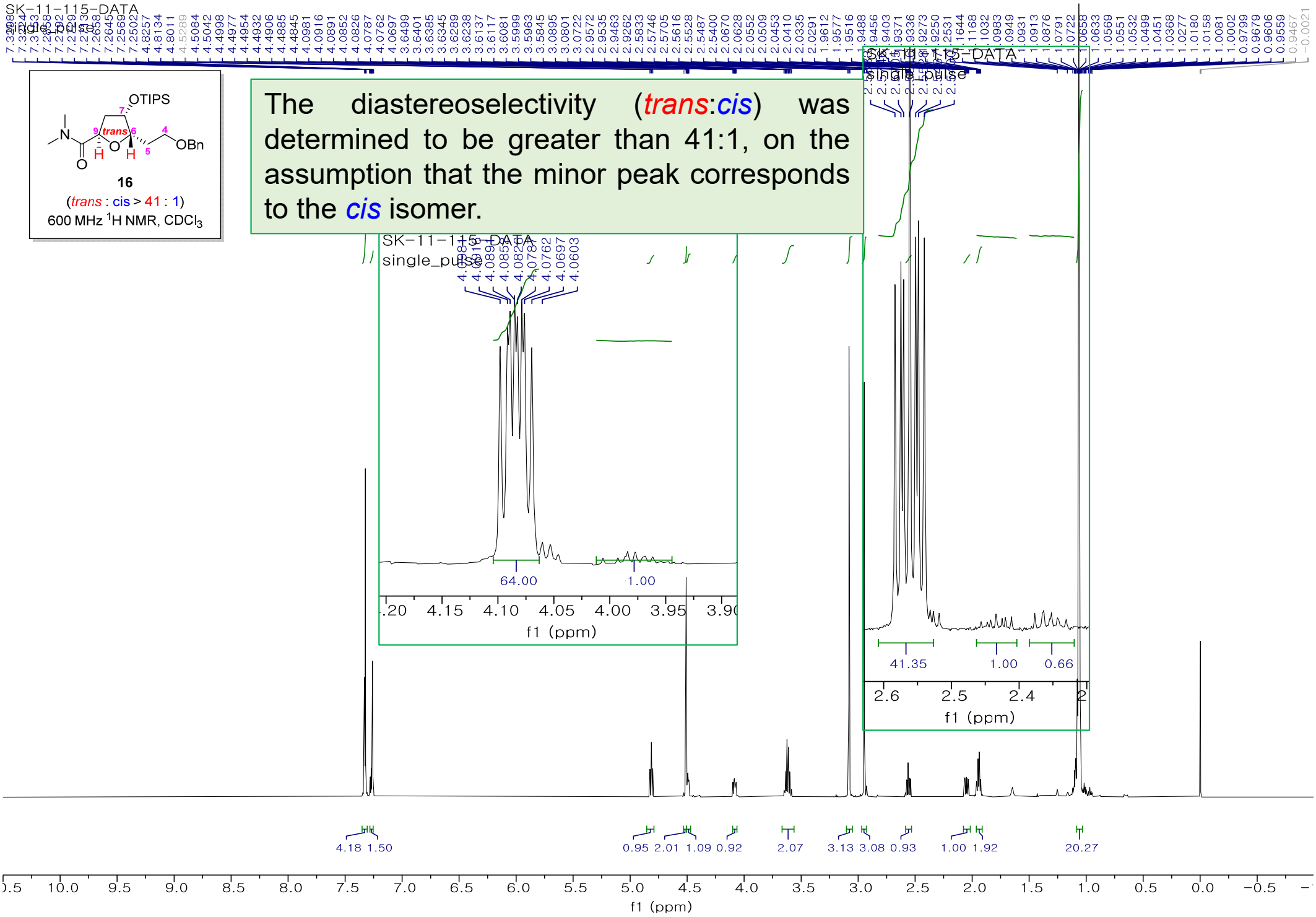
SK-11-118
single pulse decoupled gated NOE

169.0225
138.5111
128.2887
127.6076
127.4642
79.8387
73.5262
72.8833
70.1617
66.8848
36.4396
35.4132
34.6103
29.2974
18.1423
12.7212



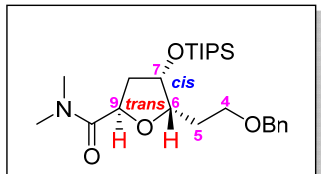
15
150 MHz ^{13}C NMR, $CDCl_3$



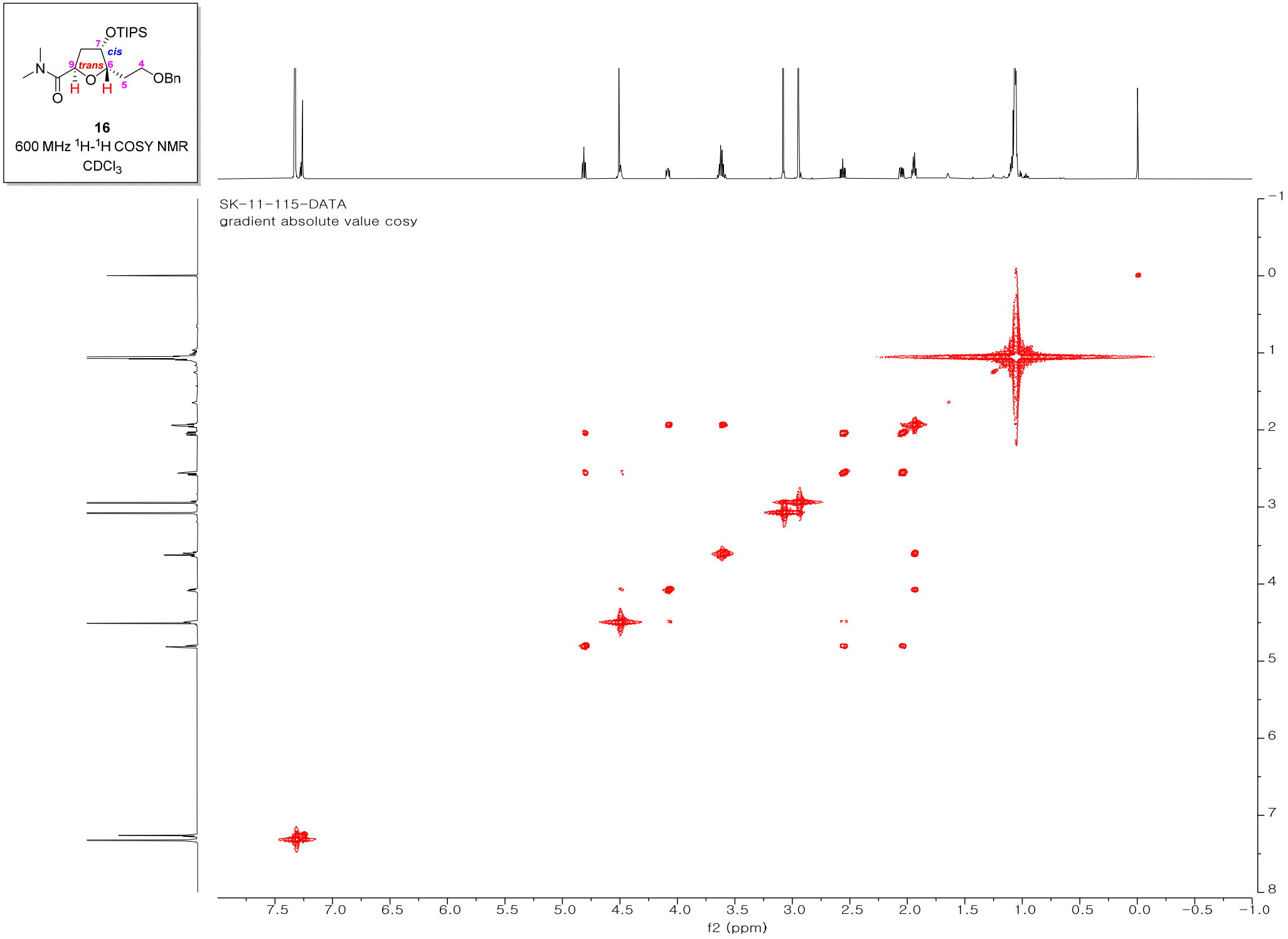

SK-11-115-DATA
single_pulse
OTIPS
trans
OBn
16
(trans : cis > 41 : 1)
600 MHz 1H NMR, CDCl3
The diastereoselectivity (trans:cis) was determined to be greater than 41:1, on the assumption that the minor peak corresponds to the cis isomer.
64.00
1.00
41.35
1.00
0.66
4.18 1.50
0.95 2.01 1.09 0.92
2.07
3.13 3.08 0.93
1.00 1.92
20.27
f1 (ppm)

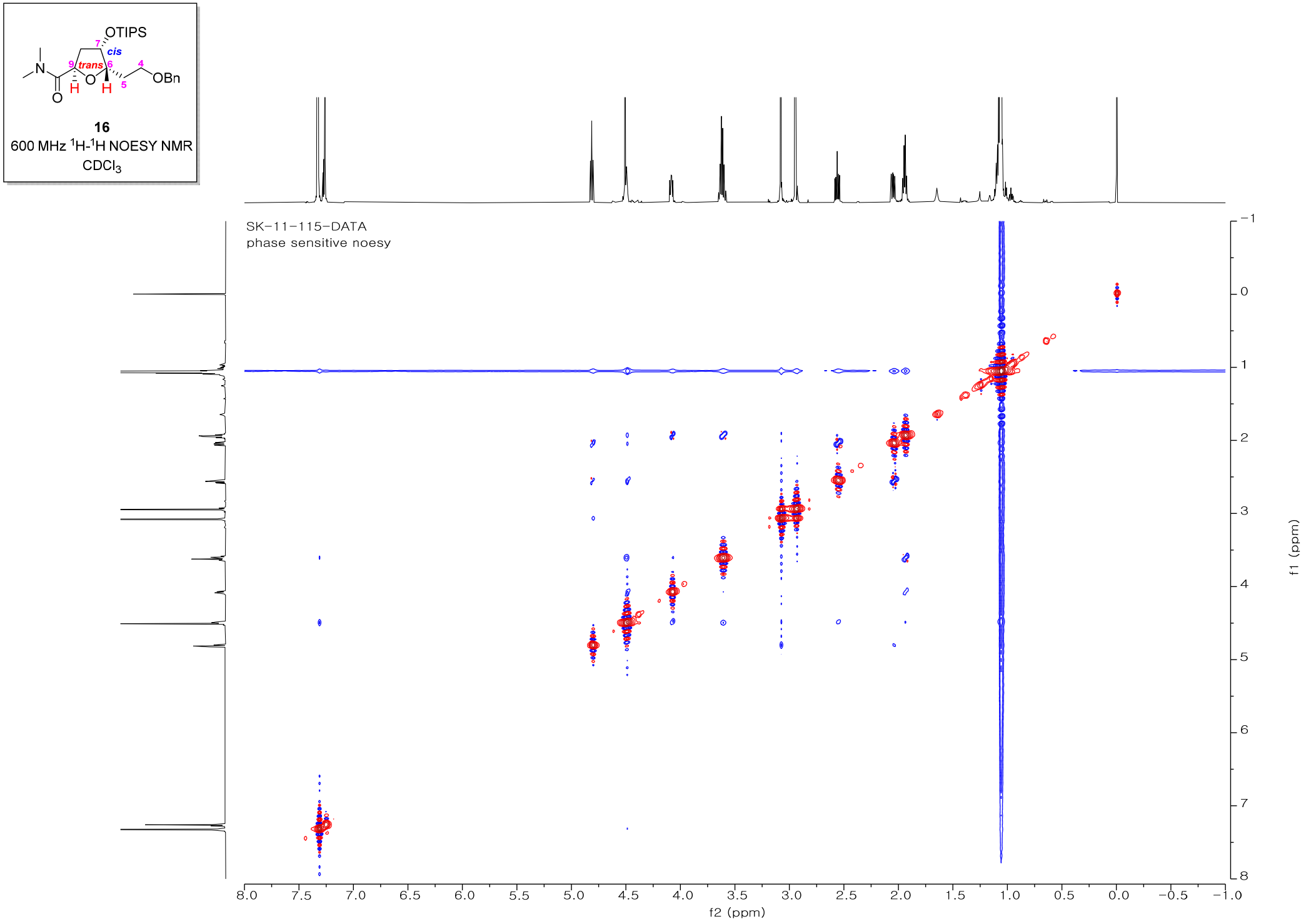
SK-11-115
single pulse decoupled gated NOE

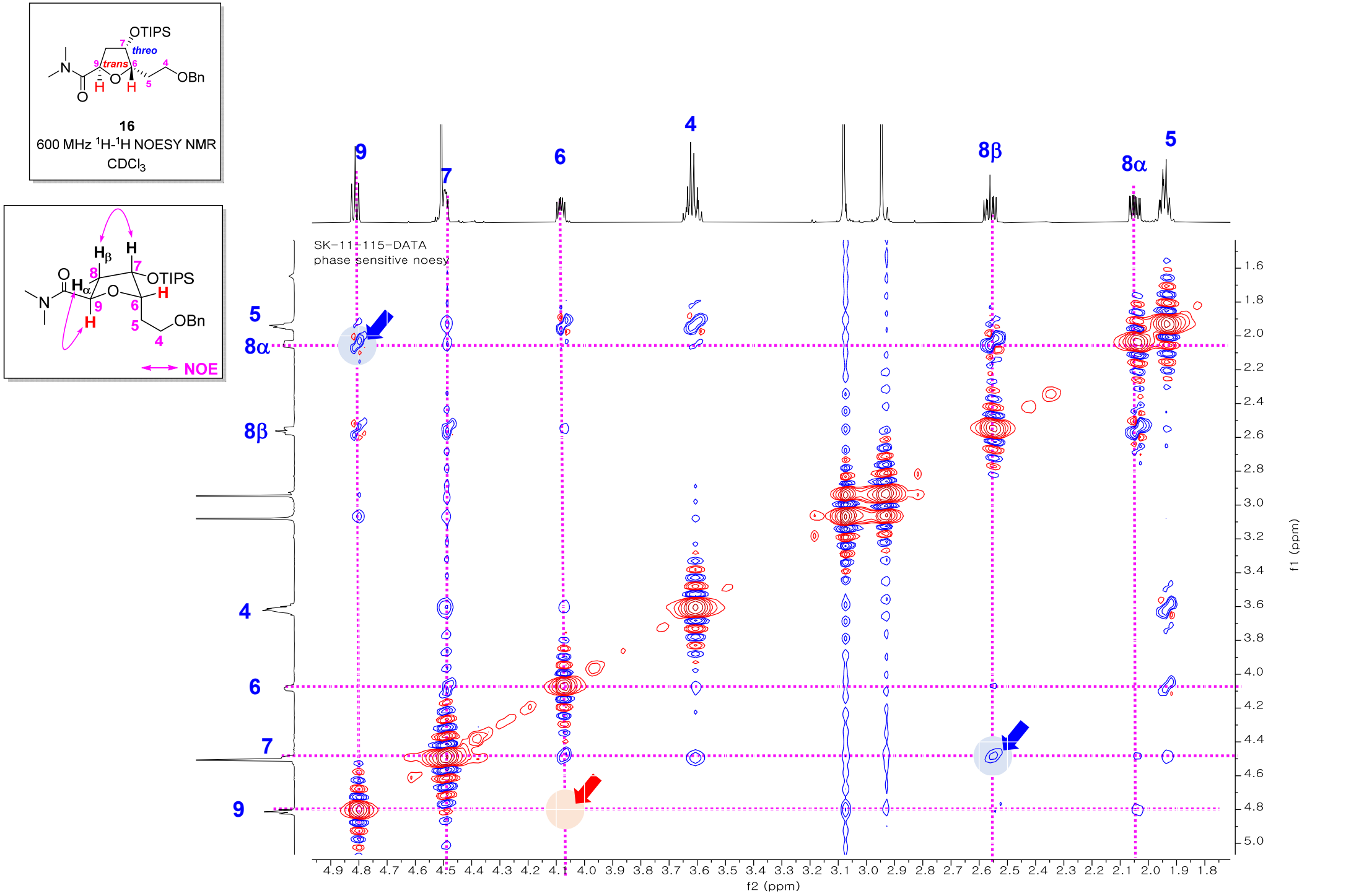
171.1628
138.6130
128.2912
127.6381
127.4316
80.5391
74.1006
73.7271
72.9876
67.9328
38.4881
36.9946
35.8063
29.9137
18.0912
18.0540
12.3512

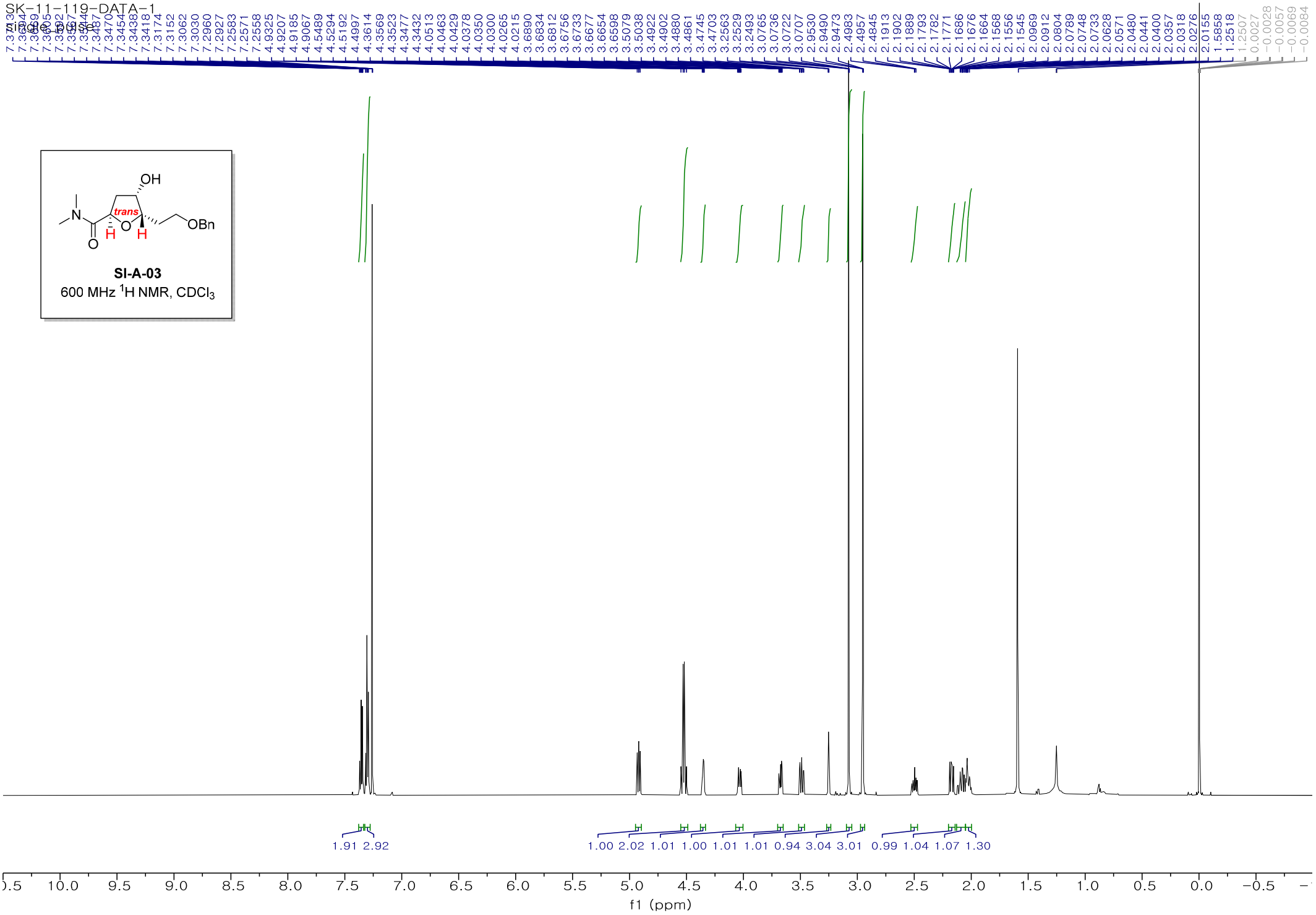


16
150 MHz ^{13}C NMR, $CDCl_3$

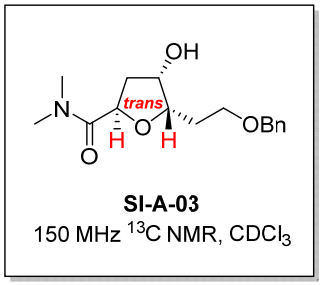

OTIPS
7
cis
9
trans
6
4
5
N
O
H
H
OBn
O
16
600 MHz ^{1}H-^{1}H COSY NMR
$CDCl_3$
SK-11-115-DATA
gradient absolute value cosy
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)
−1
0
1
2
3
4
5
6
7
8


OTIPS
7
cis
9
trans
6
4
5
N
O
H
H
OBn
O
16
600 MHz ^{1}H-^{1}H NOESY NMR
$CDCl_3$
SK-11-115-DATA
phase sensitive noesy
f2 (ppm)
f1 (ppm)

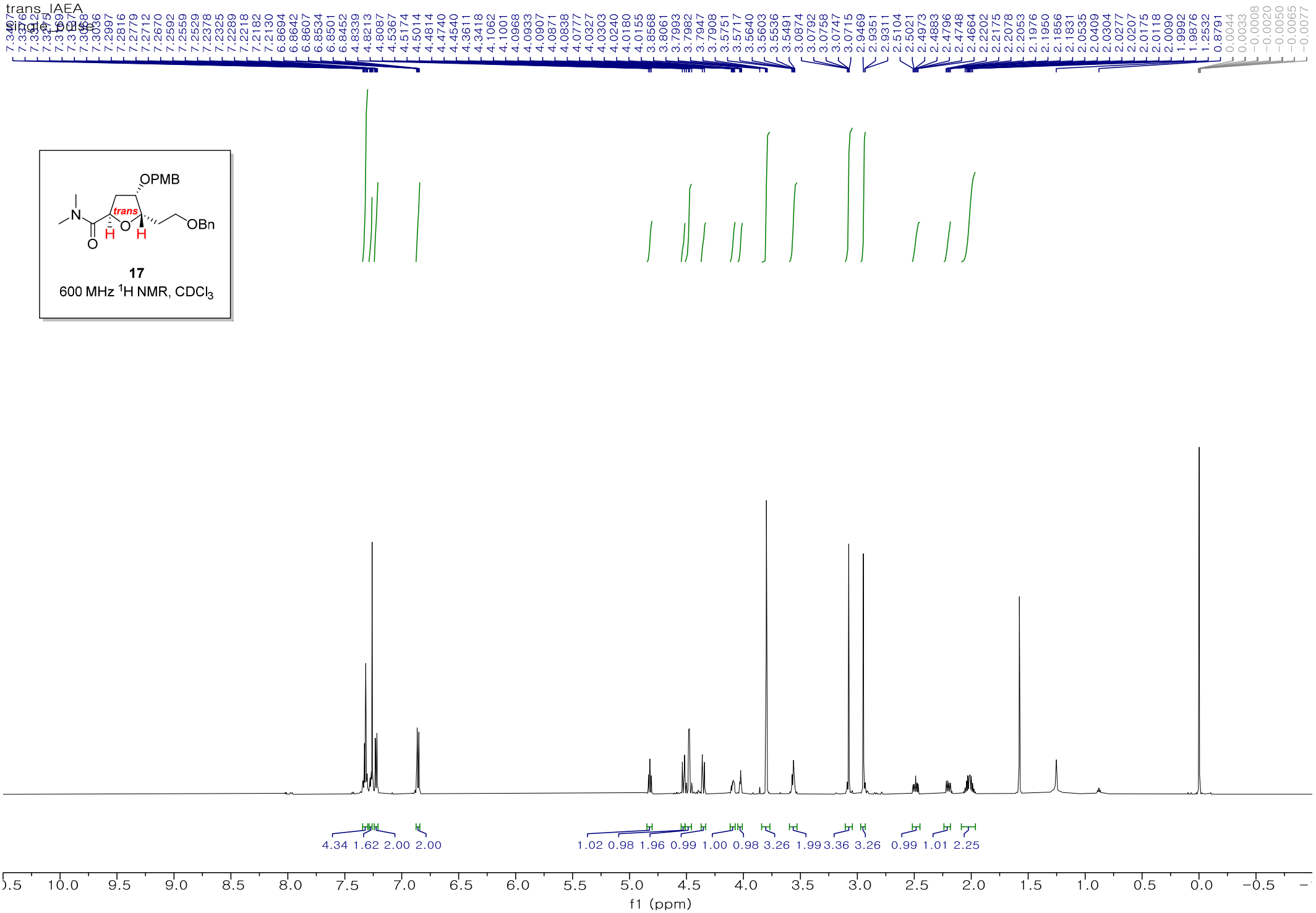

OTIPS
threo
trans
OBn
16
600 MHz ^{1}H-^{1}H NOESY NMR
$CDCl_3$
H_β
H_α
NOE
SK-11-115-DATA
phase sensitive noesy
9
7
6
4
8β
8α
5
f2 (ppm)
f1 (ppm)


SK-11-119-DATA-1
OH
trans
N
O
H
O
H
OBn
SI-A-03
600 MHz ^{1}H NMR, $CDCl_3$
1.91 2.92
1.00 2.02 1.01 1.00 1.01 1.01 0.94 3.04 3.01
0.99 1.04 1.07 1.30
f1 (ppm)

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

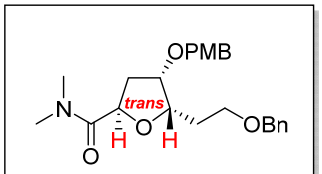


SI-A-03
150 MHz ^{13}C NMR, $CDCl_3$

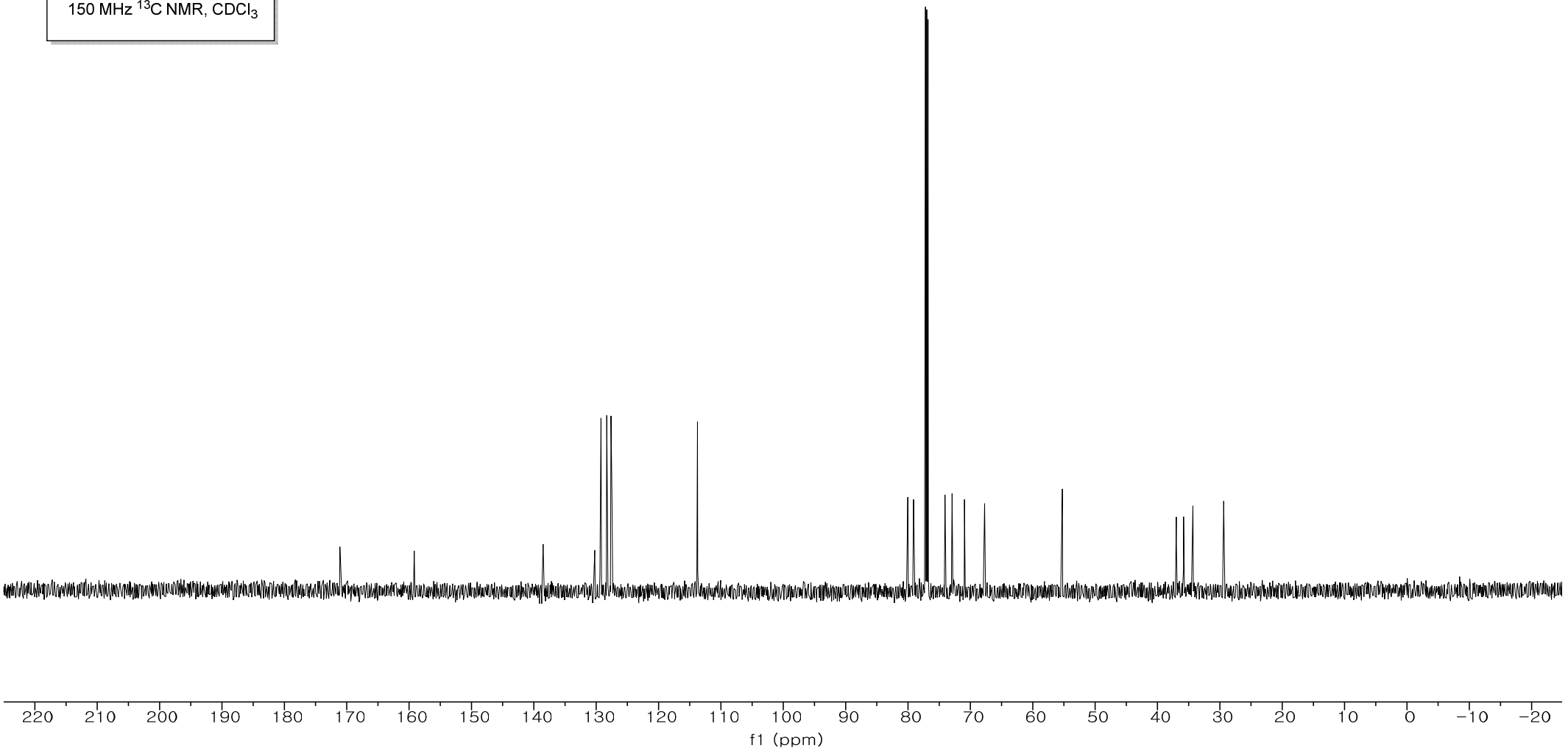

trans_IAEA
single pulse
OPMB
trans
OBn
17
600 MHz ^{1}H NMR, $CDCl_3$
4.34 1.62 2.00 2.00
1.02 0.98 1.96 0.99 1.00 0.98 3.26 1.99 3.36 3.26 0.99 1.01 2.25
f1 (ppm)

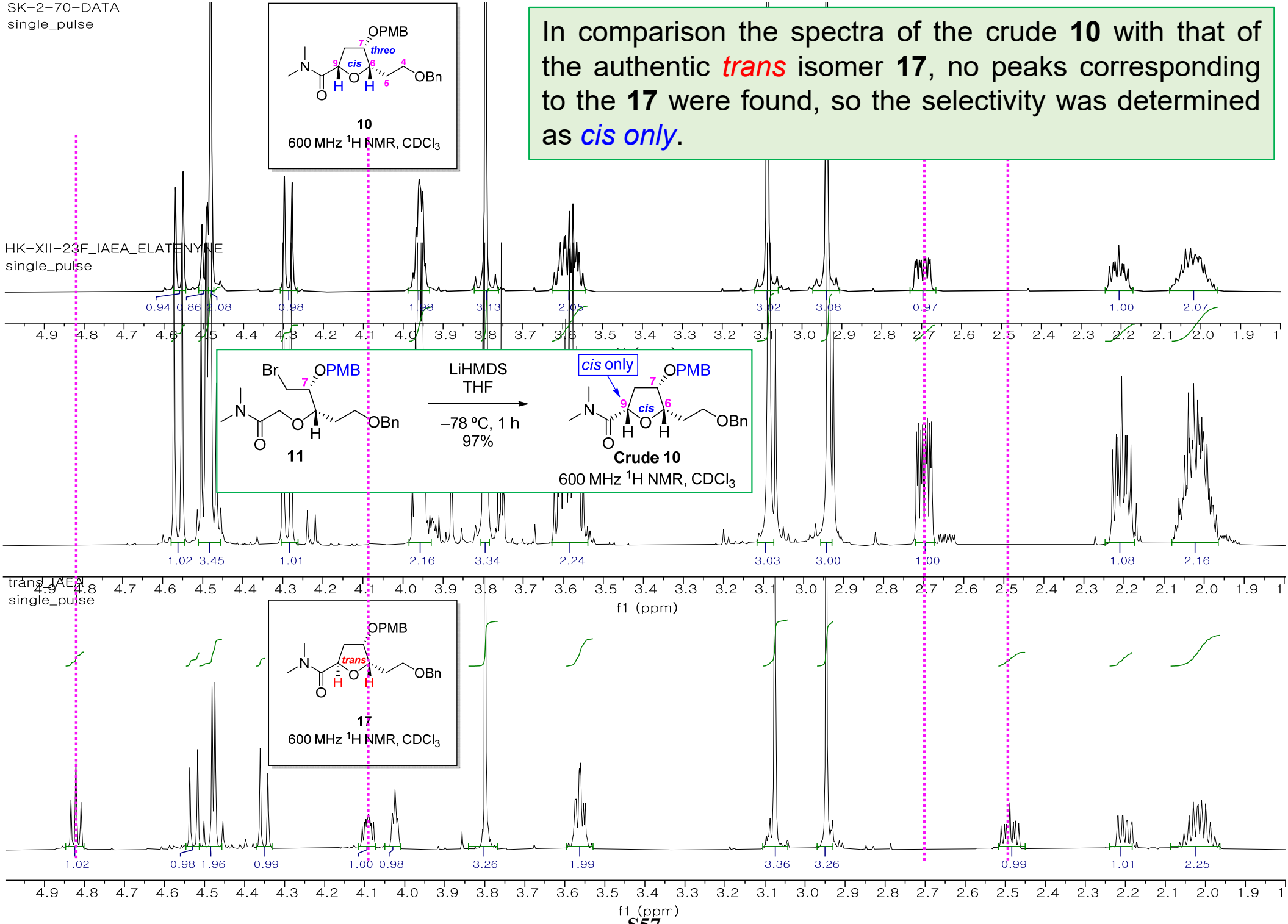
Elatenyne_IAEA-trans-2
single pulse decoupled gated NOE

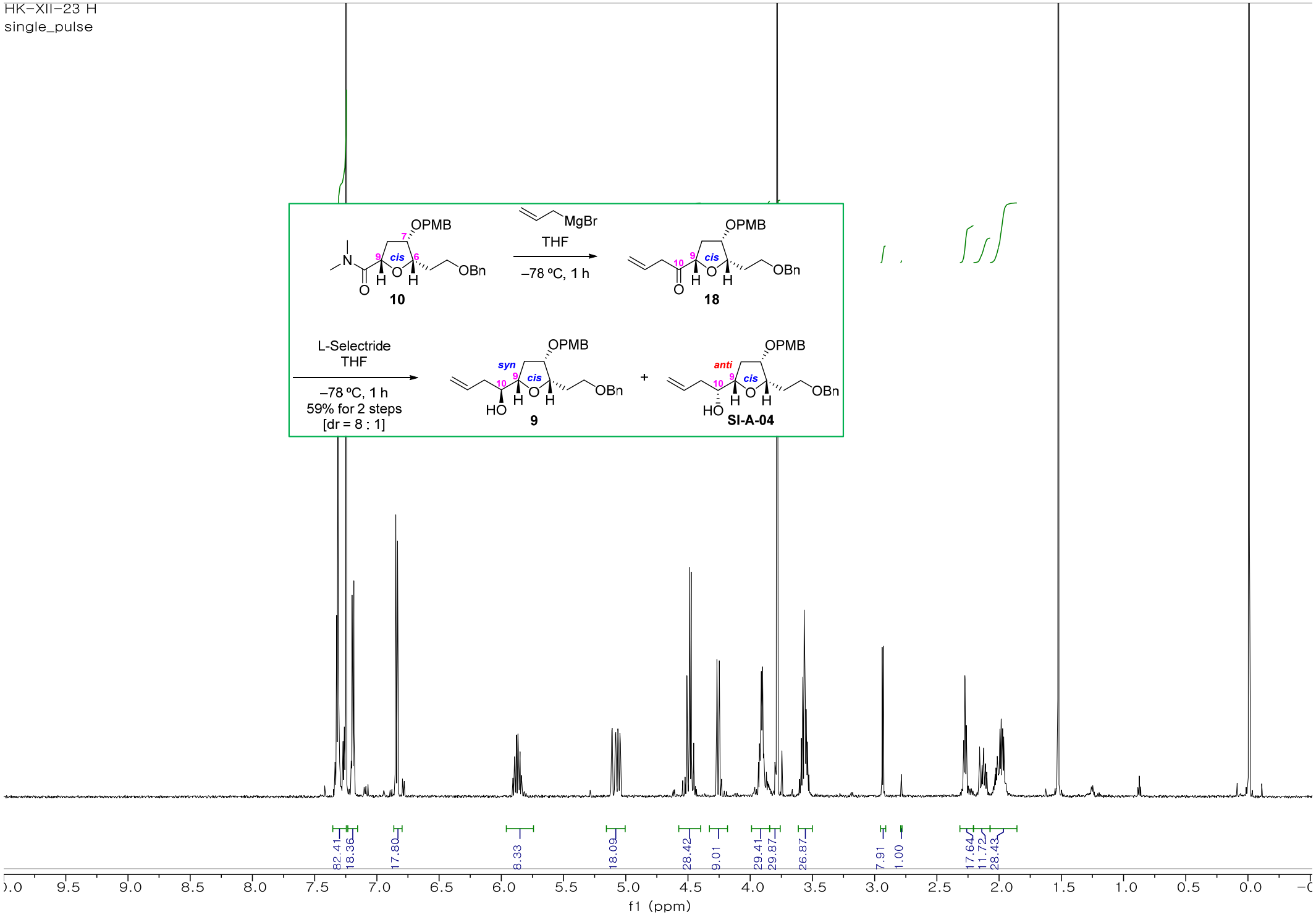
171.0887
159.1733
138.5051
130.2417
129.2292
128.3051
127.6261
127.4630
113.7478
80.0301
79.1151
74.0752
72.9350
70.9522
67.7162
55.2440
36.9760
35.8057
34.3126
29.3880

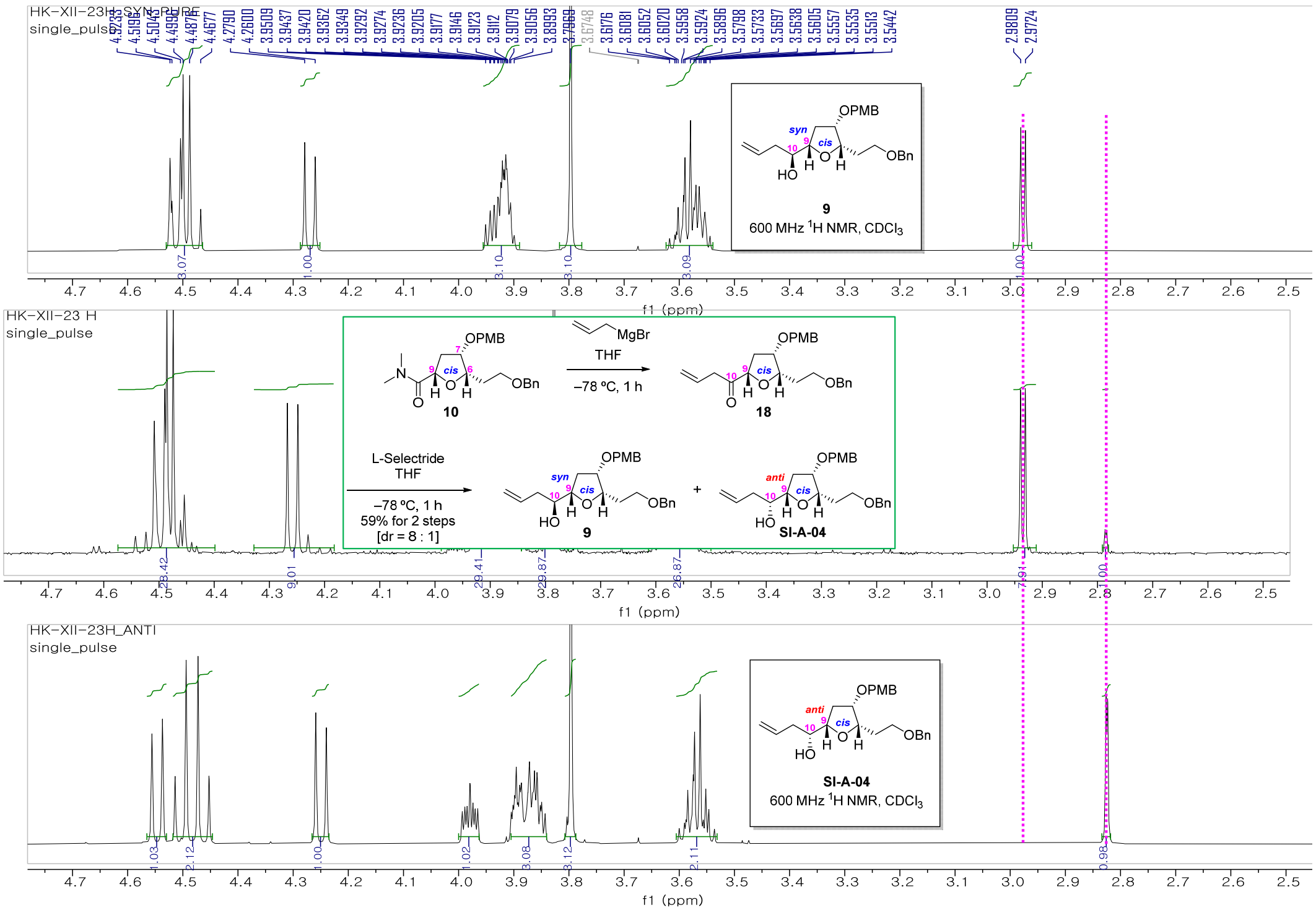


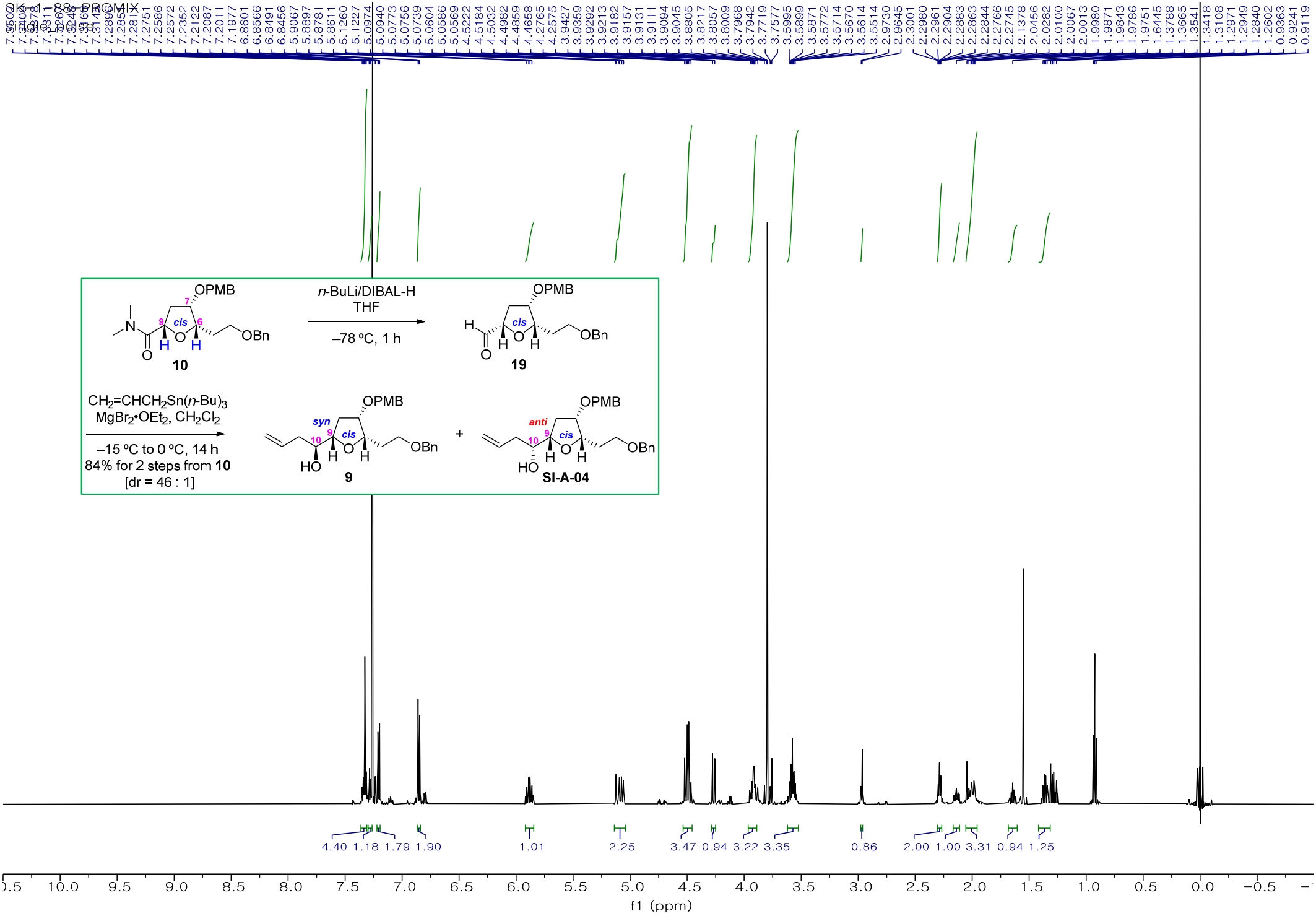
17
150 MHz ^{13}C NMR, $CDCl_3$

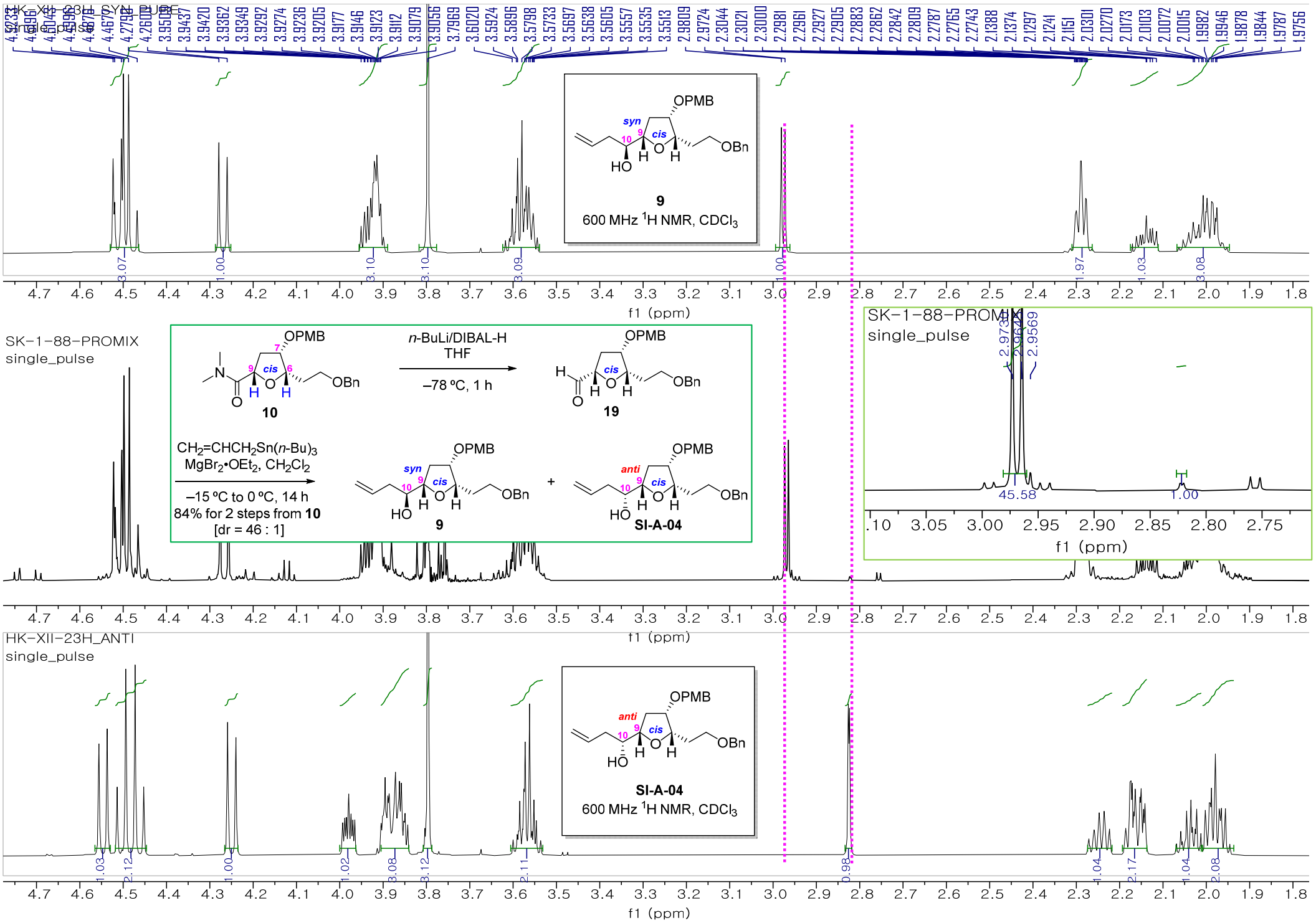


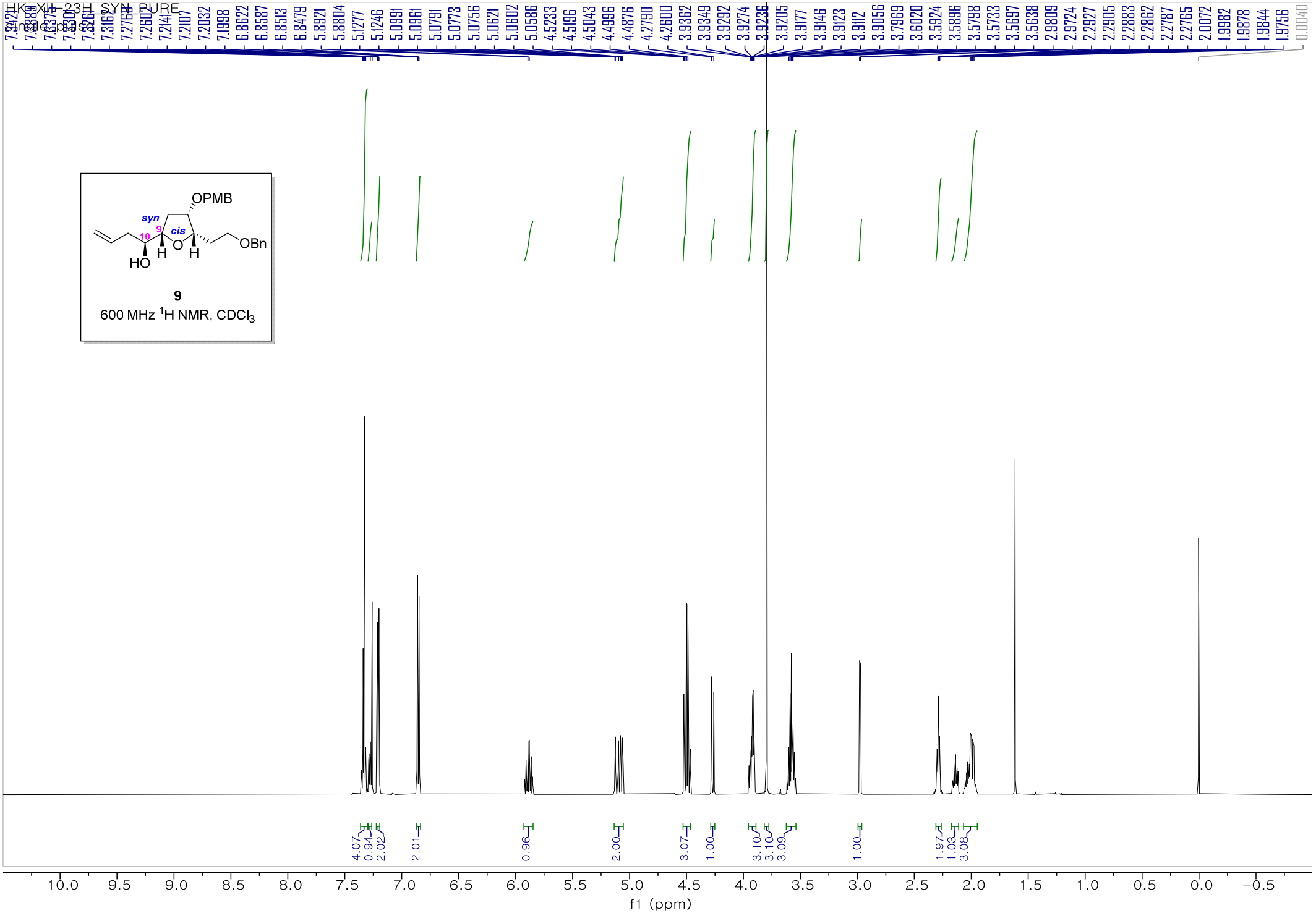

SK-2-70-DATA
single_pulse
OPMB
threo
cis
OBn
10
600 MHz ^{1}H NMR, CDCl$_3$
In comparison the spectra of the crude **10** with that of the authentic *trans* isomer **17**, no peaks corresponding to the **17** were found, so the selectivity was determined as *cis only*.
HK-XII-23F_IAEA_ELATENYNE
single_pulse
0.94 0.86 2.08 0.98 1.98 3.13 2.05 3.02 3.08 0.97 1.00 2.07
Br
OPMB
OBn
11
LiHMDS
THF
–78 °C, 1 h
97%
cis only
Crude 10
600 MHz ^{1}H NMR, CDCl$_3$
1.02 3.45 1.01 2.16 3.34 2.24 3.03 3.00 1.00 1.08 2.16
trans_IAEA
single_pulse
trans
17
600 MHz ^{1}H NMR, CDCl$_3$
1.02 0.98 1.96 0.99 1.00 0.98 3.26 1.99 3.36 3.26 0.99 1.01 2.25
f1 (ppm)


HK-XII-23 H
single_pulse
OPMB
MgBr
THF
–78 °C, 1 h
OBn
10
18
L-Selectride
THF
–78 °C, 1 h
59% for 2 steps
[dr = 8 : 1]
syn
anti
cis
HO
9
SI-A-04
82.41
18.36
17.80
8.33
18.09
28.42
9.01
29.41
29.87
26.87
7.91
1.00
17.64
11.72
28.43
f1 (ppm)


HK-XII-23H-SYN_PURE
single_pulse
OPMB
syn
cis
OBn
HO
9
600 MHz 1H NMR, CDCl3
f1 (ppm)
HK-XII-23 H
single_pulse
OPMB
cis
OBn
10
MgBr
THF
–78 °C, 1 h
18
L-Selectride
THF
–78 °C, 1 h
59% for 2 steps
[dr = 8 : 1]
9
anti
SI-A-04
HK-XII-23H_ANTI
single_pulse
SI-A-04
600 MHz 1H NMR, CDCl3
f1 (ppm)

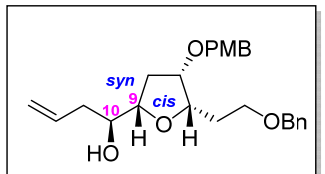

SK-I-88-PROMIX
single_pulse
OPMB
cis
OBn
10
n-BuLi/DIBAL-H
THF
–78 °C, 1 h
19
CH2=CHCH2Sn(n-Bu)3
MgBr2•OEt2, CH2Cl2
–15 °C to 0 °C, 14 h
84% for 2 steps from 10
[dr = 46 : 1]
syn
9
anti
SI-A-04
4.40 1.18 1.79 1.90
1.01
2.25
3.47 0.94 3.22 3.35
0.86
2.00 1.00 3.31 0.94 1.25
f1 (ppm)


HK-XII-23H_SYN_PURE
single_pulse
OPMB
syn
cis
OBn
HO
9
600 MHz ^{1}H NMR, CDCl$_3$
f1 (ppm)
SK-1-88-PROMIX
single_pulse
OPMB
cis
OBn
10
n-BuLi/DIBAL-H
THF
–78 °C, 1 h
19
CH$_2$=CHCH$_2$Sn(n-Bu)$_3$
MgBr$_2$•OEt$_2$, CH$_2$Cl$_2$
–15 °C to 0 °C, 14 h
84% for 2 steps from 10
[dr = 46 : 1]
anti
SI-A-04
45.58
1.00
HK-XII-23H_ANTI
single_pulse
600 MHz ^{1}H NMR, CDCl$_3$

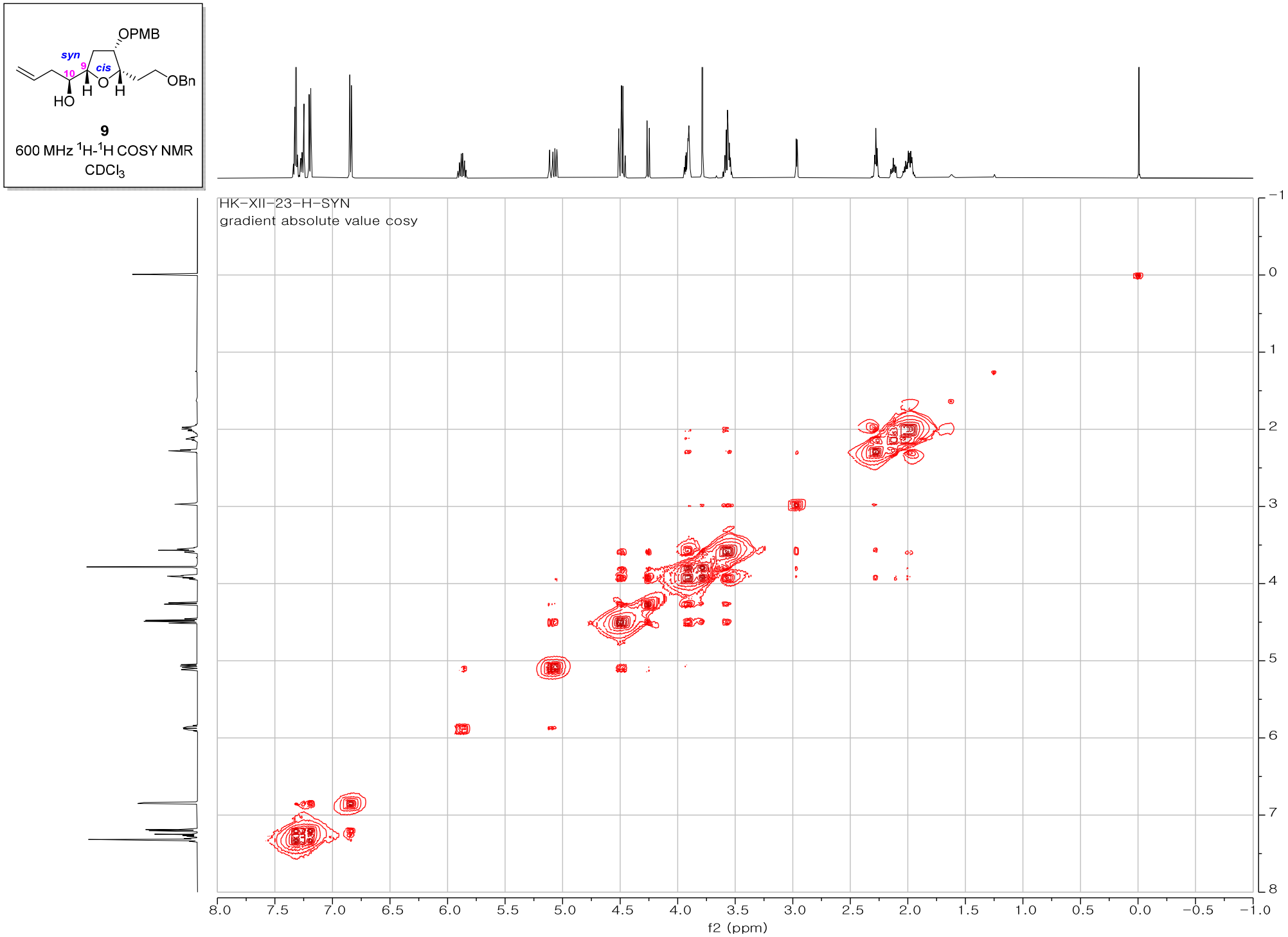

OPMB
syn
cis
10
9
H
O
H
HO
OBn
9
600 MHz ^{1}H NMR, $CDCl_3$
f1 (ppm)

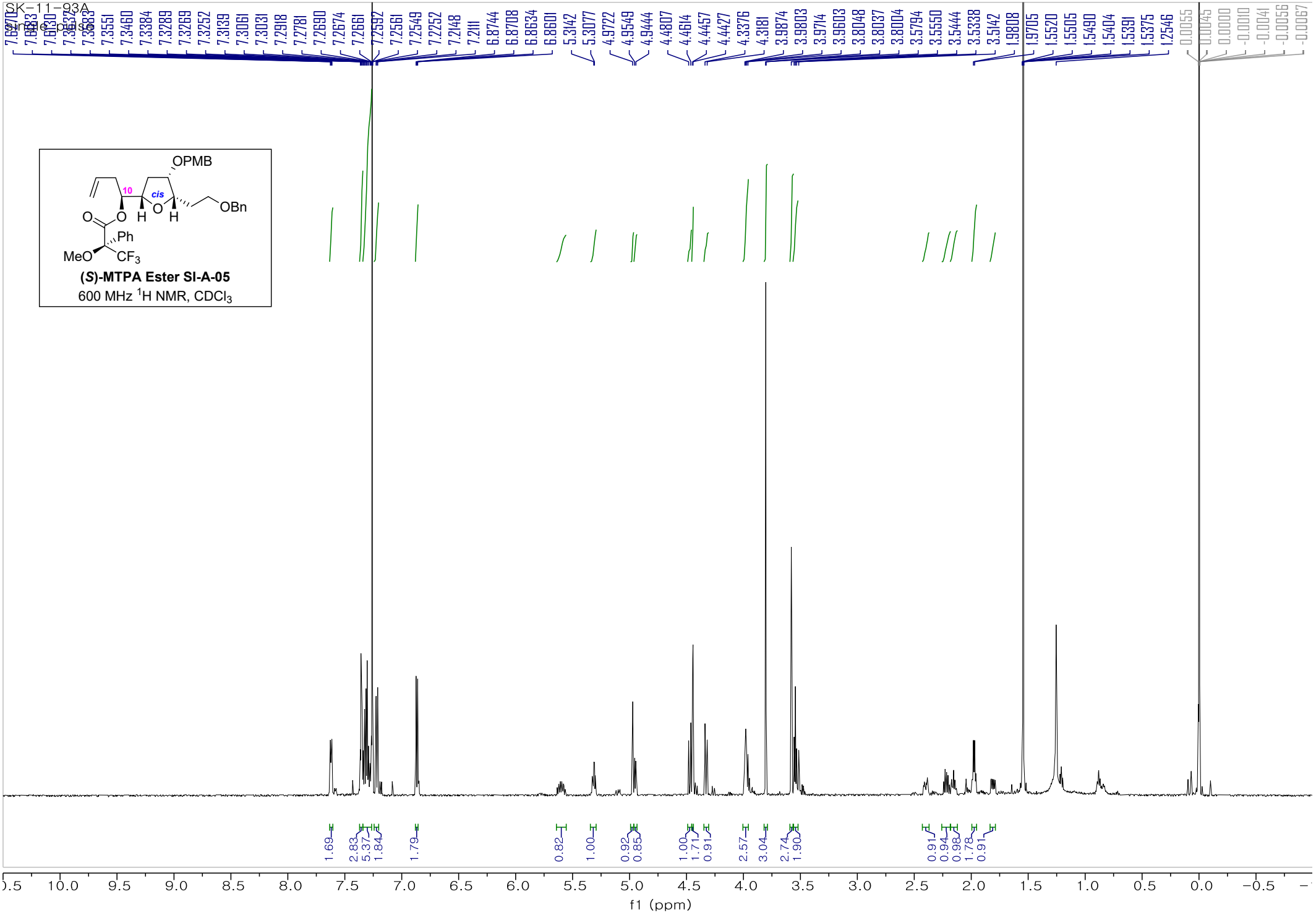
SK-3-61
single pulse decoupled gated NOE

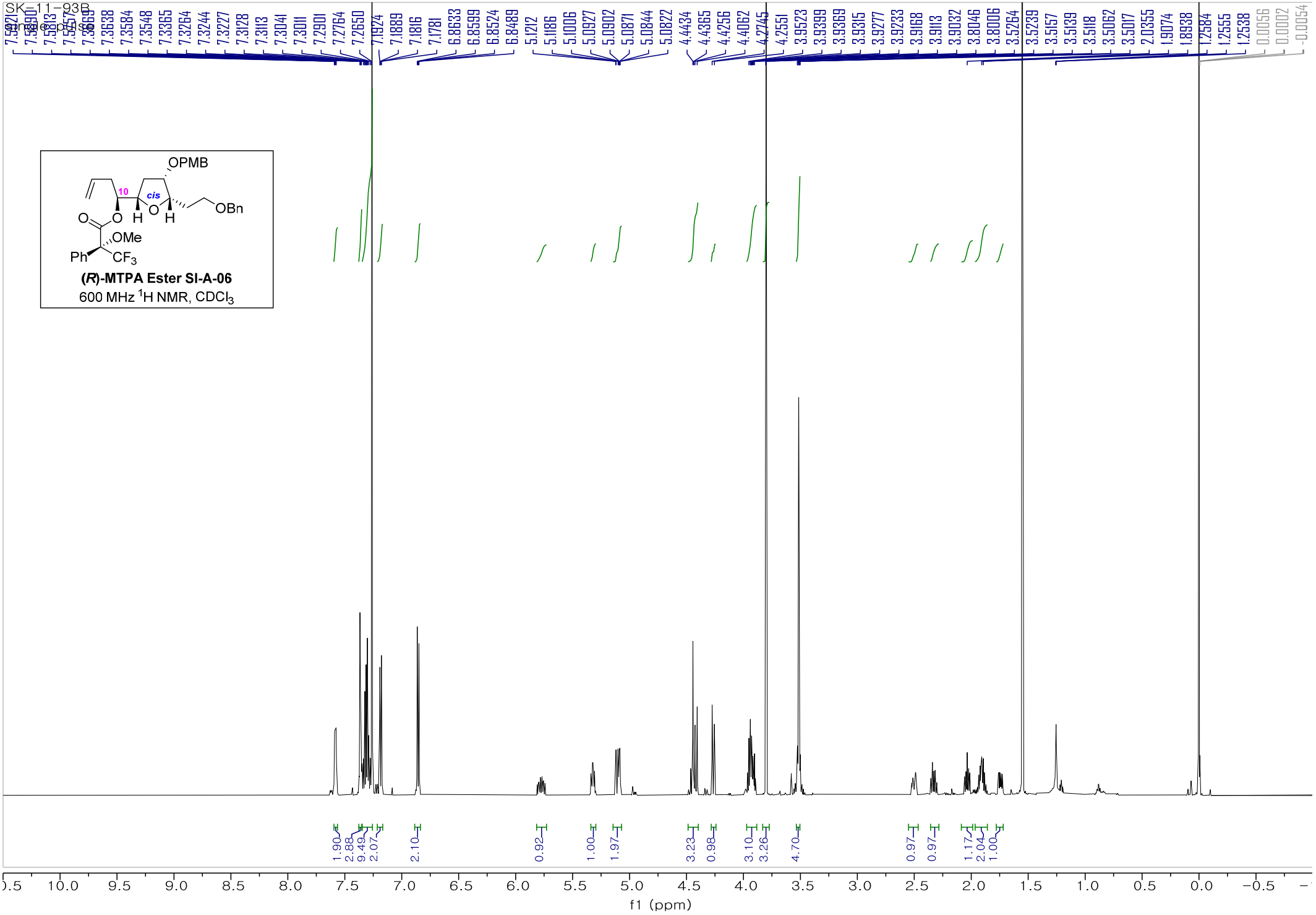
159.2344
138.4895
135.2633
129.8430
129.3632
128.3483
127.6608
127.5401
116.9007
113.7853
79.7496
79.4081
73.2181
72.9399
70.6037
67.6295
55.2619
38.5866
33.9439
29.4288
-0.0249

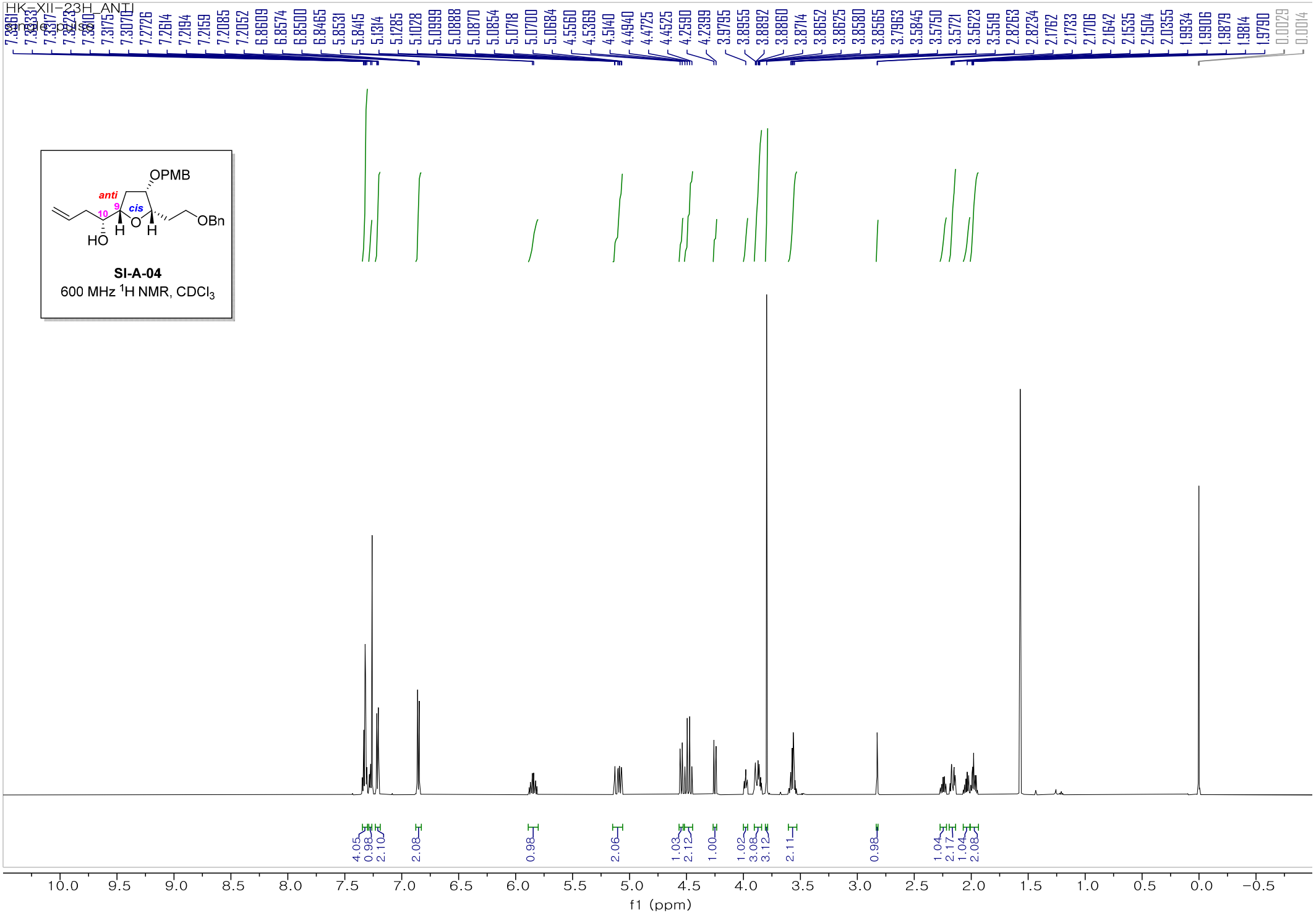


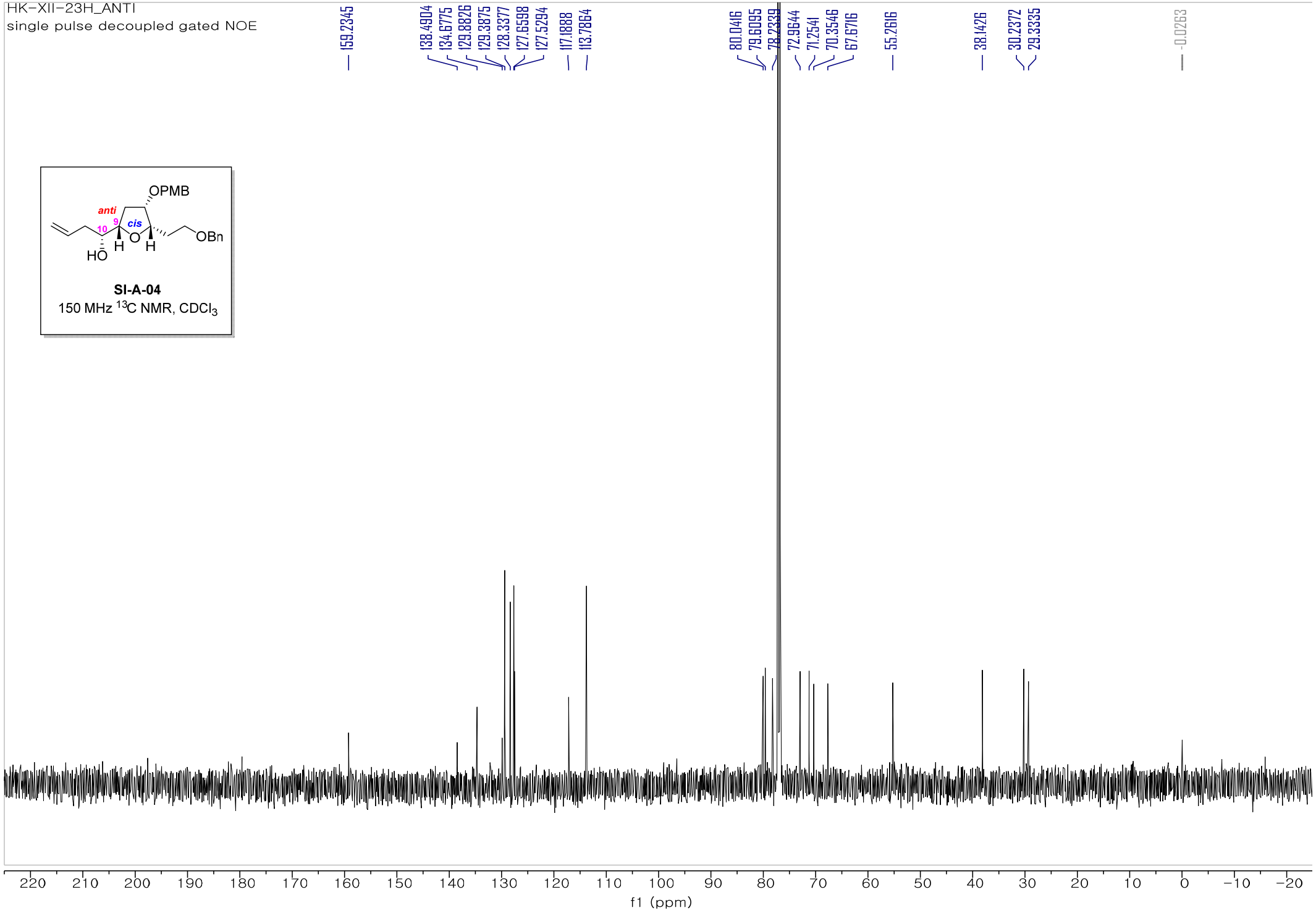
9
150 MHz ^{13}C NMR, $CDCl_3$

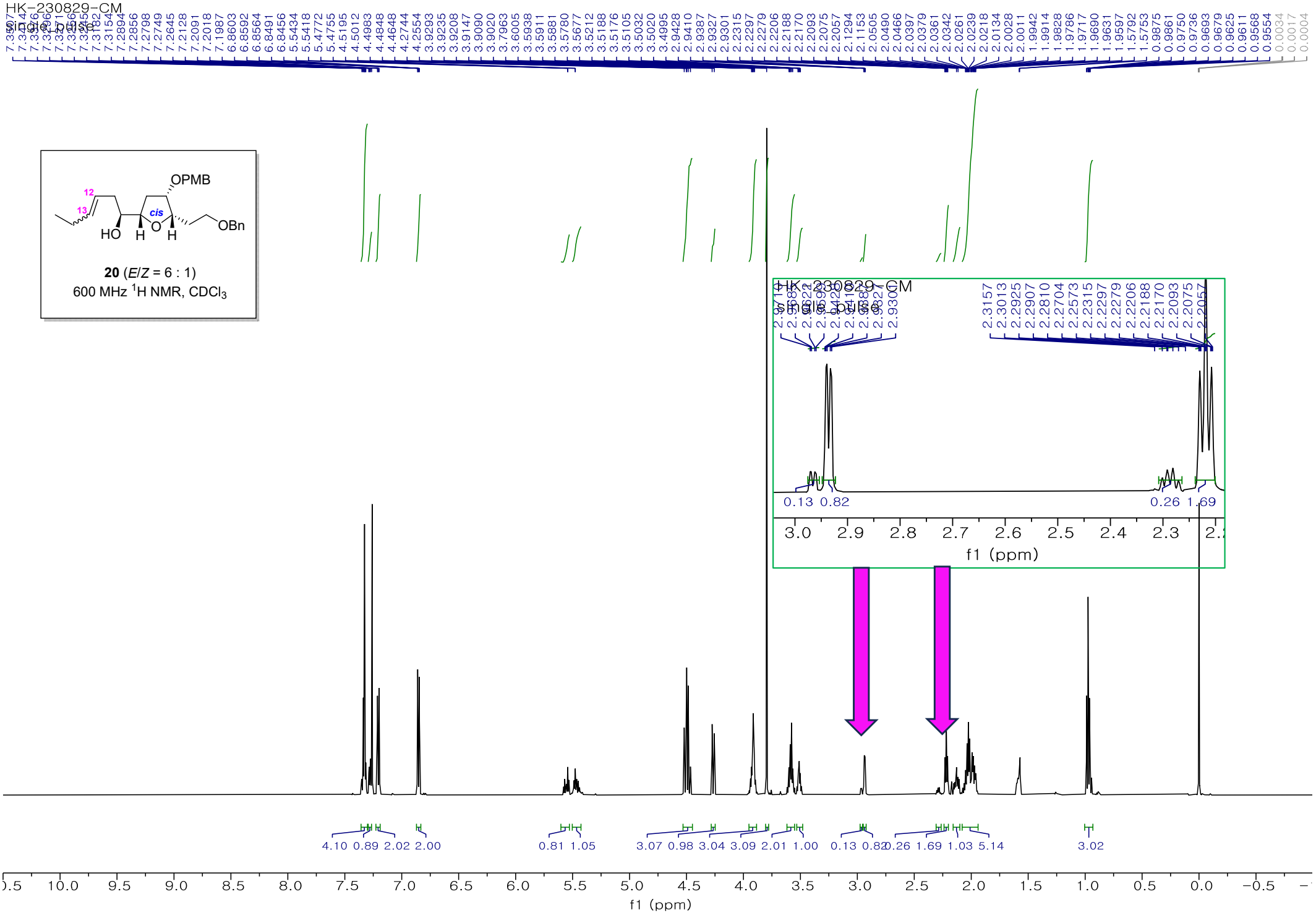

OPMB
syn
10
9
cis
HO
H
O
H
OBn
9
600 MHz ^{1}H-^{1}H COSY NMR
$CDCl_3$
HK-XII-23-H-SYN
gradient absolute value cosy
f2 (ppm)
f1 (ppm)


SK-11-93A
OPMB
10
cis
OBn
Ph
MeO
CF3
(S)-MTPA Ester SI-A-05
600 MHz 1H NMR, CDCl3
f1 (ppm)

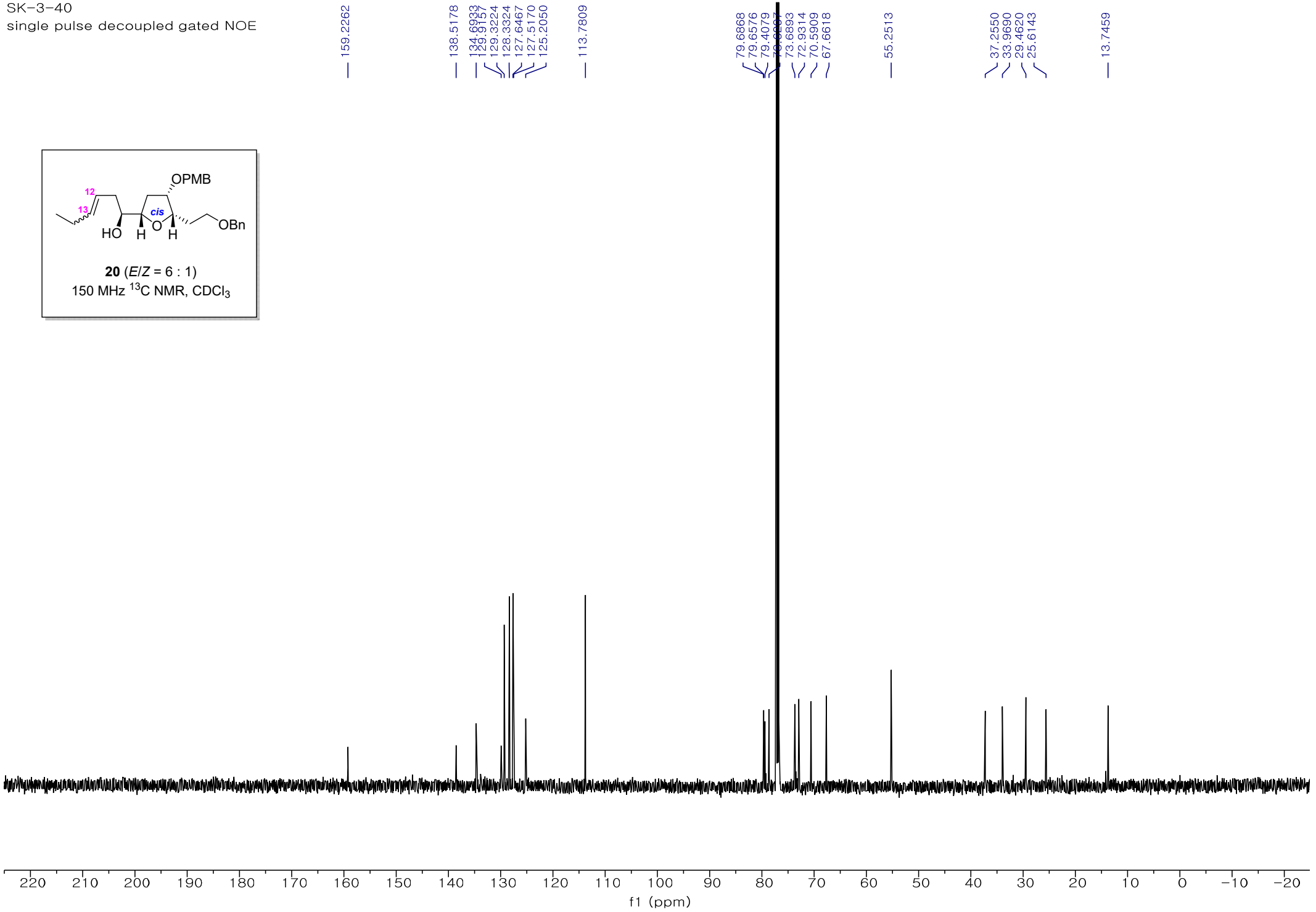

SK-11-93B
OPMB
10
cis
OBn
OMe
Ph
CF3
(R)-MTPA Ester SI-A-06
600 MHz 1H NMR, CDCl3
f1 (ppm)

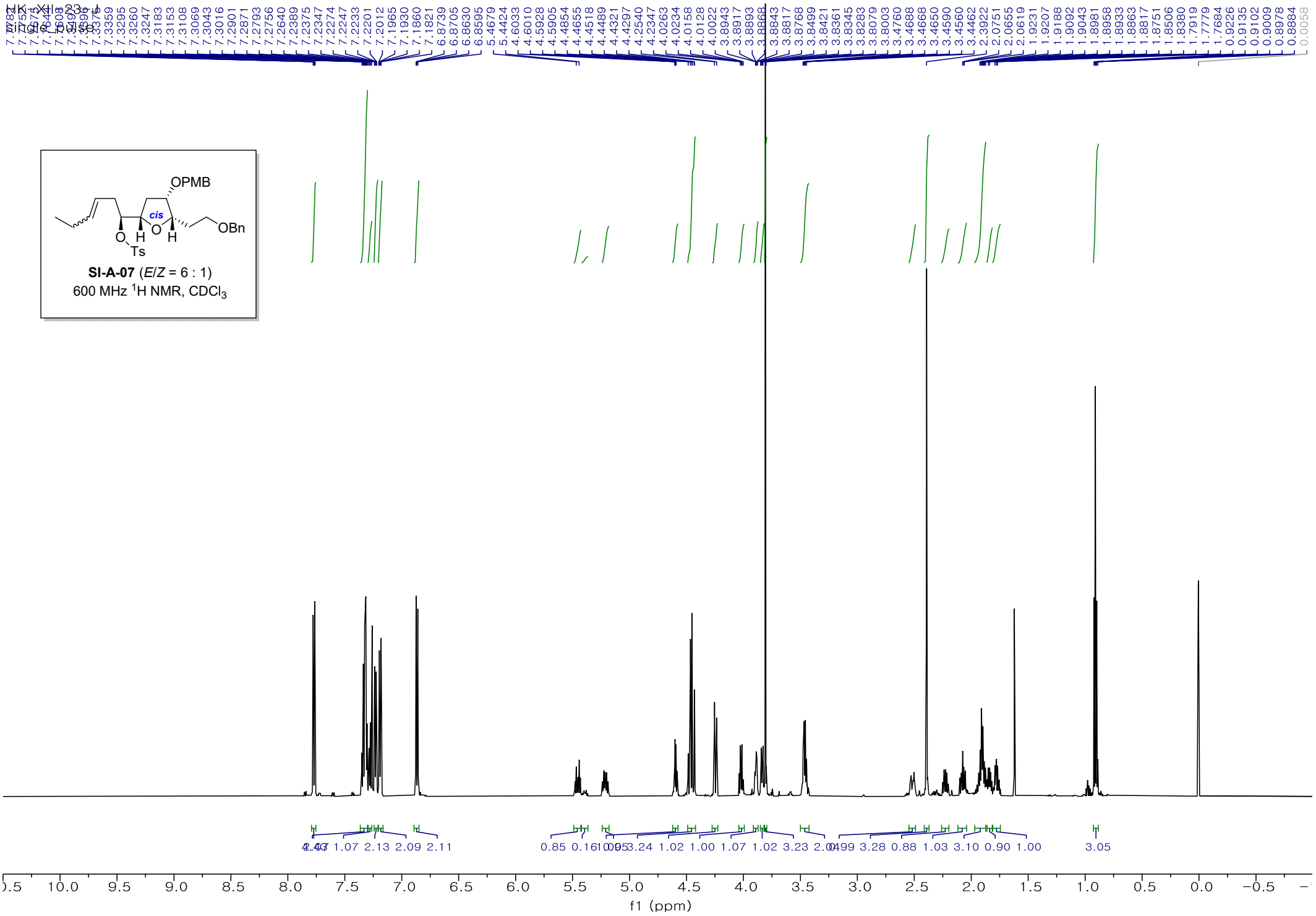

HK-XII-23H_ANTI
OPMB
anti
cis
OBn
HO
SI-A-04
600 MHz ^{1}H NMR, $CDCl_3$
f1 (ppm)


HK-XII-23H_ANTI
single pulse decoupled gated NOE
159.2345
138.4904
134.6775
129.8826
129.3875
128.3377
127.6598
127.5294
117.1888
113.7864
80.0416
79.6095
78.2339
72.9644
71.2541
70.3546
67.6716
55.2616
38.1426
30.2372
29.3335
-0.0263
OPMB
anti
cis
OBn
HO
H
O
H
SI-A-04
150 MHz 13C NMR, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

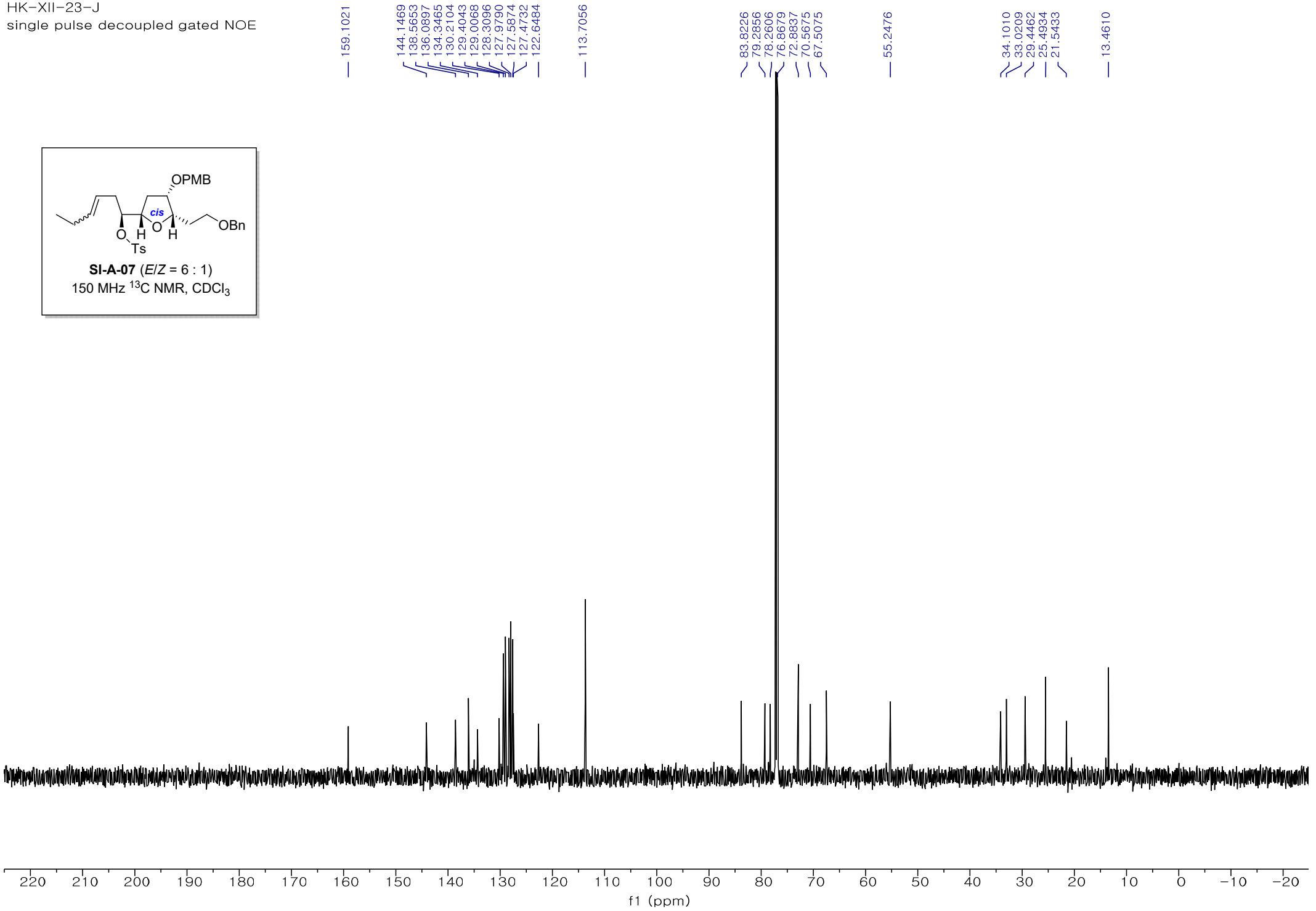

HK-230829-CM
single pulse
OPMB
12
13
cis
HO
H
O
H
OBn
20 (E/Z = 6 : 1)
600 MHz 1H NMR, CDCl3
HK-230829-CM
single pulse
0.13 0.82
0.26 1.69
f1 (ppm)
4.10 0.89 2.02 2.00
0.81 1.05
3.07 0.98 3.04 3.09 2.01 1.00
0.13 0.82
0.26 1.69 1.03 5.14
3.02
f1 (ppm)

SK-3-40
single pulse decoupled gated NOE

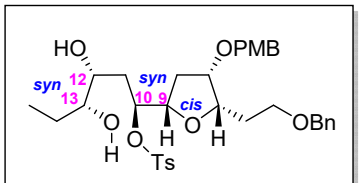



OPMB
cis
O
H
O
H
OBn
Ts
SI-A-07 (E/Z = 6 : 1)
600 MHz 1H NMR, CDCl3
f1 (ppm)

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

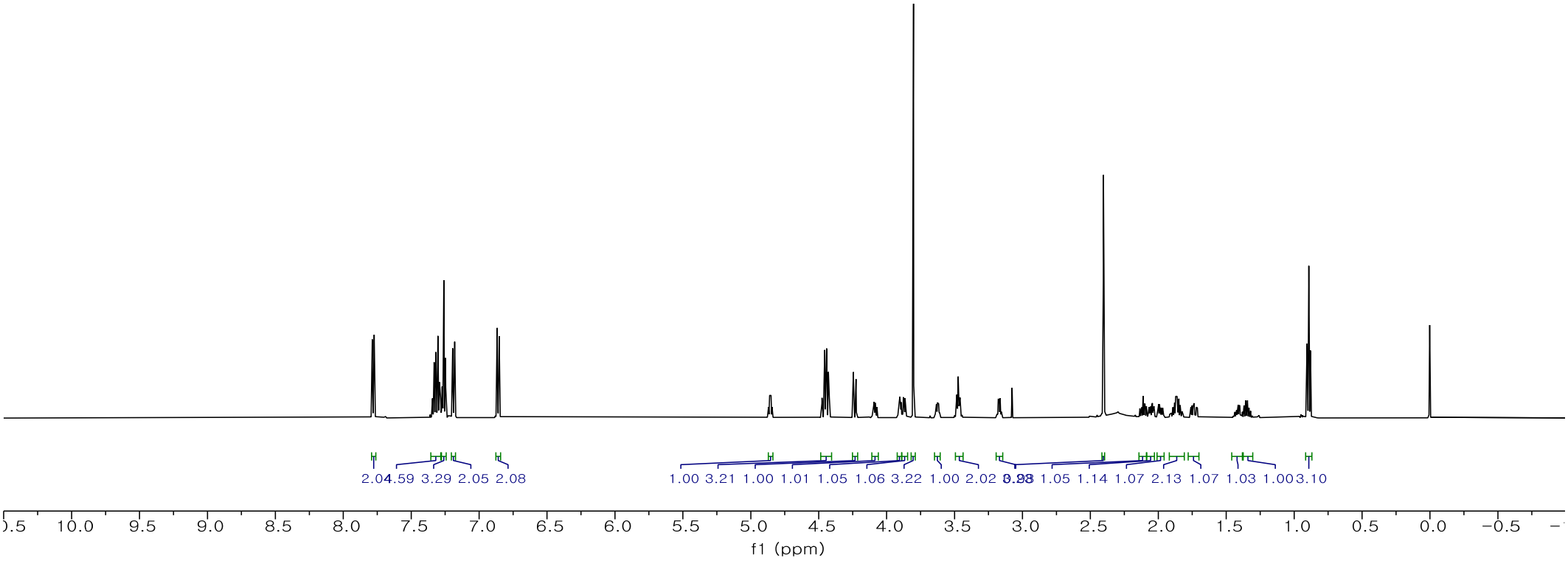


HK-230902-2H
single_pulse



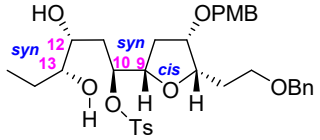
8

600 MHz ^{1}H NMR, $CDCl_3$



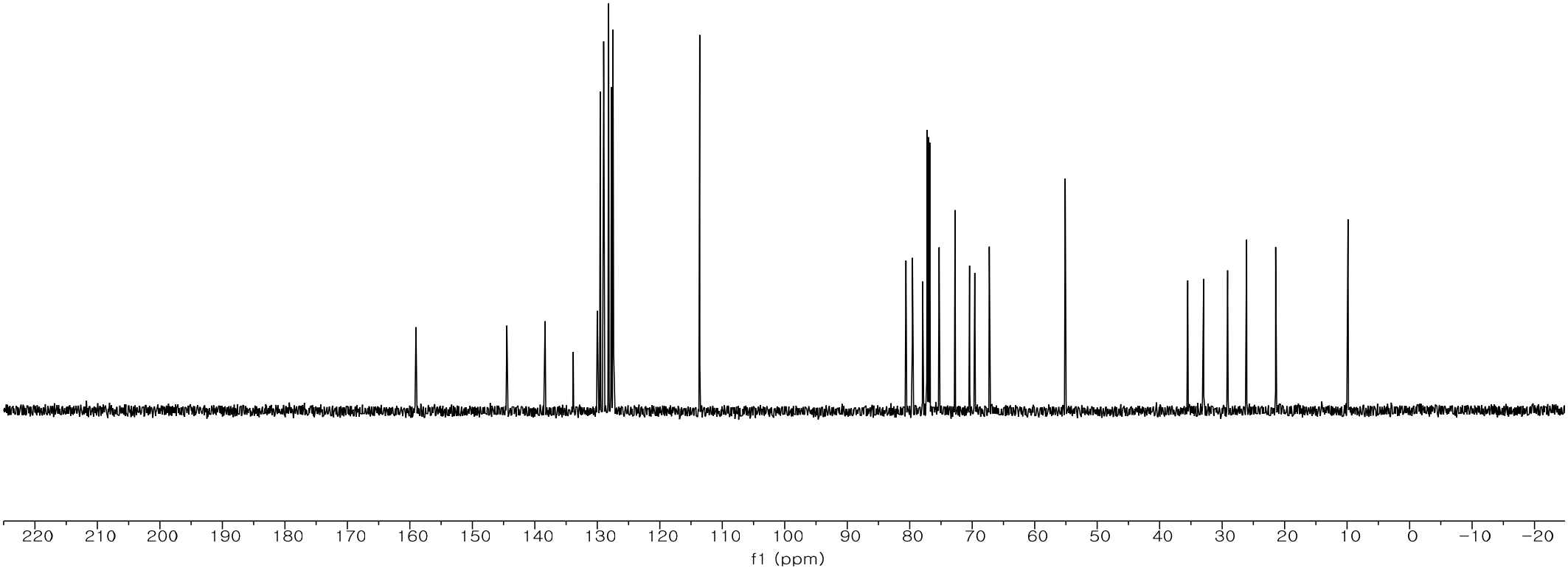
HK-230902-1C
single pulse decoupled gated NOE

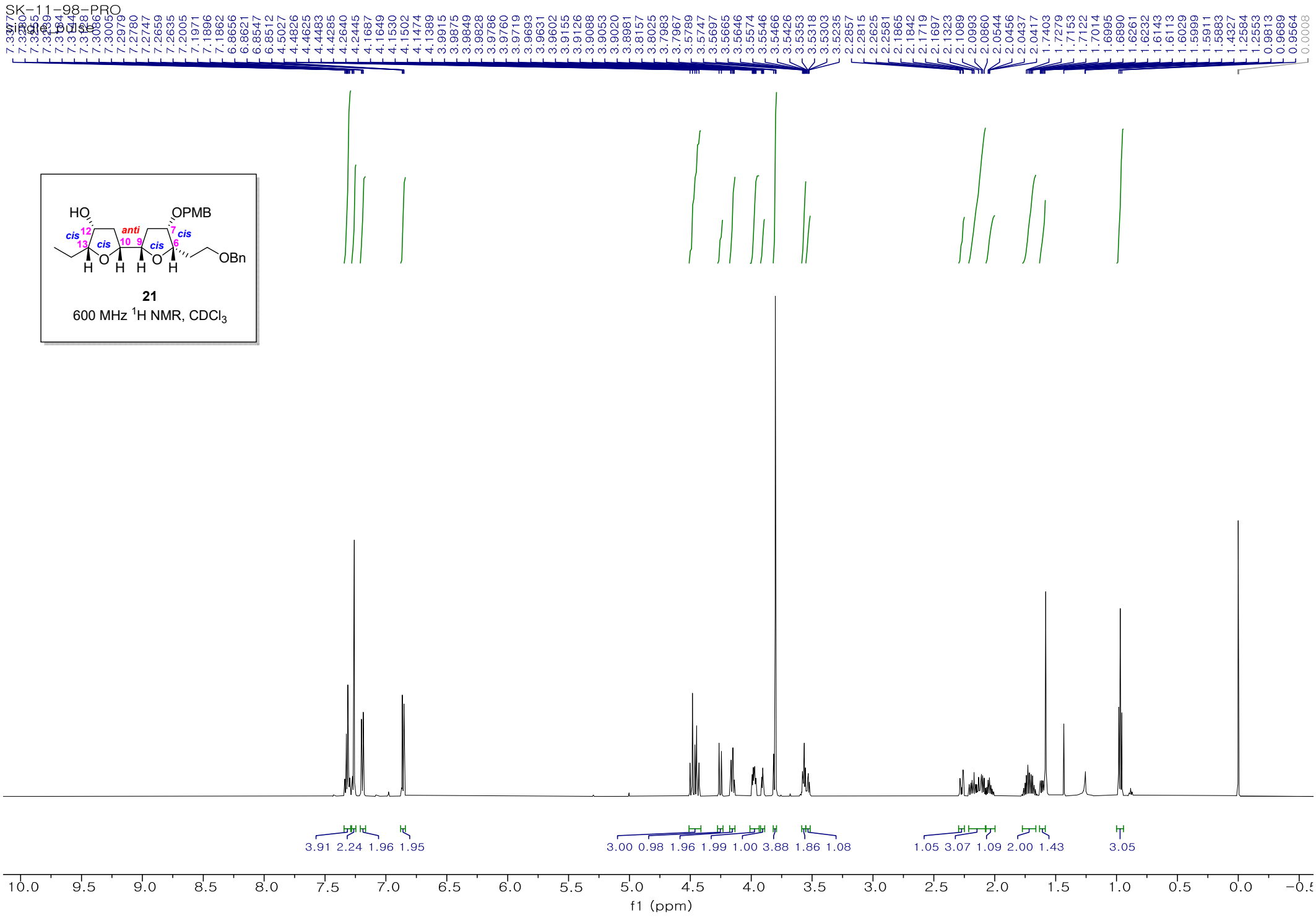
159.0302
144.4705
138.3598
133.8630
130.0062
129.5315
128.9810
128.1962
127.7405
127.4817
127.4433
127.3866
113.6124
80.6101
79.5723
77.9403
77.2632
75.2991
72.7518
70.4198
69.5861
67.2627
55.1145
35.5102
32.9679
29.1255
26.0866
21.4289
9.8613



8

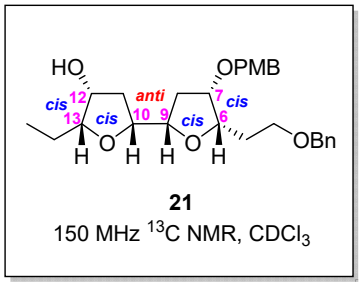
150 MHz ^{13}C NMR, $CDCl_3$




SK-11-98-PRO
single_pulse
HO
OPMB
anti
cis
cis
cis
cis
cis
OBn
21
600 MHz ^{1}H NMR, $CDCl_3$
3.91 2.24 1.96 1.95
3.00 0.98 1.96 1.99 1.00 3.88 1.86 1.08
1.05 3.07 1.09 2.00 1.43
3.05
f1 (ppm)

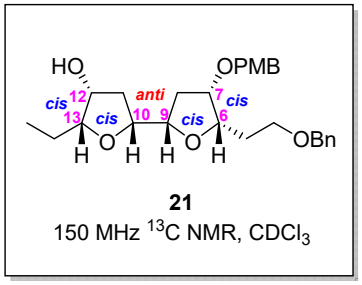
SK-04-69-DATA
single pulse decoupled gated NOE

159.1137
138.4643
130.0901
129.0085
128.3204
127.6879
127.4877
113.7556
86.2021
80.5064
79.2884
78.5832
78.2098
72.8878
70.6849
70.3588
67.3522
55.2635
34.4888
33.5929
28.9400
21.8992
10.5359
-0.0254



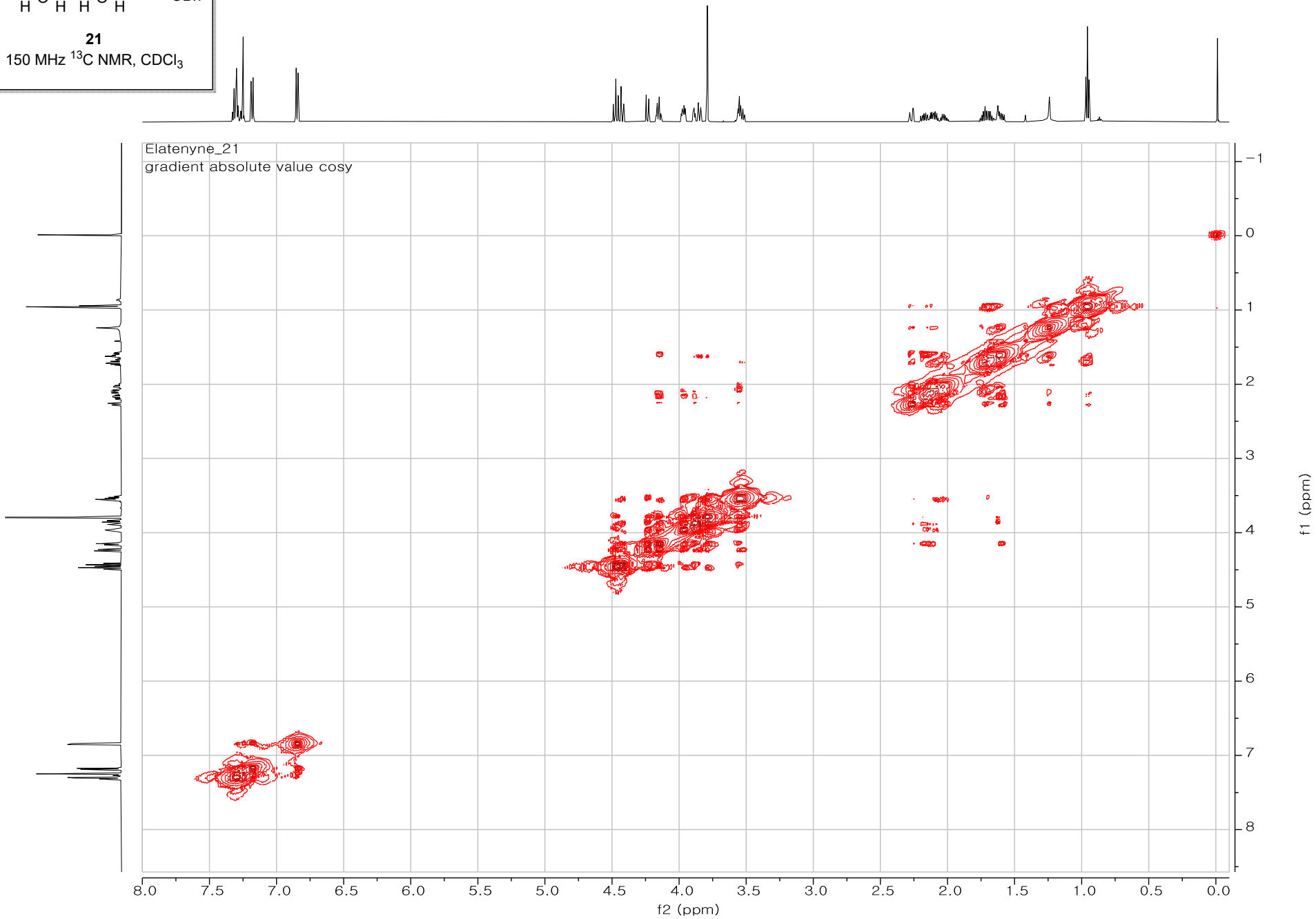
21
150 MHz ^{13}C NMR, $CDCl_3$

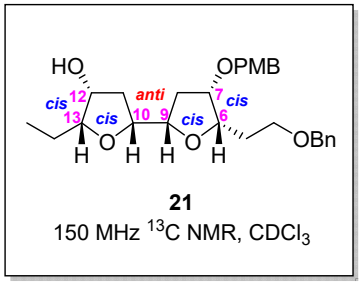
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



21

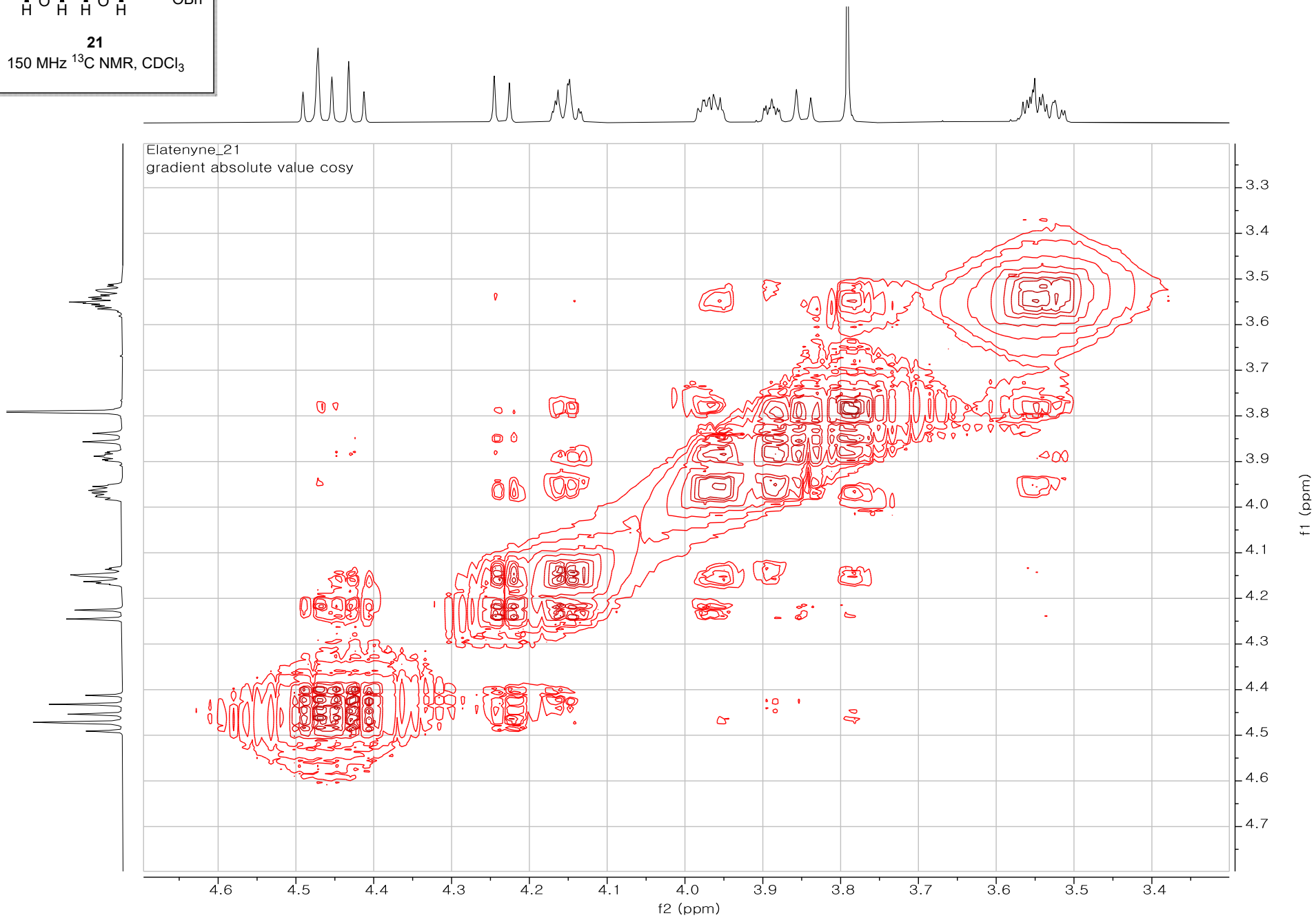
150 MHz ^{13}C NMR, $CDCl_3$

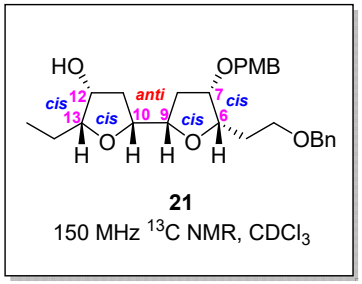




21

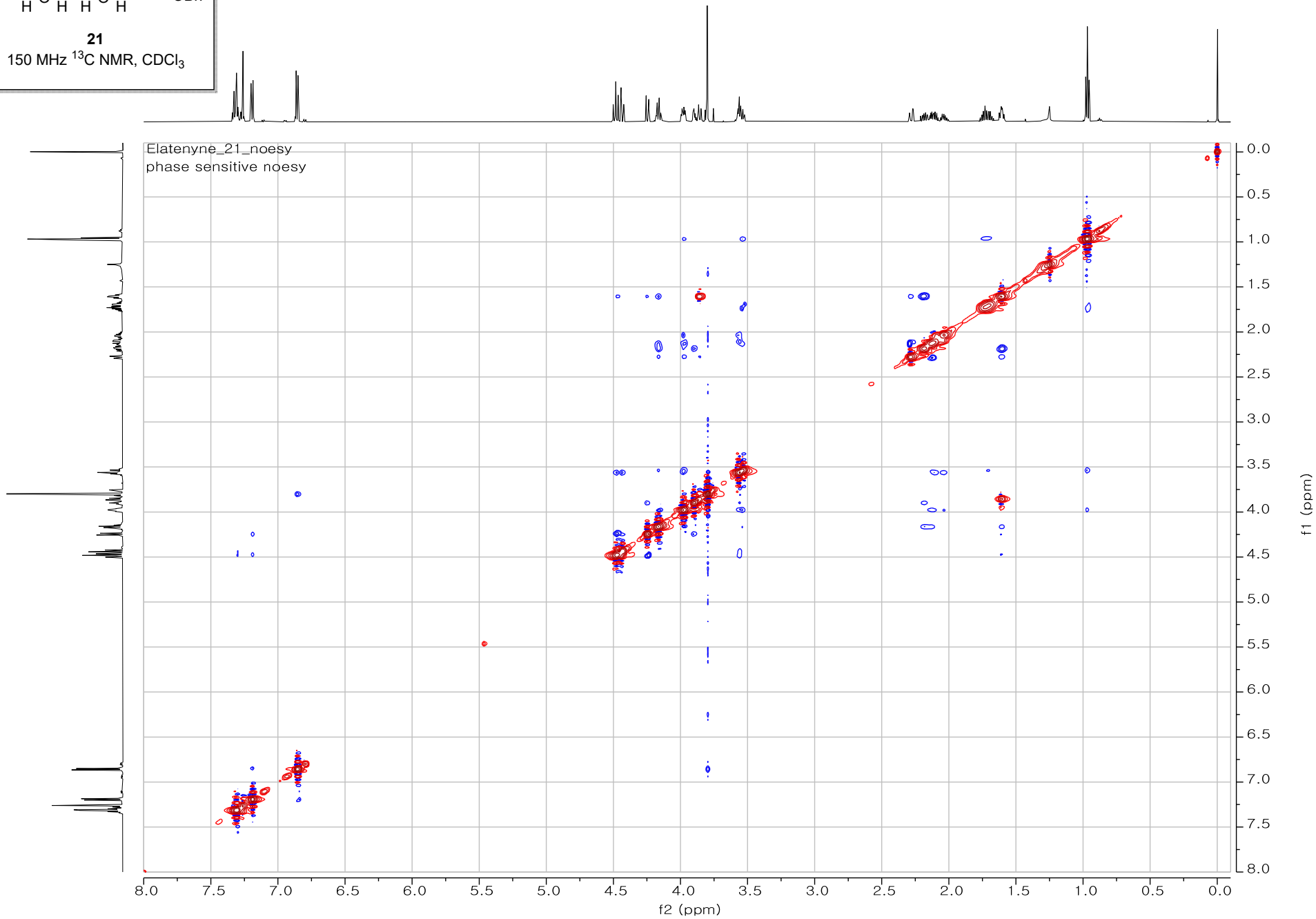
150 MHz ^{13}C NMR, $CDCl_3$

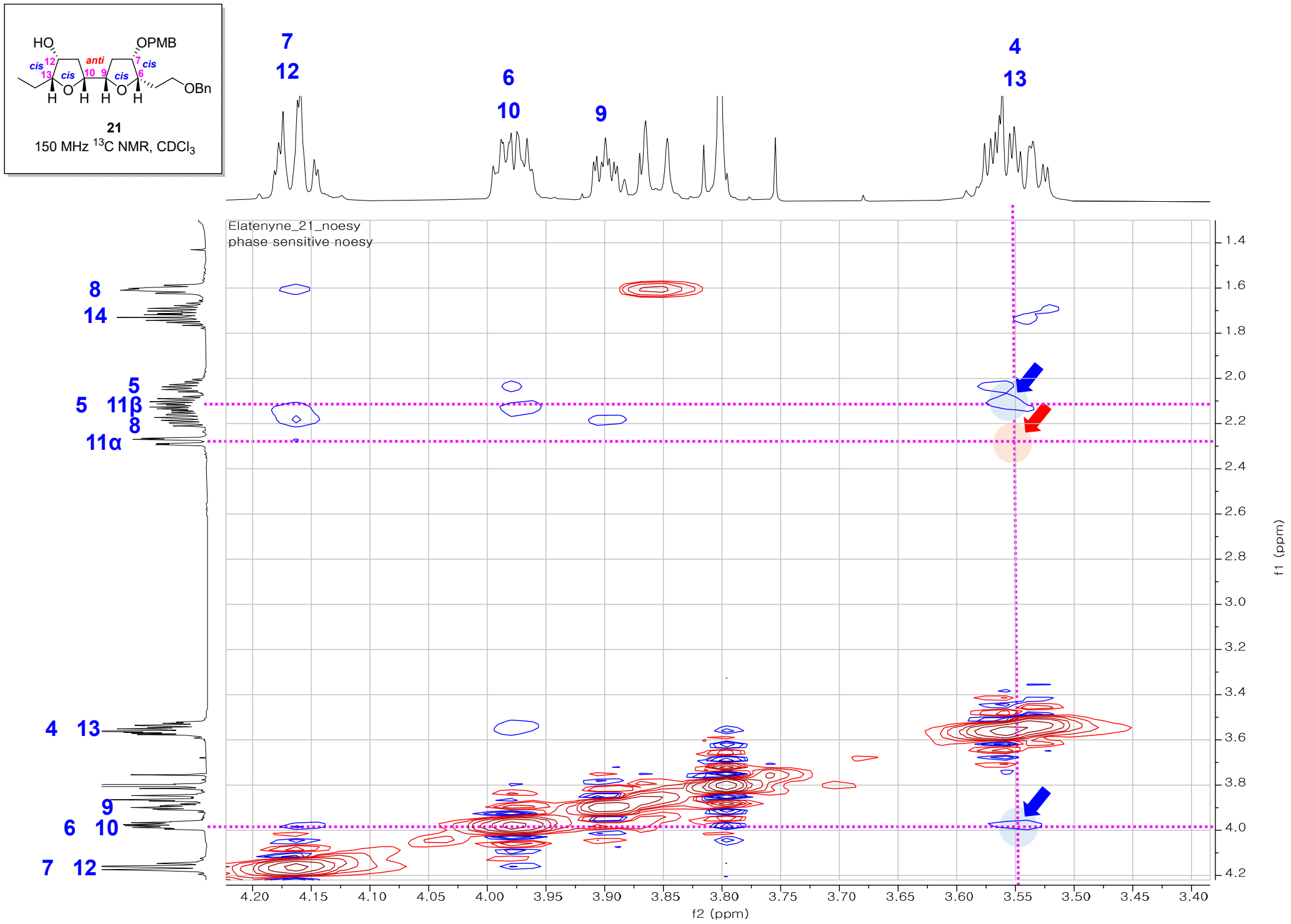


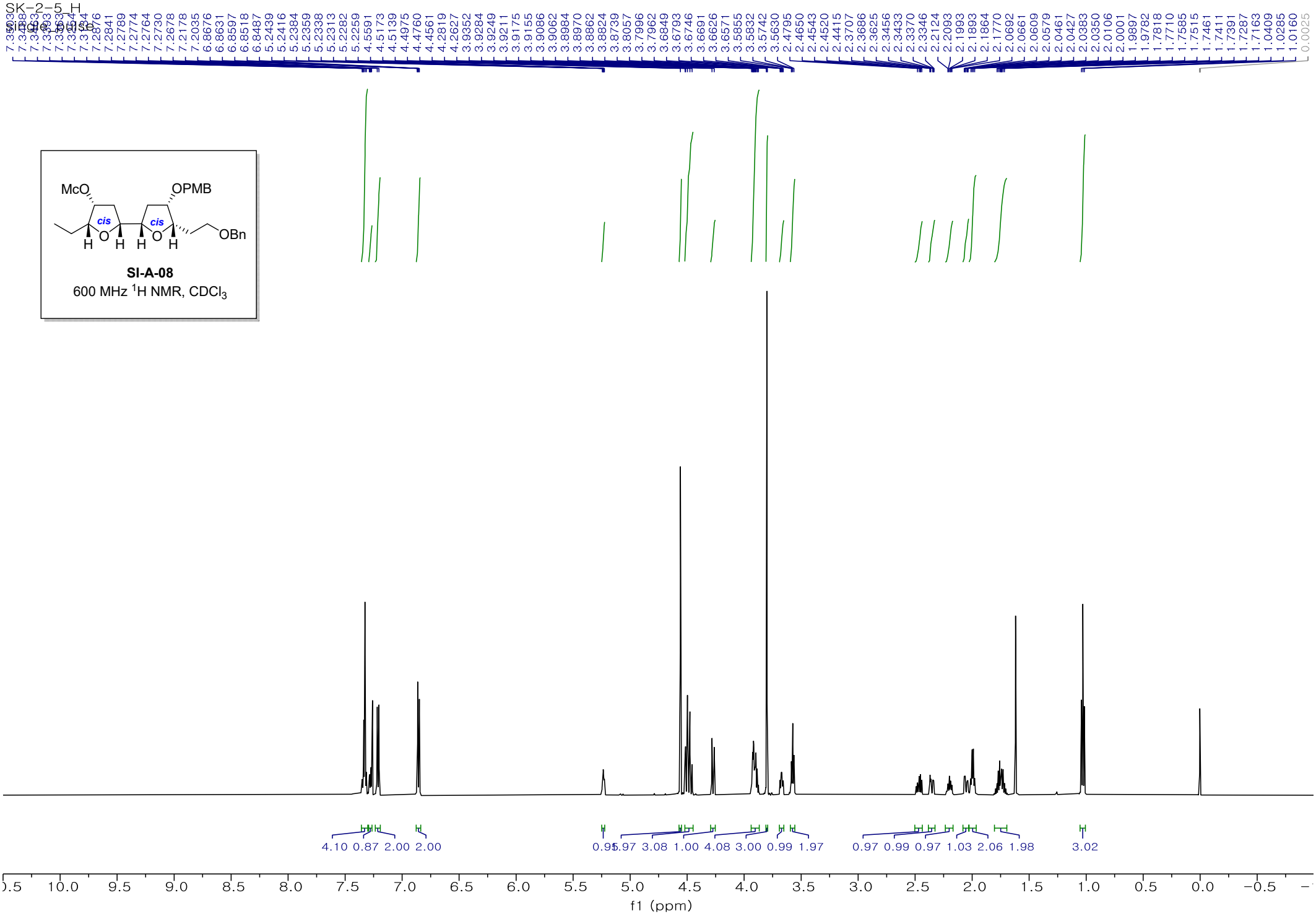


21

150 MHz ^{13}C NMR, $CDCl_3$

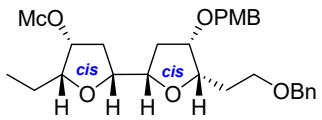



HO
OPMB
cis
anti
cis
cis
cis
cis
OBn
21
150 MHz 13C NMR, CDCl3
7
12
6
10
9
4
13
Elatenyne_21_noesy
phase sensitive noesy
8
14
5
5
11β
8
11α
4
13
9
6
10
7
12
4.20
4.15
4.10
4.05
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
3.40
f2 (ppm)
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
f1 (ppm)

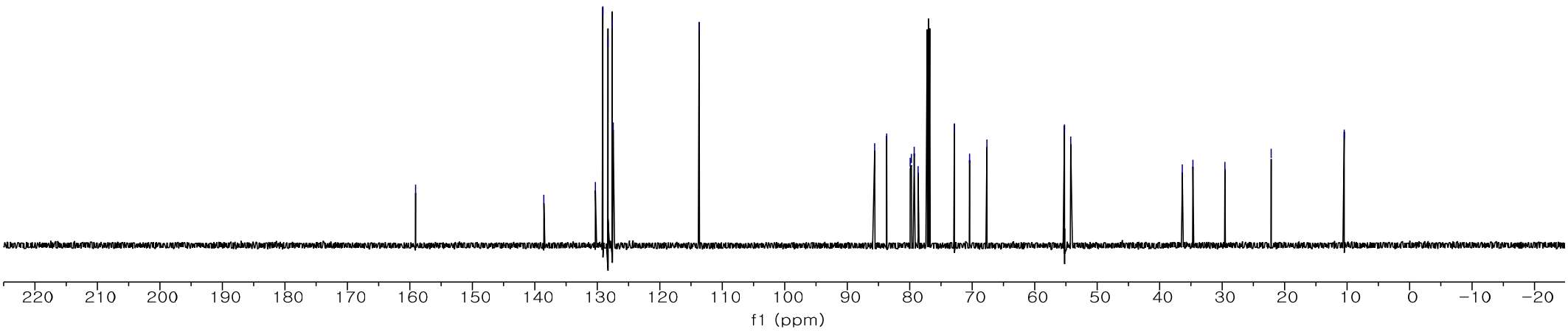

SK-2-5_H
McO
OPMB
cis
cis
OBn
SI-A-08
600 MHz 1H NMR, CDCl3
4.10 0.87 2.00 2.00
0.95 5.97 3.08 1.00 4.08 3.00 0.99 1.97
0.97 0.99 0.97 1.03 2.06 1.98
3.02
f1 (ppm)

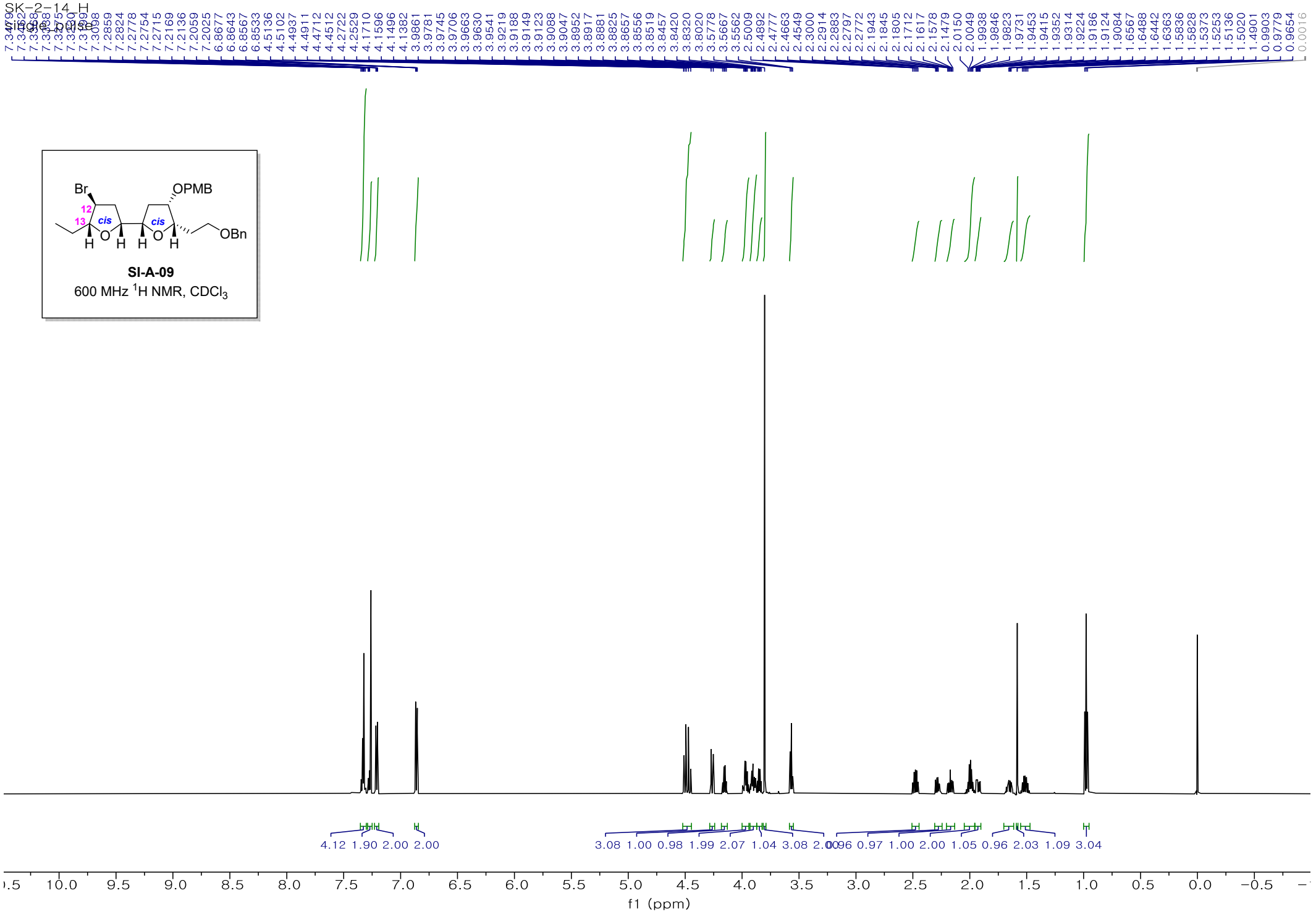
SK-2-4-C
single pulse decoupled gated NOE

159.0849
138.5527
130.3079
129.1103
128.2931
127.6019
127.4588
113.6949
85.6128
83.6775
79.9227
79.7311
79.2783
78.6504
72.8484
70.4228
67.6450
55.2284
54.2315
36.3807
34.6835
29.5625
22.1582
10.4567



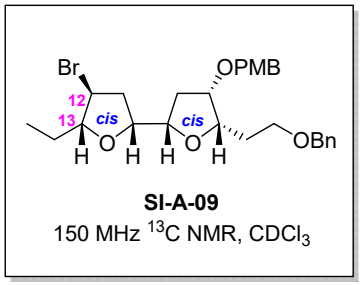
SI-A-08
150 MHz ^{13}C NMR, $CDCl_3$



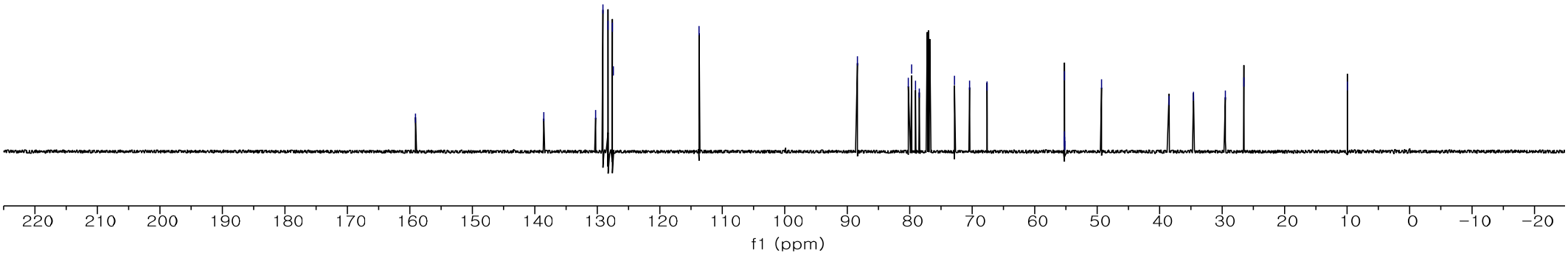

SK-2-14_H
CDCl3
Br
OPMB
12
13
cis
cis
O
H
H
H
O
H
OBn
SI-A-09
600 MHz 1H NMR, CDCl3
4.12 1.90 2.00 2.00
3.08 1.00 0.98 1.99 2.07 1.04 3.08 2.00
0.96 0.97 1.00 2.00 1.05 0.96 2.03 1.09 3.04
f1 (ppm)

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

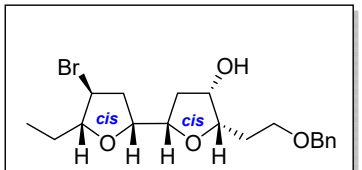
159.0877
138.5597
130.2630
129.0970
128.2803
127.5858
127.4394
113.7116
88.3697
80.2163
79.6905
79.0677
78.4707
72.8379
70.4131
67.6229
55.2558
55.2466
55.2364
55.2244
55.2102
55.1999
55.1901
49.3082
38.4877
34.5898
29.4906
26.5140
9.9512



SI-A-09
150 MHz ^{13}C NMR, $CDCl_3$



SK-1-17_H
single_pulse

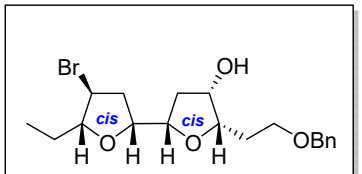


SI-A-10

600 MHz ^{1}H NMR, $CDCl_3$

SK-1-17_C
single pulse decoupled gated NOE

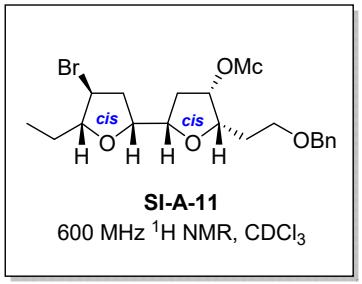
188.0391
138.1365
128.3929
127.6606
127.6388
88.8364
81.8889
79.2310
78.1937
73.1416
71.5943
67.4228
48.3598
38.5621
35.4483
29.1761
26.3993
10.1207



SI-A-10
150 MHz ^{13}C NMR, $CDCl_3$

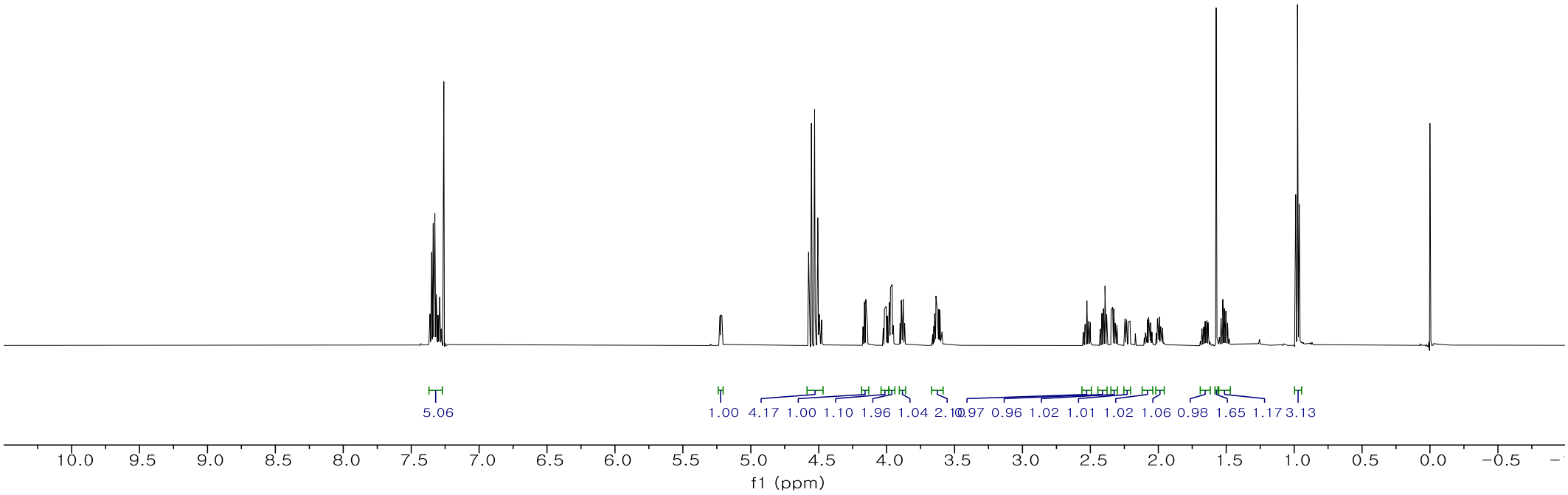
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

SK-2-18_H
single_pulse



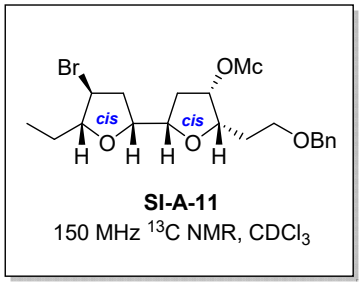
SI-A-11

600 MHz ^{1}H NMR, $CDCl_3$

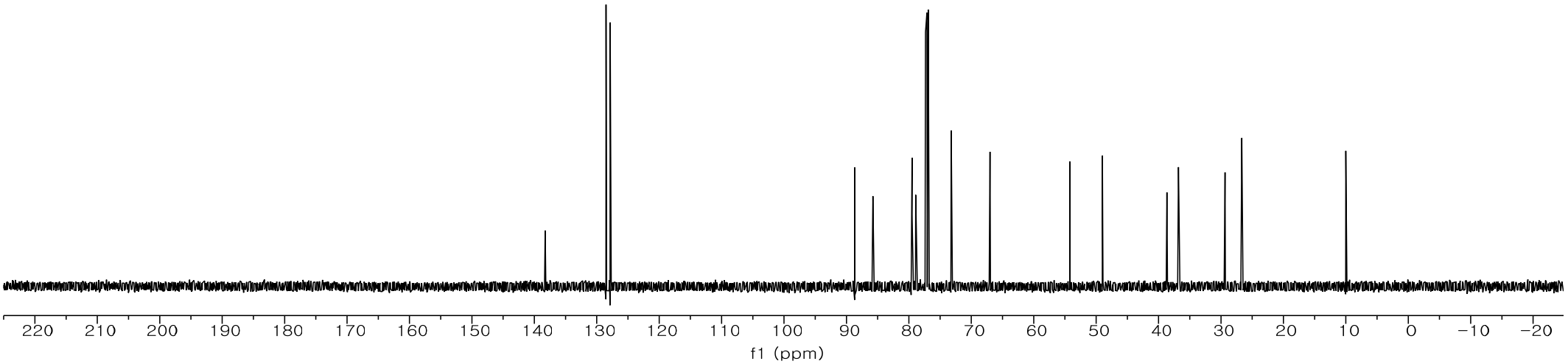


SK-2-18_C
single pulse decoupled gated NOE

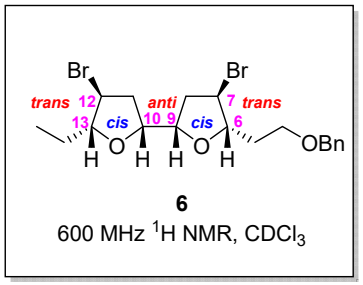
138.2982
128.5185
127.8535
127.8077
88.6855
85.7514
79.6227
79.4856
78.8966
73.2243
67.0111
54.2150
48.9970
38.6612
36.8226
29.3494
26.6735
10.0048



SI-A-11
150 MHz ^{13}C NMR, $CDCl_3$



SK-2-19_H
single_pulse

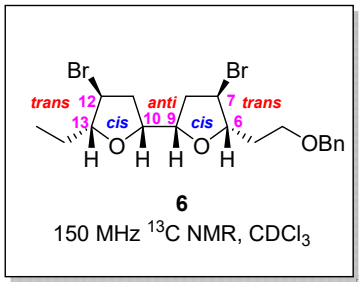


6

600 MHz ^{1}H NMR, $CDCl_3$

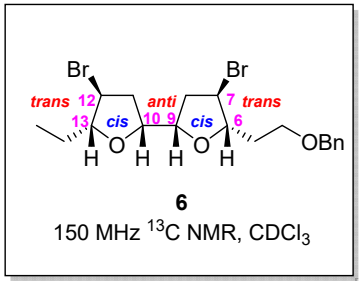
SK-2-19_C
single pulse decoupled gated NOE

138.4070
128.4834
127.7542
127.6941
90.1597
88.7676
85.1141
79.5907
79.3688
77.3357
77.1246
76.9133
73.1550
66.8250
49.6383
48.9444
39.0670
38.7321
34.0064
26.7964
10.0870



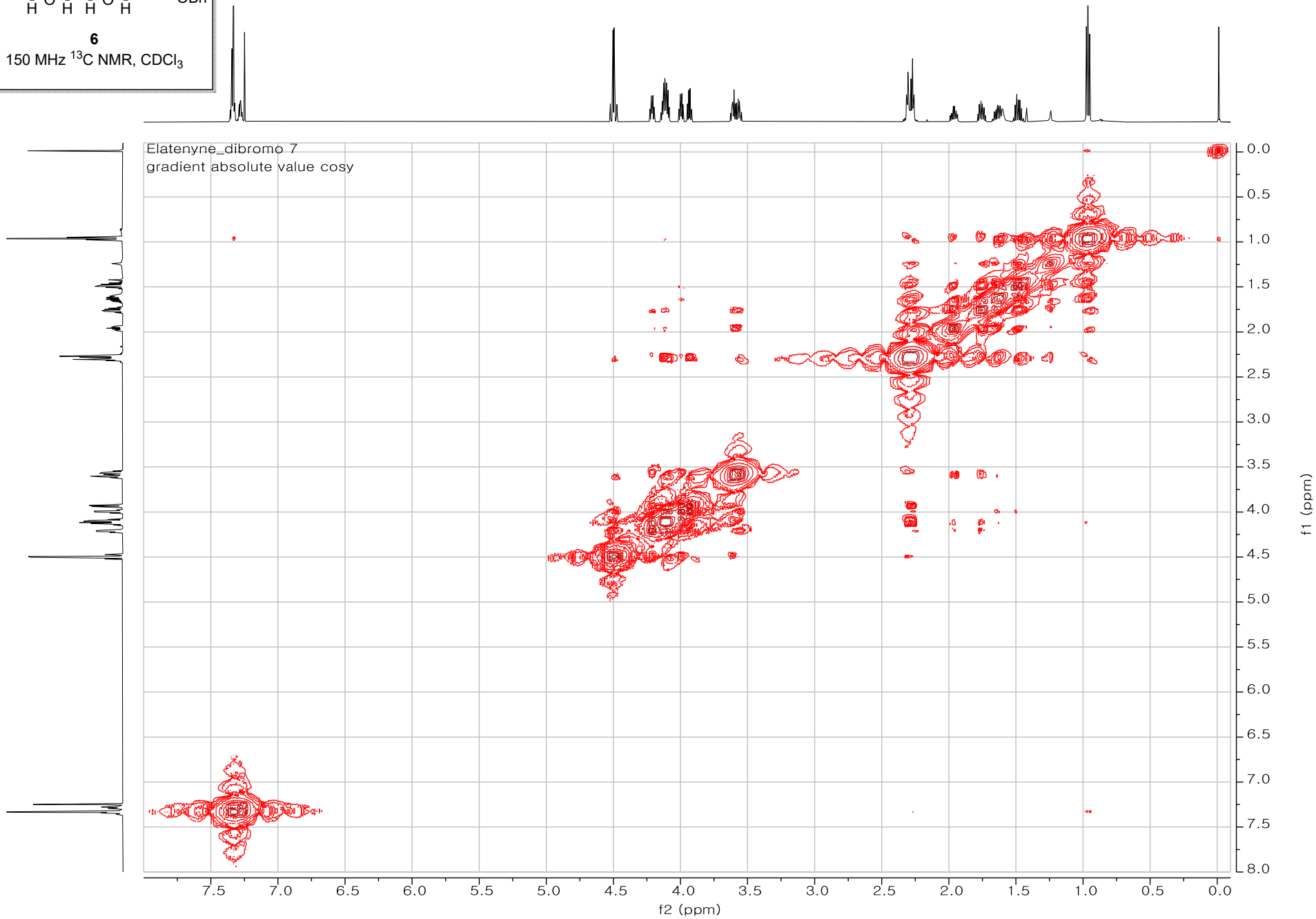
6
150 MHz ^{13}C NMR, $CDCl_3$

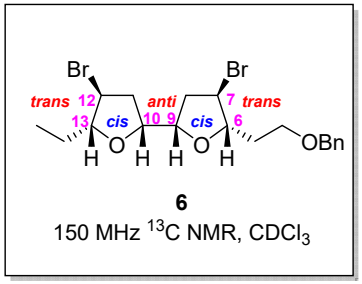
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)



6

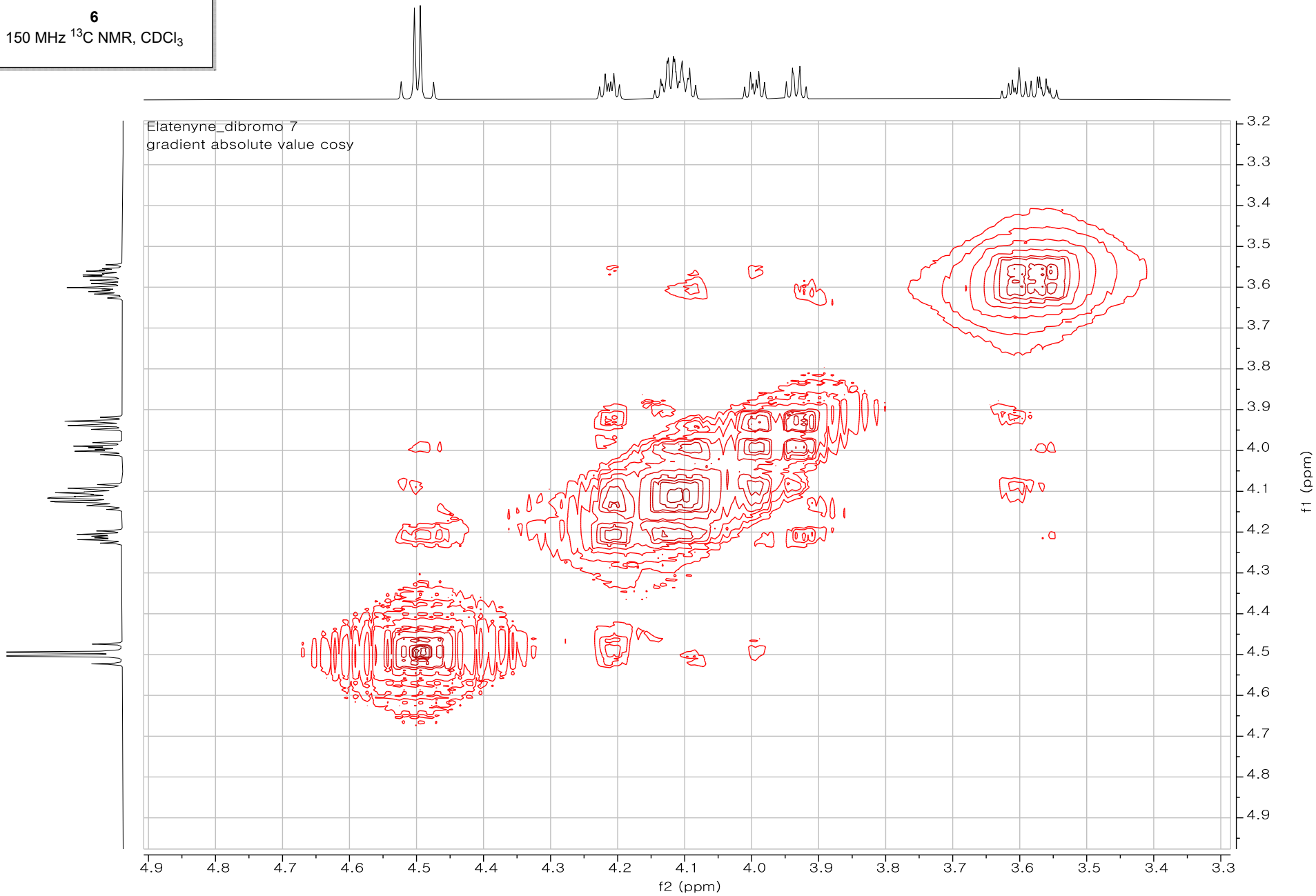
150 MHz ^{13}C NMR, $CDCl_3$

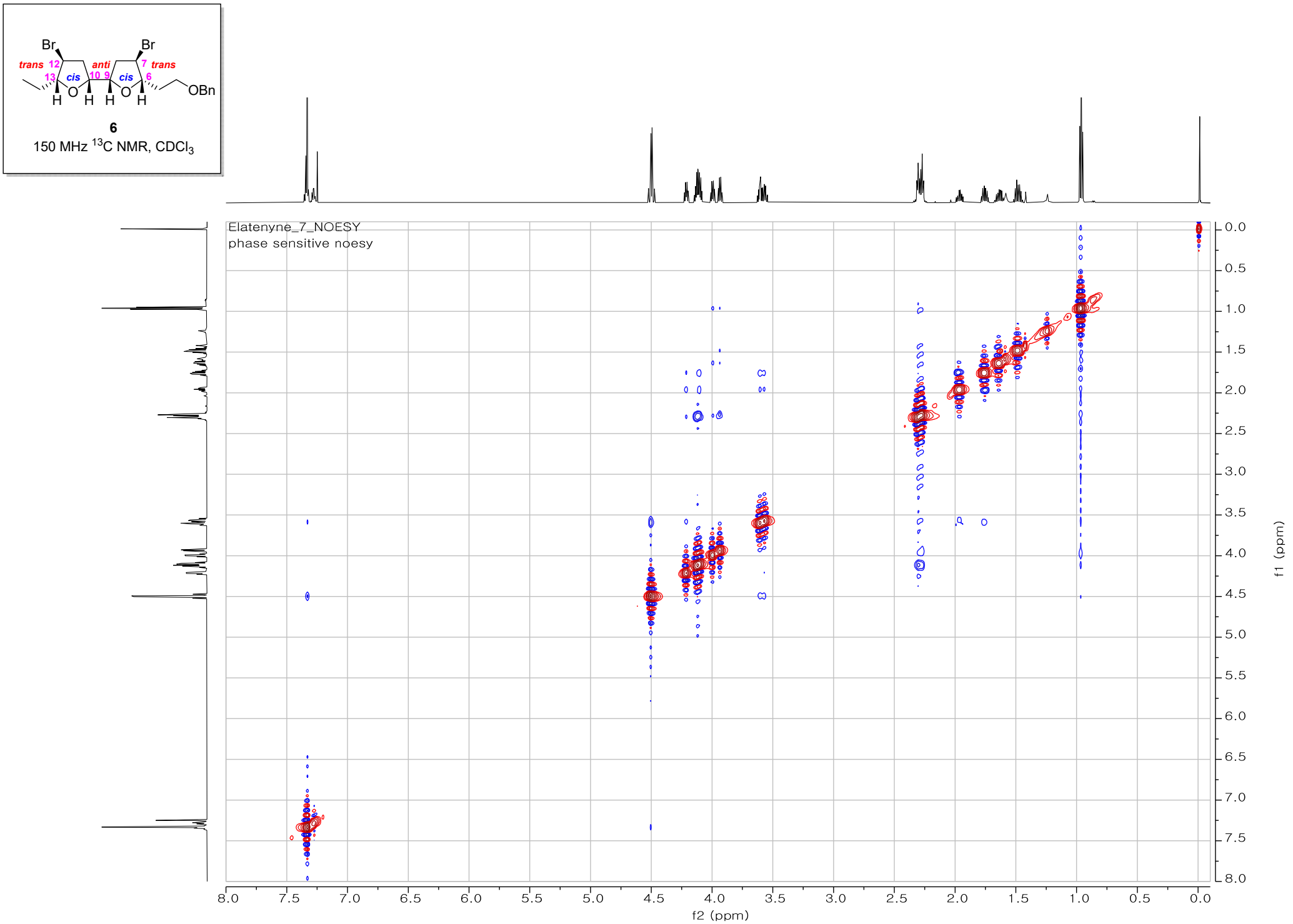


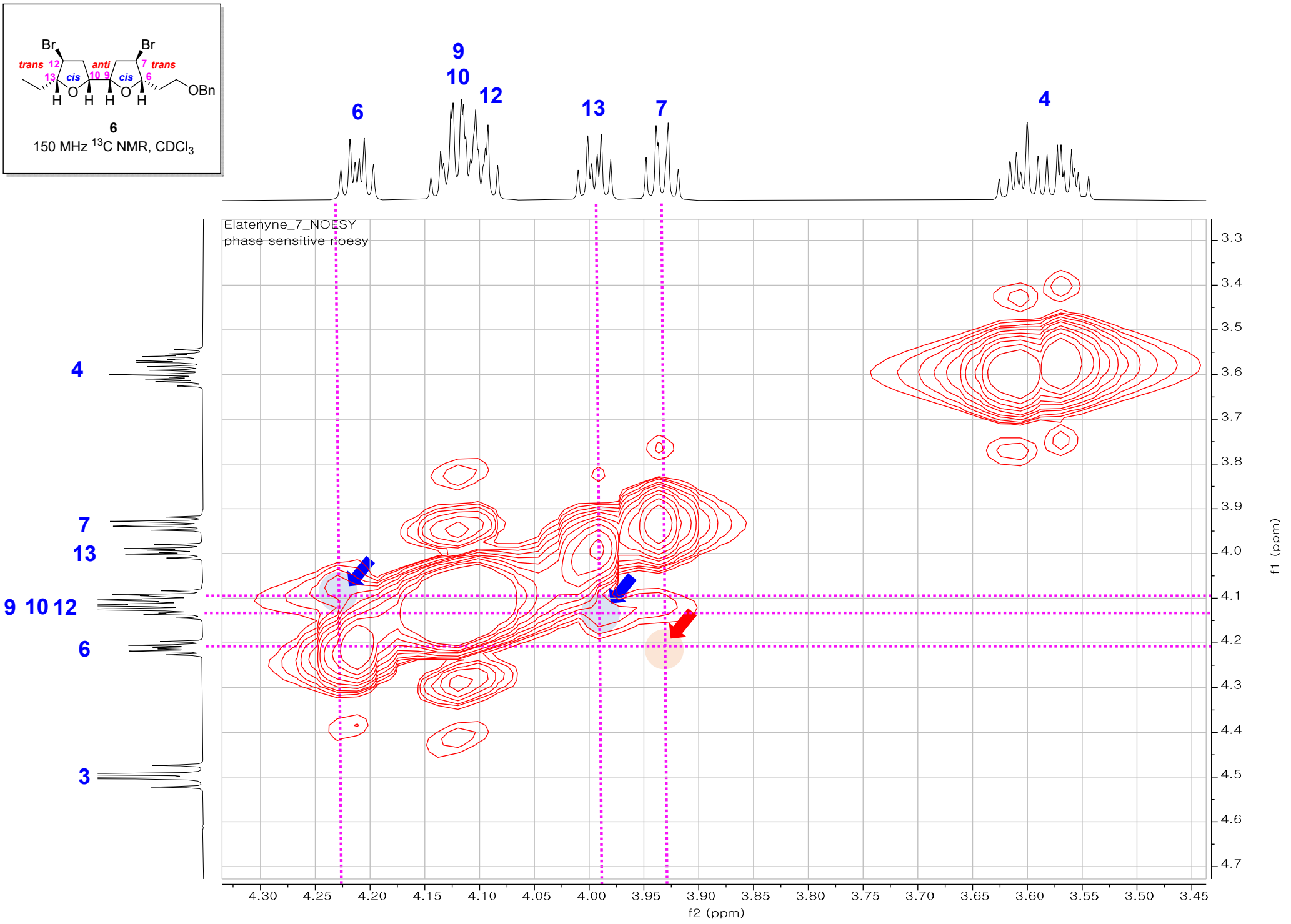


6

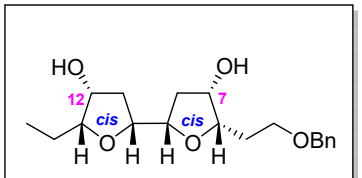
150 MHz ^{13}C NMR, $CDCl_3$



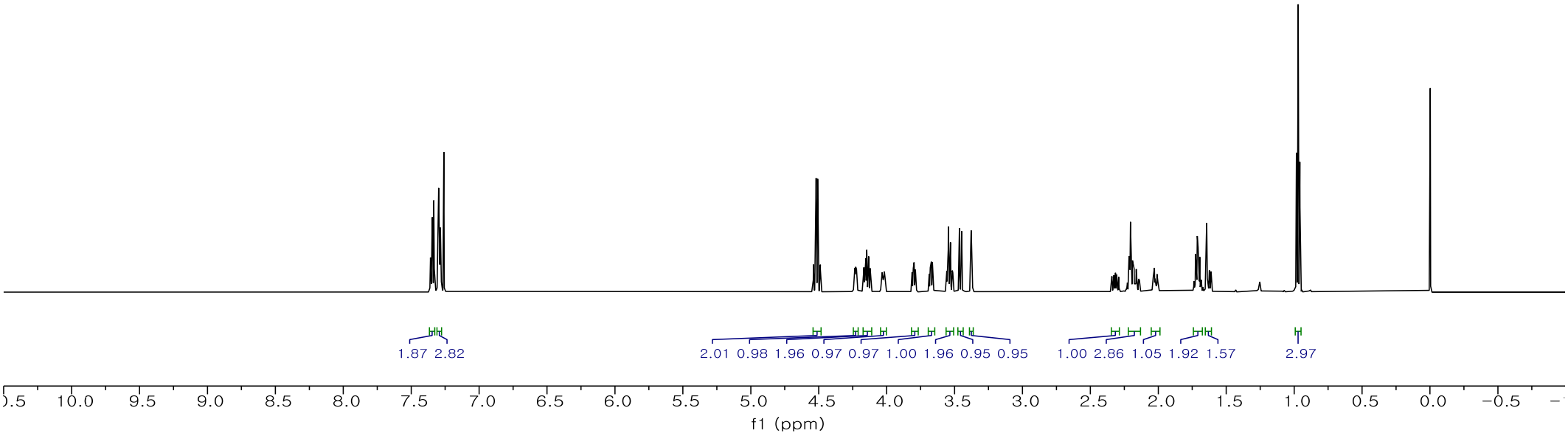

Br
Br
trans 12
anti
7 trans
13
cis
10 9
cis
6
H
O
H
H
O
H
OBn
6
150 MHz 13C NMR, CDCl3
Elatenyne_7_NOESY
phase sensitive noesy
f2 (ppm)
f1 (ppm)


Br
Br
trans 12
anti
7 trans
13
cis
10 9
cis
6
H
O
H
H
O
H
OBn
6
150 MHz 13C NMR, CDCl3
9
10
12
6
13
7
4
Elatenyne_7_NOESY
phase sensitive noesy
4
7
13
9 10 12
6
3
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
3.90
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
f2 (ppm)
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1
4.2
4.3
4.4
4.5
4.6
4.7
f1 (ppm)

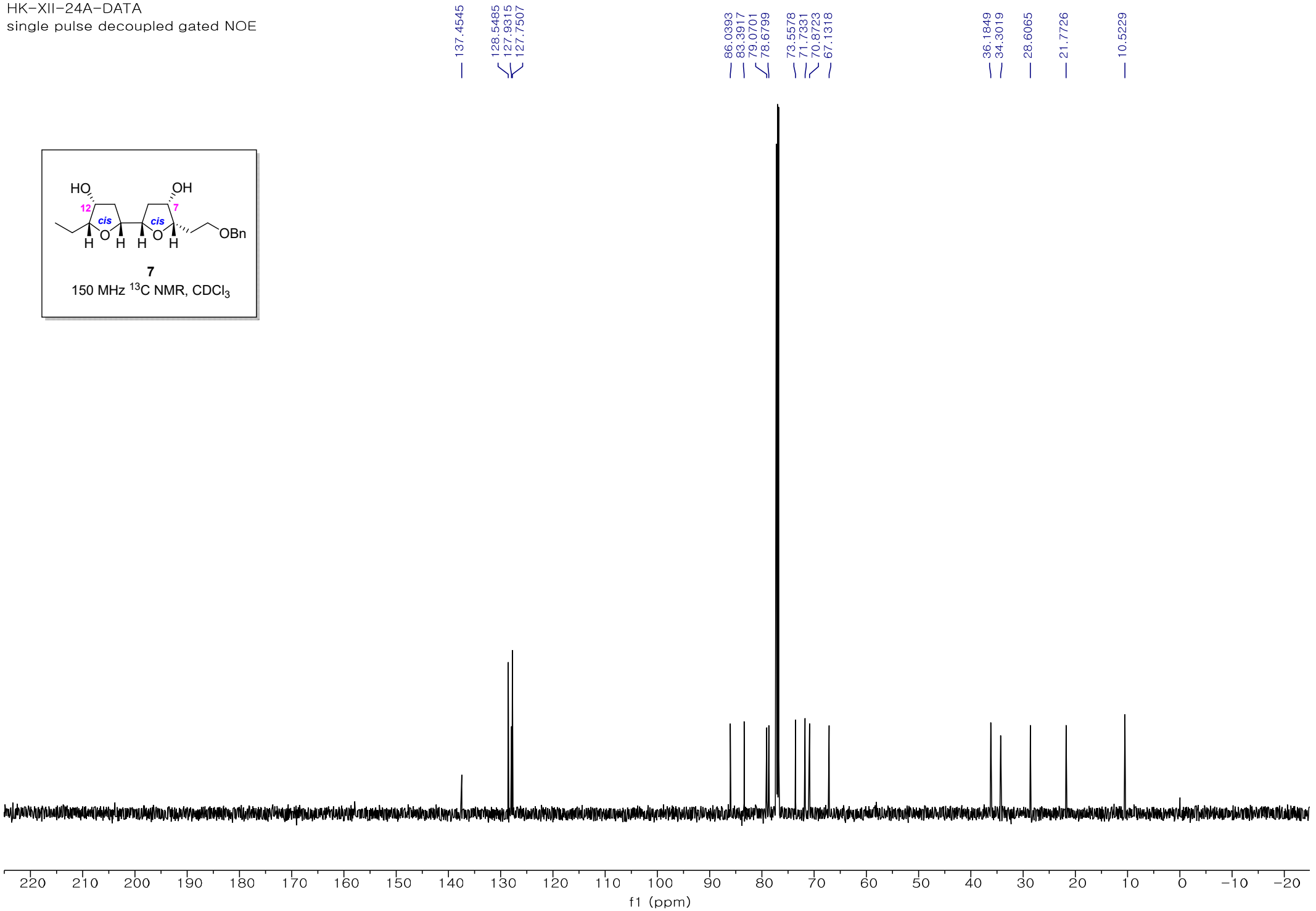
HK-XII-24A-DATA
single pulse



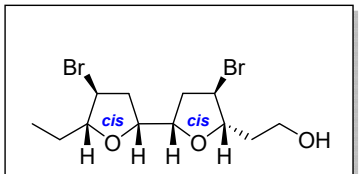
7
600 MHz ^{1}H NMR, $CDCl_3$



HK-XII-24A-DATA
single pulse decoupled gated NOE



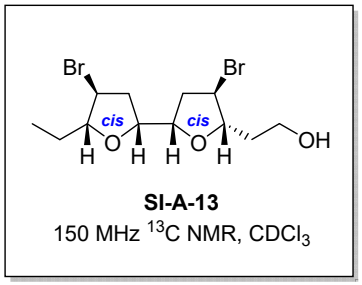
SK-2-21_H
single_pulse



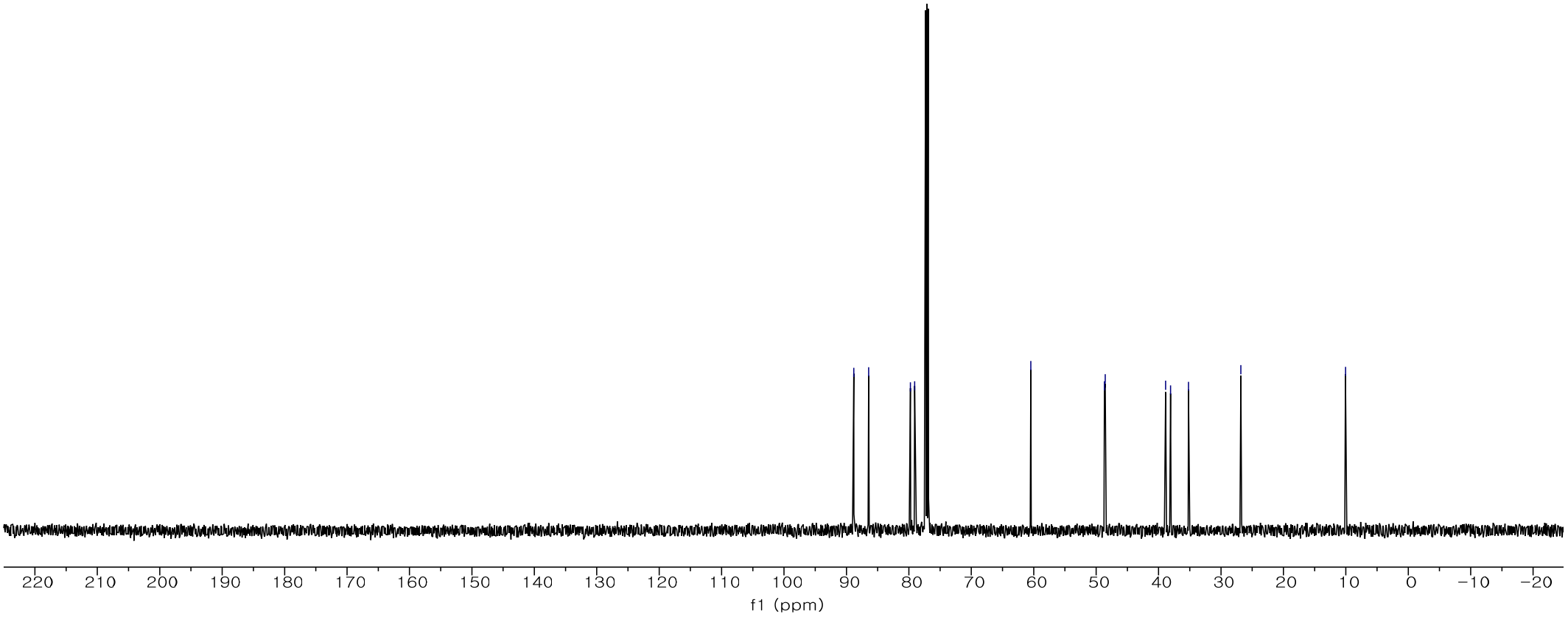
SI-A-13
600 MHz ^{1}H NMR, $CDCl_3$

SK-2-21_C
single pulse decoupled gated NOE

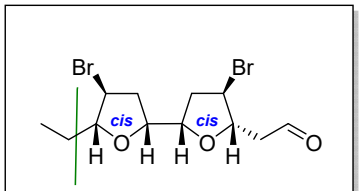
88.8278
86.4409
79.7539
79.0796
60.4733
48.6835
48.5517
38.8782
38.0820
35.2000
26.8124
10.0521



SI-A-13
150 MHz ^{13}C NMR, $CDCl_3$



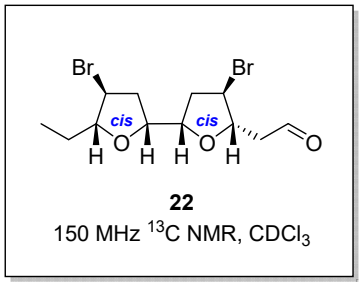
SK-11-102
single pulse



22

600 MHz ^{1}H NMR, $CDCl_3$

SK-11-102
single pulse decoupled gated NOE



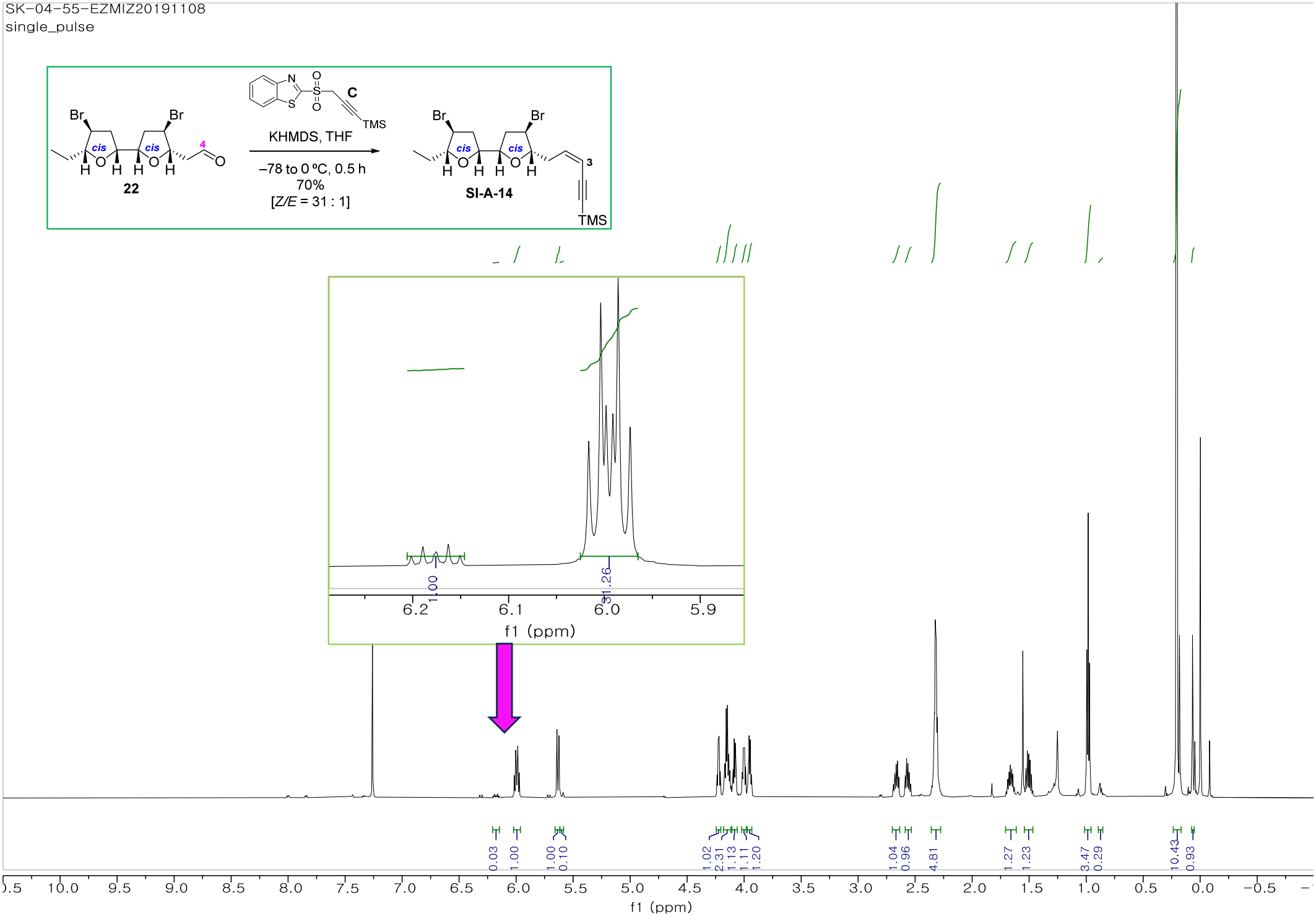
22

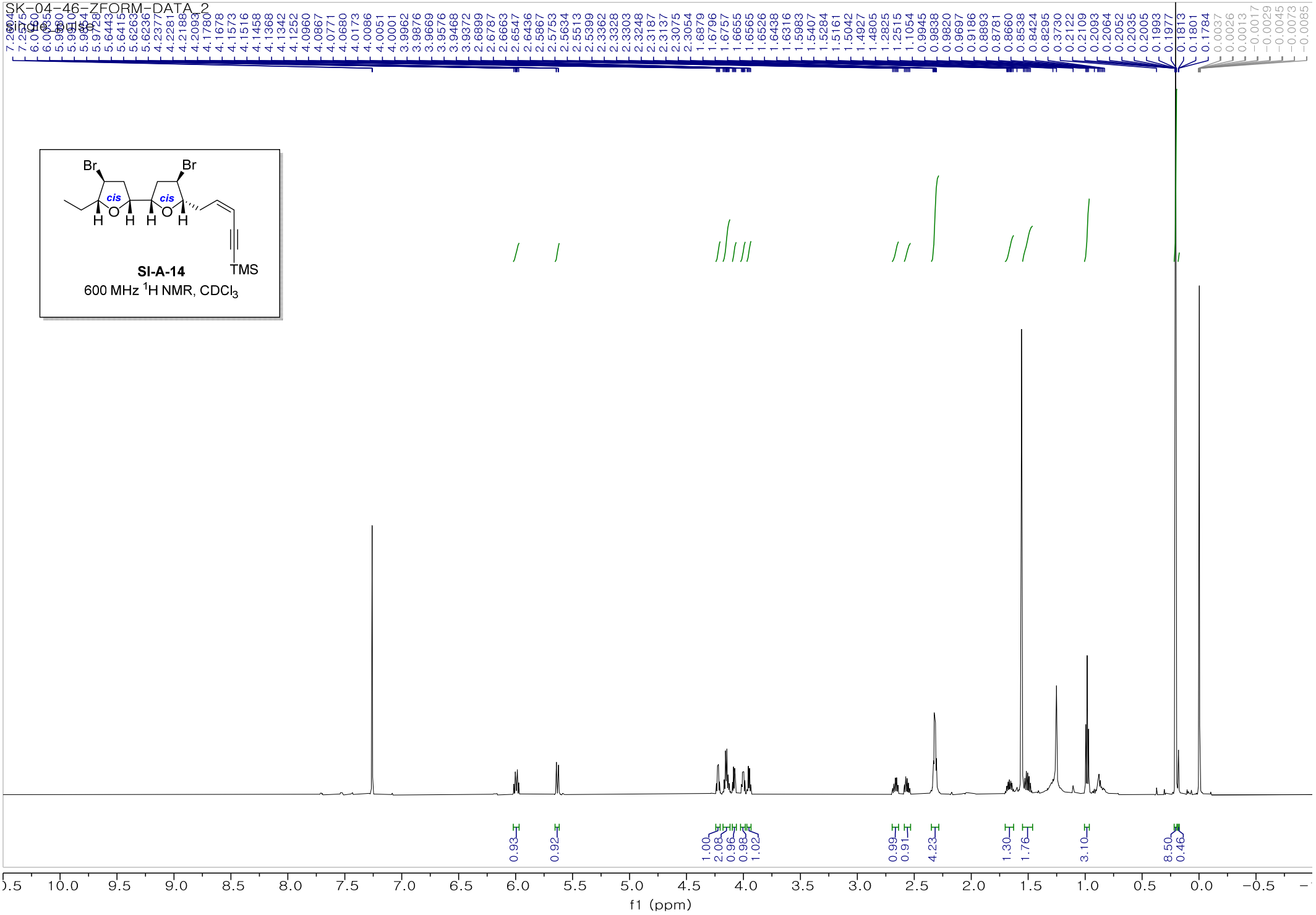
150 MHz ^{13}C NMR, $CDCl_3$

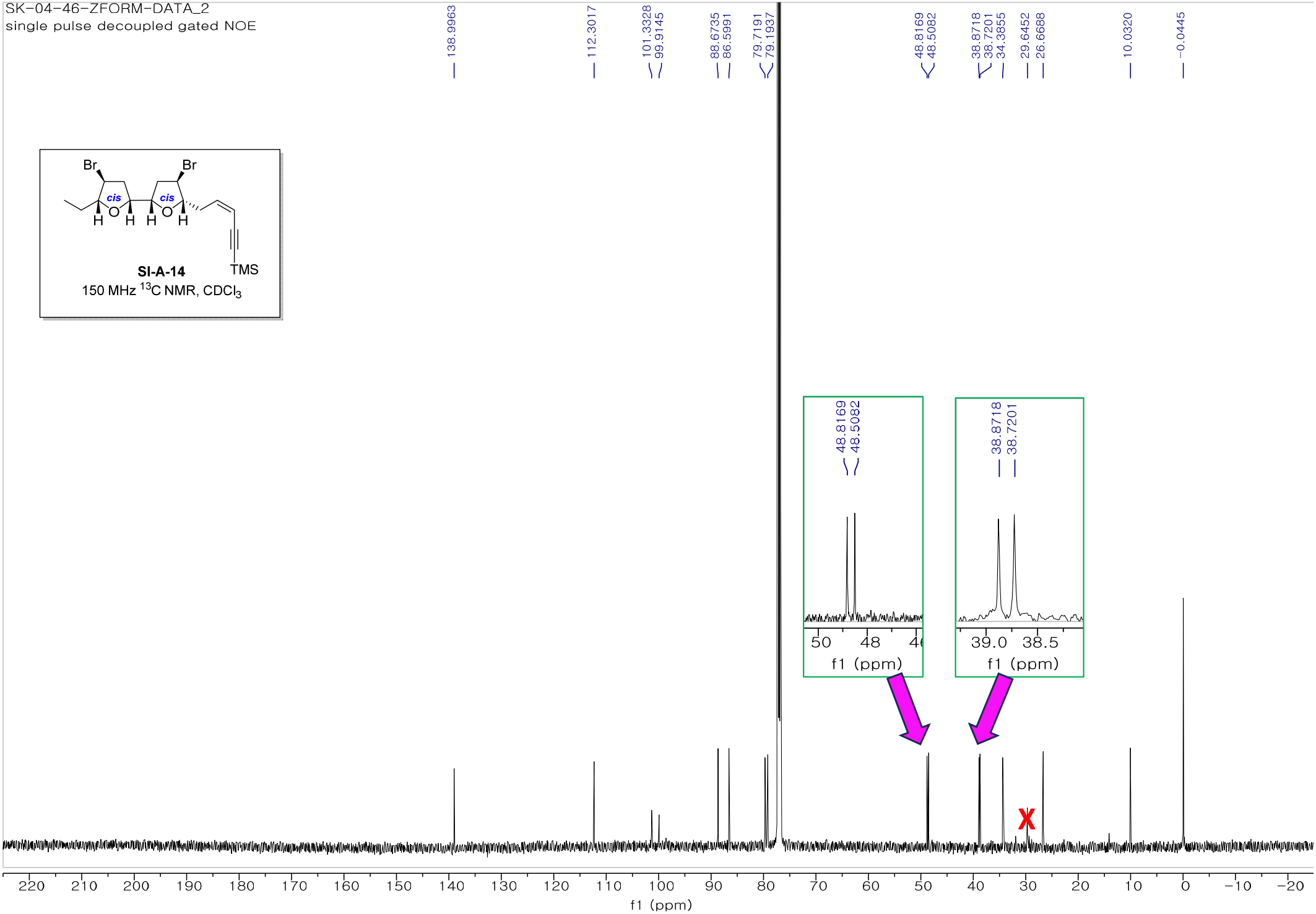
199.4187
88.7879
81.9438
81.8889
79.9284
78.9597
48.5853
47.6162
38.9056
37.8536
26.7314
9.9817

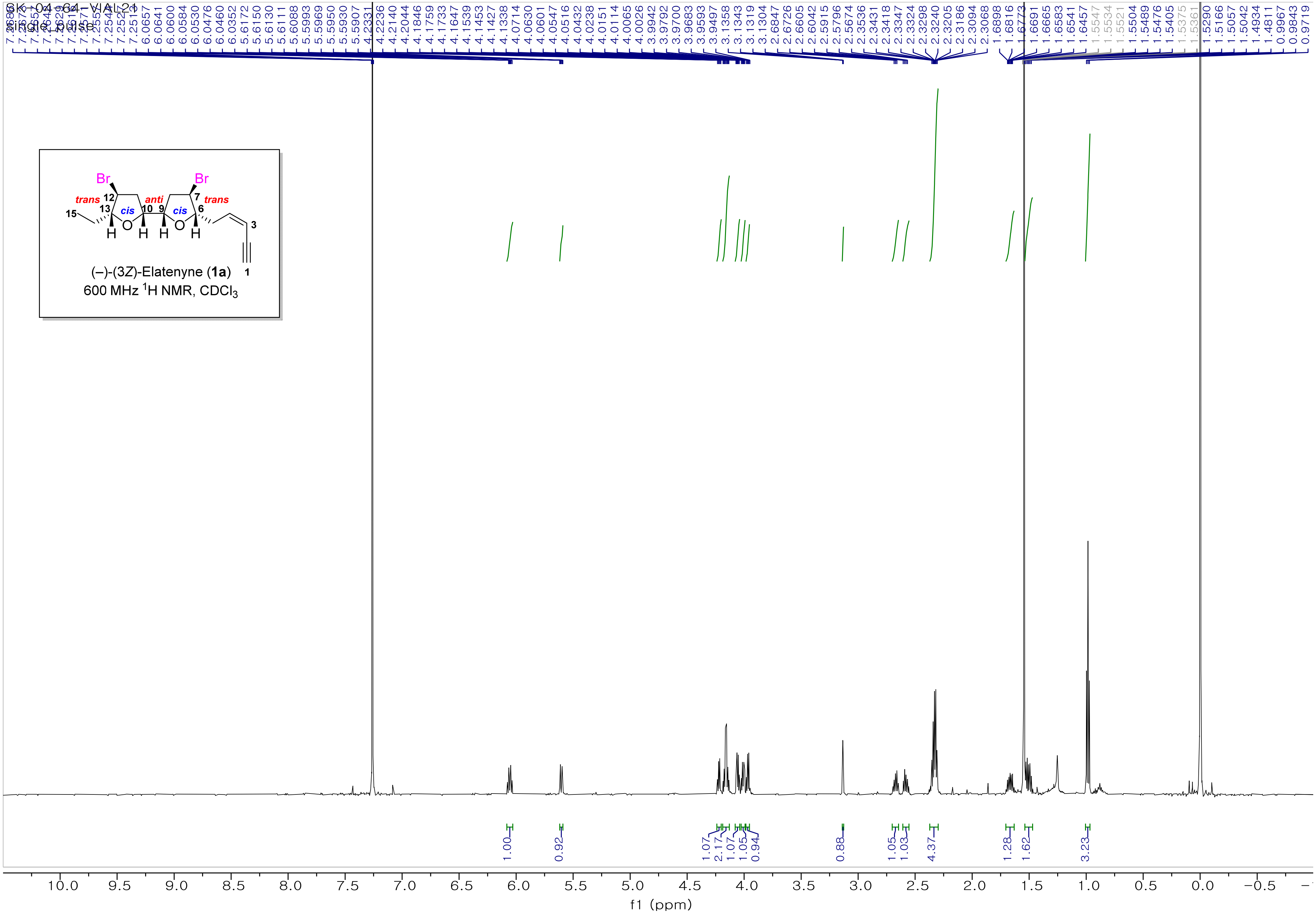
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

f1 (ppm)

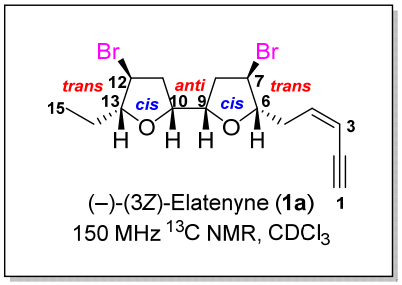

SK-04-55-EZMIZ20191108
single_pulse
Br
Br
cis
cis
4
O
H H H H
22
N
O
S
S
O
C
TMS
KHMDS, THF
–78 to 0 °C, 0.5 h
70%
[Z/E = 31 : 1]
Br
Br
cis
cis
3
H H H H
SI-A-14
TMS
1.00
1.26
6.2
6.1
6.0
5.9
f1 (ppm)
0.03
1.00
1.00
0.10
1.02
2.31
1.13
1.11
1.20
1.04
0.96
4.81
1.27
1.23
3.47
0.29
10.43
0.93
10.0
9.5
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)


SK-04-46-ZFORM-DATA_2
single pulse
Br
Br
cis
cis
H
O
H
H
O
H
TMS
SI-A-14
600 MHz ^{1}H NMR, $CDCl_3$
0.93
0.92
1.00
2.08
0.96
0.98
1.02
0.99
0.91
4.23
1.30
1.76
3.10
8.50
0.46
f1 (ppm)


SK-04-46-ZFORM-DATA_2
single pulse decoupled gated NOE
138.9963
112.3017
101.3328
99.9145
88.6735
86.5991
79.7191
79.1937
48.8169
48.5082
38.8718
38.7201
34.3855
29.6452
26.6688
10.0320
-0.0445
Br
Br
cis
cis
H
O
H
H
O
H
TMS
SI-A-14
150 MHz 13C NMR, CDCl3
48.8169
48.5082
50
48
f1 (ppm)
38.8718
38.7201
39.0
38.5
f1 (ppm)
X
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

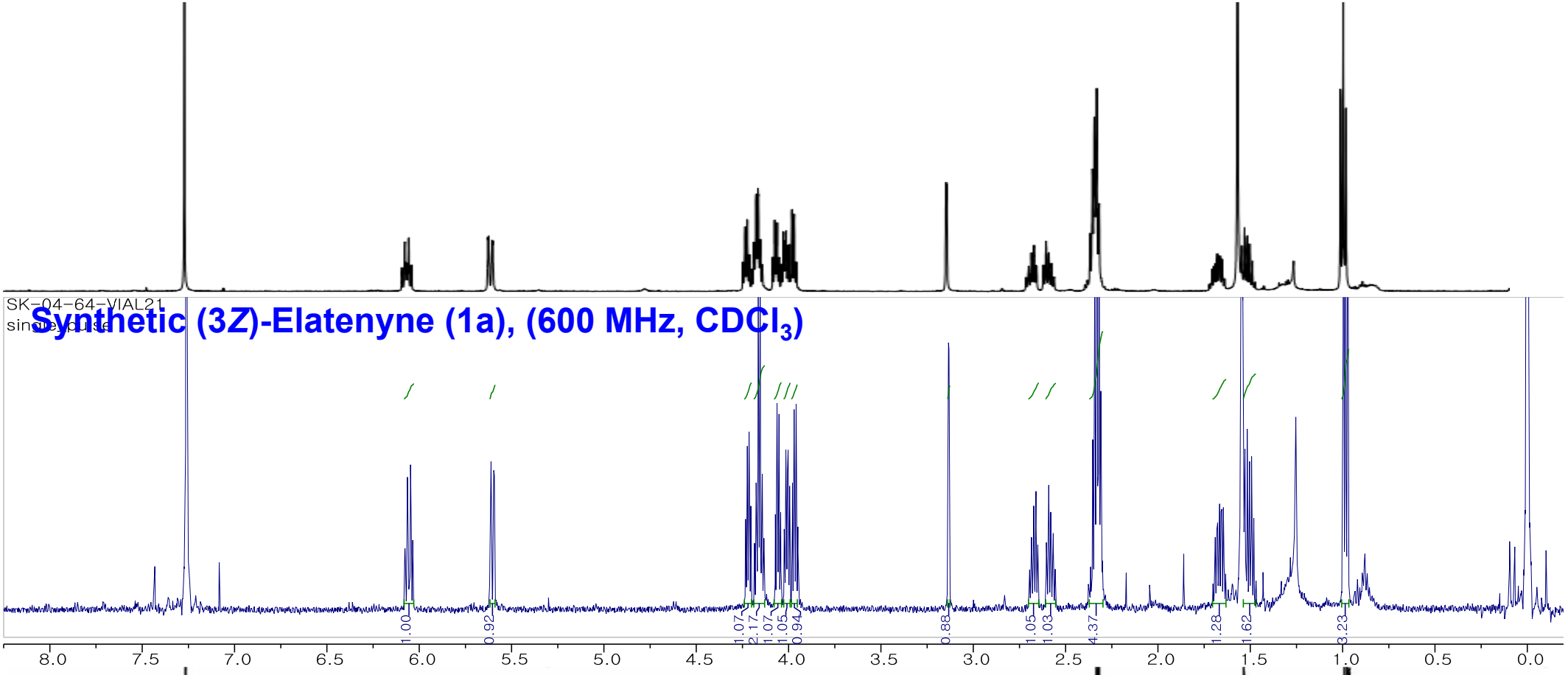

SK-04-64-VIAL21
single_pulse
(–)-(3Z)-Elatenyne (1a)
600 MHz 1H NMR, CDCl3
f1 (ppm)

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

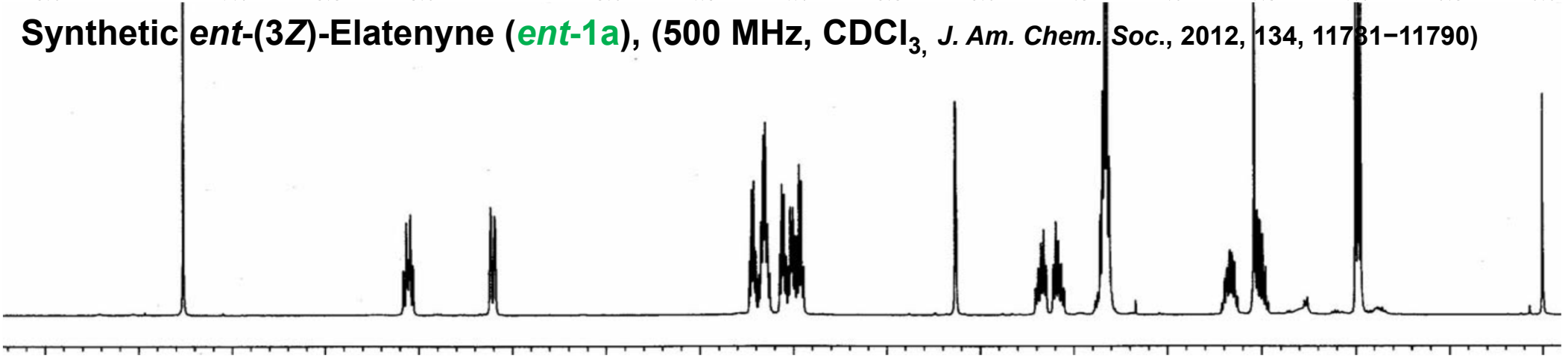


(–)-(3*Z*)-Elatenyne (**1a**)
150 MHz ^{13}C NMR, $CDCl_3$

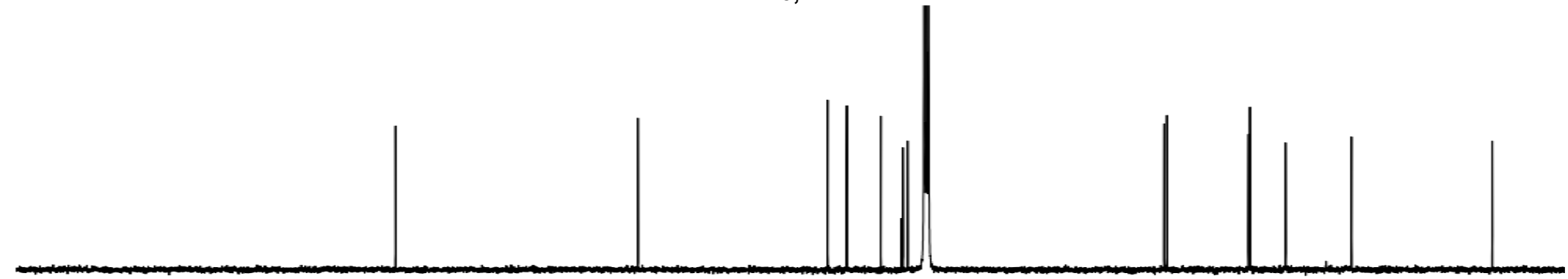
Synthetic (3*Z*)-Elatenyne (1a), (500 MHz, $CDCl_3$, *J. Am. Chem. Soc.*, 2012, 134, 11781−11790)



Synthetic *ent*-(3*Z*)-Elatenyne (*ent*-1a), (500 MHz, $CDCl_3$, *J. Am. Chem. Soc.*, 2012, 134, 11781−11790)

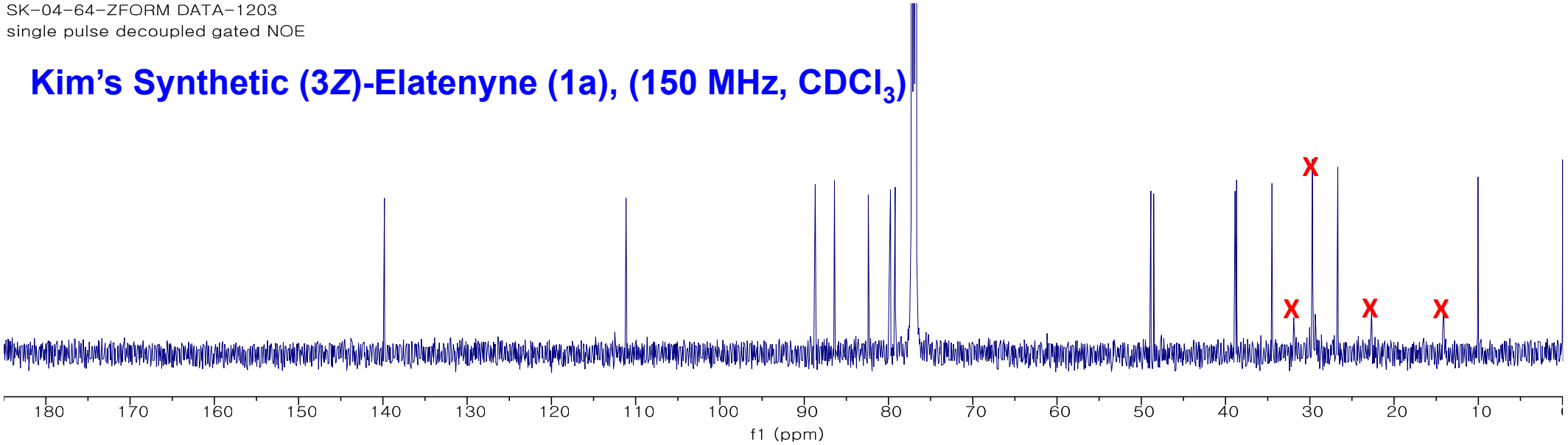


Synthetic (3*Z*)-Elatenyne (1a), (125 MHz, $CDCl_3$, *J. Am. Chem. Soc.*, 2012, 134, 11781−11790)

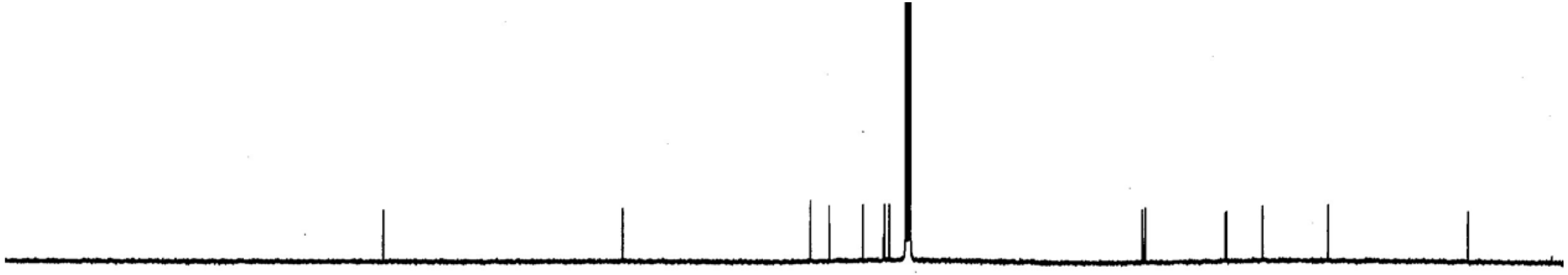


SK−04−64−ZFORM DATA−1203
single pulse decoupled gated NOE

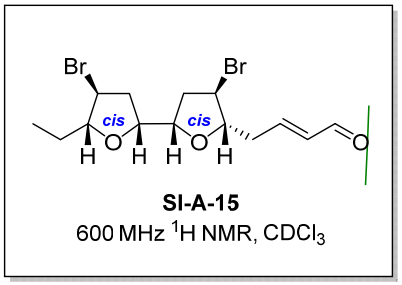
Kim's Synthetic (3*Z*)-Elatenyne (1a), (150 MHz, $CDCl_3$)



Synthetic *ent*-(3*Z*)-Elatenyne (*ent*-1a), (125 MHz, $CDCl_3$, *J. Am. Chem. Soc.*, 2012, 134, 11781−11790)



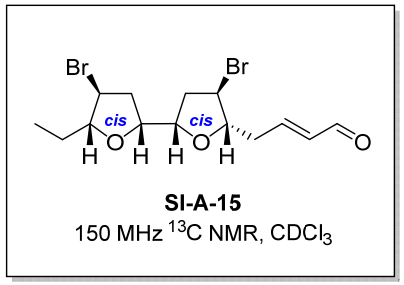
SK-11-105
single_pulse



SI-A-15
600 MHz ^{1}H NMR, $CDCl_3$

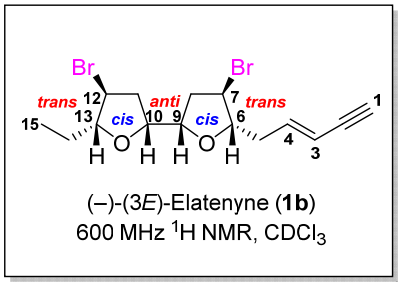
SK-11-105
single pulse decoupled gated NOE

193.2642
152.4940
135.1616
88.7834
85.1093
79.7387
78.9516
48.5528
47.4260
38.9693
37.9898
36.0537
26.7334
9.9858



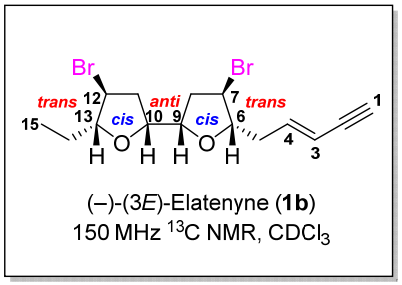
SI-A-15
150 MHz ^{13}C NMR, $CDCl_3$

SK-11-106
single_pulse



(–)-(3*E*)-Elatenyne (**1b**)
600 MHz ^{1}H NMR, $CDCl_3$

SK-11-106
single pulse decoupled gated NOE

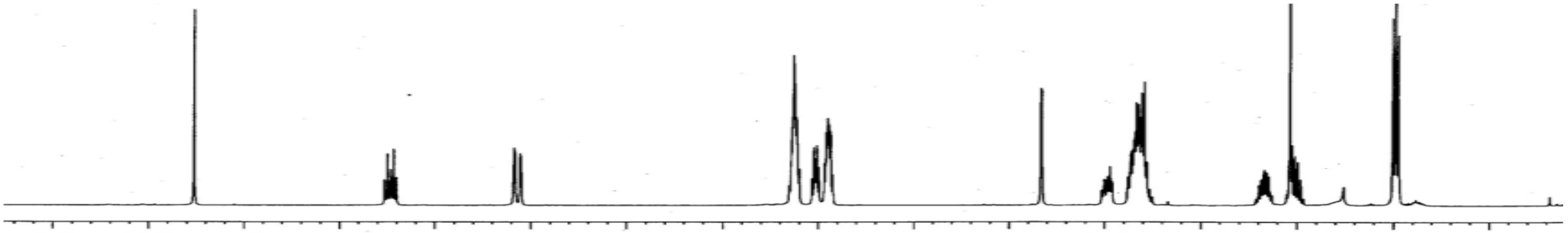


(–)-(3*E*)-Elatenyne (**1b**)
150 MHz ^{13}C NMR, $CDCl_3$

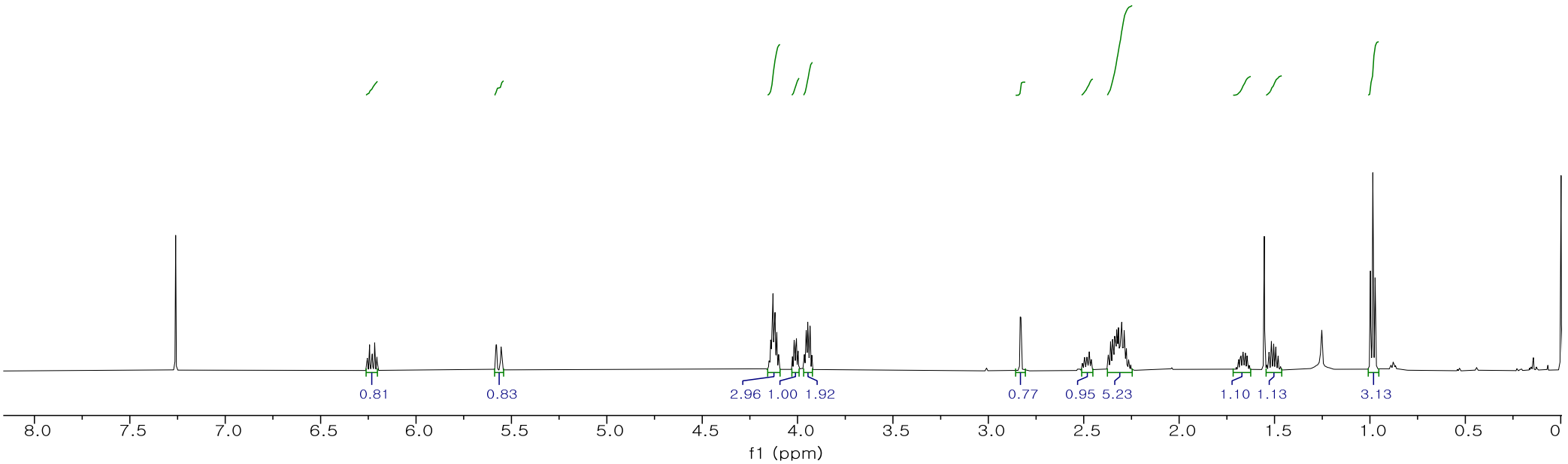
140.6206
111.8611
88.7068
85.9064
81.8340
79.6056
79.0939
77.2116 CHLOROFORM-D
77.0005 CHLOROFORM-D
76.7875 CHLOROFORM-D
76.7492
48.7304
47.7647
38.9054
38.4142
36.5115
26.6872
10.0247
-0.0214

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

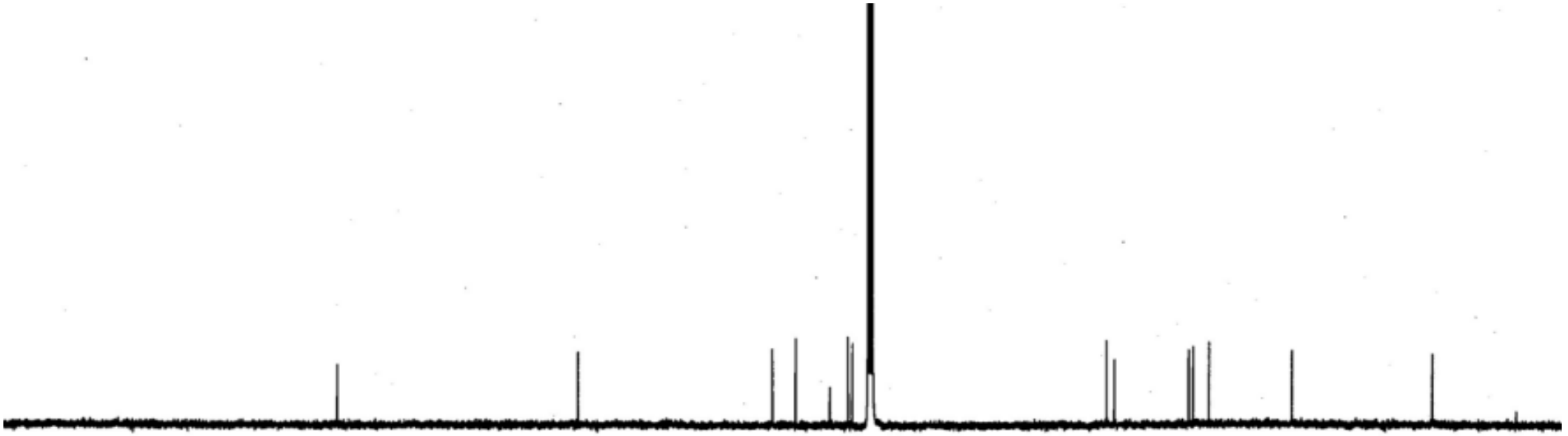
Synthetic *ent*-(*E*)-Elatenyne (*ent*-1b), (500 MHz, $CDCl_3$, *J. Am. Chem. Soc.*, 2012, 134, 11781−11790)



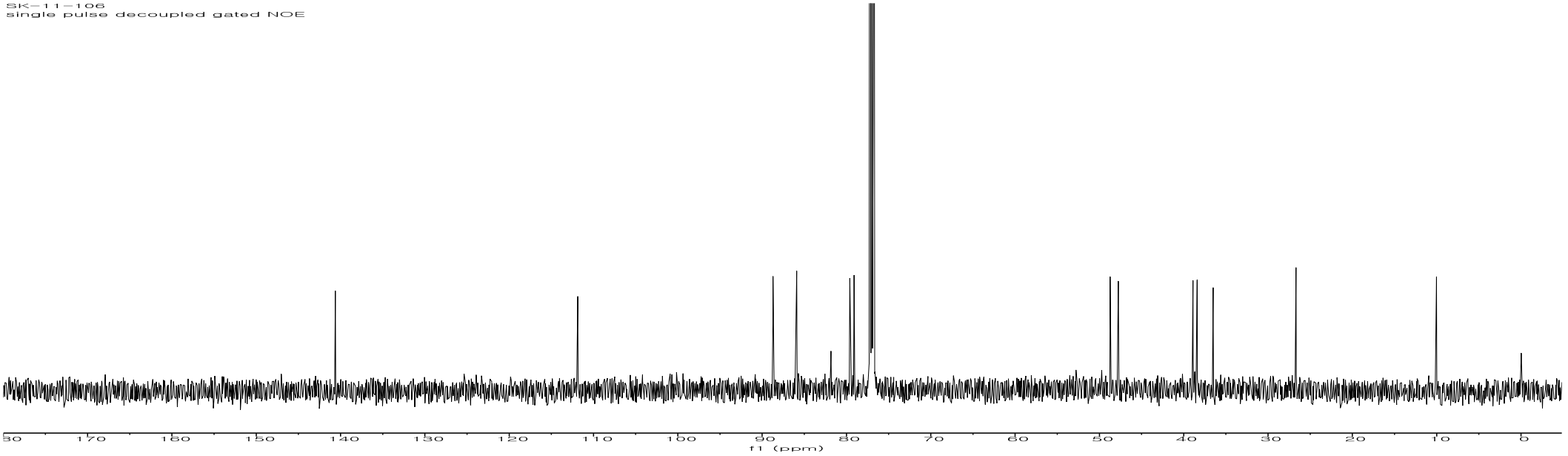
Kim's Synthetic (3*E*)-Elatenyne (1b), (600 MHz, $CDCl_3$)



Synthetic *ent*-(*E*)-Elatenyne (*ent*-1b), (500 MHz, $CDCl_3$, *J. Am. Chem. Soc.*, 2012, 134, 11781−11790)



Kim's Synthetic (3*E*)-Elatenyne (1b), (600 MHz, $CDCl_3$)



– Electronic Supplementary Information: Part C –

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

Soo Yeon Kwak,[a‡] Iljin Shin,[a‡] Hongjun jang,[a] Youngjik Park,[a] Seongju Lim,[a] Dongjoo Lee,[a] Hyoungsu Kim,*[a] and Deukjoon Kim[b]

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[‡]These authors contributed equally to this work.

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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
13	EI	$C_{16}H_{23}NO_4$	$[M]^+$	293.1627	293.1624	S117
14	EI	$C_{16}H_{24}BrNO_4$	$[M]^+$	373.0889	373.0884	S118
11	EI	$C_{24}H_{32}BrNO_5$	$[M]^+$	493.1464	493.1462	S119
10	EI	$C_{24}H_{31}NO_5$	$[M]^+$	413.2202	413.2205	S120
15	EI	$C_{25}H_{44}BrNO_4Si$	$[M]^+$	529.2223	529.2225	S121
16	EI	$C_{25}H_{43}NO_4Si$	$[M]^+$	449.2961	449.2961	S122
SI-A-03	EI	$C_{16}H_{23}NO_4$	$[M]^+$	293.1627	293.1624	S123
17	EI	$C_{24}H_{31}NO_5$	$[M]^+$	413.2202	413.2202	S124
9	EI	$C_{25}H_{32}O_5$	$[M]^+$	412.2250	412.2242	S125
SI-A-04	FAB	$C_{25}H_{33}O_5$	$[M+H]^+$	413.2328	413.2328	S126
(*S*)-MTPA-SI-A-05	FAB	$C_{35}H_{40}F_3O_7$	$[M+H]^+$	629.2726	629.2719	S127
(*R*)-MTPA-SI-A-06	FAB	$C_{35}H_{40}F_3O_7$	$[M+H]^+$	629.2726	629.2722	S128
20	EI	$C_{27}H_{36}O_5$	$[M]^+$	440.2563	440.2558	S129
SI-A-07	EI	$C_{34}H_{42}O_7S$	$[M]^+$	594.2651	594.2654	S130
8	FAB	$C_{34}H_{45}O_9S$	$[M+H]^+$	629.2784	629.2787	S131
21	EI	$C_{27}H_{36}O_6$	$[M]^+$	456.2512	456.2510	S132
SI-A-09	EI	$C_{27}H_{35}BrO_5$	$[M]^+$	518.1668	518.1669	S133
SI-A-10	EI	$C_{19}H_{27}BrO_4$	$[M]^+$	398.1093	398.1094	S134
6	EI	$C_{19}H_{26}Br_2O_3$	$[M]^+$	460.0249	460.0243	S135
7	FAB	$C_{19}H_{29}O_5$	$[M+H]^+$	337.2015	337.2017	S136
SI-A-13	FAB	$C_{12}H_{21}Br_2O_3$	$[M+H]^+$	370.9857	370.9854	S137

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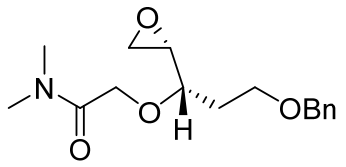
Compound	Mode	Formula	m/z	Calculated	Observed	Page
SI-A-14	EI	$C_{18}H_{28}Br_2O_2Si$	$[M]^+$	462.0225	462.0219	S138
(3*Z*)-Elatenyne (1a)	EI	$C_{15}H_{20}Br_2O_2$	$[M]^+$	389.9830	389.9825	S139
(3*E*)-Elatenyne (1a)	EI	$C_{15}H_{20}Br_2O_2$	$[M]^+$	389.9830	389.9834	S140



13

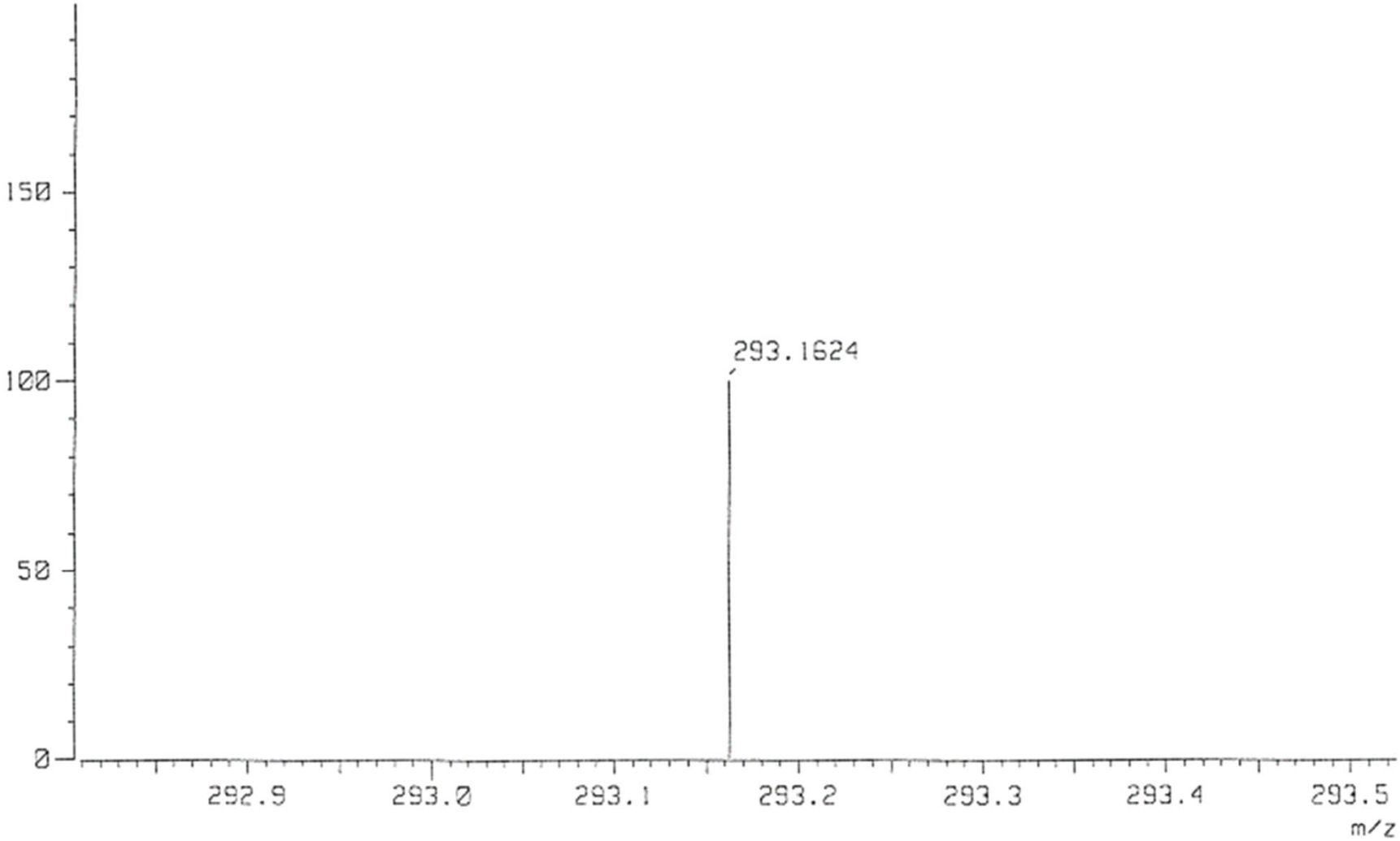
Chemical Formula: $C_{16}H_{23}NO_4$

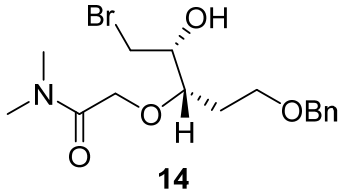
Exact Mass: 293.1627

$[M]^+$ Calcd for $C_{16}H_{23}NO_4$ 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

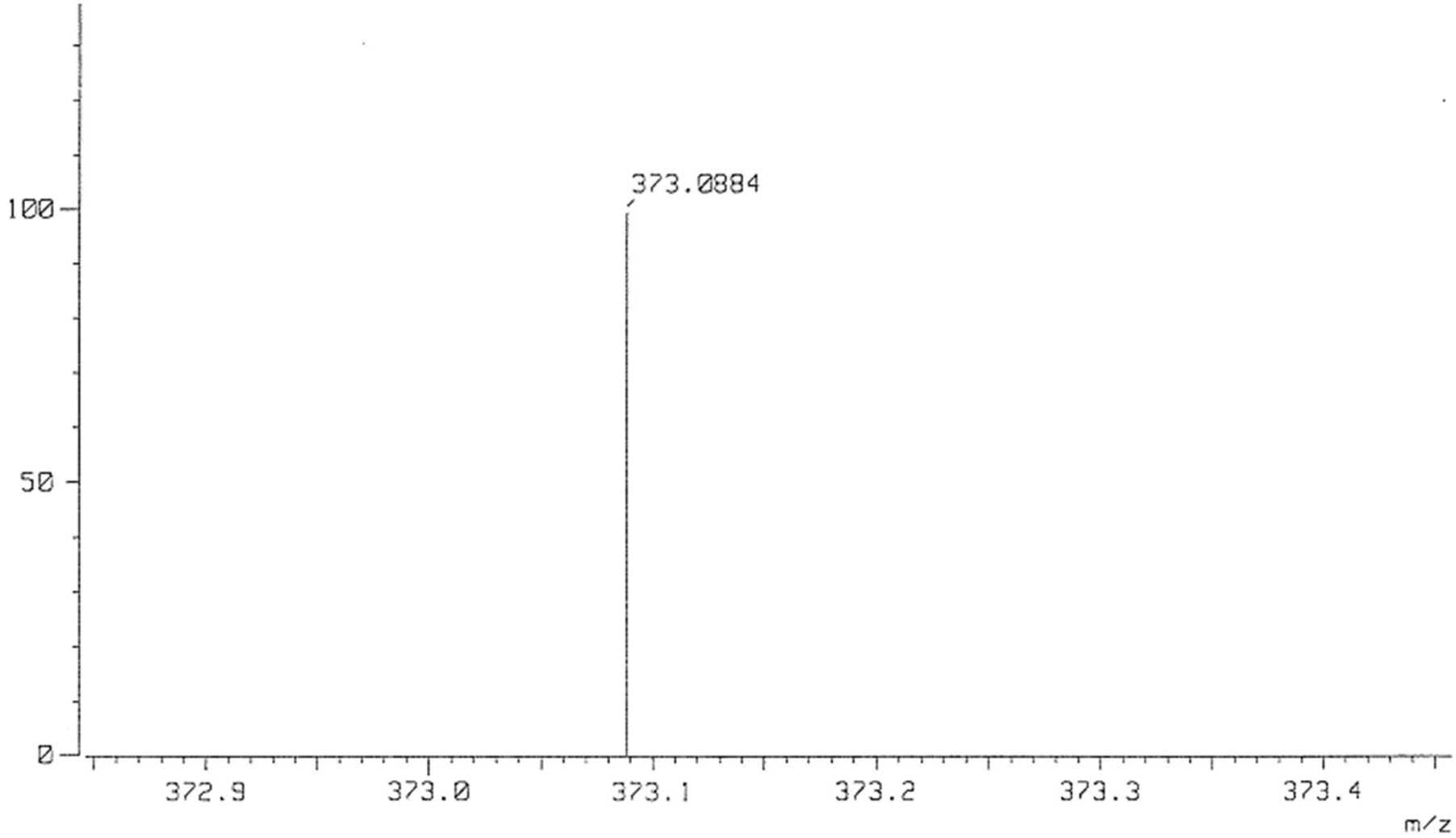
Chemical Formula: $C_{16}H_{24}BrNO_4$

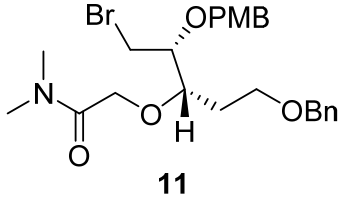
Exact Mass: 373.0889

$[M]^+$ Calcd for $C_{16}H_{24}BrNO_4$ 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
```





11

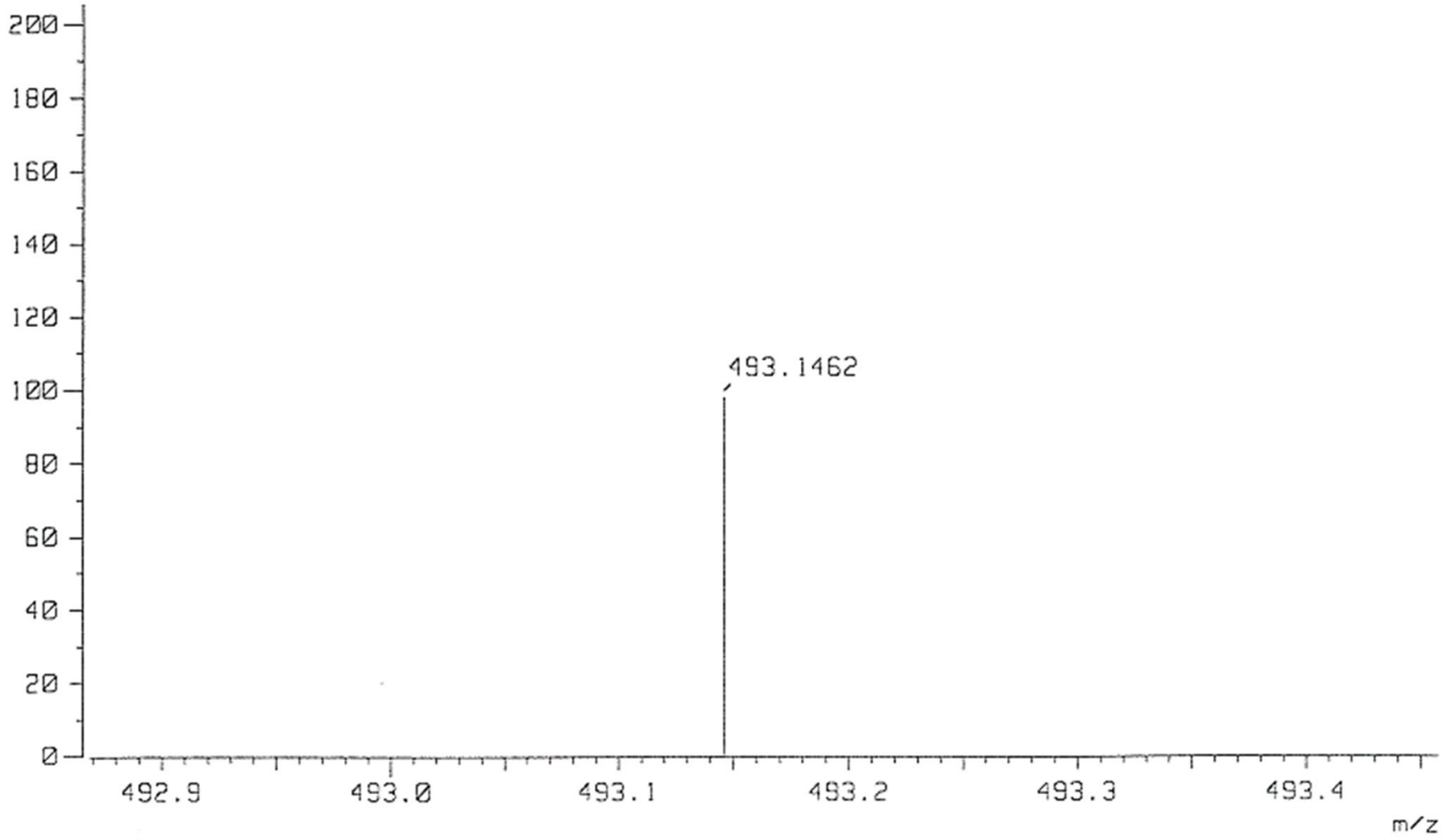
Chemical Formula: $C_{24}H_{32}BrNO_5$

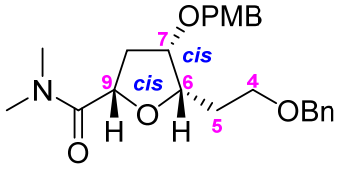
Exact Mass: 493.1464

$[M]^+$ Calcd for $C_{24}H_{32}BrNO_5$ 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

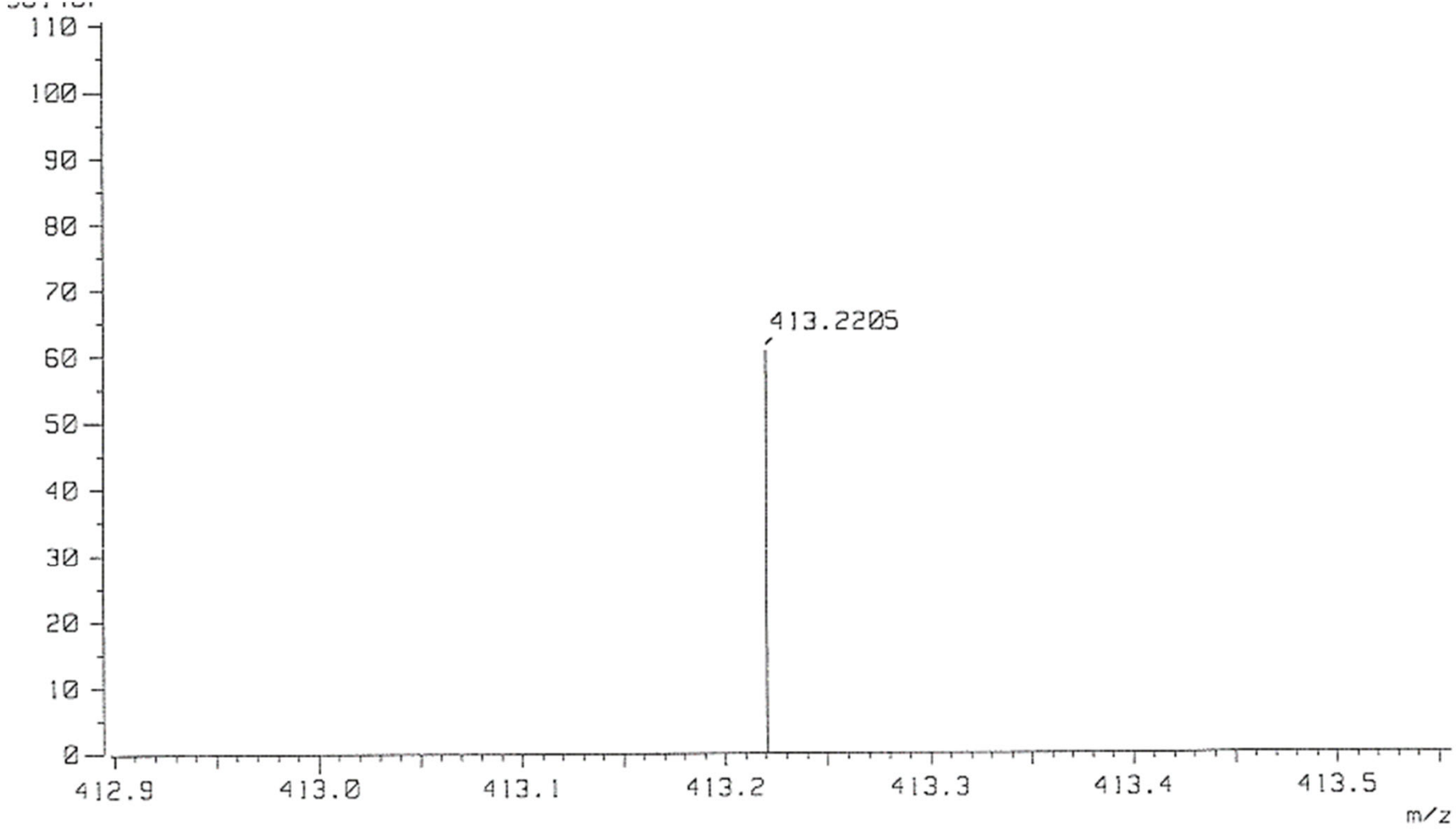
Chemical Formula: $C_{24}H_{31}NO_5$

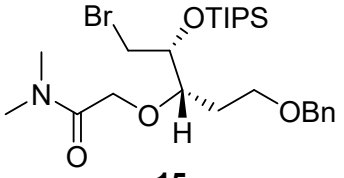
Exact Mass: 413.2202

$[M]^+$ Calcd for $C_{24}H_{31}NO_5$ 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
```





15

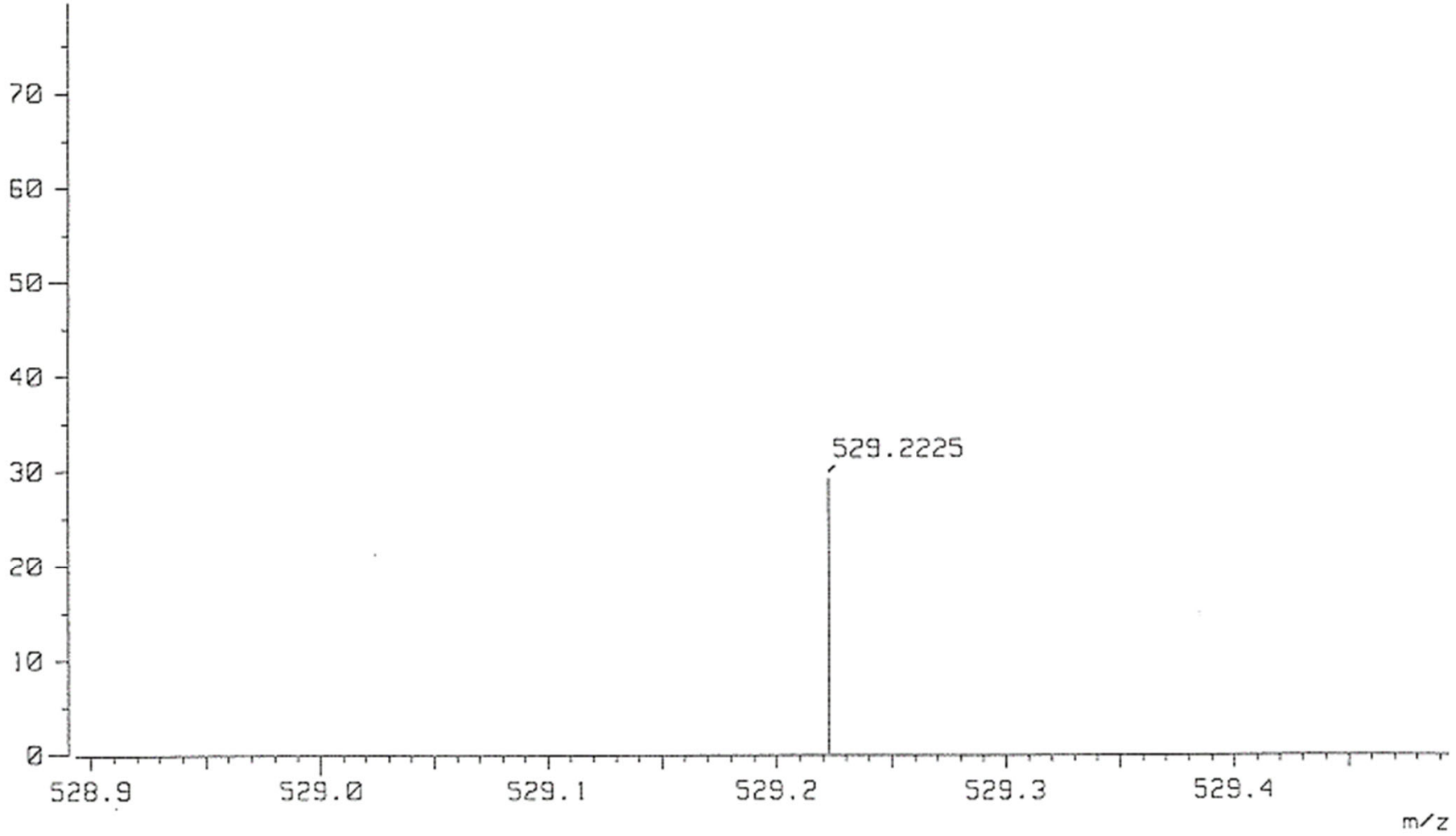
Chemical Formula: $C_{25}H_{44}BrNO_4Si$

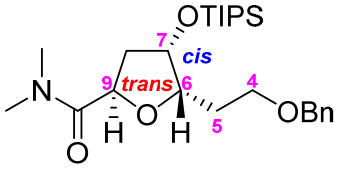
Exact Mass: 529.2223

[M]$^+$ Calcd for $C_{25}H_{44}BrNO_4Si$ 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
```





16

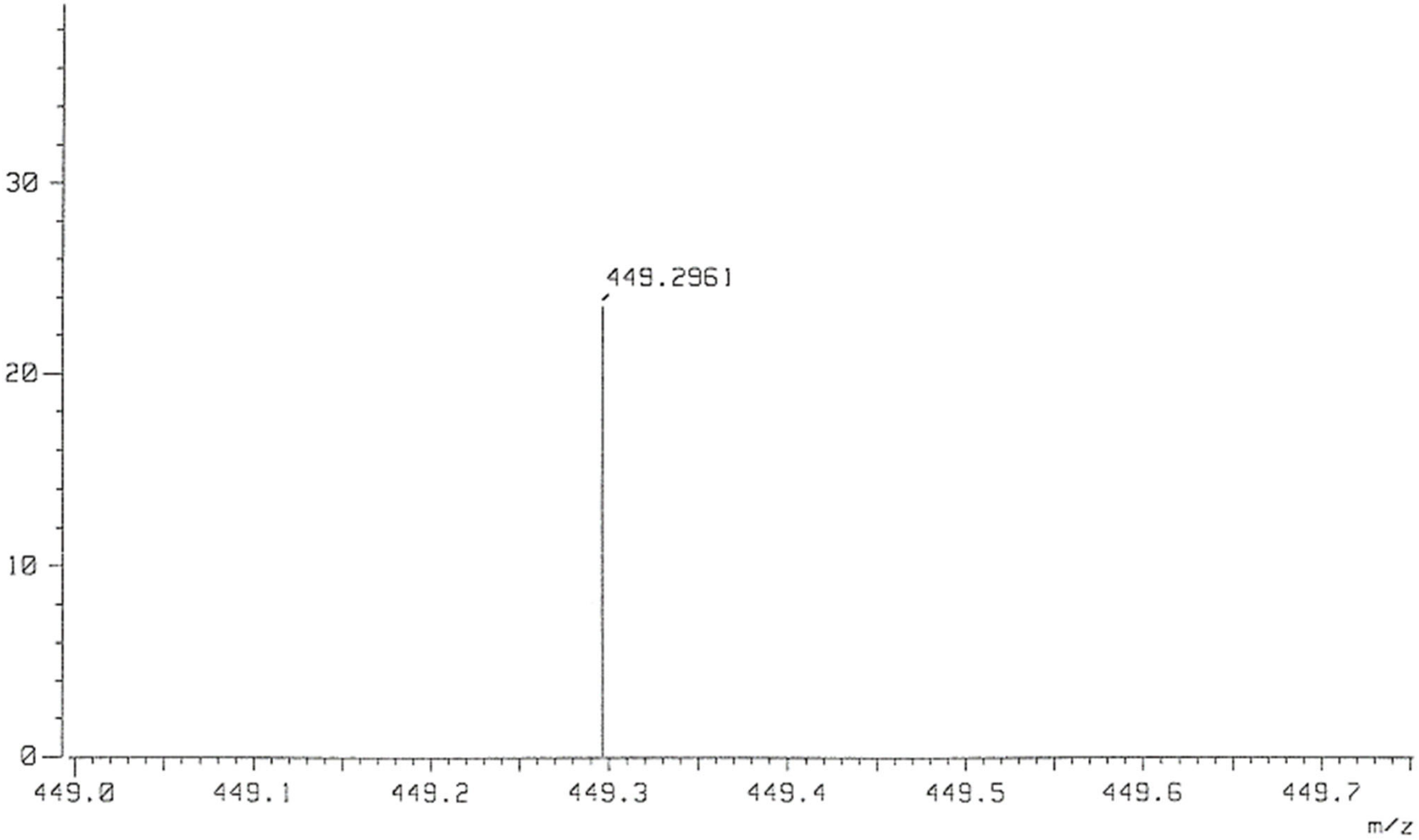
Chemical Formula: $C_{25}H_{43}NO_4Si$

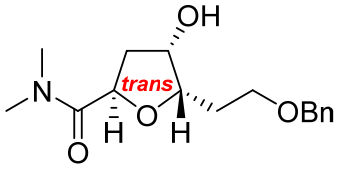
Exact Mass: 449.2961

$[M]^+$ Calcd for $C_{25}H_{43}NO_4Si$ 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

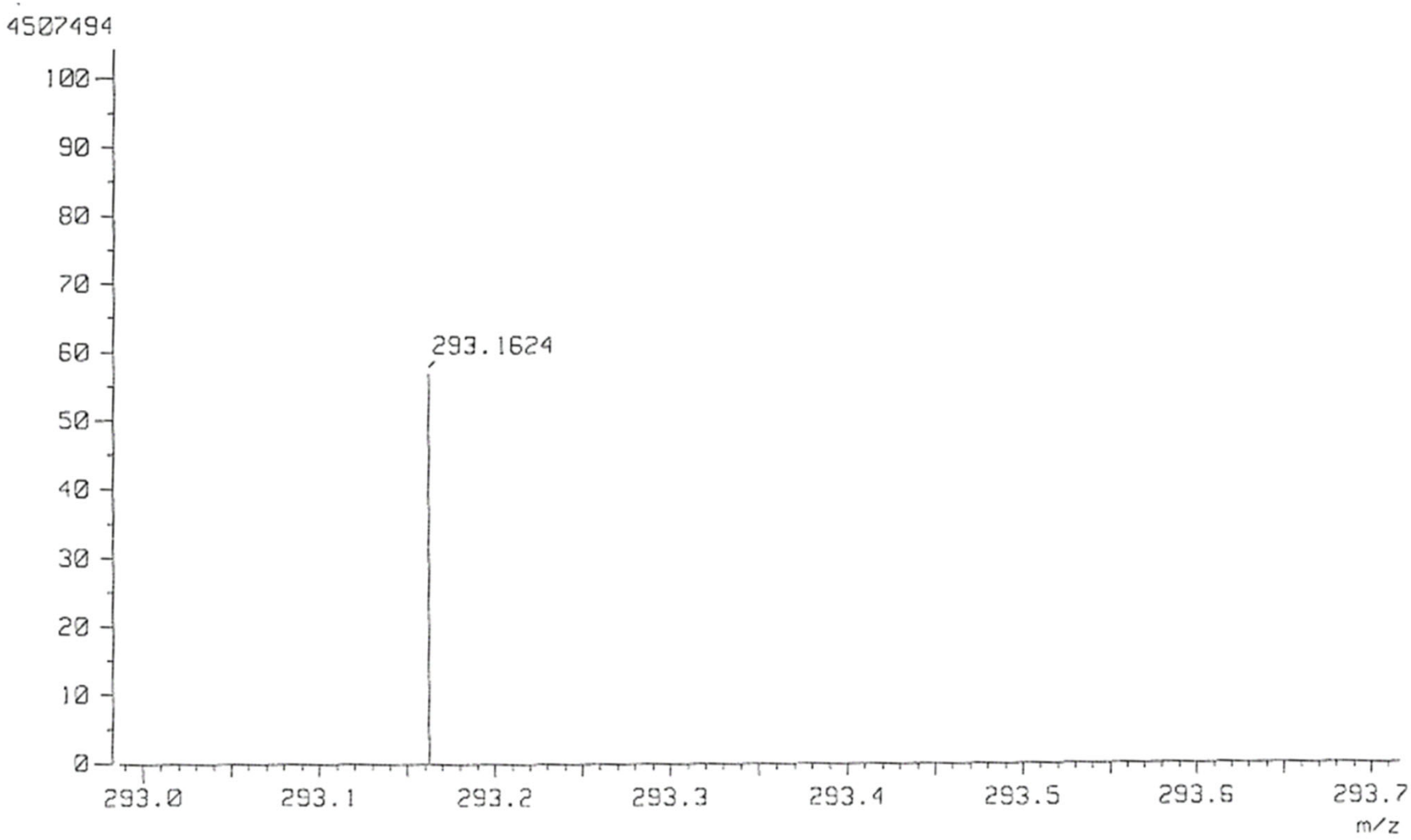
Chemical Formula: $C_{16}H_{23}NO_4$

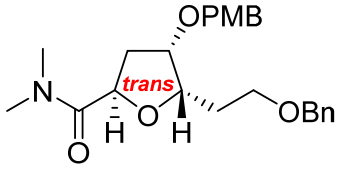
Exact Mass: 293.1627

$[M]^+$ Calcd for $C_{16}H_{23}NO_4$ 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

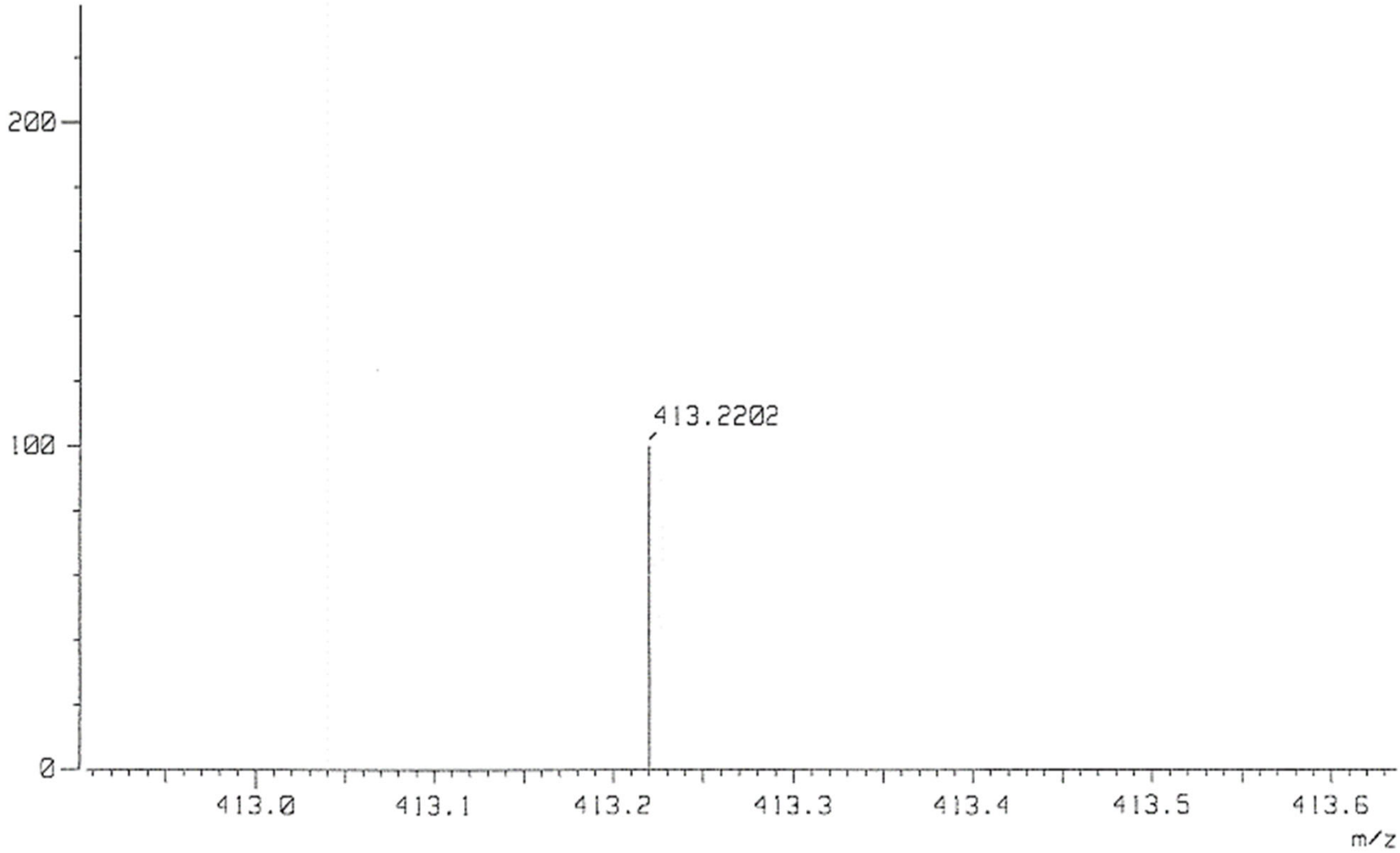
Chemical Formula: $C_{24}H_{31}NO_5$

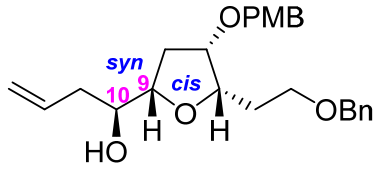
Exact Mass: 413.2202

$[M]^+$ Calcd for $C_{24}H_{31}NO_5$ 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

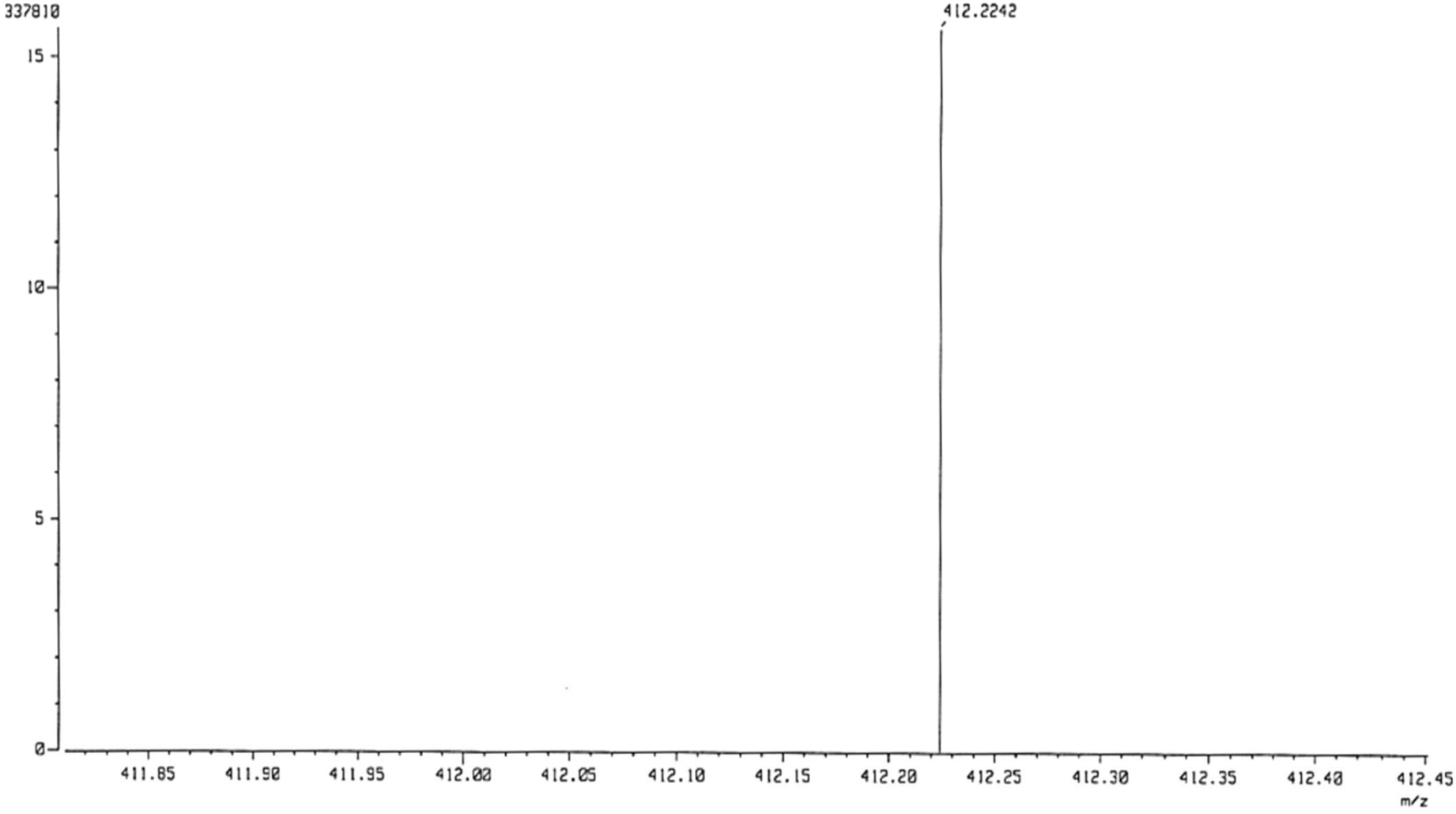
Chemical Formula: $C_{25}H_{32}O_5$

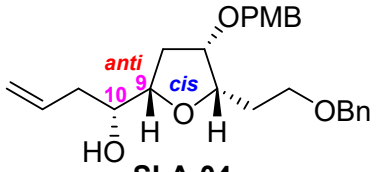
Exact Mass: 412.2250

$[M]^+$ Calcd for $C_{25}H_{32}NO_5$ 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
```





SI-A-04

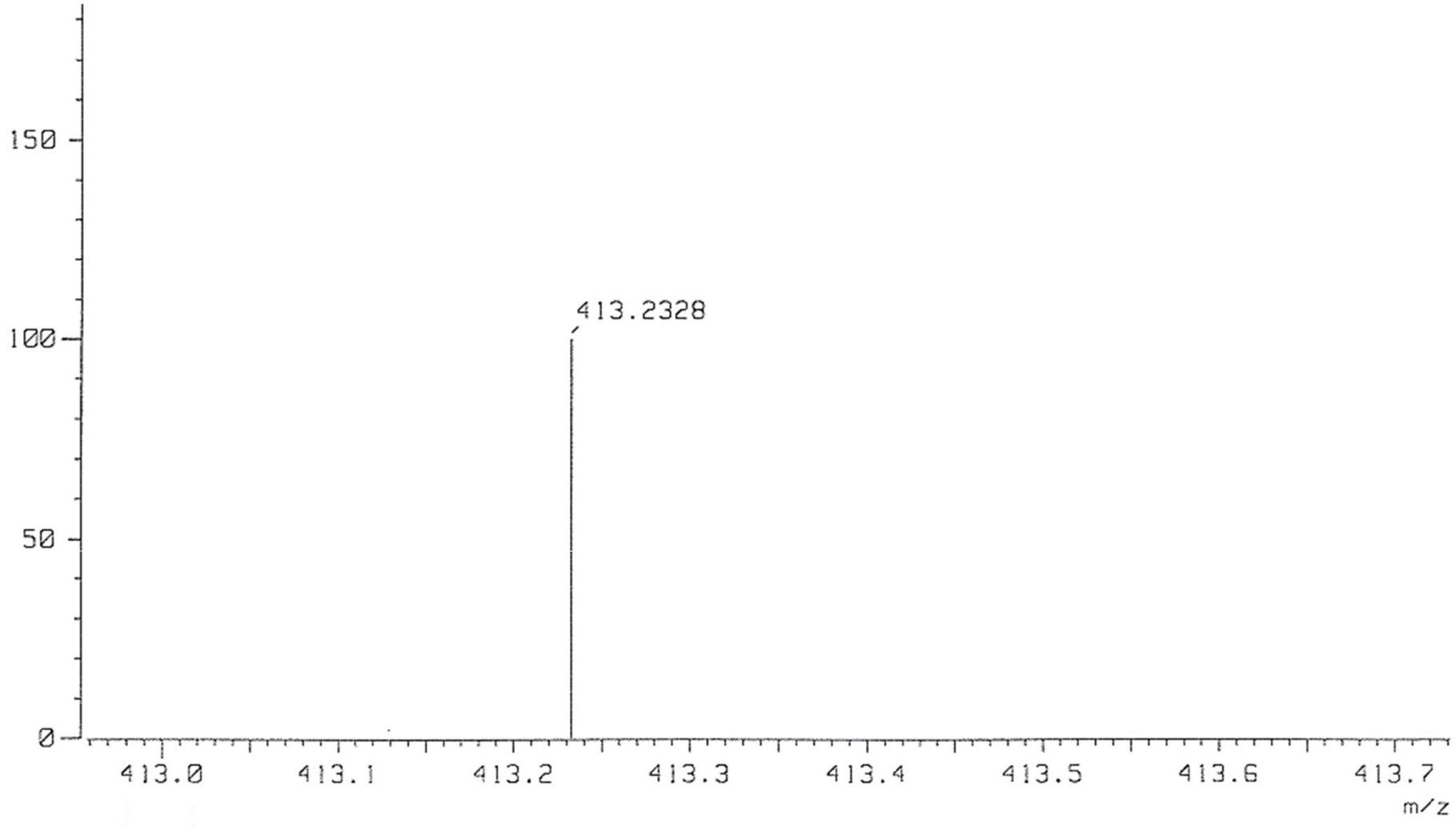
Chemical Formula: $C_{25}H_{32}O_5$

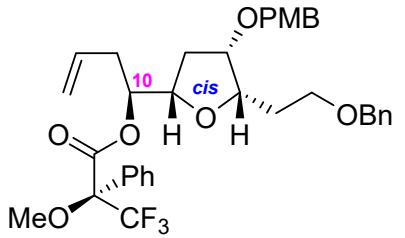
Exact Mass: 412.2250

$[M+H]^+$ Calcd for $C_{25}H_{33}NO_5$ 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

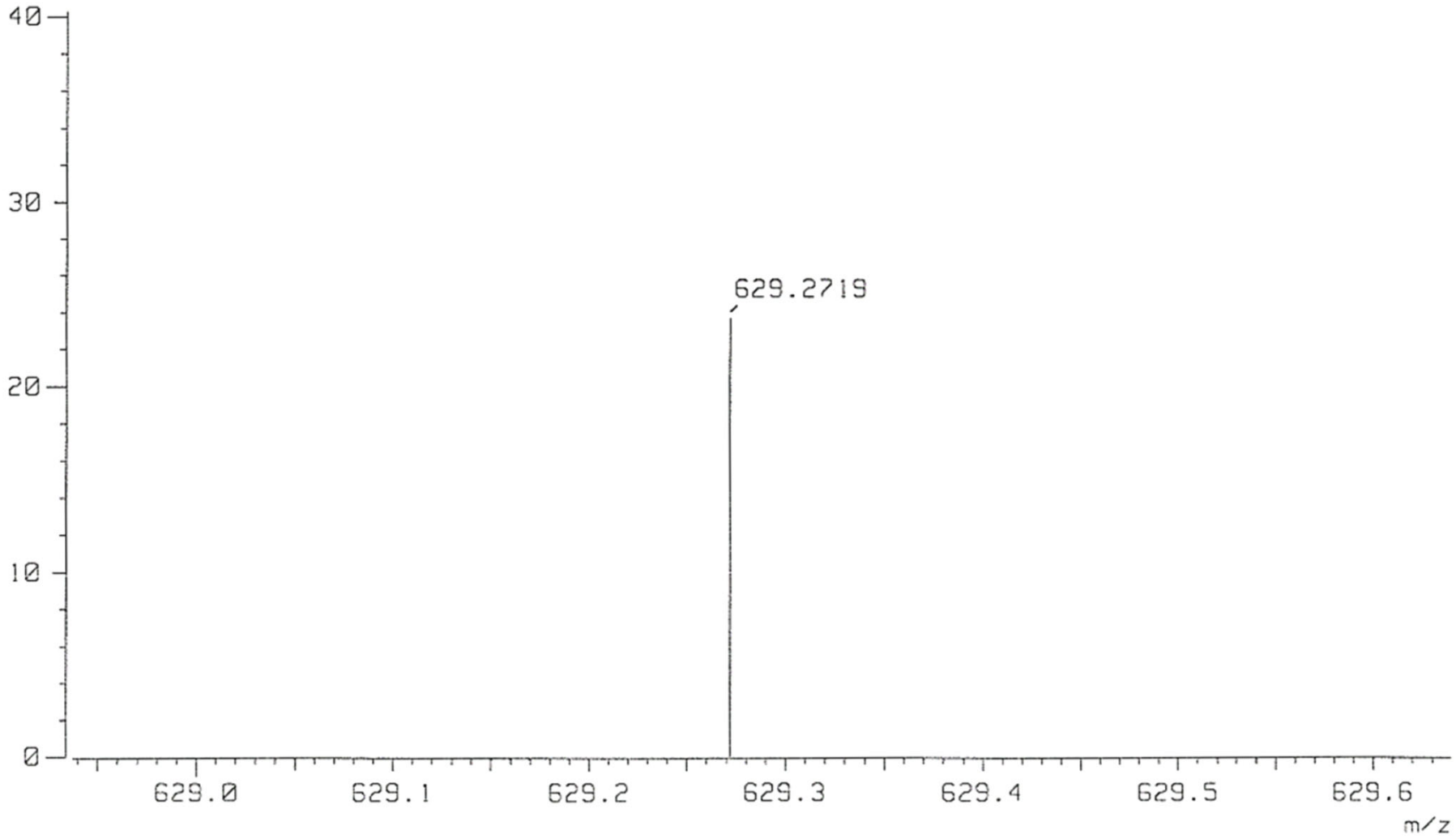
Chemical Formula: $C_{35}H_{39}F_3O_7$

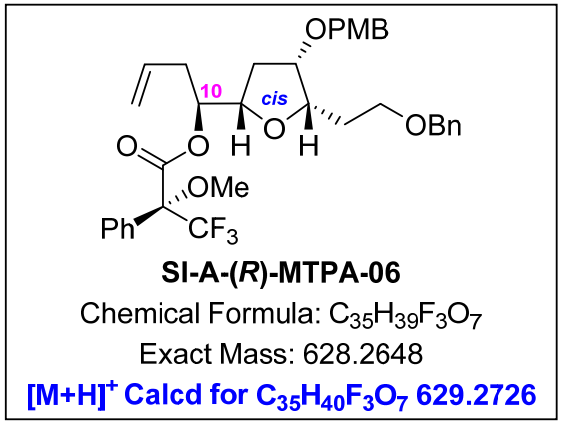
Exact Mass: 628.2648

[M+H]$^+$ Calcd for $C_{35}H_{40}F_3O_7$ 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

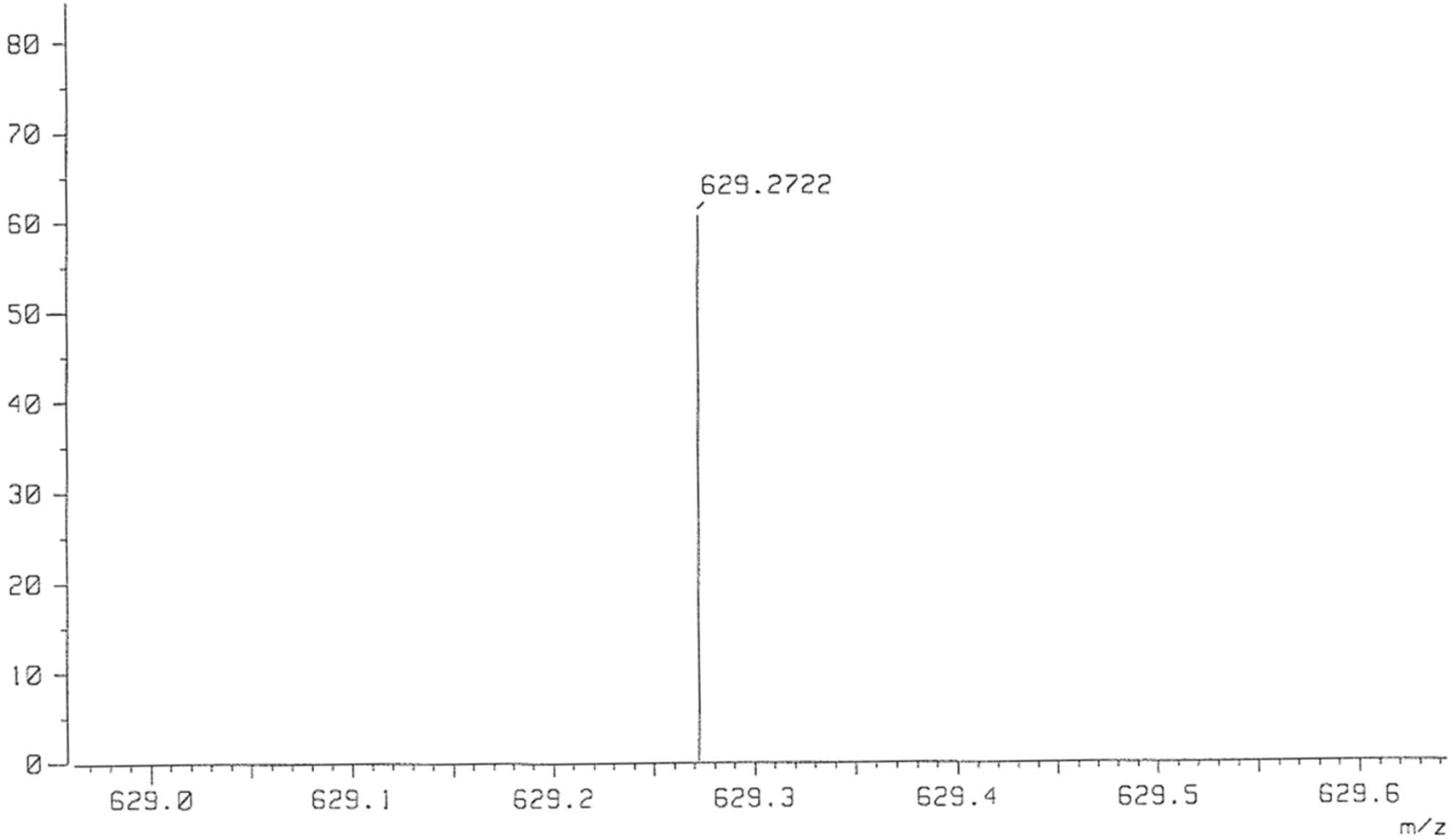
Chemical Formula: $C_{35}H_{39}F_3O_7$

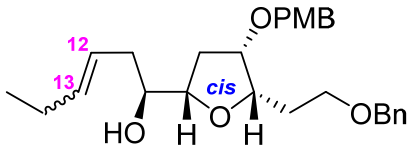
Exact Mass: 628.2648

[M+H]$^+$ Calcd for $C_{35}H_{40}F_3O_7$ 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

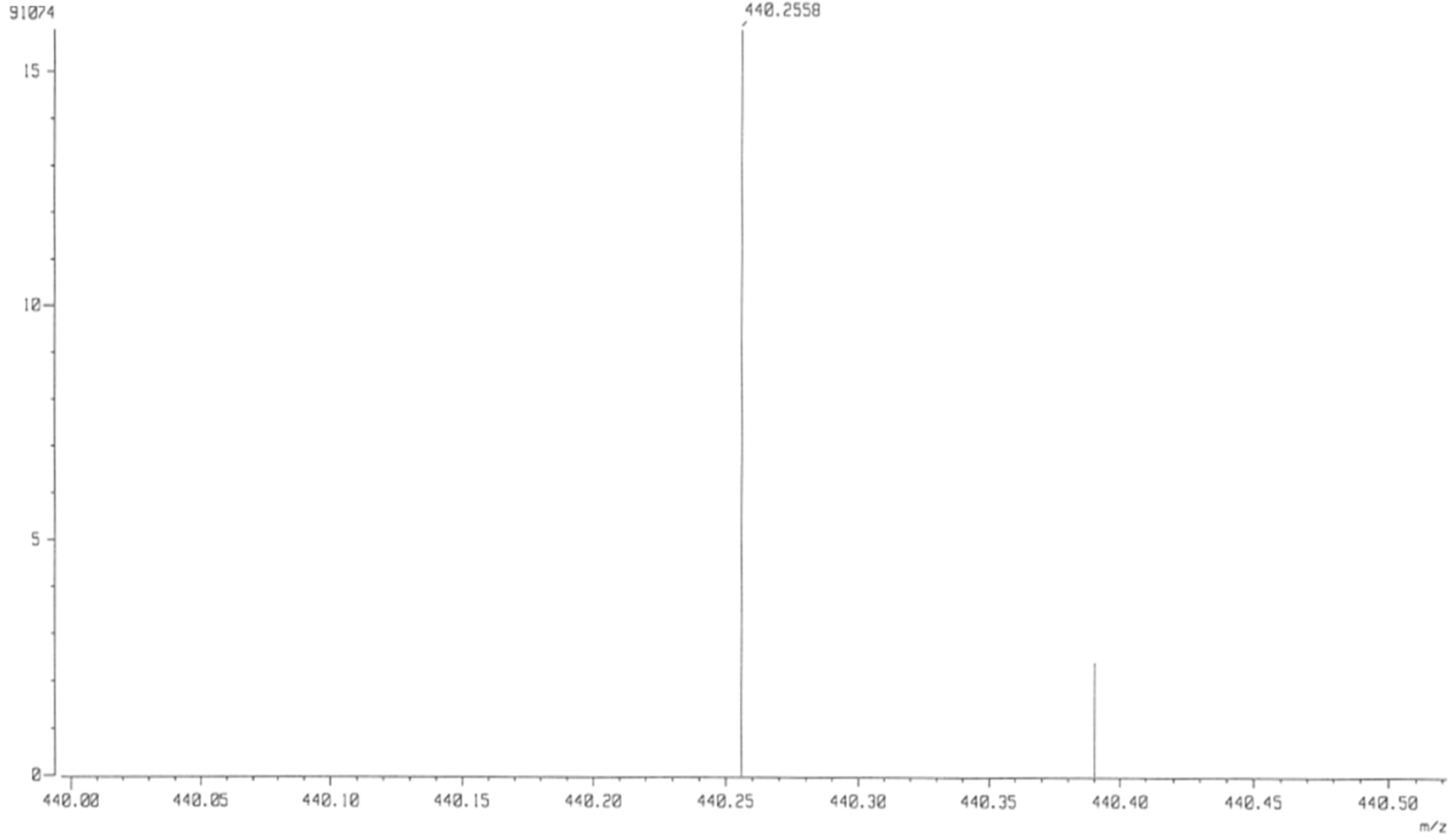
Chemical Formula: $C_{27}H_{36}O_5$

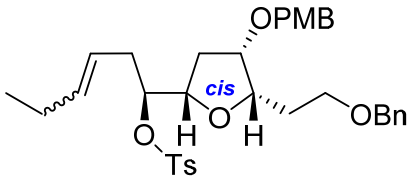
Exact Mass: 440.2563

$[M]^+$ Calcd for $C_{27}H_{36}O_5$ 440.2563

```
[ Elemental Composition ]
Data  : SK-25-017                          Date : 20-Dec-2019 16:52
Sample: Ajou-Univ.
Note : SM Lab Research institute for Analysis
Inlet : Reserv.                            Ion Mode : EI+
RT : 0.97 min                              Scan#: 30+30+31+30
Elements : C 30/0, 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
  440.2558    19.2     -1.1 /  -0.5   10.0  C 27 H 36 O 5
```





SI-A-07

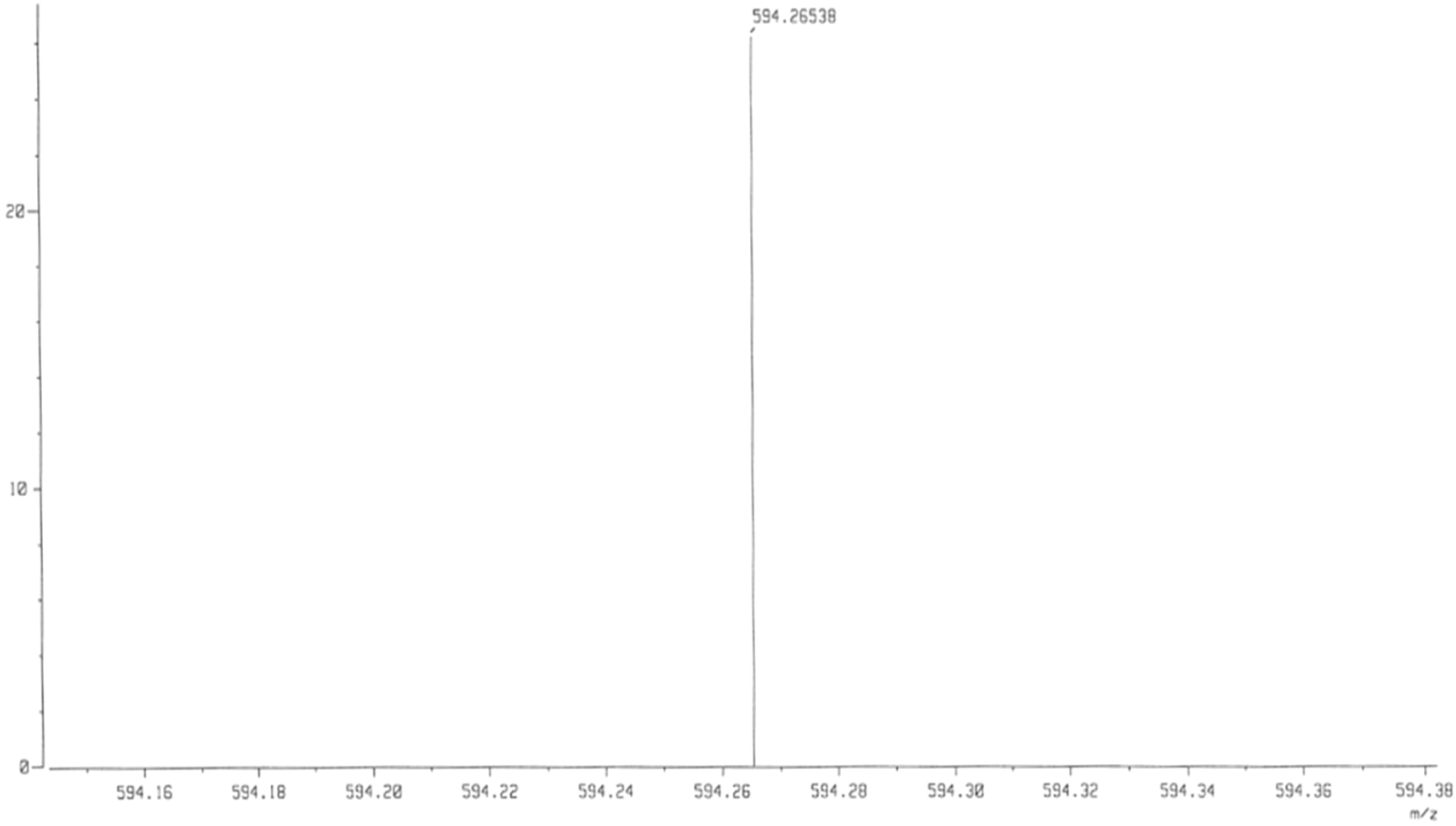
Chemical Formula: $C_{34}H_{42}O_7S$

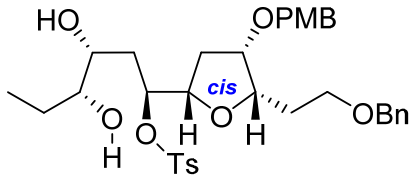
Exact Mass: 594.2651

$[M]^+$ Calcd for $C_{34}H_{42}O_7S$ 594.2651

```
[ Elemental Composition ]
Data  : SK-26-019                          Date : 20-Dec-2019 17:14
Sample: Ajou-Univ.
Note : SM Lab Research institute for Analysis
Inlet : Reserv.                            Ion Mode : EI+
RT : 1.94 min                              Scan#: 59+58+58+57+59+59+58
Elements : C 35/0, H 45/0, O 7/0, S 1/0
Mass Tolerance       : 10mmu
Unsaturation (U.S.) : -1.0 - 50.0

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

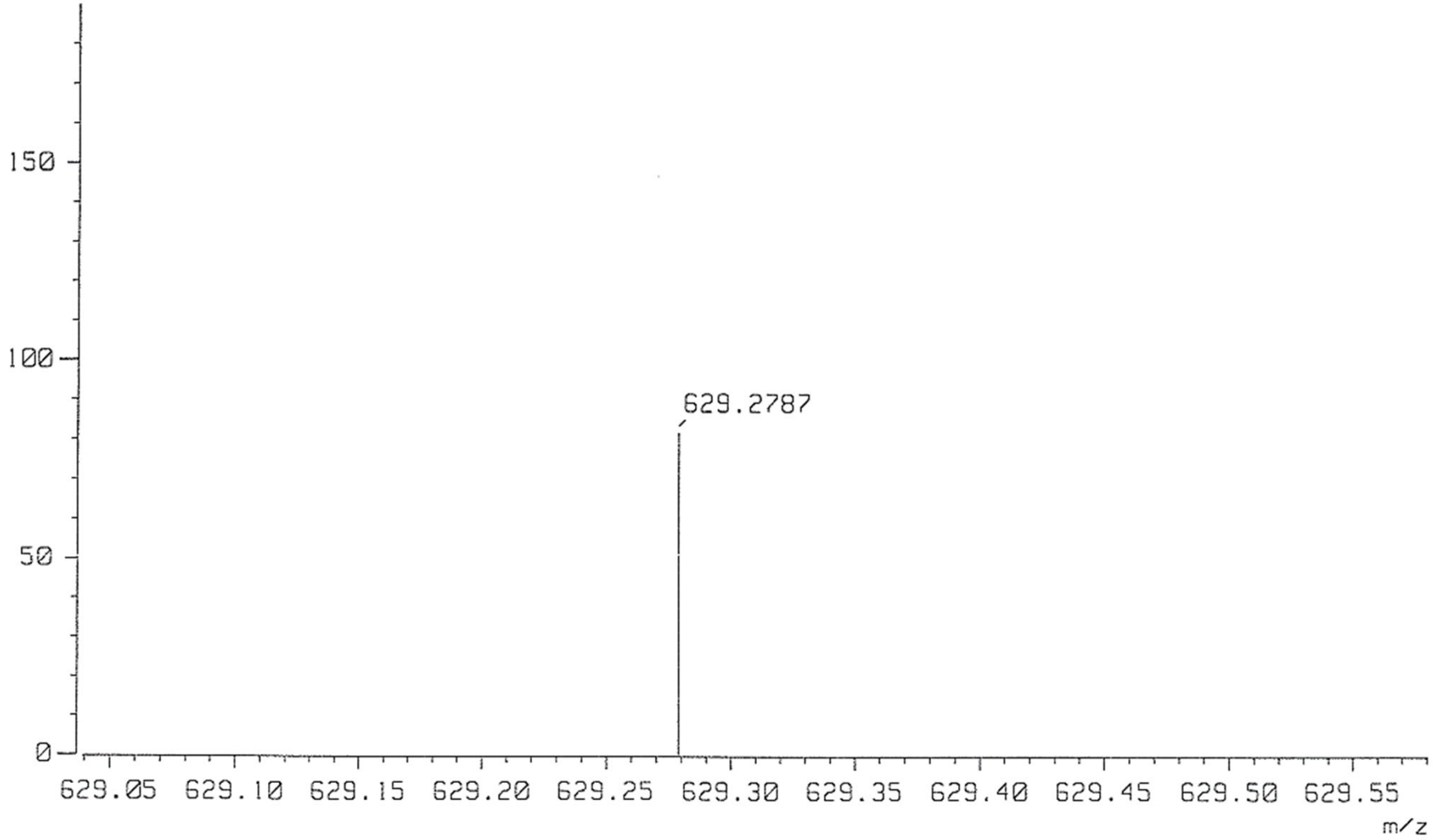
Chemical Formula: $C_{34}H_{44}O_9S$

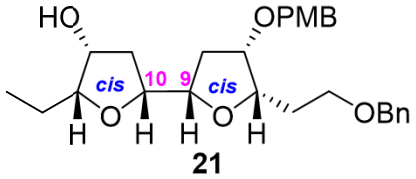
Exact Mass: 628.2706

$[M+H]^+$ Calcd for $C_{34}H_{45}O_9S$ 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
```





21

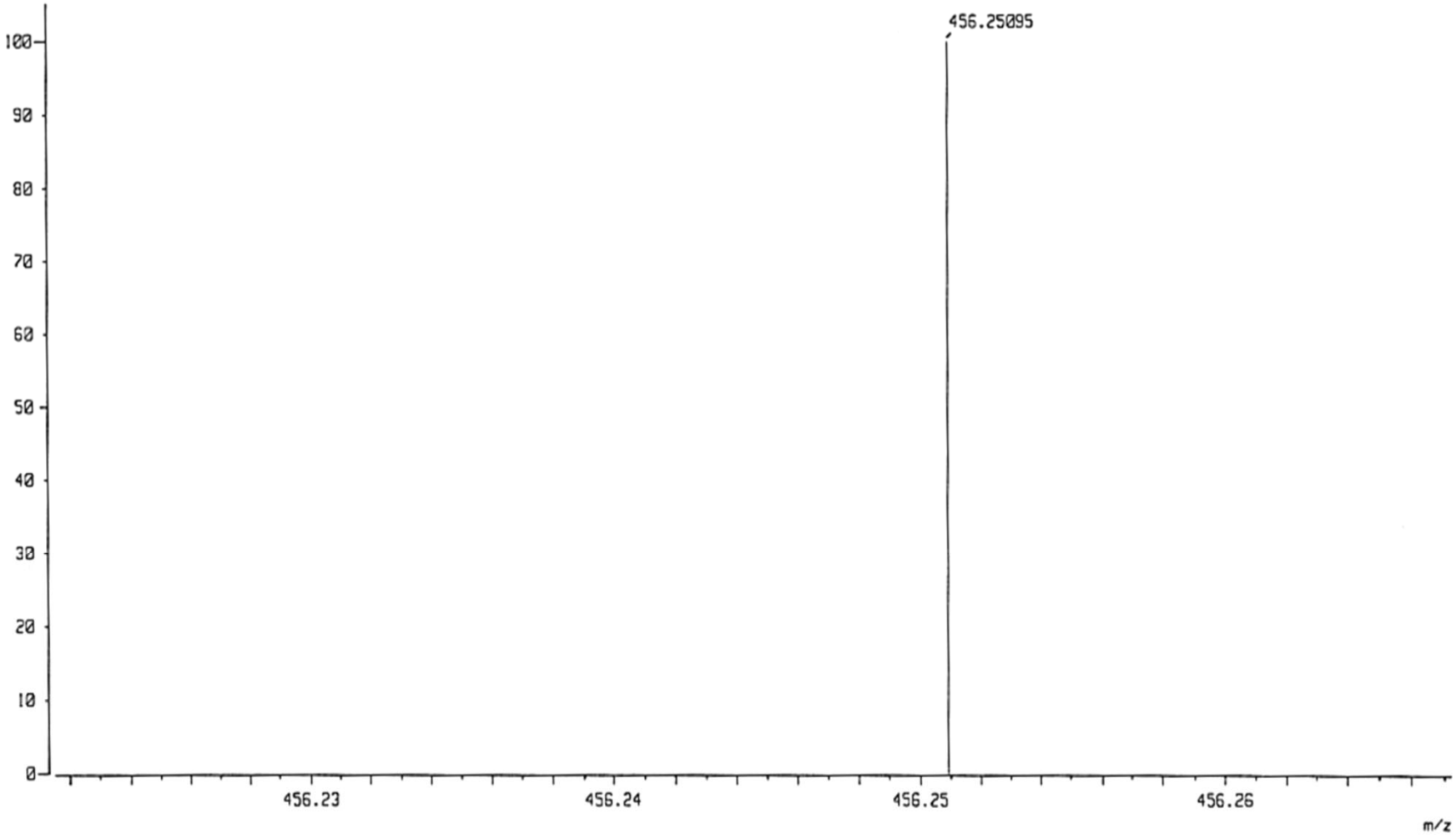
Chemical Formula: $C_{27}H_{36}O_6$

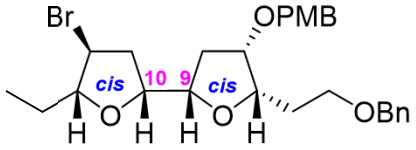
Exact Mass: 456.2512

$[M]^+$ Calcd for $C_{27}H_{36}O_6$ 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

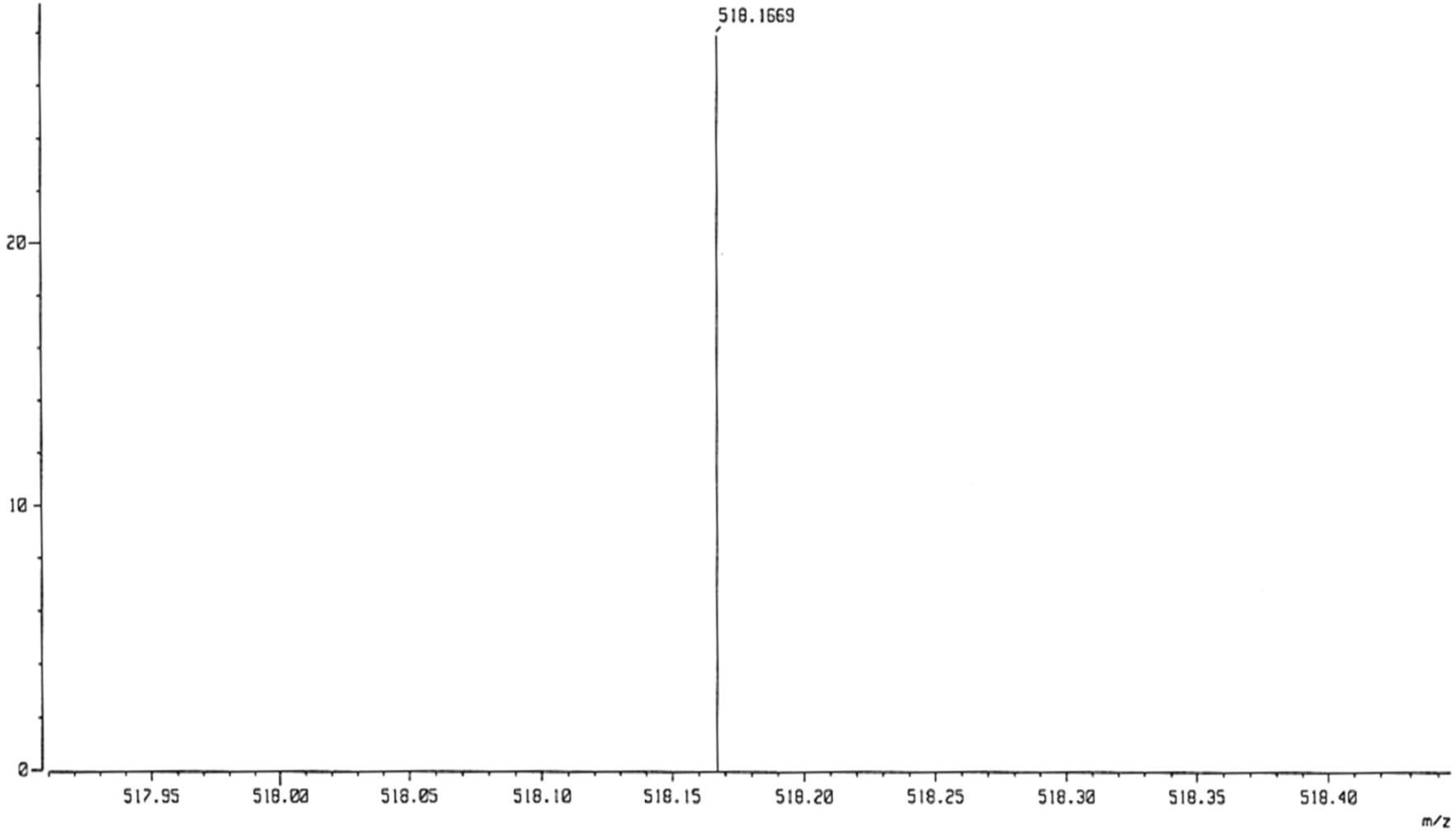
Chemical Formula: $C_{27}H_{35}BrO_5$

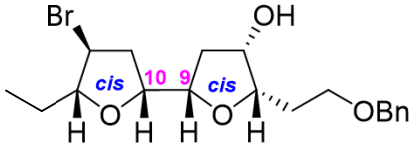
Exact Mass: 518.1668

$[M]^+$ Calcd for $C_{27}H_{35}BrO_5$ 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

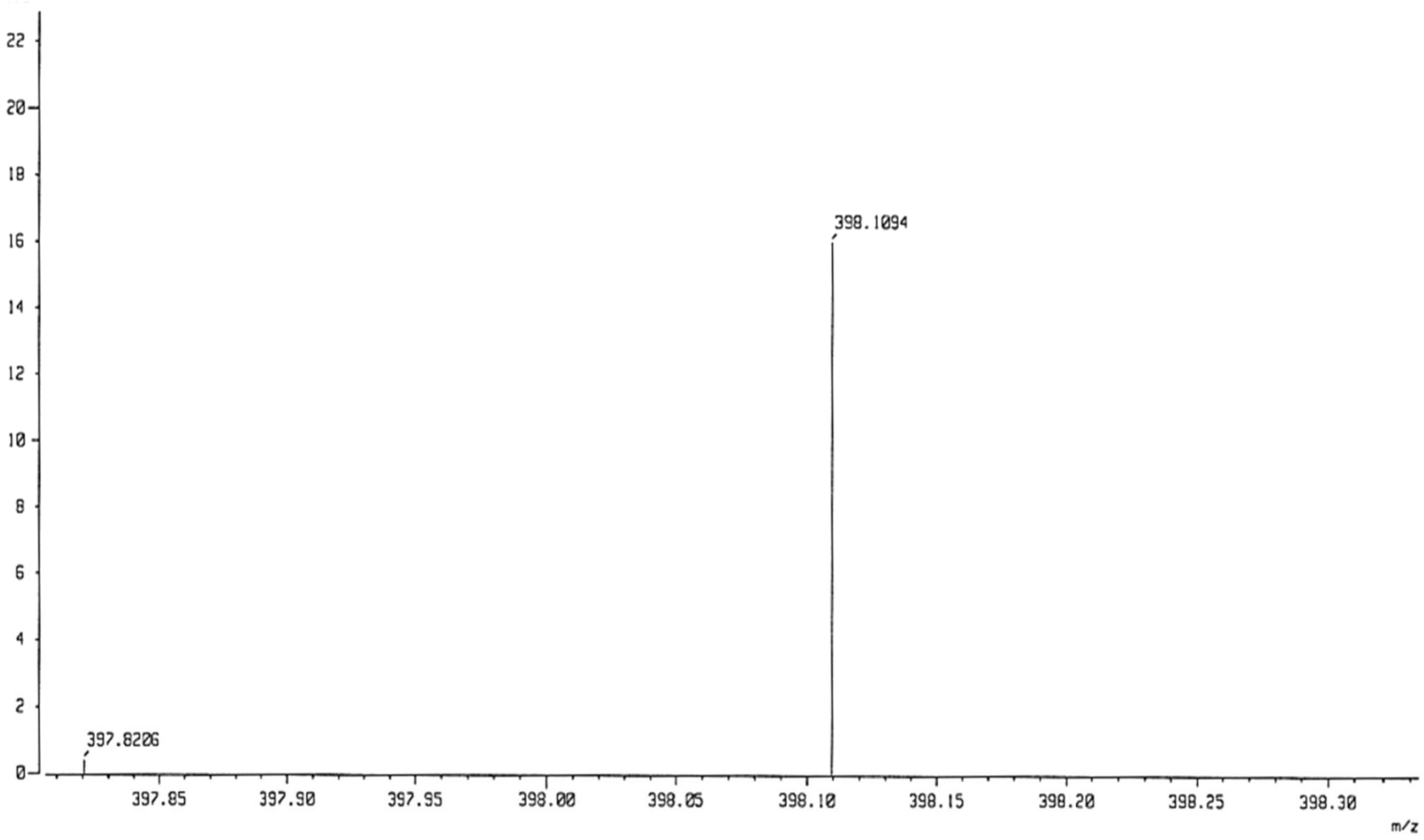
Chemical Formula: $C_{19}H_{27}BrO_4$

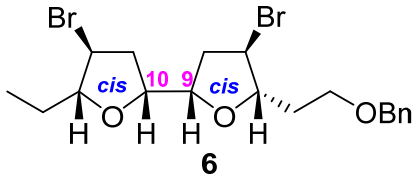
Exact Mass: 398.1093

$[M]^+$ Calcd for $C_{19}H_{27}BrO_4$ 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
```





6

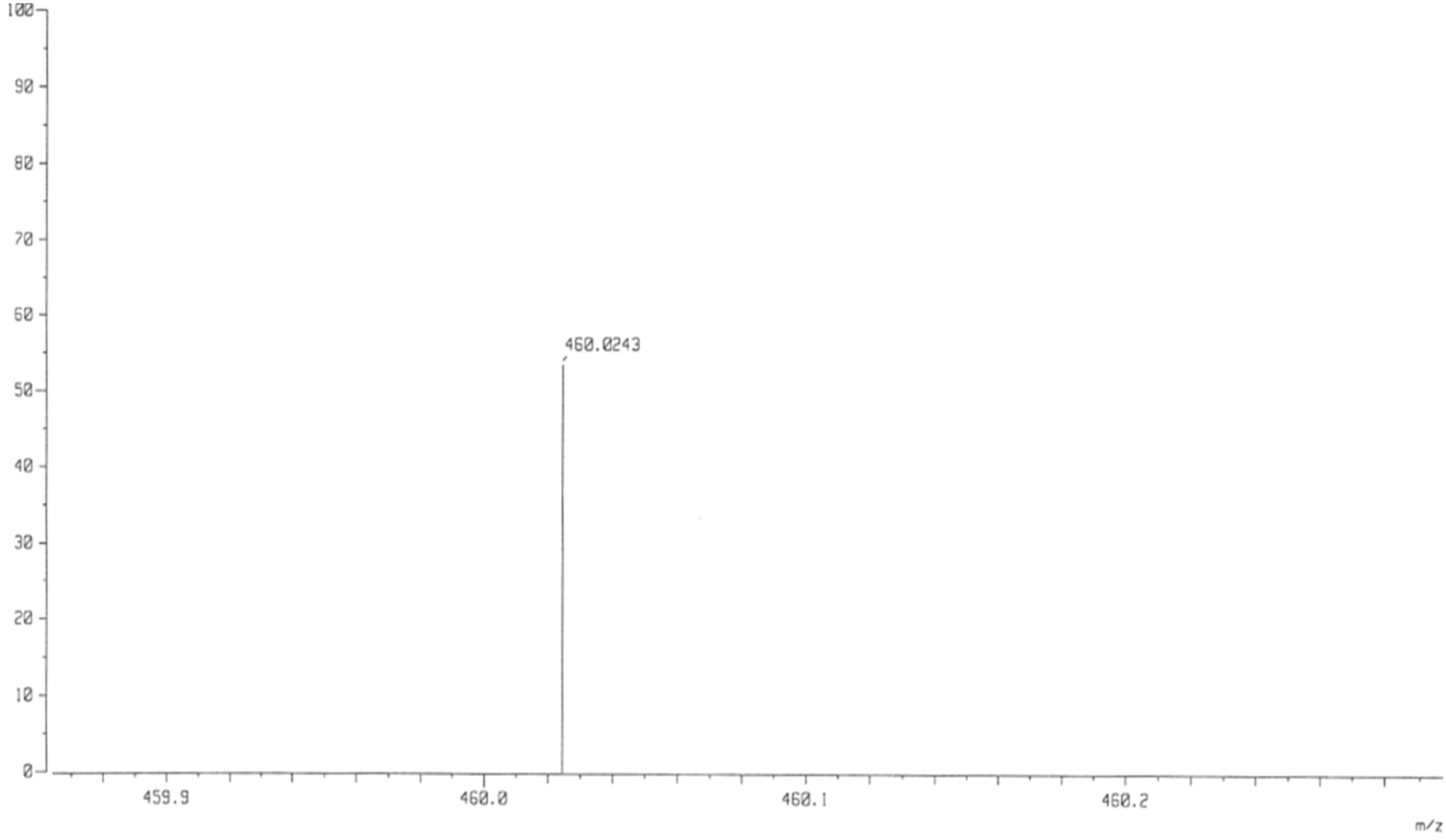
Chemical Formula: $C_{19}H_{26}Br_2O_3$

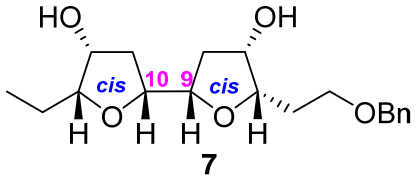
Exact Mass: 460.0249

$[M]^+$ 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
```





7

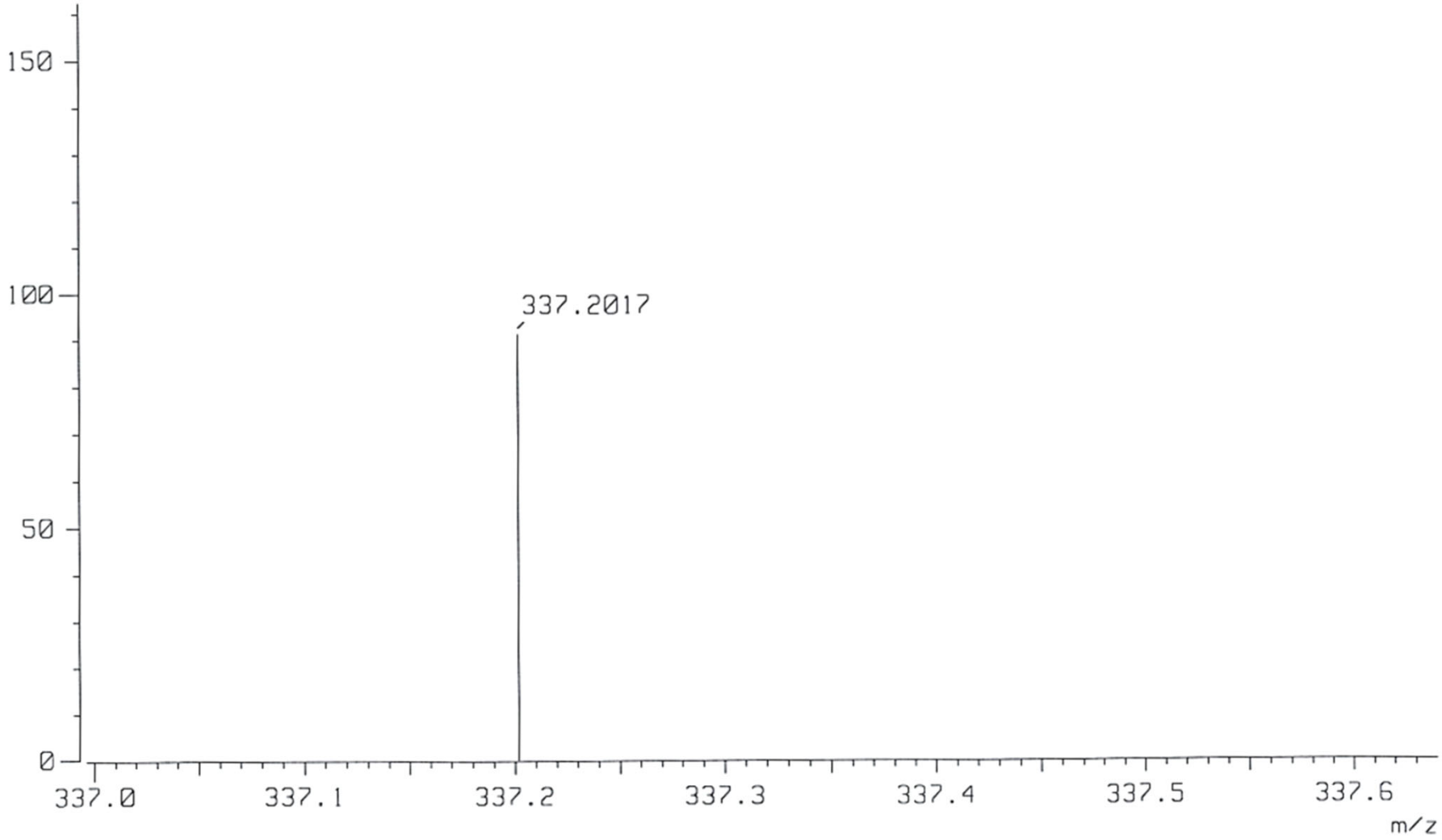
Chemical Formula: $C_{19}H_{28}O_5$

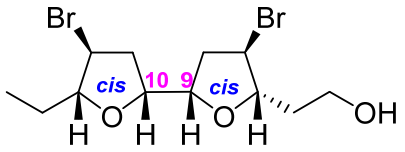
Exact Mass: 336.1937

$[M+H]^+$ Calcd for $C_{19}H_{29}O_5$ 337.2015

```
[ Elemental Composition ]
Data  : FAB-SK-13-013                    Date : 11-Oct-2023 15:05
Sample:
Note : SM Lab Research Center (Jeol JMS-700)
Inlet : Reserv.                          Ion Mode : FAB+
RT : 3.34 min                            Scan#: 101
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
  337.2017   91.3     +0.7 /  +0.2     5.5  C 19 H 29 O 5
```





SI-A-13

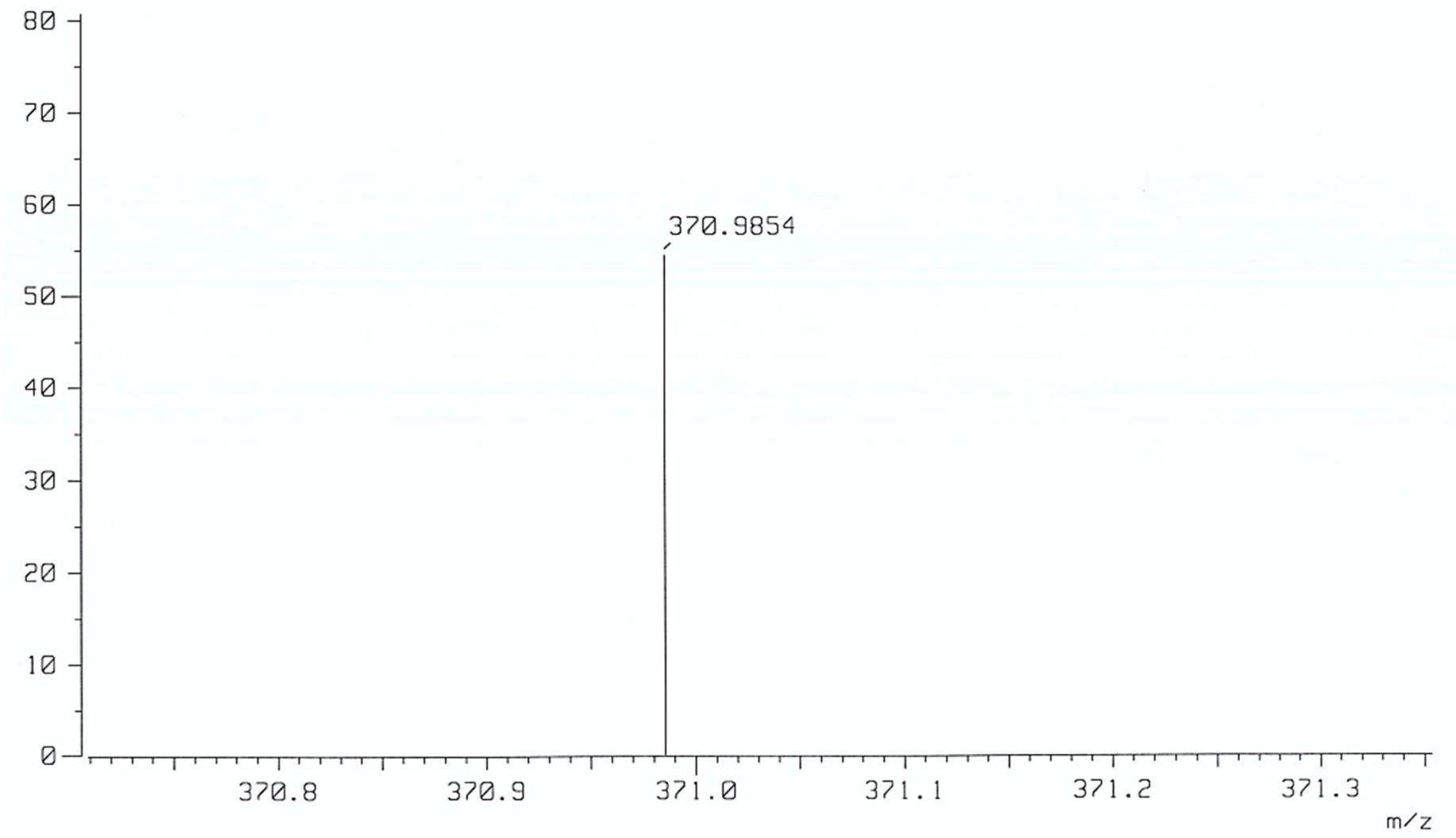
Chemical Formula: $C_{12}H_{20}Br_2O_3$

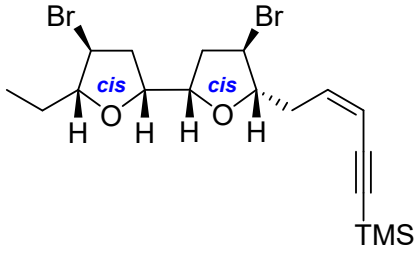
Exact Mass: 369.9779

$[M+H]^+$ 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

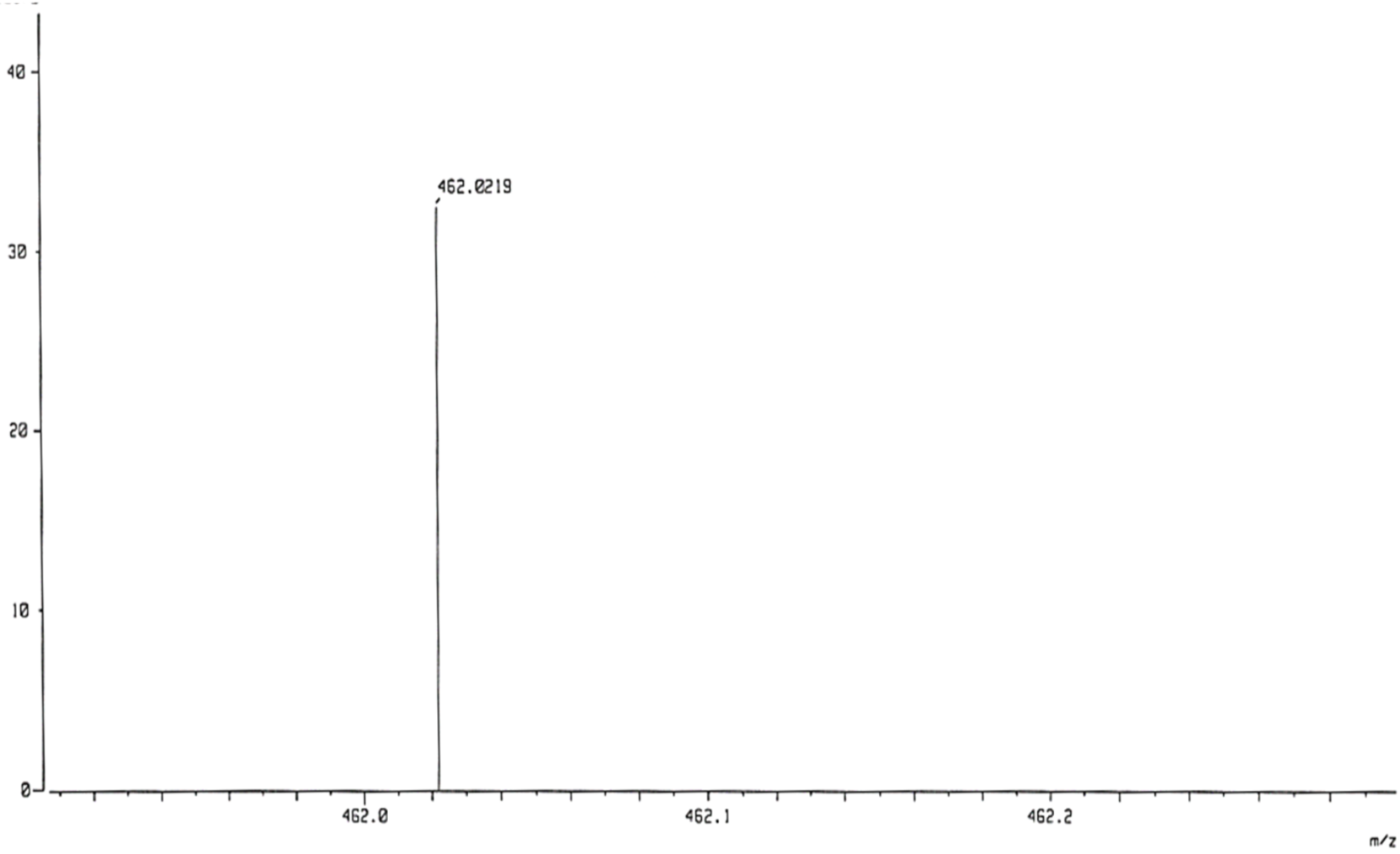
Chemical Formula: $C_{18}H_{28}Br_2O_2Si$

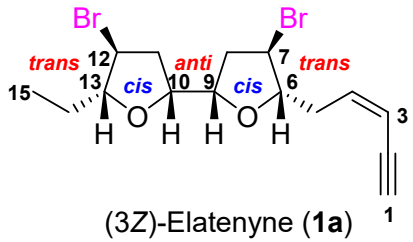
Exact Mass: 462.0225

$[M]^+$ 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
```





(3*Z*)-Elatenyne (**1a**)

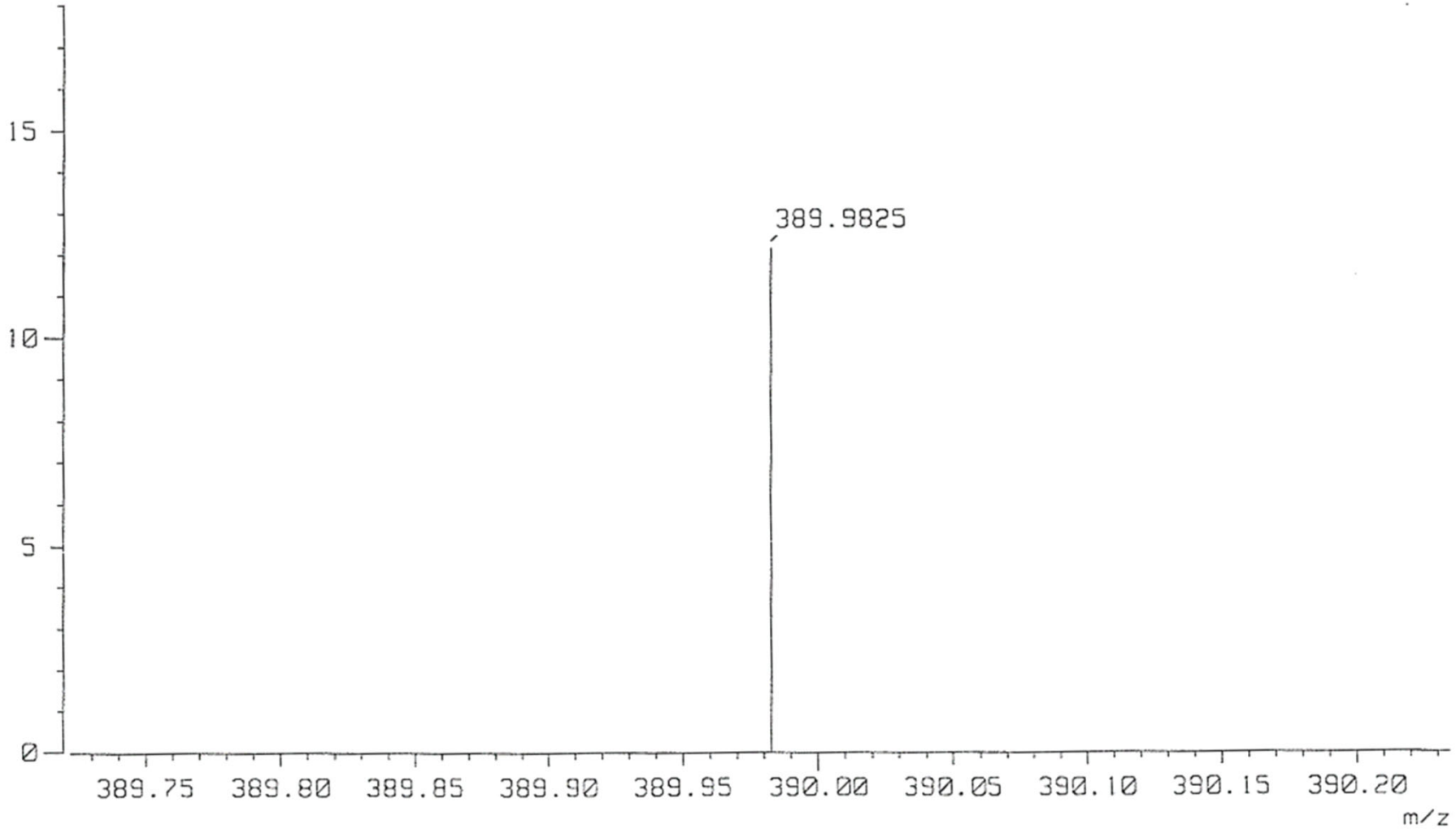
Chemical Formula: $C_{15}H_{20}Br_2O_2$

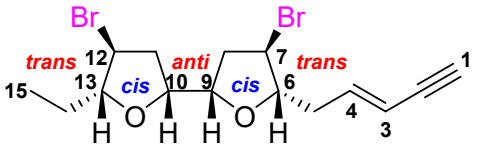
Exact Mass: 389.9830

$[M]^+$ Calcd for $C_{15}H_{20}Br_2O_2$ 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
```





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

Chemical Formula: $C_{15}H_{20}Br_2O_2$

Exact Mass: 389.9830

$[M]^+$ Calcd for $C_{15}H_{20}Br_2O_2$ 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
```