**Supplementary Information for**

# Synthesis of Fulgidic Acid and the Two Possible Stereoisomers of Chaenomic Acid D

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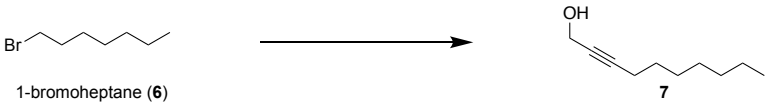
**Experimental Procedures**

**General Information**

Infrared (IR) spectra are reported in wave number ($cm^{-1}$). The $^{1}H$ NMR (400 MHz) and $^{13}C$ NMR (100 MHz) spectra were recorded in $CDCl_3$ or $CD_3OD$ with $Me_4Si$ ($\delta$ = 0 ppm), the centerline of $CDCl_3$ triplet ($\delta$ = 77.1 ppm) or residual protonated solvent as an internal standard. Signal patterns are indicated as br s, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in hertz (Hz). High-resolution mass spectroscopy (HRMS) was obtained by ionizing samples *via* field desorption (FD). After the reactions were finished, the organic extracts were concentrated by using an evaporator and then the residues were purified by chromatography on silica gel (Kanto, spherical silica gel 60 N). Dry solvents such as THF, $Et_2O$, and $CH_2Cl_2$ were obtained from commercial sources. The volume of aqueous solution used for workup was 3 to 5 times that of the reaction solvent, and the volume of organic solvent used for extraction was 2 to 4 times that of the aqueous solution.

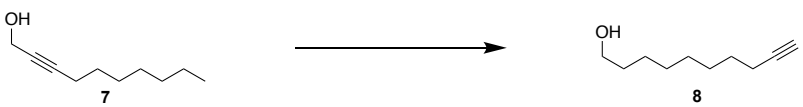
**Dec-2-yn-1-ol (7)**




1-bromoheptane (**6**) **7**

To a solution of 2-propyn-1-ol (2.83 mL, 48.0 mmol) in THF (80 mL) and HMPA (25 mL) was added *n*-BuLi (1.59 M in hexane, 60.4 mL, 96.0 mmol) at –78 ºC. After 1.5 h at –78 ºC, the mixture was warmed to –30 ºC and added 1-bromoheptane (**6**) (6.28 mL, 40.0 mmol). The mixture was stirred at room temperature for 3 d and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give alcohol **7** (4.08 g, 66%): yellow oil; $R_f$ = 0.44 (hexane/EtOAc = 3:1); $^{1}H$ NMR (400 MHz, $CDCl_3$) $\delta$ 4.25 (dt, *J* = 6.0, 2.4 Hz, 2H), 2.21 (tt, *J* = 6.8, 2.4 Hz, 2H), 1.70–1.58 (m, 1H), 1.51 (quint., *J* = 6.8 Hz, 2H), 1.43–1.18 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 86.8, 86.7, 78.3, 51.55, 51.48, 31.8, 28.90, 28.88, 28.7, 22.7, 18.8, 14.2. The spectroscopic data were in agreement with the literature values.[S1]

**Dec-9-yn-1-ol (8)**

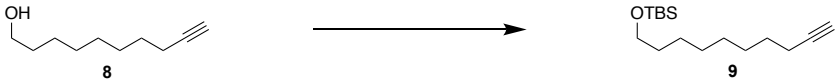



**7** **8**

NaH (55% dispersion in mineral oil, 6.92 g, 159 mmol) was suspended in 1,3-propandiamine (70 mL) at 0 °C. The mixture was stirred at room temperature for 30 min. Then the mixture

was stirred at 60 °C for 1 h. The mixture was cooled to ambient temperature and added a solution of dec-2-yn-1-ol (**7**) (4.08 g, 26.5 mmol) in 1,3-propandiamine (3 mL). The mixture was stirred at 60 °C for 4 h, and diluted with $H_2O$ and 3 N HCl at 0 °C. The resulting mixture was extracted with EtOAc four times. The combined extracts were washed with 1 N HCl and brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give acetylene **8** (3.29 g, 81%): yellow oil; $R_f$ = 0.30 (hexane/EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.64 (t, $J$ = 6.8 Hz, 2H), 2.18 (td, $J$ = 7.2, 2.8 Hz, 2H), 1.94 (t, $J$ = 2.8 Hz, 1H), 1.63–1.46 (m, 5H), 1.46–1.26 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 84.8, 68.2, 63.0, 32.8, 29.3, 29.1, 28.7, 28.5, 25.7, 18.4. The spectroscopic data were in agreement with the literature values.[S2]

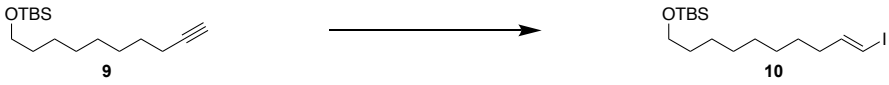
***tert*-Butyl(dec-9-yn-1-yloxy)dimethylsilane (9)**




**8** **9**

A solution of acetylene **8** (3.29 g, 21.3 mmol), imidazole (2.18 g, 32.0 mmol), and TBSCl (3.86 g, 25.6 mmol) in $CH_2Cl_2$ (43 mL) was stirred at room temperature for 13 h and diluted with $H_2O$. The resulting mixture was extracted with $CH_2Cl_2$ three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give acetylene **9** (5.61 g, 98%): colorless oil; $R_f$ = 0.45 (hexane/EtOAc = 30:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.60 (t, $J$ = 6.8 Hz, 2H), 2.18 (td, $J$ = 6.8, 2.8 Hz, 2H), 1.93 (t, $J$ = 2.8 Hz, 1H), 1.57–1.45 (m, 4H), 1.45–1.23 (m, 8H), 0.89 (s, 9H), 0.05 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 84.8, 68.1, 63.3, 32.9, 29.4, 29.2, 28.8, 28.5, 26.1, 25.8, 18.5, –5.2. The spectroscopic data were in agreement with the literature values.[S3]

**(*E*)-*tert*-Butyl[(10-iododec-9-en-1-yl)oxy]dimethylsilane (10)**

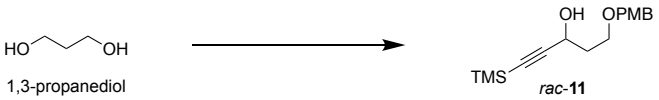



**9** **10**

To an ice-cold solution of $Cp_2ZrCl_2$ (3.95 g, 13.5 mmol) in THF (27 mL) was added DIBAL (1.02 M in hexane, 11.5 mL, 11.7 mmol). After 1 h at 0 ºC, a solution of the acetylene **9** (2.42 g, 9.01 mmol) in THF (5 mL) was added. The mixture was warmed to room temperature over 1 h and then cooled to –78 ºC. The solution of $I_2$ (4.57 g, 18.0 mmol) in THF (6 mL) was added. The mixture was stirred at –78 ºC for 40 min and diluted with saturated $Na_2S_2O_3$ and saturated Rochelle salt. The resulting mixture was extracted with hexane three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give *trans*-iodoolefin **10** (3.50 g, 97%): yellow oil; $R_f$ = 0.59 (hexane/EtOAc = 30:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.51 (dt, $J$ = 14.0, 7.2 Hz, 1H), 5.97 (dt, $J$ = 14.0, 1.2 Hz, 1H), 3.60 (t, $J$ = 6.8 Hz, 2H), 2.04 (qd, $J$

= 7.2, 1.2 Hz, 1H), 1.50 (quint., $J$ = 6.8 Hz, 2H), 1.43–1.22 (m, 10H), 0.90 (s, 9H), 0.05 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 146.8, 74.4, 63.4, 36.1, 32.9, 29.41, 29.39, 28.9, 28.4, 26.1, 25.8, 18.5, –5.2. The spectroscopic data were in agreement with the literature values.[S3]

**5-[(4-Methoxyphenyl)methoxy]-1-(trimethylsilyl)-1-pentyn-3-ol (*rac*-11)**

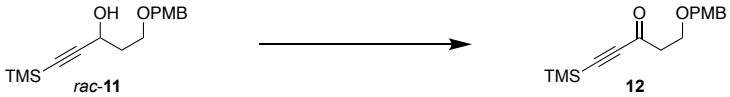



To an ice-cold solution of 1,3-propanediol (2.48 g, 32.6 mmol) in THF (55 mL) was added NaH (55% dispersion in mineral oil, 711 mg, 16.3 mmol). After 1 h, TBAI (1.20 g, 3.25 mmol) and PMBCl (2.22 mL, 16.3 mmol) were added. The mixture was stirred at room temperature for 2 d and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc four times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was semi-purified by chromatography on silica gel (hexane/EtOAc) to give alcohol, which was used for the next reaction without further purification.

To an ice-cold solution of the above alcohol in $CH_2Cl_2$ (36 mL) and DMSO (9.1 mL) were added $Et_3N$ (9.47 mL, 67.9 mmol) and $SO_3$·py (6.50 g, 40.7 mmol). The mixture was stirred at room temperature for 1 h, and diluted with $H_2O$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was passed through a short column of silica gel (hexane/EtOAc) to give the crude aldehyde, which was used for the next reaction without further purification.

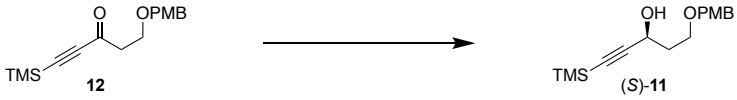
To an ice-cold solution of trimethylsilylacetylene (2.26 mL, 16.3 mmol) in THF (45 mL) was added *n*-BuLi (1.56 M in hexane, 9.59 mL, 15.0 mmol). After 1 h at 0 ºC, the solution was cooled to –78 ºC and added above aldehyde in THF (2 mL). The mixture was stirred at –78 ºC for 1.5 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give racemic alcohol *rac*-**11** (3.04 g, 64% from PMBCl): colorless oil; $R_f$ = 0.41 (hexane/EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.26 (dm, $J$ = 8.8 Hz, 2H), 6.88 (dm, $J$ = 8.8 Hz, 2H), 4.58 (dt, $J$ = 6.4, 4.4 Hz, 1H), 4.48 (d, $J$ = 11.2 Hz, 1H), 4.44 (d, $J$ = 11.2 Hz, 1H), 3.83 (ddd, $J$ = 9.2, 8.4, 4.0 Hz, 1H), 3.80 (s, 3H), 3.65 (ddd, $J$ = 9.2, 6.4, 4.4 Hz, 1H), 3.10 (d, $J$ = 6.4 Hz, 1H), 2.06 (ddt, $J$ = 14.4, 8.4, 4.4 Hz, 1H), 1.93 (ddt, $J$ = 14.4, 6.4, 4.0 Hz, 1H), 0.17 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 159.3, 130.0, 129.4, 113.9, 106.2, 89.4, 73.1, 67.5, 62.0, 55.3, 36.7, 0.0. The spectroscopic data were in agreement with the literature values.[S1]

**5-[(4-Methoxyphenyl)methoxy]-1-(trimethylsilyl)pent-1-yn-3-one (12)**



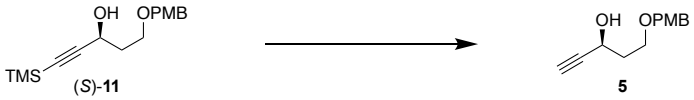

To an ice-cold solution of racemic alcohol *rac*-**11** (5.71 g, 19.5 mmol) in $CH_2Cl_2$ (66 mL) were added Celite (12.61 g) and PCC (6.32 g, 29.3 mmol). After 18 h, the mixture was diluted with hexane and filtered through a pad of Celite. The filtrate was concentrated and the residue was purified by chromatography on silica gel (hexane/EtOAc) to give ketone **12** (5.41 g, 96%): colorless oil; $R_f$ = 0.58 (hexane/EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.25 (dm, $J$ = 8.0 Hz, 2H), 6.87 (dm, $J$ = 8.0 Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.79 (t, $J$ = 6.0 Hz, 2H), 2.84 (t, $J$ = 6.0 Hz, 2H), 0.23 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 185.6, 159.3, 130.1, 129.4, 113.8, 101.8, 98.4, 72.9, 64.5, 55.3, 45.5, –0.7. The spectroscopic data were in agreement with the literature values.[S4]

**(3*S*)-5-[(4-Methoxyphenyl)methoxy]-1-(trimethylsilyl)-1-pentyn-3-ol [(*S*)-11]**




A mixture of RuCl[(*S*,*S*)-TsDPEN](*p*-cymene) (356 mg, 0.560 mmol) and KOH (623 mg, 11.1 mmol) in $CH_2Cl_2$ (3 mL) was stirred at room temperature for 15 min. The mixture was washed with $H_2O$ several times. The $CH_2Cl_2$ solution was transferred to another flask. The solution was dried over $CaH_2$, decanted, and concentrated to afford a purple solid, to which *i*-PrOH (30 mL) and a solution of ketone **12** (5.41 g, 18.5 mmol) in *i*-PrOH (7 mL) were added. After 1 h of stirring at room temperature, organic solvents were removed by evaporation. The residue was purified by chromatography on silica gel to afford optically active alcohol (*S*)-**11** (5.31 g, 98%): 96% ee by HPLC analysis (Chiralcel OD-H, hexane/*i*-PrOH = 49:1, 0.5 mL/min, 35 ºC, $t_R$/min 24.5 (*R*-isomer, minor) and 26.6 (*S*-isomer, major)); colorless oil; $R_f$ = 0.41 (hexane/EtOAc = 3:1); $[\alpha]_D^{24}$ –25 (*c* 1.24, $CHCl_3$). The $^1$H and $^{13}$C NMR spectra were identical with those of the racemic alcohol *rac*-**11**.

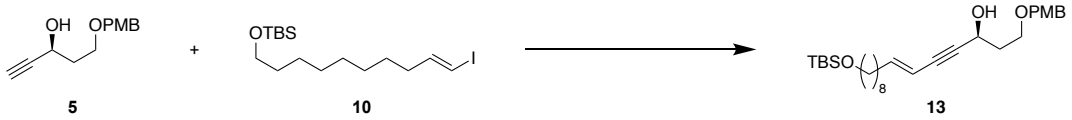
**(3*S*)-5-[(4-Methoxyphenyl)methoxy]-1-pentyn-3-ol (5)**




To an ice-cold solution of alcohol (*S*)-**11** (1.81 g, 6.19 mmol) in MeOH (20 mL) was added $K_2CO_3$ (1.29 g, 9.33 mmol). The mixture was stirred at room temperature for 1 h and concentrated. The residue was diluted with $Et_2O$ and saturated $NH_4Cl$. The mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give acetylene **5** (1.34 g, 98%): colorless oil; $R_f$ =

0.40 (hexane/EtOAc = 2:1); $[\alpha]_D^{26}$ –25 (*c* 1.01, $CHCl_3$); IR (neat) 3407, 3289, 1250, 1093 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.26 (dm, *J* = 8.8 Hz, 2H), 6.88 (dm, *J* = 8.8 Hz, 2H), 4.60 (tdd, *J* = 6.4, 4.4, 2.4 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 3.85 (ddd, *J* = 9.6, 8.4, 4.0 Hz, 1H), 3.80 (s, 3H), 3.66 (ddd, *J* = 9.6, 6.4, 4.4 Hz, 1H), 3.21 (dd, *J* = 6.4, 2.0 Hz, 1H), 2.45 (d, *J* = 2.4 Hz, 1H), 2.09 (ddt, *J* = 14.8, 8.4, 4.4 Hz, 1H), 1.94 (ddt, *J* = 14.8, 6.4, 4.0 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.4, 129.9, 129.4, 113.9, 84.4, 73.1, 73.0, 67.3, 61.4, 55.3, 36.5; HRMS (FD) calcd for $C_{13}H_{16}O_3$ $[M]^+$ 220.10994, found 220.11002.

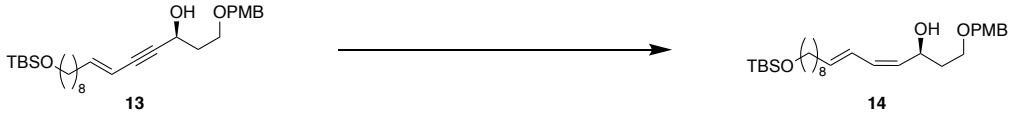
**(*S*,*E*)-15-[(*tert*-Butyldimethylsilyl)oxy]-1-[(4-methoxybenzyl)oxy]pentadec-6-en-4-yn-3-ol (13)**




**5** **10** **13**

To an ice-cold solution of acetylene **5** (3.14 g, 14.3 mmol) and *trans*-iodoolefin **10** (6.21 g, 15.7 mmol) in *t*-$BuNH_2$ (48 mL) was added CuI (271 mg, 1.42 mmol). After 5 min, $Pd(PPh_3)_4$ (824 mg, 0.713 mmol) was added and gently bubbled with Ar gas for 15 min. The mixture was stirred at room temperature for 1 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give enyne **13** (6.69 g, 96%): ocher liquid; $R_f$ = 0.41 (hexane/EtOAc = 3:1); $[\alpha]_D^{24}$ –16 (*c* 0.998, $CHCl_3$); IR (neat) 3419, 1249, 1099, 836 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.26 (dm, *J* = 8.8 Hz, 2H), 6.88 (dm, *J* = 8.8 Hz, 2H), 6.12 (dt, *J* = 16.0, 7.2 Hz, 1H), 5.47 (dq, *J* = 16.0, 1.6 Hz, 1H), 4.75–4.65 (m, 1H), 4.47 (s, 2H), 3.82 (ddd, *J* = 9.3, 8.2, 4.0 Hz, 1H), 3.80 (s, 3H), 3.65 (ddd, *J* = 9.3, 6.0, 4.4 Hz, 1H), 3.60 (t, *J* = 6.4 Hz, 2H), 3.03 (d, *J* = 6.0 Hz, 1H), 2.15–2.02 (m, 3H), 1.95 (dtd, *J* = 14.4, 6.0, 4.0 Hz, 1H), 1.50 (quint., *J* = 6.4 Hz, 2H), 1.43–1.22 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.4, 145.4, 130.1, 129.4, 113.9, 109.0, 88.0, 83.8, 73.1, 67.6, 63.4, 62.1, 55.4, 37.0, 33.1, 32.9, 29.5, 29.4, 29.1, 28.8, 26.1, 25.9, 18.5, –5.2; HRMS (FD) calcd for $C_{29}H_{48}O_4Si_1$ $[M]^+$ 488.33218, found 488.33111.

**(*S*,4*Z*,6*E*)-15-[(*tert*-Butyldimethylsilyl)oxy]-1-[(4-methoxybenzyl)oxy]pentadeca-4,6-dien-3-ol (14)**

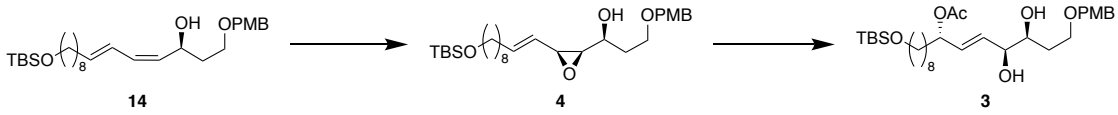



**13** **14**

A suspension of Zn powder (15.03 g, 229.9 mmol) in $H_2O$ (50 mL) was gently bubbled with argon gas for 15 min and $Cu(OAc)_2$ (2.09 g, 11.5 mmol) was added. After 20 min, $AgNO_3$ (1.95 g, 11.5 mmol) was added. The suspension was stirred for 30 min and filtered by suction and the remaining solid was washed with $H_2O$ (50 mL), MeOH (50 mL), acetone (100 mL), and $Et_2O$ (50 mL), twice

respectively. The active Zn solids were added to a solution of MeOH (30 mL) and $H_2O$ (35 mL). TMSCl (5.81 mL, 46.0 mmol) was added to the mixture. The mixture was stirred for 10 min and a solution of enyne **13** (2.25 g, 4.60 mmol) in MeOH (5 mL) was added. After being stirred for 4 d, the mixture was filtered through a pad of Celite and the filtrate was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give diene **14** (2.13 g, 94%): colorless oil; $R_f$ = 0.37 (hexane/EtOAc = 3:1); $[\alpha]_D^{25}$ +26 (*c* 1.02, $CHCl_3$); IR (neat) 3430, 1513, 1249, 1097 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.26 (dm, *J* = 8.8 Hz, 2H), 6.88 (dm, *J* = 8.8 Hz, 2H), 6.32 (ddd, *J* = 14.8, 11.0, 0.8 Hz, 1H), 6.00 (t, *J* = 11.0 Hz, 1H), 5.72 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.30 (dd, *J* = 11.0, 9.0 Hz, 1H), 4.84–4.73 (m, 1H), 4.45 (s, 2H), 3.80 (s, 3H), 3.67 (ddd, *J* = 9.5, 6.0, 4.8 Hz, 1H), 3.63–3.54 (m, 1H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.60 (d, *J* = 2.8 Hz, 1H), 2.08 (q, *J* = 7.2 Hz, 2H), 1.91 (dtd, *J* = 14.6, 8.0, 4.8 Hz, 1H), 1.75 (ddt, *J* = 14.6, 6.0, 4.8 Hz, 1H), 1.50 (quint., *J* = 6.8 Hz, 2H), 1.43–1.22 (m, 10H), 0.89 (s, 9H), 0.05 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 159.3, 137.3, 130.9, 130.2, 129.4, 125.2, 113.9, 73.0, 68.1, 67.3, 63.4, 55.4, 37.0, 33.0, 29.6, 29.5, 29.34, 29.29, 26.1, 25.9, 18.5, –5.2; HRMS (FD) calcd for $C_{29}H_{51}O_4Si_1$ $[M+H]^+$ 491.35566, found 491.35802.

**(3*S*,4*S*,7*R*,*E*)-15-[(*tert*-Butyldimethylsilyl)oxy]-3,4-dihydroxy-1-[(4-methoxybenzyl)oxy]pentadec-5-en-7-yl acetate (3)**

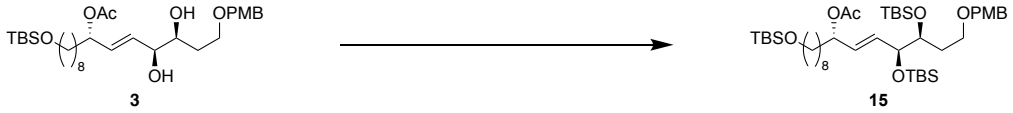



To an ice-cold mixture of diene **14** (1.41 g, 2.87 mmol) and $NaHCO_3$ (482 mg, 5.74 mmol) in $CH_2Cl_2$ (96 mL) was added *m*-CPBA (72% purity, 825 mg, 3.44 mmol). After 3 h at –10 °C, $Me_2S$ (0.064 mL, 0.87 mmol) was added. The mixture was stirred at –10 °C for 10 min, and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with $CH_2Cl_2$ three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated to give the crude epoxide **4**, which was used for the next reaction without further purification.

To an ice-cold mixture of $Pd(PPh_3)_4$ (166 mg, 0.144 mmol) and AcOH (0.25 mL, 4.4 mmol) in THF (10 mL) was added a solution of the above epoxide **4** in THF (2 mL). After 4 h at 0 °C, $H_2O_2$ (35% in $H_2O$, 0.29 mL, 9.6 mmol) was added. The mixture was stirred at room temperature for 15 min and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give acetate **3** (792 mg, 49% from diene **14**): colorless oil; $R_f$ = 0.51 (hexane/EtOAc = 1:1); $[\alpha]_D^{24}$ –12 (*c* 0.645, $CHCl_3$); IR (neat) 3452, 1735, 1247, 1097 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.24 (dm, *J* = 8.8 Hz, 2H), 6.88 (dm, *J* = 8.8 Hz, 2H), 5.76–5.65 (m, 2H), 5.27–5.19 (m, 1H), 4.45 (s, 2H), 3.99–3.93 (m, 1H), 3.81 (s, 3H), 3.73–3.61 (m,

3H), 3.59 (t, $J$ = 6.8 Hz, 2H), 3.29 (d, $J$ = 3.2 Hz, 1H), 2.78 (d, $J$ = 3.6 Hz, 1H), 2.04 (s, 3H), 1.78 (q, $J$ = 5.6 Hz, 2H), 1.70–1.42 (m, 4H), 1.39–1.20 (m, 10H), 0.89 (s, 9H), 0.46 (s, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.5, 159.4, 131.7, 131.6, 129.8, 129.5, 114.0, 75.0, 74.2, 73.9,73.1, 68.2, 63.4, 55.4, 34.4, 32.9, 32.5, 29.6, 29.44, 29.40, 26.1, 25.9, 25.2, 21.4, 18.5, –5.2; HRMS (FD) calcd for $C_{31}H_{54}O_7Si_1$ $[M]^+$ 566.36388, found 566.36581.

**(5*S*,6*S*,9*R*,*E*)-6-[(*tert*-Butyldimethylsilyl)oxy]-5-[2-[(4-methoxybenzyl)oxy]ethyl]-2,2,3,3,19,19,20,20-octamethyl-4,18-dioxa-3,19-disilahenicos-7-en-9-yl acetate (15)**




A solution of acetate **3** (780 mg, 1.38 mmol), imidazole (562 mg, 8.25 mmol), and TBSCl (830 mg, 5.51 mmol) in DMF (10 mL) was stirred at room temperature for 37 h, and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with hexane three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give trisilyl ether **15** (1.00 g, 91%): colorless oil; $R_f$ = 0.50 (hexane/EtOAc = 10:1); $[\alpha]_D^{27}$ –39 ($c$ 1.05, $CHCl_3$); IR (neat) 1741, 1249, 1103 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.24 (dm, $J$ = 8.8 Hz, 2H), 6.86 (dm, $J$ = 8.8 Hz, 2H), 5.78 (dd, $J$ = 15.6, 4.8 Hz, 1H), 5.60 (ddd, $J$ = 15.6, 6.6, 1.2 Hz, 1H), 5.26 (q, $J$ = 6.6 Hz, 1H), 4.40 (s, 2H), 4.14 (td, $J$ = 4.8, 1.2 Hz, 1H), 3.80 (s, 3H), 3.75 (ddd, $J$ = 8.8, 4.8, 2.8 Hz, 1H), 3.59 (t, $J$ = 6.8 Hz, 2H), 3.47 (dd, $J$ = 8.0, 5.6 Hz, 2H), 2.02 (s, 3H), 1.93 (dtd, $J$ = 13.8, 8.0, 2.8 Hz, 1H), 1.69–1.45 (m, 4H), 1.40 (ddt, $J$ = 13.8, 8.8, 5.6 Hz, 1H), 1.35–1.20 (m, 10H), 0.89 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 6H), 0.03 (s, 3H), 0.02 (s, 3H), 0.01 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 159.0, 131.2, 131.0, 129.3, 129.1, 113.7, 74.5, 74.3, 72.2, 72.1, 67.0, 63.4, 55.3, 34.7, 33.0, 31.1, 29.6, 29.5, 26.1, 25.9, 25.3, 21.3, 18.5, 18.3, 18.0, –4.2, –4.6, –4.8, –5.2; HRMS (FD) calcd for $C_{43}H_{82}O_7Si_3$ $[M]^+$ 794.53683, found 794.53831.

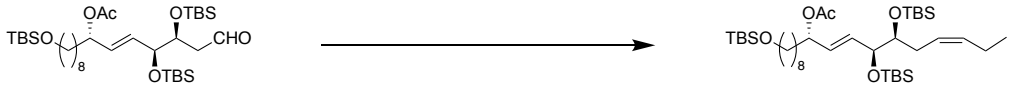
**(5*S*,6*S*,9*R*,*E*)-6-[(*tert*-Butyldimethylsilyl)oxy]-2,2,3,3,19,19,20,20-octamethyl-5-(2-oxoethyl)-4,18-dioxa-3,19-disilahenicos-7-en-9-yl acetate (16)**


To an ice-cold solution of trisilyl ether **15** (1.03 g, 1.29 mmol) in $CH_2Cl_2$ (4 mL) and $H_2O$ (0.2 mL) was added DDQ (354 mg, 1.56 mmol). The mixture was stirred at 0 °C for 1.5 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with $CH_2Cl_2$ three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was passed through a silica gel

(hexane/EtOAc) to give the crude alcohol, which was used for the next reaction without further purification.

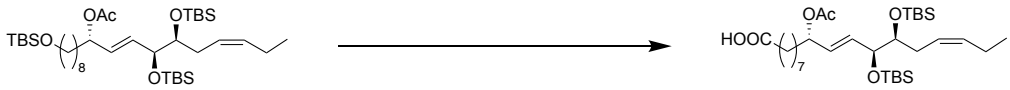
To a solution of the above alcohol in $CH_2Cl_2$ (10 mL) were added NaOAc (149 mg, 1.82 mmol), Celite (784 mg), and PCC (392 mg, 1.82 mmol). After 2 h, the mixture was diluted with hexane and filtered through a pad of Celite. The filtrate was concentrated and the residue was purified by chromatography on silica gel (hexane/EtOAc) to give aldehyde **16** (695 mg, 80% from trisilyl ether **15**): colorless oil; $R_f$ = 0.45 (hexane/EtOAc = 10:1); $[\alpha]_D^{25}$ –49 (*c* 1.14, $CHCl_3$); IR (neat) 1739, 1254, 1106 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.75 (dd, *J* = 2.4, 2.0 Hz, 1H), 5.77 (ddd, *J* = 15.6, 4.0 Hz, 1H), 5.64 (ddd, *J* = 15.6, 6.4 Hz, 1H), 5.27 (q, *J* = 6.4 Hz, 1H), 4.23–4.15 (m, 2H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.59 (ddd, *J* = 16.0, 4.0, 2.0 Hz, 1H), 2.35 (ddd, *J* = 16.0, 6.8, 2.4 Hz, 1H), 2.03 (s, 3H), 1.71–1.42 (m, 4H), 1.40–1.20 (m, 10H), 0.89 (s, 9H), 0.88 (s, 9H), 0.87 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H), 0.05 (s, 9H), 0.03 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 201.6, 170.4, 130.4, 130.2, 74.2, 73.8, 70.8, 63.4, 46.1, 34.6, 33.0, 29.6, 29.5, 29.4, 26.1, 25.84, 25.76, 25.3, 21.3, 18.5, 18.2, 17.9, –4.5, –4.7, –4.8, –4.9, –5.2; HRMS (FD) calcd for $C_{35}H_{73}O_6Si_3$ $[M+H]^+$ 673.47149, found 673.47216.

**(5*S*,6*S*,9*R*,*E*)-6-[(*tert*-Butyldimethylsilyl)oxy]-2,2,3,3,19,19,20,20-octamethyl-5-[(*Z*)-pent-2-en-1-yl]-4,18-dioxa-3,19-disilahenicos-7-en-9-yl acetate (17)**




To an ice-cold solution of propyltriphenylphosphonium bromide (3.21 g, 8.33 mmol) in THF (18 mL) and HMPA (3.0 mL, 0.017 mmol) was added NaHMDS (1.0 M solution in THF, 6.25 mL, 6.25 mmol). The mixture was stirred at 0 ºC for 1 h, and cooled to –90 ºC. A solution of aldehyde **16** (1.40 g, 2.08 mmol) in THF (2 mL) was added to the mixture dropwise. The solution was stirred at –90 ºC for 1 h and diluted with $H_2O$ and saturated $NH_4Cl$. The resulting mixture was extracted with hexane three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give *cis*-olefin **17** (1.13 g, 78%): colorless oil; $R_f$ = 0.23 (hexane/EtOAc = 30:1); $[\alpha]_D^{26}$ –44 (*c* 1.01, $CHCl_3$); IR (neat) 1743, 1255, 1101 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.80 (ddd, *J* = 15.6, 4.2, 0.8 Hz, 1H), 5.61 (ddd, *J* = 15.6, 6.8, 1.2 Hz, 1H), 5.44–5.31 (m, 2H), 5.27 (q, *J* = 6.8 Hz, 1H), 4.14 (td, *J* = 4.2, 1.2 Hz, 1H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.55 (ddd, *J* = 8.8, 4.2, 3.2 Hz, 1H), 2.30 (ddd, *J* = 14.9, 5.4, 3.2 Hz, 1H), 2.03 (s, 3H), 2.08–1.94 (m, 2H), 1.88 (ddd, *J* = 14.9, 8.8, 6.8 Hz, 1H), 1.70–1.44 (m, 4H), 1.37–1.21 (m, 10H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.88 (s, 9H), 0.045 (s, 9H), 0.038 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 132.8, 131.6, 129.1, 126.8, 76.0, 74.6, 74.5, 63.4, 34.7, 33.0, 29.6, 29.5, 29.1, 26.1, 25.92, 25.88, 25.3, 21.4, 20.6, 18.5, 18.2, 18.0, 14.4, –4.3, –4.4, –4.6, –4.8, –5.2; HRMS was not detected by FD-MS.

**(9*R*,10*E*,12*S*,13*S*,15*Z*)-9-Acetoxy-12,13-bis[(*tert*-butyldimethylsilyl)oxy]octadeca-10,15-dienoic acid (18)**



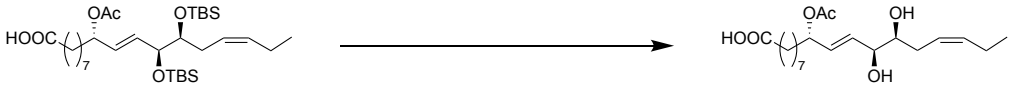

To an ice-cold solution of *cis*-orefin **17** (1.13 g, 1.62 mmol) in $CH_2Cl_2$ (3 mL) and MeOH (3 mL) was added PPTS (404 mg, 1.61 mmol). The mixture was stirred at room temperature for 3 h, and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give the crude alcohol (891 mg, 94%): colorless oil; $R_f$ = 0.37 (hexane/EtOAc = 3:1); $[\alpha]_D^{27}$ –53 (*c* 0.985, $CHCl_3$); IR (neat) 3363, 1742, 1252, 1102 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.81 (dd, *J* = 15.6, 4.8 Hz, 1H), 5.61 (ddd, *J* = 15.6, 6.8, 1.2 Hz, 1H), 5.45–5.31 (m, 2H), 5.27 (q, *J* = 6.8 Hz, 1H), 4.14 (td, *J* = 4.8, 1.2 Hz, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.55 (ddd, *J* = 9.2, 4.8, 3.2 Hz, 1H), 2.30 (ddd, *J* = 14.0, 5.4, 3.2 Hz, 1H), 2.03 (s, 3H), 2.09–1.94 (m, 2H), 1.88 (ddd, *J* = 14.0, 9.2, 6.0 Hz, 1H), 1.71–1.47 (m, 4H), 1.41–1.21 (m, 10H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.042 (s, 3H), 0.039 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 132.8, 131.6, 129.1, 126.8, 76.0, 74.6, 74.5, 63.1, 34.6, 32.9, 29.5, 29.4, 29.1, 25.92, 25.88, 25.8, 25.2, 21.4, 20.6, 18.2, 18.0, 14.4, –4.3, –4.4, –4.6, –4.8; HRMS was not detected by FD-MS.

To an ice-cold solution of the above alcohol (851 mg, 1.45 mmol) in $CH_2Cl_2$ (7 mL) were added Celite (940 mg) and PCC (470 mg, 2.18 mmol). After being stirred for 3 h, the mixture was diluted with hexane and filtered through a pad of Celite. The filtrate was concentrated and the residue was passed through a short column of silica gel (hexane/EtOAc) to give the crude aldehyde, which was used for next reaction without further purification.

To a solution of the above aldehyde in *t*-BuOH (1.8 mL) and $H_2O$ (3.0 mL) were added 2-methyl-2-butene (0.77 mL, 7.3 mmol), $NaH_2PO_4 \cdot 2H_2O$ (249 mg, 1.60 mmol), and $NaClO_2$ (70% purity, 656 mg, 5.08 mmol). The mixture was stirred at room temperature for 35 min and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give carboxylic acid **18** (804 mg, 93% from alcohol): colorless liquid; $R_f$ = 0.58 (hexane/EtOAc = 2:1); $[\alpha]_D^{25}$ –52 (*c* 0.980, $CHCl_3$); IR (neat) 2931 (br), 1742, 1712, 1239, 1101 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.81 (dd, *J* = 15.6, 4.4 Hz, 1H), 5.61 (ddd, *J* = 15.6, 6.8, 1.6 Hz, 1H), 5.46–5.31 (m, 2H), 5.27 (q, *J* = 6.8 Hz, 1H), 4.14 (td, *J* = 4.4, 1.6 Hz, 1H), 3.55 (ddd, *J* = 8.8, 4.4, 3.2 Hz, 1H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.30 (ddd, *J* = 14.0, 5.4, 3.2 Hz, 1H), 2.03 (s, 3H), 2.11–1.94 (m, 2H), 1.93–1.83 (m, 1H), 1.71–1.49 (m, 4H), 1.40–1.22 (m, 8H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.044 (s, 3H), 0.040 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$

179.8, 170.5, 132.8, 131.7, 129.0, 126.7, 75.9, 74.55, 74.52, 34.6, 34.1, 29.3, 29.2, 29.1, 25.92, 25.88, 25.2, 24.7, 21.3, 20.6, 18.2, 18.0, 14.3, –4.3, –4.4, –4.6, –4.8; HRMS was not detected by FD-MS.

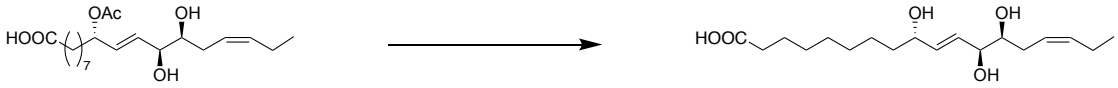
**(9*R*,10*E*,12*S*,13*S*,15*Z*)-9-Acetoxy-12,13-dihydroxyoctadeca-10,15-dienoic acid (19)**




**18** **19**

To an ice-cold solution of acetate **18** (722 mg, 1.21 mmol) in THF (3 mL) was added TBAF (1.0 M in THF 6.03 mL, 6.03 mmol). The mixture was stirred at room temperature for 2 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc four times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/EtOAc) to give diol **19** (350 mg, 78%): colorless liquid: $R_f$ = 0.31 ($CH_2Cl_2$/EtOAc = 1:2); $[\alpha]_D^{26}$ –37 (*c* 0.605, $CHCl_3$); IR (neat) 3422 (br), 1737, 1713, 1241 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.78–5.66 (m, 2H), 5.62–5.48 (m, 1H), 5.45–5.32 (m, 1H), 5.29–5.14 (m, 1H), 4.08–3.93 (m, 1H), 3.52 (dt, *J* = 6.8, 5.6 Hz, 1H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.38–2.16 (m, 2H), 2.05 (s, 3H), 2.12–1.99 (m, 2H), 1.71–1.50 (m, 4H), 1.39–1.23 (m, 8H), 0.97 (t, *J* = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 178.4, 170.6, 135.4, 132.1, 131.6, 123.7, 74.6, 74.3, 74.1, 34.2, 33.9, 30.9, 28.7, 28.6, 28.4, 24.6, 24.5, 21.4, 20.8, 14.3; HRMS (FD) calcd for $C_{20}H_{35}O_6$ $[M+H]^+$ 371.24336, found 371.24183.

**Fulgidic acid (1)**




**19** Fulgidic acid (**1**)

To an ice-cold solution of diol **19** (302 mg, 0.815 mmol) in MeOH (2.7 mL) was added NaOMe (132 mg, 2.44 mmol). The mixture was stirred at room temperature for 5 h, and added NaOMe (84.0 mg, 1.55 mmol). After being stirred at room temperature for 2 h, the mixture was diluted with a solution of AcCl in MeOH until the mixture became pH 7. The solution was removed by evaporation. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/MeOH) to give fulgidic acid (**1**) (238 mg, 89%): white solid mp 79.8–80.6 ºC; $R_f$ = 0.43 ($CH_2Cl_2$/MeOH = 5:1); $[\alpha]_D^{22}$ –14 (*c* 1.06, $CHCl_3$) [lit.[S5] $[\alpha]_D^{25}$ –12 (*c* 0.705, $CHCl_3$)]; IR (neat) 3544, 3335 (br), 3014, 1695, 1264 $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 5.78–5.66 (m, 2H), 5.55–5.40 (m, 2H), 4.05 (q, *J* = 6.8 Hz, 1H), 3.96 (t, *J* = 5.6 Hz, 1H), 3.49–3.42 (m, 1H), 2.35 (ddd, *J* = 14.5, 6.0, 4.0 Hz, 1H), 2.27 (t, *J* = 7.2 Hz, 2H), 2.19–2.00 (m, 3H), 1.60 (quint., *J* = 7.2 Hz, 2H), 1.55–1.27 (m, 10H), 0.97 (t, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CD_3OD$) $\delta$ 177.7 (–), 136.5 (+), 134.3 (+), 131.1 (+), 126.4 (+), 75.9 (+), 75.8 (+), 73.0 (+), 38.3 (–), 34.9 (–), 31.5 (–), 30.6 (–), 30.4 (–), 30.2 (–), 26.5 (–), 26.1 (–), 21.7 (–), 14.6 (+); HRMS (FD) calcd for $C_{18}H_{32}O_5$ $[M]^+$ 328.22497, found 328.22630.

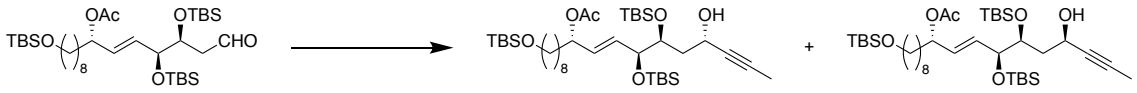
**Table S1** Comparison of $^{1}$H NMR data between the reported **1** and synthesized **1**

| NO. | reported **1** (400 MHz, $CD_3OD$)[S6] | synthesized **1** (400 MHz, $CD_3OD$) |
|---|---|---|
| 1 | 0.97, t (7.6 Hz) | 0.97, t (7.2 Hz) |
| 2 | 1.38–1.29, m | 1.55–1.27, m |
| 3 | 1.55–1.46, m | |
| 4 | 1.64–1.55, m | 1.60, quint. (7.2 Hz) |
| 5 | 2.16–2.02, m | 2.19–2.00, m |
| 6 | 2.28, t (7.5 Hz) | 2.27, t (7.2 Hz) |
| 7 | 2.35, dt (14.6, 4.9 Hz) | 2.35, ddd (14.5, 6.0, 4.0 Hz) |
| 8 | 3.48–3.43, m | 3.49–3.42, m |
| 9 | 3.96, t (4.9 Hz) | 3.96, t (5.6 Hz) |
| 10 | 4.05, q (5.1 Hz) | 4.05, q (6.8 Hz) |
| 11 | 5.50–5.41, m | 5.55–5.39, m |
| 12 | 5.77–5.67, m | 5.78–5.65, m |

**Table S2** Comparison of $^{13}C$ NMR data between the reported **1** and synthesized **1**

| NO. | reported **1** (100 MHz, $CD_3OD$)[S6] | synthesized **1** (100 MHz, $CD_3OD$) |
|---|---|---|
| 1 | 14.6 | 14.6 |
| 2 | 21.7 | 21.7 |
| 3 | 26.1 | 26.1 |
| 4 | 26.5 | 26.5 |
| 5 | 30.2 | 30.2 |
| 6 | 30.4 | 30.4 |
| 7 | 30.6 | 30.6 |
| 8 | 31.5 | 31.5 |
| 9 | 35.1 | 34.9 |
| 10 | 38.3 | 38.3 |
| 11 | 73.0 | 73.0 |
| 12 | 75.8 | 75.8 |
| 13 | 75.9 | 75.9 |
| 14 | 126.4 | 126.4 |
| 15 | 131.1 | 131.1 |
| 16 | 134.3 | 134.3 |
| 17 | 136.5 | 136.5 |
| 18 | 177.9 | 177.7 |

**(5*S*,6*S*,9*S*,*E*)-6-[(*tert*-Butyldimethylsilyl)oxy]-5-[(S)-2-hydroxypent-3-yn-1-yl]-2,2,3,3,19,19,20,20-octamethyl-4,18-dioxa-3,19-disilahenicos-7-en-9-yl acetate [(15*S*)-20] and (5*S*,6*S*,9*S*,*E*)-6-[(*tert*-butyldimethylsilyl)oxy]-5-[(R)-2-hydroxypent-3-yn-1-yl]-2,2,3,3,19,19,20,20-octamethyl-4,18-dioxa-3,19-disilahenicos-7-en-9-yl acetate [(15*R*)-20]**

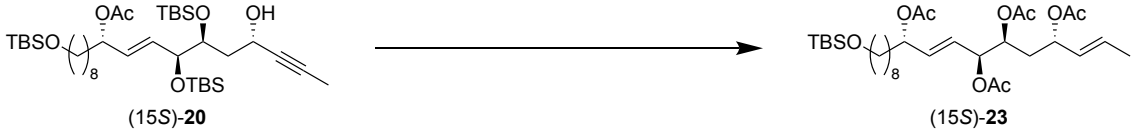



To a solution of propyne (1.0 M in THF, 3.68 mL, 3.68 mmol) in THF (12 mL) was added *n*-BuLi (1.6 M in hexane, 1.15 mL, 1.84 mmol) at –78 ºC. After 2 h at –78 ºC, a solution of aldehyde **16** (826 mg, 1.23 mmol) in THF (2 mL) was added. The solution was stirred at –78 ºC for 80 min and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give alcohol (15*S*)-**20** (239 mg, 27%) and alcohol (15*R*)-**20** (566 mg, 65%).

(15*S*)-**20**: colorless oil; $R_f$ = 0.63 (hexane/EtOAc = 5:1); $[\alpha]_D^{25}$ –45 (*c* 0.940, $CHCl_3$); IR (neat) 3480, 1742, 1253, 1104 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.79 (ddd, *J* = 15.6, 4.4, 0.8 Hz, 1H), 5.62 (ddd, *J* = 15.6, 6.4, 1.6 Hz, 1H), 5.27 (q, *J* = 6.4 Hz, 1H), 4.50–4.38 (m, 1H), 4.20 (td, *J* = 4.4, 1.6 Hz, 1H), 3.97 (dt, *J* = 8.4, 4.4 Hz, 1H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.59 (d, *J* = 5.2 Hz, 1H), 2.03 (s, 3H), 1.92 (ddd, *J* = 14.4, 8.8, 4.0 Hz, 1H), 1.83 (d, *J* = 2.4 Hz, 3H), 1.68–1.45 (m, 4H), 1.61 (dt, *J* = 14.4, 3.2 Hz, 1H), 1.39–1.22 (m, 10H), 0.90 (s, 9H), 0.89 (s, 18H), 0.12 (s, 3H), 0.10 (s, 3H), 0.07 (s, 3H), 0.05 (s, 9H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 130.5, 129.9, 80.8, 80.5, 74.4, 74.2, 72.5, 63.4, 60.0, 39.7, 34.6, 33.0, 29.6, 29.48, 29.46, 26.1, 25.9, 25.3, 21.3, 18.5, 18.3, 18.0, 3.7, –4.1, –4.67, –4.74, –4.9, –5.2; HRMS (FD) calcd for $C_{38}H_{77}O_6Si_3$ $[M]^+$ 713.50279, found 713.50166.

(15*R*)-**20**: colorless oil; $R_f$ = 0.50 (hexane/EtOAc = 5:1); $[\alpha]_D^{26}$ –40 (*c* 0.935, $CHCl_3$); IR (neat) 3437, 1741, 1255, 1102 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.78 (ddd, *J* = 15.6, 4.2, 0.8 Hz, 1H), 5.61 (ddd, *J* = 15.6, 6.4, 1.2 Hz, 1H), 5.27 (q, *J* = 6.4 Hz, 1H), 4.47–4.36 (m, 1H), 4.20 (td, *J* = 4.2, 1.2 Hz, 1H), 4.02 (dt, *J* = 7.2, 5.2 Hz, 1H), 3.59 (t, *J* = 6.8 Hz, 2H), 3.06 (d, *J* = 7.2 Hz, 1H), 2.03 (s, 3H), 1.94 (ddd, *J* = 13.9, 6.8, 5.2 Hz, 1H), 1.83 (d, *J* = 1.6 Hz, 3H), 1.69–1.44 (m, 4H), 1.64 (ddd, *J* = 13.9, 7.2, 6.0 Hz, 1H), 1.35–1.21 (m, 10H), 0.92 (s, 9H), 0.89 (s, 9H), 0.10 (s 3H), 0.09 (s, 6H), 0.07 (s, 3H), 0.05 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 130.3, 130.0, 81.3, 80.2, 74.5, 74.4, 72.7, 63.4, 60.8, 40.0, 34.6, 32.9, 29.6, 29.4, 26.1, 25.8, 25.2, 21.3, 18.5, 18.3, 18.0, 3.6, –4.3, –4.7, –4.8, –5.0, –5.2; HRMS (FD) calcd for $C_{38}H_{77}O_6Si_3$ $[M]^+$ 713.50279, found 713.50002. The stereochemistry of (15*S*)-**20** and (15*R*)-**20** was determined by $^1H$ NMR spectrum derived to MTPA ester (See S49).

**(2*E*,4*S*,6*S*,7*S*,8*E*,10*S*)-18-[(*tert*-Butyldimethylsilyl)oxy]octadeca-2,8-diene-4,6,7,10-tetrayl tetraacetate [(15*S*)-23]**



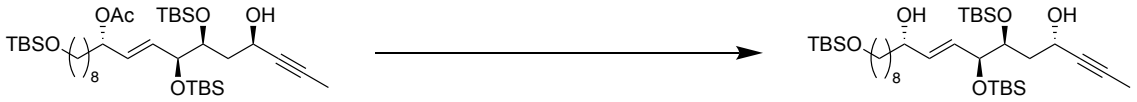

(15*S*)-**20** (15*S*)-**23**

To an ice-cold solution of alcohol (15*S*)-**20** (34.2 mg, 0.0479 mmol) in THF (3 mL) was added Red-Al (65% in toluene, 0.22 mL, 0.73 mmol). The mixture was stirred at 60 °C for 3 h and diluted with EtOAc and saturated Rochelle salt. The resulting mixture was extracted with EtOAc/THF several times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was semi-purified by chromatography on silica gel (EtOAc/MeOH) to give the crude pentaol (15*S*)-**21** and the crude tetraol (15*S*)-**22**, which was used for the next reaction without further purification.

To an ice-cold solution of the above pentaol (15*S*)-**21** in THF (5 mL) were added imidazole (0.90 mg, 0.014 mmol) and TBSCl (1.8 mg, 0.012 mmol). The mixture was stirred at –10 °C for 2 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was semi-purified by chromatography on silica gel (EtOAc) to give the crude tetraol (15*S*)-**22**, which was used for the next reaction without further purification.

To an ice-cold solution of the above tetraol (15*S*)-**22** in $CH_2Cl_2$ (3 mL) were added $Et_3N$ (0.053 mL, 0.38 mmol), DMAP (1.0 mg, 0.0082 mmol), and $Ac_2O$ (0.030 mL, 0.32 mmol). The mixture was stirred at room temperature for 15 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give tetraacetate (15*S*)-**23** [18.5 mg, 63% from alcohol (15*S*)-**20**]: colorless oil; $R_f$ = 0.34 (hexane/EtOAc = 3:1); $[\alpha]_D^{27}$ –32 (*c* 0.930, $CHCl_3$); IR (neat) 1745, 1372, 1233, 837 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.75 (dq, *J* = 15.2, 6.8 Hz, 1H), 5.68 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.57 (dd, *J* = 15.6, 6.0 Hz, 1H), 5.43–5.31 (m, 2H), 5.27–5.12 (m, 3H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.10 (s, 3H), 2.05 (s, 3H), 2.02 (s, 6H), 1.85 (ddd, *J* = 14.4, 10.6, 3.6 Hz, 1H), 1.76 (ddd, *J* = 14.4, 10.4, 4.4 Hz, 1H), 1.68 (d, *J* = 6.8 Hz, 3H), 1.64–1.44 (m, 4H), 1.36–1.19 (m, 10H), 0.89 (s, 9H), 0.04 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 170.3, 170.1, 169.9, 133.3, 129.9, 128.9, 126.5, 74.1, 73.4, 70.3, 69.4, 63.4, 35.2, 34.2, 32.9, 29.6, 29.45, 29.38, 26.1, 25.9, 25.2, 21.3, 21.1, 20.8, 18.5, 17.8, –5.2; HRMS (FD) calcd for $C_{32}H_{57}O_9Si$ $[M+H]^+$ 613.37718, found 613.37999.

**(4*S*,6*S*,7*S*,10*S*,*E*)-6,7,18-tris[(*tert*-Butyldimethylsilyl)oxy]octadec-8-en-2-yne-4,10-diol [(15*S*)-24]**

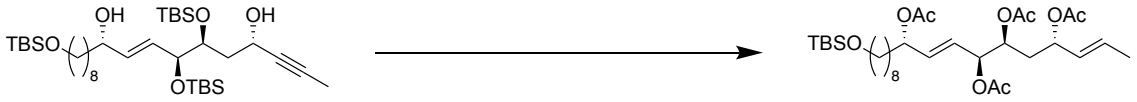



(15*R*)-**20** (15*S*)-**24**

To an ice-cold solution of alcohol (15*R*)-**20** (165 mg, 0.231 mmol) in THF (5 mL) were added $PPh_3$ (90.7 mg, 0.346 mmol), 4-nitrobenzoic acid (57.8 mg, 0.346 mmol), and DIAD (0.067 mL, 0.34 mmol). The mixture was stirred at 0 °C for 35 min and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was passed through a short column of silica gel (hexane/EtOAc) to give crude ester, which was used for the next reaction without further purification.

To an ice-cold solution of the above crude ester in THF (1 mL) and MeOH (1 mL) was added 3 N LiOH (2.31 mL, 6.93 mmol). The mixture was stirred at room temperature for 4 d, and diluted with 1 N HCl. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give diol (15*S*)-**24** [124 mg, 80% from alcohol (15*R*)-**20**]: colorless oil; $R_f$ = 0.45 (hexane/EtOAc = 4:1); $[\alpha]_D^{25}$ –31 (*c* 0.945, $CHCl_3$); IR (neat) 3431, 1472, 1256, 1101, 836 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.79 (dd, *J* = 15.8, 4.0, 1H), 5.72 (ddd, *J* = 15.8, 6.0, 1.2 Hz, 1H), 4.51–4.41 (m, 1H), 4.22 (t, *J* = 4.0 Hz, 1H), 4.15 (q, *J* = 6.0 Hz, 1H), 3.98 (dt, *J* = 8.4, 4.0 Hz, 1H), 3.59 (t, *J* = 6.8 Hz, 2H), 2.69 (d, *J* = 6.0 Hz, 1H), 1.94 (ddd, *J* = 14.6, 9.0, 4.0 Hz, 1H), 1.83 (d, *J* = 2.0 Hz, 3H), 1.68–1.60 (m, 2H), 1.59–1.23 (m, 14H), 0.91 (s, 9H), 0.90 (s, 9H), 0.89 (s, 9H), 0.13 (s 3H), 0.11 (s 3H), 0.08 (s, 3H), 0.06 (s, 3H), 0.05 (s, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 134.6, 128.6, 80.7, 80.5, 74.3, 72.7, 72.6, 63.4, 60.0, 39.7, 37.4, 33.0, 29.7, 29.6, 29.5, 26.1, 25.91, 25.89, 25.5, 18.5, 18.3, 18.0, 3.6, –4.1, –4.6, –4.7, –4.8, –5.2; HRMS (FD) calcd for $C_{36}H_{75}O_{55}Si_3$ $[M+H]^+$ 671.49223, found 671.49006.

**(2*E*,4*S*,6*S*,7*S*,8*E*,10*S*)-18-[(*tert*-Butyldimethylsilyl)oxy]octadeca-2,8-diene-4,6,7,10-tetrayl tetraacetate [(15*S*)-23]**




(15*S*)-**24** (15*S*)-**23**

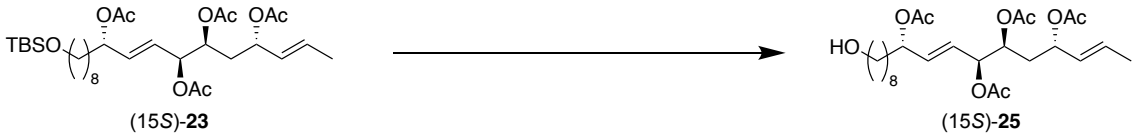
To an ice-cold solution of alcohol diol (15*S*)-**24** (124 mg, 0.185 mmol) in THF (5 mL) was added Red-Al (65% in toluene, 0.83 mL, 2.8 mmol). The mixture was stirred at 60 °C for 3 h and diluted with EtOAc and saturated Rochelle salt. The resulting mixture was extracted with EtOAc/THF several times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was semi-purified by chromatography on silica gel (EtOAc/MeOH) to give the crude pentaol (15*S*)-**21** and the crude

tetraol (15*S*)-**22**, which was used for the next reaction without further purification.

To an ice-cold solution of the above pentaol (15*S*)-**21** in THF (5 mL) were added imidazole (9.5 mg, 0.14 mmol) and TBSCl (18.2 mg, 0.121 mmol). The mixture was stirred at –10 °C for 2 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was semi-purified by chromatography on silica gel (EtOAc) to give the crude tetraol (15*S*)-**22**, which was used for the next reaction without further purification.

To an ice-cold solution of the above tetraol (15*S*)-**22** in $CH_2Cl_2$ (3 mL) were added $Et_3N$ (0.24 mL, 1.7 mmol), DMAP (7.0 mg, 0.057 mmol), and $Ac_2O$ (0.14 mL, 1.5 mmol). The mixture was stirred at room temperature for 21 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give tetraacetate (15*S*)-**23** [72.6 mg, 64% from diol (15*S*)-**24**]. The $^1$H NMR spectrum of (15*S*)-**23** was identical with that obtained from (15*S*)-**20**.

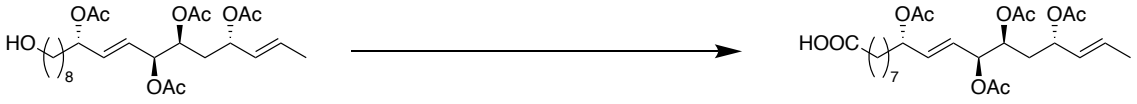
**(2*E*,4*S*,6*S*,7*S*,8*E*,10*S*)-18-Hydroxyoctadeca-2,8-diene-4,6,7,10-tetrayl tetraacetate [15*S*)-25]**




(15*S*)-**23** (15*S*)-**25**

To an ice-cold solution of tetraacetate (15*S*)-**23** (40.0 mg, 0.0653 mmol) in MeOH (1.5 mL) was added PPTS (16.4 mg, 0.0653 mmol). The mixture was stirred at room temperature for 3 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give alcohol (15*S*)-**25** (28.3 mg, 87%): colorless oil; $R_f$ = 0.42 (hexane/EtOAc = 1:1); $[\alpha]_D^{28}$ –35 (*c* 0.515, $CHCl_3$); IR (neat) 3545, 1745, 1373, 1236 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.75 (dq, *J* = 14.8, 6.4 Hz, 1H), 5.68 (dd, *J* = 16.0, 5.6 Hz, 1H), 5.57 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.43–5.30 (m, 2H), 5.27–5.12 (m, 2H), 5.17 (ddd, *J* = 10.4, 5.2, 3.6 Hz, 1H), 3.64 (t, *J* = 6.8 Hz, 2H), 2.10 (s, 3H), 2.05 (s, 3H), 2.02 (s, 6H), 1.85 (ddd, *J* = 14.8, 9.6, 3.6 Hz, 1H), 1.76 (ddd, *J* = 14.8, 10.4, 4.0 Hz, 1H), 1.71–1.47 (m, 5H), 1.68 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.40–1.19 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 170.3, 170.1, 169.9, 133.2, 129.9, 128.9, 126.6, 74.1, 73.4, 70.3, 69.5, 63.1, 35.2, 34.2, 32.8, 29.4, 29.3, 29.2, 25.7, 25.1, 21.3, 21.0, 20.8, 17.8; HRMS (FD) calcd for $C_{26}H_{43}O_9$ $[M+H]^+$ 499.29071, found 499.29240.

**(9*S*,10*E*,12*S*,13*S*,15*S*,16*E*)-9,12,13,15-Tetraacetoxyoctadeca-10,16-dienoic acid [(15*S*)-26]**

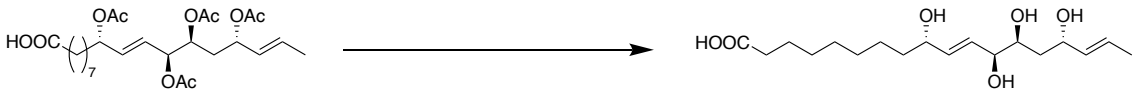



(15*S*)-**25** (15*S*)-**26**

To an ice-cold solution of alcohol (15*S*)-**25** (44.1 mg, 0.0884 mmol) in $CH_2Cl_2$ (3 mL) were added Celite (57.2 mg) and PCC (28.6 mg, 0.133 mmol). After being stirred at room temperature for 3 h, the mixture was diluted with hexane and filtered through a pad of Celite. The filtrate was concentrated to give the crude aldehyde, which was used for next reaction without further purification.

To a solution of the above aldehyde in *t*-BuOH (0.33 mL) and $H_2O$ (0.55 mL) were added 2-methyl-2-butene (0.047 mL, 0.44 mmol), $NaH_2PO_4 \cdot 2H_2O$ (15.2 mg, 0.0974 mmol), and $NaClO_2$ (70% purity, 40.0 mg, 0.310 mmol). The mixture was stirred at room temperature for 35 min and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc four times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/EtOAc) to give carboxylic acid (15*S*)-**26** [38.7 mg, 85% from alcohol (15*S*)-**25**]: colorless liquid; $R_f$ = 0.48 ($CH_2Cl_2$/EtOAc = 1:1); $[\alpha]_D^{27}$ –36 (*c* 0.940, $CHCl_3$); IR (neat) 3465, 1751, 1374, 1220 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 5.75 (dq, *J* = 15.6, 6.8 Hz, 1H), 5.68 (dd, *J* = 16.0, 5.2 Hz, 1H), 5.57 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.43–5.31 (m, 2H), 5.26–5.13 (m, 3H), 2.34 (t, *J* = 7.6 Hz, 2H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s, 6H), 1.85 (ddd, *J* = 14.8, 9.6, 3.2 Hz, 1H), 1.76 (ddd, *J* = 14.8, 10.0, 4.0 Hz, 1H), 1.68 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.67–1.48 (m, 4H), 1.39–1.17 (m, 8H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 178.4, 170.40, 170.36, 170.2, 169.9, 133.2, 129.9, 128.9,126.6, 74.1, 73.4, 70.4, 69.5, 35.2, 34.1, 33.8, 29.08, 29.05, 28.9, 25.0, 24.7, 21.3, 21.0, 20.8, 17.8; HRMS (FD) calcd for $C_{26}H_{41}O_{10}$ $[M+H]^+$ 513.26997, found 513.26950.

**Chaenomic acid D (2)**

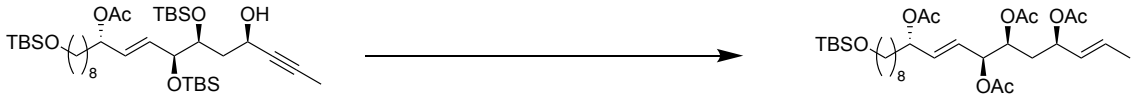



(15*S*)-**26** Chaenomic acid D (**2**)

To an ice-cold solution of diol (15*S*)-**26** (37.2 mg, 0.0726 mmol) in MeOH (2 mL) was added NaOMe (39.2 mg, 0.726 mmol). The mixture was stirred at room temperature for 5 h and diluted with a solution of AcCl in MeOH until the mixture became pH 7. The solution was removed by evaporation. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/MeOH) to give chaenomic acid D (**2**) (21.6 mg, 86%): colorless oil; $R_f$ = 0.18 ($CH_2Cl_2$/MeOH = 5:1); $[\alpha]_D^{28}$ –18 (*c* 0.455, MeOH) [lit.[S6] $[\alpha]_D$ +67 (*c* 0.30, MeOH)]; IR (neat) 3385, 1713, 1275 $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3OD$) $\delta$ 5.60–5.77 (m, 3H), 5.51 (ddq, *J* = 15.6, 6.8, 1.2 Hz, 1H), 4.26 (m, 1H), 4.04 (q, *J* = 6.0 Hz, 1H), 3.92 (t, *J* = 6.0 Hz, 1H), 3.73 (ddd, *J* = 9.6, 6.0, 2.8 Hz, 1H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.68 (d, *J* = 6.8 Hz, 3H), 1.67–1.56 (m, 3H), 1.56–1.44 (m, 3H), 1.44–1.26 (m, 8H); $^{13}C$ NMR (100 MHz, $CD_3OD$) $\delta$ 178.0 (–),

136.7 (+), 136.0 (+), 131.1 (+), 126.2 (+), 76.7 (+), 73.1 (+), 72.3 (+), 70.0 (+), 41.2 (–), 38.3 (–), 35.1 (–), 30.6 (–), 30.4 (–), 30.2 (–), 26.5 (–), 26.2 (–), 17.8 (+); HRMS (FD) calcd for $C_{18}H_{32}O_6$ $[M]^+$ 344.21989, found 344.21900.

***rac*-(2*E*,4*S*,6*S*,7*S*,8*E*,10*S*)-18-[(*tert*-Butyldimethylsilyl)oxy]octadeca-2,8-diene-4,6,7,10-tetrayl tetraacetate [*rac*-(15*R*)-23]**



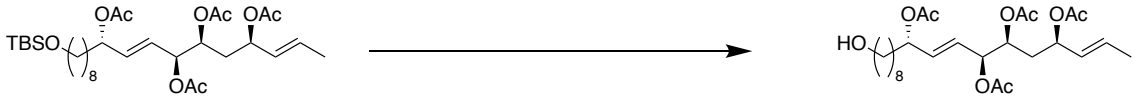

*rac*-(15*R*)-**20** *rac*-(15*R*)-**23**

To an ice-cold solution of alcohol *rac*-(15*R*)-**20** (220 mg, 0.308 mmol) in THF (4 mL) was added Red-Al (3.6 M in toluene, 0.86 mL, 3.1 mmol). The mixture was stirred at 70 °C for 3 h and diluted with EtOAc and 3N HCl. The resulting mixture was extracted with EtOAc/THF several times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was semi-purified by chromatography on silica gel (EtOAc/MeOH) to give a mixture of crude pentaol and the crude tetraol, which was used for the next reaction without further purification.

To an ice-cold solution of the above a mixture of pentaol and tetraol in THF (5 mL) were added imidazole (31.4 mg, 0.462 mmol) and TBSCl (46.4 mg, 0.308 mmol). The mixture was stirred at 0 °C for 4 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was semi-purified by chromatography on silica gel (EtOAc) to give the crude tetraol, which was used for the next reaction without further purification.

To an ice-cold solution of the above tetraol in $CH_2Cl_2$ (2 mL) were added $Et_3N$ (0.27 mL, 1.9 mmol), DMAP (9.7 mg, 0.079 mmol), and $Ac_2O$ (0.15 mL, 1.6 mmol). The mixture was stirred at room temperature for 14 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give tetraacetate *rac*-(15*R*)-**23** (48.1 mg, 55% from alcohol *rac*-(15*R*)-**20**): colorless oil; $R_f$ = 0.41 (hexane/EtOAc = 3:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.72 (dq, $J$ = 15.2, 6.8 Hz, 1H), 5.67 (dd, $J$ = 15.2, 6.4 Hz, 1H), 5.57 (dd, $J$ = 15.6, 5.6 Hz, 1H), 5.38–5.34 (m, 2H), 5.25–5.15 (m, 2H), 5.06 (ddd, $J$ = 8.8, 4.8, 4.0 Hz, 1H), 3.59 (t, $J$ = 6.8 Hz, 2H), 2.09 (s, 3H), 2.054 (s, 3H), 2.050 (s, 3H), 2.03 (s, 3H), 1.91 (ddd, $J$ = 14.6, 8.8, 2.0 Hz, 1H), 1.79 (ddd, $J$ = 14.6, 7,8, 4.0 Hz, 1H), 1.70 (dd, $J$ = 6.8, 1.6 Hz, 3H), 1.65–1.45 (m, 4H), 1.34–1.19 (m, 10H), 0.89 (s, 9H), 0.04 (s, 6H).

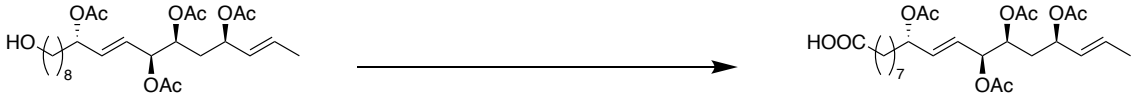
***rac*-(2*E*,4*S*,6*S*,7*S*,8*E*,10*S*)-18-Hydroxyoctadeca-2,8-diene-4,6,7,10-tetrayl tetraacetate [*rac*-(15*R*)-25]**




*rac*-(15*R*)-**23** *rac*-(15*R*)-**25**

To an ice-cold solution of tetraacetate [*rac*-(15*R*)-**23**] (48.1 mg, 0.0785 mmol) in MeOH (2 mL) was added PPTS (19.7 mg, 0.0784 mmol). The mixture was stirred at room temperature for 3 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with EtOAc three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to give alcohol [*rac*-(15*R*)-**25**] (25.4 mg, 65%): colorless oil; $R_f$ = 0.25 (hexane/EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.72 (dq, $J$ = 15.2, 6.8 Hz, 1H), 5.67 (dd, $J$ = 15.6, 6.0 Hz, 1H), 5.57 (dd, $J$ = 15.6, 6.0 Hz, 1H), 5.42–5.28 (m, 2H), 5.26–5.15 (m, 2H), 5.11–5.00 (m, 1H), 3.64 (t, $J$ = 6.8 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.91 (ddd, $J$ = 14.3, 8.8, 6.0 Hz, 1H), 1.79 (ddd, $J$ = 14.3, 7.6, 3.6 Hz, 1H), 1.71–1.40 (m, 5H), 1.70 (dd, $J$ = 6.8, 1.6 Hz, 3H), 1.39–1.19 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.3, 170.12, 170.06, 169.8, 133.2, 130.9, 128.2, 126.5, 73.8, 73.4, 71.9, 70.3, 63.0, 35.3, 34.2, 32.8, 29.4, 29.3, 29.2, 25.7, 25.1, 21.4, 21.3, 21.03, 20.98, 17.9.

***rac*-(9*S*,10*E*,12*S*,13*S*,15*S*,16*E*)-9,12,13,15-Tetraacetoxyoctadeca-10,16-dienoic acid [*rac*-(15*R*)-26]**



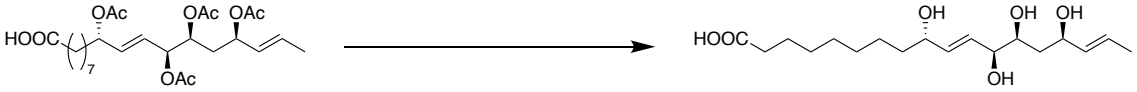

*rac*-(15*R*)-**25** *rac*-(15*R*)-**26**

To an ice-cold solution of alcohol [*rac*-(15*R*)-**25**] (25.4 mg, 0.0509 mmol) in $CH_2Cl_2$ (1.5 mL) were added Celite (32.9 mg) and PCC (16.5 mg, 0.0765 mmol). After being stirred at room temperature for 5 h, the mixture was diluted with hexane and filtered through a pad of Celite. The filtrate was concentrated to give the crude aldehyde, which was used for next reaction without further purification.

To a solution of the above aldehyde in *t*-BuOH (0.60 mL) and $H_2O$ (1.0 mL) were added 2-methyl-2-butene (0.050 mL, 0.47 mmol), $NaH_2PO_4{\cdot}2H_2O$ (8.7 mg, 0.056 mmol), and $NaClO_2$ (70% purity, 23.0 mg, 0.178 mmol). The mixture was stirred at room temperature for 1 h and diluted with saturated $NH_4Cl$. The resulting mixture was extracted with EtOAc four times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/EtOAc) to give carboxylic acid [*rac*-(15*R*)-**26**] (18.1 mg, 69%): colorless liquid; $R_f$ = 0.43 ($CH_2Cl_2$/EtOAc = 1:1); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.4 (br s, 1 H), 5.72 (dq, $J$ = 15.2, 6.8 Hz, 1H), 5.67 (dd, $J$ = 16.0, 6.0 Hz, 1H), 5.57 (dd, $J$ = 16.0, 6.0 Hz, 1H), 5.42–5.29 (m, 2H), 5.26–5.15 (m, 2H), 5.12–5.00 (m, 1H), 2.35 (t, $J$ = 7.6 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.91

(ddd, $J$ = 14.2, 8.8, 5.6 Hz, 1H), 1.79 (ddd, $J$ = 14.2, 7.8, 3.6 Hz, 1H), 1.70 (dd, $J$ = 6.8, 1.6 Hz, 3H), 1.67–1.48 (m, 4H), 1.39–1.19 (m, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 170.4, 170.2, 170.1, 169.9, 133.2, 130.9, 128.2, 126.6, 73.8, 73.4, 72.0, 70.3, 35.3, 34.1, 33.8, 29.1, 29.0, 28.9, 24.9, 24.7, 21.4, 21.3, 21.05, 21.00, 17.9.

**(15*R*)-Chaenomic acid D [(15*R*)-2]**




*rac*-(15*R*)-**26** (15*R*)-Chaenomic acid D [(15*R*)-**2**]

To an ice-cold solution of diol [*rac*-(15*R*)-**26**] (18.1 mg, 0.0351 mmol) in MeOH (2 mL) was added NaOMe (19.0 mg, 0.352 mmol). The mixture was stirred at room temperature for 5 h and diluted with a solution of AcCl in MeOH until the mixture became pH 7. The solution was removed by evaporation. The residue was purified by chromatography on silica gel ($CH_2Cl_2$/MeOH) to give *rac*-(15*R*)-chaenomic acid D [*rac*-(15*R*)-**2**] (10.3 mg, 85%): colorless oil; $R_f$ = 0.19 ($CH_2Cl_2$/MeOH = 5:1); $^1$H NMR (400 MHz, $CD_3OD$) $\delta$ 5.77–5.61 (m, 3H), 5.43 (ddq, $J$ = 15.1, 7.2, 1.2 Hz, 1H), 4.23 (q, $J$ = 7.2 Hz,, 1H), 4.05 (q, $J$ = 6.0 Hz, 1H), 3.94 (t, $J$ = 5.6 Hz, 1H), 3.60–3.50 (m, 1H), 2.27 (t, $J$ = 7.2 Hz, 2H), 1.70 (dd, $J$ = 6.4, 1.2 Hz, 3H), 1.66–1.55 (m, 4H), 1.55–1.44 (m, 2H), 1.44–1.26 (m, 8H); $^{13}$C NMR (100 MHz, $CD_3OD$) $\delta$ 178.4, 136.7, 135.0, 130.9, 127.8, 76.3, 73.8, 73.1, 72.2, 40.6, 38.3, 35.3, 30.6, 30.4, 30.2, 26.5, 26.2, 17.9.

**Table S3** Comparison of $^{1}$H NMR data between the reported **2** and synthesized **2**

| NO. | reported **2** (700 MHz, $CD_3OD$)[S7] | synthesized **2** (400 MHz, $CD_3OD$) |
|---|---|---|
| 1 | 1.36, overlap | 1.44–1.26, m |
| 2 | 1.38, overlap | |
| 3 | 1.51, ddd (14.2, 9.8, 3.0 Hz) | 1.56–1.44, m |
| 4 | 1.53, m | |
| 5 | 1.61, overlap | 1.67–1.56, m |
| 6 | 1.64, ddd (14.2, 9.8, 2.7 Hz) | |
| 7 | 1.71, ddd (6.4, 1.5, 0.6 Hz) | 1.68, d (6.8 Hz) |
| 8 | 2.29, t (7.3 Hz) | 2.27, t (7.2 Hz) |
| 9 | 3.75, ddd (9.8, 5.8, 2.7 Hz) | 3.73, ddd (9.6, 6.0, 2.8 Hz) |
| 10 | 3.94, t (5.8 Hz) | 3.92, t (6.0 Hz) |
| 11 | 4.06, q (6.1 Hz) | 4.04, q (6.0 Hz) |
| 12 | 4.28, m | 4.33–4.19, m |
| 13 | 5.54, ddq (15.3, 6.6, 1.5 Hz) | 5.51, ddq (15.6, 6.8, 1.2 Hz) |
| 14 | 5.69, dqd (15.3, 6.4, 1.1 Hz) | |
| 15 | 5.70, dd (15.9, 6.0 Hz) | 5.77–5.60, m |
| 16 | 5.74, dd (15.9, 6.1 Hz) | |

**Table S4** Comparison of $^{13}C$ NMR data between the reported **2** and synthesized **2**

| NO. | reported **2** (175 MHz, $CD_3OD$)[S7] | synthesized **2** (100 MHz, $CD_3OD$) | $\Delta\delta$ |
|---|---|---|---|
| 1 | 16.4 | 17.8 | +1.4 |
| 2 | 24.8 | 26.2 | +1.4 |
| 3 | 25.1 | 26.5 | +1.4 |
| 4 | 28.8 | 30.2 | +1.4 |
| 5 | 29.0 | 30.4 | +1.4 |
| 6 | 29.2 | 30.6 | +1.4 |
| 7 | 33.8 | 35.1 | +1.3 |
| 8 | 36.9 | 38.3 | +1.4 |
| 9 | 39.8 | 41.2 | +1.4 |
| 10 | 68.6 | 70.0 | +1.4 |
| 11 | 70.9 | 72.3 | +1.4 |
| 12 | 71.7 | 73.1 | +1.4 |
| 13 | 75.1 | 76.7 | +1.6 |
| 14 | 124.7 | 126.2 | +1.5 |
| 15 | 129.7 | 131.1 | +1.4 |
| 16 | 134.5 | 136.0 | +1.5 |
| 17 | 135.3 | 136.7 | +1.4 |
| 18 | 176.7 | 178.0 | +1.3 |

**Table S5** Comparison of $^{1}$H NMR data between the reported (15*R*)-**2** and synthesized (15*R*)-**2**

| NO. | reported **2** (700 MHz, $CD_3OD$)[S7] | synthesized (15*R*)-**2** (400 MHz, $CD_3OD$) |
|---|---|---|
| 1 | 1.36, overlap | 1.44–1.26, m |
| 2 | 1.38, overlap | |
| 3 | 1.51, ddd (14.2, 9.8, 3.0 Hz) | 1.55–1.44, m |
| 4 | 1.53, m | |
| 5 | 1.61, overlap | 1.66–1.55, m |
| 6 | 1.64, ddd (14.2, 9.8, 2.7 Hz) | |
| 7 | 1.71, ddd (6.4, 1.5, 0.6 Hz) | 1.70, dd (6.4, 1.2 Hz) |
| 8 | 2.29, t (7.3 Hz) | 2.27, t (7.2 Hz) |
| 9 | 3.75, ddd (9.8, 5.8, 2.7 Hz) | 3.60–3.50, m |
| 10 | 3.94, t (5.8 Hz) | 3.94, t (5.6 Hz) |
| 11 | 4.06, q (6.1 Hz) | 4.05, q (6.0 Hz) |
| 12 | 4.28, m | 4.23, q (7.2 Hz) |
| 13 | 5.54, ddq (15.3, 6.6, 1.5 Hz) | 5.43, ddq (15.1, 7.2, 1.2 Hz) |
| 14 | 5.69, dqd (15.3, 6.4, 1.1 Hz) | |
| 15 | 5.70, dd (15.9, 6.0 Hz) | 5.77–5.61, m |
| 16 | 5.74, dd (15.9, 6.1 Hz) | |

**Table S6** Comparison of $^{13}C$ NMR data between the reported (15*R*)-**2** and synthesized (15*R*)-**2**

| NO. | reported **2** (175 MHz, $CD_3OD$)[S7] | synthesized (15*R*)-**2** (100 MHz, $CD_3OD$) | $\Delta\delta$ |
|---|---|---|---|
| 1 | 16.4 | 17.9 | +1.5 |
| 2 | 24.8 | 26.2 | +1.4 |
| 3 | 25.1 | 26.5 | +1.4 |
| 4 | 28.8 | 30.2 | +1.4 |
| 5 | 29.0 | 30.4 | +1.4 |
| 6 | 29.2 | 30.6 | +1.4 |
| 7 | 33.8 | 35.3 | +1.5 |
| 8 | 36.9 | 38.3 | +1.4 |
| 9 | 39.8 | 40.6 | +0.8 |
| 10 | 68.6 | 72.2 | +3.6 |
| 11 | 70.9 | 73.1 | +2.2 |
| 12 | 71.7 | 73.8 | +2.1 |
| 13 | 75.1 | 76.3 | +1.2 |
| 14 | 124.7 | 127.8 | +3.1 |
| 15 | 129.7 | 130.9 | +1.2 |
| 16 | 134.5 | 135.0 | +0.5 |
| 17 | 135.3 | 136.7 | +1.4 |
| 18 | 176.7 | 178.4 | +1.7 |

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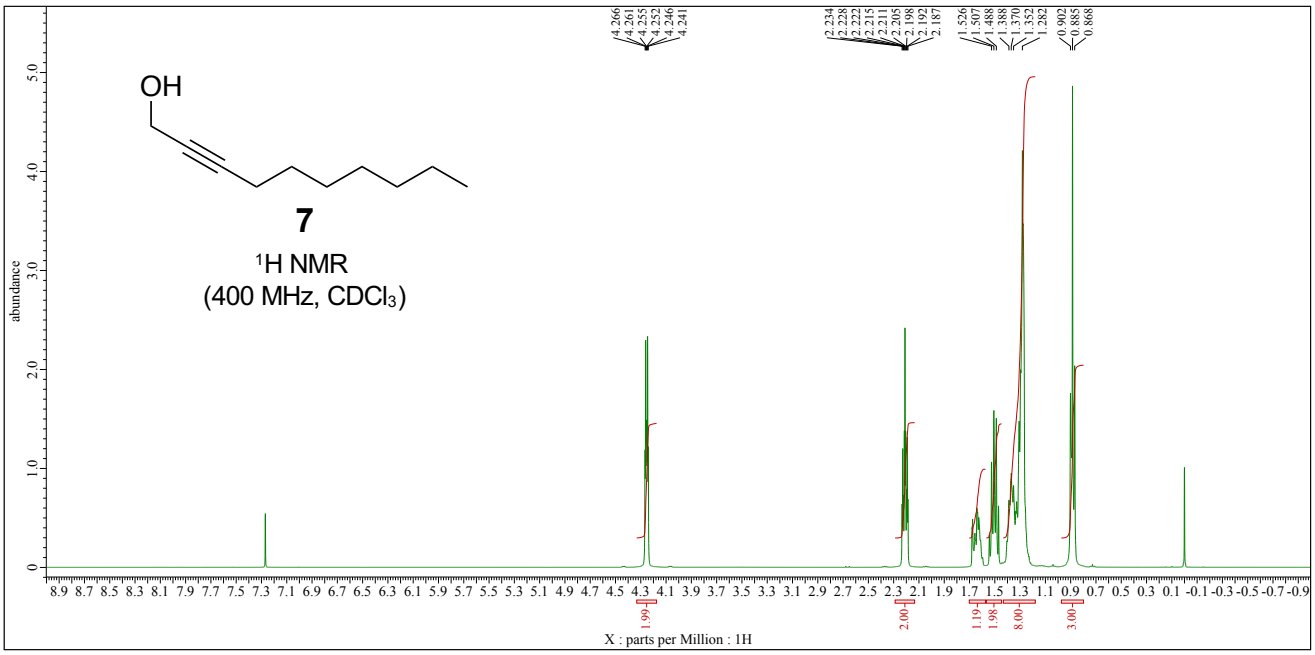
S6) C. S. Kim, O. W. Kwon, S. Y. Kim, S. U. Choi, K. H. Kim and K. R. Lee, *Lipids* **2014**, *49*, 1151–1159.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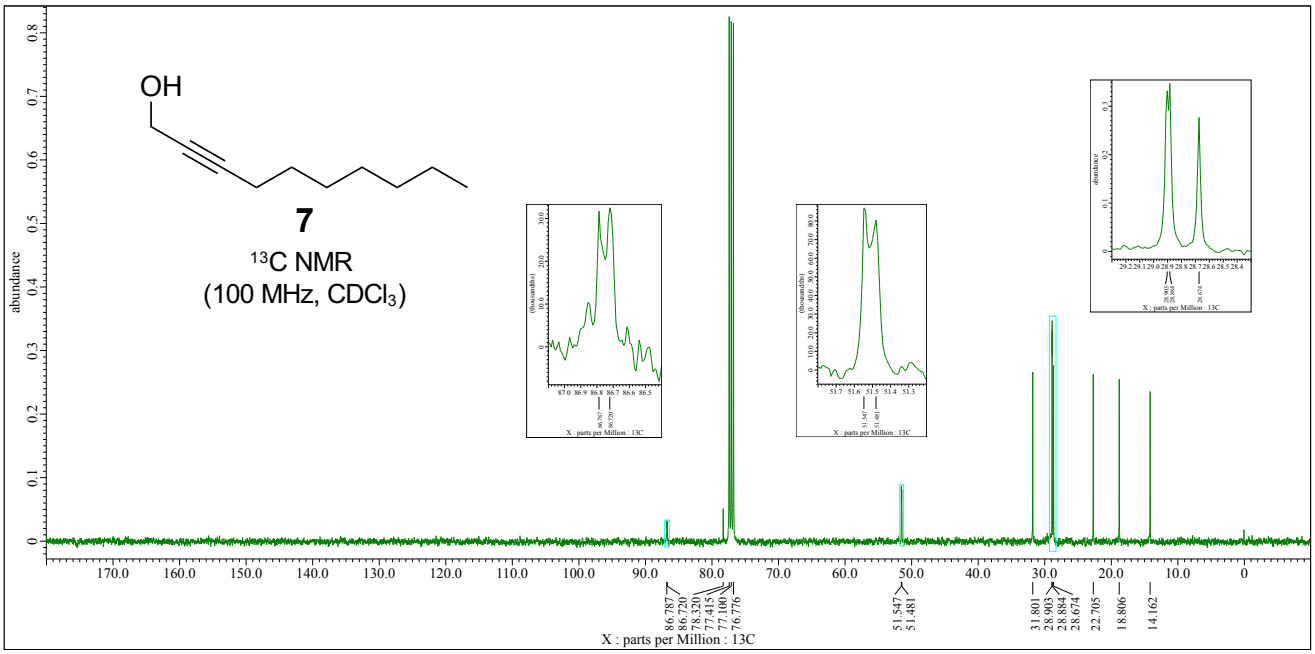
abundance
X : parts per Million : 1H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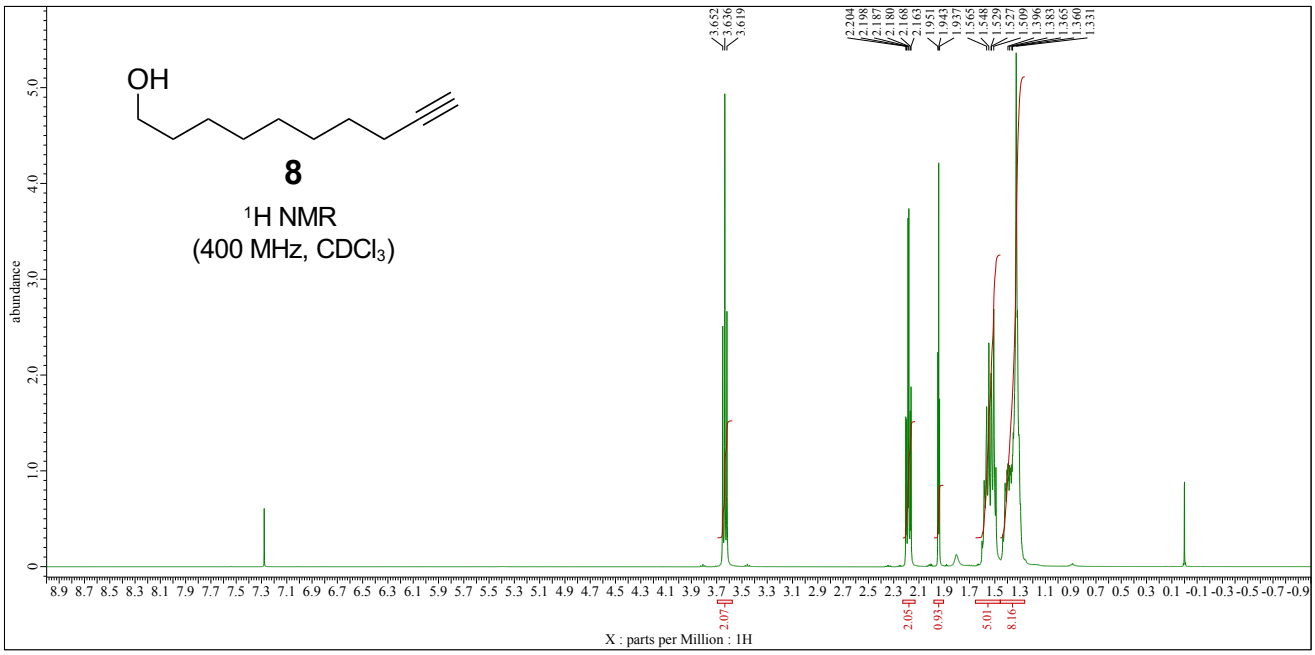
abundance
X : parts per Million : 13C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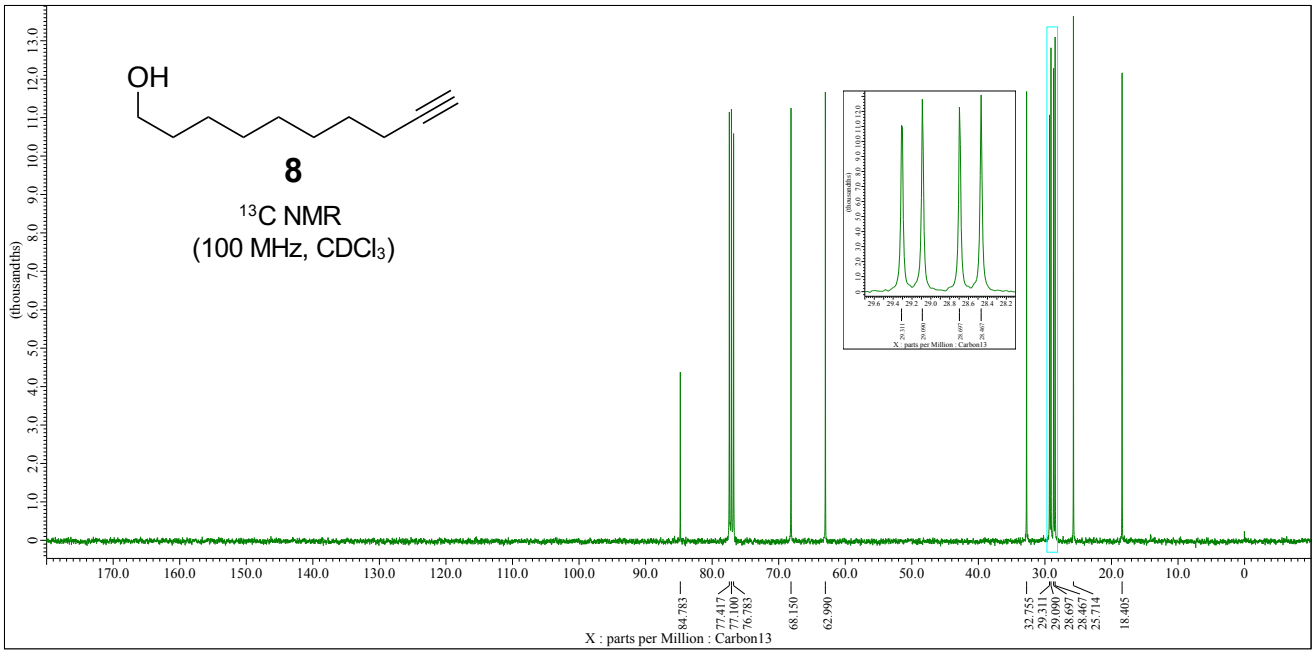
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(thousandths)
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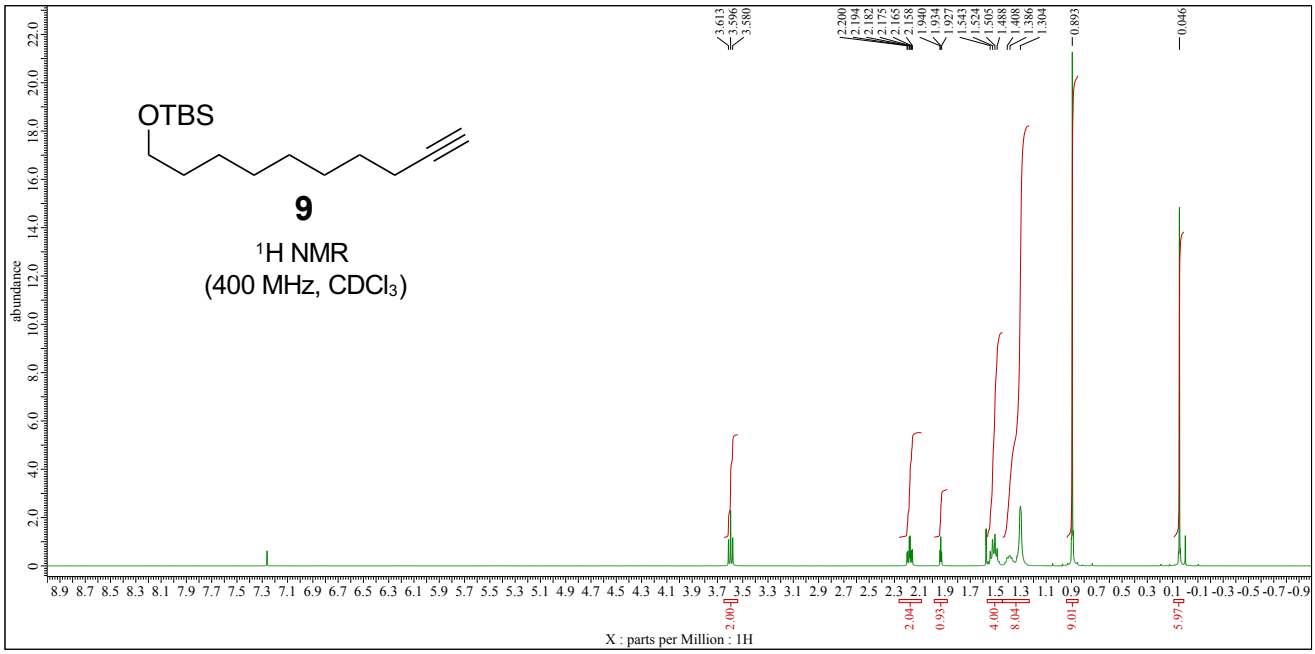
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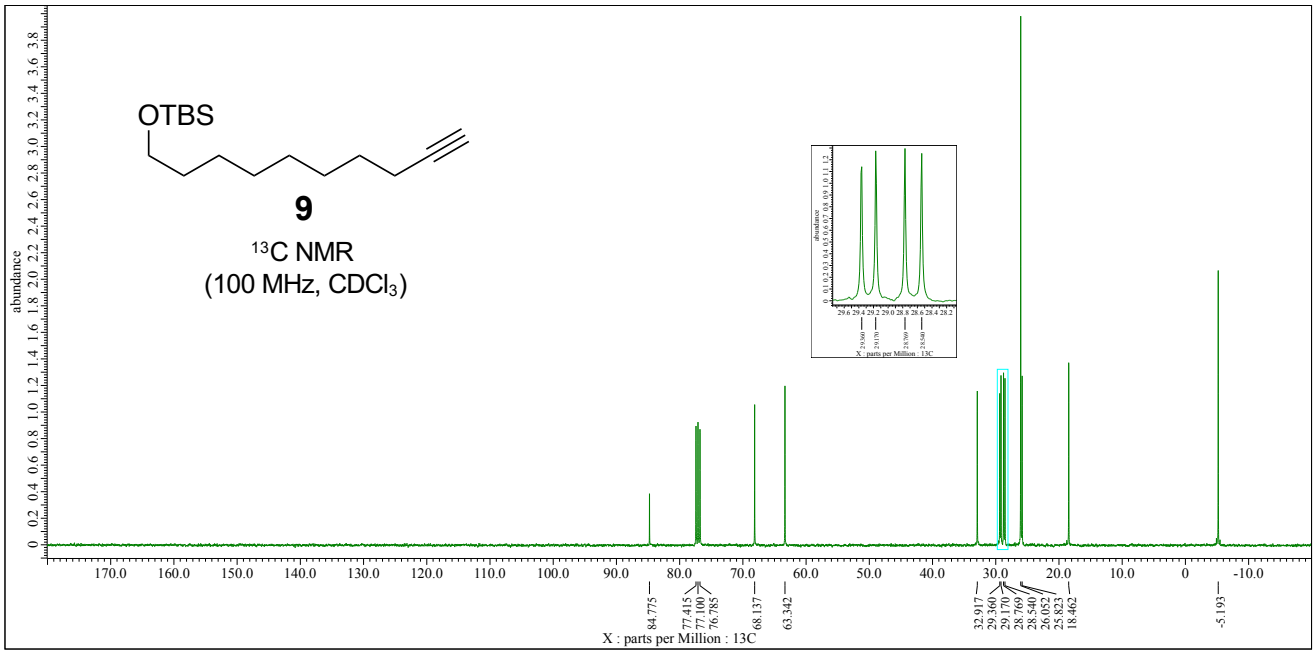
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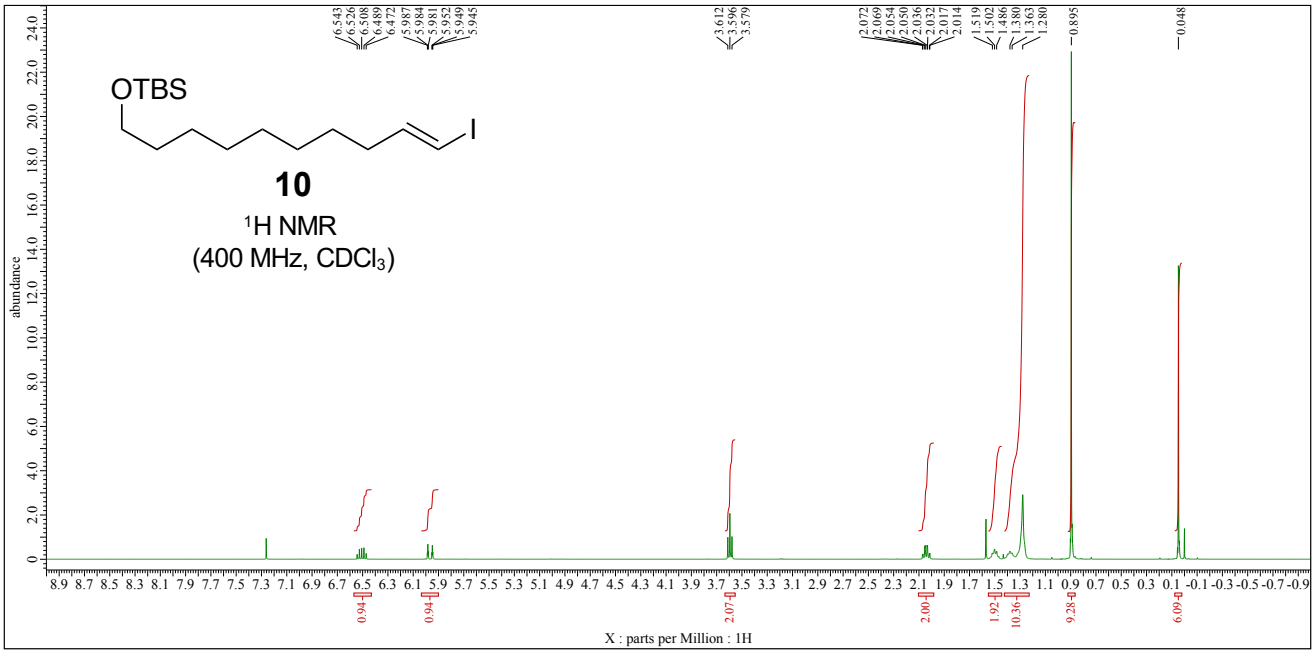
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C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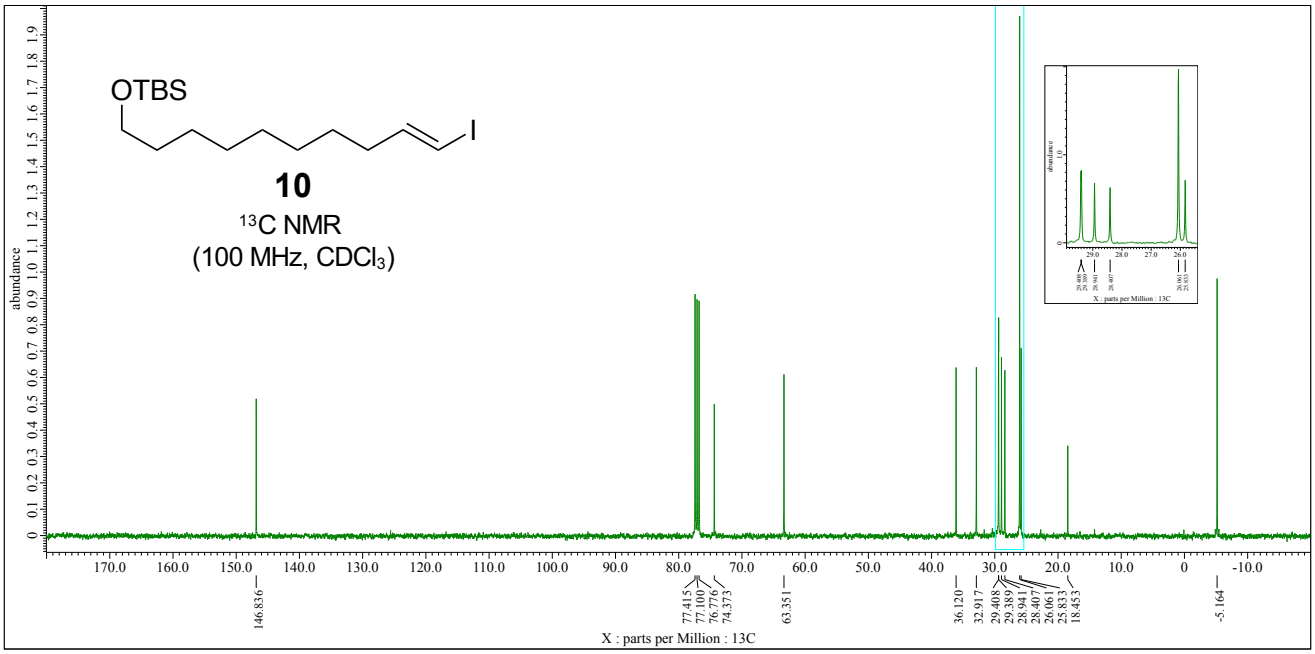
abundance
X : parts per Million : 1H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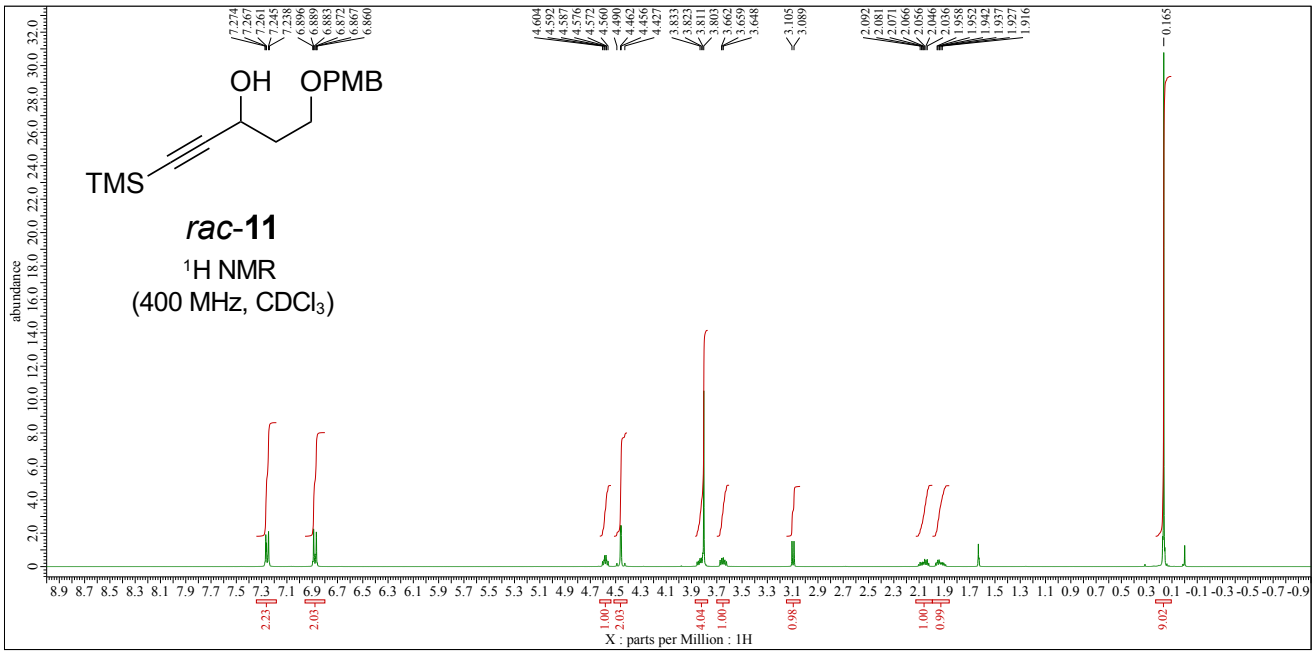
abundance
X : parts per Million : 13C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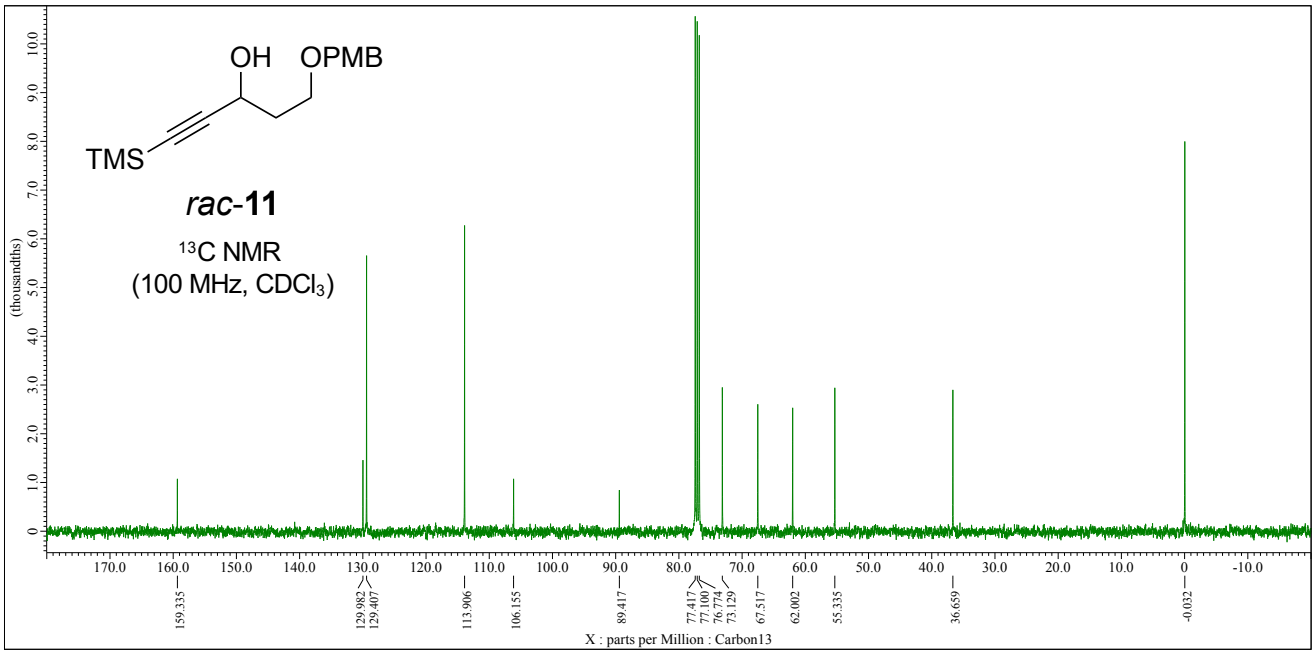
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(thousandths)
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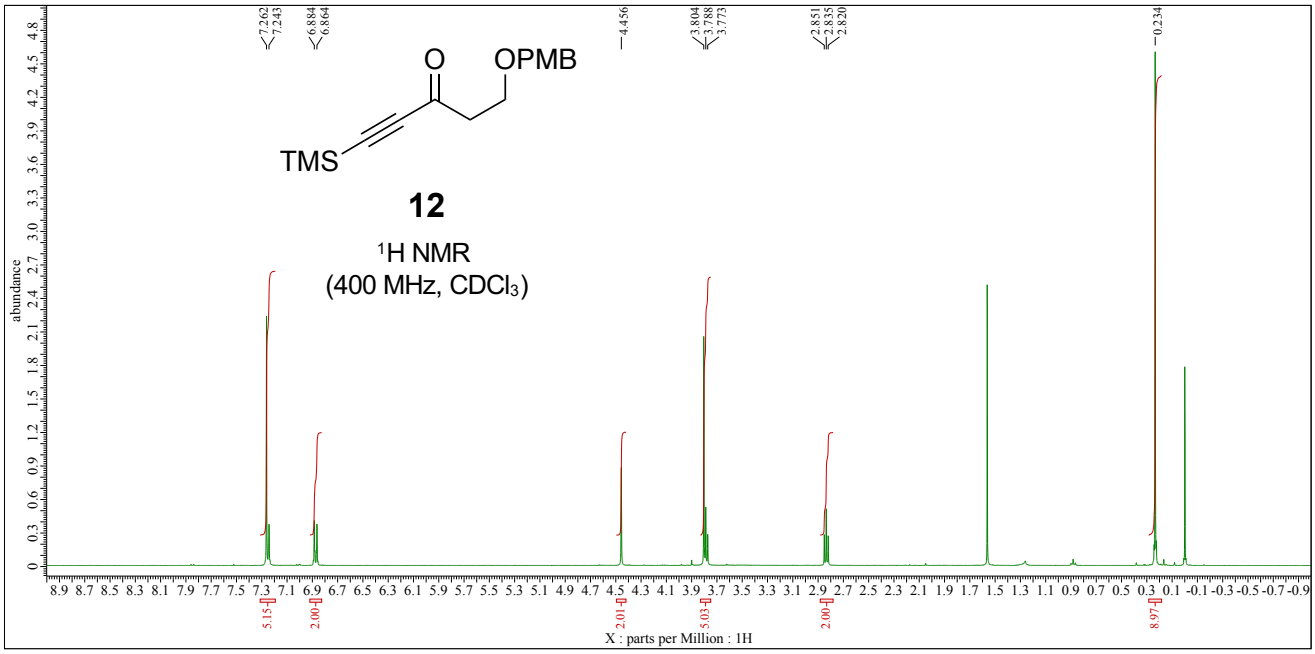
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(400 MHz, CDCl3)
abundance
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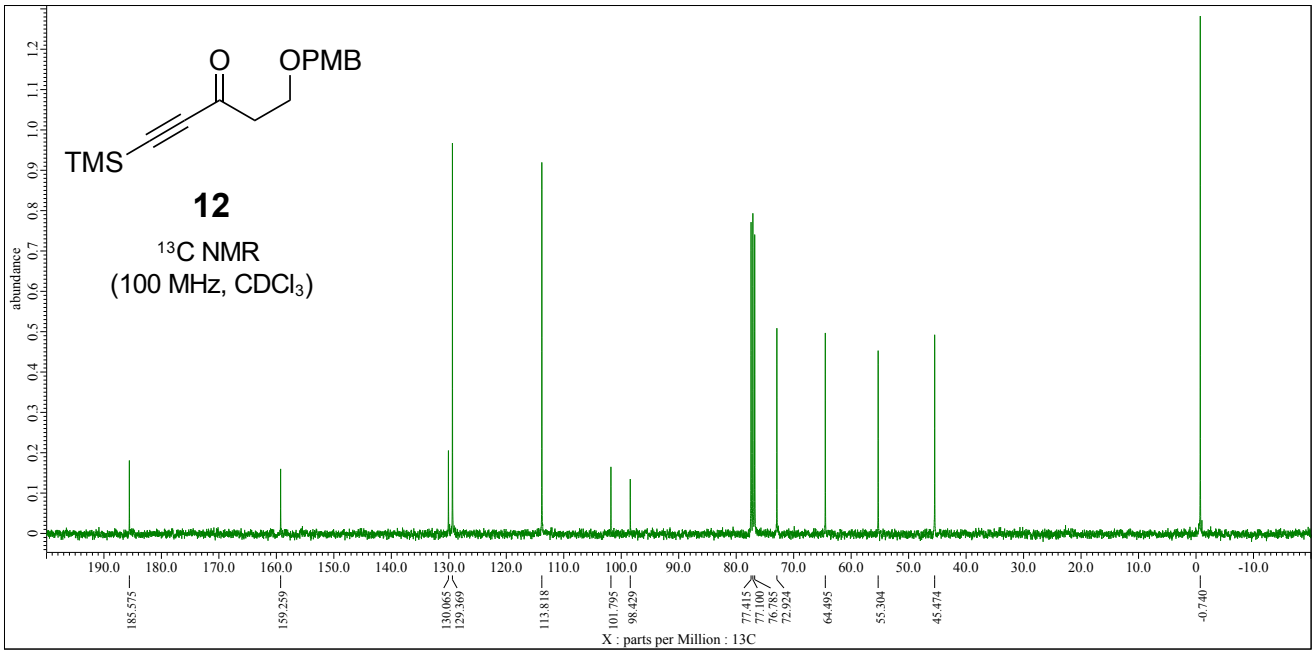
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(100 MHz, CDCl3)
abundance
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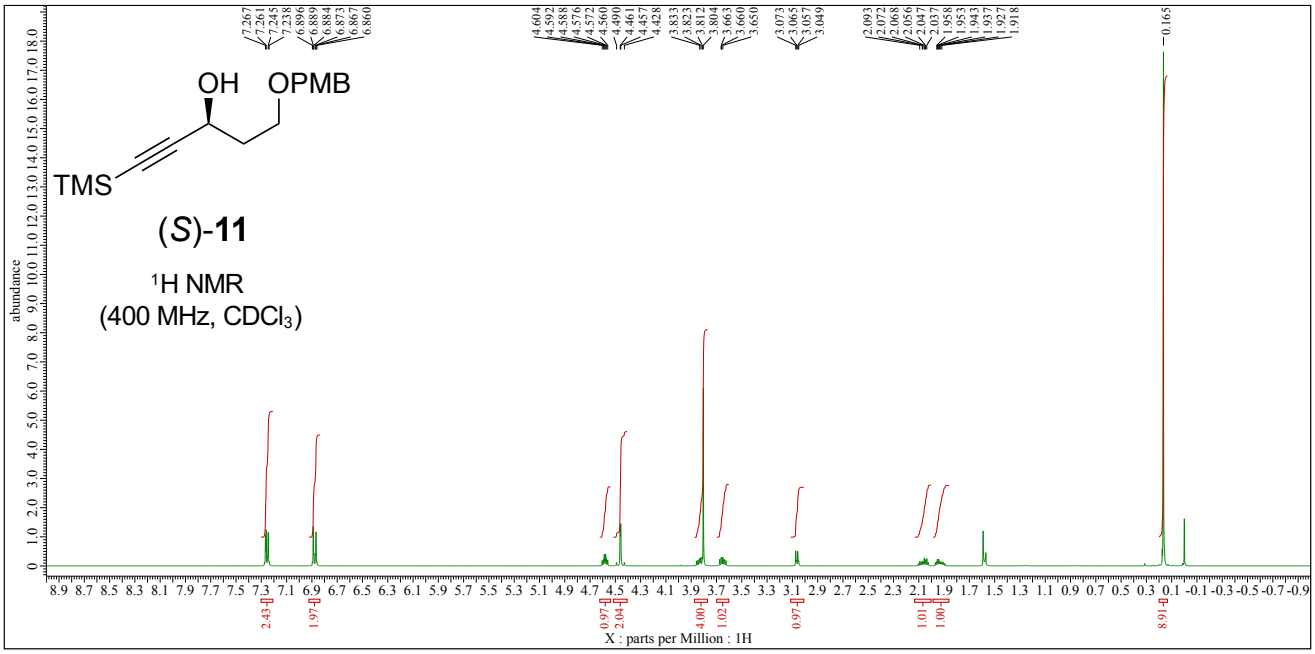
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abundance
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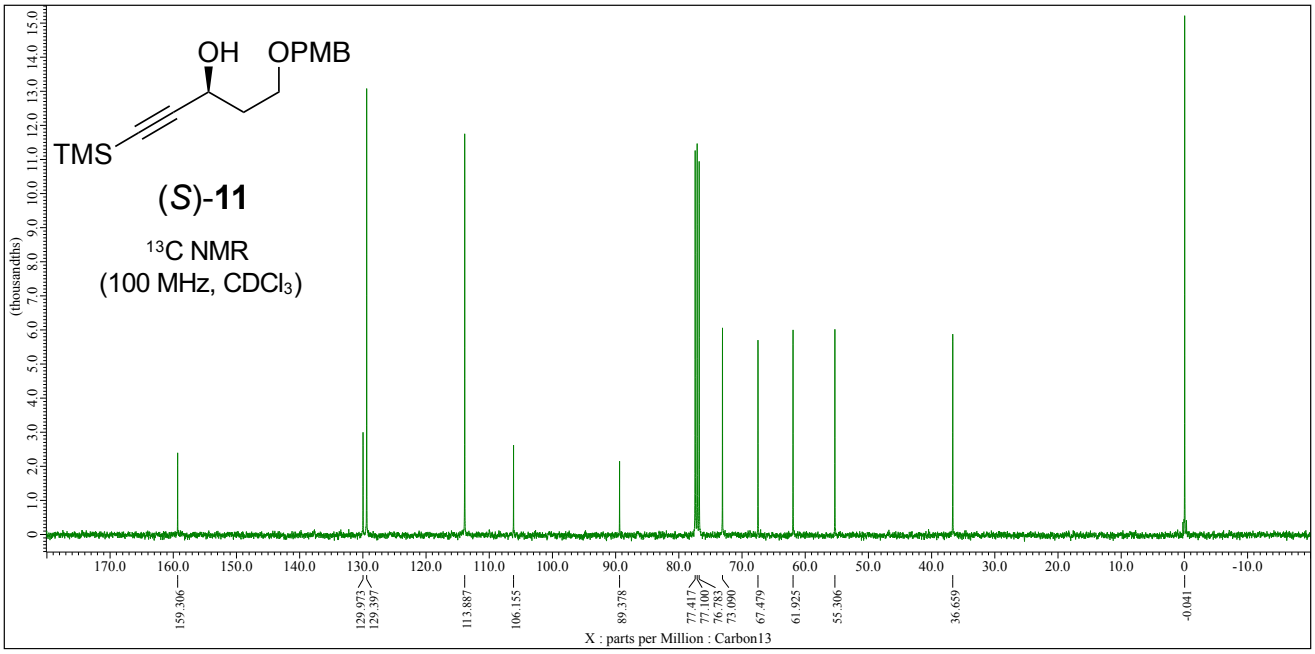
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TMS
(S)-11
13C NMR
(100 MHz, CDCl3)
(thousandths)
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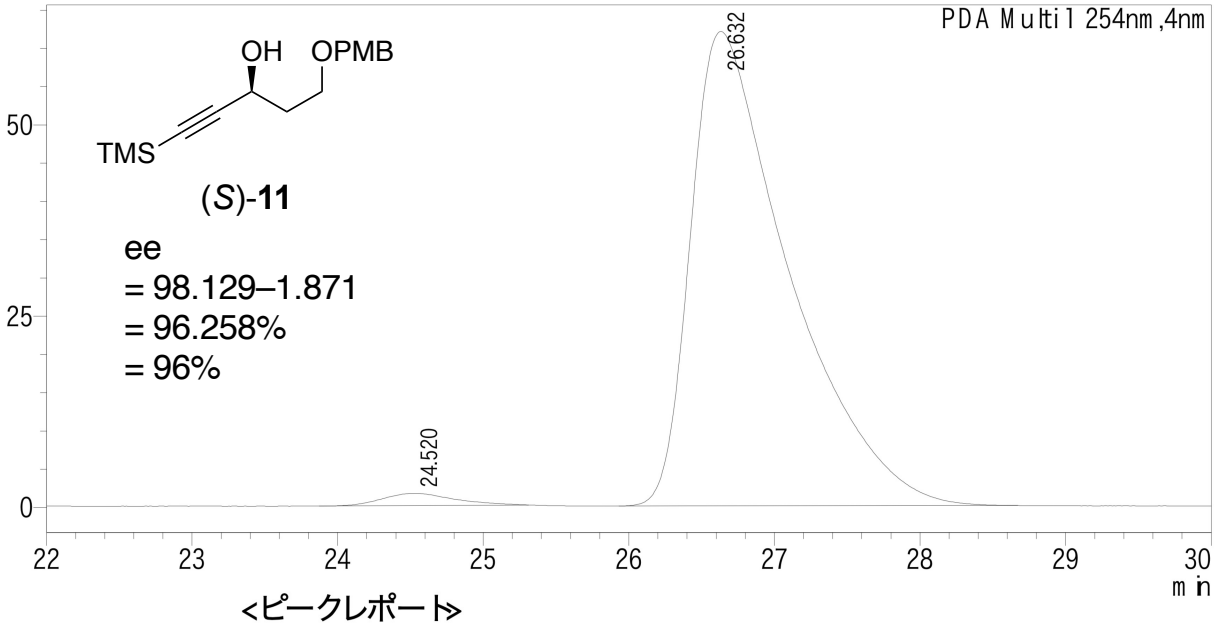
Determination of enantiopurity of alcohol by chiral HPLC

Conditions : Chiralcel OD-H, hexane/IPA = 98/2, 0.5 mL/min, 35 ºC

mAU

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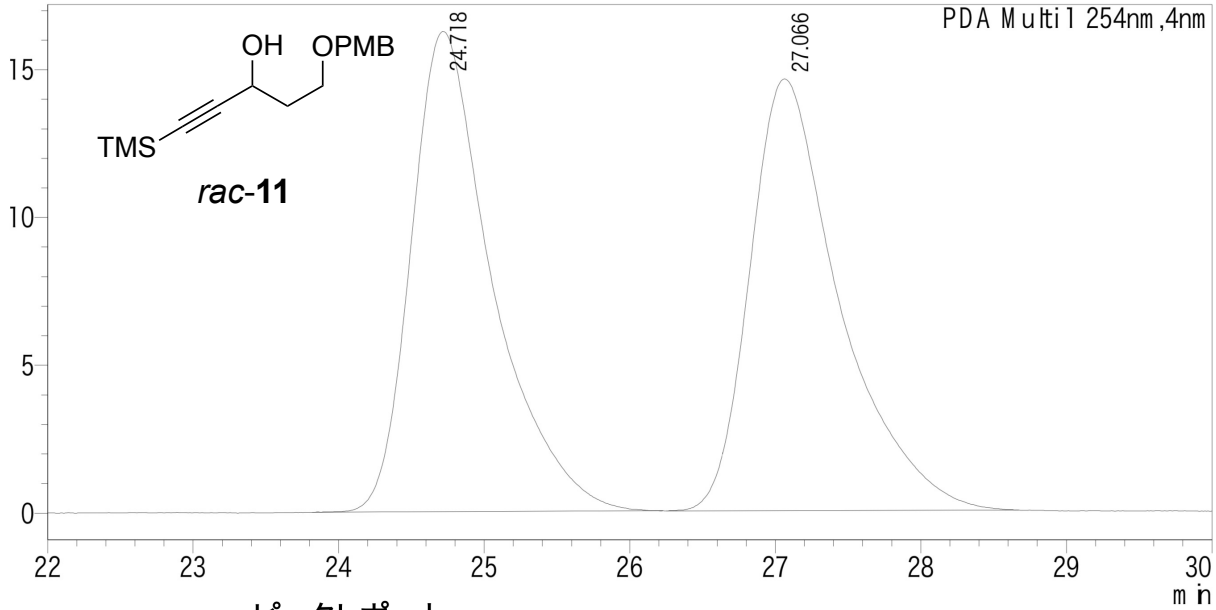
| 2 | 26.632 | 2905101 | 98.129 | 62029 | 97.468 |
| 合計 | | 2960484 | 100.000 | 63640 | 100.000 |

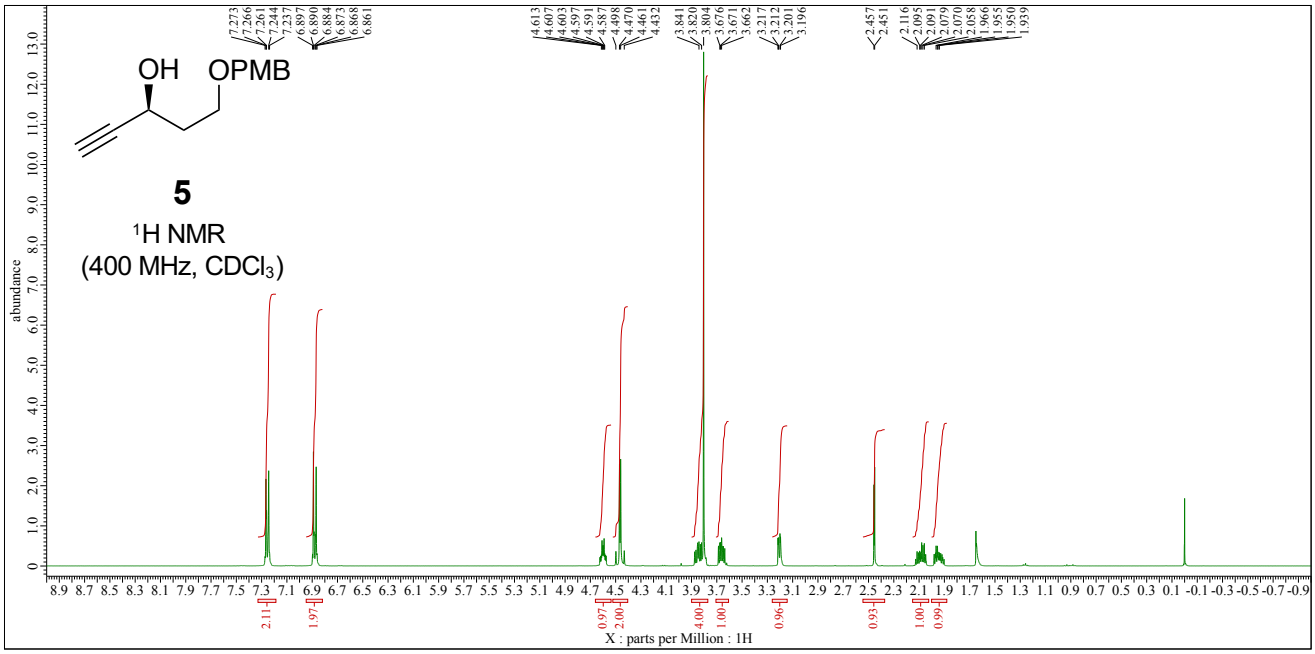
mAU

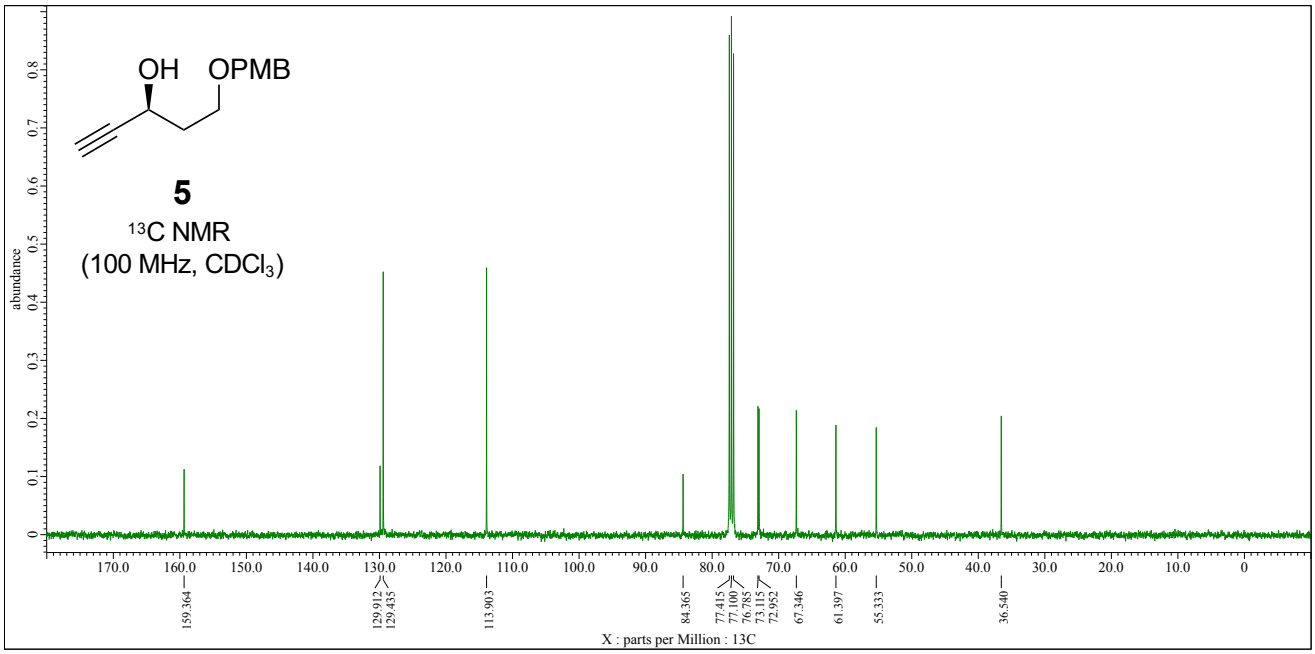


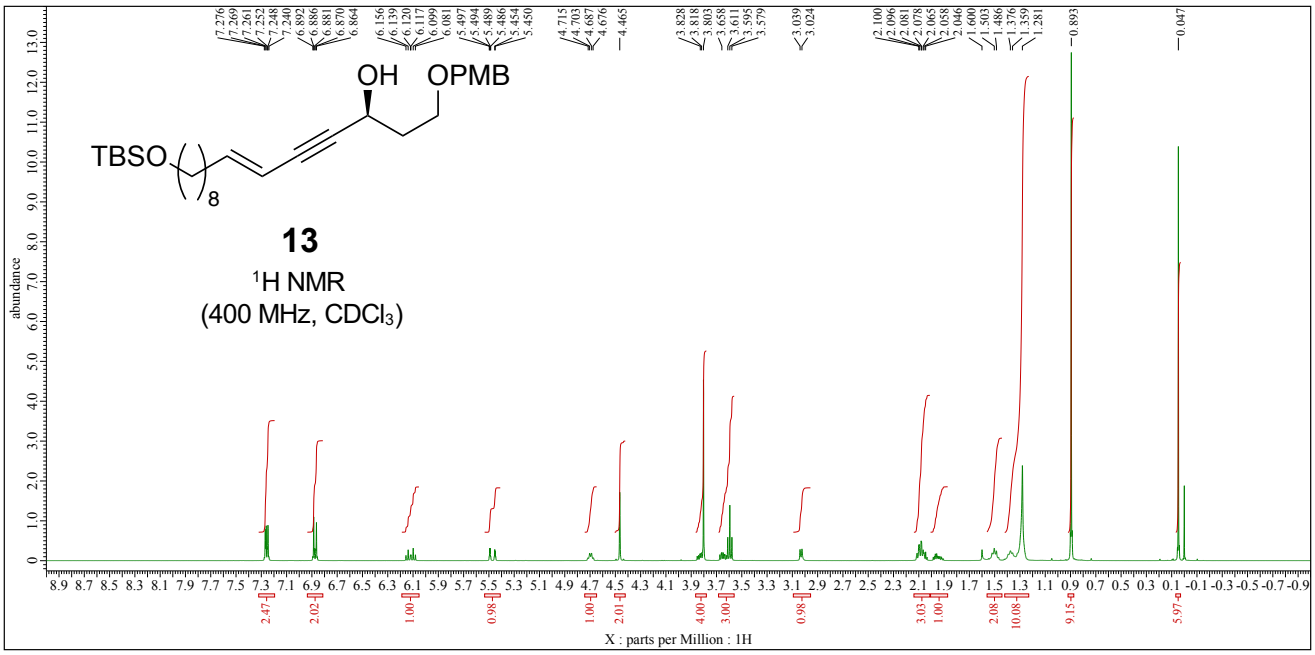

<ピークレポート>

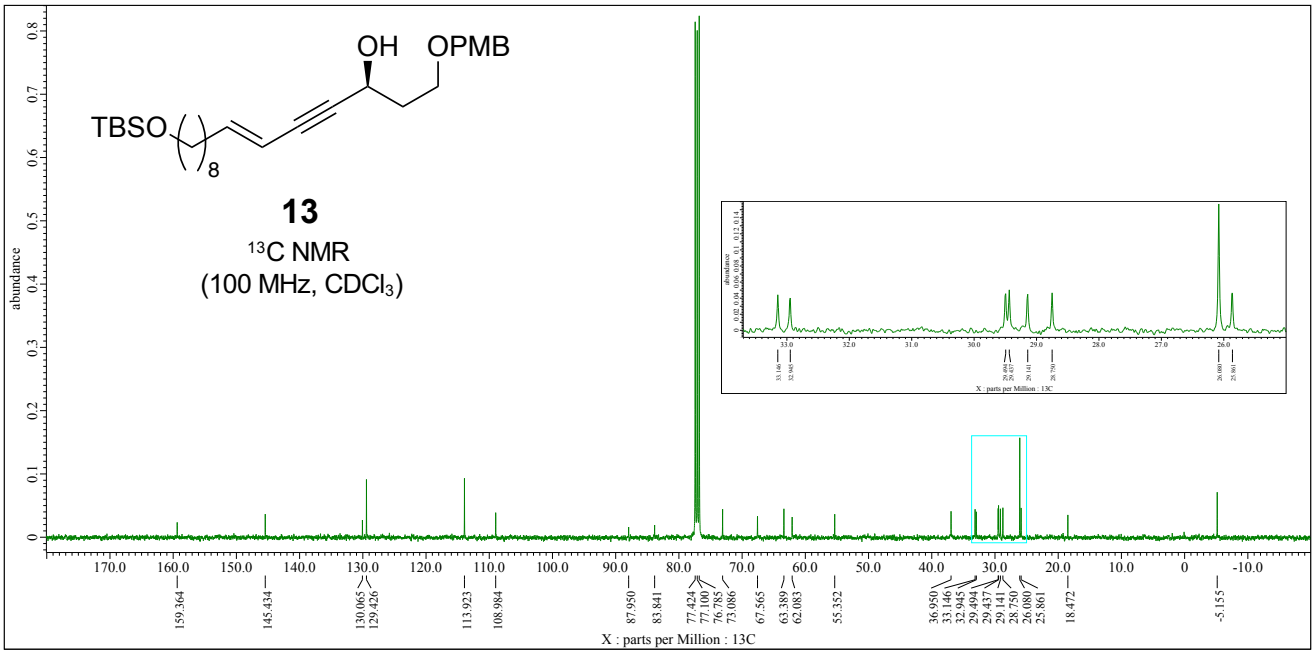
PDA Ch1 254nm

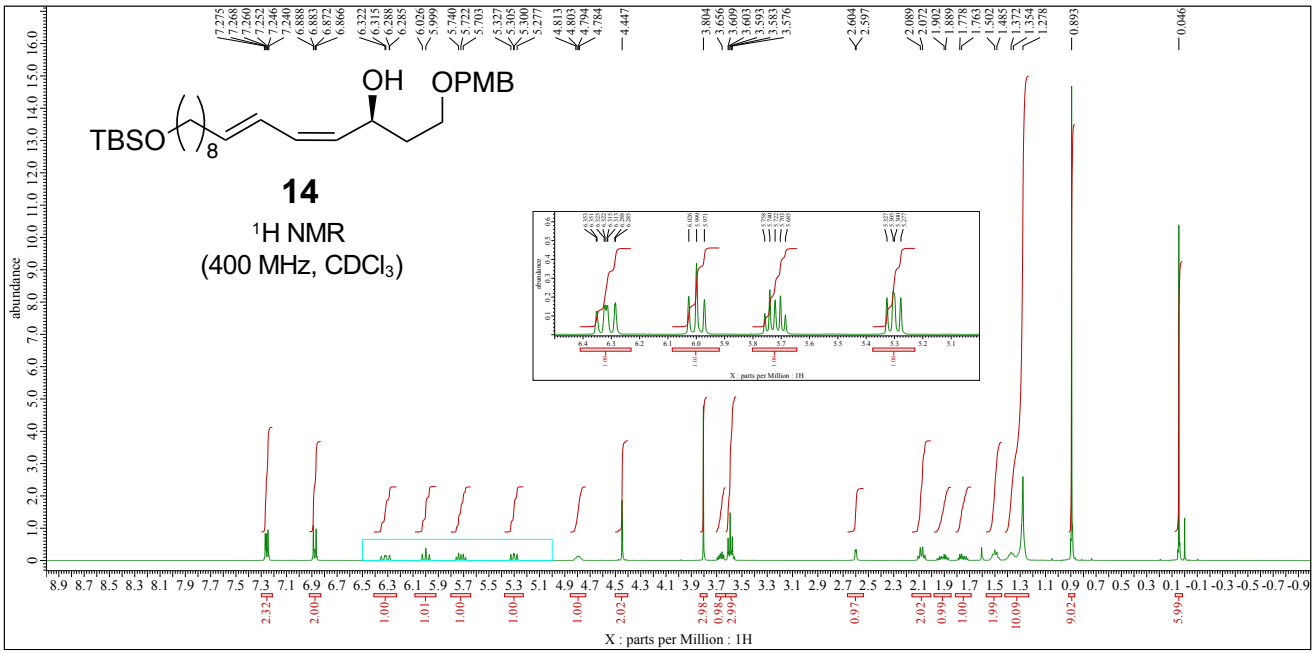
| ピーク# | 保持時間 | 面積 | 面積% | 高さ | 高さ% |
|---|---|---|---|---|---|
| 1 | 24.718 | 626980 | 50.085 | 16247 | 52.675 |
| 2 | 27.066 | 624844 | 49.915 | 14597 | 47.325 |
| 合計 | | 1251824 | 100.000 | 30843 | 100.000 |

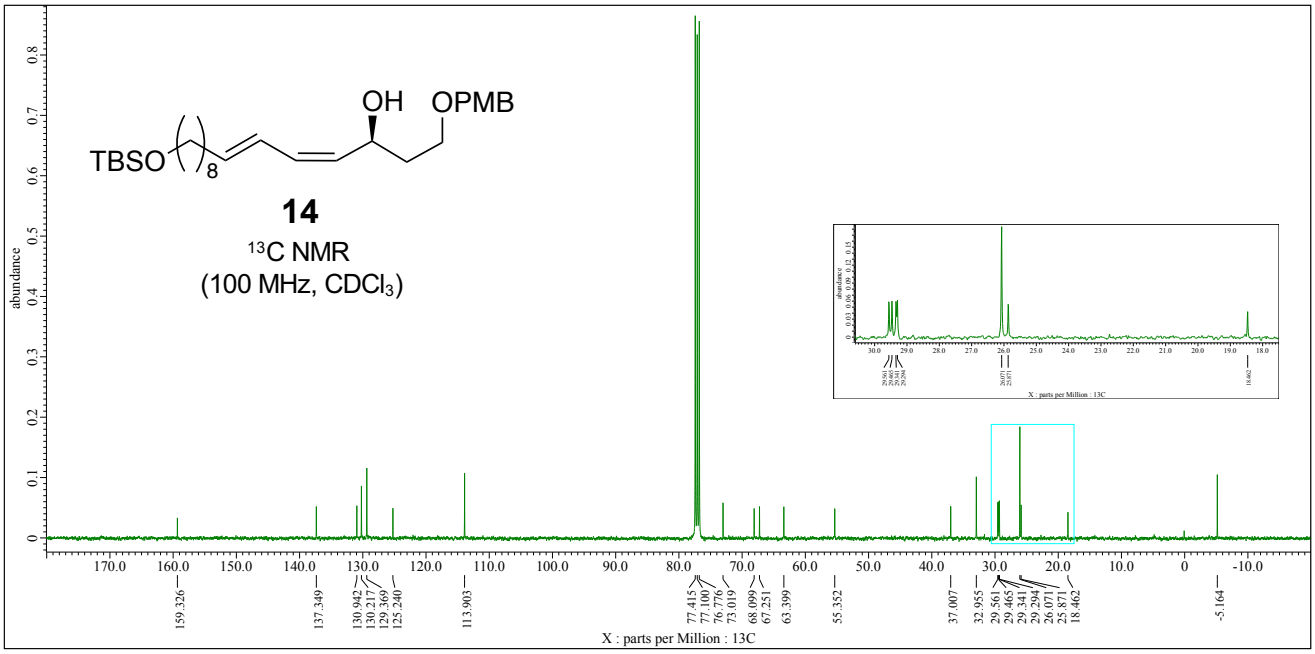

OH OPMB
5
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

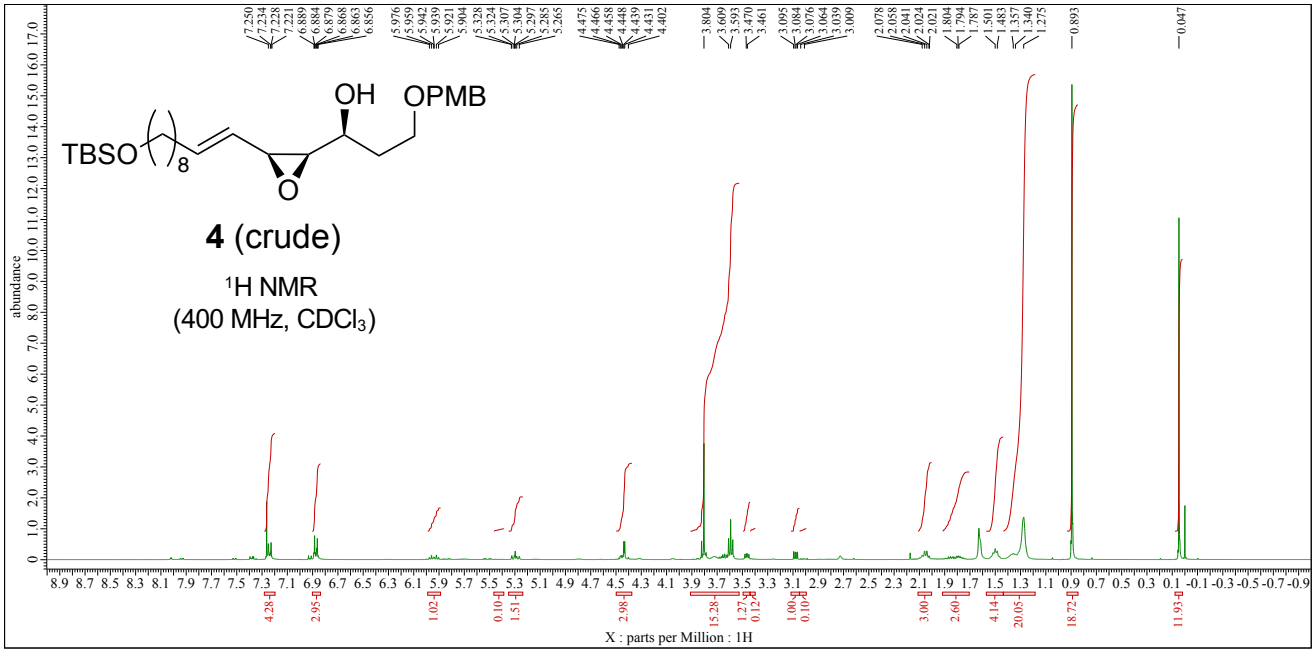

OH OPMB
5
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C


OH
OPMB
TBSO
8
13
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

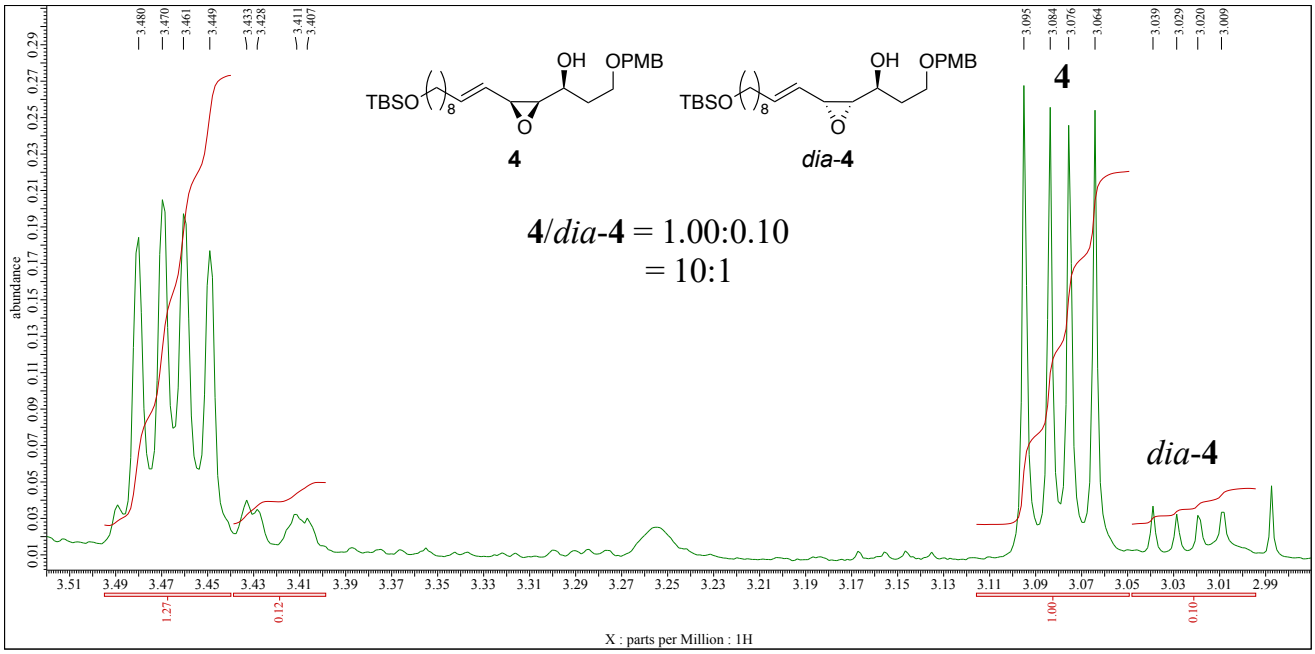

OH
OPMB
TBSO
8
13
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C

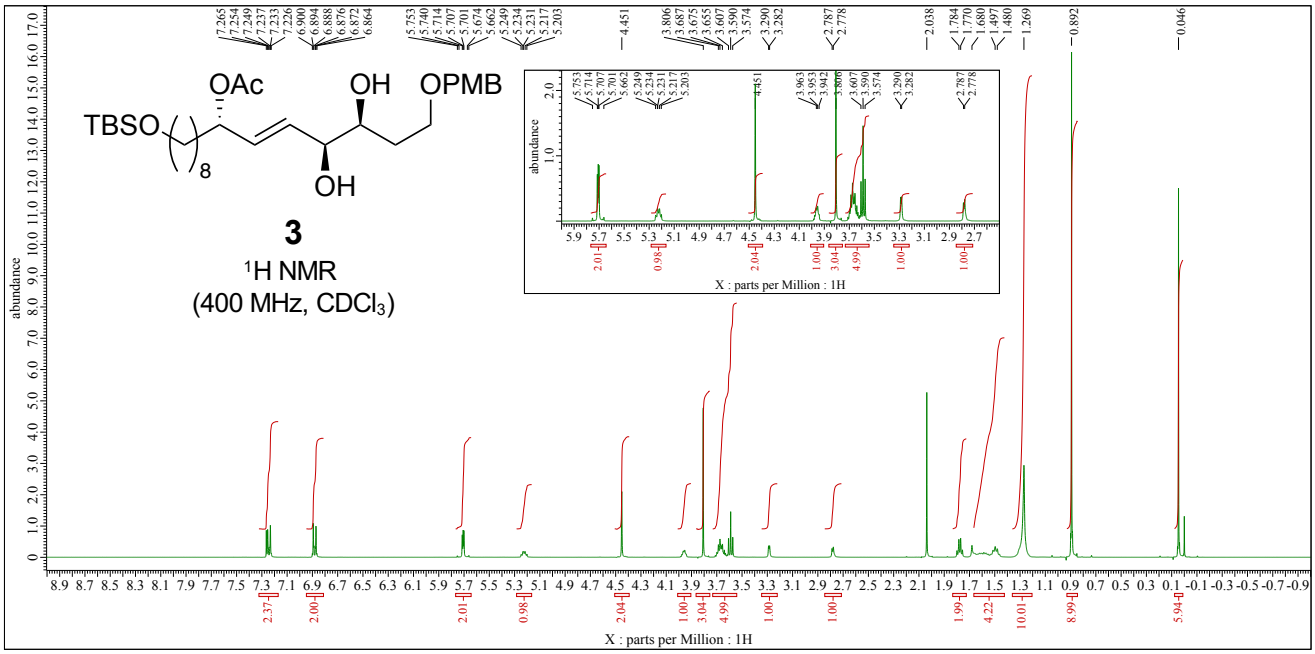

OH
OPMB
TBSO
8
14
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

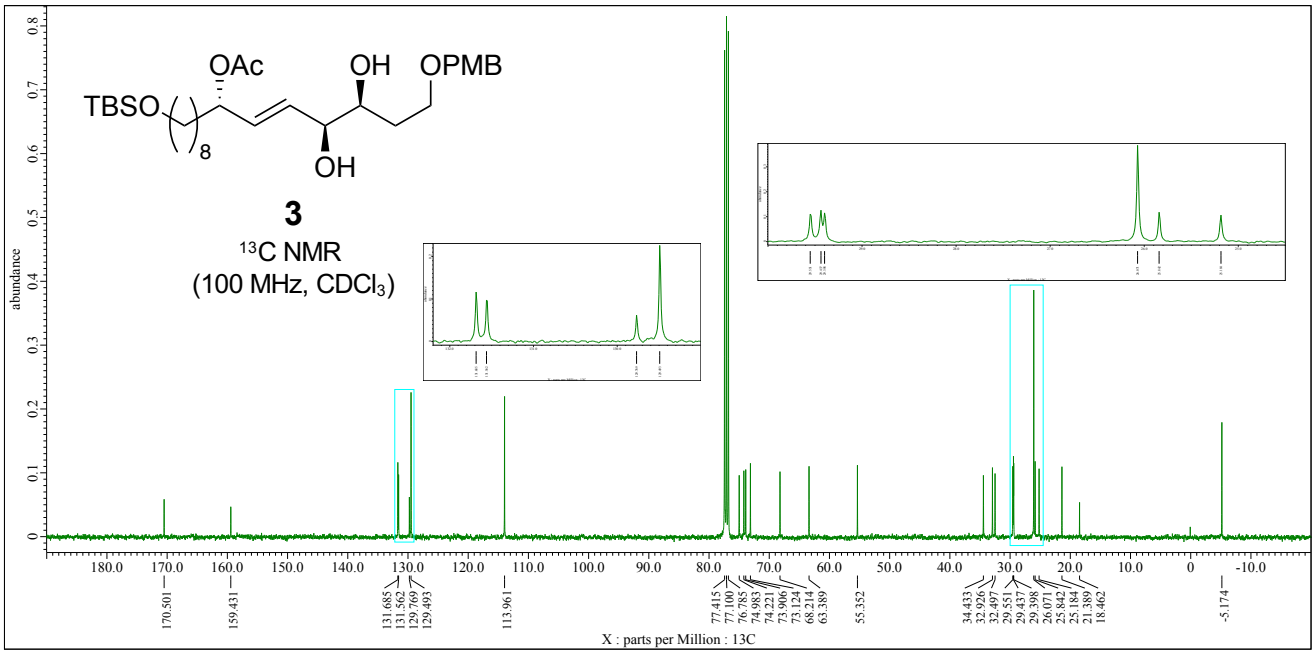

OH
OPMB
TBSO
8
14
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C

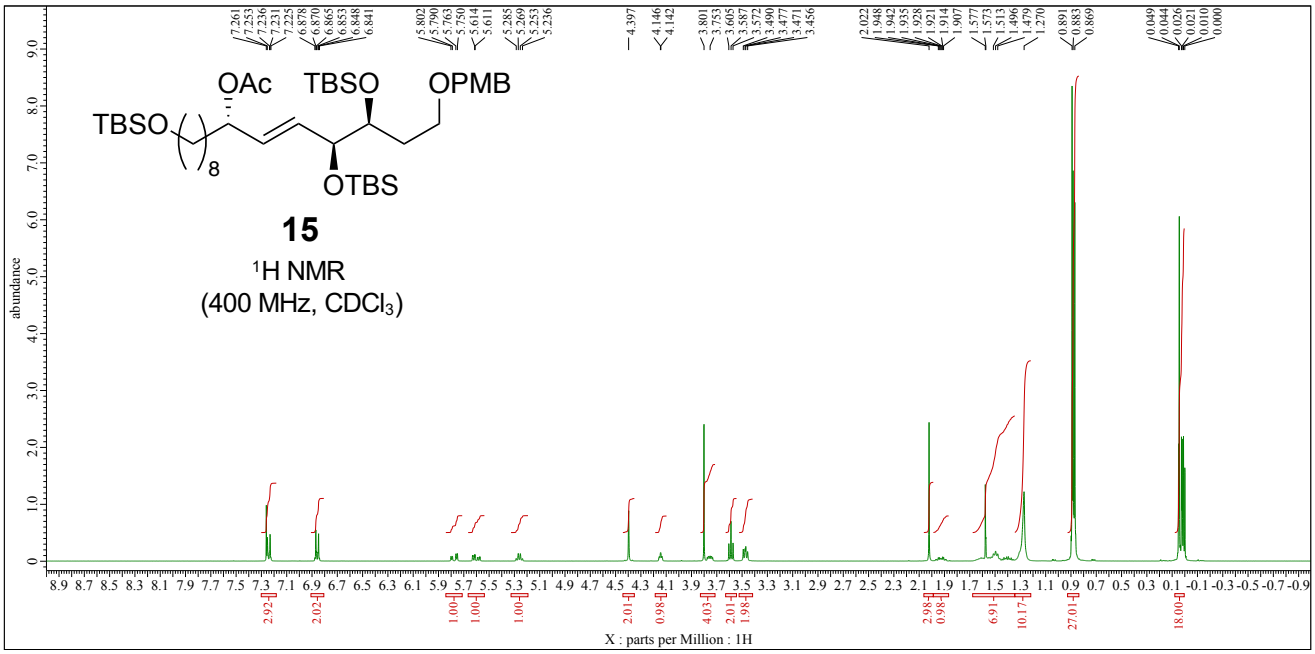


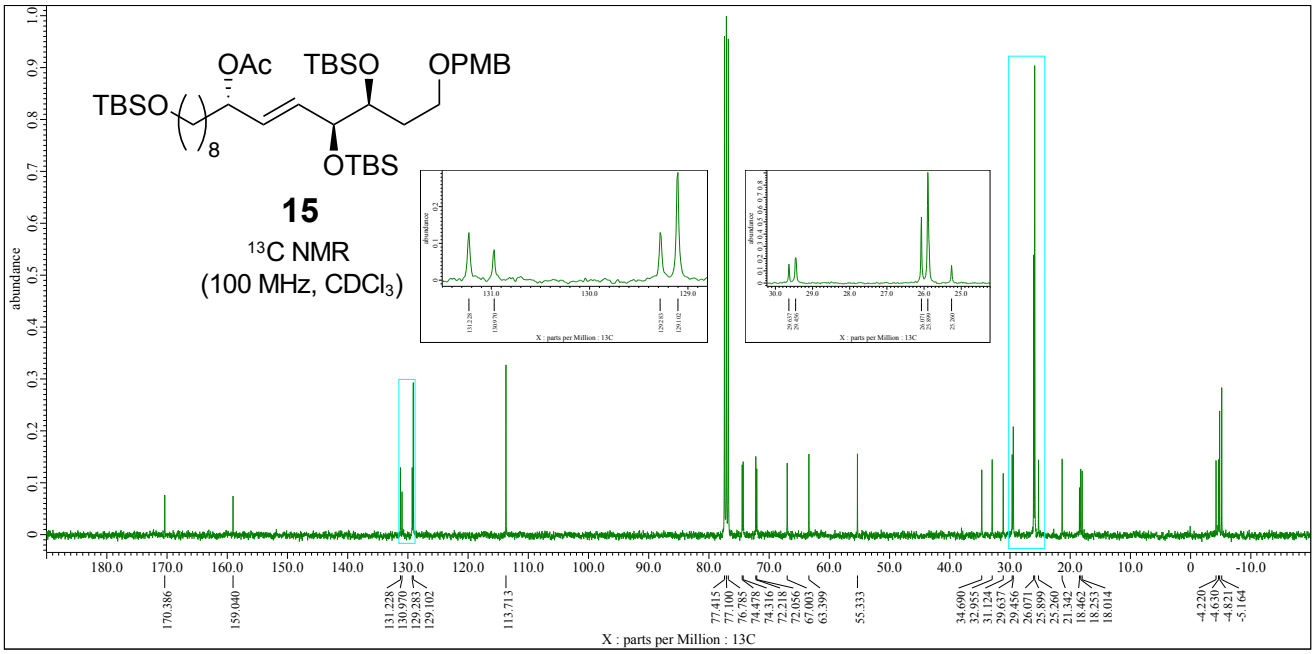

expansion of the above $^{1}$H NMR

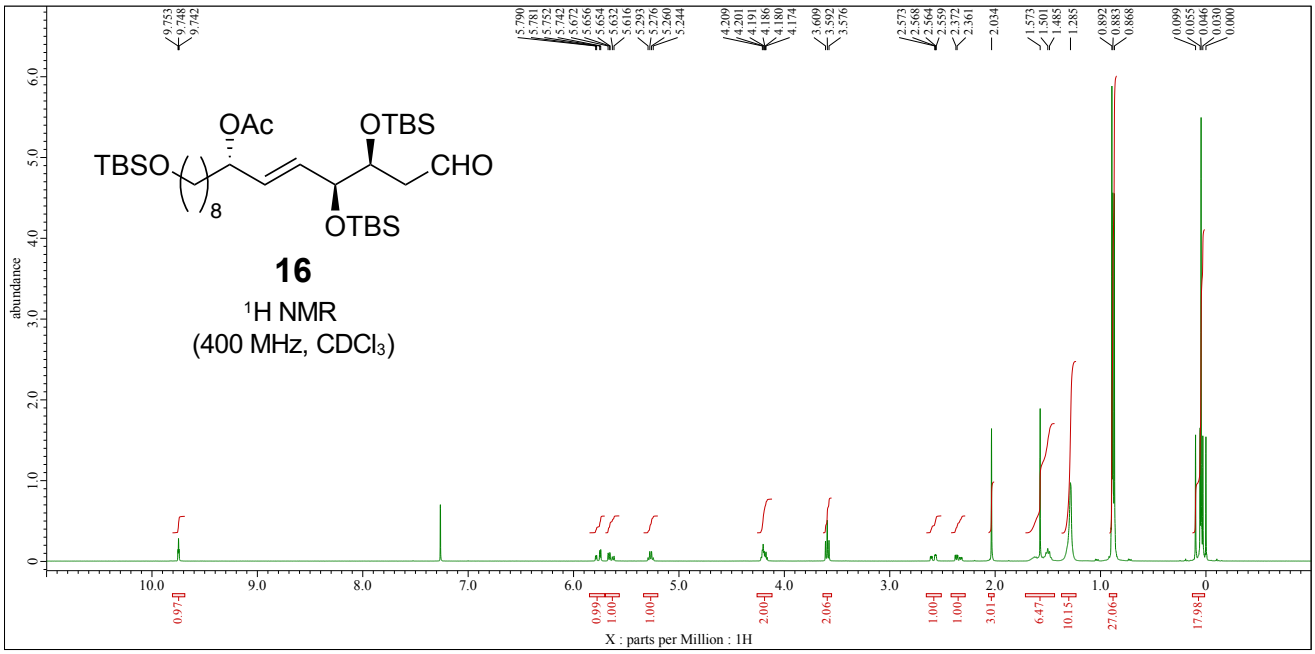


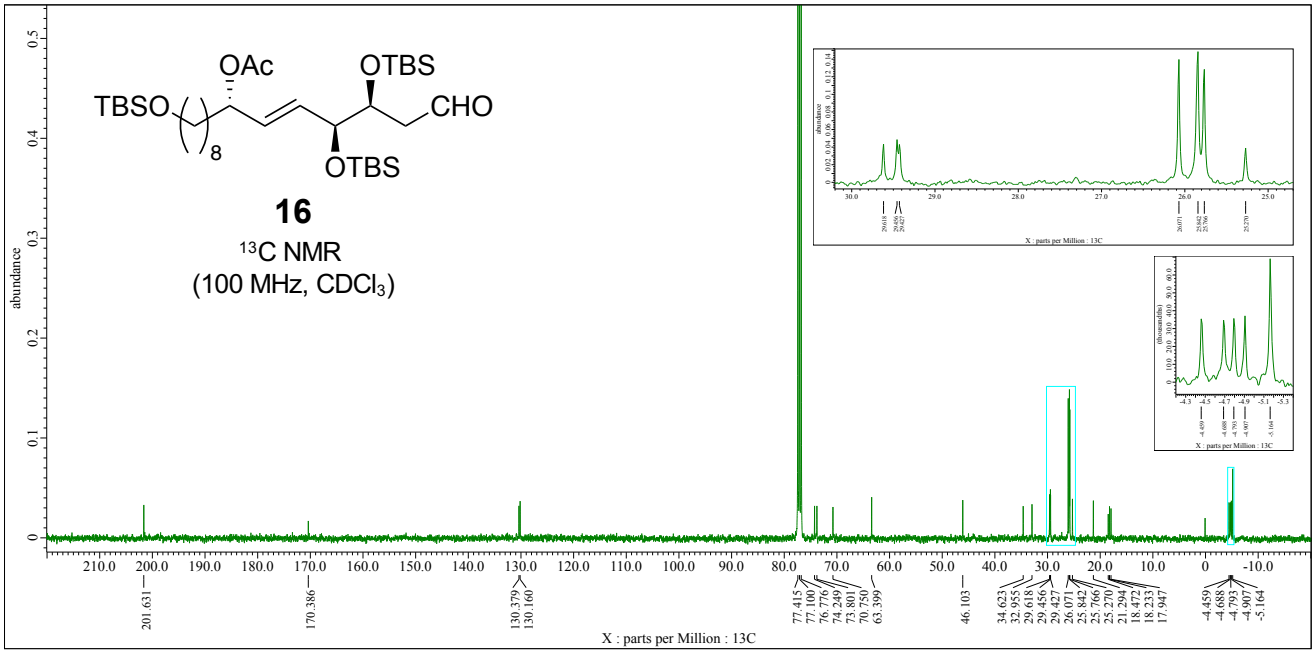

OAc
OH
OPMB
TBSO
8
OH
3
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

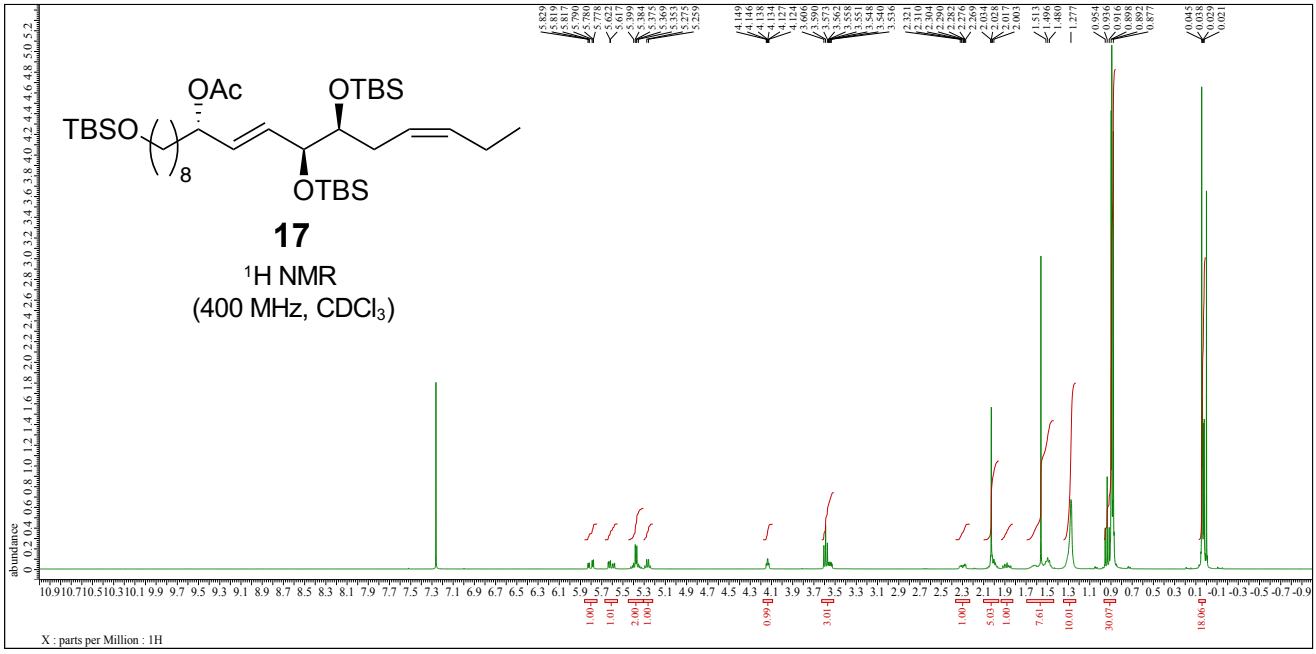

OAc
OH
OPMB
TBSO
8
OH
3
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C

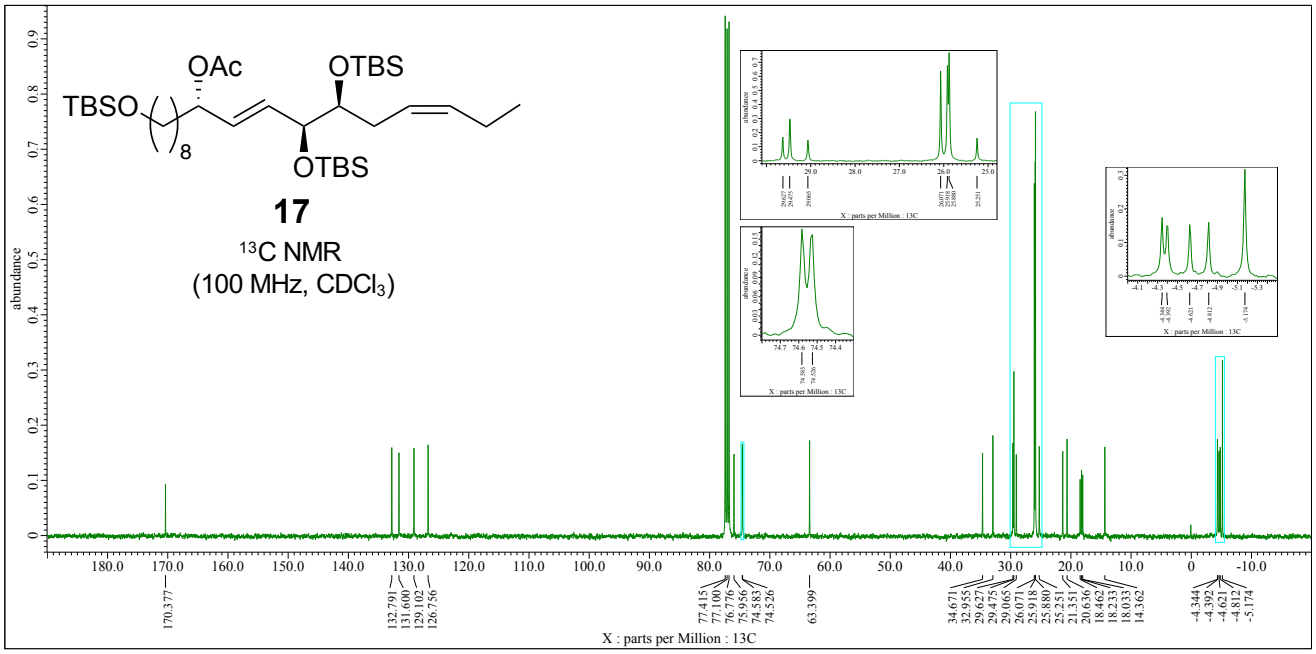

OAc
TBSO
OPMB
TBSO
8
OTBS
15
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

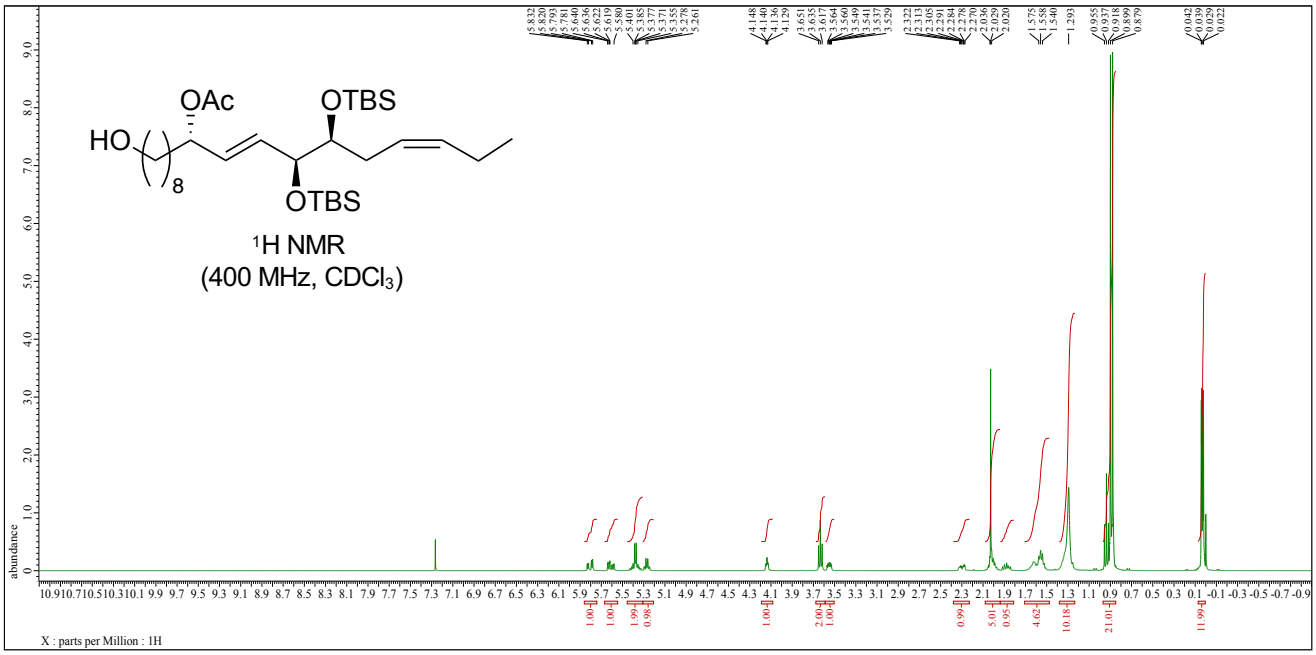

OAc
TBSO
OPMB
TBSO
8
OTBS
15
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C

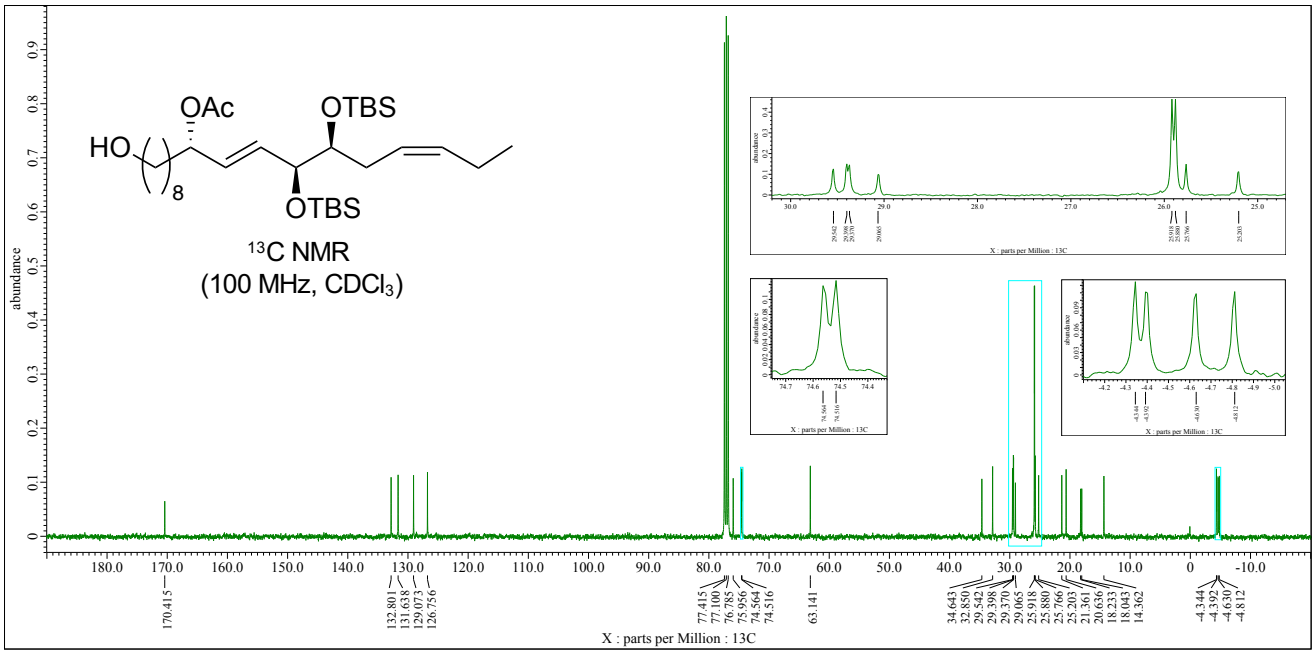

OAc
OTBS
TBSO
CHO
8
OTBS
16
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

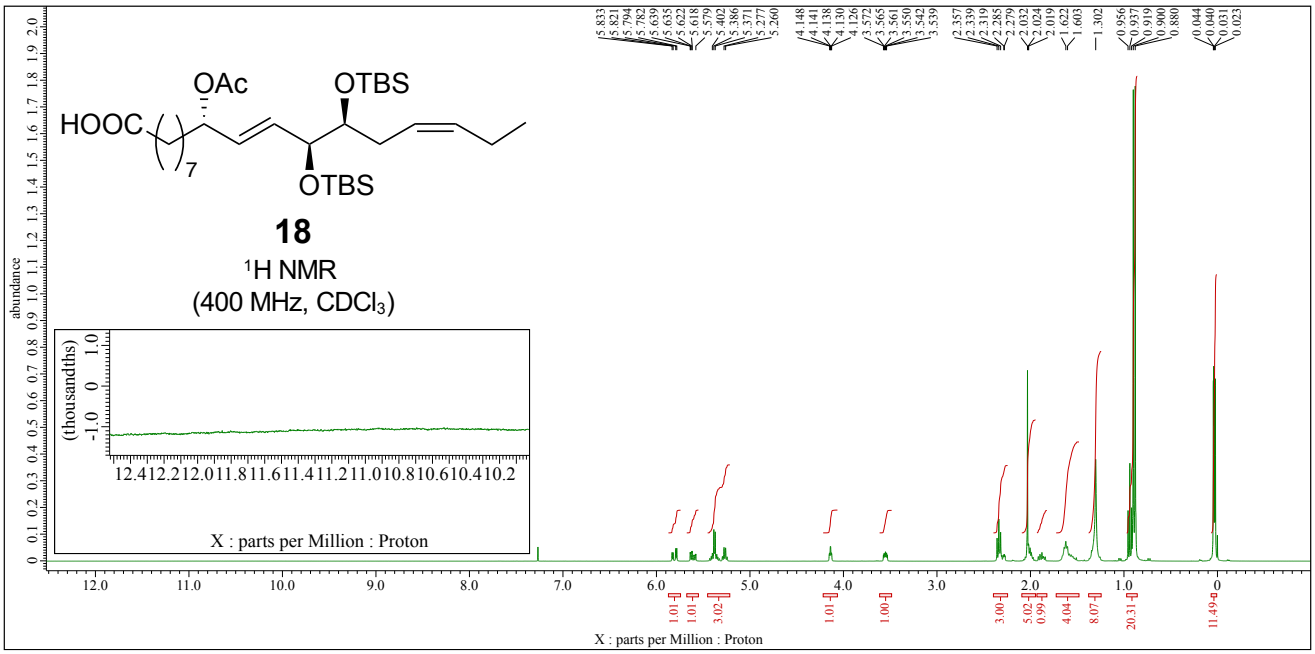

OAc
OTBS
TBSO
CHO
8
OTBS
16
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C

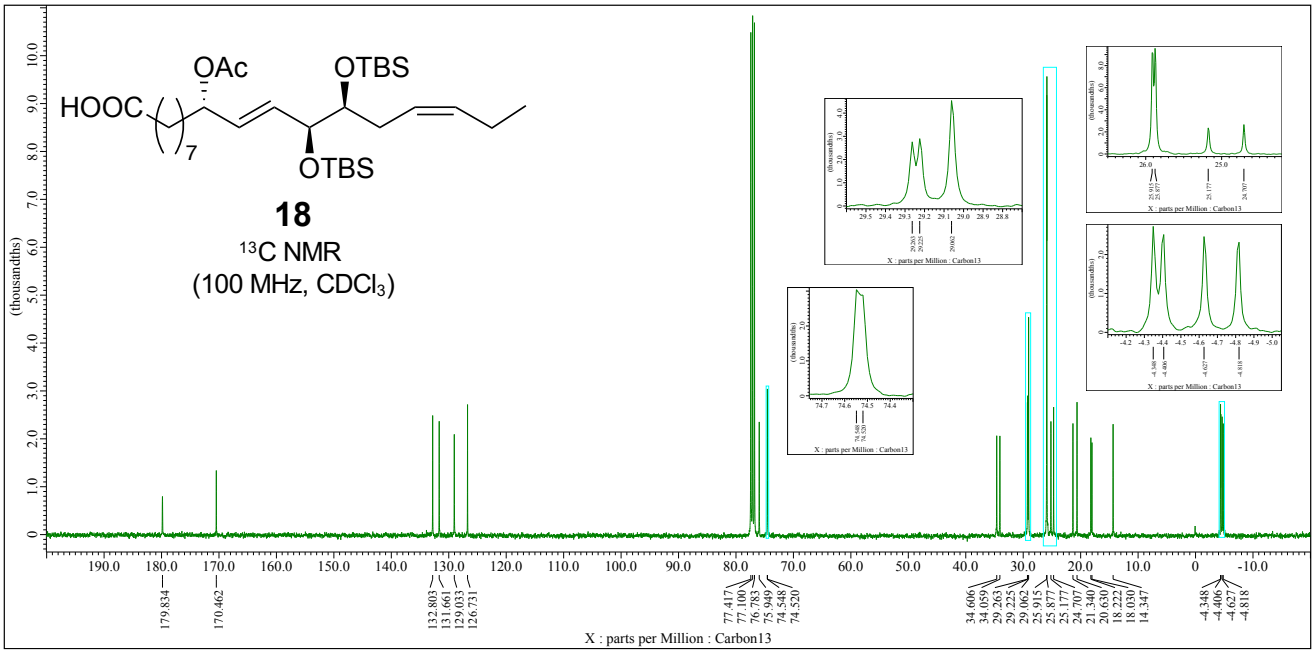

OAc
OTBS
TBSO
8
OTBS
17
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

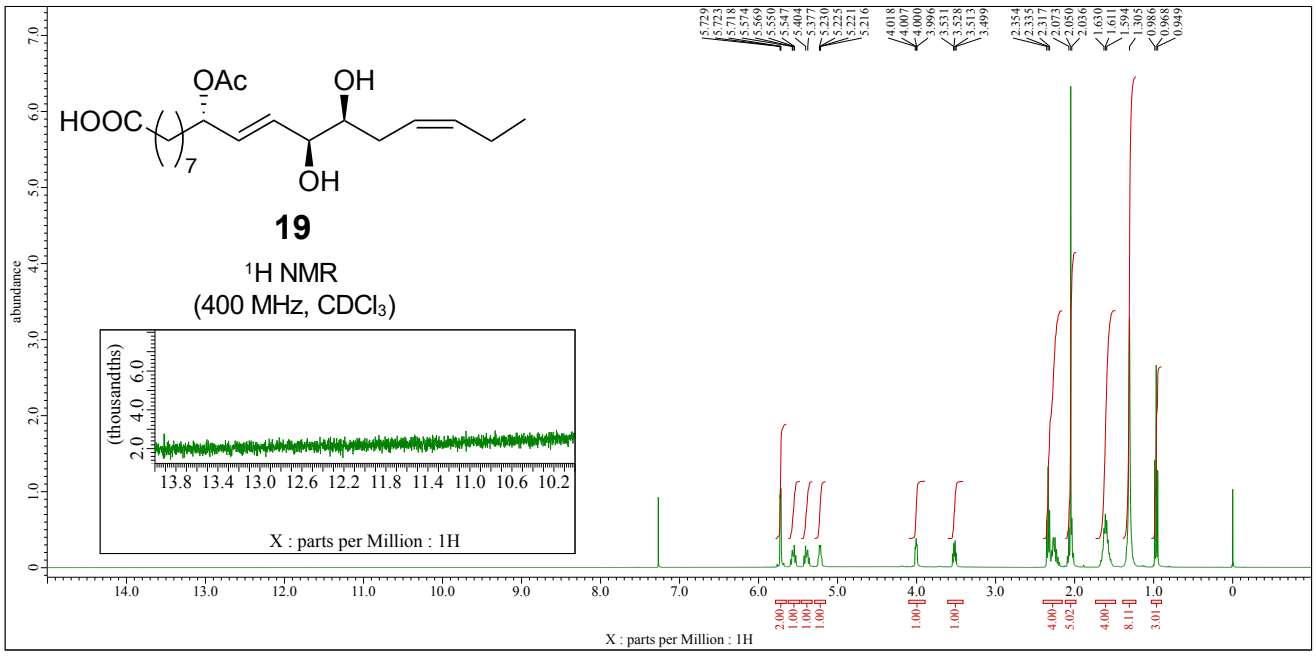

OAc
OTBS
TBSO
8
OTBS
17
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C

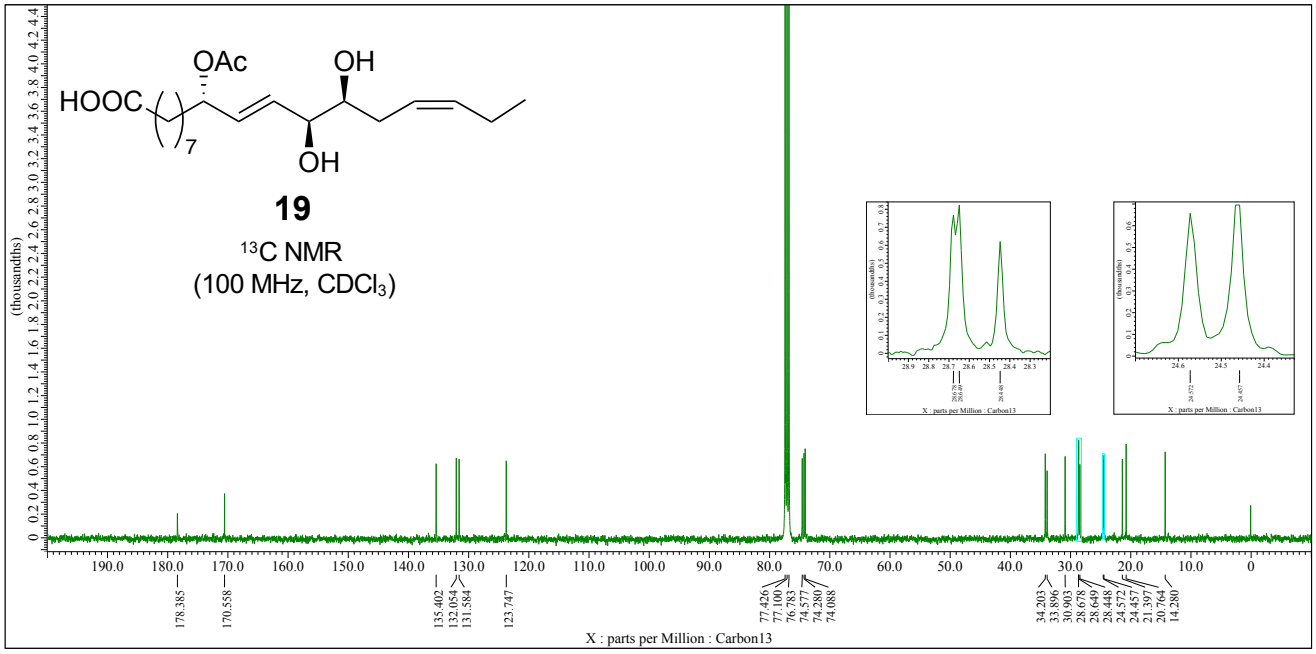

OAc
OTBS
HO
8
OTBS
$^{1}$H NMR
(400 MHz, $CDCl_3$)
abundance
X : parts per Million : 1H

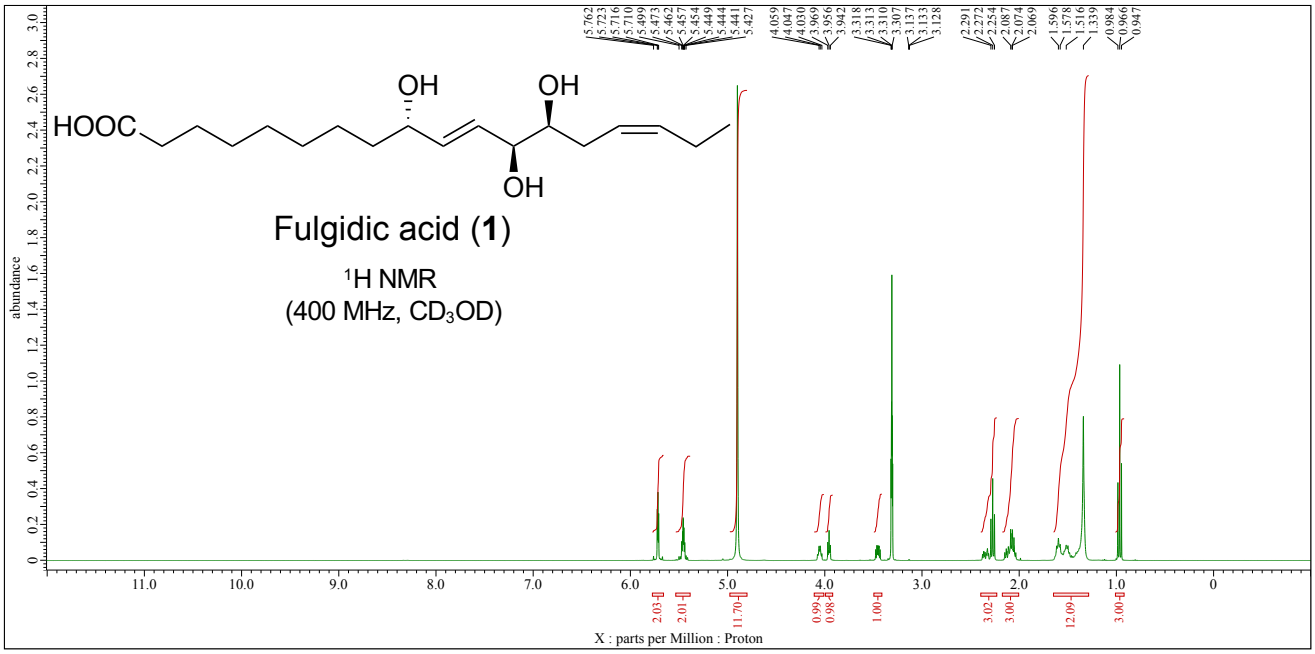

OAc
OTBS
HO
8
OTBS
$^{13}$C NMR
(100 MHz, $CDCl_3$)
abundance
X : parts per Million : 13C

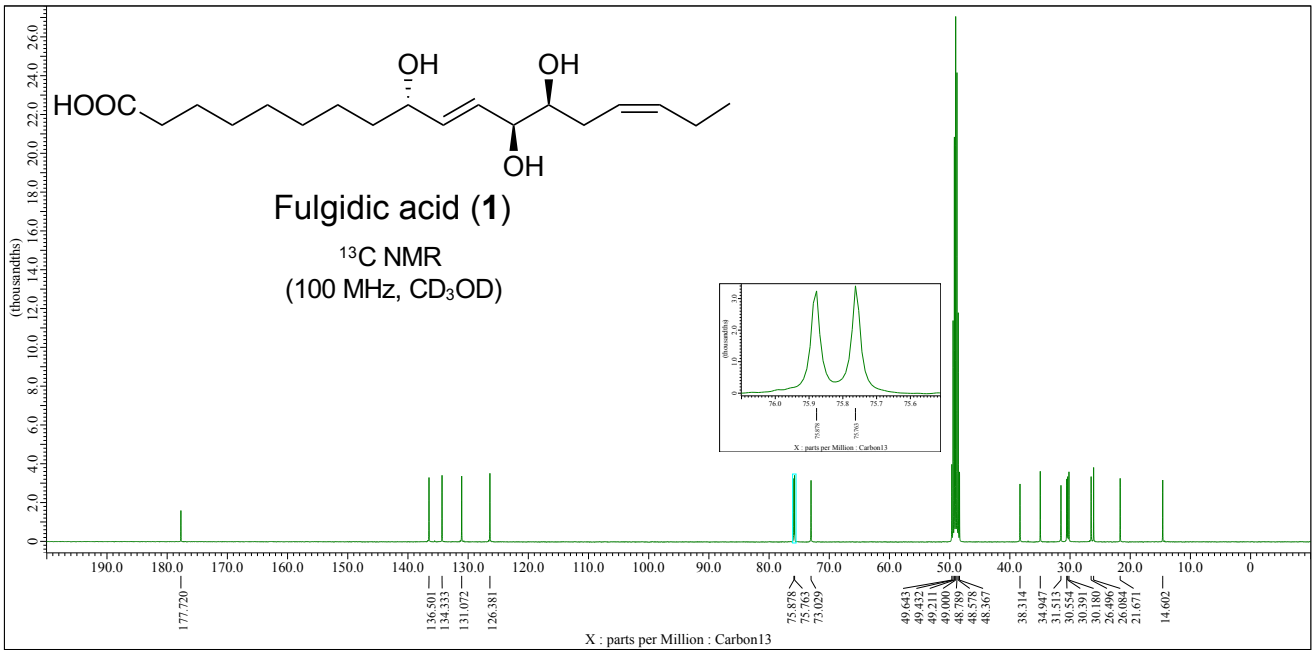

OAc
OTBS
HOOC
7
OTBS
18
1H NMR
(400 MHz, CDCl3)
X : parts per Million : Proton

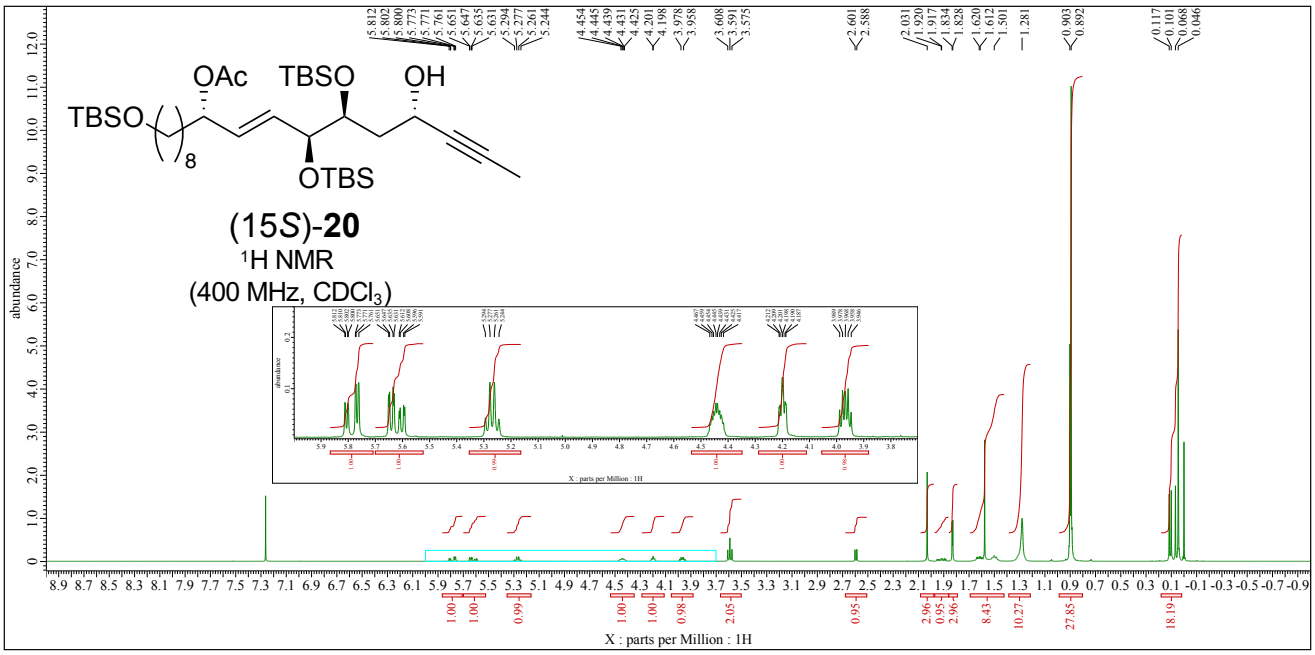

OAc
OTBS
HOOC
7
OTBS
18
13C NMR
(100 MHz, CDCl3)
X : parts per Million : Carbon13

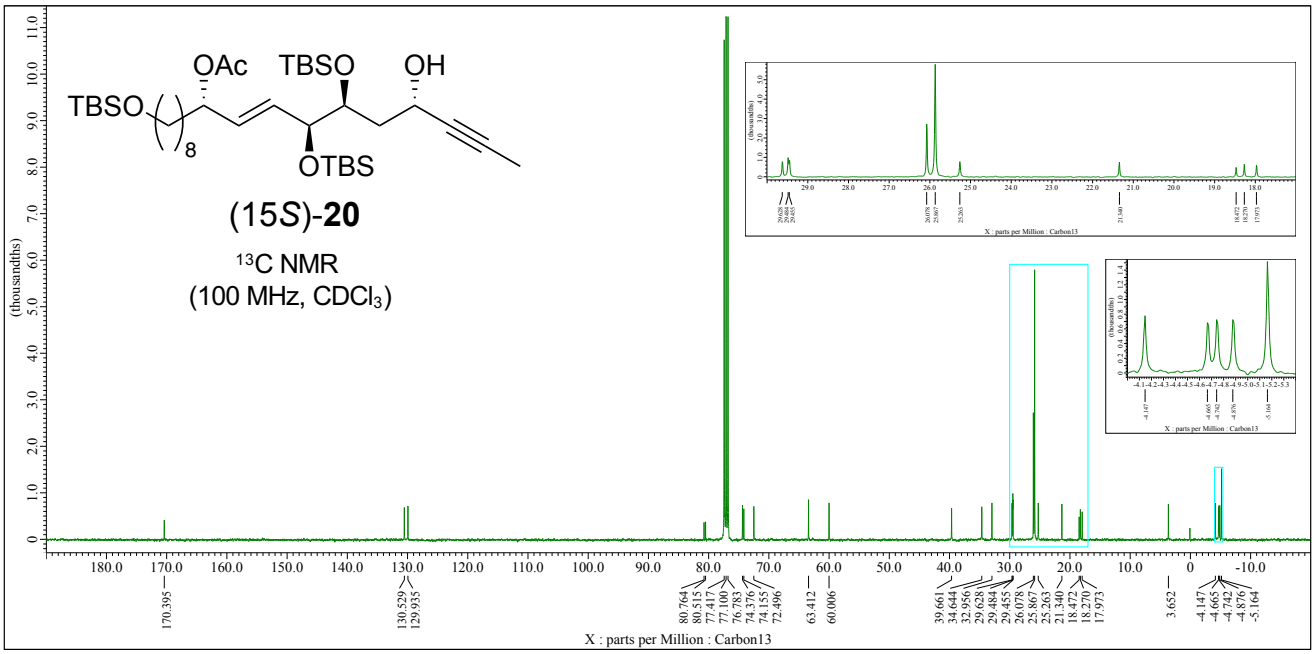

OAc
OH
HOOC
7
OH
19
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

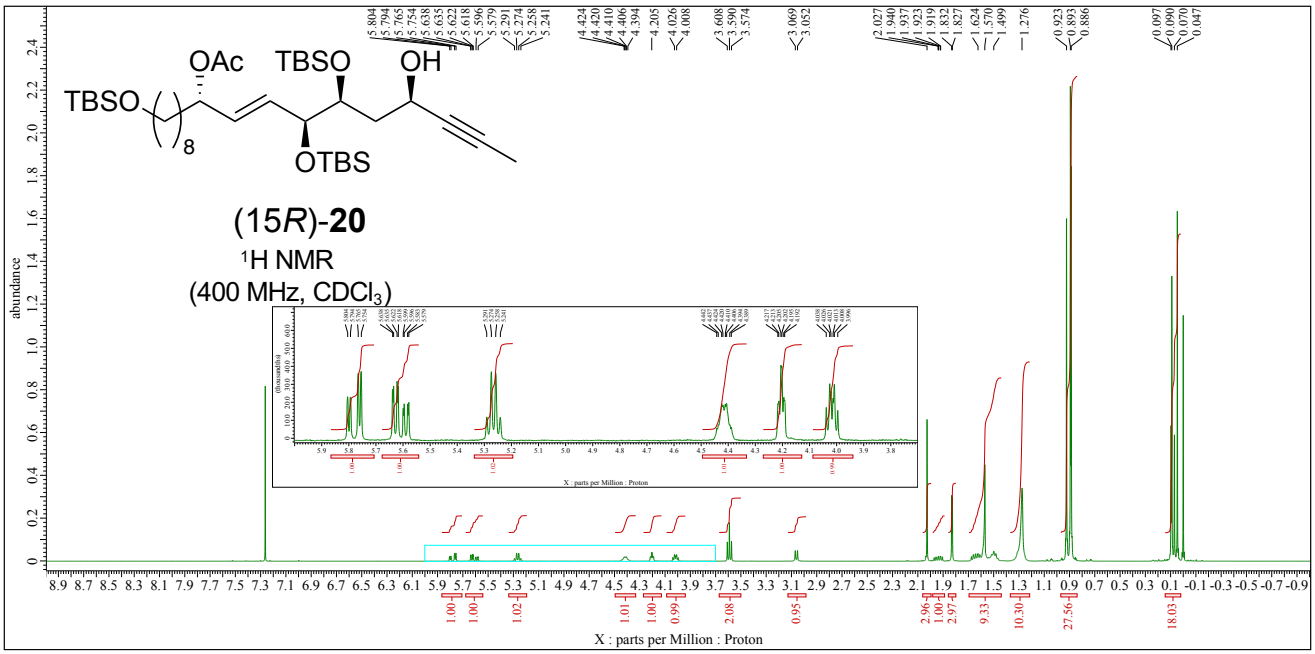

OAc
OH
HOOC
7
OH
19
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

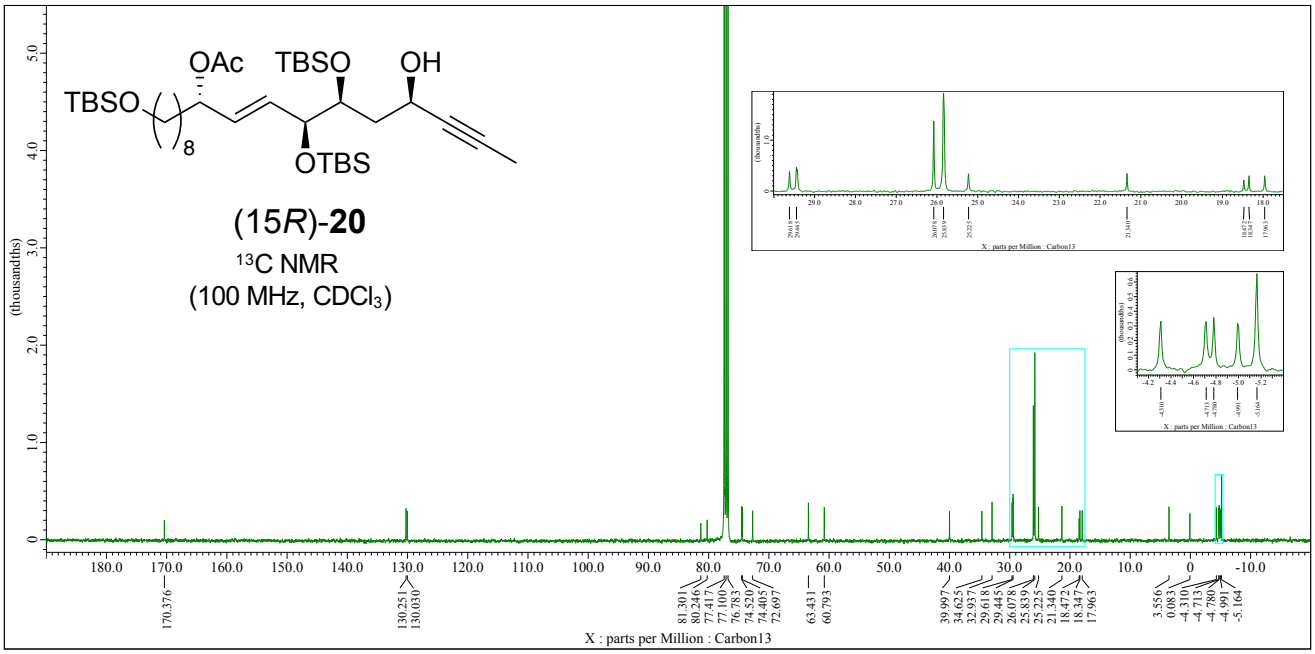

HOOC
OH
OH
OH
Fulgidic acid (1)
1H NMR
(400 MHz, CD3OD)
abundance
X : parts per Million : Proton


HOOC
OH
OH
OH
Fulgidic acid (1)
13C NMR
(100 MHz, CD3OD)
(thousandths)
X : parts per Million : Carbon13

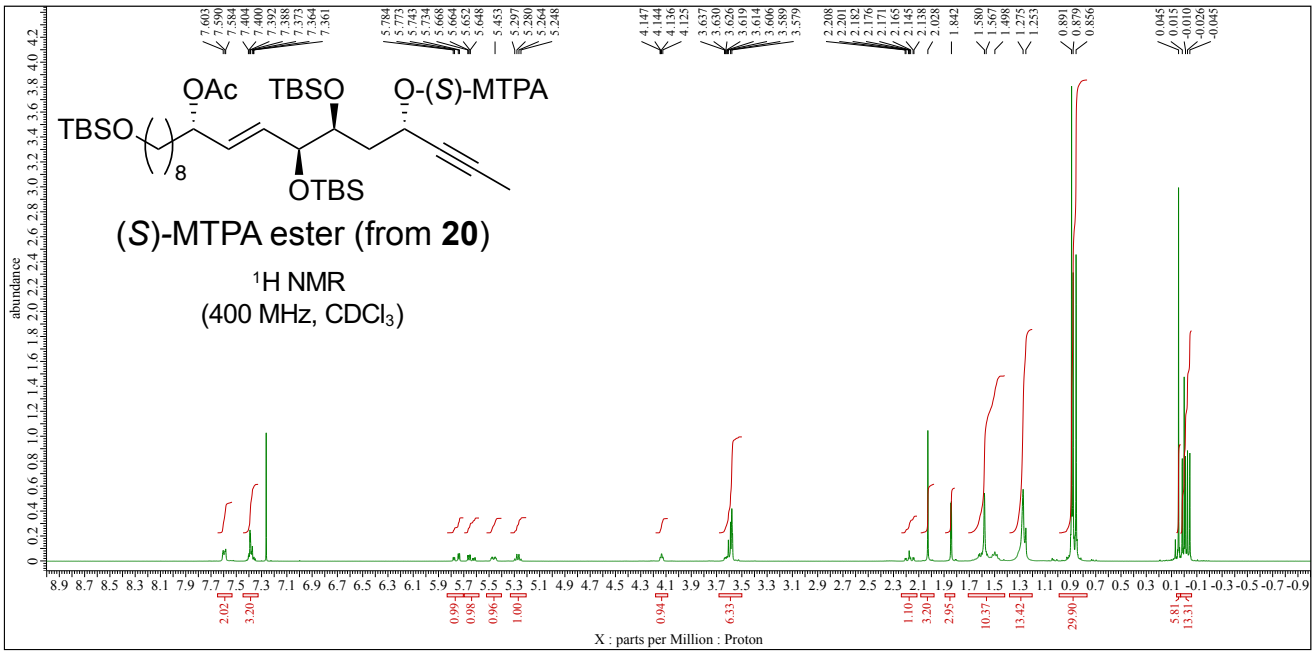

OAc
TBSO
OH
TBSO
8
OTBS
(15S)-20
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

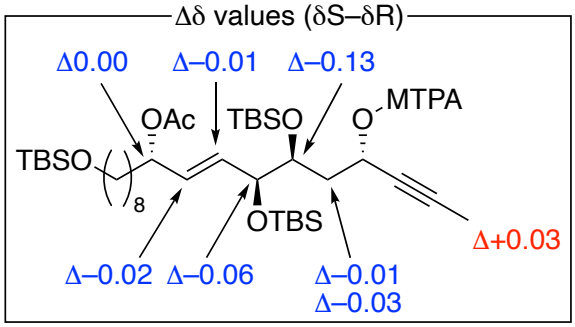

OAc
TBSO
OH
TBSO
8
OTBS
(15S)-20
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13


OAc
TBSO
OH
TBSO
8
OTBS
(15R)-20
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : Proton

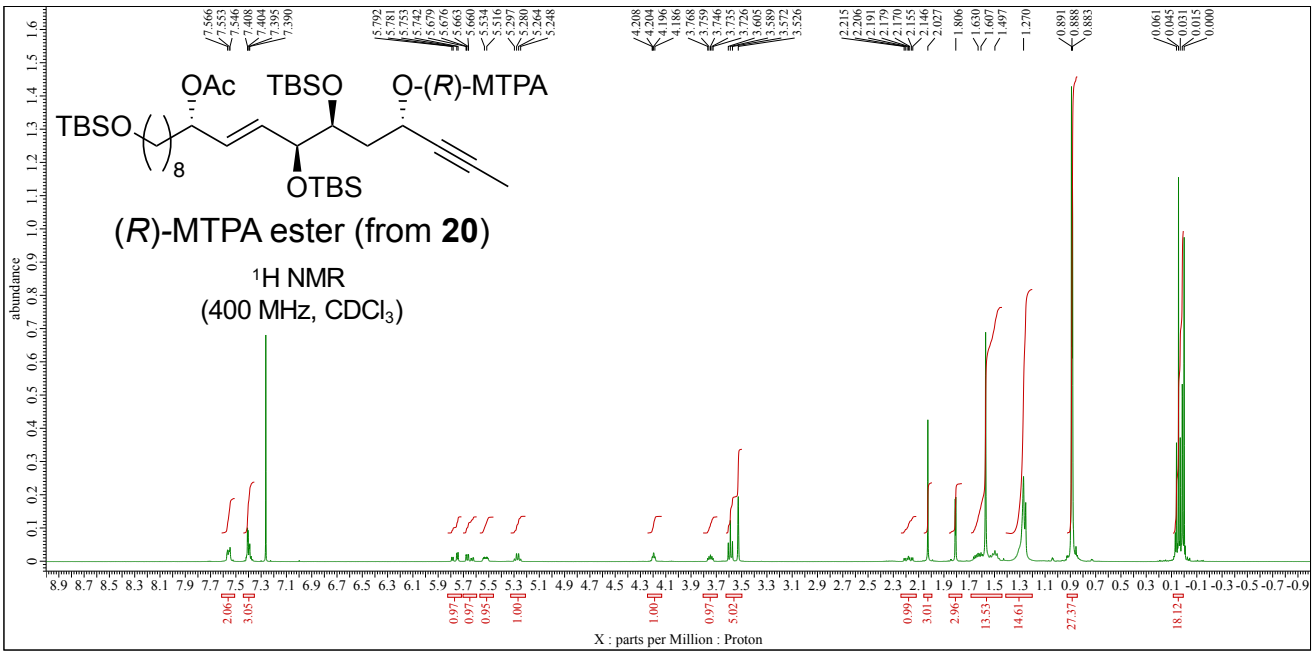

OAc
TBSO
OH
TBSO
8
OTBS
(15R)-20
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

(*S*)-MTPA ester derived from **20** (expansion => see next page )

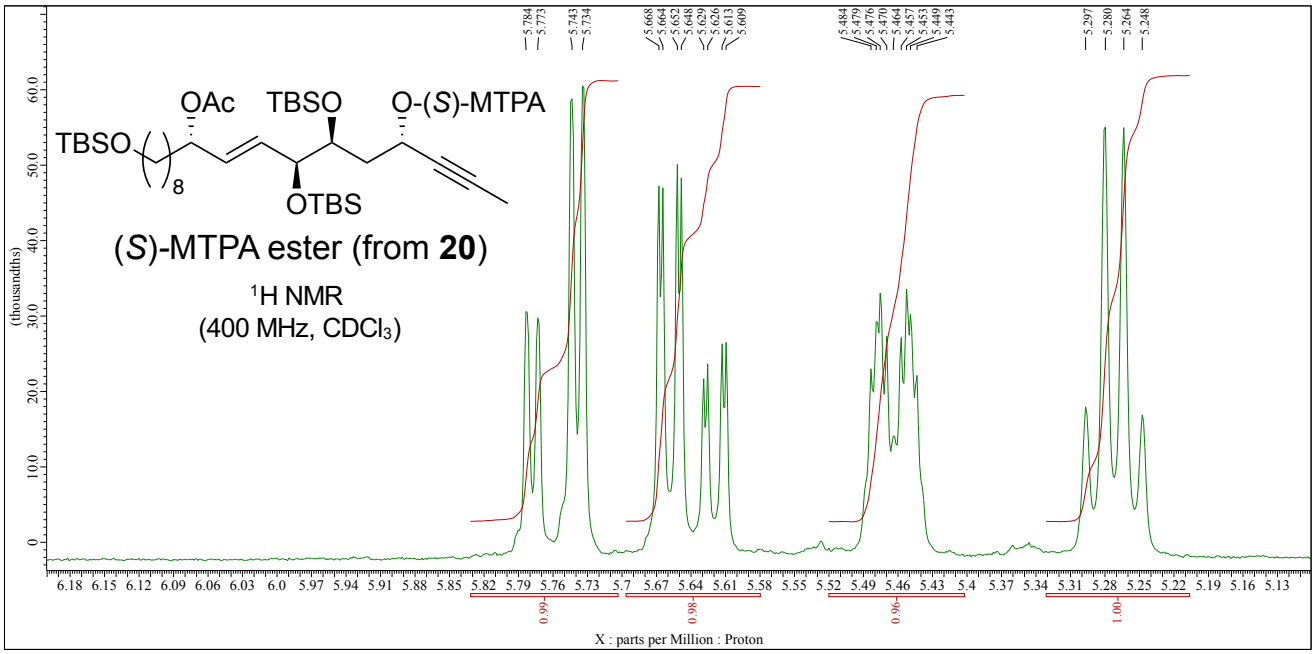


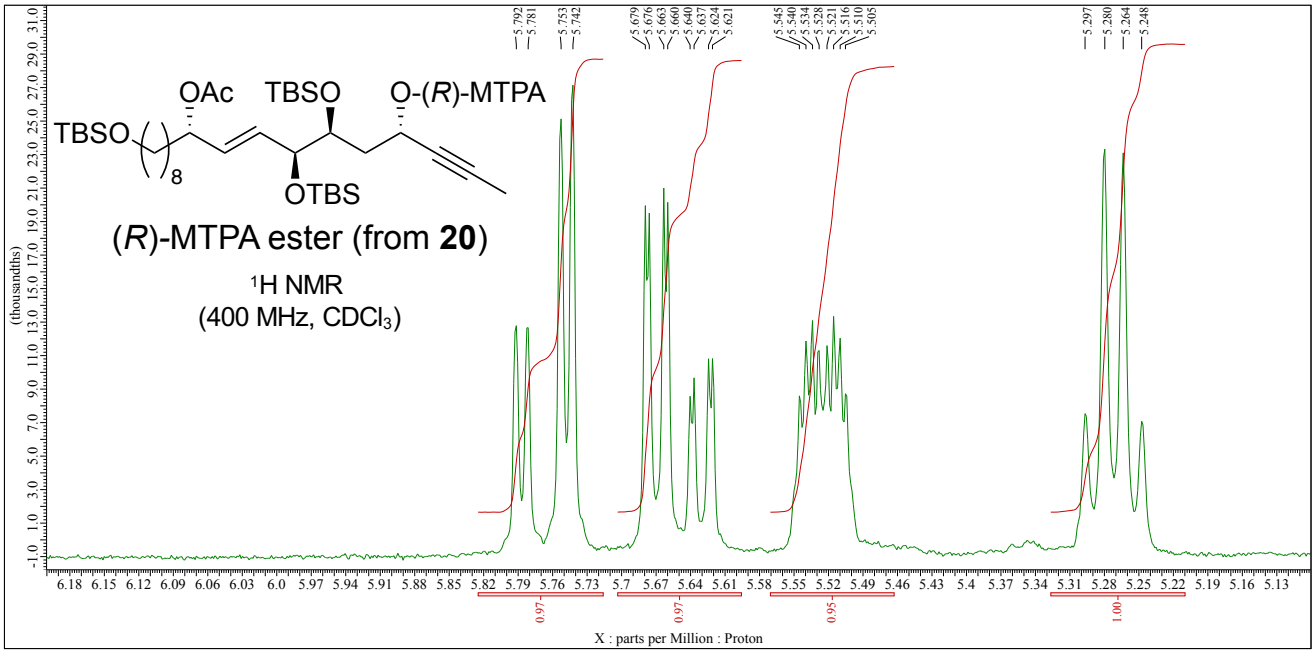

(*R*)-MTPA ester derived from **20** (expansion => see next page )



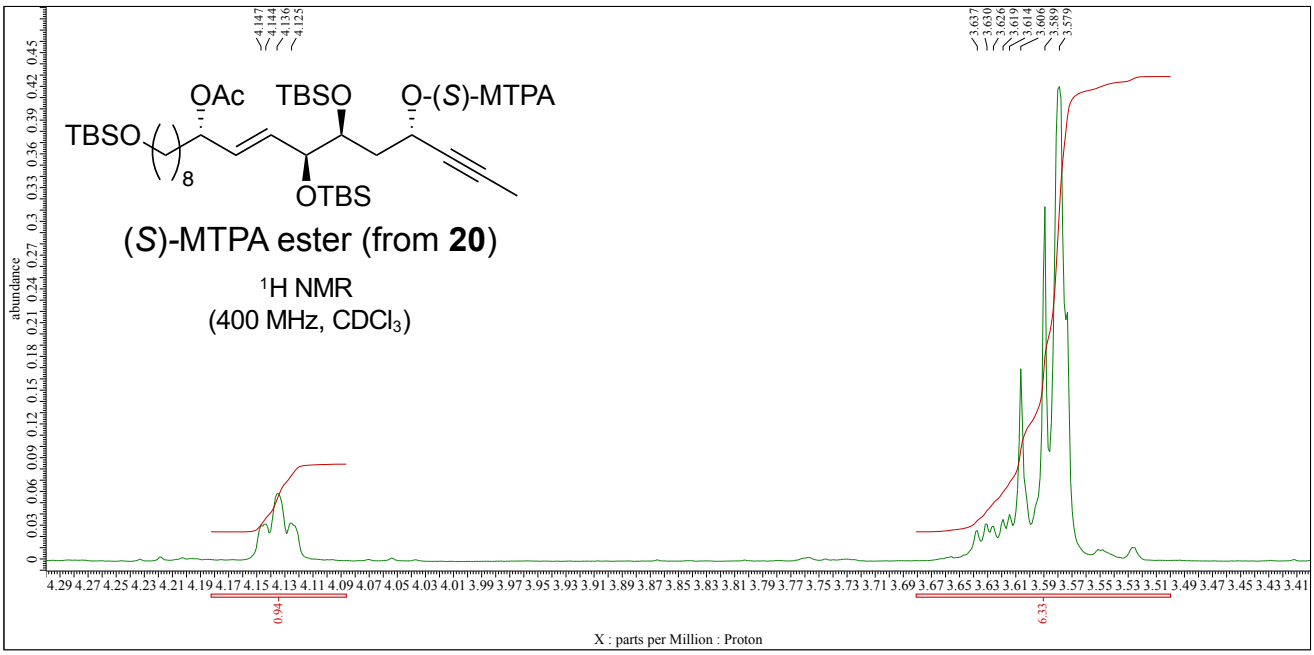
Expansion of (*S*)-MTPA ester derived from **20** at 6.2 ppm–5.1 ppm



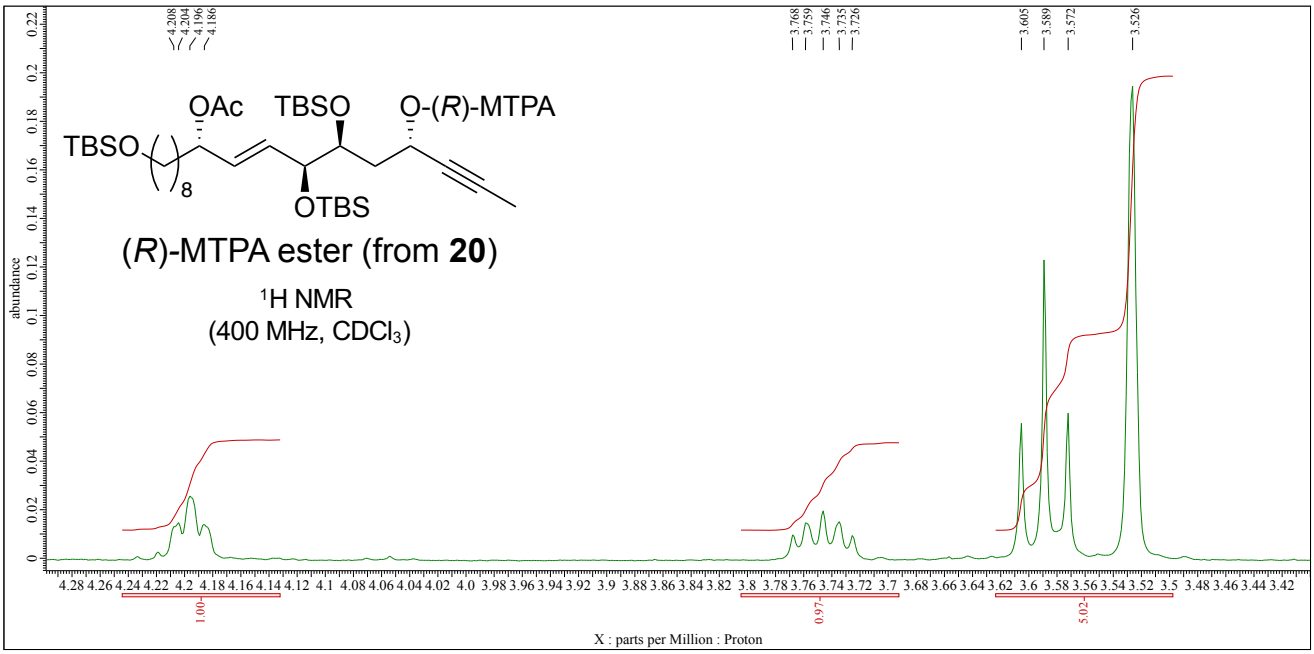

Expansion of (*R*)-MTPA ester derived from **20** at 6.2 ppm–5.1 ppm



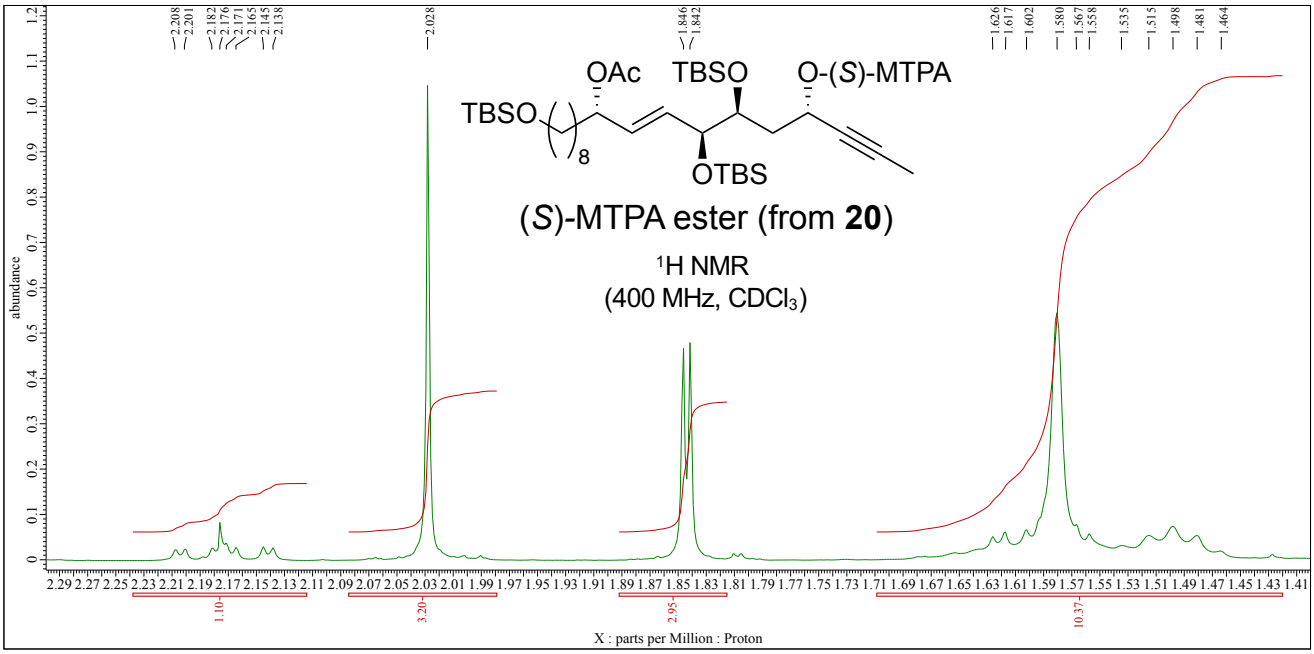
Expansion of (*S*)-MTPA ester derived from **20** at 4.3 ppm–3.4 ppm



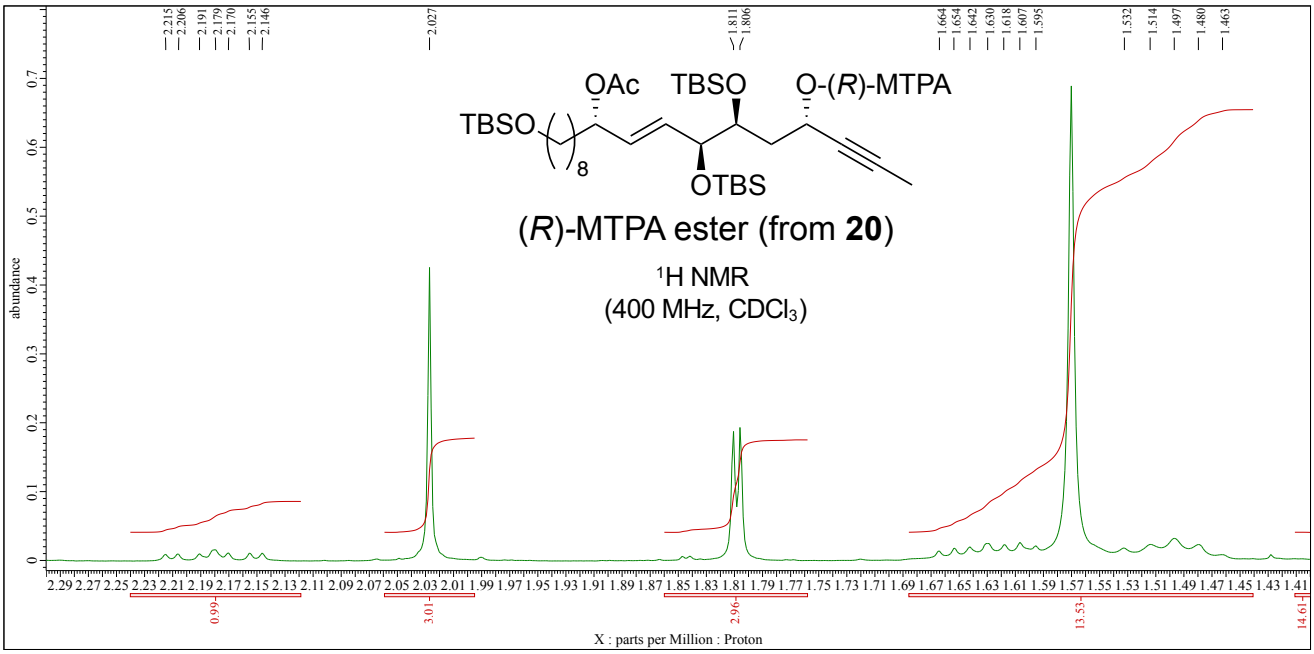

Expansion of (*R*)-MTPA ester derived from **20** at 4.3 ppm–3.4 ppm

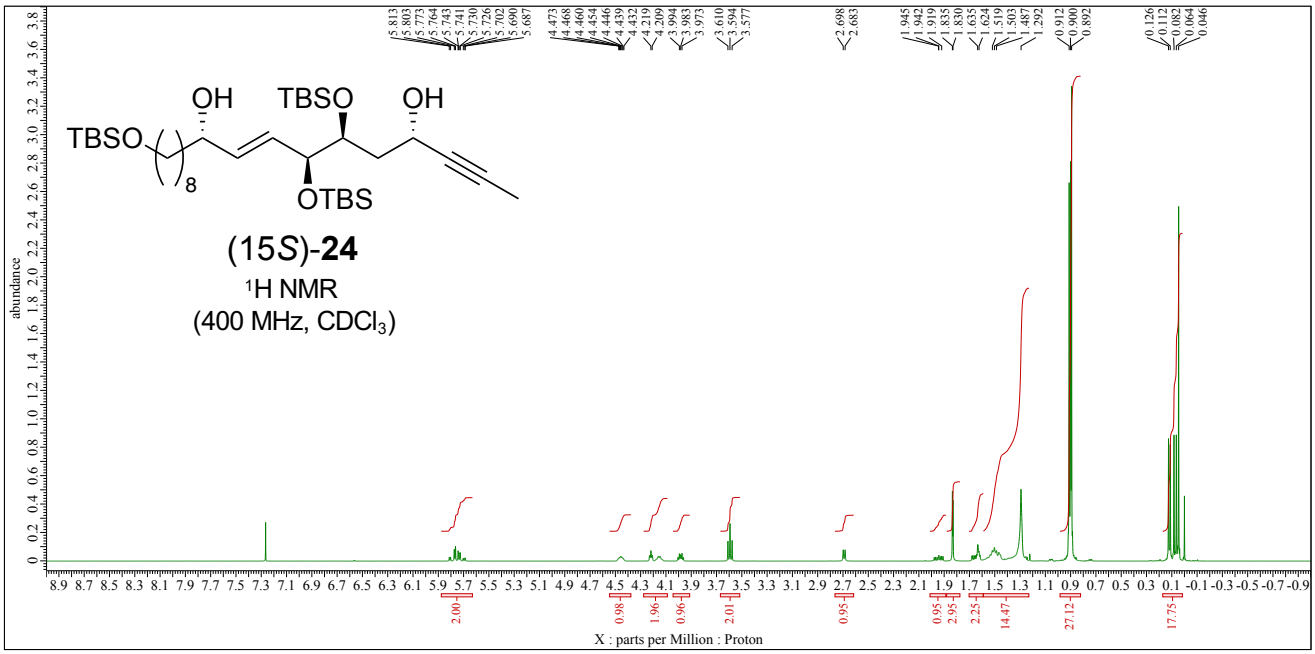


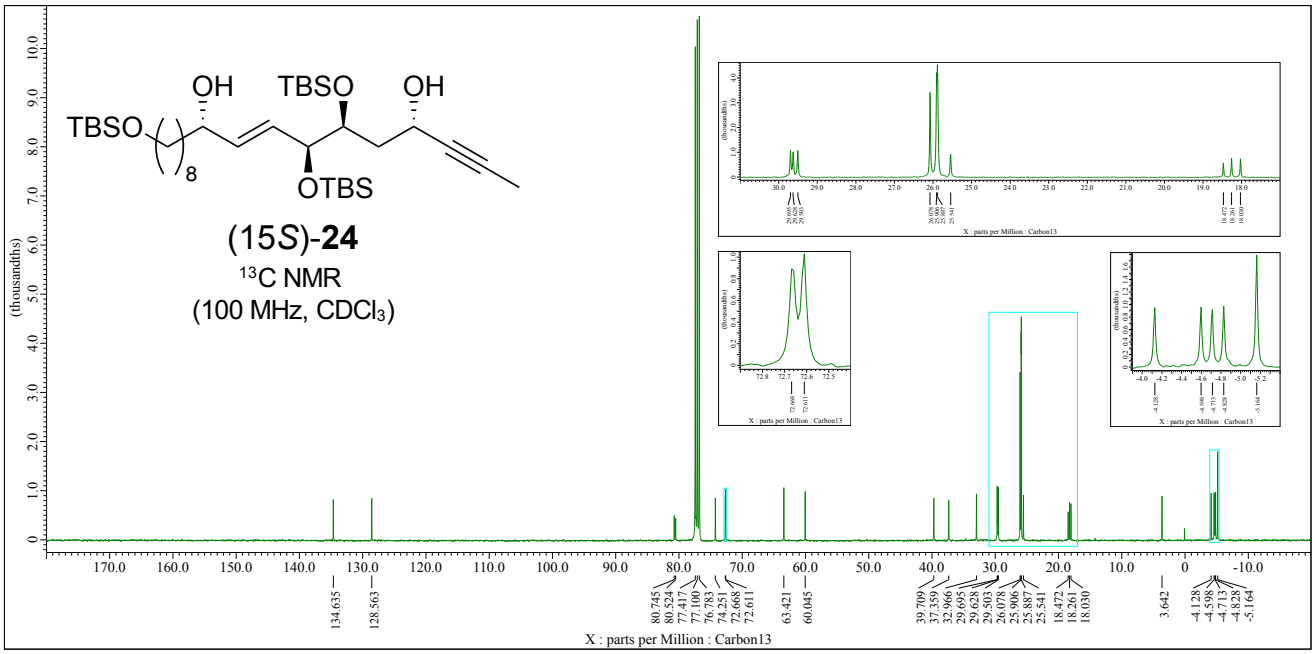
Expansion of (*S*)-MTPA ester derived from **20** at 2.3 ppm–1.4 ppm

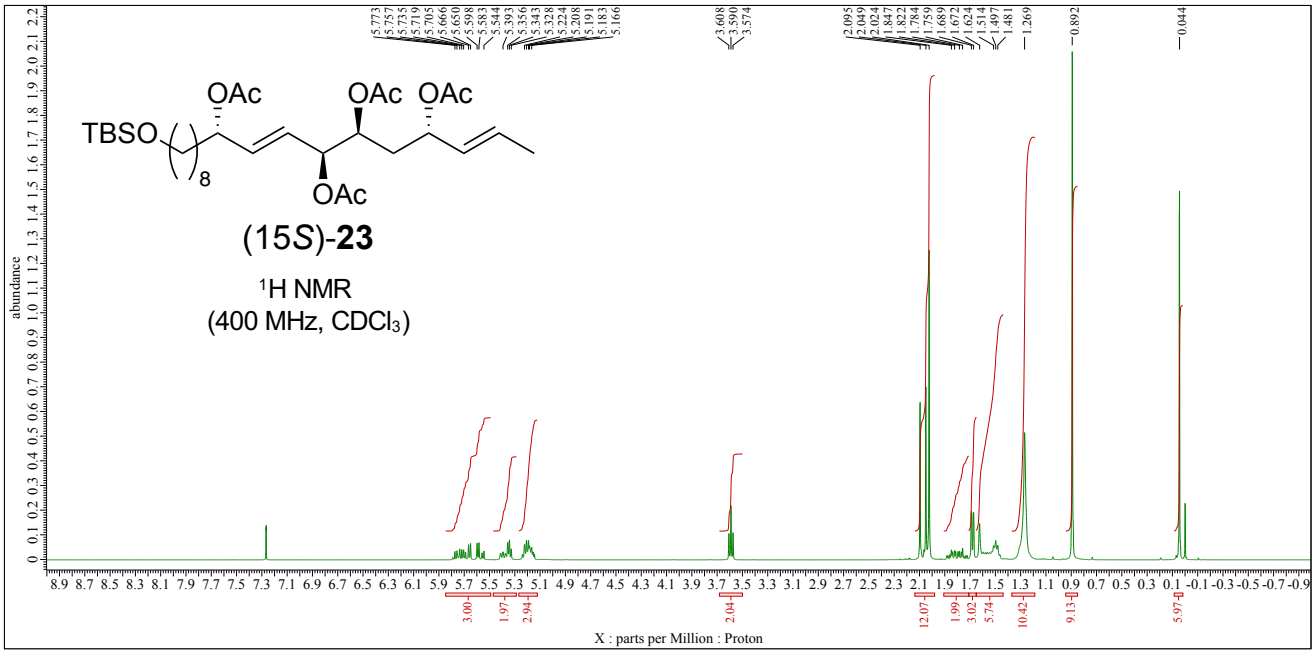


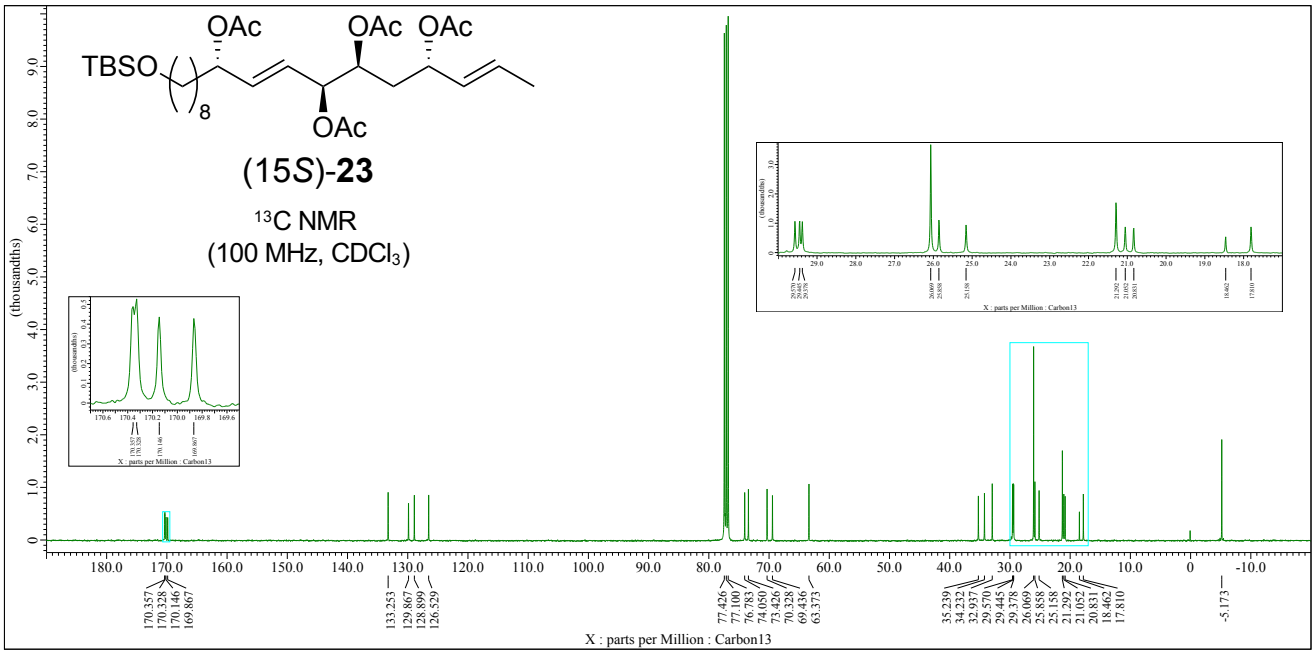

Expansion of (*R*)-MTPA ester derived from **20** at 2.3 ppm–1.4 ppm

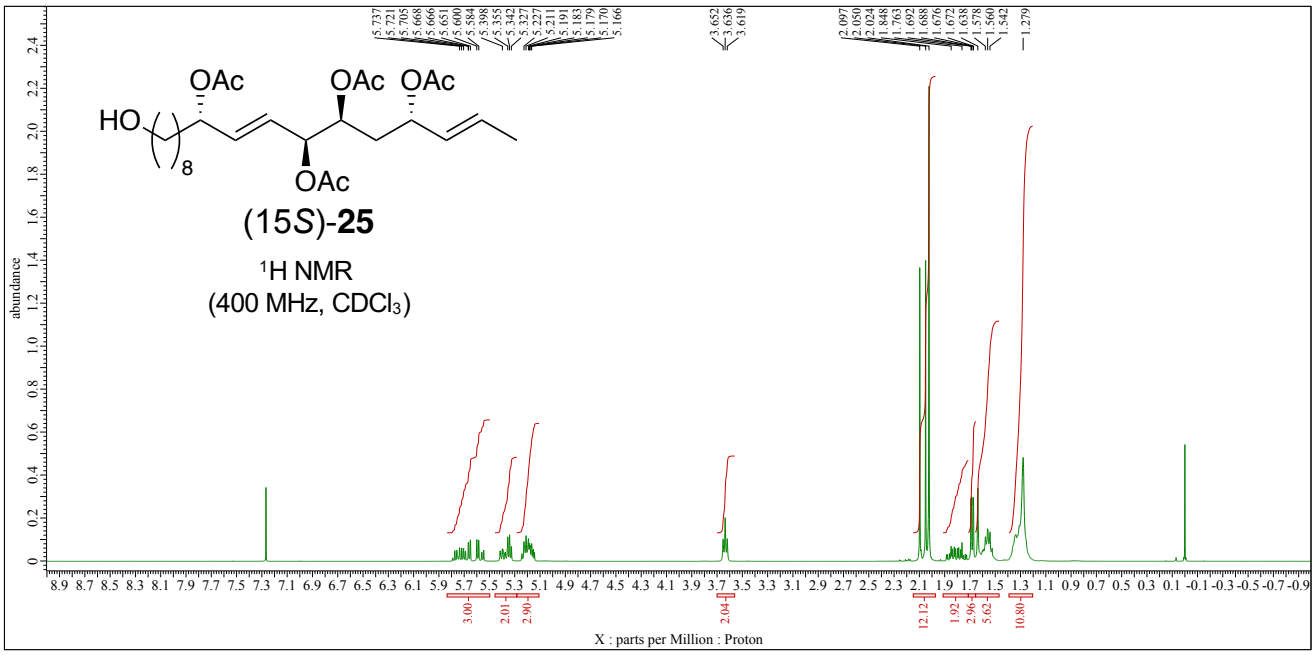


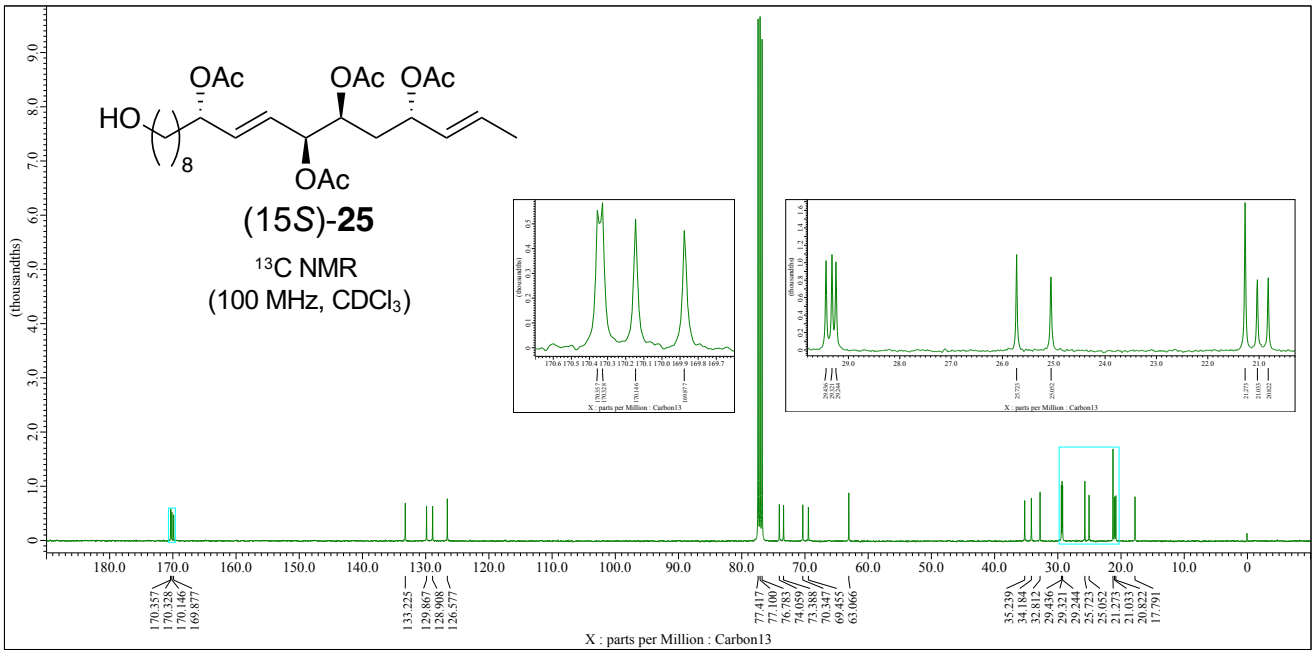

OH
TBSO
OH
TBSO
8
OTBS
(15S)-24
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : Proton

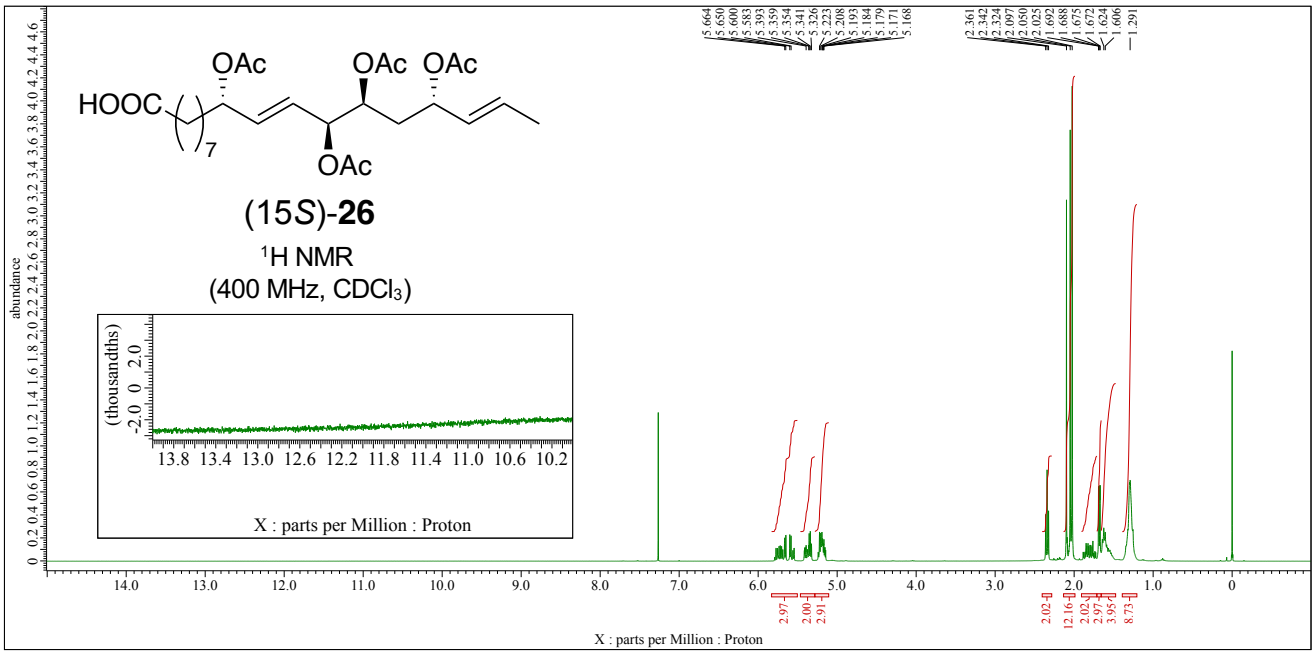

OH
TBSO
OH
TBSO
8
OTBS
(15S)-24
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

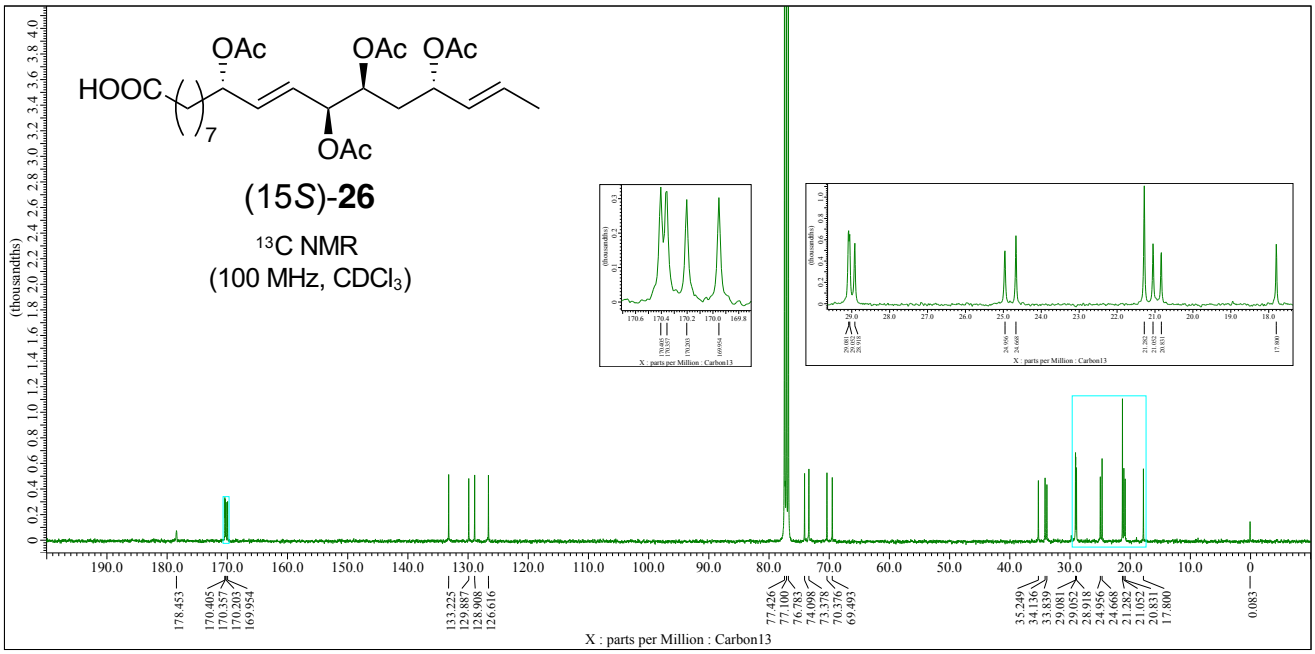

OAc
OAc
OAc
TBSO
8
OAc
(15S)-23
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : Proton

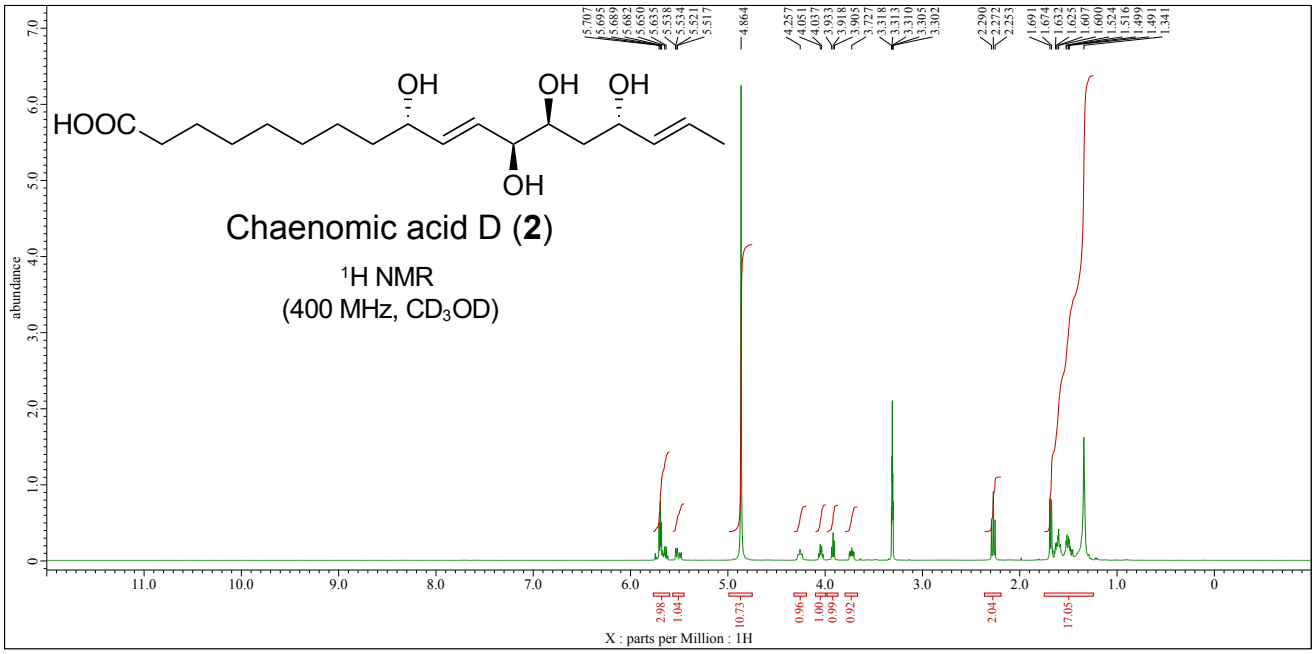

OAc
OAc
OAc
TBSO
8
OAc
(15S)-23
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

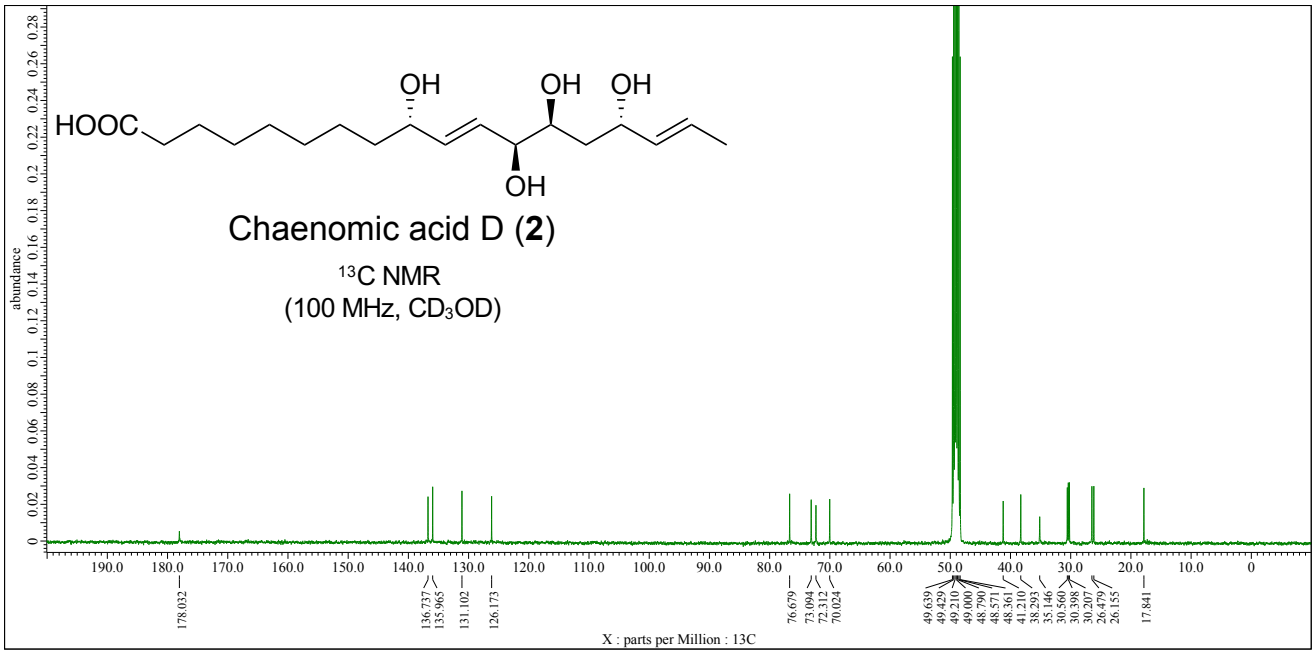

OAc
OAc
OAc
HO
8
OAc
(15S)-25
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : Proton

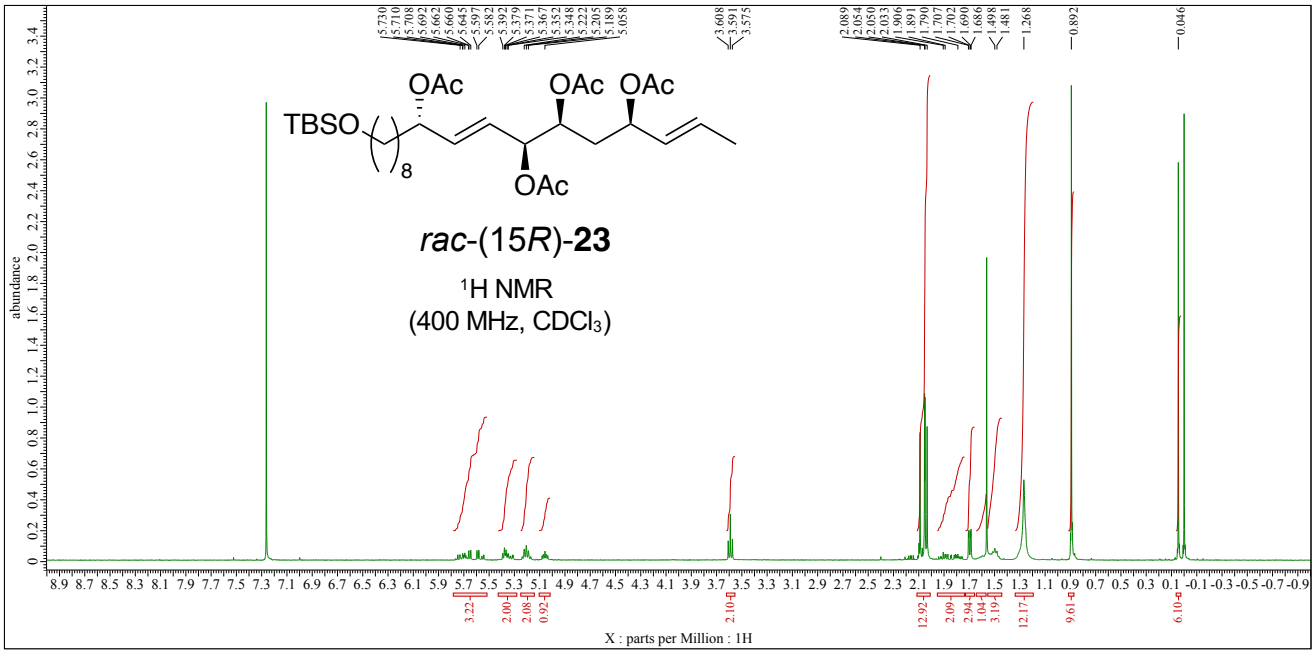

OAc
OAc
OAc
HO
8
OAc
(15S)-25
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

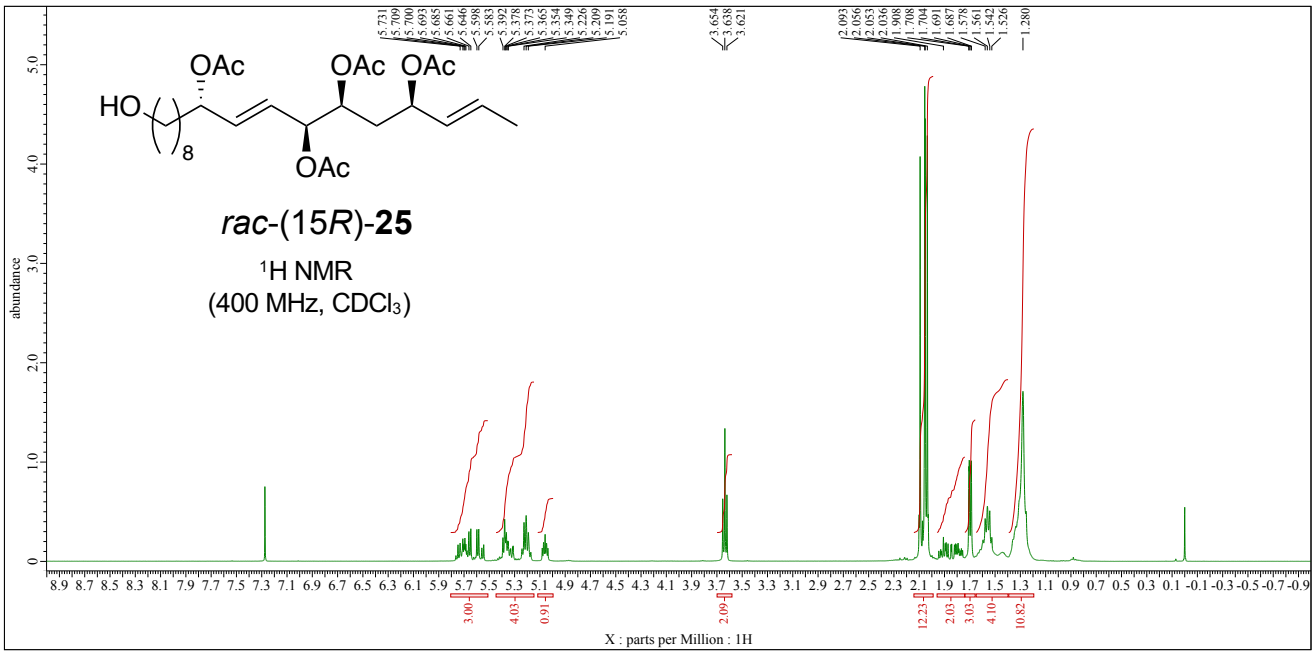

OAc
OAc
OAc
HOOC
7
OAc
(15S)-26
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : Proton
(thousandths)
X : parts per Million : Proton

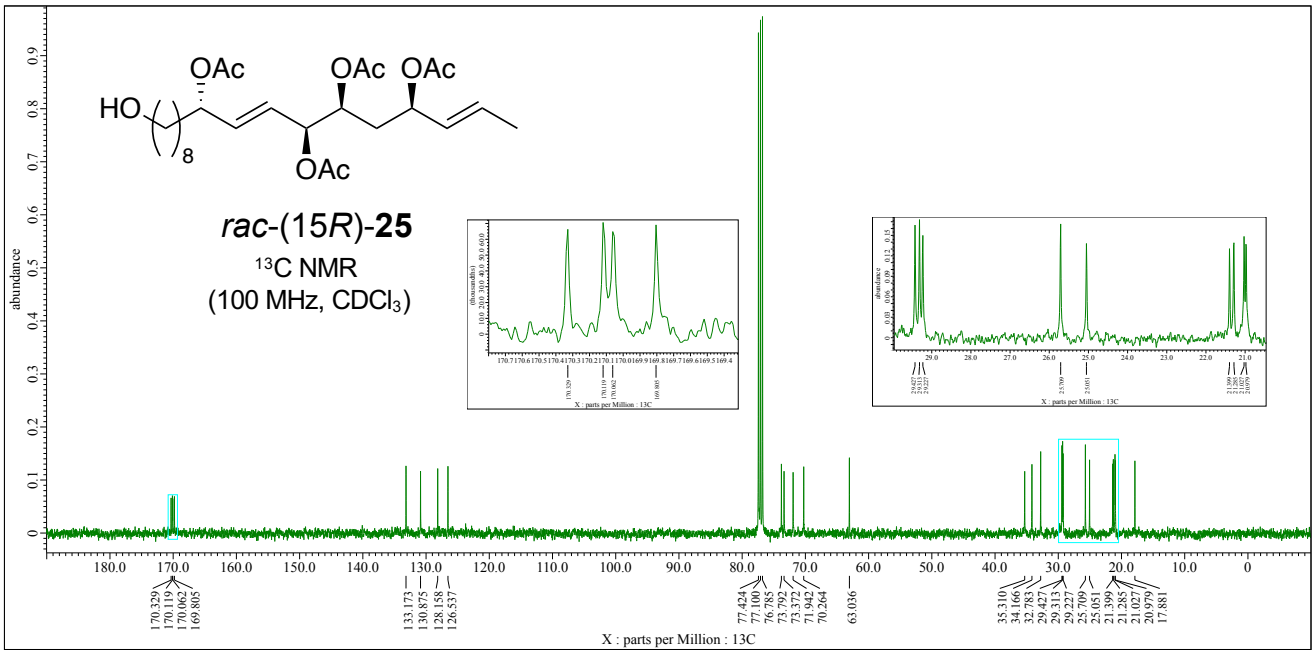

OAc
OAc
OAc
HOOC
7
OAc
(15S)-26
13C NMR
(100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13
X : parts per Million : Carbon13

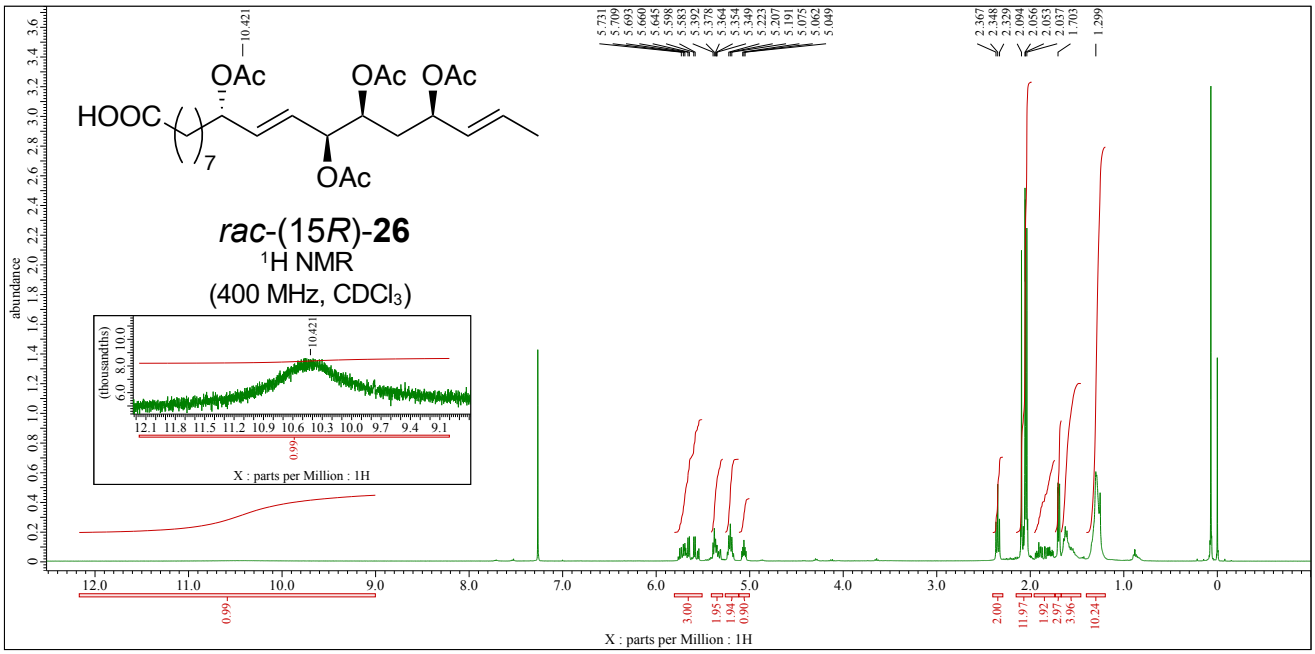

HOOC
OH
OH
OH
OH
Chaenomic acid D (2)
1H NMR
(400 MHz, CD3OD)
abundance
X : parts per Million : 1H

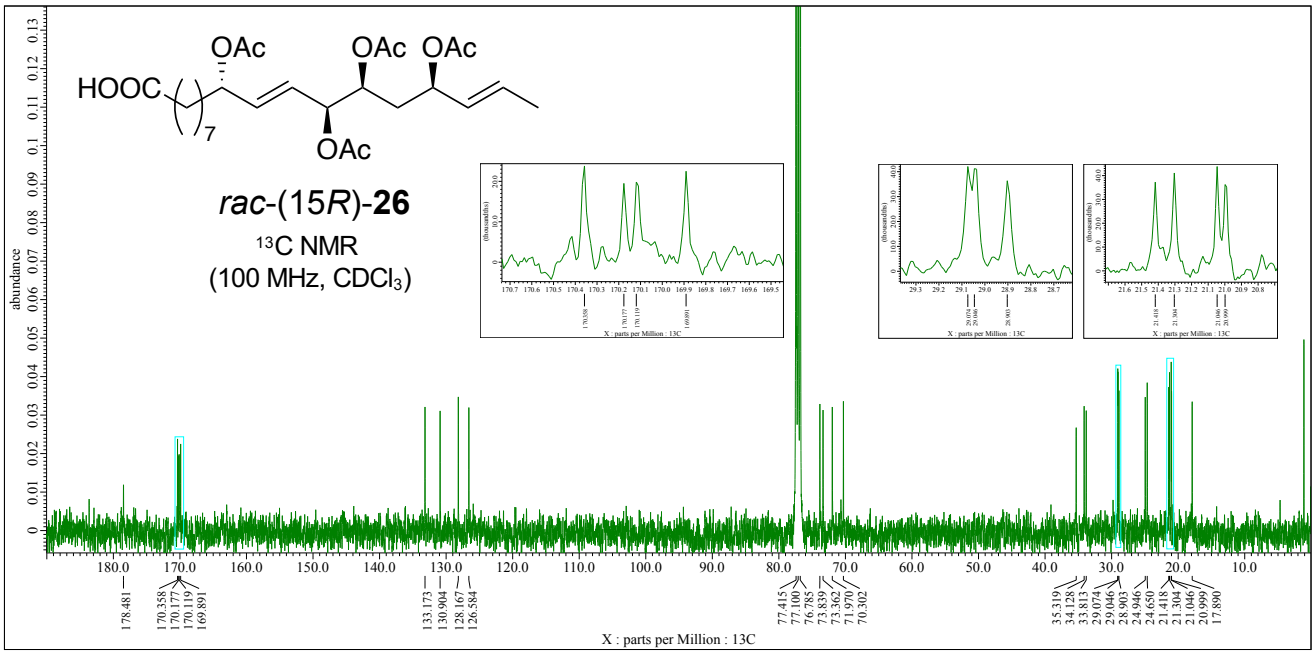

HOOC
OH
OH
OH
OH
Chaenomic acid D (2)
13C NMR
(100 MHz, CD3OD)
abundance
X : parts per Million : 13C

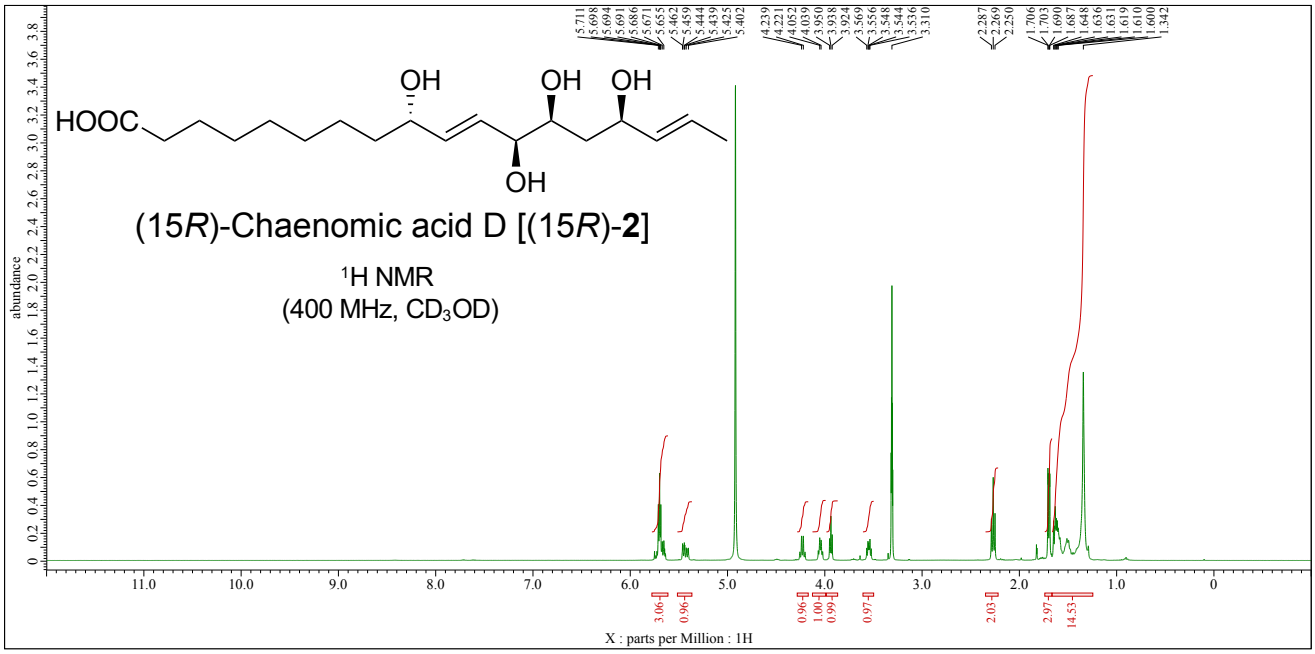

OAc
OAc
OAc
TBSO
8
OAc
rac-(15R)-23
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H

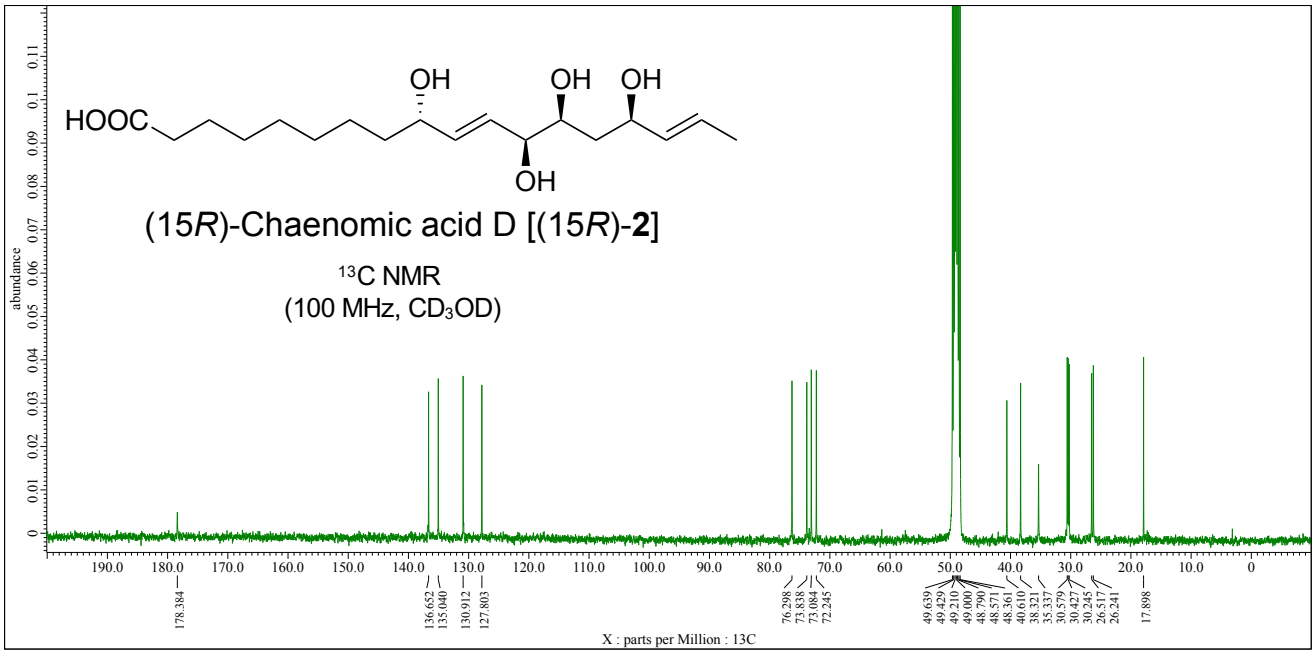

OAc
OAc
OAc
OAc
HO
8
rac-(15R)-25
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H


OAc
OAc
OAc
OAc
HO
8
rac-(15R)-25
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C


OAc
OAc OAc
HOOC
7
OAc
rac-(15R)-26
1H NMR
(400 MHz, CDCl3)
abundance
X : parts per Million : 1H


OAc
OAc OAc
HOOC
7
OAc
rac-(15R)-26
13C NMR
(100 MHz, CDCl3)
abundance
X : parts per Million : 13C


HOOC
OH
OH
OH
OH
(15R)-Chaenomic acid D [(15R)-2]
1H NMR
(400 MHz, CD3OD)
abundance
X : parts per Million : 1H


HOOC
OH
OH
OH
OH
(15R)-Chaenomic acid D [(15R)-2]
13C NMR
(100 MHz, CD3OD)
abundance
X : parts per Million : 13C