–Supporting Information for–

A minimal fluorous tagging strategy enables the synthesis of the complete stereoisomer library of Sch725674 macrolactones

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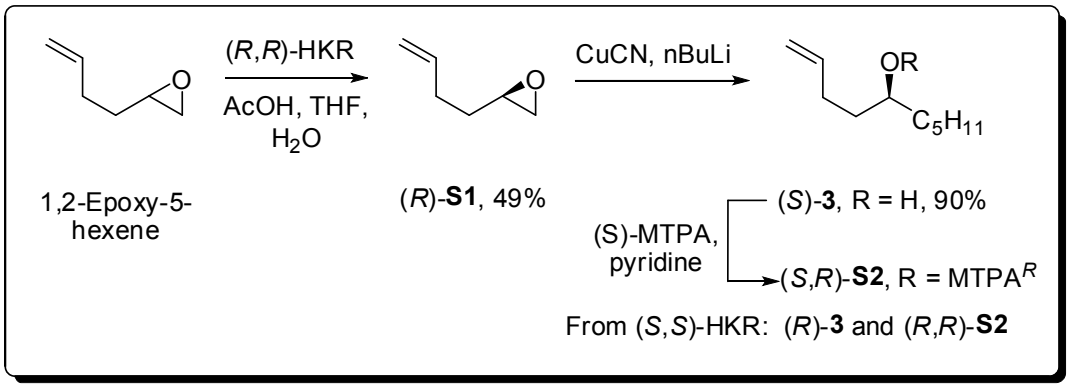
General: Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker WH-300 MHz, IBM AF-300, Bruker Avance™ 500 NMR, Bruker Avance™ 600 NMR, Bruker Avance™ 700 NMR spectrometer using deuterated chloroform as solvent, unless otherwise indicated. Signal positions are given as part per million (δ) and were determined relative to the residual proton resonance of $CDCl_3$ (7.27 ppm) or central $CDCl_3$ carbon peak carbon peak (77.03 ppm) as the internal standards. Coupling constants (*J* values) are in Hz. Spectral content is listed in the following order: chemical shift (δ), multiplicity, coupling constants (Hz), number of nuclei. All spectra were acquired at room temperature. In the case of ^{19}F NMR spectral data, an internal standard (α,α,α-trifluorotoluene) was used only for Mosher ester analyses.

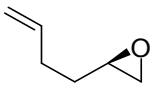
Infrared (IR) spectra were recorded on a Mattson Genesis series FTIR spectrometer as thin films on NaCl plates and peaks are reported in wave numbers (cm^{-1}). Optical rotations were measured on a Perkin-Elmer 241 polarimeter at a Na D-line (λ = 589 nm) using a 1 dm cell. Low-resolution mass spectra were obtained on a V/G 70/70 double focusing machine and were reported in units of *m/z*. HPLC analyses and separations were performed on a Waters 600E system with a Waters 2487 dual λ absorption detector. Compound names were obtained from ChemDraw Ultra 12.0 (Cambridge Soft Corp.).

All reactions were monitored by either thin layer chromatography or ^{1}H NMR spectroscopy. Visualization of the thin layer chromatography plates was achieved with ultraviolet light (254 nm), followed by development in a staining solution of anisaldehyde in ethanol, or 5% aqueous potassium permanganate. Conventional flash chromatography was performed with 230-400 mesh silica gel (E. Merck, Silica gel 60). All dry solvents were obtained by passing over activated alumina. Unless water was a cosolvent or reagent, all

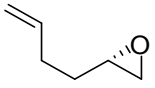
reactions were carried out under inert an atmosphere of dry argon. Deionized water was used for all workup operations. Standard syringe/septa techniques were employed throughout all reactions.

Scheme S1: Synthesis of alcohols 3



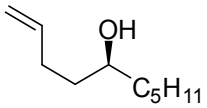


(*R*)-2-(But-3-enyl)oxirane ((*R*)-S1).[1] CAS registry number: [137688-20-1]. A 100-mL round bottom flask was charged with (*R,R*)-(–)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) catalyst (289 mg, 0.479 mmol), followed by racemic 1,2-epoxy-5-hexene (10.8 mL, 95.73 mmol) and acetic acid (110 μL). The resultant red suspension was then cooled to 0 °C and deionized water (0.95 mL) was slowly added over 5 min. The reaction mixture was stirred at 0 °C for 3 h, then at room temperature for 20 h. The mixture was concentrated by rotary evaporation and the crude product was purified by Kügelrohr distillation (60 °C, 40 torr) to afford the title compound as a colorless liquid (4.68 g, 49%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (ddt, J_1 = 16.9 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.05 (ddd, J_1 = 17.1 Hz, J_2 = 10.2 Hz, J_3 = 1.6 Hz, 2H), 2.95 (m, 1H), 2.77 (dd, J_1 = 4.9 Hz, J_2 = 4.2 Hz, 1H), 2.50 (dd, J_1 = 5.0 Hz, J_2 = 2.7 Hz, 1H), 2.24 (m, 2H).

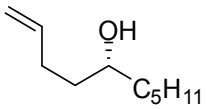


(*S*)-2-(But-3-enyl)oxirane ((*S*)-S1).[1] CAS registry number: [137688-21-2]. The literature procedure for (*R*)-**S1** was followed using 1,2-epoxy-5-hexene (11.00 mL, 97.50 mmol), acetic

acid (120 μL, 2.10 mmol), THF (1.00 mL), and (*S,S*)-(+)-*N,N′*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediaminocobalt(II) (319 mg, 0.528 mmol). Kügelrohr distillation of the crude product (60 °C, 25 torr) gave the title compound as a colorless liquid (2.01 g, 21%). The ^{1}H NMR spectrum matched that of (*R*)-**S1**.

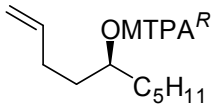


(5*S*)-Dec-1-en-5-ol ((*S*)-3).[2] A solution of butyllithium (1.6 M in hexanes, 34.2 mL, 54.7 mmol) was added dropwise to a stirred suspension of CuCN (269 g, 30.0 mmol) in THF (80 mL) at −78 °C. The reaction mixture was warmed to −20 °C and the epoxide (*R*)-**S1** (3.57 g, 36.4 mmol) in THF (35 mL) was slowly added by cannula. The original flask containing the epoxide was then washed with THF (10 mL) and the rinse was also added to the reaction mixture by cannula at −20 °C. The resultant yellow suspension was stirred for 3 h at room temperature. The reaction was quenched by addition of 90:10 saturated aqueous NH_4Cl/ NH_4OH at 0°C and the mixture was stirred for 1 h at room temperature. The quenched mixture was then filtered through a Büchner funnel and the filtrate was transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic extracts were washed with water (75 mL) and brine (75 mL), dried with $MgSO_4$, filtered, and concentrated by rotary evaporation. Flash chromatography of the crude product (1:1 pentanes/ Et_2O) gave the title compound as a colorless liquid (5.12 g, 90%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (ddt, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.02 (dd, J_1 = 17.0 Hz, J_2 = 10.2 Hz, 2H), 3.63 (m, 1H), 2.18 (m, 2H), 1.57 (m, 2H), 1.42 (m, 4H), 1.32 (broad s, 4H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 114.7, 71.6, 37.5, 36.5, 31.9, 30.1, 25.3, 22.7, 14.1; FTIR (thin film) ν_{max} 3350, 2929, 2858 cm^{-1}; HRMS calcd (EI) for $C_{10}H_{20}O$ $[M]^+$: 156.1514, found 156.1510; $[\alpha]_D^{25°C} = -16.0$, c = 1.01, $CHCl_3$.

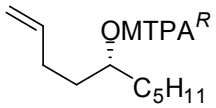


(5*R*)-Dec-1-en-5-ol ((*R*)-3). The literature precedent[2] for (*S*)-**3** (above) was followed using the epoxide (*S*)-**S1** (1.73 g, 17.63 mmol), CuCN (2.32 g, 25.92 mmol), and a solution of butyllithium (1.6 M in pentane, 29.42 mL, 47.07 mmol) in THF (75 mL). Flash chromatography (1:1 pentane/ Et_2O) of the crude product gave the title compound as a colorless liquid (1.76 g, 64%).

The 1D ^{1}H and ^{13}C NMR match those of (*S*)-**3**; HRMS calcd (EI) for $C_{10}H_{20}O$ $[M]^{+}$: 156.1514, found 156.1512; $[\alpha]_D^{25^\circ C} = +17.6$, c = 1.17, $CHCl_3$.

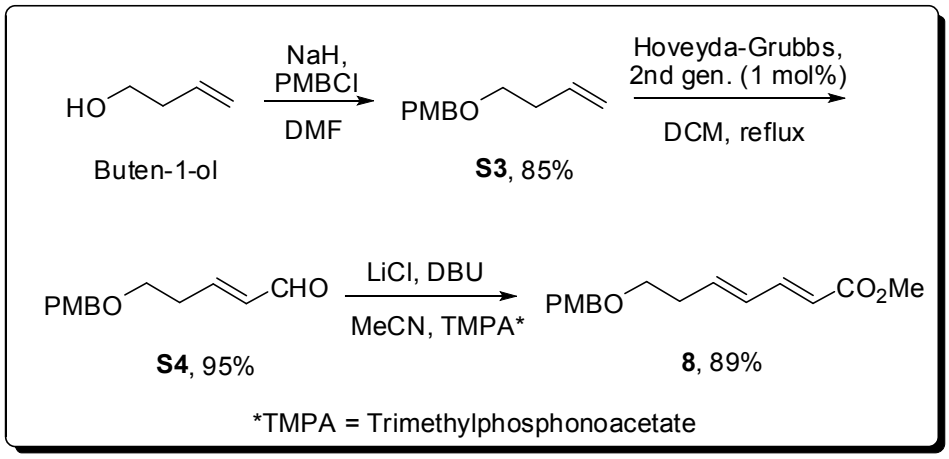


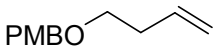
(*S,R*)-S2. Commercially available (*S*)-MTPA-Cl (29 µl, 0.155 mmol) was added dropwise to a solution of the alcohol (*S*)-**3** (12.8 mg, 0.078 mmol) in pyridine (3.00 mL) at 0 °C. The reaction mixture was stirred at this temperature for 15 min, then at room temperature for 3 h. The reaction was quenched by addition of water (3 mL) and transferred to a separatory funnel by pipet. The contents were then diluted with Et_2O (10 mL) and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with 20% aqueous $CuSO_4$ (3 x 5 mL), water (5 mL), and brine (5 mL). The organic solution was dried over $MgSO_4$, filtered and concentrated by rotary evaporation. The crude product was analyzed without purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 2H), 7.41 (m, 3H), 5.74 (ddt, J_1 = 16.4 Hz, J_2 = 9.7 Hz, J_3 = 6.6 Hz, 1H), 5.12 (m, 1H), 4.96 (m, 2H), 3.57 (s, 3H), 1.95 (m, 2H), 1.66 (m, 4H), 1.31 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.8 (s, 3F). The minor peaks in the ^{19}F NMR spectrum of (*S,R*)-**S2** match the major peaks in the spectrum of (*R,R*)-**S2** (below).



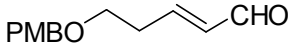
***(R,R)*-S2**. The general procedure for Mosher ester derivatization[3] was followed using the alcohol (*R*)-**3** (11.6 mg, 0.074 mmol) and (*S*)-MTPA (28 µl, 0.149 mmol) in pyridine (2 mL). The crude product was then analyzed without purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (m, 2H), 7.41 (m, 3H), 5.81 (ddt, J_1 = 16.9 Hz, J_2 = 10.2 Hz, J_3 = 6.6 Hz, 1H), 5.12 (m, 1H), 5.02 (m, 2H), 3.57 (s, 3H), 2.09 (m, 2H), 1.75 (m, 2H), 1.59 (m, 2H), 1.22 (m, 6H), 0.85 (t, J = 6.8 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.6 (s, 3F). The minor peaks in the ^{19}F NMR spectrum of (*R,R*)-**S2** match the major peaks in the spectrum of (*S,R*)-**S2** (above).

Scheme S2: Synthesis of diene 8



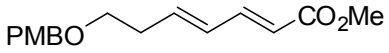


1-((But-3-enyloxy)methyl)-4-methoxybenzene (S3).[4] CAS registry number: [142860-83-1]. The literature procedure for 4-methoxy-benzyl protection was followed using buten-1-ol (5.00 mL, 58.45 mmol), NaH (95%, 1.92 g, 75.99 mmol), and 4-methoxybenzyl chloride (9.52 mL, 70.14 mmol) in dimethylformamide (200 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a yellow oil (9.52 g, 85%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.84 (ddt, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.10 (ddd, J_1 = 17.5 Hz, J_2 = 10.2 Hz, J_3= 1.7 Hz, 2H), 4.46 (s, 2H), 3.82 (s, 3H), 3.53 (t, J = 6.8 Hz, 2H), 2.38 (ddd, J_1 = 14.8 Hz, J_2 = 6.7 Hz, J_3 = 1.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 135.5, 130.5, 129.1, 115.7, 113.2, 72.4, 69.2, 55.1, 34.2.



(*E*)-5-(4-Methoxybenzyloxy)pent-2-enal (S4).[5] CAS registry number: [671232-57-8]. Alkene **S3** (10.25 g, 53.1 mmol) was dissolved in anhydrous, degassed CH_2Cl_2 (100 mL) and crotonaldehyde (22.0 mL, 266 mmol) was added by syringe at room temperature. The Grubbs-Hoveyda 2nd generation catalyst (333 mg, 0.53 mmol) was then added at room temperature in one portion. The flask was fitted with a reflux condenser and the reaction mixture was stirred at reflux for 16 h (~50 °C, bath temperature). The reaction mixture was then cooled to room temperature and concentrated by rotary evaporation. Flash chromatography of the crude product (3:1 hexanes/EtOAc) gave the title compound as a pale brown oil (11.21 g, 95%, *E*/*Z*>20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 6.8 Hz, 2H), 6.88 (dt, J_1 = 15.7

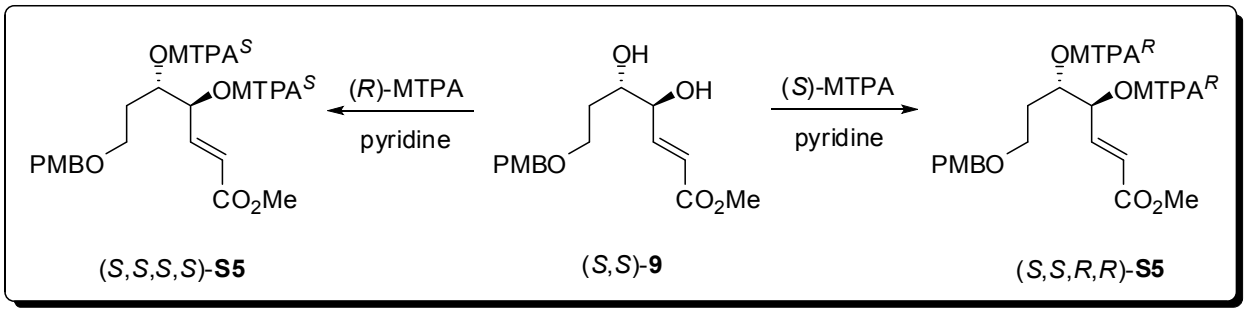
Hz, J_2 = 6.7 Hz, 1H), 6.18 (ddt, J_1 = 15.8 Hz, J_2 = 7.9 Hz, J_3 = 1.4 Hz, 1H), 4.47 (s, 2H), 3.82 (s, 3H), 3.62 (t, J = 6.2 Hz, 2H), 2.63 (qd, J_1 = 6.5 Hz, J_2 = 1.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7, 159.2, 133.9, 129.8, 129.1, 113.7, 72.6, 67.4, 55.1, 32.9.

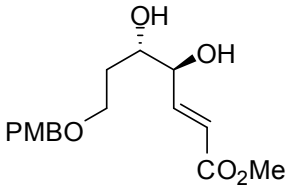


(2*E*,4*E*)-Methyl-7-(4-methoxybenzyloxy)hepta-2,4-dienoate (8). According to a modified procedure for the Horner-Wadsworth-Emmons olefination,[6] trimethylphosphonoacetate (8.79 mL, 60.79 mmol) was added dropwise by syringe to a suspension of LiCl (2.58 g, 60.79) in anhydrous MeCN (610 mL). 1,8-Diazabicyclo-[5.4.0]-undec-7-ene (8.33 mL, 55.73 mmol) was added dropwise by syringe at room temperature. The resultant suspension was cooled to 0 °C, and a solution of the aldehyde **S4** (11.21 g, 50.66 mmol) in acetonitrile (125 mL) was added dropwise by cannula transfer. The flask containing the aldehyde was rinsed with acetonitrile (25 mL) and the rinse was transferred to the reaction mixture by cannula. The resultant suspension was stirred at 0 °C for 5 min, then at room temperature for 45 min. Deionized water (300 mL) was then added to the suspension to dissolve the phosphonic acid byproduct, and the mixture was transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with Et_2O (2 x 500 mL). The combined organic extracts were washed with brine (200 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Filtration of the crude product over a silica plug afforded the title compound as a pale yellow oil (12.49 g, 89%, *E*/*Z*>20:1): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (dd, J_1= 15.4 Hz, J_2 = 10.2 Hz, 1H), 7.26 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.19 (m, 2H), 8.81 (d, J = 15.4 Hz, 1H), 4.46 (s, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 3.53 (t, J = 6.5 Hz, 2H), 2.48 (q, J = 6.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 159.3, 150.0, 140.7, 129.9, 129.3, 119.4, 113.8, 72.7, 67.8, 55.3, 51.5, 33.4.

Synthesis of *trans*-series quasiisomers 13a-d, Scheme 1 in paper

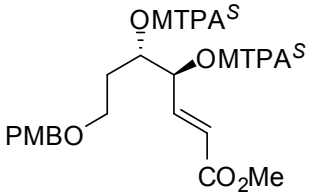
Scheme S3: Mosher ester analysis of diol (*S*,*S*)-9



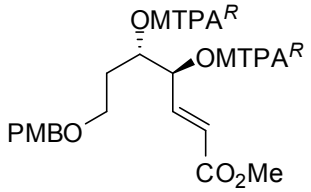


(4*S*,5*S*,2*E*)-Methyl-4,5-dihydroxy-7-(4-methoxybenzyloxy)hept-2-enoate ((*S*,*S*)-9): $K_2Os(OH)_2$ (84.5 mg, 0.230 mmol), $(DHQ)_2PHAL$ (376 mg, 0.459 mmol), $K_3Fe(CN)_6$ (22.7 g, 68.82 mmol), K_2CO_3 (9.51 g, 68.82 mmol), and methanesulfonamide (4.36 g, 45.88 mmol) were added to 1:1 *t*BuOH/H_2O (145 mL) at room temperature. The orange suspension was stirred at room temperature for 30 min, then cooled to 0 °C by Cryocooler. A solution of the diene **8** (6.34 g, 22.94 mmol) in CH_2Cl_2 (25 mL) was added to the cooled suspension dropwise by syringe, the syringe was subsequently rinsed with CH_2Cl_2 (2 x 5 mL) and the rinse was transferred to the reaction flask. The reaction mixture was stirred at 0 °C for 24 h. The reaction was quenched by addition of saturated aqueous sodium thiosulfate (75 mL) and the mixture was stirred for 1 h at room temperature. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 150 mL). The combined organic extracts were washed with brine (80 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Flash chromatography of the crude product (1:2 hexanes/EtOAc) afforded the title compound as a highly viscous, pale yellow syrup (4.89 g, 67%, 92% *ee*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.6 Hz, 2H), 6.96 (dd, J_1 = 15.3 Hz, J_2 = 4.7 Hz, 1H), 6.89 (d, J = 8.6 Hz, 2H), 6.15 (dd, J_1 = 15.7 Hz, J_2 = 1.8 Hz, 1H), 4.46 (s, 2H), 4.17 (qd, J_1= 4.9 Hz, J_2 = 1.8 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.68 (m, 2H), 3.39 (d, J = 3.4 Hz, 1H), 2.97 (d, J = 5.3 Hz, 1H), 1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.1, 147.4, 129.6, 129.2, 121.4, 113.7, 73.6, 72.7, 72.5, 67.4, 55.0, 51.5, 32.5; FTIR (thin film) ν_{max}

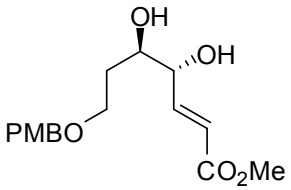
3455, 2915, 1723, 1586, 1249 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{22}O_6Na$ $[M + Na]^+$: 333.1314, found 333.1287; $[\alpha]_D^{25°C} = -4.2$, c = 1.08, $CHCl_3$.



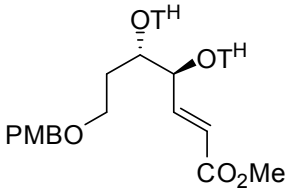
(*S,S,S,S)*-S5. The procedure for Mosher ester derivatization[3] used above in preparation of (*S*,*R*)-**S2** was followed using the diol (*S*,*S*)-**9** (12.8 mg, 0.040 mmol) and (*R*)-MTPA (31 μl, 0.162 mmol) in pyridine (1 mL). The crude product was then analyzed without purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 10H), 7.24 (d, J = 6.7 Hz, 2H), 6.89 (d, J_1 = 6.7 Hz, 2H), 6.74 (dd, J_2 = 15.8 Hz, J = 5.0 Hz, 1H), 5.81 (ddd, J_1 = 4.8 Hz, J_2 = 3.0 Hz, J_3 = 1.6 Hz, 1H), 5.77 (dd, J_1 = 15.9 Hz, J_2 = 1.6 Hz, 1H), 5.55 (ddd, J_1 = 8.0 Hz, J_2 = 5.2 Hz, J_3 = 3.1 Hz, 1H), 4.34 (d, J = 3.4 Hz, 2H), 3.81 (s, 3H), 3.72 (s, 3H), 3.49 (s, 3H), 3.44 (s, 3H), 3.38 (m, 1H), 3.25 (m, 1H), 1.84 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.7 (s, 3F), −71.9 (s, 3F). The minor peaks in the ^{19}F NMR spectrum of (*S,S,S,S)*-**S5** matched the major peaks of (*S,S,R,R)*-**S5** (below).



(*S,S,R,R)*-S5. The same procedure[3] used above in preparation of (*S*,*R*)-**S2** was followed using the diol (*S*,*S*)-**9** (21.6 mg, 0.068 mmol) and (*S*)-MTPA (51 μl, 0.273 mmol) in pyridine (2 mL). The crude product was then analyzed without purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 10H), 7.23 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 6.67 (dd, J_1 = 15.8 Hz, J_2 = 5.6 Hz, 1H), 5.80 (dd, J_1 = 15.8 Hz, J_2 = 1.5 Hz, 1H), 5.74 (ddd, J_1 = 7.1 Hz, J_2 = 2.6 Hz, J_3 = 1.6 Hz, 1H), 5.49 (td, J_1 = 6.6 Hz, J_2 = 2.7 Hz, 1H), 4.36 (s, 2H), 3.81 (s, 3H), 3.72 (s 3H), 3.47 (s, 3H), 3.40 (s, 3H), 3.35 (m, 2H), 1.82 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ −71.8 (s, 3F), −72.0 (s, 3F). The minor peaks in the ^{19}F NMR spectrum of (*S,S,R,R)*-**S5** matched the major peaks of (*S,S,S,S)*-**S5** (above).

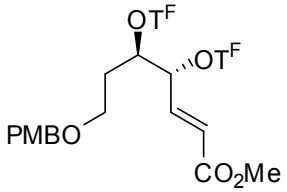


(4*R*,5*R*,2*E*)-Methyl-4,5-dihydroxy-7-(4-methoxybenzyloxy)heptenoate ((*R*,*R*)-9). The same procedure used for the preparation of (*S*,*S*)-**9** above was followed with commercially available AD-mix β (93.0 g), $(DHQD)_2PHAL$ (55 mg, 0.67 mmol), methanesulfonamide (4.23 g, 44.5 mmol), and diene **8** (6.15 g, 22.26 mmol) in 1:1 *t*BuOH/H_2O (225 mL). Flash chromatography of the crude product (1:2 hexanes/EtOAc) afforded the title compound as a highly viscous, pale yellow syrup (4.33 g, 61%). The ^1H and ^{13}C NMR spectra matched those of (*S*,*S*)-**9** (above); HRMS calcd (EI) for $C_{16}H_{22}O_6$ $[M + H]^+$: 310.1416, found 310.1421; $[\alpha]_D^{25°C} = +5.50$, c = 1.01, $CHCl_3$.

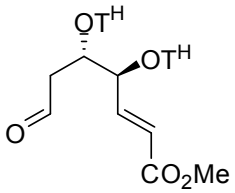


(4*S*,5*S*,*E*)-Methyl-7-(4-methoxy-benzyloxy)-4,5-bis(triisopropyl-silyloxy)hept-2-enoate ((*S*,*S*)-11). Triisopropyl trifluoromethanesulfonate (10.2 mL, 37.71 mmol) was added dropwise to a solution of the diol (*S*,*S*)-**9** (4.77 g, 15.08 mmol) and 2,6-lutidine (5.25 mL, 45.25 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min, then at room temperature for 4 h. The reaction was quenched by addition of saturated aqueous NH_4Cl (60 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 175 mL). The combined organic extracts were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the title compound as a colorless oil (9.68 g, 100%): ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 8.8 Hz, 2H), 7.19 (dd, J_1 = 15.6 Hz, J_2 = 3.4 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 6.14 (dd, J_1 = 15.7 Hz, J_2 = 1.9 Hz, 1H), 4.59 (ddd, J_1 = 5.1 Hz, J_2 = 3.4 Hz, J_3 = 2.0 Hz, 1H), 4.391 (s, 2H), 4.12 (dt, J_1 = 8.1 Hz, J_2 = 4.4 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.53 (m, 2H), 2.00 (tdd, J_1 = 11.8 Hz, J_2 = 8.0 Hz, J_3 = 3.9 Hz, 1H), 1.50 (m, 1H), 1.06 (broad s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 159.0, 148.2, 130.7, 129.0, 121.1, 113.5, 74.7, 72.3, 66.6, 55.1, 51.3, 32.4, 18.1, 18.0, 12.6, 12.3; FTIR (thin film) ν_{max} 3398, 2944, 2867,

1464, 1110 cm^{-1}; HRMS calcd (ESI) for $C_{34}H_{62}O_6Si_2Na$ [M + Na]$^+$: 645.3983, found 645.4012; $[\alpha]_D^{25°C}$ = –37.1, c = 0.98, $CHCl_3$.



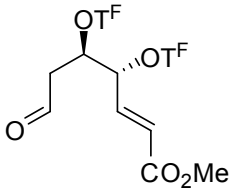
(4*R*,5*R*,2*E*)-Methyl-4,5-bis(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-7-(4-methoxybenzyloxy)-hept-2-enoate ((*R*,*R*)-10). Freshly distilled trifluoromethanesulfonic acid (2.34 mL, 26.36 mmol) was added dropwise by syringe to neat, stirring 3,3,4,4,4-pentafluorobutyl)diisopropylsilane (7.41 g, 28.24 mmol) at 0 °C. The turbid, orange reaction mixture was allowed to stir at 0 °C for 15 min, and then at room temperature for 45 min. The reaction mixture was then diluted with CH_2Cl_2 (25 mL) and the resultant solution was transferred by cannula into a separate flask (cooled to 0 °C) containing a solution of the (*R*,*R*)-**9** (3.97 g, 12.55 mmol) and 2,6-lutidine (4.37 mL, 37.65 mmol) in CH_2Cl_2 (100 mL). The reaction mixture was allowed to stir at 0 °C for 15 min, then warmed to room temperature. After 1 h, the reaction was quenched at 0 °C with saturated aqueous NH_4Cl (50 mL). The mixture was stirred at 0 °C for 15 min, after which the contents of the flask were transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 75 mL). The combined organic layers were washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Flash chromatography of the crude product (10:1 hexanes/EtOAc) afforded the title compound as a pale yellow oil (8.37 g, 86%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 8.42 Hz, 2H), 7.07 (dd, J_1 = 15.8 Hz, J_2 = 4.0 Hz, 1H), 6.86 (d, J = 8.3 Hz, 2H), 6.05 (dd, J_1 = 15.7 Hz, J_2 = 1.1 Hz, 1H), 4.44 (m, 1H), 4.38 (d, J = 2.4 Hz, 2H), 4.03 (quintet, J = 3.9 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 3.46 (m, 2H), 2.02 (m, 5H), 1.45 (m, 1H), 1.03 (broad s, 28H), 0.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 159.2, 146.8, 130.5, 129.2, 121.9, 113.7, 74.7, 72.6, 72.5, 65.9, 55.1, 51.5, 32.3, 27.6, 25.3, 17.5, 17.4, 17.4, 18.5, 17.1, 12.9, 12.8, 12.7, 12.6, 1.1, 0.8; FTIR (thin film) ν_{max} 3389, 2949, 1729, 1199 cm^{-1}; HRMS calcd (EI) for $C_{36}H_{56}O_6F_{10}Si_2Na$ [M + Na]$^+$: 853.3353, found 853.3400; $[\alpha]_D^{25°C}$ = +27.1, c = 1.08, $CHCl_3$.



(4*S*,5*S*,2*E*)-Methyl-7-oxo-4,5-bis(triisopropylsilyloxy)hept-2-enoate ((*S*,*S*)-11). The ester (*S*,*S*)-**10** (5.83 g, 9.35 mmol) was dissolved in 19:1 CH_2Cl_2/H_2O (100 mL). The mixture was cooled to 0 °C and DDQ (2.76 g, 12.16 mmol) was added in one portion. The green suspension was stirred at 0 °C for 5 min, then at room temperature for 2 h. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (40 mL). The emulsion was broken in the separatory funnel by addition of chloroform (50 mL). The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 150 mL). The combined organic extracts were washed with brine (60 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude product was taken to the next step as a mixture of the free alcohol and anisaldehyde.

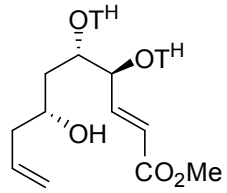
According to a literature procedure for Swern oxidations,[7] a solution of DMSO (2.00 mL, 28.06 mmol) in CH_2Cl_2 (20 mL) was slowly added by syringe to a solution of oxalyl chloride (1.61 mL, 18.71 mmol) in CH_2Cl_2 (190 mL) at −78 °C. After 15 min, the crude alcohol from above in CH_2Cl_2 (15 mL) was added dropwise by cannula transfer. The flask containing the alcohol was rinsed with CH_2Cl_2 (2 x 5 mL) and the rinse was also transferred by cannula. The resulting mixture was stirred at −78 °C for 15 min, then Et_3N (6.52 mL, 46.77 mmol) was added slowly dropwise by syringe. The reaction mixture was maintained at −78 °C for 15 min then warmed to 0 °C, and the stirring continued for 30 min. Water (30 mL) was then added and the mixture was diluted with Et_2O (50 mL). The organic layer was separated and washed with brine (30 mL). The combined aqueous layers were extracted with Et_2O (3 x 50 mL). The organic layers were combined, dried over $MgSO_4$, filtered, and then concentrated by rotary evaporation. Flash chromatography of the crude product gave the title compound as a pale yellow oil (3.67 g, 78% over two steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, J = 1.2 Hz, 1H), 7.18 (dd, J_1 = 15.8 Hz, J_2 = 3.6 Hz, 1H), 6.16 (dd, J_1 = 15.6 Hz, J_2 = 1.8 Hz, 1H), 4.67 (m, 1H), 6.90 (dd, J_1 = 11.4 Hz, J_2 = 5.5 Hz), 3.77 (s, 3H), 2.68 (ddd, J_1 = 16.0 Hz, J_2 = 5.6 Hz, J_3 = 2.2 Hz, 1H), 2.45 (ddd, J_1 = 16.1 Hz, J_2 = 6.0 Hz, J_3 = 2.2 Hz, 1H), 1.07 (broad s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.2, 166.6, 147.1, 122.2, 74.1, 70.8, 51.6, 46.7, 18.0, 12.3; FTIR (thin film) ν_{max} 3889, 2946,

2866, 1730, 1464, 1113 cm^{-1}; HRMS calcd (ESI) for $C_{26}H_{52}O_5Si_2Na$ $[M + Na]^+$: 523.3251, found 523.3234; $[\alpha]_D^{25°C} = -56.9$, c = 1.01, $CHCl_3$.



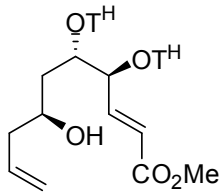
(4*R*,5*R*,2*E*)-Methyl-4,5-bis(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-7-oxohept-2-enoate ((*R*,*R*)-11)). The same deprotection conditions used above in the preparation of aldehyde (*S*,*S*)-**11** were used with (*R*,*R*)-**10** (7.43 g, 9.59 mmol) and DDQ (2.83 g, 12.5 mmol), and 18:1 CH_2Cl_2/H_2O, 100 mL). The crude product was taken to the next step without further purification as a mixture of the free alcohol and anisaldehyde byproduct.

The crude alcohol was subjected to the above procedure for Swern oxidation used in the preparation of (*S*,*S*)-**11** was followed with DMSO (2.04 mL, 28.77 mmol), oxalyl chloride (1.65 mL, 19.18 mmol), NEt_3 (6.68 mL, 47.95 mmol). Flash chromatography of the crude product gave the title compound as a pale yellow oil (5.56 g, 82% over two steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.78 (s, 1H), 7.06 (dd, J_1 = 15.6 Hz, J_2 = 3.5 Hz, 1H), 6.09 (d, J = 15.8 Hz, 1H), 4.49 (m, 2H), 3.78 (s, 3H), 2.72 (dd, J_1 = 16.8 Hz, J_2 = 2.9 Hz, 1H), 2.45 (dd, J_1 = 17.1 Hz, J_2 = 6.4 Hz, 1H), 2.02 (m, 4H), 1.04 (broad s, 28H), 0.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.3, 166.1, 145.6, 122.8, 74.0, 70.3, 51.5, 46.4; FTIR (thin film) ν_{max} 3376, 2359, 2339, 1728, 1199 cm^{-1}; HRMS calcd (ESI) for $C_{28}H_{46}O_5Si_2F_{10}Na$ $[M + Na]^+$: 731.2622, found 731.2675; $[\alpha]_D^{25°C} = +47.5$, c = 1.16, $CHCl_3$.

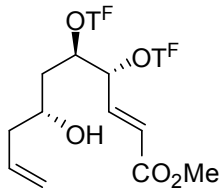


(4*S*,5*S*,7*R*,2*E*)-Methyl-7-hydroxy-4,5-bis(triisopropylsilyloxy)deca-2,9-dienoate ((*S*,*S*,*R*)-12). A commercially available solution of (+)-Ipc_2B(allyl) (5.00 mL, 5.00 mmol, 1.0 M in pentane) was added to a solution of aldehyde (*S*,*S*)-**11** (2.26 g, 4.51 mmol) in Et_2O (45 mL) at −78 °C. The reaction mixture was stirred at this temperature for 3 h, and then warmed to room temperature. The reaction was quenched by the addition of 1:2:1 30% aq. H_2O_2/MeOH/pH 7 buffer (60 mL), and the resultant suspension was stirred for 16 h. The layers were separated and

the aqueous layer extracted with ether (3 x 80 mL). The combined organic extracts were washed with water (50 mL), sat. aq. $NaHCO_3$ (50 mL), more water (50 mL), brine (50 mL), then dried over $MgSO_4$. ^1H NMR analysis of the crude product indicated an approximately 4:1 mixture of diastereomers. Flash chromatography of the crude product (10:1 hexanes/EtOAc) afforded the title compound as a single diastereomer (colorless oil) with minor impurities (1.45 g, 59%). The compound was taken to the next step for fuller characterization. Selected ^1H NMR data (300 MHz, $CDCl_3$) δ 7.20 (dd, J_1 = 15.8 Hz, J_2 = 3.7 Hz, 1H), 6.14 (dd, J_1 = 15.8 Hz, J_2 = 1.9 Hz, 1H), 5.78 (m, 1H), 5.11 (dd, J_1 = 16.0 Hz, J_2 = 11.2 Hz, 2H), 4.64 (m, 1H), 4.21 (m, 1H).

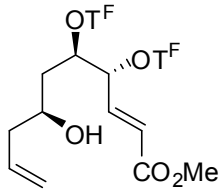


(4*S*,5*S*,7*S*,2*E*)-Methyl-7-hydroxy-4,5-bis(triisopropylsilyloxy)deca-2,9-dienoate ((*S*,*S*,*S*)-12). The same procedure employed above in the preparation of (*S*,*S*,*R*)-**12** was followed using commercially available (–)-Ipc_2B(allyl) (4.72 mL, 4.72 mmol, 1.0 M in pentane) and aldehyde (*S*,*S*)-**11** (2.15 g, 4.29 mmol) in Et_2O (45 mL). ^1H NMR analysis of the crude product indicated an approximately 4:1 mixture of diastereomers. Flash chromatography of the crude product (10:1 hexanes/EtOAc) afforded the title compound as a single diastereomer (colorless oil), with minor impurities (1.51 g, 67%). The compound was taken to the next step for fuller characterization. Selected ^1H NMR data (300 MHz, $CDCl_3$) δ 7.18 (dd, J_1 = 15.9 Hz, J_2 = 3.6 Hz, 1H), 6.14 (dd, J_1 = 15.9 Hz, J_2 = 1.8 Hz, 1H), 5.80 (ddt, J_1 = 17.4 Hz, J_2 = 10.5 Hz, J_3 = 6.9 Hz, 1H), 5.10 (dd, J_1 = 16.8 Hz, J_2 = 10.8 Hz, 2H), 4.63 (td, J_1 = 4.8 Hz, J_2 = 2.1 Hz, 1H), 4.25 (m, 1H), 3.91 (m, 1H), 3.77 (s, 3H).

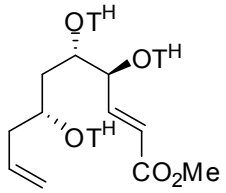


(4*R*,5*R*,7*R*,2*E*)-Methyl-4,5-bis(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-7-hydroxydeca-2,9-dienoate ((*R*,*R*,*R*)-12). The same procedure employed in the preparation of (*S*,*S*,*R*)-**12** was followed using commercially available (+)-Ipc_2B(allyl) (4.35 mL, 4.35 mmol, 1.0 M in pentane) and aldehyde (*R*,*R*)-**11** (2.57 g, 3.63 mmol) in Et_2O (45 mL). ^1H NMR analysis of

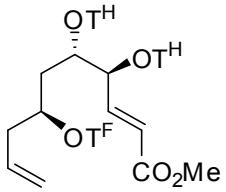
the crude product indicated an approximately 4:1 mixture of diastereomers. Flash chromatography of the crude product (10:1 hexanes/EtOAc) afforded the title compound as a single diastereomer (colorless oil), with minor impurities (1.91 g, 73%). The compound was taken to the next step for fuller characterization. Selected ^{1}H NMR data (300 MHz, $CDCl_3$) δ 7.08 (dd, J_1 = 15.8 Hz, J_2 = 4.3 Hz, 1H), 6.07 (dd, J_1 = 15.8 Hz, J_2 = 1.7 Hz, 1H), 5.76 (m, 1H), 5.12 (dd, J_1 = 18.3 Hz, J_2 = 10.7 Hz, 4.50 (td, J_1 = 4.4 Hz, J_2 = 1.8 Hz, 1H), 4.13 (m, 1H), 3.77 (s, 3H).



(4*R*,5*R*,7*S*,2*E*)-Methyl-4,5-bis(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-7-hydroxy-deca-2,9-dienoate ((*R*,*R*,*S*)-12). A solution of commercially available allyl magnesium bromide (5.50 mL, 5.50 mmol, 1.0 M in Et_2O) was added dropwise to a solution of (−)-DIP-Cl (2.15 g, 6.71 mmol) in Et_2O (20 mL) at 0 °C. The reaction was stirred at this temperature for 1 h, and the stirring was turned off to allow the magnesium mixed halide salt to settle to the bottom of the flask. The supernatant fluid was then added dropwise by cannula to a solution of the aldehyde (*R*,*R*)-**11** (2.93 g, 4.14 mmol) in Et_2O (40 mL) at −78 °C. The reaction was stirred at this temperature for 3 h and was quenched by addition of 1:2:1 pH 7 buffer/methanol/30% aq. H_2O_2 (160 mL). The mixture was stirred for 20 h at room temperature, diluted with Et_2O (150 mL) and was then transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 125 mL). The combined organic extracts were washed with water (75 mL), saturated aqueous $NaHCO_3$ (75 mL), then again with water (75 mL), and brine (75 mL). The organic solution was then dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. ^{1}H NMR analysis of the crude product indicated an approximately 4:1 mixture of diastereomers. Flash chromatography of the crude product (10:1 hexanes/EtOAc) afforded the title compound as a single diastereomer (colorless oil), with minor impurities (2.23 g, 77%). The compound was taken to the next step for fuller characterization. Selected ^{1}H NMR data (300 MHz, $CDCl_3$) δ 7.11 (dd, J_1 = 15.7 Hz, J_2 = 3.8 Hz, 1H), 6.09 (dd, J_1 =15.8 Hz, J_2 = 1.8 Hz, 1H), 5.77 (m, 1H), 5.14 (dd, J_1 = 18.4 Hz, J_2 = 10.0 Hz, 2H), 4.50 (m, 1H), 4.16 (m, 1H), 3.77 (s, 3H), 3.73 (m, 1H), 1.07 (broad s, 28H).

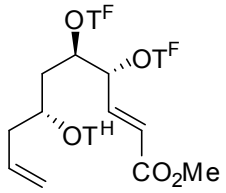


(4*S*,5*S*,7*R*,2*E*)-Methyl-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate ((*S*,*S*,*R*)-13a): The same silylation procedure used in the preparation of (*S*,*S*)-**10** was followed using the homoallylic alcohol (*S*,*S*,*R*)-**12** (1.22 g, 2.250 mmol), TIPSOTf (64 μL, 0.235 mmol), and 2,6-lutidine (0.55 mL, 0.282 mmol) in CH_2Cl_2 (25 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) afforded the title compound as a colorless oil (1.56 g, 99%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (dd, J_1 = 15.8 Hz, J_2 = 3.8 Hz, 1H), 6.15 (dd, J_1 = 15.8 Hz, J_2 = 1.8 Hz, 1H), 5.95 (m, 1H), 5.06 (d, J = 13.1 Hz, 2H), 2.30 (m, 1H), 4.17 (m, 1H), 4.08 (m, 1H), 1.082 (broad s, 42H), 1.05 (broad s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 148.5, 135.0, 121.4, 116.9, 72.6, 67.8, 51.5, 42.0, 40.9, 18.3, 18.2, 18.1, 12.7, 12.6, 12.4; FTIR (thin film) ν_{max} 2945, 2893, 2867, 1731, 1463, 1267, 1109, 1062, 883 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{38}H_{78}O_5Si_3Na$ $[M + Na]^+$: 721.5055, found 721.5074; $[\alpha]_D^{25°C} = -26.8$, c = 1.26, $CHCl_3$.

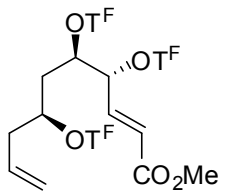


(4*S*,5*S*,7*S*,)-Methyl-7-(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-4,5-bis(triisopropyl-silyloxy)deca-2,9-dienoate ((*S*,*S*,*S*)-13b). The same fluorous tagging procedure used in preparation of (*R*,*R*)-**10** was employed using the alcohol (*S*,*S*,*S*)-**12** (1.40 g, 2.580 mmol), 3,3,4,4,4-pentafluorobutyl)diisopropylsilane (1.49 g, 5.680 mmol), trifluoromethanesulfonic acid (0.46 mL, 5.160 mmol), 2,6-lutidine (0.90 mL, 7.740 mmol) in CH_2Cl_2 (25.0 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) afforded the title compound as a colorless oil (1.38 g, 67%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, J_1 = 15.8 Hz, J_2 = 3.4 Hz, 1H), 6.14 (dd, J_1 = 15.8 Hz, J_2 = 1.8 Hz, 1H), 5.87 (ddt, J_1 = 16.7 Hz, J_2 = 9.5 Hz, J_3 = 7.1 Hz, 1H), 5.06 (d, J = 14.1 Hz, 2H), 2.31 (m, 1H), 4.01 (m, 2H), 3.75 (s, 3H), 2.39 (m, 1H), 2.06 (m, 3H), 1.84 (ddd, J_1 = 13.4 Hz, J_2 = 10.6 Hz, J_3 = 2.0 Hz, 1H), 1.51 (m, 1H), 1.10 (broad s, 21H), 1.07 (broad s, 21H), 1.01 (broad s, 14H), 0.79 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 148.0, 134.8, 121.6, 117.3, 74.2, 73.0, 69.5, 51.4, 40.8, 39.8, 25.7, 25.4, 25.1, 18.2, 18.1, 17.7,

17.6, 17.5, 13.1, 12.9, 12.5, 0.83; ^{19}F NMR (282 MHz, $CDCl_3$) –85.03 (s, 3F), –120.45 (t, $^3J_{HF}$ = 18.0 Hz, 2F); FTIR (thin film) ν_{max} 1069, 2924, 2361, 2340, 1069 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{39}H_{75}O_5F_5Si_3Na$ $[M + Na]^+$: 825.4740, found 825.4769; $[\alpha]_D^{25°C} = +5.78$, c = 1.05, $CHCl_3$.



(4*R*,5*R*,7*S*)-Methyl-4,5-bis(diisopropyl-(3,3,4,4,4-penta-fluoro-butyl)-silyloxy)-7-(triiso-propylsilyloxy)deca-2,9-dienoate (*R*,*R*,*R*)-13c). The same silylation procedure used in the preparation of (*S*,*S*)-**10** was followed using the homoallylic alcohol (*R*,*R*,*R*)-**12** (1.85 g, 2.46 mmol), TIPSOTf (1.00 mL, 3.690 mmol), and 2,6-lutidine (0.60 mL, 5.166 mmol) in CH_2Cl_2 (25 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) afforded the title compound as a colorless oil (1.88 g, 84%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07 (dd, J_1 = 15.8 Hz, J_2 = 4.7 Hz, 1H), 6.03 (dd, J_1 = 15.8 Hz, J_2 = 1.4 Hz, 1H), 5.90 (ddt, J_1 = 16.6 Hz, J_2 = 11.2 Hz, J_3 = 6.9 Hz, 1H), 5.05 (dd, J_1 = 16.8 Hz, J_2 = 10.2 Hz, 2H), 4.45 (m, 1H), 4.04 (sextet, J = 4.6 Hz, 1H), 3.94 (m, 1H), 3.76 (s, 3H), 2.40 (m, 1H), 2.38 (m, 1H), 2.19 (m, 1H), 2.05 (m, 4H), 1.86 (ddd, J_1 = 13.1 Hz, J_2 = 9.0 Hz, J_3 = 3.6 Hz, 1H), 1.51 (ddd, J_1 = 13.9 Hz, J_2 = 9.3 Hz, J_3 = 4.7 Hz, 1H), 1.04 (broad s, 49H), 0.87 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 146.9, 134.3, 122.1, 117.2, 74.3, 73.3, 68.9, 51.6, 41.1, 39.1, 25.3 (m), 18.1, 17.6, 17.5, 13.0, 12.9, 12.7, 12.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ –85.03 (s, 3F), –85.08 (s, 3F), –120.52 ($^3J_{HF}$ = 17.4 Hz, 4F); FTIR (thin film) ν_{max} 2947, 2869, 1732, 1464, 1439, 1333, 1270, 1198 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{40}H_{72}O_5F_{10}Si_3Na$ $[M + Na]^+$: 929.4426, found 929.4509; $[\alpha]_D^{25°C} = +24.1$, c = 1.32, $CHCl_3$.

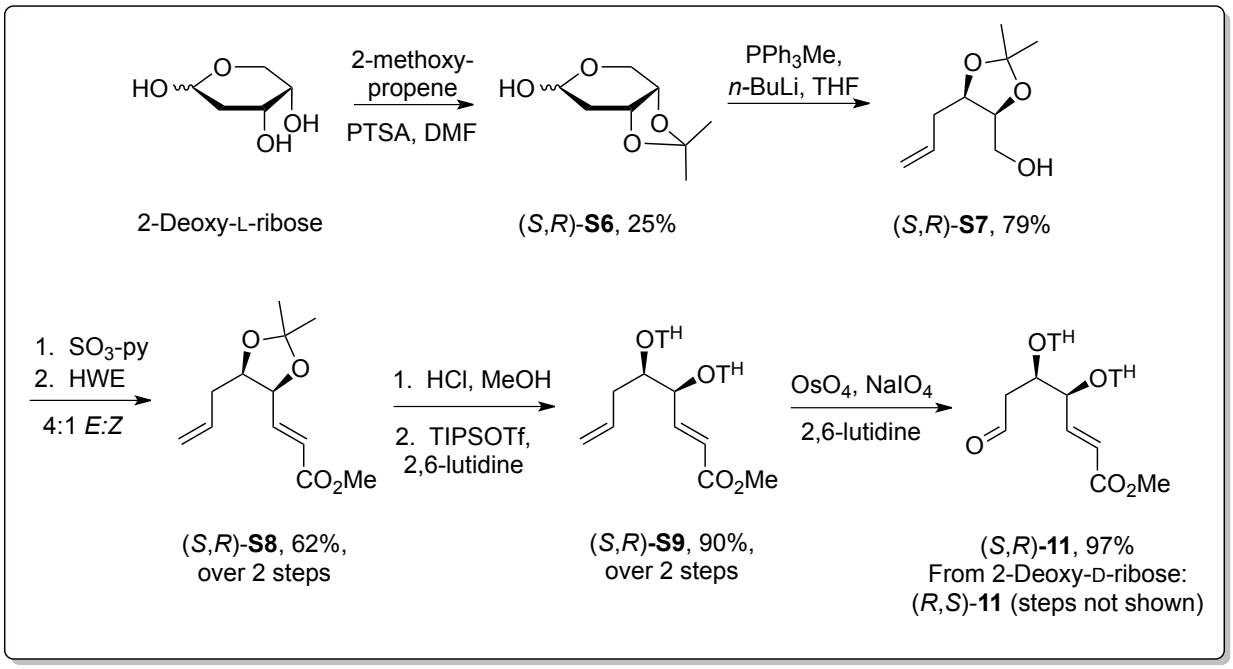


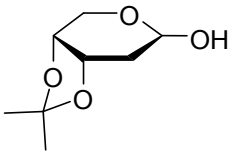
(4*R*,5*R*,7*S*,*E*)-Methyl-4,5,7-tris(diisopropyl-(3,3,4,4,4-pentafluorobutyl)silyloxy)deca-2,9-dienoate ((*R*,*R*,*S*)-13d). The same fluorous tagging procedure used above in preparation of (*R*,*R*)-**10** was employed using the alcohol (*R*,*R*,*S*)-**12** (2.38 g, 3.170 mmol), 3,3,4,4,4-

pentafluorobutyl)diisopropylsilane (1.83 g, 6.980 mmol), CF_3SO_3H (0.46 mL, 5.160 mmol), and 2,6-lutidine (1.10 mL, 9.520 mmol) in CH_2Cl_2 (32.0 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) afforded the title compound as a colorless oil (2.68 g, 84%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dd, J_1 = 15.8 Hz, J_2 = 4.3 Hz, 1H), 6.07 (dd, J_1 = 15.8 Hz, J_2 = 1.7 Hz, 1H), 5.82 (m, 1H), 5.07 (ddd, J_1 = 17.1 Hz, J_2 = 10.2 Hz J_3 = 3.5 Hz, 2H), 4.46 (td, J_1 = 4.2 Hz, J_2 = 1.6 Hz, 1H), 4.06 (m, 1H), 4.00 (m, 1H), 3.78 (s, 3H), 2.32 (m, 2H), 2.05 (m, 6H), 1.73 (m, 1H), 1.59 (m, 1H), 1.04 (broad s, 42H), 0.89 (m, 4H), 0.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 146.5, 133.9, 122.3, 117.8, 76.1, 72.7, 68.9, 51.6, 41.5, 41.2, 25.7, 25.6, 25.4, 25.3, 25.2, 25.1, 25.0, 24.9, 17.7, 17.6, 17.5, 13.0, 12.9, 12.8, 12.6, 12.5, 1.1, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −85.12 (s, 3F), −85.15 (s, 3F), −85.17 (s, 3F), −120.48 (t, $^3J_{HF}$ = 17.7 Hz, 2F), −120.58 (t, $^3J_{HF}$ = 17.5 Hz, 4F); FTIR (thin film) ν_{max} 2949, 2870, 1731, 1464, 1440, 1196, 885 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{41}H_{69}O_5F_{15}Si_3Na$ $[M + Na]^+$: 1,033.4111, found 1,033.4192; $[\alpha]_D^{25°C} = +10.8$, c = 1.09, $CHCl_3$.

Synthesis of *cis*-series quasiisomers 13e-h

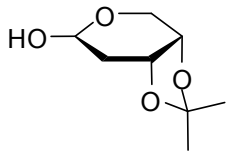
Scheme S4: Synthesis of (*S*,*R*)- and (*R*,*S*)-11



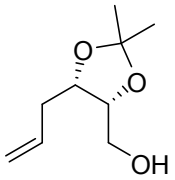


2-Deoxy-3,4-*O*-isopropylidene-D-ribose ((*R*,*S*)-S6):[8] CAS registry number: [86795-47-3]. *p*-Toluenesulfonic acid (5.61 g, 28.9 mmol) was added to a stirring solution of 2-deoxy-D-ribose (20.0 g, 0.145 mol) and 2-methoxypropene (14.3 mL, 0.145 mol) in *N,N*-dimethylformamide (300 mL) at 0 °C. After stirring at 0 °C for 1 h, another stoichiometric amount of 2-methoxypropene (14.3 mL, 0.145 mmol) was added and the reaction was stirred at 0 °C for another 2 h. The reaction was quenched at 0 °C by addition of saturated aqueous $NaHCO_3$ (~100 mL) and the resultant suspension was stirred for 1 h at 0 °C. The suspension was then transferred to a separatory funnel and partitioned with diethyl ether (~400 mL). The layers were separated and the aqueous layer was extracted with diethyl ether (3 x 300 mL). The combined organic extracts were washed with water (150 mL), brine (150 mL), dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil, isolated as a 4:1 α/β anomeric composition (6.79 g, 27%): ^{1}H NMR (300 MHz, *d*6-DMSO) δ 6.24 (d, J = 5.2 Hz, 1H), 4.94 (dt, J_1 = 7.0 Hz, J_2 = 4.3 Hz,

1H), 4.34 (dt, J_1 = 6.2 Hz, J_2 = 4.4 Hz, 1H), 4.05 (m, 1H), 3.78 (dd, J_1 = 12.6 Hz, J_2 = 3.6 Hz, 1H), 3.46 (dd, J_1 = 12.5 Hz, J_2 = 3.8 Hz, 1H), 1.93 (dt, J_1 = 14.5 Hz, J_2 = 4.2 Hz, 1H), 1.63 (ddd, J_1 = 14.5 Hz, J_2 = 7.1 Hz, J_3 = 4.4 Hz, 1H), 1.36 (s, 3H), 1.24 (s, 3H).

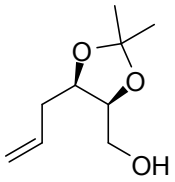


2-Deoxy-3,4-*O*-isopropylidene-L-ribose ((*S*,*R*)-S6):[8] CAS registry number: [522608-67-9]. The procedure for the preparation of (*R*,*S*)-**S6** was repeated using 2-deoxy-L-ribose (24.5 g, 0.179 mol), 2-methoxypropene (34.4 mL, 0.350 mol), and *p*-toluenesulfonic acid (6.95 g, 35.8 mmol). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil, isolated as a 4:1 α/β anomeric composition (7.81 g, 25%). The 1H NMR spectrum matched that of (*R*,*S*)-**S6** (see above); $[\alpha]_D^{25°C}$ = +47.3, c = 0.13, water, literature value reported for the D-enantiomer: $[\alpha]_D^{25°C} = -46.0$, c = 0.10, water.

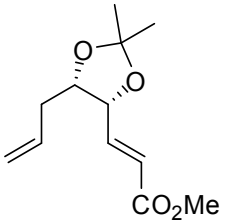


((4*R*,5*S*)-5-Allyl-2,2-dimethyl-1,3-dioxolan-4-yl)methanol ((*R*,*S*)-S7):[9] CAS registry number: [663176-89-4]. Butyllithium (1.6 M in hexanes, 68.2 mL, 0.109 mol) was added dropwise by syringe to a stirred suspension of methyltriphenylphosphonium iodide (48.8 g, 0.117 mol) in THF (450 mL) at −78 °C. The reaction was stirred at −78 °C for 15 min, then warmed to 0 °C and stirred at this temperature for 30 min. A solution of the acetonide (*R*,*S*)-**S6** (6.79 g, 39.0 mmol) in THF (50 mL) was then transferred to the stirring suspension at −78 °C by cannula (along with a 10 mL THF rinse of the original flask containing the acetonide). The reaction mixture was stirred at −78 °C for 30 min and then warmed to room temperature. After 4 h at room temperature, the reaction was quenched by addition of sat. aq. NH_4Cl (200 mL). The layers were then separated and the aqueous layer was extracted with ether (3 x 300 mL). The combined organic extracts were then washed with water (200 mL), brine (200 mL), dried over $MgSO_4$, and concentrated in vacuo. Flash chromatography of the crude product (2:1 hexanes/EtOAc) gave the title compound as a colorless oil (5.74 g, 85%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddt, J_1 = 17.1 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 4.27 (dt, J_1 = 8.2 Hz, J_2 = 6.0

Hz, 1H), 4.19 (quartet, J = 5.8 Hz, 1H), 3.66 (t, J = 5.8 Hz, 1H), 2.42 (m, 1H), 2.30 (m, 1H), 1.89 (t, J = 5.8 Hz, 1H), 1.50 (s, 3H), 1.39 (s, 3H).

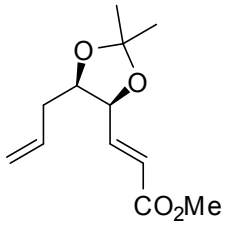


((4*S*,5*R*)-5-Allyl-2,2-dimethyl-1,3-dioxolan-4-yl)methanol ((4*S*,5*R*)-S7): The procedure above for the preparation of (*R*,*S*)-**S7** was employed using acetonide (*S*,*R*)-**S6** (7.81 g, 44.8 mmol), methyltriphenylphosphonium iodide (59.2 g, 0.144 mol), and butyllithium (1.6 M in hexanes, 81.4 mL, 0.135 mol). Flash chromatography of the crude product gave the title compound as a colorless oil (6.12 g, 79%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddt, J_1 = 17.1 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 4.27 (dt, J_1 = 8.2 Hz, J_2 = 6.0 Hz, 1H), 4.19 (quartet, J = 5.8 Hz, 1H), 3.66 (t, J = 5.8 Hz, 1H), 2.42 (m, 1H), 2.30 (m, 1H), 1.89 (t, J = 5.8 Hz, 1H), 1.50 (s, 3H), 1.39 (s, 3H); $\left[\alpha\right]_D^{25^\circ C} = -116.2$, c = 0.29, $CHCl_3$.



(*E*)-Methyl-3-((4*R*,5*S*)-5-allyl-2,2-dimethyl-1,3-dioxolan-4-yl)acrylate ((*R*,*S*)-S8): SO_3-pyridine complex (18.9 g, 0.117 mol) was added in one portion to a solution of alcohol (*R*,*S*)-**S7** (5.74 g, 33.3 mmol) and NEt_3 (23.9 mL, 0.167 mol) in 4:1 DCM/DMSO (350 mL) at 0 °C. The reaction mixture was stirred at room temperature for 30 min and quenched at 0 °C by addition of sat. aq. NH_4Cl (150 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 200 mL) and the combined organic extracts were washed with 30% aqueous $CuSO_4$ solution (3 x 100 mL), then sat. aq. $NaHCO_3$ (100 mL) and brine (100 mL). After drying over $MgSO_4$, the organic extracts were concentrated by rotary evaporation. The crude aldehyde product was taken to the next step without further purification (5.29 g, 31.1 mmol): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (d, J = 3.5 Hz, 1H), 5.84 (m, 1H), 5.17 (dq, J_1 = 7.1 Hz, J_2 = 1.5 Hz, 1H), 5.13 (t, J = 1.2 Hz, 1H), 4.44 (td, J_1 = 7.5 Hz, J_2 = 5.5 Hz, 1H), 4.32 (dd, J_1 = 7.1 Hz, J_2 = 3.1 Hz, 1H), 2.44-2.25 (m, 2H), 1.61 (s, 3H), 1.43 (s, 3H).

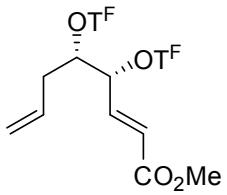
The above procedure for preparation of diene **8** by the modified Horner-Wadsworth-Emmons olefination[6] was used with the crude aldhehyde (5.29 g, 31.1 mmol), trimethylphosphonoacetate (5.56 mL, 37.3 mmol), LiCl (1.61 g, 37.3 mmol), and DBU (5.27 mL, 34.2 mmol) in acetonitrile (350 mL). ^{1}H NMR analysis of the crude product showed a 4:1 *E/Z* mixture of geometric isomers. Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the pure *E*-isomer as a colorless oil (4.01 g, 57% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88 (dd, J_1 = 15.6 Hz, J_2 = 5.9 Hz, 1H), 6.11 (dd, J_1 = 15.6 Hz, J_2 = 1.4 Hz, 1H), 5.81 (m, 1H), 5.14 (ddd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, J_3 = 6.8 Hz, 2H), 4.71 (td, J_1 = 6.3 Hz, J_2 = 1.3 Hz, 1H), 4.33 (dt, J_1 = 8.2 Hz, J_2 = 6.0 Hz, 1H), 3.77 (s, 3H), 2.24 (m, 2H), 1.54 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 143.7, 133.8, 122.6, 117.7, 109.0, 77.6, 77.1, 51.6, 35.1, 27.9, 25.4; FTIR (thin film) ν_{max} 2987, 2939, 1726, 1380, 1307, 1256, 1217, 1165 cm^{-1}; HRMS calcd (ESI) for $C_{12}H_{18}O_4Na$ $[M + Na]^+$: 249.1103, found 249.1086; $[\alpha]_D^{25^\circ C} = -2.75$, c = 1.26, $CHCl_3$.



(*E*)-Methyl 3-((4*S*,5*R*)-5-allyl-2,2-dimethyl-1,3-dioxolan-4-yl)acrylate ((*S*,*R*)-S8). The alcohol (*S*,*R*)-**S7** (6.12 g, 35.5 mmol) was taken through the same two-step oxidation/olefination procedure as (*R*,*S*)-**S8** using SO_3-pyridine complex (20.2 g, 0.124 mol), NEt_3 (25.0 mL, 0.178 mol) in 4:1 DCM/DMSO (350 mL). The crude aldehyde product was taken to the next olefination step without further purification: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (d, J = 3.5 Hz, 1H), 5.84 (m, 1H), 5.17 (dq, J_1 = 7.1 Hz, J_2 = 1.5 Hz, 1H), 5.13 (t, J = 1.2 Hz, 1H), 4.44 (td, J_1 = 7.5 Hz, J_2 = 5.5 Hz, 1H), 4.32 (dd, J_1 = 7.1 Hz, J_2 = 3.1 Hz, 1H), 2.44-2.25 (m, 2H), 1.61 (s, 3H), 1.43 (s, 3H).

The above procedure for preparation of diene **8** by the modified Horner-Wadsworth-Emmons olefination[6] was used with the crude aldhehyde (4.11 g, 24.1 mmol), trimethylphosphonoacetate (4.27 mL, 29.0 mmol), LiCl (1.25 g, 29.0 mmol), and DBU (4.05 mL, 26.6 mmol) in MeCN (250 mL). ^{1}H NMR analysis of the crude product showed a 4:1 *E/Z* mixture of geometric isomers. Flash chromatogtaphy of the crude product (10:1 hexanes/EtOAc) gave the pure *E*-isomer as a colorless oil (3.40 g, 62% over 2 steps): ^{1}H NMR

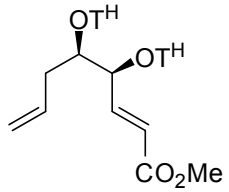
(300 MHz, $CDCl_3$) δ 6.88 (dd, J_1 = 15.6 Hz, J_2 = 5.9 Hz, 1H), 6.11 (dd, J_1 = 15.6 Hz, J_2 = 1.4 Hz, 1H), 5.81 (m, 1H), 5.14 (ddd, J_1 = 17.8 Hz, J_2 = 11.0 Hz, J_3 = 6.8 Hz, 2H), 4.71 (td, J_1 = 6.3 Hz, J_2 = 1.3 Hz, 1H), 4.33 (dt, J_1 = 8.2 Hz, J_2 = 6.0 Hz, 1H), 3.77 (s, 3H), 2.24 (m, 2H), 1.54 (s, 3H), 1.40 (s, 3H); $[\alpha]_D^{25°C}$ = +13.1, c = 1.04, $CHCl_3$.



(4*R*,5*S*,*E*)-Methyl-4,5-bis(Diisopropyl-(3,3,4,4,4-pentafluorobutyl)silyloxy)octa-2,7-dienoate ((*R*,*S*)-S9): Acetyl chloride (3.82 mL, 52.5 mmol) was added by syringe to a stirring solution of the acetal (*R*,*S*)-**S8** in MeOH (170 mL) at 0 °C. The reaction was stirred for 15 min at 0 °C, and then warmed to room temperature. The reaction was stirred at room temperature for 3 h, and then concentrated *in vacuo*. Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a pale yellow syrup which was taken to the next fluorous tagging step: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (dd, J_1 = 15.8 Hz, J_2 = 4.9 Hz, 1H), 6.16 (dd, J_1 = 15.8 Hz, J_2 = 1.8 Hz, 1H), 5.83 (m, 1H), 5.18 (m, 2H), 4.41 (m, 1H), 3.82 (m, 1H), 3.76 (s, 3H), 2.48 (m, 1H), 2.27 (m, 2H), 2.18 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 145.9, 134.1, 122.0, 118.5, 73.4, 73.0, 51.8, 36.4; FTIR (thin film) ν_{max} 3426, 2953, 1708, 1438, 1281, 1198, 1174 cm^{-1}; HRMS calcd (EI) for $C_9H_{15}O_4$ $[M]^+$: 187.0970, found 187.0964; $[\alpha]_D^{25°C}$ = +16.5, c = 1.34, $CHCl_3$.

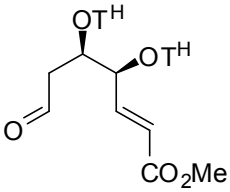
The pure diol (3.08 g, 16.5 mmol) was subjected to the same procedure used above in the preparation of (*R*,*R*)-**10** using the 3,3,4,4,4-pentafluorobutyl)diisopropylsilane (12.3 g, 45.6 mmol), CF_3SO_3H (3.85 mL, 42.9 mmol), and 2,6-lutidine (5.87 mL, 49.5 mmol) in DCM (100 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) afforded the title compound as a colorless oil (10.5 g, 87% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (dd, J_1 = 15.8 Hz, J_2 = 6.7 Hz, 1H), 5.96 (dd, J_1 = 15.8 Hz, J_2 = 1.0 Hz, 1H), 5.76 (m, 1H), 5.12 (ddd, J_1 = 16.4 Hz, J_2 = 10.9 Hz, J_3 = 5.4 Hz, 2H), 4.30 (dd, J_1 = 6.7 Hz, J_2 = 1.8 Hz, 1H), 3.89 (m, 1H), 3.76 (s, 3H), 2.29 (m, 2H), 2.05 (m, 4H), 1.04 (br s, 28H), 0.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 146.6, 133.7, 122.6, 118.5, 76.8, 75.5, 51.7, 38.7, 25.2 (m), 18.8, 17.6, 17.5 (br s), 17.4, 13.4, 12.9, 12.8, 12.7, 12.6, 10.4, 1.0, 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) −85.01 (s, 3F), −85.06 (s, 3F), −120.46 (m, 4F); FTIR (thin film) ν_{max} 2948, 2870, 1732, 1464, 1440,

1381, 1333, 1276, 1244, 1198, 1107 cm^{-1}; HRMS calcd (ESI) for $C_{29}H_{48}O_4F_{10}Si_2Na$ $[M + Na]^+$: 729.2829, found 729.2823; $[\alpha]_D^{25°C} = -1.25$, c = 1.14, $CHCl_3$.



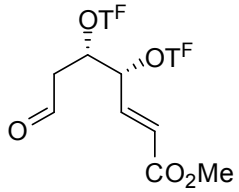
(4*S*,5*R*,*E*)-Methyl-4,5-bis(triisopropylsilyloxy)octa-2,7-dienoate ((*S*,*R*)-S9): The procedure used for the preparation of (*R*,*S*)-**S9** was repeated using (*S*,*R*)-**S8** (3.40 g, 15.0 mmol) with acetyl chloride (3.28 mL, 45.1 mmol) in MeOH (150 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the diol as a pale yellow syrup which was taken to the next step (see below): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (dd, J_1 = 15.8 Hz, J_2 = 4.9 Hz, 1H), 6.16 (dd, J_1 = 15.8 Hz, J_2 = 1.8 Hz, 1H), 5.83 (m, 1H), 5.18 (m, 2H), 4.41 (m, 1H), 3.82 (m, 1H), 3.76 (s, 3H), 2.48 (m, 1H), 2.27 (m, 2H), 2.18 (m, 1H); $[\alpha]_D^{25°C} = -16.3$, c = 1.56, $CHCl_3$.

The diol from above (2.70 g, 14.5 mmol) was subjected to the above procedure for the preparation of compound (*S*,*S*)-**10** using TIPSOTf (10.1 mL, 36.2 mmol), and 2,6-lutidine (5.15 mL, 43.5 mL) in CH_2Cl_2 (100 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (6.74 g, 90% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (dd, J_1 = 15.8 Hz, J_2 = 6.6 Hz, 1H), 5.96 (dd, J_1 = 15.8 Hz, J_2 = 1.2 Hz, 1H), 5.80 (m, 1H), 5.10 (ddd, J_1 = 16.8 Hz, J_2 = 10.7 Hz, J_3 = 7.7 Hz, 2H), 4.39 (dq, J_1 = 6.6 Hz, J_2 = 1.3 Hz, 1H), 4.01 (ddd, J_1 = 7.9 Hz, J_2 = 5.1 Hz, J_3 = 2.5 Hz, 1H), 3.76 (s, 3H), 2.35 (m, 2H), 1.07 (br s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 148.5, 134.4, 121.5, 117.8, 77.0, 75.5, 51.5, 39.2, 18.2 (br s), 12.7 (br s); FTIR (thin film) ν_{max} 2944, 2893, 2867, 1731, 1464, 1271, 1244, 1166, 1119, 1064 cm^{-1}; HRMS calcd (ESI) for $C_{27}H_{54}O_4Si_2Na$ $[M + Na]^+$: 521.3458, found 521.3481; $[\alpha]_D^{25°C} = -12.4$, c = 1.44, $CHCl_3$.

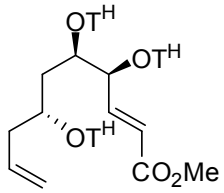


(4*S*,5*R*,*E*)-Methyl 7-oxo-4,5-bis(triisopropylsilyloxy)hept-2-enoate ((*S*,*R*)-11). The same method employed below for the preparation of (*R*,*S*)-**11** was followed using 2,6-lutidine (3.17 mL, 26.8 mmol), OsO_4 (2.5 wt. %, 3.36 mL, 0.27 mmol), $NaIO_4$ (11.6 g, 53.6 mmol), and the

alkene (*S*,*R*)-**S9** (6.68 g, 13.4 mmol) in 3:1 dioxane/water (120 mL) at room temperature. Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the title compound as a pale brown oil (5.32 g, 79%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (m, 1H), 6.90 (dd, J_1 = 15.8 Hz, J_2 = 6.4 Hz, 1H), 6.10 (dd, J_1 = 15.8 Hz, J_2 = 1.3 Hz, 1H), 4.56 (dd, J_1 = 6.3 Hz, J_2 = 1.4 Hz, 1H), 4.31 (m, 1H), 3.76 (s, 3H), 2.63 (m, 2H), 1.09 (broad s, 42H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 166.3, 147.9, 122.3, 77.3, 72.5, 51.7, 46.7, 18.1 (br s), 12.5 (br s); FTIR (thin film) ν_{max} 2945, 2892, 2867, 1728, 1463, 1274, 1243, 1166, 1131 cm^{-1}; HRMS calcd (ESI) for $C_{26}H_{52}O_5Si_2Na$ $[M + Na]^+$: 523.3251, found 523.3285; $[\alpha]_D^{25^\circ C} = +0.13$, c = 1.26, $CHCl_3$.

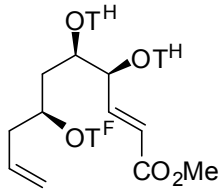


(4*R*,5*S*,2*E*)-Methyl-4,5-bis(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-7-oxohept-2-enoate ((*R*,*S*)-11): 2,6-lutidine (1.60 mL, 13.5 mmol), OsO_4 (2.5 wt. %, 1.70 mL, 0.135 mmol), and $NaIO_4$ (5.96 g, 27.1 mmol) were sequentially added to a solution of the alkene (*R*,*S*)-**S9** (4.78 g, 6.76 mmol) in 3:1 dioxane/water (80 mL) at room temperature. The resultant suspension was stirred for 4 h at room temperature, and then water (100 mL) and CH_2Cl_2 (200 mL) were added. The bilayer was then transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL) and the combined organic extracts were then washed with water (100 mL), brine (100 mL), dried over $MgSO_4$, and then concentrated in vacuo. Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the title compound as a pale brown oil (3.27 g, 68%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (m, 1H), 6.85 (dd, J_1 = 15.8 Hz, J_2 = 6.5 Hz, 1H), 5.99 (d, J = 15.8 Hz, 1H), 4.36 (m, 2H), 3.76 (s, 3H), 2.67 (m, 2H), 2.05 (m, 4H), 1.10 (broad s, 28H), 0.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 165.9, 146.1, 123.2, 76.8, 71.8, 51.7, 47.3, 25.1 (m), 17.4 (br s), 12.6 (br s), 0.9, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −84.96 (s, 3F), −85.00 (s, 3F), −120.29 (t, $^{3}J_{HF}$ = 17.5 Hz, 2F), −120.39 (t, $^{3}J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2948, 2870, 1729, 1196, 991 cm^{-1}; HRMS calcd (ESI) for $C_{28}H_{46}O_5Si_2F_{10}K$ $[M + K]^+$: 747.2361, found 747.2334; $[\alpha]_D^{25^\circ C} = -3.00$, c = 1.06, $CHCl_3$.



(4*S*,5*R*,7*R*,)-Methyl-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate ((*S*,*R*,*R*)-13e): The *in situ* preparation of the Brown reagent used for (4*R*,5*R*,7*S*)-**12** was repeated with allylmagnesium bromide (9.92 mL, 9.92 mmol), (+)-DIP-Cl (3.55 g, 10.5 mmol), and aldehyde (*S*,*R*)-**11** (1.51 g, 3.01 mmol) in Et_2O (25 mL) at −78 °C. Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the untagged homoallylic alcohol as an inseparable mixture of diastereomers (~6:1 *d.r.*) with minor impurities. This mixture was taken to the next step without further purification.

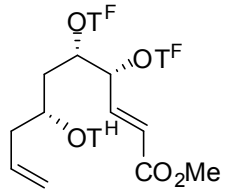
The same silylation procedure used above to obtain (*R*,*R*)-**10** was used for the inseparable mixture of diastereomers using TIPSOTf (0.90 mL, 3.26 mmol) and 2,6-lutidine (0.52 mL, 4.34 mmol) in CH_2Cl_2 (30 mL). Flash chromatography of the crude product gave the title compound as an inseparable mixture of diastereomers (1.04 g, 6:1 *d.r.*, 54% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (dd, J_1 = 15.8 Hz, J_2 = 6.3 Hz, 1H), 5.95 (d, J = 15.8 Hz, 1H), 5.82 (m, 1H), 5.04 (dd, J_1 = 17.2 Hz, J_2 = 10.1 Hz, J_2 = 9.6 Hz, 2H), 4.48 (d, J = 6.5 Hz, 1H), 4.10 (t, J = 6.5 Hz, 1H), 4.02 (quintet, J = 4.9 Hz, 1H), 3.75 (s, 3H), 2.30 (m, 2H), 1.75 (m, 2H), 1.07 (broad s, 63H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 148.7, 134.4, 121.4, 117.4, 74.2, 69.2, 51.6, 41.7, 40.8, 18.3 (br s), 12.7 (br s); FTIR (thin film) ν_{max} 2945, 2868, 1733, 1465, 1062, 996 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{38}H_{78}O_5Si_3Na$ $[M + Na]^+$: 721.5055, found 721.5110; $\left[\alpha\right]_D^{25^\circ C} = -5.10$, c = 1.93, $CHCl_3$.



(4*S*,5*R*,7*S*,2*E*)-Methyl-7-(diisopropyl-(3,3,4,4,4-pentafluorobutyl)silyloxy)-4,5-bis(triiso-propylsilyloxy)deca-2,9-dienoate ((*S*,*R*,*S*)-13f). The *in situ* preparation of the Brown reagent used for the above preparation of (*R*,*R*,*S*)-**12** was repeated with aldehyde (*S*,*R*)-**11** (1.29 g, 3.01 mmol), (−)-DIP-Cl (3.04 g, 8.99 mmol), and allylmagnesium bromide (8.48 mL, 8.48 mmol) in Et_2O (25 mL). Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the

untagged homoallylic alcohol as an inseparable mixture of diastereomers (~6:1 *d.r.*) along with 3-pinanol by-product. This mixture was taken to the next tagging step without further purification.

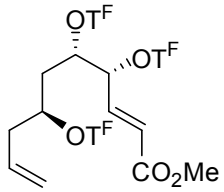
The general procedure for fluorous tagging was used for the inseparable mixture of diastereomers with 3,3,4,4,4-pentafluorobutyl)diisopropylsilane (1.17 g, 4.45 mmol), triflic acid (0.36 mL, 3.92 mmol), and 2,6-lutidine (0.64 mL, 5.34 mmol) in DCM (40 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as an inseparable mixture of diastereomers (1.27 g, 6:1 *d.r.*, 61% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (dd, J_1 = 15.8 Hz, J_2 = 6.4 Hz, 1H), 5.97 (d, J = 15.8 Hz, 1H), 5.80 (m, 1H), 5.07 (ddd, J_1 = 16.7 Hz, J_2 = 10.5 Hz, J_3 = 6.2 Hz, 2H), 4.38 (d, J = 6.5 Hz, 1H), 4.03 (t, J = 6.5 Hz), 3.87 (quintet, J = 5.6 Hz), 3.76 (s, 3H), 2.25 (m, 2H), 2.05 (m, 2H), 1.76 (m, 2H), 1.08 (broad s, 56H), 0.83 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 148.0, 134.2, 121.7, 117.7, 76.7, 74.3, 69.7, 51.6, 42.4, 41.7, 25.4 (m), 18.1 (br s), 13.2 (br s), 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) −84.97 (s, 3F), −120.35 (t, $^3J_{HF}$ = 17.7 Hz, 2F); FTIR (thin film) ν_{max} 2947, 2869, 1733, 1466, 1201, 1168, 1096, 1060, 994 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{39}H_{75}O_5F_5Si_3Na$ [M + Na]$^+$: 825.4740, found 825.4711; $[\alpha]_D^{25°C} = -6.41$, c = 1.57, $CHCl_3$.



(4*R*,5*S*,7*S*)-Methyl-4,5-bis(diisopropyl(3,3,4,4,4-pentafluorobutyl)silyloxy)-7-(triiso-propylsilyloxy)deca-2,9-dienoate ((*R*,*S*,*R*)-13g). The *in situ* preparation of the Brown reagent used above for (*R*,*R*,*S*)-**12** was repeated with aldehyde (*R*,*S*)-**11** (1.17 g, 1.65 mmol), (+)-DIP-Cl (1.95 g, 5.77 mmol), and allylmagnesium bromide (5.44 mL, 5.44 mmol) in Et_2O (30 mL). Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the untagged homoallylic alcohol as an inseparable mixture of diastereomers (~6:1 *d.r.*) along with 3-pinanol by-product.

The mixture of diastereomers was taken to the next tagging step using TIPSOTf (0.813 mL, 2.95 mmol), 2,6-lutidine (0.40 mL) in DCM (15 mL) in the same manner as above for preparation of (*S*,*S*)-**10**. Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as an inseparable mixture of diastereomers (977 mg, 6:1 *d.r.*, 65% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (dd, J_1 = 15.8 Hz, J_2 = 6.7 Hz, 1H), 5.97 (dd, J_1 =

15.8 Hz, J_2 = 1.1 Hz, 1H), 5.85 (m, 1H), 5.08 (ddd, J_1 = 17.1 Hz, J_2 = 10.3 Hz, J_3 = 8.7 Hz, 2H), 4.27 (d, J = 6.5 Hz, 1H), 4.01 (td, J_1 = 6.5 Hz, J_2 = 1.9 Hz, 1H), 3.91 (quintet, J = 6.5 Hz, 1H), 3.76 (s, 3H), 2.29 (m, 2H), 2.05 (m, 4H), 1.67 (t, J = 6.7 Hz, 1H), 1.06 (broad s, 49H), 0.86 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 146.2, 134.0, 122.7, 121.3, 117.7, 117.5, 74.4, 68.9, 51.7, 41.9, 25.4 (m), 17.6 (br s), 12.9 (br s), 1.3, 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) δ −85.01 (s, 3F), −85.04 (s, 3F), −120.47 (m, 4F); FTIR (thin film) ν_{max} 2948, 2870, 1734, 1200, 1104, 1061, 993 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{40}H_{72}O_5F_{10}Si_3Na$ $[M + Na]^+$: 929.4426, found 929.4446; $[\alpha]_D^{25^\circ C} = -3.88$, c = 1.04, $CHCl_3$.

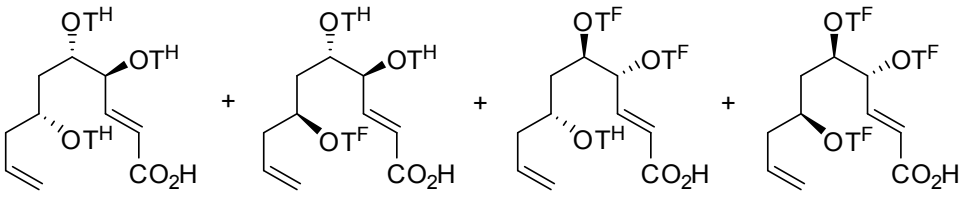


(4*R*,5*S*,7*S*,*E*)-Methyl-4,5,7-tris(diisopropyl-(3,3,4,4,4-pentafluorobutyl)silyloxy)deca-2,9-dienoate ((*R*,*S*,*S*)-13h). The *in situ* preparation of the Brown allylborane used for the preparation of (*R*,*R*,*S*)-**12** was followed using the aldehyde (*R*,*S*)-**11** (1.02 g, 1.65 mmol), (−)-DIP-Cl (1.95 g, 5.77 mmol), and allylmagnesium bromide (5.40 mL, 5.40 mmol) in Et_2O (30 mL). Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the untagged homoallylic alcohol as an inseparable mixture of diastereomers (~6:1 *d.r.*) with minor impurities.

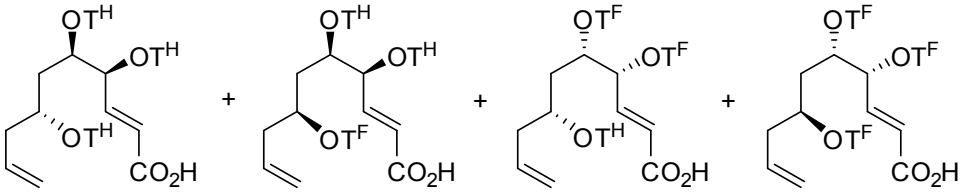
The mixture of diastereomers was taken to the next tagging step using 3,3,4,4,4-pentafluorobutyl)diisopropylsilane (0.861 g, 3.28 mmol), CF_3SO_3H (0.27 mL, 3.02 mmol), and 2,6-lutidine (0.47 mL, 3.94 mmol) in CH_2Cl_2 (13 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as an inseparable mixture of diastereomers (1.17 g, 6:1 *d.r.*, 80% over 2 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.91 (dd, J_1 = 15.8 Hz, J_2 = 6.5 Hz, 1H), 5.94 (d, J = 15.8 Hz, 1H), 5.76 (m, 1H), 5.07 (ddd, J_1 = 15.9 Hz, J_2 = 10.8 Hz J_3 = 9.0 Hz, 2H), 4.34 (d, J = 6.6 Hz, 1H), 4.02 (m, 1H), 3.95 (m, 1H), 3.77 (s, 3H), 2.27 (m, 2H), 2.05 (m, 6H), 1.68 (m, 2H), 1.05 (broad s, 42H), 0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 146.4, 133.5, 122.6, 118.1, 76.9, 74.0, 69.4, 51.7, 41.5, 40.9, 25.4 (m), 17.5 (br s), 13.0 (br s), 1.2, 0.9, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −84.97 (s, 3F), −84.99 (s, 3F), −85.03 (s, 3F), −120.45 (m, 6F); FTIR (thin film) ν_{max} 2949, 2870, 1733, 1198, 1066, 993, 886 cm^{-1};

HRMS calcd (ESI, positive mode) for $C_{41}H_{69}O_5F_{15}Si_3Na$ $[M + Na]^+$: 1,033.4111, found 1,033.4084; $[\alpha]_D^{25°C} = -5.26$, c = 1.02, $CHCl_3$.

Fluorous Mixture Synthesis, Scheme 3 in the paper

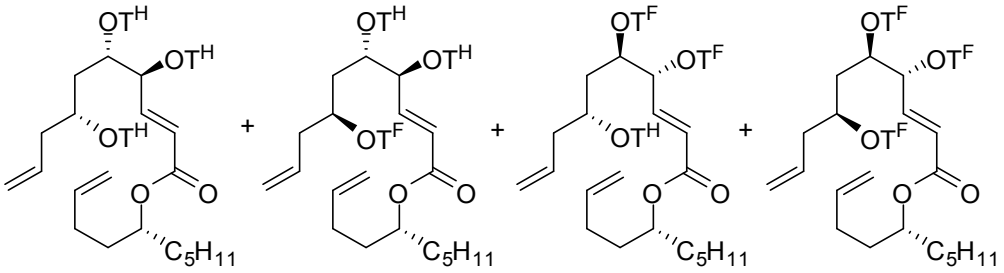


(4*S*,5*S*,7*R*,*E*)-4,5,7-Tris(triisopropylsilyloxy)deca-2,9-dienoic acid, (4*S*,5*S*,7*S*,*E*)-4,5-Bis(triisopropylsilyloxy)-7-((1,1,1,2,2)-pentafluorobutyldiisopropylsilyloxy)deca-2,9-dienoic acid, (4*R*,5*R*,7*R*,*E*)-4,5-Bis((1,1,1,2,2)-pentafluorobutyl(diisopropylsilyloxy))-7-(triisopropylsilyloxy)deca-2,9-dienoic acid, (4*R*,5*R*,7*S*,*E*)-4,5,7-Tris((1,1,1,2,2)-pentafluorobutyl(diisopropylsilyloxy))deca-2,9-dienoic acid (M-4-*trans*). Potassium trimethylsilanolate (90%, 3.05 g, 21.41 mmol) was added in one portion to a solution of (*S*,*S*,*R*)-**13a** (250 mg, 0.36 mmol), (*S*,*S*,*S*)-**13b** (287 mg, 0.36 mmol), (*R*,*R*,*R*)-**13c** (324 mg, 0.36 mmol), and (*R*,*R*,*S*)-**13d** (362 mg, 0.36 mmol) in Et_2O (13 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 15 min then at room temperature for 16 h. The reaction was quenched by addition of 0.5 M citric acid (13 mL) at 0 °C. After 10 minutes, the quenched mixture was transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic extracts were washed with water (15 mL) and brine (15 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. Flash chromatography of the crude product (10:1 hexanes/EtOAc) gave the title compound as a colorless, viscous oil (1.01 g, 84% based on average molecular weight): LRMS (ESI, positive mode) ((*S,S,R*)-**4a**) *m/z* 685 $(M)^+$; ((*S,S,S*)-**4b**) *m/z* 789 $(M)^+$; ((*R,R,R*)-**4c**) *m/z* 915 $(M + Na)^+$; **(**(*R,R,R*)-**4d**) *m/z* 1019 $(M + Na)^+$; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 9.0 min ((*S*,*S*,*R*)-**4a**), 14.9 min ((*S*,*S*,*S*)-**4b**), 20.3 min ((*R*,*R*,*R*)-**4c**), 28.6 min (*R*,*R*,*S*)-**4d**).



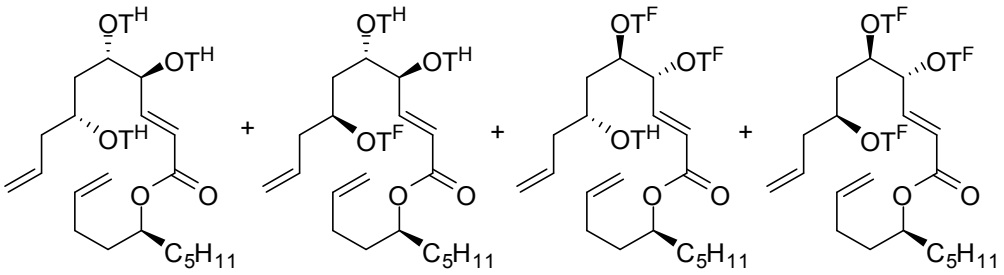
(4*S*,5*R*,7*R*,*E*)-4,5,7-Tris(triisopropylsilyloxy)deca-2,9-dienoic acid, (4*S*,5*R*,7*S*,*E*)-4,5-Bis(triisopropylsilyloxy)-7-((1,1,1,2,2)-pentafluorobutyldiisopropylsilyloxy)deca-2,9-dienoic acid, (4*R*,5*S*,7*R*,*E*)-4,5-Bis((1,1,1,2,2)-pentafluorobutyl(diisopropylsilyloxy))-7-(triiso-

propylsilyloxy)-deca-2,9-dienoic acid, (4*R*,5*S*,7*S*,*E*)-4,5,7-Tris((1,1,1,2,2)-pentafluorobutyl-(diisopropylsilyloxy))deca-2,9-dienoic acid (M-4-*cis*). The same procedure employed above for compound M-**4a-d** was repeated using (*S*,*R*,*R*)-**13e** (300 mg, 0.43 mmol), (*S*,*R*,*S*)-**13f** (345 mg, 0.43 mmol), (*R*,*S*,*R*)-**13g** (389 mg, 0.43 mmol), (*R*,*S*,*S*)-**13h** (434 mg, 0.43 mmol), and TMSOK (3.61 g, 25.36 mmol) in Et_2O (17.0 mL). Flash chromatography of the crude product (3:1 hexanes/EtOAc) gave the title compound as a colorless oil (1.14 g, 80% based on average molecular weight): LRMS (ESI, positive mode) ((*S*,*R*,*R*)-**4e**) *m/z* 708 $(M + Na)^+$; ((*S*,*R*,*S*)-**4f**) *m/z* 811 $(M + Na)^+$; ((*R*,*S*,*R*)-**4g**) *m/z* 915 $(M + Na)^+$; ((*R*,*S*,*S*)-**4h**) *m/z* 1019 $(M + Na)^+$; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 15.0 min ((*S*,*R*,*R*)-**4e**), 18.5 min ((*S*,*R*,*S*)-**4f**), 20.9 min ((*R*,*S*,*R*)-**4g**), 24.0 min ((*R*,*S*,*S*)-**4h**).

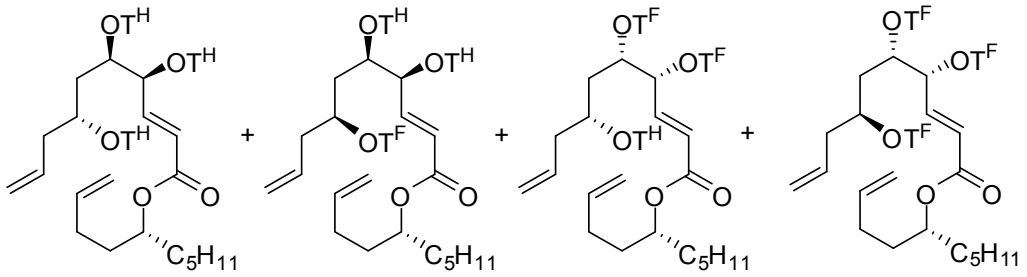


(4*S*,5*S*,7*R*)-((*R*)-Dec-1-en-5-yl)-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate, (4*S*,5*S*,7*S*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(triisopropylsilyloxy)-7-diisopropyl-(1,1,1,2,2-pentafluorobutyl-silyloxy)deca-2,9-dienoate, (4*R*,5*R*,7*R*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy))-7-triisopropylsilyloxydeca-2,9-dienoate, (4*R*,5*R*,7*S*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)) deca-2,9-dienoate (M-(*R*)-14a-d). Triethylamine (385 μL, 23.46 mmol) was added to a solution of the acid M-**4-*trans*** (1.16 g, 1.38 mmol based on average molecular weight) in toluene (14.0 mL) at room temperature. 2,4,6-Trichlorobenzoyl chloride (227 μL, 1.45 mmol) was then added by syringe and the resultant white slurry was stirred at room temperature for 1 h. A solution of the alcohol (*R*)-**3** (237 mg, 1.52 mmol) and DMAP (338 mg, 2.76 mmol) in toluene (14.0 mL) was slowly added to the reaction mixture by cannula transfer. The milky emulsion was stirred at room temperature for 3 h. Toluene (10 mL) and saturated aqueous $NaHCO_3$ (10 mL) were added and the emulsion became a clear bilayer. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation.

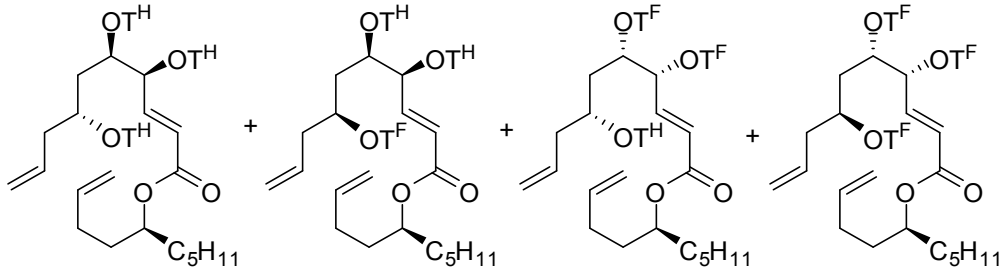
Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a pale yellow oil (1.29 g, 95% based on average molecular weight): HRMS (ESI, positive mode): calcd for $C_{47}H_{94}0_5Si_3Na$ $[M + Na]^+$ 845.6307, found 845.6340 for (*R*)-**14a**; calcd for $C_{48}H_{91}O_5F_5Si_3Na$ $[M + Na]^+$ 949.5992, found 949.6046 for (*R*)-**14b**; calcd for $C_{49}H_{88}O_5F_{10}Si_3Na$ $[M + Na]^+$ 1,053.5678, found 1,053.5725 for (*R*)-**14c**; calcd for $C_{50}H_{85}O_5F_{15}Si_3Na$ $[M+ Na]^+$ 1,157.5363, found 1,157.5360 for (*R*)-**14d**; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 22.9 min ((*R*)-**14a**), 29.5 min ((*R*)-**14b**), 33.9 min ((*R*)-**14c**), 40.5 min ((*R*)-**14d**).



(4*S*,5*S*,7*R*)-((*S*)-Dec-1-en-5-yl)-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate, (4*S*,5*S*,7*S*)-((*S*)-Dec-1-en-5-yl)-4,5-bis(triisopropylsilyloxy)-7-diisopropyl-(1,1,1,2,2-pentafluorobutyl-silyloxy)deca-2,9-dienoate, (4*R*,5*R*,7*R*)-((*S*)-Dec-1-en-5-yl)-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy))-7-triisopropylsilyloxydeca-2,9-dienoate, (4*R*,5*R*,7*S*)-((*S*)-Dec-1-en-5-yl)-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy))-deca-2,9-dienoate (M-(*S*)-14a-d): The same method employed in the preparation of M-(*R*)-**14a-d** was repeated using mixture M-**4-*trans*** (977 mg, 1.16 mmol based on average molecular weight), alcohol (*S*)-**3** (236 mg, 1.51 mmol), NEt_3 (1.78 mL), DMAP (369 mg, 3.02 mmol), and 2,4,6-trichlorobenzoyl chloride (360 μL, 2.32 mmol) in toluene (25.0 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (1.16 g, 100% based on average molecular weight): HRMS (ESI, positive mode): calcd for $C_{47}H_{94}0_5Si_3Na$ $[M + Na]^+$ 845.6307, found 845.6323 for (*S*)-**14a**; calcd for $C_{48}H_{91}O_5F_5Si_3Na$ $[M + Na]^+$ 949.5992, found 949.6074 for (*S*)-**14b**; calcd for $C_{49}H_{88}O_5F_{10}Si_3Na$ $[M + Na]^+$ 1,053.5678, found 1,053.5664 for (*S*)-**14c**; calcd for $C_{50}H_{85}O_5F_{15}Si_3Na$ $[M + Na]^+$ 1,157.5363, found 1,157.5306 for (*S*)-**14d**; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 5.1 min ((*S*)-**14a**), 7.3 min ((*S*)-**14b**), 9.9 min ((*S*)-**14c**), 15.8 min ((*S*)-**14d**).

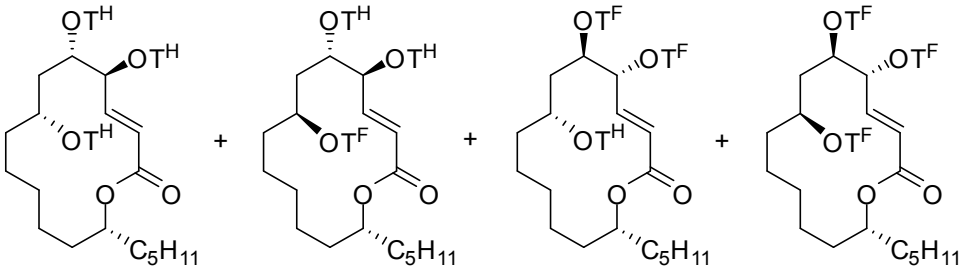


(4*S*,5*R*,7*R*)-((*R*)-Dec-1-en-5-yl)-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate, (4*S*,5*R*,7*S*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)deca-2,9-dienoate, (4*R*,5*S*,7*R*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy))-7-triisopropylsilyloxydeca-2,9-dienoate, (4*R*,5*S*,7*S*)-((*R*)-Dec-1-en-5-yl)-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy))deca-2,9-dienoate ((*R*)-M-14e-h): The same method employed above in the preparation of M-(*R*)-**14a-d** was repeated using mixture **M-4-*cis*** (548 mg, 652 μmol based on average molecular weight), alcohol (*R*)-**3** (132 mg, 847 μmol), NEt_3 (186 μL), DMAP (163 mg, 1.30 mmol), and 2,4,6-trichlorobenzoyl chloride (110 μL, 684 μmol) in toluene (13.0 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (577 mg, 90% based on average molecular weight): LRMS (ESI, positive mode) ((*R*)-**14e**) *m/z* 846 $(M + Na)^+$; ((*R*)-**14f**) *m/z* 950 $(M + Na)^+$; ((*R*)-**14g**) *m/z* 1054 $(M + Na)^+$; ((*R*)-**14h**) *m/z* 1158 $(M + Na)^+$; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 17.8 min ((*R*)-**14e**), 21.4 min ((*R*)-**14f**), 24.7 min ((*R*)-**14g**), 30.3 min ((*R*)-**14h**).



(4*S*,5*R*,7*R*)-((*S*)-Dec-1-en-5-yl)-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate, (4*S*,5*R*,7*S*)-((*S*)-Dec-1-en-5-yl)-4,5-bis(triisopropylsilyloxy)-7-diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)deca-2,9-dienoate, (4*R*,5*S*,7*R*)-((*S*)-Dec-1-en-5-yl)-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy))-7-triisopropylsilyloxydeca-2,9-dienoate, (4*R*,5*S*,7*S*)-((*S*)-Dec-1-en-5-yl)-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy))deca-2,9-dienoate (M-(*S*)-14e-h): The same method employed above in the preparation of M-(*R*)-**14a-d** was repeated

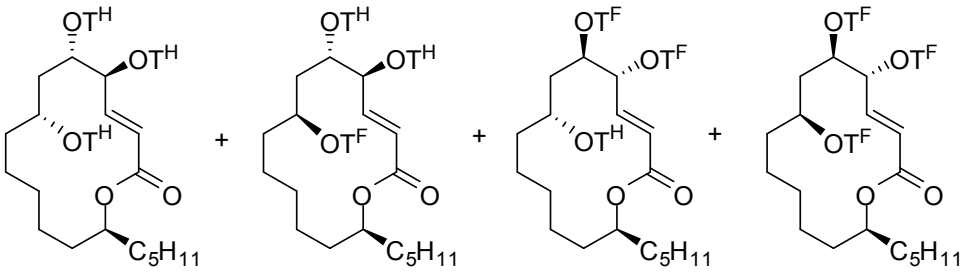
using mixture **M-4-*cis*** (584 mg, 694 μmol based on average molecular weight), alcohol (*S*)-**3** (141 mg, 902 μmol), NEt_3 (197 μL), DMAP (173 mg, 1.39 mmol), and 2,4,6-trichlorobenzoyl chloride (117 μL, 729 μmol) in toluene (14.0 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (607 mg, 89% based on average molecular weight): LRMS (ESI, positive mode) ((*S*)-**14e**) *m/z* 846 $(M + Na)^+$; ((*S*)-**14f**) *m/z* 950 $(M + Na)^+$; ((*S*)-**14g**) *m/z* 1054 $(M + Na)^+$; **(**(*S*)-**14h**) *m/z* 1158 $(M + Na)^+$; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 17.7 min ((*S*)-**14e**), 21.4 min ((*S*)-**14f**), 24.9 min ((*S*)-**14g**), 30.9 min **(**(*S*)-**14h**).



(4*S*,5*S*,7*R*,13*R*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-3-en-2-one, (4*S*,5*S*,7*S*,13*R*,*E*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl-(1,1,1,2,2-penta-fluorobutylsilyloxy)-oxacyclo-tetra-dec-2-enone, (4*R*,5*R*,7*R*,13*R*,*E*)-13-Pentyl-4,5-bis-(di-isopropyl(1,1,1,2,2-pentafluoro-butyl-silyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*R*,7*S*,13*R*,*E*)-13-Pentyl-4,5,7-tris(diisopropyl-(1,1,1,2,2-pentafluorobutyl-silyloxy)oxacyclotetradec-2-enone (M-(*R*)-15a-d): Grubbs 2nd generation catalyst (59 mg, 69.5 μmol) was added in portion to a stirring solution of the mixture M-(*R*)-**14a-d** (682 mg, 696 μmol based on average molecular weight) in CH_2Cl_2 (210 mL, degassed). The reaction flask was fitted with a reflux condenser, heated to a steady reflux (55 °C, external bath temperature), and stirred for 24 h. The reaction mixture was cooled to room temperature and an additional loading of the catalyst (59 mg, 69.5 μmol) was added in one portion. The reaction mixture was heated again to reflux (55 °C, external bath temperature) and stirred for an additional 24 h. The reaction mixture was cooled to room temperature and concentrated by rotary evaporation. Two successive rounds of flash chromatography (40:1 hexanes/EtOAc) gave the ring-closed product as a pale brown oil (630 mg, 663 μmol), which was directly subjected to the hydrogenation without further purification.

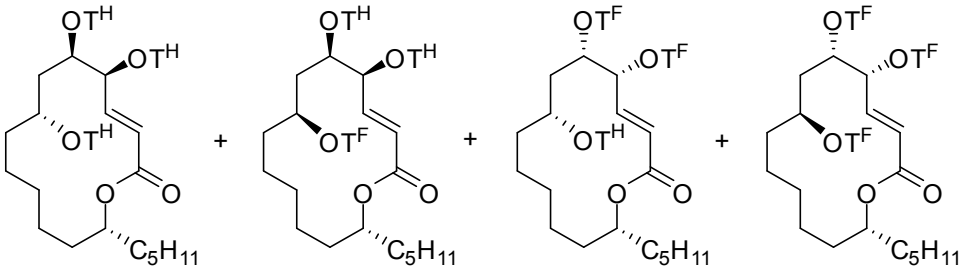
The ring-closed product (630 mg, 663 μmol) was dissolved in EtOH (20 mL) and treated with Pd/$SrCO_3$ (3.52 g, 663 μmol). The flask was fitted with a three-junction vacuum adaptor,

connected to a vacuum line and a balloon full of hydrogen gas. The flask was purged of air through the vacuum line and the flask was entrained with hydrogen gas. This "vac-fill" cycle was repeated three times to completely purge the flask with dihydrogen. The reaction mixture was stirred for exactly 60 min and the vacuum adaptor/balloon assembly was removed. The catalyst was filtered and the supernatant liquid was concentrated by rotary evaporation. Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (584 mg, 88% over two steps, based on average molecular weight): LRMS (EI) (*R*)-**15a** *m/z* 820 $(M + Na)^+$; (*R*)-**15b** *m/z* 901 $(M)^+$; (*R*)-**15c** *m/z* 1028 $(M + Na)^+$; (*R*)-**15d** *m/z* 1109 $(M)^+$; HRMS (ESI, positive mode): calcd for $C_{45}H_{92}0_5Si_3Na$ $[M + Na]^+$ 819.6145, found 819.6192 for (*R*)-**15a**; calcd for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$ 923.5836, found 923.5790 for (*R*)-**15b**; calcd for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$ 1,027.5516, found 1,027.5504 for (*R*)-**15c**; calcd for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M+ Na]^+$ 1,131.5207, found 1,131.5256 for (*R*)-**15d;** fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 5.7 min ((*R*)-**15a**), 8.0 min ((*R*)-**15b**), 11.1 min ((*R*)-**15c**), 17.2 min ((*R*)-**15d**).



(4*S*,5*S*,7*R*,13*S*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-3-en-2-one, (4*S*,5*S*,7*S*,13*S*,*E*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl-(1,1,1,2,2-penta-fluorobutylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*R*,7*R*,13*S*,*E*)-13-Pentyl-4,5-bis-(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*R*,7*S*,13*S*,*E*)-13-Pentyl-4,5,7-tris(diisopropyl-(1,1,1,2,2-pentafluorobutyl-silyloxy)oxacyclotetradec-2-enone (M-(*S*)-15a-d): The same procedure for the ring-closing metathesis in the preparation of M-(*R*)-**15a-d** was repeated using mixture M-(*S*)-**14a-d** (615 mg, 628 μmol based on average molecular weight) and the 2nd generation Grubbs catalyst (107 mg, 126 μmol) in CH_2Cl_2 (210 mL). Two successive rounds of flash chromatography (40:1 hexanes/EtOAc) gave the title compound as a pale brown oil (564 mg, 576 μmol), which was directly subjected to the hydrogenation without further purification.

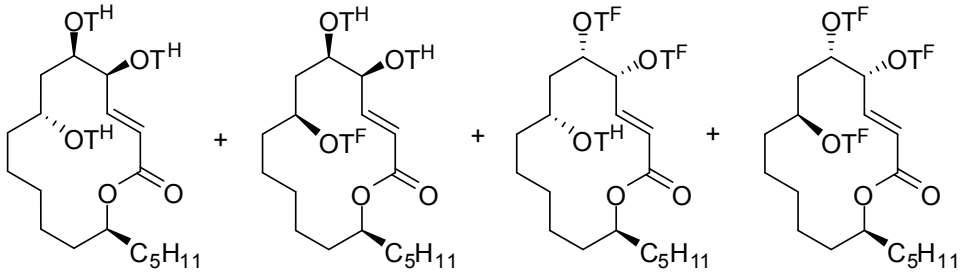
The ring-closed product (564 mg, 576 μmol) was hydrogenated by the same procedures reported for the preparation of M-(*R*)-**15a-d** (see above) using Pd/$SrCO_3$ (3.15 g, 593 μmol) in EtOH (20 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (524 mg, 87% over two steps, based on average molecular weight): LRMS (EI) (*S*)-**15a** *m/z* 797 $(M)^+$; (*S*)-**15b** *m/z* 901 $(M)^+$; (*S*)-**15c** *m/z* 1005 $(M)^+$; (*S*)-**15d** *m/z* 1109 $(M)^+$; HRMS (ESI, positive mode): calcd for $C_{45}H_{92}O_5Si_3Na$ $[M]^+$ 796.6253, found 796.6273 for (*S*)-**15a**; calcd for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$ 923.5836, found 923.5803 for (*S*)-**15b**; calcd for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$ 1,027.5516, found 1,027.5506 for (*S*)-**15c**; calcd for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M+ Na]^+$ 1,131.5207, found 1,131.5254 for (*S*)-**15d**; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 5.4 min (*S*)-**15a**, 8.5 min (*S*)-**15b**, 9.9 min (*S*)-**15c**, 17.3 min (*S*)-**15d**.



(4*S*,5*R*,7*R*,13*R*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-2-enone, (4*S*,5*R*,7*S*,13*R*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*S*,7*R*,13*R*)-13-Pentyl-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*S*,7*S*,13*R*)-13-Pentyl-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone M-(*R*)-15e-h): The procedure for the ring-closing metathesis as reported above for compound M-(*R*)-**15a-d** was repeated using mixture M-(*R*)-**14e-h** (577 mg, 589 μmol based on average molecular weight) and the 2nd generation Grubbs catalyst (103 mg, 118 μmol) in CH_2Cl_2 (200 mL). Two successive rounds of flash chromatography (40:1 hexanes/EtOAc) gave the title compound as a pale brown oil (541 mg, 569 μmol), which was taken directly to the next step without further purification.

The ring-closed product (528 mg, 555 μmol) was then directly subjected to the hydrogenation procedures as reported above for the preparation of compound M-(*R*)-**15a-d** using Pd/$SrCO_3$ (2.95 g, 555 μmol) in EtOH (27 mL). Flash chromatography of the crude product

(40:1 hexanes/EtOAc) gave the title compound as a colorless oil (463 mg, 84% over two steps, based on average molecular weight): LRMS (ESI, positive mode) (*R*)-**15e** *m/z* 820 $(M + Na)^+$; (*R*)-**15f** *m/z* 924 $(M + Na)^+$; (*R*)-**15g** *m/z* 1028 $(M + Na)^+$; (*R*)-**15h** *m/z* 1132 $(M + Na)^+$; HRMS (ESI, positive mode): calcd for $C_{45}H_{92}O_5Si_3Na$ $[M + Na]^+$ 819.6150, found 819.6223 for (*R*)-**15e**; calcd for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$ 923.5836, found 923.5826 for (*R*)-**15f**; calcd for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$ 1,027.5521, found 1,027.5491 for (*R*)-**15g**; calcd for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M+ Na]^+$ 1,131.5207, found 1,131.5283 for (*R*)-**15h**; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 15.0 min ((*R*)-**15e**), 18.0 min ((*R*)-**15f**), 22.8 min ((*R*)-**15g**), 28.4 min ((*R*)-**15e**).



(4*S*,5*R*,7*R*,13*R*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-3-en-2-one, (4*S*,5*R*,7*S*,13*R*,*E*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*S*,7*R*,13*R*,*E*)-13-Pentyl-4,5-bis(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone, (4*R*,5*S*,7*S*,13*R*,*E*)-13-Pentyl-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone (M-(*S*)-15e-h): The procedure for the ring-closing metathesis as reported above for the preparation of M-(*R*)-**15a-d** was repeated using mixture M-(*S*)-**14e-h** (607 mg, 620 μmol based on average molecular weight) and the 2nd generation Grubbs catalyst (109 mg, 124 μmol) in CH_2Cl_2 (200 mL). Two successive rounds of flash chromatography (40:1 hexanes/EtOAc) gave the ring-closed product as a pale brown oil (584 mg, 614 μmol), which was taken directly to the next step without further purification.

The ring-closed product (572 mg, 601 μmol) was hydrogenated using the same procedures as reported above for the preparation of M-(*R*)-**15a-d** using Pd/$SrCO_3$ (3.20 g, 601 μmol) in EtOH (30 mL). Flash chromatography of the crude product (40:1 hexanes/EtOAc) gave the title compound as a colorless oil (547 mg, 94% over two steps, based on average molecular weight): LRMS (ESI, positive mode) (*S*)-**15e** *m/z* 820 $(M + Na)^+$; (*S*)-**15f** *m/z* 924 $(M + Na)^+$; (*S*)-**15g** *m/z* 1028 $(M + Na)^+$; (*S*)-**15h** *m/z* 1132 $(M + Na)^+$; HRMS (ESI, positive mode):

calcd for $C_{45}H_{92}O_5Si_3$ $[M]^+$ 796.6253, found 796.6250 for (*S*)-**15e**; calcd for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$ 923.5836, found 923.5859 for (*S*)-**15f**; calcd for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$ 1,027.5521, found 1,027.5510 for (*S*)-**15g**; calcd for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M+ Na]^+$ 1,131.5207, found 1,131.5223 for (*S*)-**15h**; fluorous analytical HPLC (90:10 MeCN/H_2O for 10 min, then 100% MeCN for 60 min, 1.0 mL/min): t_R = 15.7 min ((*S*)-**15e**), 19.8 min ((*S*)-**15f**), 21.0 min ((*S*)-**15g**), 27.0 min ((*S*)-**15h)**.

Demixing of M-(*R*)-14a-d

Semi-preparative separation of M-(*R*)-**14a-d** was carried out on a Waters 600E HPLC system. The mixture M-(*R*)-**14a-d** of four compounds was dissolved in THF (4.5 mL) and filtered through a Whatman syringe filter (0.45 μm pore size) prior to injection. The separation was carried out on a FluoroFlash PF-C8 HPLC column (20 mm x 250 mm). The separation was achieved by gradient elution with 90:10 acetonitrile/water up to 100% acetonitrile in 15 minutes, followed by isocratic elution with 100% acetonitrile for 180 minutes with a constant flow rate of 10.0 mL/min. A UV detector (230 nm) was used to manually identify the peaks. Aliquots of M-(*R*)-**14a-d** (50 mg/mL) were injected per chromatographic run. The yield of the demixing over six injections was 93% and the following four compounds were isolated (see Figure S1 below): (*R*)-**14a**: 58.8 mg, t_R = 62.2 min; (*R*)-**14b**: 68.2 mg, t_R = 91.8 min; (*R*)-**14c**: 111.6 mg, t_R = 114.9 min; (*R*)-**14d**: 60.0 mg, t_R = 163.4 min.

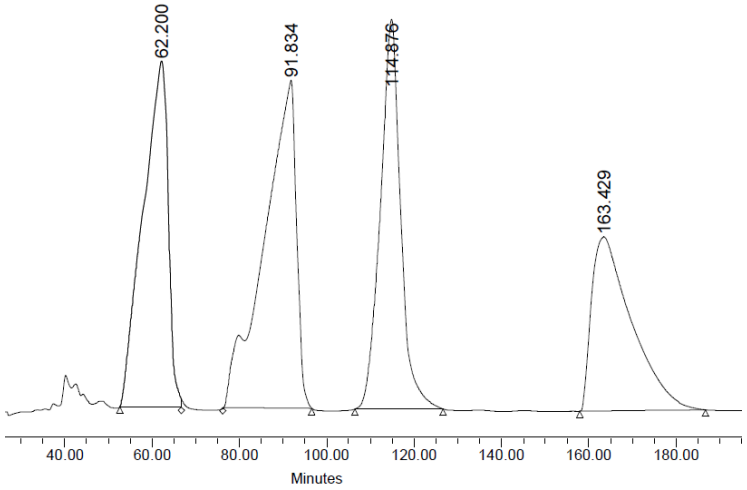
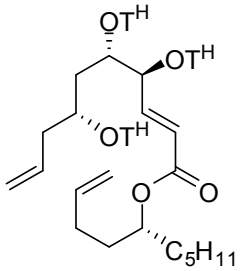
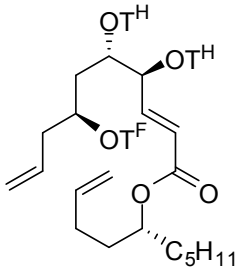


Figure S1: Fluorous semi-preparative HPLC demix trace of M-(*R*)-14a-d

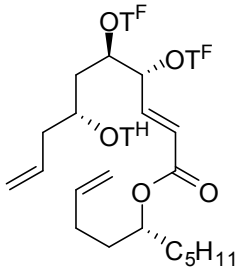


(4*S*,5*S*,7*R*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate ((*R*)-14a): From the demixing of M-(*R*)-**14a**, the first peak (*R*)-**14a** (58.8 mg) at 62.2 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J_1 = 15.8 Hz, J_2 = 4.0 Hz, 1H), 6.08 (dd, J_1 = 15.8 Hz, J_2 = 1.6 Hz, 1H), 5.93 (m, 1H), 5.80 (ddt, J_1 = 16.9 Hz, J_2 = 10.2 Hz, J_3 = 6.6

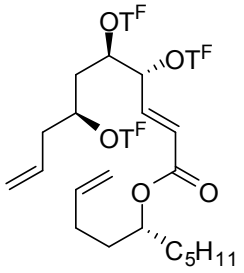
Hz, 1H), 5.01 (m, 5H), 4.58 (td, J_1 = 4.0 Hz, J_2 = 2.7 Hz, 1H), 4.20 (sextet, J = 4.0 Hz, 1H), 4.10 (m, 1H), 2.43 (m, 1H), 2.33 (ddd, J_1 = 12.9 Hz, J_2 = 8.0 Hz, J_3 = 4.4 Hz, 1H), 2.06 (m, 2H), 1.80 (ddd, J_1 = 13.5 Hz, J_2 = 8.1 Hz, J_3 = 4.9 Hz, 1H), 1.66 (m, 3H), 1.59 (2H), 1.29 (m, 6H), 1.07 (br s, 63 H), 0.88 (t, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 147.6, 138.0, 135.0, 122.5, 116.9, 114.8, 76.4, 73.7, 72.6, 68.3, 41.6, 41.2, 34.2, 33.4, 31.2, 29.7, 29.6, 25.0, 22.6, 18.3, 18.2, 18.1, 14.0, 12.8, 12.7, 12.4; FTIR (thin film) ν_{max} 2943, 2867, 1722, 1463, 1261, 1106, 1063, 994 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{47}H_{94}O_5Si_3$ $[M + Na]^+$: 845.6307, found 845.6340; $[\alpha]_D^{25^\circ C} = -24.1$, c = 1.10, $CHCl_3$.



(4*S*,5*S*,7*S*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)deca-2,9-dienoate ((*R*)-14b): From the demixing of M-(*R*)-**14a-d**, the second peak (*R*)-**14b** (68.2 mg) at 91.8 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, J_1 = 15.7 Hz, J_2 = 4.0 Hz, 1H), 6.08 (dd, J_1 = 15.7 Hz, J_2 = 1.7 Hz, 1H), 5.86 (m, 1H), 5.81 (ddt, J_1 = 16.9 Hz, J_2 = 10.3 Hz, J_3 = 6.6 Hz, 1H), 5.01 (m, 5H), 4.59 (td, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 1H), 4.07 (m, 1H), 4.02 (ddd, J_1 = 9.8 Hz, J_2 = 4.5 Hz, J_3 = 2.4 Hz, 1H), 2.38 (m, 1H), 2.09 (m, 5H), 1.89 (ddd, J_1 = 13.2 Hz, J_2 = 11.0 Hz, J_3 = 2.2 Hz, 1H), 1.66 (m, 2H), 1.50 (m, 3H), 1.28 (m, 6H), 1.10 (br s, 21H), 1.07 (br s, 21H), 1.02 (br s, 14H), 0.88 (t, J = 6.6 Hz, 3H), 0.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 147.2, 138.0, 134.8, 122.5, 117.3, 114.8, 74.2, 73.7, 73.1, 69.5, 40.9, 39.8, 34.1, 33.4, 31.8, 29.7, 29.6, 25.4, 24.9, 22.6, 18.2, 18.1, 17.7, 17.6, 14.0, 13.1, 12.9, 12.5, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −85.02 (s, 3F), −120.42 (t, $^3J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2946, 2869, 1721, 1465, 1267, 1107, 994 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{48}H_{91}O_5F_5Si_3$ $[M + Na]^+$: 949.5992, found 949.6046; $[\alpha]_D^{25^\circ C} = -41.0$, c = 1.28, $CHCl_3$.



(4*R*,5*R*,7*R*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy))-7-triisopropylsilyloxydeca-2,9-dienoate ((*R*)-14c): From the demixing of M-(*R*)-**14a-d**, the third peak (*R*)-**14c** (111.6 mg) at 114.9 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, J_1 = 15.8 Hz, J_2 = 4.9 Hz, 1H), 6.00 (dd, J_1 = 15.8 Hz, J_2 = 1.5 Hz, 1H), 5.90 (ddt, J_1 = 17.0 Hz, J_2 = 10.5 Hz, J_3 = 7.2 Hz, 1H), 5.80 (ddt, J_1 = 17.0 Hz, J_2 = 10.5 Hz, J_3 = 6.5 Hz 1H), 5.02 (m, 5H), 4.44 (m, 1H), 4.04 (m, 1H), 3.95 (dt, J_1 = 13.5 Hz, J_2 = 4.0 Hz, 1H), 2.37 (m, 1H), 2.20 (m, 1H), 2.05 (m, 6H), 1.88 (ddd, J_1 = 13.5 Hz, J_2 = 9.0 Hz, J_3 = 4.0 Hz, 1H), 1.67 (m, 2H), 1.54 (m, 3H), 1.28 (br s, 21H), 1.06 (br s, 28H), 0.88 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 146.2, 137.9, 134.3, 122.9, 117.3, 114.8, 74.4, 74.0, 73.3, 68.6, 41.1, 39.1, 34.1, 33.4, 31.7, 29.6, 25.7, 25.6, 25.4, 25.3, 25.1, 22.5, 17.7, 17.6, 17.5, 14.1, 14.0, 13.0, 12.8, 12.7, 12.6, 12.5, 1.6, 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) −84.93 (s, 3F), −85.01 (s, 3F), −120.44 (m, 4F); FTIR (thin film) ν_{max} 2946, 2869, 1723, 1201, 1108 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{49}H_{88}O_5F_{10}Si_3$ $[M + Na]^+$: 1,053.5678, found 1,053.5725; $[\alpha]_D^{25°C} = +22.4$, c = 1.11, $CHCl_3$.



(4*R*,5*R*,7*S*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-tris(diisopropyl(1,1,1,2,2-penta-fluorobutylsilyloxy)) deca-2,9-dienoate ((*R*)-14d): From the demixing of M-(*R*)-**14a-d**, the fourth peak (*R*)-**14d** (60.0 mg) at 163.4 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, J_1 = 15.8 Hz, J_2 = 4.5 Hz, 1H), 6.03 (dd, J_1 = 15.8 Hz, J_2 = 1.5 Hz, 1H), 5.79 (m, 2H), 5.02 (m, 5H), 4.45 (td, J_1 = 4.5 Hz, J_2 = 1.5 Hz, 1H), 4.05 (m, 1H), 4.01 (m, 1H), 2.32 (m, 2H), 2.04 (m, 8H), 1.70 (m, 3H), 1.57 (m, 3H), 1.28 (m, 6H), 1.04 (br s, 42H), 0.88 (m, 4H), 0.82 (m, 2H); ^{13}C

NMR (75 MHz, $CDCl_3$) δ 165.4, 145.9, 137.9, 133.9, 123.1, 117.8, 114.8, 75.9, 74.1, 72.7, 69.1, 41.8, 40.8, 34.0, 33.3, 31.7, 29.7, 29.6, 25.6, 25.5, 25.4, 25.3, 25.2, 25.0, 24.9, 22.5, 17.8, 17.7, 17.6, 17.5, 13.9, 13.1, 13.0, 12.9, 12.8, 12.6, 12.5, 1.3, 1.2, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −84.99 (s, 3F), −85.03 (s, 3F), −85.05 (s, 3F) −120.42 (m, 6F); FTIR (thin film) ν_{max} 2947, 2871, 1723, 1200, 1107, 1063, 993, 887 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{50}H_{85}O_5F_{15}Si_3$ $[M + Na]^+$: 1,157.5363, found 1,157.5360; $[\alpha]_D^{25^\circ C} = +18.6$, c = 1.11, $CHCl_3$.

Demixing of M-(*S*)-14a-d

The semi-preparative separation of the four-compound mixture M-(*S*)-**14a-d** was carried out in the same manner as M-(*R*)-**14a-d**. Aliquots of M-(*S*)-**14a-d** (50 mg/mL) were injected per chromatographic run. The yield of the demixing over six injections was 80% and the following four compounds were isolated (see Figure S2 below): (*S*)-**14a**: 83.0 mg, t_R = 37.8 min; (*S*)-**14b**: 92.4 mg, t_R = 54.9 min; (*S*)-**14c**: 90.4 mg, t_R = 68.1 min; (*S*)-**14d**: 105.7 mg, t_R = 91.5 min.

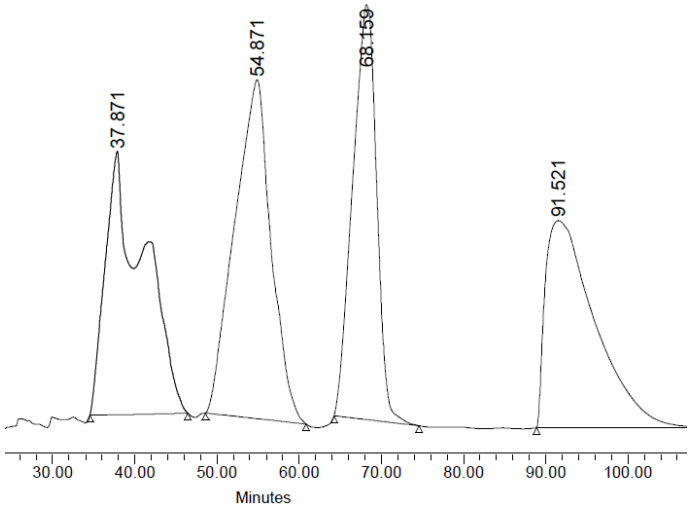
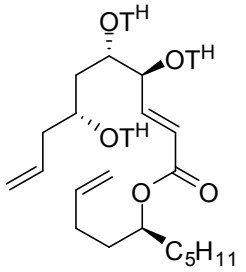
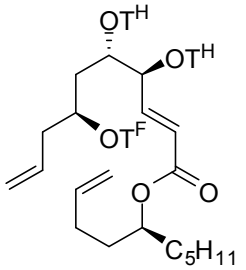


Figure S2: Fluorous semi-preparative HPLC demix trace of M-(*S*)-14a-d

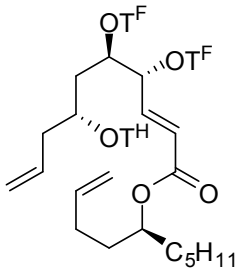


(4*S*,5*S*,7*R*,*E*)-((*S*)-Dec-1-en-5-yl) 4,5,7-tris(triisopropylsilyloxy)deca-2,9-dienoate ((*S*)-14a): From the demixing of M-(*S*)-**14a-d**, the first peak (*S*)-**14a** (83.0 mg) at 37.8 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 6.08 (dd, J_1 = 16.0 Hz, J_2 = 1.5 Hz, 1H), 5.94 (m, 1H), 5.81 (ddt, J_1 = 17.0 Hz, J_2 = 10.0 Hz, J_3 = 6.5 Hz, 1H), 5.01 (m, 5H), 4.58 (m, 1H), 4.20 (m, 1H), 4.10 (m, 1H), 2.43 (m, 1H), 2.34 (ddd, J_1 = 13.0 Hz, J_2 = 8.5 Hz, J_3 = 4.5 Hz, 1H), 2.09 (m, 2H), 1.80 (ddd, J_1 = 13.5 Hz, J_2 = 8.o Hz, J_3 = 5.0 Hz, 1H), 1.68 (m, 3H), 1.57 (m, 2H), 1.29 (m, 6H), 1.10 (br s, 42 H), 1.05 (br s, 21H), 0.88 (t, J = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 147.6, 138.0, 135.0, 122.5, 116.9, 114.8, 76.4, 73.7, 72.6, 68.3, 41.6, 41.2, 34.0, 33.4, 31.8, 29.7, 24.9, 22.6, 18.3, 18.2, 18.1, 14.0, 12.8,

12.7, 12.4; FTIR (thin film) ν_{max} 2946, 2868, 1722, 1465, 1262, 1201, 1111, 1064, 995 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{47}H_{94}O_5Si_3$ $[M + Na]^+$: 845.6307, found 845.6323; $[\alpha]_D^{25°C} = -22.8$, c = 1.07, $CHCl_3$.

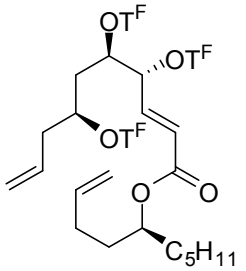


(4*S*,5*S*,7*S*,*E*)-((*S*)-Dec-1-en-5-yl)-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)deca-2,9-dienoate ((*S*)-14b): From the demixing of M-(*S*)-**14a-d**, the second peak (*S*)-**14b** (92.4 mg) at 54.9 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (dd, J_1 = 16.0 Hz, J_2 = 4.0 Hz, 1H), 6.08 (dd, J_1 = 16.0 Hz, J_2 = 1.5 Hz, 1H), 5.86 (m, 1H), 5.80 (ddt, J_1 = 17.0 Hz, J_2 = 10.0 Hz, J_3 = 6.5 Hz, 1H), 5.01 (m, 5H), 4.59 (m, 1H), 4.08 (m, 1H), 4.03 (m, 1H), 2.38 (m, 1H), 2.09 (m, 5H), 1.89 (ddd, J_1 = 13.0 Hz, J_2 = 10.5 Hz, J_3 = 2.0 Hz, 1H), 1.67 (m, 2H), 1.52 (m, 3H), 1.29 (m, 6H), 1.10 (br s, 21H), 1.07 (br s, 21H), 1.02 (br s, 14H), 0.88 (t, J = 6.5 Hz, 3H), 0.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 147.2, 138.0, 134.8, 122.5, 117.3, 114.7, 74.3, 73.7, 73.1, 69.5, 40.9, 39.8, 34.1, 33.4, 31.7, 29.7, 25.7, 25.4, 24.9, 22.6, 18.2, 18.1, 17.7, 17.6, 14.0, 13.1, 12.9, 12.5, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −85.03 (s, 3F), −120.43 (t, $^3J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2946, 2869, 1722, 1465, 1267, 1107, 994 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{48}H_{91}O_5F_5Si_3$ $[M + Na]^+$: 949.5992, found 949.6074; $[\alpha]_D^{25°C} = -46.4$, c = 1.08, $CHCl_3$.



(4*R*,5*R*,7*R*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5-bis(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy))-7-triisopropylsilyloxydeca-2,9-dienoate ((*S*)-14c): From the demixing of M-(*S*)-**14a-d**, the third peak (*S*)-**14c** (90.4 mg) at 68.1 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz,

$CDCl_3$) δ 7.05 (dd, J_1 = 16.0 Hz, J_2 = 5.0 Hz, 1H), 6.00 (dd, J_1 = 16.0 Hz, J_2 = 1.5 Hz, 1H), 5.90 (ddt, J_1 = 17.0 Hz, J_2 = 10.5 Hz, J_3 = 7.0 Hz, 1H), 5.80 (ddt, J_1 = 17.0 Hz, J_2 = 10.5 Hz, J_3 = 6.5 Hz 1H), 5.02 (m, 5H), 4.44 (t, J = 3.5 Hz, 1H), 4.04 (sextet, J = 4.5 Hz, 1H), 3.95 (m, 1H), 2.38 (m, 1H), 2.21 (m, 1H), 2.05 (m, 6H), 1.88 (ddd, J_1 = 13.5 Hz, J_2 = 9.0 Hz, J_3 = 4.0 Hz, 1H), 1.66 (m, 2H), 1.55 (m, 3H), 1.33 (m, 6H), 1.06 (br s, 49H), 0.88 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 146.2, 137.9, 134.3, 122.9, 117.3, 114.8, 74.3, 74.0, 73.3, 68.6, 41.0, 39.1, 34.1, 33.4, 31.7, 29.6, 25.7, 25.6, 25.4, 25.3, 25.1, 24.9, 22.5, 17.6, 17.5, 14.0, 13.0, 12.7, 12.6, 1.6, 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) −84.95 (s, 3F), −85.02 (s, 3F), −120.42 (t, $^3J_{HF}$ = 17.0 Hz, 2F), −120.48 (t, $^3J_{HF}$ = 17.0 Hz, 2F); FTIR (thin film) ν_{max} 2947, 2870, 1723, 1466, 1266, 1201, 1107, 1065, 994, 885 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{49}H_{88}O_5F_{10}Si_3$ $[M + Na]^+$: 1,053.5678, found 1,053.5664; $[\alpha]_D^{25°C} = +22.9$, c = 1.08, $CHCl_3$.



(4*R*,5*R*,7*S*,*E*)-((*S*)-Dec-1-en-5-yl)-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)) deca-2,9-dienoate ((*S*)-14d): From the demixing of M-(*S*)-**14a-d**, the fourth peak (*S*)-**14d** (105.7 mg) at 91.5 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (dd, J_1 = 16.0 Hz, J_2 = 4.5 Hz, 1H), 6.03 (dd, J_1 = 16.0 Hz, J_2 = 1.5 Hz, 1H), 5.79 (m, 2H), 5.02 (m, 5H), 4.45 (m, 1H), 4.05 (m, 1H), 4.01 (m, 1H), 2.32 (m, 2H), 2.04 (m, 8H), 1.70 (m, 3H), 1.57 (m, 3H), 1.28 (m, 6H), 1.04 (br s, 42H), 0.88 (m, 4H), 0.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 145.9, 137.9, 133.9, 123.1, 117.8, 114.8, 75.9, 74.1, 72.7, 69.1, 41.8, 40.8, 34.1, 33.3, 31.7, 29.6, 25.7, 25.6, 25.4, 25.3, 25.2, 25.1, 25.0, 24.9, 22.5, 17.8, 17.7, 17.6, 17.5, 14.0, 13.1, 13.0, 12.9, 12.8, 12.6, 12.5, 1.3, 1.2, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −84.99 (s, 3F), −85.03 (s, 3F), −85.05 (s, 3F), −120.40 (t, $^3J_{HF}$ = 18.0 Hz, 2F), −120.47 (t, $^3J_{HF}$ = 18.0 Hz, 2F), −120.48 (t, $^3J_{HF}$ = 18.0 Hz, 2F); FTIR (thin film) ν_{max} 2949, 2870, 1723, 1200, 1107, 1065, 993, 886 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{50}H_{85}O_5F_{15}Si_3$ $[M + Na]^+$: 1,157.5363, found 1,157.5306; $[\alpha]_D^{25°C} = +18.7$, c = 1.12, $CHCl_3$.

Demixing of M-(*R*)-15a-d

The semi-preparative separation of M-(*R*)-**15a-d** was carried out in the same manner as M-(*R*)-**14a-d**. Aliquots of M-(*R*)-**15a-d** (90 mg/mL) were injected per chromatographic run. The yield of the demixing over six injections was 48% and the following four compounds were isolated (see Figure S3 below): (*R*)-**15a**: 82.4 mg, t_R = 34.7 min; ((*R*)-**15b**: 80.5 mg, t_R = 49.7 min; ((*R*)-**15c**: 66.8 mg, t_R = 64.7 min; ((*R*)-**15d**: 52.3 mg, t_R = 87.0 min

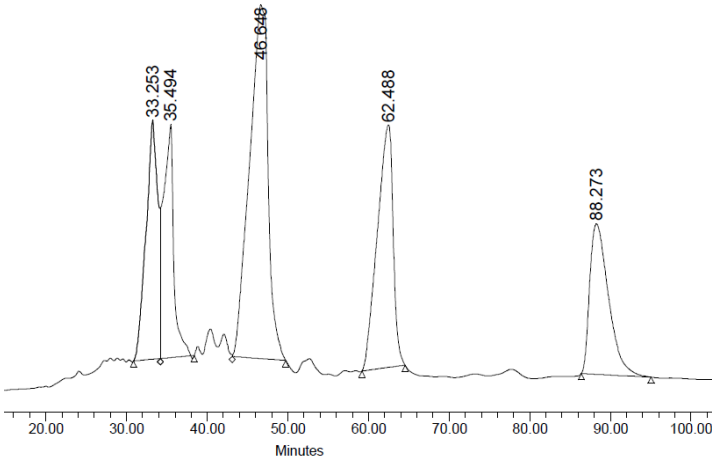
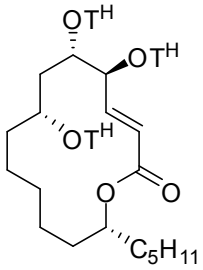
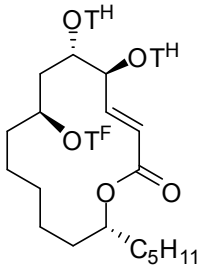


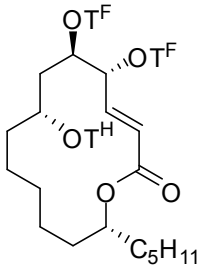
Figure S1: Fluorous semi-preparative HPLC demix trace of M-(*R*)-15a-d



(4*S*,5*S*,7*R*,13*R*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-2-en-one ((*R*)-15a): From the demixing of M-(*R*)-**15a-d**, the first peak (*R*)-**15a** (82.4 mg) at 34.7 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 6.11 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 5.04 (m, 1H), 4.65 (t, J = 2.5 Hz, 1H), 4.32 (quintet, J = 5.0 Hz, 1H), 4.14 (m, 1H), 2.08 (m, 1H), 1.86 (m, 1H), 1.64 (m, 5H), 1.50 (m, 3H), 1.37 (m, 4H), 1.30 (m, 6H), 1.10 (br s, 63H), 0.89 (t, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 149.0, 122.6, 74.9, 74.5, 73.1, 69.4, 37.0, 35.3, 33.5, 33.1, 31.8, 30.3, 25.3, 23.3, 22.6, 21.1, 18.3, 18.2, 18.1, 14.0, 13.1, 12.5; FTIR (thin film) ν_{max} 2943, 2867, 1718, 1463, 1255, 1200, 1106, 1059, 996, 883 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{45}H_{92}O_5Si_3Na$ $[M + Na]^+$: 819.6145, found 819.6192; $[\alpha]_D^{25^\circ C} = -34.6$, c = 0.76, $CHCl_3$.

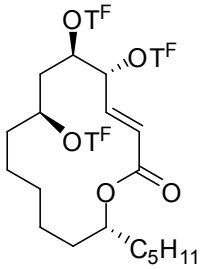


(4*S*,5*S*,7*S*,13*R*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone ((*R*)-15b): From the demixing of M-(*R*)-**15a-d**, the second peak (*R*)-**15b** (80.5 mg) at 49.7 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 6.11 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 4.99 (m, 1H), 4.62 (m, 1H), 4.25 (quintet, J = 3.0 Hz, 1H), 3.96 (m, 1H), 2.18 (dt, J_1 = 14.5 Hz, J_2 = 3.0 Hz, 1H), 2.05 (m, 3H), 1.69 (m, 3H), 1.51 (m, 5H), 1.31 (br s, 10H), 1.11 (br s, 42H), 1.03 (br s, 14H), 0.89 (t, J = 6.5 Hz, 3H), 0.78 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 148.7, 120.9, 74.1, 73.9, 73.3, 71.0, 40.7, 35.6, 32.5, 31.8, 30.0, 25.7, 25.4, 23.4, 22.5, 19.8, 18.2, 18.1, 18.0, 17.9, 17.8, 14.0, 12.9, 12.7, 12.5, 12.4, 1.6; ^{19}F NMR (282 MHz, $CDCl_3$) −84.98 (s, 3F), −120.08 (t, $^{3}J_{HF}$ = 18.0 Hz, 2F); FTIR (thin film) ν_{max} 2944, 2868, 1717, 1463, 1258, 1199, 1106, 1056, 1014, 995, 883 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$: 923.5836, found 923.5790; $[\alpha]_D^{25^\circ C} = -21.4$, c = 0.89, $CHCl_3$.



(4*R*,5*R*,7*R*,13*R*)-13-Pentyl-4,5-bis(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone ((*R*)-15c): From the demixing of M-(*R*)-**15a-d**, the third peak (*R*)-**15c** (66.8 mg) at 64.7 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (dd, J_1 = 16.0 Hz, J_2 = 6.5 Hz, 1H), 5.95 (d, J = 16.0 Hz, 1H), 5.02 (m, 1H), 4.44 (t, J = 5.3 Hz, 1H), 4.14 (m, 1H), 4.05 (quintet, J = 3.0 Hz, 1H), 2.05 (m, 4H), 1.79 (m, 2H), 1.72 (m, 1H), 1.64 (m, 1H), 1.56 (m, 5H), 1.27 (m, 11H), 1.06 (br s, 49H), 0.88 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 146.7, 123.7, 77.2, 75.9, 73.9, 69.9, 42.1, 37.3, 33.8, 31.7, 31.0, 28.4, 25.4, 25.3, 25.2, 24.1, 22.5, 18.3, 17.7, 17.6, 17.5, 14.0, 13.0, 12.7, 12.6, 12.5, 0.9, 0.8; ^{19}F NMR

(282 MHz, $CDCl_3$) −84.91 (s, 3F), −84.93 (s, 3F), −120.19 (t, $^3J_{HF}$ = 17.5 Hz, 2F), −120.29 (t, $^3J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2944, 2867, 1721, 1199, 1104, 1065 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$: 1,027.5516, found 1,027.5504; $[\alpha]_D^{25°C}$ = +2.04, c = 0.90, $CHCl_3$.



(4*R*,5*R*,7*S*,13*R*)-13-Pentyl-4,5,7-tris(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)oxa-cyclotetradec-2-enone ((*R*)-15d): From the demixing of M-(*R*)-**15a-d**, the fourth peak (*R*)-**15d** (52.3 mg) at 87.0 minutes was isolated as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86 (dd, J_1 = 16.0 Hz, J_2 = 5.5 Hz, 1H), 6.06 (d, J = 16.0 Hz, 1H), 4.99 (m, 1H), 4.41 (t, J = 10.0 Hz, 1H), 4.08 (dt, J_1 = 10.0 Hz, J_2 = 7.5 Hz 1H), 3.85 (m, 1H), 2.05 (m, 6H), 1.71 (m, 2H), 1.61 (m, 3H), 1.54 (m, 3H), 1.46 (m, 1H), 1.33 (m, 11H), 1.20 (m, 2H), 1.05 (br s, 42H), 0.89 (7H), 0.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 145.8, 124.3, 75.6, 74.9, 72.7, 69.7, 38.9, 36.6, 34.6, 32.5, 31.7, 29.4, 25.5, 25.3, 25.1, 25.0, 24.6, 23.1, 22.5, 17.7, 17.6, 17.4, 14.0, 13.2, 13.0, 12.8, 12.6, 1.4, 1.3, 0.8; ^{19}F NMR (282 MHz, $CDCl_3$) −84.93 (s, 3F), −84.95 (s, 3F), −84.98 (s, 3F), −120.09 (t, $^3J_{HF}$ = 17.5 Hz, 2F), −120.24 (t, $^3J_{HF}$ = 17.5 Hz, 2F), −120.39 (t, $^3J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2930, 2360, 2340, 1610, 1465, 1195, 1023 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M + Na]^+$: 1,131.5207, found 1,131.5256; $[\alpha]_D^{25°C}$ = +16.1 c = 1.30, $CHCl_3$.

Demixing of M-(*S*)-15a-d

The semi-preparative separation of M-(*S*)-**15a-d** was carried out in the same manner as M-(*R*)-**15a-d**. Aliquots of M-(*S*)-**15a-d** (90 mg/mL) were injected per chromatographic run. The yield of the demixing over six injections was 60% and the following four compounds were isolated (see Figure S4 below): (*S*)-**15a**: 89.1 mg, t_R = 50.3 min; (*S*)-**15b**: 69.6 mg, t_R = 85.5 min; (*S*)-**15c**: 69.9 mg, t_R = 99.8 min; (*S*)-**15d**: 87.4 mg, t_R = 161.7 min.

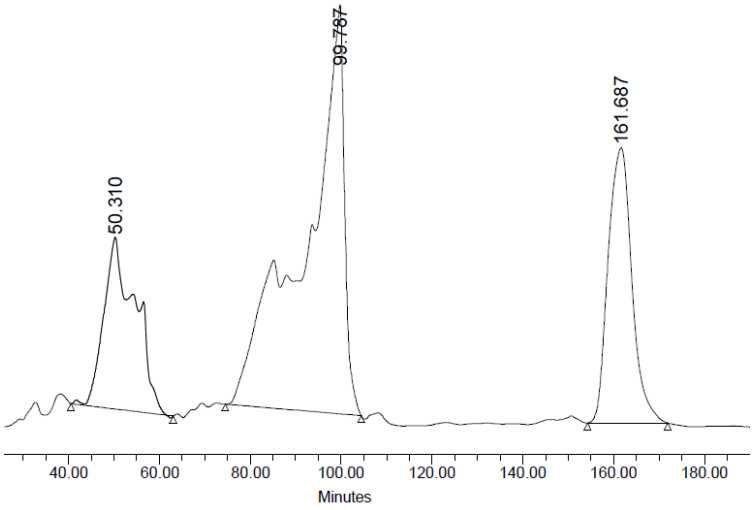
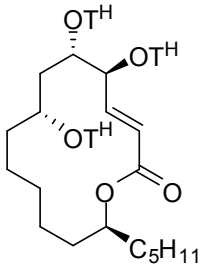
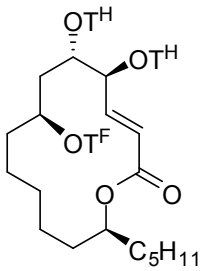


Figure S4: Fluorous semi-preparative HPLC demix trace of M-(*S*)-15a-d

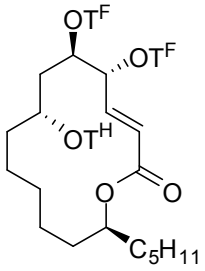


(4*S*,5*S*,7*R*,13*S*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-2-enone ((*S*)-15a): From the demixing of (*S*)-**15a-d**, the first peak (*S*)-**15a** (89.1 mg) at 50.3 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (dd, J_1 = 16.0 Hz, J_2 = 4.5 Hz, 1H), 6.10 (d, J = 16.0 Hz, 1H), 5.00 (m, 1H), 4.58 (t, J = 4.5 Hz, 1H), 4.30 (dt, J_1 = 9.0 Hz, J_2 = 4.5 Hz, 1H), 4.02 (m, 1H), 2.07 (m, 1H), 1.81 (m, 1H), 1.65 (m, 3H), 1.56 (m, 2H), 1.44 (m, 1H), 1.32 (m, 6H), 1.26 (m, 6H), 1.07 (br s, 63H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 147.7, 123.5, 75.3, 74.5, 72.7, 69.3, 37.3, 37.2, 34.7, 32.7, 31.8, 29.7, 25.1, 24.9, 22.6, 22.4, 18.3, 18.1, 14.0, 13.0, 12.9, 12.3; FTIR (thin film) ν_{max} 2942, 2866, 1722, 1462,

1261, 1106, 1063, 1016 cm^{-1}; HRMS calcd (EI) for $C_{45}H_{92}O_5Si_3$ $[M]^+$: 796.6253, found 796.6273; $[\alpha]_D^{25°C} = -30.4$, c = 1.12, $CHCl_3$.

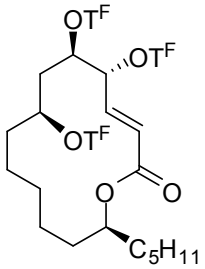


(4*S*,5*S*,7*S*,13*S*)-13-Pentyl-4,5-bis-(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-penta-fluoro-butylsilyloxy)oxacyclotetradec-2-enone ((*S*)-15b): From the demixing of M-(*S*)-**15a-d**, the second peak (*S*)-**15b** (69.6 mg) at 85.5 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.88 (dd, J_1 = 16.0 Hz, J_2 = 6.5 Hz, 1H), 5.98 (d, J = 16.0 Hz, 1H), 4.98 (m, 1H), 4.57 (t, J = 6.5 Hz, 1H), 4.22 (m, 1H), 4.08 (t, J = 6.5 Hz, 1H), 2.08 (septet, J = 9.0 Hz, 2H), 1.94 (m, 1H), 1.79 (quintet, J = 7.0 Hz, 3H), 1.65 (m, 4H), 1.53 (m, 4H), 1.40 (m, 2H), 1.30 (br s, 6H), 1.20 (m, 2H), 1.08 (br s, 56H), 0.89 (t, J = 6.5 Hz, 3H), 0.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 148.0, 123.3, 76.3, 75.5, 73.3, 71.5, 41.9, 37.1, 34.2, 31.7, 31.0, 29.7, 28.0, 25.0, 24.3, 23.9, 22.6, 18.2, 18.1, 18.0, 17.9, 17.8, 14.0, 13.4, 13.1, 12.4, 12.3, 1.5; ^{19}F NMR (282 MHz, $CDCl_3$) −84.95 (s, 3F), −120.26 (t, $^3J_{HF}$ = 18.0 Hz, 2F); FTIR (thin film) ν_{max} 2943, 2867, 1722, 1463, 1261, 1200, 1103, 1065, 996, 884 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$: 923.5836, found 923.5803; $[\alpha]_D^{25°C} = -1.15$, c = 1.08, $CHCl_3$.



(4*R*,5*R*,7*R*,13*S*)-13-Pentyl-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutyl-silyloxy)-7-triiso-propylsilyloxy)oxacyclotetradec-2-enone ((*S*)-15c): From the demixing of M-(*S*)-**15a-d**, the third peak (*S*)-**15c** (69.9 mg) at 99.8 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz,

$CDCl_3$) δ 7.31 (dd, J_1 = 16.0 Hz, J_2 = 2.5 Hz, 1H), 6.06 (dd, J_1 = 16.0 Hz, J_2 = 2.5 Hz, 1H), 4.97 (m, 1H), 4.46 (m, 1H), 4.11 (m, 1H), 3.93 (m, 1H), 2.08 (m, 6H), 1.94 (m, 1H), 1.66 (m, 4H), 1.53 (m, 5H), 1.31 (br s, 8H), 1.08 (br s, 28H), 1.04 (br s, 21H), 0.90 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.3, 147.1, 121.6, 74.5, 74.3, 73.7, 70.1, 40.9, 37.1, 34.2, 32.8, 31.8, 31.0, 30.3, 29.7, 28.0, 26.9, 25.4, 25.3, 25.2, 25.0, 24.3, 23.9, 23.6, 22.6, 22.5, 20.6, 18.3, 18.2, 17.5, 14.0, 13.4, 13.1, 12.9, 12.6, 12.4, 12.3, 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) −84.85 (s, 3F), −84.99 (s, 3F), −120.31 (t, $^3J_{HF}$ = 17.5 Hz, 2F), −120.48 (t, $^3J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2944, 2868, 1719, 1463, 1260, 1199, 1106, 1054, 995, 884 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$: 1,027.5521, found 1,027.5506; $\left[\alpha\right]_D^{25^\circ C} = +2.04$, c = 0.90, $CHCl_3$.



(4*R*,5*R*,7*S*,13*S*)-13-Pentyl-4,5,7-tris(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)oxa-cyclotetradec-2-enone ((*S*)-15d): From the demixing of M-(*S*)-**15a-d**, the fourth peak (*S*)-**15d** (87.4 mg) at 161.7 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (dd, J_1 = 16.0 Hz, J_2 = 2.5 Hz, 1H), 6.06 (dd, J_1 = 16.0 Hz, J_2 = 2.0 Hz, 1H), 5.04 (m, 1H), 4.50 (t, J = 2.5 Hz, 1H), 4.14 (quintet, J = 5.0 Hz, 1H), 4.00 (m, 1H), 2.05 (m, 6H), 1.85 (m, 1H), 1.68 (m, 1H), 1.62 (m, 1H), 1.57 (m, 2H), 1.50 (m, 4H), 1.31 (m, 5H), 1.26 (br s, 6H), 1.10 (br s, 14H), 1.1.06 (br s, 14H), 1.01 (br s, 14H), 0.89 (7H), 0.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 147.0, 75.3, 74.5, 72.9, 69.8, 37.1, 35.8, 33.7, 32.9, 31.8, 30.4, 30.2, 29.7, 25.7, 25.6, 25.4, 25.2, 25.1, 24.9, 23.6, 22.7, 22.5, 21.7, 17.6, 17.5, 17.4, 14.1, 14.0, 13.0, 12.9, 12.8, 12.7, 12.6, 1.5, 0.8, 0.7; ^{19}F NMR (282 MHz, $CDCl_3$) −84.90 (s, 3F), −84.95 (s, 3F), −84.96 (s, 3F), −120.32 (t, $^3J_{HF}$ = 17.5 Hz, 2F), −120.38 (t, $^3J_{HF}$ = 17.5 Hz, 2F), −120.48 (t, $^3J_{HF}$ = 17.5 Hz, 2F); FTIR (thin film) ν_{max} 2944, 2869, 1719, 1199, 1106, 1051, 996 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M + Na]^+$: 1,131.5207, found 1,131.5254; $\left[\alpha\right]_D^{25^\circ C} = +16.1$, c = 1.30, $CHCl_3$.

Demixing of M-(*R*)-15e-h

The semi-preparative separation of M-(*R*)-**15e-h** was carried out in the same manner as M-(*R*)-**15a-d**. Aliquots of M-(*R*)-**15e-h** (90 mg/mL) were injected per chromatographic run. The yield of the demixing over five injections was 69% and the following four compounds were isolated (see Figure S5 below): (*R*)-**15e**: 59.2 mg, t_R = 29.2 min; (*R*)-**15f**: 94.1 mg, t_R = 39.4 min; (*R*)-**15g**: 114 mg, t_R = 58.9 min; (*R*)-**15h**: 41.5 mg, t_R = 78.4 min.

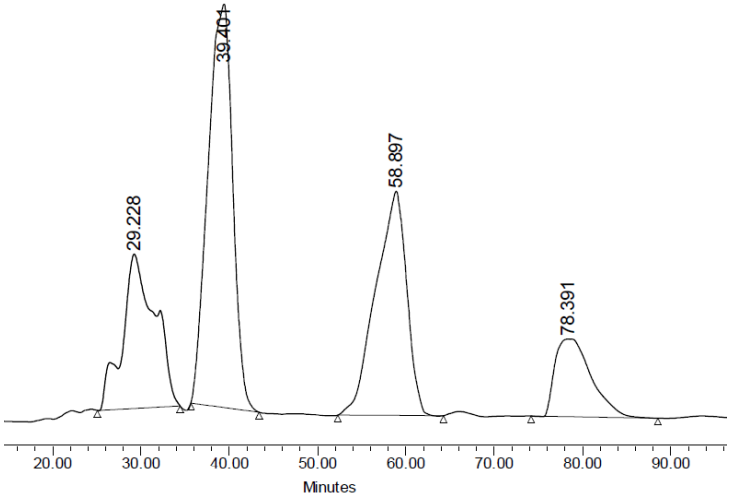
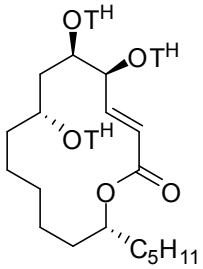
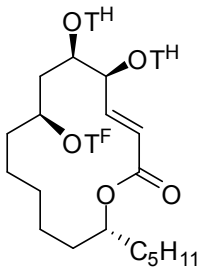


Figure S5: Fluorous semi-preparative HPLC demix trace of M-(R)-15e-h

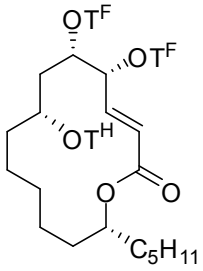


(4*S*,5*R*,7*R*,13*R*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-2-en-one ((*R*)-15e): From the demixing of M-(*R*)-M-**15e-h**, the first peak (*R*)-**15e** (59.2 mg) at 29.2 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (dd, J_1 = 15.8 Hz, J_2 = 3.0 Hz, 1H), 6.00 (d, J = 15.8 Hz, 1H), 4.98 (m, 1H), 4.24 (m, 1H), 3.91 (d, J = 9.0 Hz, 1H), 3.73 (d, J = 9.0 Hz, 1H), 2.36 (td, J_1 = 12.6 Hz, J_2 = 8.4 Hz, 1H), 2.05 (t, J = 12.1 Hz, 1H), 1.95 (m, 1H), 1.89 (m, 1H), 1.78-1.58 (m, 5H), 1.57-1.43 (m, 5H), 1.40-1.22 (m, 6H), 1.10 (br s, 63H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 148.5, 128.4, 77.3, 74.5, 72.3, 68.7, 36.8, 34.6, 32.5, 32.3, 32.1, 31.8, 31.6, 30.6, 30.3, 22.6 (br s), 18.4 (br s), 14.1; FTIR (thin film) ν_{max}

2944, 2867, 1731, 1464, 1255, 1200, 1106, 1059, 998, 883 cm^{-1}; HRMS calcd (ESI) for $C_{45}H_{92}O_5Si_3Na$ $[M + Na]^+$: 819.6150, found 819.6223; $[\alpha]_D^{25°C} = -1.36$, c = 1.26, $CHCl_3$.

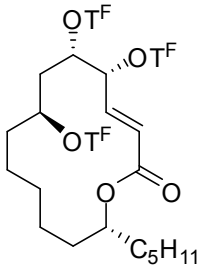


(4*S*,5*R*,7*S*,13*R*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone ((*R*)-15f): From the demixing of M-(*R*)-**15e-h**, the second peak (*R*)-**15f** (94.1 mg) at 39.4 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (dd, J_1 = 15.8 Hz, J_2 = 2.9 Hz, 1H), 6.07 (dd, J_1 = 15.8 Hz, J_2 = 2.2 Hz, 1H), 4.96 (m, 1H), 4.77 (m, 1H), 3.95 (d, J = 9.0 Hz, 1H), 3.64 (td, J_1 = 10.3 Hz, J_2 = 6.6 Hz, 1H), 2.45 (td, J_1 = 12.8 Hz, J_2 = 4.1 Hz, 1H), 2.05 (m, 2H), 1.70 (m, 2H), 1.62-1.45 (m, 8H), 1.40-1.25 (m, 6H), 1.20 (m, 3H), 1.10 (br s, 42H), 1.07 (br s, 14H), 0.89 (t, J = 6.8 Hz, 3H), 0.83 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 148.4, 121.6, 77.0, 74.3, 73.7, 69.5, 42.4, 34.0, 33.4, 32.7, 32.3, 32.2, 31.7, 30.3, 29.9, 25.4, 23.1, 22.6, 20.0, 18.3, 17.8, 1.5; ^{19}F NMR (282 MHz, $CDCl_3$) −84.99 (s, 3F), −120.26 (t, $^3J_{HF}$ = 18.0 Hz, 2F); FTIR (thin film) ν_{max} 2945, 2868, 1720, 1464, 1257, 1120, 1054, 992, 884 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$: 923.5836, found 923.5826; $[\alpha]_D^{25°C} = -12.7$, c = 1.37, $CHCl_3$.



(4*R*,5*S*,7*R*,13*R*)-13-Pentyl-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone ((*R*)-15g): From the demixing of M-(*R*)-**15e-h**, the third peak (*R*)-**15g** (114.0 mg) at 58.9 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.68 (dd, J_1 = 15.9 Hz, J_2 = 8.7 Hz, 1H), 5.86 (d, J = 15.9 Hz, 1H), 4.91 (m, 1H), 4.54 (d, J = 8.6 Hz, 1H), 3.92 (td, J_1 = 10.2 Hz, J_2 = 2.0 Hz, 1H), 3.74 (d, J = 8.6 Hz, 1H), 2.05 (m, 4H), 1.72-1.60 (m, 4H), 1.60-1.48 (m, 4H), 1.41 (m, 2H), 1.30 (br s, 6H), 1.08 (br s, 49

H), 0.88 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.7, 147.2, 122.7, 76.2, 75.5, 69.7, 69.5, 42.8, 42.2, 36.1, 35.1, 34.7, 34.5, 33.4, 32.0, 30.3, 27.2, 25.6, 22.5, 18.3, 14.0, 13.4, 13.0, 12.8, 1.5, 0.9; ^{19}F NMR (282 MHz, $CDCl_3$) −85.00 (s, 3F), −85.03 (s, 3F), −120.19 (m, 4F); FTIR (thin film) ν_{max} 2946, 2869, 1723, 1465, 1200, 1106, 1051, 993, 885 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$: 1,027.5521, found 1,027.5491; $[\alpha]_D^{25°C} = +15.6$, c = 1.17, $CHCl_3$.



(4*R*,5*S*,7*S*,13*R*)-13-Pentyl-4,5,7-tris(diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone ((*R*)-15h): From the demixing of M-(*R*)-**15e-h**, the fourth peak (*R*)-**15h** (41.5 mg) at 78.4 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (dd, J_1 = 16.0 Hz, J_2 = 7.9 Hz, 1H), 5.88 (d, J = 16.0 Hz, 1H), 4.92 (m, 1H), 4.47 (d, J = 7.9 Hz, 1H), 3.97 (m, 1H), 3.54 (m, 1H), 2.05 (m, 6H), 1.72-1.58 (m, 8H), 1.58-1.43 (m, 4H), 1.30 (m, 6H), 1.18 (m, 2H), 1.07 (br s, 42H), 0.88 (9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 147.8, 122.7, 76.2, 76.0, 75.7, 69.2, 35.1, 34.8, 34.2, 31.7, 28.2, 24.8 (m), 22.5, 17.7, 13.2, 12.8, 1.5, 0.8, 0.7; ^{19}F NMR (282 MHz, $CDCl_3$) −85.01 (s, 3F), −85.04 (s, 3F), −85.09 (s, 3F), −120.45 (m, 6F); FTIR (thin film) ν_{max} 2947, 2870, 1724, 1465, 1200, 1105, 1052, 993, 886, 750 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M + Na]^+$: 1,131.5207, found 1,131.5283; $[\alpha]_D^{25°C} = +8.88$, c = 1.08, $CHCl_3$.

Demixing of M-(*S*)-15e-h

The semi-preparative separation of M-(*S*)-**15e-h** was carried out in the same manner as M-(*R*)-**15a-d**. Aliquots of M-(*S*)-**15e-h** (50 mg/mL) were injected per chromatographic run. The yield of the demixing over ten injections was 56% and the following four compounds were isolated (see Figure S6 below): (*S*)-**15e**: 73.4 mg, t_R = 30.2 min; (*S*)-**15f**: 52.0 mg, t_R = 42.8 min; (*S*)-**15g**: 60.3 mg, t_R = 42.1 min; (*S*)-**15h**: 65.8 mg, t_R = 70.9 min. Four additional injections were needed for compound (*S*)-**15g** to improve its isomeric purity.

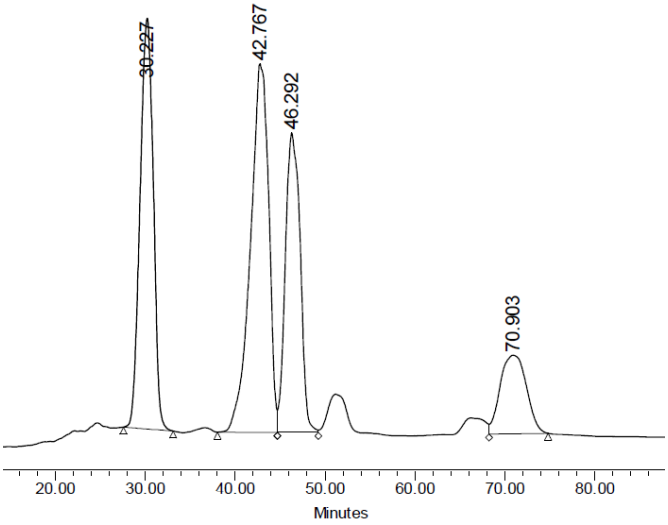
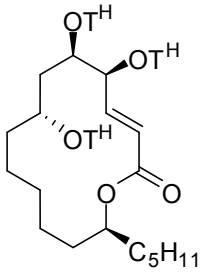
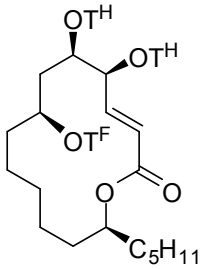


Figure S6: Fluorous semi-preparative HPLC demix trace of M-(*S*)-15e-h

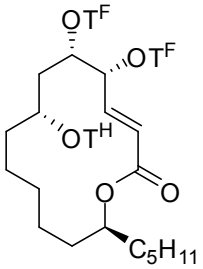


(4*S*,5*R*,7*R*,13*S*,*E*)-14-Pentyl-5,6,8-tris(triisopropylsilyloxy)oxacyclotetradec-2-enone ((*S*)-15e): From the demixing of M-(*S*)-**15e-h**, the first peak (*S*)-**15e** (73.4 mg) at 30.2 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (dd, J_1 = 16.0 Hz, J_2 = 8.2 Hz, 1H), 5.84 (dd, J_1 = 16.0 Hz, J_2 = 4.7 Hz, 1H), 4.91 (m, 1H), 4.57 (d, J = 8.2 Hz, 1H), 4.09 (m, 1H), 3.59 (br s, 1H), 2.00 (t, J = 14.3 Hz, 1H), 1.79 (ddd, J_1 = 11.5 Hz, J_2 = 7.0 Hz, J_3 = 3.7 Hz, 1H), 1.70 (m, 2H), 1.63 (m, 3H), 1.55 (m, 2H), 1.48 (m, 1H), 1.42 (m, 1H), 1.30 (br s, 6H), 1.17 (m, 3H), 1.07 (br s, 63 H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 150.1,

121.5, 77.6, 76.3, 75.7, 68.9, 34.7, 34.3, 31.8, 31.6, 29.7, 28.6, 24.7, 22.6, 20.1, 18.3 (br s), 14.0, 13.0 (br s); FTIR (thin film) ν_{max} 2944, 2867, 1723, 1464, 1259, 1058, 1014, 995, 883 cm^{-1}; HRMS calcd (EI) for $C_{45}H_{92}O_5Si_3$ $[M]^+$: 796.6253, found 796.6250; $[\alpha]_D^{25°C} = -12.0$, c = 1.10, $CHCl_3$.

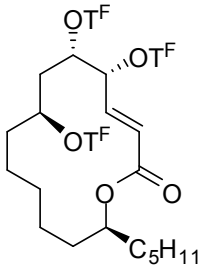


(4*S*,5*R*,7*S*,13*S*)-13-Pentyl-4,5-bis(triisopropylsilyloxy)-7-diisopropyl(1,1,1,2,2-pentafluorobutylsilyloxy)oxacyclotetradec-2-enone ((*S*)-15f): From the demixing of M-(*S*)-**15e-h**, the second peak (*S*)-**15f** (52.0 mg) at 42.8 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.73 (dd, J_1 = 15.9 Hz, J_2 = 8.6 Hz, 1H), 5.86 (d, J = 15.9 Hz, 1H), 4.91 (m, 1H), 4.66 (d, J = 8.5 Hz, 1H), 3.88 (td, J_1 = 10.5 Hz, J_2 = 6.5 Hz, 1H), 3.78 (dd, J_1 = 10.5 Hz, J_2 = 3.5 Hz, 1H), 2.43 (m, 1H), 2.08 (m, 4H), 1.74-1.45 (m, 9H), 1.44-1.21 (m, 8H), 1.08 (br s, 56H), 0.89 (t, J = 6.8 Hz, 3H), 0.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 149.3, 121.6, 178.9, 75.7, 75.5, 70.3, 42.6, 35.1, 34.3, 31.8, 31.7, 27.1, 25.1, 23.2, 18.2, 14.5, 12.5, 1.5; ^{19}F NMR (282 MHz, $CDCl_3$) −84.98 (s, 3F), −120.34 (t, $^3J_{HF}$ = 18.0 Hz, 2F); FTIR (thin film) ν_{max} 2945, 2868, 1722, 1465, 1261, 1200, 1052, 993, 884 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{46}H_{89}O_5F_5Si_3Na$ $[M + Na]^+$: 923.5836, found 923.5859; $[\alpha]_D^{25°C} = -20.0$, c = 1.01, $CHCl_3$.



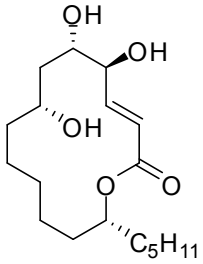
(4*R*,5*S*,7*R*,13*S*)-13-Pentyl-4,5-bis(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)-7-triisopropylsilyloxy)oxacyclotetradec-2-enone ((*S*)-15g): From the demixing of M-(*S*)-**15e-h**, the third peak (*S*)-**15g** (60.3 mg) at 42.1 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (d, J = 15.6 Hz, 1H), 6.03 (dd, J_1 = 15.6 Hz, J_2 = 2.2 Hz, 1H), 4.97 (m, 1H), 4.64 (m, 1H), 3.91 (d, J = 10.3 Hz, 1H), 3.68 (m, 1H), 2.43 (t, J = 9.7 Hz, 1H), 2.05 (m, 4H), 1.71 (m,

2H), 1.60-1.47 (m, 4H), 1.42 (m, 2H), 1.30 (br s, 9H), 1.21 (m, 2H), 1.08 (br s, 49 H), 0.92 (m, 4H), 0.89 (t, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 146.8, 122.0, 77.2, 74.5, 73.9, 68.8, 42.7, 33.9, 31.8, 30.2, 26.5, 25.7, 25.5, 25.4 (m), 23.3, 22.6, 18.2, 1.0, 0.7; ^{19}F NMR (282 MHz, $CDCl_3$) −85.01 (br s, 6F), −120.38 (m, 4F); FTIR (thin film) ν_{max} 2946, 2869, 1720, 1464, 1260, 1201, 1108, 1054, 992, 885 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{47}H_{86}O_5F_{10}Si_3Na$ $[M + Na]^+$: 1,027.5521, found 1,027.5510; $[\alpha]_D^{25°C} = +9.27$, c = 1.12, $CHCl_3$.



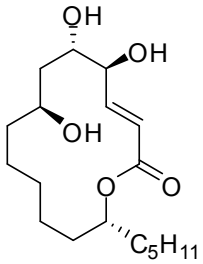
(4*R*,5*S*,7*S*,13*S*)-13-Pentyl-4,5,7-tris(diisopropyl-(1,1,1,2,2-pentafluorobutylsilyloxy)oxa-cyclotetradec-2-enone ((*S*)-15h): From the demixing of M-(*R*)-**15e-h**, the fourth peak (*S*)-**15h** (65.8 mg) at 70.9 minutes was isolated as a colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (d, J = 15.9 Hz, 1H), 6.00 (d, J = 15.9 Hz, 1H), 5.05 (m, 1H), 4.48 (br s, 1H), 3.95 (m, 2H), 2.05 (m, 6H), 1.81 (m, 1H), 1.74 (m, 1H), 1.71-1.60 (m, 3H), 1.59-1.48 (m, 5H), 1.40-1.21 (m, 10H), 1.09 (br s, 42H), 0.89 (t, J = 6.5 Hz, 3H), 0.83 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 146.5, 125.5, 76.0, 73.0, 69.4, 68.7, 40.3, 37.2, 34.3, 32.5, 31.7, 30.3, 29.7, 25.7, 25.3 (m), 22.5 (br s), 17.8, 17.5 (br s), 14.0, 1.5, 0.8, 0.7; ^{19}F NMR (282 MHz, $CDCl_3$) −84.96 (s, 3F), −85.02 (s, 3F), −85.05 (s, 3F), −120.44 (m, 6F); FTIR (thin film) ν_{max} 2948, 2871, 1730, 1466, 1200, 1105, 1062, 995, 886, 750 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{48}H_{83}O_5F_{15}Si_3Na$ $[M + Na]^+$: 1,131.5207, found 1,131.5223; $[\alpha]_D^{25°C} = +0.19$, c = 1.17, $CHCl_3$.

Detaggings

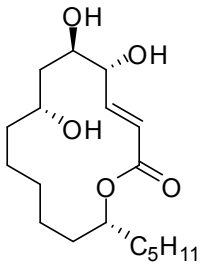


(5*S*,6*S*,8*R*,14*R*,*E*)-4,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*S*,7*R*,13*R*)-1): Tetrabutylammonium fluoride (TBAF, 0.61 mL, 0.61 mmol, 6 equiv) was added dropwise to a solution of the ester (*R*)-**15a** (81.1 mg, 102 μmol) in THF (1.00 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 5 min, and then warmed to room temperature. After stirring at room temperature for 4 h, the reaction was quenched by addition of sat. aq. NH_4Cl (3.0 mL) at 0 °C. After stirring at 0 °C for 15 minutes, the white suspension was diluted with water (1.0 mL) and ether (3.0 mL) and transferred to a separatory funnel. The aqueous layer was separated and extracted with ether (3 x 10 mL). The combined organic extracts were then washed with brine, dried over $MgSO_4$, filtered, and concentrated in vacuo. The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was dissolved in THF (3.0 mL), filtered using a Whatman syringe filter (0.45 μm pore size), and then further purified using a (*S,S*)-Whelk-O-1 column (25 cm x 21.1 mm). The purification was achieved by isocratic elution first with 90:10 hexanes/isopropanol for the first 15 minutes, then isocratic elution with 80:20 hexanes/isopropanol for 30 minutes. A constant flow rate of 10.0 mL/min was run throughout the separation and a UV detector (230 nm) was used to manually identify the peaks. The reaction after purification on the (*S,S*)-Whelk-*O*-1 column after three injections furnished the title compound as an amorphous white solid (6.4 mg): ^{1}H NMR (700 MHz, CD_3OD) δ 7.04 (dd, J_1 = 15.8 Hz, J_2 = 5.3 Hz, 1H), 6.11 (dd, J_1 = 15.8 Hz, J_2 = 1.5 Hz, 1H), 4.95 (dddd, J_1 = 12.5 Hz, J_2 = 7.6 Hz, J_3 = 5.0 Hz, J_4= 2.3 Hz, 1H), 4.26 (ddd, J_1 = 7.0 Hz, J_2 = 5.3 Hz, J_3 = 1.5 Hz, 1H), 3.92 (m, 1H), 3.77 (dt, J_1 = 7.4 Hz, J_2 = 4.5 Hz, 1H), 1.72 (m, 1H), 1.70 (dd, J_1 = 5.4 Hz, J_2 = 4.5 Hz, 2H), 1.62 (m, 1H), 1.54 (m, 2H), 1.43 (m, 4H), 1.33 (br s, 7H), 1.19 (br s, 3H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (175 MHz, CD_3OD) δ 168.0, 148.7, 123.5, 77.6, 75.8, 74.4, 69.2, 37.9, 36.8, 36.4, 34.2, 33.0, 29.7, 26.6, 26.4, 25.3, 23.8, 14.5; FTIR (thin film) ν_{max} 2926, 2857,

1705, 1270, 1100 cm^{-1}; HRMS calcd (EI) for $C_{18}H_{32}O_5$ $[M]^+$: 328.2250, found 328.2243; $[\alpha]_D^{25°C} = -9.43$, c = 0.54, MeOH.

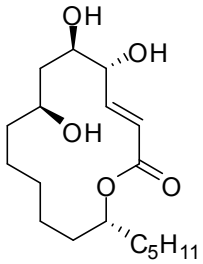


(5*S*,6*S*,8*S*,14*R*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*S*,7*S*,13*R*)-1): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**15b** (79.3 mg, 88.0 μmol) and TBAF (0.53 mL, 0.53 mmol, 6 equiv) in THF (0.90 mL). Flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) of the crude product gave the title compound as an amorphous white solid (14.6 mg, 51%): ^{1}H NMR (700 MHz, CD_3OD) δ 6.96 (dd, J_1 = 15.8 Hz, J_2 = 5.9 Hz, 1H), 6.10 (dd, J_1 = 15.8 Hz, J_2 = 1.3 Hz, 1H), 4.93 (m, 1H), 4.03 (ddd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, J_3 = 1.5 Hz, 1H), 3.54 (td, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 3.47 (m, 1H), 1.76 (ddd, J_1 = 14.6 Hz, J_2 = 8.5 Hz, J_3 = 2.7 Hz, 1H), 1.67 (m, 2H), 1.64 (m, 1H), 1.55 (m, 2H), 1.52 (m, 2H), 1.34 (br s, 9H), 1.26 (br s, 3H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 168.1, 149.4, 123.1, 77.8, 75.9, 74.6, 68.3, 43.8, 35.8, 35.6, 33.3, 33.0, 27.6, 26.4, 24.2, 23.9, 23.8, 14.5; FTIR (thin film) ν_{max} 3318, 2930, 2854, 1708, 1284 cm^{-1}; HRMS calcd (EI) for $C_{18}H_{32}O_5$ $[M]^+$: 328.2250, found 328.2260; $[\alpha]_D^{25°C} = -18.8$, c = 0.77, MeOH.

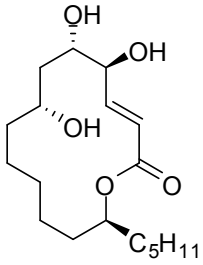


(5*R*,6*R*,8*R*,14*R*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*R*,7*R*,13*R*)-1): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**15c** (66.0 mg, 65.8 μmol) and TBAF (0.40 mL, 0.40 mmol, 6 equiv) in THF (0.66 mL). Flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) of the crude product gave the title compound as an amorphous white solid (13.1 mg, 60%): ^{1}H NMR (700 MHz, CD_3OD) δ 6.91 (dd, J_1 = 15.8 Hz, J_2 = 6.4 Hz, 1H), 6.11 (d, J = 15.8 Hz, 1H), 5.03 (m, 1H), 4.16 (t, J =

6.0 Hz, 1H), 3.82 (ddd, J_1 = 9.2 Hz, J_2 = 6.0 Hz, J_3 = 3.8 Hz, 1H), 3.79 (m, 1H), 1.78 (m, 1H), 1.63 (m, 2H), 1.56 (m, 1H), 1.45 (m, 4H) 1.39 (m, 2H), 1.33 (m, 7H), 1.18 (m, 2H), 1.11 (m, 1H) 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 168.2, 148.4, 124.3, 77.6, 77.5, 73.4, 67.6, 42.0, 37.0, 36.0, 34.5, 32.9, 30.1, 26.6, 26.5, 25.2, 23.8, 14.5; FTIR (thin film) ν_{max} 3384, 2927, 2858, 1716, 1650, 1267 cm^{-1}; HRMS calcd (EI) for $C_{18}H_{33}O_5$ $[M+H]^+$: 329.2338, found 329.2328; $[\alpha]_D^{25°C}$ = +24.8, c = 1.25, MeOH.

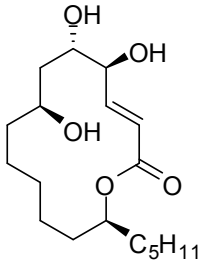


(5*R*,6*R*,8*S*,14*R*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*R*,7*S*,13*R*)-1): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**15d** (50.0 mg, 45.0 μmol) and TBAF (0.27 mL, 0.27 mmol, 6 equiv) in THF (0.45 mL). Flash chromatography of the crude product (3:1 hexanes/EtOAc, then 100% EtOAc) gave the title compound as an amorphous white solid (7.6 mg, 51%): ^{1}H NMR (700 MHz, CD_3OD) δ 7.07 (dd, J_1 = 15.8 Hz, J_2 = 5.4 Hz, 1H), 6.12 (dd, J_1 = 15.8 Hz, J_2 = 1.5 Hz, 1H), 4.97 (m, 1H), 4.26 (td, J_1 = 6.5 Hz, J_2 = 1.5 Hz, 1H), 3.90 (td, J_1 = 6.5 Hz, J_2 = 2.8 Hz, 1H), 3.78 (septet, J = 4.20 Hz, 1H), 1.70 (m, 4H), 1.63 (m, 2H), 1.54 (m, 2H), 1.42 (m, 2H), 1.31 (m, 9H), 1.21 (m, 1H), 0.91 (t, J = 6.9 Hz, 3H); ^{13}C NMR (175 MHz, CD_3OD) δ 168.8, 149.8, 123.2, 75.8, 75.3, 73.8, 68.9, 38.3, 35.8, 35.5, 33.7, 33.0, 27.8, 26.5, 25.1, 24.5, 23.8, 14.5; FTIR (thin film) ν_{max} 3195, 2924, 2854, 1709, 1554, 1272 cm^{-1}; HRMS calcd (EI) for $C_{18}H_{32}O_5$ $[M]^+$: 328.2250, found 328.2242; $[\alpha]_D^{25°C}$ = +7.66, c = 0.38, MeOH.

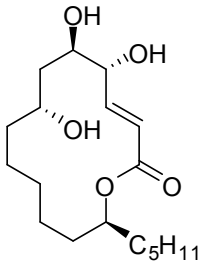


(5*S*,6*S*,8*R*,14*S*,*E*)-5,6,8-Trihydroxy-13-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*S*,7*R*,13*S*)-1): The same method employed in the preparation of (4*R*,5*R*,7*R*,13*R*)-**1** was followed using (*S*)-

15a (88.1 mg, 111 μmol) and TBAF (0.66 mL, 0.66 mmol, 6 equiv) in THF (1.11 mL). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as described for compound (4*S*,5*S*,7*R*,13*R*)-**1** (see above) and the title compound was isolated as an amorphous white solid (5.4 mg, 15%). The ^{1}H NMR spectrum matched that of (4*R*,5*R*,7*S*,13*R*)-**1** (see above); $[\alpha]_D^{25°C} = -4.04$, c = 0.27, MeOH.

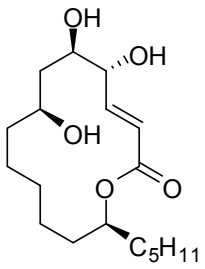


(5*S*,6*S*,8*S*,14*S*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*S*,7*S*,13*S*)-1): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*S*)-**15b** (68.0 mg, 75.4 μmol) and TBAF (0.45 mL, 0.45 mmol, 6 equiv) in THF (0.75 mL). Flash chromatography of the crude product (3:1 hexanes/EtOAc, then 100% EtOAc) gave the title compound as an amorphous white solid (16.5 mg, 67%). The ^{1}H NMR spectrum matched that of (4*R*,5*R*,7*R*,13*R*)-**1** (see above); $[\alpha]_D^{25°C} = -25.9$, c = 0.83, MeOH.

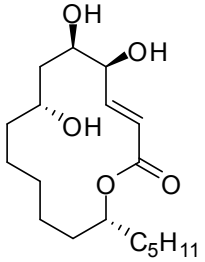


(5*R*,6*R*,8*R*,13*S*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*R*,7*R*,13*S*)-1): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*S*)-**15c** (68.8 mg, 68.4 μmol) and TBAF (0.41 mL, 0.41 mmol, 6 equiv) in THF (0.68 mL). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was dissolved in 1:1 hexanes/isopropanol (1.0 mL), filtered through a Whatman syringe filter (0.45 μm pore size), and further purified using a Chiralcel OD semi-preparative HPLC column. The purification was done with isocratic elution (92:8 hexanes/isopropanol, 4.5 mL/min), a UV detector (230 nm) was used to identify the peaks, and the desired compound (4*R*,5*R*,7*R*,13*S*)-**11**

was isolated as an amorphous white solid (1 injection, 3.2 mg, 14%) The ^{1}H NMR spectrum matched that of (4*S*,5*S*,7*S*,13*R*)-**1** (see above); $[\alpha]_D^{25°C}$ = +16.5, c = 0.32, MeOH.

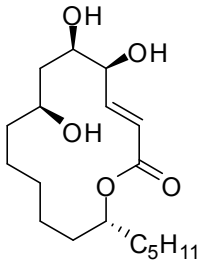


(5*R*,6*R*,8*S*,14,E*S*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*R*,7*S*,13*S*)-1): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** during the single isomer pilot synthesis (see Chapter 2.0) was followed using (*S*)-**15d** (84.9 mg, 76.5 μmol) and TBAF (0.46 mL, 0.46 mmol, 6 equiv) in THF (0.77 mL). Flash chromatography of the crude product (3:1 hexanes/EtOAc, then 100% EtOAc) gave the title compound as an amorphous white solid (16.5 mg, 66%). The ^{1}H NMR spectrum matched that of (4*S*,5*S*,7*R*,13*R*)-**1** (see above); $[\alpha]_D^{25°C}$ = +11.3, c = 0.89, MeOH.

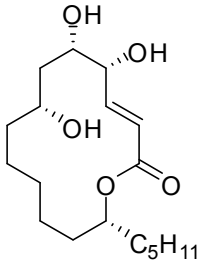


(5*S*,6*R*,8*R*,14*R*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*R*,7*R*,13*R*)-1): The tagged lactone (*R*)-**15e** (91.4 mg, 115 μmol) was dissolved in CH_2Cl_2 (3.0 mL) and transferred to a polyethylene culture tube. The solution was diluted with acetonitrile (8.0 mL). Aqueous hydrofluoric acid (48 wt. %, 0.60 mL) was then added to the solution at room temperature and the reaction mixture was stirred for 16 h at room temperature. The reaction was then quenched by dropwise addition of sat. aq. $NaHCO_3$ (10.0 mL) at 0 °C and the layers were separated. The aqueous layer was extracted with ether (3 x 20 mL). The combined organic extracts were then washed with brine, dried over MgSO4, and concentrated in vacuo. The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as described for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound

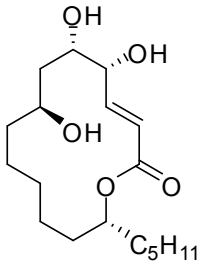
was isolated as an amorphous white solid (6 injections, 11.0 mg, 29%): ^{1}H NMR (700 MHz, CD_3OD) δ 6.94 (dd, J_1 = 15.8 Hz, J_2 = 4.7 Hz, 1H), 6.09 (dd, J_1 = 15.8 Hz, J_2 = 1.8 Hz, 1H), 5.01 (m, 1H), 4.47 (ddd, J_1 = 4.7 Hz, J_2 = 3.0 Hz, J_3 = 1.8 Hz, 1H), 3.89 (ddd, J_1 = 7.2 Hz, J_2 = 4.7 Hz, J_3 = 3.0 Hz, 1H), 3.71 (m, 1H), 1.76 (m, 2H), 1.71 (ddd, J_1 = 14.6 Hz, J_2 = 7.2 Hz, J_3 = 4.7 Hz, 1H), 1.63 (m, 1H), 1.56 (m, 1H), 1.45 (m, 5H), 1.33 (m, 8H) 1.21 (m, 2H), 1.11 (m, 1H), 0.90 (t, J = 6.9 Hz, 3H); δ ^{13}C NMR (175 MHz, CD_3OD) δ 168.0, 148.6, 123.4, 77.4, 74.6, 72.3, 68.8, 39.1, 36.4, 35.7, 34.4, 33.0, 30.3, 26.6, 26.0, 24.3, 23.8, 14.5; FTIR (thin film) ν_{max} 3288, 2922, 2855, 1703, 1265, 1183, 990 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{18}H_{32}O_5Na$ [M + Na]$^+$: 351.2147, found 351.2142; $[\alpha]_D^{25°C} = +15.5$, c = 0.55, MeOH.



(5*S*,6*R*,8*S*,14*R*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*R*,7*S*,13*R*)-1): The same method employed above in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**15f** (91.1 mg, 101 μmol) and TBAF (0.60 mL, 0.60 mmol, 6 equiv). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (12.4 mg, 37%, 12:1 *d.r.*): ^{1}H NMR (700 MHz, CD_3OD) δ 7.00 (dd, J_1 = 15.8 Hz, J_2 = 3.6 Hz, 1H), 6.06 (dd, J_1 = 15.8 Hz, J_2 = 2.2 Hz, 1H), 4.95 (m, 1H), 4.46 (m, 1H), 3.95 (ddd, J_1 = 7.6 Hz, J_2 = 4.5 Hz, J_3 = 2.2 Hz, 1H), 3.68 (septet, J = 4.5 Hz, 1H), 2.02 (ddd, J_1 = 14.1 Hz, J_2 = 8.1 Hz, J_3 = 4.5 Hz, 1H, 1H), 1.69 (m, 2H), 1.61 (m, 2H), 1.54 (m, 3H), 1.34 (m, 9H), 1.28 (m, 3H), 0.90 (t, J = 6.9 Hz, 3H); δ ^{13}C NMR (175 MHz, CD_3OD) δ 168.0, 150.2, 122.3, 76.1, 75.7, 72.1, 68.8, 39.5, 34.9, 34.6, 33.0, 32.8, 28.6, 26.6, 24.9, 23.4, 14.5; FTIR (thin film) ν_{max} 2932, 2360, 2340, 1717, 1270, 1009 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{18}H_{32}O_5Na$ [M + Na]$^+$: 351.2147, found 351.2171; $[\alpha]_D^{25°C} = +1.66$, c = 0.54, MeOH.

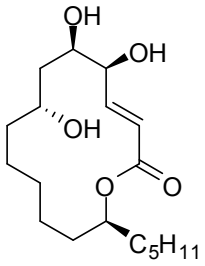


(5*R*,6*S*,8*R*,14*R*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*S*,7*R*,13*R*)-1, (+)-*nat*-Sch 725674): The same method employed above in the preparation of (4*S*,5*R*,7*R*,13*R*)-**1** was followed using (*R*)-**15g** (55.1 mg, 54.8 μmol). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (6 injections, 5.7 mg, 32%). The NMR spectroscopic data of (4*R*,5*S*,7*R*,13*R*)-**1** are in complete agreement with those of the natural product[10]: ^{1}H NMR (700 MHz, CD_3OD) δ 6.87 (dd, J_1 = 15.8 Hz, J_2 = 6.1 Hz, 1H), 6.08 (dd, J_1 = 15.8 Hz, J_2 = 1.5 Hz, 1H), 4.95 (dddd, J_1 = 10.4 Hz, J_2 = 7.9 Hz, J_3 = 5.4 Hz, J_4 = 2.9 Hz,1H), 4.49 (ddd, J_1 = 5.8 Hz, J_2 = 2.7 Hz, J_3 = 1.5 Hz, 1H), 3.99 (quintet, J = 6.2 Hz, 1H), 3.85 (m, 1H), 1.83 (dt, J_1 = 14.7 Hz, J_2 = 6.1 Hz, 1H), 1.71 (dddd, J_1 = 14.2 Hz, J_2 = 6.7 Hz, J_3 = 4.6 Hz, J_4 = 2.0 Hz, 1H), 1.65 (dt, J_1 = 14.7 Hz, J_2 = 5.0 Hz,1H), 1.61 (m, 1H), 1.55 (m, 2H), 1.46 (m, 1H), 1.34 (m, 10H) 1.18 (m, 3H), 0.90 (t, J = 6.9 Hz, 3H); δ ^{13}C NMR (175 MHz, CD_3OD) δ 168.4, 149.3, 123.1, 77.6, 76.0, 72.9, 69.5, 38.3, 36.8, 36.5, 34.1, 33.0, 29.5, 27.0, 26.4, 25.8, 23.8, 14.5; FTIR (thin film) ν_{max} 3436, 2926, 2857, 1703, 1461, 1274, 1077 cm^{-1}; HRMS calcd (EI) for $C_{18}H_{32}O_5$ $[M]^+$: 328.2250, found 328.2248; $[\alpha]_D^{25^\circ C} = +5.15$, c = 0.27, MeOH.

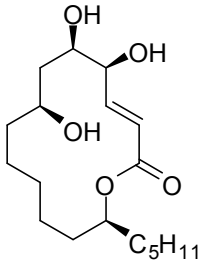


(5*R*,6*S*,8*S*,14*R*,*E*)-5,6,8-Trihydroxy-13-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*S*,7*S*,13*R*)-1): The same method employed above in the preparation of (4*S*,5*R*,7*R*,13*R*)-**1** was followed using (*R*)-**15h** (40.1 mg, 36.1 μmol). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as

described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (3 injections, 4.7 mg, 40%). ^{1}H NMR (700 MHz, CD_3OD) δ 6.95 (dd, J_1 = 15.8 Hz, J_2 = 4.2 Hz, 1H), 6.14 (dd, J_1 = 15.8 Hz, J_2 = 1.4 Hz, 1H), 4.93 (m,1H), 4.54 (m, 1H), 3.89 (dt, J_1 = 8.8 Hz, J_2 = 2.1 Hz, 1H), 3.38 (m, 1H), 2.02 (ddd, J_1 = 14.6 Hz, J_2 = 8.8 Hz, J_3 = 2.4 Hz, 1H), 1.65 (m, 3H), 1.54 (m,1H), 1.48 (m, 2H), 1.40 (m, 1H), 1.32 (m, 10H), 1.20 (m, 3H), 0.90 (t, J = 6.9 Hz, 3H); δ ^{13}C NMR (175 MHz, CD_3OD) δ 169.0, 150.0, 121.8, 75.5, 75.0, 72.1, 68.8, 40.5, 36.2, 35.9, 33.9, 33.0, 27.2, 26.5, 24.7, 24.5, 23.8, 14.5; FTIR (thin film) ν_{max} 3360, 2935, 2340, 1715, 1286 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{18}H_{32}O_5Na$ $[M + Na]^+$: 351.2147, found 351.2174; $[\alpha]_D^{25°C} = -38.6$, c = 0.24, MeOH.

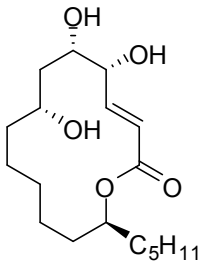


(5*S*,6*R*,8*R*,14*S*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*R*,7*R*,13*S*)-1): The same method employed in the preparation of (4*S*,5*R*,7*R*,13*R*)-**1** was followed using (*S*)-**15e** (72.7 mg, 91.2 μmol). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)- Whelk-*O*-1 column as described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (5 injections, 13.4 mg, 45%). The ^{1}H NMR spectrum matched that of (4*R*,5*S*,7*S*,13*R*)-**1** (see above); $[\alpha]_D^{25°C} = -38.7$, c = 0.67, MeOH.

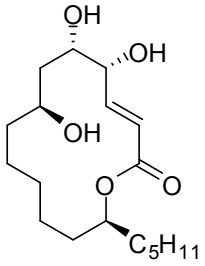


(5*S*,6*R*,8*S*,14*S*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*S*,5*R*,7*S*,13*S*)-1): The same method employed above in the preparation of (4*S*,5*R*,7*R*,13*R*)-**1** was followed using (*S*)-**15f** (87.0 mg, 96.5 μmol). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as

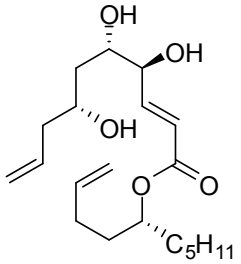
described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (3 injections, 5.5 mg, 17%). The ^{1}H NMR spectrum matched that of (4*R*,5*S*,7*R*,13*R*)-**1** (see above); $[\alpha]_D^{25^\circ C} = -2.93$, c = 0.21, MeOH.



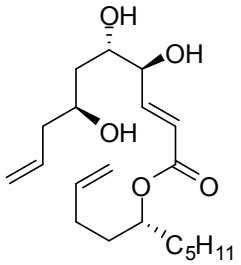
(*5R*,6*S*,8*R*,14,E*S*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*S*,7*R*,13*S*)-1): The same method employed above in the preparation of (4*S*,5*R*,7*R*,13*R*)-**1** was followed using (*S*)-**15g** (59.1 mg, 58.8 μmol). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (4 injections, 14.0 mg, 73%). The ^{1}H NMR spectrum matched that of (4*S*,5*R*,7*S*,13*R*)-**1** (see above); $[\alpha]_D^{25^\circ C} = -2.14$, c = 0.70, MeOH.



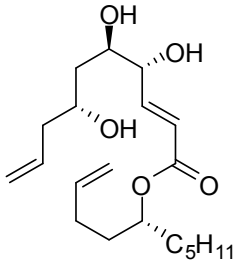
(5*R*,6*S*,8*S*,14*S*,*E*)-5,6,8-Trihydroxy-14-pentyloxacyclotetradec-3-en-2-one ((4*R*,5*S*,7*S*,13*S*)-1): The same method employed above in the preparation of (4*S*,5*R*,7*R*,13*R*)-**1** was followed using (*S*)-**15h** (59.1 mg, 58.8 μmol). The product after flash chromatography (3:1 hexanes/EtOAc, then 100% EtOAc) was further purified using a (*S,S*)-Whelk-*O*-1 column as described above for (4*S*,5*S*,7*R*,13*R*)-**1**, and the desired compound was isolated as an amorphous white solid (3 injections, 6.9 mg, 36%). The ^{1}H NMR spectrum matched that of (4*S*,5*R*,7*R*,13*R*)-**1** (see above); $[\alpha]_D^{25^\circ C} = -13.8$, c = 0.35, MeOH.



(4*S*,5*S*,7*R*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*S*,5*S*,7*R*,13*R*)-16): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**14a**. Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil (16.5 mg, 65%). The ^{1}H NMR spectrum matched that of (4*R*,5*R*,7*S*,13*S*)-**16** (see below); $[\alpha]_D^{25°C} = -30.7$, c = 1.08, MeOH.

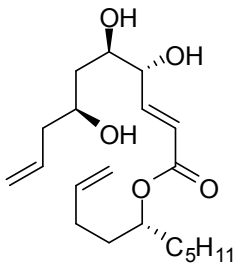


(4*S*,5*S*,7*S*,*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*S*,5*S*,7*S*,13*R*)-16): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**14b** (68.2 mg, 44.1 μmol) and TBAF (0.27 mL, 0.27 mmol, 6 equiv) in THF (0.44 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil (15.6 mg, 94%). The ^{1}H NMR spectrum matched that of (4*R*,5*R*,7*R*,13*S*)-**16** (see below); $[\alpha]_D^{25°C} = -15.1$, c = 0.83, MeOH.

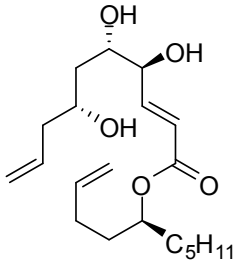


(4*R*,5*R*,7*R*,2*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*R*,5*R*,7*R*,13*R*)-16): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**14c** (112 mg, 108 μmol) and TBAF (0.65 mL, 0.65 mmol, 6 equiv) in THF (1.10 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a

colorless oil (26.4 mg, 69%). The ^{1}H NMR spectrum matched that of (4*S*,5*S*,7*S*,13*S*)-**16** (see below); $[\alpha]_D^{25°C}$ = +17.9, c = 1.02, MeOH.

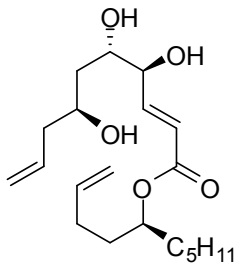


(4*R*,5*R*,7*S*,2*E*)-((*R*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*R*,5*R*,7*S*,13*R*)-16): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*R*)-**14d** (137 mg, 120 μmol) and TBAF (0.72 mL, 0.72 mmol, 6 equiv) in THF (1.20 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil (11.0 mg, 63%). The ^{1}H NMR spectrum matched that of (4*S*,5*S*,7*R*,13*S*)-**16** (see below); $[\alpha]_D^{25°C}$ = +34.6, c = 1.43, MeOH.

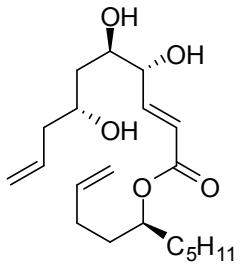


(4*S*,5*S*,7*R*)-((*S*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*S*,5*S*,7*R*,13*S*)-16): The same method employed in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*S*)-**14a** (83.0 mg, 101 μmol) and TBAF (0.61 mL, 0.61 mmol, 6 equiv) in THF (1.00 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil (23.9 mg, 67%): ^{1}H NMR (600 MHz, CD_3OD) δ 7.05 (dd, J_1 = 15.7 Hz, J_2 = 4.7 Hz, 1H), 6.10 (dd, J_1 = 15.7 Hz, J_2 = 1.7 Hz, 1H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 7.0 Hz, 1H), 5.82 (ddt, J_1 = 16.9 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.02 (m, 5H), 4.19 (td, J_1 = 4.7 Hz, J_2 = 1.7 Hz, 1H), 3.87 (m, 2H), 2.24 (m, 2H), 2.07 (m, 2H), 1.68 (m, 2H), 1.58 (m, 2H), 1.54 (m, 2H), 1.32 (br s, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 149.8, 139.2, 136.5, 122.8, 117.5, 115.6, 75.5, 75.2, 71.8, 68.8, 43.9, 40.6, 35.4, 34.8, 32.9, 30.9, 26.2, 23.8, 14.5; FTIR (thin film) ν_{max} 3364, 2925, 2857, 1696, 1641, 1271, 1172, 1066, 990 cm^{-1};

HRMS calcd (ESI, positive mode) for $C_{20}H_{34}O_5Na$ $[M+Na]^+$: 377.2304, found 377.2276; $[\alpha]_D^{25°C} = -23.0$, c = 1.20, MeOH.

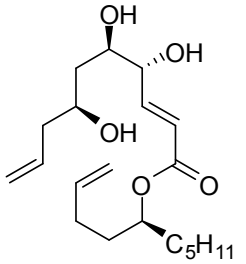


(4*S*,5*S*,7*S*)-((*S*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*S*,5*S*,7*S*,13*S*)-16): The same method employed above in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*S*)-**14b** (92.4 mg, 99.6 μmol) and TBAF (0.60 mL, 0.60 mmol, 6 equiv) in THF (1.00 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil (30.1 mg, 85%): ^{1}H NMR (600 MHz, CD_3OD) δ 7.05 (dd, J_1 = 15.7 Hz, J_2 = 4.6 Hz, 1H), 6.11 (dd, J_1 = 15.7 Hz, J_2 = 1.8 Hz, 1H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 7.0 Hz 1H), 5.82 (ddt, J_1 = 16.9 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.00 (m, 5H), 4.22 (td, J_1 = 4.5 Hz, J_2 = 1.8 Hz, 1H), 3.87 (m, 1H), 3.82 (quintet, J = 4.3 Hz, 1H), 2.25 (m, 2H), 2.08 (m, 2H), 1.74 (dt, J_1 = 14.2 Hz, J_2 = 4.4 Hz, 1H), 1.67 (m, 2H), 1.59 (m, 2H), 1.55 (dt, J_1 = 17.2 Hz, J_2 = 8.7 Hz, 1H), 1.32 (br s, 6H), 0.90 (t, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 149.9, 139.2, 136.2, 122.8, 117.7, 115.6, 75.2, 74.7, 73.8, 70.9, 43.1, 39.8, 35.4, 34.8, 32.9, 31.0, 26.2, 23.7, 14.5; FTIR (thin film) ν_{max} 3364, 2925, 2858, 1697, 1274, 1172 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{20}H_{34}O_5Na$ $[M+Na]^+$: 377.2304, found 377.2279; $[\alpha]_D^{25°C} = -13.3$, c = 1.51, MeOH.



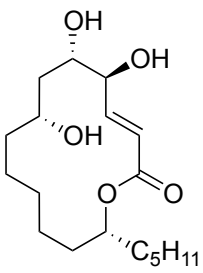
(4*R*,5*R*,7*R*)-((*S*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*R*,5*R*,7*R*,13*S*)-16): The same method employed above in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*S*)-**14c** (90.4 mg, 87.6 μmol) and TBAF (0.53 mL, 0.53 mmol, 6 equiv) in THF (0.88 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a

colorless oil (23.8 mg, 77%): ^{1}H NMR (600 MHz, CD_3OD) δ 7.05 (dd, J_1 = 15.7 Hz, J_2 = 4.6 Hz, 1H), 6.11 (dd, J_1 = 15.7 Hz, J_2 = 1.7 Hz, 1H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 7.1 Hz 1H), 5.82 (ddt, J_1 = 16.9 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.01 (m, 5H), 4.22 (td, J_1 = 4.4 Hz, J_2 = 1.8 Hz, 1H), 3.87 (m, 1H), 3.82 (quintet, J = 4.4 Hz, 1H), 2.25 (m, 2H), 2.08 (m, 2H), 1.74 (dt, J_1 = 14.1 Hz, J_2 = 4.4 Hz, 1H), 1.68 (m, 2H), 1.59 (m, 2H), 1.54 (dt, J_1 = 14.1 Hz, J_2 = 8.7 Hz, 1H), 1.32 (br s, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 149.9, 139.2, 136.2, 122.8, 117.7, 115.6, 75.2, 74.7, 73.8, 70.9, 43.1, 39.8, 35.4, 34.8, 32.9, 31.0, 26.2, 23.8, 14.5; FTIR (thin film) ν_{max} 3388, 2927, 2859, 1698, 1656, 1270, 1077 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{20}H_{34}O_5Na$ $[M+Na]^+$: 377.2304, found 377.2305; $\left[\alpha\right]_D^{25^\circ C} = +15.2$, c = 1.19, MeOH.

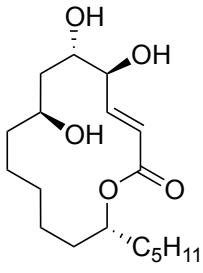


(4*R*,5*R*,7*S*)-((*S*)-Dec-1-en-5-yl)-4,5,7-trihydroxydeca-2,9-dienoate ((4*R*,5*R*,7*S*,13*S*)-16): The same method employed above in the preparation of (4*S*,5*S*,7*R*,13*R*)-**1** above was followed using (*S*)-**14d** (106 mg, 93.1 μmol) and TBAF (0.56 mL, 0.56 mmol, 6 equiv) in THF (0.93 mL). Flash chromatography of the crude product (1:1 hexanes/EtOAc) gave the title compound as a colorless oil (29.0 mg, 88%): ^{1}H NMR (600 MHz, CD_3OD) δ 7.05 (dd, J_1 = 15.7 Hz, J_2 = 4.7 Hz, 1H), 6.11 (dd, J_1 = 15.7 Hz, J_2 = 1.7 Hz, 1H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 7.1 Hz 1H), 5.82 (ddt, J_1 = 17.0 Hz, J_2 = 10.2 Hz, J_3 = 6.7 Hz, 1H), 5.00 (m, 5H), 4.19 (td, J_1 = 4.7 Hz, J_2 = 1.7 Hz, 1H), 3.88 (m, 2H), 2.24 (m, 2H), 2.08 (m, 2H), 1.68 (m, 2H), 1.55 (m, 4H), 1.32 (br s, 6H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.1, 149.8, 139.2, 136.5, 122.8, 117.5, 115.6, 75.5, 75.2, 71.8, 68.8, 44.0, 40.6, 35.4, 34.8, 32.9, 31.0, 26.2, 23.8, 14.5; FTIR (thin film) ν_{max} 3344, 2924, 2857, 1695, 1642, 1269, 1172 cm^{-1}; HRMS calcd (ESI, positive mode) for $C_{20}H_{34}O_5Na$ $[M+Na]^+$: 377.2304, found 377.2277; $\left[\alpha\right]_D^{25^\circ C} = +33.2$, c = 1.45, MeOH.

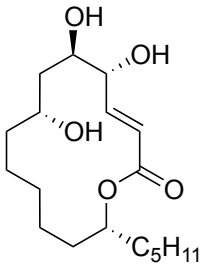
Figure S7: Stereostructures of Sch 725674 lactone library members 1



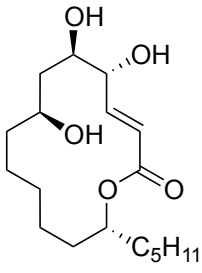
(4*S*,5*S*,7*R*,13*R*)-**1**



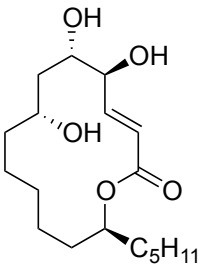
(4*S*,5*S*,7*S*,13*R*)-**1**



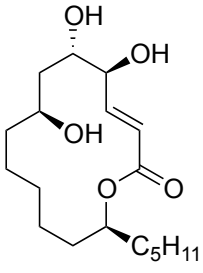
(4*R*,5*R*,7*R*,13*R*)-**1**



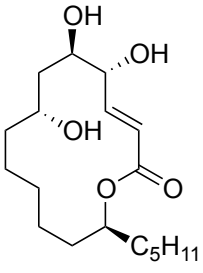
(4*R*,5*R*,7*S*,13*R*)-**1**



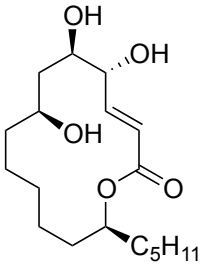
(4*S*,5*S*,7*R*,13*S*)-**1**



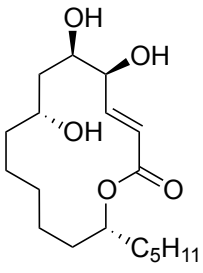
(4*S*,5*S*,7*S*,13*S*)-**1**



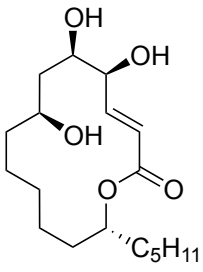
(4*R*,5*R*,7*R*,13*S*)-**1**



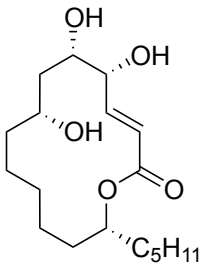
(4*R*,5*R*,7*S*,13*S*)-**1**



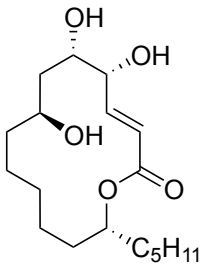
(4*S*,5*R*,7*R*,13*R*)-**1**



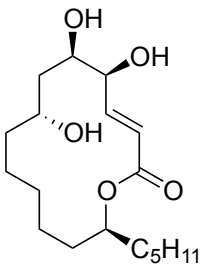
(4*S*,5*R*,7*S*,13*R*)-**1**



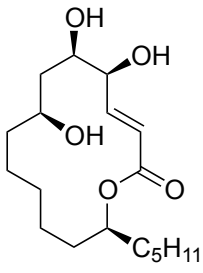
(4*R*,5*S*,7*R*,13*R*)-**1**



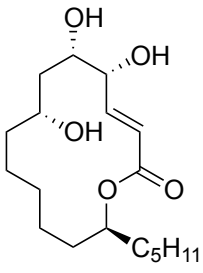
(4*R*,5*S*,7*S*,13*R*)-**1**



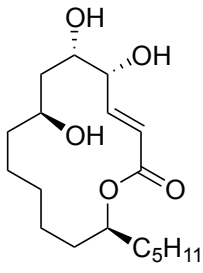
(4*S*,5*R*,7*R*,13*S*)-**1**



(4*S*,5*R*,7*S*,13*S*)-**1**

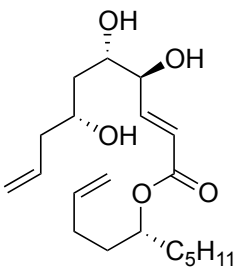


(4*R*,5*S*,7*R*,13*S*)-**1**

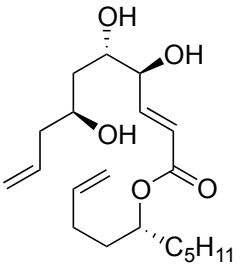


(4*R*,5*S*,7*S*,13*S*)-**1**

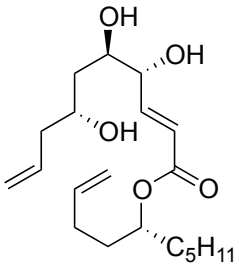
Figure S8: Stereostructures of ring-open ester library members 16



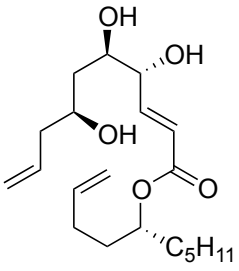
(4*S*,5*S*,7*R*,13*R*)-**16**



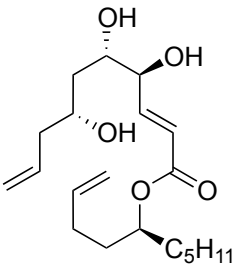
(4*S*,5*S*,7*S*,13*R*)-**16**



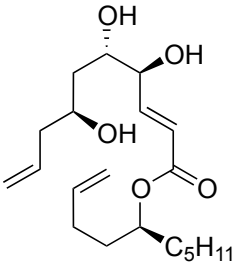
(4*R*,5*R*,7*R*,13*R*)-**16**



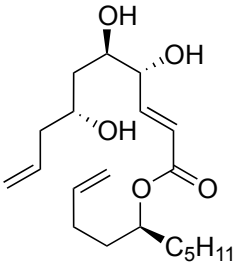
(4*R*,5*R*,7*S*,13*R*)-**16**



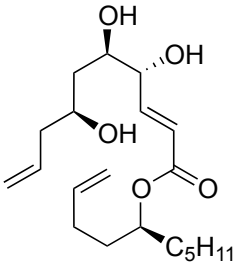
(4*S*,5*S*,7*R*,13*S*)-**16**



(4*S*,5*S*,7*S*,13*S*)-**16**



(4*R*,5*R*,7*R*,13*S*)-**16**



(4*R*,5*R*,7*S*,13*S*)-**16**

Table S1: ^{1}H NMR data (700 MHz) of the ring-closed 4,5-*trans*-13*R*-1 series in d_4-MeOD

C no.	(4*S*,5*S*,7*R*,13*R*)-**1**	(4*S*,5*S*,7*S*,13*R*)-**1**	(4*R*,5*R*,7*R*,13*R*)-**1**	(4*R*,5*R*,7*S*,13*R*)-**1**
2	6.11 (dd, 15.8, 1.5, 1H)	6.10 (dd, 15.8, 1.3, 1H)	6.11 (d, 15.8, 1H)	6.12 (dd, 15.8, 1.5, 1H)
3	7.04 (dd, 15.8, 5.3, 1H)	6.96 (dd, 15.8, 5.9, 1H)	6.91 (dd, 15.8, 6.4, 1H)	7.07 (dd, 15.8, 5.4, 1H)
4	4.95 (dddd, 12.5, 7.6, 5.0, 2.3, 1H)	4.03 (ddd, 7.6, 6.0, 1.5, 1H)	4.16 (t, 6.0, 1H)	4.26 (td, 6.5, 1.5, 1H)
5	3.77 (dt, 7.4, 4.5, 1H)	3.54 (td, 8.5, 1.5, 1H)	3.82 (ddd, 9.2, 6.0, 3.8, 1H)	3.90 (td, 6.5, 2.8, 1H)
6	1.70 (dd, 5.4, 4.5, 2H)	1.76 (ddd, 14.6, 8.5, 2.7, 1H) 1.67 (m, 1H)	1.63 (m, 1H) 1.45 (m, 1H)	1.70 (m, 2H)
7	3.92 (m, 1H)	3.47 (m, 1H)	3.79 (m, 1H)	3.78 (sept, 4.20, 1H)
8	1.43 (m, 1H) 1.33 (m, 1H)	1.55 (m, 1H) 1.34 (m, 1H)	1.45 (m, 2H)	1.31 (m, 2H)
9	1.19 (m, 2H)	nd*	nd	nd
10	nd	nd	nd	nd
11	nd	nd	nd	nd
12	1.62 (m, 1H) 1.54 (m, 1H)	1.67 (m, 2H)	1.78 (m, 1H) 1.56 (m, 1H)	1.70 (m, 2H)
13	4.95 (dddd, 12.5, 7.6, 5.0, 2.3, 1H)	4.93 (m, 1H)	5.03 (m, 1H)	4.97 (m, 1H)
14	1.62 (m, 1H) 1.54 (m, 1H)	1.67 (m, 1H) 1.64 (m, 1H)	1.56 (m, 1H) 1.45 (m, 1H)	1.63 (m, 2H)
15	1.33 (m, 2H)	1.34 (m, 2H)	1.33 (m, 2H)	1.31 (m, 2H)
16	1.33 (m, 2H)	1.34 (m, 2H)	1.33 (m, 2H)	1.31 (m, 2H)
17	1.33 (m, 2H)	1.34 (m, 2H)	1.33 (m, 2H)	1.31 (m, 2H)
18	0.91 (t, 6.9, 3H)	0.91 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)	0.91 (t, 6.9, 3H)

* nd = not determined

Table S2: ^{1}H NMR data (700 MHz) of the ring-closed 4,5-*cis*-13*R*-1 series in d_4-MeOD

C no.	(4*S*,5*R*,7*R*,13*R*)-**1**	(4*S*,5*R*,7*S*,13*R*)-**1**	(4*R*,5*S*,7*R*,13*R*)-**1**	(4*R*,5*S*,7*S*,13*R*)-**1**
2	6.09 (dd, 15.8, 1.8, 1H)	6.06 (dd, 15.8, 2.2, 1H)	6.08 (dd, 15.8, 1.5, 1H)	6.14 (dd, 15.8, 1.4, 1H)
3	6.94 (dd, 15.8, 4.7, 1H)	7.00 (dd, 15.8, 3.6, 1H)	6.87 (dd, 15.8, 6.1, 1H)	6.95 (dd, 15.8, 4.2, 1H)
4	4.47 (ddd, 4.7, 3.0, 1.8, 1H)	4.46 (m, 1H)	4.49 (ddd, 5.8, 2.7, 1.5, 1H)	4.54 (m, 1H)
5	3.89 (ddd, 7.2, 4.7, 3.0, 1H)	3.95 (ddd, 7.6, 4.5, 2.2, 1H)	3.85 (m, 1H)	3.89 (dt, 8.8, 2.1, 1H)
6	1.71 (ddd, 14.6, 7.2, 4.7, 1H) 1.33 (m, 1H)	2.02 (ddd, 14.1, 8.1, 4.5, 1H) 1.54 (m, 1H)	1.83 (dt, 14.7, 6.1, 1H) 1.65 (dt, 14.7, 5.0,1H)	1.32 (m, 2H)
7	3.71 (m, 1H)	3.68 (sept, 4.5, 1H)	3.99 (quint, 6.2, 1H)	3.38 (m, 1H)
8	1.45 (m, 2H)	1.28 (m, 2H)	1.34 (m, 2H)	1.32 (m, 2H)
9	nd*	nd	nd	nd
10	nd	nd	nd	nd
11	nd	nd	nd	nd
12	1.76 (m, 1H) 1.63 (m, 1H)	1.69 (m, 2H)	1.65 (m, 2H) 1.71 (dddd, 14.2, 6.7, 4.6, 2.0, 1H)	nd
13	5.01 (m, 1H)	4.95 (m, 1H)	4.95 (dddd, 10.4, 7.9, 5.4, 2.9, 1H)	4.93 (m, 1H)
14	1.56 (m, 1H) 1.45 (m, 1H)	1.61 (m, 2H)	1.55 (m, 1H) 1.61 (m, 1H)	1.65 (m, 1H) 1.54 (m, 1H)
15	1.33 (m, 2H)	1.34 (m, 2H)	1.34 (m, 2H)	1.32 (m, 2H)
16	1.33 (m, 2H)	1.34 (m, 2H)	1.34 (m, 2H)	1.32 (m, 2H)
17	1.33 (m, 2H)	1.34 (m, 2H)	1.34 (m, 2H)	1.32 (m, 2H)
18	0.90 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)

* nd = not determined

Table S3: ^{13}C NMR data (175 MHz) for the full ring-closed (13*R*)-1 enantioseries in d_4-MeOD

C no.	(4*S*,5*S*,7*R*,13*R*)-**1**	(4*S*,5*S*,7*S*,13*R*)-**1**[a]	(4*R*,5*R*,7*R*,13,*R*)-**1**[a]	(4*R*,5*R*,7*S*,13*R*)-**1**	(4*S*,5*R*,7*R*,13*R*)-**1**	(4*S*,5*R*,7*S*,13*R*)-**1**	(4*R*,5*S*,7*R*,13*R*)-**1**	(4*R*,5*S*,7*S*,13*R*)-**1**
1	168.0	168.1	168.2	168.9	168.0	168.0	168.4	169.0
2	123.5	123.1	124.3	123.3	123.4	122.3	123.1	121.8
3	148.7	149.4	148.4	149.8	148.6	150.2	149.3	150.0
4	75.8	77.8	77.5	75.3	74.6	75.7	76.0	75.0
5	74.4	74.6	73.4	73.9	72.3	72.1	72.9	72.1
6	37.9	43.8	42.0	nd[b]	39.1	39.5	38.3	40.5
7	69.2	68.3	67.6	69.9	68.8	68.8	69.5	68.8
8	nd	nd	nd	nd	36.4	39.5	nd	nd
9	nd	nd	nd	nd	nd	nd	nd	nd
10	nd	nd	nd	nd	nd	nd	nd	nd
11	nd	nd	nd	nd	nd	nd	nd	nd
12	36.4	35.8	34.5	nd	34.4	34.9	34.1	33.9
13	77.6	75.9	77.6	75.8	77.4	76.1	77.6	75.5
14	36.8	33.3	36.0	nd	35.7	32.8	36.5	36.2
15	26.4	26.4	26.6	26.5	26.6	26.6	26.4	23.8
16	33.0	33.0	32.9	33.0	33.0	33.0	33.0	33.0
17	23.8	23.8	23.8	23.8	23.8	23.8	23.8	23.8
18	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5

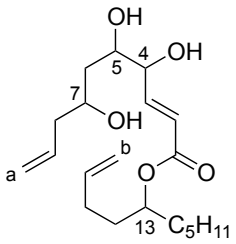
[a] Measured at 125 MHz
[b] nd = not determined

Table S4: Optical rotation measurements of all 16 lactones 1

Isomer	*c* (g/100 mL)	$[\alpha]_D^a$
(4S,5S,7R,13R)-**1**	0.54	−9.43
(4R,5R,7S,13S)-**1**	0.89	+11.3
(4S,5S,7S,13R)-**1**	0.77	−18.8
(4R,5R,7R,13S)-**1**	0.32	+16.5
(4R,5R,7R,13R)-**1**	1.25	+24.8
(4S,5S,7S,13S)-**1**	0.83	−25.9
(4R,5R,7S,13R)-**1**	0.38	+7.66
(4S,5S,7R,13S)-**1**	0.27	−4.04
(4S,5R,7R,13R)-**1**	0.55	+15.5
(4R,5S,7S,13S)-**1**	0.35	−13.8
(4S,5R,7S,13R)-**1**	0.54	+1.66
(4R,5S,7R,13S)-**1**	0.70	−2.14
(4R,5S,7R,13R)-**1**	0.27	+5.15
(4S,5R,7S,13S)-**1**	0.21	−2.93
(4S,5R,7S,13R)-**1**	0.24	−38.6
(4S,5R,7R,13S)-**1**	0.67	+38.7

[a] Measured at the same temperature in absolute MeOH

Table S5: ^{1}H NMR data (600 MHz) for the full ring-open 13*S*-16 enantioseries in d_4-MeOD



C no.	(4*S*,5*S*,7*R*,13*S*)-**16**	(4*S*,5*S*,7*S*,13*S*)-**16**	(4*R*,5*R*,7*R*,13*S*)-**16**	(4*R*,5*R*,7*S*,13*S*)-**16**
2	6.10 (dd, 15.7, 1.7, 1H)	6.11 (dd, 15.7, 1.8, 1H)	6.11 (dd, 15.7, 1.7, 1H)	6.11 (dd, 15.7, 1.7, 1H)
3	7.05 (dd, 15.7, 4.7, 1H)	7.05 (dd, 15.7, 4.6, 1H)	7.05 (dd, 15.7, 4.6, 1H)	7.05 (dd, 15.7, 4.7, 1H)
4	4.19 (td, 4.7, 1.7, 1H)	4.22 (td, 4.5, 1.8, 1H)	4.22 (td, 4.4, 1.8, 1H)	4.19 (td, 4.7, 1.7, 1H)
5	3.87 (m, 2H)	3.82 (quint, 4.3, 1H)	3.82 (quint, 4.4 Hz, 1H)	3.88 (m, 2H)
6	1.54 (m, 2H)	1.74 (dt, 14.2, 4.4, 1H) 1.55 (dt, 17.2, 8.7, 1H)	1.74 (dt, 14.1, 4.4, 1H) 1.54 (dt, 14.1, 8.7, 1H)	1.55 (m, 2H)
7	3.87 (m, 2H)	3.87 (m, 1H)	3.87 (m, 1H)	3.88 (m, 2H)
8	2.24 (m, 2H)	2.25 (m, 2H)	2.25 (m, 2H)	2.24 (m, 2H)
9	5.87 (ddt,17.2,10.2,7.0,1H)	5.87 (ddt,17.2,10.2,7.0,1H)	5.87 (ddt,17.2,10.2,7.0,1H)	5.87 (ddt,17.2,10.2,7.0,1H)
10	5.82 (ddt,16.9,10.2,6.7,1H)	5.82 (ddt,16.9,10.2,6.7,1H)	5.82 (ddt,16.9,10.2,6.7,1H)	5.82 (ddt,16.9,10.2,6.7,1H)
11	2.07 (m, 2H)	2.08 (m, 2H)	2.08 (m, 2H)	2.08 (m, 2H)
12	1.68 (m, 2H)	1.67 (m, 2H)	1.68 (m, 2H)	1.68 (m, 2H)
13	5.02 (m, 1H)	5.00 (m, 1H)	5.01 (m, 1H)	5.00 (m, 1H)
14	1.58 (m, 2H)	1.59 (m, 2H)	1.59 (m, 2H)	1.58 (m, 2H)
15	1.32 (m, 2H)	1.32 (m, 2H)	1.32 (m, 2H)	1.32 (m, 2H)
16	1.32 (m, 2H)	1.32 (m, 2H)	1.32 (m, 2H)	1.32 (m, 2H)
17	1.32 (m, 2H)	1.32 (m, 2H)	1.32 (m, 2H)	1.32 (m, 2H)
18	0.90 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)	0.90 (t, 6.9, 3H)
a	5.02 (m, 2H)	5.00 (m, 2H)	5.01 (m, 2H)	5.00 (m, 2H)
b	5.02 (m, 2H)	5.00 (m, 2H)	5.01 (m, 2H)	5.00 (m, 2H)

Table S6: ^{13}C NMR data (125 MHz) for the ring-open 13*S*-16 enantioseries in d_4-MeOD

See Table S5 structure for numbering

C no.	(4*S*,5*S*,7*R*,13*S*)-**16**	(4*S*,5*S*,7*S*,13*S*)-**16**	(4*R*,5*R*,7*R*,13*S*)-**16**	(4*R*,5*R*,7*S*,13*S*)-**16**
1	168.1	168.1	168.1	168.1
2	122.8	122.8	122.8	122.8
3	149.8	149.9	149.9	149.8
4	75.5	74.7	74.7	75.5
5	71.8	70.9	70.9	71.8
6	40.6	39.8	39.8	40.6
7	68.8	73.8	73.8	68.8
8	43.9	43.1	43.1	44.0
9	136.5	136.2	136.2	136.5
10	139.2	139.2	139.2	139.2
11	30.9	30.9	31.0	31.0
12	34.8	34.8	34.8	34.8
13	75.2	75.2	75.2	75.2
14	35.4	35.4	35.4	35.4
15	26.2	26.2	26.2	26.2
16	32.9	32.9	32.9	32.9
17	23.8	23.7	23.8	23.8
18	14.5	14.5	14.5	14.5
a	117.5	117.7	117.7	117.5
b	115.6	115.6	115.6	115.6

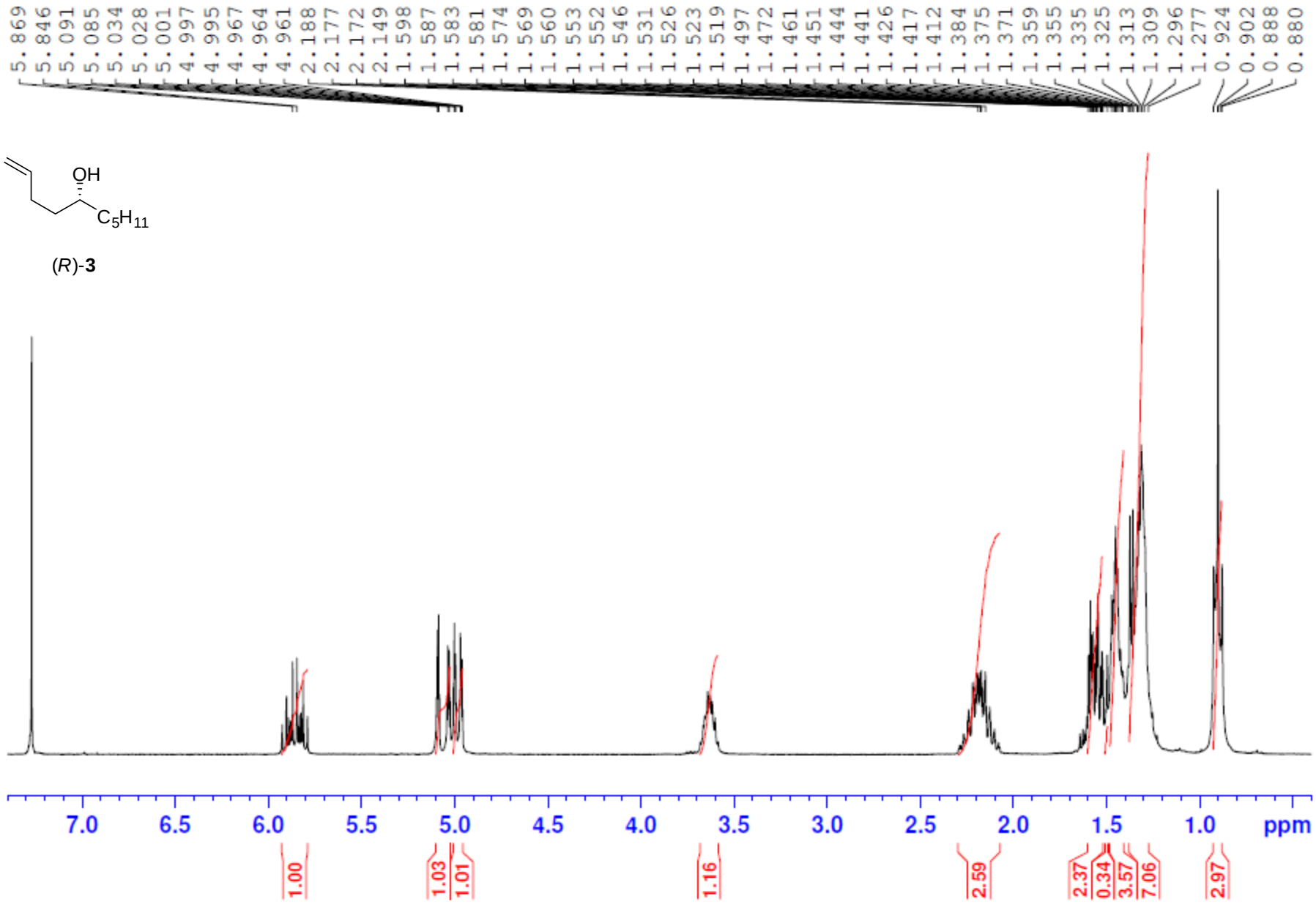
Table S7: Optical rotation measurements of the ring-open esters 16

Isomer	*c* (g/100 mL)	$[\alpha]_D^a$
(4S,5S,7R,13R)-**16**	1.08	−30.7
(4R,5R,7S,13S)-**16**	1.45	+33.2
(4S,5S,7S,13R)-**16**	0.83	−15.1
(4R,5R,7R,13S)-**16**	1.19	+15.2
(4R,5R,7R,13R)-**16**	1.02	**+**17.9
(4S,5S,7S,13S)-**16**	1.51	−13.3
(4R,5R,7S,13R)-**16**	1.02	+34.6
(4S,5S,7R,13S)-**16**	1.20	−23.0

[a] Measured at room temperature in absolute MeOH

References

1. Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307-1315.
2. Eaborn, C.; El-Hamruni, S. M.; Hill, M. S.; Hitchcock, P. B.; Smith, J. D. *J. Chem. Soc., Dalton Trans.* **2002**, *2002*, 3975-3979.
3. Hoye, T. R.; Jeffrey, C. S.; Shao, F. *Nat. Protoc.* **2007**, *2*, 2451-2458.
4. Kagawa, N.; Ihara, M.; Toyota, M. *J. Org. Chem.* **2006**, *71*, 6796-6805.
5. Furstner, A.; Kattnig, E.; Lepage, O. *J. Am. Chem. Soc.* **2006**, *128*, 9194-9204.
6. Blanchette, M. A.; Choy, W.; Davis, J. T.; Essenfeld, A. P.; Masamune, S.; Roush, W. R.; Sakai, T. *Tet. Lett.* **1984**, *25*, 2183-2186.
7. Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480-2482.
8. Barbat, J.; Gelas, J.; Horton, D. *Carbohydr. Res.* **1983**, *116*, 312-316.
9. Geng, X.; Danishefsky, S. J. *Org. Lett.* **2004**, *6*, 413-416.
10. Yang, S.-W.; Chan, T.-M.; Terracciano, J.; Loebenberg, D.; Patel, M.; Chu, M. *J. Antibiot.* **2005**, *58*, 535-538.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5.085
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5.028
5.001
4.997
4.995
4.967
4.964
4.961
2.188
2.177
2.172
2.149
1.598
1.587
1.583
1.581
1.574
1.569
1.560
1.553
1.552
1.546
1.531
1.526
1.523
1.519
1.497
1.472
1.461
1.451
1.444
1.441
1.426
1.417
1.412
1.384
1.375
1.371
1.359
1.355
1.335
1.325
1.313
1.309
1.296
1.277
0.924
0.902
0.888
0.880
OH
C5H11
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
ppm
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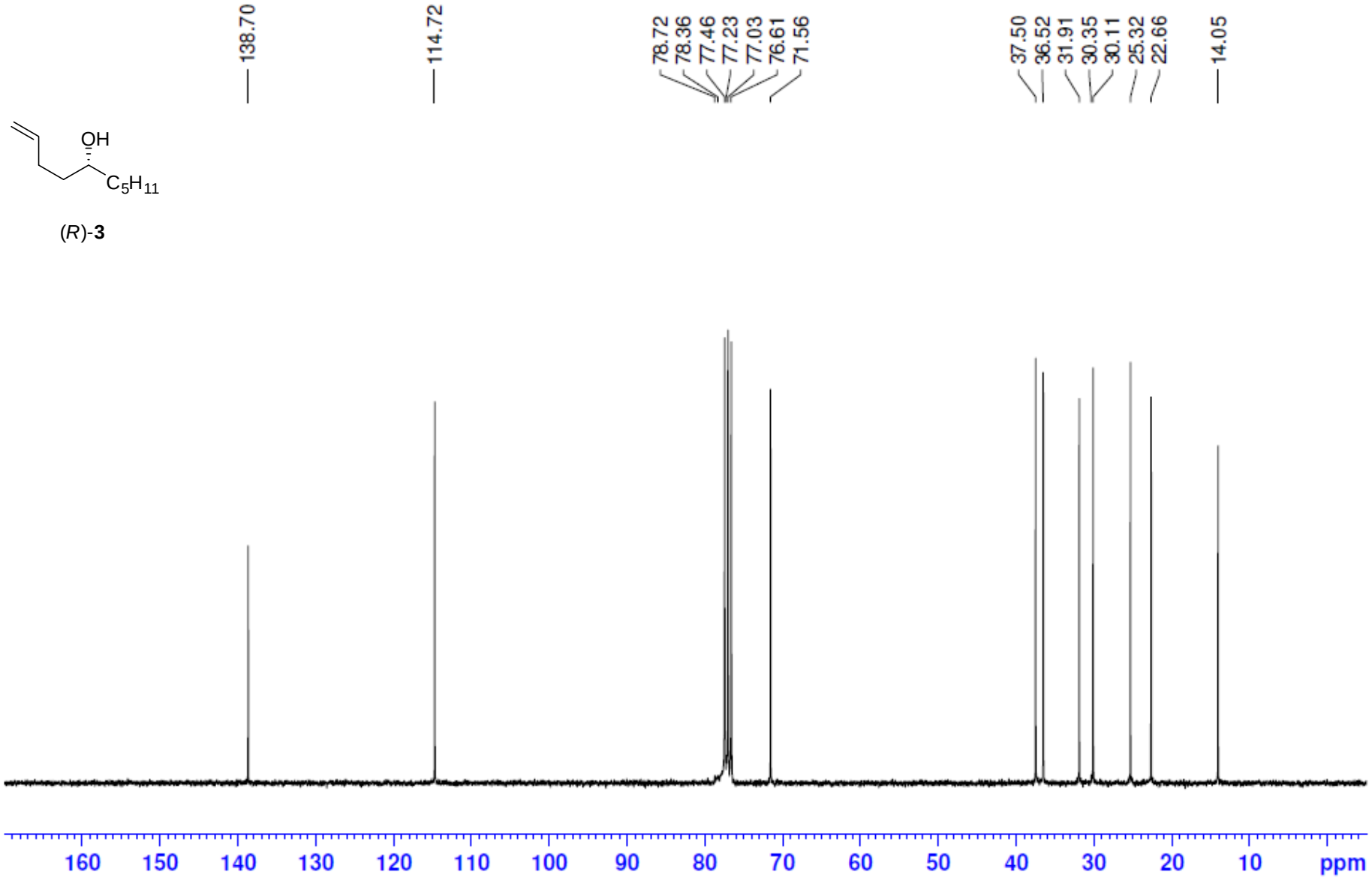
1.03
1.01
1.16
2.59
2.37
0.34
3.57
7.06
2.97

(*R*)-**3**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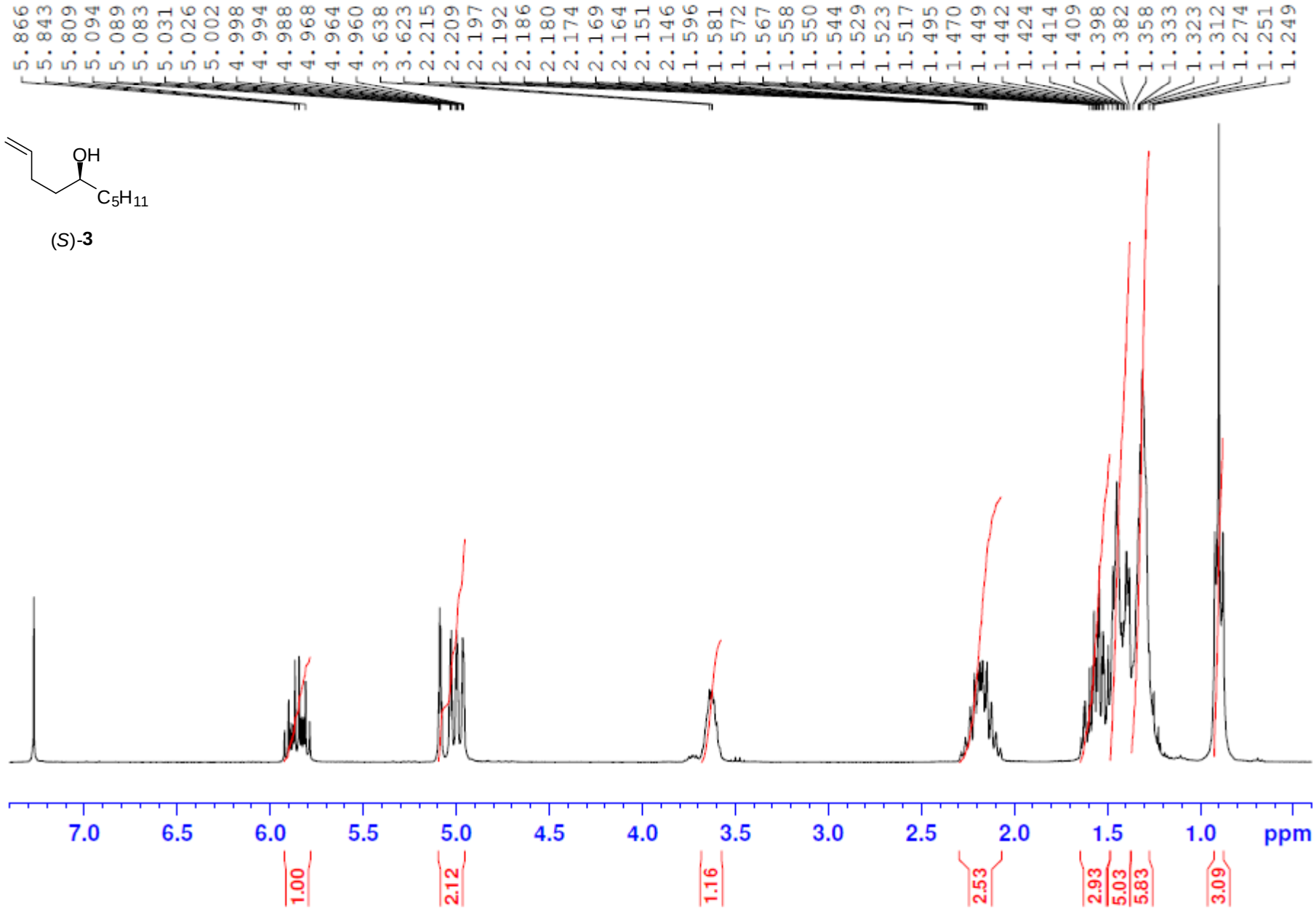
114.72
78.72
78.36
77.46
77.23
77.03
76.61
71.56
37.50
36.52
31.91
30.35
30.11
25.32
22.66
14.05
OH
C5H11
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(*R*)-**3**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5.809
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5.089
5.083
5.031
5.026
5.002
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4.994
4.988
4.968
4.964
4.960
3.638
3.623
2.215
2.209
2.197
2.192
2.186
2.180
2.174
2.169
2.164
2.151
2.146
1.596
1.581
1.572
1.567
1.558
1.550
1.544
1.529
1.523
1.517
1.495
1.470
1.449
1.442
1.424
1.414
1.409
1.398
1.382
1.358
1.333
1.323
1.312
1.274
1.251
1.249
OH
C5H11
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
ppm
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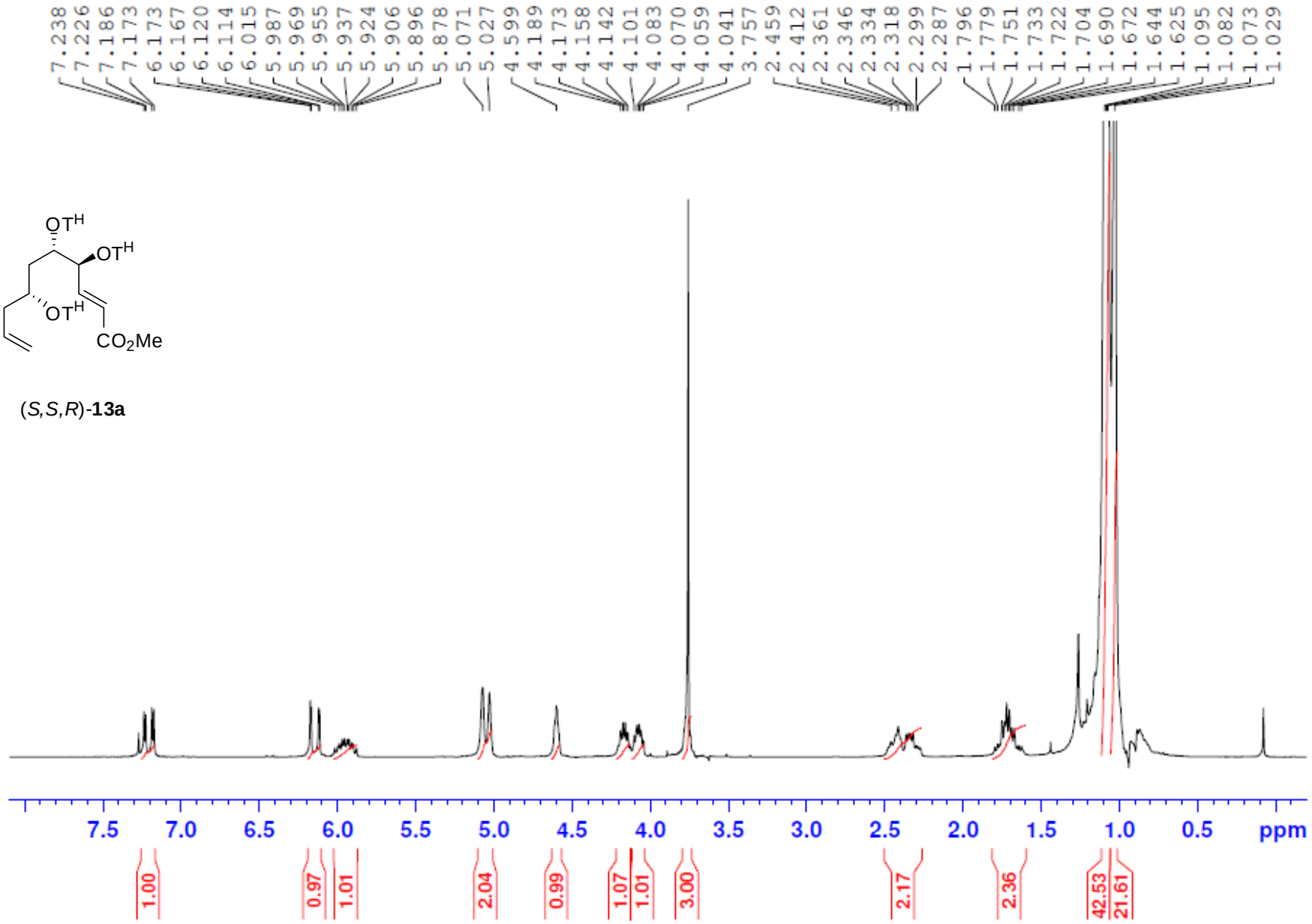
2.93
5.03
5.83
3.09

(*S*)-**3**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6.173
6.167
6.120
6.114
6.015
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5.955
5.937
5.924
5.906
5.896
5.878
5.071
5.027
4.599
4.189
4.173
4.158
4.142
4.101
4.083
4.070
4.059
4.041
3.757
2.459
2.412
2.361
2.346
2.334
2.318
2.299
2.287
1.796
1.779
1.751
1.733
1.722
1.704
1.690
1.672
1.644
1.625
1.095
1.082
1.073
1.029
OT^H
OT^H
OT^H
CO2Me
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
ppm
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0.97
1.01
2.04
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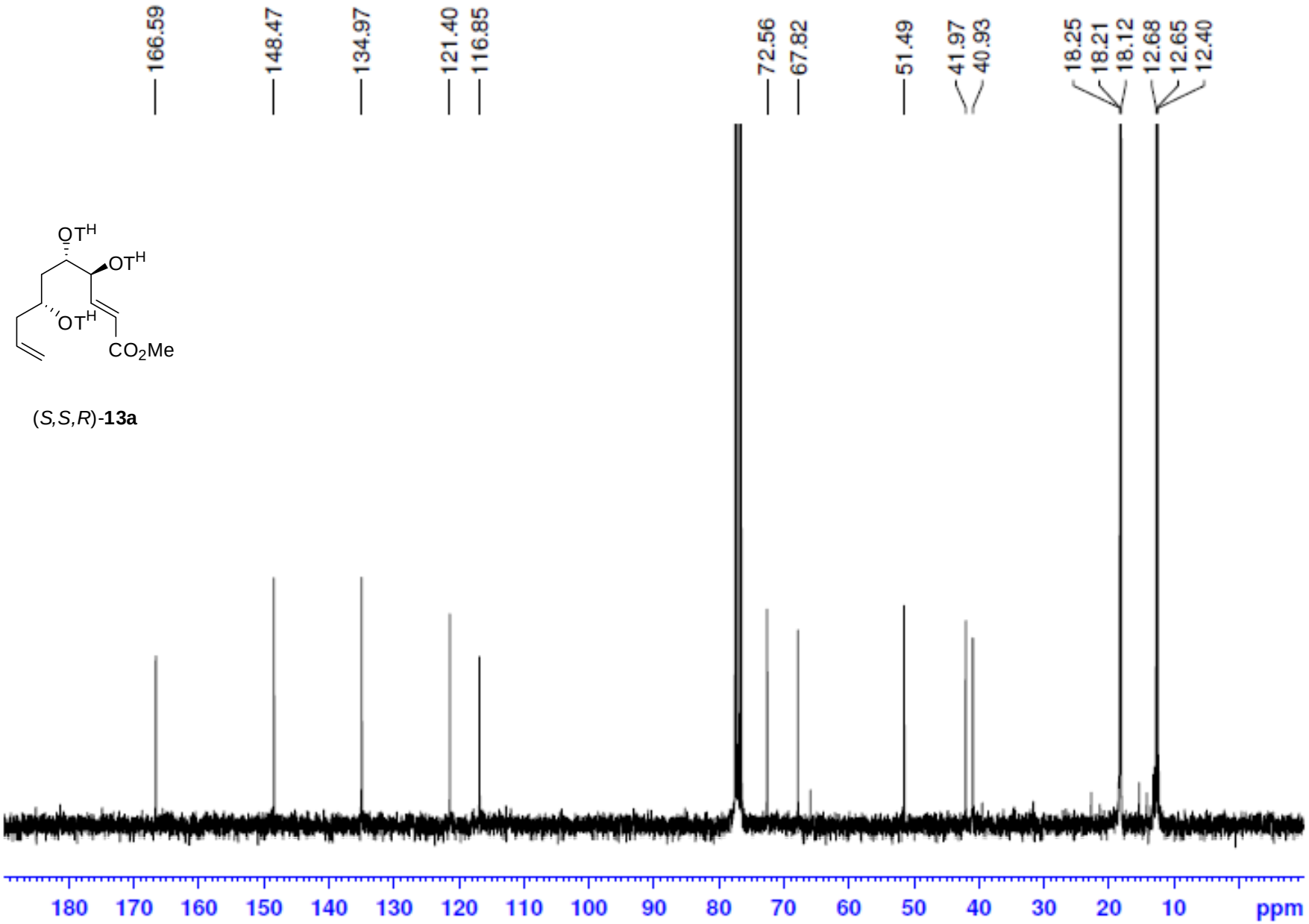
1.07
1.01
3.00
2.17
2.36
42.53
21.61

(*S*,*S*,*R*)-**13a**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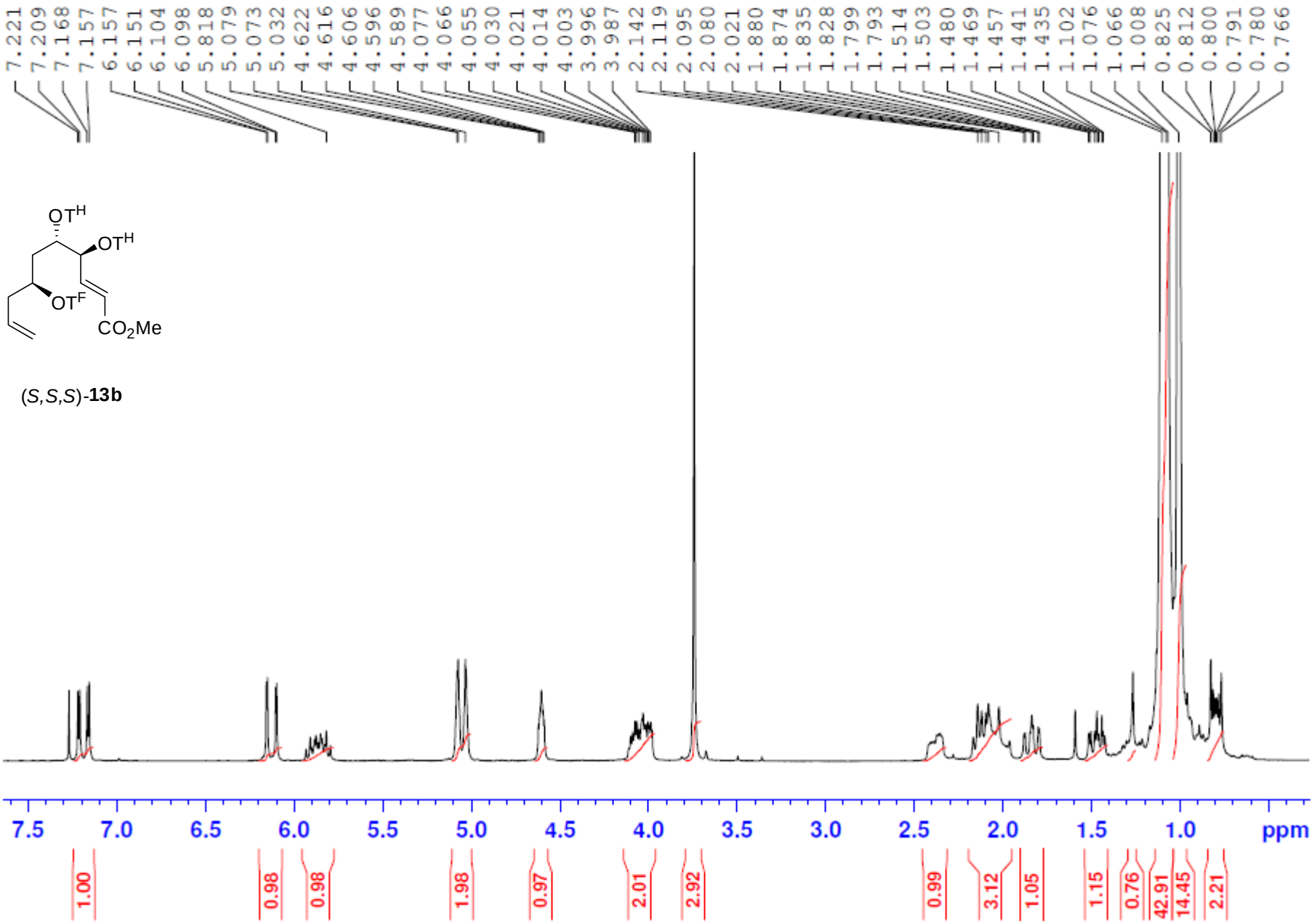
134.97
121.40
116.85
72.56
67.82
51.49
41.97
40.93
18.25
18.21
18.12
12.68
12.65
12.40
OT^H
OT^H
OT^H
CO2Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(*S*,*S*,*R*)-**13a**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6.151
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6.098
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5.079
5.073
5.032
4.622
4.616
4.606
4.596
4.589
4.077
4.066
4.055
4.030
4.021
4.014
4.003
3.996
3.987
2.142
2.119
2.095
2.080
2.021
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1.874
1.835
1.828
1.799
1.793
1.514
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1.480
1.469
1.457
1.441
1.435
1.102
1.076
1.066
1.008
0.825
0.812
0.800
0.791
0.780
0.766
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OT^H
OT^F
CO2Me
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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
ppm
1.00
0.98
0.98
1.98
0.97
2.01
2.92
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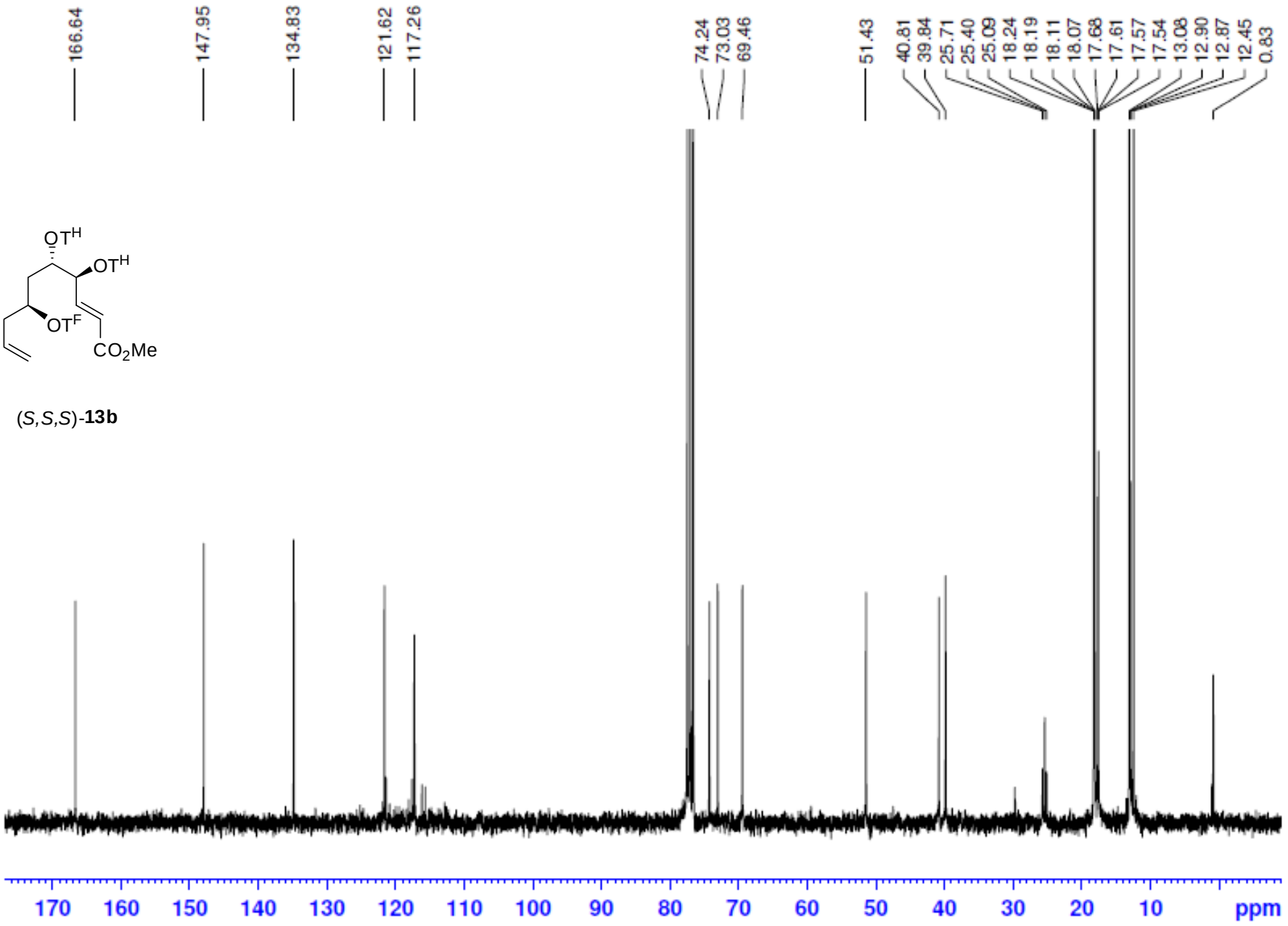
3.12
1.05
1.15
0.76
42.91
14.45
2.21

(*S*,*S*,*S*)-**13b**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117.26
74.24
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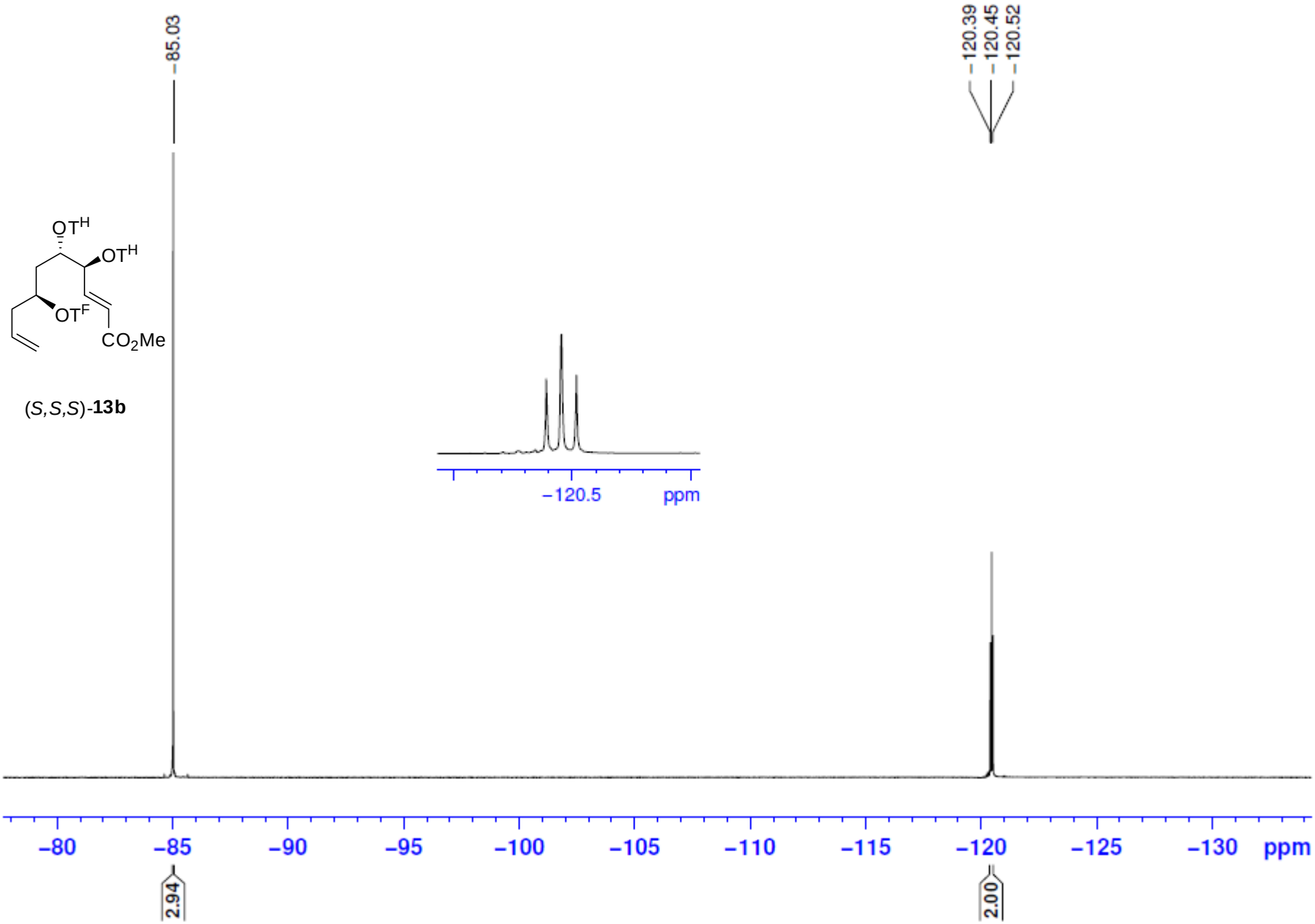
69.46
51.43
40.81
39.84
25.71
25.40
25.09
18.24
18.19
18.11
18.07
17.68
17.61
17.57
17.54
13.08
12.90
12.87
12.45
0.83
OT^H
OT^H
OT^F
CO2Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(*S*,*S*,*S*)-**13b**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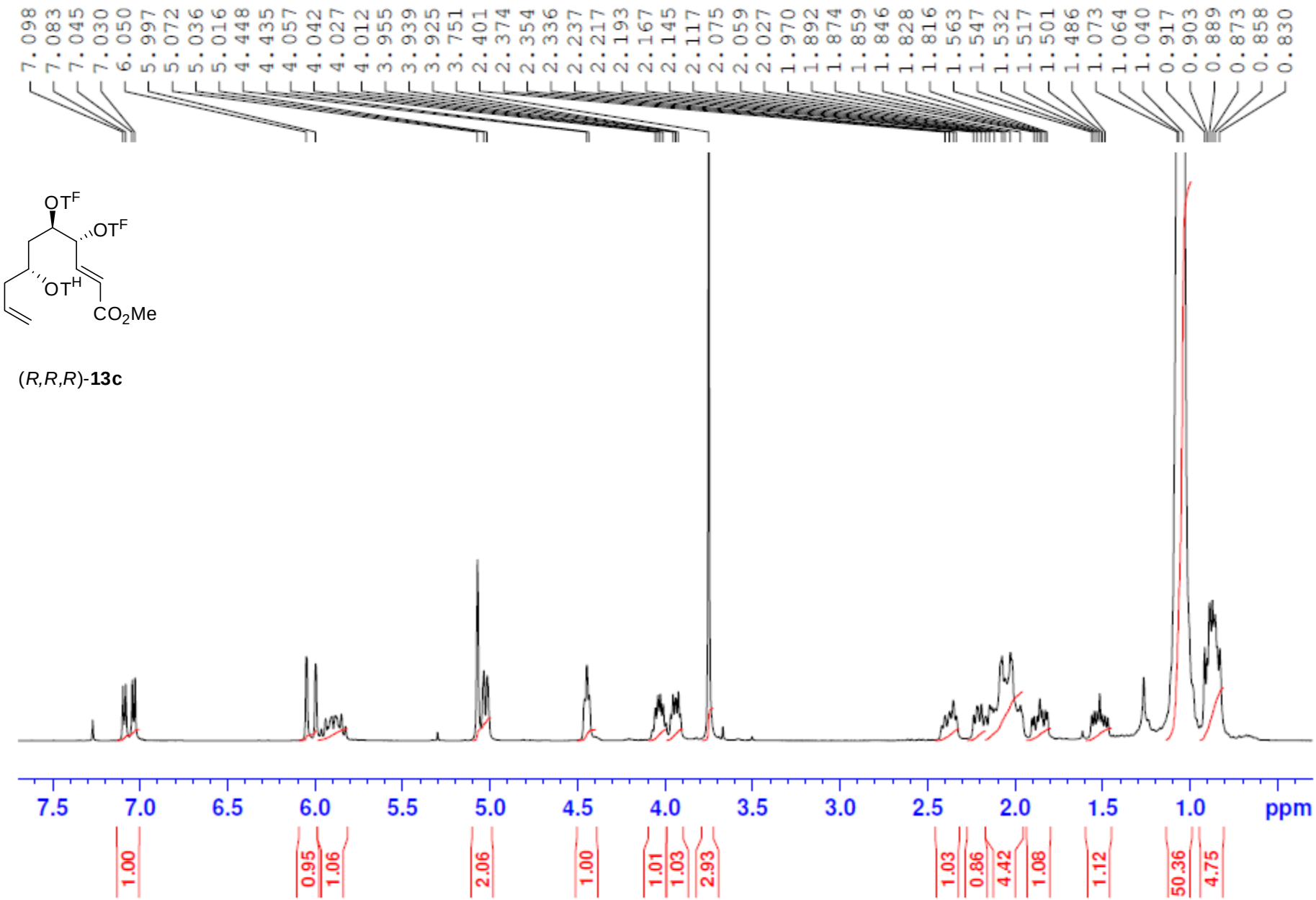
-120.45
-120.52
OT^H
OT^H
OT^F
CO2Me
(S,S,S)-13b
-120.5
ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
ppm
2.94
2.00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4.027
4.012
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3.939
3.925
3.751
2.401
2.374
2.354
2.336
2.237
2.217
2.193
2.167
2.145
2.117
2.075
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1.859
1.846
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1.547
1.532
1.517
1.501
1.486
1.073
1.064
1.040
0.917
0.903
0.889
0.873
0.858
0.830
OT^F
OT^F
OT^H
CO2Me
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
ppm
1.00
0.95
1.06
2.06
1.00
1.01
1.03
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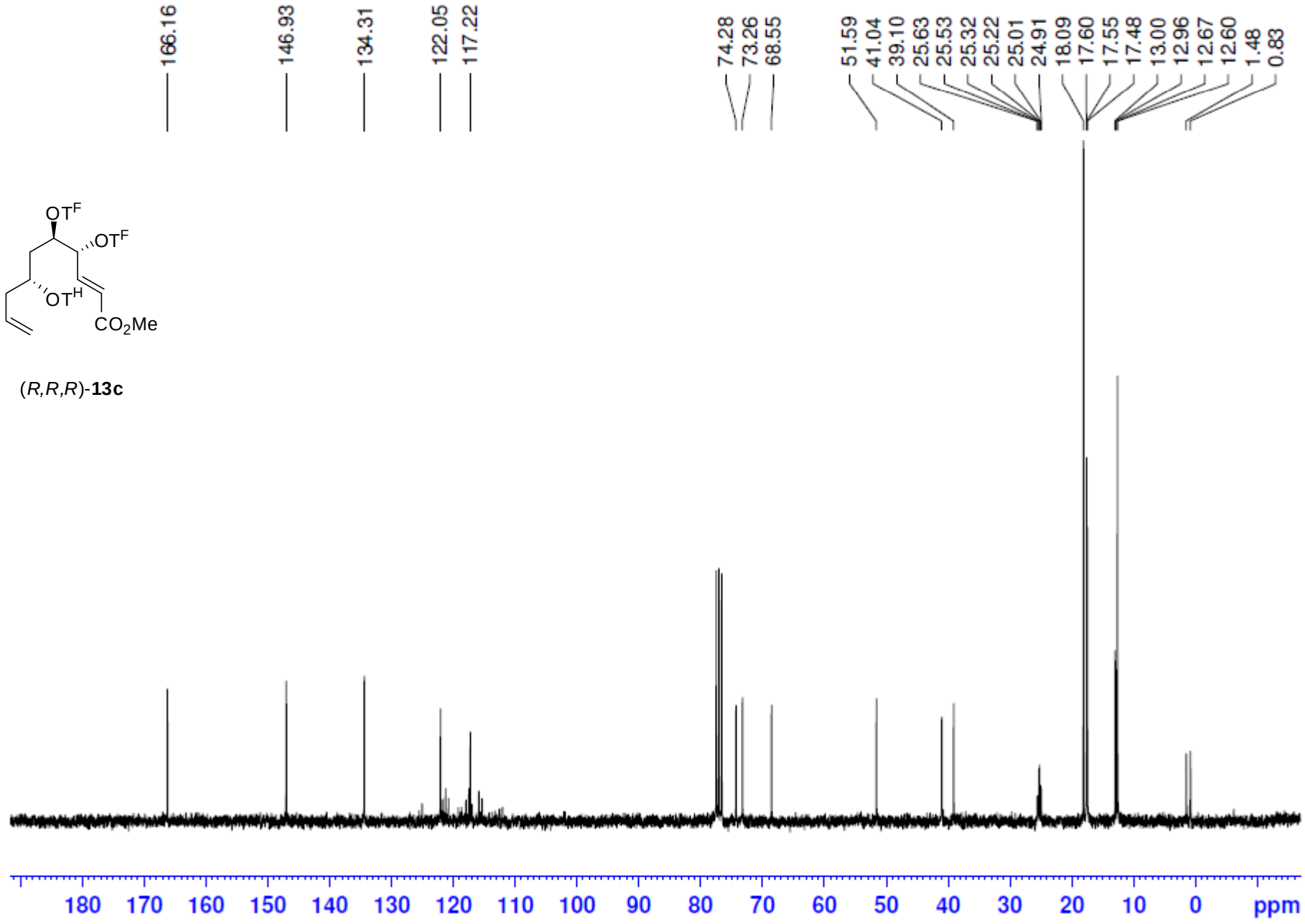
1.03
0.86
4.42
1.08
1.12
50.36
4.75

(*R,R,R*)-**13c**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74.28
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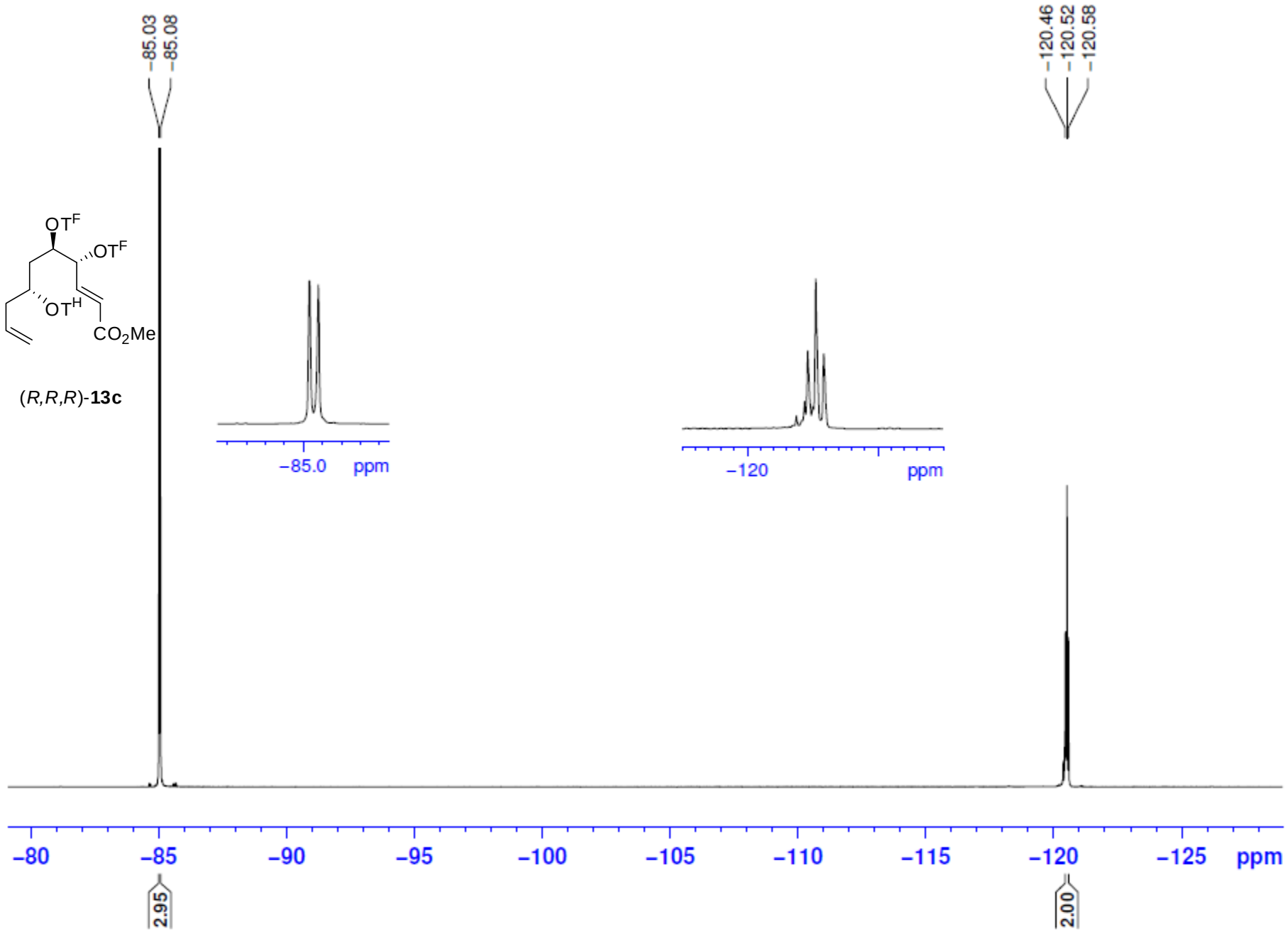
68.55
51.59
41.04
39.10
25.63
25.53
25.32
25.22
25.01
24.91
18.09
17.60
17.55
17.48
13.00
12.96
12.67
12.60
1.48
0.83
OT^F
OT^F
OT^H
CO2Me
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(*R,R,R*)-**13c**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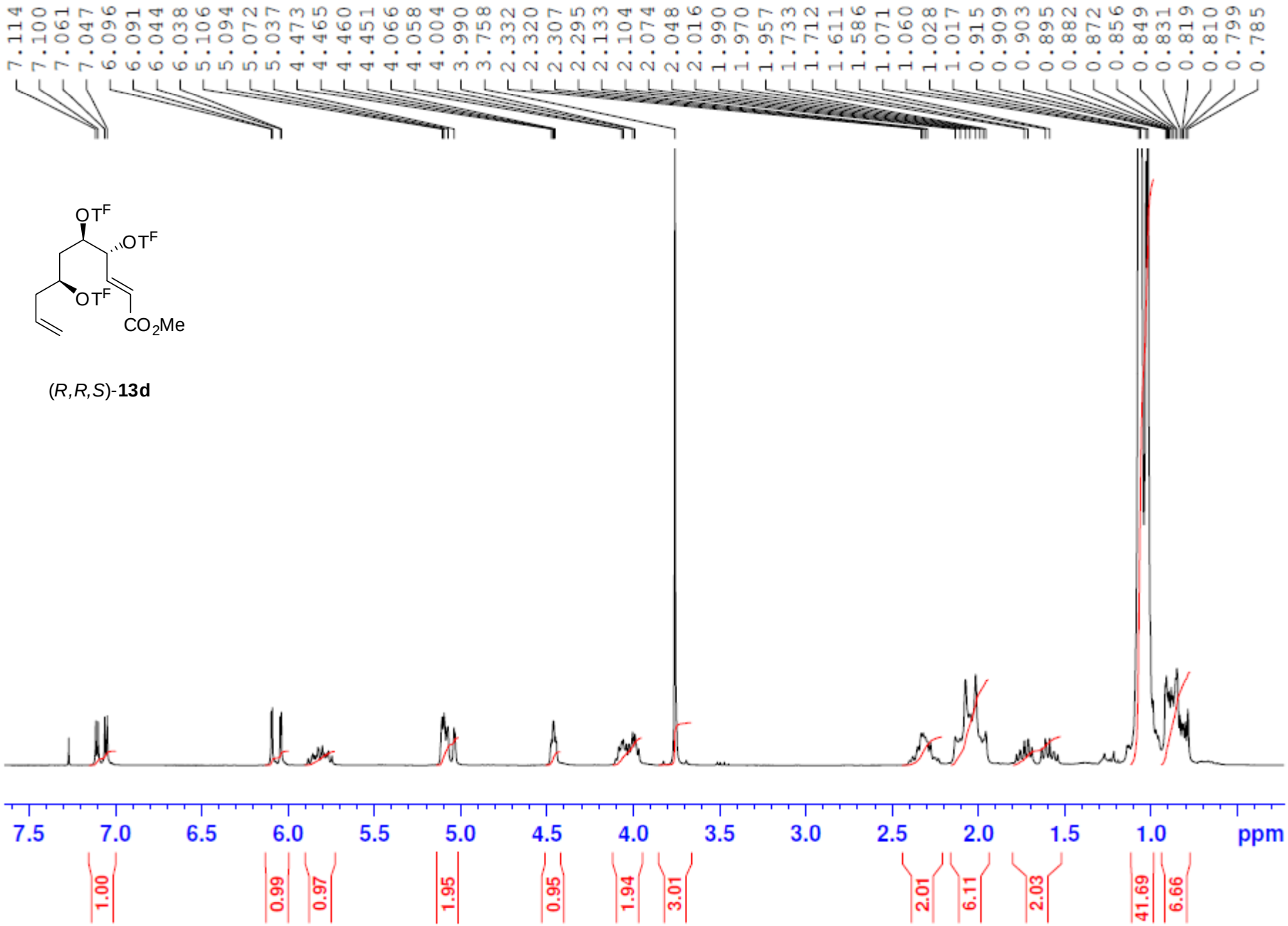
−120.46
−120.52
−120.58
OT^F
OT^F
OT^H
CO2Me
(R,R,R)-13c
−85.0 ppm
−120 ppm
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
ppm
2.95
2.00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6.038
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5.037
4.473
4.465
4.460
4.451
4.066
4.058
4.004
3.990
3.758
2.332
2.320
2.307
2.295
2.133
2.104
2.074
2.048
2.016
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1.957
1.733
1.712
1.611
1.586
1.071
1.060
1.028
1.017
0.915
0.909
0.903
0.895
0.882
0.872
0.856
0.849
0.831
0.819
0.810
0.799
0.785
OT^F
OT^F
OT^F
CO2Me
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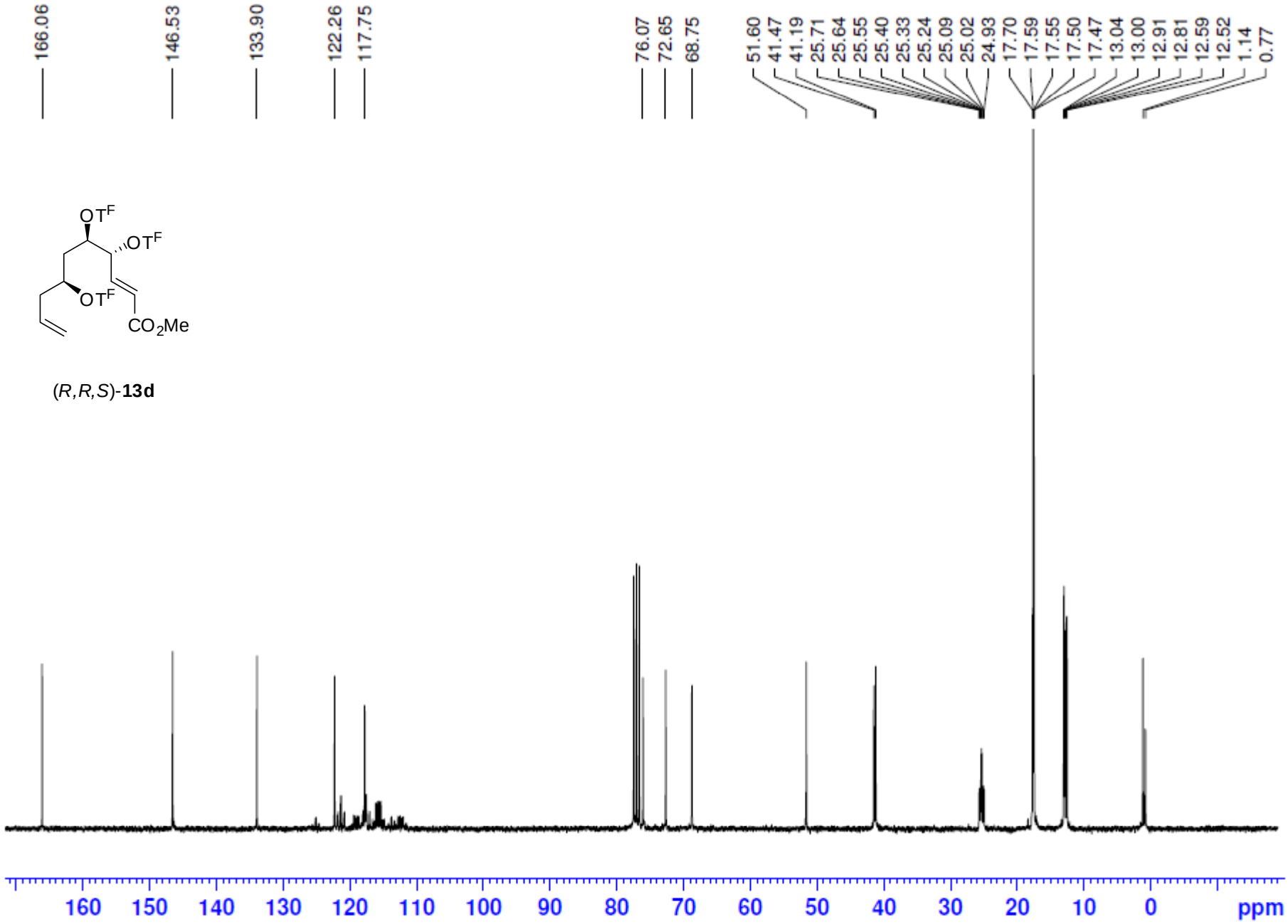
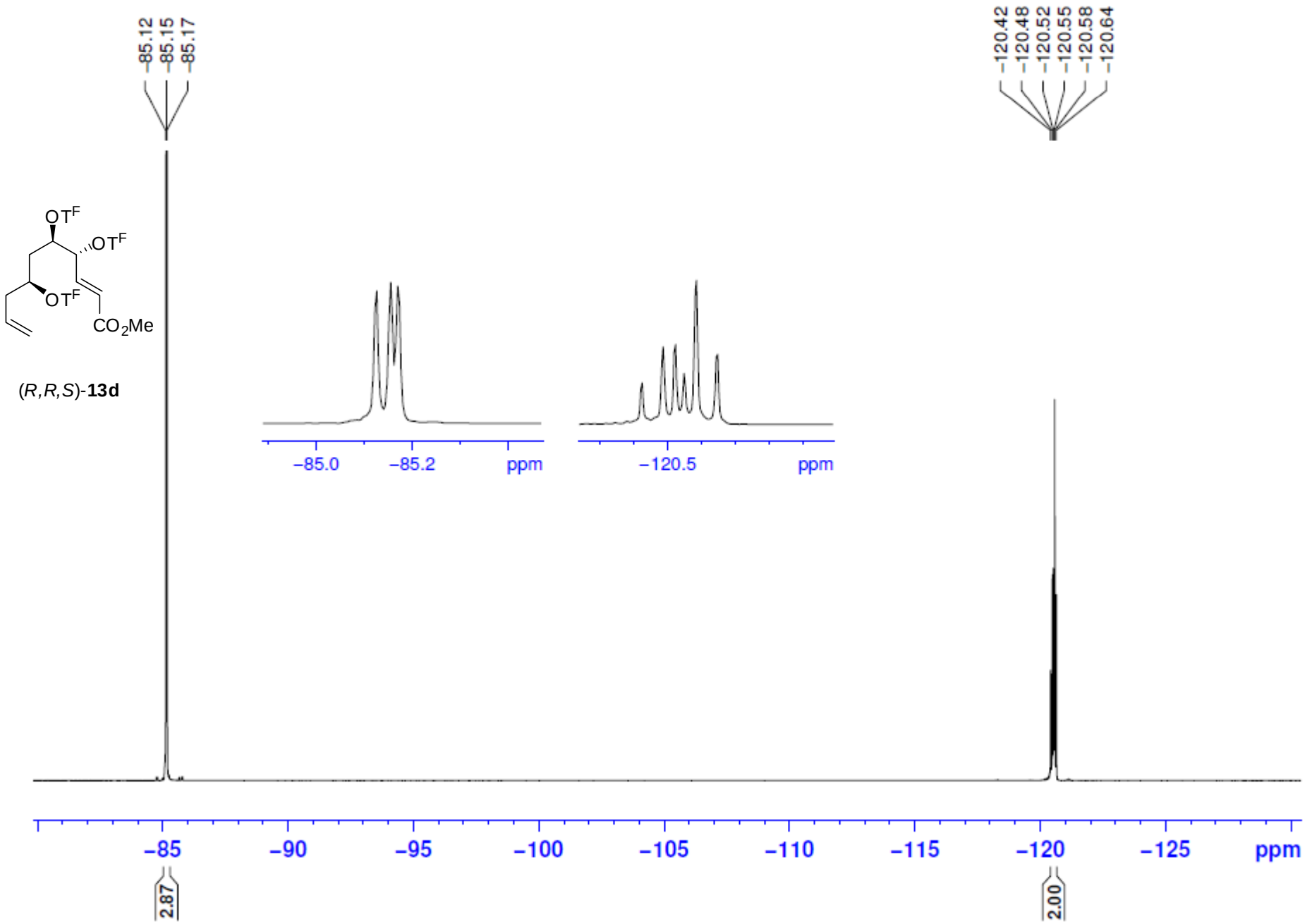
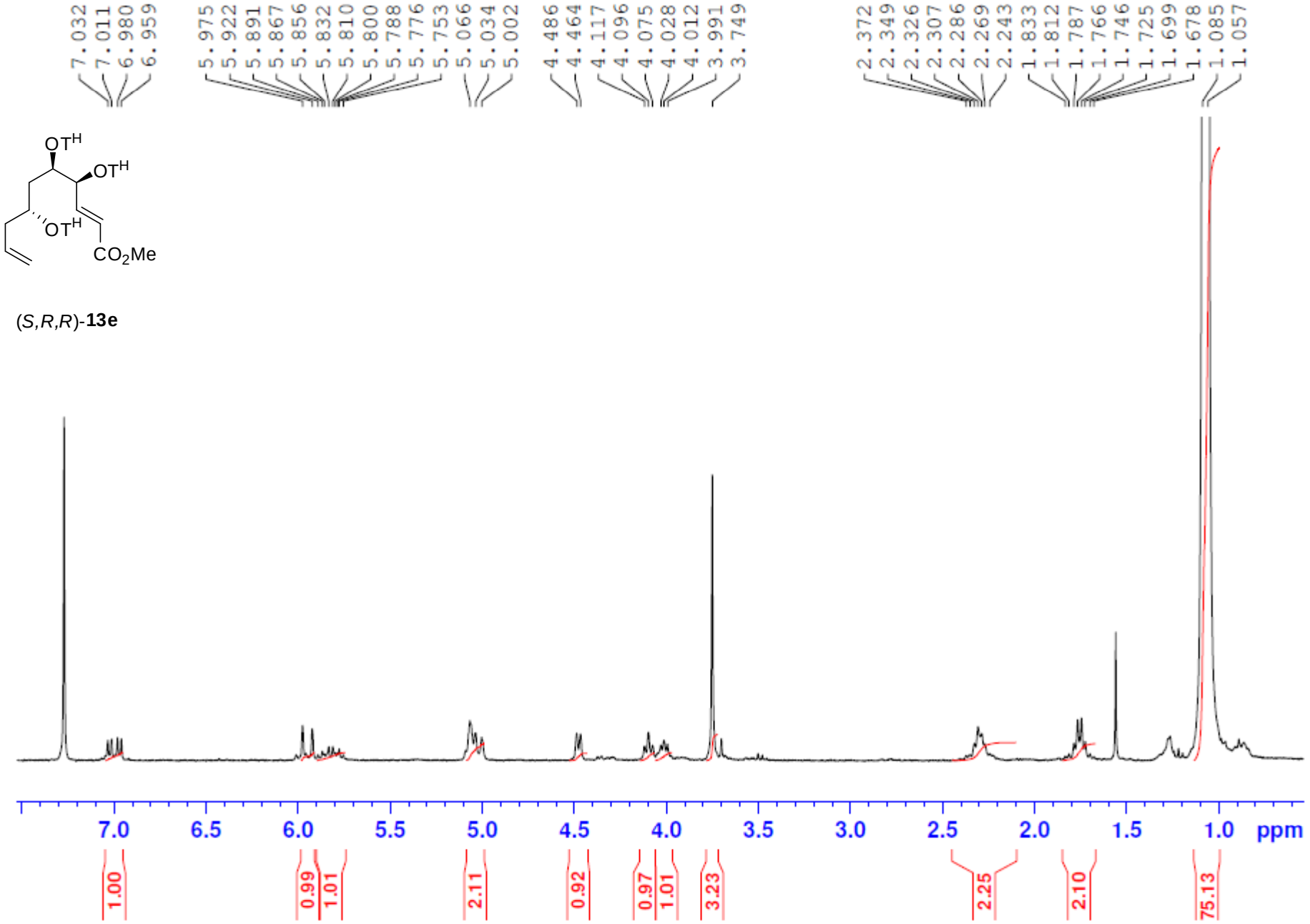
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
0.97
1.95
0.95
1.94
3.01
2.01
6.11
2.03
41.69
6.66

(*R*,*R*,*S*)-**13d**

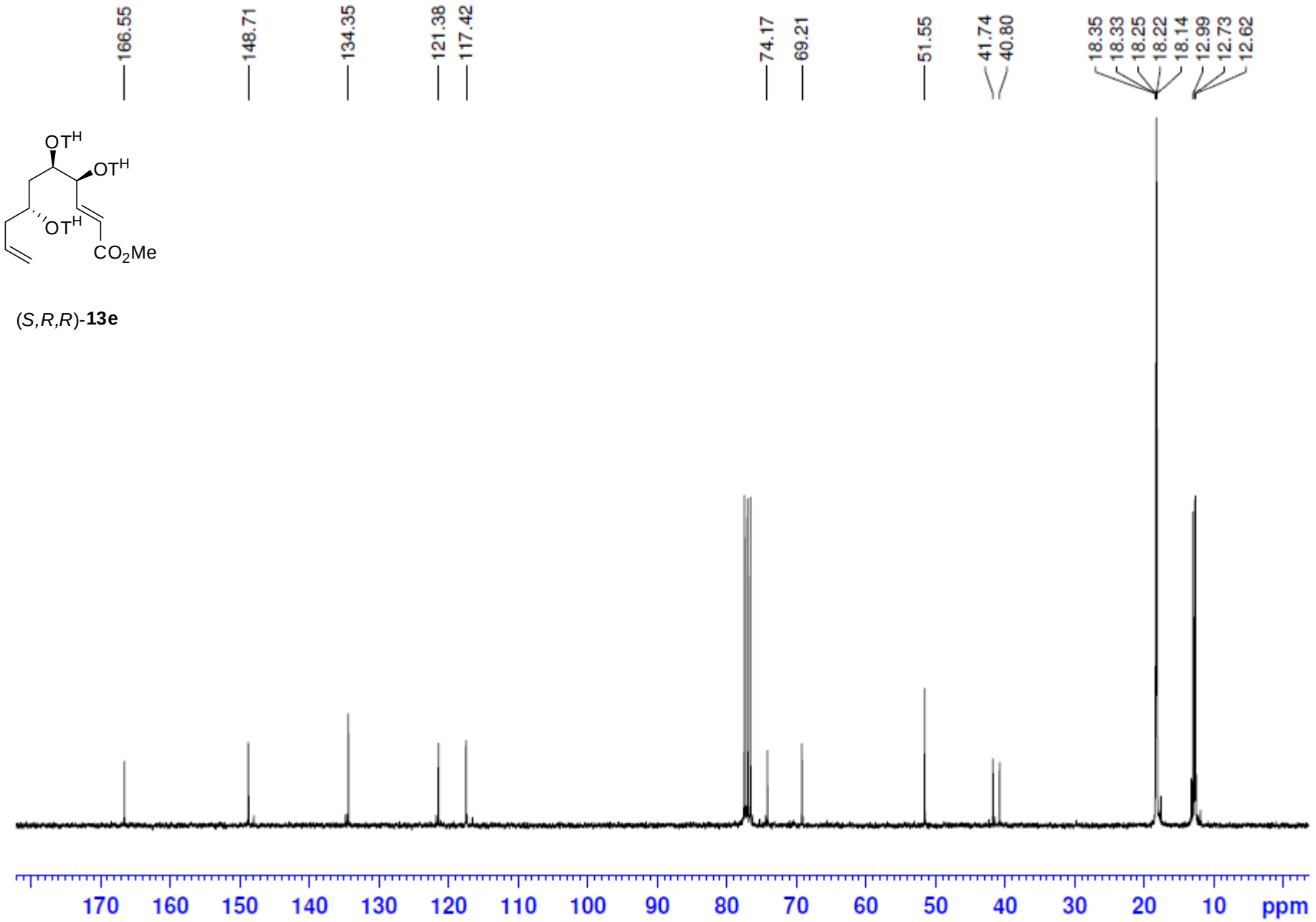

166.06
146.53
133.90
122.26
117.75
76.07
72.65
68.75
51.60
41.47
41.19
25.71
25.64
25.55
25.40
25.33
25.24
25.09
25.02
24.93
17.70
17.59
17.55
17.50
17.47
13.04
13.00
12.91
12.81
12.59
12.52
1.14
0.77
OT^F
OT^F
OT^F
CO2Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

(*R*,*R*,*S*)-**13d**

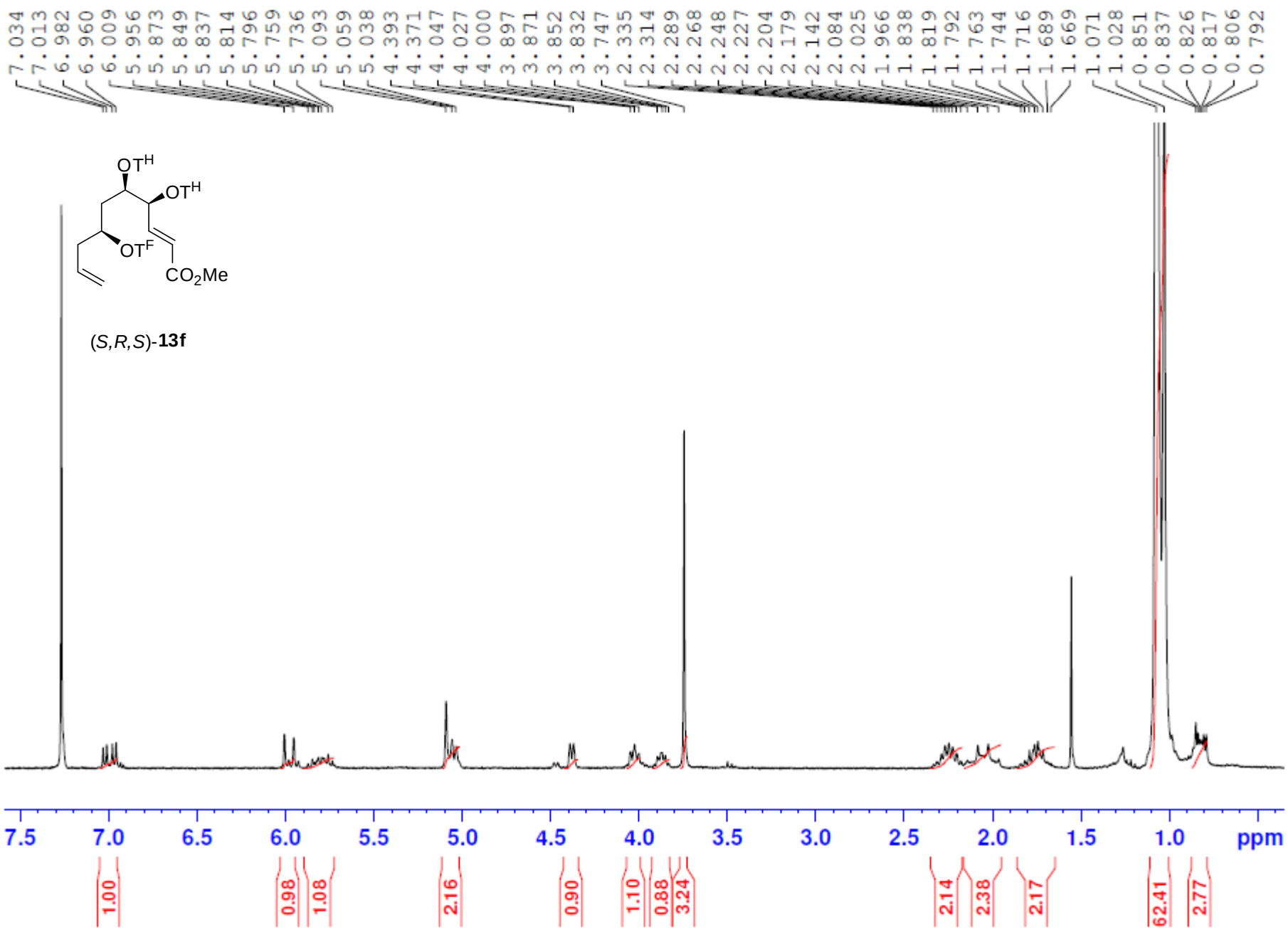

-85.12
-85.15
-85.17
-120.42
-120.48
-120.52
-120.55
-120.58
-120.64
OTF
OTF
OTF
CO2Me
(R,R,S)-13d
-85.0
-85.2
ppm
-120.5
ppm
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
2.87
2.00

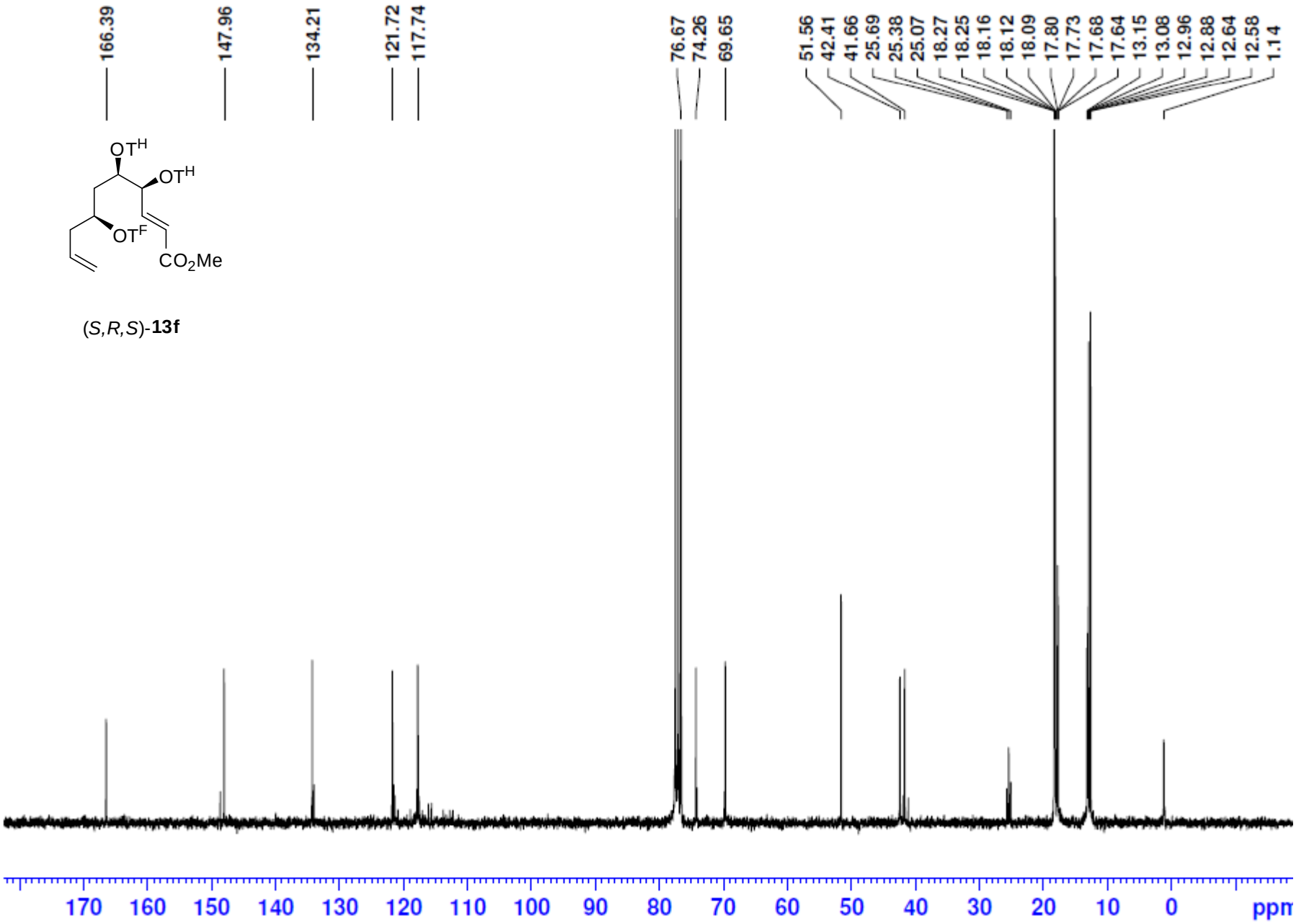

7.032
7.011
6.980
6.959
5.975
5.922
5.891
5.867
5.856
5.832
5.810
5.800
5.788
5.776
5.753
5.066
5.034
5.002
4.486
4.464
4.117
4.096
4.075
4.028
4.012
3.991
3.749
2.372
2.349
2.326
2.307
2.286
2.269
2.243
1.833
1.812
1.787
1.766
1.746
1.725
1.699
1.678
1.085
1.057
OT^H
OT^H
OT^H
CO2Me
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.99
1.01
2.11
0.92
0.97
1.01
3.23
2.25
2.10
75.13

(*S*,*R*,*R*)-**13e**

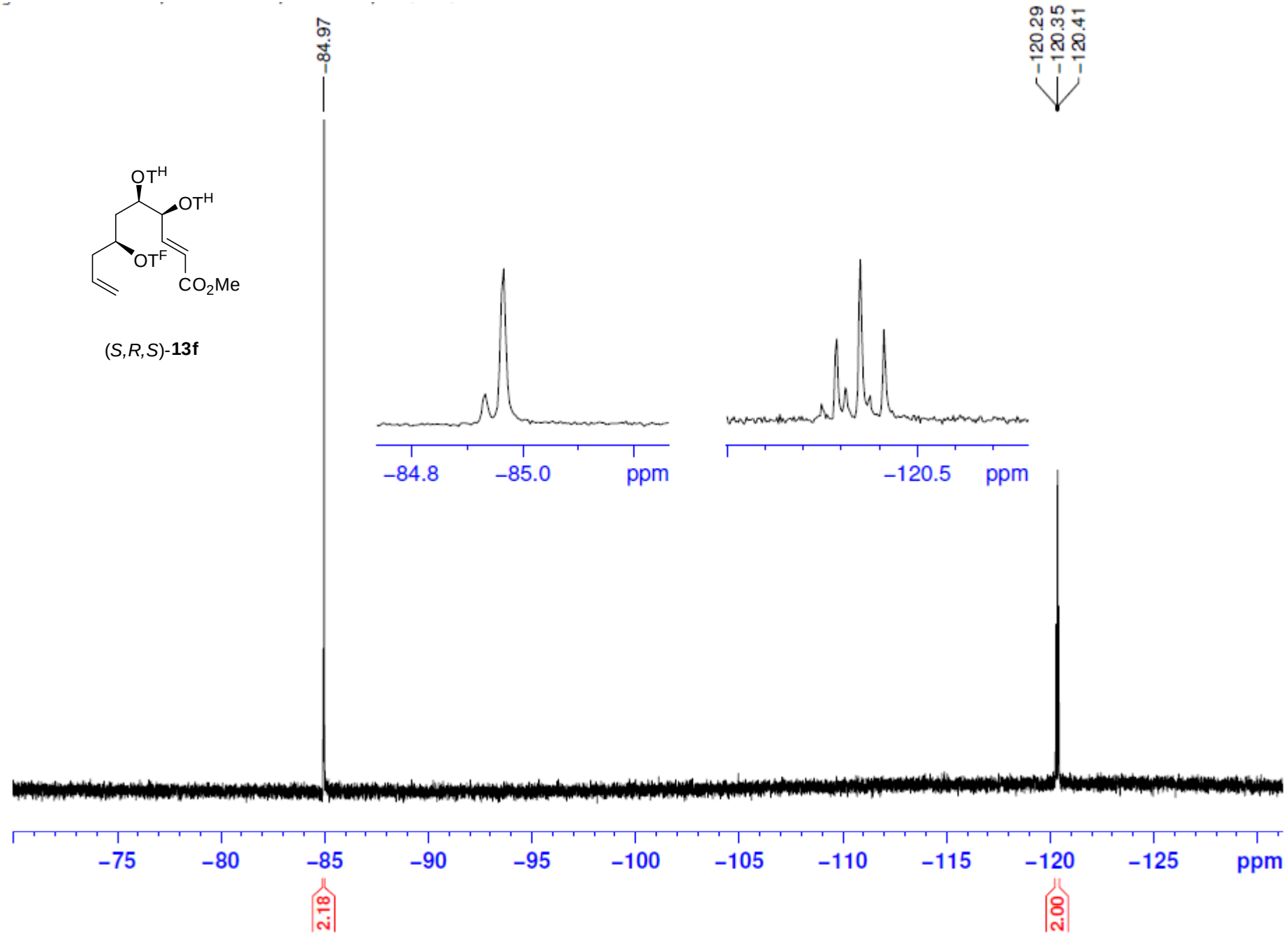

166.55
148.71
134.35
121.38
117.42
74.17
69.21
51.55
41.74
40.80
18.35
18.33
18.25
18.22
18.14
12.99
12.73
12.62
OT^H
OT^H
OT^H
CO2Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

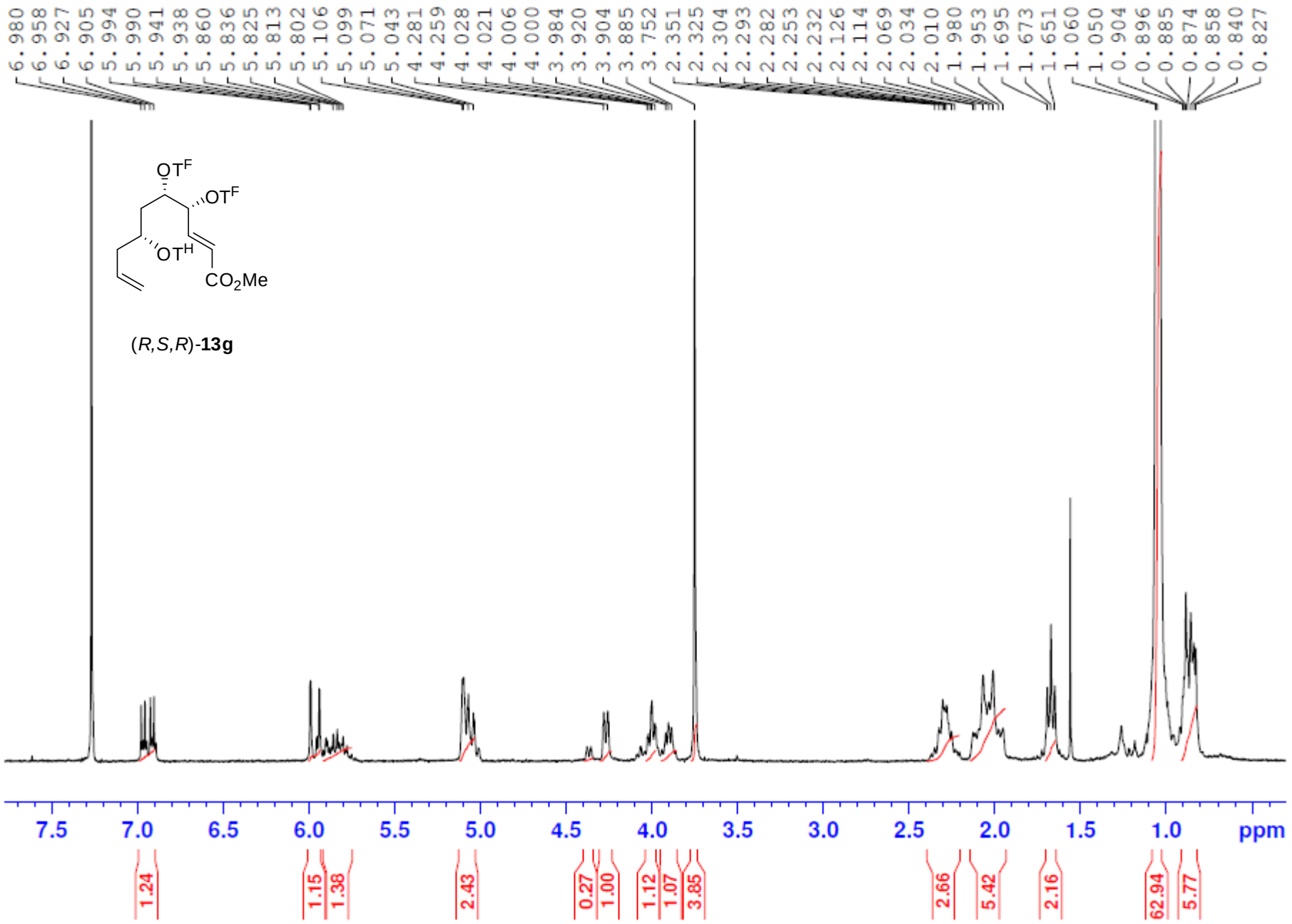
(*S*,*R*,*R*)-**13e**

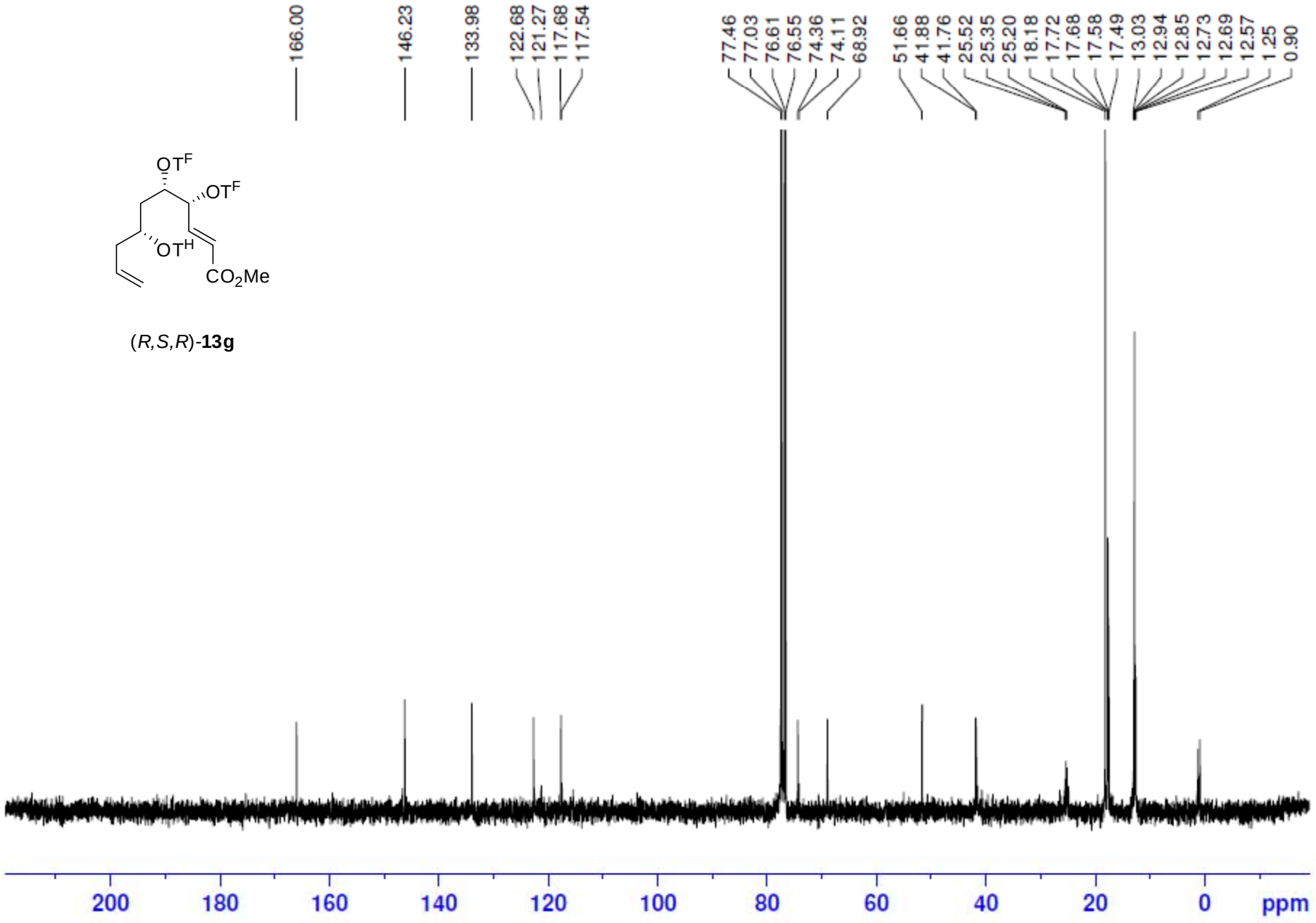

7.034
7.013
6.982
6.960
6.009
5.956
5.873
5.849
5.837
5.814
5.796
5.759
5.736
5.093
5.059
5.038
4.393
4.371
4.047
4.027
4.000
3.897
3.871
3.852
3.832
3.747
3.335
2.314
2.289
2.268
2.248
2.227
2.204
2.179
2.142
2.084
2.025
1.966
1.838
1.819
1.792
1.763
1.744
1.716
1.689
1.669
1.071
1.028
0.851
0.837
0.826
0.817
0.806
0.792
OT^H
OT^H
OT^F
CO2Me
(S,R,S)-13f
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
ppm
1.00
0.98
1.08
2.16
0.90
1.10
0.88
3.24
2.14
2.38
2.17
62.41
2.77


166.39
147.96
134.21
121.72
117.74
76.67
74.26
69.65
51.56
42.41
41.66
25.69
25.38
25.07
18.27
18.25
18.16
18.12
18.09
17.80
17.73
17.68
17.64
13.15
13.08
12.96
12.88
12.64
12.58
1.14
OT^H
OT^H
OT^F
CO2Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

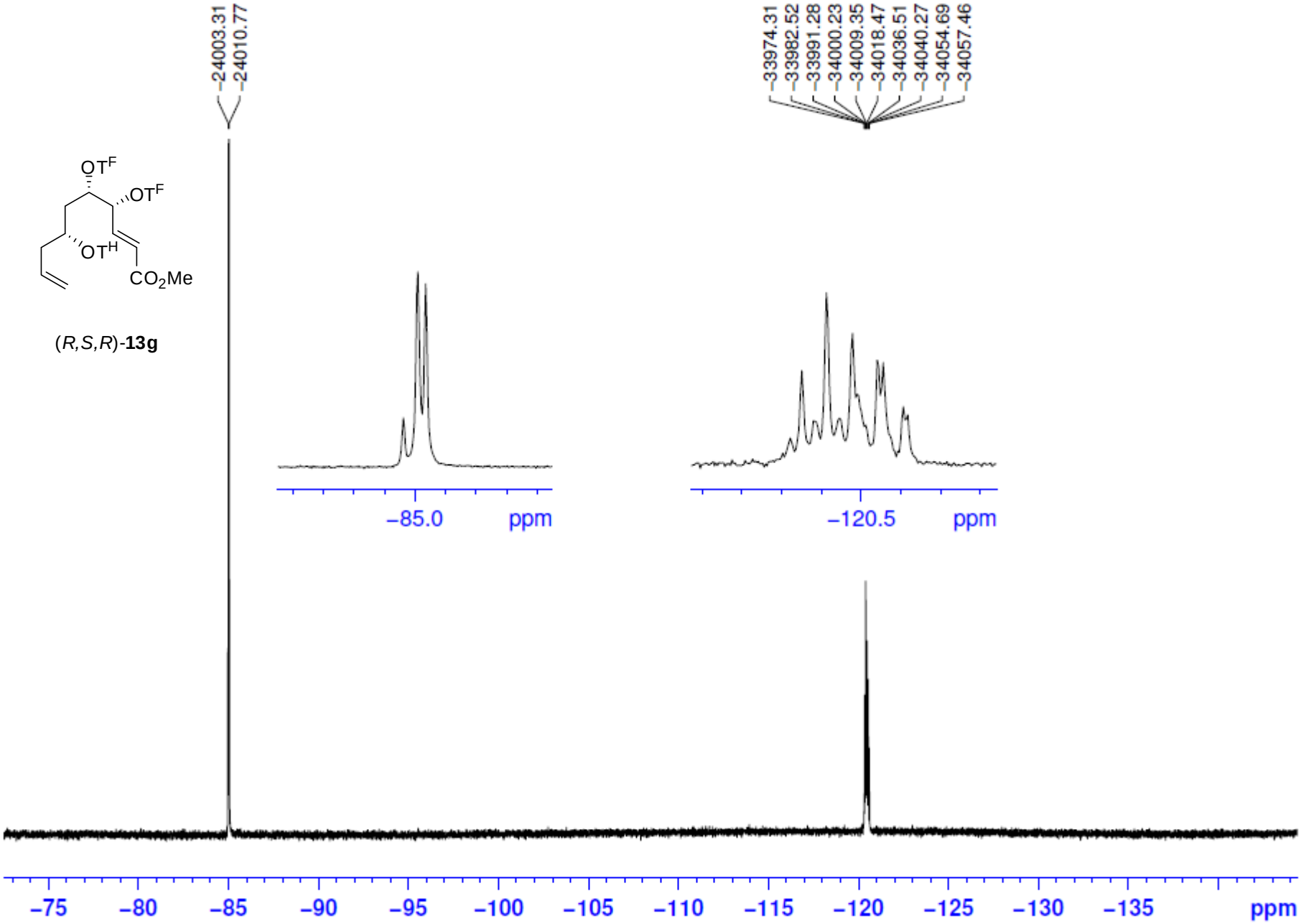
(*S*,*R*,*S*)-**13f**

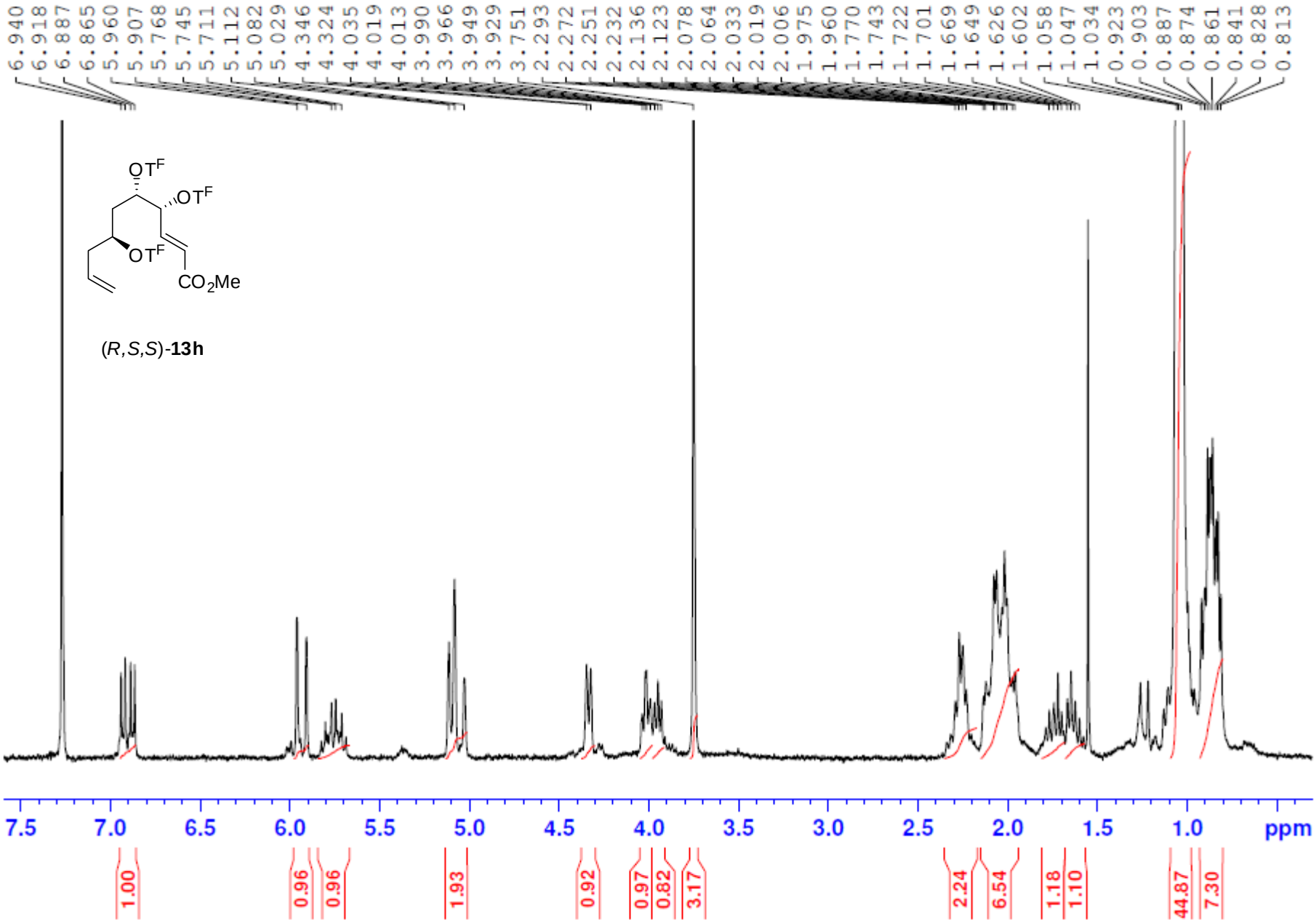

OT^H
OT^H
OT^F
CO2Me
(S,R,S)-13f
-84.97
-120.29
-120.35
-120.41
-84.8
-85.0
ppm
-120.5
ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
2.18
2.00


6.980
6.958
6.927
6.905
5.994
5.990
5.941
5.938
5.860
5.836
5.825
5.813
5.802
5.106
5.099
5.071
5.043
4.281
4.259
4.028
4.021
4.006
4.000
3.984
3.920
3.904
3.885
3.752
2.351
2.325
2.304
2.293
2.282
2.253
2.232
2.126
2.114
2.069
2.034
2.010
1.980
1.953
1.695
1.673
1.651
1.060
1.050
0.904
0.896
0.885
0.874
0.858
0.840
0.827
OT^F
OT^F
OT^H
CO2Me
(R,S,R)-13g
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
ppm
1.24
1.15
1.38
2.43
0.27
1.00
1.12
1.07
3.85
2.66
5.42
2.16
62.94
5.77

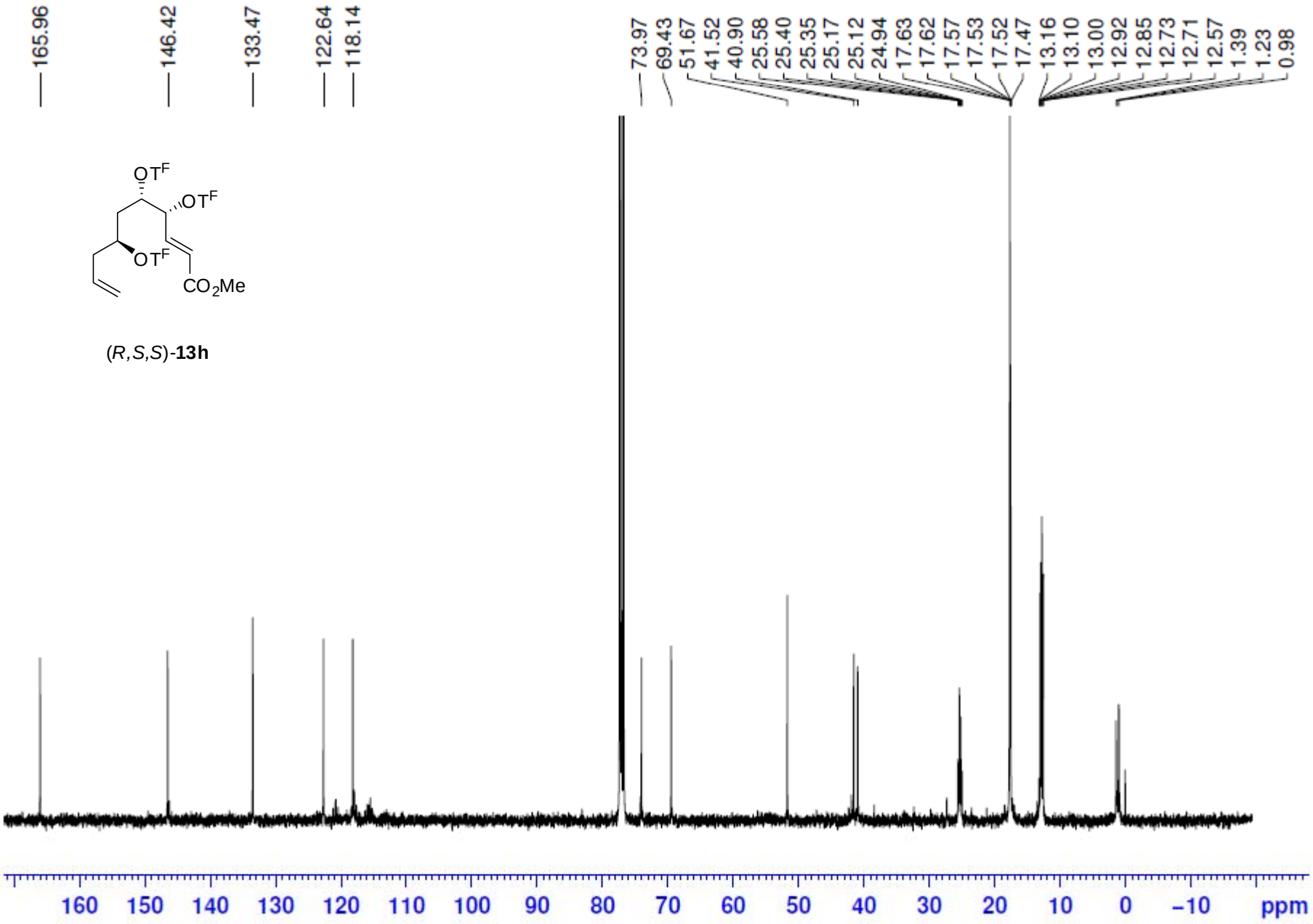

166.00
146.23
133.98
122.68
121.27
117.68
117.54
77.46
77.03
76.61
76.55
74.36
74.11
68.92
51.66
41.88
41.76
25.52
25.35
25.20
18.18
17.72
17.68
17.58
17.49
13.03
12.94
12.85
12.73
12.69
12.57
1.25
0.90
OT^F
OT^F
OT^H
CO2Me
200
180
160
140
120
100
80
60
40
20
0
ppm

(*R*,*S*,*R*)-**13g**

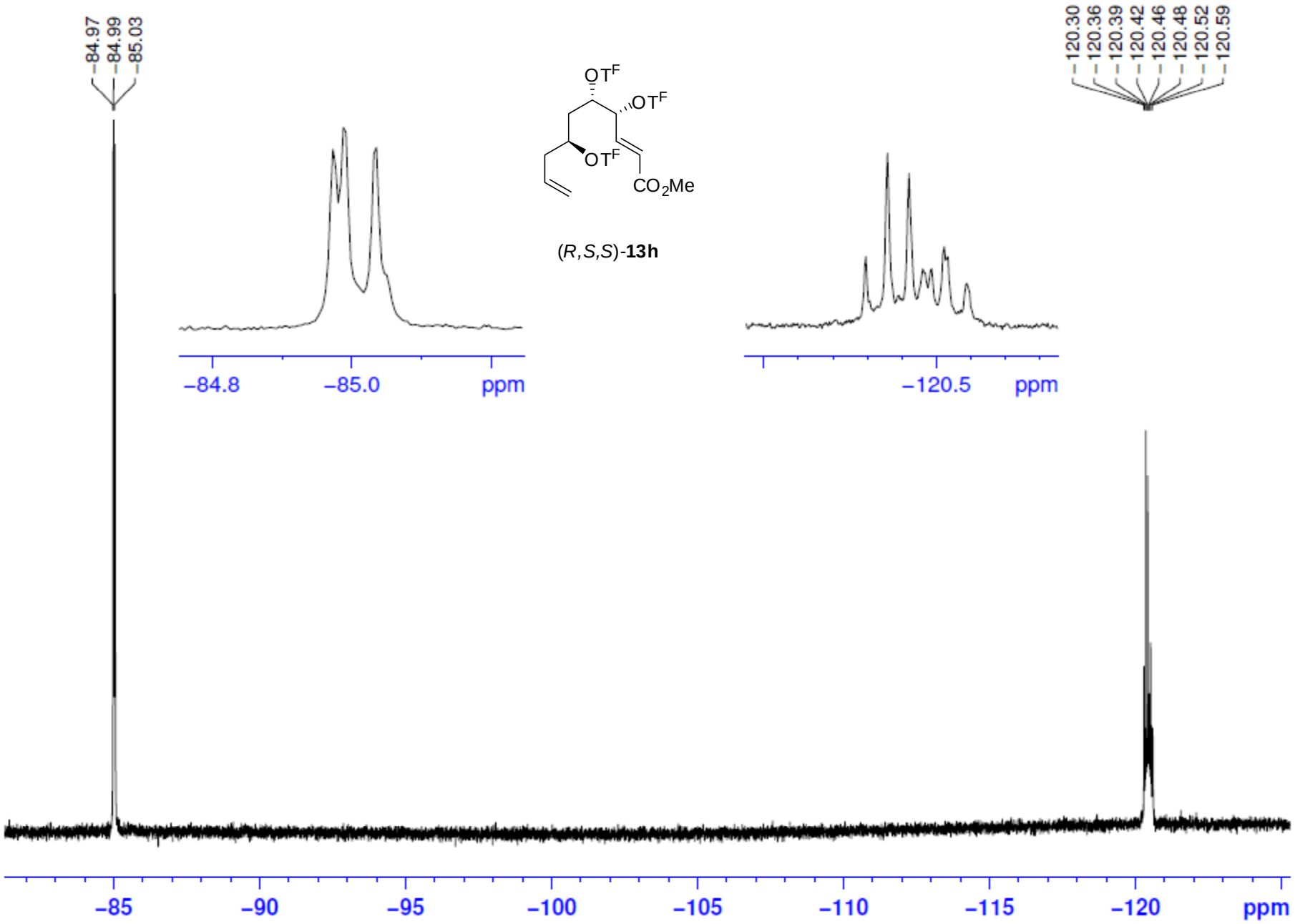

-24003.31
-24010.77
-33974.31
-33982.52
-33991.28
-34000.23
-34009.35
-34018.47
-34036.51
-34040.27
-34054.69
-34057.46
OT^F
OT^F
OT^H
CO2Me
(R,S,R)-13g
-85.0
ppm
-120.5
ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
ppm

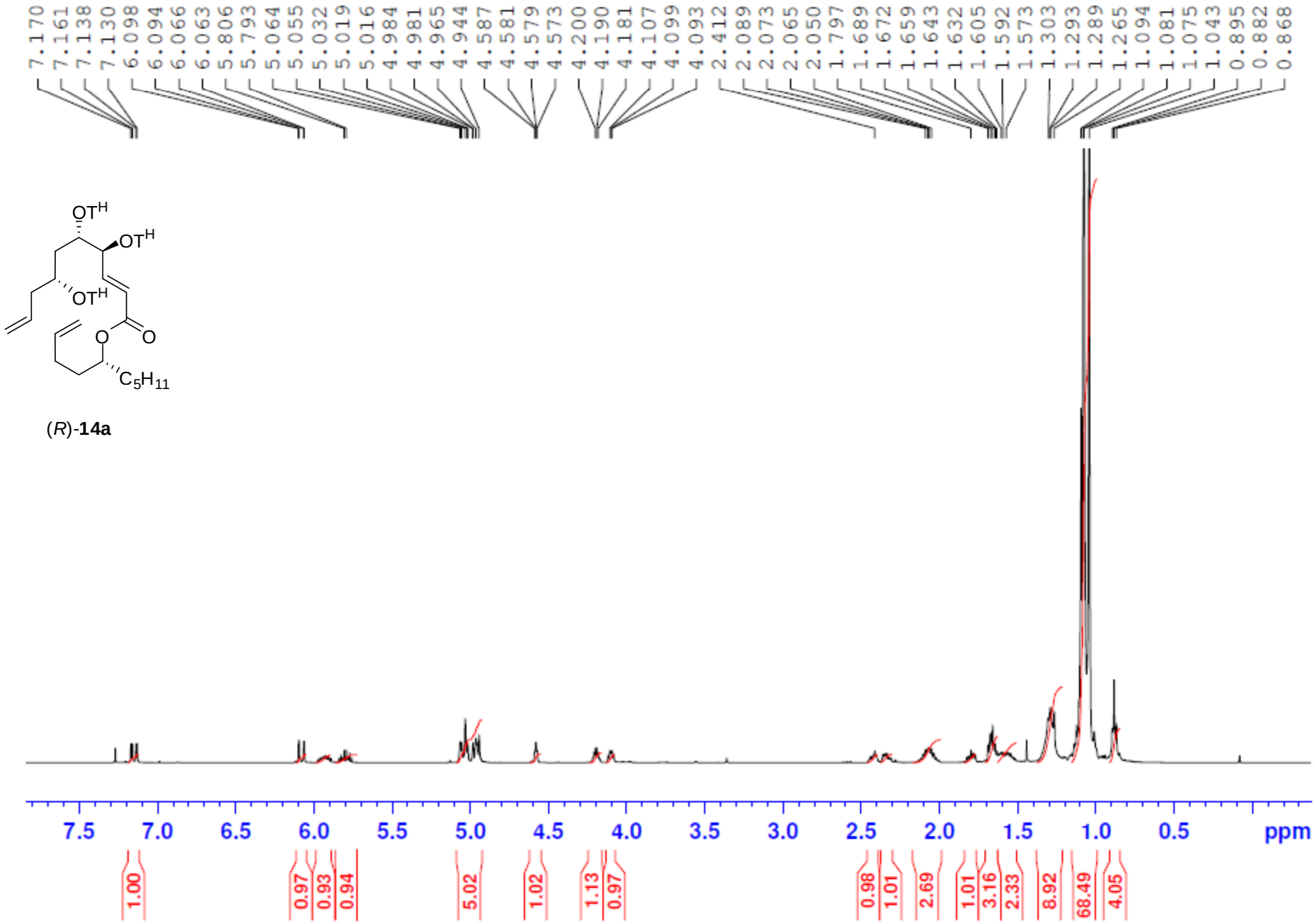

6.940
6.918
6.887
6.865
5.960
5.907
5.768
5.745
5.711
5.112
5.082
5.029
4.346
4.324
4.035
4.019
4.013
3.990
3.966
3.949
3.929
3.751
2.293
2.272
2.251
2.232
2.136
2.123
2.078
2.064
2.033
2.019
2.006
1.975
1.960
1.770
1.743
1.722
1.701
1.669
1.649
1.626
1.602
1.058
1.047
1.034
0.923
0.903
0.887
0.874
0.861
0.841
0.828
0.813
OT^F
OT^F
OT^F
CO2Me
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
ppm
1.00
0.96
0.96
1.93
0.92
0.97
0.82
3.17
2.24
6.54
1.18
1.10
44.87
7.30

(*R*,*S*,*S*)-**13h**

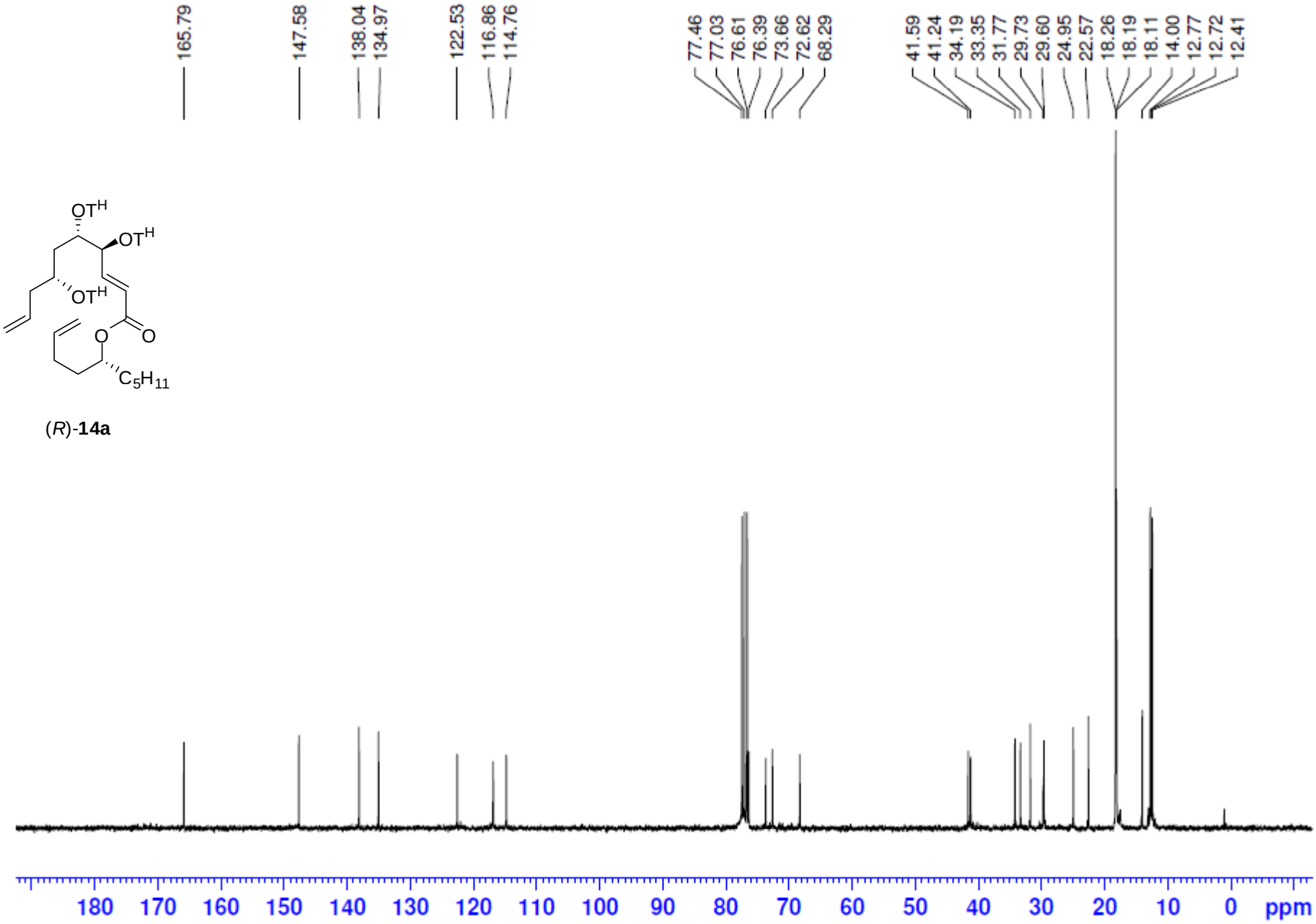

165.96
146.42
133.47
122.64
118.14
73.97
69.43
51.67
41.52
40.90
25.58
25.40
25.35
25.17
25.12
24.94
17.63
17.62
17.57
17.53
17.52
17.47
13.16
13.10
13.00
12.92
12.85
12.73
12.71
12.57
1.39
1.23
0.98
OT^F
OT^F
OT^F
CO2Me
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
ppm

(*R*,*S*,*S*)-**13h**

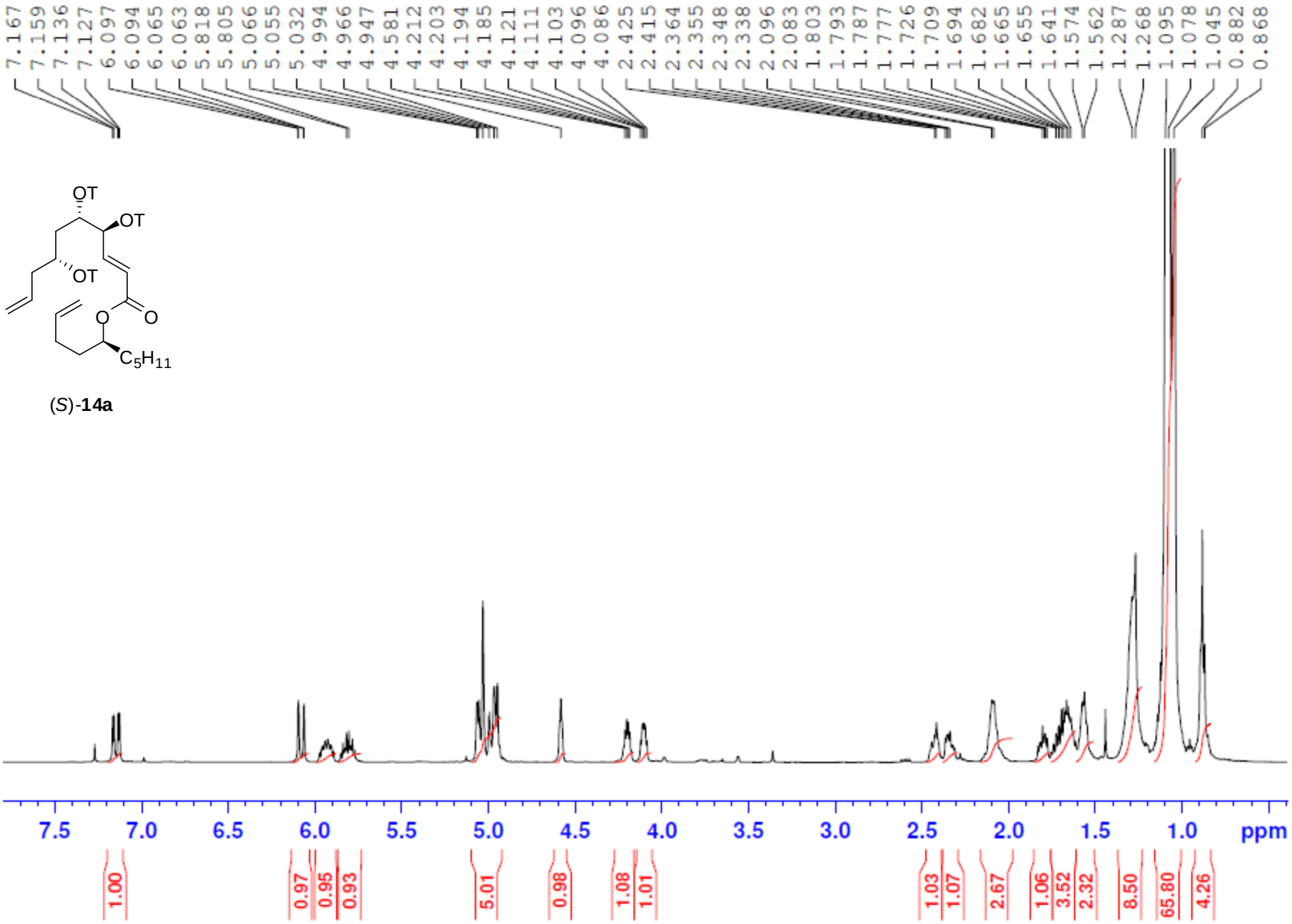

-84.97
-84.99
-85.03
OT^F
OT^F
OT^F
CO2Me
(R,S,S)-13h
-84.8
-85.0
ppm
120.30
120.36
120.39
120.42
120.46
120.48
120.52
120.59
-120.5
ppm
-85
-90
-95
-100
-105
-110
-115
-120
ppm


7.170
7.161
7.138
7.130
6.098
6.094
6.066
6.063
5.806
5.793
5.064
5.055
5.032
5.019
5.016
4.984
4.981
4.965
4.944
4.587
4.581
4.579
4.573
4.200
4.190
4.181
4.107
4.099
4.093
2.412
2.089
2.073
2.065
2.050
1.797
1.689
1.672
1.659
1.643
1.632
1.605
1.592
1.573
1.303
1.293
1.289
1.265
1.094
1.081
1.075
1.043
0.895
0.882
0.868
OT^H
OT^H
OT^H
O
O
C5H11
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
ppm
1.00
0.97
0.93
0.94
5.02
1.02
1.13
0.97
0.98
1.01
2.69
1.01
3.16
2.33
8.92
68.49
4.05

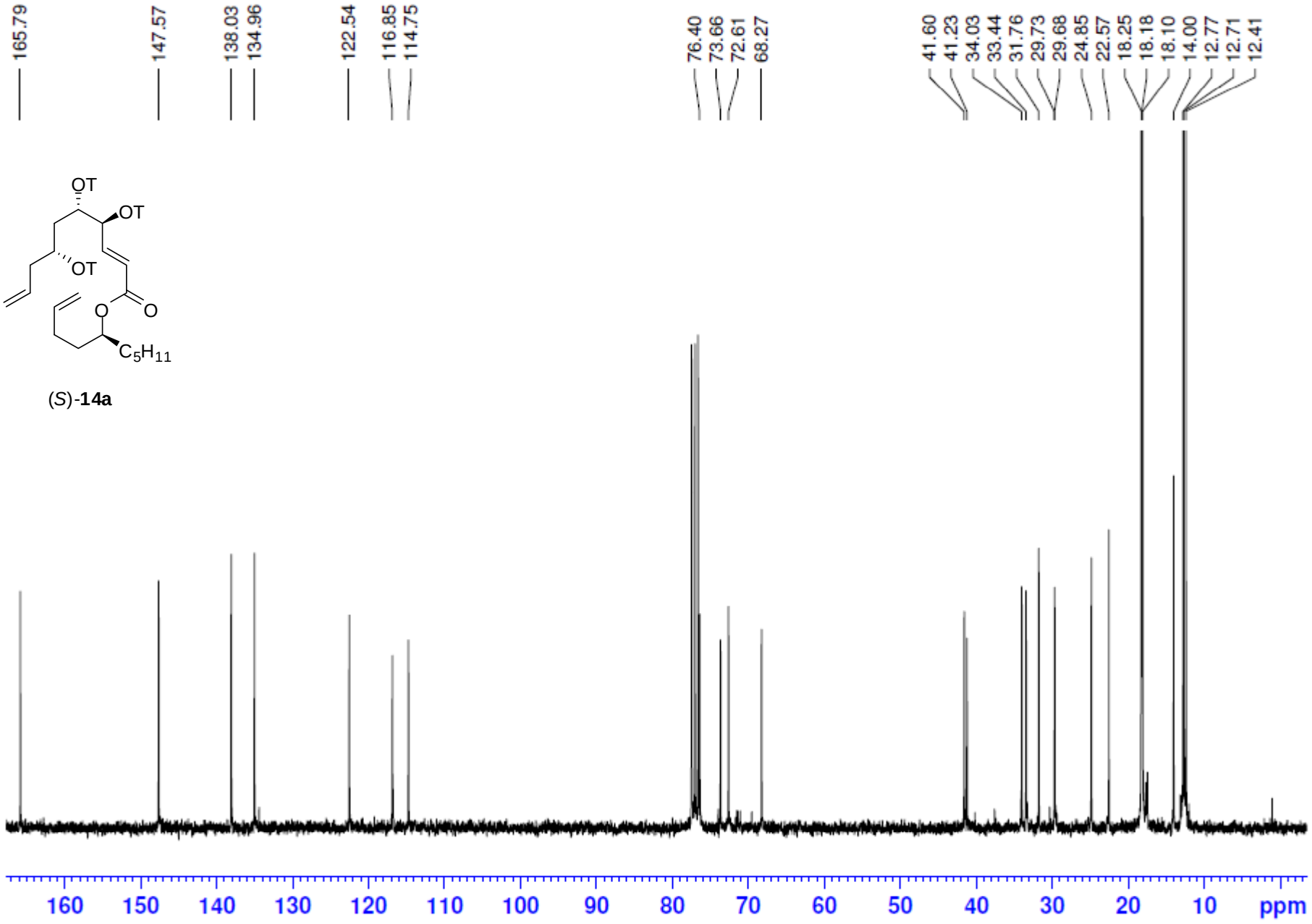
(*R*)-**14a**


165.79
147.58
138.04
134.97
122.53
116.86
114.76
77.46
77.03
76.61
76.39
73.66
72.62
68.29
41.59
41.24
34.19
33.35
31.77
29.73
29.60
24.95
22.57
18.26
18.19
18.11
14.00
12.77
12.72
12.41
OT^H
OT^H
OT^H
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

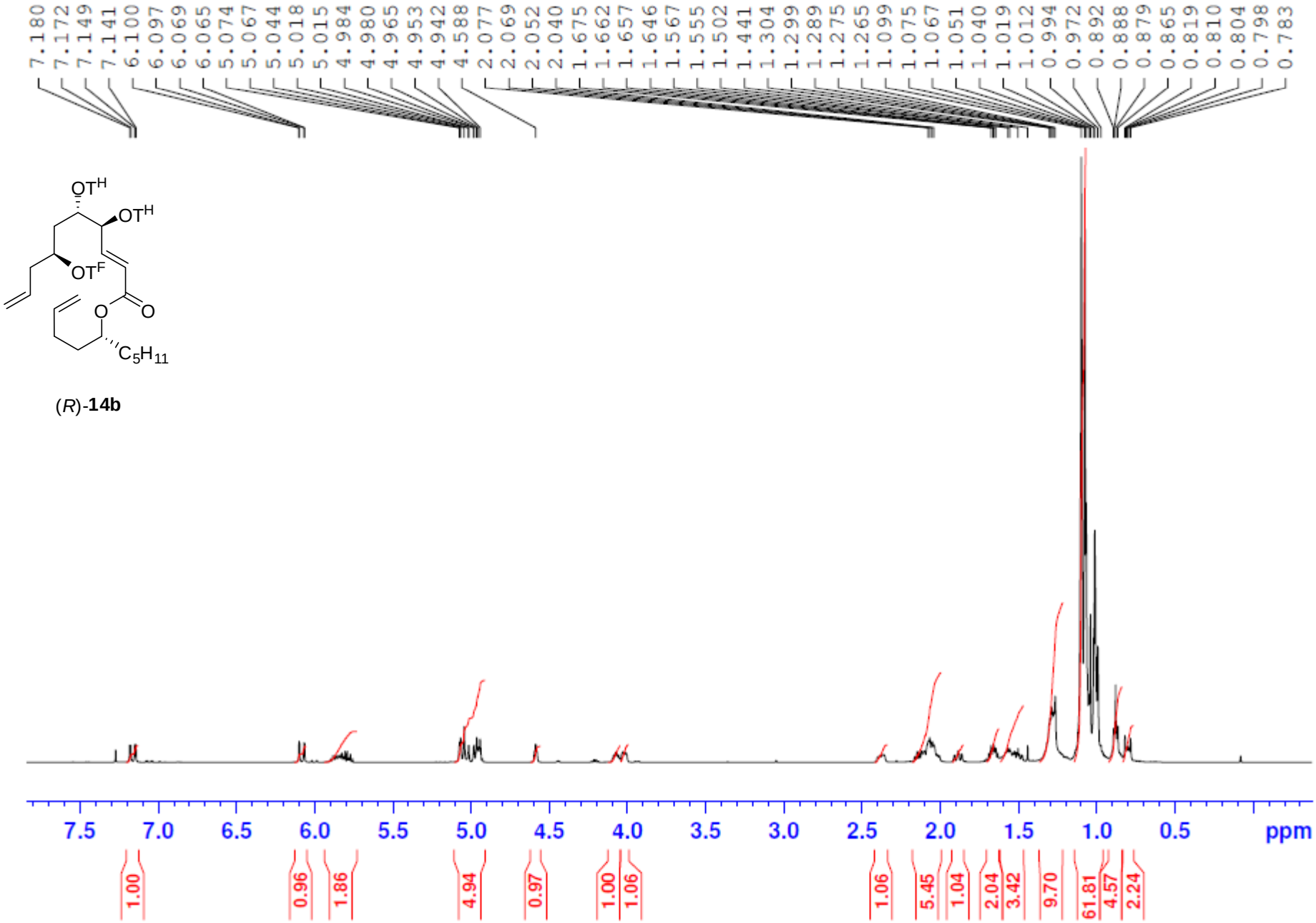
(*R*)-**14a**


7.167
7.159
7.136
7.127
6.097
6.094
6.065
6.063
5.818
5.805
5.066
5.055
5.032
4.994
4.966
4.947
4.581
4.212
4.203
4.194
4.185
4.121
4.111
4.103
4.096
4.086
2.425
2.415
2.364
2.355
2.348
2.338
2.096
2.083
1.803
1.793
1.787
1.777
1.726
1.709
1.694
1.682
1.665
1.655
1.641
1.574
1.562
1.287
1.268
1.095
1.078
1.045
0.882
0.868
OT
OT
OT
O
O
C5H11
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
ppm
1.00
0.97
0.95
0.93
5.01
0.98
1.08
1.01
1.03
1.07
2.67
1.06
3.52
2.32
8.50
65.80
4.26

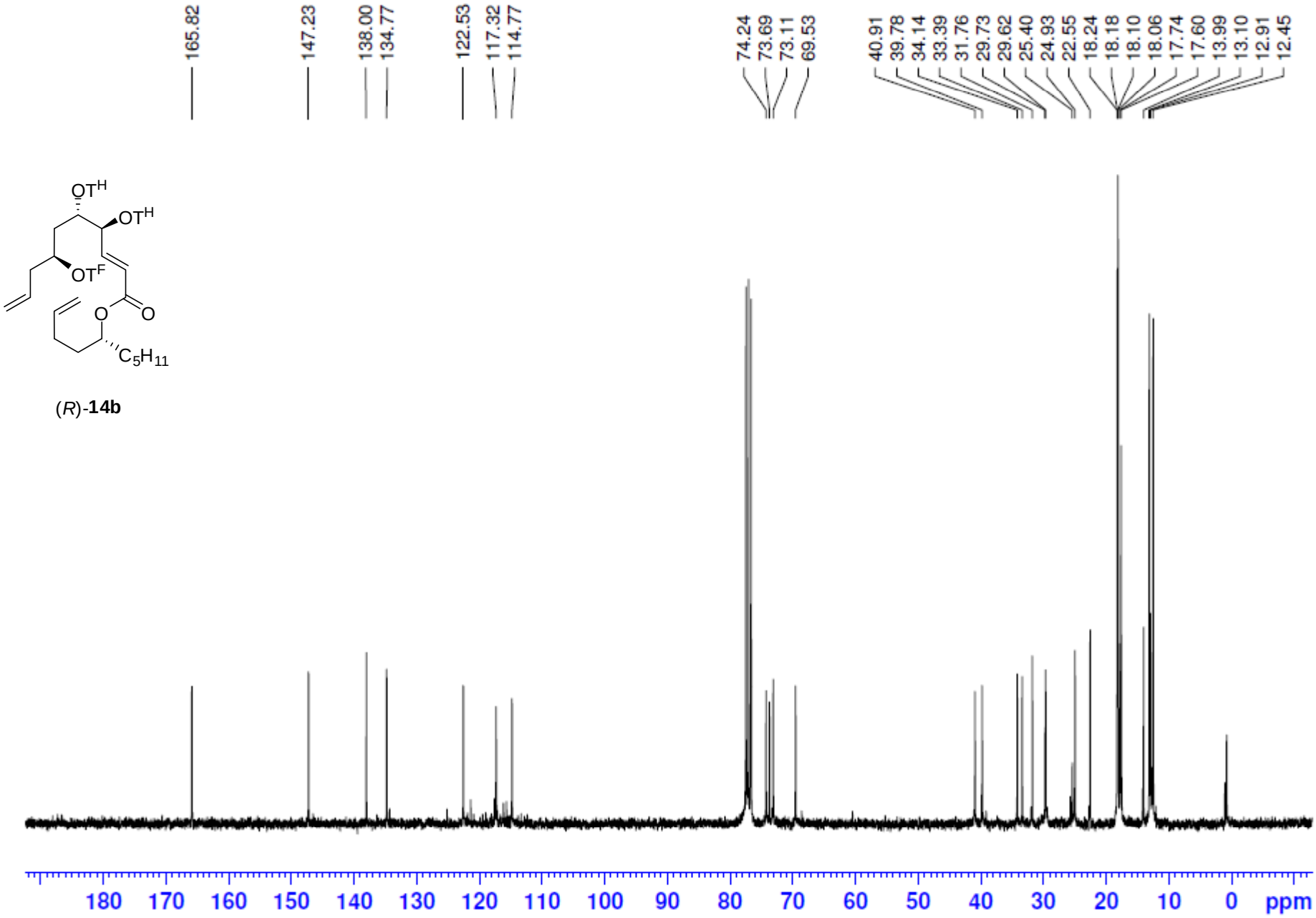
(*S*)-**14a**


165.79
147.57
138.03
134.96
122.54
116.85
114.75
76.40
73.66
72.61
68.27
41.60
41.23
34.03
33.44
31.76
29.73
29.68
24.85
22.57
18.25
18.18
18.10
14.00
12.77
12.71
12.41
OT
OT
OT
O
O
C5H11
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

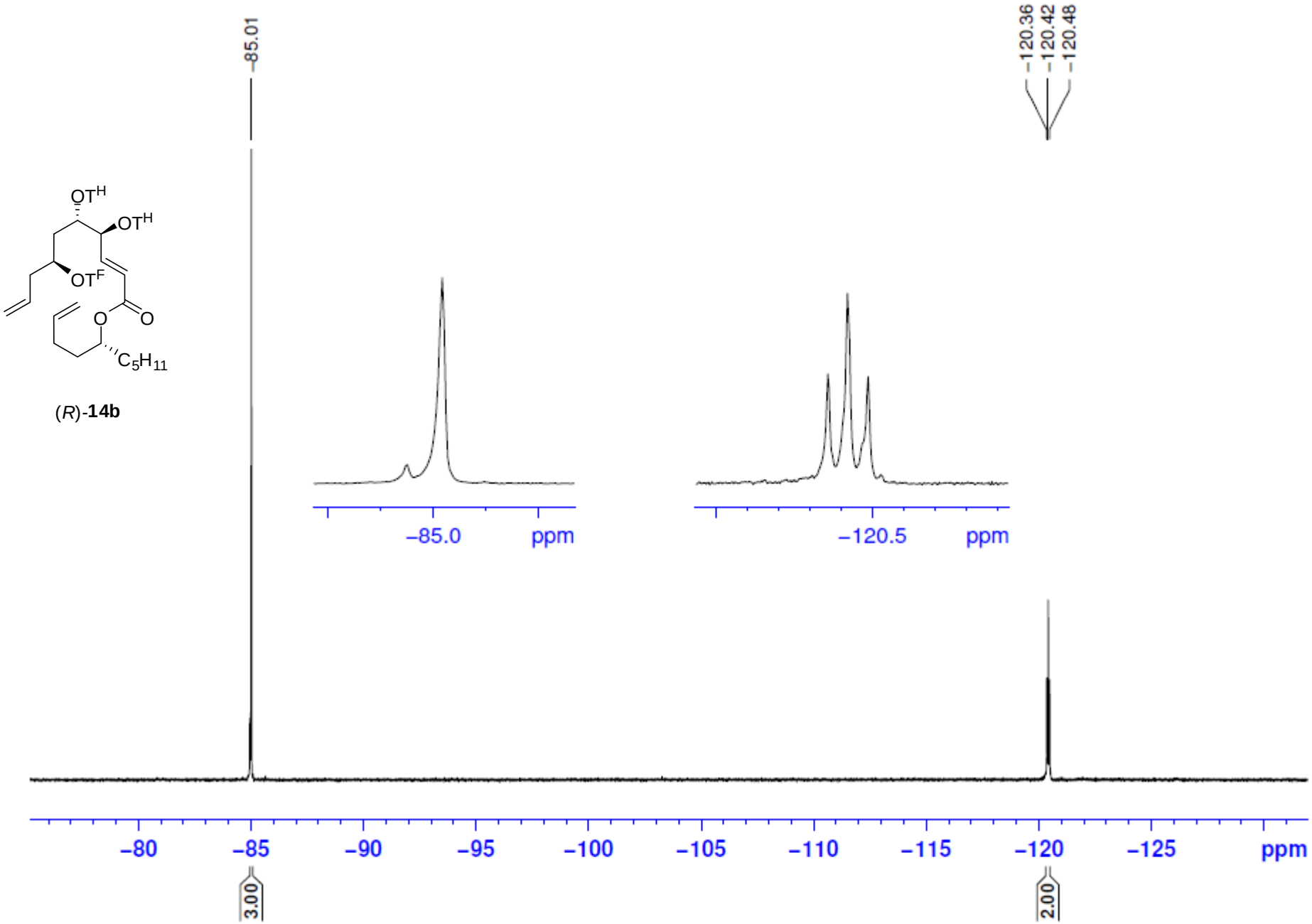
(*S*)-**14a**

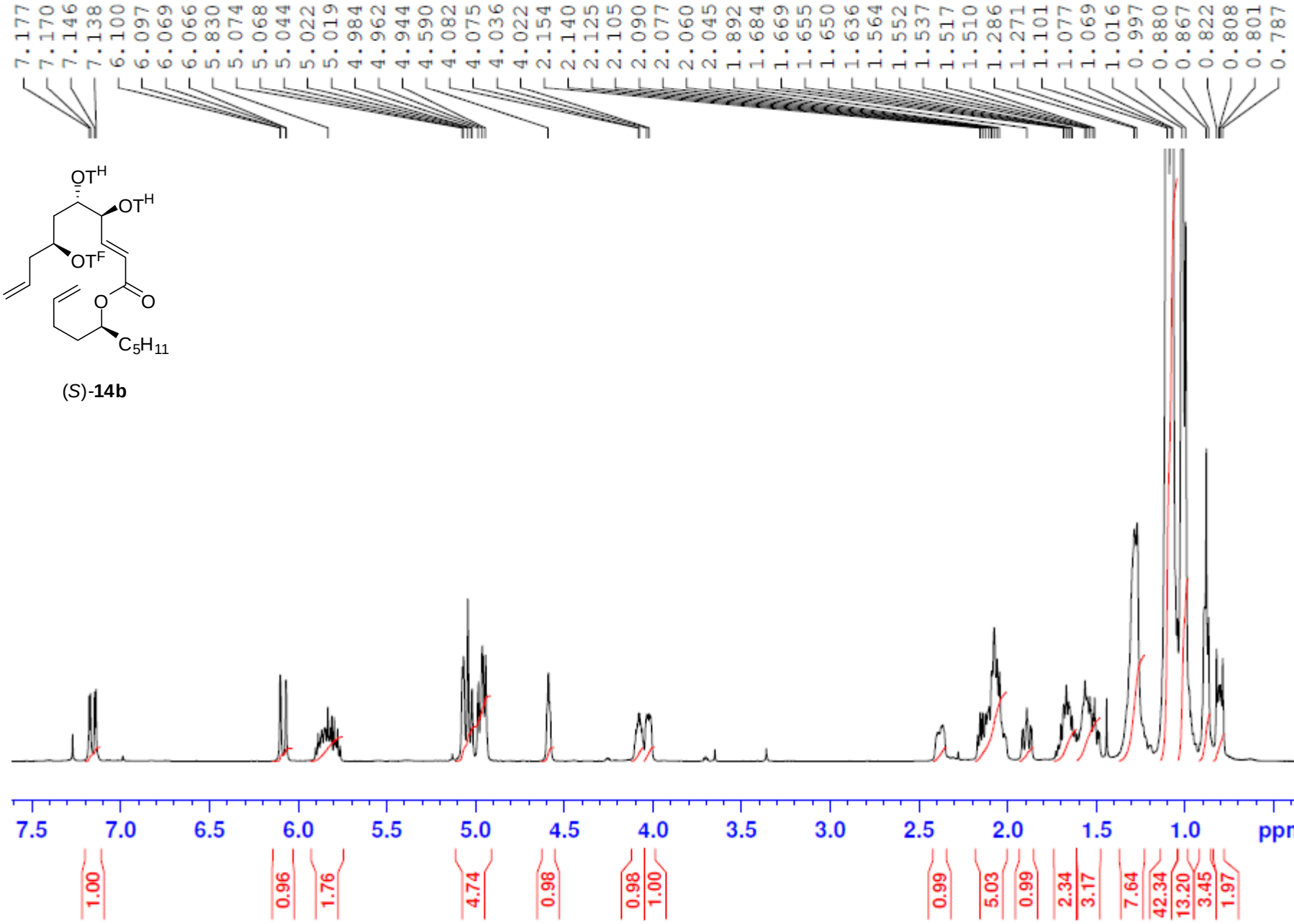

7.180
7.172
7.149
7.141
6.100
6.097
6.069
6.065
5.074
5.067
5.044
5.018
5.015
4.984
4.980
4.965
4.953
4.942
4.588
2.077
2.069
2.052
2.040
1.675
1.662
1.657
1.646
1.567
1.555
1.502
1.441
1.304
1.299
1.289
1.275
1.265
1.099
1.075
1.067
1.051
1.040
1.019
1.012
0.994
0.972
0.892
0.888
0.879
0.865
0.819
0.810
0.804
0.798
0.783
OT^H
OT^H
OT^F
O
O
C5H11
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
ppm
1.00
0.96
1.86
4.94
0.97
1.00
1.06
1.06
5.45
1.04
2.04
3.42
9.70
61.81
4.57
2.24

(*R*)-**14b**

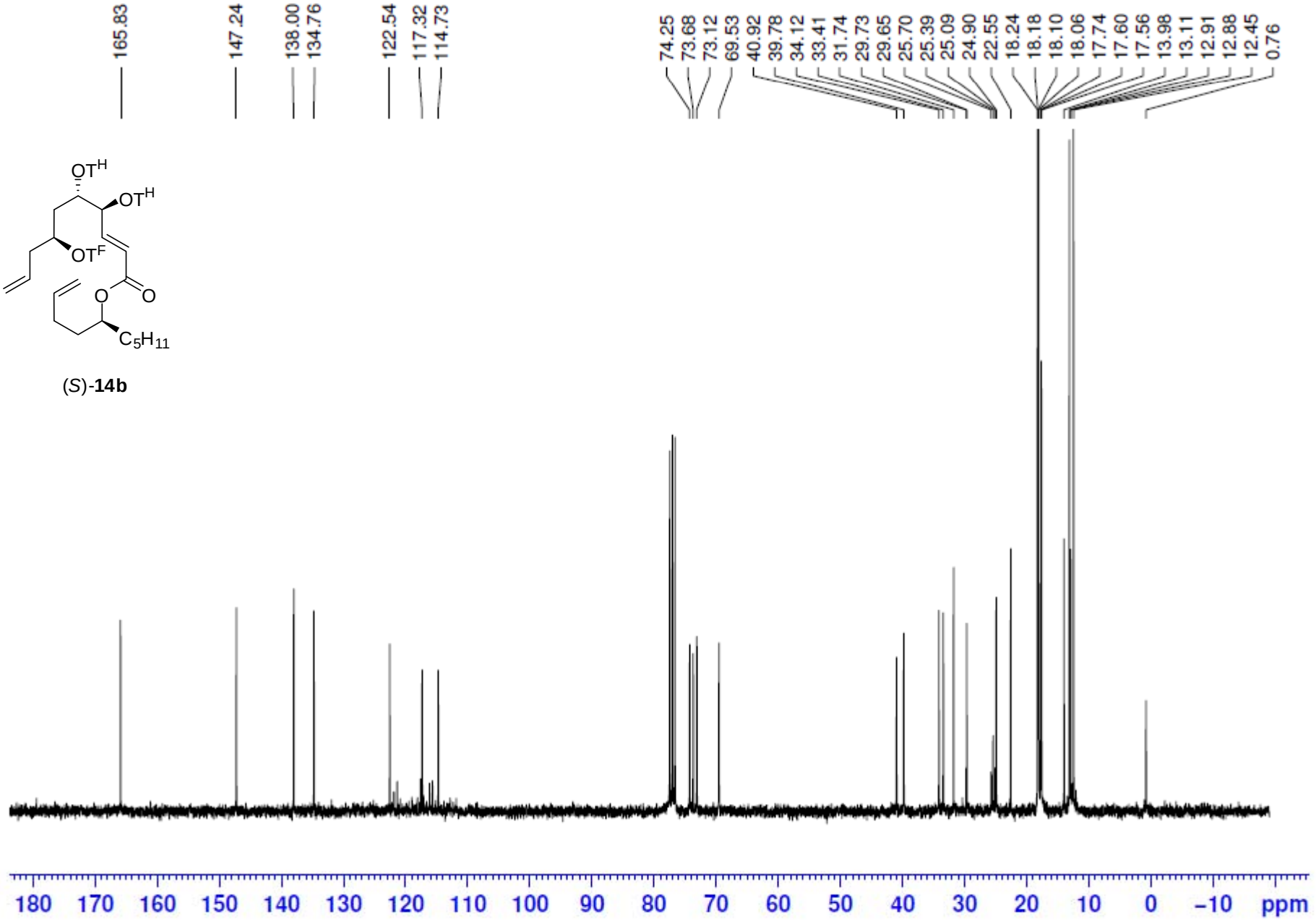

165.82
147.23
138.00
134.77
122.53
117.32
114.77
74.24
73.69
73.11
69.53
40.91
39.78
34.14
33.39
31.76
29.73
29.62
25.40
24.93
22.55
18.24
18.18
18.10
18.06
17.74
17.60
13.99
13.10
12.91
12.45
OT^H
OT^H
OT^F
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(*R*)-**14b**

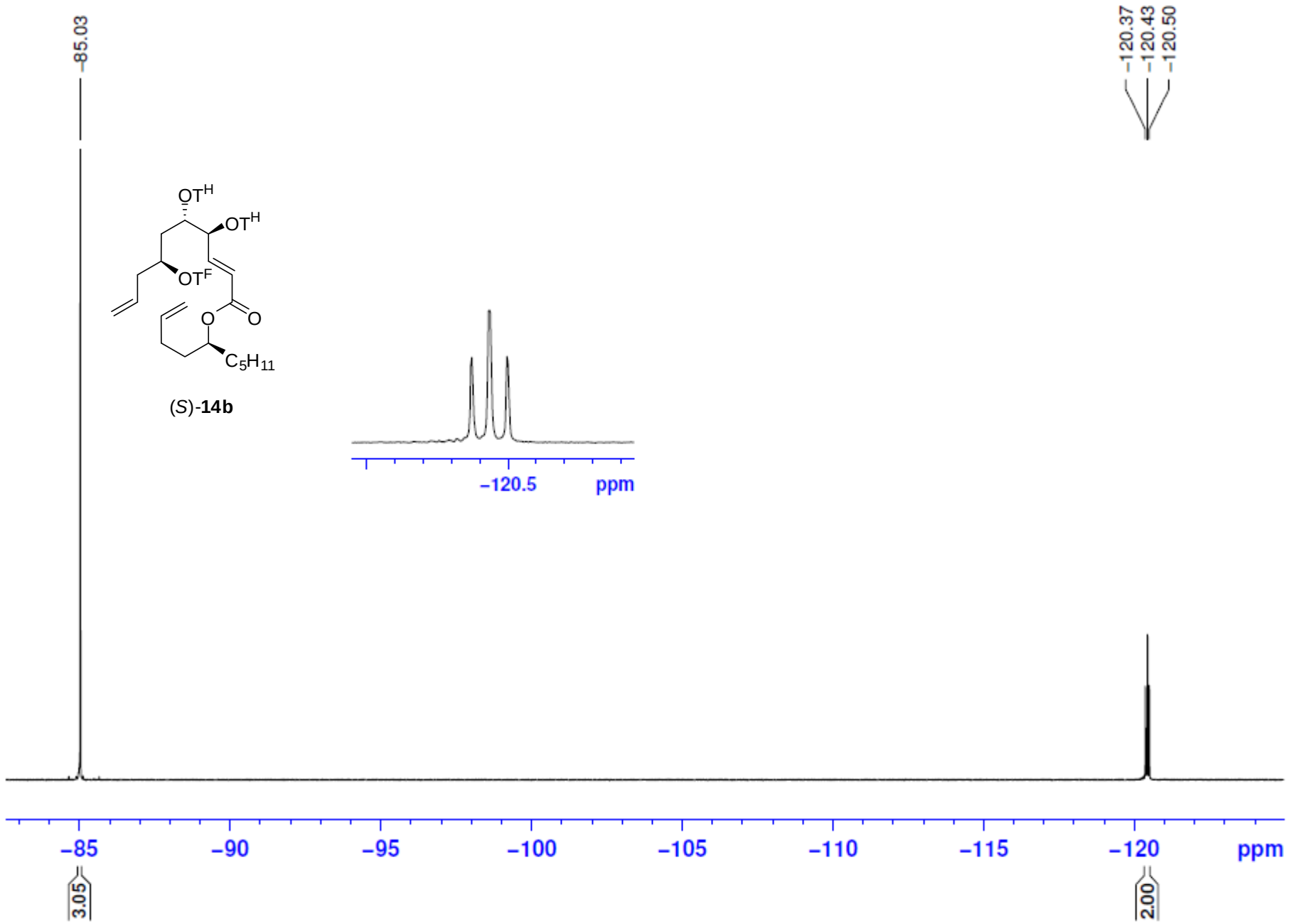

-85.01
-120.36
-120.42
-120.48
OT^H
OT^H
OT^F
O
O
C5H11
(R)-14b
-85.0 ppm
-120.5 ppm
-80 -85 -90 -95 -100 -105 -110 -115 -120 -125 ppm
3.00
2.00

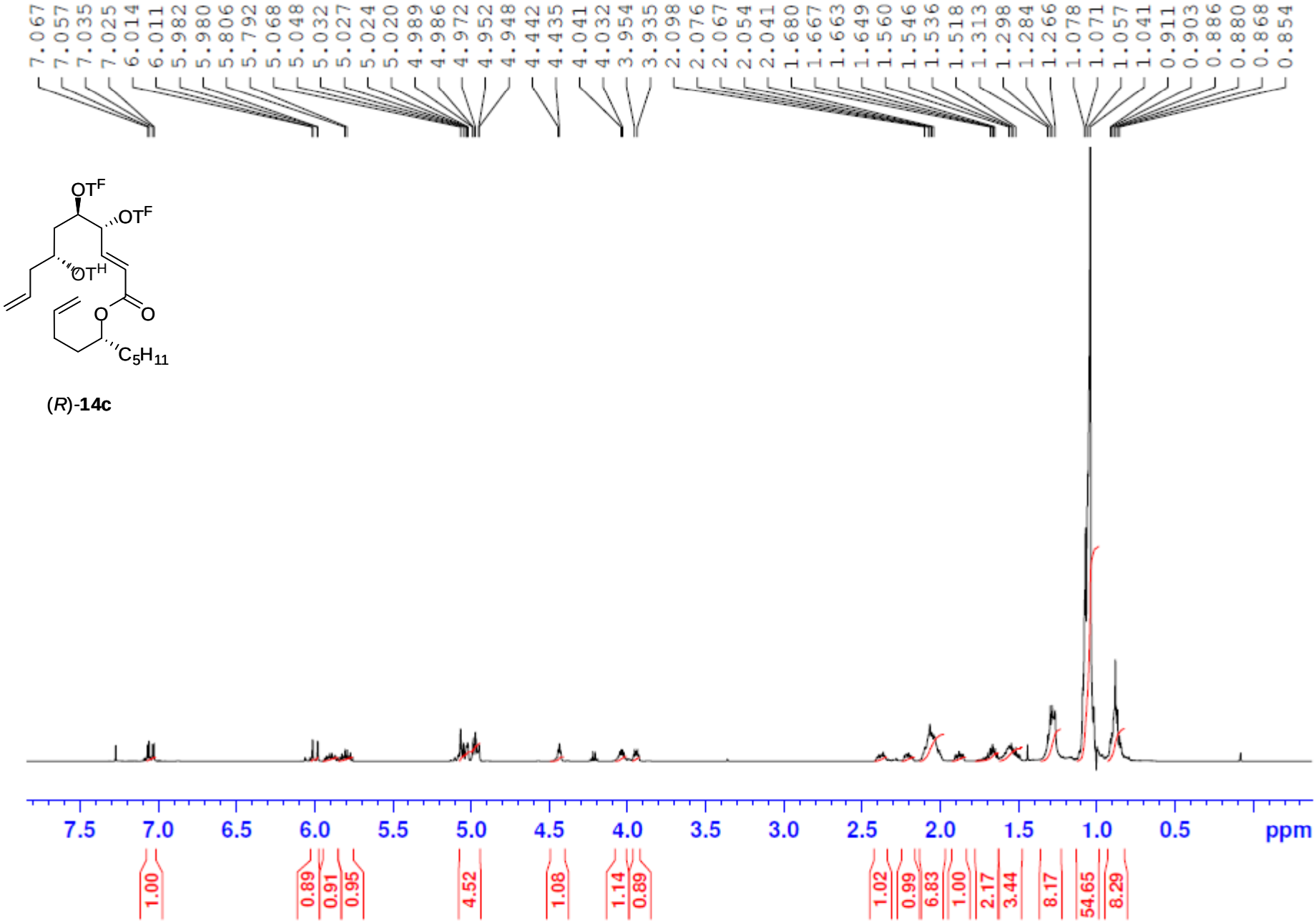

7.177
7.170
7.146
7.138
6.100
6.097
6.069
6.066
6.066
5.830
5.074
5.068
5.044
5.022
5.019
4.984
4.962
4.944
4.590
4.082
4.075
4.036
4.022
2.154
2.140
2.125
2.105
2.090
2.077
2.060
2.045
1.892
1.684
1.669
1.655
1.650
1.636
1.564
1.552
1.537
1.517
1.510
1.286
1.271
1.101
1.077
1.069
1.016
0.997
0.880
0.867
0.822
0.808
0.801
0.787
OT^H
OT^H
OT^F
O
O
C5H11
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
ppm
1.00
0.96
1.76
4.74
0.98
0.98
1.00
0.99
5.03
0.99
2.34
3.17
7.64
42.34
13.20
3.45
1.97

(*S*)-**14b**

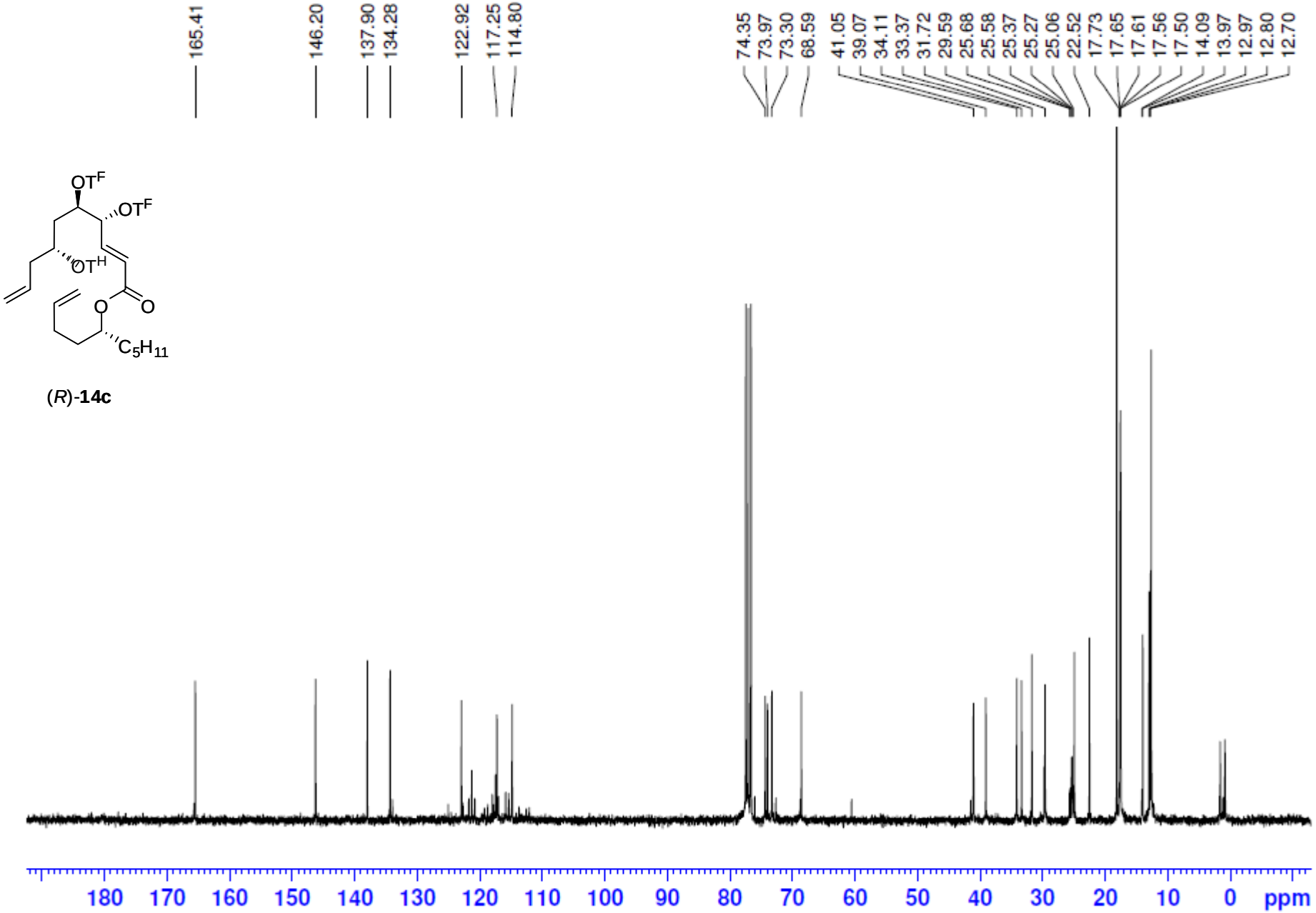

165.83
147.24
138.00
134.76
122.54
117.32
114.73
74.25
73.68
73.12
69.53
40.92
39.78
34.12
33.41
31.74
29.73
29.65
25.70
25.39
25.09
24.90
22.55
18.24
18.18
18.10
18.06
17.74
17.60
17.56
13.98
13.11
12.91
12.88
12.45
0.76
OT^H
OT^H
OT^F
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

(*S*)-**14b**

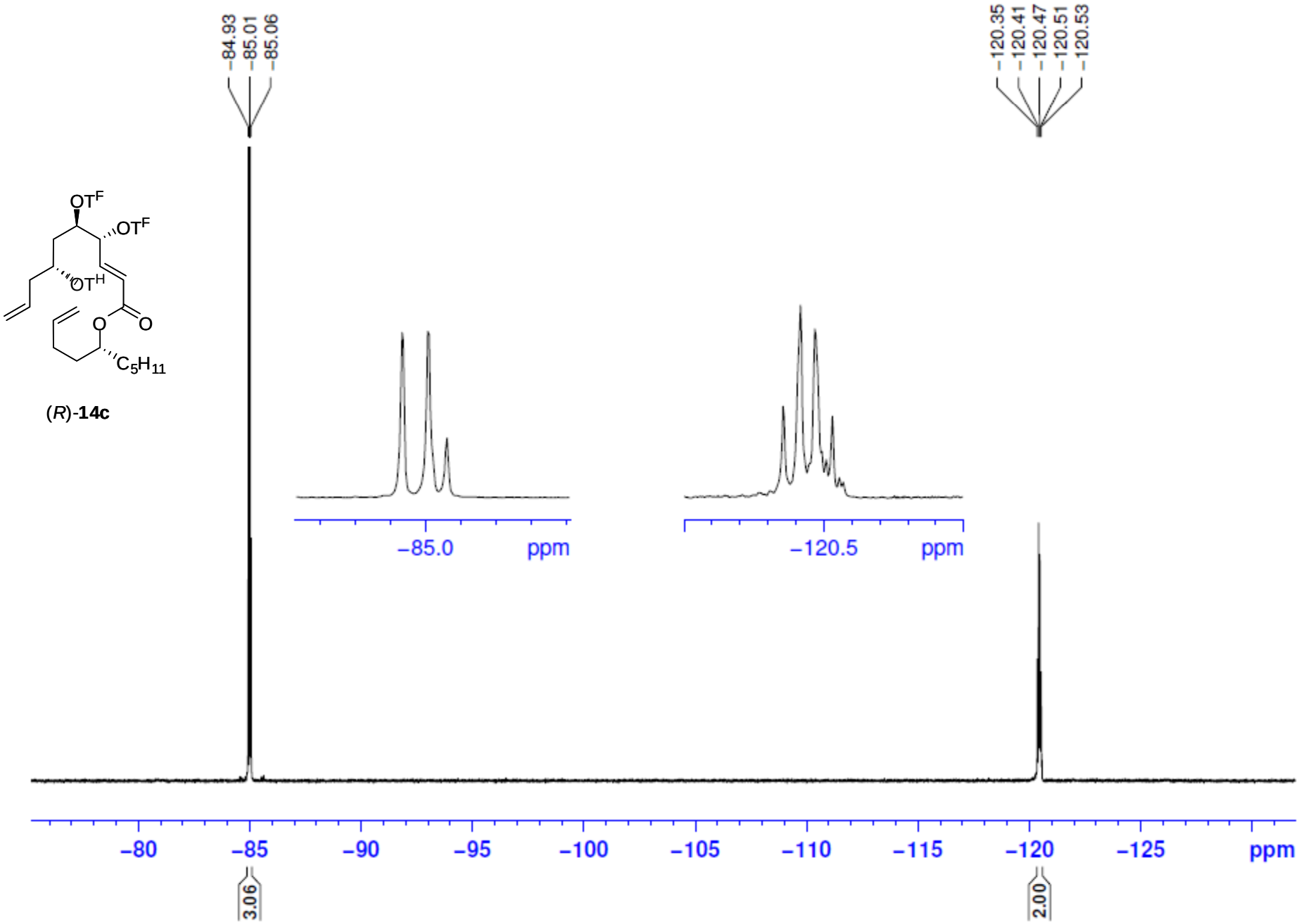

-85.03
-120.37
-120.43
-120.50
OT^H
OT^H
OT^F
O
O
C5H11
(S)-14b
-120.5
ppm
-85
-90
-95
-100
-105
-110
-115
-120
ppm
3.05
2.00


7.067
7.057
7.035
7.025
6.014
6.011
5.982
5.980
5.806
5.792
5.068
5.048
5.032
5.027
5.024
5.020
4.989
4.986
4.972
4.952
4.948
4.442
4.435
4.041
4.032
3.954
3.935
2.098
2.076
2.067
2.054
2.041
1.680
1.667
1.663
1.649
1.560
1.546
1.536
1.518
1.313
1.298
1.284
1.266
1.078
1.071
1.057
1.041
0.911
0.903
0.886
0.880
0.868
0.854
OT^F
OT^F
OT^H
O
O
C5H11
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
ppm
1.00
0.89
0.91
0.95
4.52
1.08
1.14
0.89
1.02
0.99
6.83
1.00
2.17
3.44
8.17
54.65
8.29

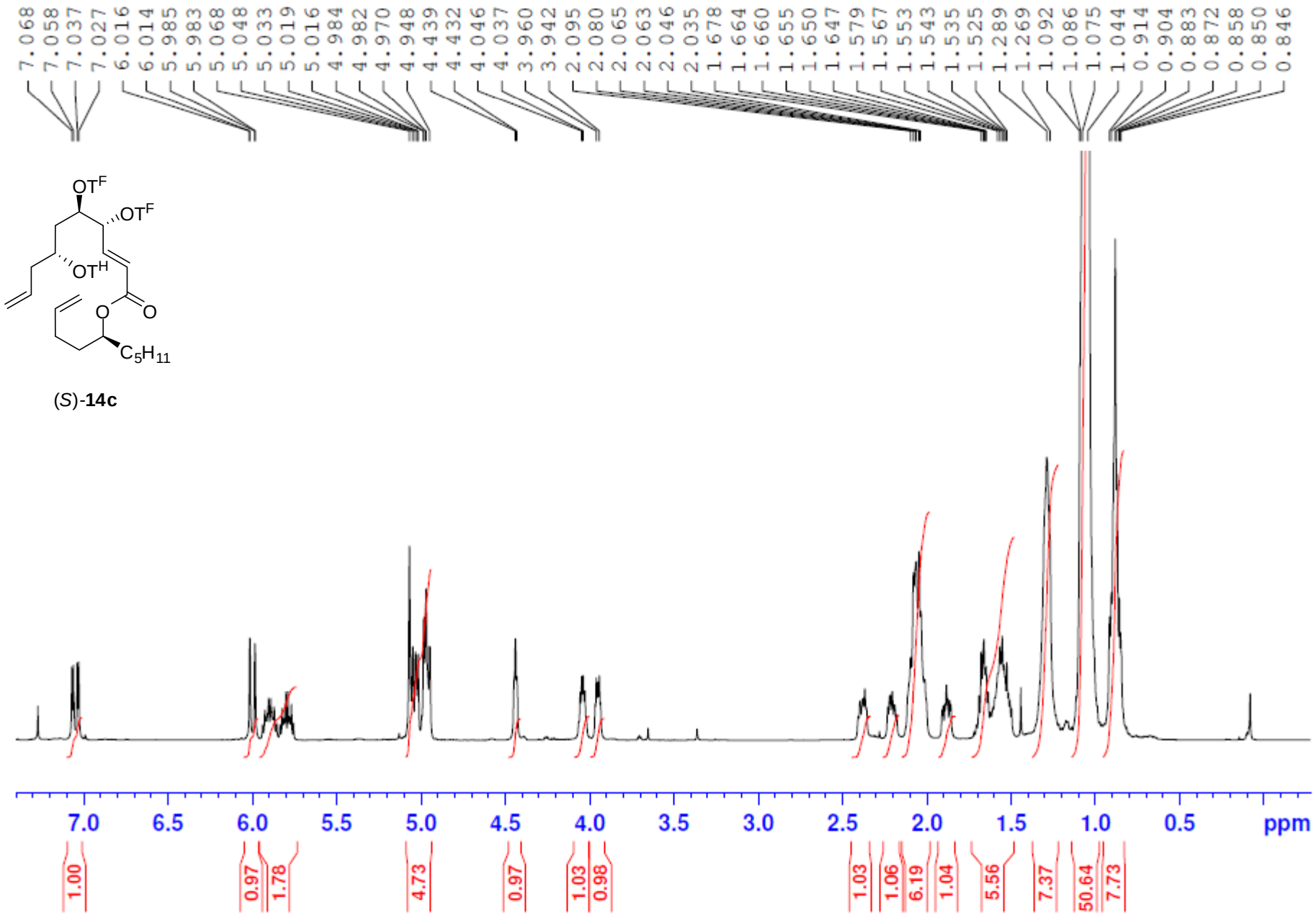
(*R*)-**14c**


165.41
146.20
137.90
134.28
122.92
117.25
114.80
74.35
73.97
73.30
68.59
41.05
39.07
34.11
33.37
31.72
29.59
25.68
25.58
25.37
25.27
25.06
22.52
17.73
17.65
17.61
17.56
17.50
14.09
13.97
12.97
12.80
12.70
OT^F
OT^F
OT^H
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

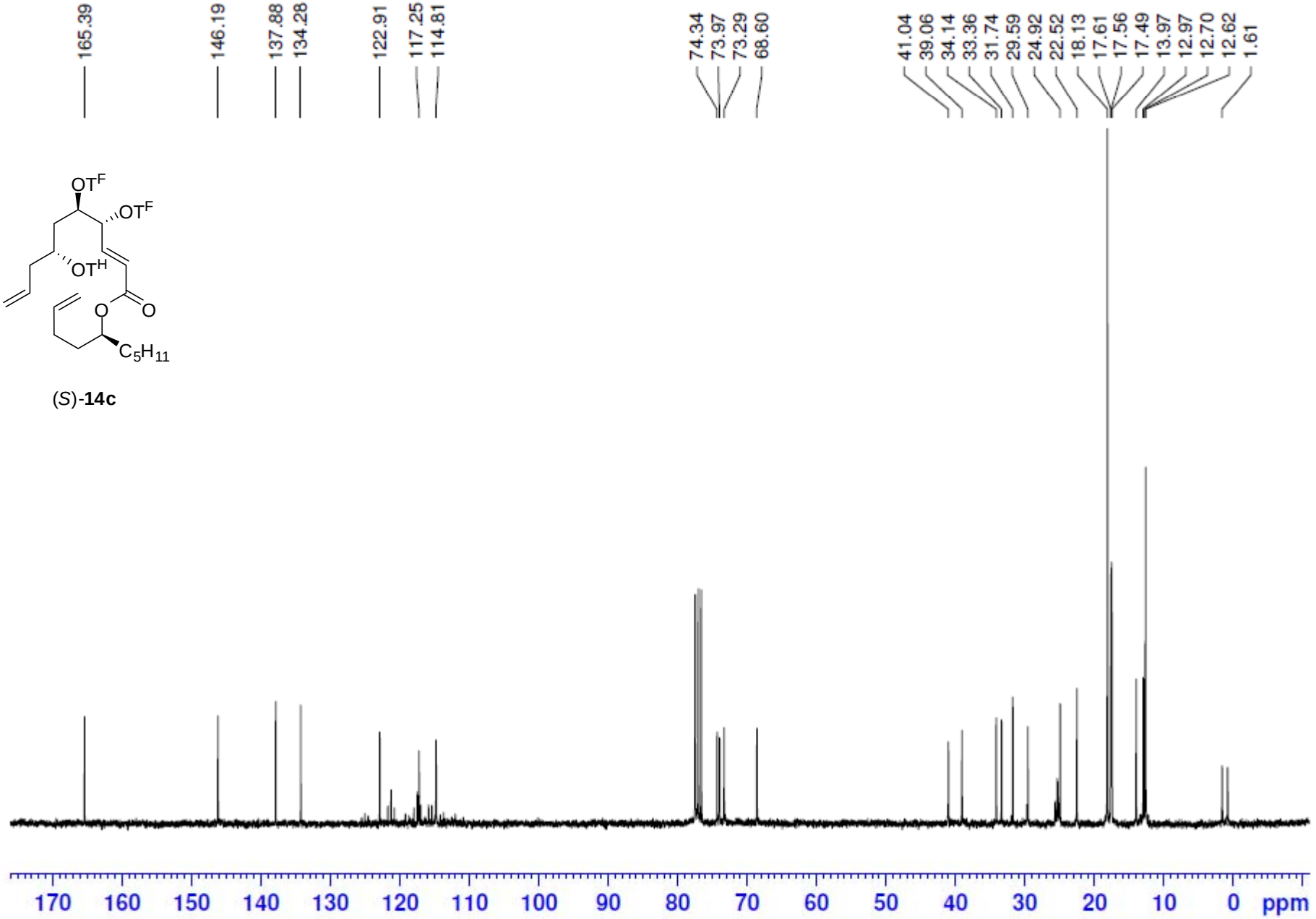
(*R*)-**14c**


-84.93
-85.01
-85.06
-120.35
-120.41
-120.47
-120.51
-120.53
OT^F
OT^F
OT^H
O
O
C5H11
-85.0 ppm
-120.5 ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
3.06
2.00

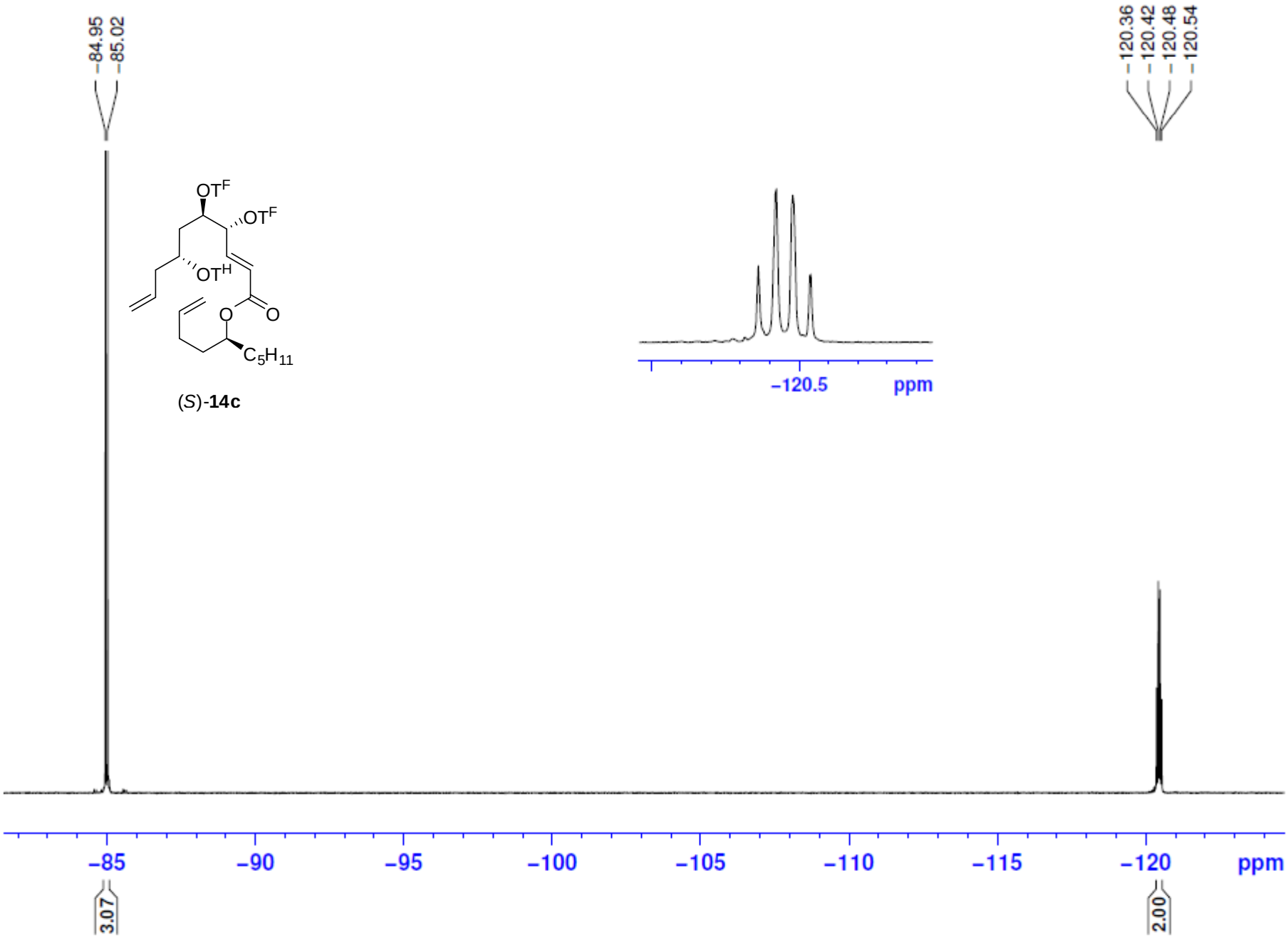
(*R*)-**14c**


7.068
7.058
7.037
7.027
6.016
6.014
5.985
5.983
5.068
5.048
5.033
5.019
5.016
4.984
4.982
4.970
4.948
4.439
4.432
4.046
4.037
3.960
3.942
2.095
2.080
2.065
2.063
2.046
2.035
1.678
1.664
1.660
1.655
1.650
1.647
1.579
1.567
1.553
1.543
1.535
1.525
1.289
1.269
1.092
1.086
1.075
1.044
0.914
0.904
0.883
0.872
0.858
0.850
0.846
OT^F
OT^F
OT^H
O
O
C5H11
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
ppm
1.00
0.97
1.78
4.73
0.97
1.03
0.98
1.03
1.06
6.19
1.04
5.56
7.37
50.64
7.73

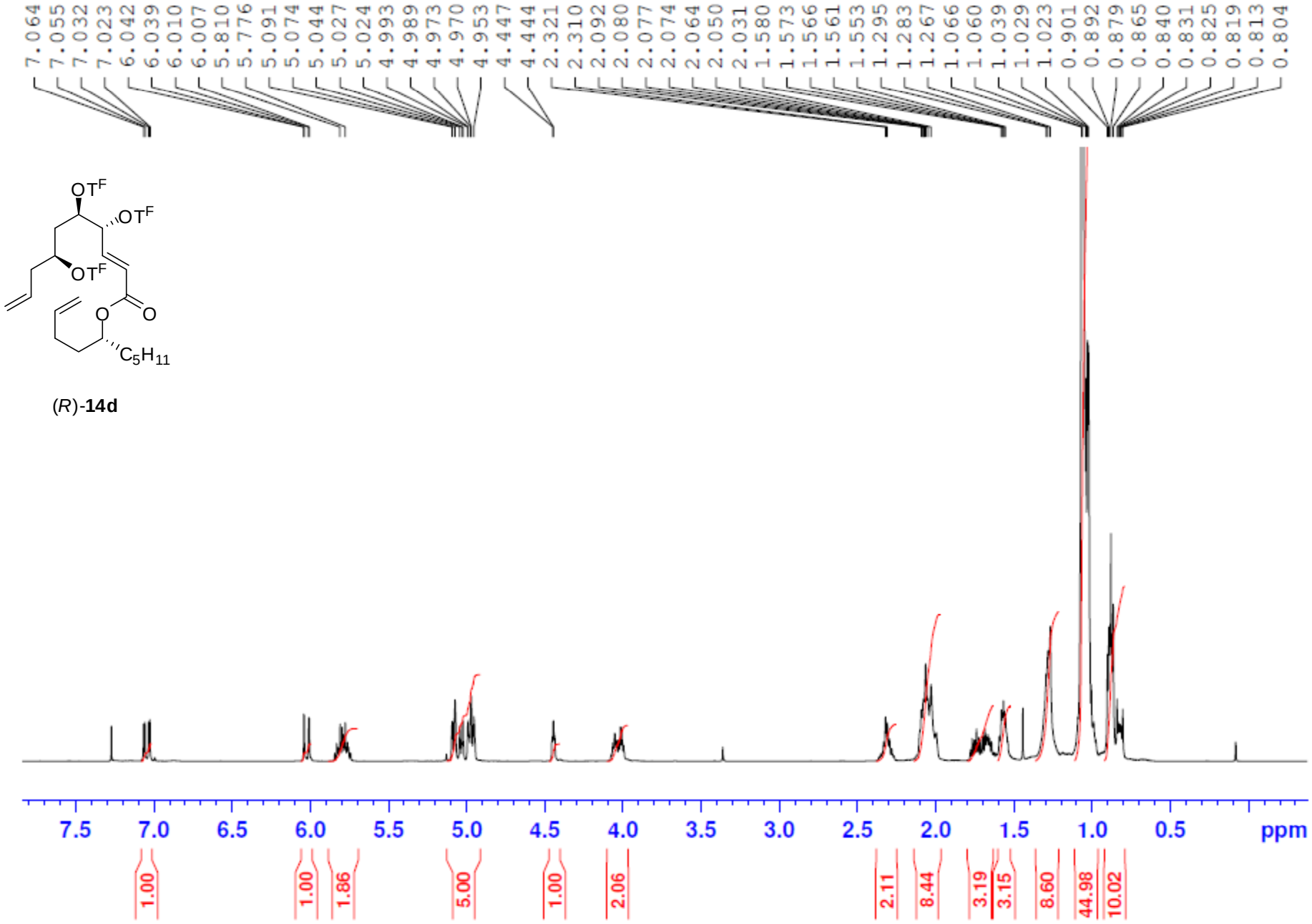
(*S*)-**14c**


165.39
146.19
137.88
134.28
122.91
117.25
114.81
74.34
73.97
73.29
68.60
41.04
39.06
34.14
33.36
31.74
29.59
24.92
22.52
18.13
17.61
17.56
17.49
13.97
12.97
12.70
12.62
1.61
OT^F
OT^F
OT^H
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

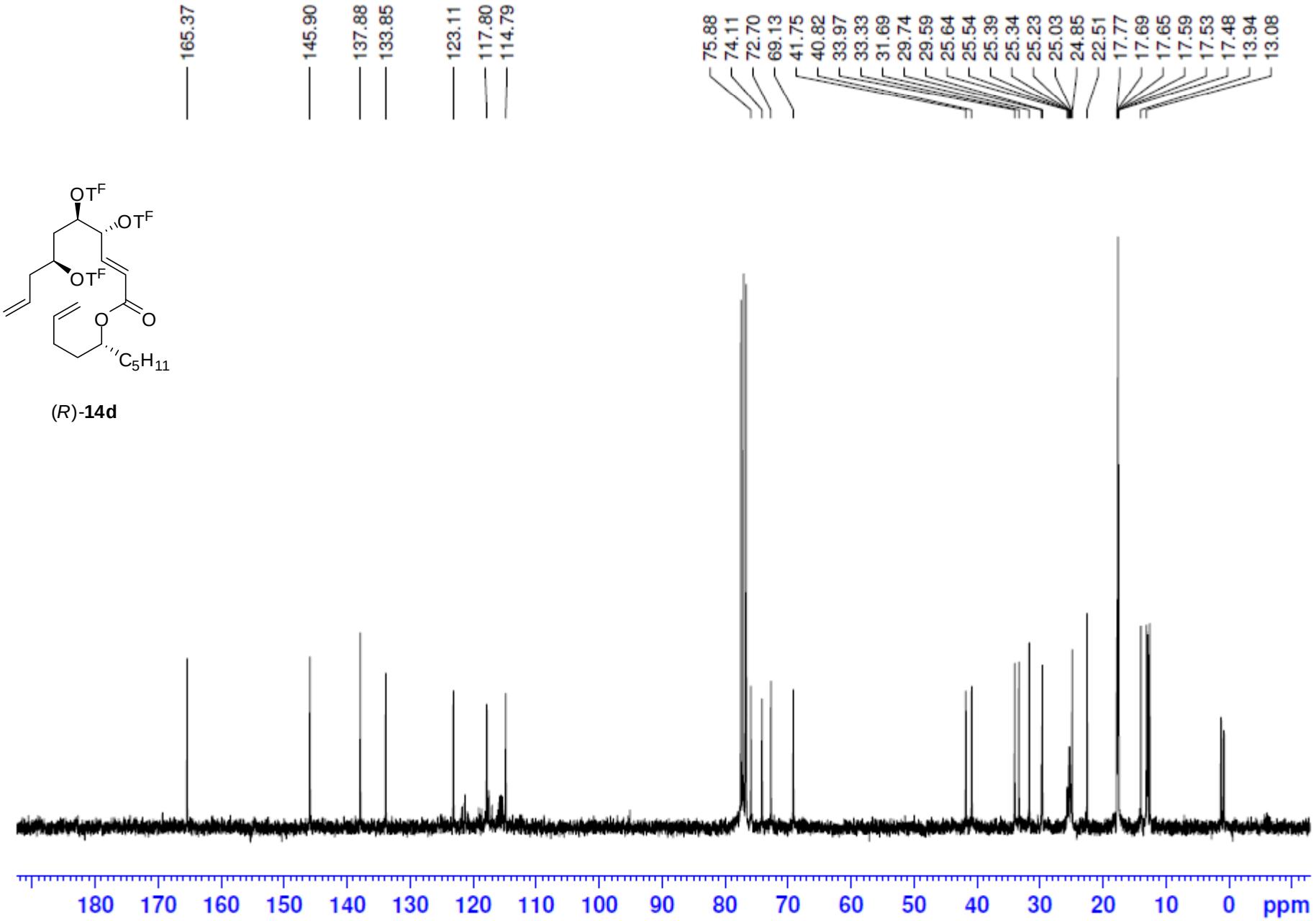
(*S*)-**14c**


-84.95
-85.02
-120.36
-120.42
-120.48
-120.54
OT^F
OT^F
OT^H
O
O
C5H11
-120.5
ppm
-85
-90
-95
-100
-105
-110
-115
-120
ppm
3.07
2.00

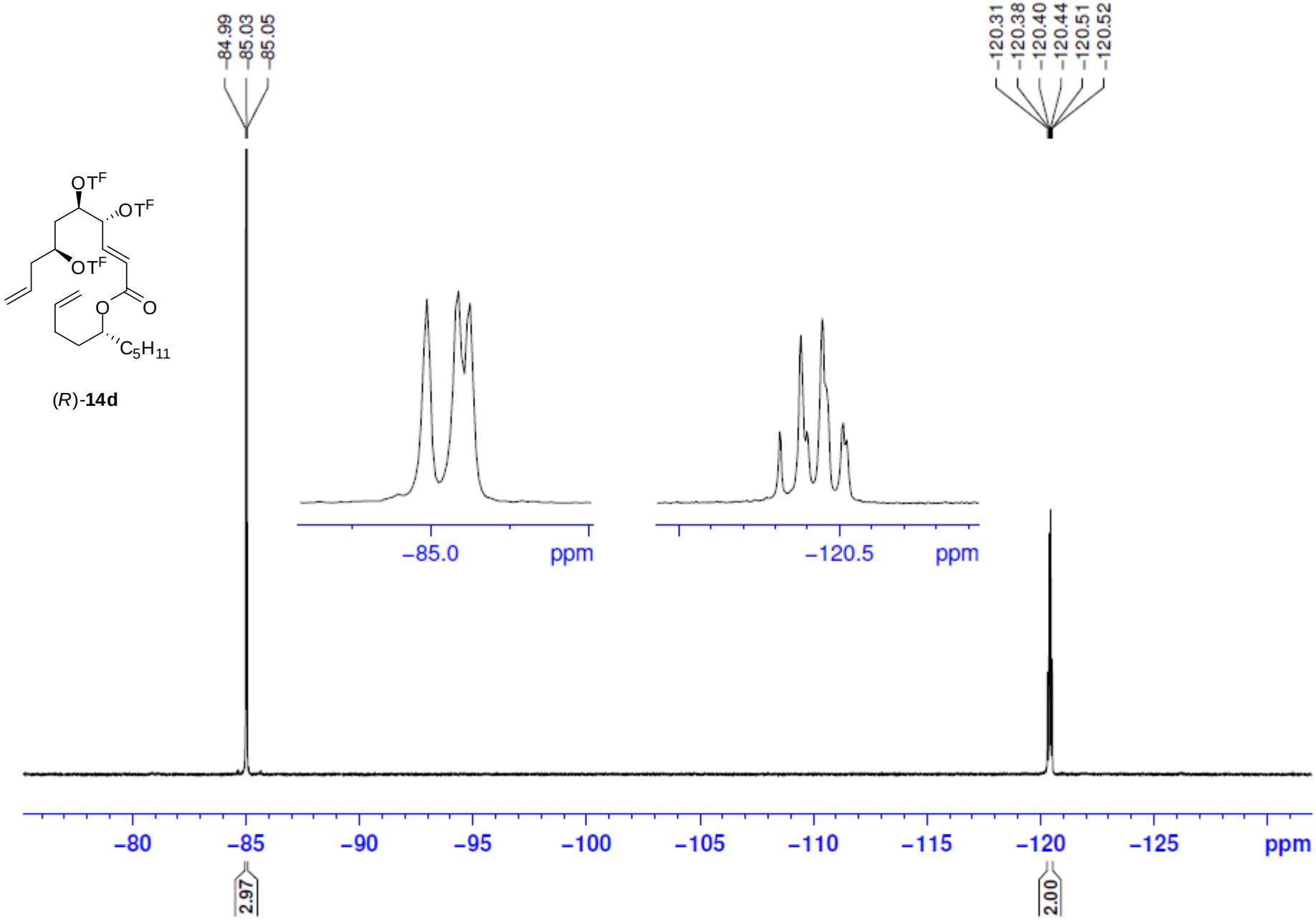
(*S*)-**14c**


7.064
7.055
7.032
7.023
6.042
6.039
6.010
6.007
5.810
5.776
5.091
5.074
5.044
5.027
5.024
4.993
4.989
4.973
4.970
4.953
4.447
4.444
2.321
2.310
2.092
2.080
2.077
2.074
2.064
2.050
2.031
1.580
1.573
1.566
1.561
1.553
1.295
1.283
1.267
1.066
1.060
1.039
1.029
1.023
0.901
0.892
0.879
0.865
0.840
0.831
0.825
0.819
0.813
0.804
OT^F
OT^F
OT^F
O
O
C5H11
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
ppm
1.00
1.00
1.86
5.00
1.00
2.06
2.11
8.44
3.19
3.15
8.60
44.98
10.02

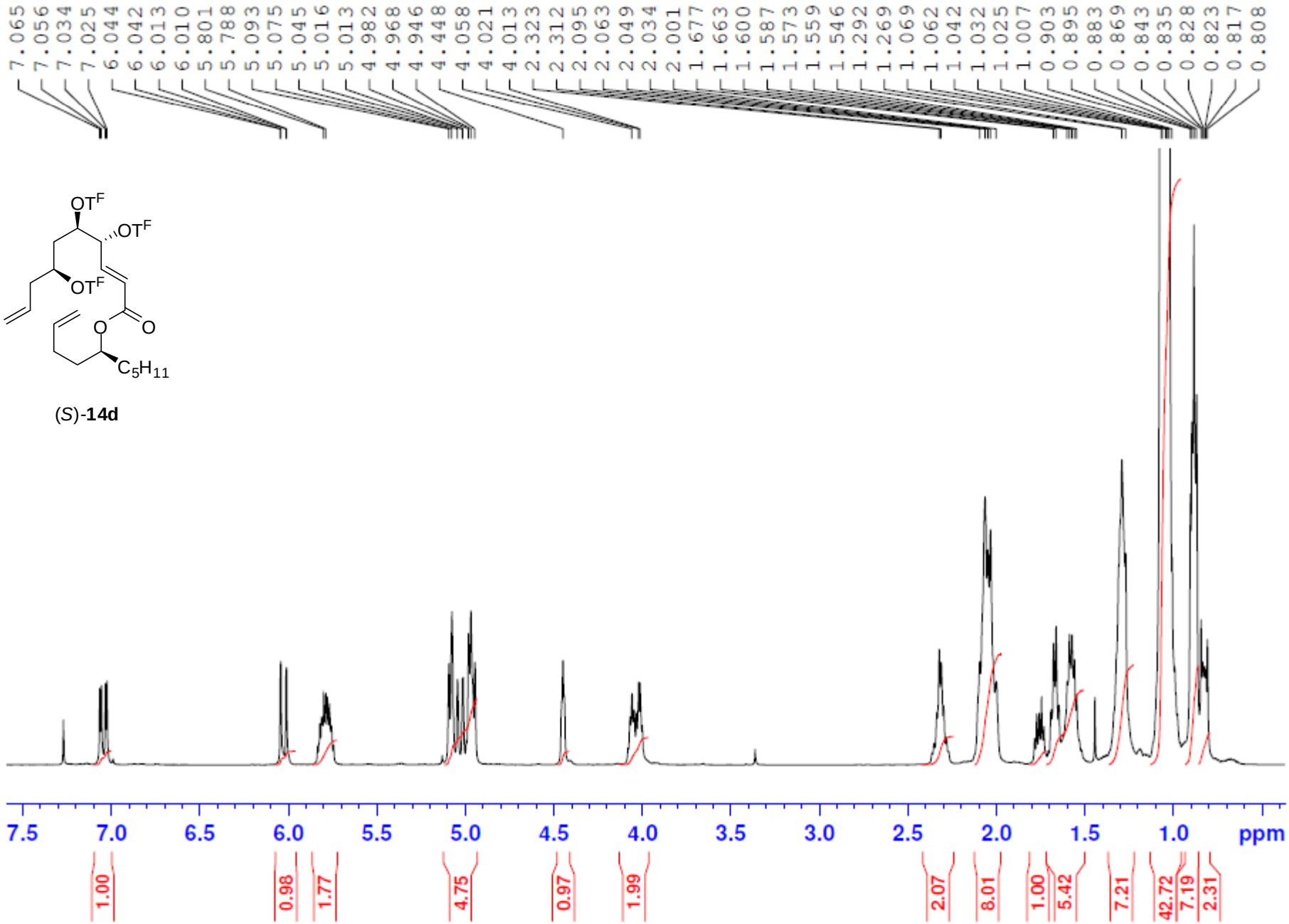
(*R*)-**14d**


165.37
145.90
137.88
133.85
123.11
117.80
114.79
75.88
74.11
72.70
69.13
41.75
40.82
33.97
33.33
31.69
29.74
29.59
25.64
25.54
25.39
25.34
25.23
25.03
24.85
22.51
17.77
17.69
17.65
17.59
17.53
17.48
13.94
13.08
OT^F
OT^F
OT^F
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

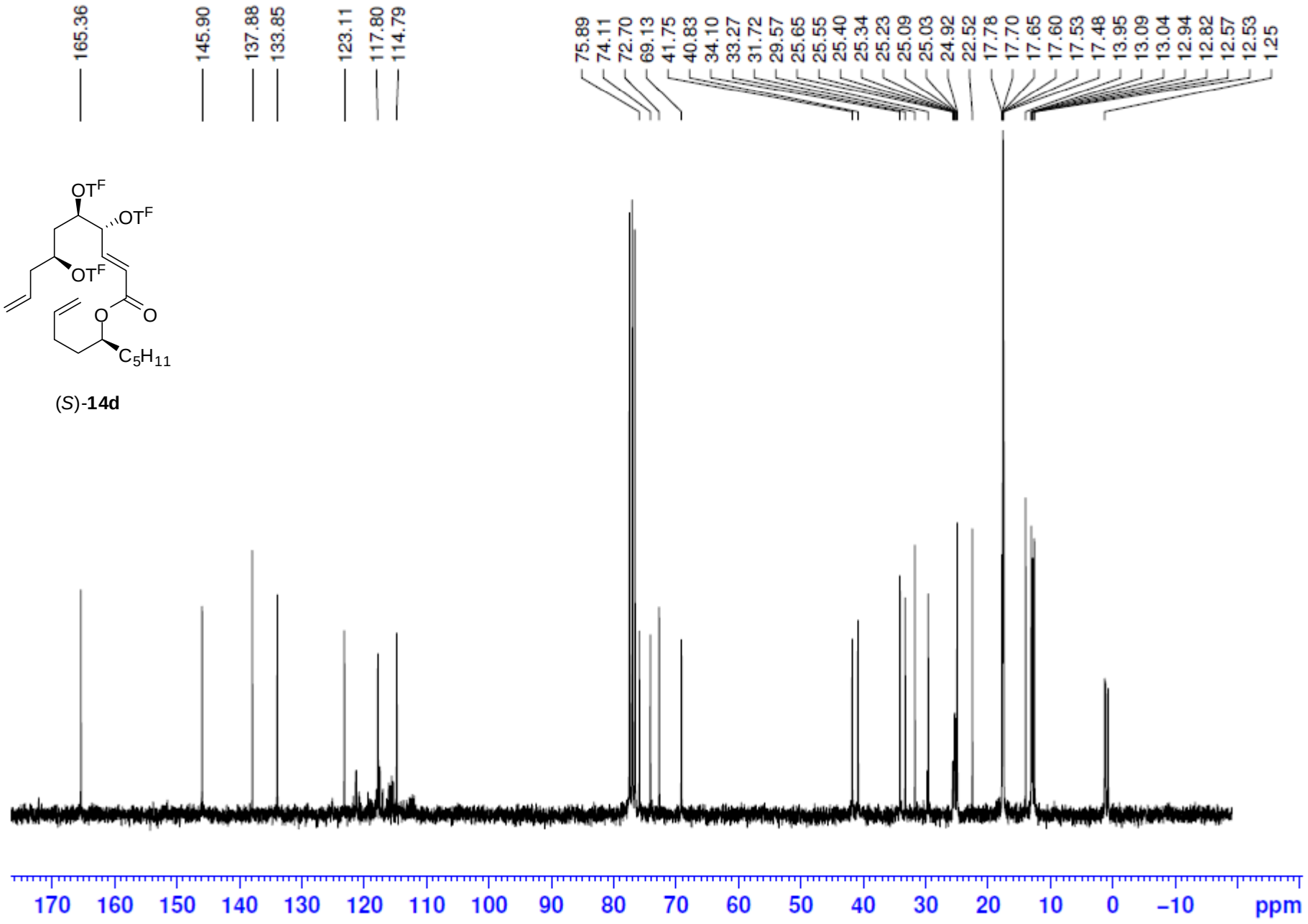
(*R*)-**14d**


-84.99
-85.03
-85.05
-120.31
-120.38
-120.40
-120.44
-120.51
-120.52
OT^F
OT^F
OT^F
O
O
C5H11
-85.0
ppm
-120.5
ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
2.97
2.00

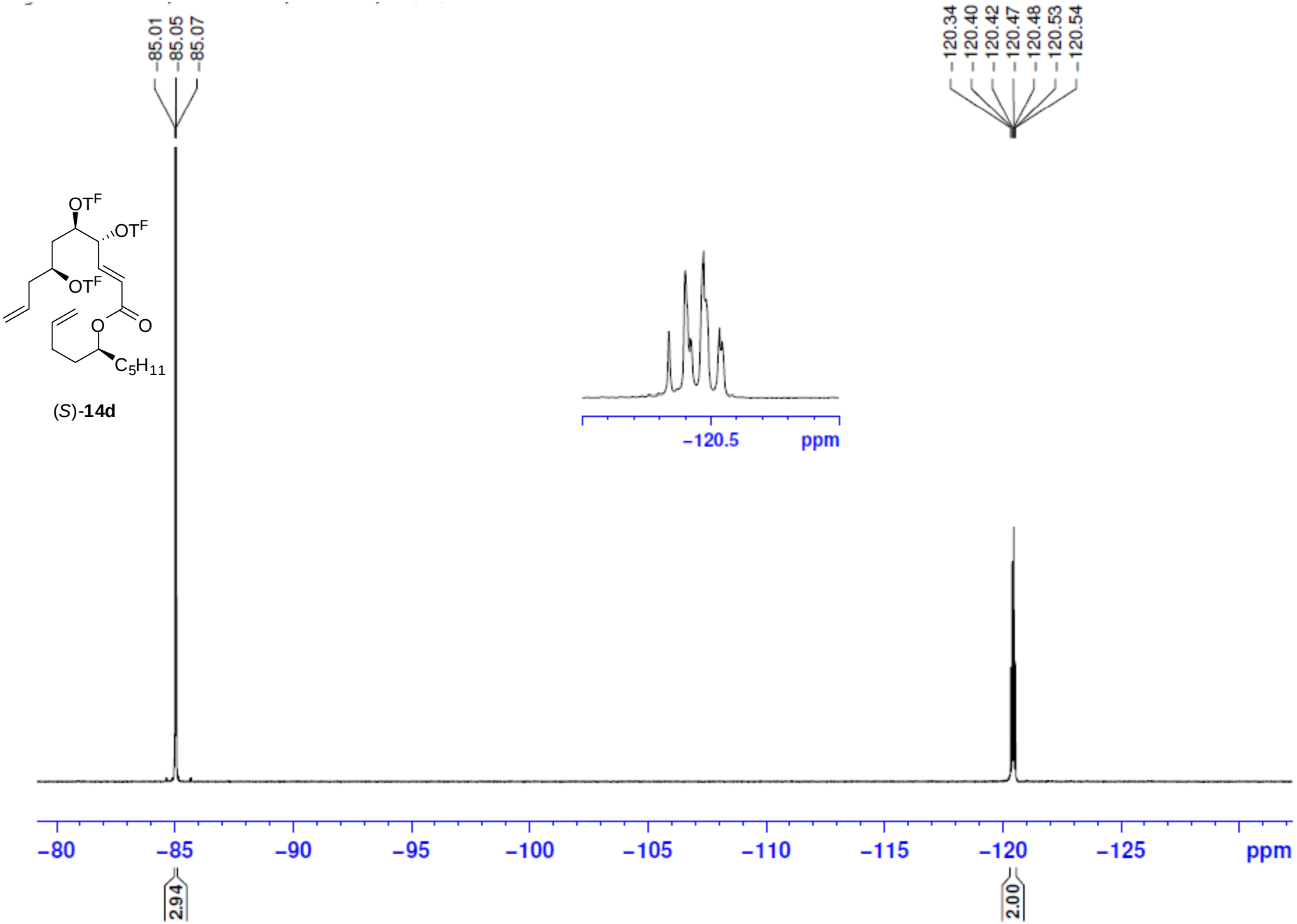
(*R*)-**14d**

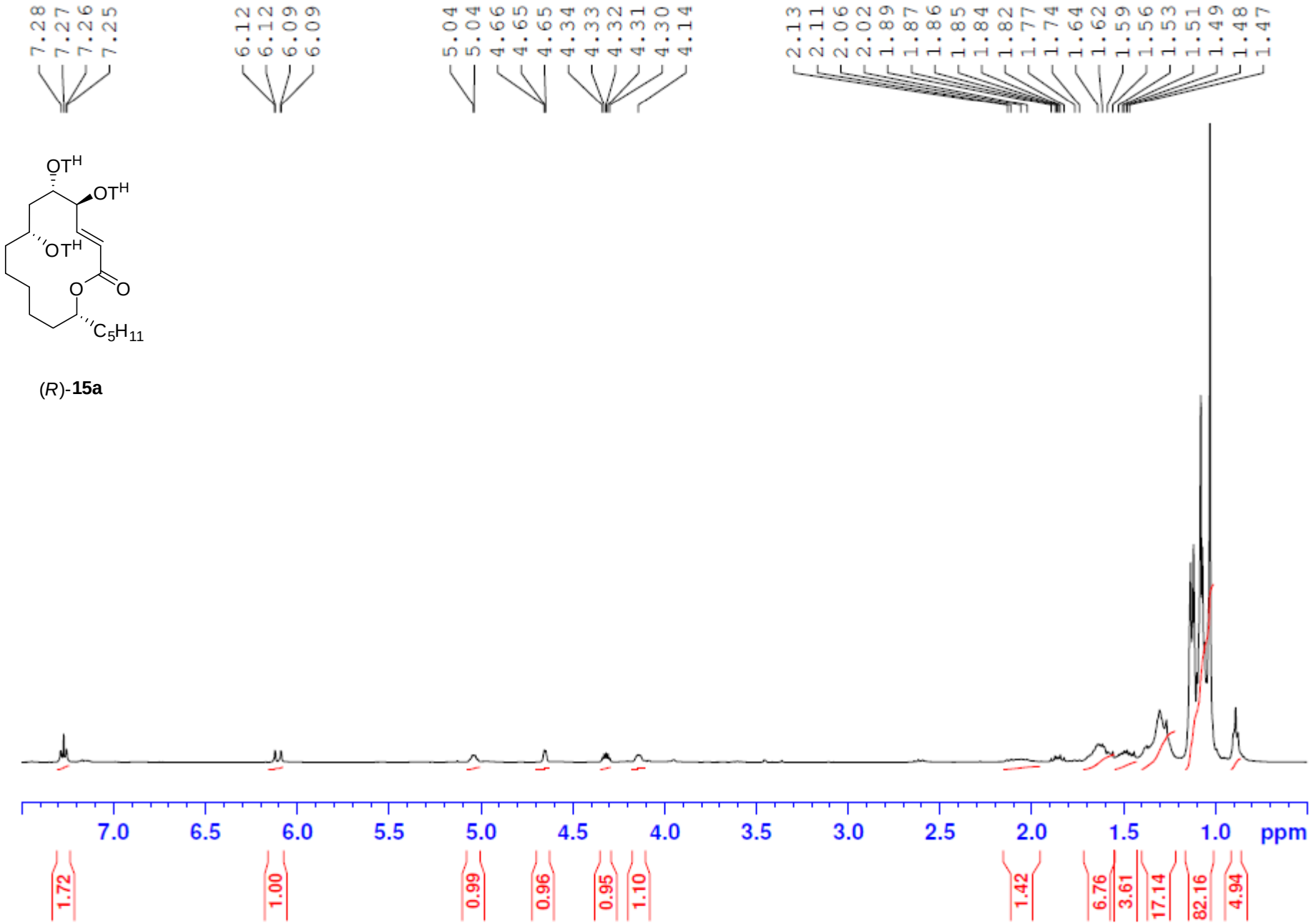

7.065
7.056
7.034
7.025
6.044
6.042
6.013
6.010
5.801
5.788
5.093
5.075
5.045
5.016
5.013
4.982
4.968
4.946
4.448
4.058
4.021
4.013
2.323
2.312
2.095
2.063
2.049
2.034
2.001
1.677
1.663
1.600
1.587
1.573
1.559
1.546
1.292
1.269
1.069
1.062
1.042
1.032
1.025
1.007
0.903
0.895
0.883
0.869
0.843
0.835
0.828
0.823
0.817
0.808
OT^F
OT^F
OT^F
O
O
C5H11
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
ppm
1.00
0.98
1.77
4.75
0.97
1.99
2.07
8.01
1.00
5.42
7.21
42.72
7.19
2.31

(*S*)-**14d**

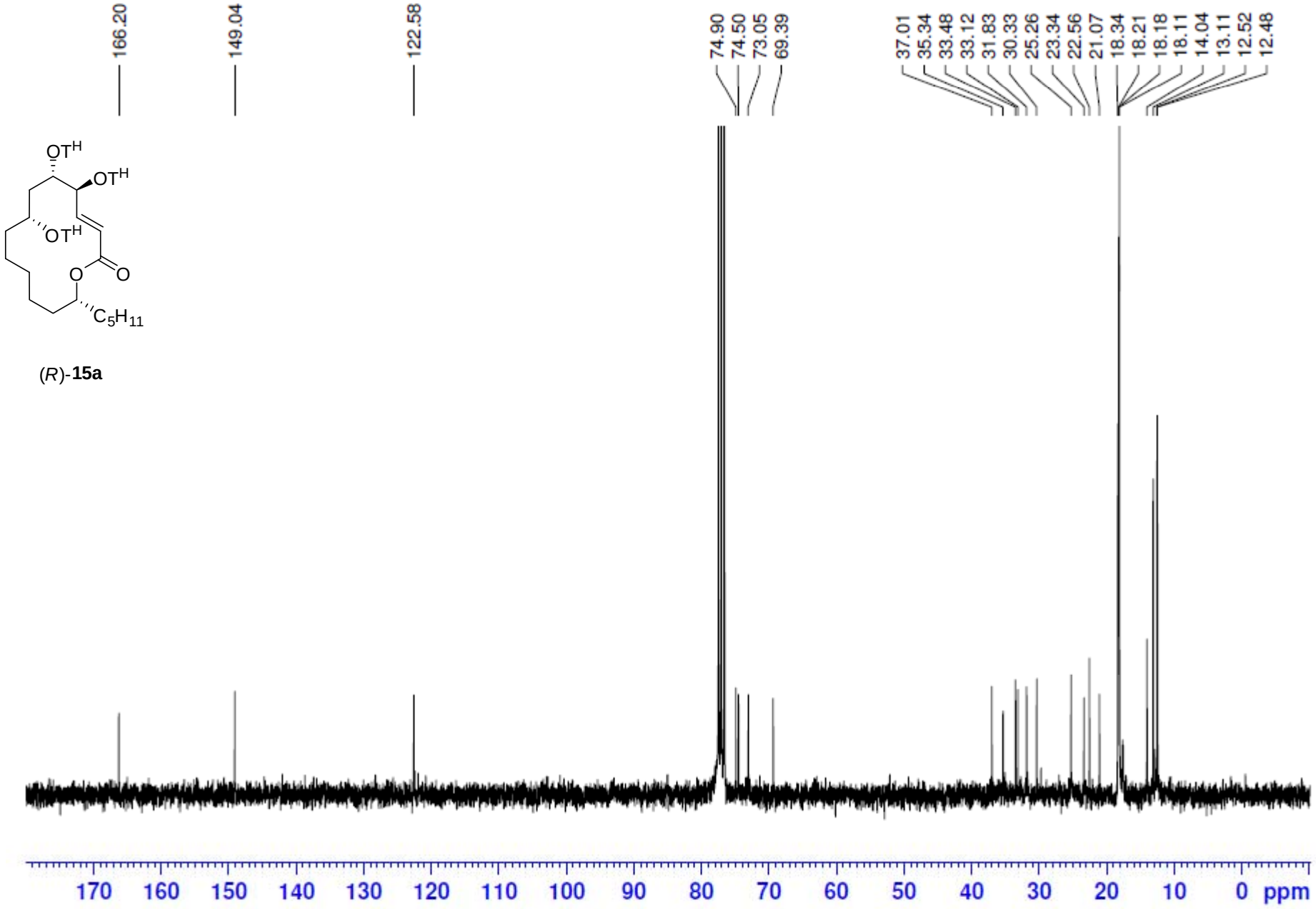

165.36
145.90
137.88
133.85
123.11
117.80
114.79
75.89
74.11
72.70
69.13
41.75
40.83
34.10
33.27
31.72
29.57
25.65
25.55
25.40
25.34
25.23
25.09
25.03
24.92
22.52
17.78
17.70
17.65
17.60
17.53
17.48
13.95
13.09
13.04
12.94
12.82
12.57
12.53
1.25
OT^F
OT^F
OT^F
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

(*S*)-**14d**

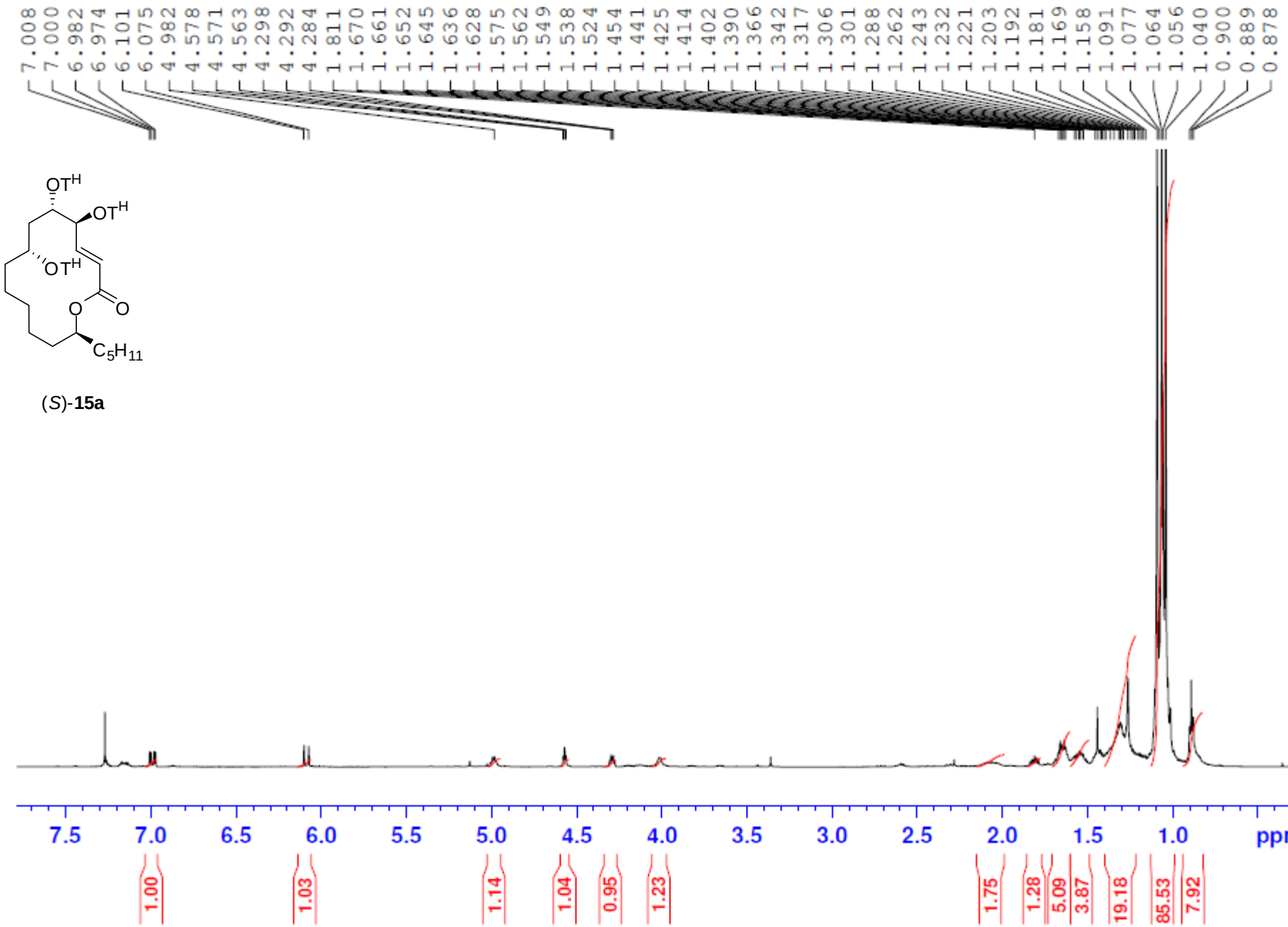

-85.01
-85.05
-85.07
120.34
120.40
120.42
120.47
120.48
120.53
120.54
OT^F
OT^F
OT^F
O
O
C5H11
(S)-14d
-120.5
ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
2.94
2.00


7.28
7.27
7.26
7.25
6.12
6.12
6.09
6.09
5.04
5.04
4.66
4.65
4.65
4.34
4.33
4.32
4.31
4.30
4.14
2.13
2.11
2.06
2.02
1.89
1.87
1.86
1.85
1.84
1.82
1.77
1.74
1.64
1.62
1.59
1.56
1.53
1.51
1.49
1.48
1.47
OTH
OTH
OTH
O
O
C5H11
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
ppm
1.72
1.00
0.99
0.96
0.95
1.10
1.42
6.76
3.61
17.14
82.16
4.94

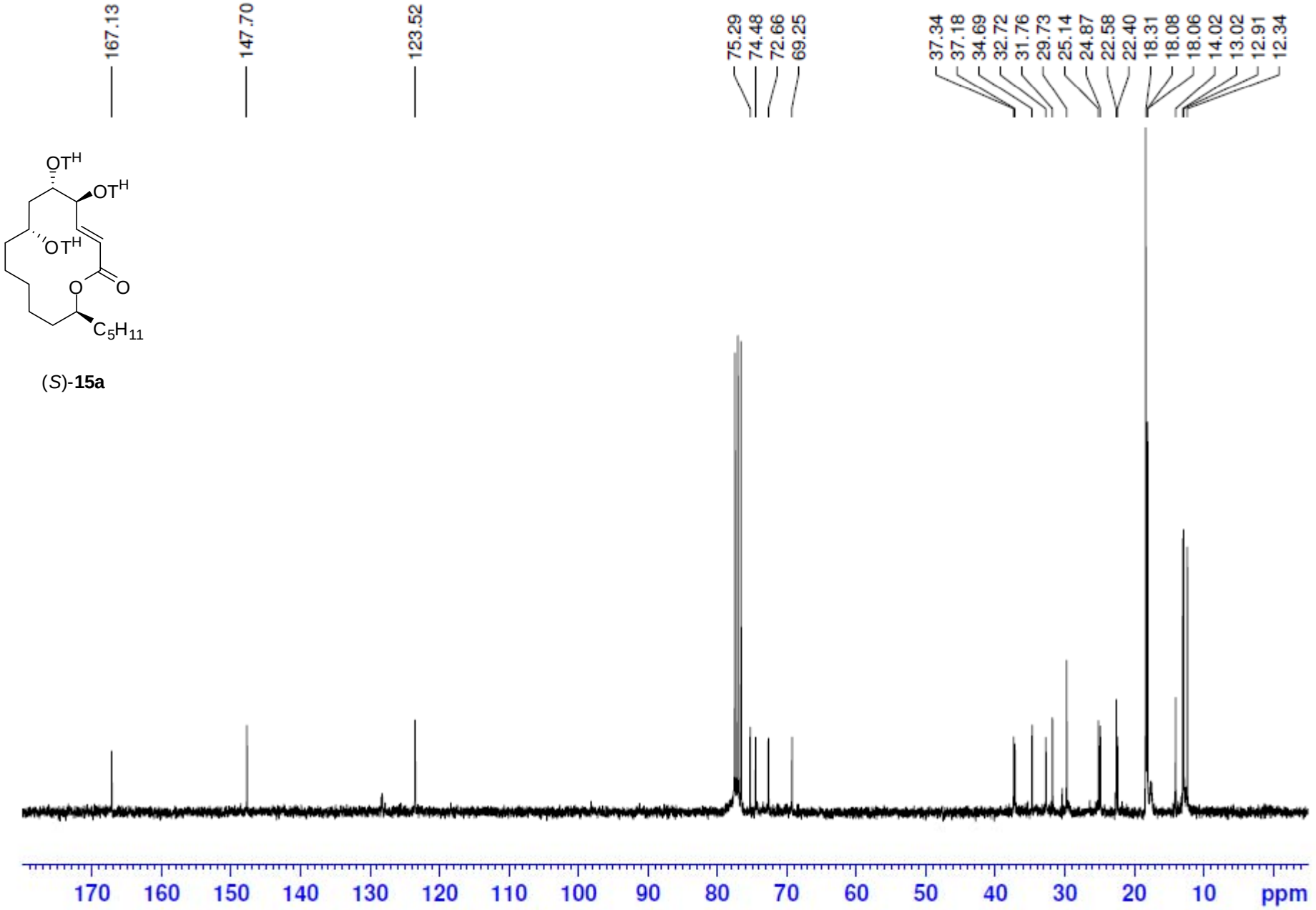
(*R*)-**15a**


166.20
149.04
122.58
74.90
74.50
73.05
69.39
37.01
35.34
33.48
33.12
31.83
30.33
25.26
23.34
22.56
21.07
18.34
18.21
18.18
18.11
14.04
13.11
12.52
12.48
OT^H
OT^H
OT^H
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

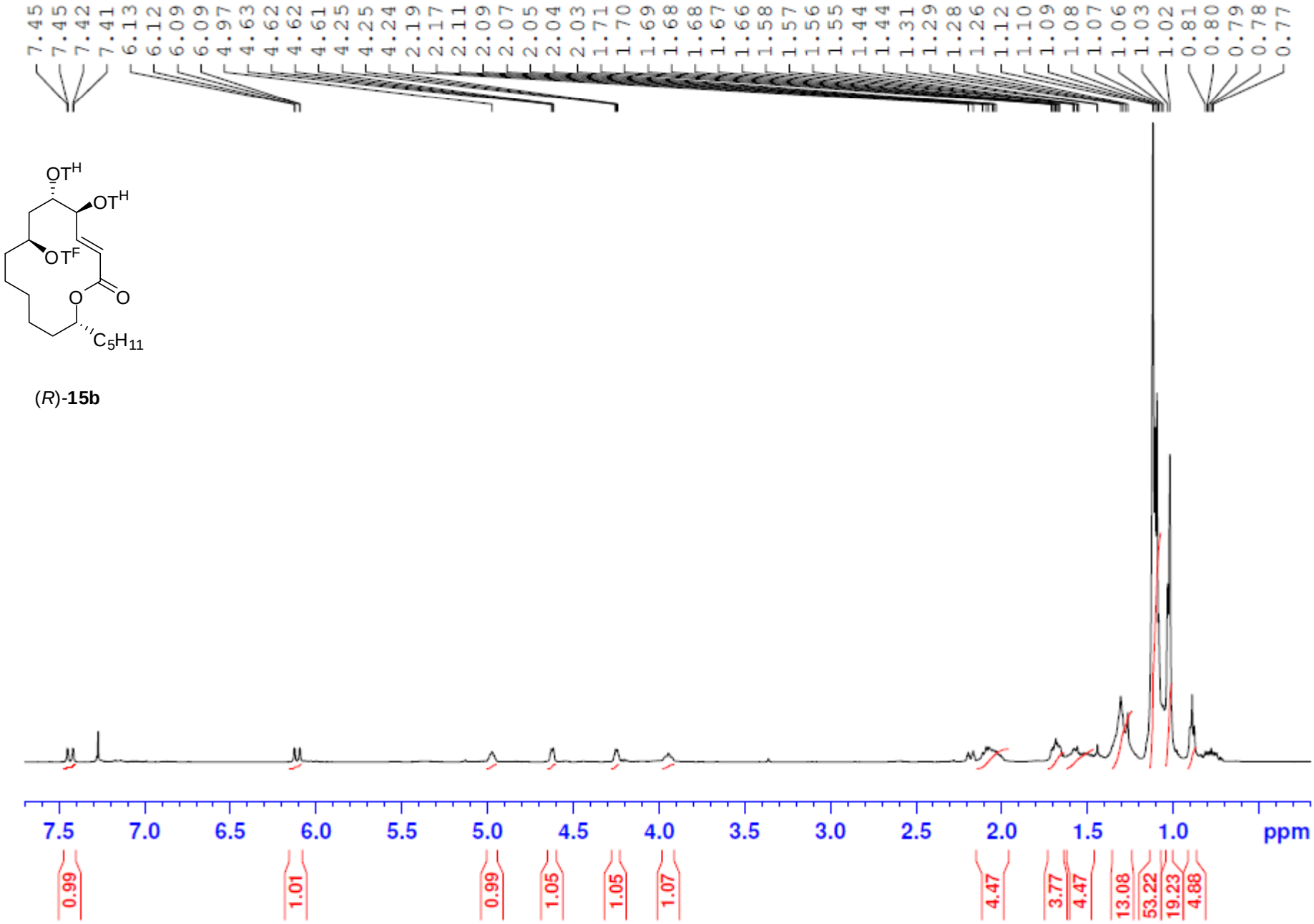
(*R*)-**15a**


7.008
7.000
6.982
6.974
6.101
6.075
4.982
4.578
4.571
4.563
4.298
4.292
4.284
1.811
1.670
1.661
1.652
1.645
1.636
1.628
1.575
1.562
1.549
1.538
1.524
1.454
1.441
1.425
1.414
1.402
1.390
1.366
1.342
1.317
1.306
1.301
1.288
1.262
1.243
1.232
1.221
1.203
1.192
1.181
1.169
1.158
1.091
1.077
1.064
1.056
1.040
0.900
0.889
0.878
OT^H
OT^H
OT^H
O
O
C5H11
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
ppm
1.00
1.03
1.14
1.04
0.95
1.23
1.75
1.28
5.09
3.87
19.18
85.53
7.92

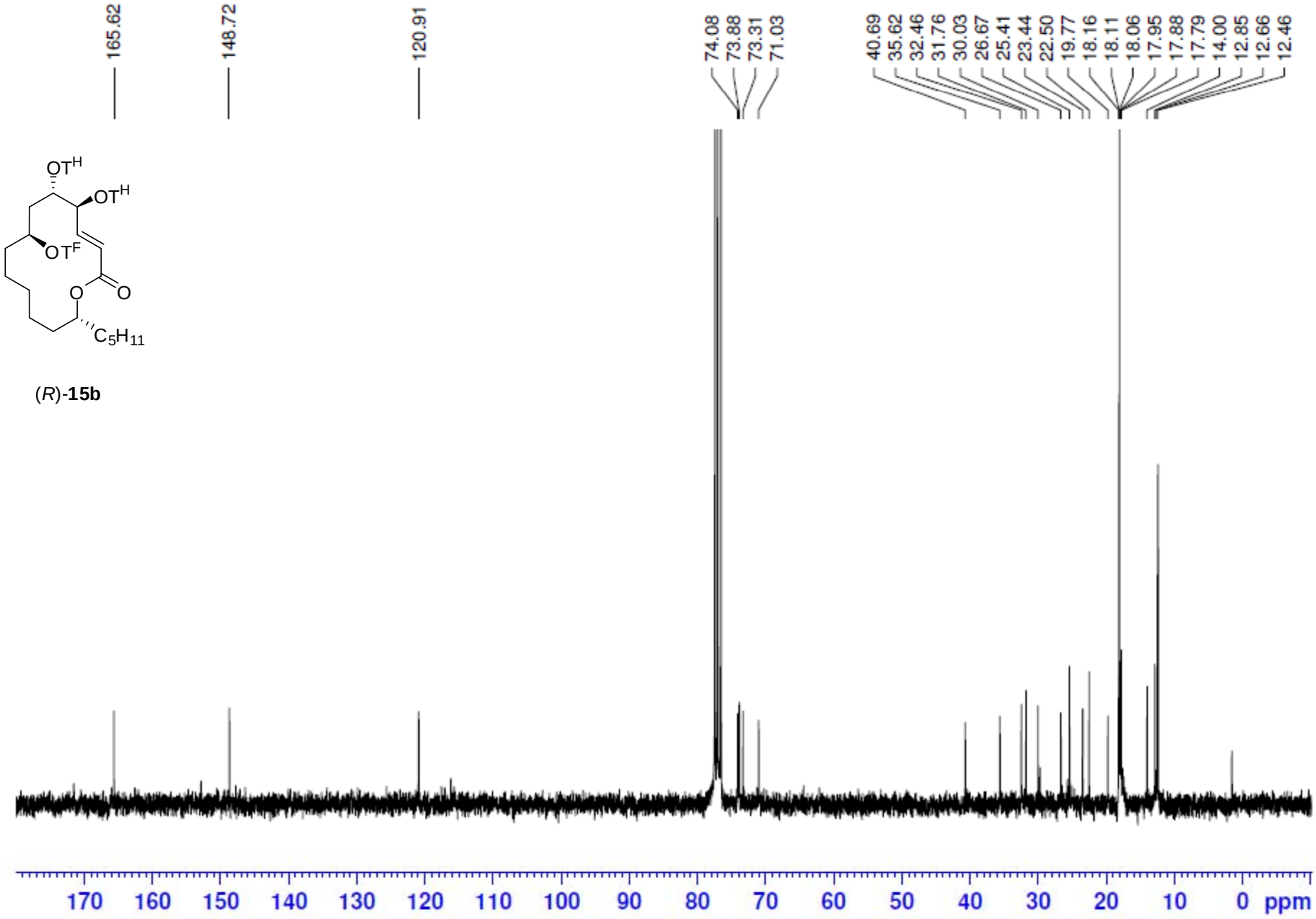
(*S*)-**15a**


167.13
147.70
123.52
75.29
74.48
72.66
69.25
37.34
37.18
34.69
32.72
31.76
29.73
25.14
24.87
22.58
22.40
18.31
18.08
18.06
14.02
13.02
12.91
12.34
OT^H
OT^H
OT^H
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

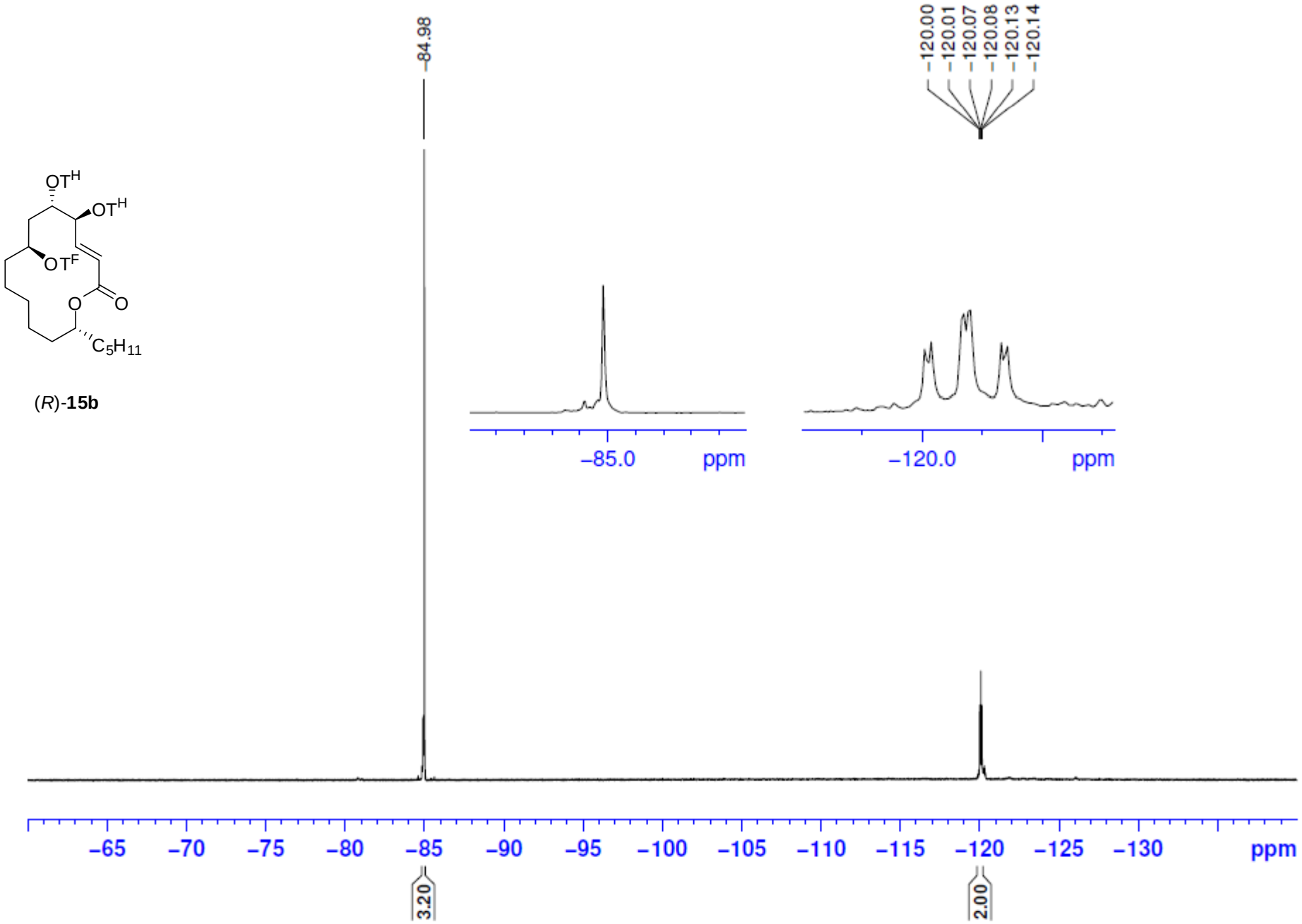
(*S*)-**15a**


7.45 7.45 7.42 7.41 6.13 6.12 6.09 6.09 4.97 4.63 4.62 4.62 4.61 4.25 4.25 4.24 2.19 2.17 2.11 2.09 2.07 2.05 2.04 2.03 1.71 1.70 1.69 1.68 1.68 1.67 1.66 1.58 1.57 1.56 1.55 1.44 1.44 1.31 1.29 1.28 1.26 1.12 1.10 1.09 1.08 1.07 1.06 1.03 1.02 0.81 0.80 0.79 0.78 0.77
OT^H
OT^H
OT^F
O
O
C5H11
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 ppm
0.99 1.01 0.99 1.05 1.05 1.07 4.47 3.77 4.47 13.08 53.22 19.23 4.88

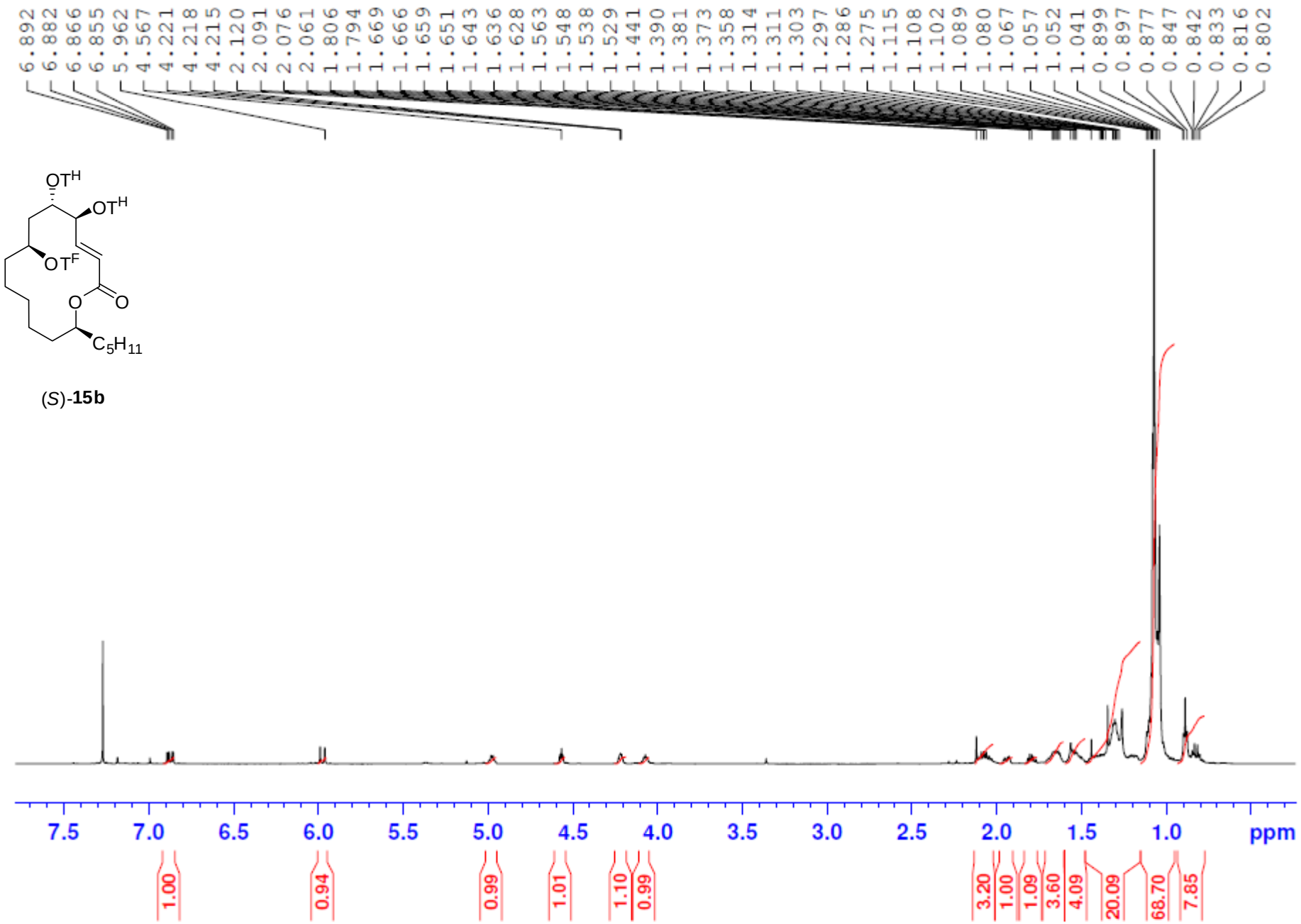
(*R*)-**15b**


165.62
148.72
120.91
74.08
73.88
73.31
71.03
40.69
35.62
32.46
31.76
30.03
26.67
25.41
23.44
22.50
19.77
18.16
18.11
18.06
17.95
17.88
17.79
14.00
12.85
12.66
12.46
OT^H
OT^H
OT^F
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

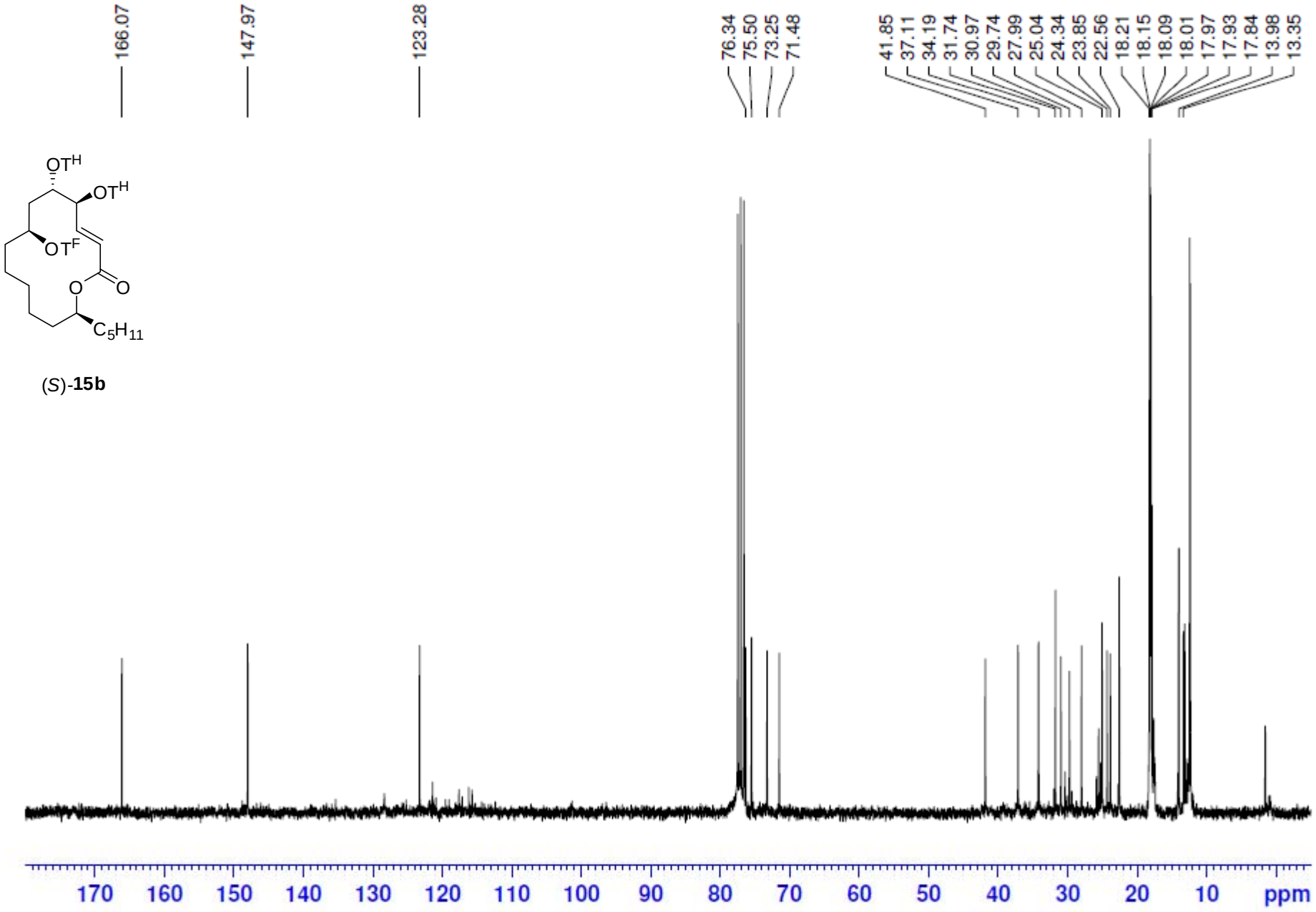
(*R*)-**15b**


-84.98
-120.00
-120.01
-120.07
-120.08
-120.13
-120.14
OT^H
OT^H
OT^F
O
O
C5H11
-85.0
ppm
-120.0
ppm
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
ppm
3.20
2.00

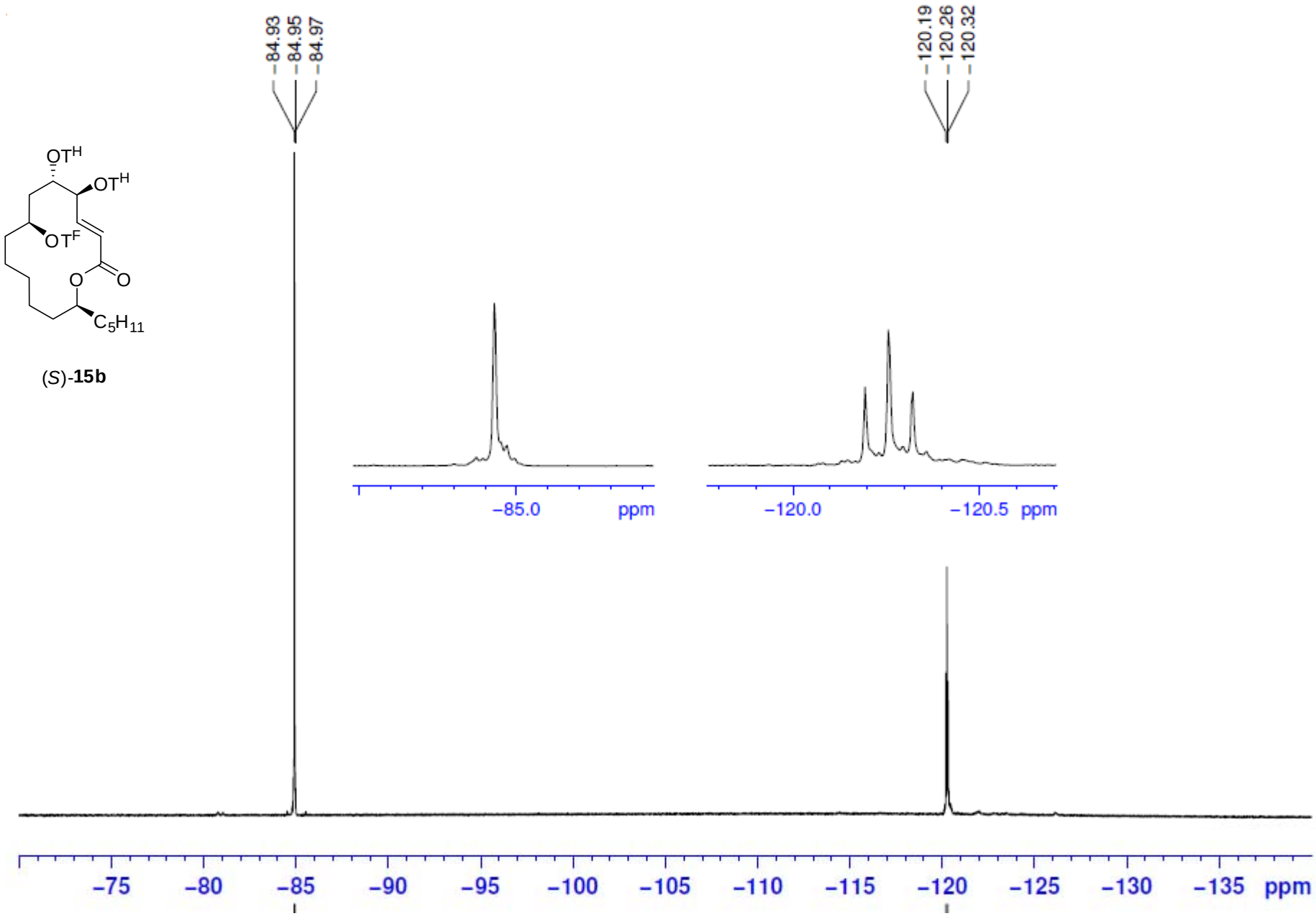
(*R*)-**15b**


6.892
6.882
6.866
6.855
5.962
4.567
4.221
4.218
4.215
2.120
2.091
2.076
2.061
1.806
1.794
1.669
1.666
1.659
1.651
1.643
1.636
1.628
1.563
1.548
1.538
1.529
1.441
1.390
1.381
1.373
1.358
1.314
1.311
1.303
1.297
1.286
1.275
1.115
1.108
1.102
1.089
1.080
1.067
1.057
1.052
1.041
0.899
0.897
0.877
0.847
0.842
0.833
0.816
0.802
OT^H
OT^H
OT^F
O
O
C5H11
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
ppm
1.00
0.94
0.99
1.01
1.10
0.99
3.20
1.00
1.09
3.60
4.09
20.09
68.70
7.85

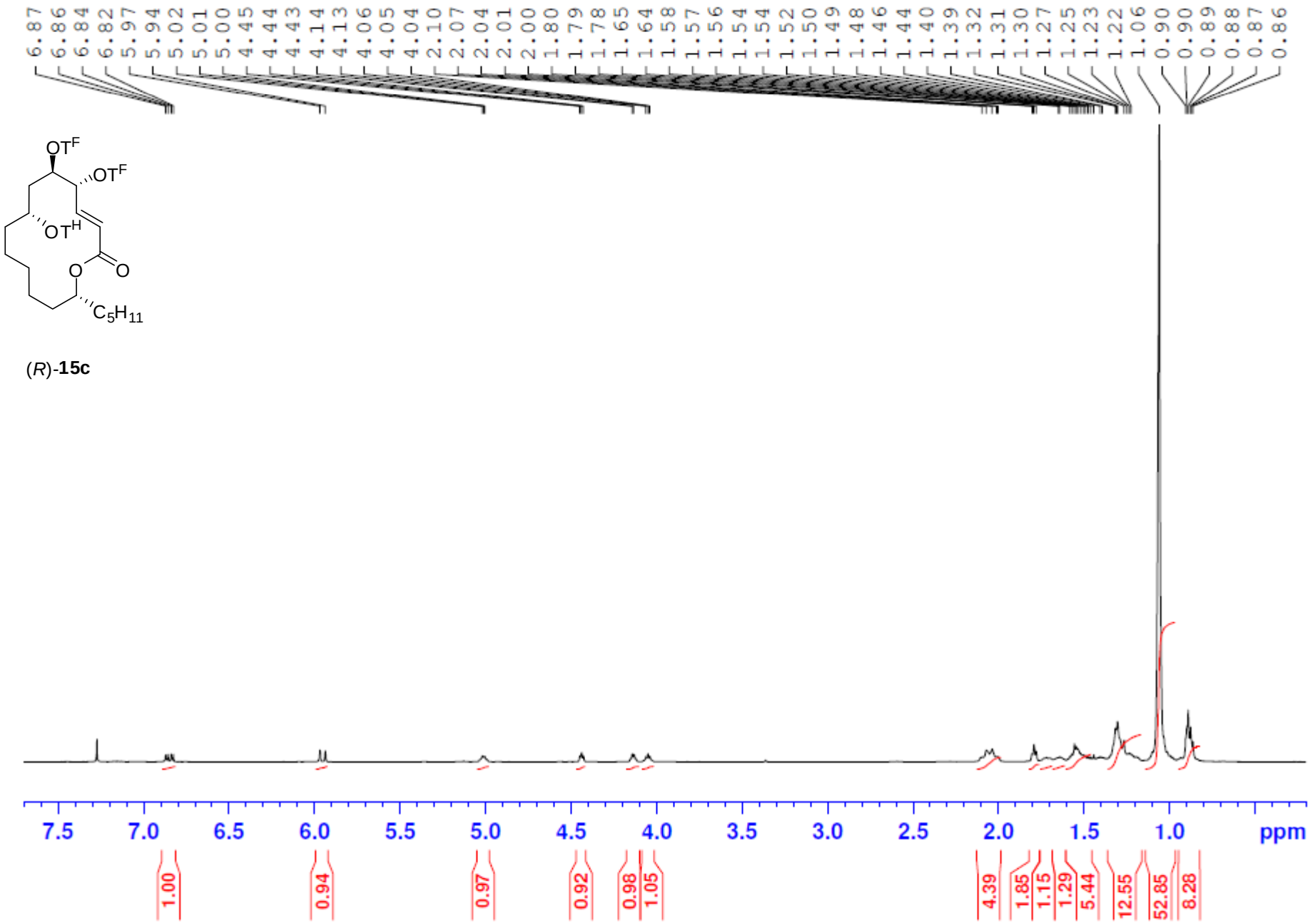
(*S*)-**15b**


166.07
147.97
123.28
76.34
75.50
73.25
71.48
41.85
37.11
34.19
31.74
30.97
29.74
27.99
25.04
24.34
23.85
22.56
18.21
18.15
18.09
18.01
17.97
17.93
17.84
13.98
13.35
OT^H
OT^H
OT^F
O
O
C5H11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

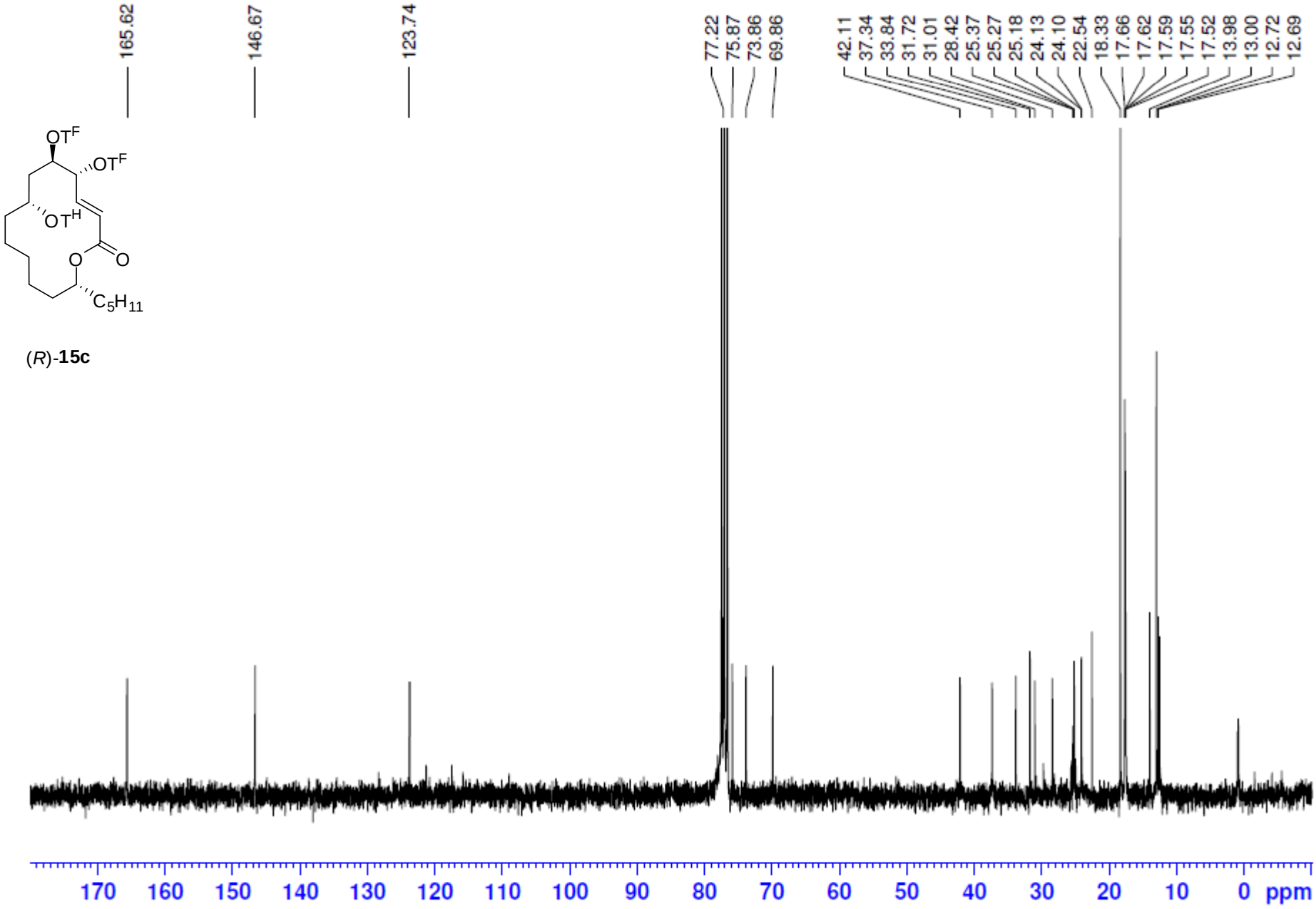
(*S*)-**15b**


-84.93
-84.95
-84.97
-120.19
-120.26
-120.32
OT^H
OT^H
OT^F
O
O
C5H11
-85.0 ppm
-120.0 -120.5 ppm
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 ppm

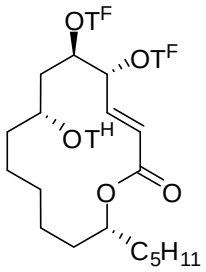
(*S*)-**15b**


6.87 6.86 6.84 6.82 5.97 5.94 5.02 5.01 5.00 4.45 4.44 4.43 4.14 4.13 4.06 4.05 4.04 2.10 2.07 2.04 2.01 2.00 1.80 1.79 1.78 1.65 1.64 1.58 1.57 1.56 1.54 1.54 1.52 1.50 1.49 1.48 1.46 1.44 1.40 1.39 1.32 1.31 1.30 1.27 1.25 1.23 1.22 1.06 0.90 0.90 0.89 0.88 0.87 0.86
OT^F
OT^F
OT^H
O
O
C5H11
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 ppm
1.00 0.94 0.97 0.92 0.98 1.05 4.39 1.85 1.15 1.29 5.44 12.55 52.85 8.28

(*R*)-**15c**

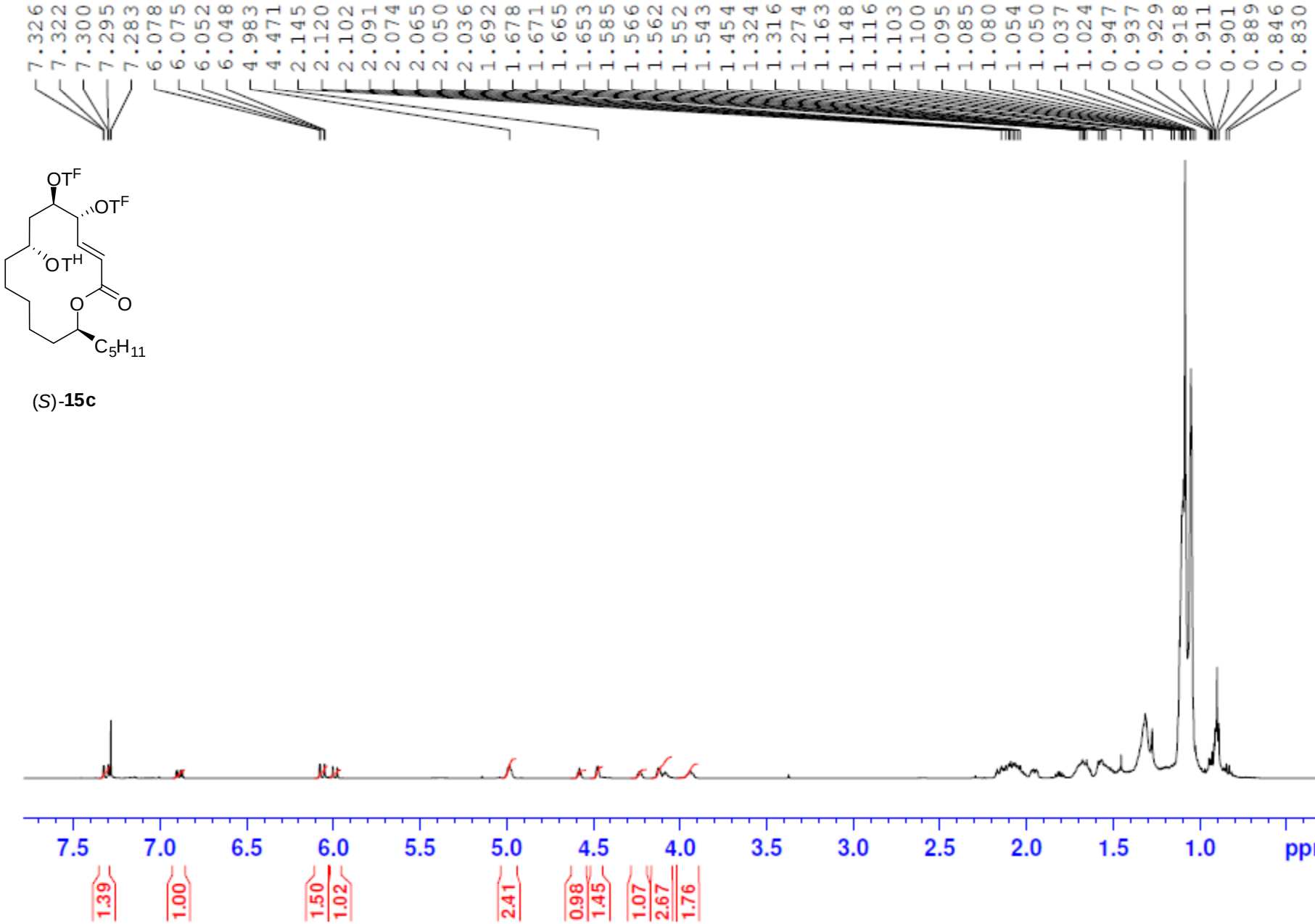

165.62
146.67
123.74
77.22
75.87
73.86
69.86
42.11
37.34
33.84
31.72
31.01
28.42
25.37
25.27
25.18
24.13
24.10
22.54
18.33
17.66
17.62
17.59
17.55
17.52
13.98
13.00
12.72
12.69
OT^F
OT^F
OT^H
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(*R*)-**15c**

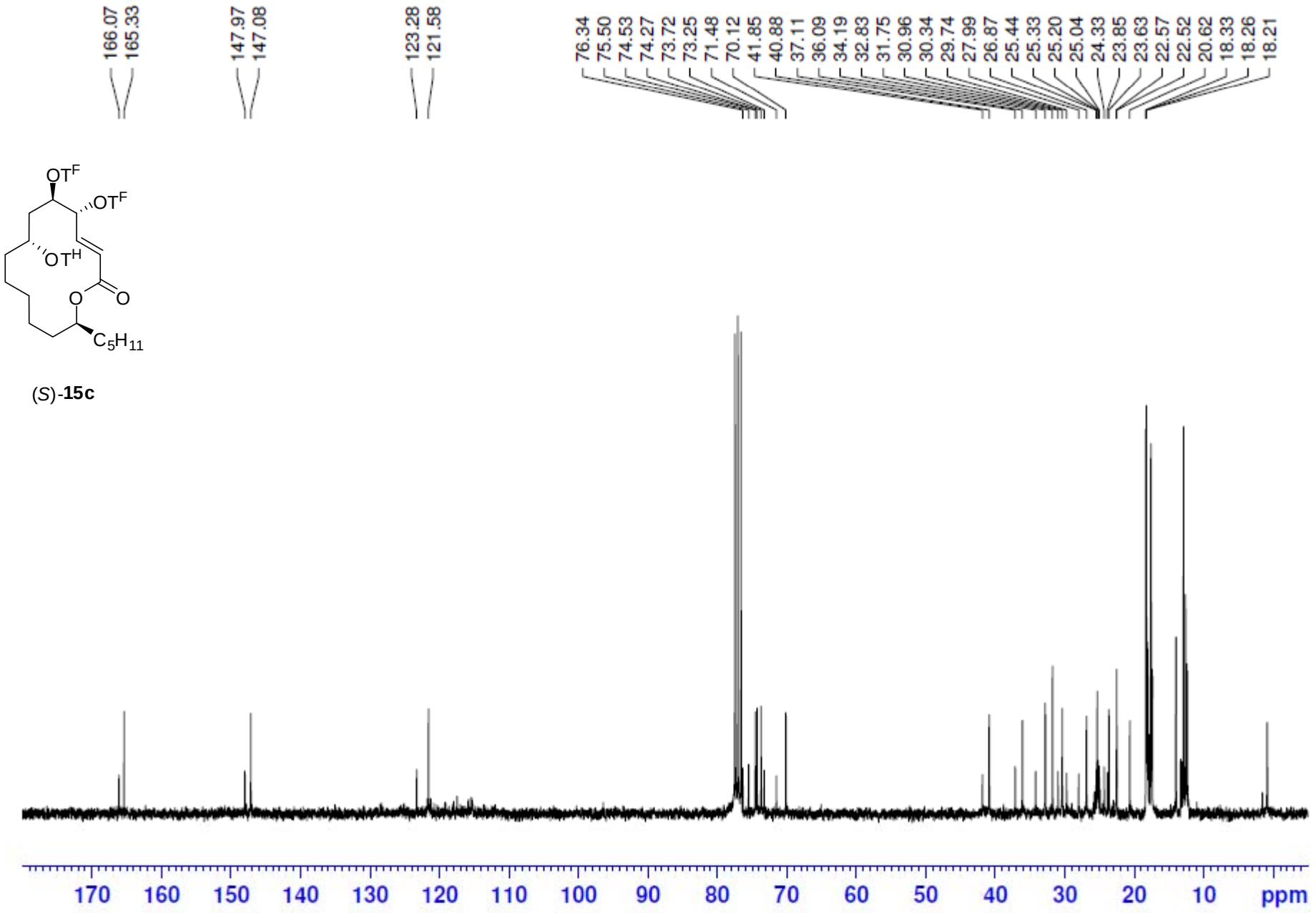

OT^F
OT^F
OT^H
O
O
C5H11

(*R*)-**15c**

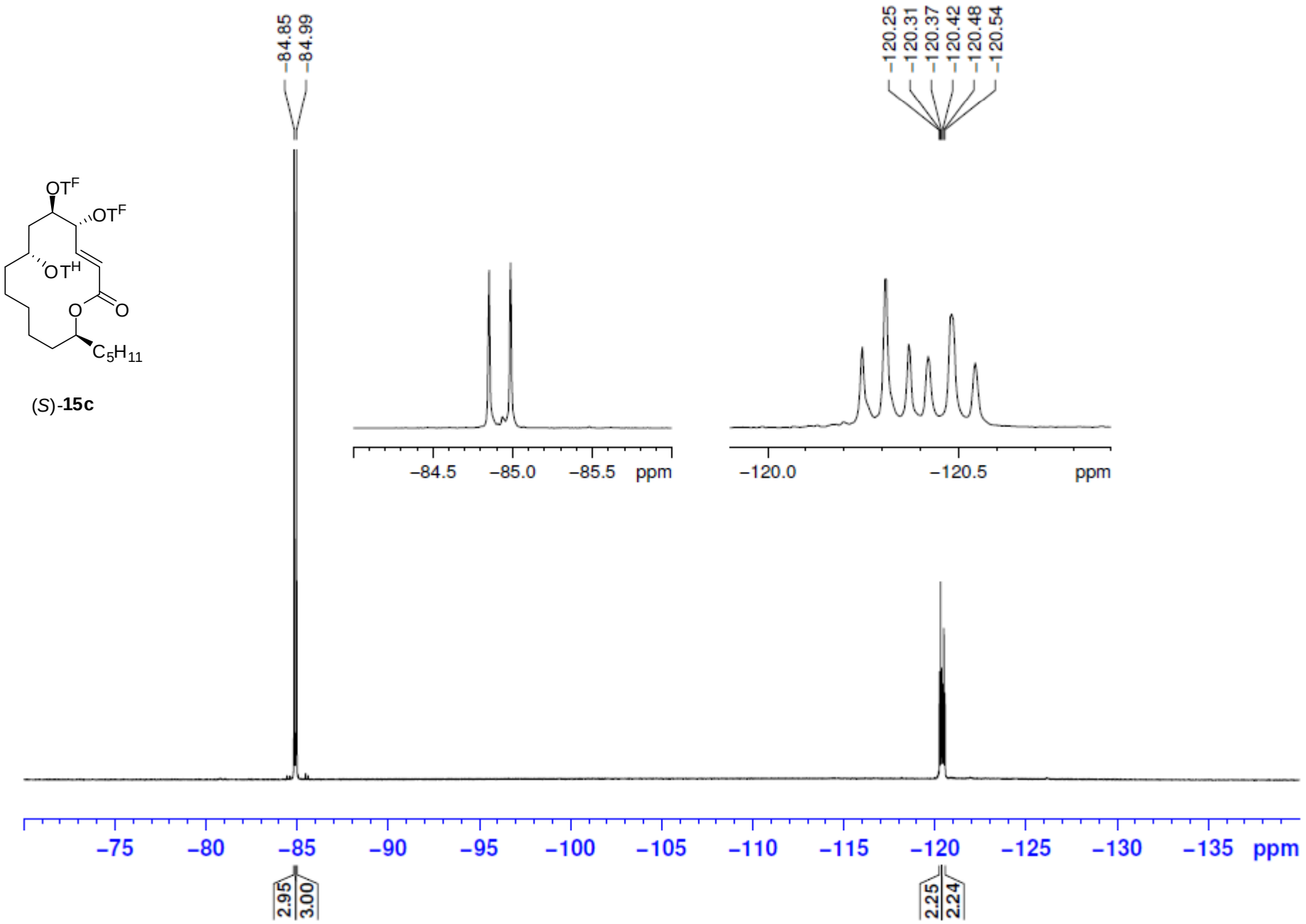
-84.91
-84.93
-120.13
-120.19
-120.23
-120.26
-120.29
-120.36
-84.8
-85.0
ppm
-120.2
ppm
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
ppm
3.03
2.00

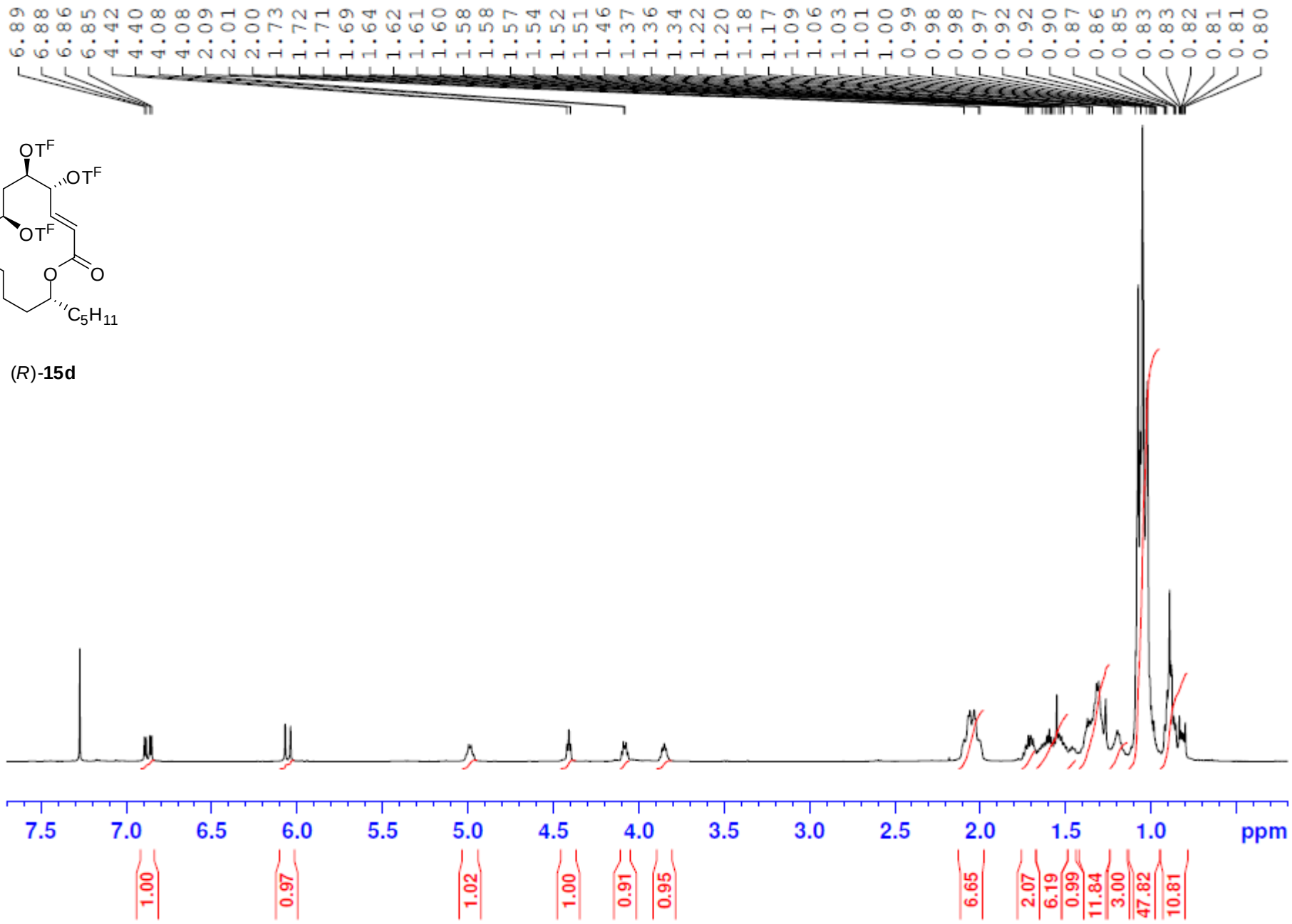

7.326
7.322
7.300
7.295
7.283
6.078
6.075
6.052
6.048
4.983
4.471
2.145
2.120
2.102
2.091
2.074
2.065
2.050
2.036
1.692
1.678
1.671
1.665
1.653
1.585
1.566
1.562
1.552
1.543
1.454
1.324
1.316
1.274
1.163
1.148
1.116
1.103
1.100
1.095
1.085
1.080
1.054
1.050
1.037
1.024
0.947
0.937
0.929
0.918
0.911
0.901
0.889
0.846
0.830
OT^F
OT^F
OT^H
O
O
C5H11
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
ppm
1.39
1.00
1.50
1.02
2.41
0.98
1.45
1.07
2.67
1.76

(*S*)-**15c**

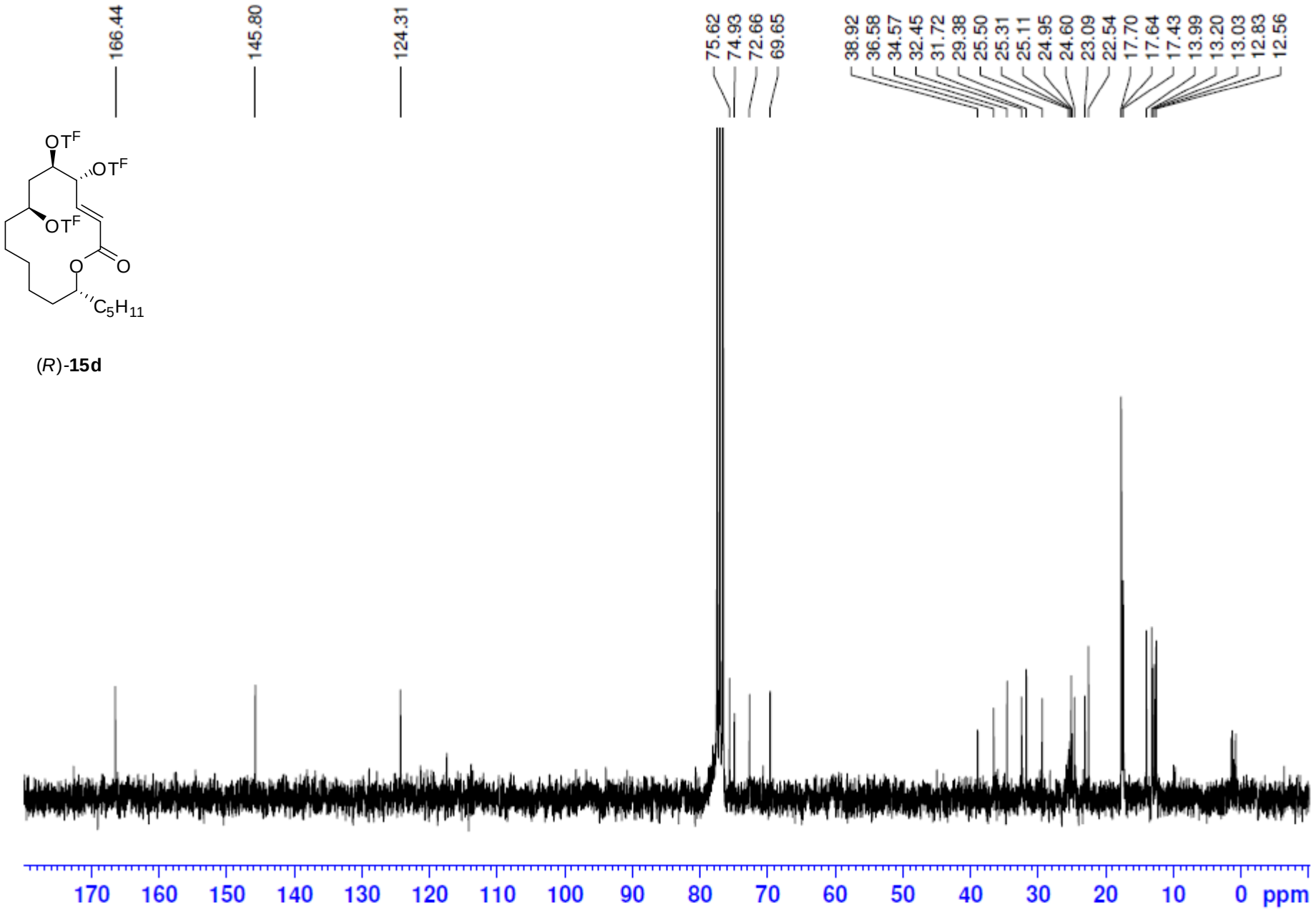

166.07
165.33
147.97
147.08
123.28
121.58
76.34
75.50
74.53
74.27
73.72
73.25
71.48
70.12
41.85
40.88
37.11
36.09
34.19
32.83
31.75
30.96
30.34
29.74
27.99
26.87
25.44
25.33
25.20
25.04
24.33
23.85
23.63
22.57
22.52
20.62
18.33
18.26
18.21
OT^F
OT^F
OT^H
O
O
C5H11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(*S*)-**15c**

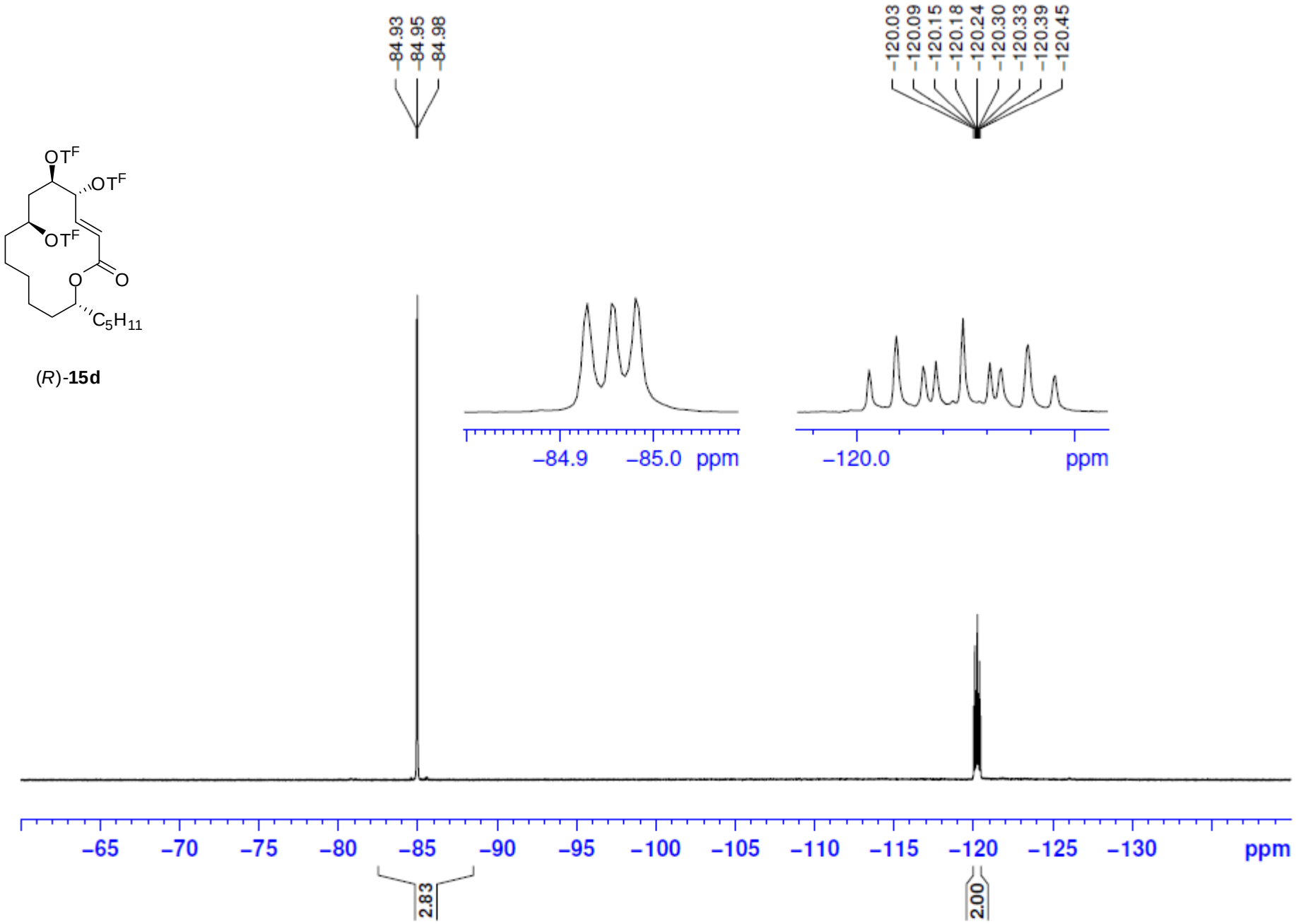

-84.85
-84.99
-120.25
-120.31
-120.37
-120.42
-120.48
-120.54
OT^F
OT^F
OT^H
O
O
C5H11
(S)-15c
-84.5
-85.0
-85.5
ppm
-120.0
-120.5
ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
ppm
2.95
3.00
2.25
2.24


6.89 6.88 6.86 6.85 4.42 4.40 4.08 4.08 2.09 2.01 2.00 1.73 1.72 1.71 1.69 1.64 1.62 1.61 1.60 1.58 1.58 1.57 1.54 1.52 1.51 1.46 1.37 1.36 1.34 1.22 1.20 1.18 1.17 1.09 1.06 1.03 1.01 1.00 0.99 0.98 0.98 0.97 0.92 0.92 0.90 0.87 0.86 0.85 0.83 0.83 0.82 0.81 0.81 0.80
OT^F
OT^F
OT^F
O
O
C5H11
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 ppm
1.00 0.97 1.02 1.00 0.91 0.95 6.65 2.07 6.19 0.99 11.84 3.00 47.82 10.81

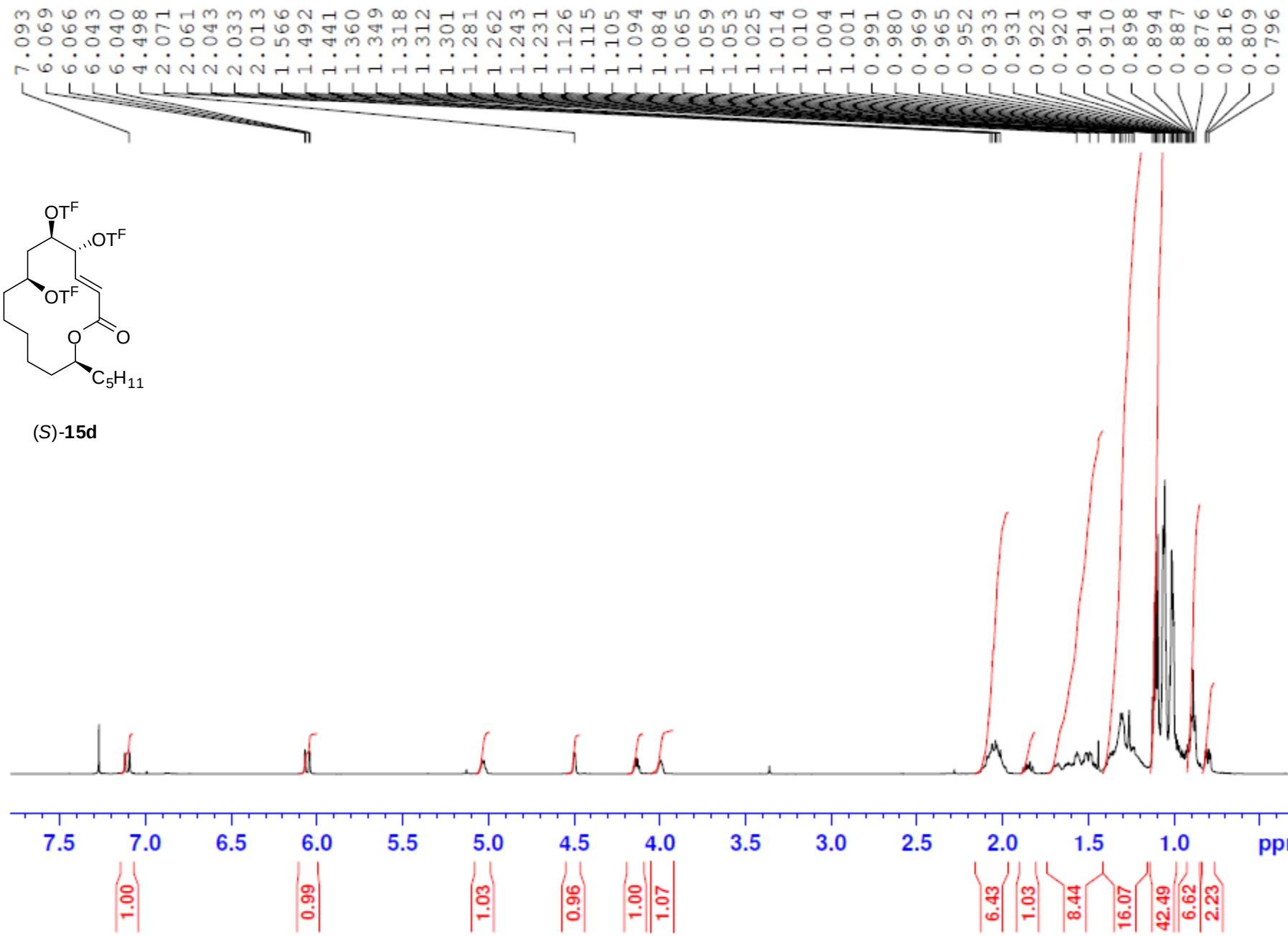
(*R*)-**15d**


166.44
145.80
124.31
75.62
74.93
72.66
69.65
38.92
36.58
34.57
32.45
31.72
29.38
25.50
25.31
25.11
24.95
24.60
23.09
22.54
17.70
17.64
17.43
13.99
13.20
13.03
12.83
12.56
OT^F
OT^F
OT^F
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

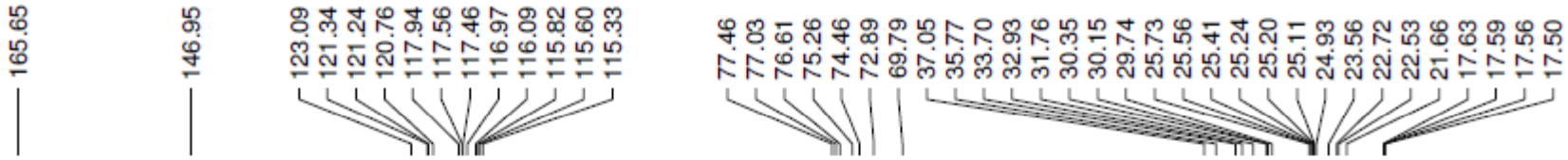
(*R*)-**15d**

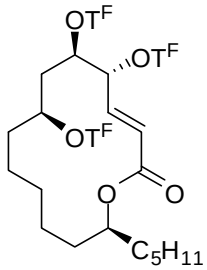

−84.93
−84.95
−84.98
−120.03
−120.09
−120.15
−120.18
−120.24
−120.30
−120.33
−120.39
−120.45
OT^F
OT^F
OT^F
O
O
C5H11
−84.9
−85.0
ppm
−120.0
ppm
−65
−70
−75
−80
−85
−90
−95
−100
−105
−110
−115
−120
−125
−130
ppm
2.83
2.00

(*R*)-**15d**


7.093
6.069
6.066
6.043
6.040
4.498
2.071
2.061
2.043
2.033
2.013
1.566
1.492
1.441
1.360
1.349
1.318
1.312
1.301
1.281
1.262
1.243
1.231
1.126
1.115
1.105
1.094
1.084
1.065
1.059
1.053
1.025
1.014
1.010
1.004
1.001
0.991
0.980
0.969
0.965
0.952
0.933
0.931
0.923
0.920
0.914
0.910
0.898
0.894
0.887
0.876
0.816
0.809
0.796
OT^F
OT^F
OT^F
O
O
C5H11
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
ppm
1.00
0.99
1.03
0.96
1.00
1.07
6.43
1.03
8.44
16.07
42.49
6.62
2.23

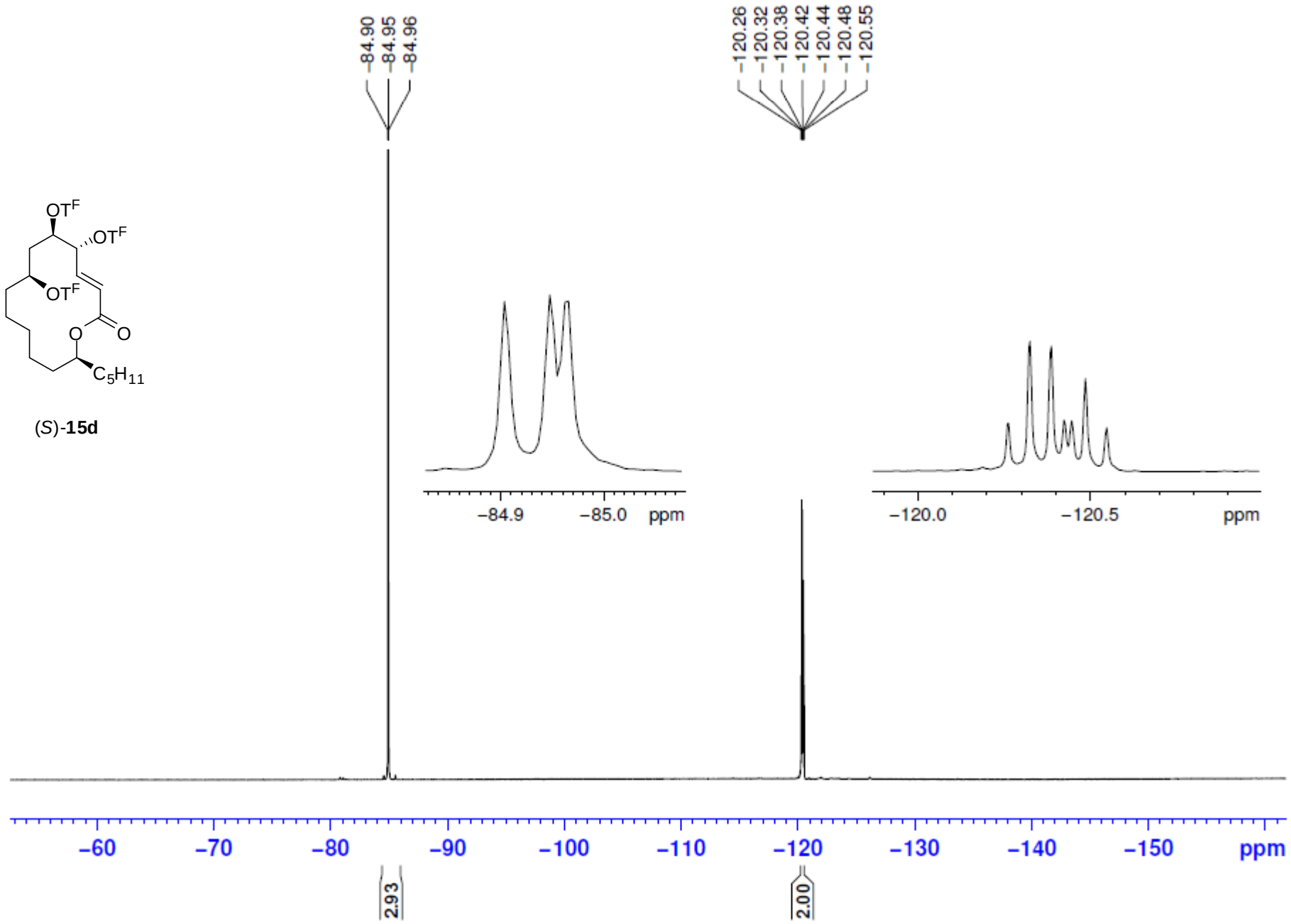
(*S*)-**15d**


165.65
146.95
123.09
121.34
121.24
120.76
117.94
117.56
117.46
116.97
116.09
115.82
115.60
115.33
77.46
77.03
76.61
75.26
74.46
72.89
69.79
37.05
35.77
33.70
32.93
31.76
30.35
30.15
29.74
25.73
25.56
25.41
25.24
25.20
25.11
24.93
23.56
22.72
22.53
21.66
17.63
17.59
17.56
17.50

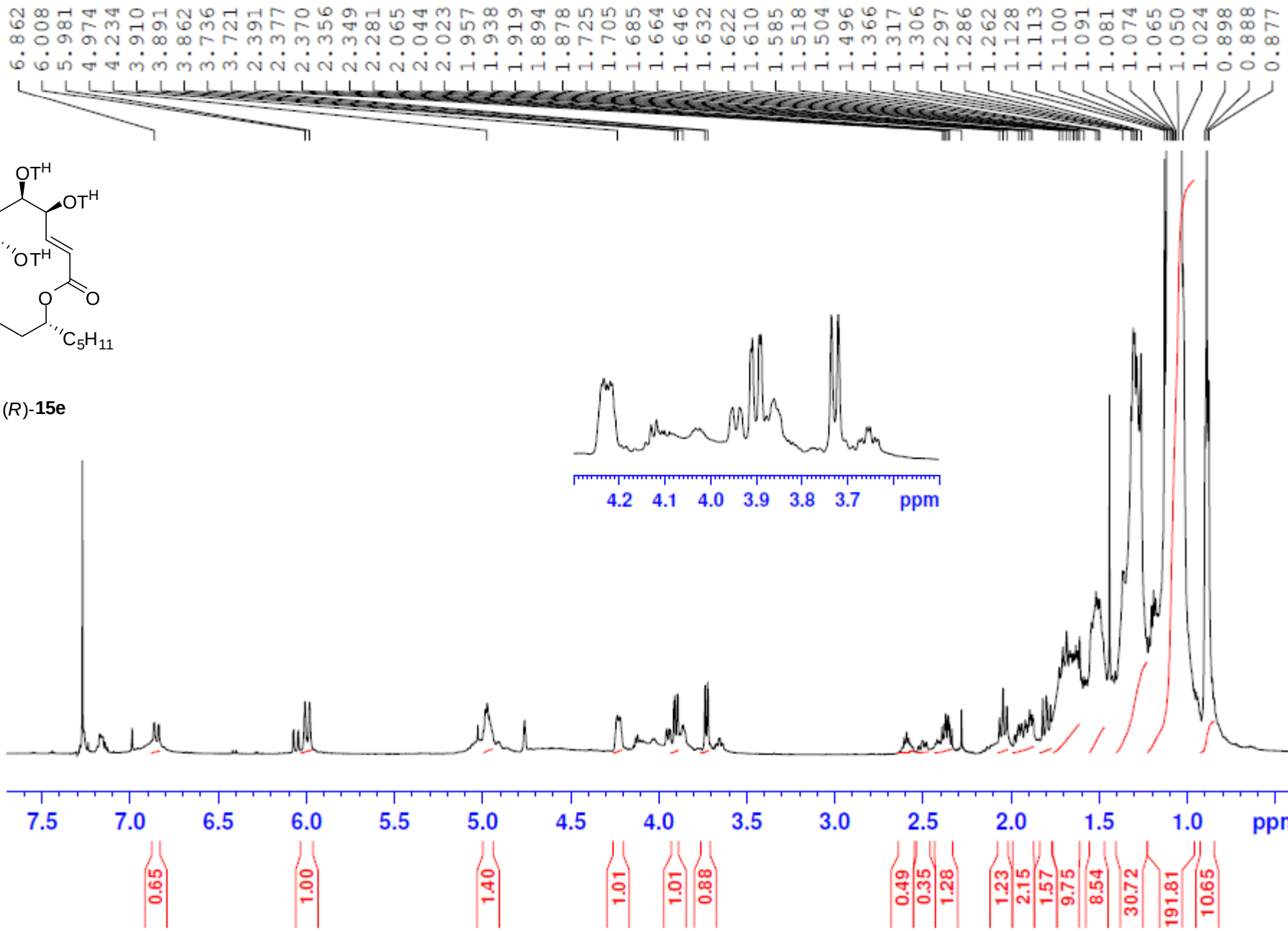

OT^F
OT^F
OT^F
O
O
C5H11

(*S*)-**15d**

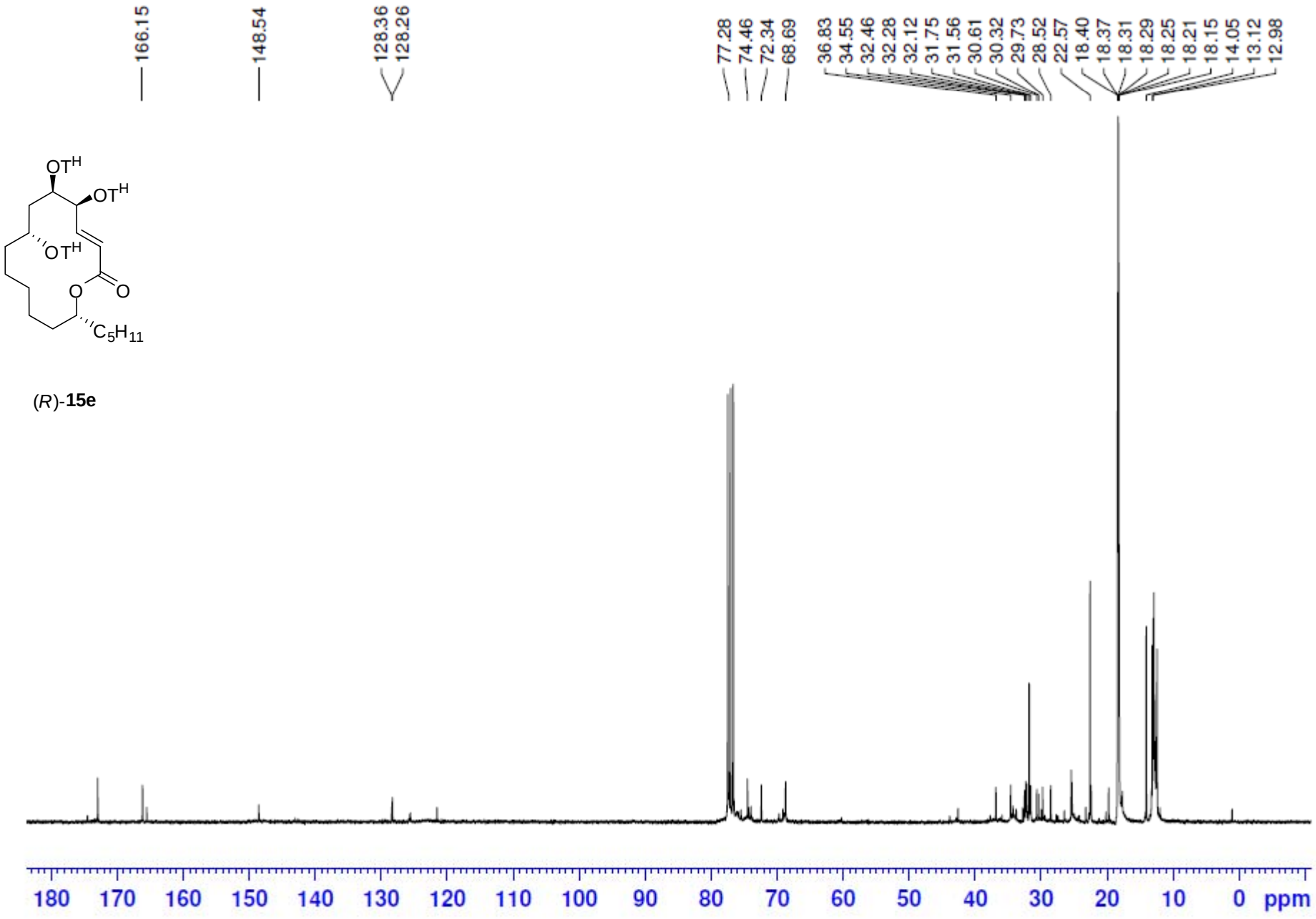
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


-84.90
-84.95
-84.96
-120.26
-120.32
-120.38
-120.42
-120.44
-120.48
-120.55
OT^F
OT^F
OT^F
O
O
C5H11
-84.9
-85.0
ppm
-120.0
-120.5
ppm
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
ppm
2.93
2.00

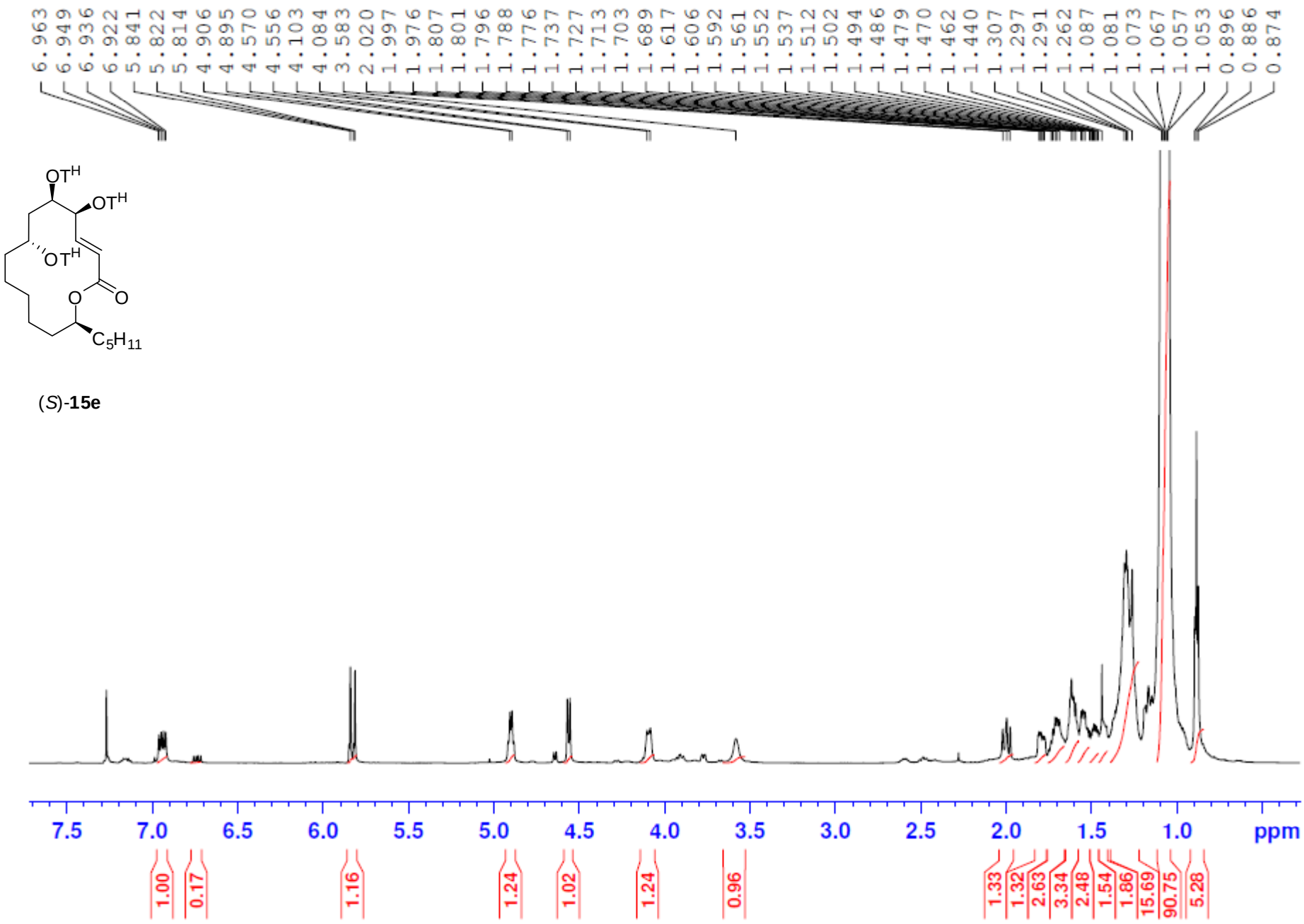
(*S*)-**15d**


6.862
6.008
5.981
4.974
4.234
3.910
3.891
3.862
3.736
3.721
2.391
2.377
2.370
2.356
2.349
2.281
2.065
2.044
2.023
1.957
1.938
1.919
1.894
1.878
1.725
1.705
1.685
1.664
1.646
1.632
1.622
1.610
1.585
1.518
1.504
1.496
1.366
1.317
1.306
1.297
1.286
1.262
1.128
1.113
1.100
1.091
1.081
1.074
1.065
1.050
1.024
0.898
0.888
0.877
OTH
OTH
OTH
O
O
C5H11
4.2 4.1 4.0 3.9 3.8 3.7 ppm
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 ppm
0.65
1.00
1.40
1.01
1.01
0.88
0.49
0.35
1.28
1.23
2.15
1.57
9.75
8.54
30.72
191.81
10.65

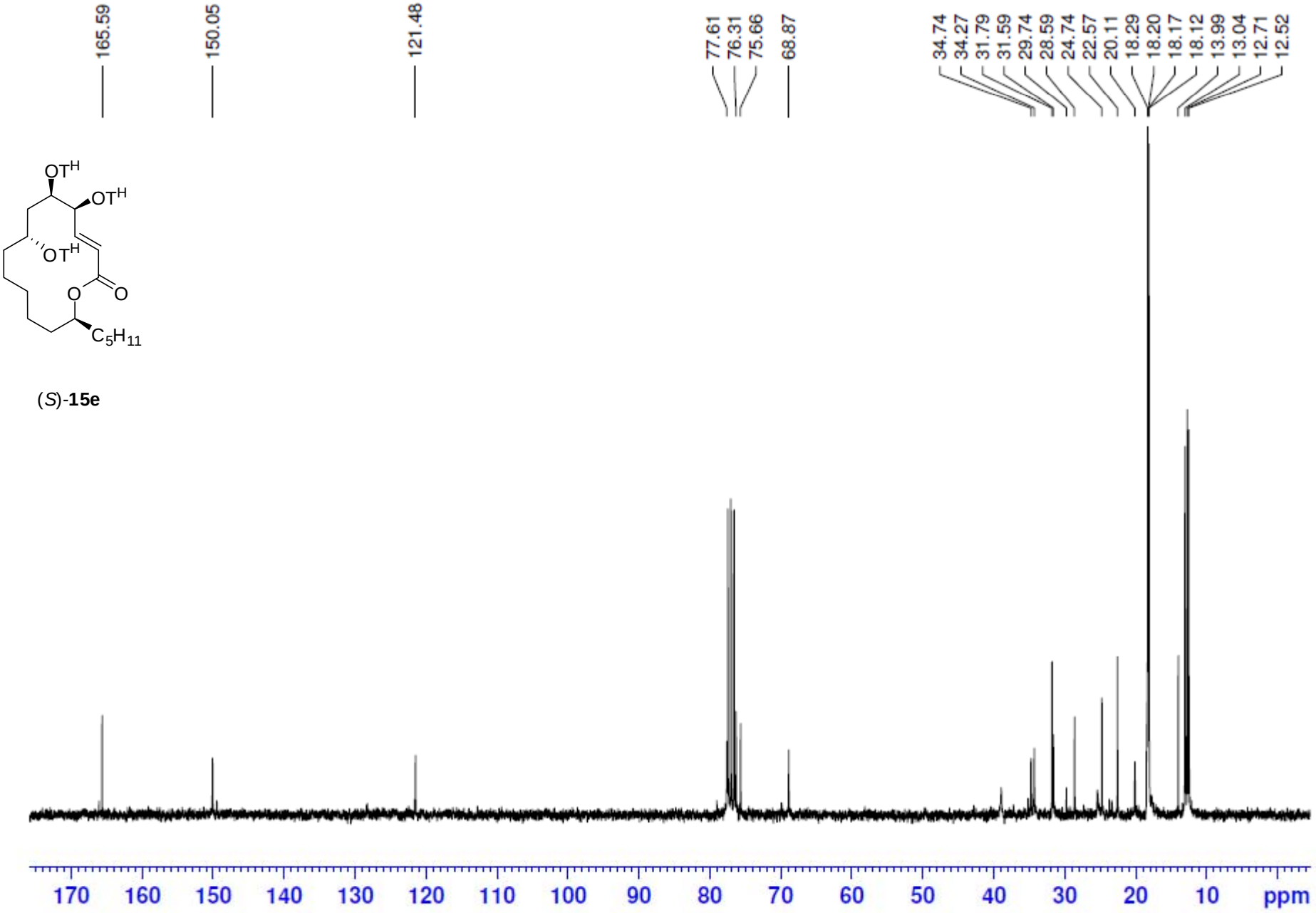
(*R*)-**15e**


166.15
148.54
128.36
128.26
77.28
74.46
72.34
68.69
36.83
34.55
32.46
32.28
32.12
31.75
31.56
30.61
30.32
29.73
28.52
22.57
18.40
18.37
18.31
18.29
18.25
18.21
18.15
14.05
13.12
12.98
OT^H
OT^H
OT^H
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

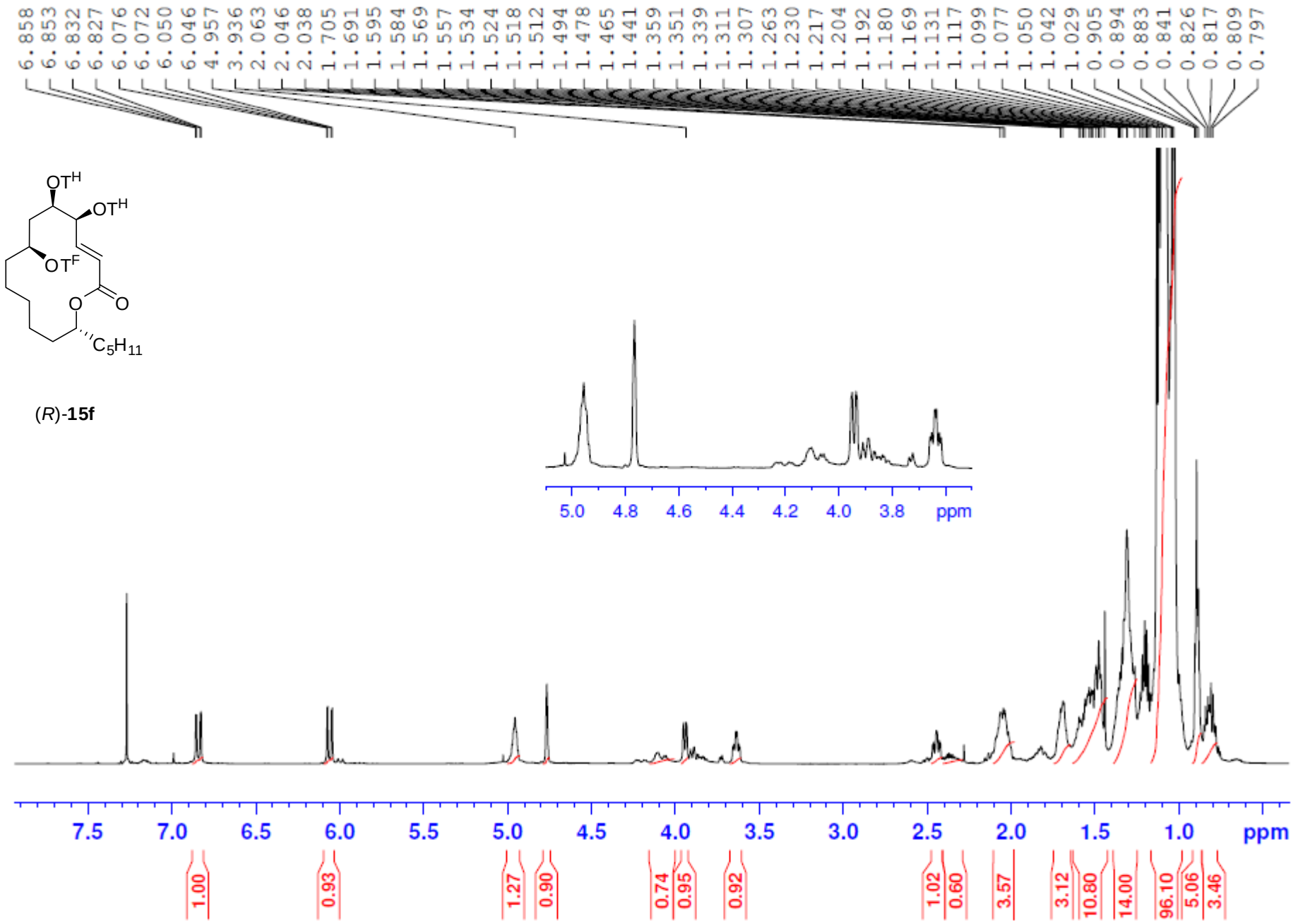
(*R*)-**15e**


6.963
6.949
6.936
6.922
5.841
5.822
5.814
4.906
4.895
4.570
4.556
4.103
4.084
3.583
2.020
1.997
1.976
1.807
1.801
1.796
1.788
1.776
1.737
1.727
1.713
1.703
1.689
1.617
1.606
1.592
1.561
1.552
1.537
1.512
1.502
1.494
1.486
1.479
1.470
1.462
1.440
1.307
1.297
1.291
1.262
1.087
1.081
1.073
1.067
1.057
1.053
0.896
0.886
0.874
OT^H
OT^H
OT^H
O
O
C5H11
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
ppm
1.00
0.17
1.16
1.24
1.02
1.24
0.96
1.33
1.32
2.63
3.34
2.48
1.54
1.86
15.69
90.75
5.28

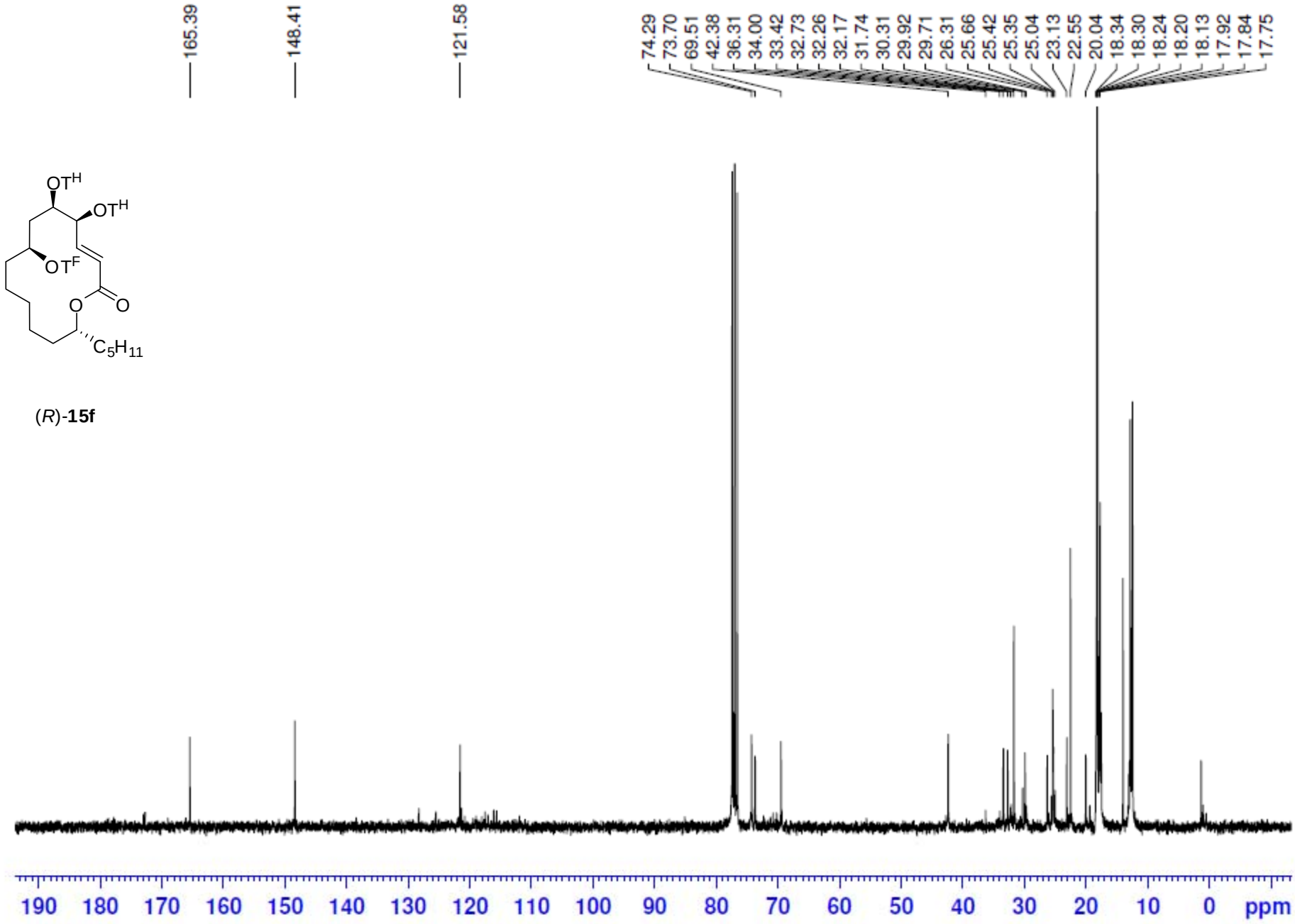
(*S*)-**15e**


165.59
150.05
121.48
77.61
76.31
75.66
68.87
34.74
34.27
31.79
31.59
29.74
28.59
24.74
22.57
20.11
18.29
18.20
18.17
18.12
13.99
13.04
12.71
12.52
OT^H
OT^H
OT^H
O
O
C5H11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

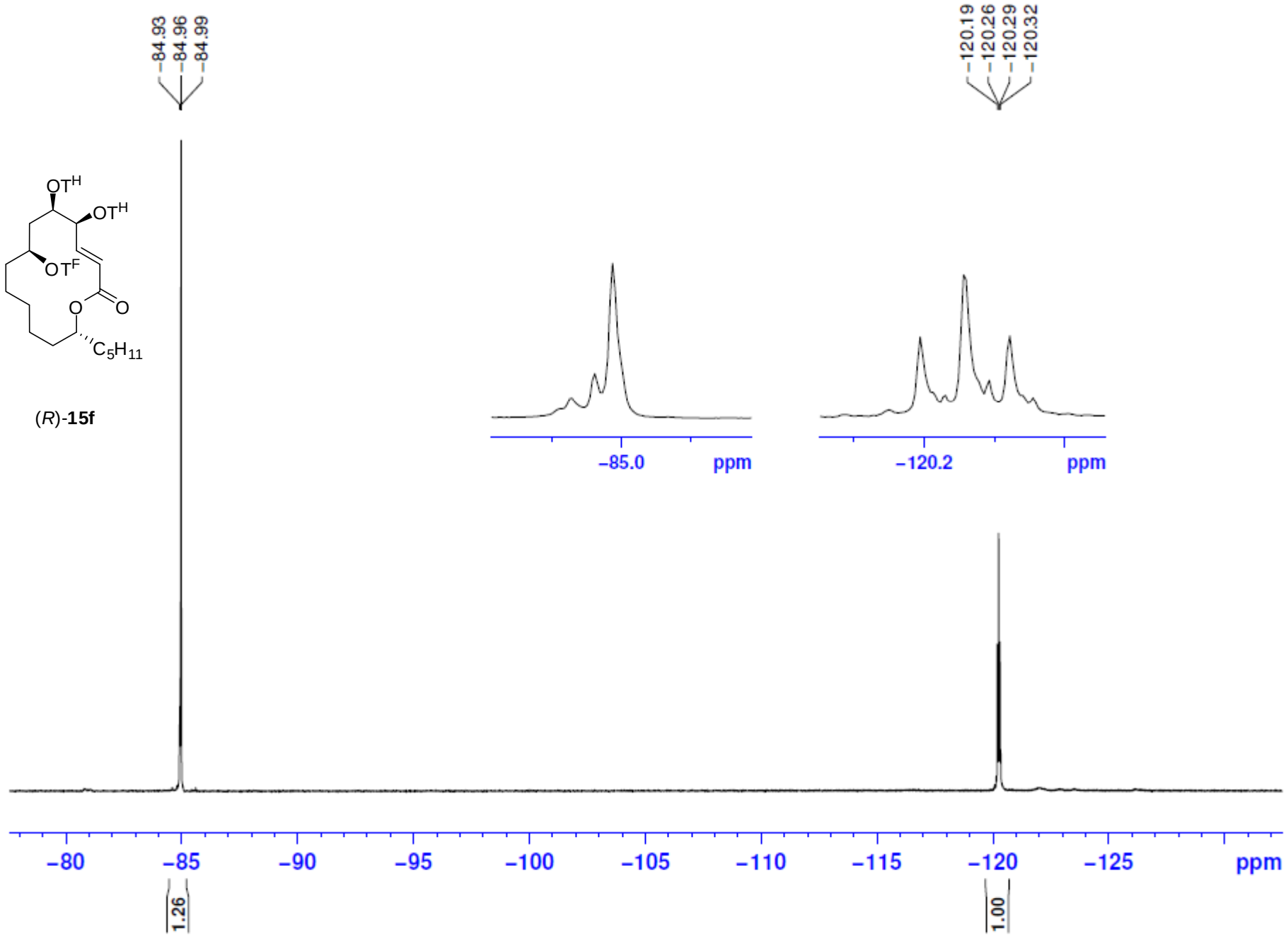
(*S*)-**15e**

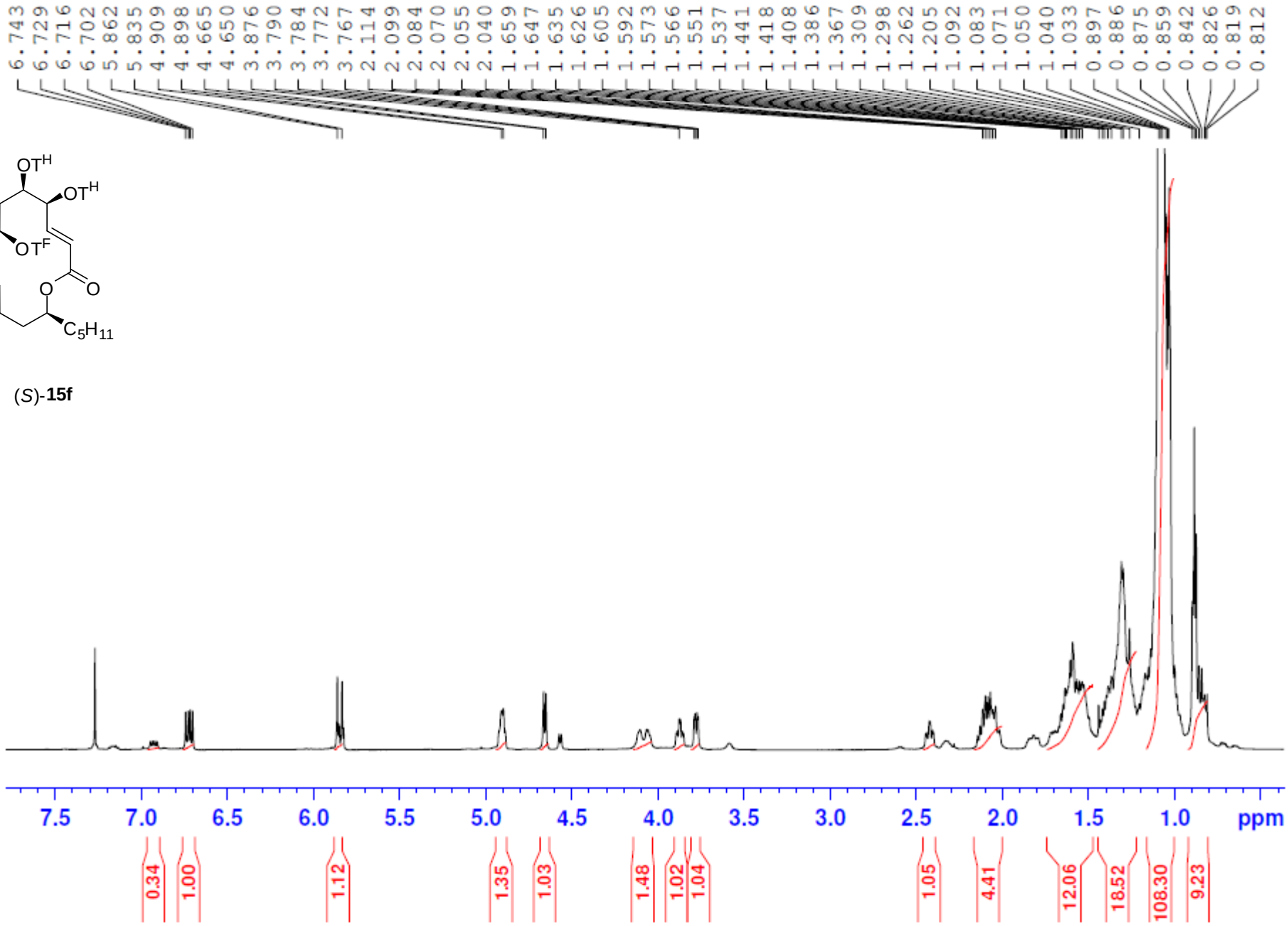

6.858
6.853
6.832
6.827
6.076
6.072
6.050
6.046
4.957
3.936
2.063
2.046
2.038
1.705
1.691
1.595
1.584
1.569
1.557
1.534
1.524
1.518
1.512
1.494
1.478
1.465
1.441
1.359
1.351
1.339
1.311
1.307
1.263
1.230
1.217
1.204
1.192
1.180
1.169
1.131
1.117
1.099
1.077
1.050
1.042
1.029
0.905
0.894
0.883
0.841
0.826
0.817
0.809
0.797
OT^H
OT^H
OT^F
O
O
C5H11
5.0
4.8
4.6
4.4
4.2
4.0
3.8
ppm
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
ppm
1.00
0.93
1.27
0.90
0.74
0.95
0.92
1.02
0.60
3.57
3.12
10.80
14.00
96.10
5.06
3.46

(*R*)-**15f**

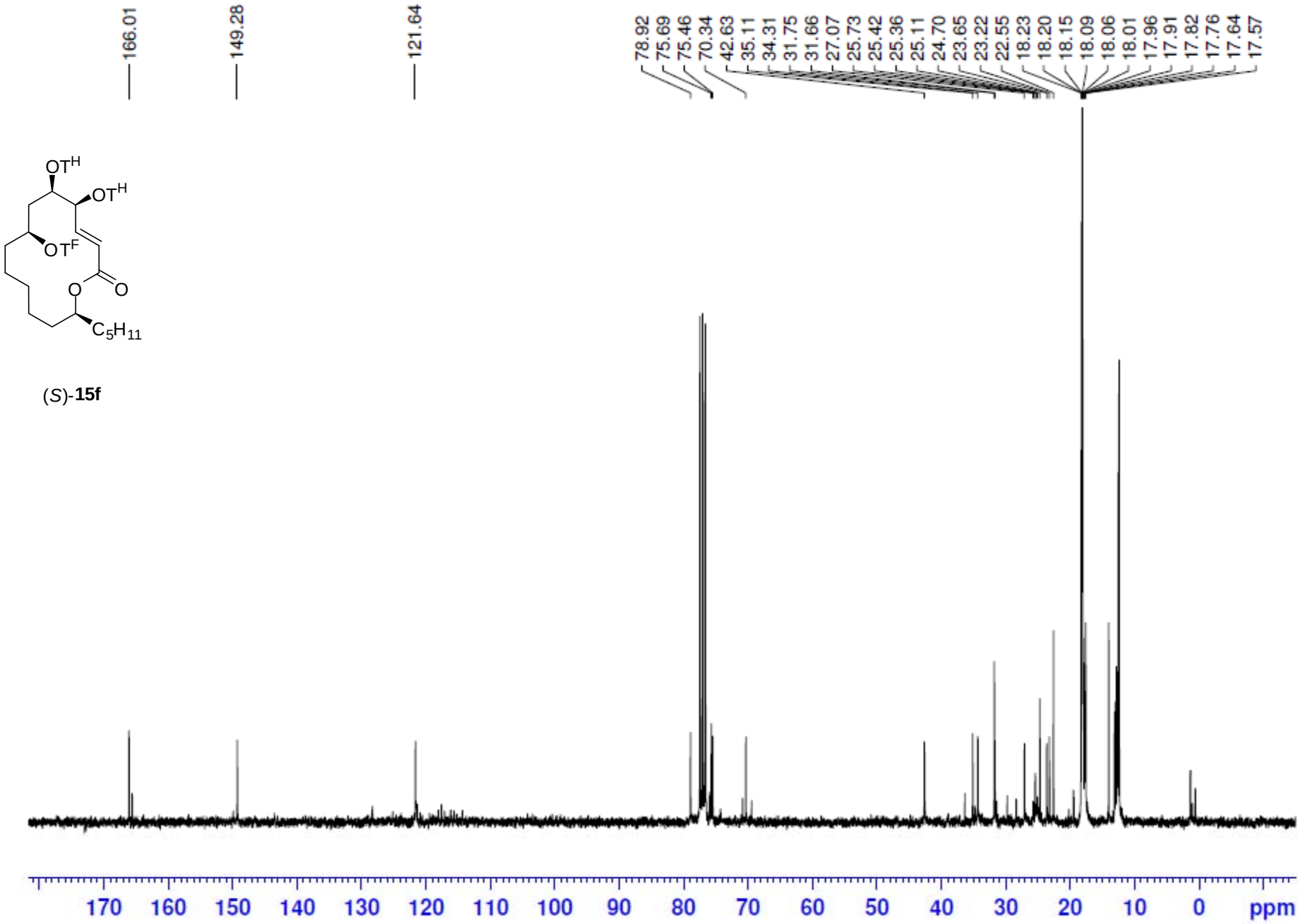

165.39
148.41
121.58
74.29
73.70
69.51
42.38
36.31
34.00
33.42
32.73
32.26
32.17
31.74
30.31
29.92
29.71
26.31
25.66
25.42
25.35
25.04
23.13
22.55
20.04
18.34
18.30
18.24
18.20
18.13
17.92
17.84
17.75
OT^H
OT^H
OT^F
O
O
C5H11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(*R*)-**15f**

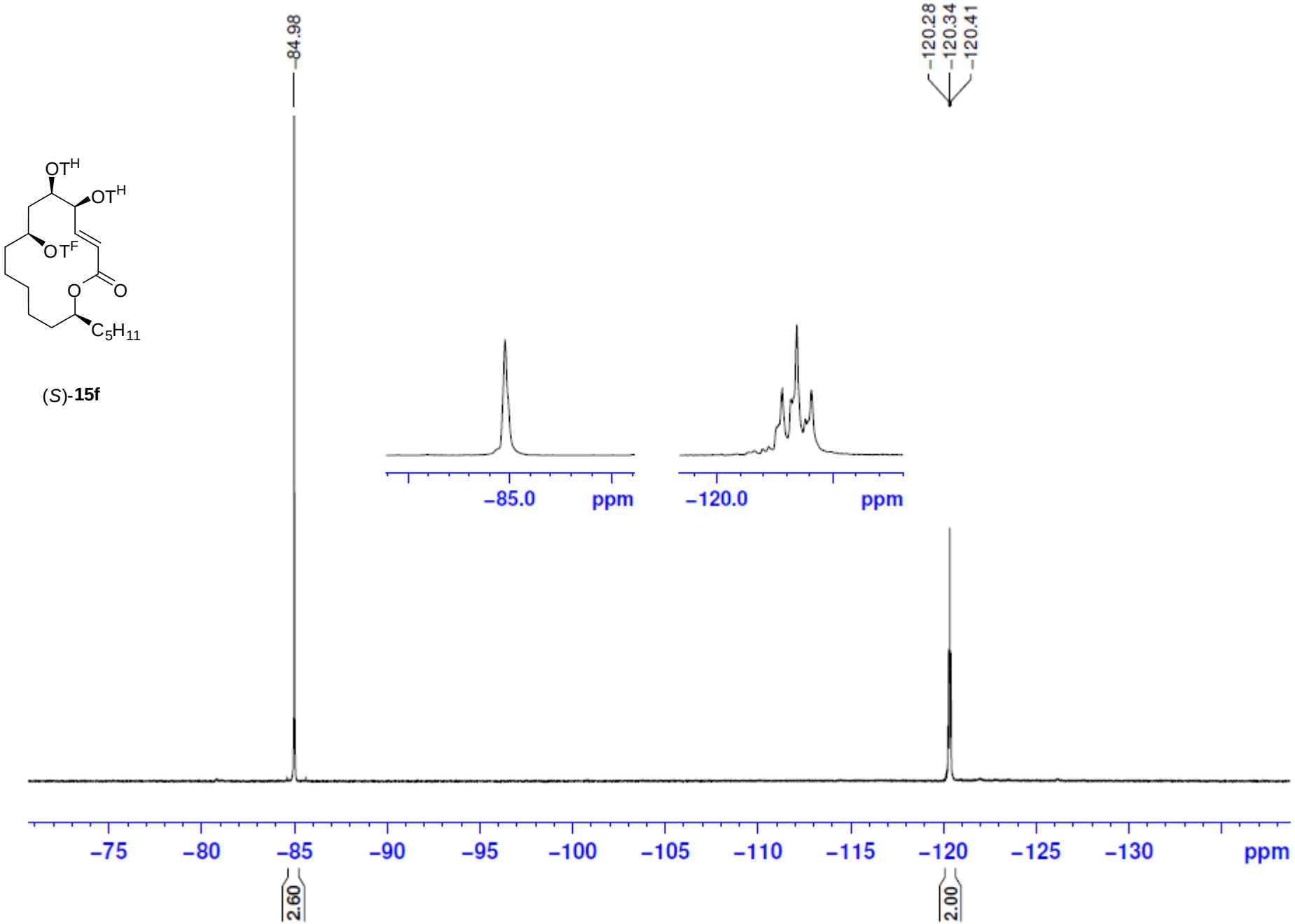

-84.93
-84.96
-84.99
-120.19
-120.26
-120.29
-120.32
OT^H
OT^H
OT^F
O
O
C5H11
(R)-15f
-85.0 ppm
-120.2 ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
1.26
1.00


6.743
6.729
6.716
6.702
5.862
5.835
4.909
4.898
4.665
4.650
3.876
3.790
3.784
3.772
3.767
2.114
2.099
2.084
2.070
2.055
2.040
1.659
1.647
1.635
1.626
1.605
1.592
1.573
1.566
1.551
1.537
1.441
1.418
1.408
1.386
1.367
1.309
1.298
1.262
1.205
1.092
1.083
1.071
1.050
1.040
1.033
0.897
0.886
0.875
0.859
0.842
0.826
0.819
0.812
OT^H
OT^H
OT^F
O
O
C5H11
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
ppm
0.34
1.00
1.12
1.35
1.03
1.48
1.02
1.04
1.05
4.41
12.06
18.52
108.30
9.23

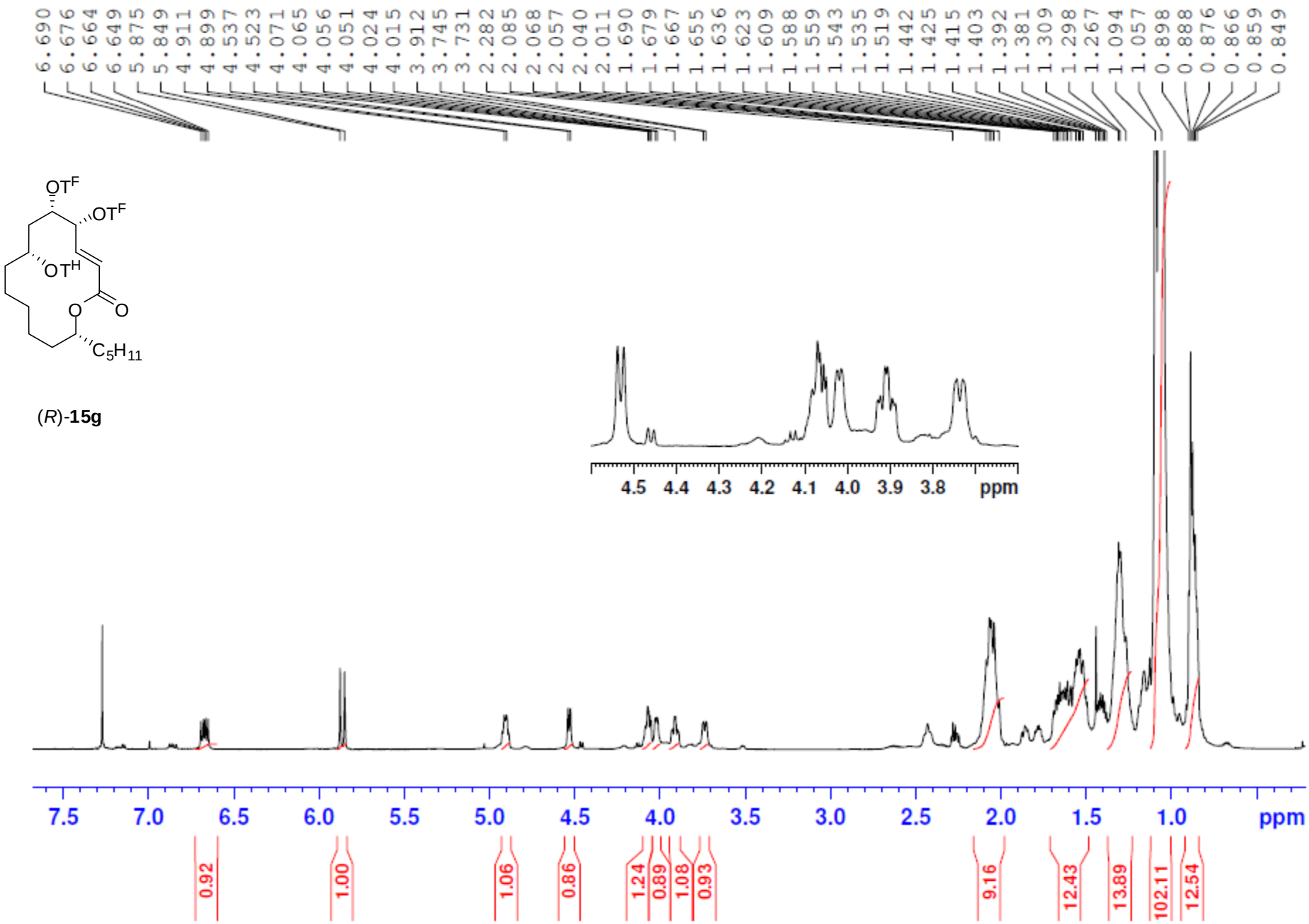
(*S*)-**15f**


166.01
149.28
121.64
78.92
75.69
75.46
70.34
42.63
35.11
34.31
31.75
31.66
27.07
25.73
25.42
25.36
25.11
24.70
23.65
23.22
22.55
18.23
18.20
18.15
18.09
18.06
18.01
17.96
17.91
17.82
17.76
17.64
17.57
OT^H
OT^H
OT^F
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

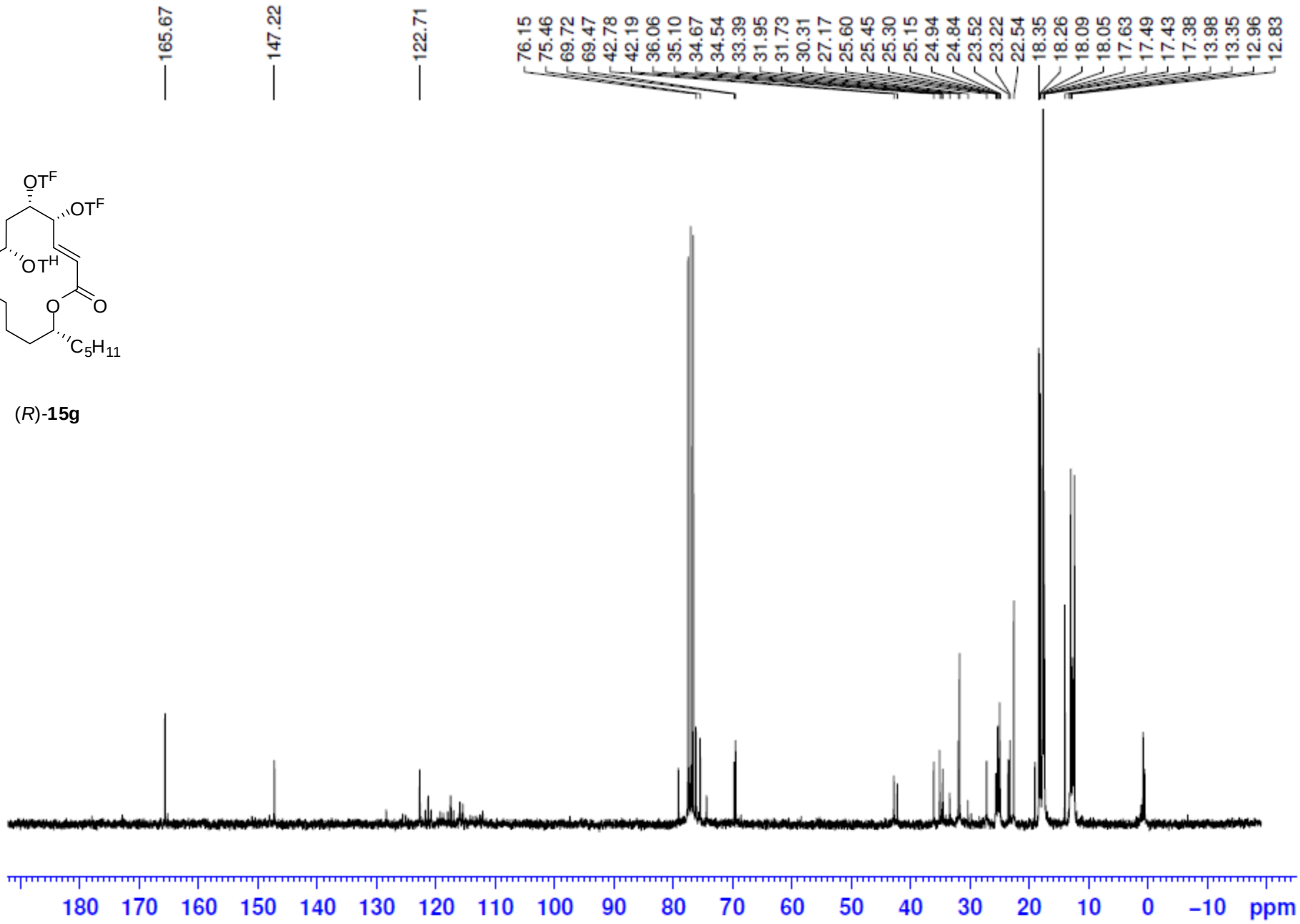
(*S*)-**15f**


-84.98
-120.28
-120.34
-120.41
OT^H
OT^H
OT^F
O
O
C5H11
-85.0
ppm
-120.0
ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
ppm
2.60
2.00

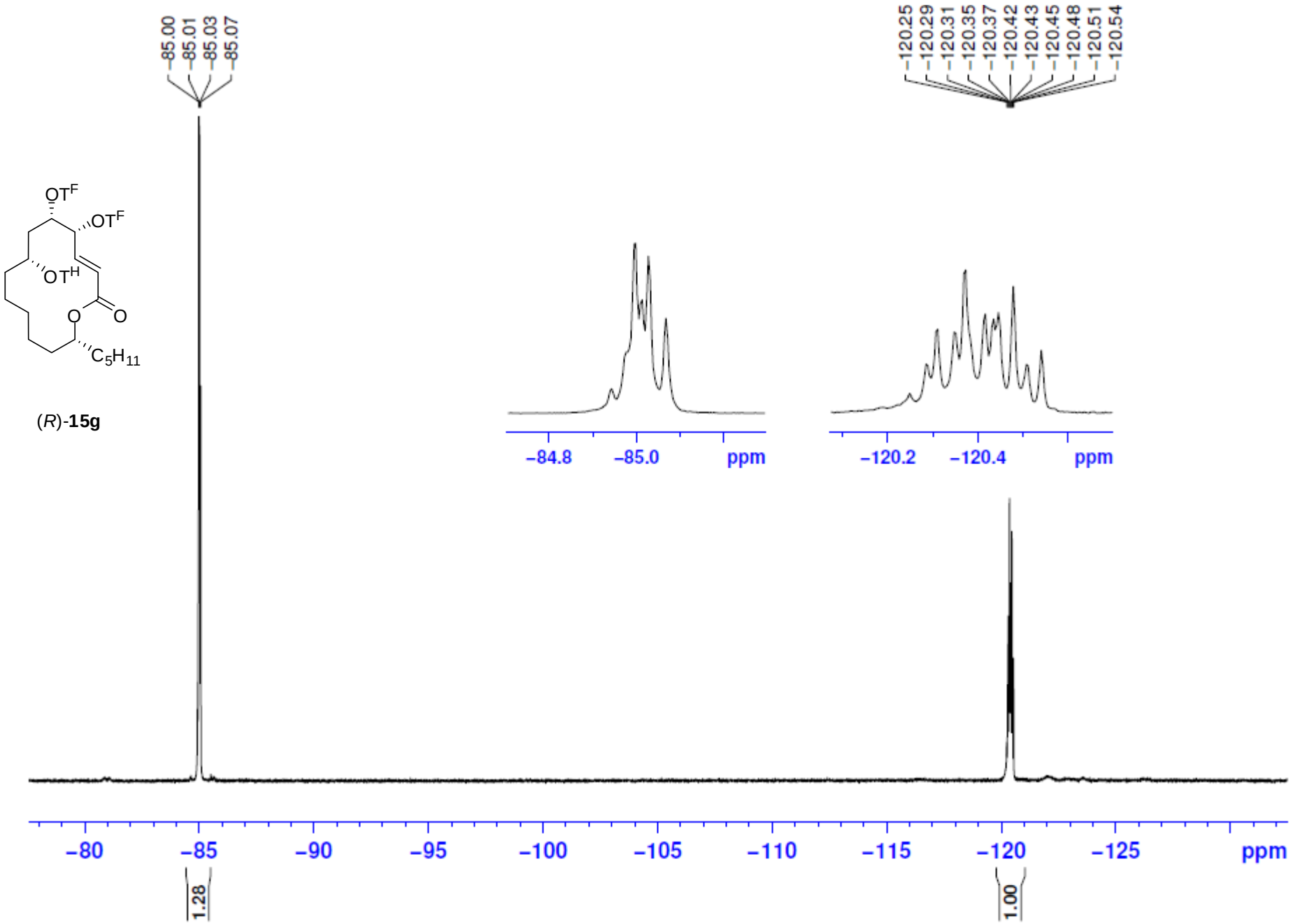
(*S*)-**15f**


6.690
6.676
6.664
6.649
5.875
5.849
4.911
4.899
4.537
4.523
4.071
4.065
4.056
4.051
4.024
4.015
3.912
3.745
3.731
2.282
2.085
2.068
2.057
2.040
2.011
1.690
1.679
1.667
1.655
1.636
1.623
1.609
1.588
1.559
1.543
1.535
1.519
1.442
1.425
1.415
1.403
1.392
1.381
1.309
1.298
1.267
1.094
1.057
0.898
0.888
0.876
0.866
0.859
0.849
OT^F
OT^F
OT^H
O
O
C5H11
4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 ppm
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 ppm
0.92
1.00
1.06
0.86
1.24
0.89
1.08
0.93
9.16
12.43
13.89
102.11
12.54

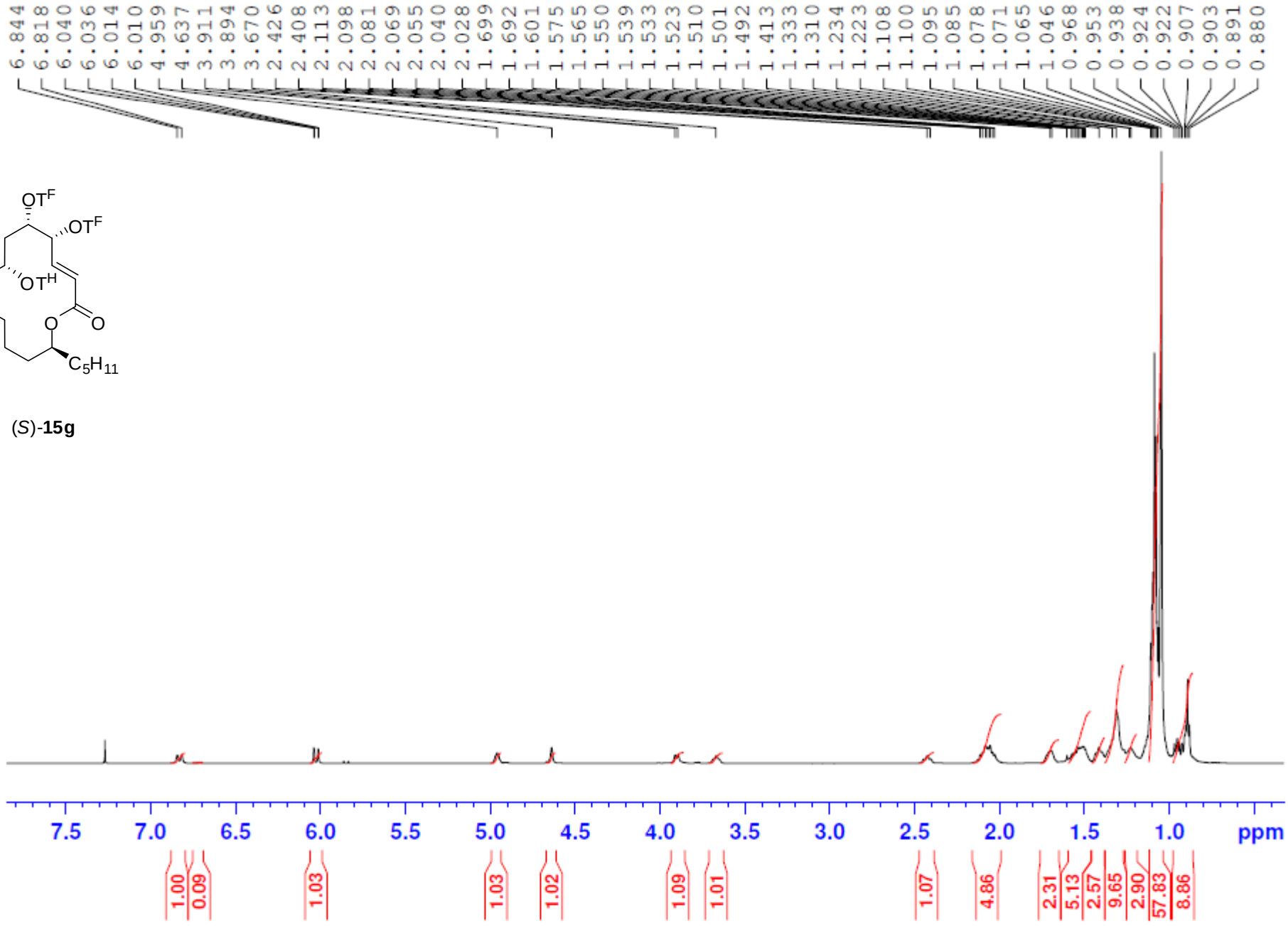
(*R*)-**15g**


165.67
147.22
122.71
76.15
75.46
69.72
69.47
42.78
42.19
36.06
35.10
34.67
34.54
33.39
31.95
31.73
30.31
27.17
25.60
25.45
25.30
25.15
24.94
24.84
23.52
23.22
22.54
18.35
18.26
18.09
18.05
17.63
17.49
17.43
17.38
13.98
13.35
12.96
12.83
OT^F
OT^F
OT^H
O
O
C5H11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

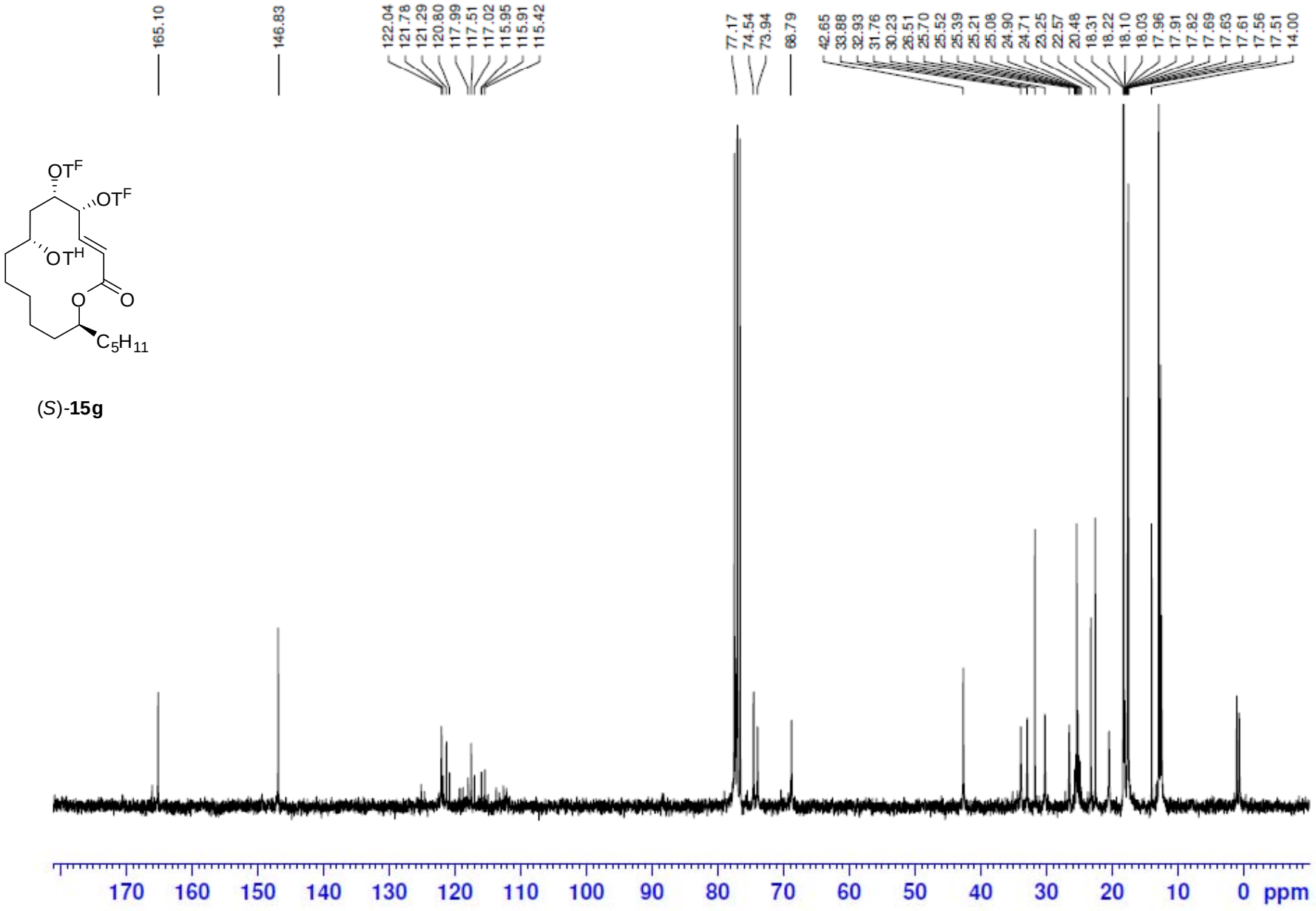
(*R*)-**15g**


-85.00
-85.01
-85.03
-85.07
-120.25
-120.29
-120.31
-120.35
-120.37
-120.42
-120.43
-120.45
-120.48
-120.51
-120.54
OT^F
OT^F
OT^H
O
O
C5H11
-84.8
-85.0
ppm
-120.2
-120.4
ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
1.28
1.00

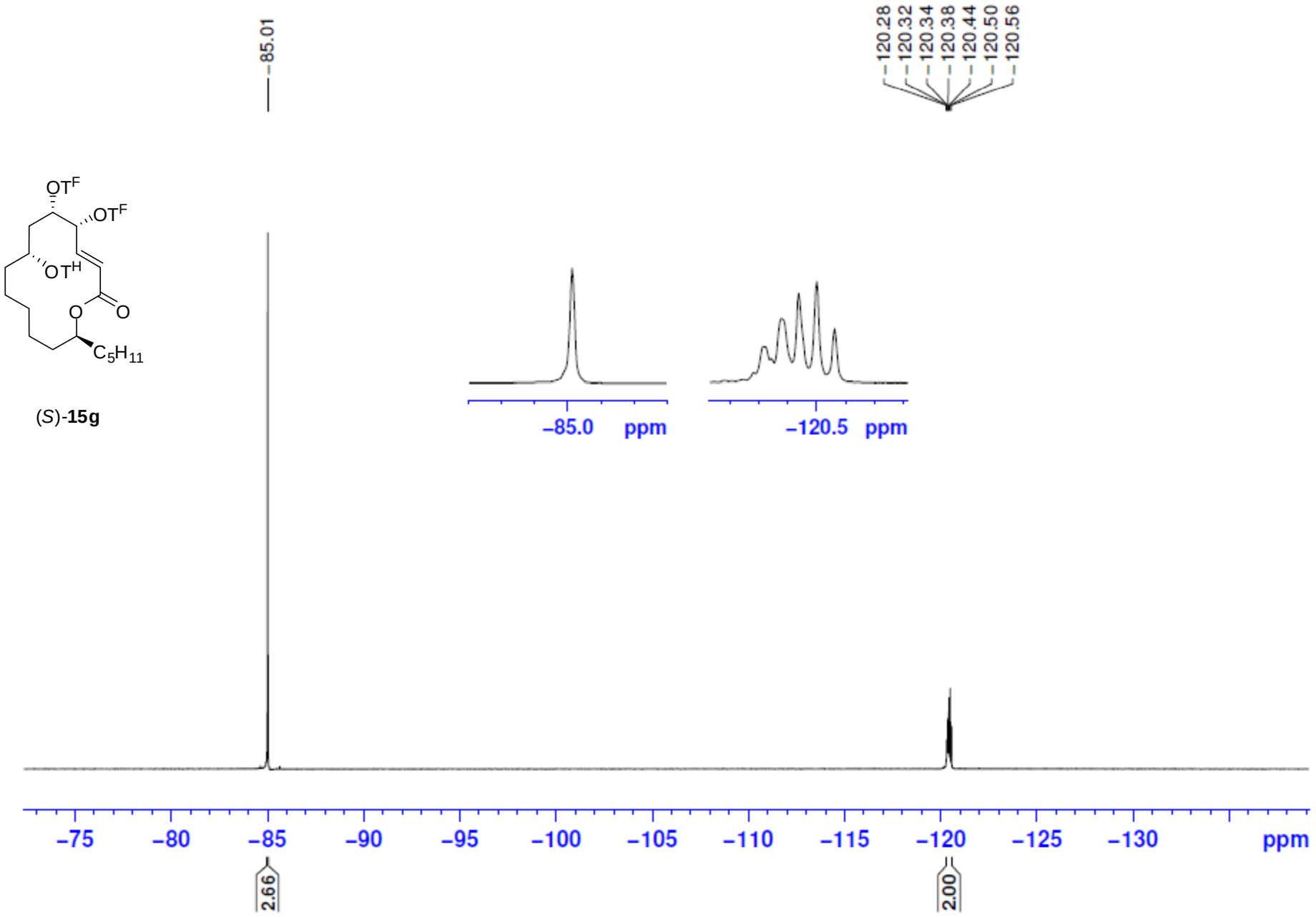
(*R*)-**15g**


6.844
6.818
6.040
6.036
6.014
6.010
4.959
4.637
3.911
3.894
3.670
2.426
2.408
2.113
2.098
2.081
2.069
2.055
2.040
2.028
1.699
1.692
1.601
1.575
1.565
1.550
1.539
1.533
1.523
1.510
1.501
1.492
1.413
1.333
1.310
1.234
1.223
1.108
1.100
1.095
1.085
1.078
1.071
1.065
1.046
0.968
0.953
0.938
0.924
0.922
0.907
0.903
0.891
0.880
OT^F
OT^F
OT^H
O
O
C5H11
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
ppm
1.00
0.09
1.03
1.03
1.02
1.09
1.01
1.07
4.86
2.31
5.13
2.57
9.65
2.90
57.83
8.86

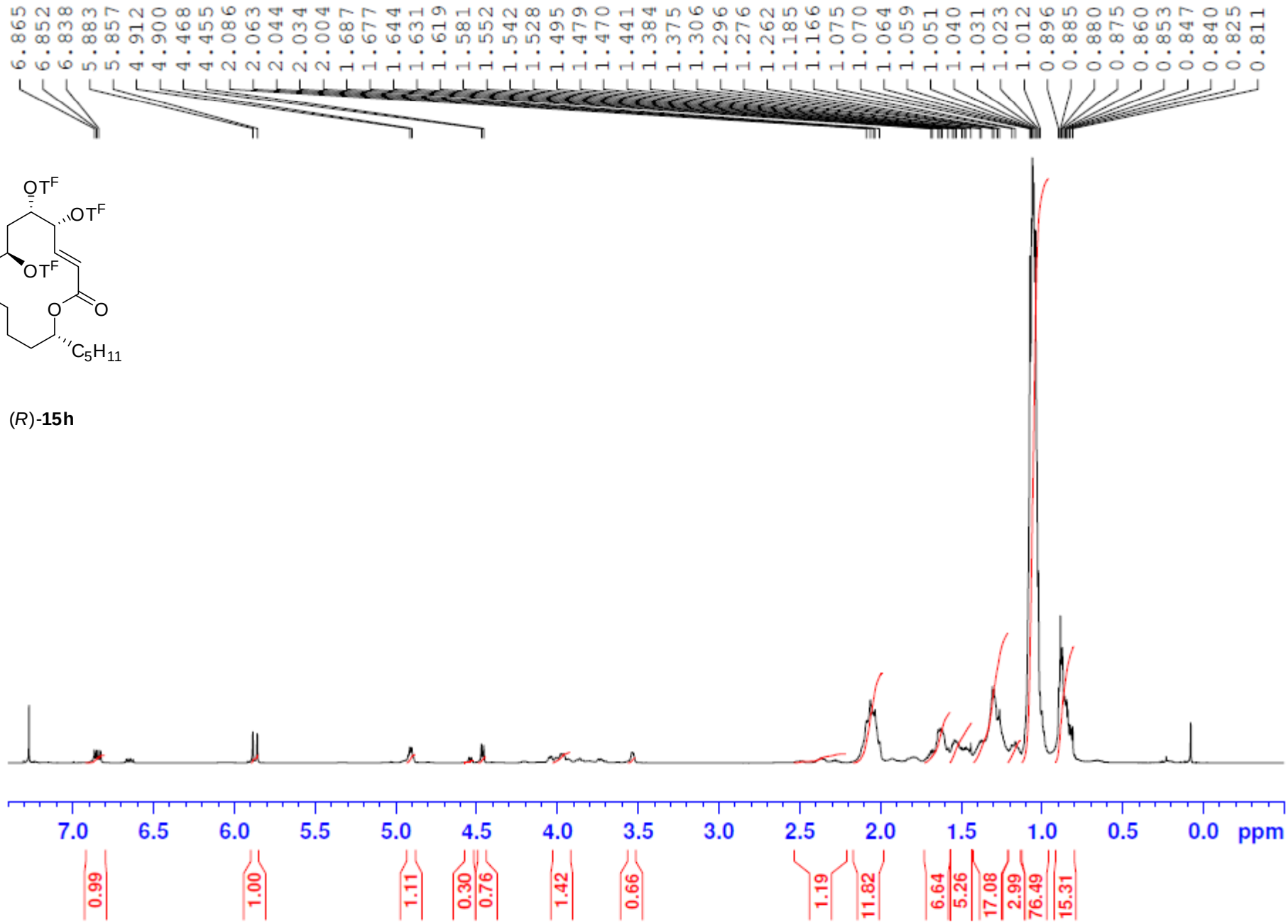
(*S*)-**15g**


165.10
146.83
122.04
121.78
121.29
120.80
117.99
117.51
117.02
115.95
115.91
115.42
77.17
74.54
73.94
68.79
42.65
33.88
32.93
31.76
30.23
26.51
25.70
25.52
25.39
25.21
25.08
24.90
24.71
23.25
22.57
20.48
18.31
18.22
18.10
18.03
17.96
17.91
17.82
17.69
17.63
17.61
17.56
17.51
14.00
OT^F
OT^F
OT^H
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

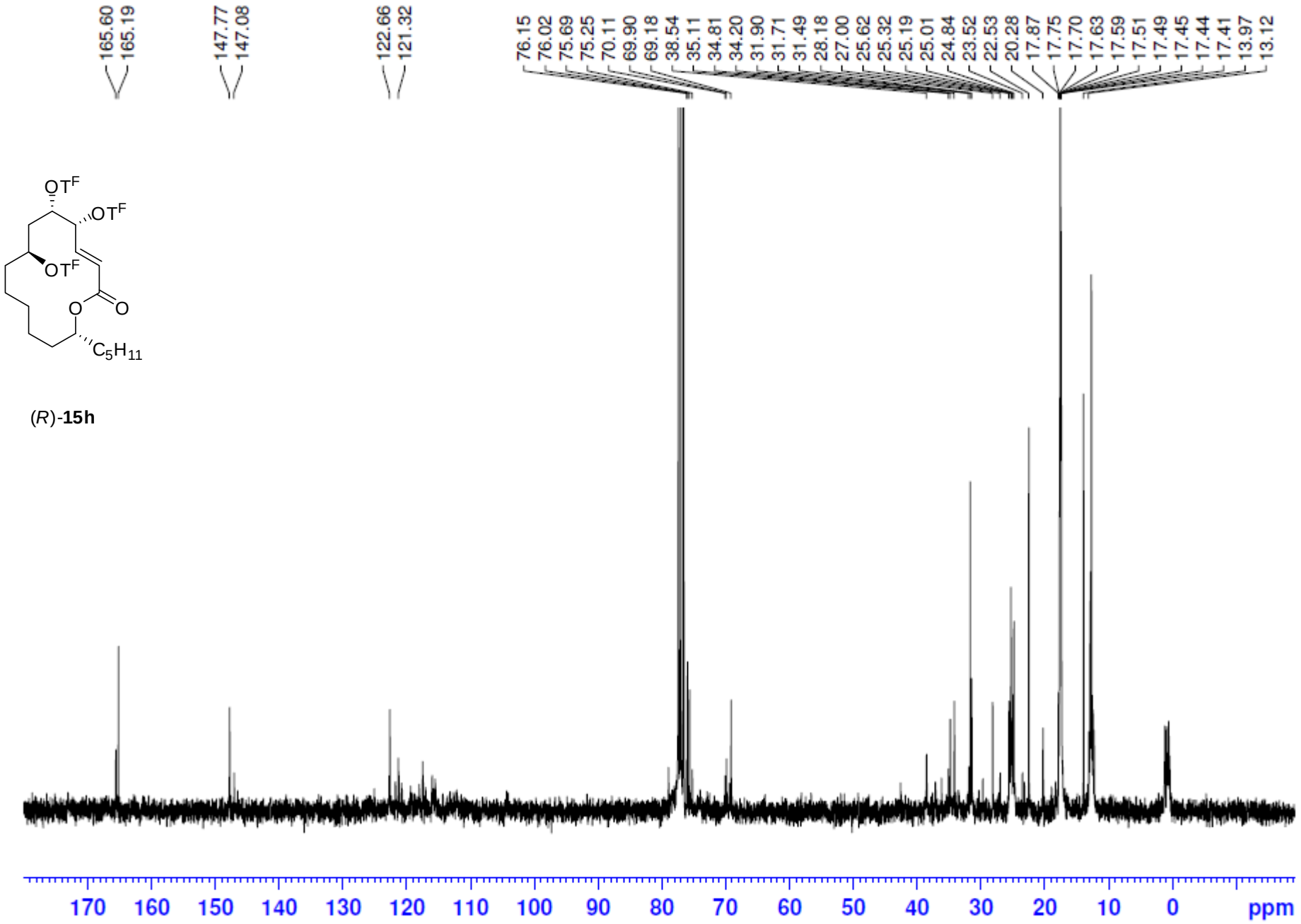
(*S*)-**15g**


-85.01
120.28
120.32
120.34
120.38
120.44
120.50
120.56
OT^F
OT^F
OT^H
O
O
C5H11
-85.0 ppm
-120.5 ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
ppm
2.66
2.00

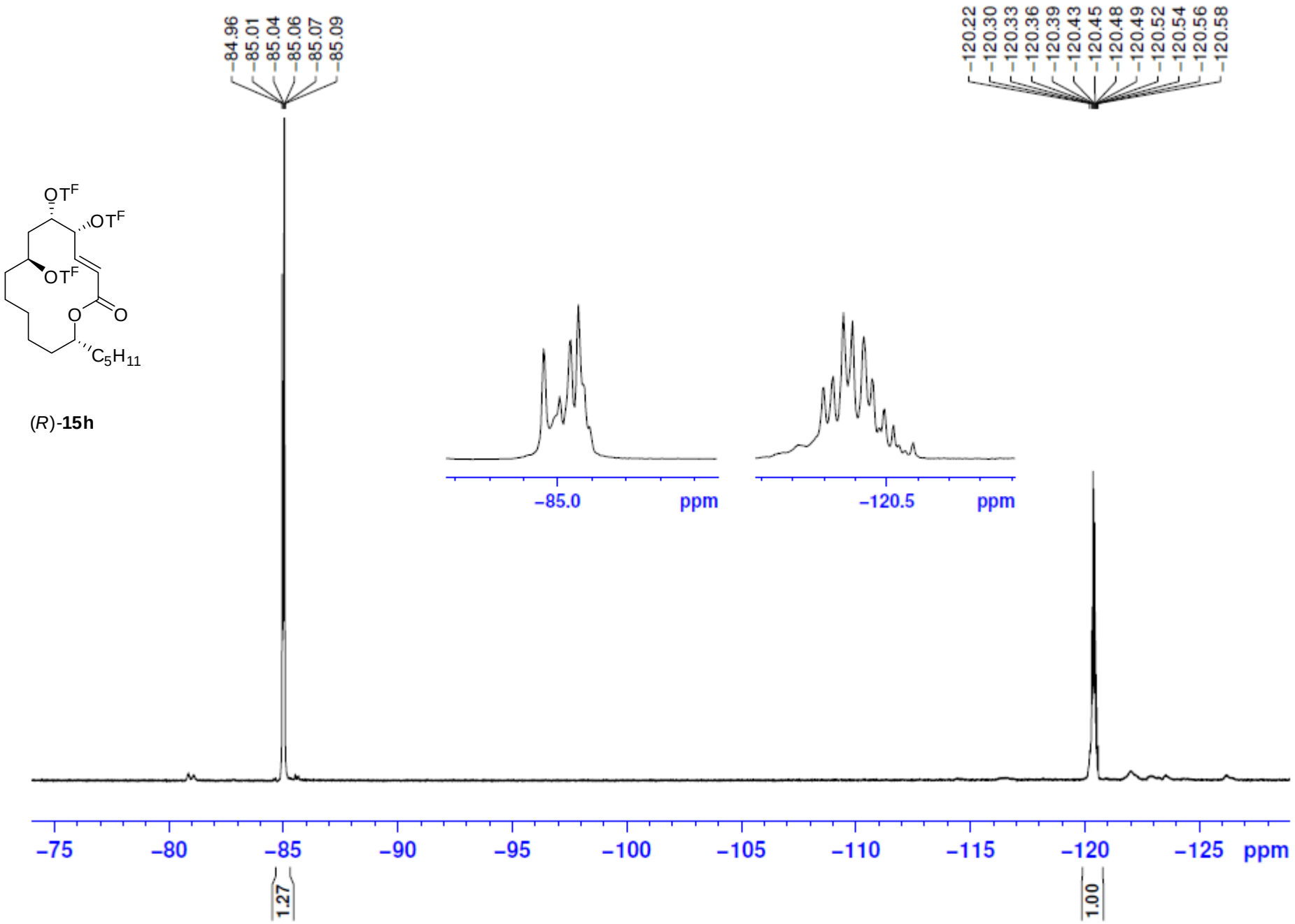
(*S*)-**15g**


6.865
6.852
6.838
5.883
5.857
4.912
4.900
4.468
4.455
2.086
2.063
2.044
2.034
2.004
1.687
1.677
1.644
1.631
1.619
1.581
1.552
1.542
1.528
1.495
1.479
1.470
1.441
1.384
1.375
1.306
1.296
1.276
1.262
1.185
1.166
1.075
1.070
1.064
1.059
1.051
1.040
1.031
1.023
1.012
0.896
0.885
0.880
0.875
0.860
0.853
0.847
0.840
0.825
0.811
OT^F
OT^F
OT^F
O
O
C5H11
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
ppm
0.99
1.00
1.11
0.30
0.76
1.42
0.66
1.19
11.82
6.64
5.26
17.08
2.99
76.49
15.31

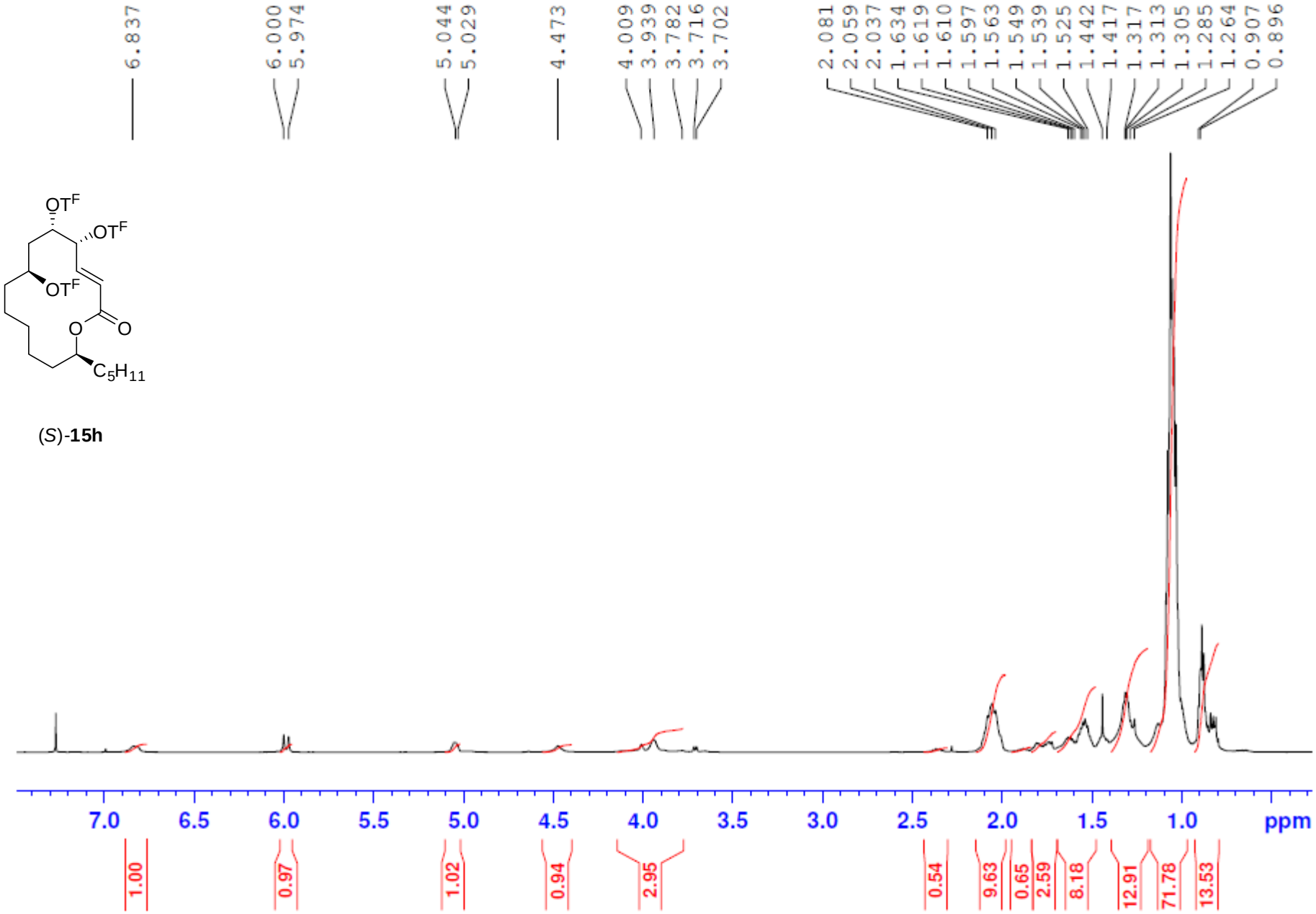
(*R*)-**15h**


165.60
165.19
147.77
147.08
122.66
121.32
76.15
76.02
75.69
75.25
70.11
69.90
69.18
38.54
35.11
34.81
34.20
31.90
31.71
31.49
28.18
27.00
25.62
25.32
25.19
25.01
24.84
23.52
22.53
20.28
17.87
17.75
17.70
17.63
17.59
17.51
17.49
17.45
17.44
17.41
13.97
13.12
OT^F
OT^F
OT^F
O
O
C5H11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

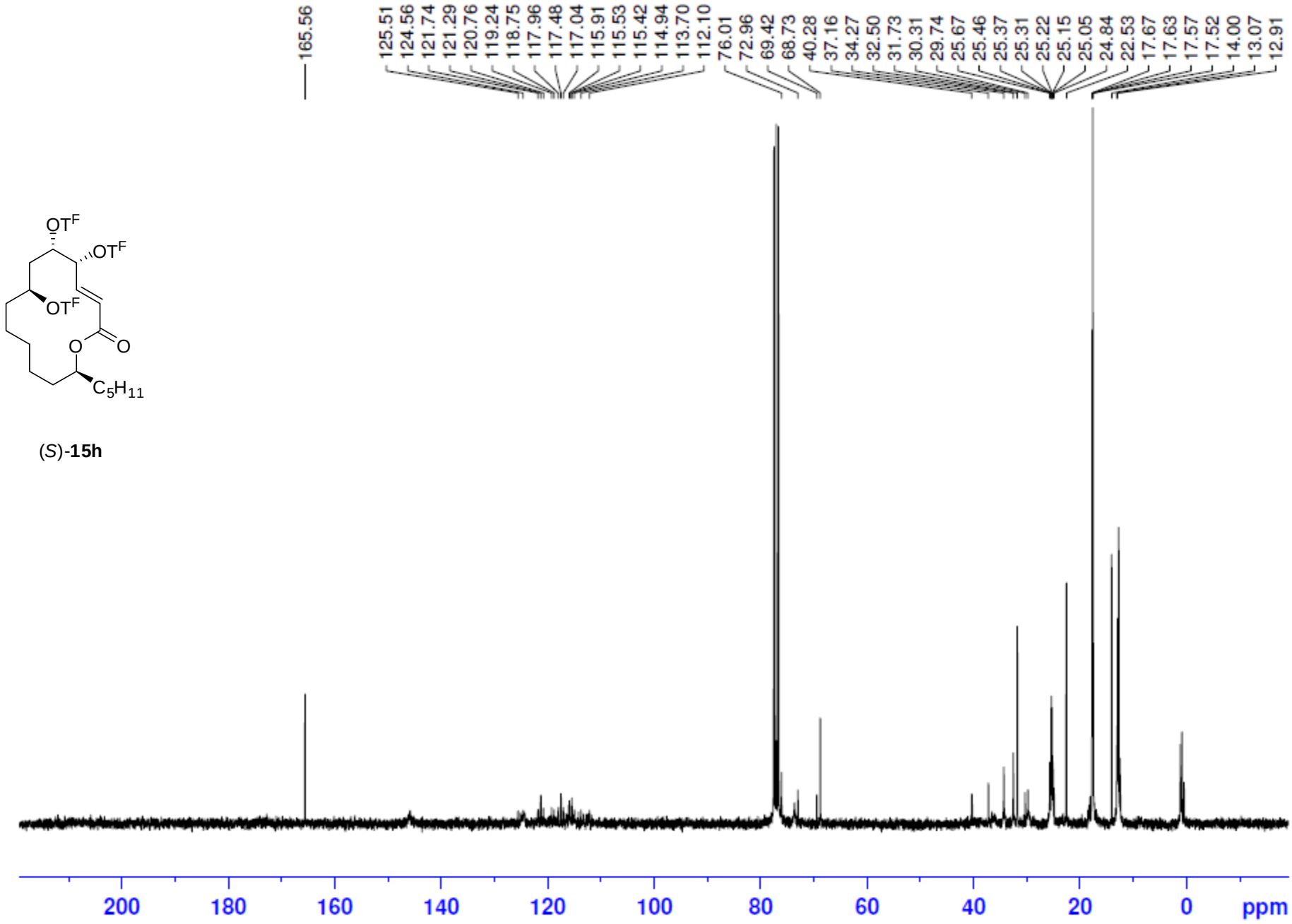
(*R*)-**15h**


-84.96
-85.01
-85.04
-85.06
-85.07
-85.09
-120.22
-120.30
-120.33
-120.36
-120.39
-120.43
-120.45
-120.48
-120.49
-120.52
-120.54
-120.56
-120.58
OT^F
OT^F
OT^F
O
O
C5H11
-85.0
ppm
-120.5
ppm
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
1.27
1.00

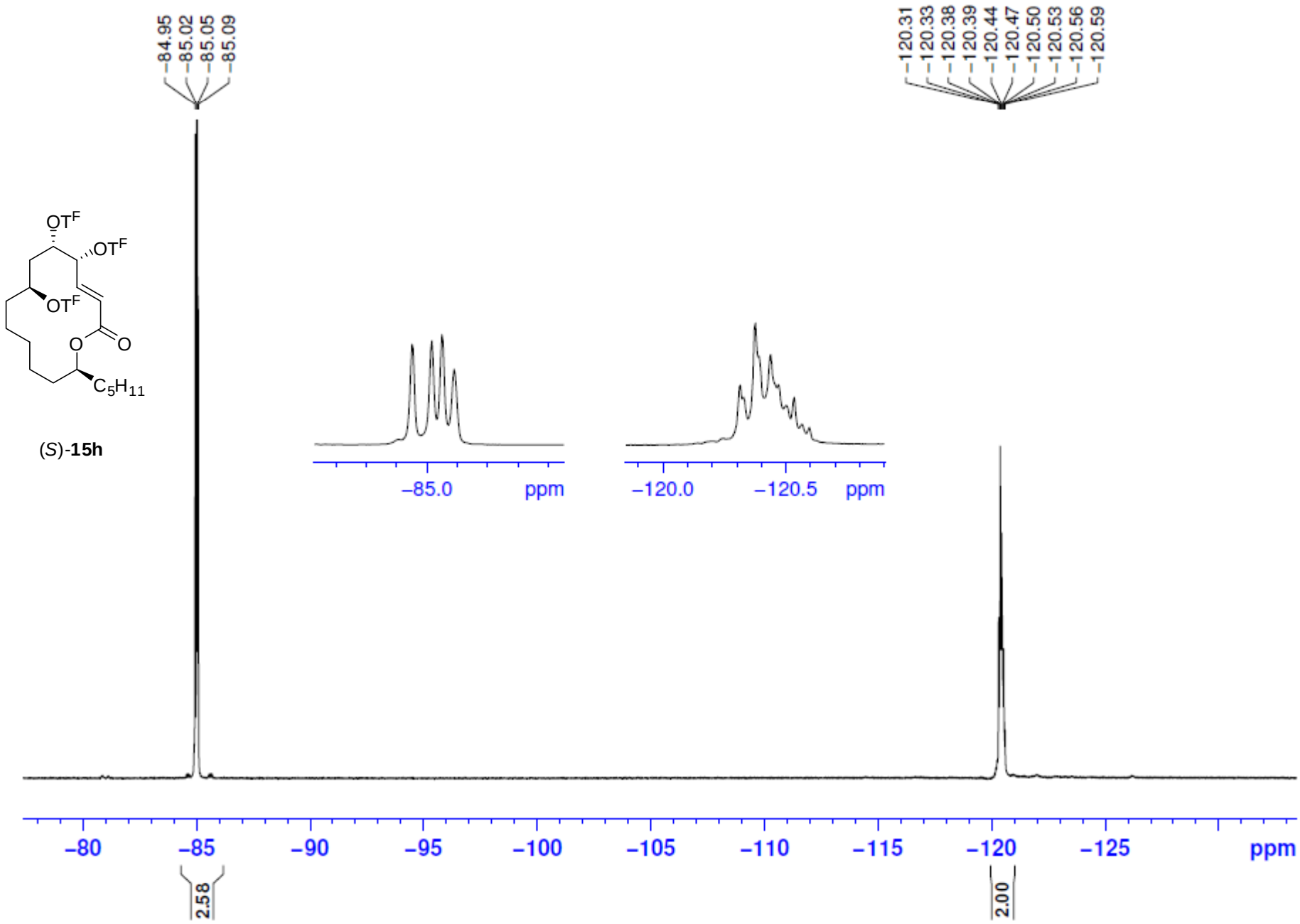
(*R*)-**15h**

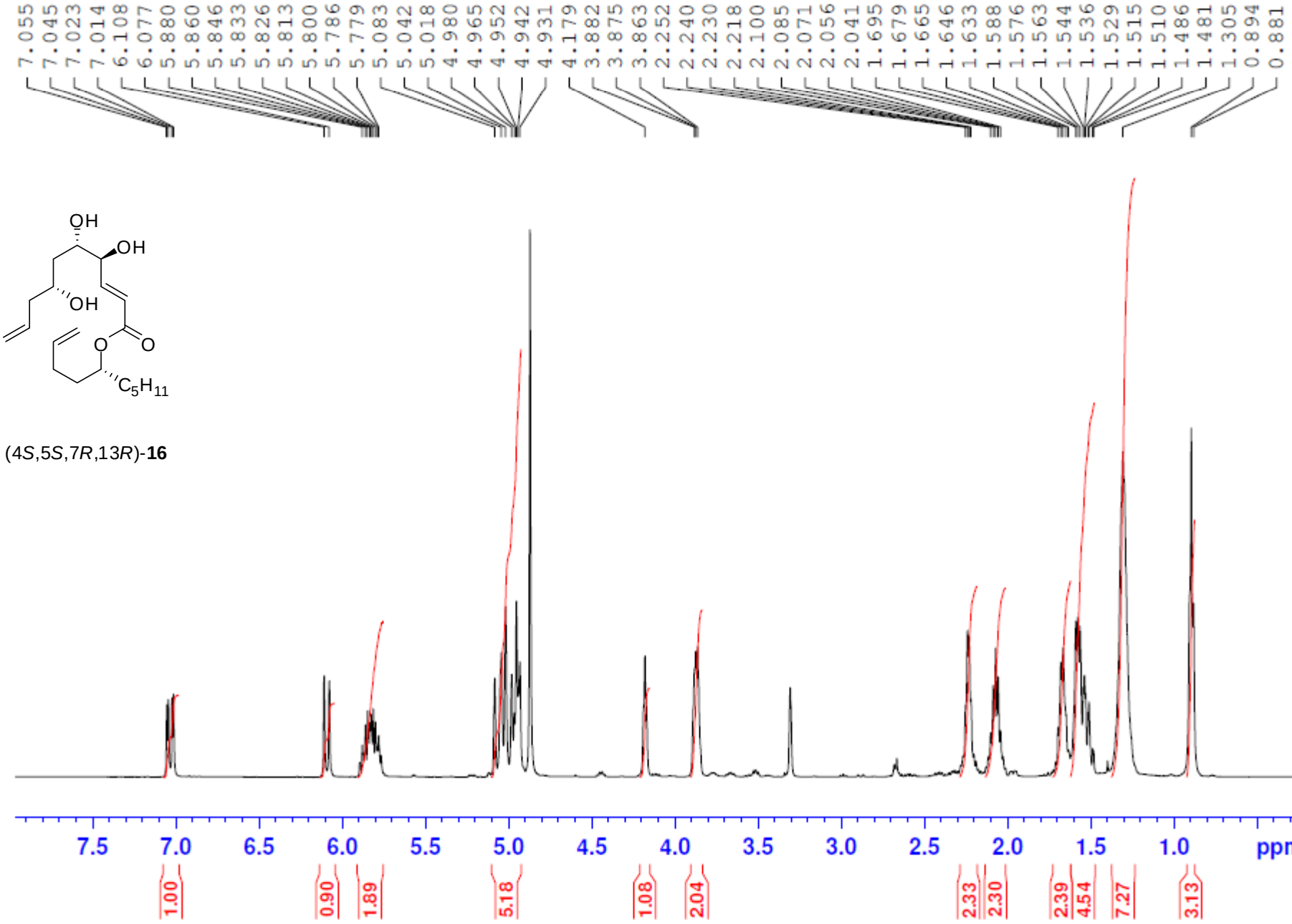

6.837
6.000
5.974
5.044
5.029
4.473
4.009
3.939
3.782
3.716
3.702
2.081
2.059
2.037
1.634
1.619
1.610
1.597
1.563
1.549
1.539
1.525
1.442
1.417
1.317
1.313
1.305
1.285
1.264
0.907
0.896
OT^F
OT^F
OT^F
O
O
C5H11
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.97
1.02
0.94
2.95
0.54
9.63
0.65
2.59
8.18
12.91
71.78
13.53

(*S*)-**15h**

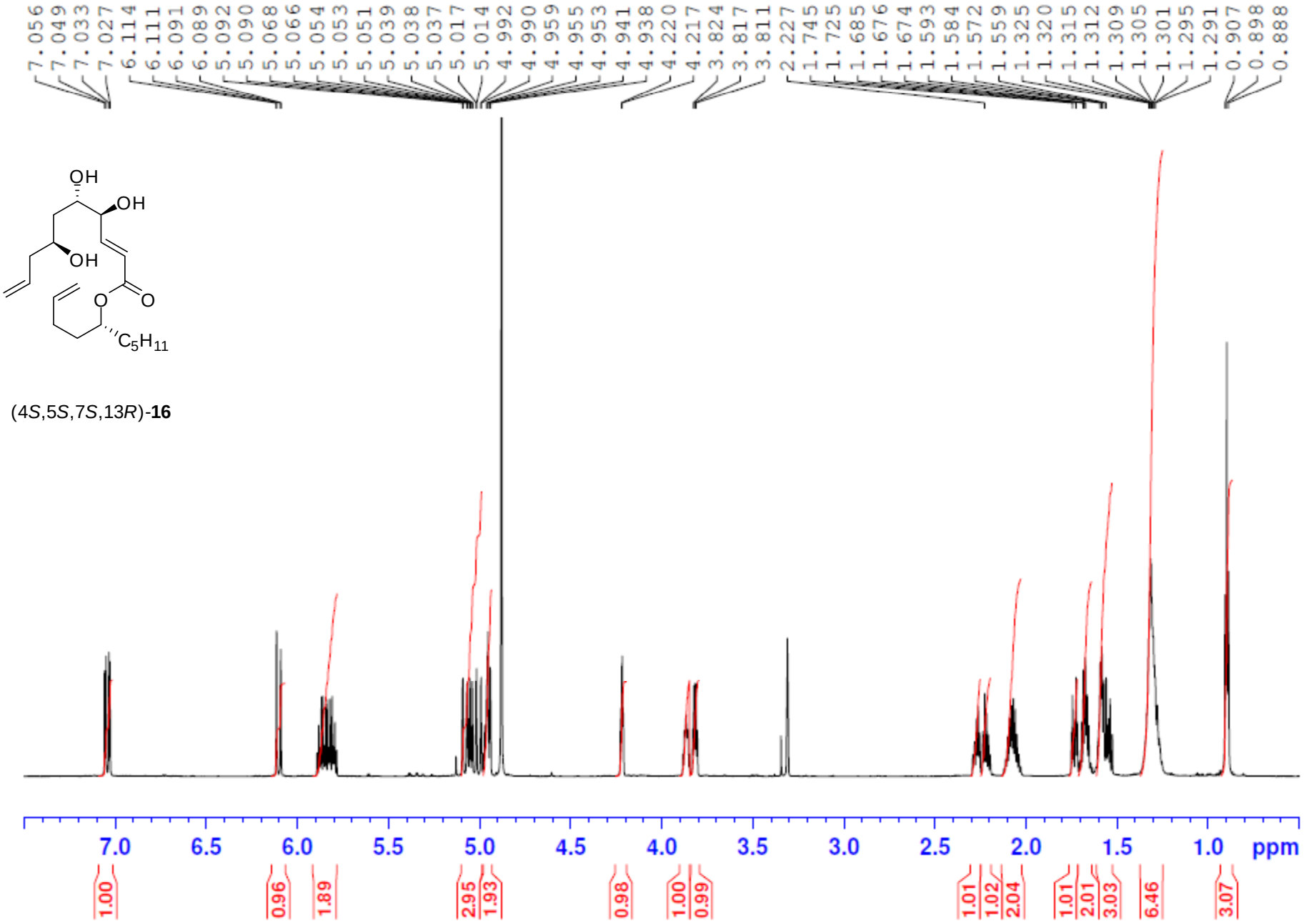

165.56
125.51
124.56
121.74
121.29
120.76
119.24
118.75
117.96
117.48
117.04
115.91
115.53
115.42
114.94
113.70
112.10
76.01
72.96
69.42
68.73
40.28
37.16
34.27
32.50
31.73
30.31
29.74
25.67
25.46
25.37
25.31
25.22
25.15
25.05
24.84
22.53
17.67
17.63
17.57
17.52
14.00
13.07
12.91
OT^F
OT^F
OT^F
O
O
C5H11
200
180
160
140
120
100
80
60
40
20
0
ppm

(*S*)-**15h**

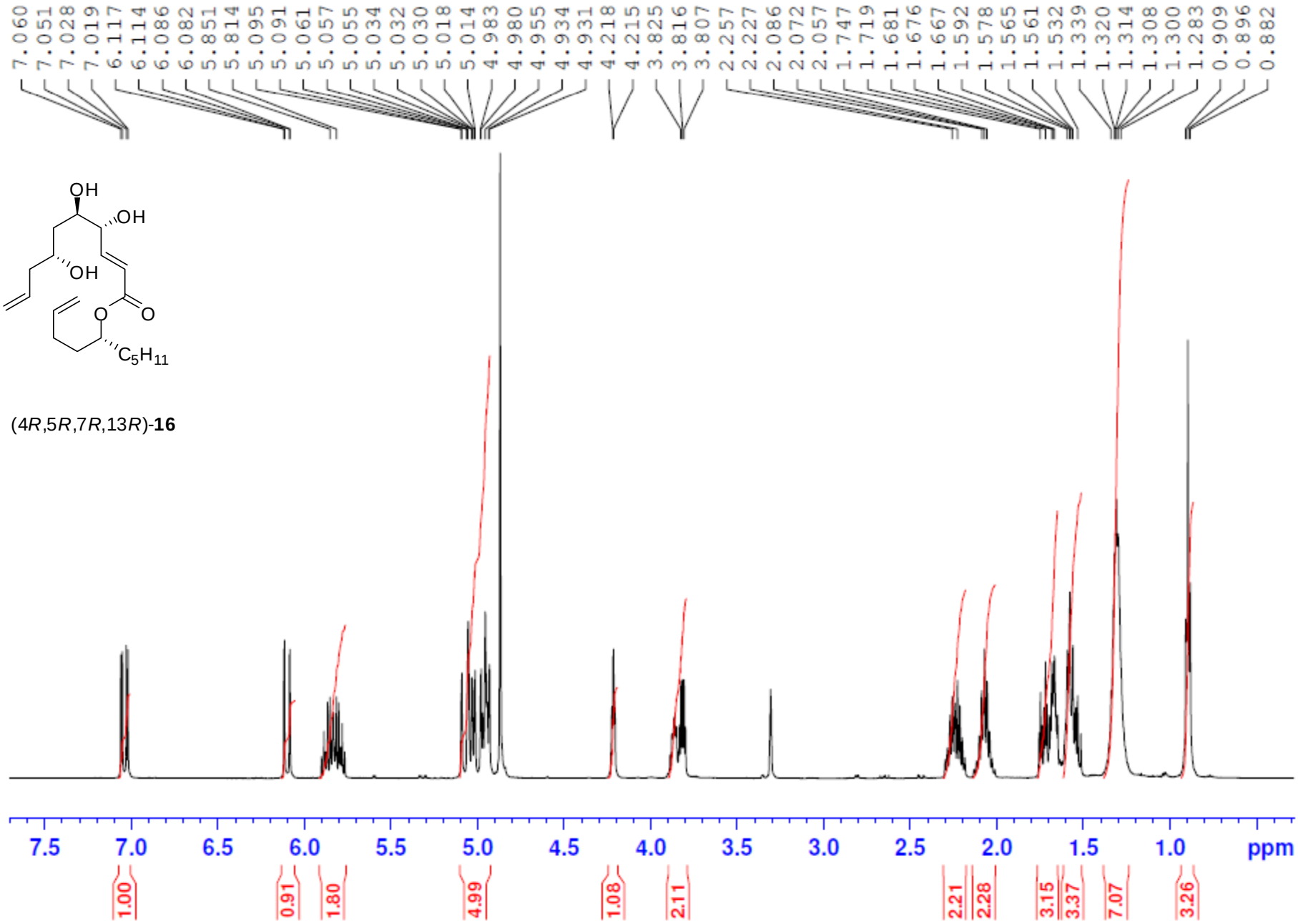

-84.95
-85.02
-85.05
-85.09
-120.31
-120.33
-120.38
-120.39
-120.44
-120.47
-120.50
-120.53
-120.56
-120.59
OT^F
OT^F
OT^F
O
O
C5H11
(S)-15h
-85.0
ppm
-120.0
-120.5
ppm
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
ppm
2.58
2.00



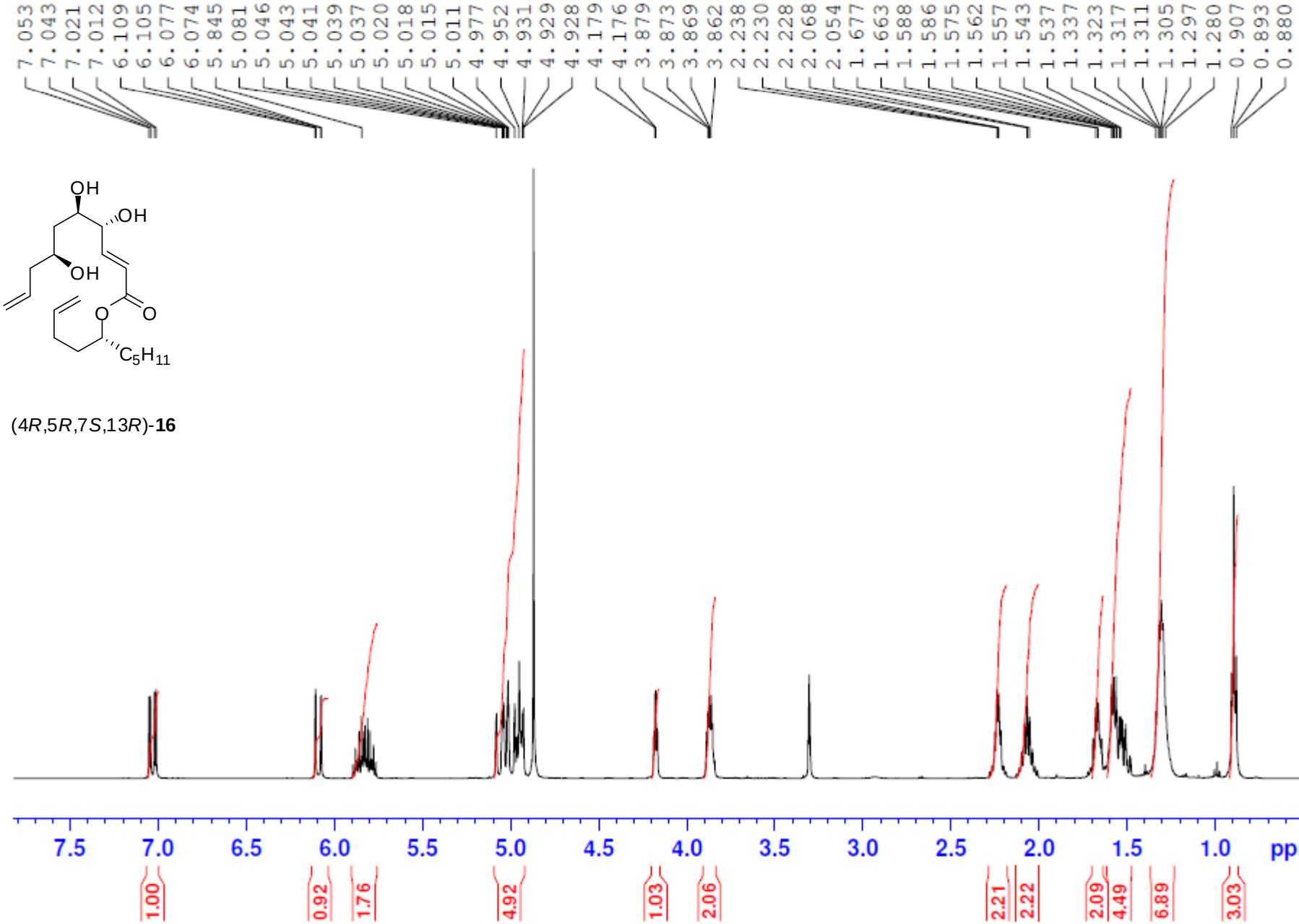
(4*S*,5*S*,7*R*,13*R*)-**16**



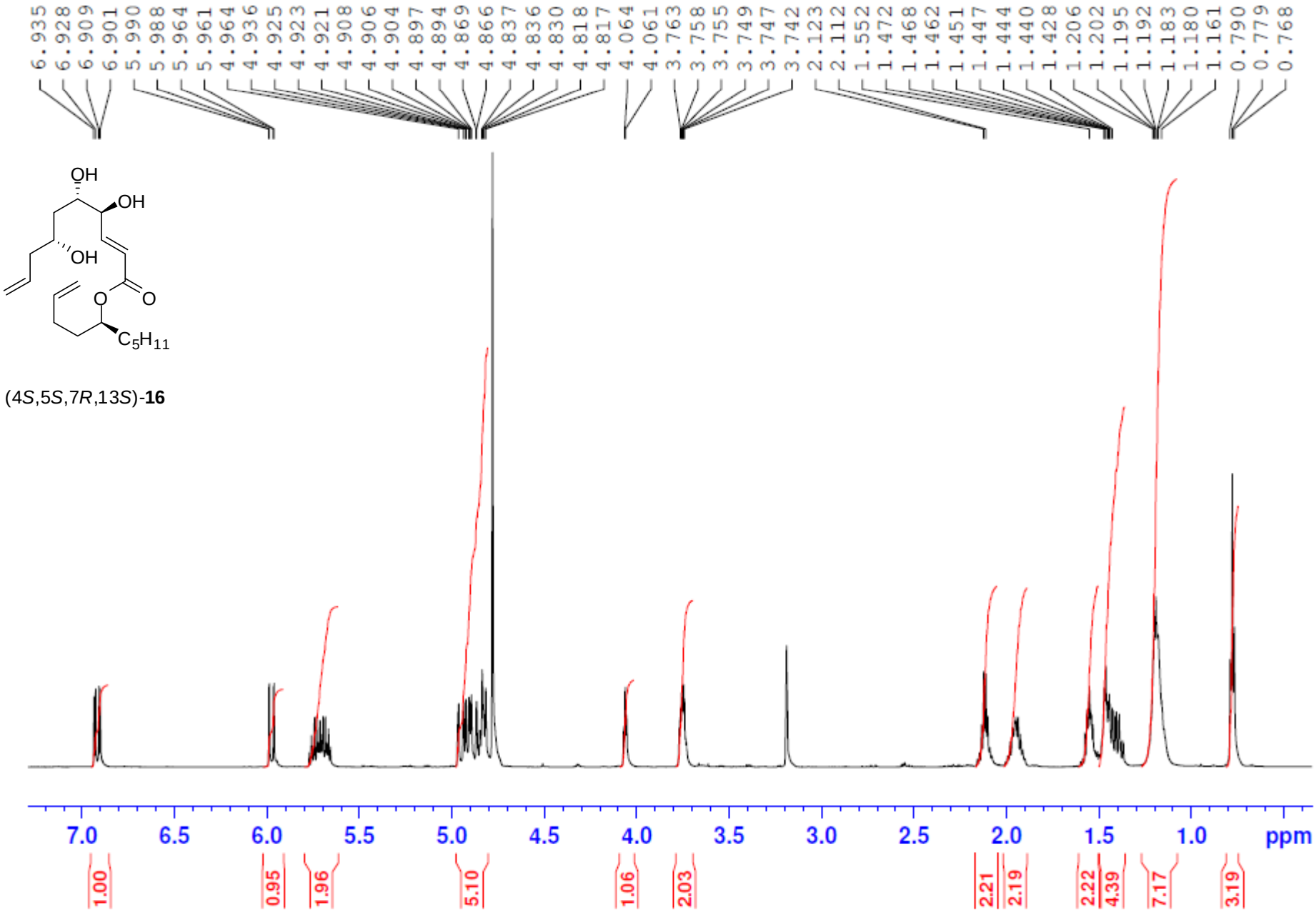
(4*S*,5*S*,7*S*,13*R*)-**16**



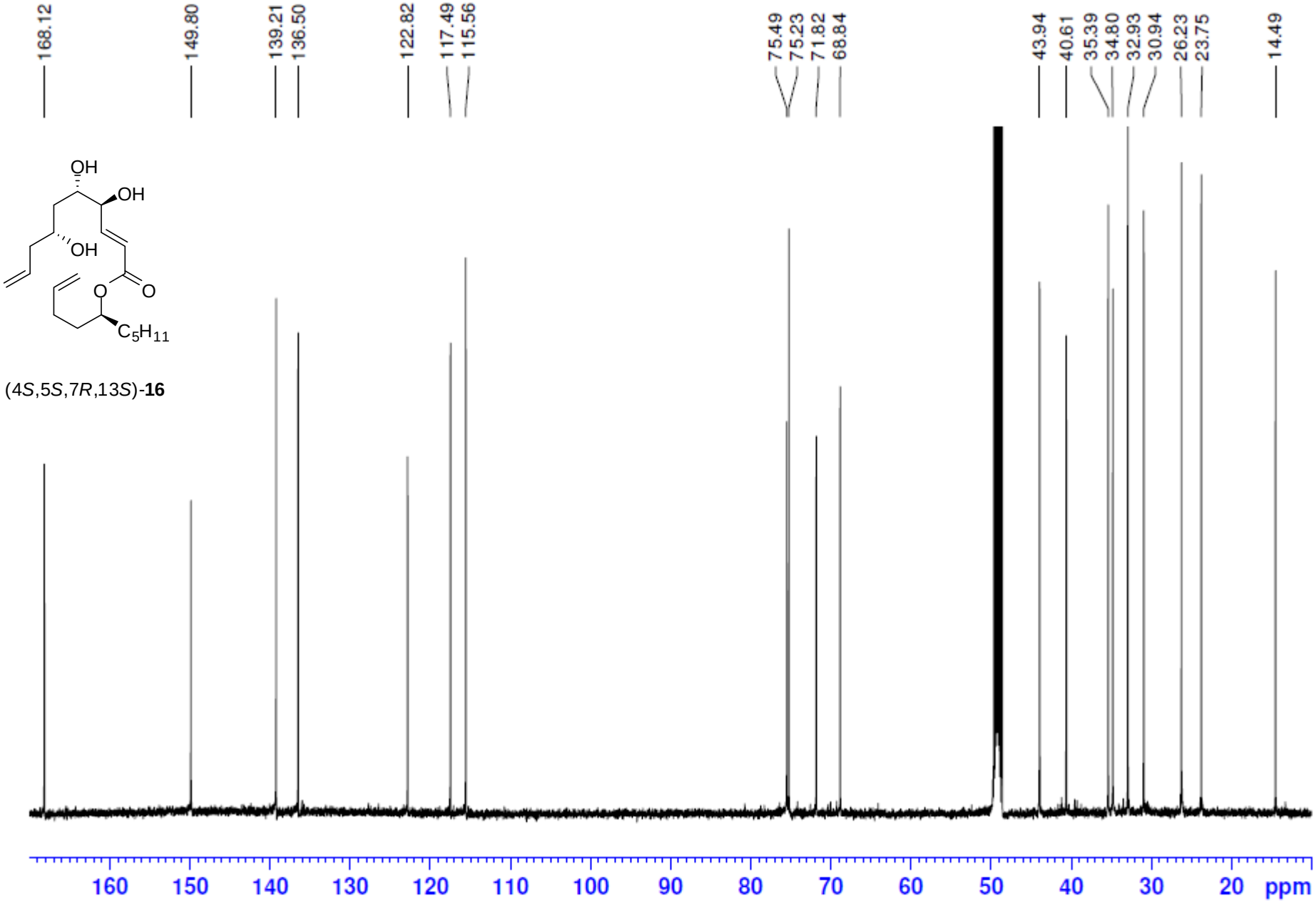
(4*R*,5*R*,7*R*,13*R*)-**16**



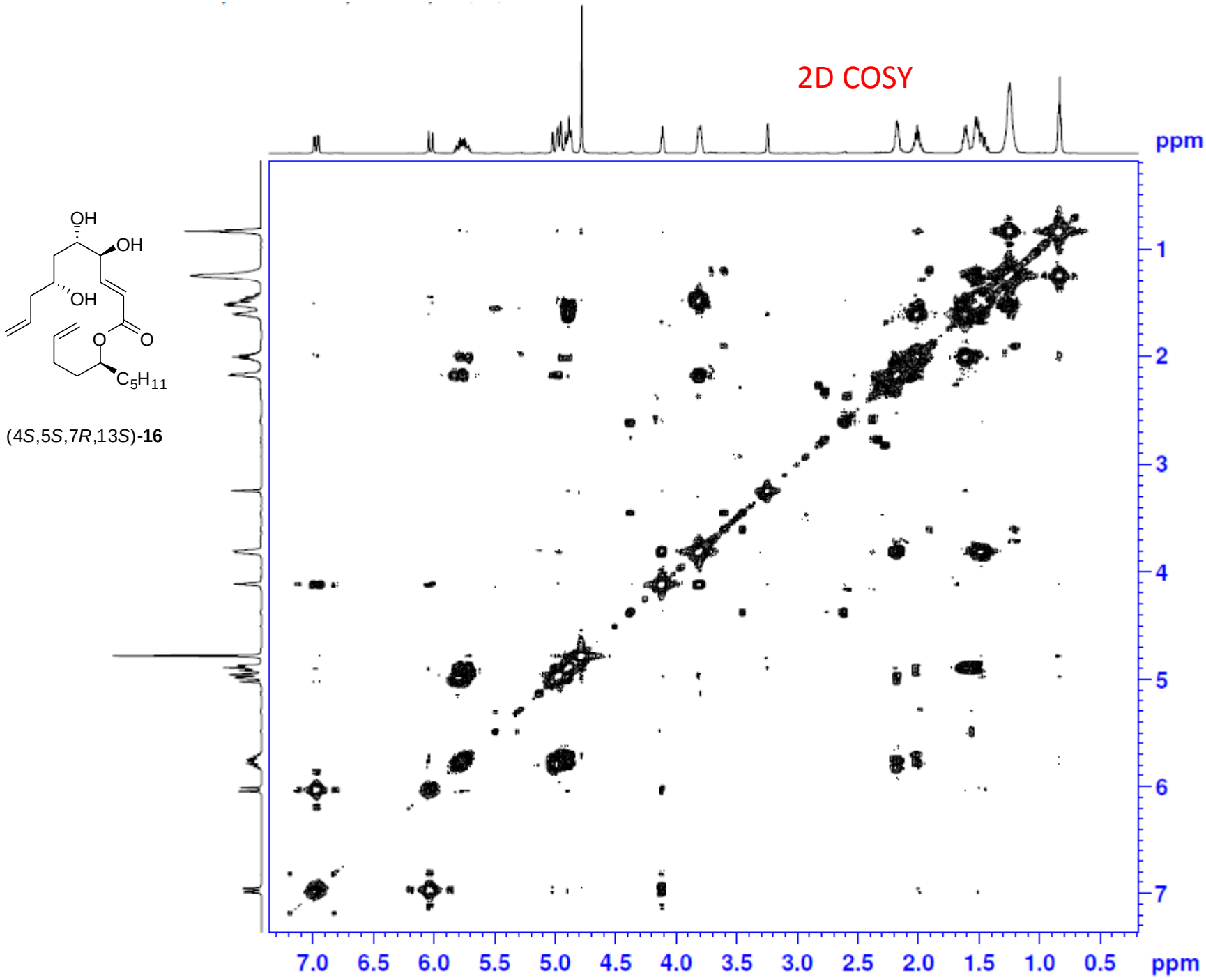
(4*R*,5*R*,7*S*,13*R*)-**16**



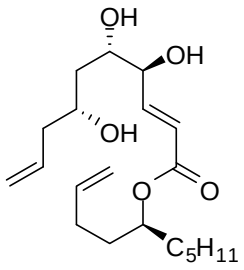
(4*S*,5*S*,7*R*,13*S*)-**16**



(4*S*,5*S*,7*R*,13*S*)-**16**

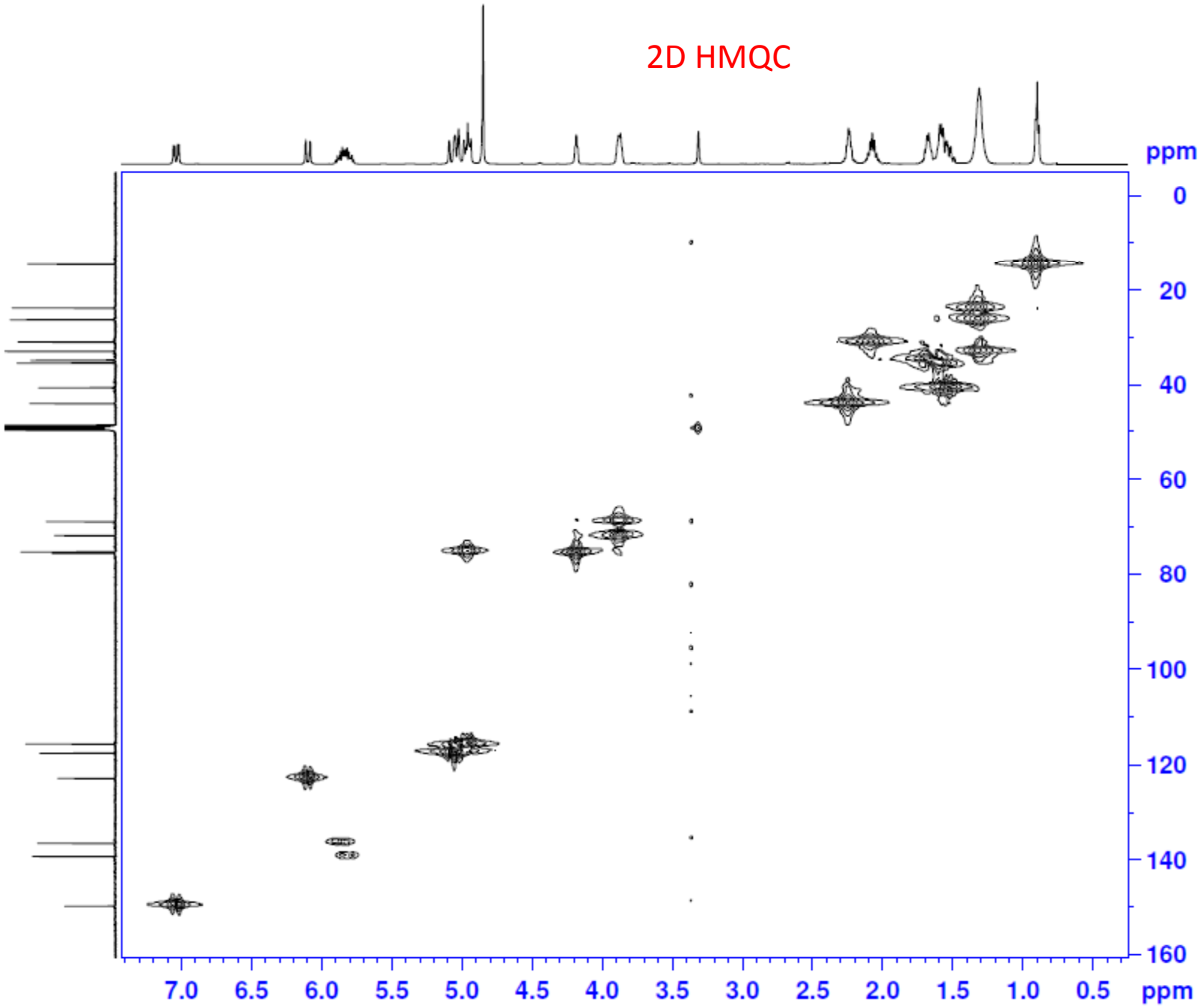


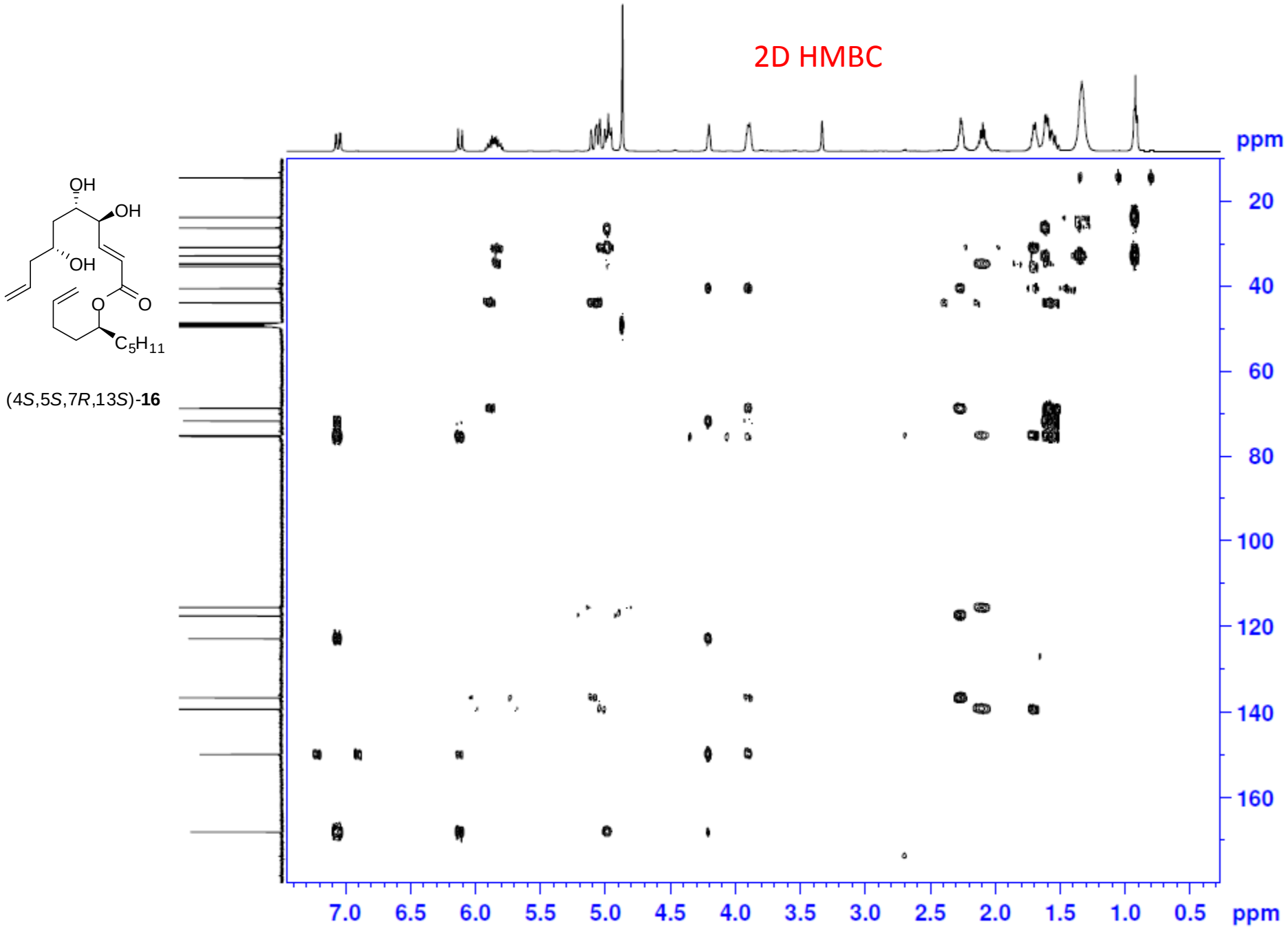
(4*S*,5*S*,7*R*,13*S*)-**16**

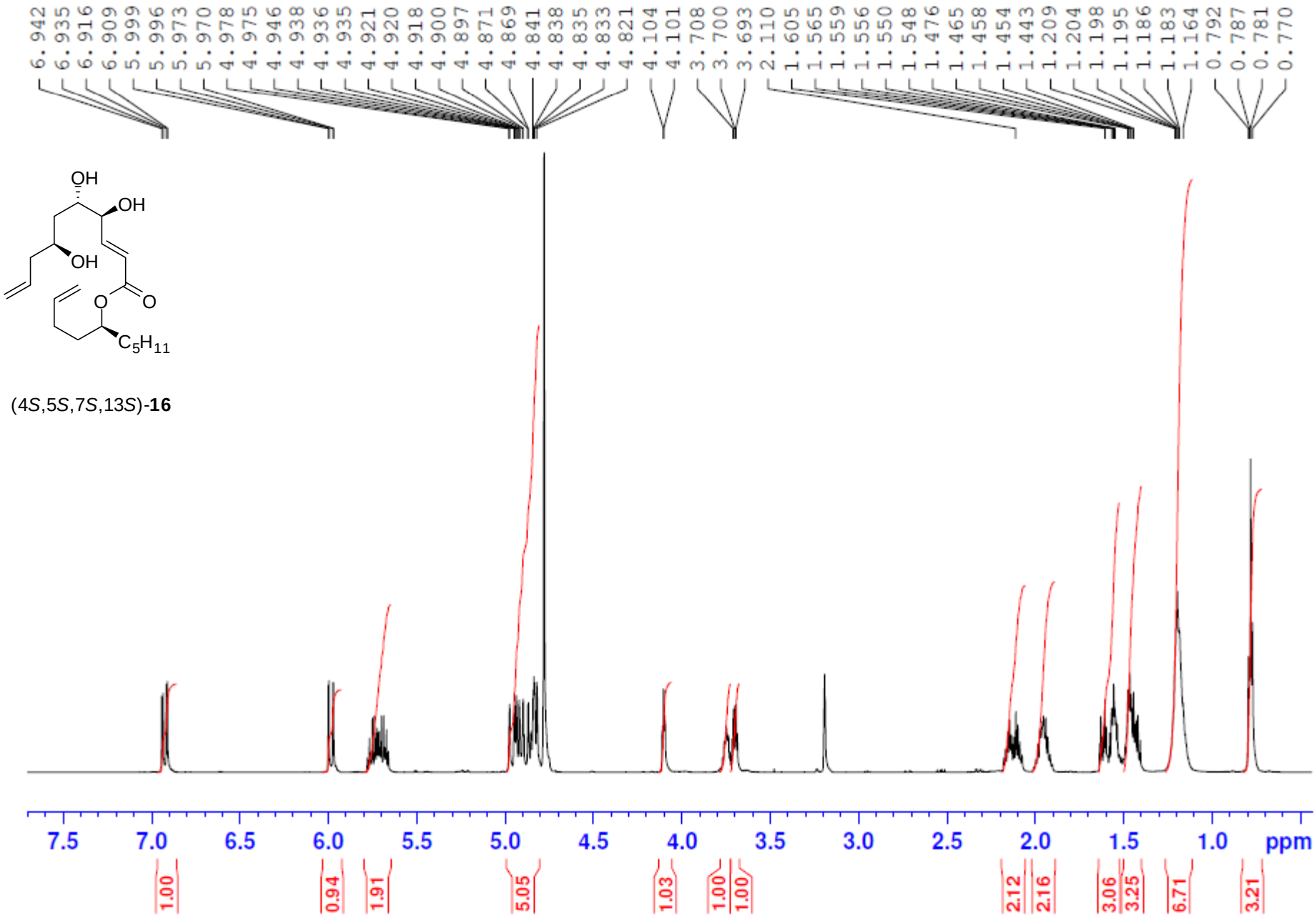


(4*S*,5*S*,7*R*,13*S*)-**16**

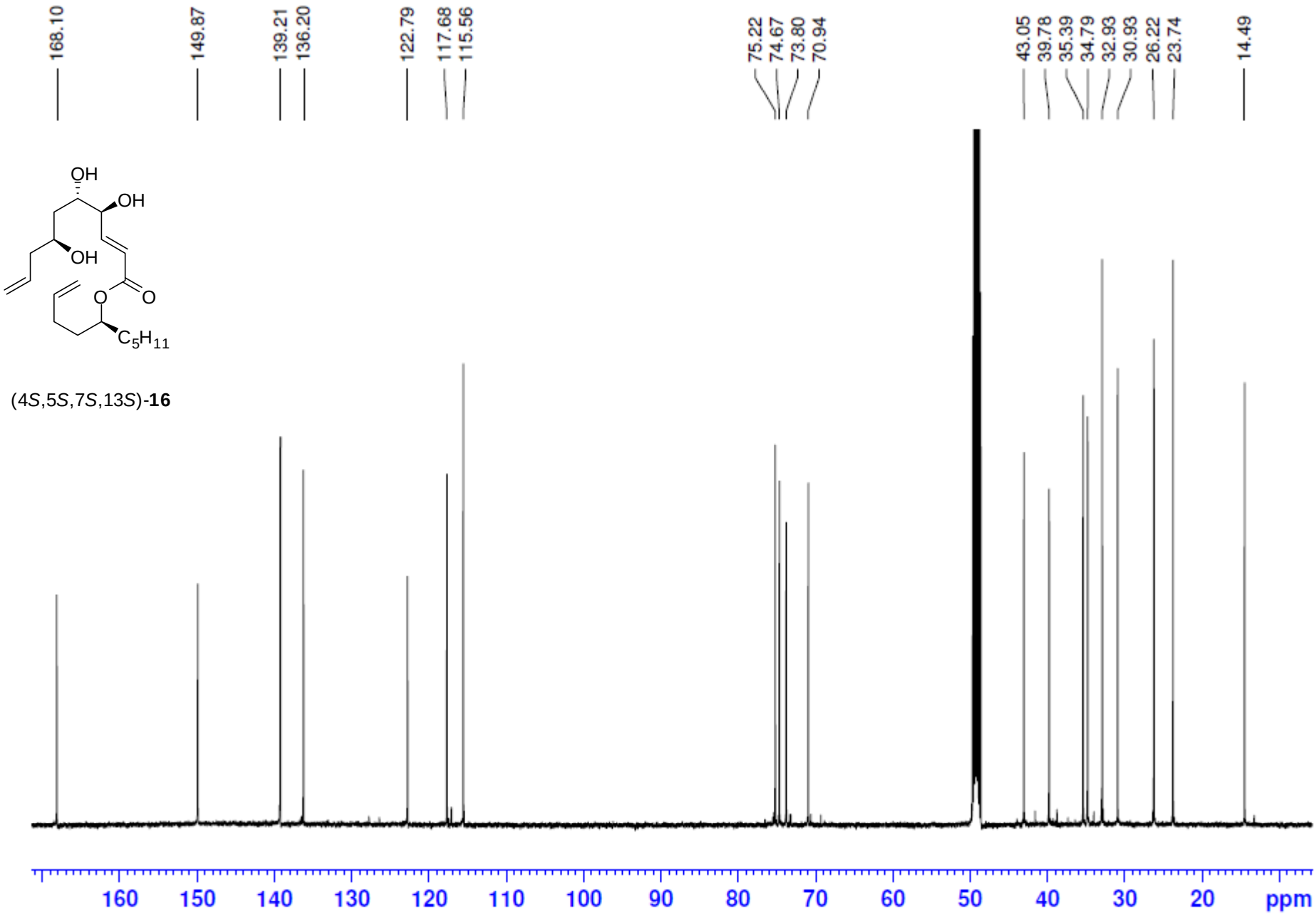
2D HMQC



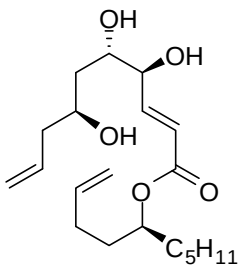

2D HMBC
OH
OH
OH
O
O
C_5H_{11}
(4*S*,5*S*,7*R*,13*S*)-**16**
ppm
20
40
60
80
100
120
140
160
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



(4*S*,5*S*,7*S*,13*S*)-**16**

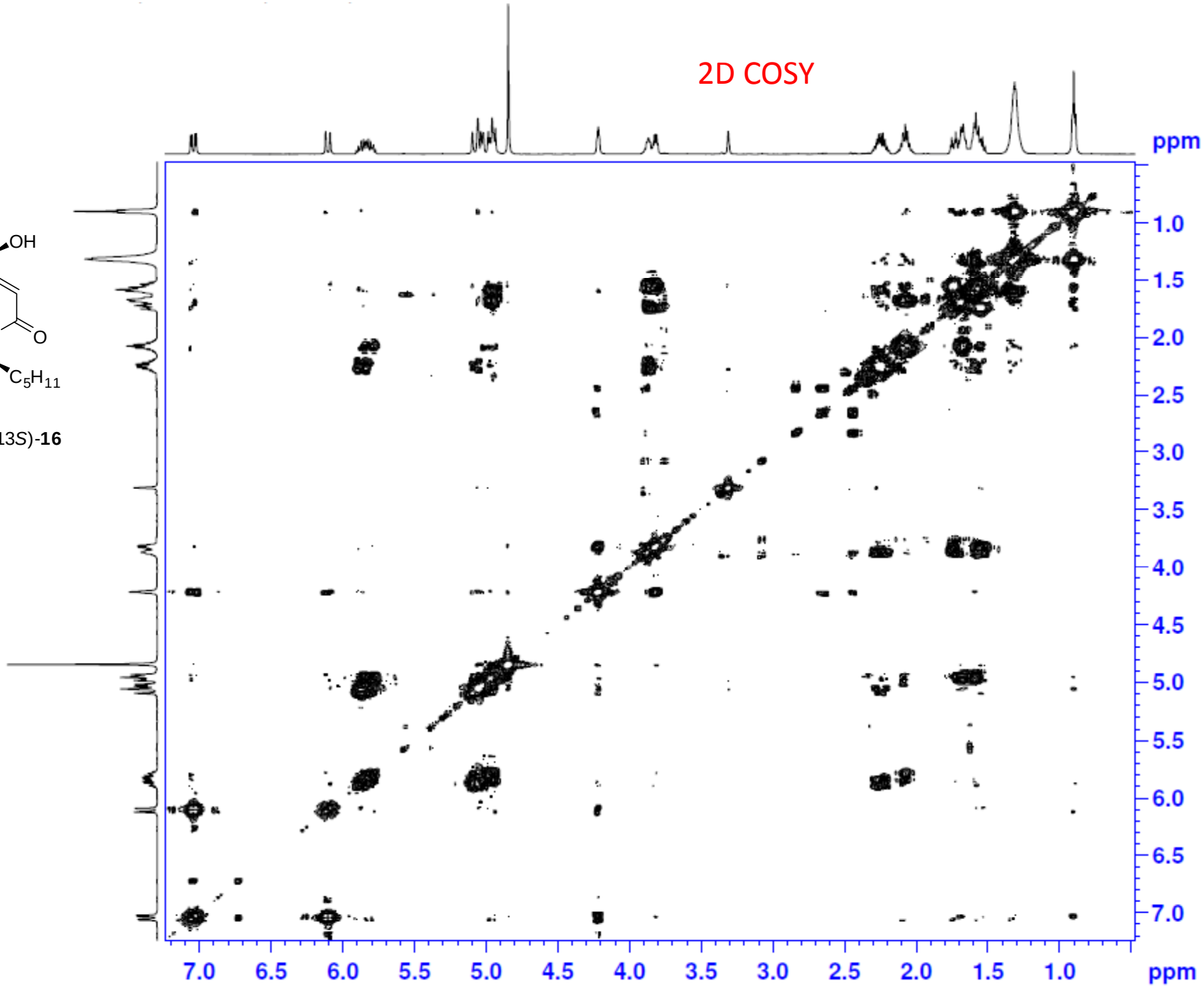


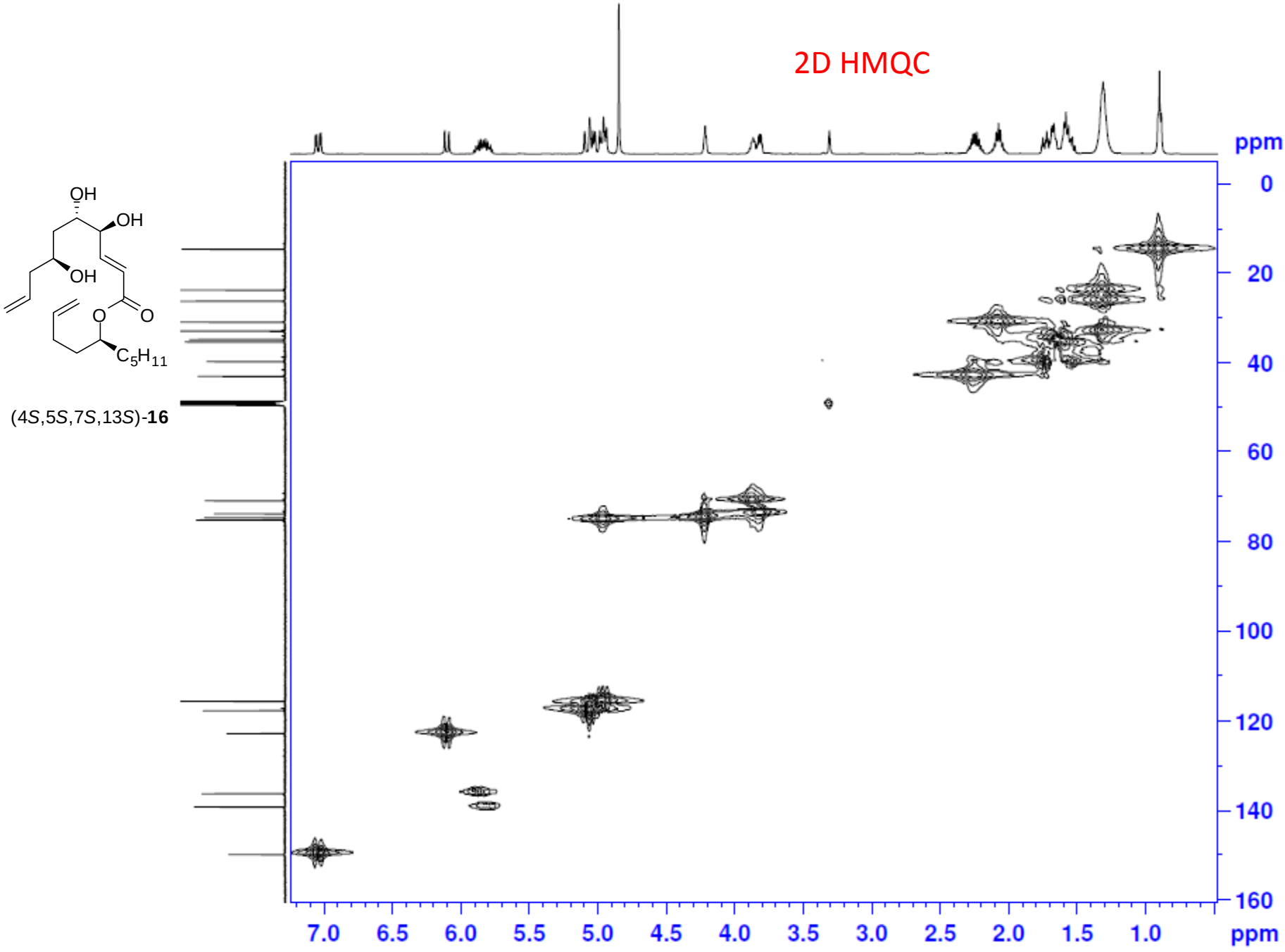
(4*S*,5*S*,7*S*,13*S*)-**16**

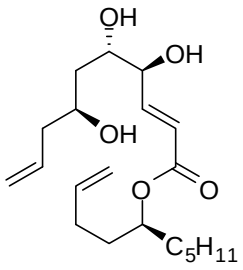


(4*S*,5*S*,7*S*,13*S*)-**16**

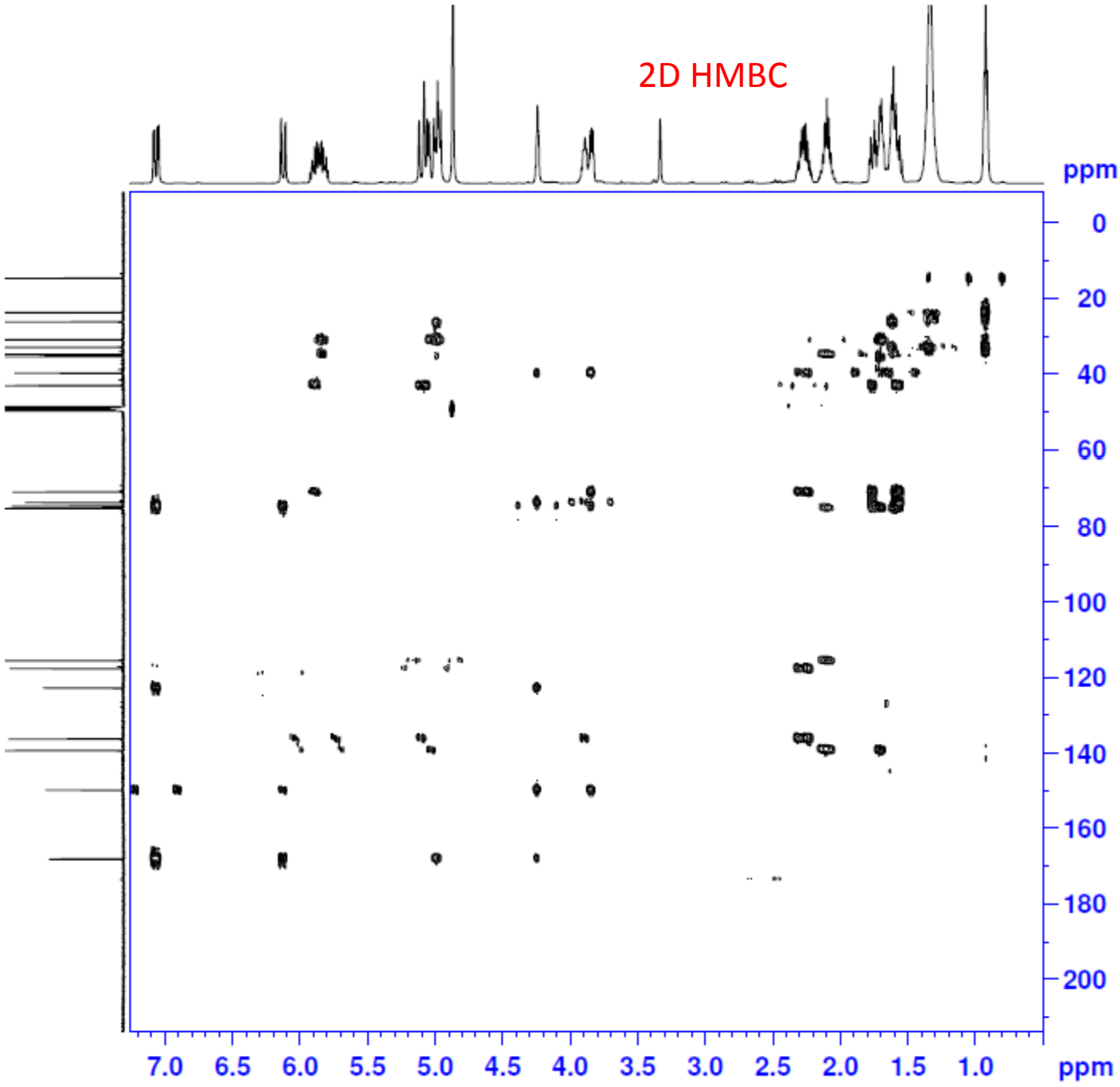
2D COSY

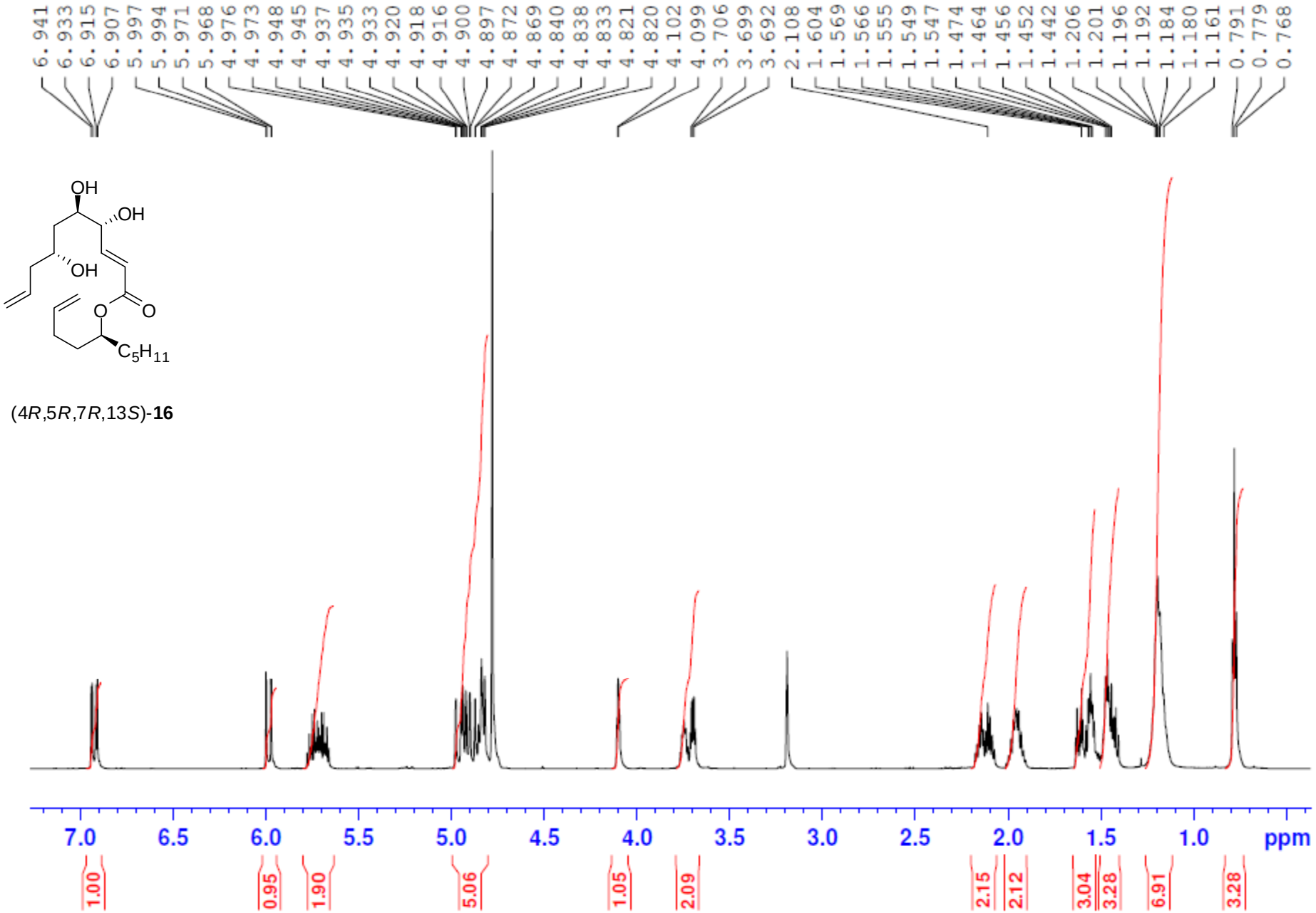



2D HMQC
OH
OH
OH
O
O
C_5H_{11}
(4*S*,5*S*,7*S*,13*S*)-**16**
ppm
0
20
40
60
80
100
120
140
160
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

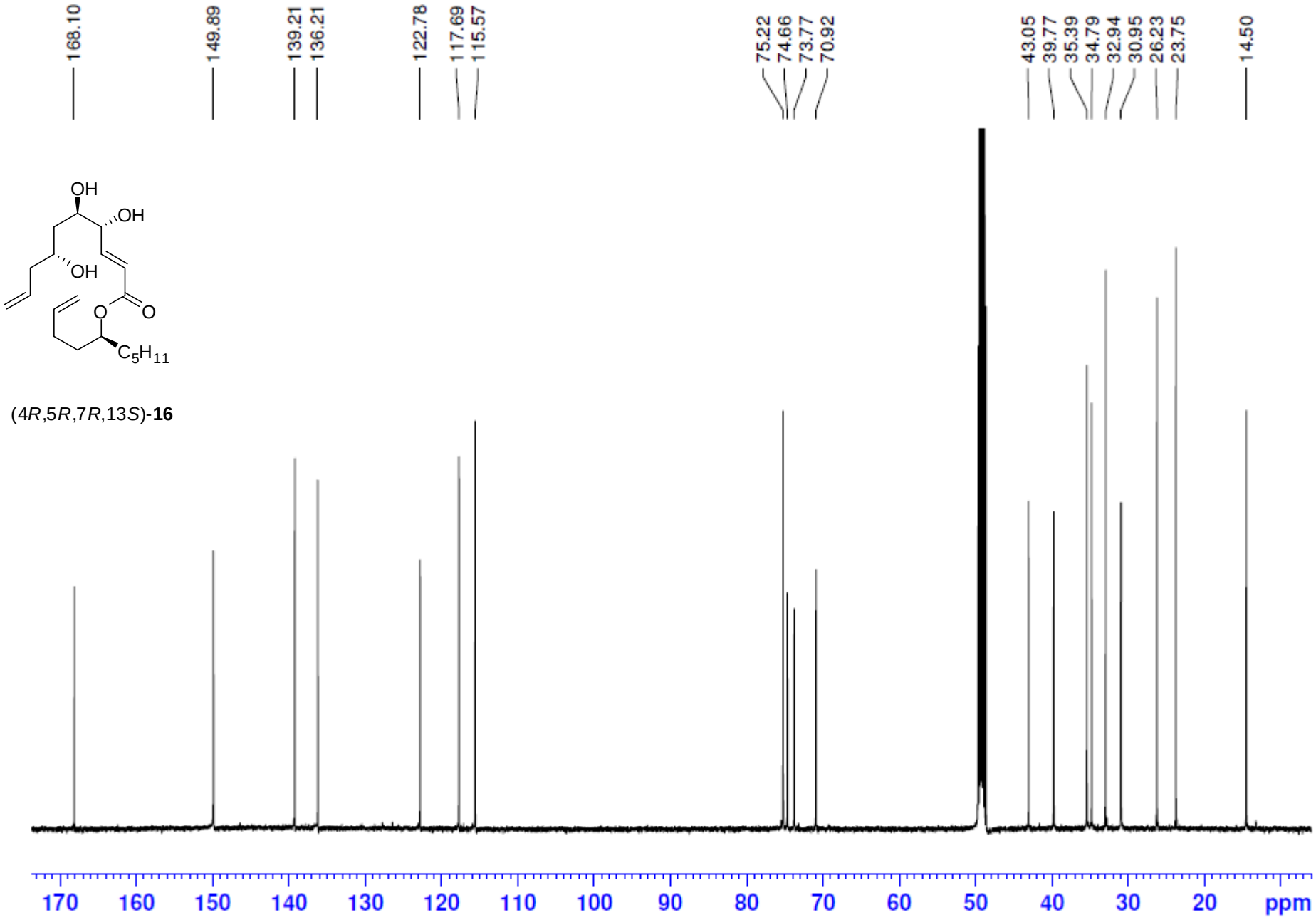


(4*S*,5*S*,7*S*,13*S*)-**16**

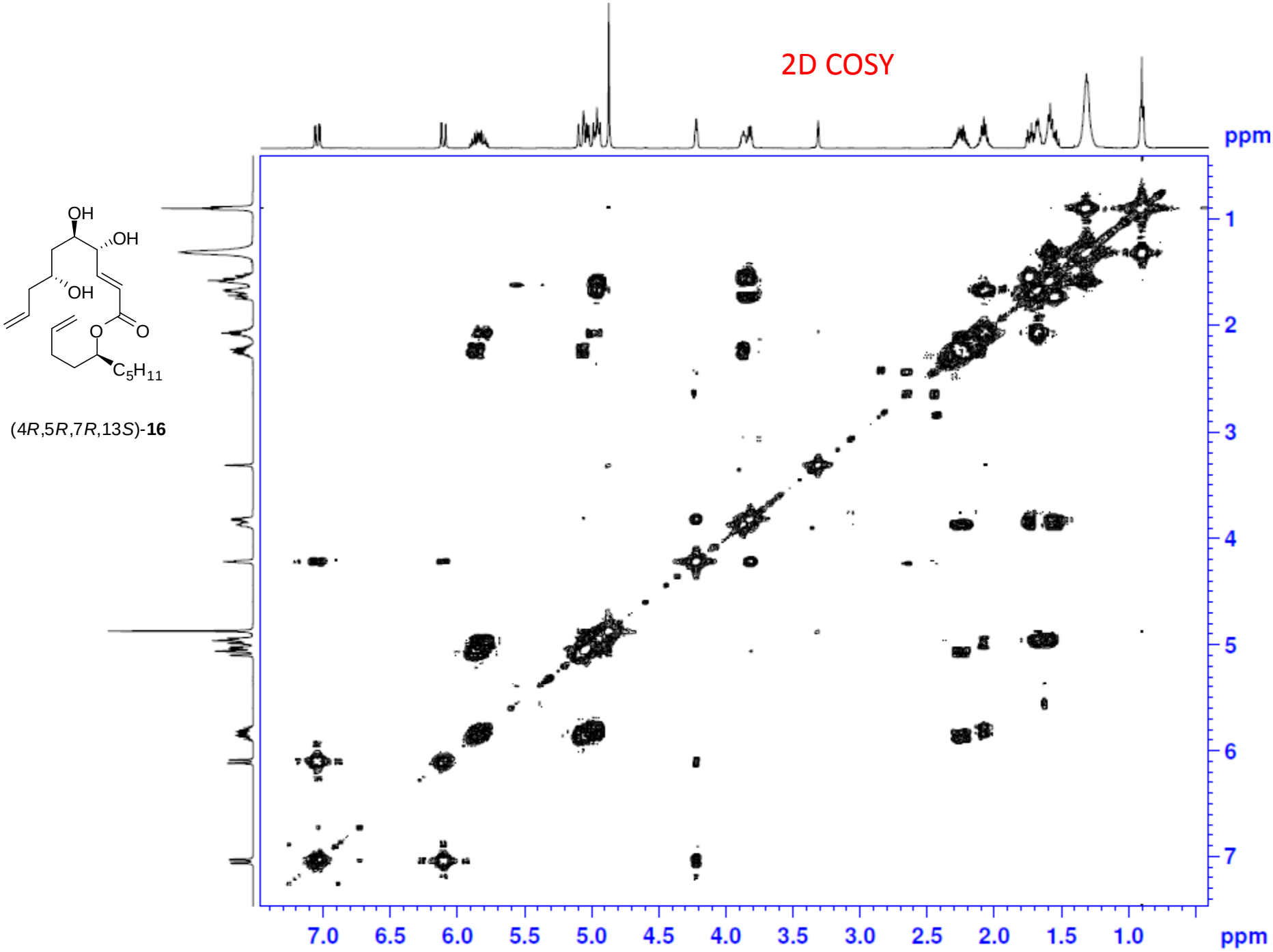




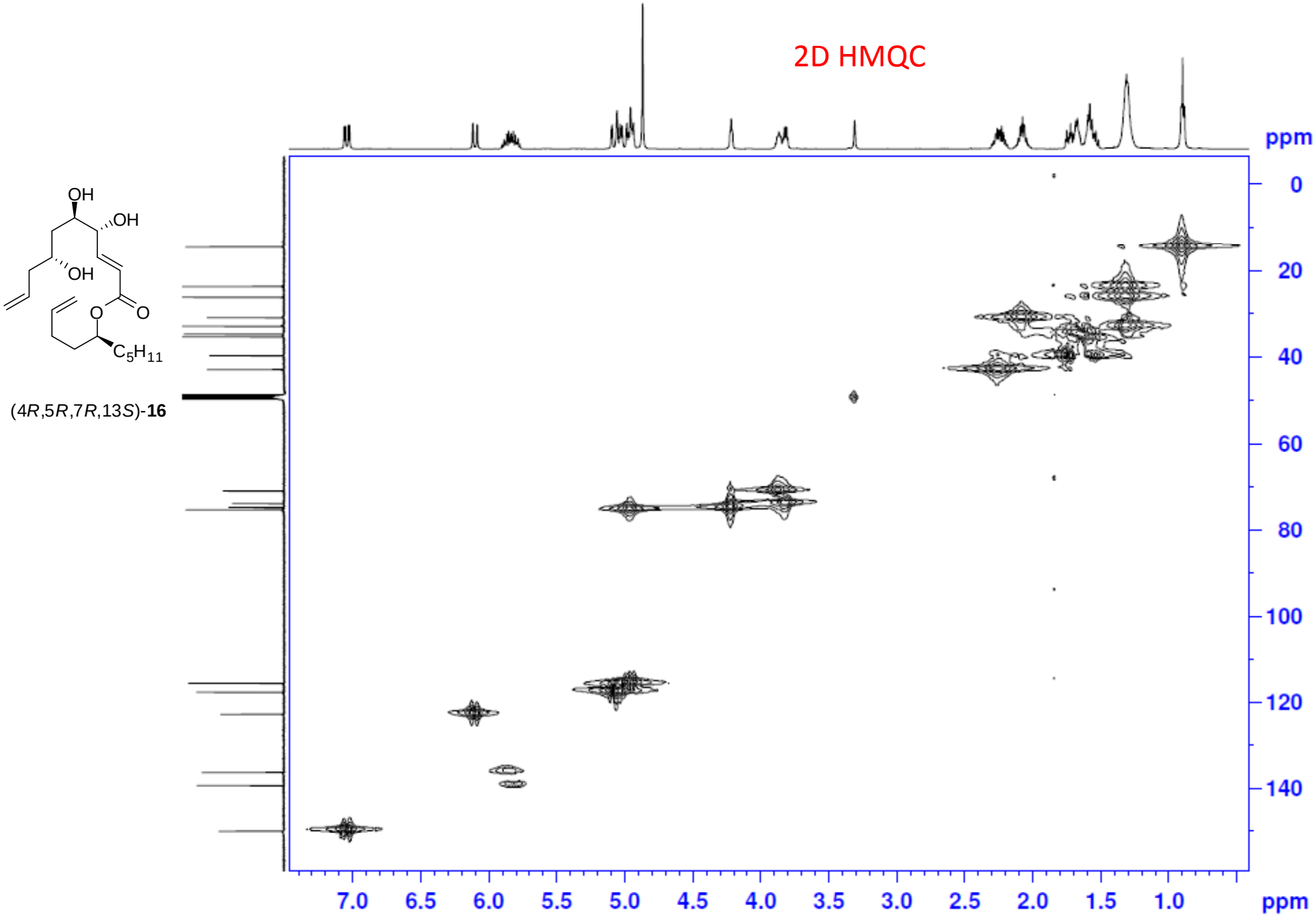
(4*R*,5*R*,7*R*,13*S*)-**16**

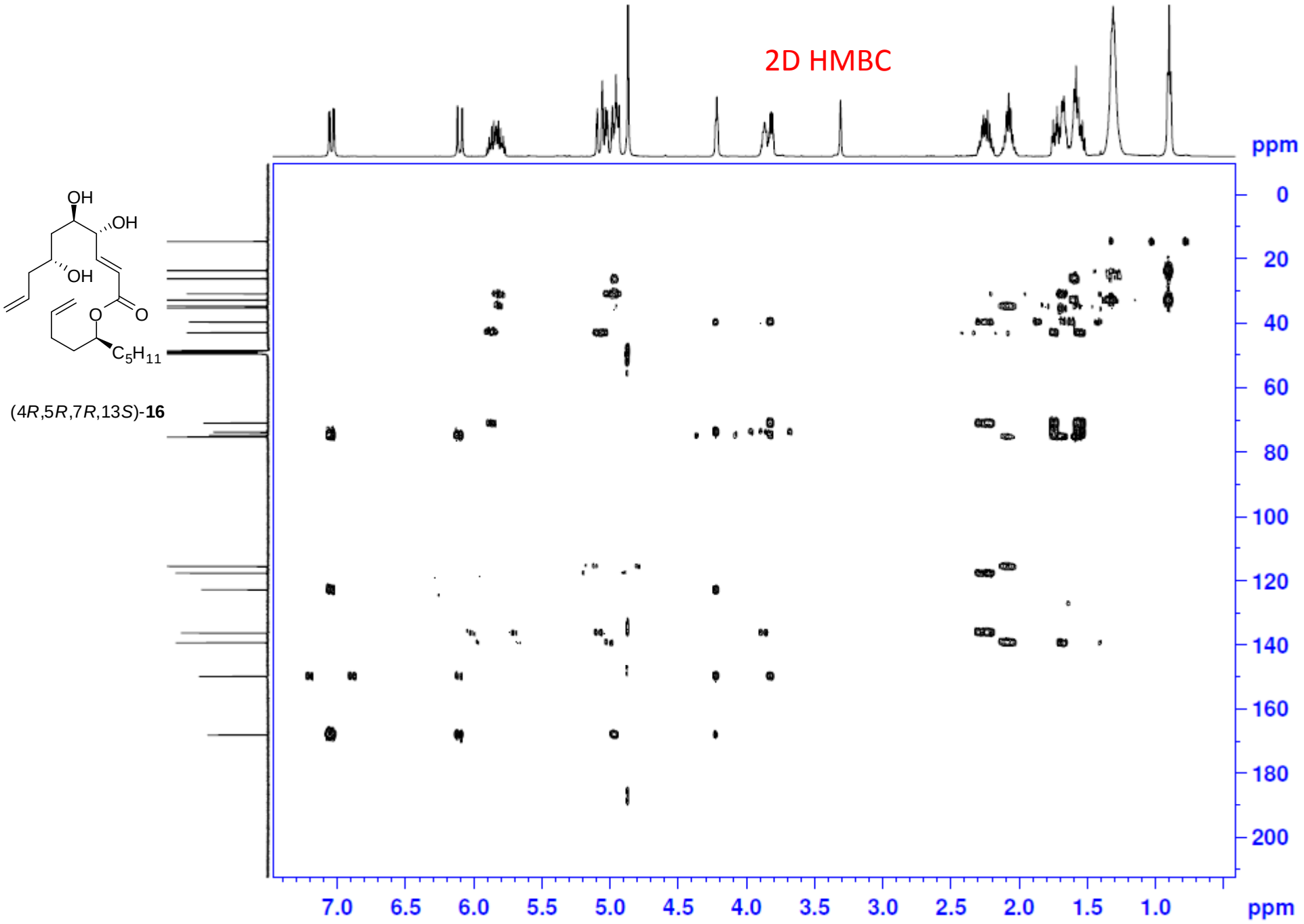


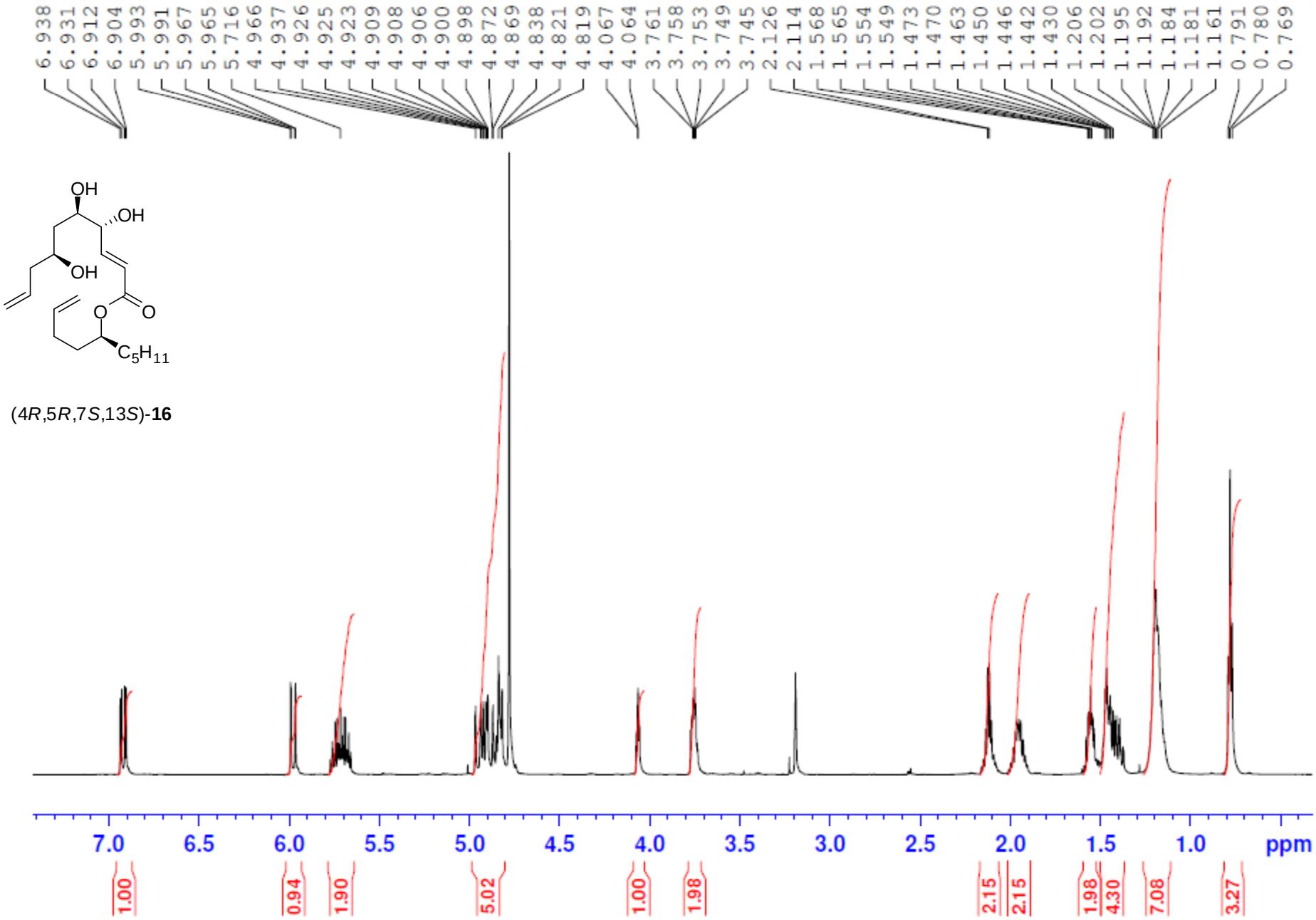
(4*R*,5*R*,7*R*,13*S*)-**16**



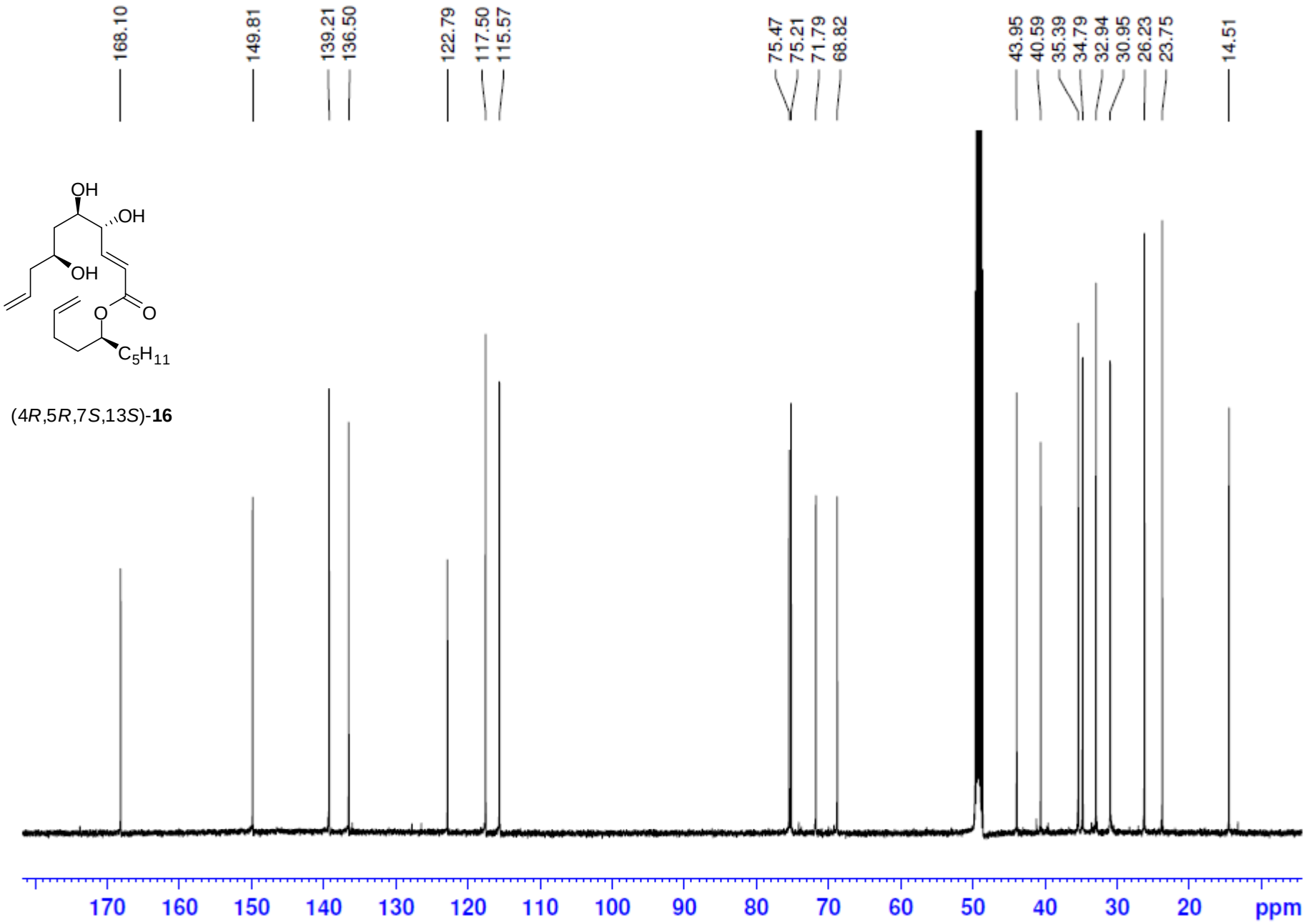
(4*R*,5*R*,7*R*,13*S*)-**16**


2D HMQC
OH
OH
OH
O
O
C_5H_{11}
(4*R*,5*R*,7*R*,13*S*)-**16**
ppm
0
20
40
60
80
100
120
140
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
ppm

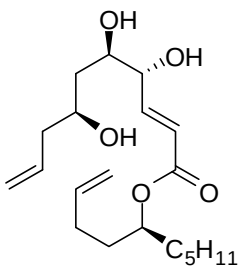

2D HMBC
OH
OH
OH
O
O
O
C_5H_{11}
(4*R*,5*R*,7*R*,13*S*)-**16**
ppm
0
20
40
60
80
100
120
140
160
180
200
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm



(4*R*,5*R*,7*S*,13*S*)-**16**

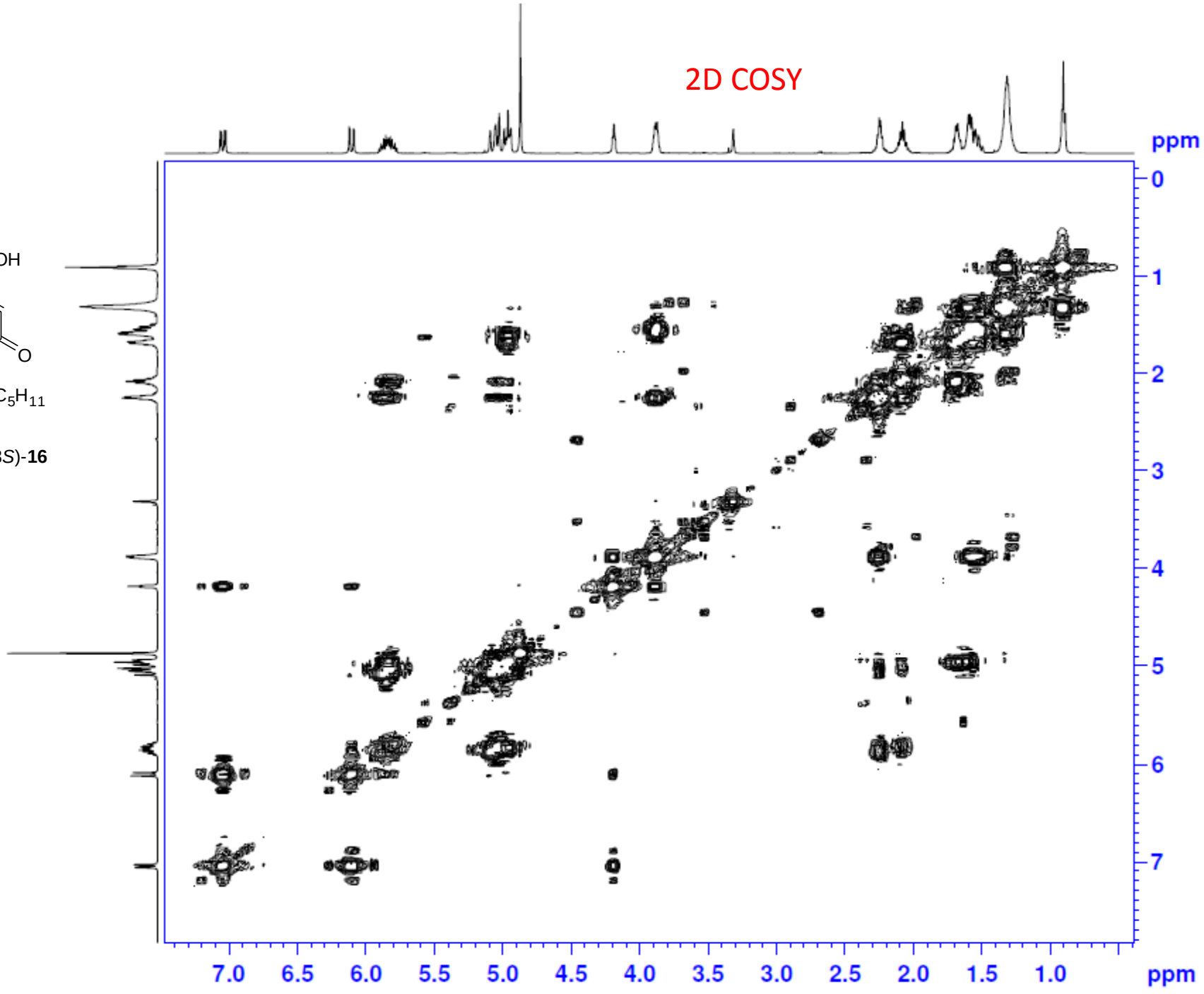


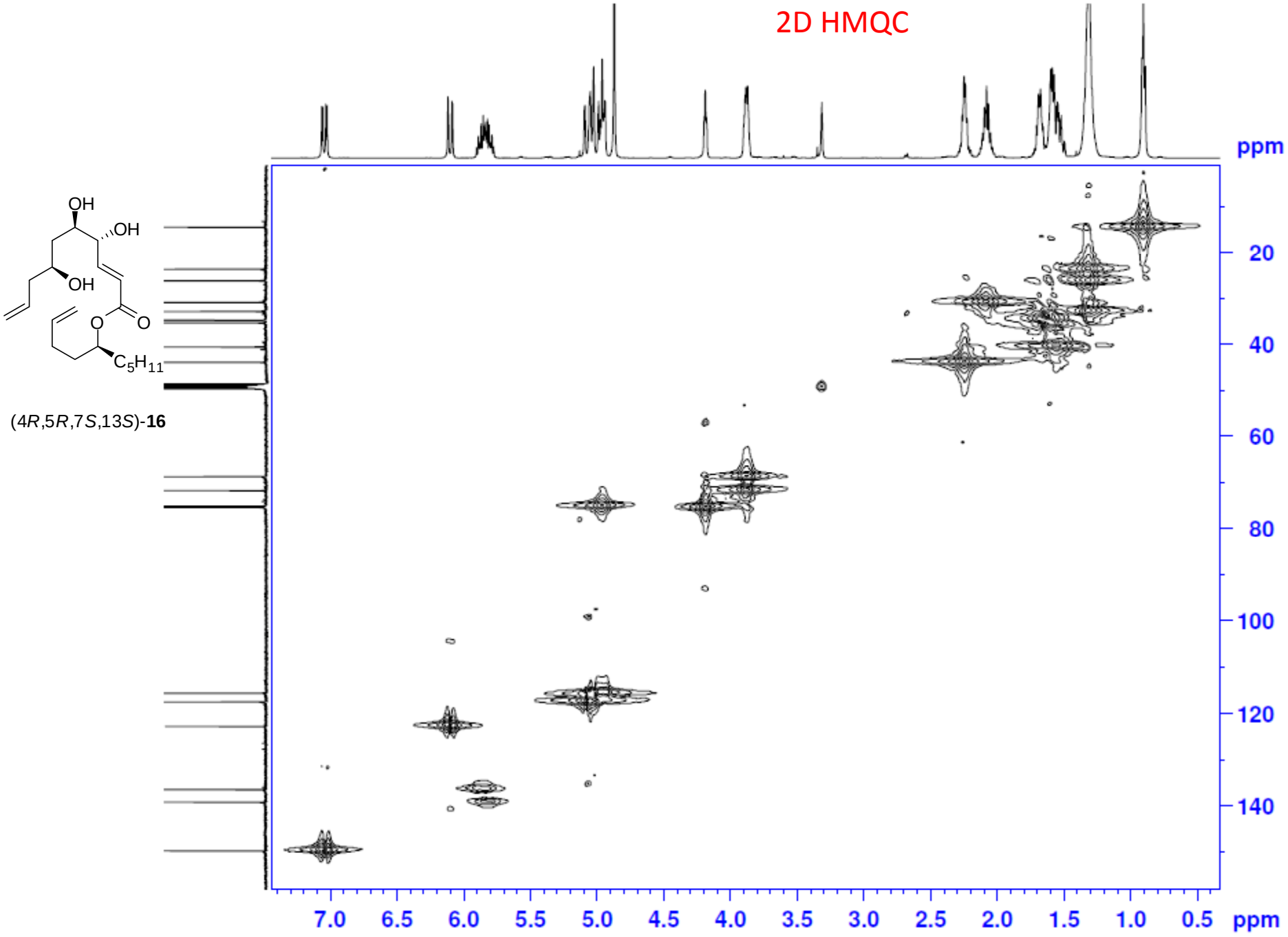
(4*R*,5*R*,7*S*,13*S*)-**16**

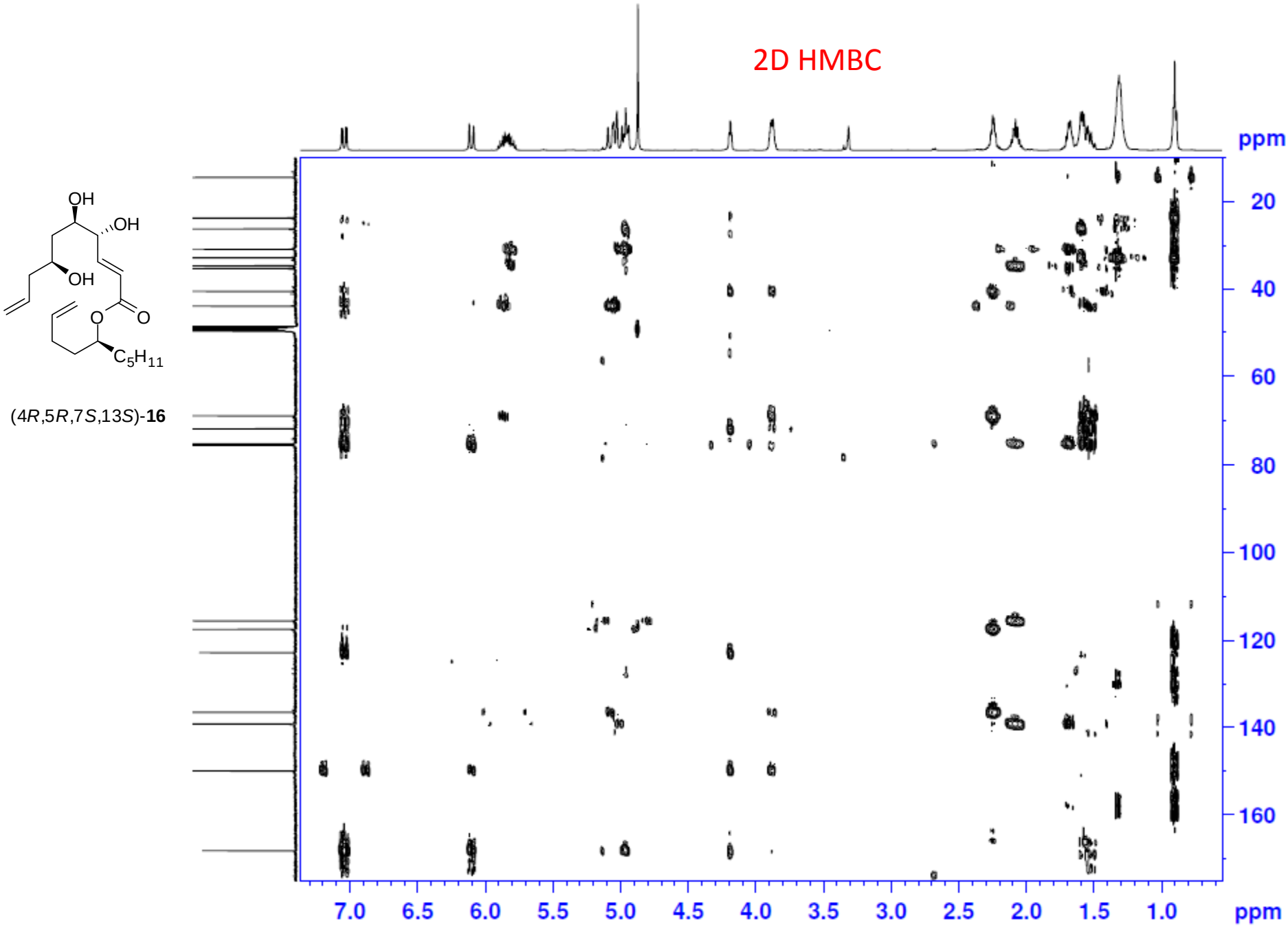


(4*R*,5*R*,7*S*,13*S*)-**16**

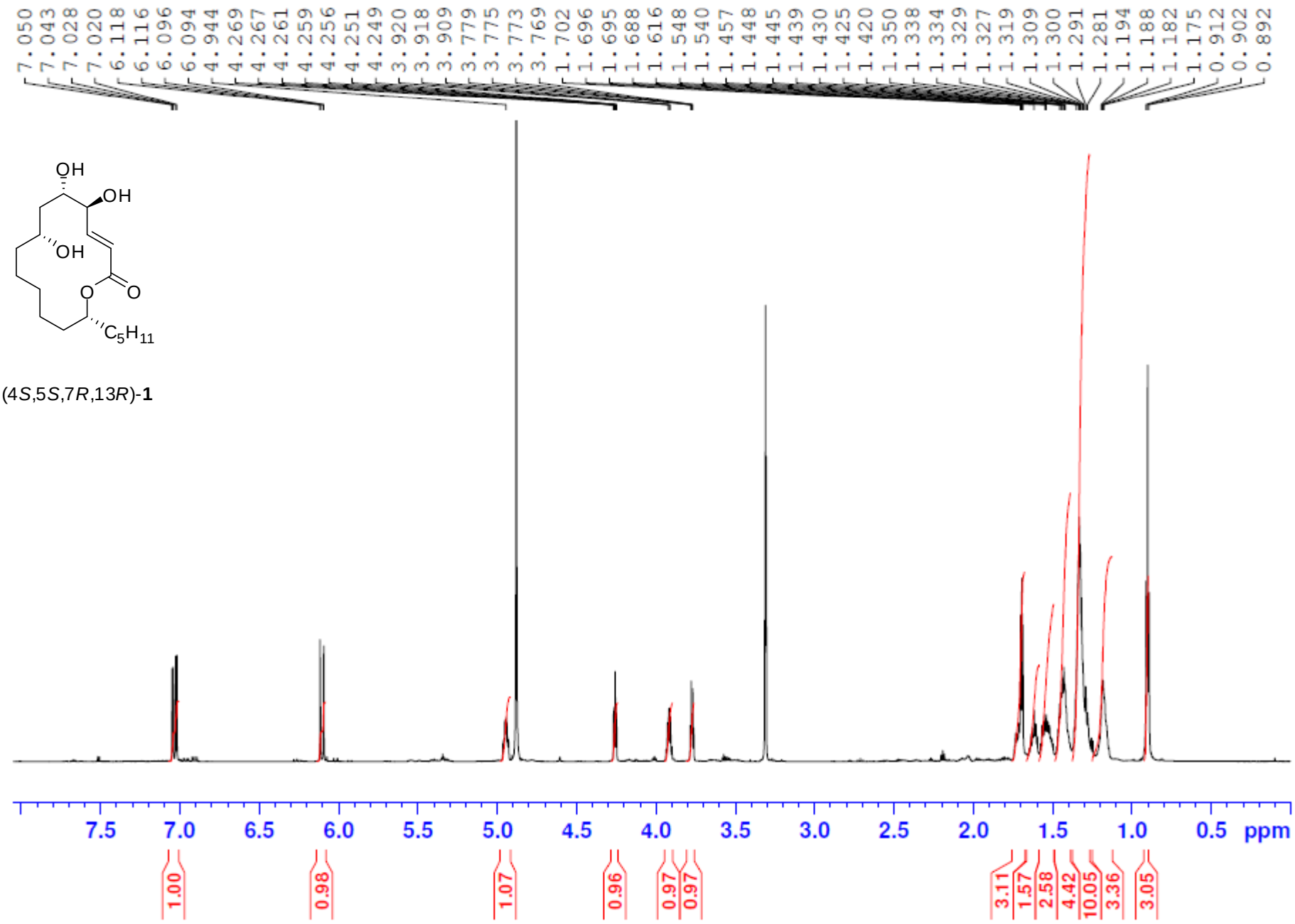
2D COSY



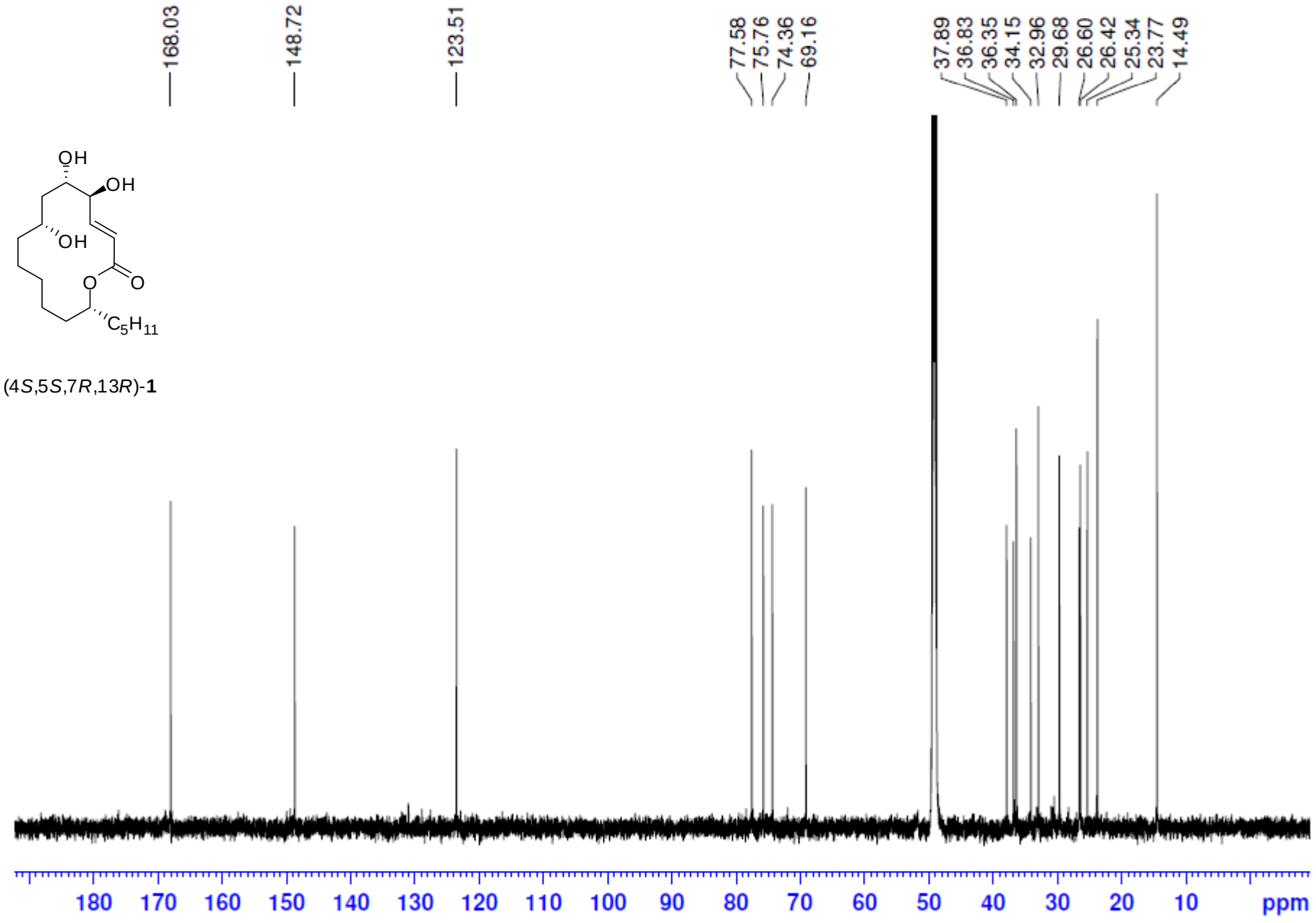

2D HMQC
OH
OH
OH
O
O
C_5H_{11}
(4*R*,5*R*,7*S*,13*S*)-**16**
ppm
20
40
60
80
100
120
140
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm



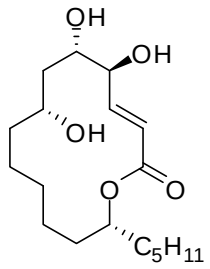
(4*R*,5*R*,7*S*,13*S*)-**16**


7.050
7.043
7.028
7.020
6.118
6.116
6.096
6.094
4.944
4.269
4.267
4.261
4.259
4.256
4.251
4.249
3.920
3.918
3.909
3.779
3.775
3.773
3.769
1.702
1.696
1.695
1.688
1.616
1.548
1.540
1.457
1.448
1.445
1.439
1.430
1.425
1.420
1.350
1.338
1.334
1.329
1.327
1.319
1.309
1.300
1.291
1.281
1.194
1.188
1.182
1.175
0.912
0.902
0.892
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.98
1.07
0.96
0.97
0.97
3.11
1.57
2.58
4.42
10.05
3.36
3.05

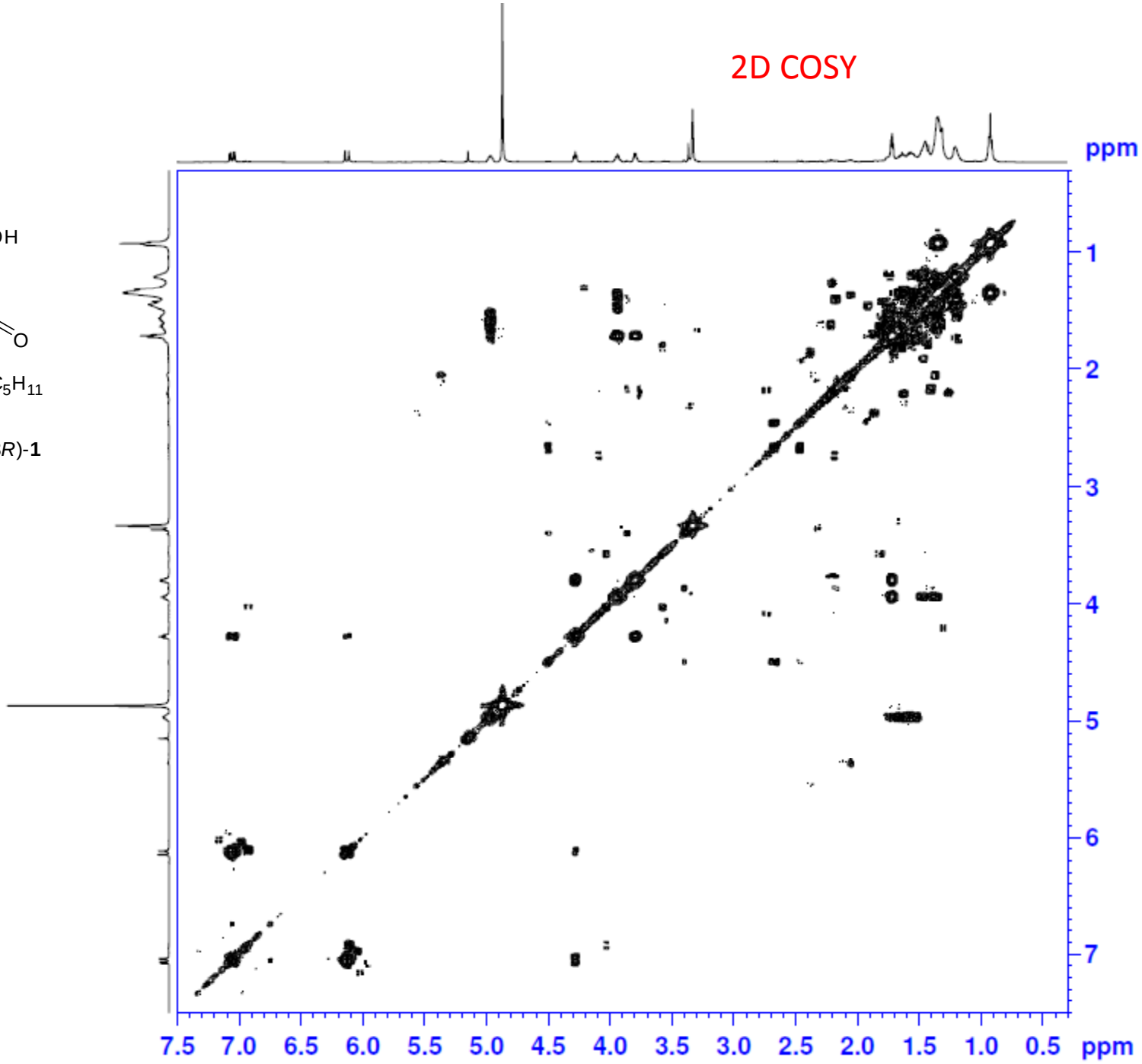
(4*S*,5*S*,7*R*,13*R*)-**1**


168.03
148.72
123.51
77.58
75.76
74.36
69.16
37.89
36.83
36.35
34.15
32.96
29.68
26.60
26.42
25.34
23.77
14.49
OH
OH
OH
O
O
C5H11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

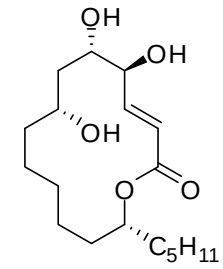
(4*S*,5*S*,7*R*,13*R*)-**1**


OH
OH
OH
O
O
C5H11

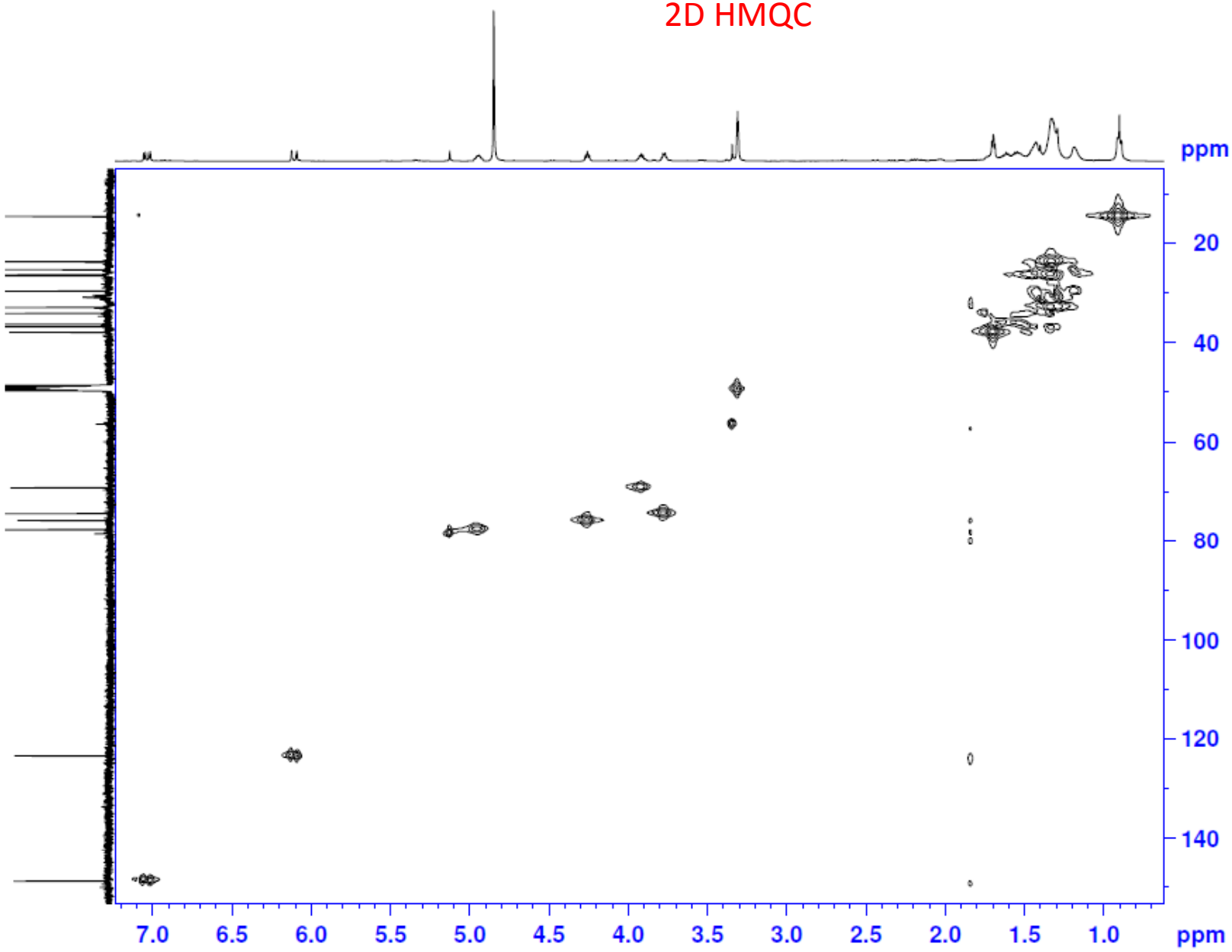
(4*S*,5*S*,7*R*,13*R*)-**1**

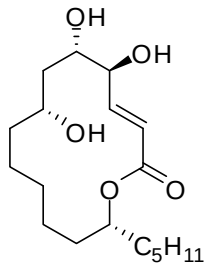

2D COSY
ppm
1
2
3
4
5
6
7
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

2D HMQC

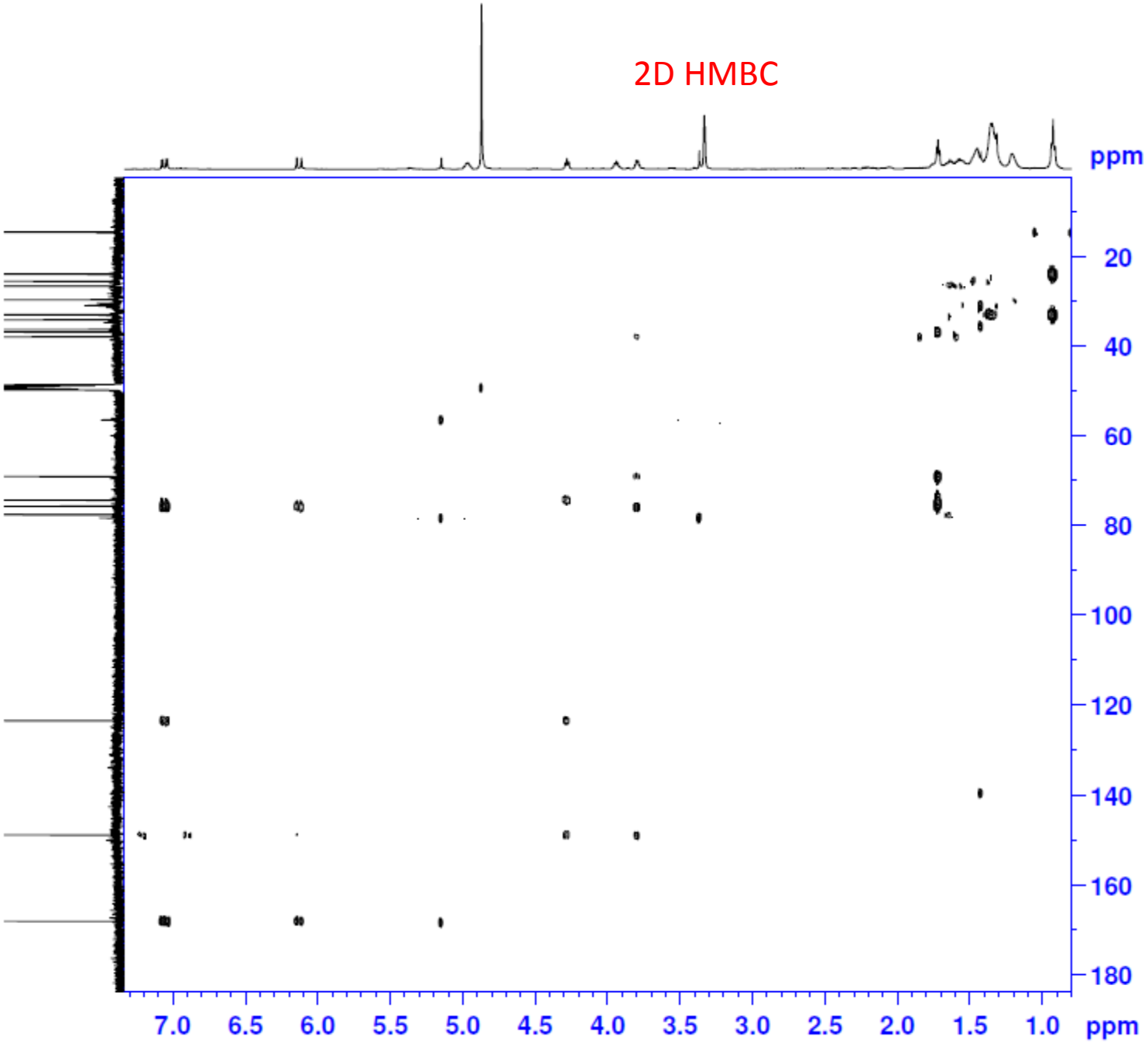


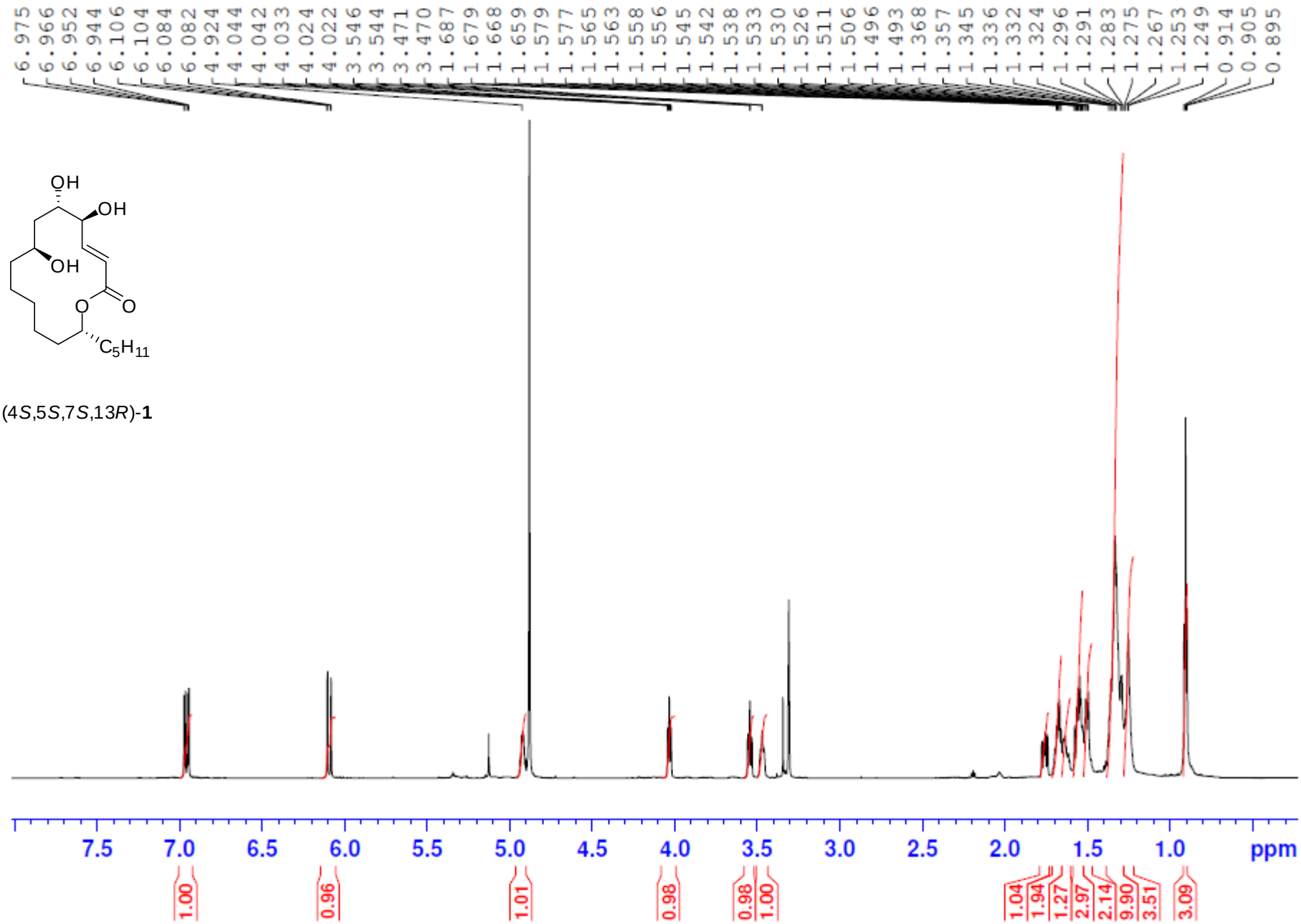
(4*S*,5*S*,7*R*,13*R*)-**1**



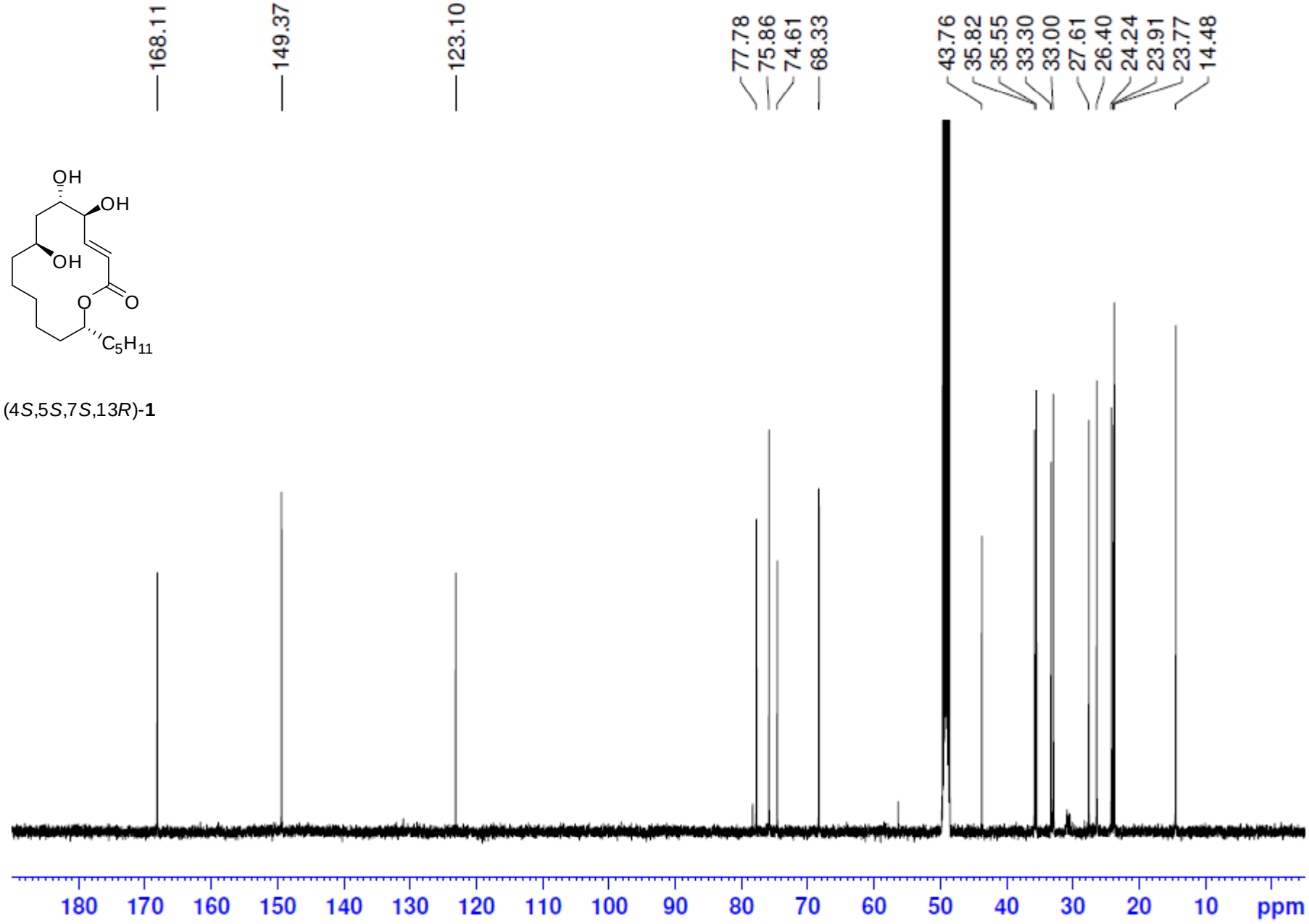

OH
OH
OH
O
O
C5H11

(4*S*,5*S*,7*R*,13*R*)-**1**


2D HMBC
ppm
20
40
60
80
100
120
140
160
180
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
ppm

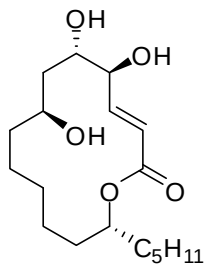

6.975
6.966
6.952
6.944
6.106
6.104
6.084
6.082
4.924
4.044
4.042
4.033
4.024
4.022
3.546
3.544
3.471
3.470
1.687
1.679
1.668
1.659
1.579
1.577
1.565
1.563
1.558
1.556
1.545
1.542
1.538
1.533
1.530
1.526
1.511
1.506
1.496
1.493
1.368
1.357
1.345
1.336
1.332
1.324
1.296
1.291
1.283
1.275
1.267
1.253
1.249
0.914
0.905
0.895
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.96
1.01
0.98
0.98
1.00
1.04
1.94
1.27
2.97
2.14
9.90
3.51
3.09

(4*S*,5*S*,7*S*,13*R*)-**1**

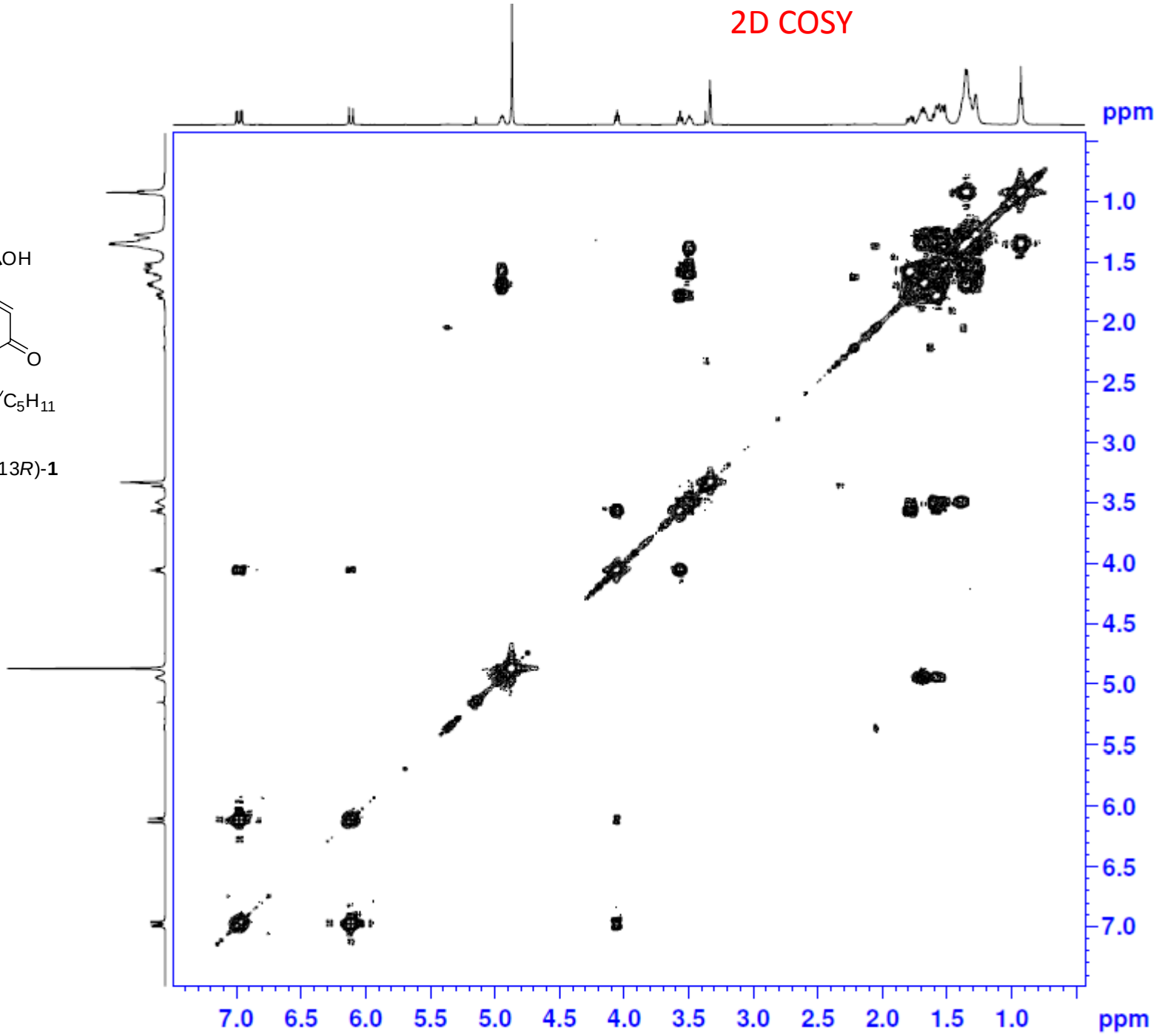

168.11
149.37
123.10
77.78
75.86
74.61
68.33
43.76
35.82
35.55
33.30
33.00
27.61
26.40
24.24
23.91
23.77
14.48
OH
OH
OH
O
O
C5H11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

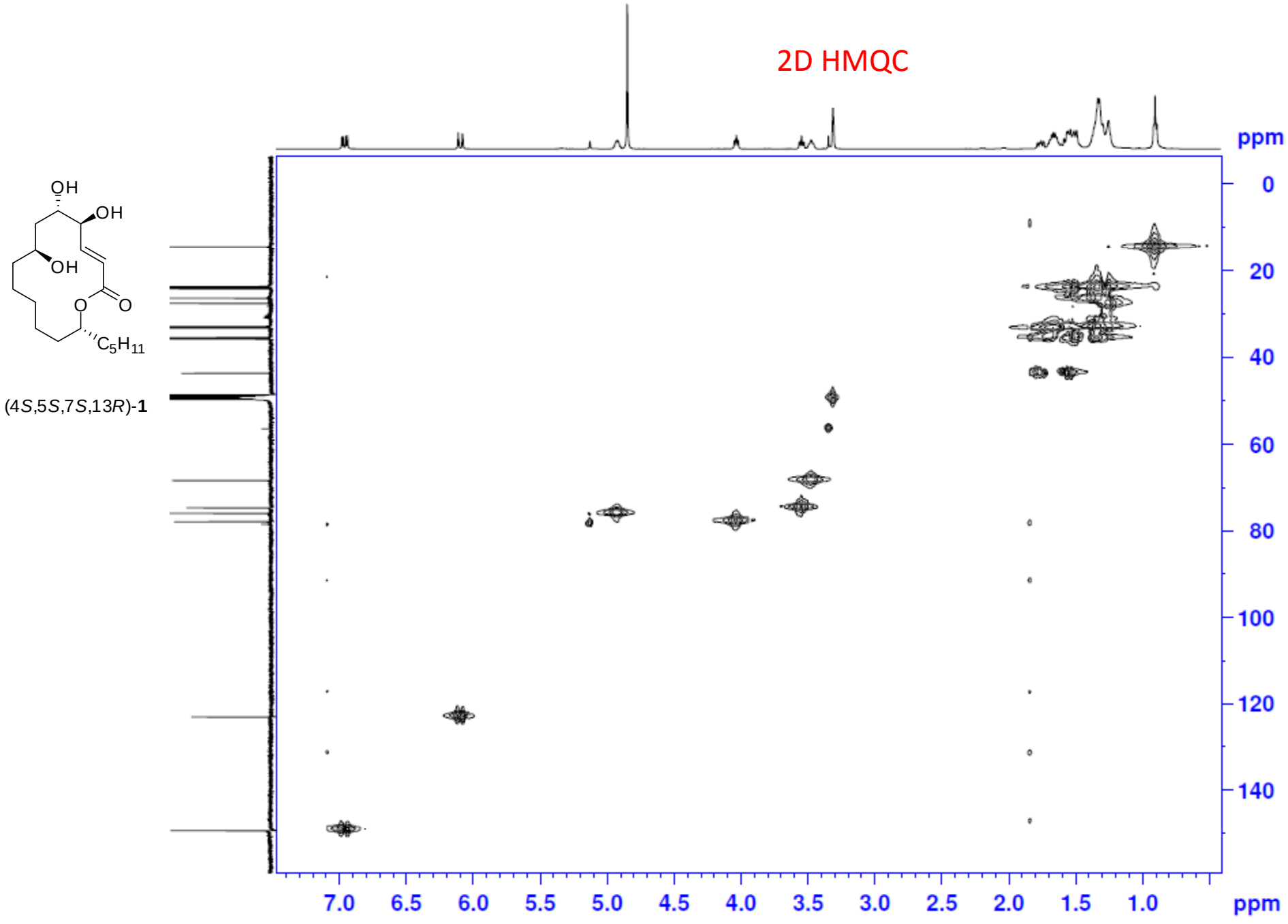
(4*S*,5*S*,7*S*,13*R*)-**1**

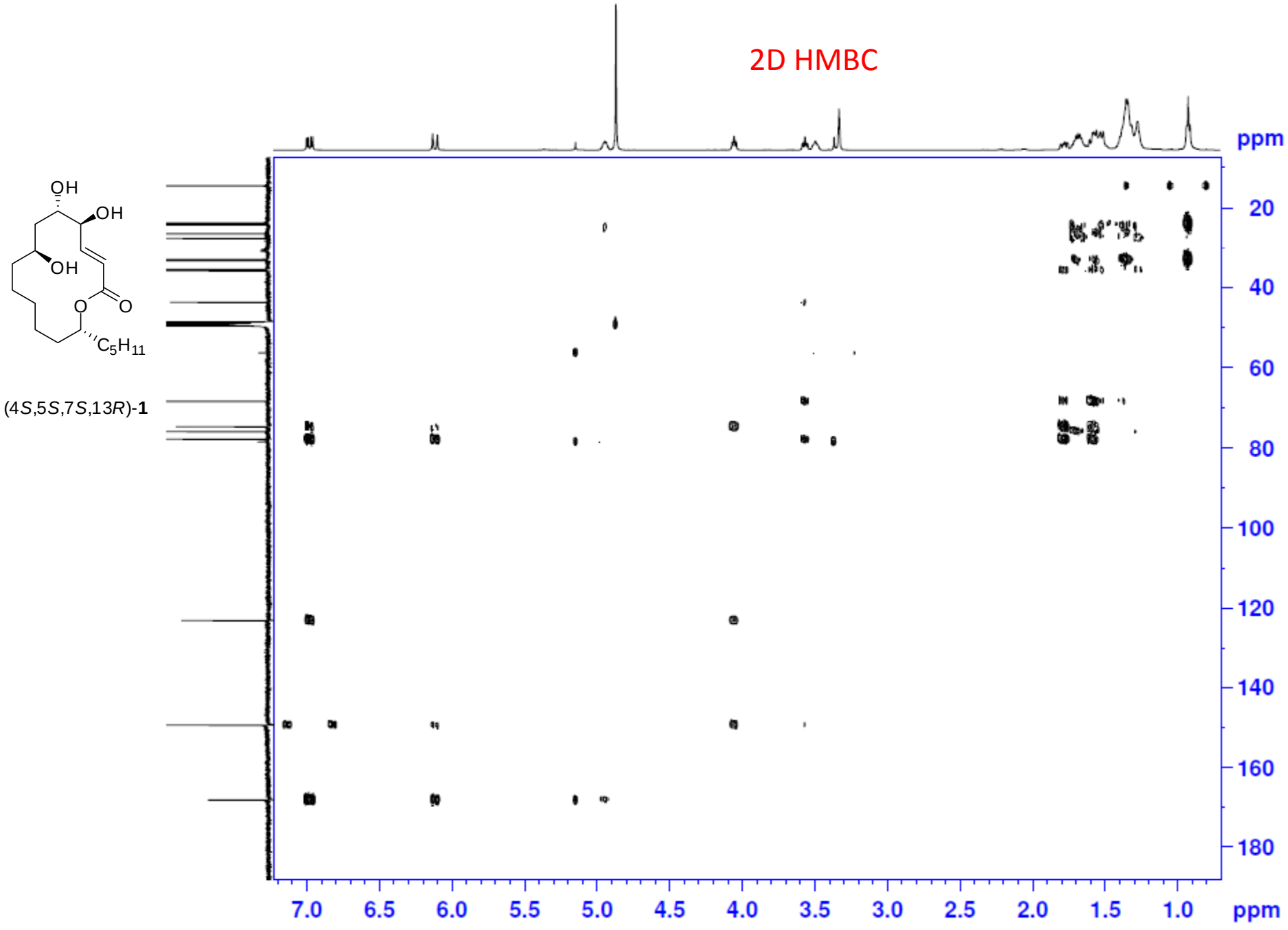
2D COSY

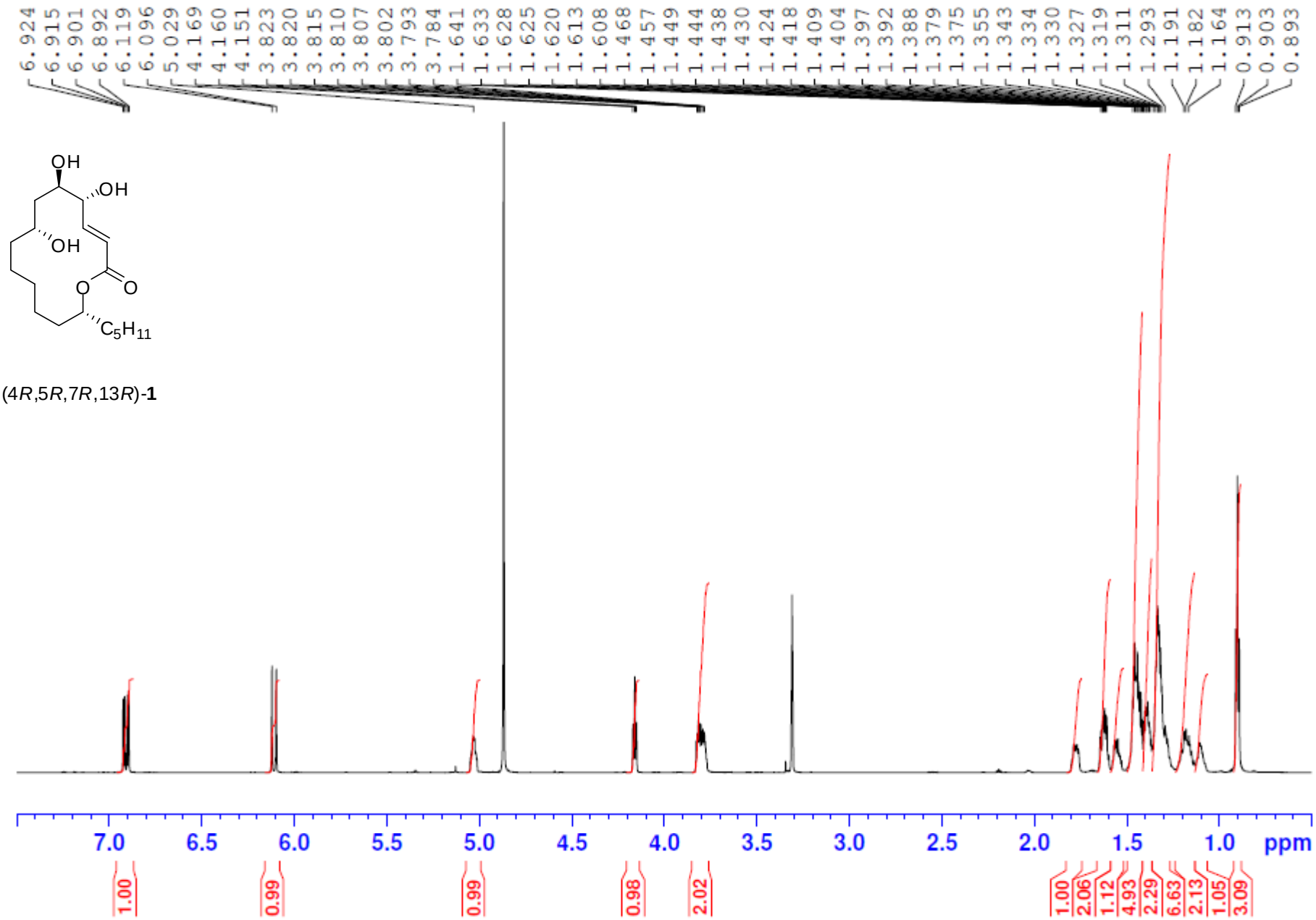


(4*S*,5*S*,7*S*,13*R*)-**1**

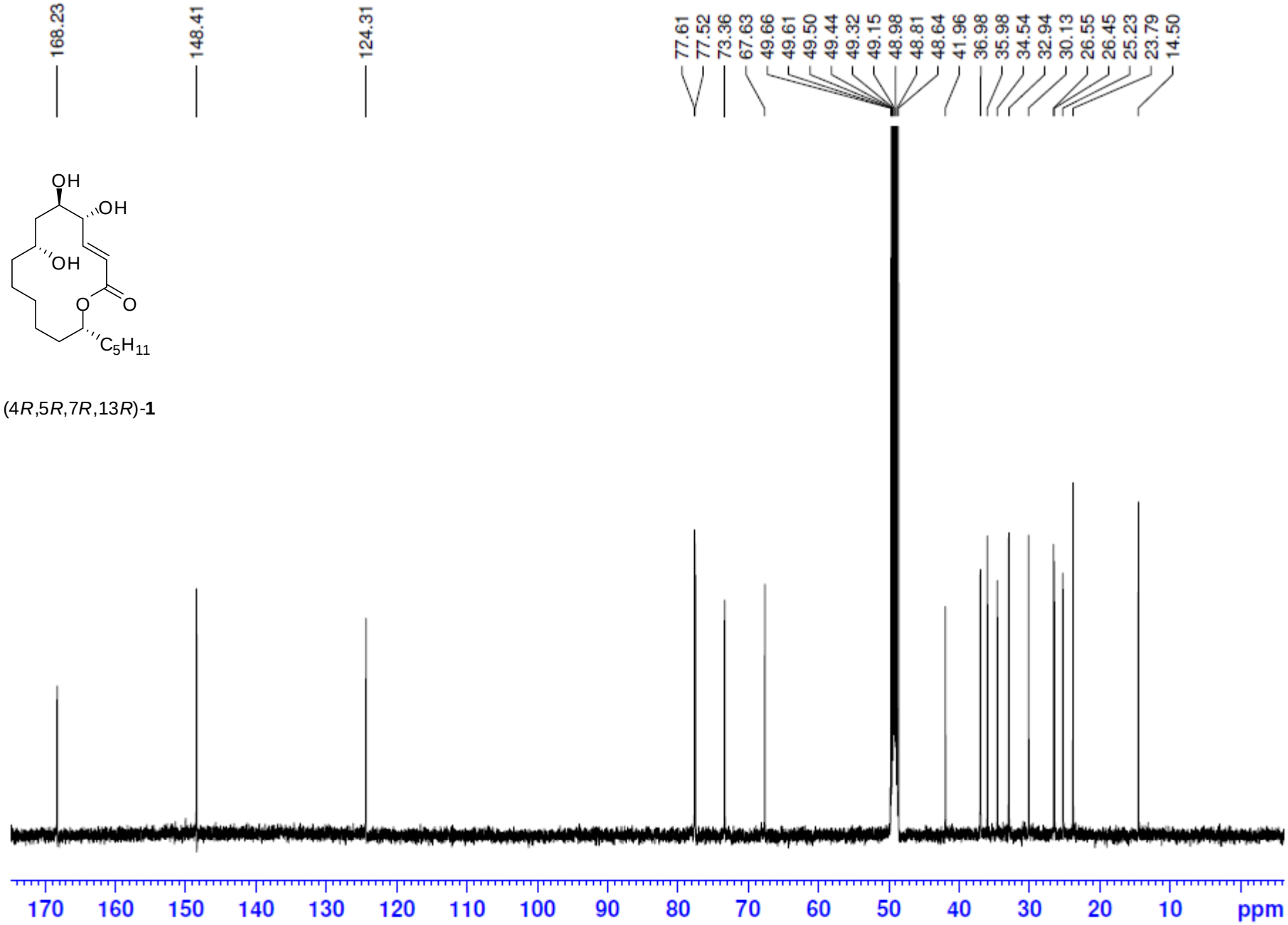



2D HMQC
OH
OH
OH
O
O
C_5H_{11}
(4*S*,5*S*,7*S*,13*R*)-**1**
ppm
0
20
40
60
80
100
120
140
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

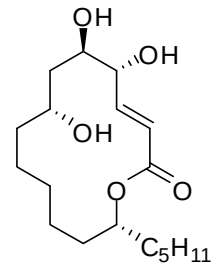

2D HMBC
OH
OH
OH
O
O
C5H11
(4S,5S,7S,13R)-1
ppm
20
40
60
80
100
120
140
160
180
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


6.924
6.915
6.901
6.892
6.119
6.096
5.029
4.169
4.160
4.151
3.823
3.820
3.815
3.810
3.807
3.802
3.793
3.784
1.641
1.633
1.628
1.625
1.620
1.613
1.608
1.468
1.457
1.449
1.444
1.438
1.430
1.424
1.418
1.409
1.404
1.397
1.392
1.388
1.379
1.375
1.355
1.343
1.334
1.330
1.327
1.319
1.311
1.293
1.191
1.182
1.164
0.913
0.903
0.893
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.99
0.99
0.98
2.02
1.00
2.06
1.12
4.93
2.29
6.63
2.13
1.05
3.09

(4*R*,5*R*,7*R*,13*R*)-**1**

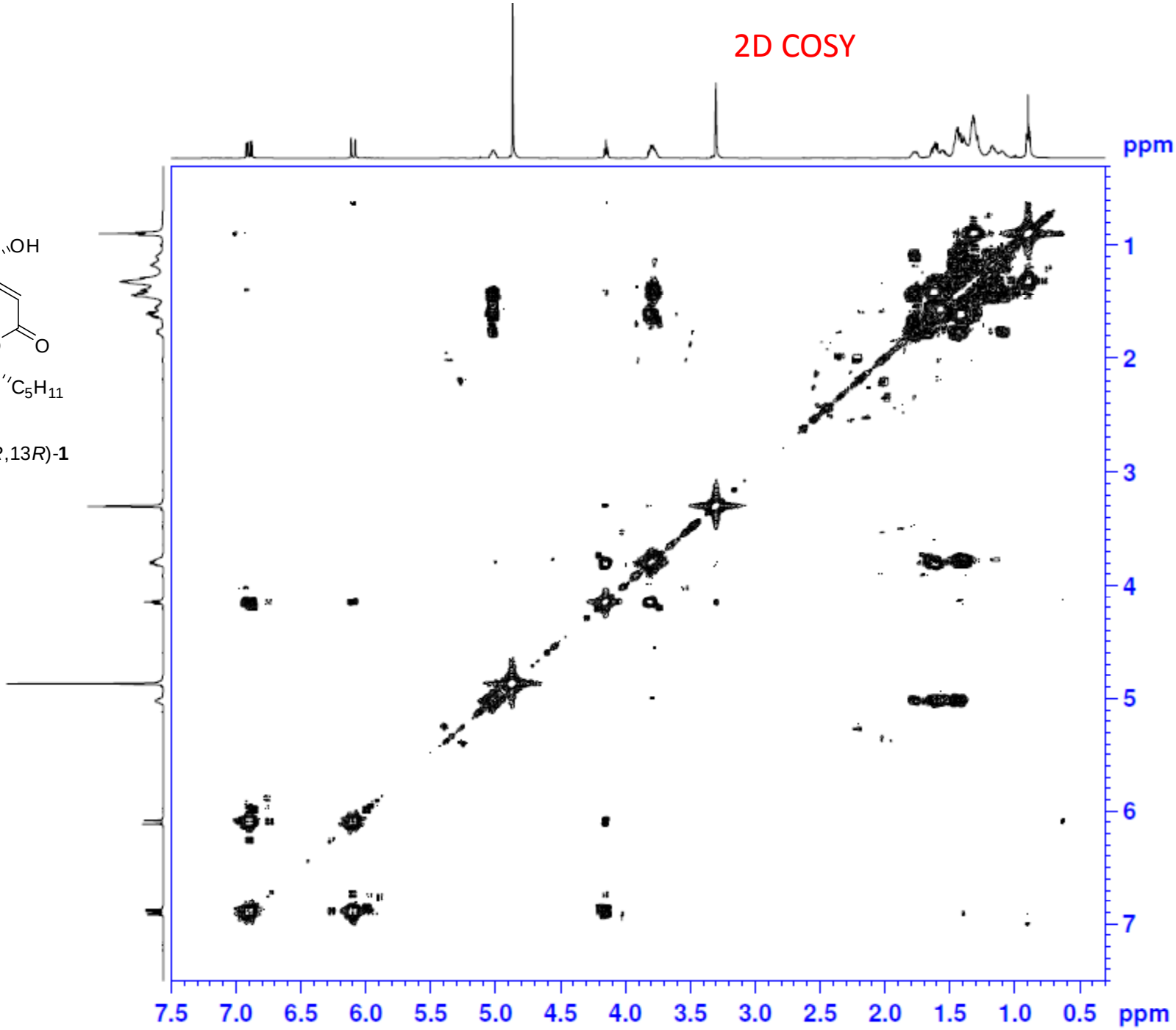

168.23
148.41
124.31
77.61
77.52
73.36
67.63
49.66
49.61
49.50
49.44
49.32
49.15
48.98
48.81
48.64
41.96
36.98
35.98
34.54
32.94
30.13
26.55
26.45
25.23
23.79
14.50
OH
OH
OH
O
O
C5H11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

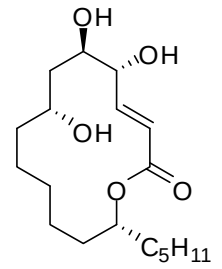
(4*R*,5*R*,7*R*,13*R*)-**1**



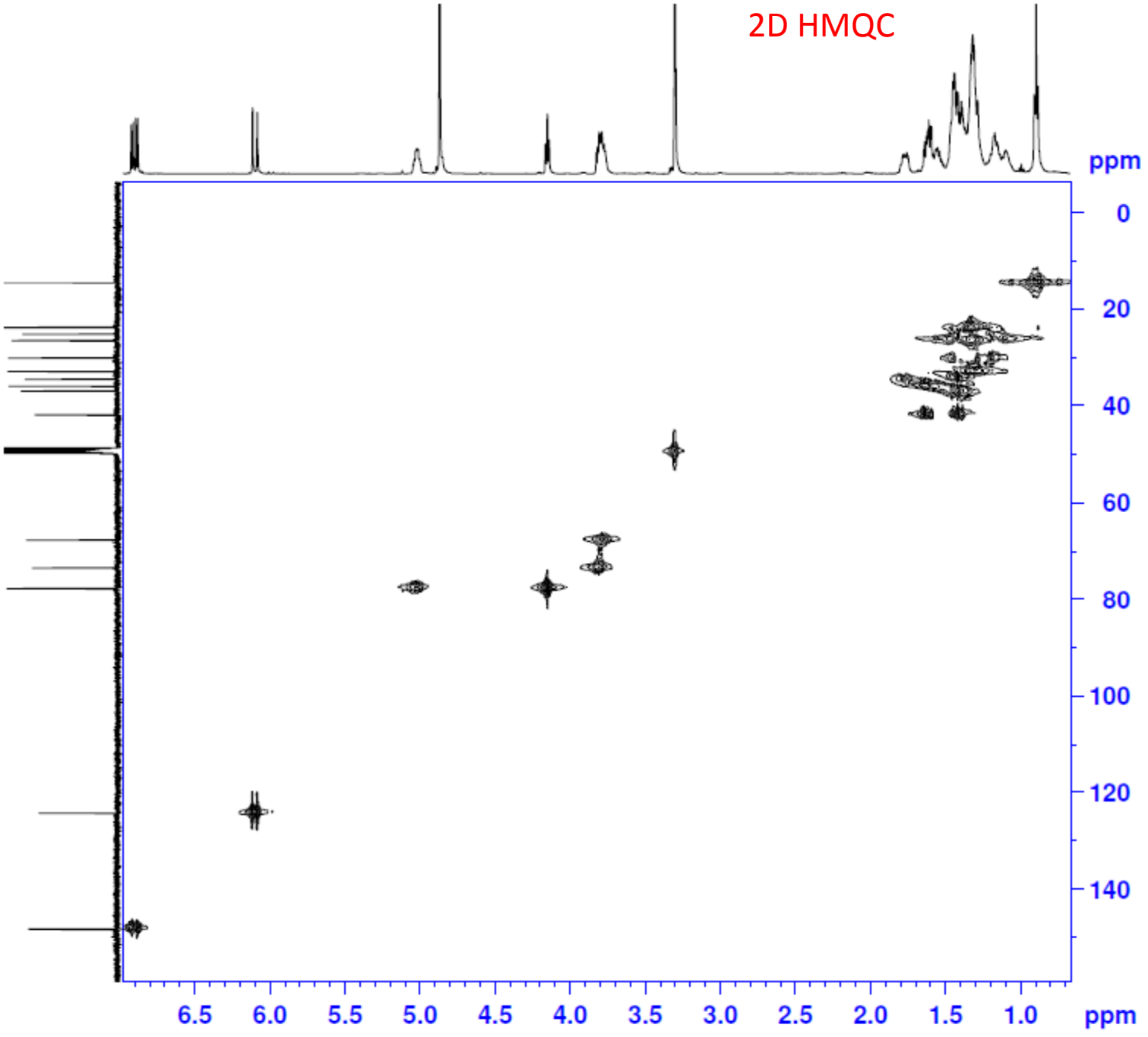
(4*R*,5*R*,7*R*,13*R*)-**1**

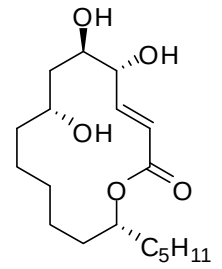
2D COSY



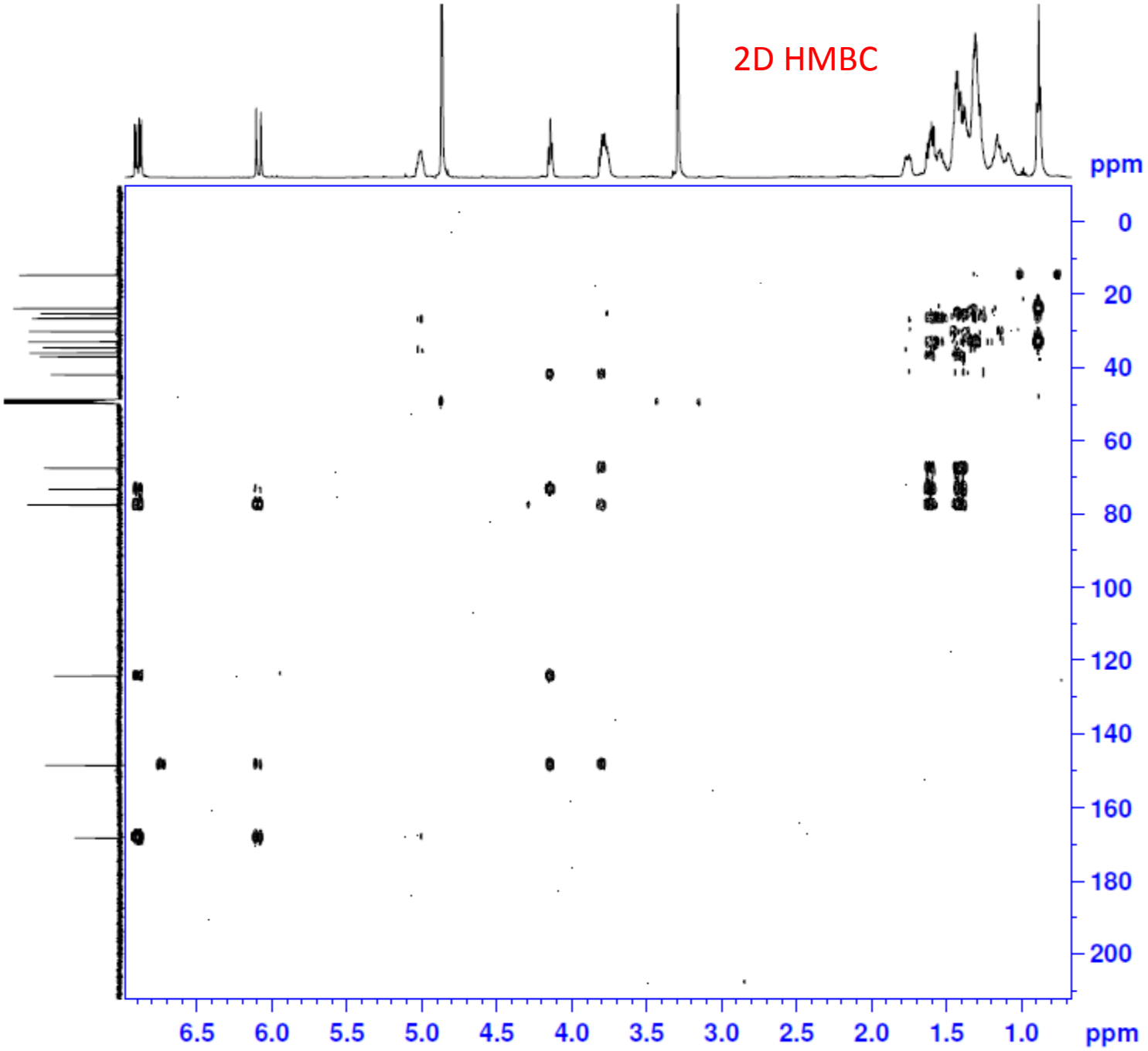

OH
OH
OH
O
O
C5H11

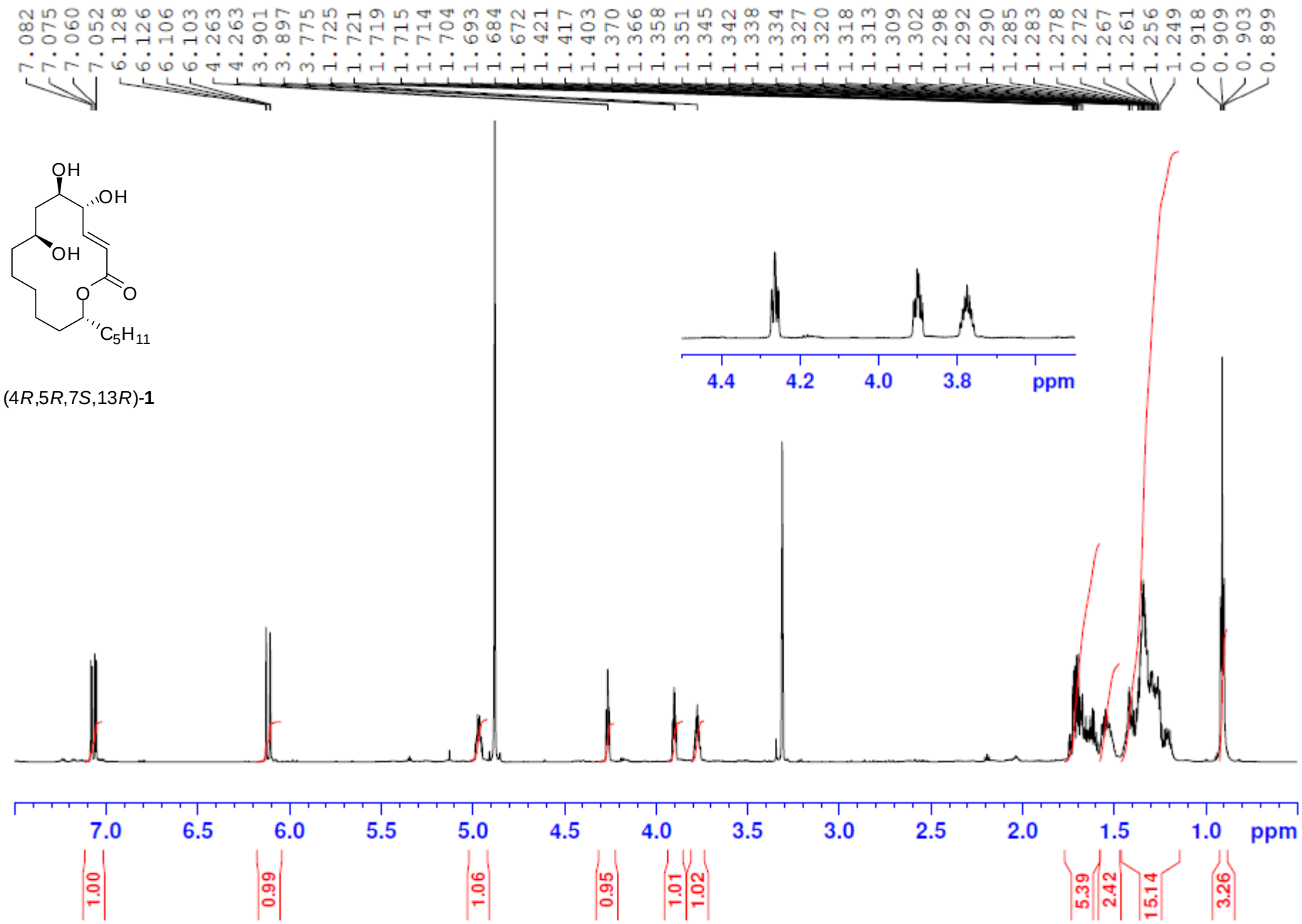
(4*R*,5*R*,7*R*,13*R*)-**1**


2D HMQC
ppm
0
20
40
60
80
100
120
140
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

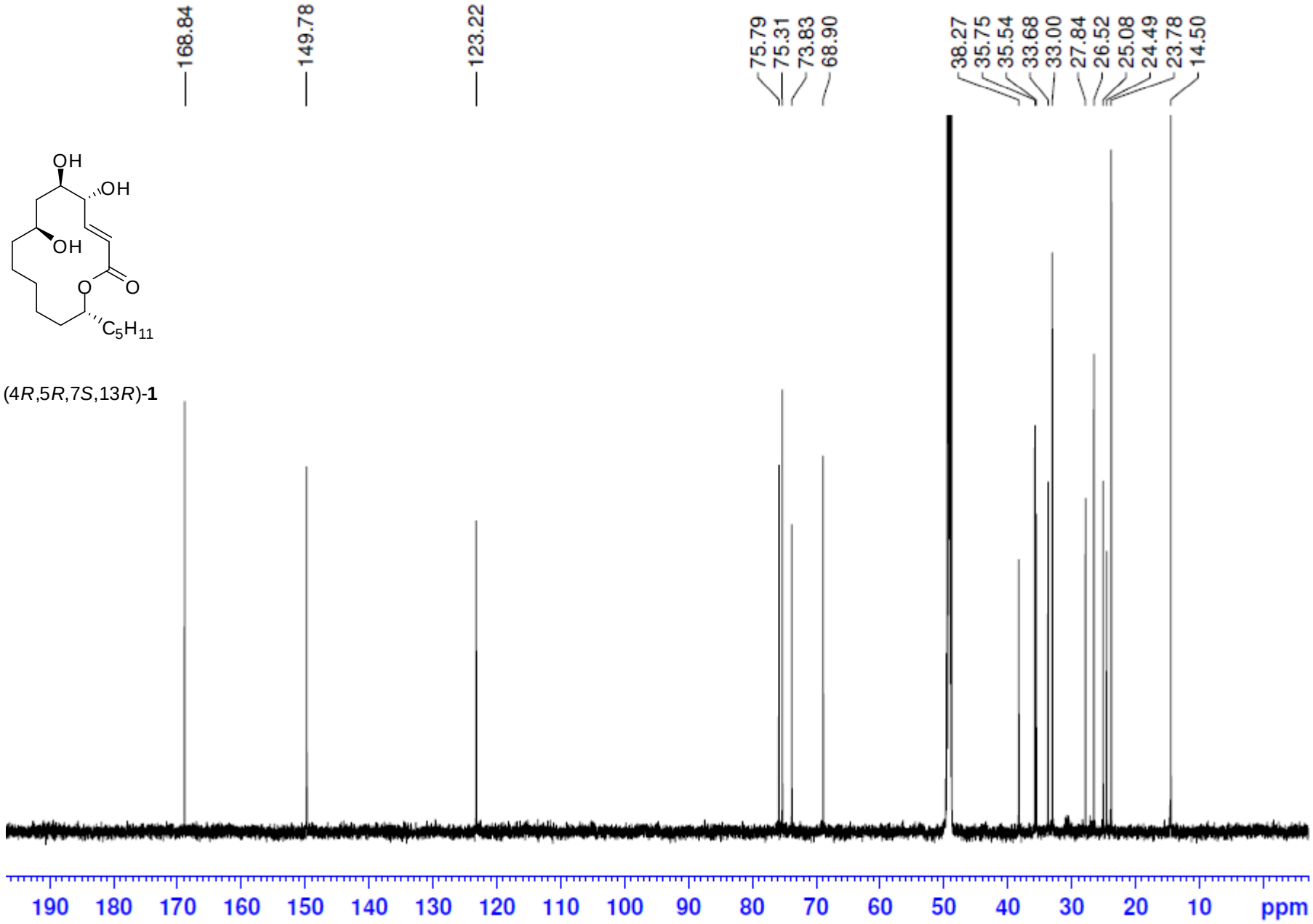

OH
OH
OH
O
O
C_5H_{11}

(4*R*,5*R*,7*R*,13*R*)-**1**

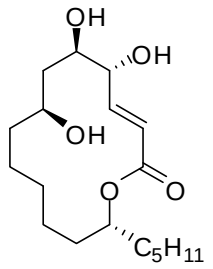

2D HMBC
ppm
0
20
40
60
80
100
120
140
160
180
200
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


7.082
7.075
7.060
7.052
6.128
6.126
6.106
6.103
4.263
4.263
3.901
3.897
3.775
1.725
1.721
1.719
1.715
1.714
1.704
1.693
1.684
1.672
1.421
1.417
1.403
1.370
1.366
1.358
1.351
1.345
1.342
1.338
1.334
1.327
1.320
1.318
1.313
1.309
1.302
1.298
1.292
1.290
1.285
1.283
1.278
1.272
1.267
1.261
1.256
1.249
0.918
0.909
0.903
0.899
OH
OH
OH
O
O
C5H11
4.4
4.2
4.0
3.8
ppm
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
ppm
1.00
0.99
1.06
0.95
1.01
1.02
5.39
2.42
15.14
3.26

(4*R*,5*R*,7*S*,13*R*)-**1**

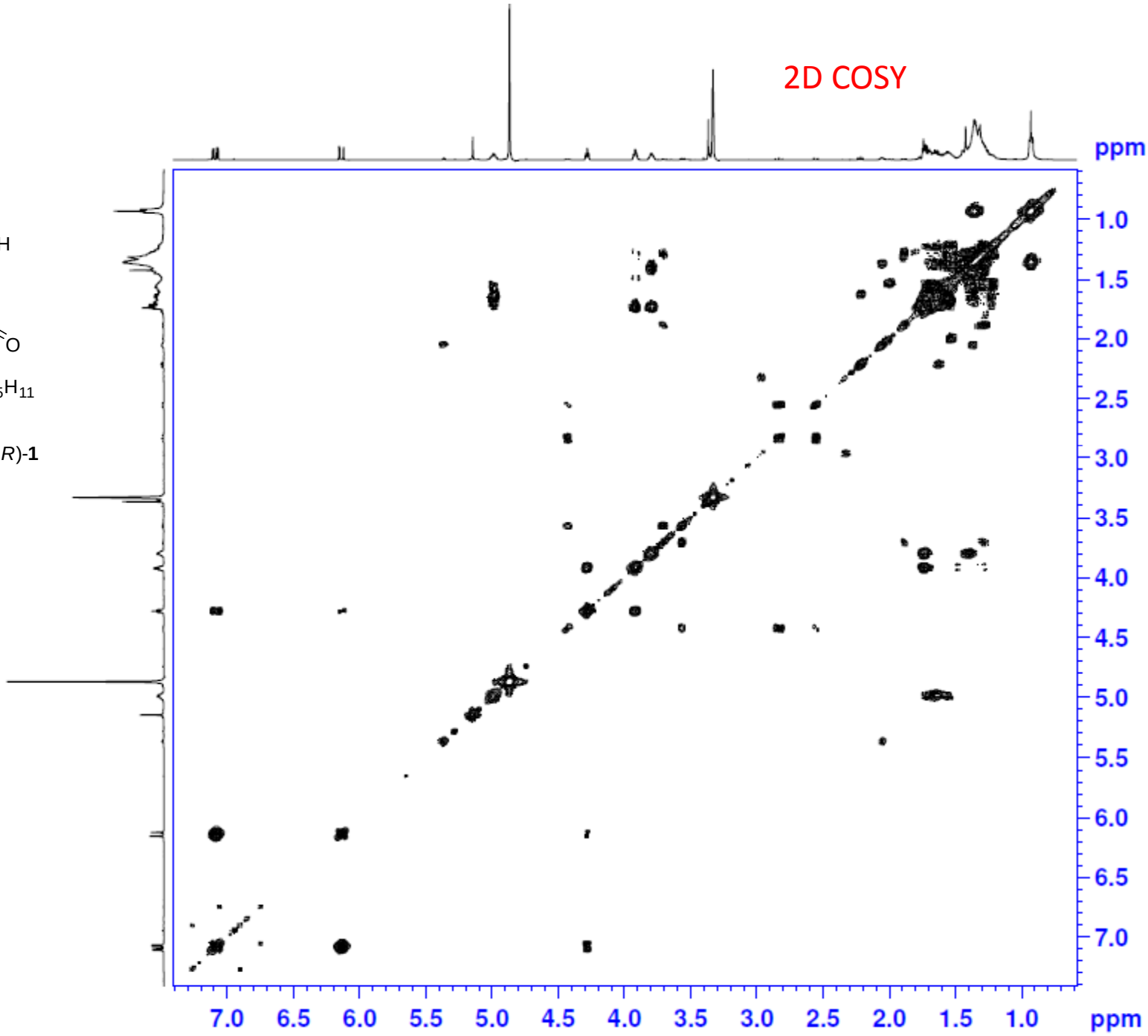

168.84
149.78
123.22
75.79
75.31
73.83
68.90
38.27
35.75
35.54
33.68
33.00
27.84
26.52
25.08
24.49
23.78
14.50
OH
OH
OH
O
O
C5H11
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(4*R*,5*R*,7*S*,13*R*)-**1**

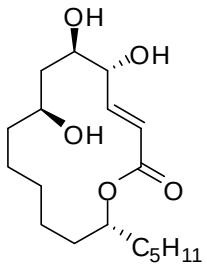


(4*R*,5*R*,7*S*,13*R*)-**1**

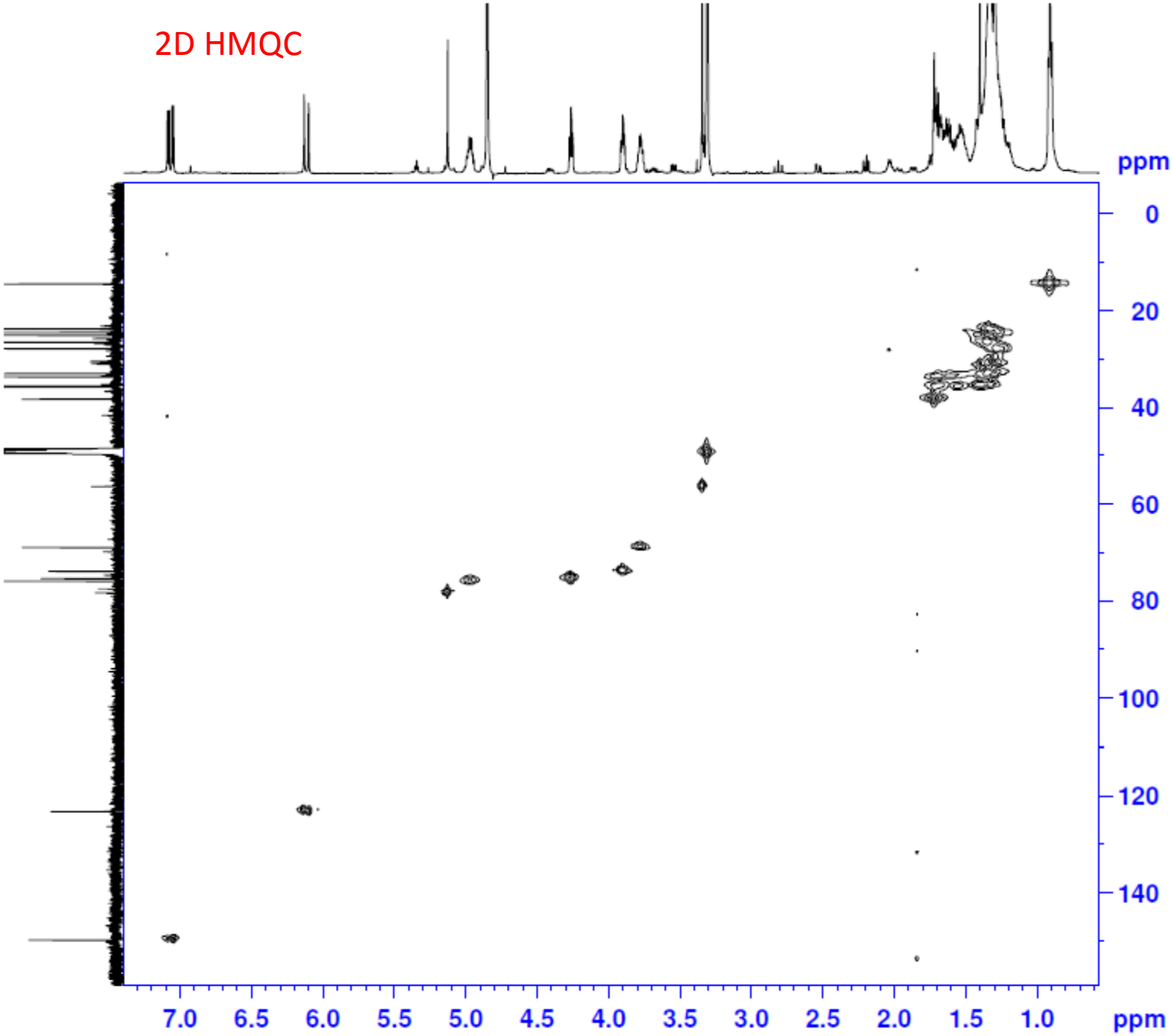
2D COSY



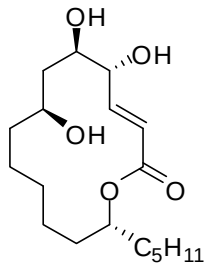
2D HMQC



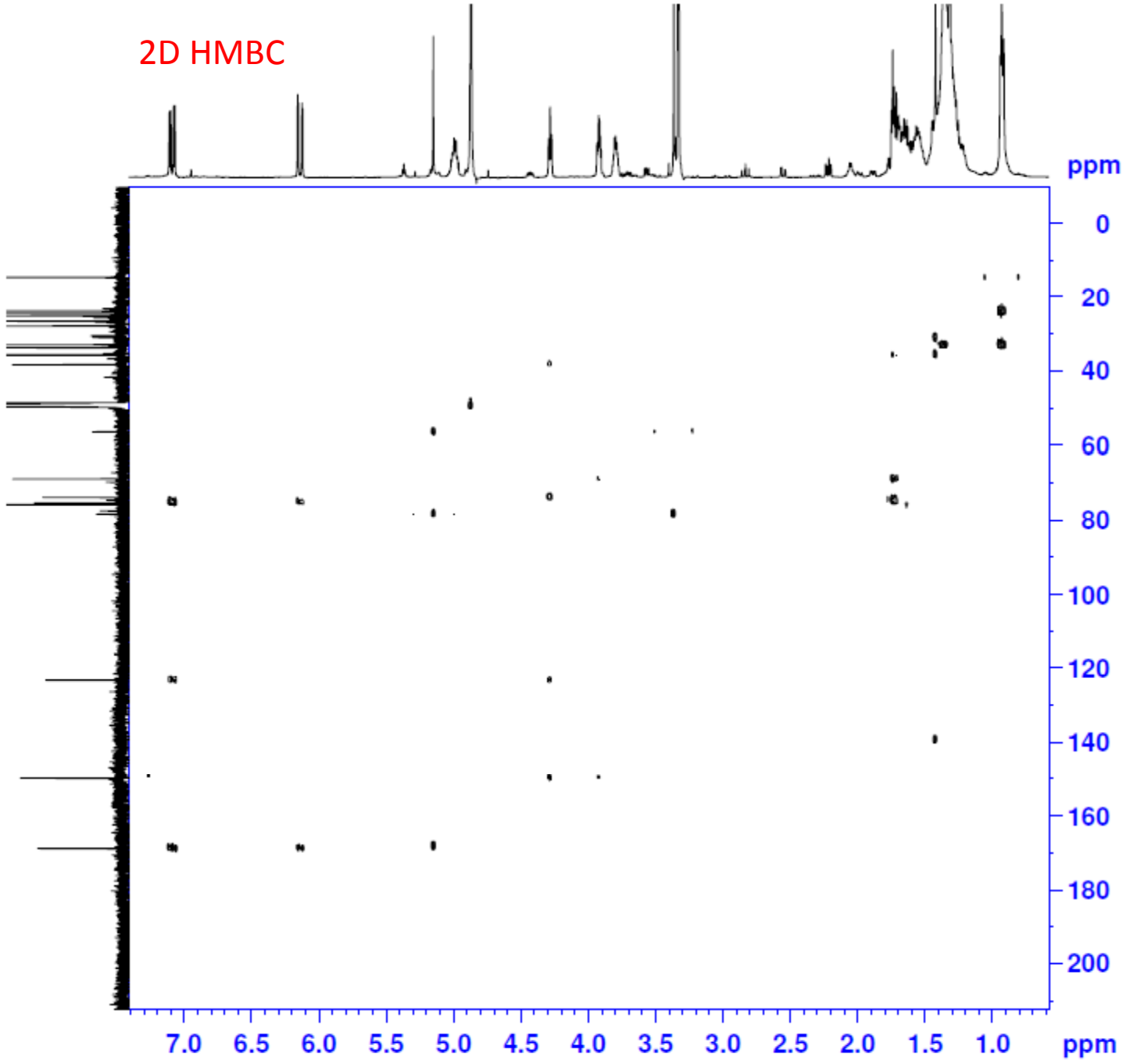
(4*R*,5*R*,7*S*,13*R*)-**1**

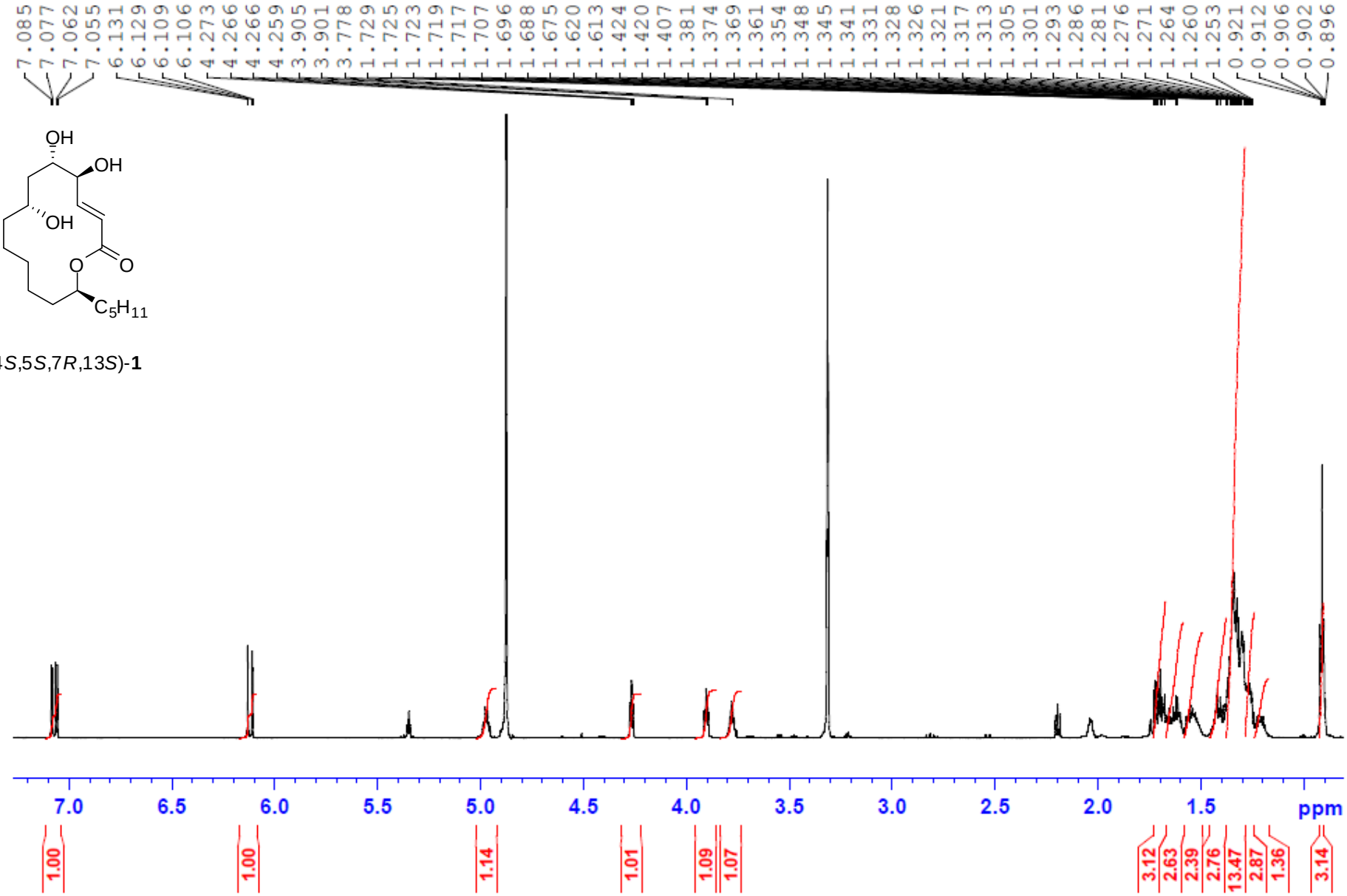


2D HMBC

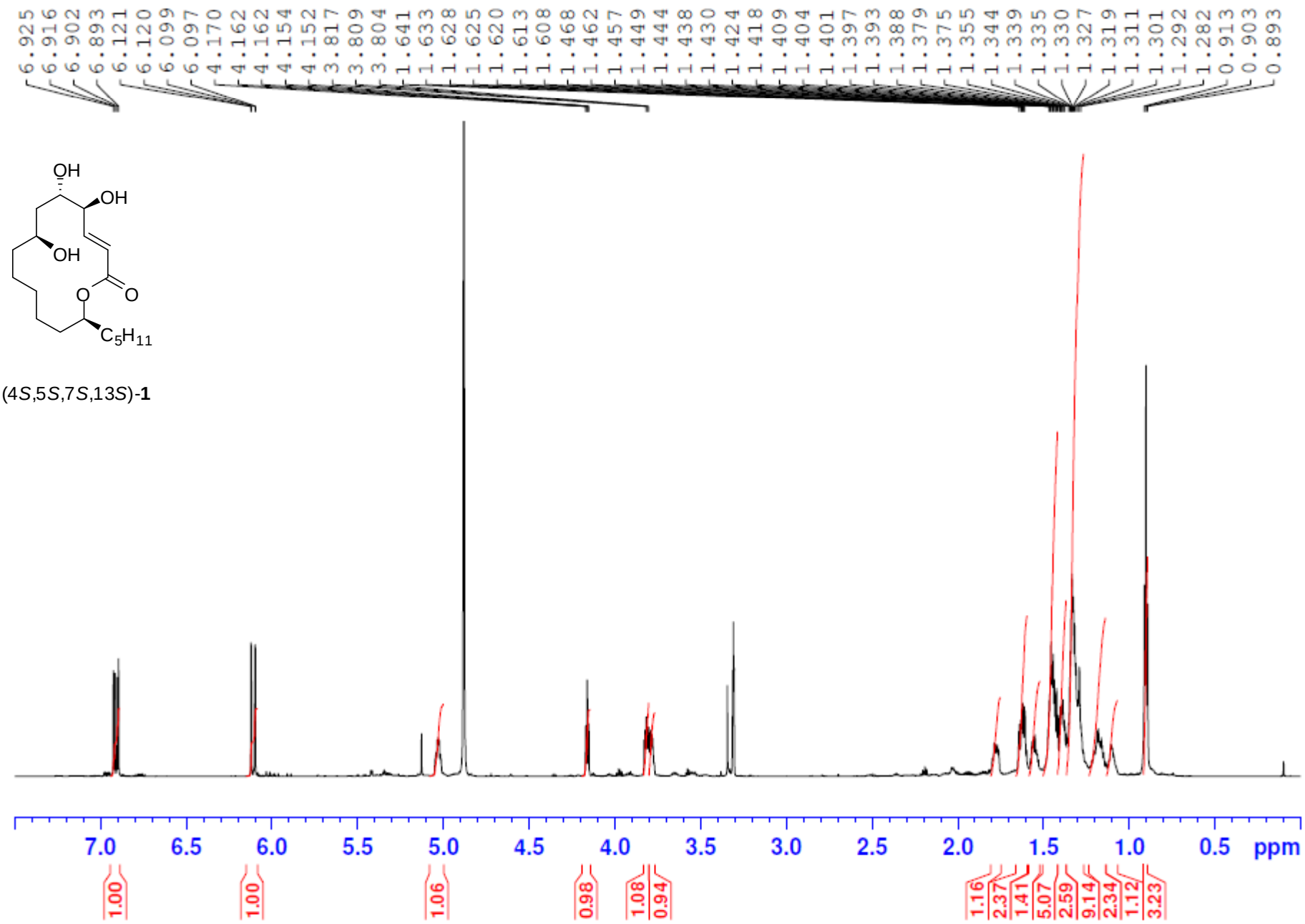


(4*R*,5*R*,7*S*,13*R*)-**1**

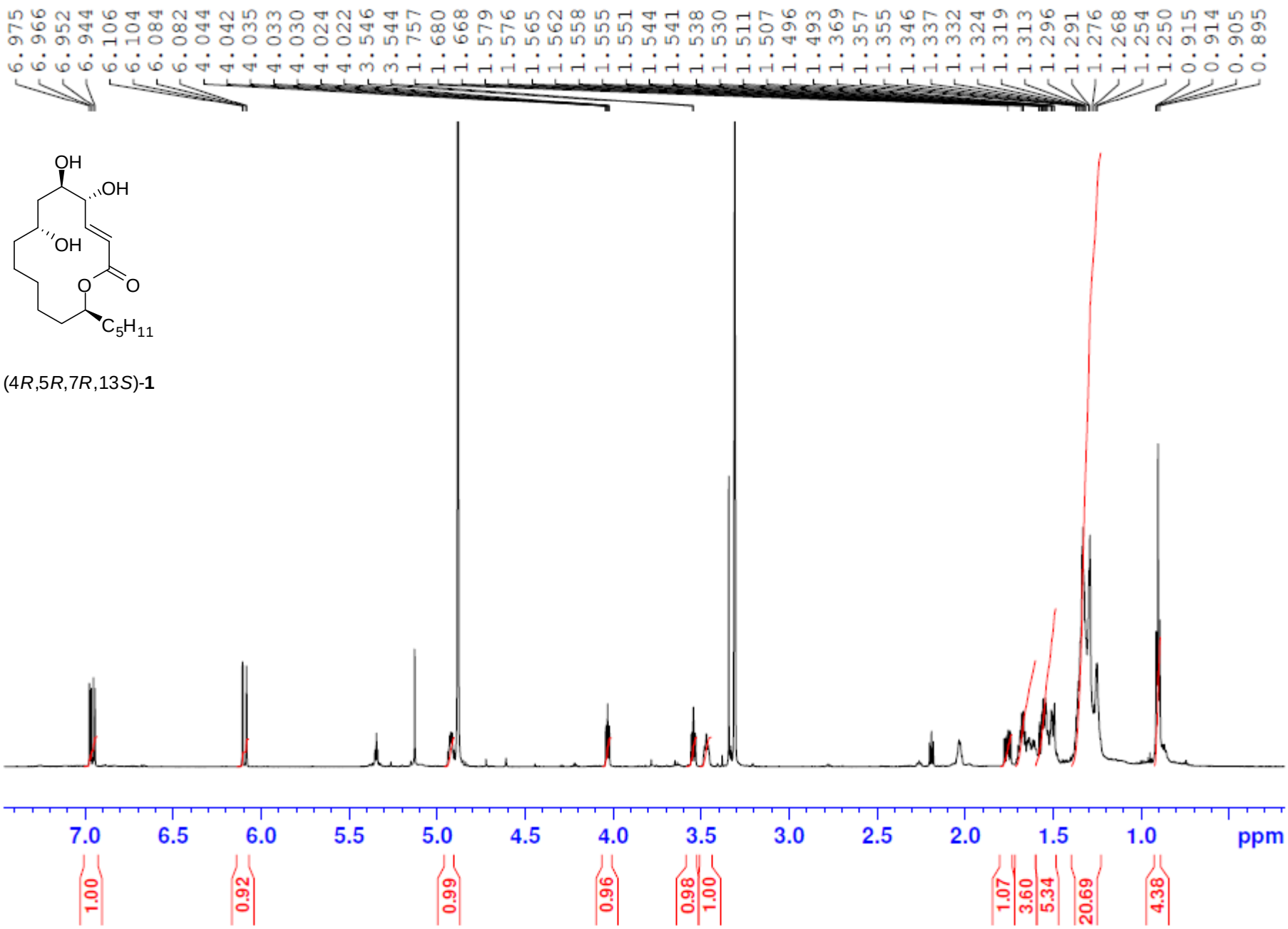



7.085
7.077
7.062
7.055
6.131
6.129
6.109
6.106
4.273
4.266
4.266
4.259
3.905
3.901
3.778
1.729
1.725
1.723
1.719
1.717
1.707
1.696
1.688
1.675
1.620
1.613
1.424
1.420
1.407
1.381
1.374
1.369
1.361
1.354
1.348
1.345
1.341
1.331
1.328
1.326
1.321
1.317
1.313
1.305
1.301
1.293
1.286
1.281
1.276
1.271
1.264
1.260
1.253
0.921
0.912
0.906
0.902
0.896
OH
OH
OH
O
O
C5H11
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.00
1.14
1.01
1.09
1.07
3.12
2.63
2.39
2.76
13.47
2.87
1.36
3.14

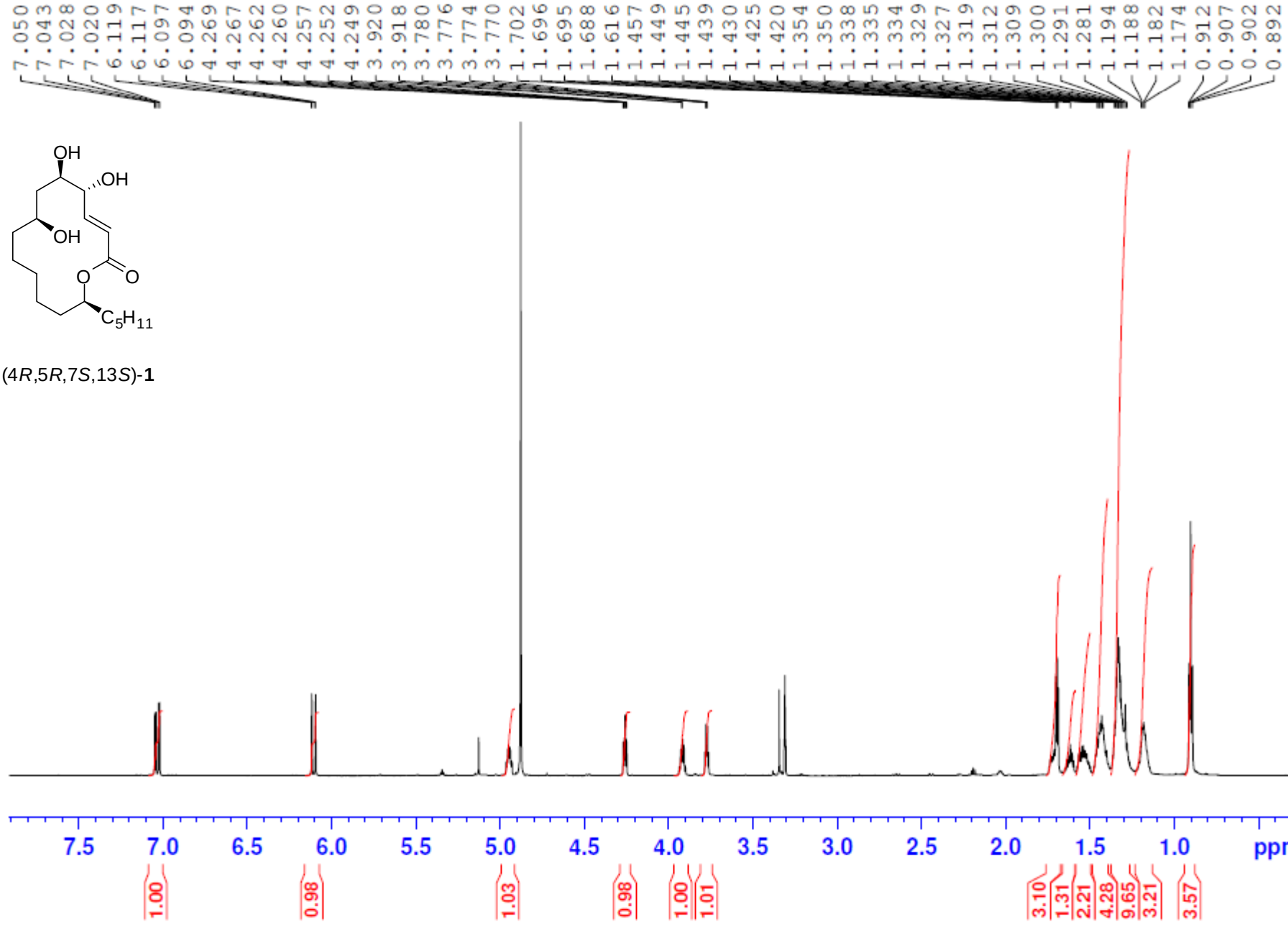
(4*S*,5*S*,7*R*,13*S*)-**1**


6.925
6.916
6.902
6.893
6.121
6.120
6.099
6.097
4.170
4.162
4.162
4.154
4.152
3.817
3.809
3.804
1.641
1.633
1.628
1.625
1.620
1.613
1.608
1.468
1.462
1.457
1.449
1.444
1.438
1.430
1.424
1.418
1.409
1.404
1.401
1.397
1.393
1.388
1.379
1.375
1.355
1.344
1.339
1.335
1.330
1.327
1.319
1.311
1.301
1.292
1.282
0.913
0.903
0.893
OH
OH
OH
O
O
C5H11
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
ppm
1.00
1.00
1.06
0.98
1.08
0.94
1.16
2.37
1.41
5.07
2.59
9.14
2.34
1.12
3.23

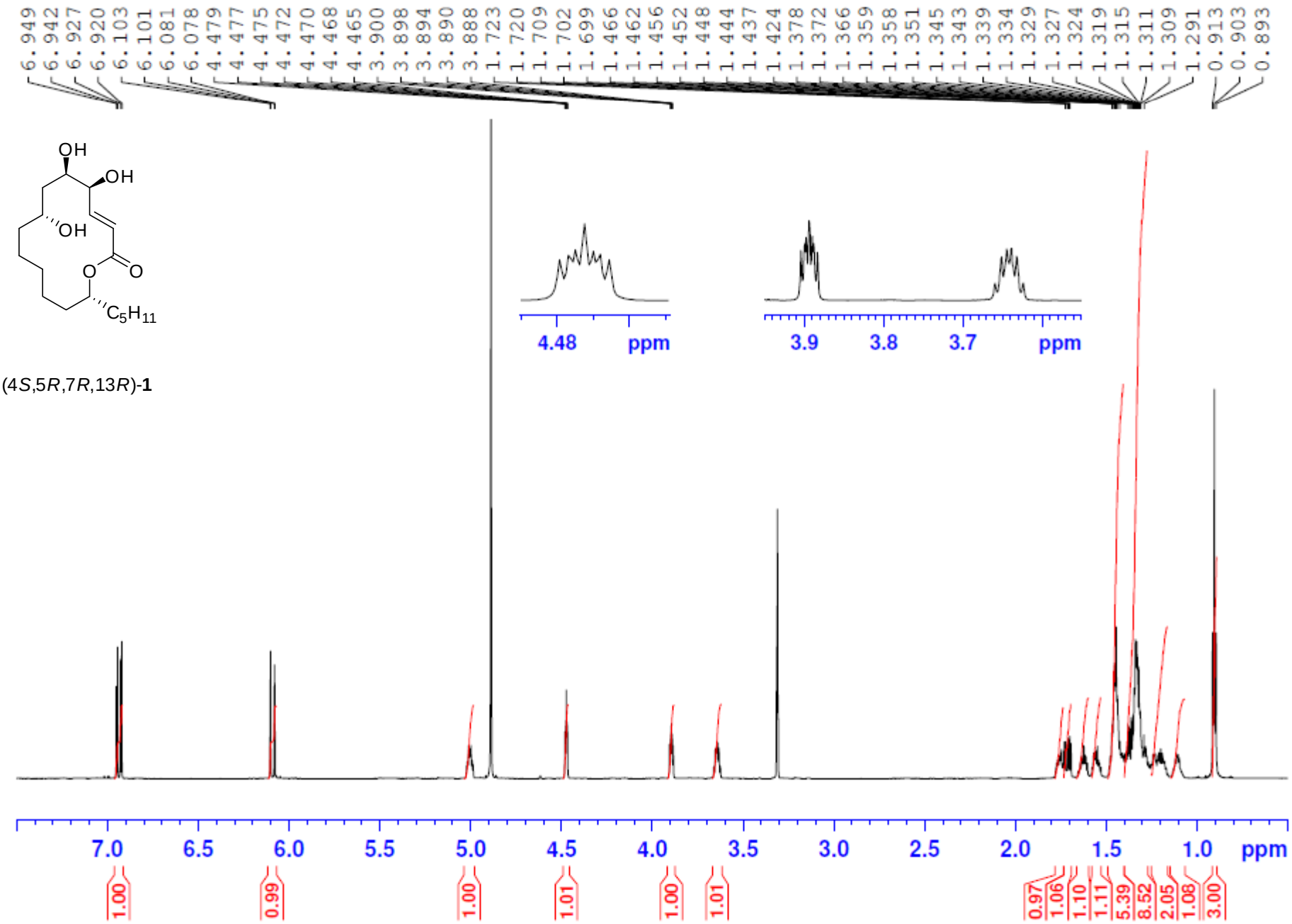
(4*S*,5*S*,7*S*,13*S*)-**1**


6.975
6.966
6.952
6.944
6.106
6.104
6.084
6.082
4.044
4.042
4.035
4.033
4.030
4.024
4.022
3.546
3.544
1.757
1.680
1.668
1.579
1.576
1.565
1.562
1.558
1.555
1.551
1.544
1.541
1.538
1.530
1.511
1.507
1.496
1.493
1.369
1.357
1.355
1.346
1.337
1.332
1.324
1.319
1.313
1.296
1.291
1.276
1.268
1.254
1.250
0.915
0.914
0.905
0.895
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.92
0.99
0.96
0.98
1.00
1.07
3.60
5.34
20.69
4.38

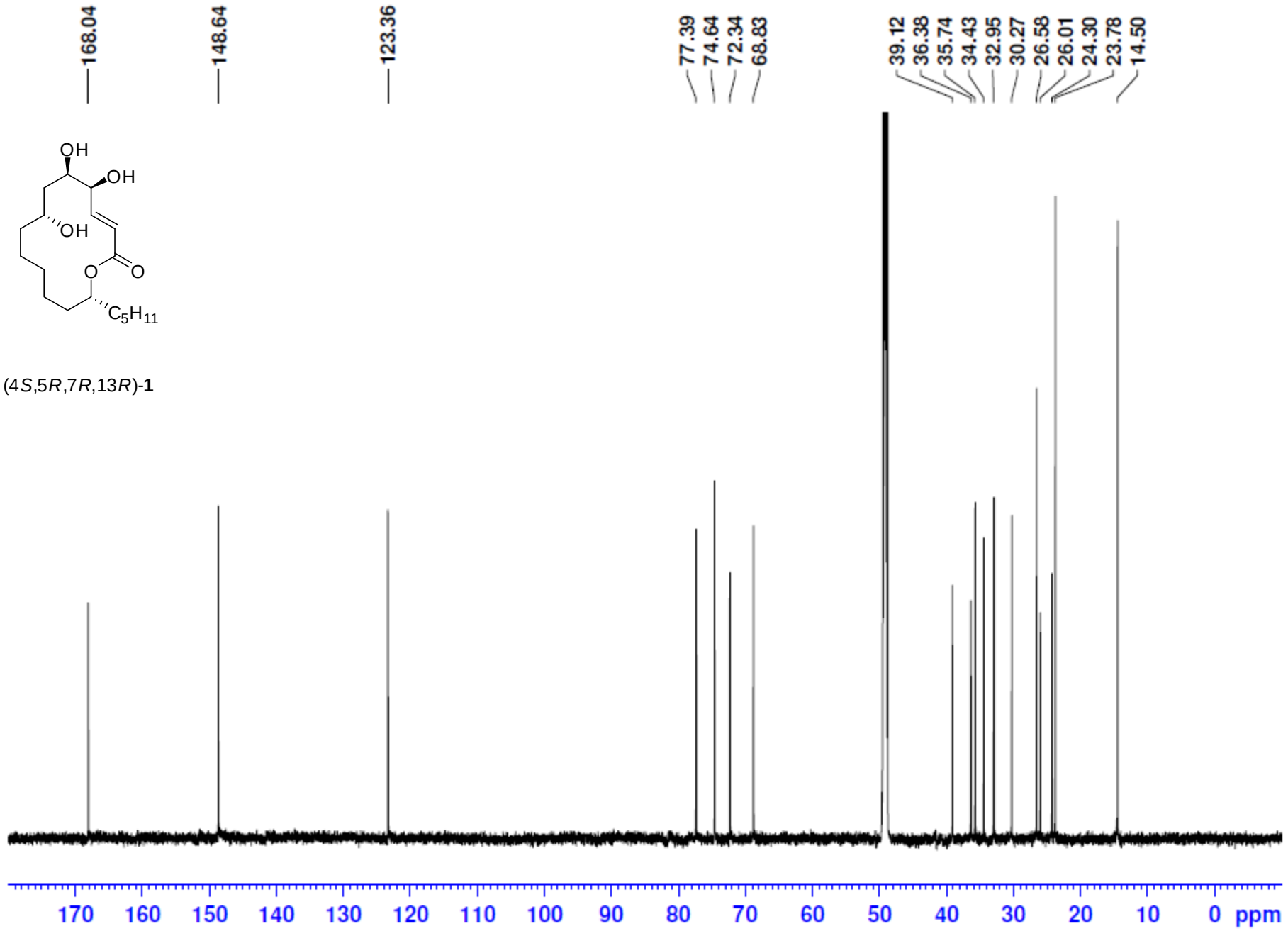
(4*R*,5*R*,7*R*,13*S*)-**1**


7.050
7.043
7.028
7.020
6.119
6.117
6.097
6.094
4.269
4.267
4.262
4.260
4.257
4.252
4.249
3.920
3.918
3.780
3.776
3.774
3.770
1.702
1.696
1.695
1.688
1.616
1.457
1.449
1.445
1.439
1.430
1.425
1.420
1.354
1.350
1.338
1.335
1.334
1.329
1.327
1.319
1.312
1.309
1.300
1.291
1.281
1.194
1.188
1.182
1.174
0.912
0.907
0.902
0.892
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.98
1.03
0.98
1.00
1.01
3.10
1.31
2.21
4.28
9.65
3.21
3.57

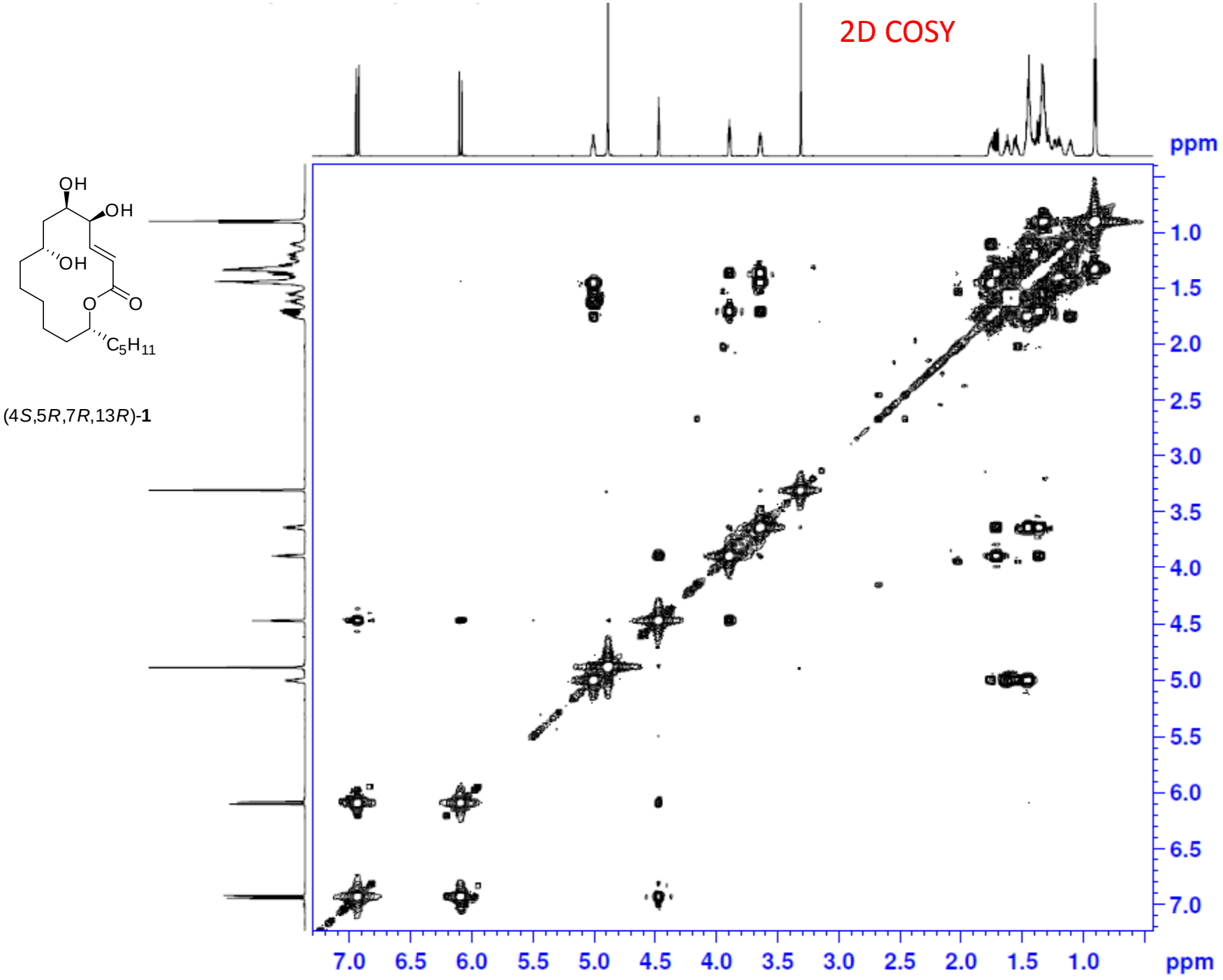
(4*R*,5*R*,7*S*,13*S*)-**1**

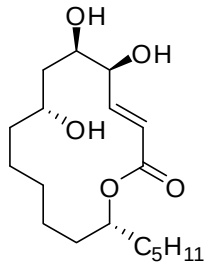

6.949
6.942
6.927
6.920
6.103
6.101
6.081
6.078
4.479
4.477
4.475
4.472
4.470
4.468
4.465
3.900
3.898
3.894
3.890
3.888
1.723
1.720
1.709
1.702
1.699
1.466
1.462
1.456
1.452
1.448
1.444
1.437
1.424
1.378
1.372
1.366
1.359
1.358
1.351
1.345
1.343
1.339
1.334
1.329
1.327
1.324
1.319
1.315
1.311
1.309
1.291
0.913
0.903
0.893
OH
OH
OH
O
O
C5H11
4.48
ppm
3.9
3.8
3.7
ppm
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
ppm
1.00
0.99
1.00
1.01
1.00
1.01
0.97
1.06
1.10
1.11
5.39
8.52
2.05
1.08
3.00

(4*S*,5*R*,7*R*,13*R*)-**1**

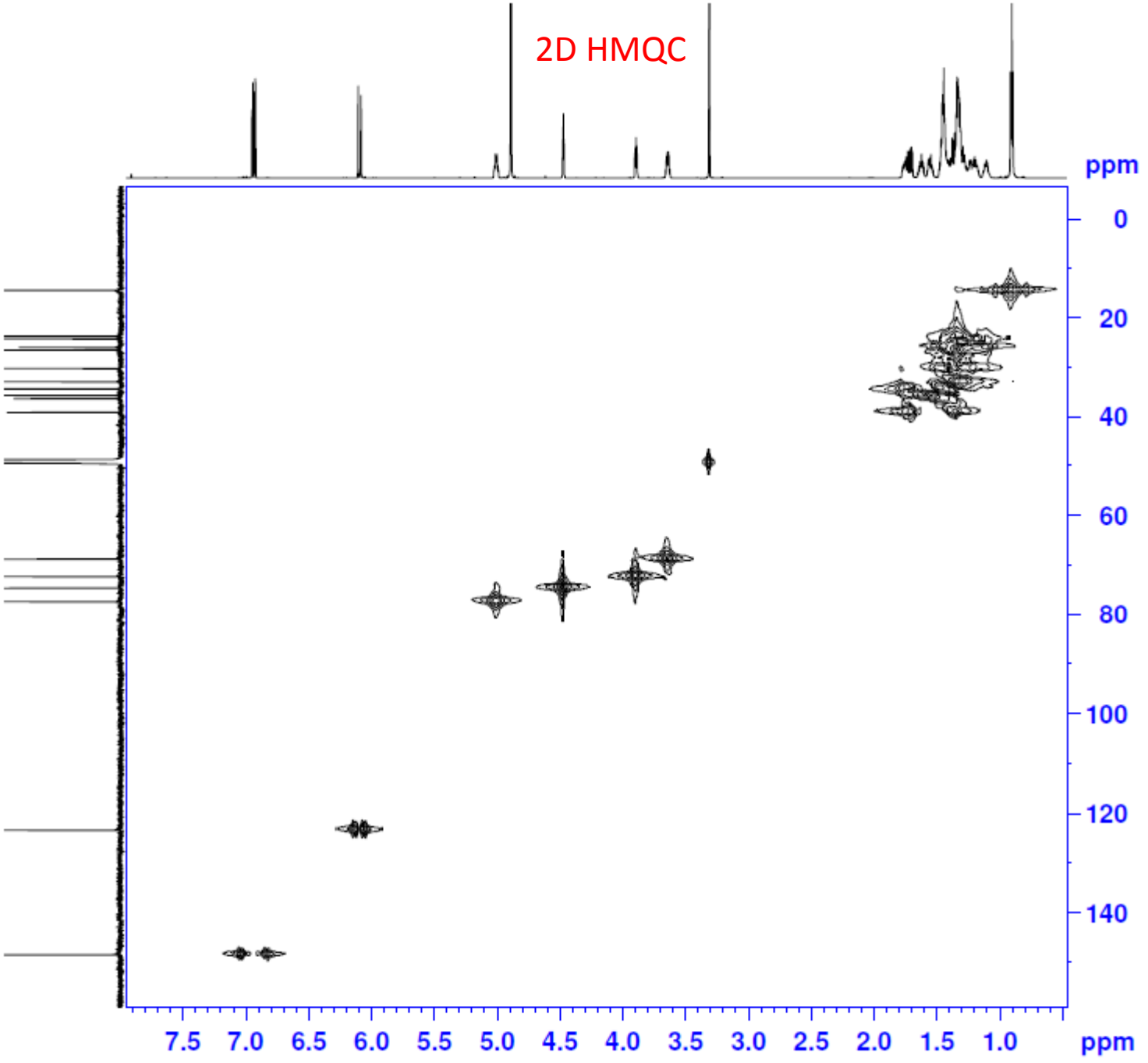

168.04
148.64
123.36
77.39
74.64
72.34
68.83
39.12
36.38
35.74
34.43
32.95
30.27
26.58
26.01
24.30
23.78
14.50
OH
OH
OH
O
O
C5H11
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

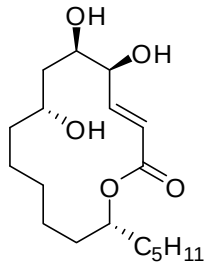
(4*S*,5*R*,7*R*,13*R*)-**1**


2D COSY
OH
OH
OH
O
O
C_5H_{11}
(4*S*,5*R*,7*R*,13*R*)-**1**
ppm
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
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 ppm

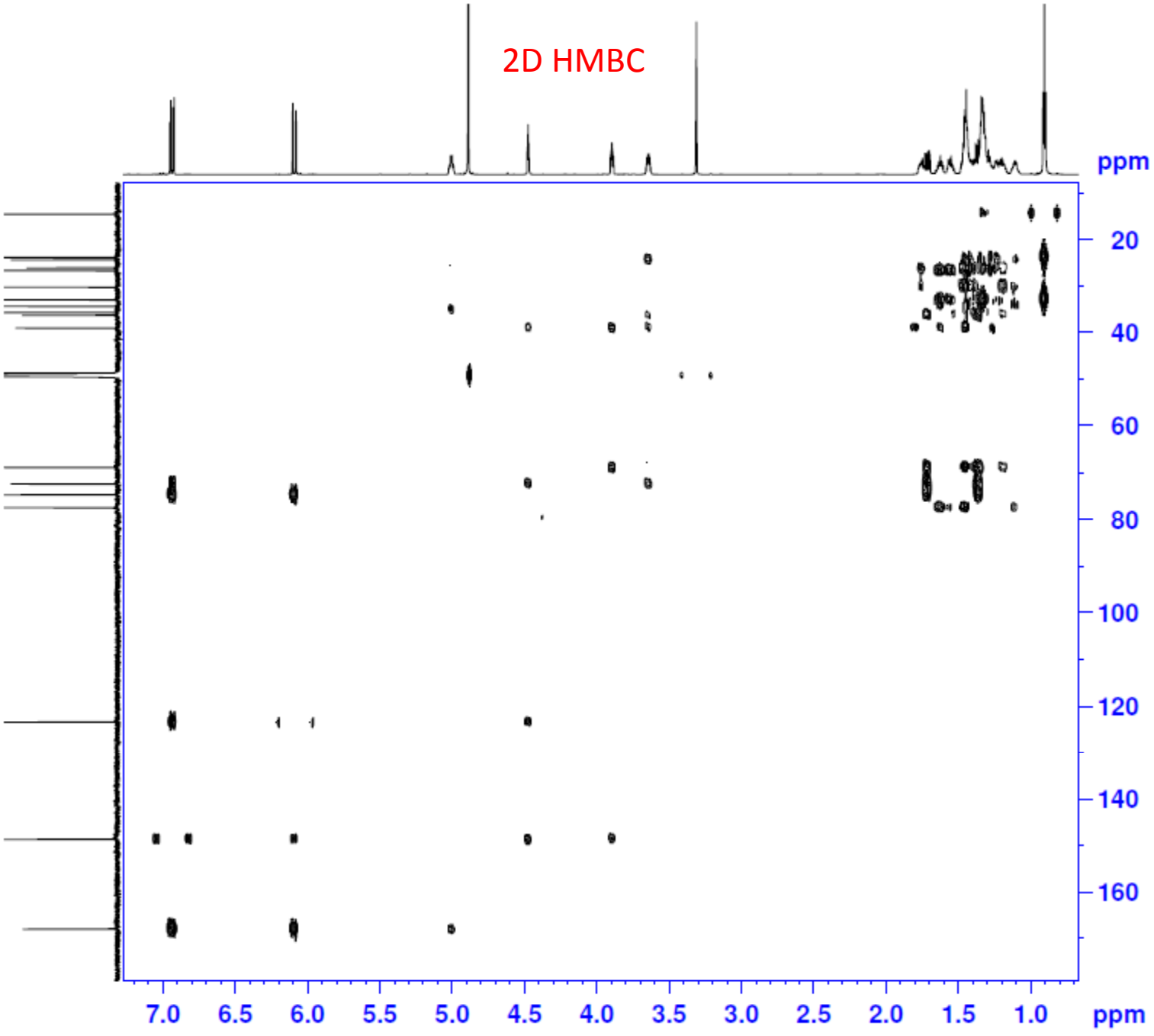

OH
OH
OH
O
O
C5H11

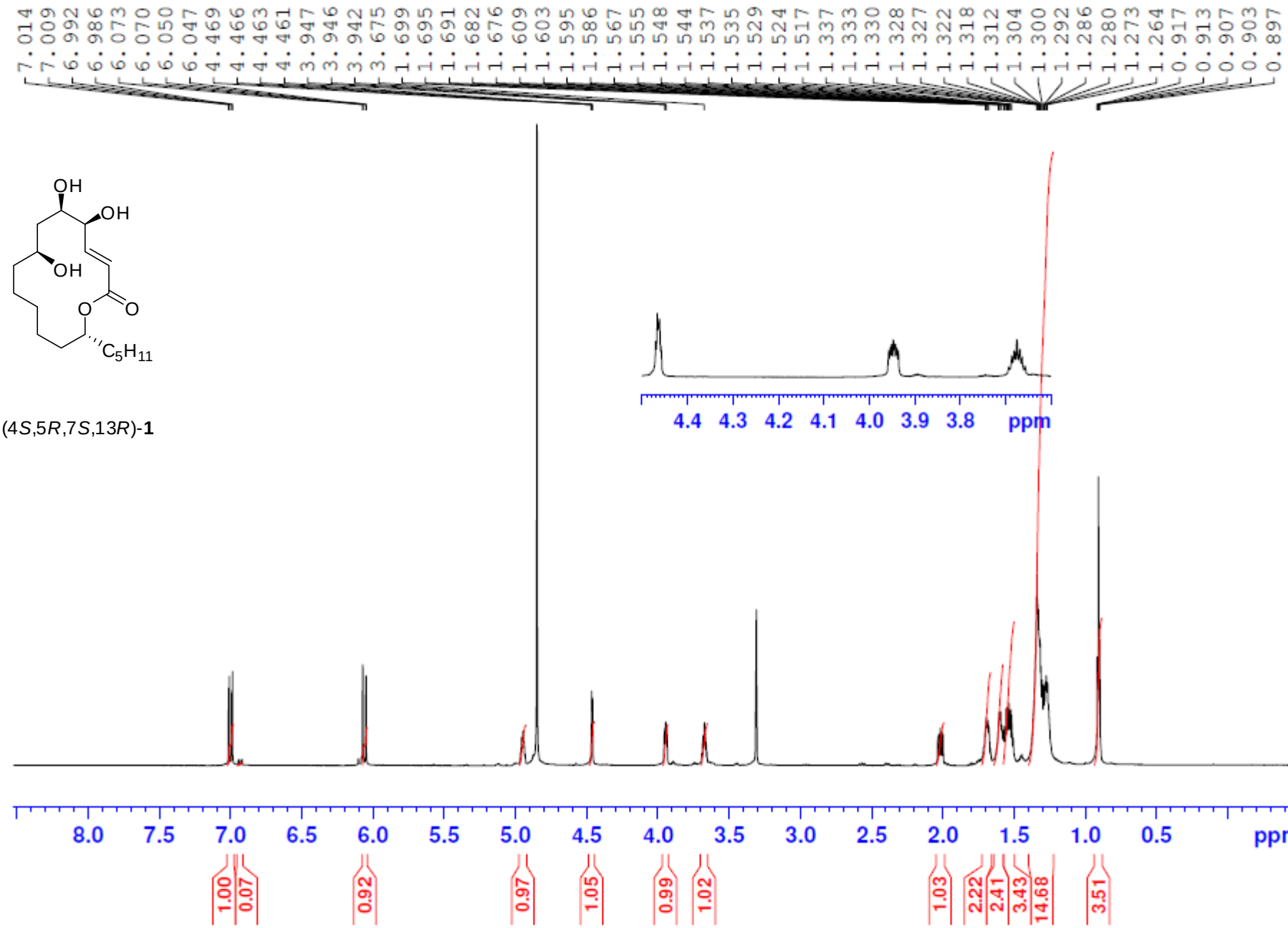
(4*S*,5*R*,7*R*,13*R*)-**1**


2D HMQC
ppm
0
20
40
60
80
100
120
140
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
ppm

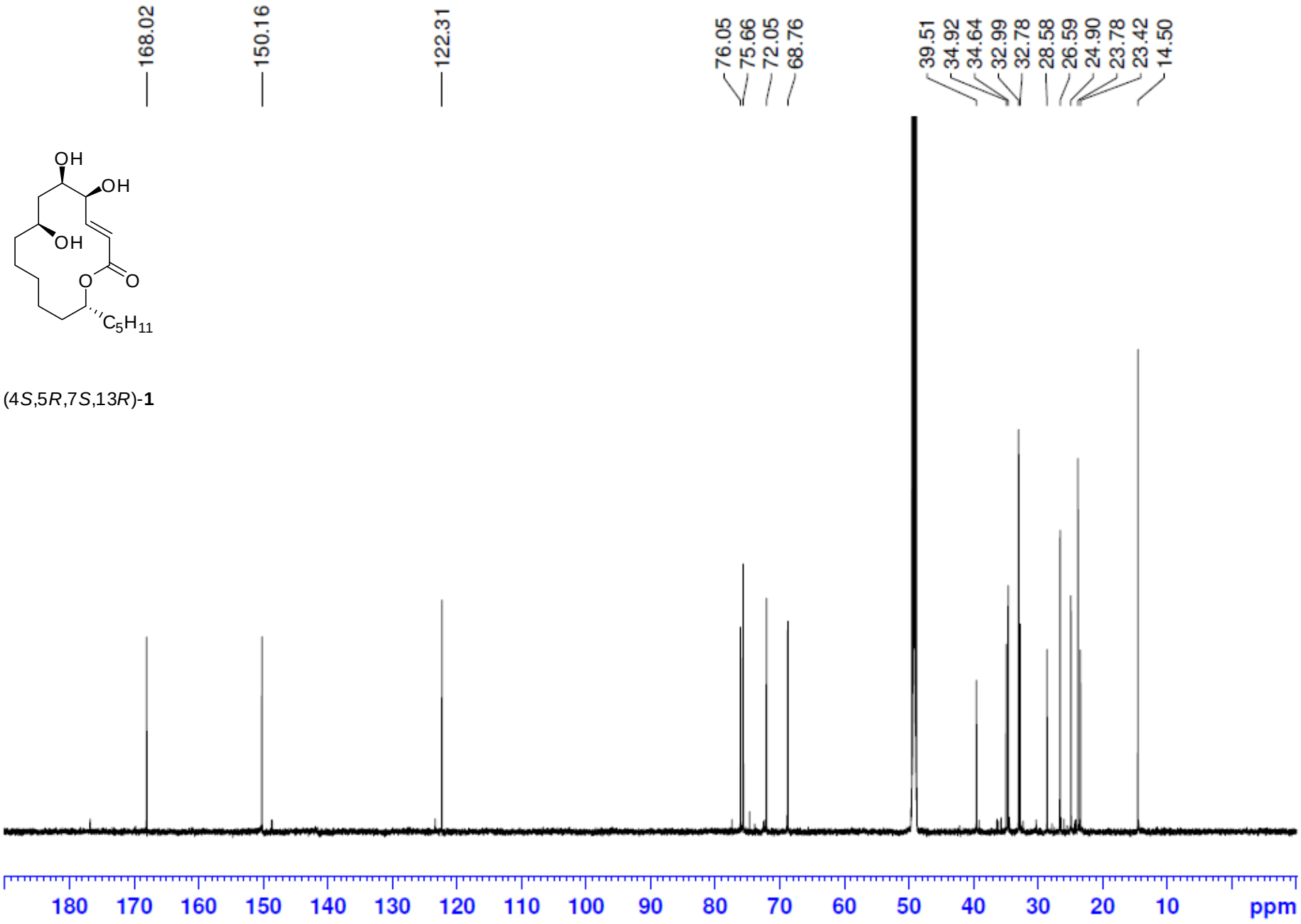

OH
OH
OH
O
O
C5H11

(4*S*,5*R*,7*R*,13*R*)-**1**

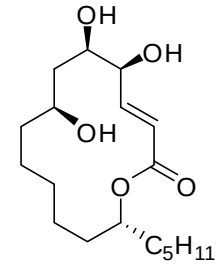

2D HMBC
ppm
20
40
60
80
100
120
140
160
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


7.014
7.009
6.992
6.986
6.073
6.070
6.050
6.047
4.469
4.466
4.463
4.461
3.947
3.946
3.942
3.675
1.699
1.695
1.691
1.682
1.676
1.609
1.603
1.595
1.586
1.567
1.555
1.548
1.544
1.537
1.535
1.529
1.524
1.517
1.337
1.333
1.330
1.328
1.327
1.322
1.318
1.312
1.304
1.300
1.292
1.286
1.280
1.273
1.264
0.917
0.913
0.907
0.903
0.897
OH
OH
OH
O
O
C5H11
4.4 4.3 4.2 4.1 4.0 3.9 3.8 ppm
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 ppm
1.00
0.07
0.92
0.97
1.05
0.99
1.02
1.03
2.22
2.41
3.43
14.68
3.51

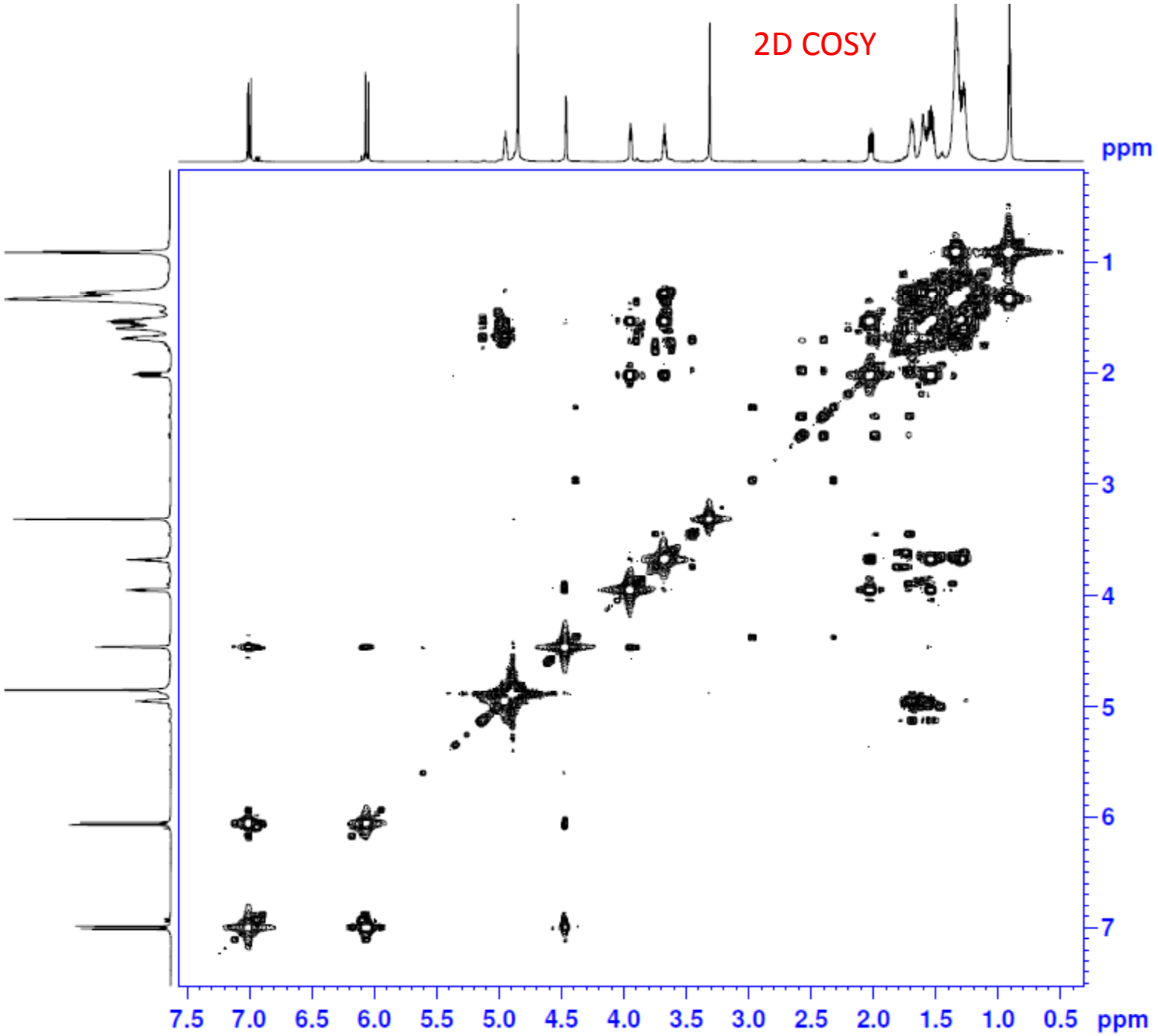
(4*S*,5*R*,7*S*,13*R*)-**1**

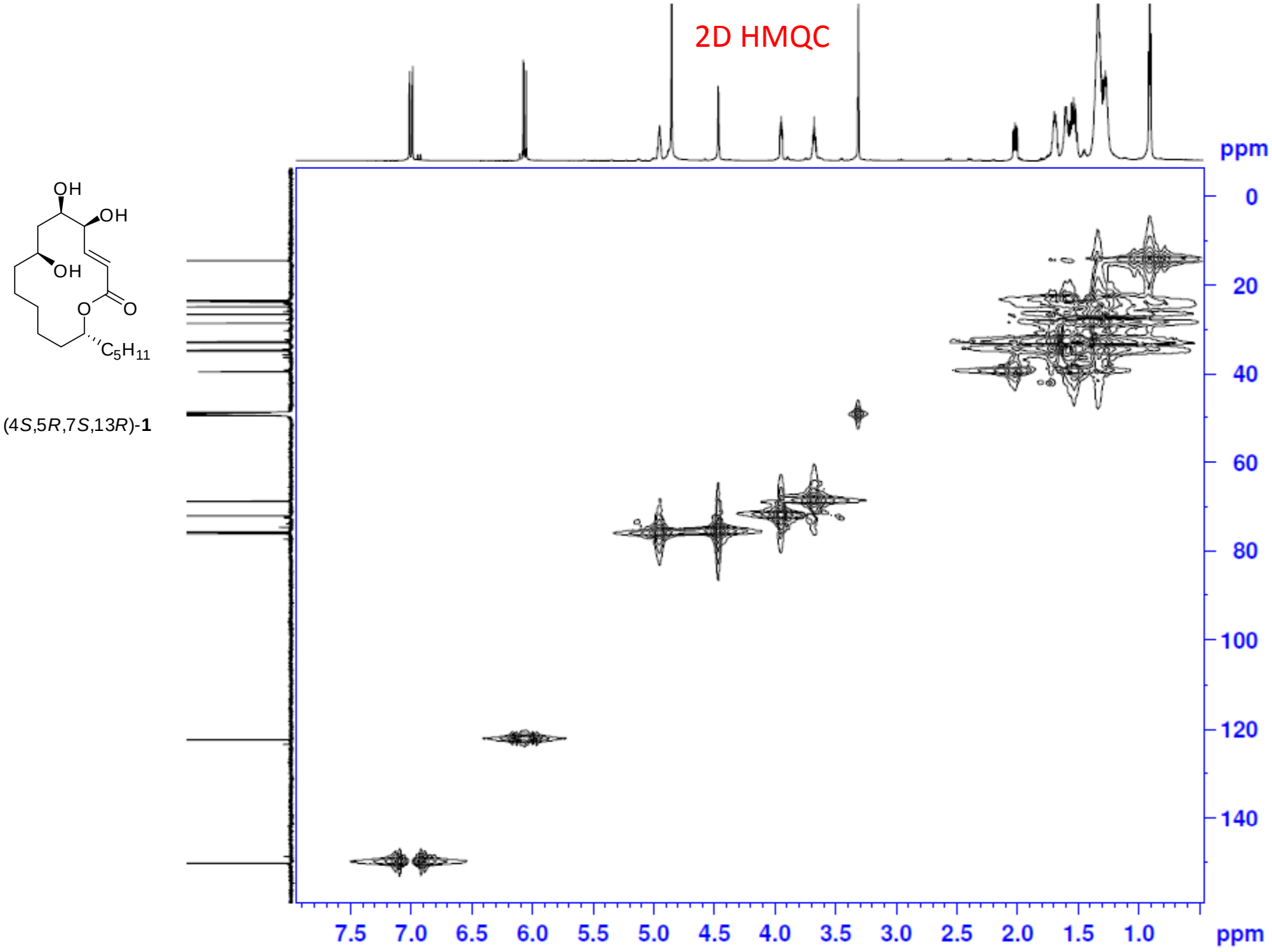

168.02
150.16
122.31
76.05
75.66
72.05
68.76
39.51
34.92
34.64
32.99
32.78
28.58
26.59
24.90
23.78
23.42
14.50
OH
OH
OH
O
O
C5H11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(4*S*,5*R*,7*S*,13*R*)-**1**

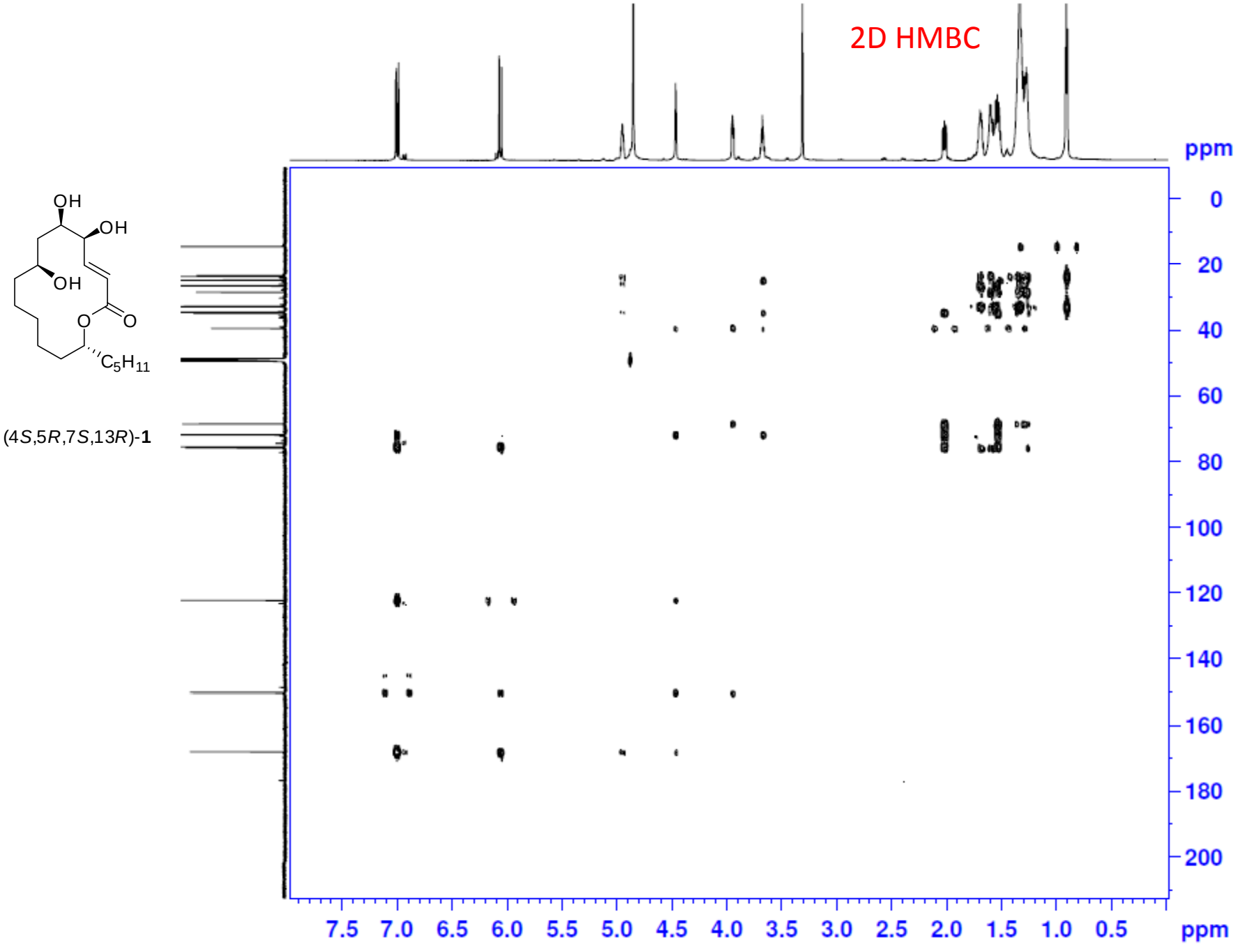

OH
OH
OH
O
O
C_5H_{11}

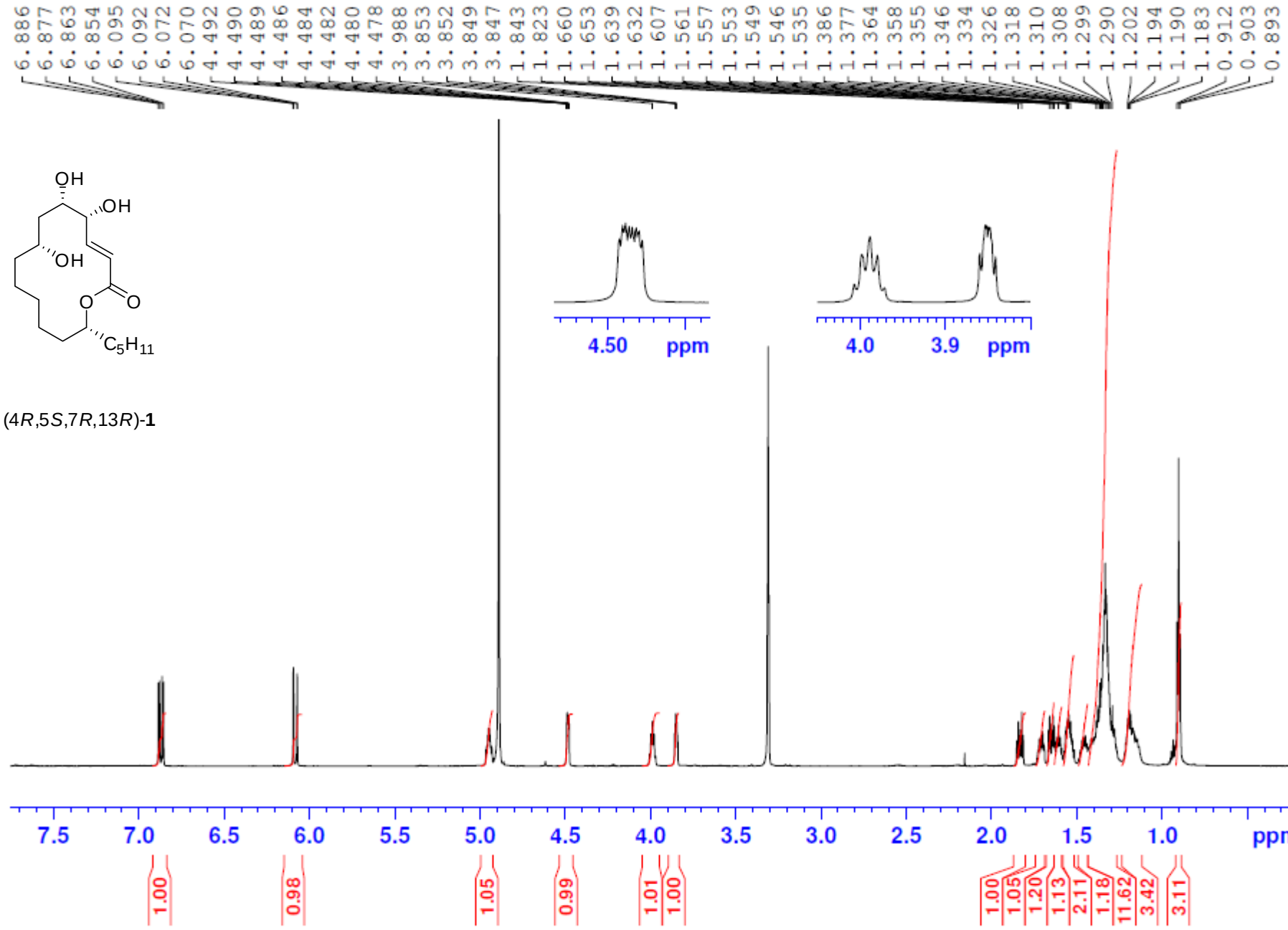
(4*S*,5*R*,7*S*,13*R*)-**1**


2D COSY
ppm
1
2
3
4
5
6
7
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 ppm

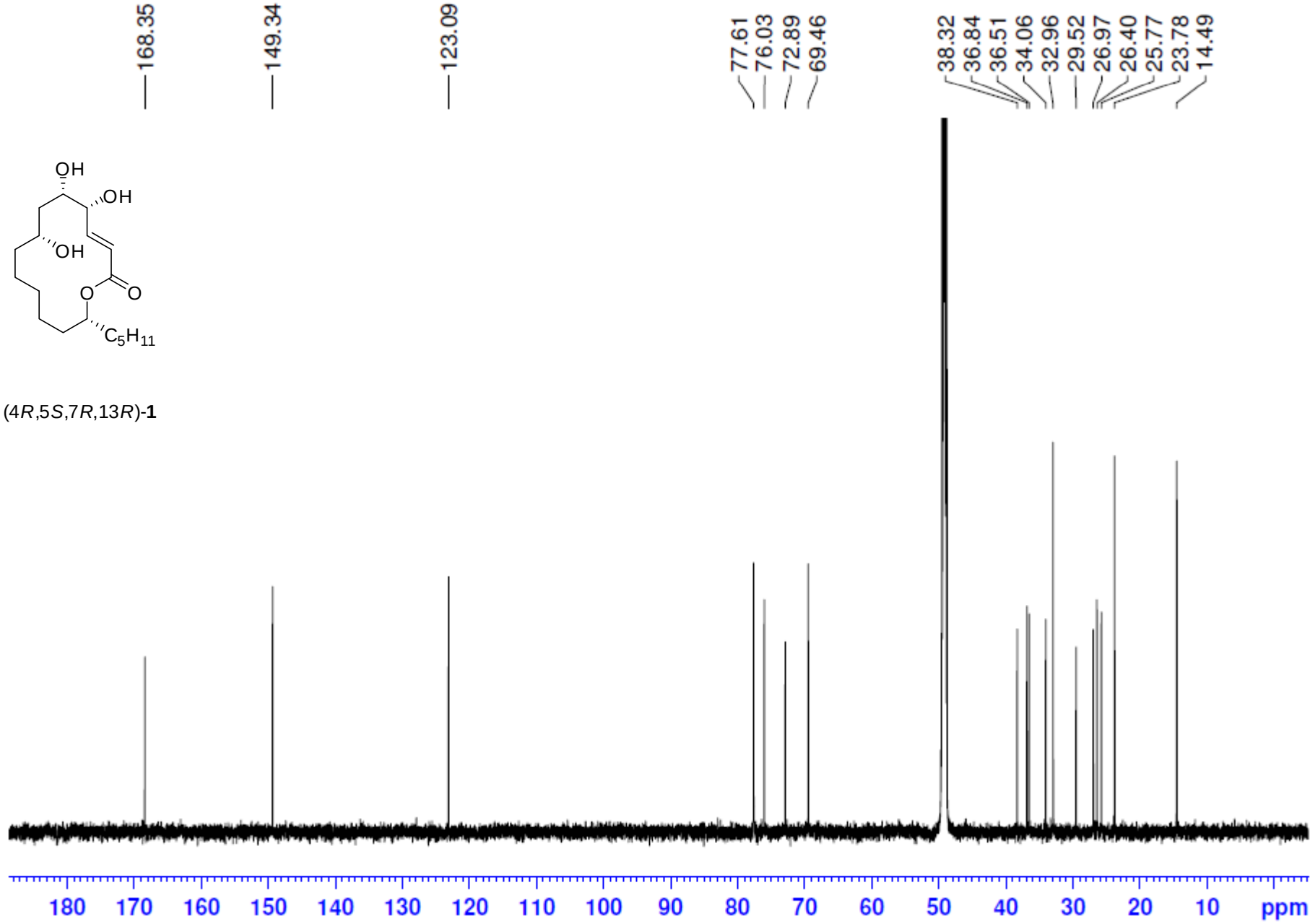

2D HMQC
OH
OH
OH
O
O
C_5H_{11}
ppm
0
20
40
60
80
100
120
140
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

(4*S*,5*R*,7*S*,13*R*)-**1**

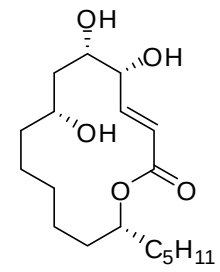

2D HMBC
OH
OH
OH
O
O
C_5H_{11}
(4*S*,5*R*,7*S*,13*R*)-**1**
ppm
0
20
40
60
80
100
120
140
160
180
200
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm


6.886
6.877
6.863
6.854
6.095
6.092
6.072
6.070
4.492
4.490
4.489
4.486
4.484
4.482
4.480
4.478
3.988
3.853
3.852
3.849
3.847
1.843
1.823
1.660
1.653
1.639
1.632
1.607
1.561
1.557
1.553
1.549
1.546
1.535
1.386
1.377
1.364
1.358
1.355
1.346
1.334
1.326
1.318
1.310
1.308
1.299
1.290
1.202
1.194
1.190
1.183
0.912
0.903
0.893
OH
OH
OH
O
O
C5H11
4.50 ppm
4.0 3.9 ppm
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 ppm
1.00
0.98
1.05
0.99
1.01
1.00
1.00
1.05
1.20
1.13
2.11
1.18
11.62
3.42
3.11

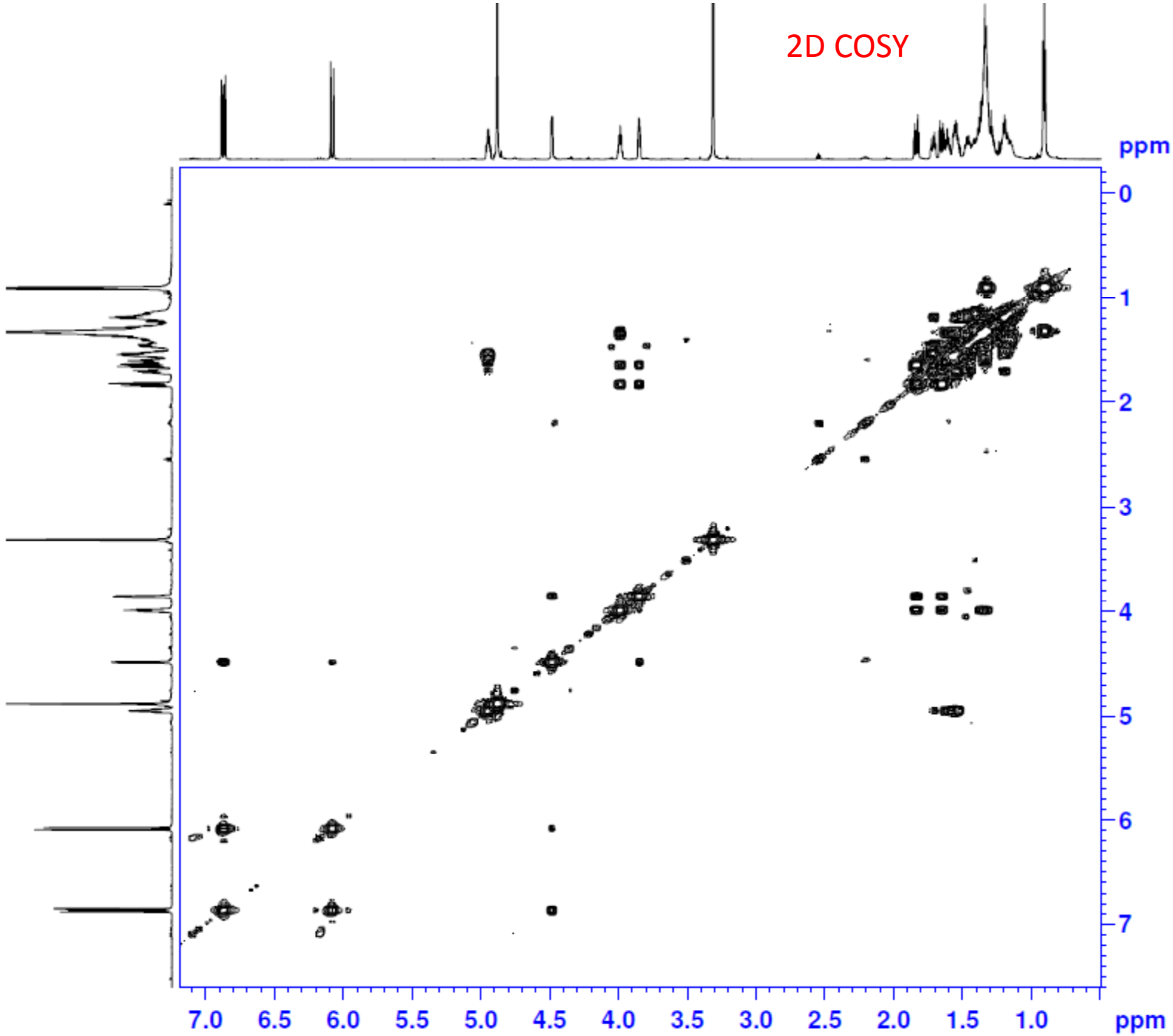
(4*R*,5*S*,7*R*,13*R*)-**1**

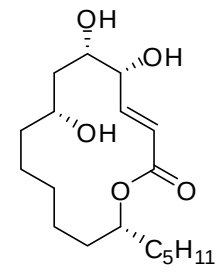

168.35
149.34
123.09
77.61
76.03
72.89
69.46
38.32
36.84
36.51
34.06
32.96
29.52
26.97
26.40
25.77
23.78
14.49
OH
OH
OH
O
O
C5H11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

(4*R*,5*S*,7*R*,13*R*)-**1**

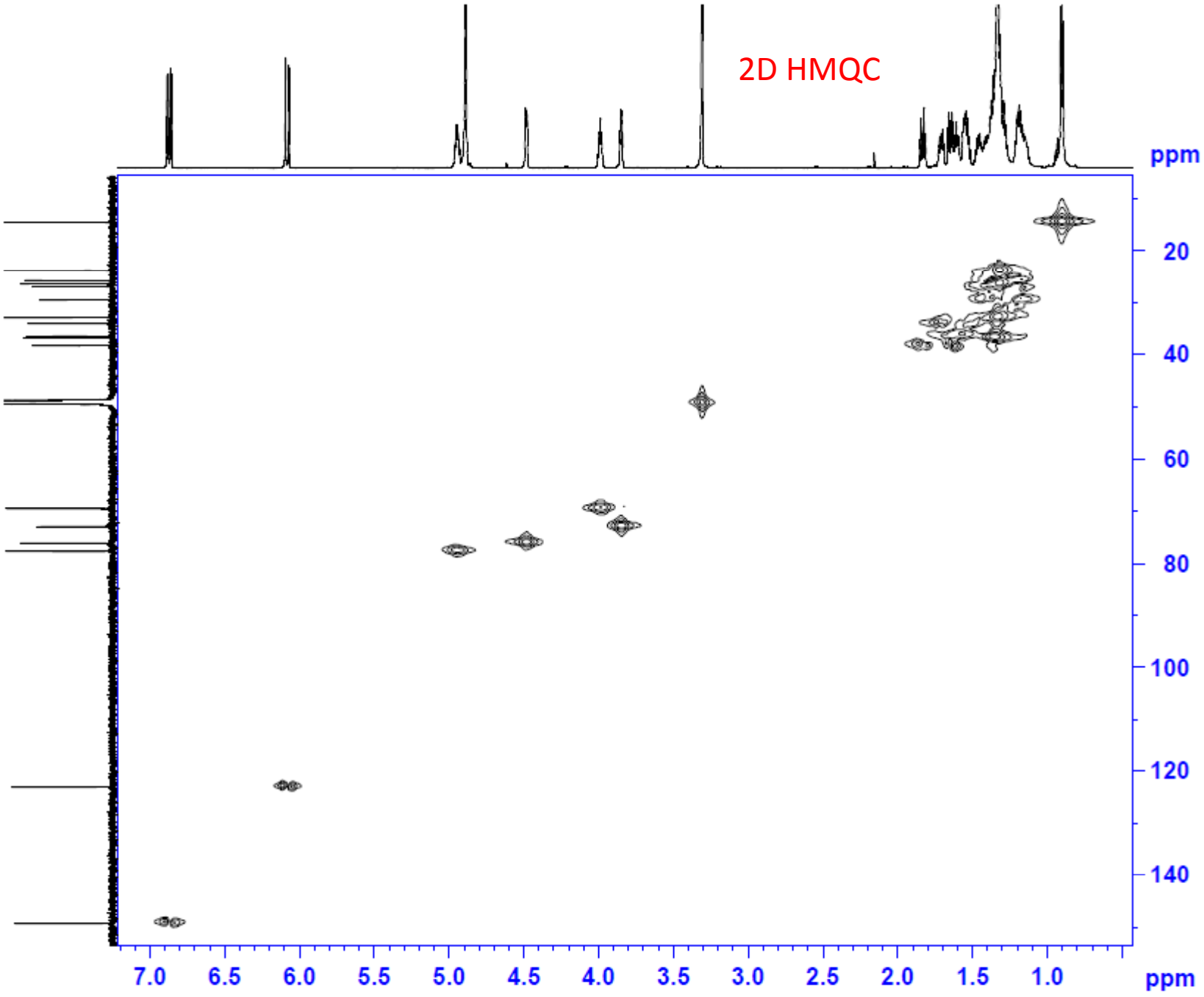

OH
OH
OH
O
O
C_5H_{11}

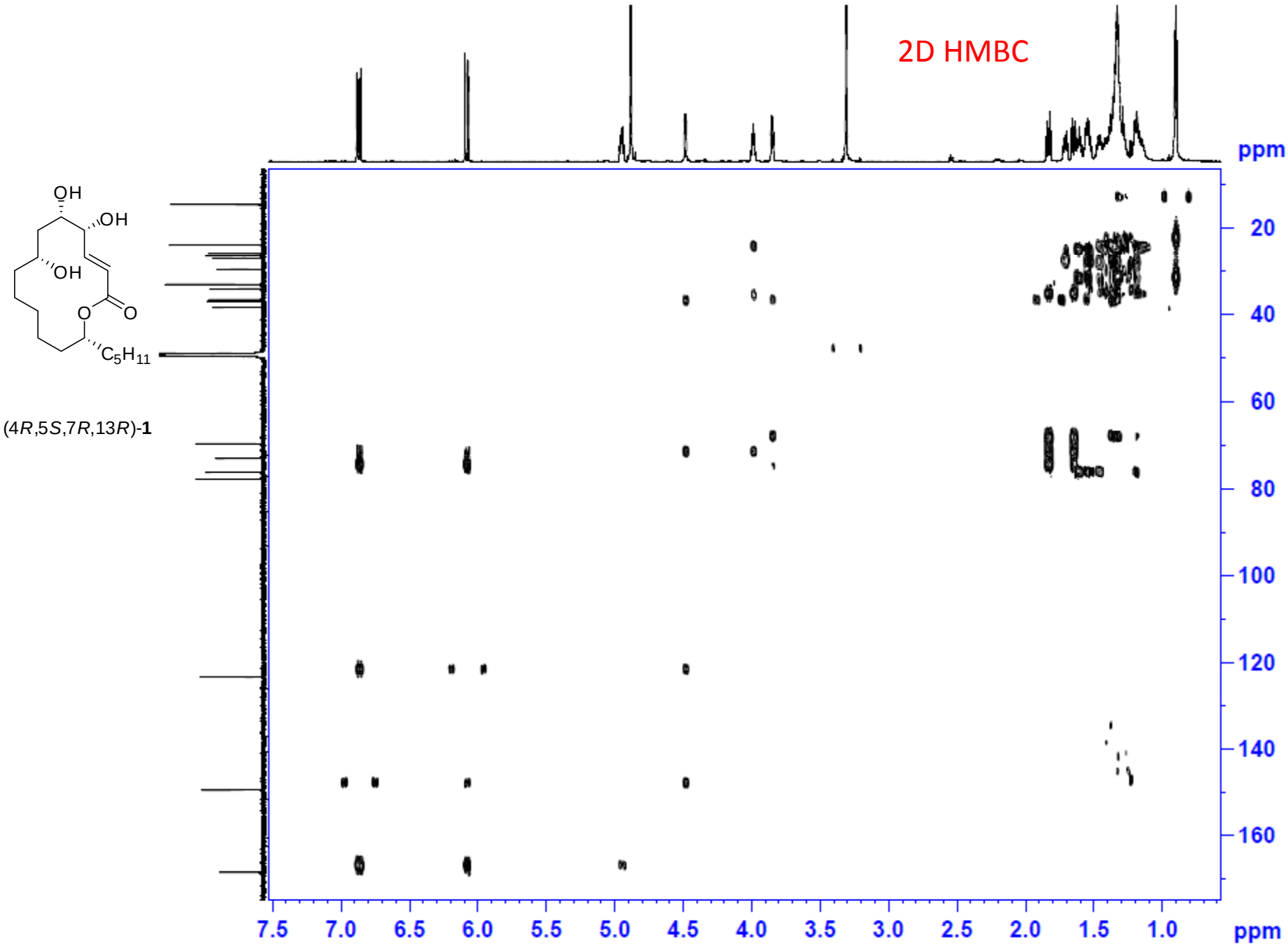
(4*R*,5*S*,7*R*,13*R*)-**1**

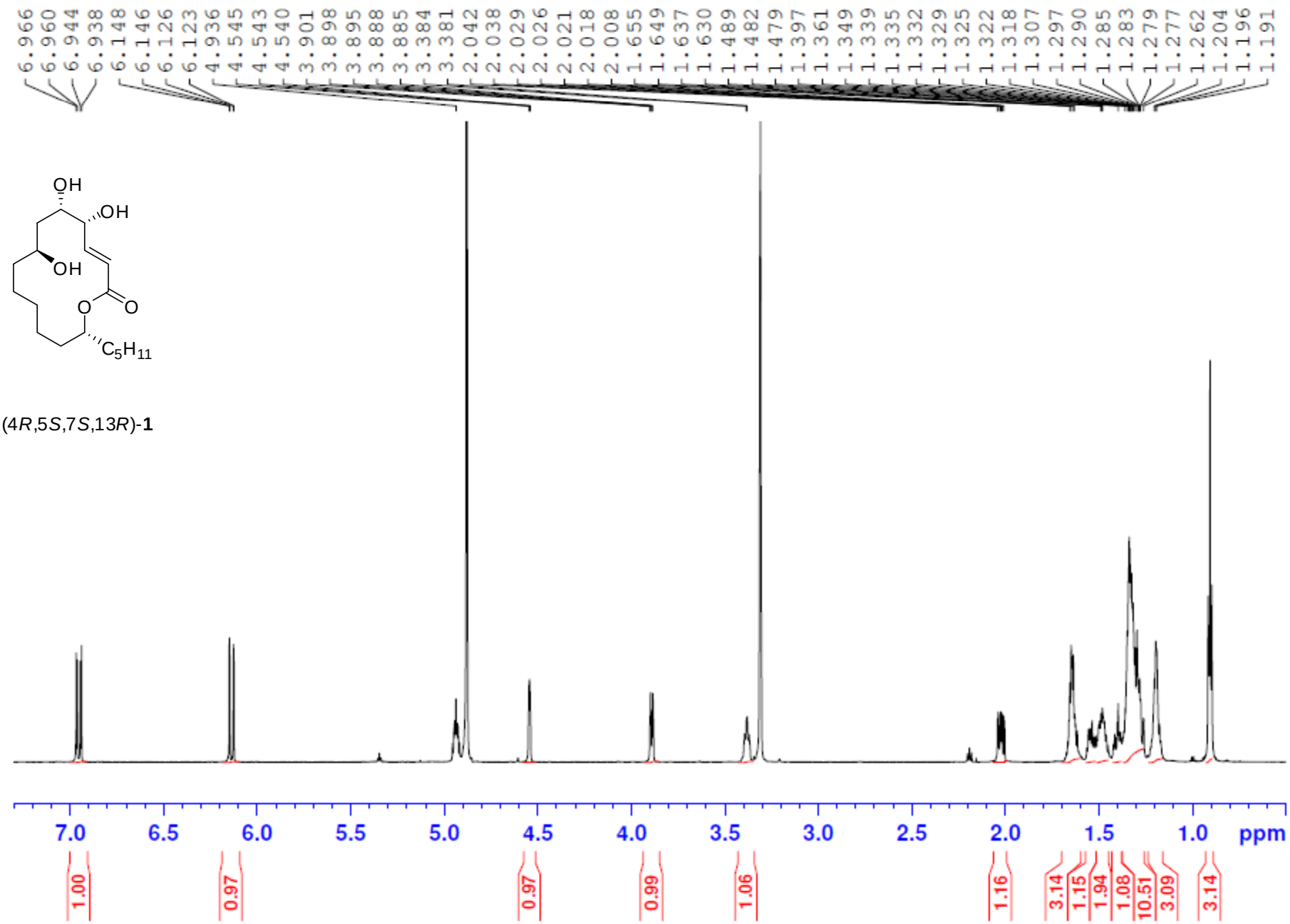

2D COSY
ppm
0
1
2
3
4
5
6
7
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


OH
OH
OH
O
O
C_5H_{11}

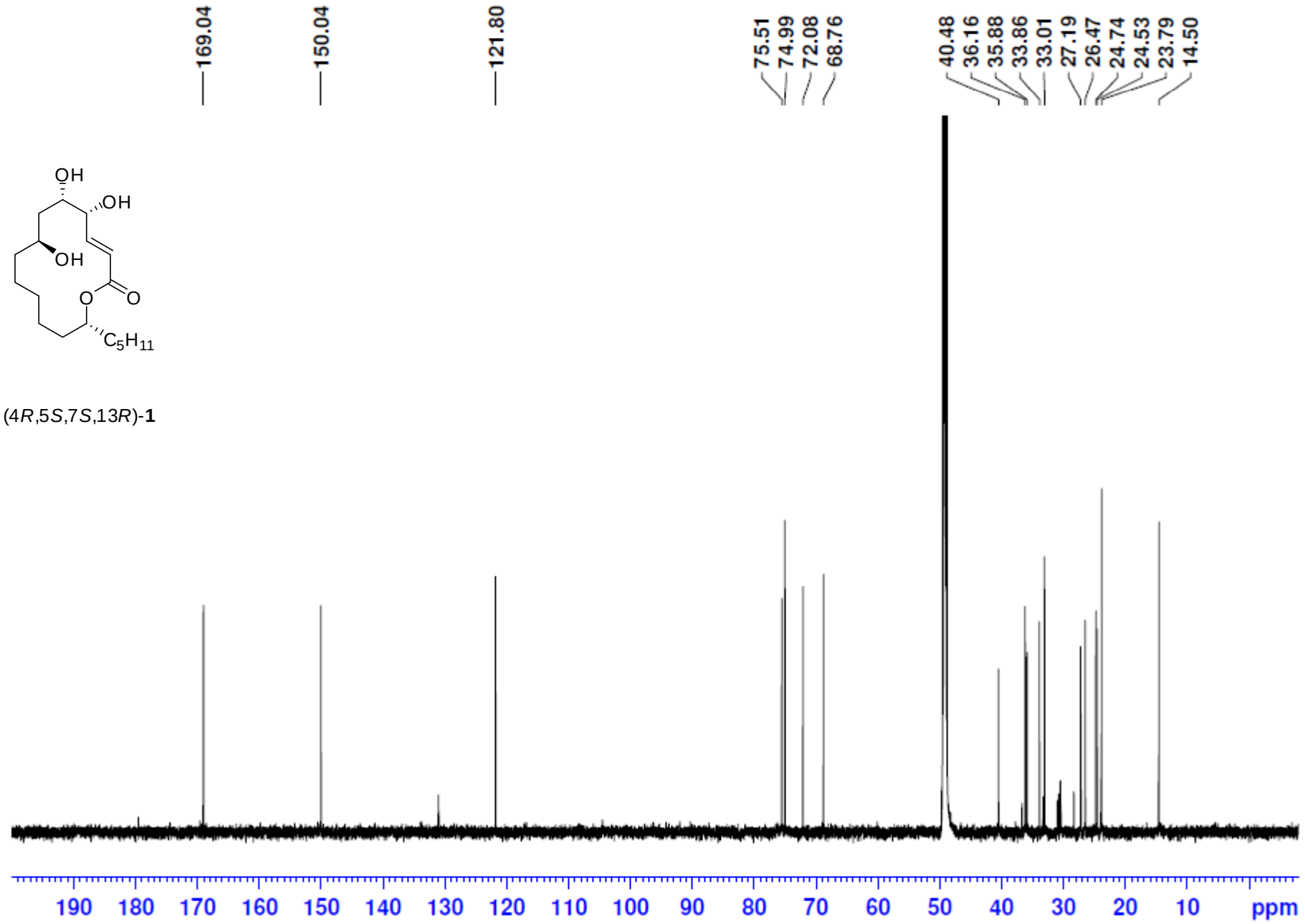
(4*R*,5*S*,7*R*,13*R*)-**1**


2D HMQC
ppm
20
40
60
80
100
120
140
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
ppm

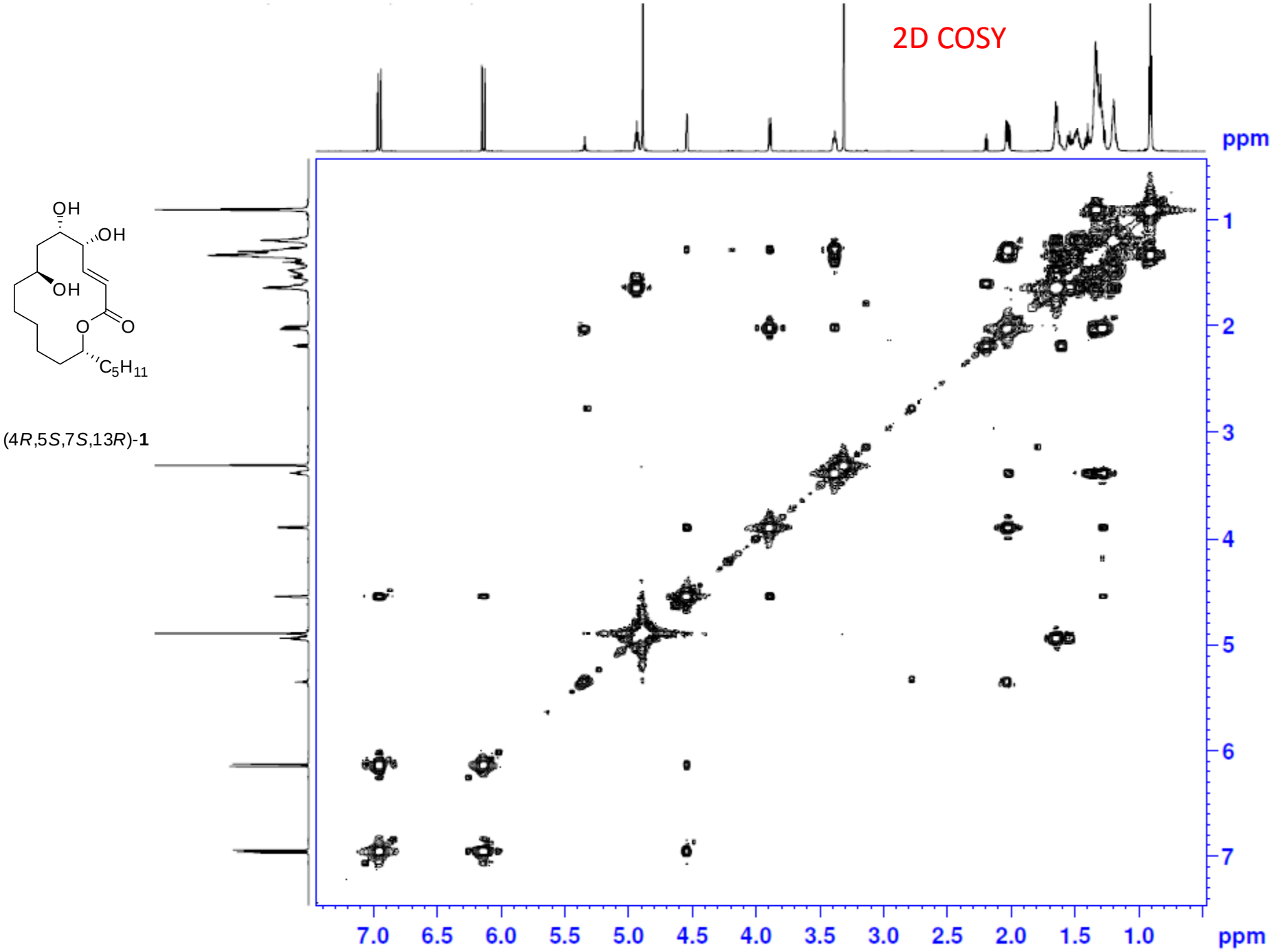

2D HMBC
OH
OH
OH
O
O
C_5H_{11}
(4*R*,5*S*,7*R*,13*R*)-**1**
ppm
20
40
60
80
100
120
140
160
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


6.966
6.960
6.944
6.938
6.148
6.146
6.126
6.123
4.936
4.545
4.543
4.540
3.901
3.898
3.895
3.888
3.885
3.384
3.381
2.042
2.038
2.029
2.026
2.021
2.018
2.008
1.655
1.649
1.637
1.630
1.489
1.482
1.479
1.397
1.361
1.349
1.339
1.335
1.332
1.329
1.325
1.322
1.318
1.307
1.297
1.290
1.285
1.283
1.279
1.277
1.262
1.204
1.196
1.191
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.97
0.97
0.99
1.06
1.16
3.14
1.15
1.94
1.08
10.51
3.09
3.14

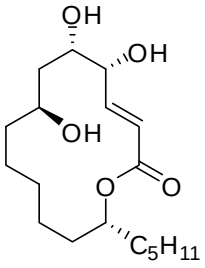
(4*R*,5*S*,7*S*,13*R*)-**1**


169.04
150.04
121.80
75.51
74.99
72.08
68.76
40.48
36.16
35.88
33.86
33.01
27.19
26.47
24.74
24.53
23.79
14.50
OH
OH
OH
O
O
C5H11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

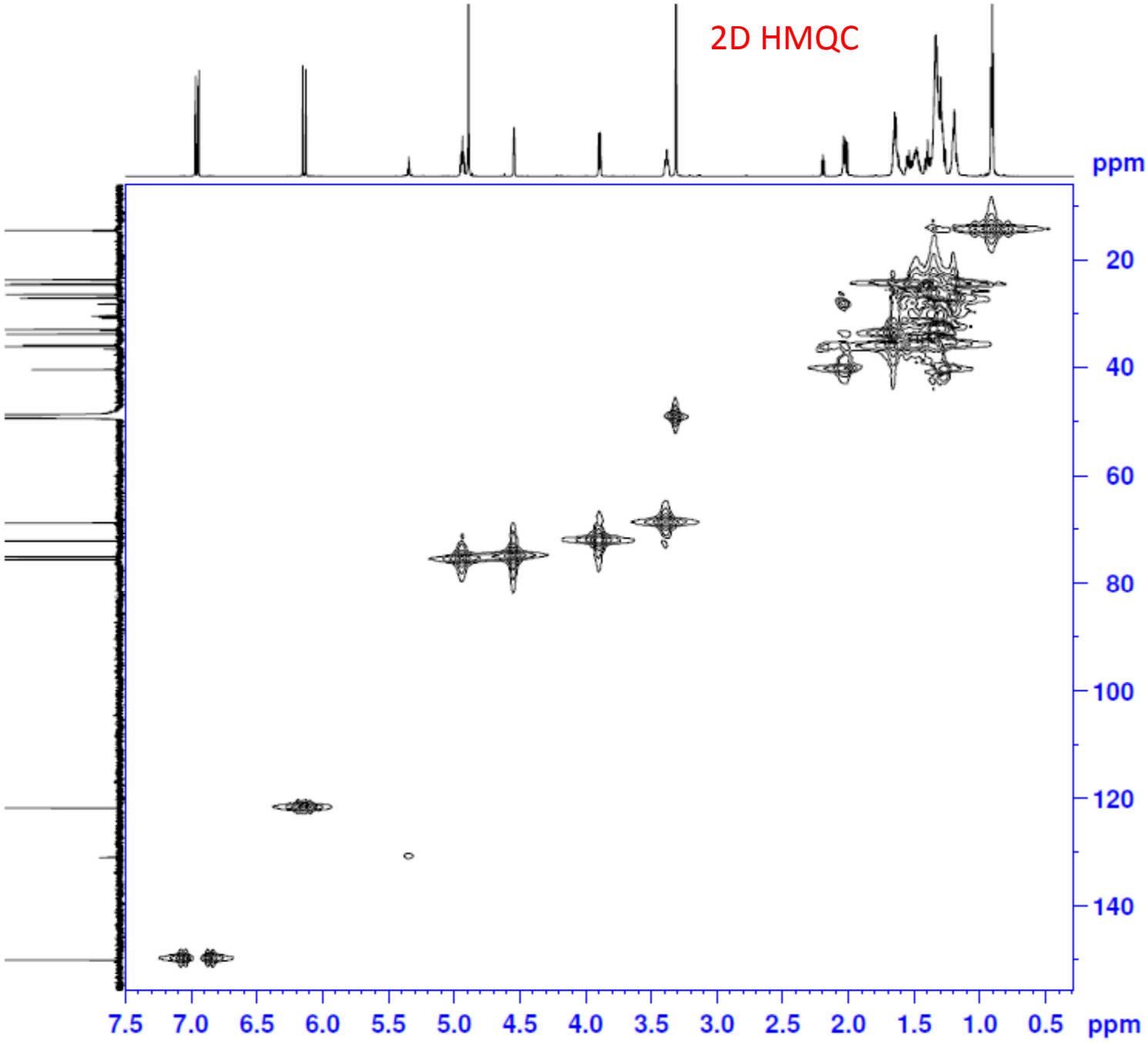
(4*R*,5*S*,7*S*,13*R*)-**1**

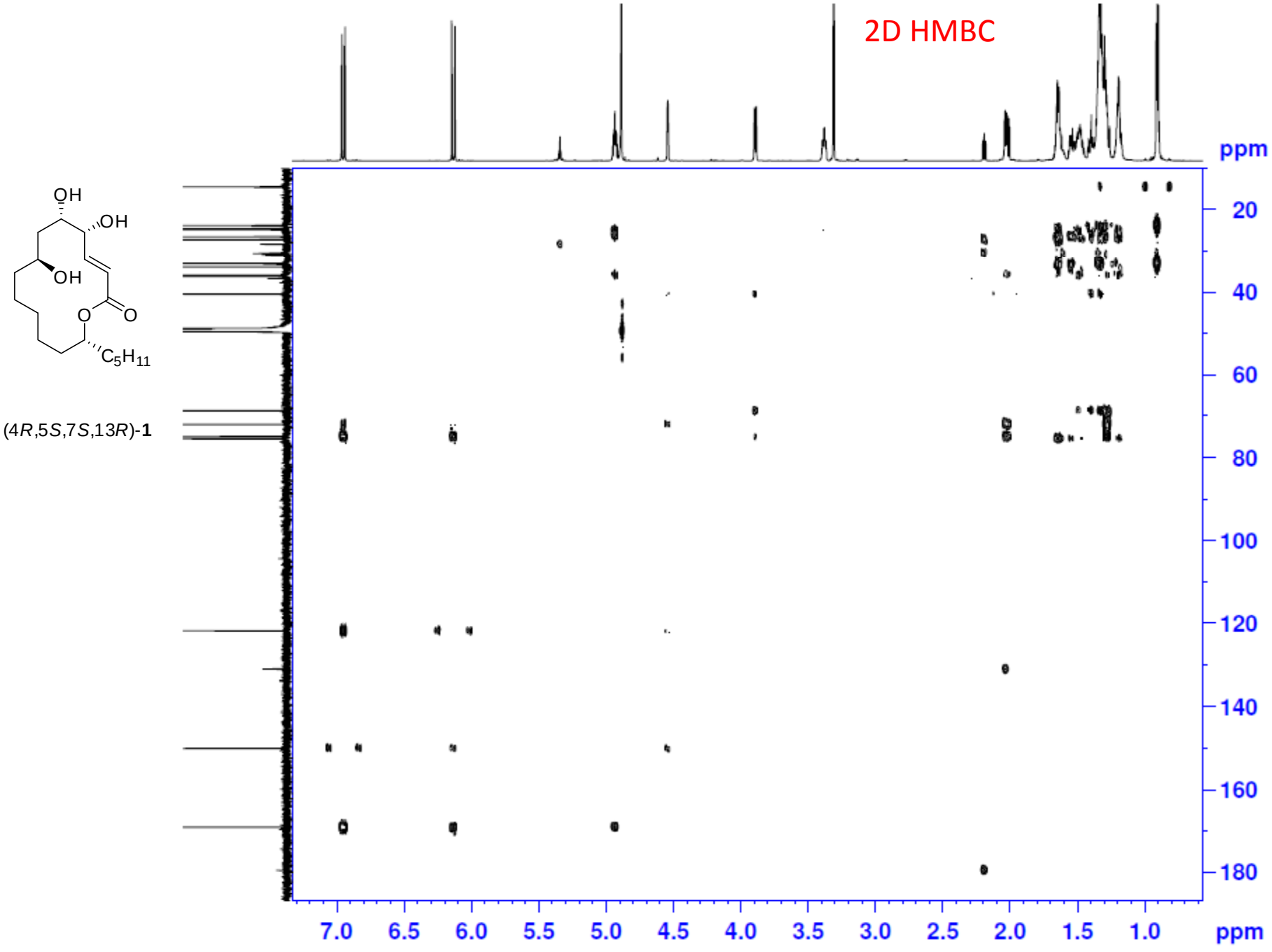

2D COSY
ppm
1
2
3
4
5
6
7
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
OH
OH
OH
O
O
C5H11

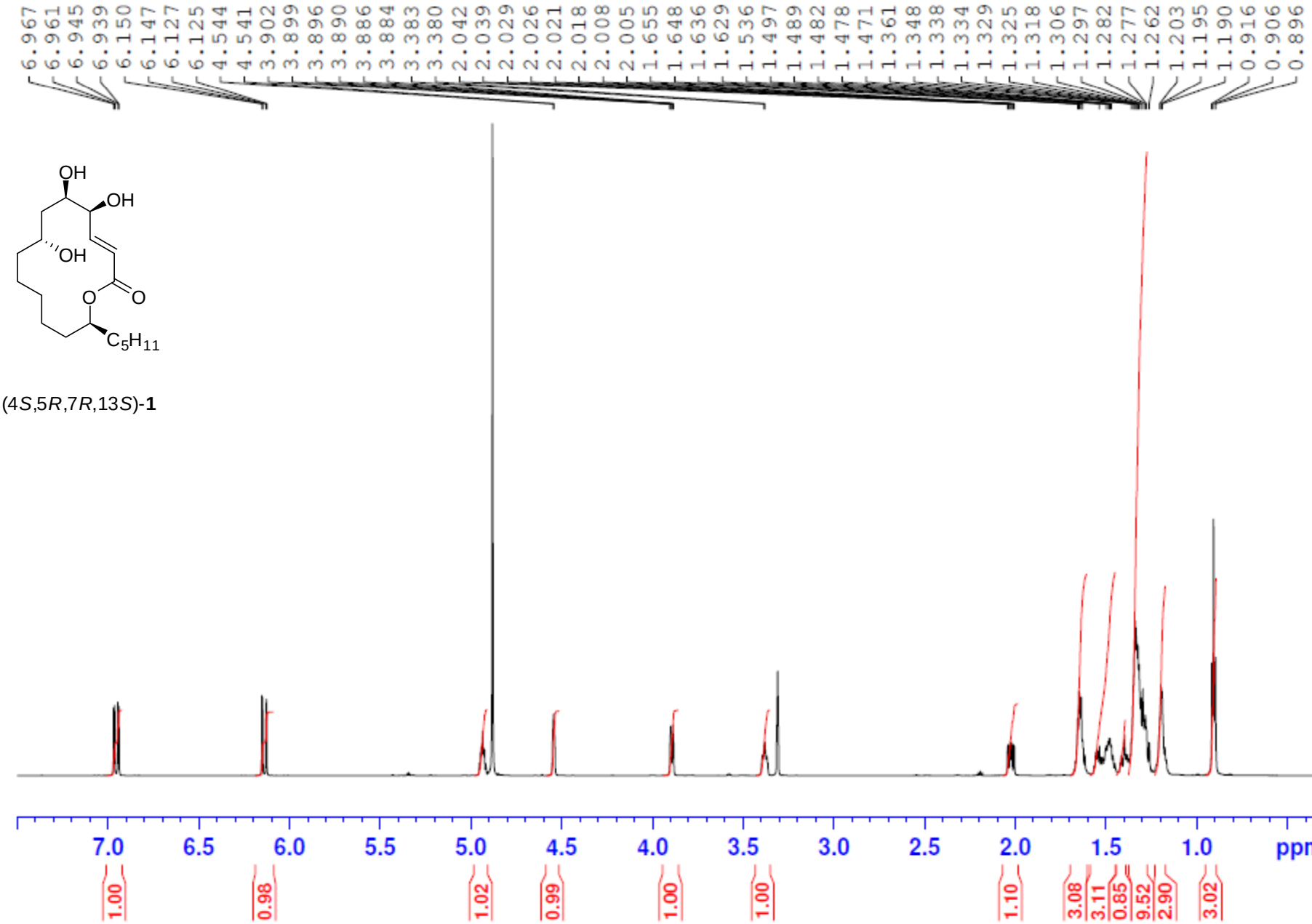
(4*R*,5*S*,7*S*,13*R*)-**1**


OH
OH
OH
O
O
C_5H_{11}

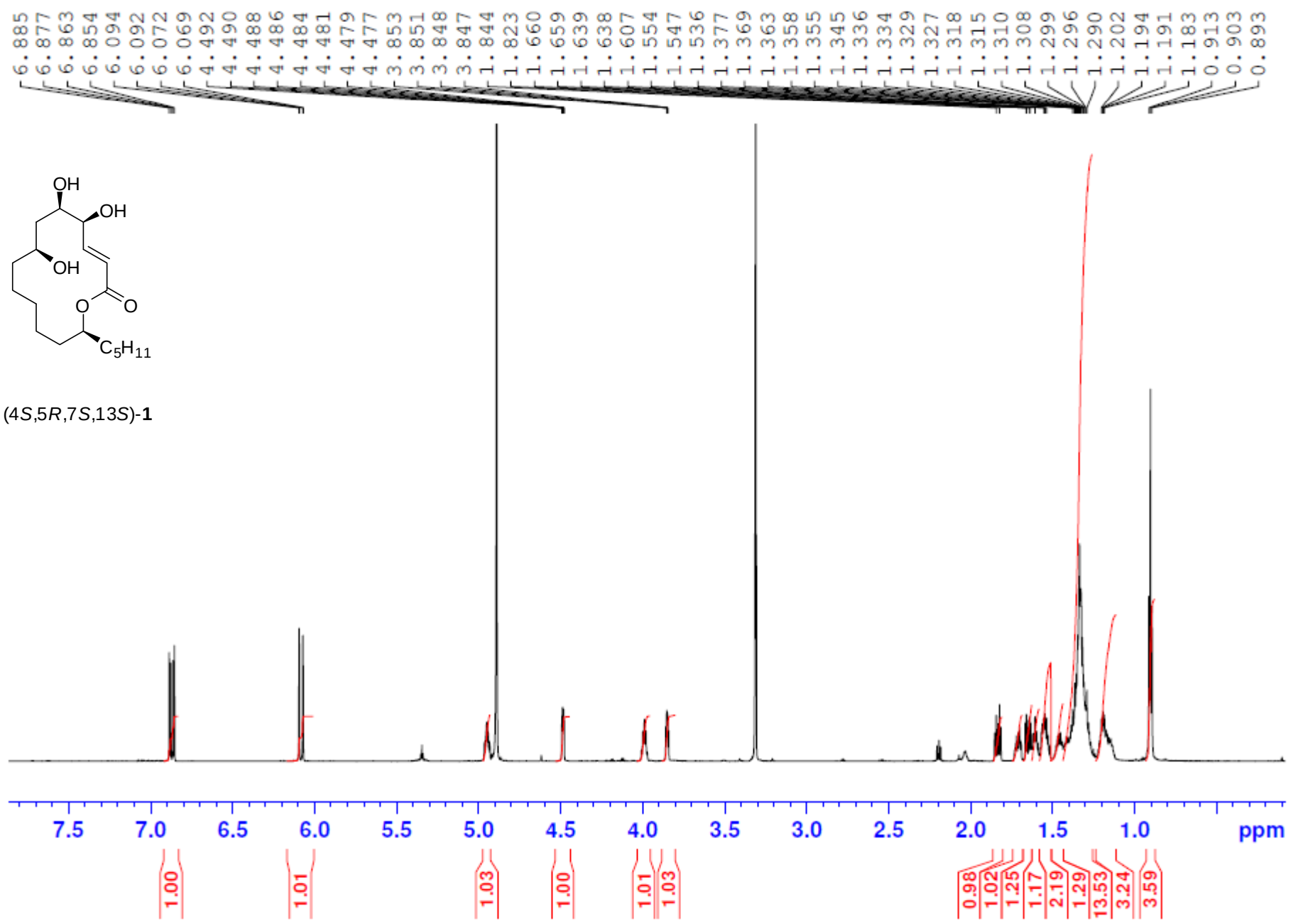
(4*R*,5*S*,7*S*,13*R*)-**1**


2D HMQC
ppm
20
40
60
80
100
120
140
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
ppm

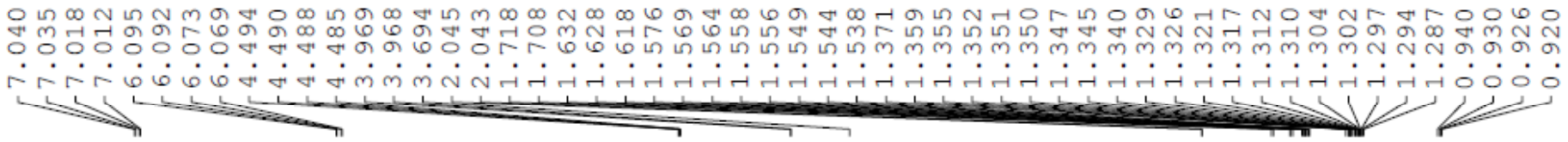

2D HMBC
OH
OH
OH
O
O
C_5H_{11}
(4*R*,5*S*,7*S*,13*R*)-**1**
ppm
20
40
60
80
100
120
140
160
180
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

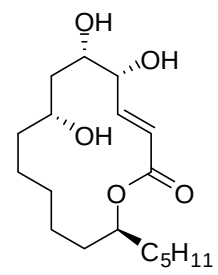

6.967
6.961
6.945
6.939
6.150
6.147
6.127
6.125
4.544
4.541
3.902
3.899
3.896
3.890
3.886
3.884
3.383
3.380
2.042
2.039
2.029
2.026
2.021
2.018
2.008
2.005
1.655
1.648
1.636
1.629
1.536
1.497
1.489
1.482
1.478
1.471
1.361
1.348
1.338
1.334
1.329
1.325
1.318
1.306
1.297
1.282
1.277
1.262
1.203
1.195
1.190
0.916
0.906
0.896
OH
OH
OH
O
O
C5H11
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
ppm
1.00
0.98
1.02
0.99
1.00
1.00
1.10
3.08
3.11
0.85
9.52
2.90
3.02

(4*S*,5*R*,7*R*,13*S*)-**1**

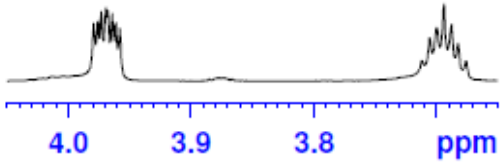

6.885
6.877
6.863
6.854
6.094
6.092
6.072
6.069
4.492
4.490
4.488
4.486
4.484
4.481
4.479
4.477
3.853
3.851
3.848
3.847
1.844
1.823
1.660
1.659
1.639
1.638
1.607
1.554
1.547
1.536
1.377
1.369
1.363
1.358
1.355
1.345
1.336
1.334
1.329
1.327
1.318
1.315
1.310
1.308
1.299
1.296
1.290
1.202
1.194
1.191
1.183
0.913
0.903
0.893
OH
OH
OH
O
O
C5H11
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
ppm
1.00
1.01
1.03
1.00
1.01
1.03
0.98
1.02
1.25
1.17
2.19
1.29
13.53
3.24
3.59

(4*S*,5*R*,7*S*,13*S*)-**1**

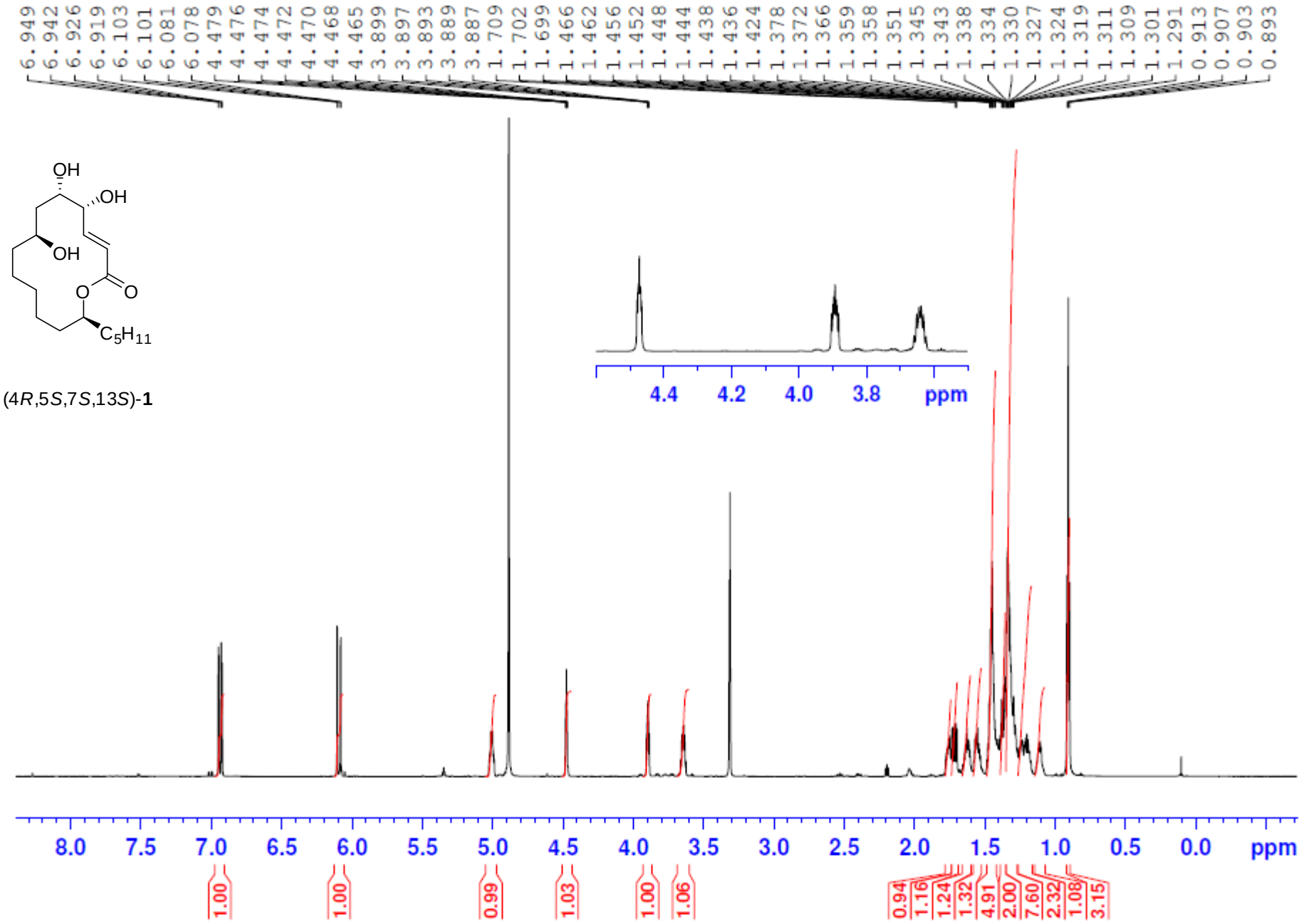

7.040
7.035
7.018
7.012
6.095
6.092
6.073
6.069
4.494
4.490
4.488
4.485
3.969
3.968
3.694
2.045
2.043
1.718
1.708
1.632
1.628
1.618
1.576
1.569
1.564
1.558
1.556
1.549
1.544
1.538
1.371
1.359
1.355
1.352
1.351
1.350
1.347
1.345
1.340
1.329
1.326
1.321
1.317
1.312
1.310
1.304
1.302
1.297
1.294
1.287
0.940
0.930
0.926
0.920


OH
OH
OH
O
O
C5H11

(4*R*,5*S*,7*R*,13*S*)-**1**


4.0
3.9
3.8
ppm

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
ppm


6.949
6.942
6.926
6.919
6.103
6.101
6.081
6.078
4.479
4.476
4.474
4.472
4.470
4.468
4.465
3.899
3.897
3.893
3.889
3.887
1.709
1.702
1.699
1.466
1.462
1.456
1.452
1.448
1.444
1.438
1.436
1.424
1.378
1.372
1.366
1.359
1.358
1.351
1.345
1.343
1.338
1.334
1.330
1.327
1.324
1.319
1.311
1.309
1.301
1.291
0.913
0.907
0.903
0.893
OH
OH
OH
O
O
C5H11
4.4
4.2
4.0
3.8
ppm
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
ppm
1.00
1.00
0.99
1.03
1.00
1.06
0.94
1.16
1.24
1.32
4.91
2.00
7.60
2.32
1.08
3.15

(4*R*,5*S*,7*S*,13*S*)-**1**