Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Stereocontrolled Total Synthesis of Resolvin D4 and 17(*R*)-Resolvin D4

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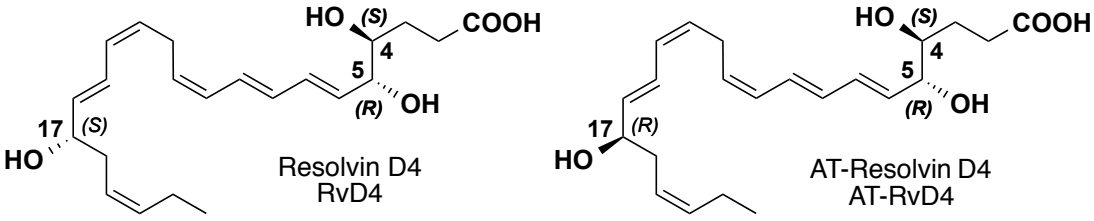

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General Methods

Unless otherwise stated, reactions were carried out in a flame-dried flask with stir bar under argon routed through a three-necked valve, using DriSolv solvents purchased from VWR. Except in cases where commercial building blocks were dried under high vacuum, all purchased reagents were used directly without further purification from Strem, Sigma Aldrich, Combi-Blocks, TCI America and Alfa Aesar. Reaction progress was monitored and recorded using EMD analytical thin layer chromatography (TLC) plates coated with Silica Gel 60 F254. TLC plates were visualized through UV absorbance, (254 nm), or staining such as vanillin, phosphomolybdic acid, potassium-permanganate, or ninhydrin followed by heating by a heat gun. Purification was carried out by flash column chromatography manually using Silica Gel (100-200 mesh) or using an automated system on a Biotage Isolera One.

Characterization was carried out using LC-MS, NMR and UV-VIS instrumentation. ^{1}H and ^{13}C spectra were procured on Varian NMR instruments at 400, 500 or 600 MHz, respectively, for ^{1}H NMR and at 101, 126 or 151 MHz, for ^{13}C NMR data. ^{1}H and ^{13}C chemical shifts, (δ), are recorded in parts per million, (ppm), and referenced to the residual protium and carbon solvent resonances converted by the TMS scale (e.g., Chloroform-*d*, ^{1}H = 7.26 ppm; ^{13}C = 77.00 ppm; and Methanol-*d*, ^{1}H = 3.31 ppm; ^{13}C = 49.00 ppm). Splitting patterns are denoted by s, d, t, dd, td, ddd, and m and refer to the respective multiplicities; singlet, doublet, triplet, doublet of doublets, triplet of doublets, doublet of doublet of doublet and multiplet. Liquid chromatography and tandem mass spectrometry data in negative polarity were recorded on a SCIEX QTRAP 6500+ coupled with an ExionLC analytical HPLC system using a C18 Kinetex 100 x 4.6 mm column, MeOH/ H_2O (0.1% formic acid) gradient at 0.5 mL/ min. UV-Vis spectra were obtained in methanol on a Hewlett-Packard 8350 spectrophotometer.

Experimental Procedures

(4*S*,5*R*)-Methyl 4,5,6-trihydroxyhex-2-enoate (10). To a solution of D-erythrose (**9**) (0.85 g, 7.1 mmol) in dry THF (10 mL) was added methyl (triphenylphosphoranylidene)acetate (2.4 g, 7.1 mmol). The reaction mixture was stirred and refluxed at 65 °C overnight (16 h). Without workup the solvent was removed *in vacuo* and the crude mixture was purified on silica gel using MeOH/ CH_2Cl_2 (10%) as the eluent to afford an *E*/*Z* isomeric mixture of triol **10** (1.1 g, 90%) as a clear colorless oil. *E*-isomer: ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.14 (dd, *J* = 15.7, 4.8 Hz, 1H), 6.10 (dd, *J* = 15.7, 1.8 Hz, 1H), 4.24 (ddd, *J* = 6.5, 4.8, 1.8 Hz, 1H), 3.73 (s, 3H), 3.61 (m, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 167.20, 148.69, 120.25, 74.35, 71.25, 62.92, 50.66.

(4*S*,5*R*)-Methyl 4,5,6-tris(*tert*-butyldimethylsilyloxy)hexanoate (11). To a solution of triol **10** (740 mg, 4.20 mmol) in EtOAc (12 mL) was added one scoop (~80 mg) of 5% palladium on charcoal. The reaction was stirred under H_2 overnight. The reaction mixture was filtered through Celite and with no workup the solvent evaporated. To a flask with imidazole (1.71 g, 25.2 mmol) and DMAP (256 mg, 2.10 mmol) in DMF (10 mL total volume) was added TBS-Cl (3.78 g, 25.2 mmol) dropwise at 0 °C. The triol (220 mg, 1.25 mmol) was cannulated to the flask and stirred overnight (15 h) at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (7 mL) and extracted with Et_2O (3 x 7 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent was removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (2%) as the eluent to afford the protected triol ester **11** (1.86 g, 89%) as a clear colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.75 (m, 1H), 3.66 (s, 3H), 3.55 (m, 1H), 3.45 (dd, *J* = 10.0, 5.9 Hz, 1H), 2.37 (m, 2H), 1.78 (m, 2H), 0.89 (m, 24H), 0.03 (m, 14H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.38, 77.10, 72.74, 64.84, 51.42, 30.11, 27.19, 25.98, 25.97, 25.93, 25.89, 25.86, 25.64, 18.19, -4.11, -4.37, -4.68, -4.88, -5.38, -5.44.

(4*S*,5*S*)-Methyl 4,5-bis((*tert*-butyldimethylsilyl)oxy)-6-oxohexanoate (12). To a solution of protected triol **11** (525 mg, 1.00 mmol) in a 1:1 mixture of CH_2Cl_2/ MeOH (14 mL) was added camphorsulfonic acid (200 mg, 0.86 mmol) at 0 °C. The reaction was monitored and quenched after 50 min with Et_3N (0.15 mL, 1.10 mmol) and the solvent was removed *in vacuo*. The crude mixture was purified on silica gel using EtOAc-Hexanes (12%) as the eluent to afford the mono-deprotected triol ester (285 mg, 70%) as a clear colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.80 (q, *J* = 5.1 Hz, 1H), 3.67 (s, 3H), 3.59 (dd, *J* = 4.5, 1.6 Hz, 2H), 2.38 (dd, *J* = 8.0, 5.6 Hz, 2H), 1.99 (dd, *J* = 7.3, 4.6 Hz, 1H), 1.84 (m, 2H), 0.90 (s, 14H), 0.03 (m, 9H). ^{13}C NMR (400 MHz, Chloroform-*d*) δ 174.11, 74.98, 72.70, 63.71, 51.54, 29.18, 28.37, 25.89, 25.85, 18.10, 18.07, -4.45, -4.60. To a solution of the primary alcohol in CH_2Cl_2 (15 mL) was added pyridine (~350 µL) and Dess-Martin periodinane (445 mg, 1.05 mmol) and the mixture was stirred at room temperature for 20 min. The reaction mixture was quenched with 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (7 mL) and extracted with Et_2O (3 x 7 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (10%) as the eluent to afford aldehyde **12** (227 mg, 80%) as clear colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.60 (d, *J* = 1.9 Hz, 1H), 3.96 (dd, *J* = 3.5, 2.1 Hz, 1H), 3.85 (m, 1H), 3.67

(s, 3H), 2.37 (t, *J* = 7.7 Hz, 2H), 1.76 (m, 2H), 0.89 (2s, 18H), 0.07 (m, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 203.06, 173.36, 80.59, 73.76, 51.34, 29.27, 28.14, 25.55, 25.54, 25.52, 17.99, 17.81, -4.66, -5.12.

(4*S*,5*R*,*E*)-Methyl 4,5-bis((*tert*-butyldimethylsilyl)oxy)-8-oxooct-6-enoate (13). To a flask with (triphenylphosphoranylidene)acetaldehyde (426 mg, 1.40 mmol) was cannulated aldehyde **12** (227mg, 0.56 mmol) in 6.5 mL of THF. The mixture was refluxed at 65 °C overnight (16 h). The reaction mixture with no workup was condensed *in vacuo* followed by purification of the crude residue on silica gel using EtOAc-Hexanes (5%) as the eluent to afford the homologated aldehyde (**13**) (180 mg, 75%) as a dark red oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.57 (d, *J* = 7.9 Hz, 1H), 6.83 (dd, *J* = 15.7, 5.2 Hz, 1H), 6.25 (ddd, *J* = 15.7, 7.9, 1.4 Hz, 1H), 4.27 (t, *J* = 4.6 Hz, 1H), 3.75 (q, *J* = 5.5 Hz, 1H), 3.66 (s, 3H), 2.39 (td, *J* = 7.5, 2.3 Hz, 2H), 1.77 (m, 2H), 0.88 (2s, 18H), 0.04 (m, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 193.26, 173.66, 157.17, 132.42, 75.63, 75.07, 51.55, 29.42, 28.35, 25.86, 25.82, 18.09, -4.05, -4.48, -4.79, -4.81.

(4*S*,5*R*,6*E*,8*E*)-Methyl 4,5-bis((*tert*-butyldimethylsilyl)oxy)-9-iodonona-6,8-dienoate (14). To a solution of $CrCl_2$ (516 mg, 4.2 mmol) dissolved in THF (8 mL total volume) was cannulated a mixture of aldehyde **13** (180 mg, 0.42 mmol) and CHI_3 (827 mg, 2.1 mmol) dissolved in anhydrous THF (3 mL) under argon at 0 °C. The reaction was stirred at 0 °C for 3 h and an additional 1 h at room temperature. The reaction mixture was quenched with brine (50 mL) extracted with Et_2O (3 x 50 mL) and dried over $MgSO_4$. The organic phase was filtered, and the solvent was removed *in vacuo* to afford a crude oil which was purified on silica gel, first using pure pentanes and then EtOAc-Hexanes (2%) as the eluent to afford the (*E*)-vinyl iodide **14** (150 mg, 64%) as a yellow oil, along with an insignificant amount (unquantified) of the (*Z*)-isomer. (*E*)-isomer: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.01 (dd, *J* = 14.3, 10.7 Hz, 1H), 6.30 (d, *J* = 14.4 Hz, 1H), 6.06 (m, 1H), 5.67 (dd, *J* = 15.3, 7.0 Hz, 1H), 3.94 (ddd, *J* = 6.9, 4.4, 1.1 Hz, 1H), 3.66 (s, 3H), 3.63 (t, *J* = 5.4 Hz, 1H), 2.38 (td, *J* = 7.4, 2.6 Hz, 2H), 1.80 (dd, *J* = 7.3, 1.4 Hz, 2H), 0.87 (2s, 18H), 0.04 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.19, 144.63, 135.19, 131.16, 78.97, 74.97(2), 51.49, 29.53, 28.16, 25.97, 25.93, 25.90, 18.22, 18.13, -4.03, -4.72, -4.74.

(4*S*,5*R*,6*E*,8*E*)-Methyl 4,5-bis((*tert*-butyldimethylsilyl)oxy)-12-hydroxydodeca-6,8-dien-10-ynoate (15). To a solution of vinyl iodide **14** (283 mg, 0.51 mmol) in Piperidine (2 mL) was added $Pd(OAc)_2$/PPh_3 (40 mg, 0.052 mmol) and propargyl alcohol (0.32 mL, 5.6 mmol). The reaction was quenched after 1 h with NH_4Cl (5 mL) and extracted with Et_2O (3 x 5 mL). The solvent was removed *in vacuo* and the resulting crude mixture of compound **15** was taken into the next step without further chromatographic purification. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.58 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.17 (m, 1H), 5.75 (dd, *J* = 15.3, 6.6 Hz, 1H), 5.59 (d, *J* = 15.7 Hz, 1H), 4.41 (s, 2H), 3.96 (m, 1H), 3.66 (s, 3H), 3.63 (q, *J* = 5.2 Hz, 1H), 2.38 (dd, *J* = 9.1, 6.8 Hz, 2H), 1.78 (m, 2H), 0.88 (2s, 18H), 0.03 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.23, 135.87 (2), 127.54 (2), 111.20, 109.51, 91.21, 89.10, 73.80, 29.70, 27.02, 26.99, 25.93, 25.90, 20.55, 19.35, 18.21, 18.11, 14.07, -4.02, -4.09, -4.68, -4.76.

(4*S*,5*R*,6*E*,8*E*)-Methyl 12-bromo-4,5-bis((*tert*-butyldimethylsilyl)oxy)dodeca-6,8-dien-10-ynoate (4). To a solution of the propargyl alcohol **15** (255 mg, 0.53 mmol) in dry CH_2Cl_2 (10 mL) was added PPh_3 (125 mg, 0.48 mmol) and *N*-bromosuccinimide (85 mg, 0.48 mmol) at 0 °C. After 30 min the reaction was quenched with $NaHCO_3$ (10 mL)

and extracted with Et_2O (3 x 10 mL). The solvent was removed *in vacuo* and the crude mixture was purified on silica gel using EtOAc-Hexanes (2%) as the eluent to afford propargyl bromide **(4)** as a clear colorless oil (240 mg, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.60 (dd, *J* = 15.5, 11.0 Hz, 1H), 6.17 (dd, *J* = 15.4, 10.9 Hz, 1H), 5.77 (dd, *J* = 15.2, 6.9 Hz, 1H), 5.59 (d, *J* = 15.6 Hz, 1H), 4.09 (d, *J* = 2.3 Hz, 2H), 3.96 (m, 1H), 3.65 (s, 3H), 3.59 (m, 1H), 2.38 (m, 2H), 1.81 (dd, *J* = 7.1, 1.7 Hz, 2H), 0.87 (2s, 18H), 0.03 (m, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.16, 142.60, 138.10, 130.37, 109.92, 86.49, 86.04, 76.47, 75.02, 51.48, 29.43, 28.23, 25.95, 25.91, 25.88, 18.20, 18.10, 15.55, -4.04, -4.15, -4.70, -4.77.

(*S*)-*tert*-Butyldimethyl(oxiran-2-ylmethoxy)silane (6A). To a solution of TBS-Cl (15.3 g, 101.5 mmol), imidazole (6.9 g, 101.5 mmol) and DMAP (412 mg, 3.4 mmol) dissolved in 125 mL dry CH_2Cl_2 at 0 °C was added *R*-glycidol (5.0 g, 67.5 mmol) at 0 °C. The reaction was allowed to stir overnight at room temperature. It was then quenched with saturated aqueous NH_4Cl (125 mL) and extracted with Et_2O (3 x 125 mL). The combined extract was dried with Na_2SO_4 and evaporated to give a crude clear oil which was then chromatographed on silica gel using EtOAc-Hexanes (0.5%) as the eluent to afford the (*S*)-protected glycidol **(6A)** as a viscous and colorless oil (12.2 g, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.84 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.65 (dd, *J* = 11.9, 4.8 Hz, 1H), 3.05 (m, 1H), 2.76 (dd, *J* = 5.2, 4.1 Hz, 1H), 2.60 (m, 1H), 0.89 (s, 9H), 0.07 (d, *J* = 3.7 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 63.72, 52.38, 44.42, 25.84, 18.33, -5.34, -5.38.

(*R*)-*tert*-Butyldimethyl(oxiran-2-ylmethoxy)silane (6B). This compound was prepared from *S*-Glycidol similarly to its enantiomer **6A** to furnish **6B** (11.8 g, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.84 (dd, *J* = 11.9, 3.2 Hz, 1H), 3.65 (dd, *J* = 11.9, 4.8 Hz, 1H), 3.07 (m, 1H), 2.76 (dd, *J* = 5.2, 4.0 Hz, 1H), 2.63 (dd, *J* = 5.2, 2.7 Hz, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 63.91, 52.55, 44.55, 26.03, 18.51, -5.16, -5.21.

2*S*, 1-(*tert*-Butyldiphenylsilyloxy)hept-4-yn-2-ol (16). To a flask at –78 °C was added 1-butyne (0.29 g, 5.3 mmol). *n*-BuLi (2.12 mL, 5.3 mmol) was added next, dropwise at –78 °C. After 0.25 h BF_3•Et_2O (0.64 mL, 5.3 mmol) was added dropwise at –78 °C. To the reaction mixture was added protected glycidol (0.5 g, 2.65 mmol) and stirred for 3 h at –78 °C. The reaction mixture was warmed to room temperature, quenched with saturated aqueous NH_4Cl (15 mL) and extracted with Et_2O (3 x 15 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (4%) as the eluent to afford compound **(16)** (600 mg, 94%) as a clear colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.72 (d, *J* = 6.2 Hz, 1H), 3.68 (dd, *J* = 9.9, 4.3 Hz, 1H), 3.60 (d, *J* = 5.8 Hz, 1H), 2.48 (d, *J* = 5.0 Hz, 1H), 2.36 (dd, *J* = 4.1, 2.0 Hz, 2H), 2.14 (d, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 83.91, 75.04, 70.44, 65.62, 25.83, 23.36, 18.26, 14.14, 12.36, -5.43.

2*R*, 1-(*tert*-Butyldiphenylsilyloxy)hept-4-yn-2-ol (20). This compound was prepared from protected *S*-Glycidol **(6B)** similarly to its enantiomer, compound **(16**), to yield **20** (611 mg, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.77 – 3.72 (m, 1H), 3.70 (dd, *J* = 9.9, 4.2 Hz, 1H), 3.60 (dd, *J* = 9.8, 5.8 Hz, 1H), 2.46 (d, *J* = 4.8 Hz, 1H), 2.42 – 2.33 (m, 2H), 2.22 – 2.10 (m, 2H), 1.11 (t, 3H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 84.15, 75.21, 70.63, 65.81, 26.03, 23.55, 18.46, 14.33, 12.55, -

5.23, -5.26.

(*S*), 2-(*tert*-Butyldiphenylsilyloxy)hept-4-yn-1-ol (17). To a flask with imidazole (95 mg, 1.39 mmol) and DMAP (8 mg, 0.06 mmol) in CH_2Cl_2 (5 mL total volume) was added TBDPS-Cl (0.36 mL, 1.39 mmol) dropwise at 0 °C. The alcohol **(16)** (280 mg, 1.15 mmol) was cannulated to the flask and stirred overnight at room temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (7 mL) and extracted with Et_2O (3 x 7 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (1%) as the eluent to afford the protected diol (525 mg, 90%) as a clear colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.65 (m, 4H), 7.55 – 7.29 (m, 6H), 3.83 (p, *J* = 5.5 Hz, 1H), 3.55 (dd, *J* = 5.4, 3.3 Hz, 2H), 2.44 – 2.34 (m, 1H), 2.32 – 2.23 (m, 1H), 2.12 (qt, *J* = 7.5, 2.4 Hz, 2H), 1.10 (t, 3H), 1.07 (s, 9H), 0.84 (s, 9H), -0.03 (s, 3H), -0.06 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.10, 136.03, 134.47, 134.34, 129.69, 129.66, 127.62, 83.29, 76.47, 72.78, 65.80, 27.09, 26.05, 24.12, 19.54, 18.46, 14.34, 12.62, -5.34, -5.35. To a solution of protected diol (0.5 g, 1.04 mmol) in CH_2Cl_2 (5 mL) was added camphor sulfonic acid (144 mg, 0.62 mmol) at room temperature and monitored for 1 h. The reaction was quenched with Et_3N (0.09 mL, 0.62 mmol) and the solvent was evaporated *in vacuo* without workup. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (12%) as the eluent to afford alcohol **(17)** (370 mg, 97%) as a clear colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (m, 4H), 7.43 (m, 6H), 3.93 (m, 1H), 3.67 (m, 2H), 2.42 (m, 1H), 2.30 (m, 1H), 2.10 (m, 2H), 1.12 (s, 9H), 1.08 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.77, 135.62, 133.52, 133.50, 129.82, 129.77, 127.73, 127.60, 75.26, 72.52, 65.54, 26.92, 23.81, 19.24, 13.99, 12.31

(*R*), 2-(*tert*-Butyldiphenylsilyloxy)hept-4-yn-1-ol (21). This compound was prepared from alcohol **(20)** similarly to its enantiomer, compound **(17**), to give **21** (378 mg, 89%) over 2 steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.72 (m, 4H), 7.57 – 7.37 (m, 6H), 4.06 – 3.87 (m, 1H), 3.70 (d, *J* = 4.6 Hz, 2H), 2.47 (ddt, *J* = 16.4, 7.7, 2.5 Hz, 1H), 2.36 (ddt, *J* = 16.4, 4.9, 2.4 Hz, 1H), 2.18 – 2.06 (m, 3H), 1.16 (s, 9H), 1.10 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.86, 135.71, 133.64, 133.62, 129.89, 129.85, 127.80, 127.68, 83.83, 75.43, 72.62, 65.56, 27.01, 23.91, 19.33, 14.10, 12.41.

2*S*, 4*Z*, 2-(*tert*-Butyldiphenylsilyloxy)-1-oxohept-4-enal (18). To a solution of alcohol **(17)** (3.9 g, 10.6 mmol) in EtOAc (100 mL) was added Lindlar catalyst (200 mg) and quinoline (~80 µL). The reaction mixture was placed under a H_2 atmosphere using a balloon (1 atm) and stirred for 2 h. The reaction was filtered through Celite and the solvent was removed *in vacuo*. To a solution of the crude alcohol residue (0.5 g, 1.36 mmol) in CH_2Cl_2 (20 mL) was added pyridine (~400 µL) and Dess-Martin periodinane (1.189 g, 2.80 mmol) the mixture was stirred at room temperature for 20 minutes. The reaction mixture was quenched with 1:1 mixture of saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$ (15 mL) and extracted with Et_2O (3 x 15 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (10%) as the eluent to afford the aldehyde **(18)** (404 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.57 (d, *J* = 1.7 Hz, 2H), 7.71 – 7.61 (m, 4H), 7.49 – 7.33 (m, 6H), 5.52 – 5.41 (m, 1H), 5.40 – 5.27 (m, 1H), 4.06 (td, *J* = 6.5, 1.7 Hz, 1H), 2.44 (dt, *J* = 14.1, 6.7 Hz, 1H), 2.34 (dt, *J* = 13.9, 6.5 Hz, 1H), 1.99 – 1.87 (m, 2H), 1.12 (s, 9H), 0.90 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101

MHz, Chloroform-*d*) δ 203.52, 135.95, 135.95, 135.11, 133.24, 133.12, 130.18, 130.13, 127.95, 127.89, 122.17, 77.94, 31.15, 27.08, 20.74, 19.49, 14.14.

2*R*, 4*Z*, 2-(*tert*-Butyldiphenylsilyloxy)-1-oxohept-4-enal (22). This compound was prepared from alcohol **(21)** similarly to its enantiomer, compound **(18**), to produce **22** (425 mg, 85%) over 2 steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.59 (d, *J* = 1.7 Hz, 1H), 7.64 (m, 4H), 7.35 (m, 6H), 5.44 (m, 1H), 5.37 (dt, *J* = 9.7, 1.3 Hz, 1H), 4.09 (ddd, *J* = 6.4, 5.6, 1.6 Hz, 1H), 2.42 (m, 1H), 2.33 (m, 1H), 1.90 (m, 2H), 1.15 (s, 9H), 0.92 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 203.27, 135.77, 134.92, 133.06, 132.94, 130.00, 129.96, 127.77, 127.71, 122.00, 77.77, 30.97, 26.90, 20.56, 19.31, 13.97.

(*S*,2*E*,6*Z*)-4-((*tert*-Butyldiphenylsilyl)oxy)nona-2,6-dienal (19). To a flask with (Triphenylphosphoranylidene)acetaldehyde (500 mg, 1.63 mmol) was cannulated aldehyde **(18)** (300mg, 0.82 mmol) in 7 mL of THF. The mixture was refluxed at 65 °C overnight. The reaction mixture with no workup was condensed *in vacuo* followed by purification of the crude mixture on silica gel using EtOAc-Hexanes (5%) as the eluent to afford the extended aldehyde **(19)** (240 mg, 75%) as a dark red colored oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.46 (d, *J* = 8.0 Hz, 1H), 7.57 (m, 4H), 7.32 (m, 6H), 6.72 (dd, *J* = 15.6, 4.9 Hz, 1H), 6.22 (ddd, *J* = 15.6, 8.0, 1.5 Hz, 1H), 5.37 (m, 1H), 5.17 (m, 1H), 4.42 (m, 1H), 2.27 (m, 2H), 1.74 (m, 2H), 1.09 (s, 9H), 0.84 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.59, 158.94, 135.83, 135.75, 134.92, 133.49, 133.16, 130.93, 129.94, 129.92, 127.68, 127.65, 122.31, 72.34, 34.97, 26.96, 20.56, 19.30, 14.00.

(*R*,2*E*,6*Z*)-4-((*tert*-Butyldiphenylsilyl)oxy)nona-2,6-dienal (23). This compound was prepared from aldehyde **22** similarly to its enantiomer, compound **(19**), to obtain **23** (232 mg, 72% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.46 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 4H), 7.40 (m, 6H), 6.73 (dd, *J* = 15.6, 4.9 Hz, 1H), 6.23 (ddd, *J* = 15.6, 8.0, 1.5 Hz, 1H), 5.41 (m, 1H), 5.20 (m, 1H), 4.46 (m, 1H), 2.26 (m, 2H), 1.79 (m, 2H), 1.09 (s, 9H), 0.84 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.53, 158.92, 135.83, 135.75, 134.92, 133.49, 133.16, 130.93, 129.94, 129.92, 127.68, 127.65, 122.31, 72.34, 34.97, 26.96, 20.56, 19.30, 14.02.

***tert*-Butyl(((*S*,3*E*,7*Z*)-deca-3,7-dien-1-yn-5-yl)oxy)diphenylsilane (5A).** To a solution of CBr_4 (440 mg, 1.33 mmol) at 0 °C in anhydrous CH_2Cl_2 (25 mL total volume) was cannulated PPh_3 (692 mg, 2.65 mmol) to give a clear yellow solution. To the reaction mixture at 0 °C was added aldehyde **(19)** (278 mg, 0.66 mmol). The reaction was run for 1 h. Upon completion and without workup, the solvent was evaporated *in vacuo* and the crude mixture was purified on silica gel using EtOAc-Hexanes (1%) as the eluent to afford the dibromide intermediate (351 mg, 97%) as a viscous and yellow colored oil. To a solution of this intermediate (351 mg, 64 mmol) at –78 °C in anhydrous THF (15 mL) was added 2.0 M solution of LDA (1.92 mL, 3.84 mmol) dropwise and stirred for 0.5 h. The reaction was quenched with water (30 mL) and extracted with Et_2O (3 x 30 mL), dried using $MgSO_4$, filtered and concentrated. The crude was then purified using silica gel with a EtOAc-Hexanes eluent (2%) to afford the alkyne product (213 mg, 86%) as a viscous and yellow colored oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (m, 4H), 7.39 (m, 6H), 6.26 (dd, *J* = 16.1, 5.7 Hz, 1H), 5.63 (dt, *J* = 15.9, 1.9 Hz, 1H), 5.36 (m, 1H), 5.18 (m, 1H), 4.26 (q, *J* = 5.1 Hz, 1H), 2.87 (d, *J* = 2.2 Hz, 1H), 2.13 (m, 2H), 1.83 (td, *J* = 7.5, 6.7, 3.2 Hz, 2H), 1.12 (s, 9H), 0.88 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.18, 135.85, 135.83, 134.24, 133.96, 133.50, 129.72, 129.69, 127.56, 123.04, 108.22, 82.04, 73.01, 35.36, 27.00, 20.54, 19.33, 14.06.

***tert*-Butyl(((*R*,3*E*,7*Z*)-deca-3,7-dien-1-yn-5-yl)oxy)dimethylsilane (5B).** Following the above procedure for TBDPS-protected (**5A**), the silyl group of **5B** was switched from TBDPS to TBS ether. In THF (4 mL) the residue (255 mg, 0.65 mmol) was added to a 1.0 M solution of TBAF (1.6 mL, 1.60 mmol) at 0 °C and stirred for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (7 mL) and extracted with Et_2O (3 x 7 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was dissolved in CH_2Cl_2 (3 mL) and cooled to 0 °C, then 2,6-lutidine (0.135 mL 1.16 mmol) and TBDMS triflate (0.27 mL 1.16 mmol) were added and the reaction mixture was allowed to stir overnight at room temperature. It was then quenched with saturated aqueous NH_4Cl (125 mL) and extracted with Et_2O (3 x 125 mL). The combined extract was dried with Na_2SO_4 and evaporated to give a crude yellow oil which was then chromatographed on silica gel using EtOAc-Hexanes (2%) as the eluent to afford the TBS-protected terminal alkyne (**5B**) as a viscous and yellow oil (127 mg, 73%) over two steps. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.25 (dd, *J* = 15.9, 5.1 Hz, 1H), 5.66 (d, *J* = 15.9 Hz, 1H), 5.43 (m, 1H), 5.28 (m, 1H), 4.14 (m, 1H), 2.86 (d, *J* = 2.3 Hz, 1H), 2.20 (m, 2H), 1.95 (m, 2H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.90 (s, 9H), 0.05 (d, *J* = 6.0 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.66, 133.76, 123.48, 107.31, 107.30, 81.76, 71.94, 35.41, 25.50, 20.41, 17.89, 13.81, -4.98, -5.14.

Methyl-(4*S*, 5*R*, 17*R*, 6*E*, 8*E*, 15*E*, 19*Z*)-tris-(*tert*-butyldimethylsilyloxy)-docosa- 6,8,15,19-tetraen-10,13-diynoate (3B). To a flame dried flask with CuI (42 mg, 0.22 mmol), NaI (33 mg, 0.22 mmol), and K_2CO_3 (30 mg, 0.22 mmol) in dry DMF (5 mL total volume) was cannulated alkyne **(5B)** (60 mg, 0.22 mmol) and allylic bromide (**4)** (60 mg, 0.11 mmol) at –20 °C. The reaction was allowed to warm up to room temperature and, stirred for 18 h, and quenched with saturated NH_4Cl (5 mL). The mixture was extracted with Et_2O (3 x 5 mL), rinsed with water to remove any DMF, and the organic layer was dried with $MgSO_4$, filtered and the solvent removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (1%) as the eluent to afford compound (**3B)** as a clear colorless oil (71 mg, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.55 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.14 (m, 2H), 5.72 (dd, *J* = 10.5, 5.3 Hz, 1H), 5.58 (m, 2H), 5.47 (m, 1H), 5.34 (d, *J* = 7.4 Hz, 1H), 4.16 (q, *J* = 5.6, 5.0 Hz, 1H), 3.96 (dd, *J* = 7.0, 4.8 Hz, 1H), 3.65 (s, 3H), 3.61 (q, *J* = 5.0 Hz, 1H), 3.44 (s, 2H), 2.33 (m, 2H), 2.18 (m, 2H), 1.97 (m, 2H), 1.77 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.88 (m, 27H), -0.02 (m, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.20, 145.99, 141.09, 136.79, 133.89, 130.72, 124.01, 110.86, 108.44, 85.91, 83.29, 79.85, 79.06, 76.55, 75.01, 72.43, 35.84, 29.41, 28.24, 25.91, 20.72, 18.19, 18.09, 14.14, 11.29, -4.04, -4.12, -4.61, -4.70, -4.78, -4.83.

Methyl-(4*S*, 5*R*, 17*R*, 6*E*, 8*E*, 15*E*, 19*Z*)-4,5-bis((*tert*-butyldimethylsilyl)oxy)-17-((*tert*-butyldiphenylsilyl)oxy)docosa-6,8,15,19-tetraen-10,13-diynoate (3A). This compound was prepared from allylic bromide **(4)**, and alkyne **(5A)** similarly to its epimer, compound **(3B**), in 84% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.63 (m, 4H), 7.42 (m, 2H), 7.37 (m, 4H), 6.55 (dd, *J* = 15.6, 10.8 Hz, 1H), 6.16 (dd, *J* = 15.3, 10.9 Hz, 2H), 5.71 (dd, *J* = 15.3, 7.2 Hz, 1H), 5.57 (m, 2H), 5.35 (m, 1H), 5.16 (m, 1H), 4.15 (m, 1H), 3.96 (dd, *J* = 7.1, 4.8 Hz, 1H), 3.66 (s, 3H), 3.62 (q, *J* = 5.1 Hz, 1H), 3.44 (t, *J* = 2.2 Hz, 2H), 2.39 (m, 2H), 2.17 (m, 1H), 1.89 (m, 2H), 1.76 (m, 2H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.24 (s, 9H), 0.89 (s, 15H), 0.82 (s, 3H), 0.03 (s, 12H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 174.25, 145.26, 141.11, 135.86, 134.09, 129.63, 127.54, 123.24, 110.86, 109.01, 85.94,

83.31, 79.87, 79.11, 76.55, 75.01, 73.12, 51.48, 35.43, 29.43, 28.25, 27.01, 25.93, 20.54, 18.21, 18.11, 14.06, 11.32, -4.03, -4.10, -4.69, -4.77.

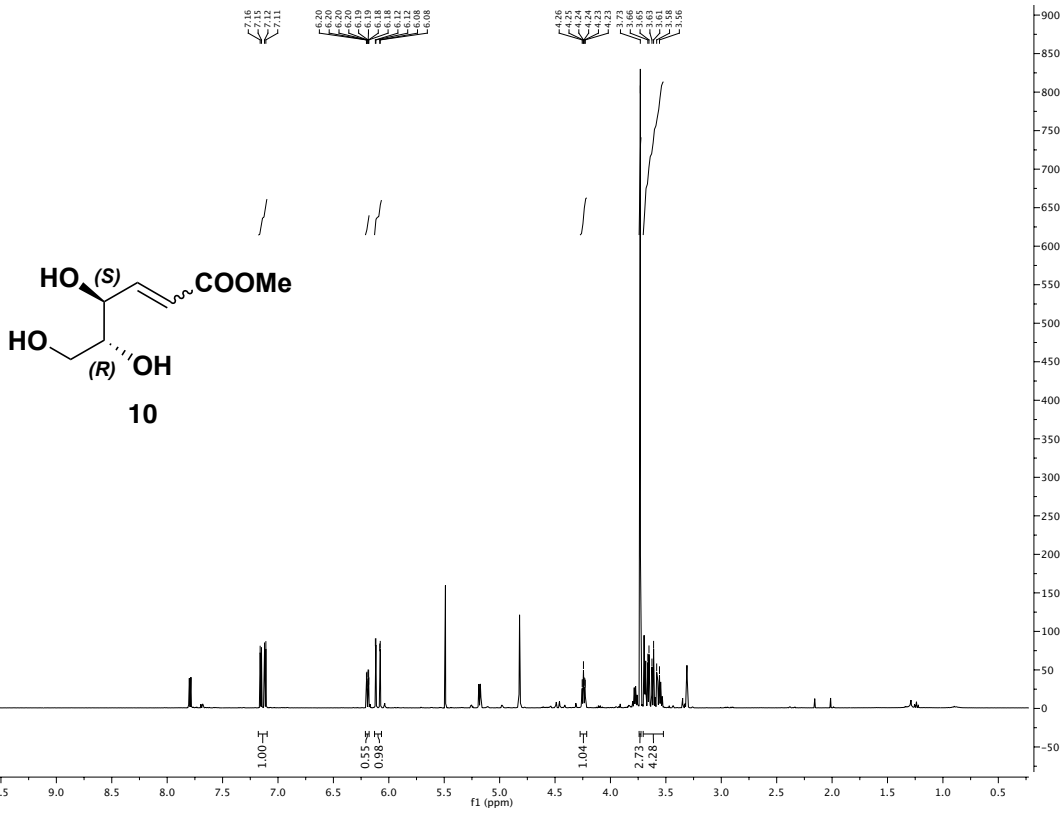
(4*S*,5*R*,6*E*,8*E*,10*Z*,13*Z*,15*E*,17*R*,19*Z*)-4,5,17-trihydroxydocosa-6,8,10,13,15,19-hexaenoic acid (1B). Part 1: To a solution of compound **(3B)** (71 mg, 0.097 mmol) in EtOAc, (4 mL), Octene, (0.4 mL), and Pyridine (0.4 mL) was added Lindlar catalyst (20 mg) and the reaction mixture was allowed to stir at room temperature under a H_2 atmosphere (1 atm). After 6 h the reaction mixture was filtered through Celite and the solvents were removed *in vacuo*. The crude reaction mixture was purified on silica gel using EtOAc-Hexanes (1%) as the eluent to afford compound **(2B)** as a clear colorless oil (51 mg, 72%). ^{1}H NMR (400 MHz, Methanol-d_4) δ 6.56 (m, 2H), 6.23 (m, 2H), 6.03 (m, 2H), 5.64 (m, 2H), 5.40 (m, 4H), 4.26 (dd, *J* = 6.4, 1.0 Hz, 1H), 4.06 (dd, *J* = 7.7, 4.2 Hz, 1H), 3.69 (q, *J* = 5.3 Hz, 1H), 3.65 (s, 3H), 3.05 (m, 2H), 2.38 (m, 2H), 2.25 (t, *J* = 7.4 Hz, 2H), 2.03 (m, 3H), 1.83 (dd, *J* = 13.2, 7.7 Hz, 2H), 1.27 (m, 4H), 0.88 (m, 27H), 0.03 (m, 15H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 175.78, 141.83, 137.98, 134.41, 133.63, 130.85, 129.82, 129.40, 129.11, 125.84, 78.48, 76.33, 74.36, 54.78, 37.31, 32.75, 30.41, 29.44, 27.56, 26.57, 26.54, 26.52, 26.42, 26.21, 23.70, 21.72, 19.17, 19.15, 19.06, 14.45, -3.60, -4.04, -4.34, -4.37, -4.42.

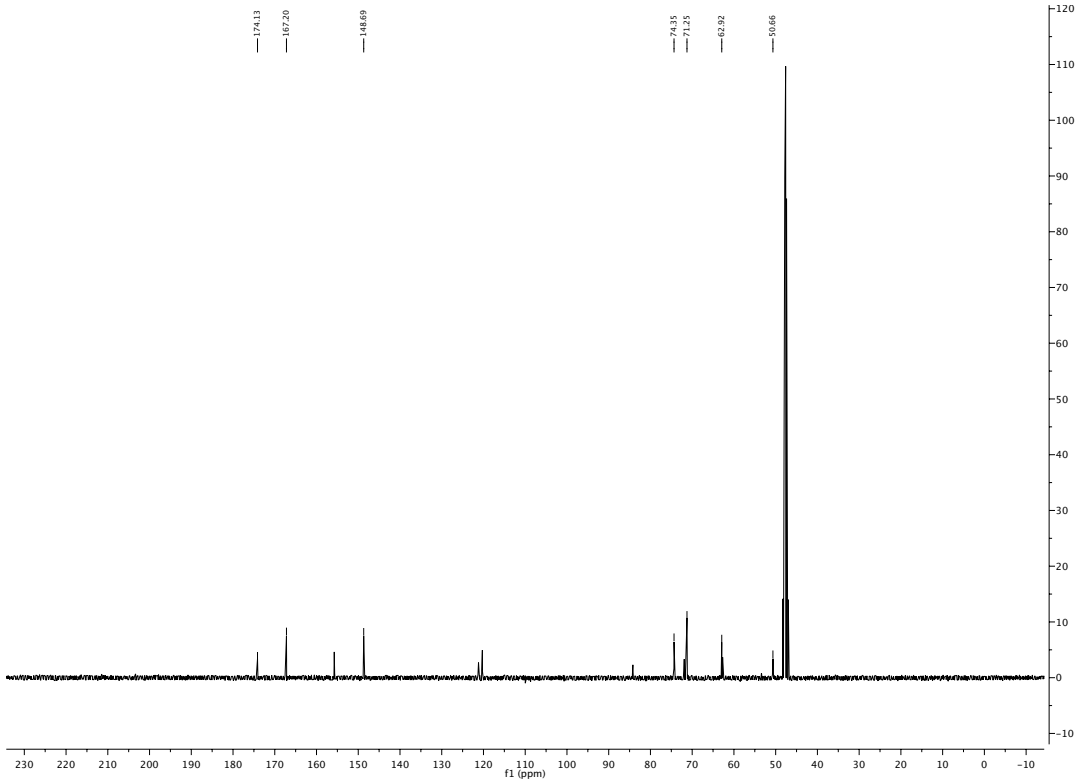
Part 2: To the hydrogenated material (4 mg, 5.5 µmol) dissolved in THF (0.5 mL) was added dropwise 10 equiv of 1M TBAF (55 µL, 55 µmol) at 0 °C. The reaction was monitored closely via thin layer chromatography and after 4 h the reaction was quenched with saturated NH_4Cl (10 mL) and extracted with Et_2O (5 x 10 mL). The organic layer was rinsed with brine, dried over $MgSO_4$ and filtered. The solvent was then concentrated and freshly prepared CH_2N_2 was added to convert any acid back to the methyl ester. The solvent was completely removed *in vacuo* and the compound was purified on silica gel using MeOH/ CH_2Cl_2 (1%) as the eluent to afford an ester/ lactone mixture which we also previously observed on a similar intermediate for Resolvin D3 (*Org. Lett.* **2013**, *15*, 1424, [ref. 12]). Without further chromatographic isolation, this product mixture was then suspended in a H_2O/ MeOH system (1:1, 1 mL) and 10 equiv of LiOH (1.34 mg, 55 µmol) were added. After 3 h the reaction mixture was dried and purified via C-18 reversed Phase HPLC using H_2O/ MeOH mixture (37%) to afford compound **(1B)** (1.15 mg, 58%) as colorless oil. ^{1}H NMR (600 MHz, Methanol-d_4) δ 6.61 – 6.54 (m, 2H), 6.37 (dd, *J* = 15.0, 10.9 Hz, 1H), 6.26 (dd, *J* = 14.6, 11.0 Hz, 1H), 6.08 – 5.97 (m, 2H), 5.83 (dd, *J* = 15.2, 6.8 Hz, 1H), 5.69 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.49 – 5.45 (m, 1H), 5.41 – 5.35 (m, 3H), 4.14 (d, *J* = 6.7 Hz, 1H), 4.01 – 3.97 (m, 1H), 3.55 – 3.50 (m, 1H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.39 – 2.24 (m, 4H), 2.05 (dd, *J* = 15.5, 7.9 Hz, 2H), 1.90 – 1.83 (m, 1H), 1.70 – 1.63 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, Methanol-d_4) δ 182.79, 137.52, 134.62, 134.47, 134.18, 133.14, 132.34, 130.46, 130.24, 130.18, 129.57, 126.27, 125.49, 76.52, 76.22, 73.18, 36.25, 32.75, 27.48, 23.70, 21.68, 14.43. ESI-MS/MS for AT-Resolvin D4 (**1B**), $C_{22}H_{31}O_5^-$, $[M\text{-}H]^-$, *m*/*z* 375 = M-H parent ion and daughter ions at *m*/*z* 357 = M-H-H_2O, *m*/*z* 339 = M-H-2H_2O, *m*/*z* 313 = M-H-H_2O-CO_2, *m*/*z* 295 = M-H-2H_2O-CO_2, *m*/*z* 259 = 277-H_2O, *m*/*z* 225 = 243-H_2O, *m*/*z* 215 = 277-H_2O-CO_2, *m*/*z* 131, *m*/*z* 113 = 131-H_2O, and *m*/*z* 101. UV (Methanol) λ_{max} 228, 276 nm.

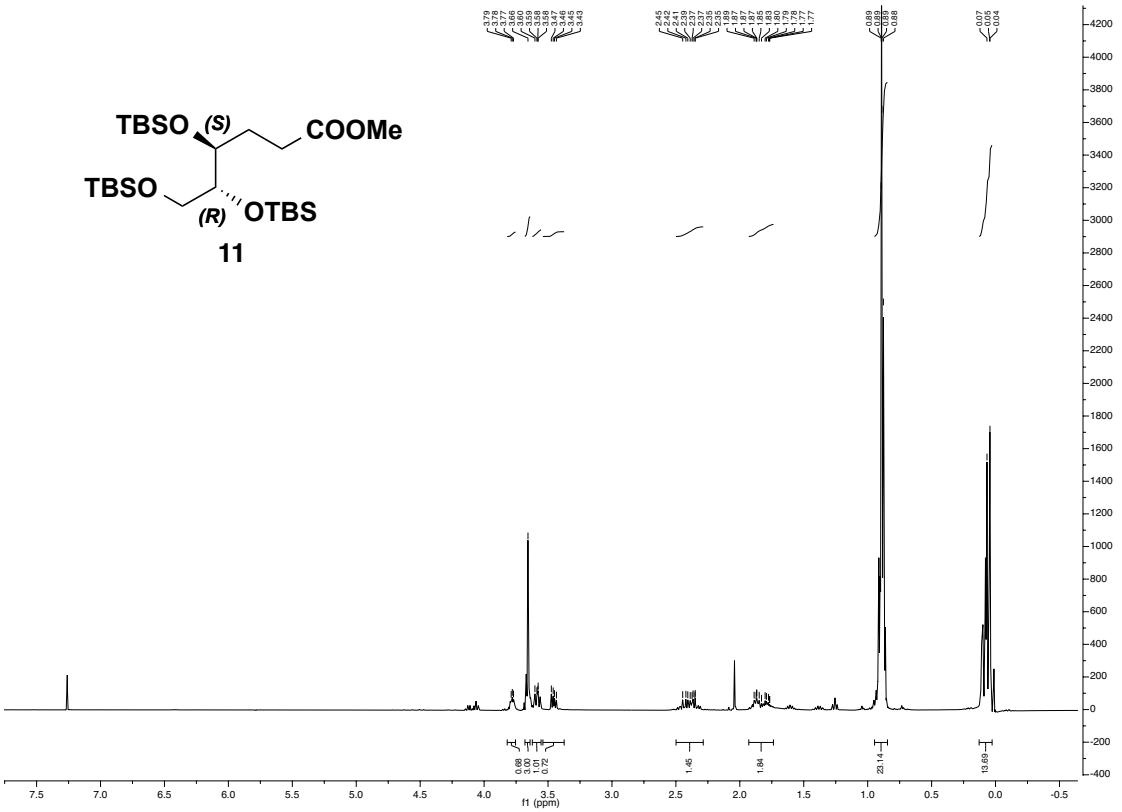
(4*S*,5*R*,6*E*,8*E*,10*Z*,13*Z*,15*E*,17*S*,19*Z*)-4,5,17-trihydroxydocosa-6,8,10,13,15,19-hexaenoic acid (1A). This compound was prepared from **(3A)** similarly to its epimer (**1B**) to furnish **1A** (1.11 mg, 56%) over 3 steps. ^{1}H NMR (600 MHz,

Methanol-d_4) δ 6.57 (t, *J* = 13.0 Hz, 2H), 6.37 (dd, *J* = 15.2, 10.6 Hz, 1H), 6.26 (dd, *J* = 14.8, 10.7 Hz, 1H), 6.08 – 5.97 (m, 2H), 5.83 (dd, *J* = 15.2, 6.8 Hz, 1H), 5.69 (dd, *J* = 15.2, 6.5 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.39 (dt, *J* = 18.0, 8.4 Hz, 3H), 4.14 (d, *J* = 6.5 Hz, 1H), 3.99 (t, *J* = 6.1 Hz, 1H), 3.52 (d, *J* = 6.2 Hz, 1H), 3.11 (t, *J* = 7.7 Hz, 2H), 2.38 – 2.23 (m, 4H), 2.06 (dt, *J* = 15.6, 7.9 Hz, 2H), 1.91 – 1.84 (m, 1H), 1.66 (dd, *J* = 14.8, 7.3 Hz, 1H), 0.96 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, Methanol-d_4) δ 182.81, 137.49, 134.63, 134.44, 134.18, 133.12, 130.56, 130.43, 130.24, 130.18, 129.57, 126.27, 125.47, 76.54, 76.21, 73.16, 36.28, 32.78, 27.50, 23.70, 21.71, 14.62. UV (Methanol) λ_{max} 228, 276 nm. ESI-MS/MS for Resolvin D4 (**1A**), $C_{22}H_{31}O_5^-$, $[M-H]^-$, *m*/*z* 375 = M-H parent ion and daughter ions at *m*/*z* 357 = M-H-H_2O, *m*/*z* 339 = M-H-2H_2O, *m*/*z* 313 = M-H-H_2O-CO_2, *m*/*z* 295 = M-H-2H_2O-CO_2, *m*/*z* 259 = 277-H_2O, *m*/*z* 225 = 243-H_2O, *m*/*z* 215 = 277-H_2O-CO_2, *m*/*z* 131, and *m*/*z* 101. In comparison to the reported syntheses for Resolvin D4 by Kobayashi (*J. Org. Chem.* **2018**, *83*, 3906, ref. 7) and by us and collaborators (*Sci. Rep.* **2016**, *6* (18972), ref. 5; and *J. Leukoc. Biol.* **2018**, *103*, 995, ref. 6), our ^{1}H and ^{13}C NMR spectra of **1A** were consistent with the published data.

Selected ^{1}H NMR and ^{13}C NMR Spectra of Compounds



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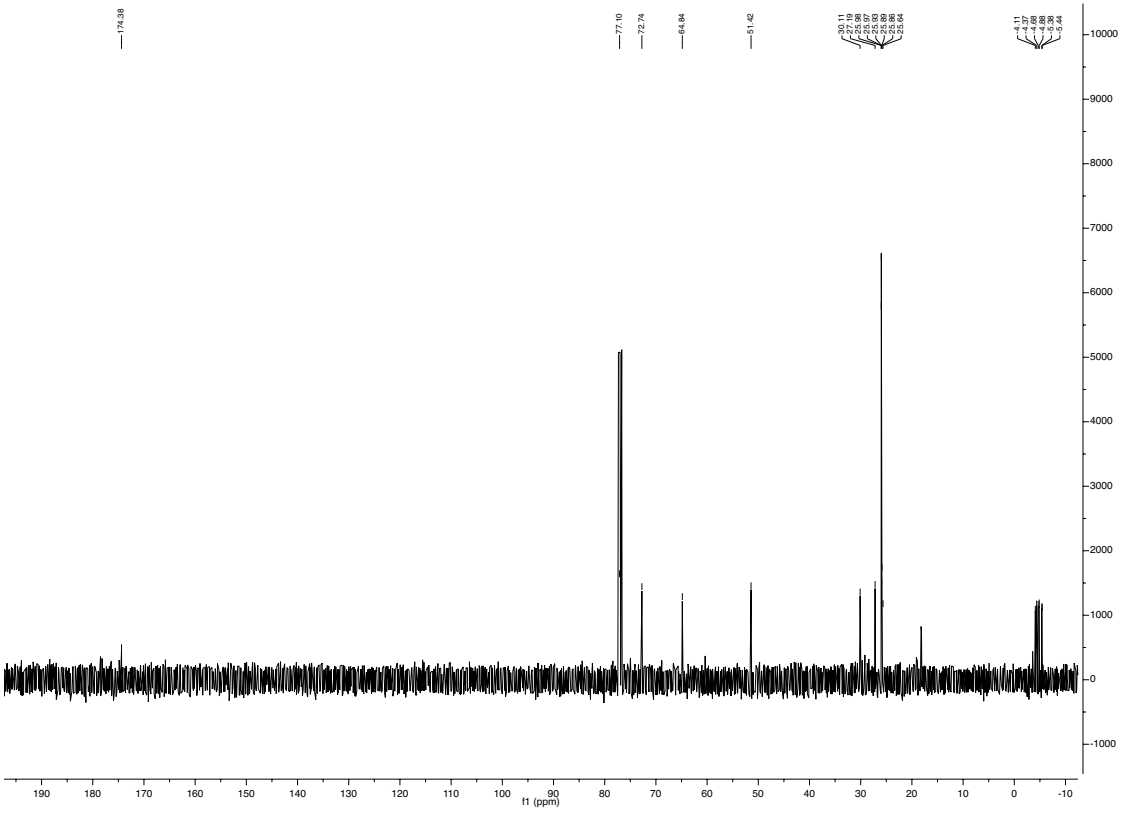
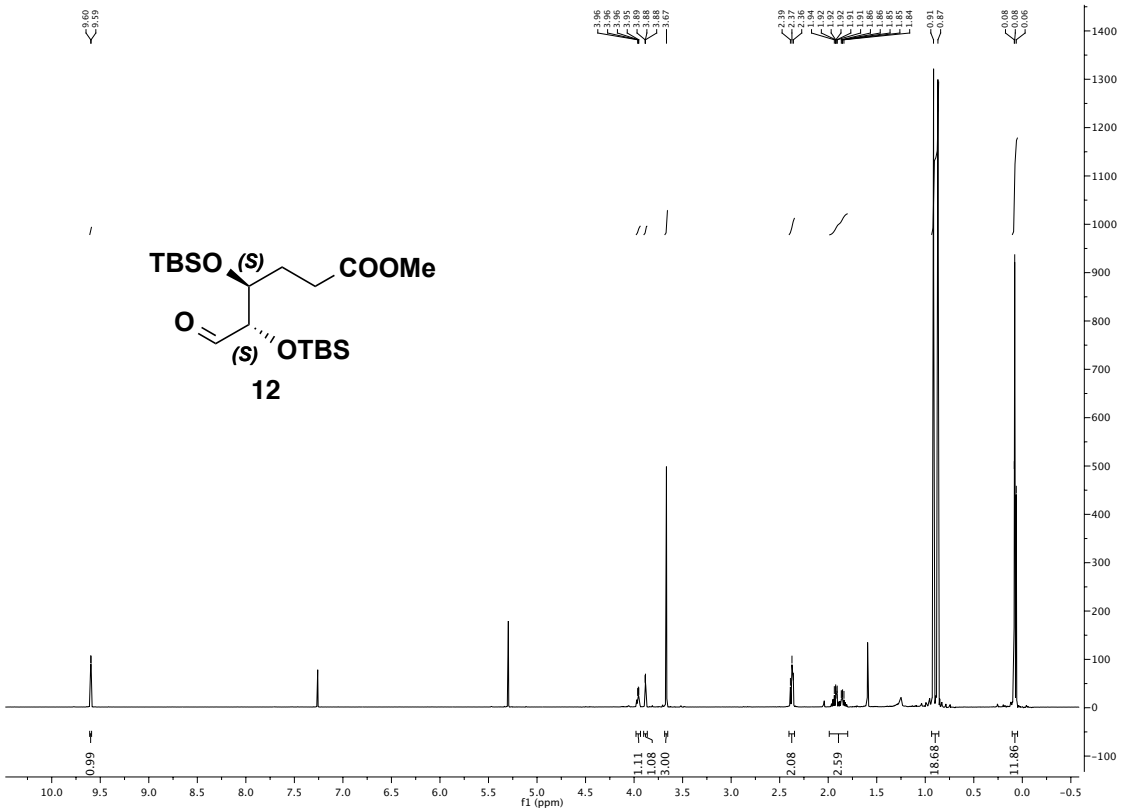
(R)
OTBS
11

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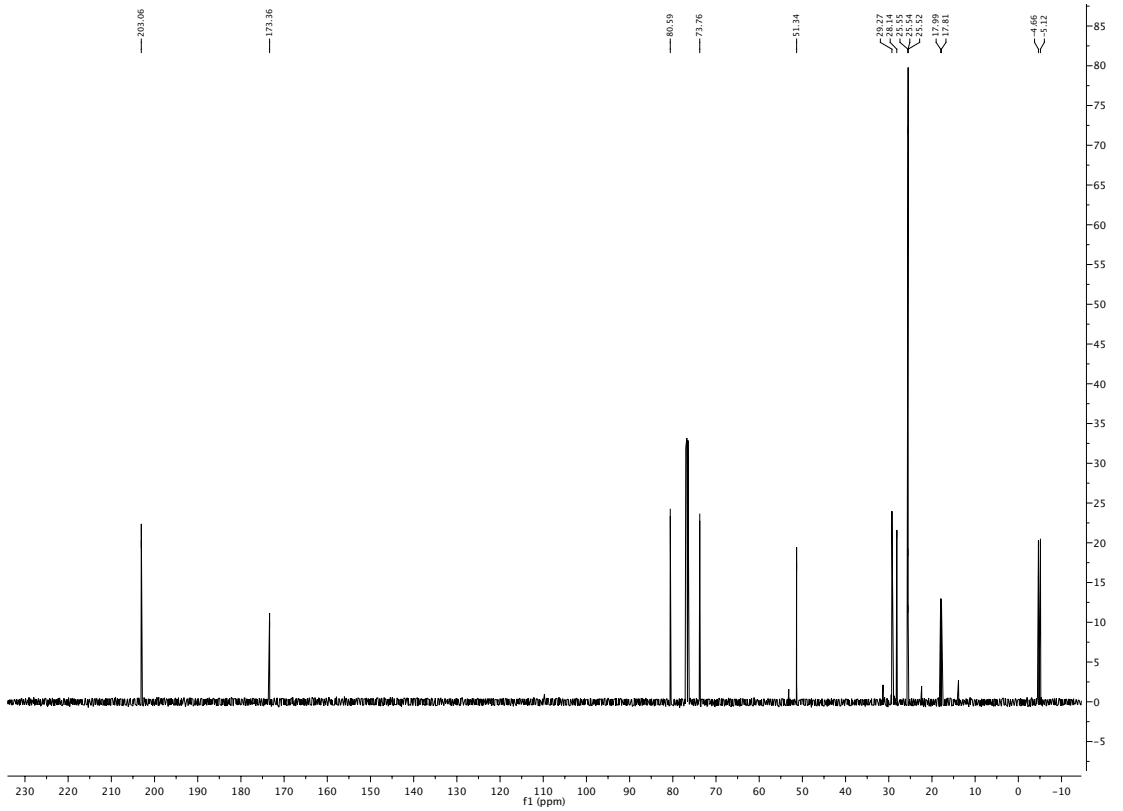
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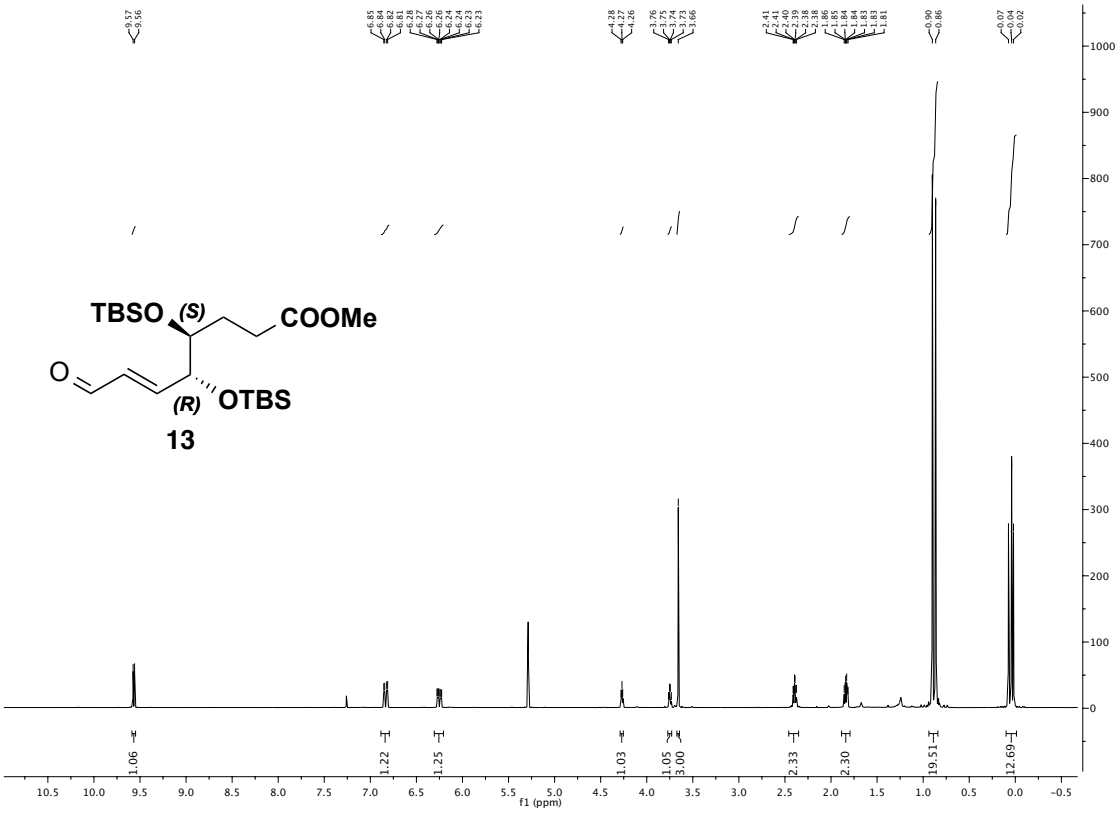
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(R)
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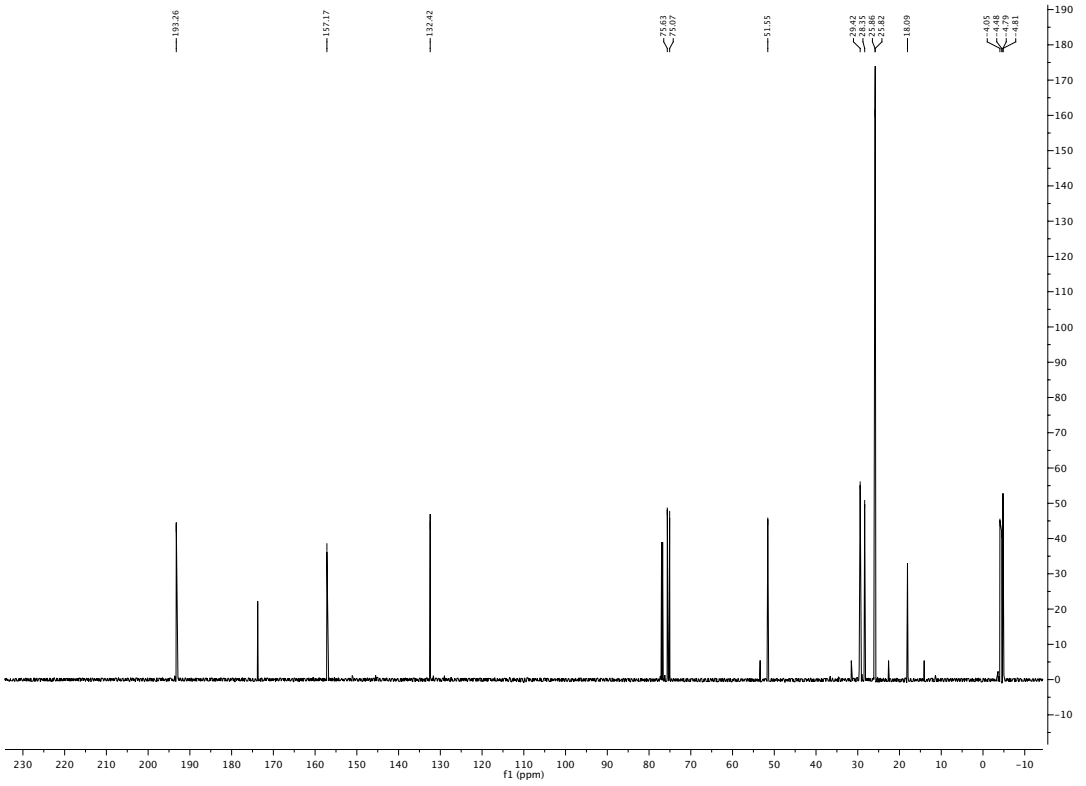
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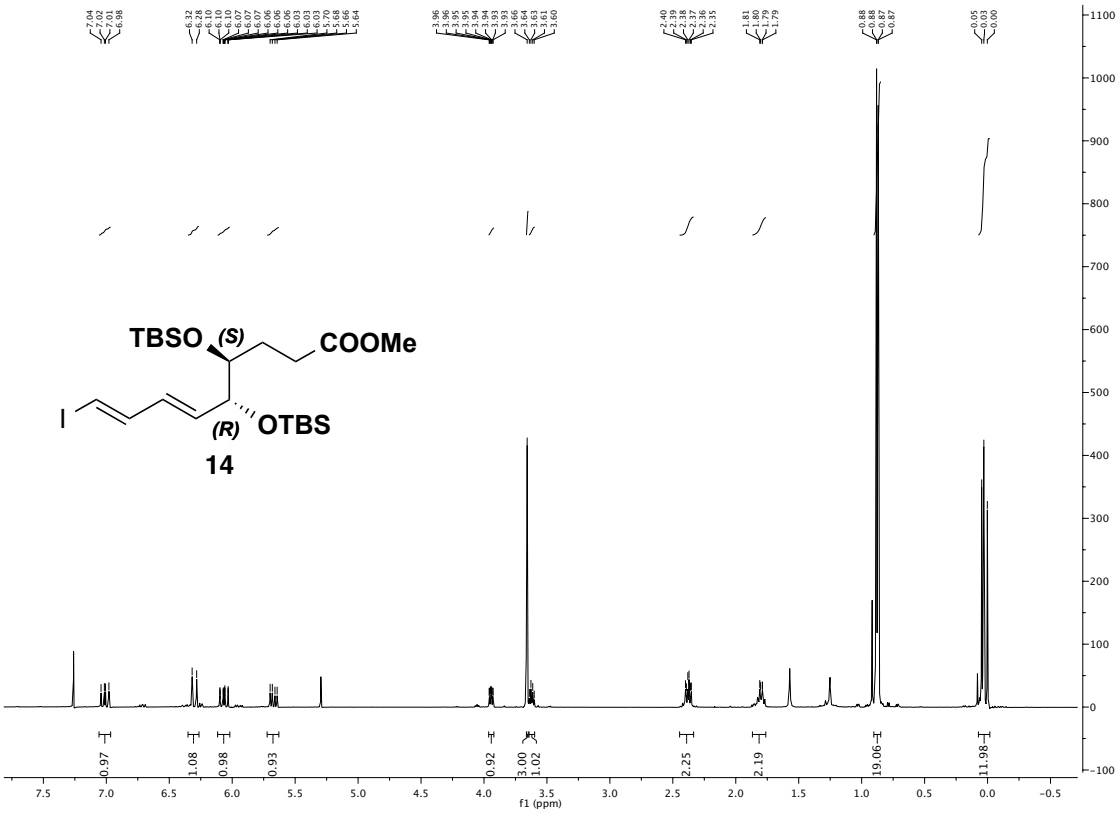
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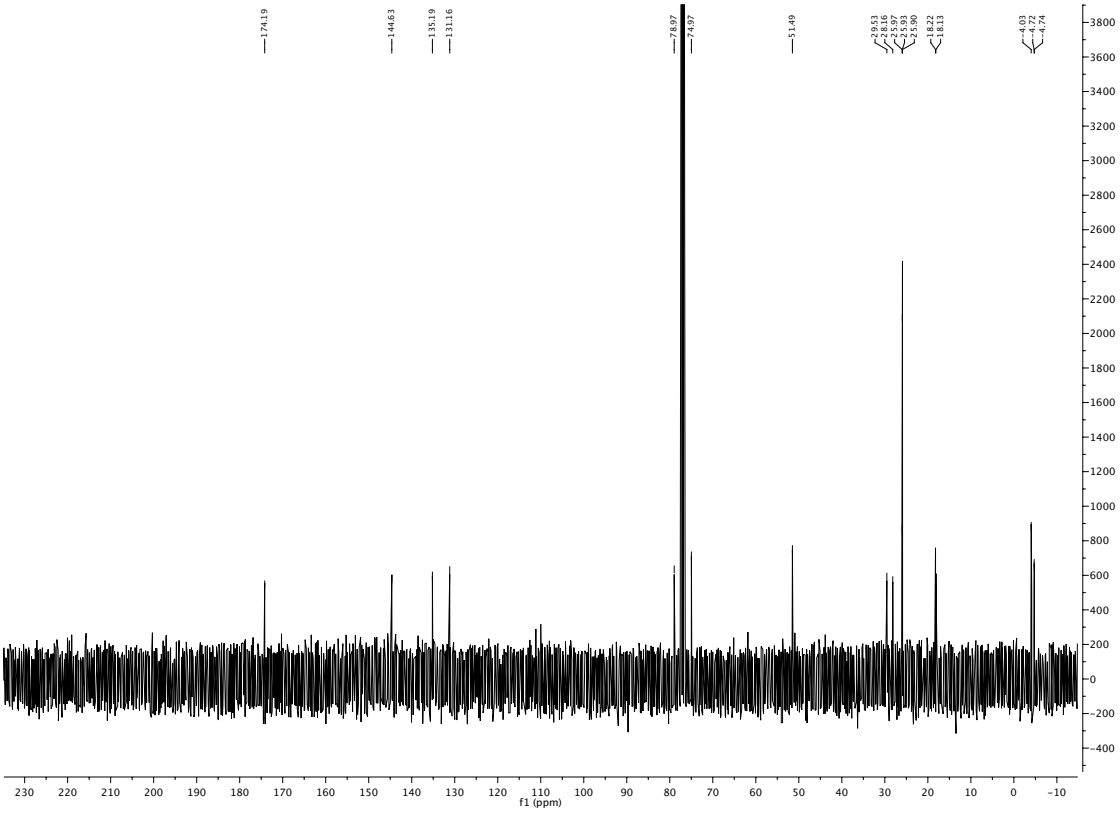
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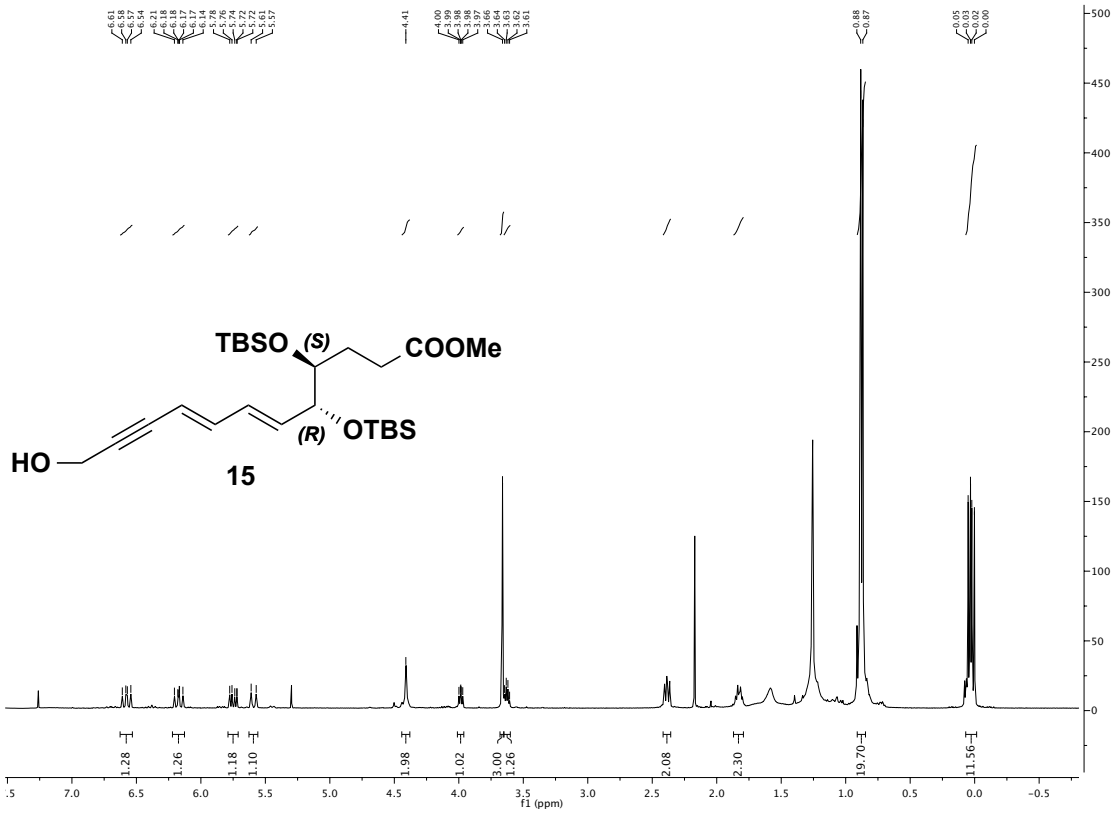
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(R)
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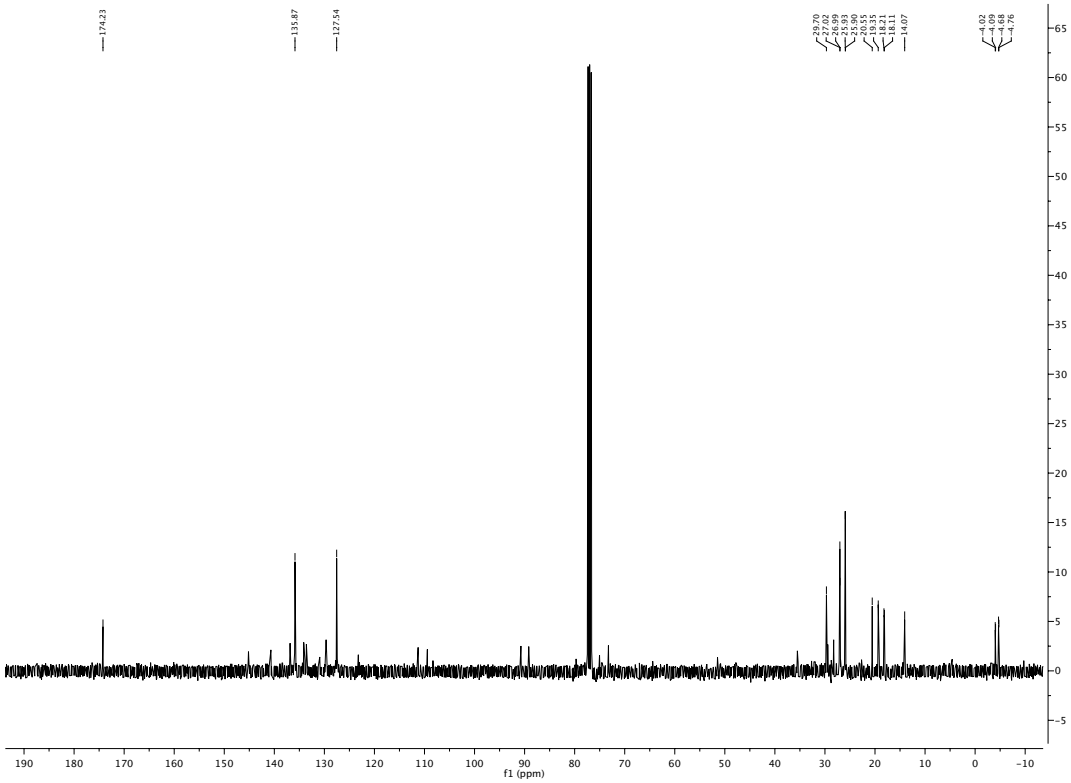
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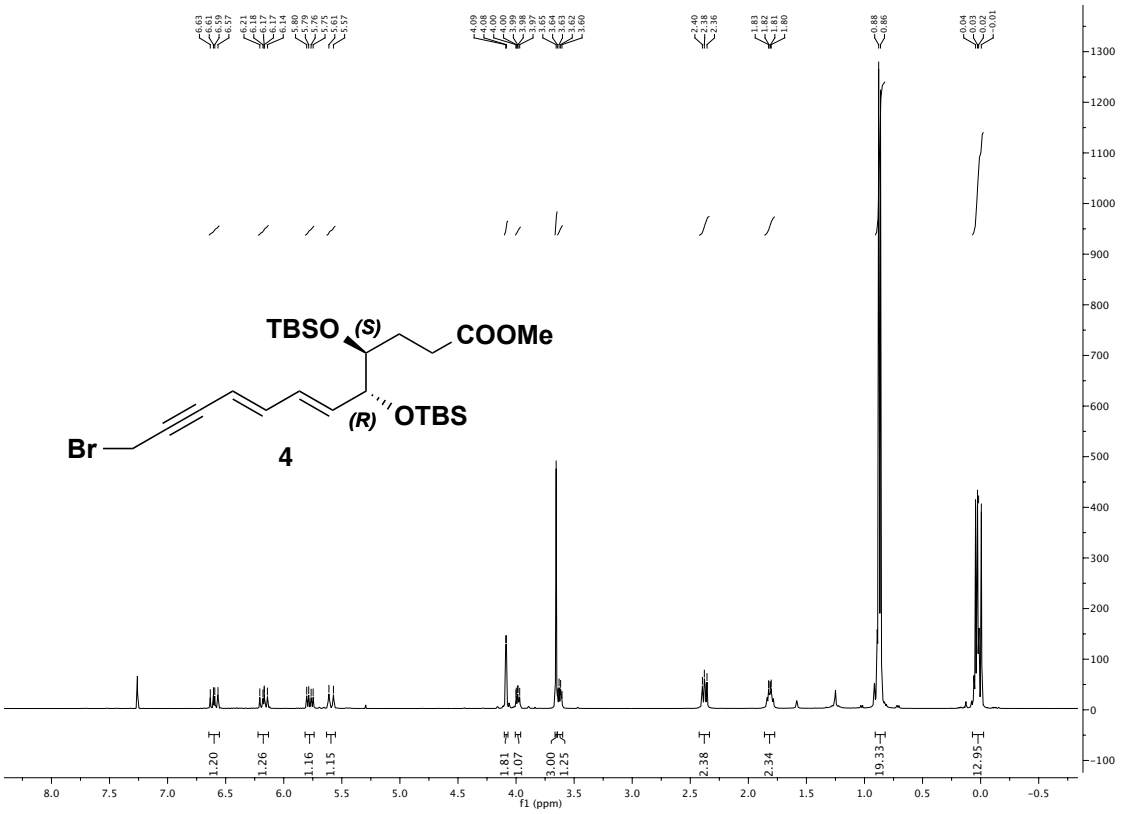
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(S)
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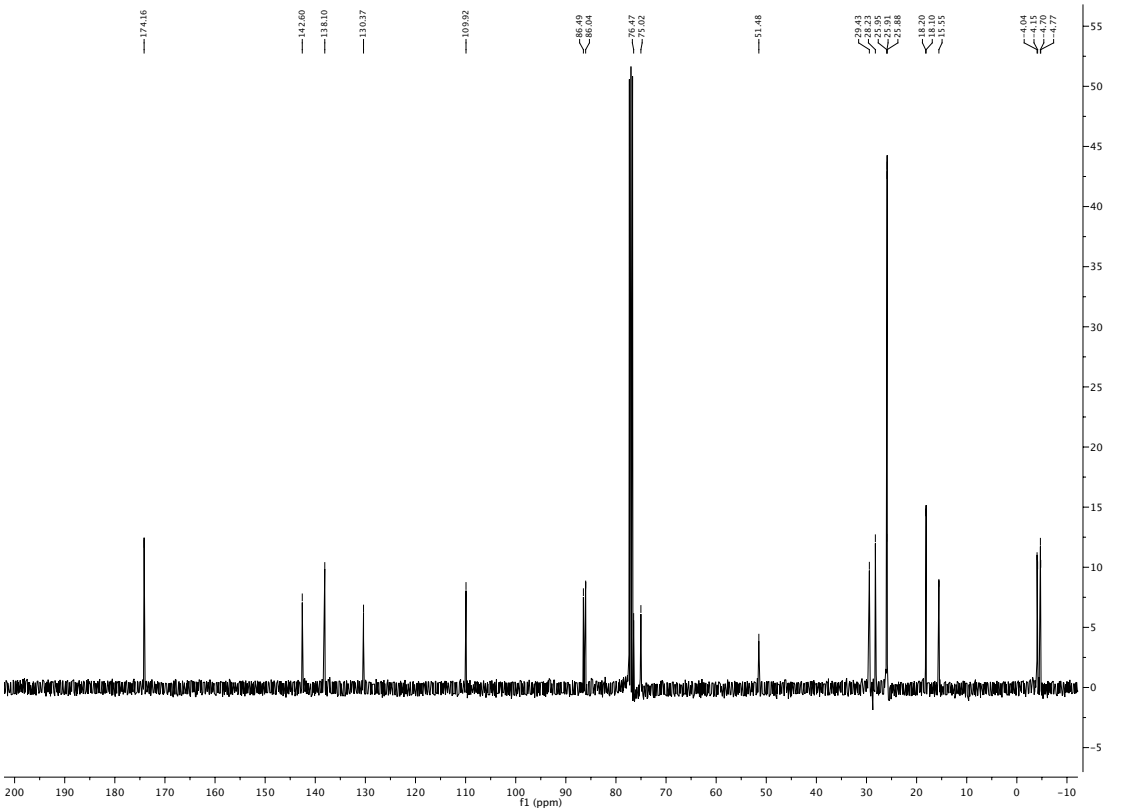
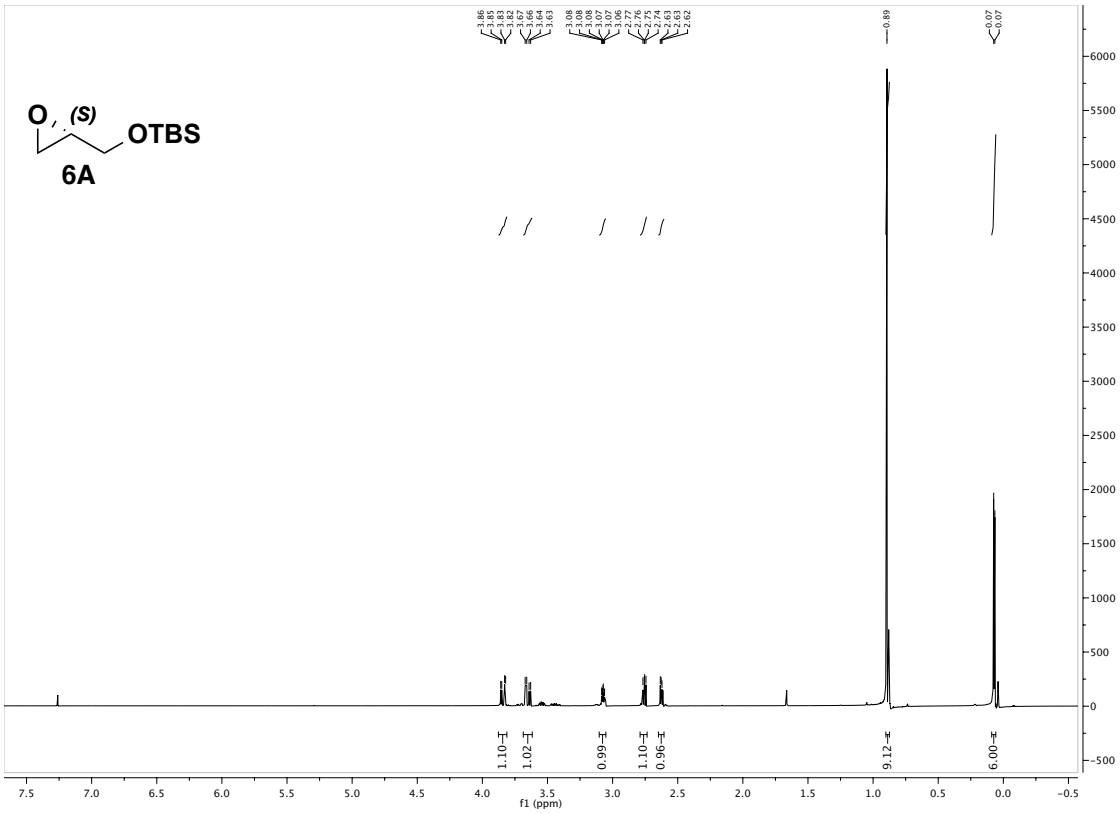
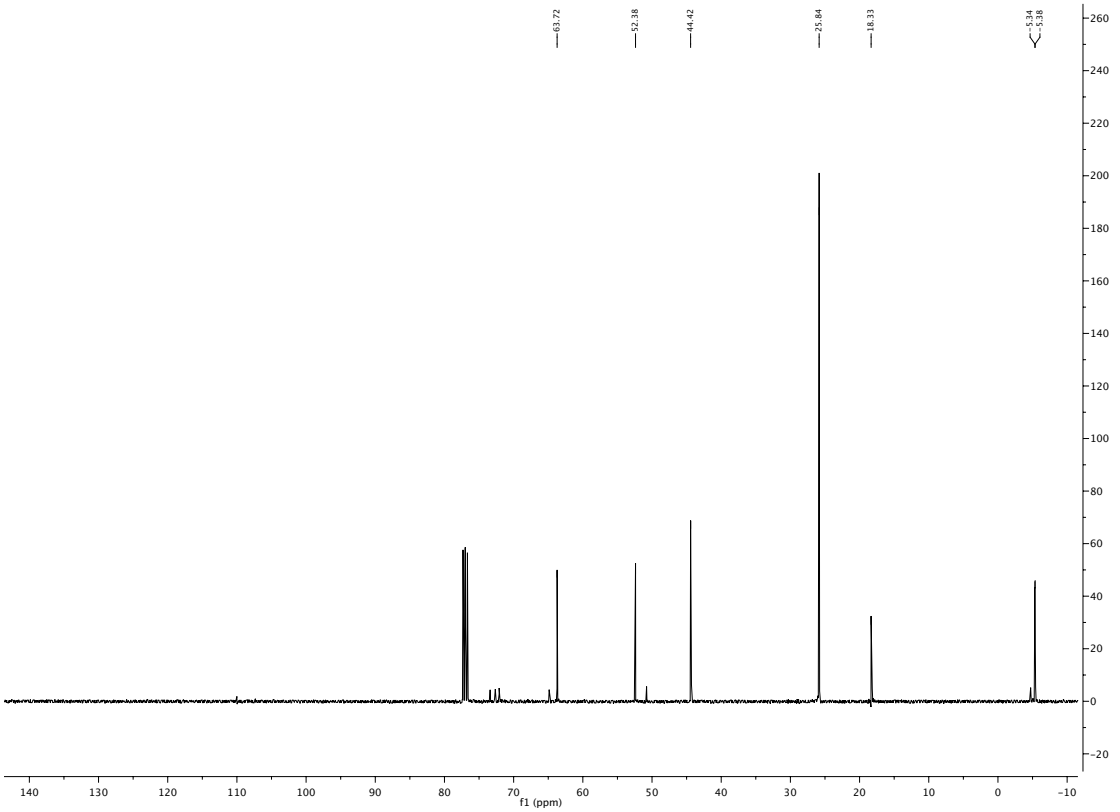
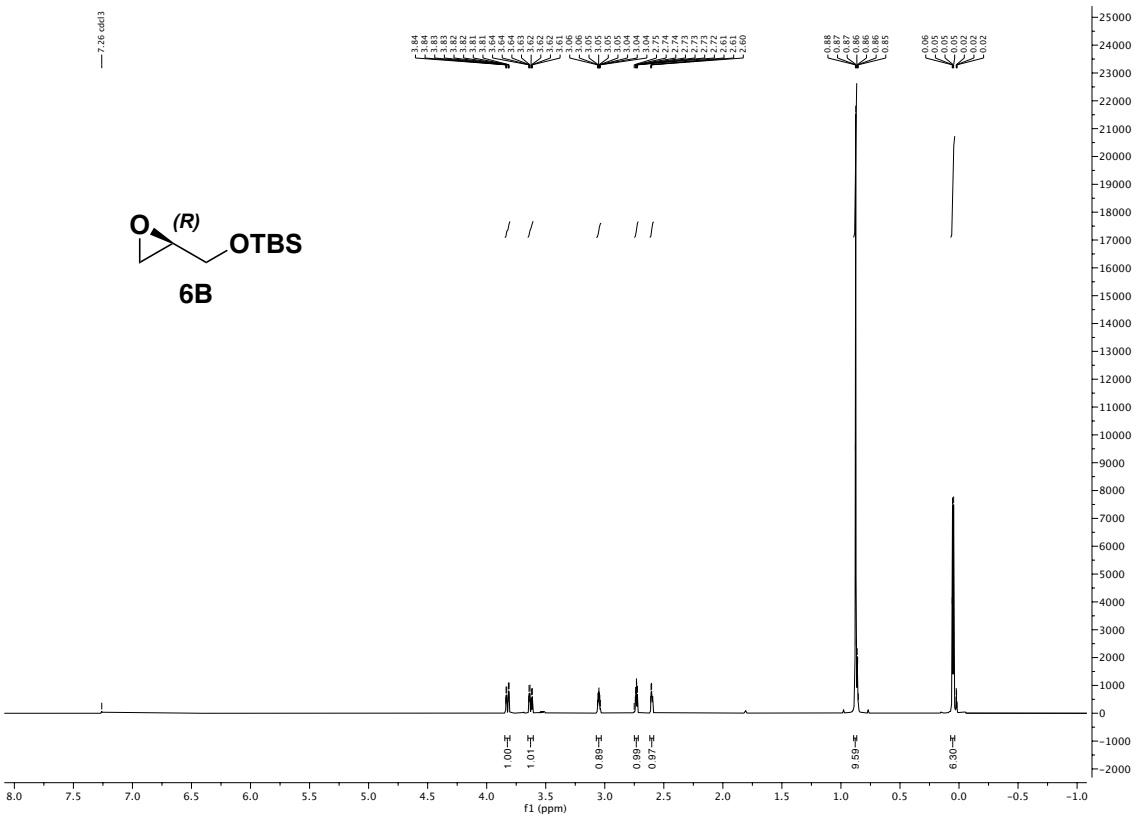
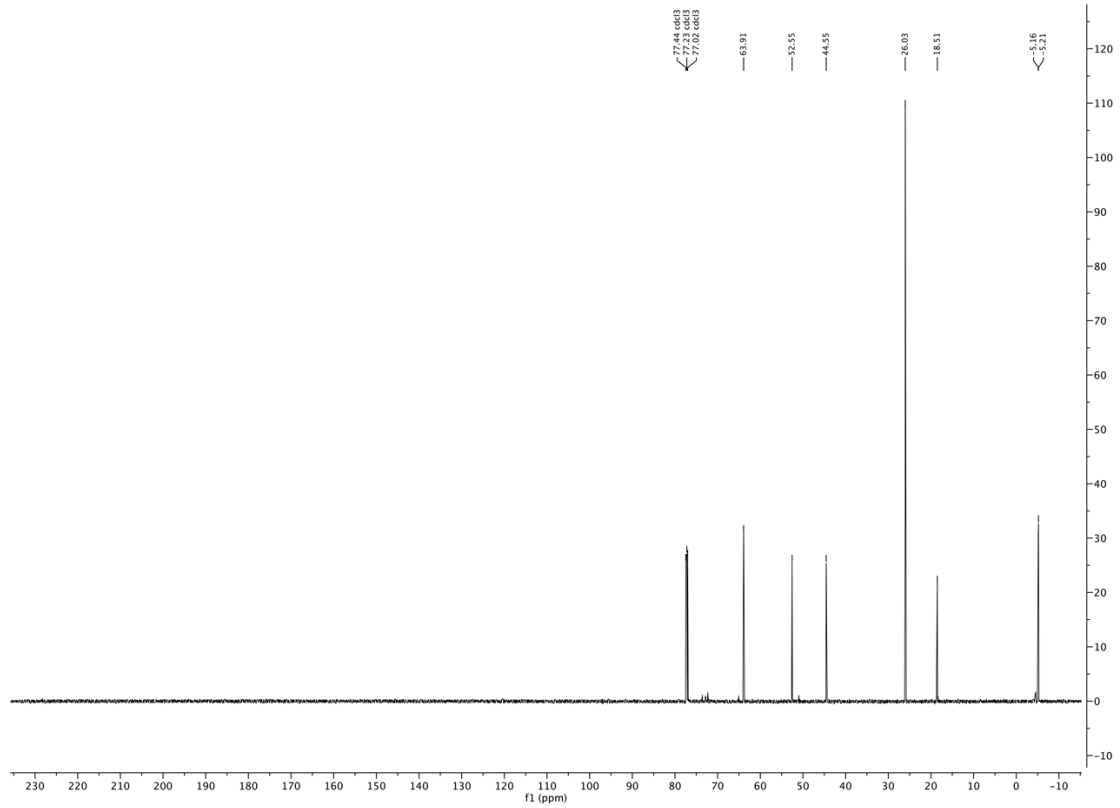
f1 (ppm)

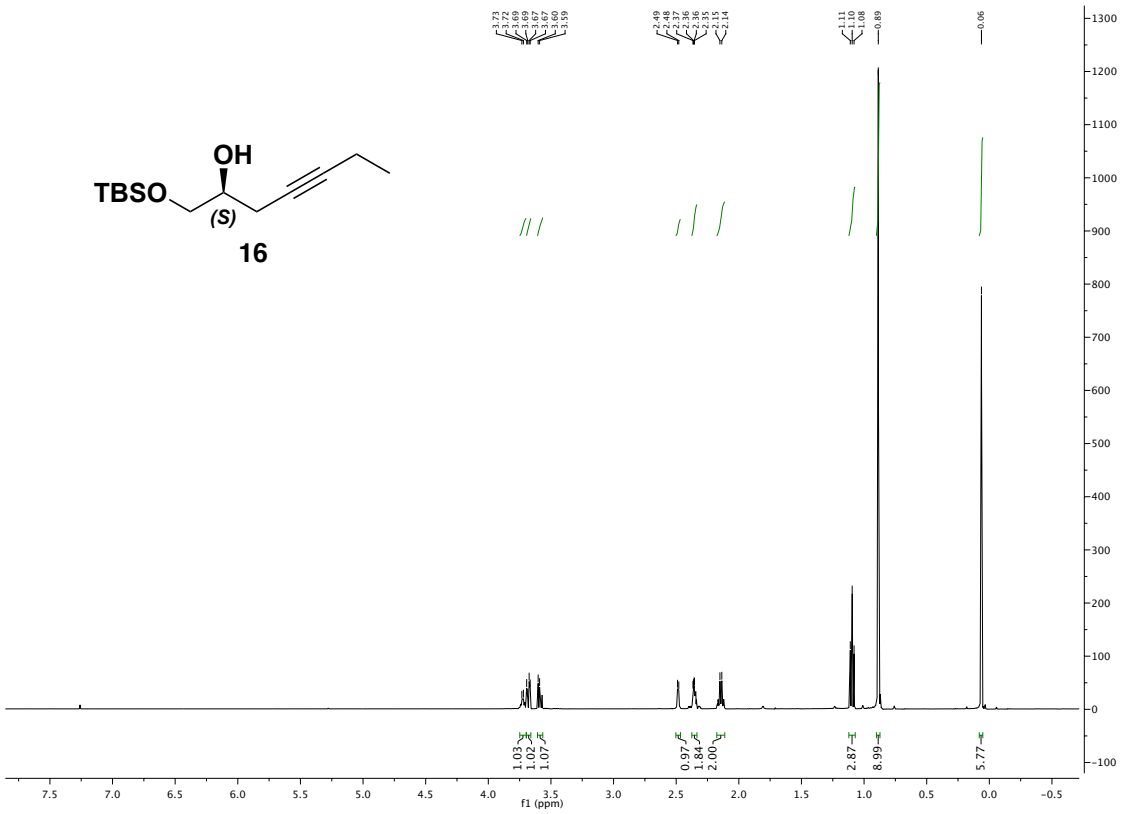

f1 (ppm)

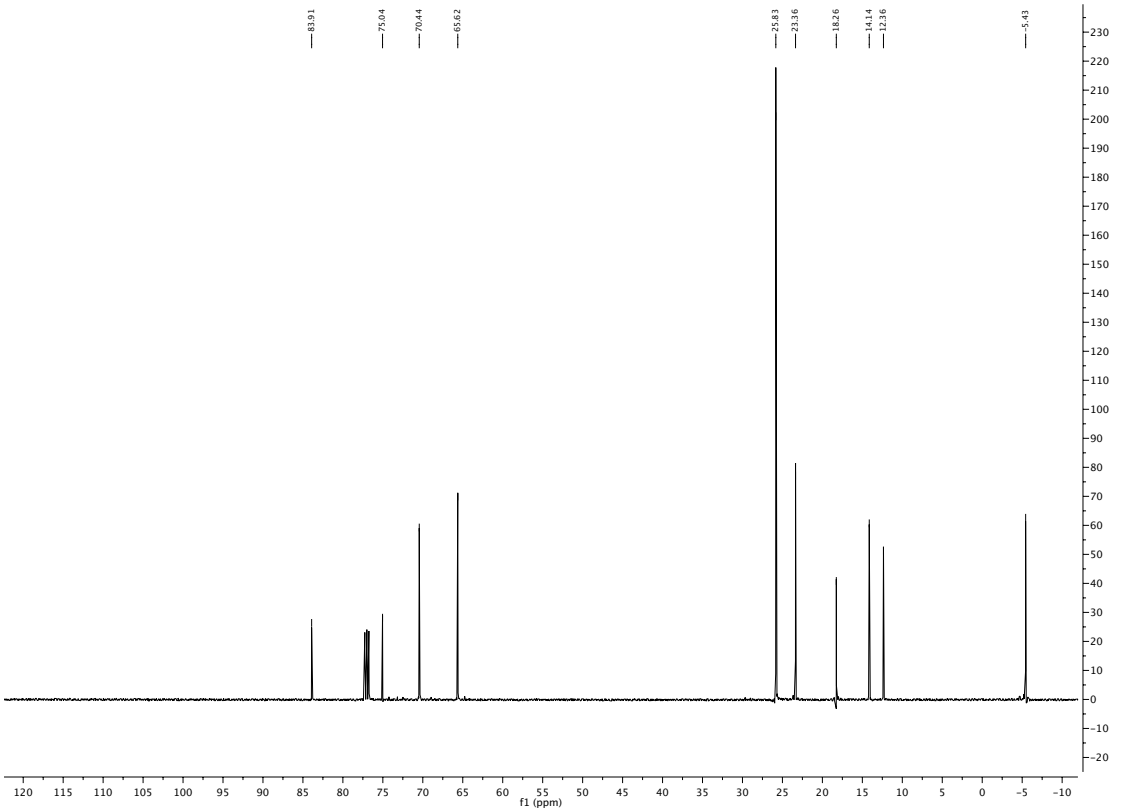

O
(S)
OTBS
6A
3.86
3.85
3.83
3.82
3.67
3.66
3.64
3.63
3.08
3.08
3.08
3.07
3.07
3.06
2.77
2.76
2.75
2.74
2.63
2.63
2.62
0.89
0.07
0.07
1.10
1.02
0.99
1.10
0.96
9.12
6.00
f1 (ppm)

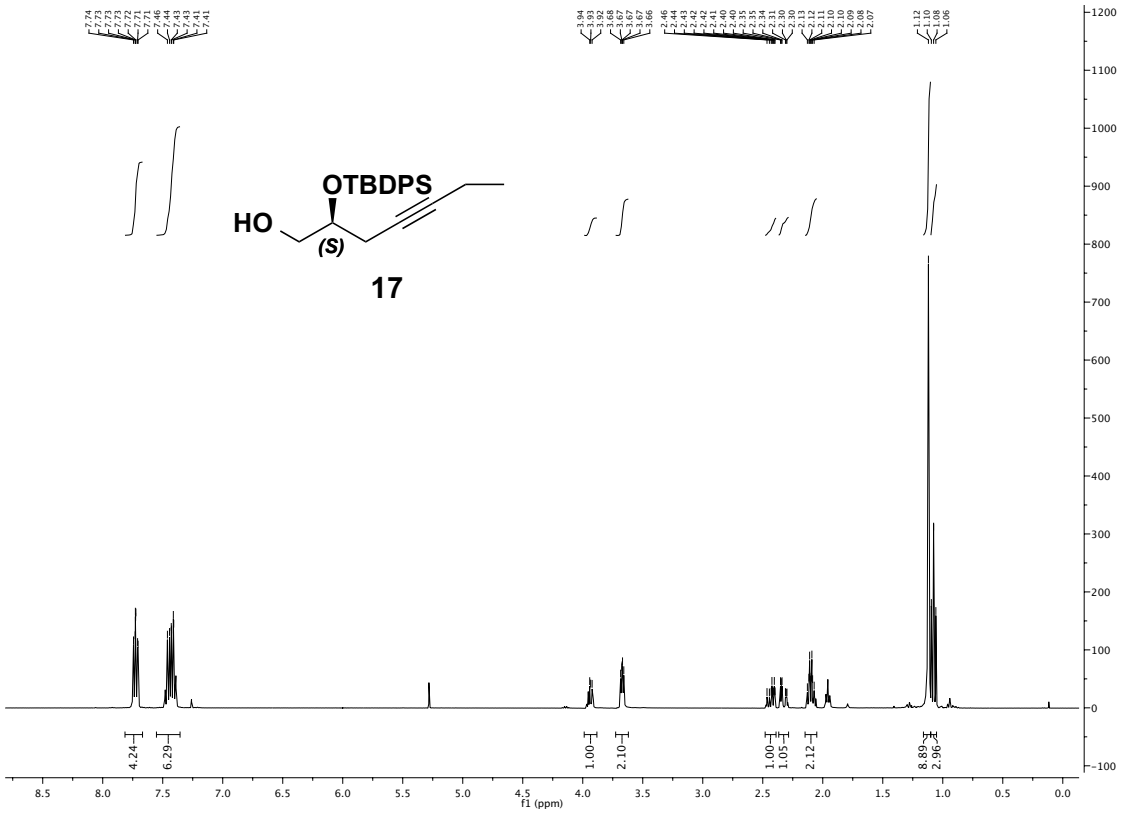

63.72
52.38
44.42
25.84
18.33
5.34
5.38
f1 (ppm)

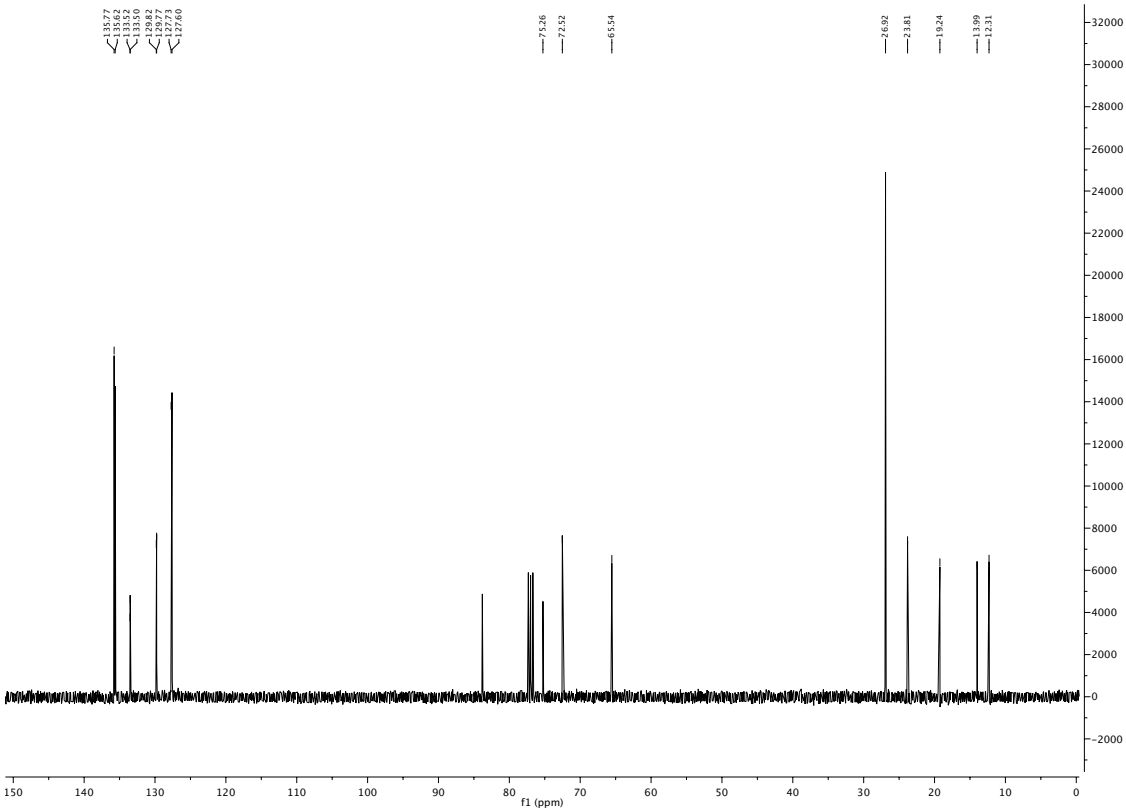

O
(R)
OTBS
6B
f1 (ppm)

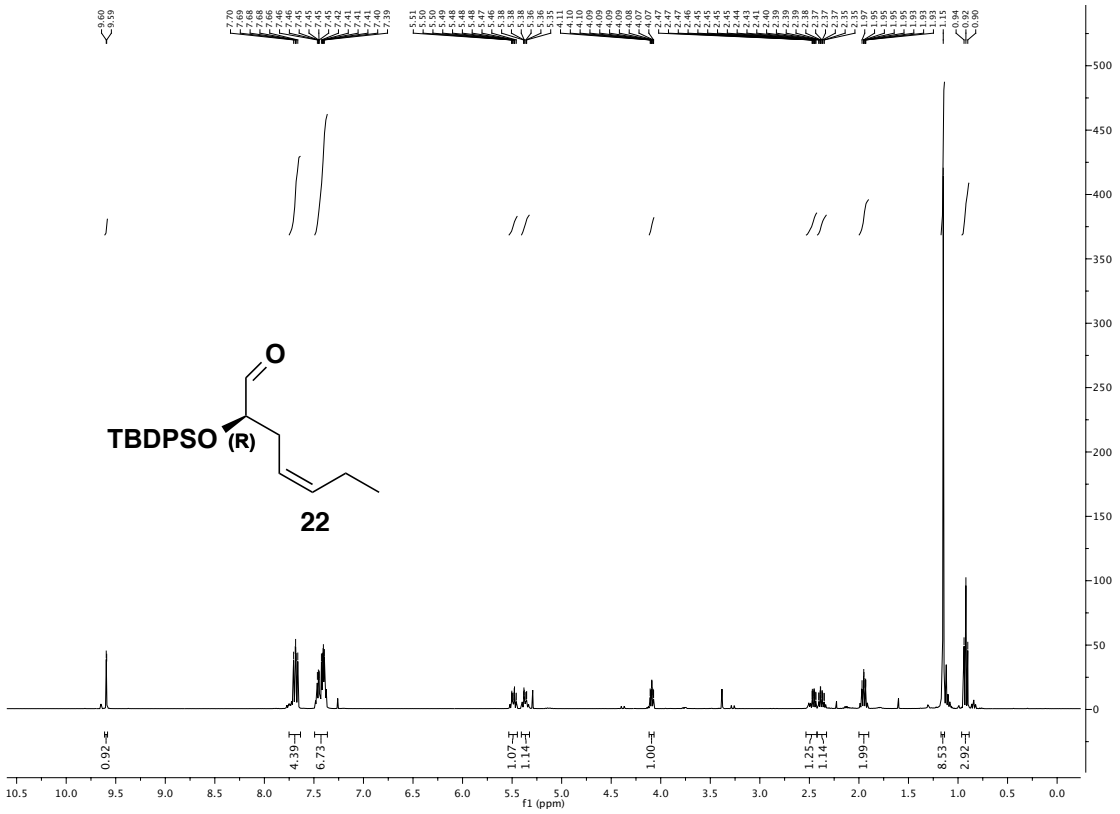

f1 (ppm)

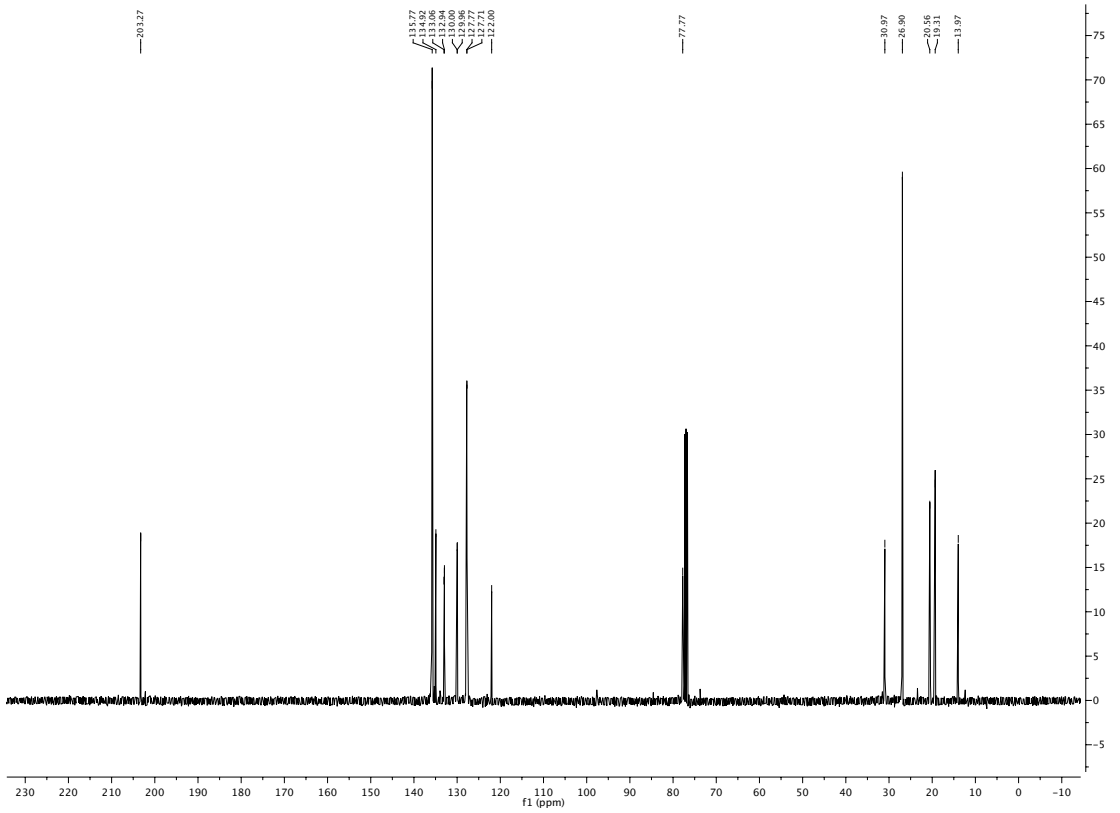

OH
TBSO
(S)
16
3.73
3.72
3.69
3.68
3.67
3.60
3.59
2.49
2.48
2.37
2.36
2.35
2.15
2.14
1.11
1.10
1.08
0.89
0.06
1.03
1.02
1.07
0.97
1.84
2.00
2.87
8.99
5.77
f1 (ppm)

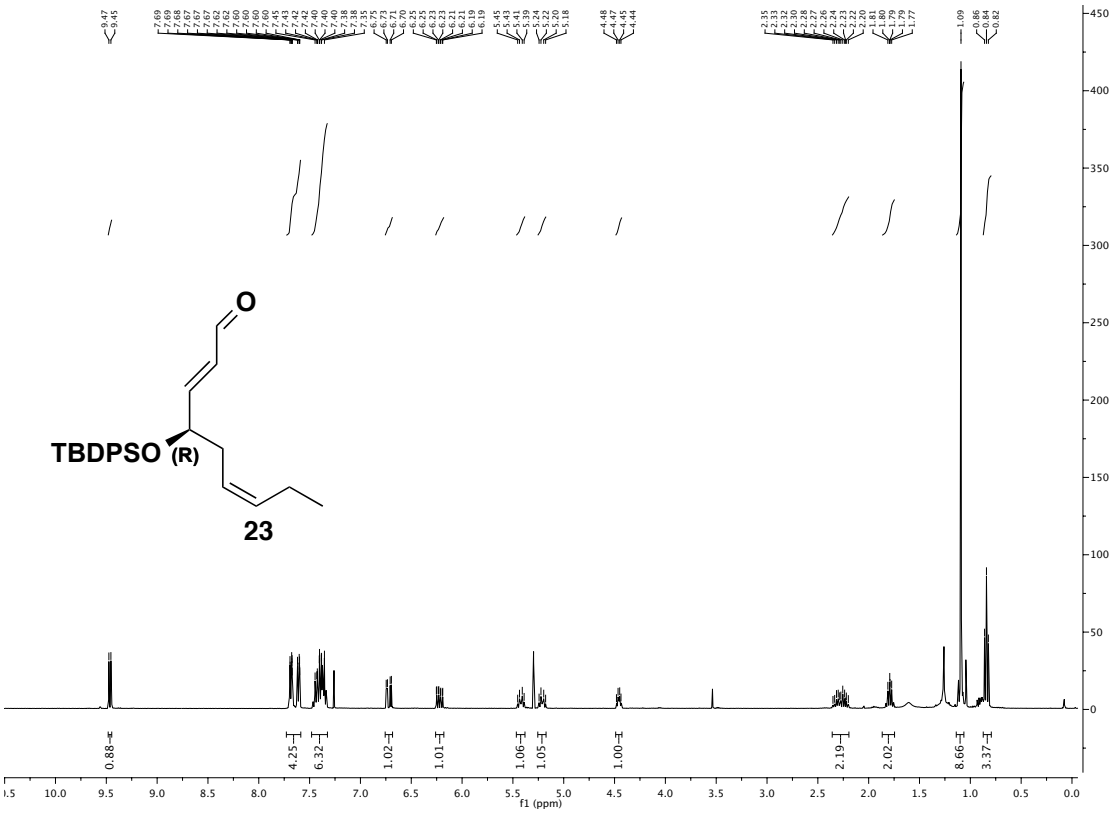

83.91
75.04
70.44
65.62
25.83
23.36
18.26
14.14
12.36
-5.43
f1 (ppm)

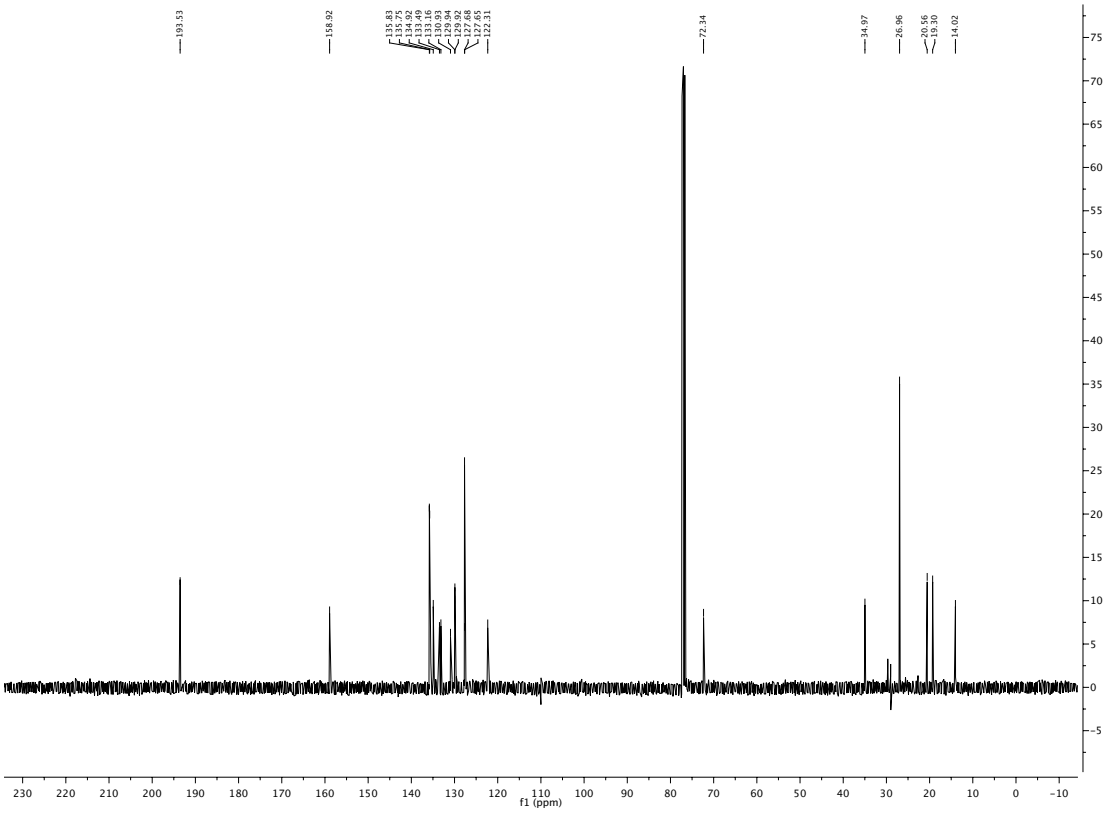

OTBDPS
HO
(S)
17
f1 (ppm)

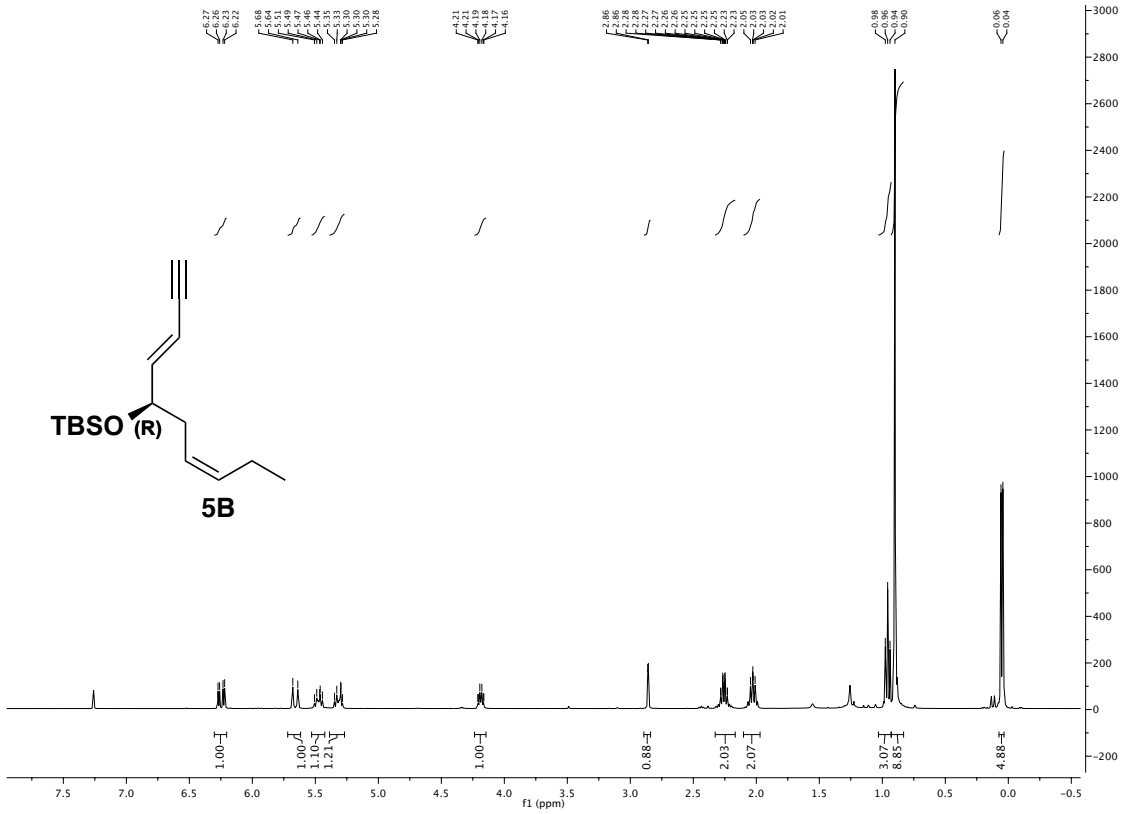

f1 (ppm)

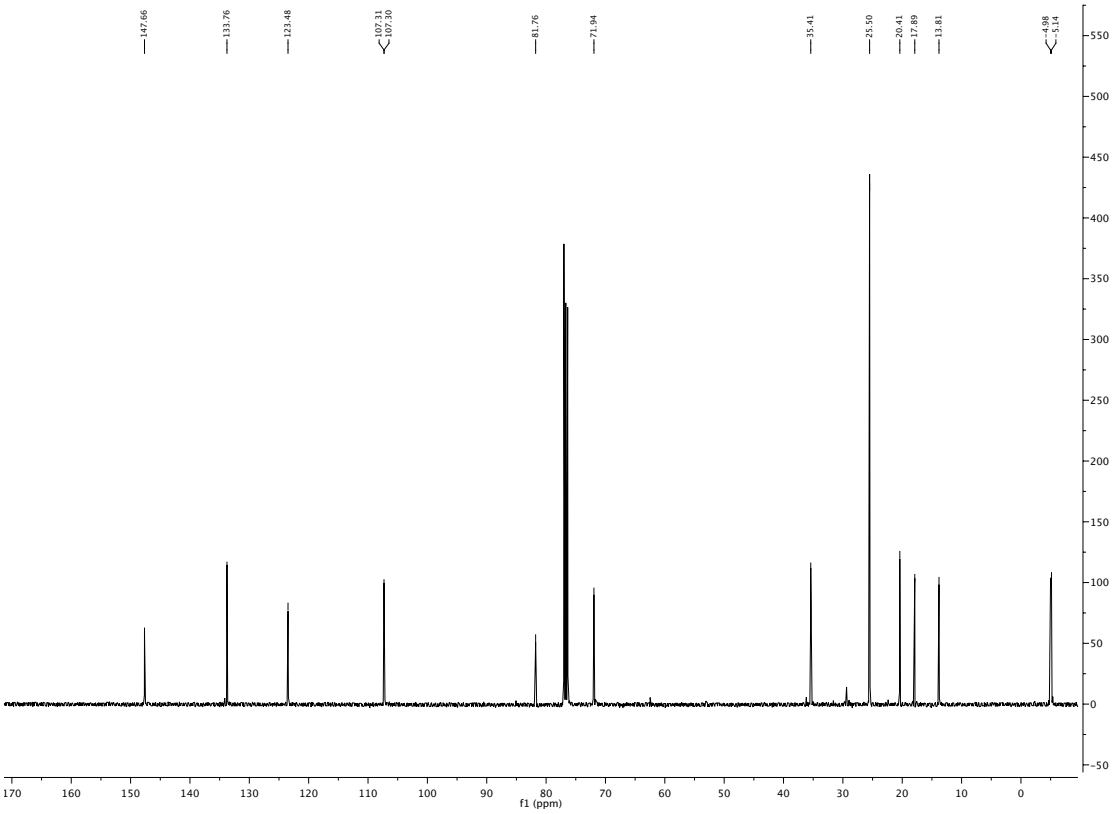

TBDPSO (R)
O
22
f1 (ppm)

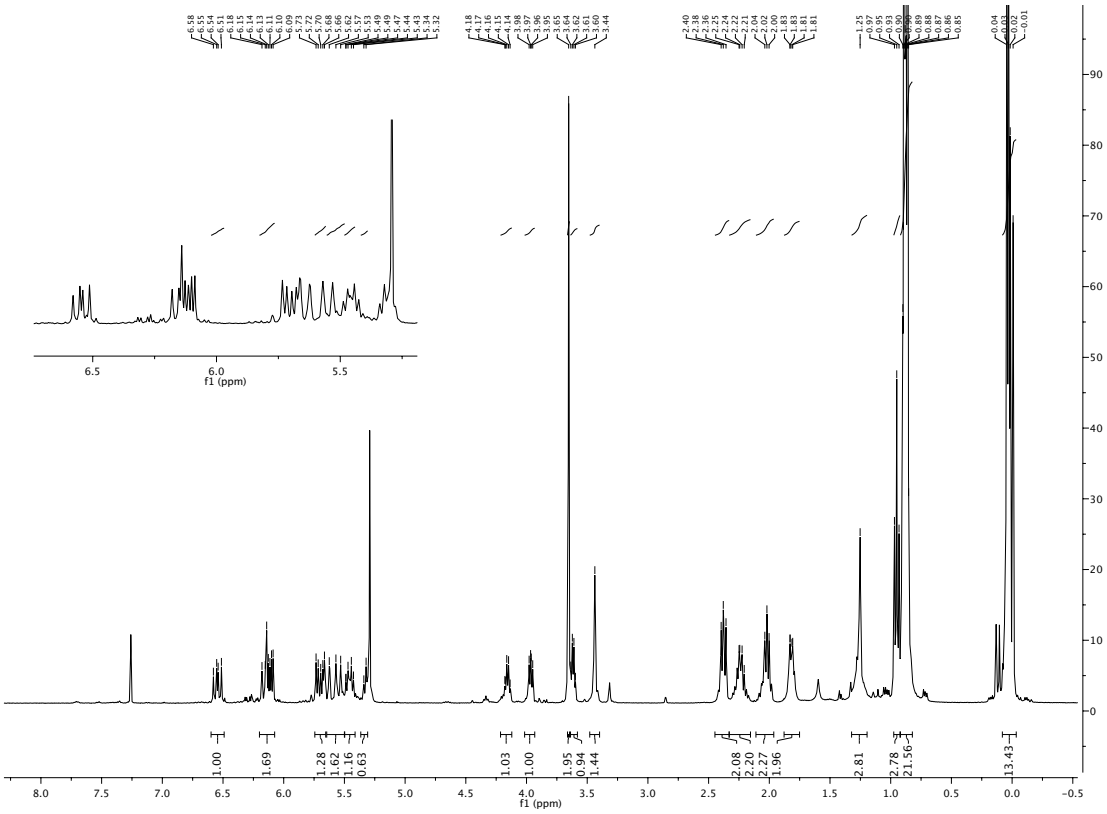

f1 (ppm)

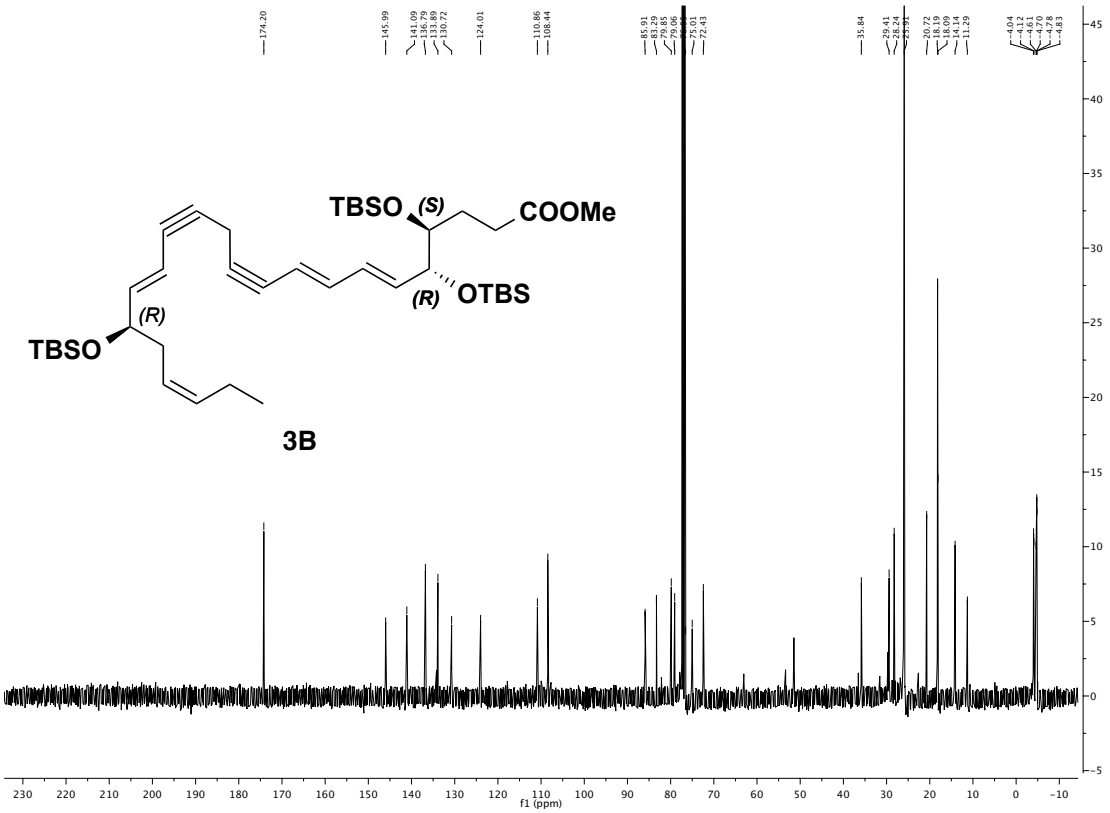

O
TBDPSO (R)
23
f1 (ppm)


f1 (ppm)

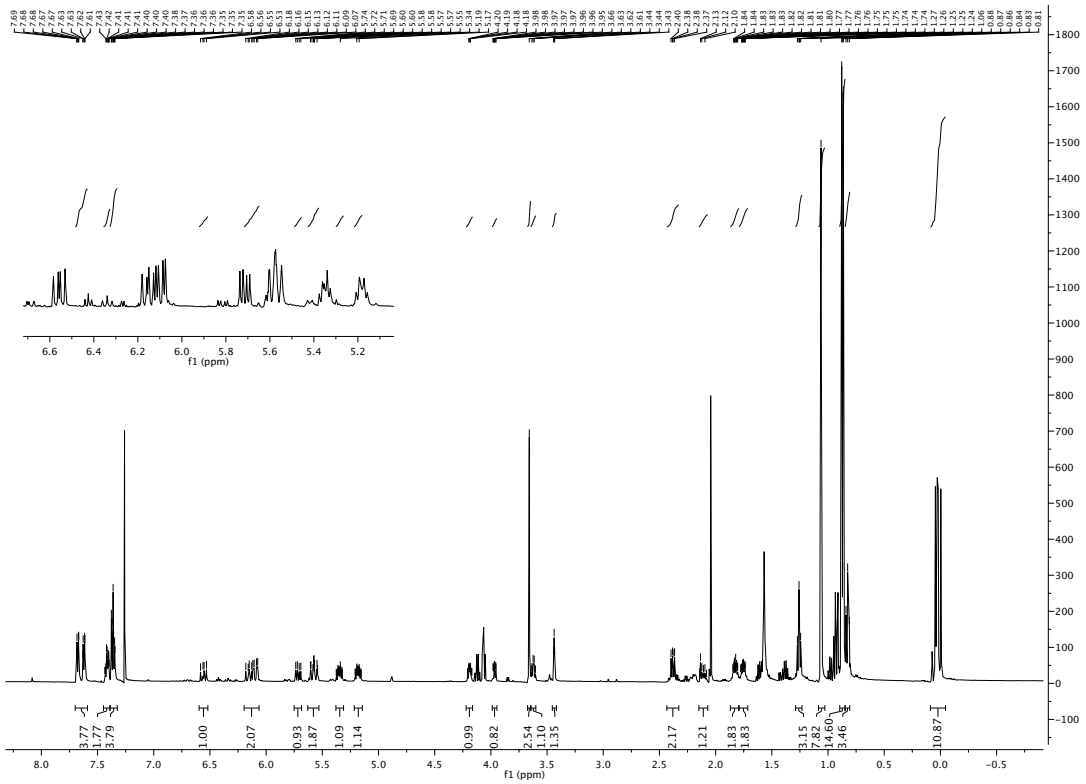

TBSO (R)
5B
f1 (ppm)

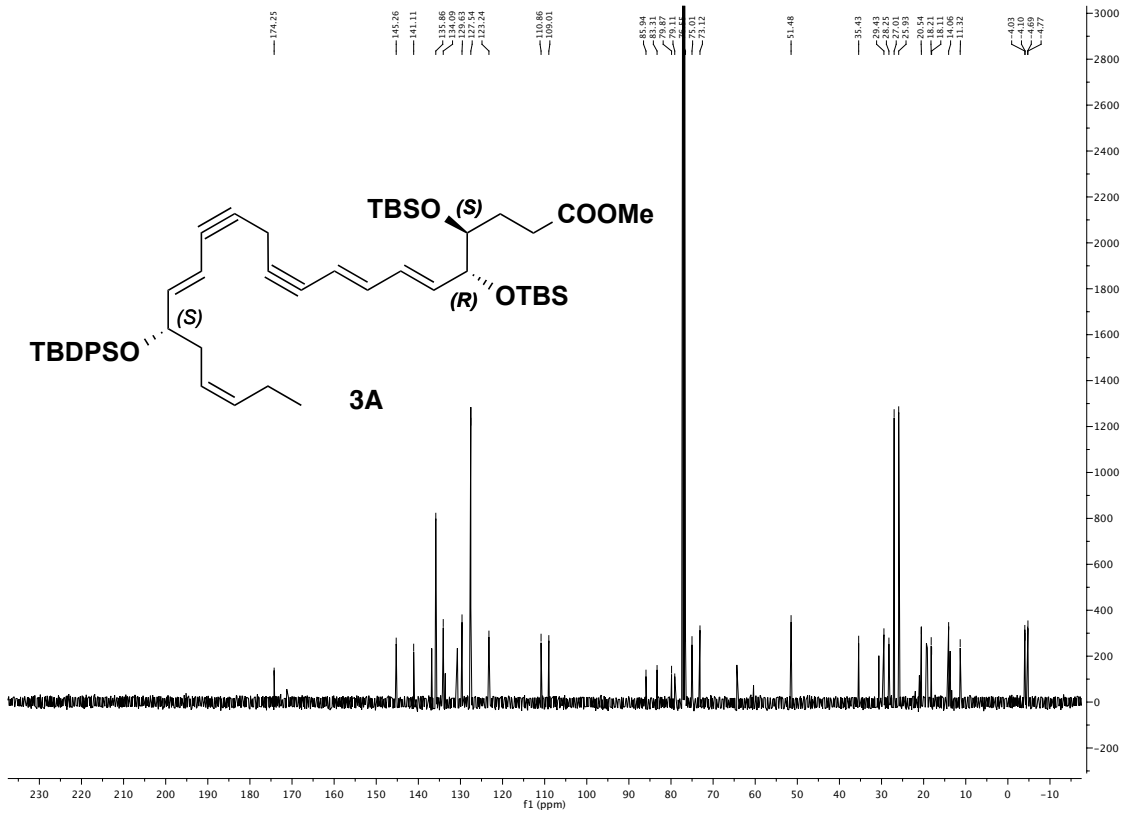

f1 (ppm)

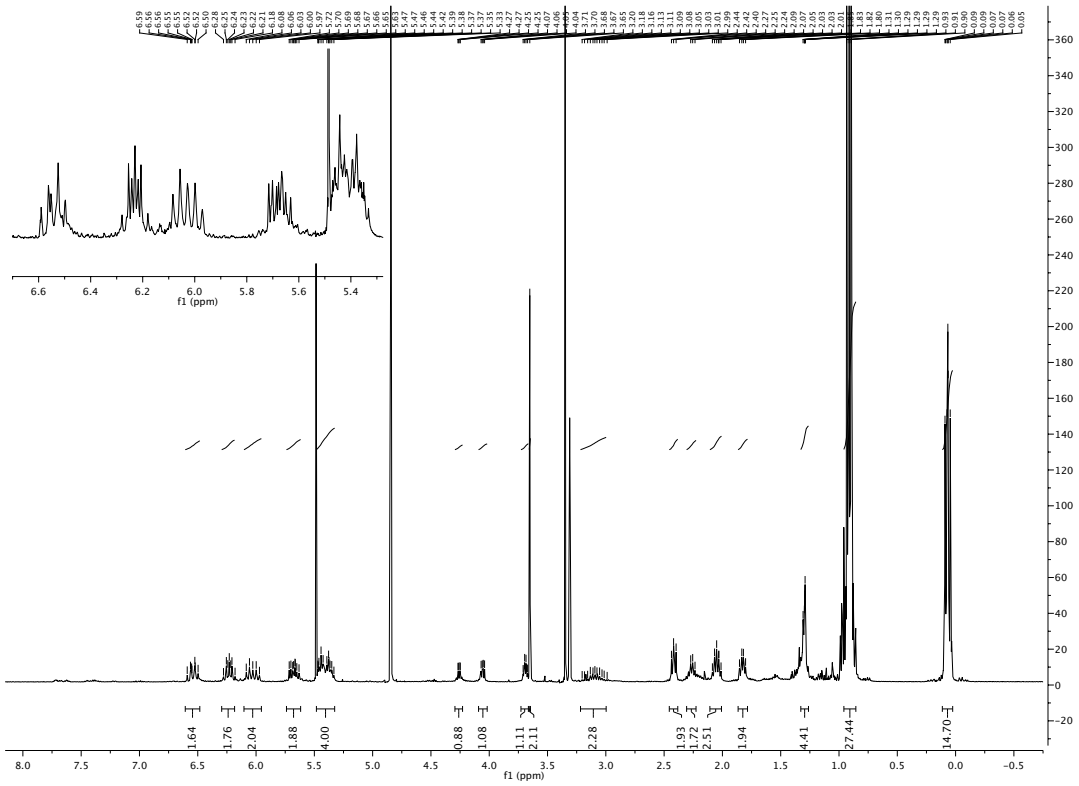


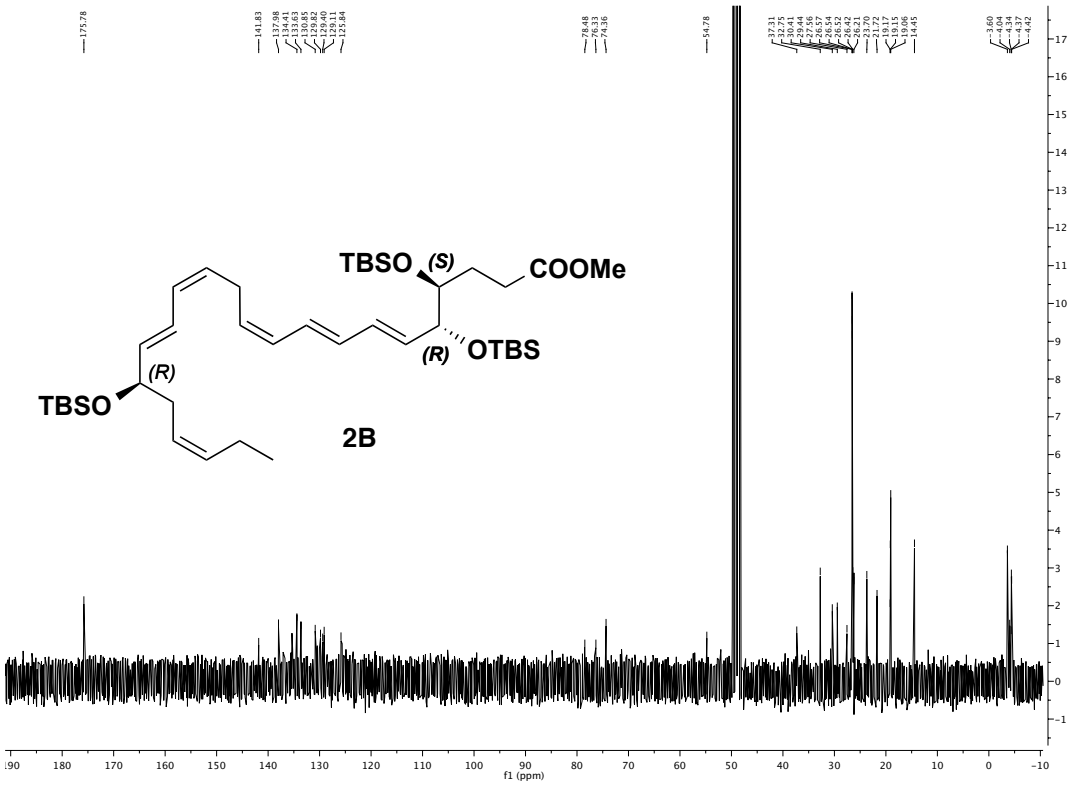


3B

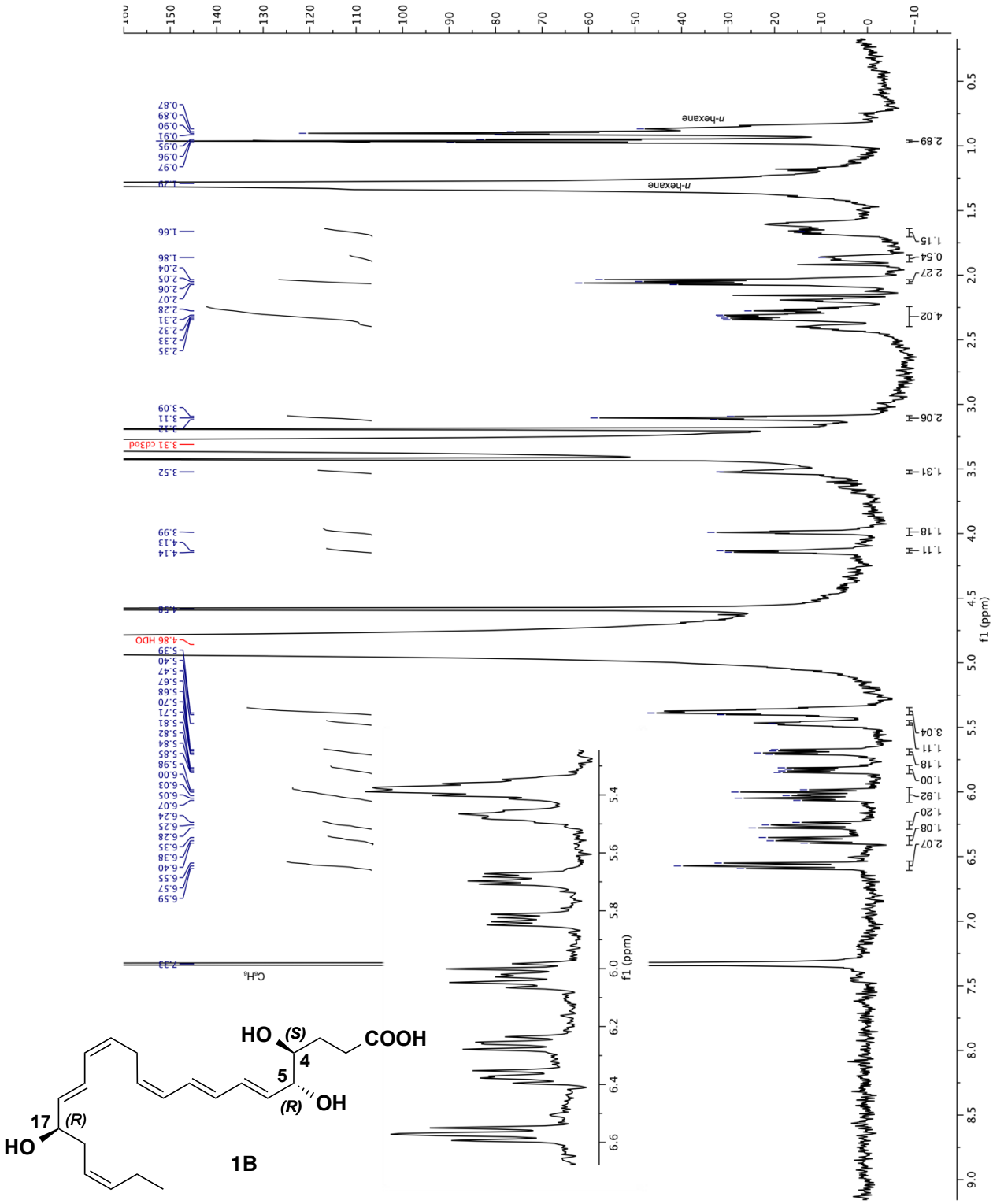

f1 (ppm)

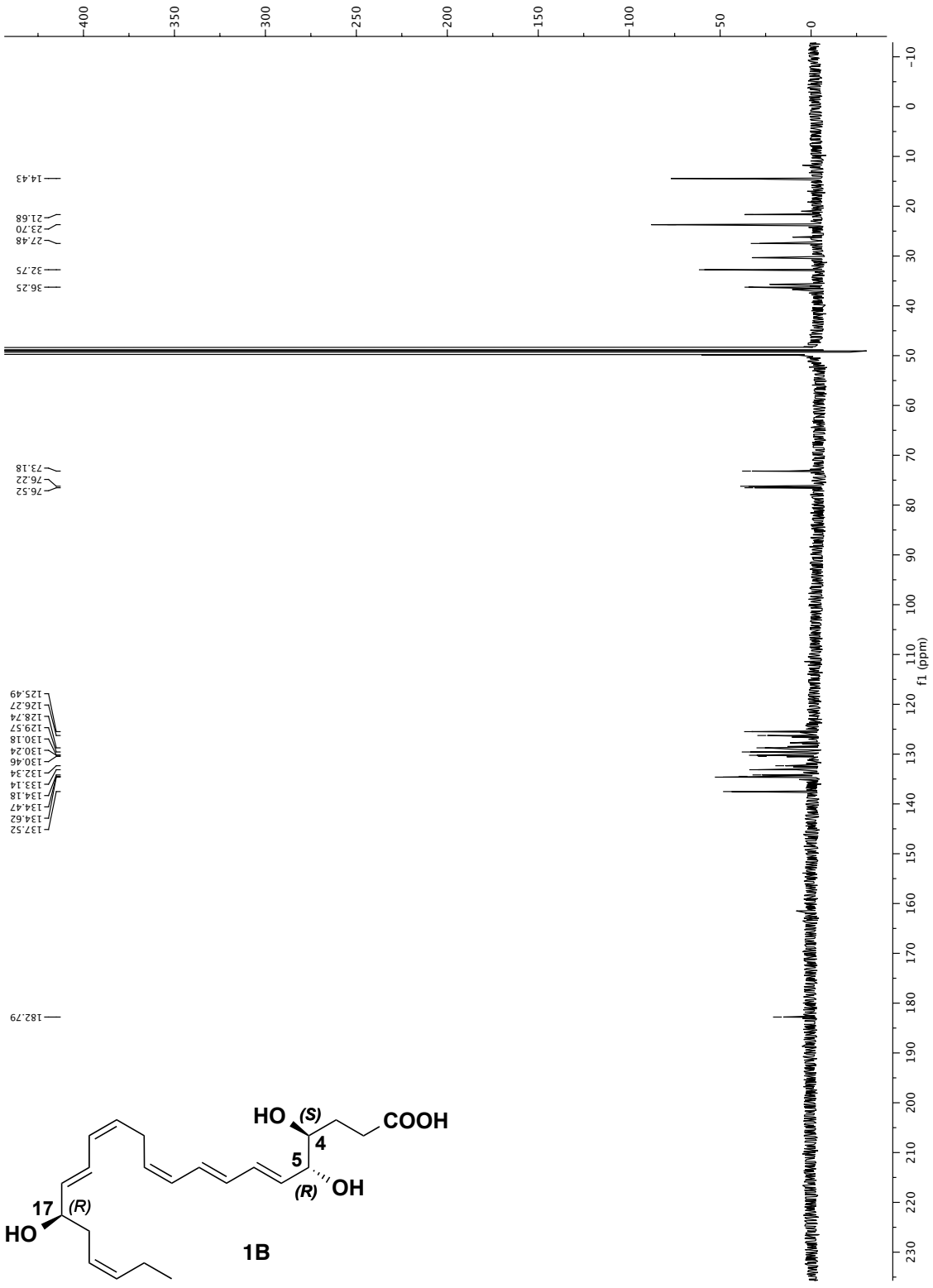

TBSO
(S)
COOMe
(R)
OTBS
(S)
TBDPSO
3A
f1 (ppm)


f1 (ppm)
1.64
1.76
2.04
1.88
4.00
0.88
1.08
1.11
2.11
2.28
1.93
1.72
2.51
1.94
4.41
27.44
14.70

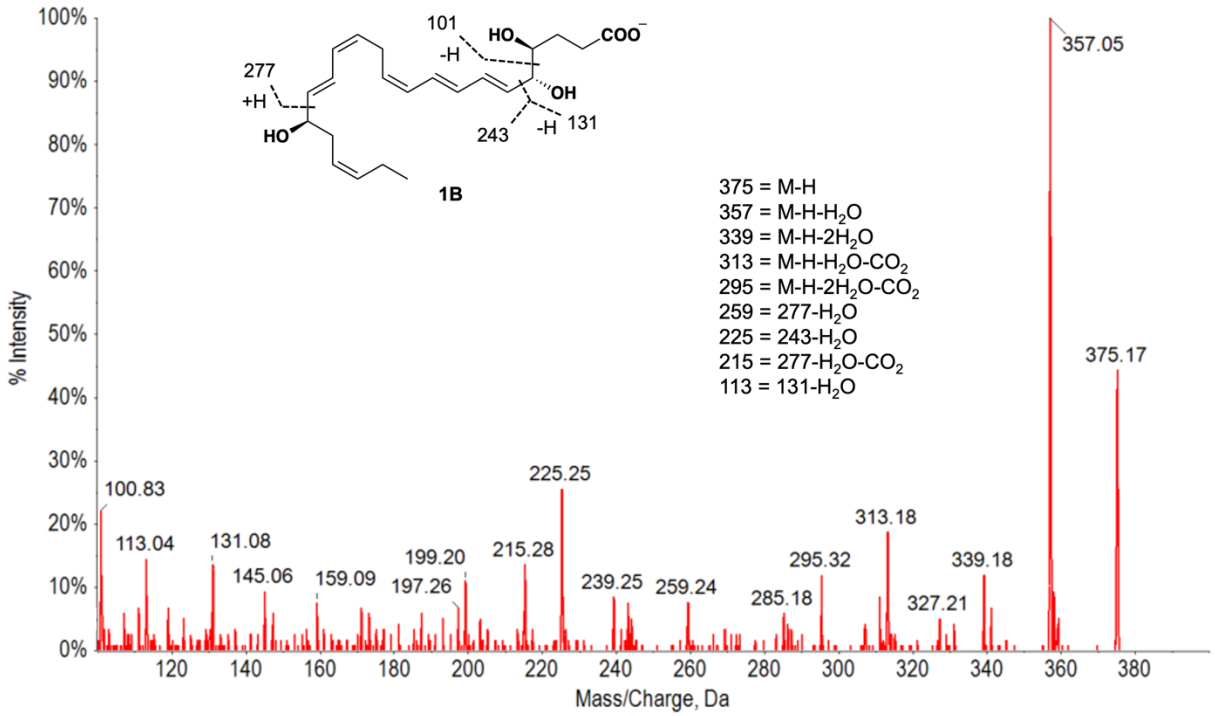

f1 (ppm)

TBSO
(S)
COOMe
(R)
OTBS
(R)
TBSO
2B

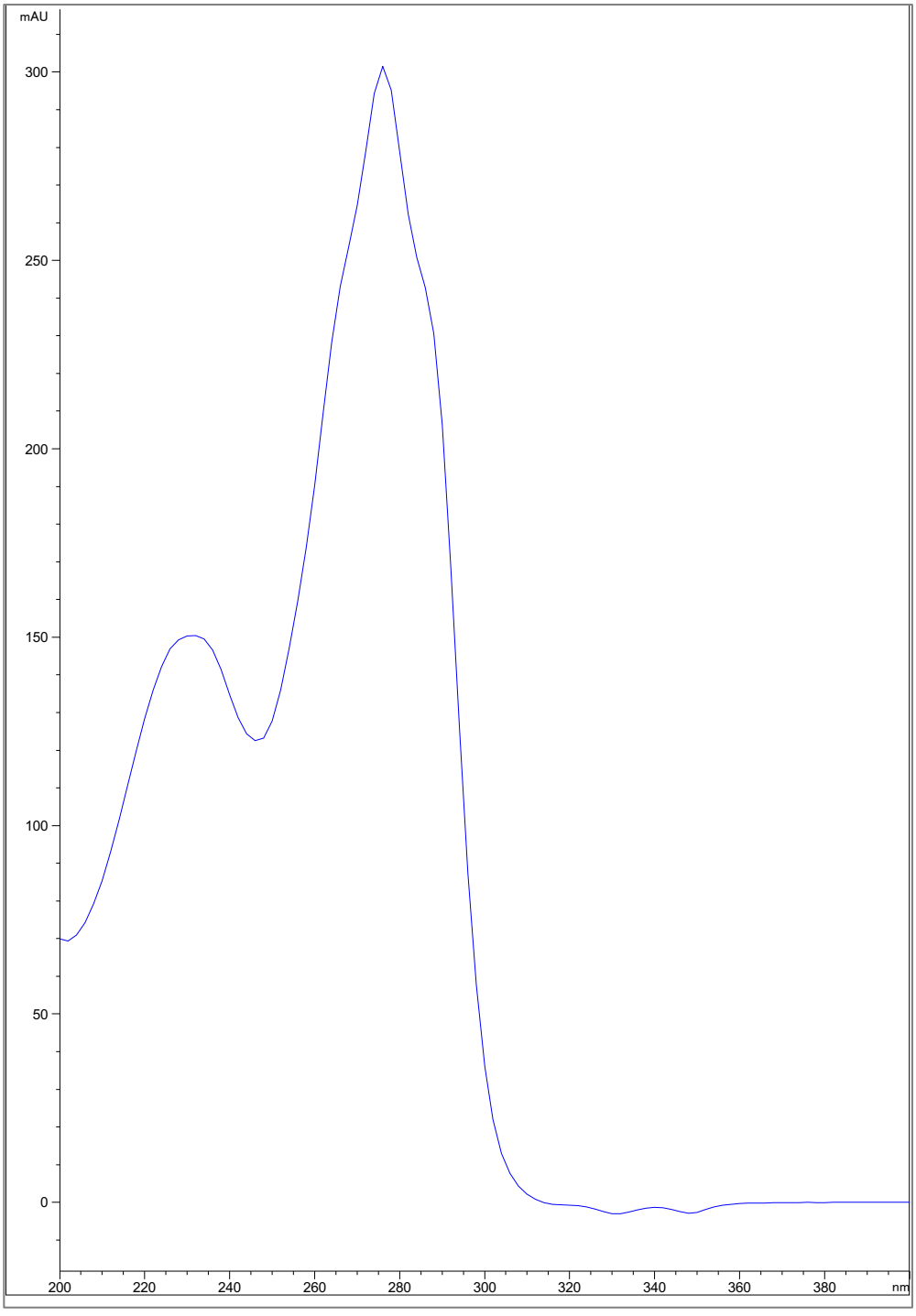

HO
(S)
COOH
4
5
(R)
OH
17
(R)
HO
1B
n-hexane
n-hexane
C6H6
4.86 HDO
3.31 cd3od
f1 (ppm)
f1 (ppm)

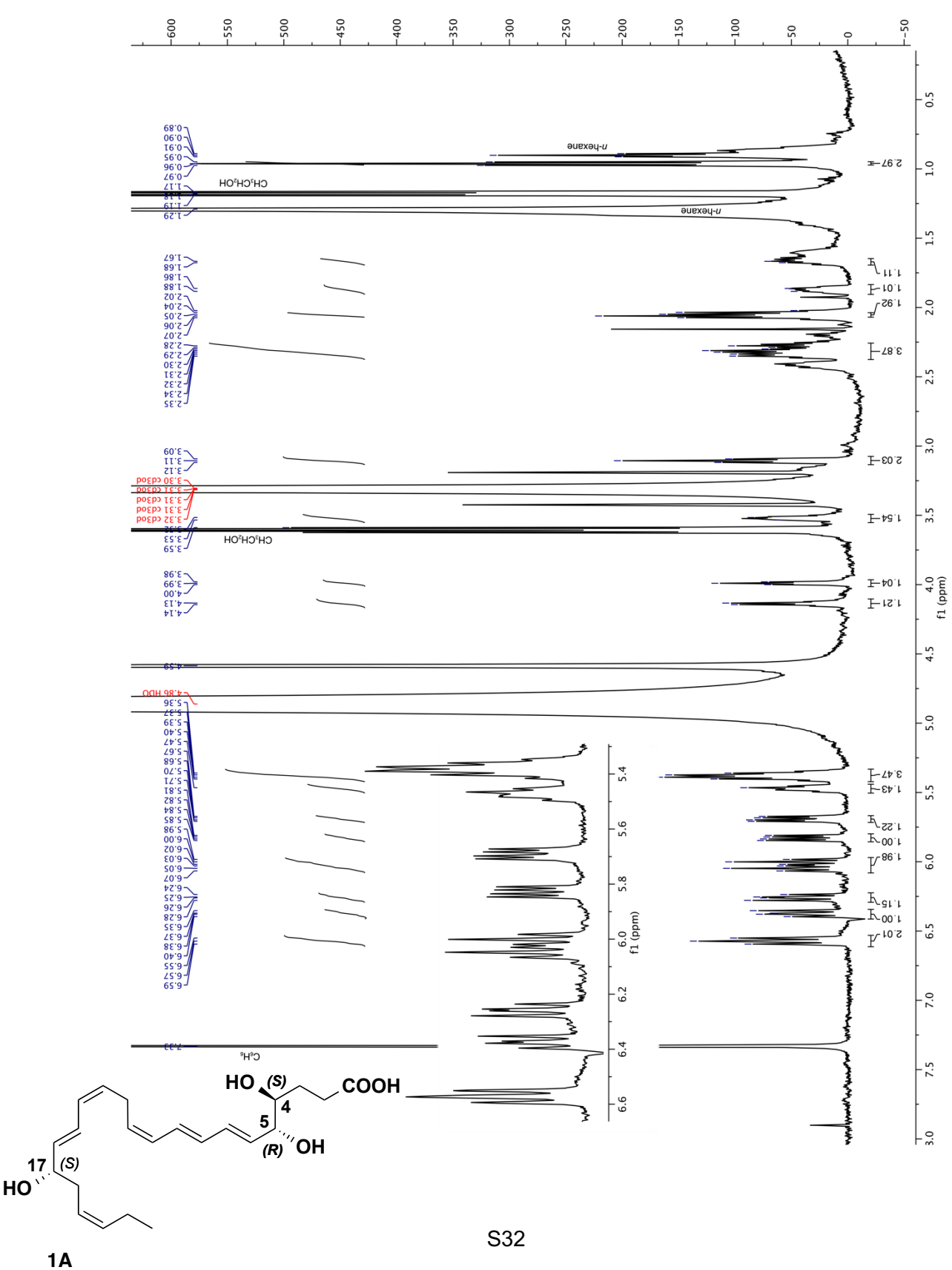

14.43
21.68
23.70
27.48
32.75
36.25
73.18
76.22
76.52
125.49
126.27
128.74
129.57
130.18
130.24
130.46
132.34
133.14
134.18
134.47
134.62
137.52
182.79
f1 (ppm)
HO
(S)
COOH
4
5
(R)
OH
17
(R)
HO
1B

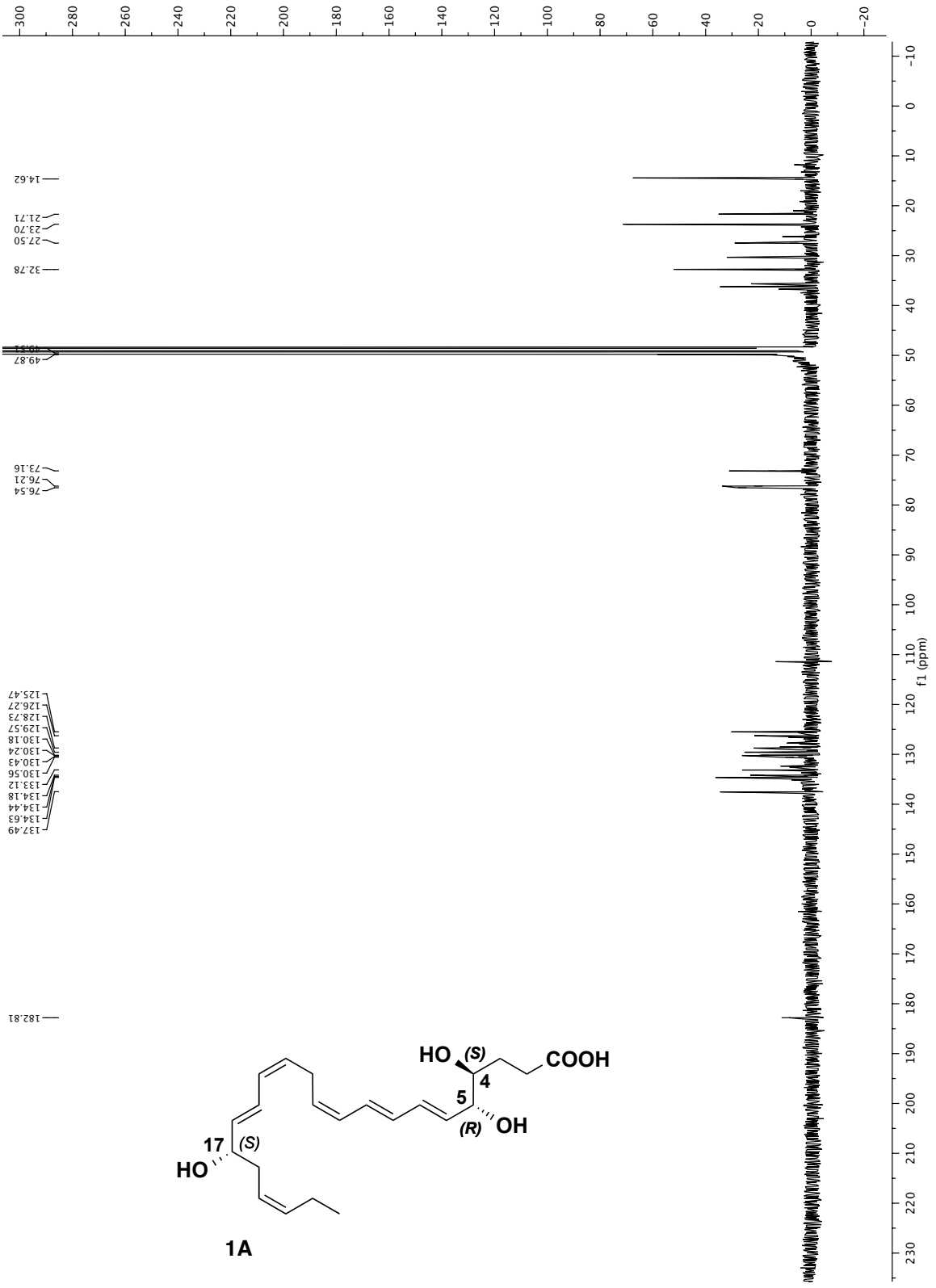
MS/MS Spectrum of 17R-Resolvin D4 (**1B**)



UV Spectrum of AT-Resolvin D4 (**1B**)

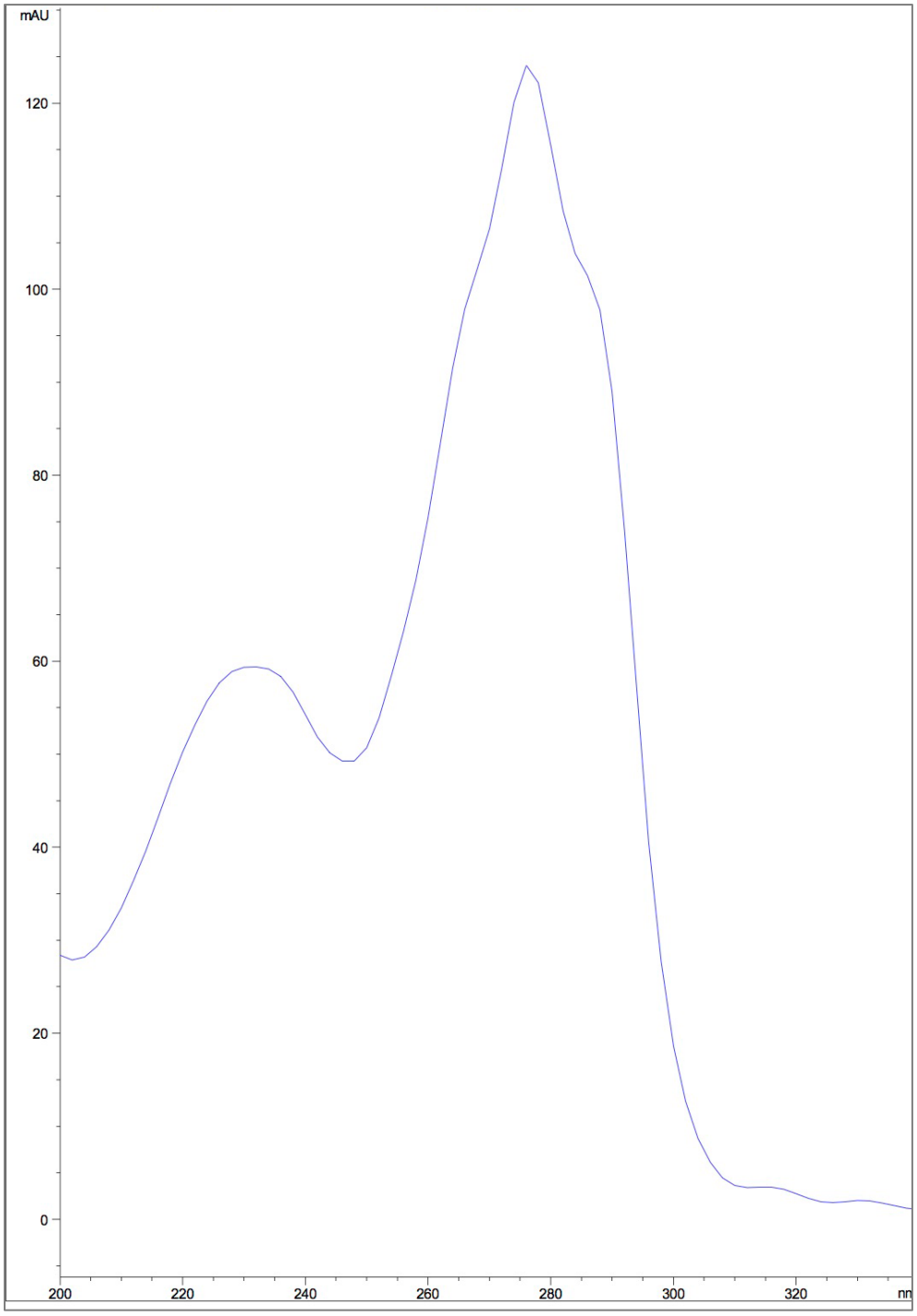



HO
17
(S)
HO
(S)
COOH
4
5
(R)
OH
1A
f1 (ppm)
n-hexane
CH3CH2OH
CH3OH
C6H6
HDO
cd3od

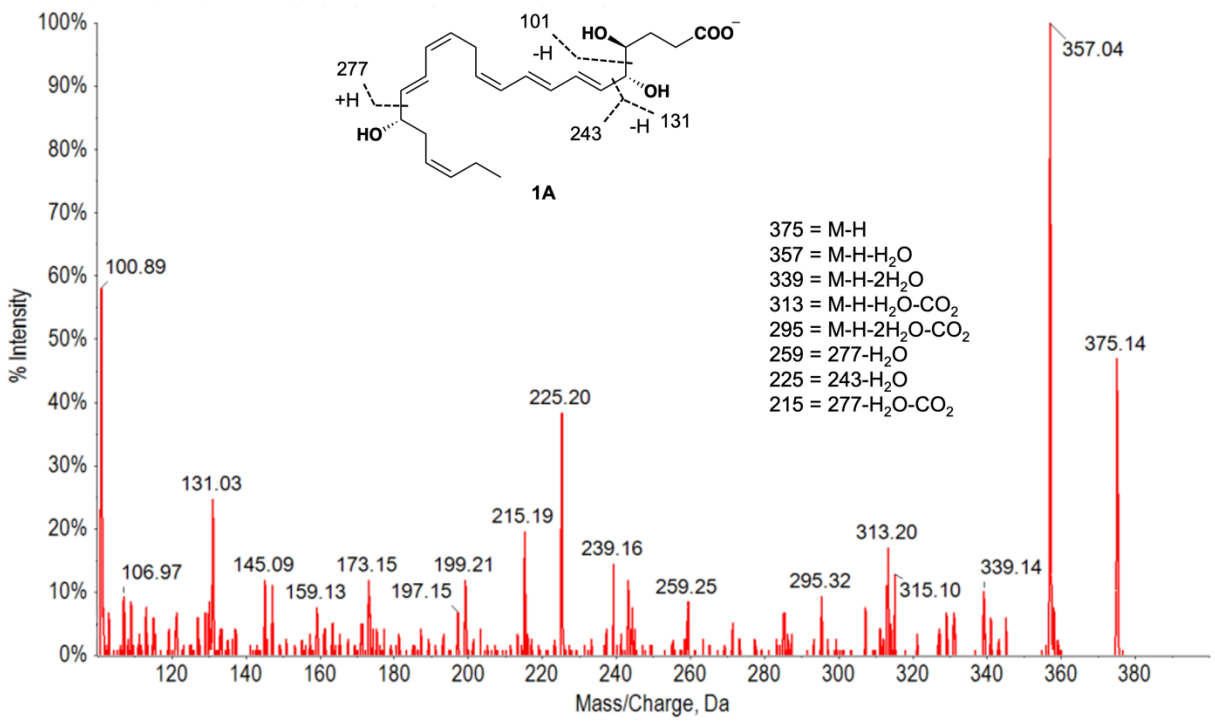

182.81
137.49
134.63
134.44
134.18
133.12
130.56
130.43
130.24
130.18
129.57
128.73
126.27
125.47
76.54
76.21
73.16
49.87
49.51
32.78
27.50
23.70
21.71
14.62
f1 (ppm)
HO
(S)
COOH
4
5
(R)
OH
17
(S)
HO

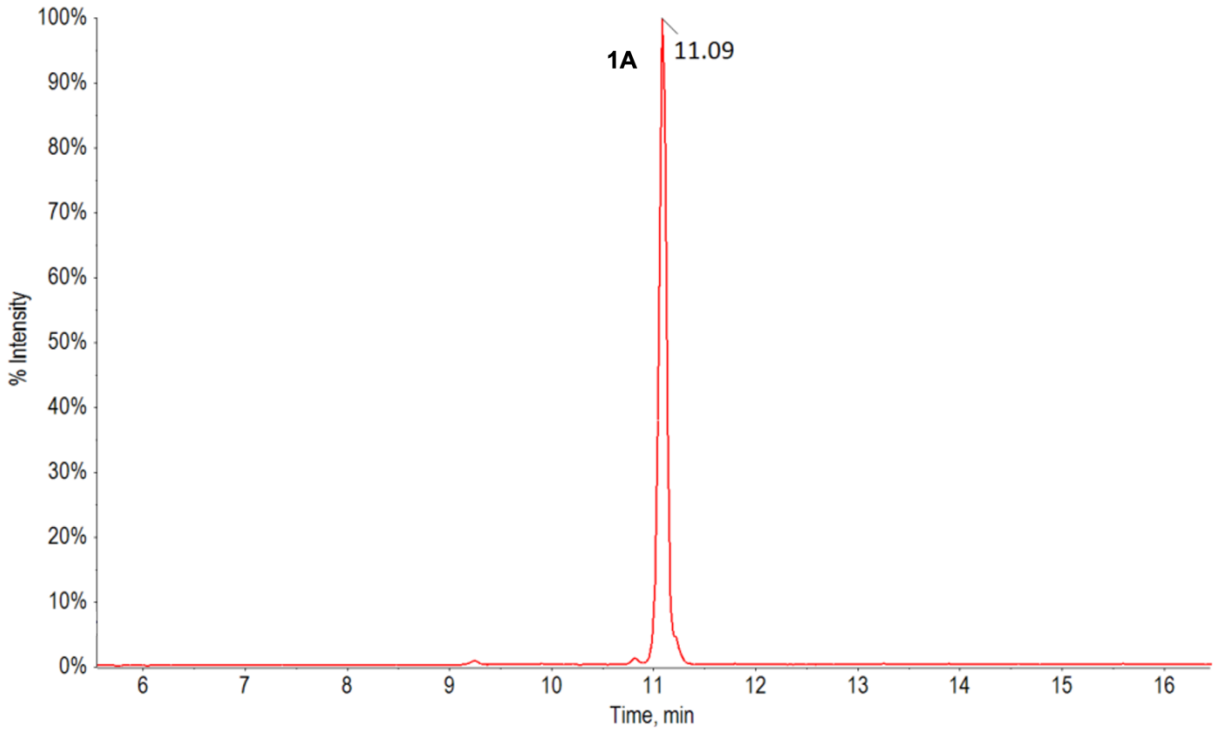
1A

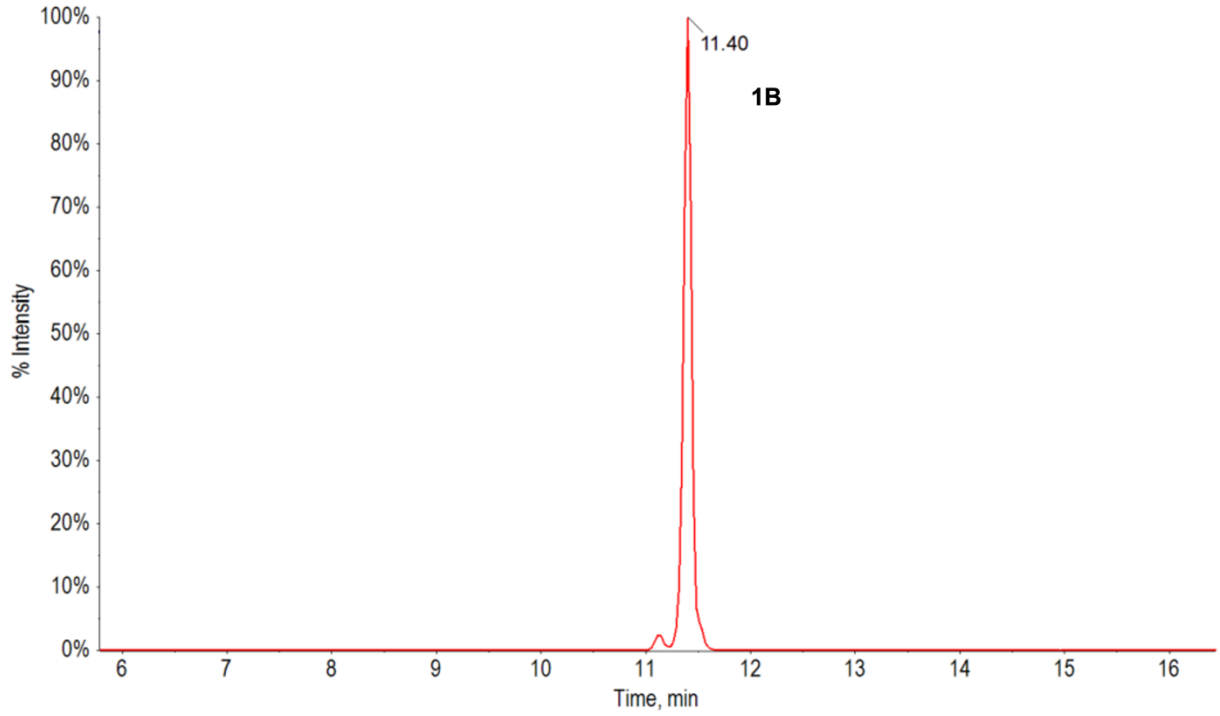
UV Spectrum of Resolvin D4 (**1A**)

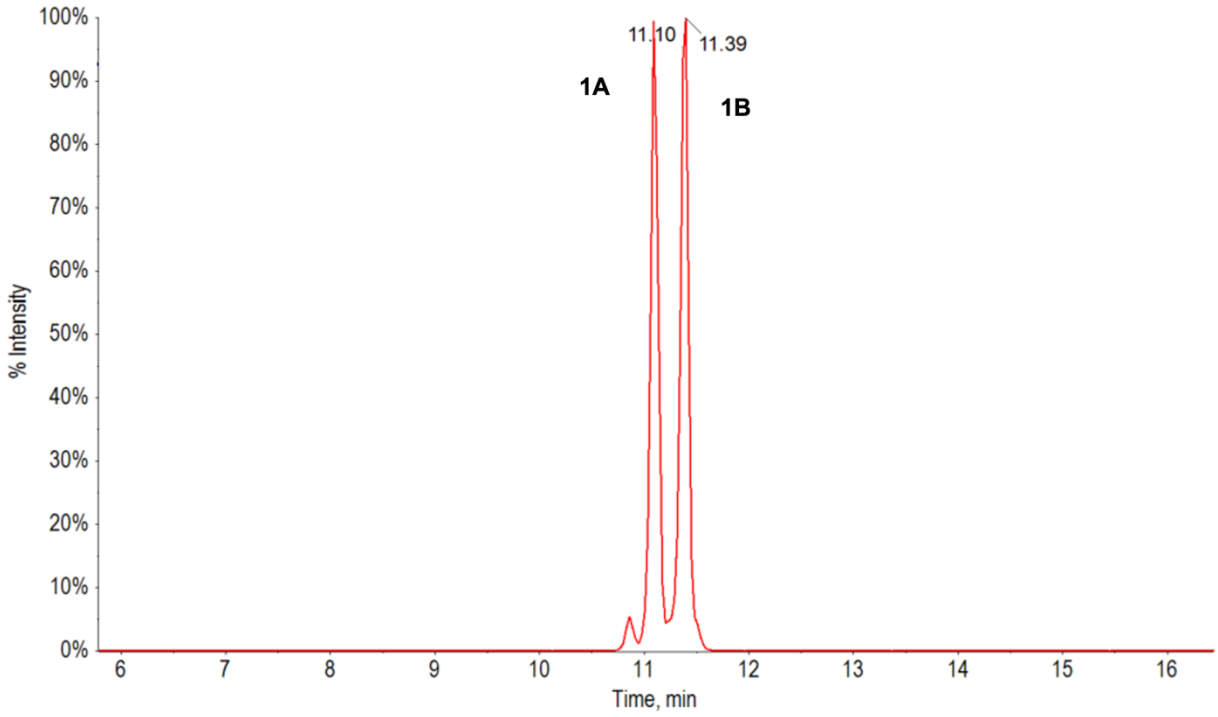


MS/MS Spectrum of Resolvin D4 (**1A**)




1A
11.09
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
% Intensity
6
7
8
9
10
11
12
13
14
15
16
Time, min


11.40
1B
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
% Intensity
6
7
8
9
10
11
12
13
14
15
16
Time, min


100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
% Intensity
11.10
11.39
1A
1B
6
7
8
9
10
11
12
13
14
15
16
Time, min