Supporting Information

Synthesis Enables a Structural Revision of the *M. Tuberculosis*-produced Diterpene, Edaxadiene

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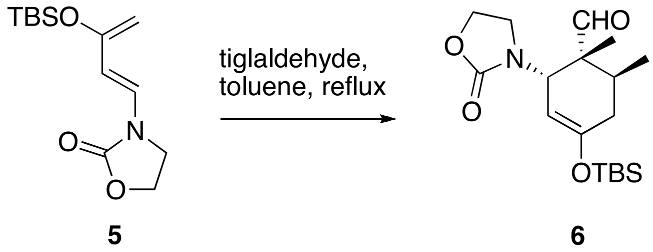
Experimental Section

General Methods. All reactions were carried out under an argon atmosphere unless otherwise indicated. Tetrahydrofuran (THF), dichloromethane, toluene, benzene, acetonitrile, dimethyl sulfoxide (DMSO) and triethylamine were dried and deoxygenated by passing the argon-purged solvents through activated alumina columns. Other commercial reagents were purchased from Strem, Aldrich, Gelest or Acros and used without further purification. Reactions were monitored by thin layer chromatography (TLC) performed on 0.25 mm Whatman silica gel plates (60 Å) with fluorescent indicator using UV light as a visualizing agent. The plates were subsequently developed using basic potassium permanganate, ceric ammonium molybdate or *p*-anisaldehyde stain. Flash silica gel (32-63 μm) was purchased from Dynamic Absorbents, Inc.

Instrumentation. FT-IR spectra were obtained on a Perkin-Elmer Paragon 500 infrared spectrometer. Samples were prepared as thin films on sodium chloride plates. Nuclear magnetic resonance (NMR) spectra were obtained on 500 MHz Bruker AVANCE spectrometers. ^{1}H-NMR spectra are referenced to the residual solvent peak ($CDCl_3$: 7.26 ppm, C_6D_6: 7.16 ppm) and ^{13}C-NMR spectra are referenced to the deuterated solvent signal ($CDCl_3$: 77.16 ppm, C_6D_6: 128.06 ppm).[1] The multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal. High-resolution mass spectra were obtained on an Agilent 6210 High-Resolution Time-of-Flight LC/MS using electrospray ionization (ESI+) or a Kratos MS50 instrument using electron ionization (EI+). Preparative SFC (supercritical fluid chromatography) was performed by Lotus Separations, LLC at Princeton University. Optical rotations were obtained on a Perkin-Elmer model 341 polarimeter and *c* is expressed as g/100 mL. Semi-preparative gas chromatography was performed using a GOW-MAC series 400 thermal conductivity gas chromatograph equipped with a 8' × 1/8" column (20% DC-200 on Chromasorb P AW DMCS, 80/100 mesh).

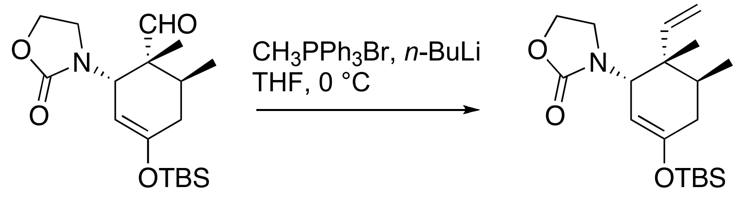
Experimental Procedures and Compound Characterization



Diene **5**[2] (14.5 g, 53.8 mmol) and tiglaldehyde aldehyde (*trans*-2-methyl-2-butenal, 13.1 g, 156 mmol) were dissolved in toluene (50 mL) and the mixture was refluxed for two days. Upon cooling, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (15% ethyl acetate in hexanes). Aldehyde **6** was obtained as a white solid (15.2 g, 43.0 mmol, 80%).

^{1}H-NMR (500 MHz, CDCl$_3$): δ 9.57 (s, 1H), 4.62 (d, *J* = 5.5 Hz, 1H), 4.54 (d, *J* = 5.5 Hz, 1H), 4.24 (t, *J* = 8.0 Hz, 2H), 3.65-3.41 (m, 2H), 2.32 (m, 1H), 2.15 (dd, *J* = 18.0, 5.9 Hz, 1H), 1.76 (dd, *J* = 18.0, 11.2 Hz, 1H), 1.17 (s, 3H), 0.92 (s, 9H), 0.90 (d, *J* = 6.6 Hz, 3H), 0.16 (s, 3H), 0.16 (s, 3H); ^{13}C-NMR (125 MHz, CDCl$_3$): δ 204.5, 158.5, 155.4, 98.2, 62.4, 55.4, 52.2, 43.0, 35.2, 28.8, 25.7, 18.1, 16.6, 13.7, −4.1, −4.5; IR (neat): 2930, 2853, 1736, 1663, 1412, 1372, 1221 cm^{-1}; HRMS calculated for $C_{18}H_{32}NO_4Si$

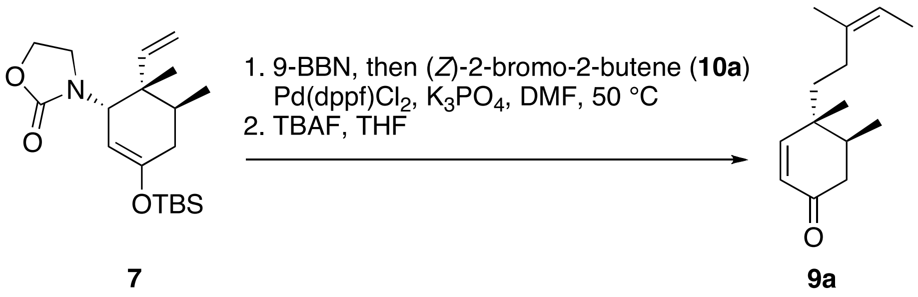
$[M+H]^+$ = 354.2101, found 354.2097 (ESI+).



6 **7**

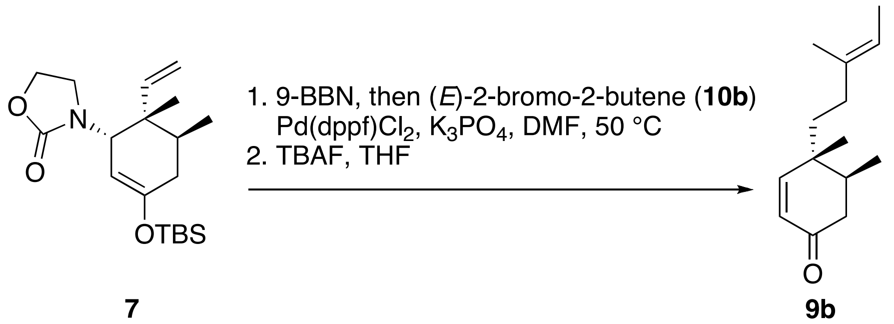
Methyltriphenylphosphonium bromide (23.0 g, 64.4 mmol) was suspended in THF (250 mL) and treated with *n*-butyllithium (25.0 mL, 62.5 mmol) at 0 °C. After 30 minutes, a solution of aldehyde **6** (15.2 g, 43.0 mmol) in THF (180 mL) was added *via* cannula. The mixture was then removed from the ice bath and stirred for 30 minutes. Upon completion, the reaction was quenched with 1 M aqueous phosphate buffer (pH 7), diluted with ethyl acetate and transferred to a separatory funnel. The organic phase was washed successively with distilled water and saturated aqueous sodium chloride and was dried over anhydrous magnesium sulfate. Once filtered and concentrated, the crude product was purified by flash column chromatography (5-15% ethyl acetate in hexanes). Compound **7** (10.2 g, 29.0 mmol, 67%) was obtained as a white solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.80 (dd, *J* = 17.3, 11.0 Hz, 1H), 5.15 (d, *J* = 11.0 Hz, 1H), 5.14 (d, *J* = 17.3 Hz, 1H), 4.64 (d, *J* = 4.9 Hz, 1H), 4.28-4.20 (m, 3H), 3.64-3.54 (m, 2H), 2.17 (dd, *J* = 17.4, 5.3 Hz, 1H), 1.84 (m, 1H), 1.76 (dd, *J* = 17.4, 9.6 Hz, 1H), 1.03, (s, 3H), 0.92 (s, 9H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 158.6, 154.3, 142.9, 115.0, 100.9, 62.0, 58.4, 43.5, 42.4, 35.6, 34.0, 25.7, 18.1, 16.4, 16.4, –4.0, –4.4; IR (neat): 2957, 2896, 2857, 1738, 1668, 1421, 1372, 1251, 1220, 834 cm^{-1}; HRMS calculated for $C_{19}H_{34}NO_3Si$ $[M+H]^+$ = 352.2308, found 352.2296 (ESI+).



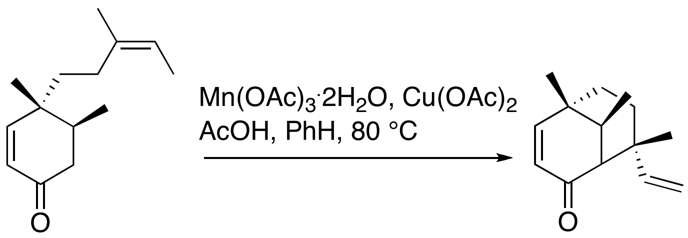
Alkene **7** (702 mg, 2.00 mmol) was dissolved in a solution of 9-borabicyclo(3.3.1)nonane (9-BBN, 0.5 M in THF, 8.0 mL, 4.0 mmol), heated to 70 °C for three hours and cooled to room temperature. In a separate flask, (*Z*)-2-bromo-2-butene (**10a**, 375 mg, 2.78 mmol) was dissolved in degassed DMF (8 mL) and treated with [1,1′-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (1:1 complex with dichloromethane, 163 mg, 0.200 mmol) and aqueous potassium phosphate (2.4 M, 1.7 mL, 4.1 mmol). After 20 minutes, the hydroboration solution was added *via* cannula and the mixture was heated to 50 °C for two hours. Upon cooling, the mixture was diluted with distilled water and ethyl acetate. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with a saturated aqueous solution of sodium chloride, dried over anhydrous magnesium sulfate, filtered and concentrated. The residue (containing compound **8a**) was dissolved in THF (15 mL), and cooled to 0 °C. Tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 4.0 mL, 4.0 mmol) was added and the solution was stirred for two hours. The mixture was concentrated and the crude product was purified by flash column chromatography (5% ethyl acetate in hexanes). Compound **9a** (355 mg, 1.72 mmol, 86%) was obtained as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.69 (d, *J* = 10.1 Hz, 1H), 5.91 (d, *J* = 10.1 Hz, 1H), 5.20 (q, *J* = 6.6 Hz, 1H), 2.35-2.16 (m, 3H), 1.97 (ddd, *J* = 13.0, 13.0, 5.0 Hz, 1H), 1.78 (ddd, *J* = 13.0, 13.0, 4.0 Hz, 1H), 1.64 (m, 1H), 1.60 (s, 3H), 1.54 (d, *J* = 6.6 Hz, 3H), 1.46 (m, 1H), 0.98 (s, 3H), 0.93 (d, *J* = 6.6 Hz, 3H); δ ^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.4, 160.5, 135.6, 128.0, 118.8, 42.2, 39.2, 38.2, 34.5, 33.9, 19.7, 16.0, 15.5, 13.5; IR (neat): 2964, 1682, 1455, 1373, 1280 cm^{-1}; HRMS calculated for $C_{14}H_{23}O$ $[M+H]^+$ = 207.1749, found 207.1746 (ESI+).



Alkene **7** (702 mg, 2.00 mmol) was dissolved in a solution of 9-BBN (0.5 M in THF, 8.0 mL, 4.0 mmol), heated to 70 °C for three hours and cooled to room temperature. In a separate flask, (*E*)-2-bromo-2-butene (**10b**, 375 mg, 2.78 mmol) was dissolved in degassed DMF (8 mL) and treated with [1,1′-Bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (1:1 complex with dichloromethane, 163 mg, 0.200 mmol) and aqueous potassium phosphate (2.4 M, 1.7 mL, 4.1 mmol). After 20 minutes, the hydroboration solution was added *via* cannula and the mixture was heated to 50 °C for two hours. Upon cooling, the mixture was diluted with distilled water and ethyl acetate. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, filtered and concentrated. The residue (containing compound **8b**) was dissolved in THF (15 mL), and cooled to 0 °C. TBAF (1.0 M in THF, 4.0 mL, 4.0 mmol) was added and the solution was stirred for two hours. The mixture was concentrated and the crude product was purified by flash column chromatography (5% ethyl acetate in hexanes). Compound **9b** (412 mg, 1.72 mmol, quantitative) was obtained as a colorless oil.

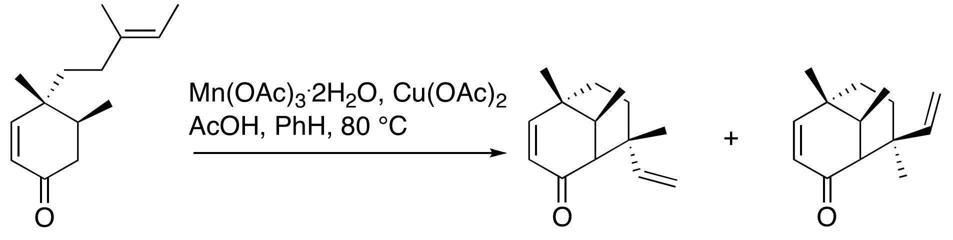
^{1}H-NMR (500 MHz, CDCl$_3$): δ 6.73 (d, J = 10.1 Hz, 1H), 5.94 (d, J = 10.1 Hz, 1H), 5.20 (q, J = 6.7 Hz, 1H), 2.35-2.22 (m, 3H), 2.03 (ddd, J = 12.7, 12.7, 5.2 Hz, 1H), 1.83 (ddd, J = 12.7, 12.7, 4.2 Hz, 1H), 1.68 (t, J = 1.4 Hz, 3H), 1.62, (ddd, J = 13.8, 12.7, 5.2 Hz, 1H), 1.54 (d, J = 6.7 Hz, 3H), 1.41 (m, 1H), 1.00 (s, 3H), 0.97 (d, J = 6.4 Hz, 3H); ^{13}C-NMR (125 MHz, CDCl$_3$): δ 200.4, 160.4, 135.8, 128.2, 119.3, 42.2, 39.4, 37.6, 33.8, 26.6, 23.6, 19.7, 15.5, 13.3; IR (neat): 2964, 2936, 1682, 1456, 1388, 1277 cm^{-1}; HRMS calculated for $C_{14}H_{23}O$ [M+H]$^+$ = 207.1749, found 207.1751 (ESI+).



9a **12a**

Compound **9a** (44 mg, 0.21 mmol) was dissolved in a benzene-acetic acid mixture (3:1, 4 mL) and treated with manganese(III) acetate dihydrate (225 mg, 0.839 mmol) and copper(II) acetate (38 mg, 0.21 mmol). The mixture was heated to 80 °C for 12 hours, 100 °C for two hours, and cooled to room temperature. The reaction was quenched with a 10% aqueous solution of sodium bisulfate, diluted with ether and transferred to a separatory funnel. The layers were separated and the organic phase was washed with saturated aqueous sodium bicarbonate (3 times) followed by saturated aqueous sodium chloride. Once filtered and concentrated, the crude product was purified by flash column chromatography (1-8% diethyl ether in hexanes). Compound **12a** (25 mg, 0.12 mmol, 57%) was isolated as a colorless oil.

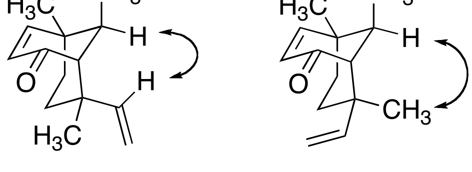
^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.24 (dd, *J* = 10.0, 1.9 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 5.78 (dd, *J* = 17.5, 10.9 Hz, 1H), 4.91 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 17.5 Hz, 1H), 2.10 (br q, *J* = 7.0 Hz, 1H), 1.94 (br s, 1H), 1.79-1.67 (m, 2H), 1.43 (m, 1H), 1.37 (m, 1H), 1.16 (s, 3H), 1.11 (s, 3H), 0.93 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 201.6, 152.4, 147.4, 129.9, 110.7, 62.1, 39.8, 38.0, 38.0, 33.1, 29.0, 25.8, 24.4, 15.4; IR (neat): 2930, 1676, 1456, 1230 cm^{-1}; HRMS calculated for $C_{14}H_{21}O$ $[M+H]^+$ = 205.1592, found 205.1587 (ESI+).



9b **12a** **12b**

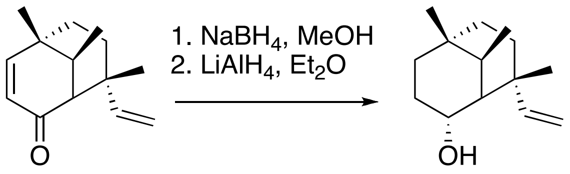
Compound **9b** (182 mg, 0.882 mmol) was dissolved in a benzene-acetic acid mixture (3:1, 18 mL) and treated with manganese(III) acetate dihydrate (816 mg, 3.04 mmol) and copper(II) acetate (160 mg, 0.882 mmol). The mixture was heated to 80 °C for 12 hours, 100 °C for two hours, and cooled to room temperature. The reaction was quenched with a 10% aqueous solution of sodium bisulfate, diluted with ether and transferred to a separatory funnel. The layers were separated and the organic phase was washed with saturated aqueous sodium bicarbonate (3 times) followed by saturated aqueous sodium chloride. Once filtered and concentrated, the crude product was purified by flash column chromatography (1-8% diethyl ether in hexanes). Compound **12b** and compound **12a** (92 mg, 0.25 mmol, 51%) were isolated as a 1.4:1 mixture of diastereomers that could be separated by flash column chromatography (1-8% diethyl ether in hexanes).

Compound **12b**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.29 (dd, *J* = 10.0, 2.2 Hz, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 5.70 (dd, *J* = 17.8, 10.9 Hz, 1H), 5.09 (d, *J* = 10.9 Hz, 1H), 5.06 (d, *J* = 17.8 Hz, 1H), 2.03 (br s, 1H), 1.96 (qdd, *J* = 7.0, 2.2, 2.2 Hz, 1H), 1.73-1.68 (m, 1H), 1.64 (dd, *J* = 13.2, 4.1 Hz, 1H), 1.51 (m, 1H), 1.31 (m, 1H), 1.06 (s, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.87 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 201.9, 153.5, 146.0, 130.1, 112.9, 61.0, 40.7, 38.8, 37.7, 33.7, 30.0, 28.7, 25.8, 15.4; IR (neat): 2928, 1674, 1456, 1233 cm^{-1}; HRMS calculated for $C_{14}H_{21}O$ $[M+H]^+$ = 205.1590, found 205.1587 (ESI+).



12a **12b**

Key nOe correlations supporting the stereochemical assignment of **12a** and **12b**.

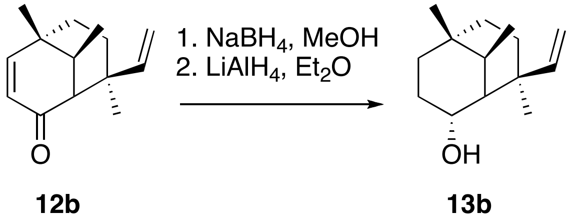


12a **13a**

Enone **12a** (62 mg, 0.30 mmol) was dissolved in methanol (2.5 mL) and treated with sodium borohydride (46 mg, 1.2 mmol). After one hour, the reaction was quenched with saturated aqueous ammonium chloride, diluted with methylene chloride and transferred to a separatory funnel. The organic phase was washed three times with distilled water and dried over anhydrous sodium sulfate. Once filtered and concentrated, the residue was dissolved in diethyl ether (2.5 mL), cooled to 0 °C and treated with lithium aluminum hydride (1.0 M in THF, 450 μL, 4.5 mmol). The mixture was allowed to warm to room temperature over one hour. The reaction was quenched with distilled water (100 μL) followed by 1 M aqueous sodium hydroxide (200 μL). An additional portion of distilled water (300 μL) was added and the mixture was stirred for 10 minutes before being filtered through a pad of Celite. The filtrate was dried over anhydrous magnesium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography (5-10% ethyl acetate in hexanes) to yield compound **13a** (54 mg, 0.26 mmol, 87%) as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.26 (dd, *J* = 17.5, 11.1 Hz, 1H), 5.01 (d, *J* = 17.5 Hz, 1H), 4.99 (d, *J* = 11.1 Hz, 1H), 4.01 (m, 1H), 2.31 (m, 1H), 2.05 (br s, 1H), 1.96 (br q, *J* = 7.2 Hz, 1H), 1.83 (m, 1H), 1.77-1.55 (m, 5H), 1.38 (dd, *J* = 13.8, 6.4 Hz, 1H), 1.30 (m, 1H), 1.09 (s, 3H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.78 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$):

δ 151.4, 109.5, 70.4, 52.5, 40.7, 38.6, 37.9, 32.4, 32.3, 32.3, 30.9, 29.1, 28.7, 15.1; IR (neat): 3461, 2930, 1461, 1372, 1075, 1052, 1004 cm^{-1}; HRMS calculated for $C_{14}H_{25}O$ $[M+H]^+$ = 209.1905, found 209.1900 (ESI+).

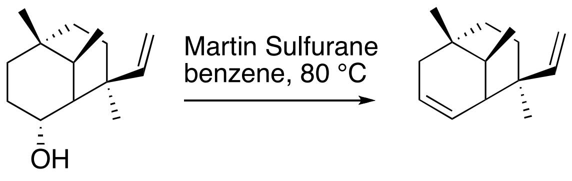


Enone **12b** (62 mg, 0.30 mmol) was dissolved in methanol (2.5 mL) and treated with sodium borohydride (46 mg, 1.2 mmol). After one hour, the reaction was quenched with saturated aqueous ammonium chloride, diluted with methylene chloride and transferred to a separatory funnel. The organic phase was washed three times with distilled water and dried over anhydrous sodium sulfate. Once filtered and concentrated, the residue was dissolved in diethyl ether (2.5 mL), cooled to 0 °C and treated with lithium aluminum hydride (1.0 M in THF, 450 μL, 4.5 mmol). The mixture was allowed to warm to room temperature over one hour. The reaction was quenched with distilled water (100 μL) followed by 1 M aqueous sodium hydroxide (200 μL). An additional portion of distilled water (300 μL) was added and the mixture was stirred for 10 minutes before being filtered through a pad of Celite. The filtrate was dried over anhydrous magnesium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography (5-10% ethyl acetate in hexanes) to yield compound **13b** (46 mg, 0.26 mmol, 73%) as a crystalline solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.76 (dd, *J* = 17.8, 10.7 Hz, 1H), 4.96 (d, *J* = 17.8 Hz, 1H), 4.95 (d, *J* = 10.7 Hz, 1H), 4.25 (ddd, *J* = 12.6, 5.9, 4.5 Hz, 1H), 2.05-1.94 (m, 2H), 1.83-1.71 (m, 3H), 1.64 (dddd, 13.8, 13.8, 6.9, 2.3 Hz, 1H), 1.56 (br s, 1H), 1.52-1.37 (m, 3H), 1.19 (s, 3H), 0.92 (d, *J* = 7.3 Hz, 3H), 0.73 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 150.3, 110.1, 70.6, 51.6, 42.6, 39.0, 39.0, 33.2, 32.5, 32.1, 31.1, 30.3, 29.1, 15.6; IR (neat): 3379, 2930, 1456, 1076, 1046, 1002 cm^{-1}; HRMS calculated for $C_{14}H_{24}O$ $[M]^+$ = 208.1827, found 208.1826 (EI+).

Compound **13a** (30 mg, 0.14 mmol) was dissolved in benzene (500 μL) and treated with a solution of Martin Sulfurane (194 mg, 0.29 mmol) in benzene (500 μL). The mixture was heated to 80 °C for 30 minutes and cooled to room temperature. Half of the solvent volume was removed under reduced pressure (care should be taken to avoid co-distillation of the volatile product) and then the solution was purified by column chromatography (0.05% diethyl ether in pentane). The fractions containing compound **14a** were concentrated to a volume of ~150 μL under reduced pressure. This solution was subsequently purified by semi-preparative gas chromatography (helium flow: 30 mL/min, current: 140 mA, oven temperature: 150 °C (isothermal), successive 15 μL injections) to yield compound **14a** (6.3 mg, 0.033 mmol, 23%) as a colorless oil.

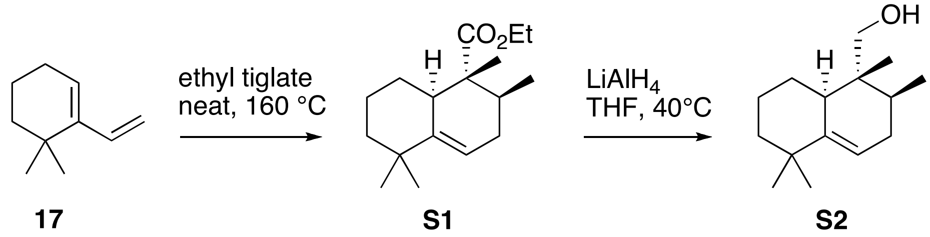
^{1}H-NMR (500 MHz, C_6D_6): δ 5.83 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.70 (ddd, *J* = 9.9, 3.3, 3.3 Hz, 1H), 5.62 (m, 1H), 4.96 (dd, *J* = 10.9, 1.4 Hz, 1H), 4.93 (dd, *J* = 17.6, 1.4 Hz, 1H), 1.86-1.79 (m, 2H), 1.70 (d, *J* = 7.2 Hz, 1H), 1.65 (br q, *J* = 6.8 Hz, 1H), 1.60 (m, 1H), 1.38 (m, 1H), 1.22 (ddd, *J* = 13.4, 4.9, 2.2 Hz, 1H), 1.10 (m, 1H), 1.08 (s, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.81 (s, 3H); ^{13}C-NMR (125 MHz, C_6D_6): δ 149.5, 128.6, 127.5, 110.1, 49.0, 40.3, 39.4, 36.3, 35.2, 32.8, 29.1, 29.1, 23.5, 15.6; IR (neat): 2962, 2925, 1636, 1454, 1256 cm^{-1}; HRMS calculated for $C_{14}H_{22}$ $[M]^+$ = 190.1722, found 190.1722 (EI+).



13b **14b**

Compound **13b** (40 mg, 0.19 mmol) was dissolved in benzene (500 μL) and treated with a solution of Martin Sulfurane (260 mg, 0.39 mmol) in benzene (500 μL). The mixture was heated to 80 °C for 30 minutes and cooled to room temperature. Half of the solvent volume was removed under reduced pressure (care should be taken to avoid co-distillation of the volatile product) and then the solution was purified by column chromatography (0.05% diethyl ether in pentane). The fractions containing compound **14a** were concentrated to a volume of ~150 μL under reduced pressure. This solution was subsequently purified by semi-preparative gas chromatography (helium flow: 30 mL/min, current: 140 mA, oven temperature: 150 °C (isothermal), successive 15 μL injections) to yield compound **14b** (12.2 mg, 0.064, 34%) as a colorless oil.

^{1}H-NMR (500 MHz, CDCl$_3$): δ 5.80 (dd, *J* = 17.7, 11.0, Hz, 1H), 5.75 (ddd, *J* = 9.9, 3.3, 3.3 Hz, 1H), 5.62 (m, 1H), 5.05 (dd, *J* = 11.0, 1.4 Hz, 1H), 5.02 (dd, *J* = 17.7, 1.4 Hz, 1H), 1.84 (br d, *J* = 19.0 Hz, 1H), 1.78 (br d, *J* = 6.1 Hz, 1H), 1.66 (br q, *J* = 6.9 Hz, 1H), 1.64-1.56 (m, 2H), 1.46 (m, 1H), 1.41 (m, 1H), 1.16 (m, 1H), 0.92 (s, 3H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.80 (s, 3H); ^{13}C-NMR (125 MHz, CDCl$_3$): δ 147.8, 129.7, 126.3, 111.8, 48.8, 41.4, 39.8, 36.5, 36.3, 32.6, 29.9, 29.2, 28.7, 15.7; IR (neat): 2926, 1633, 1454, 1370, 908 cm^{-1}; HRMS calculated for $C_{14}H_{22}$ $[M]^+$ = 190.1722, found 190.1725 (EI+).

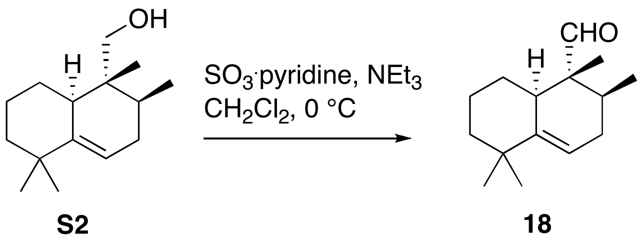


Diene **17**^{3} (600 mg, 4.40 mmol) was dissolved in ethyl tiglate (1.69 mL, 12.2 mmol) and the mixture was heated to 160 °C in a sealed vial for three days. The mixture was then cooled and the excess dienophile was removed under reduced pressure. The crude product was purified by flash column chromatography (5% ethyl acetate in hexanes) to yield compound **S1** (838 mg, 3.17 mmol, 71%) as a ~2:1 mixture of diastereomers in favor of the desired *exo* isomer. Ester **S1** (1.217 g, 4.603 mmol) was dissolved in THF (20 mL) and treated with a solution of lithium aluminum hydride (1M in THF, 9.20 mL, 9.20 mmol). The solution was heated to 40 °C for one hour, cooled to 0 °C and quenched distilled water. The mixture was diluted with diethyl ether, transferred to a separatory funnel and washed successively with 10% aqueous hydrochloric acid, distilled water and saturated aqueous sodium chloride. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, concentrated and purified by flash column chromatography (10% ethyl acetate in hexanes). Alcohol **S2** (890 mg, 4.00 mmol, 87%) was obtained as a colorless oil. The *endo*/*exo* diastereomers, as well as the two enantiomers of the *exo* isomer were successfully separated by preparative SFC [AD-H column (2 x 25 cm), 8% ethanol (0.1% DEA)/CO_2, 100 bar, 60 mL/min, 15 mg/mL, 1 mL/injection] to yield 249 mg of *endo*-**S2**, 289 mg of (+)-*exo*-**S2** ($[\alpha]_D$ = +27° (c = 0.20, $CHCl_3$)) and 291 mg of (–)-*exo*-**S2** ($[\alpha]_D$ = –30° (c = 0.24, $CHCl_3$)). The single enantiomers solidified upon standing.

Endo-**S2**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.29 (m, 1H), 3.51 (AB, J = 10.7 Hz, 1H), 3.47 (AB, J = 10.7 Hz, 1H), 2.00-1.93 (m, 2H), 1.83 (m, 1H), 1.75 (br s, 1H), 1.73-1.56 (m, 4H), 1.44 (br d, J = 12.8 Hz, 1H), 1.20-1.05 (m, 2H), 1.01 (s, 3H), 1.00 (s, 3H), 0.78 (s, 3H), 0.75 (d, J = 6.6 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 147.1, 114.5, 68.5, 42.5, 42.1, 38.5, 36.9, 31.9, 30.0, 29.5, 29.3, 26.0, 23.2, 16.3, 15.1; IR (neat): 3390, 2956, 2923, 1453, 1383, 1035 cm^{-1}; HRMS calculated for $C_{15}H_{27}O$ $[M+H]^+$ = 223.2062, found 223.2055 (ESI+).

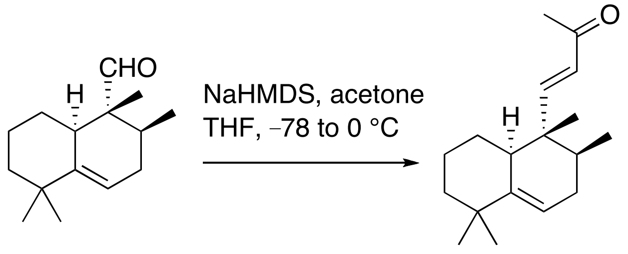
Exo-**S2**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.43 (m, 1H), 3.48, (AB, J = 11.3 Hz, 1H), 3.39 (AB, J = 11.3 Hz, 1H), 2.35 (m, 1H), 1.86 (m, 1H), 1.80-1.72 (m, 2H), 1.70-1.62 (m, 1H), 1.58-1.52 (m, 2H), 1.39 (m, 1H), 1.32 (br s, 1H), 1.19 (m 1H), 1.05 (s, 3H), 0.99 (s, 3H), 0.99-0.92 (m, 1H), 0.86 (d, J = 6.8 Hz, 3H), 0.50 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 146.1, 116.1, 65.7, 41.0, 39.3, 38.0, 36.3, 31.9, 31.3, 29.9, 28.9, 27.7, 22.2, 15.1, 11.6; IR (neat): 3360, 2928, 1455, 1382, 1037 cm^{-1}; HRMS calculated for $C_{15}H_{27}O$

$[M+H]^+$ = 223.2062, found 223.2055 (ESI+).



Alcohol **S2** (261 mg, 1.17 mmol) was dissolved in a mixture of methylene chloride and DMSO (4:1, 10 mL) and cooled to 0 °C. Triethylamine (982 μL, 7.05 mmol) was added, followed by sulfur trioxide pyridine complex (560 mg, 3.52 mmol) in one portion. The reaction was stirred for two hours and then quenched with distilled water. The mixture was diluted with diethyl ether and transferred to a separatory funnel. The organic layer was washed successively with 10% aqueous hydrochloric acid, distilled water, and saturated aqueous sodium chloride and was dried over anhydrous magnesium sulfate. After filtration and concentration, the crude product was purified by flash column chromatography (2% ethyl acetate in hexanes). Aldehyde **18** (223 mg, 1.01 mmol, 86%) was obtained as a white crystalline solid.

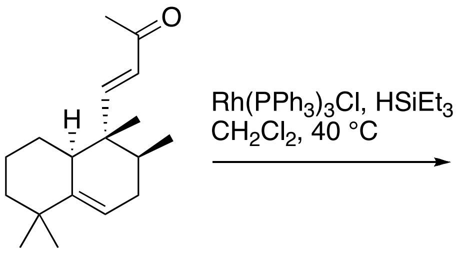
^{1}H-NMR (500 MHz, CDCl$_3$): δ 9.39 (s, 1H), 5.30 (m, 1H), 2.51 (m, 1H), 1.96 (m, 1H), 1.86 (m, 1H), 1.76 (dddd, *J* = 16.9, 11.2, 3.4, 2.0 Hz, 1H), 1.56-1.50 (m, 2H), 1.41 (ddd, *J* = 13.0, 5.1, 3.1 Hz, 1H), 1.32 (m, 1H), 1.20 (m, 1H), 1.08 (s, 3H), 1.08-1.00 (m, 1H), 1.04 (s, 3H), 0.81 (s, 3H), 0.78 (d, *J* = 6.7 Hz, 3H); ^{13}C-NMR (125 MHz, CDCl$_3$): δ 207.3, 143.9, 116.6, 52.3, 40.6, 38.1, 36.3, 32.6, 30.4, 29.7, 29.1, 28.7, 21.8, 16.2, 7.5; IR (neat): 2961, 1728, 1456, 1384 cm^{-1}; HRMS calculated for $C_{15}H_{25}O$ $[M+H]^+$ = 221.1905, found 221.1896 (ESI+); $[\alpha]_D$ = +106° (c = 0.22, $CHCl_3$).



18 **S3**

A solution of sodium bis(trimethylsilyl)amide (NaHMDS, 1 M in THF, 1.36 mL, 1.36 mmol) was cooled to −78 °C and treated with acetone (100 μL, 1.36 mmol). The mixture was stirred at this temperature for 30 minutes and then a solution of aldehyde **18** (60 mg, 0.27 mmol) in THF (2 mL) was added. After one hour, the $CO_{2(s)}$/acetone bath was removed and the mixture was allowed to warm to room temperature. After another hour, the reaction was quenched with saturated aqueous sodium bicarbonate, diluted with diethyl ether, and transferred to a separatory funnel. The organic layer was washed successively with distilled water and saturated aqueous sodium chloride and was dried over anhydrous magnesium sulfate. After filtration and concentration, the crude product was purified by flash column chromatography (2% ethyl acetate in hexanes). Enone **S3** (62 mg, 0.24 mmol, 87%) was obtained as a white crystalline solid.

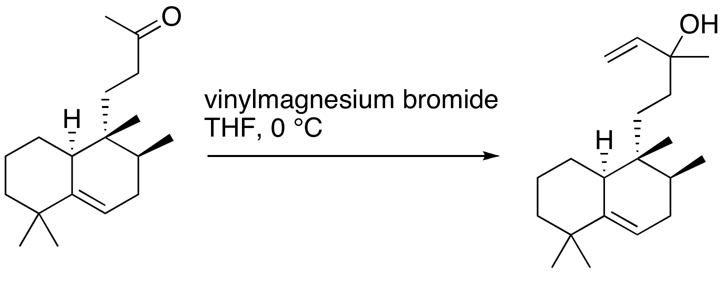
^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.61 (d, J = 16.3 Hz, 1H), 6.02 (d, J = 16.3 Hz, 1H), 5.49 (m, 1H), 2.28 (s, 3H), 2.13 (m, 1H), 1.93 (m, 1H), 1.74 (m, 1H), 1.59-1.42 (m, 4H), 1.38 (m, 1H), 1.19 (ddd, J = 12.8, 12.8, 4.8 Hz, 1H), 1.07 (s, 3H), 1.00 (s, 3H), 0.98 (m, 1H), 0.78 (s, 3H), 0.72 (d, J = 6.8 Hz, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.9, 158.3, 144.7, 129.6, 116.5, 43.6, 43.0, 40.7, 36.6, 36.2, 31.1, 29.7, 29.3, 28.3, 27.5, 21.9, 16.4, 10.3; IR (neat): 2930, 1676, 1620, 1456, 1384 cm^{-1}; HRMS calculated for $C_{18}H_{29}O$ $[M+H]^+$ = 261.2218, found 261.2210 (ESI+); $[\alpha]_D$ = +79° (*c* = 0.18, $CHCl_3$).



S3 **20**

Enone **S3** (56 mg, 0.22 mmol) was dissolved in methylene chloride (3 mL), treated with Wilkinson's catalyst (20 mg, 0.022 mmol) and triethylsilane (172 μL, 1.08 mmol) and heated to 40 °C overnight. The mixture was cooled to room temperature and treated with 6 M aqueous hydrochloric acid (3 mL). After 30 minutes, the solution was diluted with diethyl ether and washed successively with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride. The organic phase was dried over anhydrous magnesium sulfate, filtered and concentrated. The crude product was purified by flash column chromatography (3% ethyl acetate in hexanes) to yield ketone **20** (47 mg, 0.18 mmol, 83%) as a colorless oil.

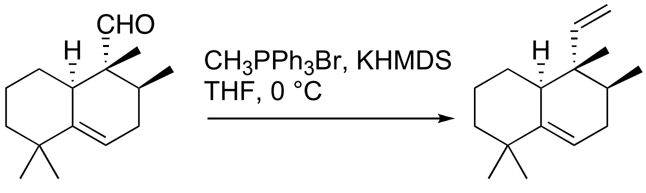
^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.44 (m, 1H), 2.42-2.28 (m, 2H), 2.17 (s, 3H), 2.01 (m, 1H), 1.84 (m, 1H), 1.79-1.64 (m, 3H), 1.60-1.36 (m, 5H), 1.19 (ddd, *J* = 13.1, 13.1, 4.3 Hz, 1H), 1.06 (s, 3H), 1.03-0.99 (m, 1H), 0.99 (s, 3H), 0.80 (d, *J* = 6.3 Hz, 3H), 0.64 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 210.0, 146.0, 116.4, 41.0, 40.1, 37.8, 36.7, 36.2, 33.6, 31.6, 30.2, 30.1, 29.9, 29.1, 27.6, 22.3, 16.1, 15.1; IR (neat): 2962, 1716, 1456, 1384, 1261 cm^{-1}; HRMS calculated for $C_{18}H_{31}O$ $[M+H]^+$ = 263.2375, found 263.2365 (ESI+); $[\alpha]_D$ = +30° (*c* = 0.44, $CHCl_3$).



20 **15**

Ketone **20** (15 mg, 0.057 mmol) was dissolved in THF (1 mL) and cooled to 0 °C. Vinylmagnesium bromide (1 M in THF, 74 μL, 0.074 mmol) was added and the mixture was stirred for 30 minutes. The reaction was then quenched with saturated aqueous sodium bicarbonate, diluted with diethyl ether, and transferred to a separatory funnel. The organic layer was washed successively with saturated aqueous sodium bicarbonate, distilled water and saturated aqueous sodium chloride and was dried over anhydrous magnesium sulfate. After filtration and concentration, the crude product was purified by flash column chromatography (3% ethyl acetate in hexanes). Tertiary allylic alcohol **15** (16 mg, 0.053 mmol, 93%) was obtained as a 3:2 mixture of alcohol epimers (based on ^{1}H-NMR). For comparisons of the NMR data of compound **15** with those of edaxadiene[4] and nosyberkol[5] see pages S25 and S30 respectively.

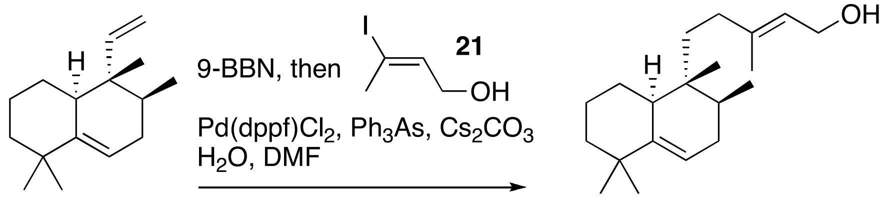
^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.92 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.43 (m, 1H), 5.21, (d, *J* = 17.4 Hz, 1H), 5.07 (d, *J* = 10.8 Hz, 1H), 2.12 (m, 1H), 1.80 (m, 1H), 1.75 (m, 1H), 1.70 (m, 1H), 1.60-1.35 (m, 7H), 1.29 (s, 3H), 1.26 (m, 1H), 1.19 (m, 1H), 1.05 (s, 3H), 1.00 (s, 3H), 1.00 (m, 1H), 0.79 (d, $J = 6.8$ Hz, 3H), 0.61 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$, signals highlighted in red appear split due to the presence of epimers): δ 146.2, 145.2, 116.3, 112.0, 73.7, 41.0, 39.8, 36.8, 36.2, 35.3, 33.5, 31.8, 30.2, 29.9, 29.2, 27.8, 27.4, 22.3, 16.3, 15.1; ^{1}H-NMR (500 MHz, C_6D_6): δ 5.77 (dd, $J = 17.3$, 10.7 Hz, 1H), 5.55 (m, 1H), 5.17 (d, $J = 17.3$ Hz, 1H), 4.96 (d, $J = 10.7$, 1H), 2.25 (m, 1H), 1.87-1.76 (m, 3H), 1.56 (m, 2H), 1.55-1.30 (m, 6H), 1.26 (m, 1H), 1.14 (s, 3H), 1.12 (s, 3H), 1.09, (s, 3H), 1.07 (m, 1H), 0.89 (br s, 1H), 0.84 (d, $J = 6.8$ Hz, 3H), 0.71 (s, 3H);^{13}C-NMR (125 MHz, C_6D_6, signals highlighted in red appear split due to the presence of epimers): δ 146.2, 145.7, 116.9, 111.5, 73.0, 41.3, 40.2, 37.0, 36.3, 35.5, 33.7, 32.1, 30.4, 30.1, 29.3, 28.3, 27.7, 22.6, 16.5, 15.3; IR (neat): 3438, 2931, 1456, 1384 cm^{-1}; HRMS calculated for $C_{20}H_{34}O$ $[M]^+$ = 290.2610, found 290.2608 (EI+), 272 $[M{-}H_2O]^+$ fragment present in +EI mass spectrum, base peak = 191; $[\alpha]_D$ = +19° (*c* = 0.16, $CHCl_3$).



18 **19**

Methyltriphenylphosphonium bromide (632 mg, 1.77 mmol) was suspended in THF (10 mL) and treated with potassium bis(trimethylsilyl)amide (KHMDS, 0.5 M in toluene, 3.36 mL, 1.68 mmol) at 0 °C. After 30 minutes, a solution of aldehyde **18** (195 mg, 0.885 mmol) in THF (10 mL) was added *via* cannula and the mixture was stirred for two hours. Upon completion, the reaction was quenched with saturated aqueous sodium bicarbonate, diluted with diethyl ether and transferred to a separatory funnel. The organic phase was washed successively with distilled water and saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate. Once filtered and concentrated, the crude product was purified by flash column chromatography (hexanes). Compound **19** (175 mg, 0.802 mmol, 91%) was obtained as a colorless liquid.

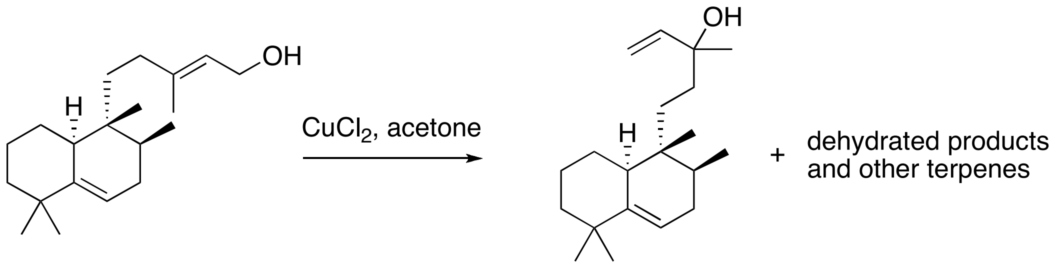
^{1}H-NMR (500 MHz, $CDCl_3$): δ 5.55 (dd, *J* = 17.5, 10.8 Hz, 1H), 5.48 (m, 1H), 5.06 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.92 (dd, *J* = 17.5, 1.5 Hz, 1H), 1.99 (m, 1H), 1.90 (m, 1H), 1.74 (m, 1H), 1.63 (m, 1H), 1.56-1.36 (m, 4H), 1.20 (ddd, *J* = 12.9, 12.9, 4.5 Hz, 1H), 1.07 (s, 3H), 1.01 (s, 3H), 0.94 (dddd, *J* = 12.8, 12.8, 12.8, 4.3 Hz, 1H), 0.75 (d, *J* = 6.8 Hz, 3H), 0.71, (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ 148.5, 145.6, 116.3, 112.4, 43.9, 42.5, 41.1, 36.6, 36.2, 31.5, 29.8, 29.4, 27.9, 22.2, 16.2, 9.9; IR (neat): 2930, 1456, 1384 cm^{-1}; HRMS calculated for $C_{16}H_{26}O$ $[M]^+$ = 218.2035, found 218.2036 (EI+); $[\alpha]_D$ = +61° (*c* = 0.45, $CHCl_3$).



19 **16**

Alkene **19** (39 mg, 0.18 mmol) was dissolved in a solution of 9-BBN (0.5 M in THF, 536 μL, 0.27 mmol), heated to 70 °C for three hours, and cooled to room temperature. In a separate flask, (*E*)-3-iodobut-2-en-1-ol[6] (**21**, 71 mg, 0.36 mmol) was dissolved in degassed DMF (1 mL) and treated with [1,1′-Bis(diphenylphosphino)ferrocene]-dichloropalladium(II) (1:1 complex with dichloromethane, 16 mg, 0.018 mmol), triphenylarsine (5 mg, 0.018 mmol), cesium carbonate (172 mg, 0.045 mmol) and distilled water (129 μL, 7.14 mmol). After 20 minutes, the hydroboration solution was added *via* cannula, rinsing with THF (500 μL). After six hours, the mixture was diluted with distilled water and diethyl ether. The aqueous phase was washed with three portions of diethyl ether, and the combined organic layers were washed once with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (5-15% diethyl ether in hexanes) to yield compound **16** (37 mg, 0.13 mmol, 73%), which had spectroscopic properties consistent with those of tuberculosinol.[7]

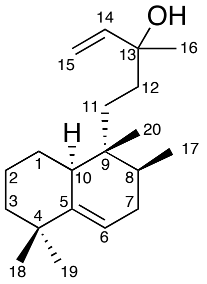
^{1}H-NMR (500 MHz, C_6D_6): δ 5.55 (m, 1H), 5.43 (tq, *J* = 6.7, 1.2 Hz, 1H), 4.00 (d, *J* = 6.7 Hz, 2H), 2.26 (m 1H), 1.94 (ddd, *J* = 13.0, 13.0, 5.0 Hz, 1H), 1.90-1.80 (m, 3H), 1.75 (m, 1H), 1.58-1.48 (m, 4H), 1.51 (s, 3H), 1.43-1.34 (m, 2H), 1.27 (m, 1H), 1.15 (s, 3H), 1.10 (s, 3H), 1.11-1.05 (m, 1H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.70 (s, 3H); ^{13}C-NMR (125 MHz, C_6D_6): δ 146.2, 139.2, 124.5, 116.8, 59.5, 41.3, 40.3, 37.2, 36.3, 35.3, 33.7, 33.0, 32.0, 30.1, 29.2, 27.8, 22.6, 16.5, 16.5, 15.3; IR (neat): 3410, 2929, 1457, 1383 cm^{-1}; HRMS calculated for $C_{20}H_{34}O$ $[M+H]^+$ = 291.2688, found 291.2678 (ESI+); $[\alpha]_D$ = +16° (*c* = 0.24, $CHCl_3$).



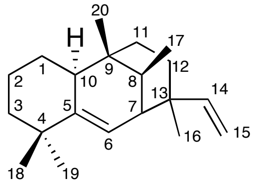
16 (tuberculosinol) **15**

Compound **16** (88 mg, 0.30 mmol) was dissolved in acetone (1 mL) and treated with copper(**II**) chloride (4 mg, 0.03 mmol). After four hours, a second portion of copper(**II**) chloride (4 mg, 0.03 mmol) was added and stirring was continued for another two hours. The reaction was then diluted with diethyl ether and washed with distilled water and saturated aqueous sodium chloride. The organic phase was dried over anhydrous magnesium sulfate, filtered, concentrated and purified by flash column chromatography (0-15% diethyl ether in hexanes). Compound **15** (18 mg, 0.062, 20%) was obtained as a 1:1 mixture of alcohol epimers. A mixture of dienes (28 mg, 0.10 mmol, 34%) resulting from dehydration was also isolated, as well as some residual tuberculosinol contaminated with other terpene byproducts (16 mg). In our hands, the addition of DCC (*N,N'*-dicyclohexylcarbodiimide) inhibited the transformation, resulting in the quantitative recovery of starting material. For a comparison of the ^{1}H-NMR spectrum of compound **15** as prepared from tuberculosinol to compound **15** prepared *via* an *exo*-selective Diels Alder reaction (as depicted in scheme 4), see page S29. For a comparison of the same spectrum to that of edaxadiene, see page S28.

Comparison of NMR Data for Compound **15** to Edaxadiene[4]



15



edaxadiene

Carbon Position	**δ ^{1}H (ppm)**, C$_6$D$_6$		**δ ^{13}C (ppm)**, C$_6$D$_6$	
	Compound **15**[1,2]	Edaxadiene	Compound **15**[2]	Edaxadiene[3]
1	1.90, 1.17	1.894, 1.164	27.7	27.53
2	1.66 (2H)[4]	1.651, 0.957	22.6	22.48
3	1.48, 1.36	1.481, 1.359	41.3	41.15
4			36.3	36.13
5			146.2	145.80
6	5.65	5.643	116.9	116.69
7	1.92	1.920	32.1	31.84
8	1.59	1.580	33.7	33.53
9			37.0	36.14[5]
10	2.35	2.346	40.2	40.07
11	1.53, 1.46	1.561, 1.453	30.4	30.24
12	~1.56-1.45 (2H)	1.549, 1.473	35.5	35.35
13			73.0	72.90
14	5.87	5.871	145.7	145.60
15	5.27, 5.05	5.273, 5.051	111.5	111.49
16	1.22	1.211	28.3	27.55[6]
17	0.91, 0.93[7]	0.909	15.3	15.20
18	1.24	1.239	30.1	29.97
19	1.19	1.186	29.3	29.22
20	0.81	0.806	16.5	16.42

[1] Due to an apparent inconsistency in the referencing of the ^{1}H-NMR spectra, the ^{1}H-NMR data of compound **15** presented in this table has been referenced such that the chemical shift of the C20 methyl protons matches that reported in ref. 4 (0.806 ppm). The g-HSQC spectrum was used to aid in the assignment of chemical shifts. The ^{1}H-NMR data for compound **15** presented on page S20 (and the spectrum included on page S53) have been referenced to the residual solvent peak of benzene-*d*6 (7.16 ppm).

[2] Peaks highlighted in red appear split due to the presence of C13 epimers.

[3] Chromium(III) acetylacetonate was added as a relaxation enhancement agent.

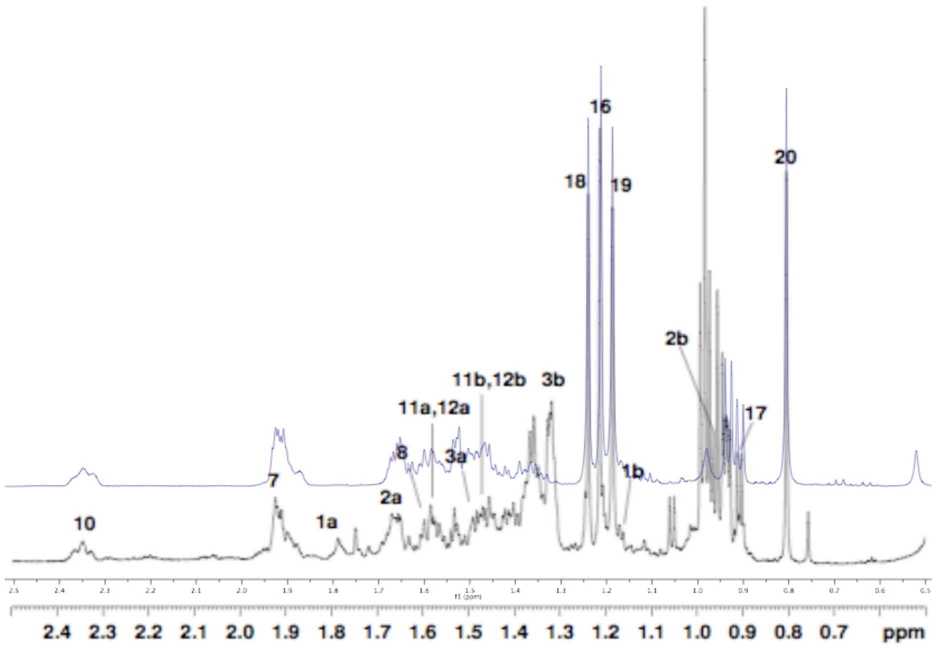
[4] There is no C2 proton at δ = 0.96 ppm in compound **15**. The OH proton appears at δ = 0.99 ppm (confirmed using a D$_2$O shake and supported by the absence of a g-HSQC correlation).

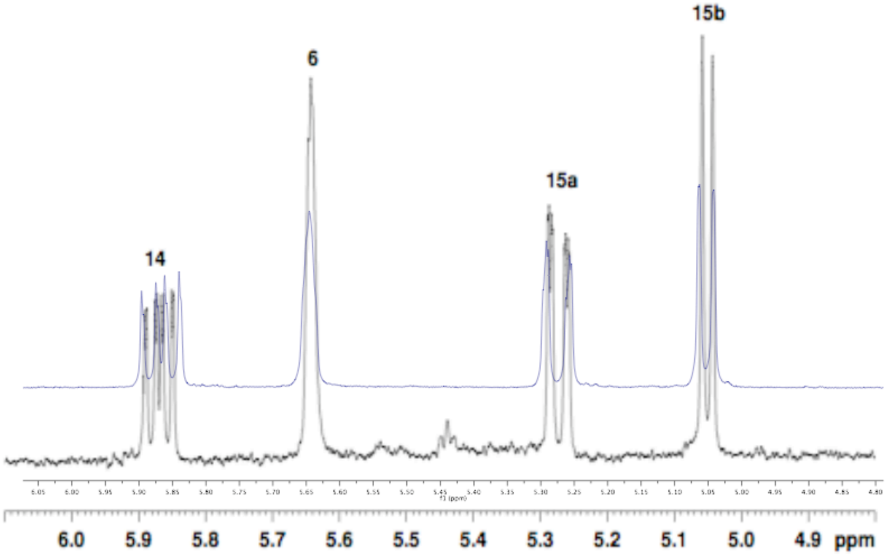
[5] The chemical shift reported for carbon 9 does not match the peak labeled in the ^{13}C-NMR spectrum. The chemical shift of C9 in edaxadiene appears as though it should be near 37 ppm.

[6] The chemical shift reported for carbon 16 does not match the peak labeled in the ^{13}C-NMR spectrum. The chemical shift of C16 in edaxadiene appears as though it should be greater than 28 ppm.

[7] There are two distinct signals for the C17 methyl group (due to the presence of C13 epimers) at 0.91 and 0.93 ppm.

Comparison of the ^{1}H-NMR Spectra of Edaxadiene (black lower trace, 700 MHz)[4] and Compound **15** (3:2 dr, blue upper trace, 500 MHz)* in C_6D_6





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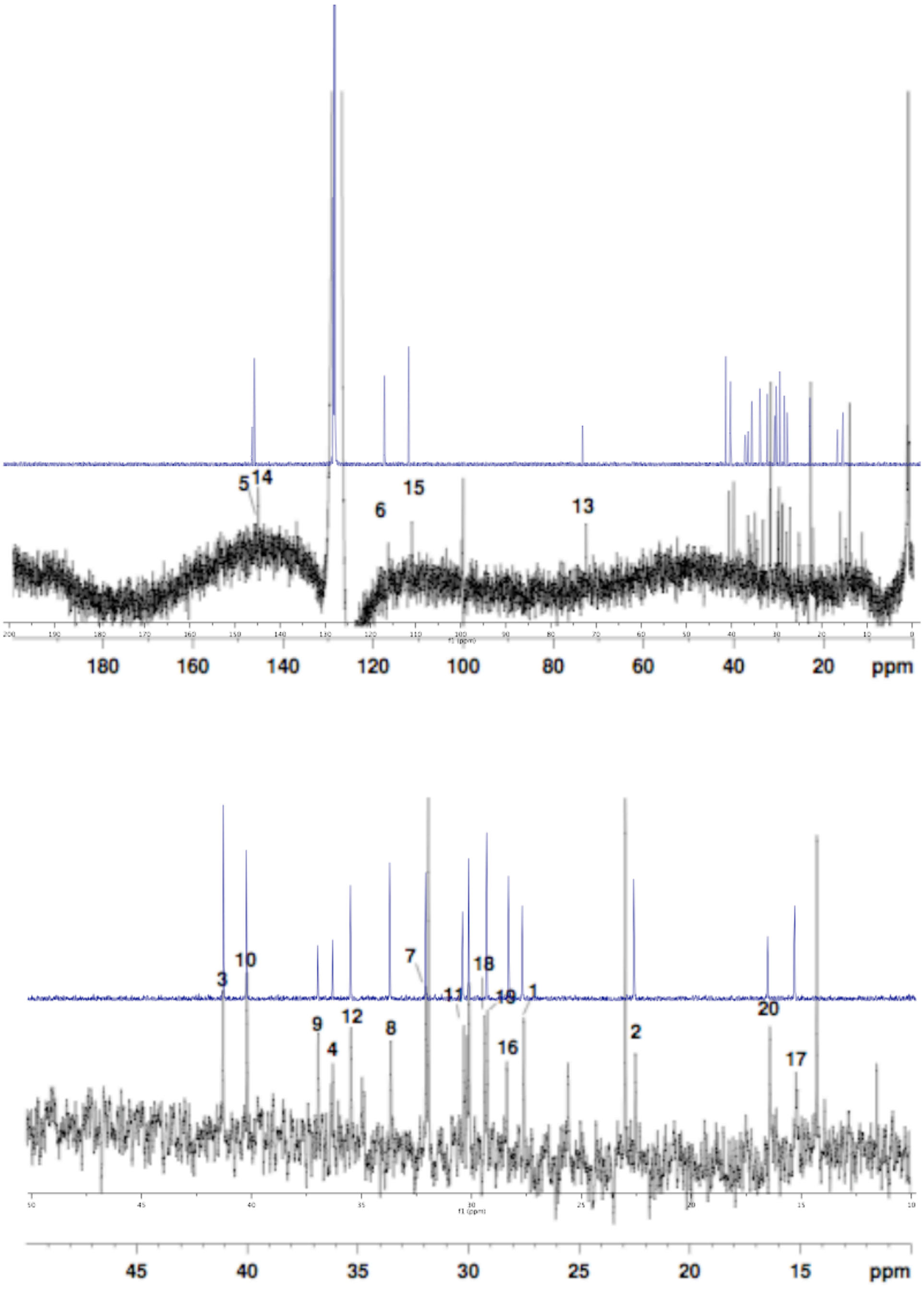
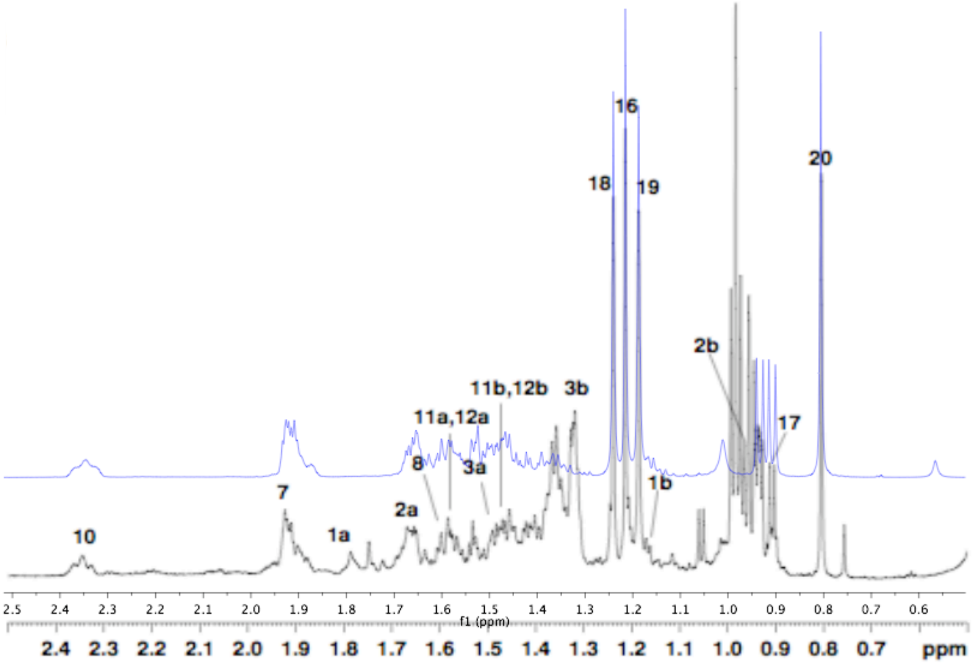
* The spectrum of compound **15** has been referenced such that the C20 methyl protons coincide with the chemical shift reported for the C20 methyl group of edaxadiene (0.806 ppm, ref. 4).

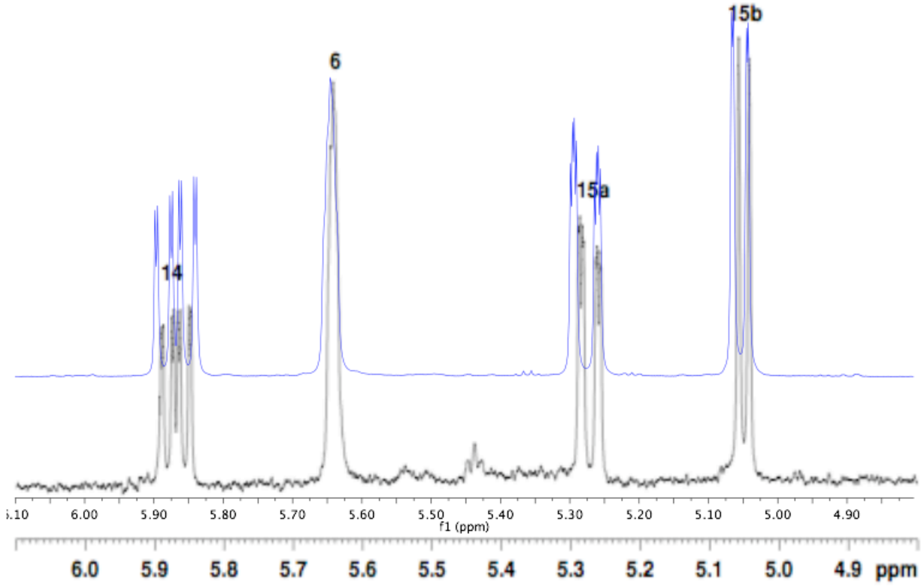
Comparison of the ^{13}C-NMR Spectra of Edaxadiene (black lower trace, 175 MHz)[4†] and Compound **15** (3:2 dr, blue upper trace, 125 MHz) in C_6D_6



[†] The peak labeled **18** in the edaxadiene spectrum does not correspond to the numerical value listed in the table of the supplementary information of ref. 4.

Comparison of the ^{1}H-NMR Spectra of Edaxadiene (black lower trace, 700 MHz)[4] and Compound **15** (1:1 dr, from tuberculosinol, blue upper trace, 500 MHz)[‡] in C_6D_6

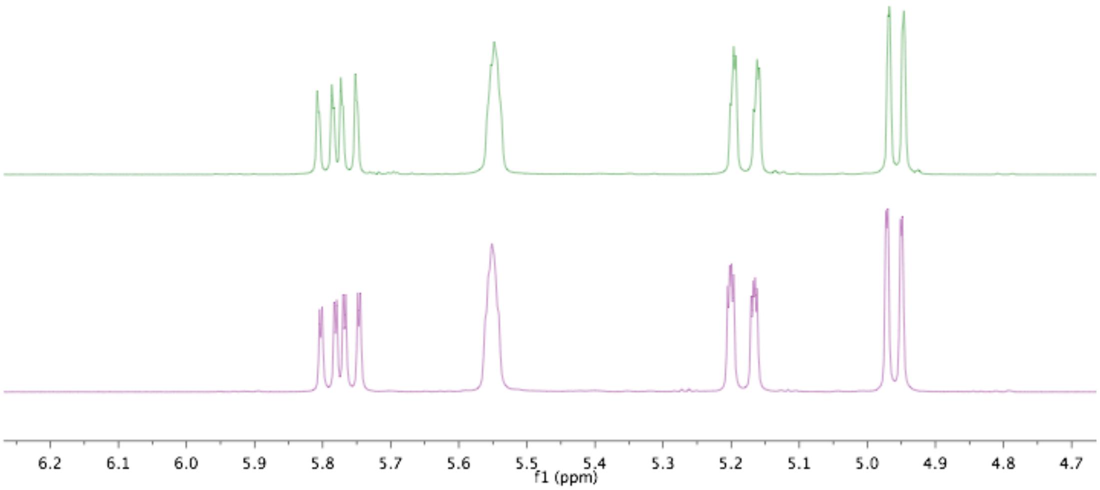


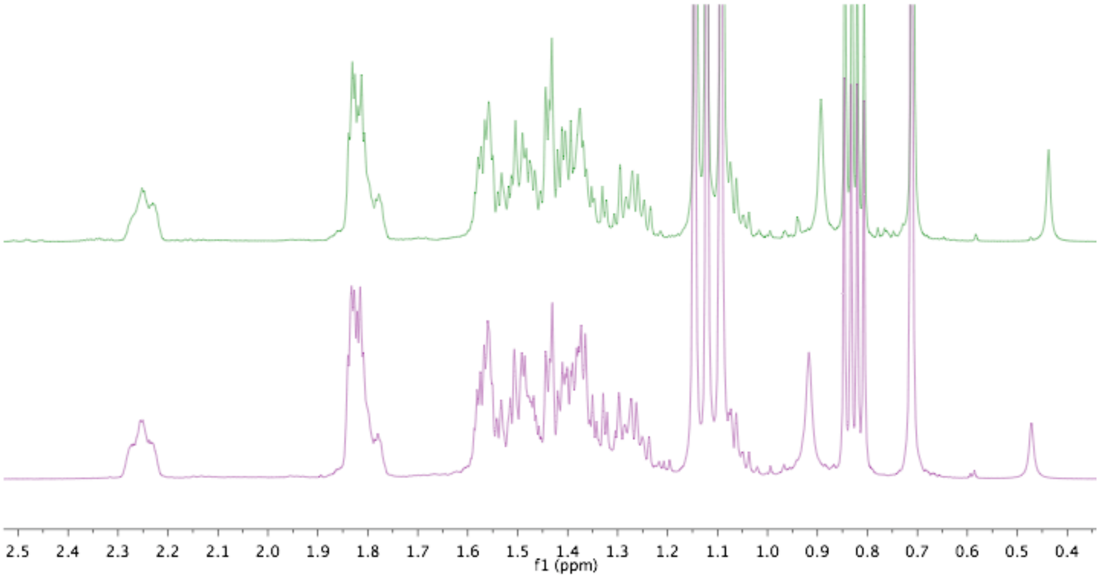


[‡] The spectrum of compound **15** has been referenced such that the C20 methyl protons coincide with the chemical shift reported for the C20 methyl group of edaxadiene (0.806 ppm, ref. 4).

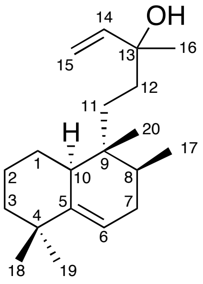
Comparison of the ^{1}H-NMR Spectra of Compound **15** (500 MHz, C_6D_6)

pink trace: compound **15** prepared from tuberculosinol (1:1 dr)
green trace: compound **15** prepared *via* an *exo*-selective Diels Alder reaction (3:2 dr, see scheme 4)





Comparison of NMR Data for Compound **15** to Nosyberkol[5]



15

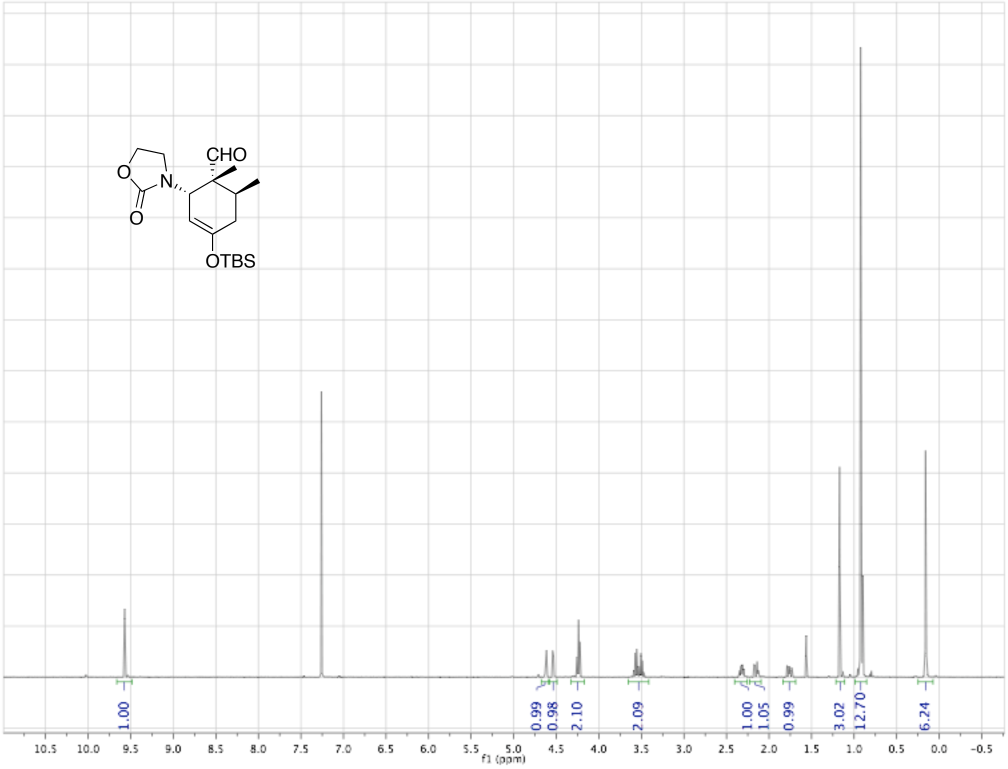
Carbon Position	δ ^{1}H (ppm), $CDCl_3$		δ ^{13}C (ppm), $CDCl_3$[1]	
	Compound **15**[2,3]	Nosyberkol	Compound **15**[3]	Nosyberkol
1	1.70, 1.00	1.68, 1.03	27.4	27.6
2	1.56, 1.50	1.56, 1.50	22.3	22.2
3	1.38, 1.19	1.40, 1.20	41.0	40.9
4			36.8	36.6
5			146.2	146.0
6	5.43	5.43	116.3	116.2
7	1.80, 1.75	1.82, 1.70	31.8	31.6
8	1.46	1.47	33.5	33.3
9			36.2	36.0
10	2.12	2.11	39.8	39.7
11	1.36, 1.26	1.35, 1.28	30.2	30.6
12	1.45	1.45	35.3	35.1
13			73.7	73.5
14	5.92	5.92	145.2	145.1
15	5.21, 5.07	5.20, 5.07	112.0	111.8
16	1.29	1.30	27.8	27.7
17	0.78, 0.79	0.79	15.1	14.9
18	1.05	1.06	29.9	29.7
19	1.00	1.00	29.2	29.0
20	0.61	0.62	16.3	16.2

[1] The chloroform-*d* peak in the ^{13}C-NMR spectrum of nosyberkol was referenced to 77.0 ppm (ref. 5), while the spectrum of compound **15** was referenced to 77.16 ppm.

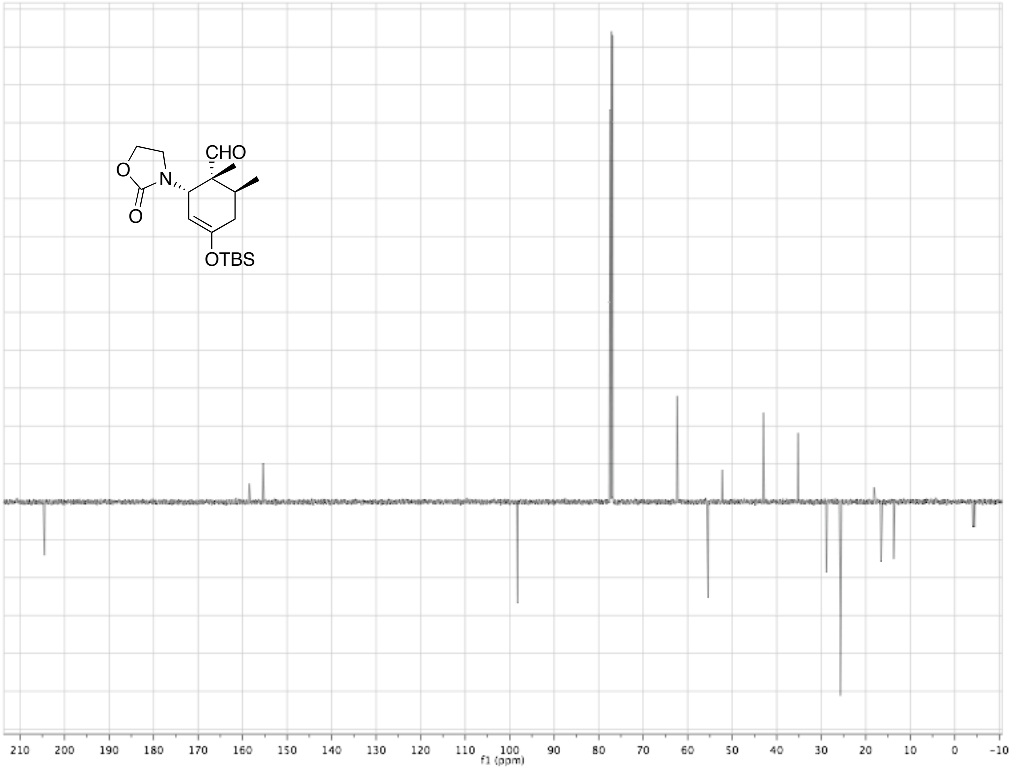
[2] The g-HSQC spectrum was used to aid in the assignment of chemical shifts.

[3] Peaks highlighted in red appear split due to the presence of C13 epimers.

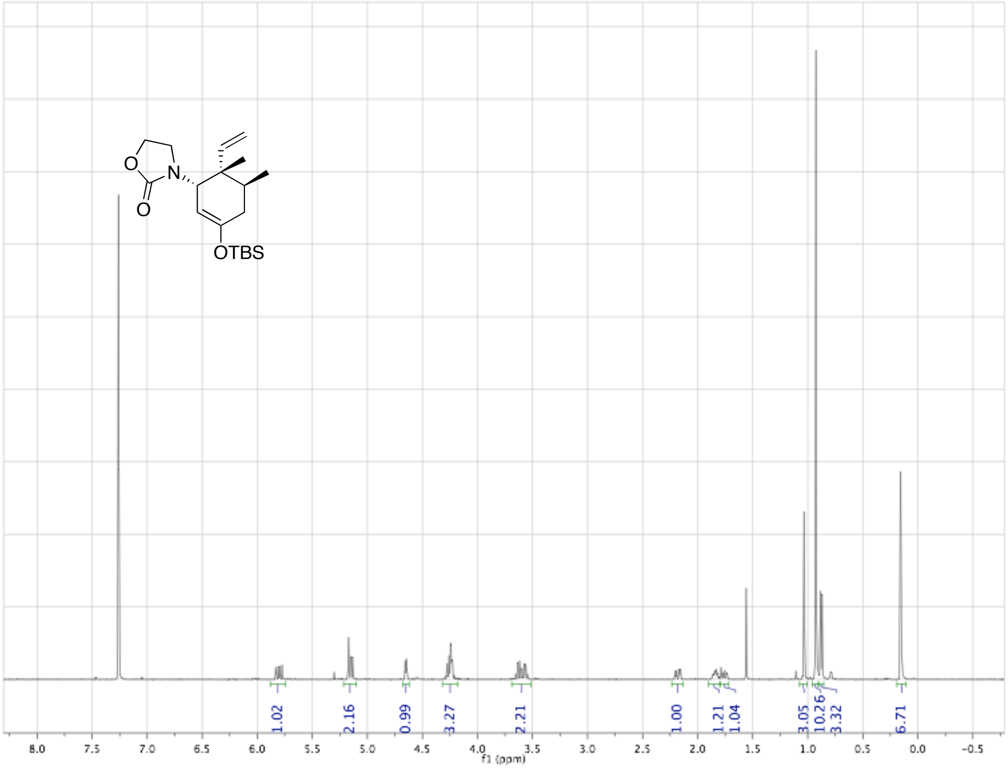
^{1}H-NMR Spectrum of Compound **6** ($CDCl_3$)



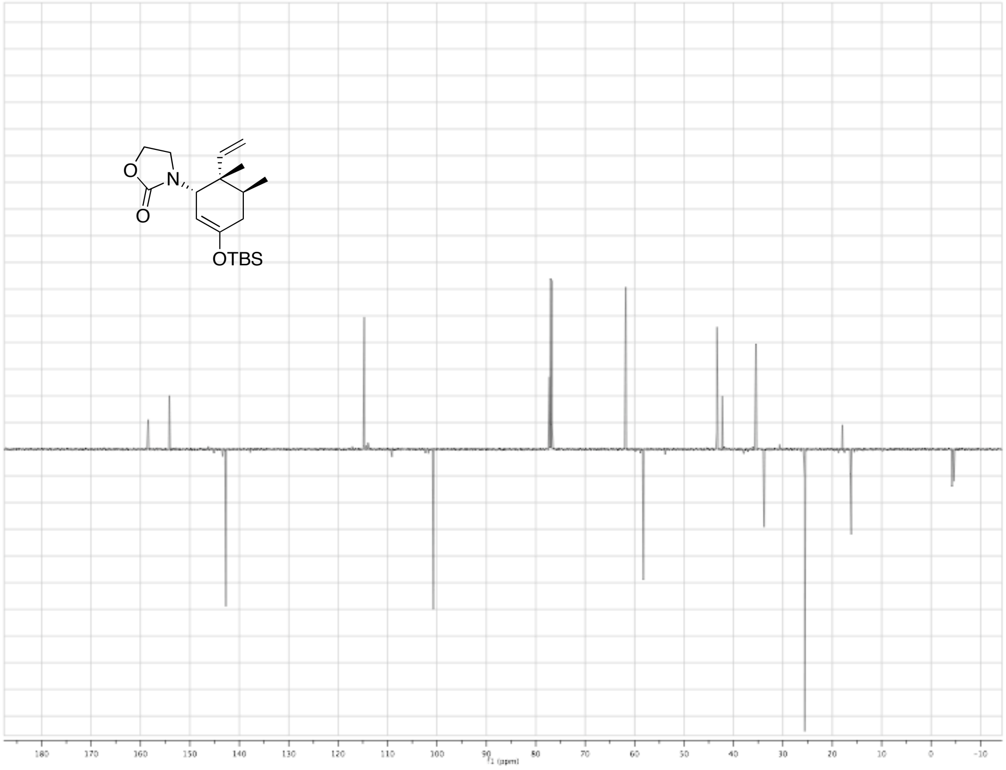
^{13}C-NMR Spectrum of Compound **6** ($CDCl_3$)



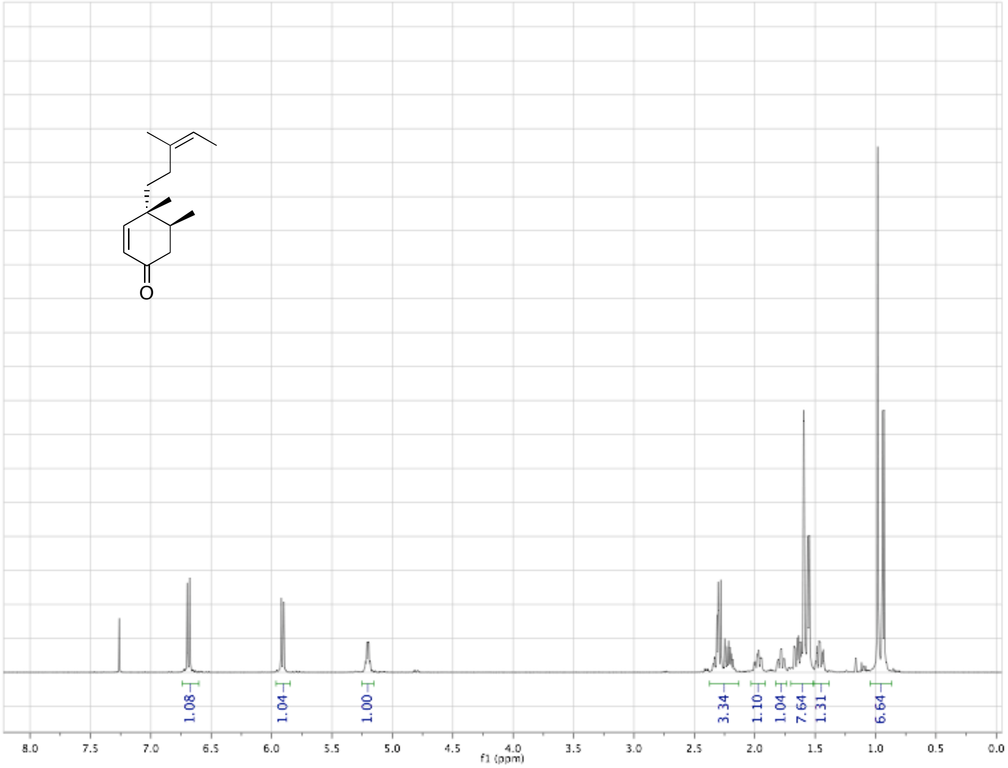
^{1}H-NMR Spectrum of Compound **7** ($CDCl_3$)



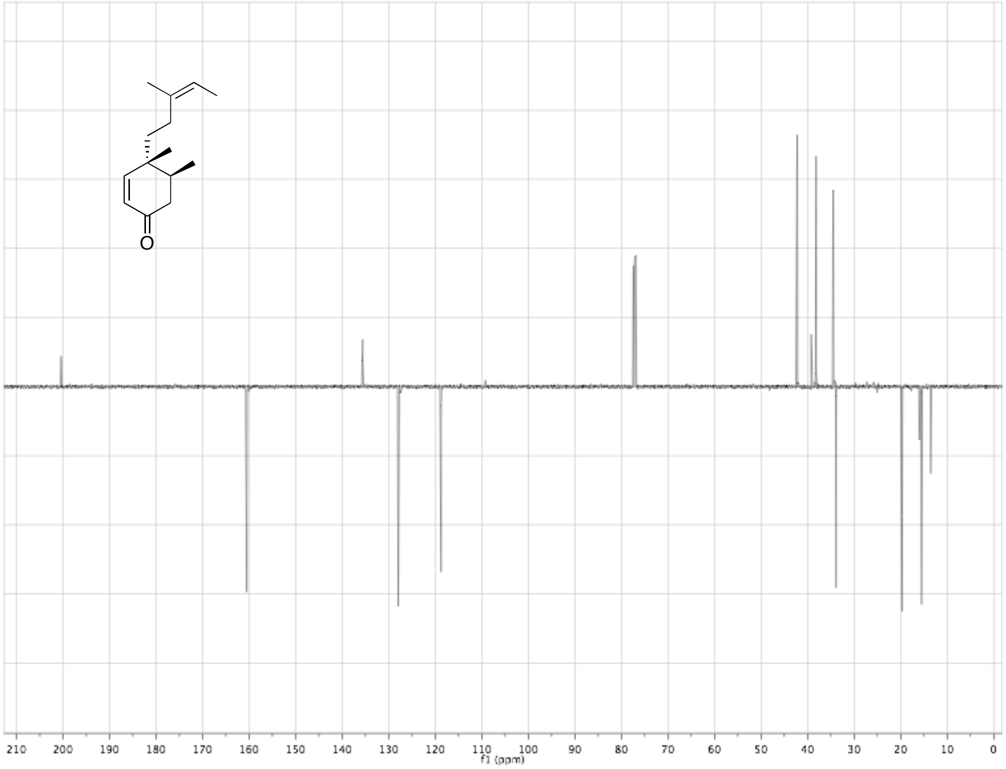
^{13}C-NMR Spectrum of Compound **7** ($CDCl_3$)



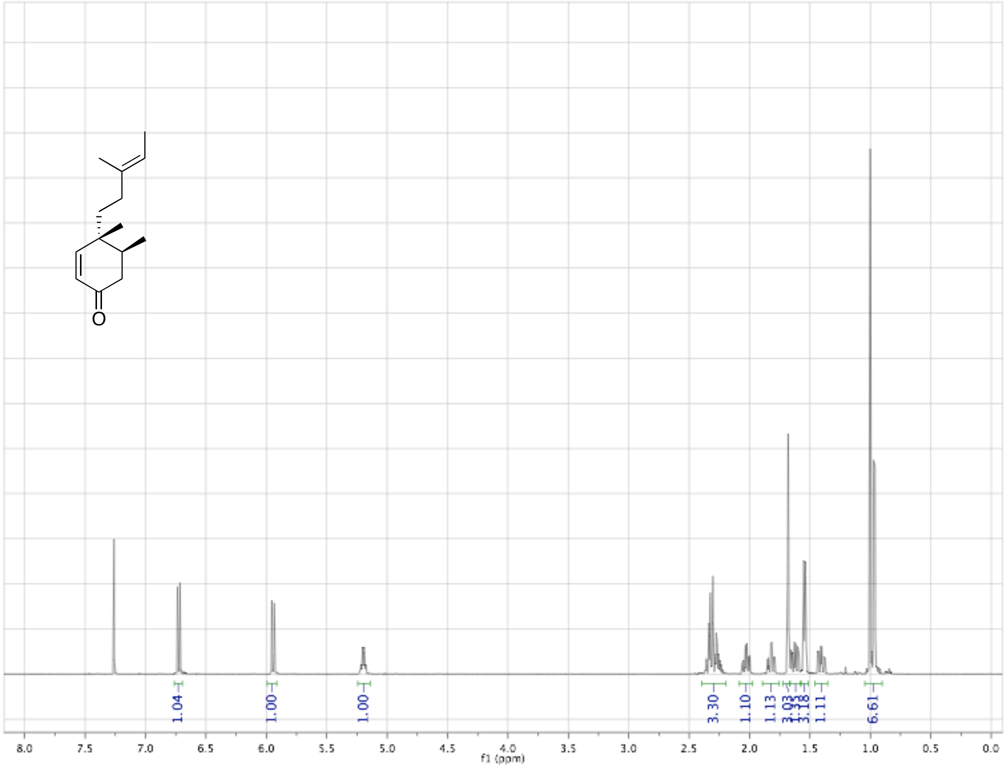
^{1}H-NMR Spectrum of Compound **9a** ($CDCl_3$)



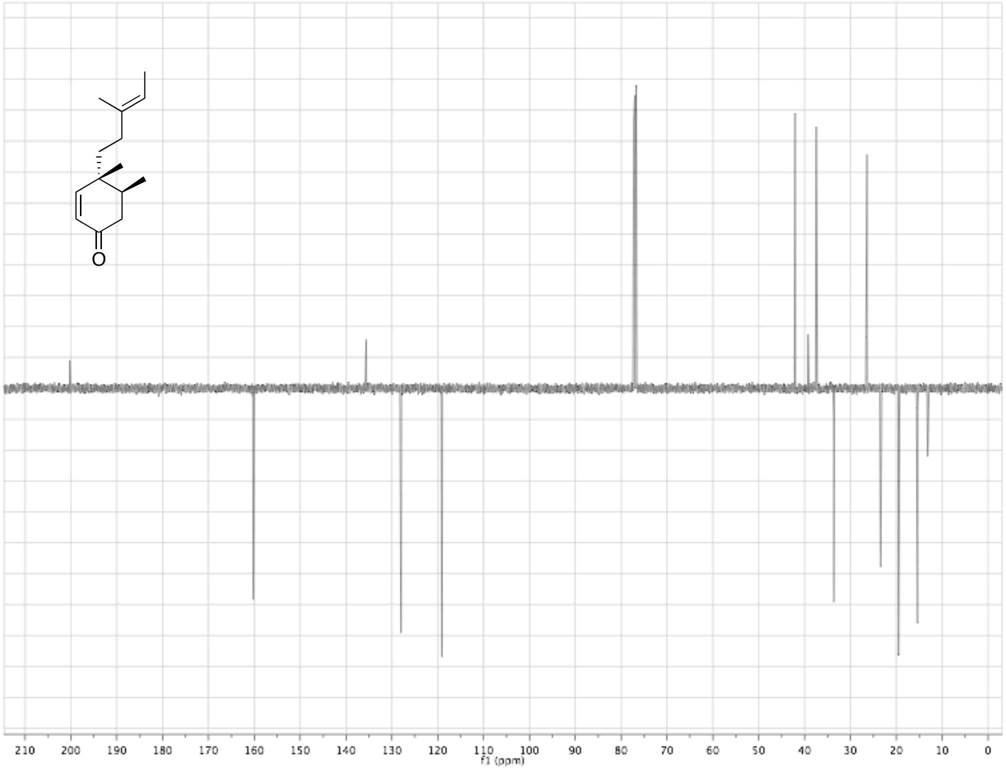
^{13}C-NMR Spectrum of Compound **9a** ($CDCl_3$)



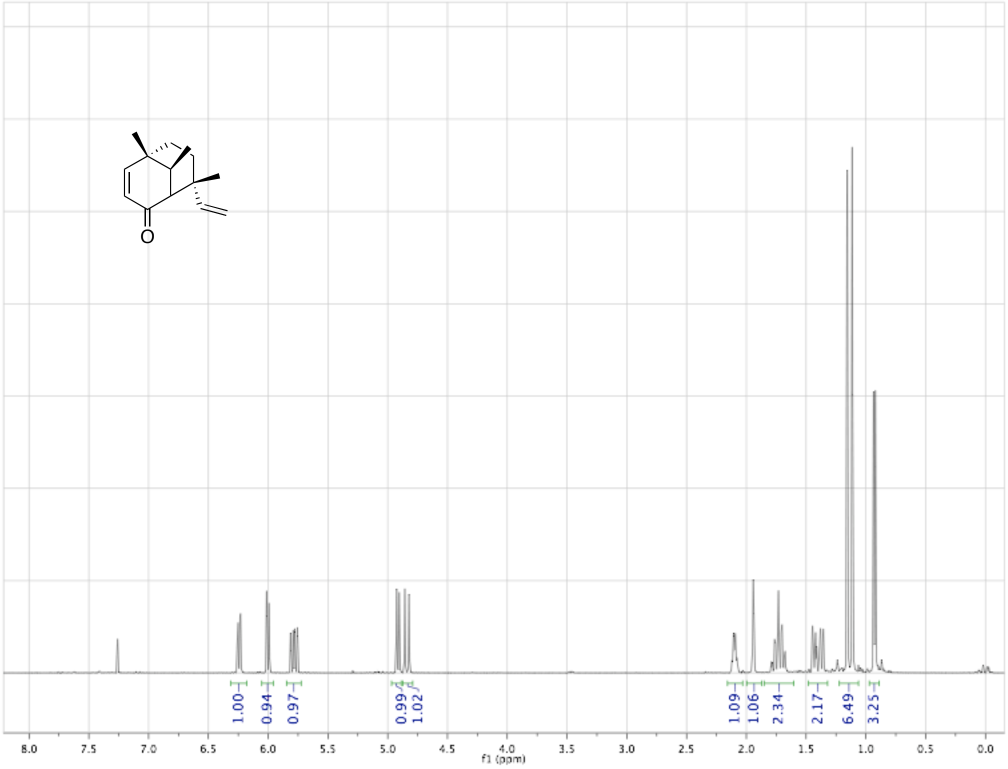
^{1}H-NMR Spectrum of Compound **9b** ($CDCl_3$)



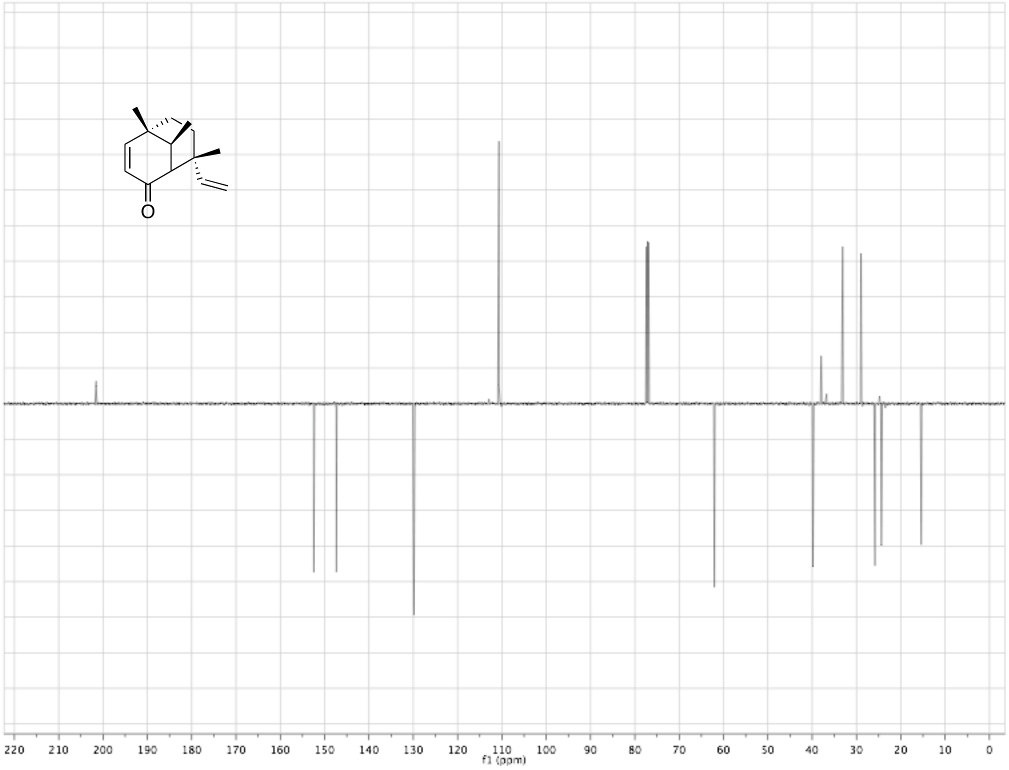
^{13}C-NMR Spectrum of Compound **9b** ($CDCl_3$)



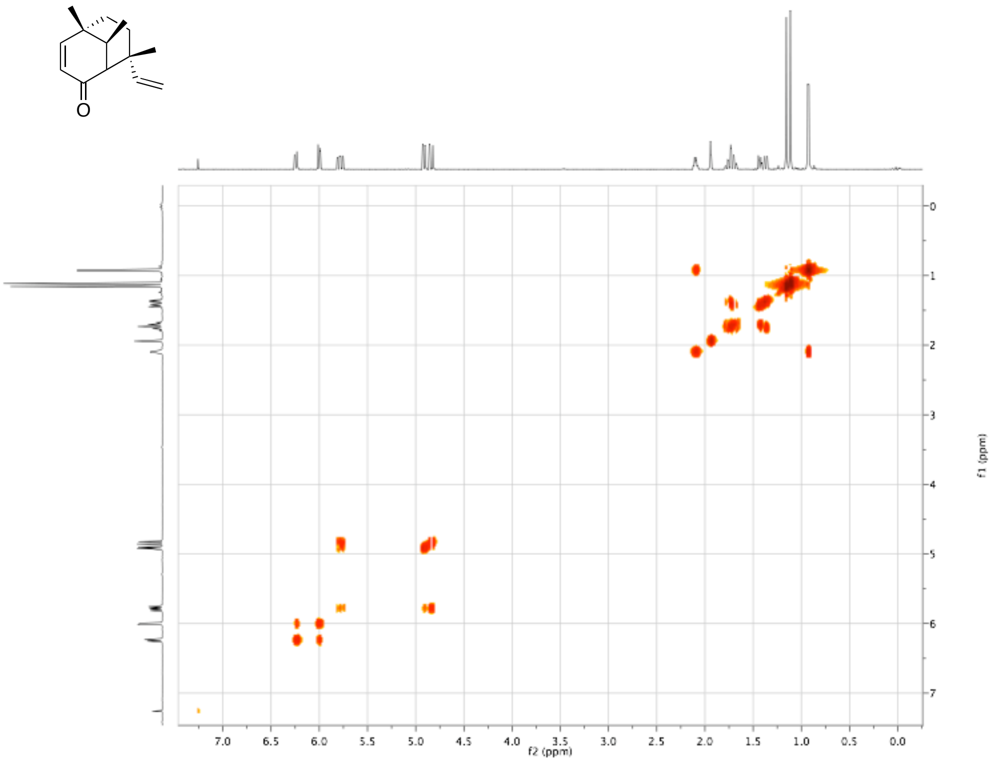
^{1}H-NMR Spectrum of Compound **12a** ($CDCl_3$)



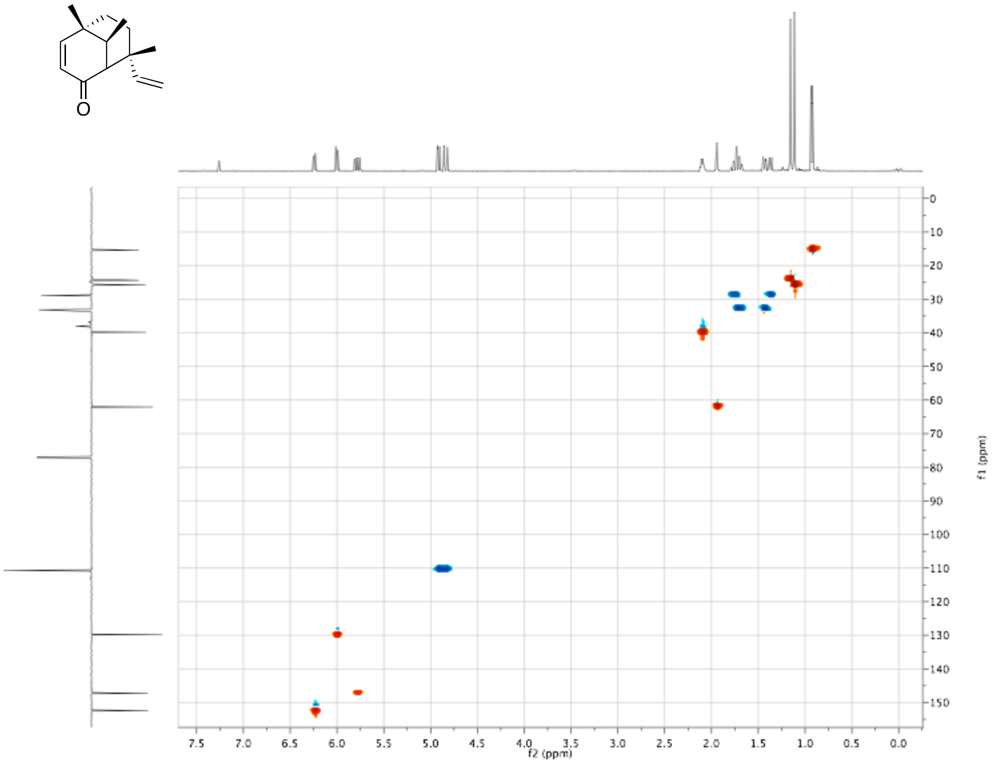
^{13}C-NMR Spectrum of Compound **12a** ($CDCl_3$)



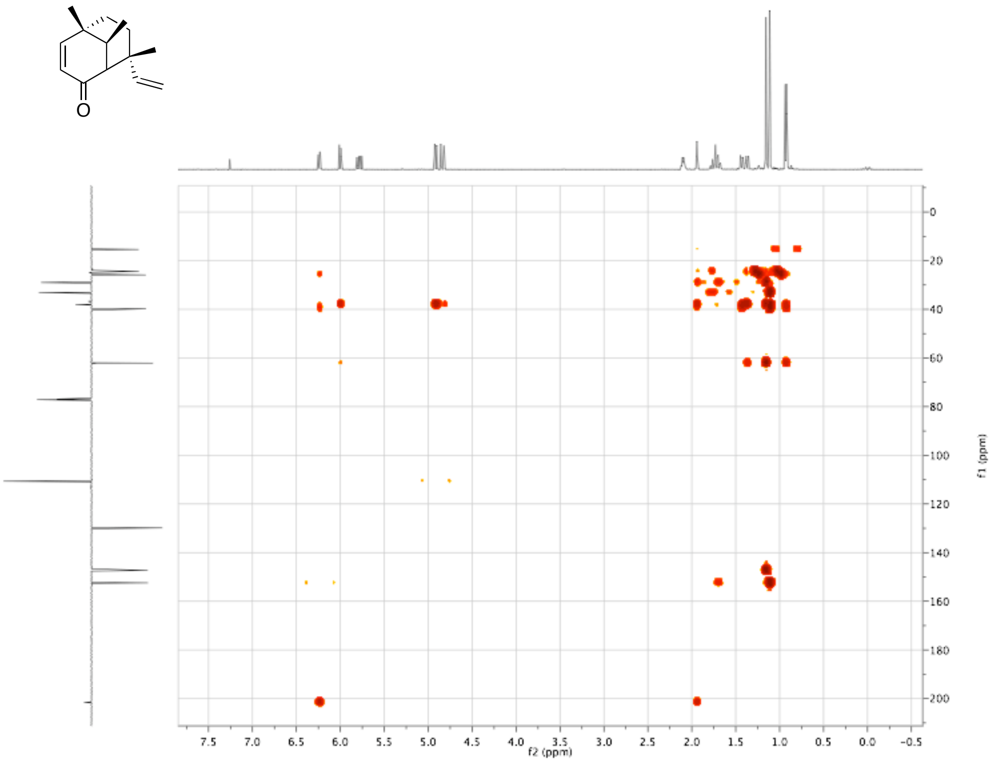
g-COSY Spectrum of Compound **12a** ($CDCl_3$)



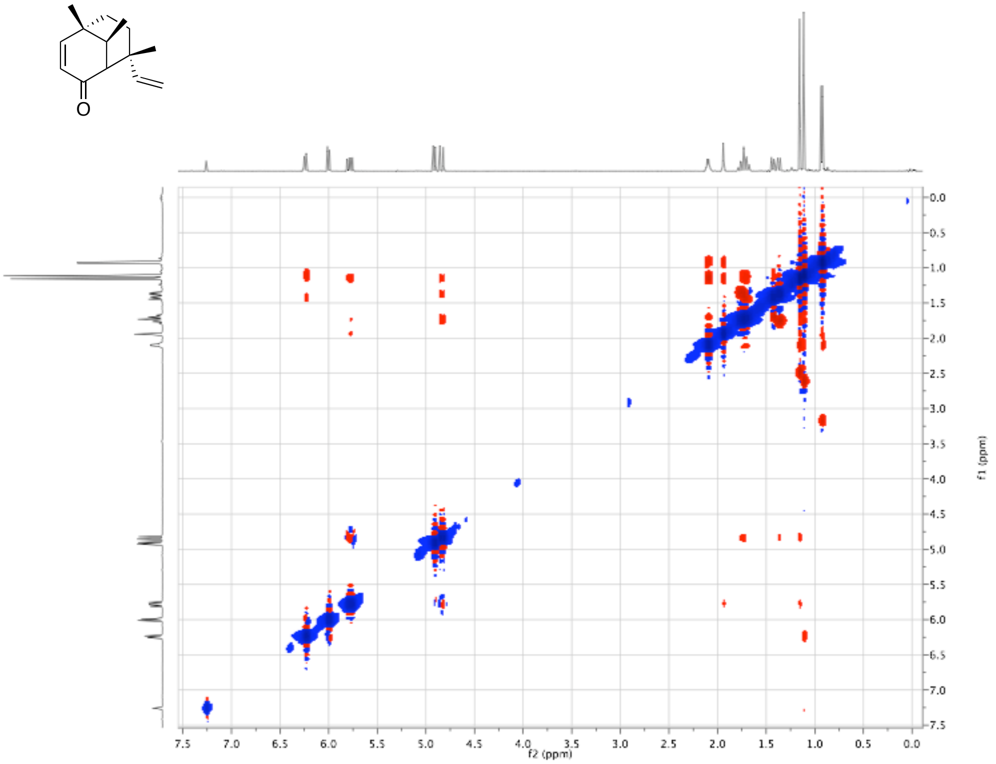
g-HSQC Spectrum of Compound **12a** ($CDCl_3$)



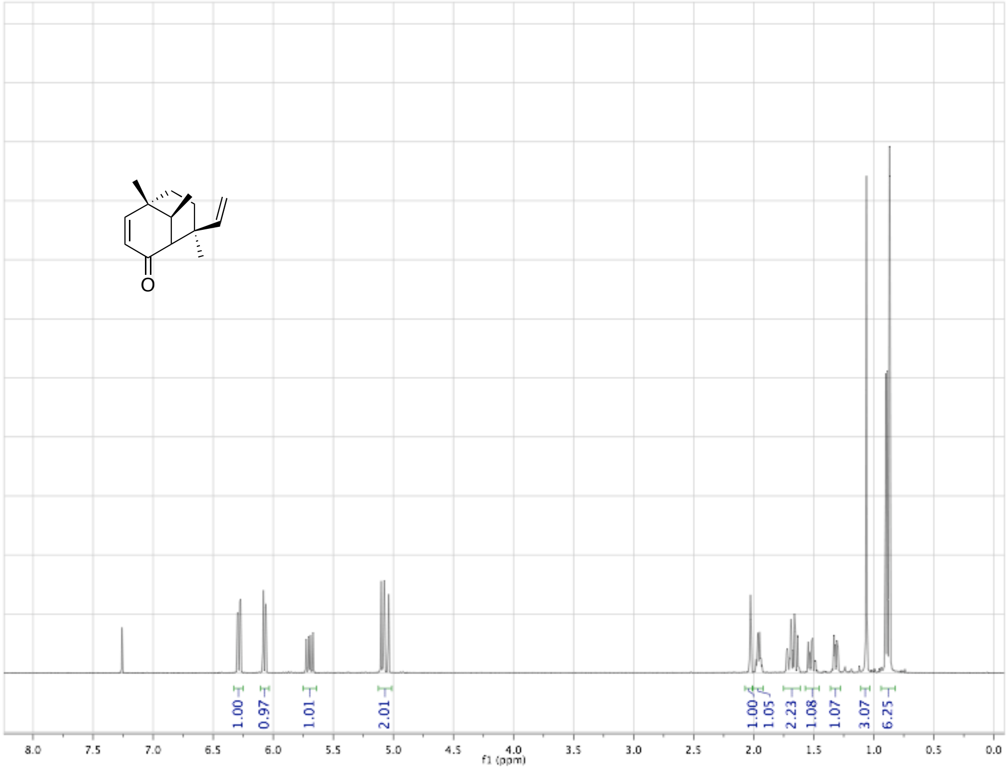
g-HMBC Spectrum of Compound **12a** ($CDCl_3$)



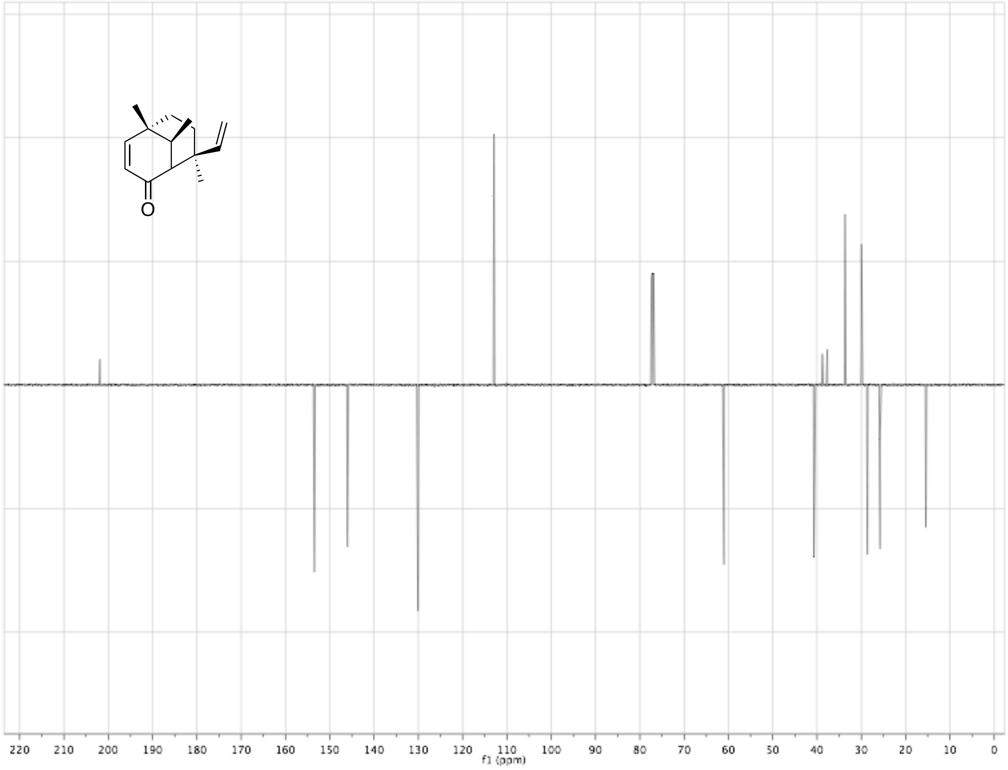
NOESY Spectrum of Compound **12a** ($CDCl_3$)



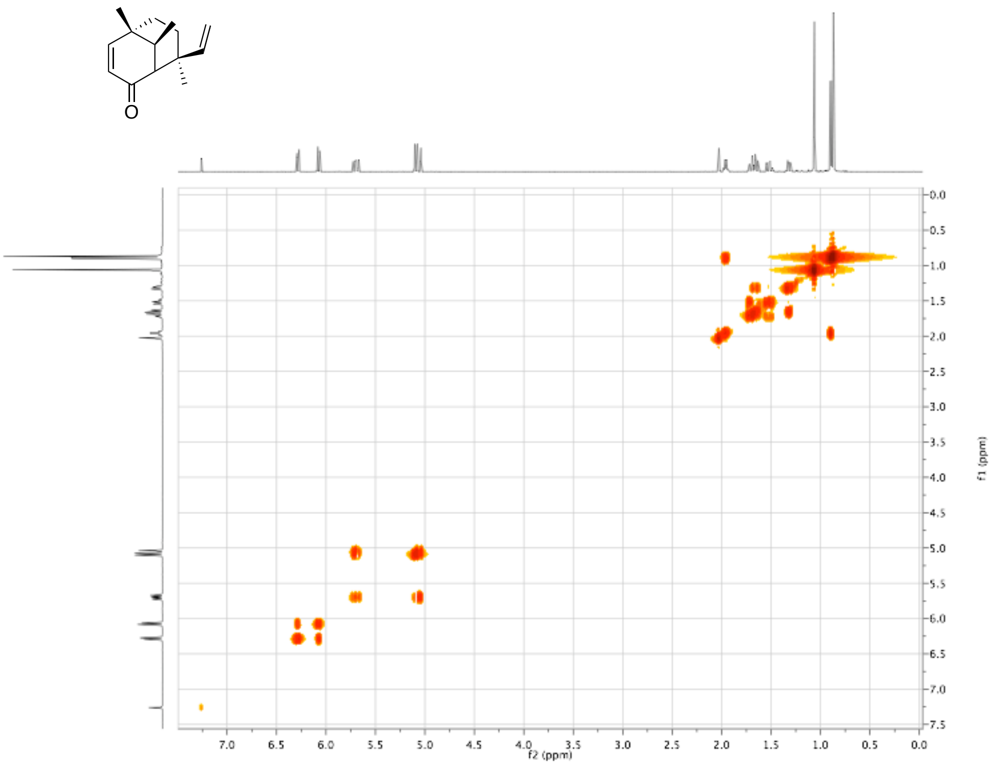
^{1}H-NMR Spectrum of Compound **12b** ($CDCl_3$)



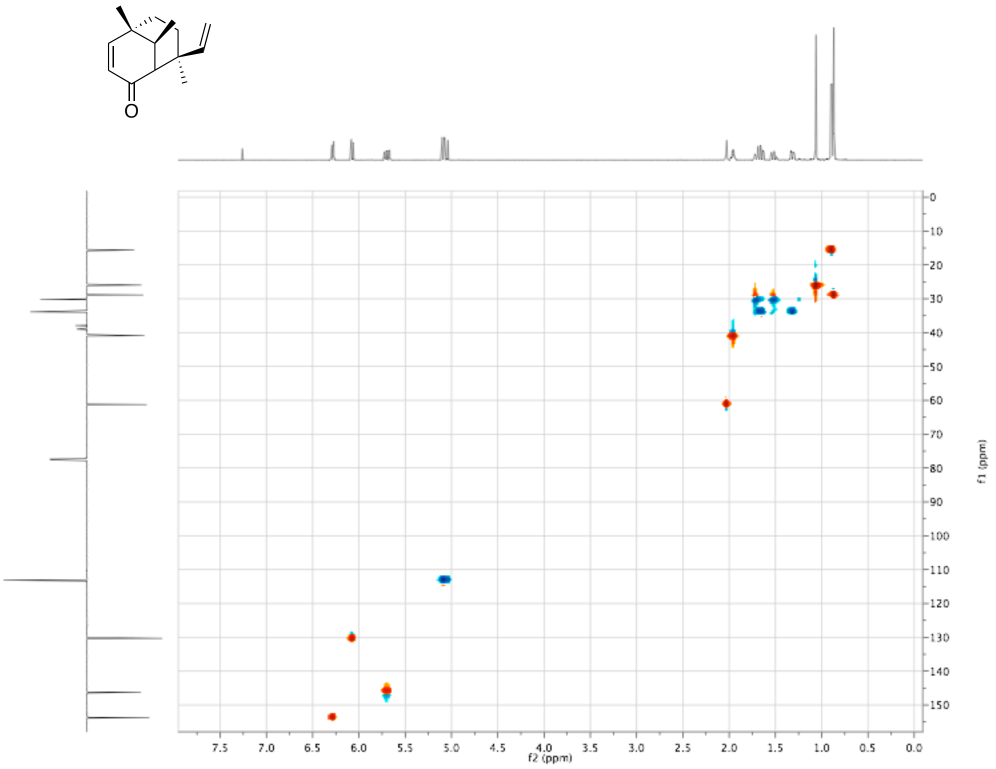
^{13}C-NMR Spectrum of Compound **12b** ($CDCl_3$)



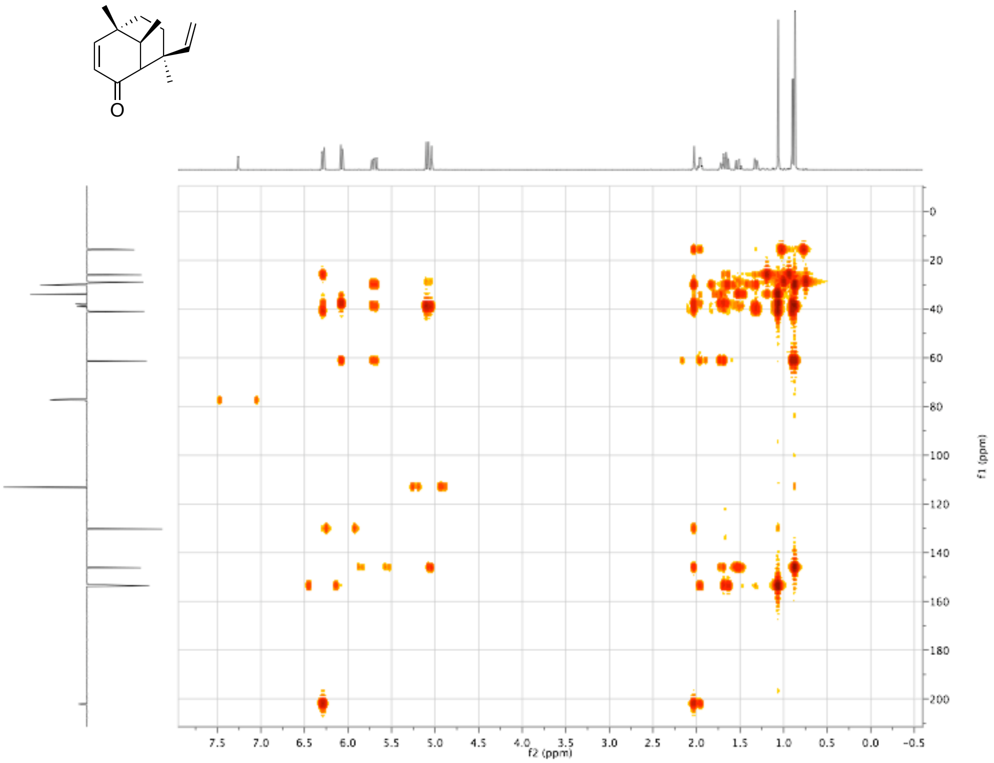
g-COSY Spectrum of Compound **12b** ($CDCl_3$)



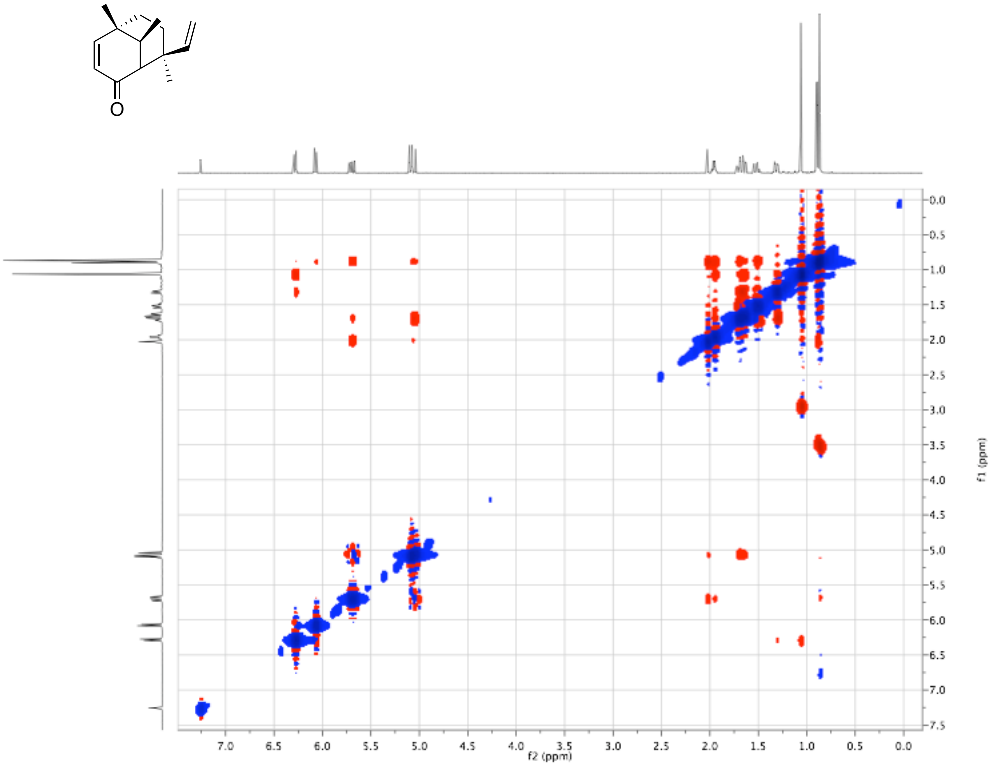
g-HSQC Spectrum of Compound **12b** ($CDCl_3$)



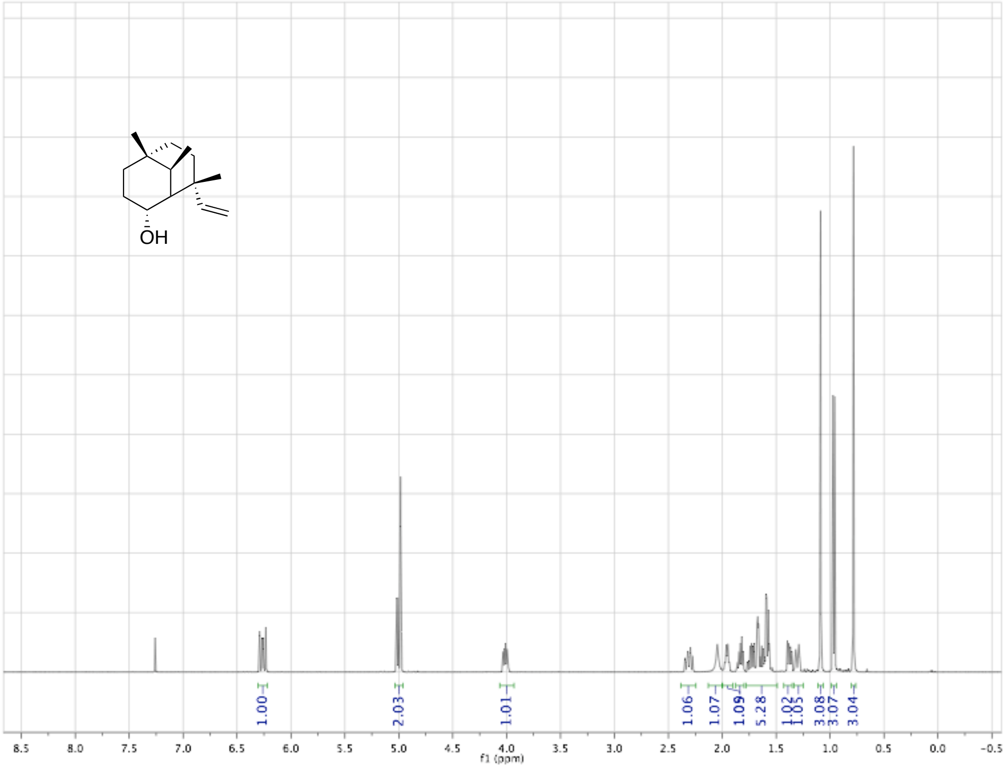
g-HMBC Spectrum of Compound **12b** ($CDCl_3$)



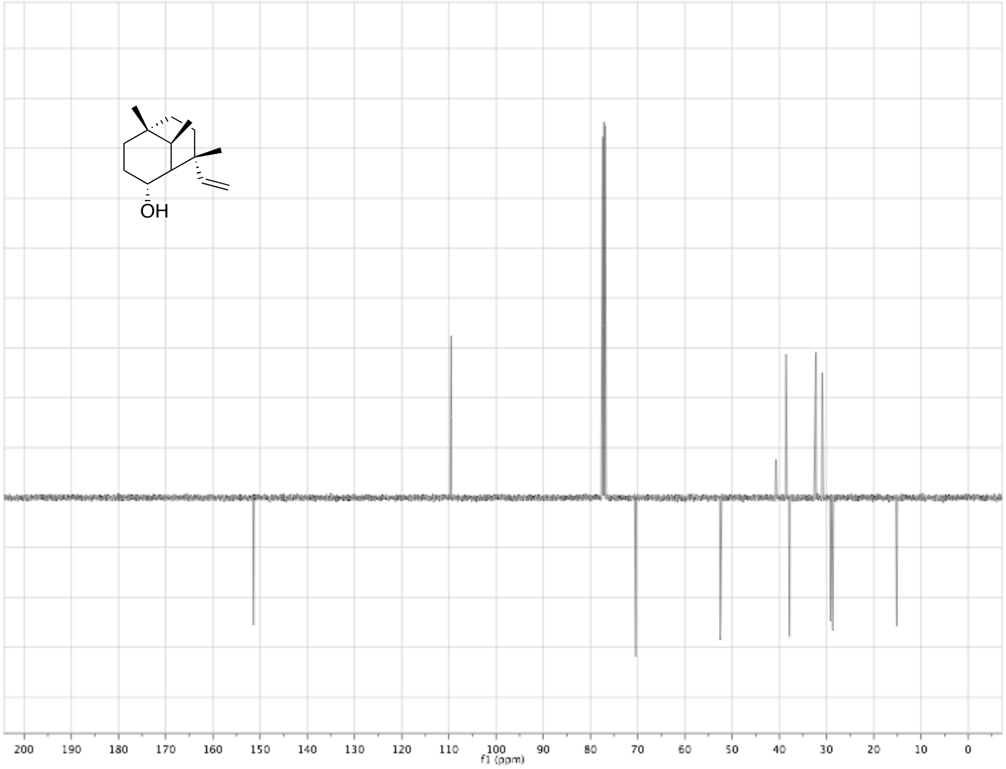
NOESY Spectrum of Compound **12b** ($CDCl_3$)



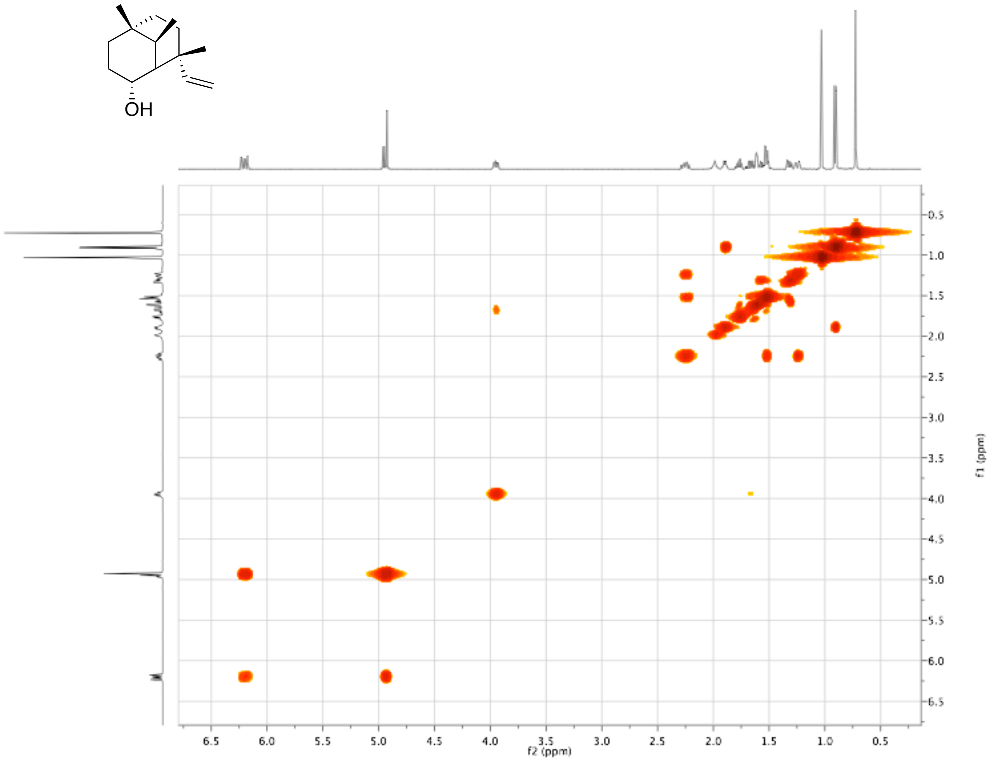
^{1}H-NMR Spectrum of Compound **13a** ($CDCl_3$)



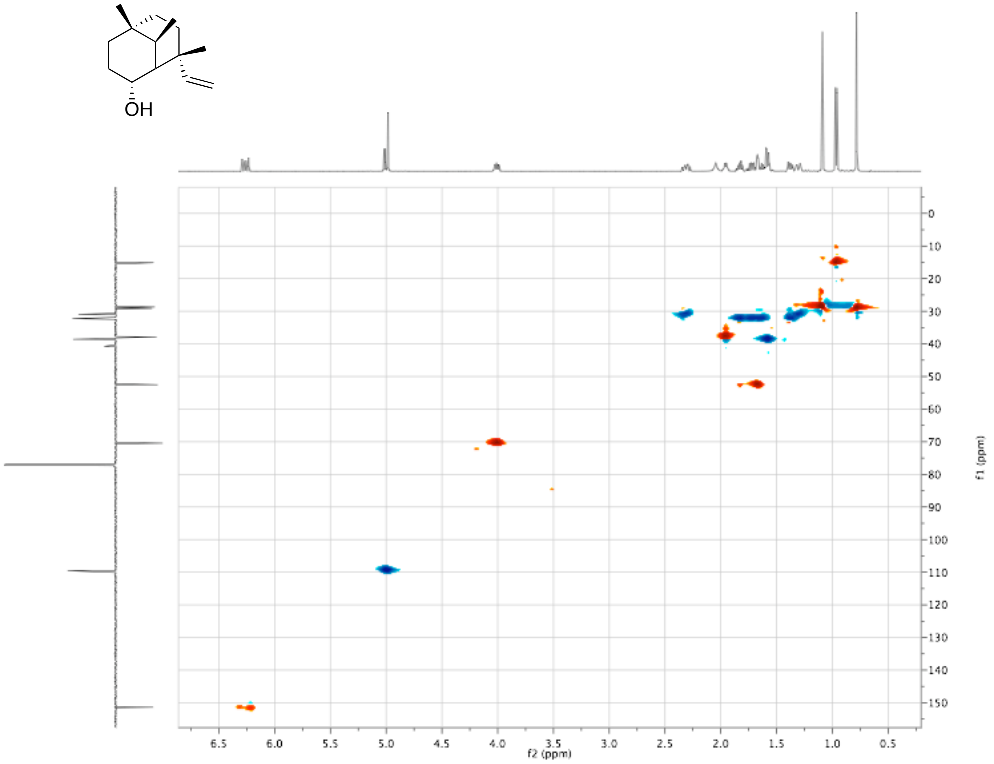
^{13}C-NMR Spectrum of Compound **13a** ($CDCl_3$)



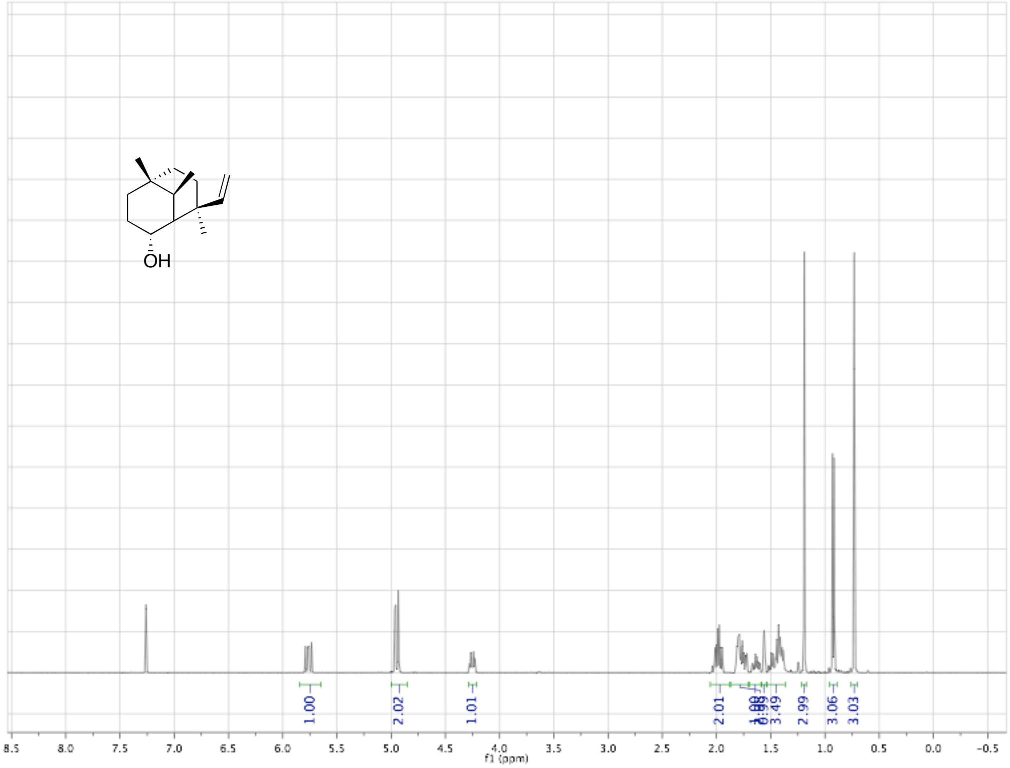
g-COSY Spectrum of Compound **13a** ($CDCl_3$)



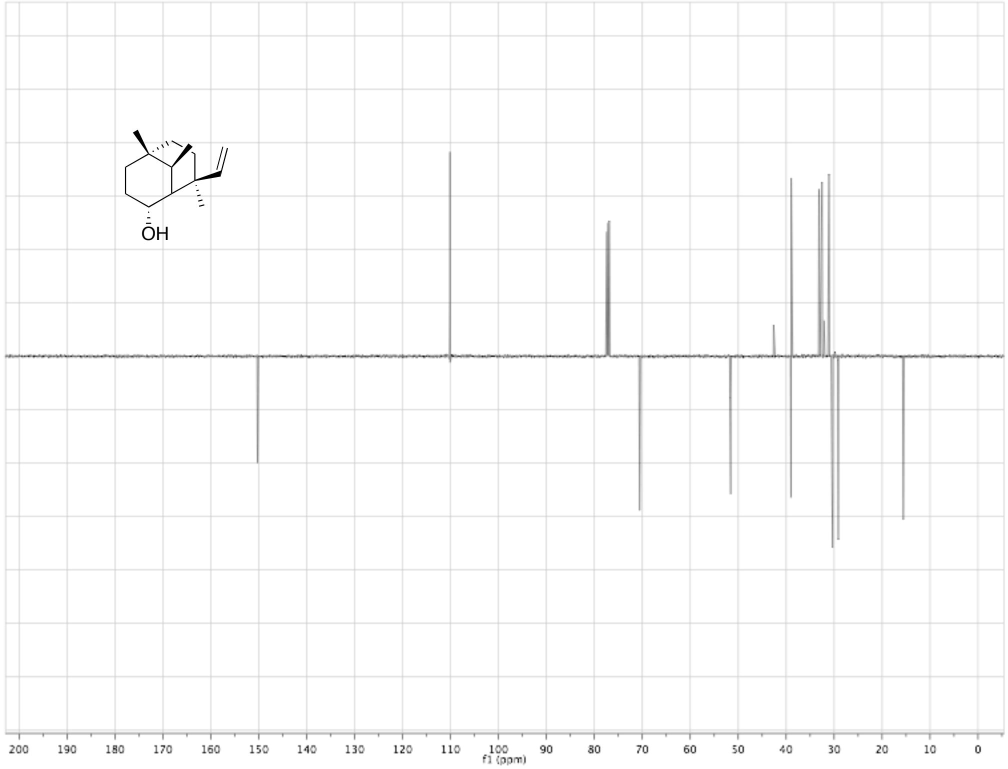
g-HSQC Spectrum of Compound **13a** ($CDCl_3$)



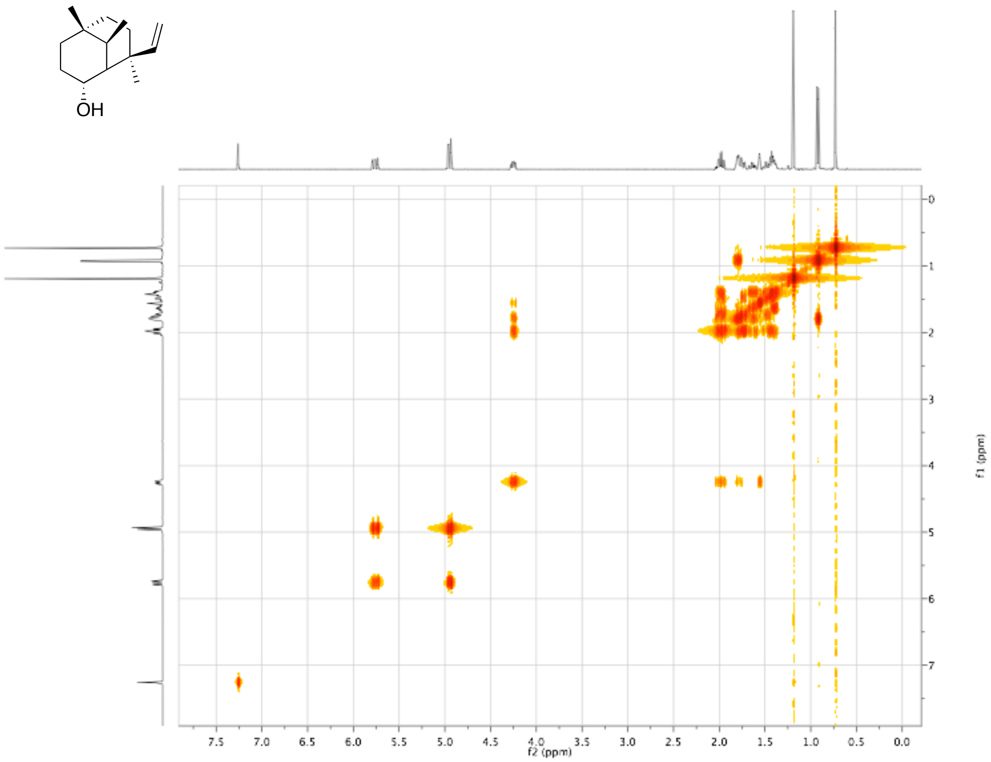
^{1}H-NMR Spectrum of Compound **13b** ($CDCl_3$)



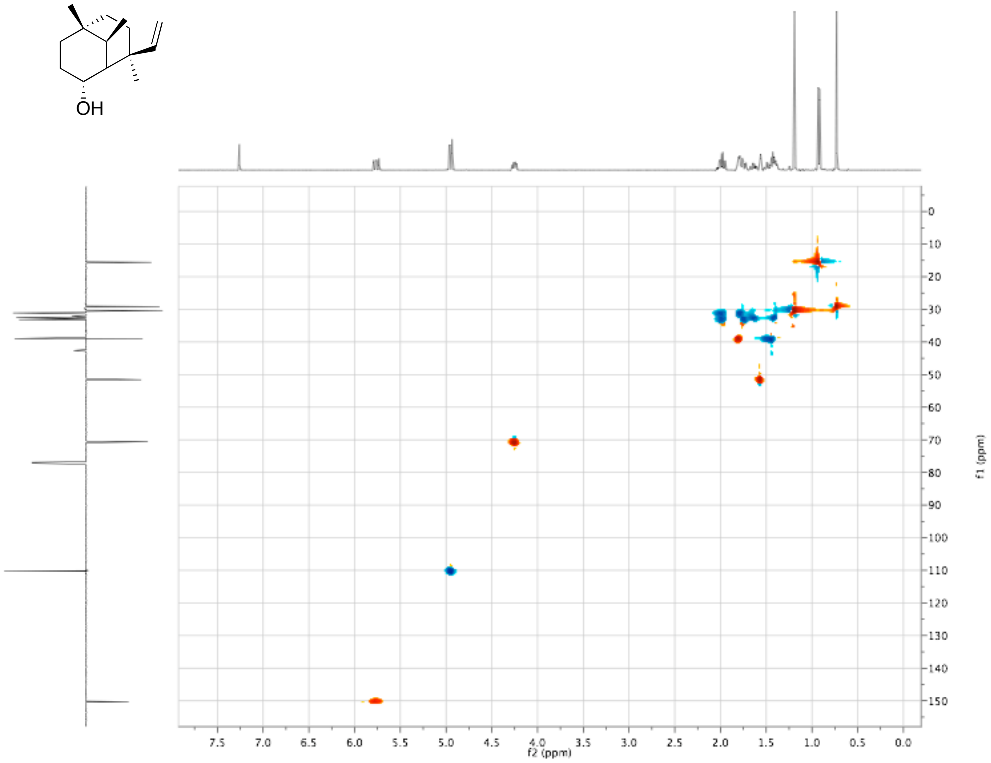
^{13}C-NMR Spectrum of Compound **13a** ($CDCl_3$)



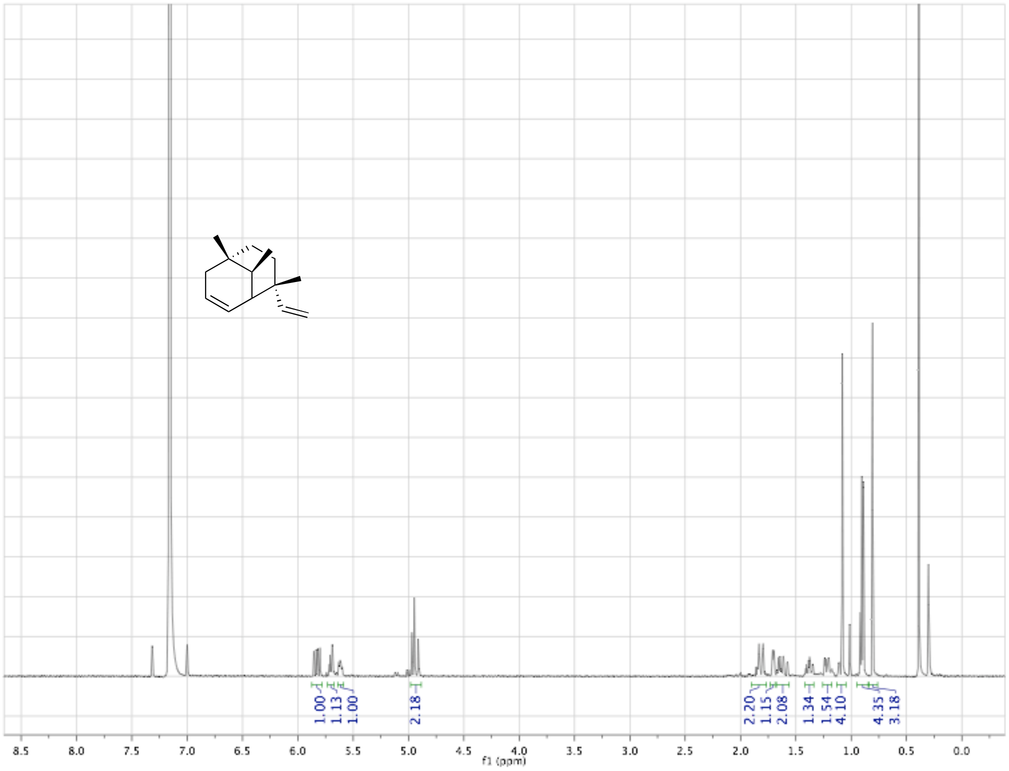
g-COSY Spectrum of Compound **13a** ($CDCl_3$)



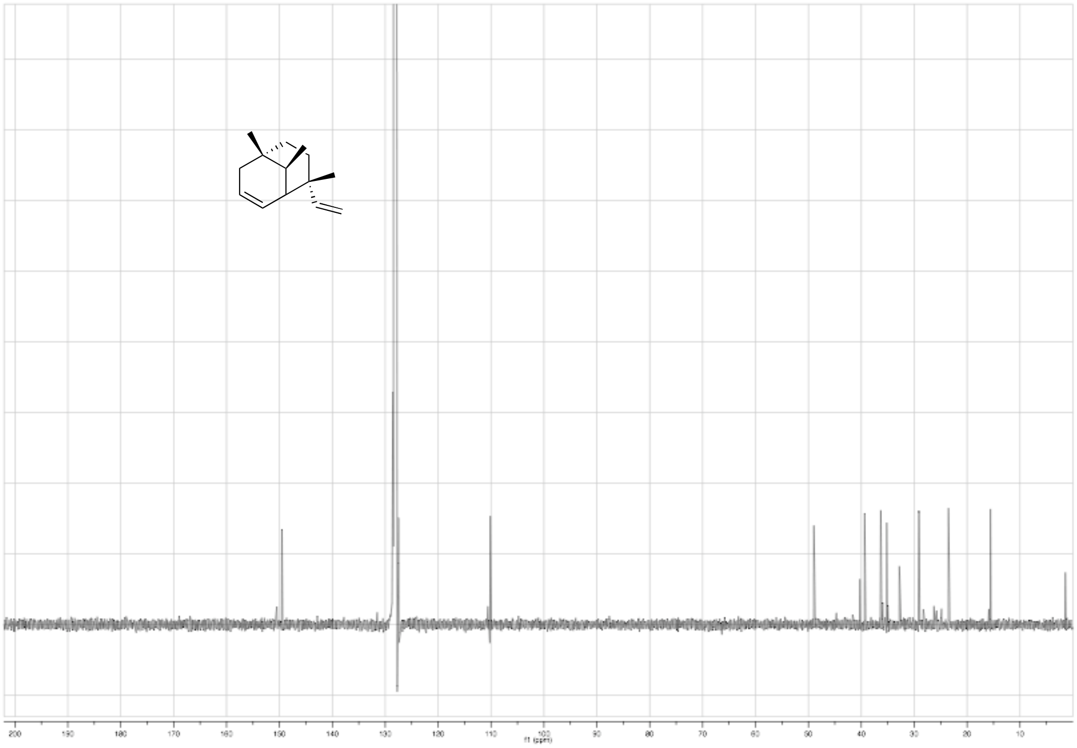
g-HSQC Spectrum of Compound **13a** ($CDCl_3$)



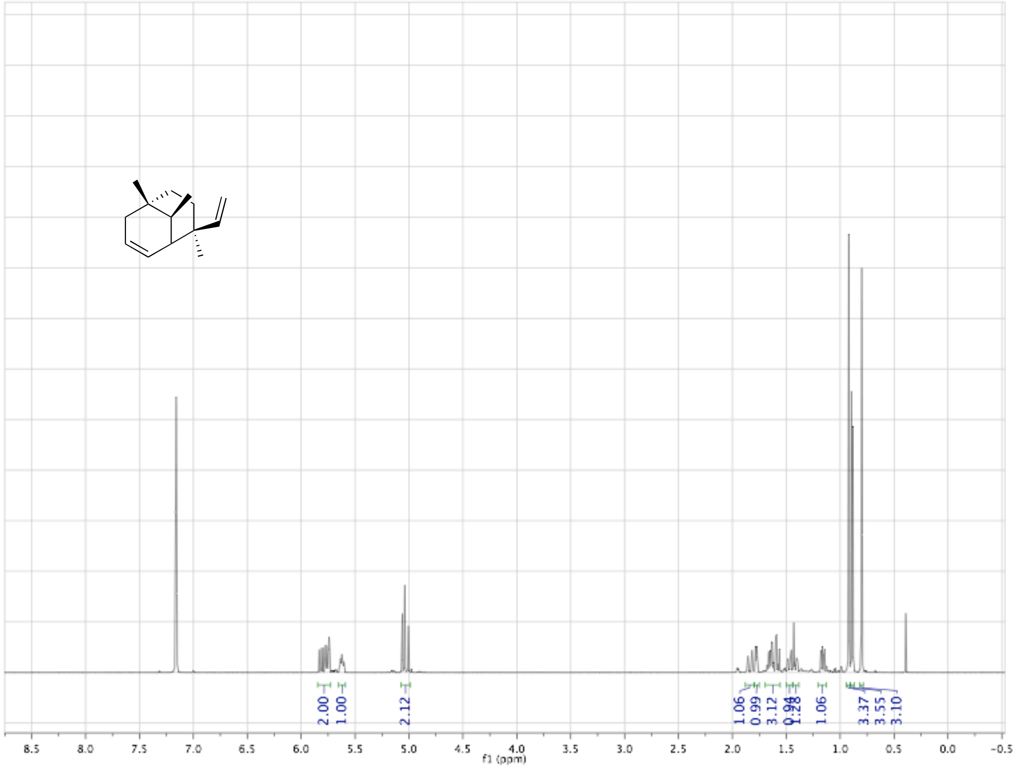
^{1}H-NMR Spectrum of Compound **14a** (C_6D_6)



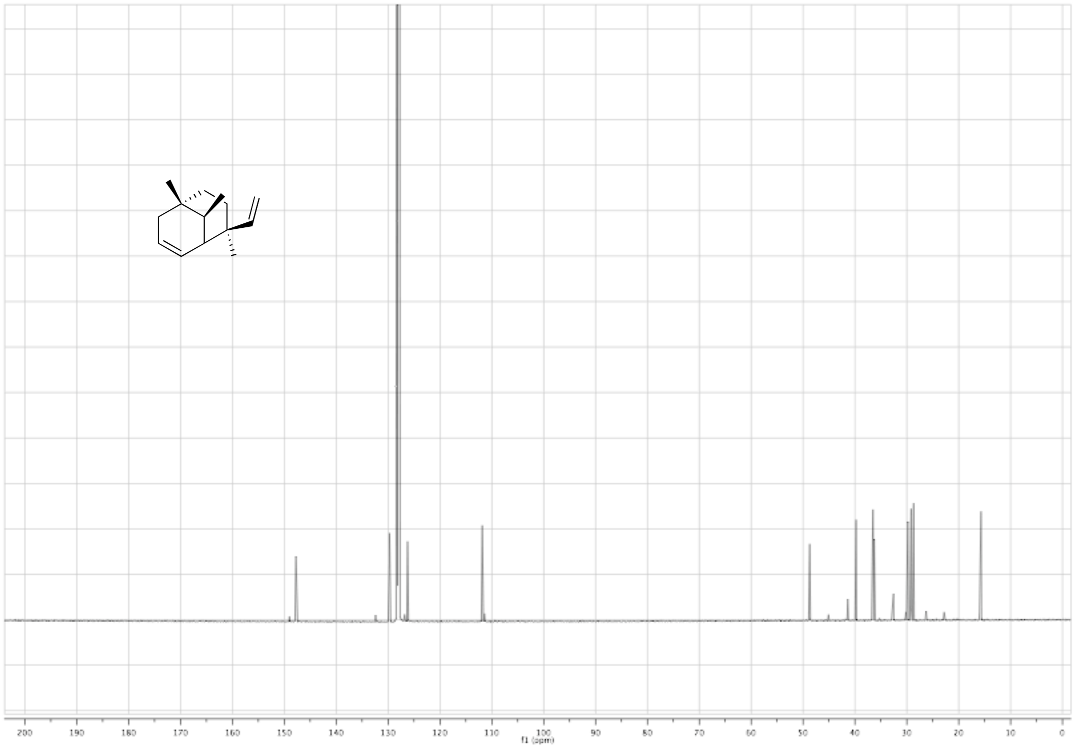
^{13}C-NMR Spectrum of Compound **14a** (C_6D_6)



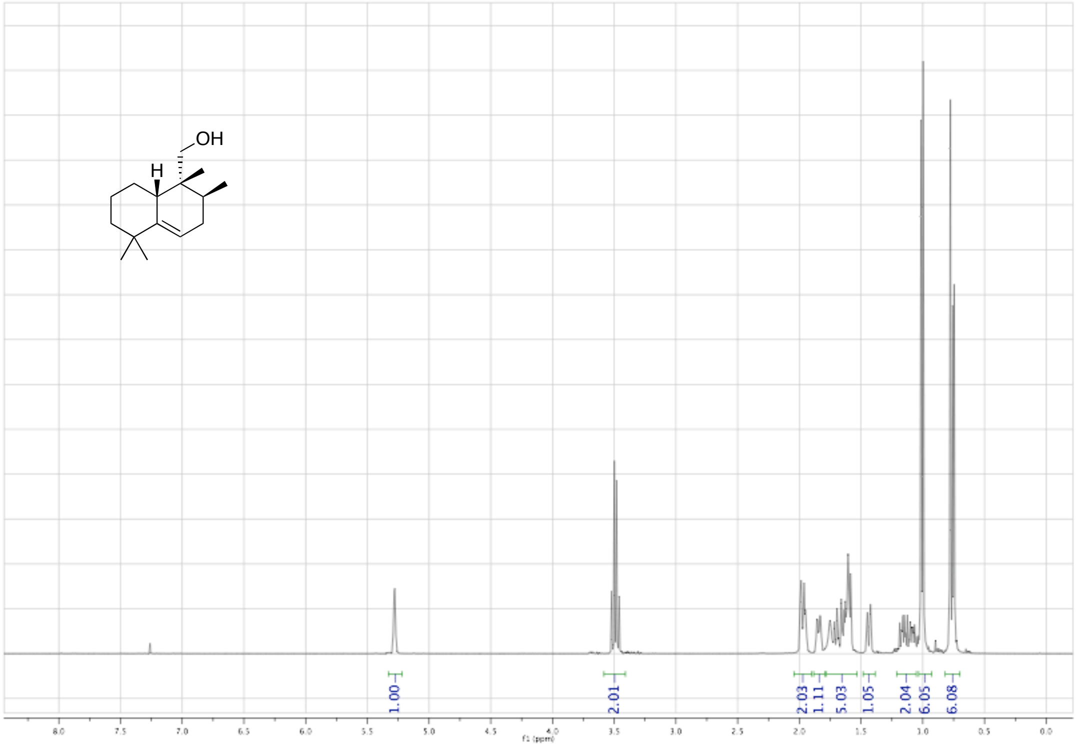
^{1}H-NMR Spectrum of Compound **14b** (C_6D_6)



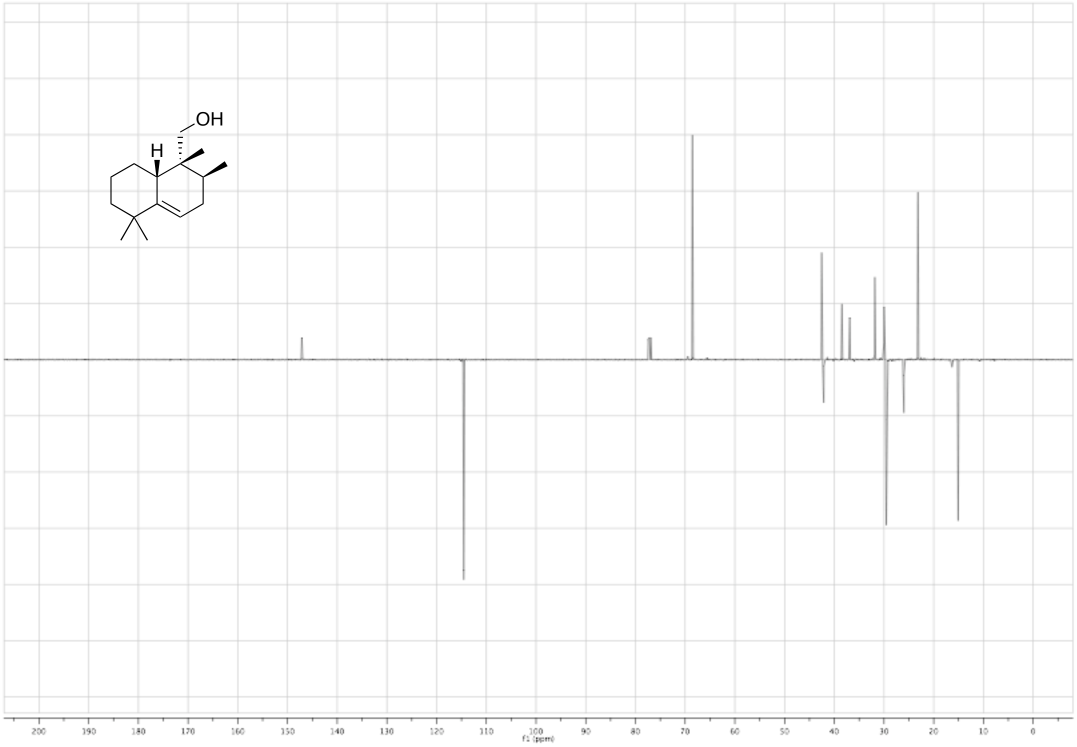
^{13}C-NMR Spectrum of Compound **14b** (C_6D_6)



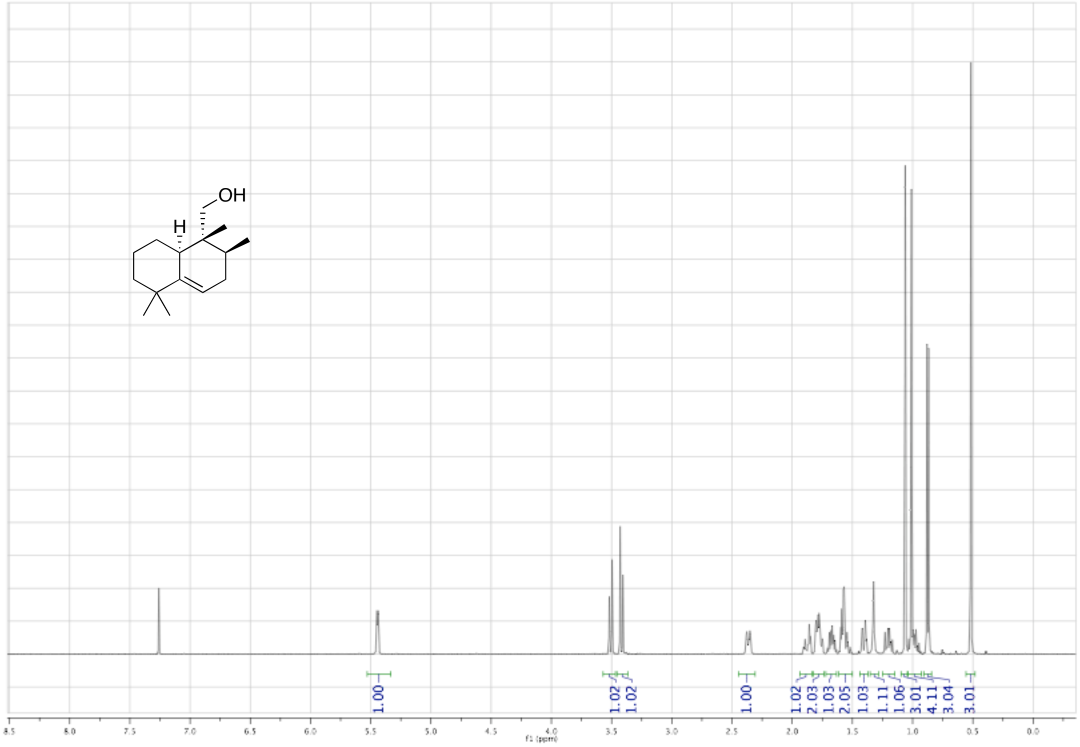
^{1}H-NMR Spectrum of Compound *endo*-**S2** ($CDCl_3$)



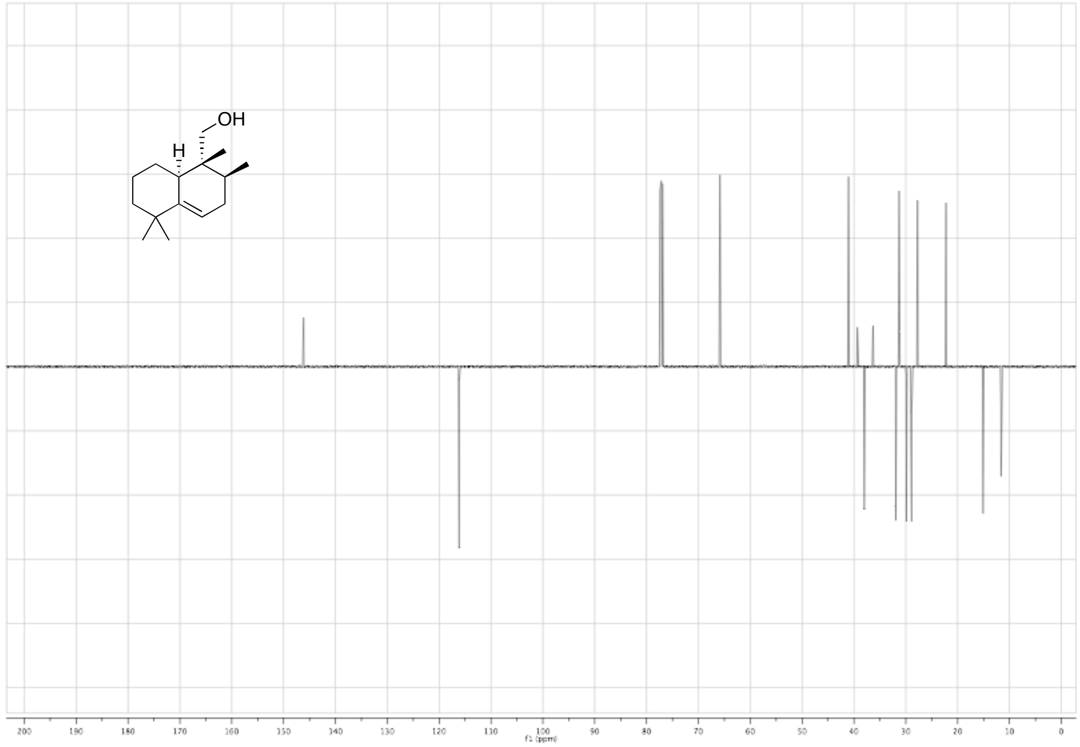
^{13}C-NMR Spectrum of Compound *endo*-**S2** ($CDCl_3$)



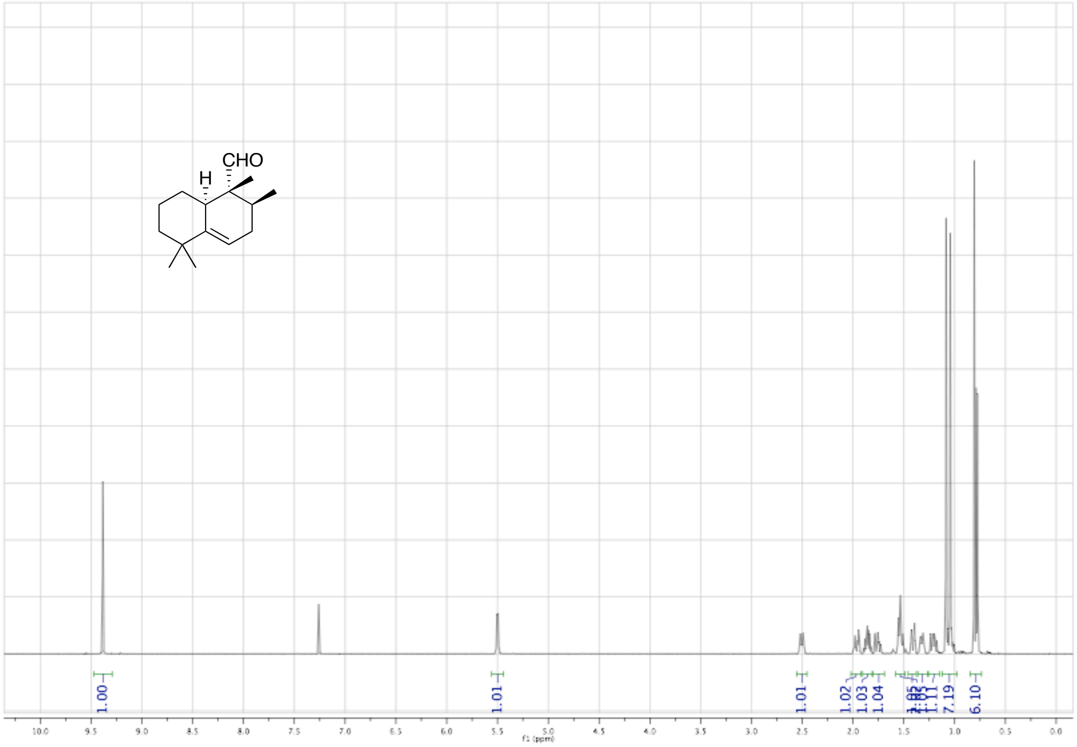
^{1}H-NMR Spectrum of Compound **S2** ($CDCl_3$)



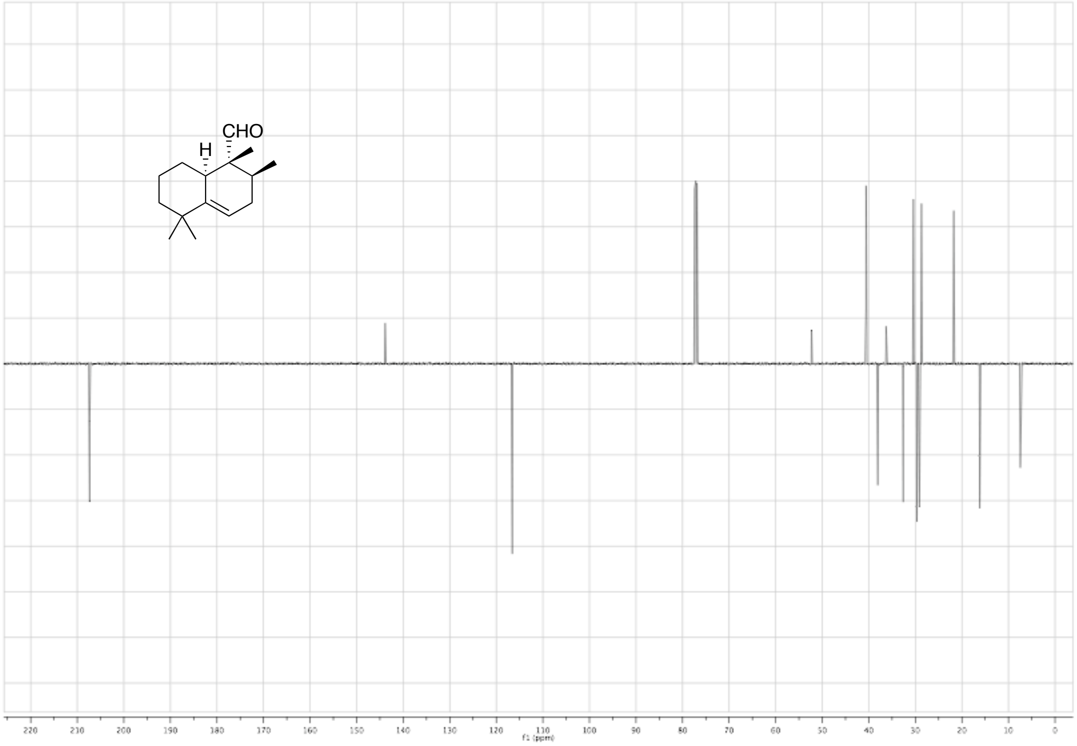
^{13}C-NMR Spectrum of Compound **S2** ($CDCl_3$)



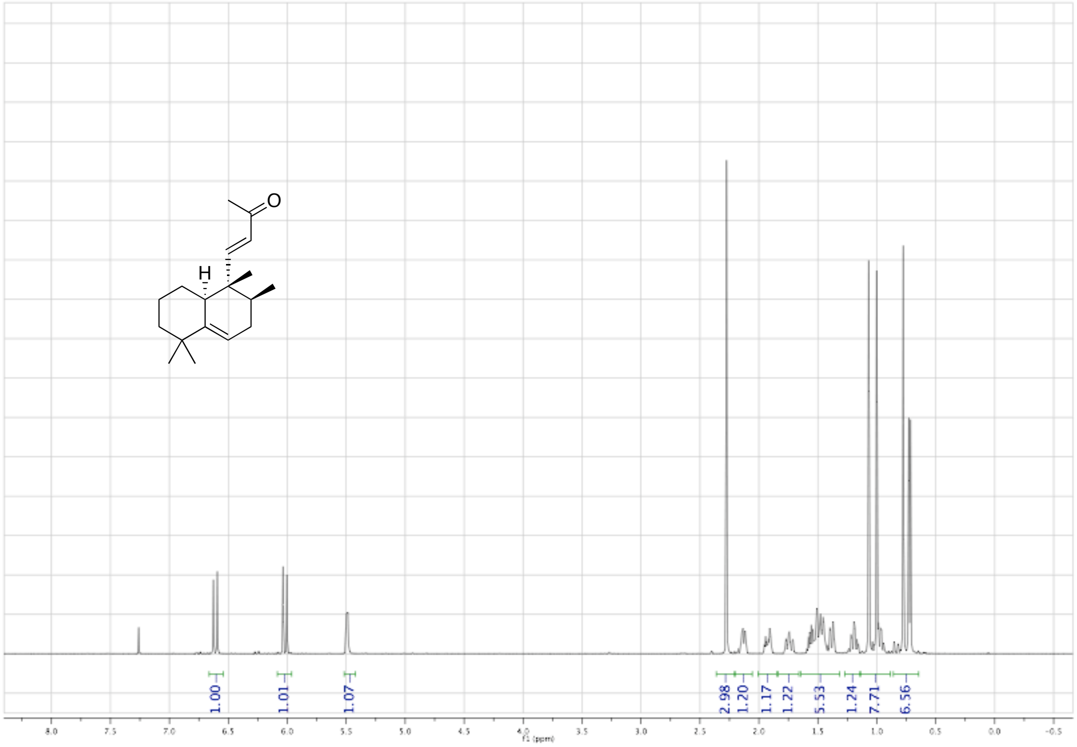
^{1}H-NMR Spectrum of Compound **18** ($CDCl_3$)



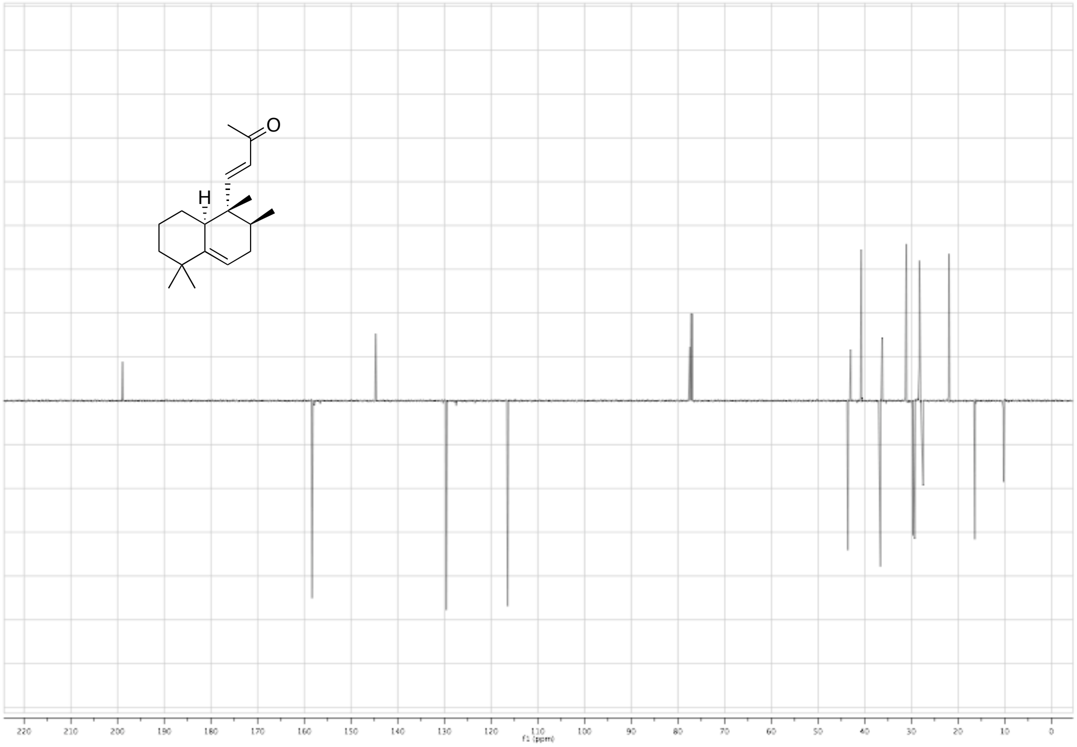
^{13}C-NMR Spectrum of Compound **18** ($CDCl_3$)



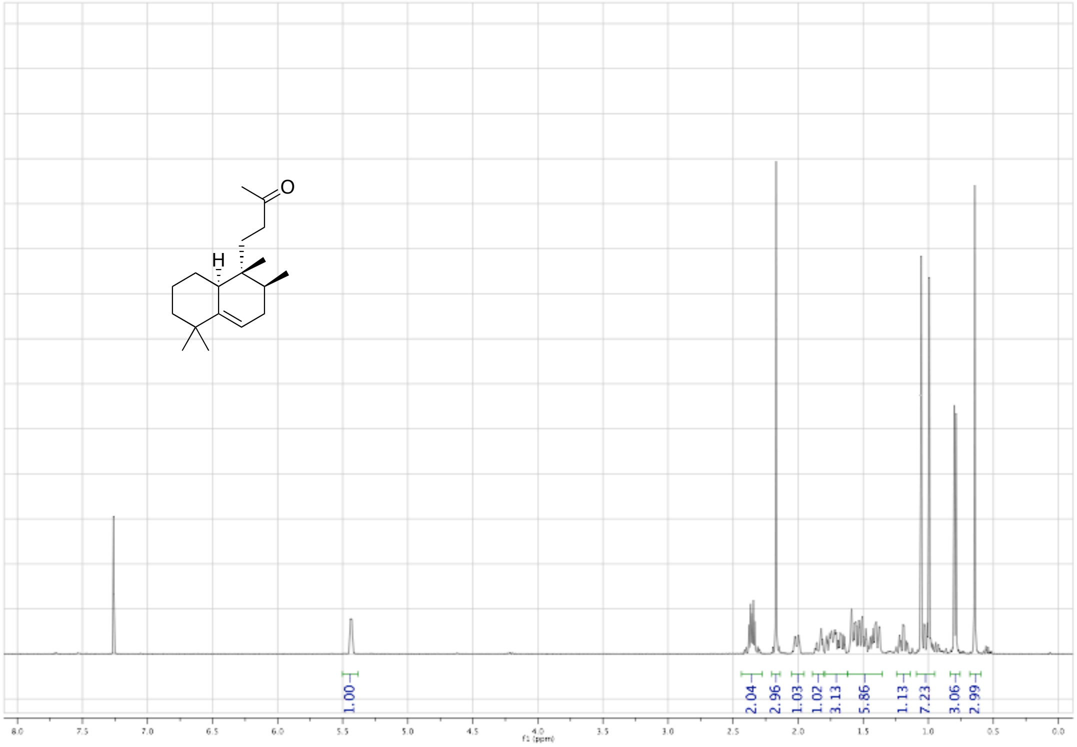
^{1}H-NMR Spectrum of Compound **S3** ($CDCl_3$)



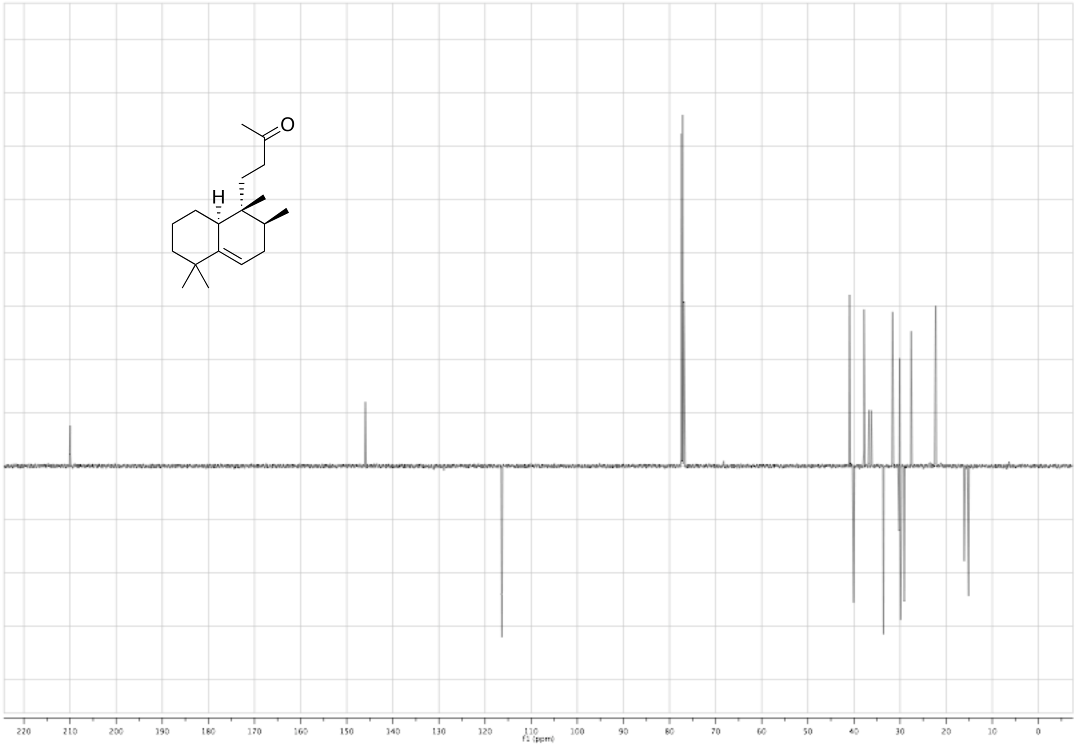
^{13}C-NMR Spectrum of Compound **S3** ($CDCl_3$)



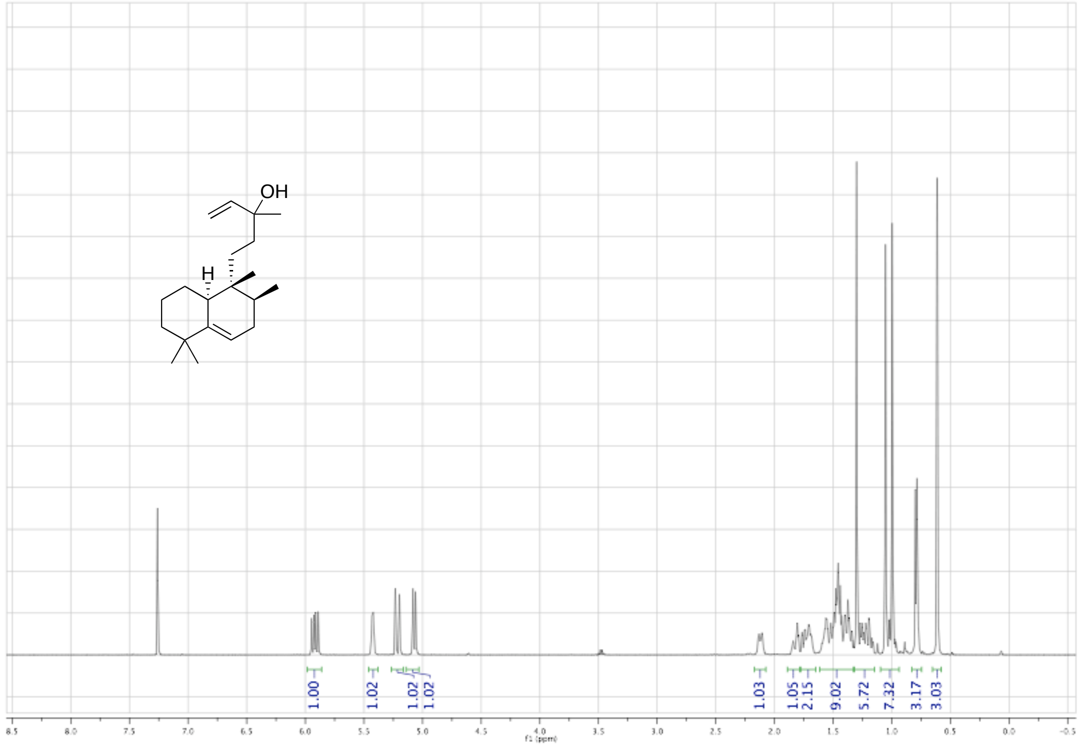
^{1}H-NMR Spectrum of Compound **20** ($CDCl_3$)



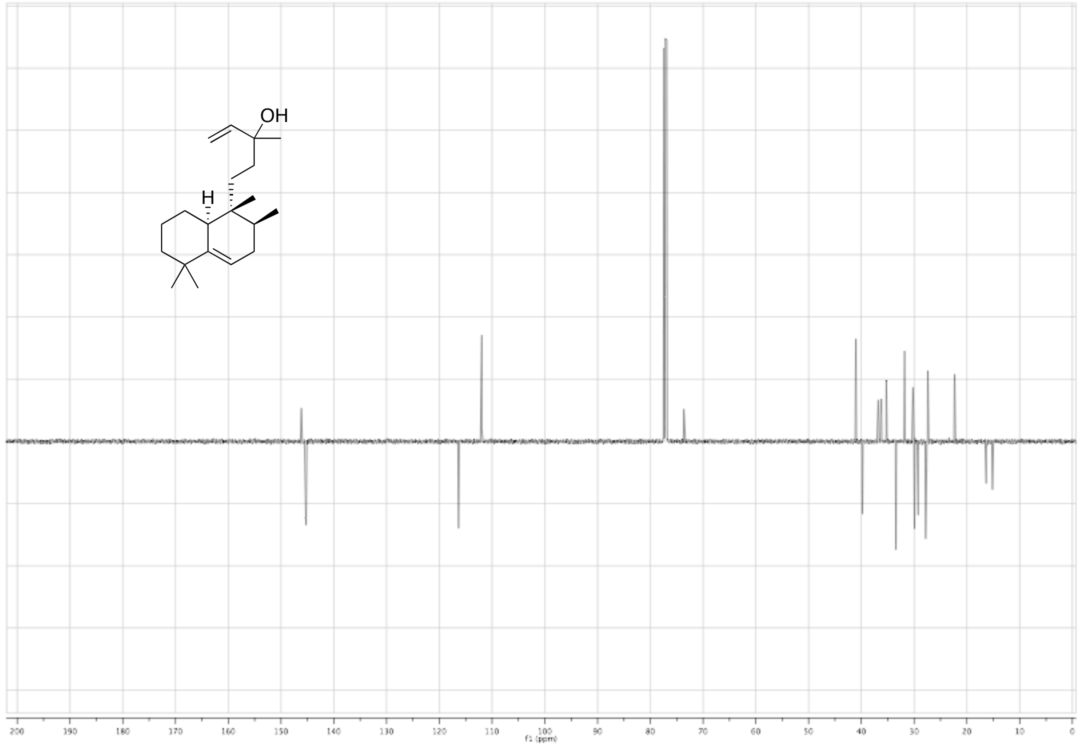
^{13}C-NMR Spectrum of Compound **20** ($CDCl_3$)



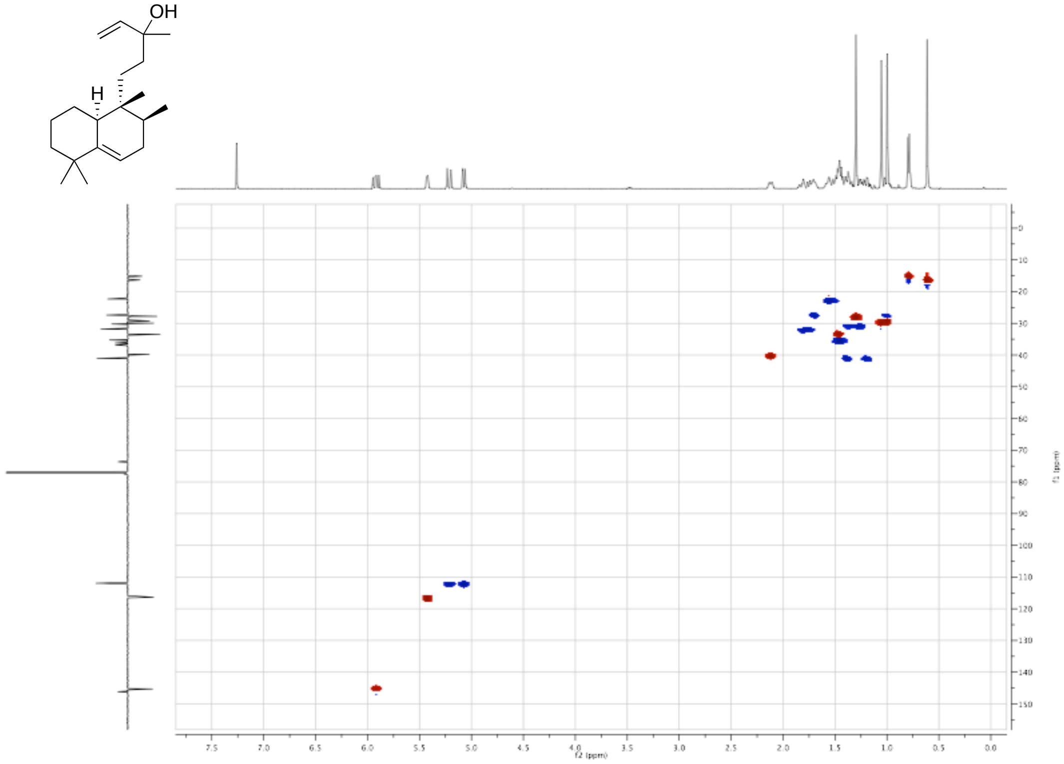
^{1}H-NMR Spectrum of Compound **15** (3:2 dr, $CDCl_3$)



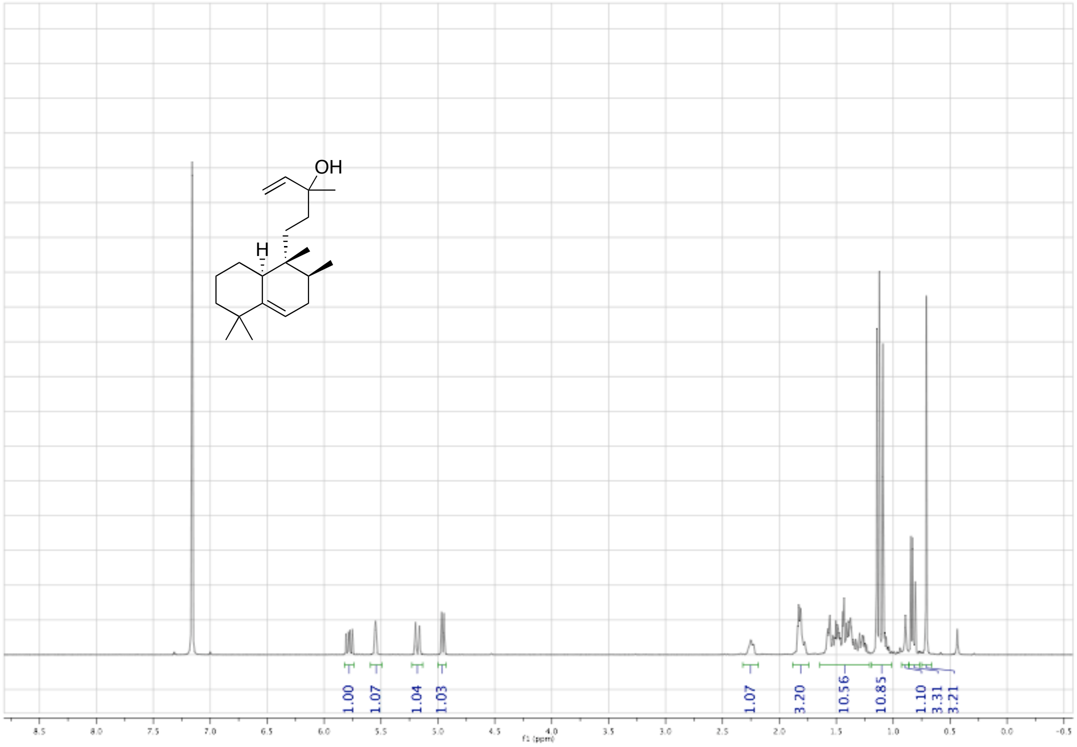
^{13}C-NMR Spectrum of Compound **15** (3:2 dr, $CDCl_3$)



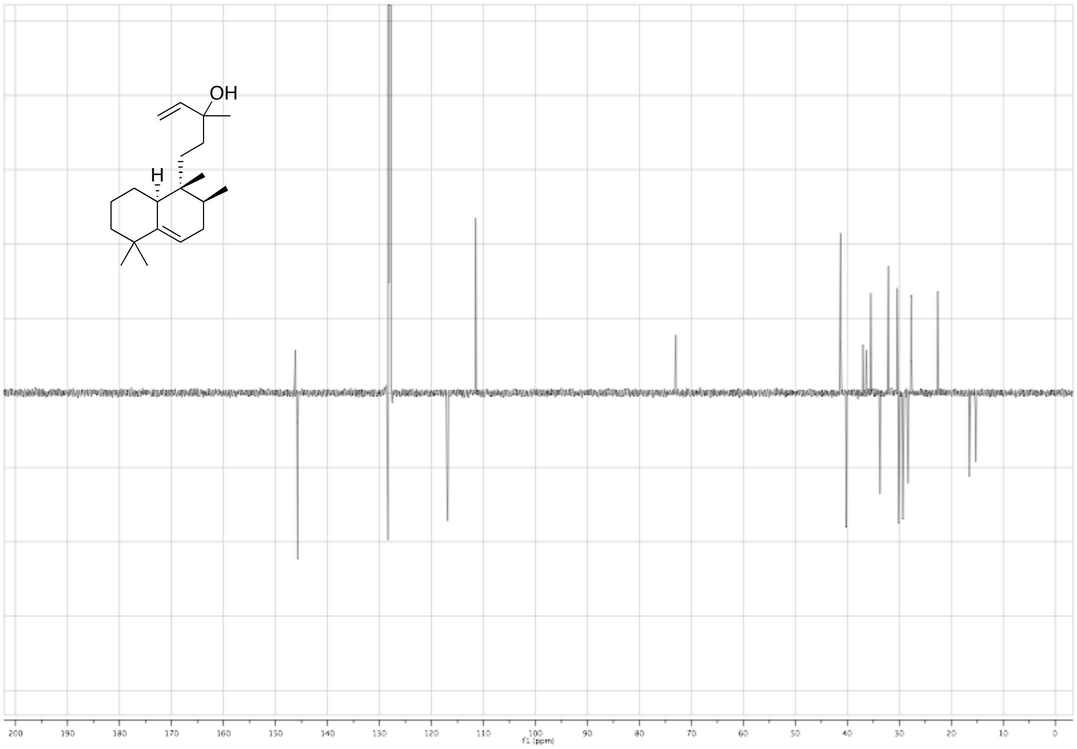
g-HSQC Spectrum of Compound **15** (3:2 dr, $CDCl_3$)



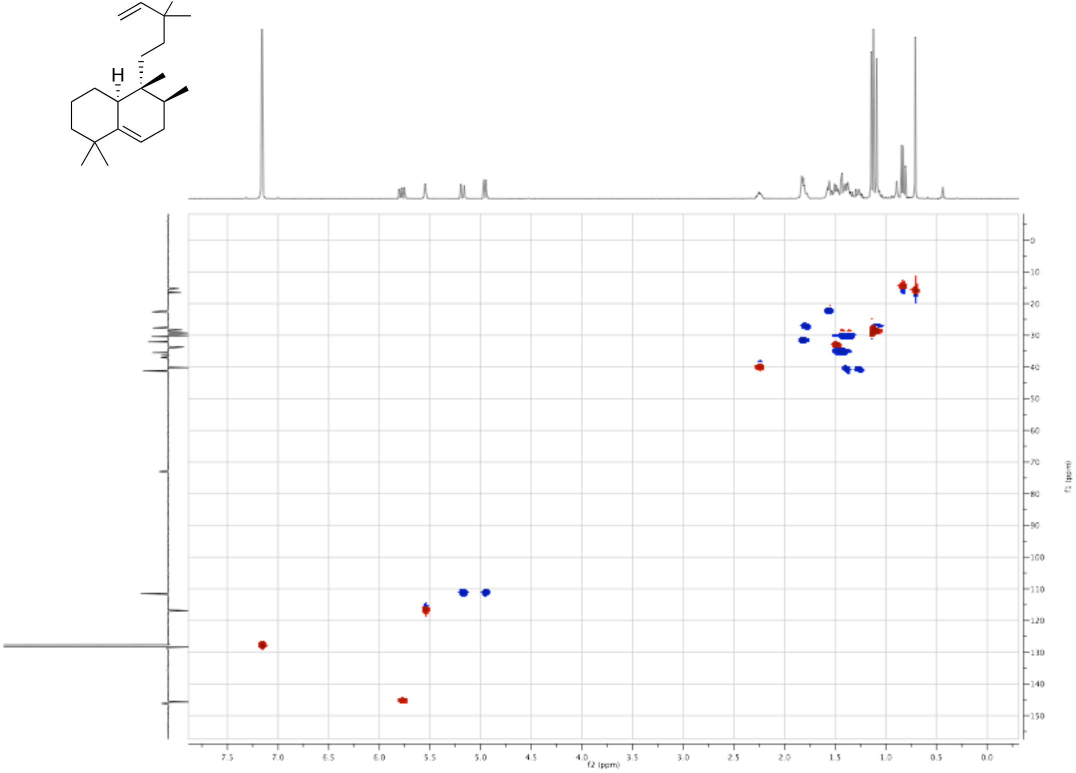
^{1}H-NMR Spectrum of Compound **15** (3:2 dr, C_6D_6)



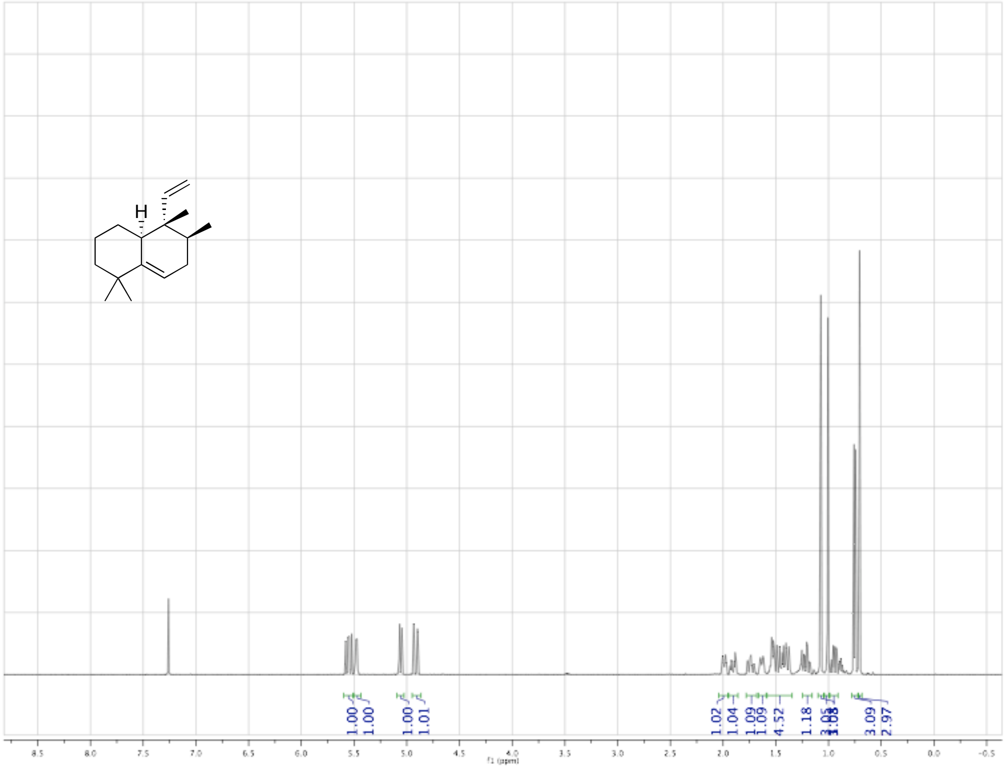
^{13}C-NMR Spectrum of Compound **15** (3:2 dr, C_6D_6)



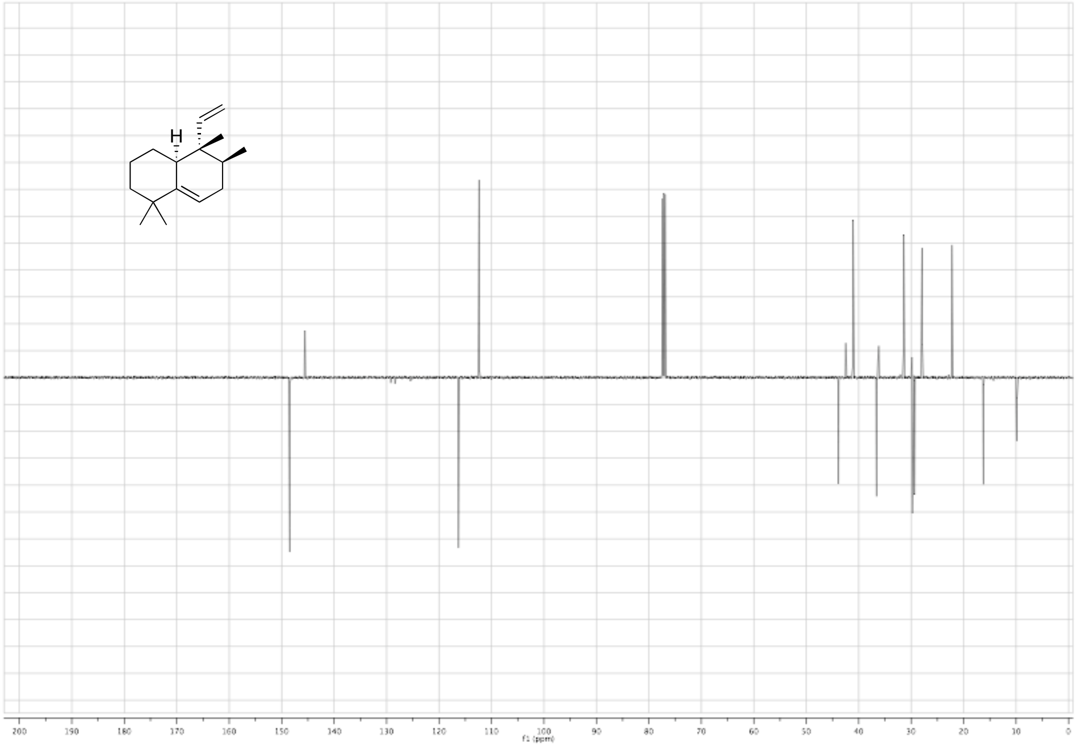
g-HSQC Spectrum of Compound **15** (3:2 dr, C_6D_6)



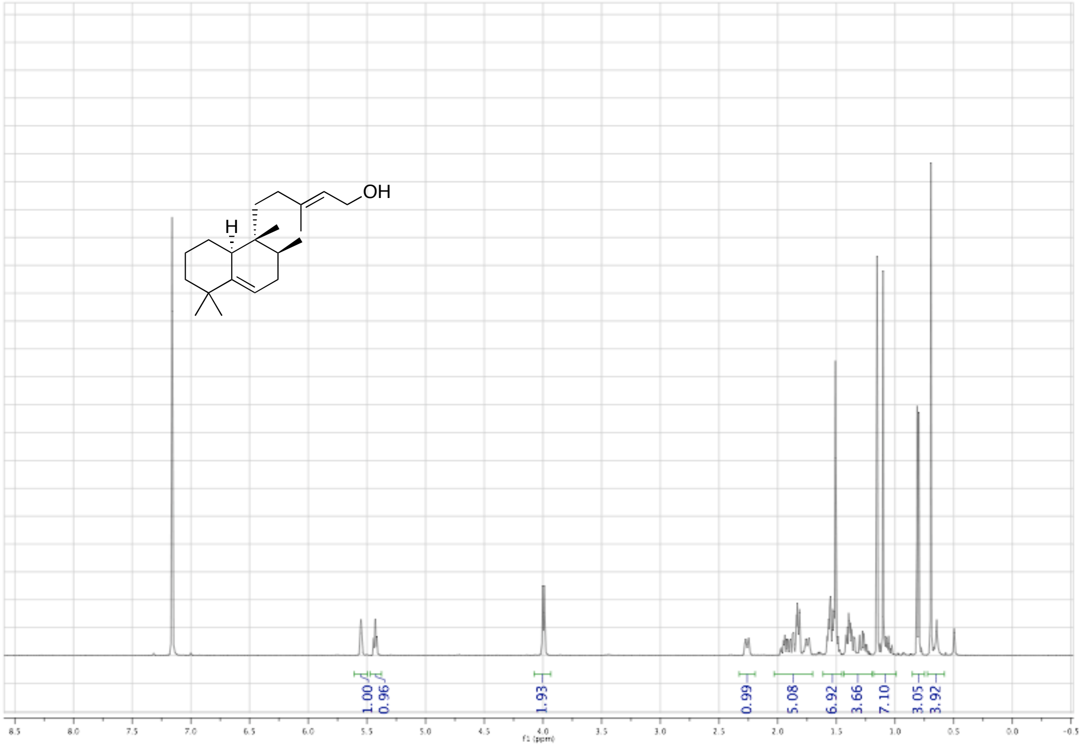
^{1}H-NMR Spectrum of Compound **19** ($CDCl_3$)



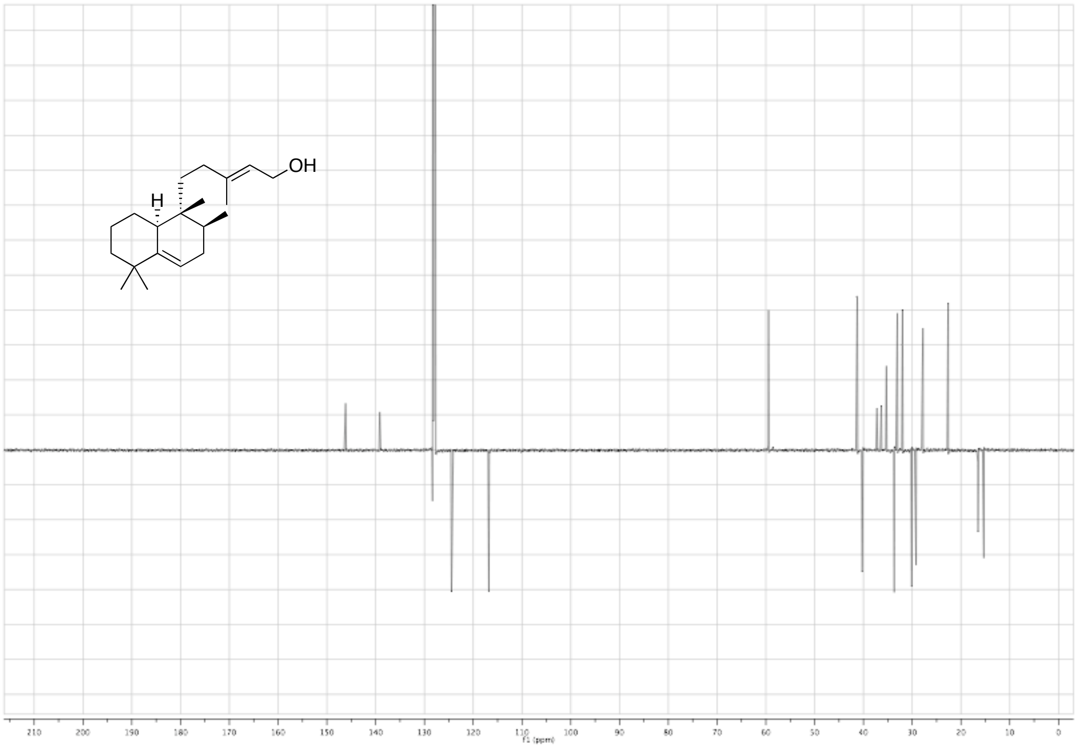
^{13}C-NMR Spectrum of Compound **19** ($CDCl_3$)



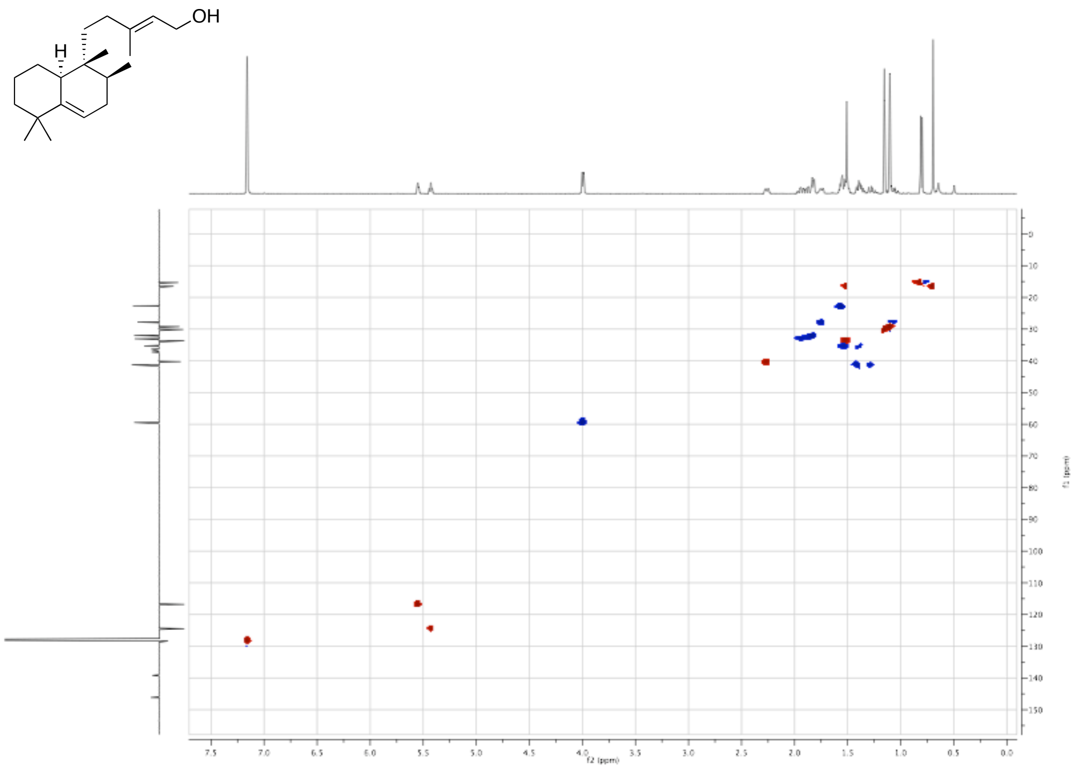
^{1}H-NMR Spectrum of Compound **16** (C_6D_6)



^{13}C-NMR Spectrum of Compound **16** (C_6D_6)



g-HSQC Spectrum of Compound **16** (C_6D_6)



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