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Supplementary Information

Enantioselective Total Synthesis of (+)-Ieodomycin A, (+)-Ieodomycin B, and Their Three Stereoisomers

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Table of contents

1 General Experimental Information S2

2 Synthetic Procedures S2

3 Absolute Configuration Assignment S11

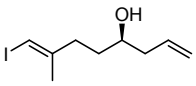
4 Diastereomeric Ratio S12

5 ^{1}H and ^{13}C NMR Spectra of Compounds S13

1. General Experimental Information

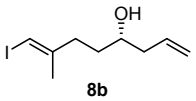
All reagents and solvents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar and TCI). Reactions were monitored by thin layer chromatography (TLC) with 0.25-mm pre-coated silica gel plates (Kieselgel $60F_{254}$). Flash column chromatography was performed on silica gel (70-230 mesh) using distilled organic solvents. ^{1}H and ^{13}C Spectra were recorded on Varian Unity-Inova 500 MHz and Bruker 600 MHz spectrometer. Chemical shifts are reported as δ (ppm) values relative to chloroform ($CDCl_3$, δ 7.26) and methanol-d_4 (CD_3OD, δ 3.31) and coupling constant was noted by Hz units. High-resolution mass spectrometry (HRMS) was performed using electrospray ionization (ESI-TOF) on Waters spectrometer by Korea Basic Science Institute (KBSI). Optical rotations were obtained using a Rudolph Research Analytical Autopol III automatic polarimeter. Melting points were measured on a Fisher Jones apparatus.

2. Synthetic Procedures



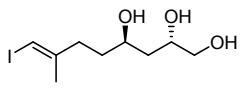
8a

(*R,E*)-8-Iodo-7-methylocta-1,7-dien-4-ol (8a). To a flame dried round-bottomed flask was added zirconocene dichloride (21.4 g, 148.5 mmol, 2.5 equiv.) and CH_2Cl_2 (373 mL), followed by the dropwise addition of $AlMe_3$ (25% w/w in hexane, 130 mL, 297.0 mmol, 5.0 equiv.) at 0 °C, while stirring at 0 °C, homoallylic alcohol **7a** (7.38 g, 59.4 mmol) in CH_2Cl_2 (25 mL) was added. The mixture was warmed to room temperature and stirred for 23 h at which point carboalumination was complete, as determined by TLC. The mixture was then cooled to -50 °C, a solution of iodine (37.7 g, 297.0 mmol, 5.0 equiv.) dissolved in THF (300 mL) was added dropwise and the reaction mixture stirred at 0 °C. After 2 h, the reaction mixture was quenched with saturated aqueous K_2CO_3 and filtered through a pad of celite with Et_2O. The aqueous layer was extracted with Et_2O, then the combined organic phase was washed with saturated aqueous Na_2SO_3 and brine, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 10/1, v/v) on silica to afford the product (**8a**) as pale yellow oil (9.3 g, 34.9 mmol, 59% yield over 3 steps). $[\alpha]^{25}_{D}$ = +11.33 ($CHCl_3$, c = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93 (q, J = 1.2 Hz, 1H), 5.81 (dddd, J = 16.8, 10.8, 8.0, 6.5 Hz, 1H), 5.16 (s, 1H), 5.15 – 5.12 (dq, 1H), 3.62 (tt, J = 8.2, 4.3 Hz, 1H), 2.38 (dddd, J = 15.2, 9.8, 5.6, 1.3 Hz, 1H), 2.34 – 2.26 (m, 2H), 2.15 (dtt, J = 13.9, 7.9, 1.1 Hz, 1H), 1.84 (d, J = 1.1 Hz, 3H), 1.66 – 1.53 (m, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 147.80, 134.52, 118.68 ,75.07, 69.94, 42.18, 35.87, 34.79, 24.06; HRMS (ESI): *m/z* calculated for $C_9H_{15}OINa^+$ $[M + Na]^+$ 289.0065, found 289.0062.



8b

(*S,E*)-8-Iodo-7-methylocta-1,7-dien-4-ol (8b). The compound was prepared by the same procedure as **8a**: pale yellow oil (11.7 g, 44.1 mmol, 74% yield over 3 steps), purified by flash column chromatography (*n*-Hexane/EtOAc = 10/1, v/v) on silica. $[\alpha]^{25}_{D}$ = -11.33 ($CHCl_3$, c = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.93 (q, J = 1.2 Hz, 1H), 5.81 (dddd, J = 16.8, 10.8, 8.0, 6.5 Hz, 1H), 5.16 (s, 1H), 5.13 (dq, J = 9.1, 1.4 Hz, 1H), 3.62 (tq, J = 7.7, 3.8 Hz, 1H), 2.38 (dddd, J = 15.1, 9.7, 5.5, 1.3 Hz, 1H), 2.33 – 2.26 (m, 2H), 2.19 – 2.12 (m, 1H), 1.84 (d, J = 1.1 Hz, 3H), 1.66 – 1.53 (m, 3H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 147.81, 134.52, 118.68, 75.07, 69.95, 42.18, 35.87, 34.80, 24.06; HRMS (ESI): *m/z* calculated for $C_9H_{15}OINa^+$ $[M + Na]^+$ 289.0065, found 289.0055.

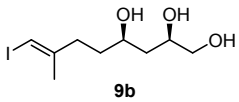


9a

(2*S*,4*R,E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (9a). To a solution of $(DHQ)_2PYR$ (8.3 mg, 0.0094 mmol, 0.01 equiv.), $K_3Fe(CN)_6$ (930.4 mg, 2.83 mmol, 3.0 equiv.), K_2CO_3 (390.6 mg, 2.83 mmol, 3.0 equiv.), $K_2OsO_4{\cdot}2H_2O$ (1.7 mg, 4.7 μmol, 0.5 mol%) in *t*-BuOH (19 mL) and H_2O (19 mL) (*t*-BuOH/H_2O = 1/1, v/v) was added vinyl iodide **8a** (250.6 mg, 0.94 mmol) at 0 °C. The reaction mixture was stirred vigorously at 0 °C for 72 h, at which point hydroxylation was complete, as determined by TLC. Na_2SO_3 was added

to the mixture, which was allowed to warm to room temperature. After stirring for 1 h, CH_2Cl_2 was added to the reaction mixture. The organic phase was washed with sat. $NaHCO_3$, brine and dried over Na_2SO_4. Purification by flash chromatography (CH_2Cl_2 : MeOH : Acetone = 20 : 1 : 1, v/v) provided triols **9a** (146.2 mg, 0.49 mmol, 52%) and **9b** (56.8 mg, 0.19 mmol, 20%) as colorless oil.

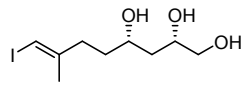
Triol 9a. $[\alpha]^{25}_D$ = +2.00 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (q, *J* = 1.1 Hz, 1H), 4.03 (ddt, *J* = 8.6, 7.0, 3.4 Hz, 1H), 3.90 (tdd, *J* = 8.2, 4.4, 2.8 Hz, 1H), 3.66 (dd, *J* = 11.0, 3.4 Hz, 1H), 3.54 (dd, *J* = 11.0, 7.3 Hz, 1H), 2.38 (dddd, *J* = 15.3, 9.7, 5.5, 1.2 Hz, 1H), 2.29 (dddd, *J* = 14.2, 9.5, 6.3, 1.1 Hz, 1H), 2.15 (s, 3H), 1.85 (d, *J* = 0.9 Hz, 3H), 1.71 – 1.65 (m, 2H), 1.65 – 1.59 (m, 1H), 1.56 (ddd, *J* = 14.5, 8.5, 3.4 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.64, 75.31, 69.53, 68.15, 67.01, 39.41, 35.92, 35.64, 24.12; HRMS (ESI): *m/z* calculated for $C_9H_{17}O_3NaIN^+$ [M + Na]$^+$ 323.0120, found 323.0125.



9b

(2*R*,4*R*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (9b). Triols **9a** (302.5 mg, 0.10 mmol, 5%) and **9b** (3.86 g, 12.86 mmol, 71%) were obtained as colorless oil from vinyl iodide **8a** (4.81 g, 18.07 mmol) by the same procedure as **9a** except using $(DHQD)_2PYR$ instead of $(DHQ)_2PYR$.

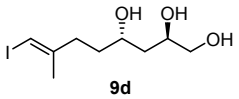
Triol 9b. $[\alpha]^{25}_D$ = +8.00 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (q, *J* = 1.1 Hz, 1H), 3.98 (tt, *J* = 7.5, 3.6 Hz, 1H), 3.89 (tt, *J* = 8.0, 4.7 Hz, 1H), 3.68 – 3.63 (m, 1H), 3.49 (dd, *J* = 10.3, 7.1 Hz, 1H), 3.26 (s, 1H), 2.90 (s, 1H), 2.39 – 2.27 (m, 2H), 2.03 (s, 1H), 1.85 (d, *J* = 1.1 Hz, 3H), 1.64 – 1.60 (m, 1H), 1.60 – 1.56 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.64, 75.24, 72.74, 71.53, 66.89, 39.02, 36.07, 35.52, 24.07; HRMS (ESI): *m/z* calculated for $C_9H_{17}O_3IN^+$ [M + Na]$^+$ 323.0120, found 323.0127.



9c

(2*S*,4*S*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (9c). Triols **9c** (4.34 g, 14.5 mmol, 65%) and **9d** (505.3 mg, 1.68 mmol, 8%) were obtained as colorless oil from vinyl iodide **8b** (5.91 g, 22.2 mmol) by the same procedure as **9a**.

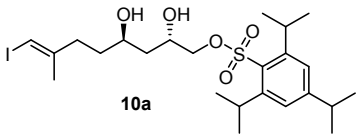
Triol 9c. $[\alpha]^{25}_D$ = -6.00 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (s, 1H), 3.96 (tt, *J* = 7.6, 3.7 Hz, 1H), 3.87 (tt, *J* = 8.0, 4.5 Hz, 1H), 3.64 (dd, *J* = 11.1, 3.3 Hz, 1H), 3.47 (dd, *J* = 11.1, 6.6 Hz, 1H), 2.91 (s, 3H), 2.39 – 2.25 (m, 2H), 1.84 (s, 3H), 1.65 – 1.54 (m, 4H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.64, 75.24, 72.74, 71.53, 66.89, 39.02, 36.07, 35.52, 24.07; HRMS (ESI): *m/z* calculated for $C_9H_{17}O_3IN^+$ [M + Na]$^+$ 323.0120, found 323.0129.



9d

(2*R*,4*S*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (9d). Triols **9c** (33.0 mg, 0.11 mmol, 13%) and **9d** (163.6 mg, 0.55 mmol, 66%) were obtained as colorless oil from vinyl iodide **8b** (219.8 mg, 0.83 mmol) by the same procedure as **9a** except using $(DHQD)_2PYR$ instead of $(DHQ)_2PYR$.

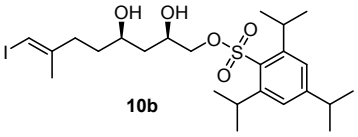
Triol 9d. $[\alpha]^{25}_D$ = -2.00 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (q, *J* = 1.2 Hz, 1H), 4.03 (tt, *J* = 7.2, 3.2 Hz, 1H), 3.95 – 3.87 (m, 1H), 3.66 (dd, *J* = 11.1, 3.3 Hz, 1H), 3.54 (dd, *J* = 11.0, 7.2 Hz, 1H), 2.38 (ddd, *J* = 14.7, 9.8, 5.6 Hz, 1H), 2.29 (ddd, *J* = 14.6, 9.5, 6.3 Hz, 1H), 2.22 (s, 3H), 1.85 (d, *J* = 0.8 Hz, 3H), 1.71 – 1.64 (m, 2H), 1.64 – 1.59 (m, 1H), 1.56 (ddd, *J* = 14.4, 8.6, 3.3 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.67, 75.26, 69.65, 68.55, 66.99, 39.15, 35.97, 35.56, 24.07; HRMS (ESI): *m/z* calculated for $C_9H_{17}O_3IN^+$ [M + Na]$^+$ 323.0120, found 323.0129.



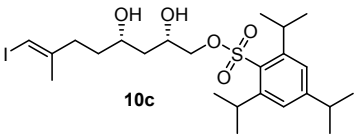
10a

(2*S*,4*R*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (10a). To a flame dried round-bottomed flask was added DMAP (190.6 mg, 1.56 mmol, 0.2 equiv.), Et_3N (1.18 g, 11.7 mmol, 1.5 equiv.) and triol **9a** (2.34 g, 7.80 mmol) in CH_2Cl_2 (21 mL). The mixture was subsequently cooled to -78°C and a solution of 2,4,6-triisopropylsulfonyl chloride (9.45 g, 31.2 mmol, 4.0 equiv.) dissolved in CH_2Cl_2 (10 ml) was added dropwise. The reaction was slowly warmed to -20 °C, at which temperature it was stirred over the next 22 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 2/1, v/v) on silica to afford the product (**10a**) (4.32 g, 7.63 mmol, 98%) as a white solid. $[\alpha]^{25}_D$ = +4.00 ($CHCl_3$, *c* = 0.5); m.p.: 104-106 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (s, 2H), 5.93

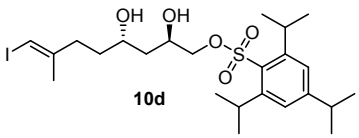
(q, *J* = 1.2 Hz, 1H), 4.22 (ddt, *J* = 8.8, 7.1, 3.6 Hz, 1H), 4.11 (p, *J* = 6.8 Hz, 2H), 4.07 (dd, *J* = 10.3, 3.9 Hz, 1H), 3.99 (dd, *J* = 10.3, 7.1 Hz, 1H), 3.90 (tdd, *J* = 8.5, 4.5, 2.7 Hz, 1H), 2.91 (p, *J* = 6.9 Hz, 1H), 2.39 – 2.24 (m, 4H), 1.83 (d, *J* = 1.1 Hz, 3H), 1.69 – 1.55 (m, 4H), 1.26 (d, *J* = 6.8 Hz, 12H) , 1.26 (d, *J* = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 154.18, 151.00, 147.59, 129.07, 124.03, 75.28, 72.87, 68.25, 67.26, 38.86, 35.90, 35.57, 34.41, 29.82, 24.90, 24.87, 24.03, 23.67; HRMS (ESI): *m/z* calculated for $C_{24}H_{39}O_5SINa^+$ $[M + Na]^+$ 589.1461, found 589.1469.



(2*R*,4*R*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (10b). Sulfonate **10b** (498.2 mg, 0.88 mmol, 88%) was obtained as a white solid from vinyl iodide **9b** (299.9 mg, 1.0 mmol) by the same procedure as **10a**. $[\alpha]^{25}_D$ = +0.67 ($CHCl_3$, *c* = 0.5); m.p.: 104-106 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.19 (s, 2H), 5.93 (s, 1H), 4.17 (ddq, *J* = 9.9, 6.8, 4.1, 3.5 Hz, 1H), 4.11 (p, *J* = 6.7 Hz, 2H), 4.00 (dt, *J* = 10.7, 5.4 Hz, 2H), 3.87 (dddd, *J* = 9.7, 7.3, 4.9, 2.3 Hz, 1H), 2.92 (hept, *J* = 6.9 Hz, 1H), 2.37 – 2.25 (m, 2H), 2.19 (s, 2H), 1.84 (s, 3H), 1.68 – 1.52 (m, 4H), 1.26 (dd, *J* = 6.8, 2.4 Hz, 18H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 154.21, 151.02, 147.56, 129.05, 124.04, 75.28, 72.59, 71.37, 70.57, 38.85, 35.93, 35.44, 34.42, 29.84, 24.90, 24.88, 24.05, 23.69; HRMS (ESI): *m/z* calculated for $C_{24}H_{39}O_5SINa^+$ $[M + Na]^+$ 589.1461, found 589.1469.

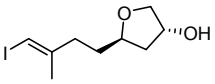


(2S,4S,E)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (10c). Sulfonate **10c** (392.2 mg, 0.69 mmol, 85%) was obtained as a white solid from vinyl iodide **9c** (243.7 mg, 0.81 mmol) by the same procedure as **10a**. $[\alpha]^{25}_D$ = -3.00 ($CHCl_3$, *c* = 0.5); m.p.: 104-106 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.19 (s, 2H), 5.92 (s, 1H), 4.17 (ddt, *J* = 9.9, 6.8, 3.4 Hz, 1H), 4.11 (p, *J* = 6.7 Hz, 2H), 4.01 – 3.96 (m, 2H), 3.87 (dddd, *J* = 9.9, 7.4, 4.9, 2.2 Hz, 1H), 3.25 (s, 2H), 2.91 (p, *J* = 6.9 Hz, 1H), 2.30 (dddd, *J* = 33.7, 14.5, 9.0, 6.2 Hz, 2H), 1.83 (s, 3H), 1.60 (dddd, *J* = 33.4, 14.4, 10.8, 3.6 Hz, 4H), 1.26 (d, *J* = 6.8 Hz, 18H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 154.21, 151.01, 147.52, 129.02, 124.04, 75.29, 72.57, 71.41, 70.55, 38.77, 35.88, 35.40, 34.41, 29.83, 24.90, 24.87, 24.04, 23.68; HRMS (ESI): *m/z* calculated for $C_{24}H_{39}O_5SINa^+$ $[M + Na]^+$ 589.1461, found 589.1459.



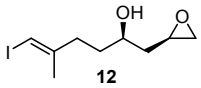
(2*R*,4*S*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (10d). Sulfonate **10d** (5.04 g, 8.90 mmol, 77%) was obtained as a white solid from vinyl iodide **9d** (3.49 g, 11.6 mmol) by the same procedure as **10a**. $[\alpha]^{25}_D$ = -2.00 ($CHCl_3$, *c* = 0.5); m.p.: 104-106 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.20 (s, 2H), 5.93 (q, *J* = 1.2 Hz, 1H), 4.22 (ddt, *J* = 8.7, 7.1, 3.6 Hz, 1H), 4.12 (p, *J* = 6.8 Hz, 2H), 4.08 (dd, *J* = 10.3, 3.8 Hz, 1H), 4.00 (dd, *J* = 10.3, 7.0 Hz, 1H), 3.91 (tt, *J* = 7.9, 2.8 Hz, 1H), 2.92 (hept, *J* = 6.8 Hz, 1H), 2.36 (dddd, *J* = 15.2, 9.7, 5.8, 1.2 Hz, 1H), 2.27 (dddd, *J* = 14.1, 9.4, 6.5, 1.2 Hz, 1H), 1.84 (d, *J* = 0.9 Hz, 3H), 1.71 – 1.54 (m, 6H), 1.27 (d, *J* = 6.8, 2.0 Hz, 12H), 1.26 (d, *J* = 6.9, 2.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 154.18, 150.99, 147.58, 129.06, 124.03, 75.28, 72.88, 68.23, 67.24, 38.86, 35.89, 35.57, 34.41, 29.82, 24.90, 24.87, 24.03, 23.68; HRMS (ESI): *m/z* calculated for $C_{24}H_{39}O_5SINa^+$ $[M + Na]^+$ 589.1461, found 589.1464.

(3*R*,5*R*)-5-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)tetrahydrofuran-3-ol (11). To a solution of sulfonate **10b** (23.6 mg, 0.042 mml) in DMSO (0.4 mL) was added NaCN (2.65 mg, 0.054 mmol, 1.3 equiv.). The reaction mixture was stirred at 70 °C for 1 h. The reaction was quenched with water, extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4. Purification by flash chromatography (*n*-Hexane/EtOAc = 2/1, v/v) provided compound **12** (3.0 mg, 0.01 mmol, 23%) and compound **11** (10.0 mg, 0.035 mmol, 76%) as colorless oil.



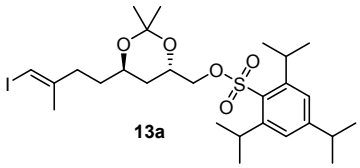
11

Compound 11. $[\alpha]^{23}_{D}$ = +7.41 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, CD_3OD) δ 6.00 (q, *J* = 1.2 Hz, 1H), 4.42 (td, *J* = 5.1, 4.2, 1.9 Hz, 1H), 4.05 (ddt, *J* = 9.9, 7.2, 5.5 Hz, 1H), 3.95 (dd, *J* = 9.5, 4.4 Hz, 1H), 3.63 (ddd, *J* = 9.5, 2.0, 1.0 Hz, 1H), 2.38 – 2.32 (m, 1H), 2.32 – 2.25 (m, 1H), 1.97 (ddt, *J* = 13.1, 5.5, 1.2 Hz, 1H), 1.84 (d, *J* = 1.1 Hz, 3H), 1.69 – 1.60 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 148.79, 78.75, 76.09, 75.20, 72.95, 42.07, 36.96, 34.70, 23.95; HRMS (ESI): *m/z* calculated for $C_9H_{15}O_2INa$+ [M + Na]+ 305.0014, found 305.0020.



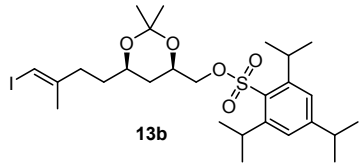
12

Compound 12. $[\alpha]^{23}_{D}$ = +21.85 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.94 (q, *J* = 1.2 Hz, 1H), 3.88 (s, 1H), 3.09 (dtd, *J* = 7.9, 3.9, 2.7 Hz, 1H), 2.79 (dd, *J* = 4.9, 4.0 Hz, 1H), 2.50 (dd, *J* = 4.9, 2.7 Hz, 1H), 2.38 (dddd, *J* = 14.6, 8.7, 6.8, 1.2 Hz, 1H), 2.31 (dddd, *J* = 14.1, 8.2, 7.0, 1.1 Hz, 1H), 2.15 (s, 1H), 1.90 (dt, *J* = 14.4, 3.7 Hz, 1H), 1.85 (d, *J* = 1.1 Hz, 3H), 1.66 – 1.60 (m, 2H), 1.47 (dt, *J* = 14.4, 8.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.65, 75.20, 70.00, 50.68, 46.69, 39.88, 35.66, 35.44, 24.06; HRMS (ESI): *m/z* calculated for $C_9H_{15}O_2INa^+$ [M + Na]$^+$ 305.0014, found 305.0017.



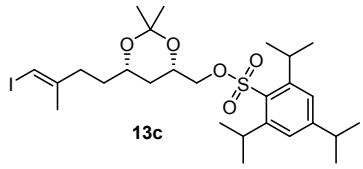
13a

((4*S*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (13a). To a stirred solution of sulfonate **10a** (139.0 mg, 0.25 mmol) in acetone (1 mL) was added 2,2-dimethoxypropane (260.4 mg, 2.5 mmol, 10 equiv.) and *p*-toluenesulfonic acid (9.5 mg, 0.05 mmol, 0.2 equiv.) at room temperature. The resulting colorless solution was stirred at room temperature for 3 h. The reaction mixture was quenched with sat. aq. $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 20/1, v/v) on silica to afford acetonide **13a** (147.0 mg, 0.24 mmol, 97%) as a white solid. $[\alpha]^{25}_{D}$ = +0.55 (CH_3OH, *c* = 1.0); m.p.: 55-57 °C; ^{1}H NMR (600 MHz, CD_3OD) δ 7.29 (s, 2H), 5.95 (q, *J* = 1.2 Hz, 1H), 4.15 (hept, *J* = 6.8 Hz, 2H), 4.10 – 4.05 (m, 2H), 3.98 (dd, *J* = 11.1, 7.5 Hz, 1H), 3.70 (ddt, *J* = 9.6, 7.8, 5.4 Hz, 1H), 2.95 (hept, *J* = 6.9 Hz, 1H), 2.33 – 2.23 (m, 2H), 1.81 (d, *J* = 0.9 Hz, 3H), 1.63 (ddd, *J* = 13.1, 9.4, 5.9 Hz, 1H), 1.60 – 1.51 (m, 3H), 1.26 (d, *J* = 6.9 Hz, 18H), 1.24 (s, 3H), 1.22 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 155.40, 152.04, 148.63, 131.00, 125.00, 101.80, 75.37, 72.22, 66.79, 66.19, 36.26, 35.51, 34.74, 34.58, 30.80, 25.08, 25.02, 24.96, 23.95, 23.75; HRMS (ESI): *m/z* calculated for $C_{27}H_{43}O_5SINa^+$ [M + Na]$^+$ 629.1774, found 629.1767.



13b

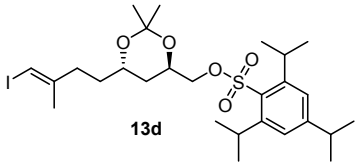
((4*R*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (13b). Acetonide **13b** (157.6 mg, 0.26 mmol, 96%) was obtained as a white solid from sulfonate **10b** (153.5 mg, 0.27 mmol) by the same procedure as **13a**. $[\alpha]^{25}_{D}$ = +2.00 (CH_3OH, *c* = 0.5); m.p.: 55-57 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (s, 2H), 5.87 (q, *J* = 1.2 Hz, 1H), 4.16 – 4.10 (m, 3H), 3.98 (d, *J* = 5.2 Hz, 2H), 3.75 (dddd, *J* = 11.7, 7.9, 4.4, 2.5 Hz, 1H), 2.91 (hept, *J* = 6.9 Hz, 1H), 2.26 (dd, *J* = 8.1, 6.9 Hz, 2H), 1.82 (d, *J* = 1.1 Hz, 3H), 1.62 – 1.55 (m, 1H), 1.55 – 1.51 (m, 1H), 1.49 (dt, *J* = 12.7, 2.7 Hz, 1H), 1.33 (s, 3H), 1.29 (s, 3H), 1.26 (d, *J* = 6.6 Hz, 12H), 1.25 (d, *J* = 7.2 Hz, 6H), 1.22 – 1.16 (q, *J* = 12.0 Hz 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 153.83, 150.91, 147.38, 129.59, 123.88, 98.98, 75.14, 71.55, 67.38, 67.19, 34.96, 34.39, 34.16, 33.02, 29.94, 29.75, 24.90, 24.86, 23.91, 23.69, 19.71; HRMS (ESI): *m/z* calculated for $C_{27}H_{43}O_5SINa^+$ [M + Na]$^+$ 629.1774, found 629.1777.



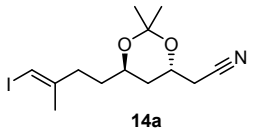
13c

((4*S*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (13c). Acetonide **13c** (1.054 g, 1.74 mmol, 94%) was obtained as a white solid from sulfonate **10c** (1.046 g, 1.85 mmol) by the same procedure as **13a**. $[\alpha]^{25}_{D}$ = -5.44 (CH_3OH, *c* = 0.5); m.p.: 55-57 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (s, 2H), 5.87 (t, *J* = 1.2 Hz, 1H), 4.13 (p, *J* = 6.5 Hz, 3H), 3.98 (d, *J* = 5.2 Hz, 2H), 3.78 – 3.72 (m, 1H), 2.91 (q, *J* = 6.9 Hz, 1H), 2.26 (t, *J* = 7.7 Hz, 2H), 1.82

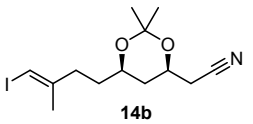
(s, 3H), 1.62 – 1.56 (m, 1H), 1.55 – 1.51 (m, 1H), 1.51 – 1.47 (m, 1H), 1.33 (s, 3H), 1.29 (s, 3H), 1.26 (dd, *J* = 6.9, 3.8 Hz, 18H), 1.19 (q, *J* = 11.9 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 153.86, 150.94, 147.41, 129.57, 123.91, 99.00, 75.17, 71.57, 67.39, 67.20, 34.98, 34.41, 34.17, 33.04, 29.96, 29.77, 24.92, 24.88, 23.93, 23.71, 19.73; HRMS (ESI): *m/z* calculated for $C_{27}H_{43}O_5SINa^+$ [M + Na]$^+$ 629.1774, found 629.1776.



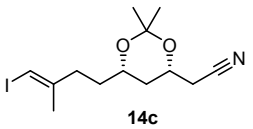
((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (13d). Acetonide **13d** (195.8 mg, 0.32 mmol, 98%) was obtained as a white solid from sulfonate **10d** (188.9 mg, 0.33 mmol) by the same procedure as **13a**. $[\alpha]^{25}_D$ = -0.87 (CH_3OH, *c* = 1.0); m.p.: 55-57 °C; ^1H NMR (600 MHz, CD_3OD) δ 7.28 (s, 2H), 5.94 (q, *J* = 1.3 Hz, 1H), 4.14 (hept, *J* = 6.7 Hz, 2H), 4.09 – 4.03 (m, 2H), 3.97 (dd, *J* = 11.0, 7.5 Hz, 1H), 3.72 – 3.66 (m, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 2.27 (hept, *J* = 7.4 Hz, 2H), 1.80 (s, 3H), 1.62 (ddd, *J* = 13.0, 9.4, 5.9 Hz, 1H), 1.59 – 1.49 (m, 3H), 1.25 (d, *J* = 6.7 Hz, 18H), 1.23 (s, 3H), 1.21 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 155.41, 152.05, 148.64, 131.01, 125.00, 101.80, 75.35, 72.23, 66.80, 66.20, 36.26, 35.52, 34.74, 34.59, 30.81, 25.07, 25.02, 24.96, 23.94, 23.73; HRMS (ESI): *m/z* calculated for $C_{27}H_{43}O_5SINa^+$ [M + Na]$^+$ 629.1774, found 629.1769.



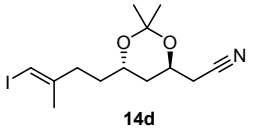
2-((4*R*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (14a). To a solution of acetonide **13a** (30.79 mg, 0.05 mmol) in DMSO (1 mL) was added NaCN (9.8 mg, 0.2 mmol, 4.0 equiv.). The reaction mixture was stirred at 70 °C for 6 h. The reaction was quenched with H_2O. The aqueous layer was extracted with EtOAc, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 20/1, v/v) on silica to afford cyanide **14a** (15.3 mg, 0.044 mmol, 88%) as colorless oil. $[\alpha]^{25}_D$ = -3.33 (CH_3OH, *c* = 0.5); ^1H NMR (600 MHz, CD_3OD) δ 5.98 (q, *J* = 1.2 Hz, 1H), 4.08 (dtd, *J* = 8.6, 6.9, 4.5 Hz, 1H), 3.79 (tdd, *J* = 8.3, 6.9, 4.9 Hz, 1H), 2.67 (dd, *J* = 16.8, 4.5 Hz, 1H), 2.59 (dd, *J* = 16.8, 7.1 Hz, 1H), 2.32 (hept, *J* = 7.3 Hz, 2H), 1.84 (d, *J* = 1.1 Hz, 3H), 1.71 (ddd, *J* = 8.6, 6.7, 3.0 Hz, 2H), 1.62 (tdd, *J* = 8.0, 5.5, 3.6 Hz, 2H), 1.35 (s, 3H), 1.33 (s, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, CD_3OD) δ 148.66, 118.84, 102.06, 75.36, 66.86, 64.33, 38.22, 36.28, 34.64, 25.18, 24.92, 24.52, 23.75; HRMS (ESI): *m/z* calculated for $C_{13}H_{20}NO_2INa^+$ [M + Na]$^+$ 372.0436, found 372.0437.



2-((4*S*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (14b). Cyanide **14b** (93.3 mg, 0.27 mmol, 87%) was obtained as colorless oil from acetonide **13b** (185.4 mg, 0.31 mmol) by the same procedure as **14a**. $[\alpha]^{25}_D$ = +18.67 (CH_3OH, *c* = 0.5); ^1H NMR (600 MHz, $CDCl_3$) δ 5.90 (dt, *J* = 2.0, 1.1 Hz, 1H), 4.14 – 4.08 (m, 1H), 3.81 – 3.75 (m, 1H), 2.54 (dd, *J* = 16.7, 5.8 Hz, 1H), 2.47 (dd, *J* = 16.6, 6.3 Hz, 1H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.83 (s, 3H), 1.66 – 1.60 (m, 2H), 1.59 – 1.55 (m, 1H), 1.42 (s, 3H), 1.39 (s, 3H), 1.28 (q, *J* = 12.0, 11.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 147.32, 116.98, 99.45, 75.26, 67.44, 65.33, 36.05, 34.97, 33.99, 29.99, 25.15, 23.92, 19.84; HRMS (ESI): *m/z* calculated for $C_{13}H_{20}NO_2INa^+$ [M + Na]$^+$ 372.0436, found 372.0438.

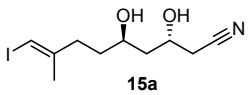


2-((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (14c). Cyanide **14c** (589.2 mg, 1.69 mmol, 93%) was obtained as colorless oil from acetonide **13c** (1.11 g, 1.82 mmol) by the same procedure as **14a**. $[\alpha]^{25}_D$ = -22.00 (CH_3OH, *c* = 0.5); ^1H NMR (600 MHz, $CDCl_3$) δ 5.89 (q, *J* = 1.1 Hz, 1H), 4.11 (dtd, *J* = 11.8, 6.1, 2.6 Hz, 1H), 3.80 – 3.75 (m, 1H), 2.53 (dd, *J* = 16.6, 5.9 Hz, 1H), 2.47 (dd, *J* = 16.6, 6.3 Hz, 1H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.83 (s, 3H), 1.65 – 1.60 (m, 2H), 1.56 (ddt, *J* = 13.8, 8.1, 4.3 Hz, 1H), 1.41 (s, 3H), 1.39 (s, 3H), 1.31 – 1.24 (m, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 147.30, 116.97, 99.42, 75.25, 67.42, 65.30, 36.03, 34.95, 33.97, 29.97, 25.13, 23.91, 19.83; HRMS (ESI): *m/z* calculated for $C_{13}H_{20}NO_2INa^+$ [M + Na]$^+$ 372.0436, found 372.0440.



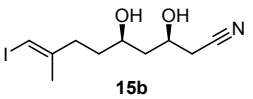
14d

2-((4*S*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (14d). Cyanide **14d** (19.5 mg, 0.056 mmol, 90%) was obtained as colorless oil from acetonide **13d** (37.5 mg, 0.062 mmol) by the same procedure as **14a**. $[\alpha]^{25}_{D}$ = +2.00 (CH_3OH, *c* = 0.5); ^{1}H NMR (600 MHz, CD_3OD) δ 5.98 (q, *J* = 1.2 Hz, 1H), 4.11 – 4.05 (m, 1H), 3.82 – 3.76 (m, 1H), 2.67 (dd, *J* = 16.9, 4.6 Hz, 1H), 2.59 (dd, *J* = 16.8, 7.1 Hz, 1H), 2.37 – 2.27 (m, 2H), 1.84 (d, *J* = 1.1 Hz, 3H), 1.74 – 1.69 (m, 2H), 1.62 (tdd, *J* = 7.9, 5.5, 3.4 Hz, 2H), 1.35 (s, 3H), 1.33 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 148.64, 118.82, 102.04, 75.40, 66.84, 64.30, 38.21, 36.28, 34.63, 25.18, 24.93, 24.52, 23.77; HRMS (ESI): *m/z* calculated for $C_{13}H_{20}NO_2INa^+$ [M + Na]$^+$ 372.0436, found 372.0434.



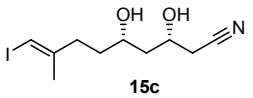
15a

(3*R*,5*R*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (15a). To a stirred solution of cyanide **14a** (69.0 mg, 0.20 mmol) in THF (2.0 mL) was added 1N HCl (1.6 mL) at room temperature. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was quenched with $NaHCO_3$ to adjust pH of 7. The aqueous layer was extracted with CH_2Cl_2, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 1.5/1, v/v) on silica to afford diol **15a** (58.0 mg, 0.19 mmol, 95%) as colorless oil. $[\alpha]^{25}_{D}$ = -4.00 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.96 (q, *J* = 1.2 Hz, 1H), 4.28 (dtd, *J* = 8.9, 5.9, 2.9 Hz, 1H), 3.94 (tdd, *J* = 8.2, 4.4, 2.9 Hz, 1H), 2.69 – 2.52 (m, 2H), 2.60 (s, 2H), 2.36 (ddd, *J* = 14.7, 9.3, 5.8 Hz, 1H), 2.29 (ddd, *J* = 14.7, 8.7, 6.7 Hz, 1H), 1.85 (d, *J* = 0.9 Hz, 3H), 1.81 – 1.76 (m, 1H), 1.72 – 1.60 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.35, 117.82, 75.53, 68.49, 65.28, 41.91, 35.86, 35.27, 26.34, 24.01; HRMS (ESI): *m/z* calculated for $C_{10}H_{16}NO_2INa^+$ [M + Na]$^+$ 332.0123, found 332.0121.



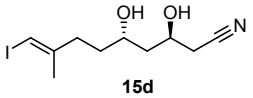
15b

(3*S*,5*R*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (15b). Diol **15b** (28.7 mg, 0.093 mmol, 94%) was obtained as colorless oil from acetonide **14b** (34.4 mg, 0.10 mmol) by the same procedure as **15a**. $[\alpha]^{25}_{D}$ = +6.00 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.97 (s, 1H), 4.19 (dtd, *J* = 8.7, 5.8, 2.7 Hz, 1H), 3.90 (dtd, *J* = 9.1, 6.2, 2.6 Hz, 1H), 2.85 (s, 2H), 2.55 (d, *J* = 5.8 Hz, 2H), 2.38 – 2.26 (m, 2H), 1.85 (s, 3H), 1.79 – 1.68 (m, 2H), 1.68 – 1.62 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.27, 117.49, 75.57, 72.05, 68.33, 41.76, 36.11, 35.39, 26.40, 24.00; HRMS (ESI): *m/z* calculated for $C_{10}H_{16}NO_2INa^+$ [M + Na]$^+$ 332.0123, found 332.0123.



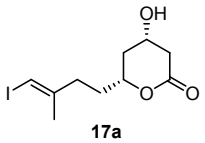
15c

(3*R*,5*S*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (15c). Diol **15c** (34.4 mg, 0.45 mmol, 98%) was obtained as colorless oil from acetonide **14c** (39.9 mg, 0.11 mmol) by the same procedure as **15a**. $[\alpha]^{25}_{D}$ = -8.67 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.98 (q, *J* = 1.2 Hz, 1H), 4.19 (dtd, *J* = 9.7, 5.8, 2.6 Hz, 1H), 3.91 (dtd, *J* = 10.0, 6.1, 2.6 Hz, 1H), 2.55 (d, *J* = 5.9 Hz, 2H), 2.32 (tt, *J* = 14.3, 7.4 Hz, 2H), 1.86 (d, *J* = 1.2 Hz, 3H), 1.80 – 1.74 (m, 1H), 1.74 – 1.68 (m, 1H), 1.66 (td, *J* = 7.8, 6.1 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.27, 117.53, 75.55, 71.94, 68.28, 41.74, 36.07, 35.36, 26.40, 24.00; HRMS (ESI): *m/z* calculated for $C_{10}H_{16}NO_2INa^+$ [M + Na]$^+$ 332.0123, found 332.0126.



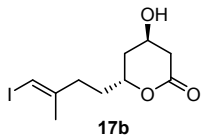
15d

(3*S*,5*S*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (15d). Diol **15d** (14.8 mg, 0.048 mmol, 94%) was obtained as colorless oil from acetonide **14d** (17.8 mg, 0.051 mmol) by the same procedure as **15a**. $[\alpha]^{25}_{D}$ = +2.67 ($CHCl_3$, *c* = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.98 (q, *J* = 1.1 Hz, 1H), 4.29 (dtd, *J* = 8.9, 6.0, 3.0 Hz, 1H), 3.97 (tdd, *J* = 8.1, 4.4, 3.0 Hz, 1H), 2.59 (dd, *J* = 6.0, 2.7 Hz, 2H), 2.37 (dddd, *J* = 14.1, 9.5, 5.9, 1.2 Hz, 1H), 2.30 (dddd, *J* = 14.1, 9.1, 6.5, 1.2 Hz, 1H), 2.04 (s, 2H), 1.86 (d, *J* = 1.1 Hz, 3H), 1.84 – 1.78 (m, 1H), 1.74 – 1.62 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.34, 117.75, 75.54, 68.57, 65.34, 41.85, 35.88, 35.26, 26.33, 24.01; HRMS (ESI): *m/z* calculated for $C_{10}H_{16}NO_2INa^+$ [M + Na]$^+$ 332.0123, found 332.0126.



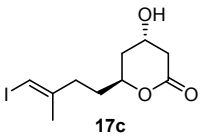
17a

(4*S*,6*R*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (17a). To a solution of diol **15a** (1.13 g, 3.65 mmol) in MeOH (73 mL) was added 7.5 N NaOH (4.87 mL). The reaction mixture was stirred at 55 °C for 38 h. at which point carboxylic acid was complete as determined by TLC. The reaction was quenched with 1N HCl to adjust pH of 7, evaporated *in vacuo.* Crude **16a** was used without further purification. To a solution of crude **16a** and Et_3N (1.33 g, 13.14 mmol, 3.6 equiv.) in CH_2Cl_2 (80 ml) was added dropwise to a solution of 2-chloro-1-methylpyridinium iodide (4.66 g, 18.25 mmol, 5.0 equiv.) in CH_2Cl_2 (11 mL). After the reaction was stirred at room temperature for 13 h. The organic phase was washed with brine, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 1/2, v/v) on silica to afford lactone **17a** (863.3 mg, 2.78 mmol, 76% yield over 2 steps) as white oil. $[\alpha]^{23}_D$ = +37.41 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.97 (q, *J* = 1.1 Hz, 1H), 4.26 (ddt, *J* = 9.2, 7.9, 5.7 Hz, 1H), 4.19 – 4.13 (m, 1H), 2.91 (ddd, *J* = 17.1, 5.9, 1.4 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.47 (dd, *J* = 17.0, 7.9 Hz, 1H), 2.39 – 2.33 (m, 1H), 2.24 (dddd, *J* = 13.6, 5.5, 3.0, 1.4 Hz, 1H), 1.90 – 1.83 (m, 4H), 1.77 (dddd, *J* = 13.8, 9.6, 6.6, 4.2 Hz, 1H), 1.61 (ddd, *J* = 13.7, 11.7, 9.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.32, 146.55, 76.09, 76.00, 63.99, 39.65, 37.95, 34.84, 33.70, 23.98; HRMS (ESI): *m/z* calculated for $C_{10}H_{15}O_3INa^+$ [M + Na]$^+$ 332.9964, found 332.9968.



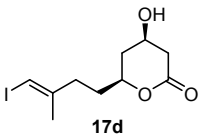
17b

(4*R*,6*R*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (17b). Lactone **17b** (54.5 mg, 0.18 mmol, 65% yield over 2 steps) was obtained as white oil from acetonide **15b** (82.6 mg, 0.27 mmol) by the same procedure as **17a**. $[\alpha]^{23}_D$ = +39.63 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.97 (q, *J* = 1.2 Hz, 1H), 4.67 (ddt, *J* = 11.6, 7.8, 3.6 Hz, 1H), 4.42 – 4.38 (m, 1H), 2.73 (dd, *J* = 17.7, 4.9 Hz, 1H), 2.63 (ddd, *J* = 17.7, 3.6, 1.8 Hz, 1H), 2.51 – 2.44 (m, 1H), 2.39 – 2.32 (m, 1H), 1.95 (dtd, *J* = 14.3, 3.3, 1.8 Hz, 1H), 1.85 (s, 3H), 1.81 (ddd, *J* = 9.9, 8.4, 5.1 Hz, 1H), 1.78 – 1.71 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.19, 146.77, 75.86, 74.89, 62.88, 38.76 , 36.09, 34.91, 33.78, 24.05; HRMS (ESI): *m/z* calculated for $C_{10}H_{15}O_3INa^+$ [M + Na]$^+$ 332.9964, found 332.9967.



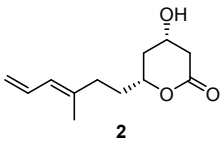
17c

(4*S*,6*S*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (17c). Lactone **17c** (77.8 mg, 0.25 mmol, 56% yield over 2 steps) was obtained as white oil from acetonide **15c** (138.1 mg, 0.45 mmol) by the same procedure as **17a**. $[\alpha]^{23}_D$ = -40.74 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.97 (q, *J* = 1.2 Hz, 1H), 4.67 (ddt, *J* = 11.6, 7.8, 3.6 Hz, 1H), 4.39 (dq, *J* = 7.0, 3.6 Hz, 1H), 2.73 (dd, *J* = 17.7, 4.9 Hz, 1H), 2.63 (ddd, *J* = 17.6, 3.5, 1.8 Hz, 1H), 2.50 – 2.44 (m, 1H), 2.38 – 2.32 (m, 1H), 1.95 (dtd, *J* = 14.3, 3.3, 1.8 Hz, 1H), 1.85 (s, 3H), 1.81 (ddd, *J* = 9.8, 8.4, 5.3 Hz, 1H), 1.78 – 1.71 (m, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.26, 146.76, 75.86, 74.92, 62.84, 38.75, 36.06, 34.90, 33.77, 24.05; HRMS (ESI): *m/z* calculated for $C_{10}H_{15}O_3INa^+$ [M + Na]$^+$ 332.9964, found 332.9970.



17d

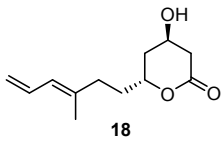
(4*R*,6*S*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (17d). Lactone **17d** (23.8 mg, 0.077 mmol, 84% yield over 2 steps) was obtained as white oil from acetonide **15d** (69.2 mg, 0.22 mmol) by the same procedure as **17a**. $[\alpha]^{23}_D$ = -39.26 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.97 (q, *J* = 1.1 Hz, 1H), 4.27 (ddt, *J* = 9.2, 7.9, 5.7 Hz, 1H), 4.19 – 4.13 (m, 1H), 2.92 (ddd, *J* = 17.2, 5.9, 1.4 Hz, 1H), 2.50 – 2.42 (m, 2H), 2.36 (dddd, *J* = 14.3, 9.4, 6.6, 1.1 Hz, 1H), 2.24 (dddd, *J* = 13.6, 5.4, 3.0, 1.4 Hz, 1H), 1.91 – 1.82 (m, 4H), 1.80 – 1.74 (m, 1H), 1.61 (ddd, *J* = 13.6, 11.7, 9.2 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.29, 146.55, 76.08, 76.00, 64.00, 39.65, 37.96, 34.85, 33.71, 23.99; HRMS (ESI): *m/z* calculated for $C_{10}H_{15}O_3INa^+$ [M + Na]$^+$ 332.9964, found 332.9967.



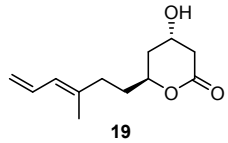
2

Ieodomycin B (2). A solution of lactone **17a** (34.9 mg, 0.11 mmol) and the tributyl(vinyl)tin (69.8 mg, 0.22 mmol, 2.0 equiv.) in NMP (1.1 mL) was treated with DIPEA (71.1 mg, 0.55 mmol, 5.0 equiv.) and Pd_2dba_3 (10.1 mg, 0.011 mmol, 10 mol%) at room temperature under N_2. The flask was covered with aluminum foil. The reaction mixture was stirred for 5 h. The reaction was quenched with aq.

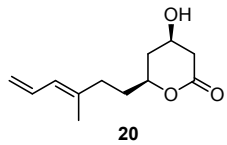
NH_4Cl. The aqueous layer was extracted with Et_2O. The combined organic phase was washed with 1 N KF solution, brine, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 1/1, v/v) on silica to afford ieodomycin B **2** (15.6 mg, 0.074 mmol, 67%) as colorless oil. $[\alpha]^{23}_D$ = +22.22 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, CD_3OD) δ 6.59 (dt, *J* = 16.8, 10.5 Hz, 1H), 5.89 (dd, *J* = 10.8, 0.5 Hz, 1H), 5.08 (dd, *J* = 16.8, 2.1 Hz, 1H), 4.97 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.26 (dddd, *J* = 12.1, 7.7, 4.9, 3.1 Hz, 1H), 4.20 (ddt, *J* = 8.6, 7.2, 5.8 Hz, 1H), 2.86 (ddd, *J* = 16.9, 5.8, 1.1 Hz, 1H), 2.37 (dd, *J* = 16.9, 7.1 Hz, 1H), 2.30 – 2.24 (m, 2H), 2.18 (ddd, *J* = 14.5, 8.9, 6.6 Hz, 1H), 1.85 – 1.76 (m, 2H), 1.78 (s, 3H), 1.52 (ddd, *J* = 13.7, 11.7, 8.5 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 173.93, 138.93, 134.40, 127.50, 115.47, 78.40, 64.26, 40.07, 38.60, 36.01, 34.83, 16.51; HRMS (ESI): *m/z* calculated for $C_{12}H_{18}O_3INa^+$ [M + Na]$^+$ 233.1154, found 233.1161.



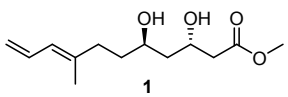
3-*epi*-Ieodomycin B (18). Compound **18** (2.3 mg, 0.011 mmol, 64%) was obtained as colorless oil from acetonide **17b** (5.2 mg, 0.017 mmol) by the same procedure as ieodomycin B **2**. $[\alpha]^{23}_D$ = +24.44 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, CD_3OD) δ 6.59 (dt, *J* = 16.8, 10.5 Hz, 1H), 5.90 (ddd, *J* = 10.9, 2.3, 1.1 Hz, 1H), 5.08 (dd, *J* = 16.8, 2.2 Hz, 1H), 4.97 (dd, *J* = 10.2, 2.2 Hz, 1H), 4.68 (dddd, *J* = 11.2, 7.9, 4.8, 3.2 Hz, 1H), 4.28 – 4.24 (m, 1H), 2.72 (dd, *J* = 17.7, 4.7 Hz, 1H), 2.54 (ddd, *J* = 17.7, 3.3, 1.9 Hz, 1H), 2.28 (ddd, *J* = 14.8, 9.7, 5.5 Hz, 1H), 2.19 (ddd, *J* = 14.2, 9.2, 6.8 Hz, 1H), 1.96 (dddd, *J* = 14.3, 4.0, 3.2, 2.0 Hz, 1H), 1.85 – 1.73 (m, 3H). 1.79 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 173.53, 138.96, 134.41, 127.52, 115.44, 77.28, 63.32, 39.14, 36.36, 35.96, 34.98, 16.54; HRMS (ESI): *m/z* calculated for $C_{12}H_{18}O_3INa^+$ [M + Na]$^+$ 233.1154, found 233.1157.



5-*epi*-Ieodomycin B (19). Compound **19** (25.3 mg, 0.12 mmol, 48%) was obtained as colorless oil from acetonide **17c** (77.8 mg, 0.25 mmol) by the same procedure as ieodomycin B **2**. $[\alpha]^{23}_D$ = -25.93 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, CD_3OD) δ 6.59 (dt, *J* = 16.8, 10.4 Hz, 1H), 5.90 (dd, *J* = 10.9, 1.2 Hz, 1H), 5.08 (dd, *J* = 16.8, 2.1 Hz, 1H), 4.97 (dd, *J* = 10.2, 2.1 Hz, 1H), 4.71 – 4.65 (m, 1H), 4.26 (p, *J* = 3.8 Hz, 1H), 2.72 (dd, *J* = 17.7, 4.7 Hz, 1H), 2.57 – 2.51 (m, 1H), 2.28 (ddd, *J* = 14.8, 9.6, 5.6 Hz, 1H), 2.19 (ddd, *J* = 14.6, 9.2, 6.8 Hz, 1H), 1.96 (dddd, *J* = 14.3, 4.0, 3.2, 1.9 Hz, 1H), 1.85 – 1.73 (m, 3H), 1.79 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 173.54, 138.96, 134.42, 127.52, 115.44, 77.28, 63.32, 39.14, 36.36, 35.96, 34.98, 16.54; HRMS (ESI): *m/z* calculated for $C_{12}H_{18}O_3INa^+$ [M + Na]$^+$ 233.1154, found 233.1156.



3,5-*epi*-Ieodomycin B (20). Compound **20** (16.0 mg, 0.076 mmol, 93%) was obtained as colorless oil from acetonide **17d** (25.4 mg, 0.082 mmol) by the same procedure as ieodomycin B **2**. $[\alpha]^{23}_D$ = -24.81 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, CD_3OD) δ 6.59 (dt, *J* = 16.8, 10.5 Hz, 1H), 5.89 (ddt, *J* = 10.8, 2.4, 1.2 Hz, 1H), 5.08 (dd, *J* = 16.8, 2.1 Hz, 1H), 4.98 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.26 (dddd, *J* = 12.0, 7.7, 4.9, 3.1 Hz, 1H), 4.20 (ddt, *J* = 8.5, 6.9, 5.8 Hz, 1H), 2.86 (ddd, *J* = 16.9, 5.8, 1.2 Hz, 1H), 2.37 (dd, *J* = 16.9, 7.1 Hz, 1H), 2.32 – 2.23 (m, 2H), 2.18 (ddd, *J* = 14.4, 9.1, 6.7 Hz, 1H), 1.87 – 1.72 (m, 2H), 1.78 (s, 3H), 1.52 (ddd, *J* = 13.6, 11.7, 8.6 Hz, 1H); ^{13}C{^{1}H} NMR (151 MHz, CD_3OD) δ 173.93, 138.93, 134.40, 127.50, 115.47, 78.39, 64.26, 40.07, 38.59, 36.00, 34.83, 16.51; HRMS (ESI): *m/z* calculated for $C_{12}H_{18}O_3INa^+$ [M + Na]$^+$ 233.1154, found 233.1160.



Ieodomycin A (1). To a solution of ieodomycin B (**2**) (1.6 mg, 0.008 mmol) in CH_3OH (0.27 mL) was added K_2CO_3(2.8 mg, 0.02 mmol, 2.5 equiv.). After stirring at room temperature for 3 h, the reaction was diluted with EtOAc. The combined organic phase was washed with aq. NH_4Cl and brine, dried over Na_2SO_4. The residue was purified by flash column chromatography (*n*-Hexane/EtOAc = 2/1, v/v) on silica to afford ieodomycin A **1** (1.8 mg, 0.0074 mmol, 93%) as colorless oil. $[\alpha]^{23}_D$ = +17.78 ($CHCl_3$, *c* = 0.9); ^{1}H NMR (600 MHz, CD_3OD) δ 6.58 (dt, *J* = 16.8, 10.5 Hz, 1H), 5.88 (d, *J* = 10.8 Hz, 1H), 5.05 (dd, *J* = 16.8, 2.2 Hz, 1H), 4.95 (dd, *J* = 10.2, 2.2 Hz, 1H), 4.26 (tdd, *J* = 8.5, 4.7, 3.2 Hz, 1H), 3.78 (dddt,

J = 9.9, 7.8, 5.2, 2.2 Hz, 1H), 3.68 (s, 3H), 2.50 (dd, *J* = 15.1, 4.7 Hz, 1H), 2.45 (dd, *J* = 15.1, 8.3 Hz, 1H), 2.21 (ddd, *J* = 15.0, 9.4, 6.6 Hz, 1H), 2.11 (ddd, *J* = 14.3, 9.1, 6.7 Hz, 1H), 1.77 (s, 3H), 1.57 (m, 3H), 1.51 (ddd, *J* = 14.2, 9.4, 3.3 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3OD) δ 173.85, 139.98, 134.58, 126.94, 114.96, 68.72, 66.49, 52.03, 45.25, 43.81, 37.42, 36.89, 16.66; HRMS (ESI): *m/z* calculated for $C_{13}H_{22}O_4INa^+$ $[M + Na]^+$ 265.1416, found 256.1414.

3. Absolute Configuration Assignment

Confirmation of the absolute configuration of homoallylic alcohols 7a and 7b

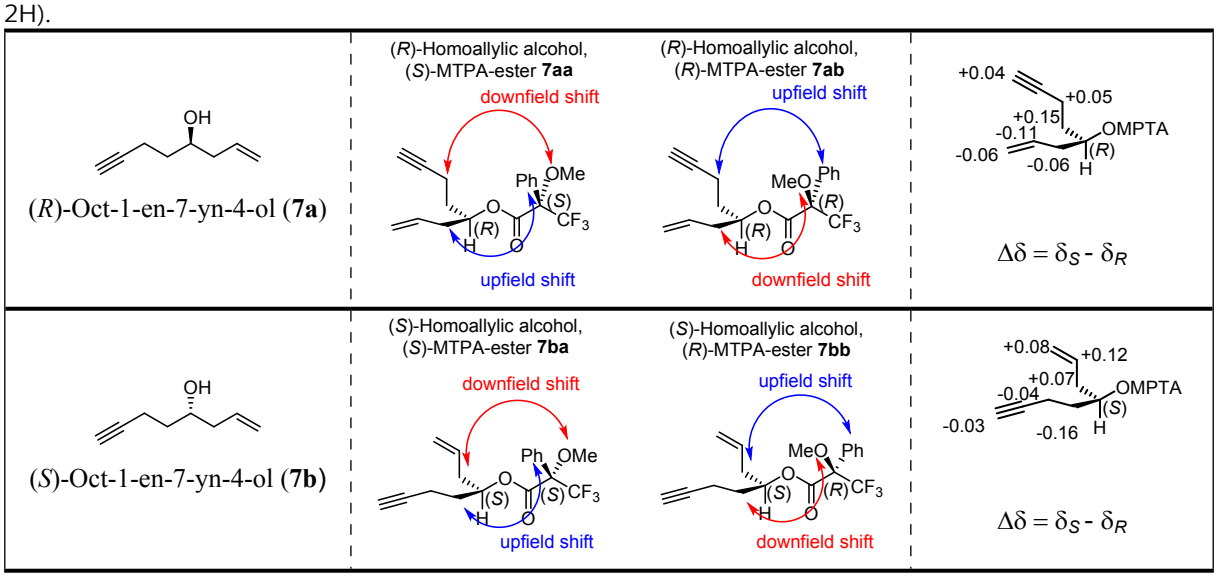
Homoallylic alcohol **7a** was treated with (*R*)-(-)- and (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (MTPA-Cl) in dry pyridine independently to yield (*S*)- and (*R*)-MTPA ester derivatives **7aa** and **7ab**, respectively.[1-2] All of the protons of (*S*)- and (*R*)-MTPA ester derivatives **7aa** and **7ab** were assigned by ^{1}H NMR. The ^{1}H chemical shift values of (*R*)-MTPA ester **7ab** were subtracted from the corresponding values of (*S*)-MTPA ester **7aa**. Negative Δδ values [$\Delta\delta = \delta_S - \delta_R$] for H-1 (-0.06), H-2 (-0.11), H-3 (-0.16) and positive values for H-5 (+0.15), H-6 (+0.05), H-8 (+0.04) confirmed the (*R*)-configuration of the originated H-4 hydroxyl center.[1-2] Similarly, homoallylic alcohol **7b** was converted to corresponding (*S*)- and (*R*)-MTPA ester derivatives **7ba** and **7bb**, respectively. The absolute configuration of the H-4 hydroxyl center of homoallylic alcohol **7b** was confirmed as (*S*)-configuration by the same method described above [positive Δδ values for H-1 (+0.08), H-2 (+0.12), H-3 (+0.07) and negative values for H-5 (-0.16), H-6 (-0.04), H-8 (-0.03)].

(*S*)-MTPA ester (7aa). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.44 – 7.37 (m, 3H), 5.65 (ddt, *J* = 17.0, 9.7, 7.1 Hz, 1H), 5.28 (dq, *J* = 8.2, 5.6 Hz, 1H), 5.07 (d, *J* = 4.3 Hz, 1H), 5.04 (s, 1H), 3.54 (s, 3H), 2.41 (t, *J* = 6.6 Hz, 2H), 2.29 – 2.15 (m, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.87 (qd, *J* = 8.0, 5.5 Hz, 2H).

(*R*)-MTPA ester (7ab). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 2H), 7.40 (dd, *J* = 5.1, 1.9 Hz, 3H), 5.82 – 5.71 (m, 1H), 5.34 – 5.27 (m, 1H), 5.14 (d, *J* = 5.5 Hz, 1H), 5.11 (s, 1H), 3.57 (s, 3H), 2.47 (t, *J* = 6.7 Hz, 2H), 2.12 (dtd, *J* = 15.6, 6.5, 2.1 Hz, 1H), 2.01 (td, *J* = 7.9, 2.6 Hz, 1H), 1.98 – 1.95 (m, 1H), 1.82 (q, *J* = 8.5, 7.7 Hz, 2H).

(*S*)-MTPA ester (7ba). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 2H), 7.40 (qd, *J* = 4.5, 2.2 Hz, 3H), 5.81 – 5.73 (m, 1H), 5.31 (pd, *J* = 5.9, 1.6 Hz, 1H), 5.14 (dt, *J* = 6.7, 1.5 Hz, 1H), 5.13 – 5.10 (m, 1H), 3.57 (t, *J* = 1.6 Hz, 3H), 2.50 – 2.45 (m, 2H), 2.16 – 2.08 (m, 1H), 2.03 – 1.98 (m, 1H), 1.97 (d, J = 2.3 Hz, 1H), 1.82 (dtd, *J* = 10.9, 6.2, 5.4, 2.3 Hz, 2H).

(*R*)-MTPA ester (7bb). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.43 – 7.39 (m, 3H), 5.69 – 5.61 (m, 1H), 5.27 (dtd, *J* = 8.3, 5.8, 4.6 Hz, 1H), 5.08 – 5.05 (m, 1H), 5.05 – 5.02 (m, 1H), 3.54 (q, *J* = 1.3 Hz, 3H), 2.41 (ddq, *J* = 7.1, 4.6, 1.3 Hz, 2H), 2.29 – 2.16 (m, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.92 – 1.81 (m, 2H).



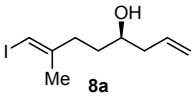
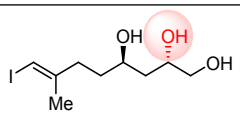
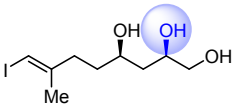
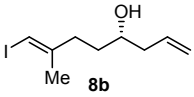
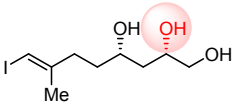
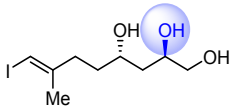
δ_S: (*S*)-MTPA-ester, δ_R: (*R*)-MTPA-ester

1. T. R. Hoye, C. S. Jeffrey and F. Shao, *Nat. Protoc.* 2007, **2**, 2451-2458.

2. J. M. Seco, E. Quiñoa and R. Riguera, *Chem. Rev.* 2004, **104**, 17-118.

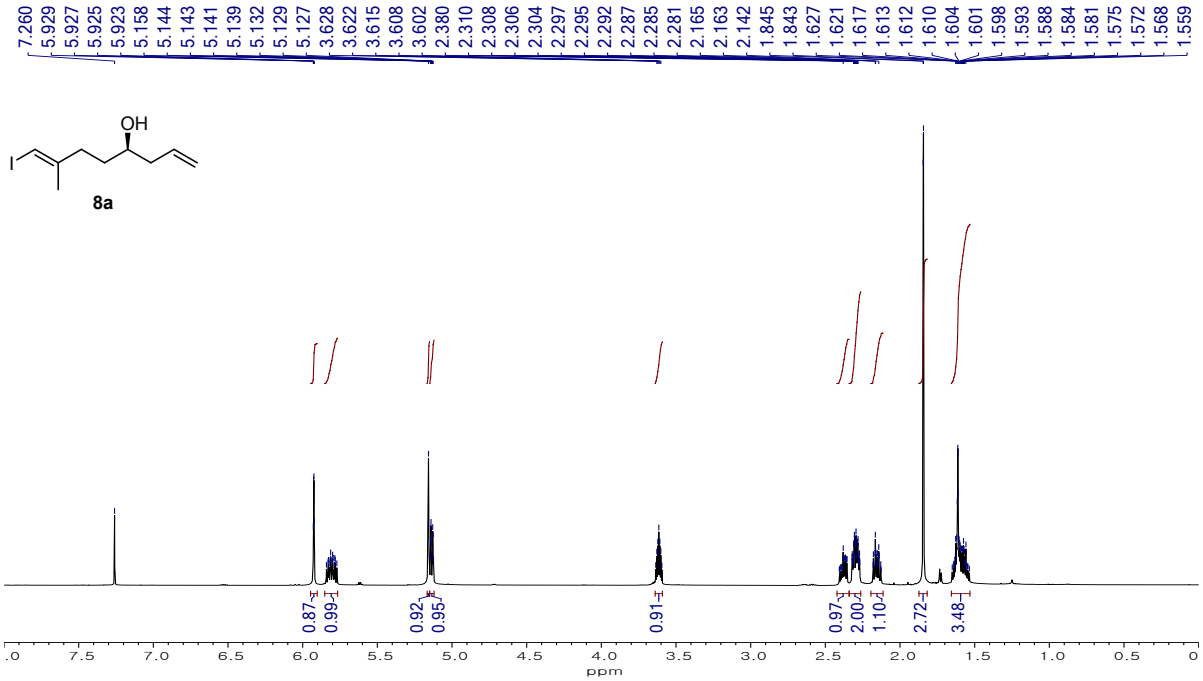
4. Diastereomeric Ratio

Table S1 Diastereomeric Ratio After Dihydroxylation by Ligands of Homoallylic Alcohols **8a** and **8b**.

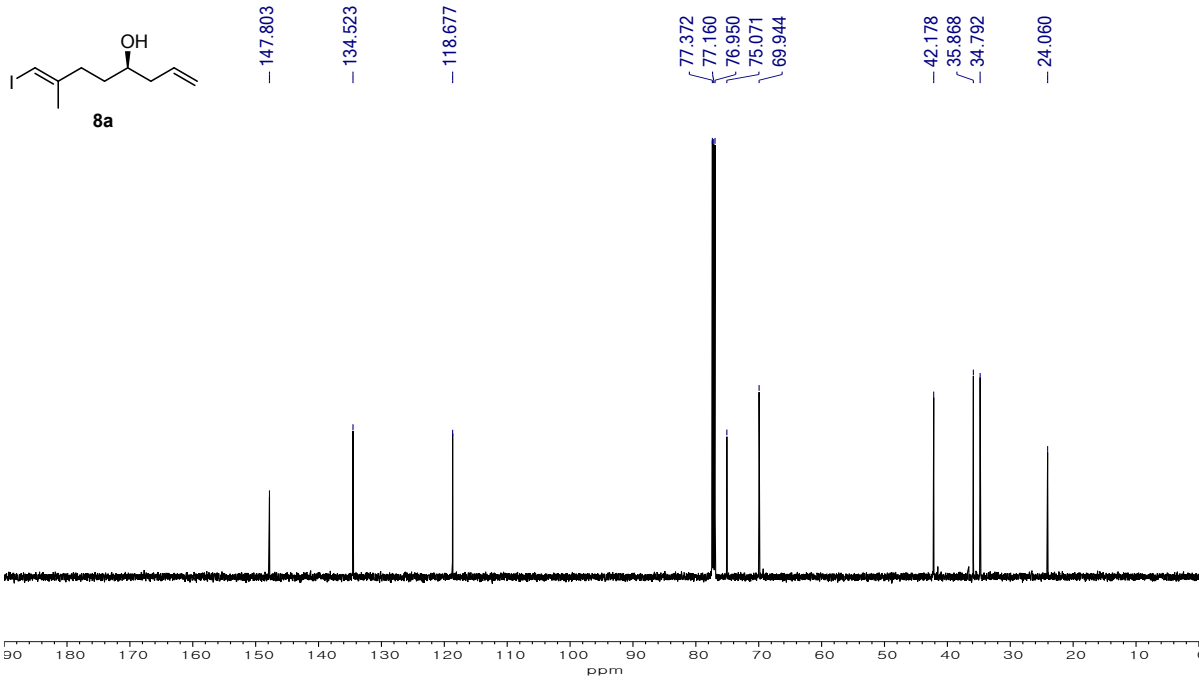
Entry	Olefins	Ligands	Crude ratio	Products
1	 **8a**	$(DHQ)_2PHAL$	**9a** : **9b** = 1.4 : 1	 **9a**, 52%, *dr* = 2.6 : 1
2		**$(DHQ)_2PYR$**	**9a** : **9b** = 2.6 : 1	
3		$(DHQ)_2AQN$	**9a** : **9b** = 1 : 1	
4		$(DHQD)_2PHAL$	**9a** : **9b** = 1 : 1	 **9b**, 71%, *dr* = 14.2 : 1
5		**$(DHQD)_2PYR$**	**9a** : **9b** = 1 : 14.9	
6		$(DHQD)_2AQN$	**9a** : **9b** = 1 : 1	
7	 **8b**	$(DHQ)_2PHAL$	**9c** : **9d** = 1.1 : 1	 **9c**, 65%, *dr* = 8.1 : 1
8		**$(DHQ)_2PYR$**	**9c** : **9d** = 6.3 : 1	
9		$(DHQ)_2AQN$	**9c** : **9d** = 1.2 : 1	
10		**$(DHQD)_2PYR$**	**9c** : **9d** = 1 : 5	 **9d**, 66%, *dr* = 5.1 : 1

The reactions were carried out with 0.01 equiv. of the ligand, 3 equiv. of $K_3Fe(CN)_6$, 3 equiv. of K_2CO_3, 0.005 equiv. of $K_2OsO_4 \cdot 2H_2O$ in *t*-BuOH/H_2O (1:1)

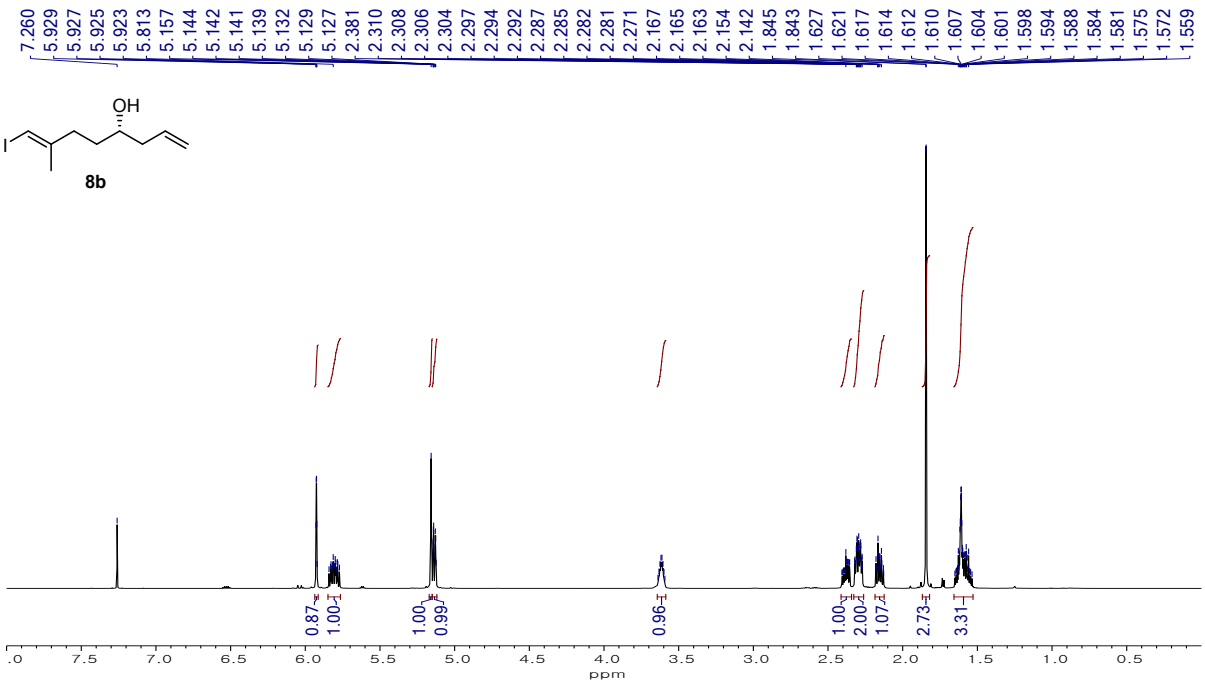
5. ^{1}H and ^{13}C NMR Spectra of Compounds



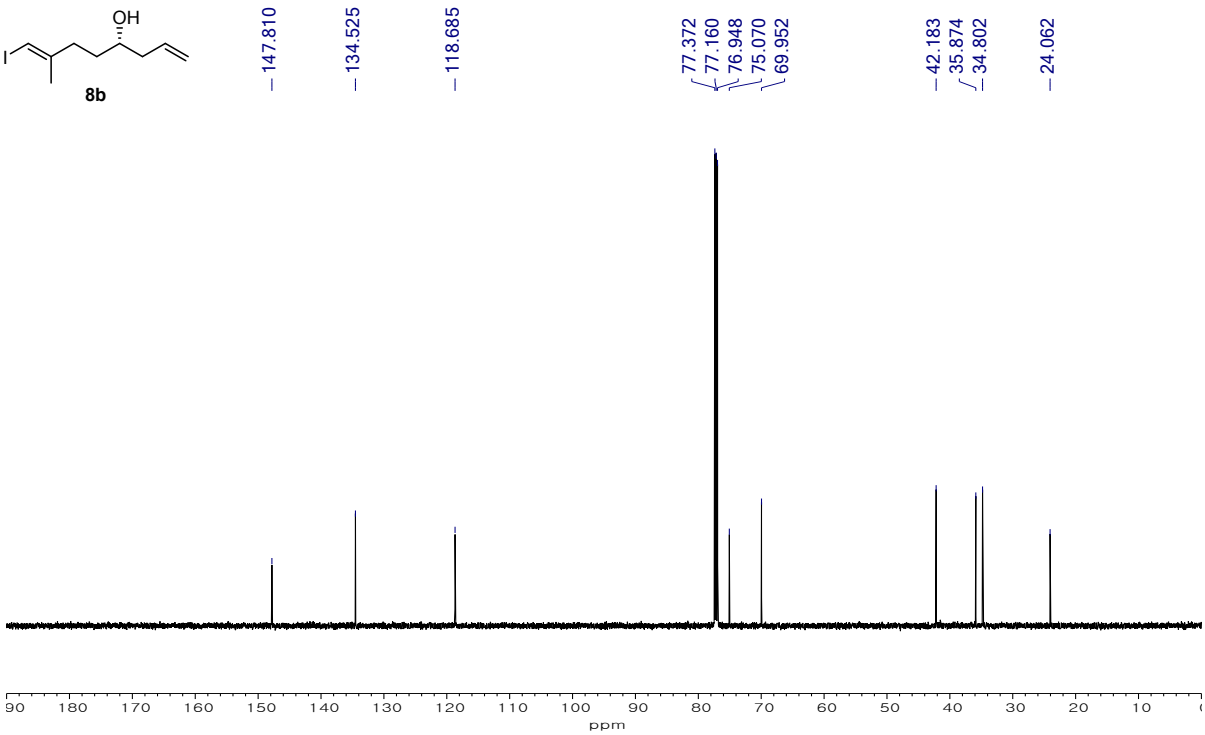
^{1}H NMR Spectrum of (*R,E*)-8-Iodo-7-methylocta-1,7-dien-4-ol (**8a**) in $CDCl_3$



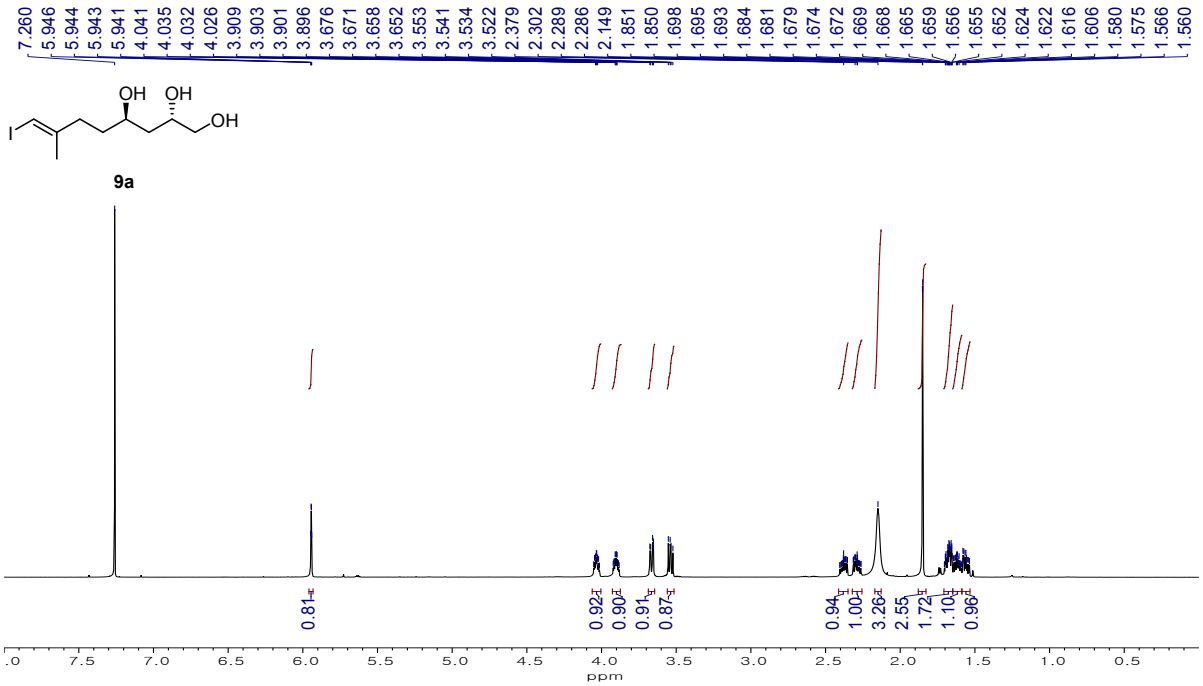
^{13}C NMR Spectrum of (*R,E*)-8-Iodo-7-methylocta-1,7-dien-4-ol (**8a**) in $CDCl_3$



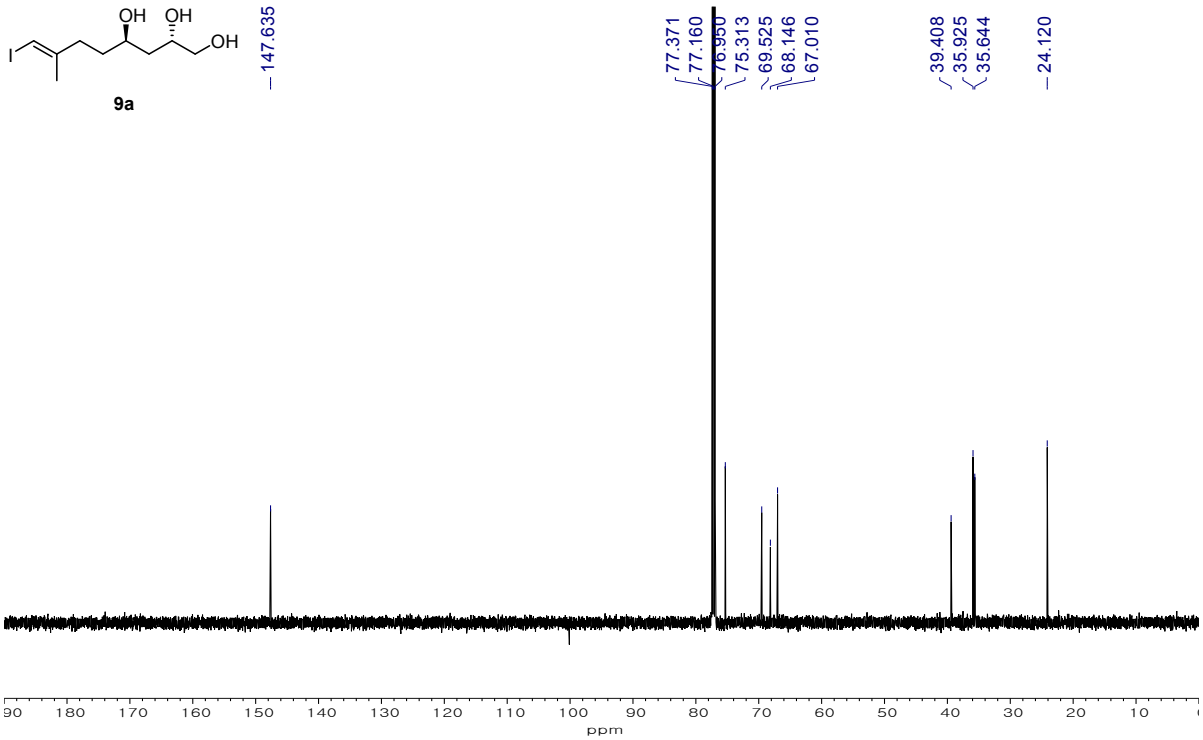
^{1}H NMR Spectrum of (*S,E*)-8-Iodo-7-methylocta-1,7-dien-4-ol (**8b**) in $CDCl_3$



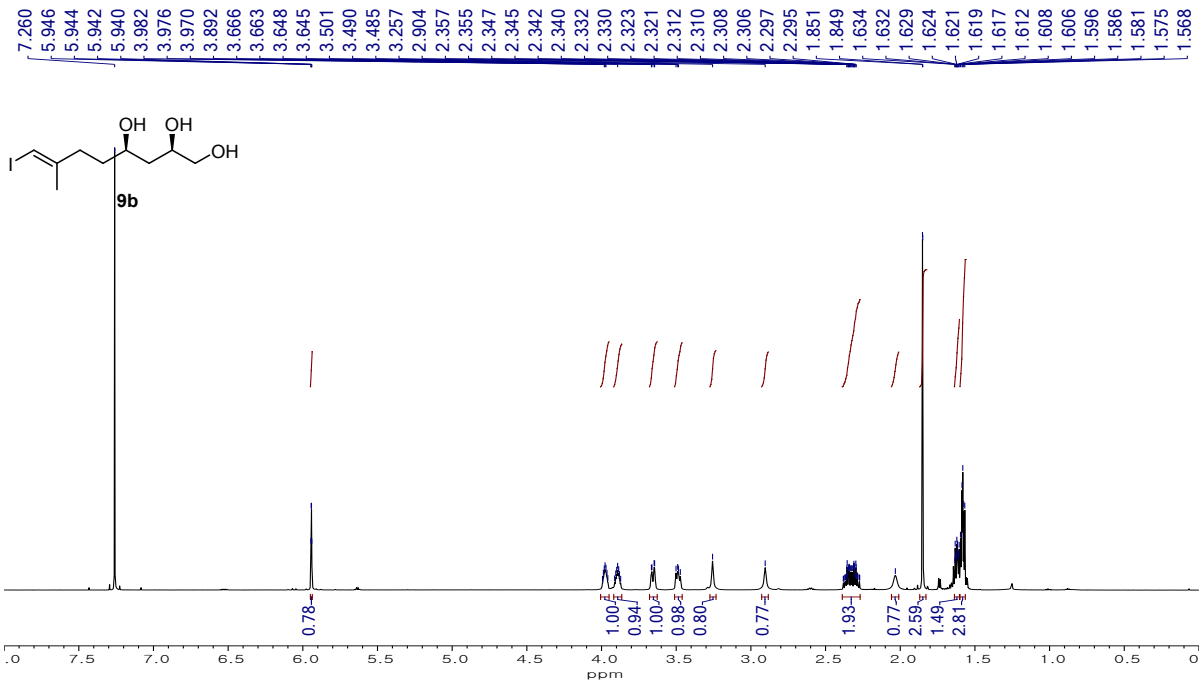
^{13}C NMR Spectrum of (*S,E*)-8-Iodo-7-methylocta-1,7-dien-4-ol (**8b**) in $CDCl_3$



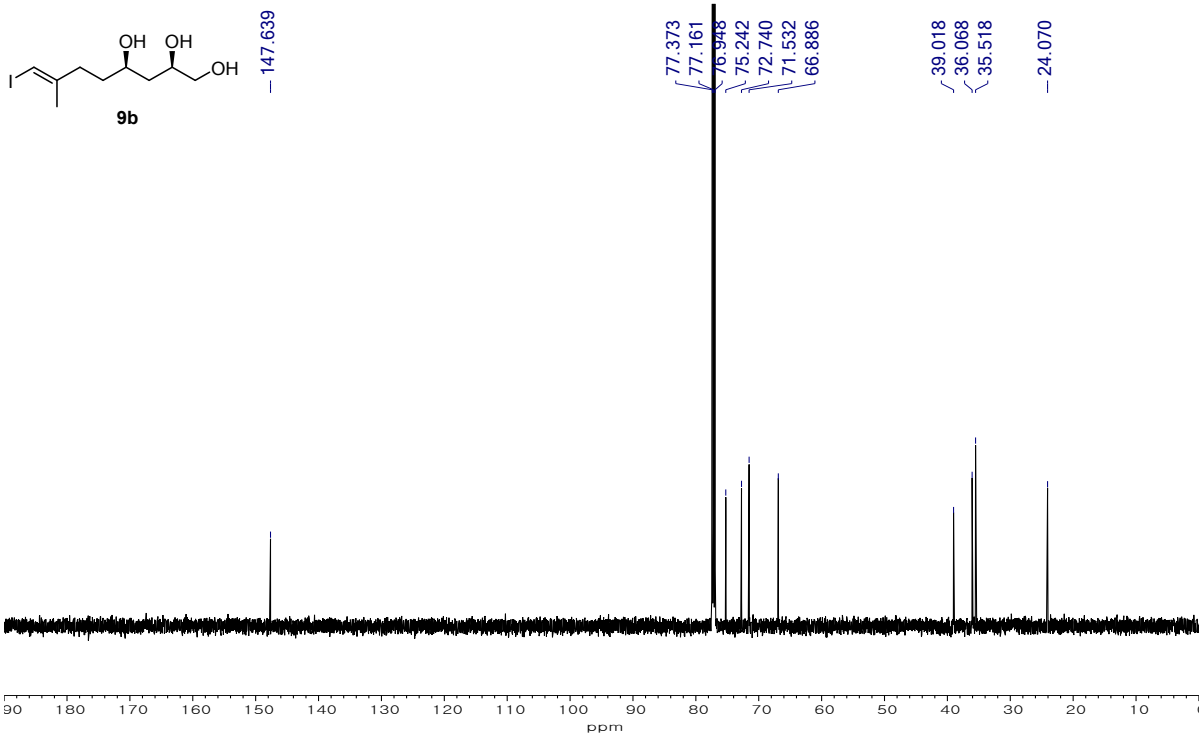
^{1}H NMR Spectrum of (2*S*,4*R*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9a**) in $CDCl_3$



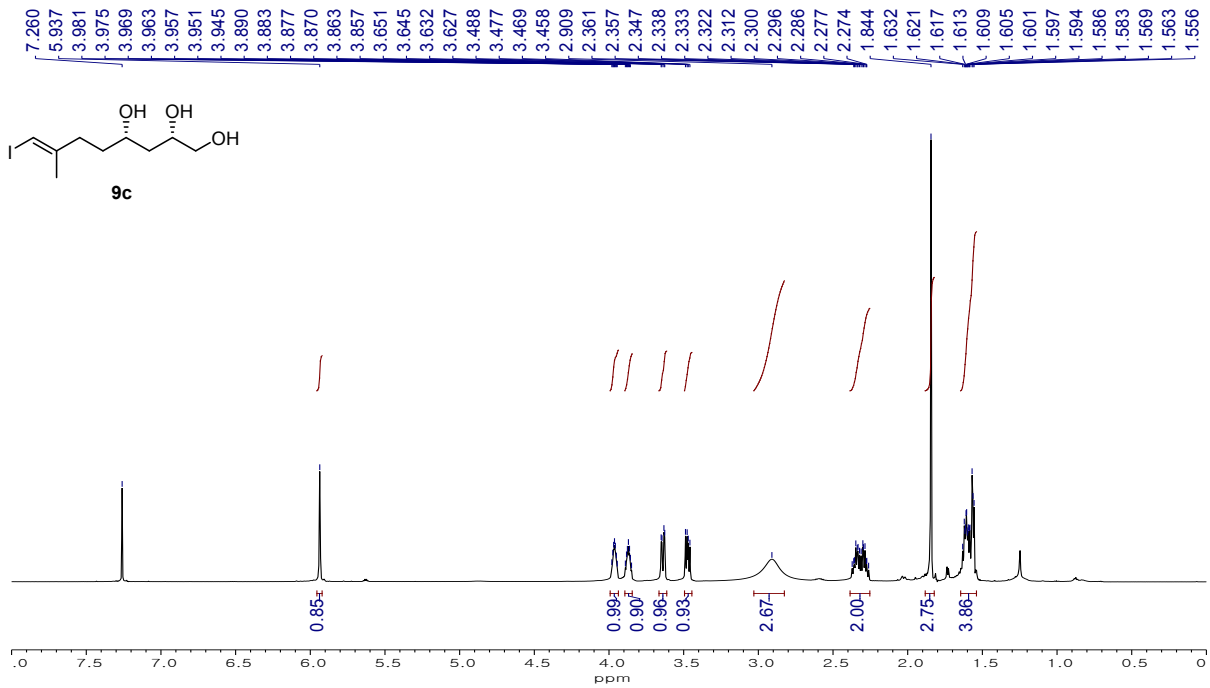
^{13}C NMR Spectrum of (2*S*,4*R*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9a**) in $CDCl_3$



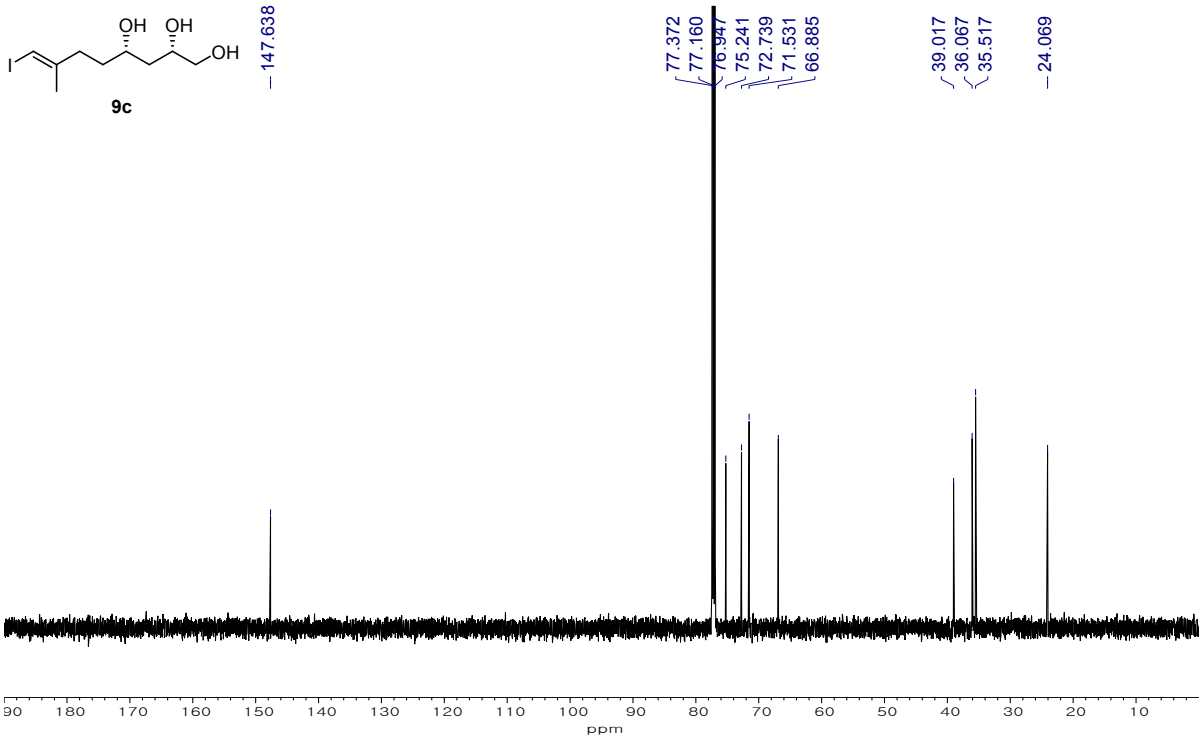
^{1}H NMR Spectrum of (2*R*,4*R*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9b**) in $CDCl_3$



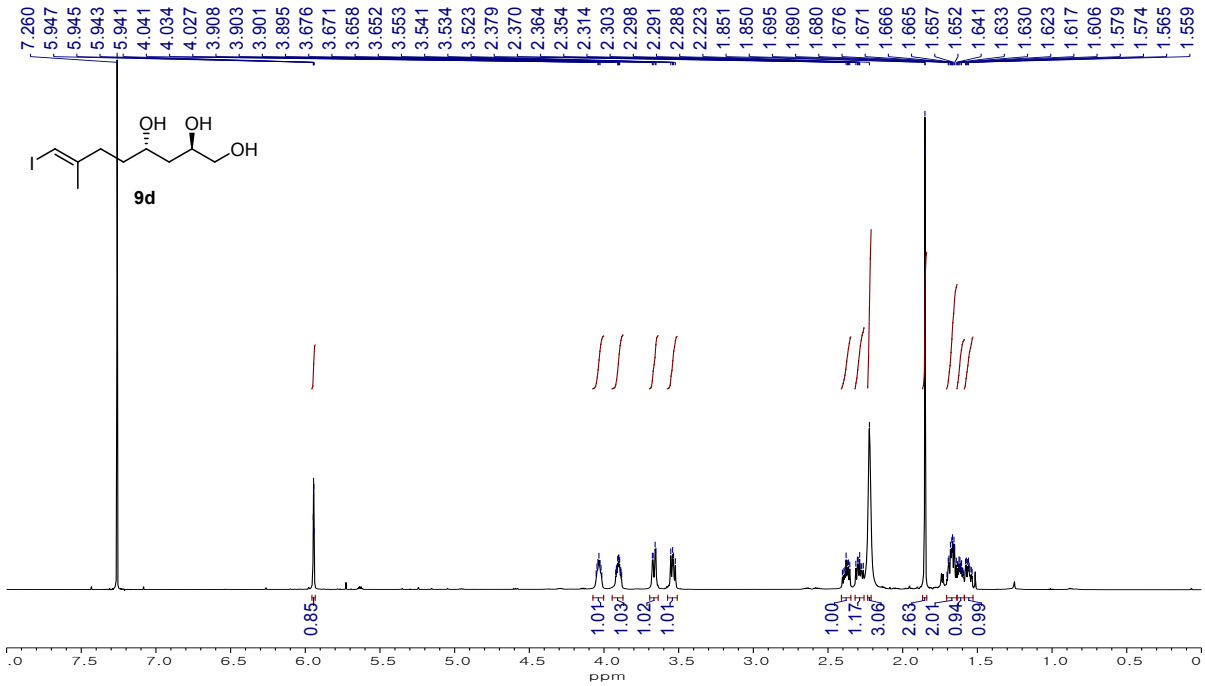
^{13}C NMR Spectrum of (2*R*,4*R*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9b**) in $CDCl_3$



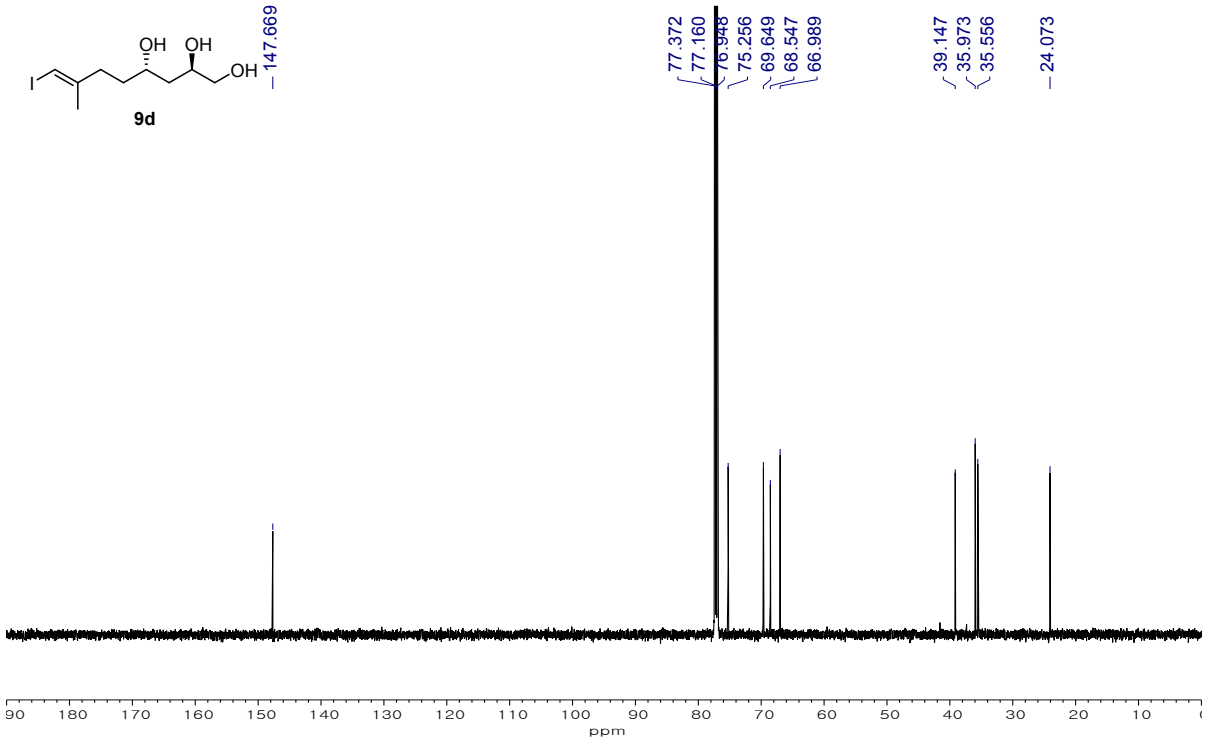
^{1}H NMR Spectrum of (2*S*,4*S*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9c**) in $CDCl_3$



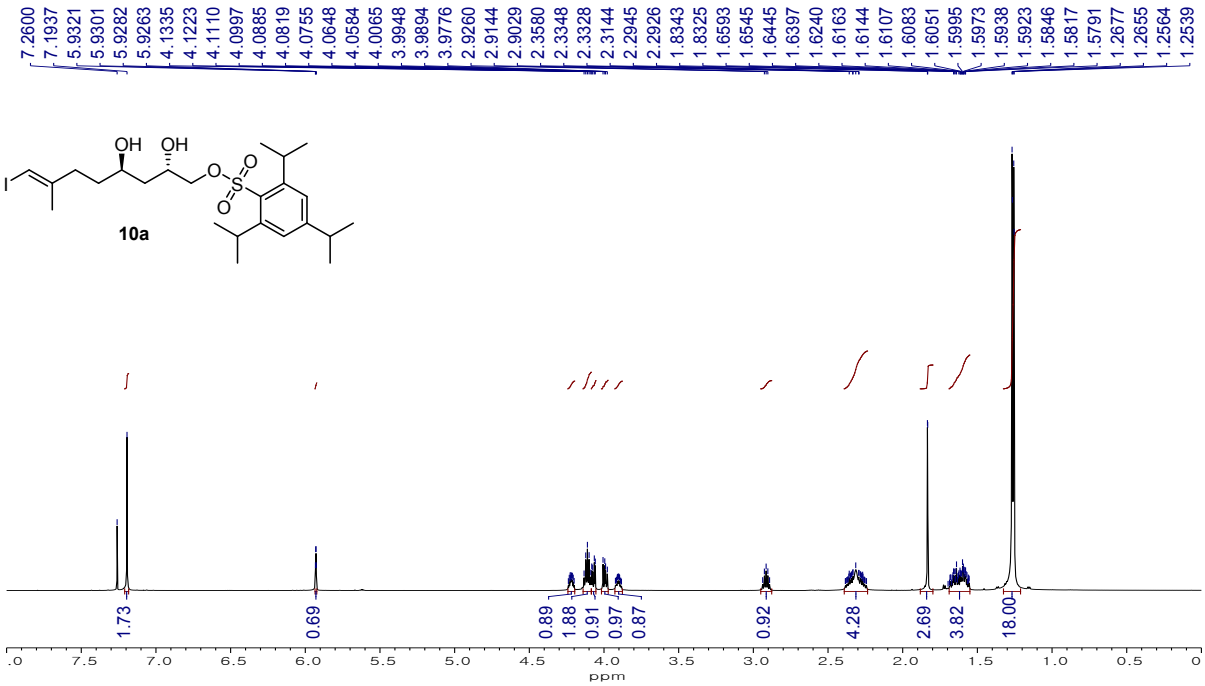
^{13}C NMR Spectrum of (2*S*,4*S*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9c**) in $CDCl_3$



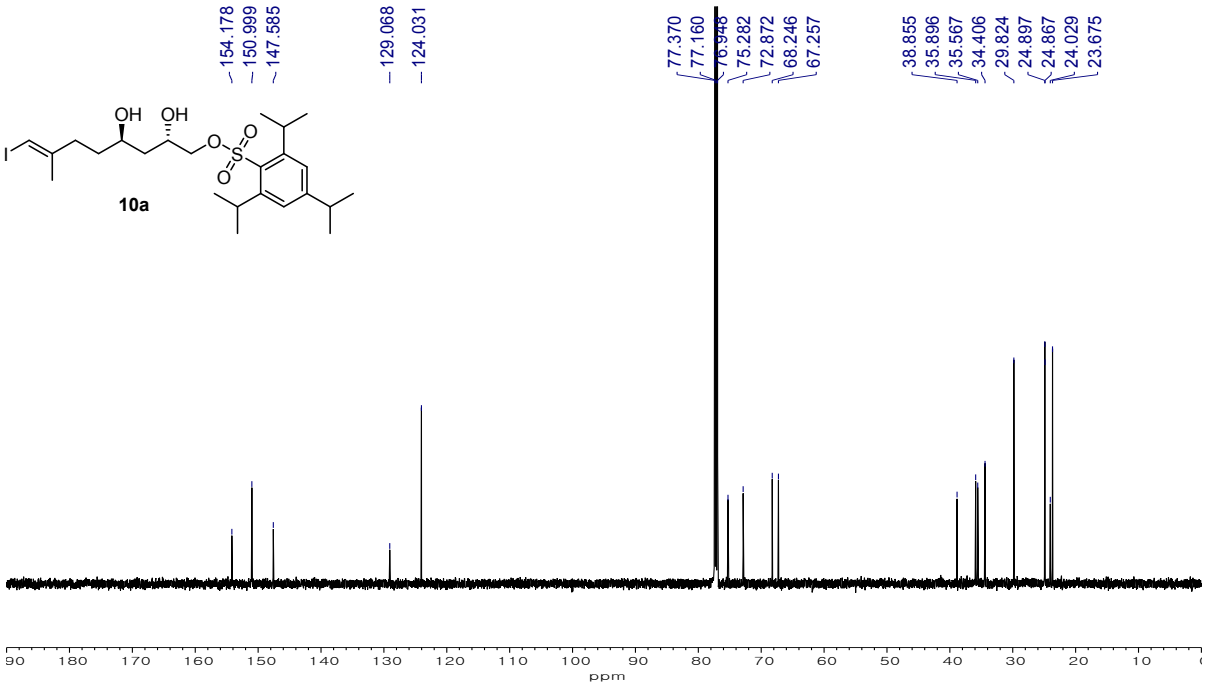
^{1}H NMR Spectrum of (2R,4S,E)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9d**) in $CDCl_3$



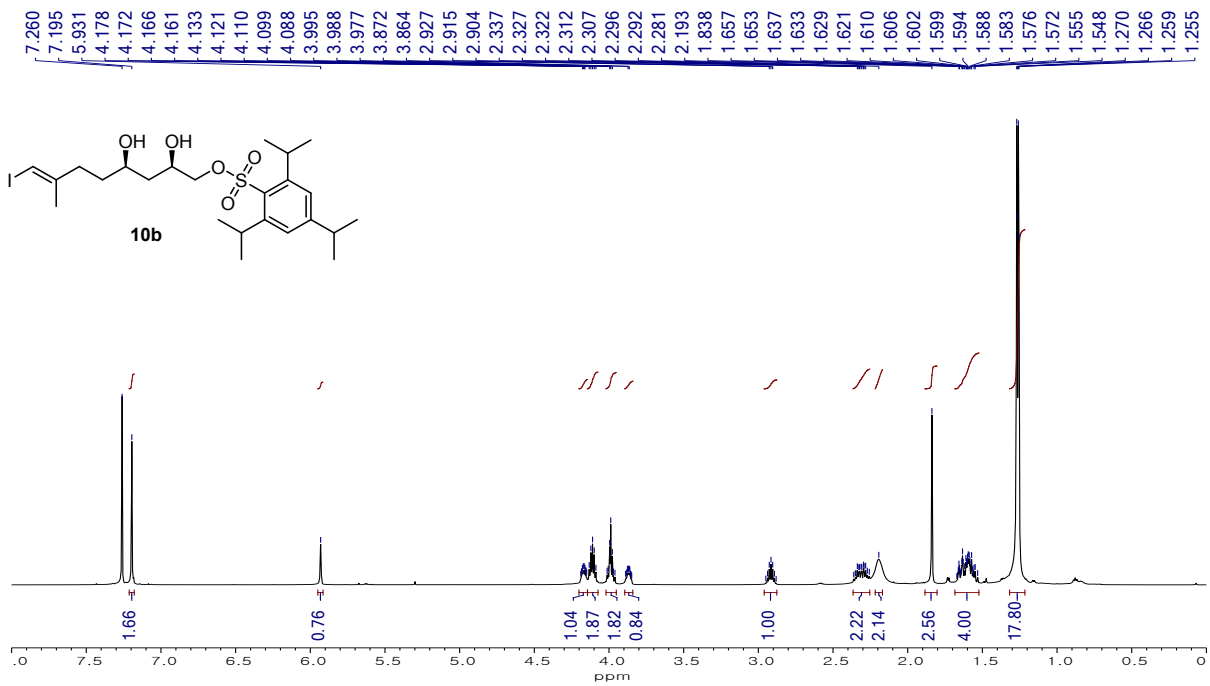
^{13}C NMR Spectrum of (2*R*,4*S*,*E*)-8-Iodo-7-methyloct-7-ene-1,2,4-triol (**9d**) in $CDCl_3$



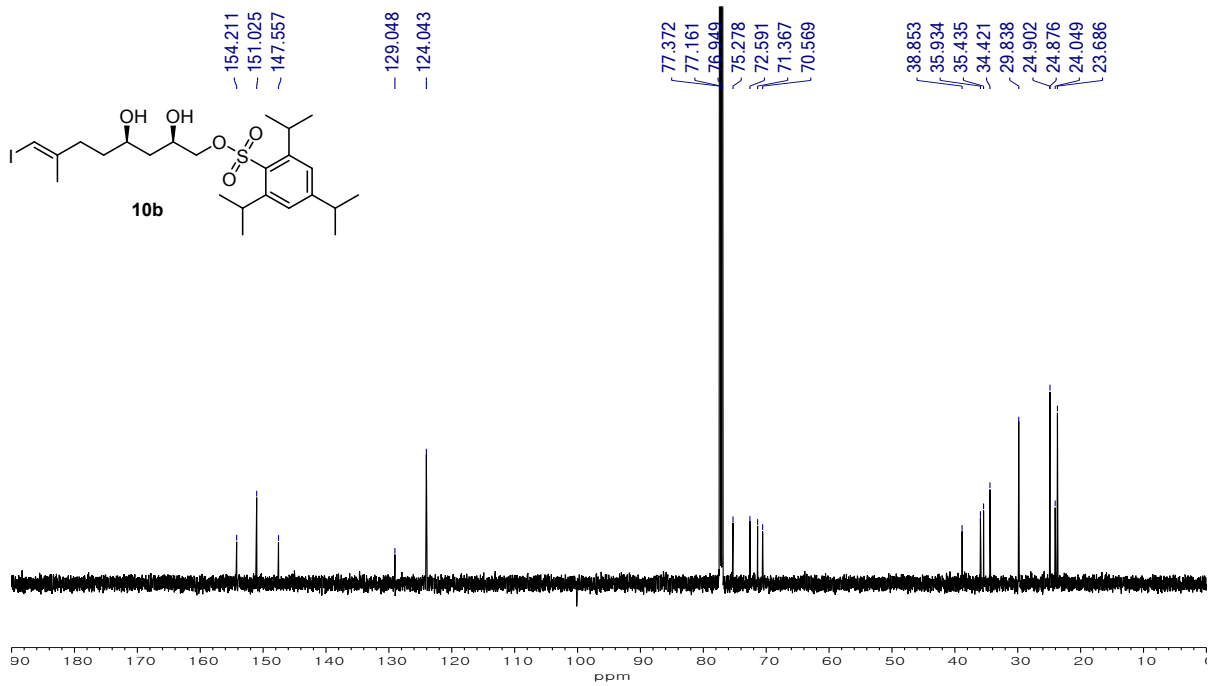
^{1}H NMR Spectrum of (2*S*,4*R*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10a**) in $CDCl_3$



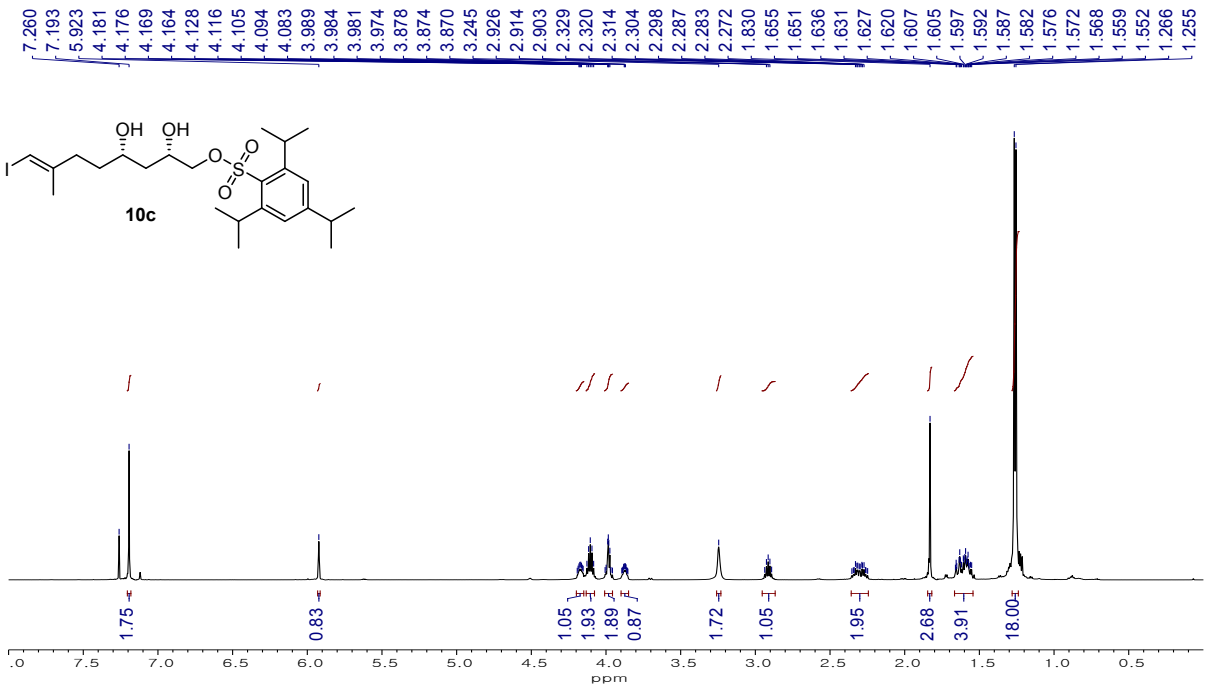
^{13}C NMR Spectrum of (2*S*,4*R*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10a**) in $CDCl_3$



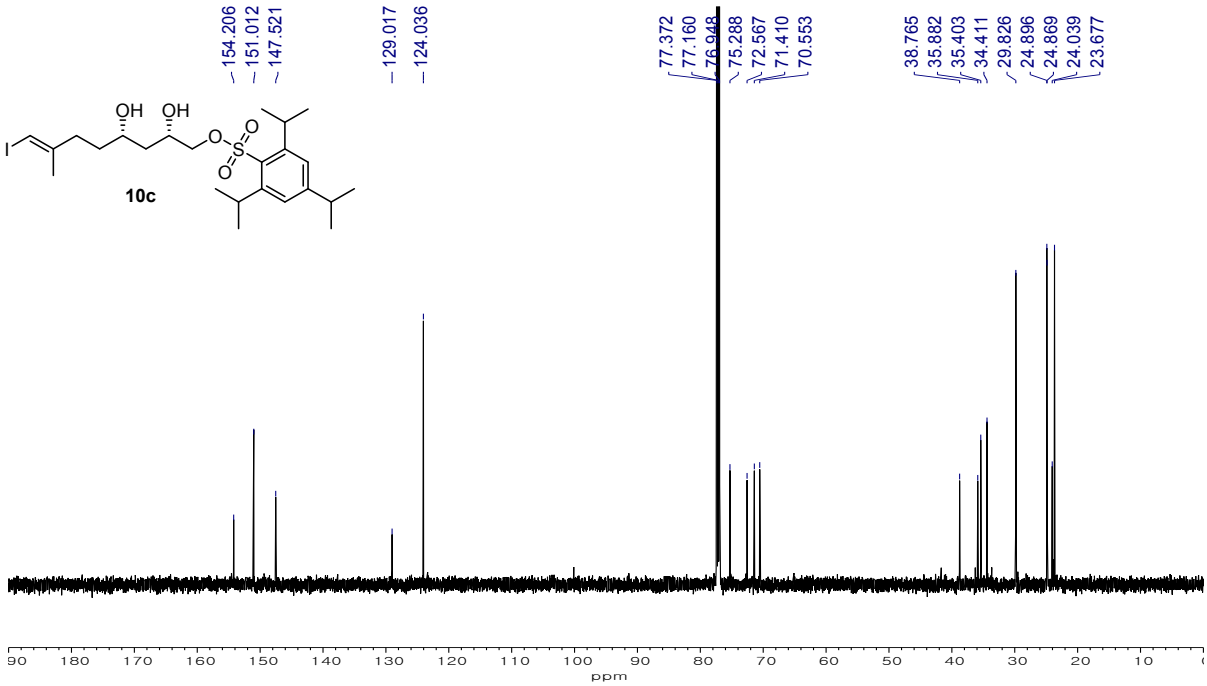
^{1}H NMR Spectrum of (2*R*,4*R*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10b**) in $CDCl_3$



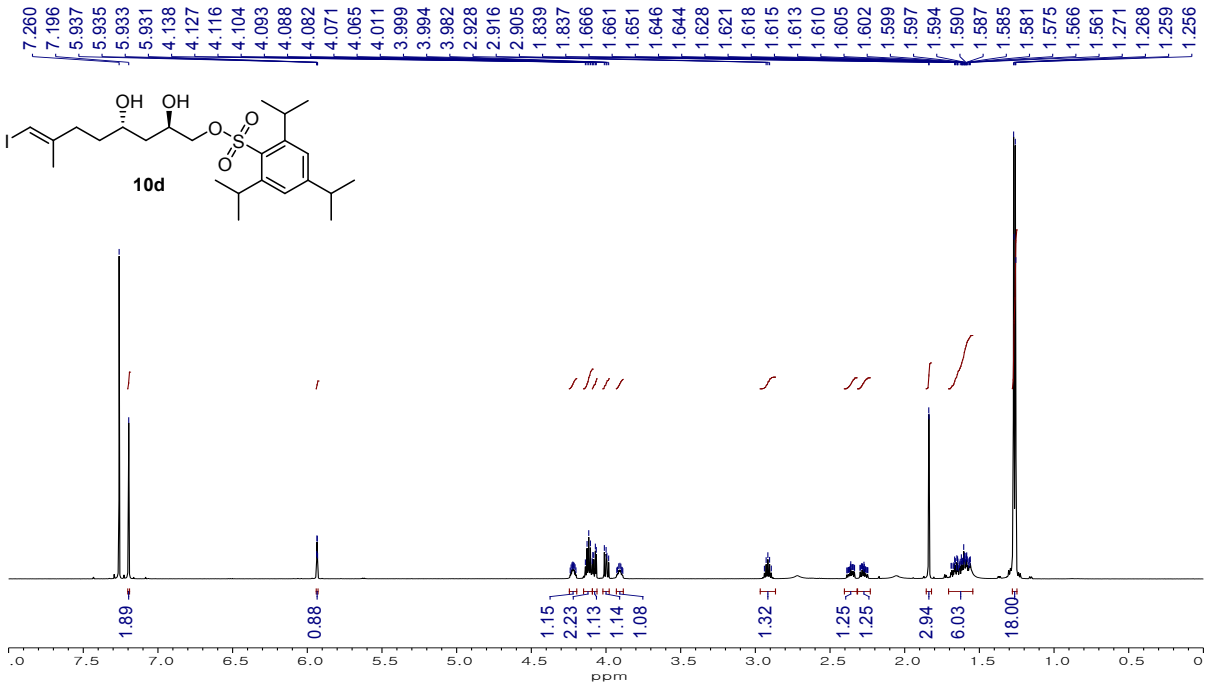
^{13}C NMR Spectrum of (2*R*,4*R*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10b**) in $CDCl_3$



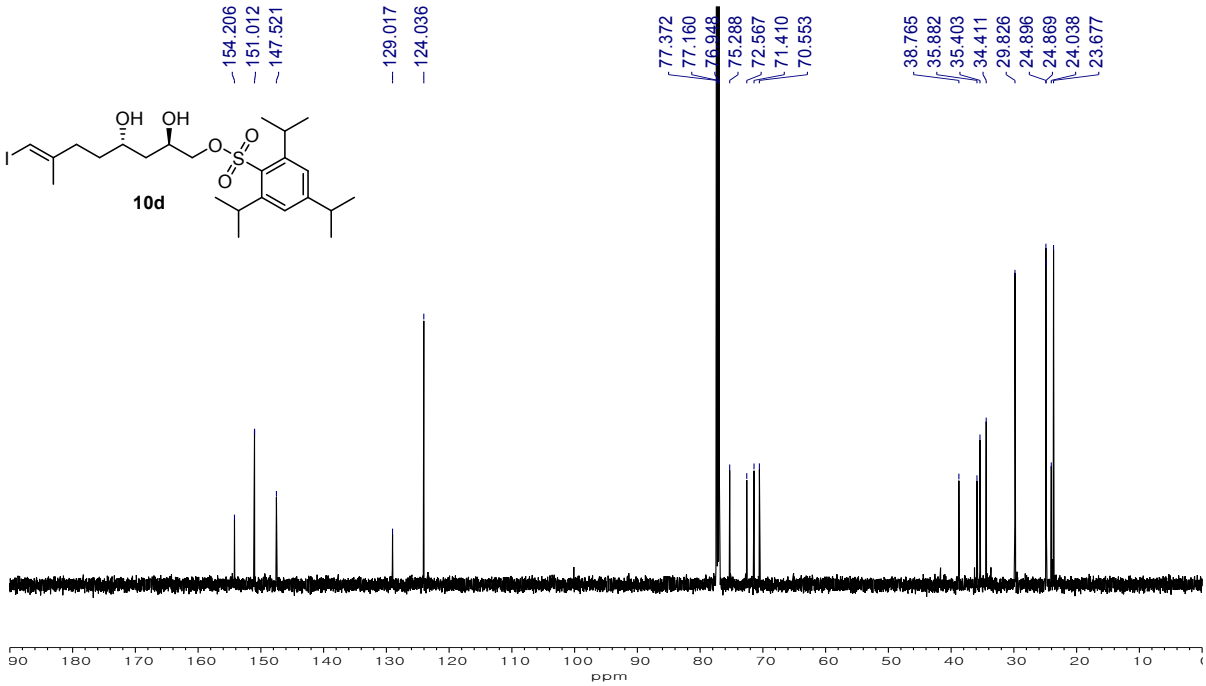
^{1}H NMR Spectrum of (2*S*,4*S*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10c**) in $CDCl_3$



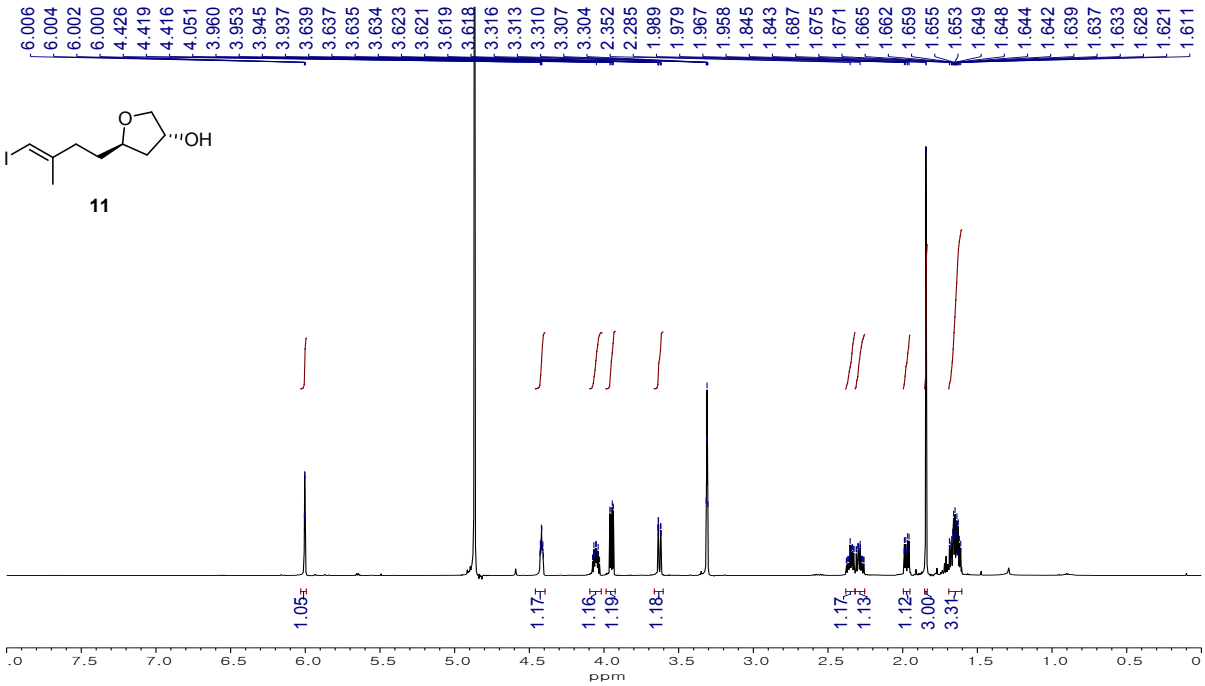
^{13}C NMR Spectrum of (2*S*,4*S*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10c**) in $CDCl_3$



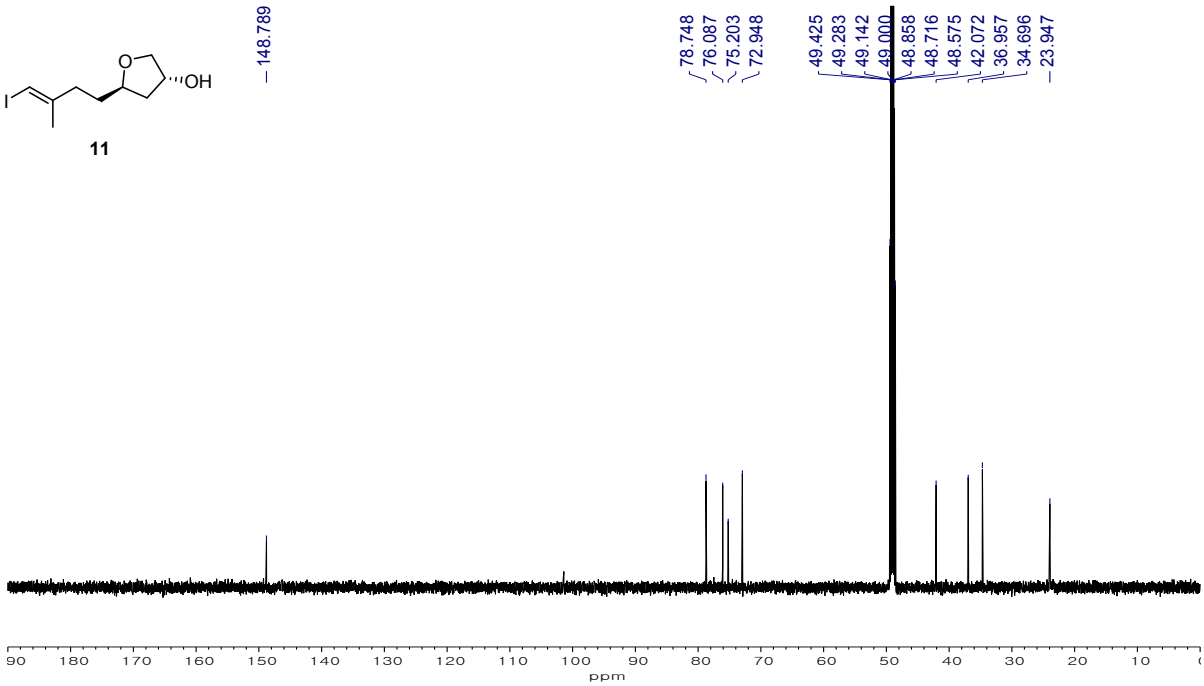
^{1}H NMR Spectrum of (2*R*,4*S*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10d**) in $CDCl_3$



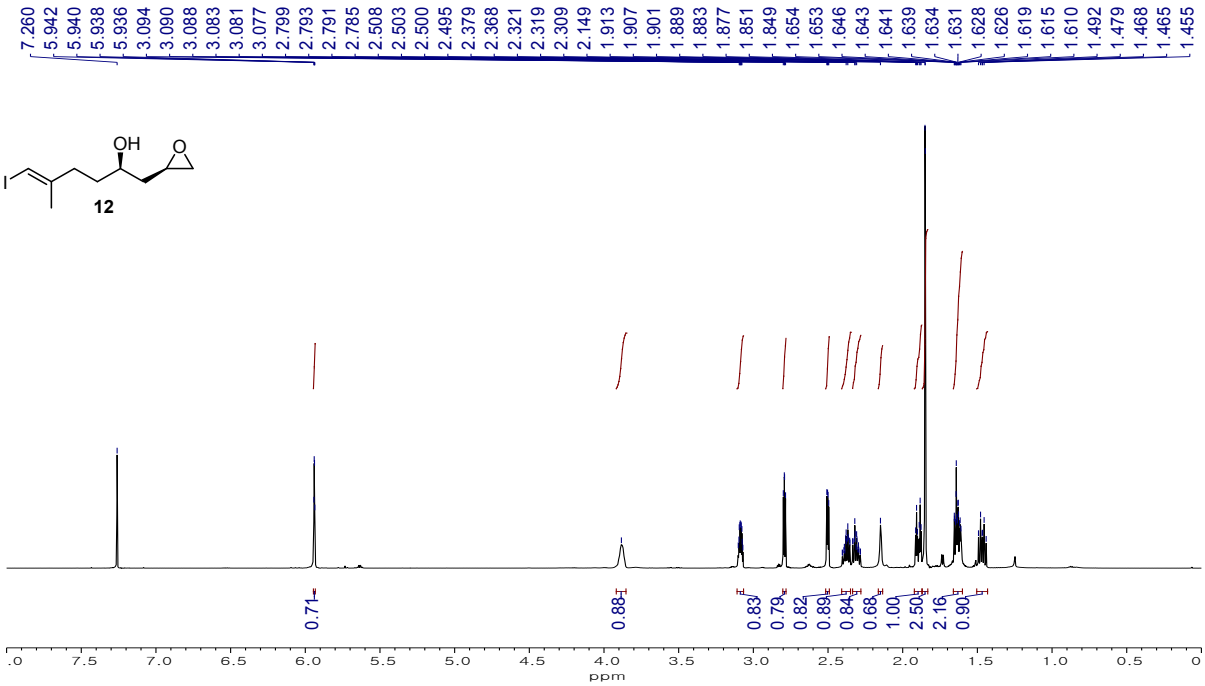
^{13}C NMR Spectrum of (2*R*,4*S*,*E*)-2,4-Dihydroxy-8-iodo-7-methyloct-7-en-1-yl 2,4,6-triisopropylbenzenesulfonate (**10d**) in $CDCl_3$



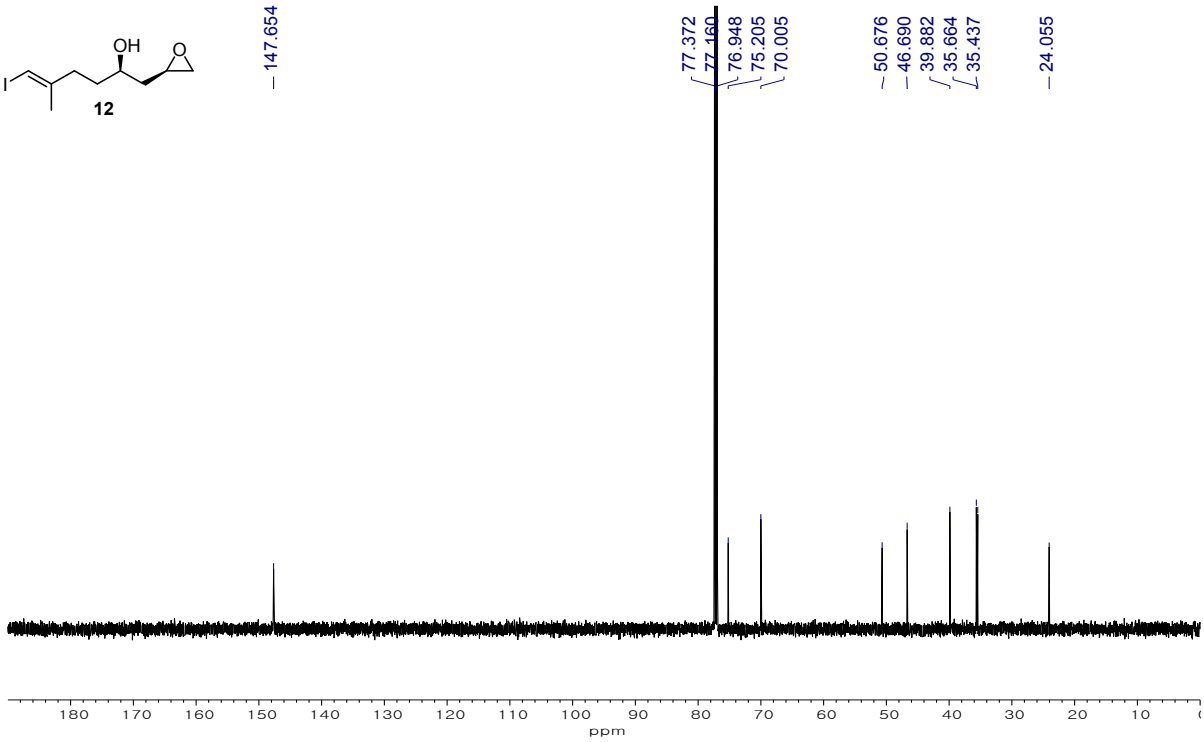
^{1}H NMR Spectrum of (3*R*,5*R*)-5-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)tetrahydrofuran-3-ol (**11**) in $CDCl_3$



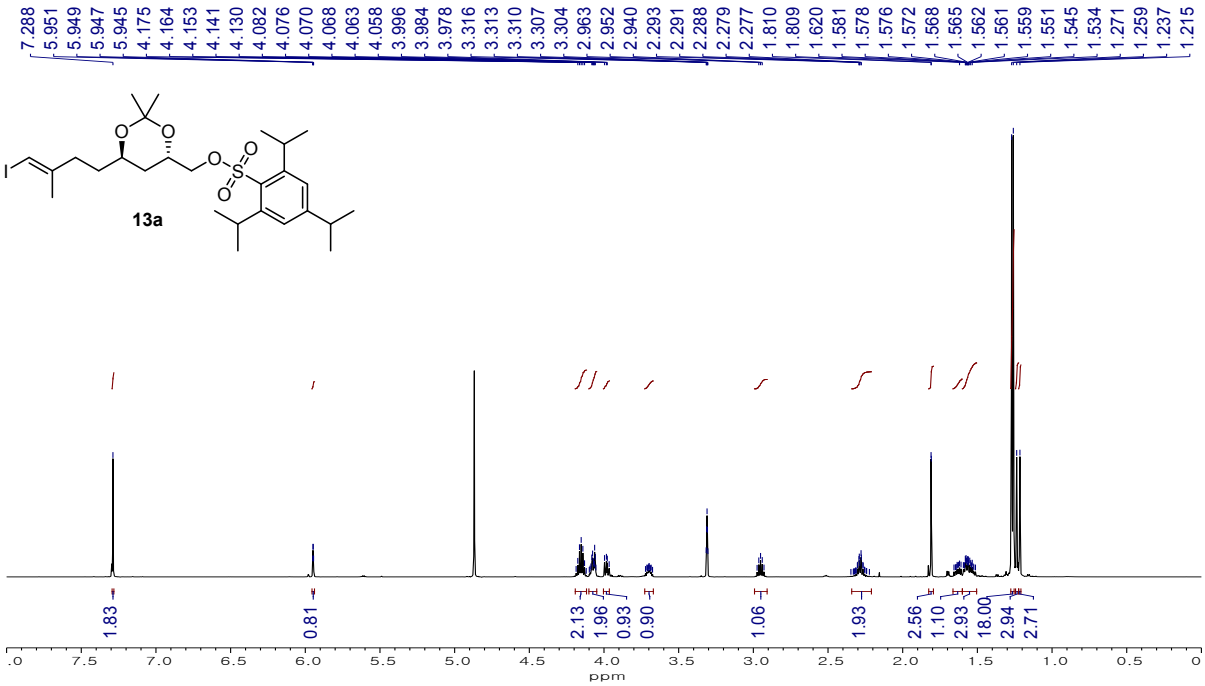
^{13}C NMR Spectrum of (3*R*,5*R*)-5-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)tetrahydrofuran-3-ol (**11**) in $CDCl_3$



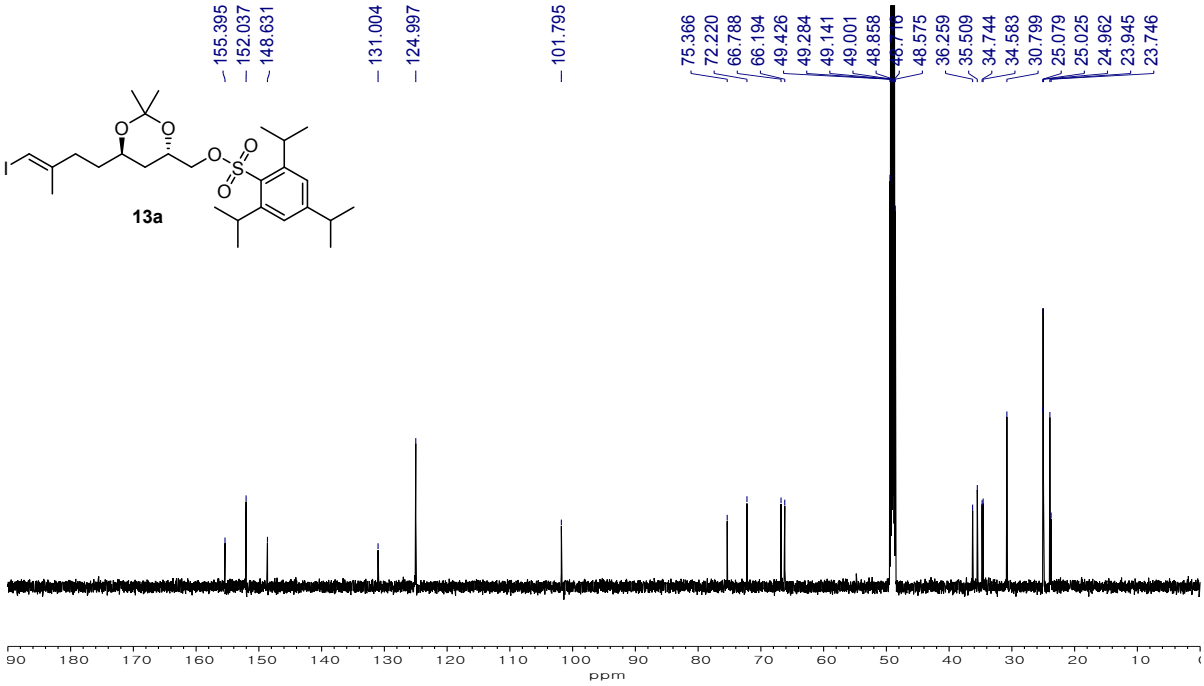
^{1}H NMR Spectrum of (*R,E*)-6-Iodo-5-methyl-1-((*R*)-oxiran-2-yl)hex-5-en-2-ol (**12**) in $CDCl_3$



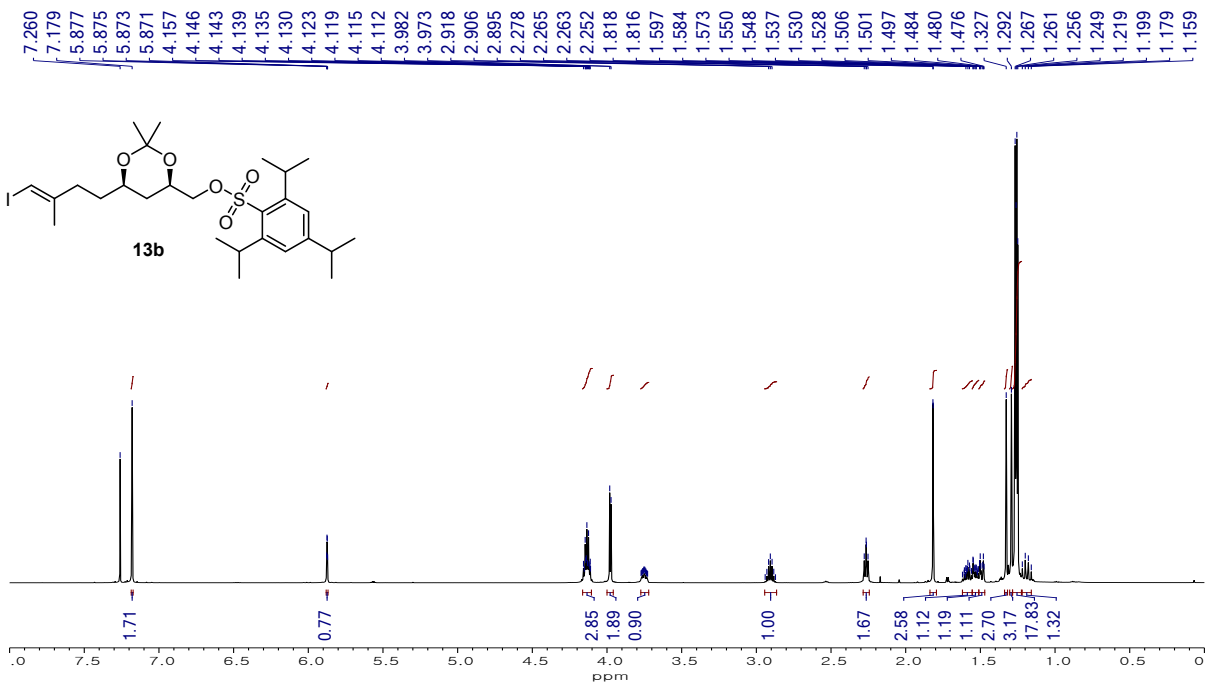
^{13}C NMR Spectrum of (*R,E*)-6-Iodo-5-methyl-1-((*R*)-oxiran-2-yl)hex-5-en-2-ol (**12**) in $CDCl_3$



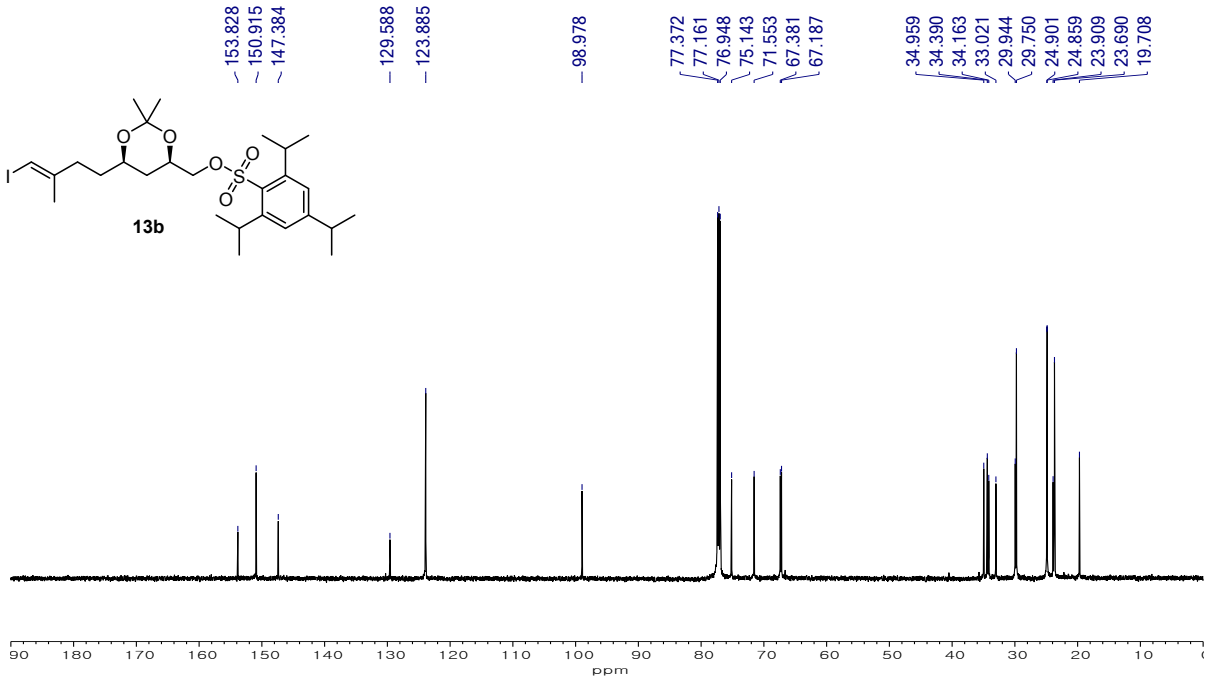
^{1}H NMR Spectrum of ((4*S*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13a**) in CD_3OD



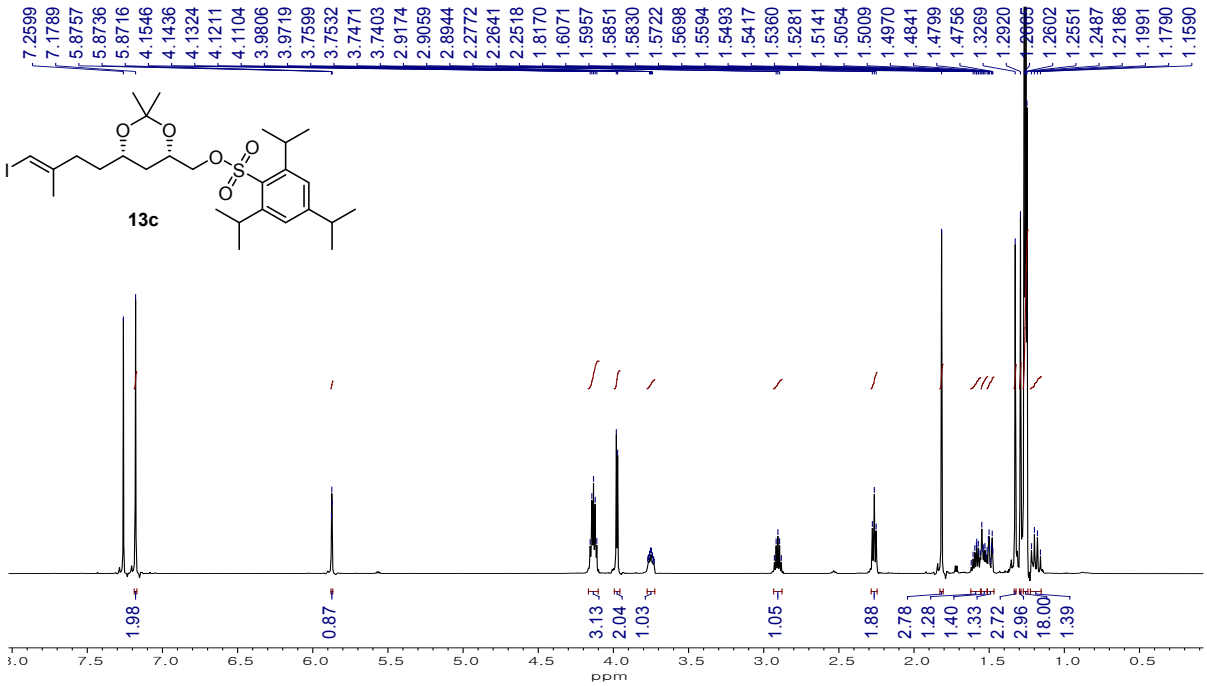
^{13}C NMR Spectrum of ((4*S*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13a**) in CD_3OD



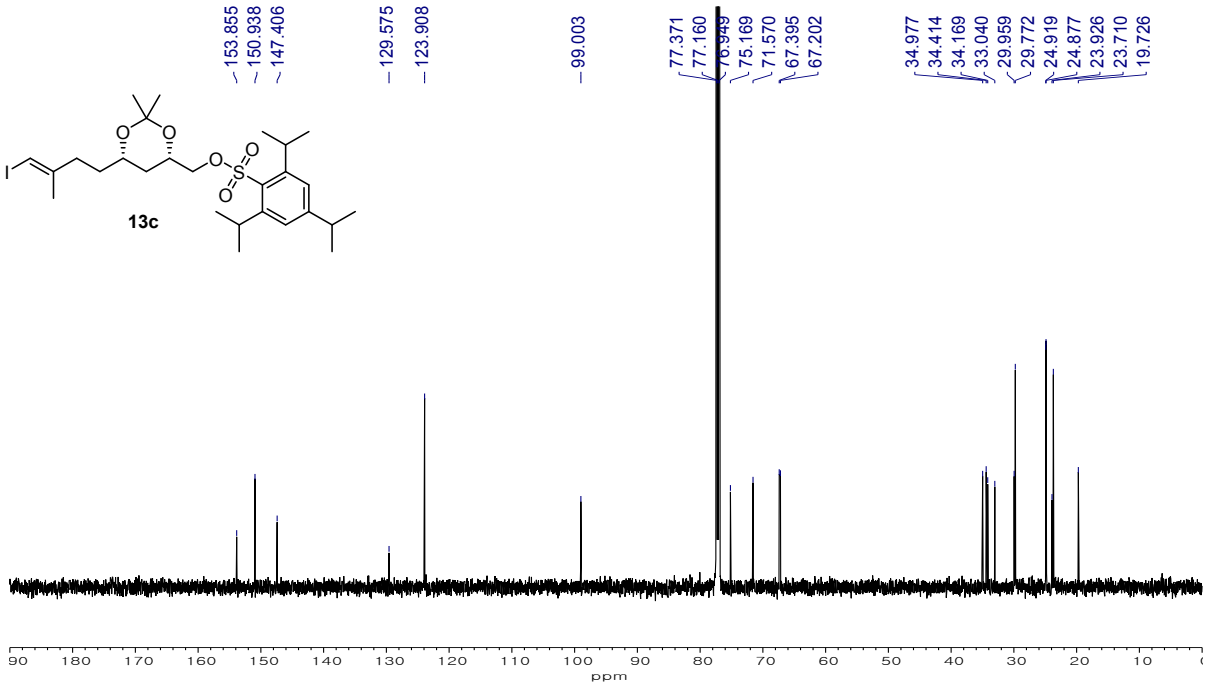
^{1}H NMR Spectrum of ((4*R*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13b**) in $CDCl_3$



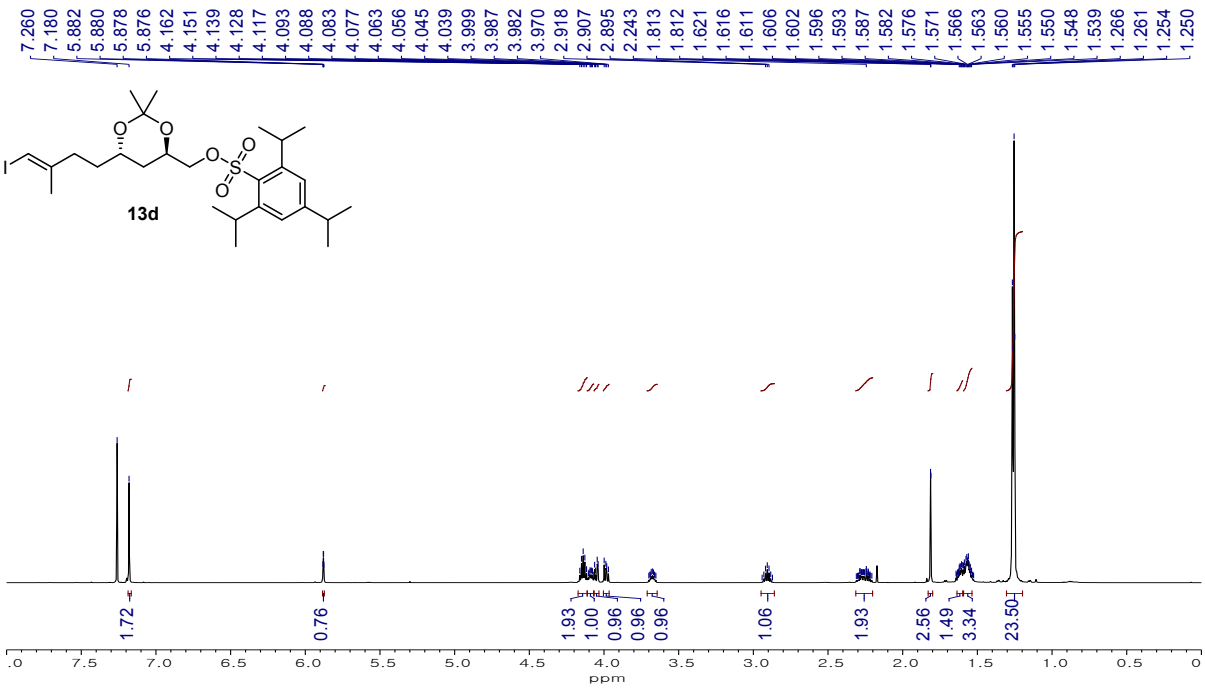
^{13}C NMR Spectrum of ((4*R*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13b**) in $CDCl_3$



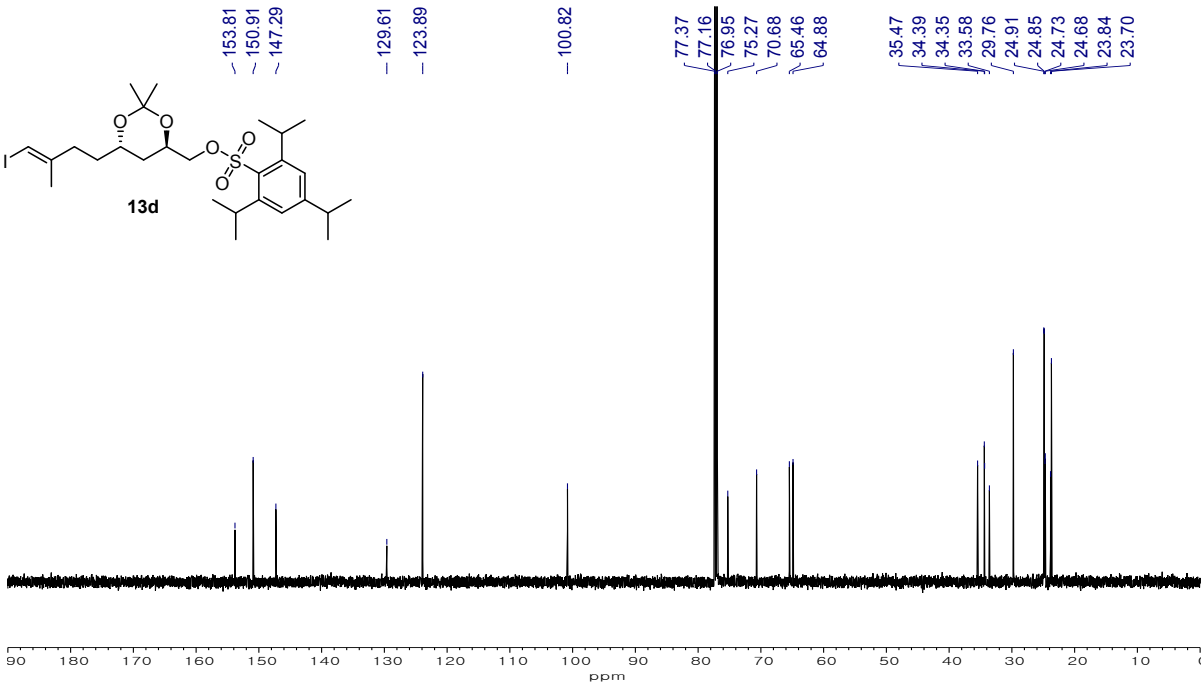
^{1}H NMR Spectrum of ((4*S*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13c**) in $CDCl_3$



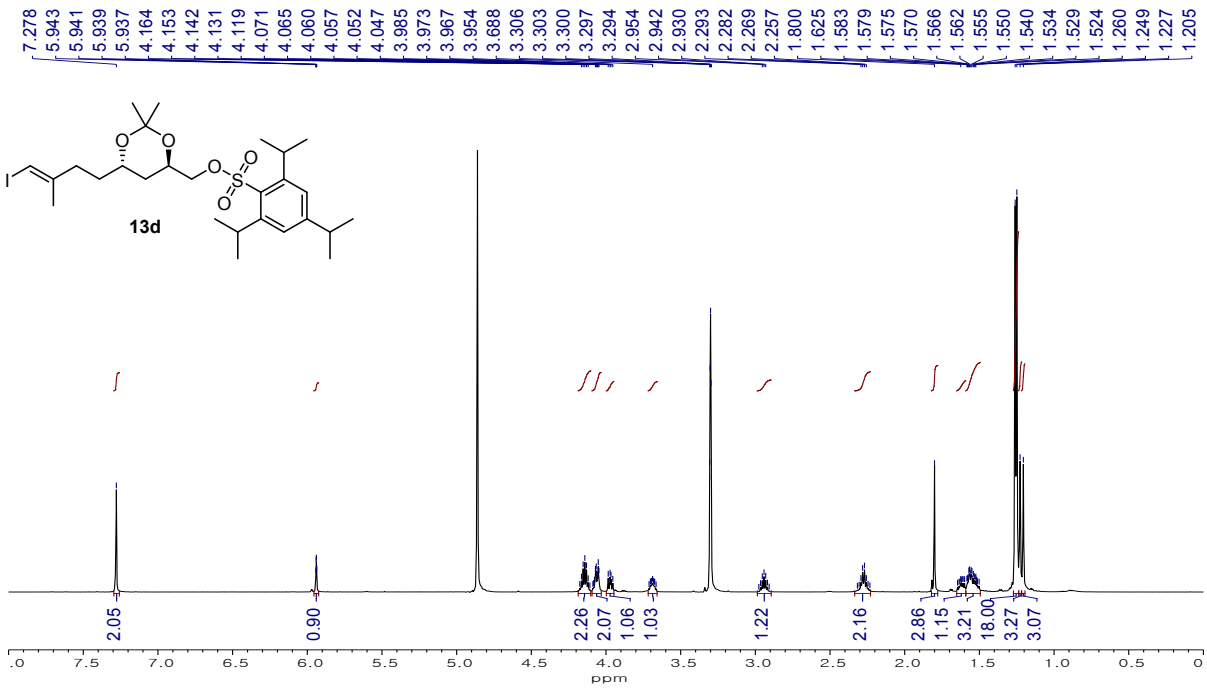
^{13}C NMR Spectrum of ((4*S*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13c**) in $CDCl_3$



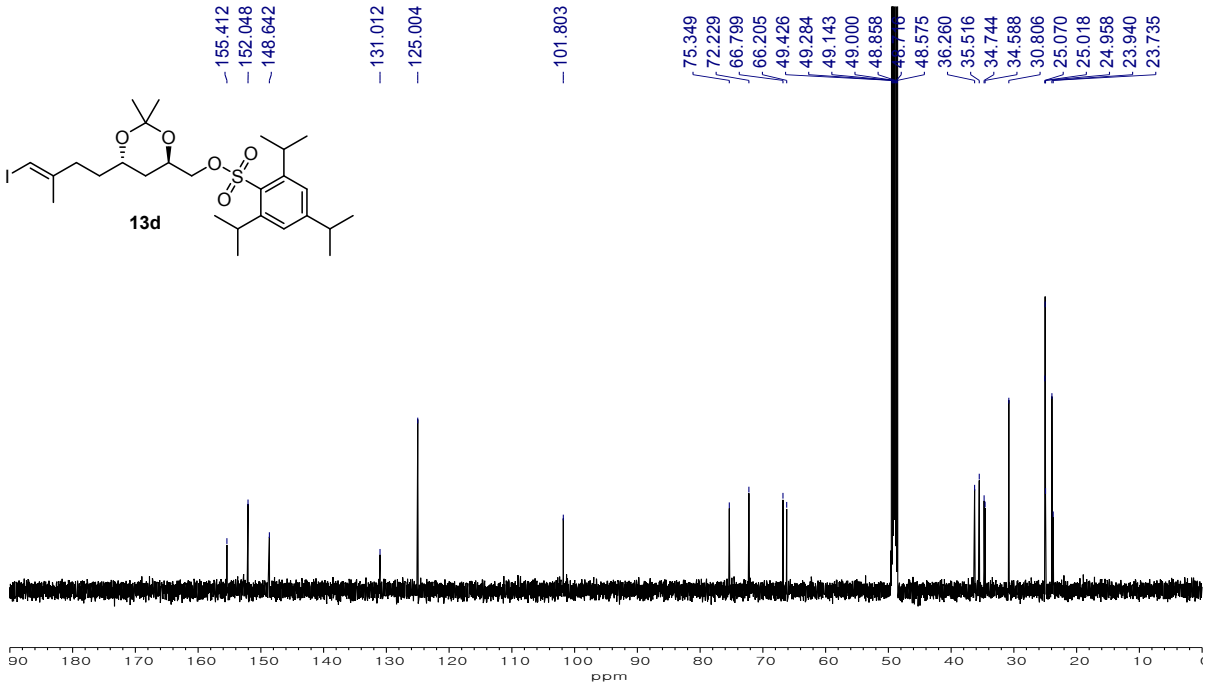
^{1}H NMR Spectrum of ((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13d**) in $CDCl_3$



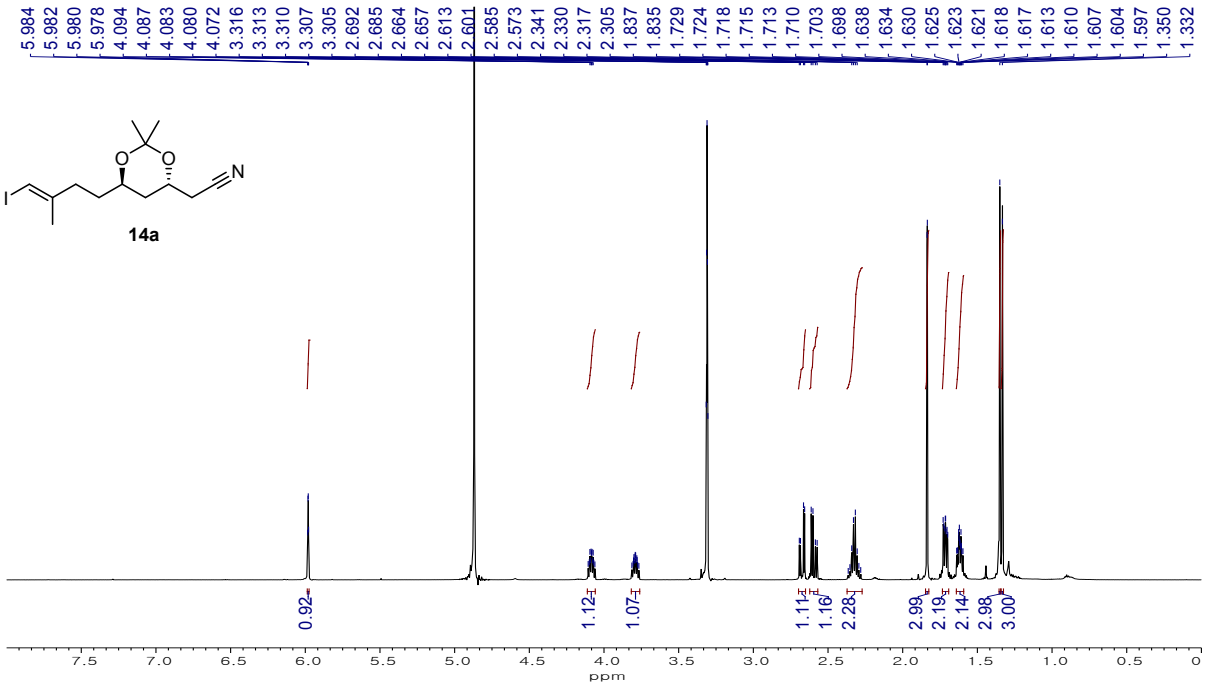
^{13}C NMR Spectrum of ((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13d**) in $CDCl_3$



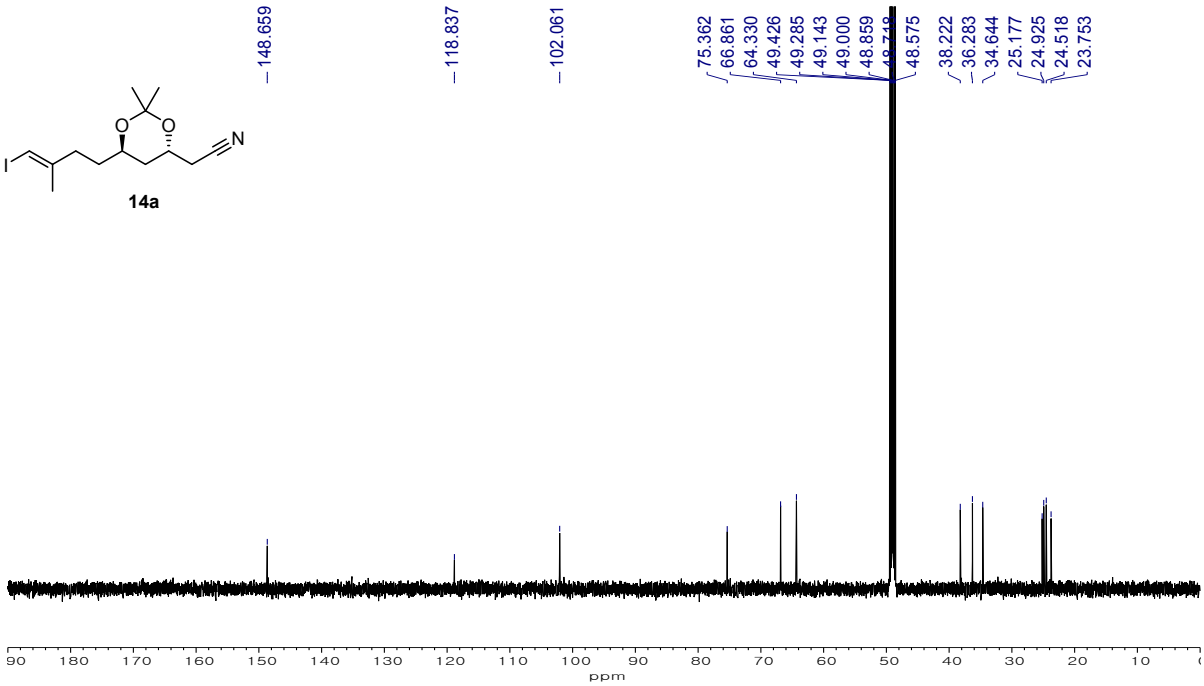
^{1}H NMR Spectrum of ((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13d**) in CD_3OD



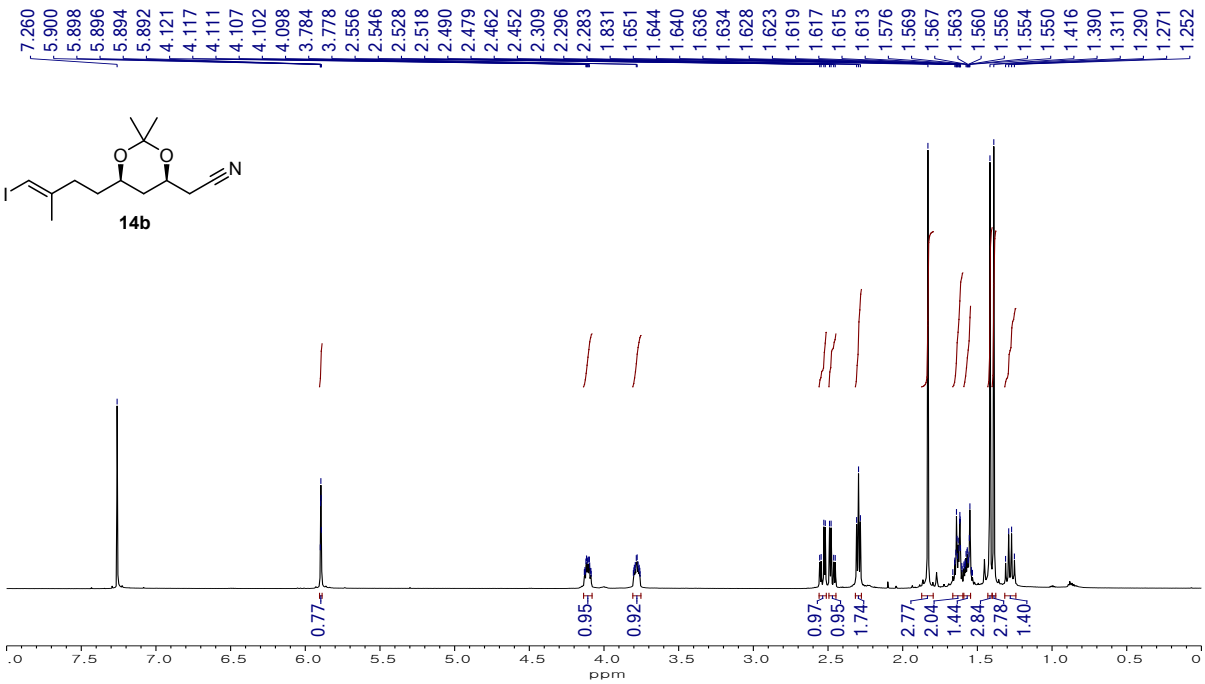
^{13}C NMR Spectrum of ((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)methyl 2,4,6-triisopropylbenzenesulfonate (**13d**) in $CDCl_3$



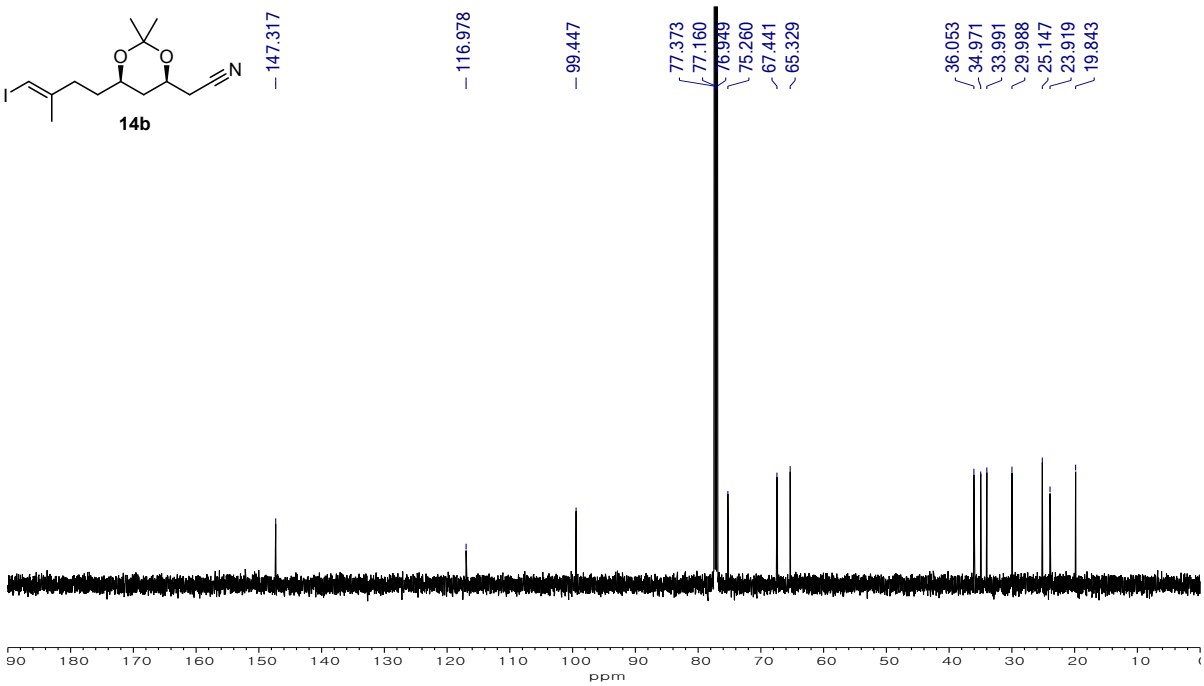
^{1}H NMR Spectrum of 2-((4*R*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14a**) in CD_3OD



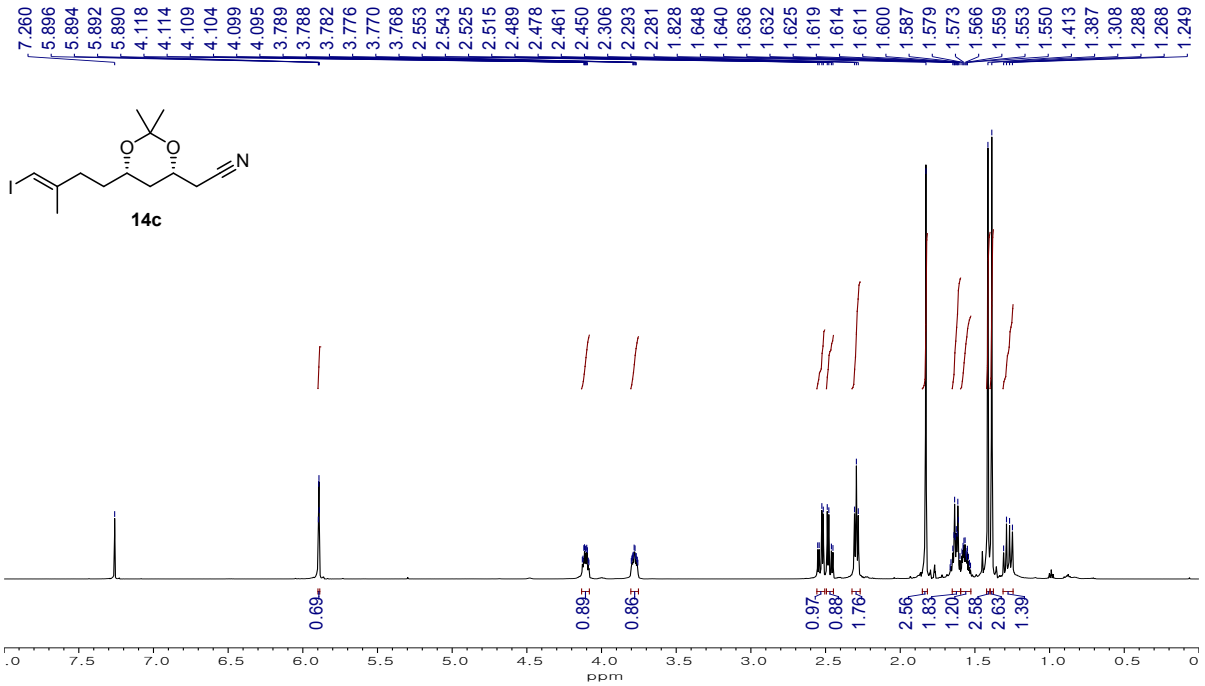
^{13}C NMR Spectrum of 2-((4*R*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14a**) in CD_3OD



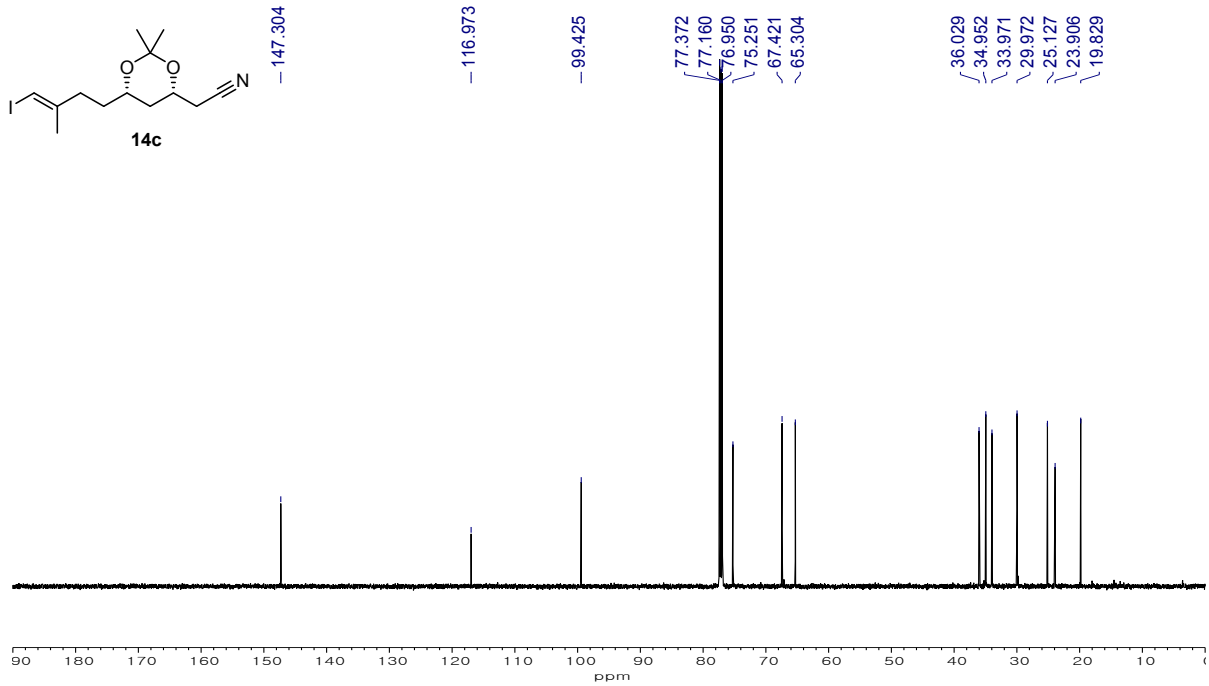
^{1}H NMR Spectrum of 2-((4*S*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14b**) in $CDCl_3$



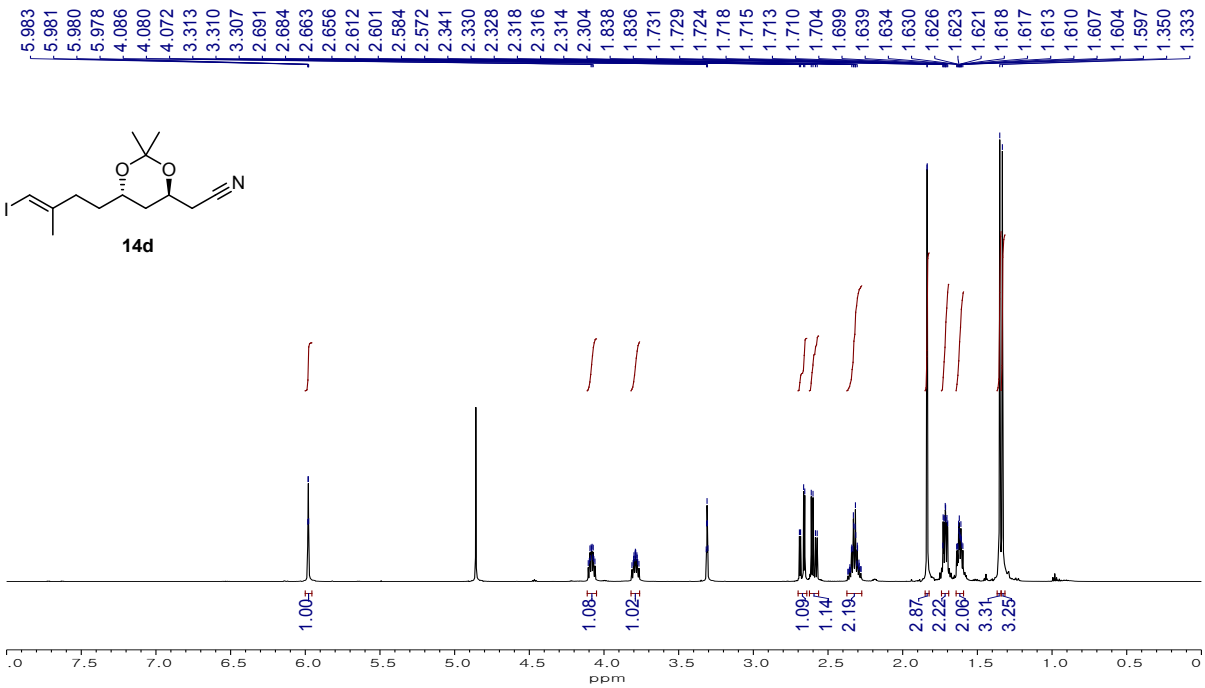
^{13}C NMR Spectrum of 2-((4*S*,6*R*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14b**) in $CDCl_3$



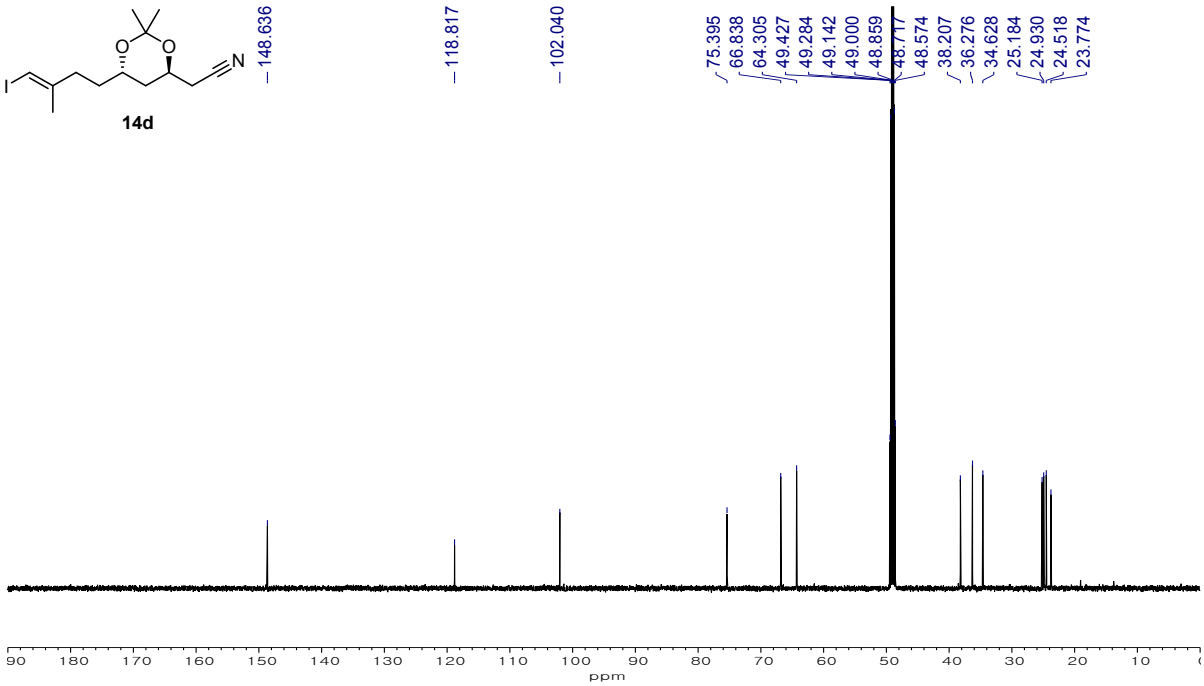
^{1}H NMR Spectrum of 2-((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14c**) in $CDCl_3$



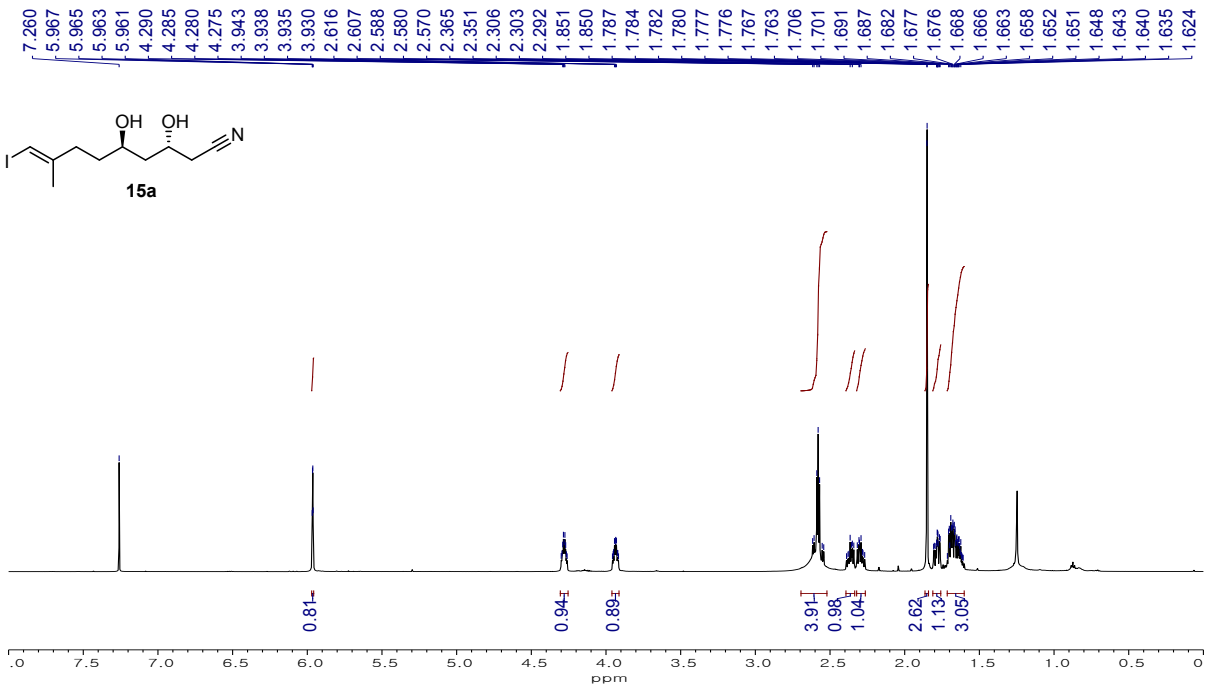
^{13}C NMR Spectrum of 2-((4*R*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14c**) in $CDCl_3$



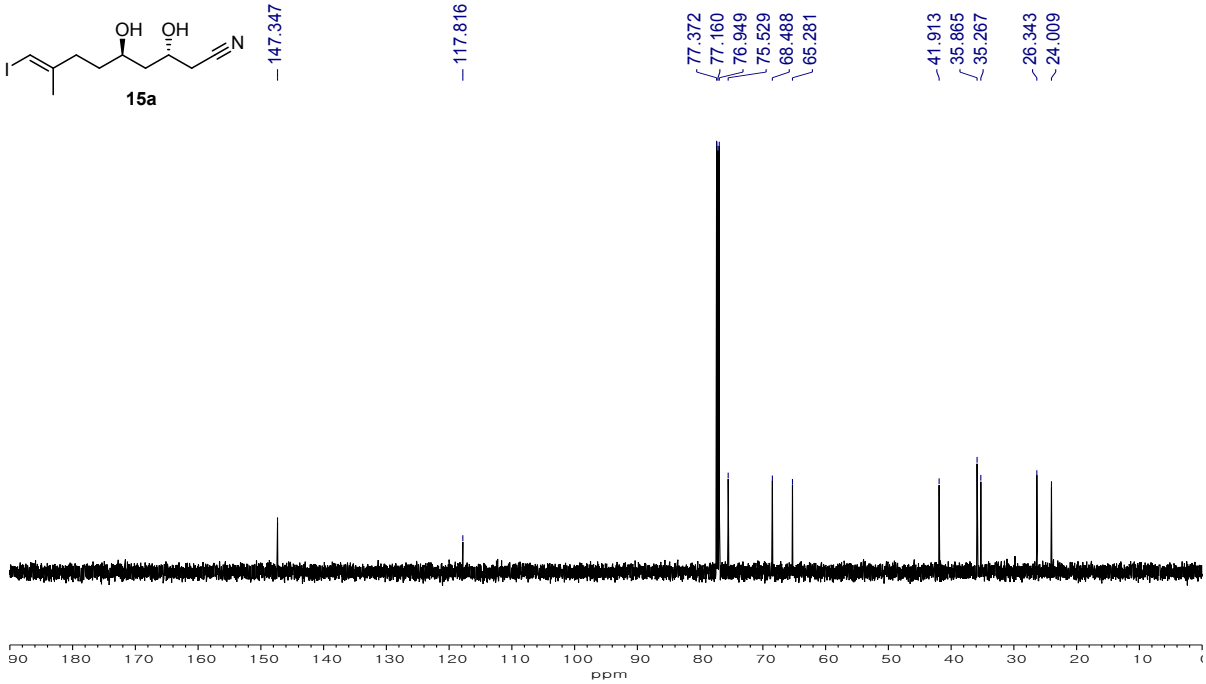
^{1}H NMR Spectrum of 2-((4*S*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14d**) in CD_3OD



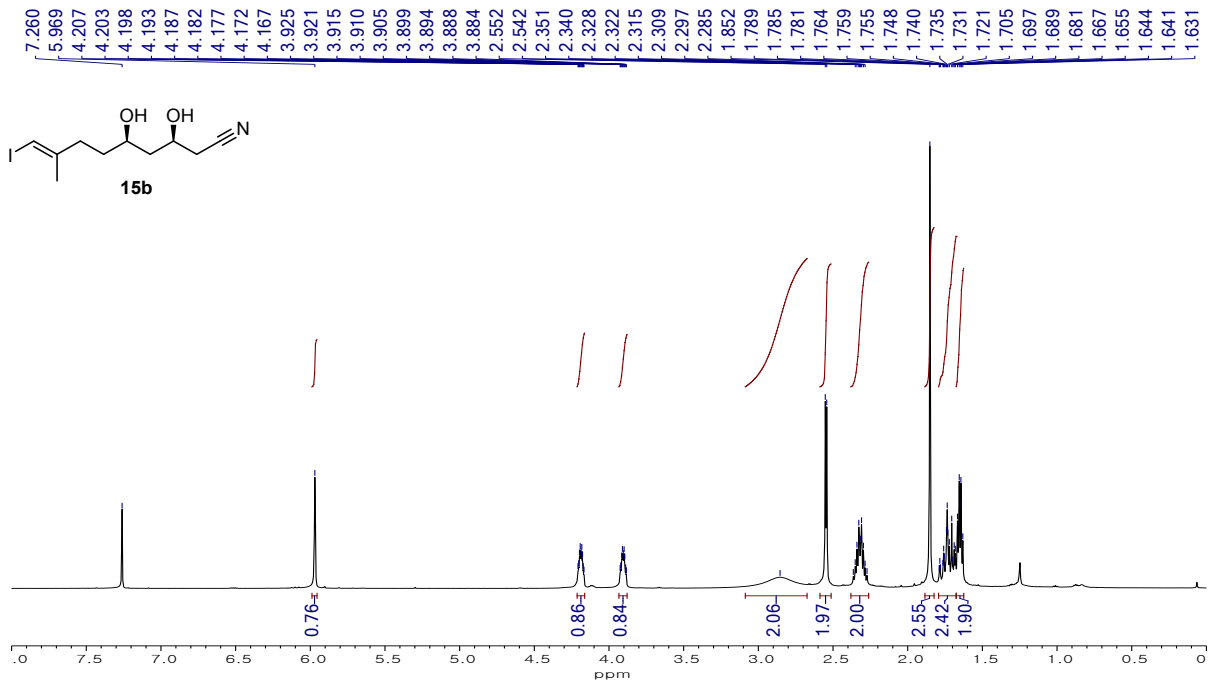
^{13}C NMR Spectrum of 2-((4*S*,6*S*)-6-((*E*)-4-Iodo-3-methylbut-3-en-1-yl)-2,2-dimethyl-1,3-dioxan-4-yl)acetonitrile (**14d**) in CD_3OD



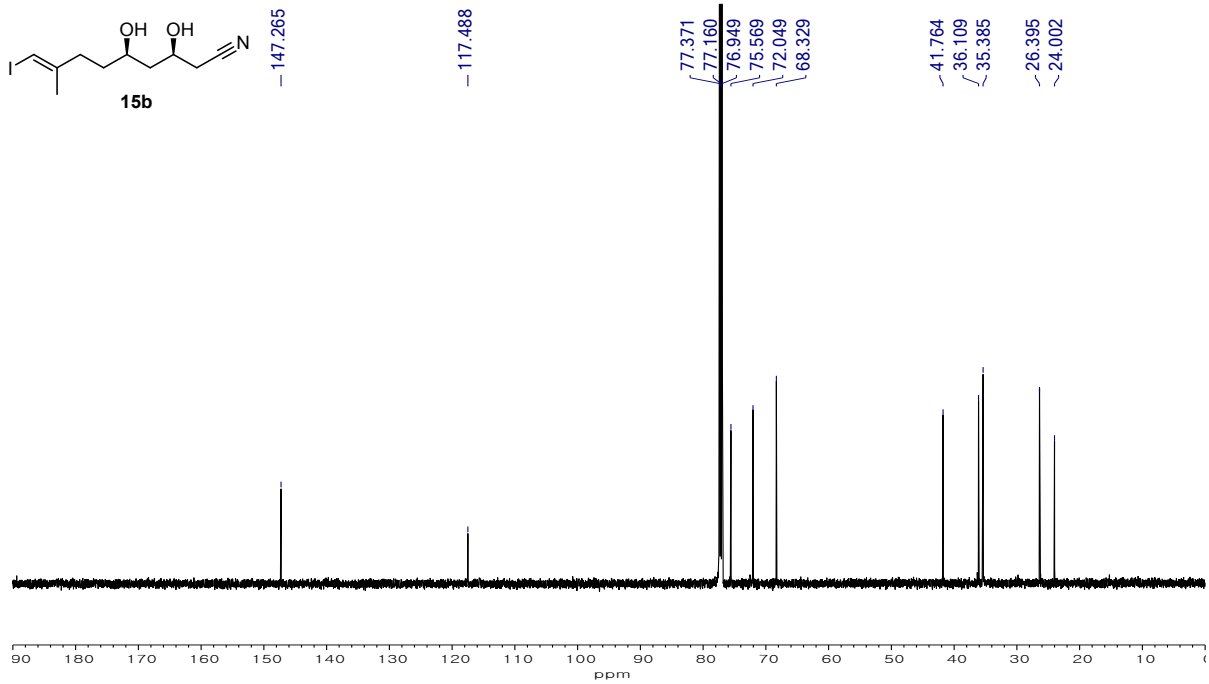
^{1}H NMR Spectrum of (3*R*,5*R*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15a**) in $CDCl_3$



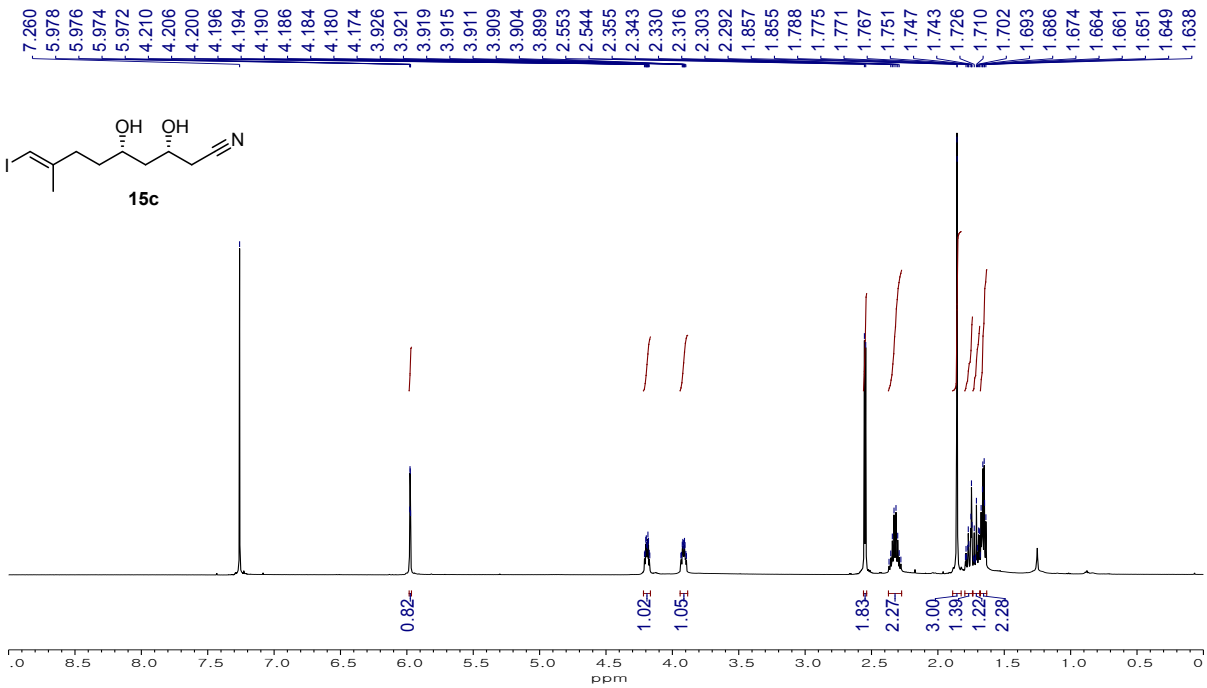
^{13}C NMR Spectrum of (3*R*,5*R*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15a**) in $CDCl_3$



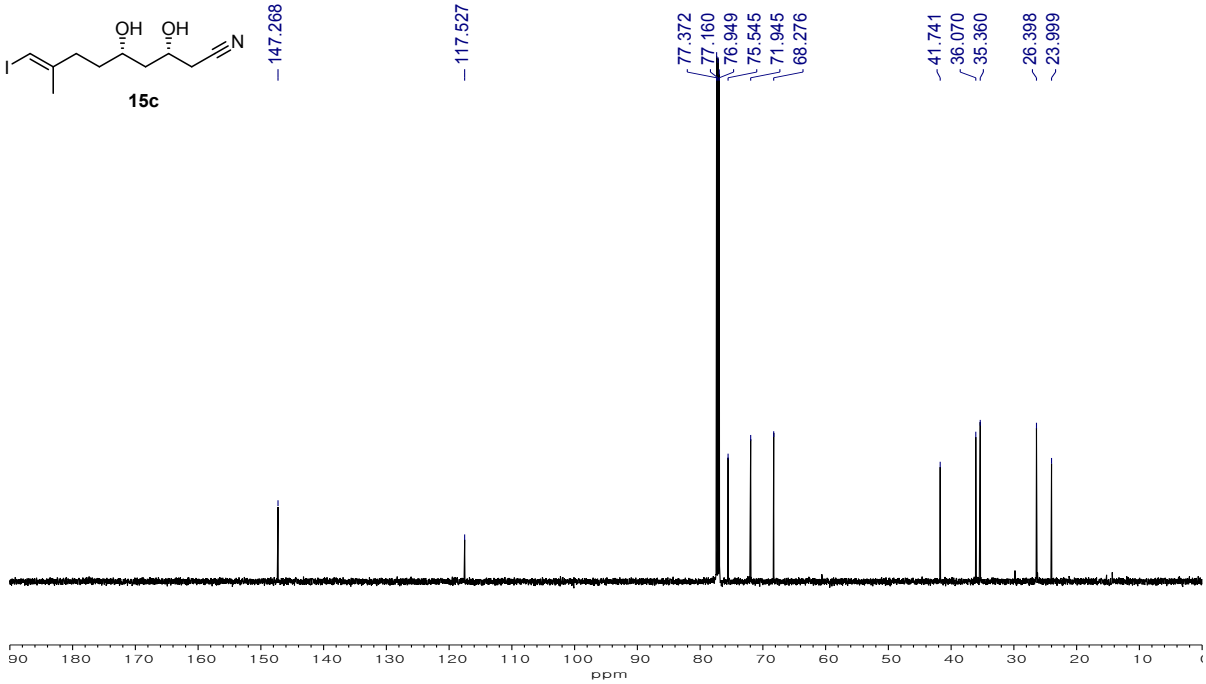
^{1}H NMR Spectrum of (3*S*,5*R*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15b**) in $CDCl_3$



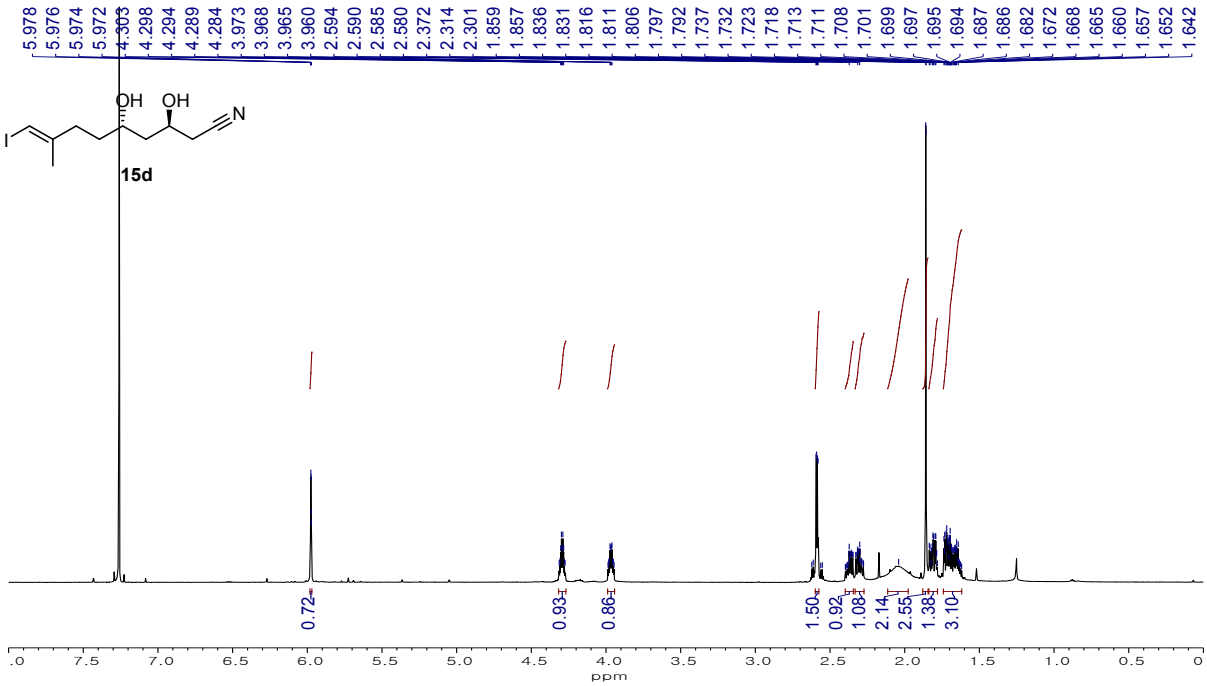
^{13}C NMR Spectrum of (3*S*,5*R*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15b**) in $CDCl_3$



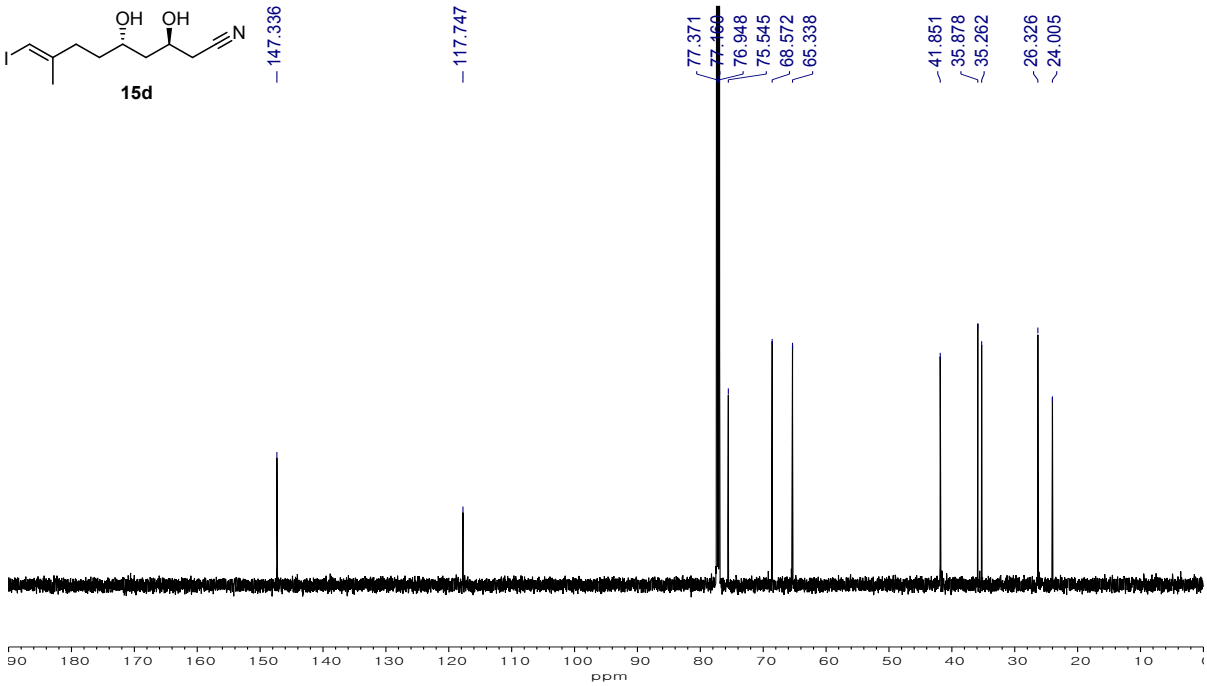
^{1}H NMR Spectrum of (3*R*,5*S*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15c**) in $CDCl_3$



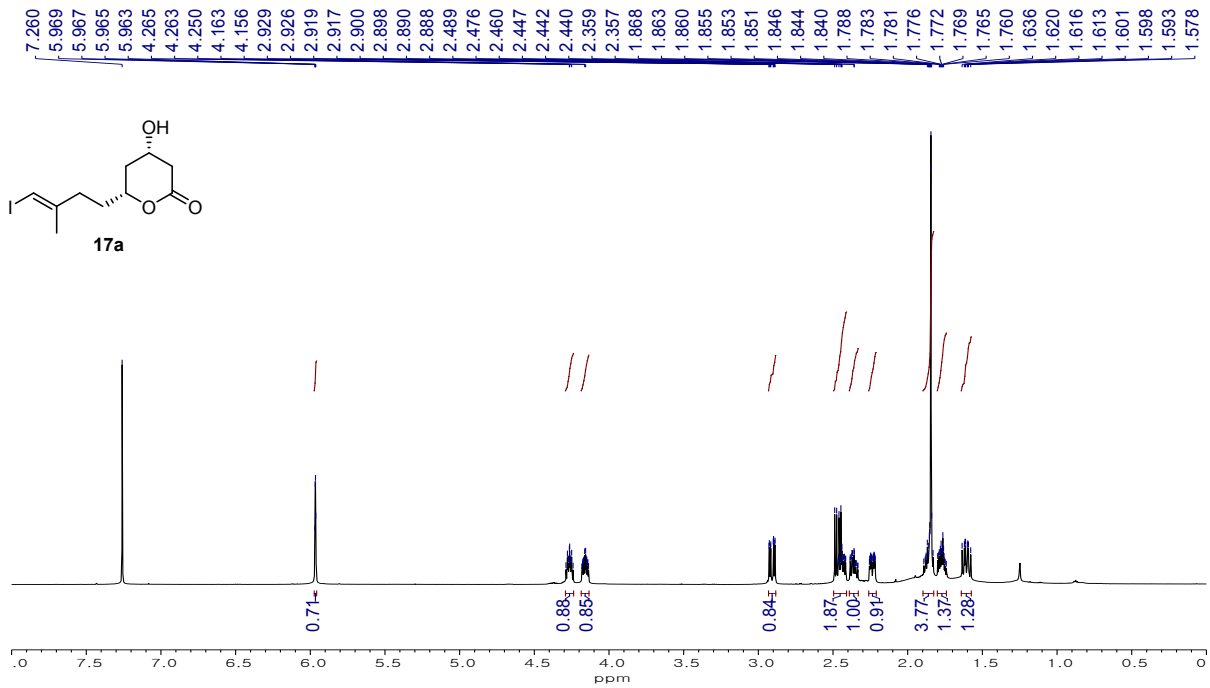
^{13}C NMR Spectrum of (3*R*,5*S*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15c**) in $CDCl_3$



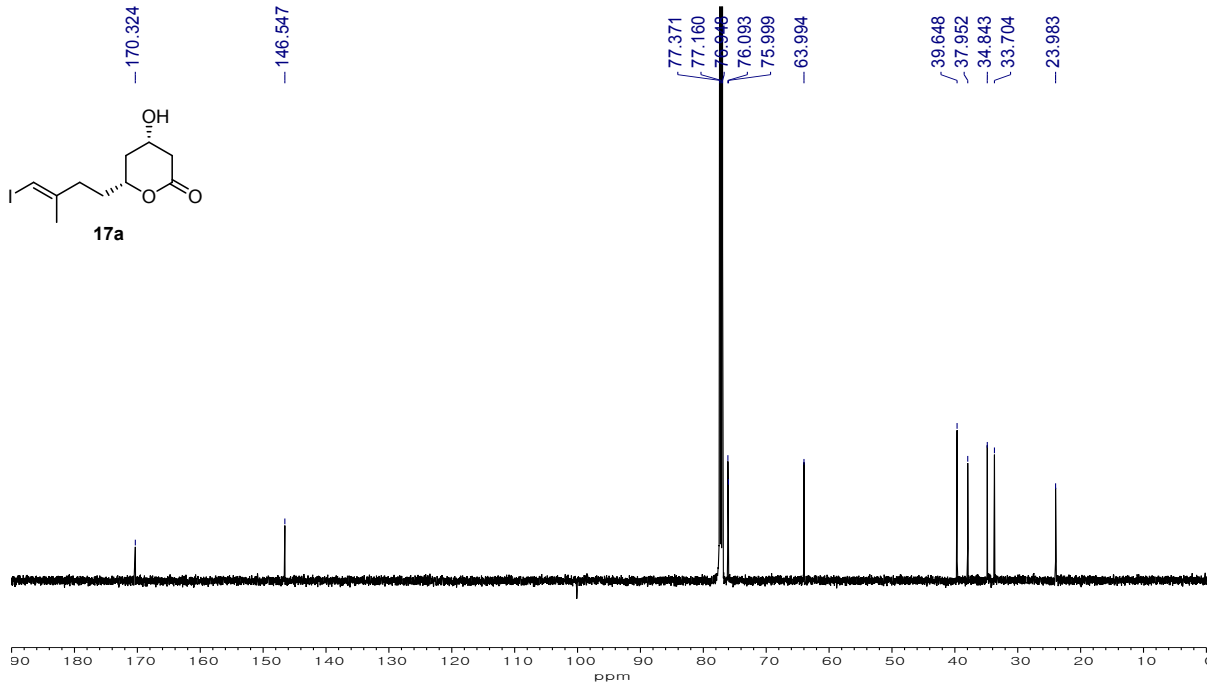
^{1}H NMR Spectrum of (3*S*,5*S*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15d**) in $CDCl_3$



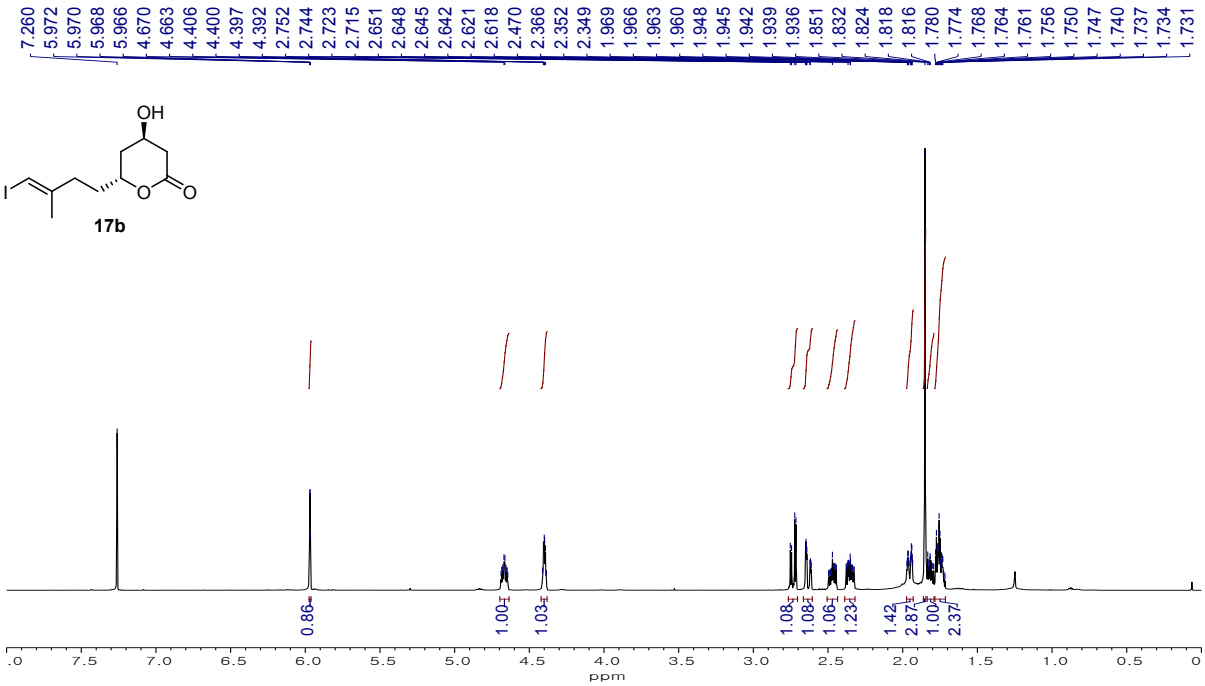
^{13}C NMR Spectrum of (3*S*,5*S*,*E*)-3,5-Dihydroxy-9-iodo-8-methylnon-8-enenitrile (**15d**) in $CDCl_3$



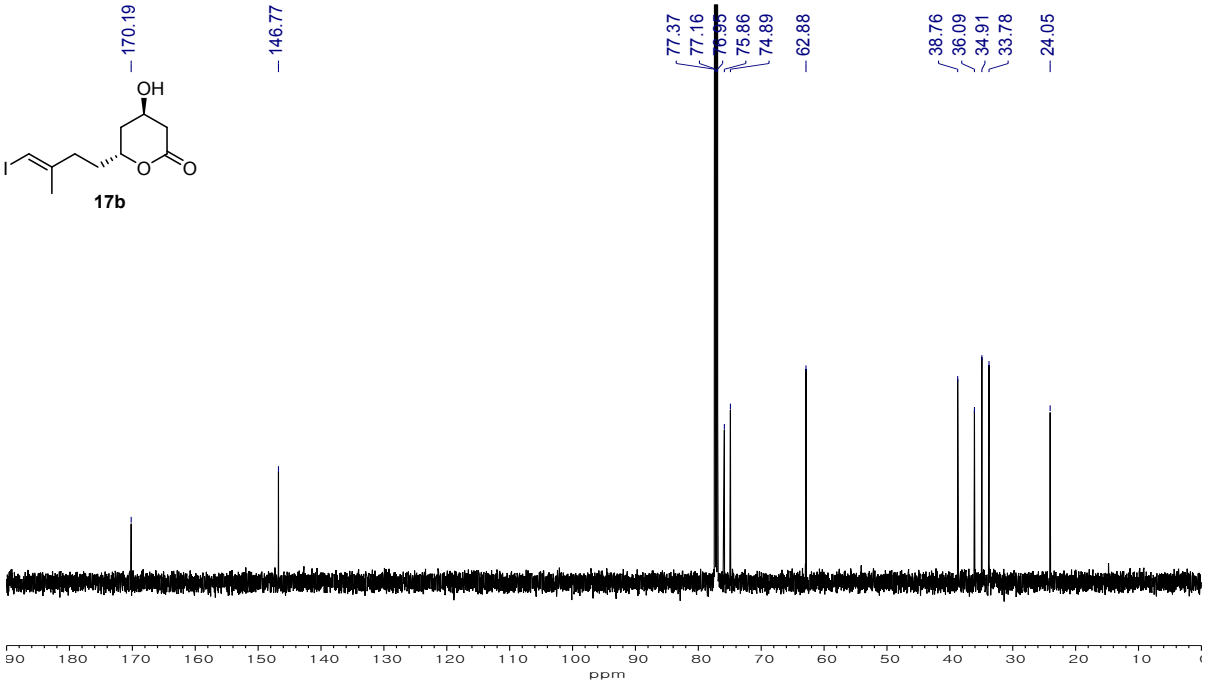
^{1}H NMR spectrum of (4*S*,6*R*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17a**) in $CDCl_3$



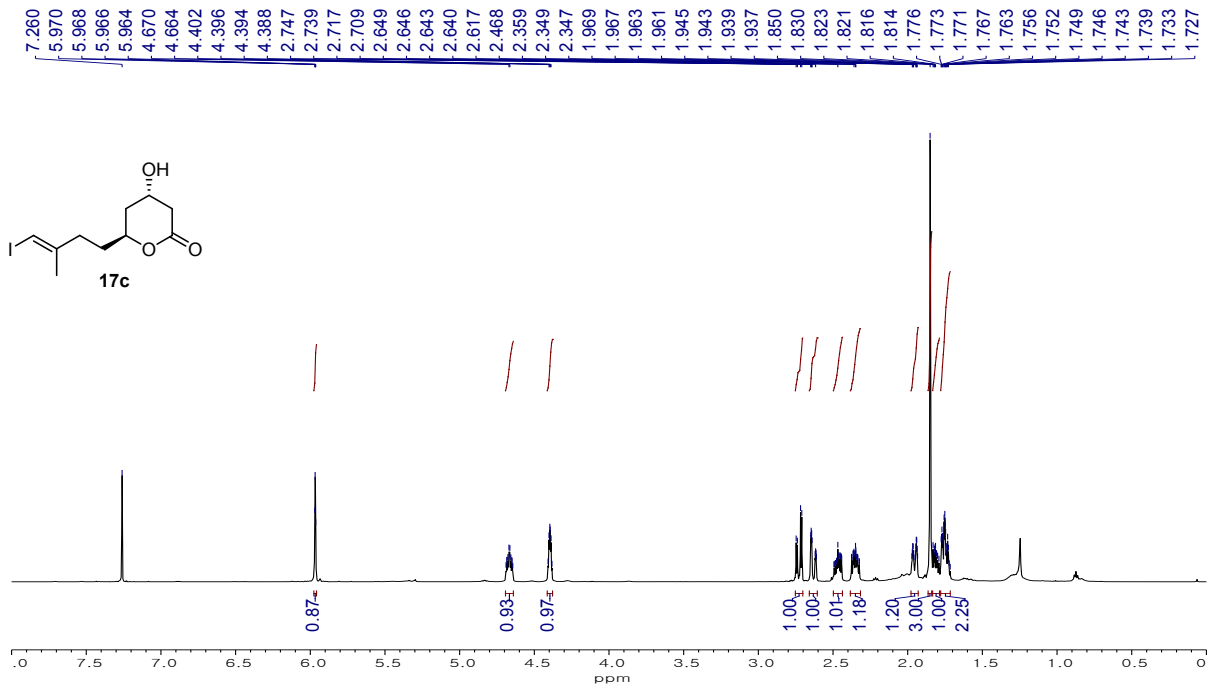
^{13}C NMR Spectrum of (4*S*,6*R*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17a**) in $CDCl_3$



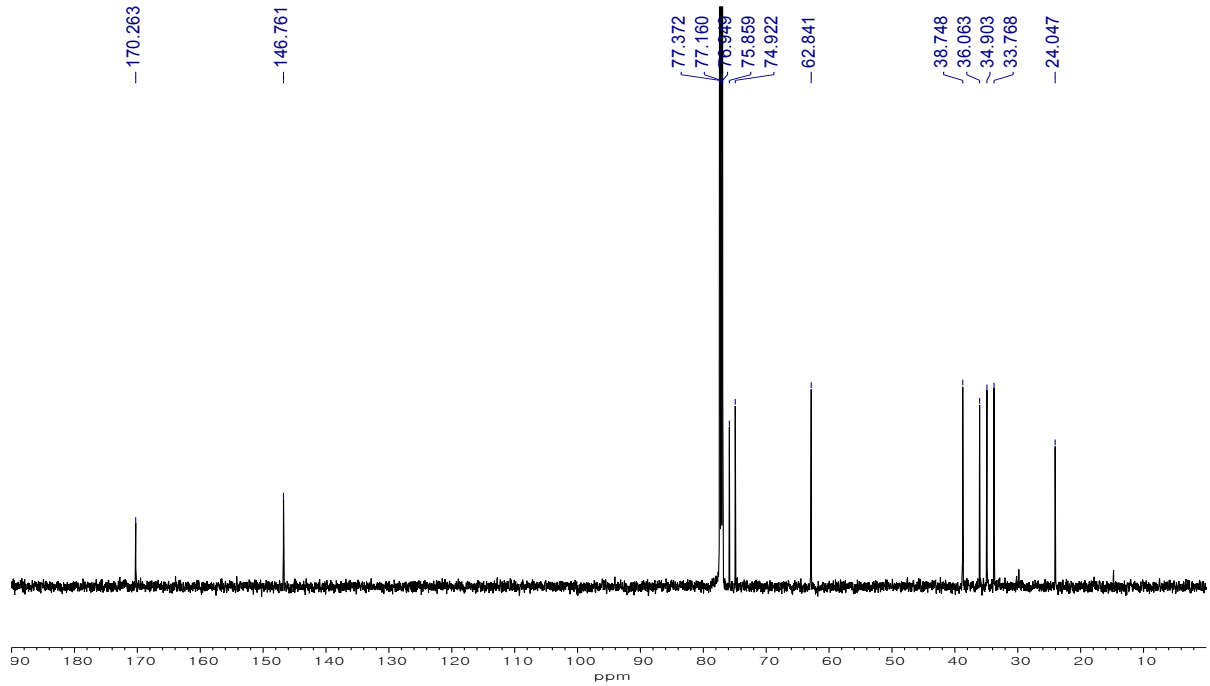
^{1}H NMR spectrum of (4*R*,6*R*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17b**) in $CDCl_3$



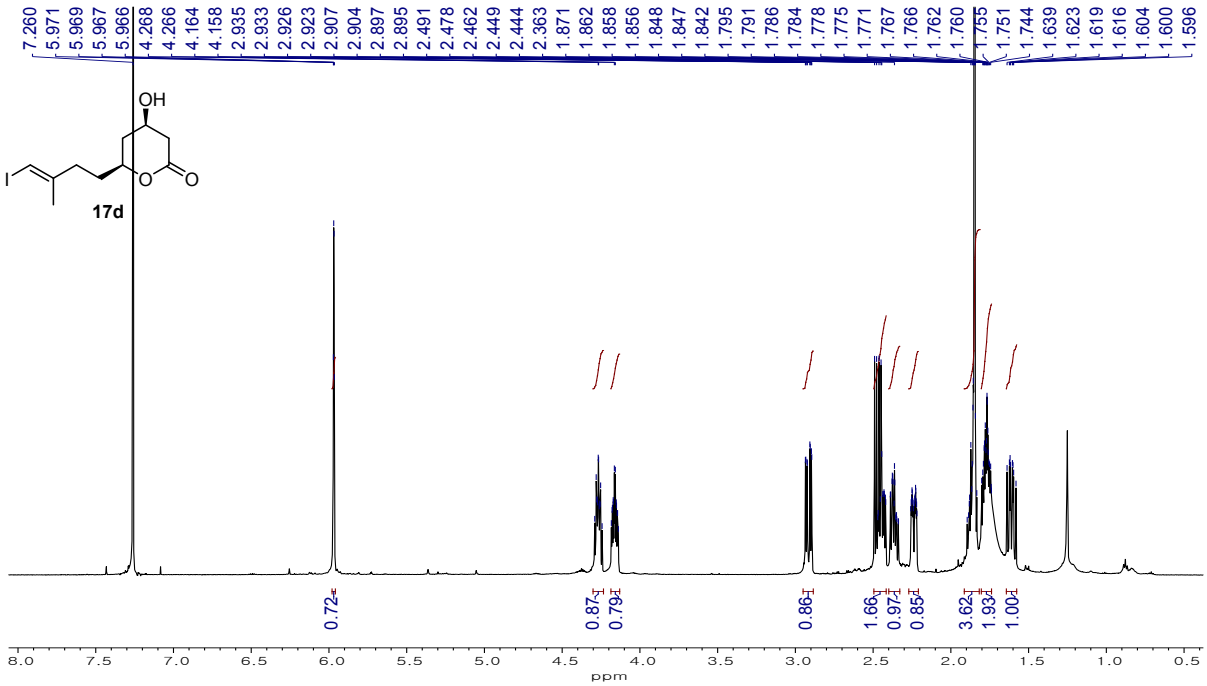
^{13}C NMR Spectrum of (4*R*,6*R*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17b**) in $CDCl_3$



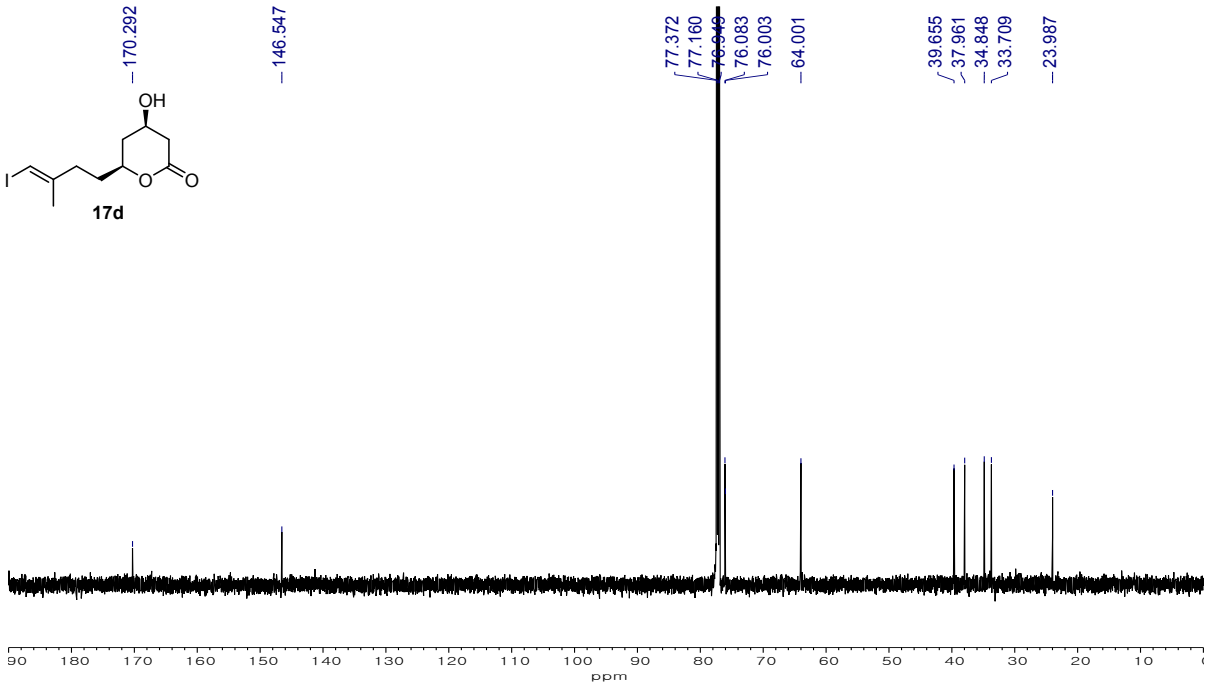
^{1}H NMR spectrum of (4*S*,6*S*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17c**) in $CDCl_3$



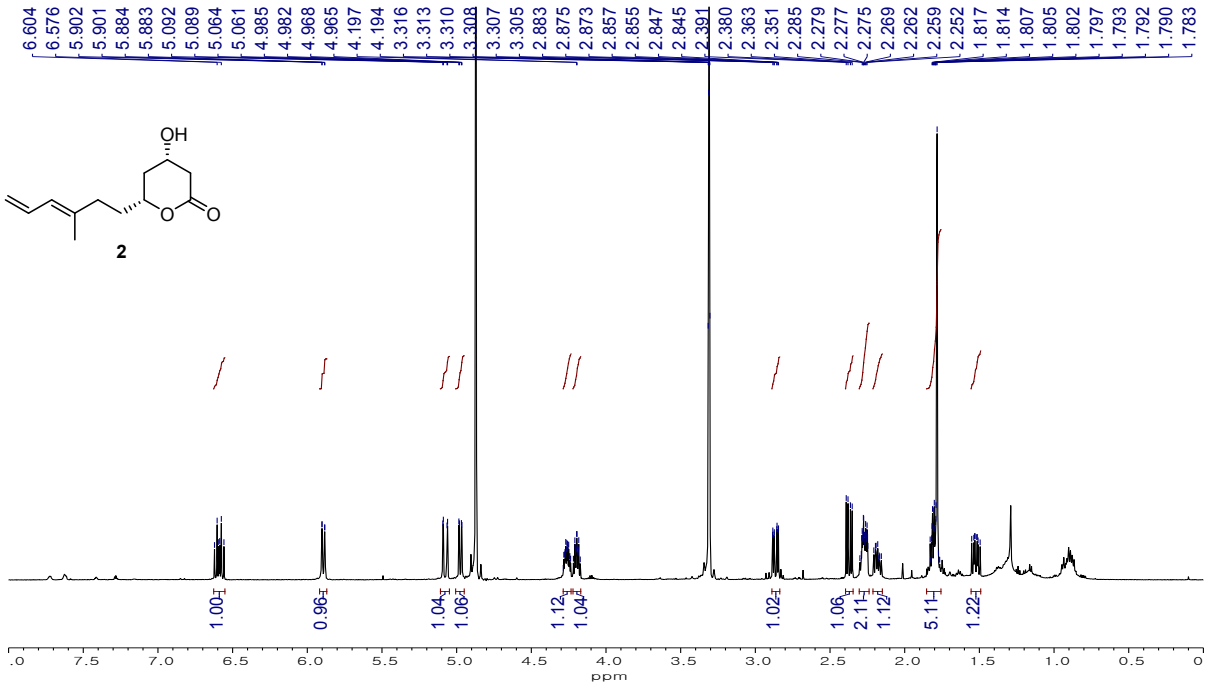
^{13}C NMR Spectrum of (4*S*,6*S*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17c**) in $CDCl_3$



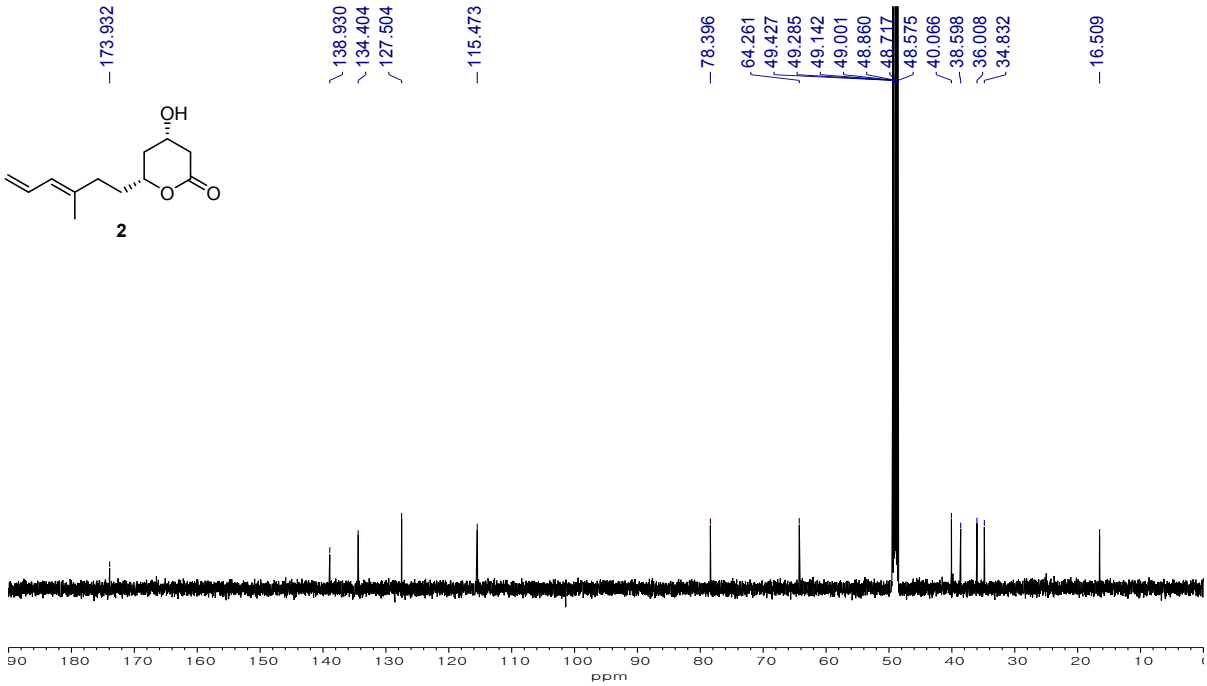
^{1}H NMR spectrum of (4*R*,6*S*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17d**) in $CDCl_3$



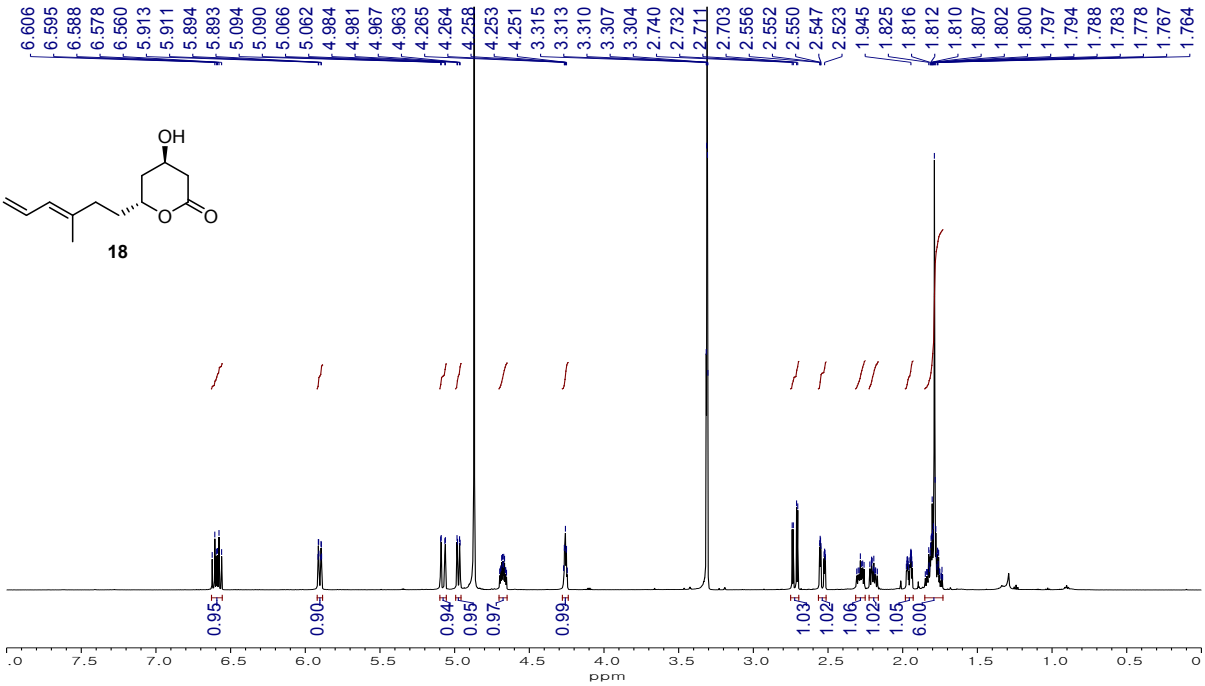
^{13}C NMR Spectrum of (4*R*,6*S*)-4-Hydroxy-6-((*E*)-4-iodo-3-methylbut-3-en-1-yl)tetrahydro-2H-pyran-2-one (**17d**) in $CDCl_3$



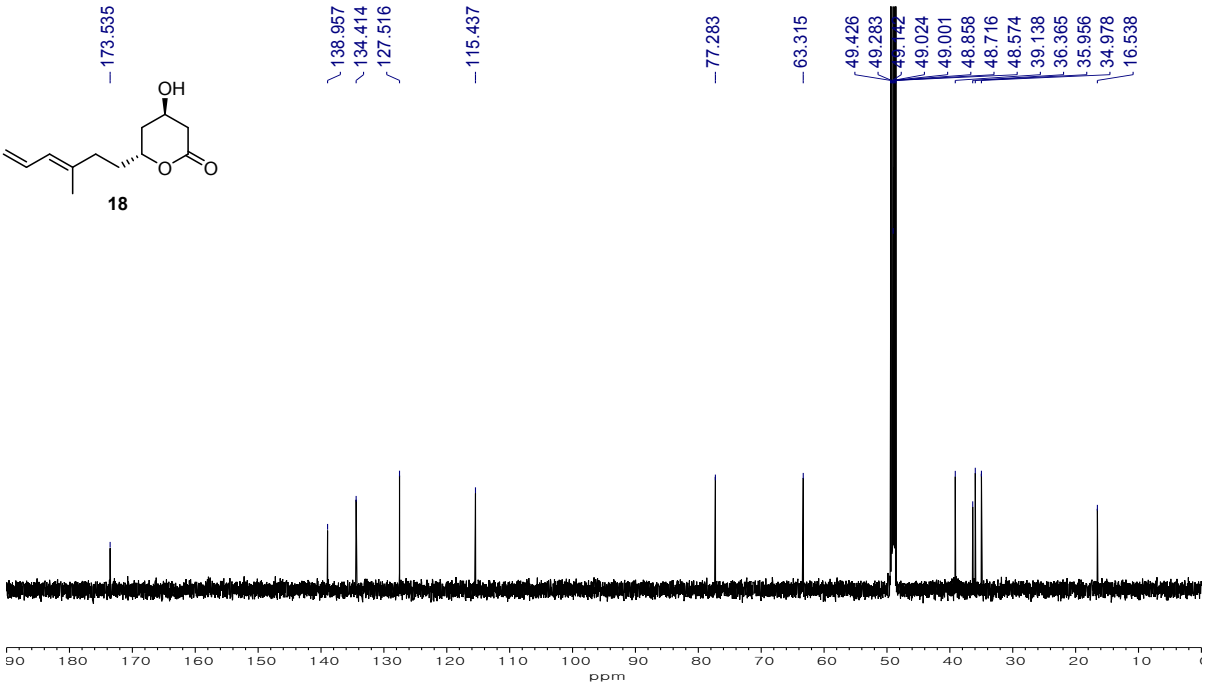
^{1}H NMR spectrum of (4*S*,6*R*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one, Ieodomycin B (**2**) in CD_3OD



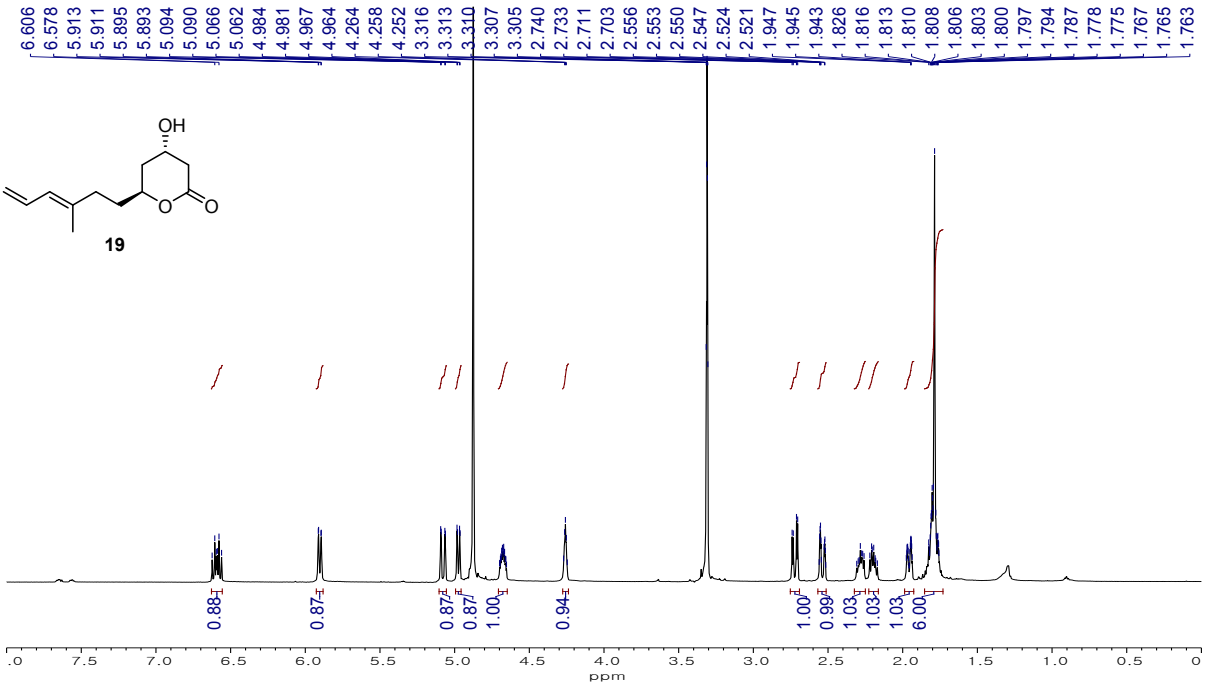
^{13}C NMR Spectrum of (4*S*,6*R*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one, Ieodomycin B (**2**) in CD_3OD



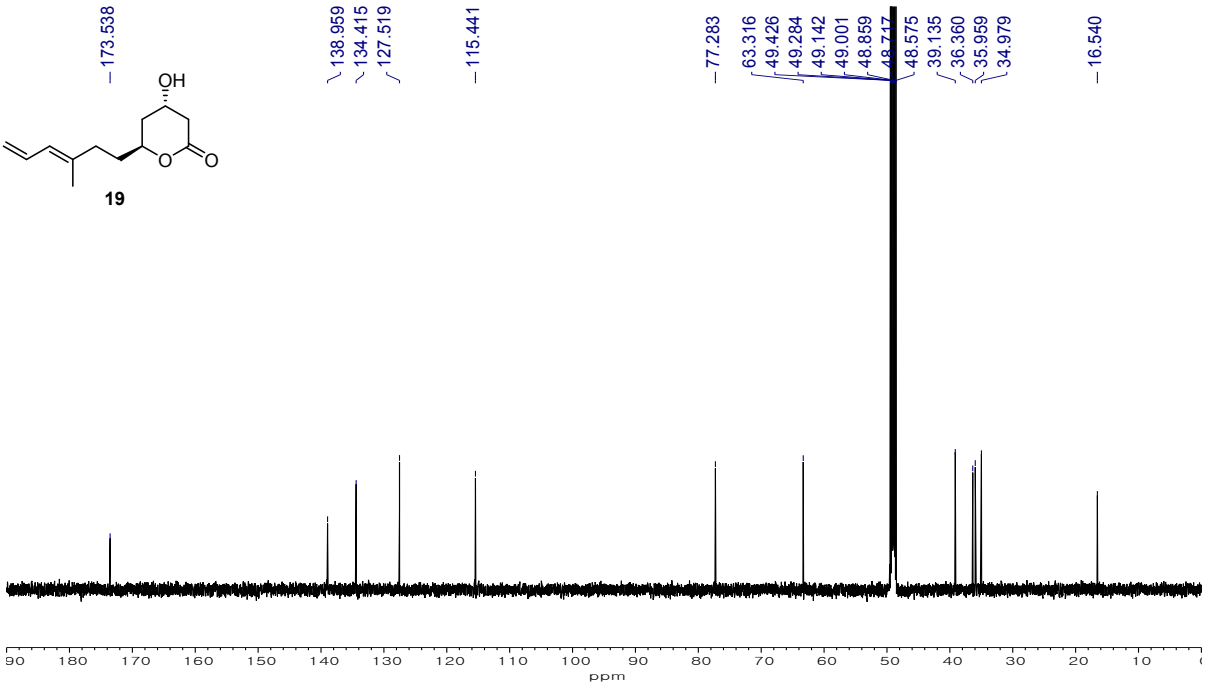
^{1}H NMR spectrum of (4*R*,6*R*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one (**18**) in CD_3OD



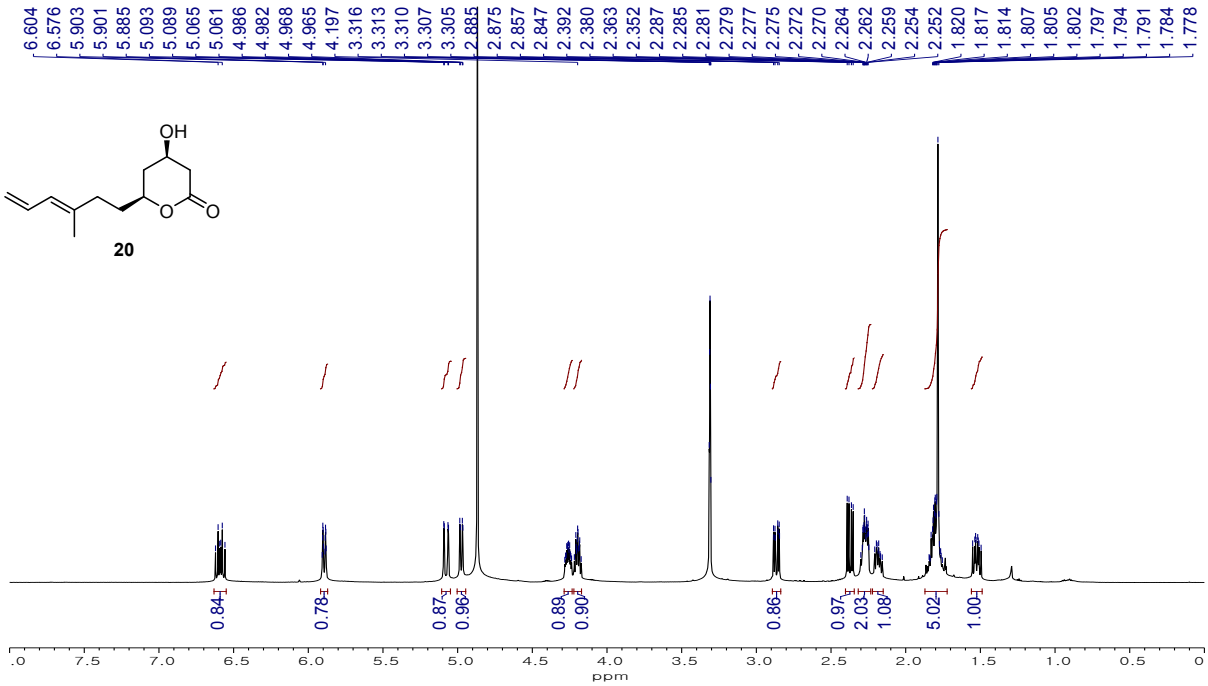
^{13}C NMR Spectrum of (4*R*,6*R*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one (**18**) in CD_3OD



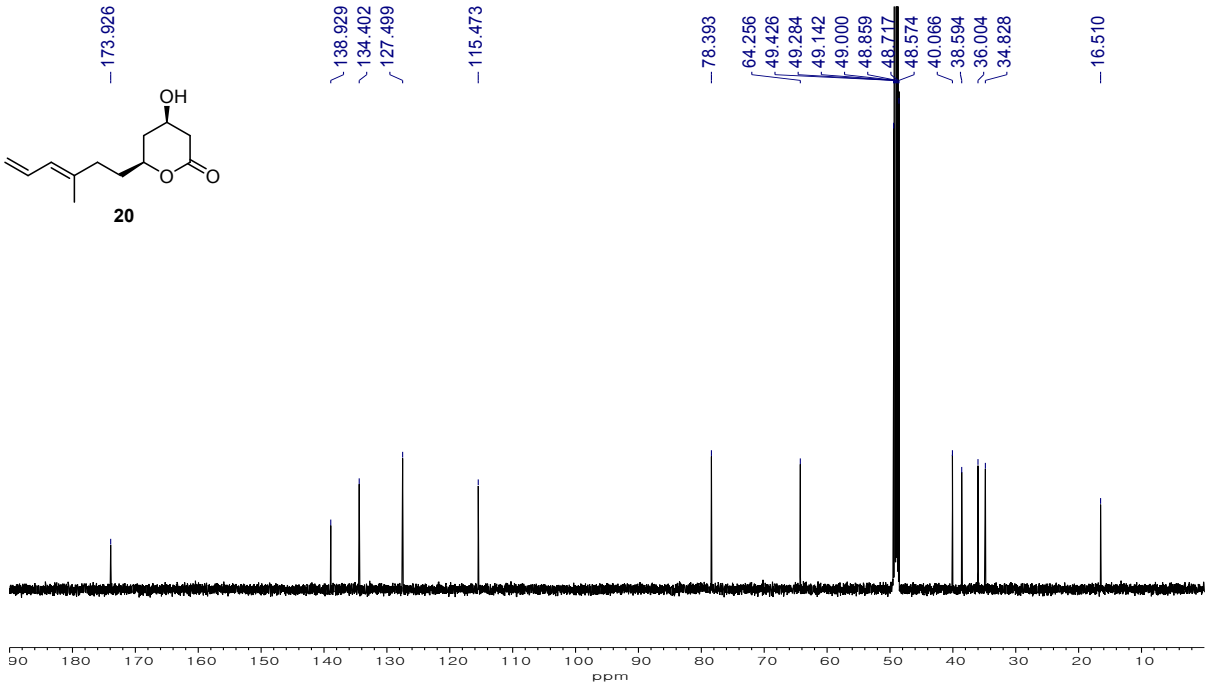
^{1}H NMR spectrum of (4*S*,6*S*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one (**19**) in CD_3OD



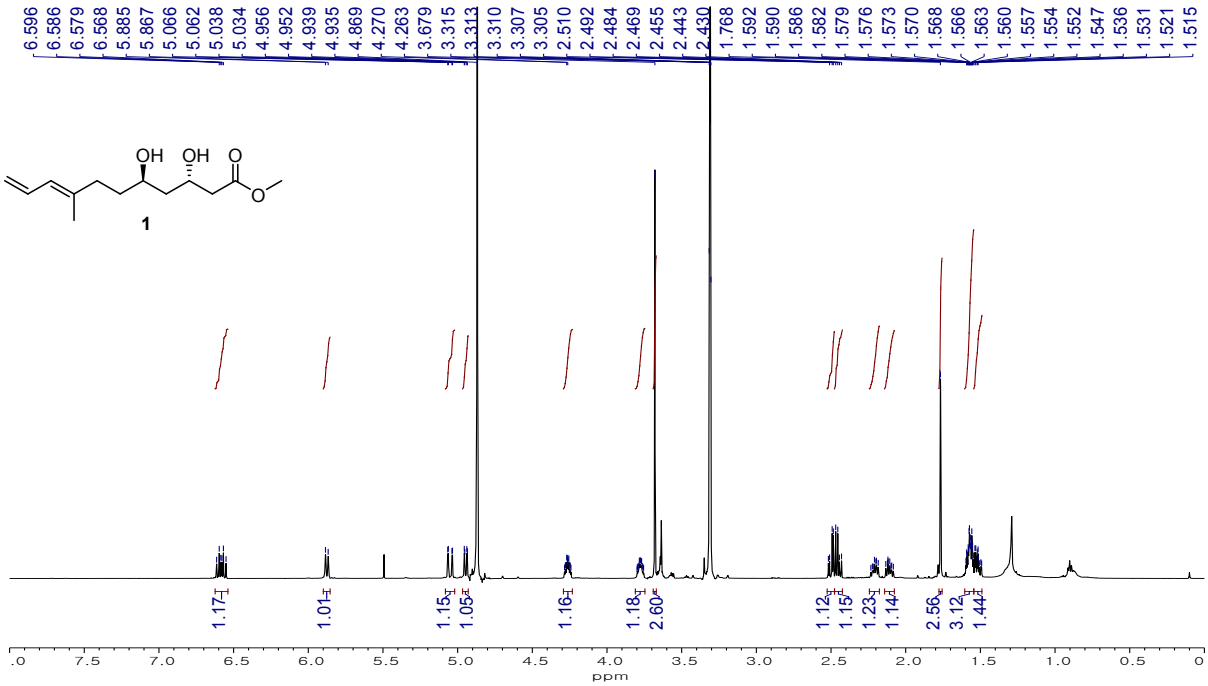
^{13}C NMR Spectrum of (4*S*,6*S*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one (**19**) in CD_3OD



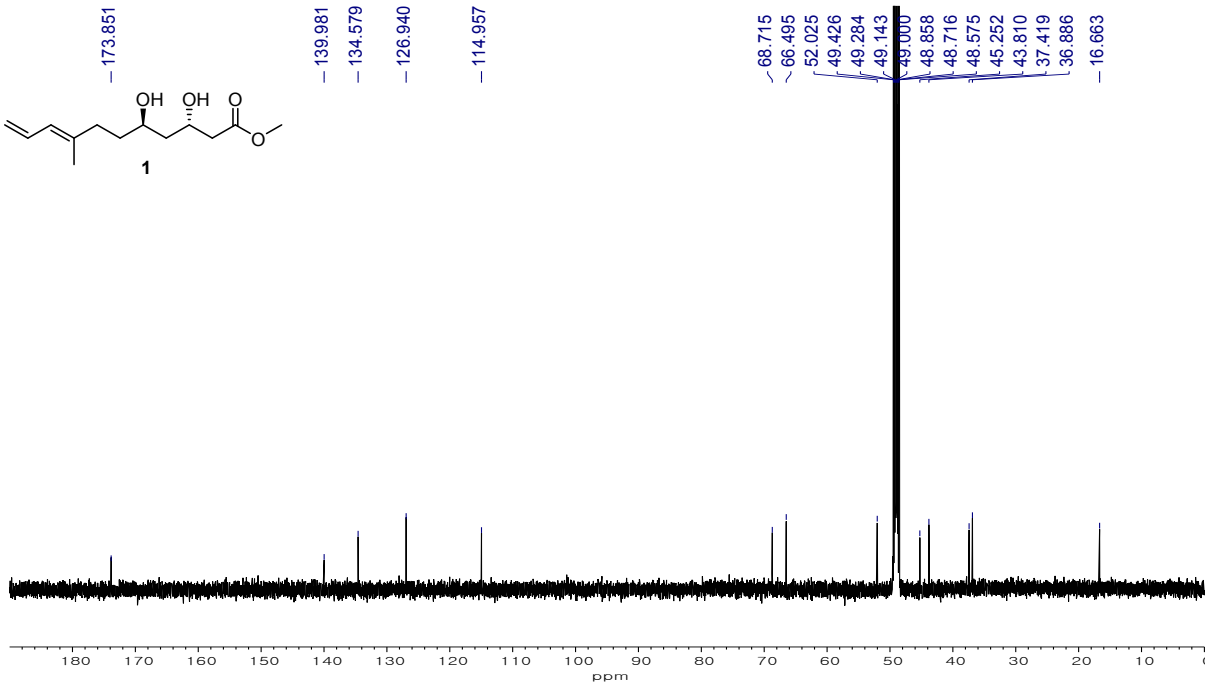
^{1}H NMR spectrum of (4*R*,6*S*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one (**20**) in CD_3OD



^{13}C NMR Spectrum of (4*R*,6*S*)-4-Hydroxy-6-((*E*)-3-methylhexa-3,5-dien-1-yl)tetrahydro-2H-pyran-2-one (**20**) in CD_3OD



^{1}H NMR spectrum of Methyl (3*S*,5*R*,*E*)-3,5-dihydroxy-8-methylundeca-8,10-dienoate (**1**) in $CDCl_3$



^{13}C NMR Spectrum of Methyl (3*S*,5*R*,*E*)-3,5-dihydroxy-8-methylundeca-8,10-dienoate (**1**) in $CDCl_3$