Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

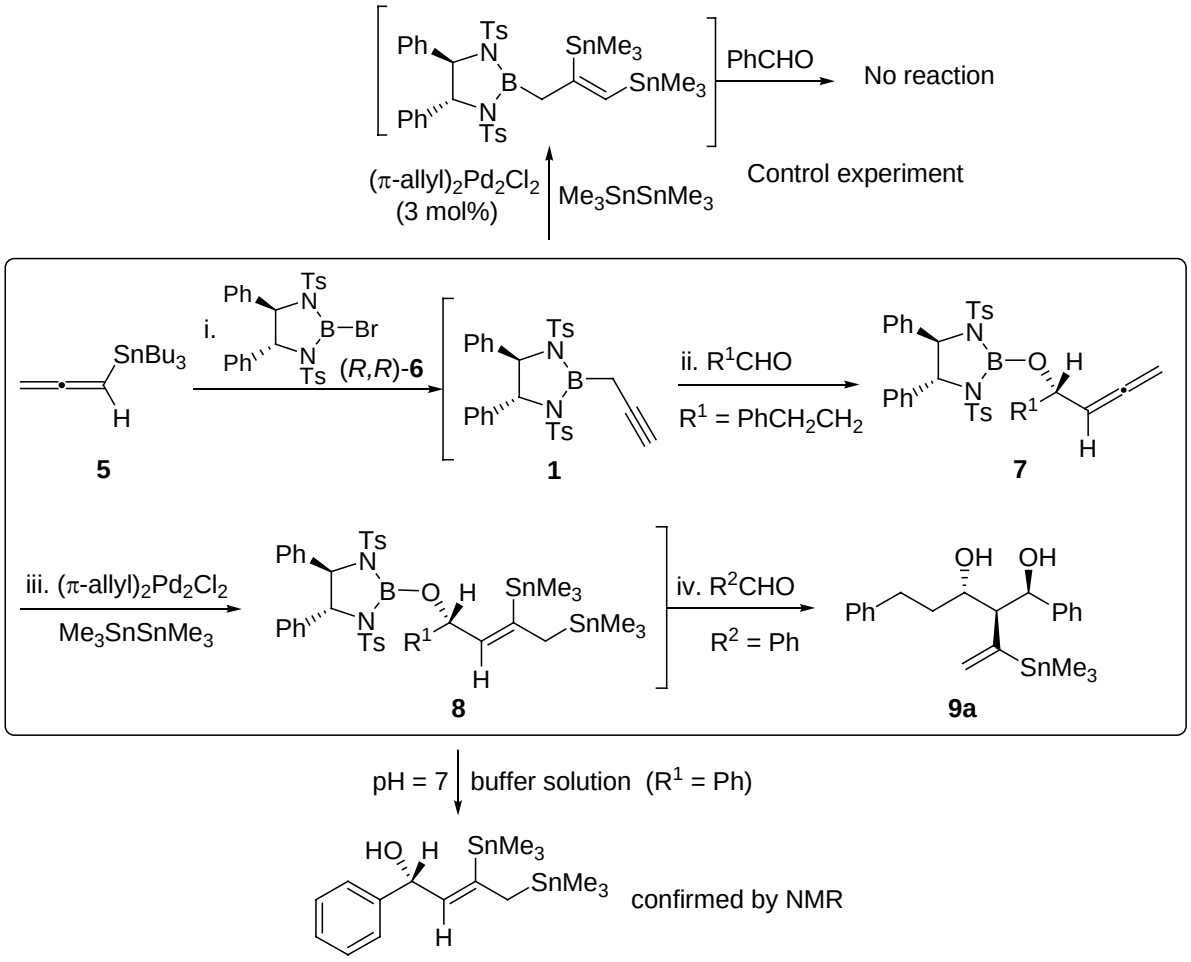
69451 Weinheim, Germany

Asymmetric Sequential Allylic Transfer Reaction for the Synthesis of 2-(1-Stannylvinyl)-1,3-diols: Concise Synthesis of (–)-Avenaciolide and (–)-Isoavenaciolide

Chan-Mo Yu,* Jinsuop Youn, and Juyoung Jung
Department of Chemistry and Institute of Basic Sciences, Sungkyunkwan University, Suwon 440-746, Korea

General: All reactions were run in flame-dried glassware under an atmosphere of nitrogen or argon. Tetrahydrofuran (THF) was dried by refluxing over sodium/benzophenone ketyl until a permanent purple coloration was presented, and distilled prior to use. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 prior to use. All liquid reagents and substrates purchased from the Aldrich were distilled properly prior to use, unless otherwise indicated. 1,2-Propadienyltributylstannane (**5**) was prepared according to the literature procedure (Tanaka, H.; Abdul Hai, A. K. M.; Ogawa, H.; Torri, S. *Synlett* 1993, 835). BBr_3 (99.99+%) was purchased from Aldrich and used without further purification. (*R*,*R*)- and (*S*,*S*)-1,2-diphenyl-1,2-diaminoethane were used as purchased from TCI. Purification was conducted by flash column chromatography on silica gel (230-400 mesh), eluting with a mixture of hexane and ethyl acetate, unless otherwise stated. All reactions were monitored by thin layer chromatography carried out on Merck silica gel plate (60 F_{254}) using UV light as visualizing agent and ethanolic anisaldehyde solution and heat as developing agent. Silica gel 60 (TA792685, 230-400 mesh) from Merck was used for column chromatography. The reported yields are for chromatographically pure isolated products. FT-IR spectra were recorded on a Nicolet 320. ^{1}H NMR spectra were recorded on a Varian Unity Inova at 500 MHz in $CDCl_3$ as a solvent with TMS or residual chloroform as the internal standard. ^{13}C NMR spectra were measured on a Varian Unity Inova at 125 MHz in $CDCl_3$ as a solvent. Optical rotations were measured on a JASCO P-1020 digital polarimeter at ambient temperature.

General Procedure: (*1R,2S,3S*)-1,5-Diphenyl-2-{1-(trimethylstannyl)vinyl}pentane-1,3-diol (8a).



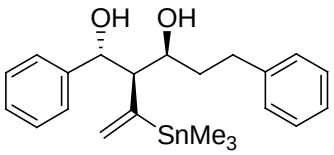
A flame-dried 20 mL Schlenk flask containing (+)-(*1R,2R*)-1,2-diphenyl-1,2-bis-*p*-toluenesulfonylamide (0.50 g, 0.96 mmol) was charged with dry CH_2Cl_2 (7 mL). The resulting mixture was cooled to 0 ^oC and treated with BBr_3 (freshly prepared 1 M solution in CH_2Cl_2, 1.1 mL, 1.1 mmol). The solution was stirred at 0 ^oC for 1 h, warmed to 20 ^oC and kept for additional 5 h, and then concentrated under vacuum (1 mmHg) through a side neck of the flask connected with three hold-cork valve. Dryness of the vacuum line was maintained with a drying tube containing anhydrous $CaSO_4$ and two traps (NaOH pellets and cold trap at –78 ^oC). Freshly distilled CH_2Cl_2 (5 mL) was added and evaporated under vauum as above. Freshly distilled CH_2Cl_2 (4 mL) was added and the homogeneous solution of (*R,R*)-**6** was cooled to –10 ^oC, and treated dropwise with 1,2-propadienyl-tributylstannane (**5**, 0.33 g, 1.00 mmol) in CH_2Cl_2 (1 mL). The reaction mixture was allowed to proceed at –10 ^oC overnight (ca 11 h). After cooling to –78 ^oC, hydrocinnamaldehyde (purified and distilled, 100 mg, 0.74 mmol) in CH_2Cl_2 (1 mL) was added over 10 min along the wall of the flask while keeping the temperature below –78 ^oC, and then stirred for 2 h. To the resulting mixture was added hexamethyldistannane (0.21 mL, 0.33 g, 1.01 mmol) in CH_2Cl_2 (0.5 mL)

followed by (π-allyl)$_2$Pd$_2$Cl$_2$ (8.3 mg, 0.022 mmol) in CH_2Cl_2 (0.5 mL). After warmed up to –40 ^oC, the mixture was stirred for 4 h. The resulting solution of 7 was cooled to –78 ^oC and a solution of benzaldehyde (0.08 mL, 83.6 mg, 0.78 mmol) in CH_2Cl_2 (1 mL) was added dropwise as same manner. The reaction was allowed to proceed for 4 h at –78 ^oC, and then quenched by addition of aqueous buffer solution (pH 7, 10 mL) followed by CH_2Cl_2 (ca 10 mL) to dissolve white precipitate (bis-sulfonamide). The aqueous layer was extracted with CH_2Cl_2 (ca 10 mL x 2). The combined organic extracts were washed with saturated $NaHCO_3$ (1x), brine (1x), dried over anhydrous Na_2SO_4, filtered, evaporated, and taken up ether (ca 30 mL). The solution was cooled to 0 ^oC for 20 min to complete precipitation of (+)-(*1R,2R*)-1,2-diphenyl-1,2-bis-*p*-toluenesulfonylamide by filtration through a sintered glass funnel, the filtrate was washed with cold 20 % KF (1x) and saturated aqueous $NaHCO_3$ (1x). The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product as fairly pure form. Final purification was effected by SiO_2 chromatography (Hexanes:EtOAc = 4:1) to afford **9a** (0.255 g, 0.57 mmol, 77%) as a colorless oil. R_f 0.29 (hexane:EtOAc = 3:1). $[\alpha]^{23}_D$ +18.15 (c 1.3, $CHCl_3$). IR (neat) 3435.2, 3026.6, 2948.0, 2922.3, 1062.8 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.04 (s, 9H; $J_{119Sn–1H}$ = 26.37 Hz), 1.60-1.68 (m, 1H), 1.81-1.88 (m, 1H), 2.08 (bs, 1H) 2.52 (bs, 1H), 2.58 (dd, 1H, *J* = 7.81, 3.91 Hz), 2.62-2.68 (m, 1H), 2.79-2.86 (m, 1H), 3.86-3.91 (m, 1H), 5.19 (d, 1H, *J* = 2.93 Hz), 5.29 (d, 1H, *J* = 1.95 Hz; $J_{119Sn–1H}$ = 35.65 Hz), 5.49 (d, 1H, *J* = 1.95 Hz; $J_{119Sn–1H}$ = 74.22 Hz), 7.15-7.21 (m, 4H), 7.21-7.34 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = –7.19 ($J_{119Sn–13C}$ = 170.42 Hz), 32.13, 37.98, 64.30, 71.78, 74.27, 126.14, 126.72, 127.46, 128.33, 128.70, 130.52, 130.63, 142.25, 143.32, 153.17. Anal. Calcd for $C_{22}H_{30}O_2Sn$: C, 59.35; H, 6.79. Found: C, 59.21; H, 6.69.

Formation of the intermedate 8 (R^1 = Ph) was confirmed by NMR after quenching with pH = 7 buffer solution (short columm on deactivated SiO_2 with Et_3N). R_f 0.83 (hexanes:EtOAc = 3:1). ^1H NMR (500MHz, $CDCl_3$) δ = 0.10 (s, 9H; $J_{119Sn–1H}$ = 25.88 Hz), 0.12 (s, 9H; $J_{119Sn–1H}$ = 26.13 Hz), 1.70 (d, 1H, *J* = 3.91 Hz), 2.20 (d, 1H, *J* = 10.26 Hz), 2.27 (d, 1H, *J* = 10.26 Hz), 5.44 (dd, 1H, *J* = 7.81, 3.91 Hz), 5.55 (d, 1H, *J* = 7.81 Hz), 7.32-7.36 (m, 3H), 7.37-7.41 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –9.23 ($J_{119Sn–13C}$ = 167.65 Hz), –8.66 ($J_{119Sn–13C}$ = 160.98 Hz), 20.26, 70.20, 126.56, 127.60, 128.76, 135.94, 144.39, 147.69.

Control Experiment (one third scale): After formation of **1** from the reaction of **5** with (*R,R*)-**6** as described above, the reaction mixture was cooled to –40 ^oC. To this mixture was treated with hexamethyldistannane followed by (π-allyl)$_2$Pd$_2$Cl$_2$ as exactly same conditions for the conversion of **7** to **8** (–40 ^oC for 4 h). After cooled to –78 ^oC, benzaldehyde was added, and then stirred for 5 h at same temperature. Most of benzaldehyde was recovered without the formation of any products.

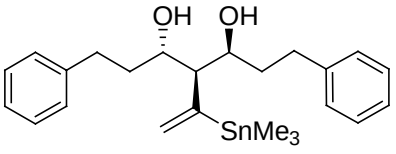
(*1R,2R,3S*)-1,5-Diphenyl-2-{1-(trimethylstannyl)vinyl}pentane-1,3-diol (9b).



9b

R_f 0.32 (hexane:EtOAc = 3:1). $[\alpha]^{23}_D$ +27.34 (c 0.8, $CHCl_3$). IR (neat) 3433.1, 3022.5, 2948.7, 2923.1, 1061.9 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.13 (s, 9H; $J_{119Sn–1H}$ = 26.37 Hz), 1.59-1.66 (m, 1H), 1.71-1.79 (m, 1H), 2.33 (d, 1H, *J* = 3.91 Hz), 2.46-2.53 (m, 1H), 2.56-2.63 (m, 2H), 2.69-2.75 (m, 1H), 4.16-4.21 (m, 1H), 4.90 (d, 1H, *J* = 7.81 Hz), 5.30 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 36.38 Hz), 5.56 (d, 1H, *J* = 1.95 Hz; $J_{119Sn–1H}$ = 76.42 Hz), 7.12-7.18 (m, 4H), 7.23-7.34 (m, 6H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.65 ($J_{119Sn–13C}$ = 172.10 Hz), 32.66, 37.41, 62.62, 70.41, 76.40, 126.03, 126.79, 127.80, 128.56, 128.64, 128.84, 130.53, 142.32, 143.65, 152.73. Anal. Calcd for $C_{22}H_{30}O_2Sn$: C, 59.35; H, 6.79. Found: C, 59.21; H, 6.69.

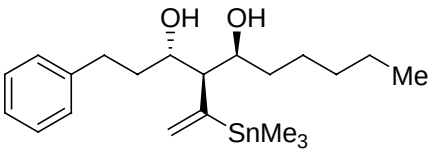
(*3S,5S*)-1,7-Diphenyl-4-(1-(trimethylstannyl)vinyl)heptane-3,5-diol (9c).



9c

R_f 0.33 (hexane:EtOAc = 3:1). $[\alpha]^{24}_D$ –26.83 (c 0.7, $CHCl_3$). IR (neat) 3437.1, 3023.6, 2948.5, 2924.4, 1061.9 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.06 (s, 9H; $J_{119Sn–1H}$ = 26.70 Hz), 1.58-1.67 (m, 2H), 1.68-1.78 (m, 2H), 1.85-1.93 (m, 1H), 1.95 (bs, 1H), 2.22(dd, 1H, *J* = 8.43, 2.45 Hz), 2.61-2.68 (m, 2H), 2.69-2.77(m, 1H), 2.79-2.87 (m, 1H), 3.81 (m, 1H), 4.17 (m, 1H), 5.39 (d, 1H, *J* = 2.25 Hz; $J_{119Sn–1H}$ = 35.14 Hz), 5.73 (d, 1H, *J* = 2.81 Hz; $J_{119Sn–1H}$ = 75.61 Hz), 7.15-7.21 (m, 6H), 7.25-7.31 (m, 4H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.91, 32.16, 32.69, 37.39, 37.81, 62.74, 70.48, 71.72, 126.11, 128.66, 128.74, 129.92, 142.27, 153.31. Anal. Calcd for $C_{24}H_{34}O_2Sn$: C, 60.91; H, 7.24. Found: C, 60.93; H, 7.18.

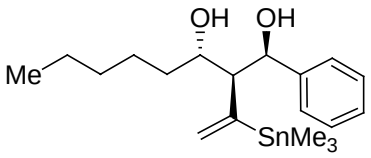
(*3S,4R,5S*)-1-Phenyl-4-{1-(trimethylstannyl)vinyl}decane-3,5-diol (9d).



9d

R_f 0.53 (hexane:EtOAc = 3:1). $[\alpha]^{24}_D$ –33.80 (c 0.7, $CHCl_3$). IR (neat) 3438.2, 3022.6, 2945.0, 2854.6, 1066.7 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.06 (s, 9H; $J_{119Sn–1H}$ = 26.28 Hz), 0.88 (t, 3H, *J* = 6.75 Hz), 0.25-1.33 (m, 6H), 1.34-1.40 (m, 2H), 1.60-1.68 (m, 1H), 1.81 (d, 1H, *J* = 3.37 Hz), 1.86 (d, 1H, *J* = 5.62 Hz), 1.87-1.93 (m, 1H), 2.20 (dd, 1H, *J* = 7.87, 2.25), 2.63-2.69 (m, 1H), 2.81-2.87 (m, 1H), 3.85 (m, 1H), 4.11 (m, 1H), 5.39 (d, 1H, *J* = 2.81 Hz; $J_{119Sn–1H}$ = 35.98 Hz), 5.72 (d, 1H, *J* = 2.81 Hz; $J_{119Sn–1H}$ = 76.17 Hz), 7.16-7.22 (m, 2H), 7.25-7.30 (m, 3H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.92, 14.23, 22.83, 25.74, 31.95, 32.22, 35.52, 37.83, 62.32, 70.99, 71.83, 126.10, 128.63, 128.71, 129.73, 142.32, 153.48. Anal. Calcd for $C_{21}H_{36}O_2Sn$: C, 57.43; H, 8.26. Found: C, 57.36; H, 8.11.

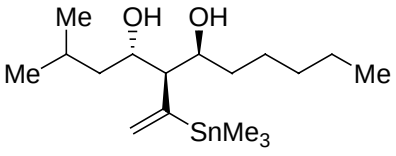
(*1R,2S,3S*)-1-Phenyl-2-{1-(trimethylstannyl)vinyl}octane-1,3-diol (9e).



9e

R_f 0.40 (hexane:EtOAc = 3:1). $[\alpha]^{23}_D$ –31.55 (c 0.9, $CHCl_3$). IR (neat) 3438.5, 3021.6, 2944.3, 2855.7, 1066.6 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.10 (s, 9H; $J_{119Sn–1H}$ = 25.72 Hz), 0.90 (t, 3H, *J* = 6.50 Hz), 1.29-1.32 (m, 6H), 1.48-1.54 (m, 2H), 1.91 (dd, 1H, *J* = 2.25, 2.25 Hz), 2.19 (bs, 1H), 2.57-2.59 (m, 1H), 3.87 (m, 1H), 5.22 (dd, 1H, *J* = 3.75, 3.75 Hz), 5.32 (d, 1H, *J* = 2.76 Hz; $J_{119Sn–1H}$ = 36.74 Hz), 5.53 (d, 1H, *J* = 2.76 Hz; $J_{119Sn–1H}$ = 77.15 Hz), 7.23-7.35 (m, 5H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.91, 22.39, 23.63, 32.21, 37.85, 44.54, 62.77, 68.74, 71.80, 126.11, 128.10, 128.71, 129.78, 142.32, 153.60. Anal. Calcd for $C_{19}H_{32}O_2Sn$: C, 55.50; H, 8.84. Found: C, 55.44; H, 8.80.

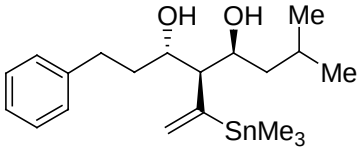
(*4S,5R,6S*)-2-Methyl-5-{1-(trimethylstannyl)vinyl}undecane-4,6-diol (9f).



9f

R_f 0.57 (hexane:EtOAc = 3:1). $[\alpha]^{24}_D$ –83.34 (c 0.6, $CHCl_3$). IR (neat) 3435.3, 2948.0, 2925.4, 2851.6, 1061.5 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.12 (s, 9H; $J_{119Sn–1H}$ = 27.10 Hz), 0.86-0.91 (m, 3H), 0.93 (d, 6H, *J* = 6.86 Hz), 1.24-1.34 (m, 6H), 1.24-1.34 (m, 2H), 1.34-1.43 (m, 2H), 1.80 (septet, 1H, *J* = 6.84 Hz), 1.83-1.89 (m, 1H), 2.06-2.11 (m, 1H), 2.11 (dd, 1H, *J* = 7.81, 1.95 Hz), 3.85 (dt, 1H, *J* = 6.84, 6.84 Hz), 4.09-4.14 (m, 1H), 5.40 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 36.62 Hz), 5.72 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 77.15 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.80 ($J_{119Sn–13C}$ = 168.20 Hz), 14.24, 21.88, 22.84, 24.15, 24.87, 25.77, 32.07, 35.47, 45.52, 62.73, 70.69, 70.93, 129.61, 153.76. Anal. Calcd for $C_{17}H_{36}O_2Sn$: C, 52.20; H, 9.28. Found: C, 52.41; H, 9.11.

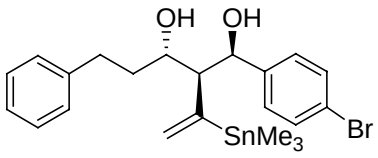
(*3S,4S,5S*)-7-Methyl-1-phenyl-4-{1-(trimethylstannyl)vinyl}octane-3,5-diol (9g).



9g

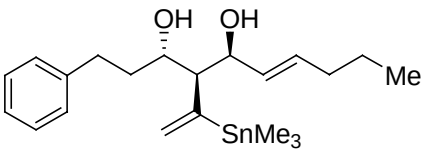
R_f 0.32 (hexane:EtOAc = 3:1). $[\alpha]^{25}_D$ –44.13 (c 0.9, $CHCl_3$). IR (neat) 3443.6, 3028.6, 2955.2, 1062.4, 1495.1 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.12 (s, 9H; $J_{119Sn–1H}$ = 27.10 Hz) , 0.96 (d, 3H, *J* = 11.72 Hz), 1.95 (d, 3H, *J* = 11.72 Hz), 1.12-1.77 (m, 1H), 1.38-1.44 (m, 1H), 1.67-1.78 (m, 2H), 1.90 (br, 1H), 1.92-1.99 (m, 2H), 2.22 (dd, 1H, *J* = 7.81, 1.95 Hz), 2.70-2.76 (m, 1H), 2.88-2.94 (m, 1H), 3.87 (m, 1H), 4.30 (m, 1H), 5.46 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 36.01 Hz), 5.78 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 76.54 Hz), 7.23-7.27 (m, 3H), 7.32-7.36 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –8.25, 22.39, 23.63, 24.67, 32.21, 37.85, 44.54, 62.62, 68.75, 71.83, 126.12, 128.70, 128.72, 129.79, 142.31, 153.58. Anal. Calcd for $C_{20}H_{34}O_2Sn$: C, 56.50; H, 8.06. Found: C, 56.28; H, 8.13.

(*1R,2S,3S*)-1-(4-Bromophenyl)-5-phenyl-2-{1-(trimethylstannyl)vinyl}pentane-1,3-diol (9h). R_f 0.34 (hexane:EtOAc = 3:1). $[\alpha]^{23}_D$ +39.84 (c 0.7, $CHCl_3$). IR (film) 3435.2, 3028.5, 2941.5, 2918.9, 1069.9 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.08 (s, 9H; $J_{119Sn–1H}$ = 26.35 Hz), 1.63-1.76 (m, 1H), 1.84-1.96 (m, 1H), 2.11 (d, 1H, *J* = 6.01 Hz), 2.54 (dd, 1H, *J* = 8.02, 3.34 Hz), 2.65-2.76 (m, 2H), 2.82-2.92 (m, 1H), 3.89-3.98 (m, 1H), 5.27 (dd, 1H, *J* = 3.34, 3.34 Hz), 5.30 (d, 1H, *J* = 2.67 Hz; $J_{119Sn–1H}$ = 34.78 Hz), 5.45 (d, 1H, *J* = 2.67 Hz; $J_{119Sn–1H}$ = 74.48 Hz), 7.12-7.14 (m, 2H), 7.18-7.20 (m, 3H), 7.28-7.31 (m, 2H), 7.42-7.43 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –7.13, 32.12, 37.95, 65.29, 71.73, 73.27, 120.94, 126.22, 128.38, 128.68, 128.70, 128.77, 130.93, 131.22, 142.07, 142.60, 152.46, 207.25. Anal. Calcd for $C_{22}H_{29}BrO_2Sn$: C, 50.42; H, 5.58. Found: C, 50.41; H, 5.71.



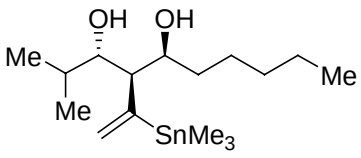
9h

(*3S,4S,5S*)-(*6E*)-1-Phenyl-4-{1-(trimethylstannyl)vinyl}dec-6-ene-3,5-diol (9i). R_f 0.40 (hexane:EtOAc = 3:1). $[\alpha]^{23}_D$ –28.76 (c 0.9, $CHCl_3$). IR (neat) 3442.1, 3020.5, 2941.5, 2850.7, 1057.1 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.08 (s, 9H; $J_{119Sn–1H}$ = 26.37 Hz), 0.89 (t, 3H, *J* = 7.32 Hz), 1.39 (sextet, 2H, *J* = 7.42 Hz), 1.60-1.66 (m, 1H), 1.81-1.86 (m, 1H), 1.88 (bs, 1H), 2.00 (q, 2H, *J* = 7.49 Hz), 2.23-2.26 (m, 1H), 2.35 (dd, 1H, *J* = 8.79, 3.91 Hz), 2.62-2.68 (m, 1H), 2.81-2.87 (m, 1H), 3.81-3.87 (m, 1H), 4.44-4.48 (m, 1H), 5.39 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 35.40 Hz), 5.50 (dd, 1H, *J* = 15.63, 7.81 Hz), 5.65 (dt, 1H, *J* = 15.63, 6.84 Hz), 5.72 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 75.20 Hz), 7.16-7.19 (m, 3H), 7.25-7.29 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –7.12 ($J_{119Sn–13C}$ = 174.31 Hz), 13.91, 22.49, 32.03, 34.55, 37.74, 63.23, 71.41, 73.45, 126.05, 128.67, 128.72, 130.07, 131.73, 133.58, 142.45, 153.55. Anal. Calcd for $C_{21}H_{34}O_2Sn$: C, 57.69; H, 7.84. Found: C, 57.58; H, 7.99.



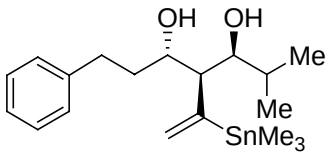
9i

(*3S,4R,5S*)-2-Methyl-4-{1-(trimethylstannyl)vinyl}decane-3,5-diol (9j). R_f 0.43 (hexane:EtOAc = 3:1). $[\alpha]^{24}_D$ –29.33 (c 0.9, $CHCl_3$); IR (film) 3445.9, 2958.1, 2930.7, 2872.3, 1465.3 cm^{-1}. ^1H NMR(500MHz, $CDCl_3$) δ = 0.11 (s, 9H; $J_{119Sn–1H}$ = 26.37 Hz), 0.83 (d, 3H, *J* = 6.84 Hz), 0.88 (t, 3H, *J* = 6.84 Hz), 0.97 (d, 3H, *J* = 6.84 Hz), 1.24-1.33 (m, 6H), 1.33-1.41(m, 2H), 1.65 (d, 1H, *J* = 5.86 Hz), 1.71-1.76 (m, 1H), 1.93 (d, 1H, *J* = 2.93 Hz), 2.29 (dd, 1H, *J* = 8.79, 1.95 Hz), 3.65-3.69 (m, 1H), 4.05-4.10 (m, 1H), 5.38 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 36.62 Hz), 5.73 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 76.68 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.79, 14.26, 14.31, 20.56, 22.85, 25.84, 30.21, 32.10, 35.58, 59.41, 71.18, 76.31, 129.13, 153.47. Anal. Calcd for $C_{16}H_{34}O_2Sn$: C, 50.95; H, 9.09. Found: C, 51.11; H, 8.97.



9j

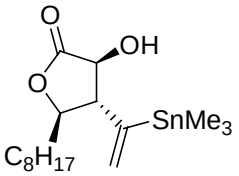
(*3S,4S,5S*)-6-Methyl-1-phenyl-4-{1-(trimethylstannyl)vinyl}heptane-3,5-diol (9k).



9k

R_f 0.42 (hexane:EtOAc = 3:1). $[\alpha]^{25}_D$ –49.85 (c 1.2, $CHCl_3$); IR (film) 3443.0, 3027.1, 2956.3, 2926.5, 1602.6, 1454.4 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.13 (s, 9H; $J_{119Sn–1H}$ = 27.10 Hz), 0.88 (d, 3H, *J* = 6.84 Hz), 1.06 (d, 3H, *J* = 6.84 Hz), 1.65-1.76 (m, 2H), 1.97 (d, 1H, *J* = 5.86 Hz), 1.97-2.02 (m, 1H), 2.22 (d, 1H, *J* = 2.93 Hz), 2.47 (dd, 1H, *J* = 8.79, 1.95 Hz), 2.71-2.78 (m, 1H), 2.91-2.98 (m, 1H), 3.70-3.74 (m, 1H), 3.84-3.90 (m, 1H), 5.48 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 18.07 Hz), 5.85 (d, 1H, *J* = 2.93 Hz; $J_{119Sn–1H}$ = 76.91 Hz), 7.25-7.30 (m, 3H), 7.33-7.39 (m, 2H). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.73 ($J_{119Sn–13C}$ = 172.64 Hz), 18.63, 19.60, 31.05, 32.32, 37.72, 60.01, 71.72, 76.74, 126.11, 128.71, 129.61, 142.37, 153.21. Anal. Calcd for $C_{19}H_{32}O_2Sn$: C, 55.50; H, 7.84. Found: C, 55.38; H, 7.83.

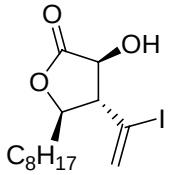
(*3S,4S,5R*)-3-Hydroxy-5-octyl-4-{1-(trimethylstannyl)vinyl}-dihydrofuran-2(*3H*)-one (13). Compound **13** was prepared according to the above general procedure for **9a** except the use of (*1S,2S*)-1,2-diphenyl-1,2-bis-*p*-toluenesulfonylamide instead of (*R,R*)-5 (R^1 = $C_8H_{17}CHO$, R^2 = MeO_2CCHO). After usual work up procedure, column chromatography on silica gel gave **13** in 75% yield as a sole product.



13

R_f 0.43 (hexane:EtOAc = 3:1). $[\alpha]^{23}_D$ +31.80 (c 1.3, $CHCl_3$). IR (neat) 3445.4, 2927.3, 2856.7, 1775.1 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ = 0.23 (s, 9H; $J_{119Sn–1H}$ = 53.00 Hz), 0.88 (t, 3H, *J* = 6.84 Hz), 1.22-1.43 (m, 12H), 1.51-1.60 (m, 1H), 1.70-1.76 (m,1H), 2.71 (d, 1H, *J* = 2.93 Hz), 2.88 (dd, 1H, *J* = 10.25, 10.25 Hz), 4.20 (ddd, 1H, *J* = 10.25, 10.25, 2.93 Hz), 4.26 (dd, 1H, *J* = 10.25, 2.93 Hz), 5.45 (d, 1H, *J* = 1.95 Hz; $J_{119Sn–1H}$ = 65.92 Hz), 5.90 (d, 1H, *J* = 1.95 Hz; $J_{119Sn–1H}$ = 136.23 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = –8.18, 14.29, 22.86, 25.79, 29.38, 29.52, 29.57, 32.05, 33.35, 61.35, 73.75, 80.9, 130.56, 149.92, 176.23. Anal. Calcd for $C_{17}H_{32}O_3Sn$: C, 50.65; H, 8.00. Found: C, 50.78; H, 8.11.

(*3S,4S,5R*)-3-Hydroxy-4-(1-iodovinyl)-5-octyl-dihydrofuran-2(*3H*)-one (14). To a stirred solution of **13** (250 mg, 0.62 mmol) in CH_2Cl_2 (10 mL) was added N-iodosuccinimide (280 mg, 1.24 mmol) at –78 °C. The pink mixture was stirred for 2 h at –78 °C and then quenched by addition of aqueous $Na_2S_2O_3$ (10%, 5 mL). The aqueous layer was extracted with CH_2Cl_2 (ca 10 mL x 2). The combined organic extracts were washed with brine (1x), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Fresh column chromatography on silica gel (hexanes:EtOAc = 3:1) afforded **14** (200 mg, 0.55 mmol, 88%) as a colorless liquid.

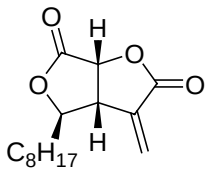


14

R_f 0.25 (hexane:EtOAc = 3:1). $[\alpha]^{24}_D$ +35.70 (c 1.2, $CHCl_3$). IR (neat): 3432.8, 2926.4, 2855,5, 1781.7 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.88 (t, 3H, *J* = 6.84

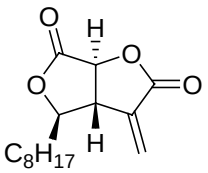
Hz), 1.23-1.37 (m, 10H), 1.38-1.46 (m, 1H), 1.49-1.57 (m, 1H), 1.60-1.67 (m, 1H), 1.69-1.76 (m, 1H), 2.34 (dd, 1H, *J* = 9.77, 9.77 Hz), 2.77 (bs, 1H), 4.28 (ddd, 1H, *J* = 9.77, 9.77, 3.58 Hz), 4.48 (d, 1H, *J* = 9.77 Hz), 6.05 (d, 1H, *J* = 1.95 Hz), 6.50 (d, 1H, *J* = 1.95 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = 14.30, 22.86, 25.41, 29.37, 29.53, 31.13, 32.04, 33.11, 61.37, 73.25, 80.57, 107.79, 132.03, 174.92. Anal. Calcd for $C_{14}H_{23}IO_3$: C, 45.91; H, 6.33. Found: C, 45.88; H, 6.41.

(–)-Avenaciolide (3). A stainless steel autoclave was charged with **14** (183 mg, 0.50 mmol), anhydrous K_2CO_3 (207 mg, 1.5 mmol), and $Pd(PPh_3)_4$ (13 mg, 0.01 mmol) in CH_3CN (7 mL). The system was flushed three times with CO (20 atm), and then the autoclave was pressurized to 100 atm. The mixture was stirred at 70 °C for 1 h. The solution was then cooled and filtered on celite using a sintered glass funnel and then washed with ether (2x). Combined organics were concentrated under reduced pressure to give crude products. The diastereomeric ratio turned out to be 95:5 as judged by the analysis of 500 MHz ^{1}H NMR of crude products (after short filteration on silicagel). Final purification was effected by column chromatography to give the cyclized product **3** (89.3 mg, 0.335 mmol, 67%) as a white solid. R_f 0.41 (hexane:EtOAc = 3:1). $[\alpha]^{24}_D$ –44.62 (c 0.9, $CHCl_3$). IR (neat) 3951.2, 2859.5, 1785.3, 1662.8 cm^{-1}. ^{1}H NMR (500MHz, $CDCl_3$) δ = 0.89 (t, 3H, *J* = 7.30 Hz), 1.23-1.57 (m, 12H), 1.77-1.85 (m, 2H), 3.55 (m, 1H), 4.42 (m, 1H), 5.04 (d, 1H, *J* = 7.80 Hz), 5.87 (d, 1H, *J* = 1.95 Hz), 6.48 (d, 1H, *J* = 1.95 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = 14.3, 22.84, 25.06, 29.35, 29.55, 29.93, 32.00, 36.34, 44.48, 74.48, 85.29, 126.39, 134.89, 167.60, 169.81. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.45; H, 8.38.



(–)-Avenaciolide (**3**)

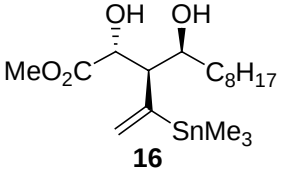
Compound 15. R_f 0.56 (hexane:EtOAc = 3:1). $[\alpha]^{27}_D$ –36.43 (c 0.4, $CHCl_3$). IR (neat) 3951.8, 2859.3, 1785.8, 1662.1 cm^{-1}. ^{1}H NMR (500MHz, $CDCl_3$) δ = 0.88 (t, 3H, *J* = 6.84 Hz), 1.21-1.45 (m, 12H), 1.61-1.71 (m, 1H), 1.72-1.82 (m, 1H), 3.48 (dd, 1H, *J* = 10.58, 10.58 Hz), 4.48 (td, 1H, *J* = 10.58, 2.93 Hz), 5.53 (d, 1H, *J* = 10.58 Hz), 5.85 (d, 1H, *J* = 2.81 Hz), 6.48 (d, 1H, *J* = 2.81 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = 14.29, 22.86, 25.60, 29.37, 29.43, 29.93, 32.02, 33.34, 48.94, 74.87, 80.24, 128.76, 135.13, 165.38, 170.24. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.55; H, 8.41.



15

(*2S,3S,4R*)-Methyl 2,4-dihydroxy-3-(1-(trimethylstannyl)vinyl)dodecanoate (16).

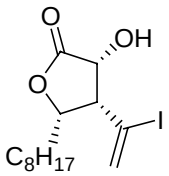
Compound **16** was prepared according to the above general procedure for **9a** except reaction time for the second allylic transfer reaction with $C_8H_{17}CHO$ for 12 h at –78 °C. After usual work up procedure, column chromatography on silica gel gave **16** in 54%



16

yield as a sole product. R_f 0.36 (hexanes:EtOAc = 3:1). $[\alpha]^{25}_D$ –47.03 (c 1.2, $CHCl_3$). IR (film) 3466.8, 2926.8, 2854.9, 1733.1 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.13 (s, 9H; $J_{119Sn–1H}$ = 20.04 Hz), 0.88 (t, 3H, J = 6.63 Hz), 1.15-1.63 (m, 14H), 1.90-1.98 (bs, 1H), 2.39 (dd, 1H, J = 8.05, 2.24 Hz), 2.78 (m, 1H), 3.69 (s, 3H), 4.00-4.09 (bs, 1H), 4.36 (dd, 1H, *J* = 8.03 Hz), 5.36 (d, 1H, *J* = 2.79 Hz; $J_{119Sn–1H}$ = 20.04 Hz), 5.68 (d, 1H, *J* = 2.79 Hz; $J_{119Sn–1H}$ = 20.04 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = –6.59, 14.31, 22.89, 25.88, 29.45, 29.74, 29.74, 32.09, 35.46, 51.82, 61.73, 70.43, 72.95, 129.60, 152.22, 175.52. Anal. Calcd for $C_{18}H_{36}O_4Sn$: C, 49.68; H, 8.34. Found: C, 49.75; H, 8.33. Enantiomeric purity was confirmed by following experiments: First allylated product, allenyl carbinol, was isolated and then immediately reduced with $LiAlH_4$ at –78 °C in ether to give the diol. This diol was treated with (+)-MTPA-Cl at –20 °C and pyridine in CH_2Cl_2 to afford the corresponding mono Mosher ester. We could not detect any minor diasteromer by the analysis of 500 MHz ^1H NMR.

(*3R,4S,5S*)-3-Hydroxy-4-(1-iodovinyl)-5-octyl-dihydrofuran-2(*3H*)-one (18).

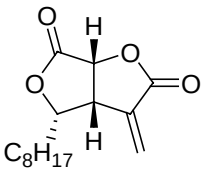


18

To a stirred solution of **16** (205 mg, 0.47 mmol) in CH_2Cl_2 (10 mL) was added N-iodosuccinimide (211 mg, 0.94 mmol) at –78 °C. The pink mixture was stirred for 1 h at –78 °C. At this time, compounds **17** [^1H NMR (500MHz, $CDCl_3$) δ = 0.88 (t, 3H, *J* = 6.90 Hz), 1.21-1.40 (m, 12H), 1.52-1.69 (m, 2H), 2.26 (bs, 1H), 2.70 (dd, 1H, *J* = 4.70, 4.70 Hz), 3.20 (bs, 1H), 3.82 (s, 3H), 4.00 (m, 1H), 4.53 (d, 1H, *J* = 5.40 Hz), 6.11 (d, 1H, *J* = 1.63 Hz), 6.53 (d, 1H, *J* = 1.63 Hz)] and **18** were formed about 1:1 mixture. Without isolation, to the resulting mixture CF_3CO_2H (5.3 mg, 0.047 mmol) was added at –78 °C and stirred for an additional 2 h. Reaction was quenched by the addition of aqueous $Na_2S_2O_3$ (10%, 5 mL). The aqueous layer was extracted with CH_2Cl_2 (ca 10 mL x 2). The combined organic extracts were washed with brine (1x), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Fresh column chromatography on silica gel (hexanes:EtOAc = 3:1) afforded **18** (132.5 mg, 0.361 mmol, 77%) as a colorless liquid. R_f 0.66 (hexanes:EtOAc = 1:1). $[\alpha]^{25}_D$ –29.83 (c 1.1, $CHCl_3$). IR (film) 3388.5, 2922.8, 2853.3, 1760.6 cm^{-1}. ^1H NMR (500MHz, $CDCl_3$) δ = 0.89 (t, 3H, J = 7.00 Hz), 1.22-1.32 (m, 12H), 1.49-1.58 (m, 1H), 1.70-1.78 (m, 1H), 1.97-2.05 (m, 1H), 3.47 (dd, 1H, J = 7.89, 5.20 Hz), 4.52 (ddd, 1H, J = 8.73, 5.20, 5.20 Hz), 4.56 (d, 1H, J = 7.89 Hz), 6.16 (d, 1H, J = 1.65 Hz), 6.36 (d, 1H, J = 1.65 Hz). ^{13}C NMR (125MHz, $CDCl_3$): δ 14.30, 22.87, 26.10, 29.44, 29.56, 29.87, 29.93, 32.04, 54.91, 71.38, 79.54, 116.54, 133.58, 175.87. Anal. Calcd for $C_{14}H_{23}IO_3$: C, 45.91; H, 6.33. Found: C, 45.78; H, 6.6.44.

(–)-Isoavenaciolide (4). Compound **4** was prepared according to the above procedure for **3**. After usual work up procedure, column chromatography on silica gel gave (–)-Isoavenaciolide (**4**) in 78% yield as a sole product. R_f 0.50 (hexane:EtOAc = 1:1). $[\alpha]^{27}_D$ –

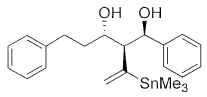
124.2 (c 1.2, EtOH). IR (film) 2924.0, 2853.3, 1767.3 cm^{-1}. ^{1}H NMR (500MHz, $CDCl_3$) δ = 0.90 (t, 3H, J = 7.00 Hz), 1.21-1.51 (m, 10H), 1.53-1.73 (m, 4H), 4.00 (ddt, 1H, J = 8.33, 8.33, 2.41 Hz), 4.77 (m, 1H), 5.12 (d, 1H, J = 8.73 Hz), 5.89 (d, 1H, J = 2.23 Hz), 6.63 (d, 1H, J = 2.59 Hz). ^{13}C NMR (125MHz, $CDCl_3$) δ = 14.28, 22.85, 26.78, 29.37, 29.56, 29.93, 32.00, 32.63, 41.98, 74.94, 80.63, 129.06, 131.12, 167.93, 170.08. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.57; H, 8.55.



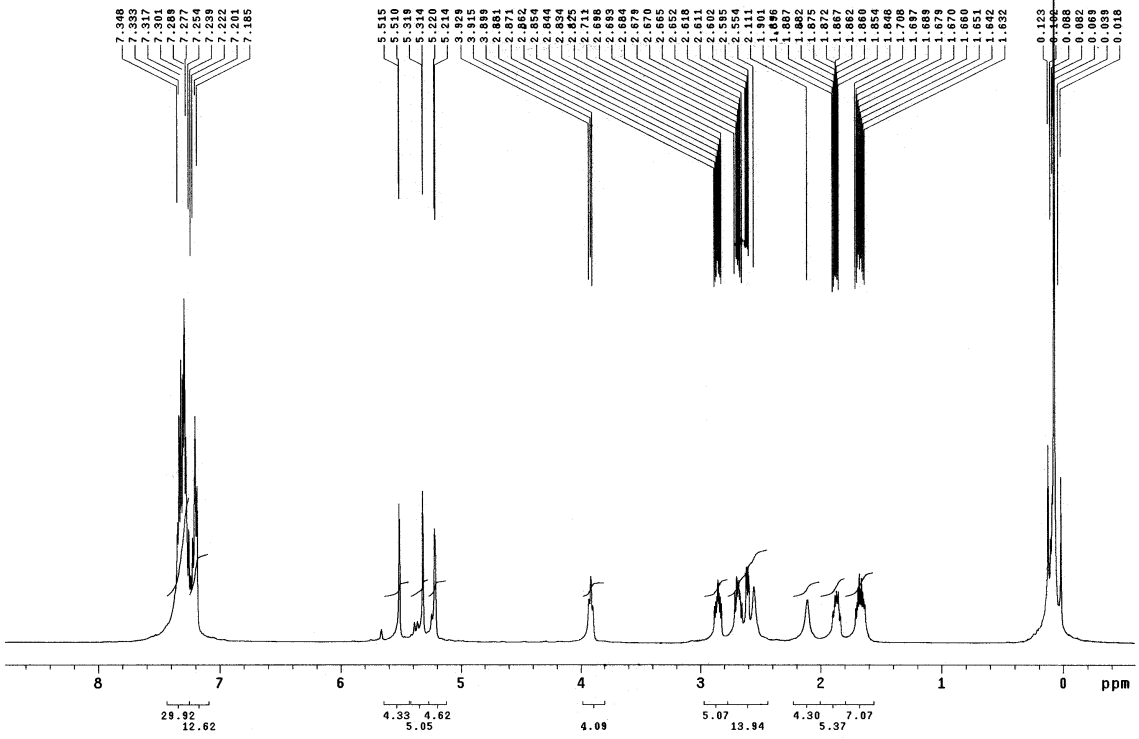
(–)-Isoavenaciolide (**4**)

JSY2-112

Pulse Sequence: s2pul

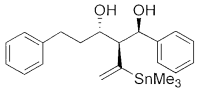


9a

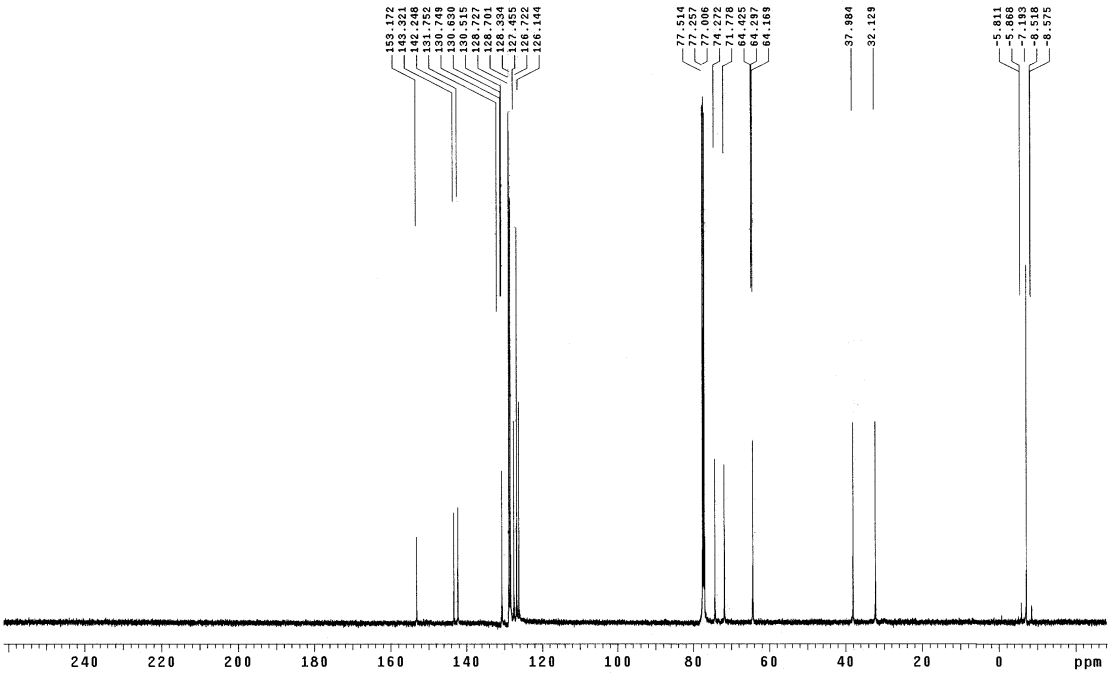


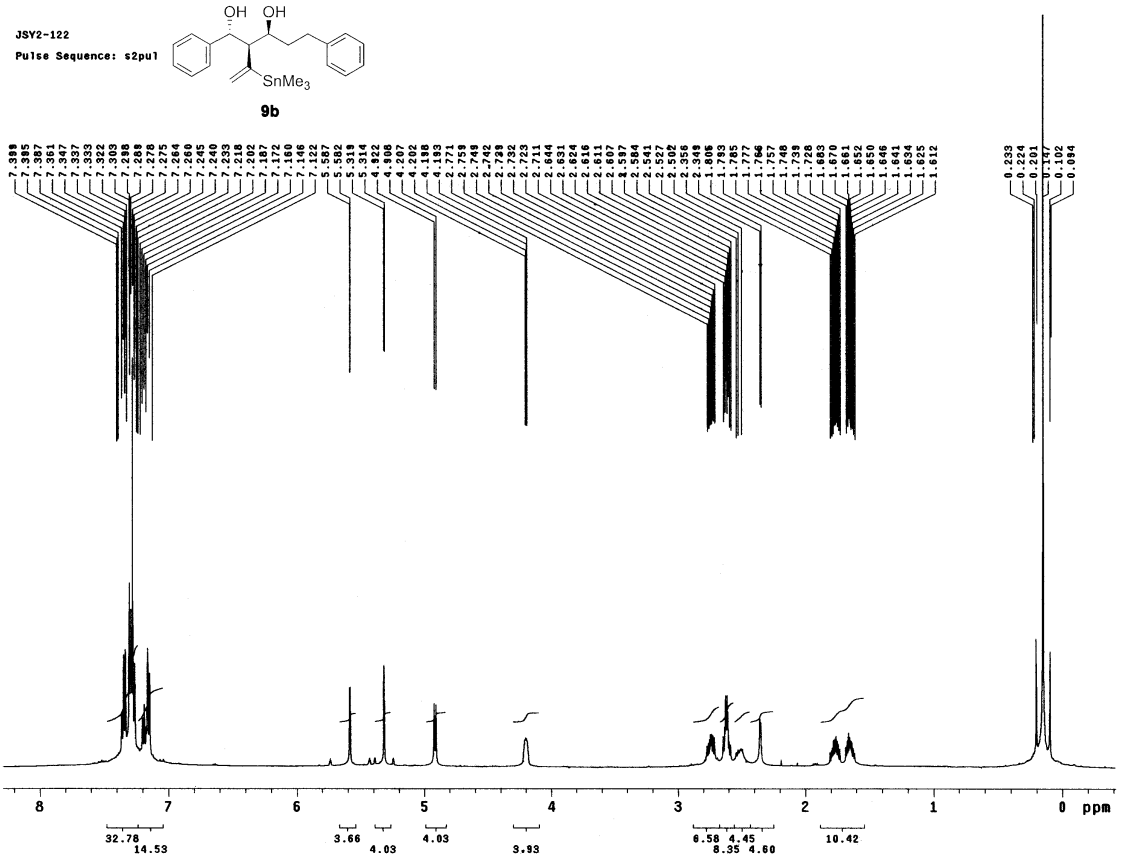
JSY2-112-13C

Pulse Sequence: s2pul



9a

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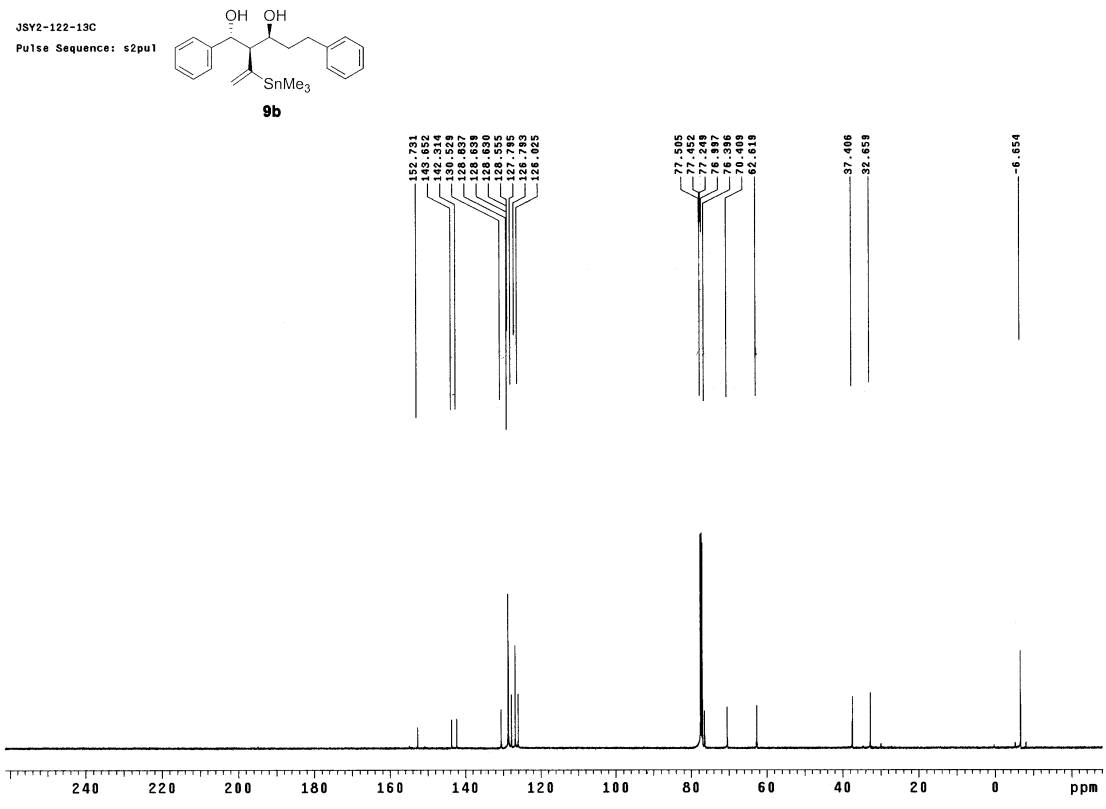
3.93
6.58
4.45
8.35
4.60
10.42


JSY2-122-13C
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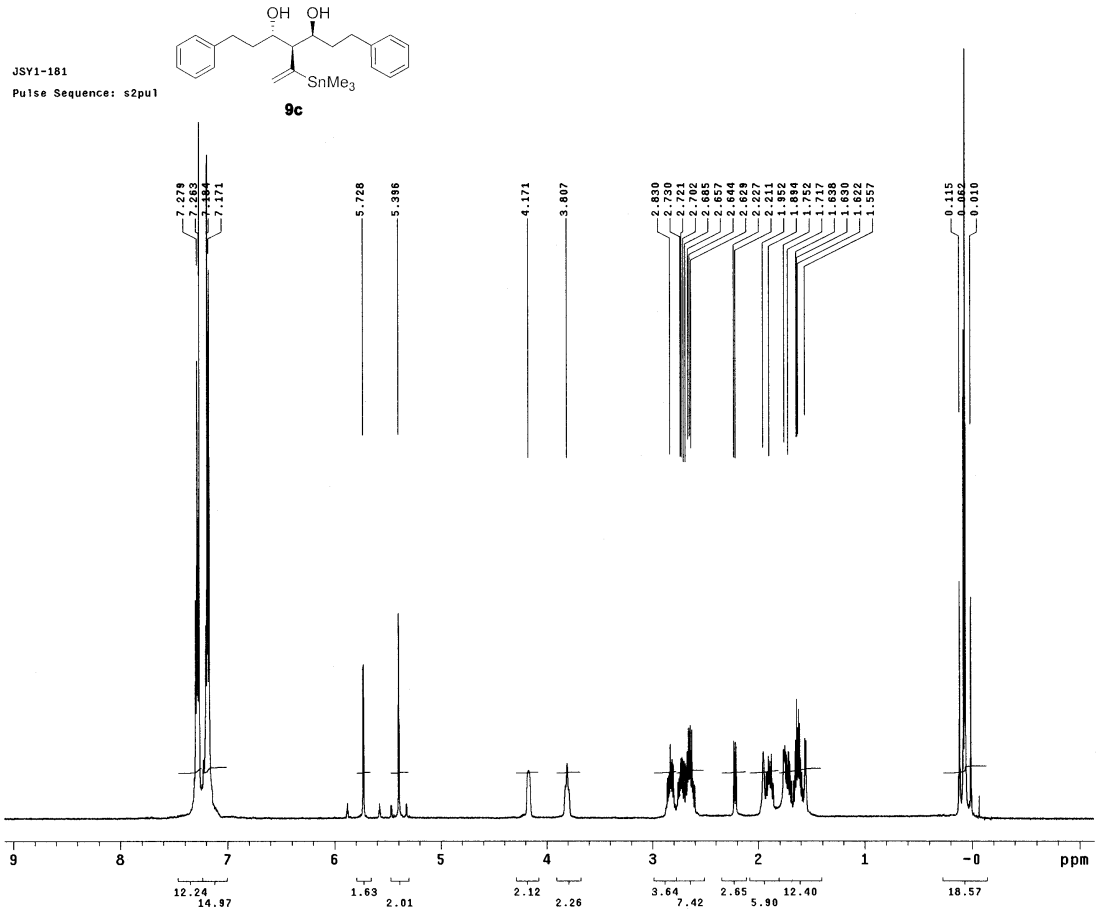
SnMe3
9b
ppm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Pulse Sequence: s2pul
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7.171
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2.730
2.721
2.702
2.685
2.657
2.644
2.628
2.227
2.211
1.952
1.894
1.752
1.717
1.638
1.630
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1.557
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9
8
7
6
5
4
3
2
1
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1.63
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2.12
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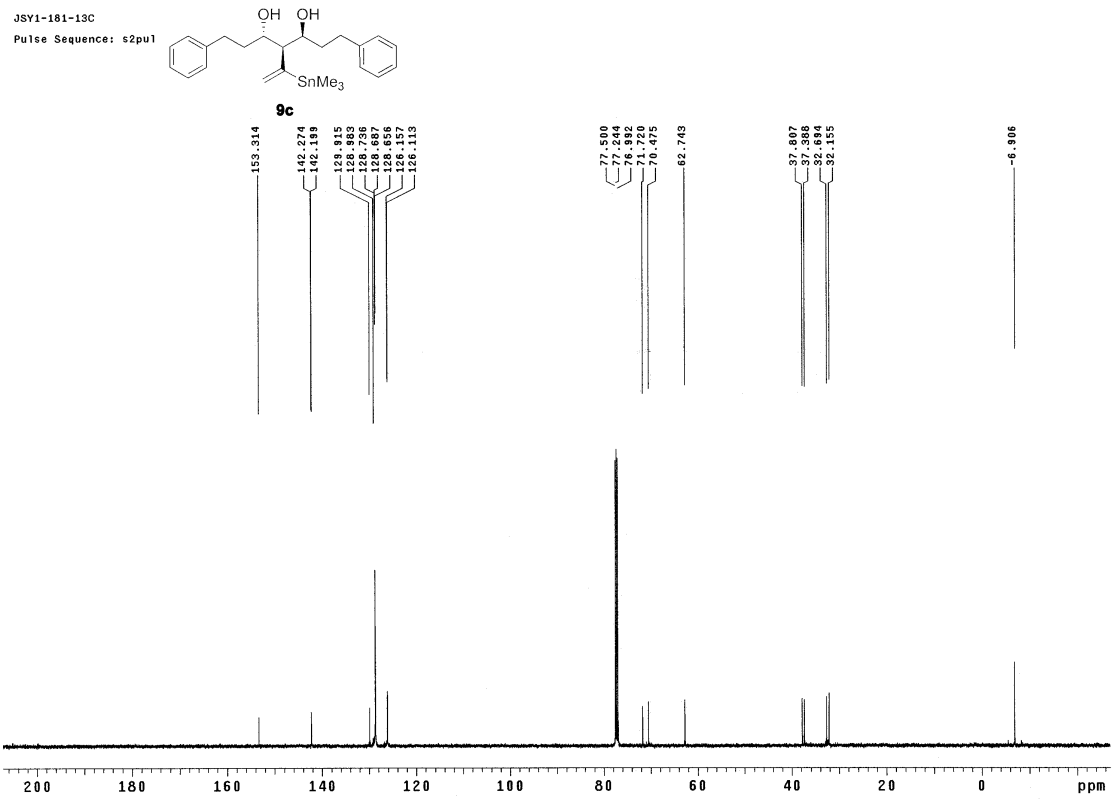
3.64
7.42
2.65
5.90
12.40
18.57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76.992
71.720
70.475
62.743
37.807
37.388
32.684
32.155
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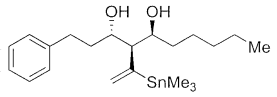
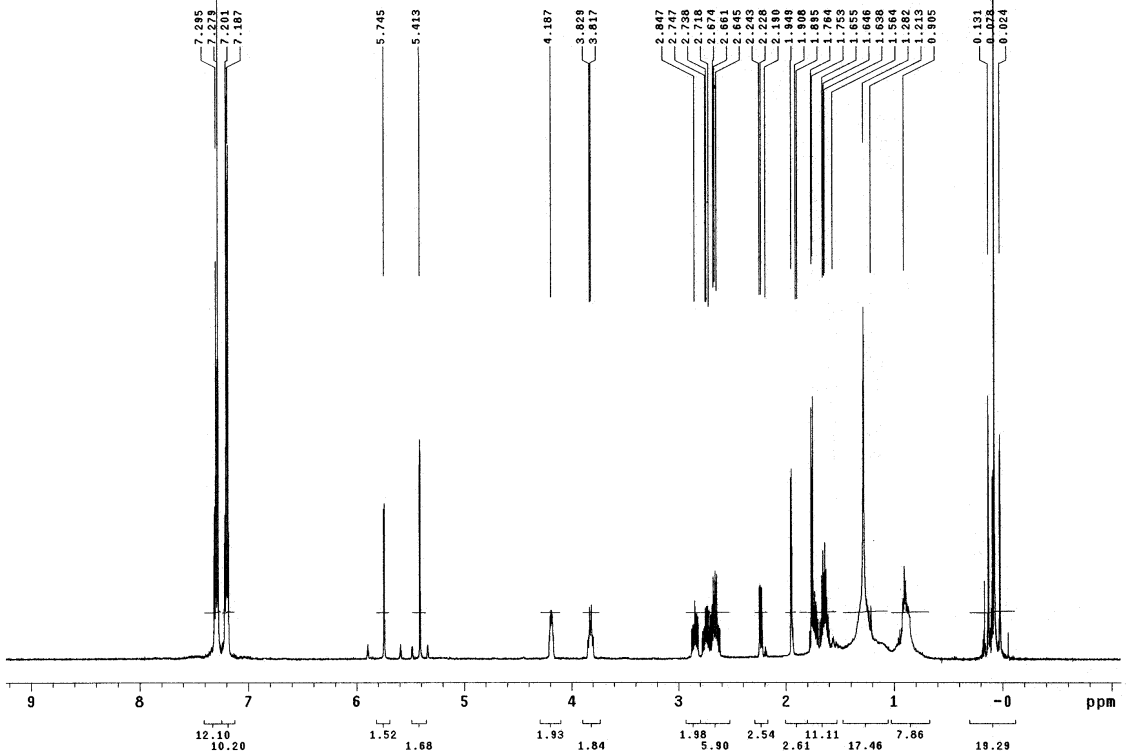
200
180
160
140
120
100
80
60
40
20
0
ppm

JSY1-182

Pulse Sequence: s2pul

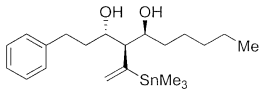


9d

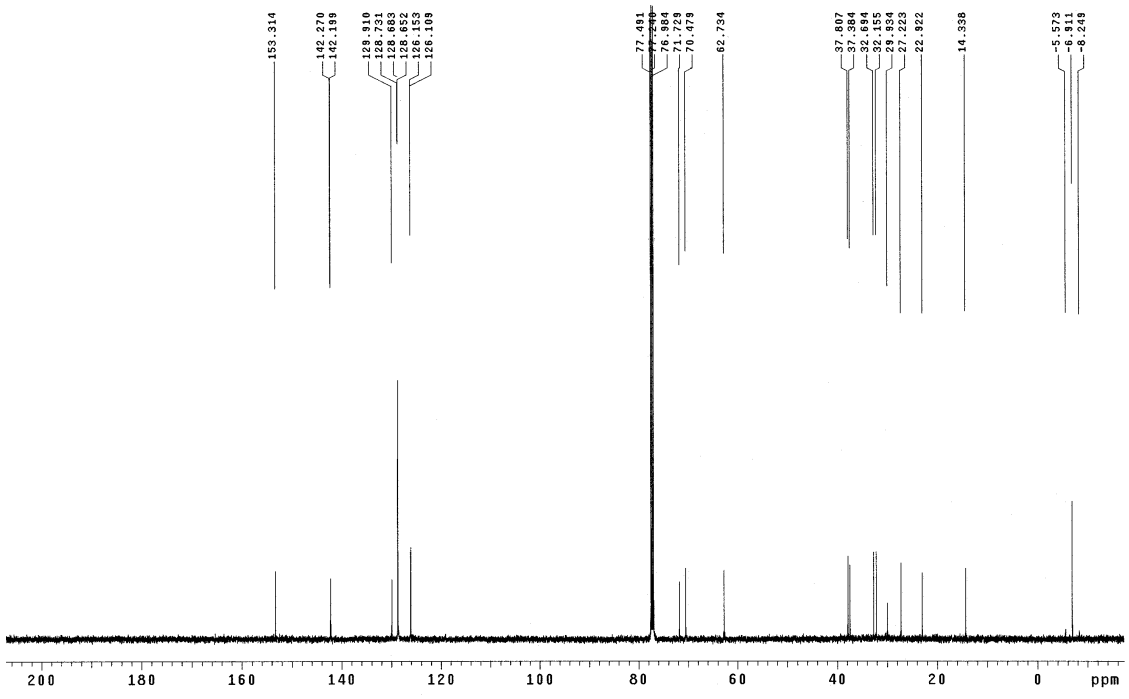


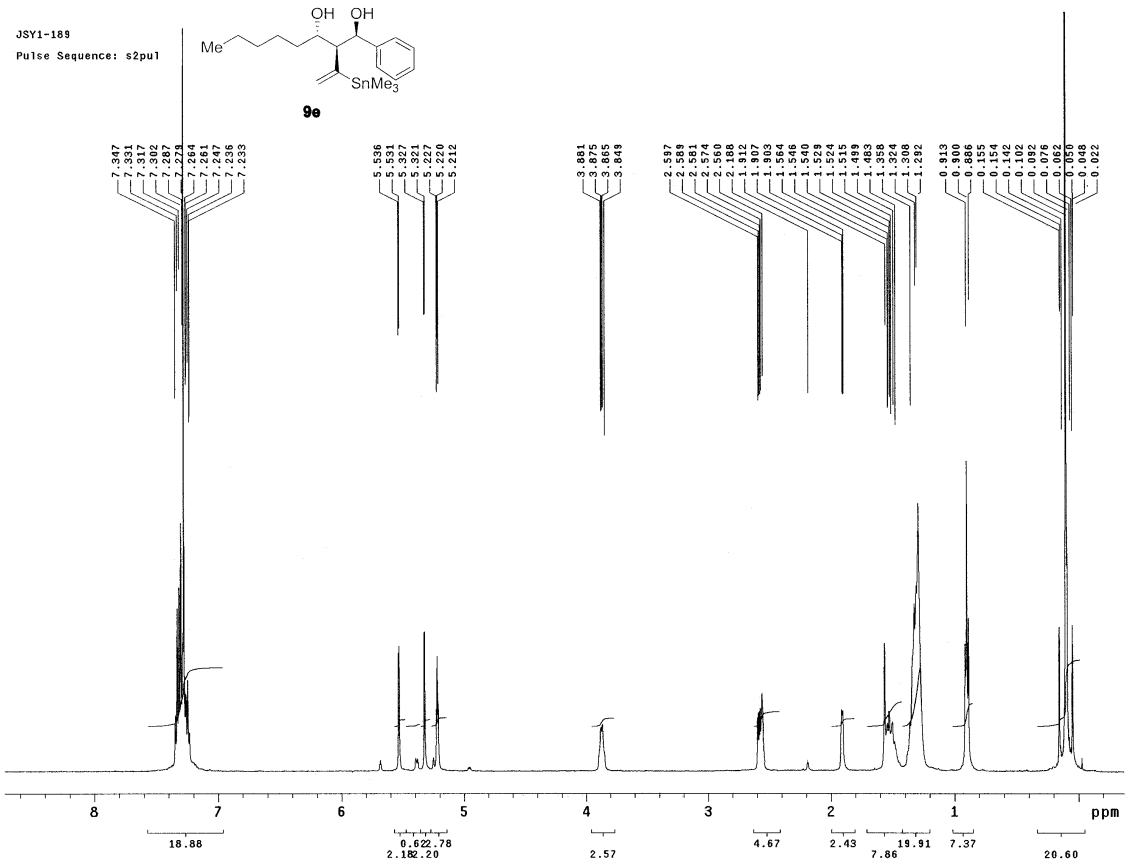
JSY1-182-13C

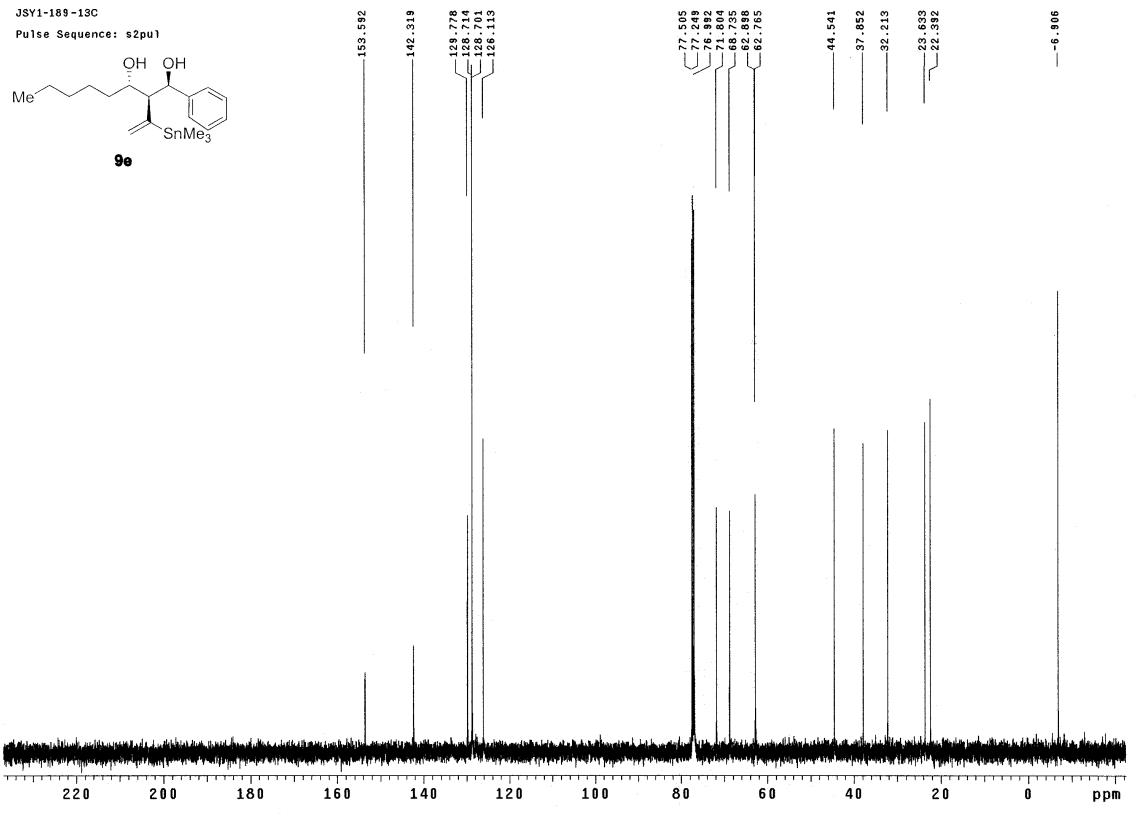
Pulse Sequence: s2pul



9d

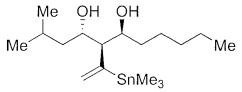



JSY1-189
Pulse Sequence: s2pul
OH OH
Me
SnMe3
9e
7.347 7.331 7.317 7.302 7.287 7.278 7.264 7.261 7.247 7.236 7.233
5.536 5.531 5.327 5.321 5.227 5.220 5.212
3.881 3.875 3.865 3.849
2.597 2.589 2.581 2.574 2.560 2.118 2.112 1.907 1.903 1.564 1.546 1.540 1.529 1.524 1.515 1.483 1.358 1.324 1.308 1.292
0.913 0.900 0.886 0.155 0.154 0.142 0.102 0.092 0.076 0.062 0.050 0.048 0.022
8 7 6 5 4 3 2 1 ppm
18.88
0.62 2.78
2.18 2.20
2.57
4.67
2.43
7.86 19.91
7.37
20.60

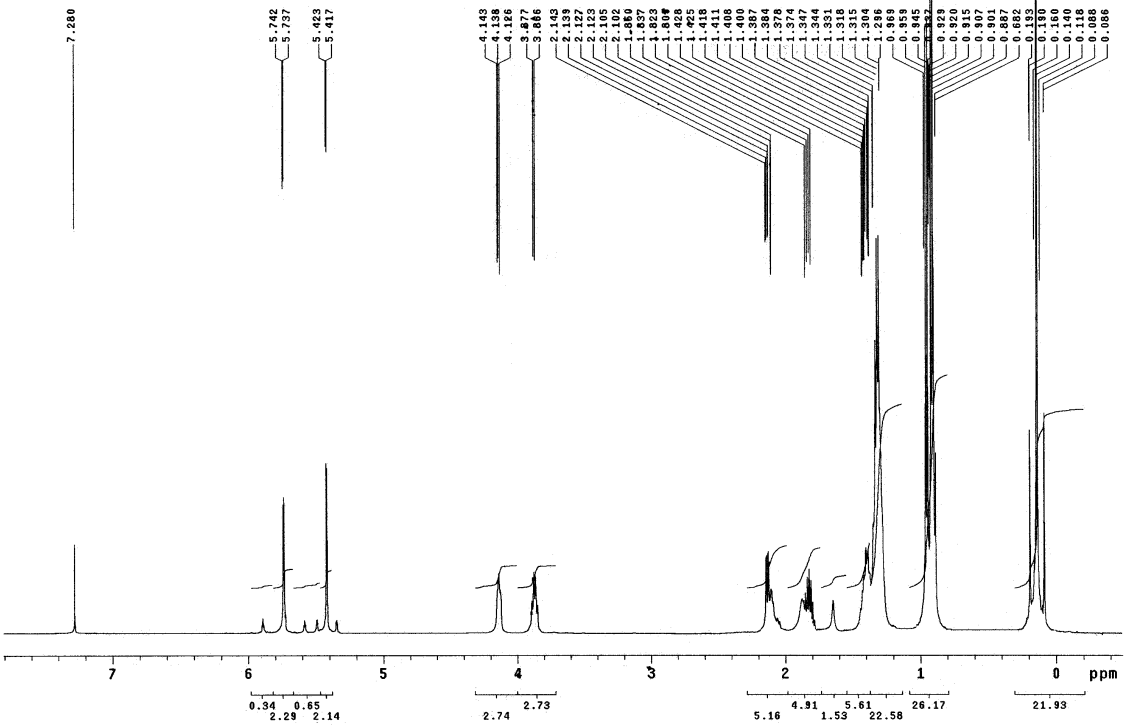

JSY1-189-13C
Pulse Sequence: s2pul
OH OH
Me
SnMe3
9e
153.592 142.319 129.778 128.714 128.701 126.113
77.505 77.249 76.992 71.804 68.735 62.898 62.765
44.541 37.852 32.213 23.633 22.392
-6.906
220 200 180 160 140 120 100 80 60 40 20 0 ppm

JSY2-114

Pulse Sequence: s2pul

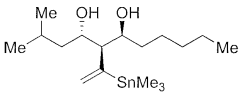


9f

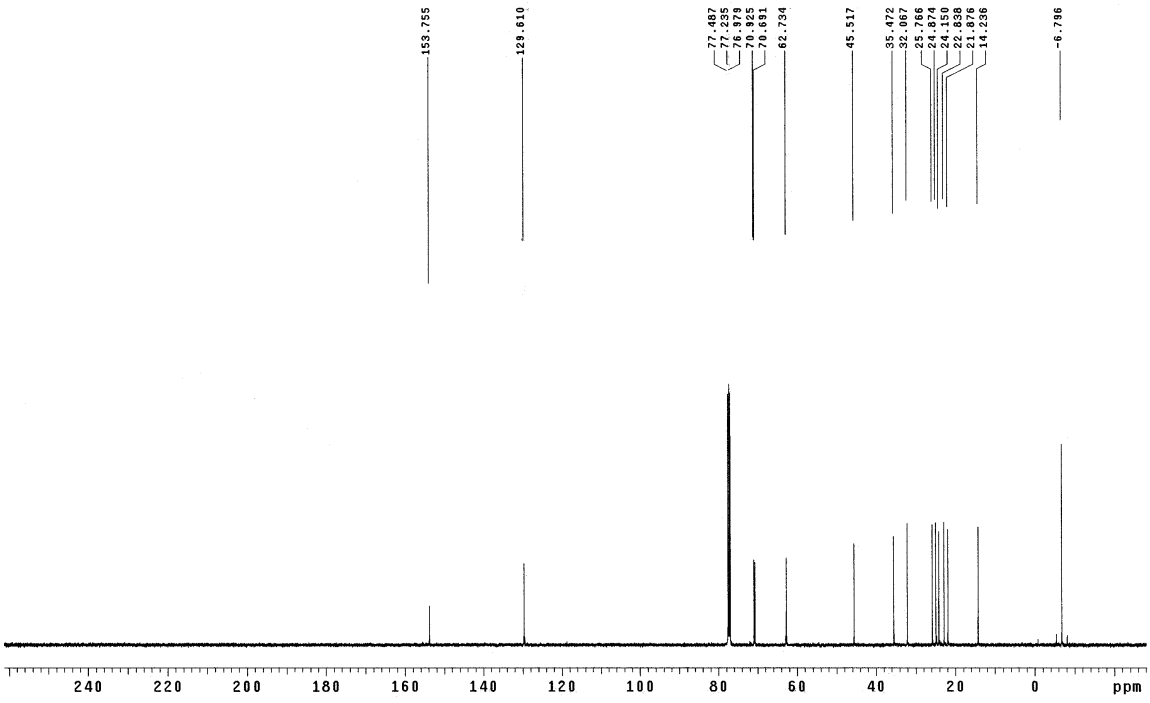


JSY2-114-13C

Pulse Sequence: s2pul

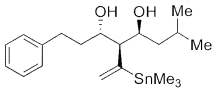


9f

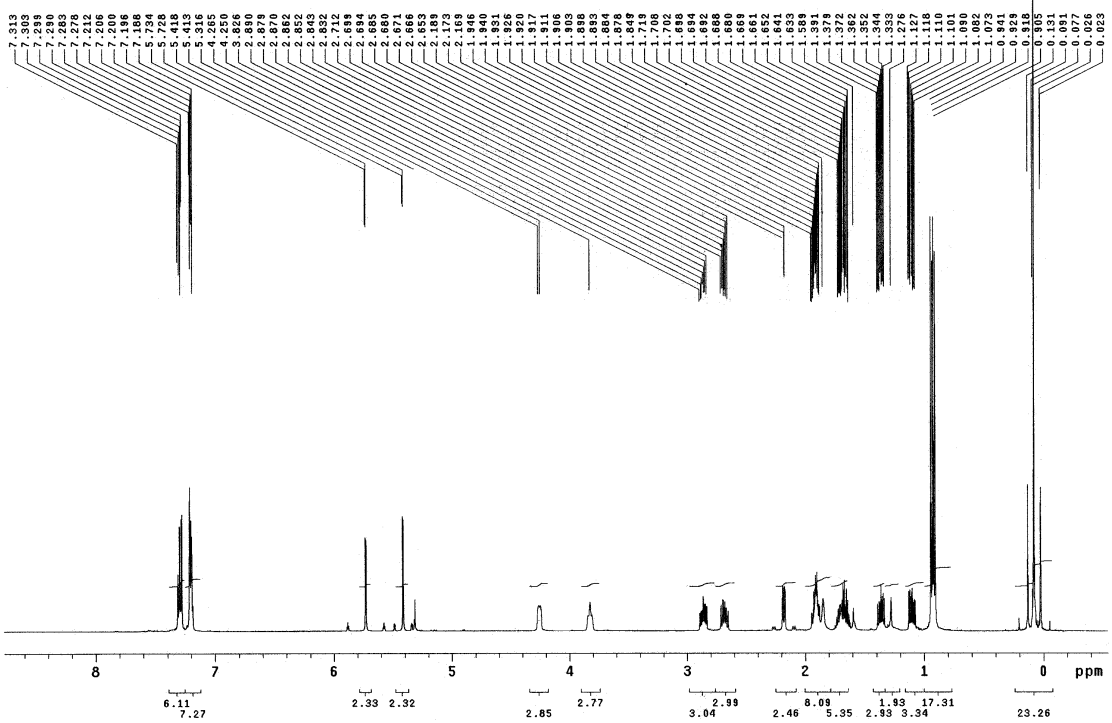


JSY1-187

Pulse Sequence: s2pul

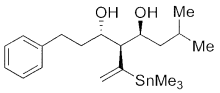


9g

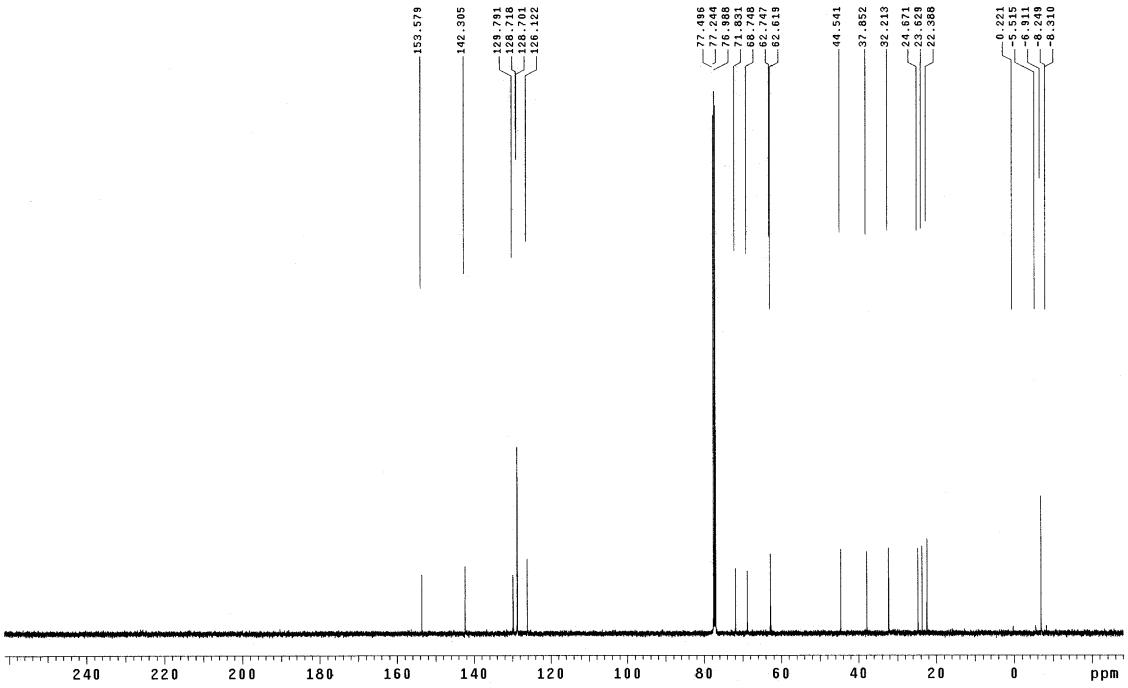


JSY1-187-13C

Pulse Sequence: s2pul

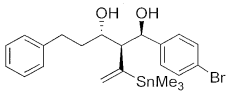


9g

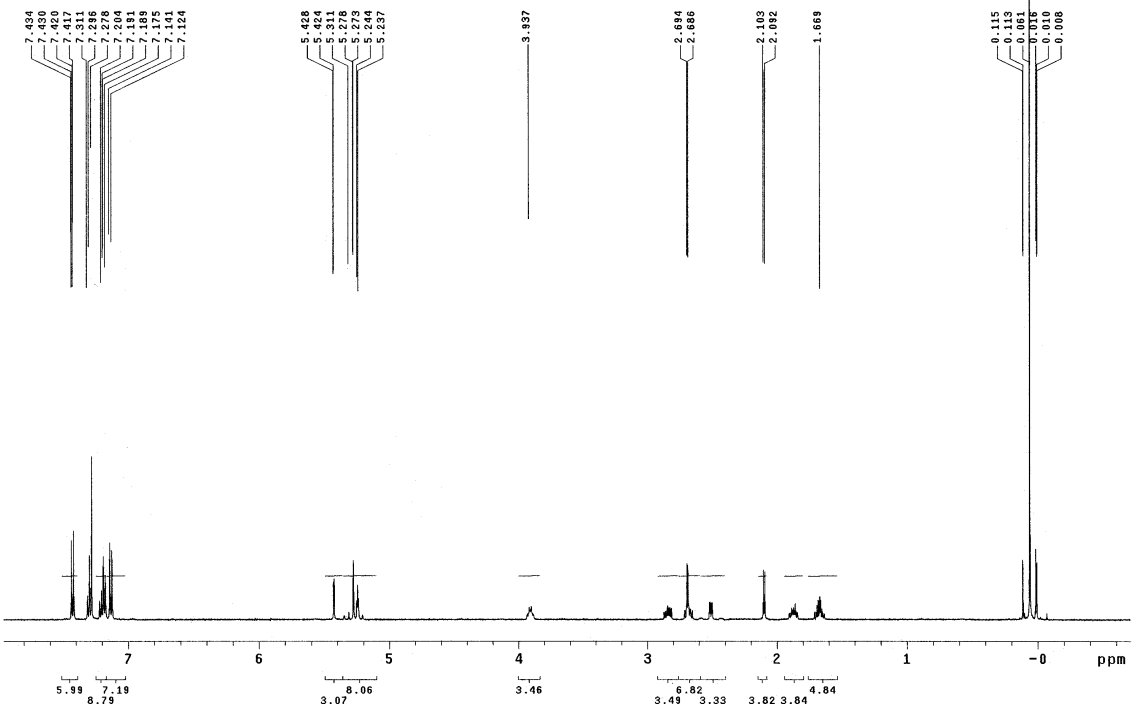


JSY1-197

Pulse Sequence: s2pul

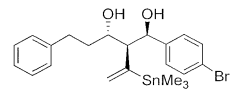


9h

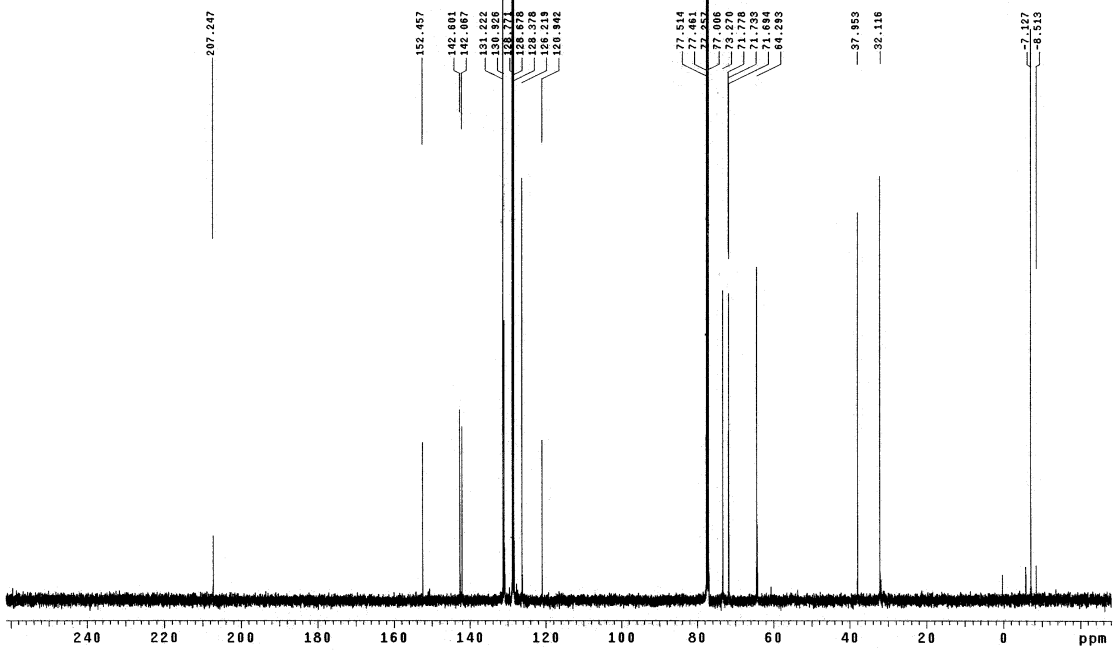


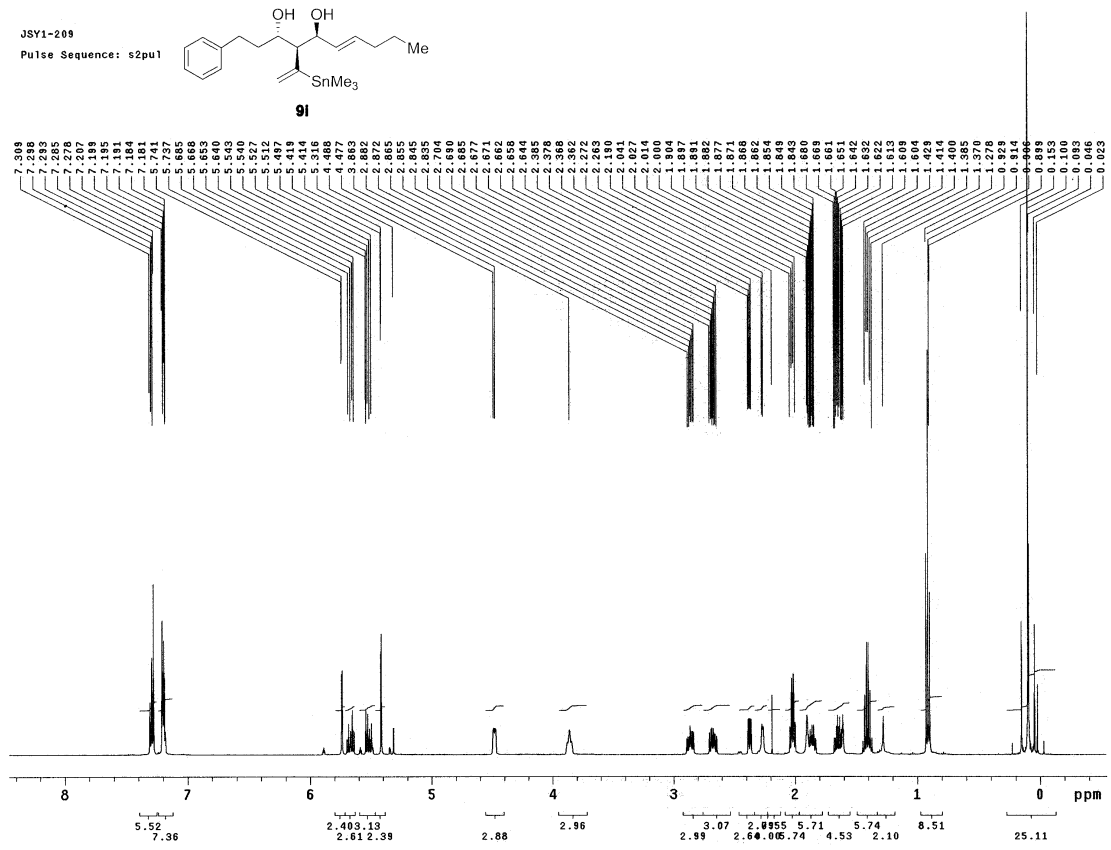
JSY1-197-13C

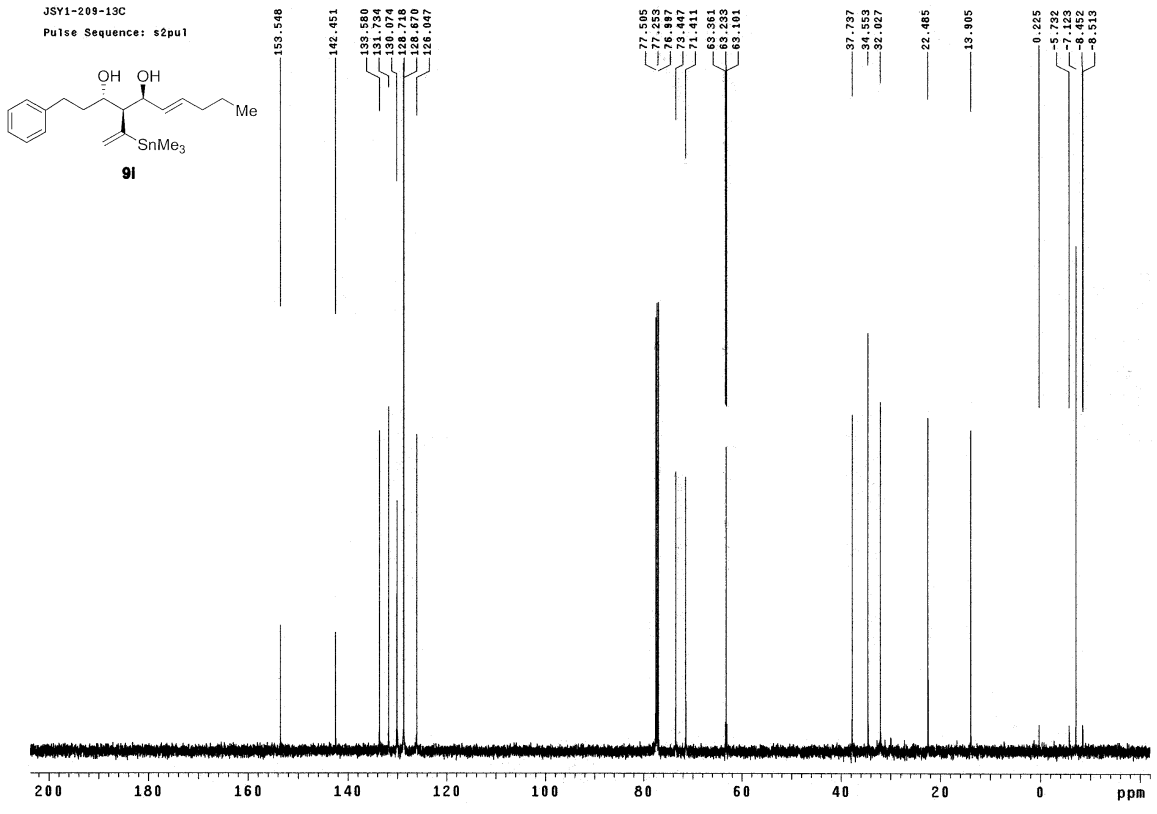
Pulse Sequence: s2pul



9h

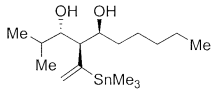



JSY1-209
Pulse Sequence: s2pul
OH
OH
Me
SnMe3
9l
7.309
7.298
7.293
7.285
7.278
7.207
7.199
7.195
7.191
7.184
7.181
5.741
5.737
5.685
5.668
5.653
5.640
5.543
5.540
5.527
5.512
5.497
5.419
5.414
5.316
4.488
4.477
3.883
2.892
2.882
2.865
2.855
2.845
2.835
2.704
2.690
2.685
2.677
2.671
2.662
2.658
2.644
2.385
2.378
2.368
2.362
2.272
2.263
2.190
2.041
2.027
2.014
2.000
1.904
1.897
1.891
1.882
1.877
1.871
1.868
1.862
1.854
1.849
1.843
1.680
1.669
1.661
1.651
1.642
1.632
1.622
1.613
1.609
1.604
1.423
1.414
1.400
1.395
1.370
1.278
0.929
0.914
0.906
0.899
0.153
0.100
0.093
0.046
0.023
8
7
6
5
4
3
2
1
0
ppm
5.52
7.36
2.40
3.13
2.61
2.38
2.88
2.96
3.07
2.99
2.00
2.05
5.74
5.71
4.53
5.74
2.10
8.51
25.11

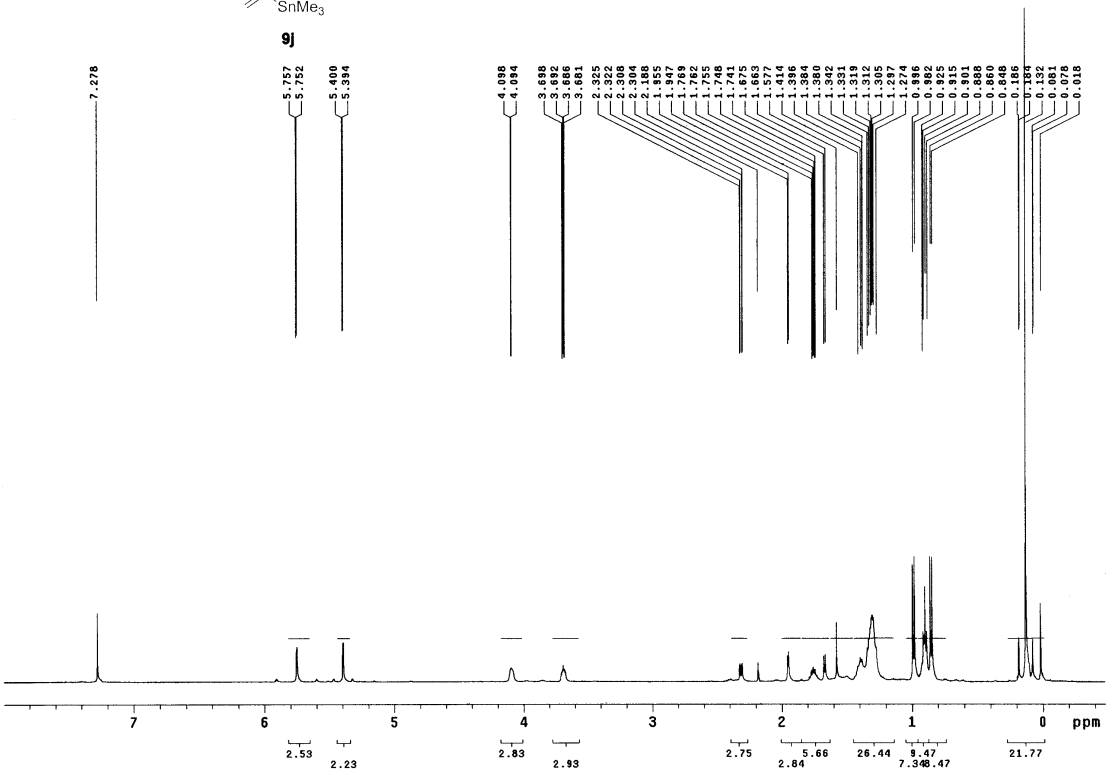

JSY1-209-13C
Pulse Sequence: s2pul
OH
OH
Me
SnMe3
9l
153.548
142.451
133.580
131.734
130.074
128.718
128.670
126.047
77.505
77.253
76.997
73.447
71.411
63.361
63.233
63.101
37.737
34.553
32.027
22.485
13.905
0.225
-5.732
-7.123
-8.452
-9.513
200
180
160
140
120
100
80
60
40
20
0
ppm

JSY2-125

Pulse Sequence: s2pul

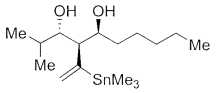


9j

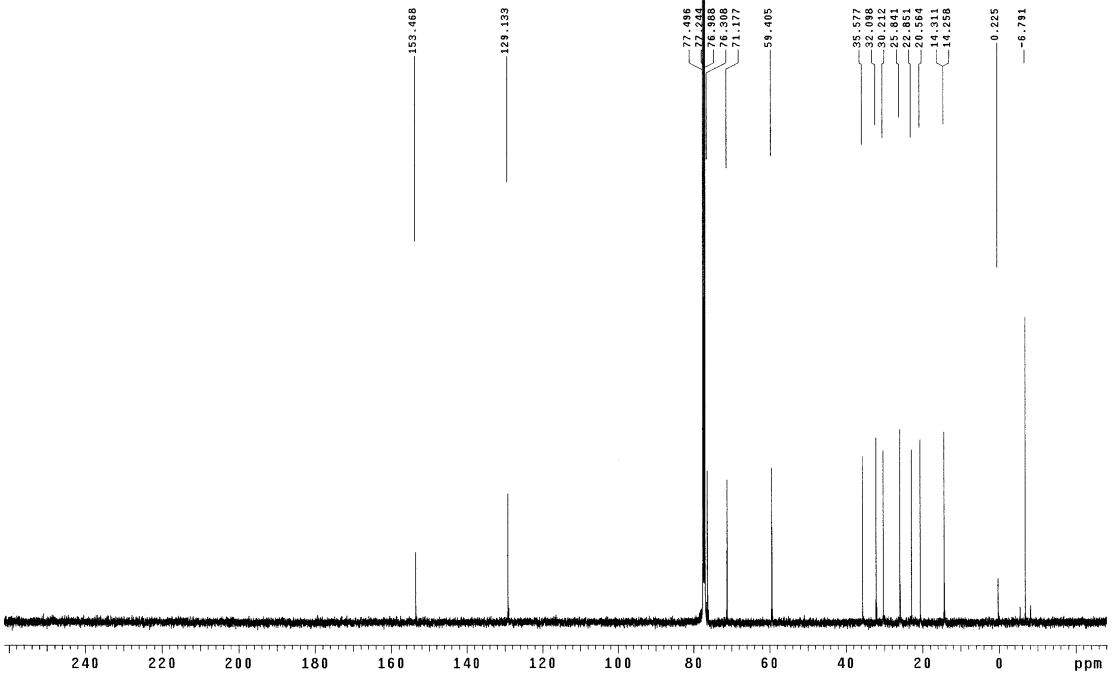


JSY2-125-13C

Pulse Sequence: s2pul

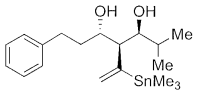


9j

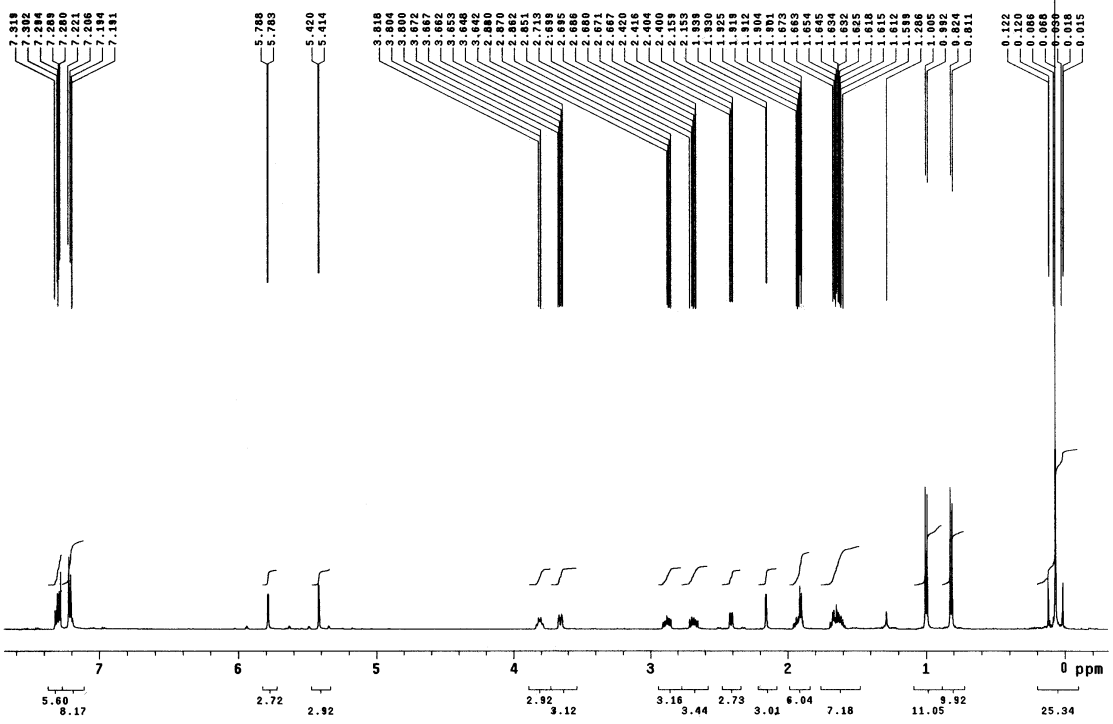


JSY2-127

Pulse Sequence: s2pul

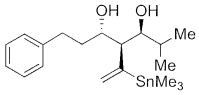


9k

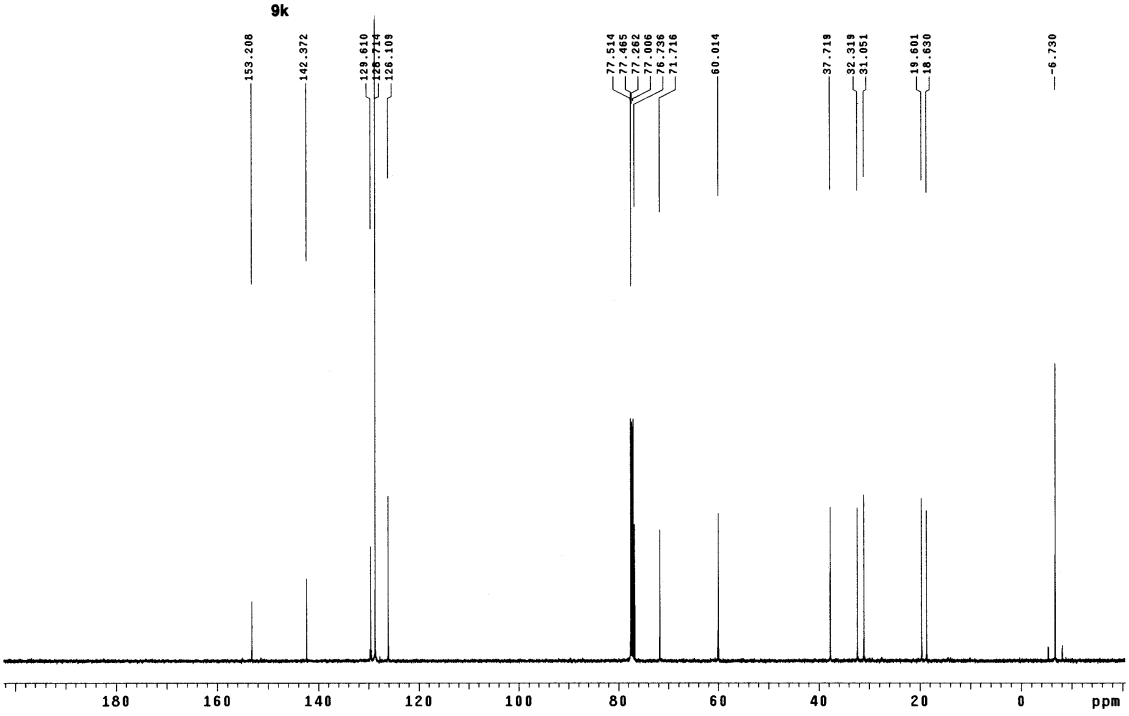


JSY2-127-13C

Pulse Sequence: s2pul

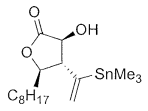


9k

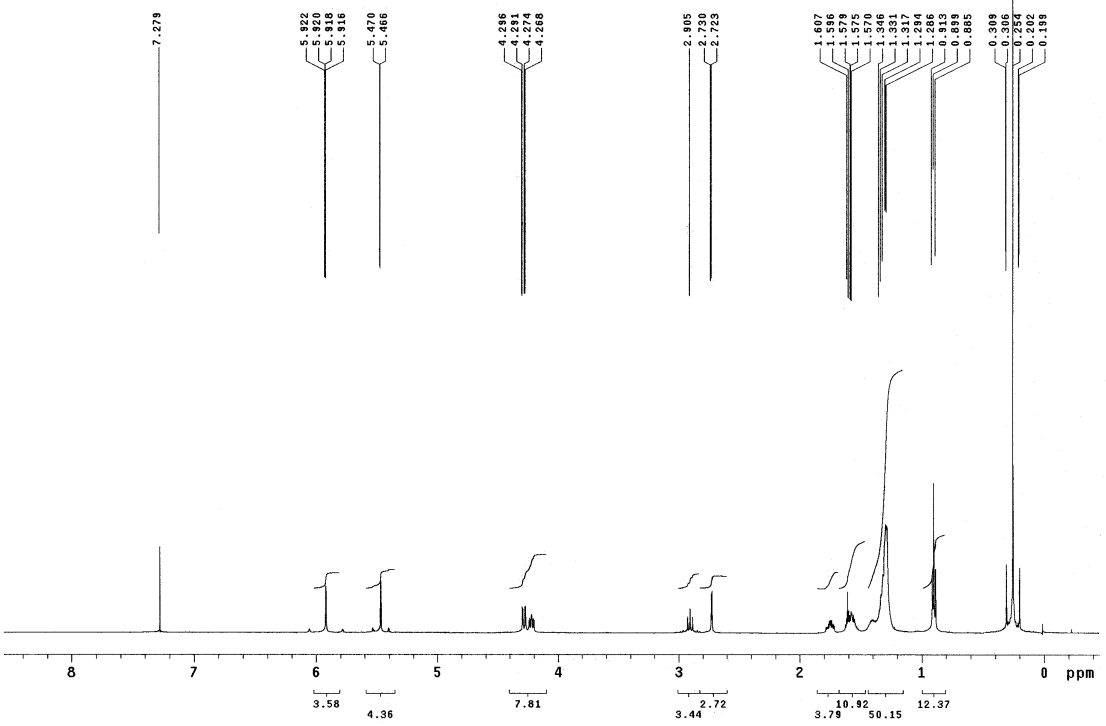


JSY2-98

Pulse Sequence: s2pul

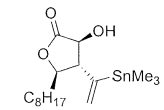


13

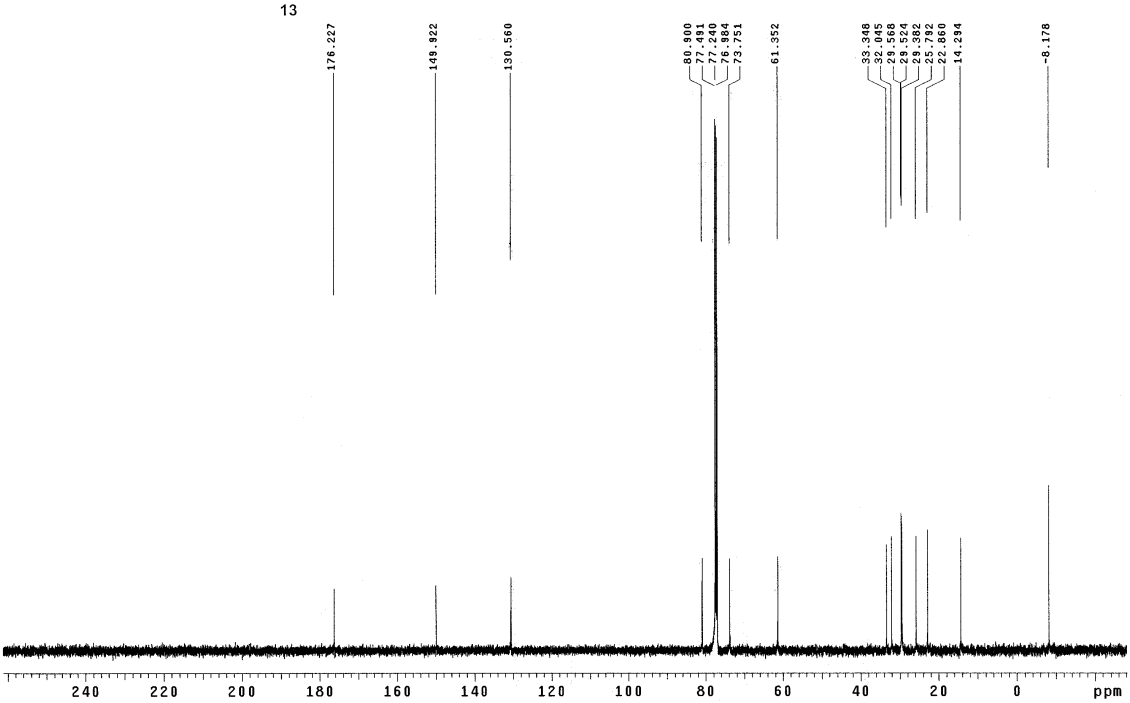


JSY2-98-13C

Pulse Sequence: s2pul

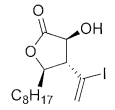


13

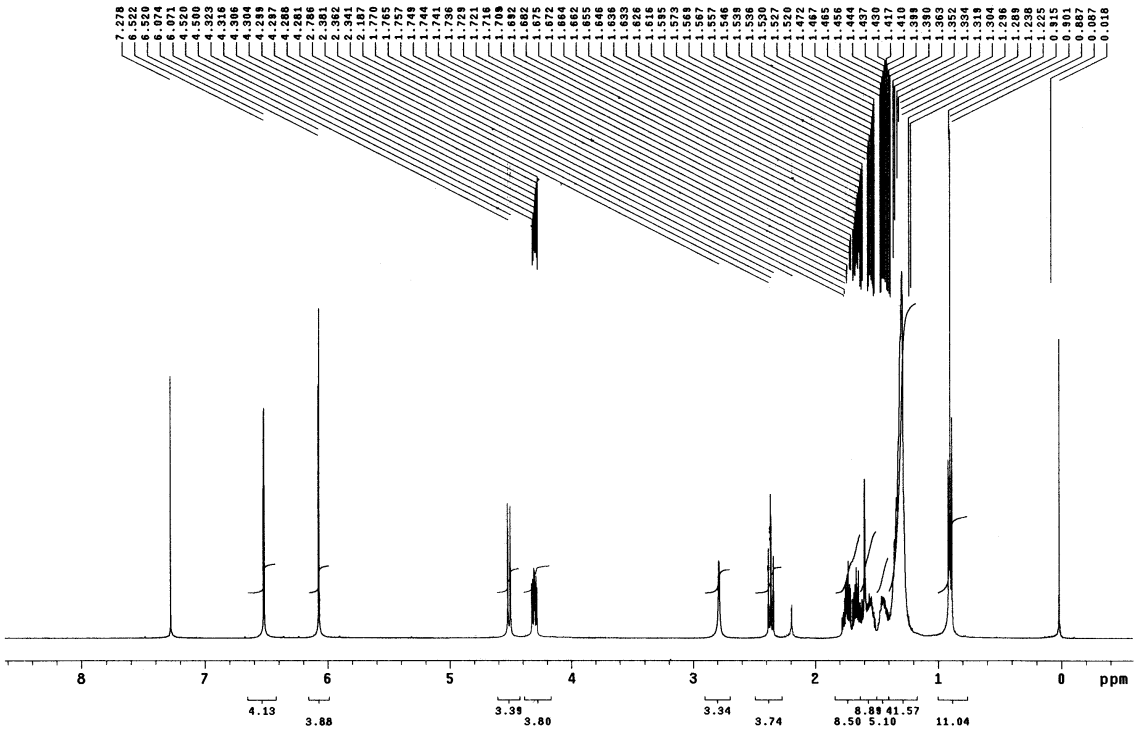


JSY2-83

Pulse Sequence: s2pul

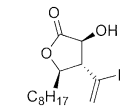


14

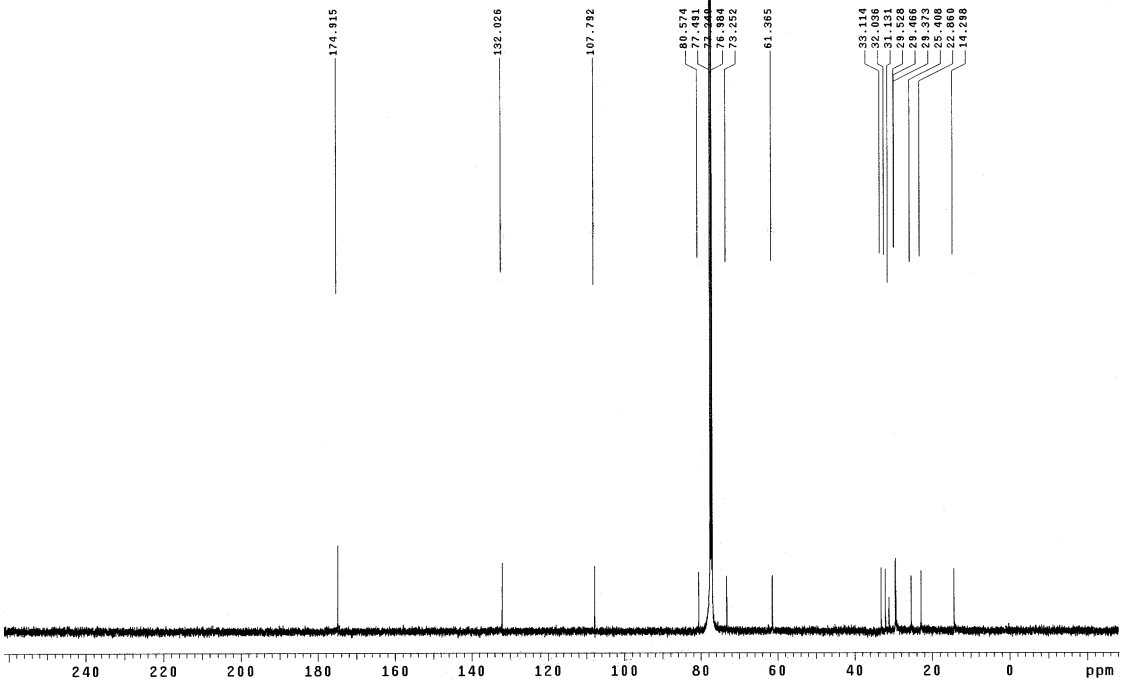


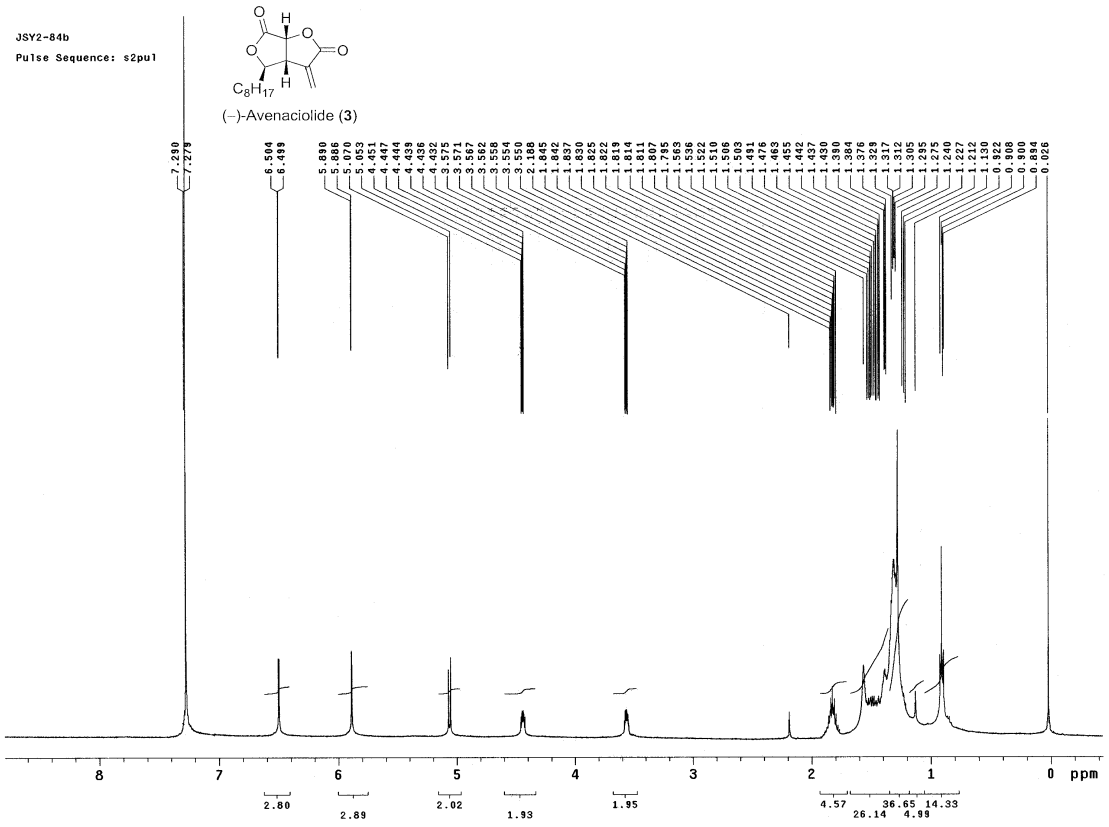
JSY2-83-13C

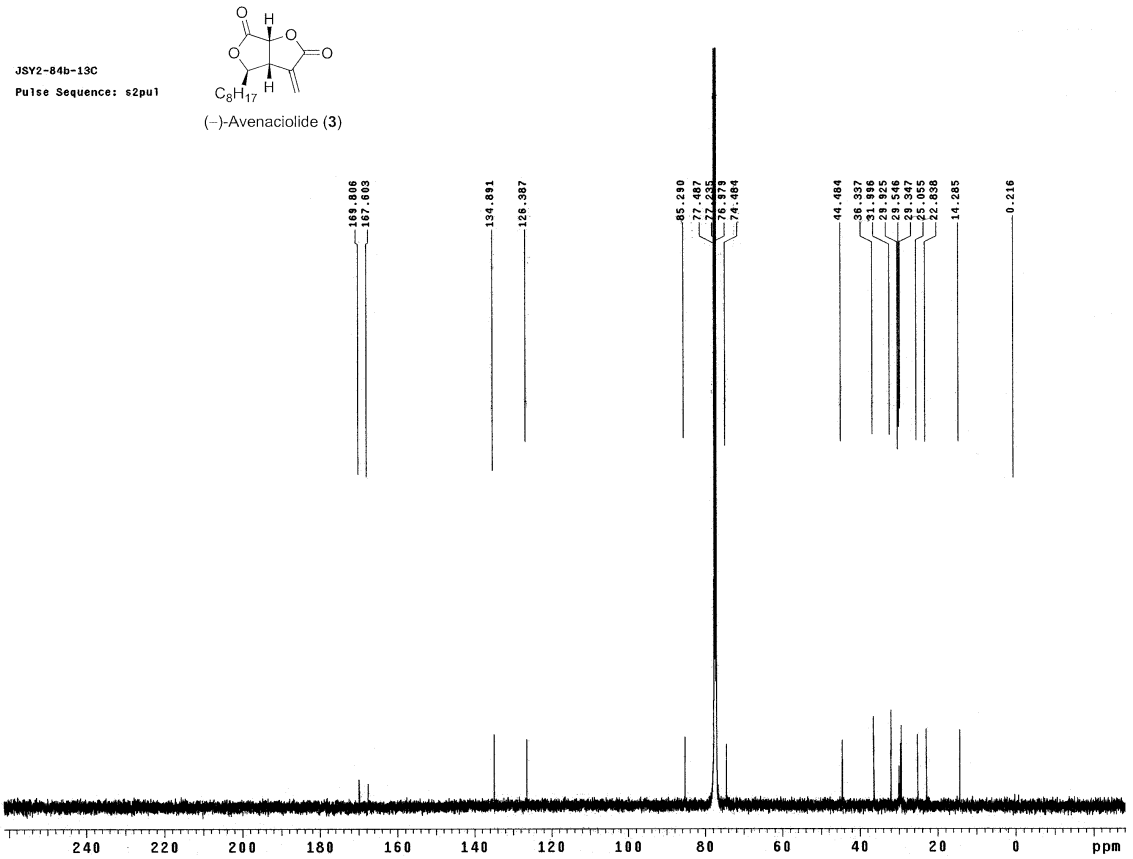
Pulse Sequence: s2pul



14

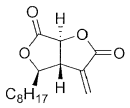



JSY2-84b
Pulse Sequence: s2pul
(–)-Avenaciolide (3)
ppm

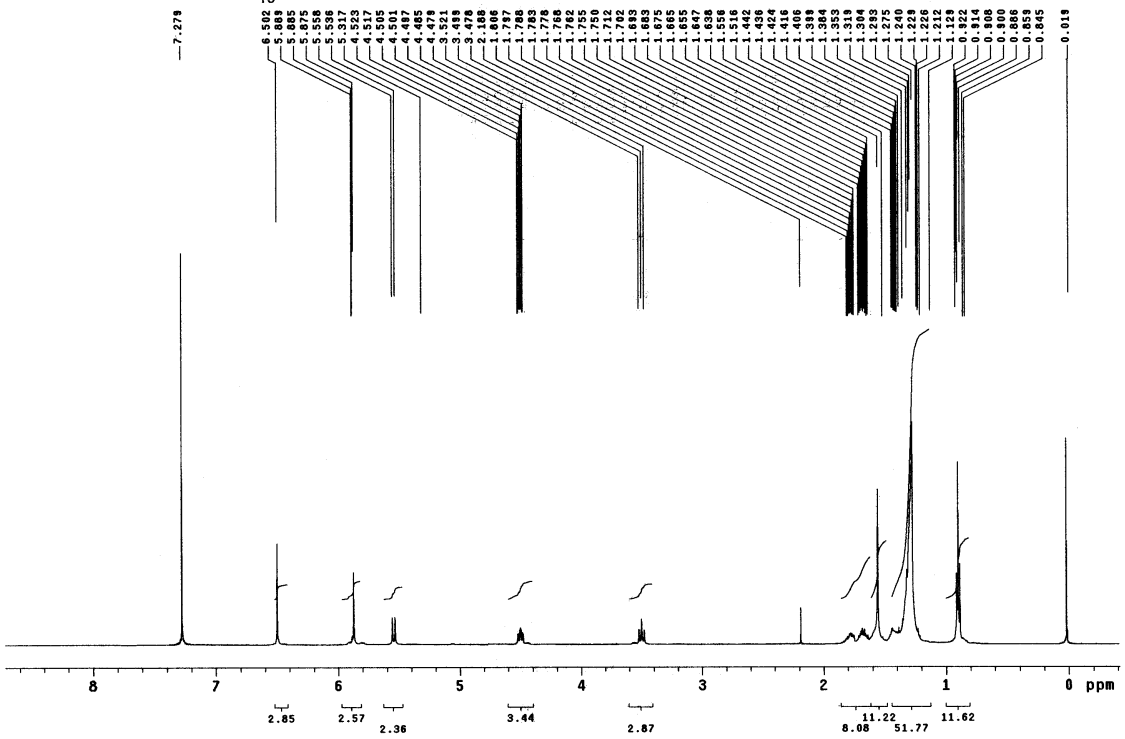

JSY2-84b-13C
Pulse Sequence: s2pul
(–)-Avenaciolide (3)
ppm

JSY2-84a

Pulse Sequence: s2pul

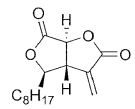


15

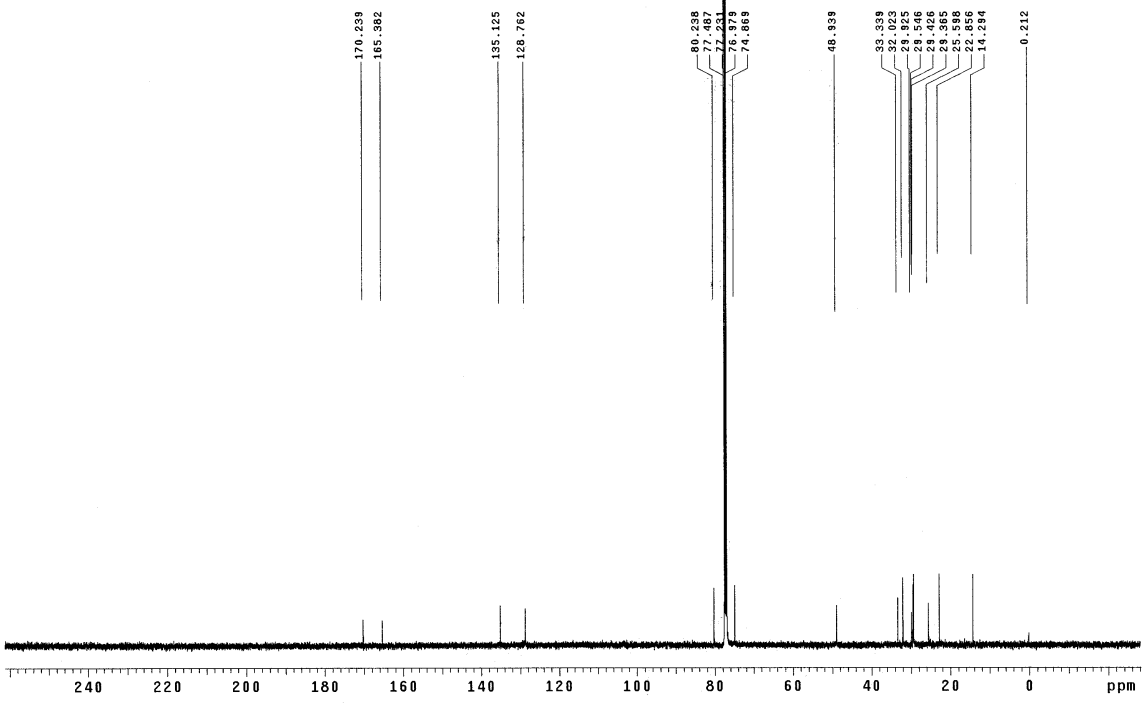


JSY2-84a-13C

Pulse Sequence: s2pul

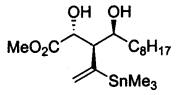


15

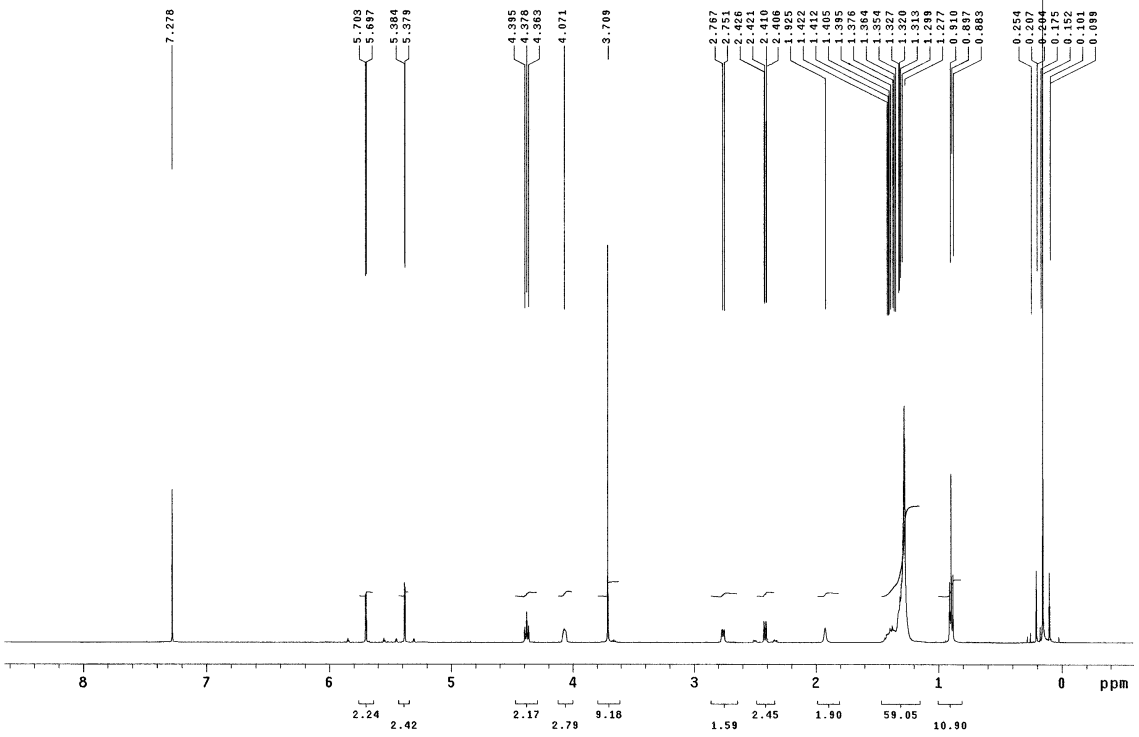


JJY1-165

Pulse Sequence: s2pul

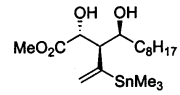


16

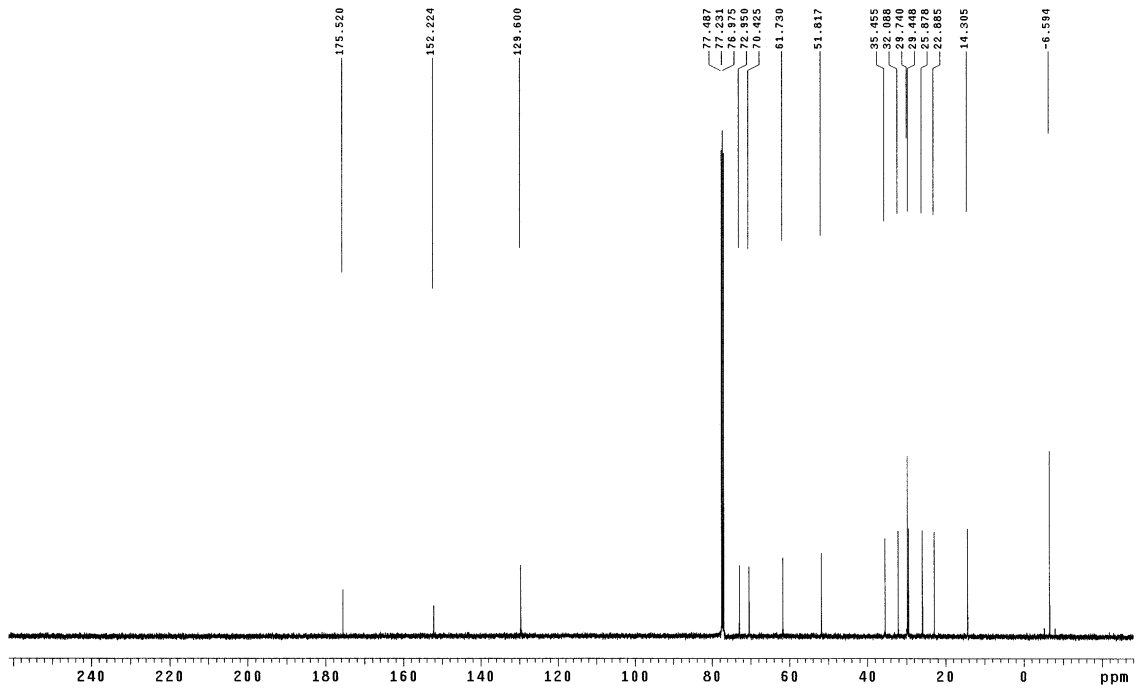


JJY1-165-13C

Pulse Sequence: s2pul

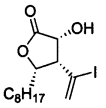


16

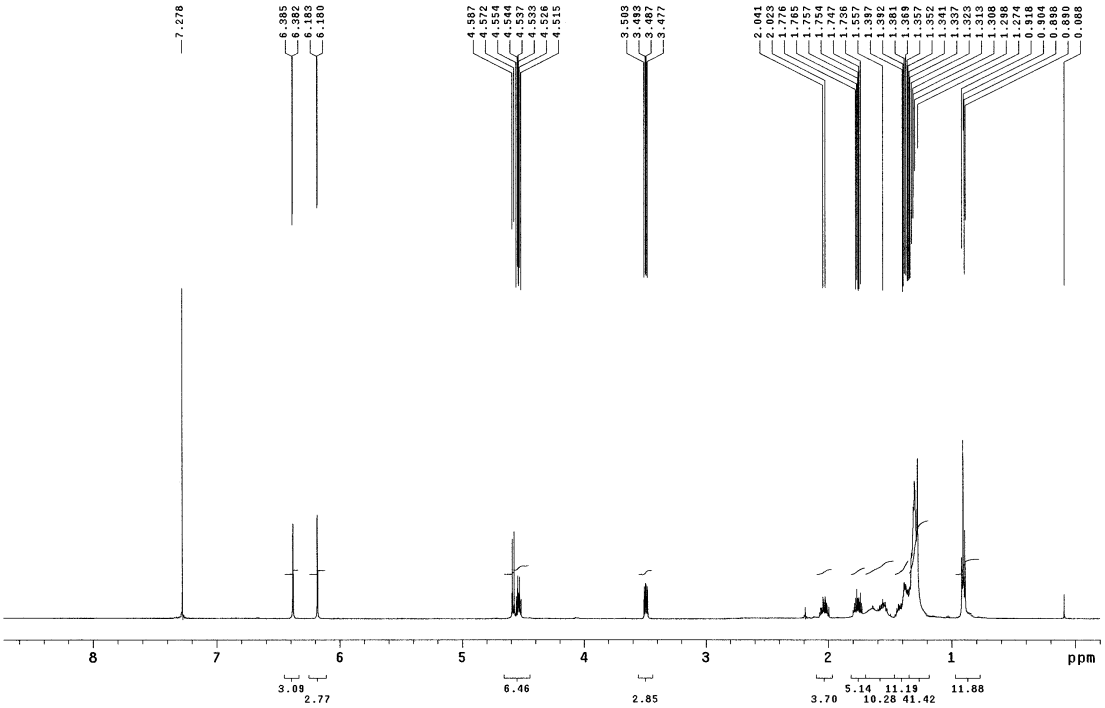


JJY1-cycle

Pulse Sequence: s2pul

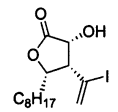


17



JJY1-cycle-13C

Pulse Sequence: s2pul



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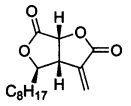
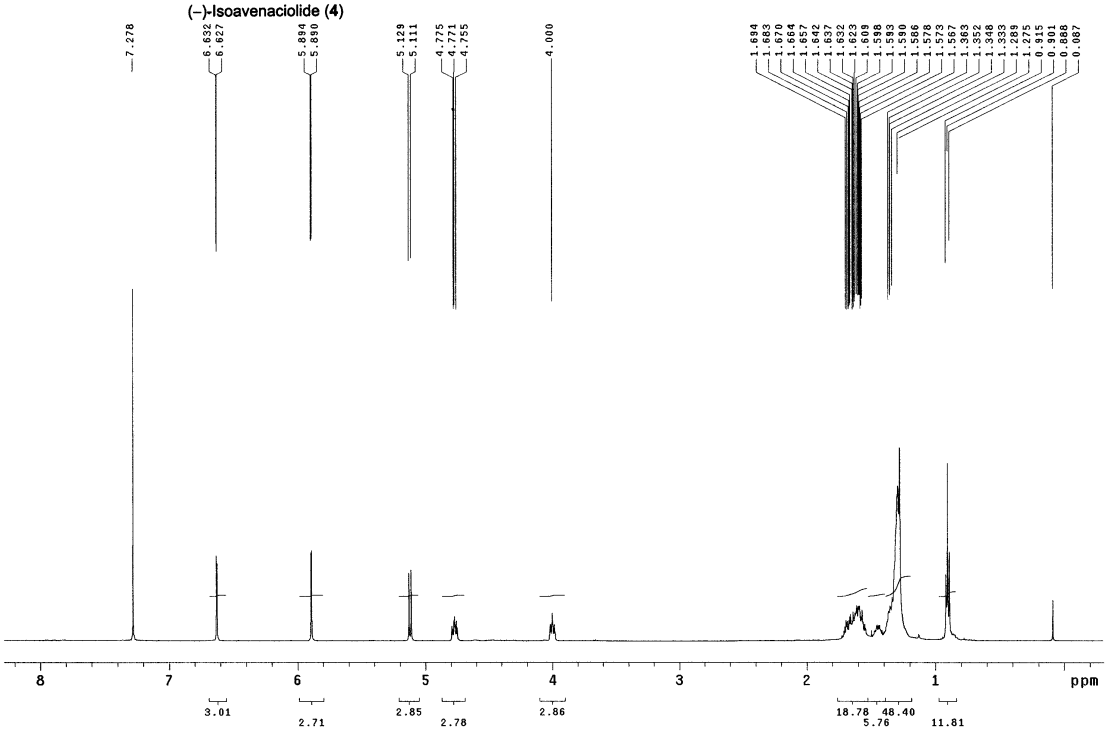
JJY1-final

Pulse Sequence: s2pul

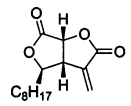


(–)-Isoavenaciolide (**4**)

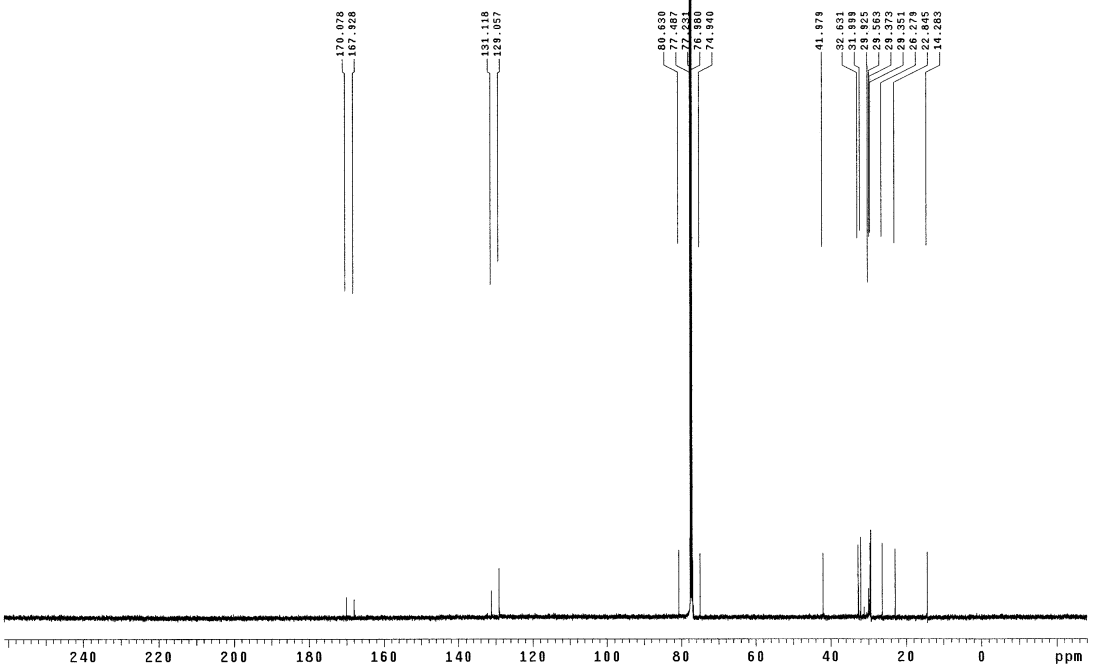


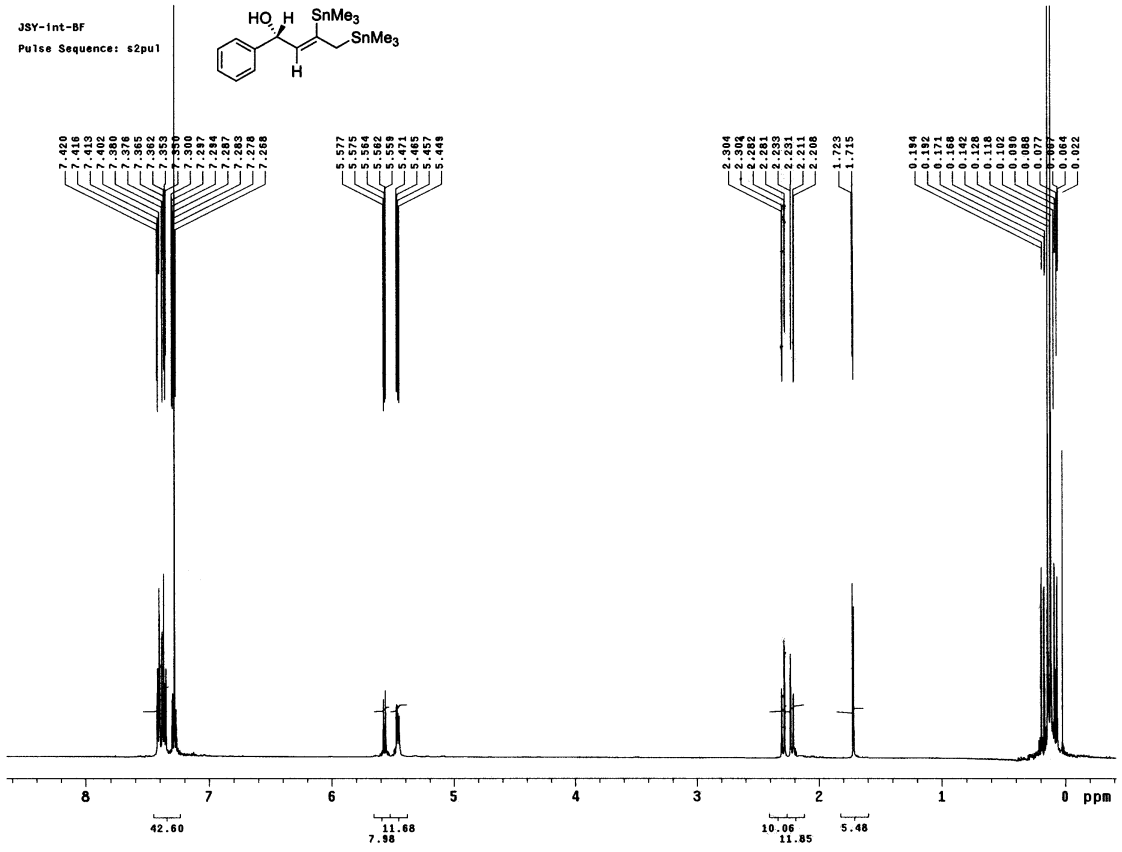
JJY1-final-13C

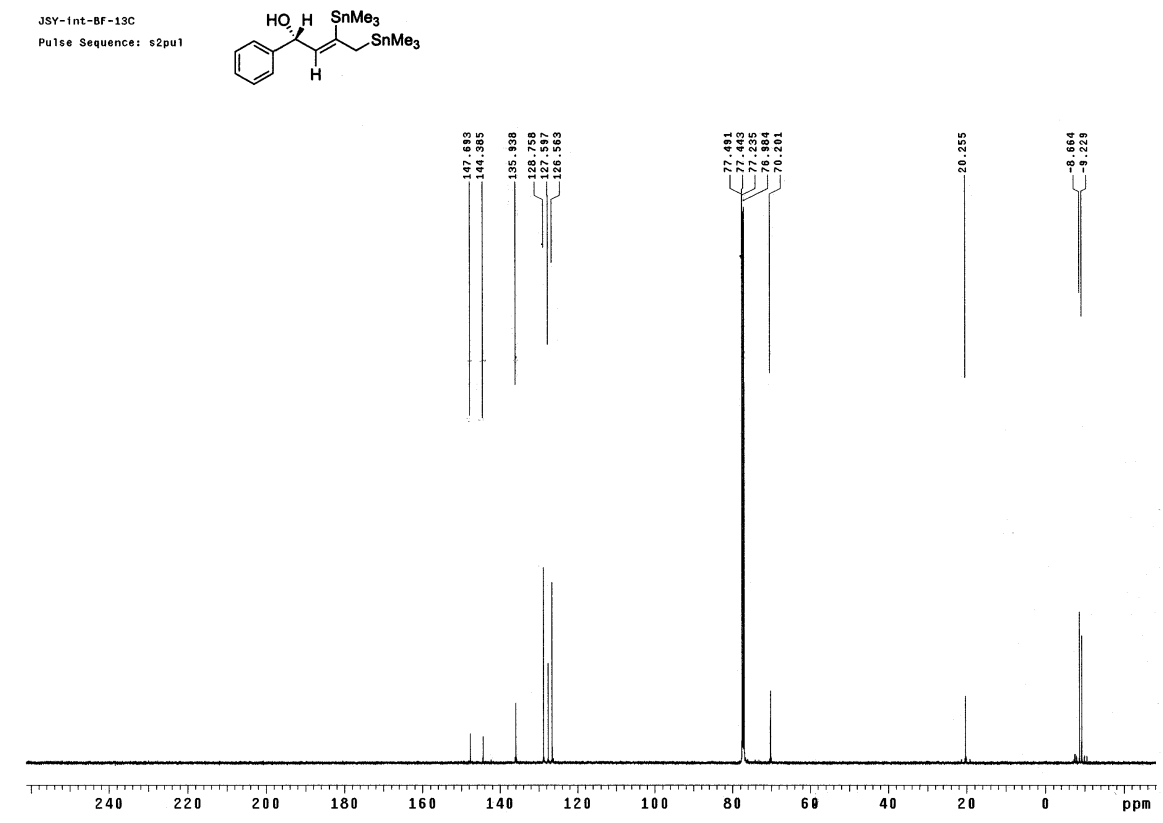
Pulse Sequence: s2pul



(–)-Isoavenaciolide (**4**)




JSY-int-BF
Pulse Sequence: s2pul
HO
H
SnMe3
SnMe3
H
7.420
7.416
7.413
7.402
7.380
7.376
7.365
7.362
7.353
7.350
7.300
7.297
7.294
7.287
7.283
7.278
7.268
5.577
5.575
5.564
5.562
5.559
5.471
5.465
5.457
5.448
2.304
2.301
2.282
2.281
2.233
2.231
2.211
2.208
1.723
1.715
0.194
0.192
0.171
0.168
0.142
0.138
0.118
0.102
0.090
0.088
0.077
0.067
0.064
0.022
8
7
6
5
4
3
2
1
0 ppm
42.60
11.68
7.98
10.06
11.85
5.48


JSY-int-BF-13C
Pulse Sequence: s2pul
HO
H
SnMe3
SnMe3
H
147.693
144.385
135.938
128.758
127.597
126.563
77.491
77.443
77.235
76.984
70.201
20.255
-8.664
-9.229
240
220
200
180
160
140
120
100
80
60
40
20
0
ppm