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Supporting Information

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Catalytic Enantioselective Additions of Allyl- and Crotylboronates to Aldehydes Using Chiral BrØnsted Acids. Efficient Catalyst-Controlled Diastereofacial-Selective Formation of Dipropionate Units.

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1. General information

Unless otherwise noted, all reactions were performed under an argon atmosphere using flame-dried glassware. Toluene, hexanes and CH_2Cl_2 were distilled over CaH_2. THF and Et_2O were distilled over sodium / benzophenone ketyl. Aldehydes were purified by Kugelrohr distillation, prior to use. Molecular sieves were prepared by heating under vacuum at 130^0C (over-night) and then stored inside oven maintained at 125^0C. Thin layer chromatography (TLC) was performed on Merck Silica Gel 60 F254 plates and, visualized with UV light and $KMnO_4$ and 5% phosphomolybdic acid / EtOH (PMA). NMR spectra were recorded on Varian INOVA-300, INOVA-400, INOVA-500 or Unity 500 instruments. The residual solvent protons (^{1}H) or the solvent carbons (^{13}C) were used as internal standards. Boron NMR spectra are referenced to external $BF_3{\cdot}OEt_2$; ^{19}F spectra are referenced to external $CFCl_3$. ^{1}H NMR data are presented as follows: chemical shift in ppm downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; qt, quartet of triplets; dd, doublet of doublets; dt, doublet of triplets; AB, AB quartet; m, multiplet. High-resolution mass-spectra was recorded by the University of Alberta Mass Spectrometry Services Laboratory, using either electron impact (EI) or electrospray (ES) ionization techniques. Infrared-spectra and optical rotations were recorded by University of Alberta Spectral Services and combustion analyses were performed by the University of Alberta Micro-Analytical Lab.

Preparation of Diols: (*R, R)*-1,2-Diarylethane-1,2-diols were either commercially available or prepared[1] by Sharpless *syn*-dihydroxylations of the corresponding (*E,E*)-1,2-diarylethanes, which in turn were obtained by McMurry coupling of the corresponding aldehydes[1]. 1,2-Bis-(3,4-bis-trifluoromethyl-phenyl)-ethane-1,2-diol[14] was generously gifted by Prof. Hisashi Yamamoto (at University of Chicago).

(*R,R*)-1,2-Diphenyl-ethane-1,2-diol (1a): Commercially available from Aldrich.

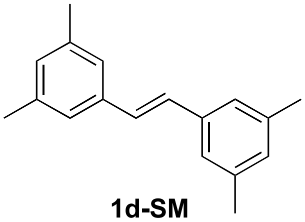
(*R,R*)-2-Methoxy-1,2-diphenyl-ethanol (1b)[2]: Prepared by monomethylation of **1a.** To a solution of (*R,R*)-(+)-Hydrobenzoin 100 mg (0.466 mmol, 1 equiv) in 2 ml of DMF under argon was added Ag_2O 108 mg (0.466 mmol, 1 equiv) and MeI 32 μl (0.513 mmol, 1.1 equiv) and this mixture was stirred under dark for 24 hrs. This resulting solution was then filtered over a short pad of celite and the celite was subsequently washed with DCM. The resulting solution was evaporated under vacuo and purified by flash chromatography (5% EtOAc / Hexanes) to give the title compound in 68% yield. The ^{1}H NMR, ^{13}C NMR. IR, HRMS properties were identical to those reported.

(*R,R*)-2-Benzyloxy-1,2-Diphenyl-ethanol (1c)[3]: To a solution of **1a** 200mg (0.934 mmol, 1 Equiv) in 10 ml of reagent grade benzene was added 17.7 mg (0.09 mmol, 0.1 Equiv) of *p*-TsOH and to this mixture was added freshly distilled benzaldehyde 113.8 μl (1.12 mmol, 1.2 Equiv) and the reaction mixture was refluxed for 3 hrs using a dean-stark trap to remove water, after which, the reaction mixture was concentrated under vacuo. The resulting solid was dissolved in 2 ml of toluene and cooled to 0^0 C, after which 2.8 ml of 1.0 M DIBAL-H in Toluene (3 Equiv) was added and the reaction mixture was stirred at 0^0C for 2 hours. The reaction was quenched with 2 ml of MeOH and this was followed by dilution with Et_2O (25ml) and addition of 10 % NaOH and then the resulting mixture was transferred to a seperatory funnel and washed with brine followed by drying over Na_2SO_4. The resulting solution was concentrated under vacuo and purified by flash chromatography (5% EtOAc/Hexane) to yield 241 mg (84% yield) of the title compound. The ^{1}H NMR, ^{13}C NMR. IR, HRMS properties were identical to those reported.

1,2-Bis-(3,4-bis-trifluoromethyl-phenly)-ethane-1,2-diol (1e)[14]: Gift from Prof. H. Yamamoto at University of Chicago.

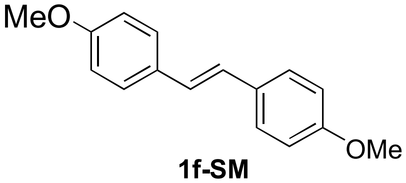
Diols **1e, 1f, 1g, 1h, 1i** were prepared by the highly enantioselective sharpless syn-dihydroxilation of the corresponding *(E)*-1,2-diarylethenes following the literature procedure.[1]

Preparation of the *(E)*-1,2-diarylethene starting materials:



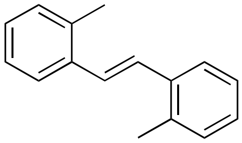
1d-SM

(*E*)-1,2-Di-(3,5-bistrimethylphenyl)-ethene (1d-SM): Into a 250 ml 2-neck round bottom flask equipped with a condenser and a magnetic stirrer under argon was added 2.02 g (45 mmol, 3.0 equiv) of Zn dust and 150 ml of freshly distilled THF. To this suspension was carefully added 2.47 ml (22.5 mmol, 1.5 equiv) of $TiCl_4$ (to avoid plugging of the needle, the syringe needle should be immediately rinsed with dilute HCl after the addition of $TiCl_4$). This mixture was stirred for 30 min until a dark green color was observed after which, 2.017 ml (15 mmol, 1 equiv) of freshly distilled 3,5-dimethylbenzaldehyde was added and the reaction was refluxed overnight. The next day, after the reaction was judged complete by TLC, the reaction mixture was poured over ice cold solution of $NaHCO_3$ and this solution was filtered through a pad of celite and the resulting mixture was extracted with DCM, washed with brine and dried over Na_2SO_4 and concentrated under vacuo and purified by flash chromatography (1-5% EtOAc/hexanes). Further recrystallization from MeOH gave 1.5 g (85%) of isomerically pure (*E*)-alkene. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.351 (s, 12H), 6.914 (s, 2H), 7.045 (s, 2H), 7.146 (s, 4H) ^{13}C NMR (125.7 MHz, $CDCl_3$) δ 21.348, 124.418, 128.535, 129.307, 137.475, 138.113. IR Cast Film: 697.0, 847.0, 961.9, 1558.8, 1599.3, 2859.1, 2912.0, 3020.8. HRMS (EI) Calcd. 236.1565, found 236.1568. Anal. Calcd for $C_{18}H_{20}$: C, 91.47, H, 8.53, found C, 91.62, H, 8.54.



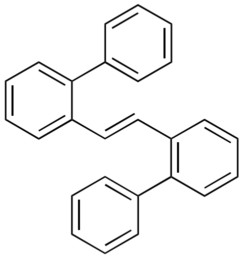
1f-SM

(*E*)-1,2-Di-(4-methoxyphenyl)-ethene (1f-SM): Following general procedure for **1e-SM**, Yield (40%) ^{1}H NMR δ (400 MHz, $CDCl_3$) 3.829 (s, 6H), 6.892 (d, *J* = 8.8 Hz, 4H), 6.933 (s, 2H), 7.428 (d, *J* = 8.8 Hz), ^{13}C NMR δ (100.58 MHz, $CDCl_3$) 55.367, 14.166, 126.249, 127.462, 130.556, 159.076, IR Cast Film: 833.8, 1029.5, 1269.8, 1517.2, 1608.0, 2837.7, 2911.3, 2937.0, 2955.6, 3020.7, 3093.6. HRMS (EI) Calcd: 240.11503, found 240.11502 , Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97, H, 6.71, found C, 79.82, 6.71.



1g-SM

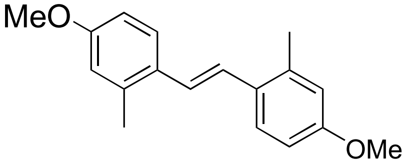
(*E*)-1,2-Di-(2-methylphenyl)-ethene (1g-SM): Following general procedure for **1e-SM**, the product was isolated as 17:14 mixture of *E*/*Z* alkenes as determined by ^{1}H NMR, and this isomeric mixture was subjected to iodine catalyzed isomerization[1] in refluxing xylenes for 24 hr. Yield (50%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.509 (s, 12H), 7.259-7.328 (m,6H), 7.688-7.691 (d, 1.2 Hz) ^{13}C NMR δ (100.58 MHz, $CDCl_3$) δ 19.967, 125.604, 126.229, 127.560, 128.058, 130.421, 135.854, 136.853. IR Cast Film: 722.8, 763.2, 978.3, 1492.2, 1954.1, 2860.0, 2946.4, 3014.5, 3061.7, 3094.2. HRMS (EI) Calcd. 208.1252, found 208.1251. Anal. Calcd for $C_{16}H_{16}$: C, 92.26, H, 7.74, found C, 92.06, H, 7.77.



1h-SM

(*E*)-1,2-Di-(2-phenylphenyl)-ethene (1h-SM): Following general procedure for **1e-SM**, the product was isolated as a 5.7 : 1 mixture of *E* / *Z* alkenes and the mixture was subjected to iodine catalyzed isomerization in refluxing xylenes[1] for 24 hr to give isomerically pure *E*-alkene which was purified by recrystallization from DCM/MeOH. Yield (60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.118 (s, 2H), 7.301-7.382 (m, 6H), 7.414-

7.561 (m, 12H),) ^{13}C NMR (100.58 MHz, $CDCl_3$) δ 125.932, 127.081, 127.498, 128.130, 129.862, 130.210, 135.660, 140.930, 141.077, IR Cast Film: 700.9, 720.2, 741.7, 761.1, 774.6, 965.0, 1072.7, 1478.7, 1498.2, 1595.3, 3019.9, 3055.9, HRMS (EI) Calcd. 332.15650, found 332.15657. Anal. Calcd. for $C_{26}H_{20}$: C, 93.94, H, 6.06, found 93.22, H, 6.05

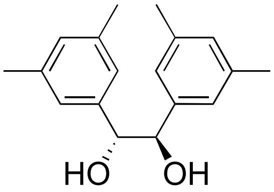


1i-SM

(*E*)-1,2-Di-(2-methyl-4-methoxy-phenyl)ethene (1i-SM): Following general procedure for **1e-SM**. The product was purified by recrystallization to give isomerically pure *E*-alkene. Yield (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.411 (s, 6H), 3.826 (s, 6H), 6.742-6.796 (m, 4H), 7.046 (s, 1H), 7526 (d, *J* = 8.8 Hz), ^{13}C NMR (100.58 MHz, $CDCl_3$) δ 20.251, 55.297, 111.786, 115.682, 125.719, 126.598, 129.952, 137.161, 158.924, IR Cast Film: 800.7, 1053.9, 1212.4, 1256.8, 1500.1, 1606.9, 2835.5, 2955.2, 3033.2, HRMS(EI) Cald. 268.14633, found 268.14648 Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56, H, 7.51, O, 11.92, found 80.40, H, 7.52

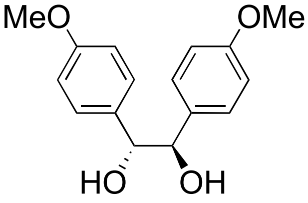
Preparation of Diols via Sharpless Asymmetric Dihydroxylation of *E*-Olefins.

General Procedure for sharpless AD for 1 mmol of olefin[1]: In a round bottom flask equipped with a magnetic stirrer was charged 3 equiv of $K_3Fe(CN)_6$, 3 equiv. of K_2CO_3, and 0.01 equiv. of $(DHDQ)_2PHAL$, 5 ml H_2O and 5 ml *t*BuOH, and this mixture was cooled to 0^0C and vigorously stirred for 10 min. after which a thick orange slurry is obtained. To above at 0^0C is added 0.002 mmol of $K_2OsO_2(OH)_4$ followed by 1 mmol of $MeSO_2NH_2$ and 1 mmol of *E* olefin, and the reaction mixture is allowed to warm up to room temperature overnight. The progress of the reaction was, monitored by TLC and upon completion of the reaction, to the reaction mixture is added 1.5 gram of Na_2SO_3 and after 1 hr, the reaction mixture is extracted with EtOAc and washed with 1N KOH and then with brine and dried over Na_2SO_4 and concentrated under vacuo. The resulting product is purified by flash chromatography, and recrystallized twice from hot CCl_4 to give the requisite diol. Model diols are obtained by this method in greater than 95 % ee (Reference)[1] and were directly used for catalytic asymmetric allylboration reaction.



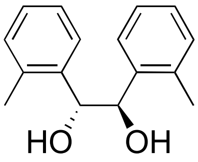
1d

(*R,R*)-(+)-1,2-Bis-(3,5-dimethyl-phenyl)-ethane-1,2-diol (1d) : Yield (75%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.271 (s, 12H), 2.673 (brs, 2H), 4.650 (s, 1H), 6.822 (s, 4H), 6.895 (s, 2H), ^{13}C NMR (100.58 MHz, $CDCl_3$) δ 21.291, 78.441, 124.527, 129.422, 137.634, 140.158, IR (cast film): 704.0, 726.9, 848.2, 1072.8, 1159.4, 1464.4, 1607.9, 2906.6, 3003.6, 3293.0, 3373.1, HRMS (EI) $[M-H_2O]^+$ 252.15162, Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96, H, 8.20, found C, 79.61, H, 8.17, $[\alpha]_D = 66.36$, (c =2.97, $CHCl_3$).



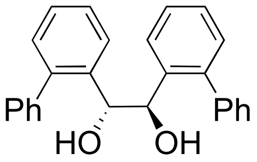
1f

(*R*,*R*)-(+)-1,2-Bis-(4-methoxy-phenyl)-ethane-1,2-diol (1f): Yield (72%) ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.748 (brs, 2H), 3.771 (s, 6H), 4.643 (s, 2H), 6.768 (d, *J* = 9 Hz), 7.051 (d, *J* = 8.7 Hz), ^{13}C NMR (100.58 MHz, CDCl$_3$) δ 55.207, 78.786, 113.512, 128.197, 132.163, 159.179, IR (cast film): 831.0, 1032.7, 1247.5, 1513.2, 1611.5, 2835.6, 2929.3, 3405.1, HRMS (EI) cacld. 274.12051, found 274.12051, Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.06, H, 6.61, found 71.11, H, 6.47, $[\alpha]_D$ = 101.56 (c = 1.23, CHCl$_3$).



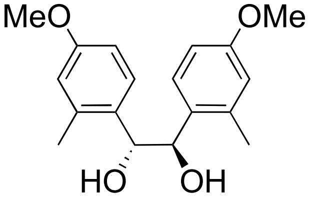
1g

(*R*,*R*)-(+)-1,2-Bis-(2-methyl-phenyl)-ethane-1,2-diol (1g): Yield (80%) ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.680 (s, 6H), 2.905 (brs, 2H), 4.991 (s, 2H), 6.93 (d, *J* = 7.5 Hz), 7.113-7.262 (m, 4H), 7.628 (d, *J* = 7.5 Hz), ^{13}C NMR (125.7 Hz, CDCl$_3$) δ 18.761, 74.652, 125.970, 127.216, 127.744, 130.211, 135.934, 138.015, IR (cast film) 762.2, 791.7, 1042.5, 1197.9, 1490.6, 1604.4, 2928.2, 3023.2, 3062.3, 3388.3, HRMS (EI) calcd. 242.13068, found 242.13068, Anal. Calcd for $C_{16}H_{18}O_2$, C, 79.31, H, 7.49, found C, 79.22, H, 7.44, $[\alpha]_D$ = 63.87 (c = 1.43, CHCl$_3$).



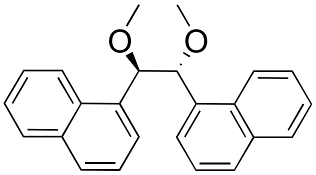
1h

(*R,R*)-(+)-1,2-Bis-(2-phenyl-phenyl)-ethane-1,2-diol (1h): Yield (56%) ^{1}H NMR (400 MHz, CDCl$_3$) δ 2.610 (brs, 2H), 4.944 (s, 2H), 6.77 (brs, 4H), 6.990-7.331 (m, 14H), ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 74.436, 126.725, 127.386, 127.402, 127.936, 129.208, 129.676, 136.629, 140.597, 141.951, IR (cast film) 707.47, 744.71, 997.69, 1074.65, 1189.90, 1436.67, 1451.60, 1596.94, 2929.78, 2976.37, 3025.38, 3066.08, 3348.87, 3468.23, HRMS (EI) Calcd. 366.16198, found 366.16179. Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.22, H, 6.05, found C, 84.65, H, 6.14, $[\alpha]_D = 88.68$ (c = 0.98, CHCl$_3$).



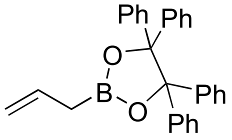
1i

(*R,R*)-(+)-1,2-Bis-(4-methoxy-2-methyl-phenyl)-ethane-1,2-diol (1g): Yield (77%) ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.689 (s, 6H), 3.009 (brs, 2H), 3.745 (s, 6H), 4.867 (s, 2H), ^{13}C NMR (125.7 MHz, CDCl$_3$) δ 19.079, 55.108, 74.497, 111.294, 115.388, 128.404, 130.460, 137.453, 158.755, IR (cast film), 1045.6, 1197.2, 1252.6, 1289.0, 1504.2, 1608.6, 2835.5, 2852.2, 2925.1, 2999.8, 3414.0, HRMS (EI) $[M\text{-}H_2O]^+$ 284.14210, Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50, H, 7.33, found 71.03, 7.45, $[\alpha]_D = 104.60$ (c = 0.55, CHCl$_3$).

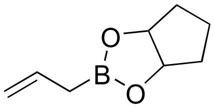


Preparation of (*R,R*)-(+)-Di-(1-Napthyl)-1,2-dimethoxy-ethane: Into a flame-dried 25 ml RB flask is added 50.0 mg (0.16 mmol, 1.0 equiv) of diol **1j** and the diol is dissolved in 2 ml of freshly distilled THF after which is added 20.3 μl (0.33 mmol, 2.05 equiv) of MeI and this mixture is cooled to 0^0C and to above is added in portions, 22.0 mg (0.56 mmol, 3.5 equiv) of NaH (60 % in mineral oil) in portions, and the reaction mixture is sealed and stirred at RT over-night after which the reaction is quenched with addition of water the product is extracted with Et_2O and washed with brine and dried over Na_2SO_4 and filtered and concentrated under vacuo and finally, purified by column chromatography (0-5% EtOAc/Hexane) to give 55.0 mg of product (>99% yield). %) ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.335 (s, 6H), 5.347 (s, 2H), 7.100-7.158 (m, 4H), 7.276-7.360 (m, 4H), 7.539 (d, 2H, *J* = 8.4 Hz), 7.667 (d, *J* = 8.0 Hz), 8.150 (brs, 2H), ^{13}C NMR (100.58 Hz, $CDCl_3$) δ 57.266, 123.869, 124.732, 125.144, 125.472, 128.312, 128.493, 131.670, 133.590, 134.042, IR (cast film) 767.7, 801.9, 1227.7, 1447.0, 1509.3, 1595.7, 2820.3, 2925.5, 3046.2, HRMS (EI) Calcd. 342.16198, found 342.15982. Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.18, H, 6.48, O, 9.34, found C, 83.39, H, 6.54, $[\alpha]_D$ = 158.88 (c = 0.11, $CHCl_3$).

Allyl (3), Cis-crotyl (7) and Trans-crotyl pinacol boronic esters (5) were prepared by literature method[4].



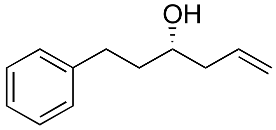
Benzopinacol-allylboronate[5]: Into a flame dried RB flask equipped with a magnetic stir bar was added 3.68g (10.0 mmol, 1 equiv) of 1,1,2,2-Tetraphenylethylene diol and to this was added 10.0 ml of toluene followed by 2.31 ml (10.0 m mol, 1 equiv) of $B(O^iPr)_3$. The RB flask was then assembled into a dean-stark trap and refluxed for 24 hr at 105^0C after which, toluene was distilled off to give a colorless glassy solid, which, was put under high vaccum overnight. To the resulting solid under argon was added 10.0 ml of anhydrous ether and the resulting mixture was cooled to -78^0C followed by addition of 10.0 ml (10.0 mmol, 1.0 equiv) of allylmagnesium bromide (1.0 M in Et_2O), which results in a white suspension and this mixture was stirred at -78^0C for 2 hr and this was followed by additional stirring at 0^0C, after which, the reaction was quenched with 8 ml (1.0 N) HCl and the mixture was then extracted with DCM (2 X 50 ml) and the organic extracts were washed with water (25 ml) and finally brine (25 ml) and dried over Na_2SO_4, filtered, and concentrated under vacuo to give the crude product which, was purified by flash chromatography (5% EtOAc/Hexane) to give 3.0 g (72%) of white solid. The product is very stable to air and moisture and remains intact even on bench. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.251-2.281 (m, 2H), 5.131-5.172 (m, 1H), 5.258-5.318 (m, 1H), 6.160-6.270 (m, 1H), 7.134-7.252 (m, 20H), ^{13}C NMR (100.58 MHz, $CDCl_3$) δ 17.949, 95.982, 115.614, 126.913, 127.194, 128.347, 133.515, 142.401, ^{11}B NMR (128.3 MHz) δ 33.176, IR (Cast film) 696.9, 768.1, 1000.1, 1190.3, 1327.9, 1445.3, 1634.9, 2935.9, 2974.2, 3039.0, 3056.6, HRMS (EI) calcd : 416.19476, found 416.19382. Anal Calcd. for $C_{29}H_{25}BO_2$: C, 83.66, H, 6.05, found C, 83.02, H, 6.16.



Allylboronic cyclopentane-diol ester: Into a flame dried 100 ml RB flask under argon was added 2.31 ml (10 mmol, 1 equiv) of $B(O^iPr)_3$ and diluted with 10 ml of anhydrous Et_2O, and cooled to -78^{0}C. To above is added 11.0 ml (11 mmol, 1.1 equiv) of allylmagnesium bromide (1.0 M in Et_2O) and the reaction mixture is stirred at -78^{0}C for 3 hrs, after which 20 ml of 1N HCl is added to the reaction mixture and the reaction mixture is brought to room temperature and stirred for 1 hr, and extracted with Et_2O and washed with brine and finally concentrated under vacuo (to leave a minimal amount of solvent,. To this crude mixture is added 714 mg (7.0 mmol, 0.7 equiv) of cis-1,2-cyclopentane diol along with 5 grams of anhydrous $MgSO_4$, and 15 ml of THF and the reaction mixture is stirred under argon overnight, followed by filtration and concentration under vacuo (10 mm Hg, bath temperature 20^{0}C) and, the allylboronate product is purified by flash chromatography (5% Et_2O/Pentane) to provide the requisite product 530 mg (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.492-1.644 (m, 4H), 1.746 (d, *J* = 7.2 Hz), 1.869-1.933 (m, 2H), 4.809-4.911 (m, 2H), 4.911-5.025 (m, 2H), 5.810-5.915 (m, 1H), ^{13}C NMR (100.58 MHz, $CDCl_3$) δ 21.473, 34.622, 82.366, 114.911, 134.209, ^{11}B NMR (128.3 MHz, $CDCl_3$) 32.893, IR (Cast film) 1033.0, 1307.0, 1329.4, 1361.1, 1385.8, 1441.8, 1637.7, 2876.3, 2964.7, 3077.3, HRMS (EI) calcd: 152.10086, found 152.10081. Anal Calcd for $C_8H_{13}BO_2$: C, 63.21, H, 8.62, found C, 63.82, H, 8.72.

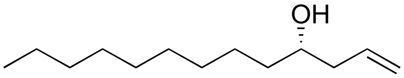
Determination of absolute configuration of homoallylic alcohol products: This was done by comparing the signs of rotation of compound **8a** with literature.[13] All other absolute stereochemistry were deduced by analogy.

General procedure for catalytic enantioselective and diastereoselective allylboration:



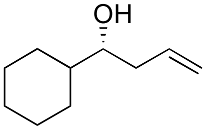
4a

(3S)-1-Phenyl-hex-5-en-3-ol (4a)[6]: Into a flame dried 25 ml round bottom flask equipped with a rice needle stir bar was added 8.65 mg (0.025 mmol, 0.11 equiv) of (*R,R*) 1,2-di-naphthyl-ethanediol, 5.6 mg (0.05 mmol, 0.05 equiv) of anhydrous Na_2CO_3 and 50 mg of activated 4 A^0 Molecular sieves, and to this mixture, under argon was added 0.5 ml of freshly distilled toluene. To above was added 25 μl (0.025 mmol, 0.10 equiv) of 1.0 M solution of $SnCl_4$ in DCM (in order to get reproducible results, it is necessary to use a gas tight 25μl syringe, and that all of the $SnCl_4$ drops into the diol-solution without touching the side walls, and hence, pyrex test-tubes were not good for this purpose). The resulting mixture was stirred for 5 minutes and cooled to -78^0C and maintained at this temperature for 15 minutes after which 46.2 mg of allyl boronic pinacol ester **3** (1.1 Equiv) dissolved in 0.5 ml of toluene was added via syringe and this mixture was maintained at -78^0C for 15 minute, after which, 32.6 μl (0.25 mmol, 1.0 equiv) of freshly distilled hydrocinnamaldehyde was added. The reaction mixture was stirred at -78^0C for 12 hrs after which 0.5 ml (0.50 mmol, 2.0 equiv) of DIBAL-H in toluene was added to quench any remaining aldehyde and after 30 minutes, 2 ml of 1 N HCl was added (to neutralize DIBAL-H and hydrolyze the borate ester to corresponding alcohol), after which the reaction mixture was brought to room temperature and stirred for 1 hr. At this point, dark brown biphasic solution is obtained which upon extraction with (2 X 25 ml) of Et_2O gives a clear etheral solution which is then washed with brine and dried over Na_2SO_4 and concentrated under vacuo to give the crude product (TLC of which gives two spots, one of the diol, and the other of the product, which, are easily separated), which, was purified by flash chromatography (5% EtOAc/Hexanes) to give 37.4 mg of the corresponding homoallylic alcohol in 85 % yield. Analytical data of this product are in complete accordance with literature.[6] HPLC analysis with chiracel-OD column (5% IPA/Hexane, 254 nm) at 0.5ml / min gives the major isomer (89%, t_r = 26.19 min) and the minor isomer (11 % t_r = 37.62 min). $[\alpha]_D$ = - 4.54 (c = 0.41, $CHCl_3$).



4b

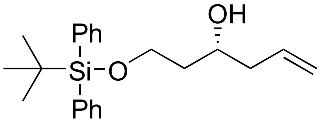
(4*S*)-Tridecen-4-ol (4b)[7]: Following general procedure for **4a**, yield (76%). The spectroscopic data of this are identical with those reported in literature.[7] HPLC analysis of the *p*-Nitro benzoyl derivative with chiracel-OD column (100% hexane) 1ml / minute gave the major isomer (90%, t_r = 24.83 min) and the minor isomer (10%, t_r = 28.57 min). $[\alpha]_D$ = -6.64 (c = 0.39, $CHCl_3$)



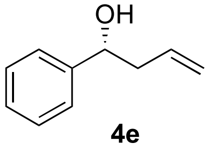
4c

(1*R*)-1-Cyclohexyl-3-buten-1-ol (4c)[8]: Following general procedure for **4a**, except that the product was purified by 5% Et_2O/Pentane eluent system, yield (90%). The spectroscopic data of the product are identical with those reported in literature.[8] Enantiomeric excess was determined from the integration of the diastereomeric peaks in the ^{19}F NMR of the corresponding (*R*) Mosher ester, major (71.544 ppm, 85%), minor

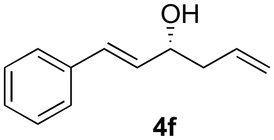
(71.605 ppm, 15%). $[\alpha]_D$ = -0.43 (c = 0.46, $CHCl_3$)


4d

(3*R*)-1–(*tert*-Butyl-diphenyl-silanoxy)-hex-5-en-3-ol (4d)[6]: Following general procedure for **4a**, except, that the aldehyde was dissolved in 0.5 ml of toluene, and injected into the reaction mixture, and reaction time was 24 hrs, yield (90%). The spectroscopic data of this are identical with those reported in literature.[6] HPLC analysis using chiracel OD (2.5% IPA/hexane, 1ml/min, 254 nm) gave the minor isomer (17.1%, t_r = 24.3 min), and the major isomer (82.9%, t_r = 29.6 min). $[\alpha]_D$ = 1.47, (c = 0.58, $CHCl_3$)

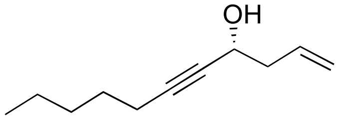

4e

(1*R*)-1-phenyl-3-butene-1-ol (4e)[6]: Following general procedure for **4a**. Yield (99%). The spectroscopic data of this are identical with those reported in literature.[6] HPLC analysis using chiracel OD (5% IPA/hexanes, 0.5 ml/min, 254 nm) gave the minor isomer (48.9%, t_r = 29.8 min), and the major isomer (51.1%, t_r = 31.9 min). $[\alpha]_D$ = -4.9, (c = 0.49, $CHCl_3$)


4f

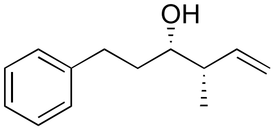
(1*E*,3*R*)-1-phenyl-1,5-hexadien-3-ol (4f)[9]: Following general procedure for **4a**. Yield (72%). The spectral properties of the obtained compound are identical with those reported in literature. HPLC analysis of the product using Chiracel OD (5%

IPA/hexanes, 0.5 ml/ml, 254 nm) gave the major isomer (59.5%, t_r = 42.6 min) and the minor isomer (41.5%, t_r = 75.3 min). $[\alpha]_D$ = -5.69, (c = 0.13, $CHCl_3$)



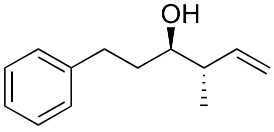
4g

(4*R*)-Undec-1-en-5-yn-1-ol (4g)[10]: Following general procedure for **4a**. Yield (99%). The spectroscopic data of this are identical with those reported in literature. Enatiomeric excess was determined by integration of the diastereomeric peaks of the corresponding (*S*)- Mosher-ester. ^{19}F NMR (376.141 MHz) Major 71.961 ppm (55.98%) and minor 72.183 ppm (44.02%). $[\alpha]_D$ = - 4.0, (c = 0.40, $CHCl_3$)



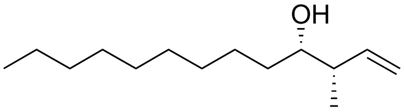
8a

(3*S*,4*S*)-4-Methyl-1-Phenyl-5-hexen-3-ol (8a)[11]: Following general procedure for **4a**, except that cis-crotyl boronic pinacol ester **7** was used and the reaction time was 24 hr. Yield (87%). The spectroscopic data of this are identical with those reported in literature[6]. HPLC analysis of the product using Chiracel OD (10% IPA/Hexane, 1 ml/min, 250 nm) gave the major isomer (70%, t_r = 10.8 min), and minor isomer (30%, t_r = 15.8 min). $[\alpha]_D$ = - 20.36, (c = 0.72, $CHCl_3$).



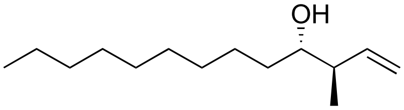
6a

(3*R*,4*S*)-4-Methyl-1-Phenyl-5-hexen-3-ol (6a)[11]: Following general procedure for **8a**, except that trans-crotyl boronic pinacolester **5** and the isomer (S,S)-(-)-1,2-Di(1-Napthyl)-1,2-ethane diol of **1j** was used and the reaction time was 24 hr. Yield (99%). The spectroscopic data of this are identical with those reported in literature.[11] HPLC analysis of the product using Chiracel OD (10% IPA/Hexane, 1 ml/min, 220 nm) gave the major isomer (86%, t_r = 12.6 min), and minor isomer (14%, t_r = 18.5 min). $[\alpha]_D$ = 13.20, (c = 0.45, $CHCl_3$).



6a

(S)-3-Methyl-tridec-1-en-4-ol (6a)[7]: Following procedure for **8a**, Yield (70%). The spectroscopic data of this are identical with those reported in literature[12] Enatiomeric excess was determined by integration of the diastereomeric peaks of the corresponding (*S*)- Mosher-ester. ^{19}F NMR (376.141 MHz) minor -71.426 ppm (27%), major 71.517 ppm (73%). $[\alpha]_D$ = -15.92, (c = 0.23, $CHCl_3$).



6b

3-Methyl-tridec-1-en-4-ol (2k)[7]: Following general procedure for **6a**, yield (70%). The spectroscopic data of this are identical with those reported in literature.[7] Enatiomeric excess was determined by integration of the diastereomeric peaks of the corresponding (*S*)- Mosher-ester. ^{19}F NMR (376.141 MHz) minor -71.467 ppm (14%), major 71.530 (86%). $[\alpha]_D$ = -23.94, (c = 0.75, $CHCl_3$).

Double diastereoselective reactions[12]:

General: **(S)-2-Methyl-3-[(tert-butyldimethylsilyl)oxy]propionaldehyde 9** was prepared following literature procedure[12]. The crude aldehyde that is obtained (after the work-up, and evaporation of the solvent) of swern oxidation is filtered through a short plug (~10 cm, 1 inch diameter) of silica using 30% EtOAc / Hexanes to free the aldehyde from any residual Et_3N-HCl and other inorganic impurities. Allyl and crotyl reagents were freshly prepared and used for the following reactions. Temperature control during reaction was provided by cryo-cool systems.

Procedure for the reaction of allyl or cis- crotyl boronic pinacol esters with aldehyde 3: Into a flame-dried 25 ml RB flask was charged 17.3mg (0.055 mmol, 0.11 equiv) of diol **1j** or its isomer **1i**, 10.3 mg of Na_2CO_3, and 50 mg of 4 A^0 activated molecular seives and the flask was capped with a septa and put under argon. To this mixture is added 0.75 ml of anhydrous toluene followed by 50 µl of $SnCl_4$ (1.0 M in DCM) (0.05mmol, 0.10 equiv) and the resulting mixture is stirred for 5 min, after which, it is cooled to -78^{0}C and maintained at this temperature for 15 minutes, after which 84 mg of allylboronic pinacol ester **3** or 100.1 mg of freshly prepared cis-crotyl boronic pinacol ester **7** (0.55 mmol, 1.1 equiv) in 0.5 ml of toluene is slowly added and this mixture is maintained at -78^{0}C for another 15 minutes. After this, 101 mg (0.50 mmol, 1.0 equiv) of freshly prepared aldehyde **3** dissolved in 0.25 ml of toluene is added dropwise and the reaction is maintained for 24 hrs at -78^{0}C. After the elapsed time, 1.0 ml of DIBAL-H (2 equiv, 2 mmol) 1.0 M in toluene, is slowly added to the reaction mixture (in-order to quench any unreacted aldehyde) and the mixture is stirred for 30 min at -78^{0}C, after which 2.0 ml of 1 N HCl is added in one portion, and the reaction mixture is gradually brought to room temperature and stirred for additional 1 hr. At this point, the biphasic reaction mixture appears dark brown. This mixture is extracted for product with 2 X 25 ml portions of Et_2O and washed with 10 ml of water and 10 ml of brine and finally dried over Na_2SO_4. The etheral extract is then filtered and concentrated under vacuo to give the crude mixture, which was analyzed for diastereomeric composition by ^{1}H-NMR. The diastereomeric mixture is determined by integration of the doublet signals of the methyl groups of the diastereomers. (See attached NMR insets). The product is purified by column chromatography using 5% EtOAc/Hexane.

Compound **10**, **11** elute together and give a combined yield of 83% for matched-case using diol **1j**, and give 84 :16 ratio of **10: 11.**

In the mis-matched case using the ***(S,S)*** isomer of diol **1j**, the combined yield is 60 % and gives a ratio of 64 :36 of **11 : 10.** The spectral characteristics of these mixture is identical with reported literature.[12]

Compounds **12** and **13** in the diastereomeric crude mixture is are purified by the same system as above, and in this case, care is made in order to get both diastereomers into same fractions in order to get accurate ratio of the diastereomers. In the case of diol **1j**, the isolates yield is 77% and the ratio of **12 : 13** is 95 : 5.

In the case of the ***(S,S)*** isomer of diol **1j**, the ratio of 12 : 13 is **68 : 32**. In this case, the results are analogous to Ref 12 as it is difficult to get 1,2,3 *syn* relationship in such type of cis- crotylboration. Spectral characteristic of these mixtures are in accordance with literature. [12]

For $SnCl_4$ catalyzed reaction of allyl **3**, cis- crotyl **5** pinacol boronic esters procedure is analogous except that no molecular sieves, or Na_2CO_3 or the diol auxiliary is used. The product is purified by column chromatography using 5% EtOAc/Hexanes as eluent to give 70% combined yield of diastereomers in the ratio of 54: 46 of **10 : 11.**

For cis-crotylation with $SnCl_4$, similar purification as the one described above is used to give a combined yield of 81% and a ratio of 66 : 34 for **12 : 13**.

NMR Studies: Into a flame dried NMR tube was charged 31.4 mg (0.1 mmol, 1 equiv) of diol **1j**, and 21.2 mg (0.20 mmol, 2 equiv) of anhydrous Na_2CO_3 and the NMR tube was sealed and flushed with argon, and 0.8 ml of toluene-d_8 from a new bottle was added to the above mixture, followed by 11.7 μl (0.1 mmol, 1.0 equiv) of $SnCl_4$. The minimally soluble diol **1j** is immediately taken into solution via complex formation. This tube is cooled to -78^{0}C and analyzed by ^{1}H NMR and ^{119} Sn NMR at -78^{0}C. The results indicate presence of 3 alcoholic protons that have shifted downfield, and the ^{119} Sn NMR indicates three peaks in the region of hexa-coordinate Sn complexes. The same result is obtained in the absence of Na_2CO_3. In the case of a complex between diol **1a**, and $SnCl_4$, only one alcoholic proton is noticed, which is shifted downfield and only one complex of hexa-coordinated Sn is observed. Possible scenarios are listed in the attached NMR spectra copies.

Also, allylboration under the general conditions for diol **1j**, (page 14-15) except, using the (*R,R*)-(+)-1,2-Di-(1-Napthyl)-1,2-dimthoxy ethane (page 11), gave no catalysis and the minimal amount of product that was formed was racemic. As such, the necessity for protons on the chiral auxiliary is demosnstrated.

References:

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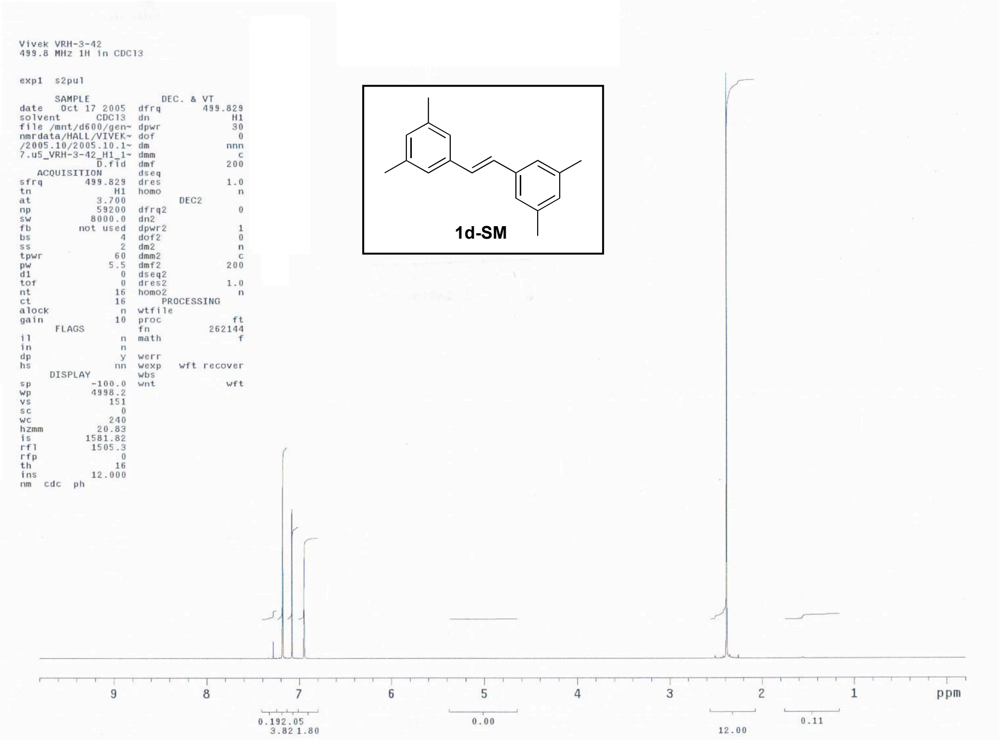

```
Vivek VRH-3-42
499.8 MHz 1H in CDCl3

exp1  s2pul

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date   Oct 17 2005  dfrq       499.829
solvent      CDCl3  dn              H1
file /mnt/d600/gen~ dpwr            30
nmrdata/HALL/VIVEK~ dof              0
/2005.10/2005.10.1~ dm             nnn
7.u5_VRH-3-42_H1_1~ dmm              c
             D.fid  dmf            200
   ACQUISITION      dseq
sfrq       499.829  dres           1.0
tn              H1  homo             n
at           3.700           DEC2
np           59200  dfrq2            0
sw          8000.0  dn2
fb        not used  dpwr2            1
bs               4  dof2             0
ss               2  dm2              n
tpwr            60  dmm2             c
pw             5.5  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt              16  homo2            n
ct              16      PROCESSING
alock            n  wtfile
gain            10  proc            ft
      FLAGS         fn          262144
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp   wft recover
     DISPLAY        wbs
sp          -100.0  wnt            wft
wp          4998.2
vs             151
sc               0
wc             240
hzmm         20.83
is         1581.82
rfl         1505.3
rfp              0
th              16
ins         12.000
nm  cdc  ph
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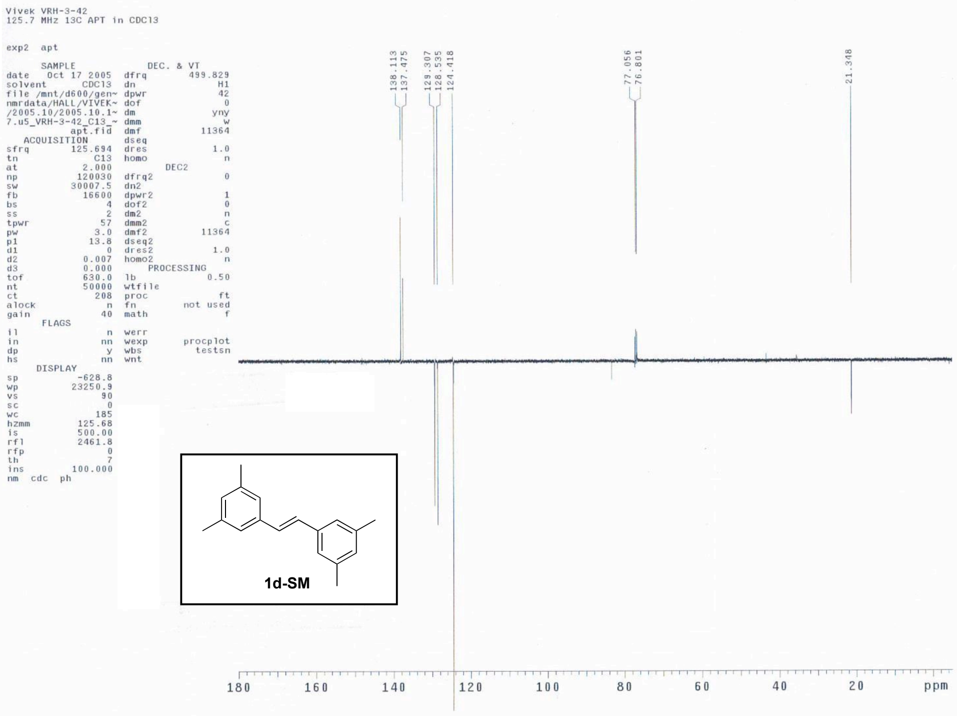
1d-SM



```
Vivek VRH-3-42
125.7 MHz 13C APT in CDCl3

exp2  apt

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solvent      CDCl3  dn              H1
file /mnt/d600/gen~ dpwr            42
nmrdata/HALL/VIVEK~ dof              0
/2005.10/2005.10.1~ dm             yny
7.u5_VRH-3-42_C13_~ dmm              w
           apt.fid  dmf          11364
   ACQUISITION      dseq
sfrq       125.694  dres           1.0
tn             C13  homo             n
at           2.000           DEC2
np          120030  dfrq2            0
sw         30007.5  dn2
fb           16600  dpwr2            1
bs               4  dof2             0
ss               2  dm2              n
tpwr            57  dmm2             c
pw             3.0  dmf2         11364
p1            13.8  dseq2
d1               0  dres2          1.0
d2           0.007  homo2            n
d3           0.000      PROCESSING
tof          630.0  lb            0.50
nt           50000  wtfile
ct             208  proc            ft
alock            n  fn        not used
gain            40  math             f
      FLAGS
il               n  werr
in              nn  wexp      procplot
dp               y  wbs         testsn
hs              nn  wnt
     DISPLAY
sp          -628.8
wp         23250.9
vs              90
sc               0
wc             185
hzmm        125.68
is          500.00
rfl         2461.8
rfp              0
th               7
ins        100.000
nm  cdc  ph
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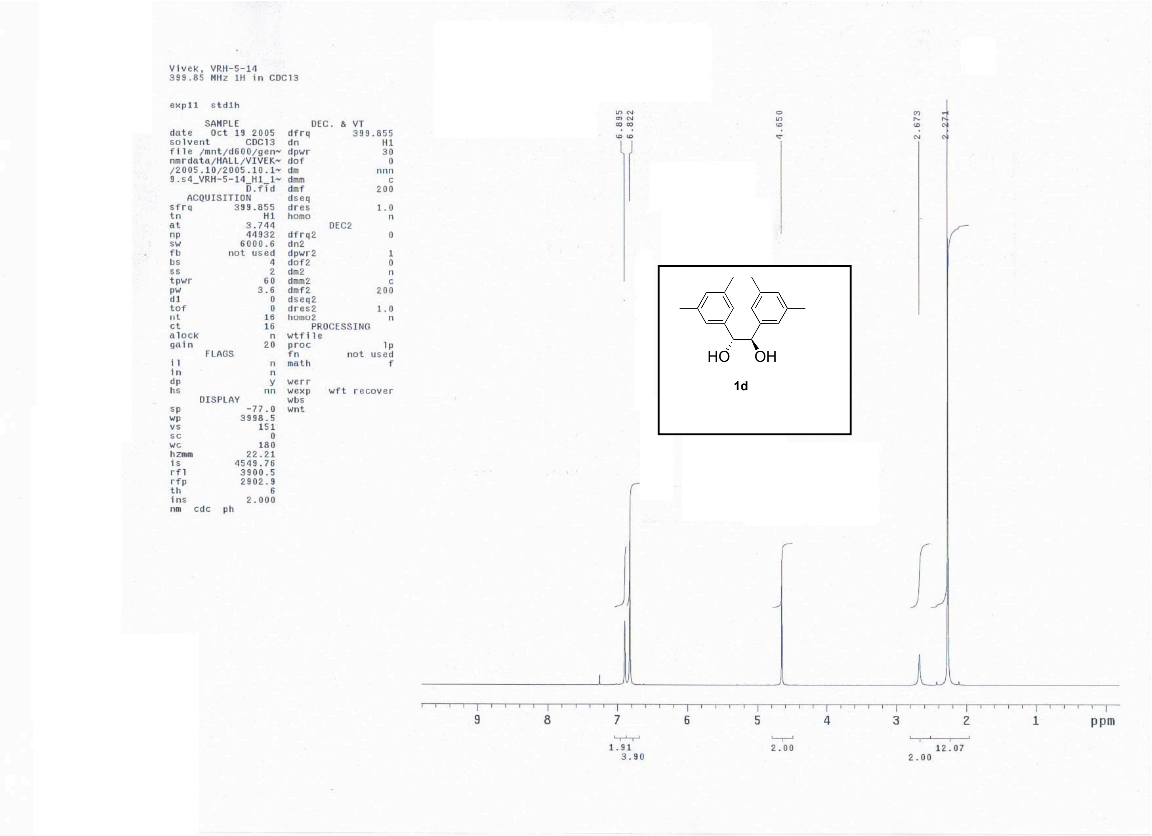
1d-SM



1d

```
Vivek, VRH-5-14
399.85 MHz 1H in CDCl3

exp11  std1h

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date   Oct 19 2005  dfrq         399.855
solvent      CDCl3  dn                H1
file /mnt/d600/gen~ dpwr              30
nmrdata/HALL/VIVEK~ dof                0
/2005.10/2005.10.1~ dm               nnn
9.s4_VRH-5-14_H1_1~ dmm                c
             D.fid  dmf              200
   ACQUISITION      dseq
sfrq       399.855  dres             1.0
tn              H1  homo               n
at           3.744          DEC2
np           44932  dfrq2              0
sw          6000.6  dn2
fb        not used  dpwr2              1
bs               4  dof2               0
ss               2  dm2                n
tpwr            60  dmm2               c
pw             3.6  dmf2             200
d1               0  dseq2
tof              0  dres2            1.0
nt              16  homo2              n
ct              16      PROCESSING
alock            n  wtfile
gain            20  proc              lp
      FLAGS         fn          not used
il               n  math               f
in               n
dp               y  werr
hs              nn  wexp   wft recover
     DISPLAY        wbs
sp           -77.0  wnt
wp          3998.5
vs             151
sc               0
wc             180
hzmm         22.21
is         4549.76
rfl         3900.5
rfp         2902.9
th               6
ins          2.000
nm  cdc  ph
```
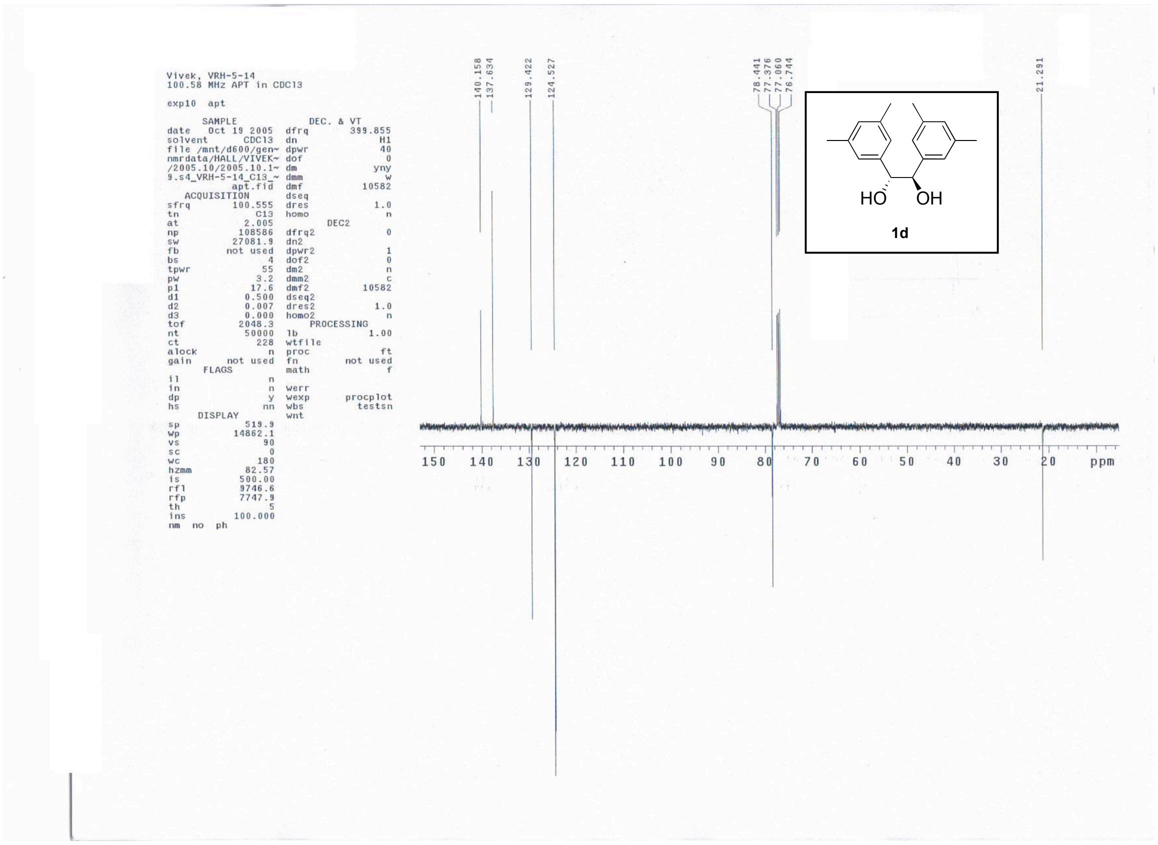
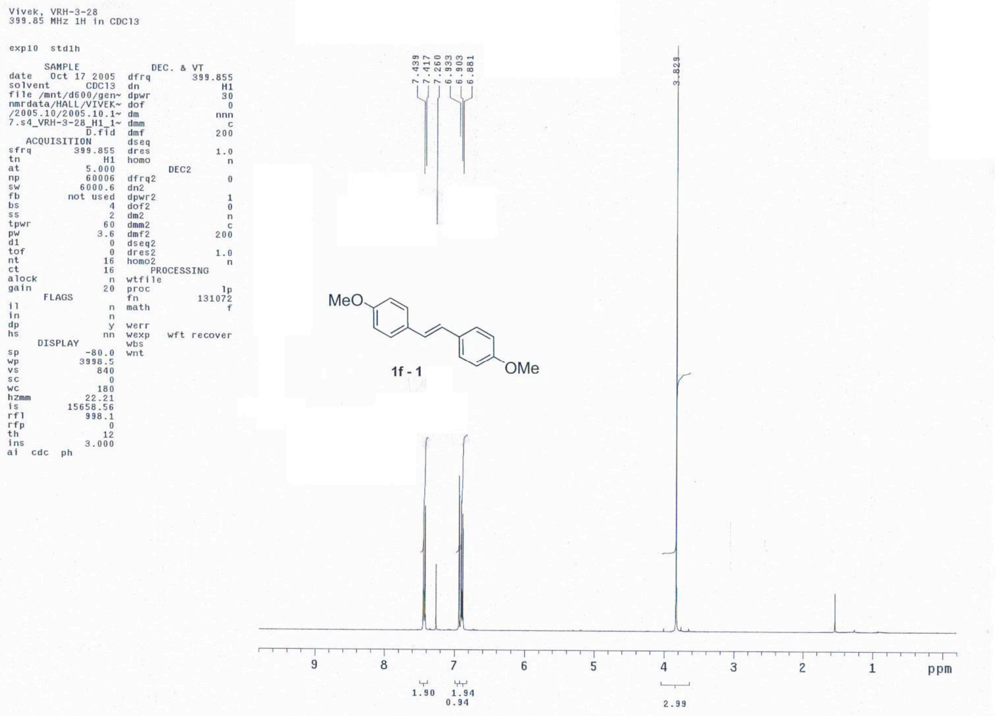



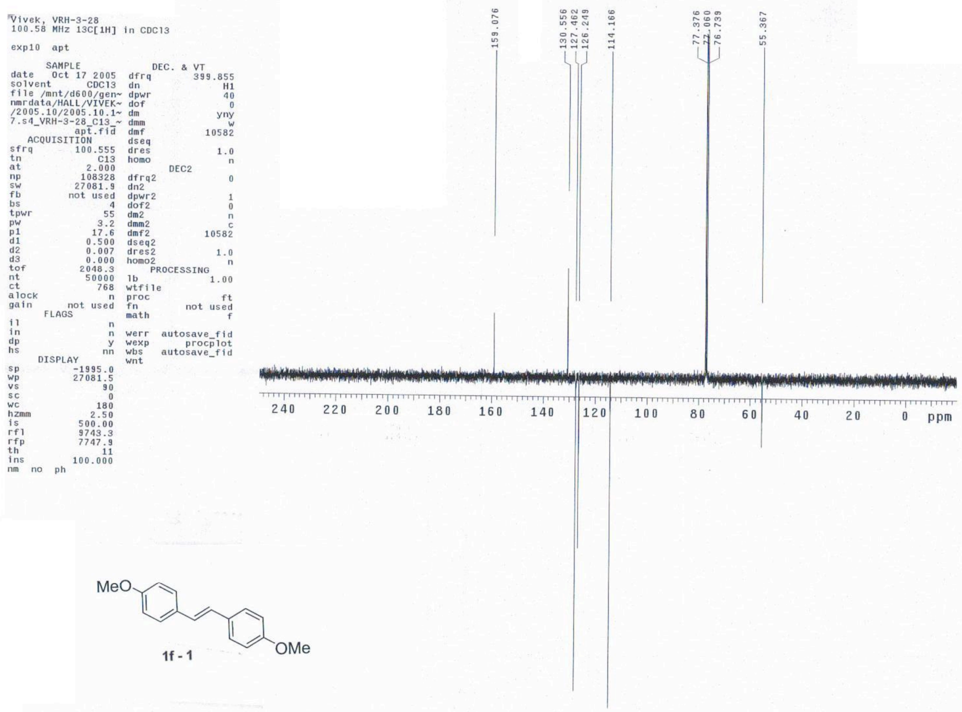
1d

```
Vivek, VRH-5-14
100.58 MHz APT in CDCl3

exp10  apt

      SAMPLE              DEC. & VT
date   Oct 19 2005  dfrq         399.855
solvent      CDCl3  dn                H1
file /mnt/d600/gen~ dpwr              40
nmrdata/HALL/VIVEK~ dof                0
/2005.10/2005.10.1~ dm               yny
9.s4_VRH-5-14_C13_~ dmm                w
           apt.fid  dmf            10582
   ACQUISITION      dseq
sfrq       100.555  dres             1.0
tn             C13  homo               n
at           2.005          DEC2
np          108586  dfrq2              0
sw         27081.9  dn2
fb        not used  dpwr2              1
bs               4  dof2               0
tpwr            55  dm2                n
pw             3.2  dmm2               c
p1            17.6  dmf2           10582
d1           0.500  dseq2
d2           0.007  dres2            1.0
d3           0.000  homo2              n
tof         2048.3      PROCESSING
nt           50000  lb              1.00
ct             228  wtfile
alock            n  proc              ft
gain      not used  fn          not used
      FLAGS         math               f
il               n
in               n  werr
dp               y  wexp        procplot
hs              nn  wbs           testsn
     DISPLAY        wnt
sp           519.9
wp         14862.1
vs              90
sc               0
wc             180
hzmm         82.57
is          500.00
rfl         9746.6
rfp         7747.9
th               5
ins        100.000
nm  no  ph
```



```
Vivek, VRH-3-28
399.85 MHz 1H in CDC13

exp10  stdlh

      SAMPLE              DEC. & VT
date   Oct 17 2005  dfrq        399.855
solvent      CDC13  dn               H1
file /mnt/d600/gen~ dpwr             30
nmrdata/HALL/VIVEK~ dof               0
/2005.10/2005.10.1~ dm              nnn
7.s4_VRH-3-28_H1_1~ dmm               c
             D.fid  dmf             200
   ACQUISITION      dseq
sfrq       399.855  dres            1.0
tn              H1  homo              n
at           5.000          DEC2
np           60006  dfrq2             0
sw          6000.6  dn2
fb        not used  dpwr2             1
bs               4  dof2              0
ss               2  dm2               n
tpwr            60  dmm2              c
pw             3.6  dmf2            200
d1               0  dseq2
tof              0  dres2           1.0
nt              16  homo2             n
ct              16     PROCESSING
alock            n  wtfile
gain            20  proc             lp
      FLAGS         fn           131072
il               n  math              f
in               n
dp               y  werr
hs              nn  wexp   wft recover
     DISPLAY        wbs
sp           -80.0  wnt
wp          3998.5
vs             840
sc               0
wc             180
hzmm         22.21
is        15658.56
rfl          998.1
rfp              0
th              12
ins          3.000
ai  cdc  ph
```

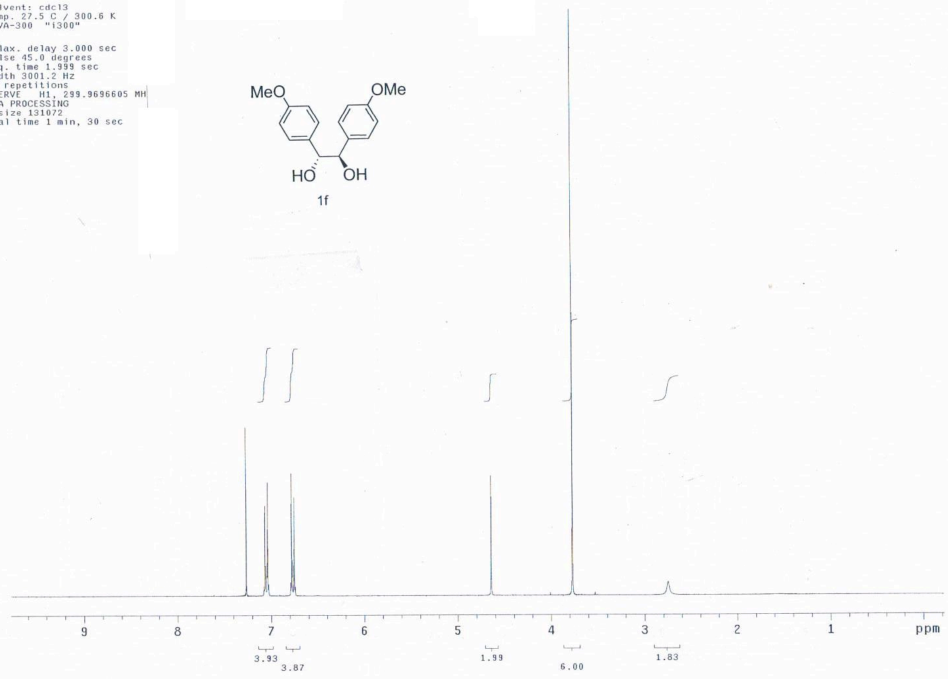
1f - 1



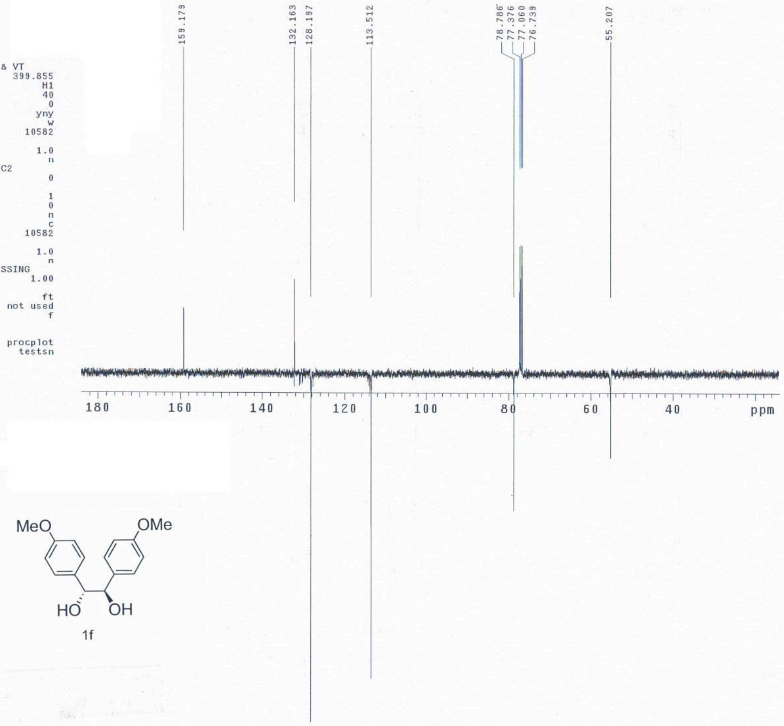
```
Vivek, VRH-3-28
100.58 MHz 13C[1H] in CDC13

exp10  apt

      SAMPLE              DEC. & VT
date   Oct 17 2005  dfrq        399.855
solvent      CDC13  dn               H1
file /mnt/d600/gen~ dpwr             40
nmrdata/HALL/VIVEK~ dof               0
/2005.10/2005.10.1~ dm              yny
7.s4_VRH-3-28_C13_~ dmm               w
           apt.fid  dmf           10582
   ACQUISITION      dseq
sfrq       100.555  dres            1.0
tn             C13  homo              n
at           2.000          DEC2
np          108328  dfrq2             0
sw         27081.9  dn2
fb        not used  dpwr2             1
bs               4  dof2              0
tpwr            55  dm2               n
pw             3.2  dmm2              c
p1            17.6  dmf2          10582
d1           0.500  dseq2
d2           0.007  dres2           1.0
d3           0.000  homo2             n
tof         2048.3     PROCESSING
nt           50000  lb             1.00
ct             768  wtfile
alock            n  proc             ft
gain      not used  fn         not used
      FLAGS         math              f
il               n
in               n  werr  autosave_fid
dp               y  wexp      procplot
hs              nn  wbs   autosave_fid
     DISPLAY        wnt
sp         -1995.0
wp         27081.5
vs              90
sc               0
wc             180
hzmm          2.50
is          500.00
rfl         9743.3
rfp         7747.9
th              11
ins        100.000
nm  no  ph
```

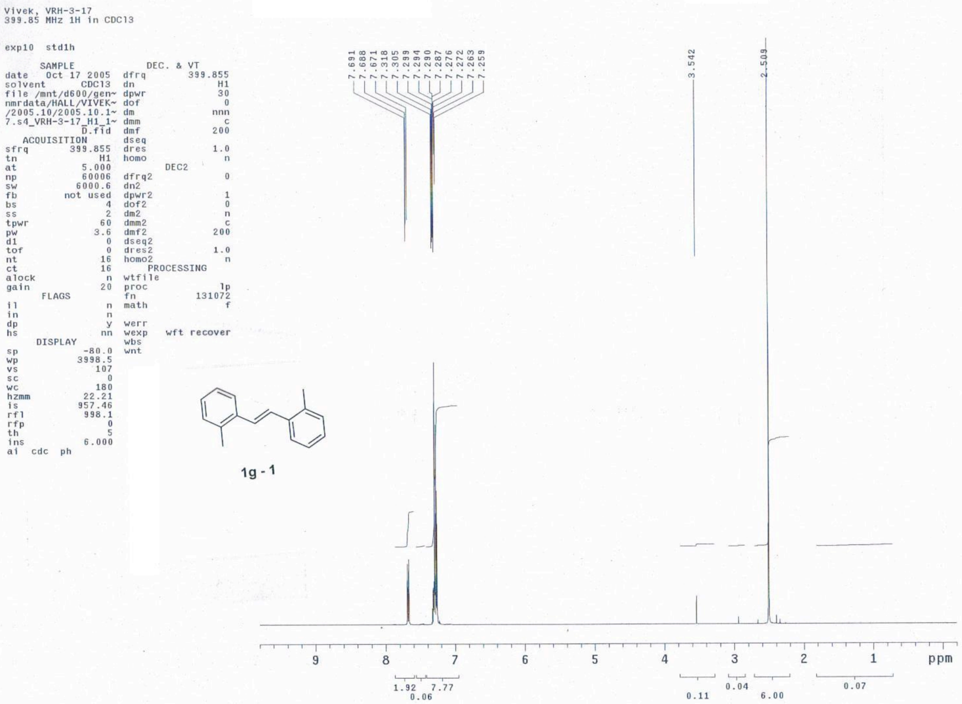
1f - 1

```
VRH-3-29B
300 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.5 C -> actual temp = 27.0 C, id probe

 Solvent: cdcl3
 Temp. 27.5 C / 300.6 K
INOVA-300  "i300"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.999 sec
 Width 3001.2 Hz
 16 repetitions
OBSERVE   H1, 299.9696605 MH
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

Pulse Sequence: s2pul
```



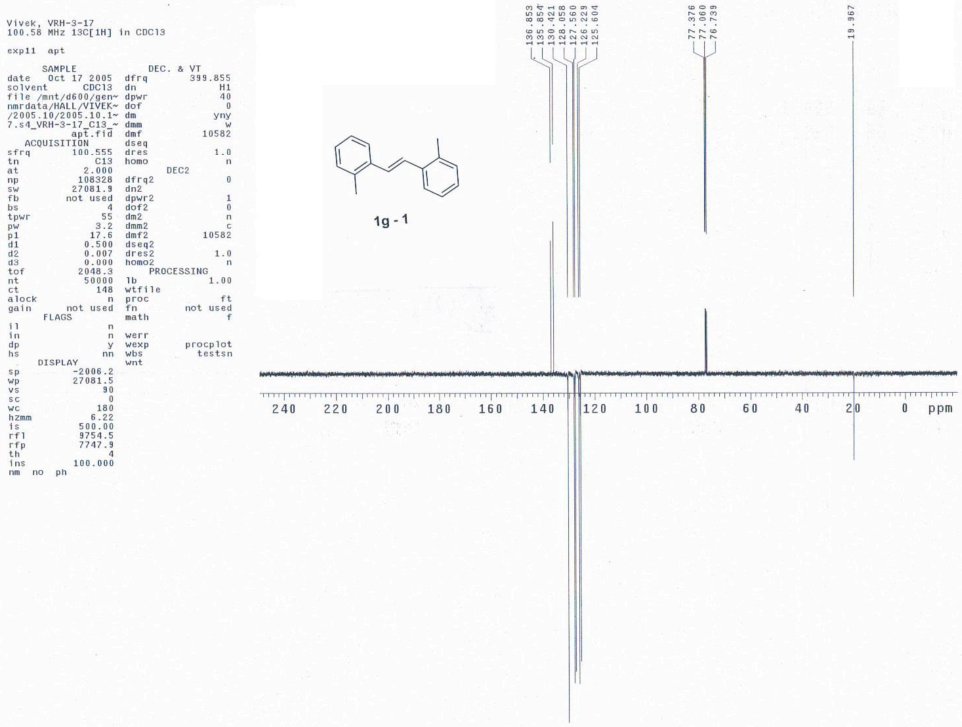
```
Vivek, VRH-3-29
100.58 MHz 13C[1H] in CDCl3

exp11  apt

      SAMPLE            DEC. & VT
date   Oct 17 2005  dfrq       399.855
solvent      CDCl3  dn              H1
file /mnt/d600/gen~ dpwr            40
nmrdata/HALL/VIVEK~ dof              0
/2005.10/2005.10.1~ dm             yny
7.s4_VRH-3-29_C13_~ dmm              w
           apt.fid  dmf          10582
   ACQUISITION      dseq
sfrq       100.555  dres           1.0
tn             C13  homo             n
at           2.000          DEC2
np          108328  dfrq2            0
sw         27081.9  dn2
fb        not used  dpwr2            1
bs               4  dof2             0
tpwr            55  dm2              n
pw             3.2  dmm2             c
p1            17.6  dmf2         10582
d1           0.500  dseq2
d2           0.007  dres2          1.0
d3           0.000  homo2            n
tof         2048.3      PROCESSING
nt           50000  lb            1.00
ct             268  wtfile
alock            n  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp      procplot
hs              nn  wbs         testsn
     DISPLAY        wnt
sp          1422.4
wp         17073.7
vs              90
sc               0
wc             180
hzmm         94.85
is          500.00
rfl         9746.6
rfp         7747.9
th               7
ins        100.000
nm  no  ph
```





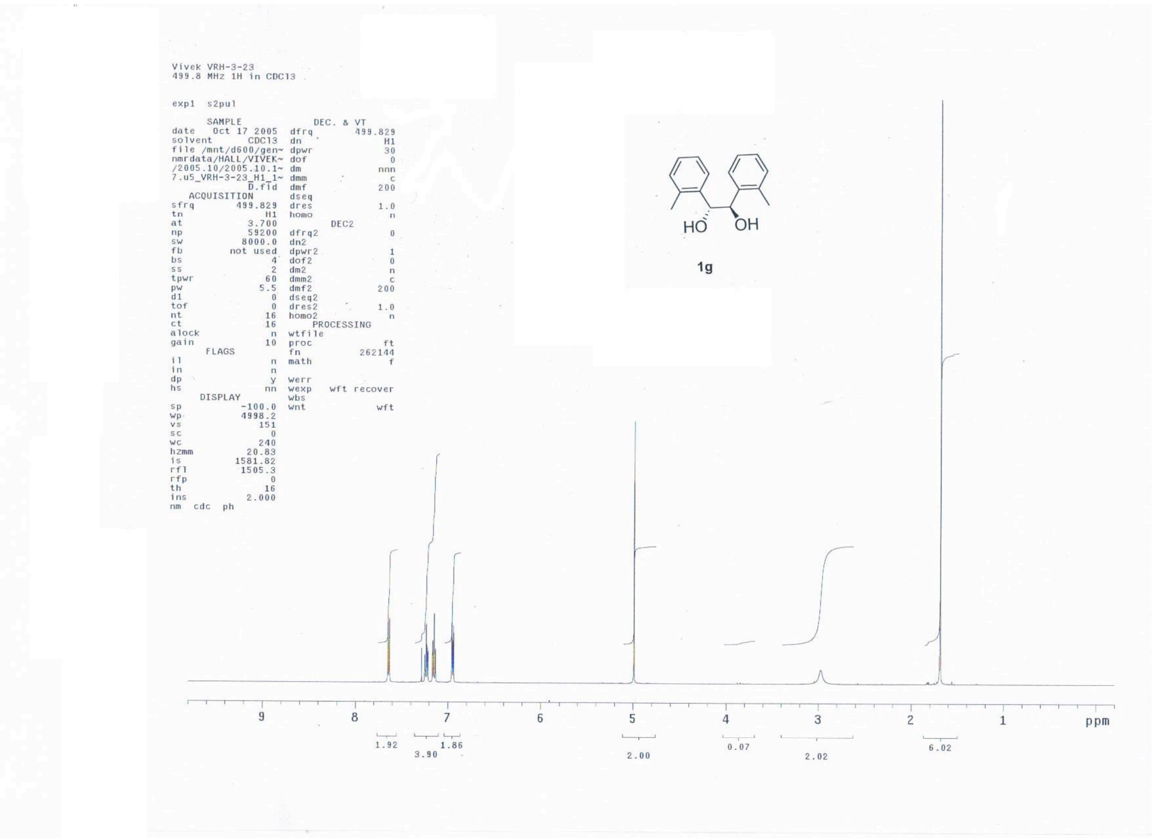
```
Vivek, VRH-3-17
399.85 MHz 1H in CDC13

exp10  std1h

       SAMPLE              DEC. & VT
date   Oct 17 2005  dfrq         399.855
solvent      CDC13  dn                H1
file /mnt/d600/gen~ dpwr              30
nmrdata/HALL/VIVEK~ dof                0
/2005.10/2005.10.1~ dm               nnn
7.s4_VRH-3-17_H1_1~ dmm                c
             D.fid  dmf              200
   ACQUISITION      dseq
sfrq       399.855  dres             1.0
tn              H1  homo               n
at           5.000           DEC2
np           60006  dfrq2              0
sw          6000.6  dn2
fb        not used  dpwr2              1
bs               4  dof2               0
ss               2  dm2                n
tpwr            60  dmm2               c
pw             3.6  dmf2             200
d1               0  dseq2
tof              0  dres2            1.0
nt              16  homo2              n
ct              16      PROCESSING
alock            n  wtfile
gain            20  proc              lp
      FLAGS         fn            131072
il               n  math               f
in               n
dp               y  werr
hs              nn  wexp    wft recover
     DISPLAY        wbs
sp           -80.0  wnt
wp          3998.5
vs             107
sc               0
wc             180
hzmm         22.21
is          957.46
rfl          998.1
rfp              0
th               5
ins          6.000
ai  cdc  ph
```

1g - 1



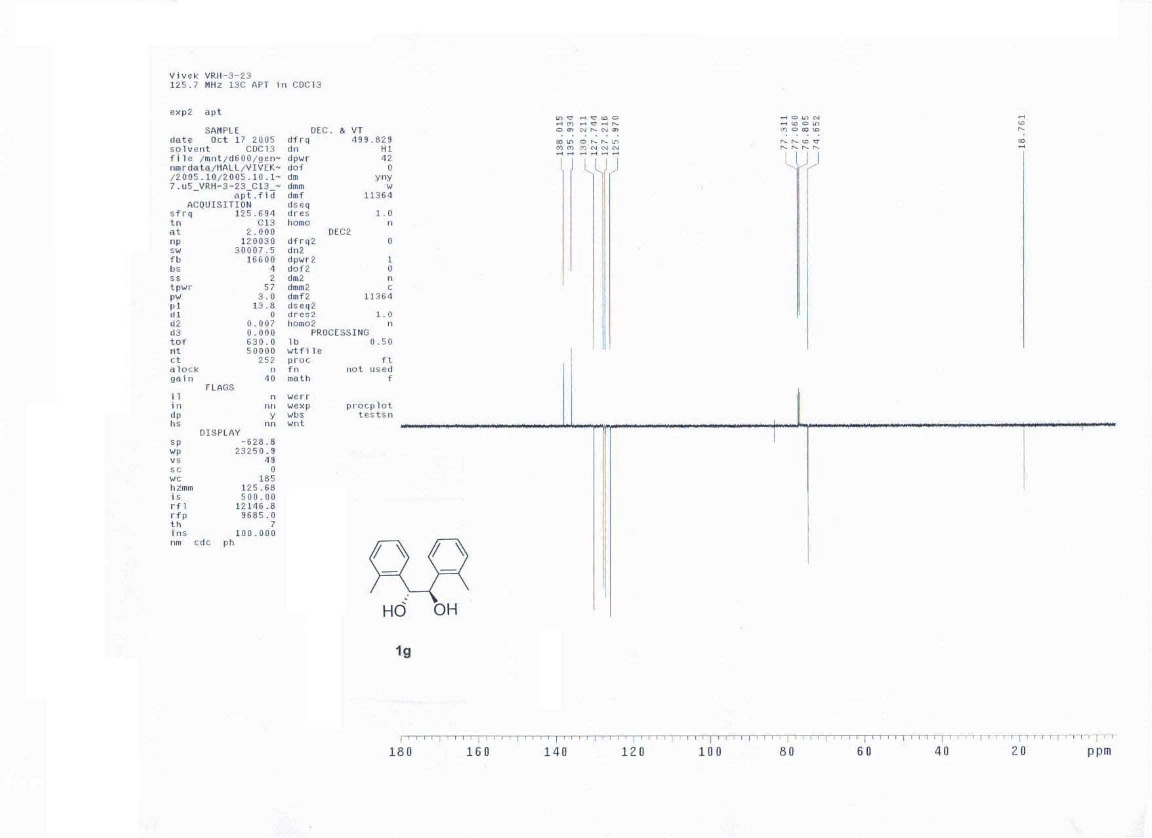
```
Vivek, VRH-3-17
100.58 MHz 13C[1H] in CDC13

exp11  apt

       SAMPLE              DEC. & VT
date   Oct 17 2005  dfrq         399.855
solvent      CDC13  dn                H1
file /mnt/d600/gen~ dpwr              40
nmrdata/HALL/VIVEK~ dof                0
/2005.10/2005.10.1~ dm               yny
7.s4_VRH-3-17_C13_~ dmm                w
           apt.fid  dmf            10582
   ACQUISITION      dseq
sfrq       100.555  dres             1.0
tn             C13  homo               n
at           2.000           DEC2
np          108328  dfrq2              0
sw         27081.9  dn2
fb        not used  dpwr2              1
bs               4  dof2               0
tpwr            55  dm2                n
pw             3.2  dmm2               c
p1            17.6  dmf2           10582
d1           0.500  dseq2
d2           0.007  dres2            1.0
d3           0.000  homo2              n
tof         2048.3      PROCESSING
nt           50000  lb              1.00
ct             148  wtfile
alock            n  proc              ft
gain      not used  fn          not used
      FLAGS         math               f
il               n
in               n  werr
dp               y  wexp        procplot
hs              nn  wbs           testsn
     DISPLAY        wnt
sp         -2006.2
wp         27081.5
vs              90
sc               0
wc             180
hzmm          6.22
is          500.00
rfl         9754.5
rfp         7747.9
th               4
ins        100.000
nm  no  ph
```

1g - 1



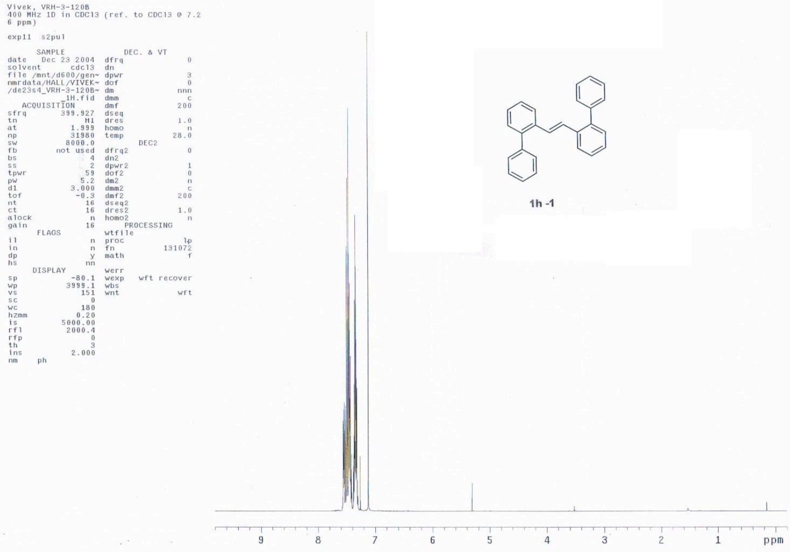
```
Vivek VRH-3-23
499.8 MHz 1H in CDC13

exp1  s2pul

      SAMPLE                  DEC. & VT
date   Oct 17 2005  dfrq          499.829
solvent       CDC13  dn                  H1
file /mnt/d600/gen~ dpwr                30
nmrdata/HALL/VIVEK~ dof                  0
/2005.10/2005.10.1~ dm                 nnn
7.u5_VRH-3-23_H1_1~ dmm                  c
              D.fid  dmf               200
   ACQUISITION       dseq
sfrq        499.829  dres              1.0
tn               H1  homo                n
at            3.700          DEC2
np            59200  dfrq2               0
sw           8000.0  dn2
fb         not used  dpwr2               1
bs                4  dof2                0
ss                2  dm2                 n
tpwr             60  dmm2                c
pw              5.5  dmf2              200
d1                0  dseq2
tof               0  dres2             1.0
nt               16  homo2               n
ct               16       PROCESSING
alock             n  wtfile
gain             10  proc               ft
      FLAGS          fn             262144
il                n  math                f
in                n
dp                y  werr
hs               nn  wexp    wft recover
     DISPLAY         wbs
sp           -100.0  wnt               wft
wp           4998.2
vs              151
sc                0
wc              240
hzmm          20.83
is          1581.82
rfl          1505.3
rfp               0
th               16
ins           2.000
nm  cdc  ph
```

1g



```
Vivek VRH-3-23
125.7 MHz 13C APT in CDC13

exp2  apt

      SAMPLE                  DEC. & VT
date   Oct 17 2005  dfrq          499.829
solvent       CDC13  dn                  H1
file /mnt/d600/gen~ dpwr                42
nmrdata/HALL/VIVEK~ dof                  0
/2005.10/2005.10.1~ dm                 yny
7.u5_VRH-3-23_C13_~ dmm                  w
            apt.fid  dmf             11364
   ACQUISITION       dseq
sfrq        125.694  dres              1.0
tn              C13  homo                n
at            2.000          DEC2
np           120030  dfrq2               0
sw          30007.5  dn2
fb            16600  dpwr2               1
bs                4  dof2                0
ss                2  dm2                 n
tpwr             57  dmm2                c
pw              3.0  dmf2            11364
p1             13.8  dseq2
d1                0  dres2             1.0
d2            0.007  homo2               n
d3            0.000       PROCESSING
tof           630.0  lb               0.50
nt            50000  wtfile
ct              252  proc               ft
alock             n  fn           not used
gain             40  math                f
      FLAGS
il                n  werr
in               nn  wexp         procplot
dp                y  wbs            testsn
hs               nn  wnt
     DISPLAY
sp           -628.8
wp          23250.9
vs               49
sc                0
wc              185
hzmm         125.68
is           500.00
rfl         12146.8
rfp          9685.0
th                7
ins         100.000
nm  cdc  ph
```

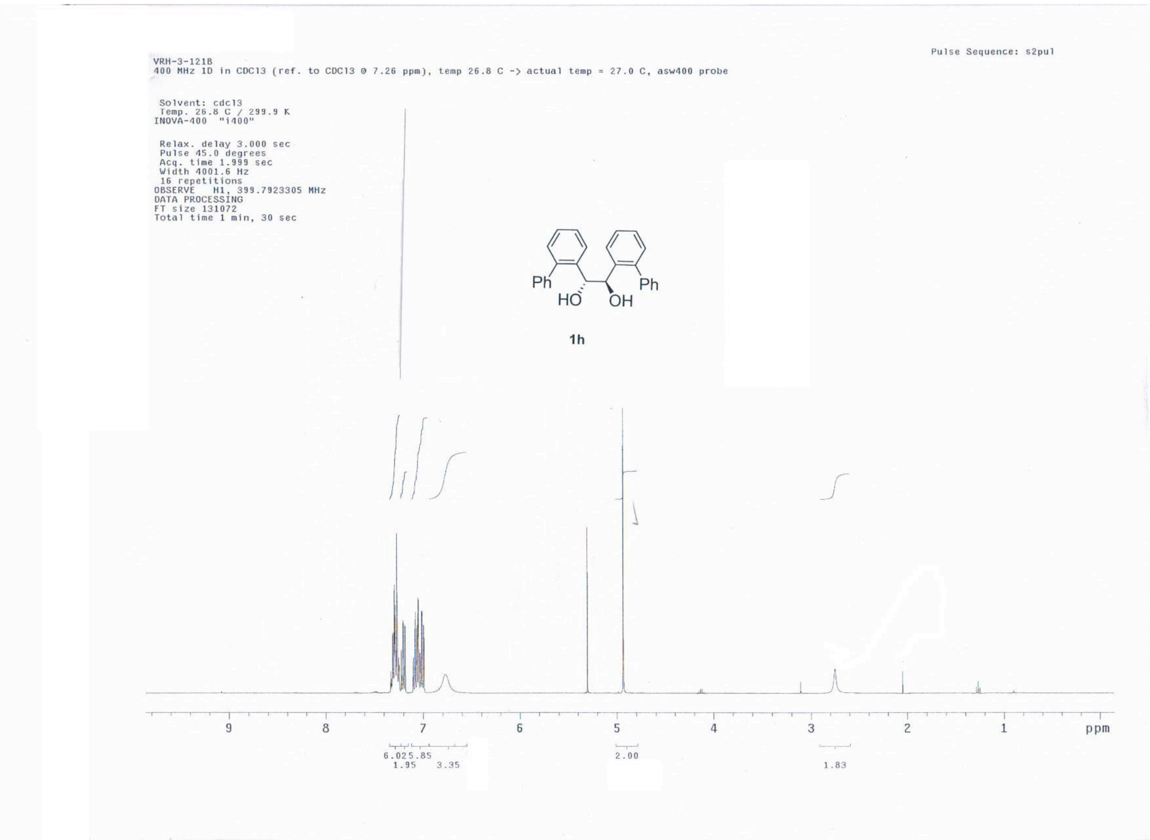
1g



```
Vivek, VRH-3-120B
400 MHz 1D in CDC13 (ref. to CDC13 @ 7.2
6 ppm)

exp11  s2pul

      SAMPLE              DEC. & VT
date   Dec 23 2004  dfrq             0
solvent      cdc13  dn
file /mnt/d600/gen~ dpwr             3
nmrdata/HALL/VIVEK~ dof              0
/de23s4_VRH-3-120B~ dm             nnn
            _1H.fid dmm              c
   ACQUISITION      dmf            200
sfrq        399.927 dseq
tn               H1 dres           1.0
at            1.999 homo             n
np            31980 temp          28.0
sw           8000.0          DEC2
fb         not used dfrq2            0
bs                4 dn2
ss                2 dpwr2            1
tpwr             59 dof2             0
pw              5.2 dm2              n
d1            3.000 dmm2             c
tof            -0.3 dmf2           200
nt               16 dseq2
ct               16 dres2          1.0
alock             n homo2            n
gain             16     PROCESSING
      FLAGS         wtfile
il                n proc            lp
in                n fn          131072
dp                y math             f
hs               nn
     DISPLAY        werr
sp            -80.1 wexp   wft recover
wp           3999.1 wbs
vs              151 wnt            wft
sc                0
wc              180
hzmm           0.20
is          5000.00
rfl          2000.4
rfp               0
th                3
ins           2.000
nm    ph
```

```
Vivek, VRH-3-120B
     1D APT in CDC13 (ref. to CDC13 @ 77.0 ppm)
```

```
Pulse Sequence: apt
```

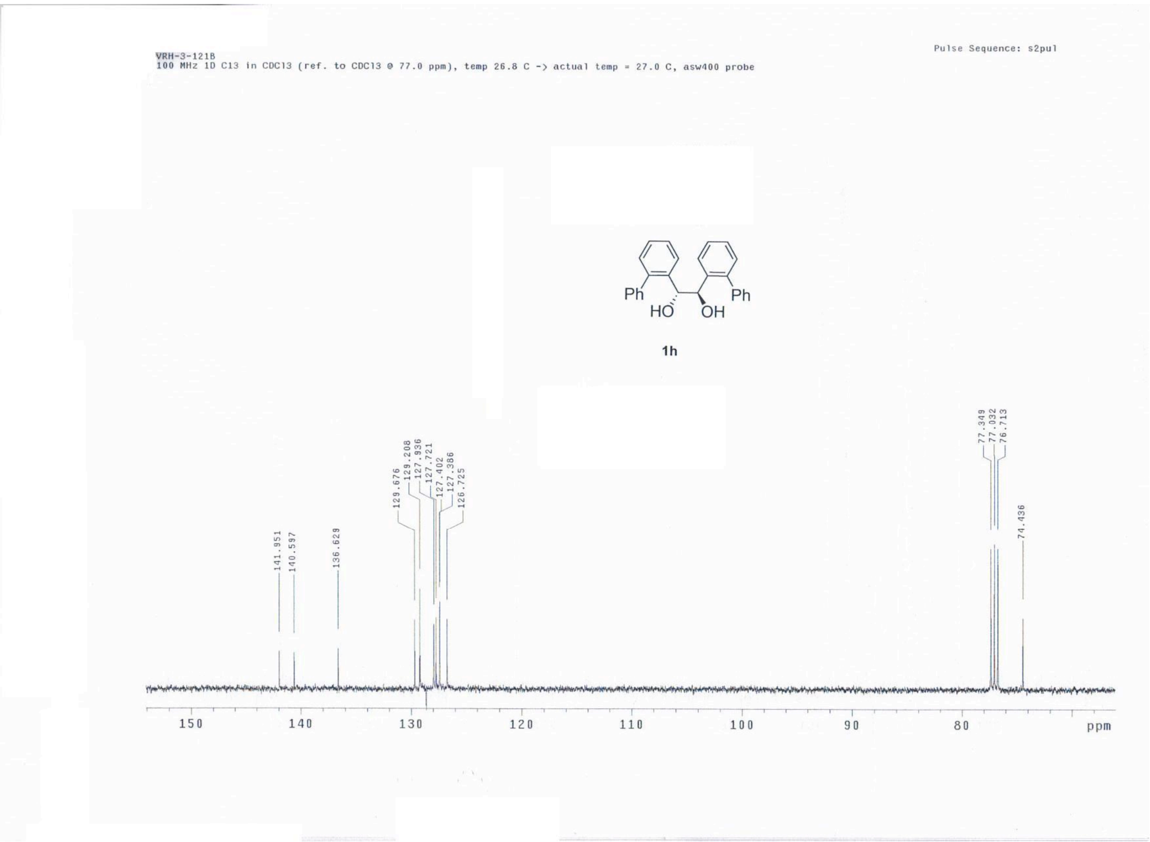


VRH-3-121B
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe

Pulse Sequence: s2pul

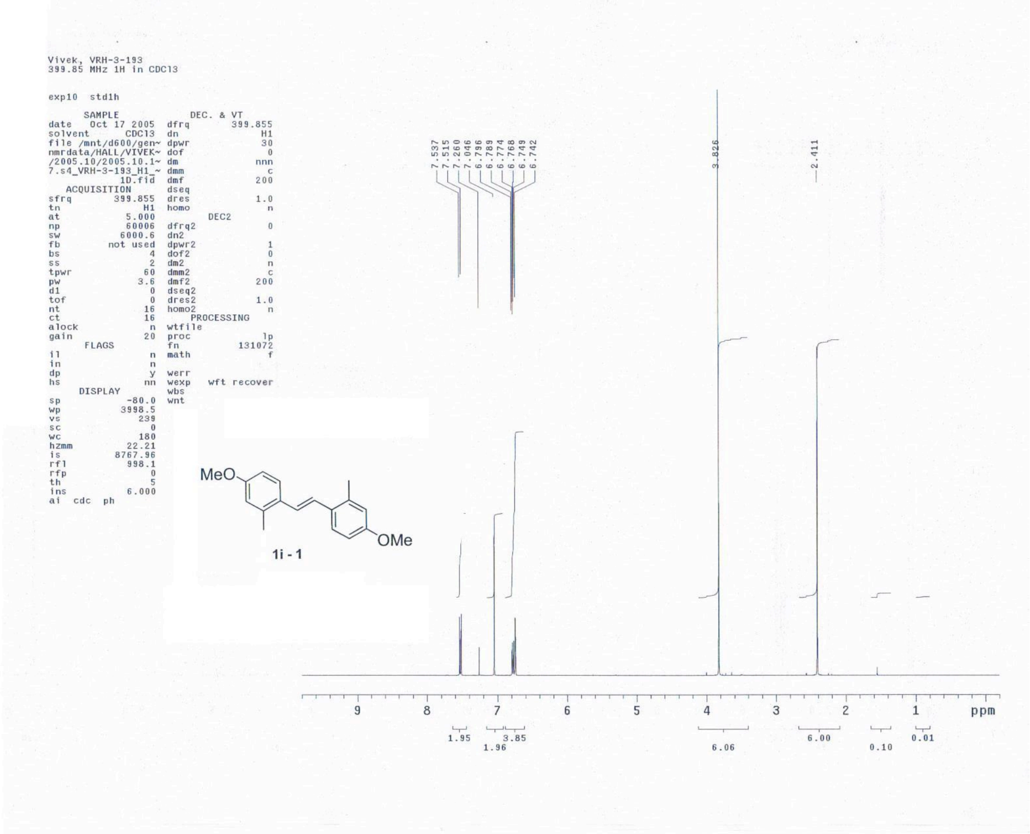
Solvent: cdcl3
Temp. 26.8 C / 299.9 K
INOVA-400 "i400"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 4001.6 Hz
16 repetitions
OBSERVE H1, 399.7923305 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

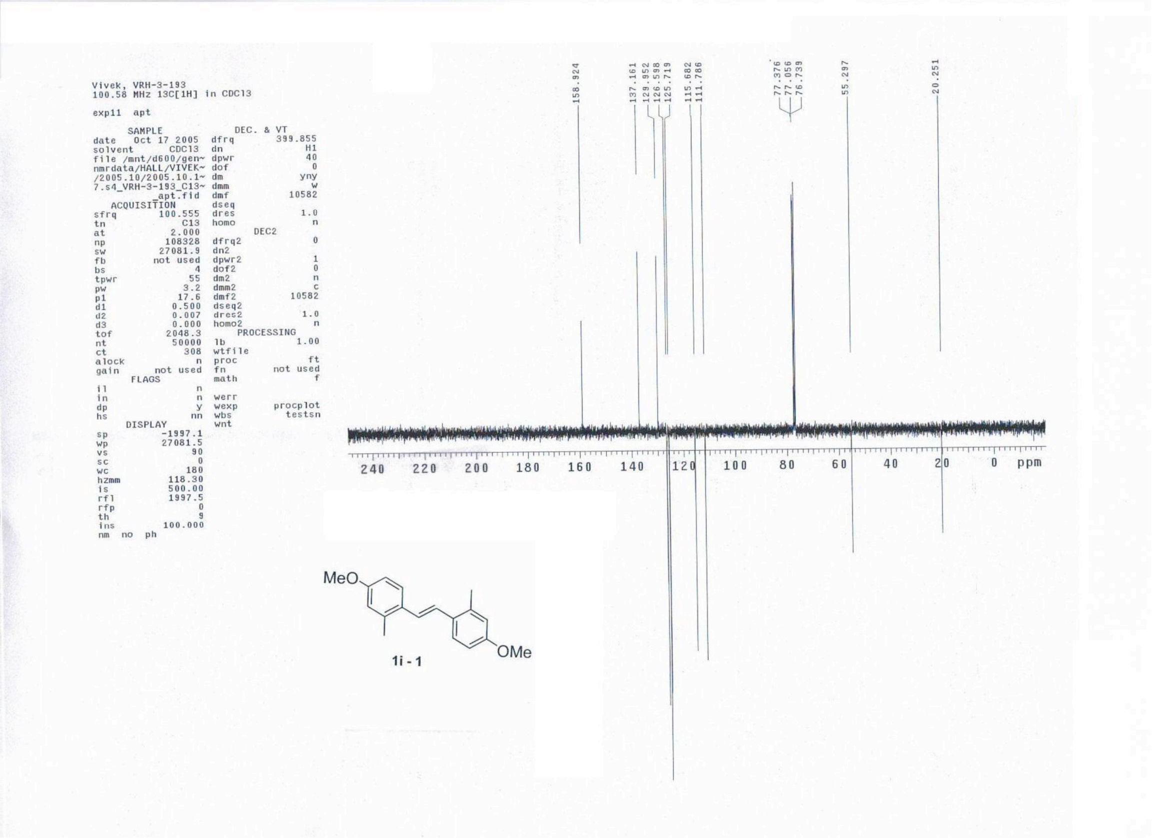


VRH-3-121B
100 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe

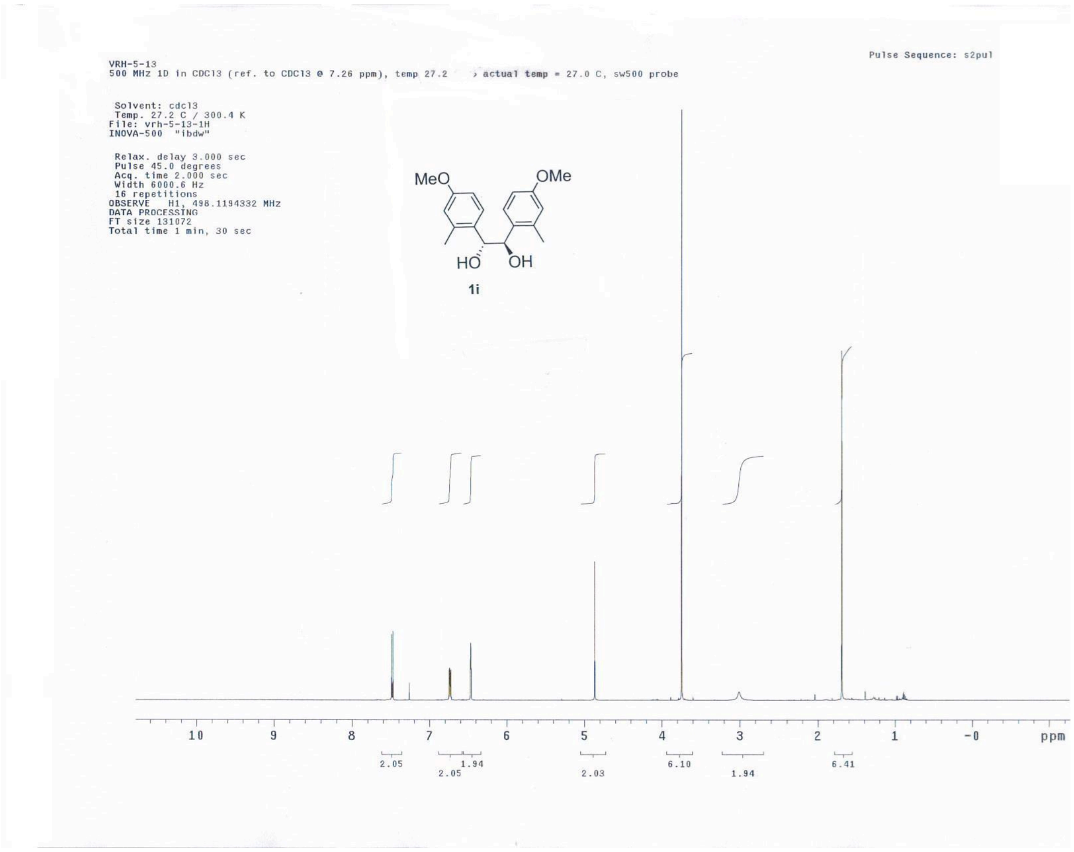
Pulse Sequence: s2pul



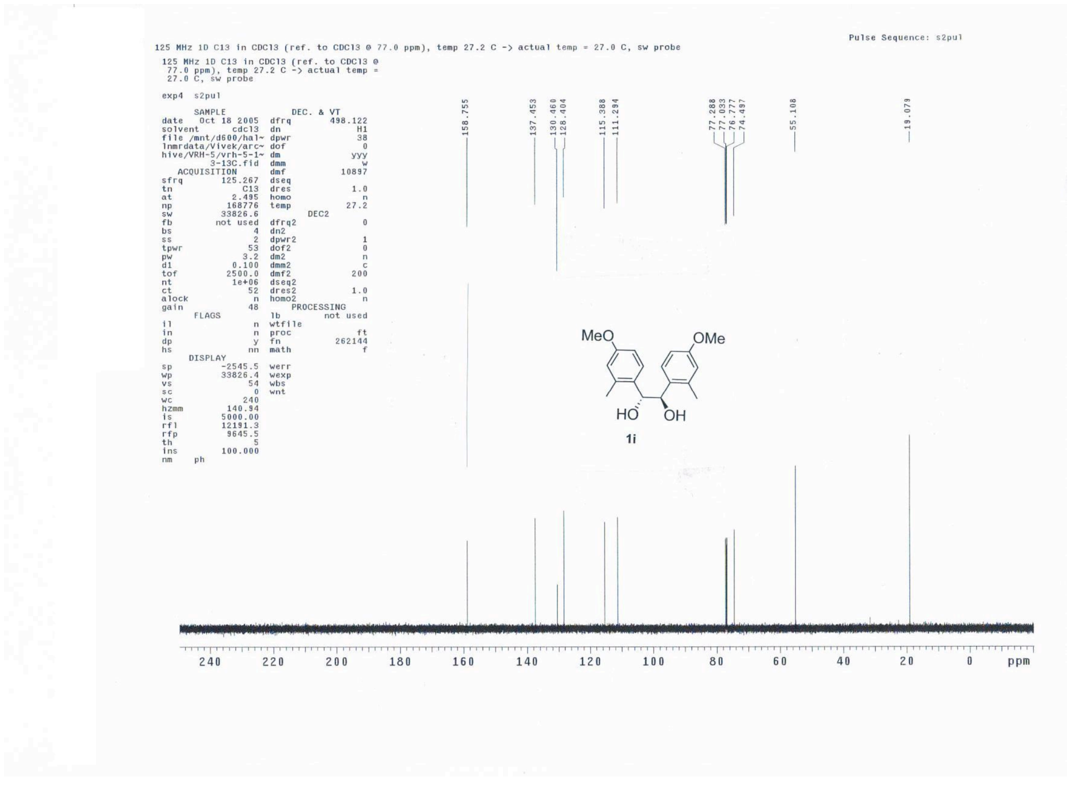
```
Vivek, VRH-3-193
399.85 MHz 1H in CDCl3

exp10  std1h

      SAMPLE              DEC. & VT
date   Oct 17 2005  dfrq       399.855
solvent      CDCl3  dn              H1
file /mnt/d600/gen~ dpwr            30
nmrdata/HALL/VIVEK~ dof              0
/2005.10/2005.10.1~ dm             nnn
7.s4_VRH-3-193_H1_~ dmm              c
            1D.fid  dmf            200
   ACQUISITION      dseq
sfrq       399.855  dres           1.0
tn              H1  homo             n
at           5.000          DEC2
np           60006  dfrq2            0
sw          6000.6  dn2
fb        not used  dpwr2            1
bs               4  dof2             0
ss               2  dm2              n
tpwr            60  dmm2             c
pw             3.6  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt              16  homo2            n
ct              16      PROCESSING
alock            n  wtfile
gain            20  proc            lp
      FLAGS         fn          131072
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp   wft recover
     DISPLAY        wbs
sp           -80.0  wnt
wp          3998.5
vs             239
sc               0
wc             180
hzmm         22.21
is         8767.96
rfl          998.1
rfp              0
th               5
ins          6.000
ai  cdc  ph
```



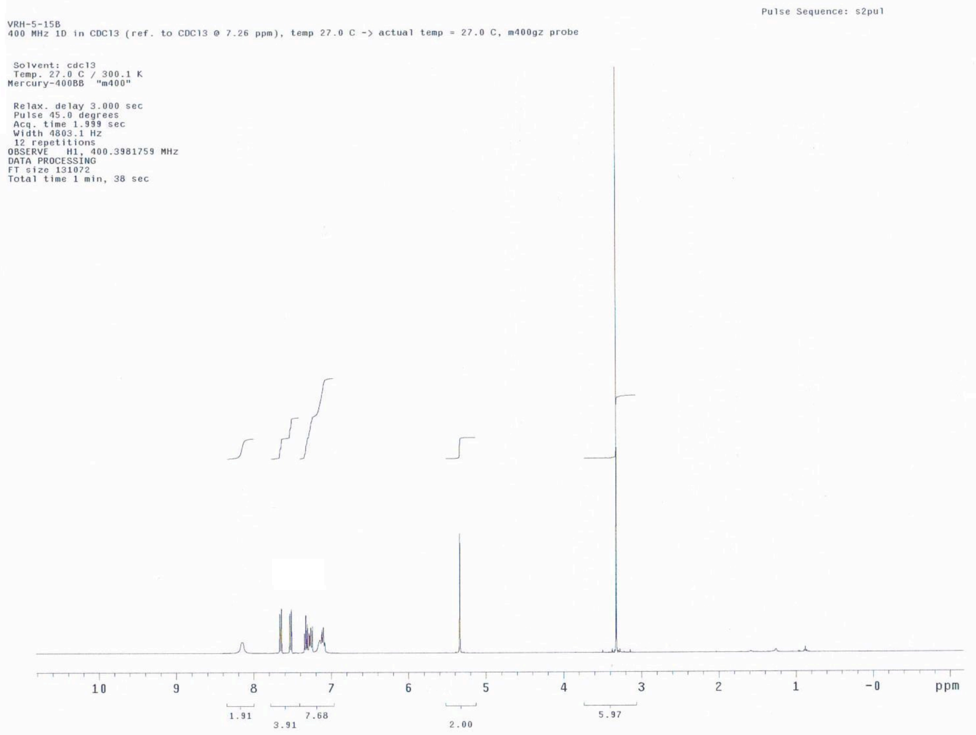
```
Vivek, VRH-3-193
100.58 MHz 13C[1H] in CDCl3

exp11  apt

      SAMPLE              DEC. & VT
date   Oct 17 2005  dfrq       399.855
solvent      CDCl3  dn              H1
file /mnt/d600/gen~ dpwr            40
nmrdata/HALL/VIVEK~ dof              0
/2005.10/2005.10.1~ dm             yny
7.s4_VRH-3-193_C13~ dmm              w
          _apt.fid  dmf          10582
   ACQUISITION      dseq
sfrq       100.555  dres           1.0
tn             C13  homo             n
at           2.000          DEC2
np          108328  dfrq2            0
sw         27081.9  dn2
fb        not used  dpwr2            1
bs               4  dof2             0
tpwr            55  dm2              n
pw             3.2  dmm2             c
p1            17.6  dmf2         10582
d1           0.500  dseq2
d2           0.007  dres2          1.0
d3           0.000  homo2            n
tof         2048.3      PROCESSING
nt           50000  lb            1.00
ct             308  wtfile
alock            n  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp      procplot
hs              nn  wbs         testsn
     DISPLAY        wnt
sp         -1997.1
wp         27081.5
vs              90
sc               0
wc             180
hzmm        118.30
is          500.00
rfl         1997.5
rfp              0
th               9
ins        100.000
nm  no  ph
```



```
VRH-5-13
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.2    › actual temp = 27.0 C, sw500 probe

 Solvent: cdcl3
 Temp. 27.2 C / 300.4 K
File: vrh-5-13-1H
INOVA-500  "ibdw"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 2.000 sec
 Width 6000.6 Hz
 16 repetitions
OBSERVE   H1, 498.1194332 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec
```

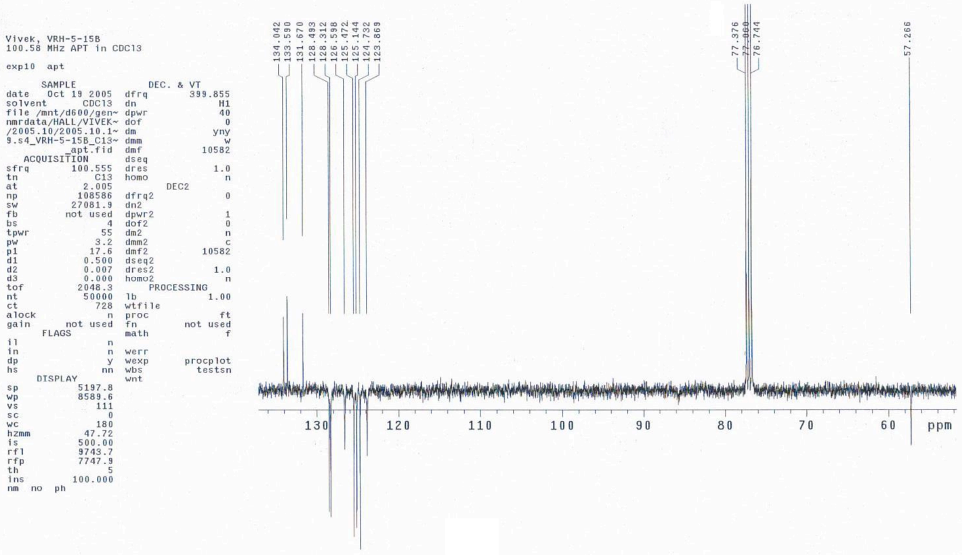


```
125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
 125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @
  77.0 ppm), temp 27.2 C -> actual temp =
  27.0 C, sw probe

 exp4  s2pul

       SAMPLE              DEC. & VT
 date   Oct 18 2005  dfrq        498.122
 solvent      cdcl3  dn               H1
 file /mnt/d600/hal~ dpwr             38
 lnmrdata/Vivek/arc~ dof               0
 hive/VRH-5/vrh-5-1~ dm              yyy
         3-13C.fid   dmm               w
    ACQUISITION      dmf           10897
 sfrq       125.267  dseq
 tn             C13  dres            1.0
 at           2.495  homo              n
 np          168776  temp           27.2
 sw         33826.6          DEC2
 fb        not used  dfrq2             0
 bs               4  dn2
 ss               2  dpwr2             1
 tpwr            53  dof2              0
 pw             3.2  dm2               n
 d1           0.100  dmm2              c
 tof         2500.0  dmf2            200
 nt           1e+06  dseq2
 ct              52  dres2           1.0
 alock            n  homo2             n
 gain            48      PROCESSING
       FLAGS         lb         not used
 il               n  wtfile
 in               n  proc             ft
 dp               y  fn           262144
 hs              nn  math              f
      DISPLAY
 sp         -2545.5  werr
 wp         33826.4  wexp
 vs              54  wbs
 sc               0  wnt
 wc             240
 hzmm        140.94
 is         5000.00
 rfl        12191.3
 rfp         9645.5
 th               5
 ins        100.000
 nm    ph
```

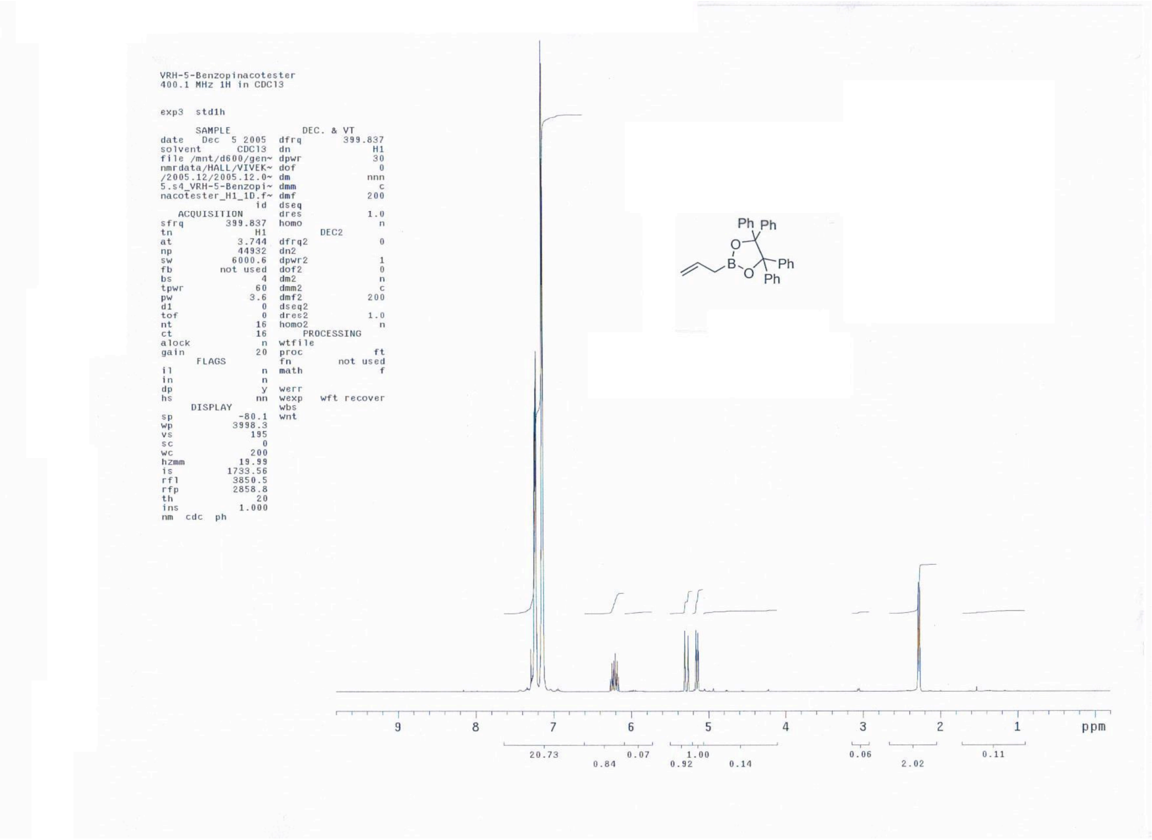


```
VRH-5-15B
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 27.0 C -> actual temp = 27.0 C, m400gz probe

 Solvent: cdcl3
 Temp. 27.0 C / 300.1 K
Mercury-400BB  "m400"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.999 sec
 Width 4803.1 Hz
 12 repetitions
OBSERVE   H1, 400.3981759 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 38 sec
```

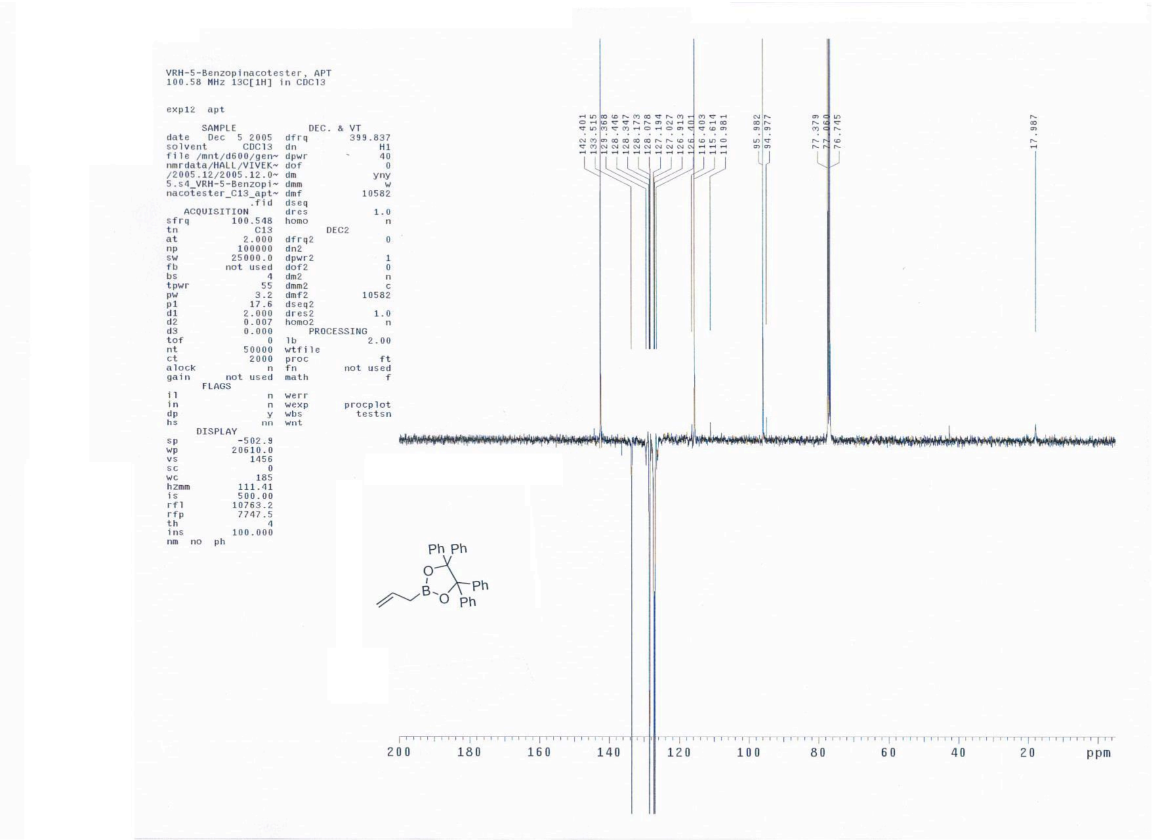
```
Pulse Sequence: s2pul
```



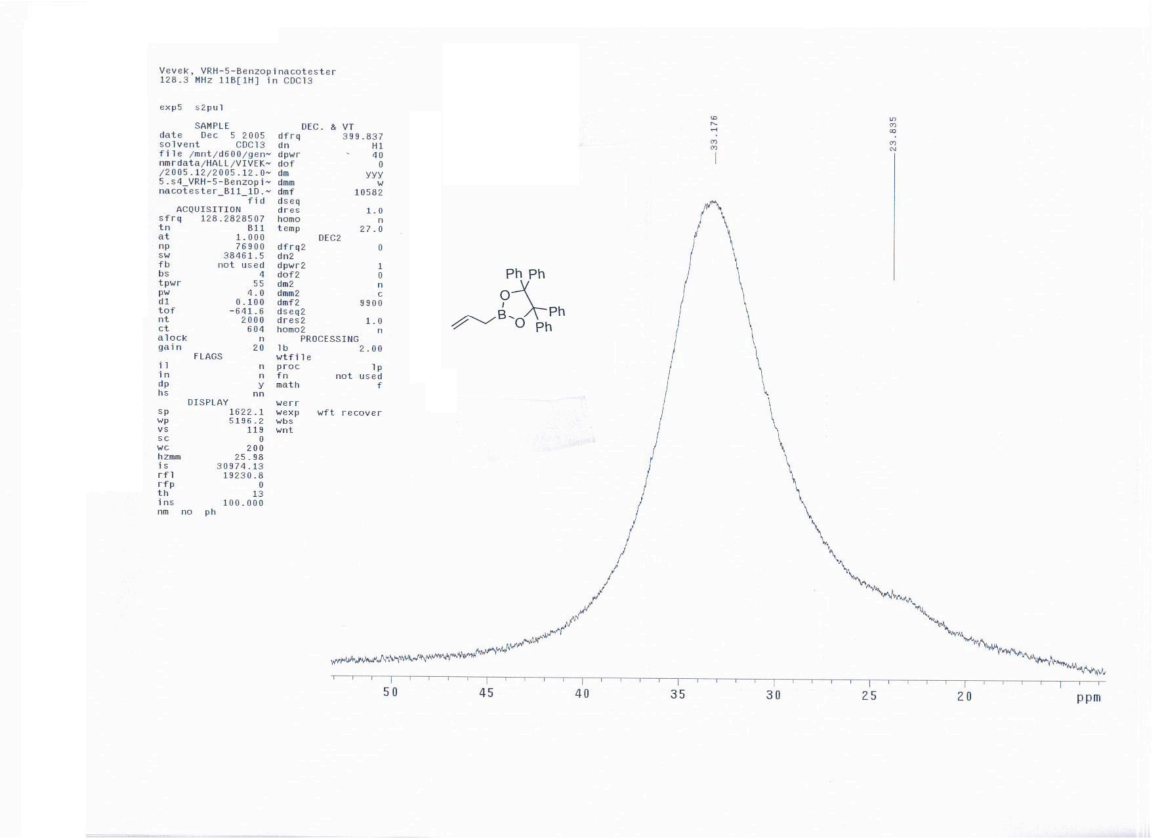
```
Vivek, VRH-5-15B
100.58 MHz APT in CDCl3

exp10  apt

      SAMPLE              DEC. & VT
date   Oct 19 2005  dfrq        399.855
solvent      CDCl3  dn               H1
file /mnt/d600/gen~ dpwr             40
nmrdata/HALL/VIVEK~ dof               0
/2005.10/2005.10.1~ dm              yny
9.s4_VRH-5-15B_C13~ dmm               w
          _apt.fid  dmf           10582
   ACQUISITION      dseq
sfrq       100.555  dres            1.0
tn             C13  homo              n
at           2.005          DEC2
np          108586  dfrq2             0
sw         27081.9  dn2
fb        not used  dpwr2             1
bs               4  dof2              0
tpwr            55  dm2               n
pw             3.2  dmm2              c
p1            17.6  dmf2          10582
d1           0.500  dseq2
d2           0.007  dres2           1.0
d3           0.000  homo2             n
tof         2048.3       PROCESSING
nt           50000  lb             1.00
ct             728  wtfile
alock            n  proc             ft
gain      not used  fn         not used
      FLAGS         math              f
il               n
in               n  werr
dp               y  wexp       procplot
hs              nn  wbs          testsn
     DISPLAY        wnt
sp          5197.8
wp          8589.6
vs             111
sc               0
wc             180
hzmm         47.72
is          500.00
rfl         9743.7
rfp         7747.9
th               5
ins        100.000
nm  no  ph
```



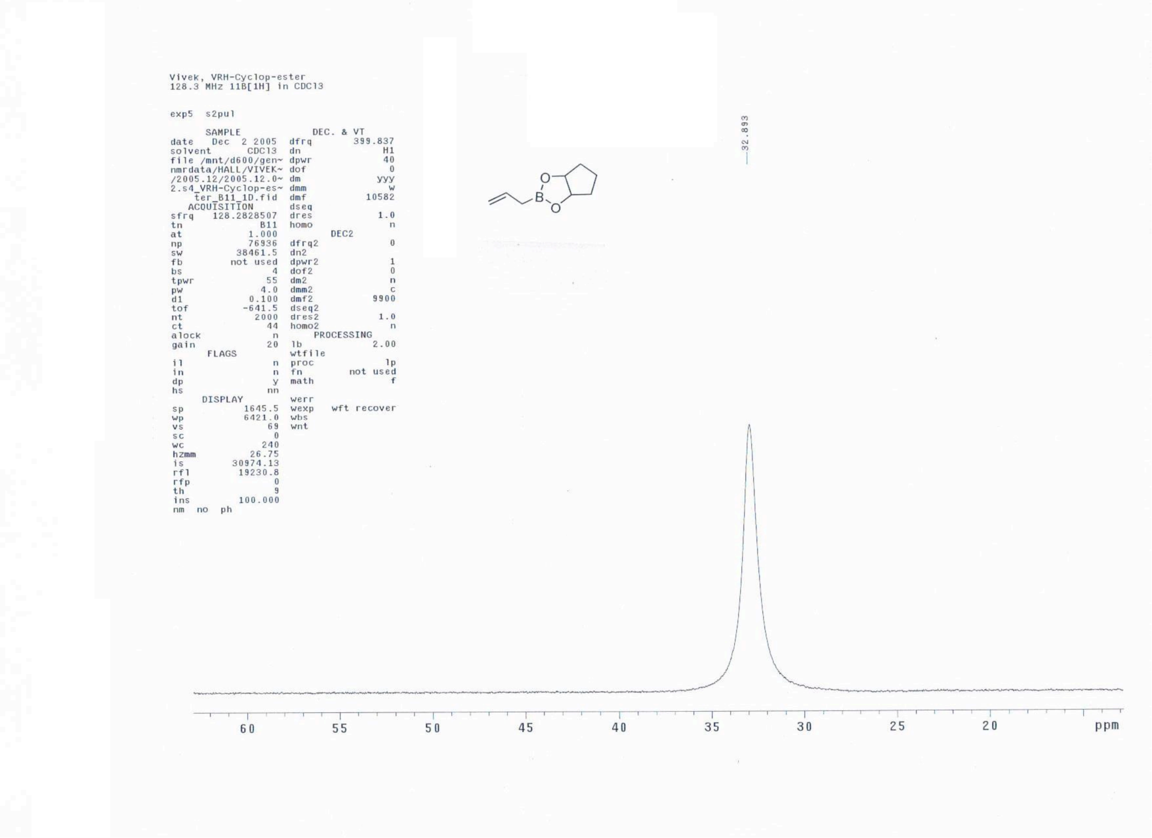
```
VRH-5-Benzopinacotester
400.1 MHz 1H in CDC13

exp3  std1h

      SAMPLE               DEC. & VT
date   Dec  5 2005  dfrq         399.837
solvent      CDC13  dn                H1
file /mnt/d600/gen~ dpwr              30
nmrdata/HALL/VIVEK~ dof                0
/2005.12/2005.12.0~ dm               nnn
5.s4_VRH-5-Benzopi~ dmm                c
nacotester_H1_1D.f~ dmf              200
                id  dseq
   ACQUISITION      dres             1.0
sfrq       399.837  homo               n
tn              H1          DEC2
at           3.744  dfrq2              0
np           44932  dn2
sw          6000.6  dpwr2              1
fb        not used  dof2               0
bs               4  dm2                n
tpwr            60  dmm2               c
pw             3.6  dmf2             200
d1               0  dseq2
tof              0  dres2            1.0
nt              16  homo2              n
ct              16      PROCESSING
alock            n  wtfile
gain            20  proc              ft
      FLAGS         fn          not used
il               n  math               f
in               n
dp               y  werr
hs              nn  wexp   wft recover
     DISPLAY        wbs
sp           -80.1  wnt
wp          3998.3
vs             195
sc               0
wc             200
hzmm         19.99
is         1733.56
rfl         3850.5
rfp         2858.8
th              20
ins          1.000
nm  cdc  ph
```



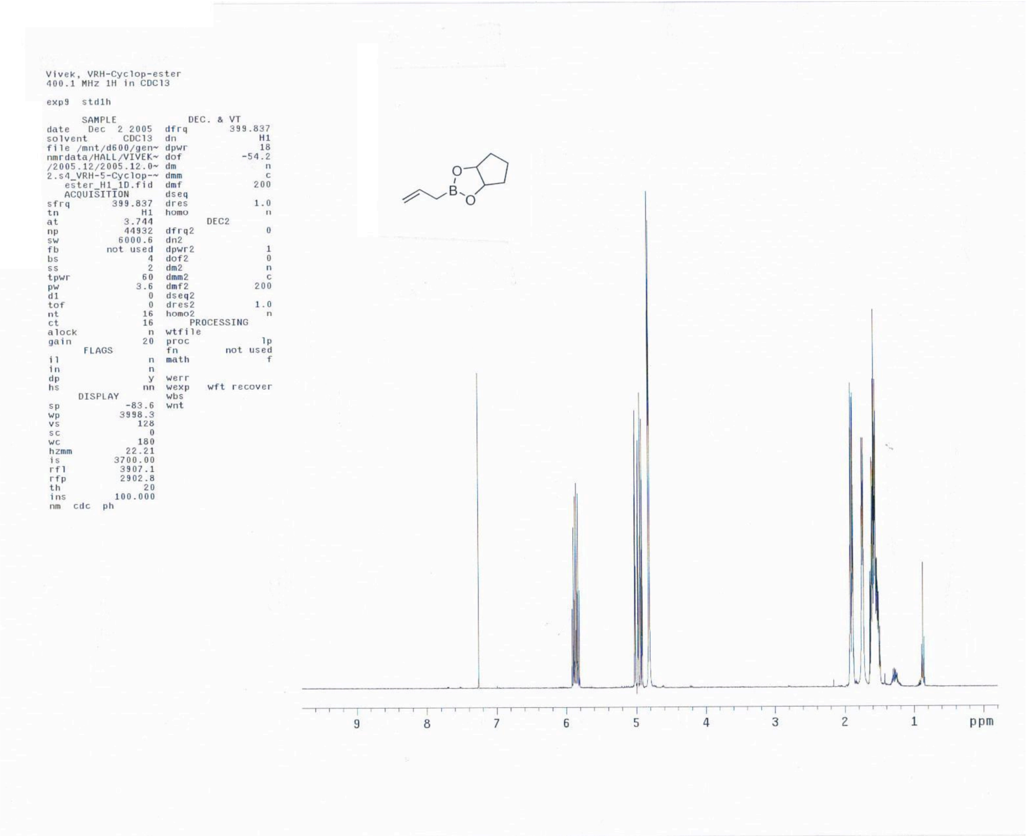
```
VRH-5-Benzopinacotester, APT
100.58 MHz 13C[1H] in CDC13

exp12  apt

      SAMPLE               DEC. & VT
date   Dec  5 2005  dfrq         399.837
solvent      CDC13  dn                H1
file /mnt/d600/gen~ dpwr              40
nmrdata/HALL/VIVEK~ dof                0
/2005.12/2005.12.0~ dm               yny
5.s4_VRH-5-Benzopi~ dmm                w
nacotester_C13_apt~ dmf            10582
              .fid  dseq
   ACQUISITION      dres             1.0
sfrq       100.548  homo               n
tn             C13          DEC2
at           2.000  dfrq2              0
np          100000  dn2
sw         25000.0  dpwr2              1
fb        not used  dof2               0
bs               4  dm2                n
tpwr            55  dmm2               c
pw             3.2  dmf2           10582
p1            17.6  dseq2
d1           2.000  dres2            1.0
d2           0.007  homo2              n
d3           0.000      PROCESSING
tof              0  lb              2.00
nt           50000  wtfile
ct            2000  proc              ft
alock            n  fn          not used
gain      not used  math               f
      FLAGS
il               n  werr
in               n  wexp        procplot
dp               y  wbs           testsn
hs              nn  wnt
     DISPLAY
sp          -502.9
wp         20610.0
vs            1456
sc               0
wc             185
hzmm        111.41
is          500.00
rfl        10763.2
rfp         7747.5
th               4
ins        100.000
nm  no  ph
```



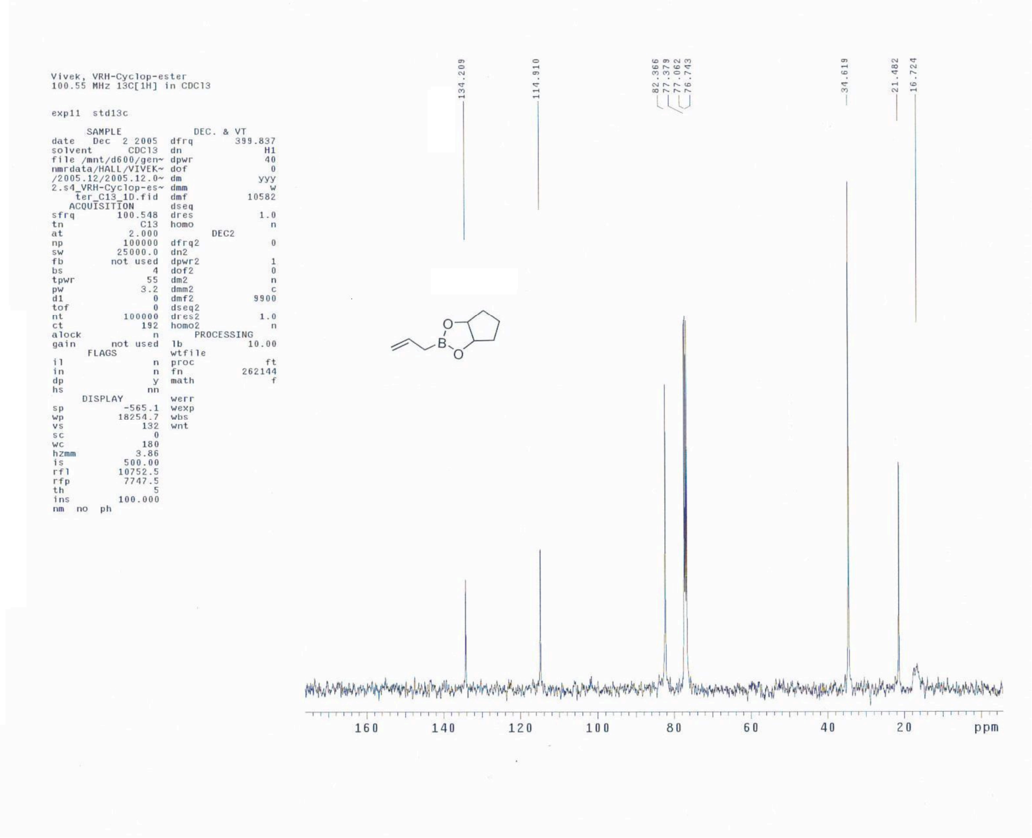
```
Vevek, VRH-5-Benzopinacotester
128.3 MHz 11B[1H] in CDCl3

exp5  s2pul

      SAMPLE              DEC. & VT
date   Dec  5 2005  dfrq        399.837
solvent       CDCl3  dn              H1
file /mnt/d600/gen~ dpwr        ~    40
nmrdata/HALL/VIVEK~ dof               0
/2005.12/2005.12.0~ dm              yyy
5.s4_VRH-5-Benzopi~ dmm               w
nacotester_B11_1D.~ dmf           10582
                fid dseq
   ACQUISITION      dres            1.0
sfrq    128.2828507 homo              n
tn              B11 temp           27.0
at            1.000          DEC2
np            76900 dfrq2             0
sw          38461.5 dn2
fb         not used dpwr2             1
bs                4 dof2              0
tpwr             55 dm2               n
pw              4.0 dmm2              c
d1            0.100 dmf2           9900
tof          -641.6 dseq2
nt             2000 dres2           1.0
ct              604 homo2             n
alock             n     PROCESSING
gain             20 lb             2.00
      FLAGS         wtfile
il                n proc             lp
in                n fn         not used
dp                y math              f
hs               nn
     DISPLAY        werr
sp           1622.1 wexp   wft recover
wp           5196.2 wbs
vs              119 wnt
sc                0
wc              200
hzmm          25.98
is         30974.13
rfl         19230.8
rfp               0
th               13
ins         100.000
nm  no  ph
```



```
Vivek, VRH-Cyclop-ester
128.3 MHz 11B[1H] in CDCl3

exp5  s2pul

      SAMPLE              DEC. & VT
date   Dec  2 2005  dfrq        399.837
solvent       CDCl3  dn              H1
file /mnt/d600/gen~ dpwr             40
nmrdata/HALL/VIVEK~ dof               0
/2005.12/2005.12.0~ dm              yyy
2.s4_VRH-Cyclop-es~ dmm               w
   ter_B11_1D.fid   dmf           10582
   ACQUISITION      dseq
sfrq    128.2828507 dres            1.0
tn              B11 homo              n
at            1.000          DEC2
np            76936 dfrq2             0
sw          38461.5 dn2
fb         not used dpwr2             1
bs                4 dof2              0
tpwr             55 dm2               n
pw              4.0 dmm2              c
d1            0.100 dmf2           9900
tof          -641.5 dseq2
nt             2000 dres2           1.0
ct               44 homo2             n
alock             n     PROCESSING
gain             20 lb             2.00
      FLAGS         wtfile
il                n proc             lp
in                n fn         not used
dp                y math              f
hs               nn
     DISPLAY        werr
sp           1645.5 wexp   wft recover
wp           6421.0 wbs
vs               69 wnt
sc                0
wc              240
hzmm          26.75
is         30974.13
rfl         19230.8
rfp               0
th                9
ins         100.000
nm  no  ph
```

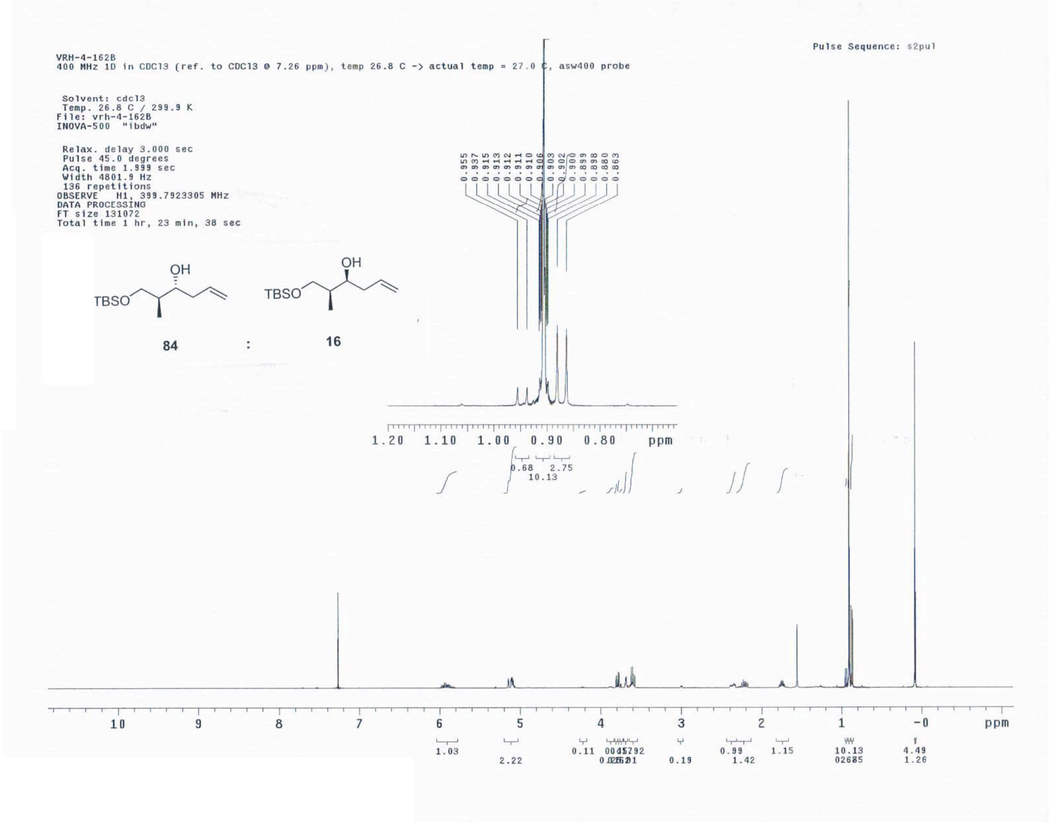


```
Vivek, VRH-Cyclop-ester
400.1 MHz 1H in CDCl3

exp9  std1h

      SAMPLE               DEC. & VT
date   Dec  2 2005  dfrq        399.837
solvent       CDCl3  dn               H1
file /mnt/d600/gen~ dpwr              18
nmrdata/HALL/VIVEK~ dof            -54.2
/2005.12/2005.12.0~ dm                 n
2.s4_VRH-5-Cyclop-~ dmm                c
   ester_H1_1D.fid  dmf              200
   ACQUISITION      dseq
sfrq        399.837  dres             1.0
tn               H1  homo               n
at            3.744           DEC2
np            44932  dfrq2             0
sw           6000.6  dn2
fb         not used  dpwr2             1
bs                4  dof2              0
ss                2  dm2               n
tpwr             60  dmm2              c
pw              3.6  dmf2            200
d1                0  dseq2
tof               0  dres2           1.0
nt               16  homo2             n
ct               16      PROCESSING
alock             n  wtfile
gain             20  proc             lp
      FLAGS          fn         not used
il                n  math              f
in                n
dp                y  werr
hs               nn  wexp   wft recover
     DISPLAY         wbs
sp            -83.6  wnt
wp           3998.3
vs              128
sc                0
wc              180
hzmm          22.21
is          3700.00
rfl          3907.1
rfp          2902.8
th               20
ins         100.000
nm  cdc  ph
```



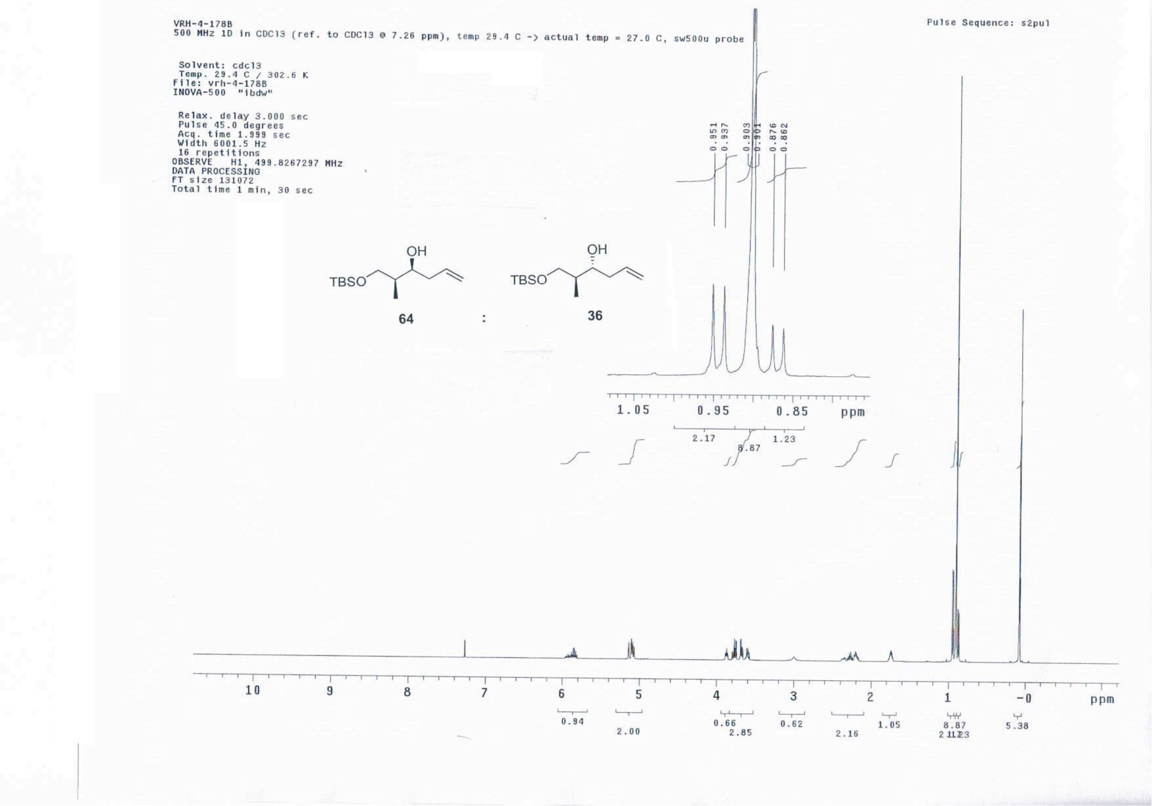
```
Vivek, VRH-Cyclop-ester
100.55 MHz 13C[1H] in CDCl3

exp11  std13c

      SAMPLE               DEC. & VT
date   Dec  2 2005  dfrq        399.837
solvent       CDCl3  dn               H1
file /mnt/d600/gen~ dpwr              40
nmrdata/HALL/VIVEK~ dof                0
/2005.12/2005.12.0~ dm               yyy
2.s4_VRH-Cyclop-es~ dmm                w
    ter_C13_1D.fid  dmf            10582
   ACQUISITION      dseq
sfrq        100.548  dres             1.0
tn              C13  homo               n
at            2.000           DEC2
np           100000  dfrq2             0
sw          25000.0  dn2
fb         not used  dpwr2             1
bs                4  dof2              0
tpwr             55  dm2               n
pw              3.2  dmm2              c
d1                0  dmf2           9900
tof               0  dseq2
nt           100000  dres2           1.0
ct              192  homo2             n
alock             n      PROCESSING
gain       not used  lb            10.00
      FLAGS          wtfile
il                n  proc             ft
in                n  fn           262144
dp                y  math              f
hs               nn
     DISPLAY         werr
sp           -565.1  wexp
wp          18254.7  wbs
vs              132  wnt
sc                0
wc              180
hzmm           3.86
is           500.00
rfl         10752.5
rfp          7747.5
th                5
ins         100.000
nm  no  ph
```

Diastereoselective Allylation with (*R*,*R*)-diol 1J and $SnCl_4$



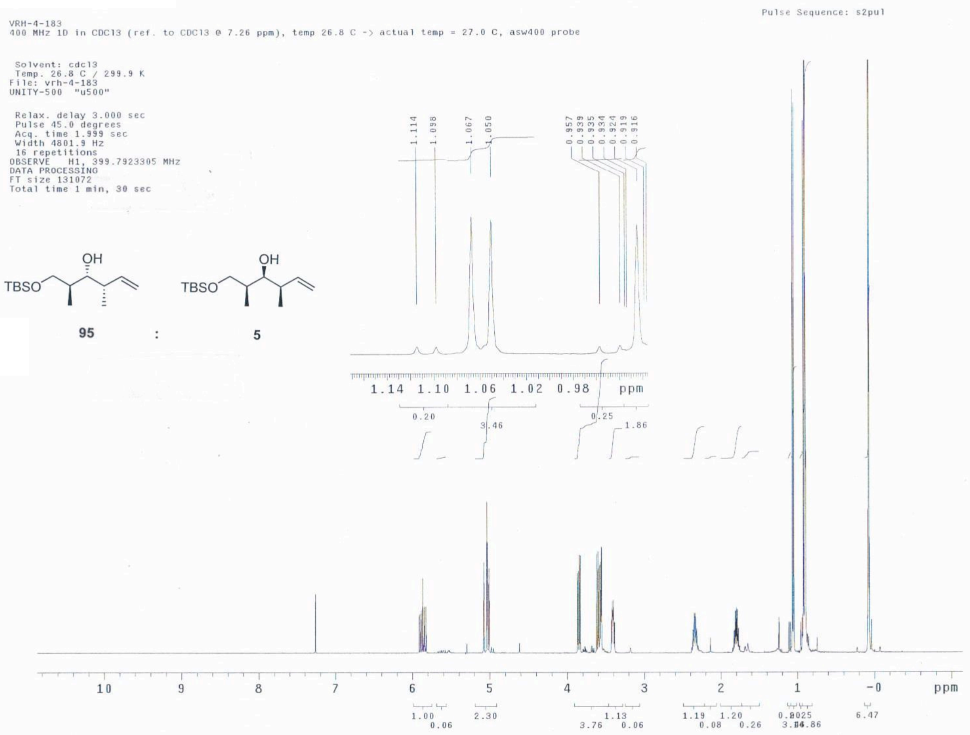
```
VRH-4-162B
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe

 Solvent: cdcl3
 Temp. 26.8 C / 299.9 K
File: vrh-4-162B
INOVA-500  "ibdw"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.999 sec
 Width 4801.9 Hz
 136 repetitions
OBSERVE   H1, 399.7923305 MHz
DATA PROCESSING
FT size 131072
Total time 1 hr, 23 min, 38 sec
```

Diastereoselective Allylation with (*S*,*S*)-diol 1j and $SnCl_4$



```
VRH-4-178B
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe

 Solvent: cdcl3
 Temp. 29.4 C / 302.6 K
File: vrh-4-178B
INOVA-500  "ibdw"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.999 sec
 Width 6001.5 Hz
 16 repetitions
OBSERVE   H1, 499.8267297 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec
```

Diastereoselective cis-crotylation with (*R*,*R*)-diol 1J and $SnCl_4$

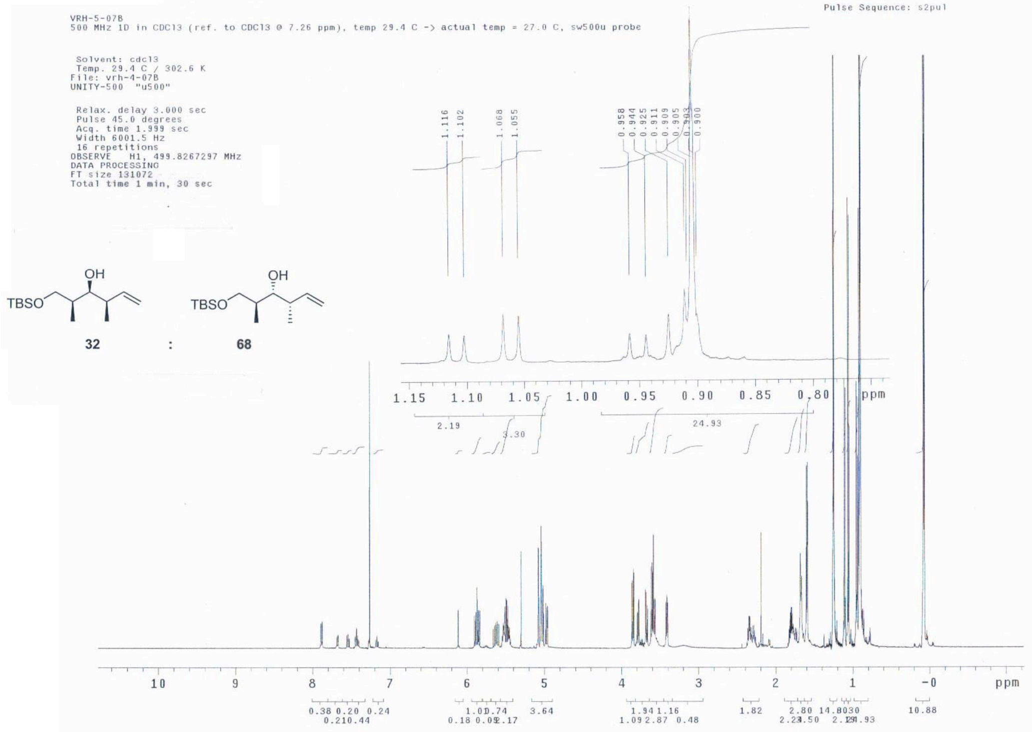

Pulse Sequence: s2pul

VRH-4-183
400 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe

Solvent: cdcl3
Temp. 26.8 C / 299.9 K
File: vrh-4-183
UNITY-500 "u500"

Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 4801.9 Hz
16 repetitions
OBSERVE H1, 399.7923305 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

Diastereoselective cis-crotylation with (*S*,*S*)-diol 1j and $SnCl_4$

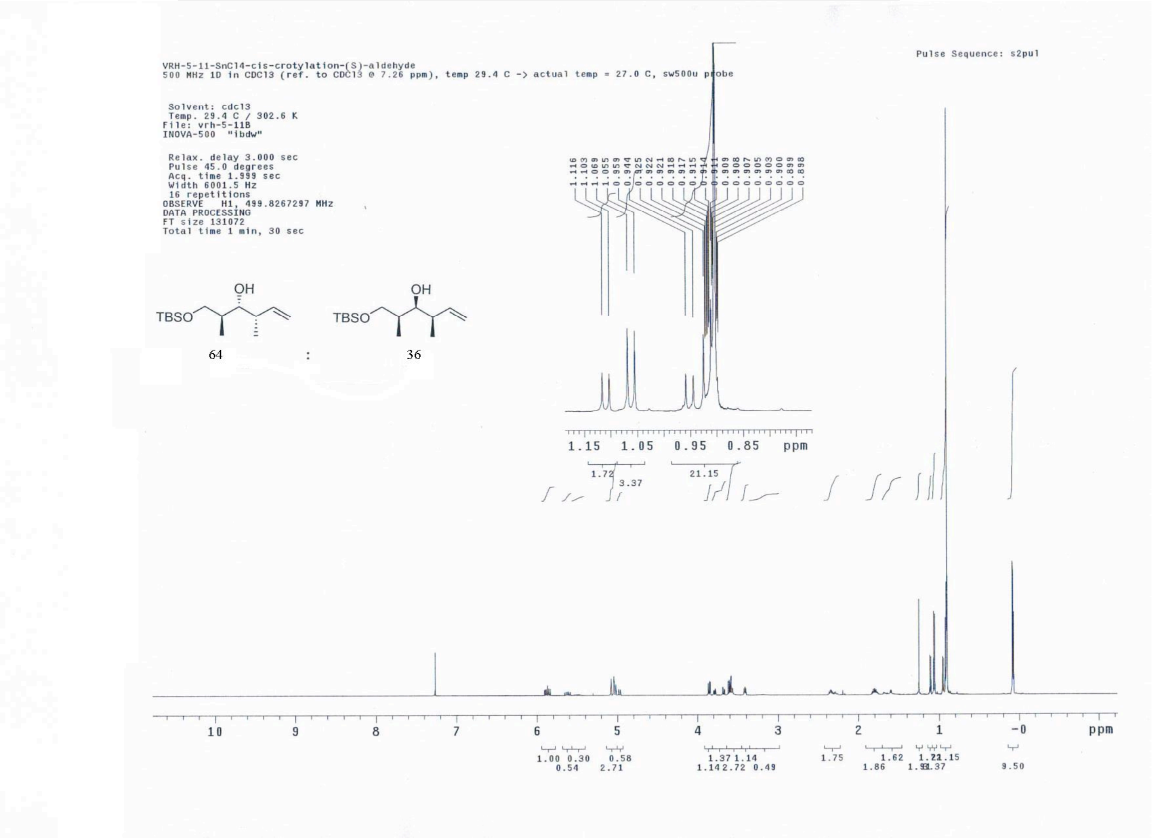

Pulse Sequence: s2pul

VRH-5-07B
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe

Solvent: cdcl3
Temp. 29.4 C / 302.6 K
File: vrh-4-07B
UNITY-500 "u500"

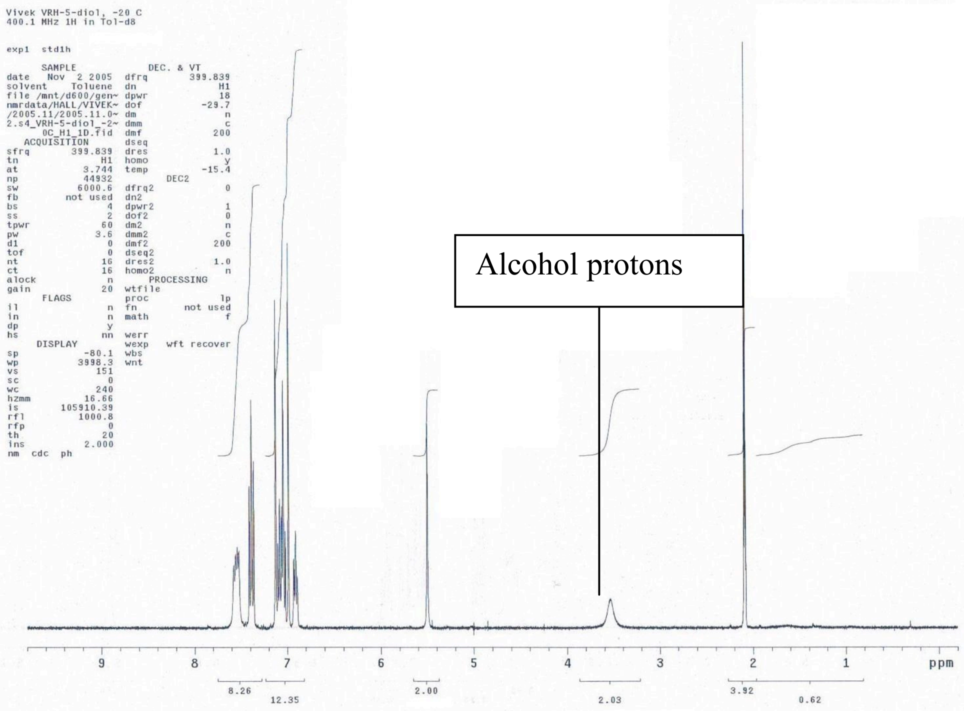
Relax. delay 3.000 sec
Pulse 45.0 degrees
Acq. time 1.999 sec
Width 6001.5 Hz
16 repetitions
OBSERVE H1, 499.8267297 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec

SnCl$_4$ catalyzed cis-crotylation of aldehyde 3



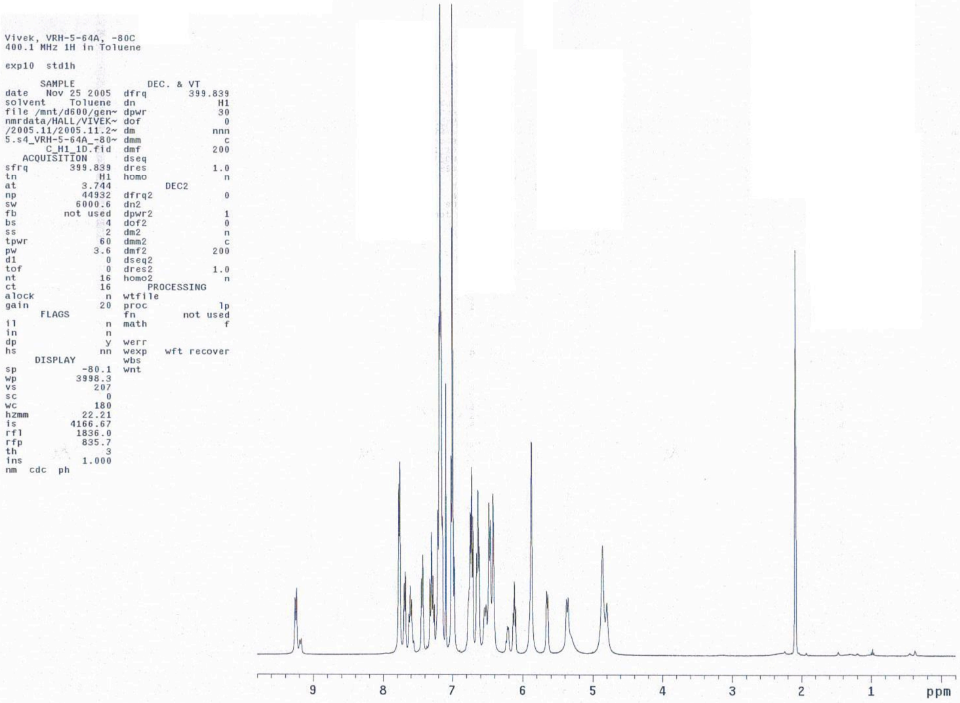
```
VRH-5-11-SnCl4-cis-crotylation-(S)-aldehyde
500 MHz 1D in CDCl3 (ref. to CDCl3 @ 7.26 ppm), temp 29.4 C -> actual temp = 27.0 C, sw500u probe

 Solvent: cdcl3
 Temp. 29.4 C / 302.6 K
File: vrh-5-11B
INOVA-500  "ibdw"

 Relax. delay 3.000 sec
 Pulse 45.0 degrees
 Acq. time 1.999 sec
 Width 6001.5 Hz
 16 repetitions
OBSERVE   H1, 499.8267297 MHz
DATA PROCESSING
FT size 131072
Total time 1 min, 30 sec
```

^{1}H NMR of diol **1j** in toluene d-8 at -20^{0}C



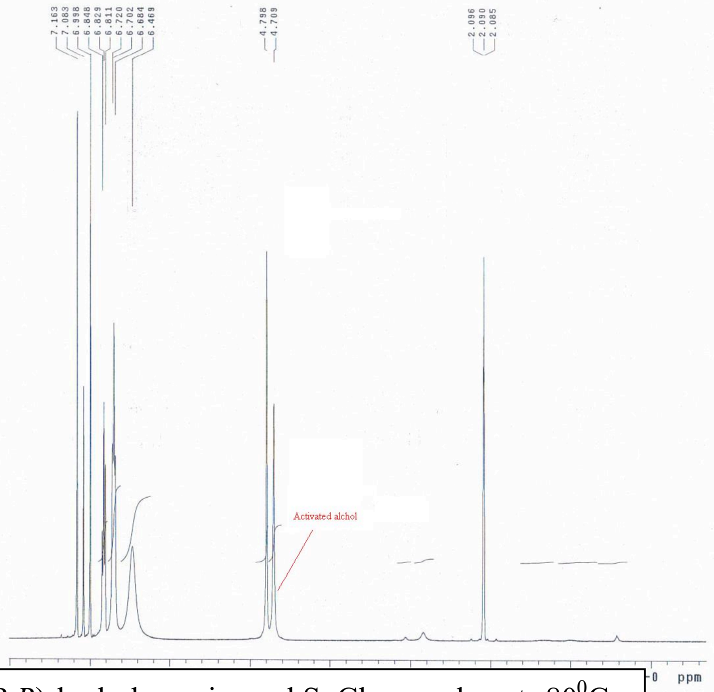
```
Vivek VRH-5-diol, -20 C
400.1 MHz 1H in Tol-d8

exp1  std1h

      SAMPLE               DEC. & VT
date   Nov  2 2005  dfrq         399.839
solvent    Toluene  dn                H1
file /mnt/d600/gen~ dpwr              18
nmrdata/HALL/VIVEK~ dof            -29.7
/2005.11/2005.11.0~ dm                 n
2.s4_VRH-5-diol_-2~ dmm                c
      0C_H1_1D.fid  dmf              200
   ACQUISITION      dseq
sfrq        399.839 dres             1.0
tn               H1 homo               y
at            3.744 temp           -15.4
np            44932          DEC2
sw           6000.6 dfrq2              0
fb         not used dn2
bs                4 dpwr2              1
ss                2 dof2               0
tpwr             60 dm2                n
pw              3.6 dmm2               c
d1                0 dmf2             200
tof               0 dseq2
nt               16 dres2            1.0
ct               16 homo2              n
alock             n     PROCESSING
gain             20 wtfile
      FLAGS         proc              lp
il                n fn          not used
in                n math               f
dp                y
hs               nn werr
     DISPLAY        wexp   wft recover
sp            -80.1 wbs
wp           3998.3 wnt
vs              151
sc                0
wc              240
hzmm          16.66
is        105910.39
rfl          1000.8
rfp               0
th               20
ins           2.000
nm  cdc  ph
```

^{1}H NMR of diol **1j** and $SnCl_4$ complex at -80^{0}C in toluene d-8



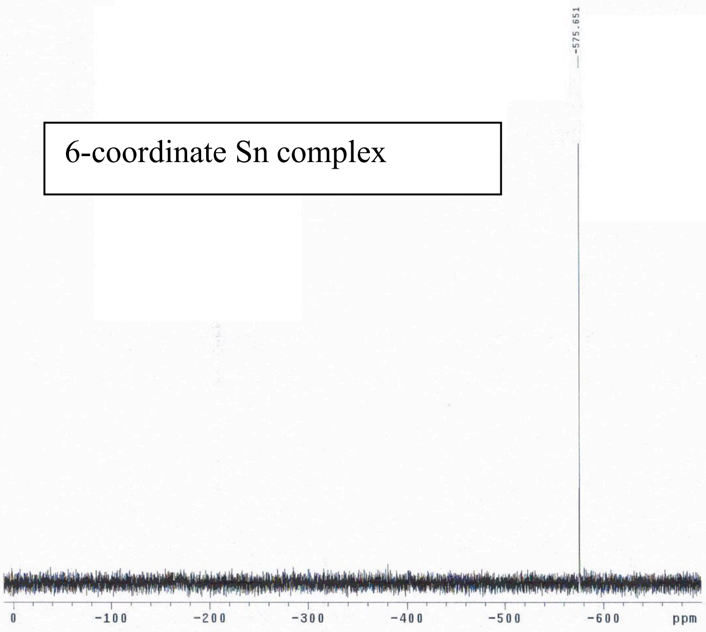
```
Vivek, VRH-5-64A, -80C
400.1 MHz 1H in Toluene

exp10  std1h

      SAMPLE               DEC. & VT
date   Nov 25 2005  dfrq         399.839
solvent    Toluene  dn                H1
file /mnt/d600/gen~ dpwr              30
nmrdata/HALL/VIVEK~ dof                0
/2005.11/2005.11.2~ dm               nnn
5.s4_VRH-5-64A_-80~ dmm                c
       C_H1_1D.fid  dmf              200
   ACQUISITION      dseq
sfrq        399.839 dres             1.0
tn               H1 homo               n
at            3.744          DEC2
np            44932 dfrq2              0
sw           6000.6 dn2
fb         not used dpwr2              1
bs                4 dof2               0
ss                2 dm2                n
tpwr             60 dmm2               c
pw              3.6 dmf2             200
d1                0 dseq2
tof               0 dres2            1.0
nt               16 homo2              n
ct               16     PROCESSING
alock             n wtfile
gain             20 proc              lp
      FLAGS         fn          not used
il                n math               f
in                n
dp                y werr
hs               nn wexp   wft recover
     DISPLAY        wbs
sp            -80.1 wnt
wp           3998.3
vs              207
sc                0
wc              180
hzmm          22.21
is          4166.67
rfl          1836.0
rfp           835.7
th                3
ins           1.000
nm  cdc  ph
```

```
Vivek, VRH-5-64B, -80C
400.1 MHz 1H in Toluene

exp10  std1h

      SAMPLE             DEC. & VT
date   Nov 25 2005  dfrq        399.839
solvent   Toluene  dn               H1
file /mnt/d600/gen~ dpwr             30
nmrdata/HALL/VIVEK~ dof               0
/2005.11/2005.11.2~ dm              nnn
5.s4_VRH-5-64B_-80~ dmm               c
    C_H1_1D.fid  dmf             200
   ACQUISITION      dseq
sfrq        399.839  dres            1.0
tn               H1  homo              n
at            3.744          DEC2
np            44932  dfrq2             0
sw           6000.6  dn2
fb         not used  dpwr2             1
bs                4  dof2              0
ss                2  dm2               n
tpwr             60  dmm2              c
pw              3.6  dmf2            200
d1                0  dseq2
tof               0  dres2           1.0
nt               16  homo2             n
ct               16       PROCESSING
alock             n  wtfile
gain             20  proc             lp
      FLAGS          fn         not used
il                n  math              f
in                n
dp                y  werr
hs               nn  wexp   wft recover
     DISPLAY         wbs
sp           -277.3  wnt
wp           3479.0
vs              151
sc                0
wc              180
hzmm          19.33
is          4166.67
rfl          1000.8
rfp               0
th               10
ins           2.000
nm  cdc  ph
```



^{119}Sn-NMR of (*R,R*)-hydrobenzoin and $SnCl_4$ complex at -80^{0}C in toluene d-8

```
Vivek, VRH-5-64B, -80C
149.05 MHz 119Sn[1H] in Toluene

exp14  s2pul

      SAMPLE             DEC. & VT
date   Nov 25 2005  dfrq        399.839
solvent   Toluene  dn               H1
file /mnt/d600/gen~ dpwr             40
nmrdata/HALL/VIVEK~ dof               0
/2005.11/2005.11.2~ dm              yyy
5.s4_VRH-5-64B_-80~ dmm               w
   C_Sn119_1D.fid  dmf           10582
   ACQUISITION      dseq
sfrq        149.050  dres            1.0
tn            Sn119  homo              n
at            1.998          DEC2
np           422962  dfrq2             0
sw         105820.1  dn2
fb         not used  dpwr2             1
bs                4  dof2              0
tpwr             55  dm2               n
pw              3.0  dmm2              c
d1                0  dmf2          10582
tof        -51976.9  dseq2
nt           100000  dres2           1.0
ct              180  homo2             n
alock             n       PROCESSING
gain             20  lb             5.00
      FLAGS          wtfile
il                n  proc             ft
in                n  fn         not used
dp                y  math              f
hs               nn
     DISPLAY         werr
sp        -104349.8  wexp   wft recover
wp         105819.7  wbs
vs              113  wnt
sc                0
wc              180
hzmm          41.39
is           500.00
rfl        104350.2
rfp               0
th               20
ins         100.000
nm  no  ph
```



6-coordinate Sn complex