SUPPORTING INFORMATION

Cobalt-Catalyzed Asymmetric Hydrovinylation of 1,3-Dienes

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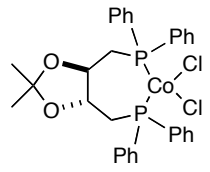
General methods. Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen or argon by using Schlenk techniques or a Vacuum Atmospheres glovebox. Ethylene (99.5%) was purchased from Matheson Inc., and passed through a column of Drierite® before use. All chemicals obtained from commercial sources were used as received unless otherwise mentioned. All dienes, unless otherwise mentioned, were prepared via Wittig reaction of the corresponding aldehydes with the Wittig reagent generated from methyl triphenylphosphonium bromide and *n*-BuLi in THF. Tetrahydrofuran and diethyl ether were distilled under nitrogen over sodium/benzophenone. Dichloromethane and toluene were purified by distillation from calcium hydride, and subsequently storing over 4 Å molecular sieve. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F254 plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Absence of polymeric impurities was ascertained by NMR of the crude materials. Except for the volatile materials, the isolated yields of the products were not significantly different from the conversions. The percentage compositions for isomeric products was determined by uncalibrated analysis of the areas. This is possible since the response of volatile isomeric hydrocarbons are essentially same in flame ionization detection as determined by comparison of GC-derived compositions with that obtained from ^{1}H NMR in several cases. Gas chromatographic analyses were performed on Agilent gas chromatographs using a HP-1 Methylsilicone column [30 m x 0.250 mm, 0.25 μm film thickness, achiral stationary phase (or ASP) GC column] and an FID detector. Enantiomeric excesses of chiral compounds were determined by chiral stationary phase gas chromatographic (CSP GC) analyses, which were performed on a Hewlett-Packard 5890 with Cyclodex-B capillary GC column (60 m x 0.25 mm, 0.25 μm film thickness) or on an Agilent 7820A using a Cyclosil-B capillary GC column (25 m x 0.25 mm, 0.25 μm film thickness) using helium or hydrogen as a carrier gas. The columns containing Chiral Stationary Phase (CSP) materials were also used for analysis of some of the geometric isomers because they gave better separation. These are indicated under appropriate chromatograms. Where ever appropriate, %ee's were determined from chromatograms where base-line separation of the enantiomers was achieved for an authentic racemic mixture. Limits of detection of the minor enantiomer were established by analyzing mixtures of both enantiomers of known compositions. Optical rotations were recorded on a Rudolph Research Analytical AUTOPOL VI polarimeter in the solvents mentioned. Unless otherwise mentioned, the measurements were done on a filtered (45 micron filter) solution at the sodium line at room temperature. ^{1}H and ^{13}C NMR spectra were recorded either on a spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C, or a machine operating at 400 MHz for ^{1}H and 162.02 MHz for ^{31}P. Proton chemical shifts were internally referenced to the residual solvent proton resonance (e.g., $CHCl_3$ at δ 7.26). In several instances where there is a minor deviation, position of a reference peak is included in the data to facilitate assignments. Coupling constants are

reported in Hz. Phosphorous (^{31}P NMR) are reported as δ in units of parts per million (ppm) relative to external H_3PO_4 (δ 0.0).

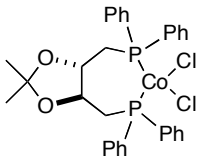
Synthesis of Cobalt Complexes

Literature methods[1] were used for preparation of complexes Co(dppm)Cl_2 and Co(dppp)Cl_2. For the preparation of Co(dppb)Cl_2, [(*RR*)-(–)(DIOP)$CoCl_2$], [(*SS*)-(+)-(DIOP)$CoCl_2$] and [(*SS*)-(–)-(BDPP)$CoCl_2$] modified procedures (see below) were used. Solid-state structures of these two complexes have been reported in our previous publication.[2]

Typical modified procedure for synthesis of cobalt complexes: [*(R,R)*-DIOP]$CoCl_2$. A 25-mL dry round bottom flask loaded with anhydrous $CoCl_2$ (10.9 mg, 0.0839 mmol) was charged with THF (5 mL). On stirring at room temperature for 15 min, a clear deep blue solution formed. A solution of (*R,R*)-DIOP (41.8 mg, 0.0839 mmol) in dry and degassed ether (5 mL) was added dropwise to yield a blue turbid solution. After stirring at room temperature for 6 h, 20 mL deoxygenated hexane was added in one portion to get a blue solid. The resulting solid was washed with diethyl ether and hexane (1:1) mixture (3 X 5 mL) to remove any unreacted DIOP. Further purification was accomplished by crystallization of the Co(II)-complex from a saturated $CHCl_3$ solution by slow vapor diffusion of pentane at room temperature. The solid state structure determined by X-ray crystallography has been reported.[2]



(4*R*,5*R*)-(-)-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane dichloro cobalt(II): (–)-[(*RR*)-(–)-(DIOP)$CoCl_2$]. Yield 94%. Elemental analysis calculated for $C_{31}H_{32}Cl_2CoO_2P_2$: C, 59.25; H, 5.13. Found: C, 56.60; H, 5.09. $[\alpha]^{25}_{405}$ ($CHCl_3$, *c* 1.25) = – 93.7



(4*S*,5*S*)-(+)-O-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane dichloro cobalt(II): (+)-[(*SS*)-(+)-(DIOP)$CoCl_2$]; Yield 92%. Elemental analysis calculated for $C_{31}H_{32}Cl_2CoO_2P_2$: C, 59.25; H, 5.13. Found C, 57.05, H, 5.12. $[\alpha]^{25}_{405}$ ($CHCl_3$, *c* 1.25) = + 88.8

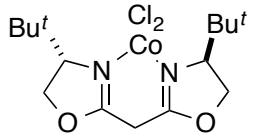
[*(S,S)*-BDPP]$CoCl_2$. Cobalt chloride (50.5 mg, 0.390 mmol) was added to a previously flame-dried 50-mL round two-necked bottom flask fitted with a flow control gas inlet and magnetic stir-bar loaded in a glove box under nitrogen. Outside the box, the nitrogen atmosphere was removed and the flask purged with dry argon. Freshly distilled, degassed THF (5 mL) was added, and upon stirring at room temperature for 15 min, a clear deep blue solution formed. A solution of (*S,S*)-BDPP (181 mg, 0.410 mmol) in freshly distilled, degassed ether (5 mL) was added dropwise to yield a blue turbid solution. After stirring at room temperature for 12 h, 20 mL freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 X 5 mL) to remove any unreacted (*SS*)-BDPP, resulting in quantitative yield of a light blue solid, which was used with no further purification. A sample was recrystallized from saturated $CHCl_3$ solution by slow vapor diffusion of pentane at room temperature. The solid-state structure determined by X-ray crystallography has been reported.[2]

(*2S,4S*)-(-)-2,4-Bis(diphenylphosphino)-pentane dichlorocobalt(II): (+)-[(*SS*)-(–)-(BDPP)$CoCl_2$]. Yield 96%. Elemental analysis calculated for $C_{29}H_{30}Cl_2CoP_2$: C, 61.07; H, 5.30. Found C, 60.69; H, 5.28.

$[\alpha]^{25}_{405}$ ($CHCl_3$, *c* 1.00) = + 271.0; $[\alpha]^{25}_{436}$ ($CHCl_3$, *c* 1.00) = + 132.0; $[\alpha]^{25}_{546}$ ($CHCl_3$, *c* 1.00) = + 164.0

Cobalt(II)-complexes of ligands listed in Table 1 and Figure 5 were similarly prepared and used for hydrovinylation under conditions listed in various tables.

Synthesis of cobalt complexes of *N*-heterocyclic carbene ligand (Figure 3). In a typical procedure the bromide salt of a carbene precursor (195 mg, 0.46 mmol, 1 equiv.) and potassium *tert*-butoxide (306 mg, 2.73 mmol, 6 equiv.) were added to a previously oven-dried 20-mL round bottom flask with magnetic stir-bar loaded in a glove box under nitrogen. Freshly distilled THF (5 mL) was added and stirred at room temperature for 36 hours under nitrogen in glove box. The reaction solution was passed through a pad of celite in dry box and the solvent was evaporated under vacuum to get free carbene. Anhydrous $CoCl_2$ (48 mg, 0.37 mmol, 0.95 equiv.) was added to a previously oven-dried 20-mL round bottom flask with sidearm fitted with a flow control gas inlet and magnetic stir-bar loaded in a glove box under nitrogen. The flask was removed from the drybox and the nitrogen atmosphere was removed and the flask purged with dry argon. Freshly distilled, degassed THF (4 mL) was added, and upon stirring at room temperature for 15 min, a clear deep blue solution formed. A solution of free carbene (104 mg, 0.39 mmol, 1 equiv.) in freshly distilled degassed THF (2 mL) was added dropwise to yield a blue solution. After stirring at room temperature for 32 h, 10 mL freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 x 10 mL) to remove any unreacted carbene, resulting in quantitative yield of a light blue solid, which was used in hydrovinylation with no further purification.



Synthesis of $CoCl_2$[*tert*-butyl bis-oxazoline] complex. Similar procedure was used for synthesis of cobalt complexes from dinitrogen based chelating ligands (–)-sparteine and the bis-oxazoline complexes (Figure 3). As a typical procedure, anhydrous $CoCl_2$ (23 mg, 0.18 mmol, 1 equiv.) was added to a previously oven-dried 20-mL round bottom flask with sidearm fitted with a flow control gas inlet under nitrogen. The nitrogen atmosphere was removed and the flask purged with dry argon. Freshly distilled, degassed THF (3 mL) was added, and upon stirring at room temperature for 20 min, a clear deep blue solution formed. A solution of the *t*-butyl bis-oxazoline ligand (51 mg, 0.19 mmol, 1.05 equiv.) in freshly distilled degassed THF (3 mL) was added dropwise to yield a blue solution. After stirring at room temperature for 36 h, 15 mL freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 x 15 mL) to remove any unreacted ligand, resulting in quantitative yield of a light blue solid, which was used for hydrovinylation of 1,3-dienes with no further purification.

Synthesis of [dppe]$FeCl_3$ complex. As a typical procedure, anhydrous $FeCl_3$ (45 mg, 0.28 mmol, 1 equiv.) was added to a previously oven-dried 20-mL round bottom flask with sidearm fitted with a flow control gas inlet under nitrogen. Freshly distilled, degassed THF (2 mL) was added, and upon stirring at room temperature for 20 min, a black-brown solution formed. A solution of DPPE (47 mg, 0.29 mmol, 1.05 equiv.) in freshly distilled degassed THF (3 mL) was added dropwise to yield a light pink solution. After stirring at room temperature for 24 h, 15 mL

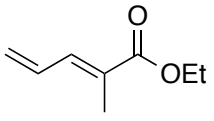
freshly distilled, degassed hexane was added in one portion to yield a blue precipitate. The resulting precipitate was filtered under argon atmosphere, and washed with diethyl ether and hexane (1:1) mixture (3 x 15 mL) to remove any unreacted dppe, resulting in good yield of a light blue solid (130 mg, 84%), which was used for hydrovinylation of 1,3-dienes with no further purification.

Synthesis of Methylaluminoxane.[3] A flame-dried 250 mL three-necked round-bottom flask equipped with a septum, flow control gas inlet, temperature probe, and magnetic stir-bar was purged with argon and charged with 3.85 g $Al_2(SO_4)_3 16\ H_2O$, 15 mL dry, distilled toluene and chilled to –10 °C using a salt/ice bath. To this slurry was added 20 mL 2 M trimethylaluminum solution in toluene stored at 0 °C dropwise via syringe with vigorous stirring. The ice bath was removed and the solution allowed to warm to room temperature slowly, and then heated to 30 °C for 4 hrs. After the first heating period, the mixture was then slowly brought to 50 °C and stirred for 8 hrs overnight. A Schlenk filter (12" column fitted with two male ground glass joints and a microporous fret in the center) and a 250 mL single-necked round-bottom were flamed dried and attached to the 250 mL three-necked flask. The solution was filtered to remove the solids and the resulting toluene filtrate was distilled to remove the toluene to give a white glassy solid that was harvested in an inert atmosphere glovebox to get the product as a white solid 0.610 g (26% yield)

Synthesis of Substrates

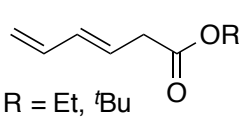
Synthesis of (*E*)-6-benzyloxy-1,3-hexadiene (12i). A 250 mL flask with sidearm equipped with a magnetic stirring bar, purged with nitrogen, was charged with methyltriphenylphosphonium bromide (6.31 g, 17.66 mmol, 1.1 equiv.) and anhydrous THF (25.0 mL). *n*-BuLi (2.5 M in hexane, 7.1 mL, 17.66 mmol, 1.1 equiv.) was added dropwise via syringe at 0 ^{0}C and the reaction mixture was allowed to stir at 0 ^{0}C for 2 h. A solution of (*E*)-5-(benzyloxy)pent-2-enal (3.0 g, 15.77 mmol) dissolved in anhydrous THF was added dropwise and the reaction mixture was allowed to stir at ambient temperature for 12 h. The reaction mixture was diluted with pentane, filtered over Celite® and the filtrate was concentrated and purified via flash column chromatography (pentane-ether, 20:1) to yield the 1,3 diene (2.04 g, 69%) as a *E*-1,3-diene. ^{1}H NMR and ^{13}C NMR agreed with published data.[2] ^{1}H NMR ($CDCl_3$, 400 MHz): 2.48 (q, J = 4 Hz, 2 H), 3.59 (t, J = 8 Hz, 2 H), 4.58 (s, 2 H), 5.05 (d, J = 8 Hz, 1 H), 5.17 (d, J = 16 Hz, 1 H), 5.75 – 5.82 (m, 1 H), 6.15 – 6. 22 (m, 1 H), 6.33 – 6.43 (m, 1 H), 7.31 – 7.43 (m, 5 H, aromatic). Gas Chromatography: CSP GC (Cyclosil, OT 150 ^{0}C/ isothermal) R_T for diene = 12.357 min. Methyl silicone SP GC (OT 150 ^{0}C/ isothermal) R_T for diene product = 10.492 min.

All the (*E*)-1,3-dienes as well as like **12a**, **12b, 12c, 12d,** and **12e** were prepared by the literature methods of Wittig olefination using the corresponding aldehyde. Dienes like β-myrcene (**12m**), isoprene (**12n**) and (*E*)-1,3-pentadiene (**12f**) were purchased directly and used after proper distillation.



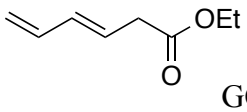
Synthesis of (*E*)-ethyl-2-methyl-penta-2,4-dienoate. A 250 mL flask with sidearm equipped with a magnetic stirring bar, purged with nitrogen, was charged with (1-ethoxycarbonylethyl)triphenylphosphonium bromide (5.0 g, 11.28 mmol, 1.0 equiv.) and anhydrous CH_2Cl_2 (20.0 mL). Potassium

hydroxide (KOH) (0.8 gm, 13.54 mmol, 1.2 equiv.) as aqueous solution was added dropwise and stirred for 3 hrs at room temperature. A solution of acrolein (0.8 g, 13.54 mmol) dissolved in anhydrous CH_2Cl_2 was added dropwise and the reaction mixture was refluxed for 3 hrs and stirred 24 hrs at room temperature. The reaction mixture was diluted with petroleum ether, filtered over Celite® and the filtrate was concentrated and purified via flash column chromatography (Hex-EtOAc, 7:1) to yield the 1,3 diene (0.6 g, 38%) as a *E*-1,3-diene. ^{1}H NMR and ^{13}C NMR agreed with published data.[5-7] ^{1}H NMR ($CDCl_3$, 400 MHz): 1.29 (t, J = 7.2 Hz, 3 H), 1.93 (s, 3 H), 4.20 (q, J = 7.2 Hz, 2 H), 5.42 (d, J = 8 Hz, 1 H), 5.53 (d, J = 16 Hz, 1 H), 6.59 – 6.68 (m, 1 H), 7.13 (d, J = 12 Hz, 1 H). CSP GC (OT 80 ^{0}C/ isothermal, H_2 carrier gas) Conditions: R_t for diene product = 14.28 min.

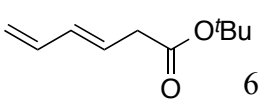


Synthesis of (*E*)-ethyl-hexa-3,5-dienoate and (*E*)-*t*-Bu-hexa-3,5-dienoate. A 250 mL flask with condenser equipped with a magnetic stirring bar, purged with nitrogen, was charged with hexa-2,4-dienoic acid (12.0 g, 107 mmol, 1.0 equiv.) and 5 drops of DMF and 3 boiling chips were added. Thionyl chloride (19 g, 161 mmol, 1.5 mmol) was added from the top of the condenser dropwise and refluxed 30 minutes. HCl and SO_2 gas were trapped by dil. NaOH solution through out the reflux period and the reaction was stopped when there was no more evolution of HCl and SO_2 gas through the NaOH solution. Hexa-2,4-dienoyl chloride (10 g, 71%) was distilled out from the same round bottom flask and directly used for the next set up reaction for diene synthesis. Freshly distilled ethyl alcohol (5.6 g, 123 mmol, 2 equiv.) and freshly distilled triethyl amine (12.4 g, 122.54 mmol, 2 equiv.) were mixed in 120 mL CH_2Cl_2 and chilled under dry ice/acetone. Hexa-2,4-dienoyl chloride (8 g, 61.27 mmol, 1 equiv.) was added dropwise via syringe. After 1 hr, a thick white precipitate appeared and the reaction was allowed to warm to room temperature and left overnight. Around 200 mL water was added and partitioned between water and DCM. The organic layer was washed (2 X 10% H_2SO_4, 1 X saturated $NaHCO_3$, 1 x H_2O, 1 X brine) and dried with $MgSO_4$ and solvent was evaporated to get crude diene. A few crystals of BHT were added to the crude product which was then distilled to afford ethyl-3,5-hexadienoate (5.1 g, 59%). ^{1}H NMR and ^{13}C NMR agreed with published data.[8-9]

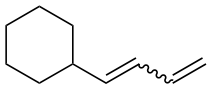
Same procedure was applied to synthesize (*E*)-*t*-Bu-3,5-hexadienoate by using *t*-butyl alcohol instead of ethyl alcohol.



^{1}H NMR ($CDCl_3$, 400 MHz): 1.21 (t, J = 7.2 Hz, 3 H), 3.07 (d, J = 6.4 Hz, 2 H), 4.12 (q, J = 4 Hz, 2 H), 5.02 (d, J = 10.4 Hz, 1 H), 5.12 (d, J = 16.4 Hz, 1 H), 5.71 – 5.78 (m, 1 H), 6.06 – 6.13 (m,1 H), 6.25 – 6.34 (m, 1 H). CSP GC (OT 90 ^{0}C/ isothermal, cyclodex-B, He carrier gas) R_T for diene product = 38.27 min.



^{1}H NMR ($CDCl_3$, 400 MHz): 1.59 (s, 9 H), 3.16 (d, J = 8 Hz, 2 H), 5.18 (d, J = 10.4 Hz, 1 H), 5.28 (d, J = 17.2 Hz, 1 H), 5.87 – 5.94 (m, 1 H), 6.22 – 6.28 (m, 1 H), 6.42 – 6.51 (m,1 H). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 28.30, 39.45, 80.99, 116.76, 126.63, 134.16, 136.79, 171.04. CSP GC (OT 100 ^{0}C/ isothermal, cyclosil, H_2 carrier gas) R_T for diene product = 12.09 min.



(*E* + Z 47:53)

Synthesis of (*Z*/*E*)-1-cyclohexyl-1,3-butadiene and other related dienes. As a typical procedure to make (*E*/*Z*)-mixture of 1-cyclohexyl-1,3-butadiene, a 250 mL flask with sidearm equipped with a magnetic stirring bar, purged with nitrogen, was charged with allyltriphenylphosphonium bromide (7.0 g, 18.0 mmol, 1.5 equiv.) and anhydrous THF (30.0 mL). Base *n*-BuLi (2.5 M in hexane, 6.5 mL, 16.2 mmol, 0.9 equiv.) was added dropwise via syringe at 0 ^{0}C and the reaction mixture was allowed to stir at 0 ^{o}C for 1 h. A solution of cyclohexanecarboxaldehyde (1.82 g, 16.2 mmol) dissolved in anhydrous THF was added dropwise and the reaction mixture was allowed to stir at ambient temperature for 12 h. The reaction mixture was diluted with pentane, filtered over Celite® and the filtrate was concentrated and purified via flash column chromatography (pentane-ether, 20:1) to yield the 1,3 diene (1.30 g, 59%) as a mixture of *Z*- and *E*-isomers (53:47, by GC). ^{1}H NMR and ^{13}C NMR agreed with published data.[10-11] ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05-1.30 (m, 11 H, both *E* and *Z*) 1.61-1.72 (m, 9 H, both *E* and *Z*), 1.96 – 1.98 (m, 1 H, *E* only), 2.41 – 2.44 (m, 1 H, *Z* only), 4.93 (d, J = 9 Hz, 1 H, *E* only), 5.03 – 5.17 (m, 3 H, overlapped *E* and *Z*), 5.29 (t, J = 10 Hz, 1 H, *Z* only), 5.64 (dd, J = 5, 16 Hz, 1 H, *E* only), 5.86 (t, J = 11 Hz, 1 H, *Z* only), 5.96 – 6.02 (m, 1 H, *E* only), 6.23 – 6.33 (m, 1 H, *E* only), 6.58 – 6.68 (m, 1 H, *Z* only). ^{13}C NMR ($CDCl_3$, 125.72 MHz): 26.07, 26.22, 26.38, 32.97, 33.45, 37.07, 40.84, (both *E* and *Z* overlapped), 114.90 (*E*), 116.88 (*Z*), 127.47 (*Z*), 128.53 (*E*), 132.81 (*Z*), 137.88 (*E*), 139.15 (*Z*), 141.51 (*E*).
Gas Chromatography: (Cyclosil, temp. 80 ^{o}C / isothermal, H_2 carrier gas) starting material R_T = 18.63 min for *Z*-diene and 26.243 min for *E* diene.

Similar procedure was used for the synthesis of (*E*/*Z*)-mixture of 1,3-dienes like (*E*/*Z*) dodeca-1,3-diene (**12d**), (*E*/*Z*)1-phenyl-1,3-butadiene (**12g**) and (*E*/*Z*) hexa-3,5-dinylbenzene (**12j**) using corresponding aldehyde and allyltriphenylphosphonium bromide.

$X_2Co(L)$-Catalyzed Hydrovinylation of 1,3-Dienes

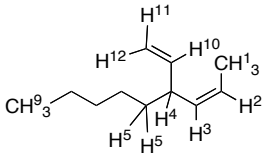
Hydrovinylation of (*E*)-nona-1,3-diene using[DPPB]$CoCl_2$ (Table 1, Entry 9, Typical procedure for ligand screening). To an oven dried round bottom flask with a sidearm, was added [DPPB]$CoCl_2$ (35 mg, 0.063 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.17 mL, 0.32 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was kept at 0 ^{o}C temperature and (*E*)-nona-1,3-diene (78 mg, 0.63 mmol) in dichloromethane (0.5 mL) solution added under ethylene and the mixture was stirred for 0.5 h. The ethylene balloon was removed and 0.1 mL of methanol was added to the flask. The reaction solution was diluted with pentane (3 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as colorless oil (96% 1,4-*Z* (**13a**) and 1,4-linear (**16a**) by GC and NMR analysis.

All the reactions in Table 1 were performed in similar fashion using the conditions described in the Table 1 using Co(II)-complexes prepared as described before. Some typical procedures are described below after details of the identification of the isomeric products from **12a**.

Identification of Products of Hydrovinylation of (*E*)-nona-1,3-diene (12a)

[The following data extracted from ref. 2, which also contains details of gas chromatographic analysis including chiral stationary phase separations of various isomers. The reported ee's were determined from these gas chromatograms.]

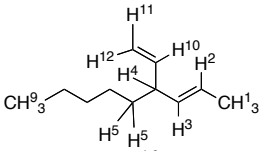
Hydrovinylation of (*E*)-nona-1,3-diene (13a) using [dppb]$CoCl_2$/Me_3Al at -10 ºC (Entry 9, Table 1), or using [DIOP]$CoCl_2$ at - 45 ºC (Entry 8, Table 4)



(*Z*)-4-Vinylnon-2-ene (13a): ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.869 (t, J = 7 Hz, 3 H, H^9), 1.21-1.35 (m, 7 H), 1.38-1.45 (m, 1 H) 1.21-1.45 total 8 H, 1.622 (dd, J = 6.5 Hz, 2 Hz, 3 H, H^1), 3.011 (m, 1 H, H^4), 4.929 (ddd, J = 10 Hz, 1.5 Hz, 1.5 Hz, 1 H, H^{11}), 4.982 (ddd, J = 17.5 Hz, 1.5 Hz, 1.5 Hz, 1 H, H^{12}), 5.216 (ddq, 10 Hz, 10 Hz, 1.5 Hz, H^3), 5.495 (dq, 10.5 Hz, 6.5 Hz, 1 Hz, H^2), 5.709 (ddd, 17 Hz, 10 Hz, 7 Hz, 1H, H^{10}). Assignments and coupling confirmed by COSY and NOESY ($CH^1{}_3$–> H^4).
^{13}C NMR ($CDCl_3$): 13.02, 14.07 22.63, 26.79, 31.90, 35.24, 41.26, 112.87, 123.78, 133.23, 141.87. The peak at δ 14.07 (due to the vinyl methyl carbon is at a higher field compared to the corresponding peak in the corresponding (*E*)-isomer , which appears at δ 17.96, see below).
IR (neat cm^{-1}): 3079 (w), 3111 (m), 2959 (s), 2927 (s), 2858 (s), 1636 (m), 992 (w), 909 (m), 724 (m)- 724 cm^{-1} is characteristic of a (*Z*)-alkene. Absence of peaks ~ 960-970 cm^{-1} indicates absence of the (*E*)-isomer, **14a**.
ESI-MS; m/z 191.1 [M+K]; mass calculated for $C_{11}H_{20}K$, 191.1.
Product from (*RR*)-(-)-DIOP $[\alpha]^{25}_D$ = – 20.9 (hexane, *c* 1.15)

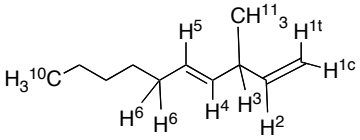
Gas Chromatography: (Polymethyldisiloxane): 80 ºC R_T **13a**: 21.169 min.; **14a**: 21.93min.; **15a** 22.77 min.; CSP GC (Cyclodex B) 60 ºC **13a:** R_T = 26.07 min. (*S*), 27.25 (*R*); **16a** 44.79 min.

Isomeric hydrovinylation products obtained from (*E*)-nona-1,3-diene (13a) using [dppm]$CoCl_2$/Me_3Al (Entries 12 and 13, Table 1)



(*E*)-4-vinylnon-2-ene (14a): ^{1}H NMR ($CDCl_3$): δ 0.85-0.91 (m, 3 H, H^9), 1.21-1.41 (m, H^5, H^6, H^7, H^8), 1.669 (dd, J = 6 Hz, 0.5 Hz, 3 H, H^1), 2.619 (pent, J = 7.5 Hz, 1 H, H^4), 4.931 (dm, J = 10 Hz, 1 H, H^{11}), 4.977 (dm, J = 17.5 Hz, 1 H, H^{12}), 5.29-5.45 (m, 2H, H^2, H^3), 5.706 (ddd, J = 17.5, 10, 7.5 Hz, 1 H, H^{10}). Chemical shifts and coupling constants assigned by COSY and double irradiation experiments.
^{13}C NMR ($CDCl_3$): δ 14.07, 17.96 (vinyl Me), 22.63, 26.84, 31.88, 34.86, 46.88, 113.24, 124.53, 134.17, 142.35. The peak at δ17.96 (due to vinyl methyl carbon is at a lower field compared to the corresponding peak in the (*Z*)-isomer **13a**, which appears at δ 17.07, see under **13a**, the previous compound.)

Gas chromatography: (polydimethylsiloxane column): see previous experiment.



(*E*)-3-methyldeca-1,4-diene (15a). ^{1}H NMR ($CDCl_3$): 0.85-0.91 (m, 3 H, H^{10}), 1.075 (d. J = 6.5 Hz, 1 H, H^{11}), 1.20-1.40 (m, H^7,

H^8, H^9), 1.990 (ddd, J = 6.5, 6.5, 6.5 Hz, 2 H, H^6), 2.807 (ddq, J = 6.0, 6.0, 6.0 Hz, H^3), 4.931 (dm, J = 10 Hz, 1H, H^{1c}), 4.977 (dm, J = 17.5 Hz, 1 H, H^{1t}), 5.352 (dd, J = 15.5, 6.5 Hz, 1 H, H^4), 5.416 (dt, J = 15.5, 6.5, 1 H, H^5), 5.791 (ddd, J = 17, 10.5, 6.5 Hz, 1 H, H^2). Chemical shifts and coupling constants assigned by COSY and double irradiation experiments.
^{13}C NMR ($CDCl_3$): 14.04, 20.00, 22.54, 29.23, 31.41, 32.55, 40.31, 112.37, 129.44, 133.86, 143.40.

Gas chromatography: (polydimethylsiloxane column) : see under **13a.**

Procedure for Co-catalyzed hydrovinylation of (*E*)-nona-1,3-diene using [dppb]$CoBr_2$ (Table 1, Ligand Screening, Entry 10). To an oven dried round-bottom-flask with a sidearm, was added [dppb]$CoBr_2$ (16 mg, 0.025 mmol) and under argon it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.12 mL, 0.24 mmol) was added dropwise and the color of the solution changed from blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -20 ^oC and (*E*)-nona-1,3-diene (30 mg, 0.24 mmol) in a dichloromethane (1 mL) added under ethylene and the mixture was stirred for 20 h. The progress of the reaction was monitored via gas chromatography until completion. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as colorless oil as 94% (Z)-1,4 HV product (**13a**) and 5% (*Z*)-1,4-linear dimerized HV product (**16a**).

Hydrovinylation of (*E*)-nona-1,3-diene using[dppp]$CoCl_2$ at room temperature (Ligand screening, Table 1, Entry 7). To an oven-dried round-bottom flask with a sidearm, was added [dppp]$CoCl_2$ (11 mg, 0.020 mmol) under argon and it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.03 mL, 0.060 mmol) was added dropwise as color of the solution quickly changed from deep blue to brown with the formation of white fumes over the solution. When all the fumes disappeared in about 5 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. When this evolution stopped, (*E*)-nona-1,3-diene (25 mg, 0.20 mmol) was added under ethylene at room temperature and the mixture was stirred for 1 h until the completion of reaction monitored via gas chromatography. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of solvent yielded the product as a colorless oil and isomeric compositions were determined by gas chromatography and NMR spectroscopy. The ratios of products are indicated in the table.

Hydrovinylation of (*E*)-nona-1,3-diene using[dppm]$CoCl_2$ at room temperature (Ligand screening, Table 1, Entry 12). To an oven-dried round-bottom flask with a sidearm, was added [dppm]$CoCl_2$ (42 mg, 0.082 mmol) under argon and it was dissolved in dichloromethane (1.5 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.13 mL, 0.25 mmol) was added dropwise as color of the solution quickly changed from bluish brown to red brown with the formation of white fumes over the solution. When all the fumes disappeared in around

5 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. When this evolution stopped, (*E*)-nona-1,3-diene (102 mg, 0.82 mmol) in dichloromethane (1 mL) was added under ethylene at room temperature and the mixture was stirred for 2 h. The progress of the reaction was monitored via gas chromatography intermittently. After 2 hours, the ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil and isomeric compositions were determined by gas chromatography and NMR spectroscopy (Table 1, entry 12).

Hydrovinylation of (*E*)-nona-1,3-diene using[BISBI]$CoCl_2$ (Ligand Screening, Table 1, Entry 14). To an oven-dried round-bottom flask with a sidearm, was added [BISBI]$CoCl_2$ (20 mg, 0.029 mmol) under argon and it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.15 mL, 0.29 mmol) was added dropwise as color of the solution quickly changed from blue to red brown with the formation of white fumes over the solution. When all the fumes disappeared in around 5 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. When this evolution stopped, (*E*)-nona-1,3-diene (36 mg, 0.29 mmol) in dichloromethane (1 mL) was added under ethylene at -12 ^oC temperature and the mixture was stirred for 6 h. The progress of the reaction was monitored via gas chromatography intermittently. After 6 hours, the ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of solvent yielded the product as a colorless oil and isomeric compositions [**13a**, 1,4-Z HV (65%) and **15a**, 1,2-E HV (34%]) were determined by gas chromatography and NMR spectroscopy.

Screening of activators in the Co-Catalyzed hydrovinylation of 1,3-dienes (Table 2)

The typical procedure described above (Hydrovinylation of (*E*)-nona-1,3-diene using[DPPB]$CoCl_2$ (Table 1, Entry 9) was used in screening various promoters for the reaction (Table 2).

The solid activators like Mn, InI_3, and Zn/ZnI_2 were added at the same time with cobalt complexes in the round bottom flask with side-arm in the nitrogen atmosphere glove box. Liquid activators like Me_3B, Et_3B, Ph_3B, *i*-BuAlH, $LiEt_3BH$ (in THF), Et_2AlOEt, Et_2AlCl, $EtAlCl_2$, PhMgBr, were added in the same way as trimethylaluminium (TMA solution in toluene) to the solution of cobalt complexes via syringe.

Typical experiments are described below:

Unsuccessful hydrovinylation of nona-1,3-diene using [dppe]$CoCl_2$ and Mn as promoter (Promoters screening, Table 2, Entry 9). As a typical procedure, to an oven dried round-bottom-flask with a sidearm, was added DPPE$CoCl_2$ (21 mg, 0.040 mmol) and Mn (22 mg, 0.40 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. After 30 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was kept in room temperature and the nona-1,3-diene (50 mg, 0.40

mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 14 h at room temperature intermittently monitoring the progress of reaction by gas chromatography. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 X 6 mL). Removal of solvent recovered the starting material back. GC and NMR analysis showed that the product was not formed at all.

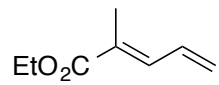
Hydrovinylation of (*E*)-dodeca-1,3-diene using [DPPP]$COBr_2$ and Zn/ZnI_2. (Promoters screening, Table 2, Entry 20) To an oven dried round-bottom-flask with a sidearm, was added [DPPP]$CoBr_2$ (20 mg, 0.032 mmol), Zn dust (4.2 mg, 0.064 mmol) and ZnI_2 (20 mg, 0.064 mmol) under argon and was dissolved in dichloromethane (2 mL) at room temperature. The solution was stirred for at least 30 minutes at room temperature, and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 ^oC and (*E*)-dodeca-1,3-diene (53 mg, 0.32 mmol) was added under ethylene. After 1 hour, first aliquot of the reaction mixture was taken out via syringe and flush through a small pad of silica and was analyzed by GC. Reaction was monitored by GC analysis until completion. Finally after stirring the reaction mixture for 4 h at ambient temperature, the ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (3 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as a mixture of hydrovinylation product (**13d**,1,4-*Z*, 79%) and linear hydrovinylation product(**16d**, 1,4-Z-linear, 21%) from GC and NMR analysis. All the reactions in Table 2 using Zn and ZnI_2 were performed exactly the same way using the conditions described therein.

Unsuccessful hydrovinylation of (*E*)-dodeca-1,3-diene using DPPB$CoCl_2$ and diethyl aluminum chloride (Et_2AlCl) as a promoter (Table 2, Entry 13). To an oven dried round-bottom-flask with a sidearm, was added DPPB$CoCl_2$ (35 mg, 0.063 mmol) and under argon it was dissolved in dichloromethane (1 mL) at room temperature. Diethylaluminium chloride (Et_2AlCl) as a 2M solution in toluene (0.16 mL, 0.32 mmol) was added dropwise and the color of the solution remain unchanged from its blue color. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -10 ^oC and (*E*)-dodeca-1,3-diene (105 mg, 0.63 mmol) in a dichloromethane (1 mL) added under ethylene and the mixture was stirred for 5 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Removal of solvent and analysis by GC and NMR gave none of the expected hydrovinylation products.

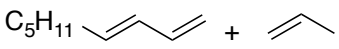
Unsuccessful hydrovinylation of nona-1,3-diene using [DPPM]$CoCl_2$ and MeMgBr and AgOTf as promoters (Promoters screening, Table 2, Entry 12). As a typical procedure, to an oven dried round-bottom-flask with a sidearm, was added [DPPM]$CoCl_2$ (19 mg, 0.037 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Methylmagnesium bromide (MeMgBr) as a 3M solution in ether (0.01 mL, 0.037 mmol) was added via syringe and the color of the solution changed from deep blue to black with the formation of white fumes over the solution. Subsequently, AgOTf (9.3 mg, 0.037 mmol) was added to the solution. After 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 ^0C and the nona-1,3-

diene (46 mg, 0.37 mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 4 h at 0 ^{0}C to rt. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (3 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 6 mL). Removal of solvent recovered the starting material back. GC and NMR analysis showed that the product was not formed at all.

Iron-catalyzed hydrovinylation of (*E*)-nona-1,3-diene using[DPPE]$FeCl_3$ (Equation 11): To an oven dried round-bottom-flask with a sidearm, was added [DPPE]$FeCl_3$ (56 mg, 0.099 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.24 mL, 0.49 mmol) was added dropwise and the color of the solution changed from light pink to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -10 ^{o}C and (*E*)-nona-1,3-diene (61 mg, 0.49 mmol) as a dichloromethane solution (0.5 mL) was added under ethylene and the mixture was stirred for 3 h at ambient temperature. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 7 mL). Removal of solvent yielded the product as a colorless oil as a mixture of (*Z*)-1,4-product (30%), 1,4-linear dimerized product (10%) and starting material (60%) by GC and NMR analysis.



Unsuccessful hydrovinylation of substrate (*E*)-ethyl-2-methylpenta-2,4-dienoate using [dppm]$CoCl_2$. To an oven dried round-bottom-flask with a sidearm, was added [dppm]$CoCl_2$ (30 mg, 0.058 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.6 ml, 1.16 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 ^{o}C and (*E*)-ethyl-2-methylpenta-2,4-dienoate (81 mg, 0.58 mmol) as a dichloromethane solution (0.5 mL) added under ethylene and the mixture was stirred for 15 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 5 mL). Removal of solvent recovered the starting material back. GC and NMR analysis showed that the product was not formed at all.



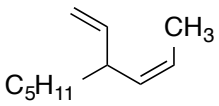
Unsuccessful attempt to dimerize (*E*)-1,3-nonadiene and propylene using [dppe]$CoCl_2$ (Equation 10). To an oven dried round-bottom-flask with a sidearm, was added (dppe)$CoCl_2$ (30 mg, 0.056 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.08 mL, 0.17 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with propylene from a balloon. The reaction vessel was cooled to -20 ^{o}C and (*E*)-1,3-nonadiene (70 mg, 0.56 mmol) as a dichloromethane solution (0.5 mL) was added under propylene and the mixture was stirred

for 14 h. The propylene balloon was removed and 0.1 mL of methanol was added to the flask. The solution was diluted with pentane (4 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 7 mL). Removal of solvent showed no codimerization reaction as all the (*E*)-1,3-nonadiene starting material was recovered as judged by GC and ^{1}H NMR.

Cobalt-Catalyzed Hydrovinylation of 1,3-Dienes. Scope of Substrates (Tables 3 and 5)

Hydrovinylation of different dienes and the major products obtained from them are listed below:

Hydrovinylation of (*E*)-nona-1,3-diene (12a)



The exploratory studies of effects of ligands and additives were conducted using this substrate. Rigorous identifications of all products from this substrate were described in our original communication.[2] For hydrovinylation procedure for (*E*)-nona-1,3-diene using[DPPB]$CoCl_2$ (Table 1, Entry 9, see under **Ligand Screening**. Details of the identification of various products were also listed earlier).

Typical procedure for asymmetric Co-catalyzed hydrovinylation reactions of (*E*)-nona-1,3-diene for ligand screening (Table 4, Entry 1-20). To an oven-dried round-bottom flask with a sidearm, was added (*RR*)-[DIOP]$CoCl_2$ (12.6 mg, 0.0201 mmol) under argon and it was dissolved in a mixture of degassed dichloromethane (2.0 mL) and toluene (0.5 mL), at 0 °C. Trimethylaluminum solution (2M) in toluene (4.3 mg, 30 μl, 0.0604 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared (typically in 5-10 min depending on complex), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3-5 min. The reaction vessel was cooled to – 45 °C (or whatever is the prescribed temperature with other ligands and substrates) and (*E*)-nona-1,3-diene (50.0 mg, 0.403 mmol) was added under ethylene and the mixture was stirred for 6 h (color of the reaction solution turned blue again at the end of the reaction). The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil (58.2 mg, 95%). Analysis by GC and NMR showed that the product was essentially pure. Isomeric compositions were determined by gas chromatography and NMR spectroscopy.

Details of the identification of the individual components of the mixture and chromatographic separation of these compounds including those of the enantiomers have been reported before.[2]

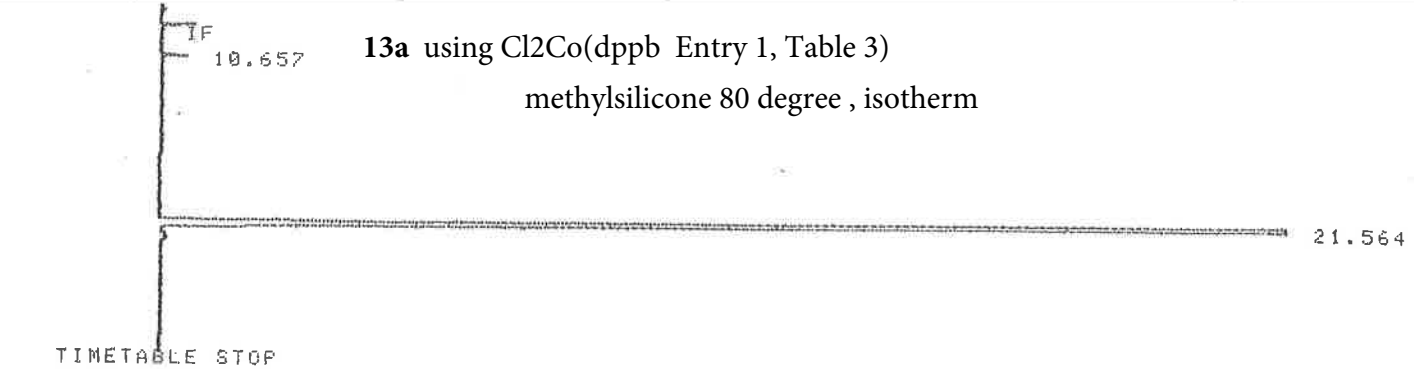
The enantioselectivities obtained with various other chiral ligands under different conditions are listed in Table 4. Typical examples are described below:

Asymmetric Co-catalyzed Hydrovinylation Reactions (*E*)-1,3-nonadiene by using (*S,S,R,R*)-Tangphos [(L14)$CoCl_2$] (Table 5, Entry 3). To an oven-dried round-bottom flask with a sidearm, was added (*S,S,R,R*)-[Tangphos]$CoCl_2$ (19 mg, 0.046 mmol) under argon and it was dissolved in a degassed dichloromethane (1.0 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.07 mL, 0.14 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution.

When all the fumes disappeared (typically in 5 min), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3 minute. The reaction vessel was cooled to – 10 ºC and (*E*)-nona-1,3-diene (57 mg, 0.46 mmol) in dichloromethane (1 mL) was added under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil. Analysis by GC and NMR showed that the product was essentially pure with two major isomers (**13a** product with 39% yield and 95% ee and the linear product **16a** product in 40% yield). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (See attached chromatograms and Spectra).

Asymmetric Co-catalyzed hydrovinylation reaction (*E*)-1,3-nonadiene by using 1 mol % Josiphos 2 [(18)$CoCl_2$] (Table 5, Entry 4). To an oven-dried round-bottom flask with a sidearm, was added [Josiphos]$CoCl_2$ (4 mg, 0.0038 mmol) under argon and it was dissolved in a degassed dichloromethane (1.0 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.0057 mL, 0.0114 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared (typically in 5 min), the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically 3 minute. The reaction vessel was cooled to – 20 ºC and (*E*)-nona-1,3-diene (47 mg, 0.38 mmol) in dichloromethane (1 mL) was added under ethylene and the mixture was stirred for 14 h until the completion of reaction monitored by gas chromatography. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 10 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil. Analysis by GC and NMR showed that the product was essentially pure with major isomer (**13a** product with 95% yield and 87% ee). Isomeric compositions were determined by gas chromatography and NMR spectroscopy.

Highest ee for this substrate was obtained using (*R,R)*-DIOP (>95% ee, >95% yield) or (*S,S*)-BDPP (>97% ee, >95% yield) at -45 ºC.[2]



13a using Cl2Co(dppb Entry 1, Table 3)

methylsilicone 80 degree , isotherm

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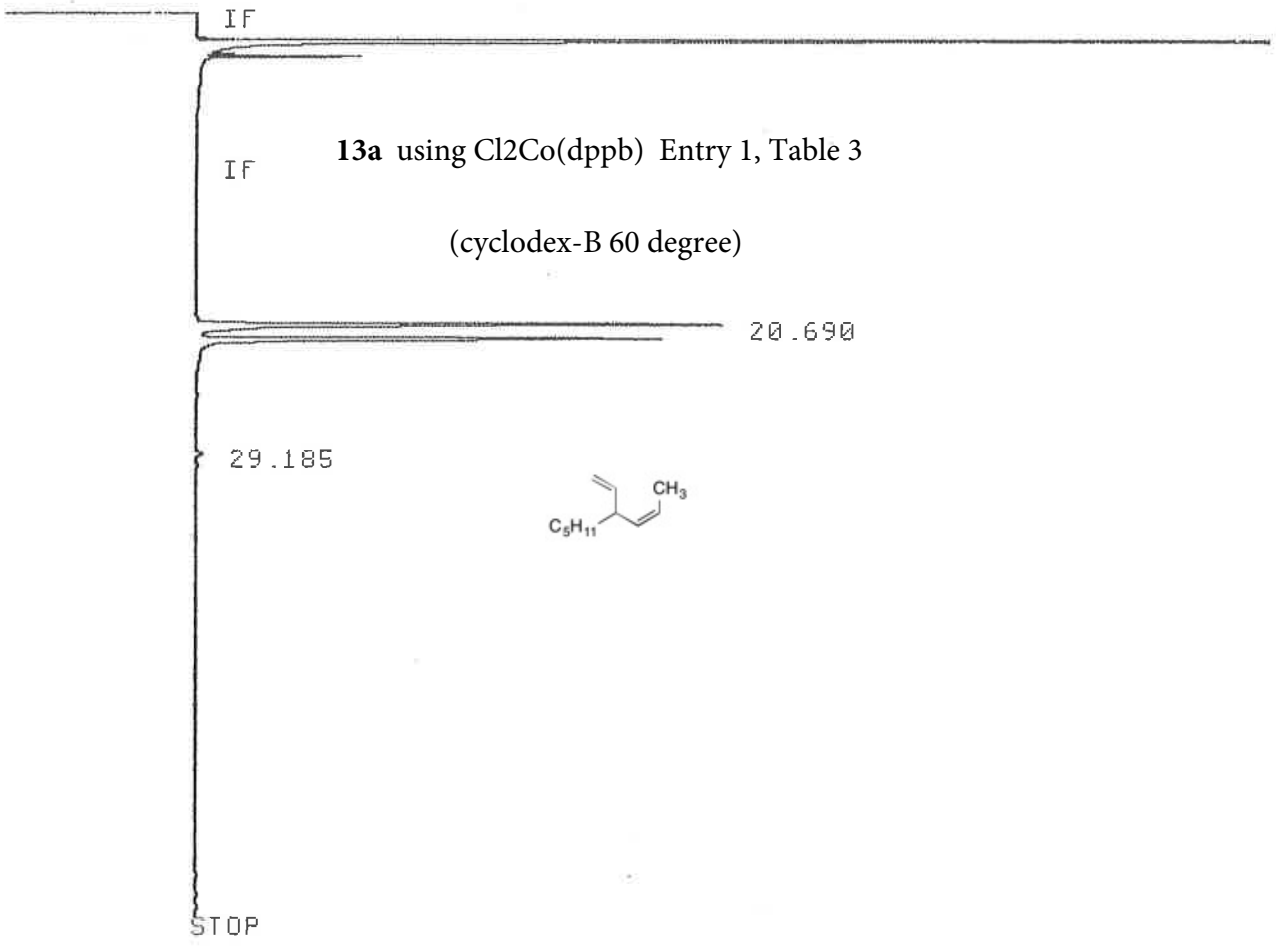

13a using Cl2Co(dppb) Entry 1, Table 3

(cyclodex-B 60 degree)

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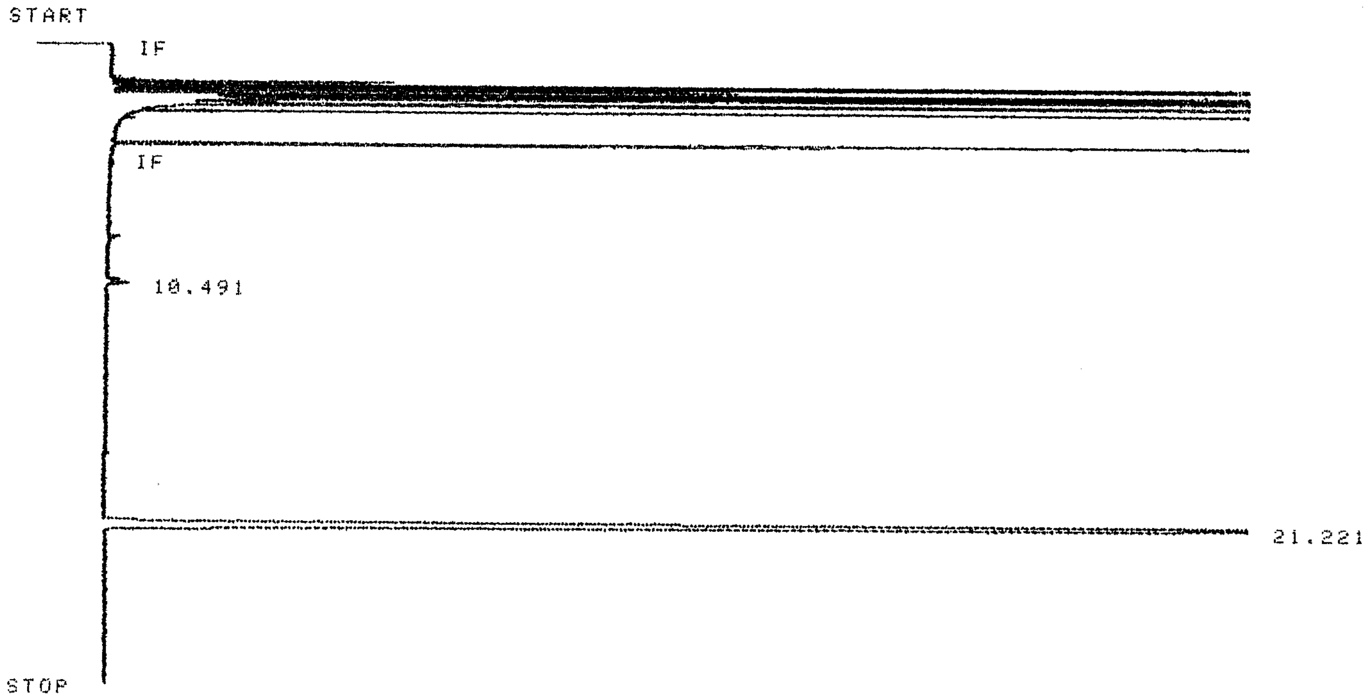
AREA%
      RT       AREA TYPE   WIDTH       AREA%
  20.690      48959   VV    .219    53.51470
  21.644      42528   VV    .215    46.48530
```



Error storing signal to M:SIGNAL .RAW
ATTEMPTED WRITE PAST END OF FILE

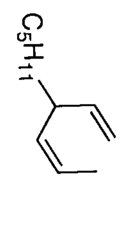
RUN# 835 JUN 24, 1901 11:20:05

AREA%

RT	AREA	TYPE	WIDTH	AREA%
21.221	1083970	PB	.168	100.00000

TOTAL AREA=1083970
MUL FACTOR=1.0000E+00

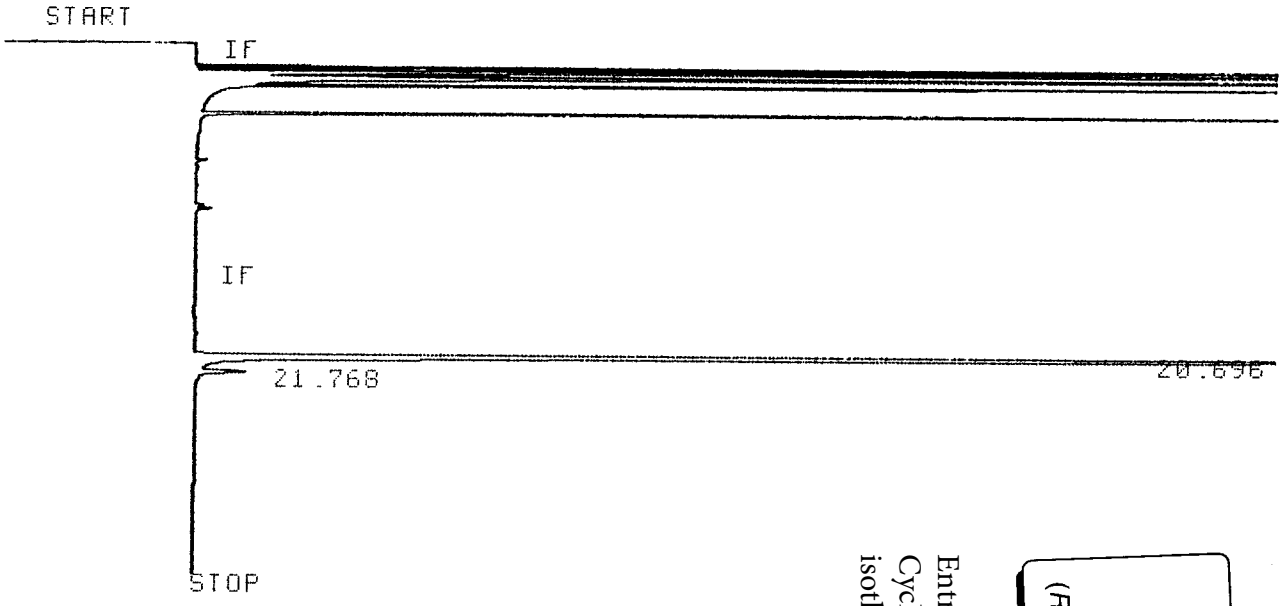
*
*
*



(RR)-(–)[DIOP]$CoCl_2$/–45 °C

(Polydimethylsiloxane, 80 °C)

(Entry1, Table 5)

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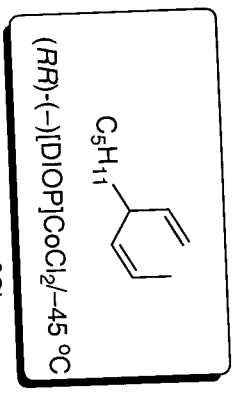
Closing signal file M:SIGNAL   .BNC

RUN#  3919          MAY 16, 2009  00:35:45

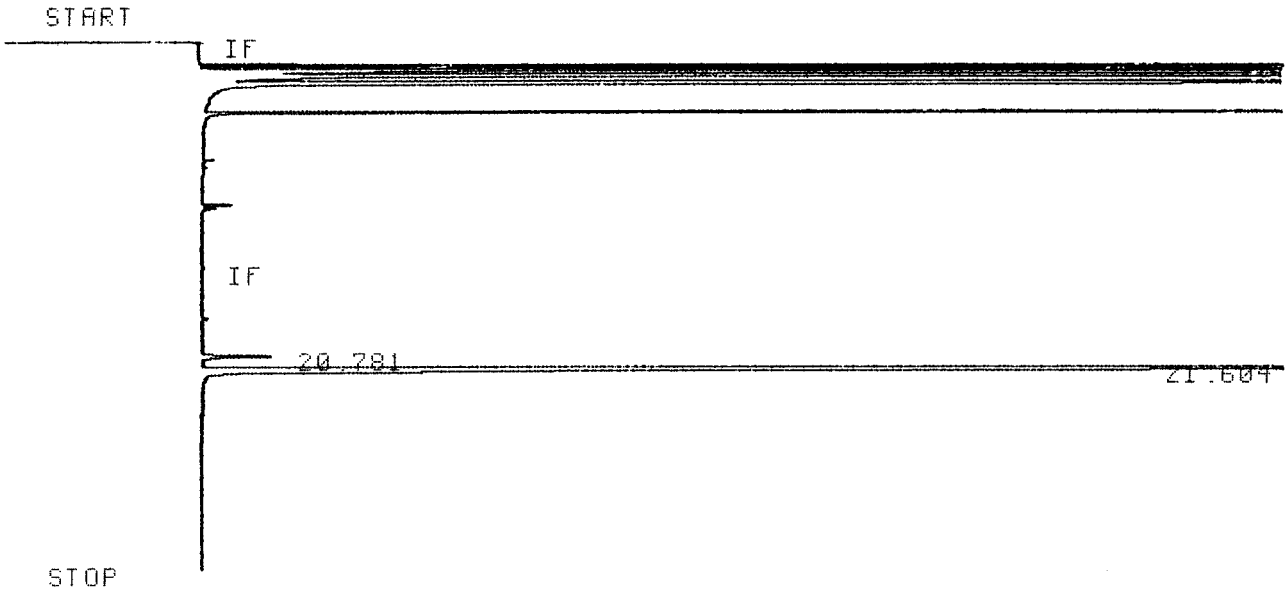
SIGNAL FILE: M:SIGNAL.BNC
AREA%
       RT       AREA TYPE  WIDTH       AREA%
   20.696      75830   BB    .203    98.01462
   21.768       1536   BP    .179     1.98537

TOTAL AREA=  77366
MUL FACTOR=1.0000E+00
```



Entryl, Tble 5
Cyclodex-B, 60 degree
isotherm)

RK1.2-152 / 5 %, (->DIOP]CoCl2 / Isotherm 60°C (-45°C)



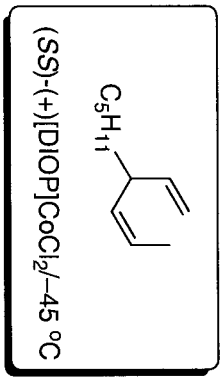
Closing signal file M:SIGNAL .BNC

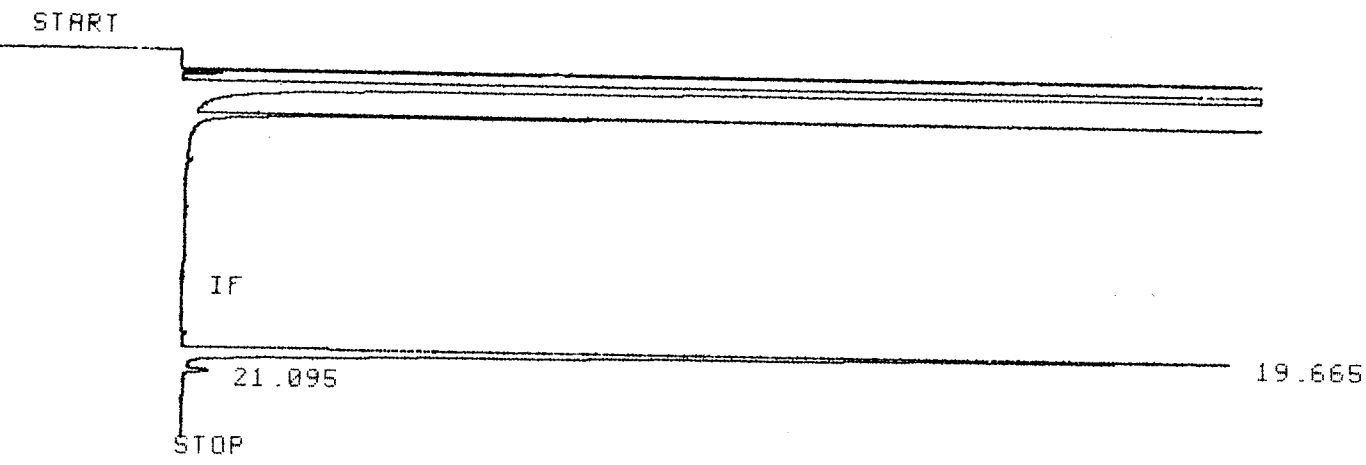
RUN# 3910 MAY 13, 2009 02:51:50

SIGNAL FILE: M:SIGNAL.BNC
AREA%

RT	AREA	TYPE	WIDTH	AREA%
20.781	2449	VV	.167	3.31879
21.604	71343	PV	.206	96.68122

TOTAL AREA= 73792
MUL FACTOR=1.0000E+00





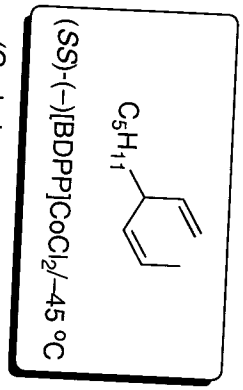
Closing signal file M:SIGNAL .BNC

RUN# 4007 AUG 3, 2009 00:35:24

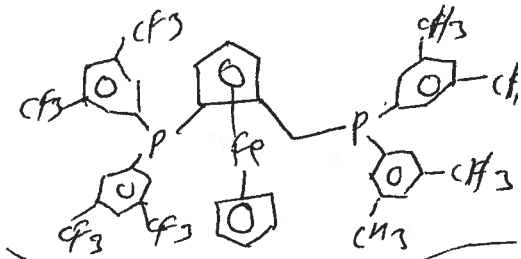
SIGNAL FILE: M:SIGNAL.BNC
AREA%

RT	AREA	TYPE	WIDTH	AREA%
19.665	592287	BB	.335	98.56893
21.095	8599	BB	.219	1.43105

TOTAL AREA= 600886
MUL FACTOR=1.0000E+00



13a using (S,S)-(BDPP) Entry 2, Table 5)



YT-03-281
OT 70°C, cyclosil, Isothermal.
(1 mol% catalyst)

RUN # 4772 FEB 17, 2012 20:24:37
ART
IF
IF
IF
25.878
47.225
STOP

GC (Cyclodex-B, 70 degree) of Compound **13a** (HV using Cl2Co(Josiphos Ligand **L18,** Entry 4, Table 5)

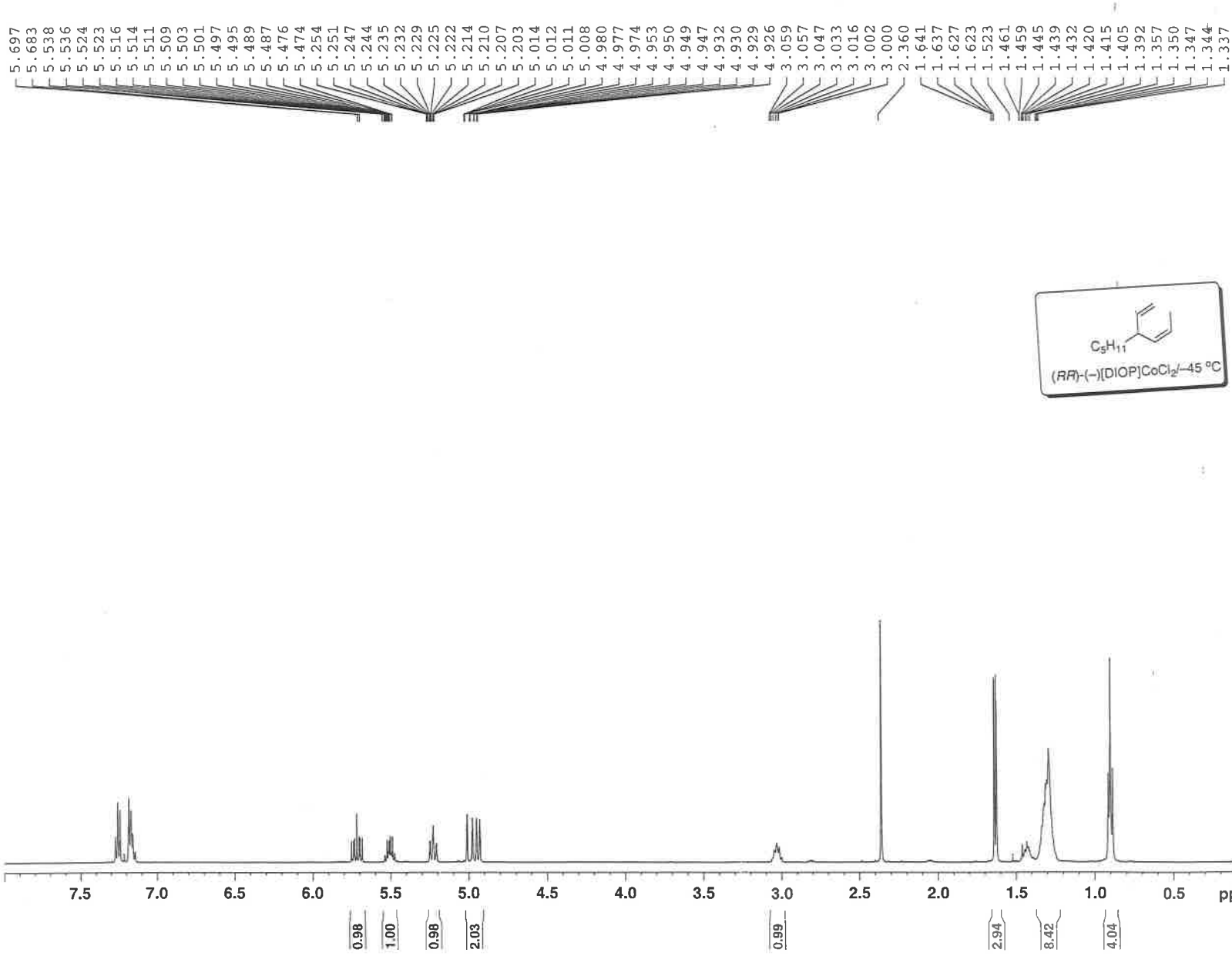
osing signal file M:SIGNAL .BNC

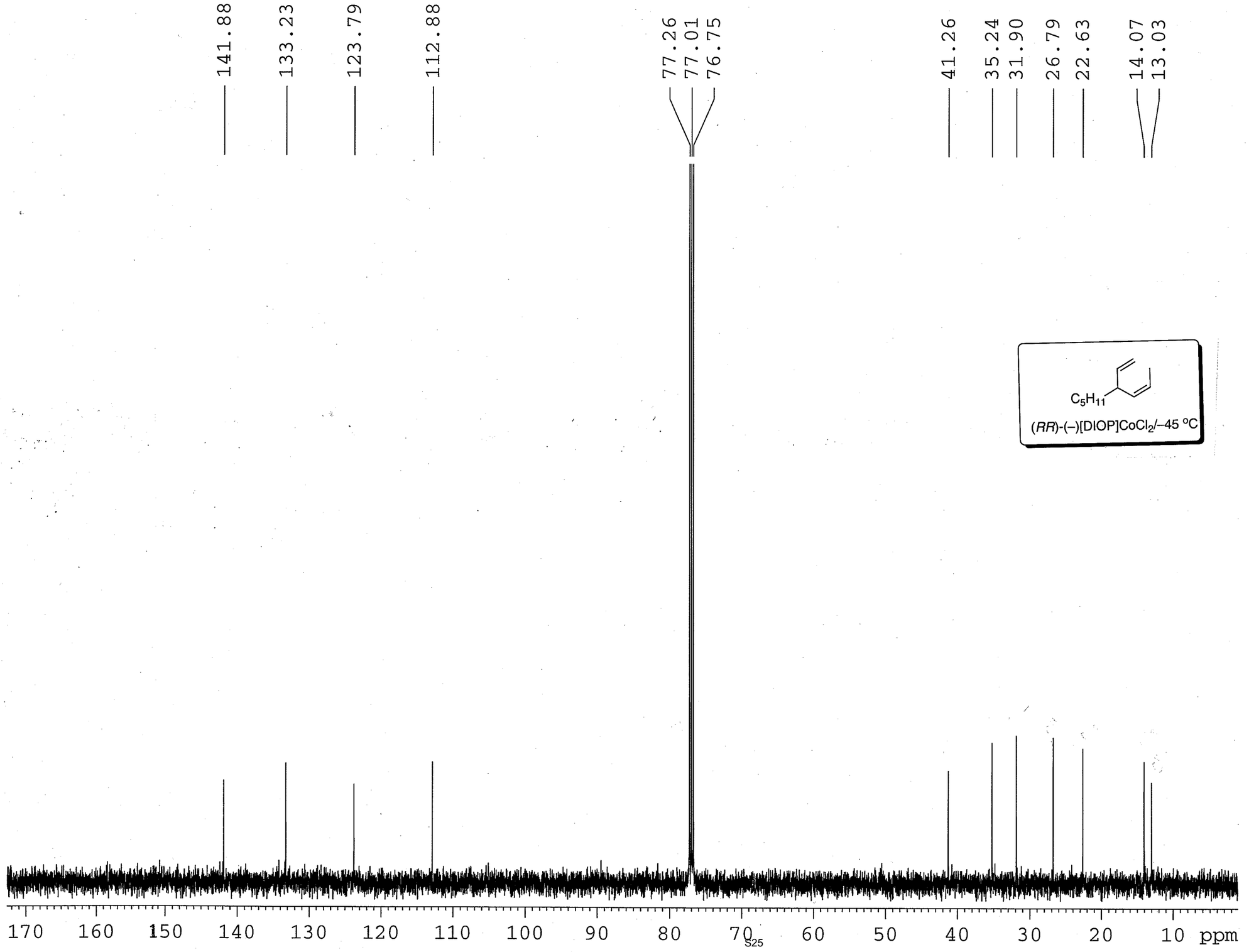
N# 4772 FEB 17, 2012 20:24:37

GNAL FILE: M:SIGNAL.BNC
EA%

RT	AREA	TYPE	WIDTH	AREA%
14.375	2058	BP	.113	1.20836
23.720	151804	BB	.204	89.13184
25.878	10506	BB	.206	6.16860
47.225	5946	BB	.349	3.49120

TAL AREA= 170314
L FACTOR=1.0000E+00


5.697
5.683
5.538
5.536
5.524
5.523
5.516
5.514
5.511
5.509
5.503
5.501
5.497
5.495
5.489
5.487
5.476
5.474
5.254
5.251
5.247
5.244
5.235
5.232
5.229
5.225
5.222
5.214
5.210
5.207
5.203
5.014
5.012
5.011
5.008
4.980
4.977
4.974
4.953
4.950
4.949
4.947
4.932
4.930
4.929
4.926
3.059
3.057
3.047
3.033
3.016
3.002
3.000
2.360
1.641
1.637
1.627
1.623
1.523
1.461
1.459
1.445
1.439
1.432
1.420
1.415
1.405
1.392
1.357
1.350
1.347
1.344
1.337
C5H11
(RR)-(−)[DIOP]CoCl2/−45 °C
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppr
0.98
1.00
0.98
2.03
0.99
2.94
8.42
4.04



BRUKER

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Current Data Parameters
NAME      RKS-2-152 again carbon
EXPNO                383
PROCNO                 1

F2 - Acquisition Parameters
Date_           20091224
Time               13.29
INSTRUM            spect
PROBHD   5 mm Multinucl
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   50
DS                    4
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ             1.0912244 sec
RG                 3251
DW               16.650 usec
DE               12.00 usec
TE               300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1               12.00 usec
PL1               3.00 dB
SFO1        125.7427020 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           100.00 usec
PL2              -1.00 dB
PL12             15.59 dB
PL13             22.50 dB
SFO2        500.0220001 MHz

F2 - Processing parameters
SI                 32768
SF          125.7301290 MHz
WDW                   EM
SSB                    0
LB                1.00 Hz
GB                     0
PC                1.00
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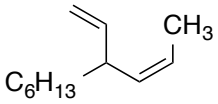
Hydrovinylation of (*E*)-deca-1,3-diene (12b)



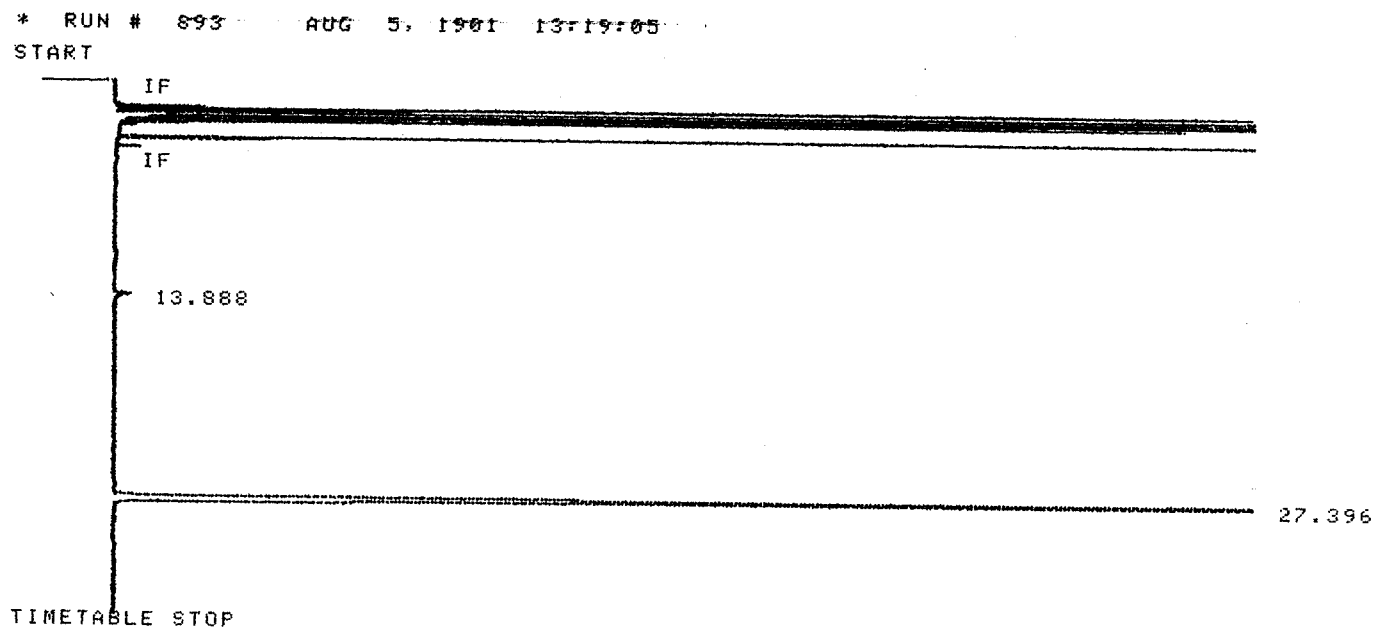
Hydrovinylation of (*E*)-deca-1,3-diene using (*R,R*)[DIOP]$CoCl_2$ (Table 5, Entry 5). To an oven dried round bottom flask with a sidearm, was added (*RR*)[DIOP]$CoCl_2$ (3 mg, 0.0028 mmol) and dichloromethane (0.5 mL) was added. Trimethylaluminium solution (2 M) (0.05 mL,0.008 mmol) was added to the solution and the color changed from deep blue to red brown with the formation of white fumes. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -45 ^{o}C and (*E*)-deca-1,3-diene (43 mg, 0.28 mmol), was added via syringe under ethylene and the mixture was stirred for 6 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 6 mL). Removal of the solvent yielded the product as colorless oil. GC showed 97% (*Z*)-1,4-product and 3% 1,4-linear dimerized product.

An authentic sample of the racemic compound was prepared by similar procedure (Table 3, Entry 2) using corresponding achiral complex [(dppb)$CoCl_2$] at the prescribed temperature.

^{1}H NMR ($CDCl_3$): δ 0.891 (t, J = 7 Hz, 3 H, H^{10}), 1.23-1.40 (m, 9 H), 1.38-1.47 (m, 1 H), 1.23-1.47 total 10 H, 1.628 (dd, J = 7, 2 Hz, 3 H, H^{1}), 3.027 (m, 1 H, H^{4}), 4.935 (dm, J = 10 Hz, H^{12}), 4.987 (ddd, J = 17.5 Hz, m, 1 H, H^{13}), 5.222 (app t m, 10.5 Hz, H^{3}), 5.502 (dqm, 11.5 Hz, 6.5 Hz, 1 Hz, H^{2}), 5.714 (ddd, 17 Hz, 10 Hz, 7 Hz, 1H, H^{11}). [toluene @ 2.364]. Also seen: (t, J = 6.5 Hz) 0.221 up-field from C_{sp3}-C*H* (3.027) ~ 2% (bis-allylic CH_2).
^{13}C ($CDCl_3$) 13.01, 14.07, 22.66, 27.10, 29.34. 31.87, 35.30, 41.26, 112.86, 123.77, 133.23, 141.86.
Mass spectrum: m/z = 167.1 (calculated for $[M+H]^{+}$, M= $C_{12}H_{23}$ 167.1)

Product from (*RR*)-(–)-DIOP $[\alpha]^{25}_{D}$ = –18.6 (hexane, *c* 1.25)

Gas chromatography: (Polydimethylsiloxane) conditions: 90 ^{o}C isotherm, retention time (min): R_T = 27.40. CSP GC (Cyclodex) conditions: 60 ^{o}C isotherm, R_T = 35.94 min. (*S*, 97.7%), 38.07 (*R*, 2.3%).



Error storing signal to M:SIGNAL .RAW
ATTEMPTED WRITE PAST END OF FILE

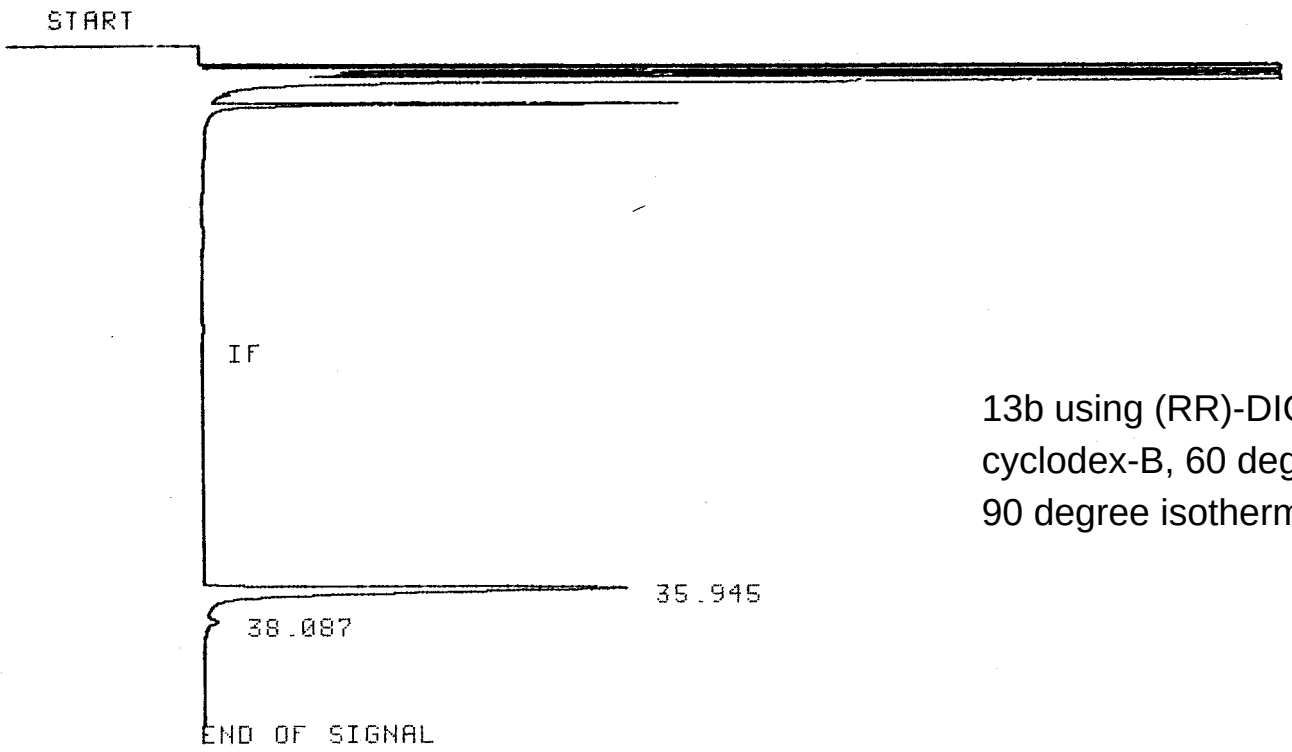
RUN# 893 AUG 5, 1901 13:19:05

AREA%

RT	AREA	TYPE	WIDTH	AREA%
13.888	11686	PV	.116	.69185
27.396	1677406	PP	.214	99.30813

TOTAL AREA=1689092
MUL FACTOR=1.0000E+00

13b using (RR)-DIOP -45 degree
methylsilicone column
90 degree isotherm, Entry 5, Table 5



13b using (RR)-DIOP -45 degree cyclodex-B, 60 degree isoterm, column 90 degree isotherm, Entry 5, Table 5

```
Closing signal file M:SIGNAL   .BNA

RUN#  3963          JUN 27, 2009  22:45:12

SIGNAL FILE: M:SIGNAL.BNA
AREA%
      RT       AREA TYPE  WIDTH      AREA%
  35.945     167914   BV    .472    97.69712
  38.087       3958   BV    .402     2.30288

TOTAL AREA= 171872
MUL FACTOR=1.0000E+00
```

1.179
1.184
1.193
1.199
1.282
1.352
1.368
1.384
1.416
1.427
1.454
1.509
1.513
1.619
1.623
1.633
1.636
1.659
1.662
1.672
1.676
1.680
1.683
2.039
2.053
2.364
2.806
2.995
3.011
3.027
3.041
4.921
4.924
4.926
4.945
4.947
4.967
4.970
4.973
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4.990
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5.005
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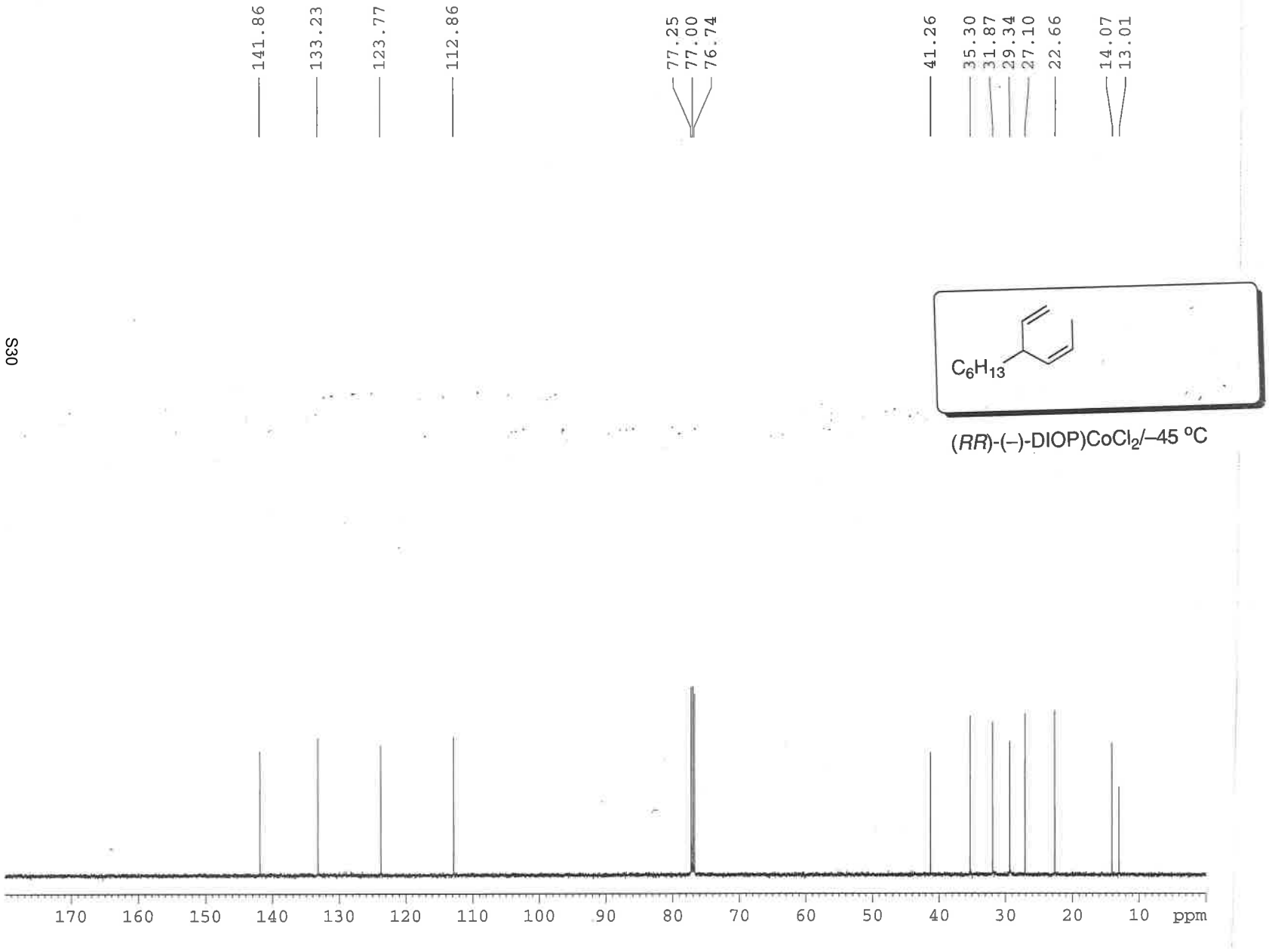
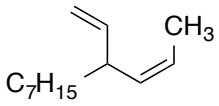
5.219
5.222
5.225
5.237
5.240
5.244
5.471
5.484
5.490
5.492
5.498
5.504
5.506
5.511
5.518
5.520
5.533
5.680
5.694
5.700
5.714
5.728
5.734
5.748
7.188
7.260
C6H13
(98%)
(RR)-(−)-DIOP)CoCl2/−45 °C
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
3.40
10.12
1.18
2.97
0.07
0.05
1.01
2.10
1.00
1.01
1.00


141.86
133.23
123.77
112.86
77.25
77.00
76.74
41.26
35.30
31.87
29.34
27.10
22.66
14.07
13.01
C_6H_{13}
(RR)-(–)-DIOP)$CoCl_2$/–45 °C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

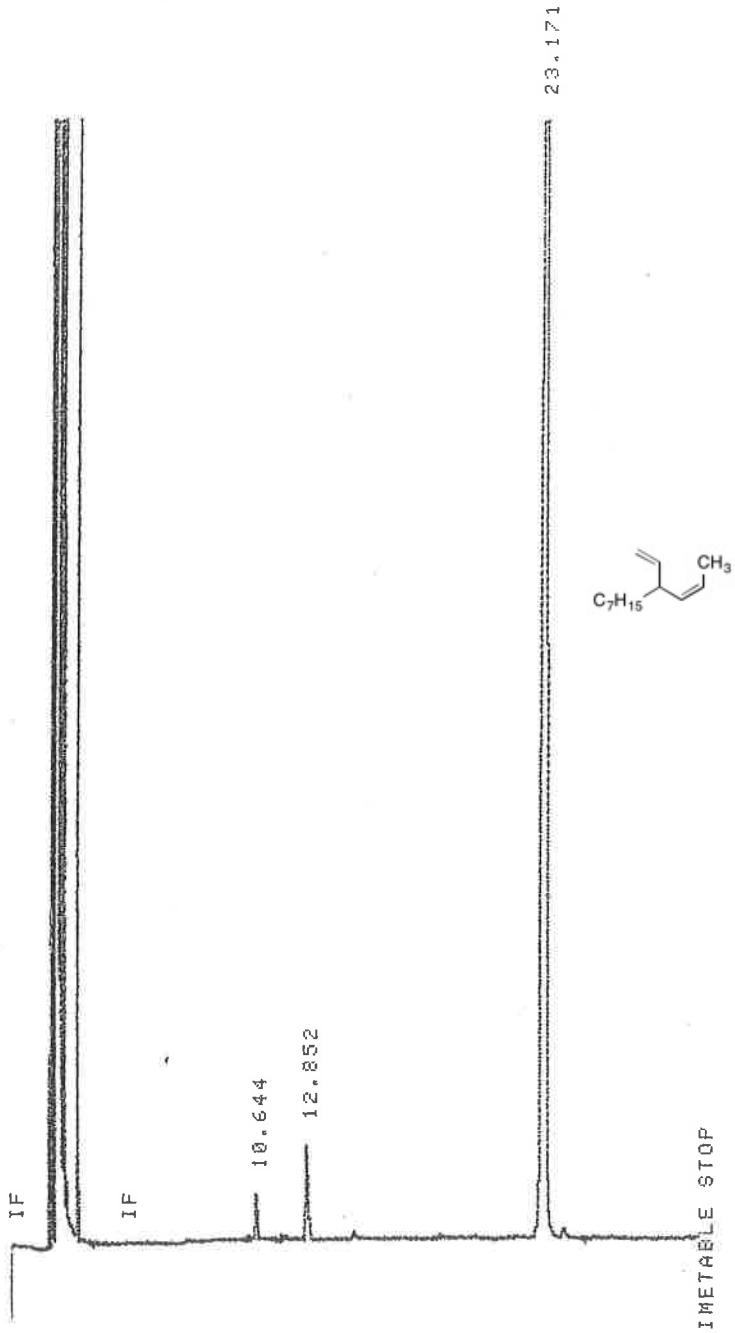
Hydrovinylation of (*E*)-undeca-1,3-diene (12c)



Hydrovinylation of (*E*)-undeca-1,3-diene using 1 mol % [L18 Josiphos-2]$CoCl_2$ Loading (Table 5, Entry 7). To an oven dried round bottom flask with a sidearm, was added [(**L18**)$CoCl_2$] (3 mg, 0.0028 mmol) and dichloromethane (0.5 mL) was added. Trimethylaluminium solution (2 M) (0.05 mL,0.008 mmol) was added to the solution and the color changed from deep blue to red brown with the formation of white fumes. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -20 ^{o}C and (*E*)-undeca-1,3-diene (43 mg, 0.28 mmol), was added via syringe under ethylene and the mixture was stirred for 7 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 6 mL). Removal of the solvent yielded the product as colorless oil. GC showed 97% (*Z*)-1,4-product and 3% 1,4-linear dimerized product.
Gas Chromatography (**13c**): CSP GC (Cyclodex-B, OT 100 ^{o}C/ isothermal, H_2 carrier gas). R_T for product = 50.0 min and 51.2 min (enantioselectivity 87 %ee).

[(*R,R*)-DIOP]$CoCl_2$ at -45 ^{o}C (6 h) gave the highest selectivity for this substrate (>95 %ee).[2]

13c using (dppb)CoCl2 (Table 3, entry 3)
methylsilicone column Oven temp 110 degrees



Error storing signal to M:SIGNAL .RAW
ATTEMPTED WRITE PAST END OF FILE

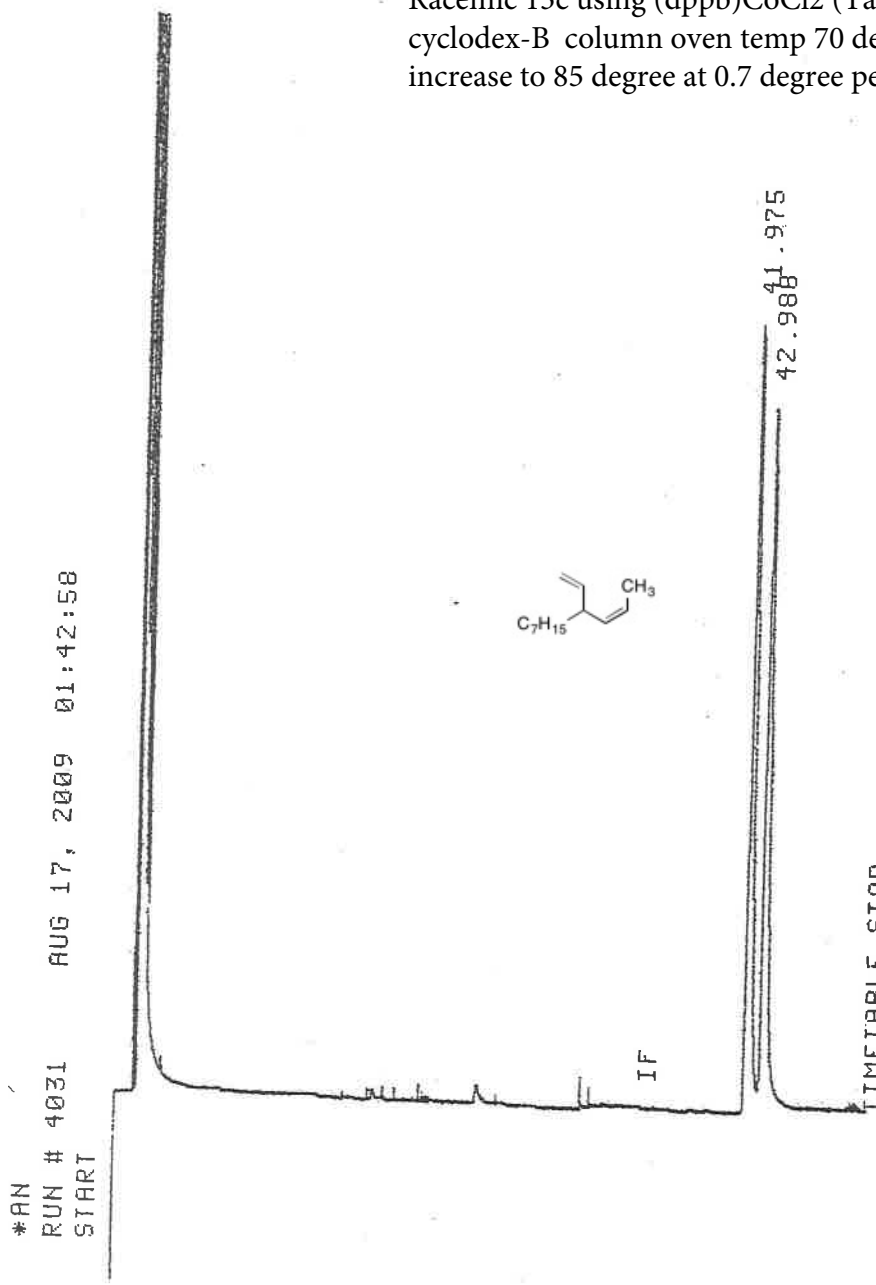
RUN# 870 JUL 11, 1901 14:02:51

AREA%

RT	AREA	TYPE	WIDTH	AREA%
10.644	14868	PP	.092	.57381
12.852	30605	PV	.095	1.18116
23.171	2545624	BV	.179	98.24502

TOTAL AREA=2591098
MUL FACTOR=1.0000E+00

Racemic 13c using (dppb)CoCl2 (Table 3, entry 3)
cyclodex-B column oven temp 70 degrees/30 min,
increase to 85 degree at 0.7 degree per minute



Closing signal file M:SIGNAL .BNA

RUN# 4031 AUG 17, 2009 01:42:58

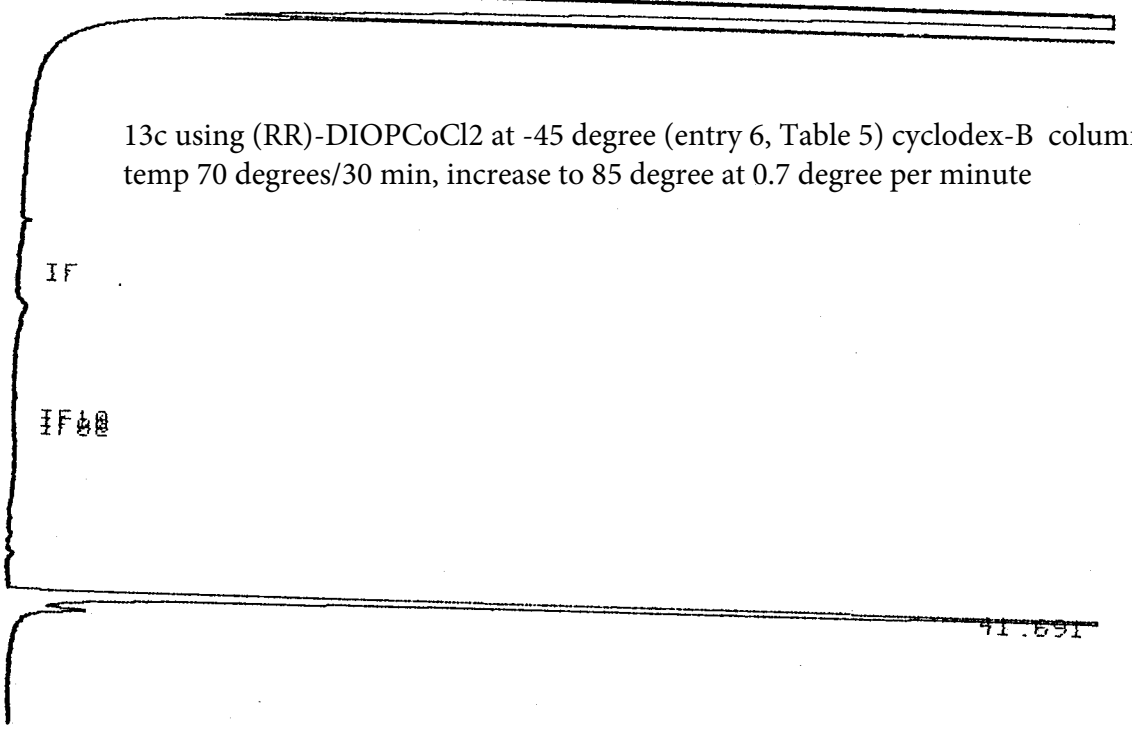
SIGNAL FILE: M:SIGNAL.BNA
AREA%

RT	AREA	TYPE	WIDTH	AREA%
41.975	105918	PU	.317	50.06784
42.988	105631	VB	.356	49.93218

TOTAL AREA= 211549
MUL FACTOR=1.0000E+00

```
*  RUN # 3956      JUN 26, 2009  23:38:42
START
```

13c using (RR)-DIOPCoCl2 at -45 degree (entry 6, Table 5) cyclodex-B column oven temp 70 degrees/30 min, increase to 85 degree at 0.7 degree per minute

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STOP

Closing signal file M:SIGNAL   .BNC

RUN#  3956            JUN 26, 2009  23:38:42

SIGNAL FILE: M:SIGNAL.BNC
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  41.691      53419   BB    .303    97.72960
  42.766       1241   PP    .255     2.27040

TOTAL AREA=  54660
MUL FACTOR=1.0000E+00
```

95.45% ee

GC (Cyclodex-B, 100 degree) of Compound **13c** (HV using Josiphos ligand **L18)** (entry 7, Table 5) 87% ee

Closing signal file M:SIGNAL .BNC

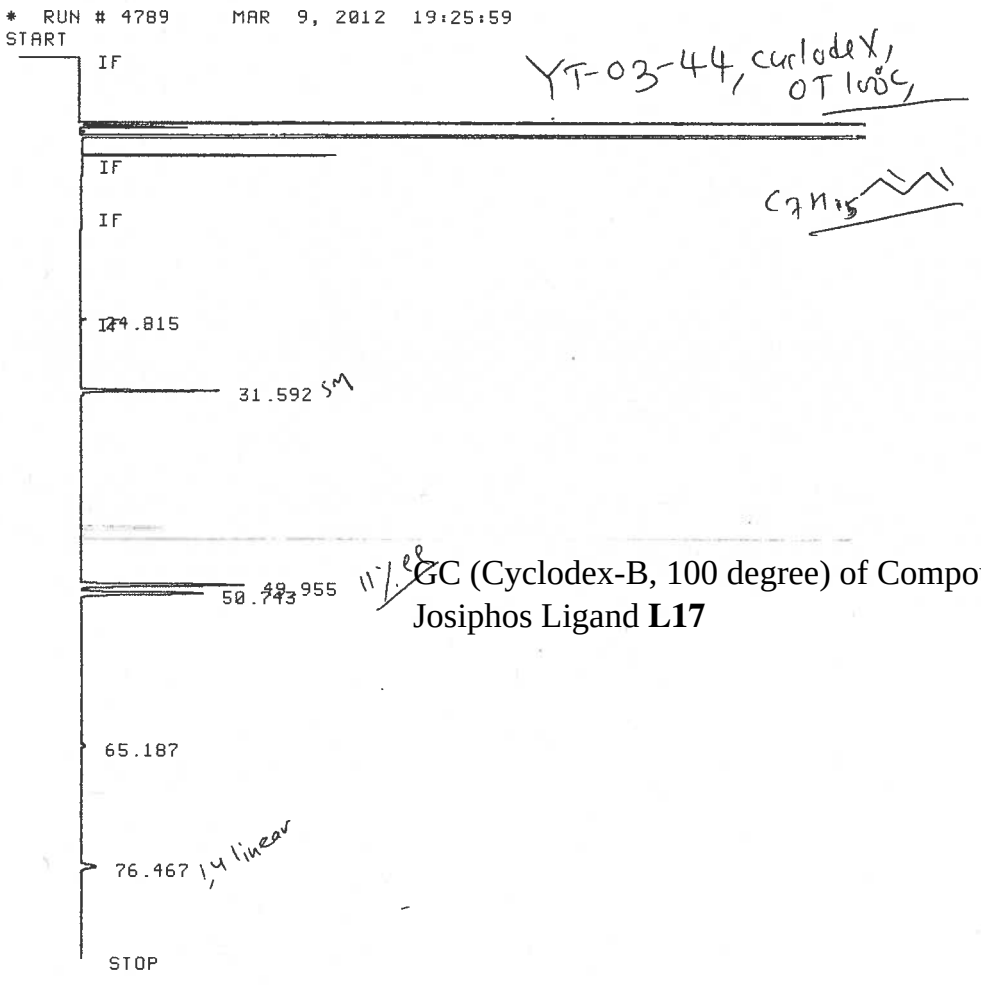
RUN# 4785 FEB 27, 2012 21:40:34

SIGNAL FILE: M:SIGNAL.BNC
AREA%

	RT	AREA	TYPE	WIDTH	AREA%
	25.067	6762	VP	.133	.45712
	25.572	1646	PB	.136	.11127
	31.955	5030	BV	.164	.34004
	32.301	5982	VB	.173	.40439
	50.000	1321737	PV	.383	89.35142
	51.225	93350	VB	.370	6.31060
	77.168	44750	BB	.408	3.02517

87% ee

TOTAL AREA=1479257
MUL FACTOR=1.0000E+00



GC (Cyclodex-B, 100 degree) of Compound **13c** Using Josiphos Ligand **L17**

```
Closing signal file M:SIGNAL   .BNC

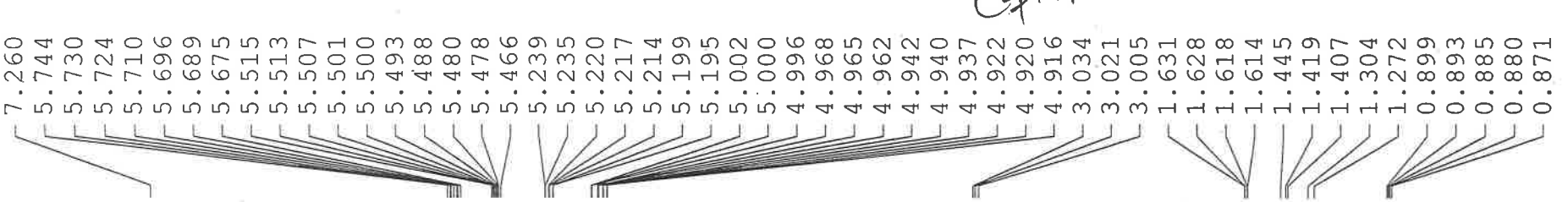
RUN#  4789          MAR  9, 2012  19:25:59

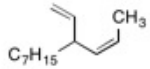
SIGNAL FILE: M:SIGNAL.BNC
AREA%
      RT       AREA TYPE  WIDTH      AREA%
  24.815       2064   PB   .128     .77326
  31.592      57986   VV   .168   21.72403
  49.955     103251   VV   .257   38.68224
  50.743      82991   VB   .275   31.09197
  65.187       4500   BB   .330    1.68589
  76.467      16129   PB   .395    6.04261

TOTAL AREA= 266921
MUL FACTOR=1.0000E+00
```

RKS-2-168

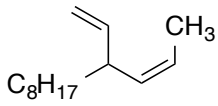
C_7H_{15}





141.88
133.23
123.78
112.87
77.26
77.00
76.75
41.26
35.29
31.89
29.65
29.30
27.14
22.67
14.08
13.02
CH3
C7H15
ppm

Hydrovinylation of (*E/Z*)-dodeca-1,3-diene (12d)



Hydrovinylation of (*E/Z*)-dodeca-1,3-diene using[DPPB]$CoCl_2$ (Table 3, Entry 5). To an oven dried round bottom flask with a sidearm, was added DPPB$CoCl_2$ (21 mg, 0.038 mmol) and methylaluminoxane (44 mg, 0.76 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -10 ^oC and (*E/Z*)-dodeca-1,3-diene (63 mg, 0.38 mmol), mixture of *E*:*Z* in the ratio of 54:46 via GC, was added via syringe under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of the solvent yielded the product as colorless oil (61 mg, 82%). GC and NMR analysis showed that the product was essentially pure. ^1H NMR ($CDCl_3$, 400 MHz): 0.836 (t, J = 7 Hz, 3 H), 1.25 – 1.43 (m, 14 H), 1.60 (dd, J = 7, 2 Hz, 3 H), 2.96 – 3.03 (m, 1 H), 4.89 - 4.99 (m, 2 H), 5.16 – 5.23 (m, 1 H), 5.43 - 5.51 (m, 1 H), 5.69 (ddd, J = 17, 10, 7 Hz, 1 H). ^{13}C NMR ($CDCL_3$, 125.02 MHz): 13.26, 14.33, 22.91, 27.37, 29.56, 29.83, 29.92, 32.14, 35.52, 41.49, 113.10, 124.01, 133.46, 142.10.
Gas Chromatography (**13d**): CSP GC (Cyclosil, OT 90 ^0C/ isothermal, H_2 carrier gas): starting material R_T = 31.19 min. for *E*-diene and 31.81 for *Z* diene. R_T for product = 51.74 min and 54.82 min (racemic). Cyclodex-B 65 ^oC/30 min increase 2 ^oC per min to 80 ^oC (He): R_T for product = 96.65 min and 99.14 min (racemic).

Hydrovinylation of (*E/Z*)-dodeca-1,3-diene using (*S,S*)[DIOP]$CoCl_2$ (Table 5, Entry 10): To an oven-dried round-bottom flask with a sidearm, was added (*SS*)-[DIOP]$CoCl_2$ (20 mg, 0.032 mmol) under argon and it was dissolved in a degassed dichloromethane (1 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.08 mL, 0.16 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 4 minutes. The reaction vessel was cooled to – 45 ^oC and (*E/Z*)-dodeca-1,3-diene (53 mg, 0.32 mmol, *E*:*Z* = 54:46) was added under ethylene and the mixture was stirred for 1 h until the completion of the reaction monitored by gas chromatography. The ethylene balloon was removed and 0.1 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 X 10 mL). Pentane was removed and product was separated as a colorless oil as a major product 1,4-Z hydrovinylation product, **13d** (53% yield) with 74% ee. Isomeric compositions were determined by gas chromatography and NMR spectroscopy. ^1H NMR ($CDCl_3$, 400 MHz): 0.836 (t, J = 7 Hz, 3 H), 1.25 – 1.43 (m, 14 H), 1.60 (dd, J = 7, 2 Hz, 3 H), 2.96 – 3.03 (m, 1 H), 4.89 - 4.99 (m, 2 H), 5.16 – 5.23 (m, 1 H), 5.43 - 5.51 (m, 1 H), 5.69 (ddd, J = 17, 10, 7 Hz, 1 H). ^{13}C NMR ($CDCL_3$, 125.02 MHz): 13.26, 14.33, 22.91, 27.37, 29.56, 29.83, 29.92, 32.14, 35.52, 41.49, 113.10, 124.01, 133.46, 142.10.
Hydrovinylation of (*E*)-dodeca-1,3-diene using(*S,S*)[DIOP]$CoCl_2$ at -45 ^oC (6 h) gave the highest ee for this substrate (>96 %ee, Table 5, Entry 8).[2]

IF

IF

13d using (dppb)CoCl2 (entry 4, Table 3)
methylsilicone 130 degree isotherm

11.540

TIMETABLE STOP

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MUL FACTOR=1.0000E+00

IF

13d using (dppb)CoCl2 (entry 4, Table 3)
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96.652
99.144

END OF SIGNAL

Closing signal file M:SIGNAL .BNA

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START

IF

IF

13d using (DIOP)CoCl2 (entry 8, Table 5)
methylsilicone 130 degree isotherm

19.240

TIMETABLE STOP

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ATTEMPTED WRITE PAST END OF FILE

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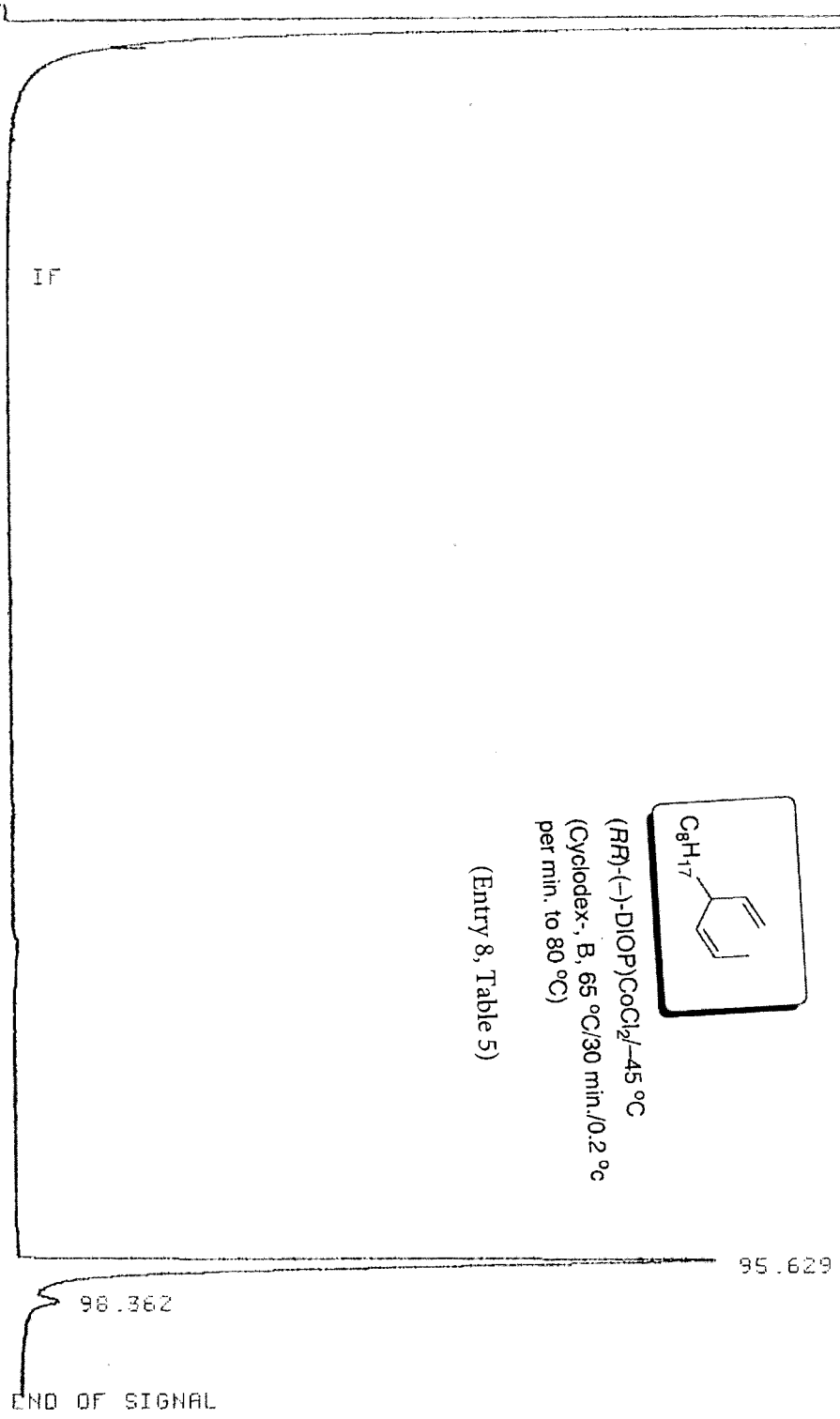

C_8H_{17}

(*RR*)-(–)-DIOP)$CoCl_2$/–45 °C
(Cyclodex-, B, 65 °C/30 min./0.2 °c
per min. to 80 °C)

(Entry 8, Table 5)

```
Closing signal file M:SIGNAL   .BNA

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MUL FACTOR=1.0000E+00
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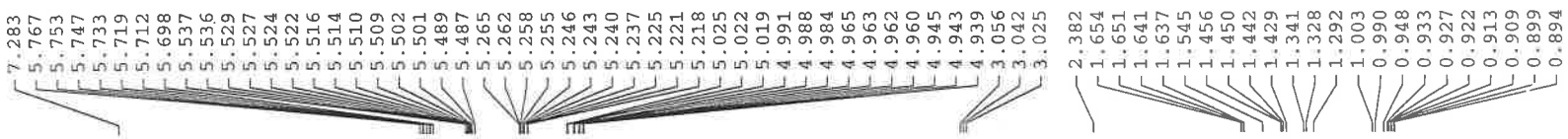
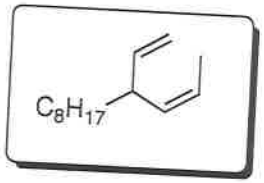
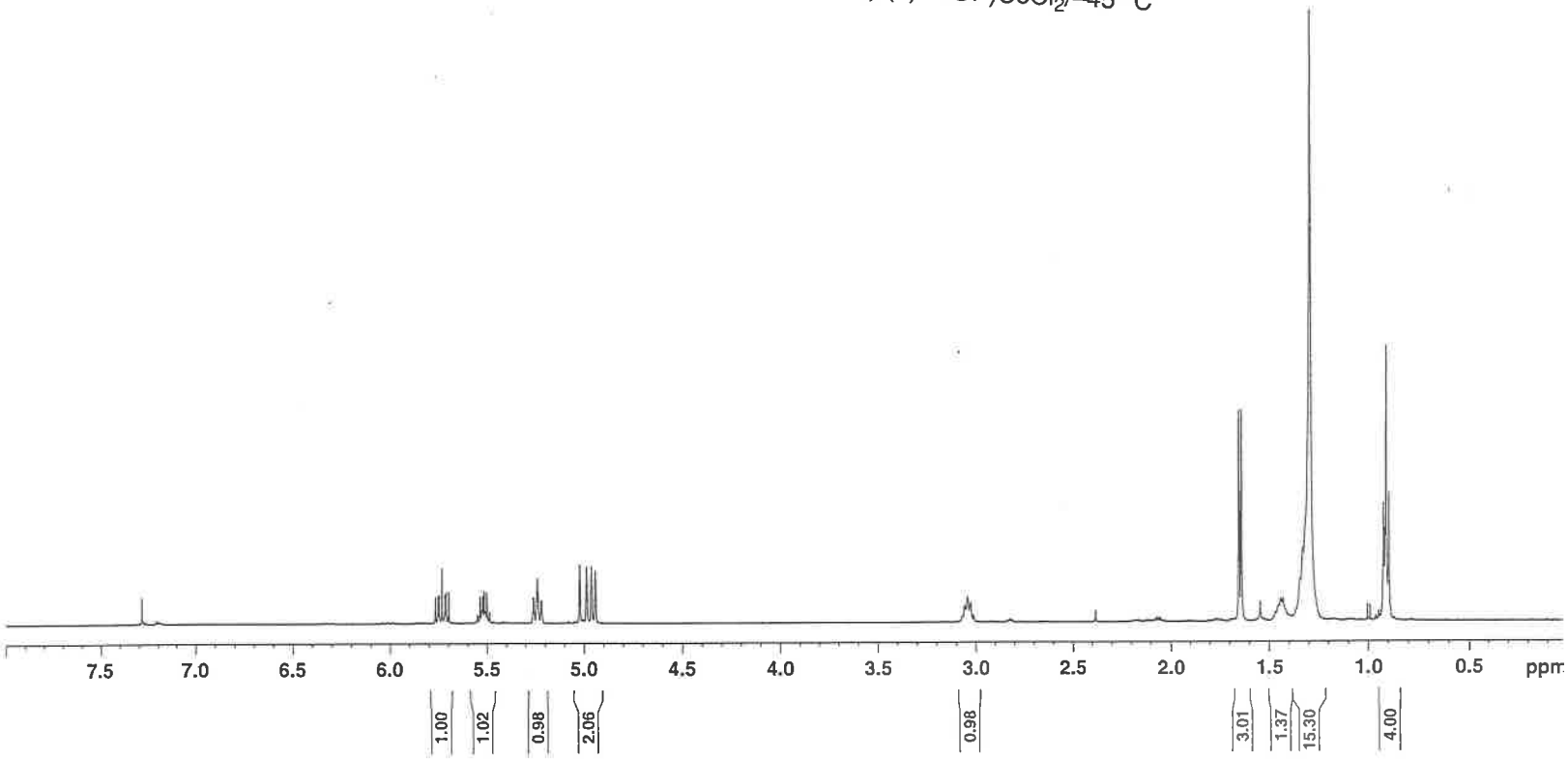
5%(-) DIOPCoCl$_2$/-45°C / 16h C_8H_{17}



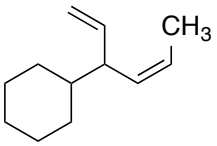


(*RR*)-(–)-DIOP)$CoCl_2$/–45 °C



141.88
133.24
123.78
112.87
77.25
77.00
76.75
41.26
35.29
31.90
29.68
29.59
29.32
27.13
22.67
14.09
13.02
C_8H_{17}
ppm

Hydrovinylation of (*E/Z*)-1-cyclohexyl-1,3-butadiene



Hydrovinylation of (*E/Z*)-1-cyclohexyl-1,3-butadiene using[DPPB]$CoCl_2$ (Table 3, Entry 6): To an oven dried round bottom flask with a sidearm, was added DPPB$CoCl_2$ (30 mg, 0.053 mmol) and methylaluminoxane (62 mg, 1.06 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -10 ^oC and (*E/Z*)-1-cyclohexyl-1,3-butadiene (72 mg, 0.53mmol), mixture of *E*:*Z* in the ratio of 45:55, was added via syringe under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of the solvent yielded the product as colorless oil (78 mg, 90%). GC and NMR analysis showed that the product (**13e**) was essentially pure. ^1H NMR ($CDCl_3$, 400 MHz): 1.07 - 1.26 (m, 6 H), 1.58 (dd, J = 1.6, 7 Hz, 3 H), 1.62 - 1.73 (m, 5 H), 2.79 (q, J = 8 Hz, 1 H), 4.91 - 4.91 (m, 1 H), 4.94 – 4.96 (m, 1 H), 5.24 - 5.30 (m, 1 H), 5.45 - 5.33 (m, 1 H), 5.62 – 5.71 (m, 1 H).^{13}C NMR ($CDCL_3$, 125.02 MHz): 13.11, 26.48, 26.54, 26.64, 30.29, 30.95, 42.16, 47.75, 113.82, 124.02, 131.75, 140.55. Gas Chromatography: Methyl silicone SP GC (OT 90 ^oC/ isothermal) R_t for product = 17.05 min. CSP GC (Cyclodex, OT 100 ^oC/ isothermal, He carrier gas): starting material R_T= 25.28 min. for Z-diene and 29.84 for E diene. R_T for product = 45.19 min and 46.35 min (enantiomers, racemic). CSP GC (Cyclosil, OT 80 ^oC/ isothermal) R_T for product = 34.52 min and 37.04 min (enantiomers, racemic).

An enantioselectivity of 84 %ee was obtained with (*S,S*)-[DIOP]$CoCl_2$ (at -10 ^{o}C, 8 h) with only the *E*-diene undergoing the conversion. With this ligand, when both *E* and *Z* are converted, maximum enantioselectivity is only 15%. With (*R,R*)-[BDPP]$CoCl_2$ and *E* and *Z* full conversion, maximum enantioselectivity is 35% [determined by CSP GC).

The following table shows the detail of HV reactions using (*E*/*Z*)-mixture of 1-cyclohexyl-1,3-diene using various ligands.

Entry	Ligand	Temp (^oC) /Time (h)	Activator	Conv.of isomer shown (%)	Product
1.	[DPPM]	-28/7	MAO	49 (*E* & *Z*)	Mixture of 1,2 and 1,4-HV
2.	(*S,S*)-[DIOP]	-15/14	MAO	98% (only *E*)	1,4- (*Z*)- HV, 84% ee.
3.	(*S,S*)-[DIOP]	-10/8	MAO	100% (*E* & *Z*)	1,4- (*Z*)- HV, 15% ee
4.	Josiphos 1 **L17**	-10/12	MAO	100% (only *E*)	1,4- (*Z*)- HV, 34% ee
5.	Josiphos 2 **L18**	-10/8	TMA	80% (only *E*)	1,4- (*Z*)- HV, 64% ee
6.	(*R,R*)-[BDPP]	-10/11	MAO	100% (*E* & *Z*)	1,4- (*Z*)- HV(78%), 35% ee, linear(21%)

Unsuccessful hydrovinylation of (only *Z*)-1-cyclohexyl-1,3-butadiene using (*S,S*)[DIOP]$CoCl_2$ and TMA (Table 5, Entry 11, but only *Z*-isomer). To an oven dried round bottom flask with a side-arm, was added (*S,S*)[DIOP]$CoCl_2$ (15 mg, 0.024 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.03 mL, 0.072 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from balloon. The reaction vessel was cooled to -12 ^{o}C and (*Z*)-1-cyclohexyl-1,3-butadiene (32 mg, 0.23 mmol) added under ethylene and the mixture was stirred for 12 h at -12 ^{o}C. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug very quickly. The plug was washed with pentane (3 x 6 mL). Removal of solvent was difficult so GC and NMR analysis showed that the product was complex mixture of many unidentified different compounds along with starting material.

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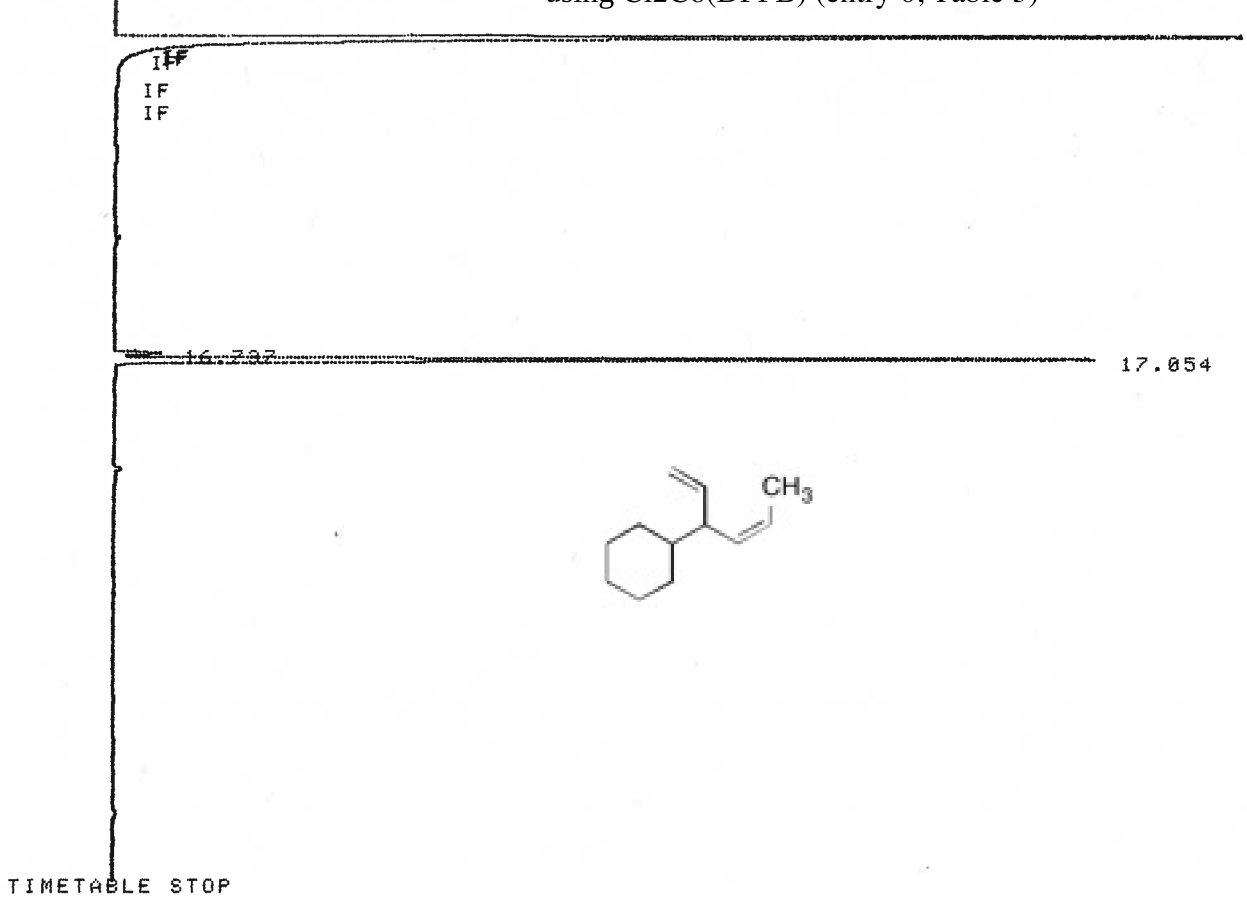
* RUN # 348 APR 12, 1901 01:23:22

START

GC (HP-5, methyl silicone, 90 degree) of Compound **13e (HV** using Cl2Co(DPPB) (entry 6, Table 3)

IF



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                                               Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
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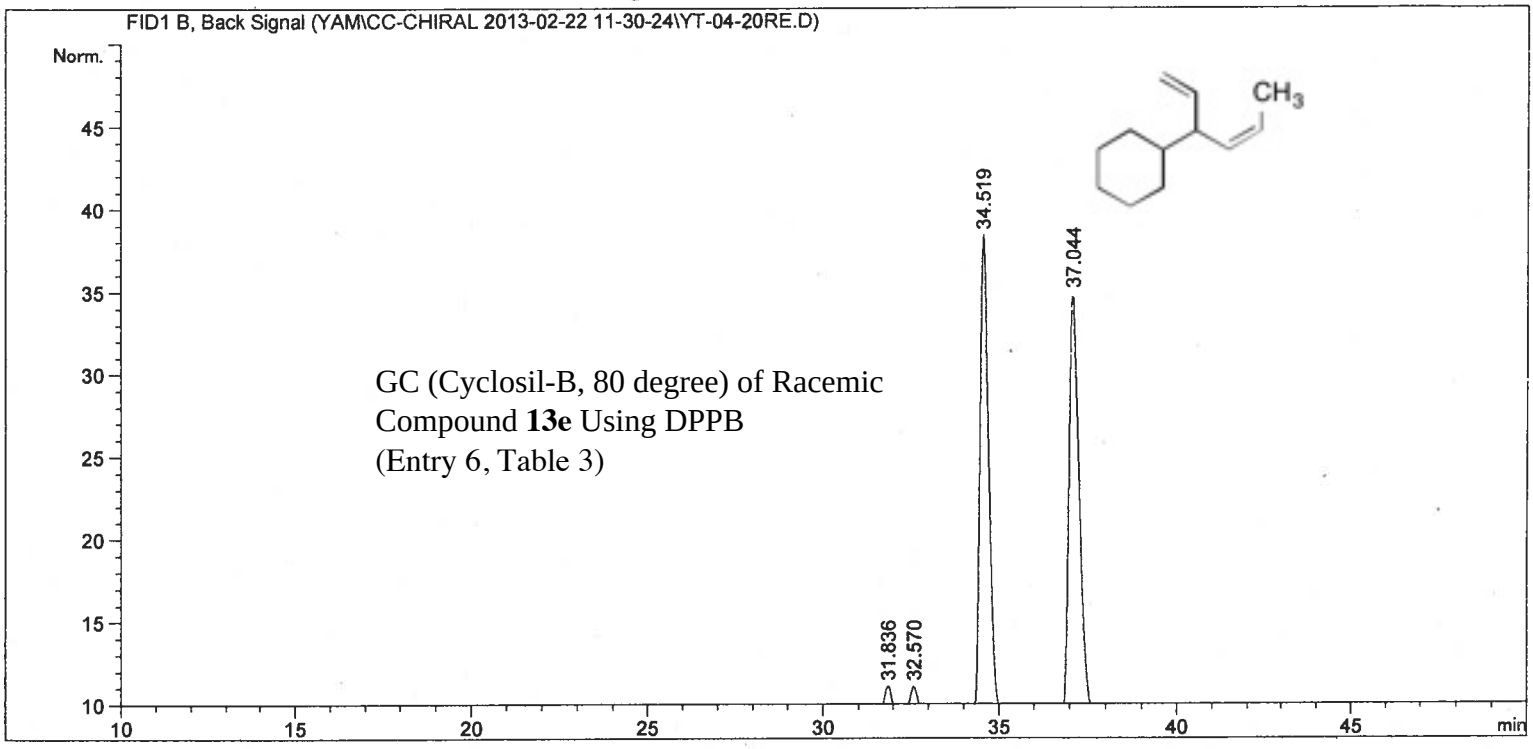

GC (Cyclosil-B, 80 degree) of Racemic Compound **13e** Using DPPB (Entry 6, Table 3)

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==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
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   2  32.570 BB    0.2370   25.28156    1.65907  2.39223
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*
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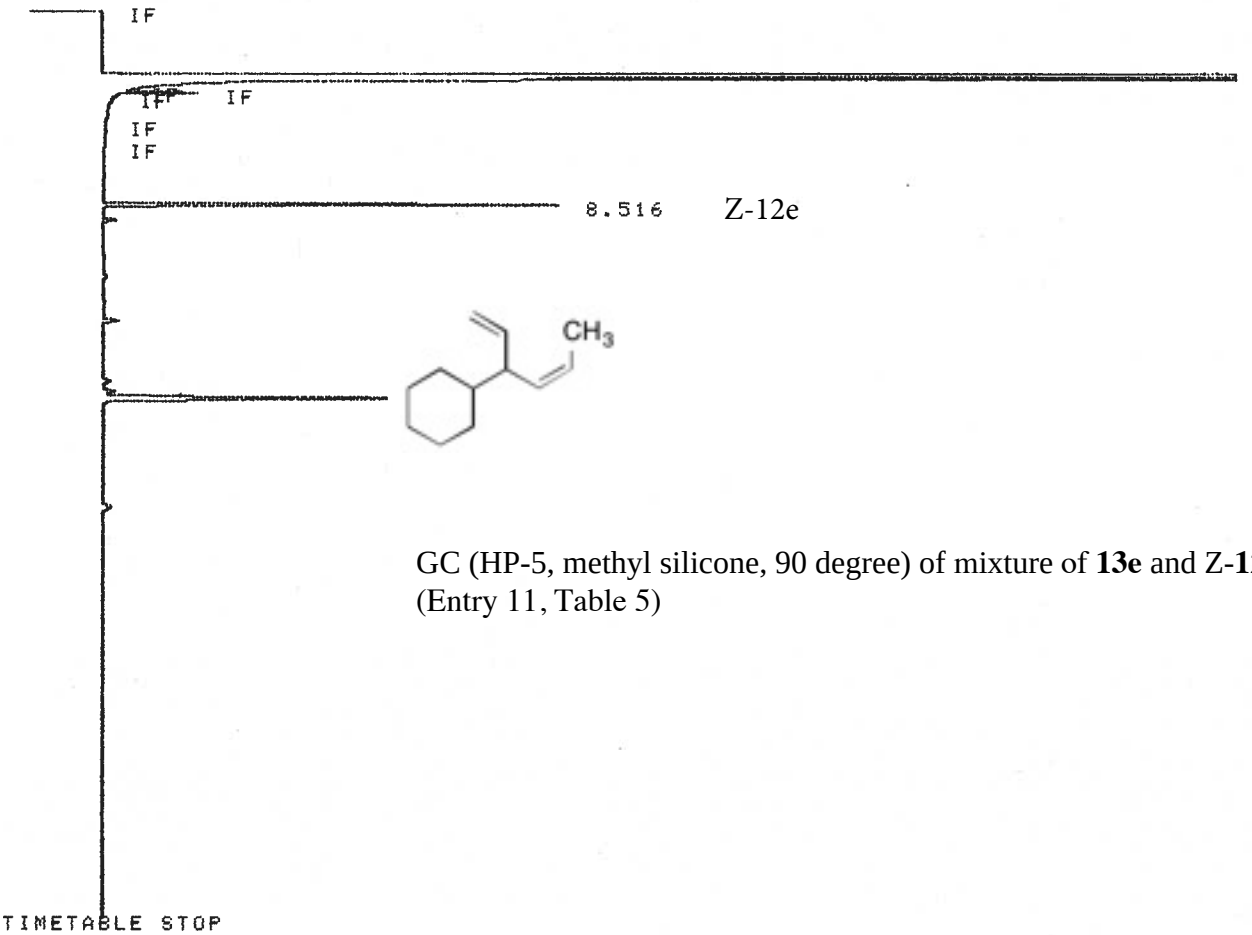

Z-12e

GC (HP-5, methyl silicone, 90 degree) of mixture of **13e** and Z-**12e** (Entry 11, Table 5)

```
TIMETABLE STOP


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                                                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
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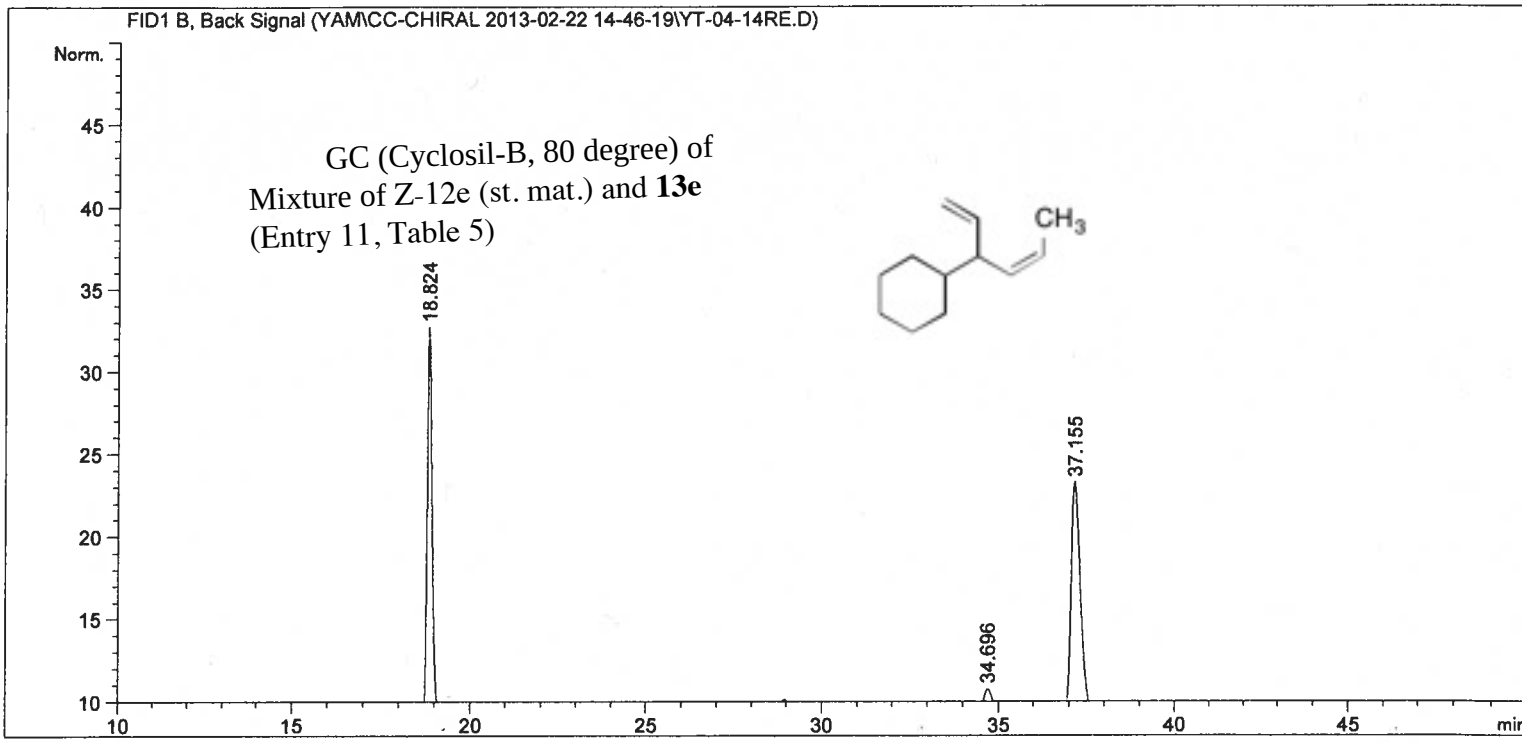


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==========================================================================
                        Area Percent Report
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Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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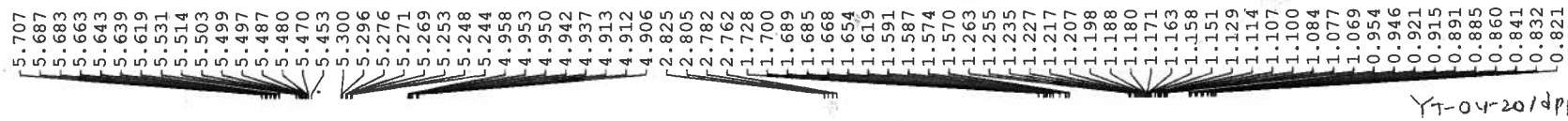

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PROCNO 1

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RG 287.4
DW 60.600 use
DE 6.00 use
TE 300.2 K
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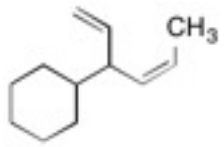
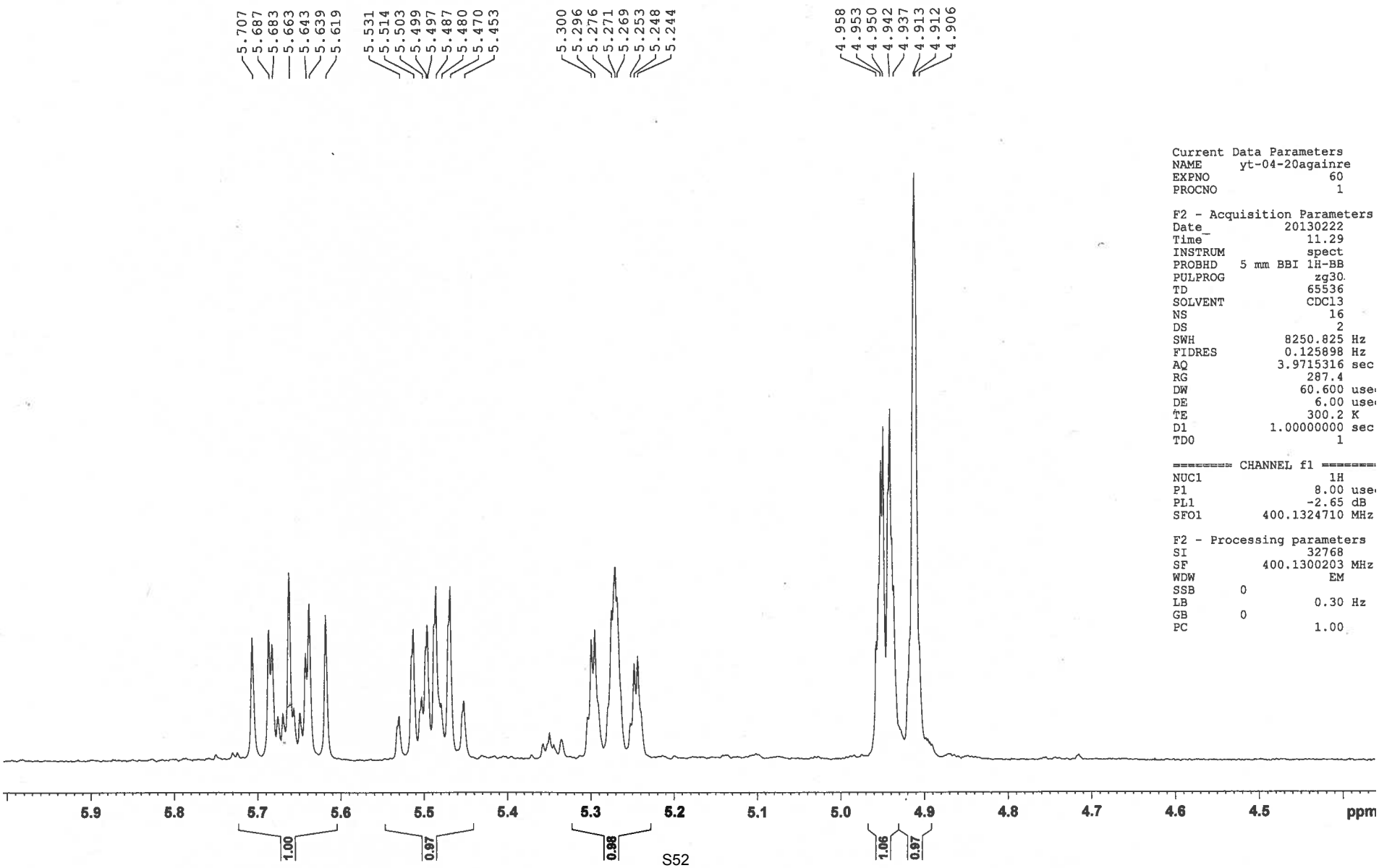
Proton NMR (400 MHz, D-chloroform) spectrum of Compound **13e** (HV using DPPB) (entry 6, Table 3)

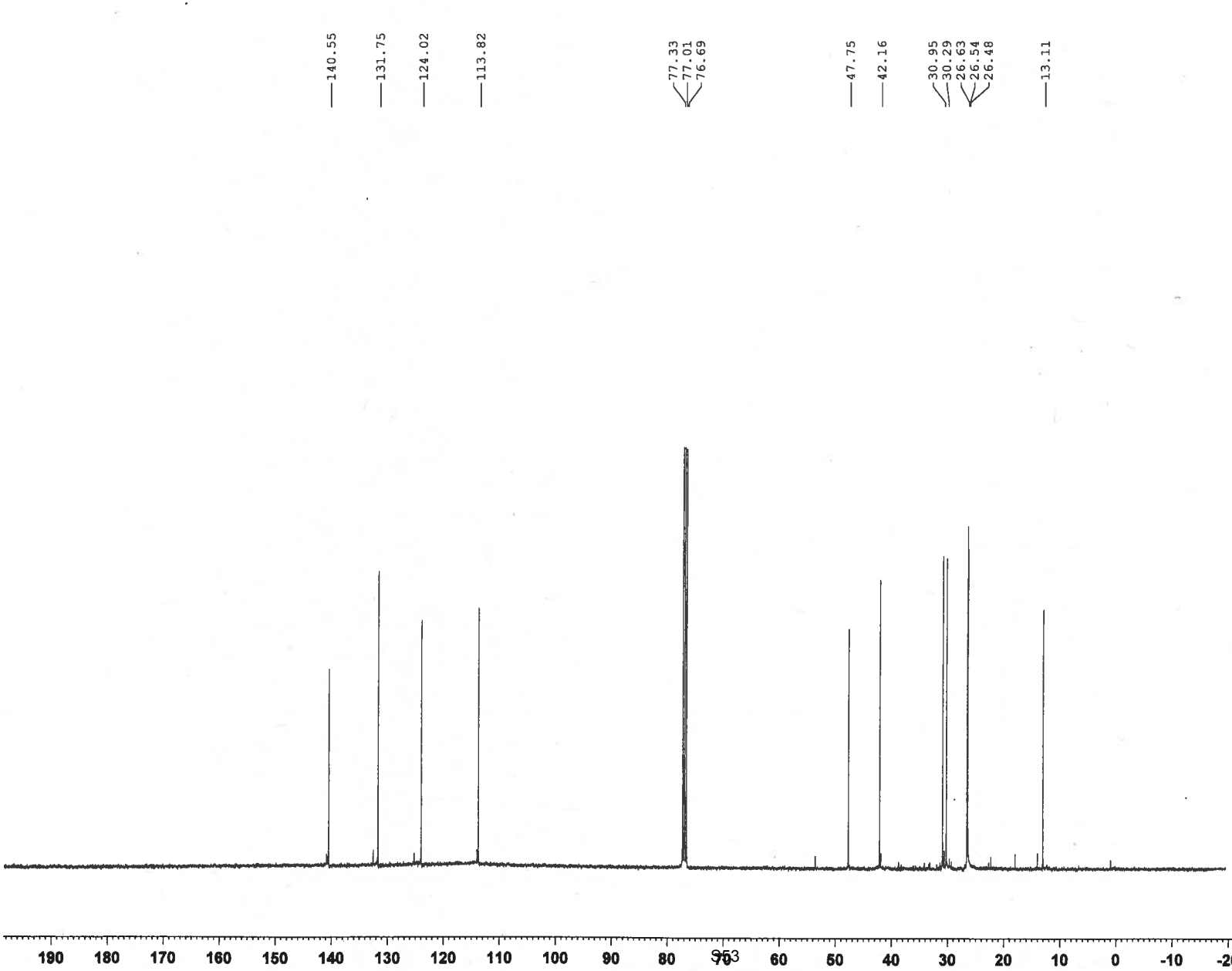


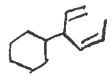
13e

Proton NMR (400 MHz, D-chloroform) spectrum of compound **13e** (HV using DPPB, Alkene Region Expansion)



Carbon NMR (100 MHz, D-chloroform) spectrum of Compound **13e**





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PROCNO                        1

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DE                        6.00 usec
TE                       300.2 K
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d11                  0.03000000 sec
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TD0                           1

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PL1                        3.00 dB
SFO1                100.6228298 MHz

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PL12                      17.35 dB
PL13                      20.00 dB
SFO2                400.1316005 MHz

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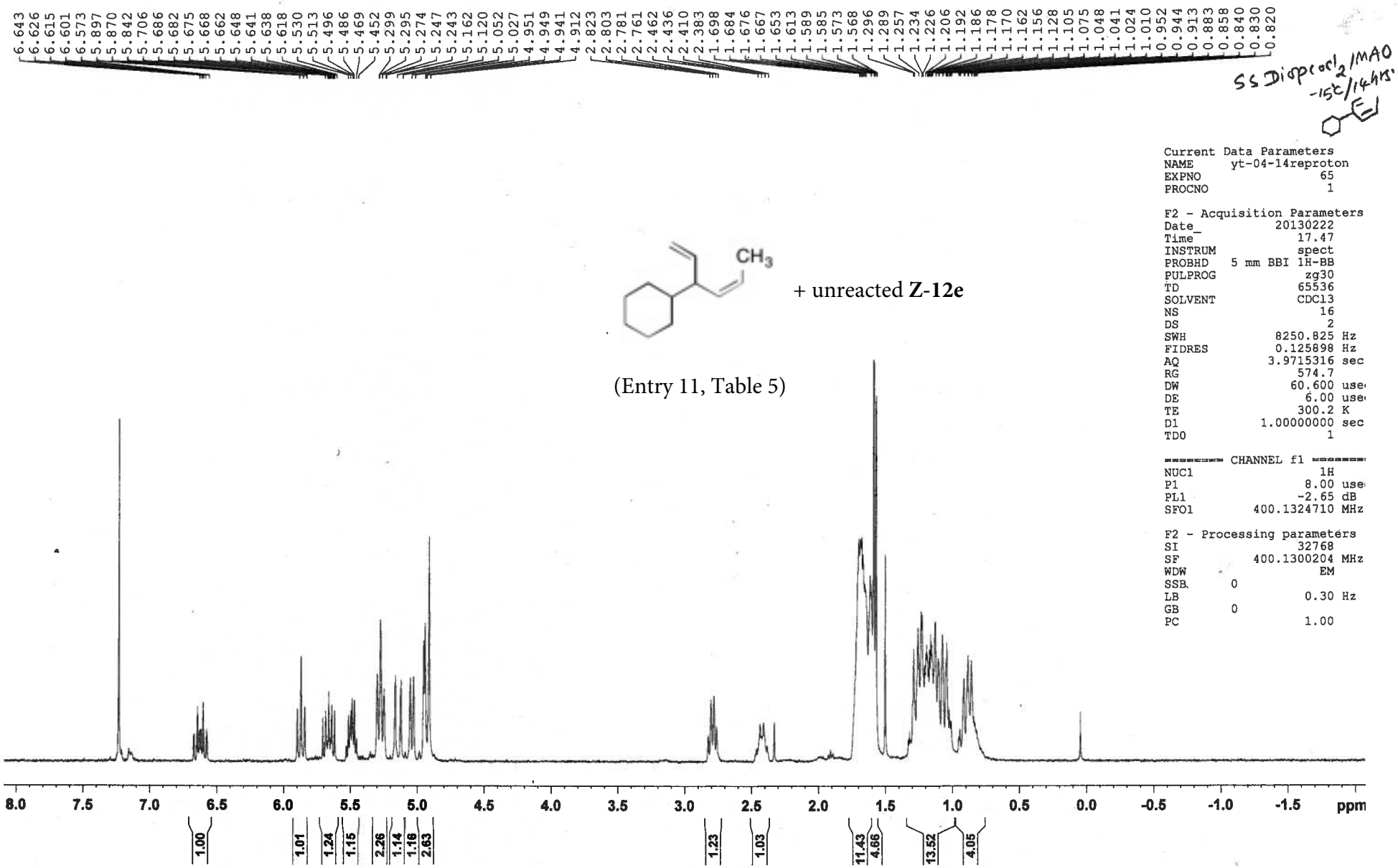
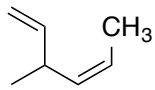


Proton NMR (400 MHz, D-Chloroform) Spectra of Mixture of 119 and Z-118 Using SS-DIOP

Hydrovinylation of (*E*)-1,3-pentadiene (12f)[2]



Hydrovinylation of (*E*)-1,3-pentadiene using [DPPB]$CoCl_2$/Me_3Al at – 10 °C (Table 3, Entry 7). [Extracted from ref. 2] To an oven-dried round-bottom flask with a sidearm, was added [dppb]$CoCl_2$ (20.4 mg, 0.037 mmol) under argon and it was dissolved in a mixture of dichloromethane and toluene (1.0 mL) at room temperature. Trimethylaluminum solution (2M) in toluene (0.06 mL 0.11 mmol) was added dropwise as color of the solution changed from deep blue to brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon and a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 5 min and the reaction vessel was cooled to – 10 °C and (*E*)-1,3-pentadiene (50.0 mg, 0.74 mmol) was added under ethylene and the mixture was stirred for 6 h. The ethylene balloon was removed and 0.1 mL of water was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 X 10 mL) and pentane was removed under vacuum in acetonitrile bath (-20 °C). Concentration yielded the product as a colorless oil (product + toluene; 501 mg). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (see attached chromatograms and spectra).

^{1}H NMR (500 MHz, $CDCl_3$): 1.072 (d, 7 Hz, 3 H), 1.570 (dd, 6.5, 1.5, Hz, 1 H), 3.167 (m, 1 H), 4.975 (ddd, 10, 1.5, 1.5, 1 H), 5.055 (ddd, 17, 1.5, 1.5, 1 H), 5.301 (ddq, 10, 10, 1.5 Hz, 1 H), 5.451 (ddq, 10, 1, 6, 1 H), 5.783 (ddd, 17.5, 11.0, 6.5, 1 H), [toluene @ 2.183]
In addition, the following minor peaks are seen in the ^{1}H NMR: a doublet at 0.009 ppm up-field from the C_{sp3}-C*H*$_3$; a triplet of multiplet at 0.417 upfield from the bis-allylic C*H* at 3.167. These minor peak might correspond to isomeric byproduct(s).
^{13}C NMR ($CDCl_3$): 12.85, 20.42, 35.20, 112.14, 123.18, 134.30, 142.89.
Isomeric purity by GC (Polydimethylsiloxane): (R_T = 6.289 min.)
CSP GC (Cyclodex-B, 28 °C): R_T = 7.36 min (*R*), 7.47 min (*S*). (*E)*-1,3-pentadiene R_T = 3.20 min., (*Z*)-1,3-pentadiene R_T = 3.47 min.
Asymmetric hydrovinylation of (*E*)-penta-1,3-diene using(*R,R*)[DIOP]$CoCl_2$ at -45 °C (6 h) gave the highest ee for this substrate (>90 %ee, Table 5, Entry 12).[2]

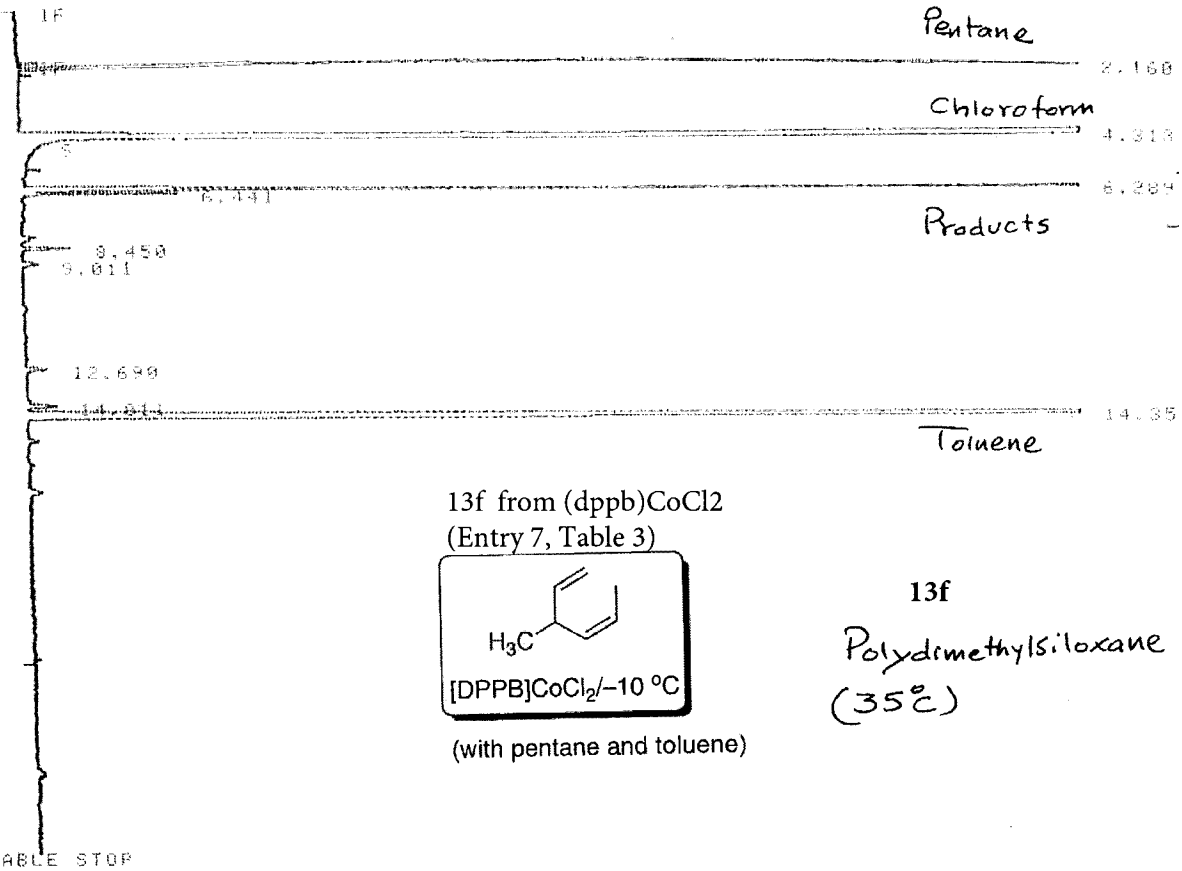
Hydrovinylation of (*E*)-1,3-pentadiene using (*R,R*)-[DIOP]$CoCl_2$ /Me_3Al at – 45 °C (Table 5, Entry 12). To an oven-dried round-bottom flask with a sidearm, was added (*RR*)-[DIOP]$CoCl_2$ (138 mg, 0.220 mmol) under argon and it was dissolved in a mixture of degassed dichloromethane (6 mL) and toluene (1.5 mL), at 0 °C. Trimethylaluminum solution (2M) in toluene (47.6 mg, 330 μl, 0.6604 mmol) was added dropwise as color of the solution changed from deep blue to red-brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon, a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 3-5 min. The reaction vessel was cooled to – 45 °C and (*E*)-1,3-pentadiene (300 mg, 440 μl, 4.404 mmol, *E*:*Z* = 99:1) was added under ethylene and the mixture was stirred for 6 h. The ethylene balloon was removed and 0.2 mL of water was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with pentane (3 x 20 mL). Pentane was removed by evacuation from a cold bath (-20 °C). Product

was distilled bulb to bulb at room temperature as a colorless oil (product + toluene; 668 mg). Isomeric compositions were determined by gas chromatography and NMR spectroscopy (see attached chromatograms and spectra).

The product from (dppb)$CoCl_2$ (Entry 7, Table 3) reaction has, the following signals in addition to the ones due to the major product: a C*H*$_3$ (?)-doublet (J = 7 Hz) δ 0.008 down-field from the C_{sp3}-C*H*$_3$; a C*H*$_3$ doublet of multiplet (J = 5 Hz, 3 H) at δ 0.035 down-field from the major C_{sp2}-C*H*$_3$ signal; a CH or CH_2 a multiplet δ 0.384 up-field from the bis-allylic C*H* proton. These peaks correspond to isomeric byproduct as determined by GC (see GC traces: isomeric purity of major product determined by GC 94.5%)

Product **13f** from hydrovinylation using [(*R,R*)-(-)-DIOP]$CoCl_2$ at –45 ^{o}C: $[\alpha]^{24}_{D}$ = – 25.6 (toluene, *c* 11.4); lit.[4] $[\alpha]^{20}_{D}$ (CH_2Cl_2, *c* 10); – 34.8 for **13f** of %ee 37% (*S)*; Because of the volatility of the product, there is some uncertainty in these optical rotation measurements. However, the enantioselectivity measured by CSP GC (Cyclodex-B, 28 ^{o}C) is unambiguous (see the attached chromatograms). Enantioselectivity determined by CSP GC: 90.1 % ee (*S)*
Product **13f** from hydrovinylation using [(*S,S*)-(+)-DIOP]$CoCl_2$ at – 45 ^{o}C: $[\alpha]^{24}_{D}$ = + 29.1 (toluene, *c* 0.39). Enantioselectivity determined by CSP GC (Cyclodex-B, 28 ^{o}C): 89.1 % ee (*R*).

START



13f from (dppb)CoCl2
(Entry 7, Table 3)

(with pentane and toluene)

13f

Polydimethylsiloxane
(35°C)

TIMETABLE STOP

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6.441	35326	I VB	.063	.05030
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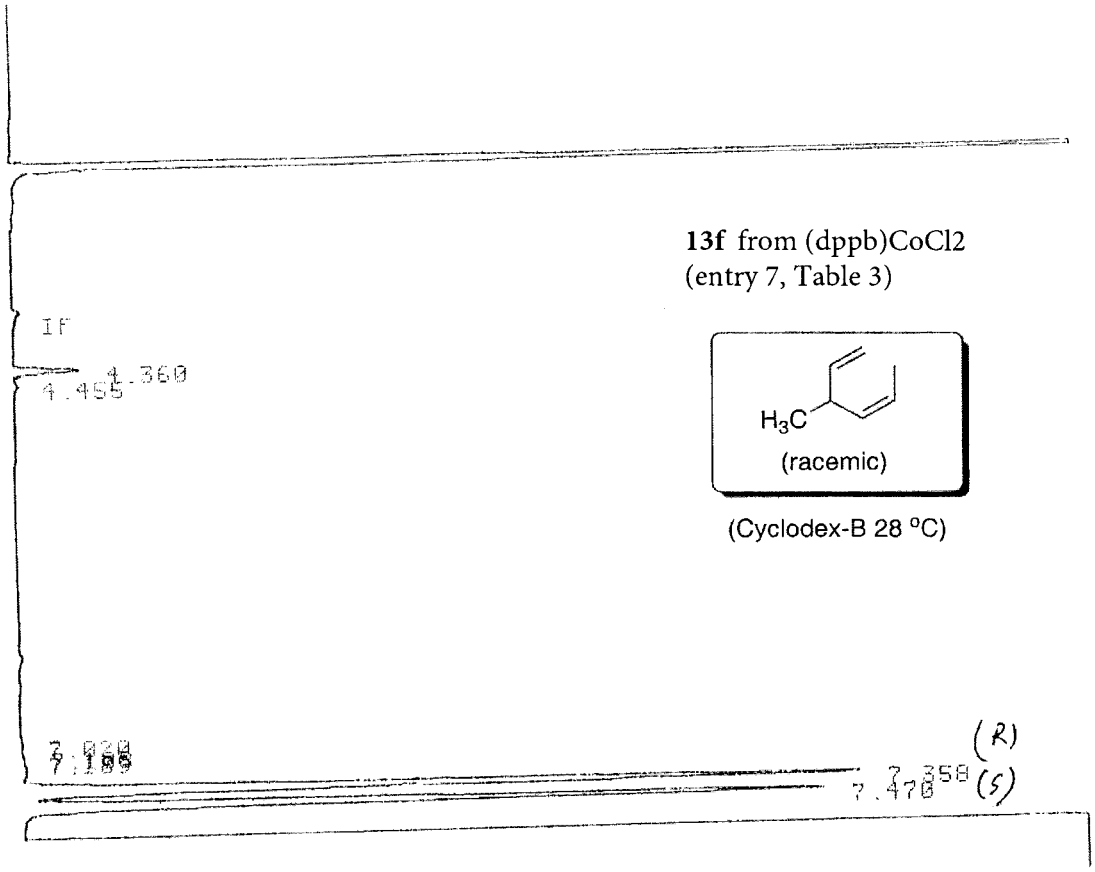
MUL FACTOR=1.0000E+00



13f from (dppb)CoCl2
(entry 7, Table 3)

(Cyclodex-B 28 °C)

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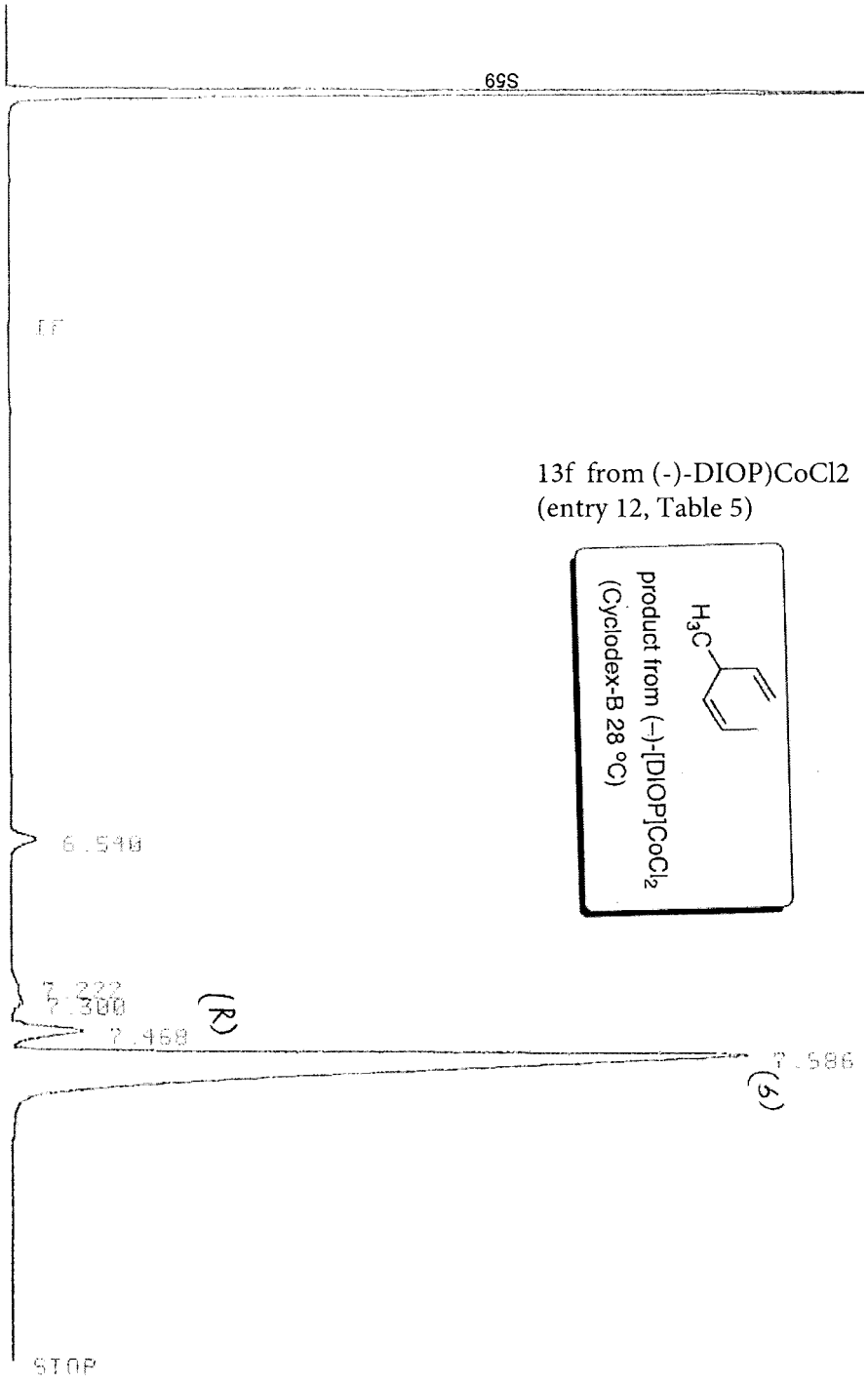

13f from (-)-DIOP)CoCl2
(entry 12, Table 5)

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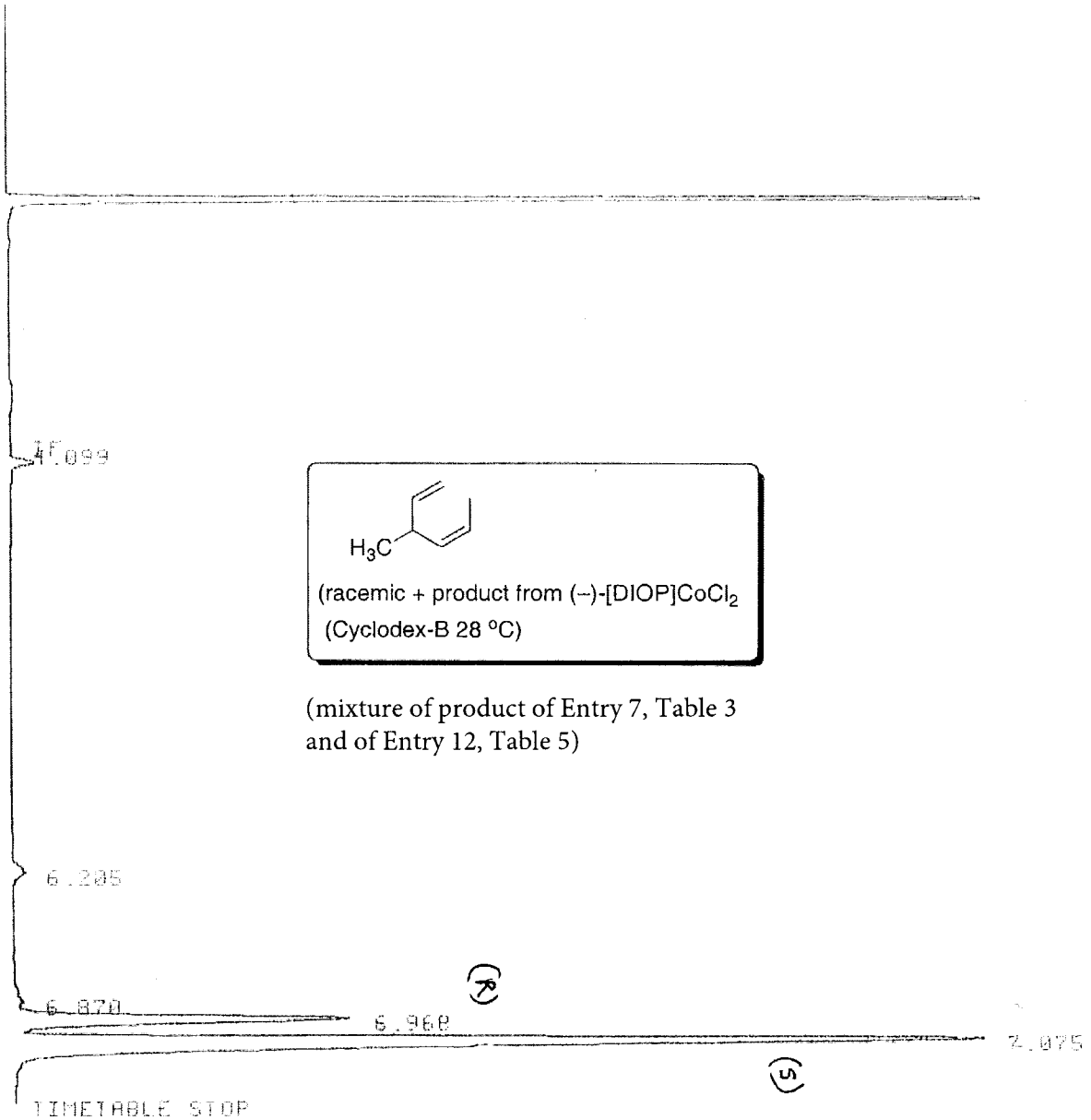
MUL FACTOR=1.0000E+00



(racemic + product from (–)-[DIOP]$CoCl_2$ (Cyclodex-B 28 °C)

(mixture of product of Entry 7, Table 3 and of Entry 12, Table 5)

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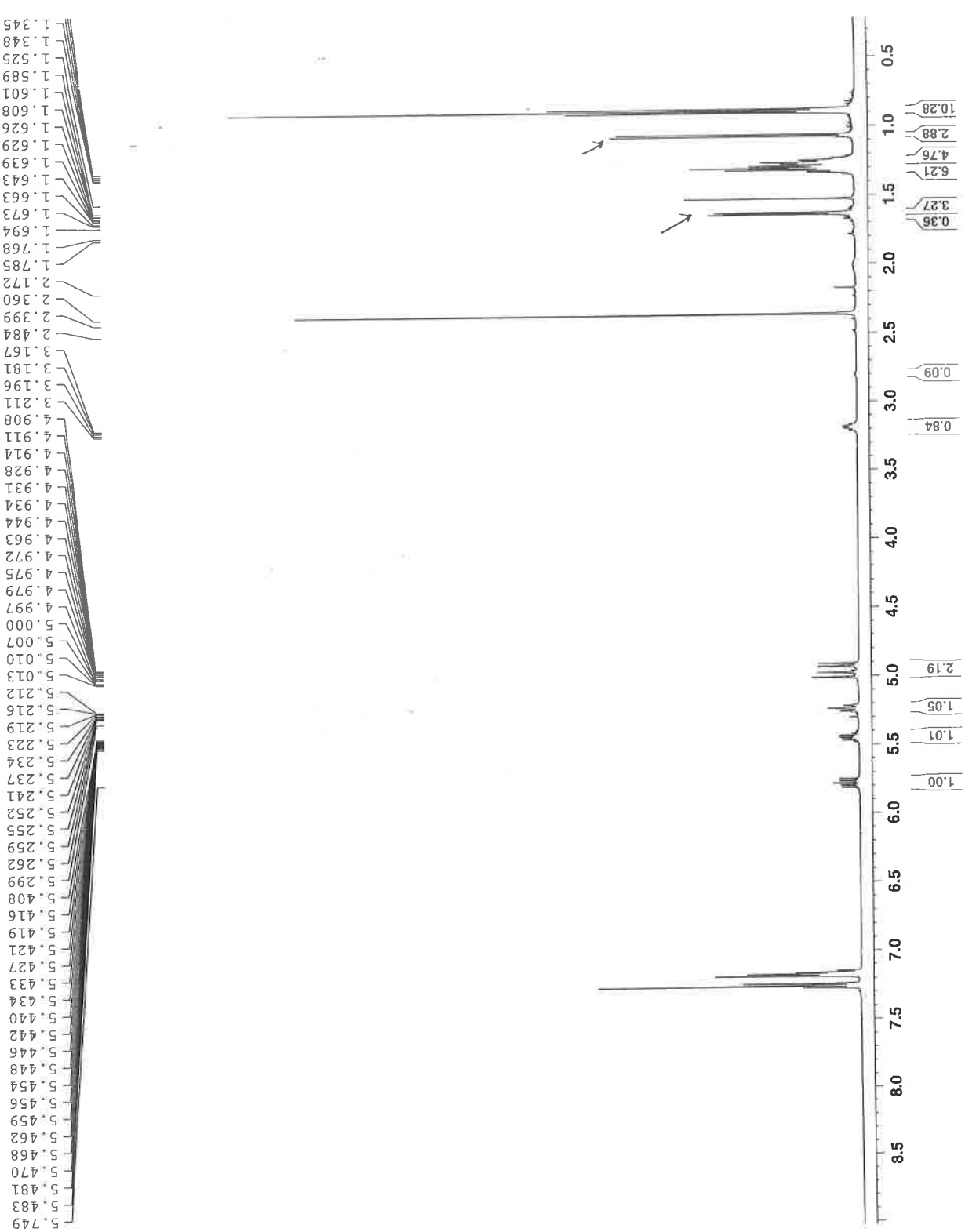
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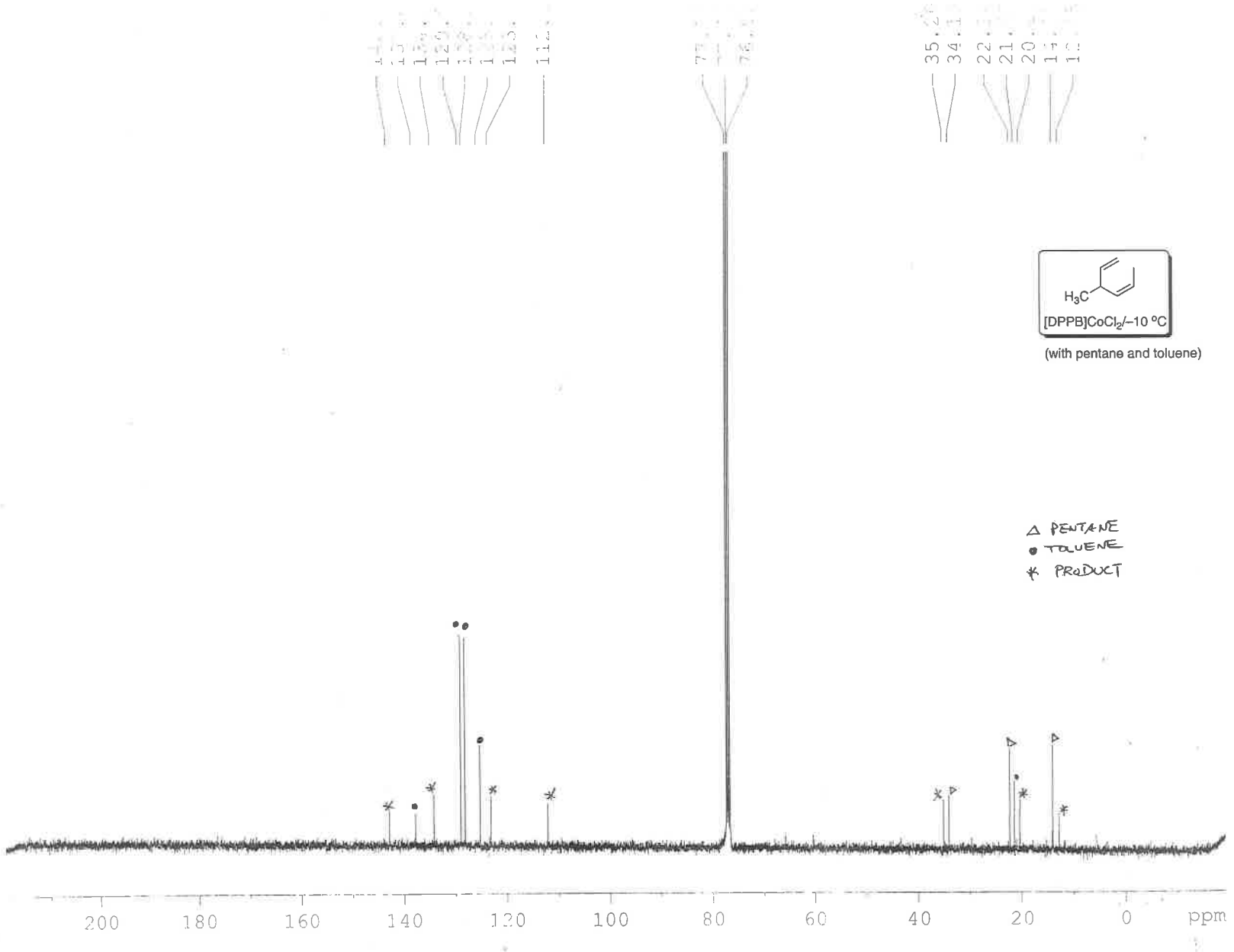
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[DPPB]CoCl2/–10 °C
(with pentane and toluene)
△ PENTANE
● TOLUENE
* PRODUCT
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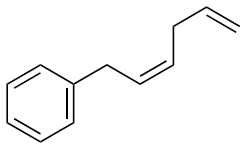
160
140
120
100
80
60
40
20
0
ppm

Hydrovinylation of (*E*)-1-phenyl-1,3-butadiene



Hydrovinylation of (*E*)-1-phenyl-1,3-butadiene using[dppp]$CoCl_2$ (Table 3, Entry 8): To an oven dried round-bottom-flask with a sidearm, was added DPPP$CoCl_2$ (45 mg, 0.083 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.13 mL, 0.25 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -20 ^{o}C and (*E*)-1-phenyl-1,3-butadiene (108 mg, 0.83 mmol) as a dichloromethane solution (0.5 mL) was added under ethylene and the mixture was stirred for 4 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as a colorless oil (113 mg, 86%). GC and NMR analysis showed that the product was essentially pure linear adduct (**16g**). ^{1}H NMR ($CDCl_3$, 500 MHz): 2.95-2.98 (m, 2 H), 3.45 (d, J = 7.5 Hz, 2 H), 5.06 (dq, J = 10, 1.5 Hz, 1 H), 5.13 (dq, J= 17, 1.5 Hz, 1 H), 5.56 - 5.62 (m, 1 H), 5.67 - 5.72 (m, 1 H), 5.89 (ddd, J = 6, 10, 17 Hz, 1 H), 7.21 - 7.23 (m, 3 H, aromatic), 7.31 - 7.34 (m, 2 H, aromatic).^{13}C NMR ($CDCl_3$, 125.02 MHz): 31.74, 33.66, 115.14, 126.12, 127.86, 128.58, 128.64, 129.53, 136.91, 141.07. Gas Chromatography: CSP GC (Cyclosil, OT 100 ^{o}C/ isothermal, H_2 carrier gas). Starting material R_t = 17.68 min. R_T for achiral linear product = 32.58 min.

This following table shows the additional experiments conducted with this diene, 1-phenyl-1,3-butadiene, employing 10 mol % catalyst (see Table 3 in the paper for details).

Entry	Catalyst	Tem(^{o}C) /Time(h)	Activator	Conv.(%)	Product
1.	DPPM$CoCl_2$	-20/7	TMA	100	1,2-HV
2.	DPPE$CoCl_2$	-10/3.5	TMA	89	1,4-linear
3.	DPPP$CoCl_2$	-20/4	TMA	97	1,4-linear
4.	DPPB$CoCl_2$	-10/6	TMA	87	1,4-linear
5.	(*S,S*)-[DIOP]$CoCl_2$	0-rt/5	MAO	97	1,4-linear (54%)+ 1,2-HV (43%, 52% ee)
6.	[DIOP]$CoCl_2$	-40/8	TMA	45	1,4-linear (40%) +1,2-HV(4%)
7.	(*SS*)-[BDPP]$CoCl_2$	-20/11	TMA	95(70+16)	1,2-HV+1,4 linear (ee not determined)
8.	DIPAMP	-12/11	TMA	6	1,4-linear
9.	DPPP$CoCl_2$	-40/8	TMA	8	1,4-linear

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                                                     Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
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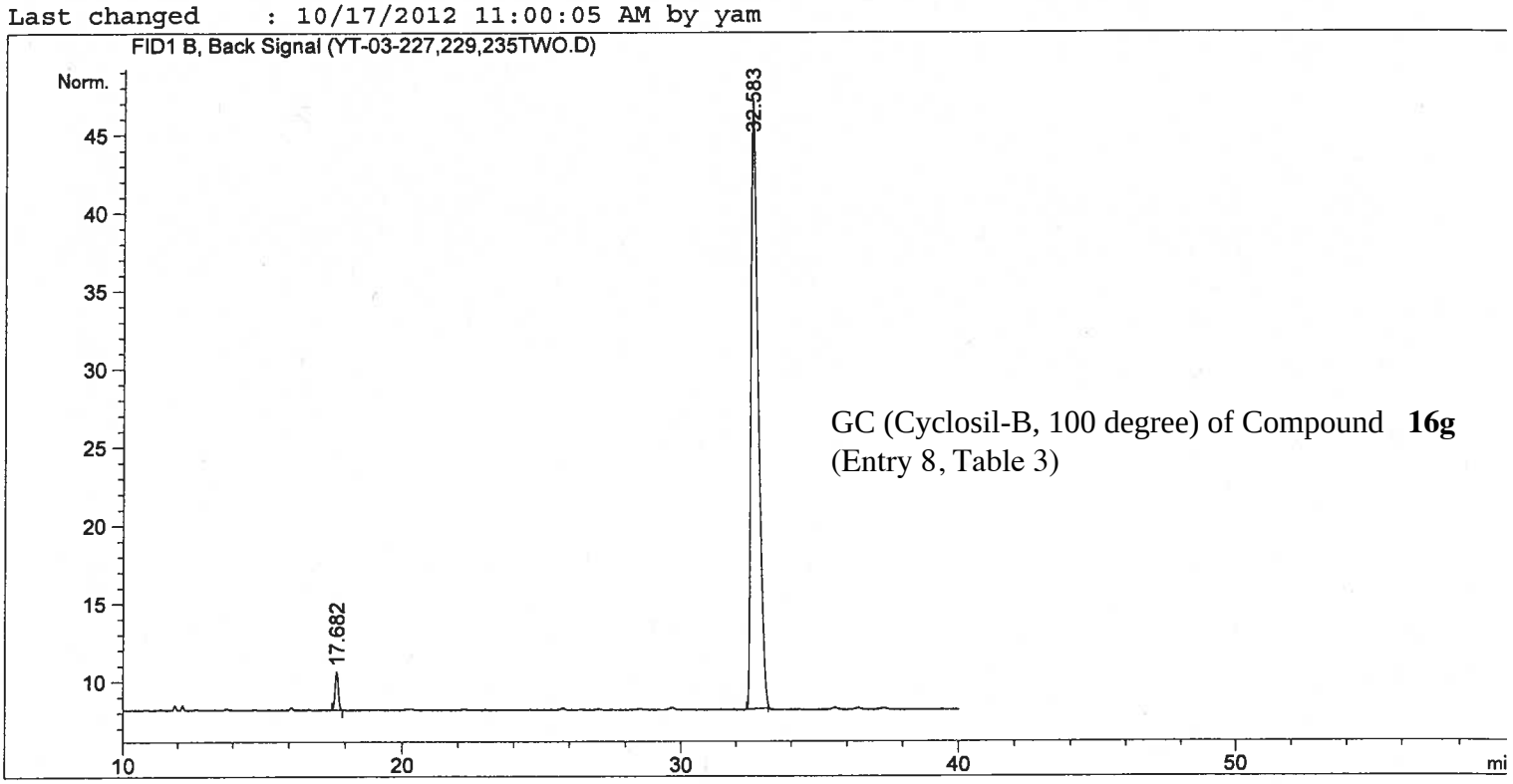

GC (Cyclosil-B, 100 degree) of Compound **16g** (Entry 8, Table 3)

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==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   6.254 BB    0.0479    1.72123 5.71427e-1  0.23561
   2  17.682 BB    0.1231   19.35352    2.43581  2.64916
   3  32.583 BB    0.2413  709.47870   38.95836 97.11524

Totals :                   730.55345   41.96559

==========================================================================
                          *** End of Report ***
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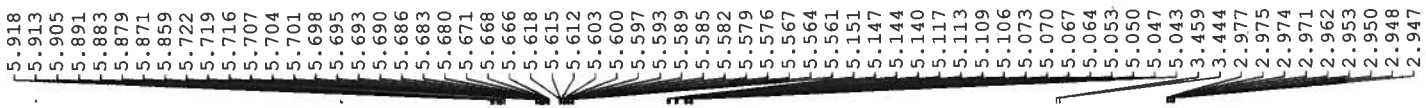
Proton NMR (500 MHz, D-Chloroform) spectrum of compound **16g** (HV using Cl2Co(DPPP)] (Entry 8, Table 3)

dpppruch2/TMA

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PROCNO                   1

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PULPROG               zg30
TD                   65536
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FIDRES           0.157632 Hz
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DE                   6.00 use
TE                  300.2 K
D1            1.00000000 sec
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MCWRK         0.01500000 sec

========== CHANNEL f1 ==========
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PL1                  -1.00 dB
SFO1         500.0030877 MHz

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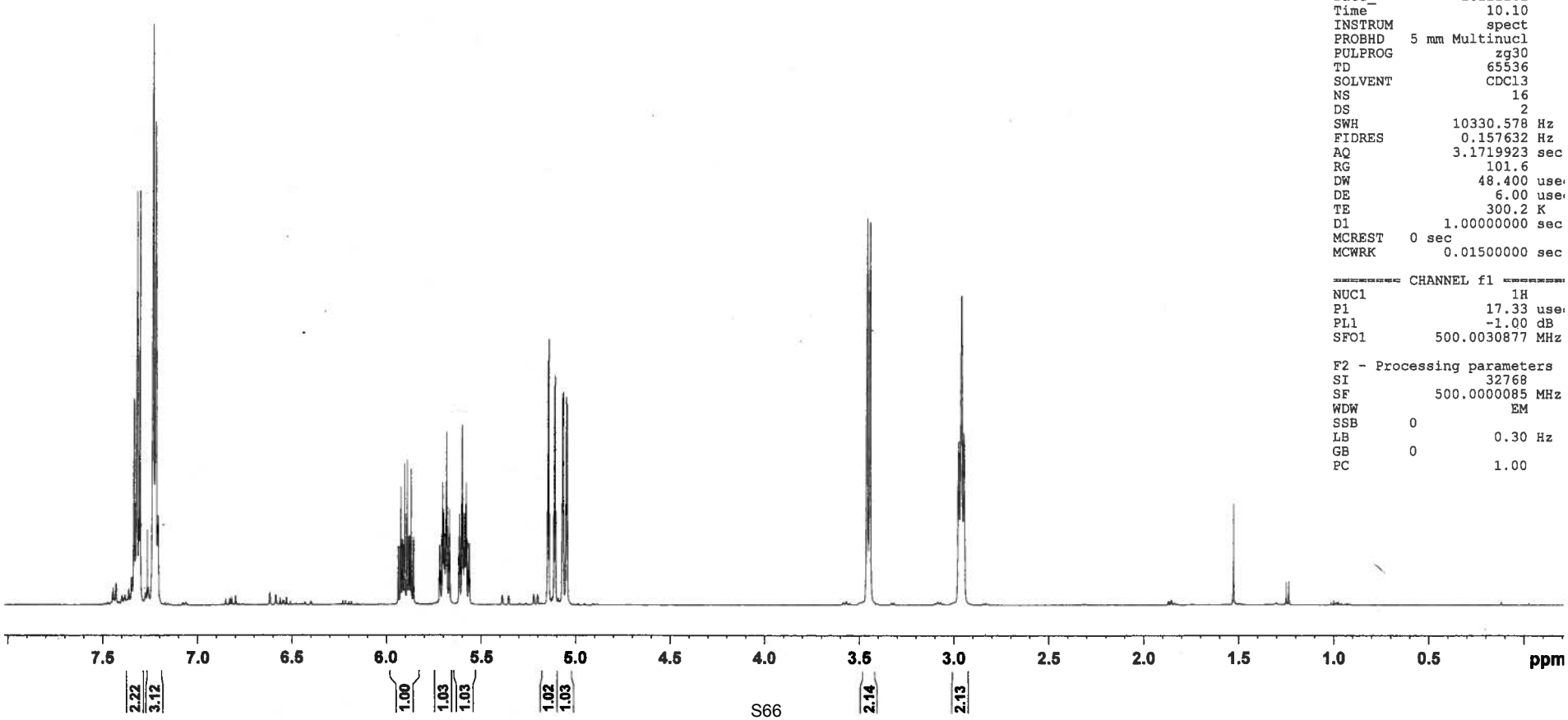
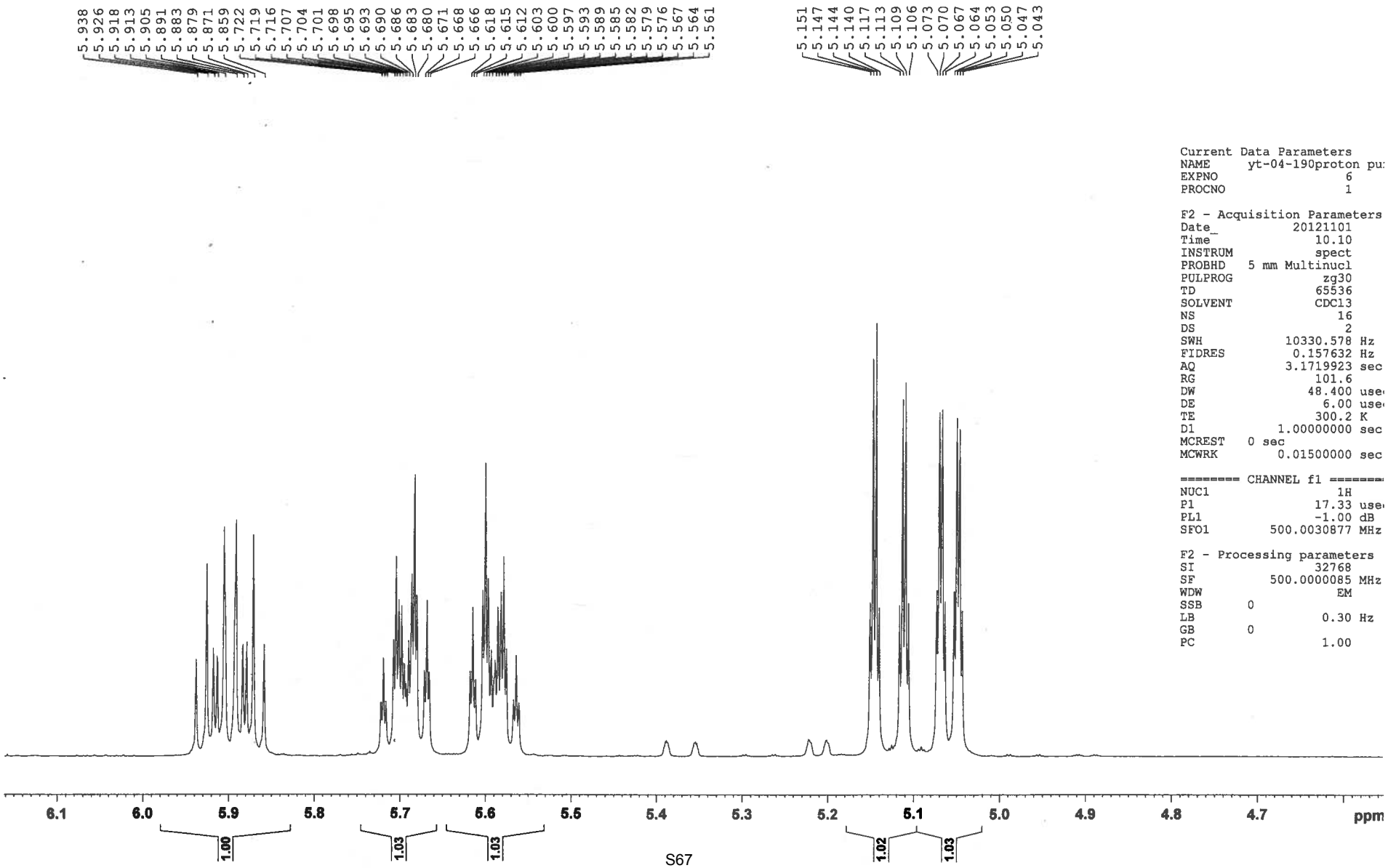
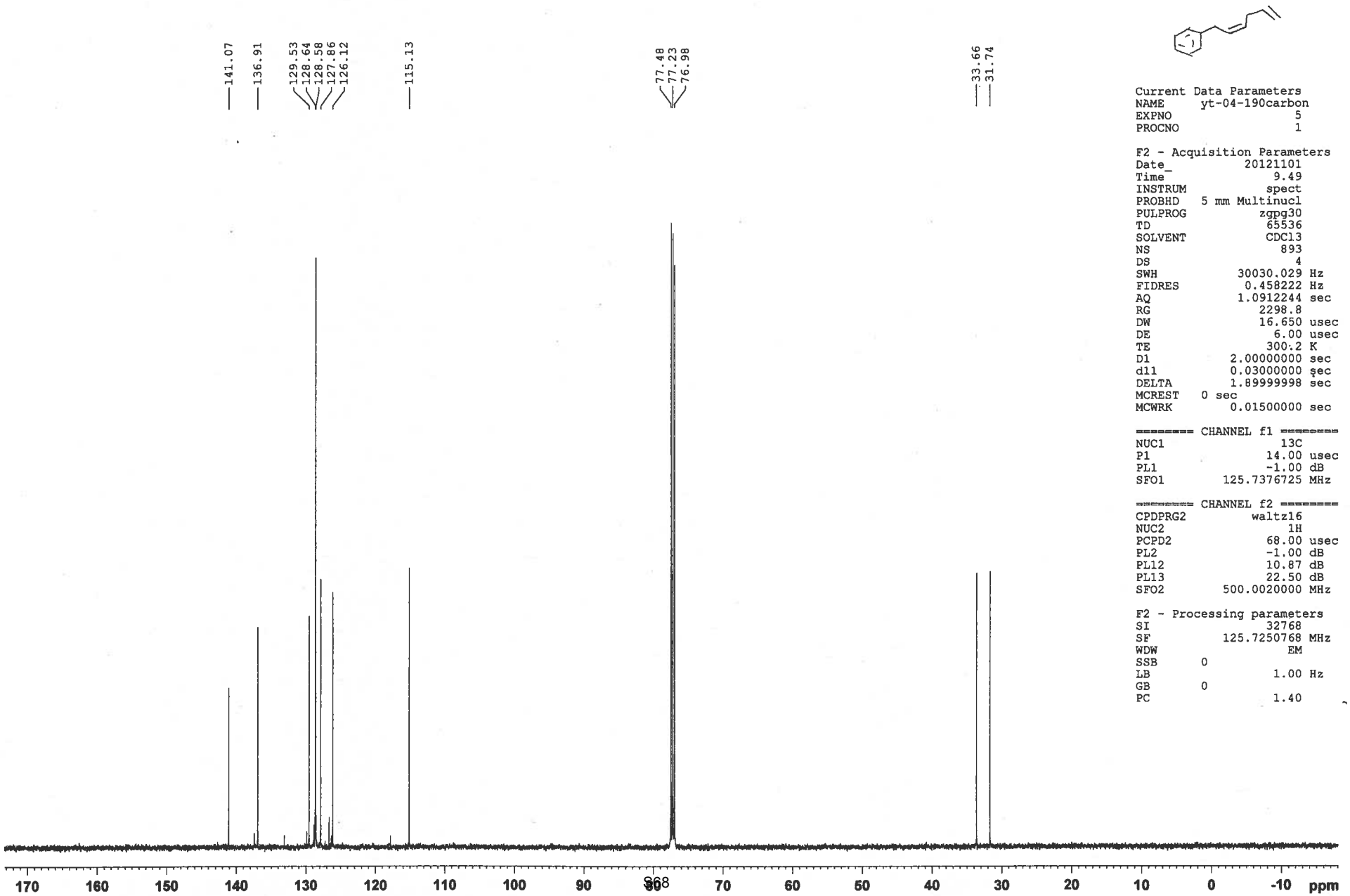


Proton NMR (500 MHz, D-Chloroform) spectrum of compound **16g** (HV using Cl2Co(DPPP)](Alkene Expansion)



Carbon NMR (500 MHz, D-Chloroform) spectrum of compound **16g** (HV using Cl2Co(DPPP)]



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PROCNO 1

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FIDRES 0.458222 Hz
AQ 1.0912244 sec
RG 2298.8
DW 16.650 usec
DE 6.00 usec
TE 300.2 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
MCREST 0 sec
MCWRK 0.01500000 sec

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PL1 -1.00 dB
SFO1 125.7376725 MHz

======== CHANNEL f2 ========
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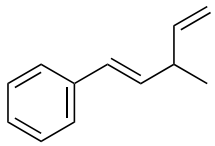
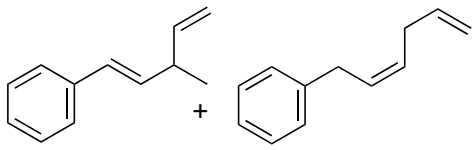
Hydrovinylation of (*E*)-1-phenyl-1,3-butadiene using [dppm]$CoCl_2$ (Table 3, Entry 10): To

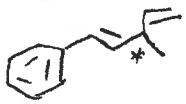


an oven dried round-bottom-flask with a sidearm, was added DPPM$CoCl_2$ (34 mg, 0.066 mmol) and under argon it was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.1 ml, 0.20 mmol) was added dropwise and the color of the solution changed from bluish brown to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to -20 ^oC and (*E*)-1-phenyl-1,3-butadiene (86 mg, 0.66 mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 7 h. The ethylene balloon was removed and 0.1 mL methanol was added to the flask. The solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 5 mL). Removal of solvent yielded the product as colorless oil (83 mg, 80%). GC and NMR analysis showed that the product was essentially pure 1,2 hydrovinylation product (**15g**). ^1H NMR ($CDCl_3$, 500 MHz): 1.19 (d, J = 7 Hz, 3 H), 2.99 – 3.05 (m, 1 H), 4.99 – 5.08 (m, 2 H), 5.87 (ddd, J = 6.5, 10, 17 Hz, 1 H), 6.17 (dd, J = 7, 16 Hz, 1 H), 6.37 (d, J = 16 Hz, 1 H), 7.18 – 7. 36 (m, aromatic, 5 H). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 20.00, 40.85, 113.54, 126.28, 127.20, 128.69, 128.86, 134.47, 137.86, 142.64. Gas Chromatography: CSP GC (Cyclosil, OT 120 ^oC/ isothermal, H_2 carrier gas) R_T for chiral 1,2 product = 14.34 and 14.58 min (enantiomers, racemic), (*SS*)-DIOP gave 52% ee with 43% yield. Methylsilicone SP GC (OT 120 ^oC/ isothermal, He carrier gas) R_t for chiral 1,2 product = 10.56 min.



Hydrovinylation of (*E*)-1-phenyl-1,3-butadiene using (*S,S*)[DIOP]$CoCl_2$ (Table 5, Entry 13): To an oven dried round bottom flask with a sidearm, was added (*S,S*)[DIOP]$CoCl_2$ (24 mg, 0.038 mmol) and methylaluminoxane (44 mg, 0.76 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1.5 mL) at room temperature. After 2 to 3 minutes when fumes stopped, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to 0 ^oC and (*E*)-1-phenyl-1,3-butadiene (49 mg, 0.38 mmol) in dichloromethane (1 mL) was added via syringe under ethylene and the mixture was stirred for 5 h in ambient temperature until the completion of reaction monitored via gas chromatography. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (5 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 X 10 mL). Removal of the solvent yielded the product as colorless oil as a mixture of two major isomers **15g** (43% with 54% ee) and **16g** (55%) (Table 5, Entry 13). GC and NMR analysis showed that the products were essentially pure and the spectra and chromatogram are attached.

dPPMCoCl2/TMA
YT-04-220RR
OT 120°C/iso/achiral



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*
*
*
*
*
*
*  RUN #  236      MAR 20, 1901  01:38:14
START
   IF
   IF
   10.555
TIMETABLE STOP


RUN#   236           MAR 20, 1901  01:38:14

AREA%
      RT       AREA TYPE  WIDTH       AREA%
  10.555      65242   BB    .096   100.00000

TOTAL AREA=  65242
MUL FACTOR=1.0000E+00
```

GC (HP-5 Methyl silicone, 120 degree) of racemic Compound **15g** (HV Using Cl2Co(DPPM) (Entry 10, Table 3)

```
*
*
*
*
*
```

Data File C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2013-01-30 09-48-53\YT-04-220RR.D (S) dppm/cl2ITM
Sample Name: YT-04-220RR.D

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                                                   Inj Volume : 1 µl
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Acq. Method      : C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2013-01-30 09-48-53\YT_85_C_CHIRAL.M
Last changed     : 1/30/2013 9:48:53 AM by YAM
Analysis Method  : C:\CHEM32\1\METHODS\YT_85_C_CHIRAL.M
Last changed     : 1/30/2013 10:37:42 AM by YAM
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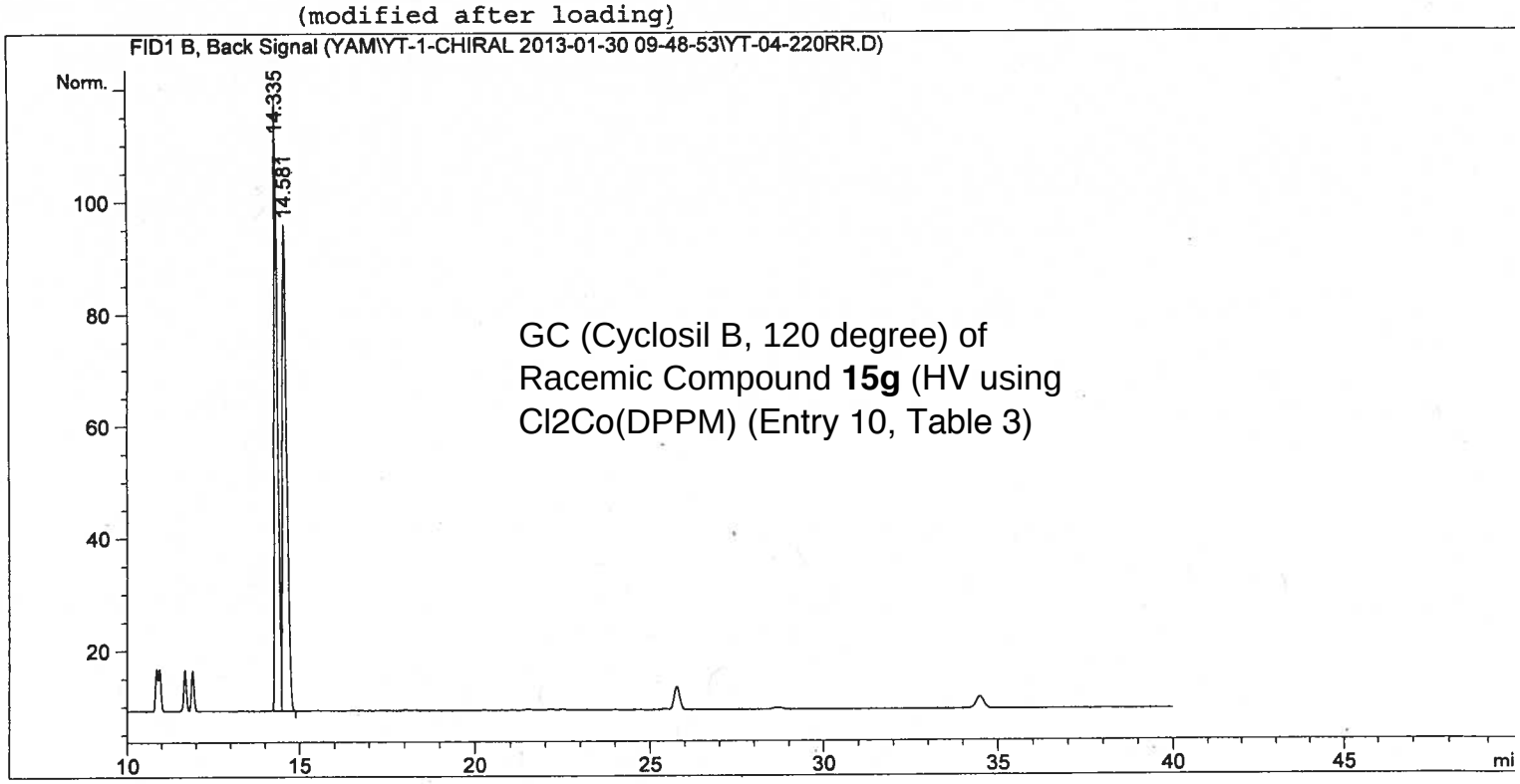

GC (Cyclosil B, 120 degree) of Racemic Compound **15g** (HV using Cl2Co(DPPM) (Entry 10, Table 3)

```
==========================================================================
                        Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
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----|-------|----|-------|----------|----------|--------|
   1  14.335 BV    0.1027  747.93854  108.62716 49.76770
   2  14.581 VB    0.1288  754.92090   86.67773 50.23230

Totals :                  1502.85944  195.30489

==========================================================================
                        *** End of Report ***
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Data File C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2012-10-12 16-55-52\YT-04-171RR.D
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                                                       Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
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Last changed     : 10/12/2012 3:42:07 PM by YAM
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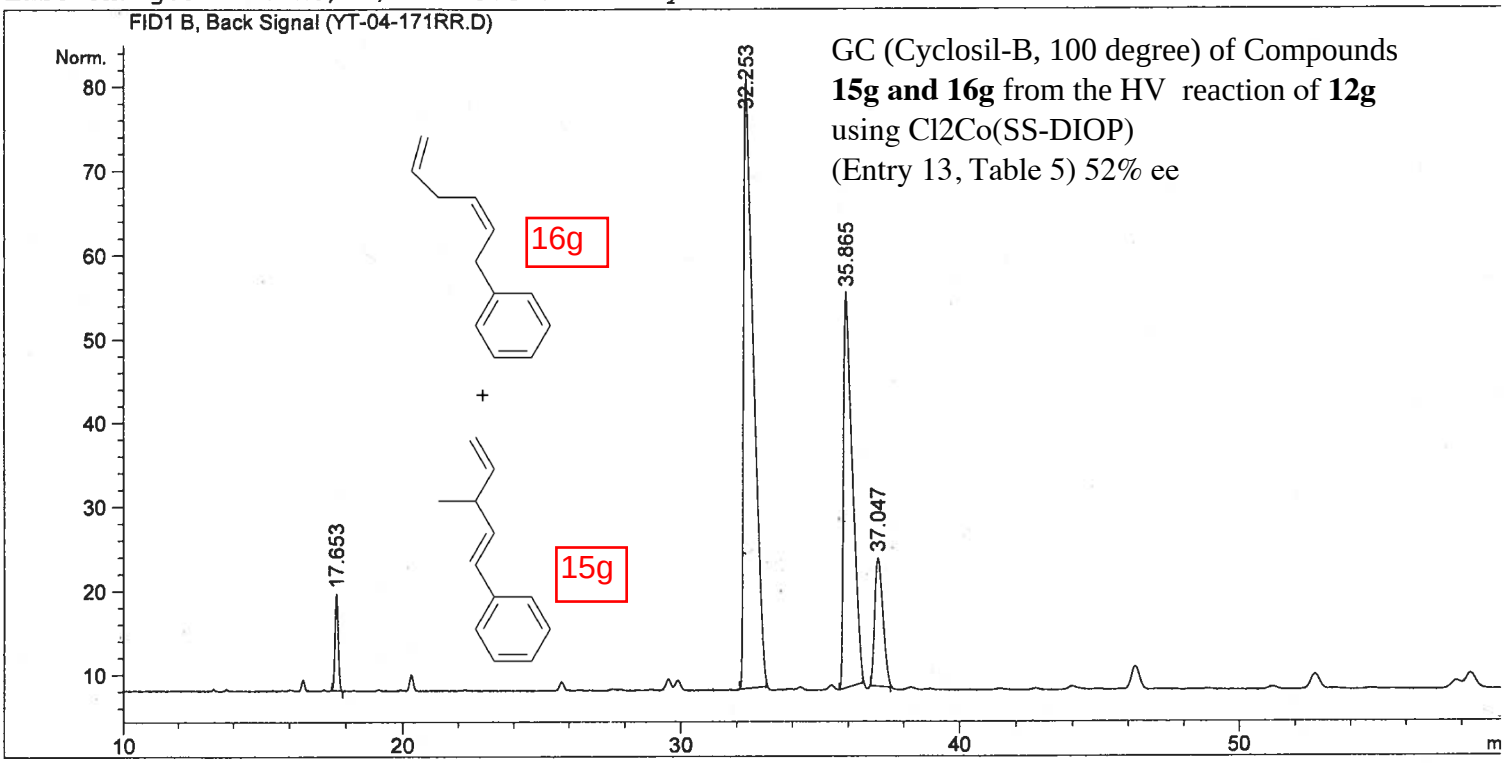

GC (Cyclosil-B, 100 degree) of Compounds **15g and 16g** from the HV reaction of **12g** using Cl2Co(SS-DIOP)
(Entry 13, Table 5) 52% ee

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  17.653 BB    0.1264   91.76698   11.54052  2.85662
   2  32.253 BB    0.3078 1760.57617   72.79673 54.80507
   3  35.865 BB    0.2973 1046.50647   47.14975 32.57676
   4  37.047 BB    0.2925  313.58331   15.26240  9.76155

Totals :                  3212.43293  146.74941


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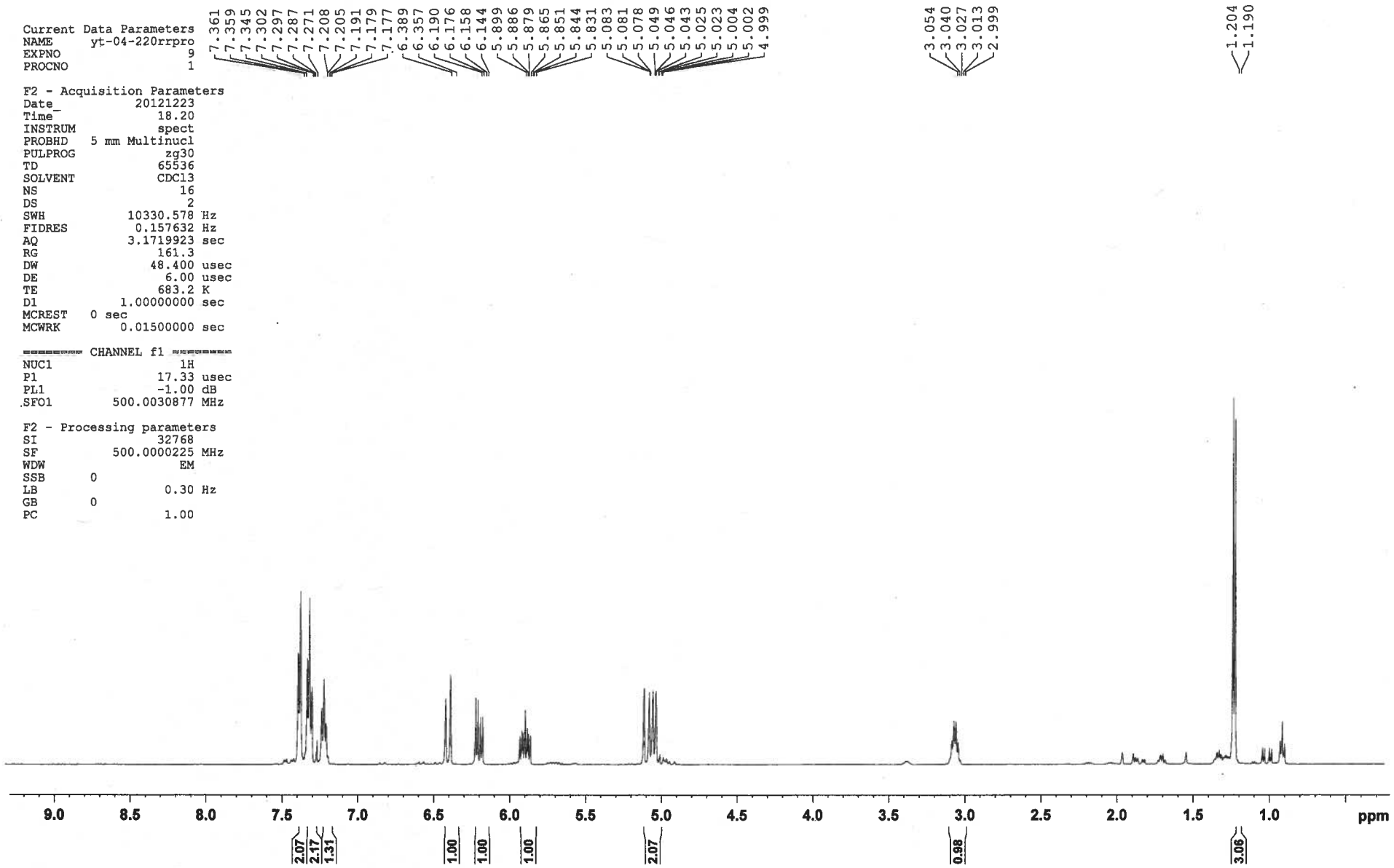
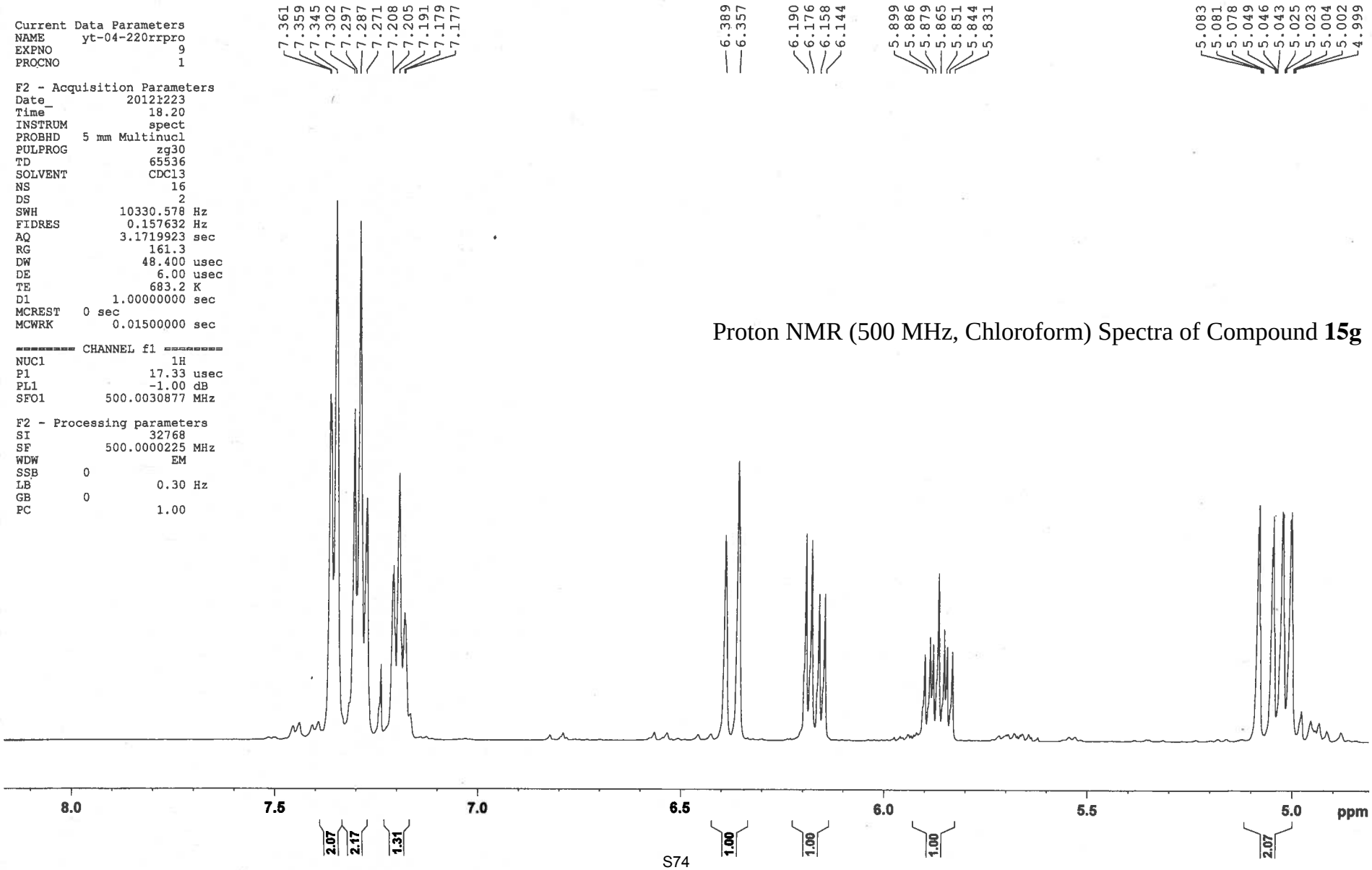
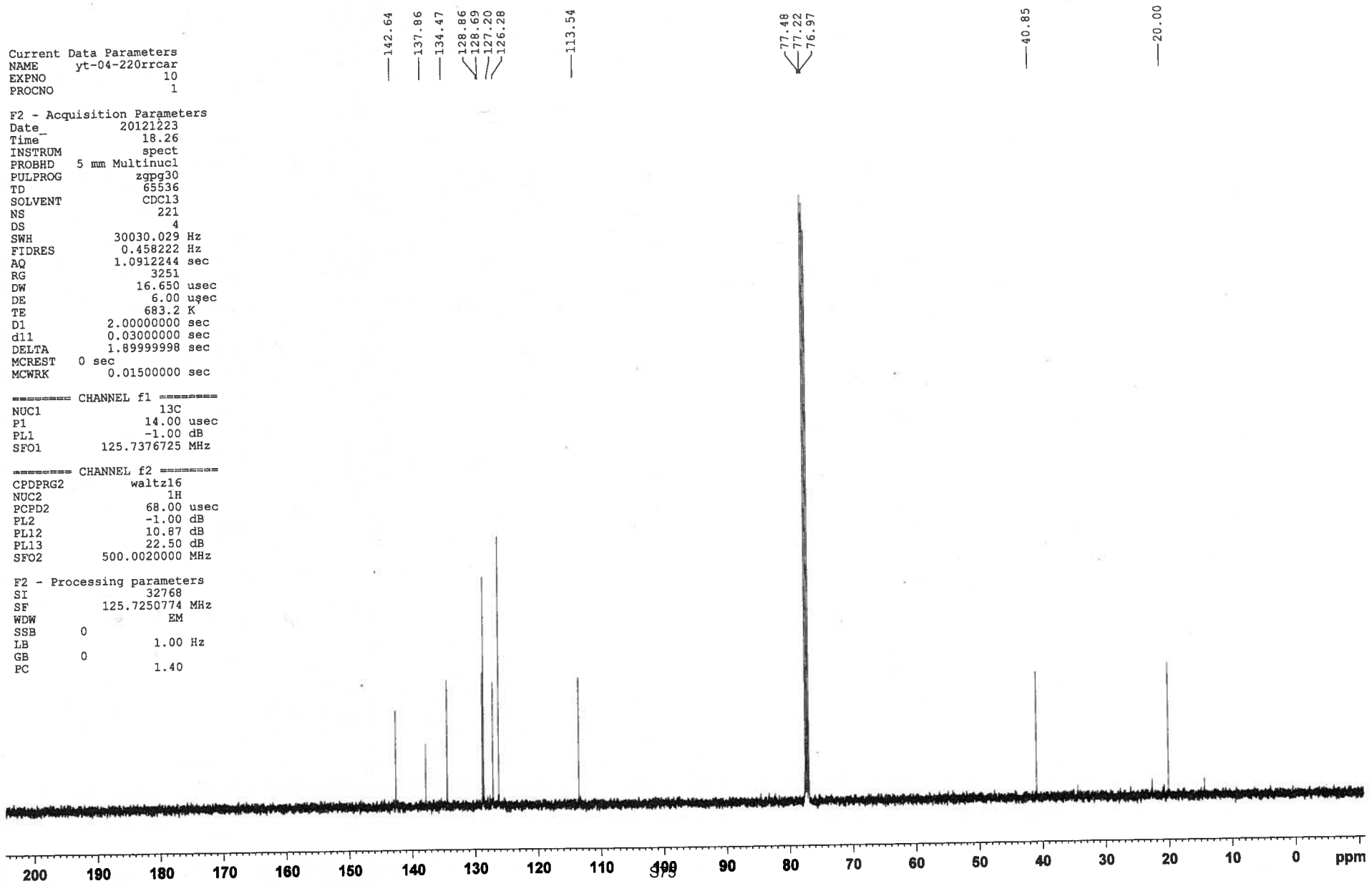


Proton NMR (500 MHz, Chloroform) Spectra of Compound **15g** Using DPPM

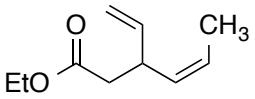


Proton NMR (500 MHz, Chloroform) Spectra of Compound **15g**

Carbon NMR (125 MHz, Chloroform) Spectra of Compound **15g**



Hydrovinylation of (*E*)-ethyl hexa-3,5-dienoate (12h)



Hydrovinylation of (*E*)-ethyl hexa-3,5-dienoate using [DPPM]$CoCl_2$ (Table 3, Entry 14): To an oven dried round-bottom-flask with a sidearm, was added [DPPM]$CoCl_2$ (31 mg, 0.060 mmol) under argon and was dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.3 mL, 0.60 mmol) was added dropwise and the color of the solution changed from bluish brown to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was cooled to 0 ^oC and (*E*)-ethyl hexa-3,5-dienoate (84 mg, 0.60 mmol) in dichloromethane (1 mL) added under ethylene and the mixture was stirred for 15 h at ambient temperature. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and diethyl ether (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with diethyl ether (3 x 5 mL). Due to low boiling nature of product, toluene solvent was first removed with flash chromatography with neat *n*-pentane as an eluent and the compound was flushed through diethyl ether to collect the product. Removal of solvent yielded the product as slight yellowish oil (84 mg, 84%). GC and NMR analysis showed that the product **(13h)** was essentially pure. ^1H NMR ($CDCl_3$, 400 MHz): 1.22 (t, J = 7.2 Hz, 3 H), 1.62 (d, J = 7 Hz, 3 H), 2.30 (dd, J = 8, 15 Hz, 1 H), 2.42 (dd, J = 7, 15 Hz, 1 H), 3.52 - 3.58 (m, 1 H), 4.09 (q, J = 7 Hz, 2 H), 5.01 (dd, J = 17, 24 Hz, 2 H), 5.20 (t, J = 10 Hz, 1 H), 5.47 - 5.55 (m, 1 H), 5.72 (ddd, J = 6.4, 10.4, 17.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 13.41, 14.69, 38.23, 40.48, 60.73, 114.54, 125.84, 131.21, 140.02, 172.45. ESI-MS; m/z 191.1061 [M + Na]; mass calculated for $C_{10}H_{16}NaO_2$, 191.1043.

CSP GC (Cyclosil, OT 80 ^oC/ isothermal, H_2 carrier gas): Starting material R_T = 19.14 min. R_T for product = 22.84 min and 23.24 min (enantiomers). Enantioselectivity is 92 % with (*S,S)*-[BDPP]$CoCl_2$ (Table 5, entry 14). (Josiphos 2)$CoCl_2$ (5 mol% catalyst) gave no conversion.

This following table shows the additional experiments conducted by using diene (*E*)-ethyl hexa-3,5-dienoate employing 10 mol % catalyst (see also Table 3 in the paper for details).

Entry	Catalyst	Temp/Time	Activator	Conversion	Product (%ee)
1.	DPPM$CoCl_2$	0-16^oC/15hr	TMA	100%	(*Z*)-1,4 HV
2.	DPPE$CoCl_2$	5^oC/9hr	TMA	No reaction	SM
3.	DPPP$CoCl_2$	5^oC/7hr	TMA	No reaction	SM
4.	DPPB$CoCl_2$	5^oC/11hr	TMA	No reaction	SM
5.	(*S,S*)-BDPP$CoCl_2$	0^oC-rt/15hr	TMA	100%	(*Z*)-1,4HV (92% ee)
6.	(*S,S*)-DIOP$CoCl_2$	10^oC/12hr	TMA	No reaction	SM
7.	Joshiphos$CoCl_2$	8^oC/8hr	TMA	No reaction	SM

Data File C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2012-08-20 15-58-05\YT-04-118.D
Sample Name: YT-04-118.D

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                                                       Inj Volume : 1 µl
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Last changed     : 11/28/2012 11:00:38 AM by Kendra Dewese
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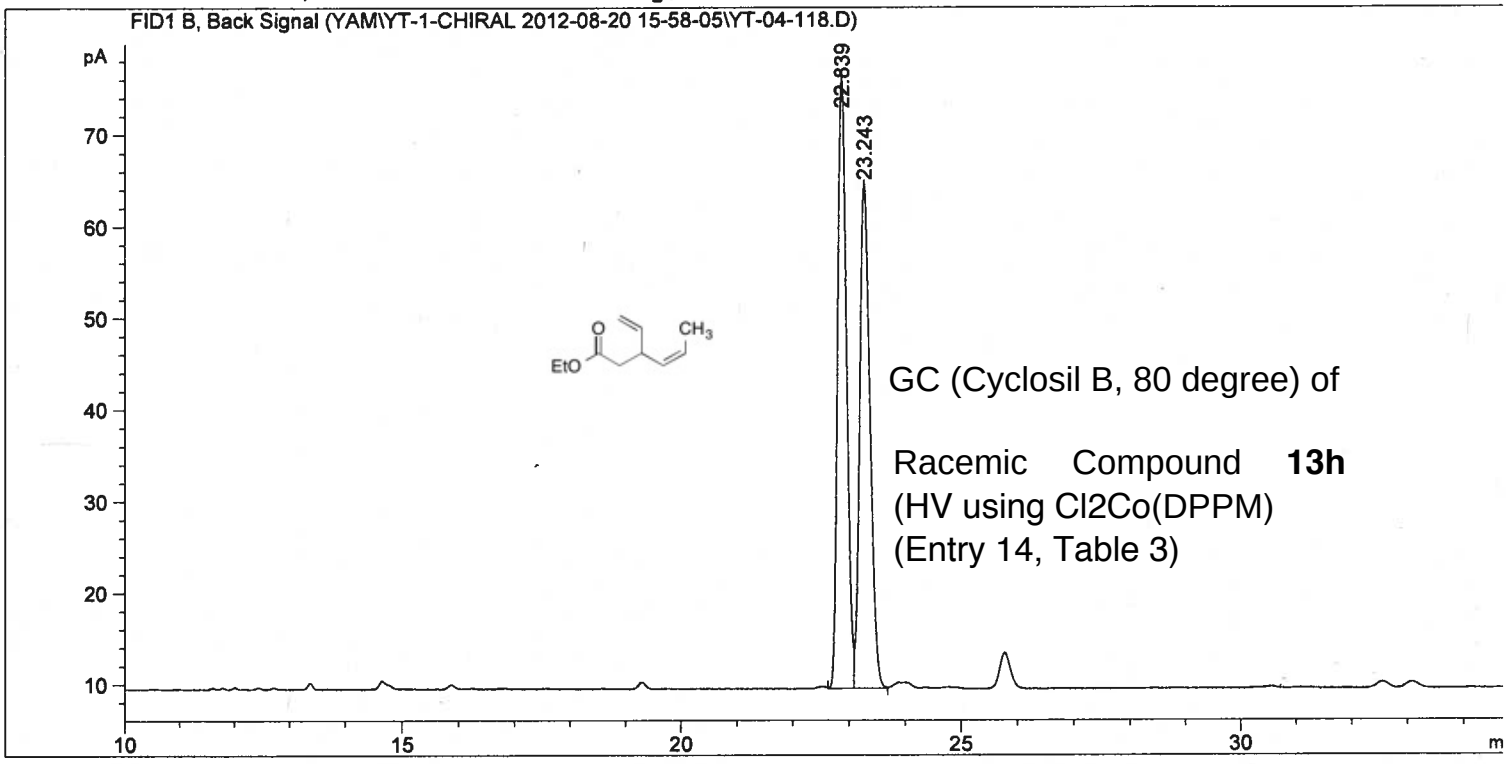

GC (Cyclosil B, 80 degree) of

Racemic Compound **13h**
(HV using Cl2Co(DPPM)
(Entry 14, Table 3)

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  22.839 VV    0.1757  744.05518   66.31979 51.50566
   2  23.243 VV    0.1938  700.55347   54.85747 48.49434

Totals :                  1444.60864  121.17726

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                        *** End of Report ***
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                                                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
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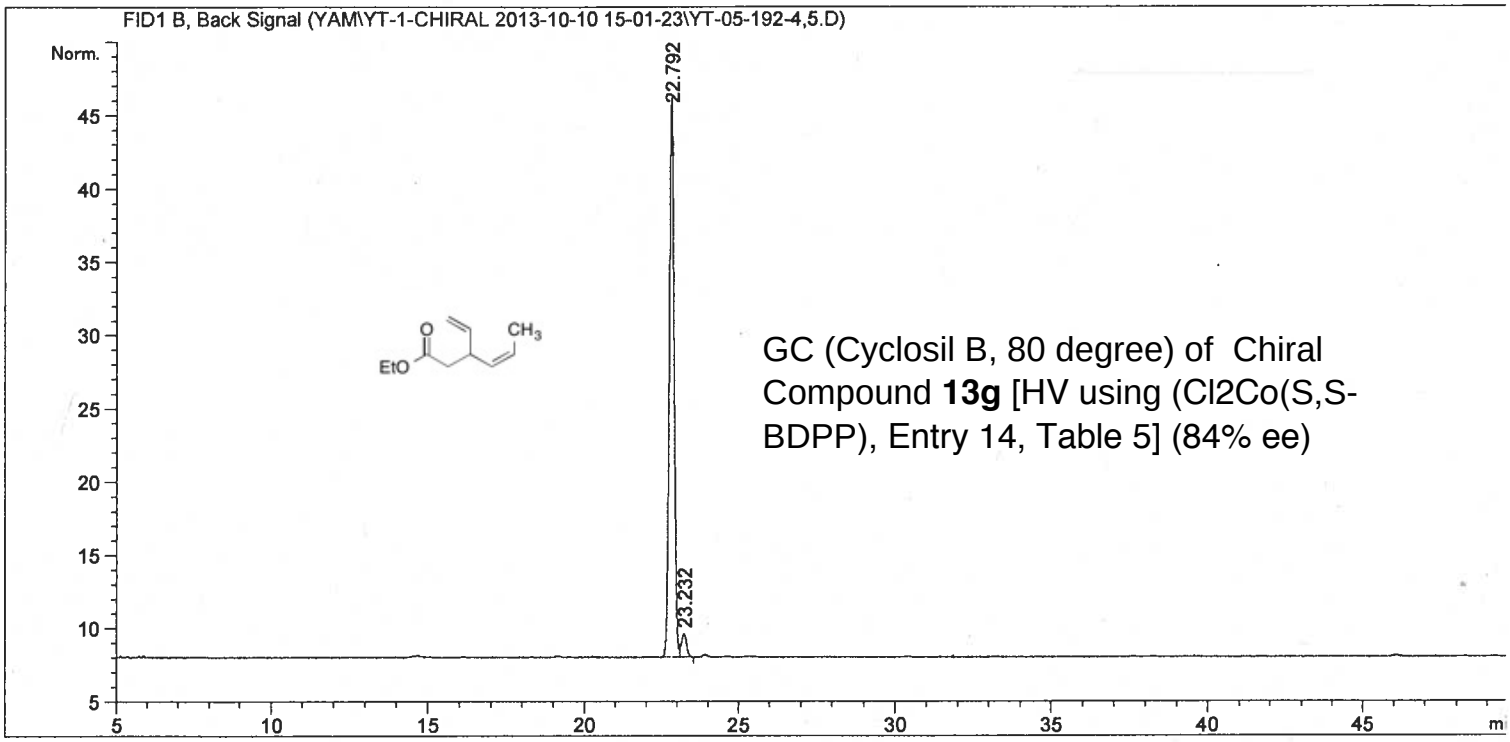

GC (Cyclosil B, 80 degree) of Chiral Compound **13g** [HV using (Cl2Co(S,S-BDPP), Entry 14, Table 5] (84% ee)

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  22.792 BV    0.1668  415.19519   38.21350 95.71836
   2  23.232 VB    0.1779   18.57237    1.60893  4.28164

Totals :                   433.76756   39.82243
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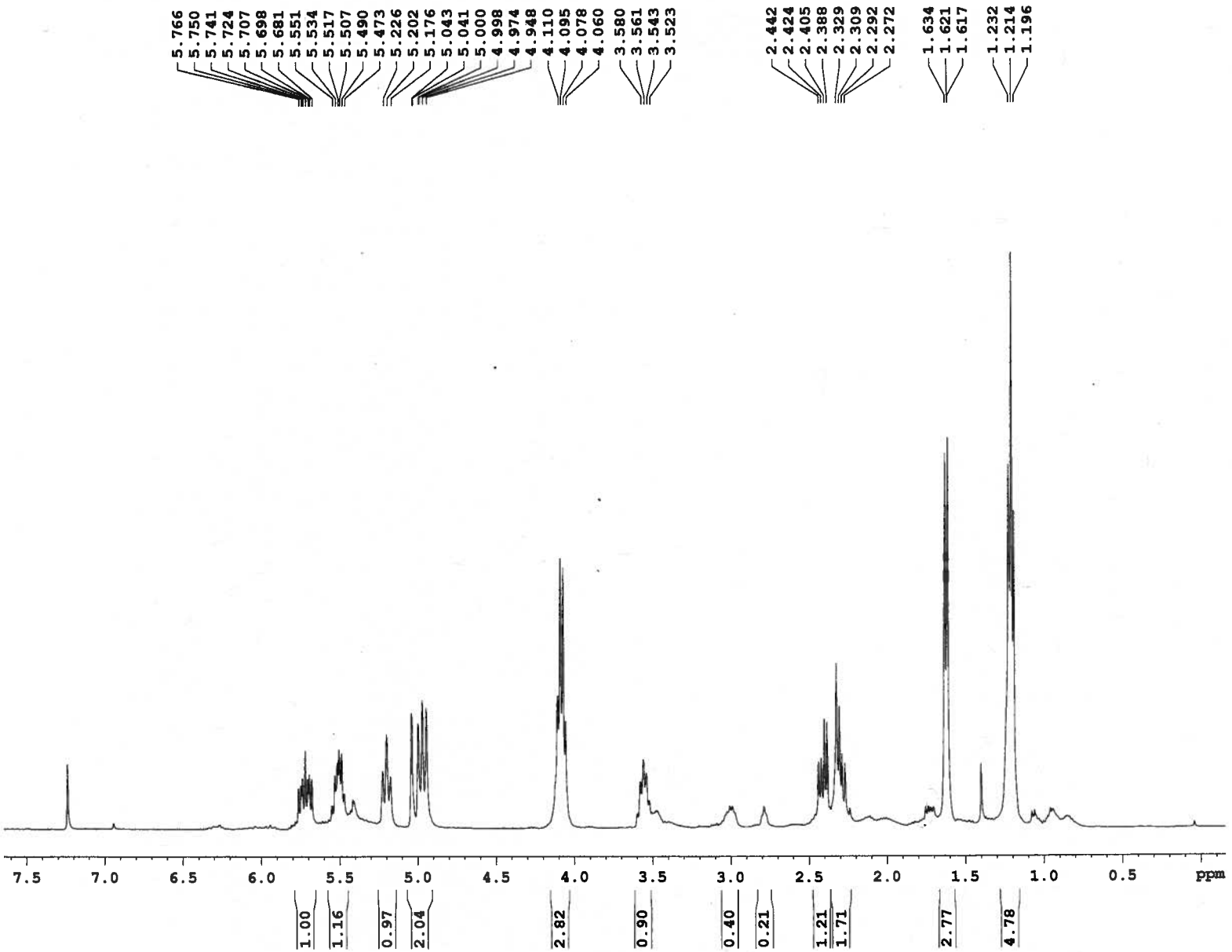


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EXPNO               702
PROCNO                1

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PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8250.825 Hz
FIDRES        0.125898 Hz
AQ           3.9715922 se
RG                40.3
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DE               6.00 us
TE              300.2 K
D1          1.00000000 se
TD0                  1

======== CHANNEL f1 ======
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PL1             -2.65 dB
SFO1          400.1324710 MH

F2 - Processing parameters
SI                32768
SF          400.1300167 MH
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
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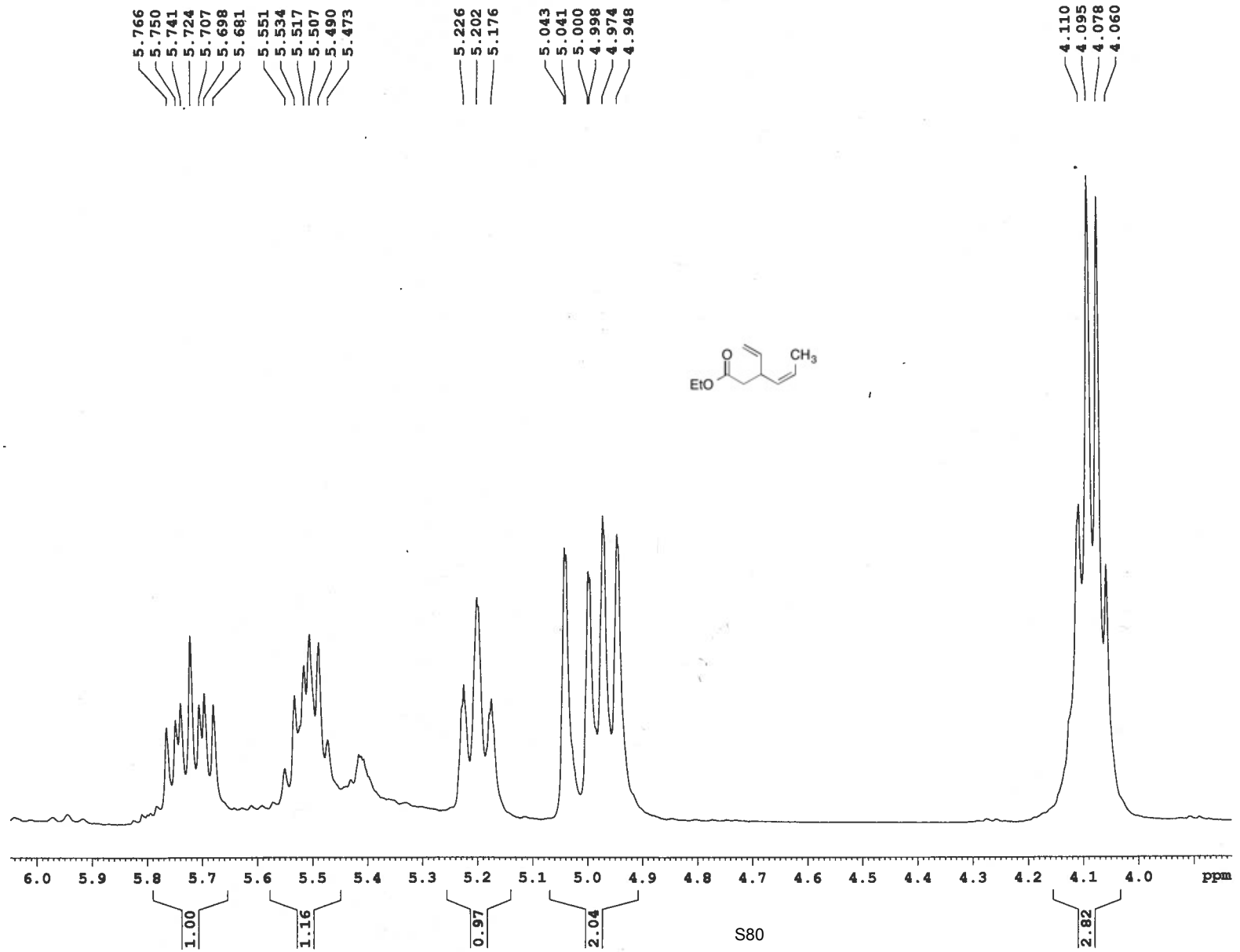
Proton NMR (400 MHz, chloroform) spectrum of compound **13h** (HV using Cl2Co(DPPM)

Proton NMR (400 MHz, Chloroform) Spectra of Compound **13h** Using DPPM (Expanded Alkene Region)

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PROCNO                   1

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TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8250.825 Hz
FIDRES           0.125898 Hz
AQ               3.9715922 se
RG                    40.3
DW                  60.600 us
DE                   6.00 us
TE                  300.2 K
D1             1.00000000 se
TD0                     1

======== CHANNEL f1 ======
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P1                   8.00 us
PL1                 -2.65 dB
SFO1         400.1324710 MH

F2 - Processing parameters
SI                  32768
SF           400.1300167 MH
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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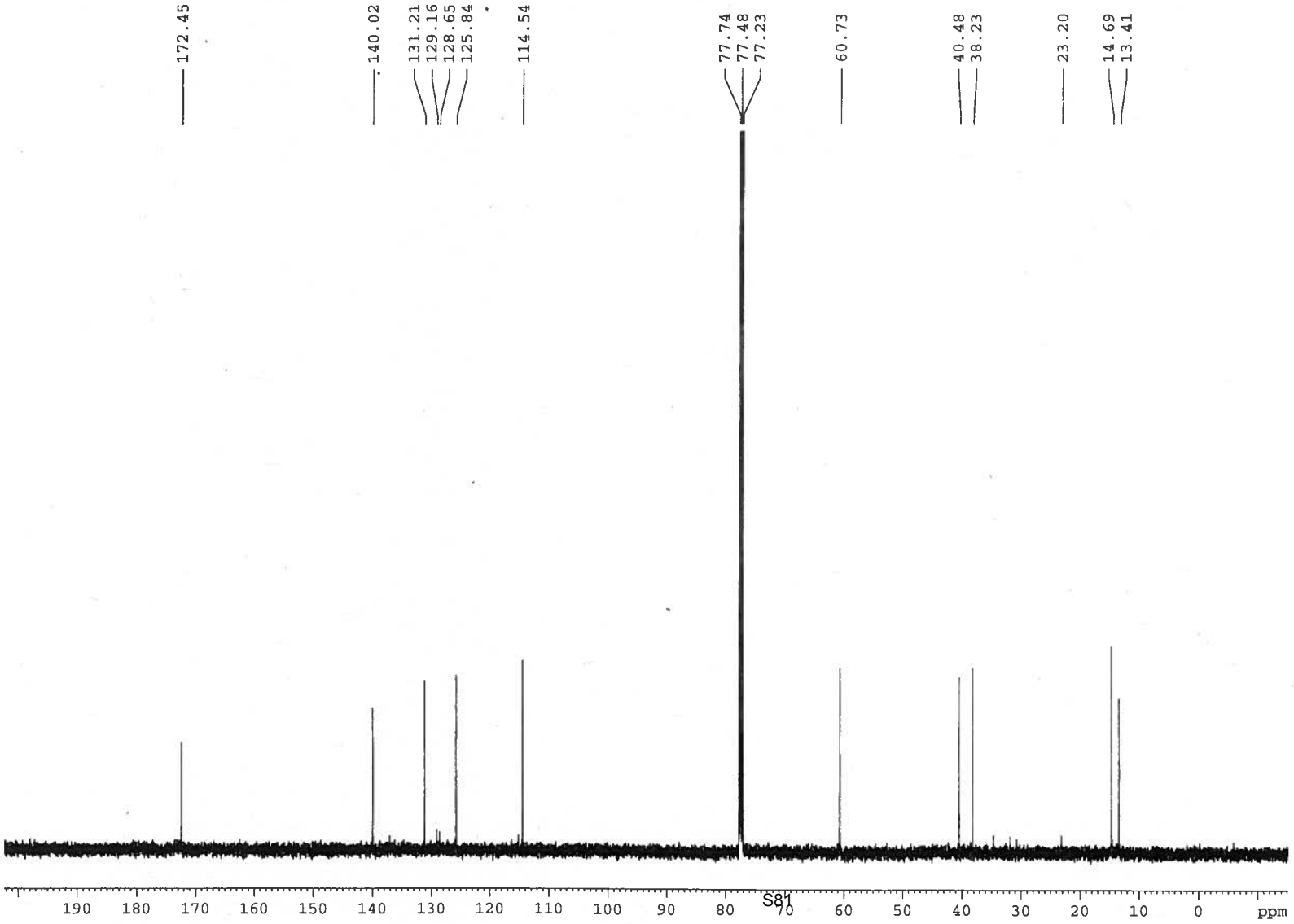
Carbon NMR (125 MHz, Chloroform) Spectra of Compound **13h** Using DPPM

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EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
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Time                18.54
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   882
DS                     4
SWH            30030.029 Hz
FIDRES          0.458222 Hz
AQ             1.0912244 sec
RG                  6502
DW               16.650 usec
DE                6.00 usec
TE                300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1                14.00 usec
PL1               -1.00 dB
SFO1         125.7376725 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2             68.00 usec
PL2               -1.00 dB
PL12              10.87 dB
PL13              22.50 dB
SFO2         500.0020000 MHz

F2 - Processing parameters
SI                 32768
SF          125.7250430 MHz
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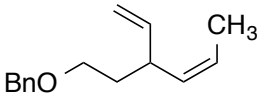
Hydrovinylation of (*E*)-6-benzyloxy-1,3-hexadiene (12i)



Hydrovinylation of (*E*)-6-benzyloxy-1,3-hexadiene using [dppb]$CoCl_2$ (Table 3, Entry 15). To an oven dried round bottom flask with a sidearm, was added [dppb]$CoCl_2$ (26 mg, 0.047 mmol) and methylaluminoxane (55 mg, 0.94 mmol) under argon and dissolved in dichloromethane (1 mL) at room temperature. After addition of dichloromethane, color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to -15 ^oC and (*E*)-6-benzyloxy-1,3-hexadiene (88 mg, 0.47 mmol) added under ethylene and the mixture was stirred for 14 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (4 mL) and diethyl ether (4 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with diethyl ether (3 x 5 mL). Flash chromatography (5 % EtOAc in hexane) and removal of solvent yielded the product as slight yellow oil (98 mg, 97%). GC and NMR analysis showed that the product (**13i**) was essentially pure. ^1H NMR ($CDCl_3$, 400 MHz): 1.54 - 1.59 (m, 1 H), 1.61 (dd, J = 1.6, 6.8 Hz, 3 H), 1.74 - 1.82 (m, 1 H), 3.21 - 3.29 (m, 1 H), 3.40 - 3.51 (m, 2 H), 4.47 (s, 2 H), 4.94 (dd, J = 1.2, 10 Hz, 1H), 4.99 (dt, J = 1.6, 17.2 Hz, 1 H), 5.19 (td, J = 1.6, 10.8 Hz, 1 H), 5.47 – 5.55 (m, 1 H), 5.71 (ddd, J = 6.8, 10.4, 17.2 Hz), 7.25 - 7.33 (m, aromatic, 5H). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 13.23, 35.17, 38.08, 68.43, 73.21, 113.61, 124.87, 127.69, 127.85, 128.54, 132.49, 138.85, 141.37. ESI-MS; m/z 239.1396 [M + Na]; mass calculated for $C_{15}H_{20}ONa$, 239.1406.

Gas Chromatography: Methylsilicone SP GC (OT 150 ^oC/isothermal, He carrier gas) starting material R_T = 10.49 min. R_T for product = 14.37 min. CSP GC (Cyclosil, OT 150 ^0C/isothermal, H_2 carrier gas). Starting material R_T = 12.36 min. R_T for product = 15.08 min. and 15.33 min (enantiomers, racemic from DPPBCoCl_2). (*S,S*)-DIOPCoCl_2 gave 94% ee. Reaction carried out with [(*S,S*)-DIOP]$CoCl_2$ at -20 ^oC gave 99% ee, albeit in lower (40%) conversion).

Asymmetric hydrovinylation of (*E*)-6-benzyloxy-1,3-hexadiene using (*S,S*)-[DIOP]$CoCl_2$ (Table 5, Entry 17): To an oven dried round bottom flask with a sidearm, was added (*SS*)-[DIOP]$CoCl_2$ (10 mg, 0.016 mmol) and methylaluminoxane (18 mg, 0.32 mmol) under argon and dissolved in dichloromethane (0.5 mL) at room temperature. After addition of dichloromethane, color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to -15 ^oC and (*E*)-6-benzyloxy-1,3-hexadiene (30 mg, 0.16 mmol) added under ethylene and the mixture was stirred for 14 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and diethyl ether (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with diethyl ether (3 x 5 mL). Flash chromatography (5 % EtOAc in hexane) and removal of solvent yielded the product as slight yellow oil (28 mg, 88%). GC and NMR analysis showed that the product was essentially pure. ^1H NMR ($CDCl_3$, 400 MHz): 1.54 - 1.59 (m, 1 H), 1.61 (dd, J = 1.6, 6.8 Hz, 3 H), 1.74 - 1.82 (m, 1 H), 3.21 - 3.29 (m, 1 H), 3.40 - 3.51 (m, 2 H), 4.47 (s, 2 H), 4.94 (dd, J = 1.2, 10 Hz, 1H), 4.99 (dt, J = 1.6, 17.2 Hz, 1 H), 5.19 (td, J = 1.6, 10.8 Hz, 1 H), 5.47 – 5.55 (m, 1 H), 5.71 (ddd, J = 6.8, 10.4, 17.2 Hz), 7.25 - 7.33 (m, aromatic,

5H). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 13.23, 35.17, 38.08, 68.43, 73.21, 113.61, 124.87, 127.69, 127.85, 128.54, 132.49, 138.85, 141.37. ESI-MS; m/z 239.1396 [M + Na]; mass calculated for $C_{15}H_{20}ONa$, 239.1406.

[(*S,S*)-DIOP]$CoCl_2$ gave 94% ee at full conversion.

This following table shows the percent conversion and percent ee's obtained using other catalysts.

Catalyst	% ee	% conversion
(*S,S*)-[BDPP]$CoCl_2$	92	100
(*S,S*)-[DIOP]$CoCl_2$	99[a]	40
L18 Joshiphos 2	71	92

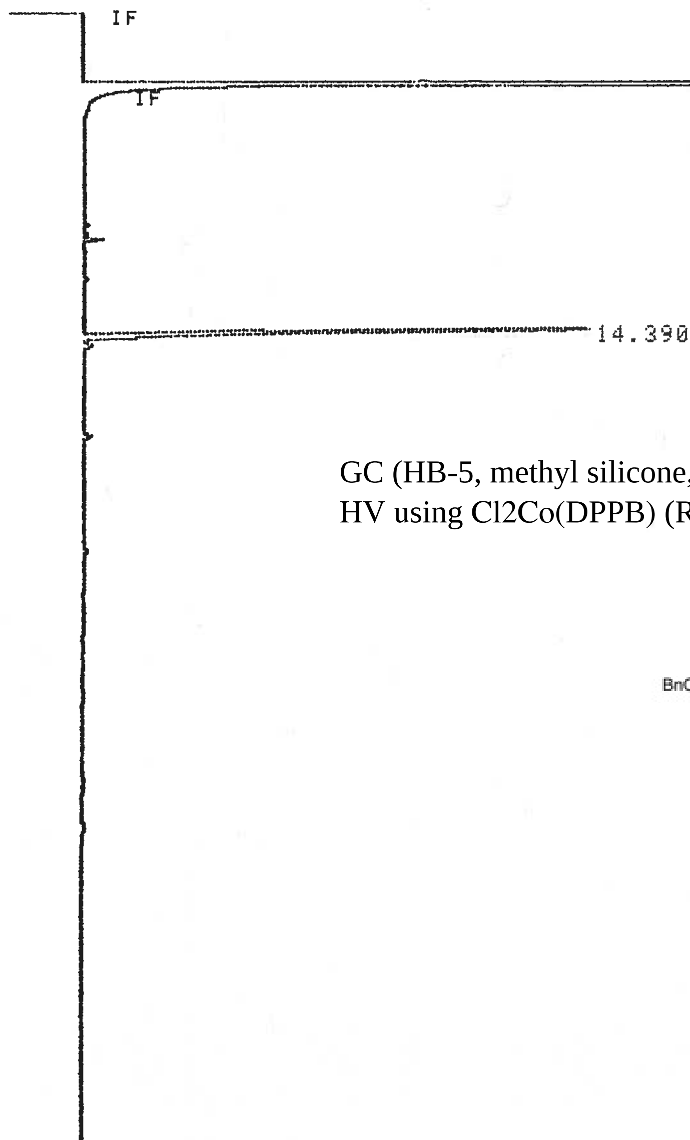
[a] at -10 ^oC/6 h, 100%, 94% ee.

dppb 150°c

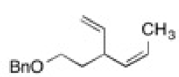
YT-04-09/dppbcocl2/MAO

*
*
*
*
*
*
*   RUN #   360   APR 15, 1901   01:41:48

START



GC (HB-5, methyl silicone, 150 degree) of Compound **13i** HV using Cl2Co(DPPB) (Racemic) Entry 15, Table 3)



13i

TIMETABLE STOP

RUN#   360   APR 15, 1901   01:41:48

AREA%

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TOTAL AREA= 215340
MUL FACTOR=1.0000E+00

*
*

Data File C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2013-02-25 11-50-11\YT-04-09DPPBRR.D
Sample Name: YT-04-09DPPBRR.D

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                                                      Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
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Last changed     : 2/25/2013 10:26:04 AM by YAM
Analysis Method : C:\CHEM32\1\METHODS\35_CYCLODEX-B.M
Last changed     : 9/9/2013 11:17:53 AM by Kendra
                   (modified after loading)
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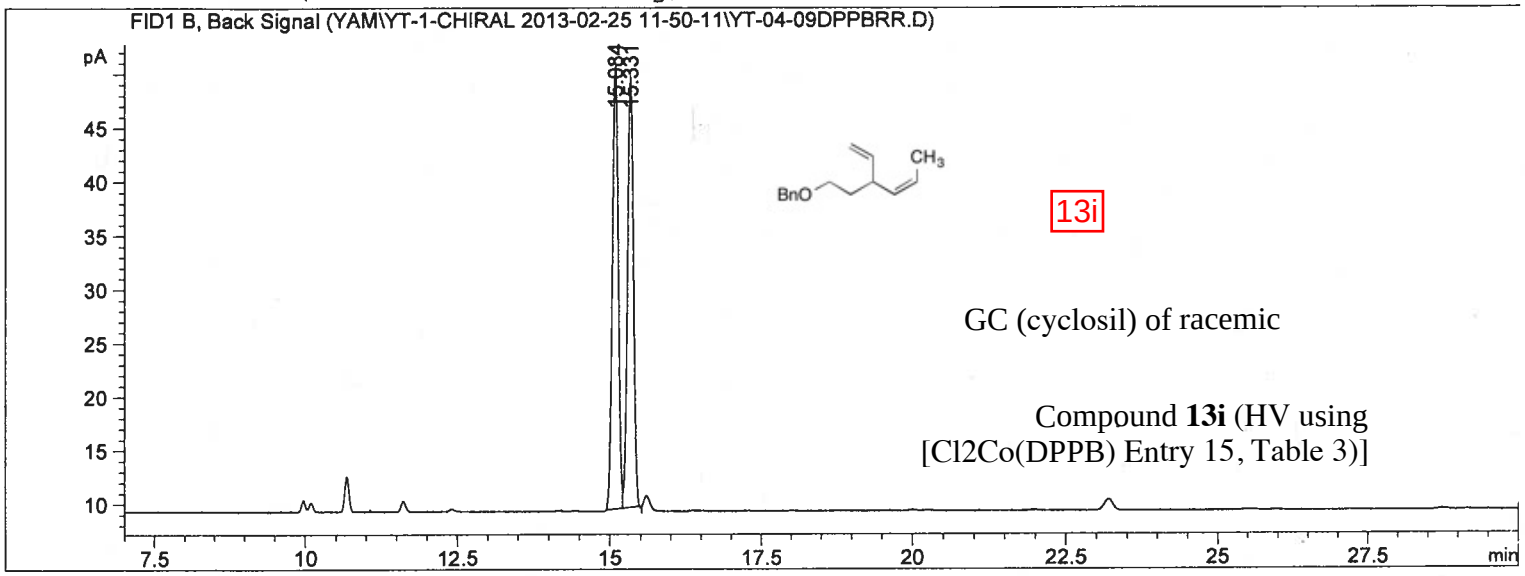

13i

GC (cyclosil) of racemic

Compound **13i** (HV using [Cl2Co(DPPB) Entry 15, Table 3)]

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  15.084 BV    0.1036  269.52896   41.15466 50.19640
   2  15.331 VB    0.1052  267.41983   39.99708 49.80360

Totals :                   536.94879   81.15174

==========================================================================
                        *** End of Report ***
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Data File C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2012-08-22 15-36-29\YT-04-138SMR.D
Sample Name: YT-04-138SMR.D

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Acq. Instrument  : Babu                          Location : Vial 201
Injection Date   : 8/22/2012 3:37:31 PM              Inj :   1
                                                Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 5 µl
Acq. Method      : C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2012-08-22 15-36-29\YT_80_C_CHIRAL.M
Last changed     : 8/22/2012 3:36:29 PM by YAM
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Last changed     : 2/25/2013 10:41:53 AM by CHANDRANI
                   (modified after loading)
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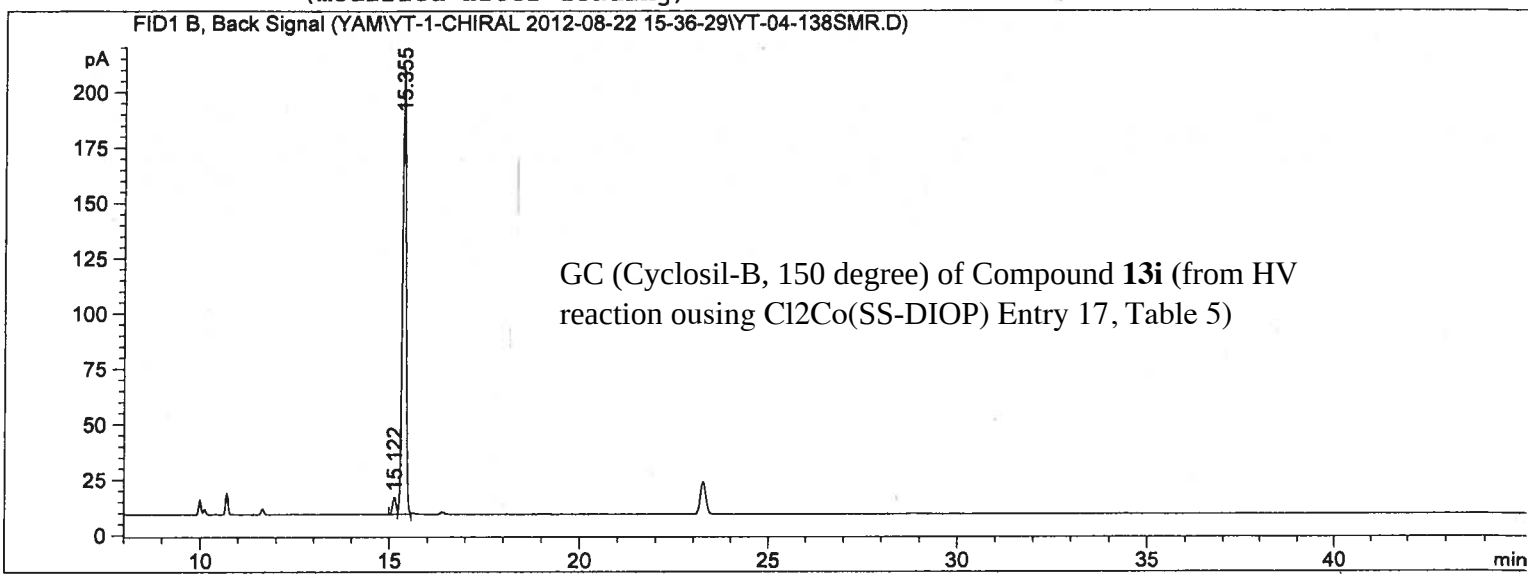

GC (Cyclosil-B, 150 degree) of Compound **13i** (from HV reaction ousing Cl2Co(SS-DIOP) Entry 17, Table 5)

```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs
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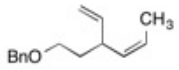

13i

```
Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  15.122 BV    0.1015   49.09645    7.70513  3.49769
   2  15.355 VV    0.1059 1354.58533  200.70699 96.50231

Totals :                  1403.68178  208.41211

==========================================================================
                        *** End of Report ***
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*
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START
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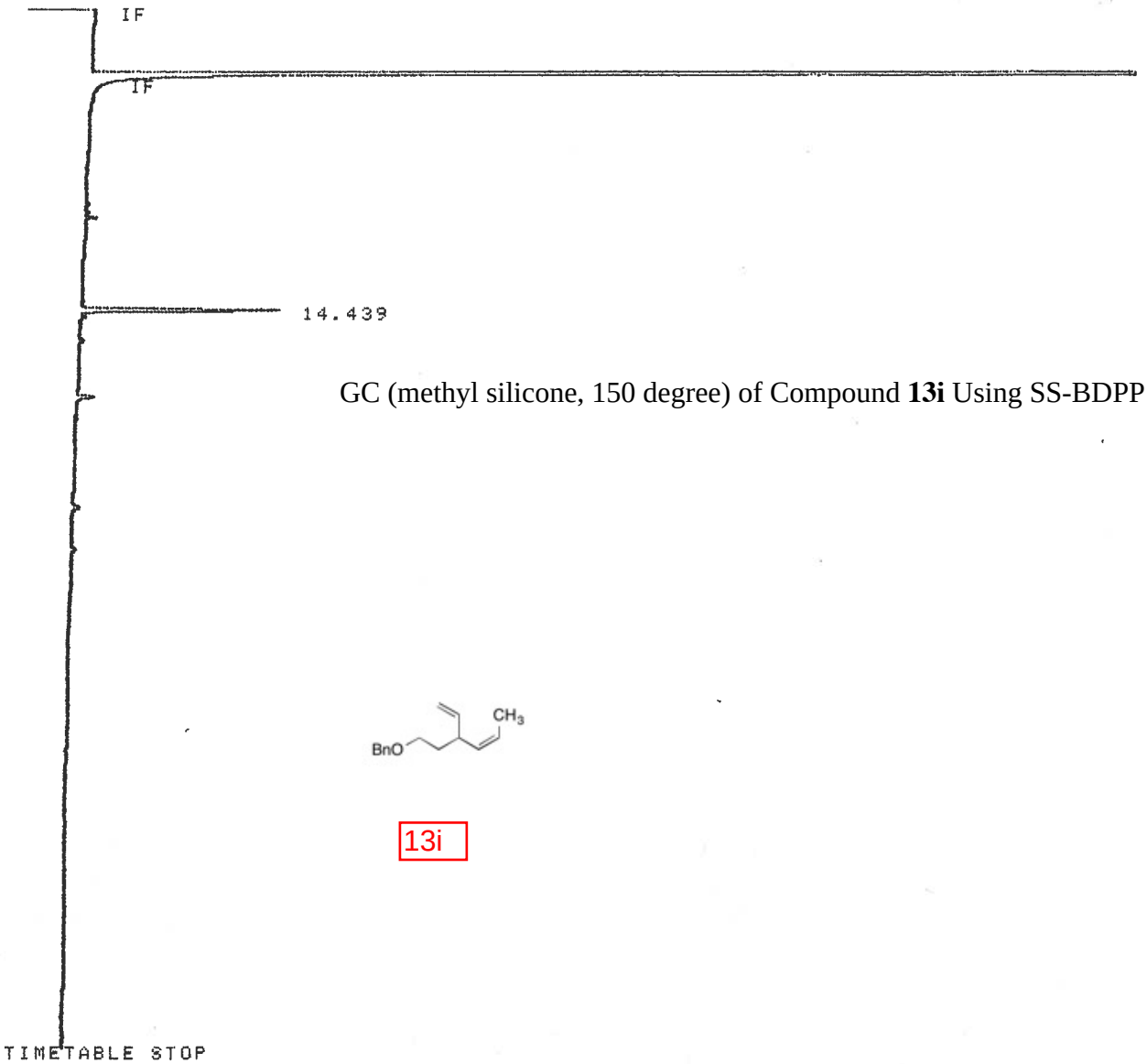
YT-03-58/SS BDPP



GC (methyl silicone, 150 degree) of Compound **13i** Using SS-BDPP (92%ee)

13i

```
TIMETABLE STOP


RUN#    358           APR 14, 1901   23:02:58

AREA%
       RT       AREA TYPE   WIDTH       AREA%
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TOTAL AREA=   97878
MUL FACTOR=1.0000E+00
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Data File C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2013-02-25 09-12-23\YT-03-58RR.D
Sample Name: YT-03-58RR.D

05/58 SS BDPP GC Column Info
OT150c/180/chiral/cyclos

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Acq. Instrument  : Babu                          Location : Vial 201
Injection Date   : 2/25/2013 9:13:37 AM              Inj :   1
                                                Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method      : C:\CHEM32\1\DATA\YAM\YT-1-CHIRAL 2013-02-25 09-12-23\YT_85_C_CHIRAL.M
Last changed     : 2/25/2013 9:12:23 AM by YAM
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Last changed     : 2/25/2013 10:22:47 AM by YAM
                   (modified after loading)
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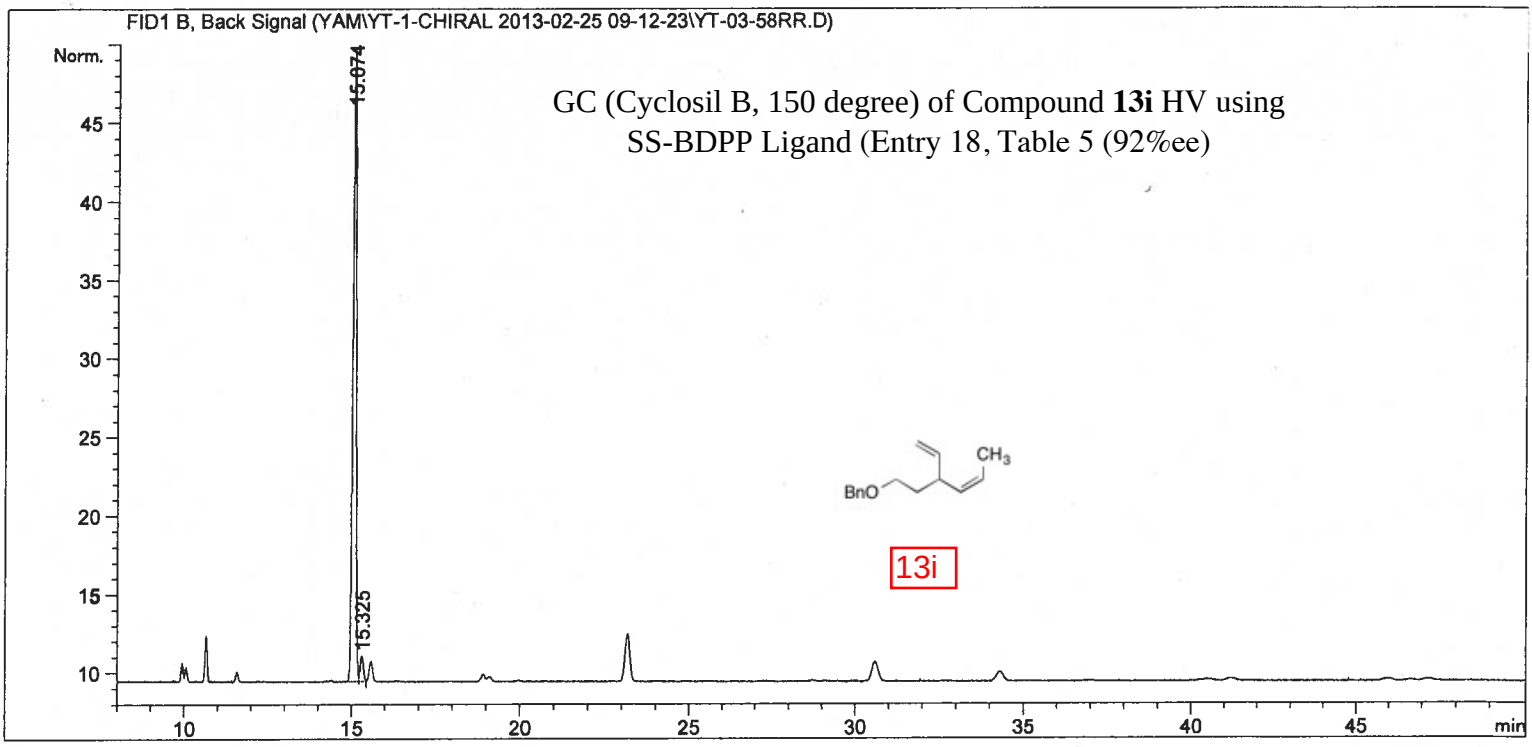


GC (Cyclosil B, 150 degree) of Compound **13i** HV using SS-BDPP Ligand (Entry 18, Table 5 (92%ee)

```
==========================================================================
                        Area Percent Report
==========================================================================

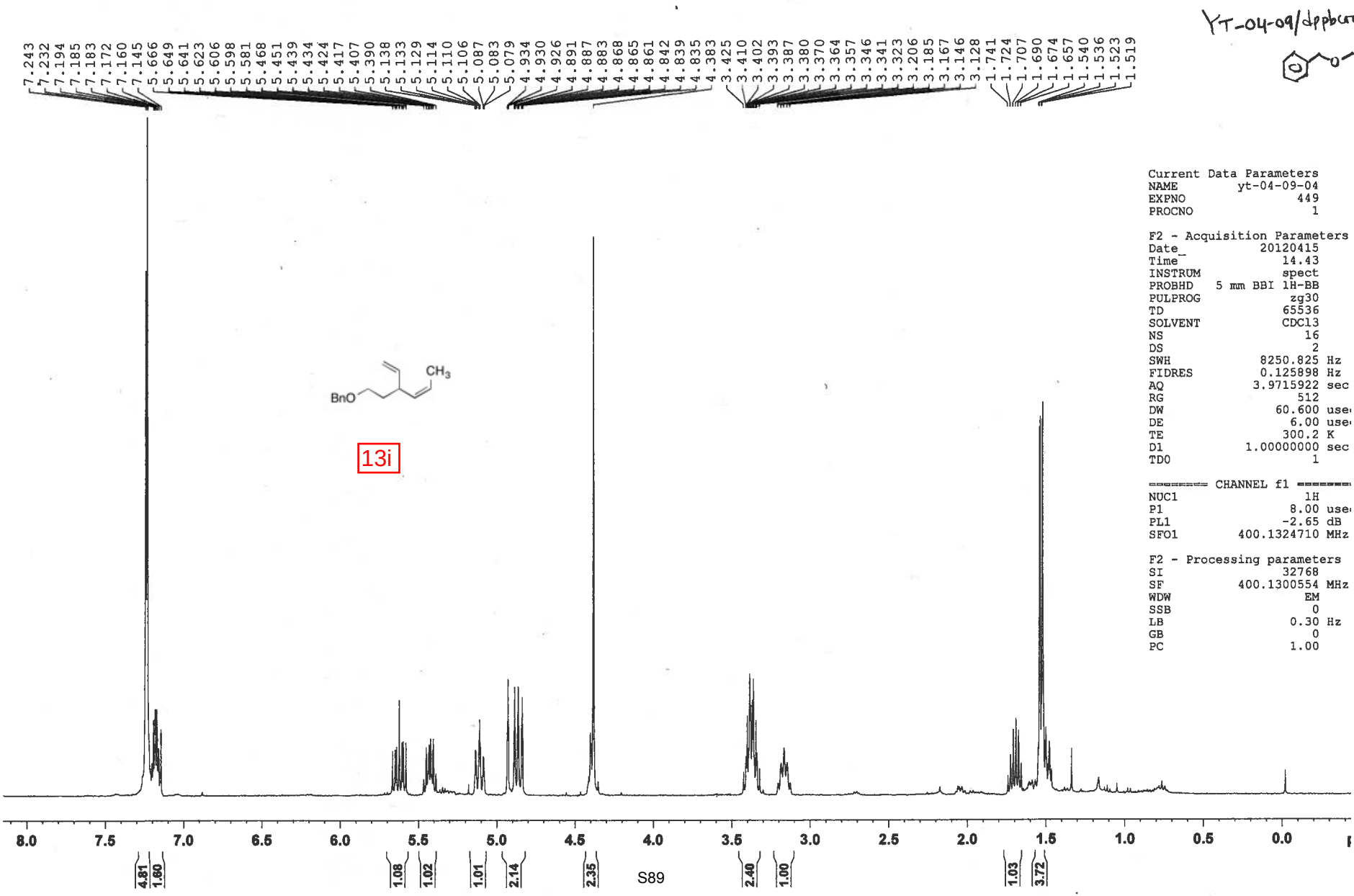
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 B, Back Signal

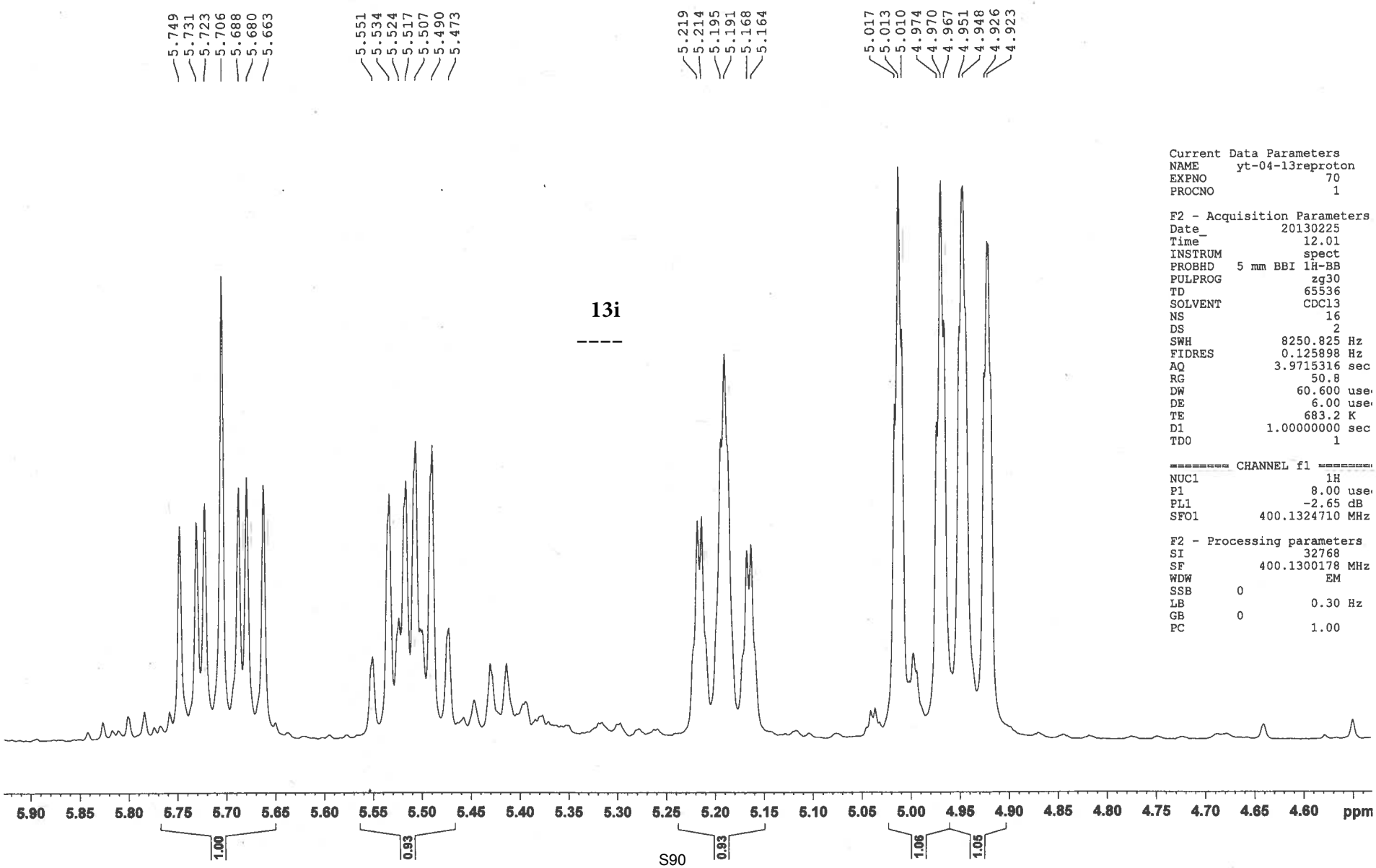
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  15.074 BV    0.1042  265.28748   40.19469 96.03125
   2  15.325 VV    0.1073   10.96372    1.62892  3.96875

Totals :                   276.25119   41.82362
```

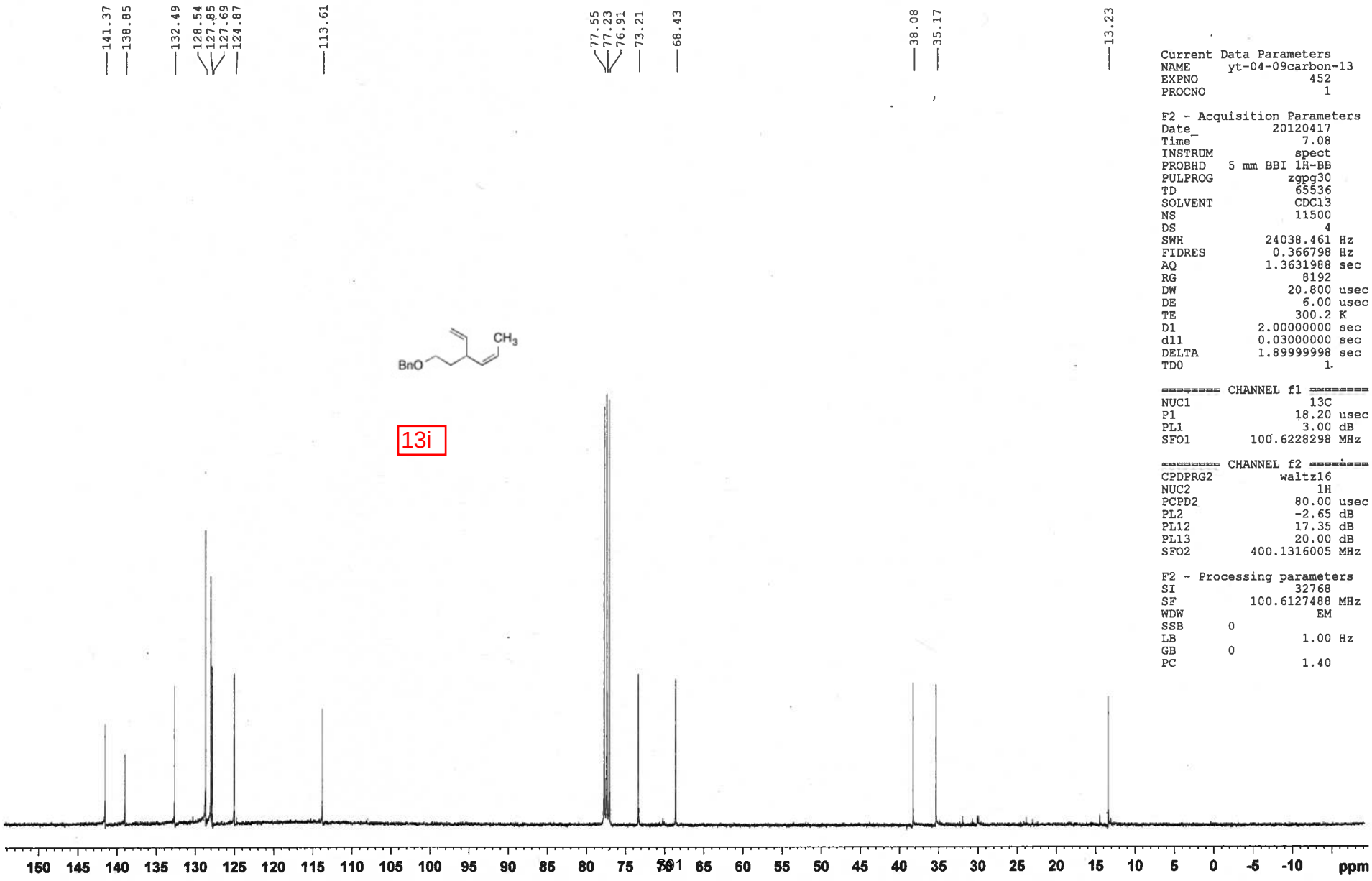
Proton NMR (400 MHz, D-chloroform) Spectra of Compound **13i**



Proton NMR (400 MHz, D-chloroform) spectrum of Compound **13i** (HV Using SS-DIOP) (Alkene Region Expansion)



Carbon NMR (400 MHz, D-chloroform) spectrum of Compound **13i** (HV Using SS-DIOP)

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EXPNO                  452
PROCNO                   1

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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                11500
DS                    4
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG                 8192
DW               20.800 usec
DE                6.00 usec
TE               300.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0                   1.

======== CHANNEL f1 ========
NUC1                 13C
P1                18.20 usec
PL1                3.00 dB
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -2.65 dB
PL12              17.35 dB
PL13              20.00 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6127488 MHz
WDW                  EM
SSB       0
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GB        0
PC                1.40
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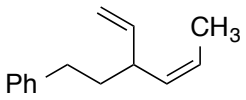
Hydrovinylation of (*E/Z*)-hexa-3,5-dienylbenzene (12j)



Hydrovinylation of (*E/Z*)-hexa-3,5-dienylbenzene using[dppb]$CoCl_2$ (Table 3, Entry 16). To an oven dried round bottom flask with a sidearm, was added [dppb]$CoCl_2$ (18 mg, 0.032 mmol) and methylaluminoxane (37 mg, 0.64 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at -10 ^{o}C and (*E/Z*)-hexa-3,5-dienylbenzene (52 mg, 0.32 mmol), mixture of *E*:*Z* in the ratio of 53:47, was added via syringe under ethylene and the mixture was stirred for 8 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of the solvent yielded the product as colorless oil (51 mg, 84%). GC and NMR analysis showed that the product (**13j**) was essentially pure. ^{1}H NMR ($CDCl_3$, 400 MHz): 1.58 (dd, J = 7, 2 Hz, 3 H), 1.57 – 1.74 (m, 1 H), 1.75 – 1.79 (m, 1 H), 2.54 – 2.63 (m, 2 H), 3.03 - 3.06 (m, 1 H), 4.94 – 5.02 (m, 2 H), 5.22 - 5.29 (m, 1 H), 5.49 – 5.58 (m, 1 H), 5.72 (ddd, J = 17, 10, 7 Hz, 1 H), 7.14 – 7.27 (m, 5 H, aromatic). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 13.33, 33.64, 37.14, 41.03, 113.65, 124.72, 125.87, 128.49, 128.67, 132.91, 141.56, 142.72.

Gas Chromatography: CSP GC (Cyclosil, OT 100 ^{o}C/ isothermal, H_2 carrier gas): starting material R_T = 37.70 min. for *E*-diene and 36.07 min. for *Z* diene. R_T for product = 54.64 min and 57.65 min (racemic).

Data File C:\CHEM32\1\DATA\DUVVURI\YT-1-CHIRAL 2014-04-04 12-30-08\YT-06-122.D
Sample Name: YT-06-122.D

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                                                   Inj Volume : 1 µl
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Last changed     : 4/4/2014 12:30:06 PM by YAM
Analysis Method : C:\CHEM32\1\METHODS\YT_85_C_CHIRAL.M
Last changed     : 4/4/2014 12:30:06 PM by YAM
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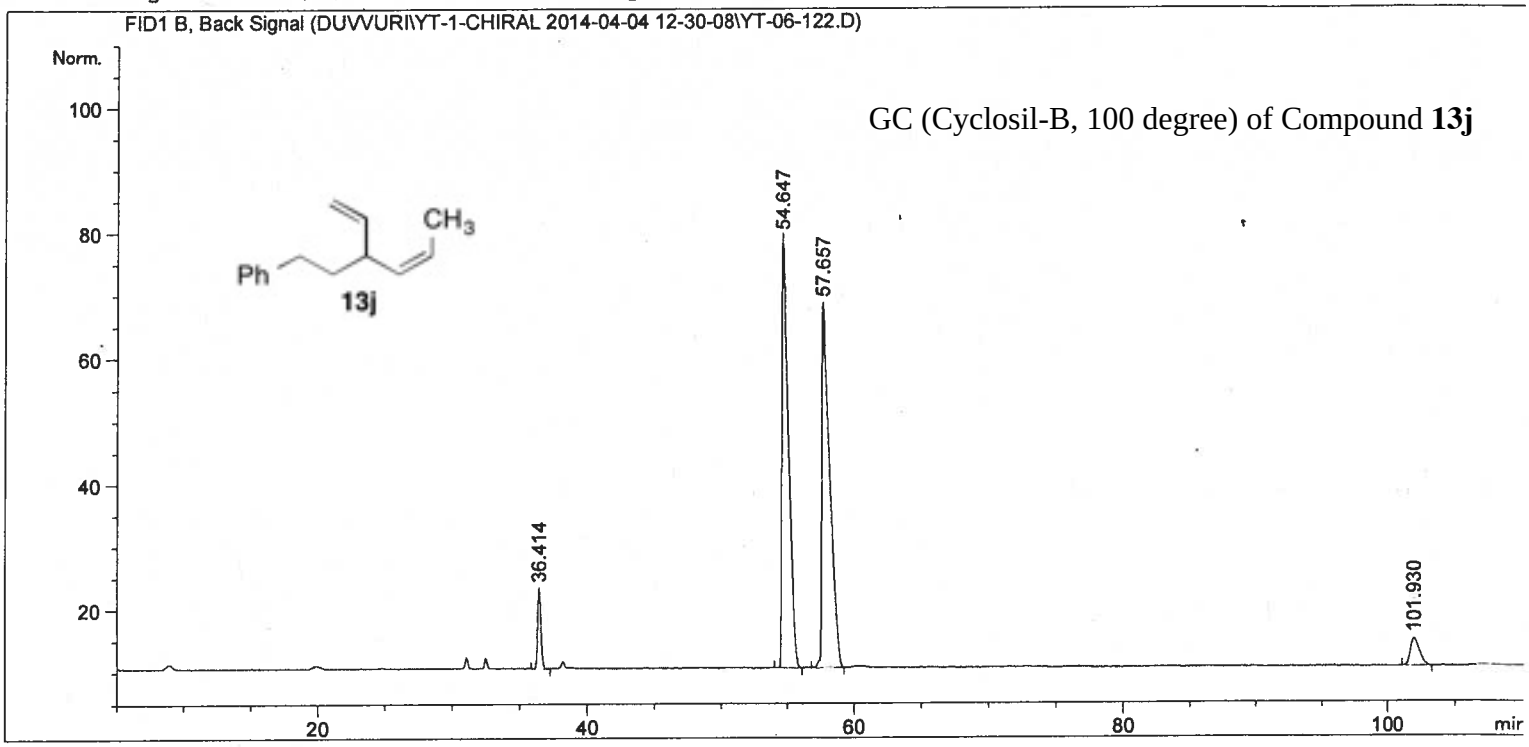


GC (Cyclosil-B, 100 degree) of Compound **13j**

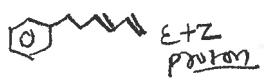
```
==========================================================================
                        Area Percent Report
==========================================================================

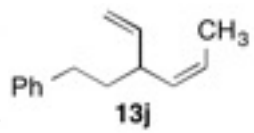
Sorted By             :      Signal
Multiplier:           :      1.0000
Dilution:             :      1.0000
Use Multiplier & Dilution Factor with ISTDs

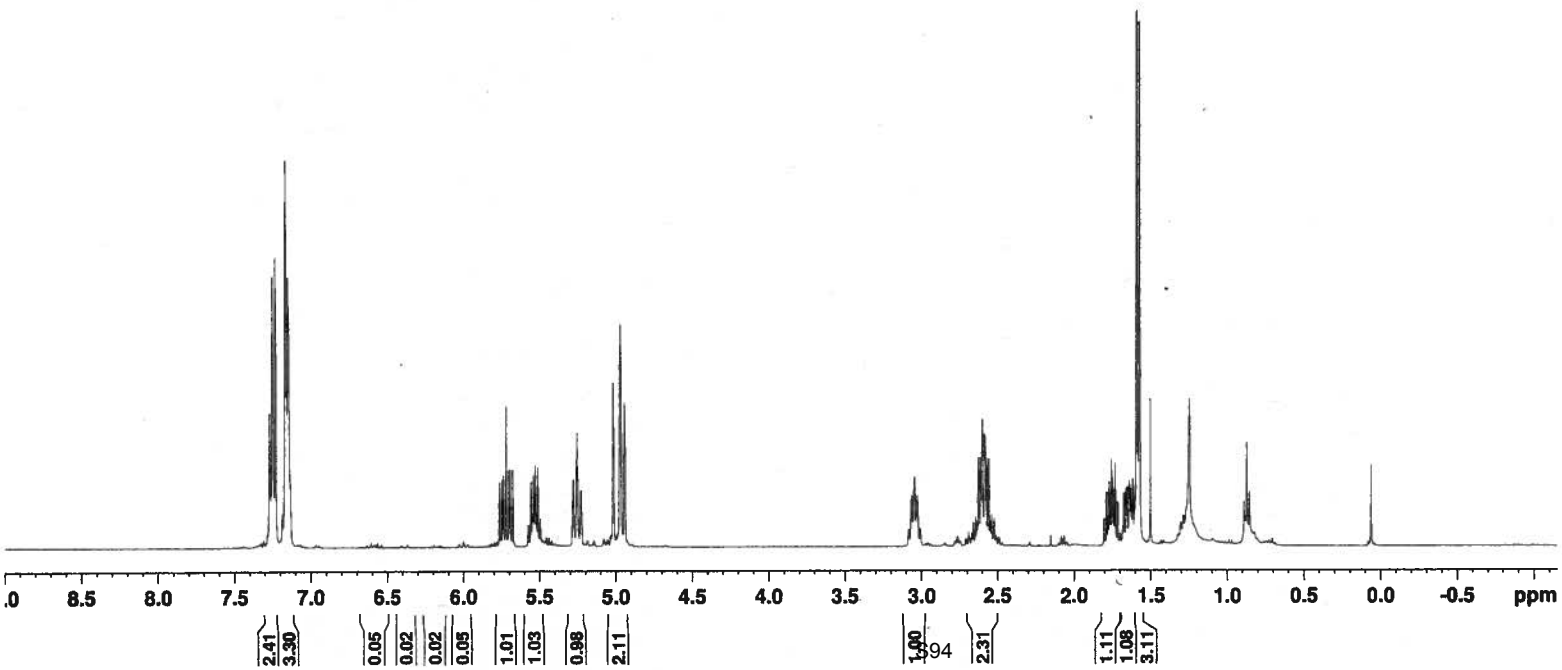

Signal 1: FID1 B, Back Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]       [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  36.414 BB    0.2539  217.92847   12.84430  4.19654
   2  54.647 BB    0.4428 2367.73975   68.85545 45.59434
   3  57.657 BB    0.5236 2403.51611   58.17712 46.28327
   4 101.930 BB    0.5638  203.87204    4.34213  3.92586
```

Proton NMR (400 MHz, D-Chloroform) spectrum of compound **13j** (HV using Cl2Co(DPPB) (Entry 16, Table 3)





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PROCNO                        1

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PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                     3.9845889 sec
RG                        112.47
DW                        60.800 use
DE                         6.50 use
TE                        300.0 K
D1                     1.00000000 sec
TD0                           1

======== CHANNEL f1 ========
NUC1                         1H
P1                        15.00 use
PLW1              12.52000046 W
SFO1              400.1724712 MHz

F2 - Processing parameters
SI                        65536
SF                400.1700196 MHz
WDW                         EM
SSB          0
LB                         0.30 Hz
GB           0
PC                         1.00
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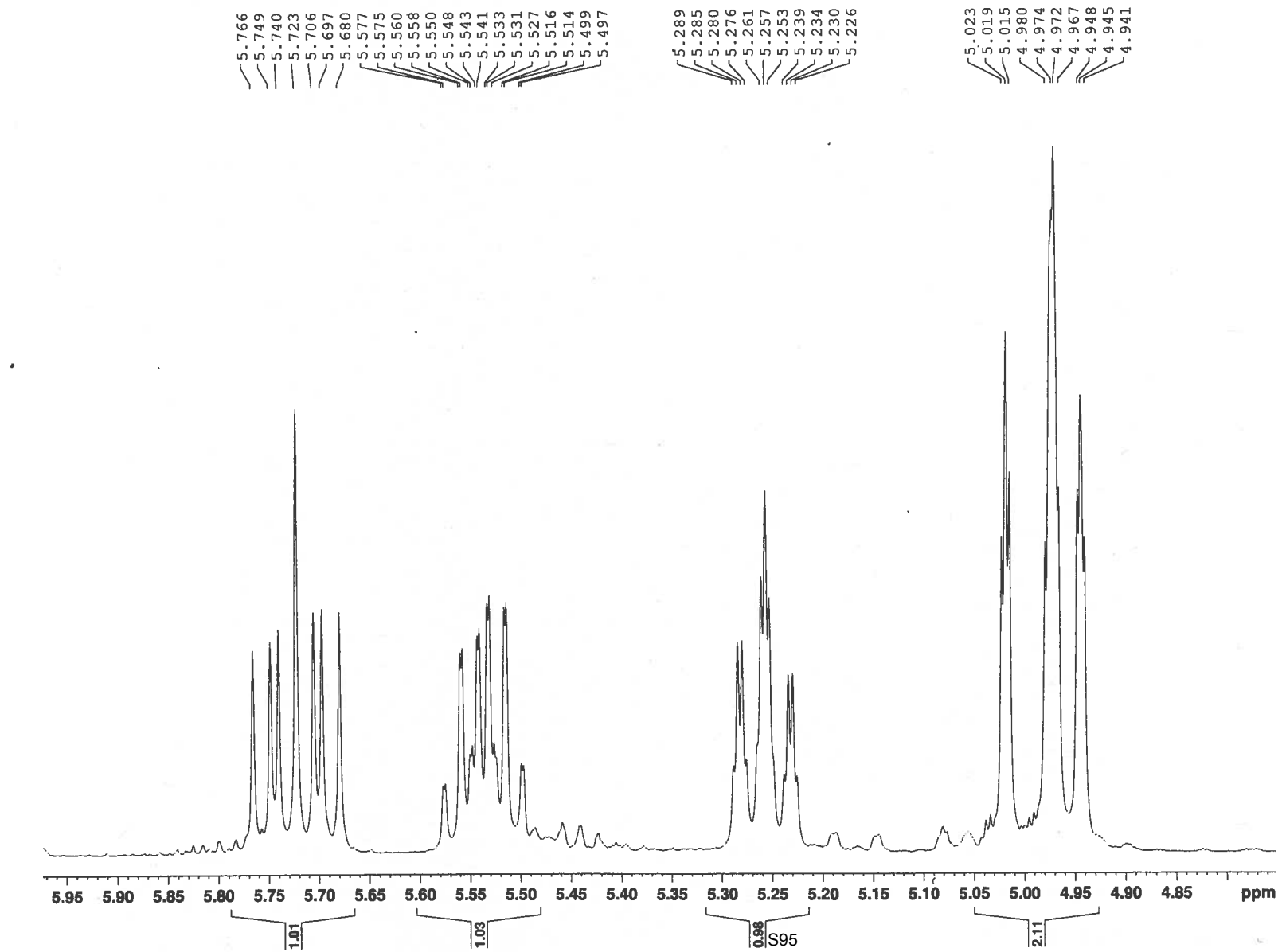
Proton NMR (400 MHz, D-Chloroform) spectrum of compound **13j** (HV using Cl2Co(DPPB(Alkene Region Expansion)

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Current Data Parameters
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EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
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Time                      19.17
INSTRUM                   spect
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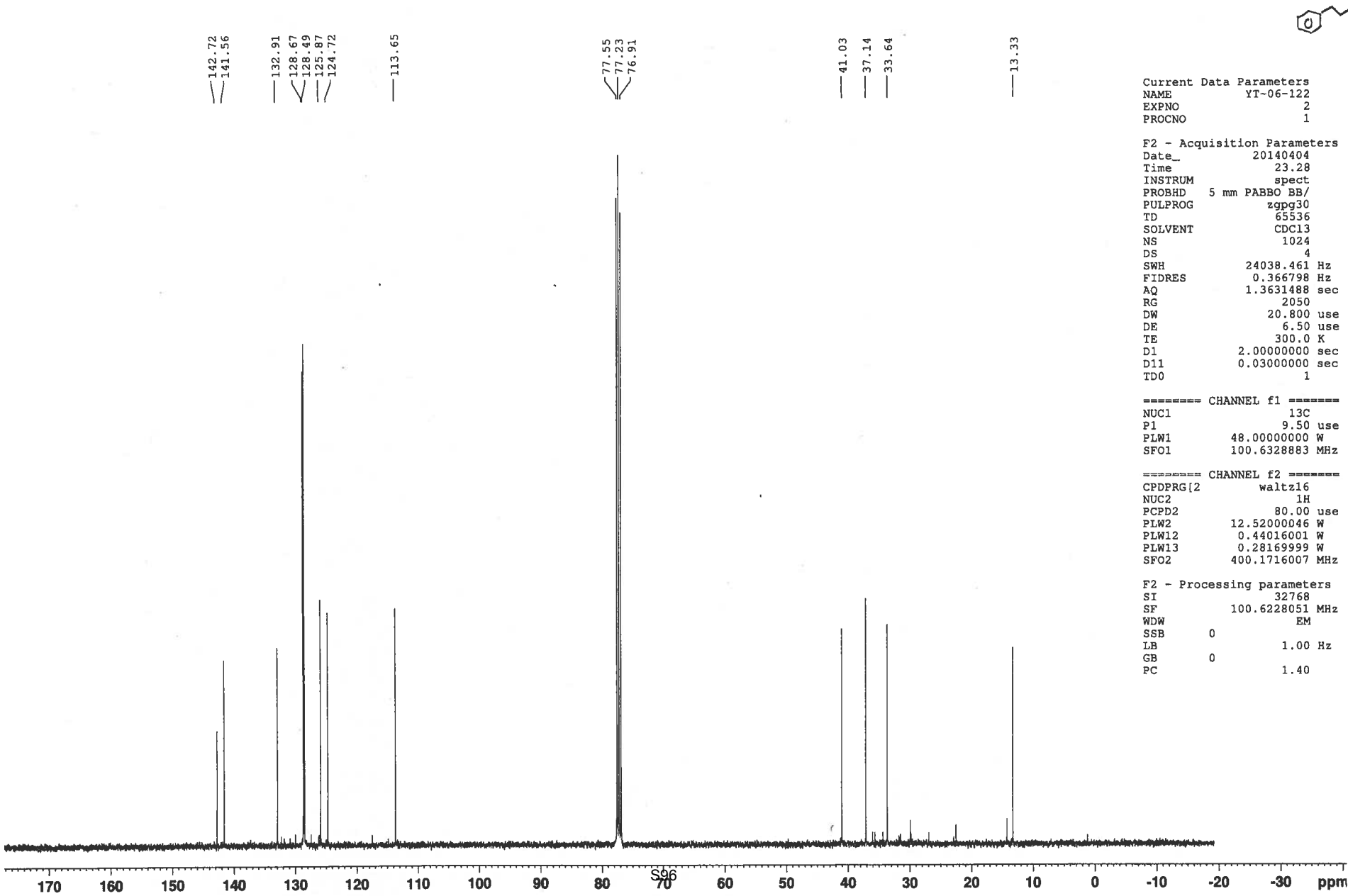
PULPROG                    zg30
TD                        65536
SOLVENT                   CDCl3
NS                           16
DS                            2
SWH                    8223.685 Hz
FIDRES                 0.125483 Hz
AQ                     3.9845889 sec
RG                       112.47
DW                       60.800 use
DE                        6.50 use
TE                       300.0 K
D1                    1.00000000 sec
TD0                           1

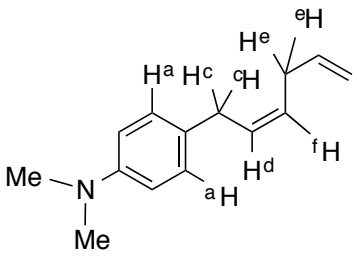
======== CHANNEL f1 =======
NUC1                         1H
P1                       15.00 use
PLW1             12.52000046 W
SFO1             400.1724712 MHz

F2 - Processing parameters
SI                        65536
SF               400.1700196 MHz
WDW                         EM
SSB          0
LB                        0.30 Hz
GB           0
PC                        1.00
```

Carbon NMR (400 MHz, D-chloroform) spectrum of compound 13j (HV using Cl2Co(DPPB)

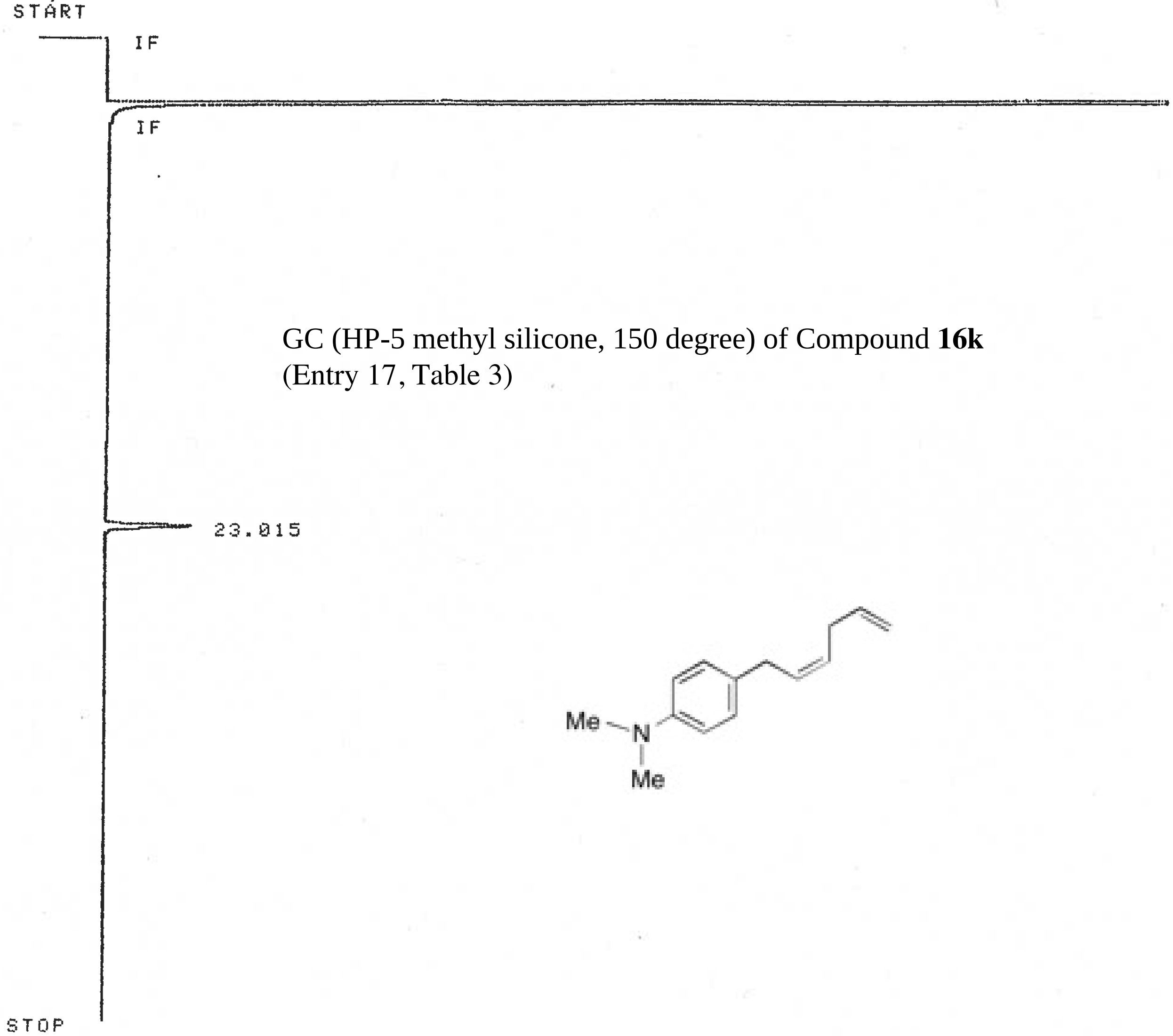


Hydrovinylation of (*E*)-4-(buta-1,3-dienyl)-*N*,*N*-dimethylaniline (12k)



Hydrovinylation of (*E*)-4-(buta-1,3-dienyl)-*N*,*N*-dimethylaniline using DPPBCoCl$_2$ (Table 3, Entry 17): To an oven dried round bottom flask with a sidearm, was added [DPPB]CoCl$_2$ (36 mg, 0.065 mmol) and methylaluminoxane (76 mg, 1.30 mmol) under argon. The color of the solution changed from deep blue to red brown with the formation of white fumes over the addition of dichloromethane solvent (1 mL). After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was kept at 0 ^{0}C and (*E*)-4-(buta-1,3-dienyl)-*N,N*-dimethylaniline (113 mg, 0.65 mmol) in dichloromethane (1 mL) added via syringe under ethylene and the mixture was stirred for 13 h at ambient temperature. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and diethyl ether (2 mL) and warmed to room temperature. After this, the reaction solution was subsequently passed through a silica plug. The plug was washed with diethyl ether (3 X 5 mL). Flash column chromatography with (5:1, hexane: ethyl acetate) yielded the product as yellowish oil (104 mg, 79%). GC and NMR analysis showed that the product (**16k**) was essentially pure. ^{1}H NMR (CDCl$_3$, 400 MHz): 2.91 (s, 6 H), 2.91 - 2.95 (overlap with 2.91) (m, 2 H), 3.32 (d, J = 7 Hz, 2 H), 5.01 (dq, J = 10, 1.6 Hz, 1 H), 5.09 (dq, J = 17, 1.6 Hz, 1 H), 5.47 - 5.54 (m, 1 H), 5.59 - 5.67 (m, 1 H), 5.86 (ddt, J = 17, 10, 6 Hz, 1 H), 6.72 (d, J = 8 Hz, 2 H, aromatic), 7.07 (d, J = 9 Hz, 2 H, aromatic).
^{13}C NMR (CDCl$_3$, 125.02 MHz): 31.71, 32.60, 41.25, 113.52, 114.99, 127.14, 129.15, 130.32, 137.13.
Gas Chromatography: Methylsilicone SP GC (OT 150 ^{o}C/ isothermal, He carrier gas): R_T for product = 23.02 min. R_T for starting material = 18.68 min. ESI-MS; m/z 202.1593 [M + H]; mass calculated for $C_{14}H_{20}N_1$, 202.1590.

* RUN # 165 MAR 1, 1901 00:09:44



GC (HP-5 methyl silicone, 150 degree) of Compound **16k** (Entry 17, Table 3)

RUN# 165 MAR 1, 1901 00:09:44

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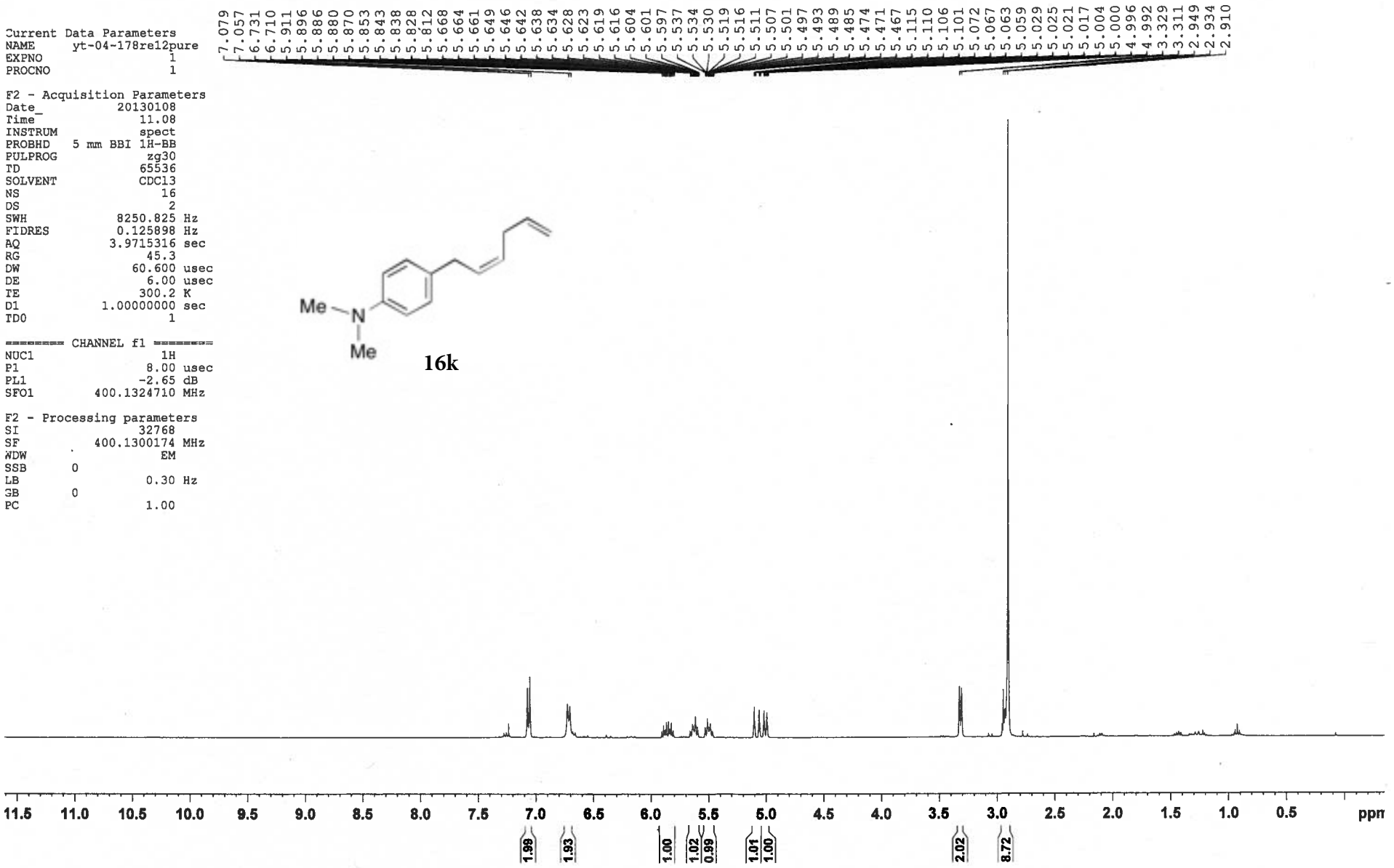

Proton NMR (400 MHz, D-Chloroform) Spectra of Compound **16k** (Entry 17, Table 3)

Proton NMR (400 MHz, D-chloroform) spectrum of compound **16k**

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EXPNO                    1
PROCNO                   1

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DS                     2
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FIDRES          0.125898 Hz
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TE                300.2 K
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TD0                    1

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PL1               -2.65 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
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WDW                   EM
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PC                 1.00
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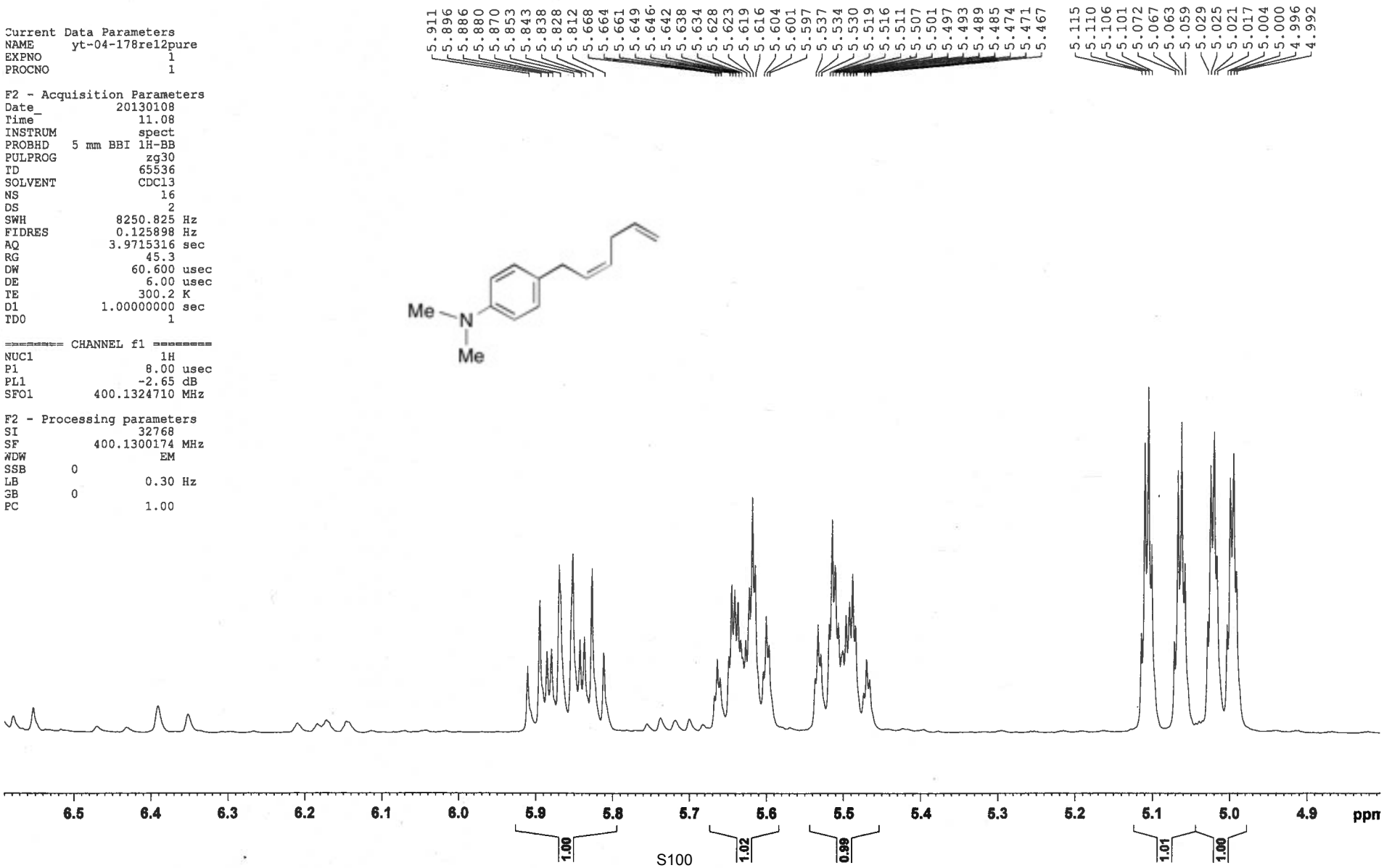
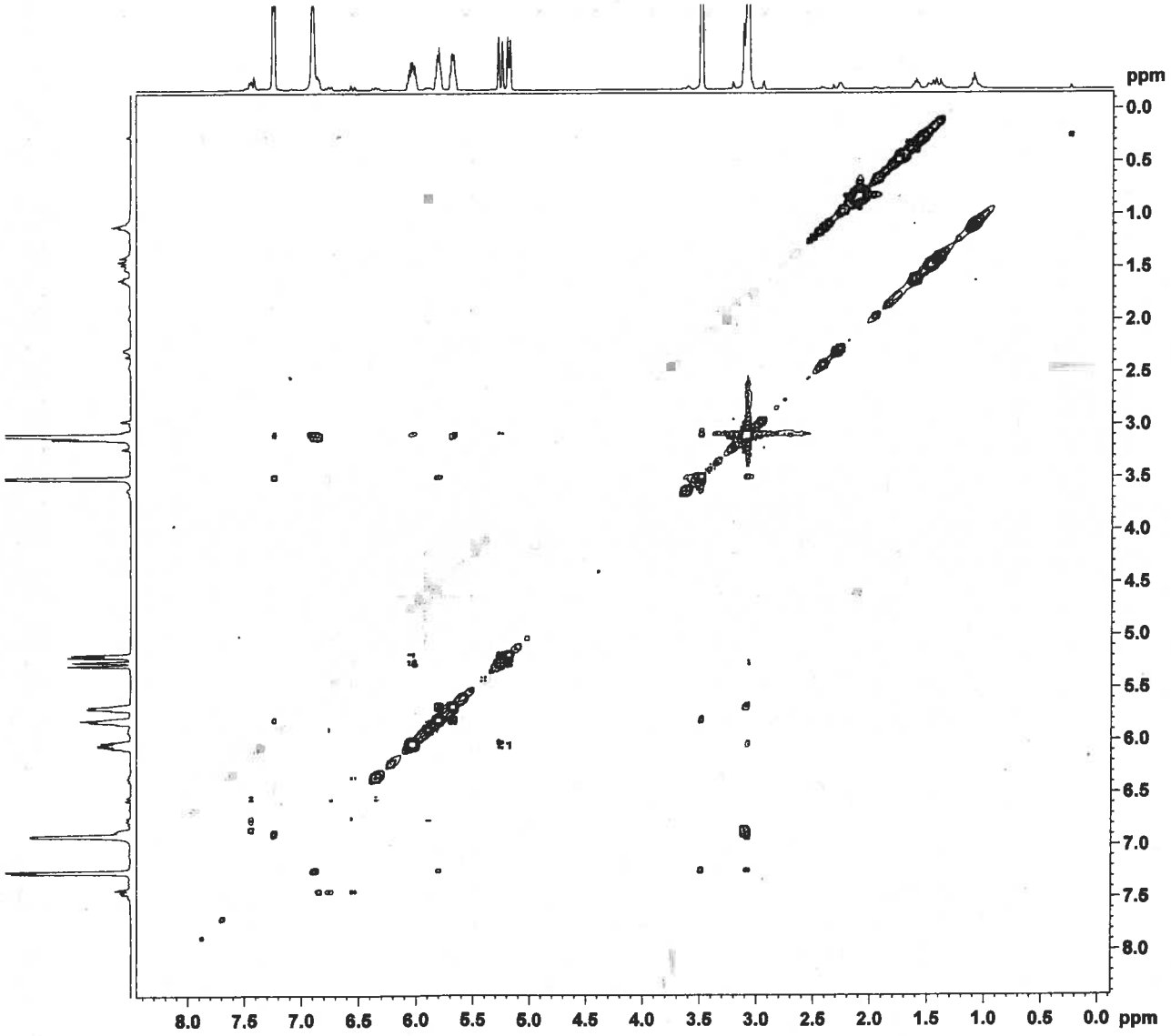
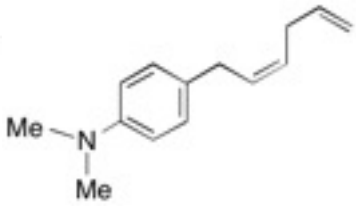
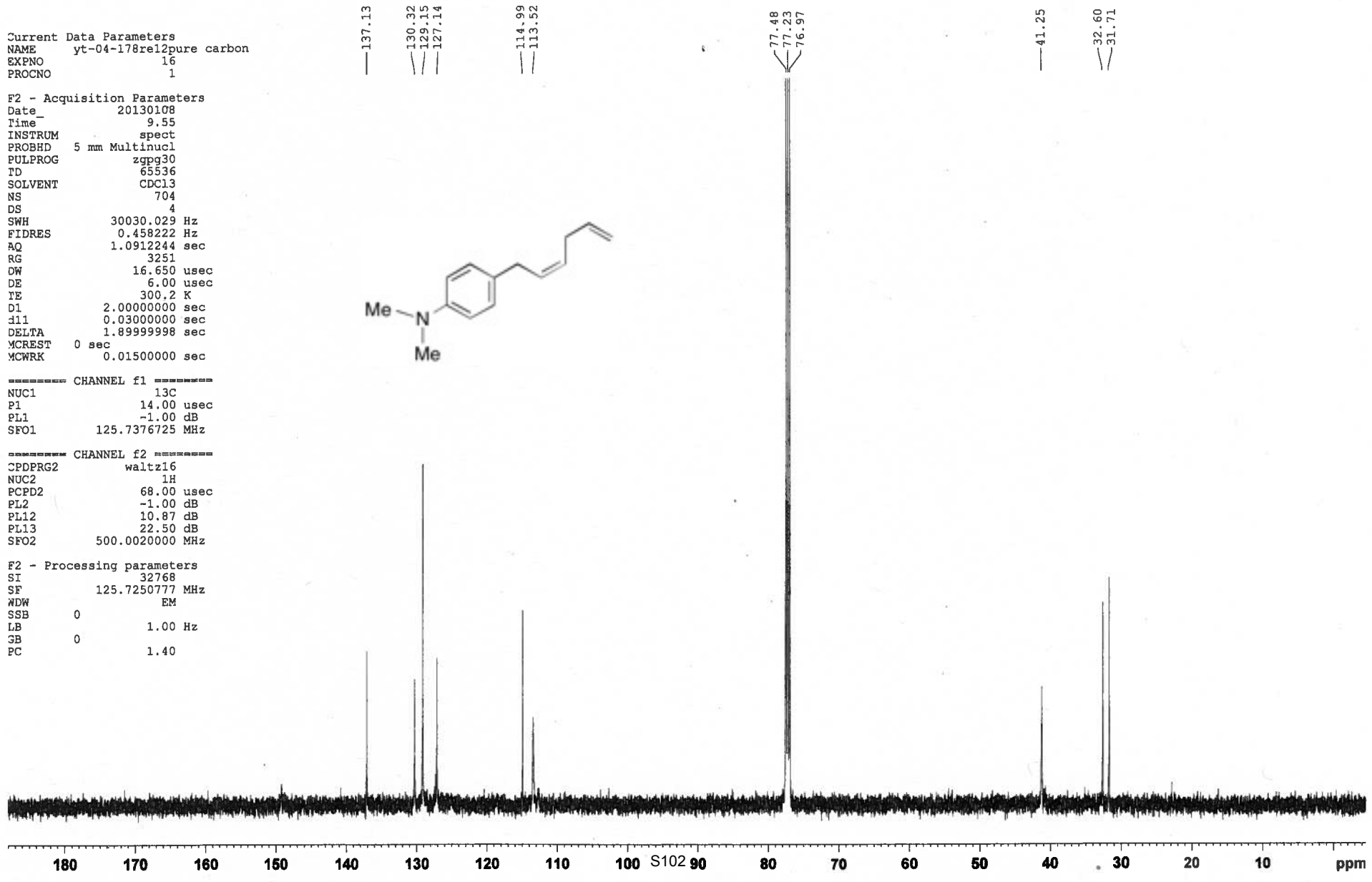




NOESY (500 MHz, D-chloroform) 2D spectrum of compound **16k**



Carbon NMR (125 MHz, D-Chloroform) Spectra of Compound **16k**

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EXPNO                 16
PROCNO                 1

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TD                65536
SOLVENT            CDCl3
NS                   704
DS                     4
SWH            30030.029 Hz
FIDRES         0.458222 Hz
AQ             1.0912244 sec
RG                  3251
DW                16.650 usec
DE                 6.00 usec
TE                300.2 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
MCREST   0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
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PL1               -1.00 dB
SFO1         125.7376725 MHz

======== CHANNEL f2 ========
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NUC2                1H
PCPD2             68.00 usec
PL2               -1.00 dB
PL12              10.87 dB
PL13              22.50 dB
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F2 - Processing parameters
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WDW                   EM
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GB       0
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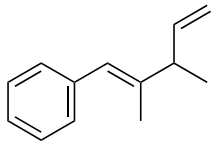
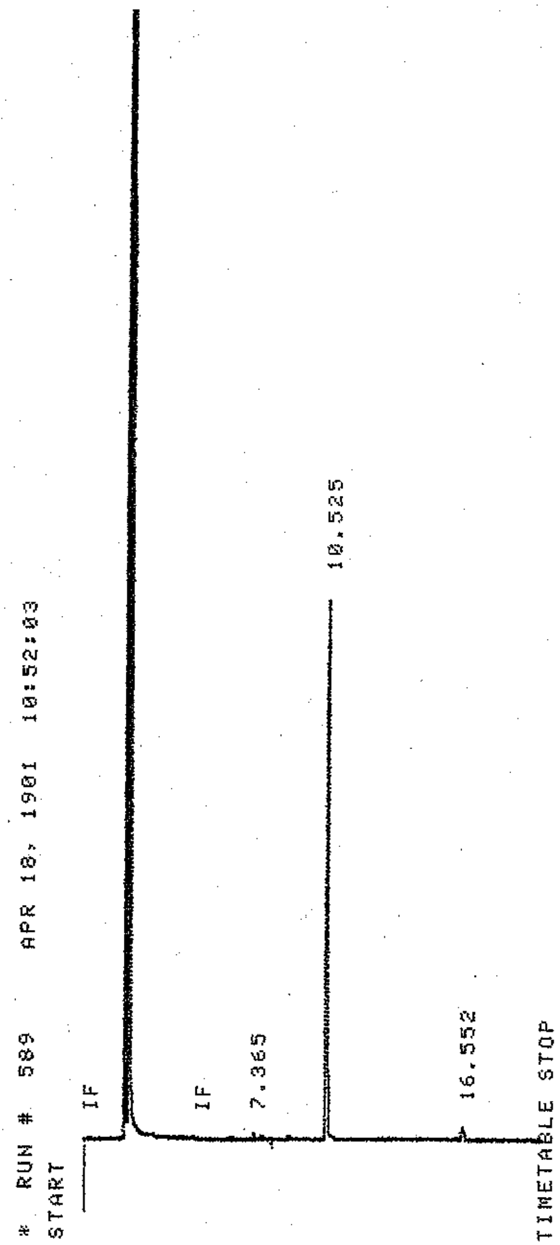
Hydrovinylation of (*E*)-1-phenyl-2-methyl-1,3-butadiene (12l)



Hydrovinylation of (*E*)-1-phenyl-2-methyl-1,3-butadiene using [dppm]$CoCl_2$ (Table 3, Entry 18 and 19). To an oven-dried 10 mL round-bottom flask with a sidearm, was added [dppm]$CoCl_2$ (35.6 mg, 0.0693 mmol) under argon and it was dissolved in a mixture of degassed dichloromethane (4.0 mL) and toluene (1 mL), at 0 ^oC. Trimethylaluminum solution (2M) in toluene (15.0 mg, 104 μl, 0.208 mmol) was added dropwise as color of the solution changed from green to brown with the formation of white fumes over the solution. When all the fumes disappeared, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The filled balloon was used to maintain the ethylene atmosphere, while a vigorous reaction with evolution of fumes was observed. This evolution stopped in typically within 5 min. The reaction vessel was cooled to -10 ^oC and (*E*)-2-methyl-1-phenyl-1,3-butadiene (100.0 mg, 0.6935 mmol) was added under ethylene and the mixture was stirred for 6 h (color of the reaction solution turned dark green again at the end of the reaction). The ethylene balloon was removed and 0.2 mL of methanol was introduced into the flask and stirring was continued for 5 minutes. The solution was warmed to room temperature and was subsequently passed through a silica plug. The plug was washed with hexane (3 X 20 mL). Concentration and removal of last traces of solvent yielded the product as a colorless oil (**15l**, 116.9 mg; 97 %). Isomeric compositions were determined by gas chromatography and NMR spectroscopy. ^1H NMR ($CDCl_3$, 500 MHz): 1.184 (d, 7 Hz, 3 H), 1.816 (dd, 1.5, 1.5, 3 H), 2.922 (m, 1 H), 5.044 (dm, 17 Hz, 1 H), 5.009 (dm, 12 Hz, 1 H), 6.295 (s, 1H), 5.842 (ddd, 17, 11, 1.5), 6.295 (s, 1 H), 7.10-7.30 (m, aromatic). NOESY: Ph*CH* —> C_{sp3}-CH_3, bis-allylic *CH*. ^{13}C NMR ($CDCl_3$): 15.72, 18.16, 46.88, 113.71, 124.61, 125.98, 128.05, 128.98, 138.61, 141.84, 142.31.

Since the HV product itself could not be separated on Cyclodex-B column, further derivatization was employed to prepare an alcohol, which was analyzed as the TMS ether. The hydrocarbon **15l** was subjected to hydroboration/oxidation using 9-BBN and the enantiomeric mixture of alcohols were converted into the corresponding –TMS ethers which were analyzed on Cyclodex-B column. The product was ascertained to be nearly racemic. Optical rotation measurements further confirmed these observations.



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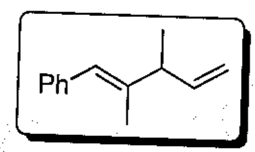
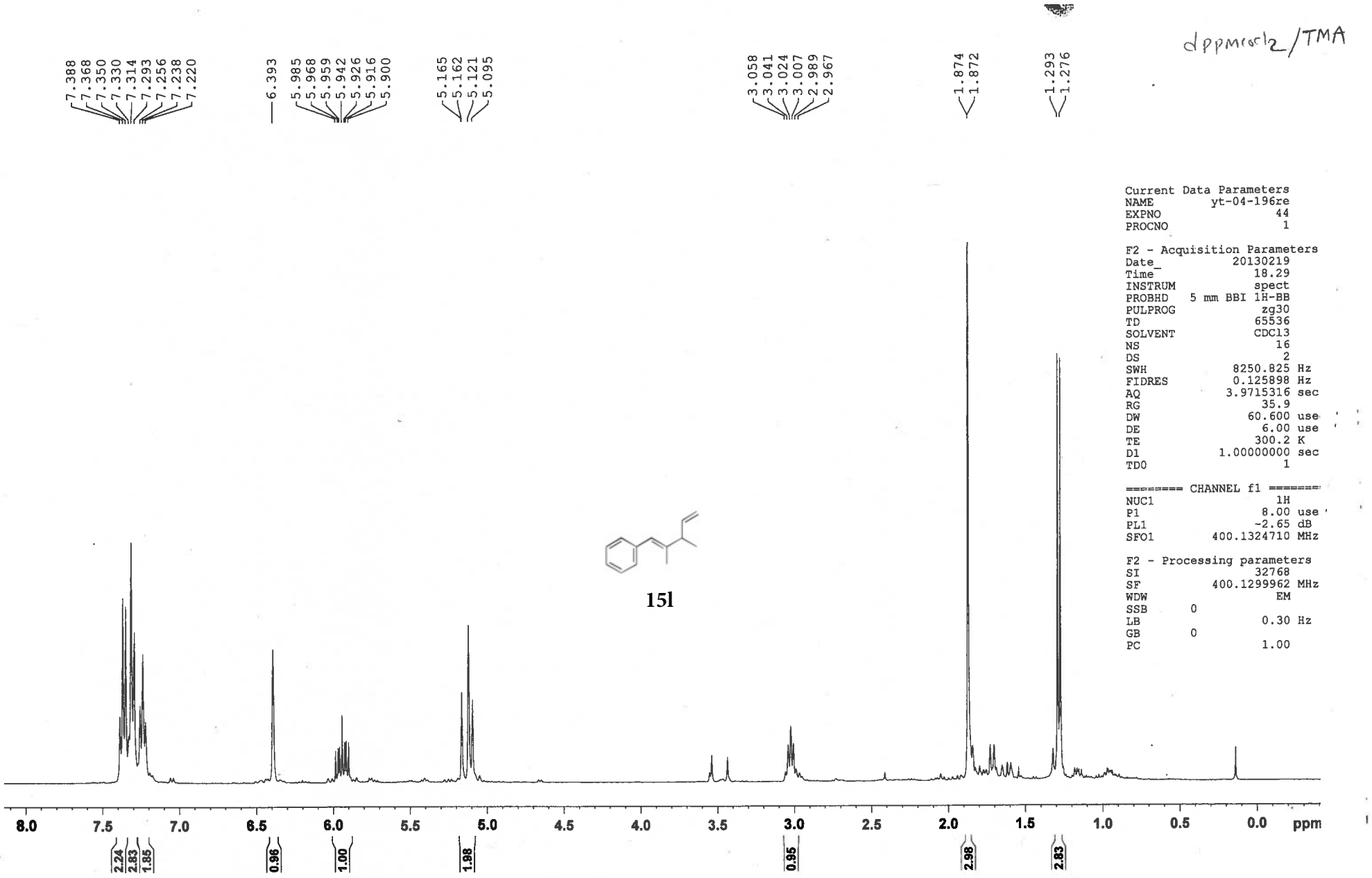
(Entry 18, Table 3)



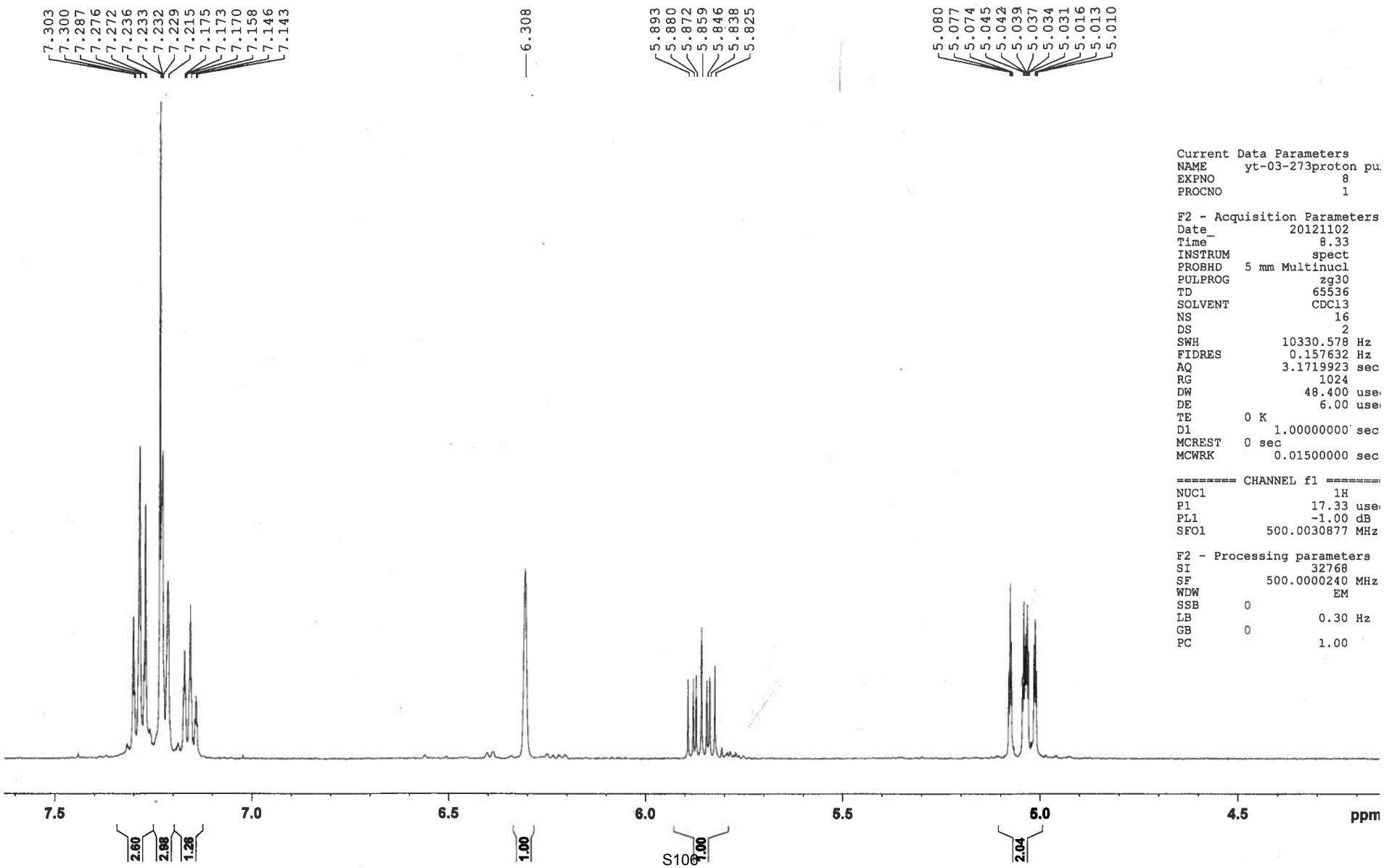
150°C
(Polydimethylsiloxane)

* *

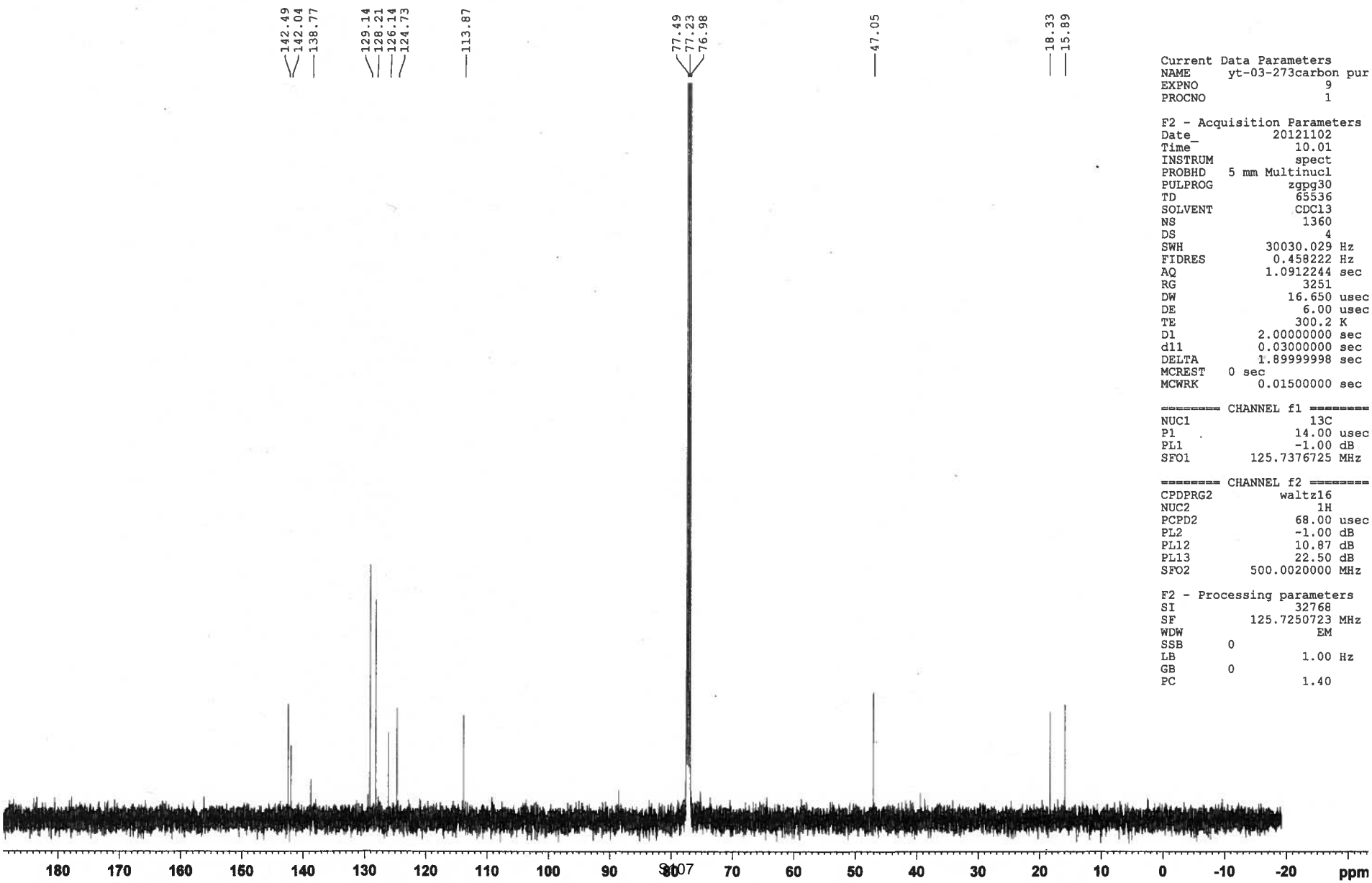


Proton NMR (400 MHz, D-chloroform) Spectra of compound **15l** (HV using Cl2Co(dppp) (Entry 19, Table 3)

Proton NMR (500 MHz, D-chloroform) Spectra of compound **15l** (Alkene Region)



Carbon NMR (125 MHz, D-Chloroform) of compound **15l** (Entry 19, Table 3)

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PROCNO                     1

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PULPROG              zgpg30
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DS                        4
SWH               30030.029 Hz
FIDRES             0.458222 Hz
AQ                1.0912244 sec
RG                     3251
DW                   16.650 usec
DE                    6.00 usec
TE                   300.2 K
D1              2.00000000 sec
d11             0.03000000 sec
DELTA           1.89999998 sec
MCREST    0 sec
MCWRK           0.01500000 sec

======== CHANNEL f1 ========
NUC1                    13C
P1                    14.00 usec
PL1                   -1.00 dB
SFO1          125.7376725 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                 68.00 usec
PL2                   -1.00 dB
PL12                  10.87 dB
PL13                  22.50 dB
SFO2          500.0020000 MHz

F2 - Processing parameters
SI                     32768
SF            125.7250723 MHz
WDW                       EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```

Hydrovinylation of 7-methyl-3-methyleneocta-1,6-diene (β-myrcene, 12m)

Hydrovinylation of (β-myrcene) using [dppp]$CoCl_2$ (Table 3, Entry 21). To an oven dried round bottom flask with a sidearm, was added [DPPP]$CoCl_2$ (49 mg, 0.090 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.14 mL, 0.27 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene from a balloon. The reaction vessel was kept at room temperature and 7-methyl-3-methyleneocta-1,6-diene (0.15 mL, 0.90 mmol) added under ethylene and the mixture was stirred for 1 h. The ethylene balloon was removed and 0.1 mL of methanol was added to the flask. The reaction solution was diluted with pentane (2 mL) and subsequently passed through a silica plug. The plug was washed with pentane (3 x 5 mL). Removal of solvent yielded the product as colorless oil (123 mg, 83%). GC and NMR analysis showed that the product (**16m**) was essentially pure. ^{1}H NMR ($CDCl_3$, 400MHz): 1.57 – 1.58 (m, 6 H), 1.66 (s, 3 H), 1.95 – 2.07 (m, 4 H), 2.77 (d, J = 6.4 Hz, 2 H), 4.94 - 5.04 (m, 2 H), 5.06 - 5.09 (m, 1 H), 5.28 (q, J = 7 Hz, 1 H), 5.68 - 5.78 (m, 1 H). NOESY: H_g ---> H_h, H_i; H_f ---> H_e, H_d; H_e ---> H_f, H_c; H_d ---> H_f, H_c. ^{13}C NMR ($CDCl_3$, 125.02 MHz): 13.43, 17.90, 25.92, 26.99, 34.81, 37.29, 115.11, 119.85, 124.59, 131.60, 136.38, 137.76. Gas Chromatography: CSP GC (Cyclosil, OT 100 ^{o}C/ isothermal, H_2 carrier gas) starting material R_t = 6.571 min. R_T for product = 9.954 min. The following table shows the additional experiments conducted by using β-myrcene employing 10 mol % catalyst and trimethylaluminium as an activator. The isomeric product has not been identified.

Entry	Catalyst	Temp(^{o}C)/Time(h)	Conv.(%)	Product
1.	[DPPM]$CoCl_2$	rt/4	71%	(55%) isomer(3%)
2.	[DPPE]$CoCl_2$	-20/3	8%	8%
3.	[DPPB]$CoCl_2$	-20/4	91%	(82%)+ iso(9%)
4.	(*SS*)-[DIOP]$CoCl_2$	-20/7	91%	(62%) +iso(15%)
5.	(*SS*)-[BDPP]$CoCl_2$	-20/7	94%	(36%)+ iso(57%)

Data File C:\CHEM32\1\DATA\YAM\YT-04-194MYRO.D
Sample Name: YT-04-194MYRO

dppp/-20°c/4hrs.

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==========================================================================
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Acq. Instrument : Babu                              Location : Vial 201
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                                                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method      : C:\CHEM32\1\METHODS\YT_ISO120_CYCLODEX-B.M
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                   (modified after loading)
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Last changed     : 11/28/2012 4:43:57 PM by Kendra Dewese
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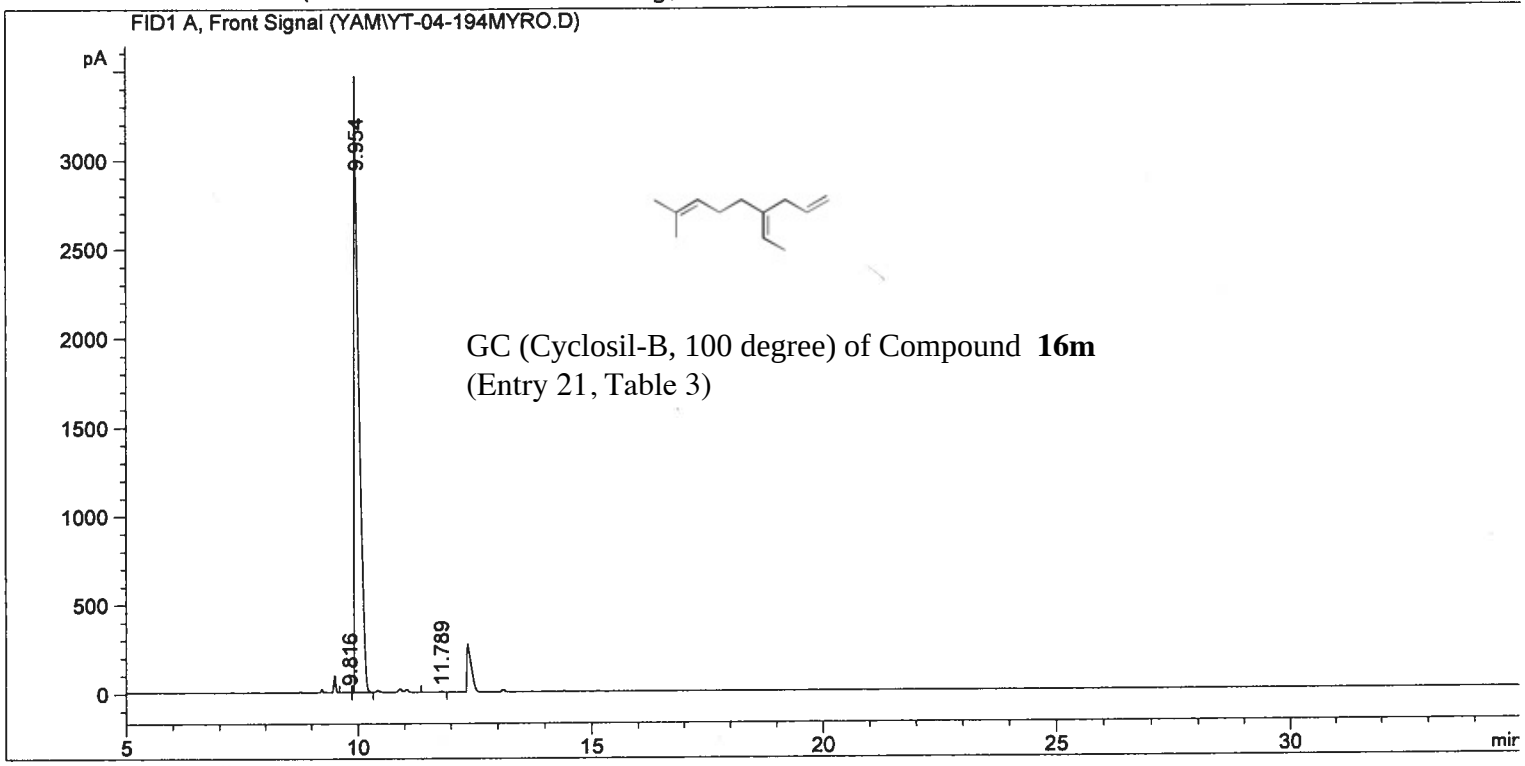

GC (Cyclosil-B, 100 degree) of Compound **16m** (Entry 21, Table 3)

```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   9.816 VV    0.0948   37.49633    5.54818  0.15672
   2   9.954 VV    0.1119 2.38449e4  2900.67920 99.66528
   3  11.789 BV    0.1006   42.58645    6.35175  0.17800

Totals :                  2.39250e4  2912.57913
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Proton NMR (400 MHz, D-chloroform) spectra of compound **16m**
(Entry 21, Table 3)

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PROCNO                 1

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FIDRES         0.125898 Hz
AQ             3.9715316 sec
RG                101.6
DW               60.600 usec
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TE                300.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
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PL1              -2.65 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
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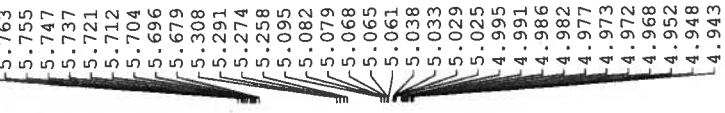
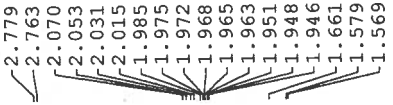
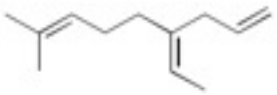




dppcacl2/TMA/β-myr



16m

Proton NMR (400 MHz, D-chloroform) spectra of compound **16m** (Expansion)

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EXPNO                   73
PROCNO                   1

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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH               8250.825 Hz
FIDRES            0.125898 Hz
AQ                3.9715316 sec
RG                   101.6
DW                  60.600 usec
DE                    6.00 usec
TE                   300.2 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                   8.00 usec
PL1                 -2.65 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
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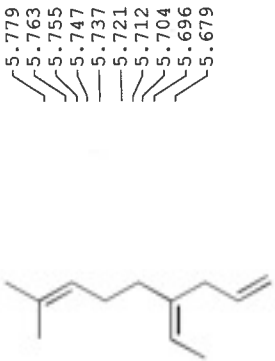
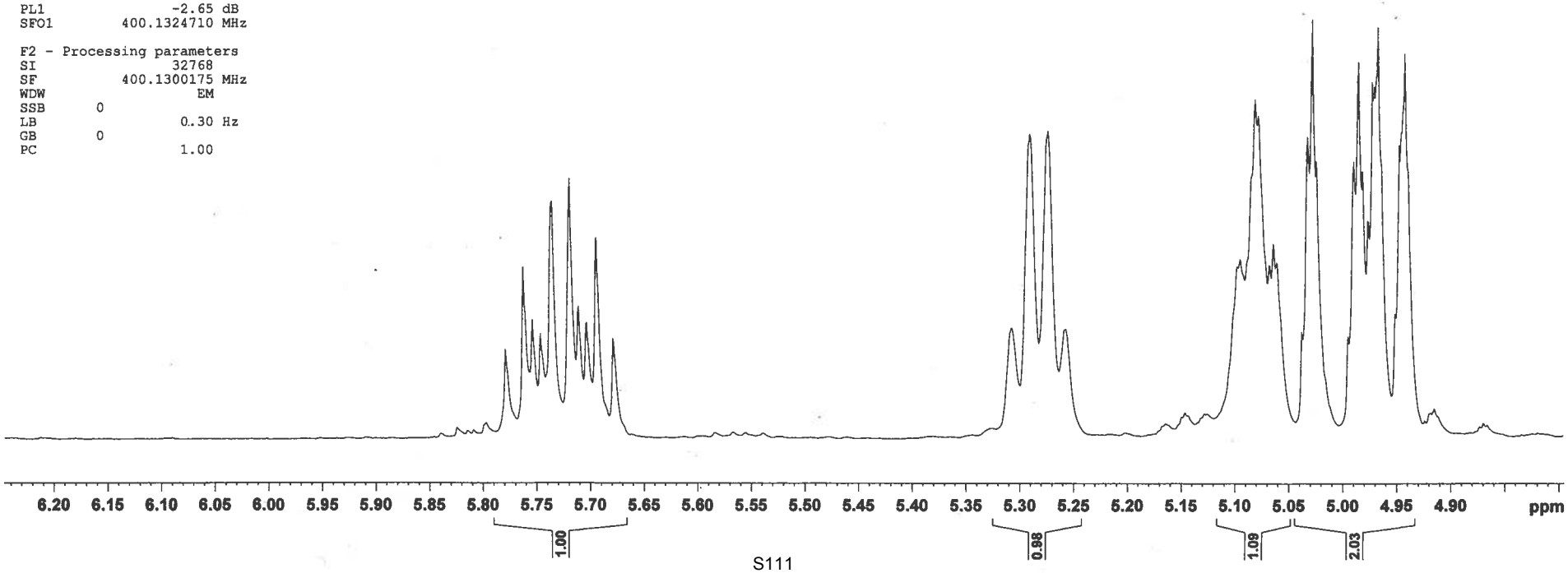
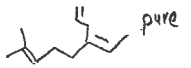
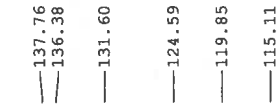




Carbon NMR (125 MHz, D-chloroform) spectra of compound **16m**



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PROCNO                 1

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TD                65536
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DS                    4
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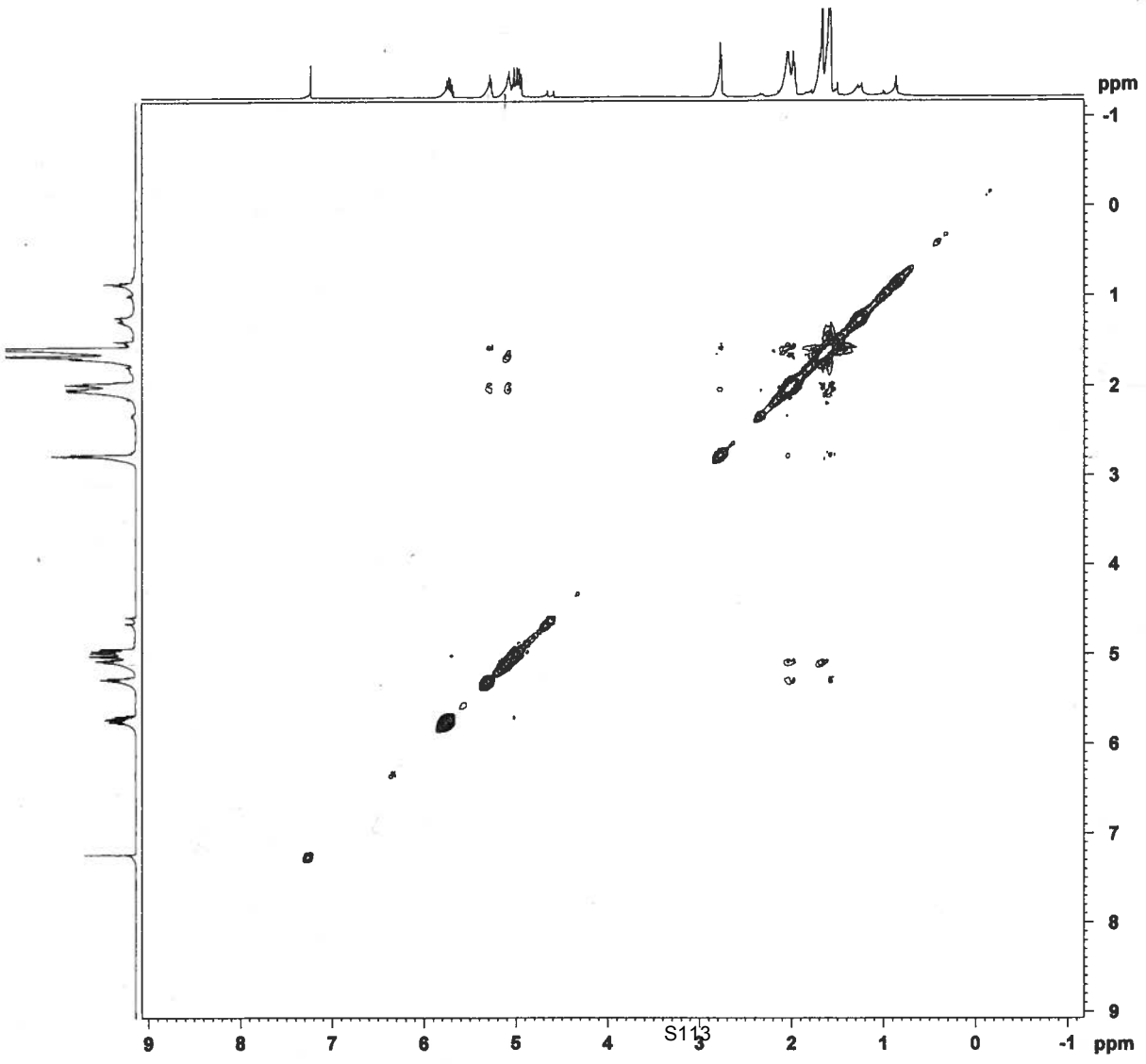
FIDRES         0.458222 Hz
AQ             1.0912244 sec
RG                3649.1
DW                16.650 usec
DE                 6.00 usec
TE                295.2 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                13C
P1                14.00 usec
PL1               -1.00 dB
SFO1         125.7376725 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2             68.00 usec
PL2               -1.00 dB
PL12              10.87 dB
PL13              22.50 dB
SFO2         500.0020000 MHz

F2 - Processing parameters
SI                 32768
SF           125.7250747 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

NOESY (500 MHz, D-chloroform) 2D spectra of compound **16m**

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Current Data Parameters
NAME      yt-04-193,67noe
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20130109
Time               14.46
INSTRUM            spect
PROBHD  5 mm Multinucl
PULPROG       noesygpph
TD                 2048
SOLVENT            CDCl3
NS                    4
DS                   16
SWH             5122.951 Hz
FIDRES          2.501441 Hz
AQ              0.1999348 sec
RG                   256
DW                97.600 usec
DE                 6.00 usec
TE                300.2 K
d0             0.00007553 sec
D1             2.00000000 sec
D8             2.00000000 sec
D16            0.00020000 sec
IN0            0.00019520 sec
MCREST   0 sec
MCWRK          2.00000000 sec
TAU            0.99879998 sec

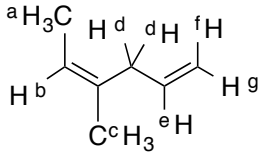
======== CHANNEL f1 ========
NUC1                   1H
P1                 17.33 usec
P2                 34.66 usec
PL1                -1.00 dB
SFO1         500.0020000 MHz

====== GRADIENT CHANNEL =====
GPNAM1           SINE.100
GPNAM2           SINE.100
GPX1      0 %
GPX2      0 %
GPY1      0 %
GPY2      0 %
GPZ1               40.00 %
GPZ2              -40.00 %
P16              1000.00 usec

F1 - Acquisition parameters
TD                   248
SFO1           500.002 MHz
FIDRES        20.657061 Hz
SW               10.246 ppm
FnMODE              TPPI

F2 - Processing parameters
SI                  1024
SF           500.0000259 MHz
WDW                 QSINE
SSB                     2
LB        0 Hz
GB        0
PC                  1.00

F1 - Processing parameters
SI                  1024
MC2                 TPPI
SF           500.0000259 MHz
WDW                   TR
SSB                     2
LB        0 Hz
GB        0
```



Hydrovinylation of Isoprene using [dppp]$CoCl_2$ (Table 3, Entry 22): To an oven dried round bottom flask with a sidearm, was added [dppp]$CoCl_2$ (50 mg, 0.092 mmol) dissolved in dichloromethane (1 mL) at room temperature. Trimethylaluminium as a 2M solution in toluene (0.14 mL, 0.28 mmol) was added dropwise and the color of the solution changed from deep blue to red brown with the formation of white fumes over the solution. After 2 to 3 minutes, the reaction vessel was carefully evacuated and then refilled with ethylene balloon. The reaction vessel was cooled to -20 ^{o}C and isoprene (63 mg, 0.92 mmol) added under ethylene and the mixture was stirred for 4 h. The ethylene balloon was removed and 0.1 mL methanol was added into the flask. The reaction solution was diluted with pentane (2 mL) and warmed to room temperature and subsequently passed through a silica plug very quickly. The plug was washed with pentane (3 x 5 mL). Removal of solvent was difficult due to high volatility of the product so GC and NMR analysis showed that the product was essentially pure (**16n**).

^{1}H NMR ($CDCl_3$, 400 MHz): 1.64 (d, J = 6.8 Hz, 3 H, H^a), 1.73 (m, 3 H, H^c), 2.83 (d, J = 6.4 Hz, 2 H, H^d ??), 5.02 (dm, J = 10 Hz, 1 H, H^g), 5.08 (dm, J = 17 Hz, 1 H, H^f), 5.35 (qm, J = 6.8 Hz, 1 H, H^b), 5.79 (ddt, J = 6, 10, 17 Hz, 1 H, H^e). ^{13}C NMR ($CDCl_3$, 125.02 MHz): 13.31, 23.50, 36.47, 115.09, 120.20, 134.04, 136.16.

Gas Chromatography: Methylsilicone SP GC (OT 35 ^{o}C/ isothermal, He carrier gas) R_T for product = 5.14 min. CSP GC (Cyclosil, OT 50 ^{o}C/ isothermal, H_2 carrier gas). R_T for product = 16.89 min.

Data File C:\CHEM32\1\DATA\YAM\YT-04-202A.D
Sample Name: YT-04-202A

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==========================================================================
Acq. Operator    : YAM
Acq. Instrument : Babu                                Location : Vial 201
Injection Date  : 11/28/2012 10:33:22 AM
                                                   Inj Volume : 1 µl
Different Inj Volume from Sequence !     Actual Inj Volume : 3 µl
Acq. Method      : C:\CHEM32\1\METHODS\YT_ISO120_CYCLODEX-B.M
Last changed     : 11/28/2012 10:31:30 AM by YAM
                   (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\YT_ISO120_CYCLODEX-B.M
Last changed     : 11/28/2012 11:27:32 AM by YAM
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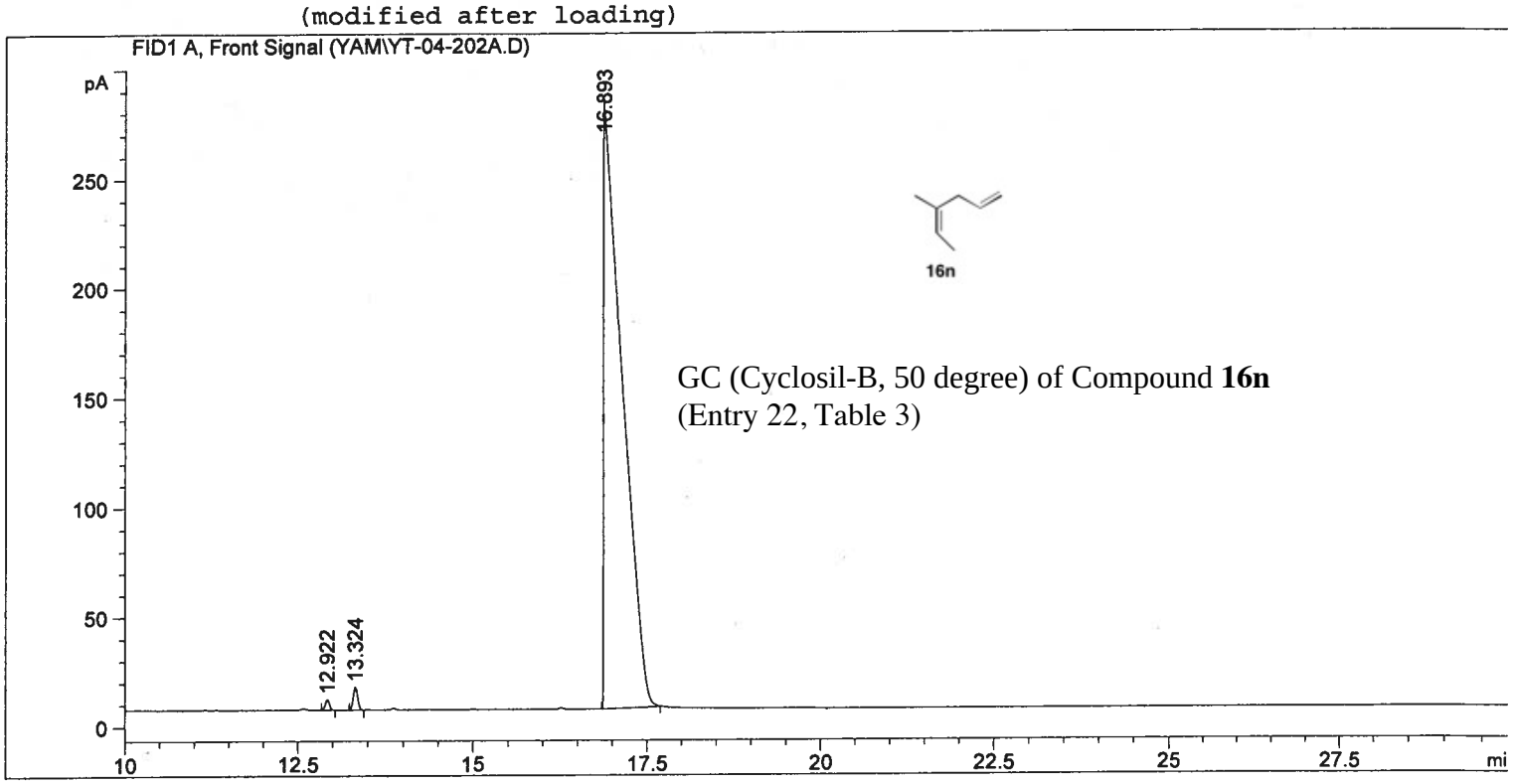


GC (Cyclosil-B, 50 degree) of Compound **16n** (Entry 22, Table 3)

```
==========================================================================
                          Area Percent Report
==========================================================================

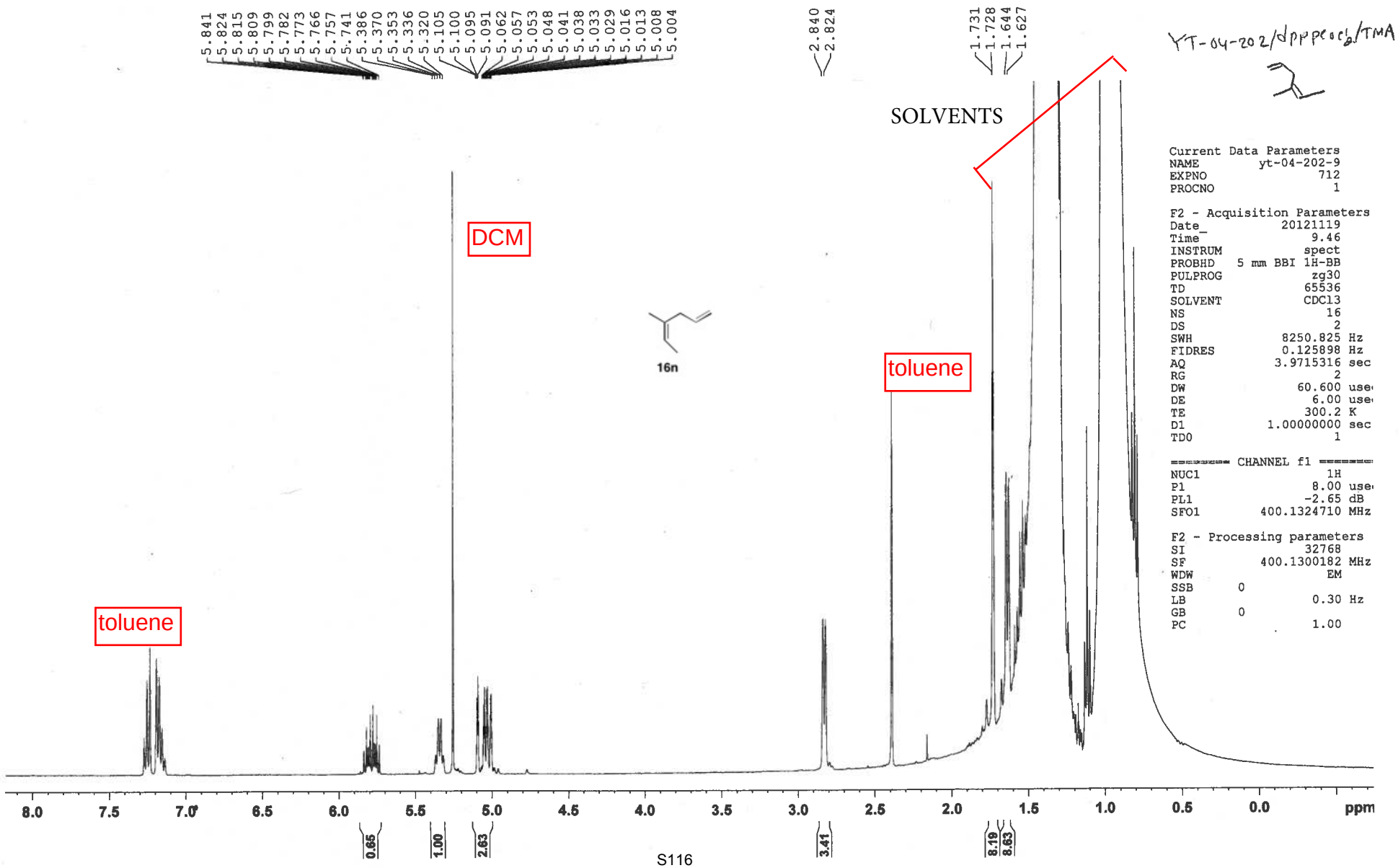
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

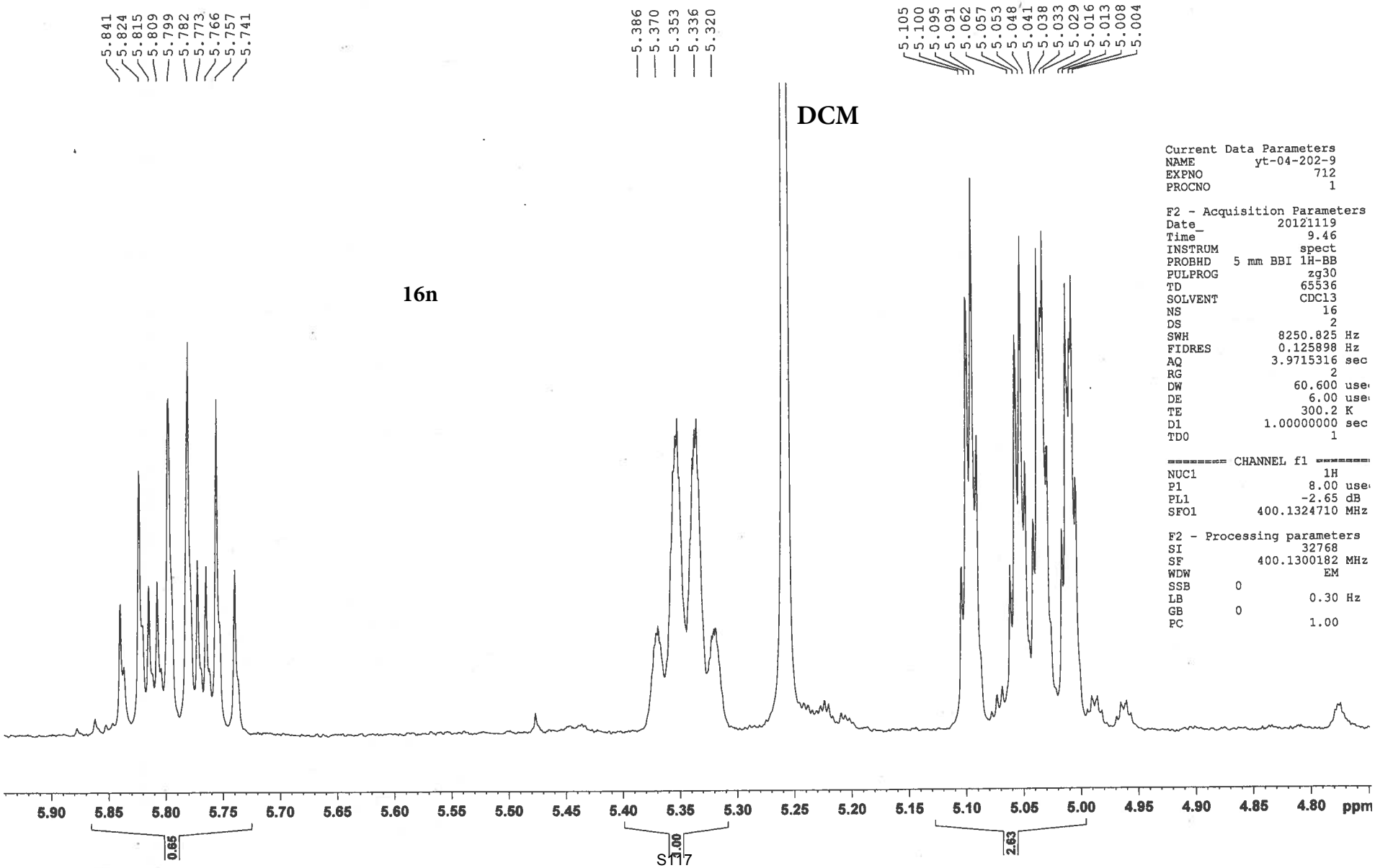
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  12.922 BB    0.0647   20.02247    4.79711  0.38776
   2  13.324 BB    0.0674   44.62691   10.29189  0.86425
   3  16.893 BB    0.2242 5099.00146  277.23431 98.74799

Totals :                  5163.65084  292.32332
```

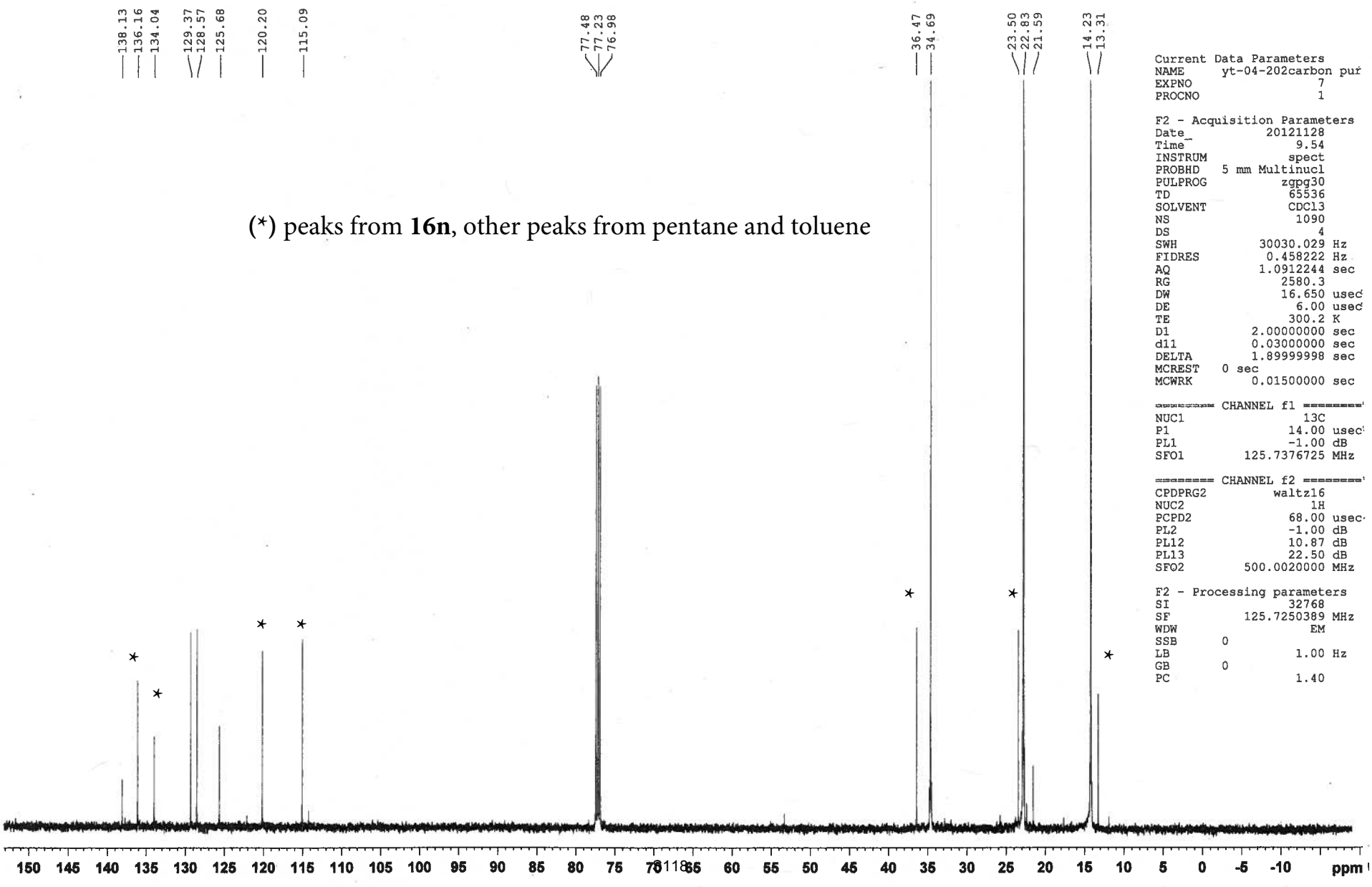
Proton NMR (400 MHz, D-chloroform) spectra of compound 16n HV of isoprene using Cl2Co(dppp) {Entry 22, Table 3)



Proton NMR (400 MHz, D-Chloroform) Spectra of Compound 16n (Expansion of Alkene Region)



Carbon NMR (125 MHz, D-chloroform) spectra of **16n** Cl2Co(DPPP) complex with solvent toulene and pentane



(*) peaks from **16n**, other peaks from pentane and toluene

References

1. Grutters, M. M. P.; Mueller, C.; Vogt, D. *J. Am. Chem. Soc.* 2006, **128**, 7414.
2. Sharma, R. K.; RajanBabu, T. V., *J. Am. Chem. Soc.* 2010**, 132**, 3295.
3. (a) Reddy, S. S.; Radhakrishnan, K.; Sivaram, S. *Polymer Bulletin* 1996, **36**, 165-171. (b) Sangokya, S. A. Preparation of Methylaluminoxanes. U.S. Patent 5,248,801, Sep 28, 1993.
4. **13f:** Ehlers, J.; König, W. A.; Lutz, S.; Wenz, G.; tom Dieck, H. *Angew. Chem. Int. Ed. Engl*. 1988, **27**, 1556.
5. Blumberg, L. C.; Costa, B.; Goldstein, R. T*etrahedron Lett.* 2011, **52**, 872.
6. House, H. O.; Rasmusson, G. H. *J. Org.Chem.* 1961, **26**, 4278.
7. Piers, E.; Jung, G. L.; Ruediger, E. H. *Can. J. Chem.* 1987, **65**, 670.
8. Hoye, T. R.; Magee, A. S.; Trumper, W. S. *Synthetic Communications* 1982, **12**, 183.
9. Martin, S. F.; Tu, C.; Chou, T. *J. Am. Chem. Soc.* 1980, **102**, 5274.
10. Ikeda, Y.; Ukai, J.; Ikeda, N.; Yamamoto, H. *Tetrahedron* 1987, **43**, 723.
11. Wang, Y.; West, F. G. *Synthesis* 2002, 99.