Supporting Information for

Substrate-Dependent Stereochemical Course of the (*Z*)-13 Desaturation Catalyzed by the Processionary Moth Multifunctional Desaturase

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Experimental Section

General Methods. All commercially available chemicals and solvents were used without further purification as supplied with the following exceptions: dimethylformamide (DMF) and hexamethylphosphotriamide (HMPA) were distilled and kept over molecular sieves (3Å), diethyl ether and tetrahydrofuran (THF) were distilled over Na/benzophenone under inert atmosphere. All moisture- and air-sensitive reactions were carried out under a dry nitrogen or argon atmosphere with dry reagents and solvents in flame-dried round bottom flasks. All the organic extracts obtained from workup of crude reaction mixtures were dried over $MgSO_4$, filtered and concentrated with a rotatory evaporator under reduced pressure. *C. antarctica* lipase type B (CALB) was supplied as an immobilized preparation on a macroporous acrylic resin. Adsorption of *T. lanuginosus* lipase onto polypropylene support (EP100) was carried out following the methodology described by Gitlesen et al.[1] The activity of both immobilized lipase preparations was measured by use of the acylation of 1-dodecanol in organic media.[2] Purification procedures were carried out by flash chromatography on silica gel (230-400 mesh) using compressed air, and most of the products were obtained as oils. Melting points (mp) were determined in soft glass capillary tubes and are uncorrected. Elemental analyses were conventional combustion analyses without discrimination between hydrogen and deuterium contents. $LiAlD_4$ and D_2 Deuterium content were 98% and 99.8%, respectively. Analytical thin layer chromatography (TLC) was performed using 0.2 mm silica gel coated Kieselgel 60 F_{254} plates. Visualization of UV-inactive materials was accomplished by soaking the TLC plates in ethanolic solution of anisaldehyde and sulfuric acid (v/v/v, 96:2:2) or in ethanolic solution of phosphomolybdic acid (5%). Unless otherwise stated, most of ^1H NMR spectra were acquired at 500 MHz, and ^{13}C NMR spectra, at 125 MHz in freshly neutralized $CDCl_3$ solutions, and chemical shifts are quoted in parts per million (ppm) on the δ scale downfield from $Si(CH_3)_4$ for ^1H, and $CDCl_3$ for ^{13}C. GC/MS analysis was performed by chemical ionization (CI) using methane as ionization gas. All IR spectra were run in film. Optical rotations were measured at 25º in $CHCl_3$ solution at the specified concentration

(g/100 mL). Enantiomeric and diasteromeric excesses (ee and de) values were calculated by HPLC or NMR analysis of the corresponding (*R*)-(-)-MPA or (*R*)-(-)-9-AMA diastereomeric esters.

$BrCH_2(CH_2)_4CH_2OMOM$ was prepared from 1,6-hexandiol in two steps on a multigram scale according a previously reported method.[3]

Preparation of alkynol 2. To a mixture of 3-butyn-1-ol (5.6 g, 80 mmol), 80 ml of dry HMPA and 100 ml of THF was added dropwise a solution of butyllitium (2.4 M) in hexanes (75 mL, 180 mmol) at –15º C. The resulting pale red mixture was stirred for 10 min and a solution of $BrCH_2(CH_2)_4CH_2OMOM$ (9 g, 40 mmol) in 20 mL of THF was added dropwise at that temperature. Stirring was continued for 4 h at 0^{o}C and then allowed to warm up to ambient temperature and stirred for another 12 h. The reaction mixture was poured into satd $NaHCO_3$ aqueous solution (200 ml) and extracted with hexane (3 x 150 ml). Solvent was evaporated and the residue purified by flash chromatography on silica gel using a gradient hexane/MTBE (0-35%) to afford 6.7 g of the expected alkynol **2** in 78% yield.

11,13-dioxatetradec-4-yn-1-ol (2). IR 3420, 2935, 2860, 1725, 1460, 1440, 1145, 1110, 1045, 920 cm $^{-1}$; ^{1}H NMR δ 4.62 (s, 2H), 3.68 (t, *J* = 6.0 Hz, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H), 2.43 (m, 2H), 2.17 (m, 2H), 2.03 (bb, 1H), 1.60 (m, 2H), 1.51 (m, 2H), 1.45-1.34 (ca, 4H); ^{13}C NMR δ 96.3 (CH_2), 82.4 (C), 76.4 (C), 67.7 (CH_2), 61.3 (CH_2), 55.0 (CH_3), 29.5 (CH_2), 28.8 (CH_2), 28.6 (CH_2), 25.7 (CH_2), 23.1 (CH_2), 18.6 (CH_2); MS m/z 183 (100, $M^{\bullet+}$-CH_3O), 165 (55), 151 (20), 135 (30), 121 (35), 109 (50), 97 (50), 83 (60); Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.26; H, 10.35. Found: C, 67.25; H, 10.32.

Deuteration of alkynol 2. To a mixture of 6.45 g (30 mmol) of alkynol **2** and 0.93 g (1 mmol) of Wilkinson catalyst,[4] 200 mL of degassed benzene was added under argon atmosphere to afford a reddish solution. The system was purged by a combination of vacuum and passing a D_2 stream throughout it, then D_2 atmosphere was kept from a balloon and the solution was stirred for 48 h. The mixture was filtered through a bed of Celite and the solvent evaporated. The residue was purified by flash chromatography on silica gel (0-3% MTBE/hexane) to give 5.06 g (75% yield) of the saturated tetradeuterated alcohol **3** after the eluent evaporation.

[3,3,4,4-$^2H_4$]-11,13-dioxatetradecan-1-ol (3). IR 3420, 2925, 2855, 2185, 2095, 1460, 1150, 1110, 1050, 920 cm $^{-1}$; ^{1}H NMR δ 4.62 (s, 2H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H), 1.63-1.51 (4H), 1.40-1.20 (8H); ^{13}C NMR δ 96.2 (CH_2), 67.8 (CH_2), 62.8 (CH_2), 55.0 (CH_3), 32.4 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.3 (CD_2, quint, *J* = 19 Hz), 26.1 (CH_2), 24.6 (CD_2, quint, *J* = 19 Hz); MS m/z 191 (100, $M^{\bullet+}$-CH_3O), 161 (55), 151 (20), 141 (40); Anal. Calcd for $C_{12}H_{22}{}^2H_4O_3$: C, 64.82; H, 11.79. Found: C, 64.82; H, 11.62.

Preparation of 1-Bromoalkane 4. This reaction was accomplished according to the procedure described by Bates et al[5] with some modifications. A solution of NBS (26 mmol, 4.63 g in 18 mL of DMF) was added dropwise at 0 ºC to a stirred DMF solution (30 mL) containing 4.44 g (20 mmol) of the tetradeuterated alcohol and 6.84 g (26 mmol) of triphenylphosphine. Stirring was continued until TLC showed absence of starting material (ca. 1 h). The reaction was quenched by addition of 5 mL of methanol to the resulting pale

yellow mixture. After 5 minutes, ethyl ether was added, the organic layer washed with brine and carefully evaporated to dryness. Residue was purified by flash chromatography on silica gel using hexane (alkanes mixture) as eluent to obtain 4.50 g (79% yield) of the tetradeuterated bromide after solvent evaporation.

[3,3,4,4-$^2H_4$]-1-Bromo-11,13-dioxatetradecane (4). IR 2925, 2855, 2190, 2095, 1460, 1440, 1280, 1215, 1145, 1110, 1050, 920 cm $^{-1}$; ^{1}H NMR δ 4.62 (s, 2H), 3.52 (t, *J* = 6.5 Hz, 4H), 3.41 (t, *J* = 6.5 Hz, 4H), 3.36 (s, 3H), 1.83 (t, J_1 = 7 Hz, 2H), 1.59 (m, 2H), 1.42-1.24 (ca, 8H); ^{13}C NMR δ 96.2 (CH_2), 67.6 (CH_2), 54.9 (CH_3), 33.8 (CH_2), 32.4 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.0 (CH_2), 27.6 (CD_2, quint, *J* = 19 Hz), 27.0 (CD_2, quint, *J* = 19 Hz), 26.1 (CH_2); MS m/z 287 (7, $M^{\bullet+}$+1), 285 (9, $M^{\bullet+}$+1), 255 (45), 253 (50), 225 (40), 223 (55), 173 (100), 155 (40), 141 (25), 123 (15), 111 (75), 97 (50). Calcd for $C_{12}H_{21}{}^2H_4BrO_2$: C, 50.53; H, 8.87. Found: C, 50.52; H, 8.92.

Kinetic enzymatic resolution of alkynols 5. Reactions were performed in 250 ml sealed round bottom flasks. To a mixture of the racemic alkynol 12 g (101 mmol) and inmobilized lipase type B from *C. antarctica* (**5a**; 1 g , **5b**; 2.2 g) in 120 mL of diisopropyl ether was added vinyl acetate (17 mL, 180 mmol). The resulting mixture was reciprocally shaken (125 rpm) at ambient temperature until GC analysis showed a 45% conversion. The chilled suspension was filtered off, the solid washed with diethyl ether and the solvent was carefully distilled to give a residue that was purified by column chromatography on silica gel. A gradient of diethyl ether in pentane (0-30%) and a careful distillation of the eluent allowed the separation of the corresponding acetate (**(*S*)-(-)-6a**; 86% ee, (**(*R*)-(+)-6b**; 76% ee) from the complementary enantiomerically enriched alkynol (**(*R*)-(+)-6a**; 80% ee, (**(*S*)-(+)-6b**; 76% ee). Acetate hydrolysis and a second chemoenzymatic resolution (**a**; 80% conversion, **b**; 70% conversion) afforded the enantiomerically pure acetates **6**.

(*S*)-(-)-3-Acetoxy-1-hexyne (6a). In this case, after both consecutive resolutions 4.2 g were obtained (29%) with 98% ee. IR 3295, 2965, 2935, 2875, 1745 (CO), 1450, 1375, 1235, 1020 cm $^{-1}$; ^{1}H NMR δ 5.36 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 1H), 2.45 (d, *J* = 2 Hz, 1H), 2.09 (s, 3H), 1.82-1.70 (2H), 1.53-1.38 (2H), 0.95 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 170.0 (CO), 81.3 (C), 73.3 (CH), 63.6, 36.5 (CH_2), 21.0 (CH_3), 18.2 (CH_2), 13.9 (CH_3); MS m/z 141 (15, $M^{\bullet+}$+1), 99 (100); Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H 8.63, Found: C; 68.47 H, 8.65; $[\alpha]_D$= -110.8 (c 1, $CHCl_3$, 96% ee).

(*R*)-(+)-3-Acetoxy-5-hexyne (6b) In this case, after both consecutive resolutions 3.1 g were obtained (22%) with 96% ee. IR 3300, 2965, 2940, 2885, 1730 (CO), 1460, 1430, 1375, 1235, 1020 cm $^{-1}$; ^{1}H NMR δ 4.88 (m, 1H), 2.48 (m, 2H), 2.08 (s, 3H), 2.00 (t, *J* = 2.5 Hz, 1H), 1.82-1.64 (2H), 0.93 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR δ 170.6 (CO), 79.6 (C), 72.8 (CH), 70.2 (CH), 25.8 (CH_2), 23.3 (CH_2), 21.0 (CH_3), 9.4 (CH_3); MS m/z 141 (75, $M^{\bullet+}$+1), 101 (100); Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H 8.63, Found: C; 68.49 H, 8.55; $[\alpha]_D$= +62.0 (c 1, $CHCl_3$, 94% ee).

Acetate Saponification. Enantiomerically pure alcohols **5** were obtained by treatment of the corresponding acetoxy derivatives **6** (0.1 mmol/mL) with a mixture of K_2CO_3 in MeOH (20 mg/mL). Reaction evolution was monitored by TLC (16 h) and then the reaction mixture was neutralized with HCl (2 N), extracted with ethyl ether and the resulting solvent

mixture distilled. The final residue was purified by column chromatography (silica gel, pentane:diethyl ether 7:3) yielding the oily pure alkynols after eluent elimination.

(*S*)-(-)-1-Hexyn-3-ol ((*S*)-(-)-5a). This compound was isolated (2.45 g, 85% yield) starting from 4.20 g of acetate $[\alpha]_D$= -15.2 (c 1, $CHCl_3$, 96% ee); **(*R*)-(-)-5-Hexyn-3-ol ((*R*)-(-)-5b),** This compound was isolated (1.82 g, 81% yield) starting from 3.20 g of acetate $[\alpha]_D$= -4.0 (c 1, $CHCl_3$, 94% ee).

Preparation of alkynols 7. Coupling of alkynol **5** with bromoderivative **4** was similarly performed by the above described procedure for the preparation of compound **2**. Thus, to a solution of the corresponding enantiomerically resolved or enriched alkynol **5** (16 mmol) dissolved in 25 ml of dry HMPA and 25 ml of THF was added dropwise a solution of butyllitium (2.5 M) in hexanes (15 mL, 37.5 mmol) at –15º C. The resulting mixture was stirred for 10 min and a solution of **4** ($BrCH_2CH_2CD_2CD_2(CH_2)_6OMOM$) (2.30 g, 8 mmol) in 5 mL of THF was added dropwise at that temperature. Stirring was continued for 6 h at 0^{o}C and then 10 h at room temperature. The reaction mixture was then poured into satd. $NaHCO_3$ (100 ml) and extracted with hexane (3 x 60 ml). Solvent was evaporated and the residue purified by flash chromatography on silica gel using a gradient hexane/MTBE (0-35%) to give the expected alkynols **7** with high yields.

[9,9,10,10-$^2H_4$]-17,19-dioxa-5-icosyn-4-ol (7a). IR 3455, 2930, 2860, 2190, 2095, 1460, 1150, 1110, 1045, 920 cm $^{-1}$; ^{1}H NMR δ 4.62 (s, 2H), 4.36 (m, 1H), 3.52 (t, *J* = 7 Hz, 2H), 3.36 (s, 3H), 2.19 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 2H), 1.74 (bs, 1H), 1.72-1.54 (4H), 1.54-1.40 (4H), 1.40-1.18 (10H), 0.95 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 85.4 (C), 81.3 (C), 67.8 (CH_2), 62.4 (CH), 55.0 (CH_3), 40.3 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.4 (CH_2), 28.1 (CD_2, quint, *J* = 19 Hz), 28.0 (CD_2, quint, *J* = 19 Hz), 26.2 (CH_2), 18.6 (CH_2), 18.5 (CH_2), 13.7 (CH_3); MS m/z (CI) 285 ($M^{\bullet+}$+1–H_2O, 15), 269 (10), 253 (100), 241 (50), 151 (15), 139 (22), 125 (20), 111 (20), 97 (25);. Anal. Calcd for $C_{18}H_{30}{}^2H_4O_3$: C, 71.47; H, 11.34 Found: C, 71.54; H, 11.37.

(*S*)-(-)-7a. This compound was obtained (2.10 g, 87% yield) from enantiomerically pure alkynol **(*S*)-(-)-5a** $[\alpha]_D$= -4.0 (c 2, $CHCl_3$, 96% ee).
Enantiomerically enriched **(*R*)-(+)-7a**. This compound was obtained (1.91 g, 79% yield) from enantiomerically enriched alkynol **(*R*)-(+)-5a** in 90% yield $[\alpha]_D$= +3.0 (c 2, $CHCl_3$, 76% ee).

[9,9,10,10-$^2H_4$]-17,19-dioxa-5-icosyn-3-ol (7b). IR 3475, 2930, 2855, 2185, 2095, 1455, 1150, 1110, 1040, 920 cm $^{-1}$; ^{1}H NMR δ 4.62 (s, 2H), 3.62 (m, 1H), 3.52 (t, *J* = 7 Hz, 2H), 3.36 (s, 3H), 2.41 (m, 1H), 2.27 (m, 1H), 2.20-2.13 (m, 2H), 1.98 (d, *J* = 4.5 Hz, 1H) 1.62-1.51 (4H), 1.47 (t, *J* = 7 Hz, 2H), 1.40-1.22 (10H), 0.96 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 83.0 (C), 76.0 (C), 71.4 (CH), 67.8 (CH_2), 55.0 (CH_3), 29.7 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 28.2 (CD_2, quint, *J* = 19 Hz), 28.0 (CD_2, quint, *J* = 19 Hz), 27.2 (CH_2), 26.1 (CH_2), 18.6 (CH_2), 9.8 (CH_3); MS m/z 285 ($M^{\bullet+}$+1–H_2O, 4), 271 (100), 253 (40), 241 (20), 213 (25), 195 (10), 181 (5), 167 (10), 153 (15), 139 (15), 125 (20), 111 (20), 97 (20);. Anal. Calcd for $C_{18}H_{30}{}^2H_4O_3$: C, 71.47; H, 11.34 Found: C, 71.45; H, 11.58.
(*R*)-(-)-7b. This compound was obtained (1.71 g, 71% yield) from enantiomerically pure alkynol **(*R*)-(-)-5b**; $[\alpha]_D$= -4.0 (c 2, $CHCl_3$, 94% ee).

Enantiomerically enriched **(*S*)-(+)-7b**. This compound was obtained (1.76 g, 73% yield) from enantiomerically enriched alkynol **(*S*)-(+)-5b**; $[\alpha]_D$= +2.5 (c 2, $CHCl_3$, 76% ee).

Kinetic enzymatic resolution of enantiomerically enriched alkynols (*R*)-(+)-7a and **(*S*)-(+)-7b.** In this case, resolutions were performed using inmobilized lipase from *Thermomyces lanuginosus* (TL) in 250 ml sealed round bottom flasks. To a mixture of the corresponding enantiomerically enriched alcohol **7** (4 mmol) and inmobilized lipase (EP100, 5 g) in 100 mL of diisopropyl ether was added vinyl acetate (0.74 mL, 8 mmol). The resulting mixture was reciprocally shaken (125 rpm) at room temperature. The reaction evolution was followed by GC and quenched according to the initial enantiomeric excess. The suspension was filtered off, the solid support washed with Et_2O and the solvent was evaporated under vacuum to give a residue that was purified by column chromatography on silica gel. A gradient of MTBE in hexane (0-30%) allowed the separation of the formed acetate **8** from the residual alcohol **7**.

(*R*)-(+)-[9,9,10,10-$^2H_4$]-4-Acetoxy-17,19-dioxa-5-icosyne ((*R*)-(+)-8a). This acetate was obtained as an enantiomerically pure compound (1.10 g, 78% yield, 82% conversion) starting from 1.21 g (4 mmol) of alkynol **(*R*)-(+)-7a**; IR 2930, 2855, 2190, 2100, 1740, 1460, 1370, 1225, 1150, 1105, 1045, 915 cm $^{-1}$; ^{1}H NMR δ 5.36 (tt, J_1 = 7 Hz, J_2 = 2 Hz, 1H), 4.62 (s, 2H), 3.52 (t, J = 6.5 Hz, 2H), 3.36 (s, 3H), 2.19 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 2H), 2.07 (s, 3H), 1.71 (m, 2H), 1.59 (m, 2H), 1.52-1.40 (m, 4H), 1.40-1.20 (m, 8H), 0.94 (t, J = 7 Hz, 3H); ^{13}C NMR δ 169.8 (CO), 96.3 (CH_2), 86.0 (C), 77.6 (C), 67.7 (CH_2), 64.3 (CH), 54.9 (CH_3), 37.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.0 (CH_2), 28.1 (CH_2), 28.0 (CD_2, quint, J = 19 Hz), 27.9 (CD_2, quint, J = 19 Hz), 26.1 (CH_2), 20.9 (CH_3), 18.5 (CH_2), 18.2 (CH_2), 13.5 (CH_3); MS m/z 345 ($M^{\bullet+}$+1, 2), 343 ($M^{\bullet+}$-1, 3), 313 (5), 285 (15), 271 (10), 253 (100), 235 (15), 165 (25), 151 (20), 137 (25), 123 (30), 109 (25), 95 (15). Anal. Calcd for $C_{20}H_{32}{}^2H_4O_4$: C, 69.72; H, 10.54 Found: C 69.41; H, 10.66; $[\alpha]_D$= +58.0 (c 2, $CHCl_3$, 98% ee).

(*S*)-(+)-[9,9,10,10-$^2H_4$]-17,19-dioxa-5-icosyn-3-ol (*S*)-(+)-7b. This alkynol was obtained enantiomerically pure (0.82 g, 68% yield) starting from alkynol **(*S*)-(+)-7b** (60% of initial ee) after a 30% enzymatic conversion to the unwanted acetate. IR 3475, 2930, 2855, 2185, 2095, 1455, 1150, 1110, 1040, 920 cm $^{-1}$; ^{1}H NMR δ 4.62 (s, 2H), 3.62 (m, 1H), 3.52 (t, J = 7 Hz, 2H), 3.36 (s, 3H), 2.41 (m, 1H), 2.27 (m, 1H), 2.20-2.13 (m, 2H), 1.98 (d, J = 4.5 Hz, 1H) 1.62-1.51 (4H), 1.47 (t, J = 7 Hz, 2H), 1.40-1.22 (10H), 0.96 (t, J = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 83.0 (C), 76.0 (C), 71.4 (CH), 67.8 (CH_2), 55.0 (CH_3), 29.7 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 28.7 (CH_2), 28.2 (CD_2, quint, J = 19 Hz), 28.0 (CD_2, quint, J = 19 Hz), 27.2 (CH_2), 26.1 (CH_2), 18.6 (CH_2), 9.8 (CH_3); MS m/z 285 ($M^{\bullet+}$+1–H_2O, 4), 271 (100), 253 (40), 241 (20), 213 (25), 195 (10), 181 (5), 167 (10), 153 (15), 139 (15), 125 (20), 111 (20), 97 (20);. Anal. Calcd for $C_{18}H_{30}{}^2H_4O_3$: C, 71.47; H, 11.34 Found: C, 71.45; H, 11.58; $[\alpha]_D$= +4 (c 2, $CHCl_3$, 94% ee).

Acetate Saponification of (*R*)-(+)-8a. Alkynol **(*R*)-(+)-7a** (1.03 g, 3 mmol) was obtained by treatment of acetate **(*R*)-(+)-8a** with a mixture of K_2CO_3 in MeOH (250 mg/10 mL) for 16 h. Neutralization with HCl (1 N), followed by the usual work up and purification by flash chromatography on silica gel according the above conditions allowed obtaining the pure alcohol in high yields. **(*R*)-(+)-7a** (0.81 g, 90%); $[\alpha]_D$= +4.0 (c 2, 96% ee).

Hydrogenation of methoxymethane protected alkynols 8. General Procedure.

To a mixture of alkynol **7** (0.76 g, 2,5 mmol) and 275 mg (0.3 mmol) of $RhCl(PPh_3)_3$, was added 15 mL of degassed benzene. The reaction mixture was purged passing a stream of H_2 through, then H_2 atmosphere was kept from the balloon and the solution was stirred for 48 h. The mixture was filtered through a bed of Celite and the solvent was evaporated. The residue was purified by flash chromatography on silica gel (0-30% MTBE/hexane) to give the pure stereoisomer **9** (64-86% yields).

[9,9,10,10-$^2H_4$]-17,19-dioxaicosan-4-ol (9a). IR 3440, 2930, 2850, 2185, 2090, 1460, 1150, 1110, 1045, 915 cm^{-1}; ^1H NMR δ 4.62 (s, 2H), 3.59 (m, 1H), 3.52 (t, *J* = 7 Hz, 2H), 3.36 (s, 3H), 1.65-1.51 (2H), 1.51-1.20 (18H), 0.93 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 71.6 (CH), 67.8 (CH_2), 55.0 (CH_3), 39.6 (CH_2), 37.5 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 28.8 (quint, *J* = 18 Hz, CD_2), 28.5 (quint, *J* = 18 Hz, CD_2), 26.2 (CH_2), 25.6 (CH_2), 18.8 (CH_2), 14.1 (CH_3); MS *m/z* 289 ($M^{\bullet+}$+1-H_2O, 15), 273 (35), 257 (100), 245 (75), 231 (25), 207 (20), 151 (30), 137 (35), 111 (45), 97 (70); Calcd for $C_{18}H_{34}{}^2H_4O_3$: C, 70.53; H, 12.50 Found: C 70.60; H, 12.56; Compounds (*S*)-**9a** (0.47 g, 62% yield; $[\alpha]_D$ = +0.5 (c=3, $CHCl_3$) and (*R*)-**9a** (0.48 g, 64% yield; $[\alpha]_D$ = -0.7 (c=2, $CHCl_3$) were obtained from compounds (*S*)-**7a** and (*R*)-**7a,** respectively.

[9,9,10,10-$^2H_4$]-17,19-dioxaicosan-3-ol (9b). IR 3430, 2925, 2855, 2185, 2085, 1460, 1150, 1105, 1035, 920 cm^{-1}; ^1H NMR δ 4.62 (s, 2H), 3.59 (m, 1H), 3.52 (t, *J* = 7 Hz, 3H), 3.36 (s, 3H), 1.65-1.20 (20H), 0.94 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 73.2 (CH), 67.8 (CH_2), 55.0 (CH_3), 36.9 (CH_2), 30.1 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.5 (quint, *J* = 18 Hz, CD_2), 26.2 (CH_2), 25.6 (CH_2), 9.8 (CH_3); MS *m/z* 289 ($M^{\bullet+}$+1-H_2O, 10), 273 (40), 257 (100), 245 (80), 229 (20), 216 (10), 169 (10), 155 (15), 138 (30), 127 (25), 113 (30), 99 (35); Calcd for $C_{18}H_{34}{}^2H_4O_3$: C, 70.53; H, 12.50 Found: C 70.47; H, 12.36; Compounds (*S*)-**9b** (0.62 g, 82% yield; $[\alpha]_D$ = +4.5 (c=3, $CHCl_3$) and (*R*)-**9b** (0.64 g, 84% yield; $[\alpha]_D$ = -4.6 (c=3, $CHCl_3$) were obtained from compounds (*S*)-**7b** and (*R*)-**7b,** respectively.

Preparation of Mesyl Esters 10. General Procedure These products were prepared by the procedure described by Abad *et al*.[6] A solution of saturated alcohol **9** (0.45 g, 1.5 mmol) and Et_3N (675 μL, 4.5 mmol) in 20 ml of CH_2Cl_2 was treated with CH_3SO_2Cl (160 μL, 2 mmol) and the mixture was stirred under argon for 2 h at ambient temperature (TLC monitoring). The reaction mixture was washed with H_2O (2 x 5 mL), dried, concentrated and the residue purified by flash chromatography on silica gel using as eluent hexane/MTBE 85:15 to give the expected products in 87-90% yields).

[9,9,10,10-$^2H_4$]-17,19-dioxaicosan-4-yl methanesulfonate 10a. IR 2930, 2850, 2185, 2090, 1460, 1355, 1170, 1110, 1045, 905 cm^{-1}; ^1H NMR δ 4.71 (m, *J* = 6 Hz, 1H), 4.62 (s, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H), 3.00 (s, 3H), 1.76-1.54 (6H), 1.50-1.20 (14H), 0.95 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.2 (CH_2), 83.9 (CH_2), 67.7 (CH_2), 54.9 (CH_2), 38.5 (CH_3), 36.4 (CH_2), 34.4 (CH_2), 34.3 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.4 (quint, *J* = 19 Hz, CD_2), 28.3 (quint, *J* = 19 Hz, CD_2), 26.1 (CH_2), 24.8 (CH_2), 18.2 (C), 13.7 (CH_3); Compounds (*S*)-(-)-**10a** (0.52 g, 90%; [α]= -3.0 (c=3, $CHCl_3$) and (*R*)-(+)-**10a** (502 mg, 87%; $[\alpha]_D$ = +3.0 (c=3, $CHCl_3$) were obtained from **(*S*)-9a** and **(*R*)-9a**, respectively.

[9,9,10,10-$^2H_4$]-17,19-dioxaicosan-3-yl methanesulfonate 10b. IR 2930, 2850, 2185, 2090, 1460, 1355, 1170, 1110, 1045, 905 cm^{-1}; ^1H NMR δ 4.66 (quint, *J* = 6 Hz, 1H), 4.62 (s, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H), 3.00 (s, 3H), 1.81-1.54 (6H), 1.50-1.20 (14H), 0.98 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 85.2 (CH), 67.8 (CH), 54.9 (CH_3), 38.5 (CH_3), 33.9 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 28.5 (quint, *J* = 19 Hz, CD_2), 27.3 (CH_2), 26.1 (CH_2), 24.9 (CH_2), 9.1 (CH_3); Compounds (*S*)-**10b** (0.51 g, 88%; $[\alpha]_D$ = ±0.0 (c=3, $CHCl_3$)) and (*R*)-**10b** (504 mg, 87%; $[\alpha]_D$ = ±0.0 (c=3, $CHCl_3$)) were obtained from **(*S*)-9b** and **(*R*)-9b**, respectively.

Reduction of mesylates . General Procedure. Mesyl derivative **10** was dissolved in Et_2O (14 ml) and treated with $LiAlD_4$ (8 molar equiv.) for 36 h at 20 ºC (TLC monitoring). The reaction mixture was quenched by carefully adding of stechiometric amounts of H_2O, the resulting white precipitate was filtered out through Celite and the organic layer concentrated to give a residue that after purification by flash chromatography on silica gel using a gradient of 0-10% MTBE in hexane, gave the corresponding pure deuterated products **11** with 93-98% yields.

[11,11,12,12,17-$^2H_5$]-2,4-dioxaicosane (11a). Compounds (*S*)-**11a** (362 mg, 93%) and (*R*)-**11a** (360 mg, 95%) were obtained from 0.52 g (1.35 mmol) of (*S*)-**10a** and 0.50 g (1.30 mmol) of (*R*)-**10a**, respectively; IR 2955, 2925, 2855, 2185, 2140, 2090, 1730, 1465, 1375, 1150, 1100, 1045, 915 cm^{-1}; ^1H NMR δ 4.62 (s, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H) 1.63-1.55 (2H), 1.40-1.18 (17H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.4 (CH_2), 67.8 (CH_2), 55.0 (CH_3), 31.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.9 (t, *J* = 19 Hz, CHD), 28.7 (quint, *J* = 19 Hz, CD_2), 28.6 (quint, *J* = 19 Hz, CD_2), 26.2 (CH_2), 22.6 (CH_2), 14.0 (CH_3); MS *m/z* 309 ($M^{\bullet+}$+28+1, 5), 290 ($M^{\bullet+}$-1, 20), 274 (10), 260 (100), 246 (20), 230 (45); Anal. Calcd for $C_{18}H_{33}{}^2H_5O_2$: C, 74.16; H, 13.15. Found: C, 74.03; H, 13.19.

[11,11,12,12,18-$^2H_5$]-2,4-dioxaicosane (11b). Compounds (*S*)-**11b** (378 mg, 98%) and (*R*)-**11b** (361 mg, 94%) were obtained from 0.51 g (1.35 mmol) of (*S*)-**10b** and 0.50 g (1.30 mmol) of (*R*)-**10b**, respectively; IR 2925, 2850, 2185, 2140, 2090, 1465, 1380, 1210, 1150, 1110, 1045, 920 cm^{-1}; ^1H NMR δ 4.62 (s, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.36 (s, 3H) 1.63-1.55 (2H), 1.40-1.18 (17H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 96.3 (CH_2), 67.8 (CH_2), 55.0 (CH_3), 31.5 (t, *J* = 19 Hz, CHD), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.9 (quint, *J* = 19 Hz, CD_2), 28.6 (quint, *J* = 19 Hz, CD_2), 26.2 (CH_2), 22.6 (CH_2), 14.0 (CH_3); MS *m/z* 309 ($M^{\bullet+}$+28+1, 5), 290 ($M^{\bullet+}$-1, 25), 274 ($M^{\bullet+}$-2, 90), 260 (100), 246 (20), 230 (45), 128 (15), 113 (10), 99 (15). Anal. Calcd for $C_{18}H_{33}{}^2H_5O_2$: C, 74.16; H, 13.15. Found: C, 74.03; H, 13.19.

Alcohol deprotection. General Procedure. Enantiotopically deuterated compounds **11a** and **11b** were deprotected to the corresponding alcohols by treatment with a 0.5M solution of HCl in MeOH for 36 h at ambient temperature (1 mmol/10 mL). The solution was neutralized with saturated aqueous $NaHCO_3$, concentrated and the residue extracted with CH_2Cl_2, dried, and purified by flash chromatography on silica gel using a gradient of 0-30% MTBE in hexane, obtaining the corresponding pure deuterated alcohols in 83-90% yields.

[7,7,8,8,13-$^2H_5$]-1-hexadecanol (12a) Compounds **(*S*)-12a** (212 mg, 86%) and (*R*)-**12a** (220 mg, 89%) were isolated from 292 mg of **(*S*)-11a** and (*R*)-**11a**, respectively; m.p. 48-49 ºC; IR 3260, 2960, 2915, 2850, 2175, 2130, 2075, 1460, 1210, 1060, 755 cm^{-1}; ^1H NMR δ 3.63

(t, *J* = 6.5 Hz, 2H), 1.64-1.48 (2H), 1.48-1.18 (21H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 62.7 (CH_2), 32.7 (CH_2), 31.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.9 (t, *J* = 19 Hz, CHD), 28.6 (quint, *J* = 19 Hz, CD_2), 25.8 (CH_2), 22.6 (CH_2), 14.0 (CH_3); MS *m/z* 246 ($M^{\bullet+}$-1, 100), 230 (95), 187 (5), 173 (10), 158 (15), 144 (10), 129 (10), 114 (10), 100 (15). Anal. Calcd for $C_{16}H_{29}{}^2H_5O$: C, 77.65; H, 13.86. Found: C, 77.57; H, 13.69.

[7,7,8,8,14-$^2H_5$]-1-hexadecanol (12b) Compounds (*S*)-**12b** (230 mg, 93%) and (*R*)-**12b** (223 mg, 90%) were obtained from 292 mg of **(*S*)-11b** and **(*R*)-11b**, respectively; m.p. 48-50 ºC; IR 3330, 2955, 2915, 2850, 2175, 2135, 2080, 1460, 1210, 1060, 755 cm^{-1}; ^{1}H NMR δ 3.64 (t, *J* = 6.5 Hz, 2H), 1.64-1.48 (2H), 1.48-1.18 (21H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 62.8 (CH_2), 32.7 (CH_2), 31.5 (t, *J* = 19 Hz, CHD), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 28.9 (quint, *J* = 19 Hz, CD_2), 28.6 (quint, *J* = 19 Hz, CD_2), 25.7 (CH_2), 22.5 (CH_2), 14.0 (CH_3); MS *m/z* 246 ($M^{\bullet+}$-1, 100), 230 (95), 187 (5), 173 (10), 158 (15), 144 (10), 129 (10), 114 (10), 100 (15); Anal. Calcd for $C_{16}H_{29}{}^2H_5O$: C, 77.65; H, 13.86 Found: C, 77.58; H, 13.71.

Preparation of Carboxylic Acids. Compounds **1** were prepared according to a method previously reported involving the alcohol oxidation in two steps.[3]

[7,7,8,8,13-$^2H_5$]-hexadecanoic acid 1a. Compounds (*S*)-**1a** (102 mg, 78%) and (*R*)-**1a** (106 mg, 81%) were obtained from 124 mg (0.5 mmol) of alcohols (*S*)-**12a** and (*R*)-**12a**, respectively. m.p. 60-62; IR 3020, 2915, 2850, 2175, 2125, 2080, 1695, 1460, 1405, 1295, 1200, 935, 755 cm^{-1}; ^{1}H NMR δ 2.35 (t, *J* = 7.5 Hz, 2H), 1.68-1.58 (m, 2H), 1.40-1.16 (21H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 180.5 (CO), 34.1 (CH_2), 31.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.9 (t, *J* = 19 Hz, CHD), 28.6 (quint, *J* = 19 Hz, CD_2), 28.6 (quint, *J* = 19 Hz, CD_2), 24.7 (CH_2), 22.7 (CH_2), 14.1 (CH_3); MS m/z (Methyl ester), 304 (20, $M^{\bullet+}$+28), 276 (100, $M^{\bullet+}$+1); Anal. Calcd for $C_{16}H_{27}{}^2H_5O_2$: C, 73.50; H, 12.34 Found: C, 73.44; H, 12.14.

[7,7,8,8,14-$^2H_5$]-hexadecanoic acid 1b. Compounds (*S*)-**1b** (104 mg, 79%) and (*R*)-**1b** (105 mg, 80%) were obtained from 124 mg (0.5 mmol) of (*S*)-**12b** and (*R*)-**12b**, respectively. m.p. 60-62º; IR 3020, 2915, 2850, 2180, 2135, 2080, 1700, 1460, 1405, 1295, 1210, 940, 755 cm^{-1}; ^{1}H NMR δ 2.35 (t, *J* = 7.5 Hz, 2H), 1.68-1.58 (m, 2H), 1.40-1.16 (21H), 0.88 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 180.5 (CO), 34.1 (CH_2), 31.5 (t, *J* = 19 Hz, CHD), (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.7 (quint, *J* = 19 Hz, CD_2), 28.6 (quint, *J* = 19 Hz, CD_2), 24.7 (CH_2), 22.6 (CH_2), 14.0 (CH_3); MS m/z (Methyl ester), 304 (20, $M^{\bullet+}$+28), 276 (100, $M^{\bullet+}$+1); Anal. Calcd for $C_{16}H_{27}{}^2H_5O_2$: C, 73.50; H, 12.34 Found: C, 73.46; H, 12.10.

Aryl acetic esters preparation of the different stereoisomers of alkynols 5 and 7 (**13** and **14**). Carbodiimide (ECD, 0.14 mmol) was added to a mixture of the corresponding alcohol (0.10 mmol), DMAP (0.10 mmol) and (*R*)-(-)-MPA (or 9-AMA) (0.14 mmol) in dry CH_2Cl_2 (3 ml). The mixture was stirred for 2 h at room temperature, washed with saturated aqueous $NaHCO_3$ solution and the organic layer concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using a gradient of 0-20% MTBE in hexane (75-90% isolated yields).

(*S*)-3-Hex-1-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*S*)-13a) (From CALB resolved acetate). IR 3290, 2960, 2930, 2870, 1750 (CO), 1450, 1240, 1170, 1100, 990 cm^{-1}; ^{1}H NMR δ 7.50-7.41 (2H), 7.40-7.30 (3H), 5.40 (dt, J_1 = 6.5 Hz, J_2 = 2 Hz, 1H), 4.79 (s, 1H), 3.43 (s, 3H), 2.46 (d, J = 2 Hz, 1H), 1.68-1.55 (2H), 1.29-1.12 (2H), 0.78 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 169.6 (CO), 135.9 (C), 128.7 (CH), 128.5 (CH), 127.2 (CH), 82.2 (CH), 80.7 (CH), 73.9 (C), 64.1 (CH), 57.3 (CH_3), 36.3 (CH_2), 17.7 (CH_2), 13.3 (CH_3); $[\alpha]_D$ = -112.0 (c 2, $CHCl_3$, 96% de).

(*R*)-3-Hex-1-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*R*)-13a) (From CALB residual alcohol). IR 3290, 2960, 2930, 2870, 1750 (CO), 1450, 1240, 1170, 1110, 990 cm^{-1}; ^{1}H NMR δ 7.50-7.42 (2H), 7.42-7.30 (3H), 5.40 (dt, J_1 = 6.5 Hz, J_2 = 2 Hz, 1H), 4.79 (s, 1H), 3.43 (s, 3H), 2.36 (d, J = 2 Hz, 1H), 1.82-1.70 (2H), 1.48-1.36 (2H), 0.92 (t, J = 6.5 Hz, 3H); ^{13}C NMR δ 169.6 (CO), 135.6 (C), 128.6 (CH), 128.4 (CH), 127.0 (CH), 82.4 (CH), 80.3 (CH), 73.8 (C), 64.3 (CH), 57.2 (CH_3), 36.3 (CH_2), 18.0 (CH_2), 13.4 (CH_3); $[\alpha]_D$ = -10.6 (c 2, $CHCl_3$, 60% de).

(*R*)-3-Hex-5-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*R*)-13b) (From CALB resolved acetate). IR 3300, 2975, 2940, 2875, 1750 (CO), 1460, 1260, 1185, 1100 cm^{-1}; ^{-1}H NMR δ 7.50-7.42 (2H), 7.42-7.30 (3H), 4.94 (m, 1H), 4.78 (s, 1H), 3.44 (s, 3H), 2.33 (m, 2H), 1.81 (t, J = 3 Hz, 1H), 1.80-1.62 (2H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 170.4 (CO), 136.2 (C), 128.6 (CH), 128.5 (CH), 127.1 (CH), 82.6 (CH), 79.1 (CH), 73.8 (C), 70.3 (CH), 57.3 (CH_3), 25.9 (CH_2), 23.2 (CH_2), 9.3 (CH_3); $[\alpha]_D$ = -62.0 (c 1, $CHCl_3$, 94% de).

(*S*)-3-Hex-5-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*S*)-13b) (From CALB residual alcohol). IR 3310, 2975, 2940, 1745 (CO), 1460, 1245, 1180, 1100 cm^{-1}; ^{1}H NMR δ 7.50-7.42 (2H), 7.42-7.30 (3H), 4.92 (m, 1H), 4.78 (s, 1H), 3.43 (s, 3H), 2.48 (m, 2H), 1.97 (t, J = 3 Hz, 1H), 1.68-1.50 (2H), 0.63 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 170.3 (CO), 136.3 (C), 128.7 (CH), 128.5 (CH), 127.2 (CH), 82.5 (CH), 79.4 (CH), 73.8 (C), 70.4 (CH), 57.3 (CH_3), 25.9 (CH_2), 23.6 (CH_2), 9.0 (CH_3); $[\alpha]_D$ = -100.6 (c 1, $CHCl_3$, 64% de).

(*S*)-[9,9,10,10-$^{2}H_4$]-17,19-dioxa-4-eico-5-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*S*)-14a) (From CALB resolved acetate). IR 2935, 2850, 2190, 2090, 1750 (CO), 1455, 1245, 1150, 1110, 1050, 920 cm^{-1}; ^{1}H NMR δ 7.47-7.41 (2H), 7.39-7.28 (3H), 5.41 (tt, J_1 = 6.5 Hz, J_2 = 2 Hz, 1H), 4.78 (s, 1H), 4.62 (s, 2H), 3.52 (t, J = 6.5 Hz, 2H), 3.42 (s, 3H), 3.36 (s, 3H), 2.17 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 2H), 1.65-1.52 (4H), 1.45 (t, J = 7 Hz, 3H), 1.42-1.10 (10H), 0.77 (t, J = 7 Hz, 3H); ^{13}C NMR δ 169.7 (CO), 136.1 (C), 128.6 (CH), 128.5 (CH), 127.2 (CH), 96.3 (CH_2), 86.6 (C), 82.3 (CH), 77.3 (C), 67.8 (CH_2), 65.0 (CH), 57.3 (CH_3), 55.0 (CH_3), 36.9 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.1 (CH_2), 26.1 (CH_2), 18.5 (CH_2), 17.9 (CH_2), 13.3 (CH_3); $[\alpha]_D$ = -60.6 (c 2, $CHCl_3$, 96% de).

(*R*)-[9,9,10,10-$^{2}H_4$]-17,19-dioxa-4-eico-5-ynyl-(*R*)-α-O-methyl-α-phenyl-acetate (Ester (*R*)-14a) (From CALB residual alcohol). IR 2935, 2850, 2190, 2090, 1750 (CO), 1455, 1245, 1150, 1110, 1050, 920 cm^{-1}; ^{1}H NMR δ 7.47-7.41 (2H), 7.39-7.28 (3H), 5.40 (tt, J_1 = 6.5 Hz, J_2 = 2 Hz, 1H), 4.78 (s, 1H), 4.62 (s, 2H), 3.52 (t, J = 6.5 Hz, 2H), 3.43 (s, 3H), 3.36 (s, 3H), 2.09 (dt, J_1 = 7 Hz, J_2 = 2 Hz, 2H), 1.72 (m, 2H), 1.59 (m, 2H), 1.46-1.16 (14H), 0.90 (t, J = 7 Hz, 3H); ^{13}C NMR δ 169.8 (CO), 135.9 (C), 128.5 (CH), 128.4 (CH), 127.1 (CH), 96.3 (CH_2), 86.5 (C), 82.6 (CH), 76.9 (C), 67.8 (CH_2), 65.3 (CH), 57.3 (CH_3), 55.0

(CH_3), 36.9 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.1 (CH_2), 26.1 (CH_2), 18.4 (CH_2), 18.2 (CH_2), 13.5 (CH_3); $[\alpha]_D$= +15.0 (c 0.5, $CHCl_3$, 96% de).

(*R*)-[9,9,10,10-$^2H_4$]-17,19-dioxa-3-eico-5-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*R*)-14b) (From CALB resolved acetate). IR 2930, 2850, 2190, 2095, 1745 (CO), 1450, 1255, 1175, 1105, 1040, 920 cm^{-1}; ^{1}H NMR δ 7.49-7.42 (2H), 7.39-7.28 (3H), 4.90 (m, 1H), 4.77 (s, 1H), 4.62 (s, 2H), 3.52 (t, *J* = 6.5 Hz, 2H), 3.44 (s, 3H), 3.36 (s, 3H), 2.28 (m, 2H), 2.00 (m, 2H), 1.80-1.50 (4H), 1.42-1.16 (10H), 0.87 (t, *J* = 7 Hz, 3H); ^{13}C NMR δ 170.3 (CO), 136.3 (C), 128.4 (CH), 128.4 (CH), 127.0 (CH), 96.3 (CH_2), 82.7 (CH), 82.4 (C), 74.7 (C), 74.6 (CH), 67.8 (CH_2), 57.3 (CH_3), 55.0 (CH_3), 29.7 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 23.5 (CH_2), 18.5 (CH_2), 9.3 (CH_3); $[\alpha]_D$= -13.0 (c 1, $CHCl_3$, 94% de).

(*S*)-[9,9,10,10-$^2H_4$]-17,19-dioxa-3-eico-5-ynyl-(*R*)-α-O-methyl-α-phenyl acetate (Ester (*S*)-14b) (From CALB and TL residual alcohol). IR 2930, 2850, 2190, 2095, 1745 (CO), 1450, 1255, 1175, 1105, 1040, 920 cm^{-1}; ^{1}H NMR δ 7.49-7.42 (2H), 7.39-7.28 (3H), 4.87 (m, 1H), 4.77 (s, 1H), 4.62 (s, 2H), 3.51 (t, *J* = 6.5 Hz, 2H), 3.42 (s, 3H), 3.36 (s, 3H), 2.43 (m, 2H), 2.10 (m, 2H), 1.70-158 (4H), 1.43 (t, *J* = 7 Hz, 2H), 1.40-1.18 (10H), 0.62 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR δ 170.2 (CO), 136.4 (C), 128.5 (CH), 128.4 (CH), 127.2 (CH), 96.3 (CH_2), 82.6 (CH), 82.4 (CH), 74.9 (C), 74.5 (CH), 67.8 (CH_2), 57.2 (CH_3), 54.9 (CH_3), 36.9 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.6 (CH_2), 26.1 (CH_2), 25.9 (CH_2), 23.8 (CH_2), 18.6 (CH_2), 8.9 (CH_3); $[\alpha]_D$= -50.1 (c 2, $CHCl_3$, 94% de).

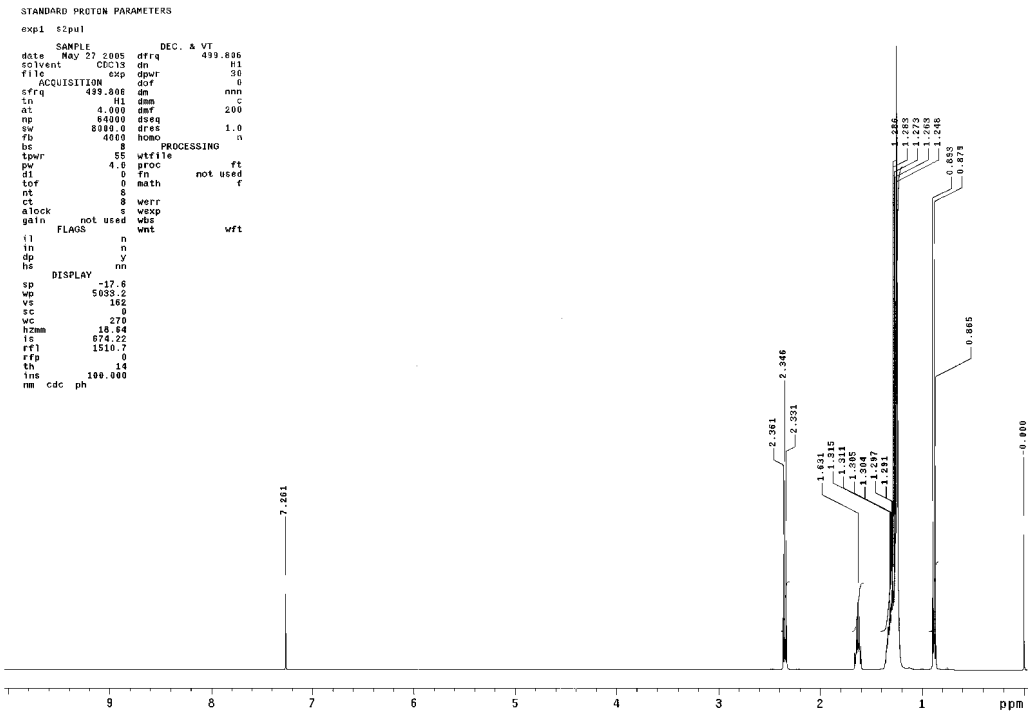
***In Vivo* Gland Culture Procedure**. In these experiments, newly-emerged virgin *T. pityocampa* females were briefly anesthetized on ice and pheromone glands were everted and impregnated (1 μL every 3 hours x 4 times) with the DMSO solutions of stereospecifically deuterated probes **1** (10 mg/mL each). The *in vivo* incubation proceeded for 36 h. In order to obtain the methyl ester derivatives of the gland lipids for analysis, the pheromone glands were excised and soaked in chloroform methanol (2:1) at 25 ºC for 1 h and base-methanolized in 0.5 M KOH for 1 h. After this time, the organic solution was neutralized with 1 N HCl, washed with satd. $NaHCO_3$ aqueous solution, extracted with hexane, concentrated and the residue was treated with a freshly prepared diazomethane solution. Ten glands were used for each assay.

Instrumental Analysis of the Biological Extracts. The GC-MS analysis of biological extracts was performed by Chemical Ionization (CI) using methane as ionization gas. The system was equipped with a non-polar HP5-MS capillary column (30 m x 0.25 mm I.D, 0.25 μm stationary phase thickness) and using the following program: from 100 ºC to 220 ºC at 5 ºC/min and then to 300 ºC at 7 ºC/min after an initial delay of 1 min. Analyses were carried out on methanolyzed lipidic extracts from pheromone glands with the equipment and conditions described above. Kinetic isotope effects were calculated from the ratios of formed products from each probe which afforded a cluster of ions, analyzed as methyl esters, and are based on the abundance of the respective molecular ions in the range *m/z* 265-274 in which the most abundant ones corresponded to the molecular ion of the resulting isotopomers.

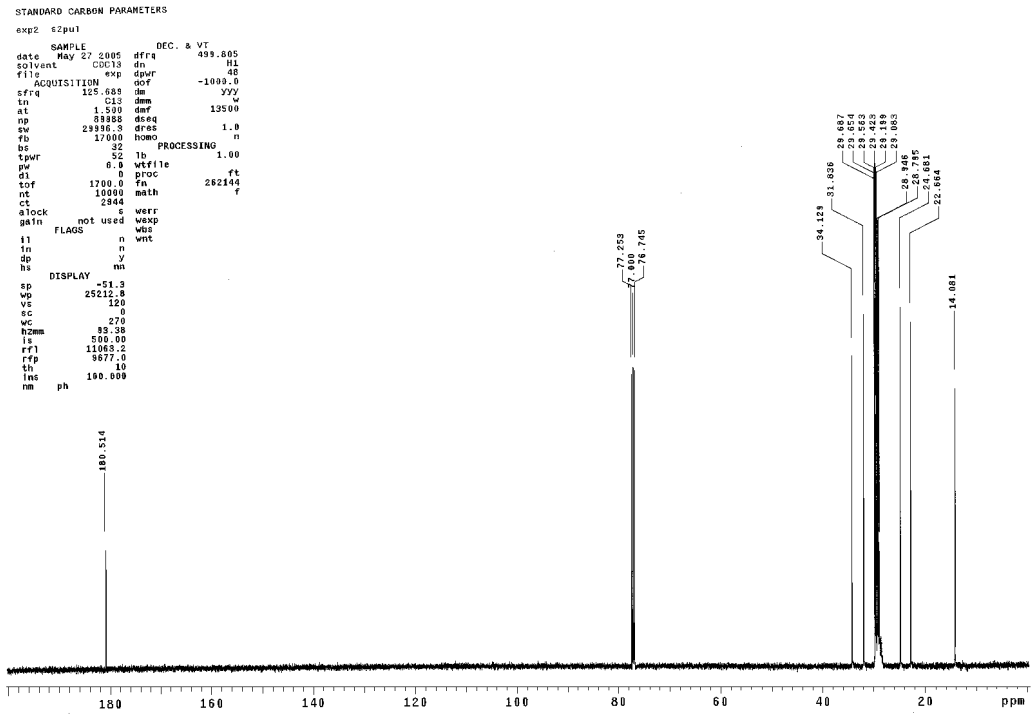
NMR Spectra

1a $CH_3CH_2CH_2CHDCH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_5COOH$

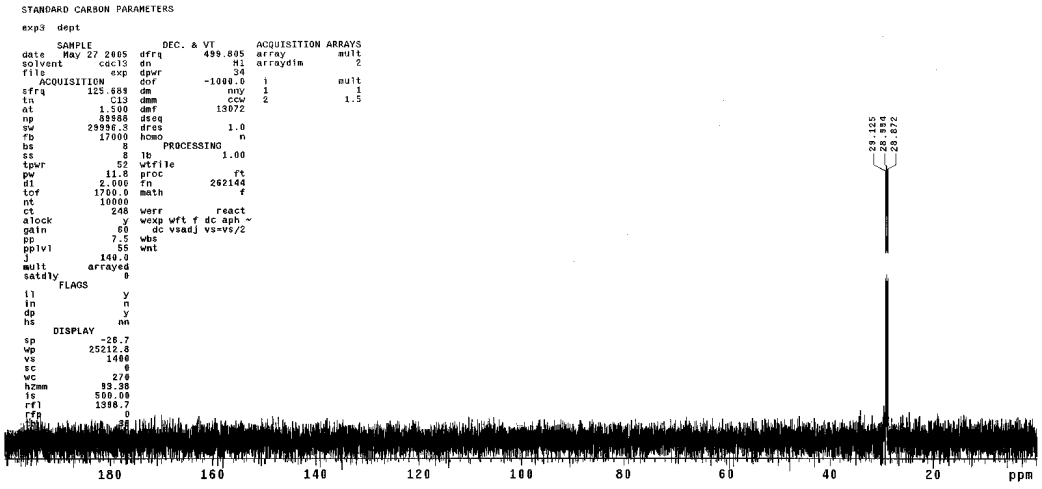
^1H NMR



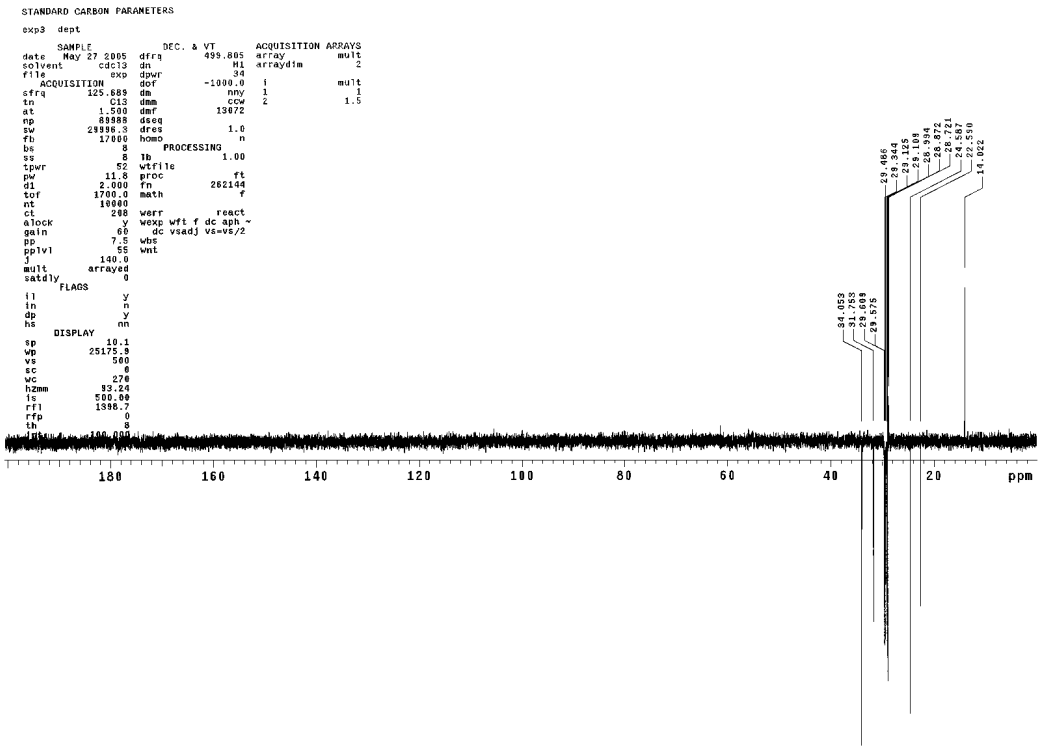
^{13}C NMR



DEPT 1(CH)

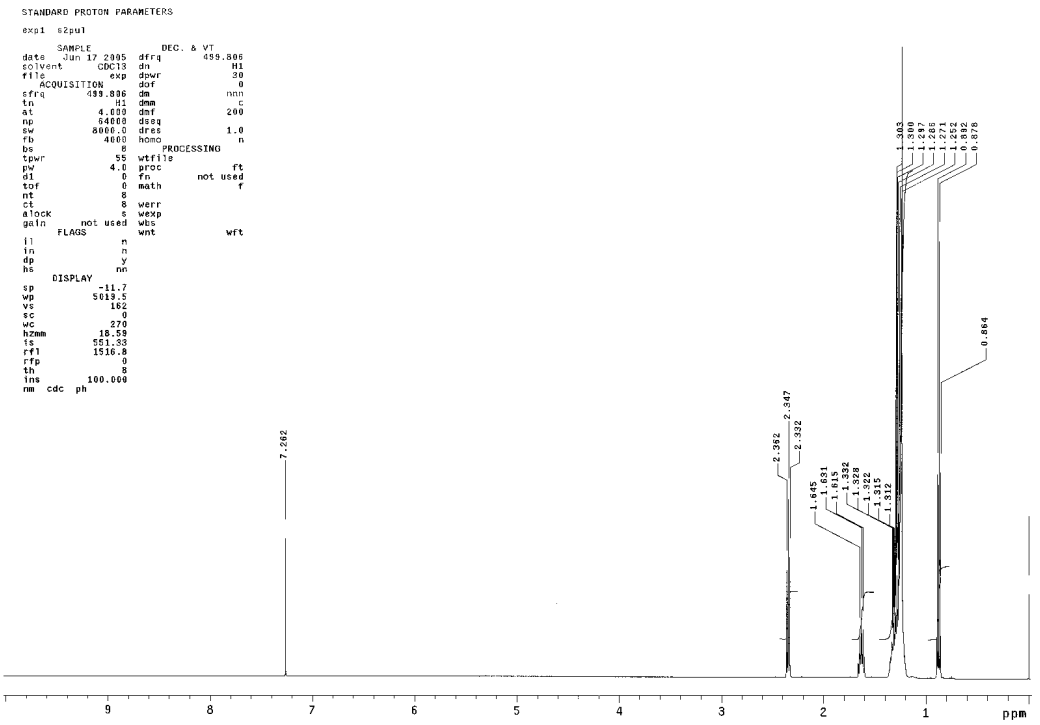


DEPT 2 (CH, CH_3/CH_2)

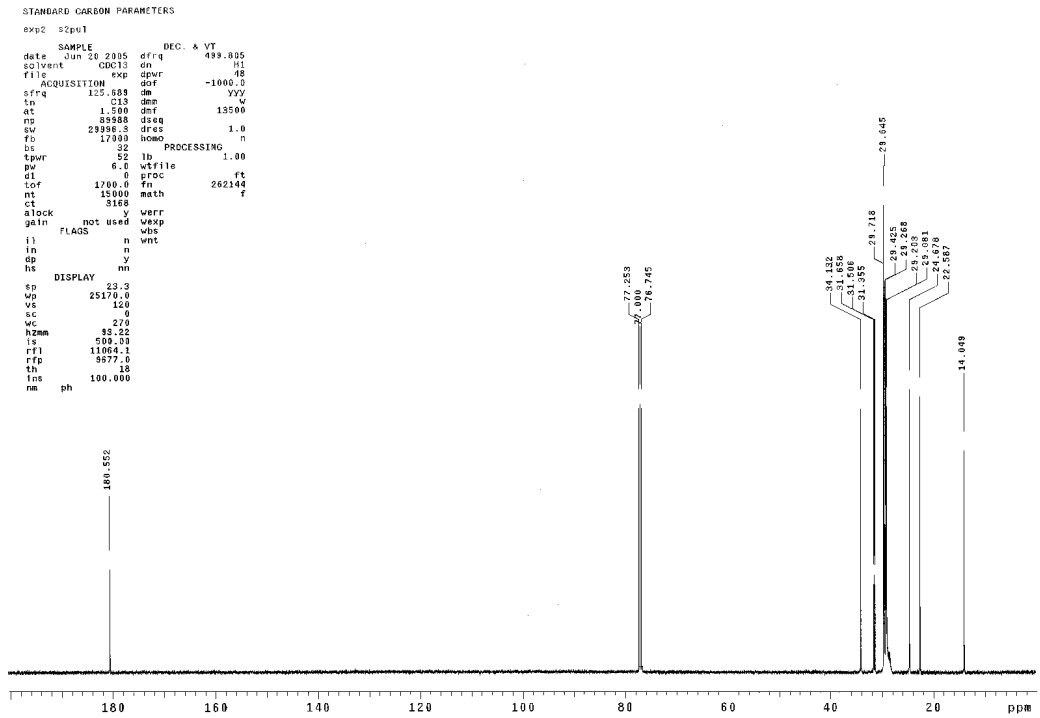


1b $CH_3CH_2CHDCH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_5COOH$

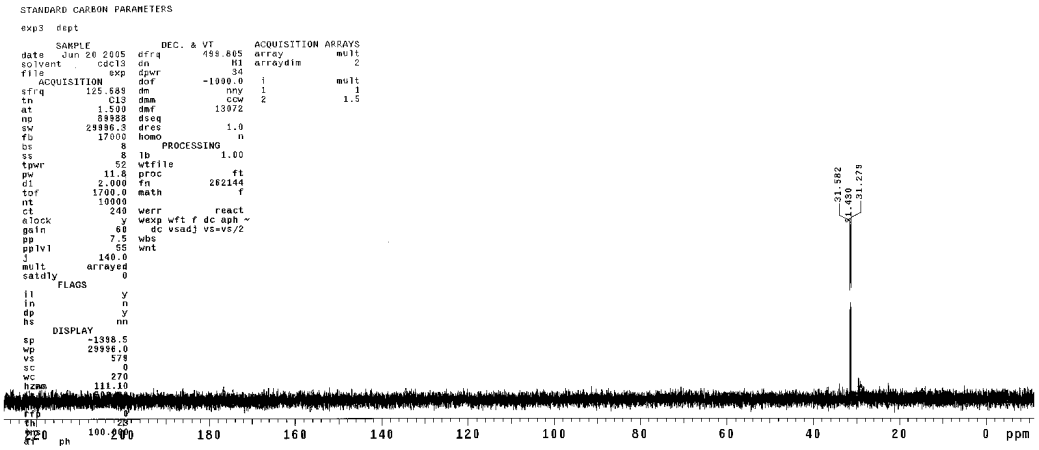
^{1}H NMR



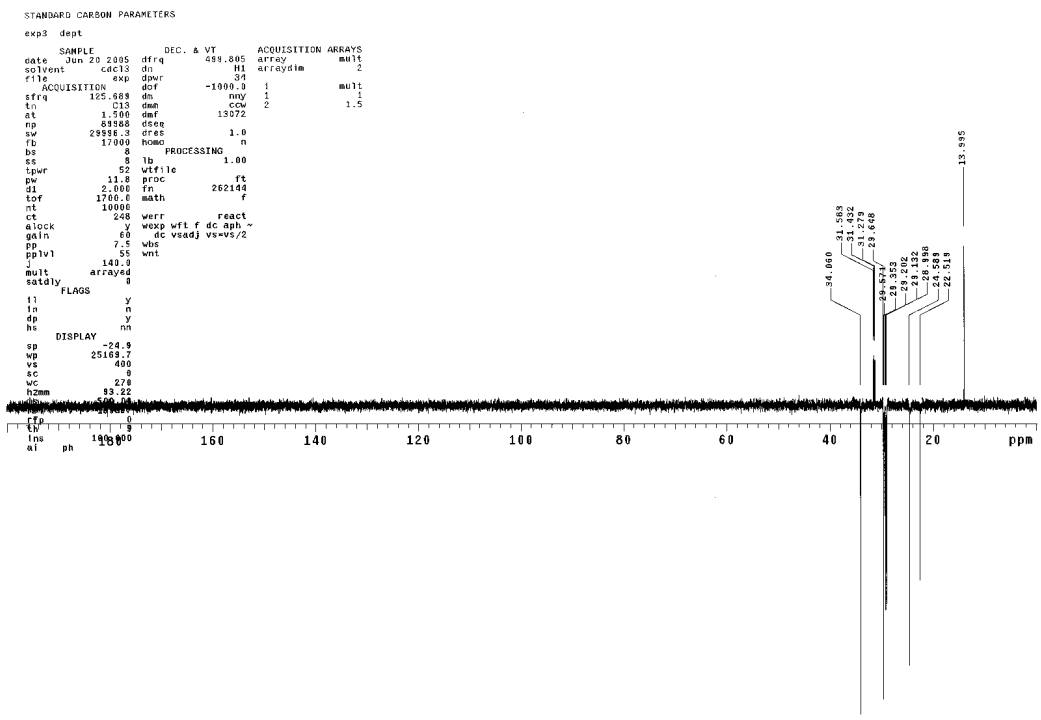
^{13}C NMR



DEPT 1(CH)

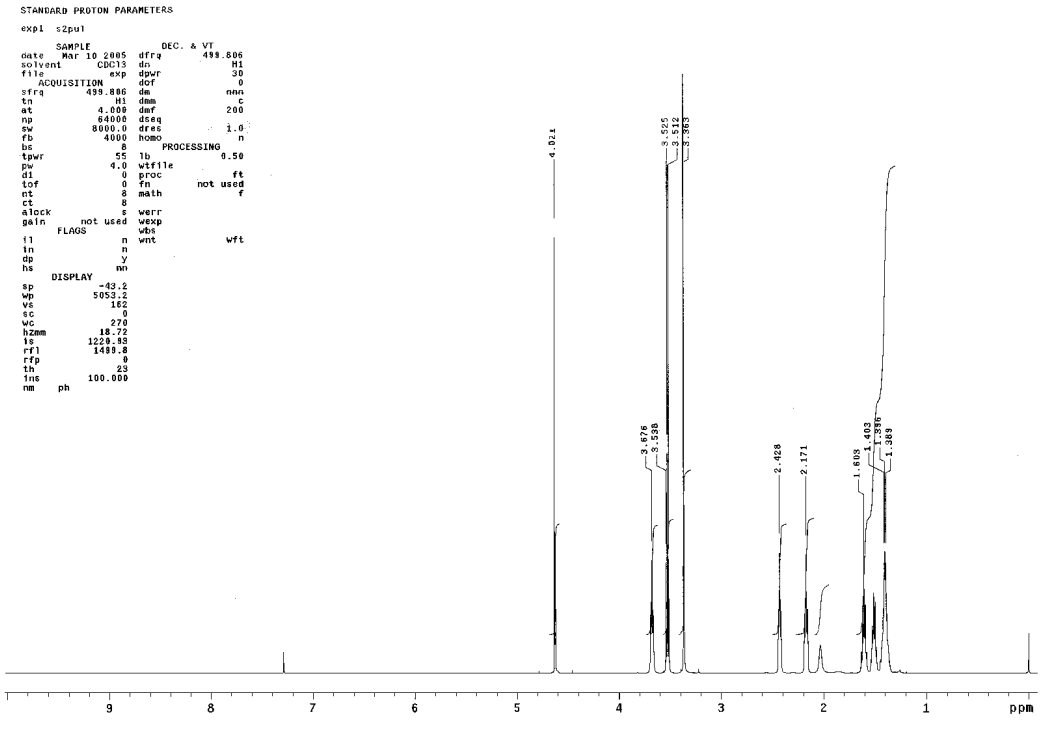


DEPT 2 (CH, CH_3/CH_2)

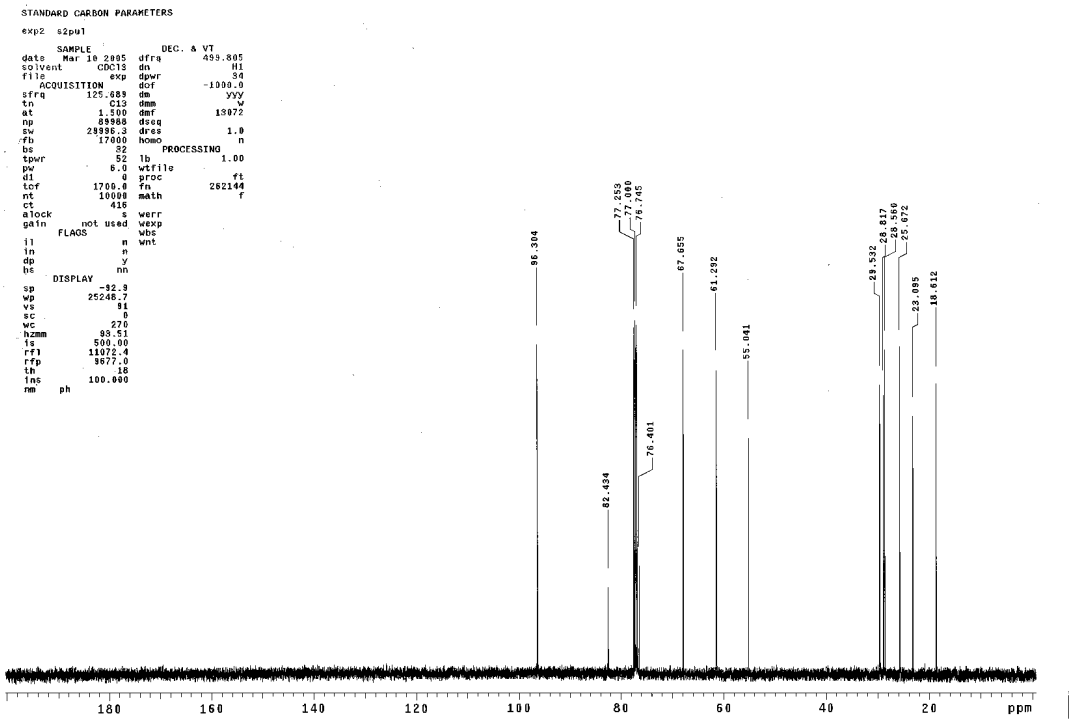


2 $HOCH_2CH_2C{\equiv}C(CH_2)_6OMOM$

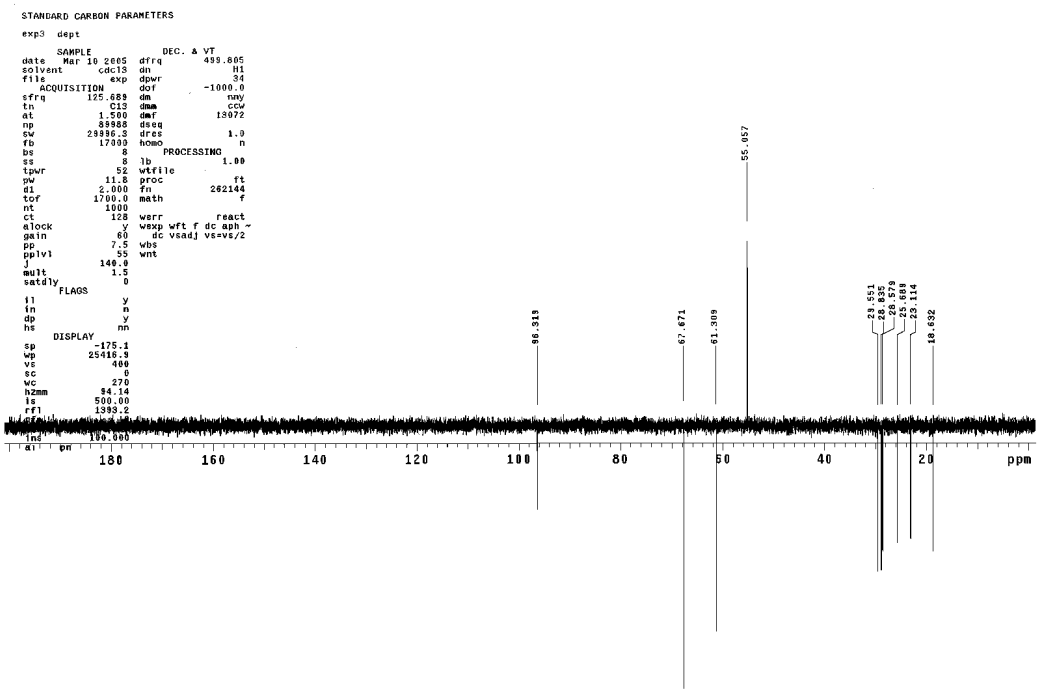
^1H NMR



^{13}C NMR

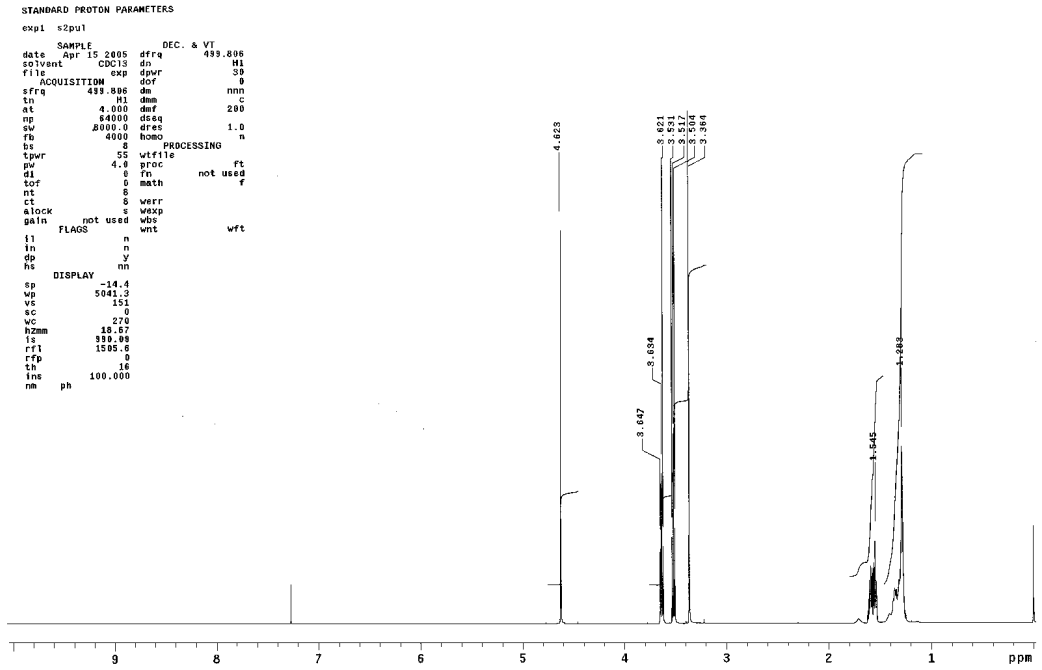


DEPT

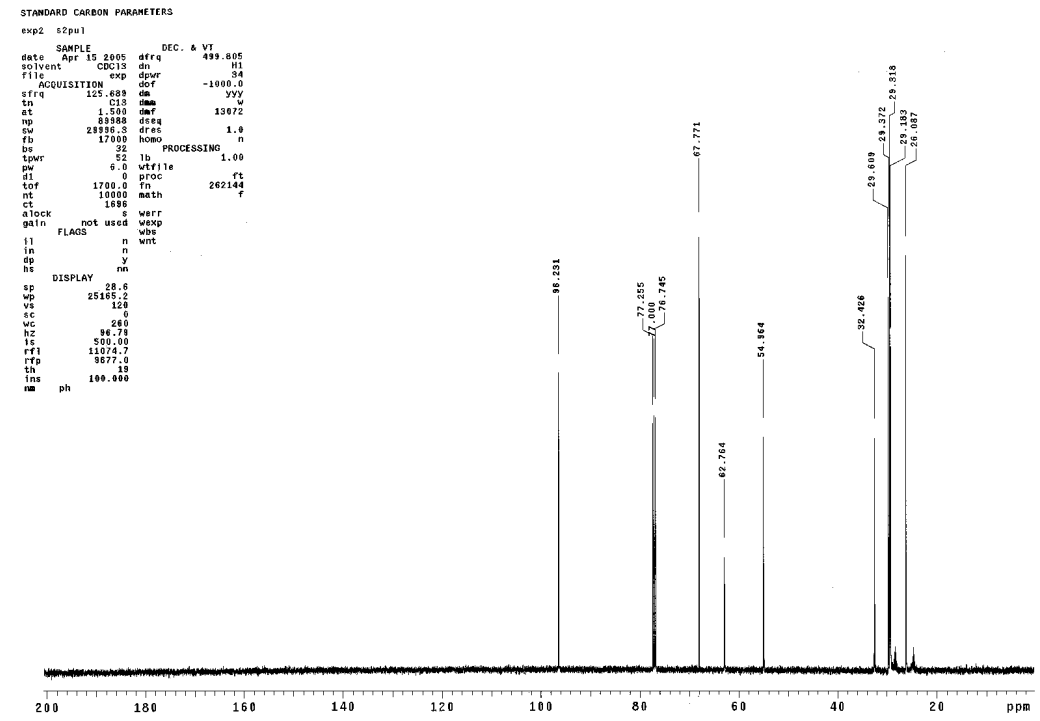


3 $HO(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

^1H NMR



^{13}C NMR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dp y
hs nn
DISPLAY
sp 28.6
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nm ph
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dres 1.0
homo n
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fn 262144
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wbs
wnt
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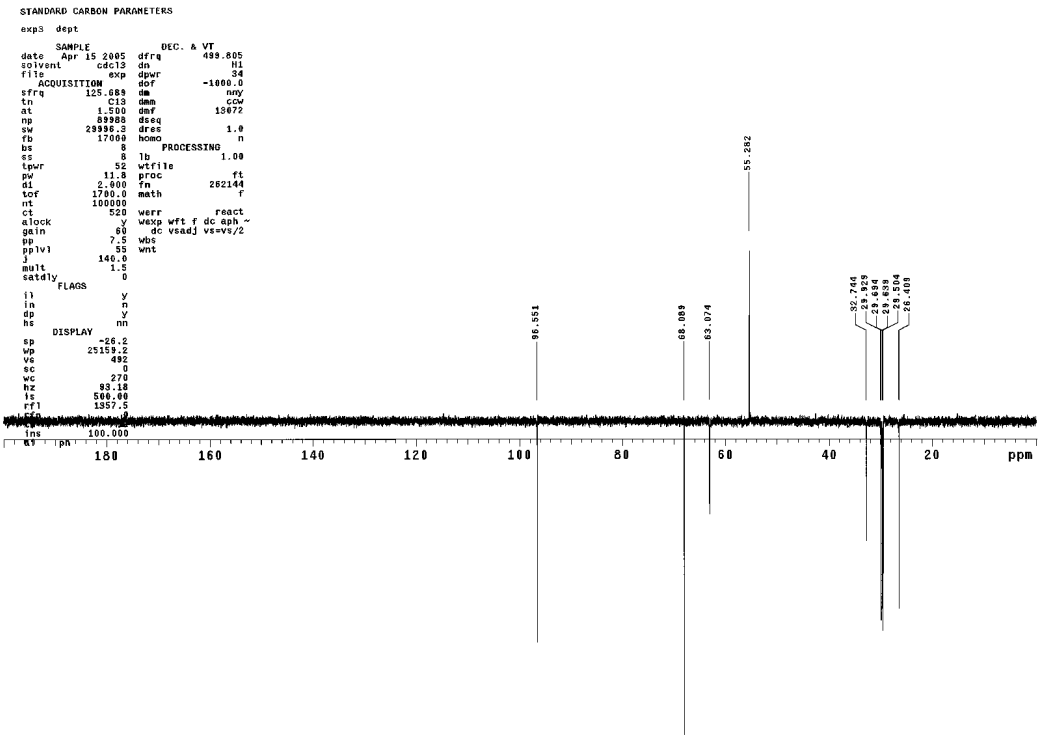
DEPT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solvent cdcl3
file exp
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tn C13
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29.464
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29.504
26.408
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140
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100
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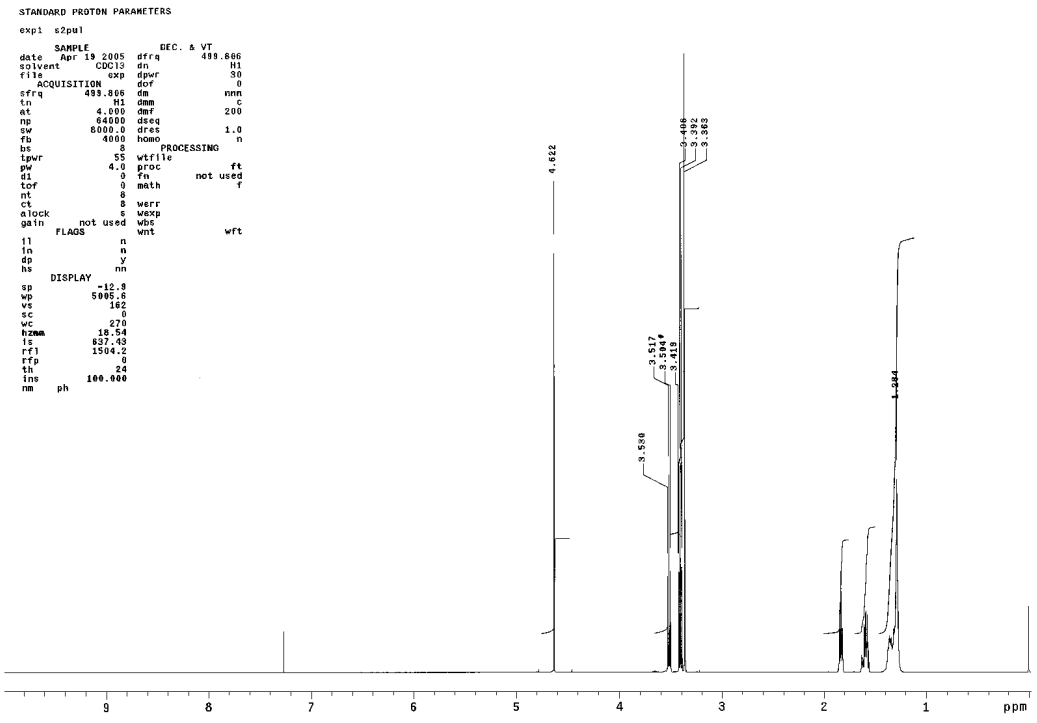
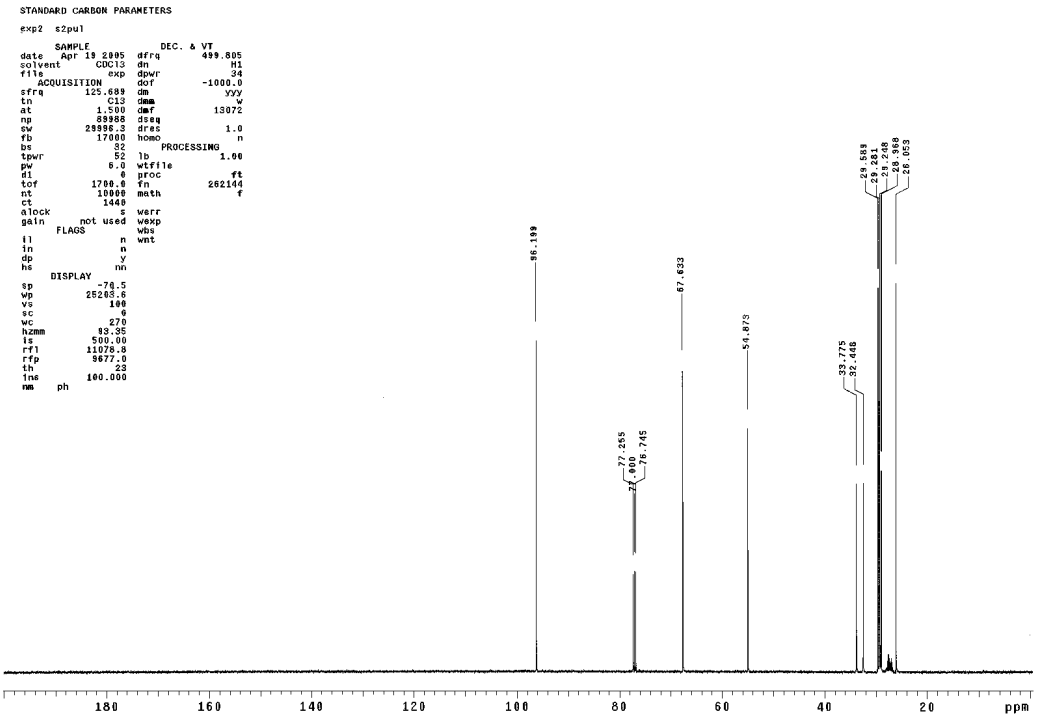
60
40
20
ppm

4 $Br(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

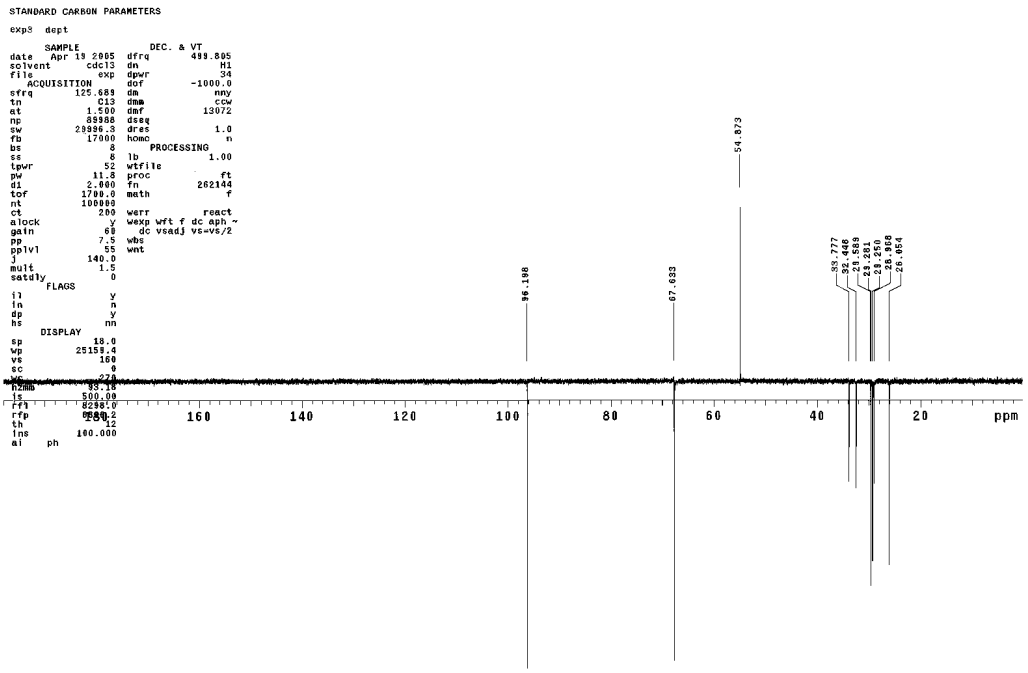
^1H NMR



^{13}C NMR

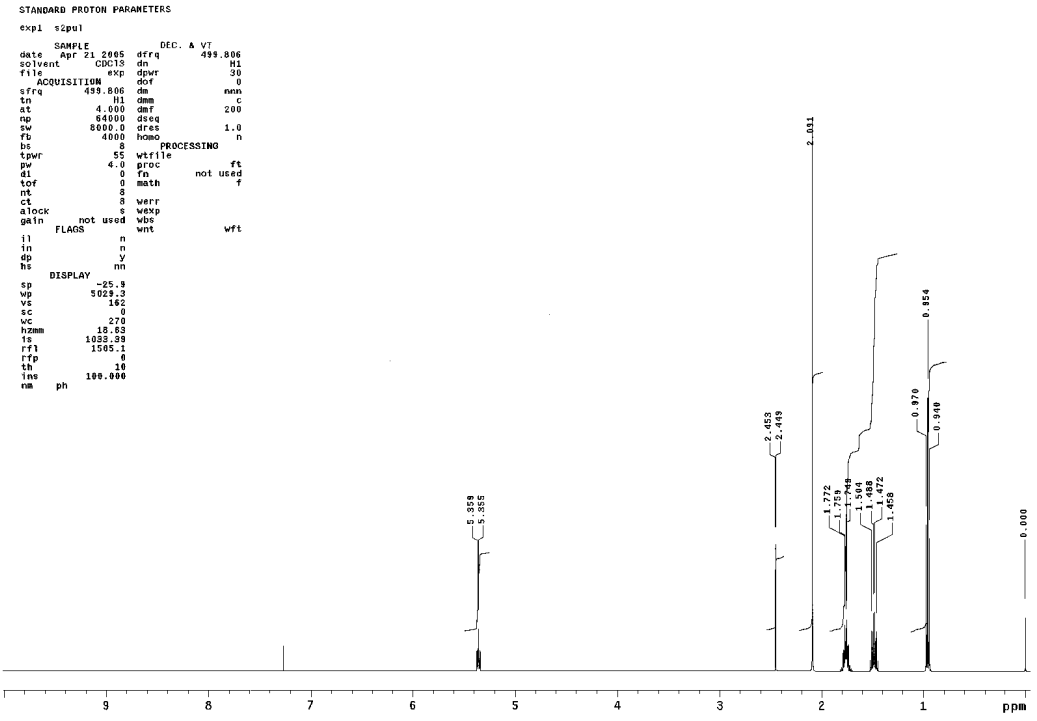


DEPT

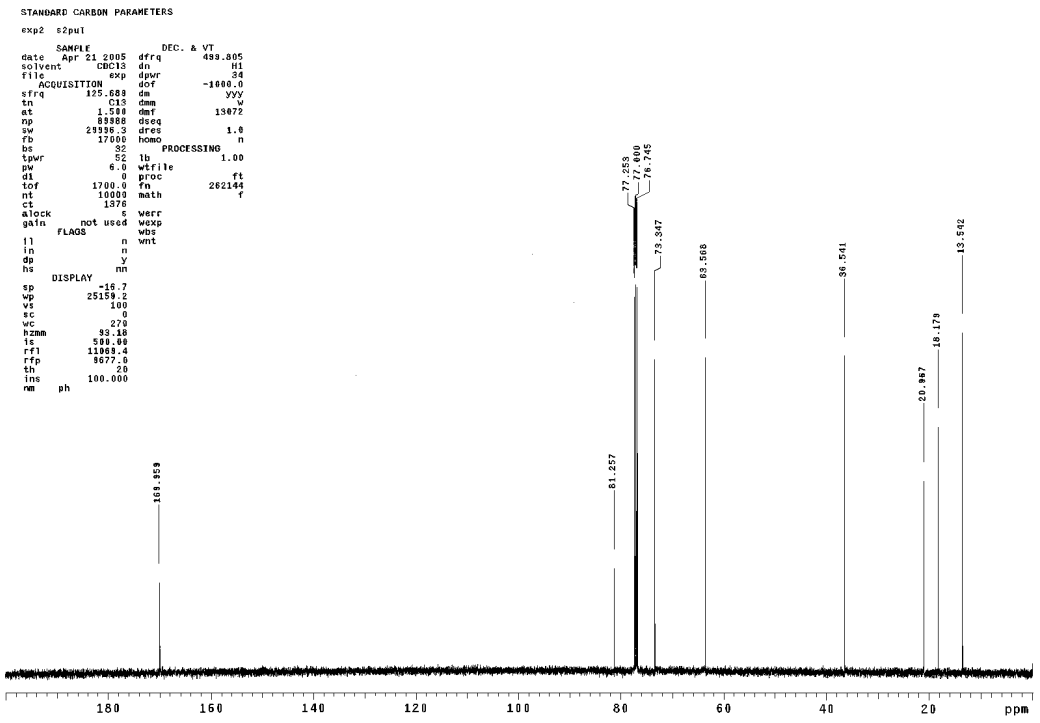


6a $CH_3(CH_2)_2CHOAcC{\equiv}C$

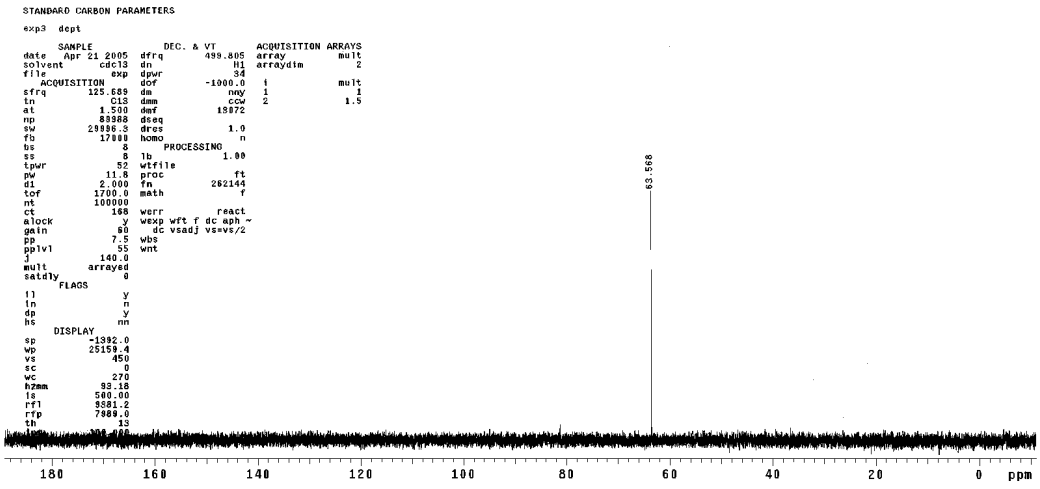
^1H NMR



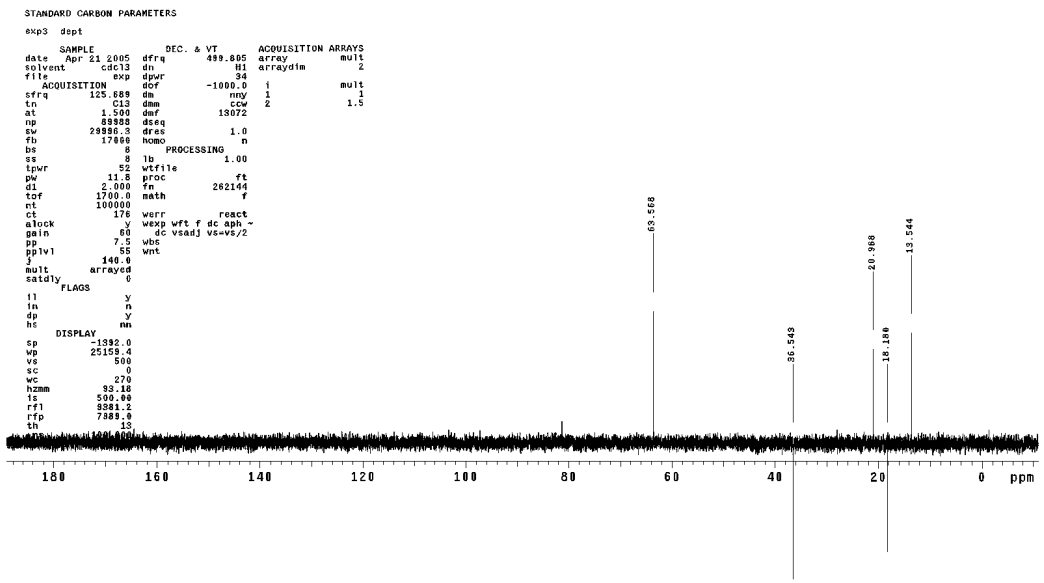
^{13}C NMR



DEPT 1(CH)

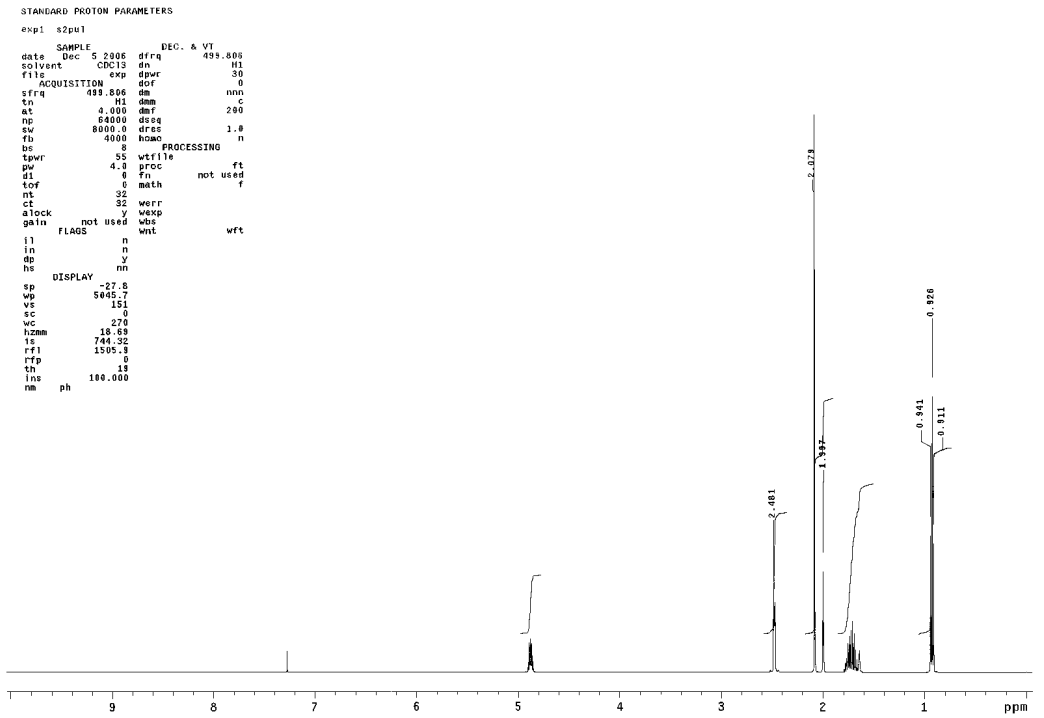


DEPT 2 (CH, CH_3/CH_2)

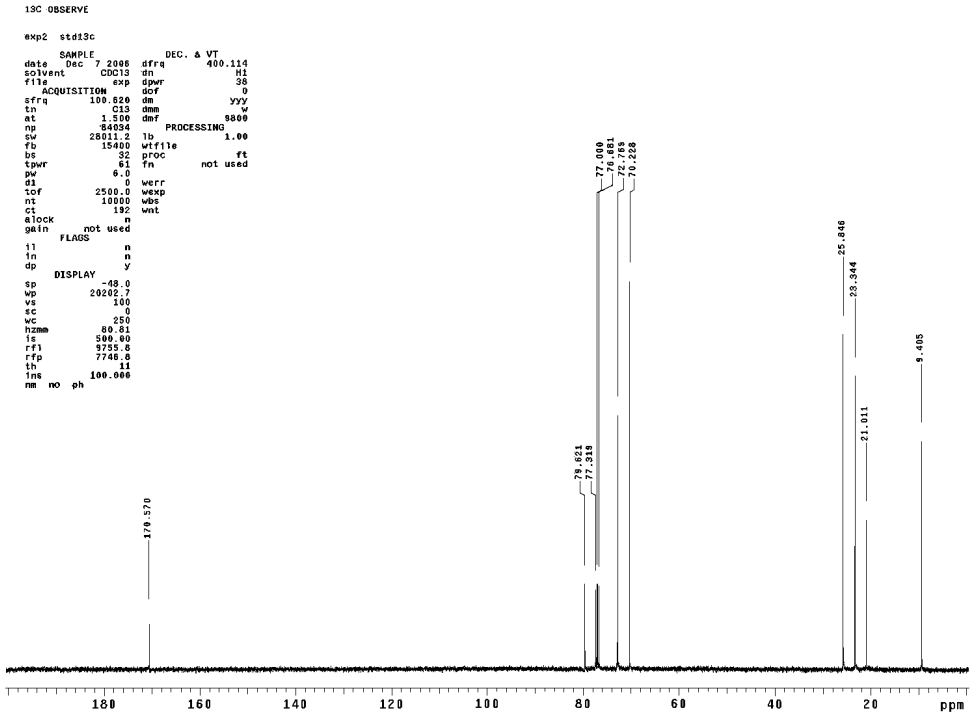


6b CH_3CH_2CHOAc $CH_2C{\equiv}C$

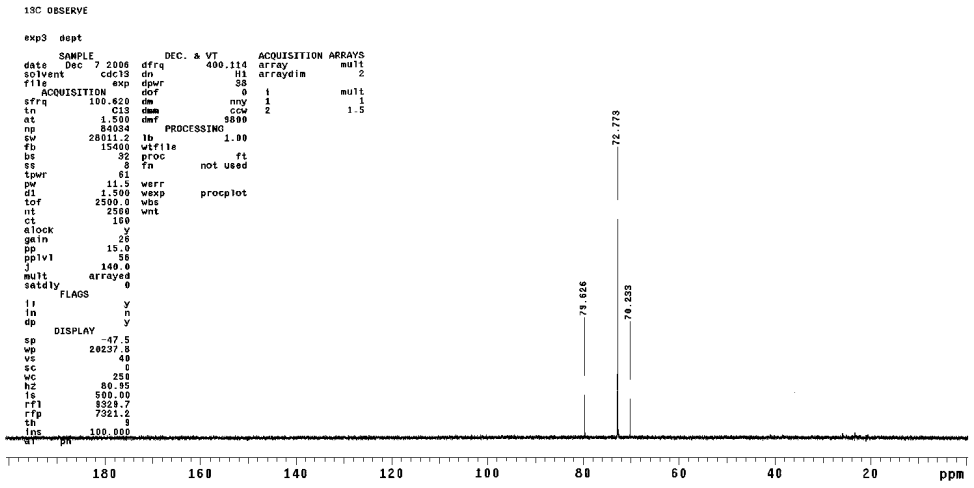
^{1}H NMR



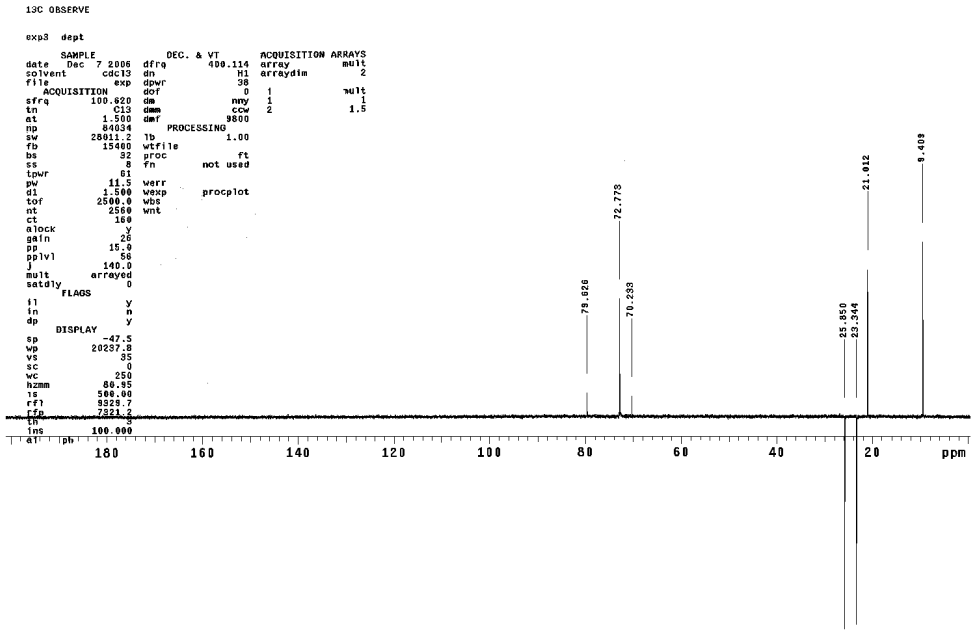
^{13}C NMR



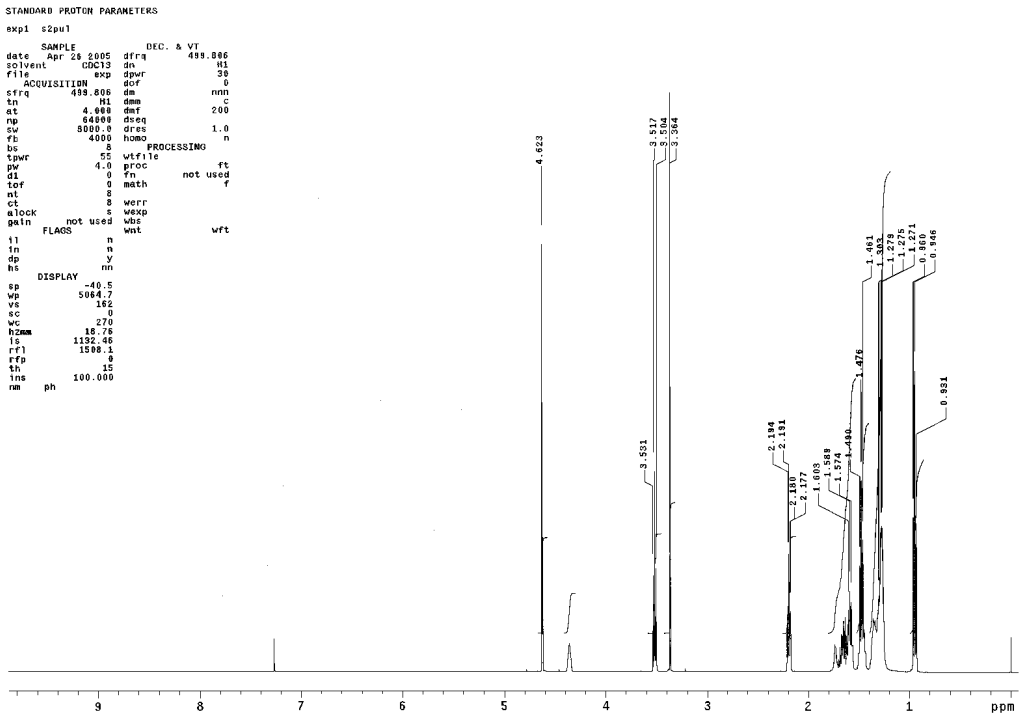
DEPT 1(CH)



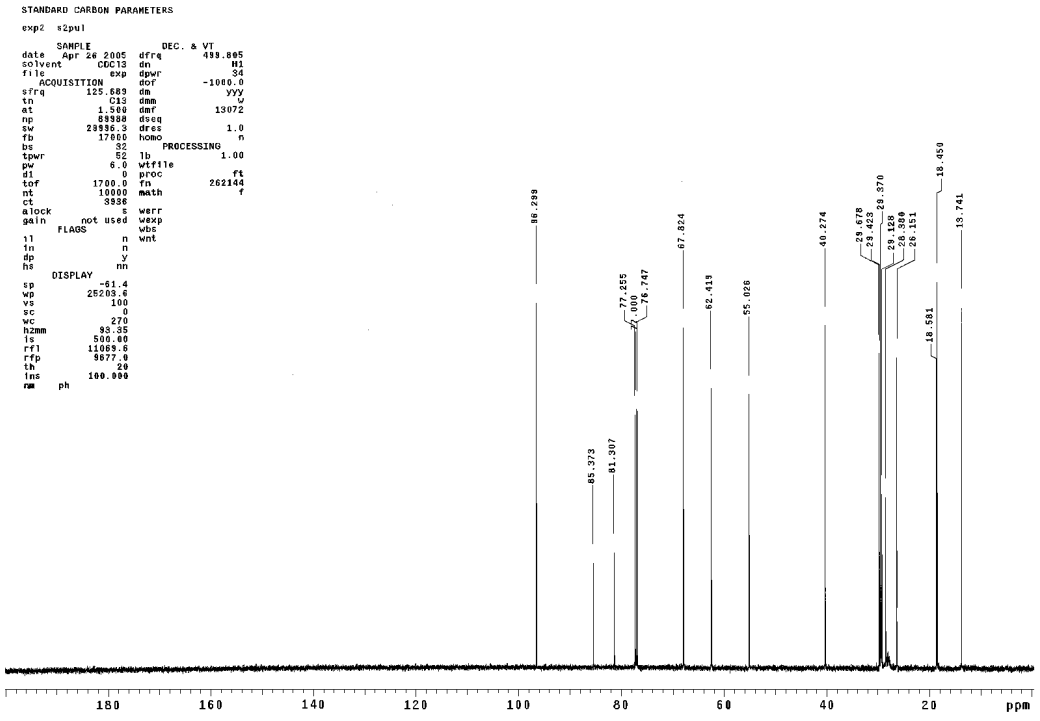
DEPT 2 (CH, CH_3/CH_2)



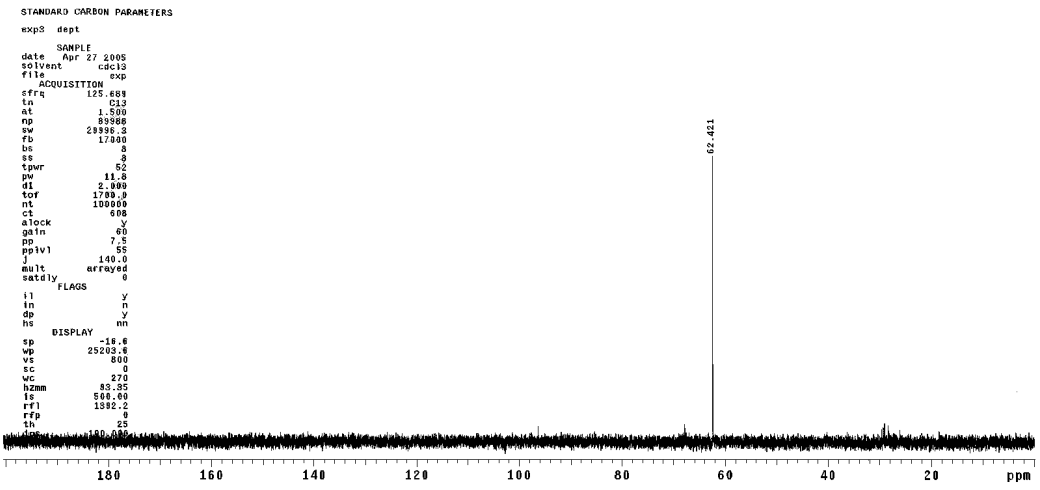
7a $CH_3(CH_2)_2CHOHC{\equiv}C(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



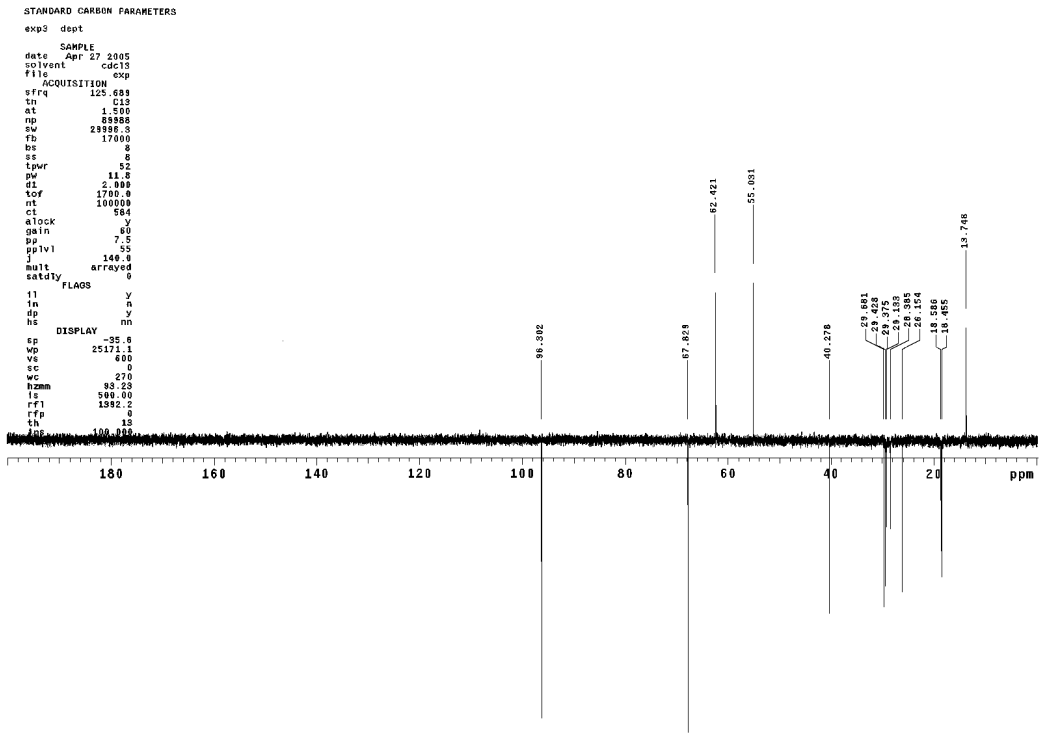
^{13}C NMR



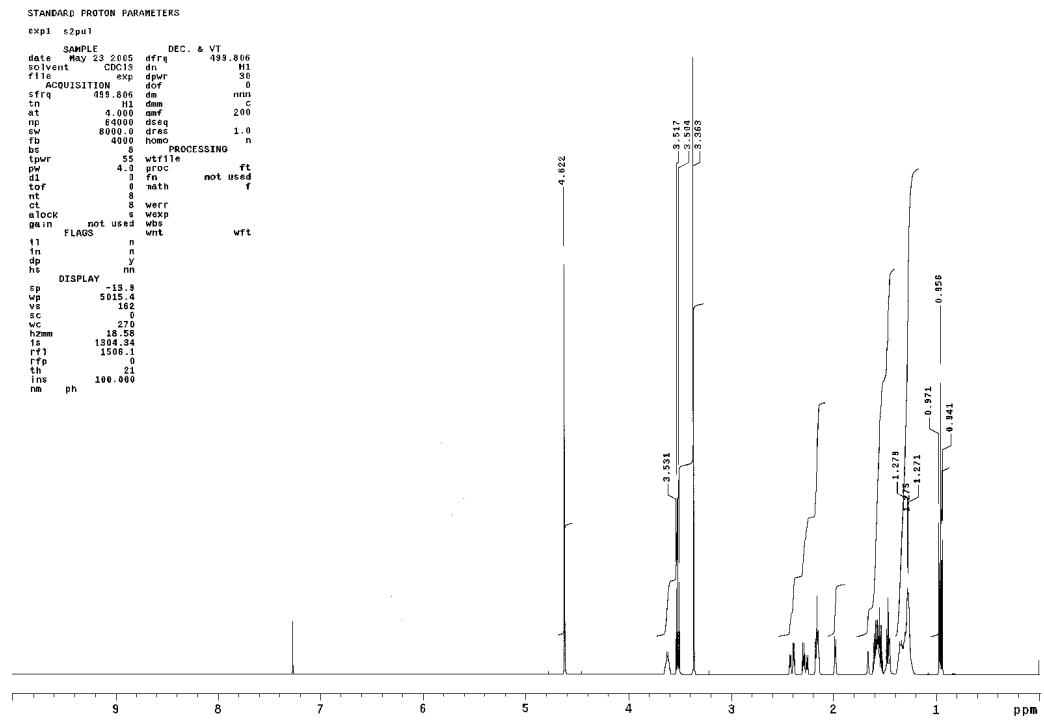
DEPT 1(CH)



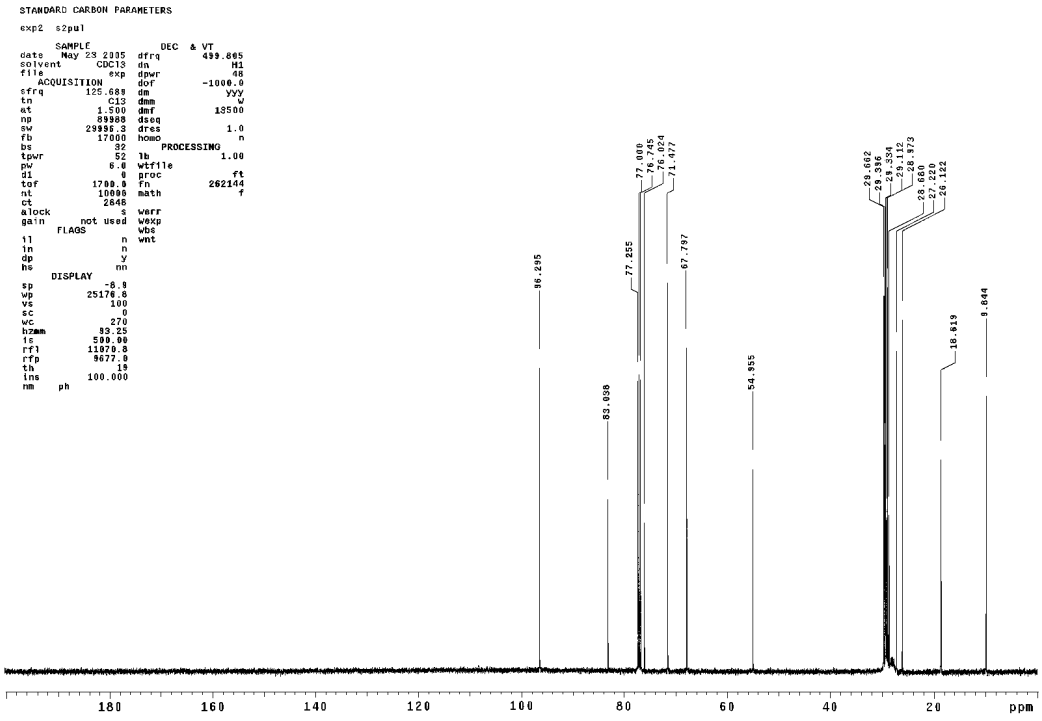
DEPT 2 (CH, CH_3/CH_2)



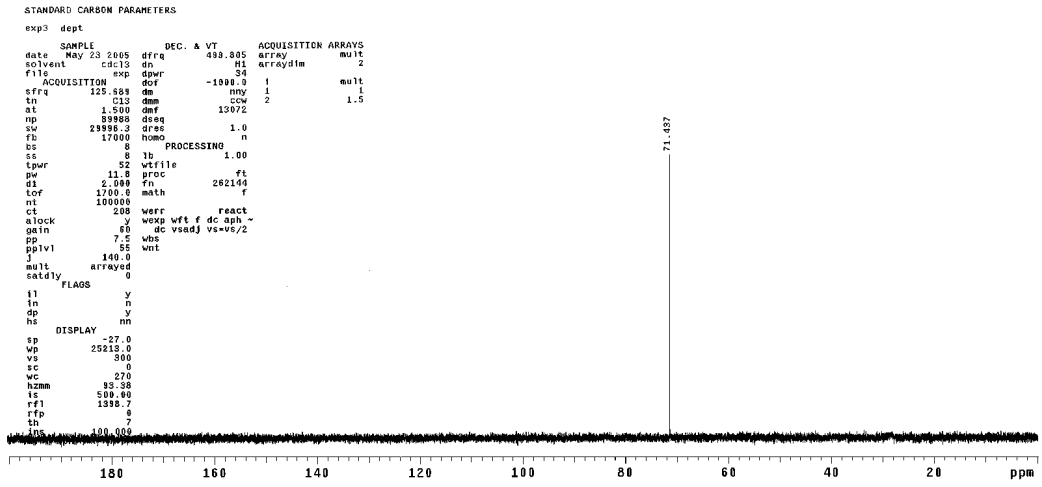
7b $CH_3CH_2CHOHCH_2C{\equiv}C(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^{1}H NMR



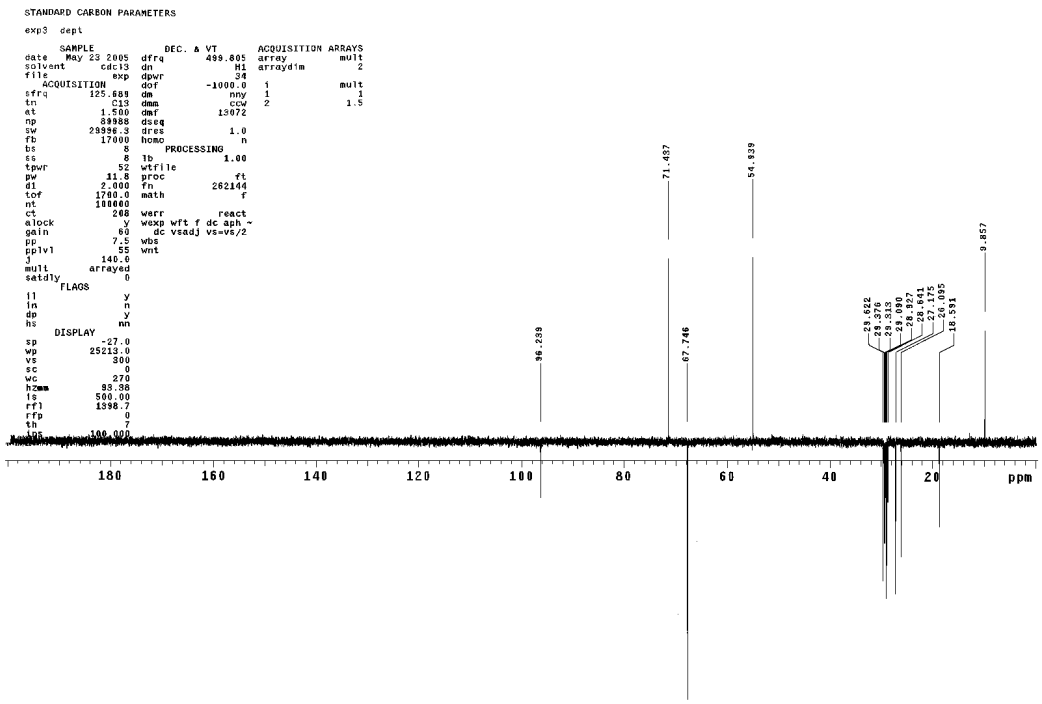
^{13}C NMR



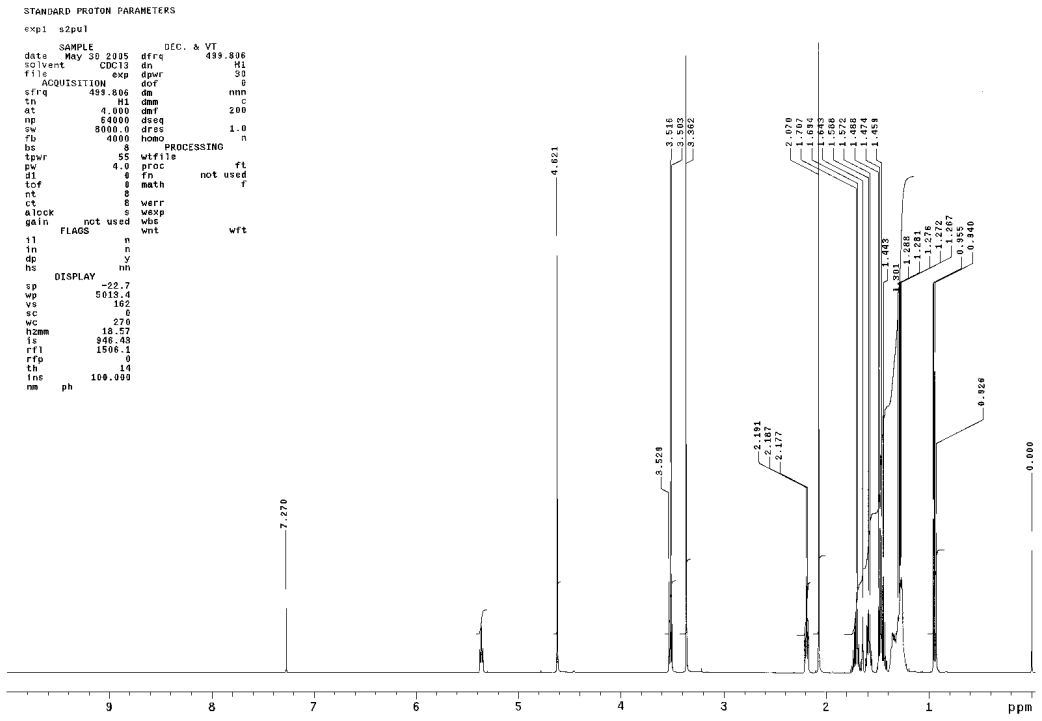
DEPT 1(CH)



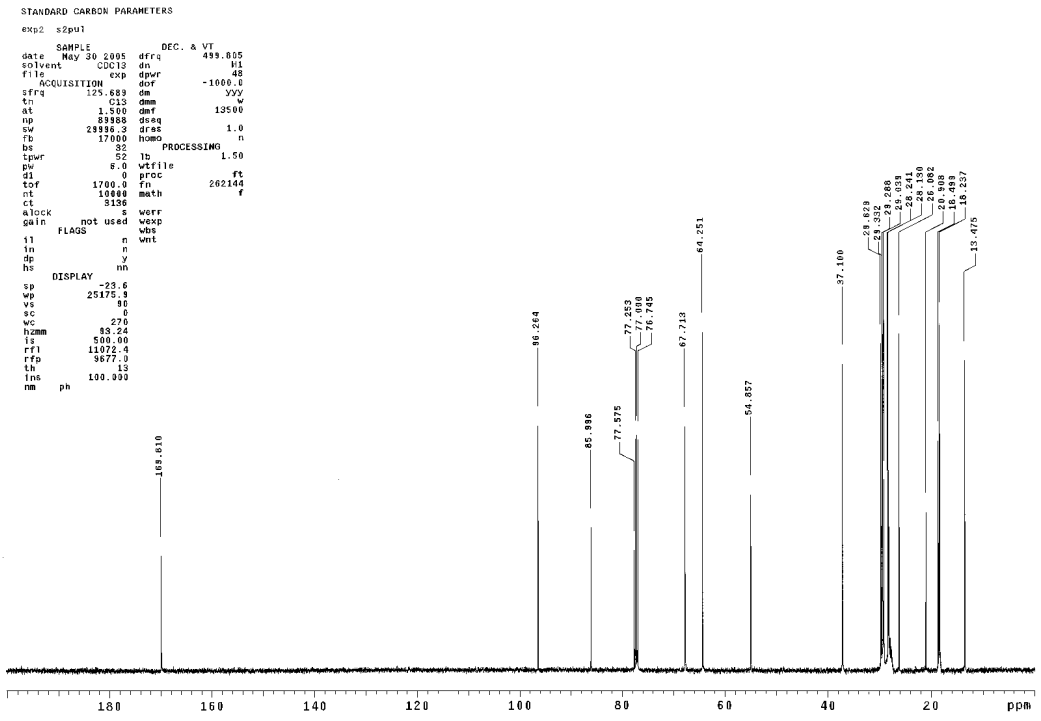
DEPT 2 (CH, CH_3/CH_2)



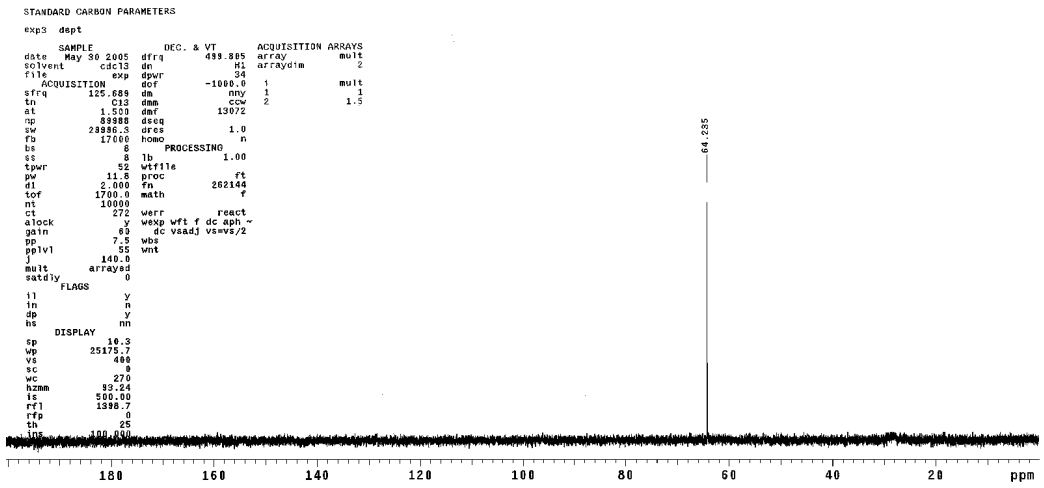
8a $CH_3(CH_2)_2CHOAcC{\equiv}C(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



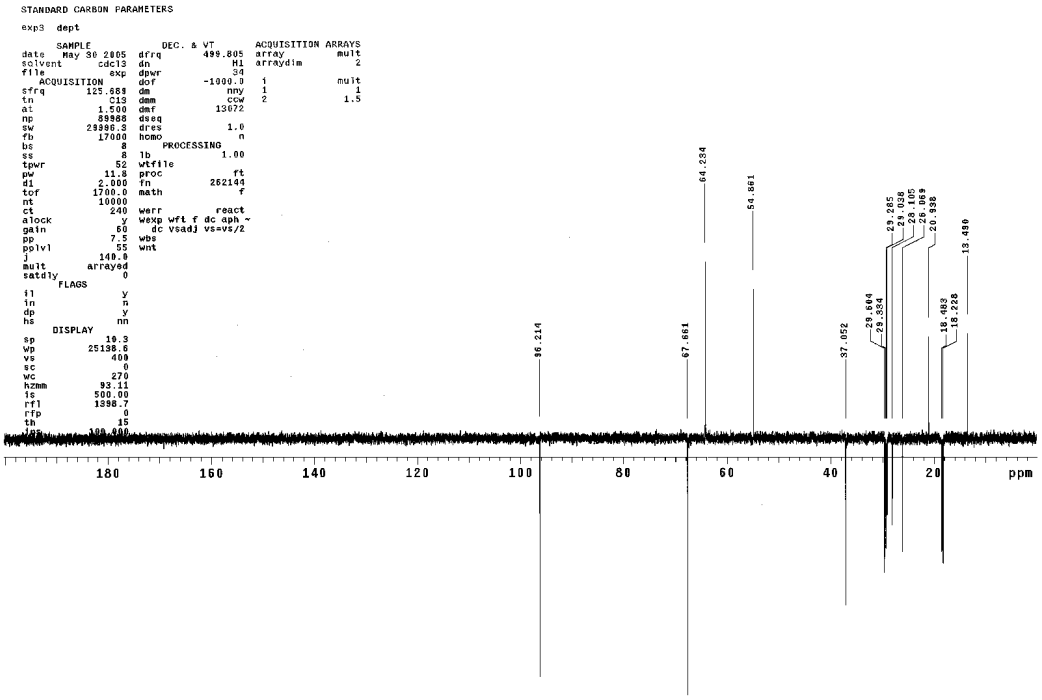
^{13}C NMR



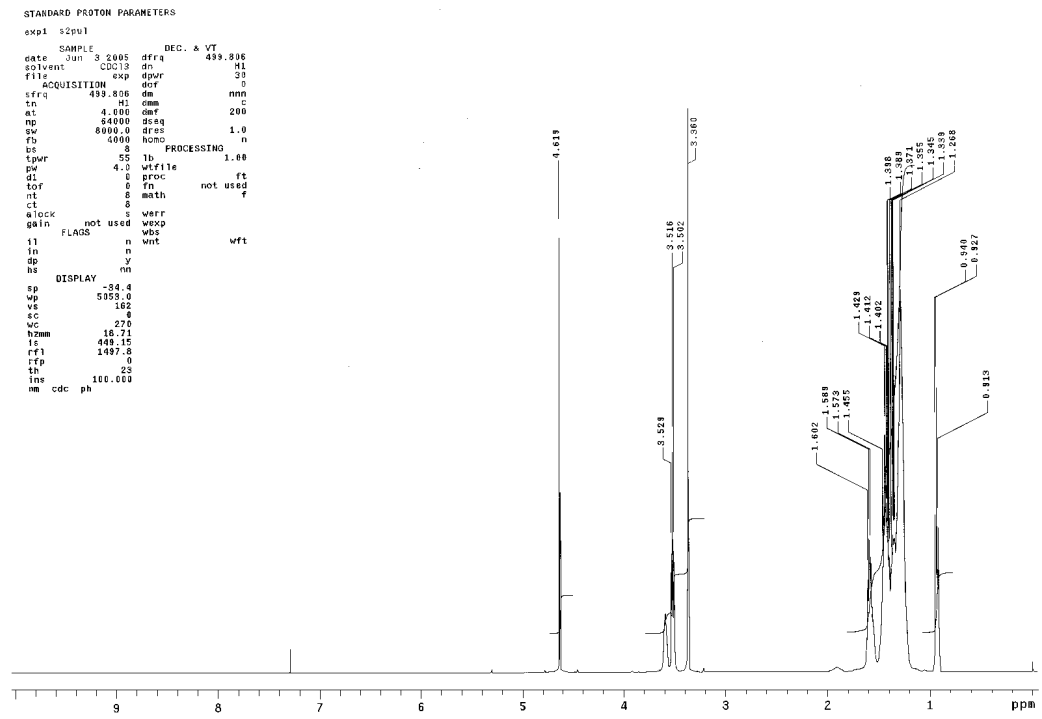
DEPT 1(CH)



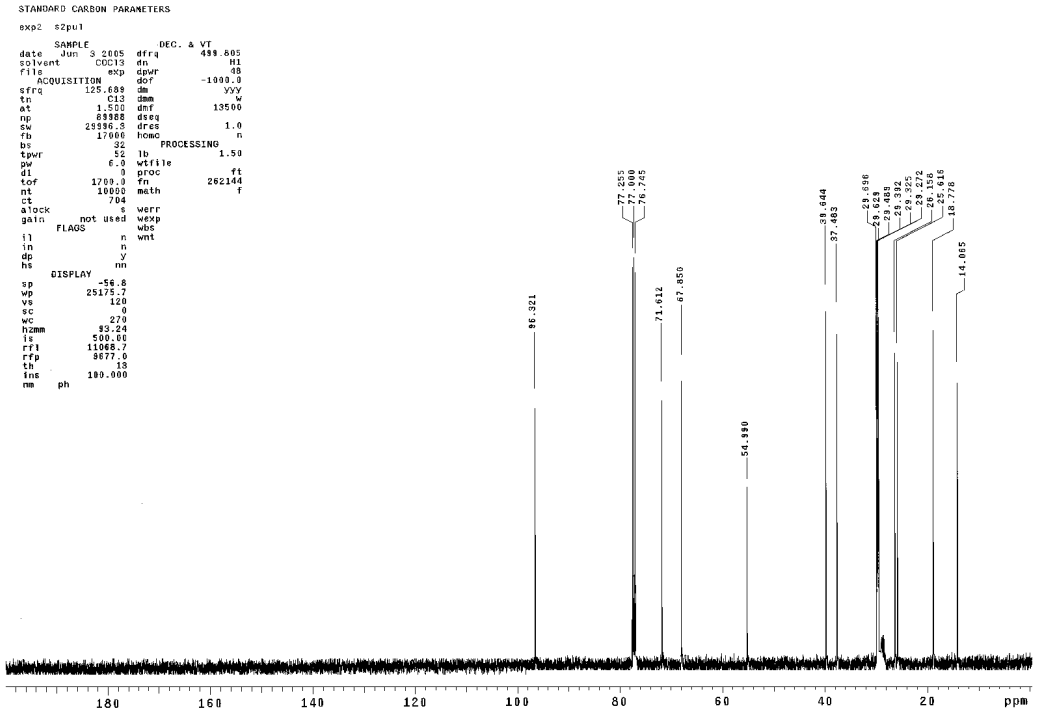
DEPT 2 (CH, CH_3/CH_2)



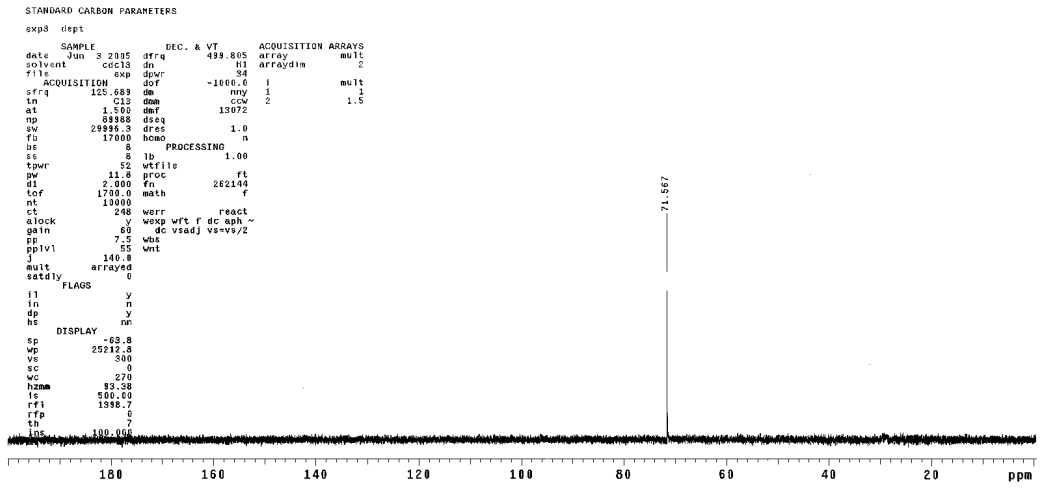
9a $CH_3(CH_2)_2CHOHCH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



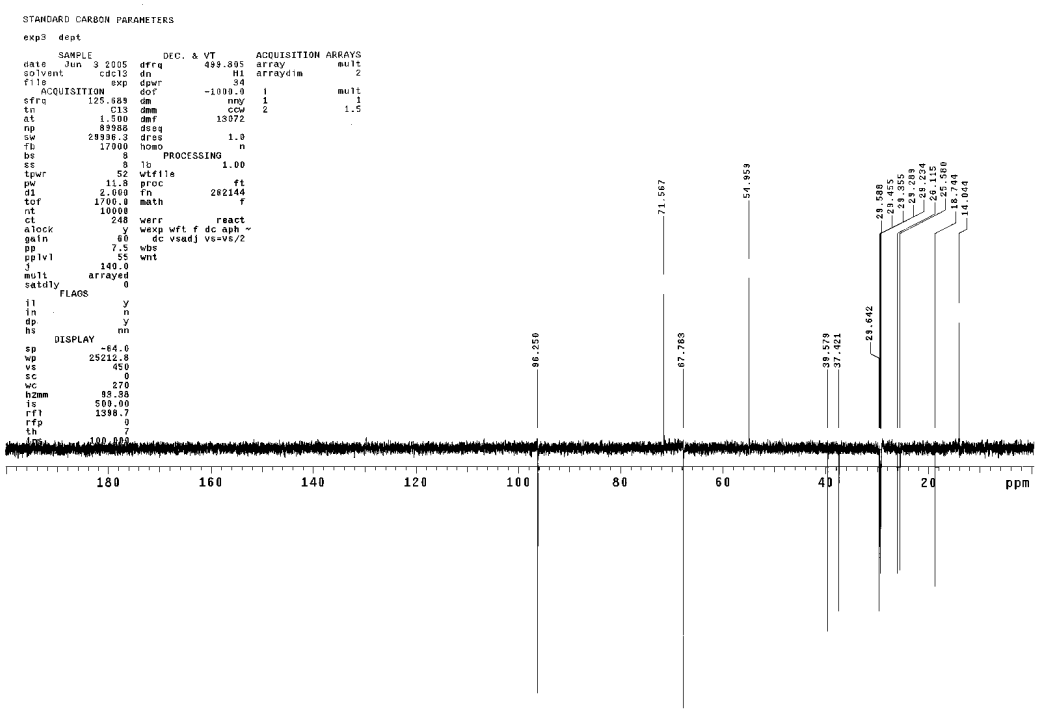
^{13}C NMR



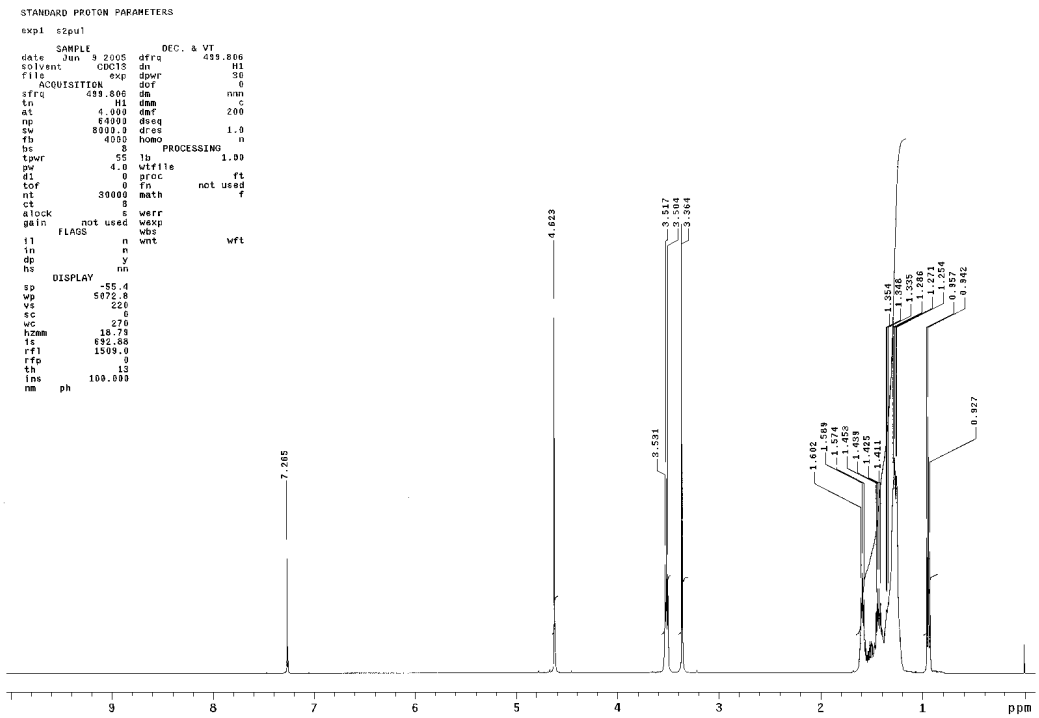
DEPT 1(CH)



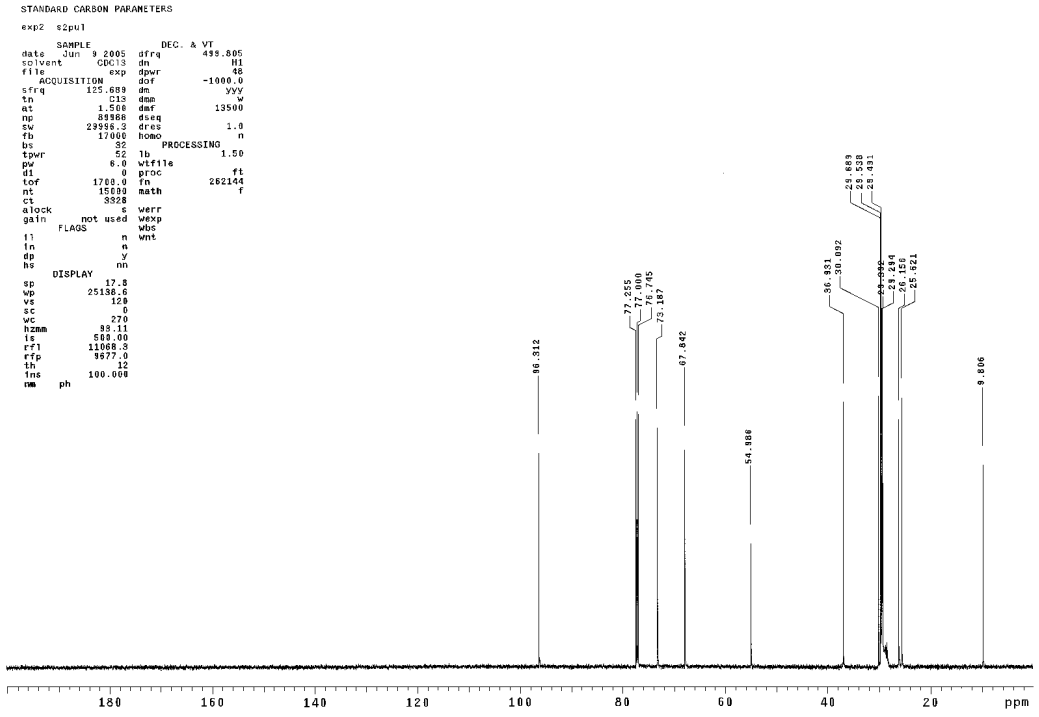
DEPT 2 (CH, CH_3/CH_2)



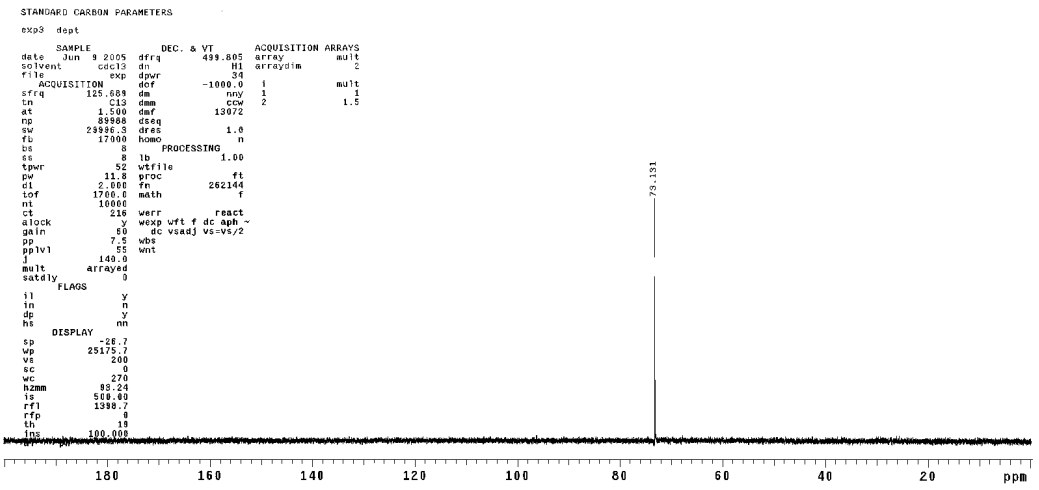
9b $CH_3CH_2CHOHCH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



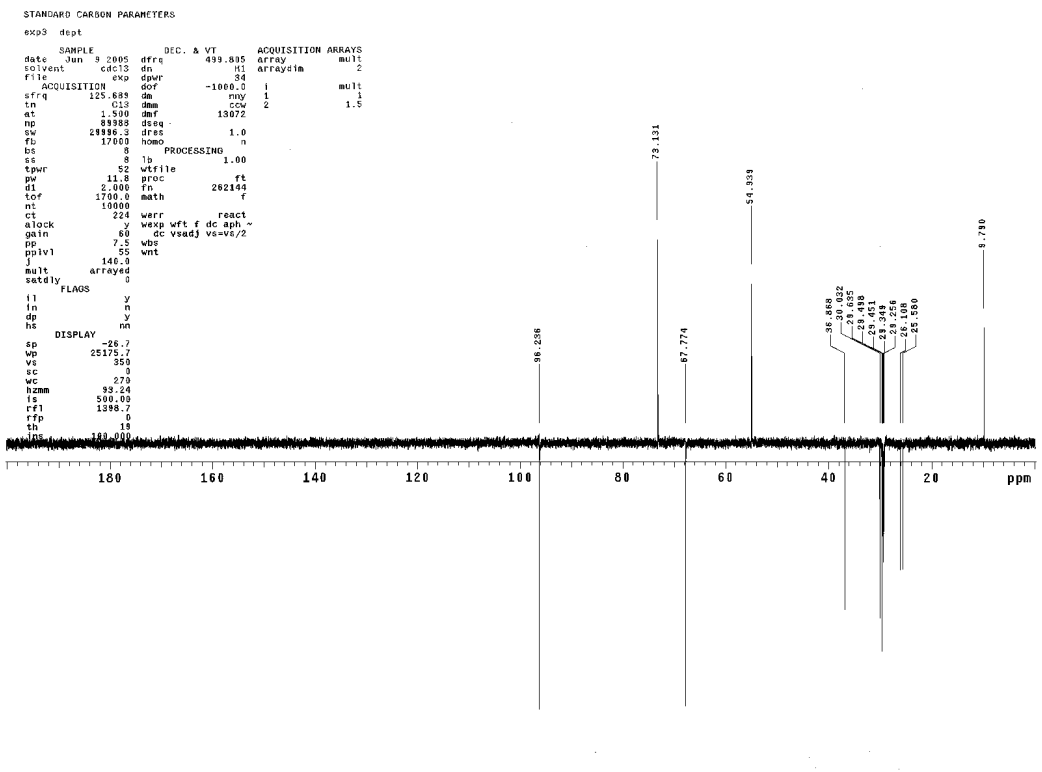
^{13}C NMR



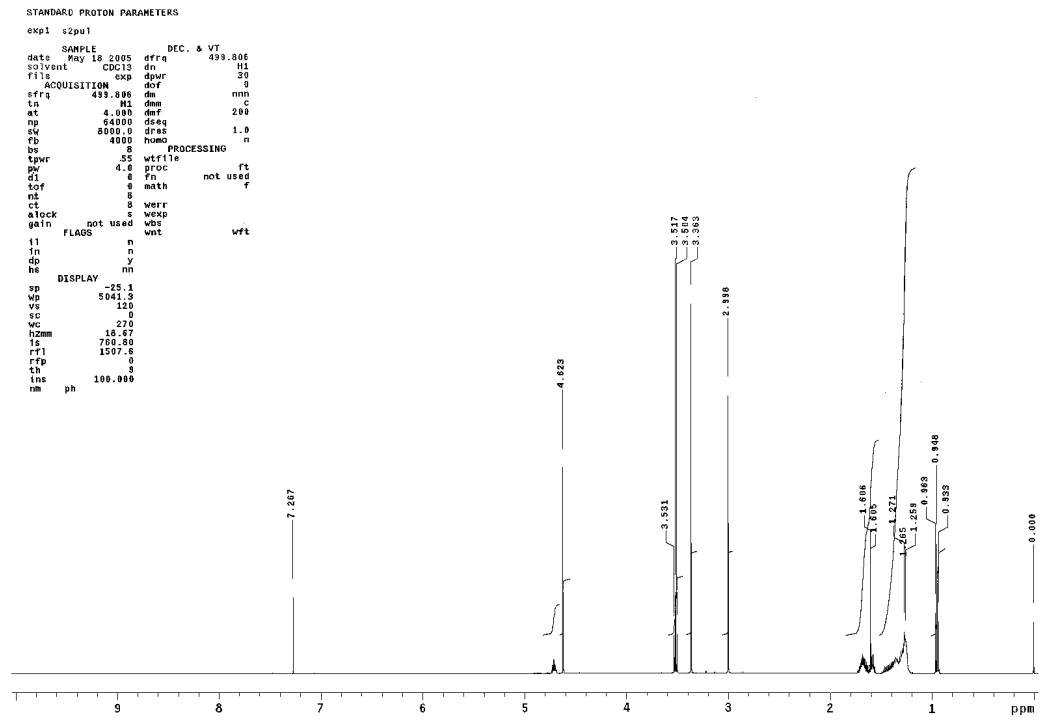
DEPT 1(CH)



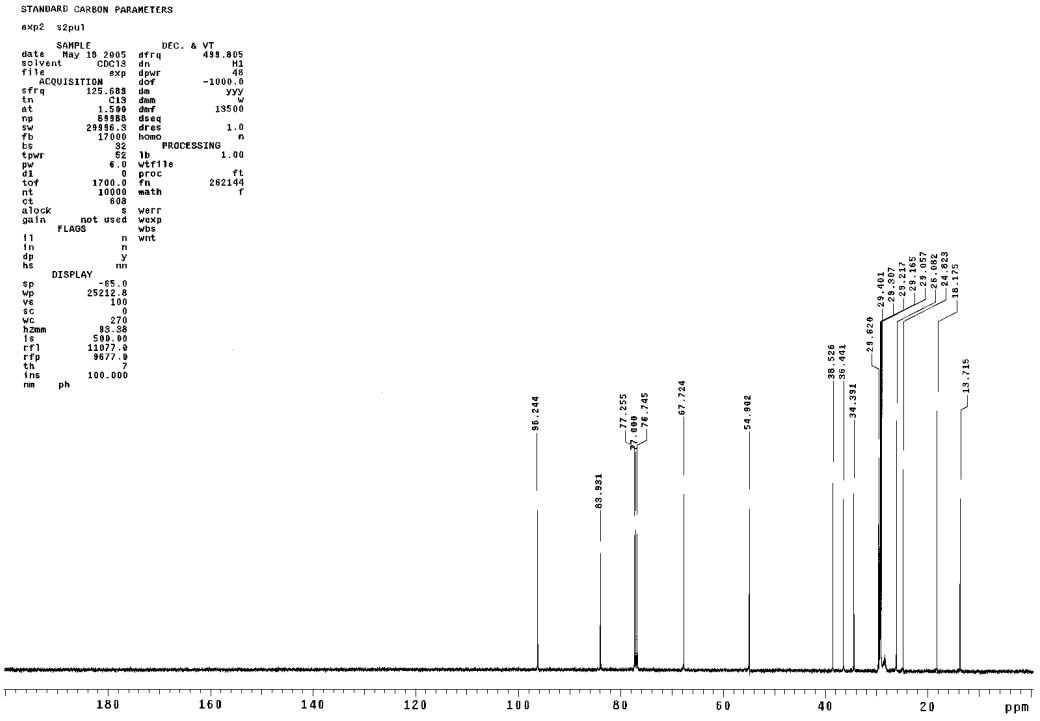
DEPT 2 (CH, CH_3/CH_2)



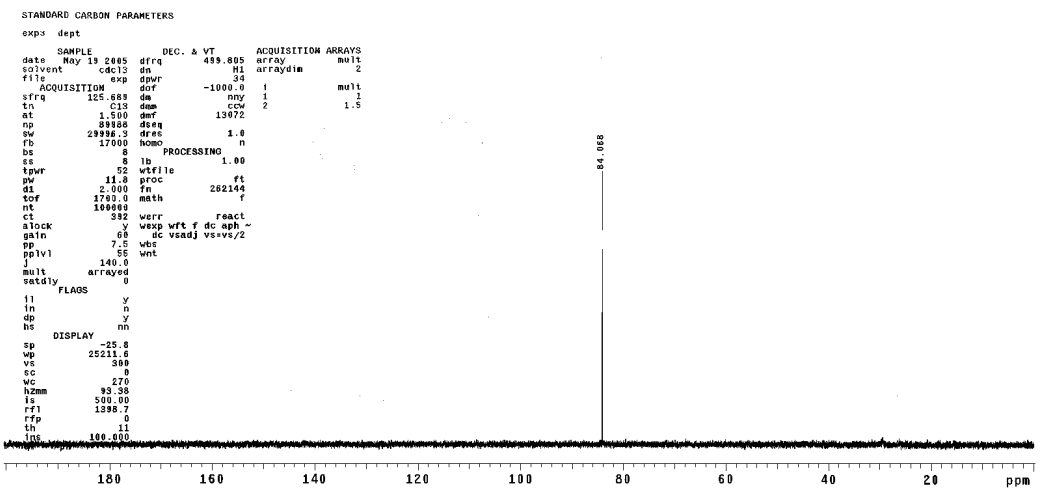
10a $CH_3(CH_2)_2CHOMsCH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



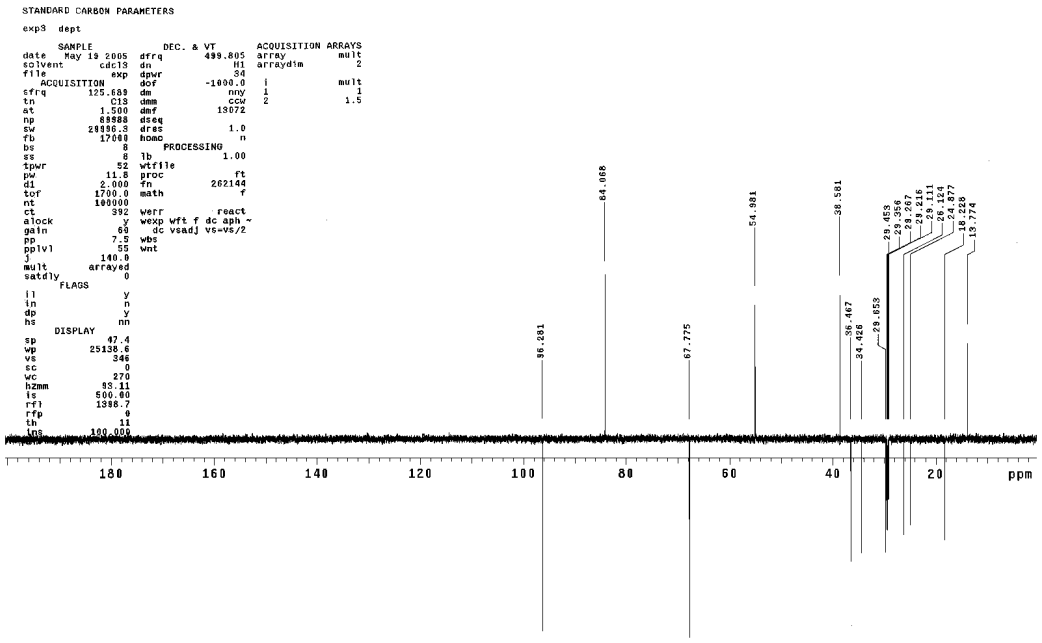
^{13}C NMR



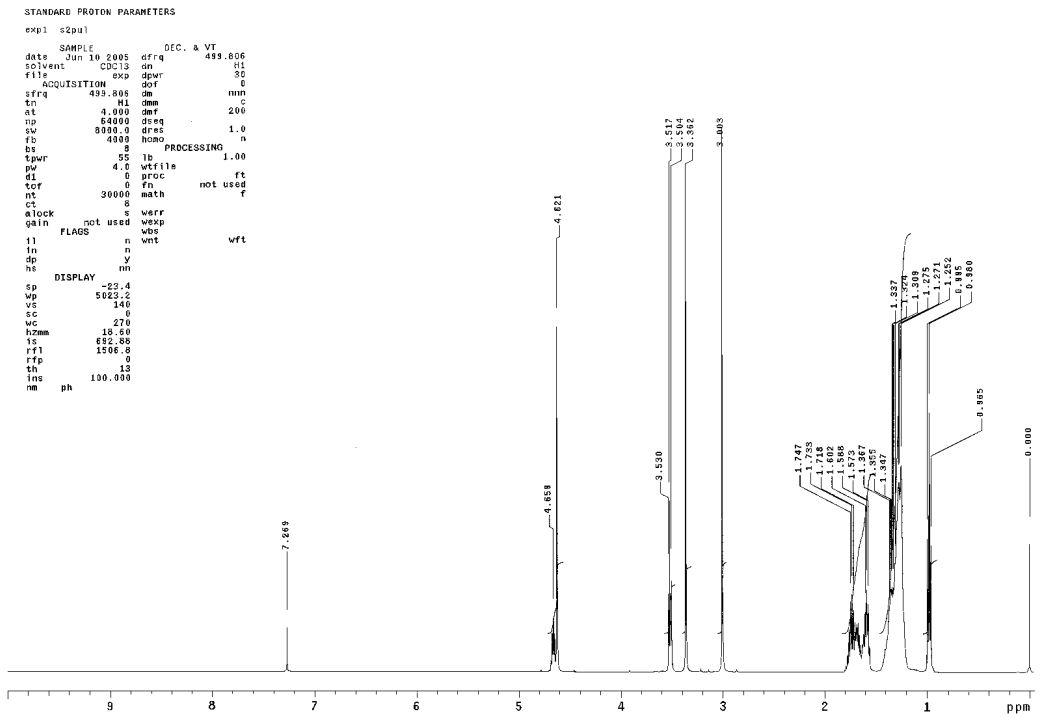
DEPT 1(CH)



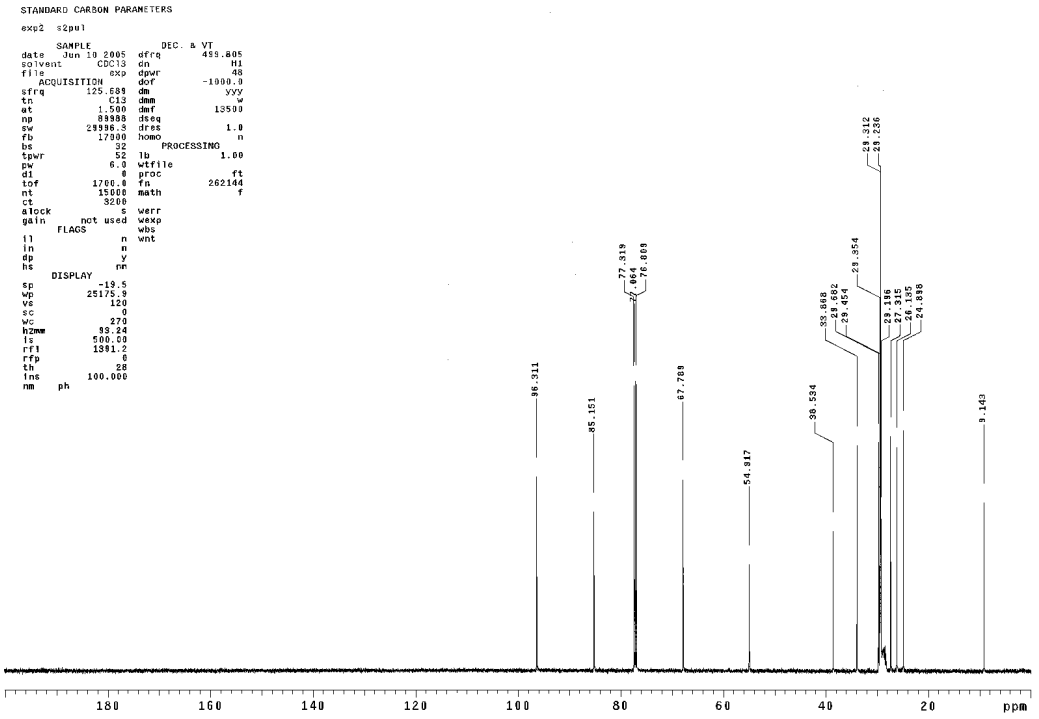
DEPT 2 (CH, CH_3/CH_2)



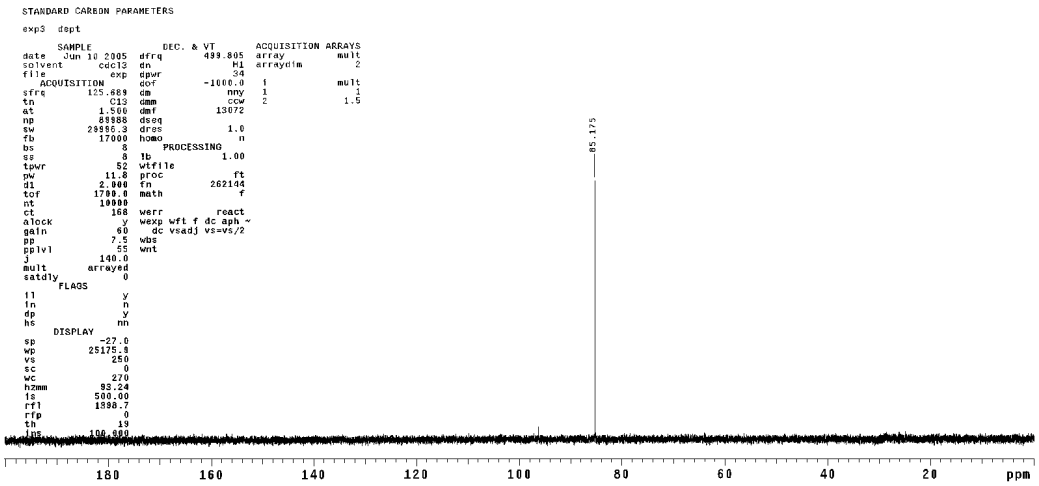
10b $CH_3CH_2CHOMsCH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



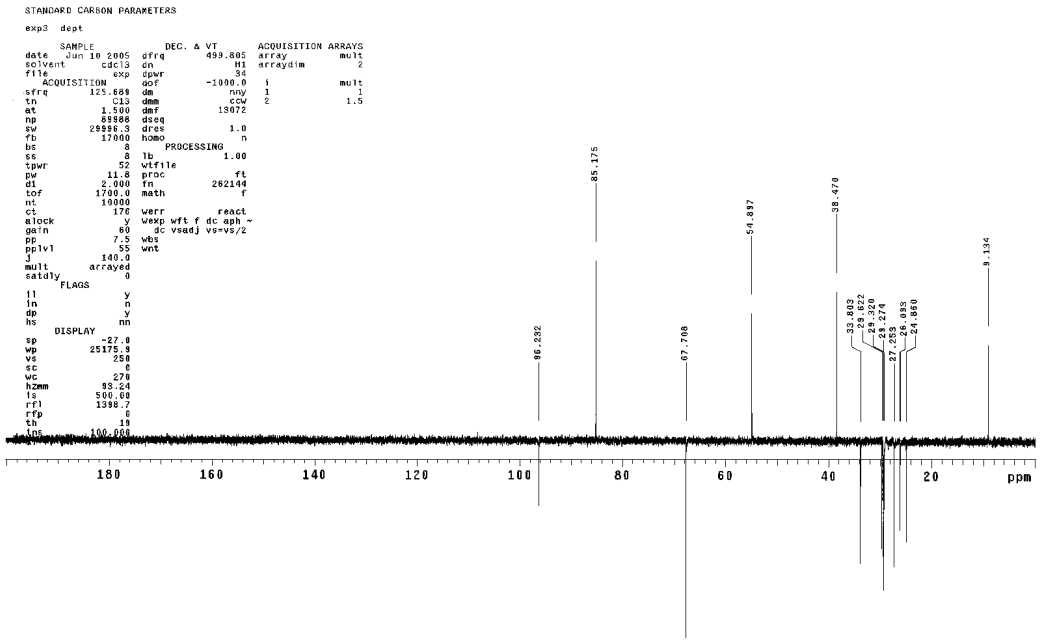
^{13}C NMR



DEPT 1(CH)

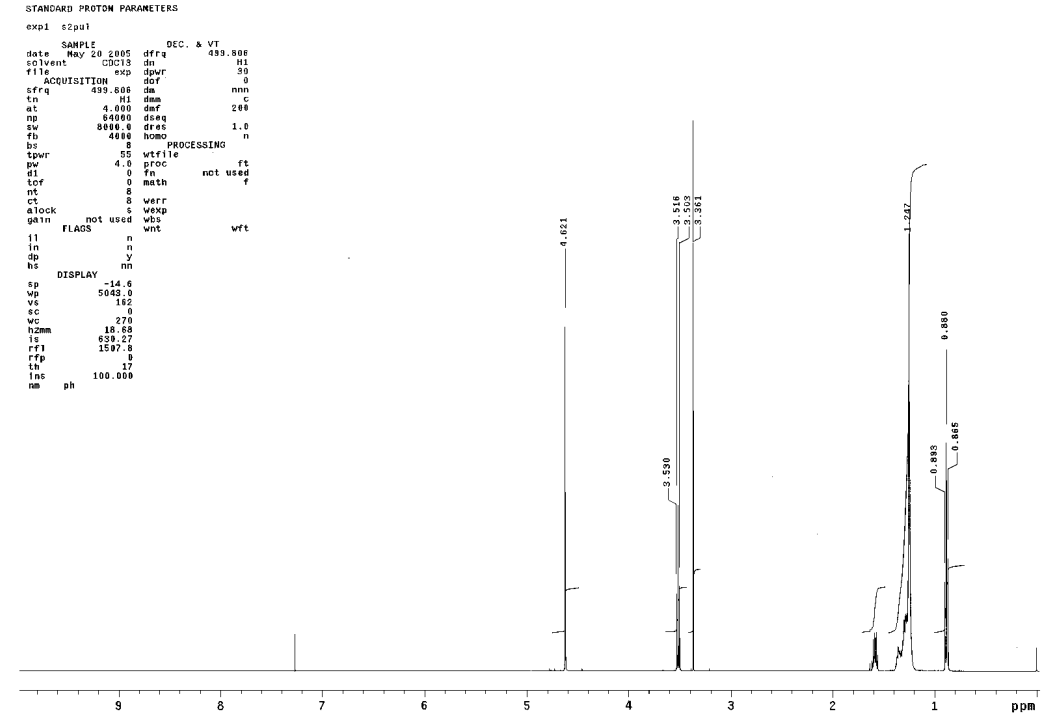


DEPT 2 (CH, CH_3/CH_2)

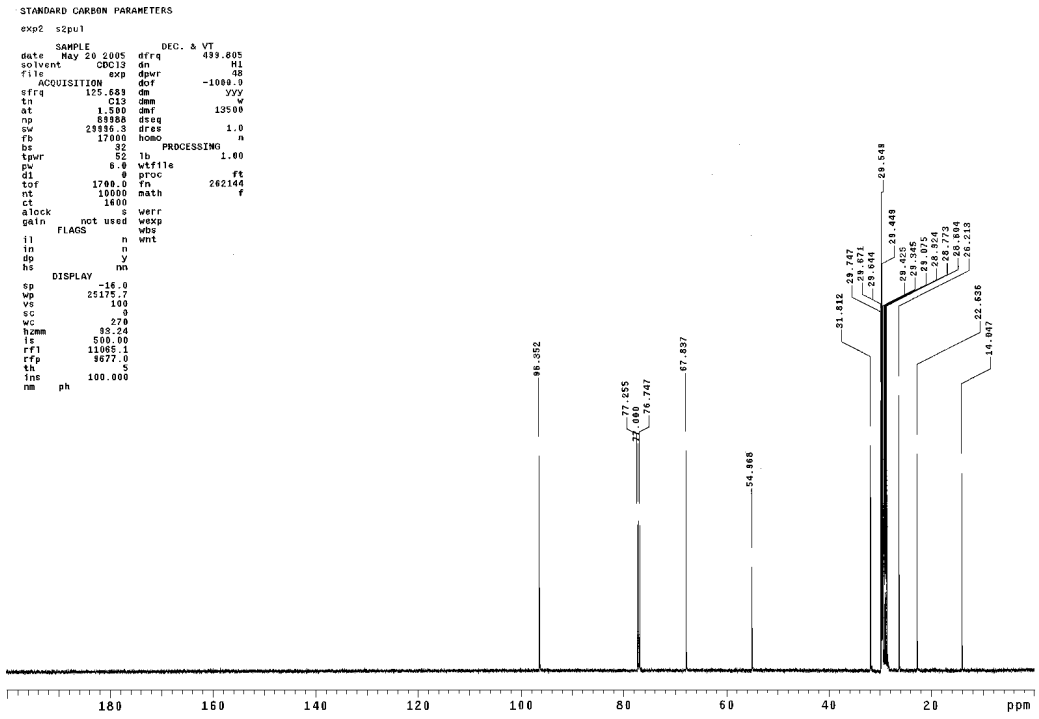


11a $CH_3(CH_2)_2CHDCH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

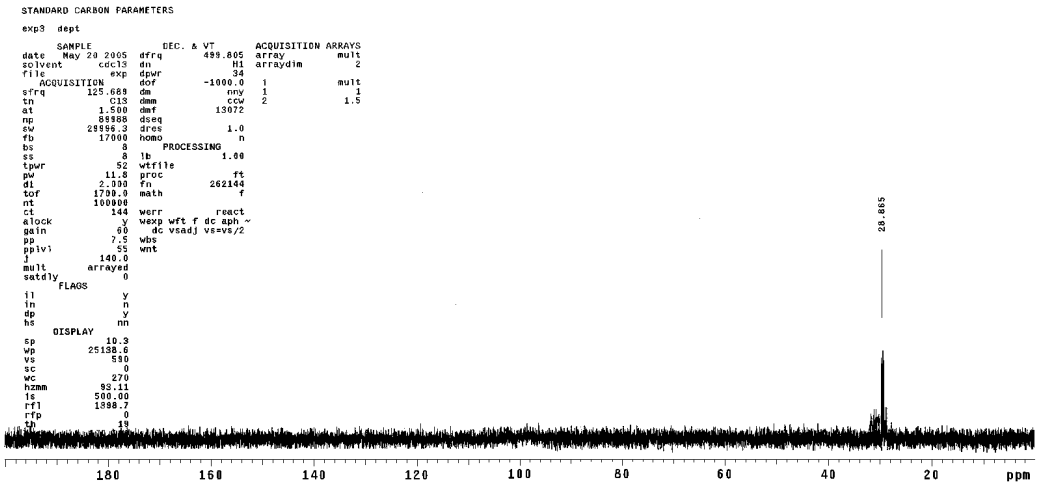
^1H NMR



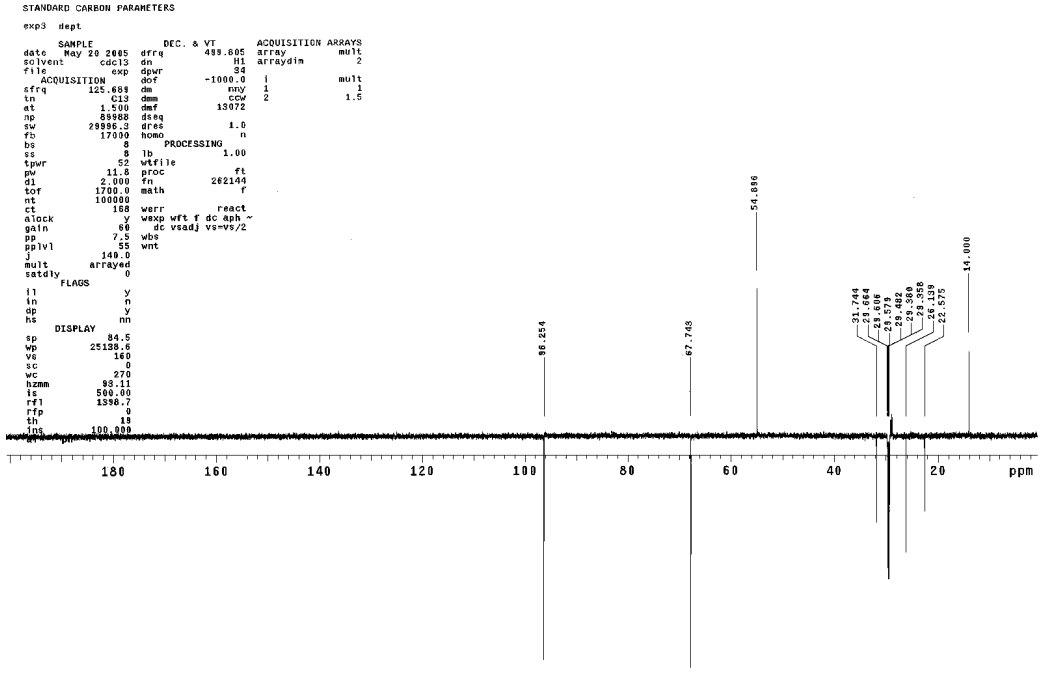
^{13}C NMR



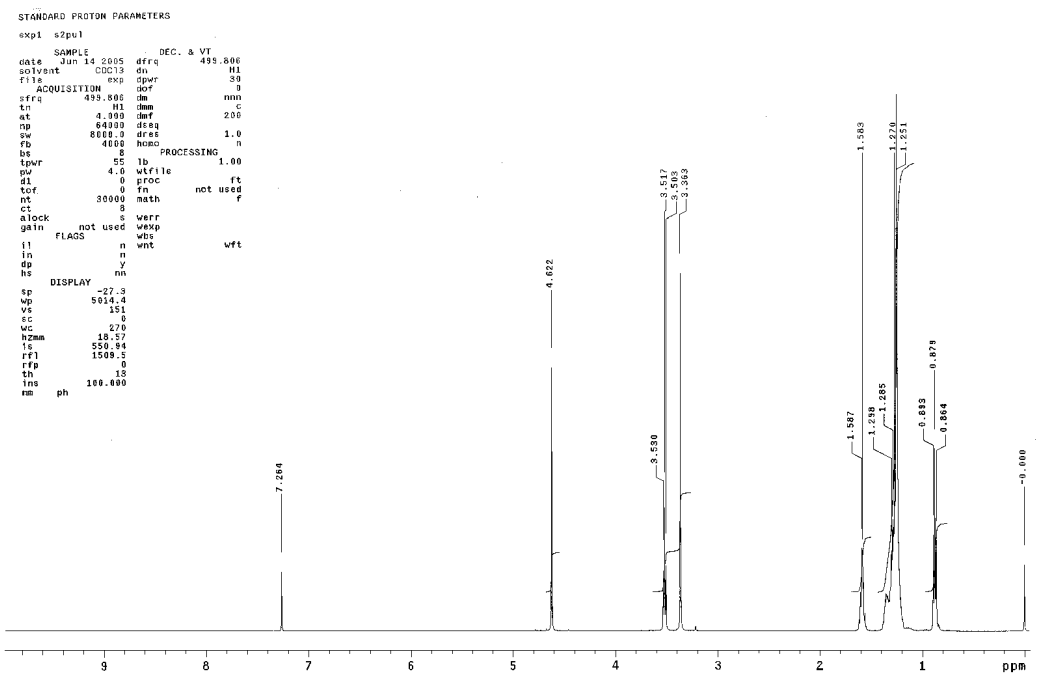
DEPT 1(CH)



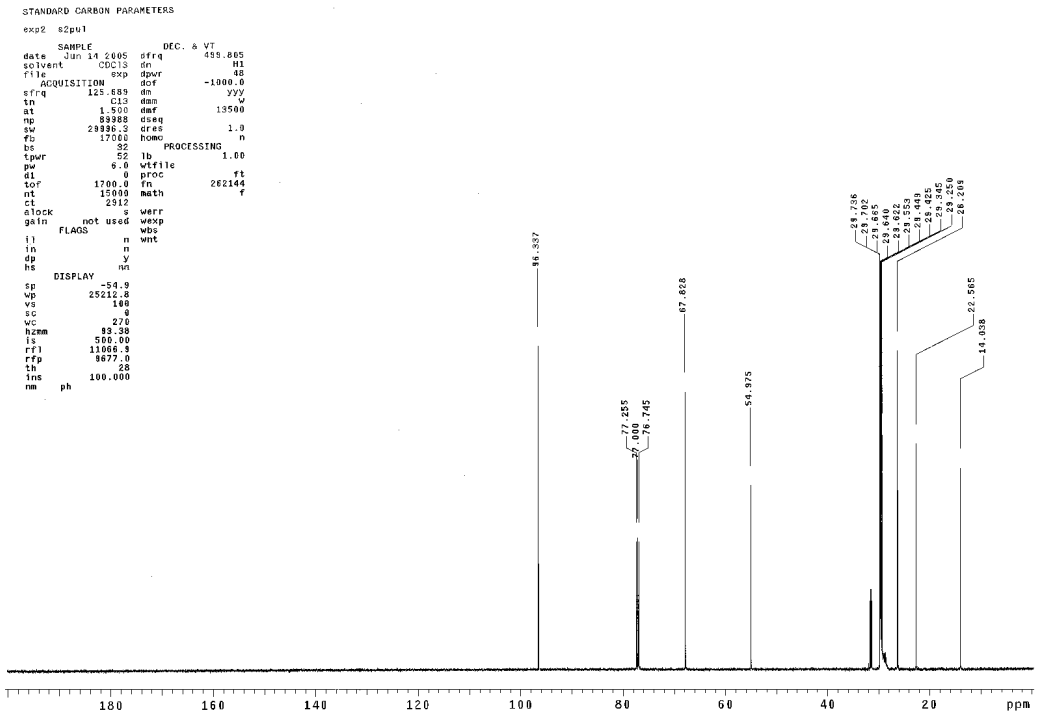
DEPT 2 (CH, CH_3/CH_2)



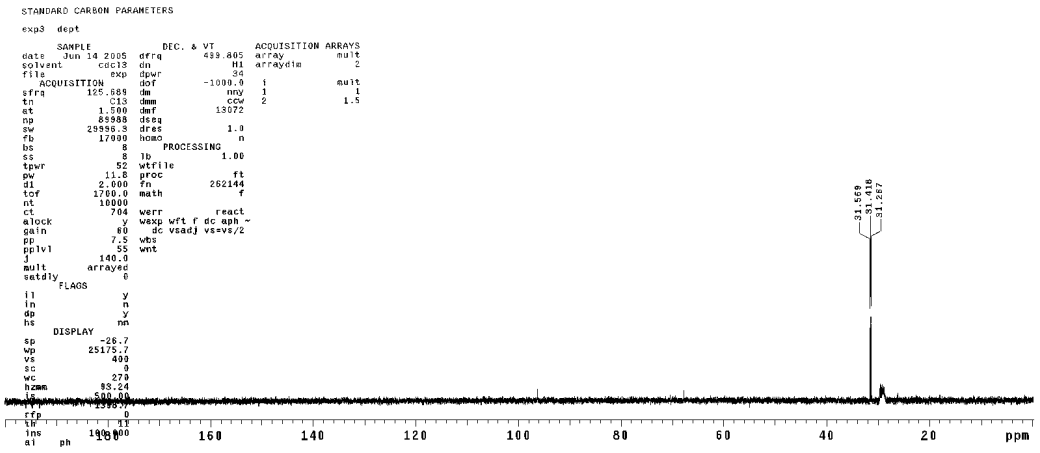
11b $CH_3CH_2CHDCH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$
^1H NMR



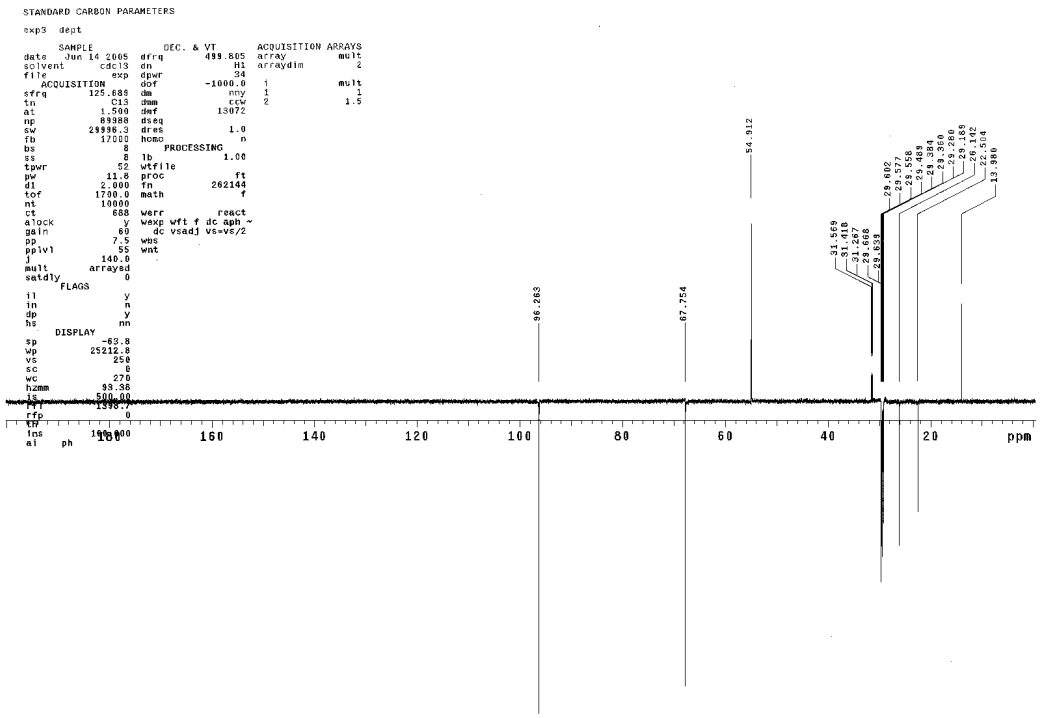
^{13}C NMR



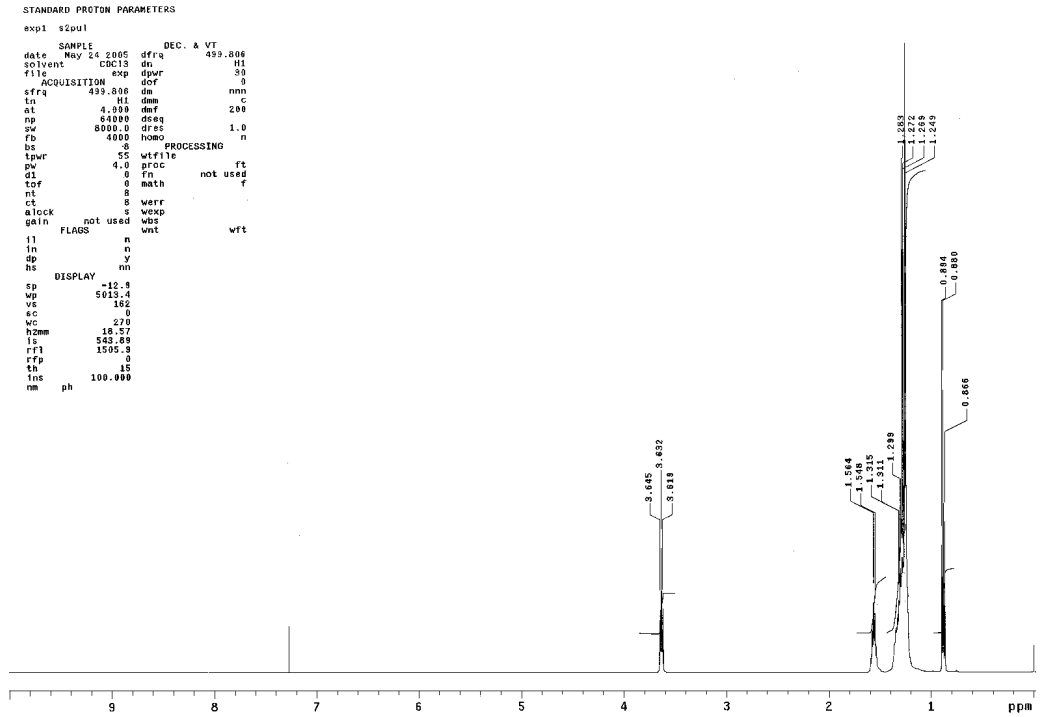
DEPT 1(CH)



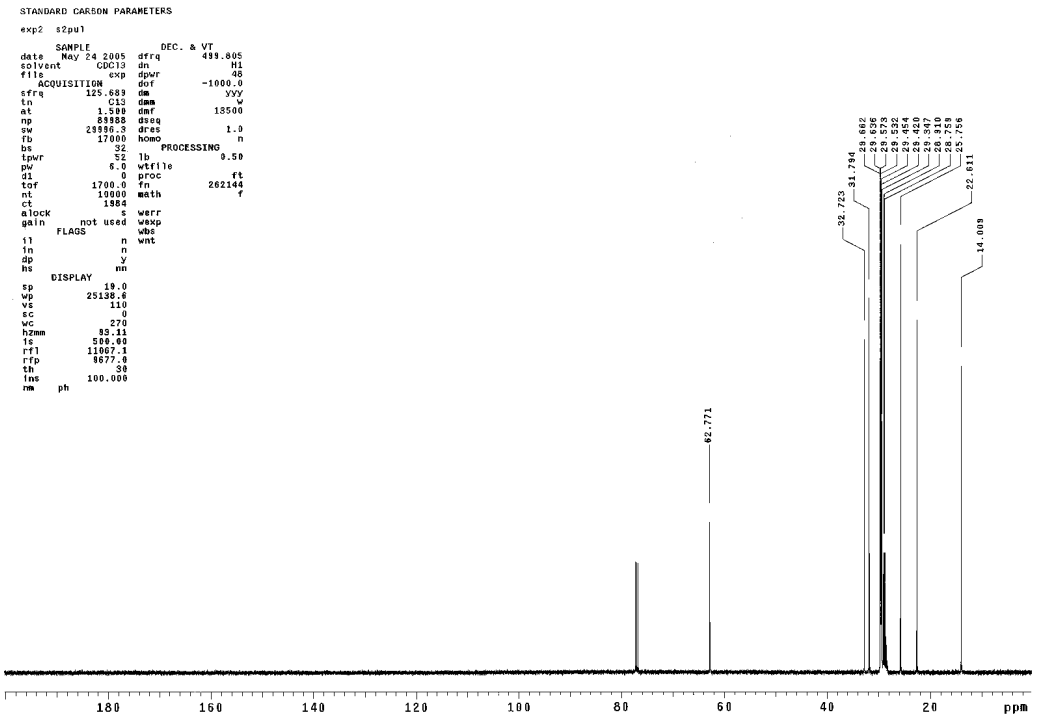
DEPT 2 (CH, CH_3/CH_2)



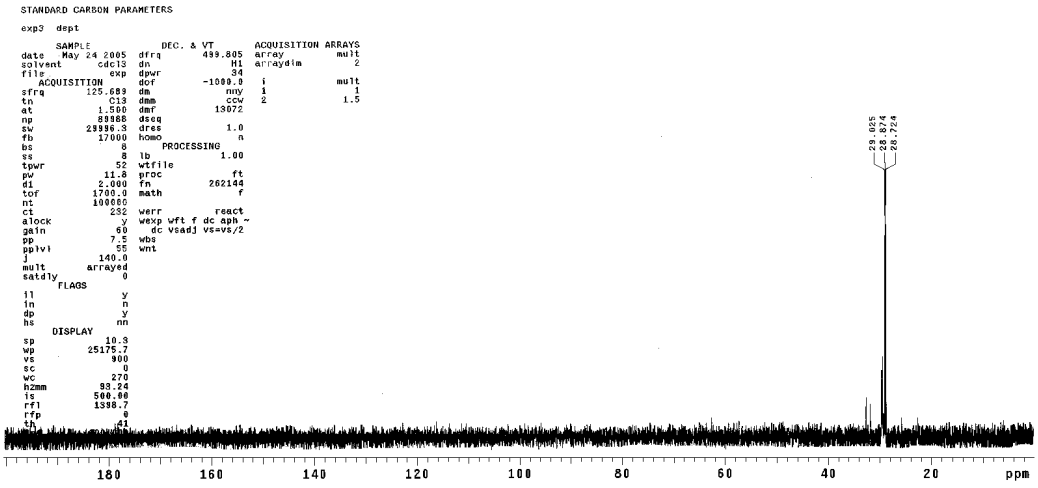
12a $CH_3CH_2CH_2CHDCH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OH$
^1H NMR



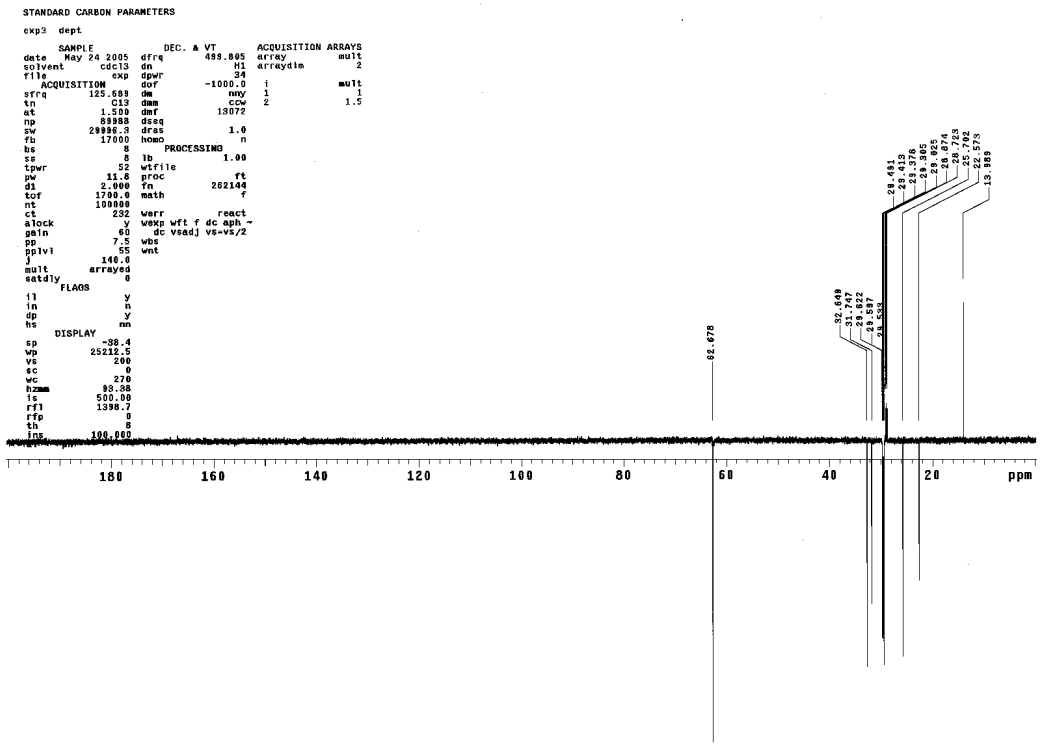
^{13}C NMR



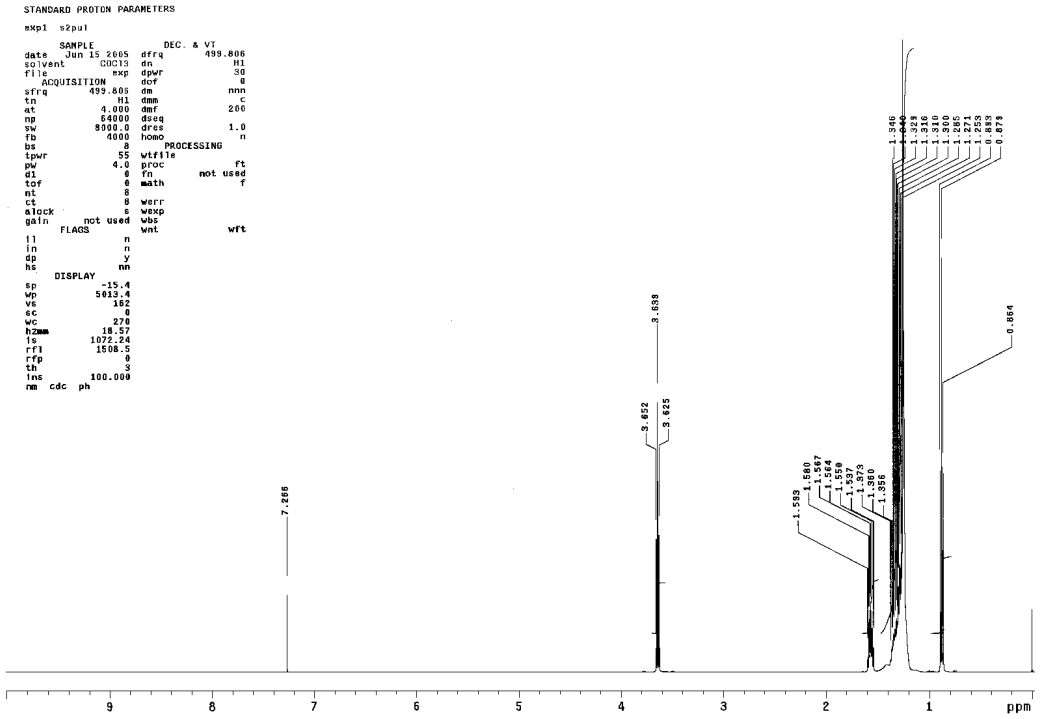
DEPT 1(CH)



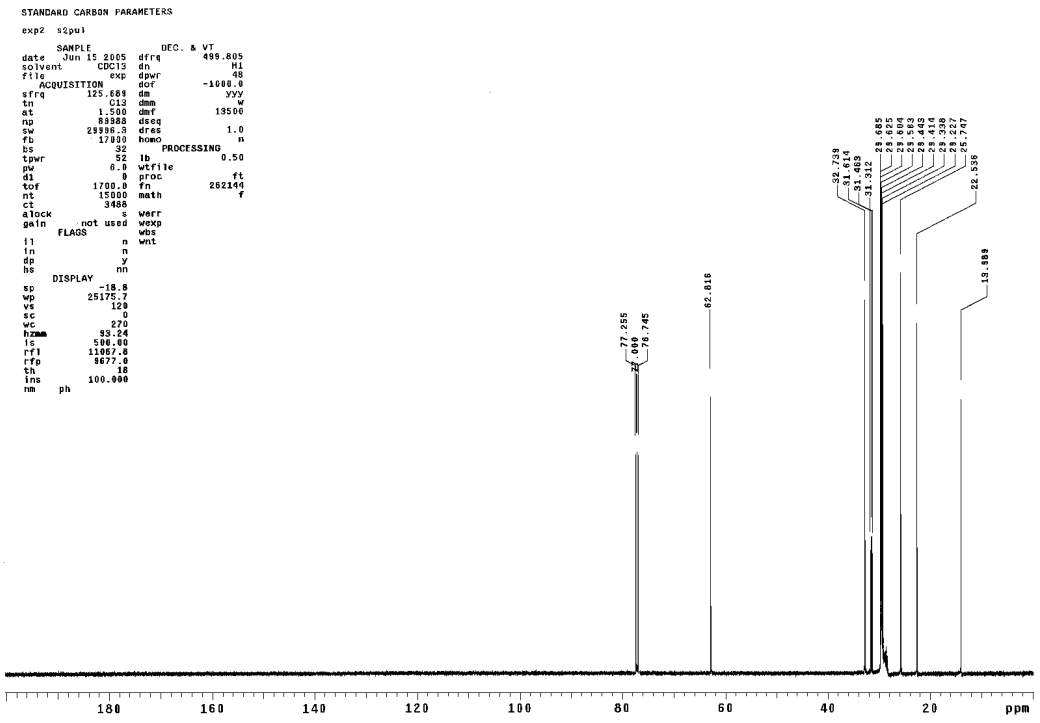
DEPT 2 (CH, CH_3/CH_2)



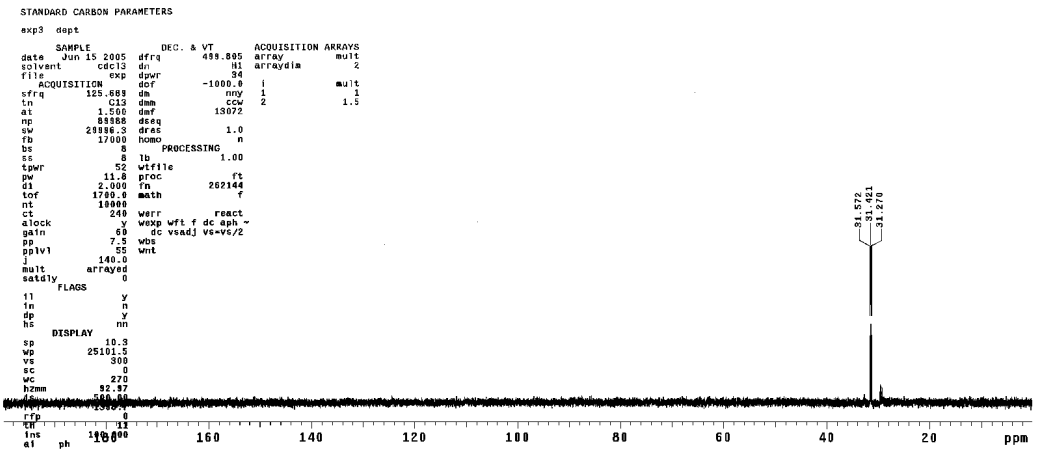
12b $CH_3CH_2CHDCH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OH$
^1H NMR



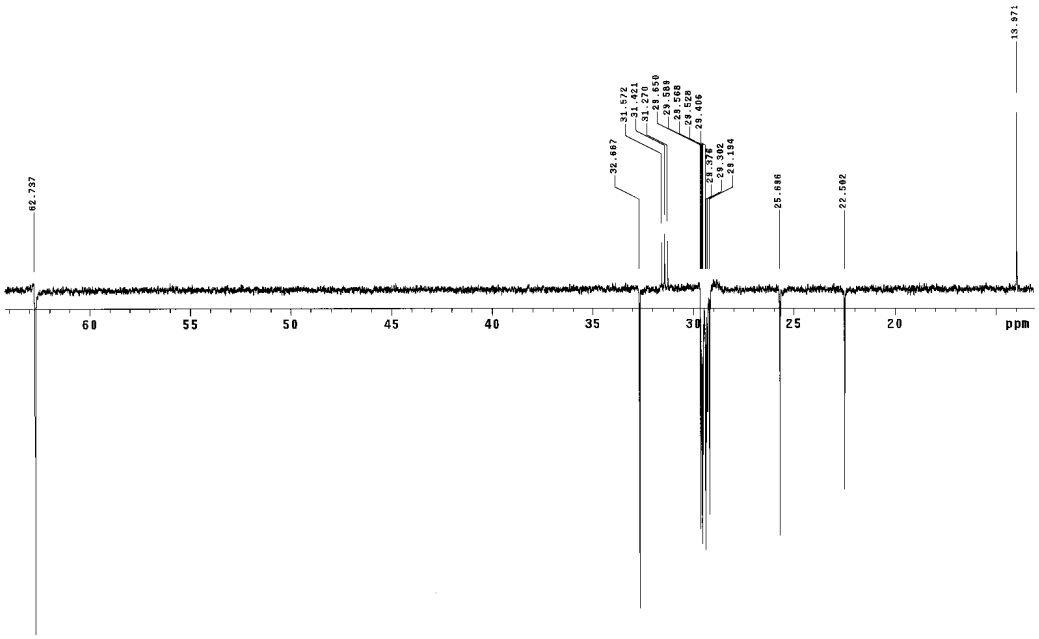
^{13}C NMR



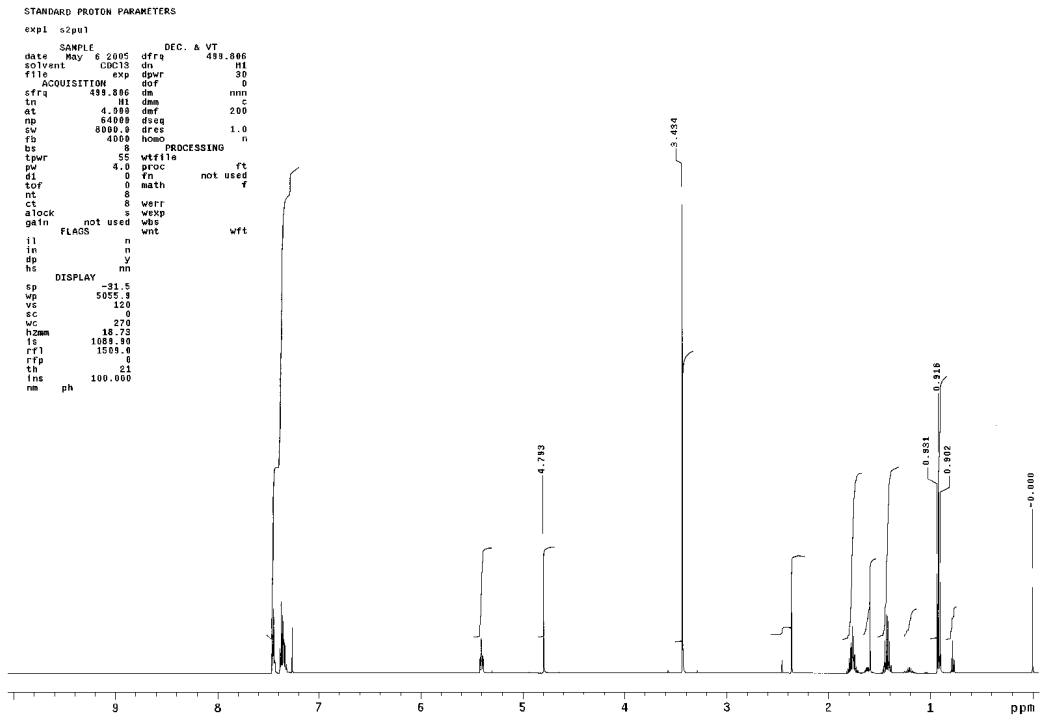
DEPT 1(CH)



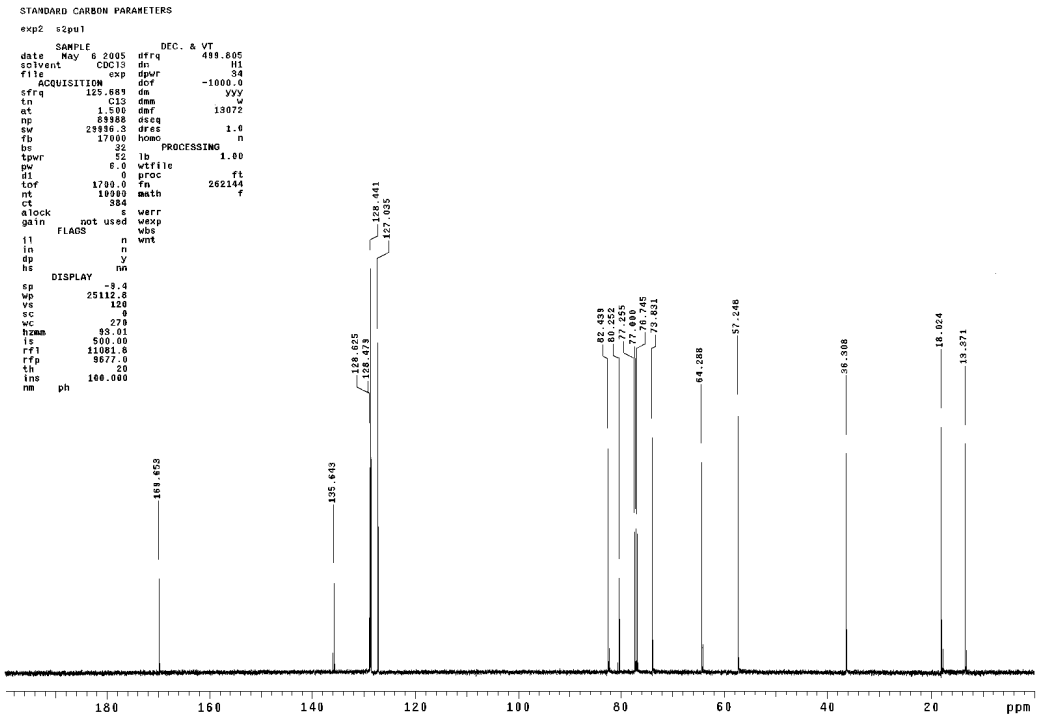
DEPT 2 (CH, CH_3/CH_2)



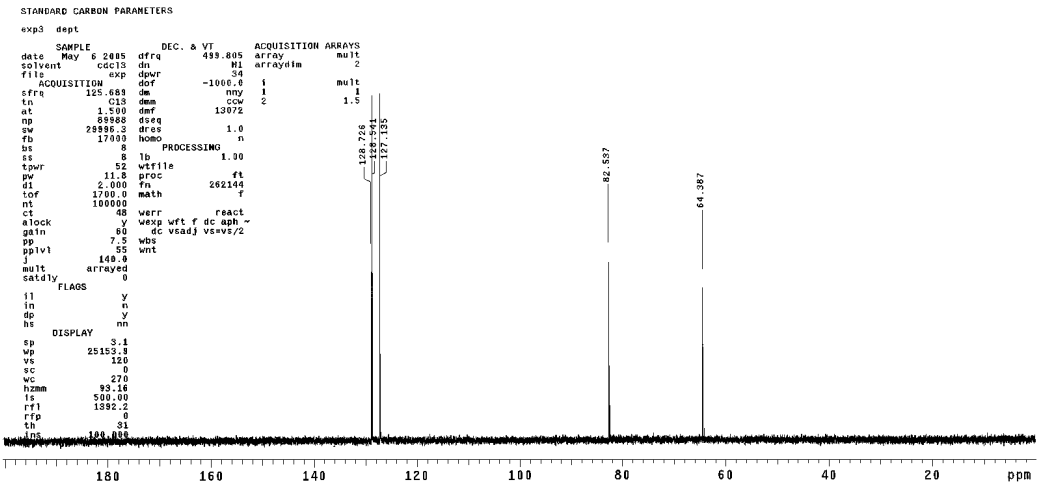
(*R*)-13a $CH_3(CH_2)_2CHO$[MPA-(*R*)]C≡C
^{1}H NMR



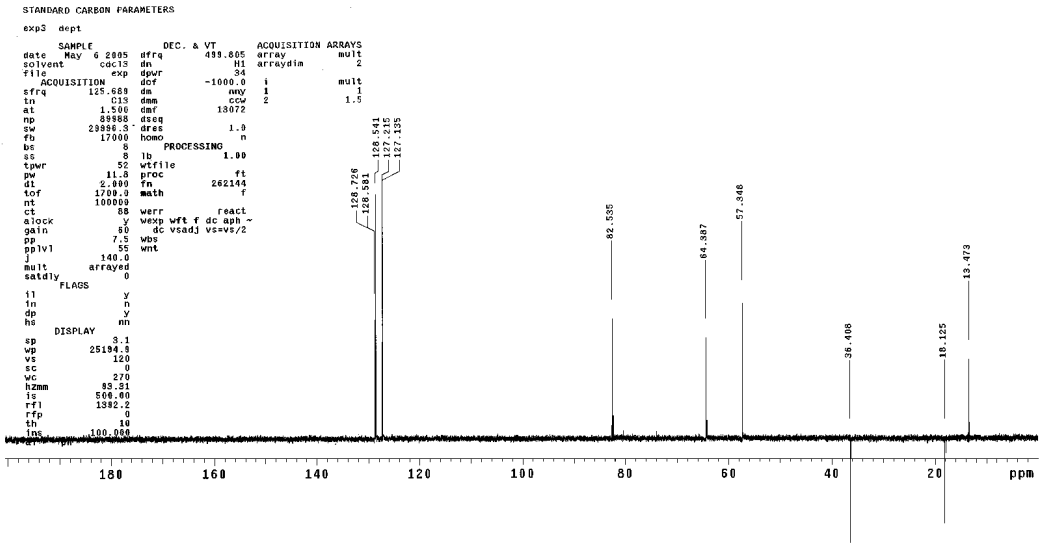
^{13}C NMR



DEPT 1(CH)



DEPT 2 (CH, CH_3/CH_2)



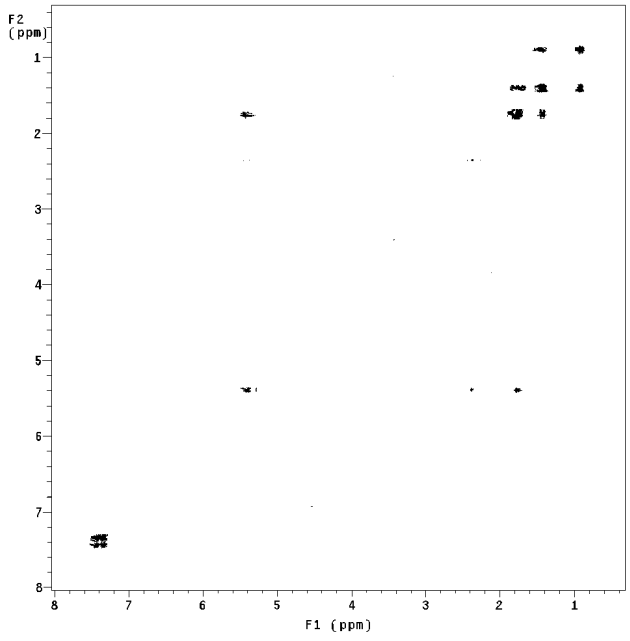
DQCOSY

STANDARD PROTON PARAMETERS

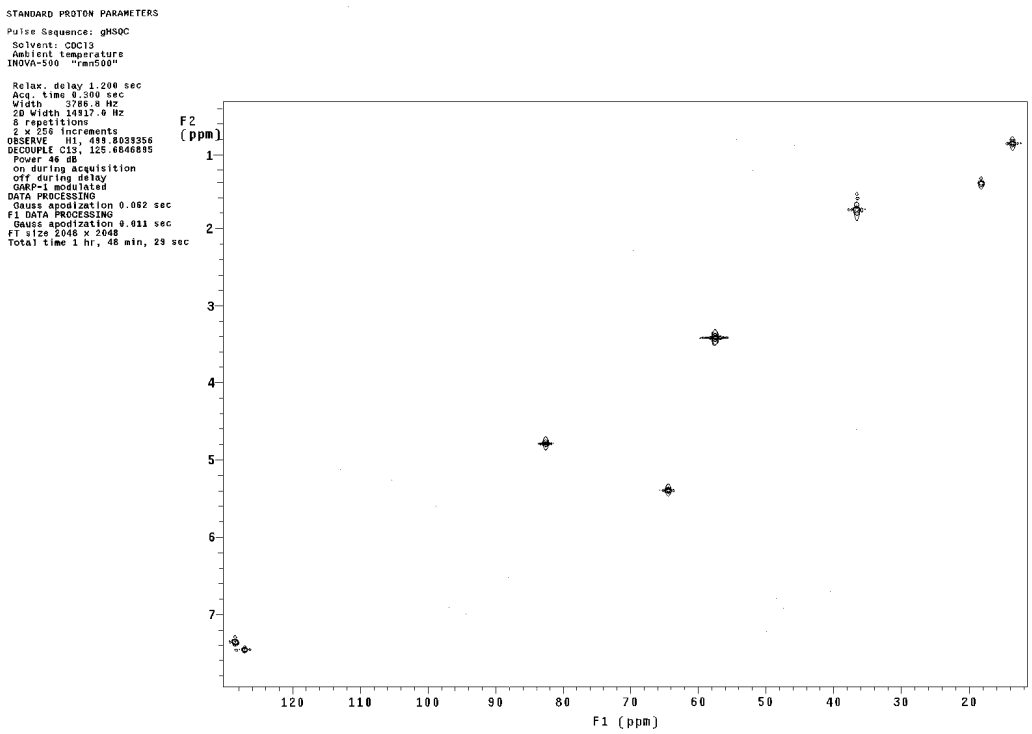
Pulse Sequence: gDQCOSY

Solvent: CDCl3
Ambient temperature
INOVA-500 "rmn500"

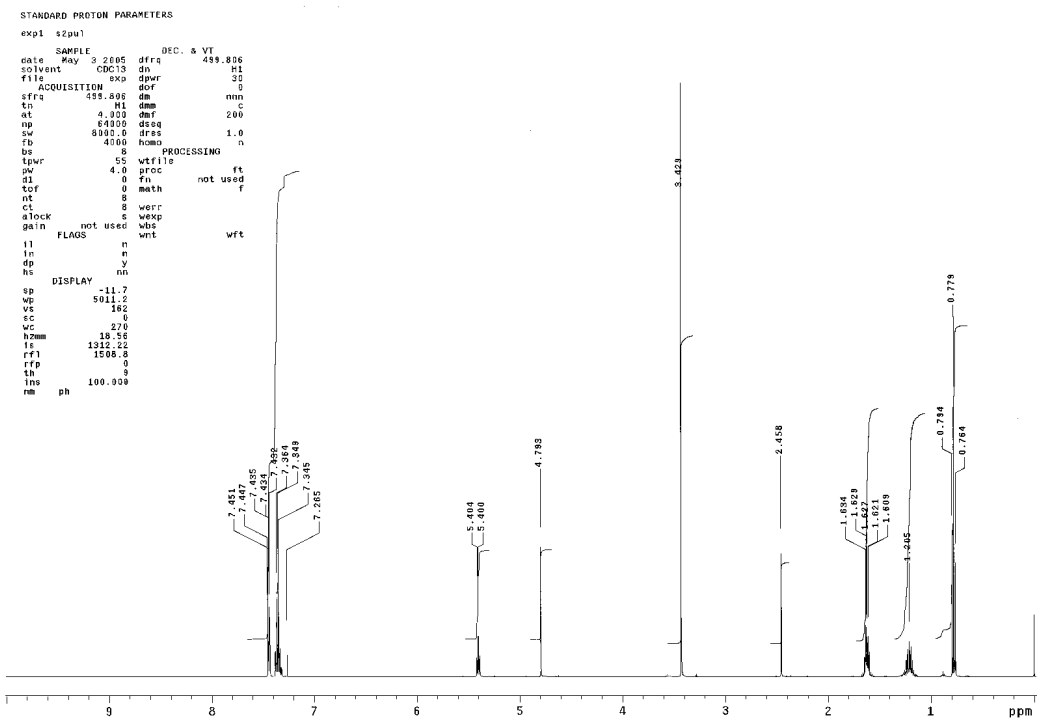
Relax. delay 1.167 sec
Acq. time 0.333 sec
Width 3861.4 Hz
20 Width 3861.4 Hz
4 repetitions
2 x 386 increments
OBSERVE H1, 499.8039406 MHz
DATA PROCESSING
Sq. sine bell 0.250 sec
Shifted by -0.167 sec
F1 DATA PROCESSING
Sq. sine bell 0.150 sec
Shifted by -0.100 sec
FT size 4096 x 4096
Total time 1 hr, 21 min, 46 sec



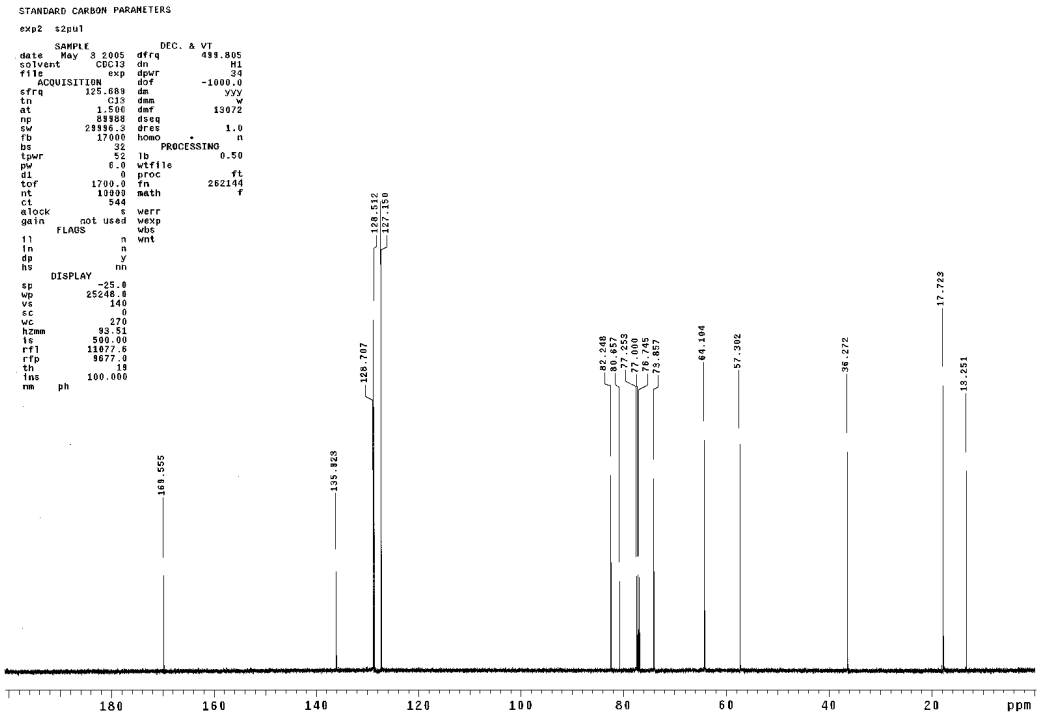
HSQC



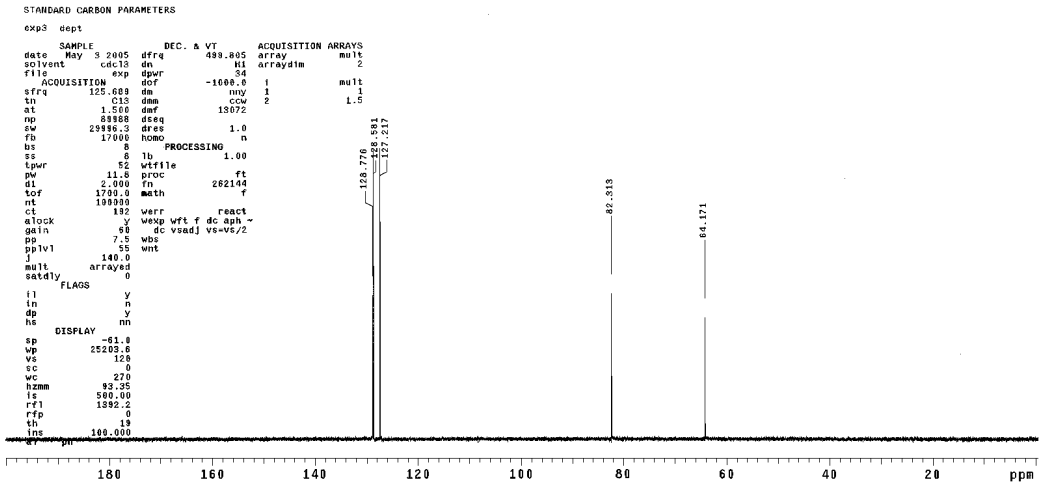
(*S*)-13a $CH_3(CH_2)_2CHO$[MPA-(*R*)]C≡C
^{1}H NMR



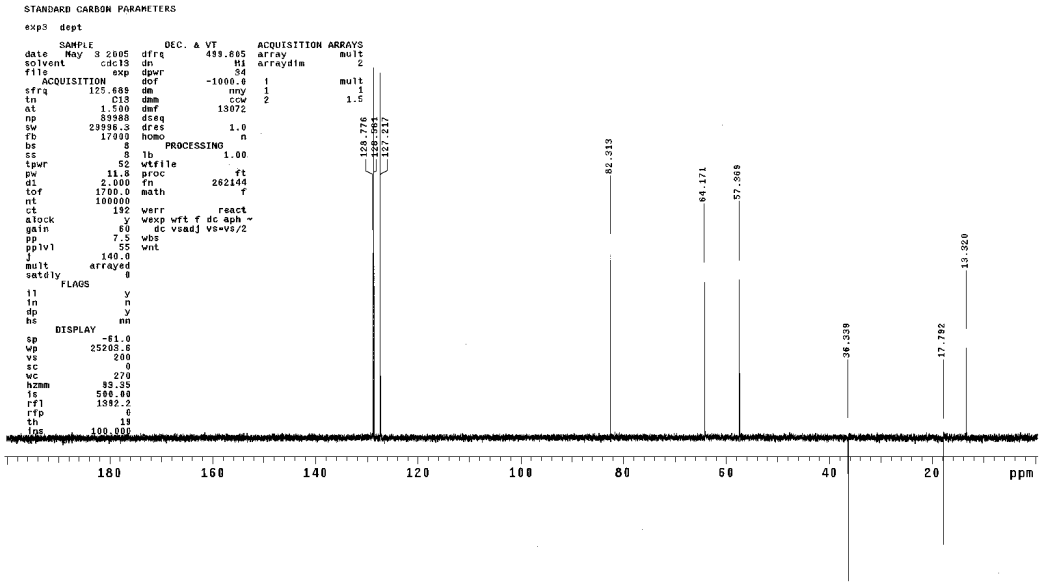
^{13}C NMR



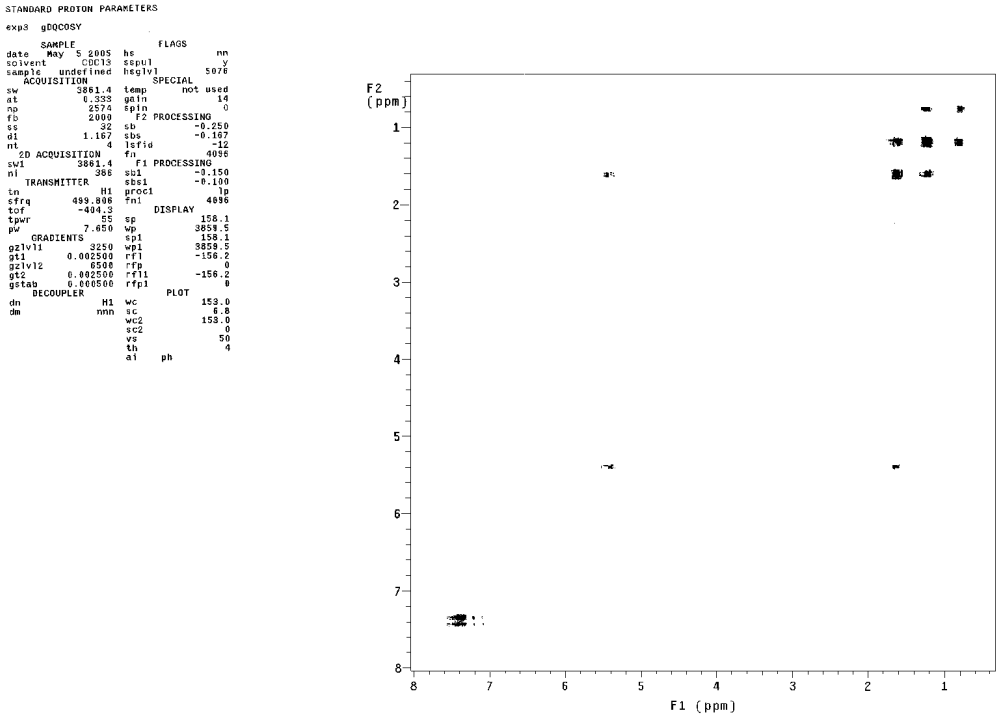
DEPT 1(CH)



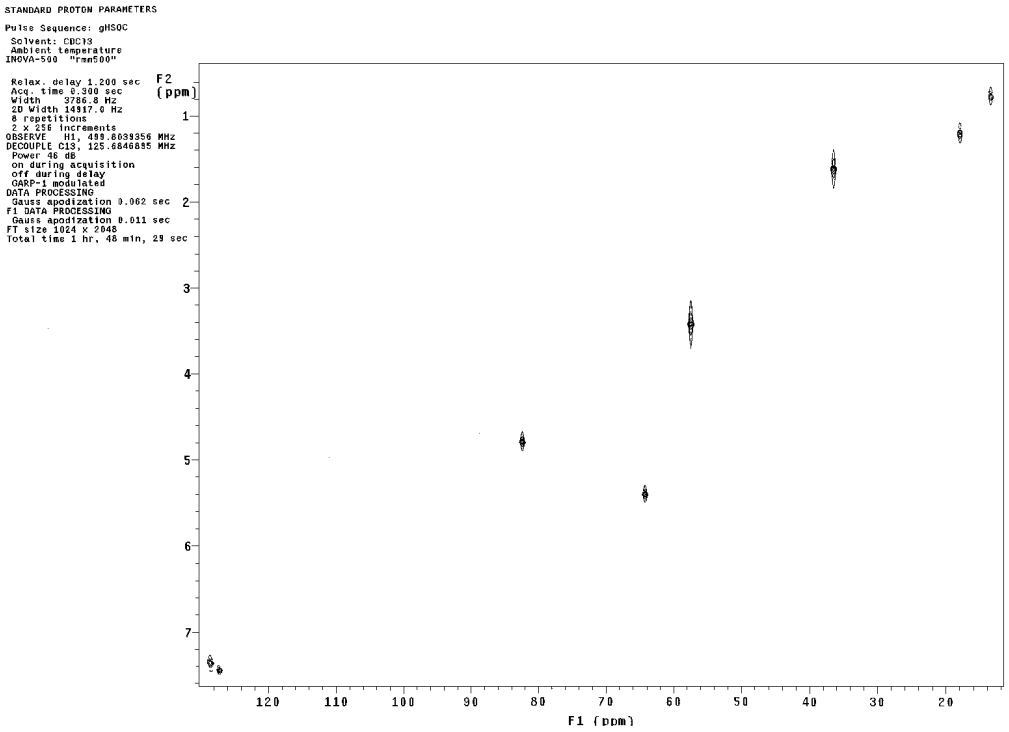
DEPT 2 (CH, CH_3/CH_2)



DQCOSY

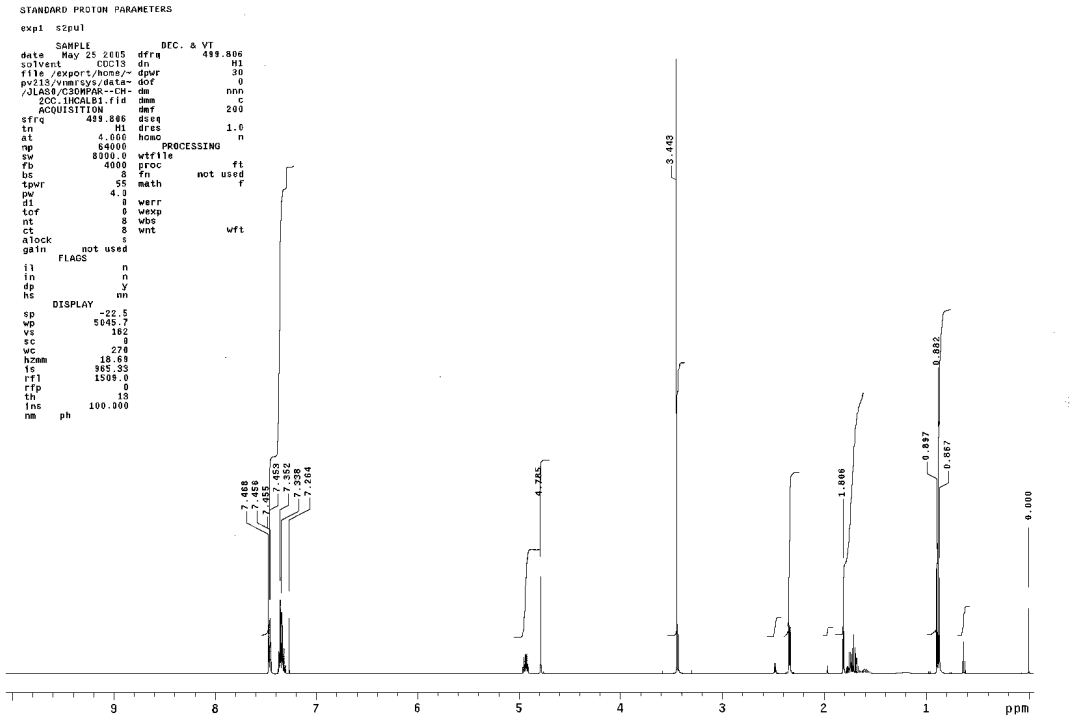


HSQC

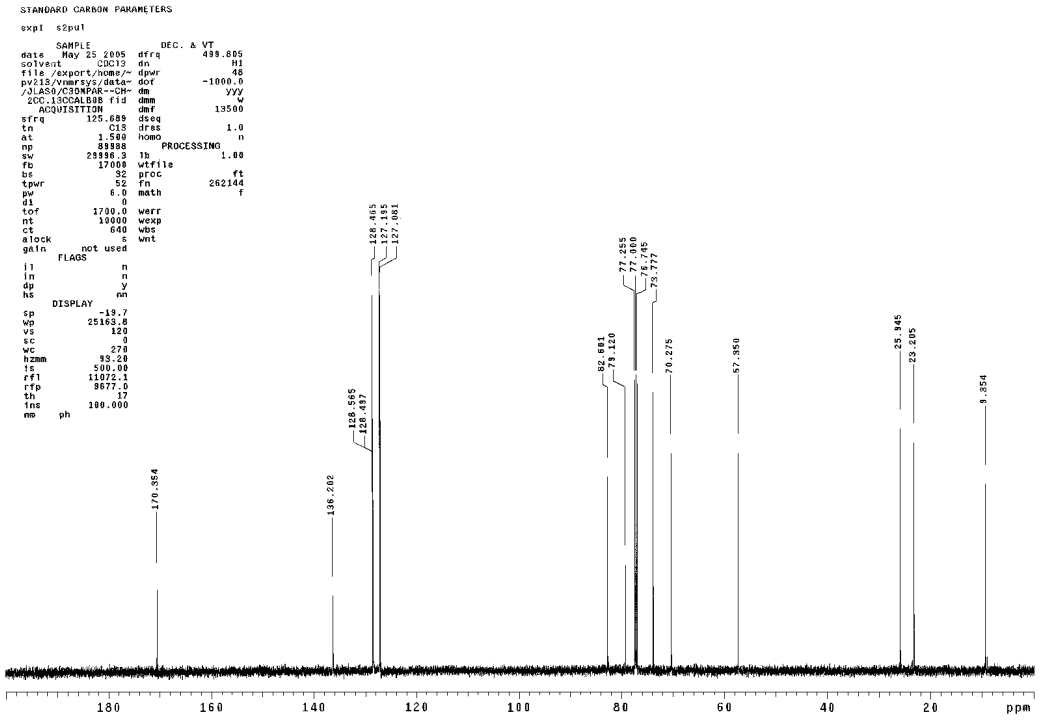


(*R*)-13b CH_3CH_2CHO[MPA-(*R*)]$CH_2C{\equiv}C$

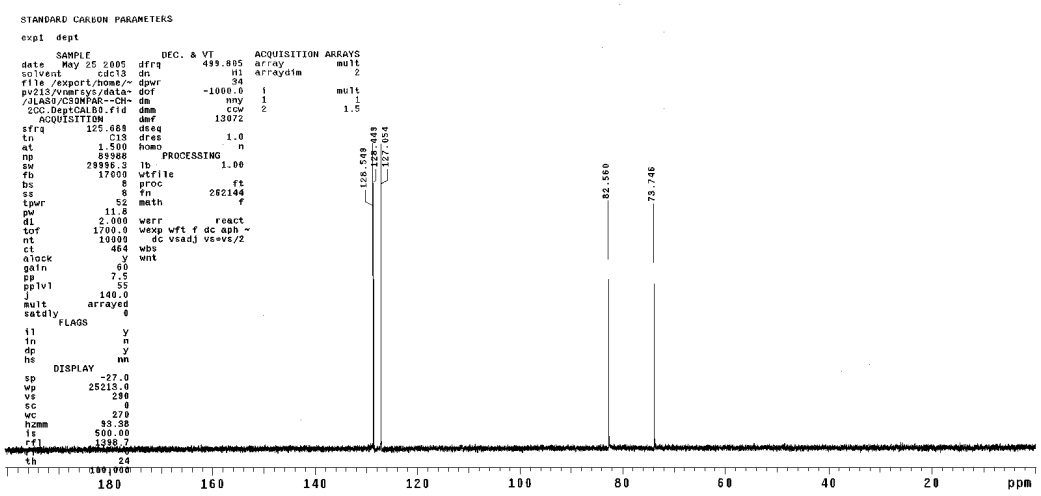
^{1}H NMR



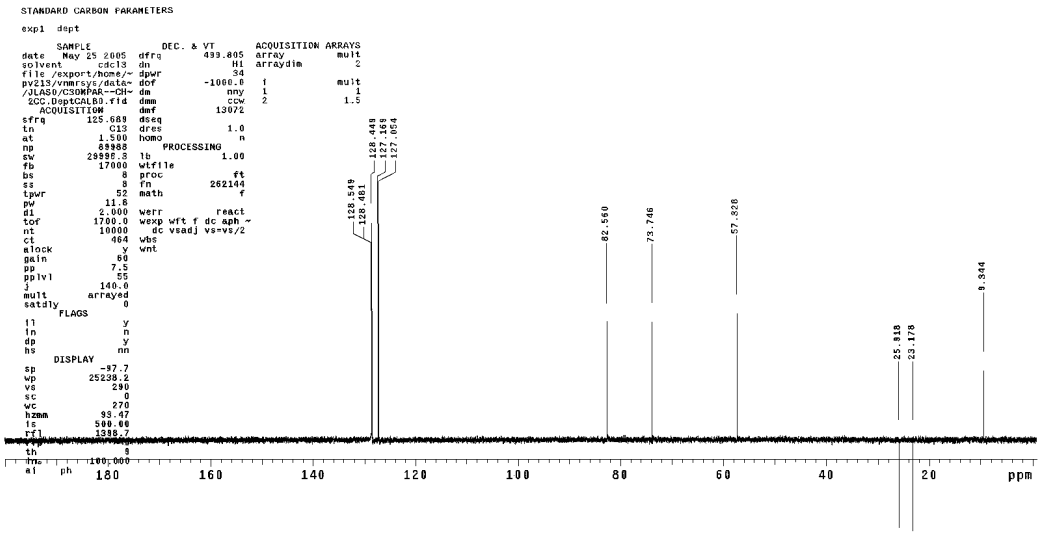
^{13}C NMR



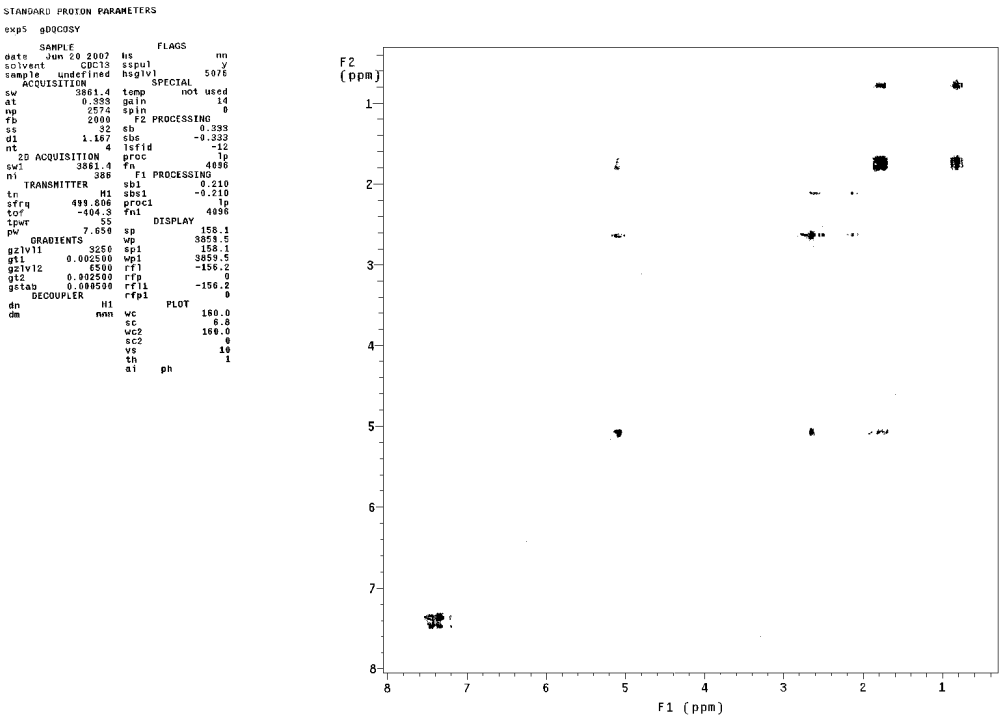
DEPT 1(CH)



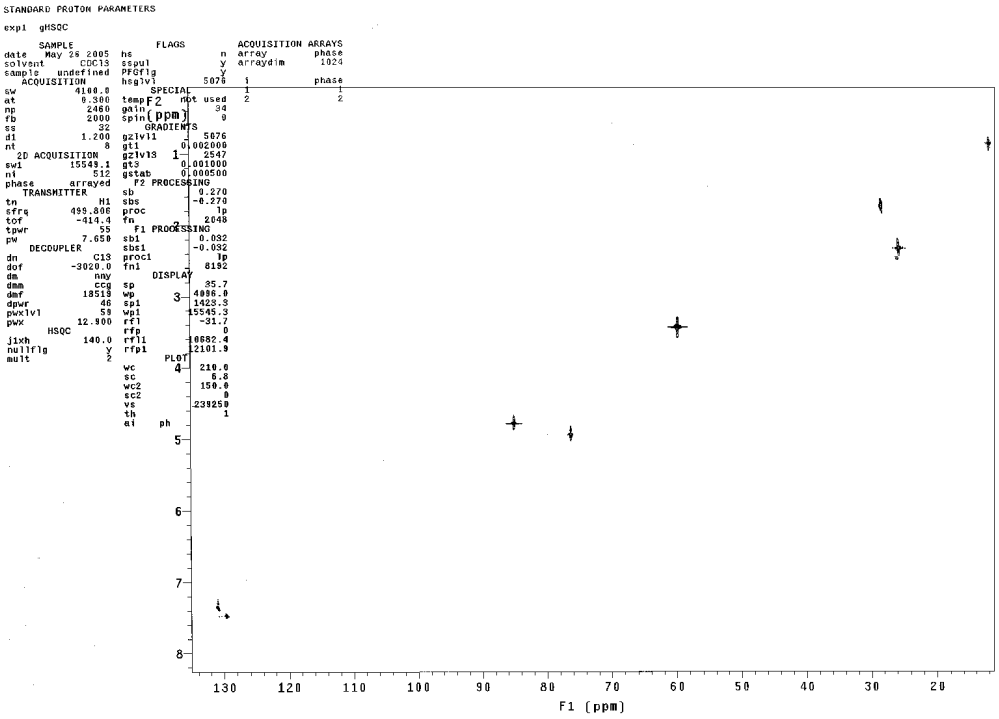
DEPT 2 (CH, CH_3/CH_2)



DQCOSY

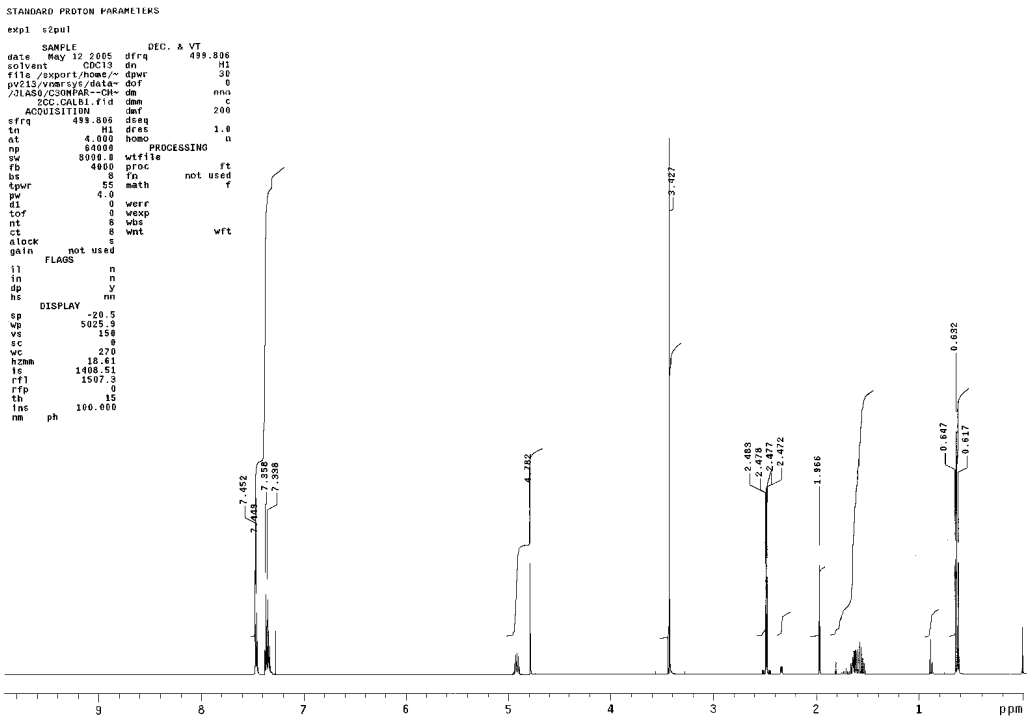


HSQC

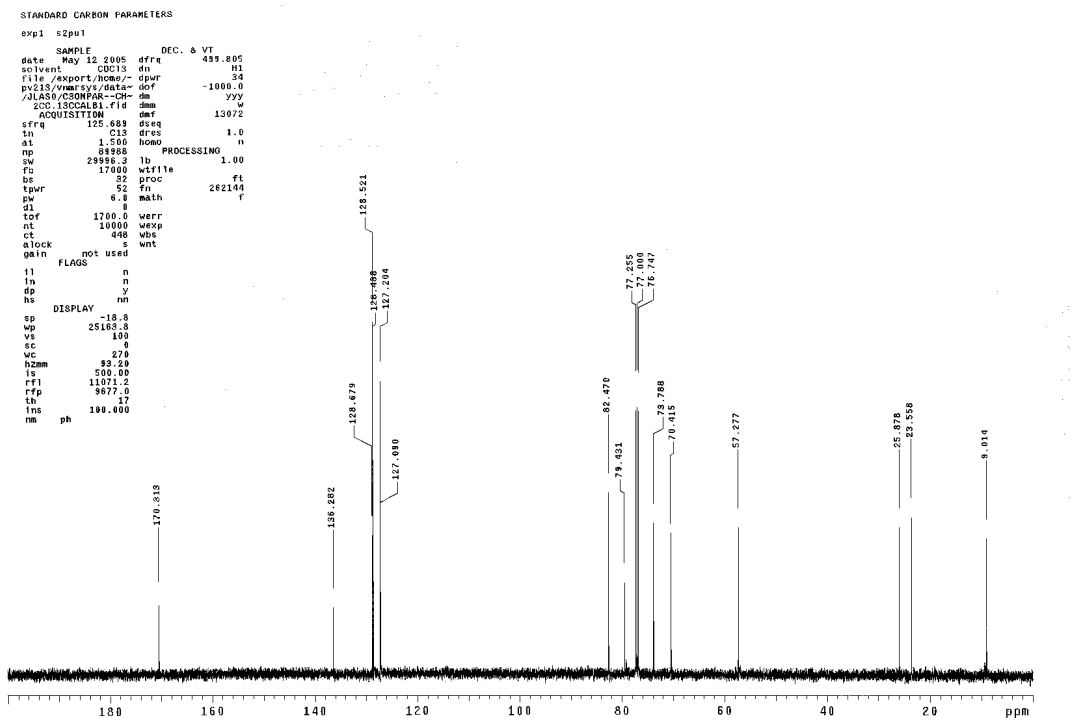


(*S*)-13b CH_3CH_2CHO[MPA-(*R*)]$CH_2C{\equiv}C$

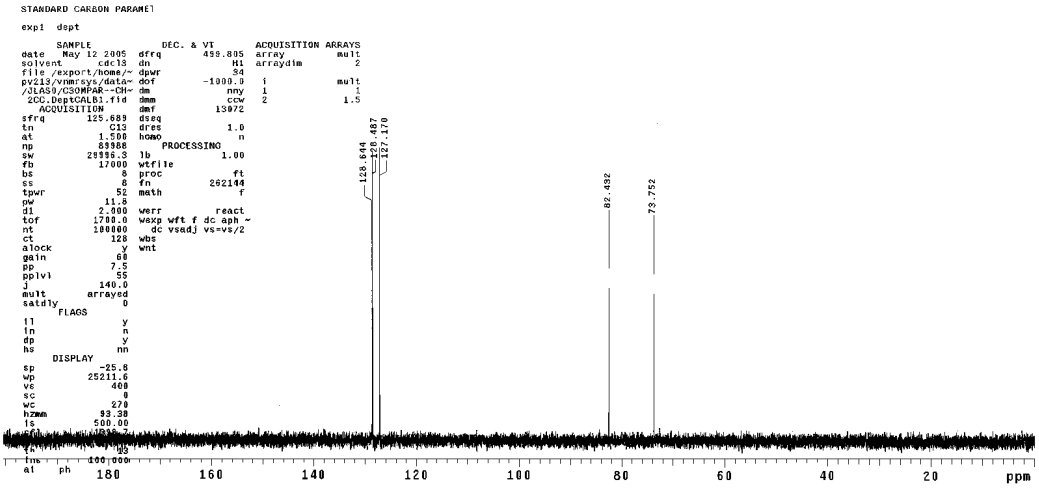
^{1}H NMR



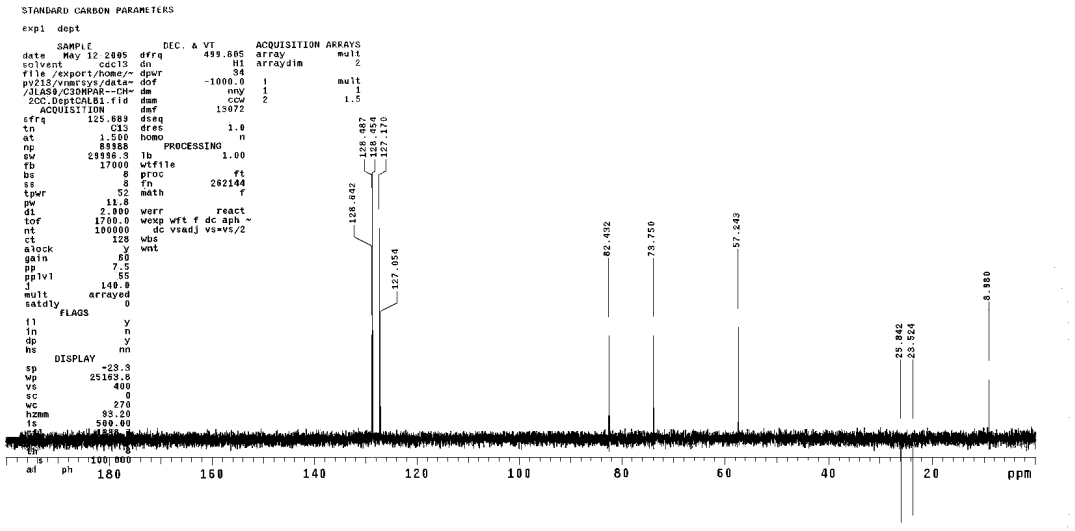
^{13}C NMR



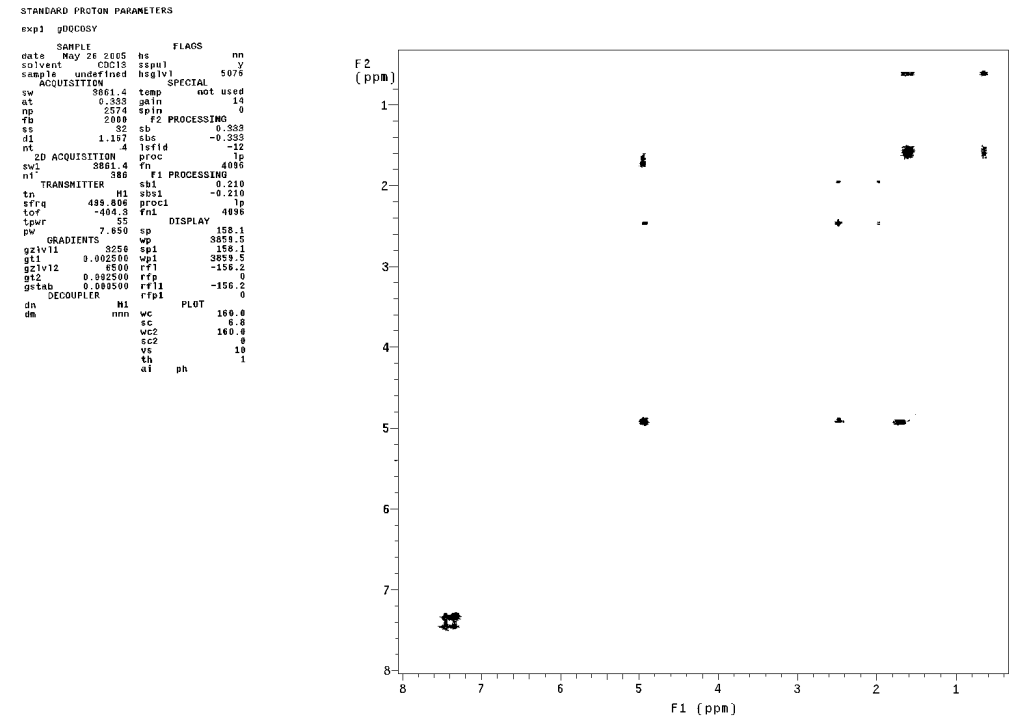
DEPT 1(CH)



DEPT 2 (CH, CH_3/CH_2)

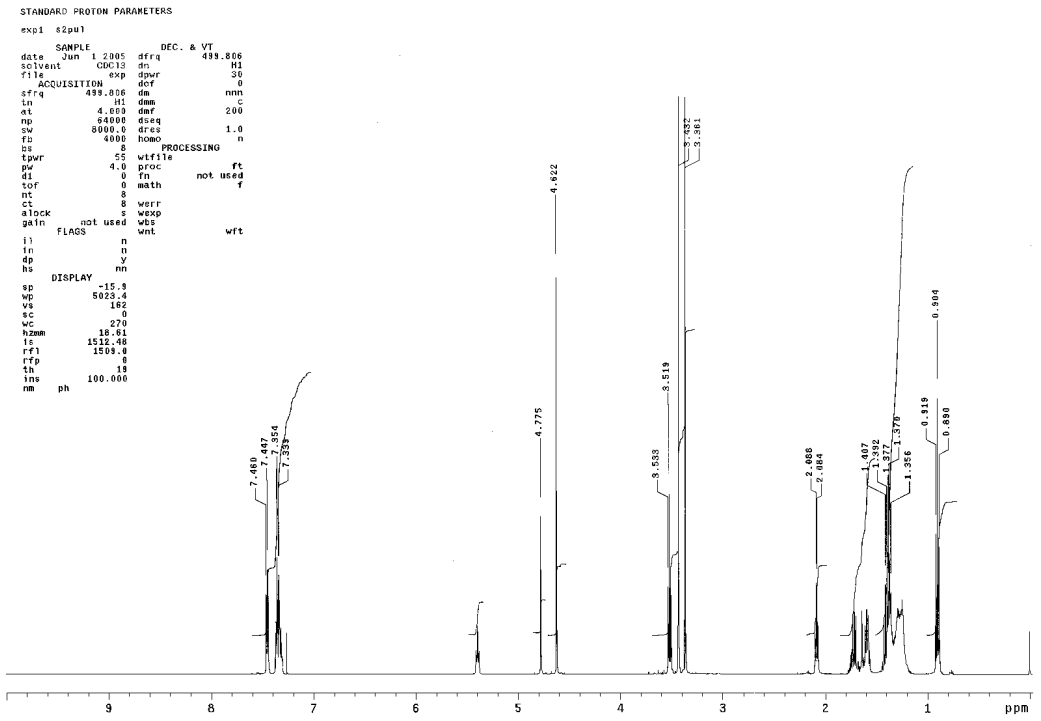


DQCOSY

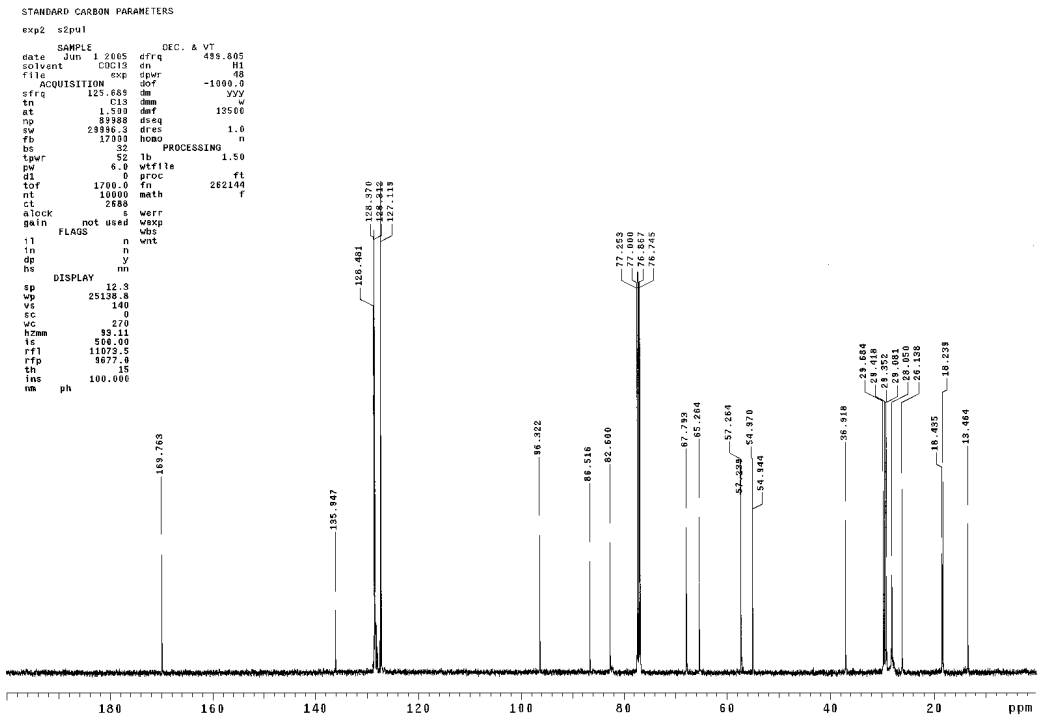


(*R*)-14a $CH_3(CH_2)_2CHO[MPA\text{-}(R)]CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

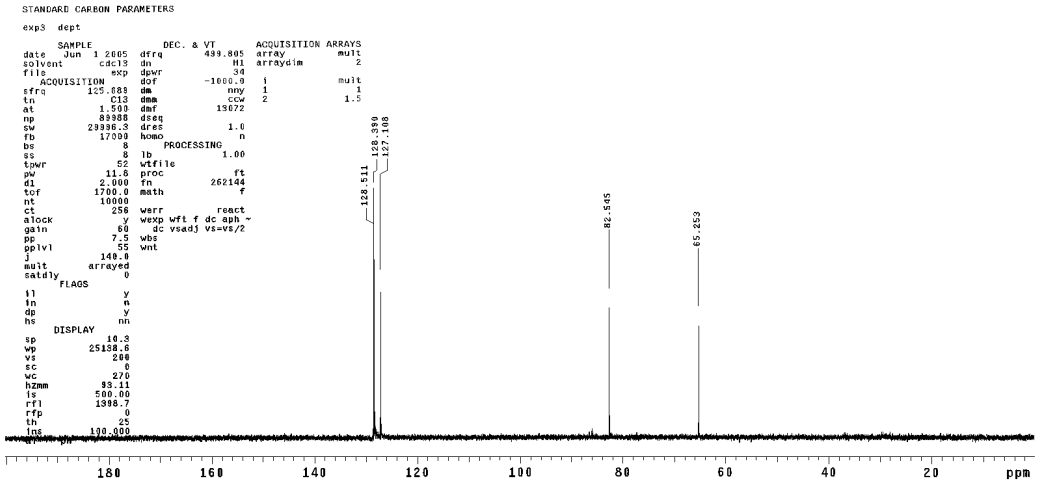
^1H NMR



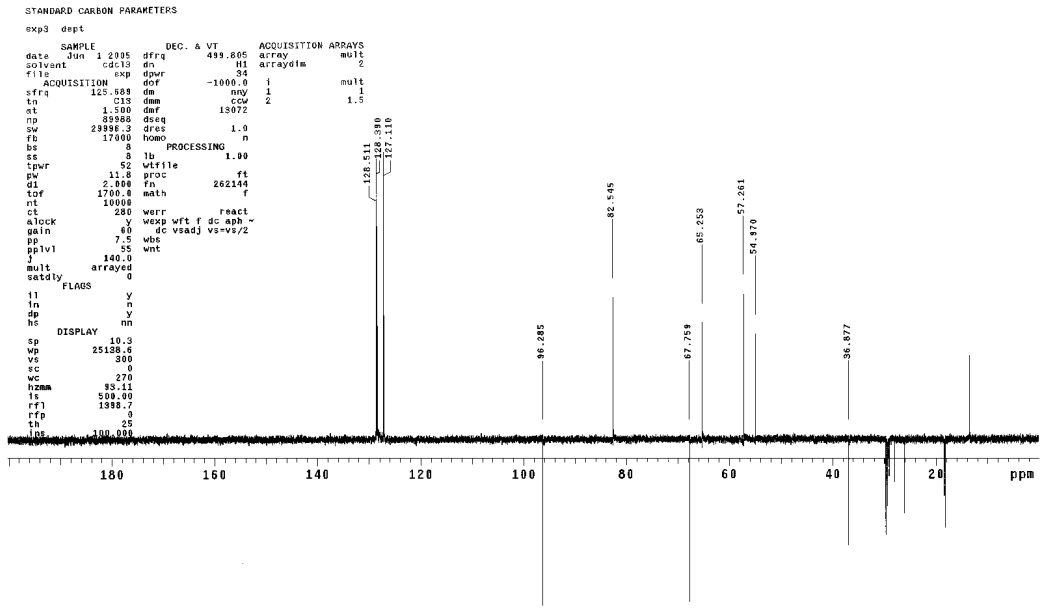
^{13}C NMR



DEPT 1(CH)



DEPT 2 (CH, CH_3/CH_2)

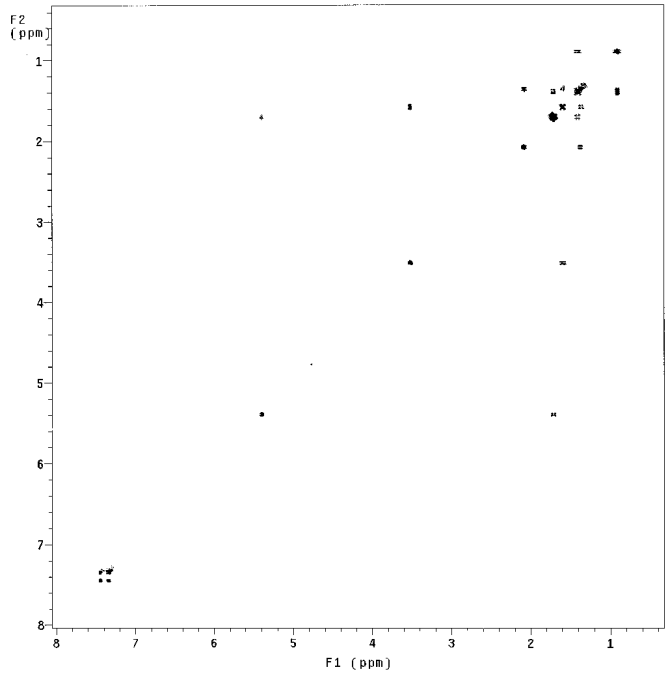


DQCOSY

STANDARD PROTON PARAMETERS

exp6 gDQCOSY

SAMPLE		FLAGS	
date	Jun 1 2005	hs	nn
solvent	CDCl3	sspul	y
sample	undefined	hsglvl	5076
ACQUISITION		SPECIAL	
sw	3861.4	temp	not used
at	0.885	gain	14
np	2574	spin	0
fb	2000	F2 PROCESSING	
ss	32	sb	0.333
d1	1.167	sbs	-0.333
nt	4	lsfid	-12
2D ACQUISITION		proc	lp
sw1	3861.4	fn	4096
n1	386	F1 PROCESSING	
TRANSMITTER		sb1	0.210
tn	H1	sbs1	-0.210
sfrq	499.806	proc1	lp
tof	-404.3	fn1	4096
tpwr	55	DISPLAY	
pw	7.650	sp	158.1
GRADIENTS		wp	3859.5
gzlvl1	3250	sp1	158.1
gt1	0.002500	wp1	3858.5
gzlvl2	8580	rfl	-156.2
gt2	0.002500	rfp	0
gstab	0.000500	rfl1	-156.2
DECOUPLER		rfp1	0
dn	H1	PLOT	
dm	nnn	wc	160.0
		sc	6.8
		wc2	160.0
		sc2	0
		vs	10
		th	1
		ai ph	

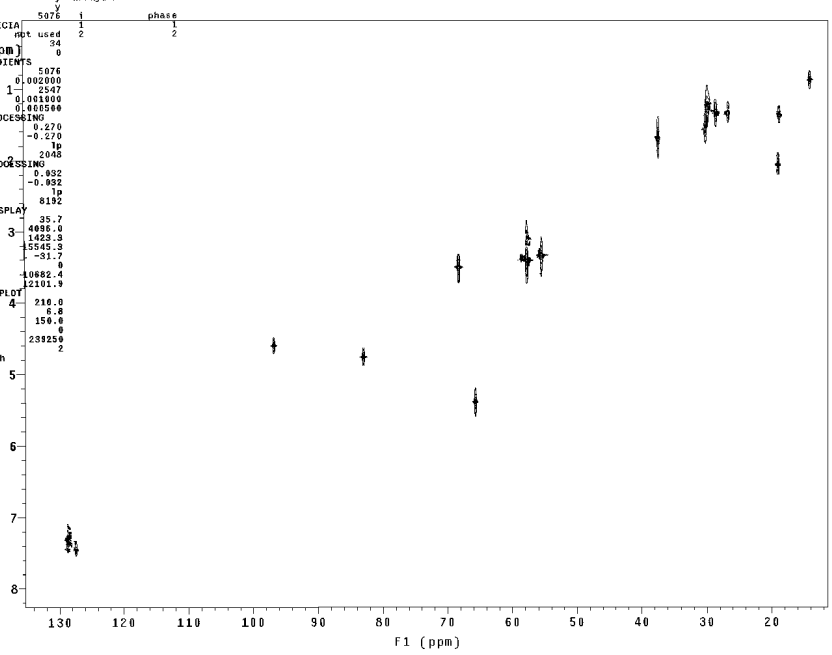


HSQC

STANDARD PROTON PARAMETERS

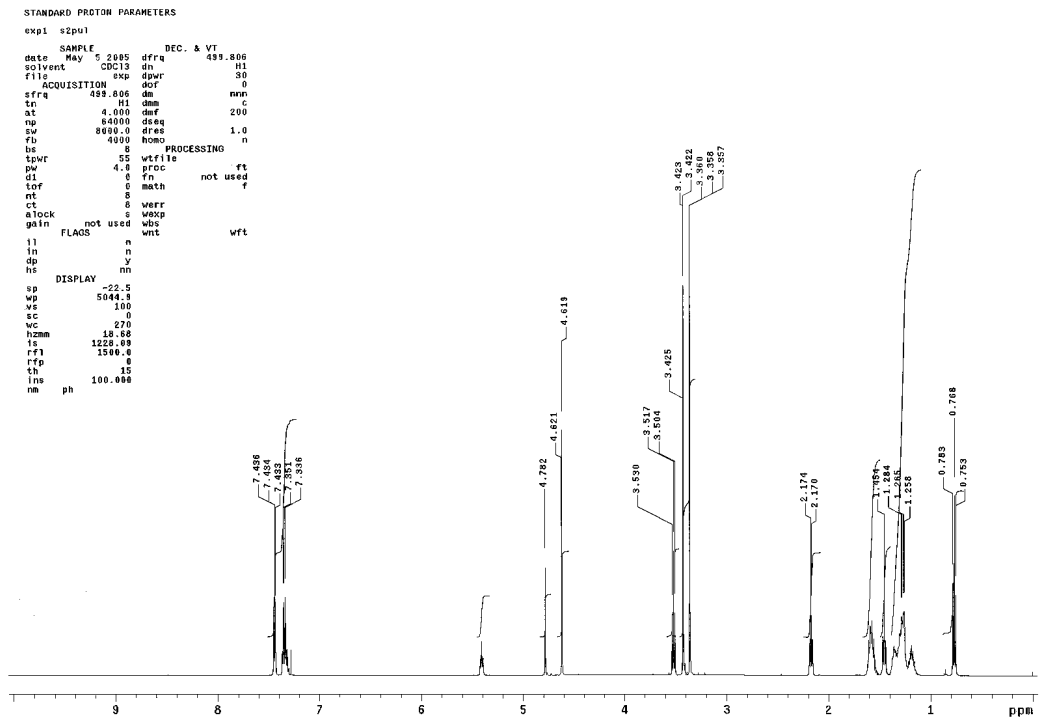
exp1 gHSQC

SAMPLE		FLAGS		ACQUISITION ARRAYS	
date	Jun 2 2005	hs	n	array	phase
solvent	CDCl3	sspul	y	arraydim	1024
sample	undefined	PFGflg	y		
ACQUISITION		hsglvl	5076	i	phase
sw	4180.0	SPECIAL		1	1
at	0.306	temp	not used	2	2
np	2460	gain	34		
fb	2000	spin	0		
ss	32	GRADIENTS			
d1	1.200	gzlvl1	5076		
nt	8	gt1	0.002000		
2D ACQUISITION		gzlvl3	2547		
sw1	15548.1	gt3	0.001800		
n1	512	gstab	0.000500		
phase	arrayed	F2 PROCESSING			
TRANSMITTER		sb	0.270		
tn	H1	sbs	-0.270		
sfrq	499.806	proc	lp		
tof	-414.4	fn	2048		
tpwr	55	F1 PROCESSING			
pw	7.650	sb1	0.032		
DECOUPLER		sbs1	-0.032		
dn	C13	proc1	lp		
dof	-3020.0	fn1	8192		
dm	nny	DISPLAY			
dmm	ccg	sp	35.7		
dmf	18519	wp	4096.0		
dpwr	46	sp1	1423.8		
pwx1vl	59	wp1	15545.3		
pwx	12.900	rfl	-31.7		
HSQC		rfp	0		
j1xh	140.0	rfl1	10682.4		
nullflg	y	rfp1	12101.9		
mult	2	PLOT			
		wc	210.0		
		sc	6.8		
		wc2	150.0		
		sc2	0		
		vs	239250		
		th	2		
		ai ph			

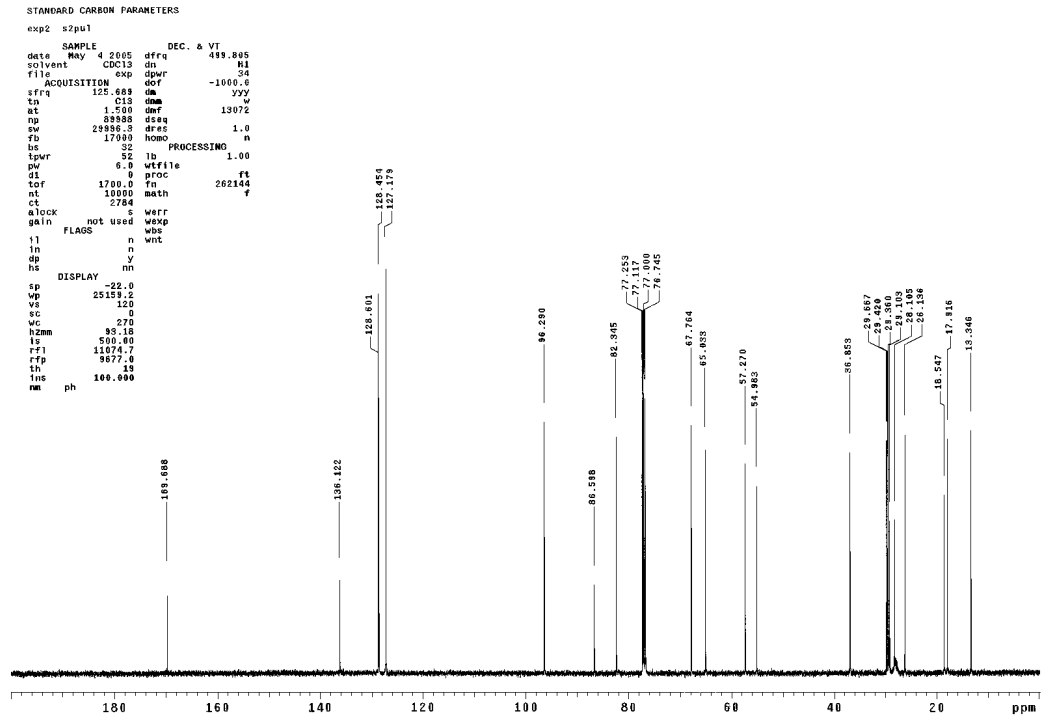


(*S*)-14a $CH_3(CH_2)_2CHO[MPA\text{-}(R)]CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

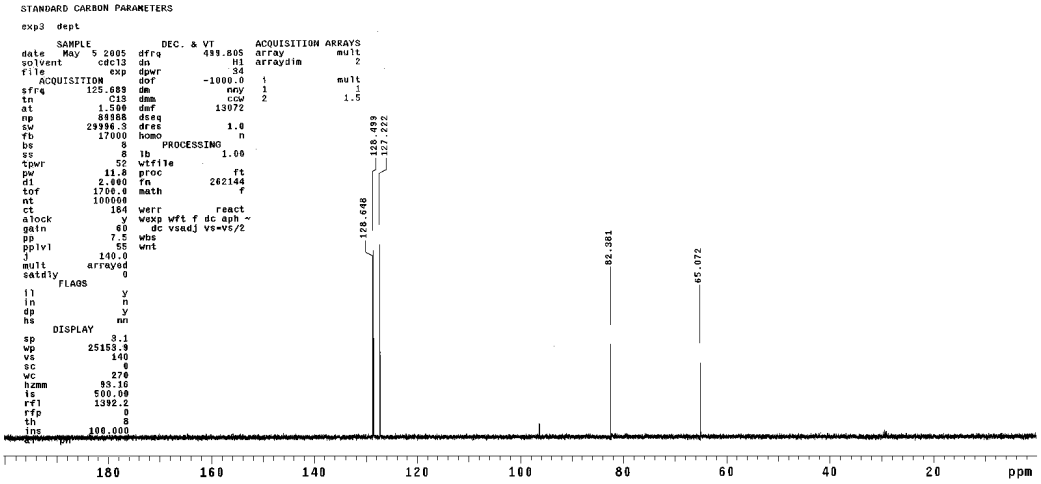
^1H NMR



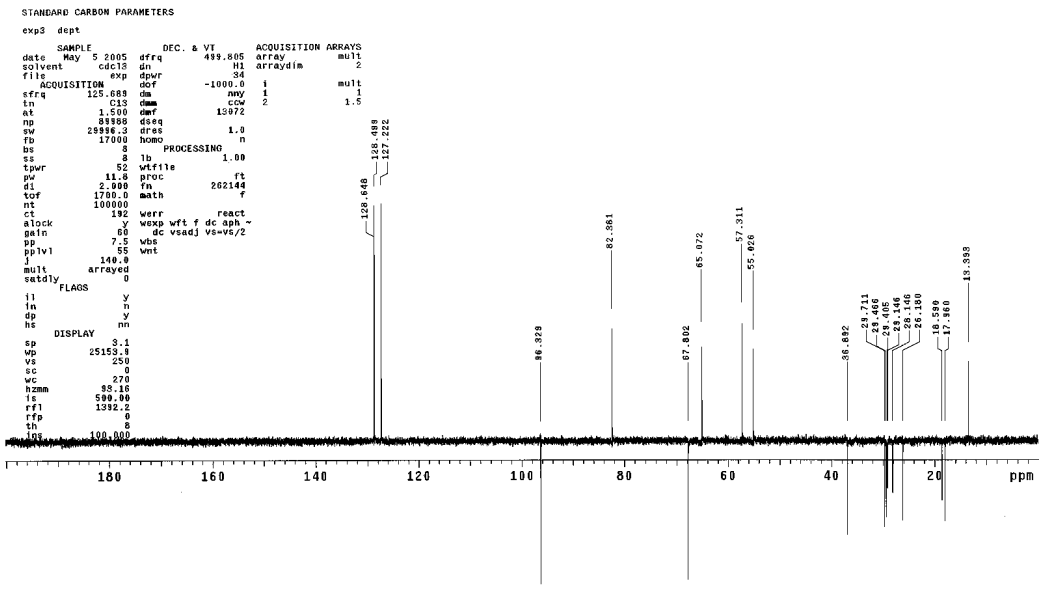
^{13}C NMR



DEPT 1(CH)



DEPT 2 (CH, CH_3/CH_2)

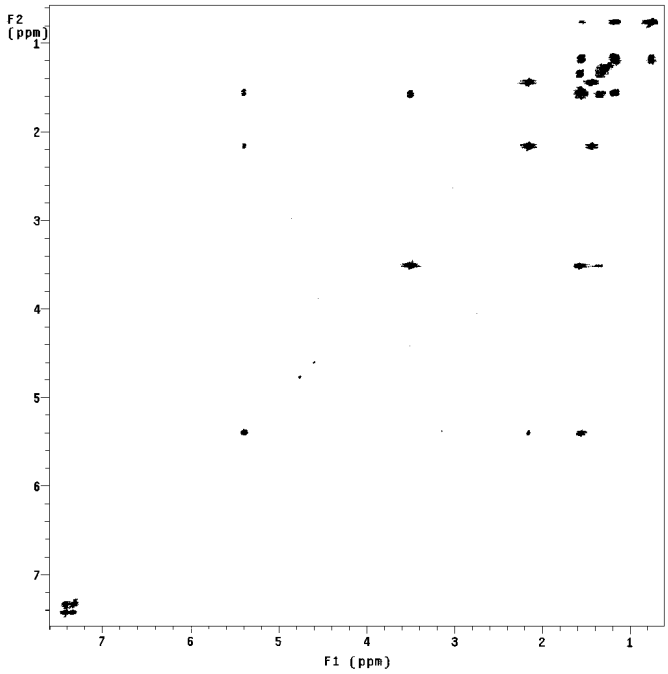


DQCOSY

STANDARD PROTON PARAMETERS

exp10 gDQCOSY

SAMPLE		FLAGS	
date	May 4 2005	hs	nn
solvent	CDCl3	sspul	y
sample	undefined	hsglv1	5076
ACQUISITION		SPECIAL	
sw	3861.4	temp	not used
at	0.933	gain	14
np	2574	spin	0
fb	2000	F2 PROCESSING	
ss	32	sb	-0.250
d1	1.167	sbs	-0.167
nt	4	lsfid	-12
2D ACQUISITION		proc	lp
sw1	3861.4	fn	4096
ni	386	F1 PROCESSING	
TRANSMITTER		sb1	-0.150
tn	H1	sbs1	-0.100
sfrq	499.806	proc1	lp
tof	-464.3	fn1	4096
tpwr	55	DISPLAY	
pw	7.650	sp	286.2
GRADIENTS		wp	3499.4
gzlvl1	3250	sp1	305.2
gt1	0.002500	wp1	3493.7
gzlvl2	6500	rf1	-156.2
gt2	0.002500	rfp	0
gstab	0.000500	rfl1	-156.2
DECOUPLER		rfp1	0
dn	H1	PLOT	
dm	nnn	wc	160.0
		sc	6.8
		wc2	160.0
		sc2	0
		vs	162
		th	8
		al ph	



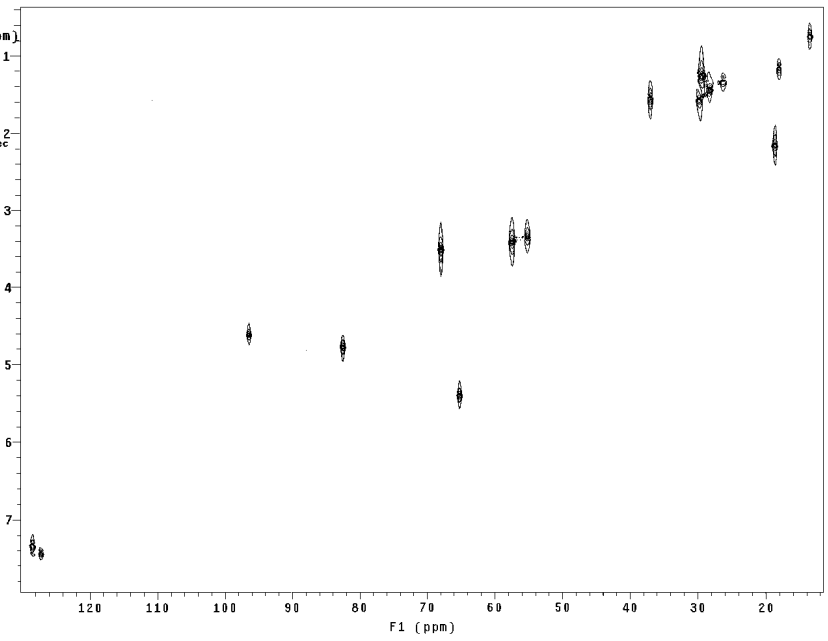
HSQC

STANDARD PROTON PARAMETERS

Pulse Sequence: gHSQC

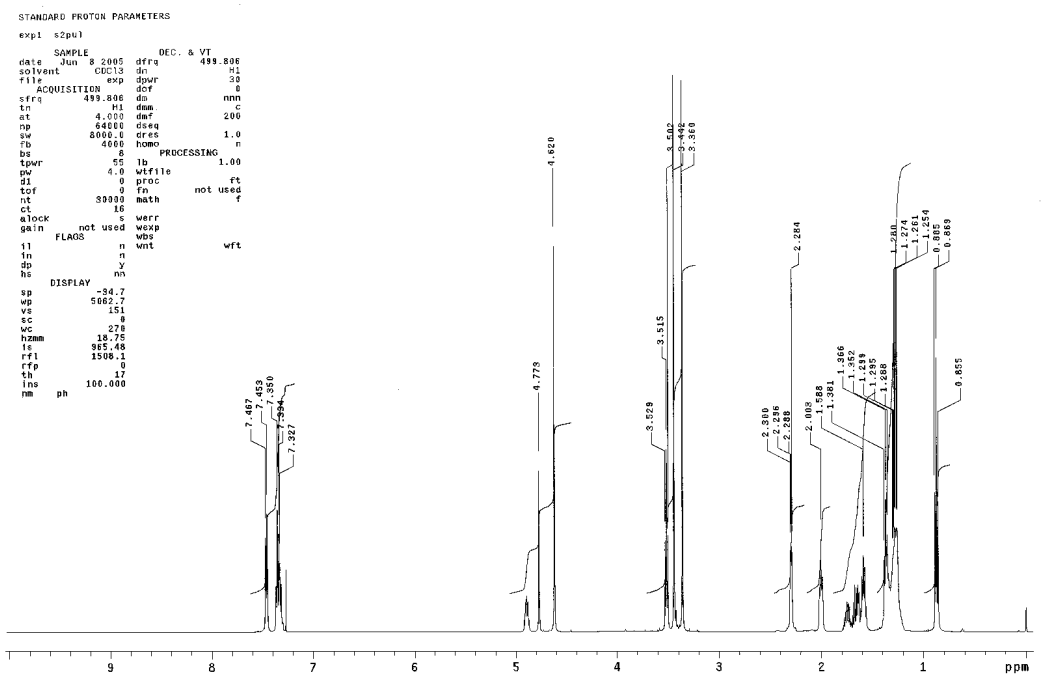
Solvent: CDCl3
Ambient temperature
INOVA-500 "rmn500"

Relax. delay 1.200 sec
Acq. time 0.300 sec
Width 3786.8 Hz
2D Width 14917.0 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 499.8039356 MHz
DECOUPLE C13, 125.6846895 MHz
Power 46 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.062 sec
F1 DATA PROCESSING
Gauss apodization 0.011 sec
FT size 1024 x 2048
Total time 1 hr, 48 min, 29 sec

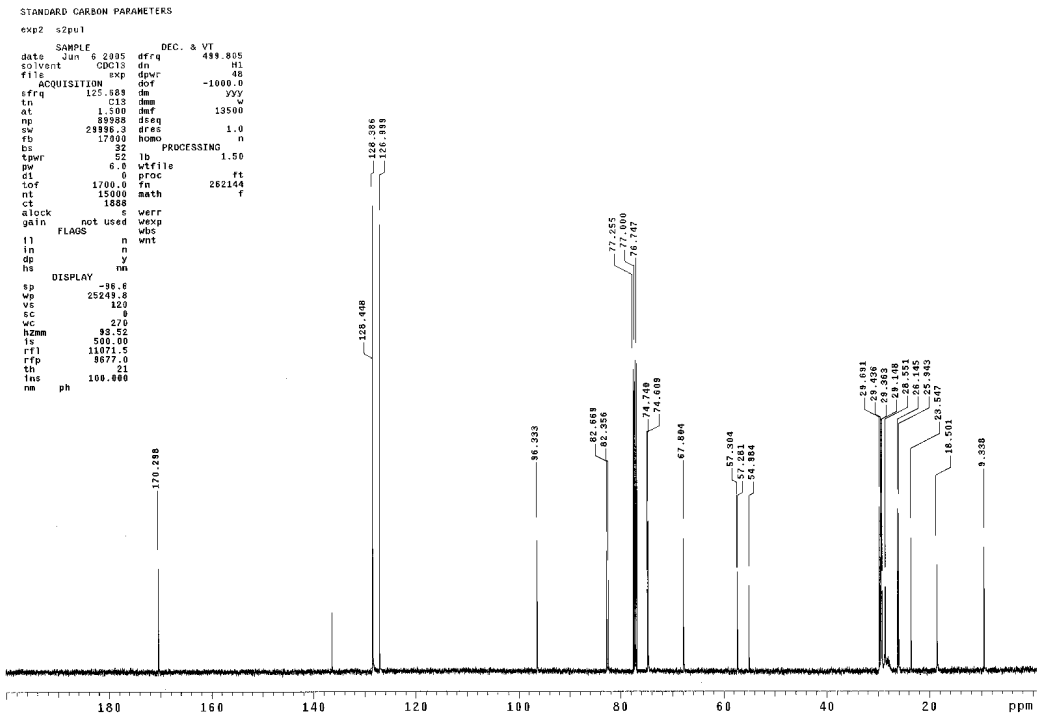


(*R*)-14b $CH_3CH_2CHO[MPA\text{-}(R)]CH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

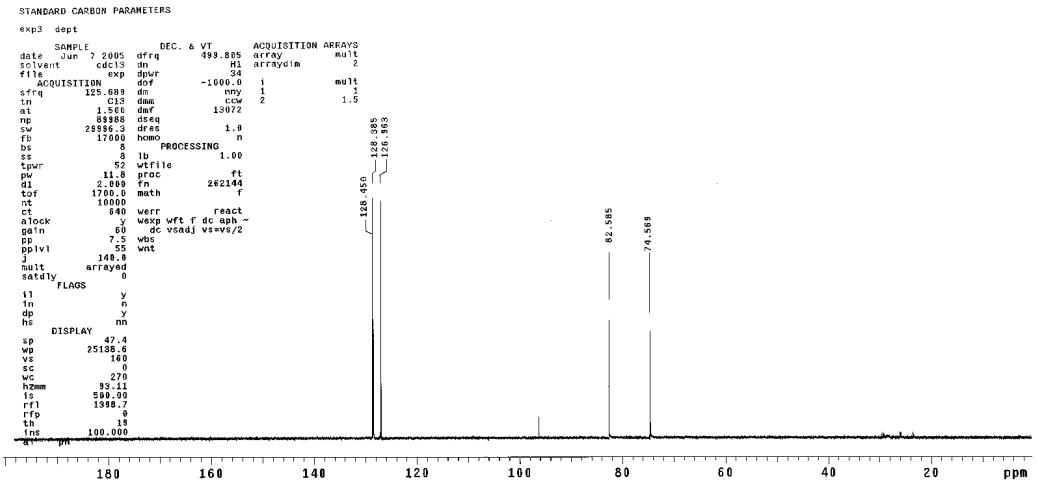
^1H NMR



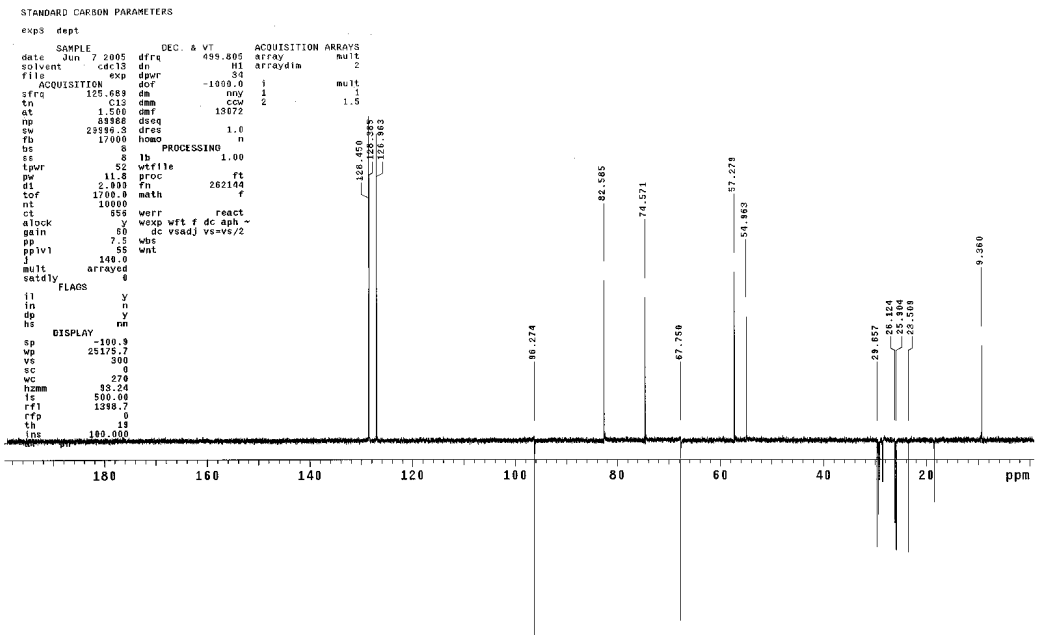
^{13}C NMR



DEPT 1(CH)



DEPT 2 (CH, CH_3/CH_2)

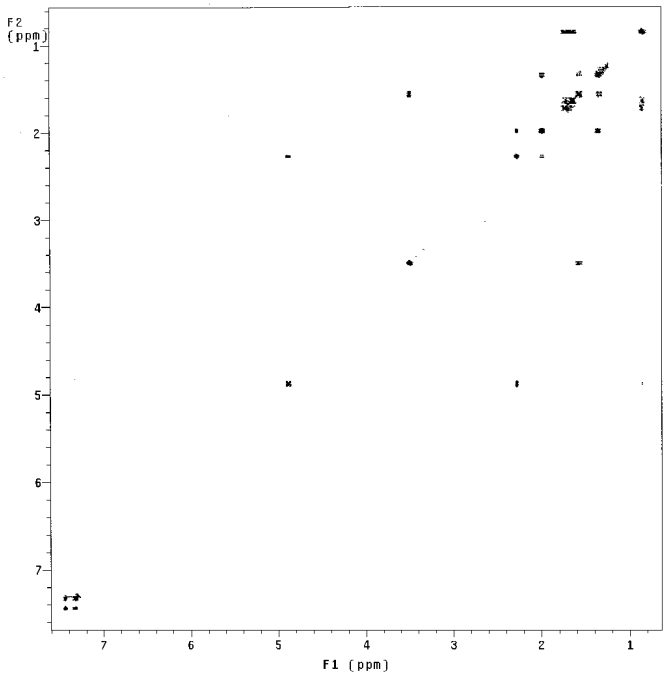


DQCOSY

STANDARD PROTON PARAMETERS

exp6 gDQCOSY

SAMPLE		FLAGS	
date	Jun 7 2005	hs	nn
solvent	CDCl3	sspul	y
sample	undefined	hsglvl	5076
ACQUISITION		SPECIAL	
sw	3861.4	temp	not used
at	0.333	gain	14
np	2574	spin	0
fb	2000	F2 PROCESSING	
ss	32	sb	0.333
d1	1.167	sbs	-0.333
nt	8	lsfid	-12
2D ACQUISITION		proc	lp
sw1	3861.4	fn	8192
ni	386	F1 PROCESSING	
TRANSMITTER		sb1	0.210
tn	H1	sbs1	-0.210
sfrq	498.806	proc1	lp
tof	-404.8	fn1	8192
tpwr	55	DISPLAY	
pw	7.656	sp	284.4
GRADIENTS		wp	3561.6
gzlvl1	8250	sp1	317.4
gt1	0.002500	wp1	3482.4
gzlvl2	8590	rfl	-156.2
gt2	0.002500	rfp	0
gstab	0.000500	rfl1	-156.2
DECOUPLER		rfp1	0
dn	H1	PLOT	
dm	nnn	wc	160.0
		sc	6.8
		wc2	160.0
		sc2	0
		vs	10
		th	1
		al ph	



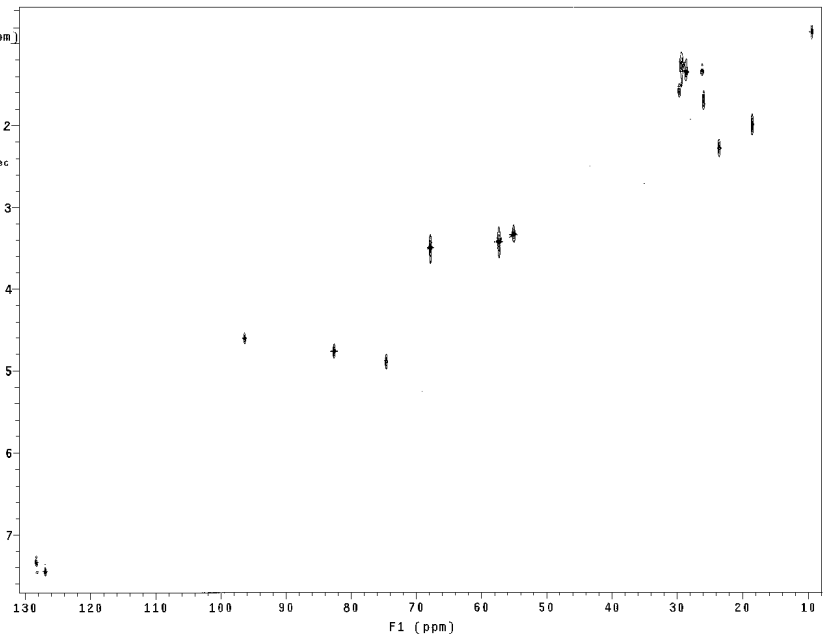
HSQC

STANDARD PROTON PARAMETERS

Pulse Sequence: gHSQC

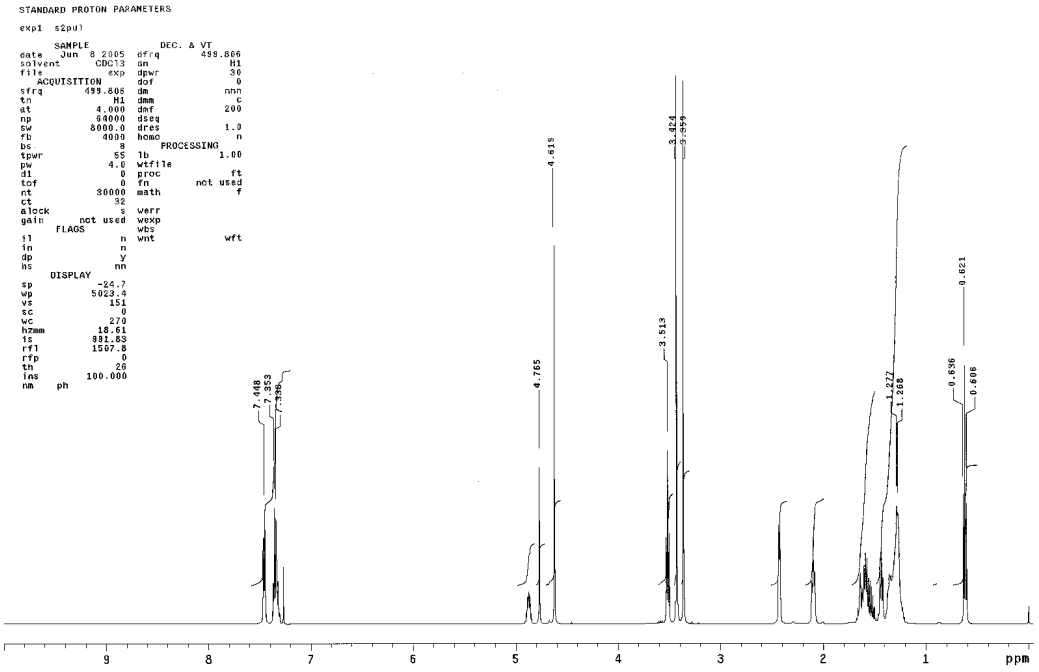
Solvent: CDCl3
Ambient temperature
INOVA-500 "rmn500"

Relax. delay 1.200 sec
Acq. time 0.300 sec
Width 4100.0 Hz
20 Width 15800.9 Hz
8 repetitions
2 x 512 increments
OBSERVE H1, 499.8039356 MHz
DECOUPLE C13, 125.6846895 MHz
Power 46 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Sine bell 0.270 sec
Shifted by -0.270 sec
F1 DATA PROCESSING
Sine bell 0.032 sec
Shifted by -0.032 sec
FT size 2048 x 8192
Total time 3 hr, 37 min, 11 sec

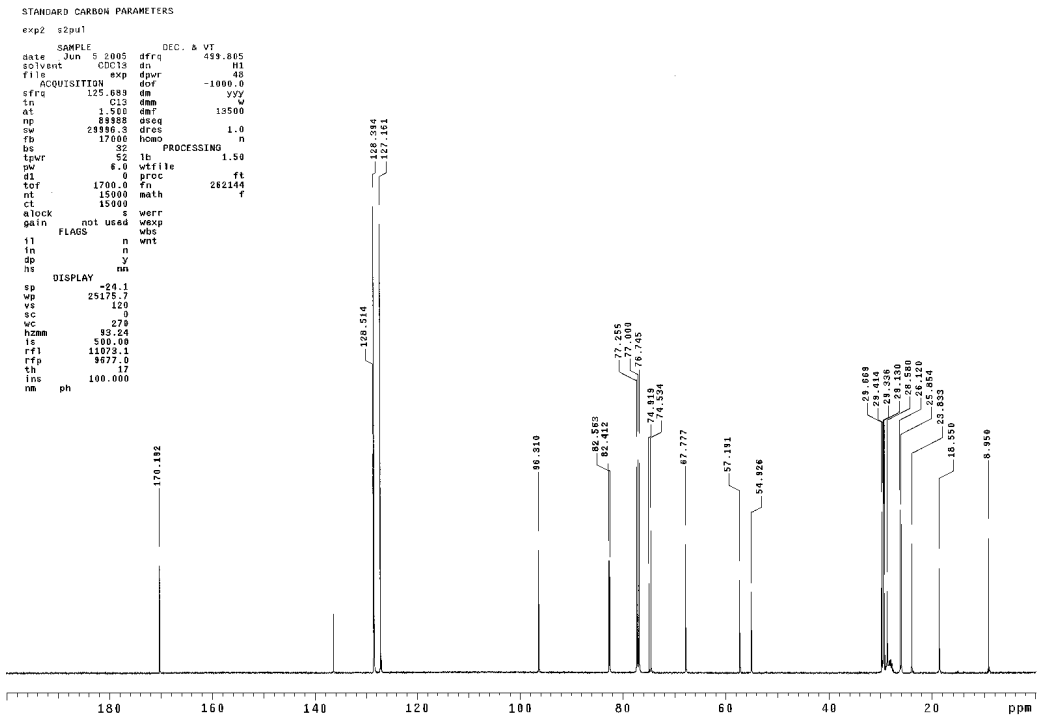


(*S*)-14b $CH_3CH_2CHO[MPA\text{-}(R)]CH_2CH_2CH_2(CH_2)_2(CD_2)_2(CH_2)_6OMOM$

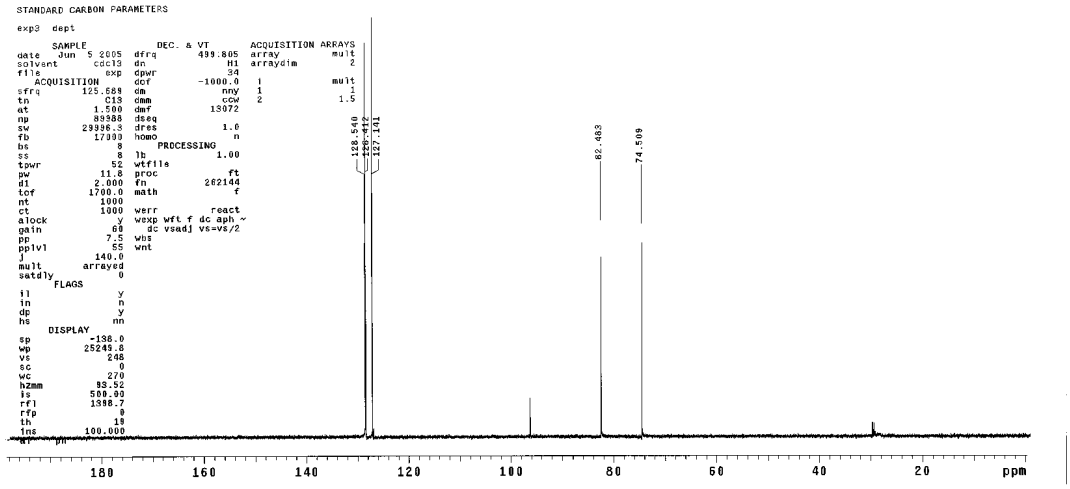
^1H NMR



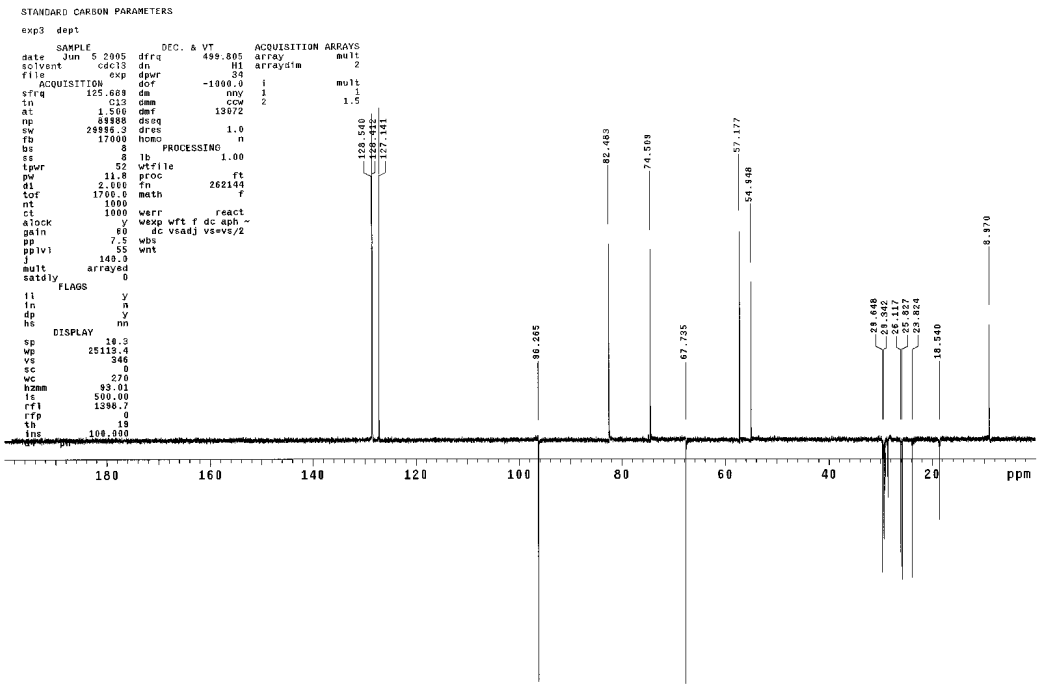
^{13}C NMR



DEPT 1(CH)



DEPT 2 (CH, CH_3/CH_2)

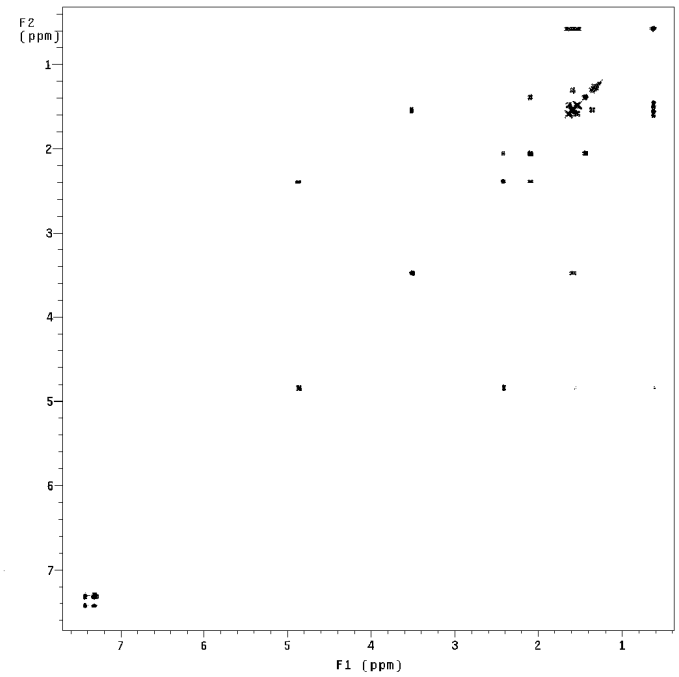


DQCOSY

STANDARD PROTON PARAMETERS

exp6 gDQCOSY

SAMPLE		FLAGS	
date	Jun 5 2005	hs	nn
solvent	CDCl3	sspul	y
sample	undefined	hsglvl	5076
ACQUISITION		SPECIAL	
sw	3861.4	temp	not used
at	0.333	gain	14
np	2574	spin	0
fb	2000	F2 PROCESSING	
ss	32	sb	0.333
d1	1.167	sbs	-0.333
nt	8	lsfid	-12
2D ACQUISITION		proc	lp
sw1	3861.4	fn	8192
n1	386	F1 PROCESSING	
TRANSMITTER		sb1	0.210
tn	H1	sbs1	-0.210
sfrq	499.806	proc1	lp
tof	-404.3	fn1	8192
tpwr	55	DISPLAY	
pw	7.650	sp	171.3
GRADIENTS		wp	3689.6
gzlvl1	3250	sp1	180.7
gt1	0.002500	wp1	3659.6
gzlvl2	4500	rf1	-156.2
gt2	0.002500	rfp	0
gstab	0.000500	rf11	-156.2
DECOUPLER		rfp1	0
dn	H1	PLOT	
dm	nnn	wc	160.0
		sc	6.8
		wc2	160.0
		sc2	0
		vs	10
		th	1
		al ph	



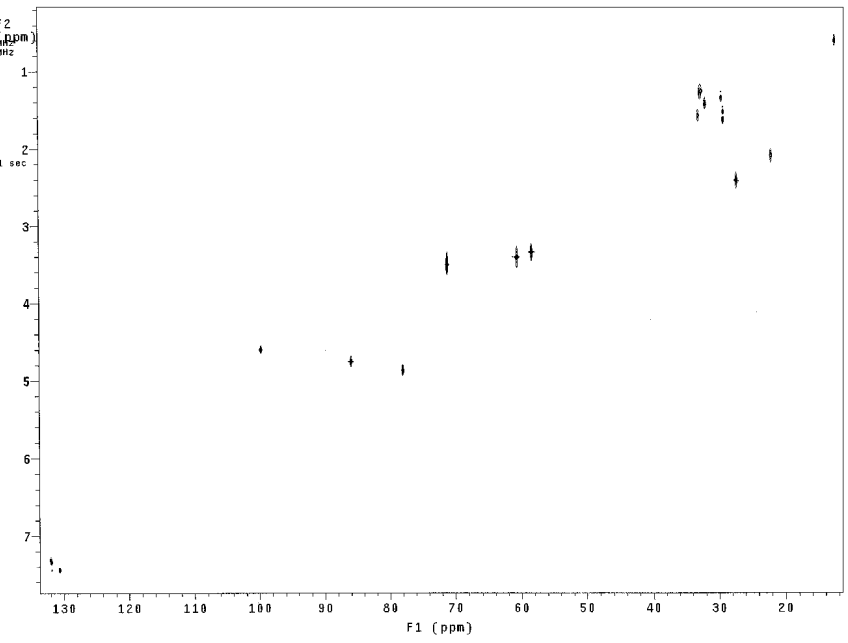
HSQC

STANDARD PROTON PARAMETERS

Pulse Sequence: gHSQC

Solvent: CDCl3
Ambient temperature
INOVA-500 "man500"

Relax. delay 1.200 sec
Acq. time 0.300 sec
Width 4100.0 Hz
20 Width 15800.9 Hz
8 repetitions
256 x 512 increments
OBSERVE H1, 499.8038356 MHz
DECOUPLE C13, 125.6846895 MHz
Power 46 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Sine bell 0.270 sec
Shifted by -0.270 sec
F1 DATA PROCESSING
Sine bell 0.032 sec
Shifted by -0.032 sec
FT size 2048 x 8192
Total time 3 hr, 37 min, 11 sec



References

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2. Abad, J.-L.; Soldevila, C.; Clapès, P.; Camps, F., *J. Org. Chem.* **2003,** *68*, 5351-5356.

3. Abad, J. L.; Serra, M.; Camps, F.; Fabriàs, G., *J. Org. Chem.* **2007,** *72*, 760-764.

4. Abad, J.-L.; Fabriàs, G.; Camps, F., *Lipids* **2004,** *39*, 397-401.

5. Bates, H. A.; Farina, J.; Tong, M., *J. Org. Chem.* **1986,** *51*, 2637-2641.

6. Abad, J.-L.; Fabriàs, G.; Camps, F., *J. Org. Chem.* **2000,** *65*, 8582-8588.