Supporting information

Tetrazolic Acid Functionalized Dihydroindol – Rational Design of a Highly Selective Cyclopropanation Organocatalyst

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General Information

Chemicals and solvents were either purchased puris p.A. from commercial suppliers or purified by standard techniques.[27] For thin layer chromatography (TLC), precoated 0.25 mm silica plates were used and spots were visualized either with UV light or by heating after soaking the TLC plate in a solution consisting of *p*-anisaldehyde (23 mL), concentrated H_2SO_4 (35 mL), acetic acid (10 mL) and 900 mL ethanol. Column chromatography was performed on silica gel. Macroporous polystyrene-sulfonic acid (MP-TsOH) was used as a catch and release resin. ^1H NMR spectra were recorded on a 500 MHz (499.9 MHz) spectrometer and ^{13}C NMR spectra were recorded on 400 MHz (100.6 MHz) spectrometer and 300MHz (75.5 MHz) spectrometer. Spectra were recorded at 23 °C, 60 °C and 80 °C using deuturated chloroform or dimethylsulfoxide-d_6 as solvent. Chemical shifts (δ) in ppm are reported using residual chloroform or dimethylsulfoxide as internal reference (1H δ 7.26, 13C δ 77.0) or (1H 2.49, 13C δ 39.5) and coupling constants (*J*) are reported in Hz. Infrared spectra were recorded on a Spectrum 100 FT/IR spectrometer. Melting point determination was done using a SMP3 melting point apparatus and are reported uncorrected. Purity of catalyst was confirmed by elemental analysis. Enantiomeric excesses were partly determined using a high pressure liquid chromatography (HPLC) system equipped with a column consisting of a chiral stationary phase (4 µm, 0.46*250 mm). Enantiomeric excess determination was also done using gas chromatography coupled to mass spectroscopy. The GC system was equipped with columns (30m*0,25mm), consisting of a fused silica capillary tubing coated with a chiral stationary phase (film thickness 0.125 µm) using helium gas at 10 psi as carrier gas and electron impact ionization (EI, 70eV). Details concerning the columns and temperature programs used are given specifically for each compound in the experimental section below.

(2*E*)-4-(Allyloxy)-but-2-enal[1] 16

The title compound was prepared as described by Garzía-Gómez et al.[1] Obtained as colorless liquid (1.16 g; 59%) after column chromatography (silica gel, 40 % diethyl ether in n-pentane), R_f=0.42. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (d, 7.88 Hz, 1H), 6.83 (dt, *J*=15.7, 4.01 Hz, 1H), 6.35 (ddt, *J*=15.7, 7.86, 2.01 Hz, 1H), 5.90 (ddt, *J*=17.6, 10.8, 5.7 Hz, 1H), 5.30 (dq, *J*=17.2, 1.65 Hz, 1H), 5.22 (dq, *J*=10.5, 1.44 Hz, 1H), 4.25 (dd, *J*=4.21, 2.01 Hz, 2H), 4.04 (dt, *J*=5.48, 1.47 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 68.5, 71.8, 117, 132, 134, 153, 193.

5-Hexenal[2] 17

The title compound was prepared as described by Diedrich et al.[2] Gave a colorless oil (2.14 g; 54%) after column chromatography (silica gel, 25 % diethyl ether in n-pentane), R_f=0.75. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (t, *J*=1.67 Hz, 1H), 5.77 (ddt, *J*=17.1, 10.2, 6.58 Hz, 1H), 5.05 (ddd, *J*=3.47, 1.47, 0.38 Hz, 1H), 5.06-4.97 (m, 1H) , 2.44 (td, *J*=7.31, 1.67, Hz, 2H), 2.10 (qt, *J*=7.1, 1.56 Hz, 2H), 1.74 (d, *J*=7.36, Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24, 36, 42, 117, 136, 203.

(*E*)-2,7-Octadienal[2] 18

The title compound was prepared as described by Diedrich et al.[2] Oxidation of (*E*)-2,7-Octadienol (1.63 g; 12.9 mmol) furnished slightly yellow liquid which was purified further by means of column chromatography (silica gel, 20 % diethyl ether in n-pentane), R_f=0.39, to yield a colorless oil (1.18g; 74 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (d, *J*=7.8 Hz, 1H), 6.84 (dt, *J*=15.6, 6.82 Hz, 1H), 6.12 (ddt, *J*=15.8, 7.82, 1.49 Hz, 1H), 5.78 (ddt, *J*=17.3, 10.3, 1.49 Hz, 1H), 5.06-4.97 (m, 2H), 2.35 (qd, *J*=6.83, 1.46 Hz, 2H), 2.11 (m, 2H), 1.62 (quin, *J*=7.57 Hz, 2H).

(*E*)-2,7-Octadienol [2] 19

Reduction of ethyl-(*E*)-2,7-octadienoate furnished crude product as colorless oil (1.63; 98%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.80 (ddt, *J*=17.1, 10.3, 6.79 Hz, 1H), 5.61-5.73 (m, 2H), 5.00 (dq, *J*=17.1, 1.46 Hz, 1H), 4.95 (ddt, *J*=10.3, 2.07, 1.21 Hz, 1H), 4.08 (m, 2H), 2.03-2.10 (m, 4H), 1.52-1.45 (m, 2H), 1.36 (brs, 1H).

Ethyl-(*E*)-2,7-octadienoate [2] 20

The crude product was obtained as an yellow oil which was further purified by means of column chromatography (silica gel, 1.5 % ethyl acetate in n-hexane). Ethyl-(*E*)-2,7-octadienoate, R$_f$=0.32, (2.26 g, 62 %) and Ethyl-(*Z*)-2,7-octadienoate R$_f$=0.40, (0.8 g, 22 %). Ethyl-(*E*)-2,7-octadienoate: ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.95 (dt, *J*=15.6, 8.67 Hz, 1H), 5.83 (dt, *J*=15.6, 1.58 Hz, 1H), 5.78 (ddt, *J*=17.1, 10.3, 6.72 Hz, 1H), 5.01 (ddq, *J*=17.1, 1.59, 0.49 Hz, 1H), 4.98 (ddt, *J*=10.3, 1.59, 0.37 Hz, 1H), 4.18 (q, *J*=7.1 Hz, 2H), 2.21 (qd, *J*=14.9, 1.71 Hz, 1H), 2.08 (t, *J*=7.1 Hz, 1H), 1.56 (qui d, *J*=7.11, 0.97 Hz, 2H), 1.28 (t, *J*=7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 13, 29, 33, 35, 63, 115, 123, 133, 148, 167.

2-(Dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone[3] and 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone[3]

The stabilized sulfur ylides 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone were prepared according to literature procedure. ^{1}H NMR and ^{13}C NMR, IR and melting points for both compounds were identical to previously reported data.[8]

(*S*)-1-(Benzyloxycarbonyl)-indoline-2-carboxylic acid (3)

Based on a reported procedure:[4] To a cold solution (5°C) of (*S*)-(-)-indoline-2-carboxylic acid (**2**) (4.5 g; 27.57 mmol) in 30 ml of 2 M sodium hydroxide was added under vigorous stirring alternating benzyl chloroformate (9.38 g; 55.15 mmol) and 30 ml of a 4 M sodium hydroxide solution. The mixture was stirred for an additional two hours at 5 °C and at room temperature for 3 hours after which the mixture was washed with 2*40 ml of diethyl ether. The aqueous layer was acidified to pH 1, saturated with sodium chloride and then extracted with ethyl acetate 3*100 ml. The combined extracts were dried with Na_2SO_4, filtered and concentrated under reduced pressure to give the crude product as a brown powder. The product was purified by means of column chromatography applying the mixture as a pad of silica using column chromatography (silica gel; 10 % methanol in dichloromethane and 1 % acetic acid), R_f=0.50 to give a white powder (7.57 g; 93 %), mp=115-116° C after evaporation of residual acetic acid using an azeotrope using toluene. ^{1}H NMR (500MHz; [D_6]-DMSO; 353.15 K) 3.08 (dd, *J*=16.6, 3.65 Hz, 1H), 3.57 (dd, *J*=16.6, 11.5 Hz, 1H), 4.91 (dd, *J*=11.5, 3.92 Hz, 1H), 5.24 (s, 2H), 6.96 (td, *J*=7.44, 0.98 Hz, 1H), 7.16-7.22 (m, 2H), 7.30-7.34 (m, 1H), 7.35-7.44 (m, 4H), 7.60 (m, 1H), 13 (brs, 1H); ^{13}C NMR (75 MHz; [D_6]-DMSO; 353.15 K) δ 31.9, 59.5, 59.6, 66.4, 113.6, 122.3, 124.4, 126.2, 127, 127.1, 127.2, 127.5, 128, 128.7, 136, 141.6, 151.9, 172.2; IR (neat): ν_{max} 3034, 1702, 1269, 1055 cm^{-1}.

(*S*)-1-(Benzyloxycarbonyl)-indoline-2-carboxamide (4)

Based on a reported procedure:[5] To a mixture of (*S*)-1-(benzyloxycarbonyl)-indoline-2-carboxylic acid (**3**) (6.95 g; 23.4 mmol), di-tert-butyl pyrocarbonate (6.65 g; 30.5 mmol), ammonium bicarbonate (2.4 g; 29.9 mmol) and acetonitrile 100 ml was slowly added pyridine (1.11 ml; 14.1 mmol) under nitrogen gas followed by stirring for 68 h at room temperature. The mixture was filtered and the collected crystals were recrystallized from hot acetonitrile to give white needle shaped crystals (4.33 g; 63 %). The mother liquor was concentrated under reduced pressure to give slightly yellow oil which was dissolved in dichloromethane 50 ml the organic phase was washed with saturated $NaHCO_3$ (3*50 ml), 0.2 M HCl (3*50 ml) and brine (50 ml). The solution was dried with Na_2SO_4, filtered and concentrated under reduced pressure to give the title compound as yellow oil which was subsequently was purified by means of column chromatography (silica gel; 5 % methanol in dichloromethane), R_f=0.33 to give white powder (1.1 g; 16 %). The combined yield amounted to (5.44g, 78 %), mp=189-190° C. ^{1}H NMR (500 MHz; [D_6]-DMSO; 353.15 K) δ 3.0 (dd, *J*=16.6, 3.91 Hz, 1H), 3.07 (d, *J*=16.6 Hz, 1H), 3.5 (dd, *J*=16.6, 11.2 Hz, 1H), 4.84 (dd, *J*=11.2, 4.12 Hz, 1H), 5.18-5.25 (m, 2H), 6.94 (td, *J*=7.44, 1.11 Hz), 7.13-7.19 (m, 2H), 7.3-7.45 (m, 5H), 7.65-7.70 (m, 1H); ^{13}C NMR (75 MHz; [D_6]-DMSO; 353.15 K) δ 27.5, 32.9, 38.6, 60.1, 66.2, 113.7, 122.1, 124.2, 126.8, 127, 127.4, 127.9, 129.2, 136.1, 142.1, 152, 172.4, 172.5; IR (neat): ν_{max} 3393, 1698, 1649, 1487, 1062, 755.

(*S*)-1-(Benzyloxycarbonyl)-indoline-2-carbonitrile (5)

Based on a reported procedure:[6] To a cold mixture 5 ºC consisting of (*S*)-1-(benzyloxycarbonyl)-indoline-2-carboxamide (**4**) (5.29 g; 17.9 mmol) and dimethylformamide 70 m capped with a drying tube ($CaCl_2$) was added cyanuric chloride (2.48 g; 13.4 mmol) in one shot where after which the solution was allowed to slowly reach room temperature upon which the stirring was continued for 24 hours. The reaction was quenched with 100 ml water upon which a precipitate was formed. The mixture was diluted with 300 ml ethyl acetate which dissolved the formed precipitate. The water and ethyl acetate phases were separated and the water phase was extracted with ethyl acetate (2*100 ml). The combined organic phases were washed with water (4*100 ml), dried with sodium sulphate, filtered and concentrated under reduced pressure to give crude product as a pale yellow oil which was further purified by means of column chromatography (silica gel; 5 % methanol in dichloromethane), R_f=0.75 to give white powder (4.39 g; 88 %), mp=104-105° C. The ^{1}H NMR (500 MHz; [D_6]-DMSO; 333.15 K) δ 3.35 (dd, *J*=16.6, 3.21 Hz, 1H), 3.62 (dd, *J*=16.6, 10.5 Hz, 1H), 5.30-5.37 (m, 2H), 5.50 (dd, *J*=10.7, 3,17 Hz, 1H), 7.05 (td, *J*=8.54, 1.09 Hz, 1H), 7.20-7.28 (m, 1H), 7.29-7.32 (m, 1H), 7.33-7.37 (m, 1H), 7.38-7.43 (m, 2H), 7.45-7.52 (m, 2H), 7.55-7.65 (m, 2H); ^{13}C NMR (75 MHz, [D_6]-DMSO; 333.15 K) δ 32.9, 48.4, 67.3, 114.1, 118.7, 123.2, 124.8, 127.5, 127.8, 127.9, 128.1, 135.5, 139.1, 151.2; IR (neat): ν_{max} 3132, 2243, 1726, 1604, 1485, 901.

(*S*)-1-(Benzyloxycarbonyl)-indoline-2-yltetrazole (6)

Based on a reported procedure:[7] A mixture of (*S*)-1-(benzyloxycarbonyl)-indoline-2-carbonitrile (**5**) (3.22 g; 11.6 mmol), sodium azide (1.51g; 23.1 mmol), and zink bromide (1.31; 5.78 mmol) in 30 ml 2-propanol and 30 ml water was stirred at reflux for 24 hours. To the reaction mixture was added 6 ml 3 M HCl upon which a white precipitate was formed and subsequently the mixture was diluted with 100 ml ethyl acetate after which the mixture was left stirring at room temperature until no solid was present and the solution was clear. The organic layer was isolated and the aqueous layer was extracted with ethyl acetate (2*40 ml). The combined organic phases were washed with brine (100 ml), dried with sodium sulphate and concentrated under reduced pressure to give the crude product as a white powder which was purified further by means of column chromatography (silica gel; 10 % methanol in dichloromethane and 1 % acetic acid), R_f=0.31 to give a white powder (3.49 g; 94 %), mp=210-212°C after evaporation of residual acetic acid using a azeotrope with toluene. ^{1}H NMR (500 MHz; [D_6]-DMSO; 353.15 K): δ 3.07 (dd, *J*=16.4, 3.40 Hz, 1H), 3.70 (dd, *J*=16.3, 10.7 Hz, 1H), 5.15 (s, 2H), 5.93 (dd, *J*=10.7, 3,7 Hz, 1H), 6.99 (td, *J*=7.44, 1.09 Hz, 1H), 7.17-7.23 (m, 4H), 7.25-7.33 (m, 3H), 7.68-7.73 (m, 1H). ^{13}C NMR (75 MHz; [D_6]-DMSO; 353.15 K): δ 35.6, 52.3, 52.4, 53.7, 108.7, 117.8, 123.8, 124.5, 126.7, 126.9, 127.0, 127.4, 127.9, 129.0, 135.8, 150.3, 159.7. IR (neat) ν_{max} 2976, 2852, 1715, 1483, 1392, 1143, 1033, 744 cm^{-1}.

(*S*)-(-)-Indoline-2-yl-1H-tetrazole (1)

Based on a reported procedure:[8] (*S*)-1-(Benzyloxycarbonyl)-indoline-2-yltetrazole (**6**) (2.91g; 9.04 mmol) was dissolved in 100 ml (9:1) (acetic acid: water). To this homogenous solution was added (0.4 g) palladium on carbon. The flask was placed under a hydrogen atmosphere and stirred at 60°C for 15 hours. The solution was filtrated through celite and concentrated under reduced pressure to give the crude product as a slightly yellow crystalline material. The crystalline material was dissolved in a mixture of dimethylformamide and methanol and 7 g of a macroporous polystyrene-sulfonic acid (MP-TsOH) was added to the homogenous solution and the mixture was stirred for one hour. The resin was washed with three times 40 ml dimethylformamide:methanol mixture and compound was released using

200 ml of sat. ammonia in dimethylformamide:methanol mixture. The solution was concentrated under reduced pressure to give a light yellow crystalline residue which was crystallized from methanol to give the title compound as an white solid (1.56 g; 92 %); mp 243-245 °C. $[\alpha]^{rt}_{D}$=-14.96 (c=1, DMF); ^{1}H NMR (500 MHz; [D$_6$]-DMSO; 273.15 K) δ 3.08 (dd, *J*=15.8, 8.79 Hz, 1H), 3.46 (dd, *J*=15.8, 9.82 Hz, 1H), 5.20 (dt, *J*=9.26, 0.85 Hz, 1H), 6.10-6.40 (brs, 1H), 6.584 (d, *J*=7.58 Hz, 1H), 6.615 (td, *J*=7.32, 0.97 Hz, 1H), 6.974 (td, *J*=7.58, 1.08 Hz, 1H), 7.055 (dd, *J*=7.32, 0.97 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]-DMSO) δ 36.1, 48.6, 52.5, 109.1, 118.2, 124.3, 126.9, 127.5, 150.6; IR (neat): ν_{max} 3348, 2936, 1604, 1568, 1243, 1052, 835; Anal. Calcd for $C_9H_9N_5$: C, 57.74; H, 4.85; N, 37.41. Found: C, 57.3; H, 4.9; N, 37.1; HPLC-MS: R_t = 5.0 min, MS (ESI) *m/z*: 188.3 $[M+H]^+$.

General procedure for catalytic asymmetric cyclopropanation

To a 30 ml flask equipped with a magnetic stirring bar was added the aldehyde (0.508 mmol) and chloroform 21 ml. The mixture was cooled to the desired temperature and stirred for an additional 20 minutes. To the chilled mixture was then added either (*S*)-(-)-indoline-2-carboxylic acid (**2)** (4.2 mg; 0.026 mmol) or (*S*)-(-)-indoline-2-yl-1H-tetrazole (**1)** (4.8 mg; 0.026 mmol) and 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone (23 mg; 0.127 mmol) or 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone (33 mg; 0.127mmol). The homogenous solution was stirred between 24-48 hours after which the cold solution was filtered through a pad of silica eluting with diethyl ether. The filtrate was concentrated under reduced pressure to give crude products as yellow oils which were further purified by means of column chromatography.

(*1R, 2S, 3R*)-2-Benzoyl-3-propyl-cyclopropanecarbaldehyde 8a (Table 2, entry 1):

Prepared according to general procedure from *trans*-2-hexenal (59 µl; 50mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a light yellow oil (22.6 g mg; 82 % yield; 99 % ee; 32:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.21 . ^{1}H NMR (500MHz; $CDCl_3$) δ 9.36 (d, *J*=6.58 Hz, 1H), 8.00-7.96 (m, 2H), 7.59 (tt, *J*=7.31, 1.21 Hz, 1H), 7.51-7.47 (m, 2H), 3.02 (dd, *J*=8.57, 6.13 Hz, 2H), 2.55-2.49 (m,1H), 2.12 (dt, *J*=8.51, 6.08 Hz, 1H), 0.96 (m, 3H). and ^{13}C NMR (100MHz; $CDCl_3$) δ 13.7, 22.0, 29.2, 30.3, 34.1, 34.7, 36.7, 40.2, 128.3, 128.7, 133.5, 137.0, 196.1, 199.3. $[\alpha]_D$=-12.23° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (155 °C isotherm for 90 minutes), ramp to (175 °C, 5 °C/min and isotherm for 18 min) and ramp to (220 °C, 10 °C/min, hold 0.5 min). *Major* diastereomer: major enantiomer t_r=31.8 min and *minor* enantiomer t_r=33.4 min. *Minor* diastereomer: major enantiomer t_r=20.1 min and *minor* enantiomer t_r=19.8 min. MS (EI): *m/z* (rel intensity): 216 (M^+, 2), 217 (M^++1, 32), 218 (2), 174 (13), 173 (100), 172 (3), 146 (5), 145 (33), 144 (4), 117(23), 116(4), 115(13), 106(7), 105(82), 104(5), 78(5), 77(44), 76(3).

(*1R, 2S, 3R*)-2-Benzoyl-3-propyl-cyclopropanecarbaldehyde 8b (Table 3, entry 1):

Prepared according to general procedure from *trans*-2-hexenal (59 µl; 50mg; 0.50 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a light yellow oil (20.3 mg; 74 % yield; 93 % ee; 31:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.21. ^{1}H NMR (500MHz; $CDCl_3$) δ 9.36 (d, *J*=6.6 Hz, 1H), 8.00-7.96 (m, 2H), 7.59 (tt, *J*=7.31, 1.21Hz, 1H), 7.51-7.47 (m, 2H), 3.02 (dd, *J*=8.57, 6.08 Hz, 2H), 2.55-2.48 (m, 1H), 2.12 (dt, *J*=8.66, 6.32 Hz, 1H), 1.65-1.45 (m, 4H), 0.96 (m, 3H). ^{13}C NMR (100MHz; $CDCl_3$) δ 13.7, 22.0, 29.2, 30.3, 34.1, 34.7, 40.2, 128.3, 128.7, 133.5, 137.0, 196.1, 199.3. $[\alpha]_D$=-15.28° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (155 °C isotherm for 90 minutes), ramp to (175 °C, 5

°C/min and isotherm for 18 min) and ramp to (220 °C, 10 °C/min, hold 0.5 min). *Major* diastereomer: major enantiomer t_r=31.8 min and *minor* enantiomer t_r=33.4 min. *Minor* diastereomer: major enantiomer t_r=20.4 min and *minor* enantiomer t_r=19.6 min. MS (EI) *m/z* (rel. intensity): 216 (M^+, 3), 217 (M^++1, 51), 218 (8), 174 (13), 173 (100), 172 (4), 146 (5), 145 (35), 144 (4), 117(25), 116(4), 115(14), 106(8), 105(90), 104(3), 78(5), 77(45), 76(3)

(*1R, 2S, 3R*)-2-(4´-bromo-benzoyl)-3-propyl-cyclopropanecarbaldehyde 9a (Table 2, entry 2): Prepared according to general procedure from *trans*-2-hexenal (59 µl; 50mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a light yellow oil (27.7 mg; 74 % yield; 99 % ee; 31:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.1 . ^{1}H NMR (500MHz, $CDCl_3$) δ 9.36 (d, *J*=6.6 Hz, 1H), 7.86-7.82 (m, 2H), 7.64-7.61 (m, 2H), 2.95 (dd, *J*=8.54, 6.09 Hz, 1H), 2.52-2.19 (m, 1H), 2.13 (dt, *J*=8.52, 6.24 Hz, 1H), 1.65-1.45 (m, 4H) 0.96 (m, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 13.7, 22.0, 29.4, 30.3, 34.1, 34.6, 40.2, 128.8, 129.8, 132.1, 135.7, 195.1, 199.0. $[\alpha]_D$=-16.28° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (180 °C isotherm for 110 minutes), ramp to (220 °C , 10 °C/min, hold 0.50 min). *Major* diastereomer: major enantiomer t_r=39.5 min and *minor* enantiomer t_r=40.6 min. *Minor* diastereomer: major enantiomer t_r=23.1 min and *minor* enantiomer t_r=22.5 min. MS (EI) *m/z* (rel. intensity): 294 (M^+, 1), 295 (M^++1, 4), 296 (2), 251 (99), 252 (15), 253 (100), 254 (13), 183 (65), 184 (8), 185(65), 186(7), 155(23), 156(4), 157(26), 158(12), 144(37), 145(9), 115(14), 116(17), 117(4), 118(1).

(*1R, 2S, 3R*)-2-(4´-bromo-benzoyl)-3-propyl-cyclopropanecarbaldehyde 9b (Table 3, entry 2): Prepared according to general procedure from *trans*-2-hexenal (59 µl; 50mg; 0.50 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a light yellow oil (24.6 mg; 66 % yield; 93 % ee; 32:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.1. ^{1}H NMR (500MHz, $CDCl_3$) δ 9.36 (d, *J*=6.6 Hz, 1H), 7.86-7.82 (m, 2H), 7.64-7.61 (m, 2H), 2.95 (dd, *J*=8.54, 6.09 Hz, 1H), 2.52-2.19 (m, 1H), 2.13 (dt, *J*=8.52, 6.24 Hz, 1H), 1.65-1.45 (m, 4H) 0.96 (m, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 13.7, 22.0, 29.2, 30.3, 34.1, 34.7, 40.2, 128.3, 128.7, 133.5, 137.0, 196.1, 199.3. $[\alpha]_D$=-14.88° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (180 °C isotherm for 110 minutes), ramp to (220 °C by 10 °C/min, hold 0.50 min). *Major* diastereomer: major enantiomer t_r=39.3 min and *minor* enantiomer t_r=40.4 min. *Minor* diastereomer: major enantiomer t_r=23.6 min and *minor* enantiomer t_r=23.1 min MS (EI) *m/z* (rel. intensity): 294 (M^+, 1), 295 (M^++1, 5), 296 (1), 251 (98), 252 (14), 253 (100), 254 (12), 183 (61), 184 (7), 185(63), 186(7), 155(22), 156(4), 157(24), 158(12), 144(35), 145(7), 115(14), 116(18), 117(4), 118(1)

(*1R, 2S, 3R*)-2-Benzoyl-3-methyl-cyclopropanecarbaldehyde 10a (Table 2, entry 3):

Prepared according to general procedure from crotonaldehyde (59 µl; 50mg; 0.50 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a light yellow oil (20.2 mg; 85 % yield; 99 % ee; 22:1 dr) after column chromatography (silica gel; 10 % Et_2O in n-pentane), R_f=0.2. ^{1}H NMR (500MHz; $CDCl_3$) δ 9.35 (d, *J*=6.58 Hz, 1H), 8.00-7.96 (m, 2H), 7.60 (tt, *J*=8.78, 1.25 Hz, 1H), 7.52-7.47 (m, 2H), 2.99 (dd, *J*=8.53, 6.09 Hz, 1H), 2.53 (ddq, *J*=12,1, 6.3, 6.1 Hz, 1H), 2.12 (ddd, *J*=8.56, 6.38, 5.56 Hz, 1H), 1.37 (d, *J*=6.11 Hz, 3H). and ^{13}C NMR (100MHz; $CDCl_3$) δ 17.3, 24.2, 35.1, 39.5, 42.3, 129.1, 129.5, 133.9, 136.4, 196.6, 199.5. $[\alpha]_D$=-7.89° (C=1.0, $CHCl_3$). The enantiomeric excess was determined by GLC using Astec Chiraldex σ-TA (30 m * 0.25 mm), column (160 °C isotherm for 60 minutes), ramp to (180 °C by 10 °C/min, hold 0.5 min). *Major* diastereomer: major enantiomer t_r=10.3 min and *minor* enantiomer t_r=11.2 min. MS (EI) *m/z* (rel. intensity): 187 (M^+, 1), 171 (4), 144 (3), 115 (10), 105 (100), 89 (2), 77 (46), 69 (5), 51(22). The diastereomeric ratio was determined by ^{1}H NMR analysis on the crude reaction mixture.

(*1R, 2S, 3R*)-2-Benzoyl-3-methyl-cyclopropanecarbaldehyde 10b (Table 3, entry 3):

Prepared according to general procedure from crotonaldehyde (59 μl; 50mg; 0.50 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a light yellow oil (16 mg; 67 % yield; 89 % ee; 20:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.2. ^{1}H NMR (500MHz; $CDCl_3$) δ 9.35 (d, *J*=6.58 Hz, 1H), 8.00-7.96 (m, 2H), 7.60 (tt, *J*=8.78, 1.25 Hz, 1H), 7.52-7.47 (m, 2H), 2.99 (dd, *J*=8.53, 6.09 Hz, 1H), 2.53 (ddq, *J*=12,1, 6.3, 6.1 Hz, 1H), 2.12 (ddd, *J*=8.56, 6.38, 5.56 Hz, 1H), 1.37 (d, *J*=6.11 Hz, 3H). and ^{13}C NMR (100MHz; $CDCl_3$) δ 17.3, 24.2, 35.1, 39.5, 42.3, 129.1, 129.5, 133.9, 136.4, 196.6, 199.5. $[\alpha]_D$=-5.67° (C=1.0, $CHCl_3$). The enantiomeric excess was determined by GLC using Astec Chiraldex σ-TA (30 m * 0.25 mm), column (160 °C isotherm for 60 minutes), ramp to (180 °C by 10 °C/min, hold 0.5 min). *Major* diastereomer: major enantiomer t_r=10.3 min and *minor* enantiomer t_r=11.4 min. MS (EI) *m/z* (rel. intensity): 187 (M^+, 1), 171 (5), 144 (3), 115 (10), 105 (100), 89 (2), 77 (45), 69 (5), 51(22). The diastereomeric ratio was determined by ^{1}H NMR analysis on the crude reaction mixture.

(*1R*, *2R*, *3S*)-2-Allyloxymethyl-3-benzoyl-cyclopropanecarbaldehyde 11a (Table 2, entry 4): Prepared according to general procedure from (*2E*)-4-(allyloxy)-but-2-enal (64 mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a colorless oil (28.3 mg; 91 % yield; 99 % ee; 41:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.09. ^{1}H NMR (500MHz; $CDCl_3$) δ 9.4 (d, *J*=6.49 Hz, 1H), 8.03-8.00 (m, 2H), 7.62-7.57 (m, 1 Hz), 7.51-7.46 (m, 2H), 5.88 (ddt, *J*=17.2, 10.3, 5.62 Hz, 1H), 5.27 (dqd, *J*=17.2, 10.3, 0.23 Hz, 1H), 5.21 (dq, *J*=10.3, 1.34 Hz, 1H), 4.03-3.99 (m, 2H), 3.72 (dd, *J*=10.3, 4.87 Hz, 1H), 3.58 (dd, *J*=10.5, 5.4 Hz, 1H), 3.25 (dd, *J*=8.81, 6.14 Hz, 1H), 2.77 (m, 1H), 2.33 (dt, *J*=8.81, 6.23 Hz, 1H).^{13}C NMR (100MHz; $CDCl_3$) δ 27.6, 30.3, 31.8, 36.6, 68.5, 71.9, 117.4, 128.4, 128.7, 133.6, 134.1, 136.8, 146.2, 195.6, 198.8. $[\alpha]_D$=-6.33° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (177° C isotherm for 120 minutes), ramp to (220° C by 10° C/min), hold 220° C for 0.5 min. *Major* diastereomer: major enantiomer t_r=28.7 min and *minor* enantiomer t_r=29.7 min. *Minor* diastereomer:

major enantiomer t_r=13.1 min and *minor* enantiomer t_r=13.4 min. MS (EI) *m/z* (rel. intensity): 244 (M^+, 2), 245 (M^++1, 52), 173 (100), 117 (26), 116 (4), 105 (75), 104 (2), 77 (38), 76 (2).

(*1R*, *2R*, *3S*)-2-Allyloxymethyl-3-benzoyl-cyclopropanecarbaldehyde 11b (Table 3, entry 4): Prepared according to general procedure from (*2E*)-4-(allyloxy)-but-2-enal (64 mg; 0.50 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a colorless oil (24 mg; 77 % yield; 91 % ee; 23:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.09. ^{1}H NMR (500MHz; $CDCl_3$) δ 9.4 (d, *J*=6.49 Hz, 1H), 8.03-8.00 (m, 2H), 7.62-7.57 (m, 1 Hz), 7.51-7.46 (m, 2H), 5.88 (ddt, *J*=17.2, 10.3, 5.62 Hz, 1H), 5.27 (dqd, *J*=17.2, 10.3, 0.23 Hz, 1H), 5.21 (dq, *J*=10.3, 1.34 Hz, 1H), 4.03-3.99 (m, 2H), 3.72 (dd, *J*=10.3, 4.87 Hz, 1H), 3.58 (dd, *J*=10.5, 5.4 Hz, 1H), 3.25 (dd, *J*=8.81, 6.14 Hz, 1H), 2.77 (m, 1H), 2.33 (dt, *J*=8.81, 6.23 Hz, 1H). ^{13}C NMR (100MHz; $CDCl_3$) δ 27.6, 30.3, 31.9, 36.6, 68.5, 71.7, 117.4, 128.6, 128.7, 133.6, 134.1, 136.8, 146.2, 195.6, 198.8. $[\alpha]_D$=-8.67° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (177° C isotherm for 120 minutes), ramp to (220° C by 10° C/min), hold 220° C for 0.5 min. *Major* diastereomer: major enantiomer t_r=28.9 min and *minor* enantiomer t_r=29.9 min. *Minor* diastereomer: major enantiomer t_r=13.0 min and *minor* enantiomer t_r=13.4 min. MS (EI) *m/z* (rel. intensity): 244 (M^+, 4), 245 (M^++1, 48), 173 (100), 117 (23), 116 (7), 105 (78), 104 (2), 77 (38), 76 (4).

(*1R*, *2R*, *3S*)-2-Allyloxymethyl-3-(4´-bromo-benzoyl)-cyclopropanecarbaldehyde 12a (Table 2, entry 5): Prepared according to general procedure from (*2E*)-4-(allyloxy)-but-2-enal (64 mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a colorless oil (34.1 mg; 83 % yield; 99 % ee; 43:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.06. ^{1}H NMR (500MHz, $CDCl_3$) δ 9.38 (d, *J*=6.34 Hz, 1H), 7.9-7.86 (m, 2H), 7.64-7.61 (m, 2H), 5.88 (ddt, *J*=17.2, 10.4, 5.6 Hz, 1H), 5.27 (dq, *J*=17.2, 1.57 Hz, 2H), 5.21 (ddq, *J*=10.4, 1.59, 1.21 Hz, 1H), 4.03-4.00 (m, 2H), 3.74 (dd, *J*=10.4, 4.59 Hz, 1H), 3.55 (dd, *J*=10.4, 5.5 Hz, 1H), 3.19 (dd, *J*=8.81, 6.11 Hz, 1H), 2.78-2.72 (m, 1H), 2.34

(dt, 8.82, 6.21). ^{13}C NMR (100MHz, $CDCl_3$) δ 27.9, 30.3, 31.8, 36.5, 68.4, 71.9, 117.5, 130.0(2C), 132.0(2C), 134.1, 135.5, 194.7, 198.5. $[\alpha]_D$=-16.9° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (200 °C isotherm for 130 minutes), ramp to (220 °C by 10 °C), hold 0.5 min. *Major* diastereomer: major enantiomer t_r=32.6 min and *minor* enantiomer t_r=33.3 min. *Minor* diastereomer: major enantiomer t_r=21.3 min and *minor* enantiomer t_r=21.9 min. MS (EI) *m/z* (rel. intensity): 323 (M^+1, 7), 325 (7), 283 (5), 281 (8), 280 (1), 253 (97), 252 (16), 251 (100), 250 (4), 185(53), 184(8), 183(55), 182(2), 157(22), 156(4), 155(21), 154(1).

(*1R*, *2R*, *3S*)-2-Allyloxymethyl-3-(4´-bromo-benzoyl)-cyclopropanecarbaldehyde 12b (Table 3, entry 5): Prepared according to general procedure from (*2E*)-4-(allyloxy)-but-2-enal (64 mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a colorless oil (32.1 mg; 78 % yield; 88 % ee; 28:1 % de) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.06. ^{1}H NMR (500MHz, $CDCl_3$) δ 9.38 (d, *J*=6.34 Hz, 1H), 7.9-7.86 (m, 2H), 7.64-7.61 (m, 2H), 5.88 (ddt, *J*=17.2, 10.4, 5.6 Hz, 1H), 5.27 (dq, *J*=17.2, 1.57 Hz, 2H), 5.21 (ddq, *J*=10.4, 1.59, 1.21 Hz, 1H), 4.03-4.00 (m, 2H), 3.74 (dd, *J*=10.4, 4.59 Hz, 1H), 3.55 (dd, *J*=10.4, 5.5 Hz, 1H), 3.19 (dd, *J*=8.81, 6.11 Hz, 1H), 2.78-2.72 (m, 1H), 2.34 (dt, 8.82, 6.21). ^{13}C NMR (100MHz, $CDCl_3$) δ 27.9, 30.3, 31.8, 36.5, 68.4, 71.9, 117.5, 130.0(2C), 132.0(2C), 134.1, 135.5, 194.7, 198.5. $[\alpha]_D$=-8.63° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (200 °C isotherm for 130 minutes), ramp to (220 °C by 10 °C), hold 0.5 min. *Major* diastereomer: major enantiomer t_r=32.8 min and *minor* enantiomer t_r=33.4 min. *Minor* diastereomer: major enantiomer t_r=21.5 min and *minor* enantiomer t_r=22.2 min. MS (EI) *m/z* (rel. intensity): 322 (M^+,1), 323 (11), 324 (3), 325 (10), 253 (100), 252 (15), 251 (96), 250 (4), 225 (19), 224 (4), 223 (19), 222 (1), 185 (46), 184(6), 183(47), 182(2), 157(18), 156(4), 155(17), 154(1).

(*1R, 2S, 3R*)-2-(4´-bromo-benzoyl)-3-hex-5-enyl-cyclopropanecarbaldehyde 13a (Table 2, entry 6): Prepared according to general procedure from (*E*)-2,7-octadienal (63.1mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a light yellow oil (32 mg; 86 % yield; 99 % ee; 29:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.1. ^{1}H NMR (500MHz; $CDCl_3$) δ 9.33 (d, *J*=6.6 Hz, 1H), 7.86-8.10 (m, 2H), 7.64-7.60 (m, 2, 1H), 5.76 (ddt, *J*=17.1, 10.3, 6.57 Hz, 1H), 5.04-4.94 (m, 2H), 2.95 (dd, *J*=8.51, 6.1 Hz, 1H), 2.50 (ddt, *J*=12.4, 6.4, 6.4 Hz, 1H), 2.15-2.07 (m, 3H), 1.64-1.50 (m, 6H). ^{13}C NMR (100MHz; $CDCl_3$) δ 27.9, 29.3, 29.7, 31.4, 33.1, 34.5, 40.2, 115.2, 128.9, 129.8, 132.1, 135.7, 137.9 195.0, 198.9. $[\alpha]_D$=-18.23° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column (195° C isotherm for 150 minutes), ramp to 220 °C by 10 °C/min, 220 °C hold 0.5 minutes. *Major* diastereomer: major enantiomer t_r=41.9 min and *minor* enantiomer t_r=42.55 min. *Minor* diastereomer: major enantiomer t_r=26.8 min and *minor* enantiomer t_r=26.3 min. MS (EI) *m/z* (rel. intensity): 334 (M^+,1), 323 (4), 322 (2), 321 (5), 320 (2), 279 (15), 278 (5), 277 (14), 276 (2), 253 (69), 252 (14), 251 (76), 250 (5), 225 (22), 224 (7), 223 (24), 222 (4), 185 (100), 184(13), 183(96), 182(3), 157(44), 156(6), 155(38), 154(3).

(*1R, 2S, 3R*)-2-(4´-bromo-benzoyl)-3-hex-5-enyl-cyclopropanecarbaldehyde 13b (Table 3, entry 6): Prepared according to general procedure from (*E*)-2,7-octadienal (63.1mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-(4´-bromophenyl)-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a light yellow oil (30.2 mg; 71 % yield; 93 % ee; 25:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), ^{1}H NMR (500MHz; $CDCl_3$) δ 9.33 (d, *J*=6.6 Hz, 1H), 7.86-8.10 (m, 2H), 7.64-7.60 (m, 2, 1H), 5.76 (ddt, *J*=17.1, 10.3, 6.57 Hz, 1H), 5.04-4.94 (m, 2H), 2.95 (dd, *J*=8.51, 6.1 Hz, 1H), 2.50 (ddt, *J*=12.4, 6.4, 6.4 Hz, 1H), 2.15-2.07 (m, 3H), 1.64-1.50 (m, 6H). ^{13}C NMR (100MHz; $CDCl_3$) δ 27.9, 29.3, 30.3, 31.4, 33.0, 34.5, 40.2, 115.2, 128.8, 129.7, 132.0, 135.6, 137.8, 195.0, 198.9. $[\alpha]_D$=-14.4° (C=1.0, $CHCl_3$). The enantiomeric excess and diastereomeric excess was determined by GLC using Astec Chiraldex β-DM (30 m * 0.25 mm), column

(195° C isotherm for 150 minutes), ramp to 220 °C by 10 °C/min, 220 °C hold 0.5 minutes. *Major* diastereomer: major enantiomer t_r=41.5 min and *minor* enantiomer t_r=42.2 min. *Minor* diastereomer: major enantiomer t_r=26.6 min and *minor* enantiomer t_r=26.2 min. MS (EI) *m/z* (rel. intensity): 334 (M^+,1), 323 (8), 322 (4), 321 (8), 320 (2), 225 (23), 224 (12), 223 (22), 222 (4), 185 (100), 184(13), 183(98), 182(4), 157(41), 156(7), 155(36), 154(4).

(*1R*, *2S*, *3R*)-2-Benzoyl-3-phenyl-cyclopropanecarbaldehyde 14a (Table 2, entry 7): Prepared according to general procedure from *trans*-cinnamaldehyde (68 mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-yl-1H-tetrazole to give the pure product as a colorless oil (29.8 mg; 94 % yield; 99 % ee; 35:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.15. ^{1}H NMR (500MHz, $CDCl_3$) δ 9.59 (d, *J*=6.08 Hz, 1H), 8.02-7.98 (m, 2H), 7.63-7.59 (m, 2H), 7.52-7.47 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.28 (m, 1H), 7.25-7.21 (m, 2H), 3.61 (t, *J*=6.11 Hz, 1H), 3.48 (dd, *J*=9.02, 6.1 Hz, 1H), 2.68 (ddd, *J*=8.91, 6.3, 6.1 Hz, 1H). ^{13}C NMR (100MHz; $CDCl_3$) δ 32.4, 36.7, 40.8, 126.6 (2C), 127.6, 128.4 (2C), 128.8 (2C), 128.9 (2C), 133.7, 136.9, 137.0, 195.0, 197.7. $[\alpha]_D$=-166.9° (C=1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis after reduction of the aldehyde to the corresponding alcohol. (*1R*, *2S*, *3R*)-2-Benzoyl-3-phenyl-cyclopropanecarbaldehyde (**14a**) (29.8 mg; 0.12 mmol) was carefully dissolved in 1 ml (methanol:AcOH/AcONa buffer pH=4.5) (1:1) after which (1.2 eq, 7.54 mg, 0.144 mmol) of sodium cyanoborohydride was added. The mixture was stirred at room temperature for 6 hours after which the mixture was concentrated at reduced pressure to give white residue. The residue was diluted with 1 ml saturated NaCl and then extracted 3 times with ethyl acetate. The combined organic phases were dried with Na_2SO_4, filtered, concentrated to give crude product which was further purified by means of column chromatography (silica gel, 30 % ethyl acetate in n-pentane), R_f=0.75, to give pure product primary alcohol (**15a**) as a colorless oil (28.8 mg, 95 %). ^{1}H NMR (500MHz; $CDCl_3$) δ 8.02-7.98 (m, 2H), 7.60-7.53 (m, 1H), 7.35-7.28 (m, 2H), 7.27-7.14 (m, 5H), 4.15 (m, 2H), 3.90 (dd, *J*=12.1, 8.29 Hz, 1H), 3.02 (dd, *J*=8.79, 5.14 Hz, 1H), 2.94 (td, *J*=5.69, 1.31 Hz, 1H), 2.42-2.33 (m, 1H). The anantiomeric excess was determined by HPLC equipped with chiral column Chiralcel AD (25

% 2-propanol in hexane, 1ml/min, 254 nm); *major* diastereomer: major enantiomer t_r= 22.15 min. *Minor* diastereomer: major enantiomer t_r=12.3 min and *minor* enantiomer t_r=13.8 min.

(*1R*, *2S*, *3R*)-2-Benzoyl-3-phenyl-cyclopropanecarbaldehyde 14b (Table 3, entry 7): Prepared according to general procedure from *trans*-cinnamaldehyde (68 mg; 0.508 mmol), 2-(dimethyl-λ^4-sulfanylidene)-1-phenyl-ethanone and (*S*)-(-)-indoline-2-carboxylic acid to give the pure product as a colorless oil (25.8 mg; 81 % yield; 93 % ee; 32:1 dr) after column chromatography (silica gel, 10 % Et_2O in n-pentane), R_f=0.15. ^1H NMR (500MHz, $CDCl_3$) δ 9.59 (d, *J*=6.08 Hz, 1H), 8.02-7.98 (m, 2H), 7.63-7.59 (m, 2H), 7.52-7.47 (m, 2H), 7.39-7.33 (m, 2H), 7.32-7.28 (m, 1H), 7.25-7.21 (m, 2H), 3.61 (t, *J*=6.11 Hz, 1H), 3.48 (dd, *J*=9.02, 6.1 Hz, 1H), 2.68 (ddd, *J*=8.91, 6.3, 6.1 Hz, 1H). ^{13}C NMR (100MHz; $CDCl_3$) δ 32.4, 36.7, 40.8, 126.6 (2C), 127.6, 128.4 (2C), 128.8 (2C), 128.9 (2C), 133.7, 136.9, 137.0, 195.0, 197.7. $[\alpha]_D$=-165.6° (C=1.0, $CHCl_3$). The enantiomeric excess was determined by HPLC analysis after reduction of the aldehyde to the corresponding alcohol. (*1R*, *2S*, *3R*)-2-Benzoyl-3-phenyl-cyclopropanecarbaldehyde (**14b**) (25.8 mg; 0.103 mmol) was carefully dissolved in 1 ml (methanol:AcOH/AcONa buffer pH=4.5) (1:1) after which (1,2 eq, 7.2 mg, 0.124 mmol) of sodium cyanoborohydride was added. The mixture was stirred at room temperature for 6 hours after which the mixture was concentrated at reduced pressure to give white residue. The residue was diluted with 1 ml saturated NaCl and extracted 3 times with ethyl acetate. The combined organic phases were dried with Na_2SO_4, filtered, concentrated to give crude product which was further purified by means of column chromatography (silica gel, 30 % ethyl acetate in n-pentane), R_f=0.75, to give pure product primary alcohol (**15b**) as a colorless oil (16.6 mg, 65 %). ^1H NMR (500MHz; $CDCl_3$) δ 8.02-7.98 (m, 2H), 7.60-7.53 (m, 1H), 7.35-7.28 (m, 2H), 7.27-7.14 (m, 5H), 4.15 (m, 2H), 3.90 (dd, *J*=12.1, 8.29 Hz, 1H), 3.02 (dd, *J*=8.79, 5.14 Hz, 1H), 2.94 (td, *J*=5.69, 1.31 Hz, 1H), 2.42-2.33 (m, 1H). The anantiomeric excess was determined by HPLC equipped with chiral column Chiralcel AD (25 % 2-propanol/hexanes, 1ml/min, 254 nm); major enantiomer t_r= 22.35 min and minor enantiomer t_r= 29.70 min. *Minor* diastereomer: major enantiomer t_r=11.8min and *minor* enantiomer t_r=13.1 min.

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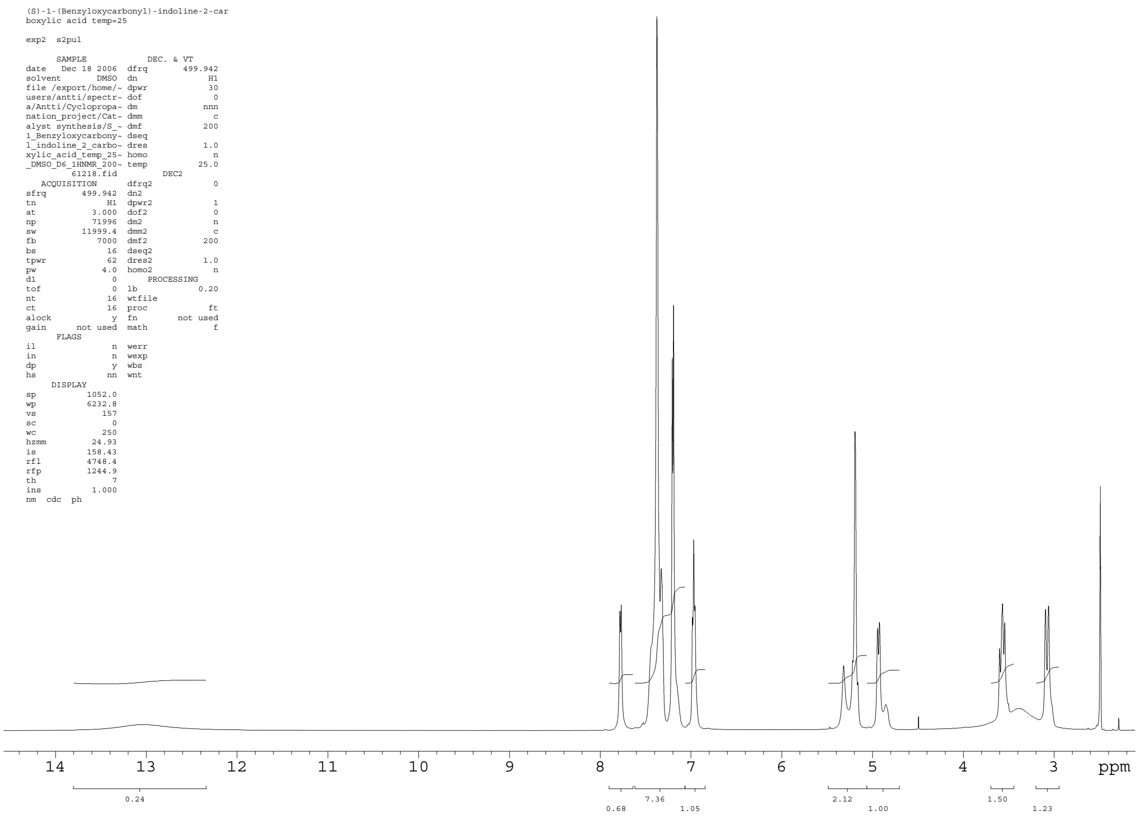
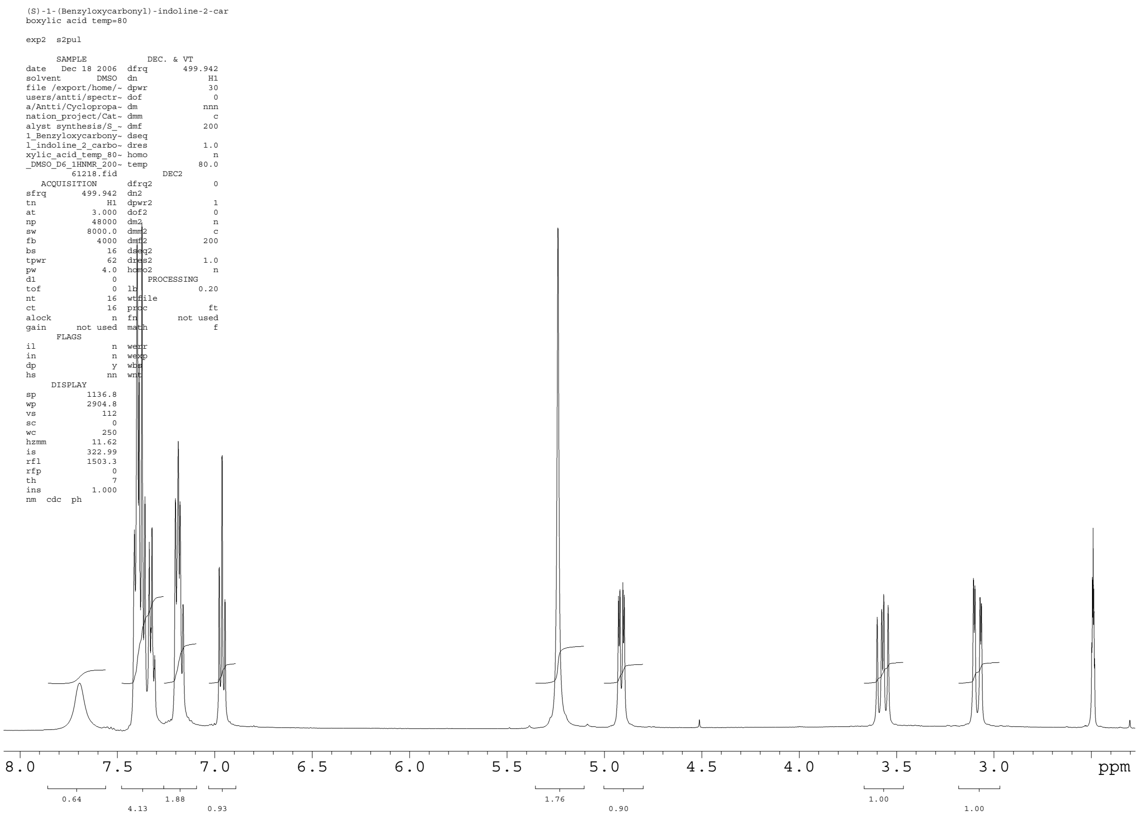
Figure 1: ^{1}H NMR of (3) at 25 °C.



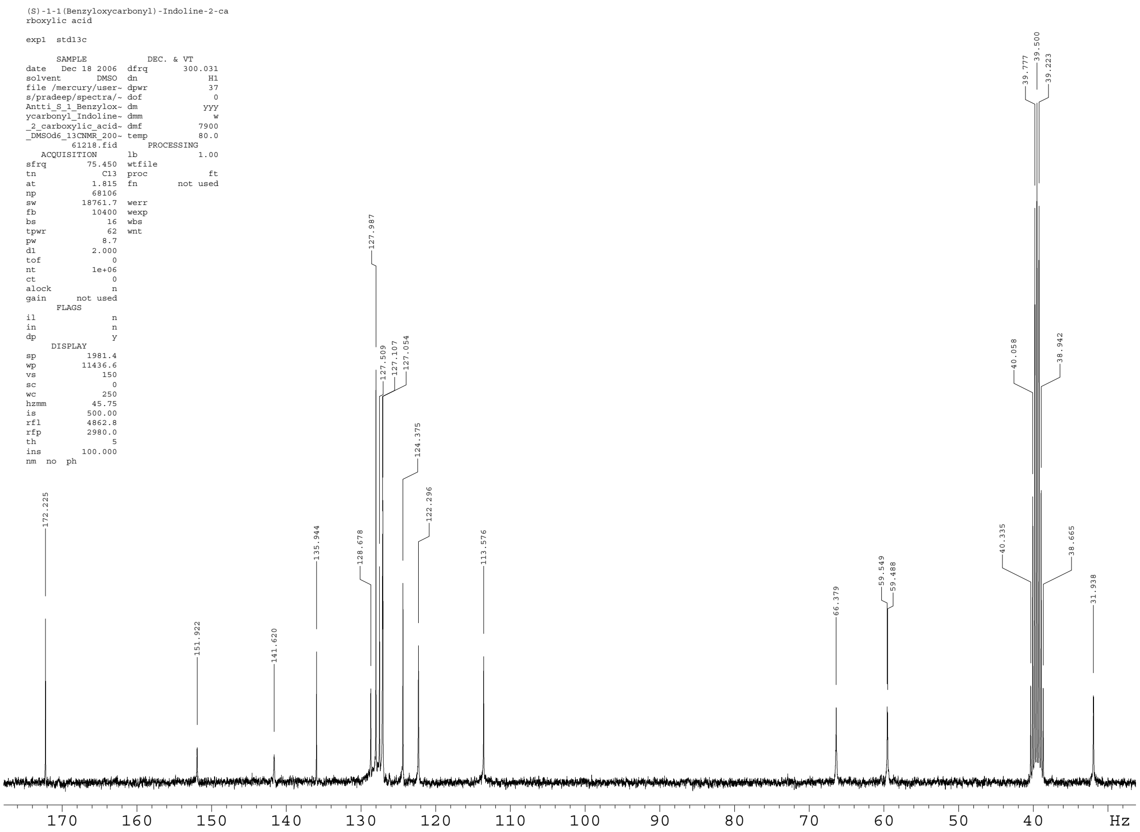
```
(S)-1-(Benzyloxycarbonyl)-indoline-2-car
boxylic acid temp=25

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 18 2006  dfrq       499.942
solvent       DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_indoline_2_carbo~ dres           1.0
xylic_acid_temp_25~ homo             n
_DMSO_D6_1HNMR_200~ temp          25.0
         61218.fid          DEC2
   ACQUISITION      dfrq2            0
sfrq       499.942  dn2
tn              H1  dpwr2            1
at           3.000  dof2             0
np           71996  dm2              n
sw         11999.4  dmm2             c
fb            7000  dmf2           200
bs              16  dseq2
tpwr            62  dres2          1.0
pw             4.0  homo2            n
d1               0      PROCESSING
tof              0  lb            0.20
nt              16  wtfile
ct              16  proc            ft
alock            y  fn        not used
gain      not used  math             f
      FLAGS
il               n  werr
in               n  wexp
dp               y  wbs
hs              nn  wnt
     DISPLAY
sp          1052.0
wp          6232.8
vs             157
sc               0
wc             250
hzmm         24.93
is          158.43
rfl         4748.4
rfp         1244.9
th               7
ins          1.000
nm  cdc  ph
```

Figure 2: ^{1}H NMR of (3) at 80 °C.



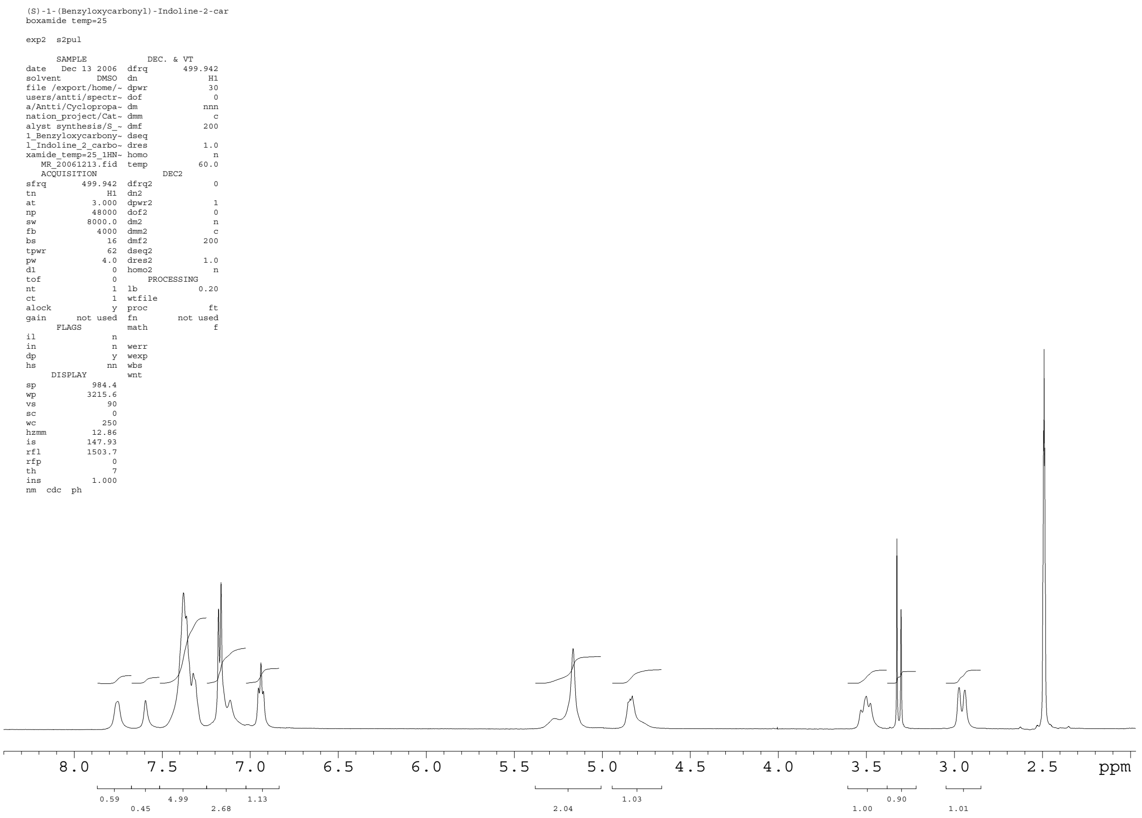
```
(S)-1-(Benzyloxycarbonyl)-indoline-2-car
boxylic acid temp=80

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 18 2006  dfrq       499.942
solvent       DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_indoline_2_carbo~ dres           1.0
xylic_acid_temp_80~ homo             n
_DMSO_D6_1HNMR_200~ temp          80.0
         61218.fid          DEC2
   ACQUISITION      dfrq2            0
sfrq       499.942  dn2
tn              H1  dpwr2            1
at           3.000  dof2             0
np           48000  dm2              n
sw          8000.0  dmm2             c
fb            4000  dmf2           200
bs              16  dseq2
tpwr            62  dres2          1.0
pw             4.0  homo2            n
d1               0      PROCESSING
tof              0  lb            0.20
nt              16  wtfile
ct              16  proc            ft
alock            n  fn        not used
gain      not used  math             f
      FLAGS
il               n  werr
in               n  wexp
dp               y  wbs
hs              nn  wnt
     DISPLAY
sp          1136.8
wp          2904.8
vs             112
sc               0
wc             250
hzmm         11.62
is          322.99
rfl         1503.3
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

Figure 3: ^{13}C NMR of (3) at 80 °C.



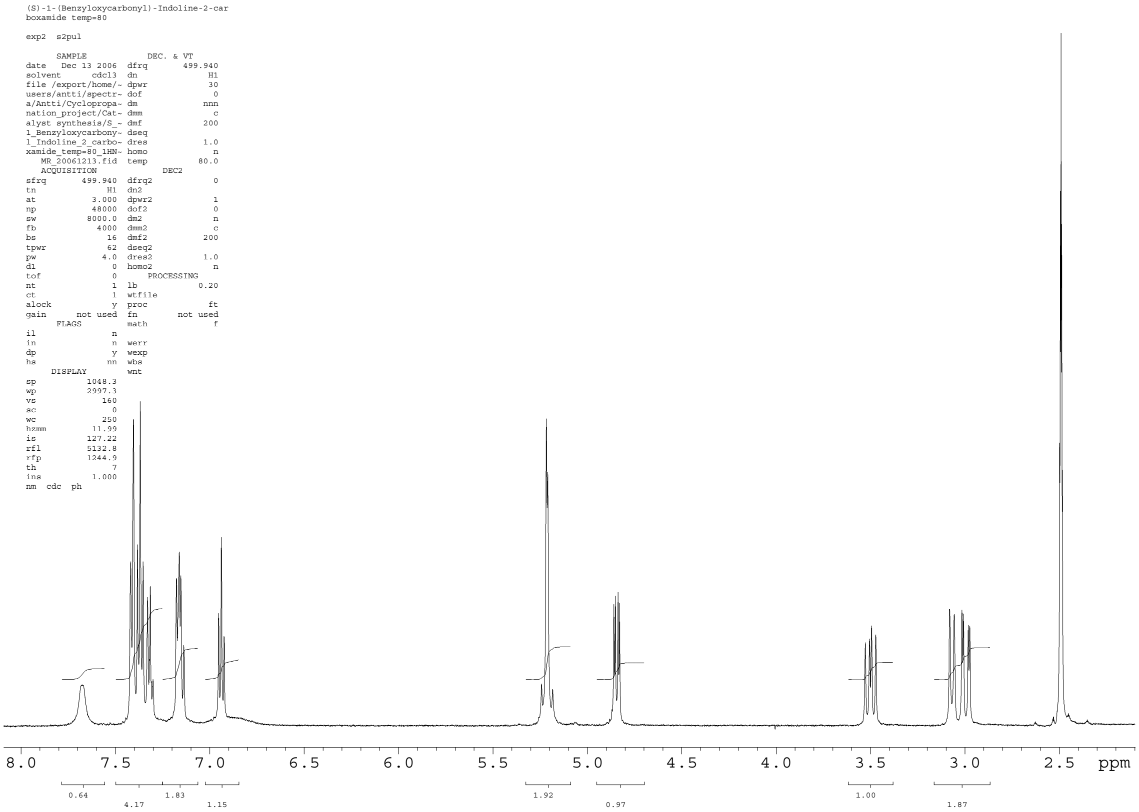
```
(S)-1-1(Benzyloxycarbonyl)-Indoline-2-ca
rboxylic acid

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec 18 2006  dfrq       300.031
solvent       DMSO  dn              H1
file /mercury/user~ dpwr            37
s/pradeep/spectra/~ dof              0
Antti_S_1_Benzylox~ dm             yyy
ycarbonyl_Indoline~ dmm              w
_2_carboxylic_acid~ dmf           7900
_DMSOd6_13CNMR_200~ temp          80.0
         61218.fid      PROCESSING
   ACQUISITION      lb            1.00
sfrq        75.450  wtfile
tn             C13  proc            ft
at           1.815  fn        not used
np           68106
sw         18761.7  werr
fb           10400  wexp
bs              16  wbs
tpwr            62  wnt
pw             8.7
d1           2.000
tof              0
nt           1e+06
ct               0
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          1981.4
wp         11436.6
vs             150
sc               0
wc             250
hzmm         45.75
is          500.00
rfl         4862.8
rfp         2980.0
th               5
ins        100.000
nm  no  ph
```

Figure 4: ^{1}H NMR of (4) at 25 °C.



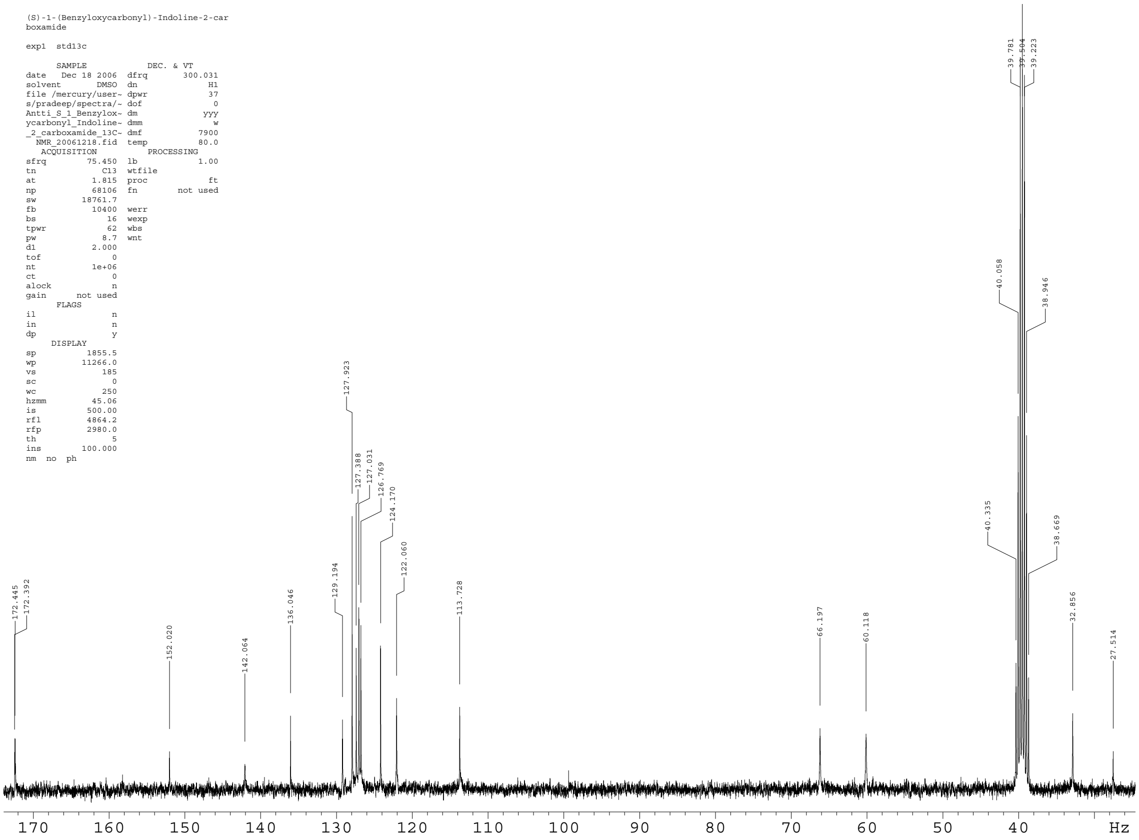
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-car
boxamide temp=25

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 13 2006  dfrq       499.942
solvent       DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_Indoline_2_carbo~ dres           1.0
xamide_temp=25_1HN~ homo             n
   MR_20061213.fid  temp          60.0
   ACQUISITION             DEC2
sfrq       499.942  dfrq2            0
tn              H1  dn2
at           3.000  dpwr2            1
np           48000  dof2             0
sw          8000.0  dm2              n
fb            4000  dmm2             c
bs              16  dmf2           200
tpwr            62  dseq2
pw             4.0  dres2          1.0
d1               0  homo2            n
tof              0      PROCESSING
nt               1  lb            0.20
ct               1  wtfile
alock            y  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp           984.4
wp          3215.6
vs              90
sc               0
wc             250
hzmm         12.86
is          147.93
rfl         1503.7
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

Figure 5: ^{1}H NMR of (4) at 80 °C.



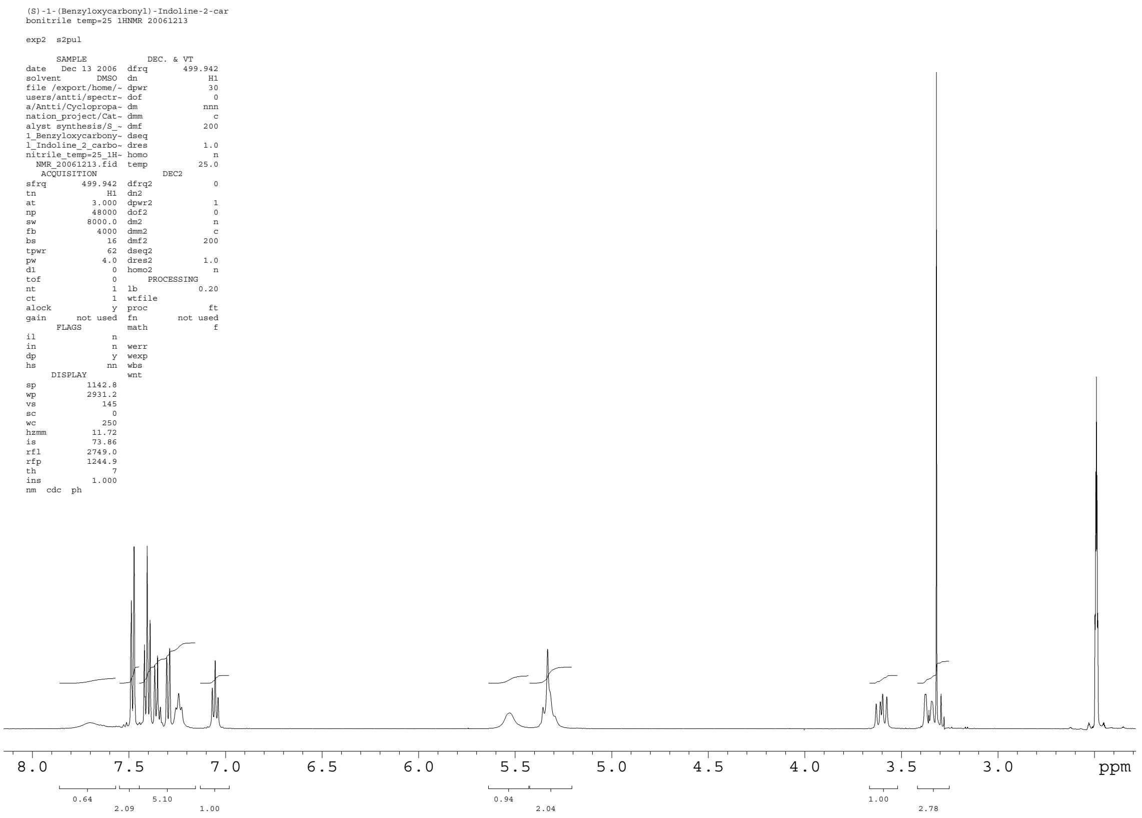
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-car
boxamide temp=80

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 13 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_Indoline_2_carbo~ dres           1.0
xamide_temp=80_1HN~ homo             n
   MR_20061213.fid  temp          80.0
   ACQUISITION              DEC2
sfrq       499.940  dfrq2            0
tn              H1  dn2
at           3.000  dpwr2            1
np           48000  dof2             0
sw          8000.0  dm2              n
fb            4000  dmm2             c
bs              16  dmf2           200
tpwr            62  dseq2
pw             4.0  dres2          1.0
d1               0  homo2            n
tof              0      PROCESSING
nt               1  lb            0.20
ct               1  wtfile
alock            y  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp          1048.3
wp          2997.3
vs             160
sc               0
wc             250
hzmm         11.99
is          127.22
rfl         5132.8
rfp         1244.9
th               7
ins          1.000
nm  cdc  ph
```

Figure 6: ^{13}C NMR of (4) at 80 °C.



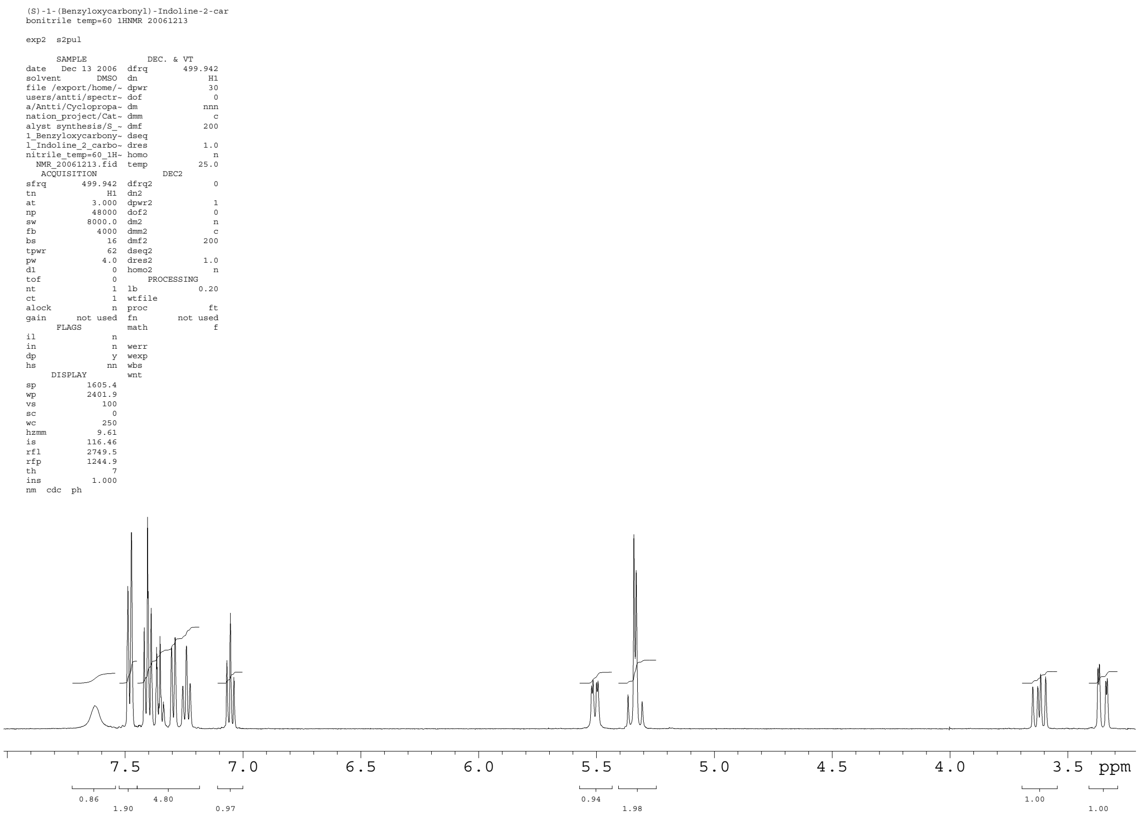
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-car
boxamide

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec 18 2006  dfrq       300.031
solvent       DMSO  dn              H1
file /mercury/user~ dpwr            37
s/pradeep/spectra/~ dof              0
Antti_S_1_Benzylox~ dm             yyy
ycarbonyl_Indoline~ dmm              w
_2_carboxamide_13C~ dmf           7900
  NMR_20061218.fid  temp          80.0
   ACQUISITION         PROCESSING
sfrq        75.450  lb            1.00
tn             C13  wtfile
at           1.815  proc            ft
np           68106  fn        not used
sw         18761.7
fb           10400  werr
bs              16  wexp
tpwr            62  wbs
pw             8.7  wnt
d1           2.000
tof              0
nt          1e+06
ct               0
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          1855.5
wp         11266.0
vs             185
sc               0
wc             250
hzmm         45.06
is          500.00
rfl         4864.2
rfp         2980.0
th               5
ins        100.000
nm  no  ph
```

Figure 7: ^{1}H NMR of (5) at 25 °C.



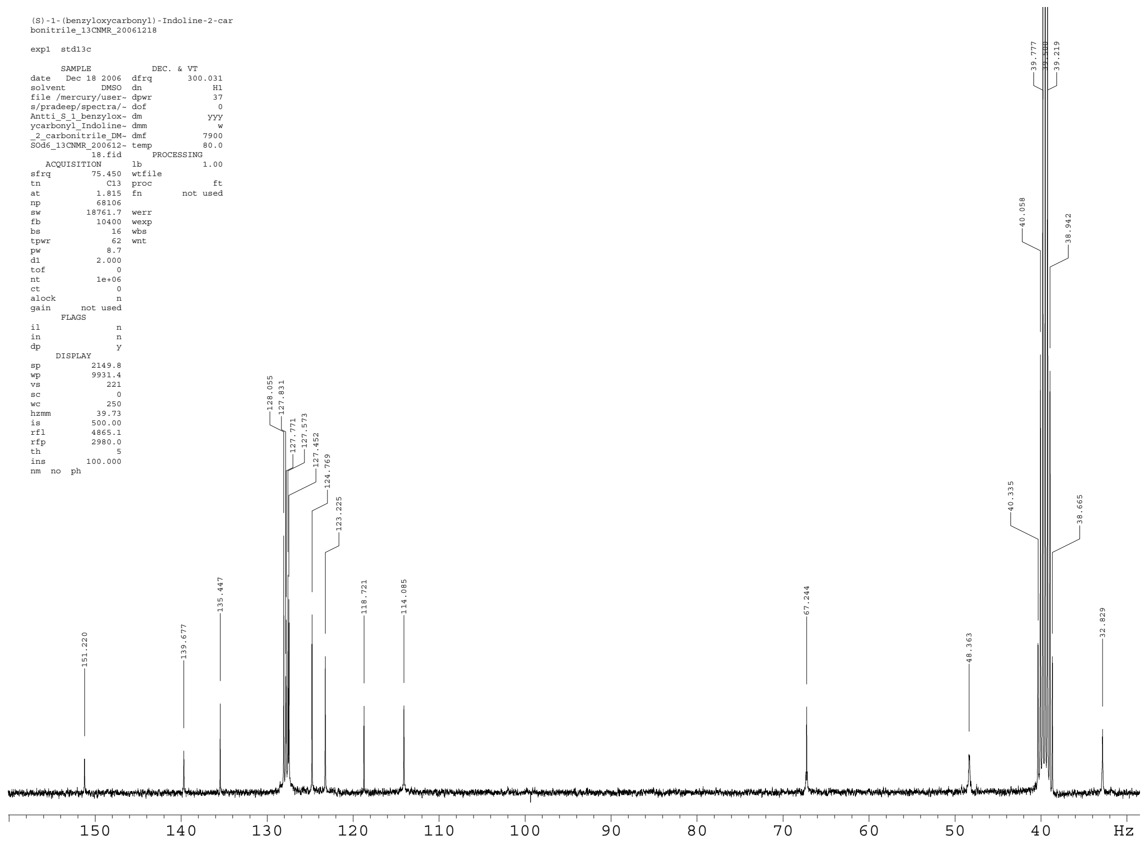
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-car
bonitrile temp=25 1HNMR 20061213

exp2  s2pul

      SAMPLE              DEC. & VT
date   Dec 13 2006  dfrq       499.942
solvent       DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_Indoline_2_carbo~ dres           1.0
nitrile_temp=25_1H~ homo             n
  NMR_20061213.fid  temp          25.0
   ACQUISITION               DEC2
sfrq       499.942  dfrq2            0
tn              H1  dn2
at           3.000  dpwr2            1
np           48000  dof2             0
sw          8000.0  dm2              n
fb            4000  dmm2             c
bs              16  dmf2           200
tpwr            62  dseq2
pw             4.0  dres2          1.0
d1               0  homo2            n
tof              0      PROCESSING
nt               1  lb            0.20
ct               1  wtfile
alock            y  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp          1142.8
wp          2931.2
vs             145
sc               0
wc             250
hzmm         11.72
is           73.86
rfl         2749.0
rfp         1244.9
th               7
ins          1.000
nm  cdc  ph
```

Figure 8: ^{1}H NMR of (5) at 60 °C.



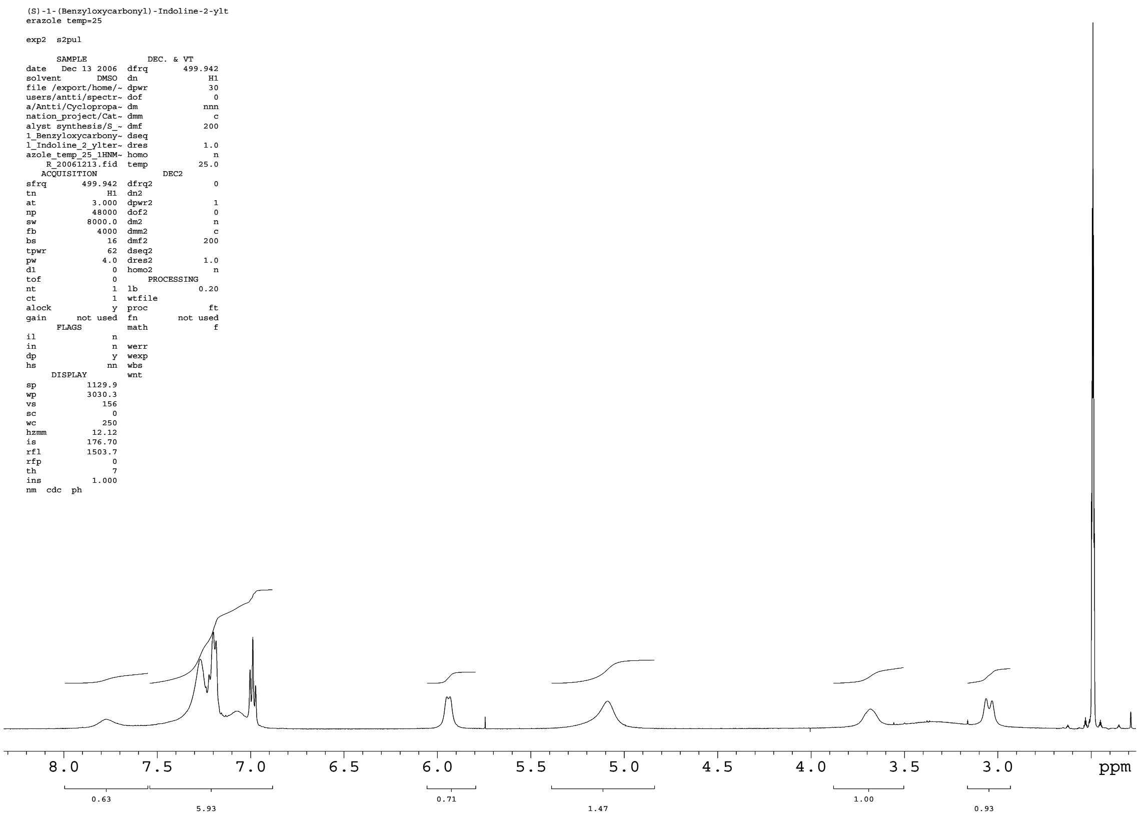
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-car
bonitrile temp=60 1HNMR 20061213

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 13 2006  dfrq       499.942
solvent       DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_Indoline_2_carbo~ dres           1.0
nitrile_temp=60_1H~ homo             n
  NMR_20061213.fid  temp          25.0
   ACQUISITION              DEC2
sfrq       499.942  dfrq2            0
tn              H1  dn2
at           3.000  dpwr2            1
np           48000  dof2             0
sw          8000.0  dm2              n
fb            4000  dmm2             c
bs              16  dmf2           200
tpwr            62  dseq2
pw             4.0  dres2          1.0
d1               0  homo2            n
tof              0      PROCESSING
nt               1  lb            0.20
ct               1  wtfile
alock            n  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp          1605.4
wp          2401.9
vs             100
sc               0
wc             250
hzmm          9.61
is          116.46
rfl         2749.5
rfp         1244.9
th               7
ins          1.000
nm  cdc  ph
```

Figure 9: ^{13}C NMR of (5) at 60 °C.



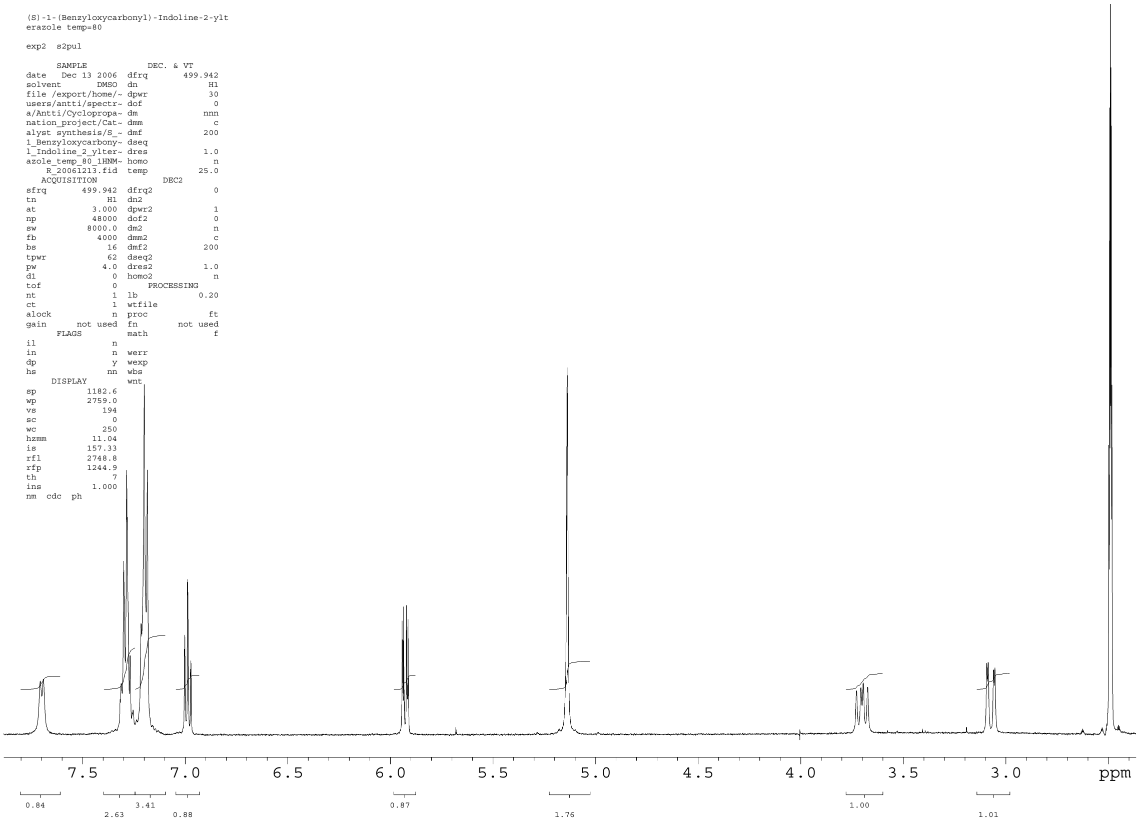
```
(S)-1-(benzyloxycarbonyl)-Indoline-2-car
bonitrile_13CNMR_20061218

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec 18 2006  dfrq       300.031
solvent       DMSO  dn              H1
file /mercury/user~ dpwr            37
s/pradeep/spectra/~ dof              0
Antti_S_1_benzylox~ dm             yyy
ycarbonyl_Indoline~ dmm              w
_2_carbonitrile_DM~ dmf           7900
SOd6_13CNMR_200612~ temp          80.0
            18.fid      PROCESSING
   ACQUISITION      lb            1.00
sfrq        75.450  wtfile
tn             C13  proc            ft
at           1.815  fn        not used
np           68106
sw         18761.7  werr
fb           10400  wexp
bs              16  wbs
tpwr            62  wnt
pw             8.7
d1           2.000
tof              0
nt           1e+06
ct               0
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          2149.8
wp          9931.4
vs             221
sc               0
wc             250
hzmm         39.73
is          500.00
rfl         4865.1
rfp         2980.0
th               5
ins        100.000
nm  no  ph
```

Figure 10: ^{1}H NMR of (6) at 25 °C.



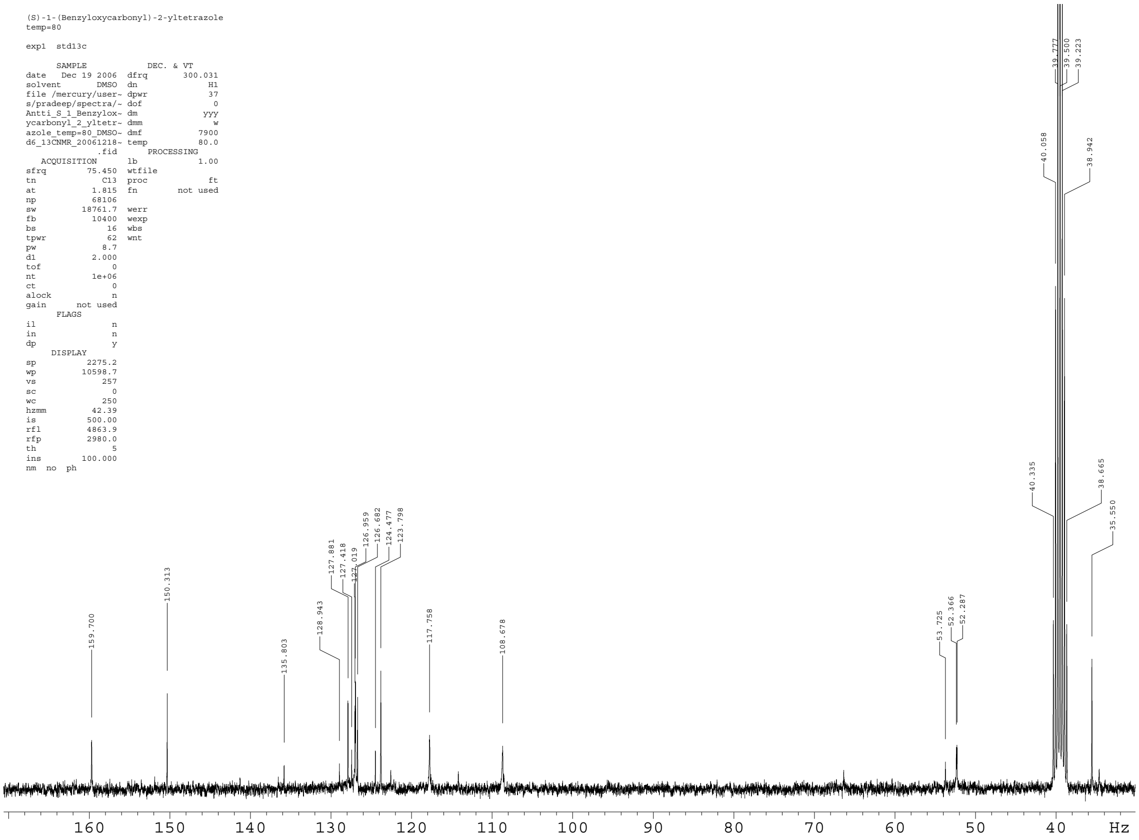
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-ylt
erazole temp=25

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 13 2006  dfrq       499.942
solvent        DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Cat~ dmm              c
alyst synthesis/S_~ dmf            200
1_Benzyloxycarbony~ dseq
l_Indoline_2_ylter~ dres           1.0
azole_temp_25_1HNM~ homo             n
    R_20061213.fid  temp          25.0
   ACQUISITION             DEC2
sfrq        499.942  dfrq2            0
tn               H1  dn2
at            3.000  dpwr2            1
np            48000  dof2             0
sw           8000.0  dm2              n
fb             4000  dmm2             c
bs               16  dmf2           200
tpwr             62  dseq2
pw              4.0  dres2          1.0
d1                0  homo2            n
tof               0      PROCESSING
nt                1  lb            0.20
ct                1  wtfile
alock             y  proc            ft
gain       not used  fn        not used
      FLAGS          math             f
il                n
in                n  werr
dp                y  wexp
hs               nn  wbs
     DISPLAY         wnt
sp           1129.9
wp           3030.3
vs              156
sc                0
wc              250
hzmm          12.12
is           176.70
rfl          1503.7
rfp               0
th                7
ins           1.000
nm  cdc  ph
```

Figure 11: ^{1}H NMR of (6) at 80 °C.



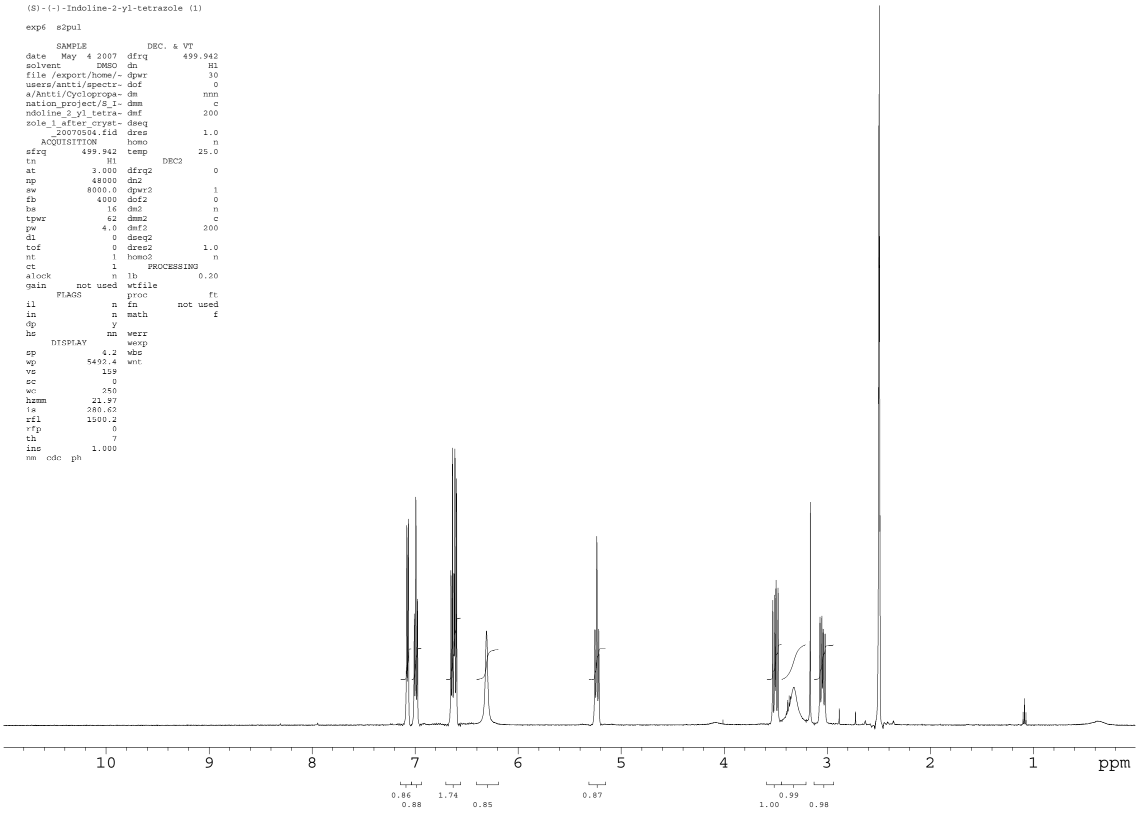
```
(S)-1-(Benzyloxycarbonyl)-Indoline-2-ylt
erazole temp=80

exp2  s2pul

      SAMPLE            DEC. & VT
date   Dec 13 2006  dfrq        499.942
solvent       DMSO  dn               H1
file /export/home/~ dpwr             30
users/antti/spectr~ dof               0
a/Antti/Cyclopropa~ dm              nnn
nation_project/Cat~ dmm               c
alyst synthesis/S_~ dmf             200
1_Benzyloxycarbony~ dseq
l_Indoline_2_ylter~ dres            1.0
azole_temp_80_1HNM~ homo              n
    R_20061213.fid  temp           25.0
   ACQUISITION               DEC2
sfrq       499.942  dfrq2             0
tn              H1  dn2
at           3.000  dpwr2             1
np           48000  dof2              0
sw          8000.0  dm2               n
fb            4000  dmm2              c
bs              16  dmf2            200
tpwr            62  dseq2
pw             4.0  dres2           1.0
d1               0  homo2             n
tof              0      PROCESSING
nt               1  lb             0.20
ct               1  wtfile
alock            n  proc             ft
gain      not used  fn         not used
      FLAGS         math              f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp          1182.6
wp          2759.0
vs             194
sc               0
wc             250
hzmm         11.04
is          157.33
rfl         2748.8
rfp         1244.9
th               7
ins          1.000
nm  cdc  ph
```

Figure 12: ^{13}C NMR of (6) at 80 °C.



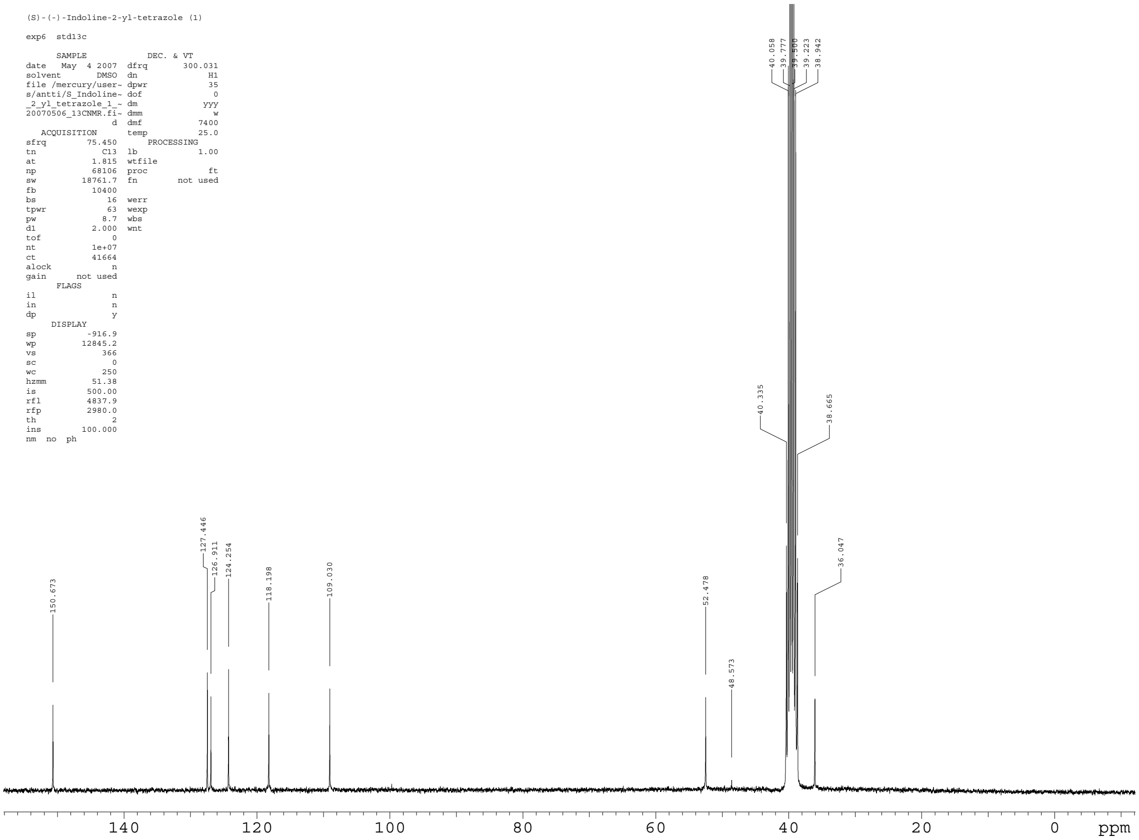
```
(S)-1-(Benzyloxycarbonyl)-2-yltetrazole
temp=80

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec 19 2006  dfrq       300.031
solvent       DMSO  dn              H1
file /mercury/user~ dpwr            37
s/pradeep/spectra/~ dof              0
Antti_S_1_Benzylox~ dm             yyy
ycarbonyl_2_yltetr~ dmm              w
azole_temp=80_DMSO~ dmf           7900
d6_13CNMR_20061218~ temp          80.0
              .fid      PROCESSING
   ACQUISITION      lb            1.00
sfrq        75.450  wtfile
tn             C13  proc            ft
at           1.815  fn        not used
np           68106
sw         18761.7  werr
fb           10400  wexp
bs              16  wbs
tpwr            62  wnt
pw             8.7
d1           2.000
tof              0
nt           1e+06
ct               0
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          2275.2
wp         10598.7
vs             257
sc               0
wc             250
hzmm         42.39
is          500.00
rfl         4863.9
rfp         2980.0
th               5
ins        100.000
nm  no  ph
```

Figure 13: ^{1}H NMR of (1) at 25 °C.



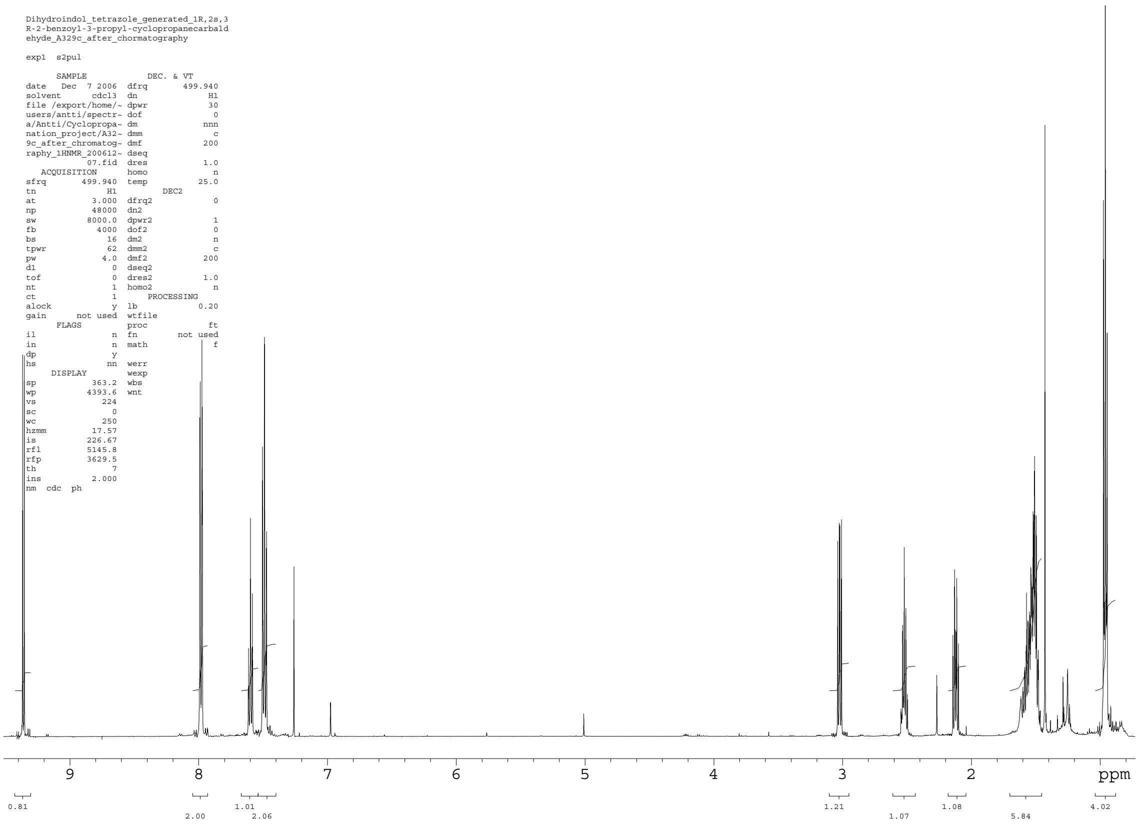
```
(S)-(-)-Indoline-2-yl-tetrazole (1)

exp6  s2pul

      SAMPLE             DEC. & VT
date   May  4 2007  dfrq       499.942
solvent       DMSO  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/S_I~ dmm              c
ndoline_2_yl_tetra~ dmf            200
zole_1_after_cryst~ dseq
     _20070504.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       499.942  temp          25.0
tn              H1         DEC2
at           3.000  dfrq2            0
np           48000  dn2
sw          8000.0  dpwr2            1
fb            4000  dof2             0
bs              16  dm2              n
tpwr            62  dmm2             c
pw             4.0  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt               1  homo2            n
ct               1      PROCESSING
alock            n  lb            0.20
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               y
hs              nn  werr
     DISPLAY        wexp
sp             4.2  wbs
wp          5492.4  wnt
vs             159
sc               0
wc             250
hzmm         21.97
is          280.62
rfl         1500.2
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

Figure 14: ^{13}C NMR of (1) at 25 °C.



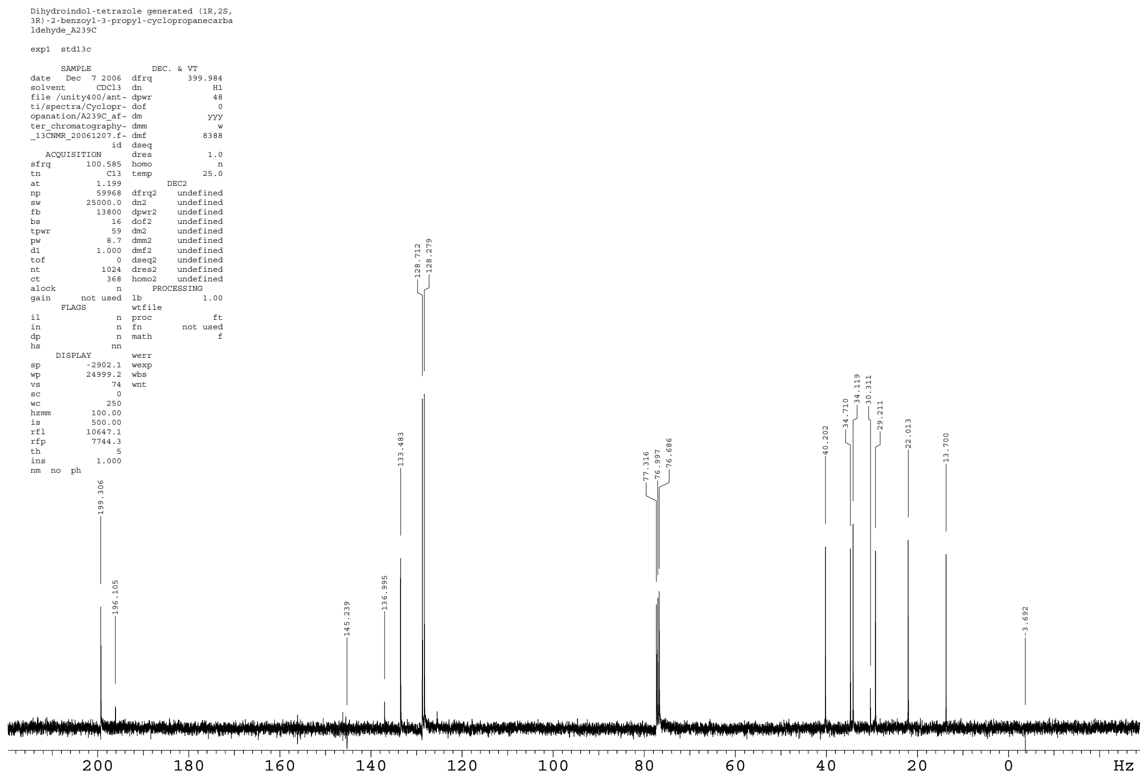
```
(S)-(-)-Indoline-2-yl-tetrazole (1)

exp6  std13c

      SAMPLE            DEC. & VT
date   May  4 2007  dfrq       300.031
solvent       DMSO  dn              H1
file /mercury/user~ dpwr            35
s/antti/S_Indoline~ dof              0
_2_yl_tetrazole_1_~ dm             yyy
20070506_13CNMR.fi~ dmm              w
                  d dmf           7400
   ACQUISITION      temp          25.0
sfrq        75.450       PROCESSING
tn             C13  lb            1.00
at           1.815  wtfile
np           68106  proc            ft
sw         18761.7  fn        not used
fb           10400
bs              16  werr
tpwr            63  wexp
pw             8.7  wbs
d1           2.000  wnt
tof              0
nt           1e+07
ct           41664
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
     DISPLAY
sp          -916.9
wp         12845.2
vs             366
sc               0
wc             250
hzmm         51.38
is          500.00
rfl         4837.9
rfp         2980.0
th               2
ins        100.000
nm  no  ph
```

Figure 15: ^{1}H NMR of 8a (Table 2, entry 1) at 25 °C.



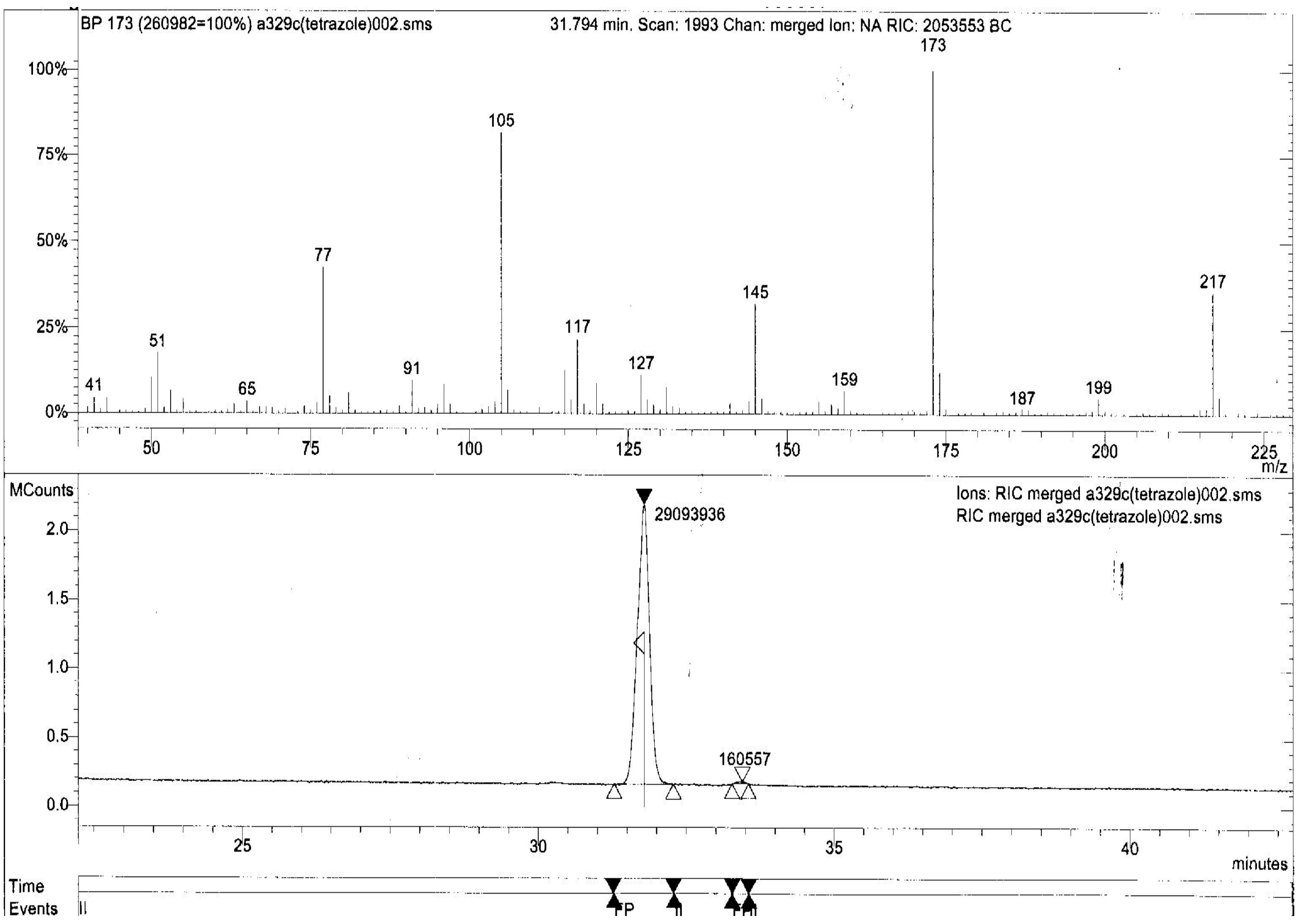
```
Dihydroindol_tetrazole_generated_1R,2s,3
R-2-benzoyl-3-propyl-cyclopropanecarbald
ehyde_A329c_after_chormatography

exp1  s2pul

      SAMPLE              DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A32~ dmm              c
9c_after_chromatog~ dmf            200
raphy_1HNMR_200612~ dseq
            07.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       499.940  temp          25.0
tn              H1         DEC2
at           3.000  dfrq2            0
np           48000  dn2
sw          8000.0  dpwr2            1
fb            4000  dof2             0
bs              16  dm2              n
tpwr            62  dmm2             c
pw             4.0  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt               1  homo2            n
ct               1      PROCESSING
alock            y  lb            0.20
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               y
hs              nn  werr
     DISPLAY        wexp
sp           363.2  wbs
wp          4393.6  wnt
vs             224
sc               0
wc             250
hzmm         17.57
is          226.67
rfl         5145.8
rfp         3629.5
th               7
ins          2.000
nm  cdc  ph
```

Figure 16: ^{13}C NMR of 8a (Table 2, entry 1) at 25 °C.



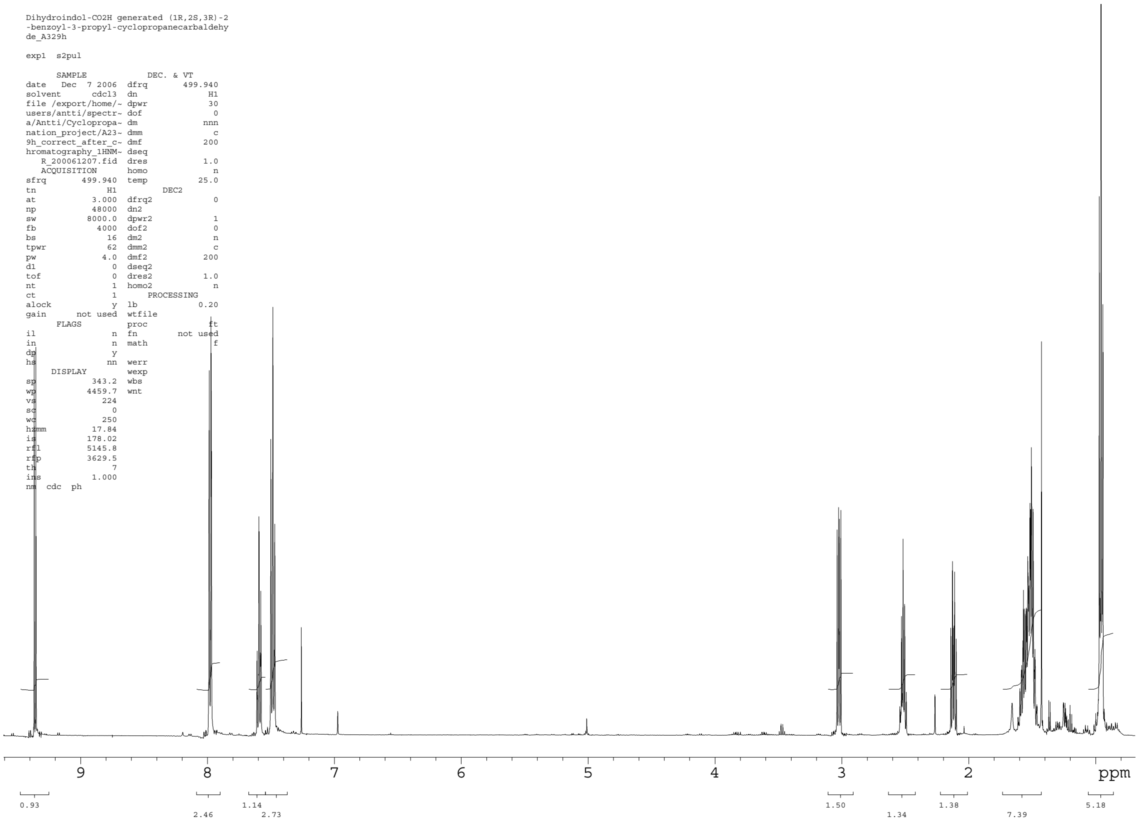
```
Dihydroindol-tetrazole generated (1R,2S,
3R)-2-benzoyl-3-propyl-cyclopropanecarba
ldehyde_A239C

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A239C_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_20061207.f~ dmf           8388
                id  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199         DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             368  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp         -2902.1  wexp
wp         24999.2  wbs
vs              74  wnt
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10647.1
rfp         7744.3
th               5
ins          1.000
nm  no  ph
```

Figure 17: GLC-MS determination of ee (major diastereomer) 8a (Table 2, entry 1).



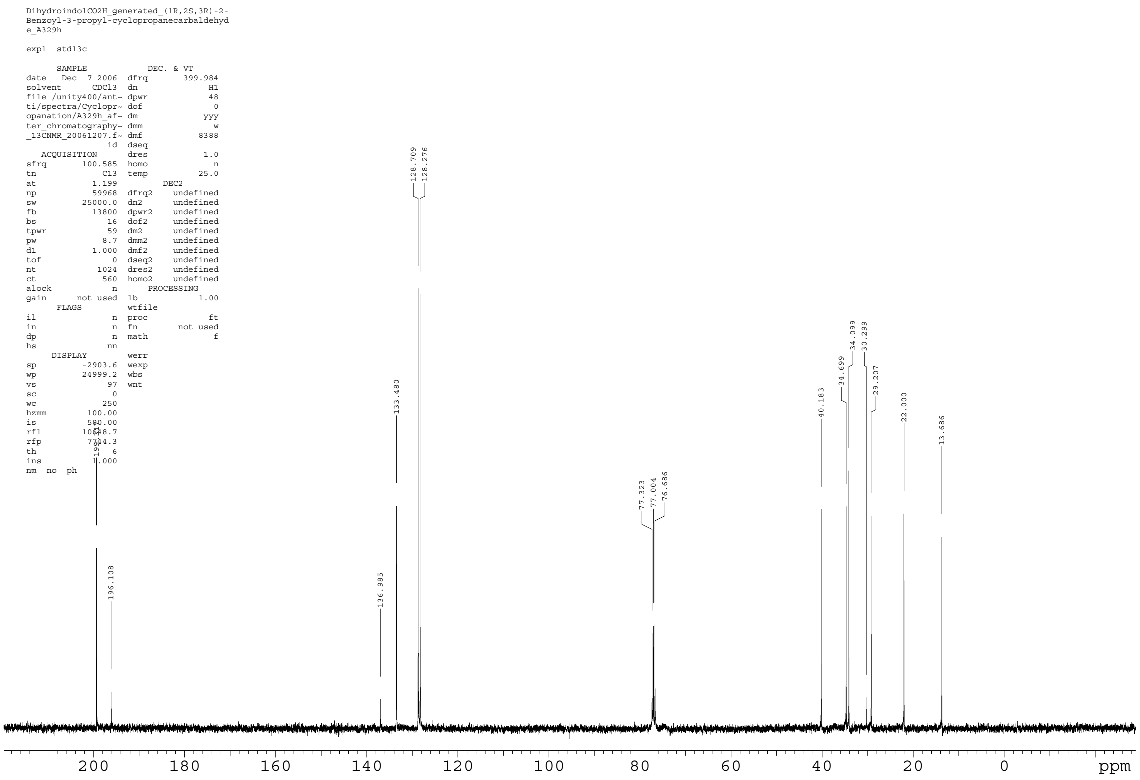
Major enantiomer	Minor enantiomer	ee %
29093936	160557	99

Figure 18: ^{1}H NMR of 8b (Table 3, entry 1) at 25 °C.



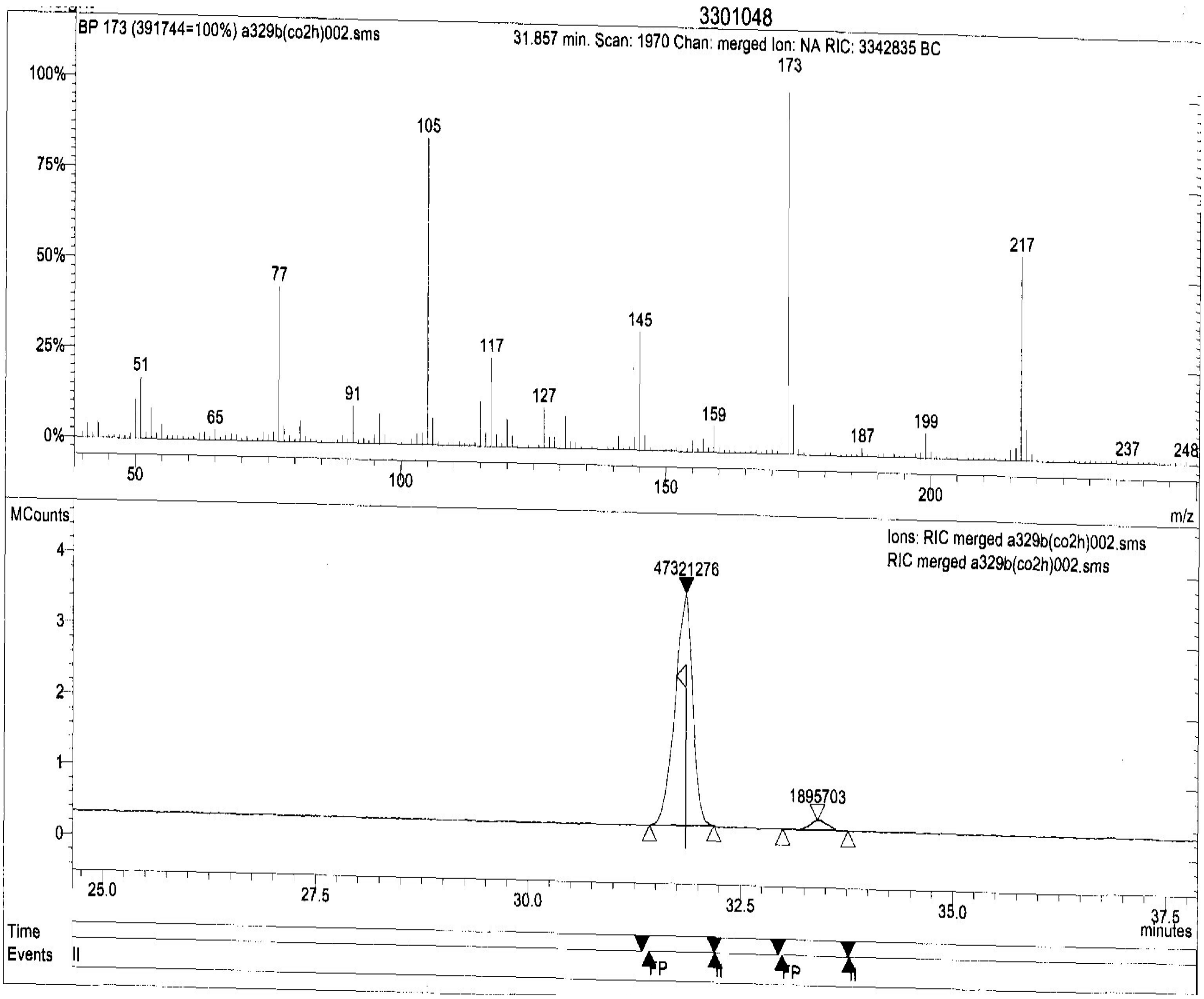
```
Dihydroindol-CO2H generated (1R,2S,3R)-2
-benzoyl-3-propyl-cyclopropanecarbaldehy
de_A329h

exp1  s2pul

      SAMPLE             DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A23~ dmm              c
9h_correct_after_c~ dmf            200
hromatography_1HNM~ dseq
   R_200061207.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       499.940  temp          25.0
tn              H1         DEC2
at           3.000  dfrq2            0
np           48000  dn2
sw          8000.0  dpwr2            1
fb            4000  dof2             0
bs              16  dm2              n
tpwr            62  dmm2             c
pw             4.0  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt               1  homo2            n
ct               1      PROCESSING
alock            y  lb            0.20
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               y
hs              nn  werr
     DISPLAY        wexp
sp           343.2  wbs
wp          4459.7  wnt
vs             224
sc               0
wc             250
hzmm         17.84
is          178.02
rfl         5145.8
rfp         3629.5
th               7
ins          1.000
nm  cdc  ph
```

Figure 19: ^{13}C NMR of 8b (Table 3, entry 1) at 25 °C.



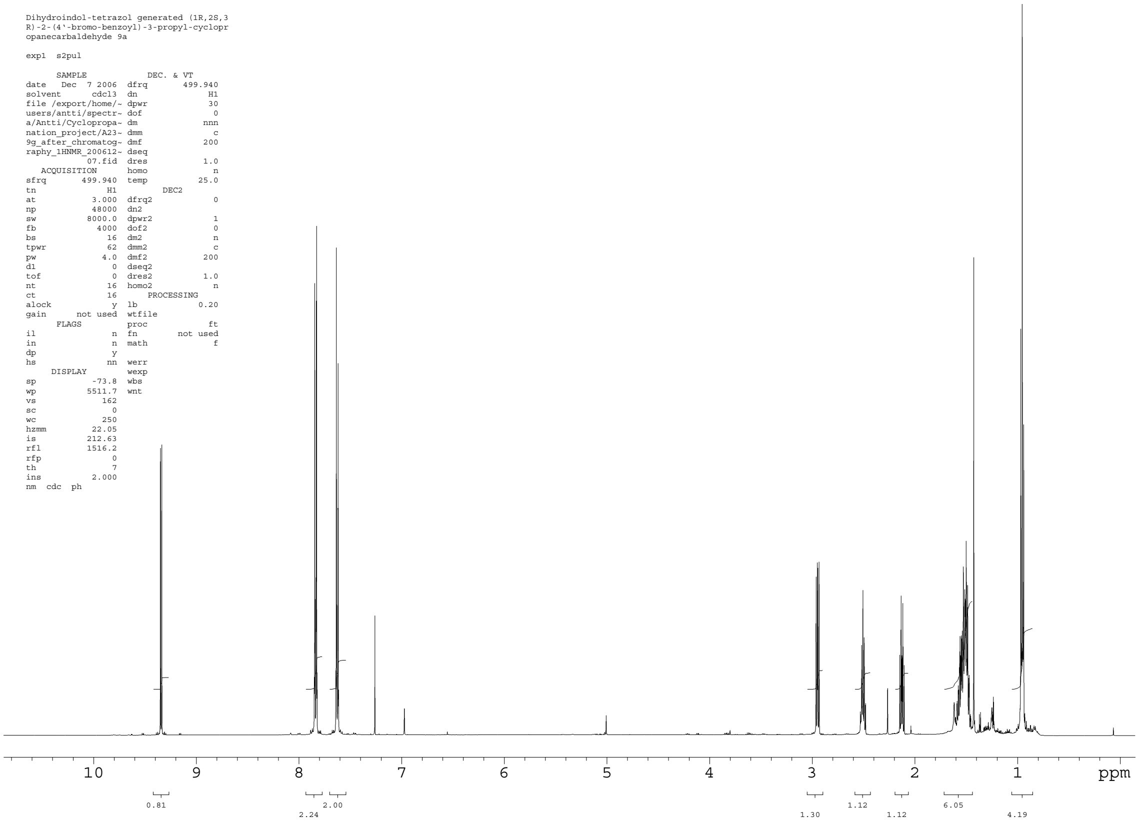
```
DihydroindolCO2H_generated_(1R,2S,3R)-2-
Benzoyl-3-propyl-cyclopropanecarbaldehyd
e_A329h

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A329h_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_20061207.f~ dmf           8388
                id  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199        DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             560  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp         -2903.6  wexp
wp         24999.2  wbs
vs              97  wnt
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10648.7
rfp         7744.3
th               6
ins          1.000
nm  no  ph
```

Figure 20: GLC-MS determination of ee (major diastereomer) 8b (Table 3, entry 1).



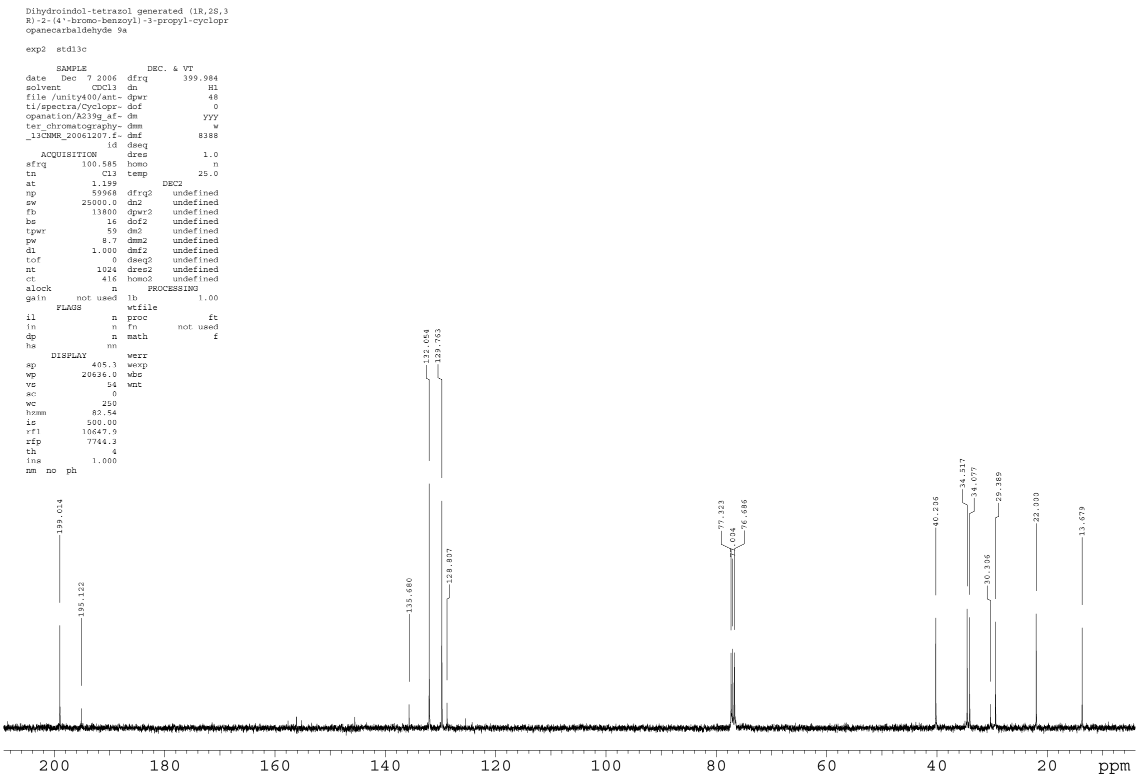
Major enantiomer	Minor enantiomer	ee %
47321276	1895703	92

Figure 21: ^{1}H NMR of 9a (Table 2, entry 2) at 25 °C.



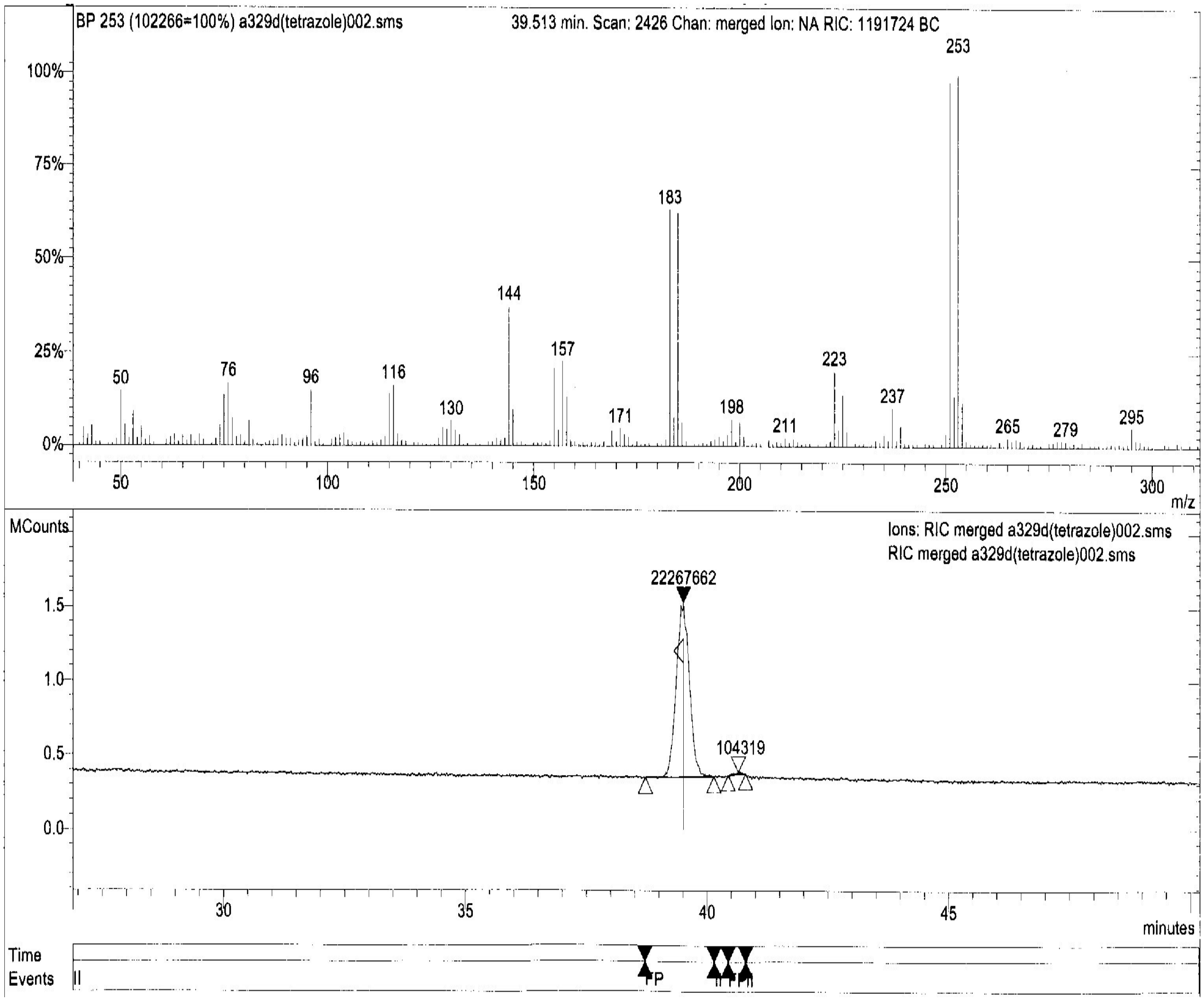
```
Dihydroindol-tetrazol generated (1R,2S,3
R)-2-(4'-bromo-benzoyl)-3-propyl-cyclopr
opanecarbaldehyde 9a

exp1  s2pul

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A23~ dmm              c
9g_after_chromatog~ dmf            200
raphy_1HNMR_200612~ dseq
            07.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       499.940  temp          25.0
tn              H1         DEC2
at           3.000  dfrq2            0
np           48000  dn2
sw          8000.0  dpwr2            1
fb            4000  dof2             0
bs              16  dm2              n
tpwr            62  dmm2             c
pw             4.0  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt              16  homo2            n
ct              16      PROCESSING
alock            y  lb            0.20
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               y
hs              nn  werr
     DISPLAY        wexp
sp           -73.8  wbs
wp          5511.7  wnt
vs             162
sc               0
wc             250
hzmm         22.05
is          212.63
rfl         1516.2
rfp              0
th               7
ins          2.000
nm  cdc  ph
```

Figure 22: ^{13}C NMR of 9a (Table 2, entry 2) at 25 °C.



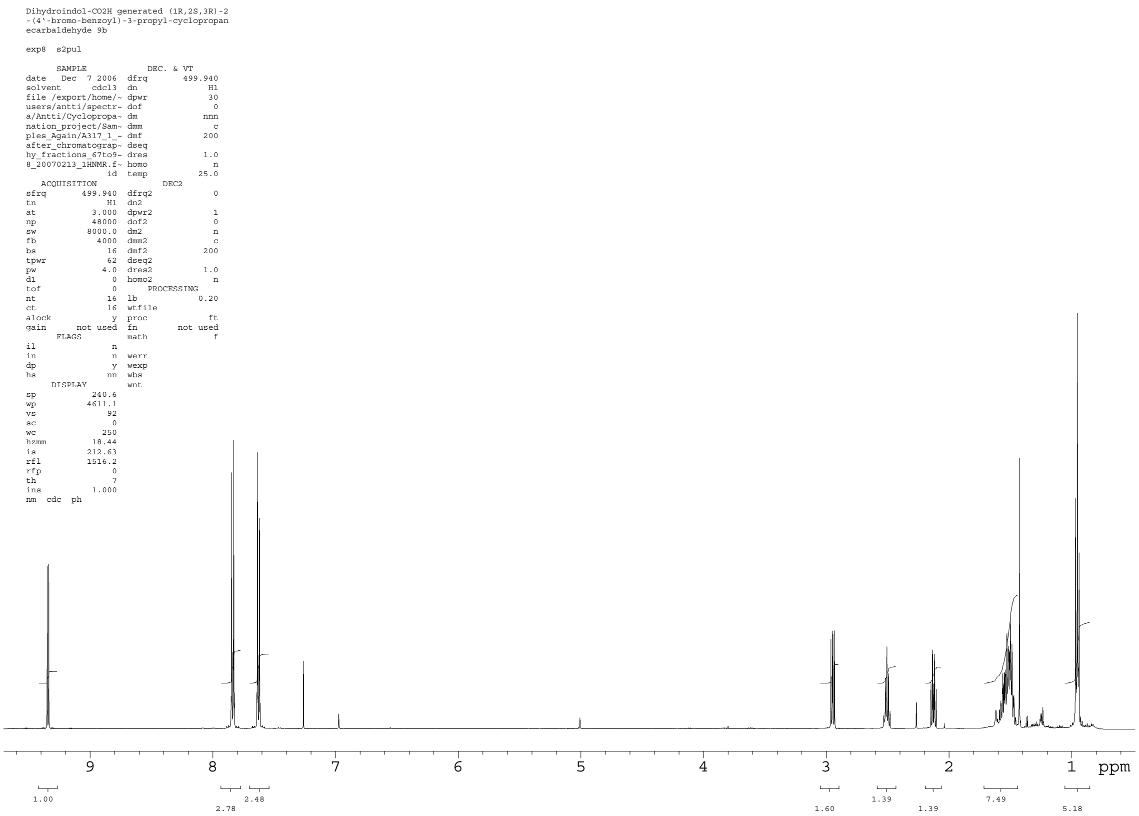
```
Dihydroindol-tetrazol generated (1R,2S,3
R)-2-(4'-bromo-benzoyl)-3-propyl-cyclopr
opanecarbaldehyde 9a

exp2  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A239g_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_20061207.f~ dmf           8388
                id  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199         DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             416  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp           405.3  wexp
wp         20636.0  wbs
vs              54  wnt
sc               0
wc             250
hzmm         82.54
is          500.00
rfl        10647.9
rfp         7744.3
th               4
ins          1.000
nm  no  ph
```

Figure 23: GLC-MS determination of ee (major diastereomer) 9a (Table 2, entry 2).



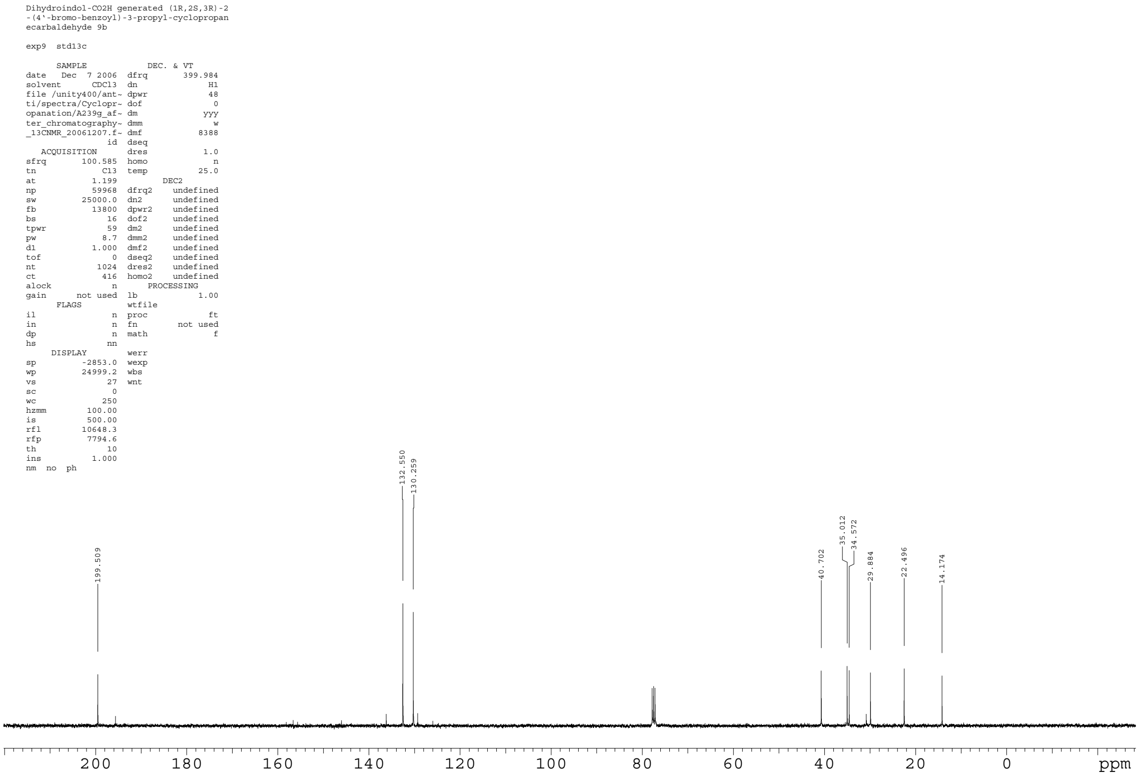
Major enantiomer	Minor enantiomer	ee %
22267662	104319	99

Figure 24: ^{1}H NMR of 9b (Table 3, entry 2) at 25 °C.



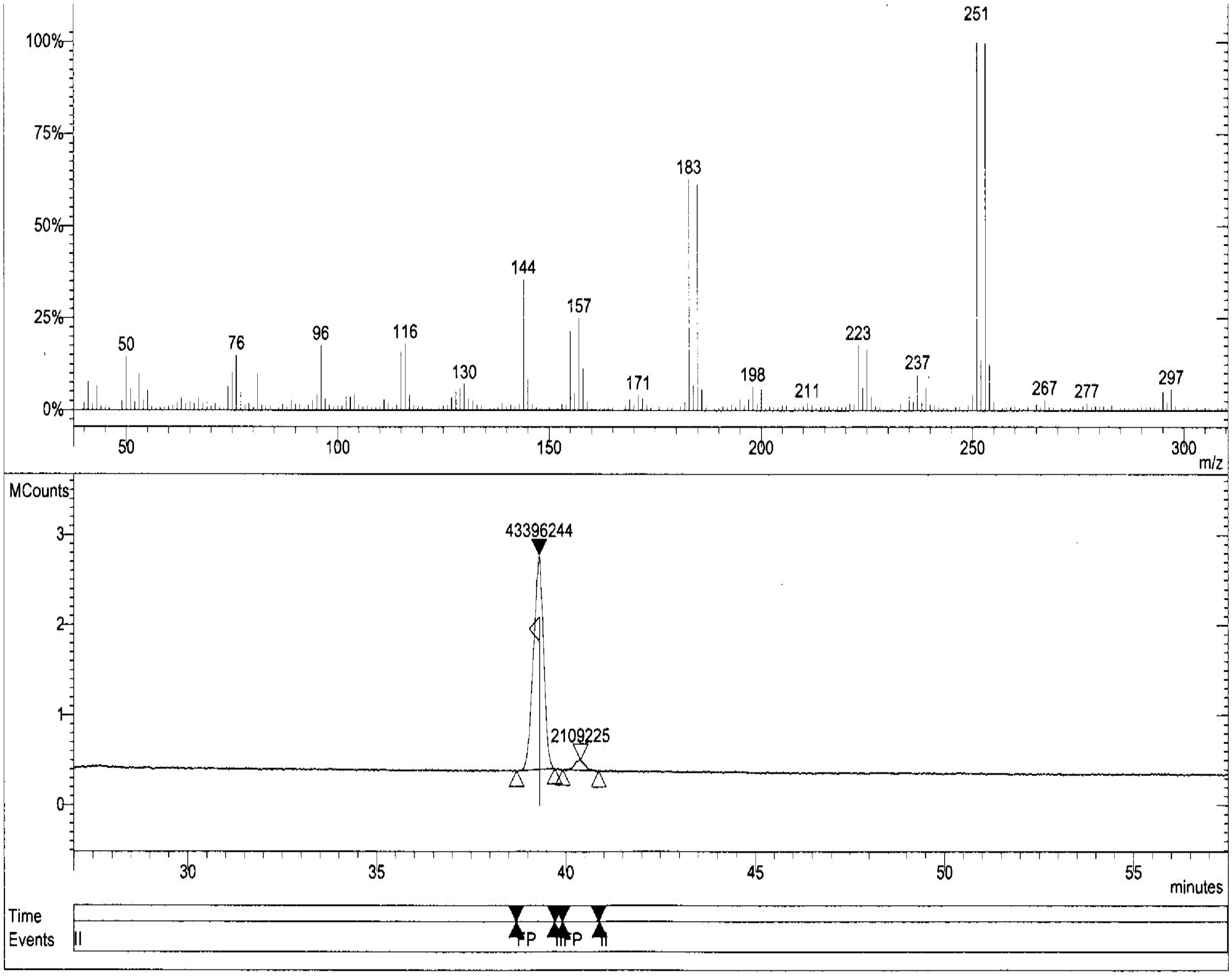
```
Dihydroindol-CO2H generated (1R,2S,3R)-2
-(4'-bromo-benzoyl)-3-propyl-cyclopropan
ecarbaldehyde 9b

exp8  s2pul

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/Sam~ dmm              c
ples_Again/A317_1_~ dmf            200
after_chromatograp~ dseq
hy_fractions_67to9~ dres           1.0
8_20070213_1HNMR.f~ homo             n
                id  temp          25.0
   ACQUISITION            DEC2
sfrq       499.940  dfrq2            0
tn              H1  dn2
at           3.000  dpwr2            1
np           48000  dof2             0
sw          8000.0  dm2              n
fb            4000  dmm2             c
bs              16  dmf2           200
tpwr            62  dseq2
pw             4.0  dres2          1.0
d1               0  homo2            n
tof              0      PROCESSING
nt              16  lb            0.20
ct              16  wtfile
alock            y  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp           240.6
wp          4611.1
vs              92
sc               0
wc             250
hzmm         18.44
is          212.63
rfl         1516.2
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

Figure 25: 13C NMR of 9b (Table 3, entry 2) at 25 °C.



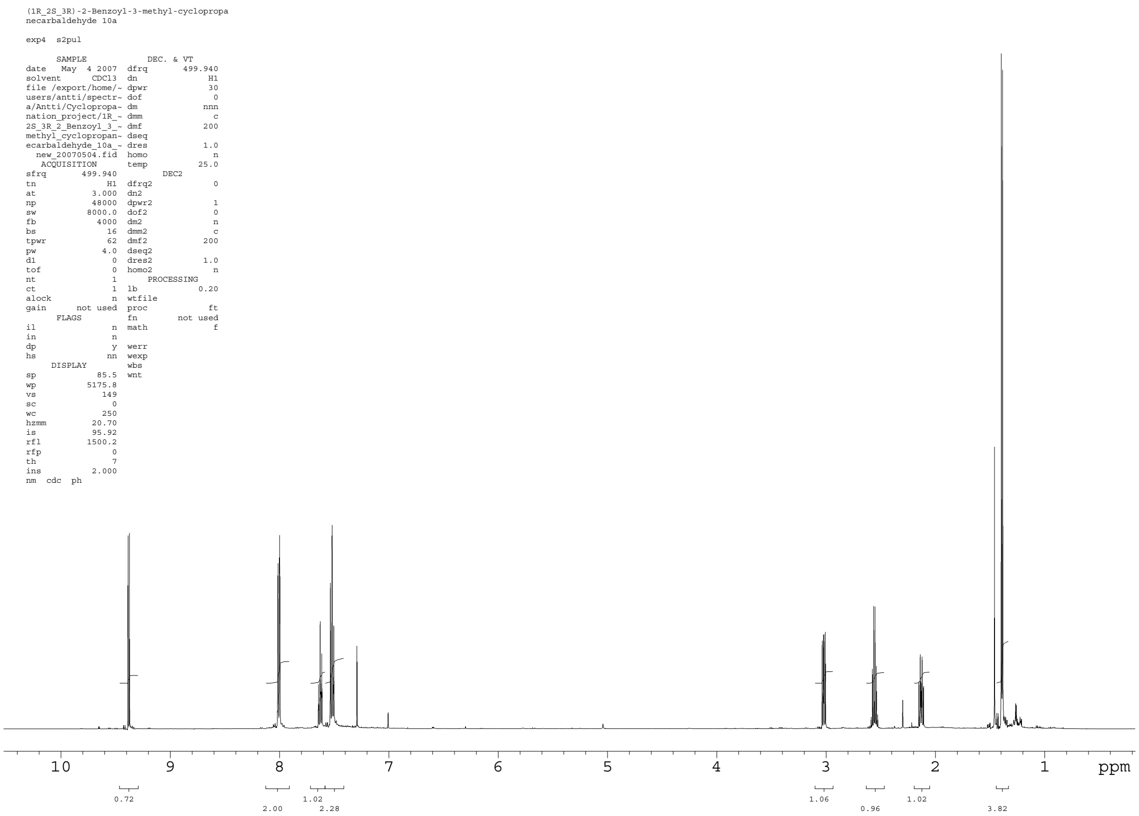
```
Dihydroindol-CO2H generated (1R,2S,3R)-2
-(4'-bromo-benzoyl)-3-propyl-cyclopropan
ecarbaldehyde 9b

exp9  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A239g_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_20061207.f~ dmf           8388
                id  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199         DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             416  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp         -2853.0  wexp
wp         24999.2  wbs
vs              27  wnt
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10648.3
rfp         7794.6
th              10
ins          1.000
nm  no  ph
```

Figure 26: GLC-MS determination of ee (major diastereomer) 9b (Table 3, entry 2).



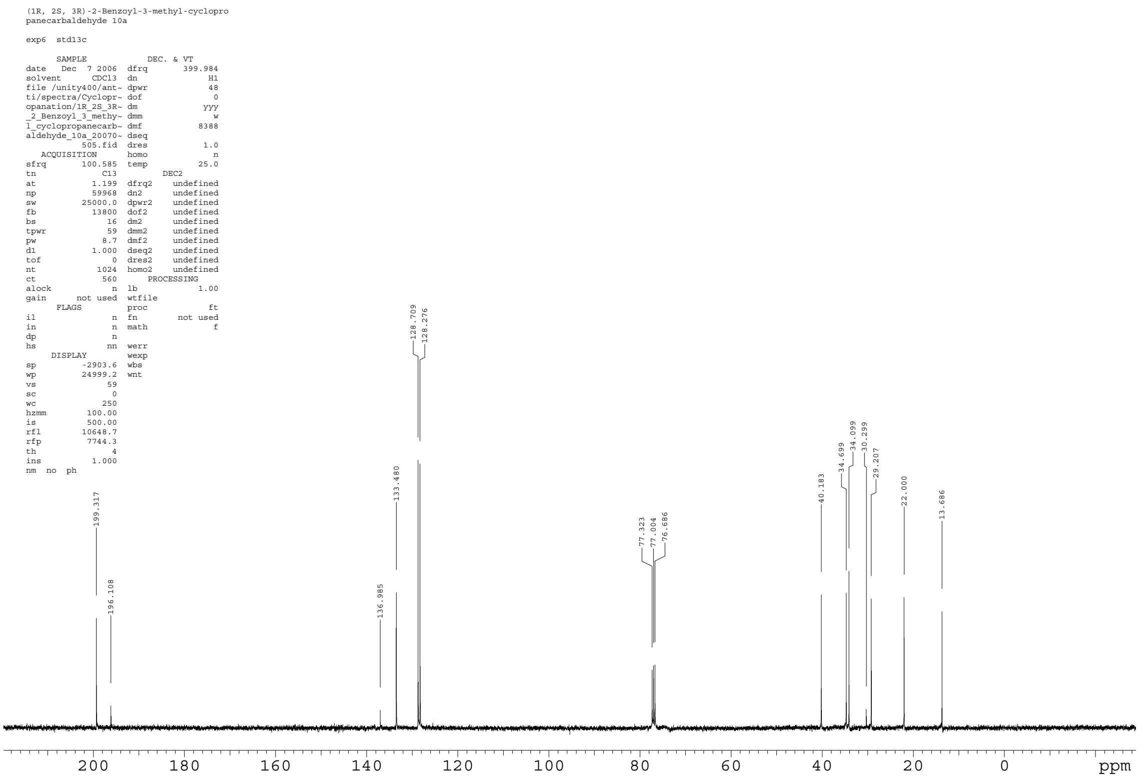
Major enantiomer	Minor enantiomer	ee %
43396244	2109225	91

Figure 27: ^{1}H NMR of 10a (Table 2, entry 3) at 25 °C.



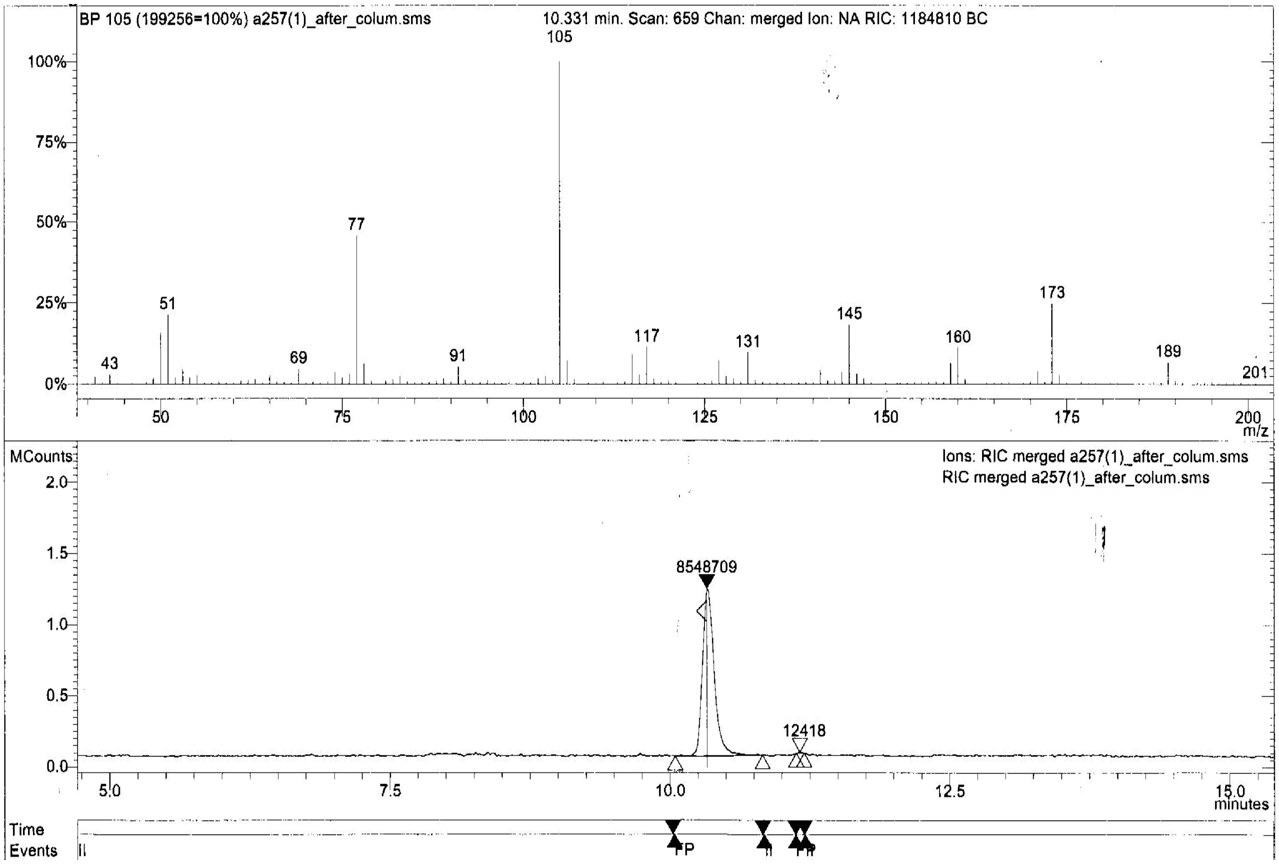
```
(1R_2S_3R)-2-Benzoyl-3-methyl-cyclopropa
necarbaldehyde 10a

exp4  s2pul

      SAMPLE            DEC. & VT
date   May  4 2007  dfrq       499.940
solvent      CDCl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/1R_~ dmm              c
2S_3R_2_Benzoyl_3_~ dmf            200
methyl_cyclopropan~ dseq
ecarbaldehyde_10a_~ dres           1.0
  new_20070504.fid  homo             n
   ACQUISITION      temp          25.0
sfrq       499.940          DEC2
tn              H1  dfrq2            0
at           3.000  dn2
np           48000  dpwr2            1
sw          8000.0  dof2             0
fb            4000  dm2              n
bs              16  dmm2             c
tpwr            62  dmf2           200
pw             4.0  dseq2
d1               0  dres2          1.0
tof              0  homo2            n
nt               1      PROCESSING
ct               1  lb            0.20
alock            n  wtfile
gain      not used  proc            ft
      FLAGS         fn        not used
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp
     DISPLAY        wbs
sp            85.5  wnt
wp          5175.8
vs             149
sc               0
wc             250
hzmm         20.70
is           95.92
rfl         1500.2
rfp              0
th               7
ins          2.000
nm  cdc  ph
```

Figure 28: ^{13}C NMR of 10a (Table 2, entry 3) at 25 °C.



```
(1R, 2S, 3R)-2-Benzoyl-3-methyl-cyclopro
panecarbaldehyde 10a

exp6  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/1R_2S_3R~ dm             yyy
_2_Benzoyl_3_methy~ dmm              w
l_cyclopropanecarb~ dmf           8388
aldehyde_10a_20070~ dseq
           505.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       100.585  temp          25.0
tn             C13          DEC2
at           1.199  dfrq2    undefined
np           59968  dn2      undefined
sw         25000.0  dpwr2    undefined
fb           13800  dof2     undefined
bs              16  dm2      undefined
tpwr            59  dmm2     undefined
pw             8.7  dmf2     undefined
d1           1.000  dseq2    undefined
tof              0  dres2    undefined
nt            1024  homo2    undefined
ct             560      PROCESSING
alock            n  lb            1.00
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               n
hs              nn  werr
     DISPLAY        wexp
sp         -2903.6  wbs
wp         24999.2  wnt
vs              59
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10648.7
rfp         7744.3
th               4
ins          1.000
nm  no  ph
```

Figure 29: GLC-MS determination of ee (major diastereomer) 10a (Table 2, entry 3).



Major enantiomer	Minor enantiomer	ee %
8548709	12418	> 99

Figure 30: ^{1}H NMR of 10b (Table 3, entry 3) at 25 °C.

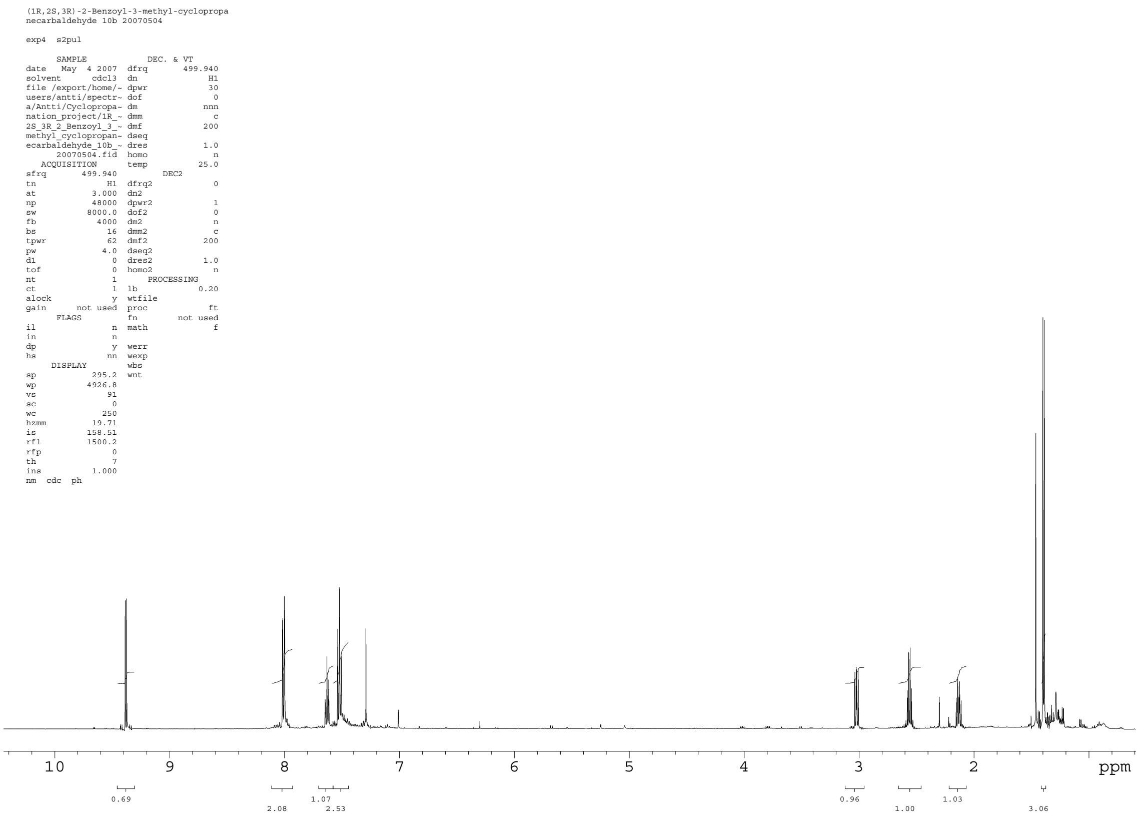
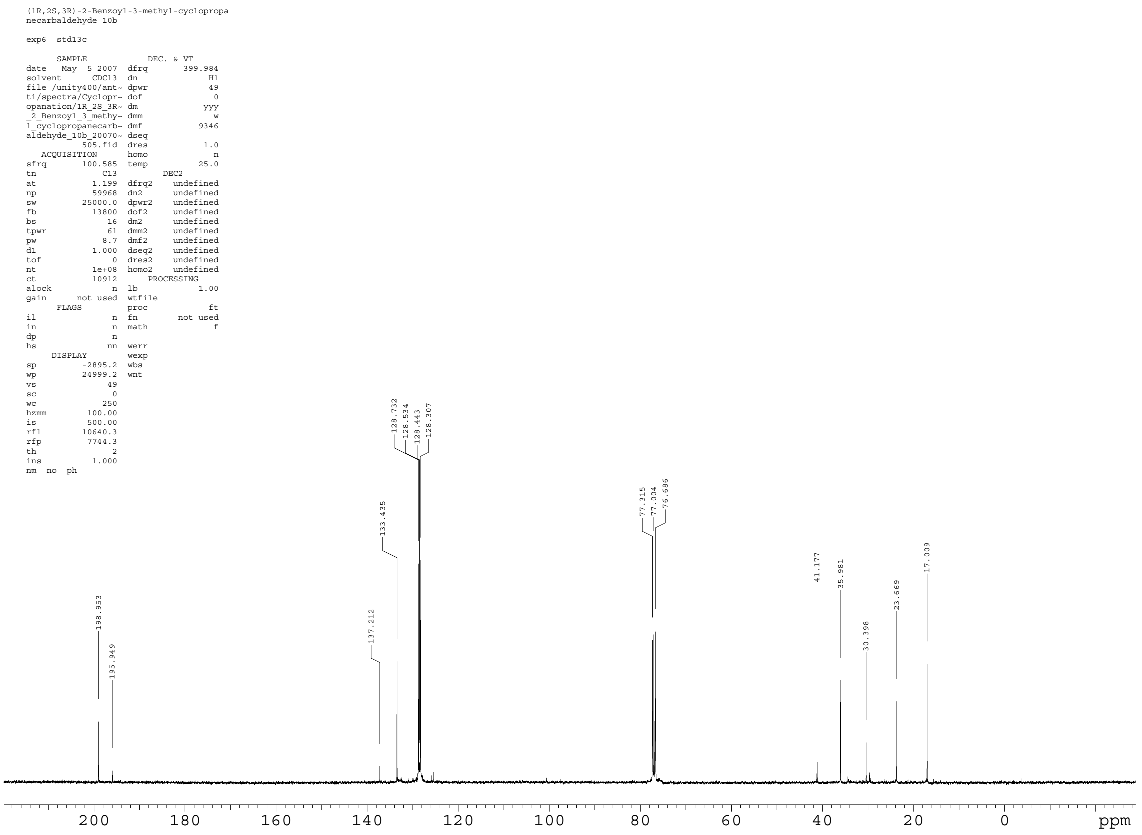
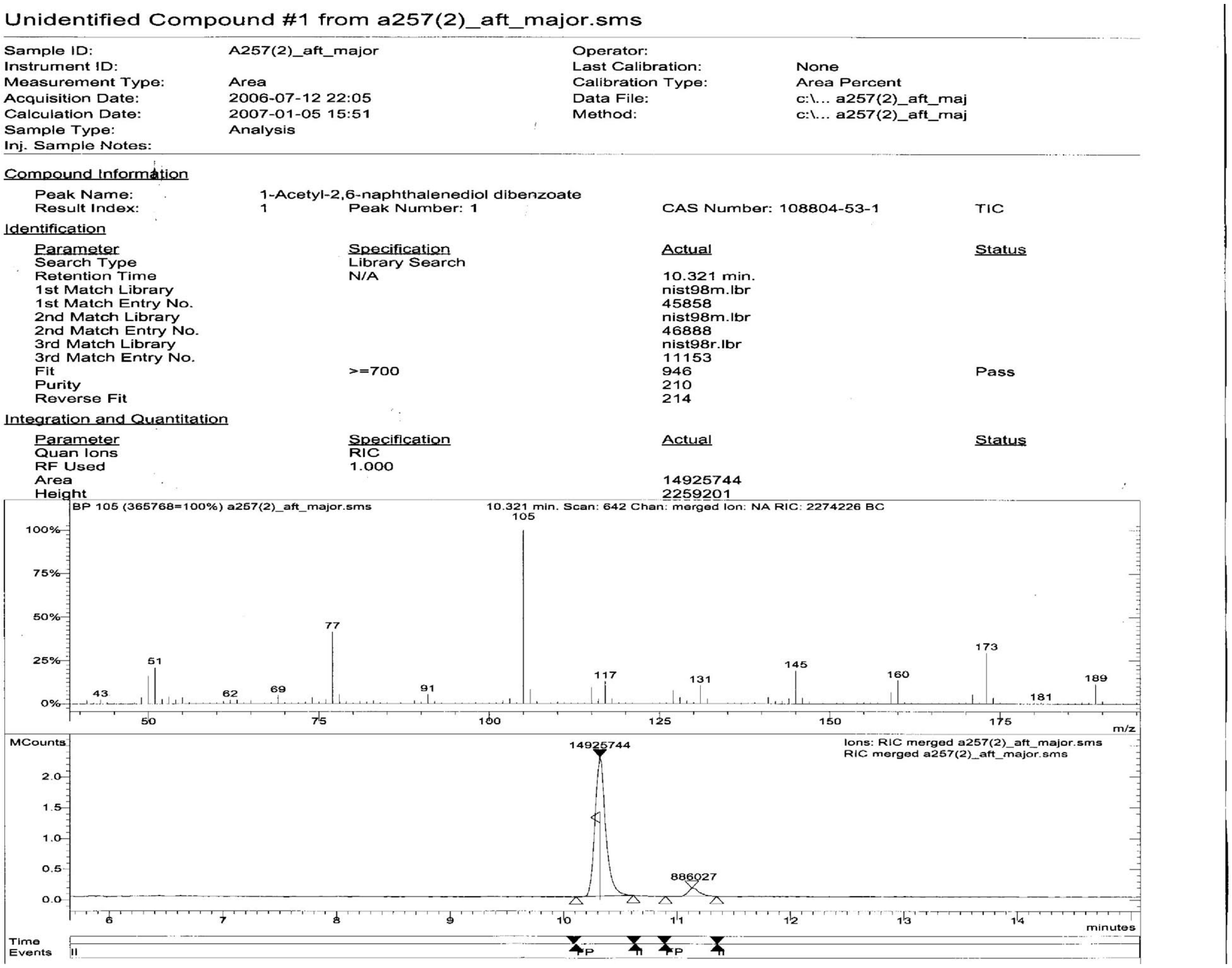

```
(1R,2S,3R)-2-Benzoyl-3-methyl-cyclopropa
necarbaldehyde 10b 20070504

exp4  s2pul

      SAMPLE              DEC. & VT
date   May  4 2007  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/1R_~ dmm              c
2S_3R_2_Benzoyl_3_~ dmf            200
methyl_cyclopropan~ dseq
ecarbaldehyde_10b_~ dres           1.0
      20070504.fid  homo             n
   ACQUISITION      temp          25.0
sfrq       499.940           DEC2
tn              H1  dfrq2            0
at           3.000  dn2
np           48000  dpwr2            1
sw          8000.0  dof2             0
fb            4000  dm2              n
bs              16  dmm2             c
tpwr            62  dmf2           200
pw             4.0  dseq2
d1               0  dres2          1.0
tof              0  homo2            n
nt               1      PROCESSING
ct               1  lb            0.20
alock            y  wtfile
gain      not used  proc            ft
      FLAGS         fn        not used
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp
     DISPLAY        wbs
sp           295.2  wnt
wp          4926.8
vs              91
sc               0
wc             250
hzmm         19.71
is          158.51
rfl         1500.2
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

Figure 31: ^{13}C NMR of 10b (Table 3, entry 3) at 25 °C.



```
(1R,2S,3R)-2-Benzoyl-3-methyl-cyclopropa
necarbaldehyde 10b

exp6  std13c

      SAMPLE            DEC. & VT
date   May  5 2007  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            49
ti/spectra/Cyclopr~ dof              0
opanation/1R_2S_3R~ dm             yyy
_2_Benzoyl_3_methy~ dmm              w
l_cyclopropanecarb~ dmf           9346
aldehyde_10b_20070~ dseq
           505.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       100.585  temp          25.0
tn             C13           DEC2
at           1.199  dfrq2    undefined
np           59968  dn2      undefined
sw         25000.0  dpwr2    undefined
fb           13800  dof2     undefined
bs              16  dm2      undefined
tpwr            61  dmm2     undefined
pw             8.7  dmf2     undefined
d1           1.000  dseq2    undefined
tof              0  dres2    undefined
nt          1e+08   homo2    undefined
ct           10912      PROCESSING
alock            n  lb            1.00
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               n
hs              nn  werr
     DISPLAY        wexp
sp         -2895.2  wbs
wp         24999.2  wnt
vs              49
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10640.3
rfp         7744.3
th               2
ins          1.000
nm  no  ph
```

Figure 32: GLC-MS determination of ee (major diastereomer) 10b (Table 3, entry 3).



Unidentified Compound #1 from a257(2)_aft_major.sms

Sample ID:	A257(2)_aft_major	Operator:	
Instrument ID:		Last Calibration:	None
Measurement Type:	Area	Calibration Type:	Area Percent
Acquisition Date:	2006-07-12 22:05	Data File:	c:\... a257(2)_aft_maj
Calculation Date:	2007-01-05 15:51	Method:	c:\... a257(2)_aft_maj
Sample Type:	Analysis		
Inj. Sample Notes:			

Compound Information

Peak Name: 1-Acetyl-2,6-naphthalenediol dibenzoate

Result Index: 1 Peak Number: 1 CAS Number: 108804-53-1 TIC

Identification

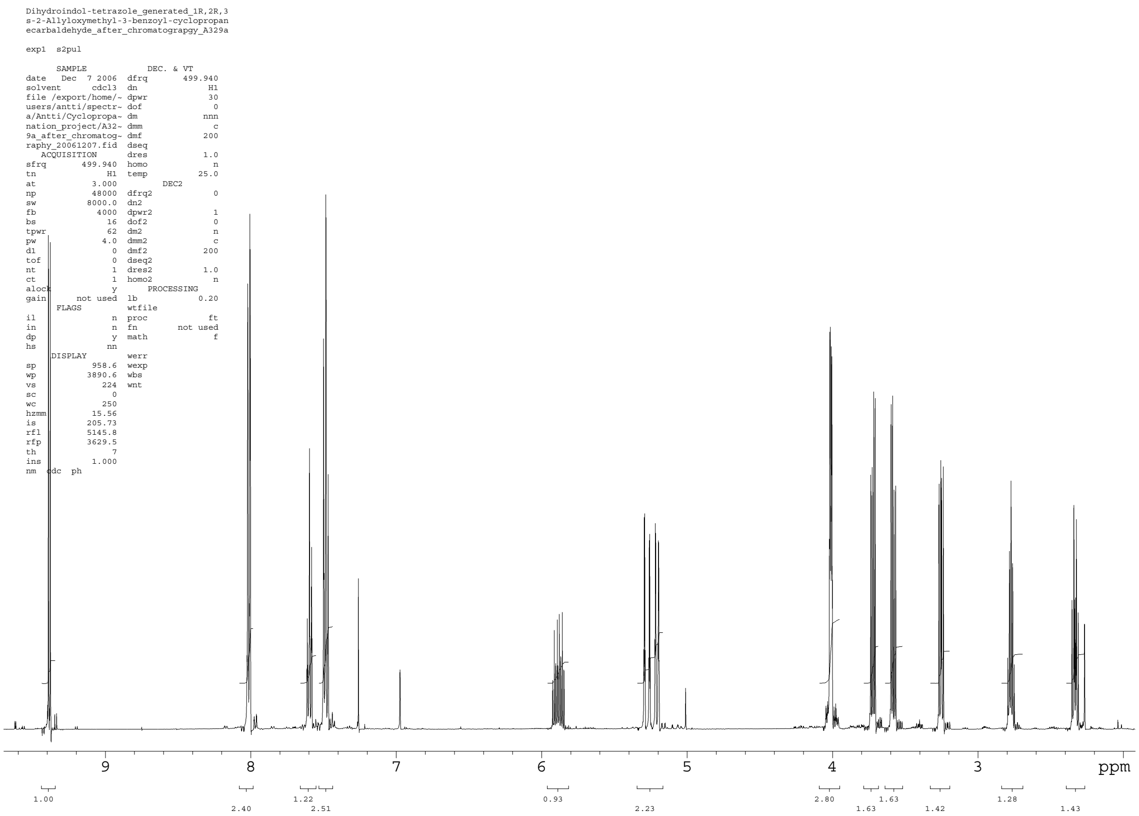
Parameter	Specification	Actual	Status
Search Type	Library Search		
Retention Time	N/A	10.321 min.	
1st Match Library		nist98m.lbr	
1st Match Entry No.		45858	
2nd Match Library		nist98m.lbr	
2nd Match Entry No.		46888	
3rd Match Library		nist98r.lbr	
3rd Match Entry No.		11153	
Fit	>=700	946	Pass
Purity		210	
Reverse Fit		214	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	RIC		
RF Used	1.000		
Area		14925744	
Height		2259201	

Major enantiomer	Minor enantiomer	ee %
14925744	886027	89

Figure 33: ^{1}H NMR of 11a (Table 2, entry 4) at 25 °C.



```
Dihydroindol-tetrazole_generated_1R,2R,3
s-2-Allyloxymethyl-3-benzoyl-cyclopropan
ecarbaldehyde_after_chromatograpgy_A329a

exp1  s2pul

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A32~ dmm              c
9a_after_chromatog~ dmf            200
raphy_20061207.fid  dseq
   ACQUISITION      dres           1.0
sfrq       499.940  homo             n
tn              H1  temp          25.0
at           3.000         DEC2
np           48000  dfrq2            0
sw          8000.0  dn2
fb            4000  dpwr2            1
bs              16  dof2             0
tpwr            62  dm2              n
pw             4.0  dmm2             c
d1               0  dmf2           200
tof              0  dseq2
nt               1  dres2          1.0
ct               1  homo2            n
alock            y      PROCESSING
gain      not used  lb            0.20
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               y  math             f
hs              nn
     DISPLAY        werr
sp           958.6  wexp
wp          3890.6  wbs
vs             224  wnt
sc               0
wc             250
hzmm         15.56
is          205.73
rfl         5145.8
rfp         3629.5
th               7
ins          1.000
nm  cdc  ph
```

Figure 34: ^{13}C NMR of 11a (Table 2, entry 4) at 25 °C.

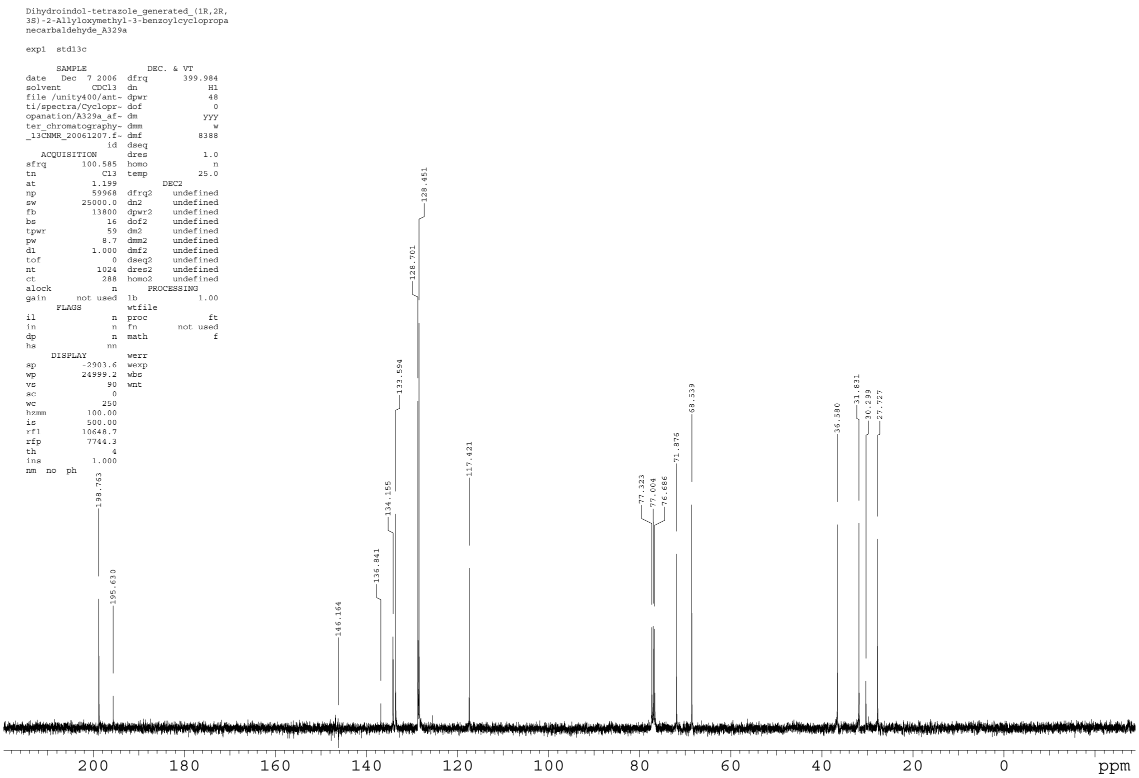
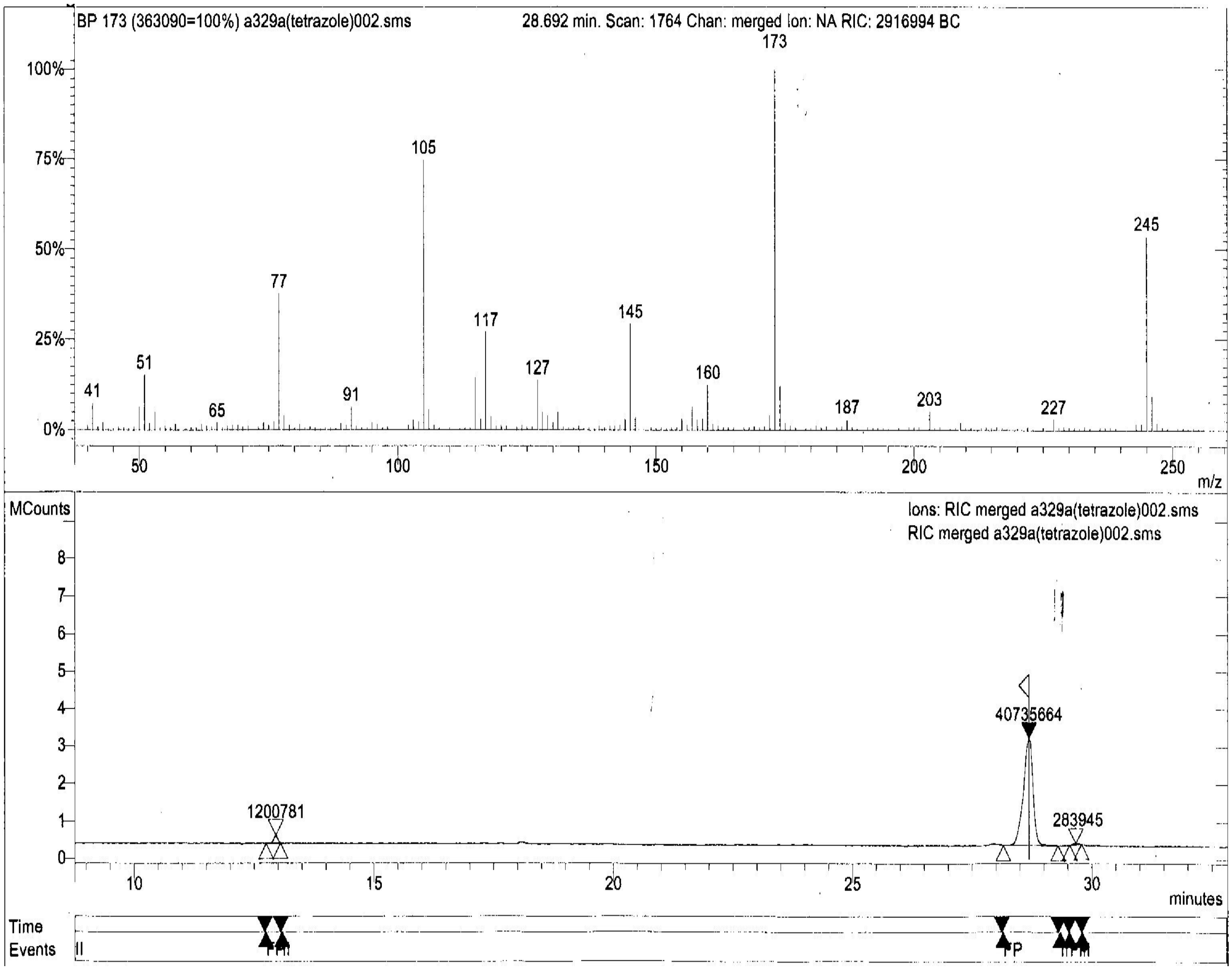
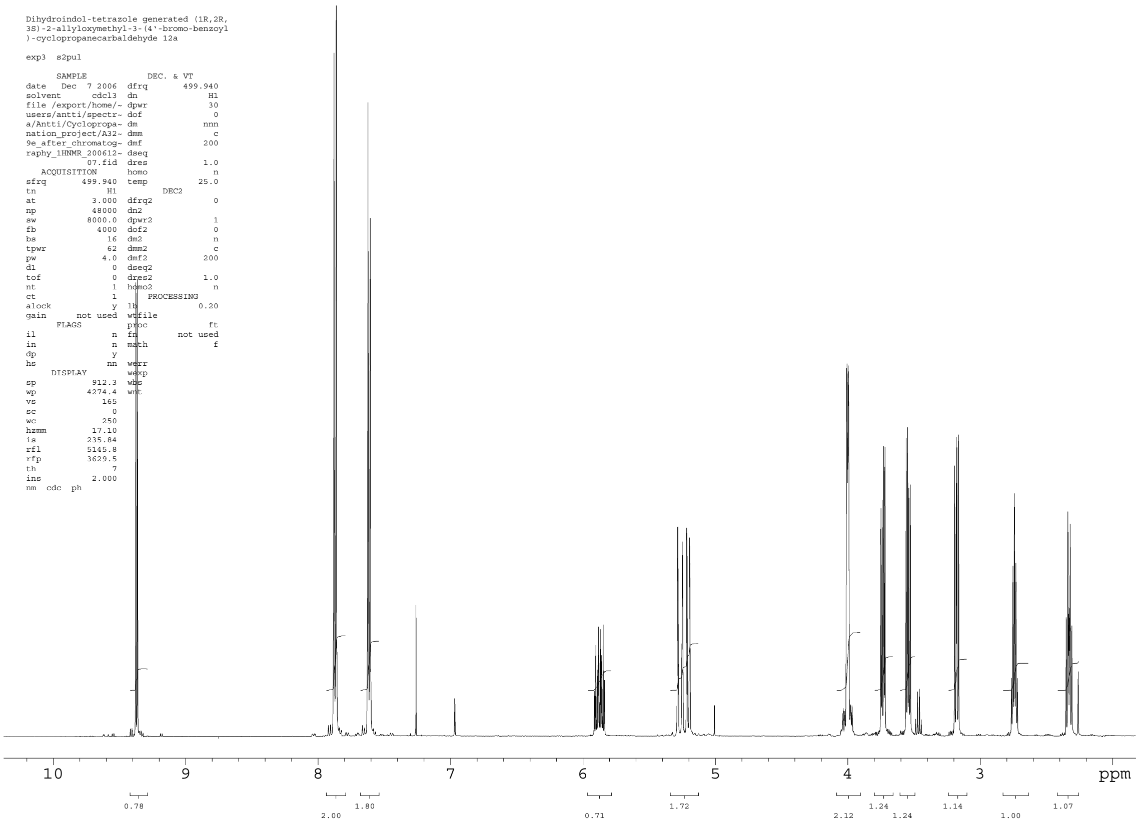

```
Dihydroindol-tetrazole_generated_(1R,2R,
3S)-2-Allyloxymethyl-3-benzoylcyclopropa
necarbaldehyde_A329a

exp1  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A329a_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_20061207.f~ dmf           8388
                id  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199         DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             288  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp         -2903.6  wexp
wp         24999.2  wbs
vs              90  wnt
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10648.7
rfp         7744.3
th               4
ins          1.000
nm  no  ph
```

Figure 35: GLC-MS determination of ee (major diastereomer) 11a (Table 2, entry 4).



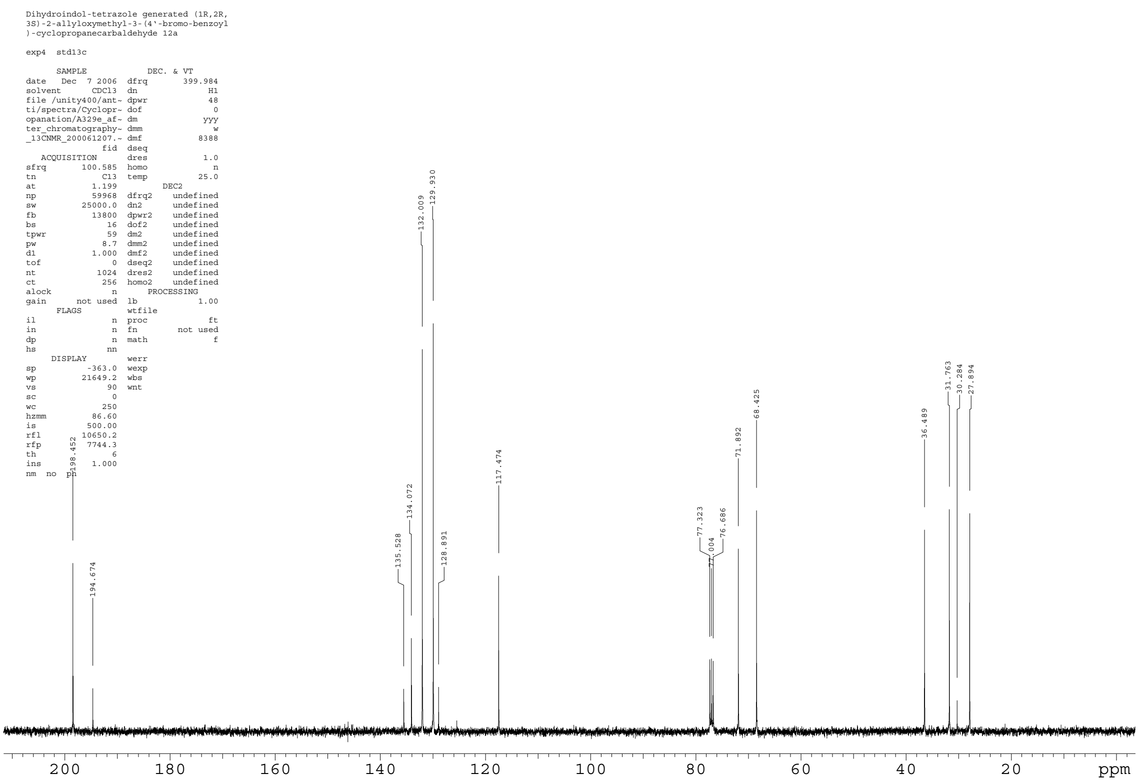
Major enantiomer	Minor enantiomer	ee %
40735664	282945	99

Figure 36: ^{1}H NMR of 12a (Table 2, entry 5) at 25 °C.



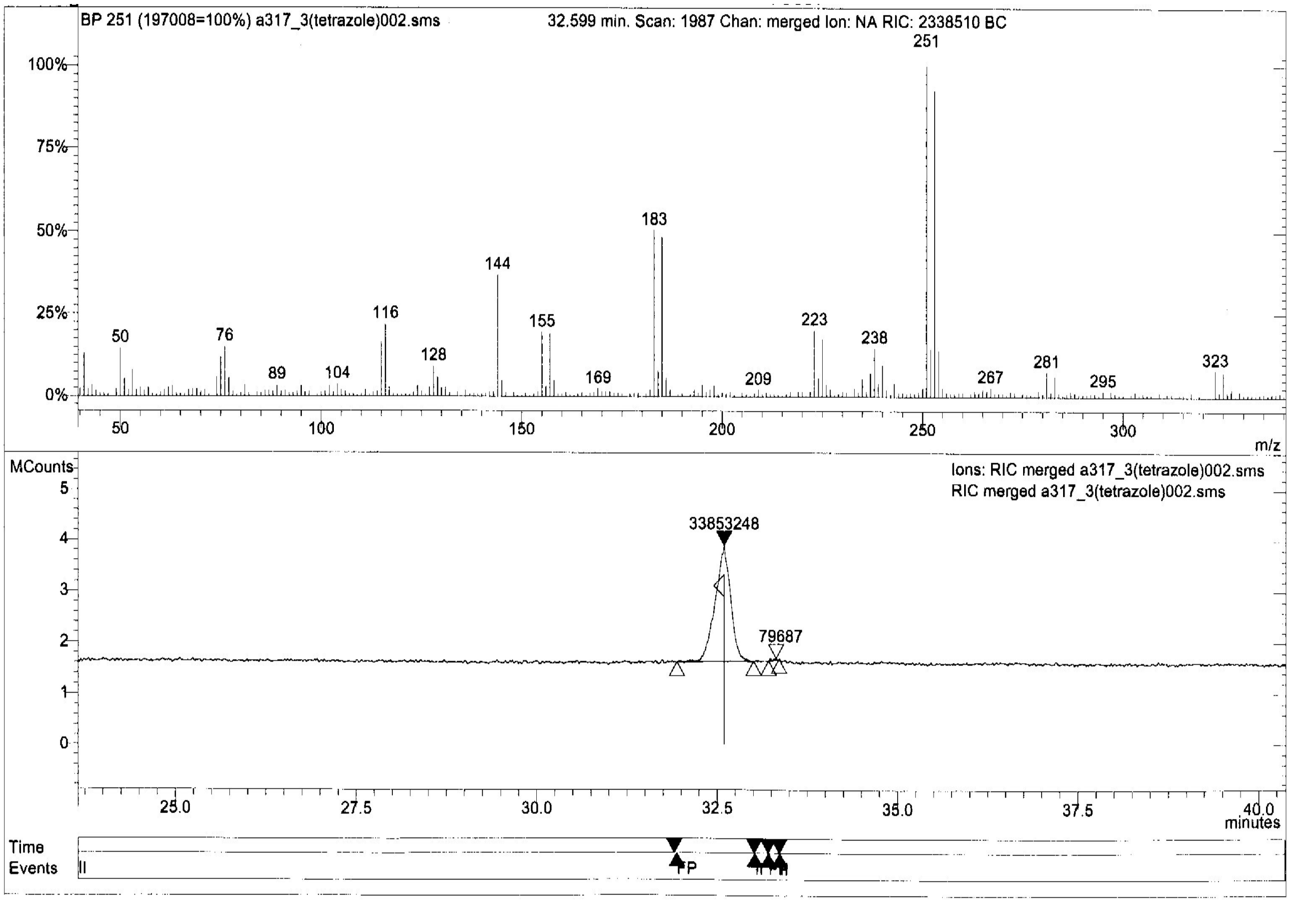
```
Dihydroindol-tetrazole generated (1R,2R,
3S)-2-allyloxymethyl-3-(4'-bromo-benzoyl
)-cyclopropanecarbaldehyde 12a

exp3  s2pul

      SAMPLE             DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A32~ dmm              c
9e_after_chromatog~ dmf            200
raphy_1HNMR_200612~ dseq
            07.fid  dres           1.0
   ACQUISITION      homo             n
sfrq       499.940  temp          25.0
tn              H1         DEC2
at           3.000  dfrq2            0
np           48000  dn2
sw          8000.0  dpwr2            1
fb            4000  dof2             0
bs              16  dm2              n
tpwr            62  dmm2             c
pw             4.0  dmf2           200
d1               0  dseq2
tof              0  dres2          1.0
nt               1  homo2            n
ct               1      PROCESSING
alock            y  lb            0.20
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               y
hs              nn  werr
     DISPLAY        wexp
sp           912.3  wbs
wp          4274.4  wnt
vs             165
sc               0
wc             250
hzmm         17.10
is          235.84
rfl         5145.8
rfp         3629.5
th               7
ins          2.000
nm  cdc  ph
```

Figure 37: ^{13}C NMR of 12a (Table 2, entry 5) at 25 °C.



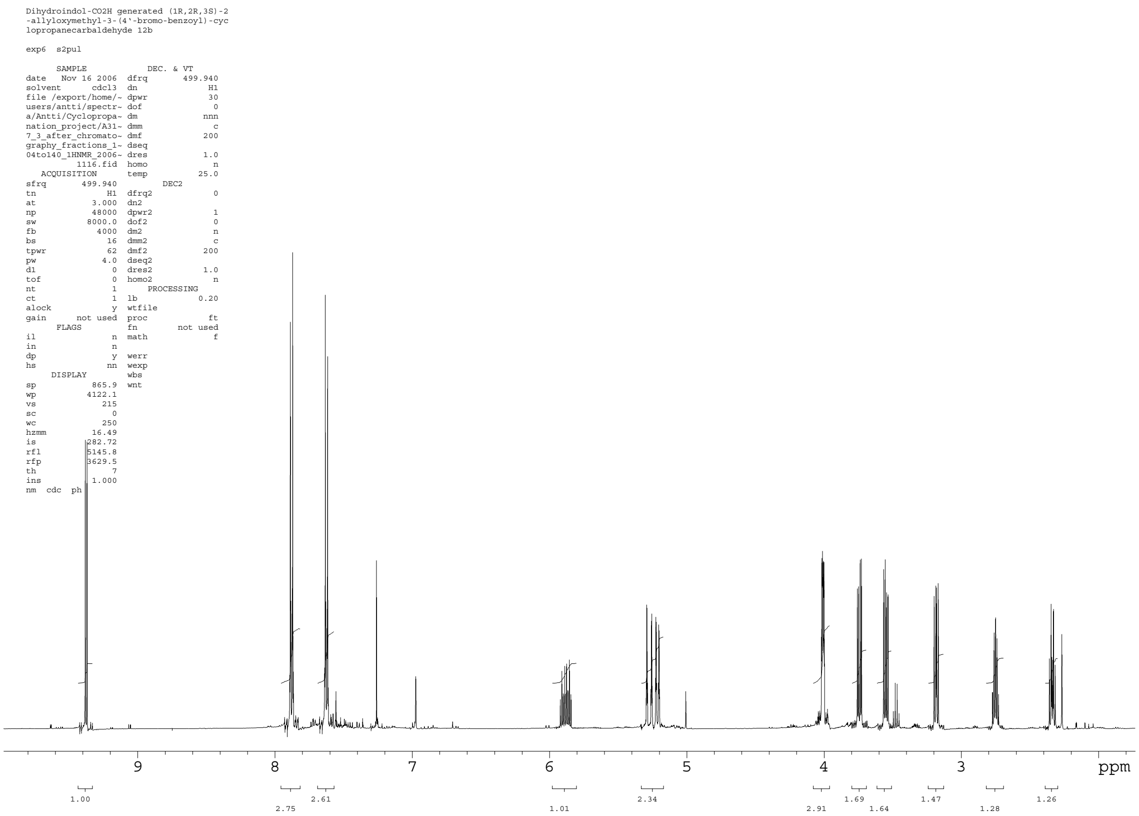
```
Dihydroindol-tetrazole generated (1R,2R,
3S)-2-allyloxymethyl-3-(4‘-bromo-benzoyl
)-cyclopropanecarbaldehyde 12a

exp4  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A329e_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_200061207.~ dmf           8388
               fid  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199         DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             256  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp          -363.0  wexp
wp         21649.2  wbs
vs              90  wnt
sc               0
wc             250
hzmm         86.60
is          500.00
rfl        10650.2
rfp         7744.3
th               6
ins          1.000
nm  no  ph
```

Figure 38: GLC-MS determination of ee (major diastereomer) 12a (Table 2, entry 5).



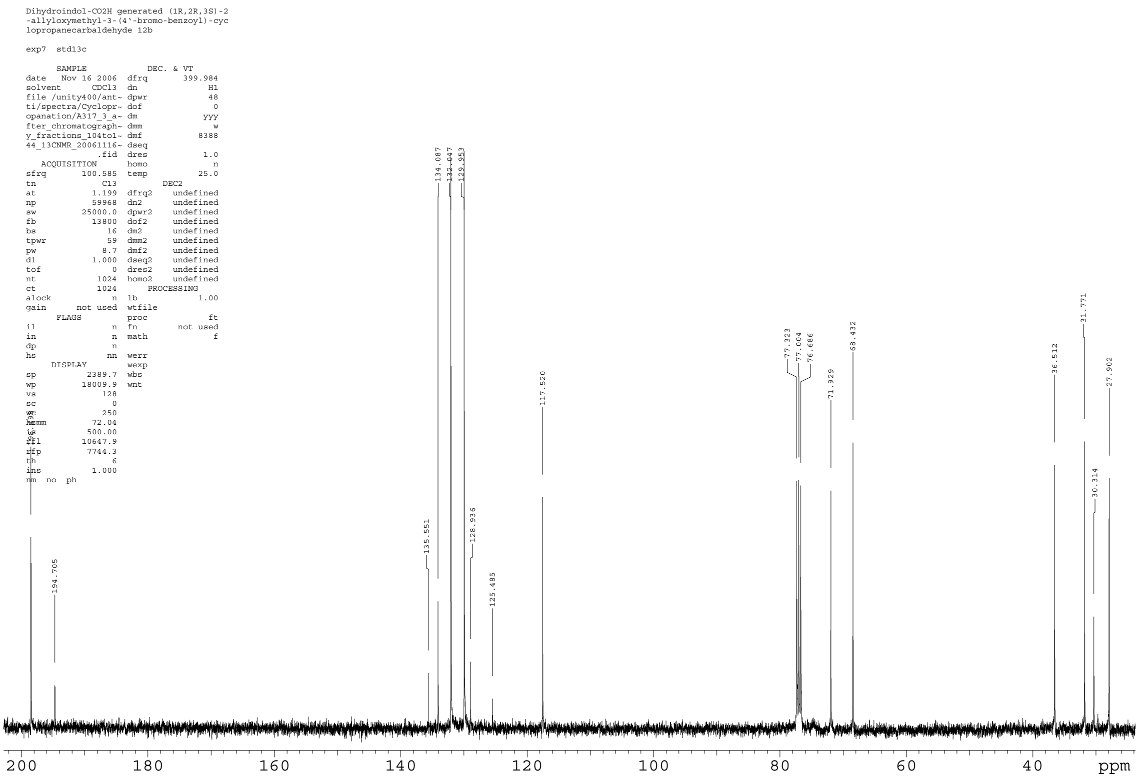
Major enantiomer	Minor enantiomer	ee %
33853248	79687	> 99

Figure 39: ^{1}H NMR of 12b (Table 3, entry 5) at 25 °C.



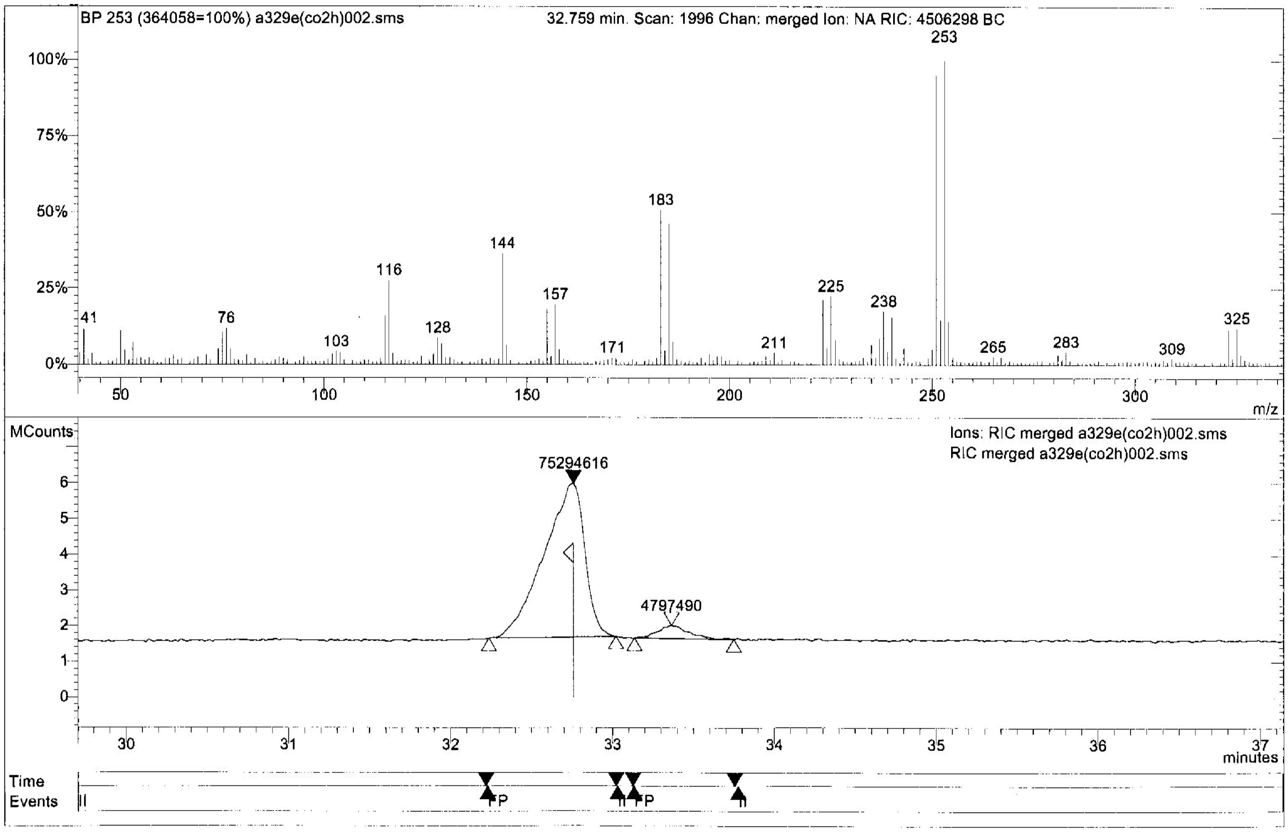
```
Dihydroindol-CO2H generated (1R,2R,3S)-2
-allyloxymethyl-3-(4‘-bromo-benzoyl)-cyc
lopropanecarbaldehyde 12b

exp6  s2pul

      SAMPLE            DEC. & VT
date   Nov 16 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A31~ dmm              c
7_3_after_chromato~ dmf            200
graphy_fractions_1~ dseq
04to140_1HNMR_2006~ dres           1.0
          1116.fid  homo             n
   ACQUISITION      temp          25.0
sfrq       499.940         DEC2
tn              H1  dfrq2            0
at           3.000  dn2
np           48000  dpwr2            1
sw          8000.0  dof2             0
fb            4000  dm2              n
bs              16  dmm2             c
tpwr            62  dmf2           200
pw             4.0  dseq2
d1               0  dres2          1.0
tof              0  homo2            n
nt               1      PROCESSING
ct               1  lb            0.20
alock            y  wtfile
gain      not used  proc            ft
      FLAGS         fn        not used
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp
     DISPLAY        wbs
sp           865.9  wnt
wp          4122.1
vs             215
sc               0
wc             250
hzmm         16.49
is          282.72
rfl         5145.8
rfp         3629.5
th               7
ins          1.000
nm  cdc  ph
```

Figure 40: ^{13}C NMR of 12b (Table 3, entry 5) at 25 °C.



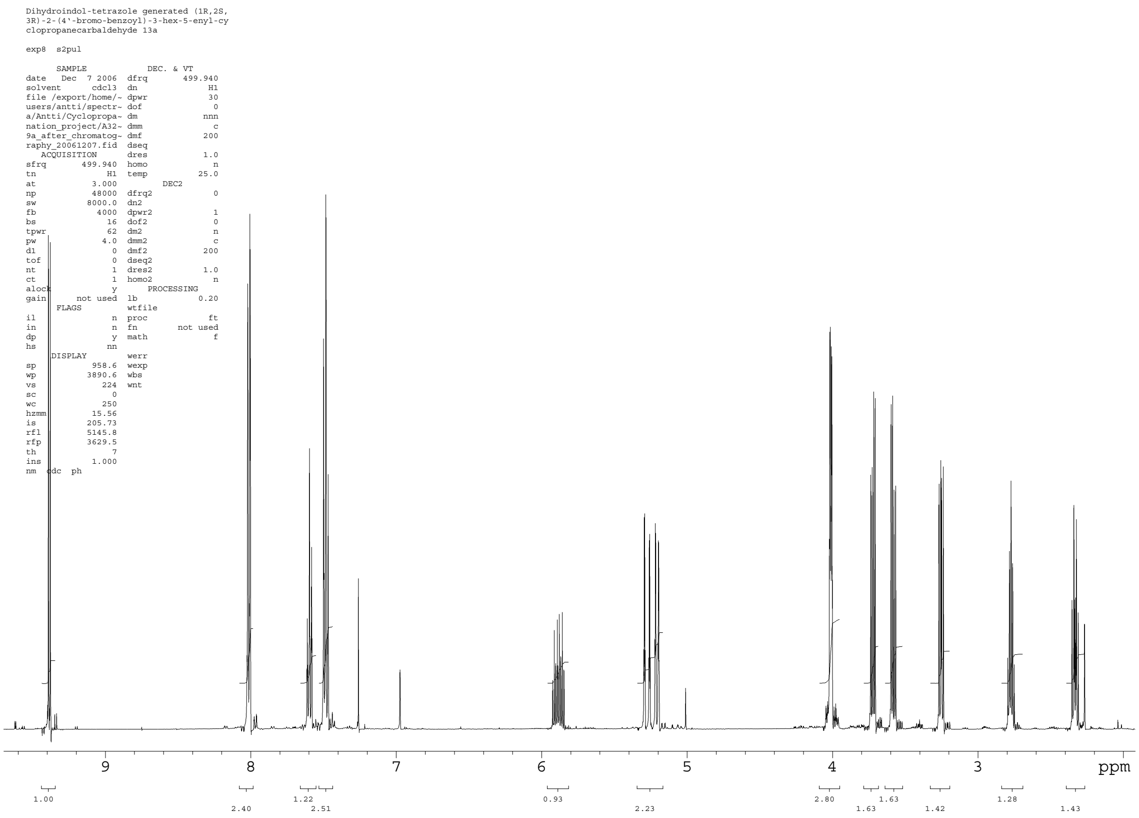
```
Dihydroindol-CO2H generated (1R,2R,3S)-2
-allyloxymethyl-3-(4‘-bromo-benzoyl)-cyc
lopropanecarbaldehyde 12b

exp7  std13c

      SAMPLE            DEC. & VT
date   Nov 16 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A317_3_a~ dm             yyy
fter_chromatograph~ dmm              w
y_fractions_104to1~ dmf           8388
44_13CNMR_20061116~ dseq
               .fid dres           1.0
   ACQUISITION      homo             n
sfrq       100.585  temp          25.0
tn             C13          DEC2
at           1.199  dfrq2    undefined
np           59968  dn2      undefined
sw         25000.0  dpwr2    undefined
fb           13800  dof2     undefined
bs              16  dm2      undefined
tpwr            59  dmm2     undefined
pw             8.7  dmf2     undefined
d1           1.000  dseq2    undefined
tof              0  dres2    undefined
nt            1024  homo2    undefined
ct            1024      PROCESSING
alock            n  lb            1.00
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               n
hs              nn  werr
     DISPLAY        wexp
sp          2389.7  wbs
wp         18009.9  wnt
vs             128
sc               0
wc             250
hzmm         72.04
is          500.00
rfl        10647.9
rfp         7744.3
th               6
ins          1.000
nm  no  ph
```

Figure 41: GLC-MS determination of ee (major diastereomer) 12b (Table 3, entry 5).



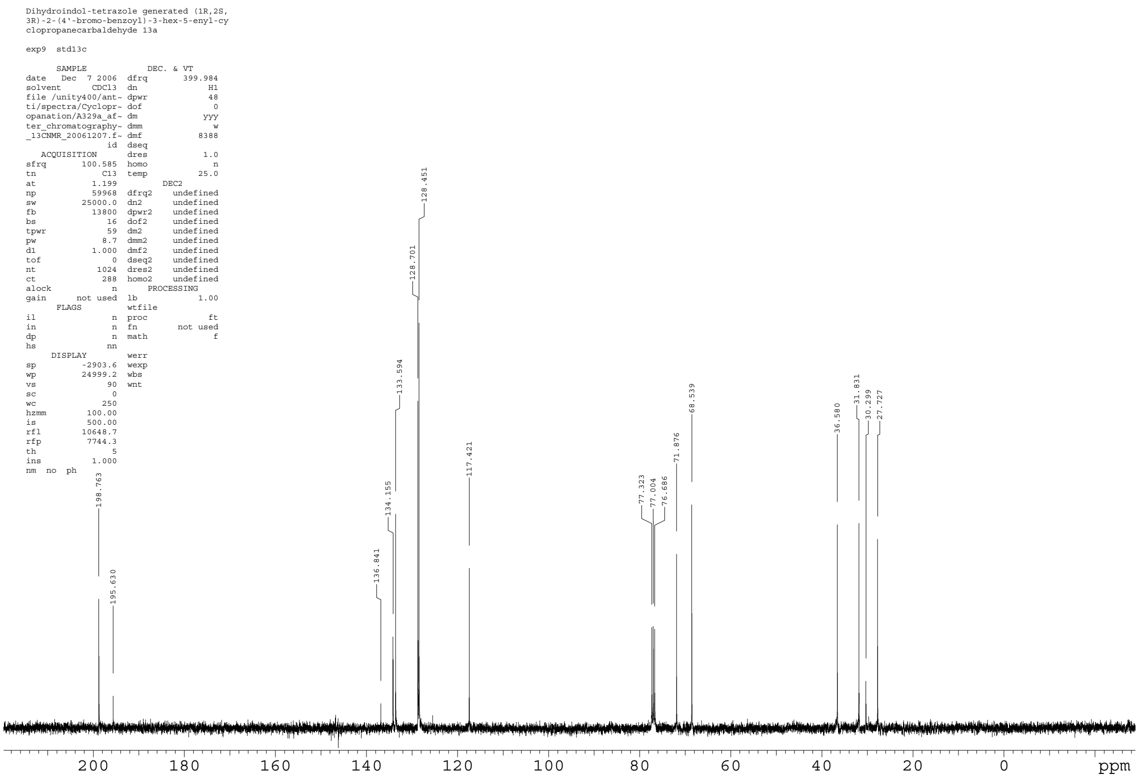
Major enantiomer	Minor enantiomer	ee %
75294616	4797490	88

Figure 42: ^{1}H NMR of 13a (Table 2, entry 6) at 25 °C.



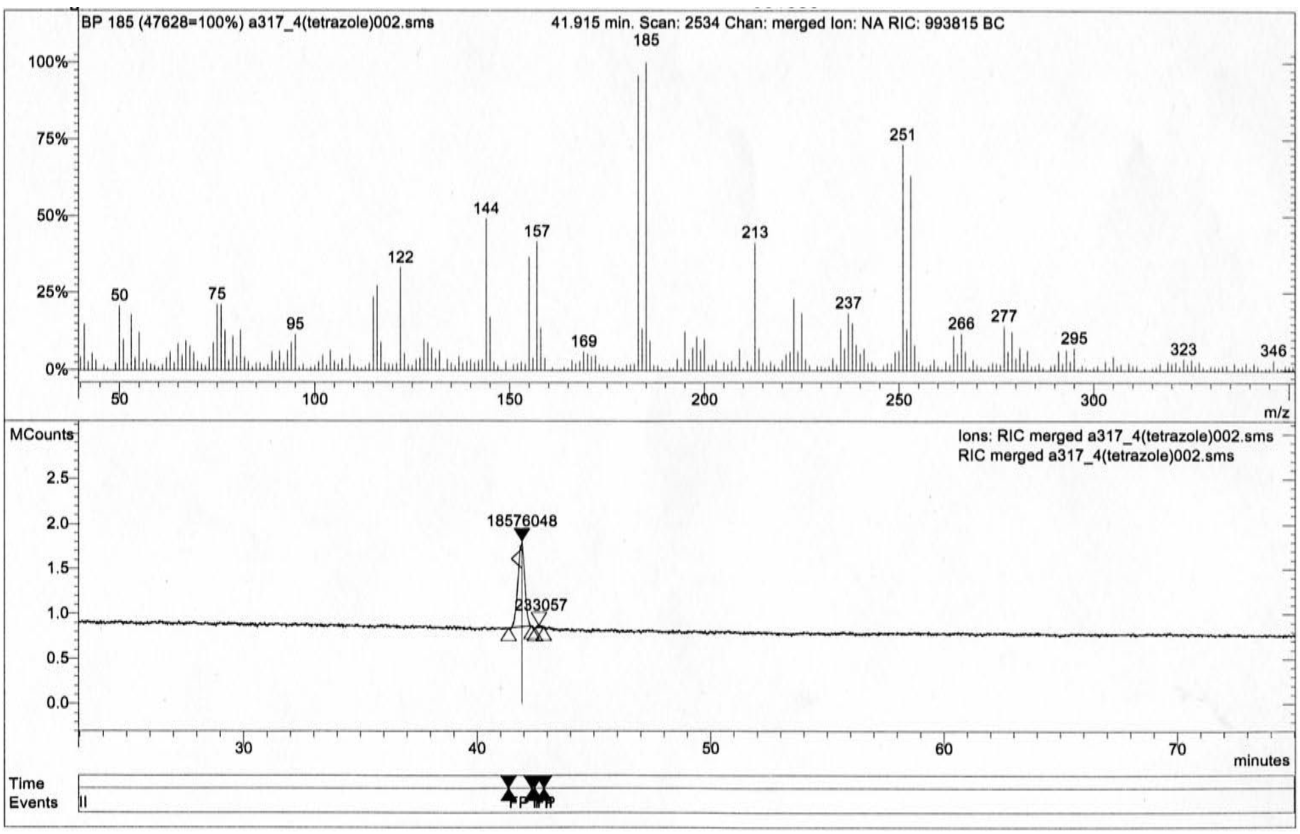
```
Dihydroindol-tetrazole generated (1R,2S,
3R)-2-(4'-bromo-benzoyl)-3-hex-5-enyl-cy
clopropanecarbaldehyde 13a

exp8  s2pul

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A32~ dmm              c
9a_after_chromatog~ dmf            200
raphy_20061207.fid  dseq
   ACQUISITION      dres           1.0
sfrq       499.940  homo             n
tn              H1  temp          25.0
at           3.000         DEC2
np           48000  dfrq2            0
sw          8000.0  dn2
fb            4000  dpwr2            1
bs              16  dof2             0
tpwr            62  dm2              n
pw             4.0  dmm2             c
d1               0  dmf2           200
tof              0  dseq2
nt               1  dres2          1.0
ct               1  homo2            n
alock            y       PROCESSING
gain      not used  lb            0.20
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               y  math             f
hs              nn
     DISPLAY        werr
sp           958.6  wexp
wp          3890.6  wbs
vs             224  wnt
sc               0
wc             250
hzmm         15.56
is          205.73
rfl         5145.8
rfp         3629.5
th               7
ins          1.000
nm  cdc  ph
```

Figure 43: ^{13}C NMR of 13a (Table 2, entry 6) at 25 °C.



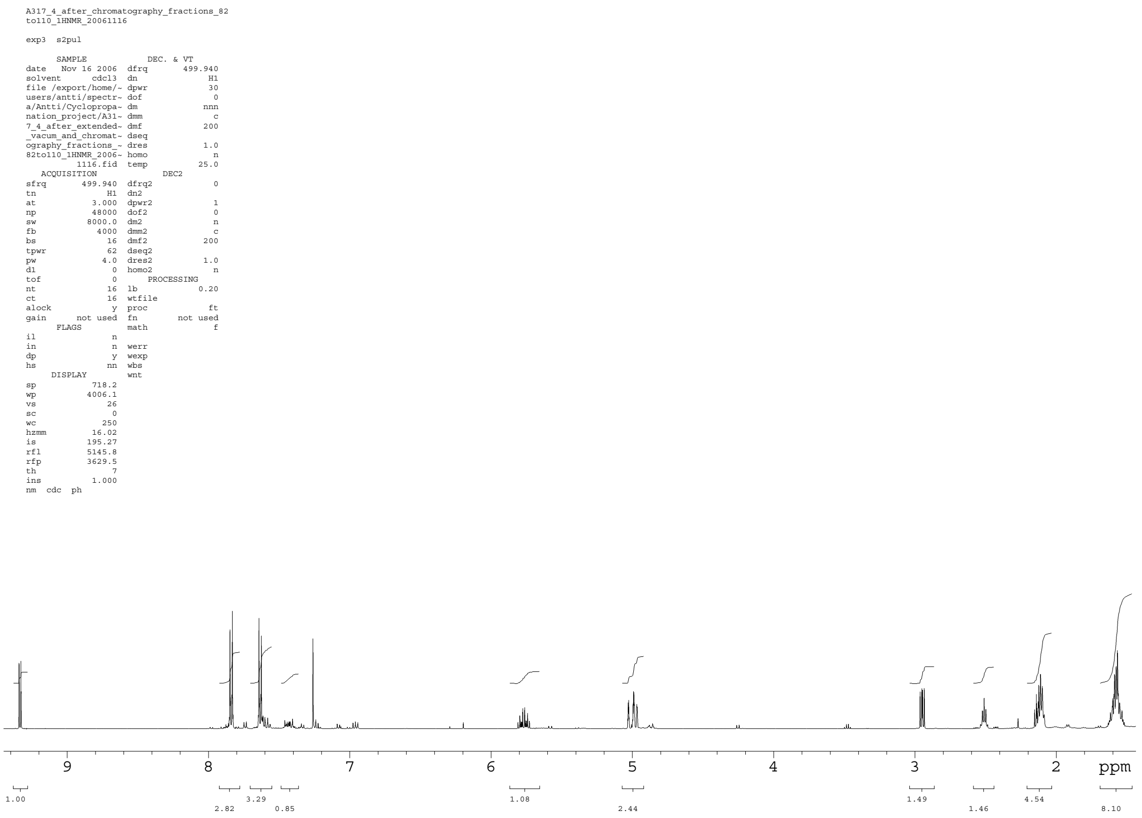
```
Dihydroindol-tetrazole generated (1R,2S,
3R)-2-(4'-bromo-benzoyl)-3-hex-5-enyl-cy
clopropanecarbaldehyde 13a

exp9  std13c

      SAMPLE            DEC. & VT
date   Dec  7 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A329a_af~ dm             yyy
ter_chromatography~ dmm              w
_13CNMR_20061207.f~ dmf           8388
                id  dseq
   ACQUISITION      dres           1.0
sfrq       100.585  homo             n
tn             C13  temp          25.0
at           1.199         DEC2
np           59968  dfrq2    undefined
sw         25000.0  dn2      undefined
fb           13800  dpwr2    undefined
bs              16  dof2     undefined
tpwr            59  dm2      undefined
pw             8.7  dmm2     undefined
d1           1.000  dmf2     undefined
tof              0  dseq2    undefined
nt            1024  dres2    undefined
ct             288  homo2    undefined
alock            n      PROCESSING
gain      not used  lb            1.00
      FLAGS         wtfile
il               n  proc            ft
in               n  fn        not used
dp               n  math             f
hs              nn
     DISPLAY        werr
sp         -2903.6  wexp
wp         24999.2  wbs
vs              90  wnt
sc               0
wc             250
hzmm        100.00
is          500.00
rfl        10648.7
rfp         7744.3
th               5
ins          1.000
nm  no  ph
```

Figure 44: GLC-MS determination of ee (major diastereomer) 13a (Table 2, entry 6).



Major enantiomer	Minor enantiomer	ee %
186786048	283057	> 99

Figure 45: ^{1}H NMR of 13b (Table 3, entry 6) at 25 °C.



```
A317_4_after_chromatography_fractions_82
to110_1HNMR_20061116

exp3  s2pul

      SAMPLE            DEC. & VT
date   Nov 16 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A31~ dmm              c
7_4_after_extended~ dmf            200
_vacum_and_chromat~ dseq
ography_fractions_~ dres           1.0
82to110_1HNMR_2006~ homo             n
          1116.fid  temp          25.0
   ACQUISITION             DEC2
sfrq       499.940  dfrq2            0
tn              H1  dn2
at           3.000  dpwr2            1
np           48000  dof2             0
sw          8000.0  dm2              n
fb            4000  dmm2             c
bs              16  dmf2           200
tpwr            62  dseq2
pw             4.0  dres2          1.0
d1               0  homo2            n
tof              0      PROCESSING
nt              16  lb            0.20
ct              16  wtfile
alock            y  proc            ft
gain      not used  fn        not used
      FLAGS         math             f
il               n
in               n  werr
dp               y  wexp
hs              nn  wbs
     DISPLAY        wnt
sp           718.2
wp          4006.1
vs              26
sc               0
wc             250
hzmm         16.02
is          195.27
rfl         5145.8
rfp         3629.5
th               7
ins          1.000
nm  cdc  ph
```

Figure 46: ^{13}C NMR of 13b (Table 3, entry 6) at 25 °C.

```
A317_4_after_Chromatography_fractions_82
to110_13CNMR_20061116

exp3  std13c

      SAMPLE            DEC. & VT
date   Nov 16 2006  dfrq       399.984
solvent      CDCl3  dn              H1
file /unity400/ant~ dpwr            48
ti/spectra/Cyclopr~ dof              0
opanation/A317_4_a~ dm             yyy
fter_Chromatograph~ dmm              w
y_fractions_82to11~ dmf           8388
0_13CNMR_20061116.~ dseq
               fid  dres           1.0
   ACQUISITION      homo             n
sfrq       100.585  temp          25.0
tn             C13          DEC2
at           1.199  dfrq2    undefined
np           59968  dn2      undefined
sw         25000.0  dpwr2    undefined
fb           13800  dof2     undefined
bs              16  dm2      undefined
tpwr            59  dmm2     undefined
pw             8.7  dmf2     undefined
d1           1.000  dseq2    undefined
tof              0  dres2    undefined
nt          100000  homo2    undefined
ct            1376      PROCESSING
alock            n  lb            1.00
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math             f
dp               n
hs              nn  werr
     DISPLAY        wexp
sp          2318.7  wbs
wp         17832.9  wnt
vs              48
sc               0
wc             250
hzmm         71.33
is          500.00
rfl        10647.1
rfp         7744.3
th               7
ins          1.000
nm  no  ph
```

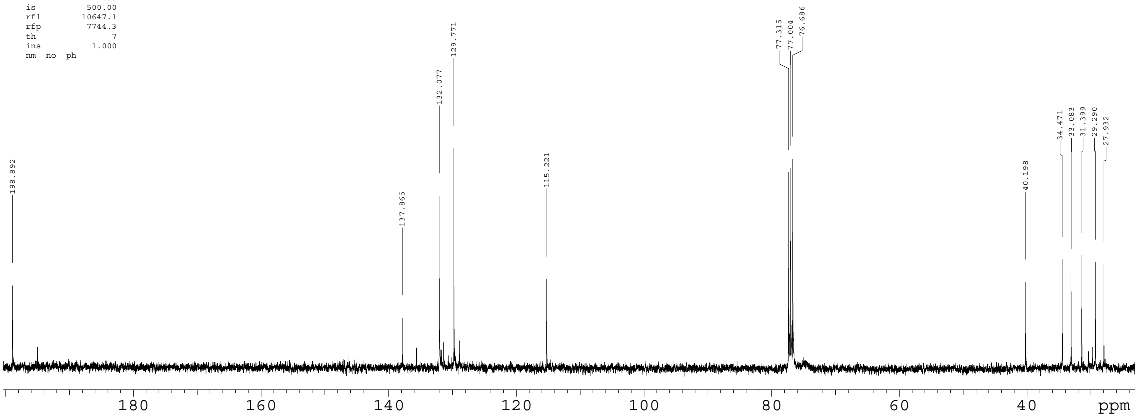
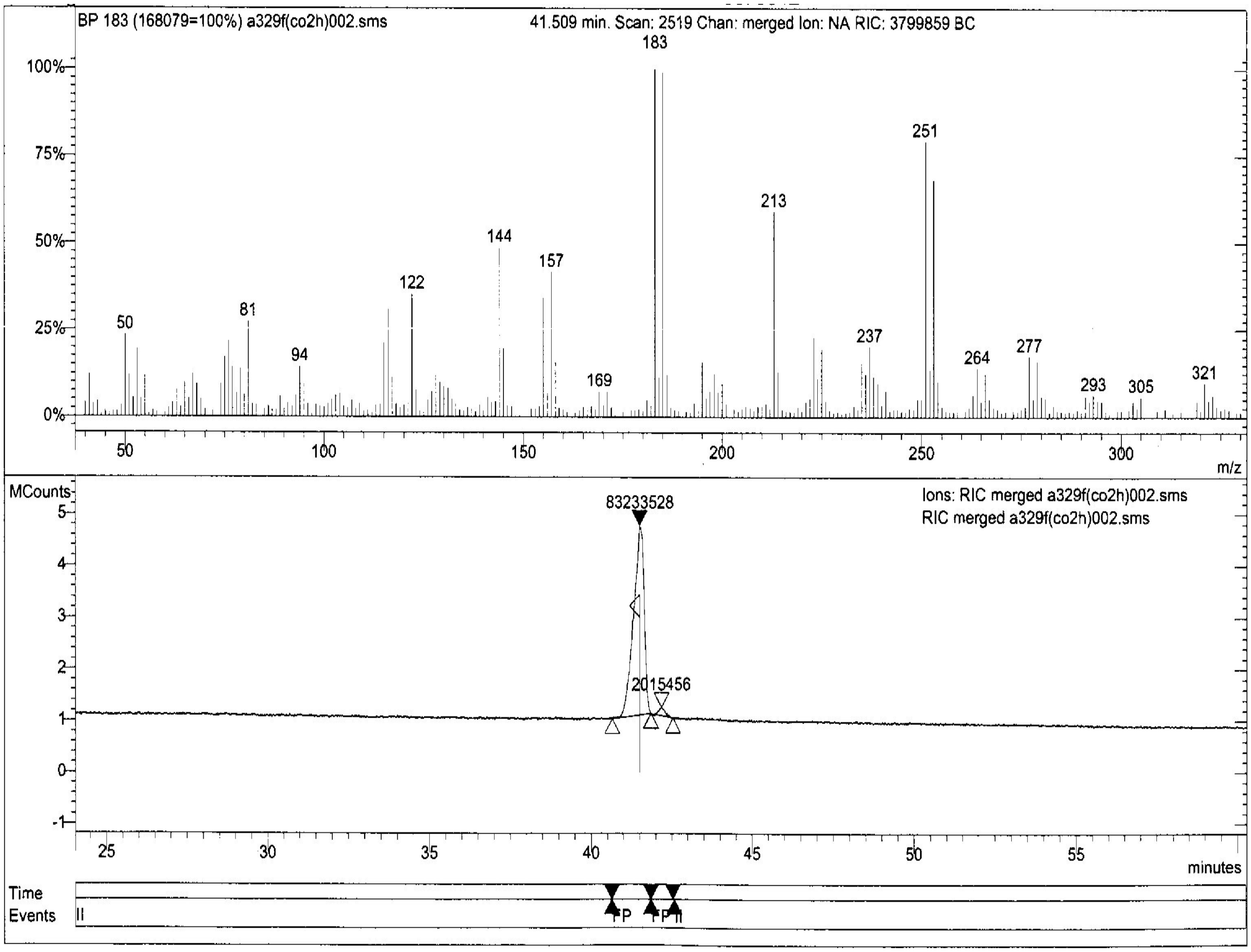


Figure 47: GLC-MS determination of ee (major diastereomer) 13b (Table 3, entry 6).



Major enantiomer	Minor enantiomer	ee %
83233528	2015456	95

Figure 48: ^{1}H NMR of 14a (Table 2, entry 7) at 25 °C.

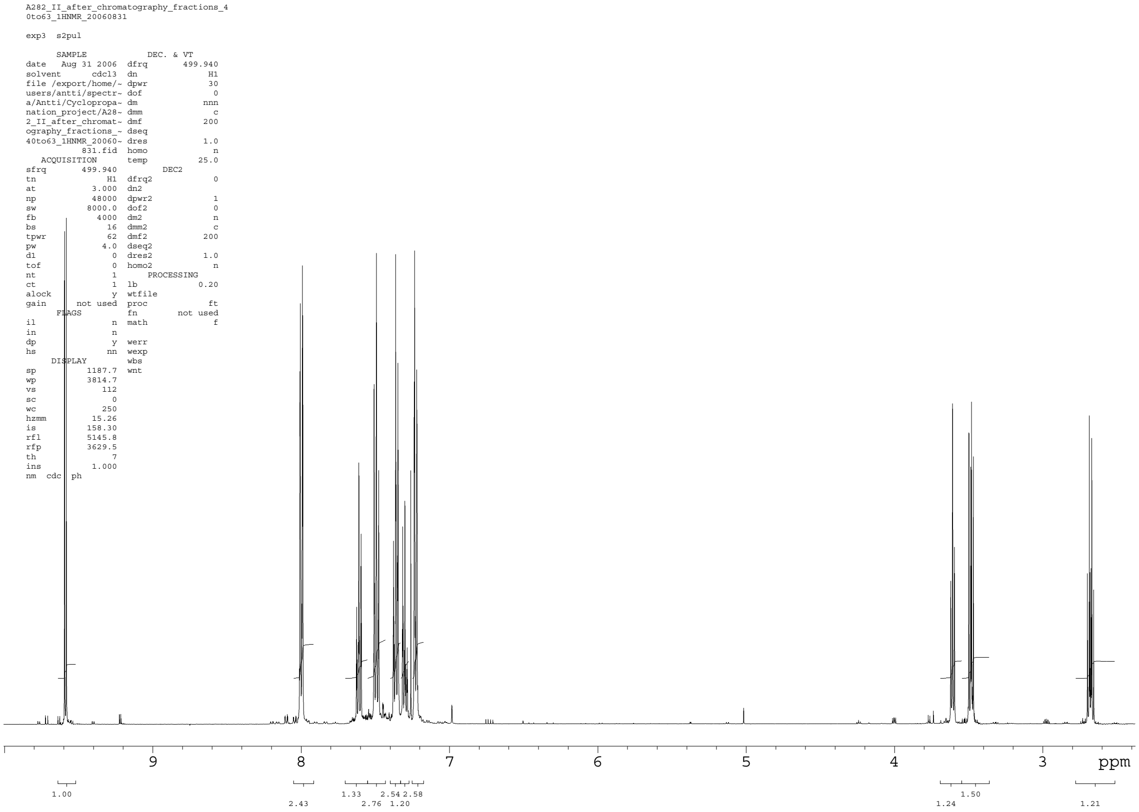
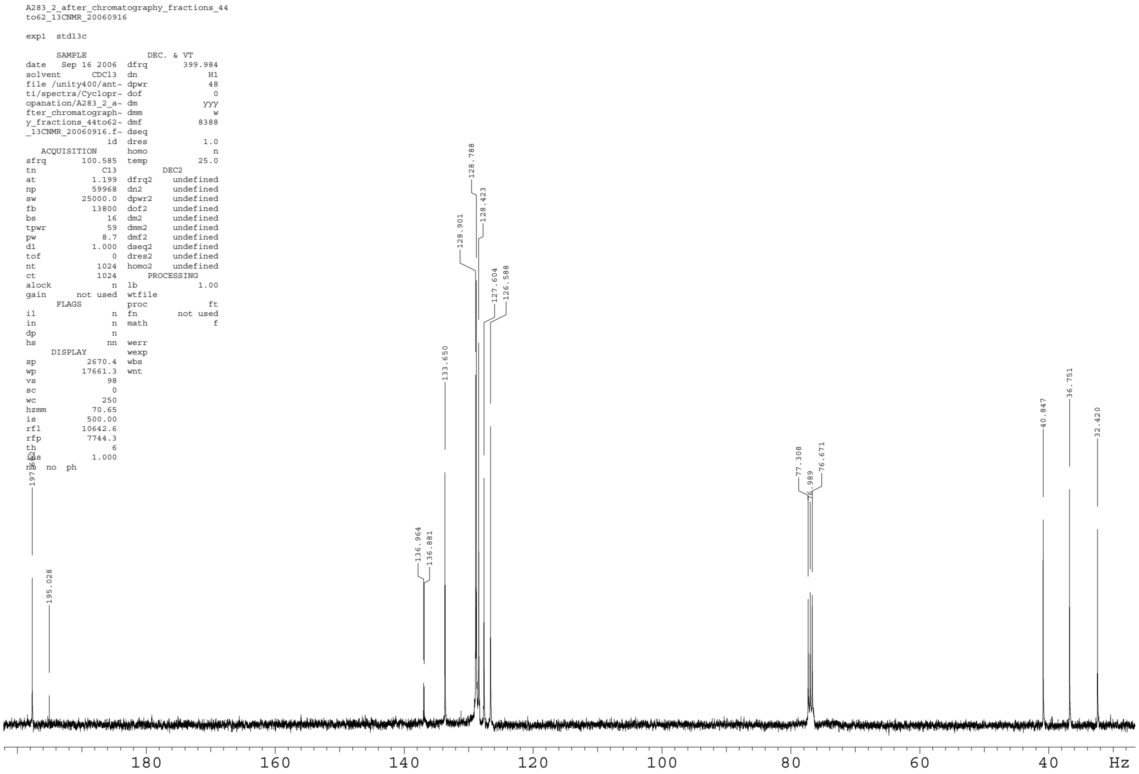
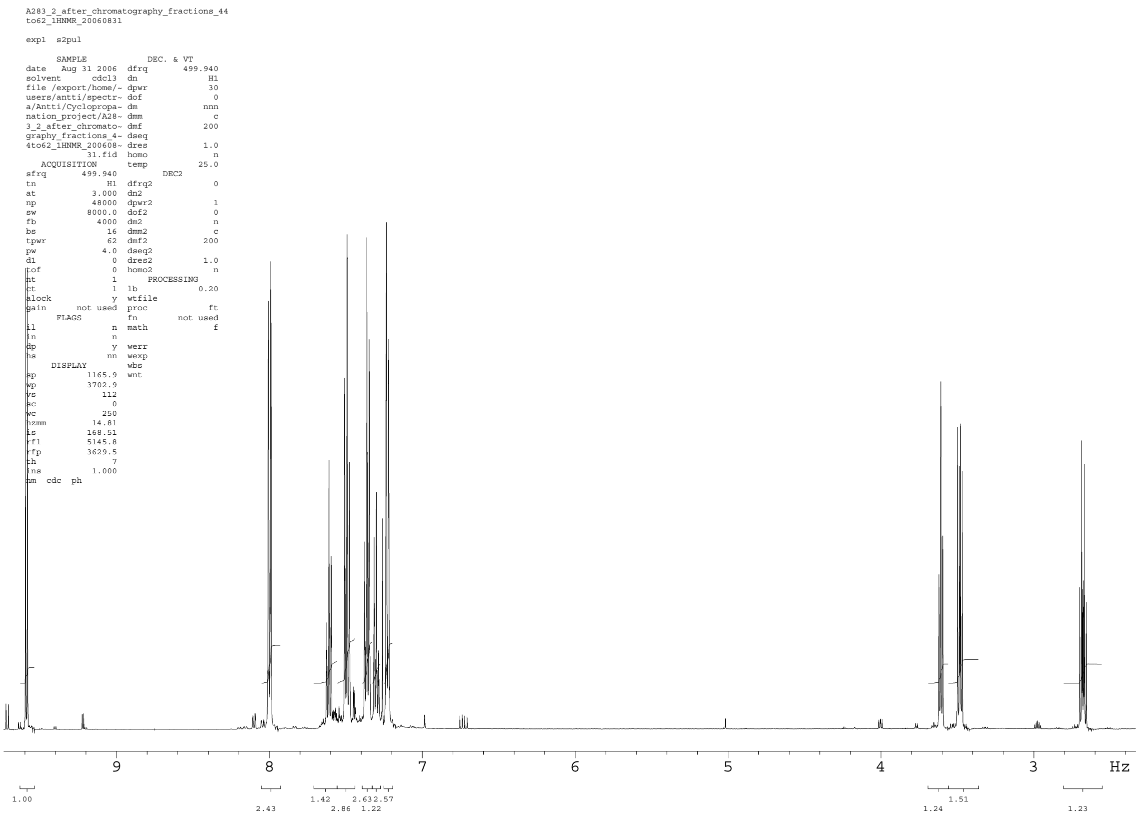


Figure 49: ^{13}C NMR of 14a (Table 2, entry 7) at 25 °C.



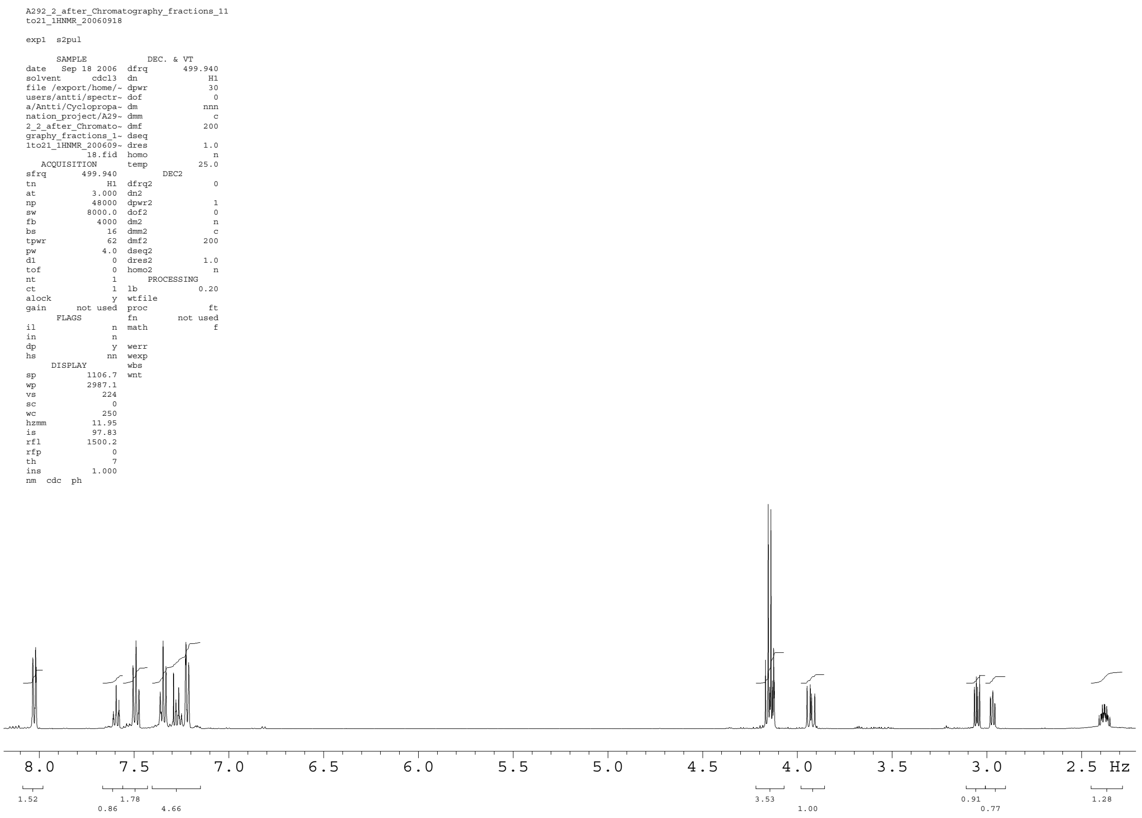
```
A283_2_after_chromatography_fractions_44
to62_13CNMR_20060916

exp1  std13c

      SAMPLE              DEC. & VT
date   Sep 16 2006  dfrq       399.984
solvent       CDCl3  dn              H1
file /unity400/ant~  dpwr            48
ti/spectra/Cyclopr~  dof              0
opanation/A283_2_a~  dm             yyy
fter_chromatograph~  dmm              w
y_fractions_44to62~  dmf           8388
_13CNMR_20060916.f~  dseq
                 id  dres           1.0
   ACQUISITION      homo             n
sfrq       100.585  temp          25.0
tn             C13         DEC2
at           1.199  dfrq2    undefined
np           59968  dn2      undefined
sw         25000.0  dpwr2    undefined
fb           13800  dof2     undefined
bs              16  dm2      undefined
tpwr            59  dmm2     undefined
pw             8.7  dmf2     undefined
d1           1.000  dseq2    undefined
tof              0  dres2    undefined
nt            1024  homo2    undefined
ct            1024      PROCESSING
alock            n  lb            1.00
gain      not used  wtfile
      FLAGS         proc            ft
il               n  fn        not used
in               n  math            f
dp               n
hs              nn  werr
     DISPLAY        wexp
sp          2670.4  wbs
wp         17661.3  wnt
vs              98
sc               0
wc             250
hzmm         70.65
is          500.00
rfl        10642.6
rfp         7744.3
th               6
ins          1.000
nm  no  ph
```

Figure 50: ^{1}H NMR of 14b (Table 3, entry 7) at 25 °C.



```
A283_2_after_chromatography_fractions_44
to62_1HNMR_20060831

exp1  s2pul

      SAMPLE            DEC. & VT
date   Aug 31 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A28~ dmm              c
3_2_after_chromato~ dmf            200
graphy_fractions_4~ dseq
4to62_1HNMR_200608~ dres           1.0
            31.fid  homo             n
   ACQUISITION      temp          25.0
sfrq       499.940          DEC2
tn              H1  dfrq2            0
at           3.000  dn2
np           48000  dpwr2            1
sw          8000.0  dof2             0
fb            4000  dm2              n
bs              16  dmm2             c
tpwr            62  dmf2           200
pw             4.0  dseq2
d1               0  dres2          1.0
tof              0  homo2            n
nt               1      PROCESSING
ct               1  lb            0.20
alock            y  wtfile
gain      not used  proc            ft
      FLAGS         fn        not used
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp
     DISPLAY        wbs
sp          1165.9  wnt
wp          3702.9
vs             112
sc               0
wc             250
hzmm         14.81
is          168.51
rfl         5145.8
rfp         3629.5
th               7
ins          1.000
nm  cdc  ph
```

Figure 51: ^{1}H NMR of reduced 14a to give 15a (referring to Table 2, entry 7) at 25 °C.



```
A292_2_after_Chromatography_fractions_11
to21_1HNMR_20060918

exp1  s2pul

      SAMPLE             DEC. & VT
date   Sep 18 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A29~ dmm              c
2_2_after_Chromato~ dmf            200
graphy_fractions_1~ dseq
1to21_1HNMR_200609~ dres           1.0
            18.fid  homo             n
   ACQUISITION      temp          25.0
sfrq       499.940           DEC2
tn              H1  dfrq2            0
at           3.000  dn2
np           48000  dpwr2            1
sw          8000.0  dof2             0
fb            4000  dm2              n
bs              16  dmm2             c
tpwr            62  dmf2           200
pw             4.0  dseq2
d1               0  dres2          1.0
tof              0  homo2            n
nt               1      PROCESSING
ct               1  lb            0.20
alock            y  wtfile
gain      not used  proc            ft
      FLAGS         fn        not used
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp
     DISPLAY        wbs
sp          1106.7  wnt
wp          2987.1
vs             224
sc               0
wc             250
hzmm         11.95
is           97.83
rfl         1500.2
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

Figure 52: ^{1}H NMR of reduced 14b to give 15b (referring to Table 3, entry 7) at 25 °C.

```
A292_1_after_chromatography_fractions_18
to27_1HNMR_20060918

exp1  s2pul

      SAMPLE           DEC. & VT
date   Sep 18 2006  dfrq       499.940
solvent      cdcl3  dn              H1
file /export/home/~ dpwr            30
users/antti/spectr~ dof              0
a/Antti/Cyclopropa~ dm             nnn
nation_project/A29~ dmm              c
2_1_after_chromato~ dmf            200
graphy_fractions_1~ dseq
8to27_1HNMR_200609~ dres           1.0
            18.fid  homo             n
   ACQUISITION      temp          25.0
sfrq       499.940         DEC2
tn              H1  dfrq2            0
at           3.000  dn2
np           48000  dpwr2            1
sw          8000.0  dof2             0
fb            4000  dm2              n
bs              16  dmm2             c
tpwr            62  dmf2           200
pw             4.0  dseq2
d1               0  dres2          1.0
tof              0  homo2            n
nt               1      PROCESSING
ct               1  lb            0.20
alock            y  wtfile
gain      not used  proc            ft
      FLAGS         fn        not used
il               n  math             f
in               n
dp               y  werr
hs              nn  wexp
     DISPLAY        wbs
sp          1090.4  wnt
wp          3046.6
vs             140
sc               0
wc             250
hzmm         12.19
is           62.07
rfl         1500.2
rfp              0
th               7
ins          1.000
nm  cdc  ph
```

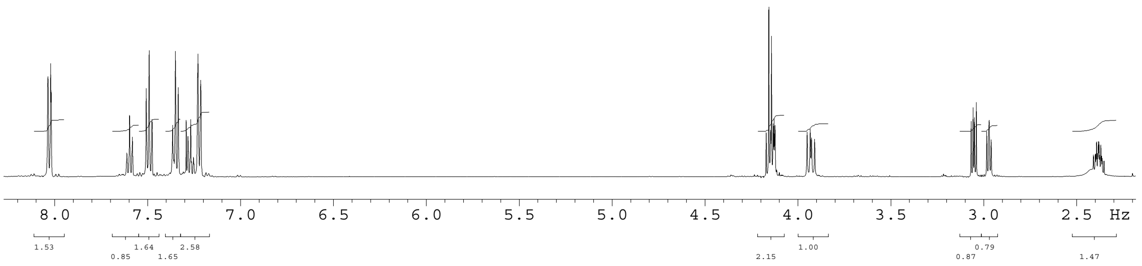
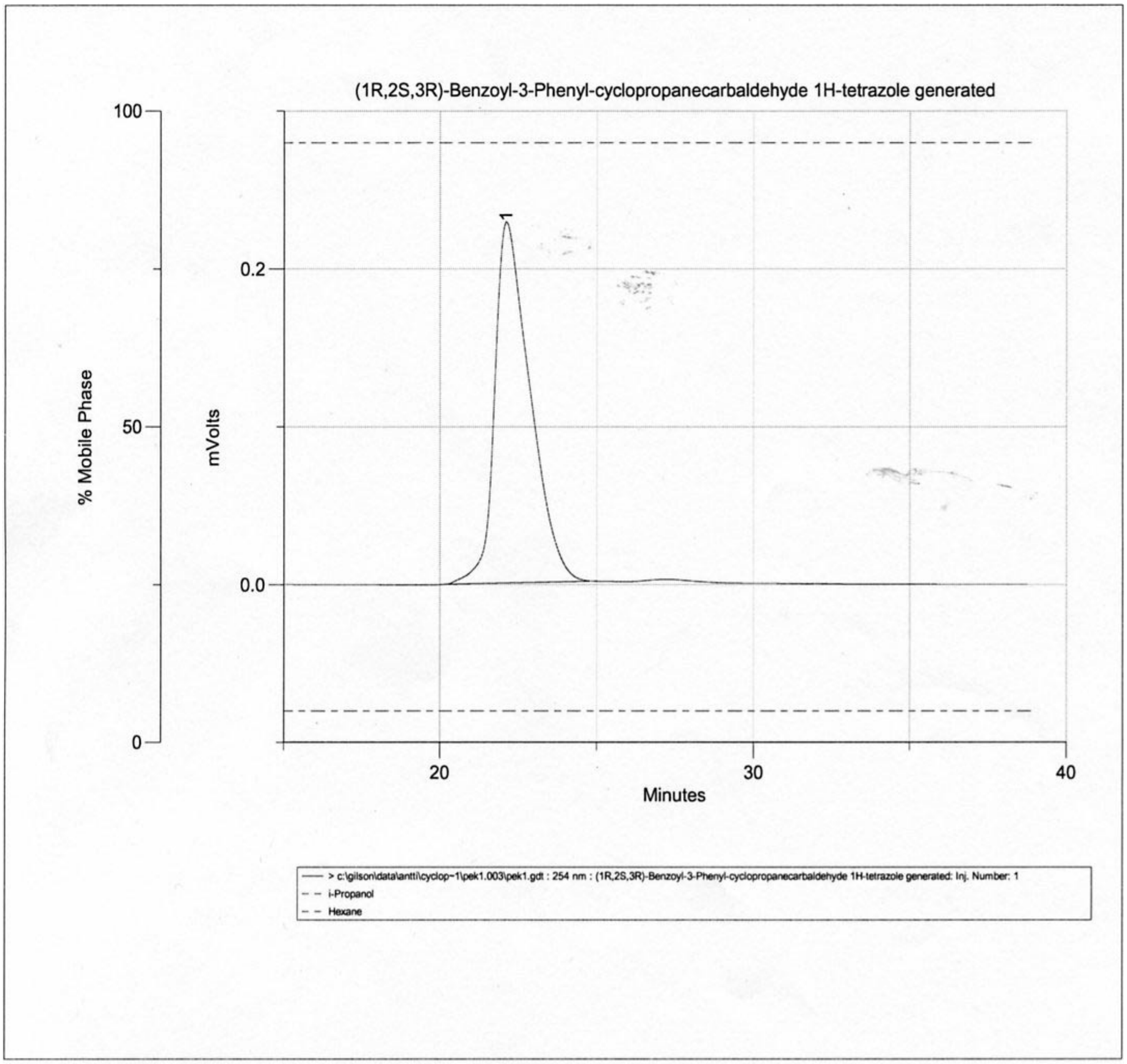
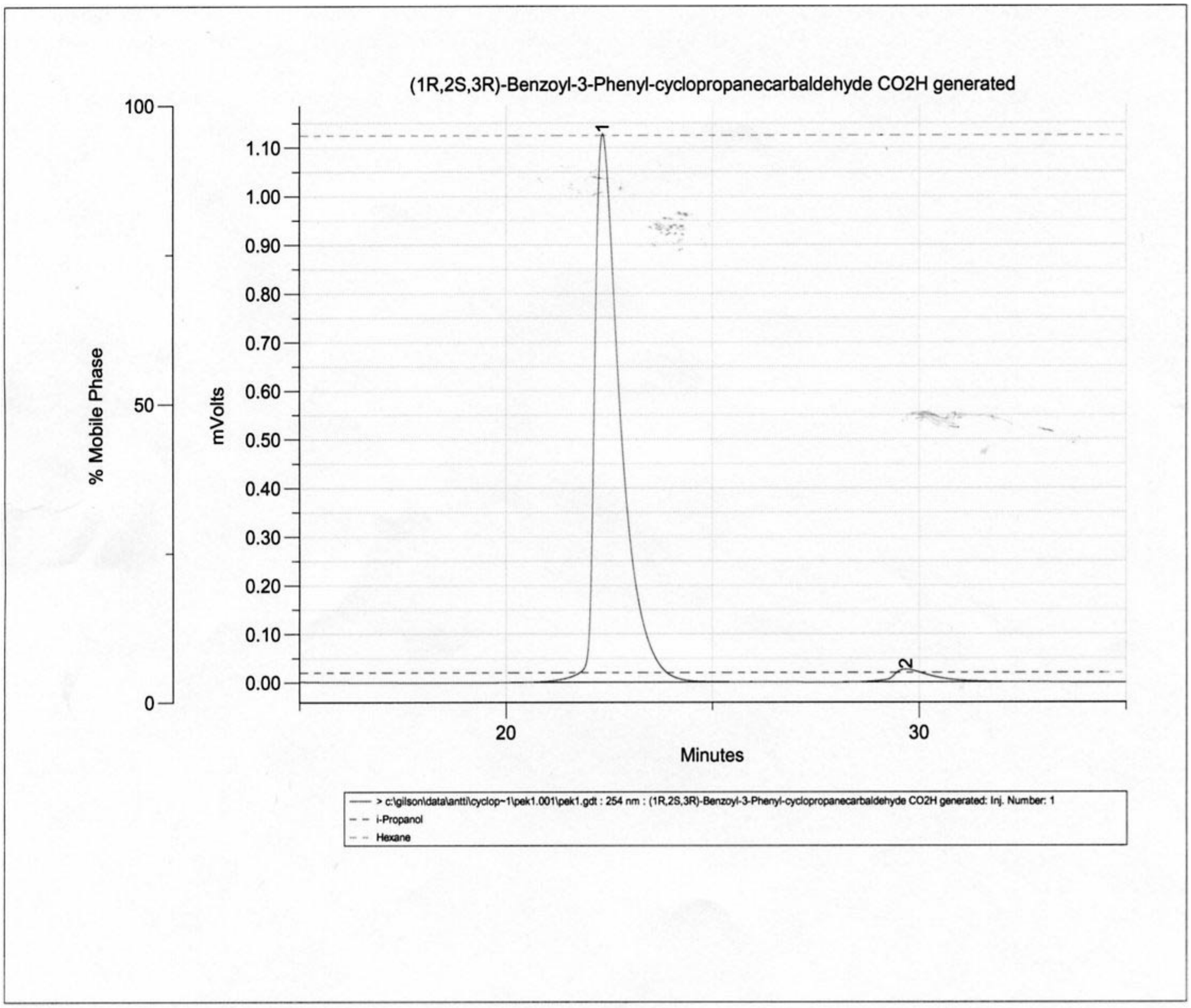


Figure 53: HPLC determination of ee (major diastereomer) 15a (referring to Table 2, entry 7).



	Inj. Number	Peak Name	R. Time	Area	Area %	Sample Descrip.				
1	1.00	1	22.15	301490560.0	100.00	lopropanecarl				

Figure 54: HPLC determination of ee (major diastereomer) 15b (referring to Table 3, entry 7).



	Inj. Number	Peak Name	R. Time	Area	Area %	Sample Descrip.				
1	1.00	1	22.35	320737216.0	96.53	cyclopropane				
2	1.00	2	29.70	29478692.00	3.47	cyclopropane				