# Supporting Information

## Catalytic Enantioselective Peroxidation of α,β-Unsaturated Ketones

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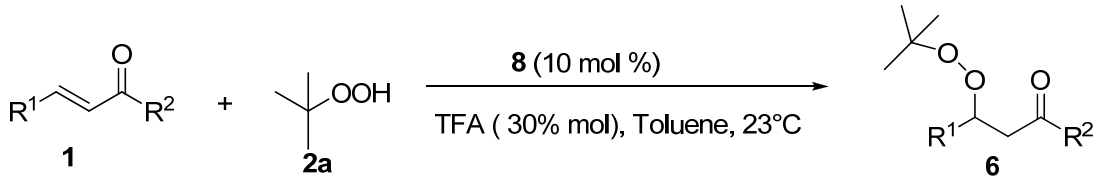
**General Information:** $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively). $^{1}H$ NMR spectra were internally referenced to tetramethylsilane signal and $^{13}C$ NMR spectra were internally referenced to $CDCl_3$ signal (δ = 77.0 ppm). Data for $^{1}H$ NMR are reported as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), and integration. Data for $^{13}C$ NMR are reported in terms of chemical shift (δ, ppm). Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrometer and are reported in frequency of absorption ($cm^{-1}$). High resolution mass spectra for all the new compounds were done by a Micromass Q-Tof instrument (ESI). Specific rotations were measured on a Jasco Digital Polarimeter. High performance liquid chromatography (HPLC) analysis was performed on a Hewlett-Packard 1100 Series instrument equipped with a quaternary pump using Daicel Chiralcel OJ or OD Columns (250 x 4.6 mm), Chiralpak AD or AS Columns (250 x 4.6 mm), or Regis Pirckle covalent (*R*, *R*) Whelk-O 1 Column (250 x 4.6 mm). UV absorption was monitored at 220 nm. Analytical gas-liquid chromatography (GLC) was performed on a Hewlett-Packard 6890 Series instrument equipped with a split mode capillary injection system and a flame ionization detector using HP chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm).

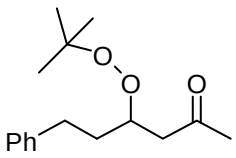
**Materials**: Enones **1** was prepared according to literature methods[1] except those which could be purchased from the Aldrich, ACROS or Alfa Aesar. Purchased compounds were used without further purification. *T*-butyl hydroperoxide (**2a,** 5.0-6.0 M in decane) and cumene hydroperoxde (**2b**, ~80% in cumene) were purchased from Aldrich, and 2-hydroperoxy-2-methoxypropane (**2c**) was prepared according to literature methods.[2] Quinine and quinidine were purchased from Aldrich., and used without further

purification. All the Cinchona alkaloid catalysts are prepared according to literature methods.[3]

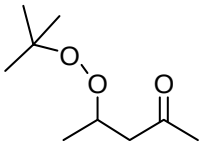
**1. General procedure for peroxidation of enones with TBHP.**



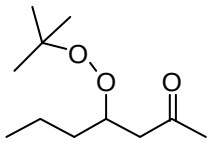

To a solution of enone **1** (0.3 mmol), catalyst **8** (0.03 mmol, 10 mol%), and trifluroacetic acid (6.9 μL, 0.09 mmol, 30 mol%) in toluene (0.3 ml) at room temperature was added *t*-butyl hydroperoxide **2a** (0.36 mmol, 1.2 equiv.). The reaction mixture was kept at room temperature for 4h, then passed through a short plug of silica gel for removal of the catalyst. The silica gel plug was washed with diethyl ether, the eluent was concentrated in *vacuo*, and the residue was subjected to silica gel flash chromatography. The racemic product for HPLC or GC analysis was prepared by mixing the products of Q-$NH_2$ and QD-$NH_2$ catalyzed reactions.



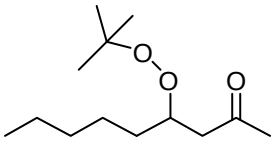

**6Aa** was obtained as a colorless oil (71.1 mg) in 90% yield after flash chromatography (Hexanes/Ethyl acetate = 10:1) and in 91% ee determined by HPLC [Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 0.8 mL/min, λ = 220 nm, 20.0°C, $t_r$ (major) = 11.12 min, $t_r$ (minor) = 10.01 min]. $[\alpha]_D^{25}$= 35.8 (*c* = 0.57, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 9H), 1.79-1.89 (m, 2H), 2.16 (s, 3H), 2.46 (dd, $J_1$ = 4.8 Hz, $J_2$ = 5.2 Hz, 1H), 2.62-2.70 (m, 1H), 2.74-2.80 (m, 1H), 2.90 (dd, $J_1$ = 6.0 Hz, $J_2$ = 6.8Hz, 1H), 4.43-4.47 (m, 1H), 7.14-7.18 (m, 3H), 7.24-7.28 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.34, 30.84, 31.85, 34.75, 47.53, 79.38, 80.33, 125.85, 128.28, 128.35, 141.69, 207.40; IR (neat) *v* 2978, 2931, 1715, 1604, 1497, 1455, 1363, 1242, 1197, 1053, 880, 748, 700. HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{16}H_{24}O_3Na$ 287.1623, found 287.1612.



**6Ba** was obtained as a colorless oil (45.2 mg) in 88% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) in 84% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after hydrogenation of the peroxide to the $\beta$-hydroxyl ketone [Inject Temp: 240 °C, FID Temp: 260 °C, Inlet pressure: 10 psi., Oven Temp: 50 °C, 5 min, 2 °C/min to 80°C, retention times: 38.4 min and 39.3 min]. $[\alpha]_D^{25} = 20$ ($c = 0.15$, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.18 (s, 9H), 2.16 (s, 3H), 2.39 (dd, $J_1 = 6.0$ Hz, $J_2 = 6.4$ Hz, 1H), 2.85 (dd, $J_1 = 6.0$ Hz, $J_2 = 6.4$ Hz, 1H), 4.42-4.49 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 18.47, 26.30, 30.91, 48.93, 76.17, 80.29, 207.28; IR (neat) $\nu$ 2976, 2926, 1717, 1457, 1364, 1242, 1198, 1094, 867. HRMS (ESI/[M+Na]$^+$) Calcd. For: $C_9H_{18}O_3Na$ 197.1154, found 197.1155.



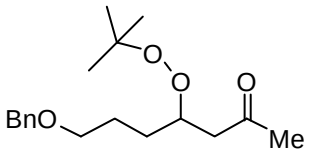
**6Ca** was obtained as a colorless oil (53.7 mg) in 91% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 90% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of the peroxide to the $\beta$-hydroxyl ketone [Inject Temp: 240 °C, FID Temp: 260 °C, Inlet pressure: 10 psi. Oven Temp: 50 °C , 5 min, 2.5°C/min to 100 °C, retention times: 38.0 min and 38.4 min]. $[\alpha]_D^{25} = 61.0$ ($c = 0.63$, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, $J = 6.8$Hz, 3H), 1.18 (s, 9H), 1.32-1.52 (m, 4H), 2.17 (s, 3H), 2.41 (dd, $J_1 = 4.8$ Hz, $J_2 = 5.2$ Hz, 1H), 2.84 (dd, $J_1 = 6.4$ Hz, $J_2 = 6.8$ Hz , 1H), 4.37-4.39 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 14.07, 18.87, 26.27, 30.89, 35.22, 47.72, 79.94, 80.29, 207.76; IR (neat) $\nu$ 2963, 2936, 2875, 1716, 1459, 1363, 1197, 1026, 886; HRMS (ESI/[M+Na]$^+$) Calcd. for: $C_{11}H_{22}O_3Na$ 225.1467, found 225.1471.



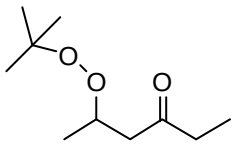
(+) **6Da** was obtained as a colorless oil (59.7 mg) in 86% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and

in 93% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of peroxide to the $\beta$-hydroxyl ketone [Inject Temp: 240 °C, FID Temp: 260 °C, Inlet pressure: 10 psi. Oven Temp: 50 °C, 5min, 5 °C/min to 100 °C, retention times: 101.0 min and 101.8 min]. $[\alpha]_D^{25}$ = 39.3 ($c$ = 0.61, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.87(t, $J$ = 6.4 Hz, 3H), 1.20 (s, 9H), 1.26-1.54 (m, 8H), 2.19 (s, 3H), 2.43 (dd, $J_1$ = $J_2$ = 4.8 Hz, 1H), 2.85 (dd, $J_1$ = $J_2$= 6.8 Hz, 1H), 4.37-4.41 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.98, 22.48, 25.25, 26.30, 30.93, 31.77, 33.00, 47.73, 80.18, 80.33, 207.82; IR (neat) $\nu$ 2932, 2862, 1716, 1460, 1363, 1197, 1054, 882. HRMS (ESI/[M+Na]$^+$) Calcd. for: $C_{13}H_{26}O_3Na$ 253.1780, found 253.1778.

**(-) 6Da** was obtained as a colorless oil (61.3mg) in 90% yield and in 90% ee from a reaction catalyzed by QD-$NH_2$ (10 mol %) in toluene (0.3 ml) at 23 °C for 4h. $[\alpha]_D^{25}$ = -41.4 ($c$ = 0.49, $CHCl_3$).

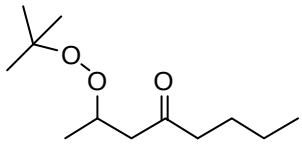



**6Ea** was obtained as a colorless oil (60.0 mg) in 65% yield after flash chromatography (Hexanes/Ethyl acetate=10:1) and in 91% ee determined by HPLC [Daicel Chiralcel AD, Hexanes / IPA = 99.5:0.5, 0.6 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 14.71 min, $t_r$ (minor) = 16.15 min]. $[\alpha]_D^{25}$= 35.1 ($c$ = 0.56, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H), 1.60-1.72 (m, 4H), 2.19 (s, 3H), 2.44 (dd, $J_1$ = 4.8 Hz, $J_2$ = 5.6 Hz, 1H), 2.88 (dd, $J_1$ =$J_2$ = 6.8Hz, 1H), 3.46-3.49 (m, 2H), 4.41-4.45 (m, 1H), 4.50 (s, 2H), 7.26-7.28 (m, 2H), 7.29-7.33 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.18, 26.61, 30.05, 31.18, 47.93, 70.40, 73.17, 80.08, 80.66, 127.76, 127.87, 128.59, 138.70, 207.77; IR (neat) $\nu$ 2978, 2935, 2859, 1715, 1454, 1363, 1197, 1101, 1028, 883, 738, 699; HRMS (ESI/[M+Na]$^+$) Calcd. for: $C_{18}H_{28}O_4Na$ 331.1885, found 331.1883.

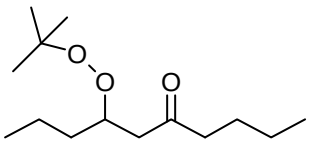



**6Fa** was obtained as a colorless oil (51.2 mg) in 90% yield after

flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 89% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of the peroxide to the $\beta$-hydroxyl ketone followed by the converting the hydroxyl group to the corresponding acetate form [Inject Temp: 250 °C, FID Temp: 220 °C, Inlet pressure: 13 psi., Oven Temp: 85 °C, retention times: 42.0 min and 42.6 min]. $\mathbf{[\alpha]_D^{25}}$ = 10.4 ($c$ = 0.67, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.03(t, $J$ = 7.2 Hz, 3H), 1.17 (s, 3H), 1.19 (s, 9H), 2.37 (dd, $J_1$ = 5.2 Hz, $J_2$ = 5.6 Hz, 1H), 2.40-2.51 (m, 2H), 2.83 (dd, $J_1$ = $J_2$ = 6.8 Hz, 1H), 4.47-4.50 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 7.55, 18.50, 26.25, 36.90, 47.68, 76.36, 80.22, 209.77; IR (neat) $\nu$ 2963, 2931, 2862, 1716, 1506, 1456, 1365, 1230, 1040, 884; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{10}H_{20}O_3Na$ 211.1310, found 211.1303.



**6Ha** was obtained as a colorless oil (61.2 mg) in 94% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 87% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of the peroxide to the $\beta$-hydroxyl ketone followed by the converting the hydroxyl group to the corresponding acetate form [Inject Temp: 250 °C, FID Temp: 220 °C, Inlet pressure: 13 psi., Oven Temp: 110 °C, retention times: 35.7 min and 37.6 min]. $\mathbf{[\alpha]_D^{25}}$ = 10.4 ($c$ = 0.52, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, $J$ = 7.2 Hz, 3H), 1.18 (s, 3H), 1.20 (s, 9H), 1.25-1.33 (m, 2H), 1.50-1.56 (m, 2H), 2.37 (dd, $J_1$ = $J_2$ = 6.0 Hz, 1H), 2.42-2.48 (m, 2H), 2.85 (dd, $J_1$ = 6.4 Hz, $J_2$ = 6.8 Hz 1H), 4.47-4.50 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.84, 18.51, 22.26, 25.64, 26.28, 43.53, 47.90, 76.25, 80.22, 209.45; IR (neat) $\nu$ 2977, 2935, 2875, 1715, 1459, 1410, 1364, 1198, 1143, 1028, 864; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{12}H_{24}O_3Na$ 239.1623, found 239.1615.

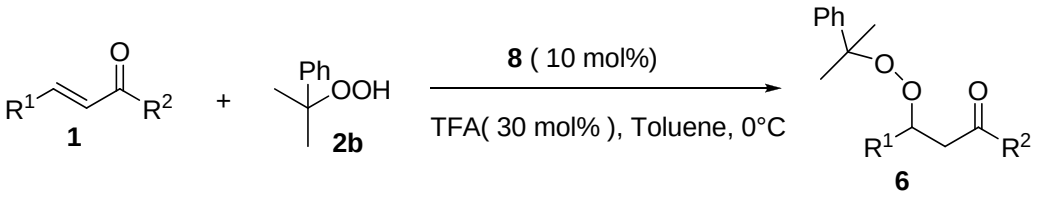


**6Ia(+)** was obtained as a colorless oil (57.1 mg) in 64%

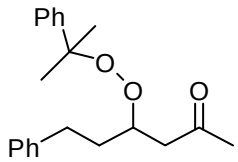
yield after flash chromatography(Hexanes/Ethyl acetate = 20:1) and in 94% ee. The ee was determined by the HPLC [Daicel Chiralcel AD-H, Hexanes / IPA = 99.2:0.8, 0.78 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 16.95 min, $t_r$ (minor) = 19.46 min] after the hydrogenation of the peroxide to the $\beta$ -hydroxyl ketone followed by the converting the hydroxyl group to the corresponding 4-chlorobenzylacetate form. $[\alpha]_D^{25}$ = 26.8 (*c* = 0.40, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 0.87(t, *J* = 6.4 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H), 1.20 (s, 9H), 1.26-1.53 (m, 8H), 2.39 (dd, $J_1$ = 4.8 Hz, $J_2$ = 5.6 Hz, 1H), 2.45-2.55 (m, 2H), 2.83 (dd, $J_1$ = $J_2$ = 6.8 Hz, 1H), 4.37-4.42 (m, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 13.86, 14.11, 18.90, 22.28, 25.35, 26.31, 35.32, 43.51, 46.75, 80.03, 80.28, 209.95; IR (neat) *v* 2961, 2935, 2874, 1714, 1465, 1363, 1198, 1050, 884; HRMS (ESI/$[M+Na]^+$) Calcd. For :$C_{14}H_{28}O_3Na$ 267.1936, found 267.1933.

**6Ia(-)** was obtained as a colorless oil (62.1 mg) in 77% yield and in 88% ee from a reaction catalyzed by QD-$NH_2$ (10% mol) in toluene (0.3 ml) at 20.0 °C for 4h.

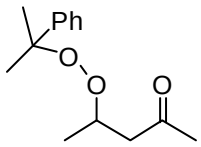
**2. General procedure for peroxidation of enones with cumene hydroperoxide.**



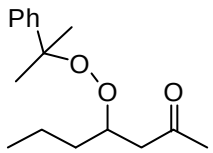

To a solution of enone **1** (0.3 mmol) catalyst **8** (0.03 mmol, 10 mol%) and trifluroacetic acid (6.9 μL, 0.09mmol, 30 mol%) in toluene(0.3 ml) at zero degree was added cumene hydroperoxide **2b** (0.36 mmol, 1.2 equiv.). The reaction mixture was kept at zero degree overnight then passed through a short plug of silica gel for removal of the catalyst. The silica gel plug was washed with diethyl ether, eluent was concentrated in *vacuo*, and the residue was subjected to silica gel flash chromatography. The racemic product for the HPLC or GC analysis was prepared by mixing the Q-$NH_2$ and QD-$NH_2$ catalyzed product.



**6Ab** was obtained as a colorless oil (69.5 mg) in 74% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 94% ee determined by HPLC [Daicel Chiralcel AS-H, Hexane / IPA = 99:1, 1.0 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 10.53 min, $t_r$ (minor) = 9.31 min]. $[\alpha]_D^{25}$ = 35.9 (*c* = 0.44, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.56 (s, 3H), 1.58 (s, 3H), 1.69-1.81 (m, 2H), 2.09 (s, 3H), 2.45 (dd, $J_1 = J_2 = 4.8$ Hz, 1H), 2.49-2.62 (m, 2H), 2.87 (dd, $J_1 = J_2 = 6.0$ Hz, 1H), 4.39-4.45 (m, 1H), 7.08-7.16 (m, 3H), 7.22-7.27 (m, 3H), 7.30-7.34 (m, 2H), 7.37-7.47 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 26.43, 26.64, 30.82, 31.67, 34.61, 47.55, 79.44, 82.90, 125.57, 125.82, 127.13, 128.00, 128.29, 128.33, 141.47, 145.21, 207.33; IR (neat) *v* 2983, 2926, 1706, 1496, 1448, 1376, 1362, 1267, 1155, 838, 764, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{21}H_{26}O_3Na$ 349.1780, found 349.1777.

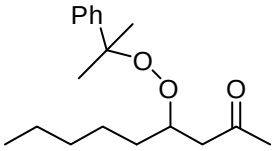


**6Bb** was obtained as a colorless oil (48.0 mg) in 70% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 92% ee determined by HPLC [Daicel Chiralcel AS-H, Hexane / IPA = 99:1, 1.0 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 11.86 min, $t_r$ (minor) = 10.36 min]. $[\alpha]_D^{25}$ = 22.4 (*c* = 0.17, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, $J = 6.4$ Hz, 3H), 1.58 (s, 3H), 1.62 (s, 3H), 2.11 (s, 3H), 2.40 (dd, $J_1 = 6.0$ Hz, $J_2 = 6.4$ Hz, 1H), 2.83 (dd, $J_1 = J_2 = 6.4$ Hz, 1H), 4.47-4.52 (m, 1H), 7.25-7.35 (m, 3H), 7.43-7.46 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 18.58, 26.33, 26.65, 30.79, 48.88, 76.18, 82.86, 125.49, 127.06, 127.99, 145.25, 207.20; IR (neat) *v* 2981, 2927, 2858, 1716, 1497, 1448, 1378, 1362, 1266, 1165, 1142, 1075, 1030, 857, 763, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{14}H_{20}O_3Na$ 229.1310, found 259.1300.

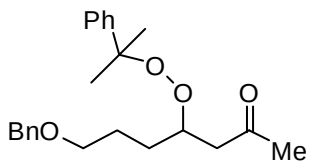


**6Cb** was obtained as a colorless oil (59.0 mg) in 75% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 92% ee determined by HPLC [Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1.0 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 6.55 min, $t_r$ (minor) = 7.07 min].

$[\alpha]_D^{25}$ = 40.9 (*c* = 0.53, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.20-1.51 (m, 4H), 1.57 (s, 6H), 2.14 (s, 3H), 2.44 (dd, $J_1$ = 5.2 Hz, $J_2$ = 5.6 Hz, 1H), 2.84 (dd, $J_1$ = $J_2$ = 6.4 Hz, 1H), 4.36-4.40 (m, 1H), 7.24-7.35 (m, 3H), 7.42-7.45 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.97, 18.71, 26.47, 26.50, 30.87, 35.11, 47.72, 79.88, 80.85, 125.51, 127.02, 127.93, 145.26, 207.66; IR (neat) *v* 2960, 2931, 2874, 1716, 1496, 1448, 1379, 1362, 1266, 1164, 1137, 1030, 848, 763, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{16}H_{24}O_3Na$ 287.1623, found 287.1618.

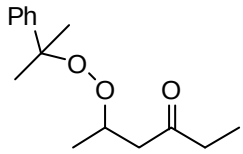



**6Db** was obtained as a colorless oil (86.7 mg) in 77% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 95% ee determined by HPLC [Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1.0 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) =7.13 min, $t_r$ (minor) = 6.85 min]. $[\alpha]_D^{25}$ = 35.1 (*c* = 1.06, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, *J* = 6.8 Hz, 3H), 1.18-1.50 (m, 8H), 1.56 (s, 3H), 1.57 (s, 3H), 2.14 (s, 3H), 2.44 (dd, $J_1$ = 4.8 Hz, $J_2$ = 5.2 Hz, 1H), 2.83 (dd, $J_1$ = 6.0 Hz, $J_2$ = 6.8 Hz 1H), 4.35-4.40 (m, 1H), 7.23-7.27 (m, 1H), 7.31-7.35 (m, 2H), 7.43-7.45 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.95, 22.46, 25.09, 26.43, 26.55, 30.87, 31.64, 32.90, 47.72, 80.10, 82.84, 125.53, 127.04, 127.93, 145.26, 207.70; IR (neat) *v* 2932, 2958, 2861, 1716, 1496, 1448, 1376, 1361, 1266, 1162, 867, 763, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{18}H_{28}O_3Na$ 315.1936, found 315.1932.

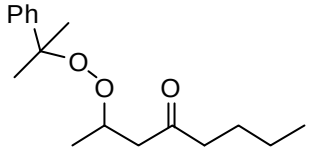



**6Eb** was obtained as a colorless oil (90.0 mg) in 82% yield after flash chromatography (Hexanes/Ethyl acetate = 10:1) and in 96% ee determined by HPLC [Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 18.07 min, $t_r$ (minor) = 19.15 min]. $[\alpha]_D^{25}$ = 17.2 (*c* = 1.41, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.55 (s, 3H), 1.57 (s, 3H), 1.57-1.63 (m, 4H), 2.13 (s, 3H), 2.44 (dd, $J_1$ = $J_2$ = 5.6 Hz, 1H), 2.85 (dd, $J_1$ = $J_2$ = 6.8 Hz, 1H), 3.35-3.38 (m, 2H), 4.36-4.42 (m, 1H), 4.44 (s, 2H),

7.25-7.38 (m, 5H), 7.42-7.56 (m, 5H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 25.68, 26.41, 26.58, 29.63, 29.68, 30.85, 31.74, 47.63, 69.98, 72.79, 79.76, 82.90, 125.53, 127.07, 127.49, 127.61, 127.96, 128.33, 138.50, 145.22, 207.45; IR (neat) *v* 2981, 2934, 2867, 1715, 1496, 1449, 1376, 1362, 1273, 1159, 1103, 1075, 1029, 862, 764, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{23}H_{30}O_4Na$ 393.2042, found 393.2040.

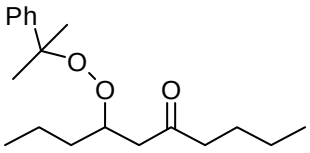


**6Fb** was obtained as a colorless oil (61.2 mg) in 75% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 94% ee determined by HPLC [Daicel Chiralcel AD-H, AD, Hexanes / IPA = 99.7:0.3, 0.6 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) =24.93 min, $t_r$ (minor) = 22.62 min]. $[\alpha]_D^{25}$ = 7.85 (*c* = 0.79, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.99(t, *J* = 7.2 Hz, 3H), 1.16(d, *J* = 6.4 Hz, 3H), 1.55 (s, 3H), 1.57 (s, 3H), 2.35 (dd, $J_1$ = 6.0 Hz, $J_2$ = 6.4Hz, 1H), 2.39-2.47 (m, 2H), 2.80 (dd, $J_1$ = 6.4 Hz, $J_2$ = 6.8 Hz, 1H), 4.47-4.53 (m, 1H), 7.23-7.26 (m, 1H), 7.33-7.42 (m, 2H), 7.42-7.44 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 7.50, 18.62, 26.30, 26.59, 36.82, 47.68, 76.37, 80.81, 125.46, 127.01, 127.94, 145.23, 209.66; IR (neat) *v* 2980, 2935, 1717, 1497, 1448, 1376, 1360, 1266, 1145, 1103, 928, 856, 764, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{15}H_{22}O_3Na$ 273.1454, found 273.1467.



**6Hb** was obtained as a colorless oil (55.4 mg) in 65% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 96% ee determined by HPLC [Daicel Chiralcel AD, AD-H, Hexanes / IPA = 99.5:0.5.0, 0.4ml/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 36.66 min, $t_r$ (minor) = 34.07 min]. $[\alpha]_D^{25}$ = 8.2 (*c* = 0.69, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88(t, *J* = 7.2Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 3H), 1.22-1.31 (m, 2H), 1.43-1.51 (m, 2H), 1.56 (s, 3H), 1.58 (s, 3H), 2.35 (dd, $J_1$ = 6.8 Hz, $J_2$ = 7.2 Hz, 1H), 2.38-2.42 (m, 2H), 2.81 (dd, $J_1$ = 6.0 Hz, $J_2$ = 6.8 Hz, 1H), 4.48-4.53 (m, 1H), 7.23-7.26 (m, 1H), 7.31-7.35 (m, 2H), 7.43-7.45 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.84, 18.62,

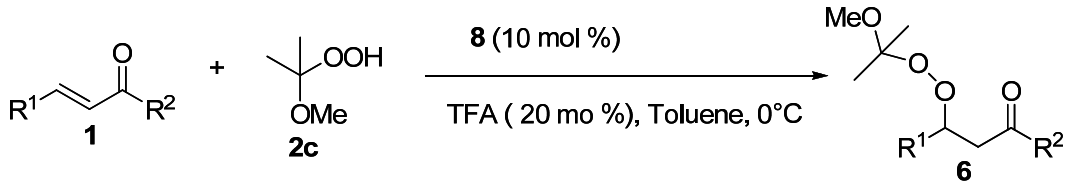
22.24, 25.60, 26.38, 26.59, 43.48, 47.89, 76.29, 82.83, 125.46, 127.02, 127.95, 145.25, 209.37; IR (neat) *v* 2959, 2935, 2872, 1717, 1459, 1448, 1410, 1376, 1363, 1266, 1144, 1031, 931, 854, 763, 699; HRMS (ESI/[M+Na]$^+$) Calcd. for: $C_{17}H_{26}O_3Na$ 301.1780, found 301.1779.

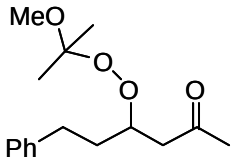


**6Ib** was obtained as a colorless oil (48.7 mg) in 55% yield after flash chromatography (Hexanes/Ethyl acetate =20:1) and in 97% ee determined by HPLC [Daicel Chiralcel AD, AD-H, Hexanes / IPA = 99.5:0.5, 0.4 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 33.14 min, $t_r$ (minor) = 30.76 min]. **$[\alpha]_D^{25}$** = 16.2 (*c* = 0.37, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 6.8Hz, 3H), 0.89 (t, *J* = 7.2Hz, 3H), 1.16-1.53 (m, 8H), 1.57 (s, 6H), 2.39 (dd, $J_1$= 5.6 Hz, $J_2$ = 6.4 Hz, 1H), 2.42-2.47 (m, 2H), 2.82(dd, $J_1$ = 6.0 Hz, $J_2$ = 6.8 Hz, 1H), 4.38-4.44 (m, 1H), 7.23-7.26 (m, 1H), 7.31-7.34 (m, 2H), 7.42-7.44 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.87, 14.00, 18.72, 22.27, 25.62, 26.44, 26.56, 35.21, 43.54, 46.76, 79.98, 82.84, 125.53, 127.01, 127.91, 145.26, 209.85; IR (neat) *v* 2960, 2874, 1715, 1496, 1449, 1378, 1360, 1266, 1157, 855, 763, 700; HRMS (ESI/[M+Na]$^+$) Calcd. For : $C_{19}H_{30}O_3Na$ 329.2093, found 329.2083.

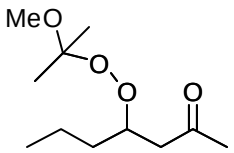
**3. General procedure for peroxidation of enones the conjugate addition between the enones and the 2-hydroperoxy-2-methoxypropane:**

To a solution of enone **1** (0.3 mmol) catalyst **8** (0.03 mmol, 10 mol%) and trifluroacetic acid ( 4.6μL, 0.06mmol, 20 mol%)in toluene (0.3 ml) was added 2-hydroperoxy-2-methoxypropane **2c** (0.36 mmol, 5M in toluene, 1.2 equiv.). The reaction mixture was kept overnight then passed through a short plug of silica gel for removal of the catalyst. The silica gel plug was washed with diethyl ether, eluent was concentrated in *vacuo*, and the residue was subjected to silica gel flash chromatography. The racemic product for the HPLC or GC analysis was prepared by mixing the Q-$NH_2$ and QD-$NH_2$ catalyzed product.

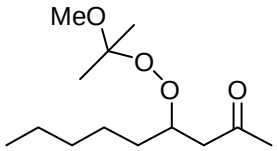


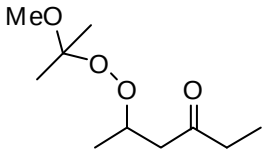
**6Ac** was obtained as a colorless oil (52.1 mg) in 62% yield after flash chromatography (Hexanes/Ethyl acetate = 10:1) and in 92% ee determined by HPLC [Daicel Chiralcel AD-H, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 11.68 min, $t_r$ (minor) = 12.96 min]. $[\alpha]_D^{25}$ = 38.4 (*c* = 1.15, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 6H), 1.83-1.93 (m, 2H), 2.19 (s, 3H), 2.53 (dd, $J_1$ =$J_2$ = 5.6 Hz, 1H), 2.68-2.74 (m, 1H), 2.77-2.81(m, 1H), 2.91 (dd, $J_1$ = $J_2$ = 6.0 Hz, 1H), 3.29 (s, 3H), 4.49-4.53 (m, 1H), 7.16-7.21 (m, 3H), 7.26-7.30 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 22.68, 22.87, 30.78, 31.72, 34.65, 47.49, 49.30, 79.42, 104.73, 125.90, 128.34, 128.38, 141.56, 206.97; IR (neat) *v* 2994, 2944, 1715, 1604, 1496, 1455, 1381, 1368, 1262, 1210, 1183, 1153, 1071, 842, 749, 700; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{16}H_{24}O_4Na$ 303.1572, found 303.1560.



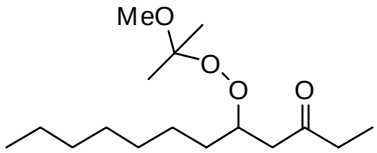
**6Cc** was obtained as a colorless oil (44.8 mg) in 70% yield after flash chromatography (Hexanes/Ethyl acetate =10:1) and in 95% ee. The ee was determined by GC HP Chiral (20% Permethylated *β*-Cyclodextrin, 30m x 0.25 mm) after hydrogenation of peroxide to the *β*-hydroxyl ketone [ Inject Temp: 240 °C, Fid Temp: 260 °C, Inlet pressure: 10 psi. Oven Temp: 50 °C, 5min, 2.5°C/min to 100°C, retention times: 38.0min and 38.3min]. $[\alpha]_D^{25}$ = 23.1 (*c* = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.95(t, *J* = 6.8 Hz, 3H), 1.26 (s, 3H), 1.37 (s, 3H), 1.40-1.58 (m, 4H), 2.22 (s, 3H), 2.50 (dd, $J_1$ = 5.2Hz, $J_2$ =5.6 Hz, 1H), 2.87 (dd, $J_1$ = $J_2$ = 6.8Hz, 1H), 3.29 (s, 3H), 4.46-4.50 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.95, 18.78, 22.61, 22.74, 30.80, 35.06, 47.62, 49.21, 79.91, 104.61, 207.29; IR (neat) *v* 2994, 2961, 1716, 1465, 1368, 1211, 1185, 1160, 1137, 1072, 839. HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{11}H_{22}O_4Na$ 241.1416, found 241.1410.



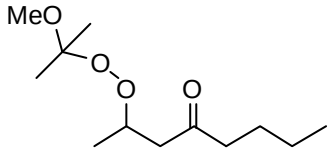

**6Dc** was obtained as a colorless oil (45.0 mg) in 62% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 95% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of peroxide to the $\beta$-hydroxyl ketone [ Inject Temp: 240 °C, Fid Temp: 260 °C, Inlet pressure: 10 psi. Oven Temp: 50 °C, 5 min, 5 °C/min to 100 °C, retention times: 82.9 min and 83.2 min]. $[\alpha]_D^{25}$ = 30.0 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88(t, $J$ = 6.4 Hz, 3H), 1.37 (s, 6H), 1.40-1.59 (m, 8H), 2.21 (s, 3H), 2.50 (dd, $J_1$=4.8 Hz, $J_2$=5.2 Hz, 1H), 2.86 (dd, $J_1$ = $J_2$ = 6.8 Hz, 1H), 3.29 (s, 3H), 4.44-4.49 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 13.98, 22.46, 22.65, 22.75, 25.13, 30.82, 31.68, 32.89, 47.61, 49.23, 80.14, 104.62, 207.33; IR (neat) $\nu$ 2999, 2935, 2858, 1716, 1465, 1368, 1265, 1211, 1072, 839; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{13}H_{26}O_4Na$ 269.1729, found 269.1728.




**6Fc** was obtained as a colorless oil (37.5 mg) in 63% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 94% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of the peroxide to the $\beta$-hydroxyl ketone followed by the converting the hydroxyl group to the corresponding acetate [ Inject Temp: 250 °C, Fid Temp: 220 °C, Inlet pressure: 13 psi., Oven Temp: 85 °C. retention times: 42.0 min and 42.6 min.]. $[\alpha]_D^{25}$ = 4.7 ($c$ = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.06 (t, $J$=7.2 Hz, 3H), 1.24 (d, $J$ = 6.0 Hz, 3H), 1.36 (s, 3H), 1.37 (s, 3H), 2.44 (dd, $J_1$ = $J_2$ = 5.6 Hz, 1H), 2.48-2.56 (m, 2H), 2.88 (dd, $J_1$ = 6.0 Hz, $J_2$ =6.4 Hz, 1H), 3.29 (s, 3H), 4.50-4.62 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 7.58, 18.66, 22.65, 22.71, 36.86, 47.66, 49.25, 76.40, 104.58, 209.46; IR (neat) $\nu$ 2980, 2942, 2862, 1716, 1459, 1378, 1369, 1211, 1185, 1142, 1072, 930, 837; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{10}H_{20}O_4Na$ 227.1259, found 227.1257.



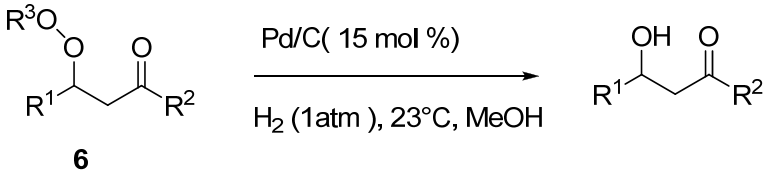
**6Gc** was obtained as a colorless oil (36.0 mg) in 41% yield after flash chromatography (Hexanes/Ethyl acetate = 10:1) and in 94% ee. The ee was determined by HPLC [ (R,R)Whelk-O 1, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 11.91min, $t_r$ (minor) = 13.82 min] after the hydrogenation of the peroxide to the $\beta$ -hydroxyl ketone followed by the converting the hydroxyl group to the corresponding benzylacetate form. $[\alpha]_D^{25}$ = 15.8 (*c* =1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 6.4 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H), 1.42 (s, 3H), 1.43(s, 3H), 1.45-1.66 (m, 12H), 2.21 (dd, $J_1$ = 7.2 Hz, $J_2$ = 7.6 Hz, 1H), 2.28-2.60 (m, 2H), 2.84 (dd, $J_1$=$J_2$=6.4Hz, 1H), 3.28 (s, 3H), 4.44-4.50 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 7.59, 14.07, 22.60, 22.65, 22.79, 25.51, 29.13, 29.49, 30.92, 31.76, 33.05, 36.85, 46.48, 49.23, 80.37, 104.61, 209.90; IR (neat) *v* 2929, 2858, 1716, 1460, 1368, 1211, 1183, 1153, 1113, 1073, 835; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{16}H_{32}O_4Na$ 311.2198, found 311.2201.



**6Hc** was obtained as a colorless oil(41.0 mg) in 60% yield after flash chromatography (Hexanes/Ethyl acetate = 20:1) and in 94% ee. The ee was determined by GC HP Chiral column (20% Permethylated $\beta$ -Cyclodextrin, 30m x 0.25 mm) after the hydrogenation of the peroxide to the $\beta$ -hydroxyl ketone followed by the converting the hydroxyl group to the acetate form [ Inject Temp: 250 °C, Fid Temp: 220 °C, Inlet pressure: 13 psi, Oven Temp: 110 °C, retention times: 37.5 min and 39.1 min]. $[\alpha]_D^{25}$ = 14.1 (*c* = 1.0, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.91(t, *J* = 7.2 Hz, 3H), 1.23 (d, *J* = 6.0 Hz, 3H), 1.25-1.36 (m, 2H), 1.37 (s, 6H), ,1.52-1.58 (m, 2H), 2.43 (dd, $J_1$ = $J_2$ = 6.4 Hz, 1H), 2.46-2.51 (m, 2H), 2.88 (dd, $J_1$ = 5.6 Hz, $J_2$ = 6.0 Hz, 1H), 3.29 (s, 3H), 4.55-4.62 (m, 1H); $^{13}$**C** NMR (100 MHz, $CDCl_3$) δ 13.84, 18.64, 22.25, 22.65, 22.72, 25.62, 43.44, 47.85, 49.23, 76.27, 104.55, 209.10; IR(neat) *v* 2960, 2935, 1715, 1461, 1369, 1211, 1142, 1072, 932, 839;. HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{12}H_{24}O_4Na$

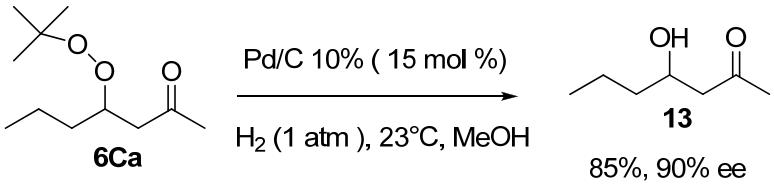
255.1572, found 255.1574.

**4. General procedure for the hydrogenation of Peroxide adducts:**



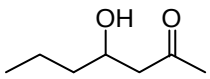

**6**

To a solution of peroxide **6** (0.1 mmlol) in methanol (5ml) at room temperature, was added 15 mol % Pd/C (10 %). The reaction mixture was kept under hydrogen atmosphere for 4 h then passed through celite. The celite was washed with diethyl ether, the eluent was concentrated in *vacuo*, and the residue was subjected to silica gel flash chromatography.

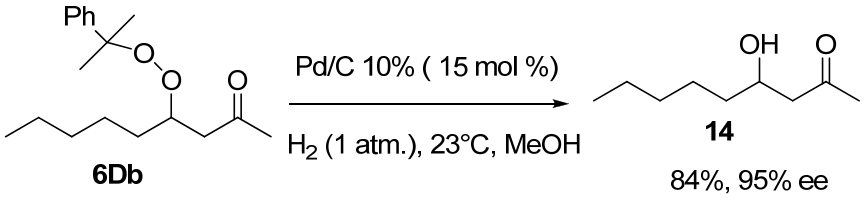


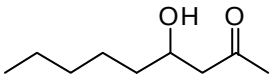

**6Ca** **13**

85%, 90% ee



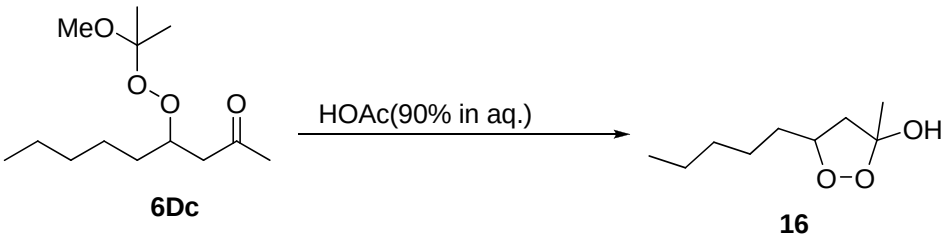

**13** was obtained as a colorless oil in 85% yield. The reaction mixture was stirred at 23 °C for 4h with 15% Pd/C (10 %) in methanol under the hydrogen atmosphere for 4 h, then passed through the celite. The celite was washed with diethyl ether, and the eluent was concentrated in vacuo, and the residue was subjected to silica gel flash chromatography (Hexanes/Ethyl acetate = 3:1) to get the product. The ee of the product is 90%, which was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) [ Inject Temp: 240 °C, FId Temp: 260 °C, Inlet pressure: 10 psi. Oven Temp: 50 °C, 5 min, 2.5 °C/min to 100 °C, retention times: 38.0 min and 38.4 min]. $[\alpha]_D^{25}$ = -48.0 (*c* = 0.38, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, $J_1$ = 7.2 Hz, 3H), 1.26-1.54 (m, 4H), 2.19 (s, 3H), 2.53 (dd, $J_1$ = 8.4 Hz, $J_2$ = 9.2 Hz, 1H), 2.63 (dd, $J_1$ = 8.4 Hz, $J_2$ = 9.2 Hz, 1H), 2.97 (s, 1H), 4.03-4.06 (m, 1H). According to literature report{($[\alpha]_D^{25}$ = -49.6 (*c* = 0.23, $CHCl_3$)}[4], the absolute configuration of **13** is *R*, therefore, the absolute configuration of **6Ca** is also ***R*.**



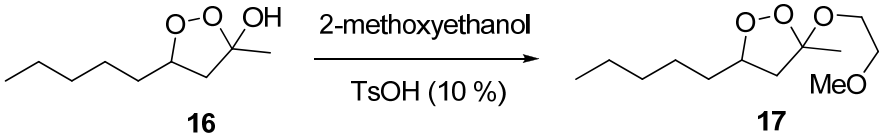

**14** was obtained as a colorless oil in 84% yield. The reaction mixture was stirred at 23 °C for 4h with 15% Pd/C (10 %) in methanol under the hydrogen atmosphere for 4 h, then passed through the celite. The celite was washed with diethyl ether, and the eluent was concentrated in vacuo, and the residue was subjected to silica gel flash chromatography (Hexanes/Ethyl acetate=3:1) to get the product. The ee of the product is 90%, which was determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) [ Inject Temp: 240 °C, FID Temp: 260°C, Inlet pressure 10 psi. Oven Temp: 50°C, 5min, 5°C/min to 100 °C, retention times: 101.0 min and 101.8 min]. $[\alpha]_D^{25}$= -48 ($c$ = 0.38, $CHCl_3$). $^1$H (400 MHz, $CDCl_3$) δ 0.89(t, $J_1$ = 6.8 Hz, 3H), 1.30-1.51 (m, 8H), 2.18 (s, 3H), 2.53 (dd, $J_1$ = $J_2$ = 9.2 Hz, 1H), 2.63 (dd, $J_1$ = $J_2$ = 9.2 Hz, 1H), 2.95 (s, 1H), 4.02-4.04 (m, 1H).

**5. Transformation from peroxide to 1,2-Dioxolane.**



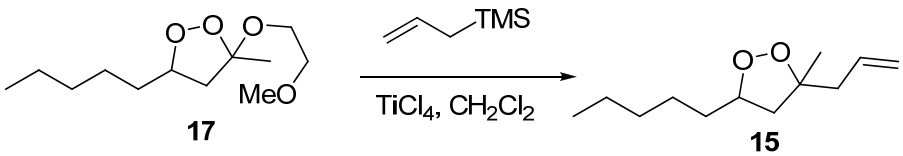

To a compound **6Dc** (100 mg, 0.41 mmol) was added 90% acetic acid in the water at room temperature. After stirring at room temperature for 1.5 h, the solvent was removed under reduced pressure. Compound **2** (56 mg, dr = 1 : 1) was obtained as a colorless oil by flash chromatography (silica gel: Hexanes : EtOAc = 5 : 1). yield: 81%, the mixture of two diasteremor $^1$H NMR (400 MHz, $CDCl_3$) δ 0.87-0.90 (m, 6H )

1.26-1.71 (m,22 H ), 2.20-2.33 (m, 2H), 2.66-2.71 (m, 1H), 2.80-2.85 (m, 2H), 4.33-4.36 (m, 1H), 4.42-4.46 (m, 1H).




**16** **17**

TsOH (5 mg) was added to the compound **16** ( 56 mg, 0.32 mmol ) in 3 mL 2-methoxyethanol, After stirred at room temperature for 24 hrs, the solvent was removed under reduced pressure. Compound **17** (57 mg, dr = 1 : 1) was obtained as a colorless oil by flash chromatography (silica gel: Hexanes : EtOAc = 7 : 1). yield: 75 %, one diasteremor **17a** $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88(t, *J* = 6.8 Hz, 3H), 1.29-1.71 (m, 11H), 2.15 (dd, *J* = 6.0 Hz, 12.4 Hz, 1H), 2.89 (dd, *J* = 7.2 Hz, 12.0 Hz, 1H), 3.39 (s, 3H), 3.50-3.77 (m, 4H), 4.42-4.45 (m, 1H). The other diasteremor **17b** $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88(t, *J* = 6.0 Hz, 3H), 1.29-1.71 (m, 11H), 2.43 (dd, *J* = 8.8 Hz, 12.8 Hz, 1H), 2.57 (dd, *J* = 8.0 Hz, 12.8 Hz, 1H), 3.40 (s, 3H), 3.47-3.76 (m, 4H), 4.29-4.36 (m, 1H).

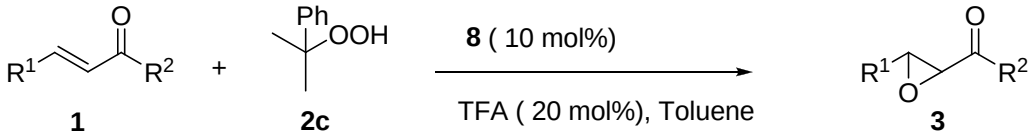



**17** **15**

Under Argon atmosphere, $TiCl_4$ ( 0.27 ml, 1 M in $CH_2Cl_2$) was added to the compound **17** ( 55 mg, 0.24 mmol ) and allyltrimethylsilane ( 114 uL, 0.71 mmol) in 2 mL $CH_2Cl_2$ at -78$^o$C, After stirred for 30 min, the reaction was quenched by saturate $NaHCO_3$, the mixture was allowed to warm up to room temperature and was extracted with ethyl acetate (5 mL X 3). The organic phase was collected together and dried over $Na_2SO_4$. The solvent was removed in *vacuo* to afford a light yellow oil. **15** ( 24 mg ) by flash chromatography (silica gel: Hexanes : EtOAc = 7 : 1). dr = 4 : 1, yield: 47 %, the major : $^1$H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.4 Hz, 1H), 1.21-1.55 (m, 7H),

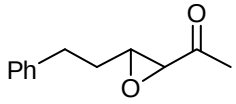
1.33 (s, 3H), 1.64-1.70 (m, 1H), 1.87 (dd, *J* = 6.8 Hz, 11.6 Hz, 1H), 2.31-2.37 (m, 2H), 2.55 (dd, *J* = 6.8 Hz, 11.6 Hz, 1H), 4.19-4.26 (m, 1H), 5.09-5.13 (m, 2H), 5.76-5.87 (m, 1H). the minor : $^1$H NMR (400 MHz, $CDCl_3$) δ 1.21-1.55 (m, 10H), 1.29 (s, 3H), 1.64-1.70 (m, 1H), 2.07 (dd, *J* = 8 Hz, 19.6 Hz, 1H), 2.27-2.46 (m, 3H), 4.19-4.29 (m, 1H), 5.09-5.13 (m, 2H), 5.76-5.87 (m, 1H).; HRMS (ESI/$[M+Na]^+$) Calcd. for: $C_{12}H_{22}O_2$: 221.1517, Found: 221.1506.

**6. General procedure for epoxidation of the enones with cumene hydroperoxide**

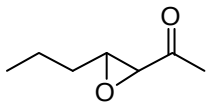



**1** **2c** **3**

To a solution of Enone **1** (0.3 mmol) catalyst **8** (0.03 mmol, 10 mol %) and trifluroacetic acid ( 4.6μL, 0.06mmol, 20 mol%) in toluene at room temperature (0.3 ml) was added **2c** (0.36 mmol, 1.2 equiv.). The reaction mixture was kept at certain temperature for 24-72h then passed through a short plug of silica gel for removal of the catalyst. The silica gel plug was washed with diethyl ether, the eluent was concentrated in *vacuo*, and the residue was subjected to silica gel flash chromatography. The racemic product was prepared according to literature methods[5].

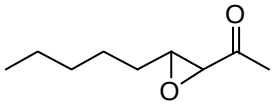



**3Ab** was obtained as a colorless oil (49.9mg) in 88% yield after flash chromatography (Hexanes/Ethyl acetate = 10:1) and in 97% ee [determined by HPLC Daicel Chiralcel AD-H, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm, 20.0 °C, $t_r$ (major) = 19.84 min, $t_r$ (minor) = 12.65 min]. $[\alpha]_D^{25}$ = -15.6 (*c* = 0.51, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 1.93-1.98 (m, 2H), 2.01(s, 3H), 2.78-2.82 (m, 2H), 3.09-3.12 (m, 1H ) 3.17 (s, 1H), 7.18-7.24 (m, 3H), 7.26-7.31 (m, 2H).

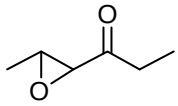



**3Cb** was obtained as a colorless oil (33.5 mg) in 91% yield after flash chromatography (Hexanes/Ethyl acetate =30:1) and in 97% ee [determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250 °C, FID Temp: 260 °C, Inlet pressure: 13 psi., Oven Temp:

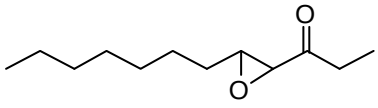
90 °C, retention times: 16.44 min and 17.32 min]. **[α]$_D^{25}$** = -52.3 (*c* = 0.91, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.2 Hz, 3H), 1.47-1.63 (m, 4H), 2.07 (s, 3H), 3.06-3.10 (m, 1H), 3.19 (d, *J* = 2 Hz, 1H).



**3Db** was obtained as colorless oil (43.4 mg) in 91% yield after flash chromatography (Hexanes/Ethyl acetate = 30:1) and in 97% ee [determined by GC HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250 °C, FID Temp: 260 °C, Inlet pressure: 13 psi., Oven Temp: 102 °C retention times: 34.48 min and 35.60 min]. **[α]$_D^{25}$** = -44.3 (*c* = 1.14, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.43-1.49 (m, 4H), 1.55-1.66 (m, 4H), 2.06 (s, 3H), 3.0 (t, *J* = 4.8 Hz, 1H), 3.18 (s, 1H). Acoording to literature report{**[α]$_D^{25}$** = -38.7 (*c* = 0.75, $CHCl_3$)}[6], the absolute configuration of **3Db** is **(**3*S***,** 4*R***).**

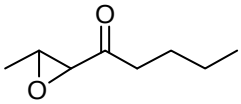


**3Fb** was obtained as colorless oil (19.5 mg) in 55% yield. The reaction mixture was heated at 55°C for 24h, then subjected to flash chromatography(Hexanes/Ethyl acetate = 30:1) to get the product. The ee of the product is 97%, which was determined by GC [HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250 °C, Fid Temp: 260 °C, Inlet pressure: 13psi., Oven Temp: 73 °C, retention times: 18.12 min and 19.40 min]. **[α]$_D^{25}$** = -13.8 (*c* = 0.13, $CHCl_3$); **$^1$**H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.6 Hz, 3H), 1.23 (d, *J* = 4.8 Hz, 3H), 2.27-2.37 (m, 1H), 2.42-2.51 (m, 1H), 3.12-3.3.15 (m, 1H), 3.19 (s, 1H).



**3Gb** was obtained as colorless oil (33.2 mg) in 58% yield. The reaction mixture was heated at 55°C for 24h, then subjected to flash chromatography (Hexanes/Ethyl acetate = 30:1) to get the product. The ee of the product is 96%, which was determined by GC [HP Chiral

column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250 °C, Fid Temp: 260 °C, Inlet pressure: 13 psi., Oven Temp: 115 °C, retention times: 97.74 min and 99.61 min]. $[\alpha]_D^{25}$ = -15.2 (*c* = 0.50, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H), 1.21-1.32 (m, 8H), 1.43-1.50 (m, 2H), 1.58-1.67 (m, 2H), 2.27-2.37 (m, 1H), 2.42-2.50 (m, 1H), 3.03-3.06 (m, 1H), 3.23 (s, 1H).



**3Hb** was obtained as colorless oil (32.5 mg) in 71% yield. The reaction mixture was heated at 55°C for 24h, then subjected to flash chromatography (Hexanes/Ethyl acetate = 30:1) to get the product. The ee of the product is 97%, which was determined by GC [HP Chiral column (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250 °C, FID Temp: 260 °C, Inlet pressure: 13 psi., Oven Temp: 80 °C, retention times: 47.97 min and 49.11 min]. $[\alpha]_D^{25}$ = -19.0 (*c* = 0.70, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.8 Hz, 3H), 1.26-1.36 (m, 3H), 1.40-1.43 (m, 2H), 1.51-1.58 (m, 2H), 2.26-2.32 (m, 1H), 2.39-2.46 (m, 1H), 3.13-3.3.14 (m, 1H), 3.18 (s, 1H).

References:

(1) Singh, R. P.; Bartelson, K.B.; Wang, Y.; Su, H.; Lu, X.; Deng, L.; *J. Am. Chem. Soc.* **2008**, *30*, 2422.

(2) Dussault, P.; Sahli, A.; *J. Org. Chem.***1992**, *57*, 1009.

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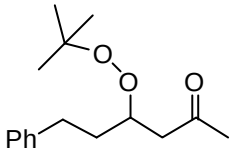
(4) Olivier, L; *ARKIVOC* (Gainesvile, FL, United States) **2007**, P94-106.

(5) Yadav, K.V.; Kaporr, K. K.; *Tetrahedron* **1995**, *51*, 8573.

(6) Bougauchi, S.; Watanabe, T.; Arai, T; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119*, 2329.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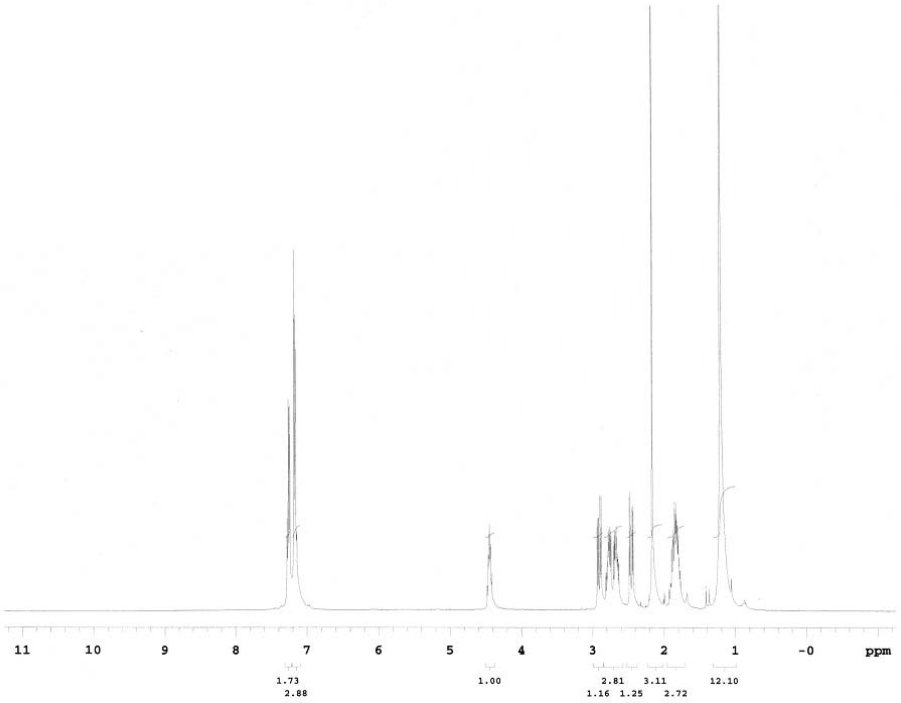
O
O
Ph

**6Aa**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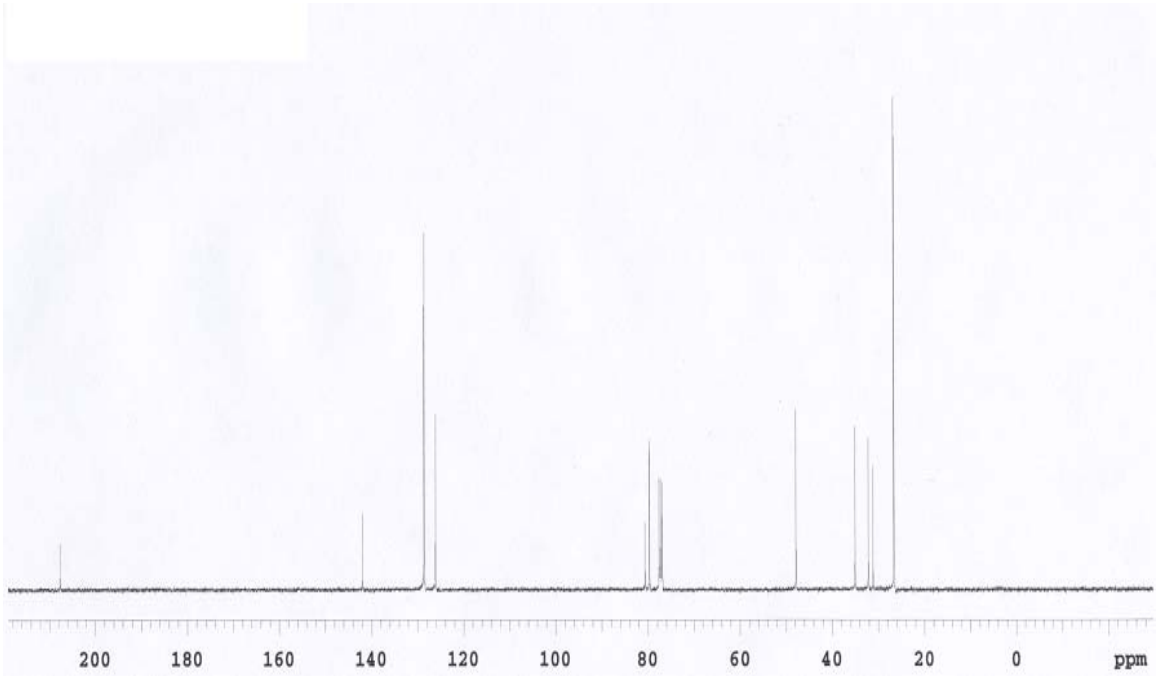
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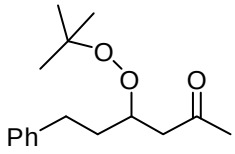
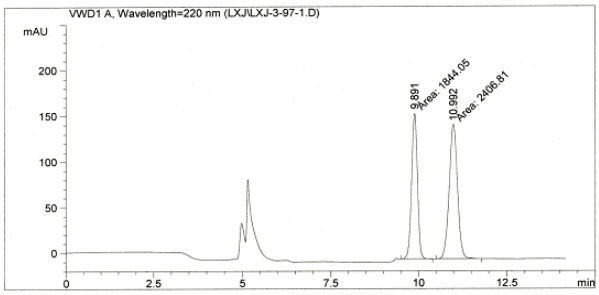



**6Aa**

Mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

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================================================================================

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Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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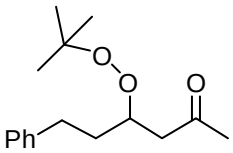
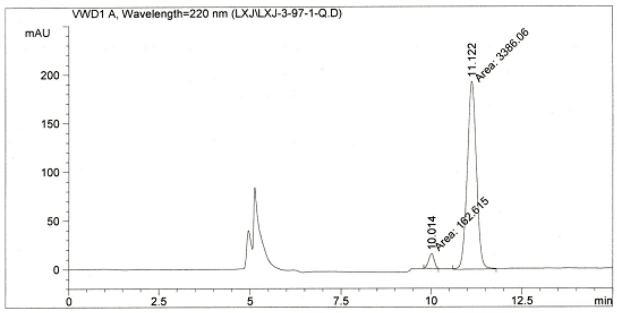



**6Aa**

91% ee obtained from Q-$NH_2$ catalyzed reaction

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================================================================================

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Dilution              :      1.0000
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Use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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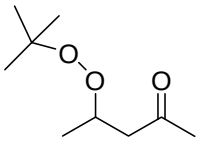
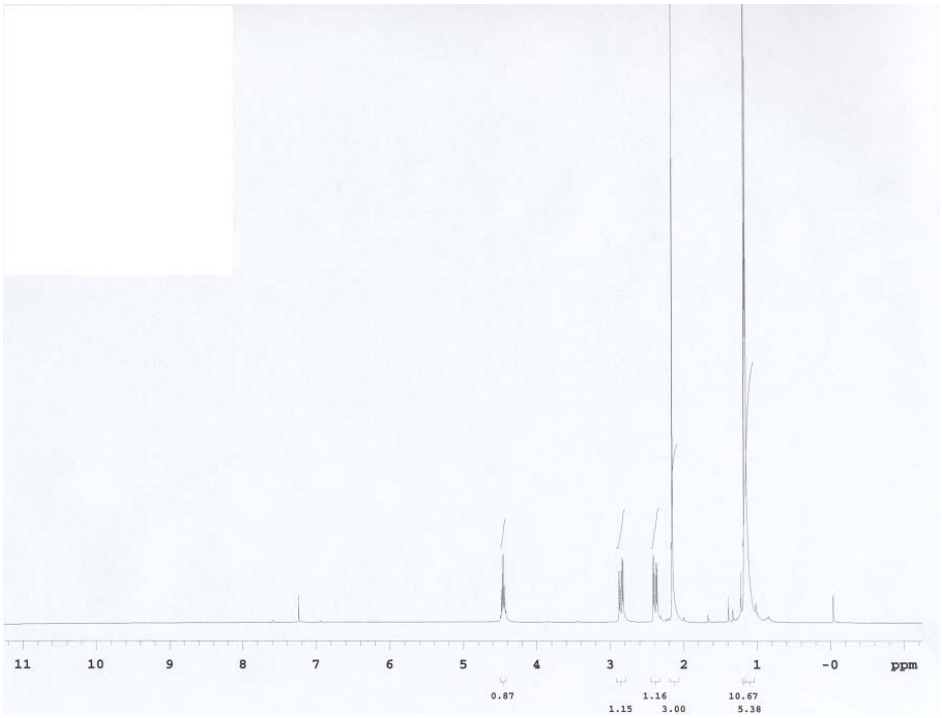

O
O
O

**6Ba**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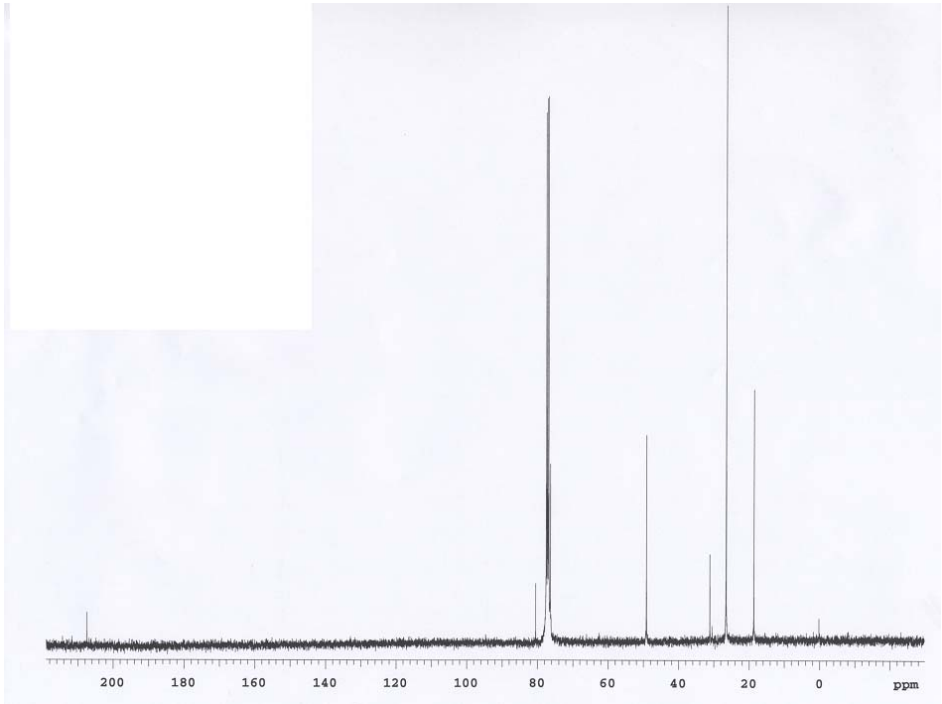
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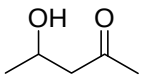
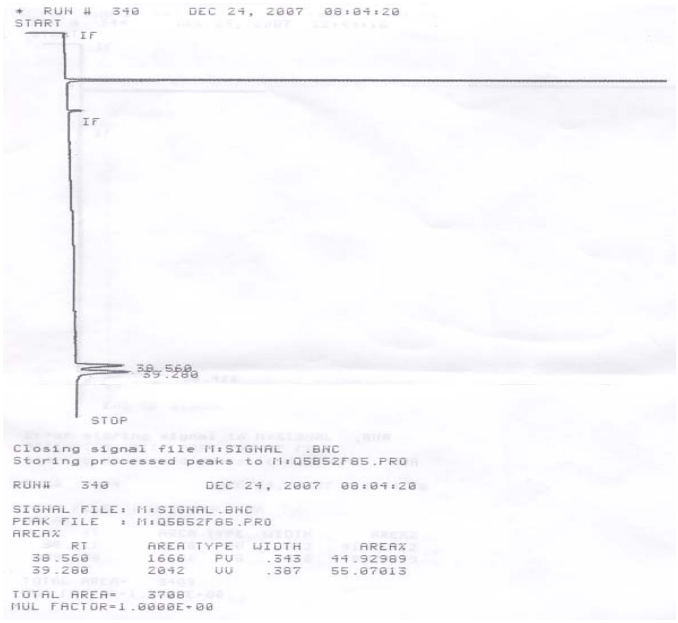
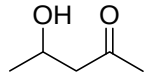
GC HP Chiral (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 240 °C, FID Temp: 260 °C, Inlet pressure :10 psi. Oven Temp, 50 °C 5 min, 2 °C/min, 80°C

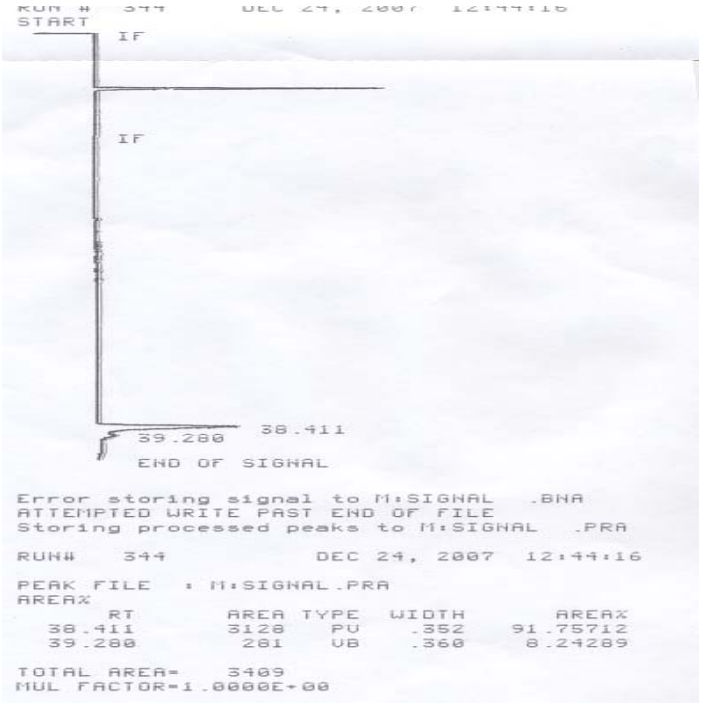


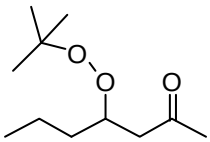

Mixture obtained from Q-$NH_2$ and QD-$NH_2$ catalyzed product **6Ba**



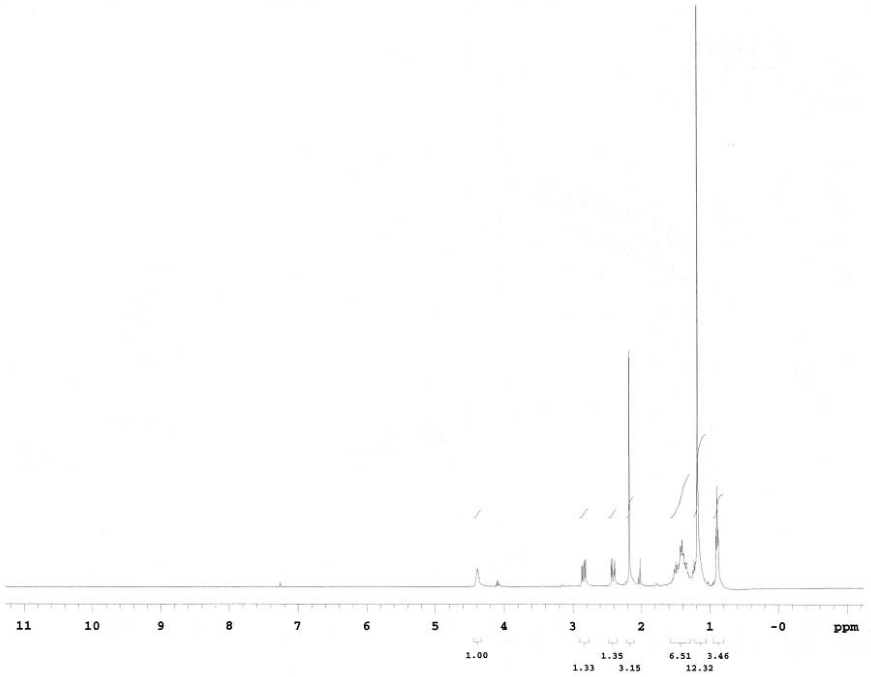



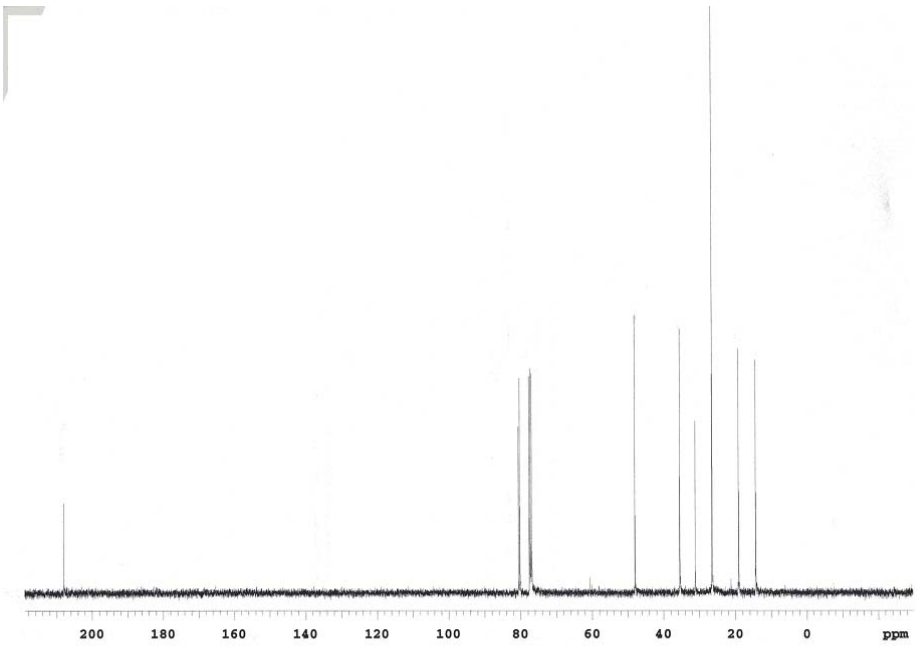

84% ee, obtained from Q-$NH_2$ catalyzed product **6Ba**



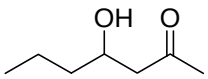


**6Ca**

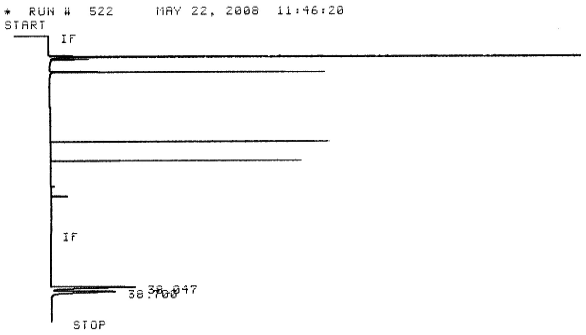

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
1.33
1.35
3.15
6.51
3.46
12.32


200
180
160
140
120
100
80
60
40
20
0
ppm

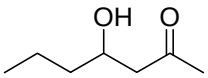
GC HP Chiral (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 240 °C, Fid Temp: 260 °C, Inlet pressure 10 psi. Oven Temp, 50 °C 5min, 2.5 °C/min, 100 °C



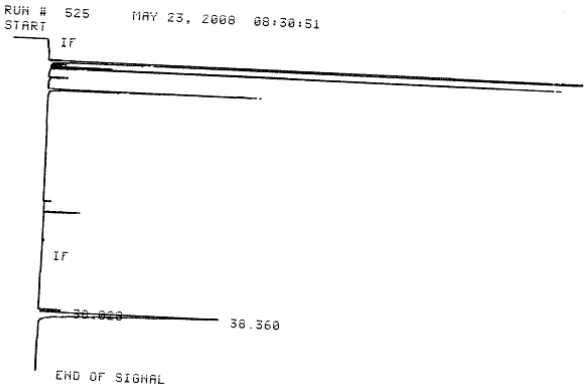

Mixture obtained from Q-$NH_2$ and QD-$NH_2$ catalyzed product **6Ca**



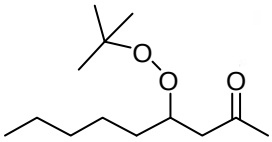

```
Closing signal file M:SIGNAL   .BHC
Storing processed peaks to M:067F190D.PRO

RUN#   522          MAY 22, 2008  11:46:20

SIGNAL FILE: M:SIGNAL.BHC
PEAK FILE  : M:067F190D.PRO
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  38.047       9015   PU    .234    52.52274
  38.700       8149   VB    .275    47.47728

TOTAL AREA=  17164
MUL FACTOR=1.0000E+00
```



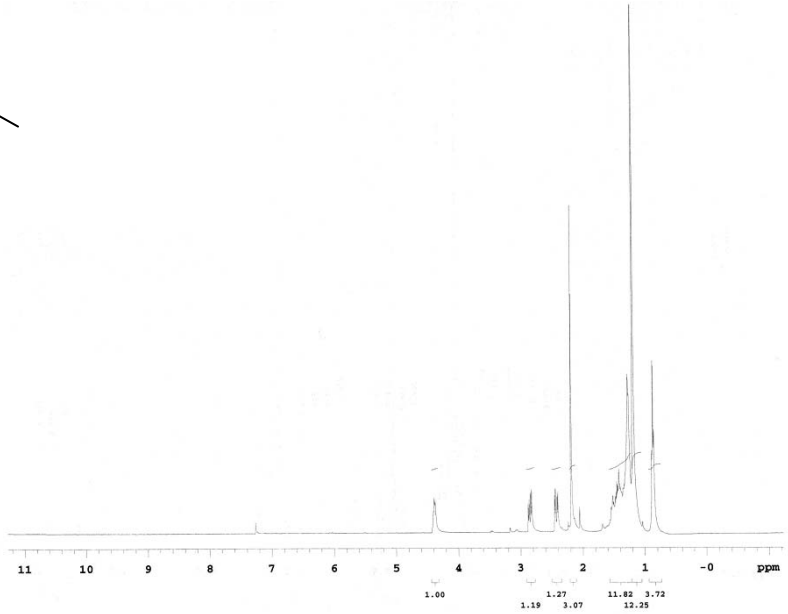

90% ee, obtained from Q-$NH_2$ c atalyzed product **6Ca**

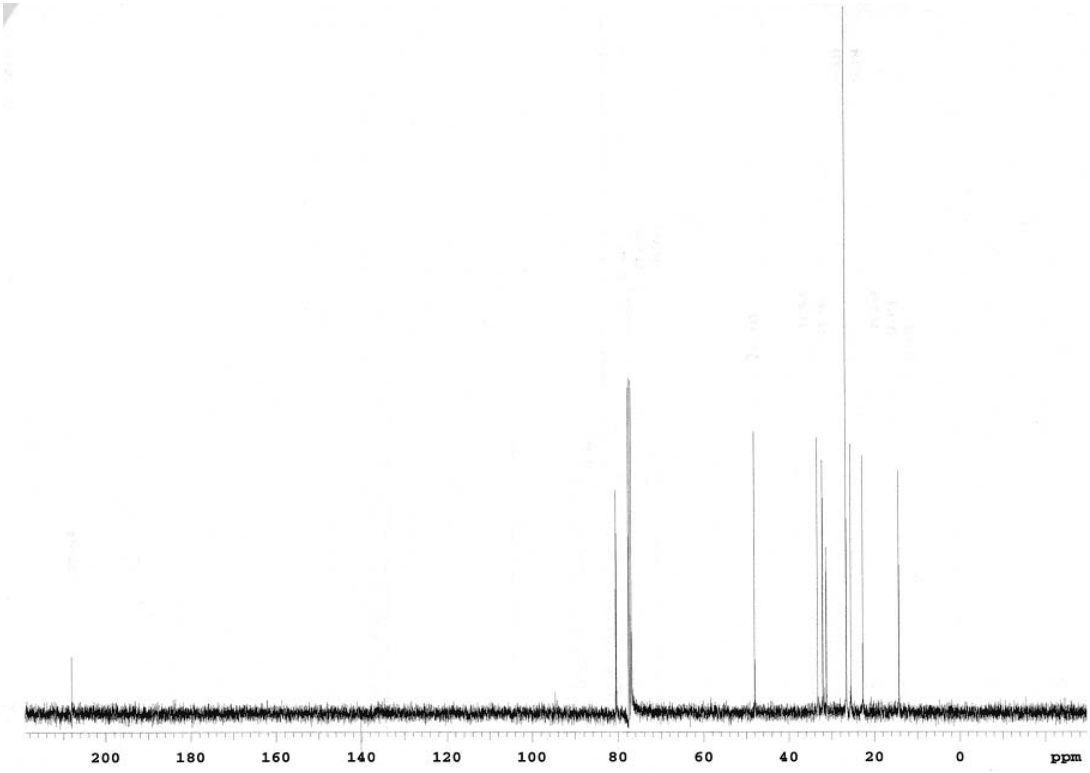



```
Closing signal file M:SIGNAL   .BHA
Storing processed peaks to M:SIGNAL   .PRA

RUN#   525          MAY 23, 2008  08:30:51

SIGNAL FILE: M:SIGNAL.BHA
PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  38.028       1696   PU    .162     5.20916
  38.360      30862   VB    .381    94.79085

TOTAL AREA=  32558
MUL FACTOR=1.0000E+00
```

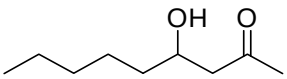


**6Da**

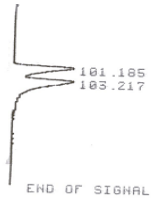

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
1.19
1.27
3.07
11.82
12.25
3.72


200
180
160
140
120
100
80
60
40
20
0
ppm

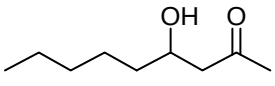
GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 240°C, Fid Temp: 260°C, Inlet pressure 10 psi. Oven Temp, 50°C 5min, 5°C/min, 100°C



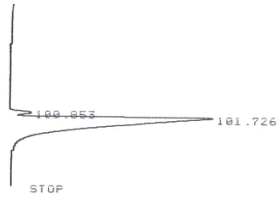

Mixture obtained from Q-$NH_2$ and QD-$NH_2$ catalyzed product **6Da**



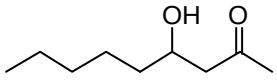

```
Closing signal file M:SIGNAL   .BNA
Storing processed peaks to M:SIGNAL   .PRA

RUN#   312            DEC  5, 2007  07:17:31

SIGNAL FILE: M:SIGNAL.BNA
PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT        AREA TYPE  WIDTH       AREA%
 101.185        6151   PU  1.005    42.09266
 103.217        8462   UU  1.410    57.90734

TOTAL AREA=  14613
MUL FACTOR=1.0000E+00
```



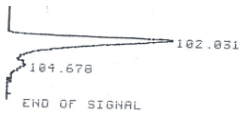

93% ee, obtained from Q-$NH_2$ catalyzed product **(+)6Da**



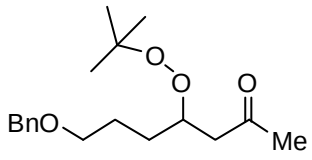

```
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q59C60C2.PRO

RUN#   314            DEC  5, 2007  12:27:44

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M:Q59C60C2.PRO
AREA%
      RT        AREA TYPE  WIDTH       AREA%
 100.853        1478   VV   .601     3.71955
 101.726       38258   VV  1.709    96.28045

TOTAL AREA=  39736
MUL FACTOR=1.0000E+00
```



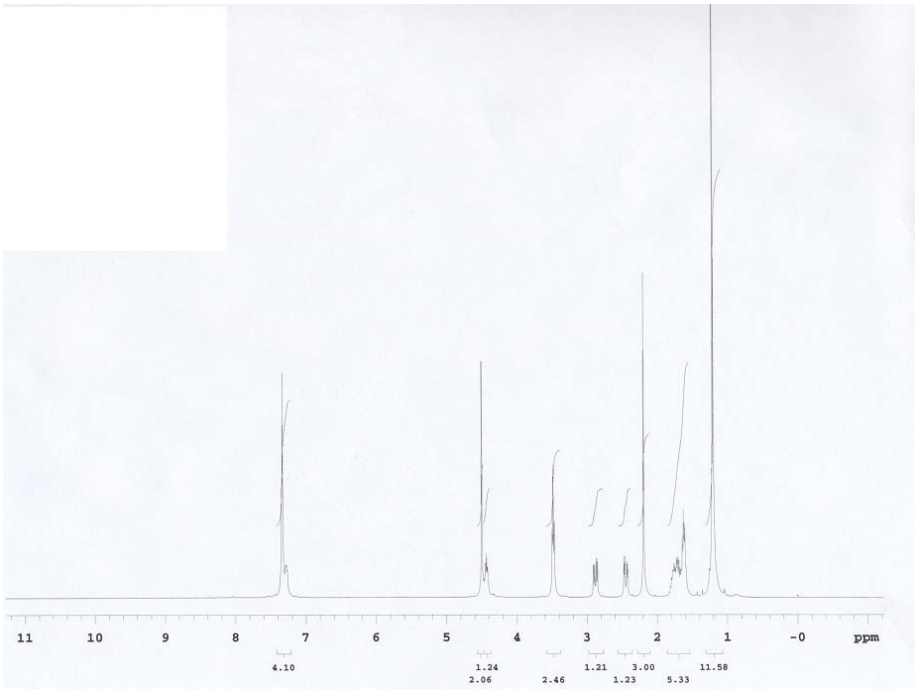

90% ee, obtained from QD-$NH_2$ catalyzed prodct **(-)6Da**

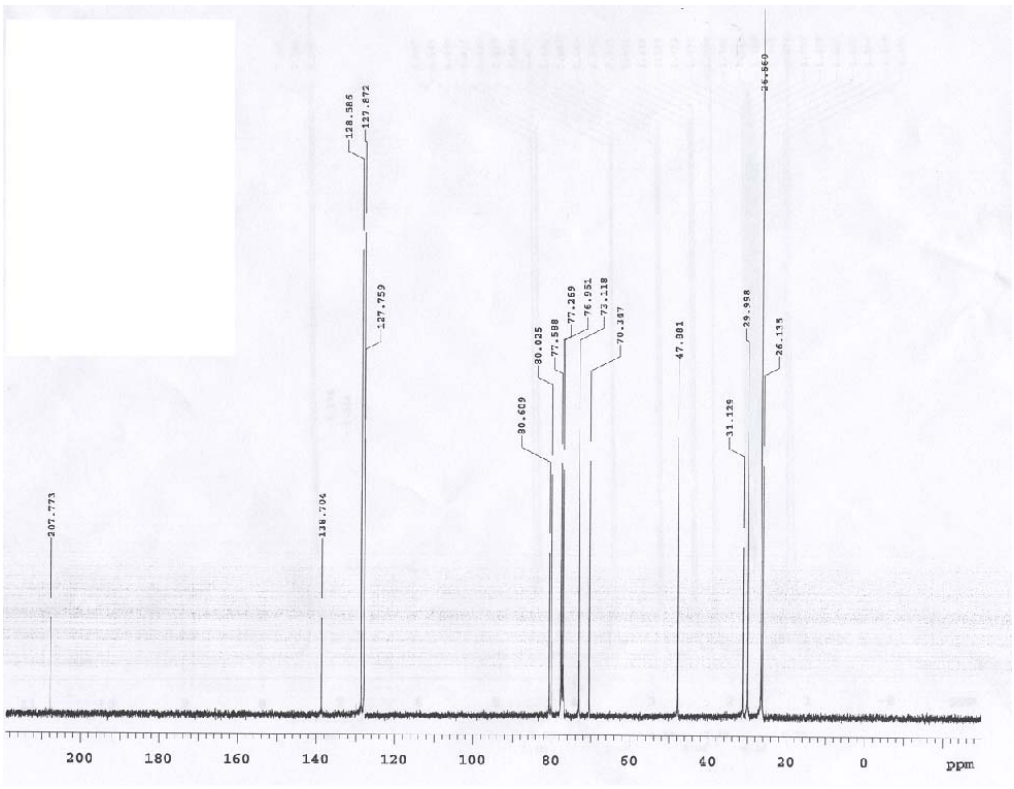



```
Closing signal file M:SIGNAL   .BNA
Storing processed peaks to M:SIGNAL   .PRA

RUN#   198            MAY 27, 1901  06:26:18

SIGNAL FILE: M:SIGNAL.BNA
PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT        AREA TYPE  WIDTH       AREA%
  34.021          34   PB   .567      .33831
  43.415          87   PP   .242      .86567
  46.435         115   PU   .958     1.14428
  59.021          28   PU   .233      .27861
  77.448          54   PU   .900      .53731
  83.749          36   PP   .600      .35821
  85.315         215   PU   .896     2.13930
  88.139         127   PB  1.058     1.26368
  90.495          41   PU   .683      .40796
 102.031        8858   PU  1.055    88.13933
 104.678         455   UB   .843     4.52736

TOTAL AREA=  10050
MUL FACTOR=1.0000E+00
```

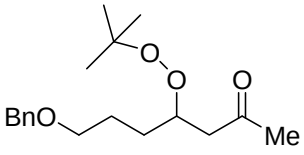

BnO
O
O
O
Me

**6Ea**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
4.10
1.24
2.06
2.46
1.21
1.23
3.00
5.33
11.58

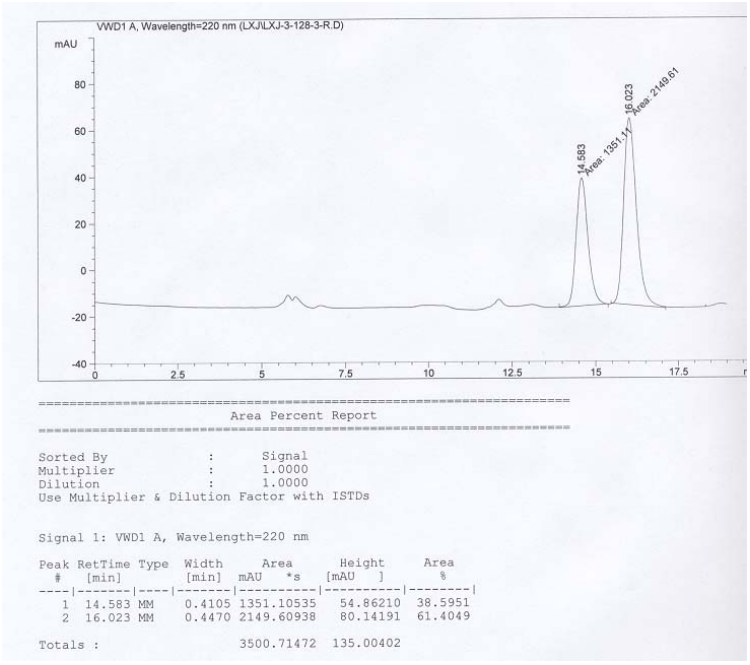

207.773
138.704
128.586
127.872
127.759
80.669
80.025
77.588
77.269
76.051
73.118
70.387
47.381
31.135
29.958
26.660
26.135
200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC [Daicel Chiralcel AD, Hexanes / IPA = 99.5:0.5, 0.6 mL/min, λ = 220 nm, 20.0 °C, $t_r$(major) = 14.71 min, $t_r$(minor) = 16.15 min]




**6Ea**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

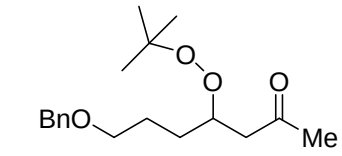



Area Percent Report

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

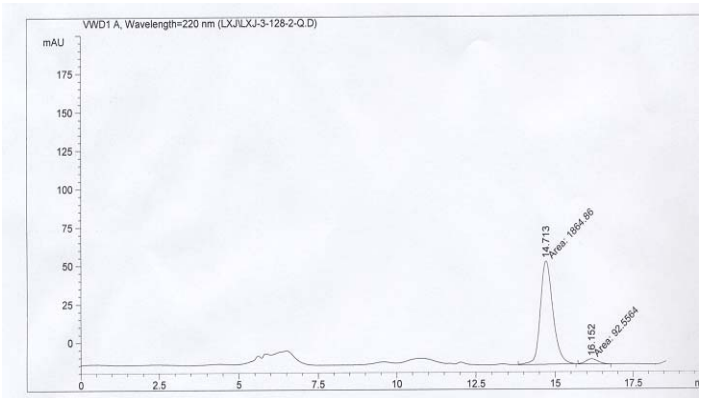
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.583 | MM | 0.4105 | 1351.10535 | 54.86210 | 38.5951 |
| 2 | 16.023 | MM | 0.4470 | 2149.60938 | 80.14191 | 61.4049 |
| Totals : | | | | 3500.71472 | 135.00402 | |




**6Ea**

91% ee, obtained from Q-$NH_2$ catalyzed reaction

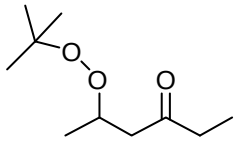



Area Percent Report

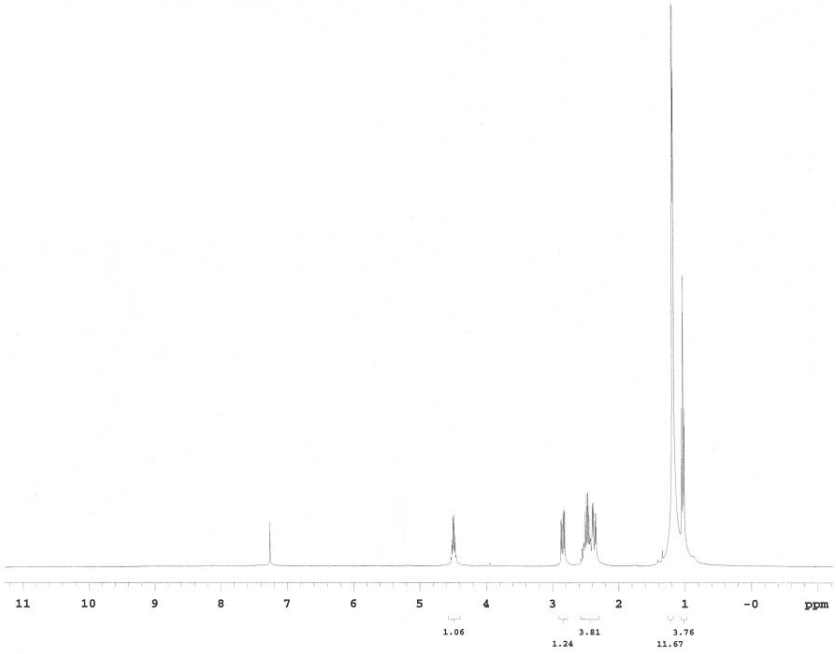
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

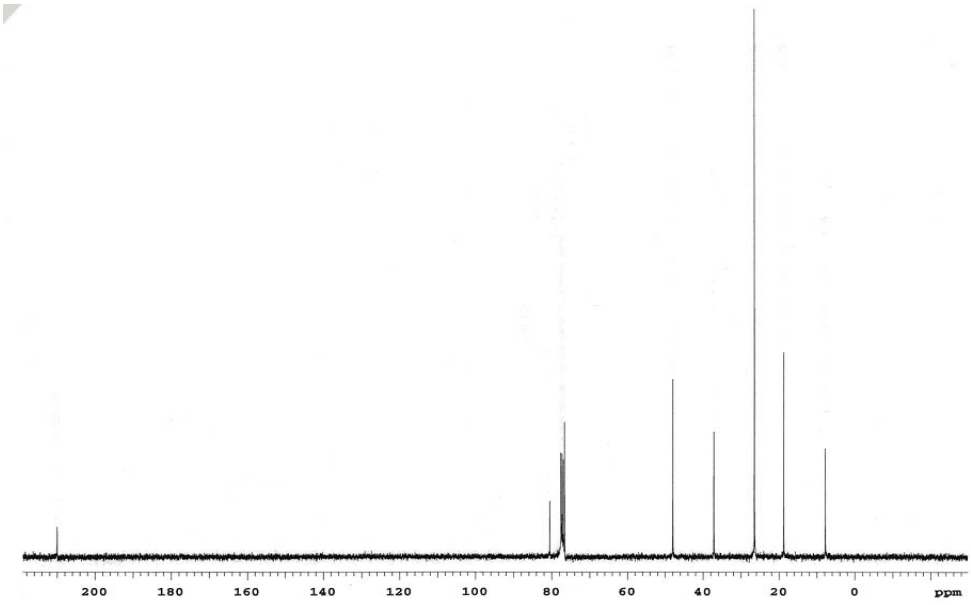
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 14.713 | MM | 0.4629 | 1864.85999 | 67.14729 | 95.2715 |
| 2 | 16.152 | MM | 0.4586 | 92.55637 | 3.36337 | 4.7285 |
| Totals : | | | | 1957.41635 | 70.51066 | |

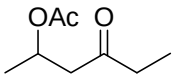


**6Fa**

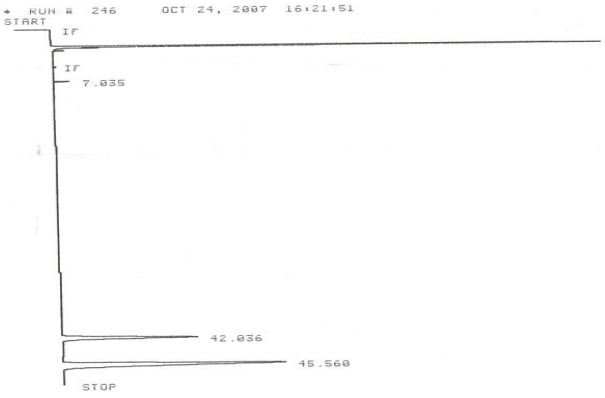

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.06
1.24
3.81
3.76
11.67


200
180
160
140
120
100
80
60
40
20
0
ppm

GC HP Chiral (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250 °C, Fid Temp: 220 °C, Inlet pressure 13 psi. Oven Temp: 85 °C.




Mixture obtained from Q-$NH_2$ and QD-$NH_2$ catalyzed product **6Fa**



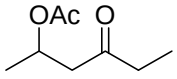

Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q563E720.PR0

RUN# 246 OCT 24, 2007 16:21:51

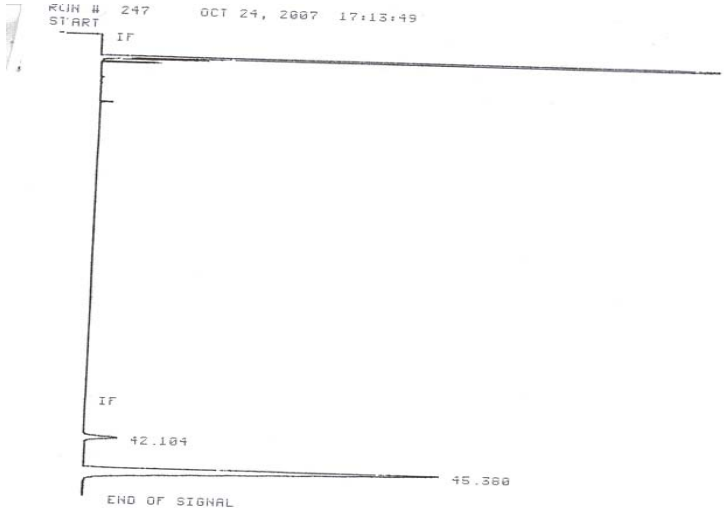
SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M:Q563E720.PR0
AREA%

| RT | AREA | TYPE | WIDTH | AREA% |
|---|---|---|---|---|
| 7.035 | 244 | UP | .064 | .79806 |
| 42.036 | 9636 | PU | .324 | 31.51697 |
| 45.560 | 20694 | BP | .426 | 67.68496 |

TOTAL AREA= 30574
MUL FACTOR=1.0000E+00




89% ee, obtained from Q-$NH_2$ catalyzed product **6Fa**



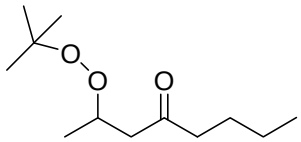

Closing signal file M:SIGNAL .BNA
Storing processed peaks to M:SIGNAL .PRA

RUN# 247 OCT 24, 2007 17:13:49

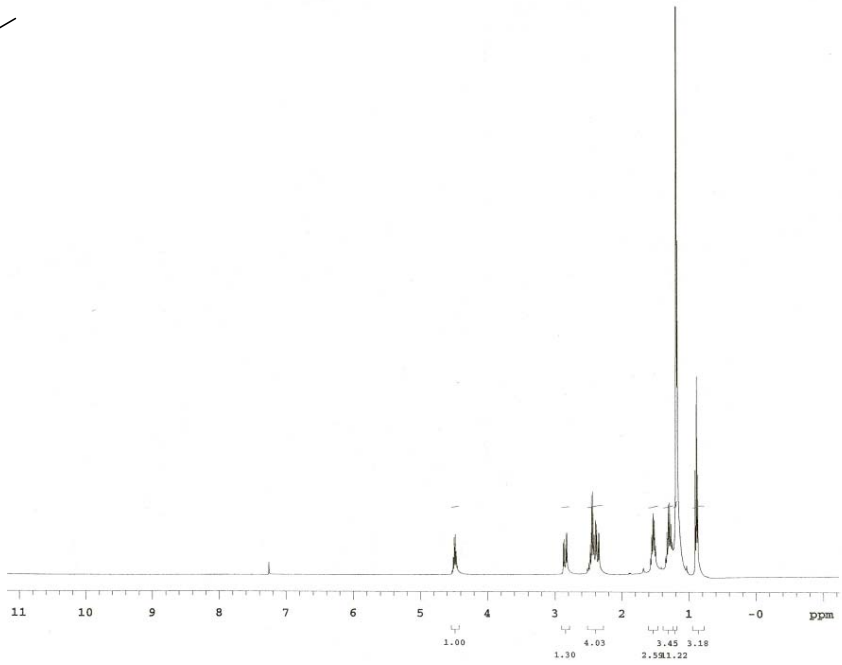
SIGNAL FILE: M:SIGNAL.BNA
PEAK FILE : M:SIGNAL.PRA
AREA%

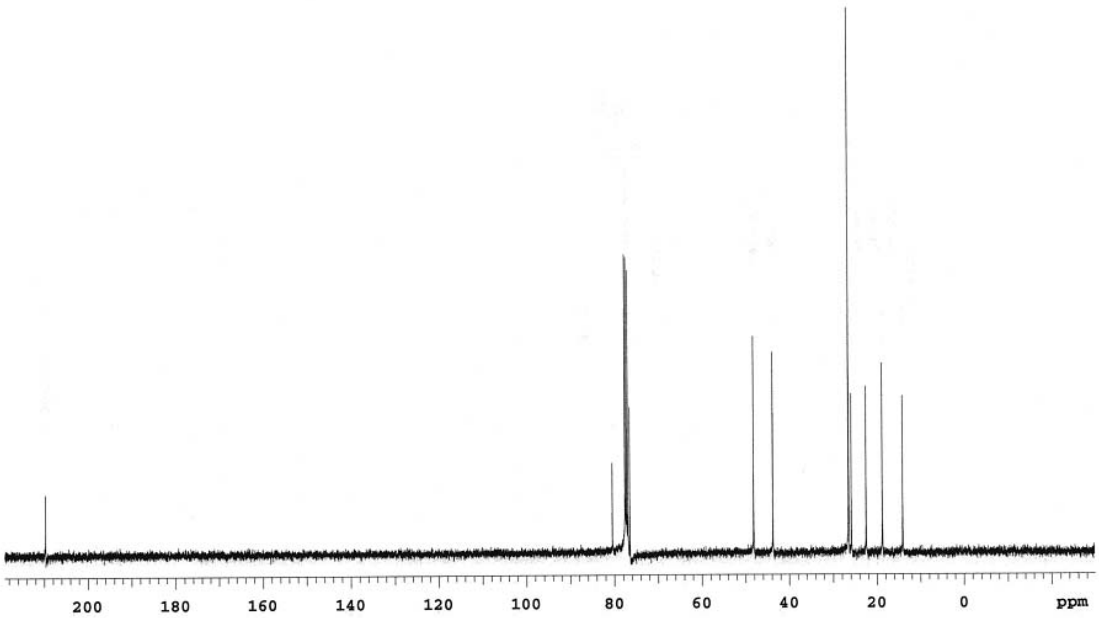
| RT | AREA | TYPE | WIDTH | AREA% |
|---|---|---|---|---|
| 42.104 | 2073 | UP | .323 | 5.77325 |
| 45.380 | 33834 | UP | .489 | 94.22675 |

TOTAL AREA= 35907
MUL FACTOR=1.0000E+00

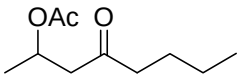


**6Ha**

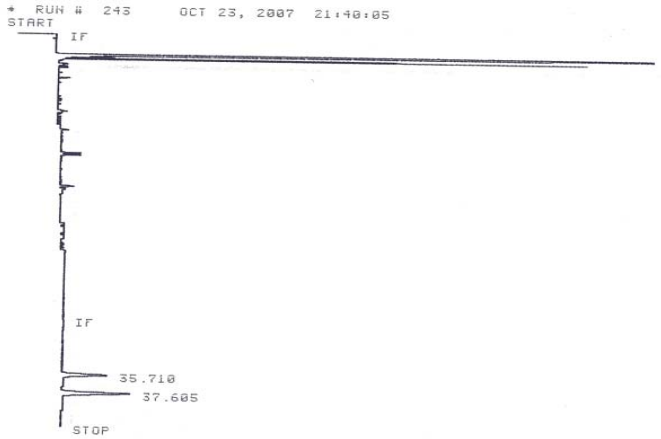

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
1.30
4.03
3.45
3.18
2.58
1.22


200
180
160
140
120
100
80
60
40
20
0
ppm

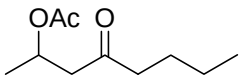
GC HP Chiral (20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 250 °C, Fid Temp: 220 °C, Inlet pressure 13 psi. Oven Temp: 110 °C



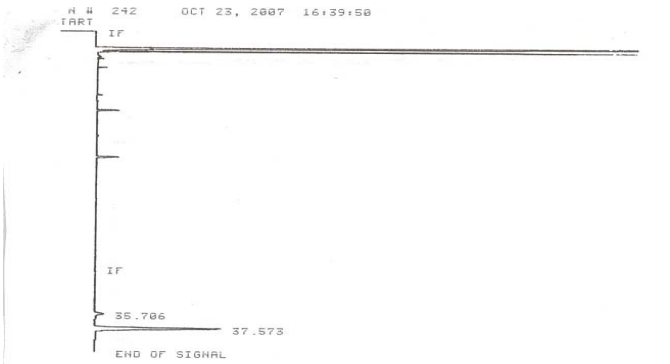

Mixture obtained from Q-$NH_2$ and QD-$NH_2$ catalyzed product **6Ha**



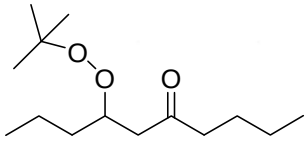

```
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q562E036.PRO

RUN#   243          OCT 23, 2007  21:40:05

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M:Q562E036.PRO
AREA%
      RT       AREA TYPE  WIDTH      AREA%
  35.710        716   PU    .298   41.31565
  37.605       1017   PP    .292   58.68435

TOTAL AREA=    1733
MUL FACTOR=1.0000E+00
```



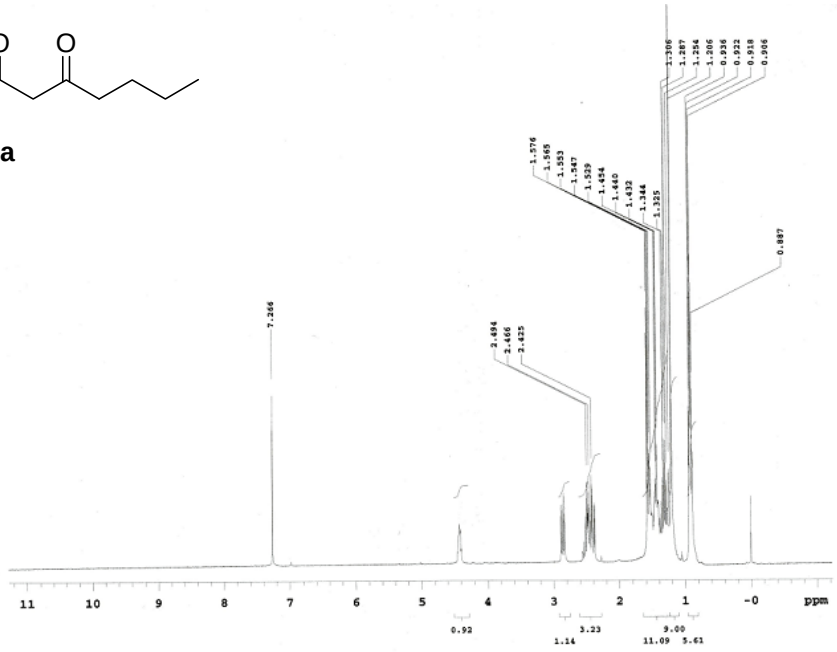

87% ee, obtained from Q-$NH_2$ catalyzed product **6Ha**

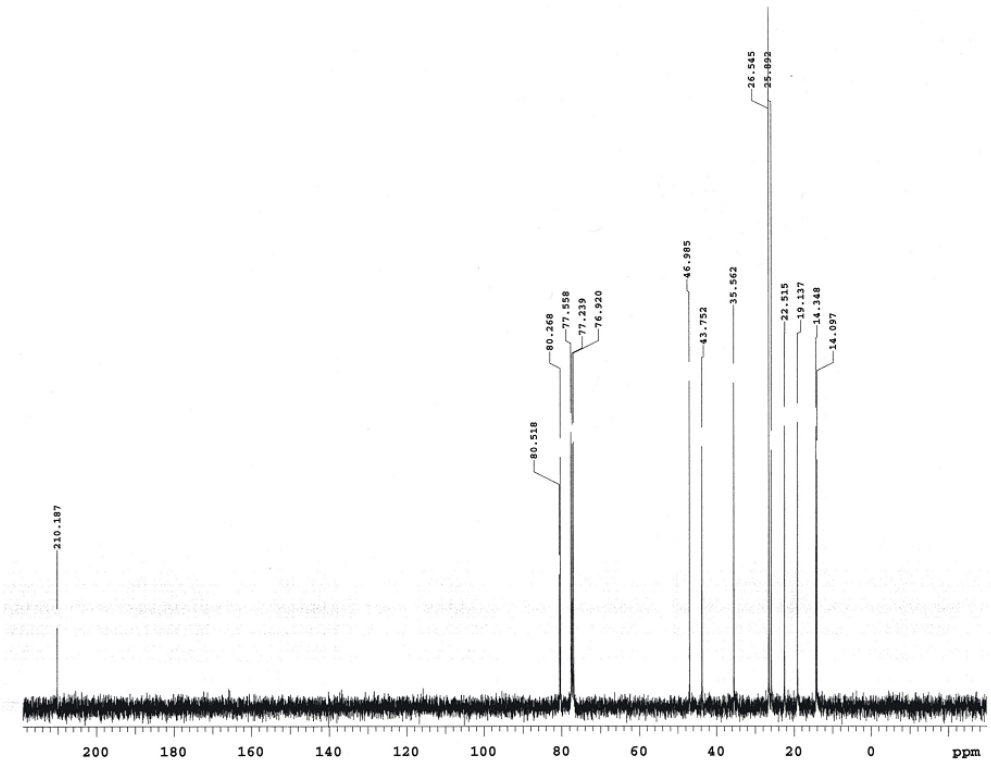



```
Closing signal file M:SIGNAL   .BNA
Storing processed peaks to M:SIGNAL   .PRA

RUN#   242          OCT 23, 2007  16:39:50

SIGNAL FILE: M:SIGNAL.BNA
PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT       AREA TYPE  WIDTH      AREA%
  35.706        570   PB    .288    6.61560
  37.573       8046   PU    .284   93.38438

TOTAL AREA=    8616
MUL FACTOR=1.0000E+00
```

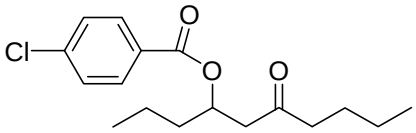


**6Ia**

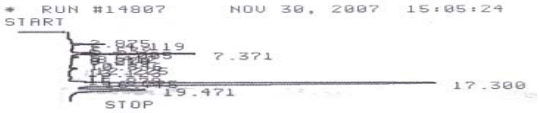

1.576
1.565
1.553
1.547
1.529
1.454
1.440
1.432
1.344
1.335
1.306
1.287
1.254
1.206
0.936
0.922
0.918
0.906
0.887
7.266
2.494
2.466
2.435
11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.92
1.14
3.23
11.09
9.00
5.61


210.187
80.518
80.268
77.558
77.239
76.920
46.985
43.752
35.562
26.545
25.899
22.515
19.137
14.348
14.097
200
180
160
140
120
100
80
60
40
20
0
ppm

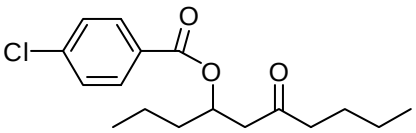
HPLC Daicel Chiralcel AD-H, Hexanes / IPA = 99.2:0.8, 0.78 mL/min, λ = 220 nm, 20.0 °C



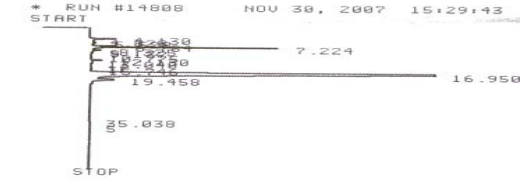
Mixture obtained from Q-$NH_2$ and QD-$NH_2$ catalyzed product **6la**



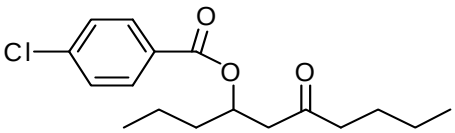

```
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q5949CB5.PRO
DIRECTORY FULL

RUN# 14807              NOV 30, 2007  15:05:24

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M?Q5949CB5.PRO
AREA%
      RT        AREA  TYPE   WIDTH        AREA%
   2.875     4011554    BH   1.051       .78864
   4.119    12022224   SHB    .262      2.36348
   5.532     1079667   TPB    .373       .21225
   7.005     8172832   SPH    .268      1.60672
   7.371    28047568   SHB    .175      5.51395
   8.412     2254054    VV    .221       .44313
   8.870      341616    VV    .162       .06716
   9.214      346425    VB    .199       .06810
  10.846      816469    VB    .261       .16051
  12.225     3288592    BV    .312       .64651
  13.123      470860    VV    .356       .09257
  15.878      537971    VV    .383       .10576
  16.775     7031264    VH    .305      1.38230
  17.300   362120960   SHH    .787     71.19040
  19.471    78123456 ISHP    .814     15.35851

TOTAL AREA=5.0867E+08
MUL FACTOR=1.0000E+00
```



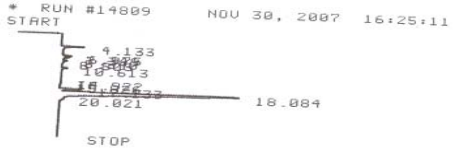
94% ee, obtained from Q-$NH_2$ catalyzed product **(+)6la**



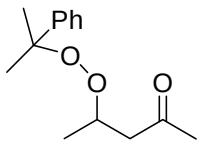

```
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q594A268.PRO
DIRECTORY FULL

RUN# 14808              NOV 30, 2007  15:29:43

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M?Q594A268.PRO
AREA%
      RT        AREA  TYPE   WIDTH        AREA%
   4.130     8617587    BV    .247      1.41360
   4.828     1837348    VV    .521       .30139
   5.528     3850368    VH    .493       .63160
   6.784     9305523   SHH    .254      1.52645
   7.224    44176576   SHB    .176      7.24660
   8.325     3280128   TBB    .245       .53806
   9.137      529292    VB    .198       .08682
  10.775     1438788    VV    .733       .23601
  12.130     5197674    VV    .310       .85261
  13.040      617510    VV    .392       .10129
  15.746      863863    BH    .362       .14171
  16.950   512495520   SHB   1.115     84.06826
  19.458    16217600   TBP    .612      2.66029
  35.038     1190707   TPB   1.028       .19532

TOTAL AREA=6.0962E+08
MUL FACTOR=1.0000E+00
```



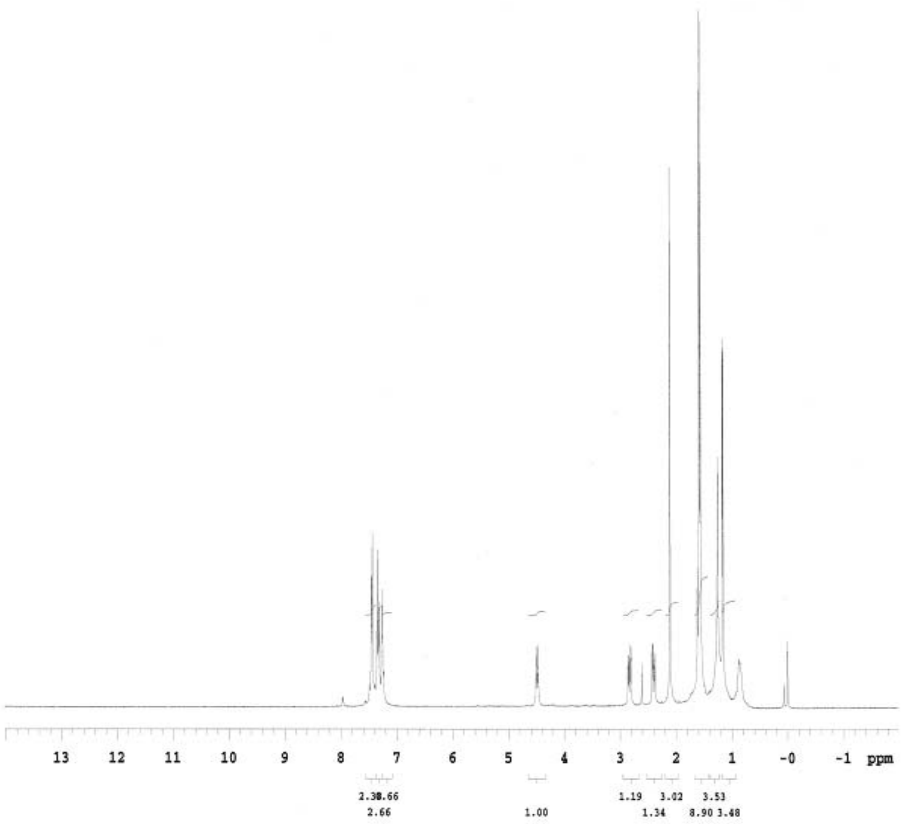
88% ee, obtained from QD-$NH_2$ catalyzed product **(-)6la**

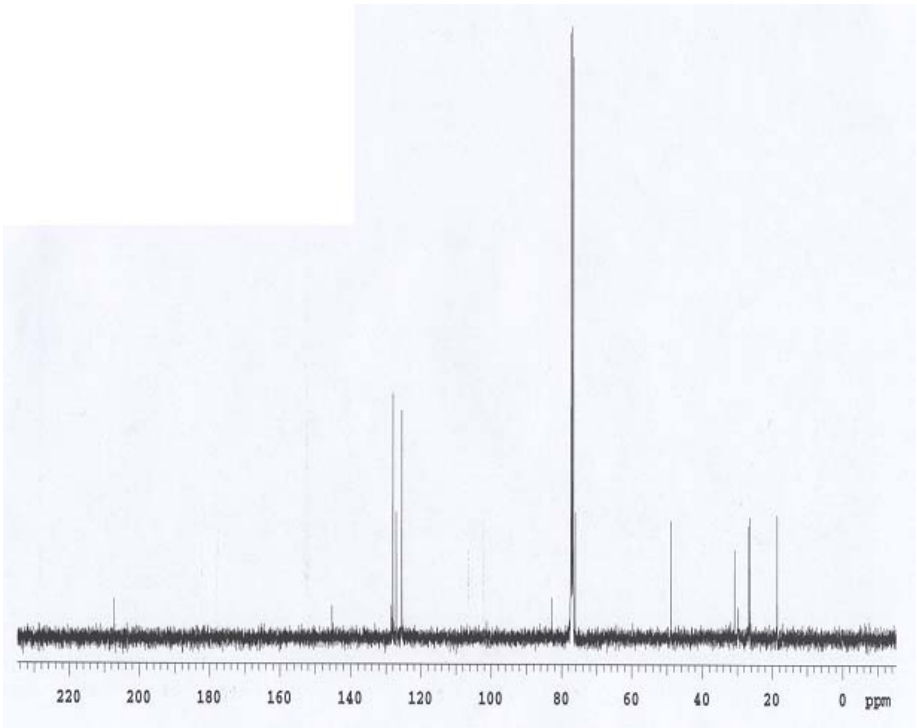



```
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q594AF68.PRO
DIRECTORY FULL

RUN# 14809              NOV 30, 2007  16:25:11

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M?Q594AF68.PRO
AREA%
      RT        AREA  TYPE   WIDTH        AREA%
   4.133     6974224    PB   .217      2.88401
   6.975     5994592    PU   .365      2.47891
   7.349     2849536    VV   .235      1.17835
   8.340     2791706    VV   .282      1.15444
   8.803     1044232    VB   .331       .43182
  10.613     2408128    PB   .247       .99582
  14.922      927914    PU   .430       .38372
  15.826      617433    VV   .469       .25532
  17.133    13319960    VH   .418      5.50813
  18.084   203735520   SHB   .798     84.24960
  20.021     1160448   TBB   .416       .47987

TOTAL AREA=2.4182E+08
MUL FACTOR=1.0000E+00
```

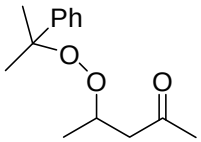

Ph
O
O
O

**6Bb**


13 12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
2.38 6.66
2.66
1.00
1.19 3.02
1.34
3.53
8.90 3.48

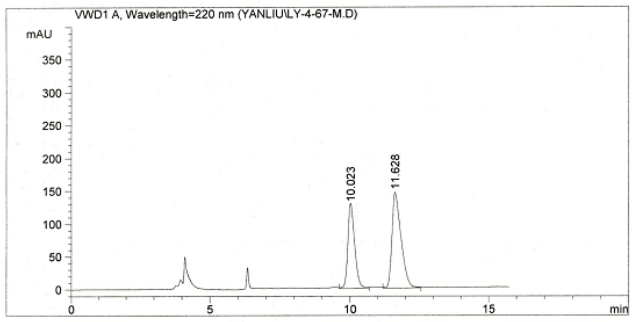

220 200 180 160 140 120 100 80 60 40 20 0 ppm

HPLC, Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1.0 mL/min, λ = 220 nm




**6Bb**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

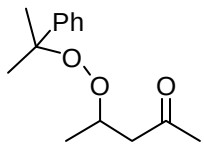



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

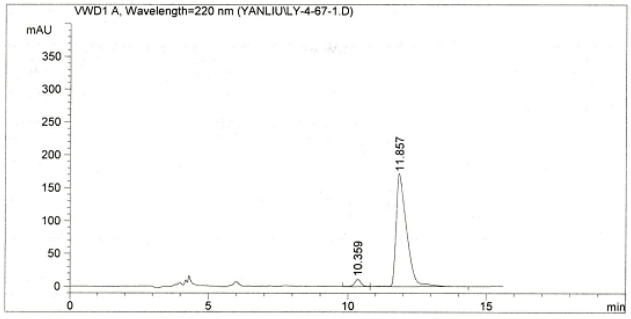
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.023 | VV | 0.2615 | 2219.10132 | 127.34330 | 39.9990 |
| 2 | 11.628 | VV | 0.3376 | 3328.79321 | 145.09052 | 60.0010 |
| Totals : | | | | 5547.89453 | 272.43382 | |




**6Bb**

92% ee obtained from Q-$NH_2$ catalyzed reaction

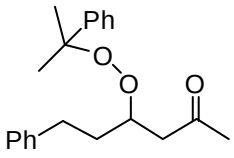



Area Percent Report

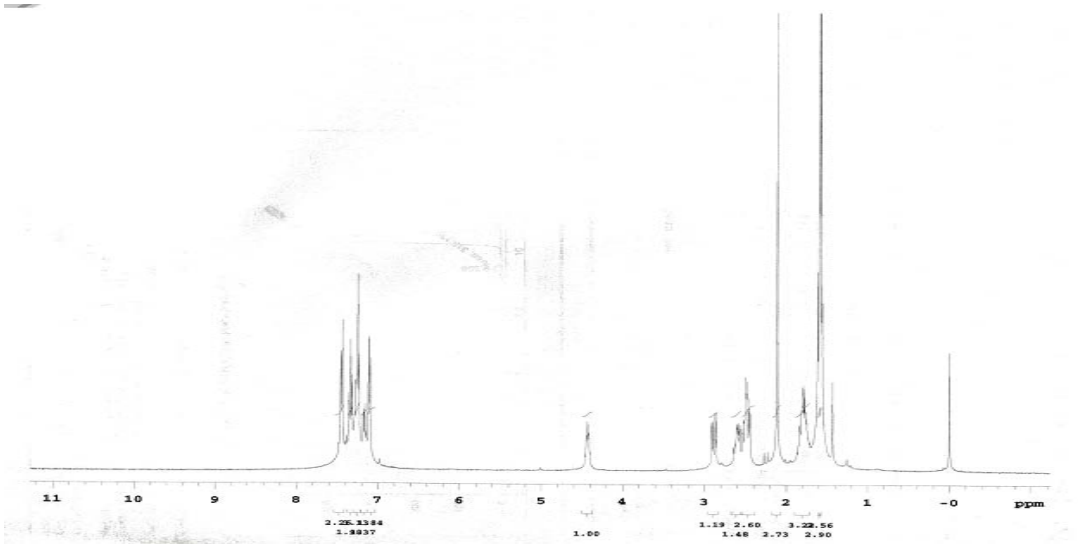
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

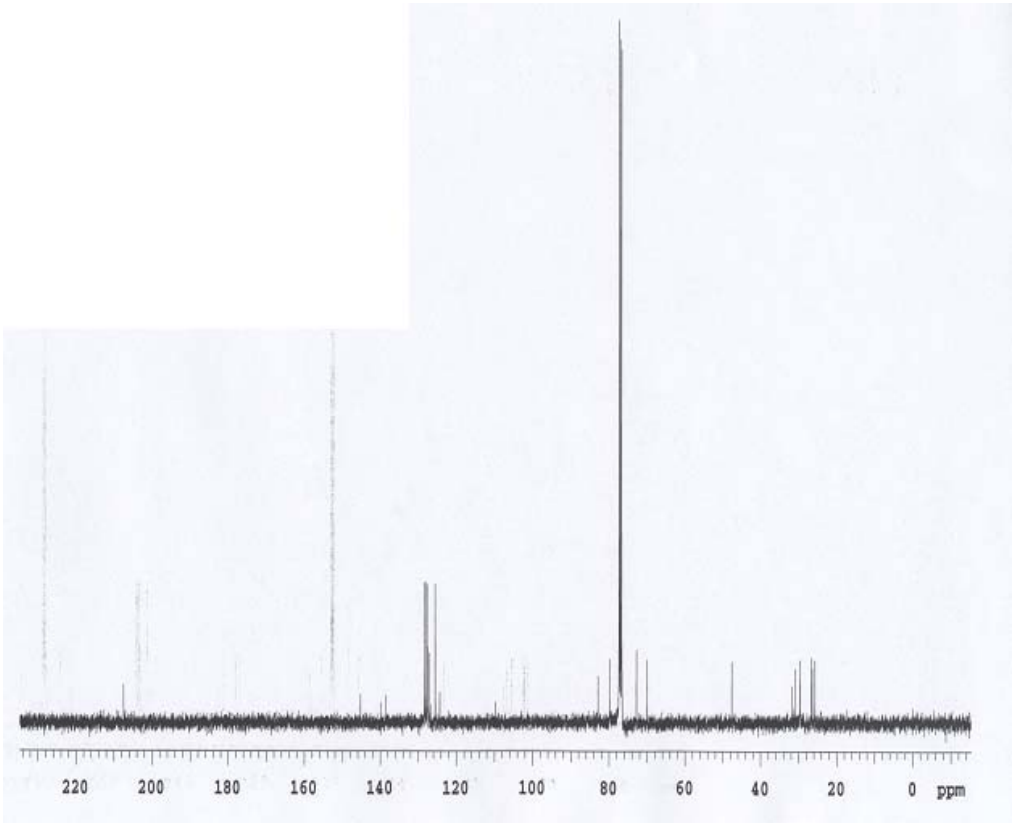
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.359 | VV | 0.2530 | 184.27620 | 11.03659 | 3.9234 |
| 2 | 11.857 | VV | 0.3799 | 4512.59424 | 169.84238 | 96.0766 |
| Totals : | | | | 4696.87044 | 180.87896 | |

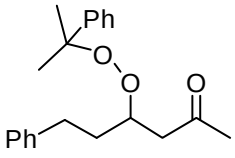

Ph
O
O
O
Ph

**6Ab**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm

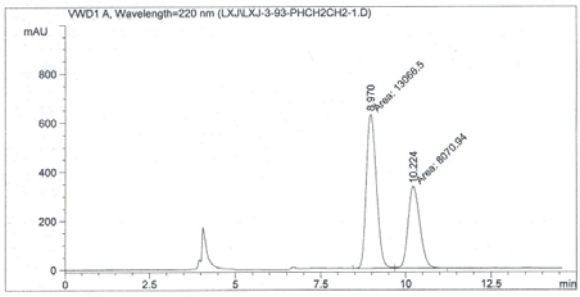

220
200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC, Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1.0 mL/min, λ = 220 nm

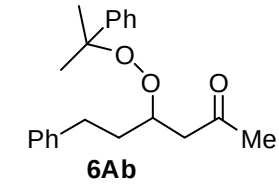



**6Ab**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

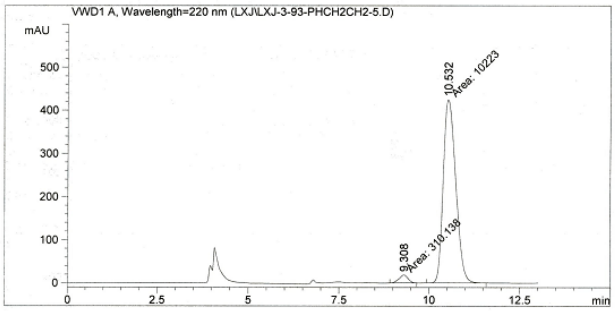



```
================================================================================
                              Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   8.970 MF    0.3461 1.30665e4   629.20129  61.8169
   2  10.224 FM    0.4023 8070.93701  334.40027  38.1831

Totals :                  2.11375e4   963.60156
```

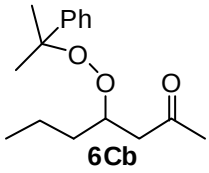



**6Ab**

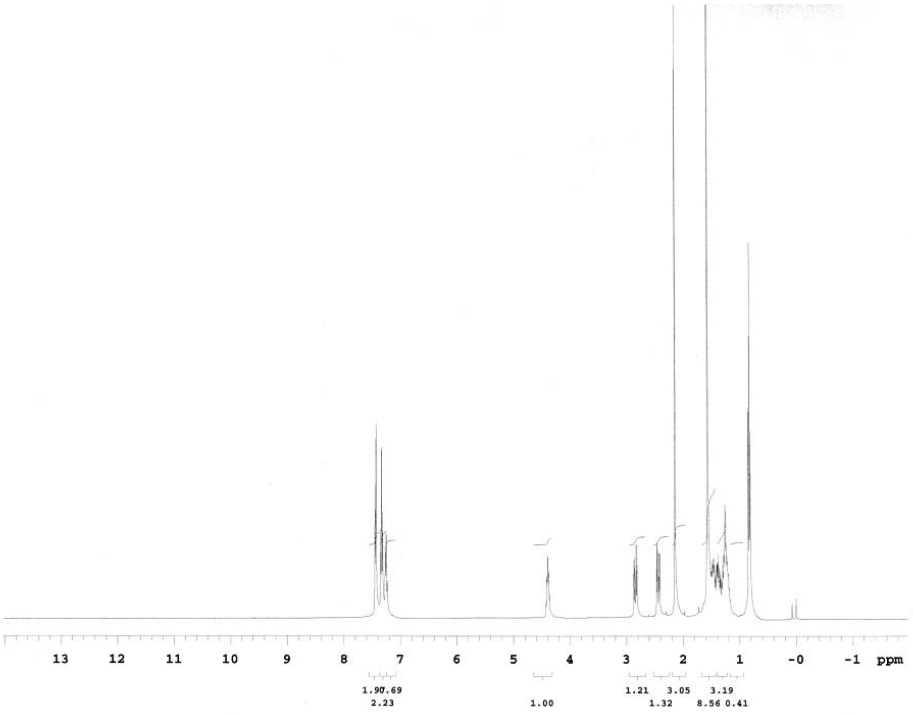
94% ee obtained from Q-$NH_2$ catalyzed reaction

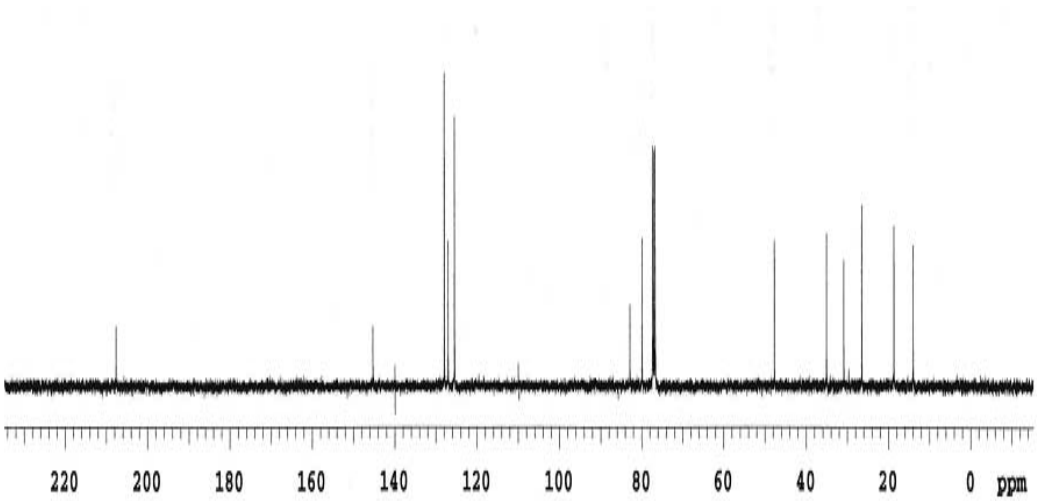



```
================================================================================
                              Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   9.308 MM    0.2790  310.13763   18.52793   2.9444
   2  10.532 MM    0.4008 1.02230e4   425.09888  97.0556

Totals :                  1.05332e4   443.62680
```

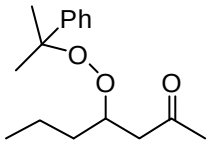

Ph
O
O
O

**6Cb**


13 12 11 10 9 8 7 6 5 4 3 2 1 -0 -1 ppm
1.90 7.69
2.23
1.00
1.21 3.05 3.19
1.32 8.56 0.41

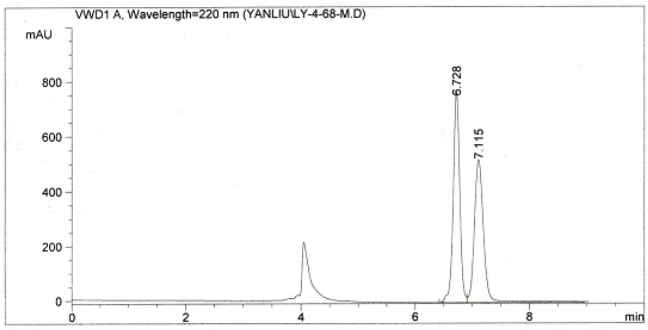

220 200 180 160 140 120 100 80 60 40 20 0 ppm

HPLC, Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1.0 mL/min




**6Cb**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

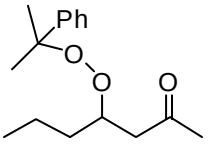



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

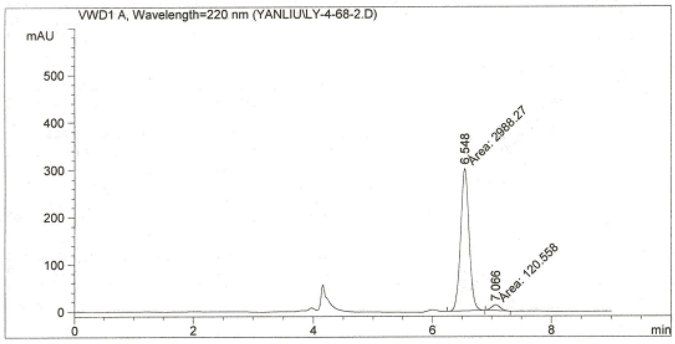
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.728 | BV | 0.1309 | 6100.17969 | 741.81171 | 50.5766 |
| 2 | 7.115 | VV | 0.1825 | 5961.08887 | 511.87125 | 49.4234 |
| Totals : | | | | 1.20613e4 | 1253.68295 | |




**6Cb**

92% ee obtained from Q-$NH_2$ catalyzed reaction

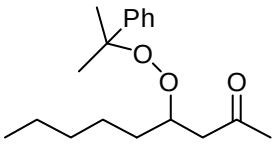



Area Percent Report

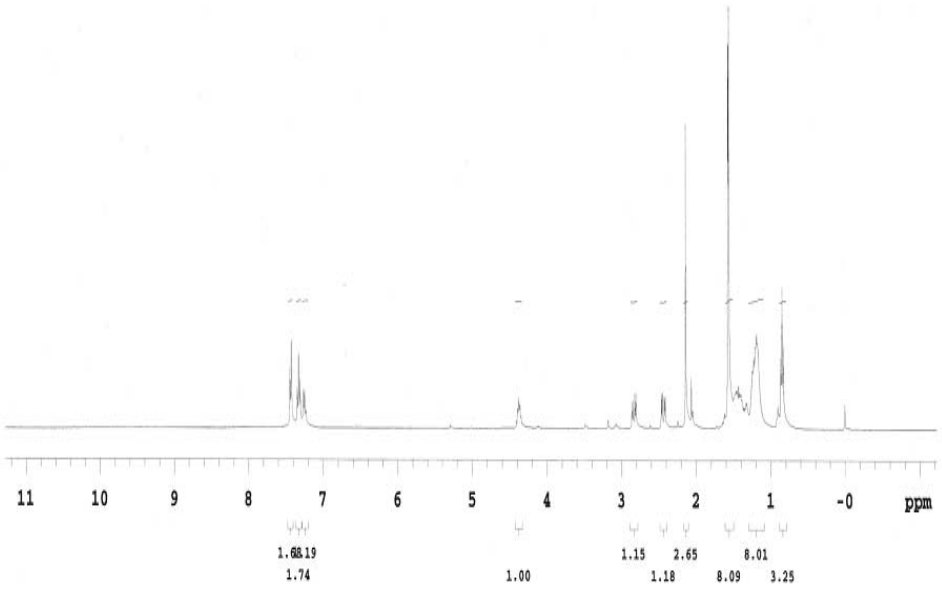
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

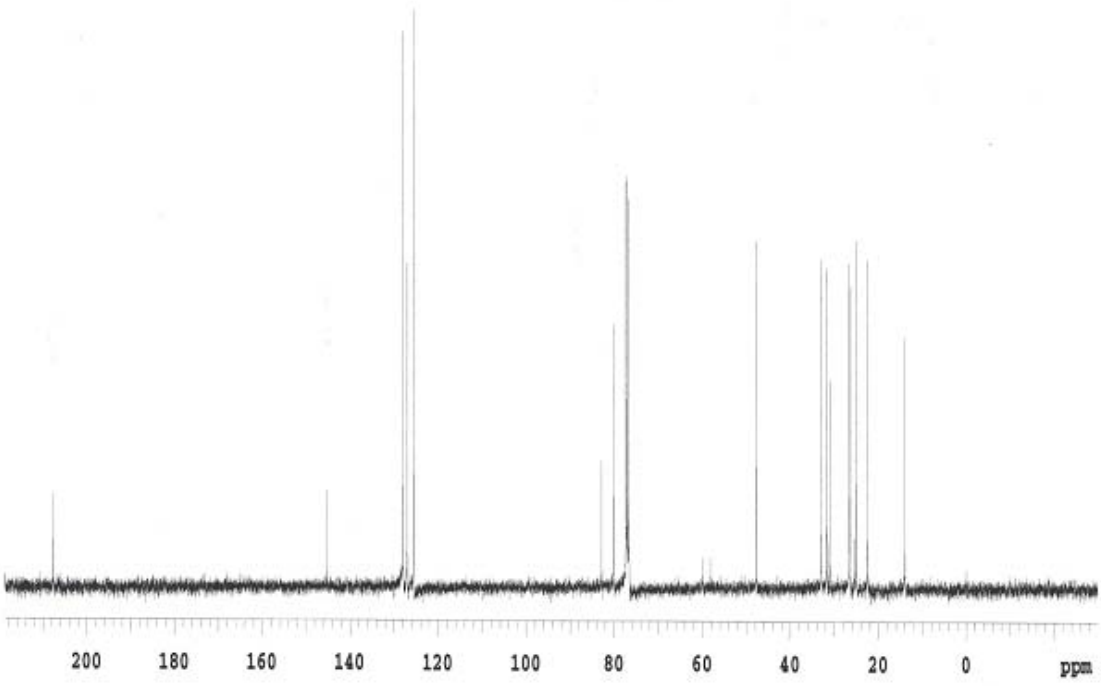
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.548 | MM | 0.1648 | 2988.27319 | 302.24094 | 96.1221 |
| 2 | 7.066 | MM | 0.1654 | 120.55843 | 12.14699 | 3.8779 |
| Totals : | | | | 3108.83163 | 314.38793 | |

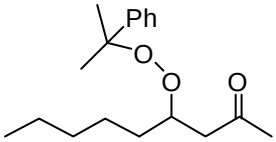

Ph
O
O
O

**6Db**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.68
1.74
1.00
1.15
1.18
2.65
8.01
8.09
3.25

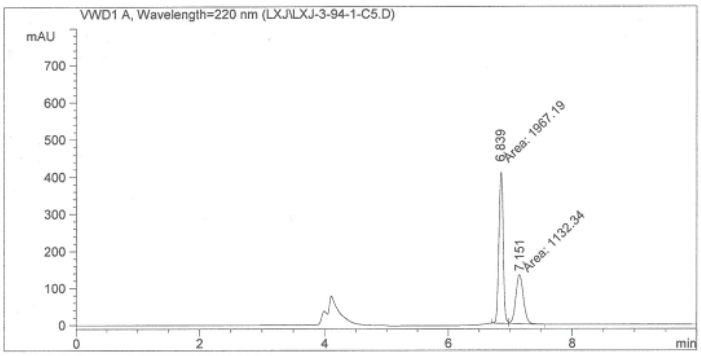

200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC, Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1.0 mL/min, λ = 220 nm

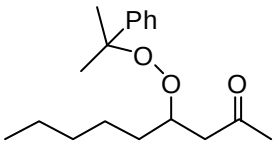



**6Db**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

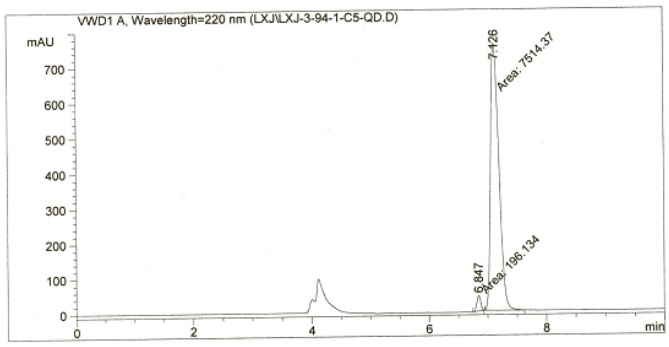



```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.839 MF    0.0769 1967.18579  426.54062  63.4673
   2   7.151 FM    0.1422 1132.33972  132.73480  36.5327

Totals :                  3099.52551  559.27542
```

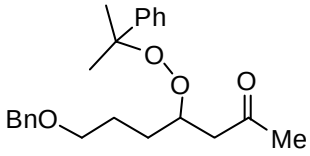



**6Db**

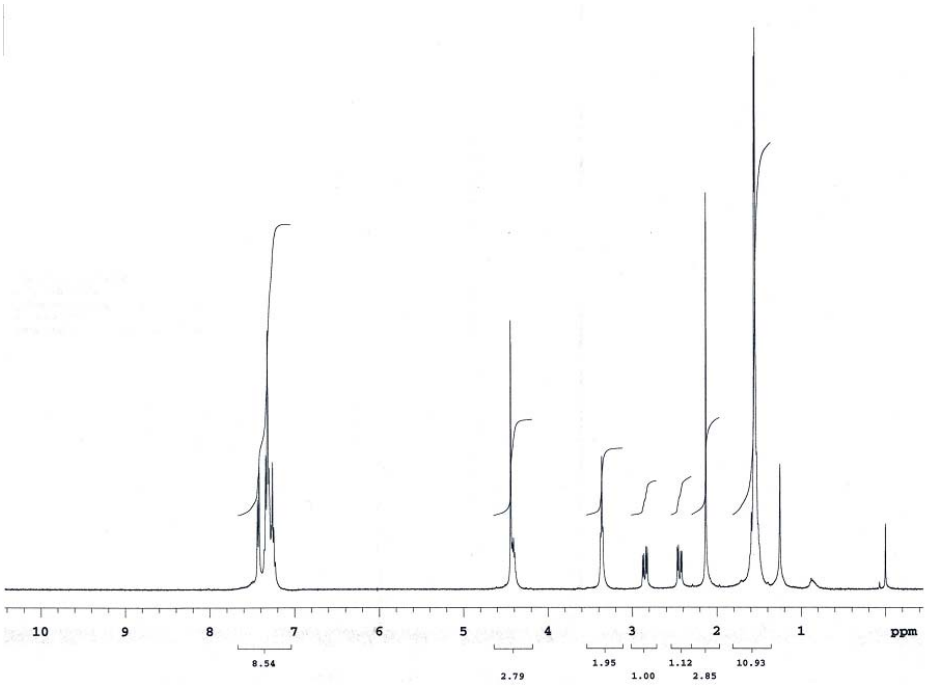
95% ee, obtained from Q-$NH_2$ catalyzed reaction

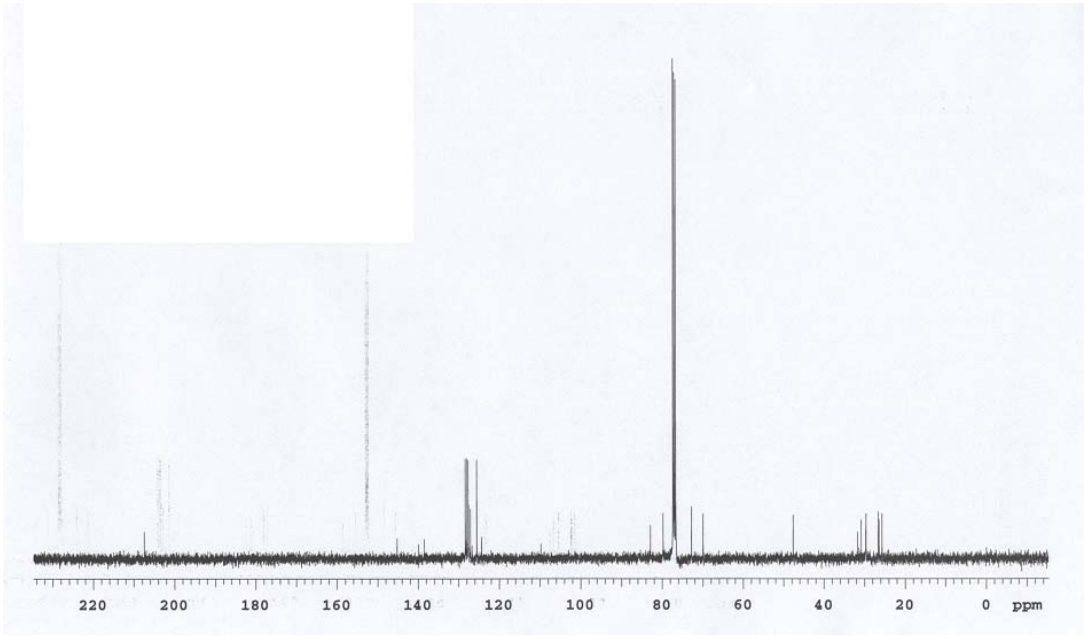



```
================================================================================
                            Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.847 MM    0.0793  196.13443   41.24803   2.5437
   2   7.126 MM    0.1653 7514.37158  757.73254  97.4563

Totals :                  7710.50601  798.98058
```

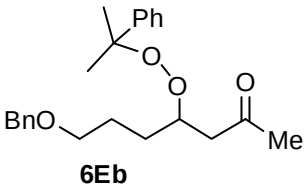

Ph
O
O
O
BnO
Me

**6Eb**


10
9
8
7
6
5
4
3
2
1
ppm
8.54
2.79
1.95
1.00
1.12
2.85
10.93

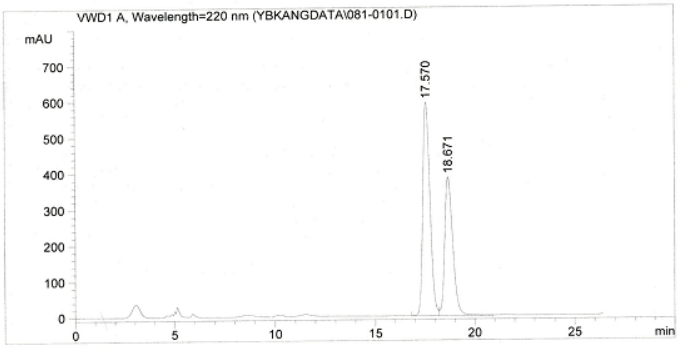

220
200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC, Daicel Chiralcel AS-H, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm




**6Eb**

mixture of Q-$NH_2$ and QD-N catalyzed reaction

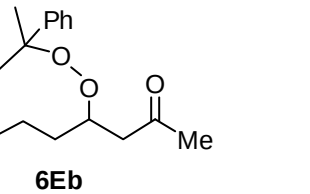



Area Percent Report

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

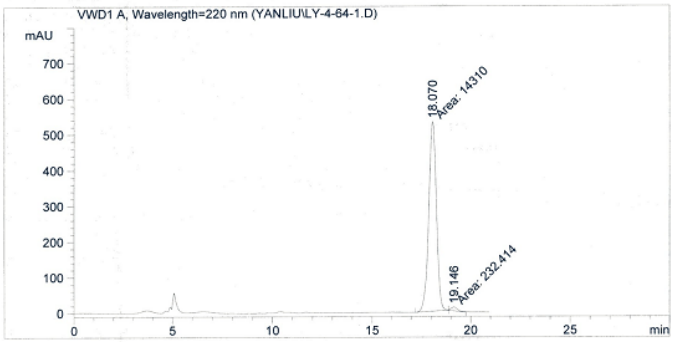
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.570 | VV | 0.3974 | 1.48768e4 | 593.28906 | 57.5092 |
| 2 | 18.671 | VV | 0.4436 | 1.09917e4 | 385.17764 | 42.4908 |
| Totals : | | | | 2.58685e4 | 978.46671 | |




**6Eb**

96% ee obtained from Q-$NH_2$ catalyzed reaction

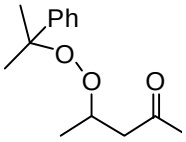



Area Percent Report

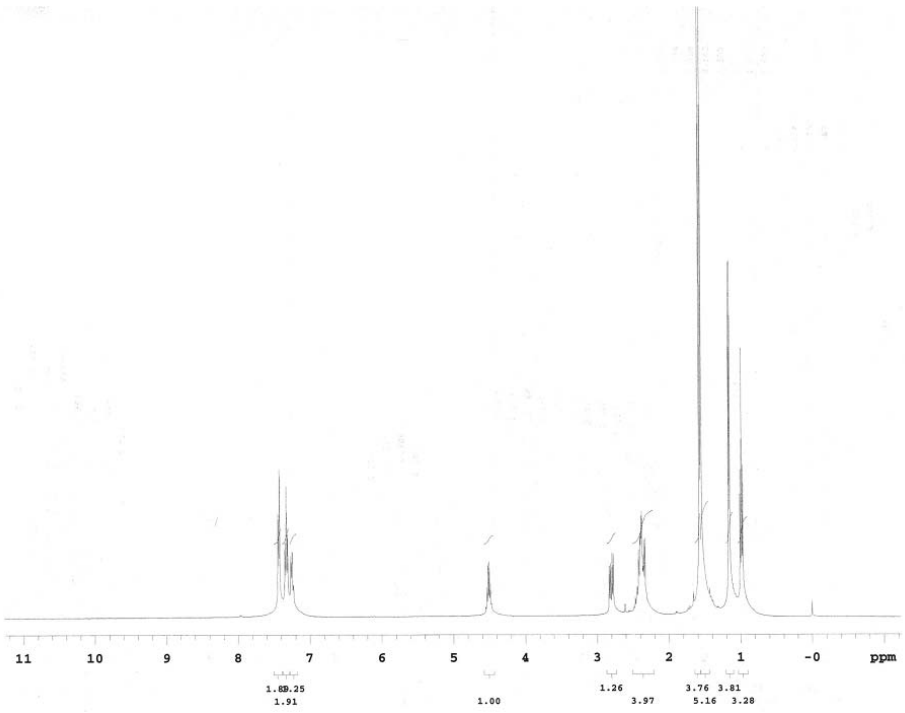
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

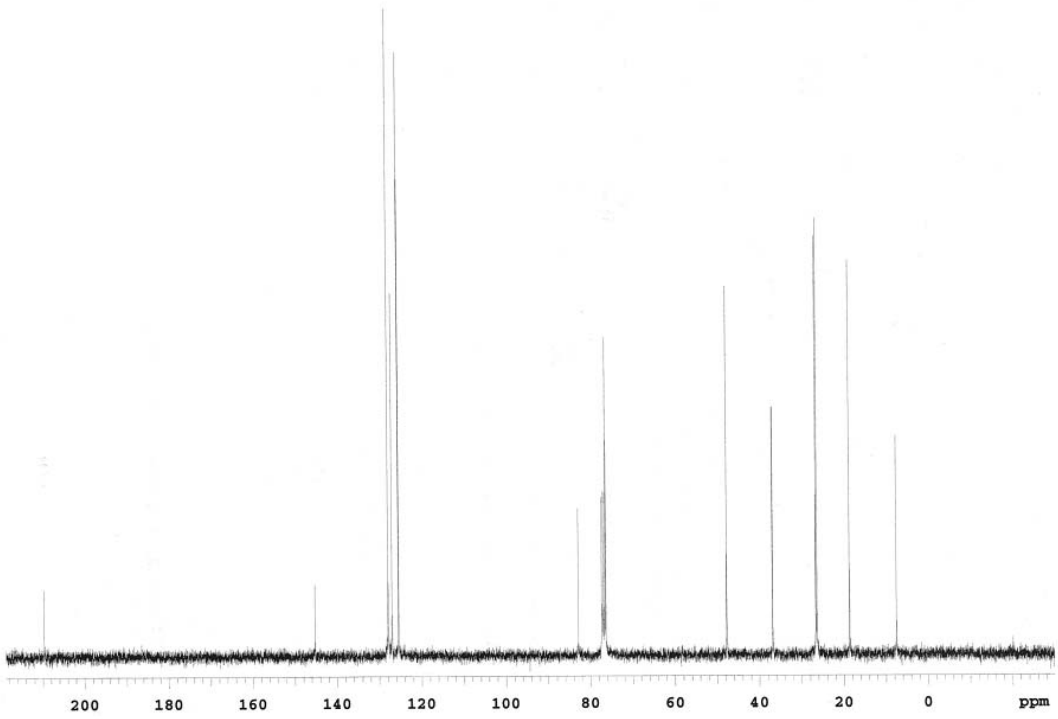
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.070 | MM | 0.4498 | 1.43100e4 | 530.19403 | 98.4018 |
| 2 | 19.146 | MM | 0.3648 | 232.41402 | 10.61706 | 1.5982 |
| Totals : | | | | 1.45424e4 | 540.81109 | |

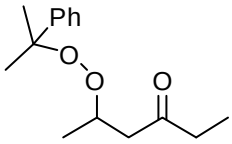

Ph
O
O
O

**6Fb**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.89
1.25
1.91
1.00
1.26
3.97
3.76
3.81
5.16
3.28

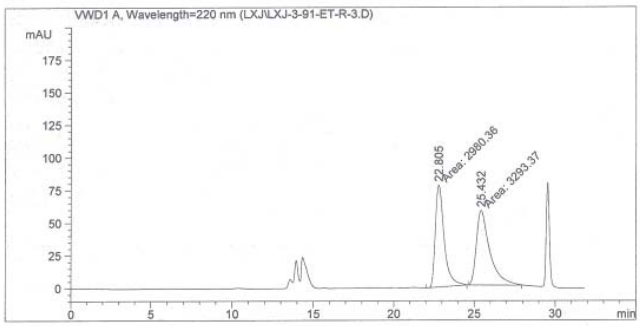

200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC, Daicel Chiralcel AD-H, AD, Hexanes / IPA = 99.7:0.3, 0.6 mL/min, λ = 220 nm




**6Fb**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

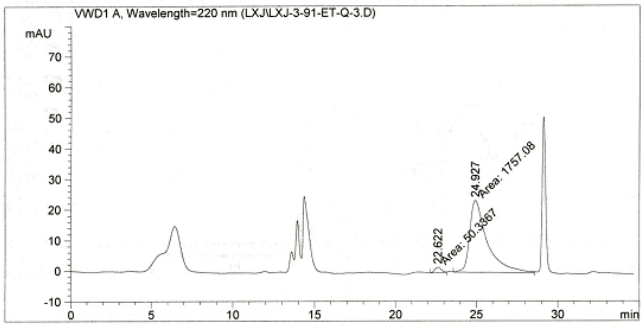



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  22.805 MM    0.6364 2980.35669   78.04903  47.5054
   2  25.432 MM    0.9600 3293.37085   57.17882  52.4946

Totals :                  6273.72754  135.22784
```

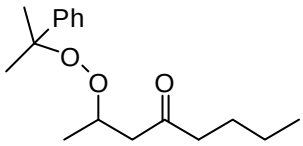



**6Fb**

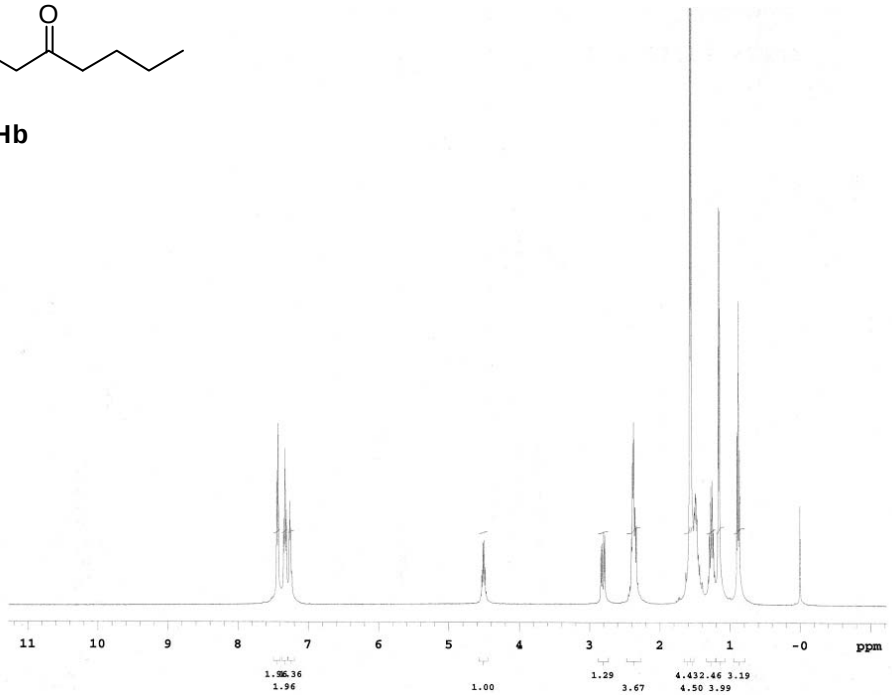
94% ee obtained from Q-N catalyzed reaction

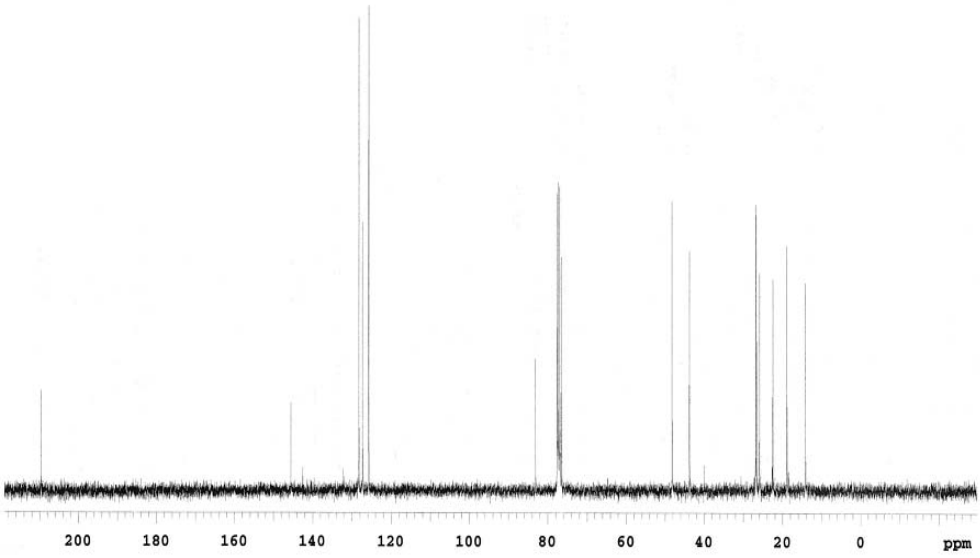



```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Sample Amount         :      1.00000  [ng/ul]   (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  22.622 MM    0.4709   50.33667    1.78161   2.7850
   2  24.927 MM    1.2465 1757.08032   23.49428  97.2150

Totals :                  1807.41699   25.27589
```

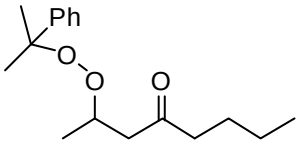

Ph
O
O
O

**6Hb**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.96
1.00
1.29
3.67
4.50
3.99

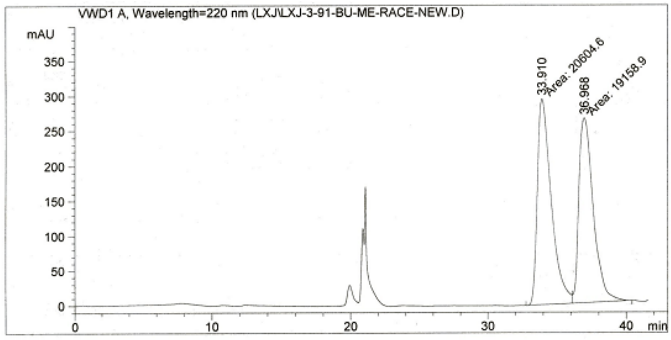

200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC, Daicel Chiralcel AD, AD-H, Hexanes / IPA = 99.5:0.5, 0.4ml/min, λ = 220 nm



**6Hb**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

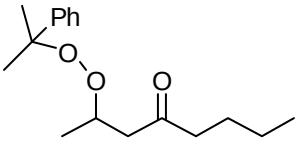



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

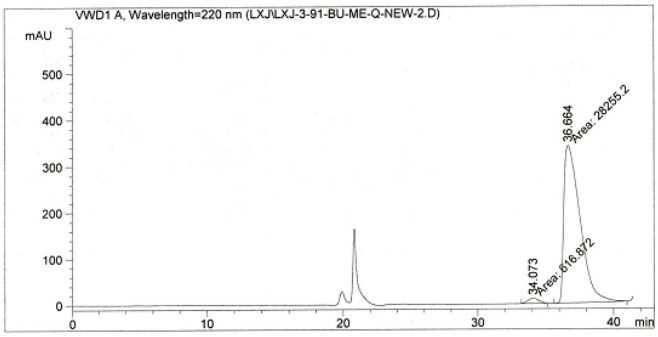
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 33.910 | MF | 1.1657 | 2.06046e4 | 294.60797 | 51.8178 |
| 2 | 36.968 | FM | 1.2074 | 1.91589e4 | 264.47162 | 48.1822 |
| Totals : | | | | 3.97635e4 | 559.07959 | |



**6Hb**

96% ee obtained from Q-NH2 catalyzed reaction

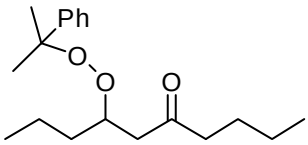



Area Percent Report

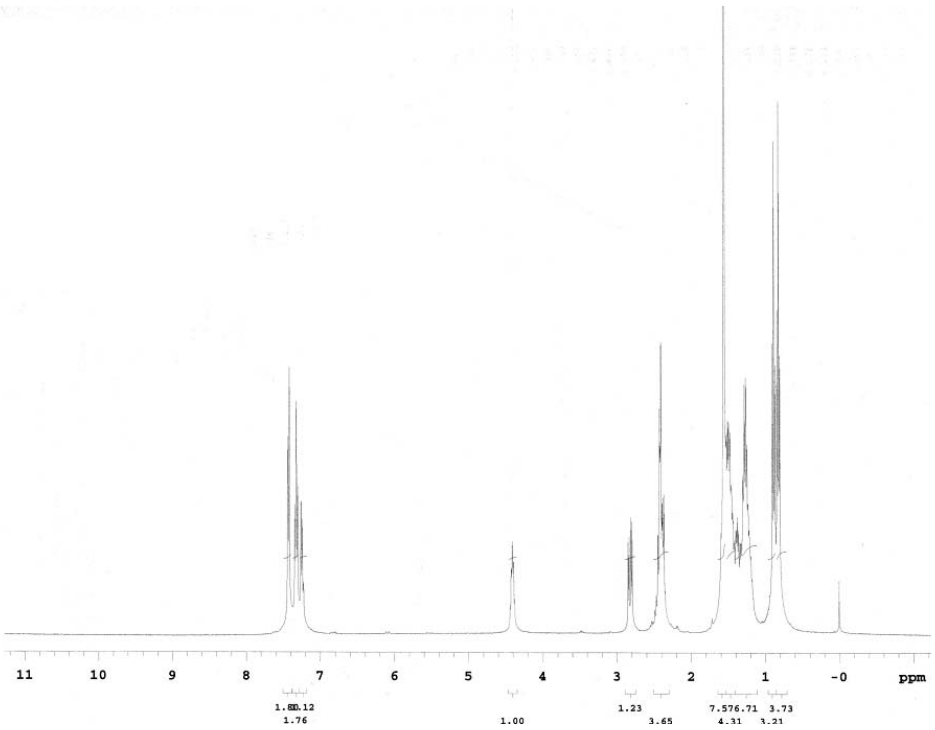
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

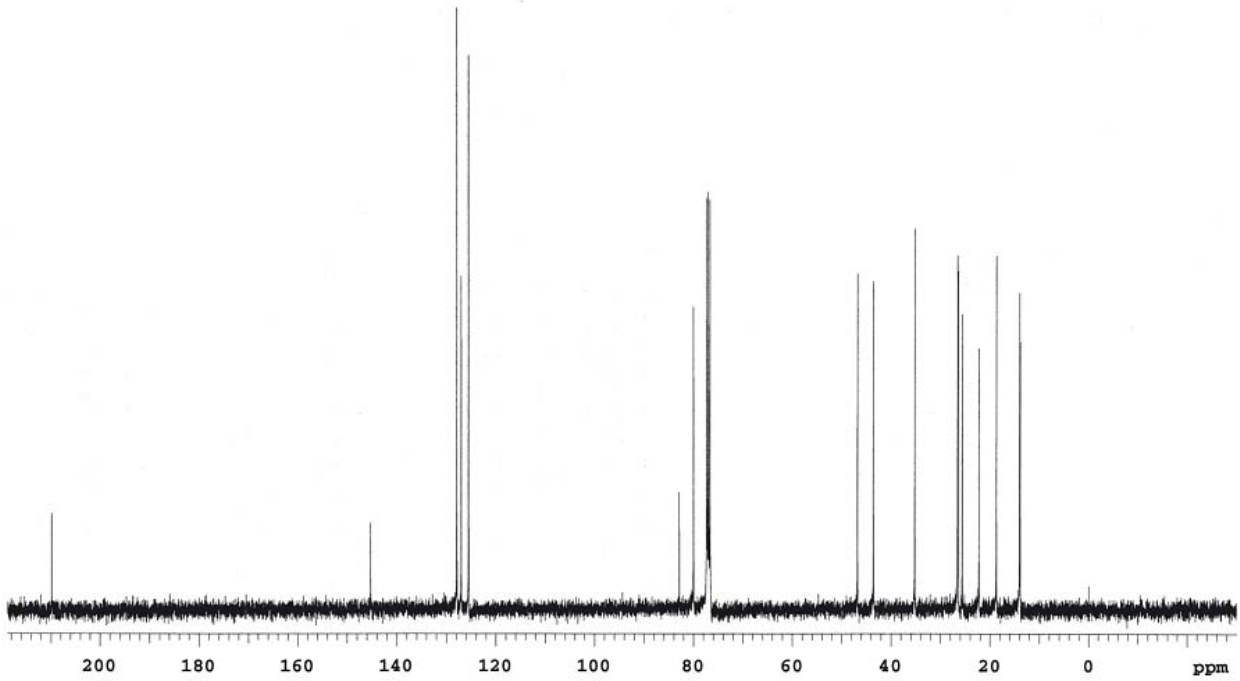
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 34.073 | MM | 0.9375 | 616.87158 | 10.96646 | 2.1366 |
| 2 | 36.664 | MM | 1.3842 | 2.82552e4 | 340.20645 | 97.8634 |
| Totals : | | | | 2.88721e4 | 351.17291 | |

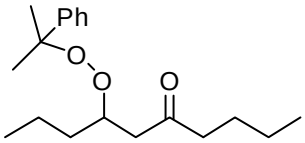

Ph
O
O
O

**6Ib**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.76
1.00
1.23
3.65
7.57
6.71
4.31
3.73

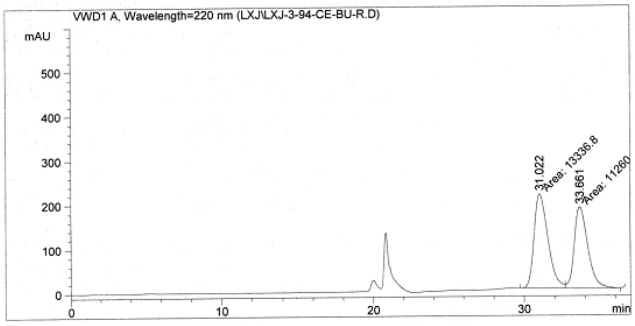

200
180
160
140
120
100
80
60
40
20
0
ppm

HPLC, Daicel Chiralcel AD, AD-H, Hexanes / IPA = 99.5:0.5, 0.4ml/min, λ = 220 nm



**6lb**

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

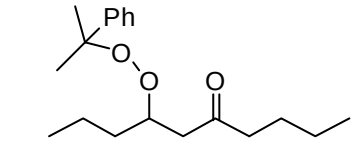



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

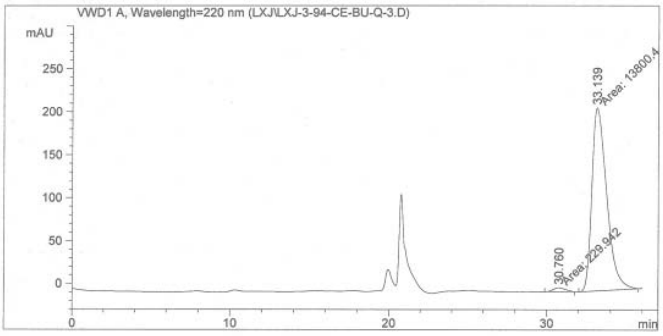
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 31.022 | MF | 1.0492 | 1.33368e4 | 211.86626 | 54.2197 |
| 2 | 33.661 | FM | 1.0290 | 1.12609e4 | 182.38411 | 45.7803 |
| Totals : | | | | 2.45977e4 | 394.25037 | |



**6lb**

97% ee obtained from Q-$NH_2$ catalyzed reaction

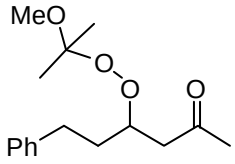



Area Percent Report

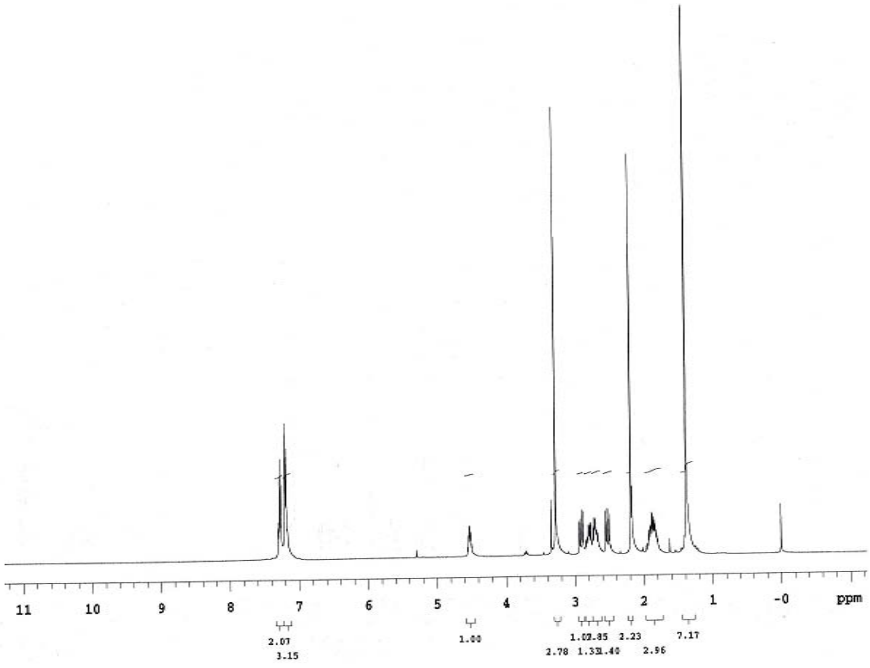
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

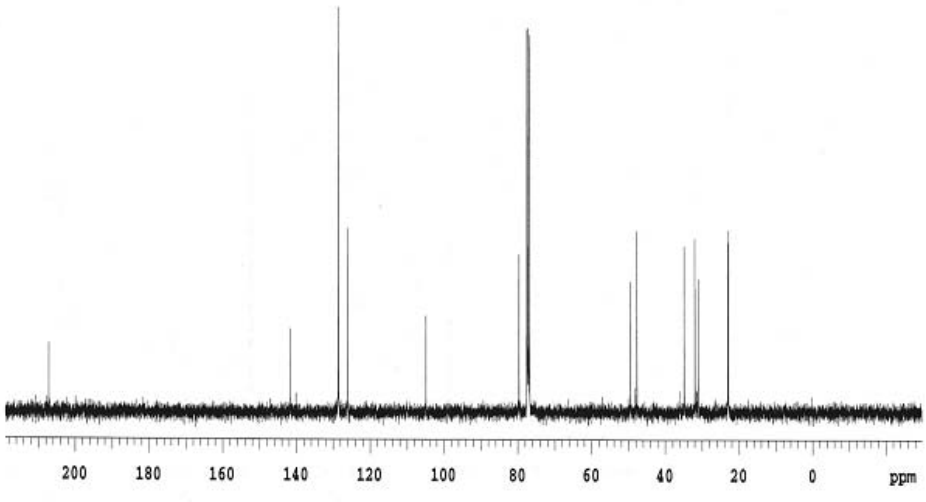
Signal 1: VWD1 A, Wavelength=220 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU ] | Area % |
|---|---|---|---|---|---|---|
| 1 | 30.760 | MM | 0.8680 | 229.94171 | 4.41534 | 1.6389 |
| 2 | 33.139 | MM | 1.0801 | 1.38004e4 | 212.94423 | 98.3611 |
| Totals : | | | | 1.40303e4 | 217.35957 | |

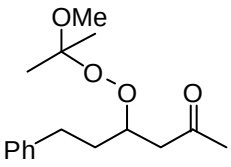

MeO
O
O
O
Ph

**6Ac**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
2.07
3.15
1.00
2.78
1.33
1.40
2.96
2.23
7.17

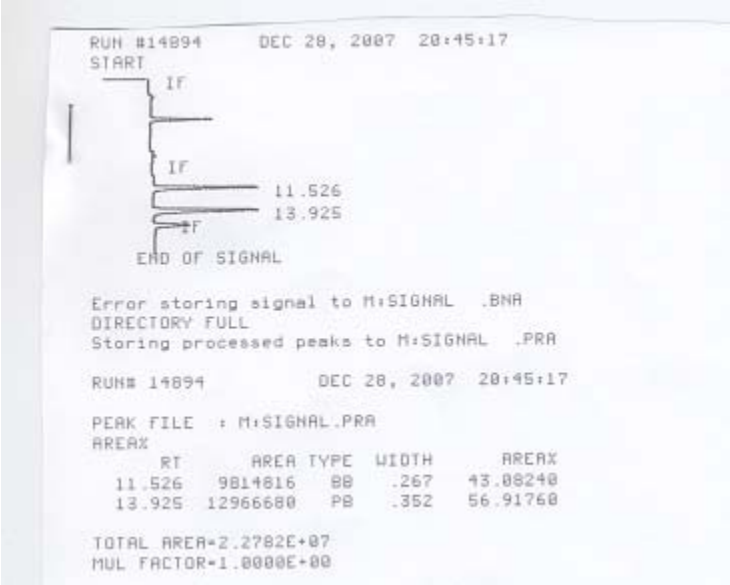

200
180
160
140
120
100
80
60
40
20
0
ppm

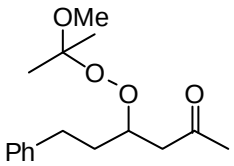
HPLC, Daicel Chiralcel AD-H, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm




**6Ac**

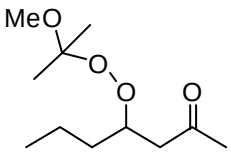
mixture of Q-$NH_2$ and QD-NH catalyzed reaction



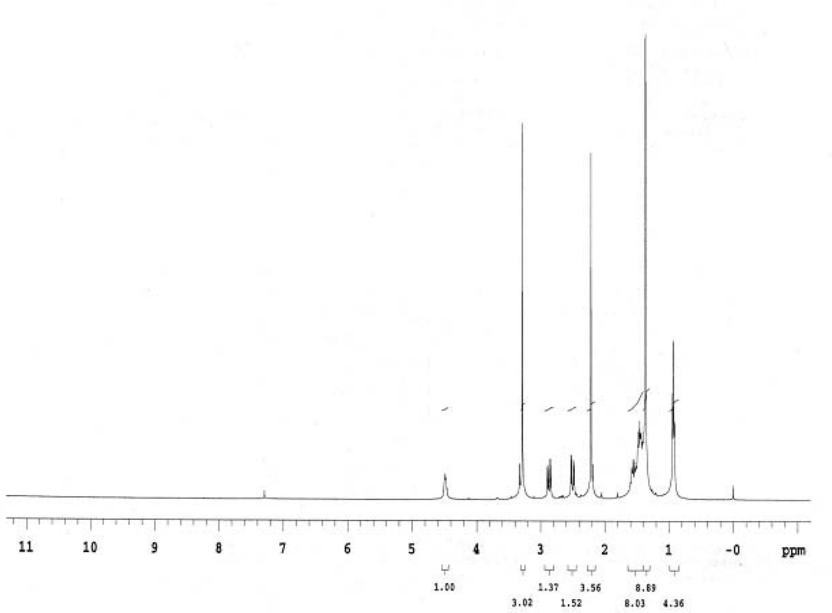



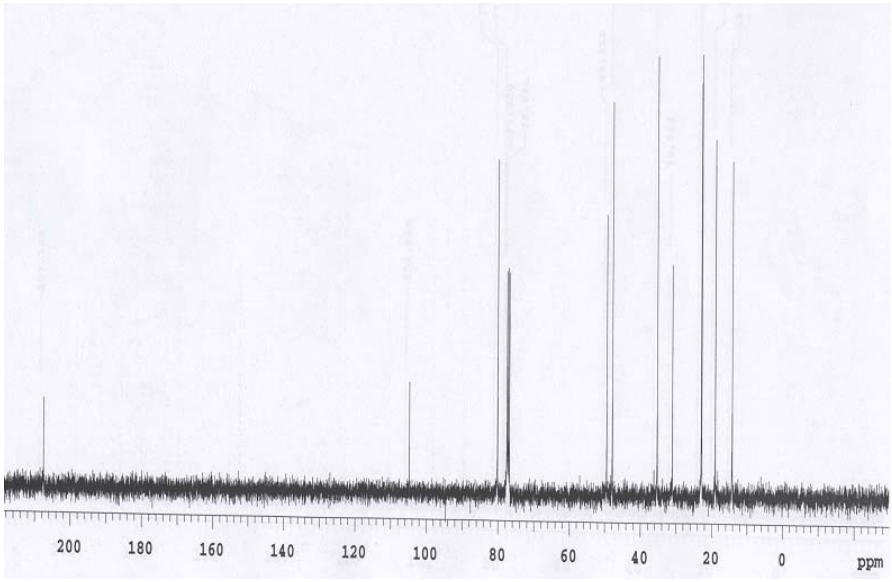

**6Ac**

92%ee, obtained from Q-$NH_2$ catalyzed reaction

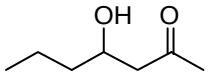

MeO
O
O
O

**6Cc**

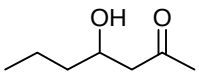

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
3.02
1.37
1.52
3.56
8.89
8.03
4.36


200
180
160
140
120
100
80
60
40
20
0
ppm

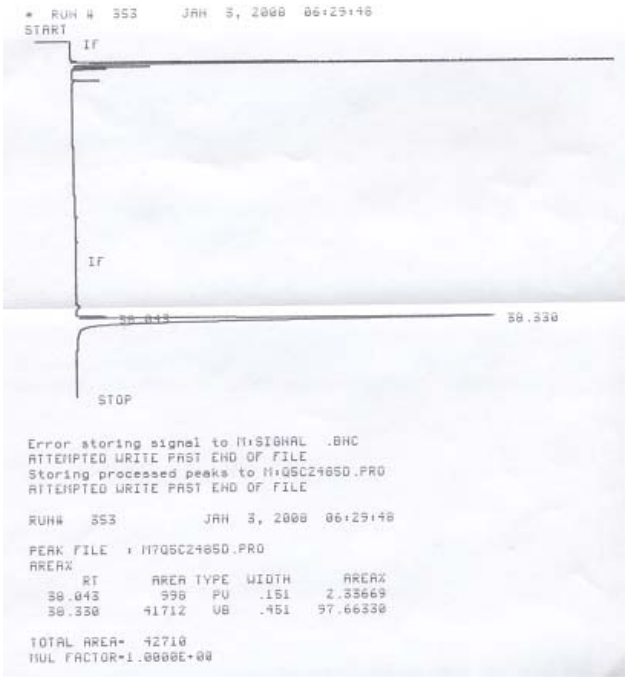
Chiral GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 240°C, Fid Temp: 260°C, Inlet pressure 10 psi. Oven Temp, 50°C 5min, 2.5°C/min, 100°C

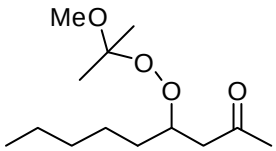



mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

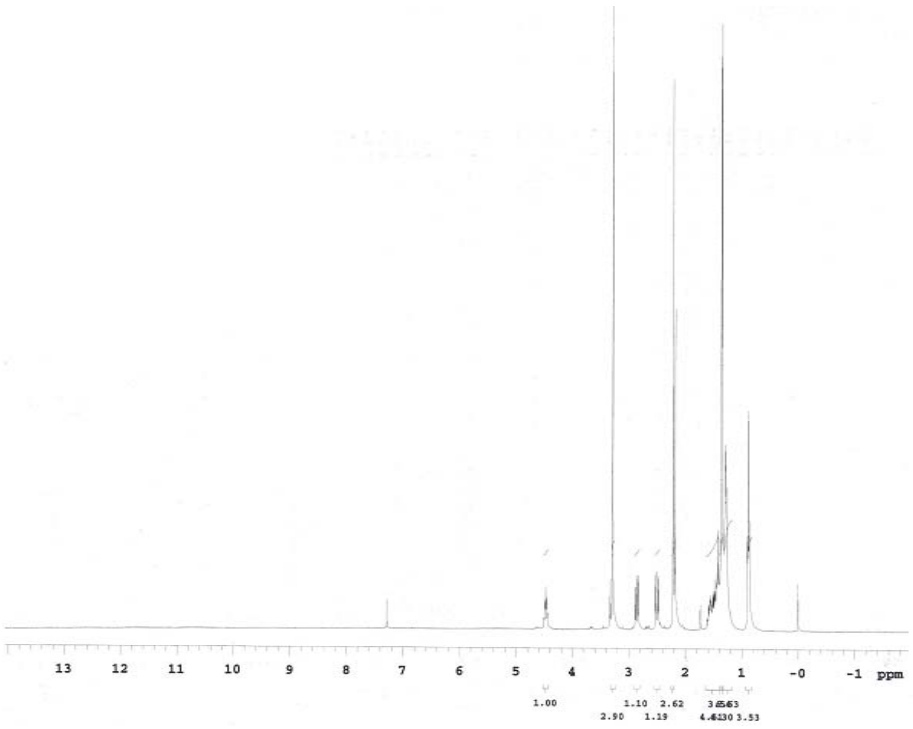



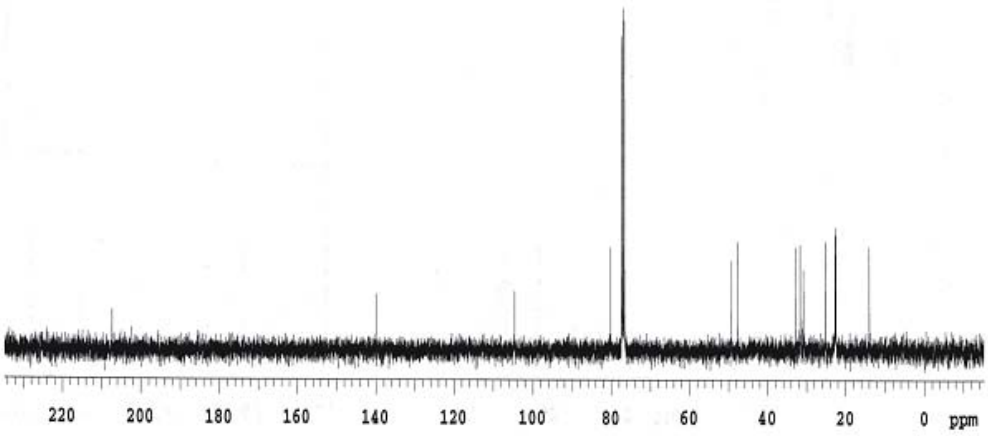

95%ee, obtained from Q-$NH_2$ catalyzed reaction



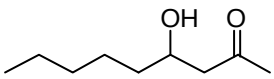

MeO
O
O
O

**6Dc**

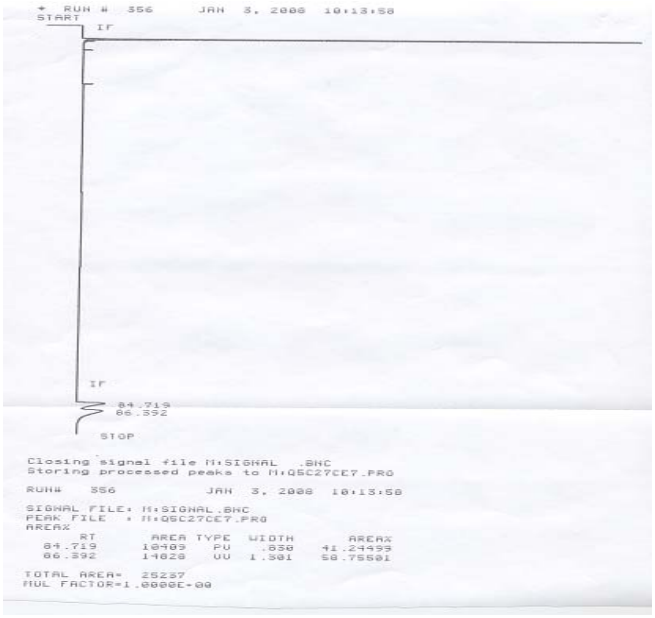

13
12
11
10
9
8
7
6
5
4
3
2
1
-0
-1
ppm
1.00
2.90
1.10
1.19
2.62
3.65
4.61
3.53

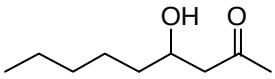

220
200
180
160
140
120
100
80
60
40
20
0
ppm

Chiral GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 240°C, Fid Temp: 260°C, Inlet pressure 10 psi. Oven Temp, 50°C 5min, 5°C/min, 100°C

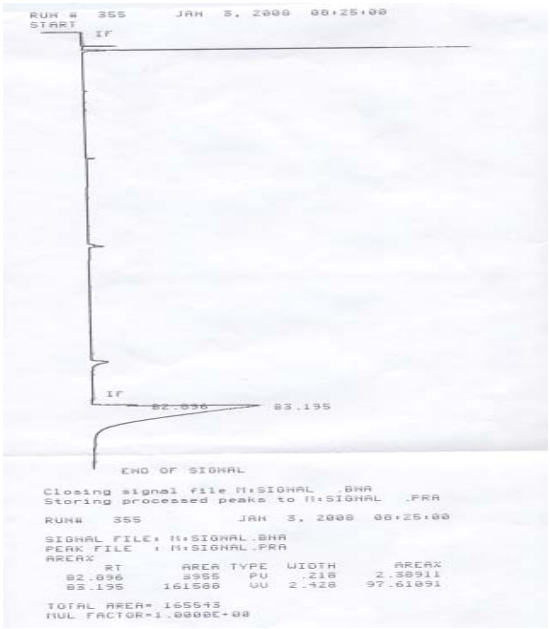


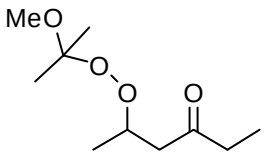

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction



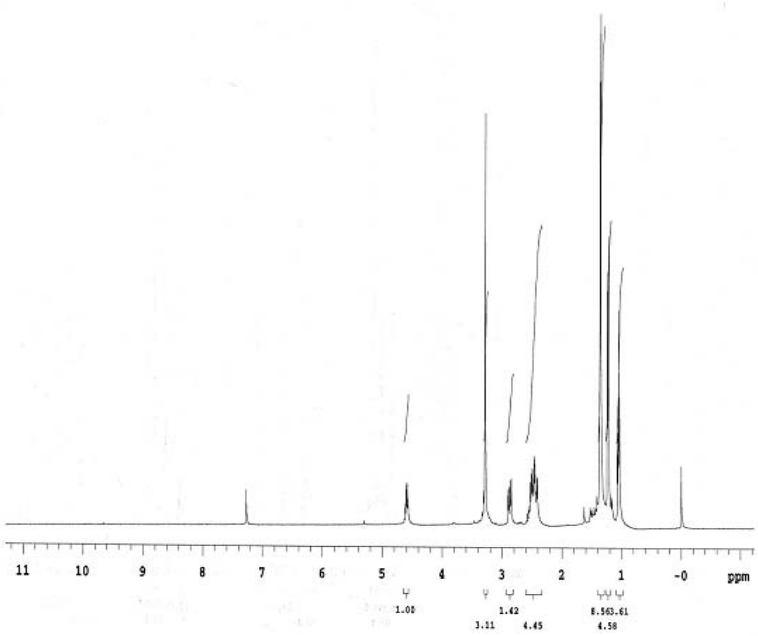



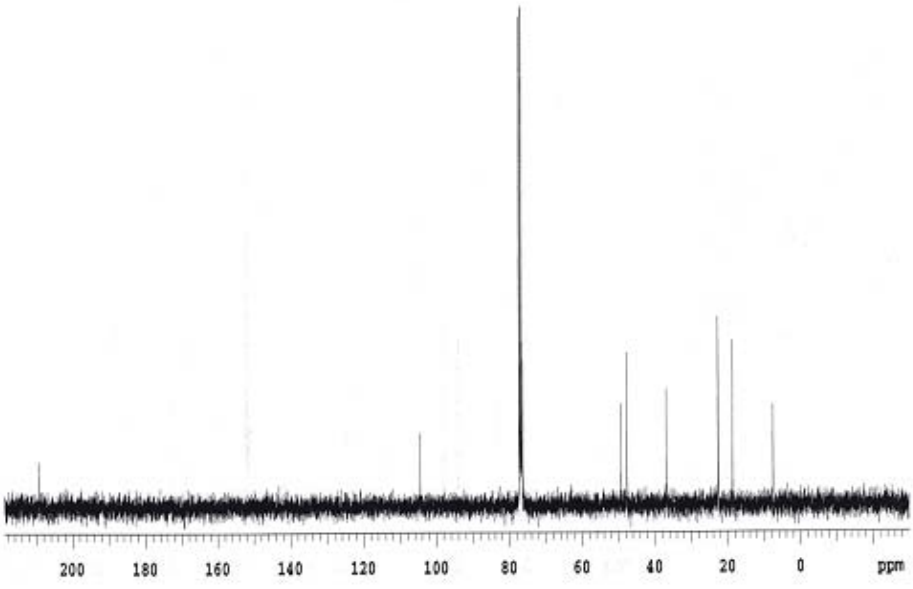

95%ee, obtained from Q-$NH_2$ catalyzed reaction



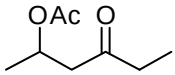

MeO
O
O
O

**6Fc**

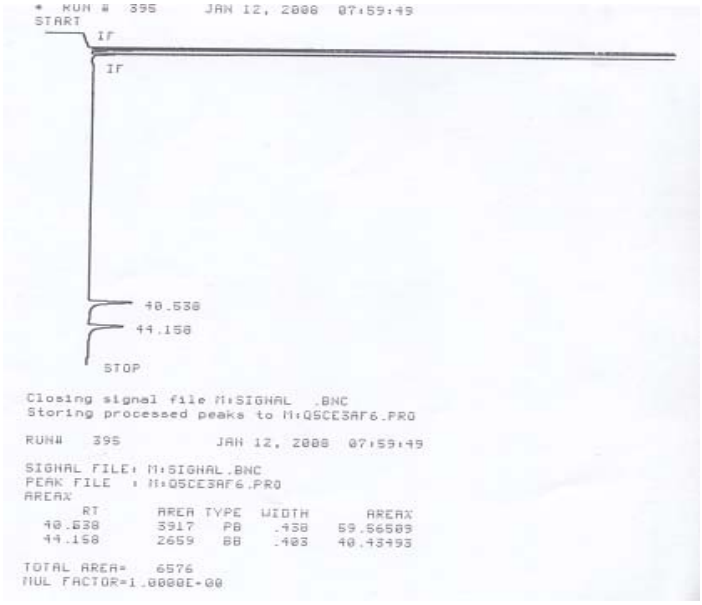

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.00
3.11
1.42
4.45
8.563.61
4.58

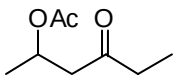

200
180
160
140
120
100
80
60
40
20
0
ppm

Chiral GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 250°C, Fid Temp: 220°C, Inlet pressure 13 psi. Oven Temp: 85°C

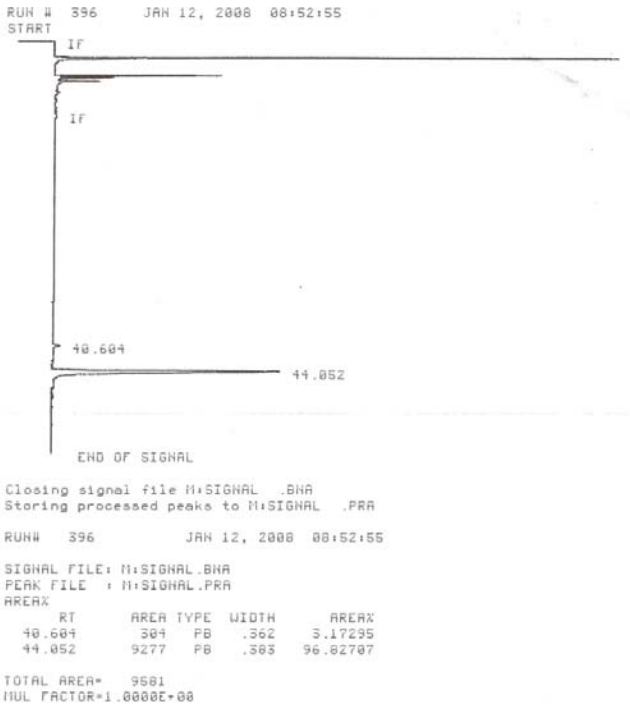


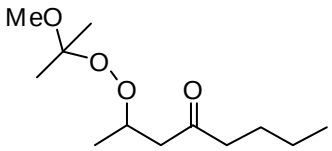

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction



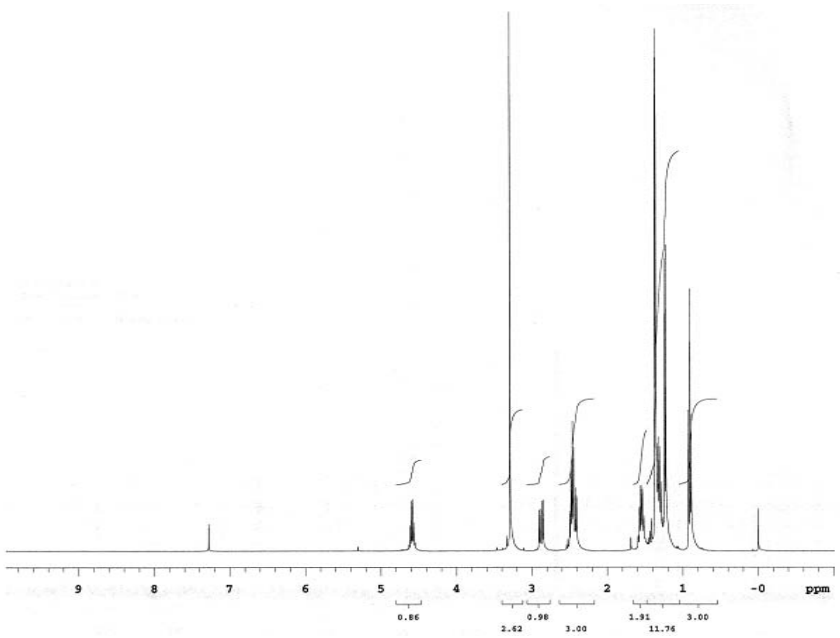



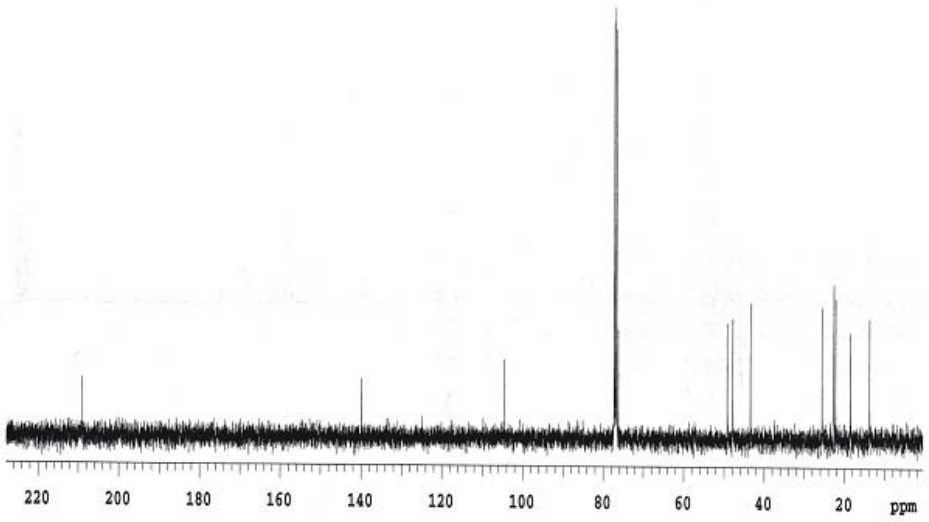

95%ee, obtained from Q-$NH_2$ catalyzed reaction



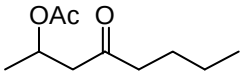

MeO
O
O
O

**6Hc**

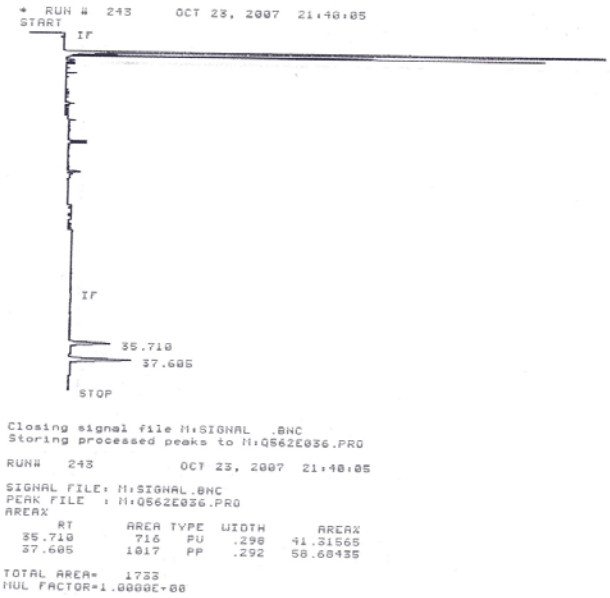

9
8
7
6
5
4
3
2
1
-0
ppm
0.86
2.62
0.98
3.00
1.91
11.76
3.00


220
200
180
160
140
120
100
80
60
40
20
ppm

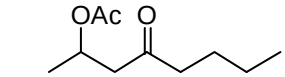
Chiral GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm), Inject Temp: 250°C, Fid Temp: 220°C, Inlet pressure 13 psi, Oven Temp: 110°C



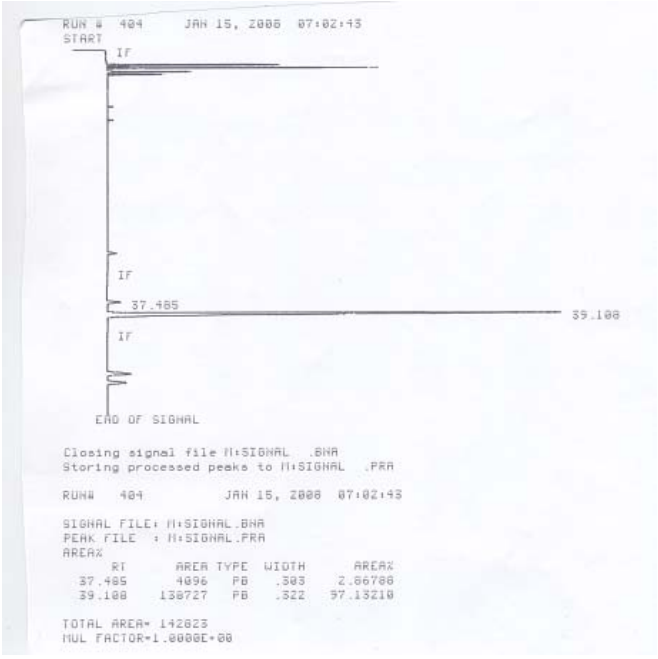

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction



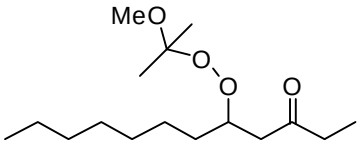

```
Closing signal file M:SIGNAL   .BNC
Storing processed peaks to M:Q562E036.PRO

RUN#   243          OCT 23, 2007  21:40:05

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M:Q562E036.PRO
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  35.710        716   PU    .298    41.31565
  37.685       1017   PP    .292    58.68435

TOTAL AREA=   1733
MUL FACTOR=1.0000E+00
```



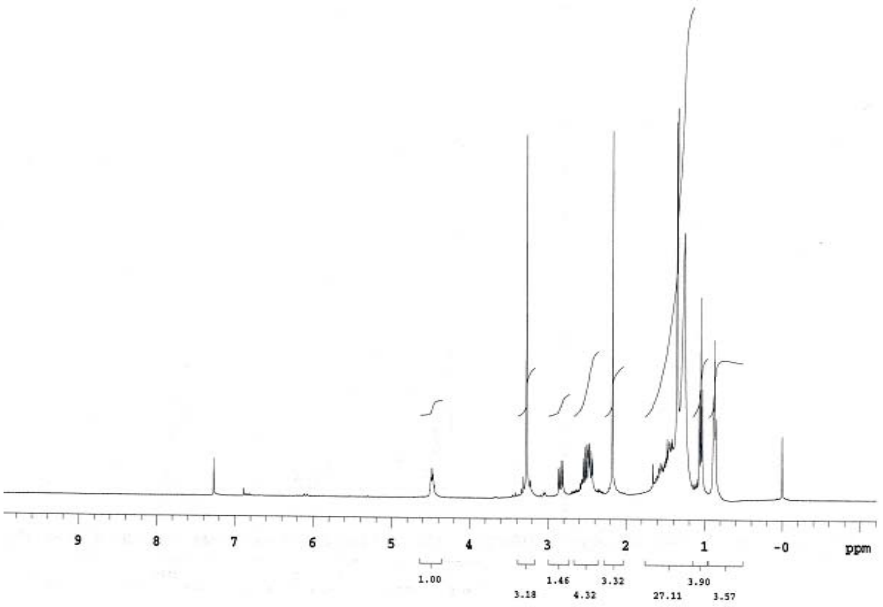

94%ee, obtained from Q-$NH_2$ catalyzed reaction

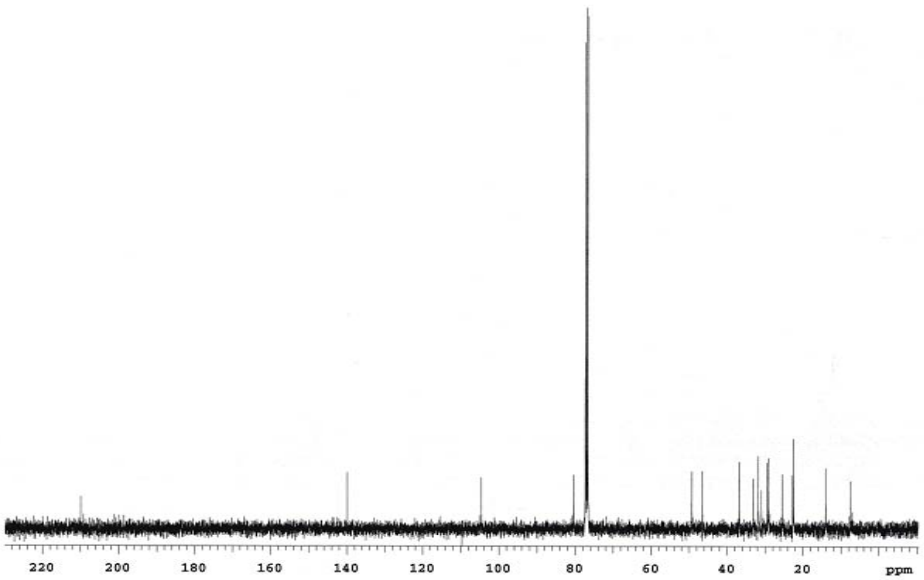



```
Closing signal file M:SIGNAL   .BNA
Storing processed peaks to M:SIGNAL   .PRA

RUN#   404          JAN 15, 2008  07:02:43

SIGNAL FILE: M:SIGNAL.BNA
PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT       AREA TYPE  WIDTH       AREA%
  37.485        4096   PB    .303     2.86788
  39.108      138727   PB    .322    97.13210

TOTAL AREA= 142823
MUL FACTOR=1.0000E+00
```

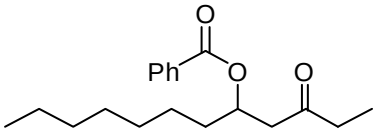

MeO
O
O
O

**6Gc**

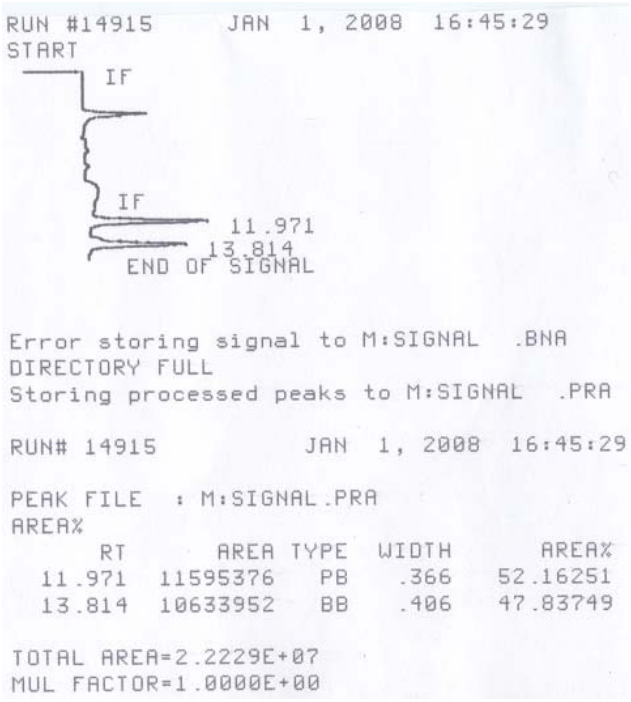

9
8
7
6
5
4
3
2
1
-0
ppm
1.00
3.18
1.46
4.32
3.32
3.90
27.11
3.57


220
200
180
160
140
120
100
80
60
40
20
ppm

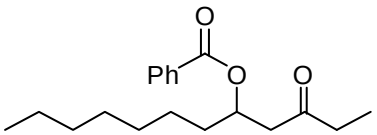
HPLC, (R,R)Whelk-O 1, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm



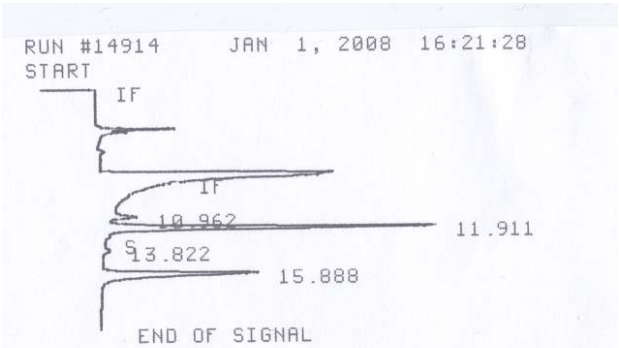

mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction



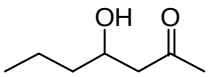

```
Error storing signal to M:SIGNAL   .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL   .PRA

RUN# 14915          JAN  1, 2008  16:45:29

PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT      AREA TYPE  WIDTH      AREA%
  11.971  11595376   PB    .366   52.16251
  13.814  10633952   BB    .406   47.83749

TOTAL AREA=2.2229E+07
MUL FACTOR=1.0000E+00
```



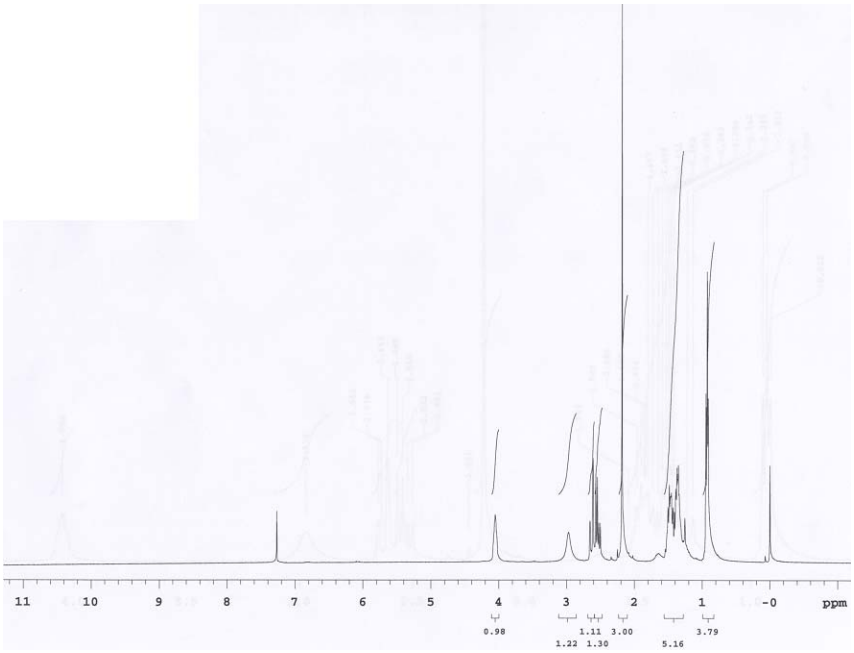

94%ee, obtained from Q-$NH_2$ catalyzed reaction

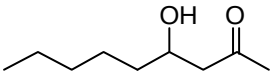



```
Error storing signal to M:SIGNAL   .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL   .PRA

RUN# 14914          JAN  1, 2008  16:21:28

PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT      AREA TYPE  WIDTH      AREA%
  10.962   2351936   BP    .317    4.31184
  11.911  31489600  SPB    .330   57.73035
  13.822    893320   BB    .446    1.63774
  15.888  19811152 ISPP    .436   36.32008

TOTAL AREA=5.4546E+07
MUL FACTOR=1.0000E+00
```

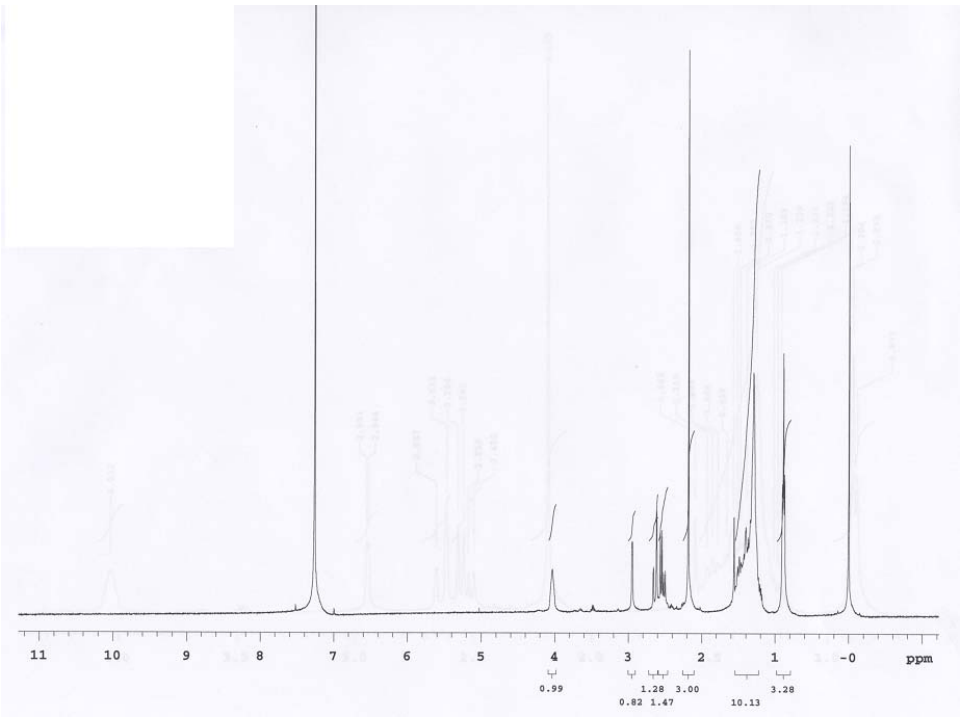

OH
O

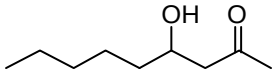
**13**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.98
1.22
1.11
1.30
3.00
5.16
3.79


OH
O

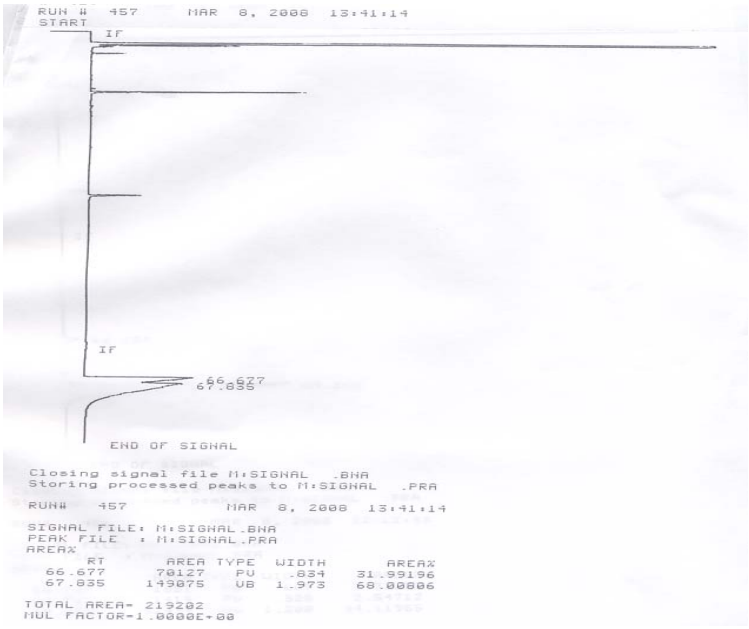
**14**

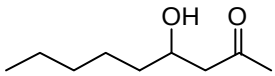

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.99
0.82
1.28
1.47
3.00
10.13
3.28




14

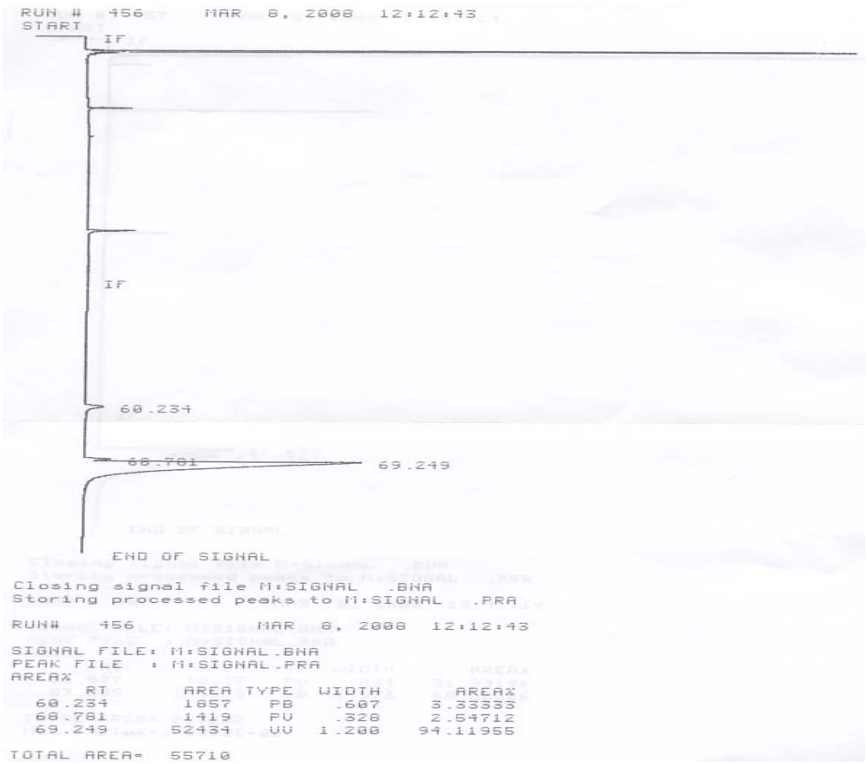
mixture of Q-$NH_2$ and QD-$NH_2$ catalyzed reaction

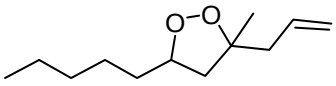


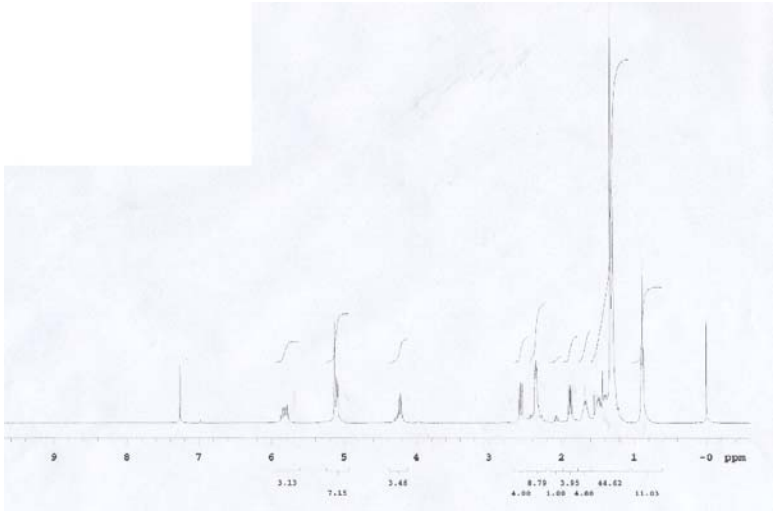

14

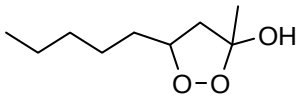
95%ee, obtained from Q-$NH_2$ catalyzed reaction



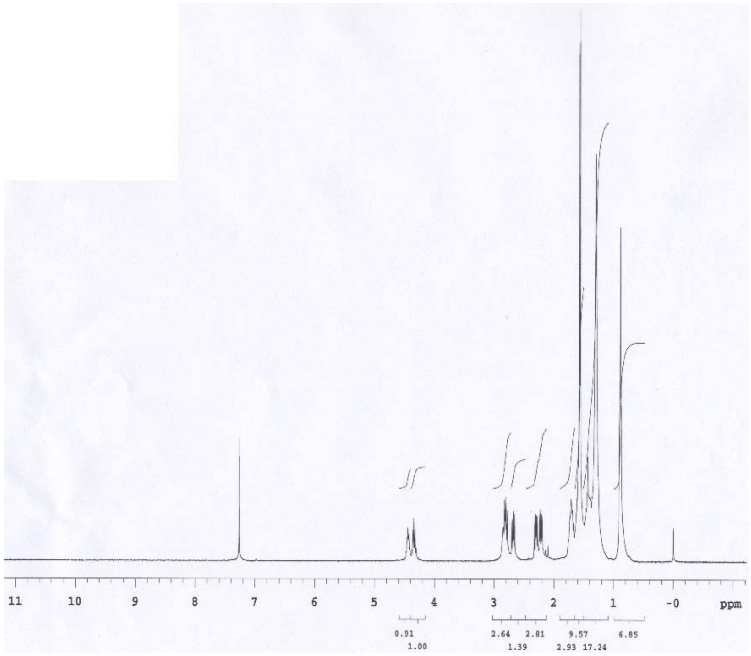


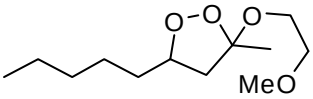
**15**



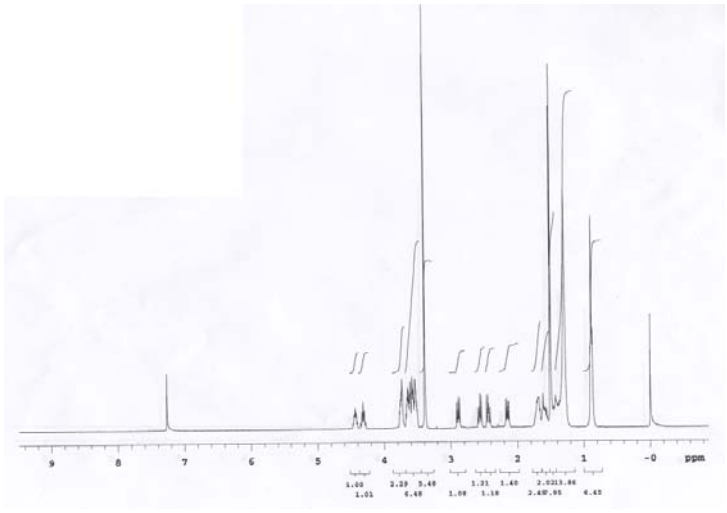


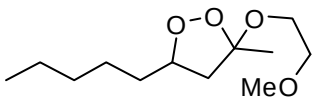
**16**



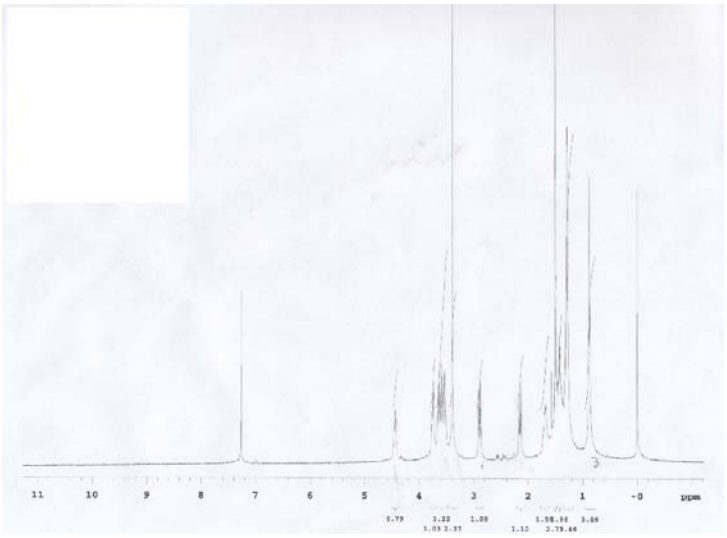


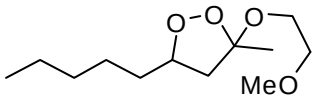
**17**



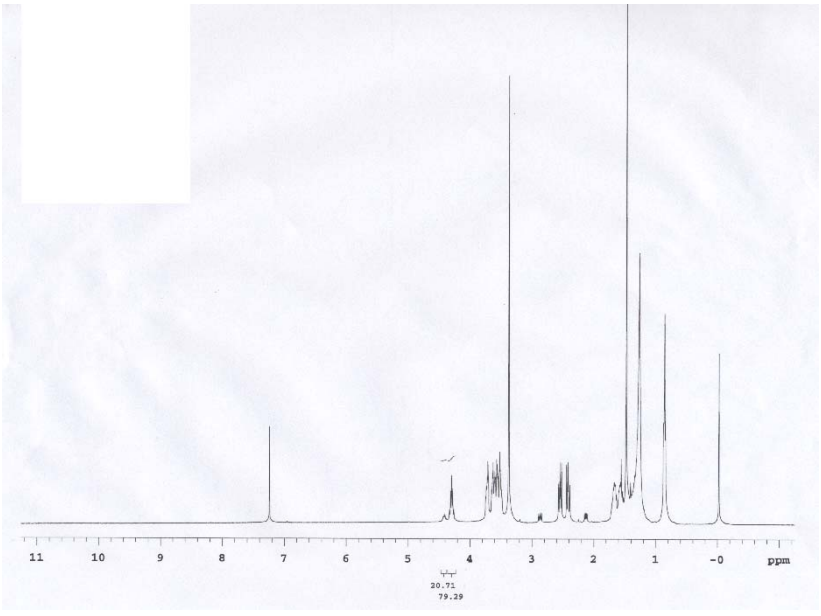

O
O
O
MeO

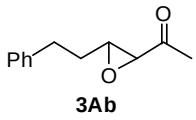
**17a**


11
10
9
8
7
6
5
4
3
2
1
-0
ppm

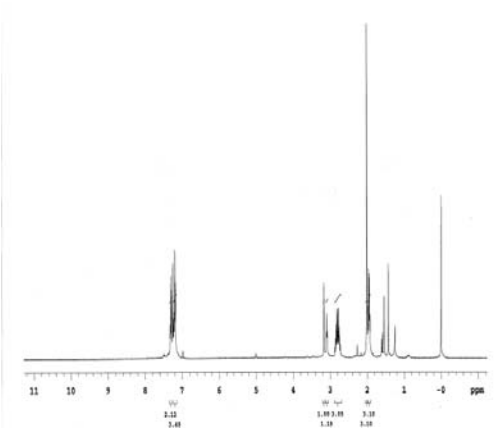

O
O
O
MeO

**17b**

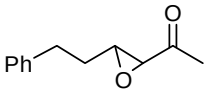

11
10
9
8
7
6
5
4
3
2
1
-0
ppm
20.71
79.29




**3Ab**

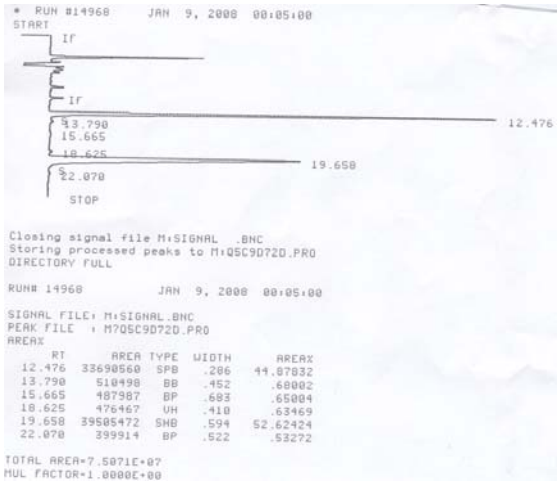


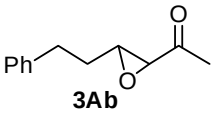
HPLC, Daicel Chiralcel AD-H, Hexanes / IPA = 99:1, 1 mL/min, λ = 220 nm




**3Ab**

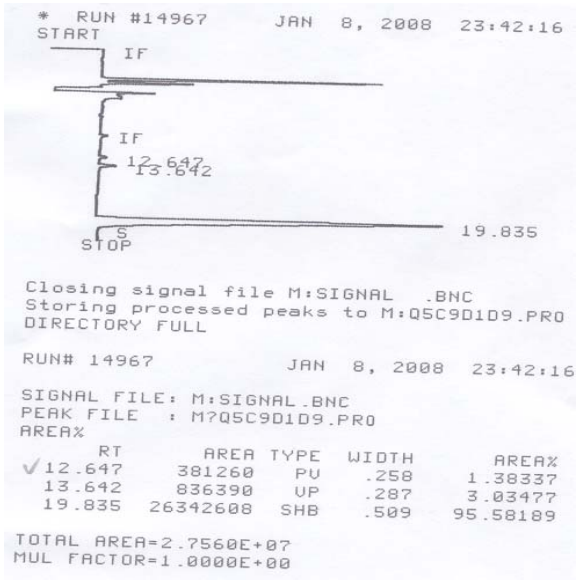
racemic

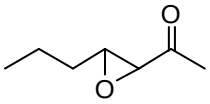


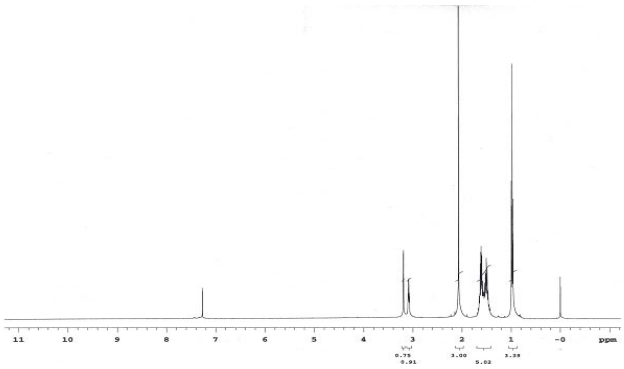

**3Ab**

97%ee, obtained from Q-$NH_2$ catalyzed reaction

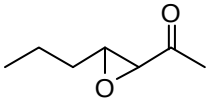




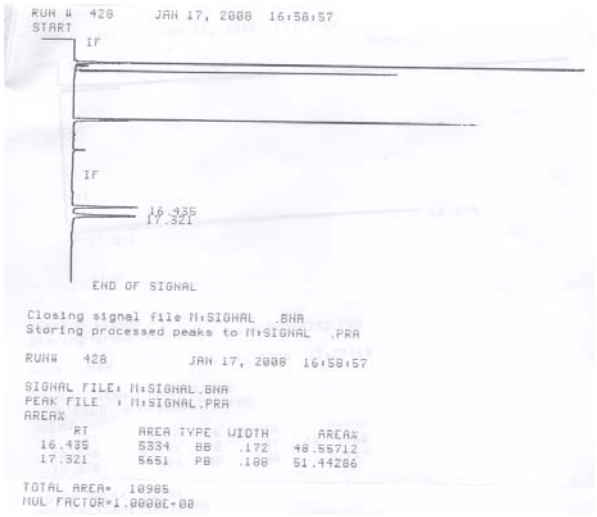
**3Cb**

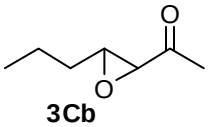


Chiral GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250°C, Fid Temp: 260°C, Inlet pressure 13 psi. Oven Temp: 90°C

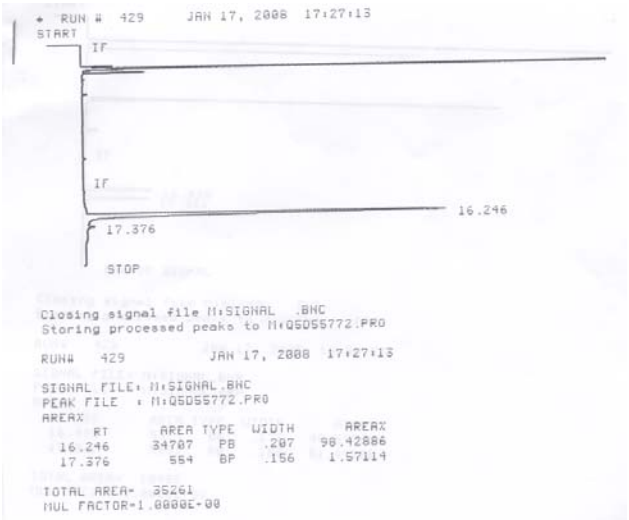


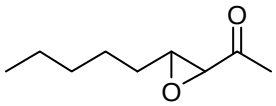
**3Cb**
racemic



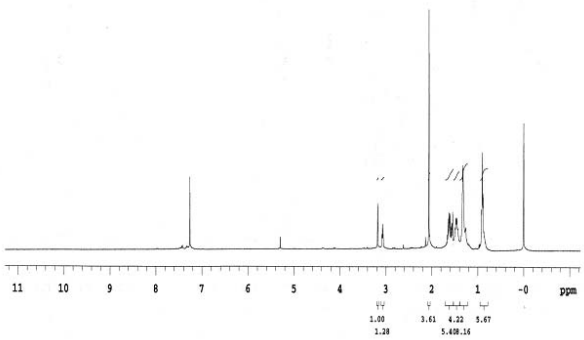



**3Cb**
97%ee, obtained from
Q-$NH_2$ catalyzed reaction

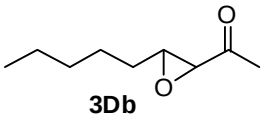




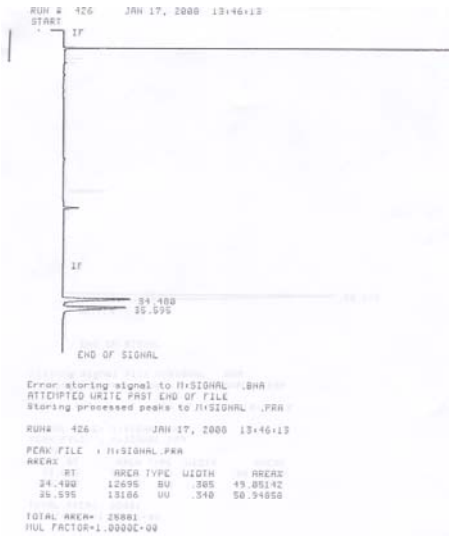
**3Db**

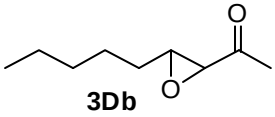



Chiral GC HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250°C, Fid Temp: 260°C, Inlet pressure 13 psi. Oven Temp: 102°C

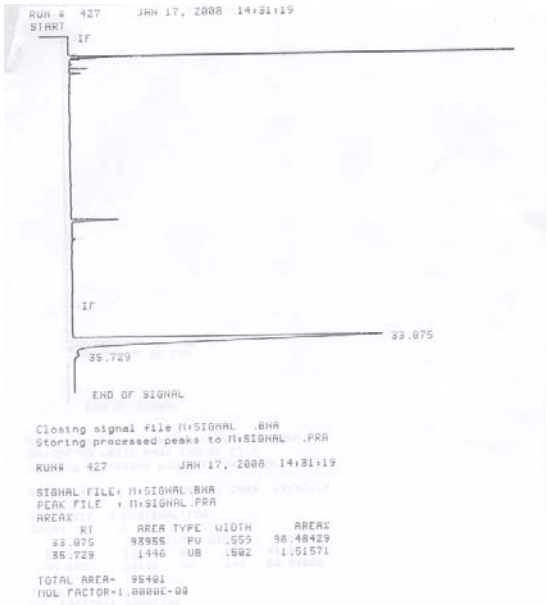


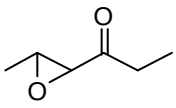
**3Db**
racemic



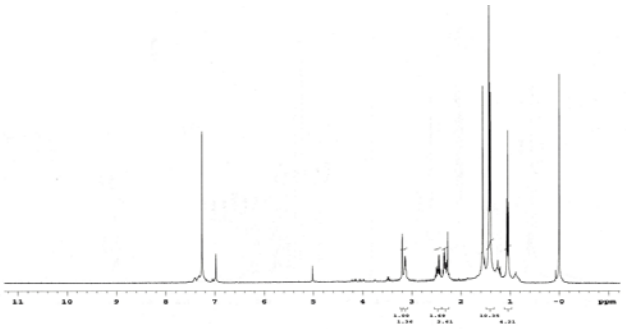



**3Db**
97%ee, obtained from Q-$NH_2$ catalyzed reaction

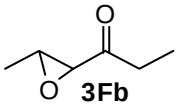




**3Fb**

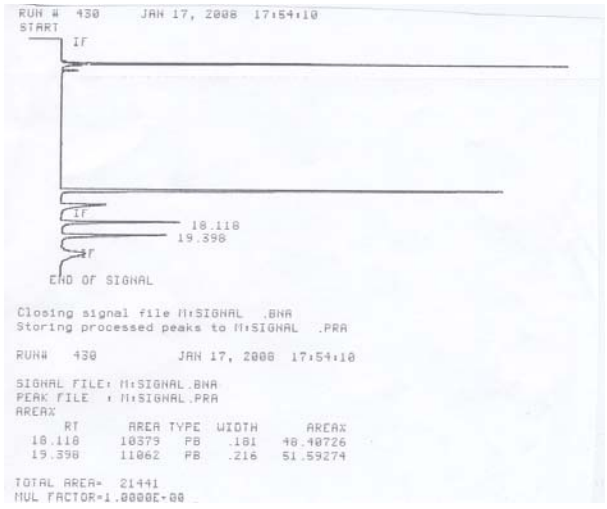


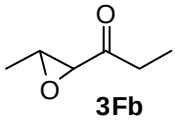
Chiral GC [HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250°C, Fid Temp: 260°C, Inlet pressure 13 psi. Oven Temp: 73°C



**3Fb**

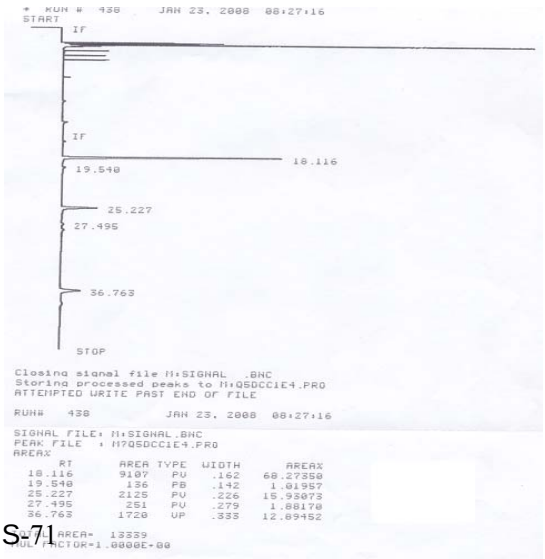
racemic

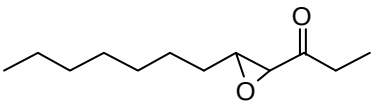


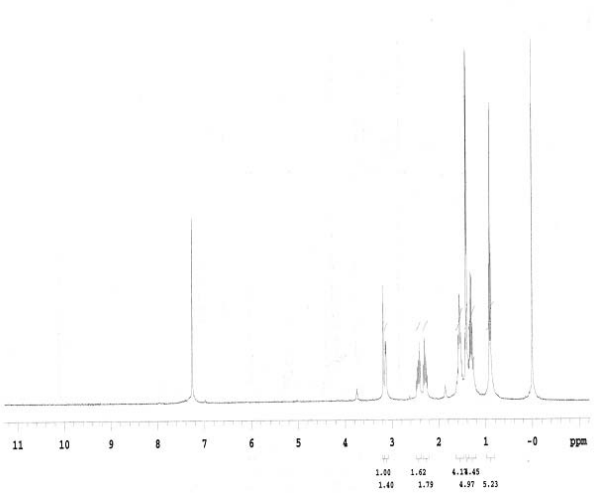
**3Fb**

97%ee, obtained from Q-$NH_2$ catalyzed reaction

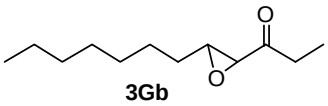




**3Gb**

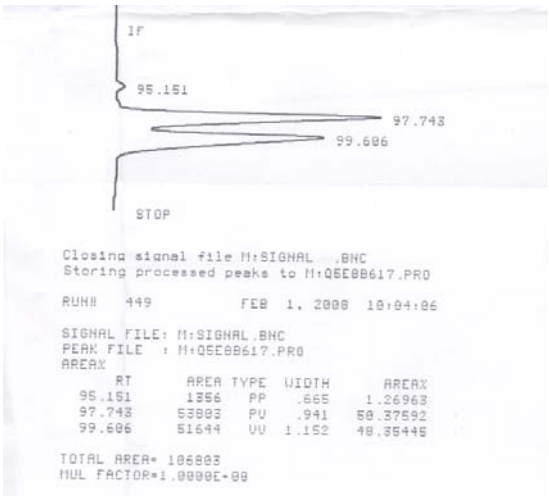


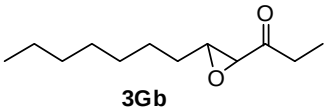

Chiral GC [HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250°C, Fid Temp: 260°C, Inlet pressure 13 psi. Oven Temp: 115°C



**3Gb**

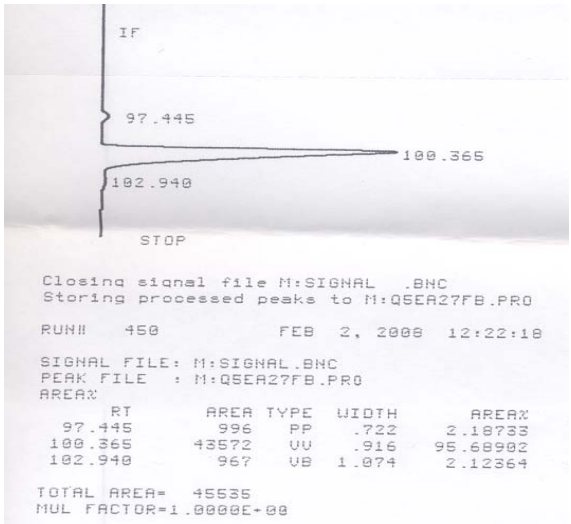
racemic

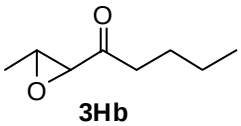


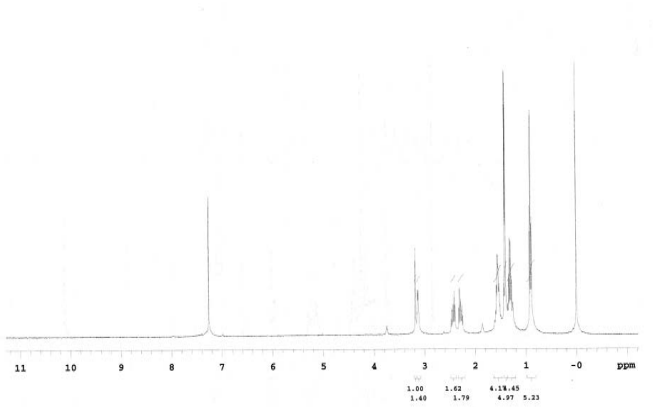
**3Gb**

96% ee, obtained from Q-$NH_2$ catalyzed reaction

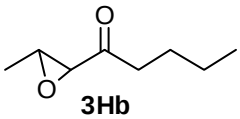




**3Hb**

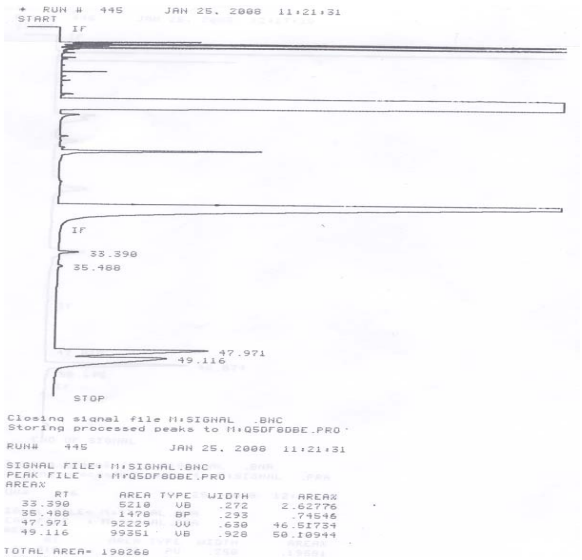


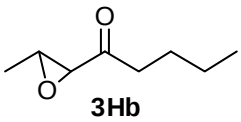

Chiral GC [HP Chiral(20% Permethylated $\beta$-Cyclodextrin, 30m x 0.25 mm) Inject Temp: 250°C, Fid Temp: 260°C, Inlet pressure 13 psi. Oven Temp: 80°C



**3Hb**

racemic



**3Hb**

97%ee, obtained from Q-$NH_2$ catalyzed reaction