Supporting Information
Asymmetric olefin isomerization of butenolides via proton transfer catalysis by an organic molecule

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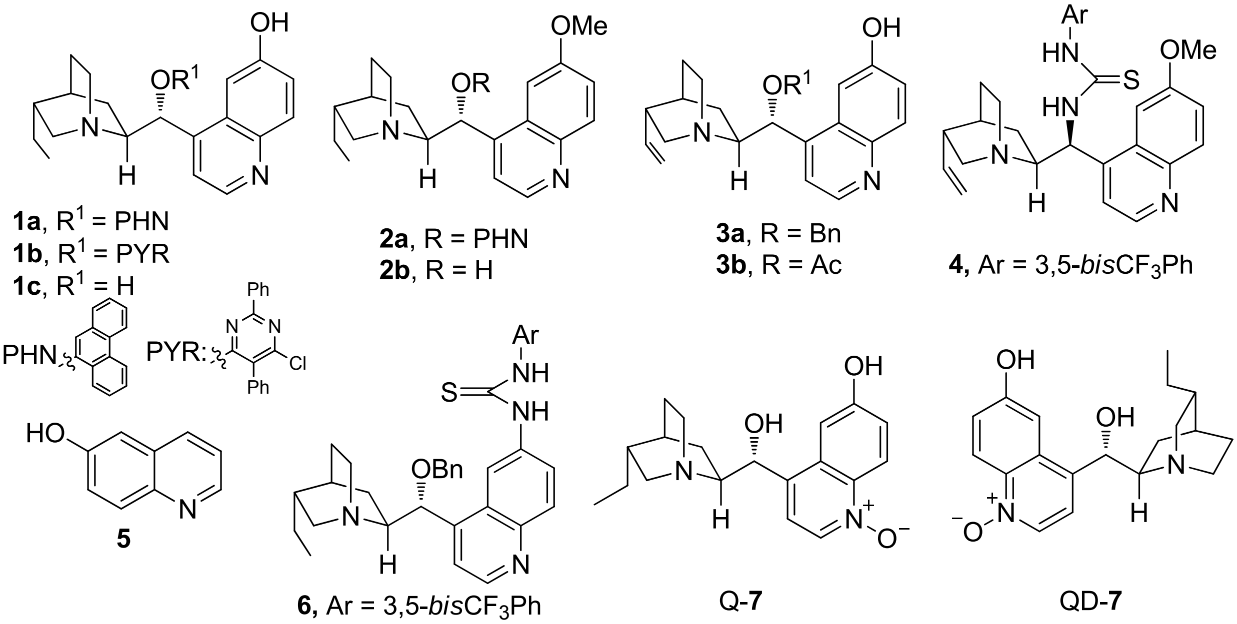
General Information. ^1H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), integration, coupling constant (Hz). 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. Low resolution and high resolution mass spectra were recorded on either a Micromass 70-VSE-B instrument (EI, CI) or a Micromass Q-TOF instrument (ESI). Specific rotations were measured on a Jasco Digital Polarimeter.

High performance liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1100 Series instrument equipped with a quaternary pump, using Daicel Chiralpak AS or AS-H Columns (250 x 4.6 mm). UV absorption was monitored at 220 nm.

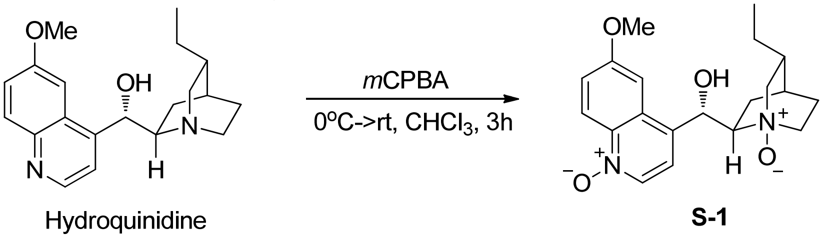
1. Materials:

Cinchona alkaloid catalysts (**S-Figure 1**): **1a**, **1b**, **1c**, **3a**, **3b** and **4** were prepared according to our reported methods.[1] **2a**, hydroquinine (**2b**) and **5** were purchased from Aldrich Inc. and used without further purification. **6** was prepared according to a reported literature.[2]

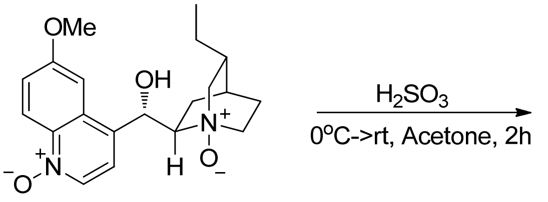


S-Figure 1. Structure of the catalysts

Preparation of Catalyst QD-7:

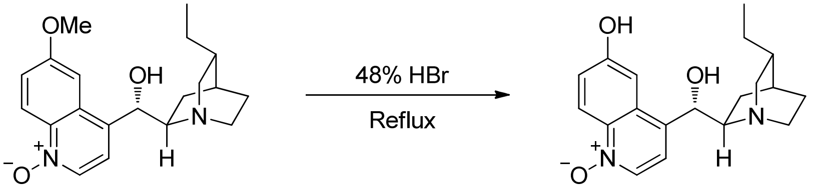


At 0 °C, *m*-chloroperoxybenzoic acid (77%, 9.20 g, 37.5 mmol) was added in portions to a solution of dihydroquinidine (4.89 g, 15.0 mmol) in chloroform (90 mL). The resulting suspension was allowed to warm to rt and stirred for 3 h at that temperature, during which time the reaction mixture became a clear yellow solution. The reaction was quenched with NaOH(aq) (10% in H_2O) until pH = 10. The resulting two-phase mixture was extracted with a mixed solvent of $CHCl_3$/MeOH (10/1, 50 mL×6). The organic phase was collected and the combined organic phase was dried over Na_2SO_4, filtered and evaporated *in vacuo* to give the crude product **S-1** as a light yellow foam (5.30 g, 99% yield). This crude product was used in the next step without further purification.



S-1 **S-2**

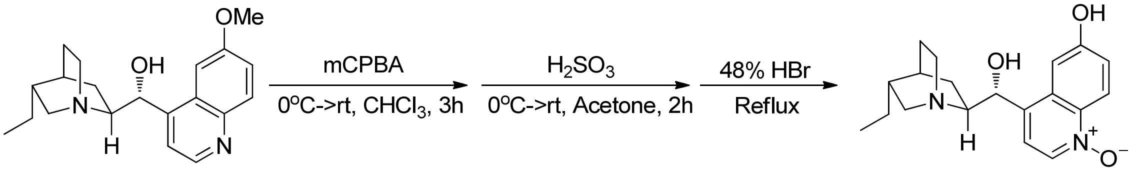
To the solution of **S-1** (5.30 g, 15.0 mmol) in acetone (60 mL) at 0 °C was added dropwise an aqueous solution of sulfurous acid (6% wt, 24 mL, 18 mmol). The resulting mixture was warmed to rt. White solid precipitated out from the solution during the next 2 h. The resulting mixture was stirred overnight until the solution became clear again. Then, the acetone was removed under vacuum and ammonium hydroxide was added to make the solution alkaline. Chloroform (50 mL×5) was used to extract the aqueous layer. The organic layers were combined, washed with brine (50 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was subjected to silica gel column chromatography (CH_2Cl_2/MeOH = 20/1 + 1% Et_3N) to afford **S-2** as a white solid (4.51 g, 86% yield). m. p. 187-188 °C; $[\alpha]_D^{23}$ = +202.9 (c = 0.27, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2Hz, 3H), 1.22-1.25 (m, 1H), 1.35-1.47 (m, 5H), 1.68 (bs, 1H), 1.93 (t, *J* = 10.0Hz, 1H), 2.65-2.74 (m, 2H), 2.78-2.94 (m, 3H), 3.85 (s, 3H), 5.17 (s, 1H), 5.49 (s, 1H), 6.90 (s, 1H), 7.14-7.20 (m, 2H), 7.93 (d, *J* = 6.4Hz, 1H), 8.45 (d, *J* = 9.2Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.0, 21.9, 25.2, 26.2, 27.3, 37.4, 50.1, 51.0, 55.6, 60.3, 71.0, 101.7, 118.4, 121.1, 122.5, 128.5, 133.7, 135.1, 142.5, 158.6; IR ($CHCl_3$) ν 3193, 2934, 2216, 1618, 1573, 1465, 1213, 1024 cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{20}H_{27}N_2O_3$ requires m/z 343.2022, found m/z 343.2019.



S-2 QD-**7**

A round bottom flask (25 mL) equipped with a reflux condenser was charged with **S-2** (1.03 g, 3 mmol) and hydrobromic acid (48% wt in water, 6.0 mL). The resulting light yellow solution was subjected to heating in an oil bath (130 °C) under stirring. The solution turned dark red after 5-10 minutes, and was allowed to heat at reflux overnight. The resulting mixture was cooled to rt, and the solution was adjusted to pH = 9 with solid NaOH. The resulting yellow solution was extracted with a mixture of DCM/MeOH (10/1, 50 mL×6). Then the combined golden yellow organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was subjected to silica gel column chromatography (DCM/MeOH = 4/1+1% NH_4OH) to give the QD-**7** as a yellow solid (885 mg, 90% yield). m.p. 212~214 °C (dec.); $[\alpha]_D^{23}$ = +250.8 (c = 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 0.95 (t, *J* = 7.2Hz, 3H), 1.17 (m, 1H), 1.56-1.62 (m, 5H), 1.80 (s, 1H), 2.17 (t, *J* = 7.2Hz, 1H), 2.89-3.17 (m, 4H), 3.43 (m, 1H), 5.55 (s, 1H), 7.19 (s, 1H), 7.37 (d, *J* = 9.6Hz, 1H), 7.59 (d, *J* = 6.0Hz, 1H), 8.38 (d, *J* = 6.4Hz, 1H), 8.50 (d, *J* = 9.6Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 12.2, 20.4, 25.9, 26.8, 27.1, 37.7, 50.7, 51.7, 60.8, 71.1, 106.3, 119.9, 122.0, 126.3, 130.8, 134.0, 135.0, 142.1, 163.0; IR ($CHCl_3$) ν 3401, 2954, 2527, 1644, 1574, 1453, 1274; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{19}H_{25}N_2O_3$ requires m/z 329.1865, found m/z 329.1857.

Preparation of Catalyst Q-7:

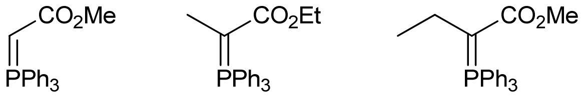


hydroquinine

Q-**7**

Catalyst Q-**7** was synthesized by the same procedure as mentioned above for catalyst QD-**7** in 40% yield (344.0 mg) over 3 steps from hydroquinine. m. p. 199~202 °C (dec); $[\alpha]_D^{23}$ = -101.6 (c = 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 0.82 (t, *J* = 6.4Hz, 3H), 1.19-1.58 (m, 5H), 1.78-1.86 (m, 3H), 2.40-2.44 (m, 1H), 2.62-2.78 (m, 1H), 3.02-3.16 (m, 2H), 3.29-3.32 (m, 2H), 3.68-3.78 (m, 1H), 5.53 (s, 1H), 7.25 (s, 1H), 7.32 (dd, *J* = 2.4, 9.2Hz, 1H), 7.62 (d, *J* = 4.4Hz, 1H), 7.89 (d, *J* = 8.8Hz, 1H), 8.58 (d, *J* = 4.8Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 12.1, 20.5, 26.5, 28.2, 28.3, 38.0, 44.3, 58.9, 60.7, 71.4, 105.1, 119.7, 124.2, 128.3, 131.4, 143.5, 146.9, 149.2, 159.2; IR ($CHCl_3$) ν 3093, 2952, 1572, 1452, 1273, 1203; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{19}H_{25}N_2O_3$ m/z 329.1865, found m/z 329.1861.

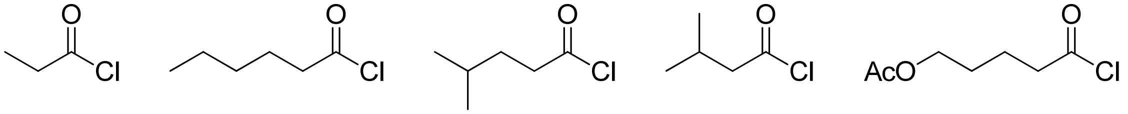
Wittig reagents (triphenyl phosphonium ylide, S-Figure 2): Y1, Y2 were purchased from VWR Inc. **Y3** was prepared according to a literature procedure.[3]



Y1 **Y2** **Y3**

S-Figure 2. Wittig Reageants

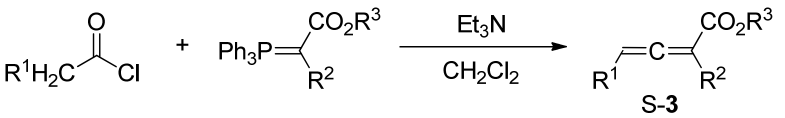
Acid chlorides (S-Figure 3): A1-A4 were purchased from Aldrich Inc. and used without further purification. **A5** was prepared according to the literature procedure.[4]



A1 **A2** **A3** **A4** **A5**

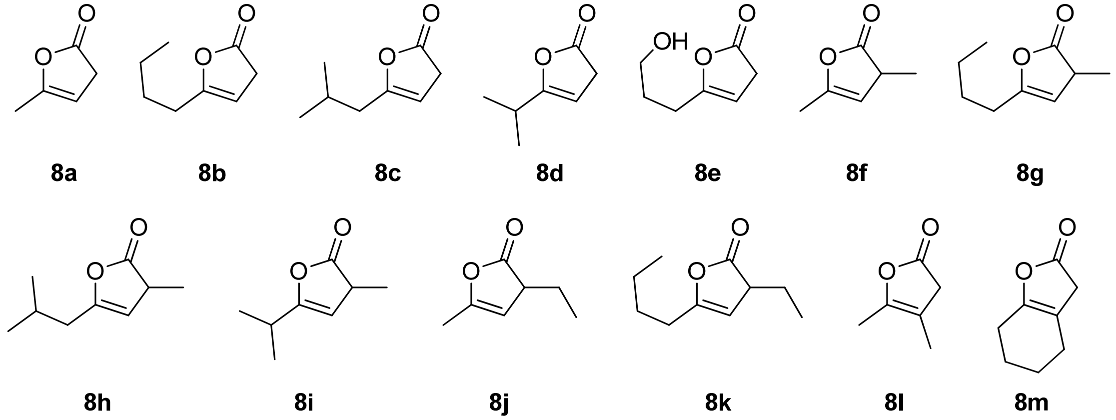
S-Figure 3. Acid chlorides

Allenoates (S-Figure 4) were prepared according to the literature procedures.[5]



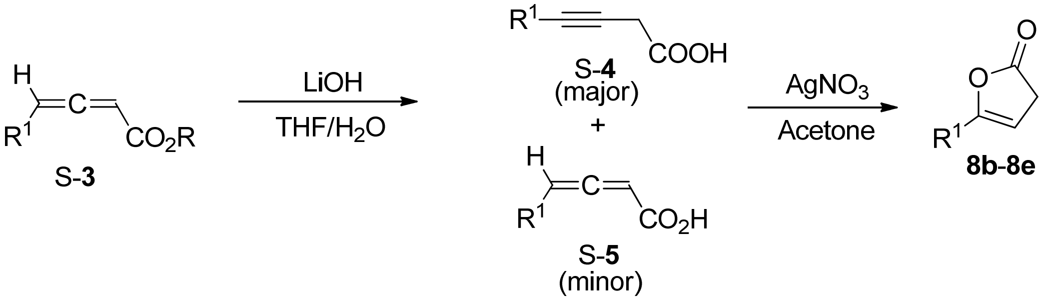
S-Figure 4. Preparation of allenoates

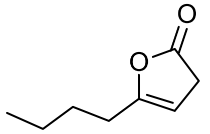
β,γ-unsaturated butenolides: 8a was purchased from Aldrich Inc. and used without further purification. **8b-8e** were prepared according to Marshall's method.[5]



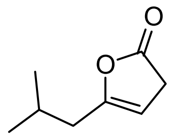
S-Figure 5. β,γ-unsaturated butenolides

Preparation of β,γ-unsaturated butenolides 8b-8e[5]

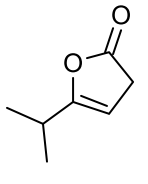




β,γ-unsaturated butenolide 8b. This compound was obtained as a clear liquid in 62% yield after flash chromatography (ethyl ether/petroleum ether = 1/50). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.93 (t, *J* = 7.2Hz, 3H), 1.31-1.42 (m, 2H), 1.49-1.60 (m, 2H), 2.30 (t, *J* = 6.0Hz, 2H), 3.17 (d, *J* = 1.6Hz, 2H), 5.09-5.12 (m, 1H). The spectral data was consistent with that reported in the literature.[6]

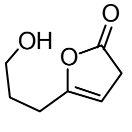


β,γ-unsaturated butenolide 8c. This compound was obtained as a clear liquid in 47% yield after flash chromatography (ethyl ether/petroleum ether = 1/50). ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.94 (d, *J* = 6.4Hz, 6H), 1.90-1.95 (m, 1H), 2.17 (d, *J* = 7.6Hz, 2H), 3.19 (d, *J* = 2.4Hz, 2H), 5.11-5.14 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 22.2, 25.6, 33.9, 37.4, 99.3, 156.3, 177.0; IR(neat) ν 3118, 2957, 2934, 2873, 1806, 1790, 1676, 1466, 1264, 1178, 1110cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_8H_{13}O_2$ m/z 141.0916, found m/z 141.0915.



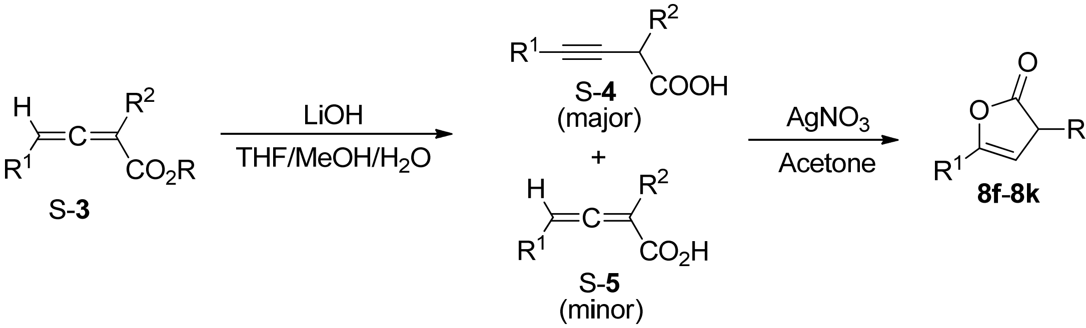
β,γ-unsaturated butenolide 8d. This compound was obtained as a clear liquid in 43% yield after flash chromatography (ethyl ether/petroleum ether = 1/50).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, *J* = 7.6Hz, 3H), 2.45-2.63 (m, 1H), 3.16-3.19 (m, 2H), 5.06-5.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 27.7, 33.8, 96.1, 162.2, 177.1; IR(neat) ν 3120, 2974, 2938, 2879, 1795, 1672, 1470, 1396, 1273, 1114, 930cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_7H_{11}O_2$ m/z 127.0759, found m/z 127.0758.

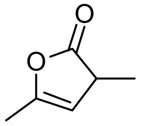


β,γ-unsaturated butenolide 8e. The acetate group was also removed via the LiOH initiated hydrolysis step in 30 min. This compound was obtained as a clear viscous liquid in 24% yield after flash chromatography (ethyl ether/petroleum ether = 1/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.66 (bs, 1H), 1.76-1.85 (m, 2H), 2.43 (t, *J* = 7.2Hz, 2H), 3.18-3.20 (m, 2H), 3.71 (t, *J* = 6.4Hz, 2H), 5.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 28.5, 33.9, 61.3, 98.7, 156.4, 177.1; IR(neat) ν 3409, 2947, 2881, 1789, 1677, 1631, 1394, 1267, 1180, 938, 848cm^{-1}; HRMS (ESI/$[M+Na]^+$) Calcd. for $C_7H_{10}NaO_3$ m/z 165.0528, found m/z 165.0534.

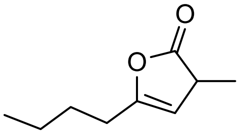
General procedure for the preparation of β,γ-unsaturated butenolides 8f-8k



A modification of Marshall's method was applied. To a solution of allenoate S-**3** (1.0 equiv.) in THF/MeOH/H_2O (4/2/1, 7 mL per mmol S-**3**) at 0°C was added LiOH(aq) (2.0 mmol in 4 mL water per mmol S-**3**). The resulting solution was stirred overnight in darkness. Saturated aqueous ammonium chloride solution (12 mL per mmol S-**3**) was added to quench the reaction. 12 N HCl solution was then used to adjust the pH of the solution to 3, at which point the solution became cloudy. Then the mixture was extracted with ethyl acetate (10 mL×3 per mmol S-**3**). The combined ethyl acetate extracts were dried over $MgSO_4$ and concentrated to give alkynoic acid S-**4** and allenic acid S-**5** as a colorless liquid mixture. This mixture was then transferred to a round bottom flask charged with a stirring bar. Acetone (4 mL per mmol S-**3**) was added followed by the addition of silver nitrate (0.2 equiv.). The resulting mixture was stirred overnight in darkness. The acetone was then removed under *vacuo* and the residue was applied to silica gel column chromatography (ethyl ether/petroleum ether = 1/50 – 1/20) to afford β,γ-unsaturated butenolides **8f-8k** as colorless liquids.

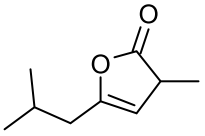


β,γ-unsaturated butenolide 8f. This compound was obtained as a clear liquid in 43% yield after flash chromatography (ethyl ether/petroleum ether = 1/10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (dd, *J* = 1.2, 7.6Hz, 3H), 1.98-2.00 (m, 3H), 3.21-3.30 (m, 1H), 5.12-5.15 (m, 1H). The spectral data was consistent with that reported in the literature.[7]

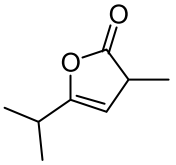


β,γ-unsaturated butenolide 8g. This compound was obtained as a clear liquid in 30% yield after flash chromatography (ethyl ether/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J*

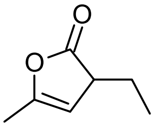
= 7.2Hz, 3H), 1.32 (d, J = 7.6Hz, 3H), 1.33-1.40 (m, 2H), 1.49-1.60 (m, 2H), 2.29 (t, J = 7.6Hz, 2H), 3.19-3.28 (m, 1H), 5.11-5.14(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 15.8, 22.0, 27.6, 27.7, 39.6, 104.7, 155.7, 180.4; IR($CHCl_3$) ν 3112, 2960, 2935, 2874, 1807, 1798, 1790, 1676, 1454, 1267, 1131, 1009, 942, 936cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_9H_{15}O_2$ m/z 155.1072, found m/z 155.1071.



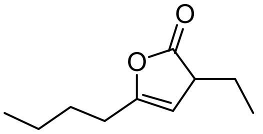
β,γ-unsaturated butenolide 8h. This compound was obtained as a clear liquid in 31% yield after flash chromatography (ethyl ether/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, J = 6.8Hz, 6H), 1.32 (d, J = 7.6Hz, 3H), 1.90-1.97 (m, 1H), 2.16 (d, J = 6.8Hz, 2H), 3.22-3.30 (m, 1H), 5.14 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 22.1, 22.2, 25.5, 37.2, 39.6, 106.0, 154.8, 180.4.; IR(film) ν 3107, 2961, 2934, 2874, 1790, 1676, 1464, 1265, 1128, 1088, 1008cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_9H_{17}O_2$ m/z 155.1072, found m/z 155.1068.



β,γ-unsaturated butenolide 8i. This compound was obtained as a clear liquid in 31% yield after flash chromatography (ethyl ether/petroleum ether = 1/15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, J = 7.2Hz, 6H); 1.32 (d, J = 7.6Hz, 3H), 2.48-2.52 (m, 1H), 3.23-3.28 (m, 1H), 5.10 (bs, 1H). The spectral data was consistent with that reported in the literature.[8]

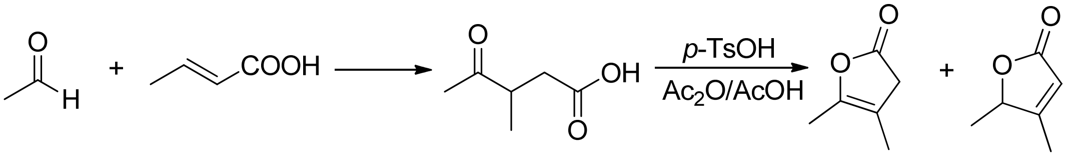


β,γ-unsaturated butenolide 8j. This compound was obtained as a clear liquid in 41% yield after flash chromatography (Ethyl acetate/Hexanes = 1/100). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.6Hz, 3H), 1.52-1.55 (m, 1H), 1.55-1.58 (m, 1H), 2.00 (s, 3H), 3.17-3.21 (m, 1H), 5.14 (bs, 1H). The spectral data was consistent with that reported in the literature.[8]



β,γ-unsaturated butenolide 8k. This compound was obtained as a clear liquid in 57% yield after flash chromatography (ethyl ether/petroleum ether = 1/20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90-0.98 (m, 6H), 1.32-1.42 (m, 2H), 1.50-1.60 (m, 2H), 1.64-1.74 (m, 2H), 1.78-1.90 (m, 2H), 2.30 (t, J = 7.6Hz, 2H), 3.16-2.23 (m, 1H), 5.12 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.8, 13.7, 22.0, 23.9, 27.7, 27.8, 46.1, 102.6, 156.2, 179.6; IR($CHCl_3$) ν 3112, 2965, 2935, 2875, 1798, 1676, 1462, 1240, 1127, 1092, 935cm^{-1}; HRMS (ESI/[M+H]$^+$) Calcd. for $C_{10}H_{17}O_2$ m/z 169.1229, found m/z 169.1228.

Preparation of β,γ-unsaturated butenolide 8l



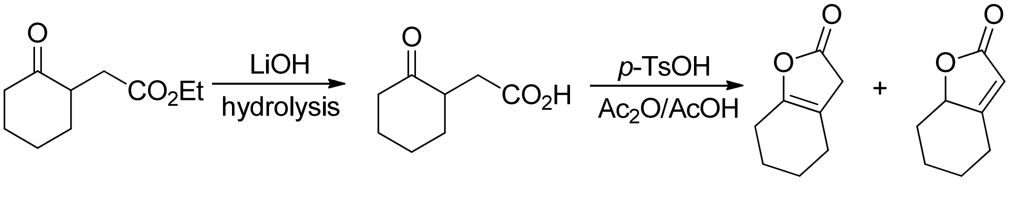
3-methyl-4-oxopentanoic acid

8l

9l

3-methyl-4-oxopentanoic acid was prepared according to a literature procedure.[9] 3-methyl-4-oxopentanoic acid (605 mg, 4.6 mmol) was dissolved in a 1:1 mixture of Ac_2O and AcOH (18 mL). p-TsOH (80 mg, 0.46 mmol) was then added. The resulting solution was heated at 60 °C. Reaction progress was followed by TLC (Hex/EA/AcOH = 5/1/0.01), and after 1 h, the red solution was moved out of the oil bath. After cooling down to rt, H_2O (20 mL) was added and the mixture was stirred for 10 min. The aqueous layer was then extracted with Et_2O (30 mL×3). The combined organic solvent was washed with $NaHCO_3$(sat) until no more bubbles were produced. Then the organic layer was dried over Na_2SO_4(s), and concentrated under vacuum. The residue was applied to silica gel columatography (CH_2Cl_2/Petroleum Ether = 1/20) to afford β,γ-unsaturated butenolide **8l** as a colorless liquid (191.1 mg, 37% yield) (α,β-unsaturated butenolide **9l** (80 mg, 16% yield) was also separated as a side product.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 3H), 1.92 (s, 3H), 3.08 (s, 2H). The spectral data was consistent with that reported in the literature.[7]

Preparation of β,γ-unsaturated butenolide 8m

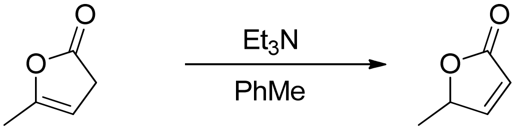


8m **9m**

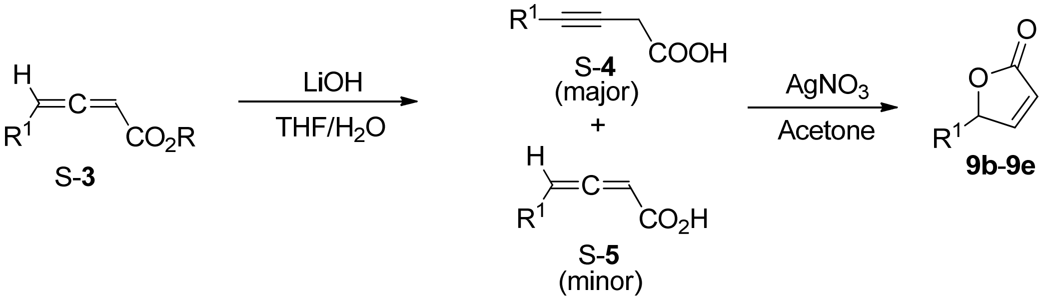
To the solution of ethyl 2-(2-oxocyclohexyl)acetate (1.84 g, 10 mmol) in a 4:2:1 mixture of THF:MeOH:H_2O (70 mL) was added LiOH·H_2O (20 mL, 20 mmol, 1.0 M in H_2O solution) in one portion. The yellow solution was stirred at rt for 1h. After that, saturated NH_4Cl (40 mL) was added. The aqueous solution was extracted with EtOAc (50 mL×4). The combined organic solvents were concentrated under vacuum to yield a crude yellow liquid (2.34 g).

One third of the yellow mixture (0.78 g) was then dissolved in a 1:1 mixture of Ac_2O and AcOH (20 mL). p-TsOH (86 mg, 0.5 mmol) was added. The resulting solution was heated at 60 oC. The reaction progress was followed by TLC (Hex/EA/AcOH = 5/1/0.01), and the red solution was moved out of the oil bath after 1.5 h. After cooling to rt, H_2O (20 mL) was added and the aqueous layer was extracted with Et_2O (30 mL×3). The combined organic solvent was washed with saturated $NaHCO_3$ until no more bubbles were produced. Then the organic layer was dried over Na_2SO_4(s), and concentrated under vacuum. The residue was applied to silica gel columatography (petroleum ether/diethyl ethyl = 50/1) to afford β,γ-unsaturated butenolide **8f** as a colorless liquid (169 mg, 38% yield) (α,β-unsaturated butenolide **9f** (130 mg, 29% yield) was also separated as a side product.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.67-1.73 (m, 2H), 1.76-1.84 (m, 2H), 2.02-2.11 (m, 2H), 2.20-2.30 (m, 2H), 3.05-3.12 (m, 2H). The data is consistent with that reported in the literature.[10]

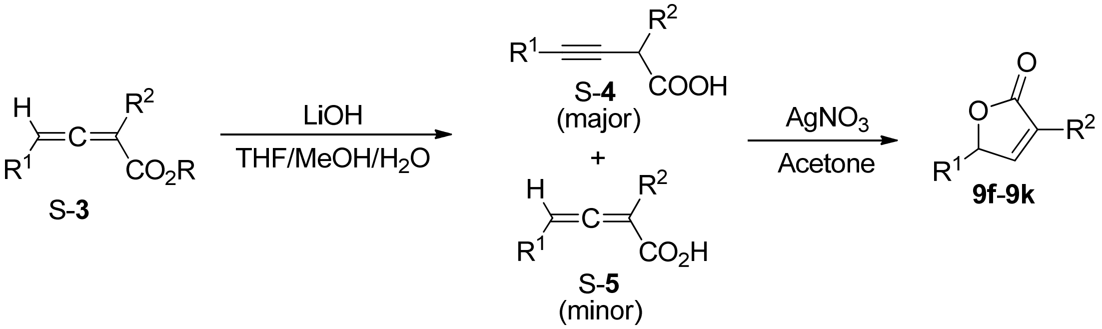
2. Preparation of racemic isomerization product



To a solution of **8a** (49 mg, 0.50 mmol) in toluene (0.5 mL) at 60 °C was added Et_3N (0.5 equiv.). When the reaction did not go any further (monitored by TLC, 6 h), the crude reaction mixture was purified by silica gel column chromatography (ether/petroleum ether = 20/1) to afford racemic **9a** as a colorless liquid (29.6 mg, 60% yield) and subjected to HPLC analysis.[11]



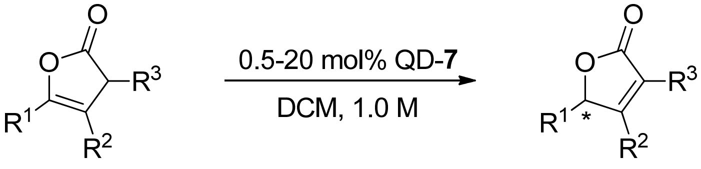
Racemic **9b-9d** were separated as colorless liquids from the preparation of **8b-8d**[5] in 5-6% yield. **9e** was separated as colorless viscous liquid from the preparation of **8e** in 14% yield.



Racemic **9f-9k** were separated as colorless liquids from the preparation of **8f-8k** (see page s-5 for details) in 8-30% yields (**9f**, 14%; **9g**, 15%; **9h**, 8%; **9i**, 28%; **9j**, 15%; **9k**, 30%).

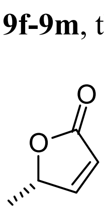
Racemic **9l** was prepared in 16% yield (see page s-6 for details) and racemic **9m** was prepared in 28% yield (see page s-7 for details).

3. General procedure for asymmetric olefin isomerization



8 **9**

At the temperature specified in table **3**, to a solution of QD-**7** (0.0005-0.02 mmol as specified in table **3**) in DCM (0.1 mL) was added **8** (0.10 mmol) in one portion. After 1-72 h as specified in table **3**, the reaction was stopped by passing the reaction mixture through a plug of silica gel to remove the catalyst. The silica gel plug was then washed with diethyl ether (2.0-4.0 mL). The filtrate was concentrated *in vacuo* to give a residue. Pure **9a-9e** were obtained by subjecting the residue to silica gel chromatography (see below for details). For **9f-9m**, the residue were found to be pure by NMR analysis.

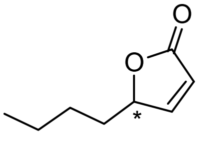


(S)-(+)-α,β-unsaturated butenolide 9a. This product was obtained as a clear liquid in 63% yield after flash chromatography (ethyl ether/petroleum ether = 1/5) and 90% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA = 80/20, 1.0 ml/min, λ 220nm, t(major) = 12.76 min, t(minor) = 14.02 min] from a reaction catalyzed by QD-**7** (10 mol%) at -20°C for 60 hrs. $[\alpha]_D^{23} = +80.3$

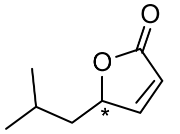
(c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (d, *J* = 6.8Hz, 3H), 5.14 (d, *J* = 6.8 Hz, 1H), 6.11 (bs, 1H), 7.46 (d, *J* = 6.4Hz, 1H). The spectral data was consistent with that reported in the literature.[12]

(-)-9a was obtained in 56% yield and 90% ee from a reaction catalyzed by Q-**7** at -20 °C for 5 days. $[\alpha]_D^{23}$ = -90.9 (c = 0.55, $CHCl_3$).

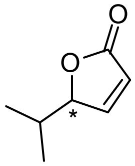
The absolute configuration of (+)-9a was determined to be S by comparing the specific optical rotation with literature value. $[\alpha]_D^{23}$ = +80.3 (c = 0.34, $CHCl_3$) for 90% ee [lit.[12a] $[\alpha]_D^{23}$ = +95 (*c* = 0.5, $CHCl_3$)].



(+)-α,β-unsaturated butenolide 9b. This product was obtained as a clear liquid in 69% yield after flash chromatography (ethyl ether/petroleum ether = 1/5, followed by pure ethyl ether) and 91% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 220nm, t(major) = 10.60 min, t(minor) = 12.85 min] from a reaction catalyzed by QD-**7** (20 mol%) at -20°C for 72h. $[\alpha]_D^{23}$ = +98.9 (c = 0.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2Hz, 3H), 1.33-1.48 (m, 4H), 1.62-1.77 (m, 2H), 5.04 (m, 1H), 6.10 (d, *J* = 4.4Hz, 1H), 7.45 (d, *J* = 5.6Hz, 1H). The data was consistent with that reported in the literature.[13]

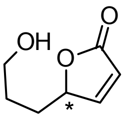


(+)-α,β-unsaturated butenolide 9c. This product was obtained as a clear liquid in 64% yield after flash chromatography (ethyl ether/petroleum ether = 1/5, followed by pure ethyl ether) and 90% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 220nm, t(major) = 10.53 min, t(minor) = 12.05 min] from a reaction catalyzed by QD-**7** (20 mol%) at -20°C for 72h. $[\alpha]_D^{23}$ = +66.4 (c = 0.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, *J* = 6.8 Hz, 6H), 1.55 (t, *J* = 6.8Hz, 3H), 1.90-1.95 (m, 1H), 5.09 (t, *J* = 6.8Hz, 1H), 6.10 (dd, *J* = 2.0, 5.6Hz, 1H), 7.47 (dd, *J* = 1.6, 5.6Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 22.0, 23.1, 25.3, 42.2, 82.1, 121.2, 156.8, 173.2; IR ($CHCl_3$) ν 3092, 2959, 2934, 2873, 1765, 1601, 1468, 1322, 1163, 1025cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_8H_{13}O_2$ requires m/z 141.0916, found m/z 141.0915.



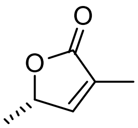
(+)-α,β-unsaturated butenolide 9d. This product was obtained as a clear liquid in 73% yield after flash chromatography (ethyl ether/petroleum ether = 1/5, then ethyl ether) and 90% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 220nm, t(major) = 13.20 min, t(minor) = 16.72 min] from a reaction catalyzed by QD-**7** (10 mol%) at rt for 1 hr. $[\alpha]_D^{23}$ = +74.6 (c = 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (dd, *J* = 1.2, 6.8Hz, 6H), 2.02-2.05 (m, 1H), 4.86 (d, *J* = 6.0Hz, 1H), 6.15 (dd, *J* = 1.6, 6.0Hz, 1H), 7.46 (dd, *J* = 1.2, 6.0Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 17.9, 31.6, 88.0, 122.2, 154.8, 173.2; IR ($CHCl_3$) ν 3091, 2968, 2935, 1783, 1754, 1600, 1468, 1165, 1092cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_7H_{11}O_2$ requires m/z 127.0759, found m/z 127.0762.

(-)-9d was obtained as a clear liquid in 69% yield and 88% ee from a reaction catalyzed by Q-**7** (10 mol%) at rt for 1 hr. $[\alpha]_D^{23}$ = -74.3 (c = 0.37, $CHCl_3$).



(+)-α,β-unsaturated butenolide 9e. This product was obtained as a clear liquid in 64% yield after flash chromatography (ethyl ether/petroleum ether = 1/2, then ethyl ether/MeOH = 10/1) and 87% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=80/20, 1.0 ml/min, λ 220nm, t(major) = 15.90

min, t(minor) = 19.36 min] from a reaction catalyzed by QD-**7** (10 mol%) at -20 °C for 36 hr. $[\alpha]_D^{23}$ = +70.7 (c = 0.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65-1.79 (m, 4H), 1.91-2.02 (m, 1H), 3.67-3.76 (m, 2H), 5.09-5.15 (m, 1H), 6.13(dd, *J* = 2.0, 5.6Hz, 1H), 7.49 (dd, *J* = 1.2, 5.6Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.9, 29.7, 61.9, 83.2, 121.6, 156.3, 173.1; IR ($CHCl_3$) ν 3416, 2946, 2876, 1744, 1600, 1333, 1171, 1014, 924cm^{-1}; HRMS (ESI/$[M+Na]^+$) Calcd. for $C_7H_{10}NaO_3$ requires m/z 165.0528, found m/z 165.0530.

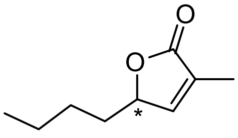


(S)-(+)-α,β-unsaturated butenolide 9f. This product was obtained as a clear liquid in 95% yield and 90% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 220nm, t(major) = 10.65 min, t(minor) = 12.58 min] from a reaction catalyzed by QD-**7** (10 mol%) at rt for 1 hr. $[\alpha]_D^{23}$ = +72.6 (c = 0.39, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.8Hz, 3H), 2.07 (s, 3H), 4.91 (q, *J* = 6.8Hz, 1H), 5.79 (s, 1H). The data was consistent with that reported in the literature.[14]

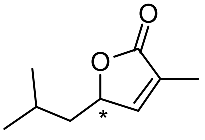
The absolute configuration of (+)-9f was determined to be S by comparing the specific optical rotation with literature value.[14] $[\alpha]_D^{23}$ = +72.6 (c = 0.39, $CHCl_3$) for 90% ee [lit. $[\alpha]_D^{23}$ = +92.3 (*c* = 0.15, $CHCl_3$)].

(+)-**9f** was obtained as a clear liquid in 95% yield and 90% ee from a reaction catalyzed by QD-**7** (0.5 mol%) at rt for 12 hr.

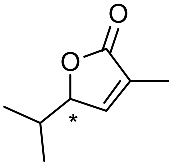
(R)-(-)-9f was obtained as a clear liquid in 92% yield and 90% ee from a reaction catalyzed by Q-**7** (10 mol%) at rt for 1 hr. $[\alpha]_D^{23}$ = -76.9 (c = 0.51, $CHCl_3$).



(+)-α,β-unsaturated butenolide 9g. This product was obtained as a clear liquid in 94% yield and 90% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 220nm, t(major) = 8.39 min, t(minor) = 11.14 min] from a reaction catalyzed by QD-**7** (0.5 mol%) at rt for 12 hr. $[\alpha]_D^{23}$ = +70.1 (c = 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 6.8Hz, 3H), 1.32-1.48 (m, 4H), 1.61-1.78 (m, 2H), 1.92 (s, 3H), 4.86-4.90 (m, 1H), 7.03 (t, *J* = 1.6Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 13.8, 22.4, 27.0, 33.1, 81.1, 129.7, 148.8, 174.3; IR (neat) ν 3079, 2958, 2932, 2863, 1755, 1660, 1457, 1207, 1097cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_9H_{15}O_2$ requires m/z 155.1072, found m/z 155.1072.

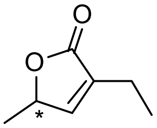


(+)-α,β-unsaturated butenolide 9h. This product was obtained as a clear liquid in 95% yield and 90% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes:IPA=90/10, 1.0 ml/min, λ 220nm, t(major) = 8.45 min, t(minor) = 10.61 min] from a reaction catalyzed by QD-**7** (0.5 mol%) at rt for 12 hr. $[\alpha]_D^{23}$ = +53.2 (c = 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 6.8Hz, 6H), 1.47 (t, *J* = 6.8Hz, 2H), 1.85-1.92 (m, 4H), 4.93 (t, *J* = 6.0Hz, 1H), 7.04 (t, *J* = 1.6Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 22.1, 23.0, 25.2, 42.5, 79.8, 129.5, 149.2, 174.3; IR (CH_3Cl) ν 3078, 2954, 2873, 1753, 1659, 1462, 1205, 1096cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_9H_{15}O_2$ requires m/z 155.1072, found m/z 155.1070.

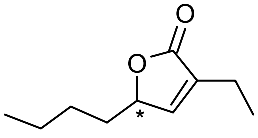


(+)-α,β-unsaturated butenolide 9i. This product was obtained as a clear liquid in 99% yield and 94% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 220nm, t(major) = 8.66

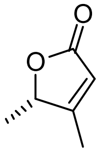
min, t(minor) = 11.44 min] from a reaction catalyzed by QD-**7** (0.5 mol%) at rt for 12 hr. $[\alpha]_D^{23}$ = +77.3 (c = 0.71, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (d, *J* = 6.4Hz, 3H), 0.99 (d, *J* = 6.8Hz, 3H), 1.91-2.00 (m, 4H), 4.68-4.70 (m, 1H), 7.05 (d, *J* = 1.6Hz, 1H). The data was consistent with that reported in the literature.[15]



(+)-α,β-unsaturated butenolide 9j. This product was obtained as a clear liquid in 95% yield and 91% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 220nm, t(major) = 9.45 min, t(minor) = 11.84 min] from a reaction catalyzed by QD-**7** (0.5 mol%) at rt for 12 hr. $[\alpha]_D^{23}$ = +73.8 (c = 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, *J* = 7.2Hz, 3H), 1.41 (d, *J* = 6.8Hz, 3H), 2.31 (q, *J* = 7.2Hz, 2H), 4.96-5.03 (m, 1H), 6.99 (d, *J* = 2.0Hz, 1H); The data was consistent with that reported in the literature.[16]

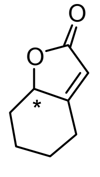


(+)-α,β-unsaturated butenolide 9k. This product was obtained as a clear liquid in 95% yield and 91% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=90/10, 1.0 ml/min, λ 220nm, t(major) = 7.13 min, t(minor) = 10.13 min] from a reaction catalyzed by QD-**7** (0.5 mol%) at rt for 12 hr. $[\alpha]_D^{23}$ = +42.4 (c = 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.2Hz, 3H), 1.17 (t, *J* = 7.2Hz, 3H), 1.25-1.46 (m, 4H), 1.56-1.73 (m, 2H), 2.30 (q, *J* = 7.2Hz, 2H), 4.86-4.91 (m, 1H), 7.00 (d, *J* = 1.6Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.7, 13.8, 18.6, 22.4, 27.0, 33.2, 81.3, 135.8, 147.2, 173.9; IR ($CHCl_3$) ν 3118, 2957, 2934, 2873, 1806, 1790, 1676, 1466, 1264, 1110, 1091, 931cm^{-1}; HRMS (ESI/$[M+H]^+$) Calcd. for $C_{10}H_{17}O_2$ requires m/z 169.1229, found m/z 169.1227.



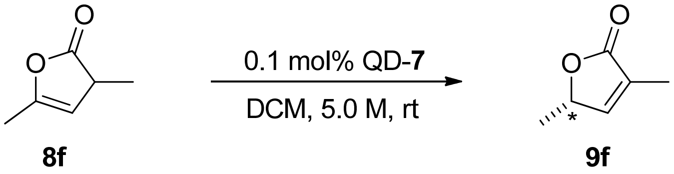
(S)-(+)-α,β-unsaturated butenolide 9l. This product was obtained as a clear liquid in 95% yield and 81% ee as determined by HPLC analysis [Daicel chiralpak AS-H, Hexanes/IPA=70/30, 1.0 ml/min, λ 220nm, t(major) = 13.05 min, t(minor) = 11.67 min] from a reaction catalyzed by QD-**7** (10 mol%) at -20°C for 24 hr. ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (d, *J* = 6.8Hz, 3H), 2.07 (s, 3H), 4.91 (q, *J* = 6.8Hz, 1H), 5.79 (s, 1H). The data was consistent with that reported in the literature.[17]

The absolute configuration of (+)-9l was determined to be S by comparing the specific optical rotation with literature value.[17] $[\alpha]_D^{23}$ = +17.2 (c = 0.39, $CHCl_3$) for 81% ee. [lit. $[\alpha]_D$ = +20.2 (*c* = 5.00, CH_2Cl_2)].



(+)-α,β-unsaturated butenolide 9m. This product was obtained as a clear liquid in 83% yield and 82% ee as determined by HPLC analysis [Daicel chiralpak AS, Hexanes/IPA=50/50, 1.0 ml/min, λ 220nm, t(major) = 12.5 min, t(minor) = 11.4 min] from a reaction catalyzed by cat. QD-**7** (10 mol%) at -20°C for 24 hr. $[\alpha]_D^{23}$ = +100.7 (c = 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23-1.41 (m, 2H), 1.42-1.54 (m, 1H), 1.88-1.98 (m, 1H), 2.00-2.09 (m, 1H), 2.22-2.34 (m, 1H), 2.50-2.60 (m, 1H), 2.83-2.94 (m, 1H), 4.68 (dd, *J* = 6.4 & 8.9 Hz, 1H), 5.71-5.77 (s, 1H). The data was consistent with that reported in the literature.[18]

4. 0.1 mol% QD-7 catalyzed isomerization of 8f to 9f



To a DCM solution of QD-**7** (0.0001 mmol, 20 uL, 0.005M) was added **8f** (0.10 mmol) in one portion. After 24 h, the reaction was stopped by passing the reaction mixture through a plug of silica gel to remove the catalyst. The silica gel plug was then washed with diethyl ether (2.0-4.0 mL). The filtrate was concentrated *in vacuo* to give **9f** in 91% yield and 86% ee.

5. Kinetic Method.

The kinetic parameters of this reaction were determined by *in situ* monitoring of the consumption of β,γ-unsaturated butenolide **8f** by following the reaction progress via NMR. The experiment was conducted according to Johnson's procedure.[19]

Plotting -ln[**8f**] versus time gave a straight line ($R^2 = 0.999$, Figure A), thus establishing first-order dependence on butenolide **8f**.

The reaction order in catalyst QD-**7** was established by determining the rate constants (k_{obs}) at various catalyst concentrations. According to the rate law (eq.1), equation 2 can be obtained. From eq.2, equation 3 can be derived. Thus the slope obtained from the plot of $-\ln(k_{obs})$ versus the catalyst concentration would be the order of catalyst. The slope = 1.18 (Figure E) indicates the first order dependence on catalyst.

$$R = -k_{obs}[S] = -k[S][C]^m \qquad \text{(eq. 1)}$$

$$k_{obs} = k[C]^m \qquad \text{(eq. 2)}$$

$$\ln(k_{obs}) = m\ln[C] + \ln(k) \qquad \text{(eq. 3)}$$

The general kinetic method will be illustrated with a specific example. To a 5 mm NMR tube was added β,γ-unsaturated butenolide **8f** (0.05 mmol, 5.6 mg) and $CDCl_3$ (0.40 mL). An initial ^1H NMR was taken to determine the ratio of substrate peak and the internal standard peak. Then catalyst QD-**7** (0.005 mmol, 1.6 mg) was added to the NMR tube in one portion. The NMR tube was well shaken and put back into the NMR machine. Every minute a ^1H NMR spectra was taken to follow the progress of the reaction until the reaction reached about 70% conversion. Substrate concentration was determined by the integration of the ^1H NMR spectra: The substrate **8f** peak at 5.10 ppm (integrated from 5.069 ppm to 5.139 ppm) was followed. The chloroform peak at 7.26 ppm was used as an internal standard. The k_{obs} for each run was determined from the slope of the line obtained by plotting the -ln[**8f**] versus time.

Figure A. Determination of the order of butenolide **8f**

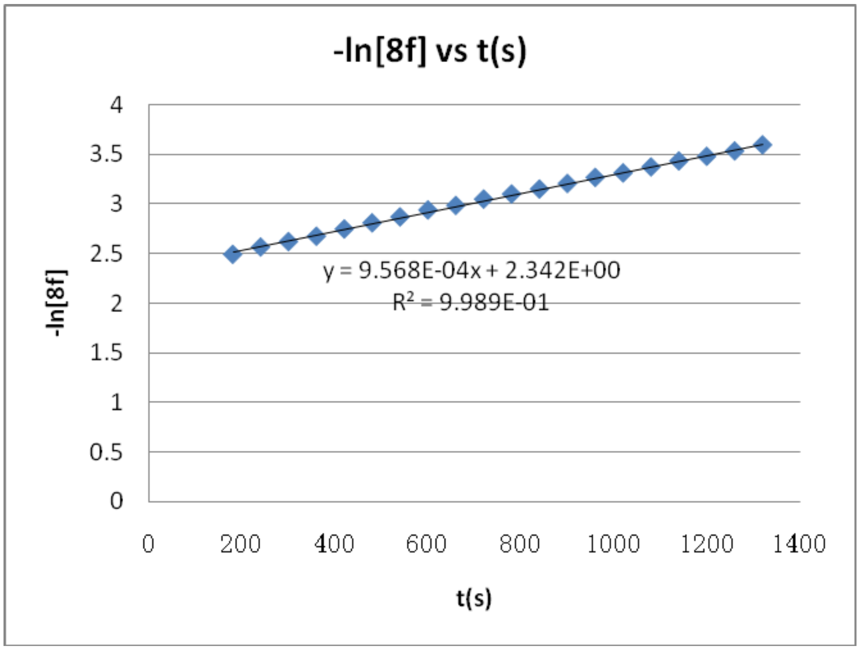


Figure A shows a linear relationship between –ln[**8f**] and time, indicating the reaction is first order in **8f**.

Figure B. Determination of the order of butenolide **8f**

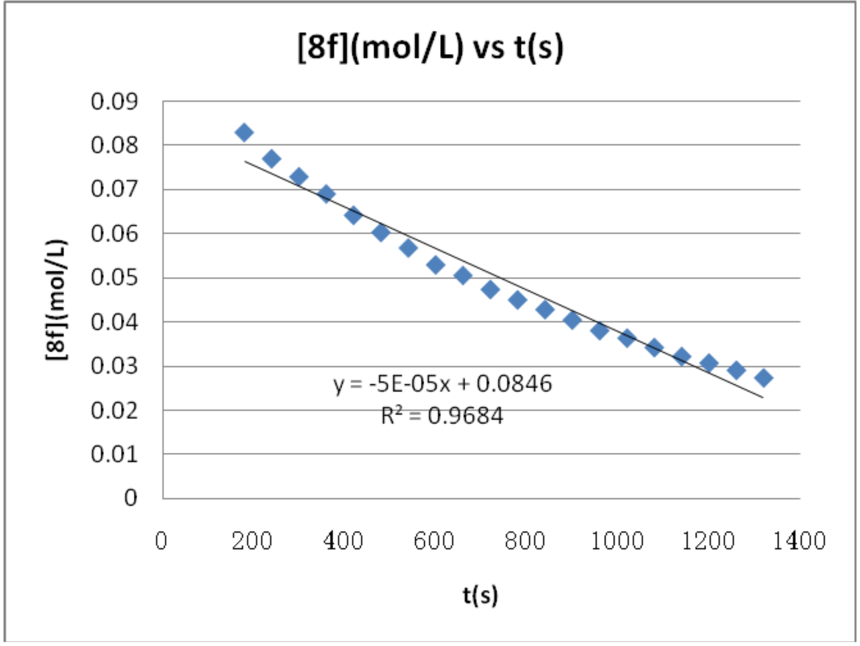


Figure B showed a nonlinear relationship between [**8f**] and time, indicating the reaction is NOT zeroth order in **8f**

Figure C. Determination of the order of butenolide **8f**

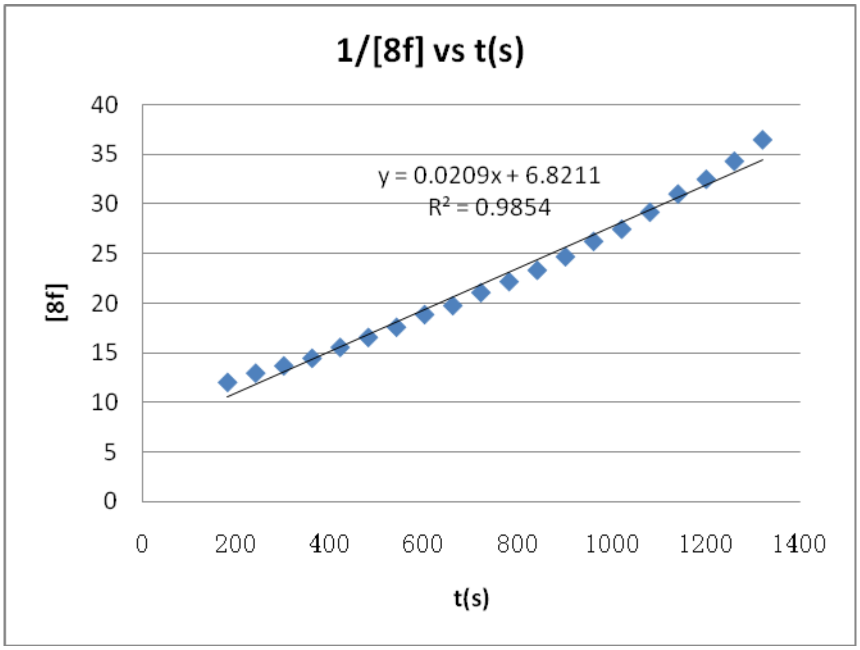
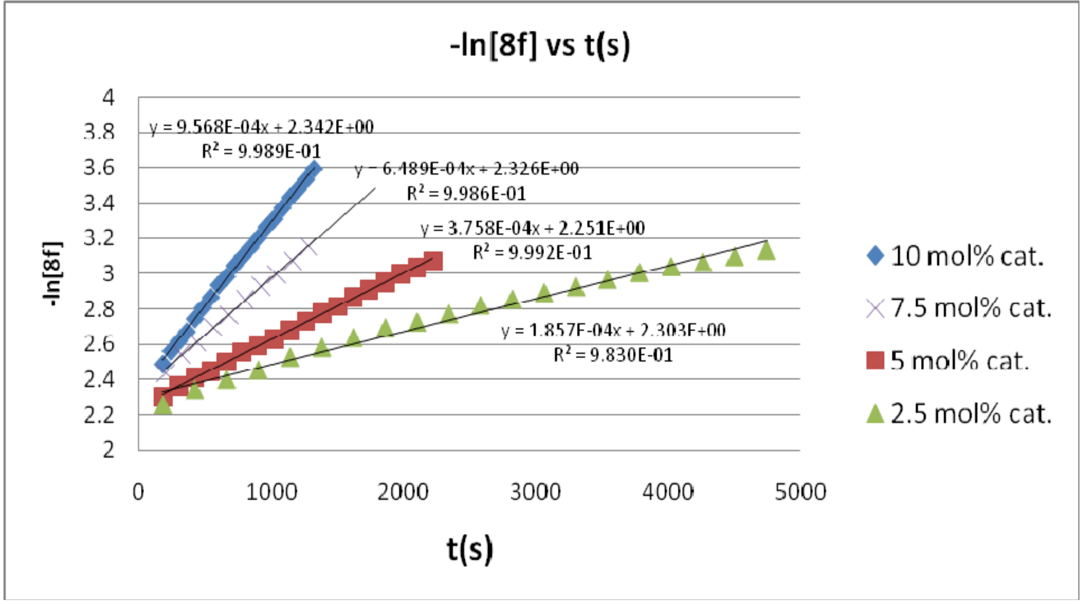


Figure C showed a nonlinear relationship between 1/[**8f**] and time, indicating the reaction is NOT second order in **8f**

Figure D. Kinetic profiles for the catalyst QD-**7**



Catalyst 10 mol%, k_{obs} = 9.568E-4, $\ln(k_{obs})$ = -6.952, R^2 = 0.999
Catalyst 7.5 mol%, k_{obs} = 6.489E-4, $\ln(k_{obs})$ = -7.340, R^2 = 0.999
Catalyst 5.0 mol%, k_{obs} = 3.758E-4, $\ln(k_{obs})$ = -7.886, R^2 = 0.992
Catalyst 2.5 mol%, k_{obs} = 1.857E-4, $\ln(k_{obs})$ = -8.591, R^2 = 0.983

Figure F. Determination of the reaction order on the catalyst QD-**7**

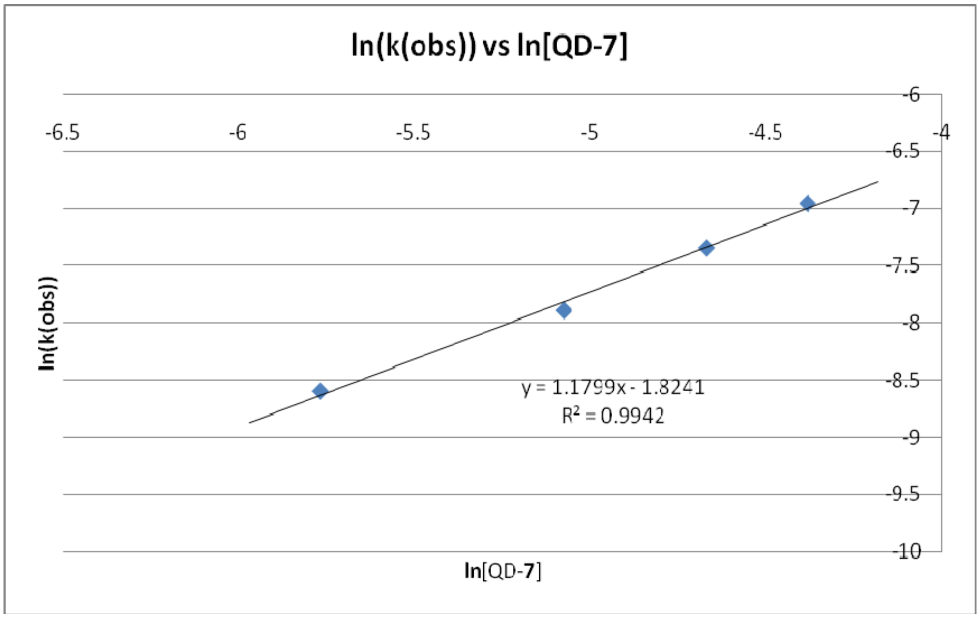


Figure F showed that the slope of ln(k_{obs}) vs ln[QD-**7**] is 1.18, which is close to 1, indicating the reaction is first order dependence on the catalyst.

6. ^{13}C Kinetic Isotope Effect Study.

β,γ-unsaturated butenolide **8f** (560 mg, 5.0 mmol) and n-Octane (28.6 mg, 0.25 mmol) were dissolved in DCM (5 mL, distilled) in a 20 ml vial charged with a stirring bar. Catalyst QD-**7** (8.2 mg, 0.025 mmol) was added in one portion and the reaction mixture was stirred at rt for 3h. An aliquot of 10 uL reaction solution was taken out, passed through a pad of silica. The silica was washed with Et_2O (0.8 mL). The organic solvents were collected, diluted to 1.0 mL and subjected to GC analysis for conversion. Meanwhile, Et_2O (5.0 mL) was added to the remaining of the reaction solution and the resulting yellow suspension was passed through a plug of silica, which was washed with Et_2O (30.0 mL). The combined organic solvent was concentrated *in vacuo*. The residue was applied to silica gel columatography (Eluent: Pentane/Et_2O = 15/1) to afford recovered β,γ-unsaturated butenolide **8f** as a clear liquid (Warning: The butenolide **8f** is very volatile, don't leave under reduced pressure for long.).

The ^{13}C NMR analysis of the recovered and virgin samples of β,γ-unsaturated butenolide **8f** was performed by following Singleton's ^{13}C NMR method.[20] The NMR sample of virgin and recovered **8f** was prepared identically as follows: a 5 mm high precision NMR tube was charged with **8f** (80 mg, 0.71 mmol), then $CDCl_3$ was added to a total height of 4.0 cm. The $^{13}C\{^1H\}$ NMR spectra were recorded with H-decoupling and 45 degree pulses on 400MHz NMR spectrometer. A 100 s delay between pulses was imposed to minimize T1 variations (d1 = 100 s, at = 5.0 s, nt = 720). Polynomial fit zeroth-order baseline correction was applied. Integrations were determined by using a range of ± 5 times the half peak width around each peak. The C**5**, which isotopic composition can be safely assumed not to change during the reaction, was employed as an "internal standard" for ^{13}C integrations. The average ^{13}C integration ratio of the recovered and virgin samples of **8f** is shown in Table S1.

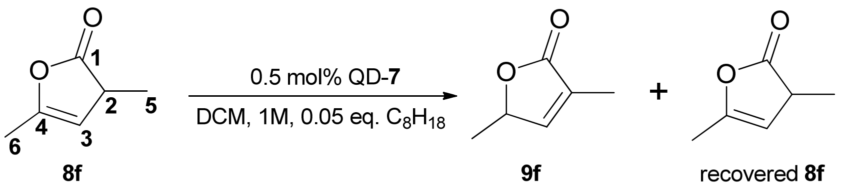


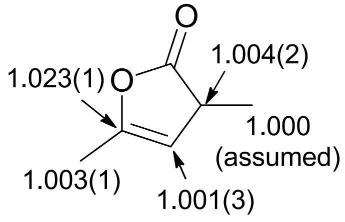
Table S1. ^{13}C integration of the recovered and virgin samples of butenolide **8f**[a]

C#	virgin	recovered (71% conv)	recovered/virgin	change(%)
2	0.969	0.973	1.004	0.4
3	0.971	0.969	0.998	-0.2
4	**0.987**	**1.010**	**1.023**	**2.3**
5(ref)	1.000	1.000	1.000	0.0
6	0.988	0.992	1.004	0.4

C#	virgin	recovered (70% conv)	recovered/virgin	change(%)
2	0.969	0.972	1.003	0.3
3	0.971	0.973	1.002	0.2
4	**0.987**	**1.011**	**1.024**	**2.4**
5(ref)	1.000	1.000	1.000	0.0
6	0.988	0.992	1.004	0.4

C#	virgin	recovered (69% conv)	recovered/virgin	change(%)
2	0.969	0.975	1.006	0.6
3	0.971	0.974	1.003	0.3
4	**0.987**	**1.011**	**1.024**	**2.4**
5(ref)	1.000	1.000	1.000	0.0
6	0.988	0.990	1.002	0.2

[a] Due to practical limitations, the NMR data was collected with a time between pulses inadequate for relaxation of the carbonyl carbon (C**1**) precluding an accurate integration.



recovered **8f**

The most pronounced carbon isotope effect was observed on the carbon 4 when the ^{13}C ratio of recovered **8f** at 71% conversion was compared to that of the virgin sample (^{13}C(recovered)/^{13}C(virgin) at C**4** = 1.023, average of three runs). This indicates that the rate limiting step is the protonation step, in which only carbon 4 is involved in the bond formation.

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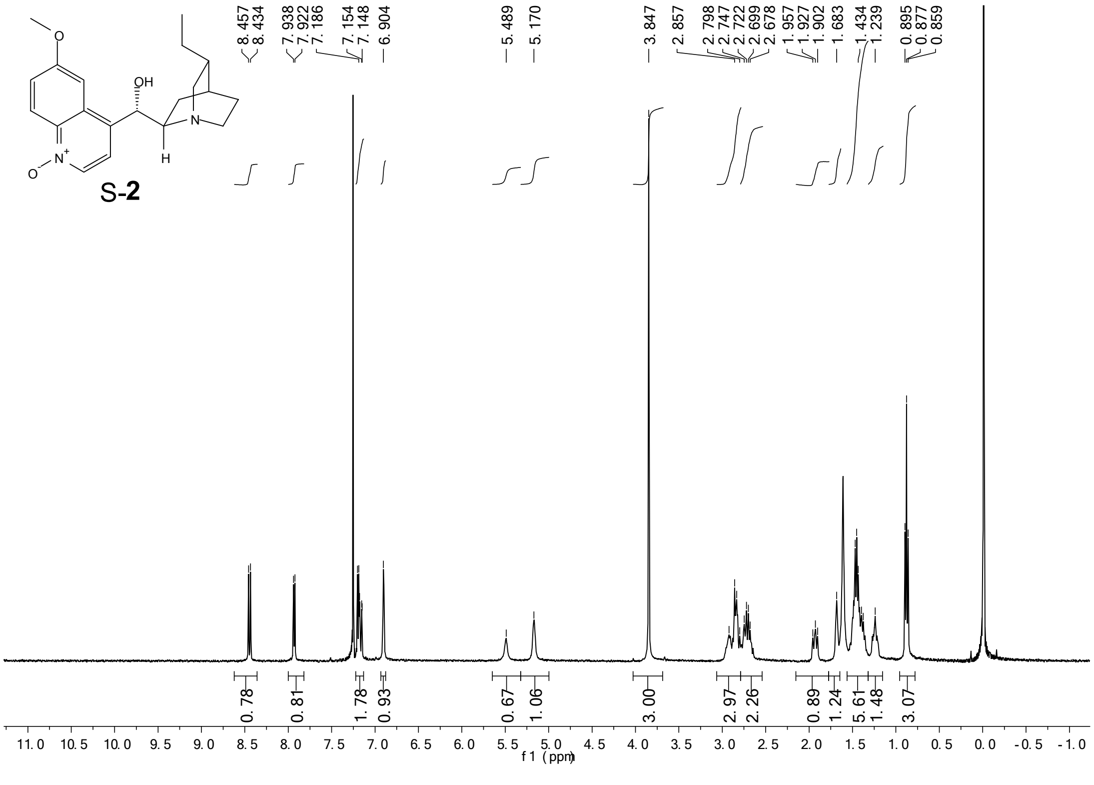
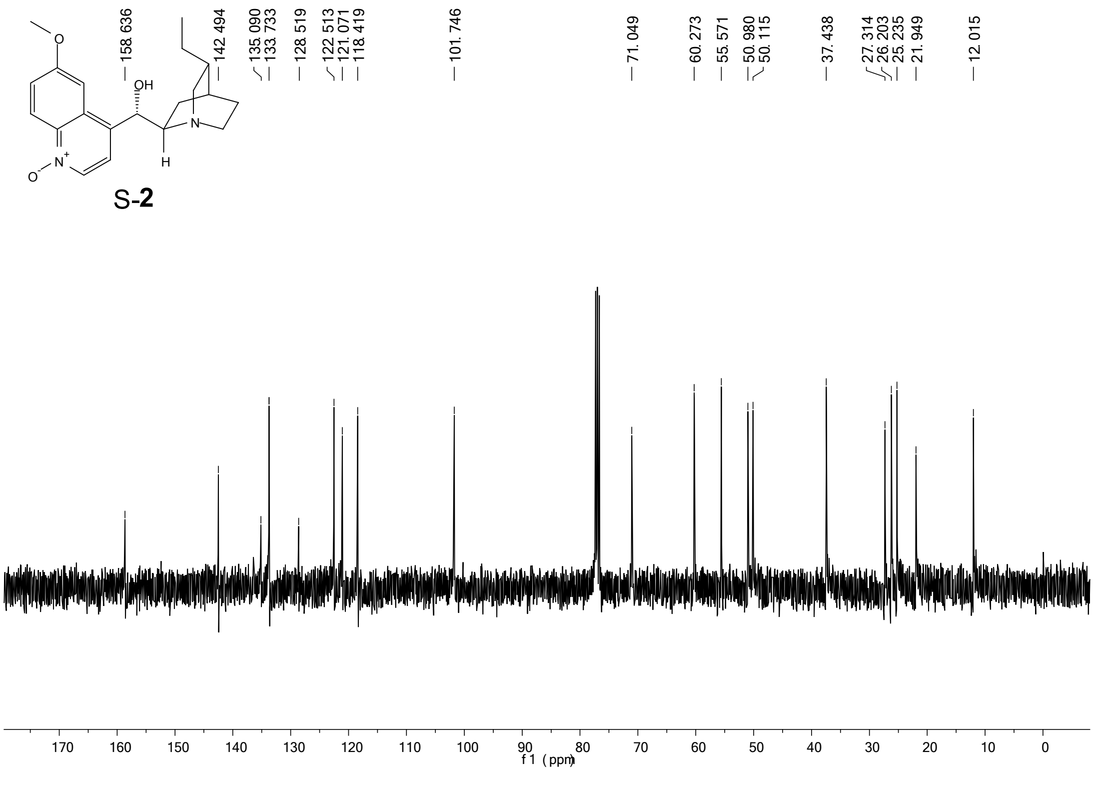
^{1}H and ^{13}C NMR spectra for the catalysts


S-**2**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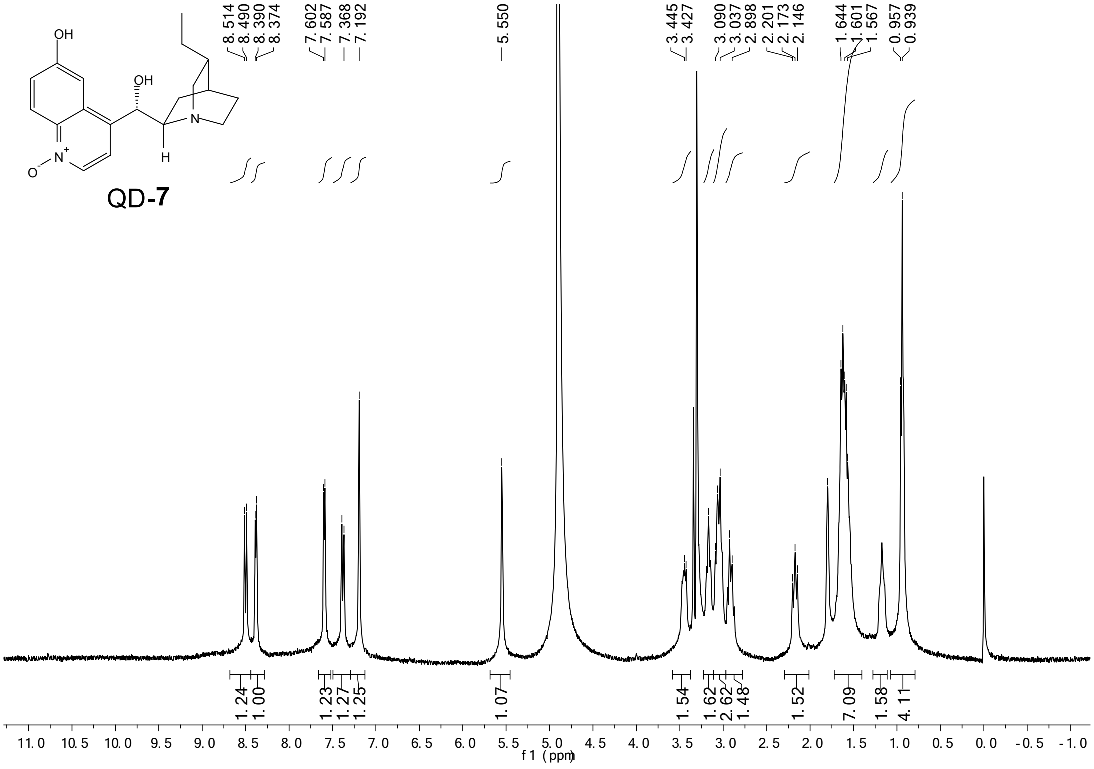
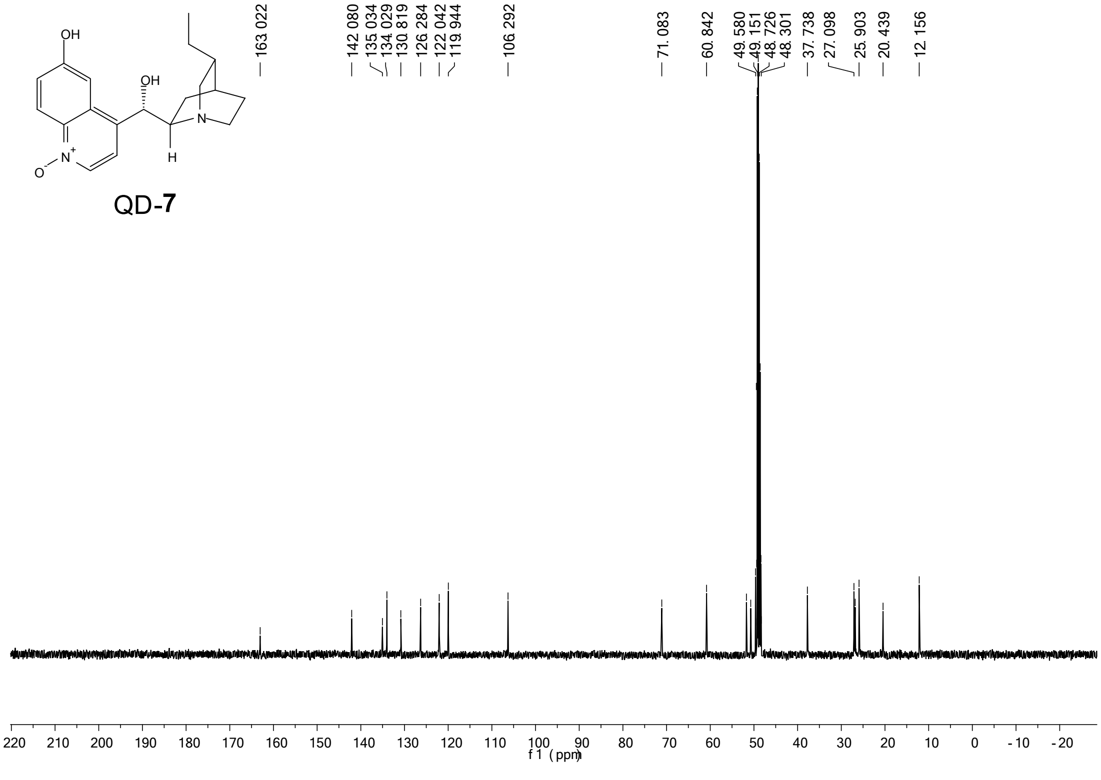
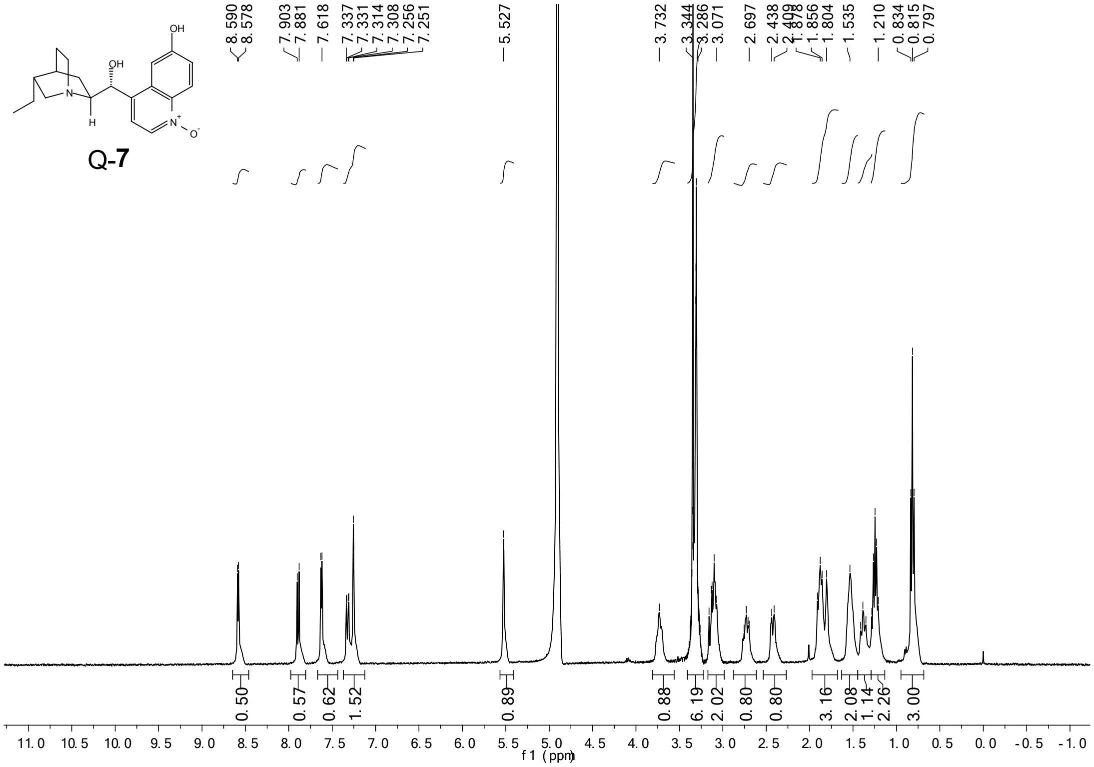

OH
OH
N
N
O
H
8.514
8.490
8.390
8.374
7.602
7.587
7.368
7.192
5.550
3.445
3.427
3.090
3.037
2.898
2.201
2.173
2.146
1.644
1.601
1.567
0.957
0.939
1.24
1.00
1.23
1.27
1.25
1.07
1.54
1.62
2.62
1.48
1.52
7.09
1.58
4.11
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

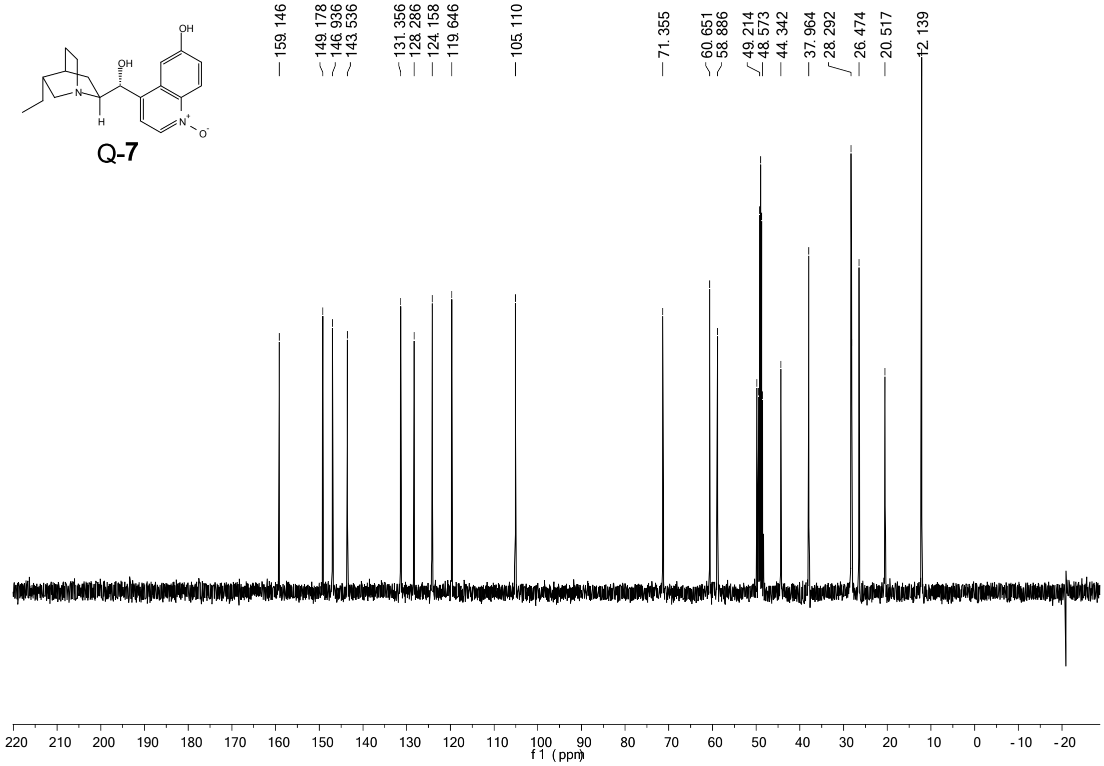
QD-**7**


OH
OH
N
N
O
H
163.022
142.080
135.034
134.029
130.819
126.284
122.042
119.944
106.292
71.083
60.842
49.580
49.151
48.726
48.301
37.738
27.098
25.903
20.439
12.156
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

QD-**7**

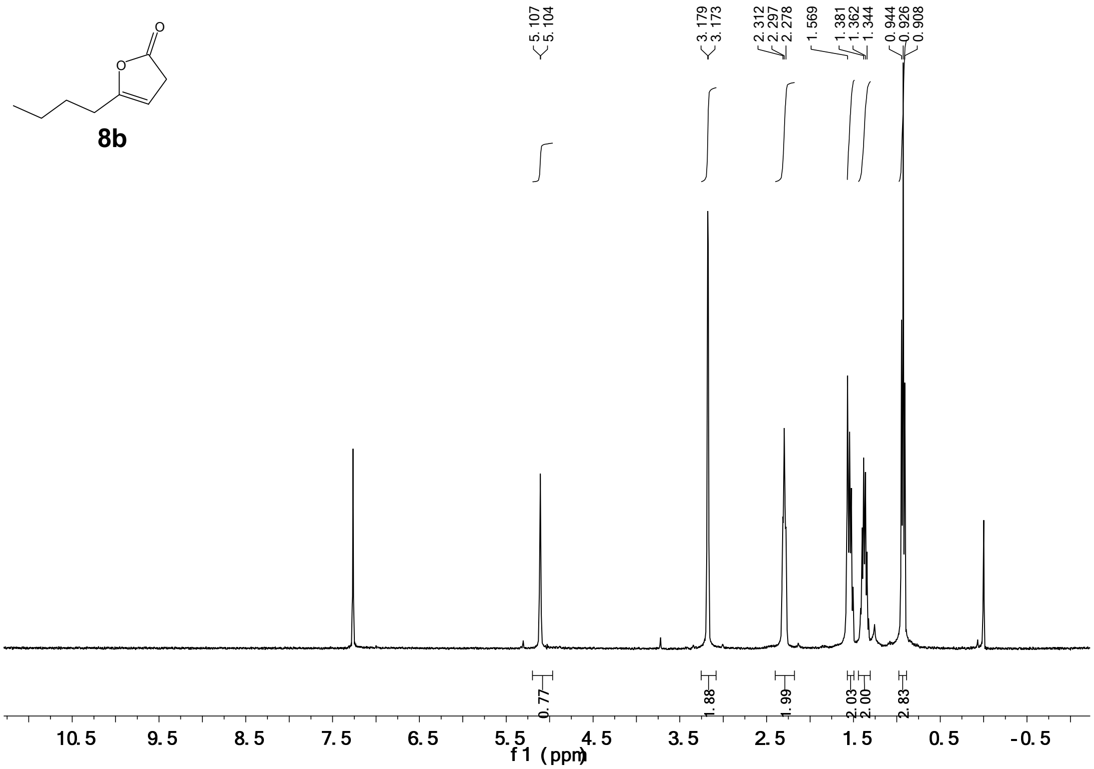


OH
OH
N
H
N+
O-
Q-7
8.590
8.578
7.903
7.881
7.618
7.337
7.331
7.314
7.308
7.256
7.251
5.527
3.732
3.344
3.286
3.071
2.697
2.438
2.409
1.878
1.856
1.804
1.535
1.210
0.834
0.815
0.797
0.50
0.57
0.62
1.52
0.89
0.88
6.19
2.02
0.80
0.80
3.16
2.08
1.14
2.26
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

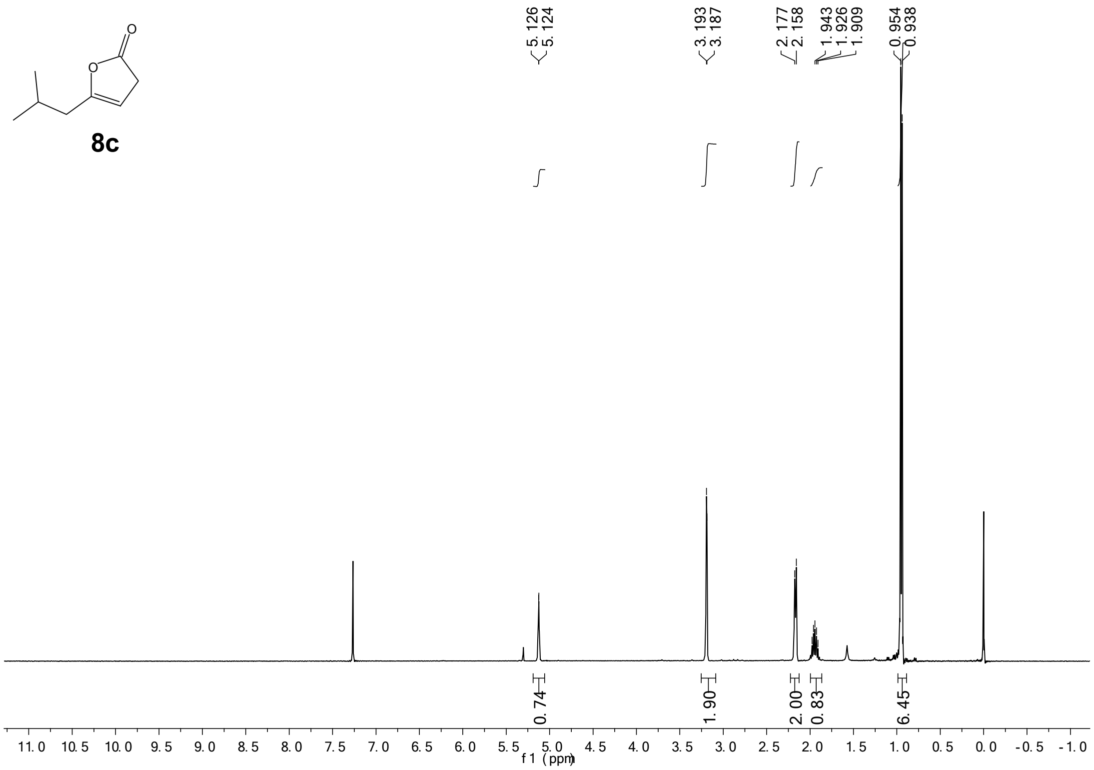


OH
OH
N
H
N+
O-
Q-7
159.146
149.178
146.936
143.536
131.356
128.286
124.158
119.646
105.110
71.355
60.651
58.886
49.214
48.573
44.342
37.964
28.292
26.474
20.517
12.139
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

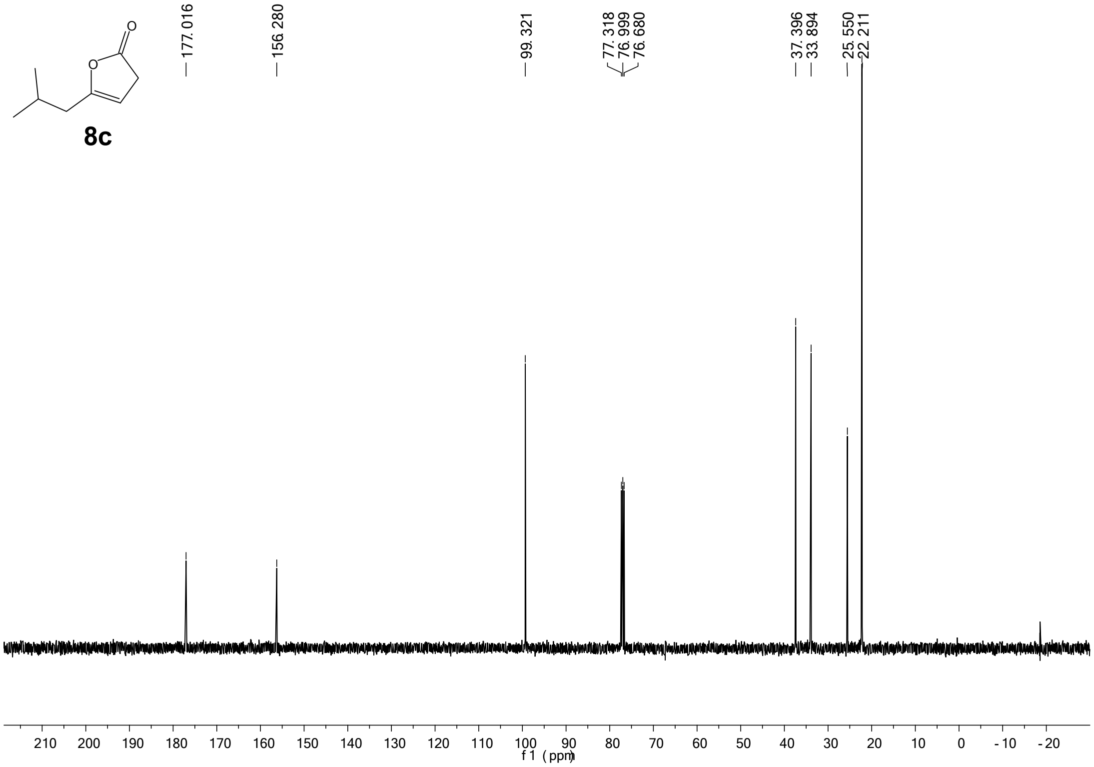
^{1}H and ^{13}C NMR spectra for β,γ-butenolides **8**



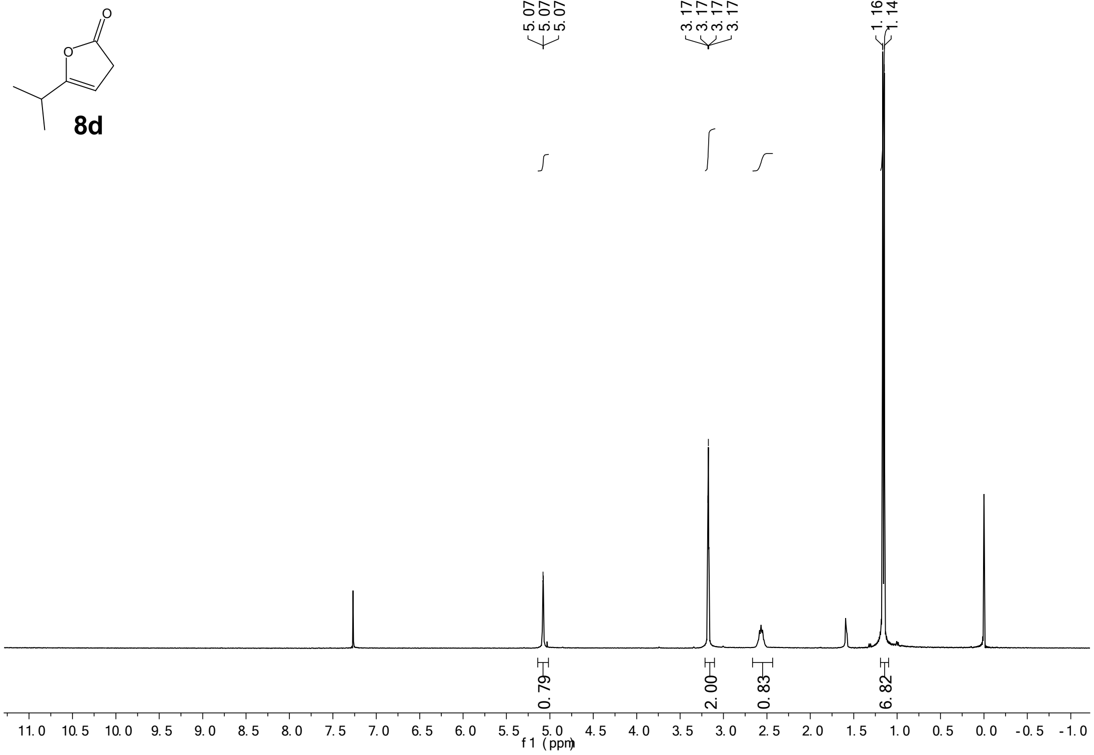
8b



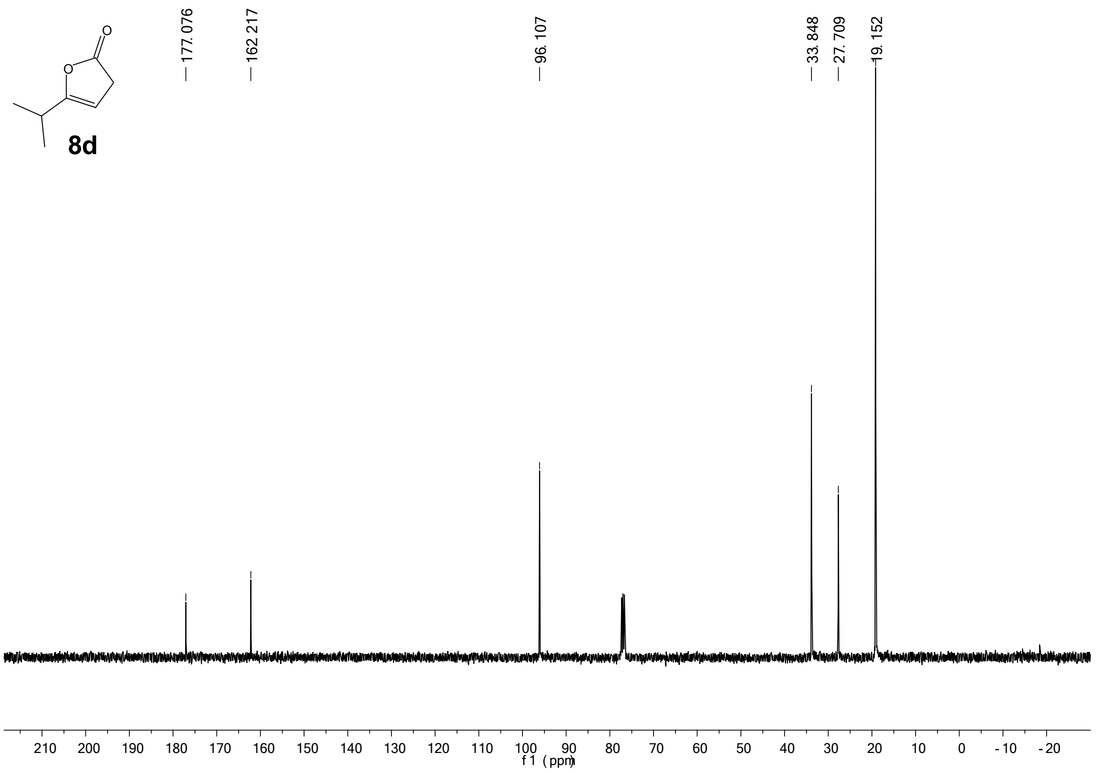
8c


8c

177.016
156.280
99.321
77.318
76.999
76.680
37.396
33.894
25.550
22.211
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

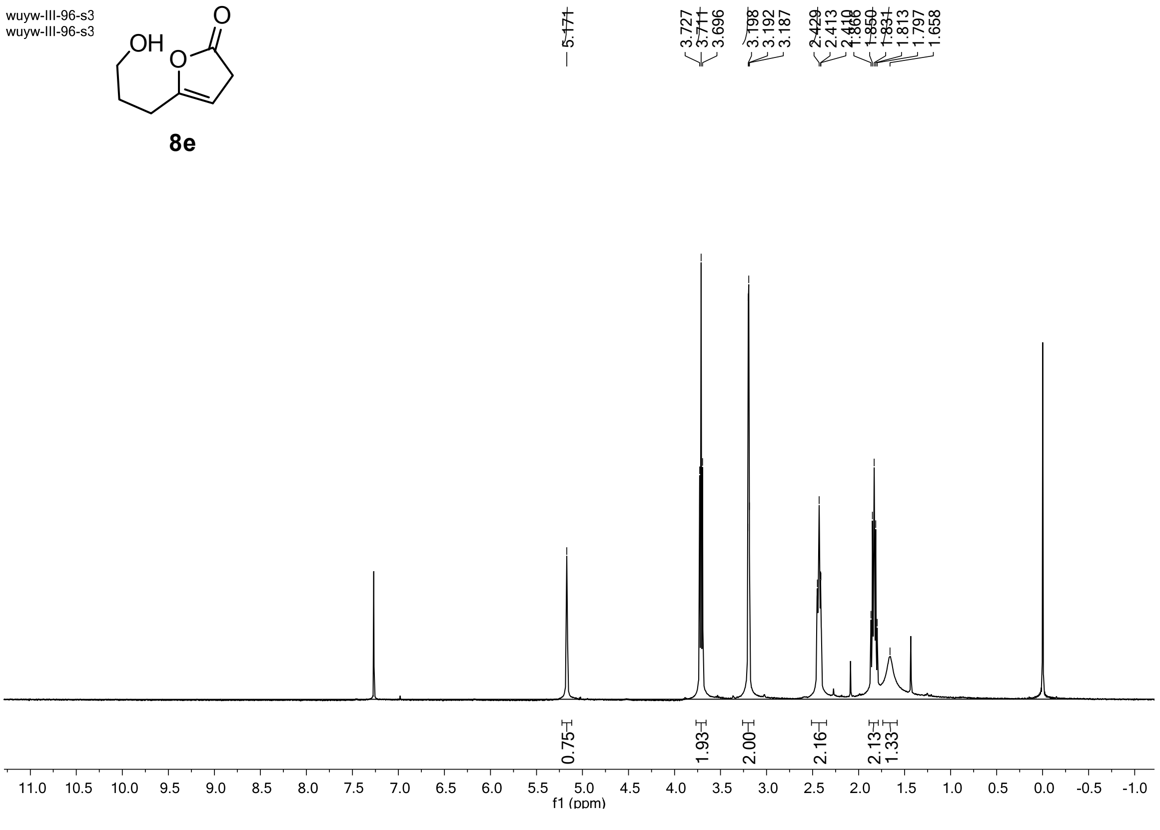

8d

5.079
5.077
5.075
3.179
3.176
3.174
3.170
1.166
1.147
O
O
0.79
2.00
0.83
6.82
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



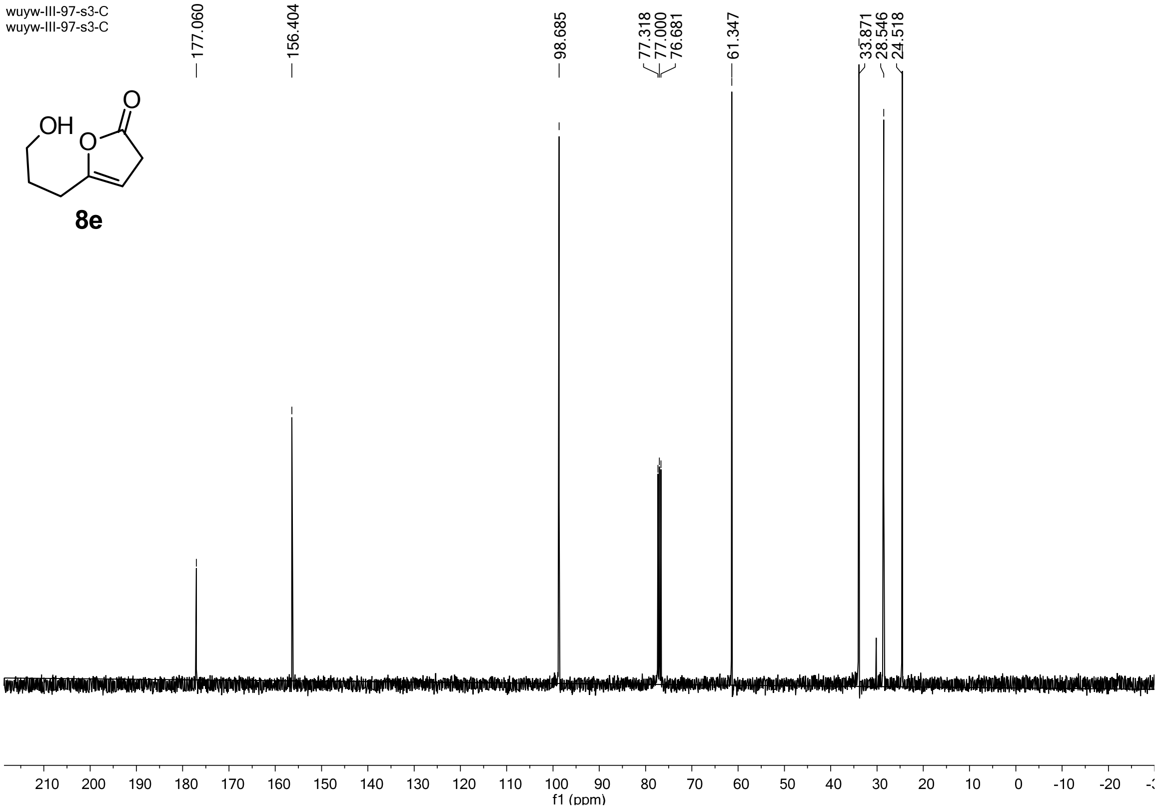
8d

177.076
162.217
96.107
33.848
27.709
19.152
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
- 10
- 20
f1 (ppm)

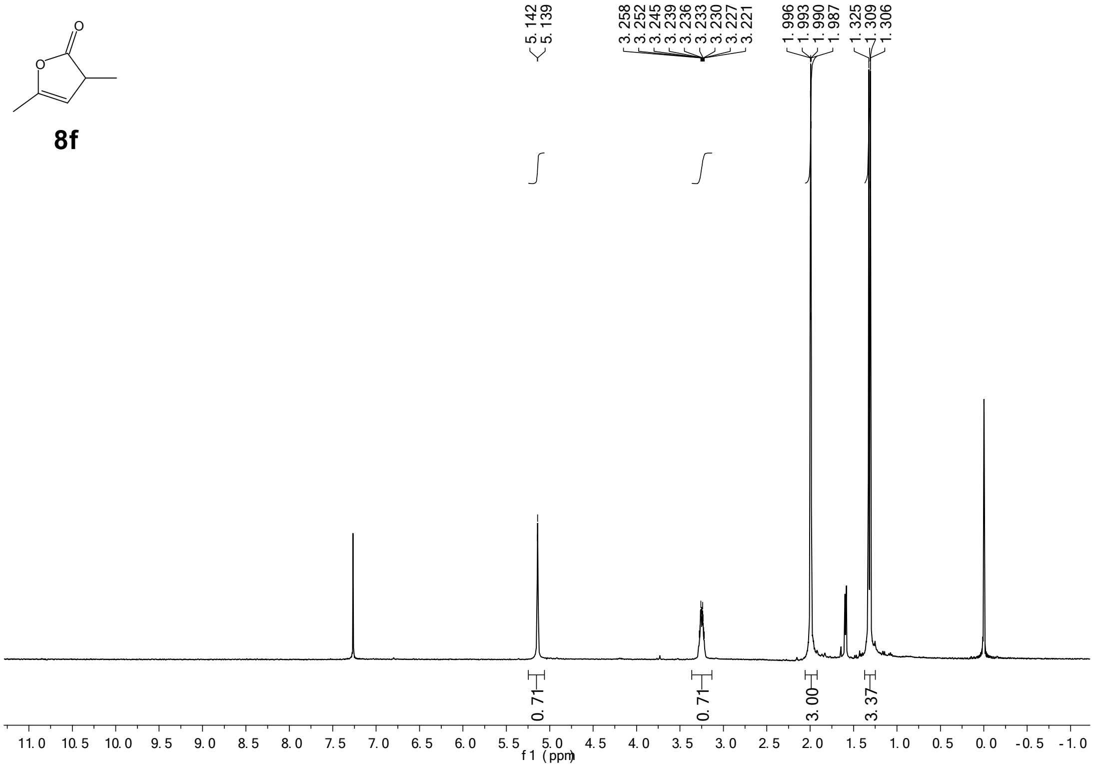


8e

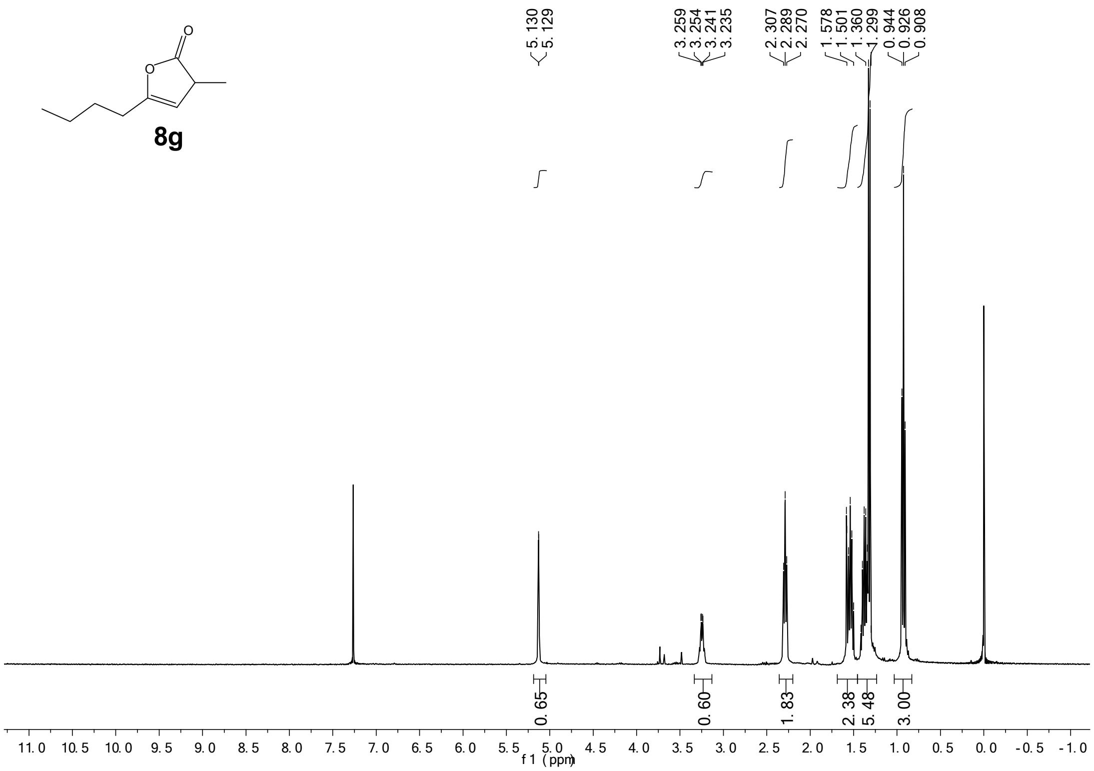
wuyw-III-96-s3
wuyw-III-96-s3
OH
O
O
5.171
3.727
3.711
3.696
3.198
3.192
3.187
2.429
2.413
2.410
1.866
1.850
1.831
1.813
1.797
1.658
0.75
1.93
2.00
2.16
2.13
1.33
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

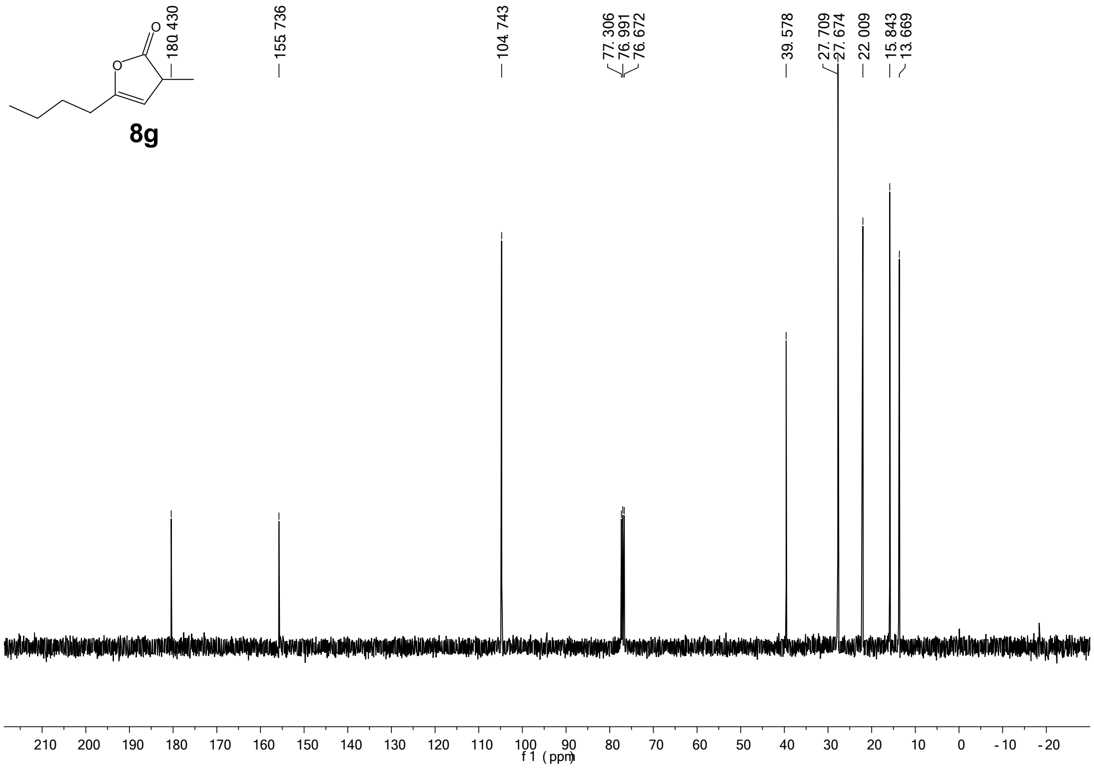

8e

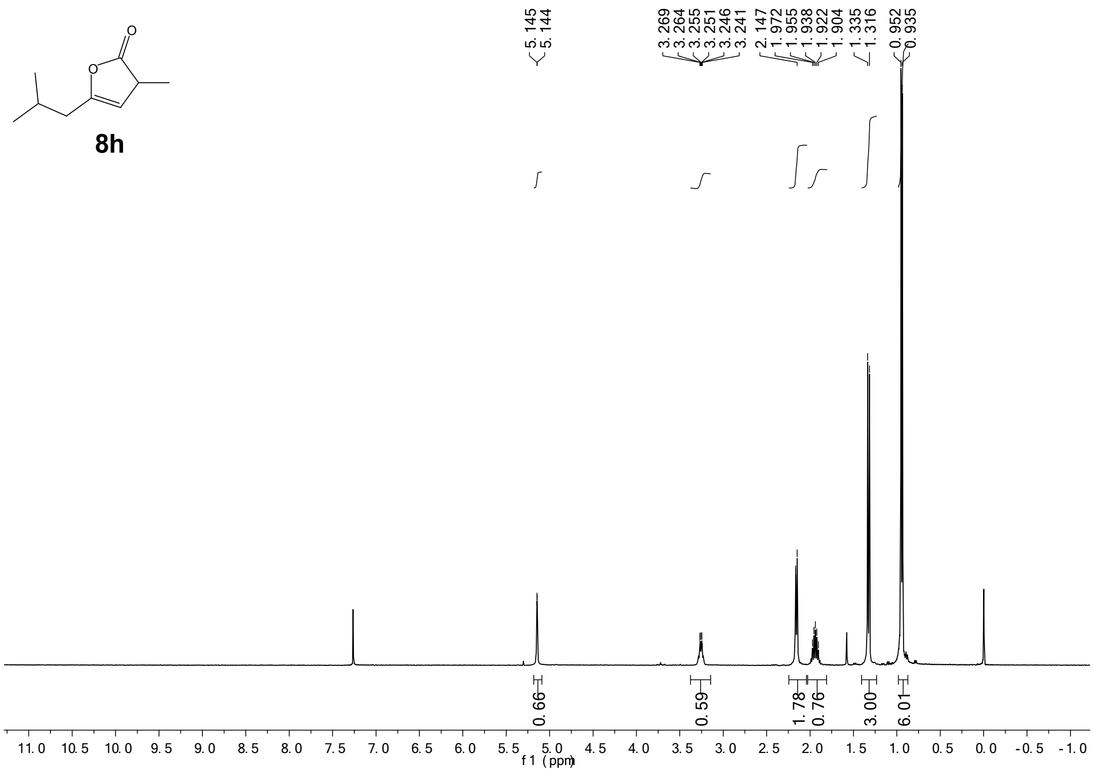
wuyw-III-97-s3-C
wuyw-III-97-s3-C
177.060
156.404
98.685
77.318
77.000
76.681
61.347
33.871
28.546
24.518
OH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

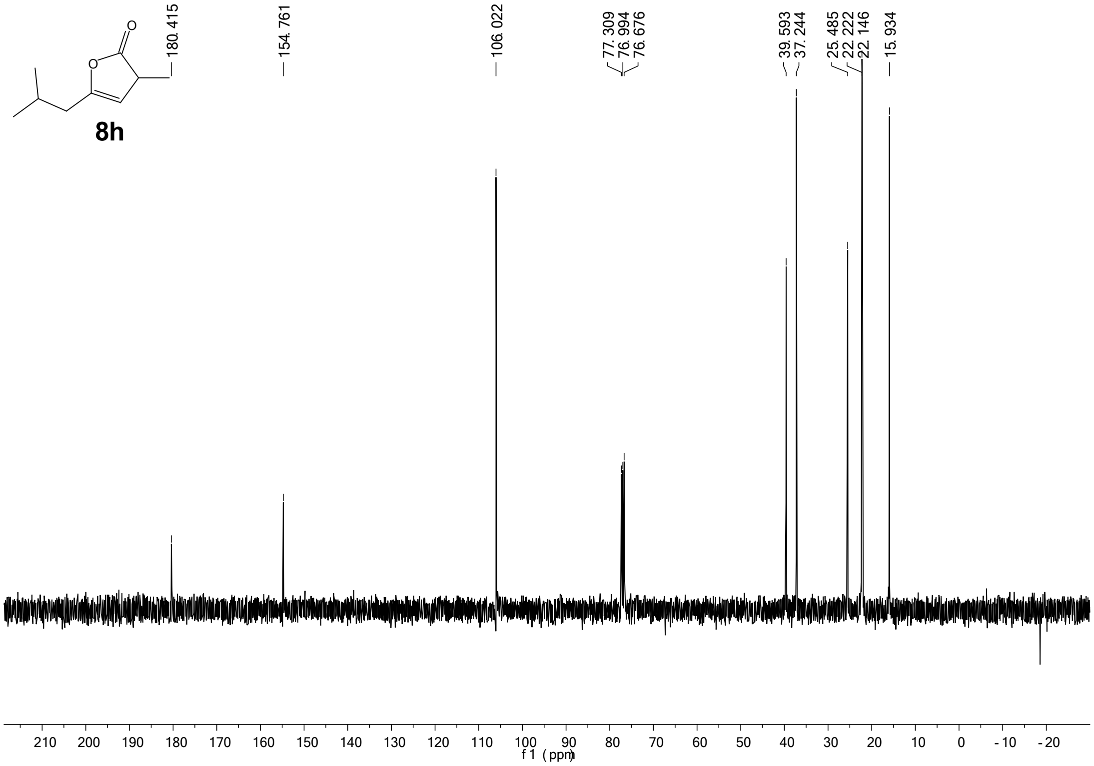

8f

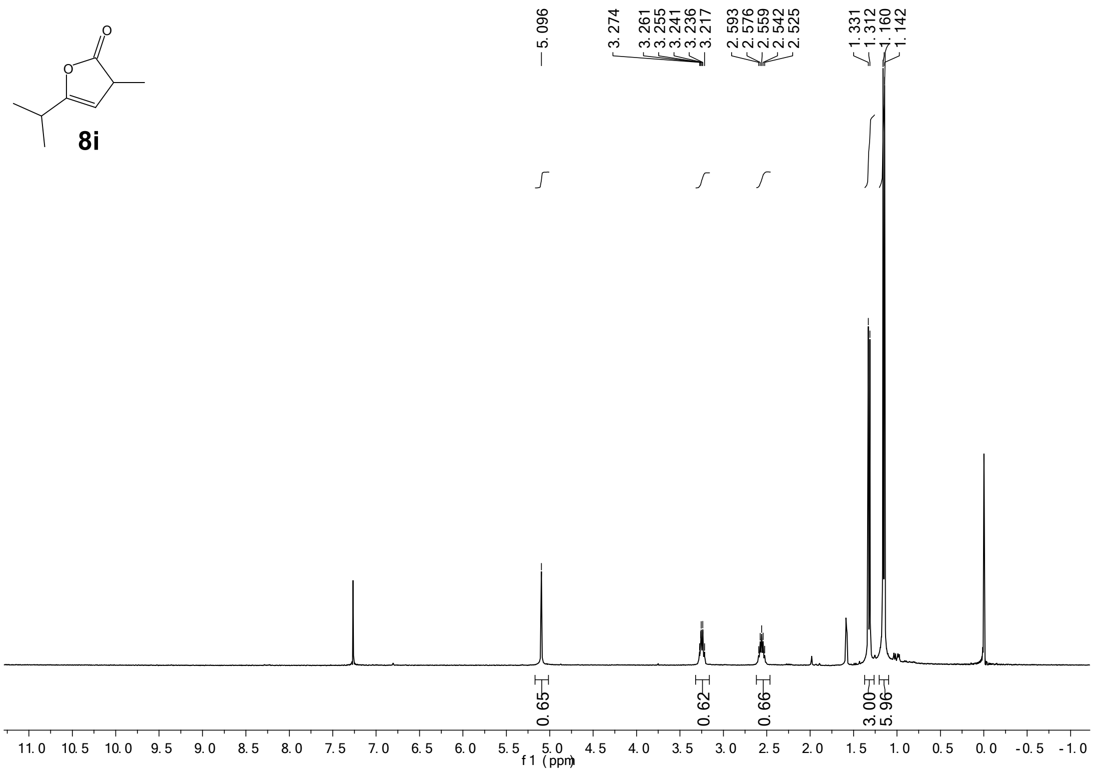
5.142
5.139
3.258
3.252
3.245
3.239
3.236
3.233
3.230
3.227
3.221
1.996
1.993
1.990
1.987
1.325
1.309
1.306
O
O
0.71
0.71
3.00
3.37
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


8g
O
O
5.130
5.129
3.259
3.254
3.241
3.235
2.307
2.289
2.270
1.578
1.501
1.360
1.299
0.944
0.926
0.908
0.65
0.60
1.83
2.38
5.48
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

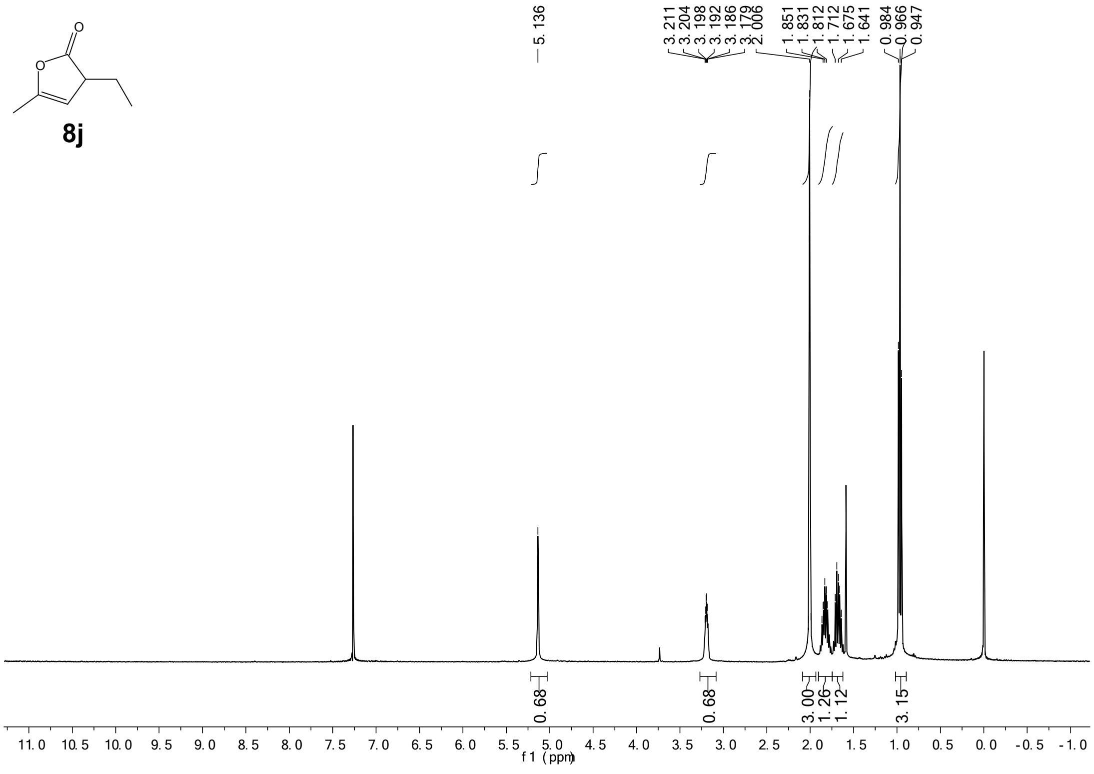

8g
O
O
180.430
155.736
104.743
77.306
76.991
76.672
39.578
27.709
27.674
22.009
15.843
13.669
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8h
O
O
5.145
5.144
3.269
3.264
3.255
3.251
3.246
3.241
2.147
1.972
1.955
1.938
1.922
1.904
1.335
1.316
0.952
0.935
0.66
0.59
1.78
0.76
3.00
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

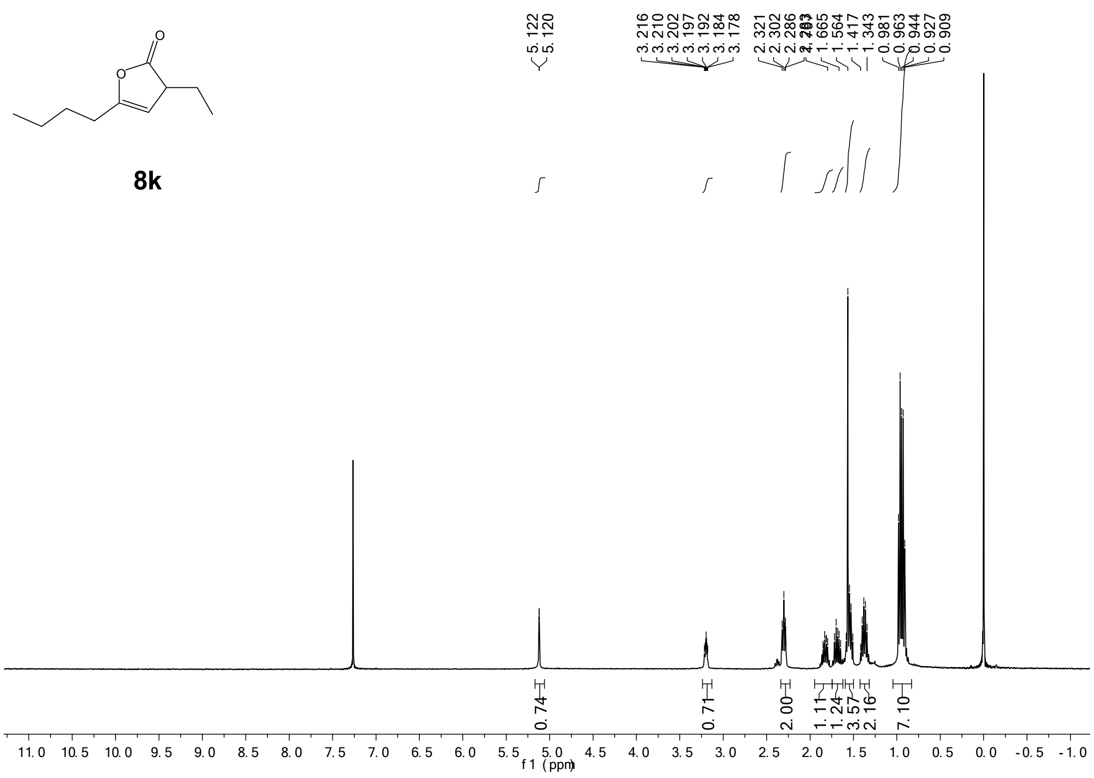

8h
O
O
180.415
154.761
106.022
77.309
76.994
76.676
39.593
37.244
25.485
22.222
22.146
15.934
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
O
5.096
3.274
3.261
3.255
3.241
3.236
3.217
2.593
2.576
2.559
2.542
2.525
1.331
1.312
1.160
1.142
0.65
0.62
0.66
3.00
5.96
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

8i

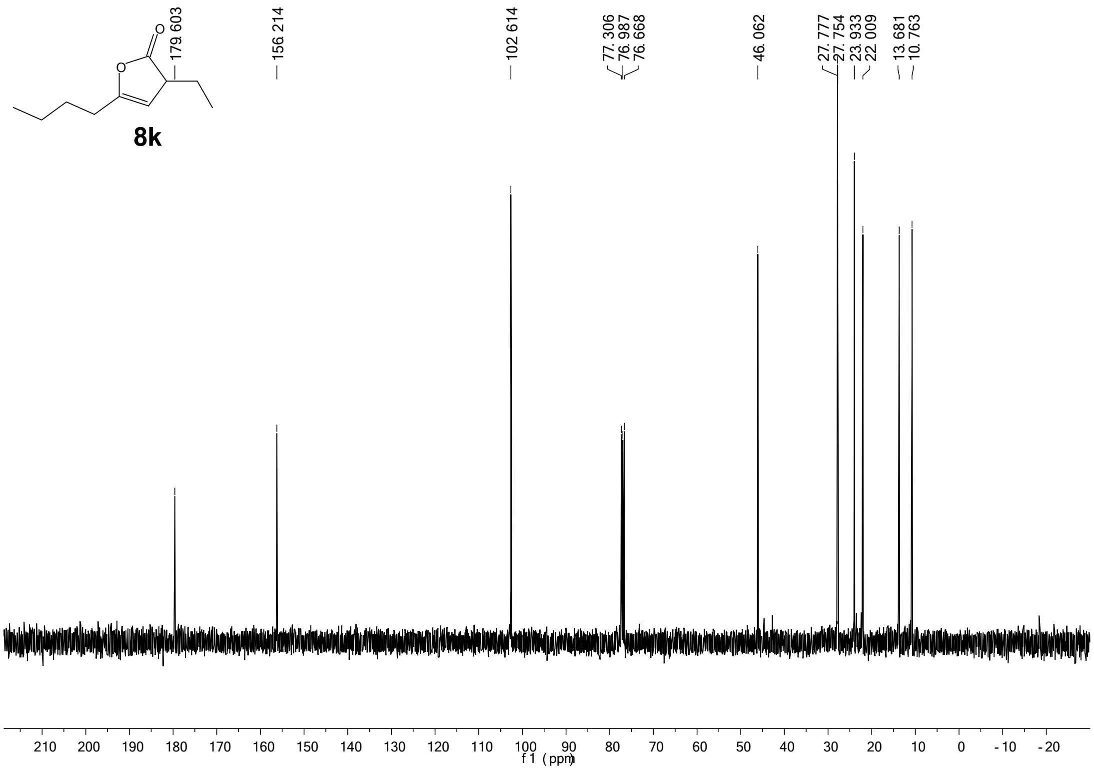

O
O
5.136
3.211
3.204
3.198
3.192
3.186
3.179
2.006
1.851
1.831
1.812
1.712
1.675
1.641
0.984
0.966
0.947
0.68
0.68
3.00
1.26
1.12
3.15
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

8j



8k

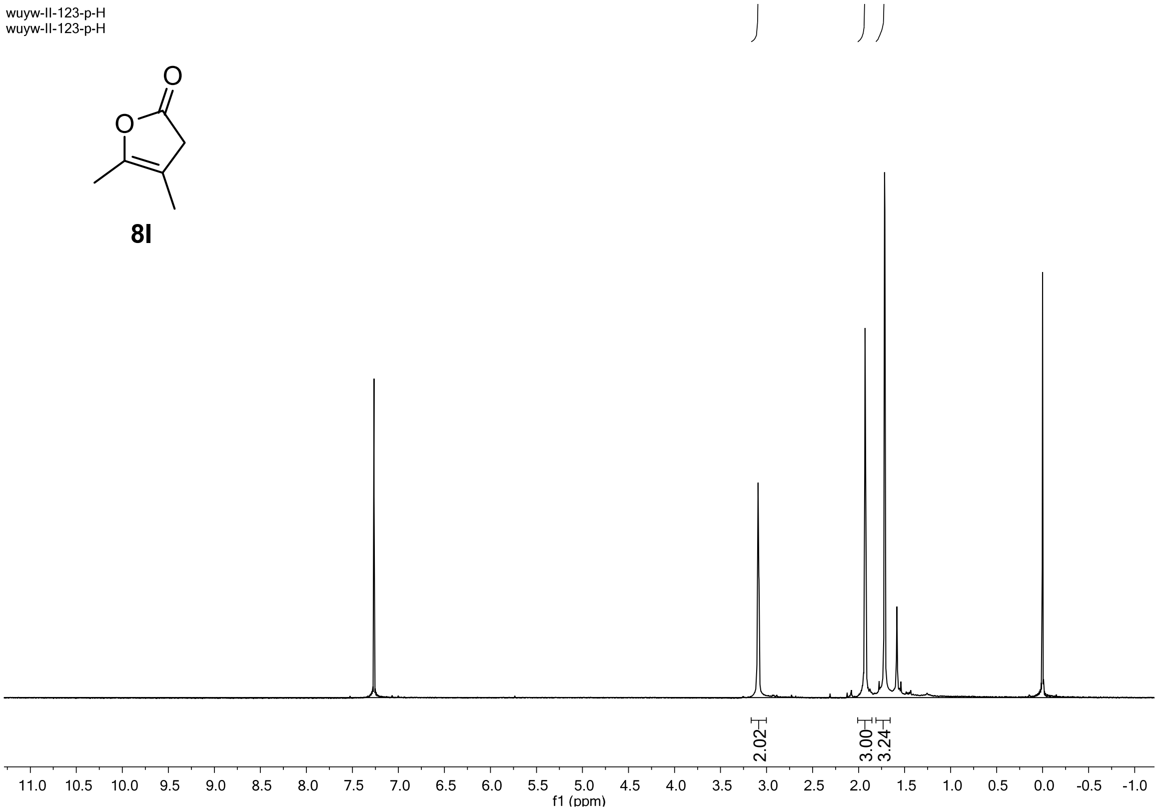
5.122
5.120
3.216
3.210
3.202
3.197
3.192
3.184
3.178
2.321
2.302
2.286
2.283
1.665
1.564
1.417
1.343
0.981
0.963
0.944
0.927
0.909
0.74
0.71
2.00
1.11
1.24
3.57
2.16
7.10
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



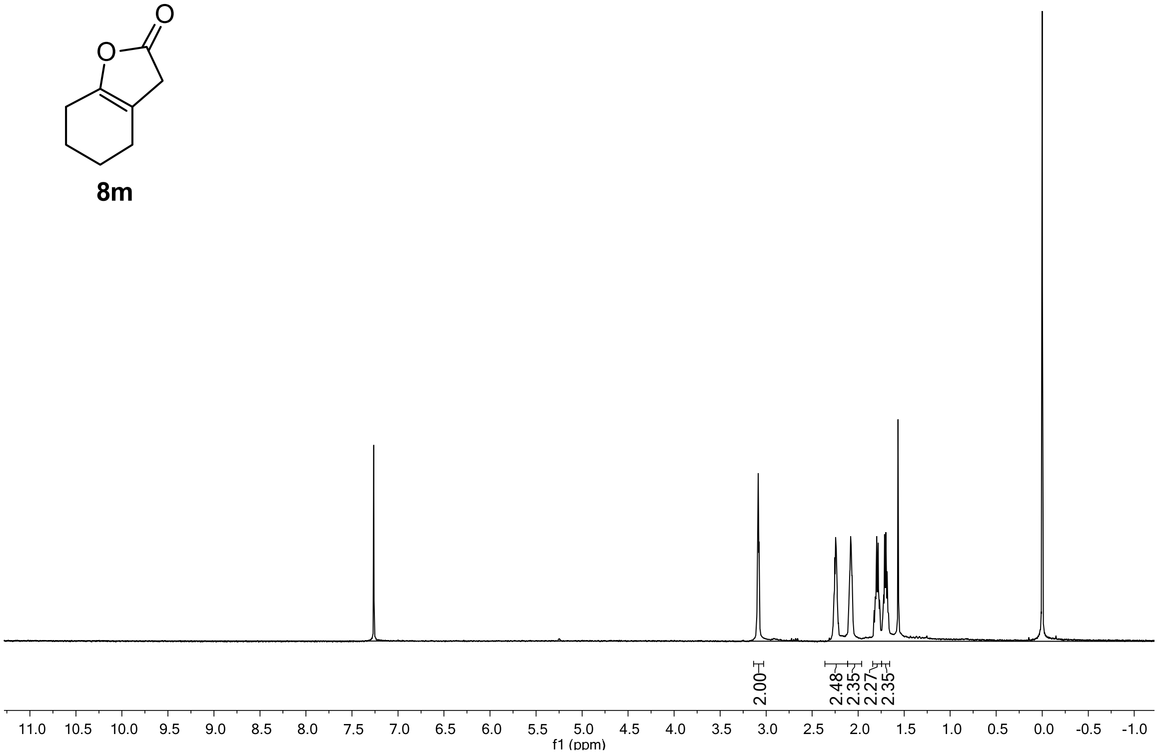
8k

179.603
156.214
102.614
77.306
76.987
76.668
46.062
27.777
27.754
23.933
22.009
13.681
10.763
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

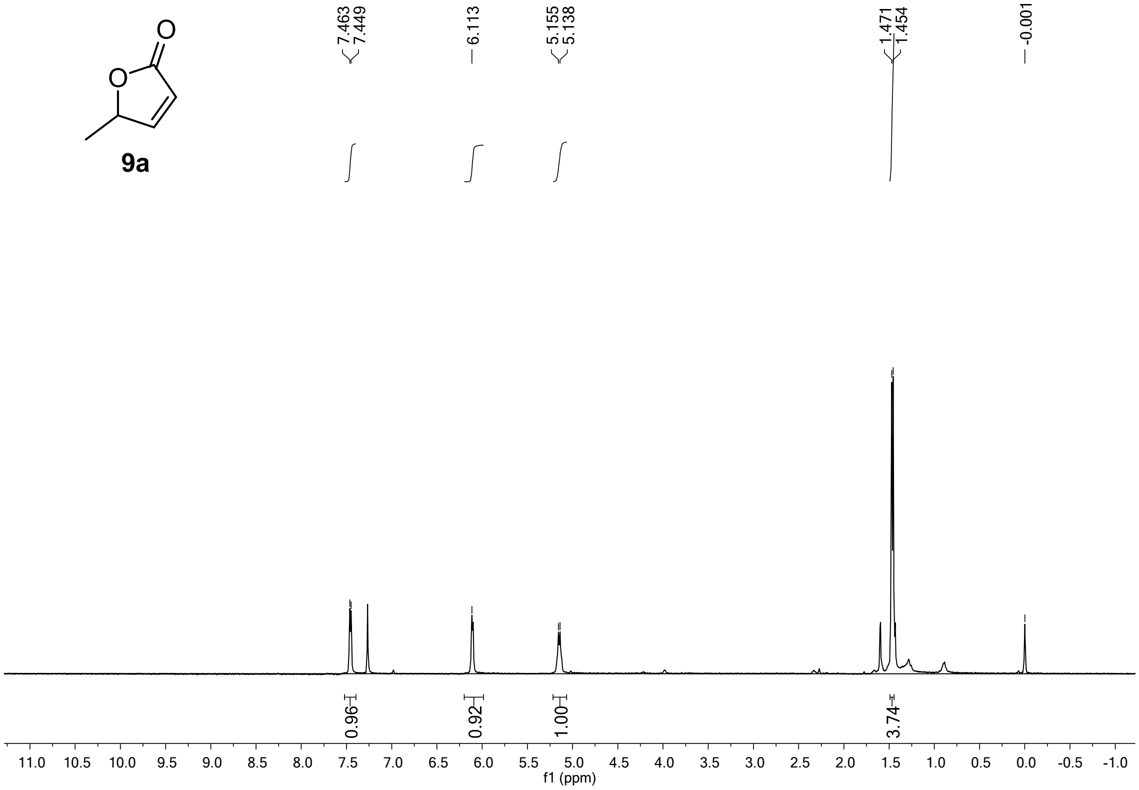
wuyw-II-123-p-H
wuyw-II-123-p-H



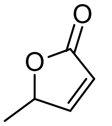
wuyw-III-102-s1
wuyw-III-102-s1

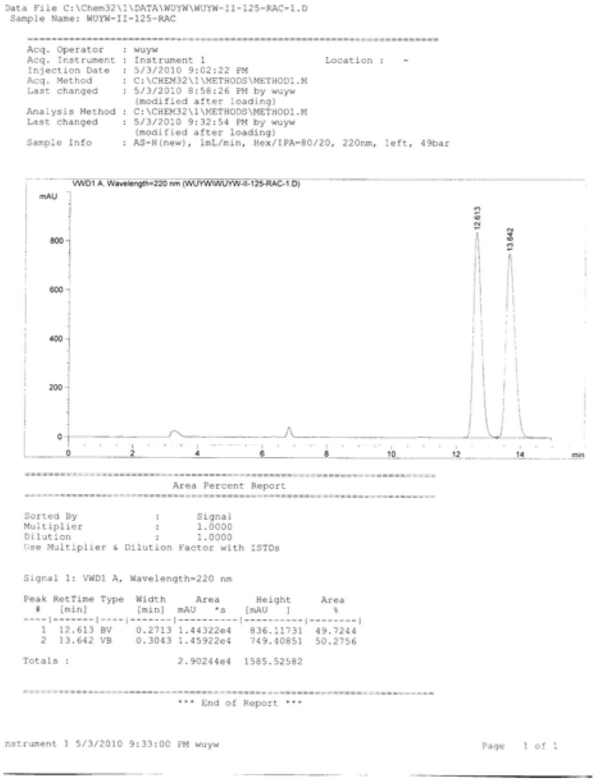


^{1}H and ^{13}C NMR spectra and HPLC spectra for α,β-butenolides **9**


9a

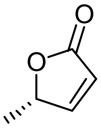
HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 80:20, 1.0 mL/min, λ= 220 nm


Racemic **9a**

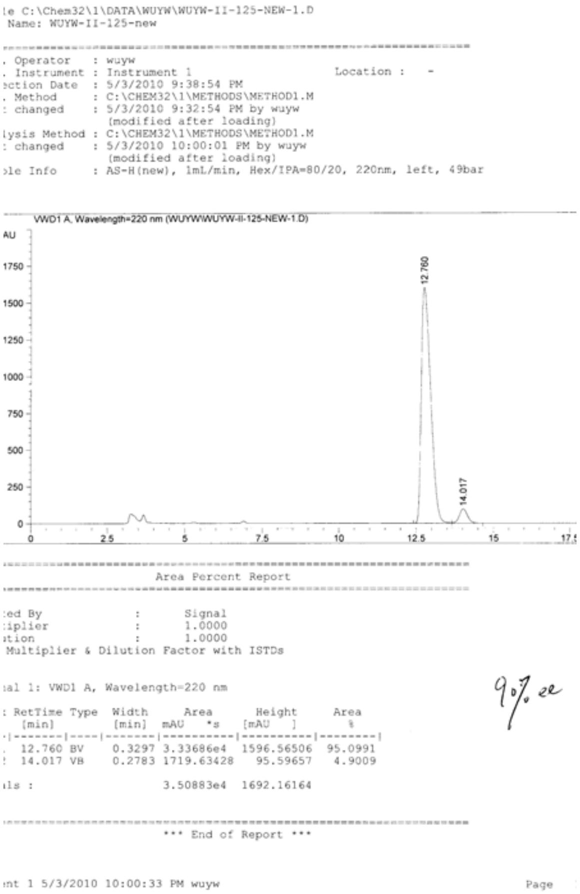


```
Data File C:\Chem32\1\DATA\WUYW\WUYW-II-125-RAC-1.D
 Sample Name: WUYW-II-125-RAC

   =====================================================================
   Acq. Operator   : wuyw
   Acq. Instrument : Instrument 1                    Location :  -
   Injection Date  : 5/3/2010 9:02:22 PM
   Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 5/3/2010 8:58:26 PM by wuyw
                     (modified after loading)
   Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 5/3/2010 9:32:54 PM by wuyw
                     (modified after loading)
   Sample Info     : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 49bar
```

```
   =====================================================================
                         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 Type  Width     Area      Height     Area
     #   [min]        [min]  mAU   *s   [mAU   ]      %
   ----|-------|----|-------|----------|----------|--------|
      1  12.613 BV    0.2713 1.44322e4  836.11731 49.7244
      2  13.642 VB    0.3043 1.45922e4  749.40851 50.2756

   Totals :                  2.90244e4 1585.52582

   =====================================================================
                         *** End of Report ***

nstrument 1 5/3/2010 9:33:00 PM wuyw                          Page    1 of 1
```



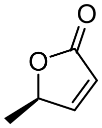
(*S*)-**9a**, 90% ee from
10 mol% QD-**7**
catalyzed reaction.



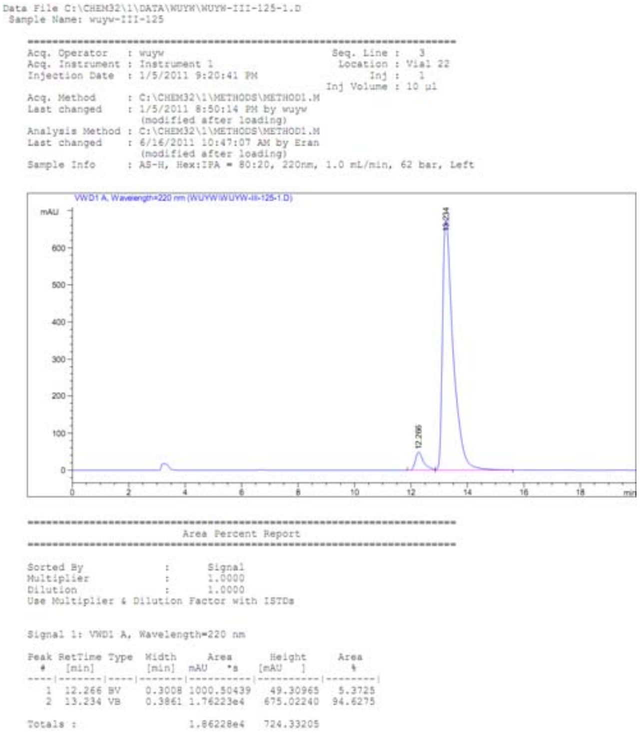
```
le C:\Chem32\1\DATA\WUYW\WUYW-II-125-NEW-1.D
 Name: WUYW-II-125-new

==================================================================
. Operator   : wuyw
. Instrument : Instrument 1                    Location :   -
ection Date  : 5/3/2010 9:38:54 PM
. Method     : C:\CHEM32\1\METHODS\METHOD1.M
: changed    : 5/3/2010 9:32:54 PM by wuyw
               (modified after loading)
lysis Method : C:\CHEM32\1\METHODS\METHOD1.M
: changed    : 5/3/2010 10:00:01 PM by wuyw
               (modified after loading)
ple Info     : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 49bar
```

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

ted By             :      Signal
iplier             :      1.0000
ition              :      1.0000
 Multiplier & Dilution Factor with ISTDs


al 1: VWD1 A, Wavelength=220 nm

: RetTime Type  Width     Area      Height     Area
   [min]        [min]  mAU   *s    [mAU   ]      %
-|-------|----|-------|----------|----------|--------|
.  12.760 BV    0.3297 3.33686e4 1596.56506  95.0991
!  14.017 VB    0.2783 1719.63428   95.59657   4.9009

ls :                   3.50883e4  1692.16164

==================================================================
                   *** End of Report ***


nt 1 5/3/2010 10:00:33 PM wuyw                                  Page
```

90% ee

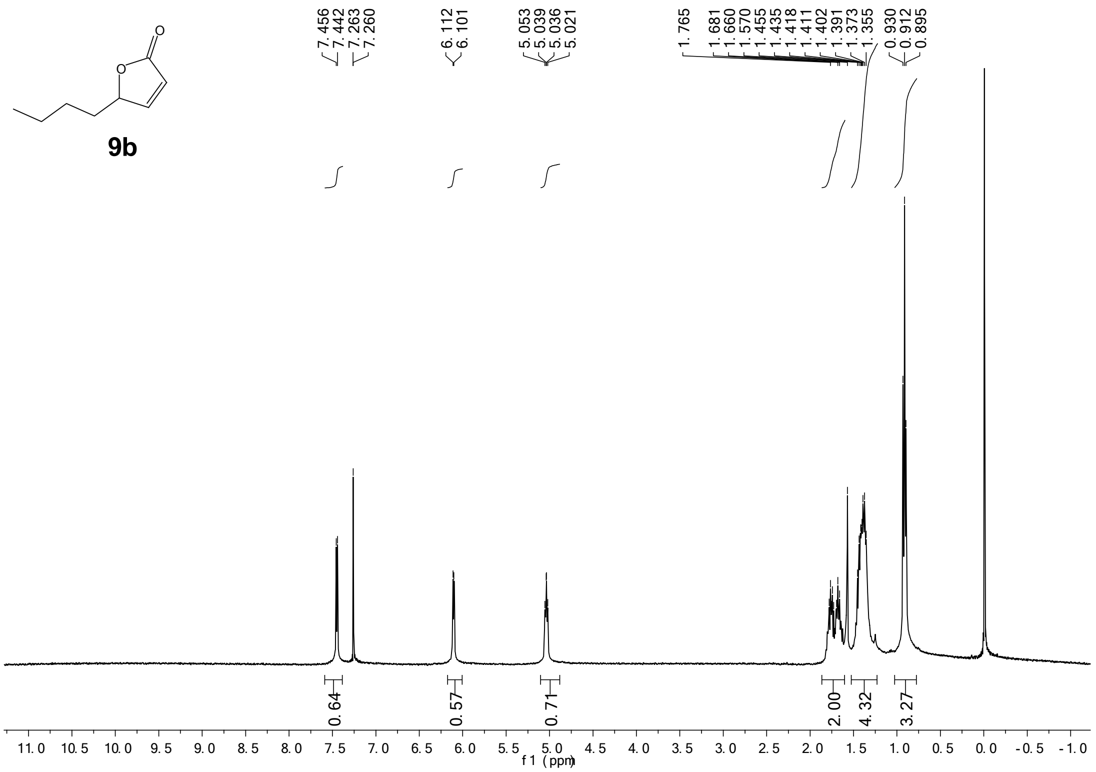


(*R*)-**9a**, 90% ee from
10 mol% Q-**7**
catalyzed reaction.



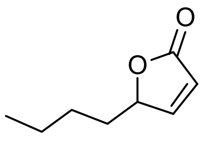
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-125-1.D
 Sample Name: wuyw-III-125

   =====================================================================
   Acq. Operator   : wuyw                           Seq. Line :    3
   Acq. Instrument : Instrument 1                    Location : Vial 22
   Injection Date  : 1/5/2011 9:20:41 PM                  Inj :    1
                                                  Inj Volume : 10 µl
   Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 1/5/2011 8:50:14 PM by wuyw
                     (modified after loading)
   Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 6/16/2011 10:47:07 AM by Eran
                     (modified after loading)
   Sample Info     : AS-H, Hex:IPA = 80:20, 220nm, 1.0 mL/min, 62 bar, Left
```

```
=====================================================================
                         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 Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.266 BV    0.3008 1000.50439   49.30965   5.3725
   2  13.234 VB    0.3861 1.76223e4   675.02240  94.6275

Totals :                  1.86228e4   724.33205
```

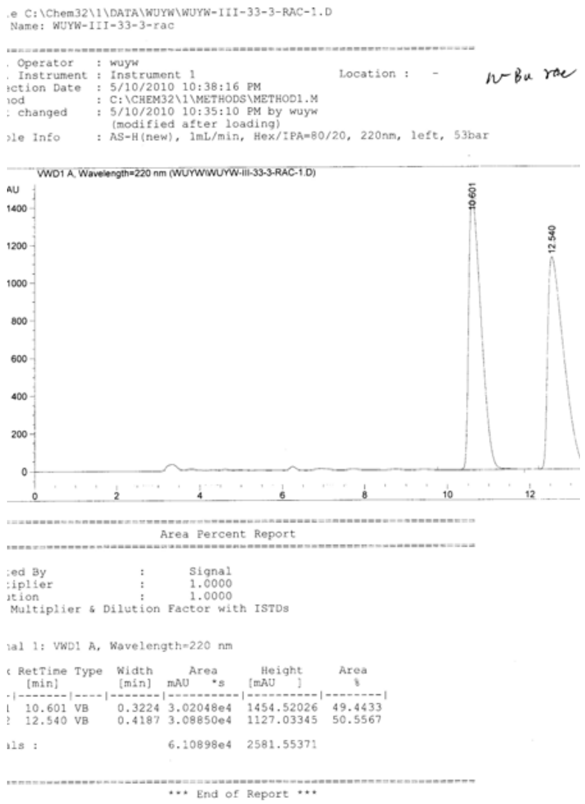


9b

HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 80:20, 1.0 mL/min, λ= 220nm



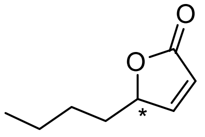
Racemic **9b**



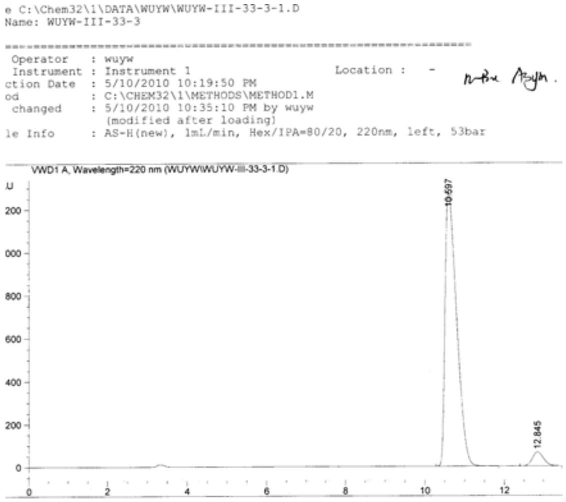
```
.e C:\Chem32\1\DATA\WUYW\WUYW-III-33-3-RAC-1.D
 Name: WUYW-III-33-3-rac

. Operator   : wuyw
. Instrument : Instrument 1                    Location :   -
ection Date  : 5/10/2010 10:38:16 PM
nod          : C:\CHEM32\1\METHODS\METHOD1.M
: changed    : 5/10/2010 10:35:10 PM by wuyw
               (modified after loading)
ole Info     : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 53bar
```

n-Bu rac

```
                       Area Percent Report

:ed By              :      Signal
:iplier             :      1.0000
ition               :      1.0000
 Multiplier & Dilution Factor with ISTDs

nal 1: VWD1 A, Wavelength=220 nm

< RetTime Type  Width     Area       Height      Area
   [min]        [min]  mAU    *s   [mAU    ]      %
-|-------|----|-------|----------|----------|--------|
1  10.601 VB    0.3224 3.02048e4  1454.52026  49.4433
2  12.540 VB    0.4187 3.08850e4  1127.03345  50.5567

als :                  6.10898e4  2581.55371

                       *** End of Report ***
```



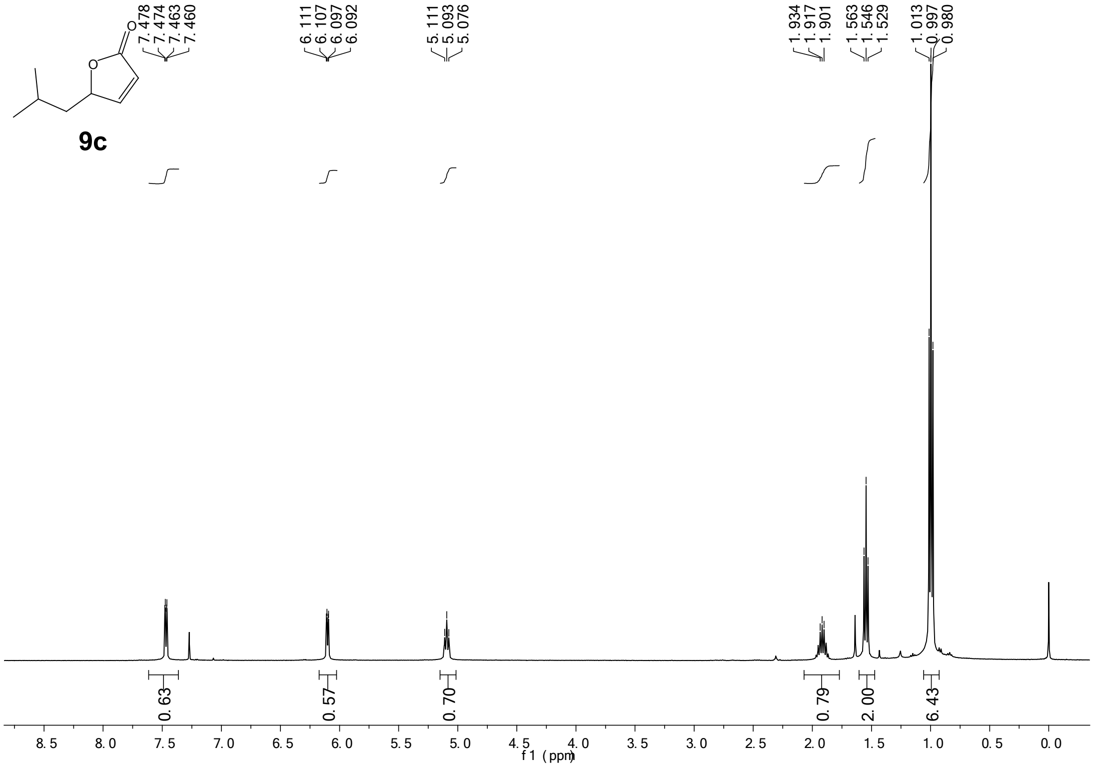
(+)-**9b**, 91% ee from 20 mol% QD-**7** catalyzed reaction.



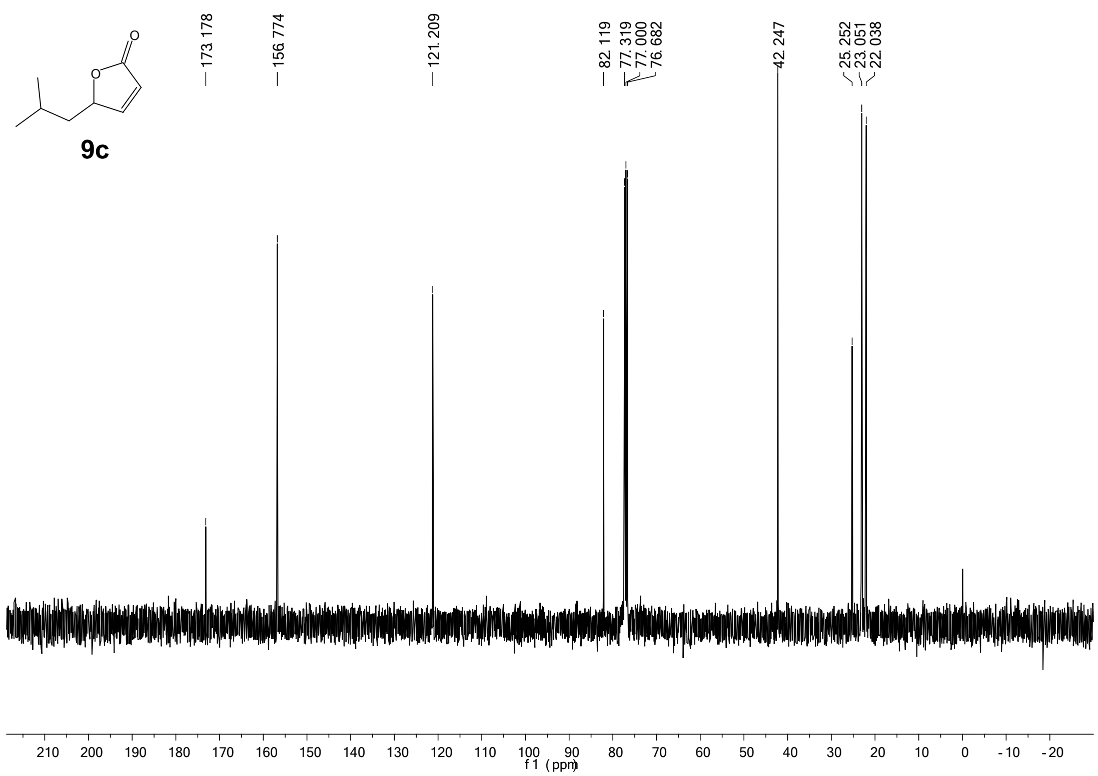
```
e C:\Chem32\1\DATA\WUYW\WUYW-III-33-3-1.D
Name: WUYW-III-33-3

=====================================================================
 Operator   : wuyw
 Instrument : Instrument 1                    Location :  -
ction Date  : 5/10/2010 10:19:50 PM
od          : C:\CHEM32\1\METHODS\METHOD1.M
 changed    : 5/10/2010 10:35:10 PM by wuyw
              (modified after loading)
le Info     : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 53bar
```

n-Bu Asym.

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

ed By             :      Signal
iplier            :      1.0000
tion              :      1.0000
Multiplier & Dilution Factor with ISTDs

al 1: VWD1 A, Wavelength=220 nm

 RetTime Type  Width     Area      Height     Area
  [min]        [min]  mAU   *s   [mAU   ]      %
|-------|----|-------|----------|----------|--------|
  10.597 BB    0.3125 2.57357e4  1276.01111  95.3877
  12.845 BB    0.3040 1244.39368   64.01481   4.6123

ls :                  2.69801e4  1340.02592
```

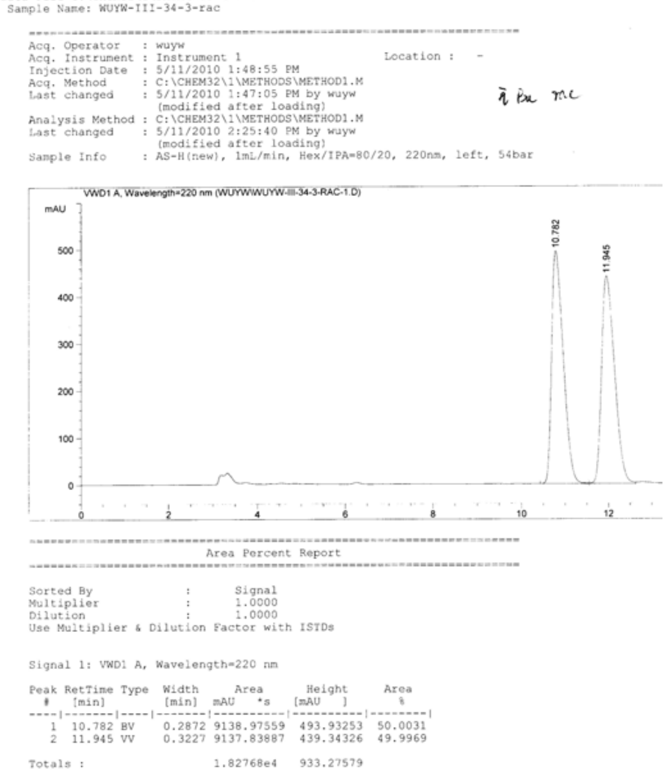


9c



9c

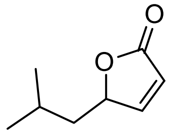
HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 80:20, 1.0 mL/min, λ= 220 nm



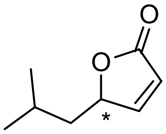
```
Data File C:\Chem32\1\DATA\WUYW\WUYW-III-34-3-RAC-1.D
Sample Name: WUYW-III-34-3-rac

=====================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                    Location :  -
Injection Date  : 5/11/2010 1:48:55 PM
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/11/2010 1:47:05 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/11/2010 2:25:40 PM by wuyw
                  (modified after loading)
Sample Info     : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 54bar
```

i Bu rac

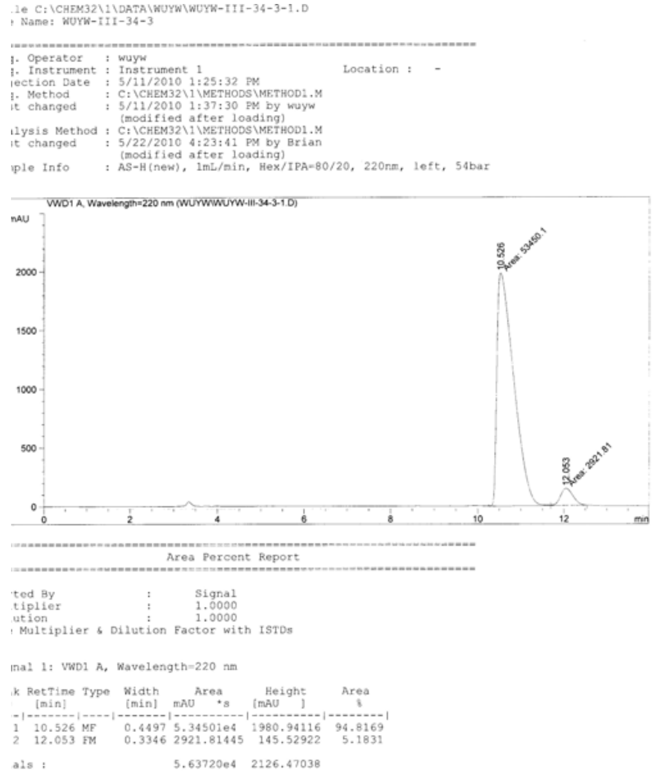
```
=====================================================================
                        Area Percent Report
=====================================================================

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

Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU  ]       %
----|-------|----|-------|----------|----------|--------|
   1  10.782 BV    0.2872 9138.97559  493.93253  50.0031
   2  11.945 VV    0.3227 9137.83887  439.34326  49.9969

Totals :                  1.82768e4   933.27579
```



Racemic **9c**

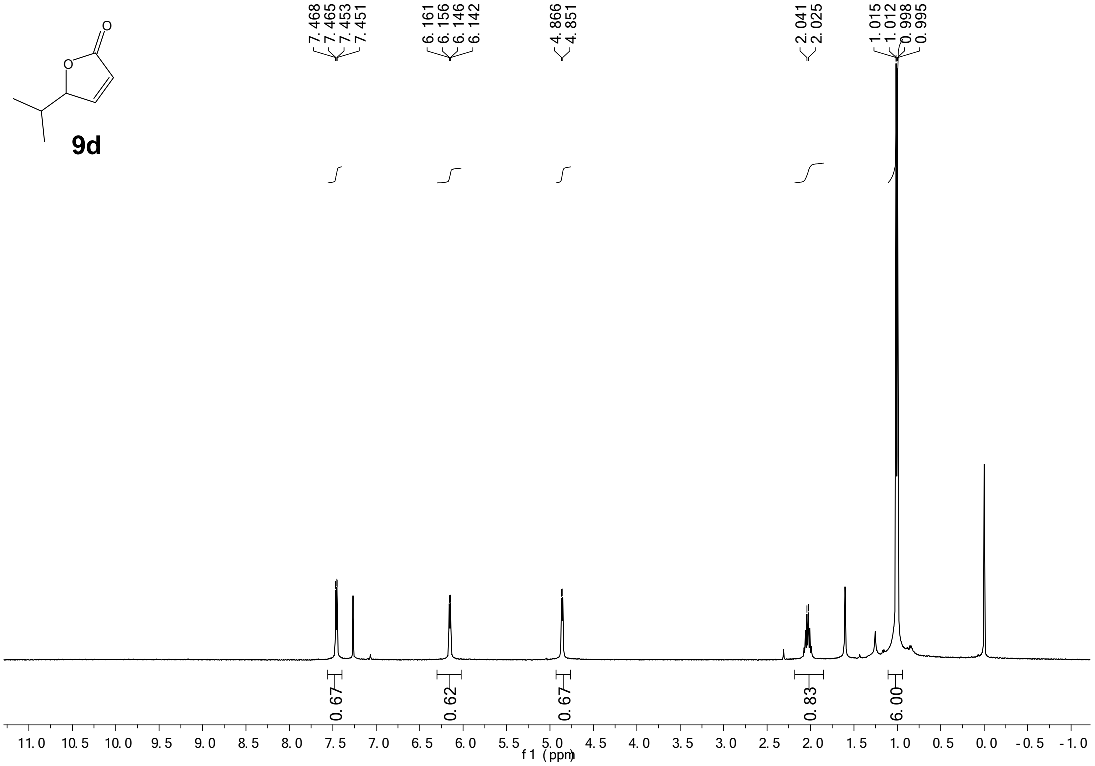


(+)-**9c**, 90% ee from 20 mol% QD-**7** catalyzed reaction.



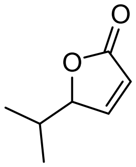
```
.le C:\CHEM32\1\DATA\WUYW\WUYW-III-34-3-1.D
: Name: WUYW-III-34-3

=====================================================================
;. Operator    : wuyw
;. Instrument  : Instrument 1                    Location :  -
jection Date   : 5/11/2010 1:25:32 PM
;. Method      : C:\CHEM32\1\METHODS\METHOD1.M
it changed     : 5/11/2010 1:37:30 PM by wuyw
                 (modified after loading)
ilysis Method  : C:\CHEM32\1\METHODS\METHOD1.M
it changed     : 5/22/2010 4:23:41 PM by Brian
                 (modified after loading)
iple Info      : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 54bar
```

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

'ted By             :      Signal
tiplier             :      1.0000
ution               :      1.0000
: Multiplier & Dilution Factor with ISTDs


nal 1: VWD1 A, Wavelength=220 nm

k RetTime Type  Width     Area      Height     Area
   [min]        [min]   mAU   *s   [mAU   ]      %
-|-------|----|-------|----------|----------|--------|
1  10.526 MF    0.4497 5.34501e4  1980.94116  94.8169
2  12.053 FM    0.3346 2921.81445  145.52922   5.1831

als :                   5.63720e4  2126.47038
```

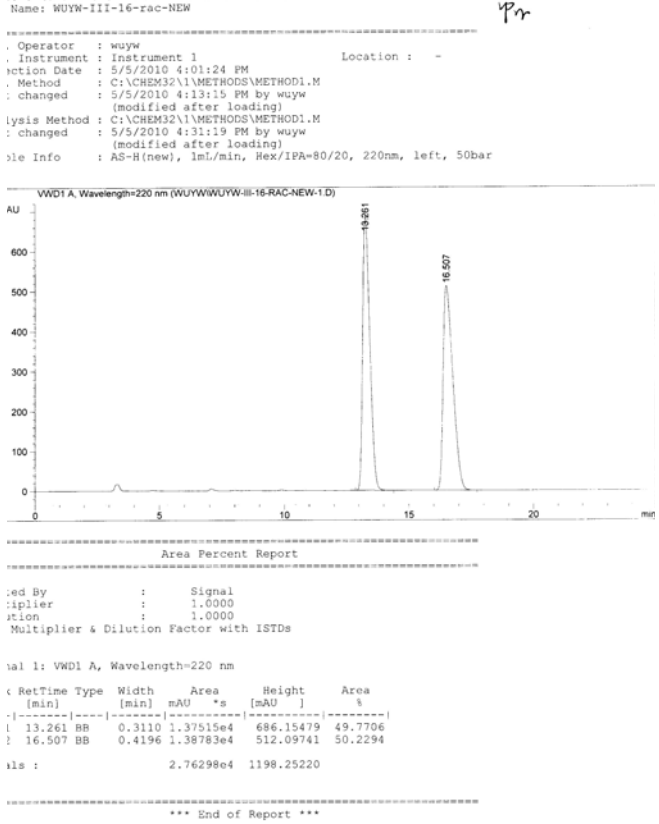


9d

HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 80:20, 1.0 mL/min, λ= 220 nm



Racemic **9d**

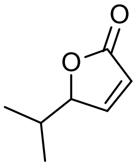


```
le C:\Chem32\1\DATA\WUYW\WUYW-III-16-RAC-NEW-1.D
 Name: WUYW-III-16-rac-NEW
```

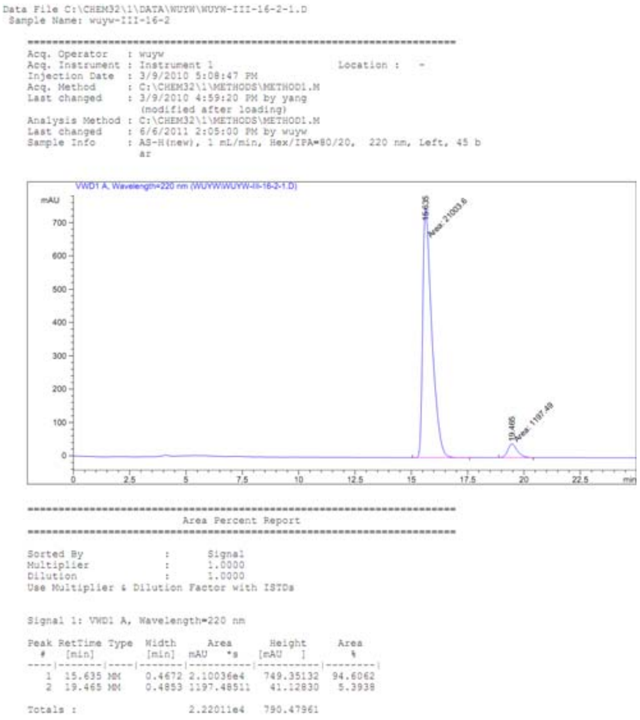
iPr

```
======================================================================
. Operator    : wuyw
. Instrument  : Instrument 1                        Location :  -
ection Date   : 5/5/2010 4:01:24 PM
. Method      : C:\CHEM32\1\METHODS\METHOD1.M
: changed     : 5/5/2010 4:13:15 PM by wuyw
                (modified after loading)
lysis Method  : C:\CHEM32\1\METHODS\METHOD1.M
: changed     : 5/5/2010 4:31:19 PM by wuyw
                (modified after loading)
ole Info      : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 50bar
```

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

ted By              :      Signal
tiplier             :      1.0000
ution               :      1.0000
 Multiplier & Dilution Factor with ISTDs


nal 1: VWD1 A, Wavelength=220 nm

 RetTime Type  Width     Area      Height     Area
  [min]        [min]  mAU   *s   [mAU   ]      %
-|-------|----|-------|----------|----------|--------|
1  13.261 BB    0.3110 1.37515e4   686.15479  49.7706
2  16.507 BB    0.4196 1.38783e4   512.09741  50.2294

als :                  2.76298e4  1198.25220

======================================================================
                        *** End of Report ***
```

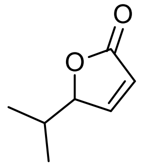


(+)-**9d**, 90% ee from
10 mol% QD-**7**
catalyzed reaction.

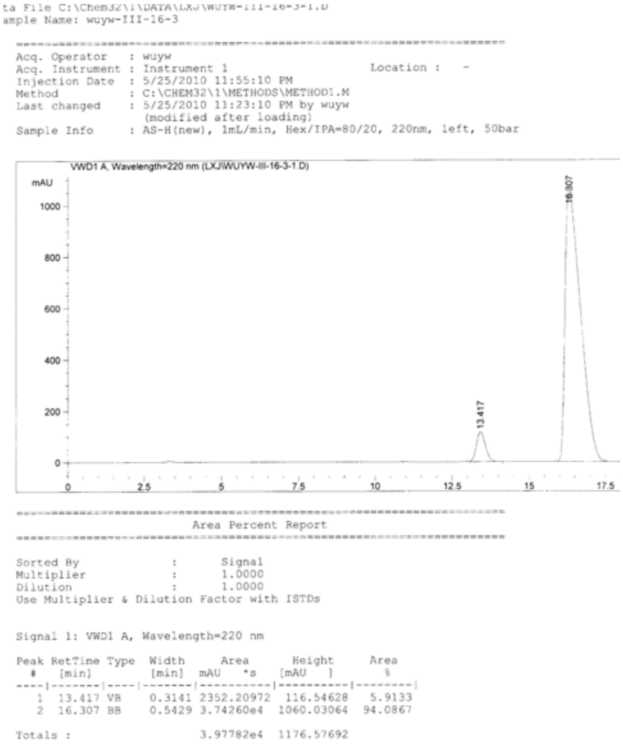


```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-16-2-1.D
 Sample Name: wuyw-III-16-2

   =====================================================================
   Acq. Operator   : wuyw
   Acq. Instrument : Instrument 1                      Location :  -
   Injection Date  : 3/9/2010 5:08:47 PM
   Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 3/9/2010 4:59:20 PM by yang
                     (modified after loading)
   Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
   Last changed    : 6/6/2011 2:05:00 PM by wuyw
   Sample Info     : AS-H(new), 1 mL/min, Hex/IPA=80/20,  220 nm, Left, 45 b
                     ar
```

```
=====================================================================
                        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 Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.635 MM    0.4672 2.10036e4  749.35132  94.6062
   2  19.465 MM    0.4853 1197.48511  41.12830   5.3938

Totals :                  2.22011e4  790.47961
```

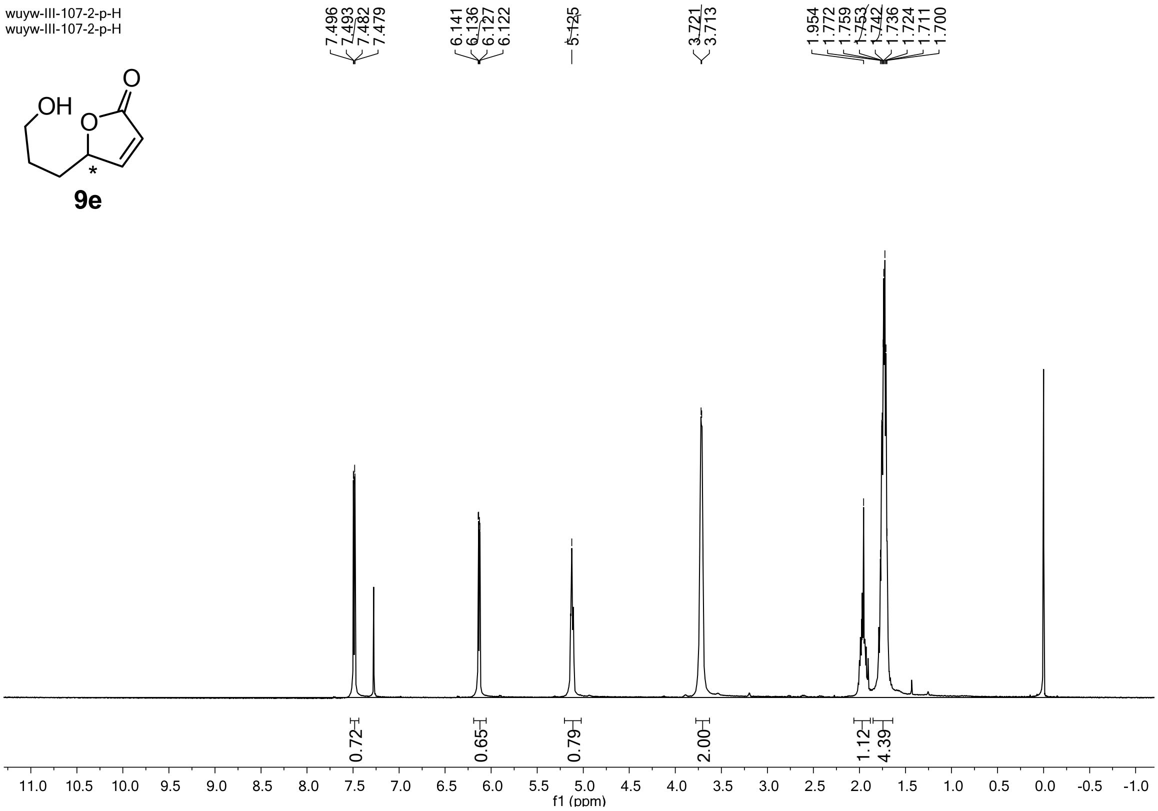


(-)-**9d**, 88% ee from 10 mol% Q-**7** catalyzed reaction.

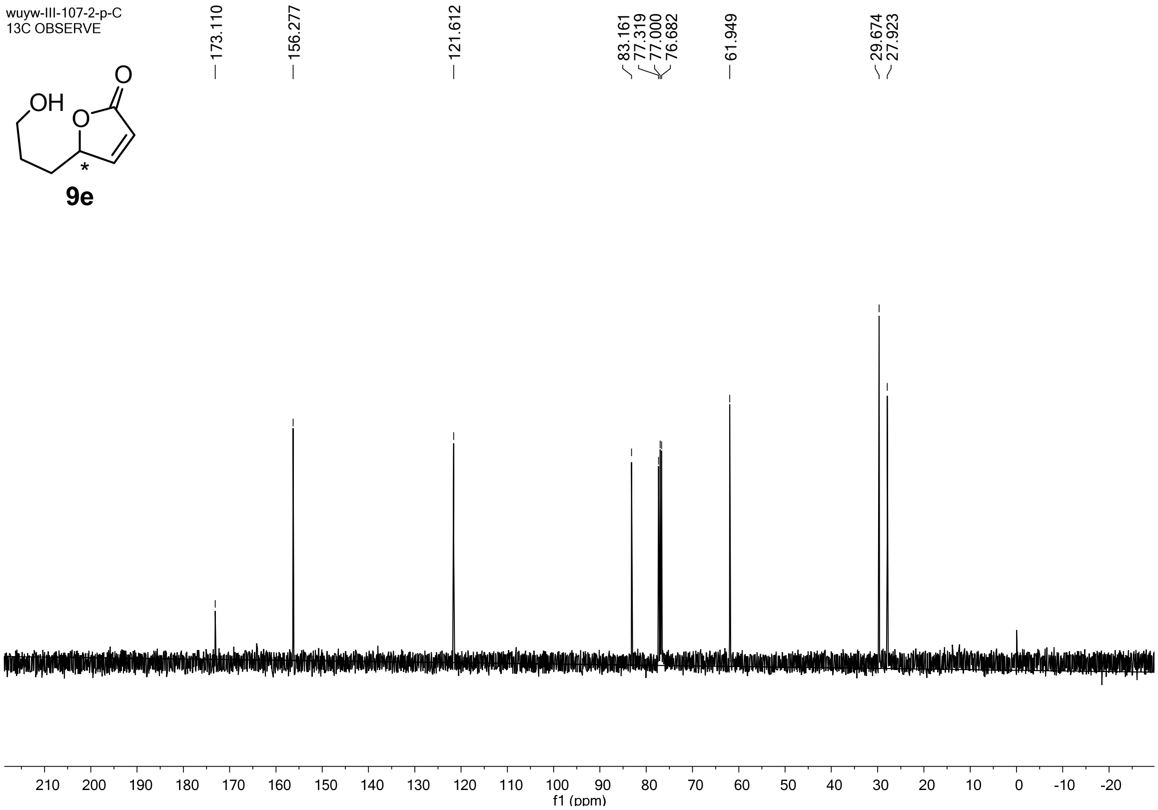


```
ta File C:\Chem32\1\DATA\LXJ\WUYW-III-16-3-1.D
ample Name: wuyw-III-16-3

=====================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 5/25/2010 11:55:10 PM
Method          : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/25/2010 11:23:10 PM by wuyw
                  (modified after loading)
Sample Info     : AS-H(new), 1mL/min, Hex/IPA=80/20, 220nm, left, 50bar
```

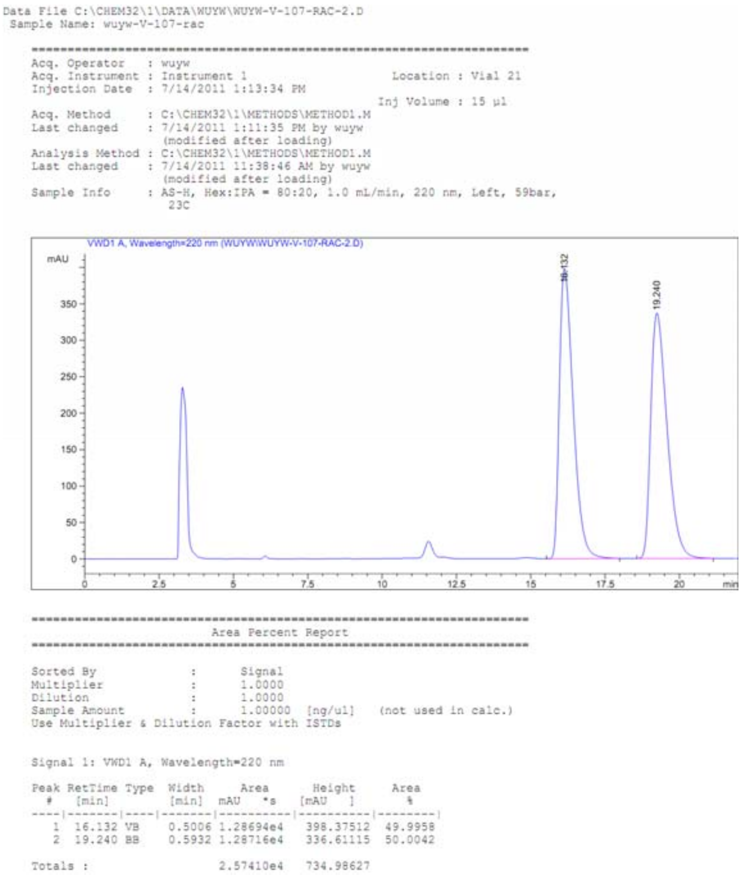
```
=====================================================================
                         Area Percent Report
=====================================================================

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


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  13.417 VB    0.3141 2352.20972  116.54628   5.9133
   2  16.307 BB    0.5429 3.74260e4  1060.03064  94.0867

Totals :                  3.97782e4  1176.57692
```



9e

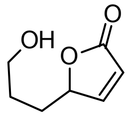


9e

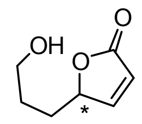


```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-107-RAC-2.D
 Sample Name: wuyw-V-107-rac

    =====================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                  Location : Vial 21
    Injection Date  : 7/14/2011 1:13:34 PM
                                                  Inj Volume : 15 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 7/14/2011 1:11:35 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 7/14/2011 11:38:46 AM by wuyw
                      (modified after loading)
    Sample Info     : AS-H, Hex:IPA = 80:20, 1.0 mL/min, 220 nm, Left, 59bar,
                       23C
```

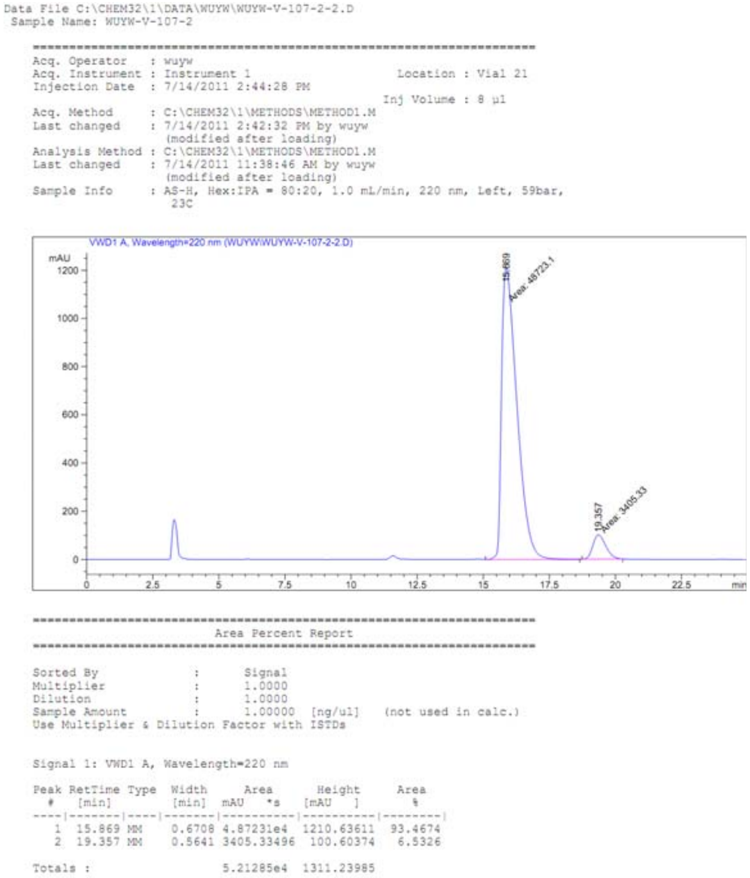
```
    =====================================================================
                            Area Percent Report
    =====================================================================

    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  16.132 VB    0.5006 1.28694e4  398.37512  49.9958
       2  19.240 BB    0.5932 1.28716e4  336.61115  50.0042

    Totals :                  2.57410e4  734.98627
```



racemic **9e**

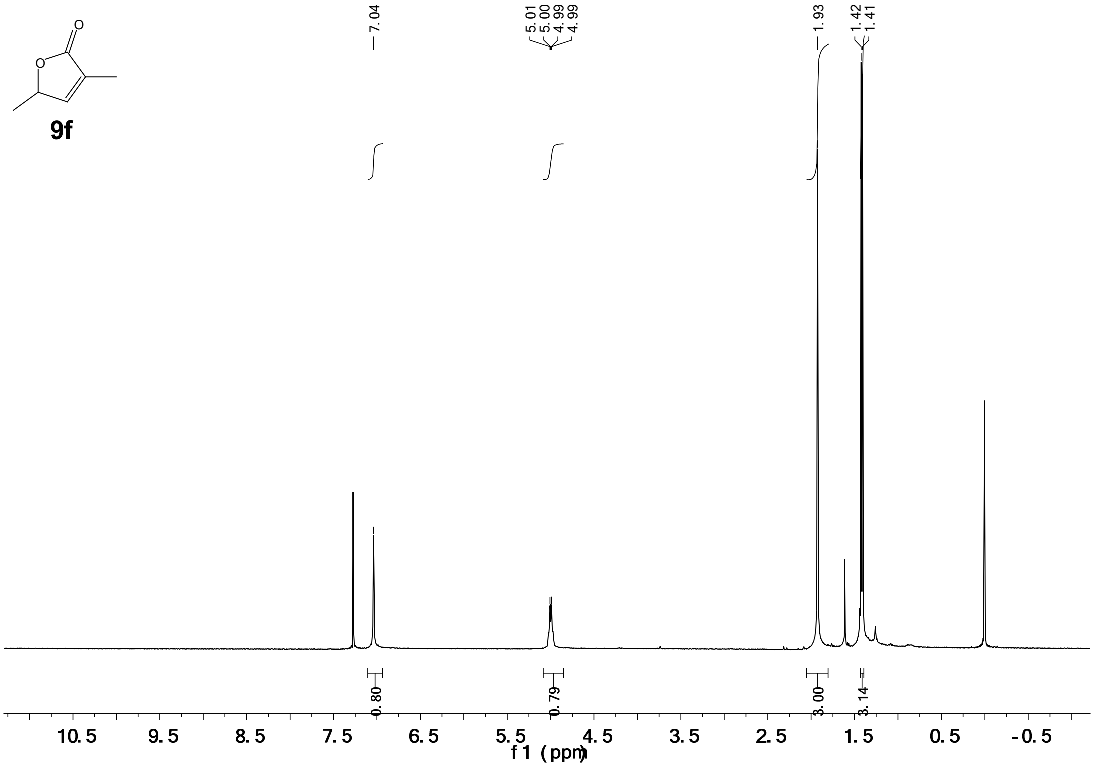


(+)-**9e**, 87% ee from
10 mol% QD-**7**
catalyzed reaction



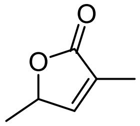
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-V-107-2-2.D
 Sample Name: WUYW-V-107-2

    =====================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                    Location : Vial 21
    Injection Date  : 7/14/2011 2:44:28 PM
                                                   Inj Volume : 8 µl
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 7/14/2011 2:42:32 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 7/14/2011 11:38:46 AM by wuyw
                      (modified after loading)
    Sample Info     : AS-H, Hex:IPA = 80:20, 1.0 mL/min, 220 nm, Left, 59bar,
                       23C
```

```
    =====================================================================
                             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  15.869 MM    0.6708 4.87231e4 1210.63611  93.4674
       2  19.357 MM    0.5641 3405.33496  100.60374   6.5326

    Totals :                  5.21285e4  1311.23985
```

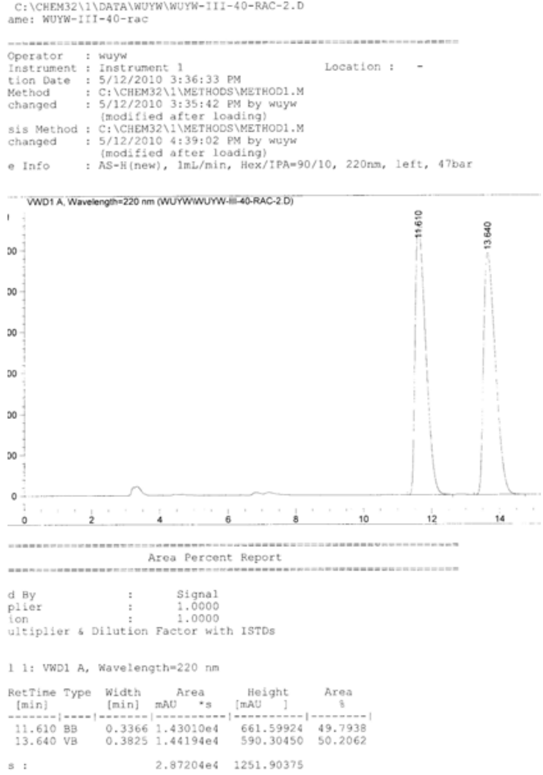


9f

HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 90:10, 1.0 mL/min, λ= 220 nm

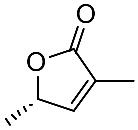


Racemic **9f**

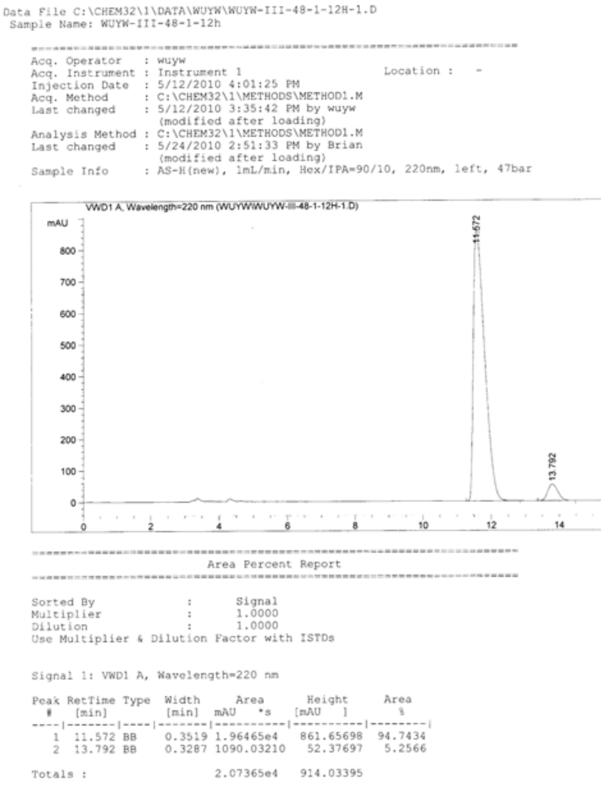


```
 C:\CHEM32\1\DATA\WUYW\WUYW-III-40-RAC-2.D
ame: WUYW-III-40-rac

=====================================================================
Operator   : wuyw
Instrument : Instrument 1                       Location :   -
tion Date  : 5/12/2010 3:36:33 PM
Method     : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/12/2010 3:35:42 PM by wuyw
             (modified after loading)
sis Method : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/12/2010 4:39:02 PM by wuyw
             (modified after loading)
e Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 47bar
```

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

d By               :      Signal
plier              :      1.0000
ion                :      1.0000
ultiplier & Dilution Factor with ISTDs


l 1: VWD1 A, Wavelength=220 nm

RetTime Type  Width     Area      Height     Area
 [min]        [min]  mAU   *s    [mAU   ]      %
-------|----|-------|----------|----------|--------|
 11.610 BB    0.3366 1.43010e4   661.59924  49.7938
 13.640 VB    0.3825 1.44194e4   590.30450  50.2062

s :                  2.87204e4  1251.90375
```

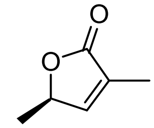


(*S*)-**9f**, 90% ee from
0.5 mol% QD-**7**
catalyzed reaction.

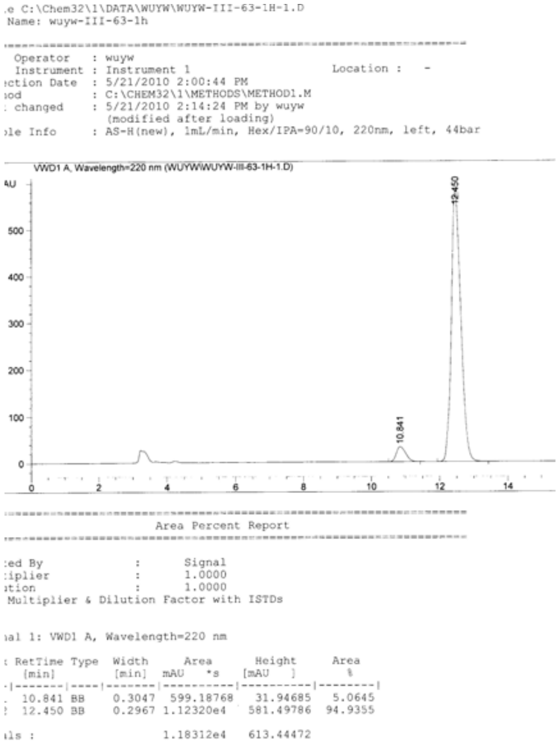


```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-48-1-12H-1.D
 Sample Name: WUYW-III-48-1-12h

     ================================================================
     Acq. Operator   : wuyw
     Acq. Instrument : Instrument 1                       Location :   -
     Injection Date  : 5/12/2010 4:01:25 PM
     Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
     Last changed    : 5/12/2010 3:35:42 PM by wuyw
                       (modified after loading)
     Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
     Last changed    : 5/24/2010 2:51:33 PM by Brian
                       (modified after loading)
     Sample Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 47bar
```

```
     ================================================================
                       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 Type  Width     Area      Height     Area
       #   [min]        [min]  mAU   *s    [mAU   ]      %
     ----|-------|----|-------|----------|----------|--------|
        1  11.572 BB    0.3519 1.96465e4   861.65698  94.7434
        2  13.792 BB    0.3287 1090.03210   52.37697   5.2566

     Totals :                  2.07365e4   914.03395
```

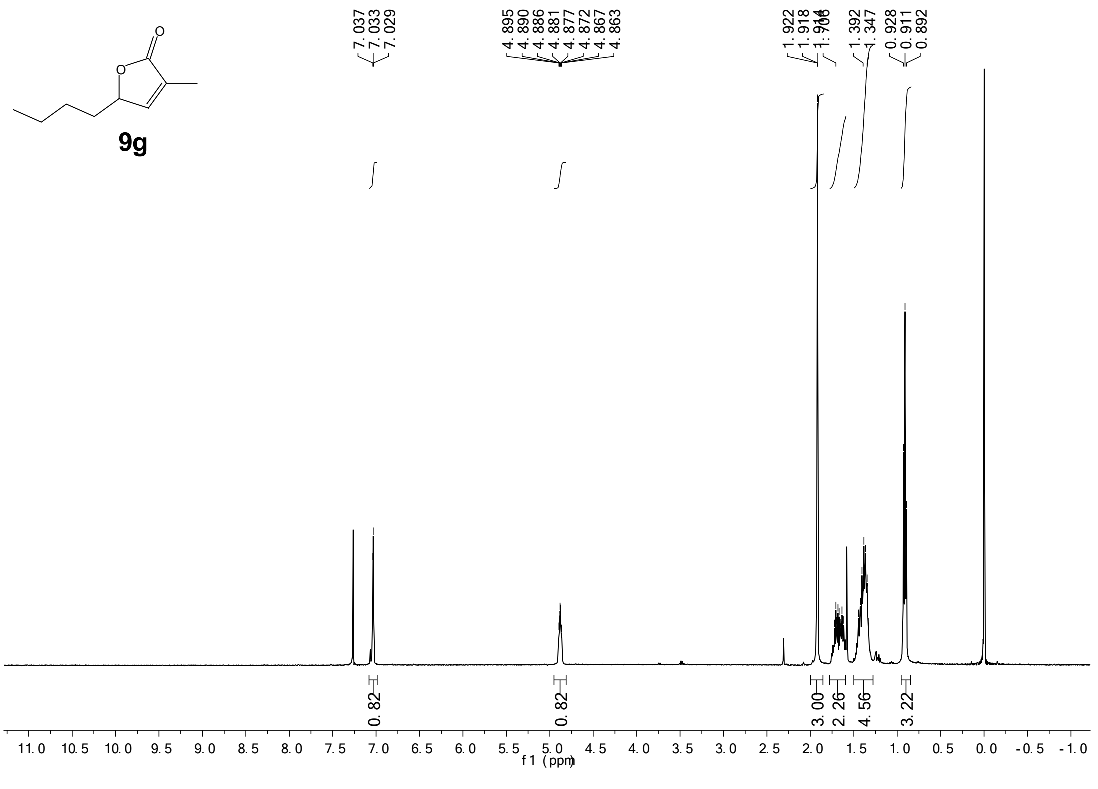


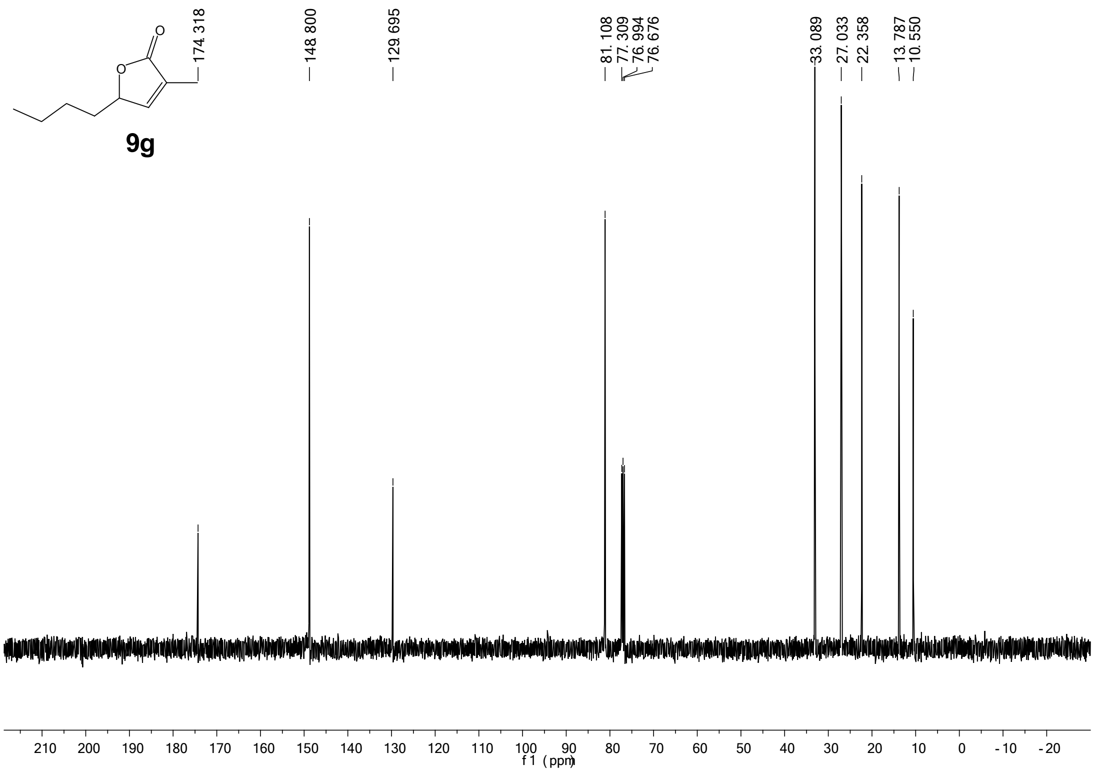
(*R*)-**9f**, 90% ee from 10 mol% Q-**7** catalyzed reaction.



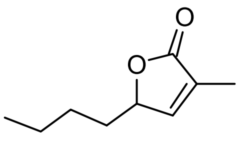
```
.e C:\Chem32\1\DATA\WUYW\WUYW-III-63-1H-1.D
 Name: wuyw-III-63-1h

=====================================================================
  Operator   : wuyw
  Instrument : Instrument 1                     Location :   -
:ction Date  : 5/21/2010 2:00:44 PM
:od          : C:\CHEM32\1\METHODS\METHOD1.M
: changed    : 5/21/2010 2:14:24 PM by wuyw
               (modified after loading)
:le Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 44bar
```

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

:ed By              :      Signal
:iplier             :      1.0000
:tion               :      1.0000
 Multiplier & Dilution Factor with ISTDs

:al 1: VWD1 A, Wavelength=220 nm

: RetTime Type  Width     Area      Height      Area
   [min]        [min]  mAU   *s   [mAU   ]       %
-|-------|----|-------|----------|----------|--------|
.  10.841 BB    0.3047  599.18768   31.94685   5.0645
:  12.450 BB    0.2967 1.12320e4   581.49786  94.9355

:ls :                  1.18312e4   613.44472
```

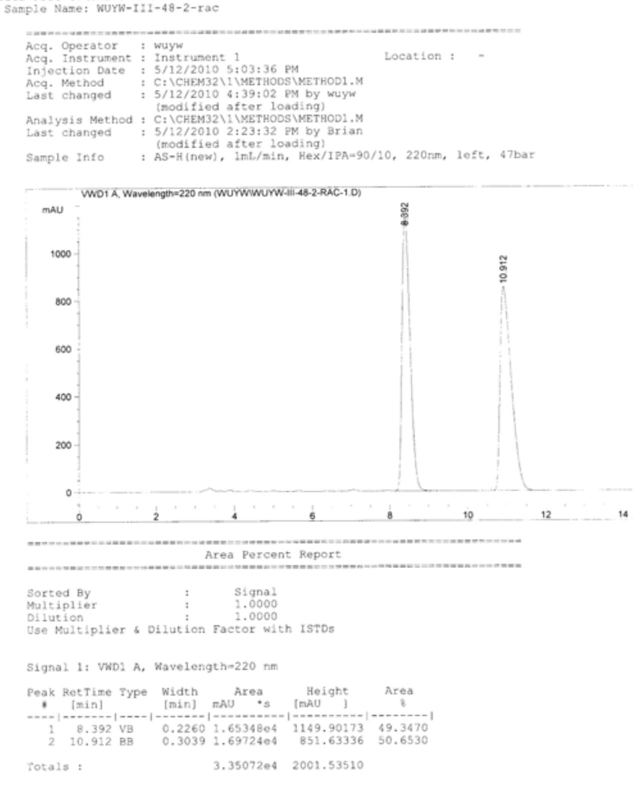




HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 90:10, 1.0 mL/min, λ= 220 nm

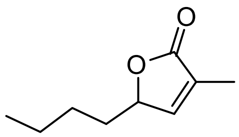


Racemic **9g**

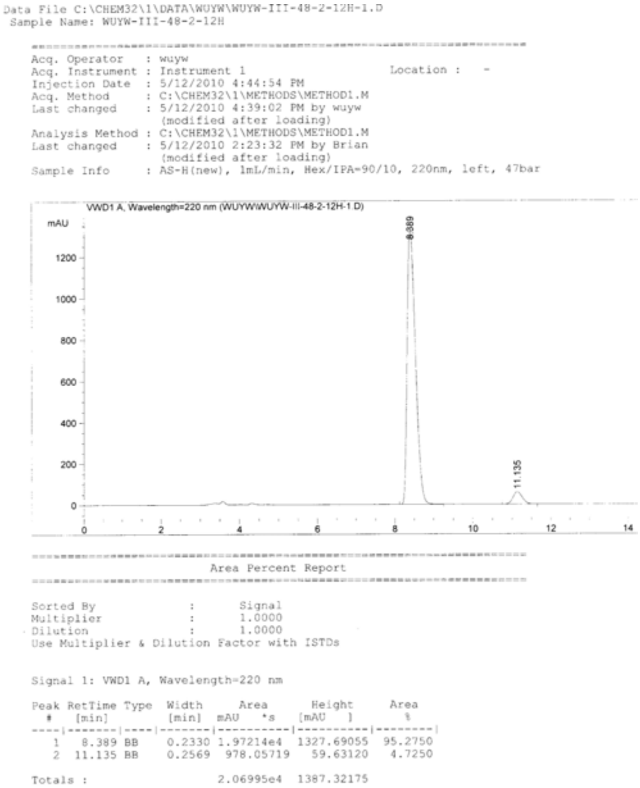


```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-48-2-RAC-1.D
Sample Name: WUYW-III-48-2-rac

=====================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                    Location :  -
Injection Date  : 5/12/2010 5:03:36 PM
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/12/2010 4:39:02 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/12/2010 2:23:32 PM by Brian
                  (modified after loading)
Sample Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 47bar
```

```
=====================================================================
                         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 Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1   8.392 VB    0.2260 1.65348e4 1149.90173 49.3470
  2  10.912 BB    0.3039 1.69724e4  851.63336 50.6530

Totals :                 3.35072e4 2001.53510
```

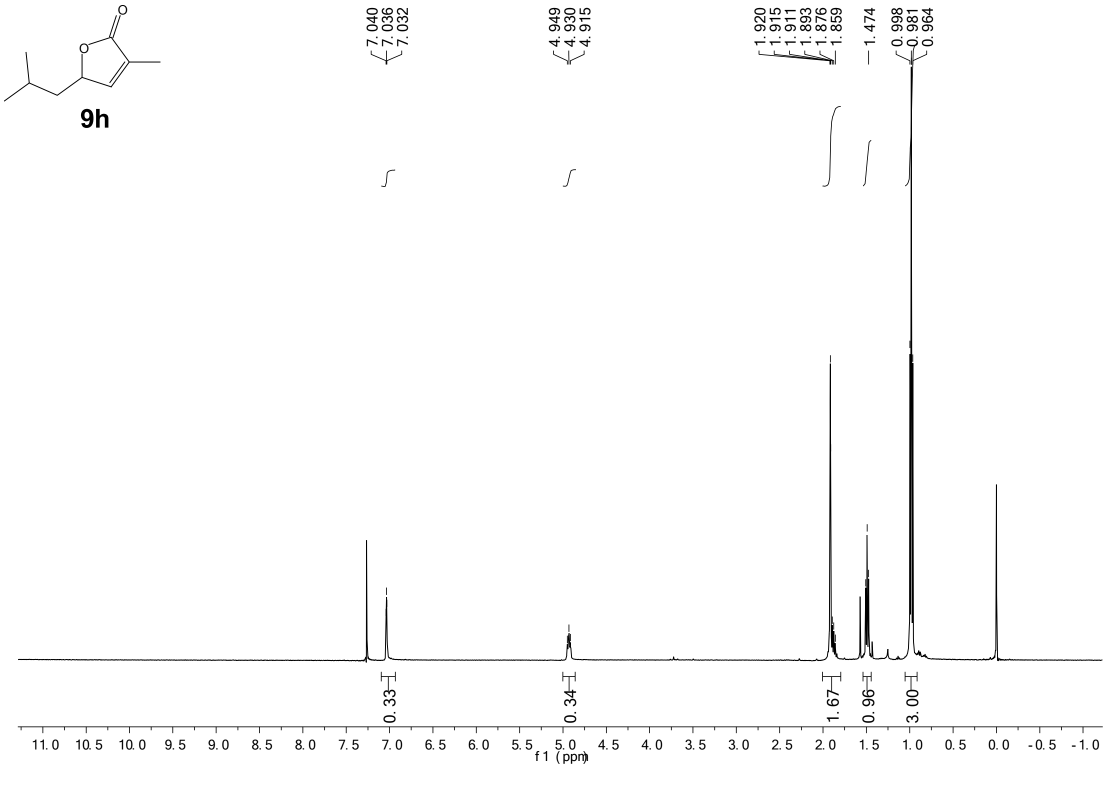


(+)-**9g**, 90% ee from 0.5 mol% QD-**7** catalyzed reaction.

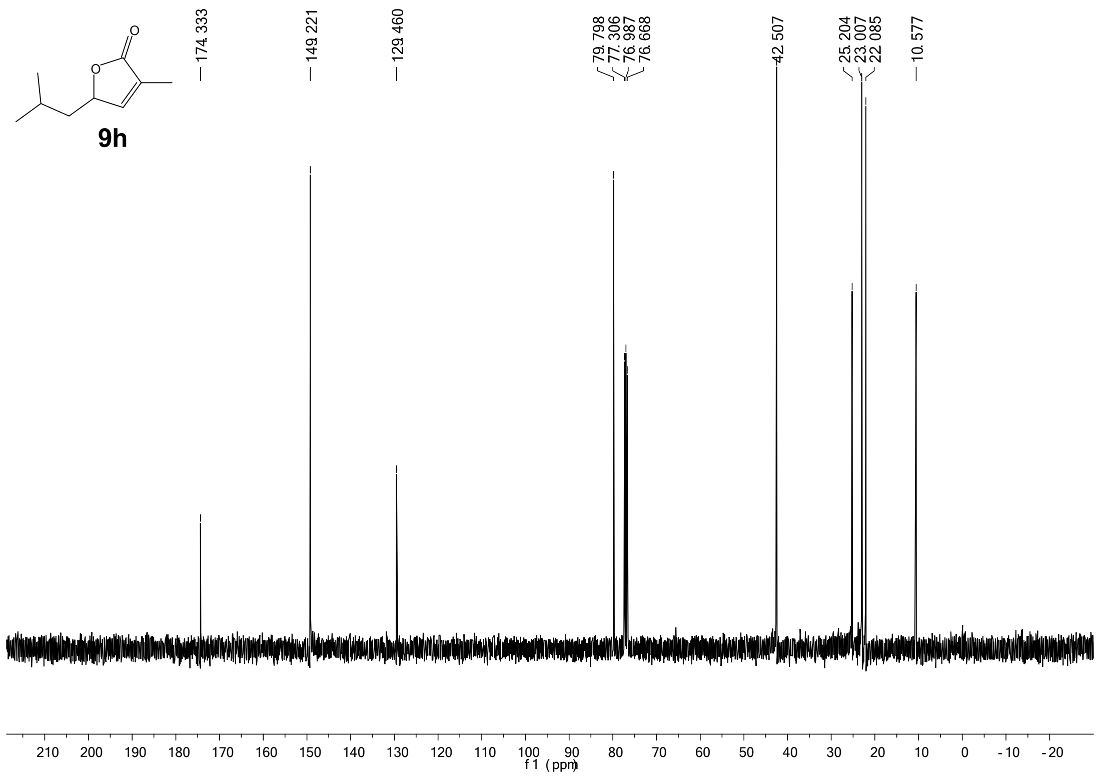


```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-48-2-12H-1.D
 Sample Name: WUYW-III-48-2-12H

    =====================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                     Location :   -
    Injection Date  : 5/12/2010 4:44:54 PM
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/12/2010 4:39:02 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/12/2010 2:23:32 PM by Brian
                      (modified after loading)
    Sample Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 47bar
```

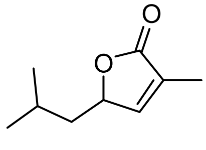
```
=====================================================================
                       Area Percent Report
=====================================================================

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


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.389 BB    0.2330 1.97214e4 1327.69055 95.2750
   2  11.135 BB    0.2569  978.05719   59.63120  4.7250

Totals :                  2.06995e4 1387.32175
```



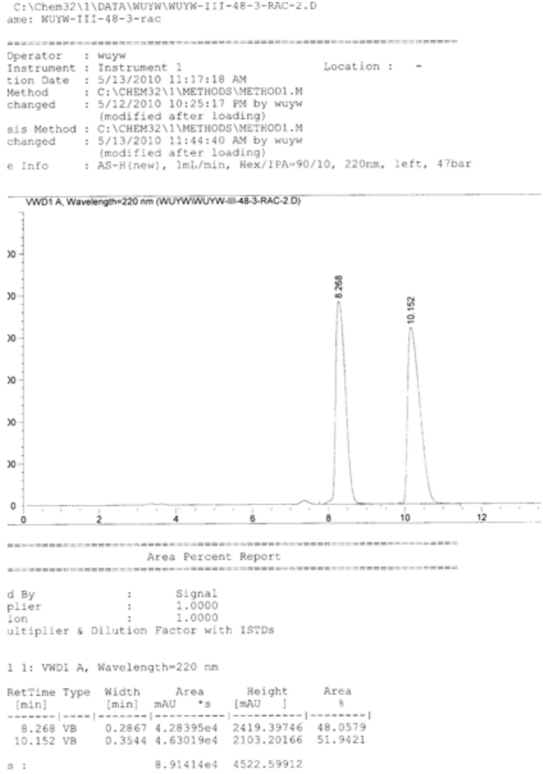
9h



HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 90:10, 1.0 mL/min, λ= 220 nm

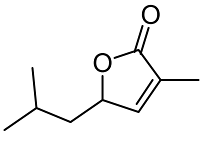


Racemic **9h**

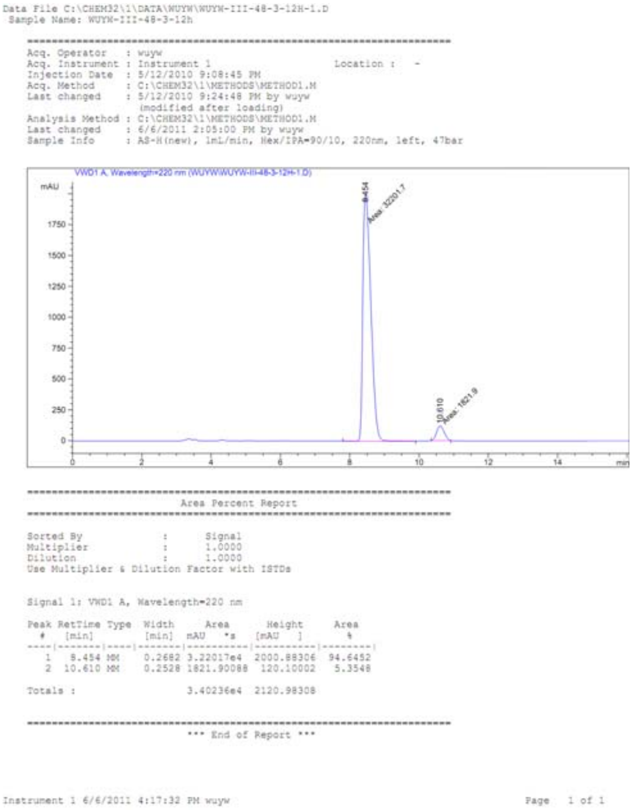


```
 C:\Chem32\1\DATA\WUYW\WUYW-III-48-3-RAC-2.D
ame: WUYW-III-48-3-rac

=====================================================================
Operator   : wuyw
Instrument : Instrument 1                    Location :   -
tion Date  : 5/13/2010 11:17:18 AM
Method     : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/12/2010 10:25:17 PM by wuyw
             (modified after loading)
sis Method : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/13/2010 11:44:40 AM by wuyw
             (modified after loading)
e Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 47bar
```

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

d By               :      Signal
plier              :      1.0000
ion                :      1.0000
ultiplier & Dilution Factor with ISTDs

l 1: VWD1 A, Wavelength=220 nm

RetTime Type  Width     Area      Height     Area
 [min]        [min]  mAU   *s   [mAU   ]      %
-------|----|-------|----------|----------|--------|
  8.268 VB    0.2867 4.28395e4  2419.39746  48.0579
 10.152 VB    0.3544 4.63019e4  2103.20166  51.9421

s :                  8.91414e4  4522.59912
```



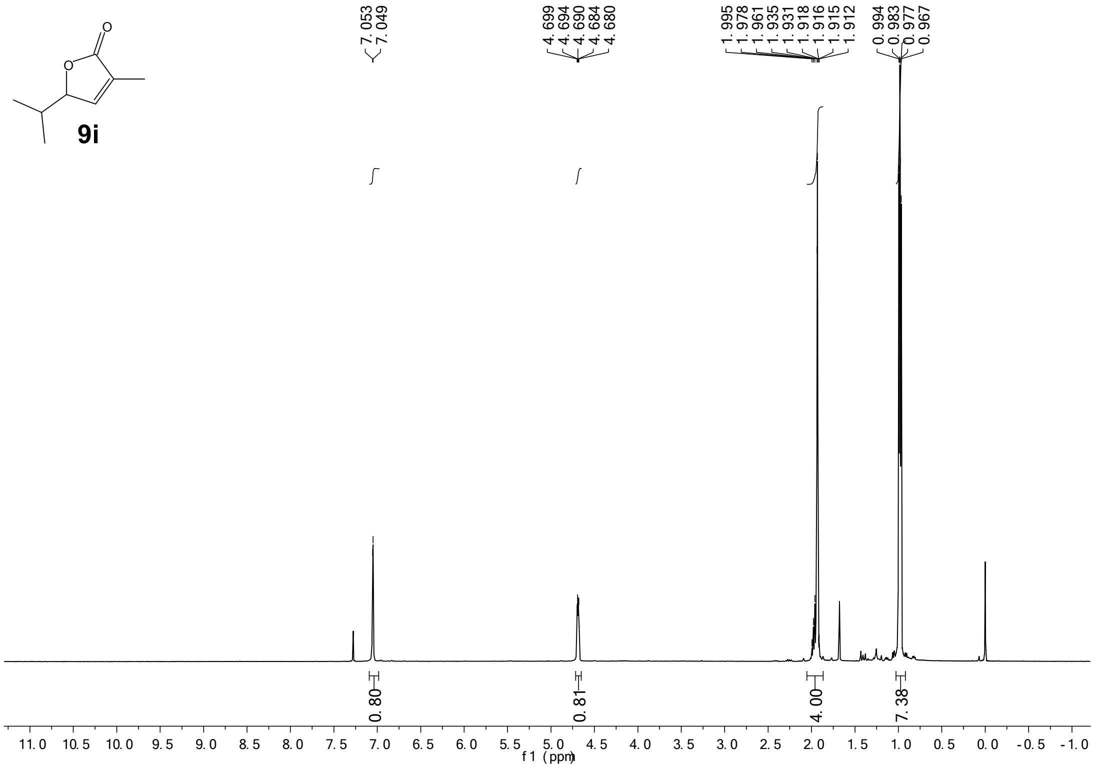
(+)-**9h**, 90% ee from 0.5 mol% QD-**7** catalyzed reaction.



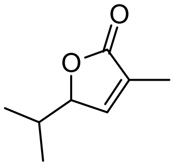
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-48-3-12H-1.D
 Sample Name: WUYW-III-48-3-12h

    =====================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 5/12/2010 9:08:45 PM
    Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/12/2010 9:24:48 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 6/6/2011 2:05:00 PM by wuyw
    Sample Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 47bar
```

```
    =====================================================================
                             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 Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   8.454 MM    0.2682 3.22017e4  2000.88306  94.6452
       2  10.610 MM    0.2528 1821.90088  120.10002   5.3548

    Totals :                  3.40236e4  2120.98308

    =====================================================================
                             *** End of Report ***


Instrument 1 6/6/2011 4:17:32 PM wuyw                                Page  1 of 1
```

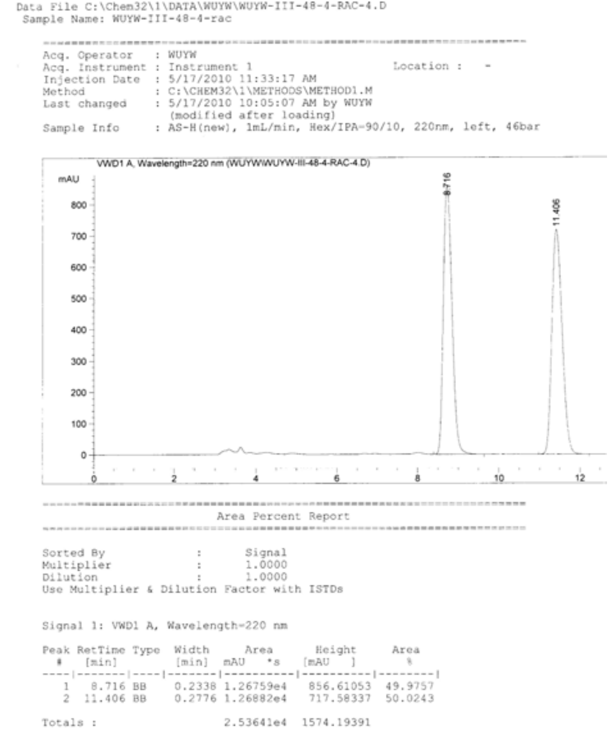
9i



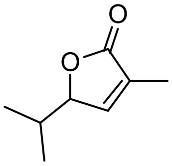
HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 90:10, 1.0 mL/min, λ= 220 nm



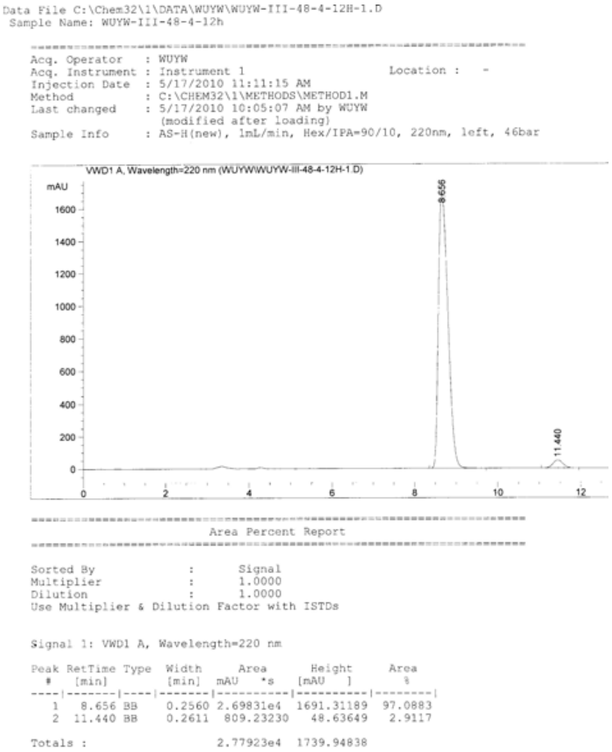
Racemic **9i**



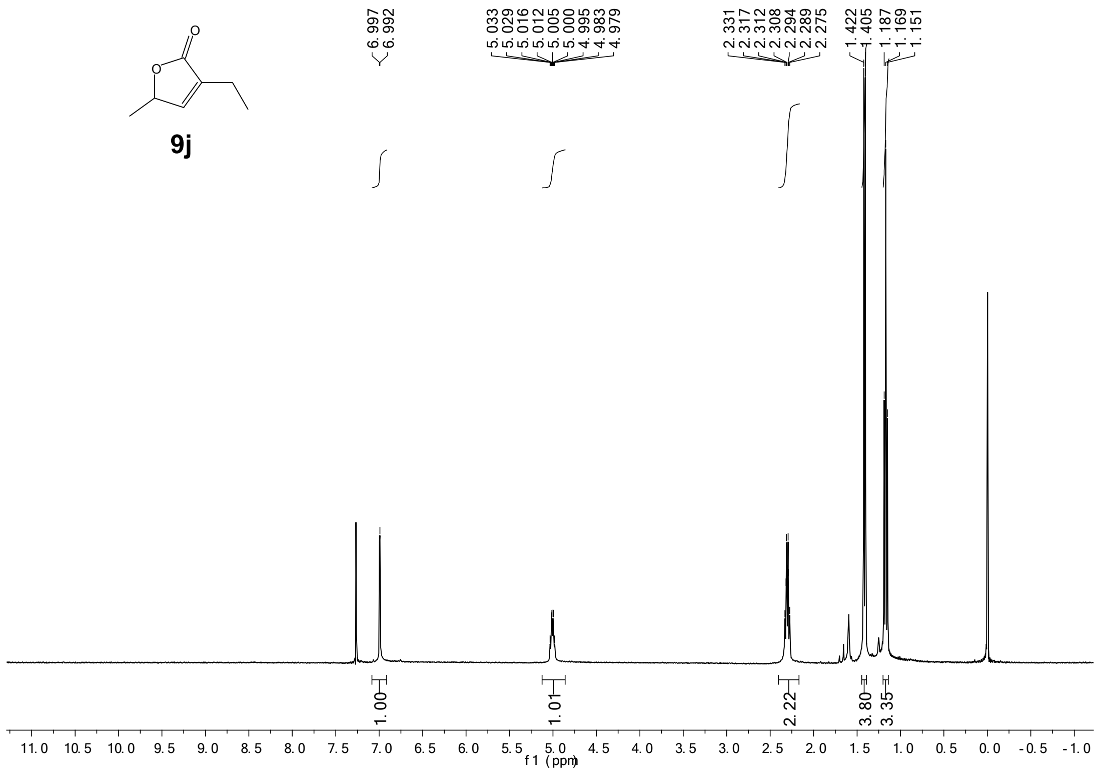
```
Data File C:\Chem32\1\DATA\WUYW\WUYW-III-48-4-RAC-4.D
 Sample Name: WUYW-III-48-4-rac

    =====================================================================
    Acq. Operator   : WUYW
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 5/17/2010 11:33:17 AM
    Method          : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/17/2010 10:05:07 AM by WUYW
                      (modified after loading)
    Sample Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 46bar

    =====================================================================
                              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 Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   8.716 BB    0.2338 1.26759e4  856.61053 49.9757
       2  11.406 BB    0.2776 1.26882e4  717.58337 50.0243

    Totals :                  2.53641e4 1574.19391
```



(+)-**9i**, 94% ee from
0.5 mol% QD-**7**
catalyzed reaction.

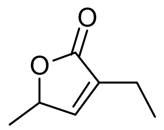


```
Data File C:\Chem32\1\DATA\WUYW\WUYW-III-48-4-12H-1.D
 Sample Name: WUYW-III-48-4-12h

    =====================================================================
    Acq. Operator   : WUYW
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 5/17/2010 11:11:15 AM
    Method          : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/17/2010 10:05:07 AM by WUYW
                      (modified after loading)
    Sample Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 46bar

    =====================================================================
                              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 Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1   8.656 BB    0.2560 2.69831e4 1691.31189 97.0883
       2  11.440 BB    0.2611  809.23230   48.63649  2.9117

    Totals :                  2.77923e4 1739.94838
```

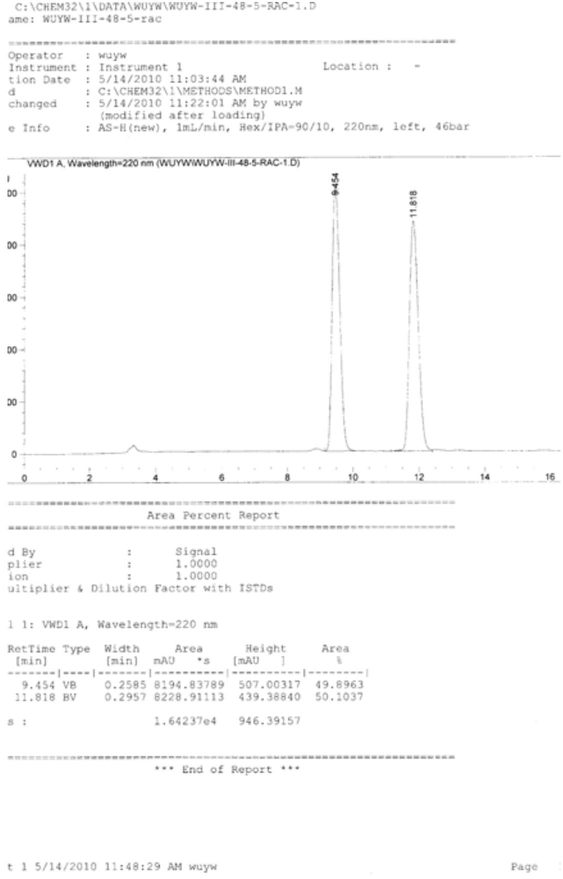


9j

HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 90:10, 1.0 mL/min, λ= 220 nm

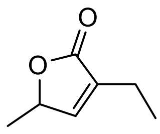


Racemic **9j**

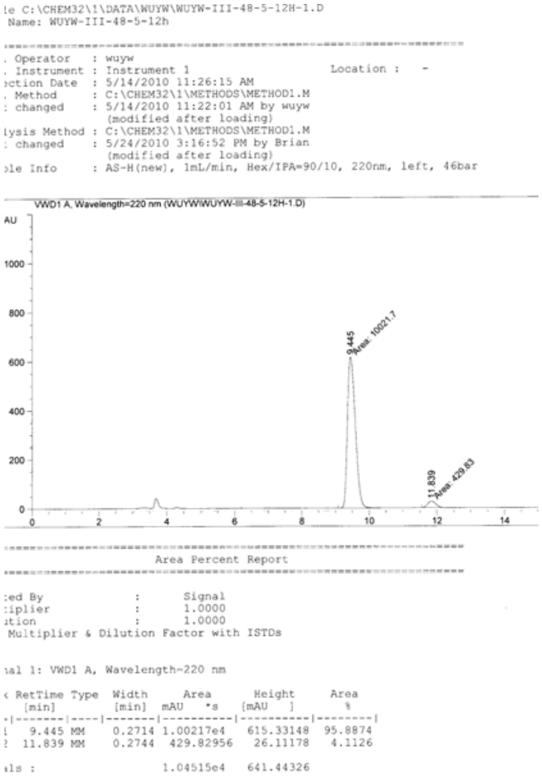


```
 C:\CHEM32\1\DATA\WUYW\WUYW-III-48-5-RAC-1.D
ame: WUYW-III-48-5-rac

=====================================================================
Operator   : wuyw
Instrument : Instrument 1                      Location :   -
tion Date  : 5/14/2010 11:03:44 AM
d          : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/14/2010 11:22:01 AM by wuyw
             (modified after loading)
e Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 46bar
```

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

d By                :      Signal
plier               :      1.0000
ion                 :      1.0000
ultiplier & Dilution Factor with ISTDs


1 1: VWD1 A, Wavelength=220 nm

RetTime Type  Width     Area      Height     Area
 [min]        [min]  mAU    *s   [mAU   ]     %
-------|----|-------|----------|----------|--------|
  9.454 VB    0.2585 8194.83789  507.00317  49.8963
 11.818 BV    0.2957 8228.91113  439.38840  50.1037

s :                  1.64237e4   946.39157

=====================================================================
                      *** End of Report ***



t 1 5/14/2010 11:48:29 AM wuyw                                   Page
```

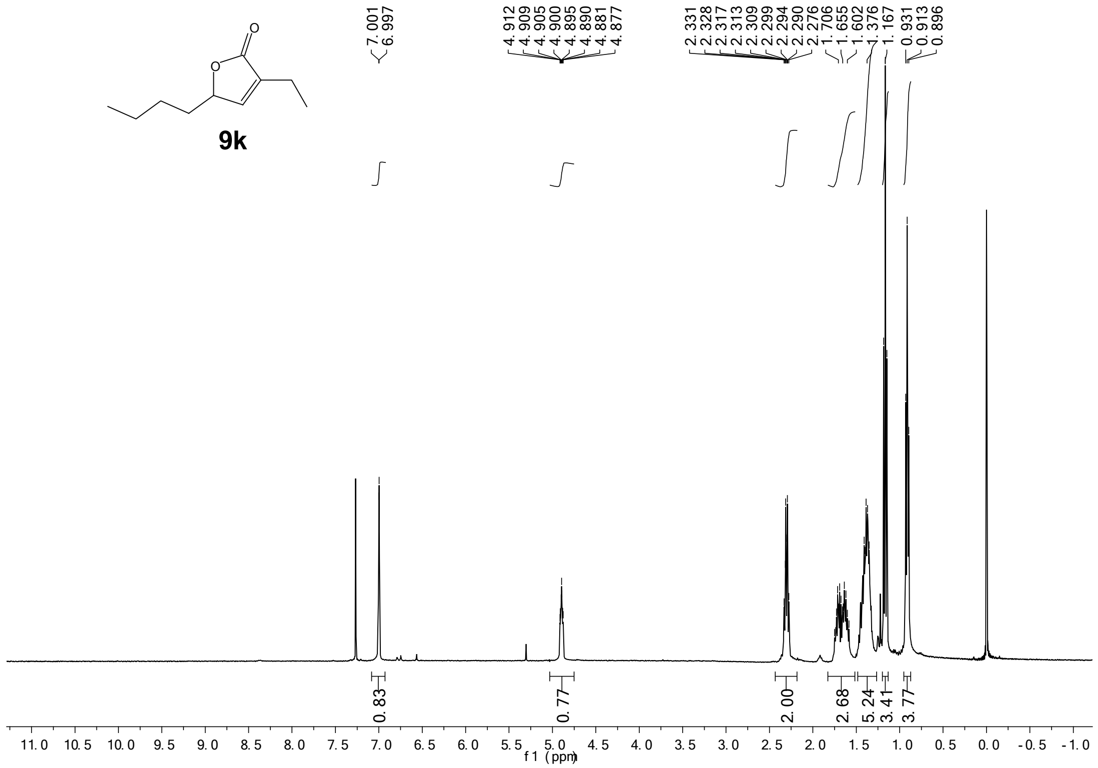


(+)-**9j**, 92% ee from 0.5 mol% QD-**7** catalyzed reaction.

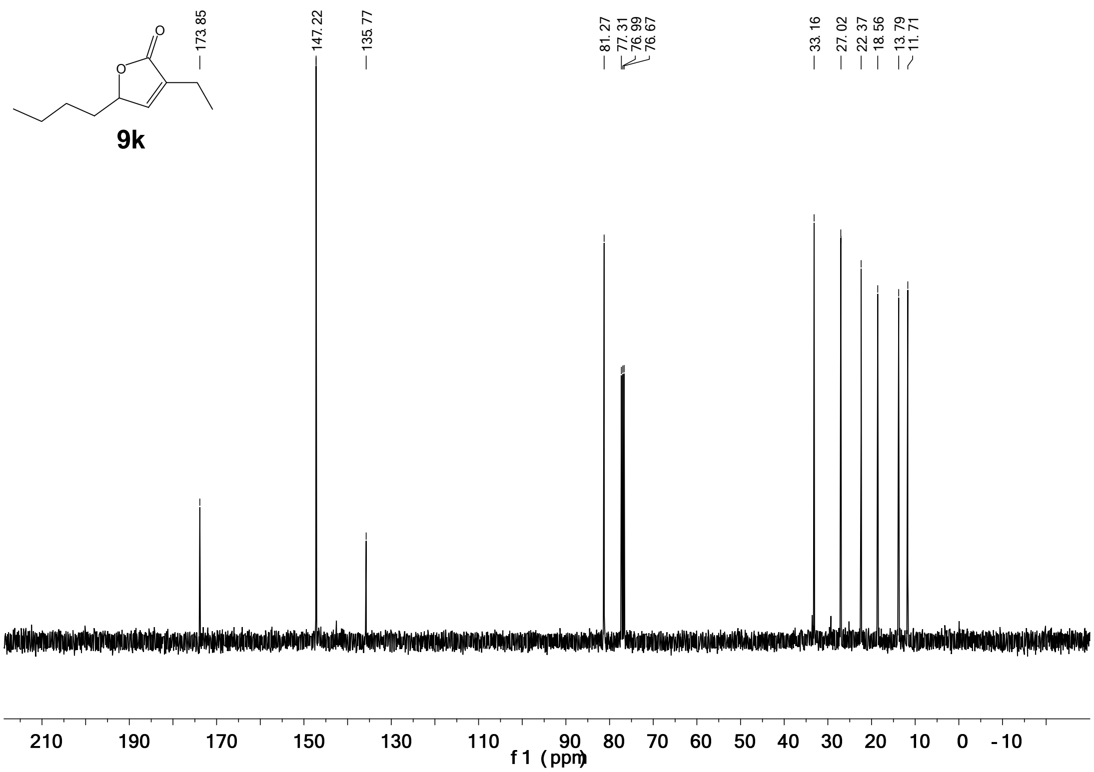


```
le C:\CHEM32\1\DATA\WUYW\WUYW-III-48-5-12H-1.D
 Name: WUYW-III-48-5-12h

=====================================================================
. Operator    : wuyw
. Instrument  : Instrument 1                      Location :   -
ection Date   : 5/14/2010 11:26:15 AM
. Method      : C:\CHEM32\1\METHODS\METHOD1.M
: changed     : 5/14/2010 11:22:01 AM by wuyw
                (modified after loading)
lysis Method  : C:\CHEM32\1\METHODS\METHOD1.M
: changed     : 5/24/2010 3:16:52 PM by Brian
                (modified after loading)
ple Info      : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 46bar
```

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

ted By              :      Signal
tiplier             :      1.0000
ution               :      1.0000
 Multiplier & Dilution Factor with ISTDs

nal 1: VWD1 A, Wavelength=220 nm

k RetTime Type  Width     Area      Height     Area
   [min]        [min]  mAU   *s   [mAU   ]      %
-|-------|----|-------|----------|----------|--------|
1   9.445 MM    0.2714 1.00217e4  615.33148  95.8874
2  11.839 MM    0.2744  429.82956   26.11178   4.1126

als :                  1.04515e4  641.44326
```

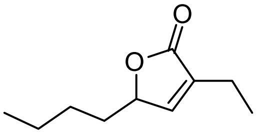


9k

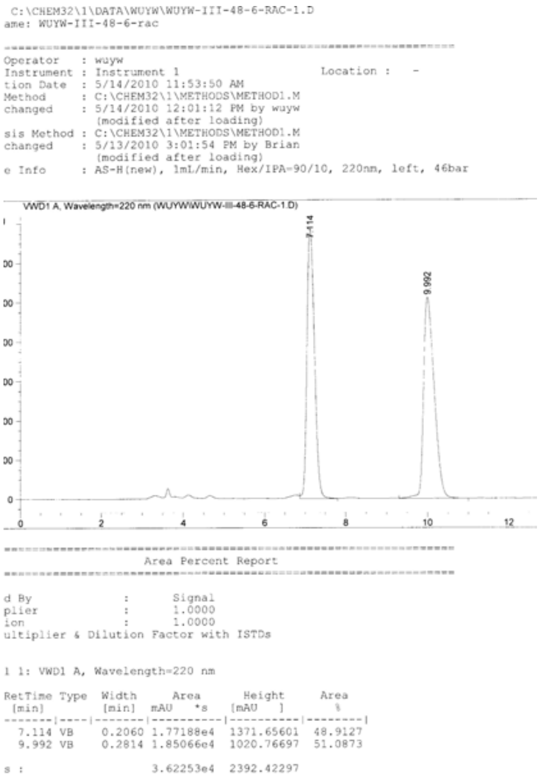


9k

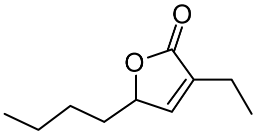
HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 90:10, 1.0 mL/min, λ= 220 nm



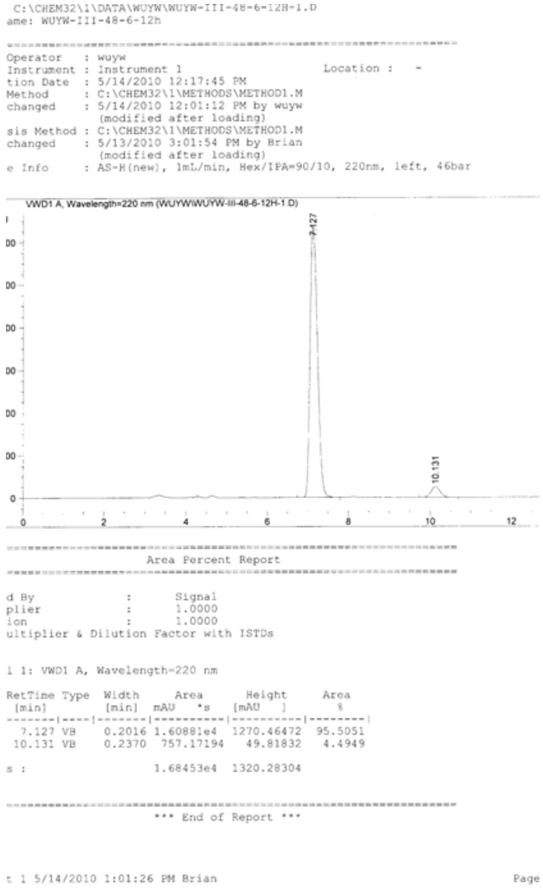
Racemic **9k**


```
 C:\CHEM32\1\DATA\WUYW\WUYW-III-48-6-RAC-1.D
ame: WUYW-III-48-6-rac

==================================================================
Operator   : wuyw
Instrument : Instrument 1                    Location :   -
tion Date  : 5/14/2010 11:53:50 AM
Method     : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/14/2010 12:01:12 PM by wuyw
             (modified after loading)
sis Method : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/13/2010 3:01:54 PM by Brian
             (modified after loading)
e Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 46bar
```

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

d By              :      Signal
plier             :      1.0000
ion               :      1.0000
ultiplier & Dilution Factor with ISTDs


1 1: VWD1 A, Wavelength=220 nm

RetTime Type  Width     Area      Height      Area
 [min]        [min]  mAU    *s   [mAU    ]      %
-------|----|-------|----------|----------|--------|
  7.114 VB    0.2060 1.77188e4  1371.65601  48.9127
  9.992 VB    0.2814 1.85066e4  1020.76697  51.0873

s :                  3.62253e4  2392.42297
```



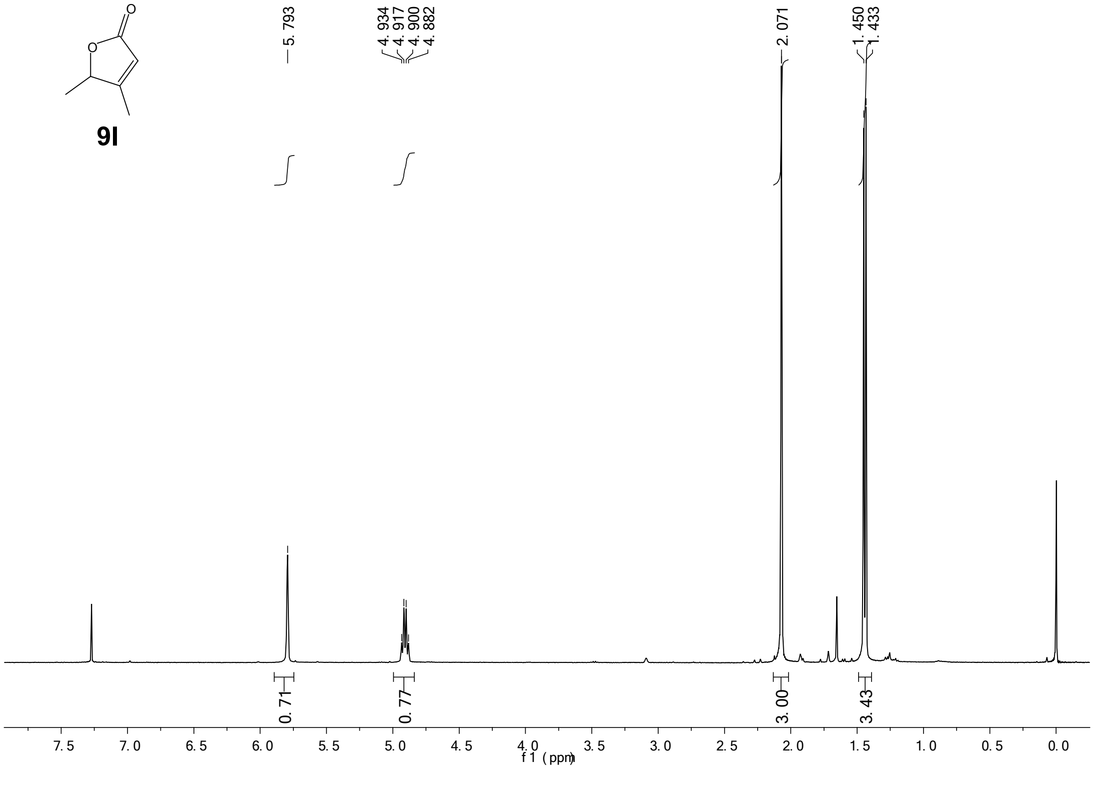
(+)-9k, 91% ee from 0.5 mol% QD-**7** catalyzed reaction.



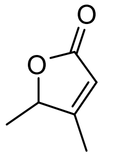
```
 C:\CHEM32\1\DATA\WUYW\WUYW-III-48-6-12H-1.D
ame: WUYW-III-48-6-12h

=====================================================================
Operator   : wuyw
Instrument : Instrument 1                        Location :   -
tion Date  : 5/14/2010 12:17:45 PM
Method     : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/14/2010 12:01:12 PM by wuyw
             (modified after loading)
sis Method : C:\CHEM32\1\METHODS\METHOD1.M
changed    : 5/13/2010 3:01:54 PM by Brian
             (modified after loading)
e Info     : AS-H(new), 1mL/min, Hex/IPA=90/10, 220nm, left, 46bar
```

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

d By              :     Signal
plier             :     1.0000
ion               :     1.0000
ultiplier & Dilution Factor with ISTDs


1 1: VWD1 A, Wavelength=220 nm

RetTime Type  Width     Area      Height     Area
 [min]        [min]  mAU   *s   [mAU   ]      %
-------|----|-------|----------|----------|--------|
  7.127 VB    0.2016 1.60881e4  1270.46472  95.5051
 10.131 VB    0.2370  757.17194   49.81832   4.4949

s :                  1.68453e4  1320.28304

=====================================================================
                    *** End of Report ***


t 1 5/14/2010 1:01:26 PM Brian                                      Page
```

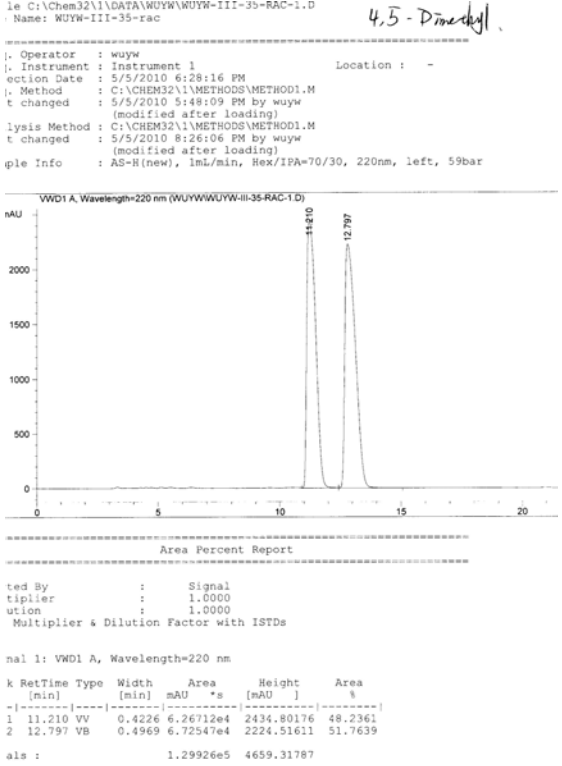
9l



HPLC, Chiralpak AS-H, Hexanes:Isopropanol = 70:30, 1.0 mL/min, λ= 220 nm



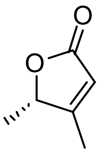
Racemic **9l**



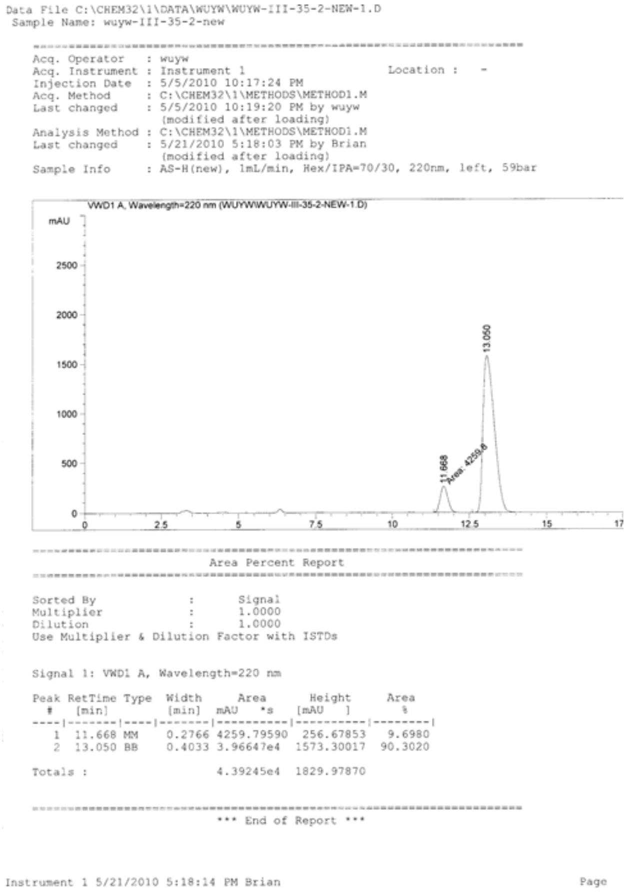
4,5 - Dimethyl .

```
le C:\Chem32\1\DATA\WUYW\WUYW-III-35-RAC-1.D
 Name: WUYW-III-35-rac

==================================================================
|. Operator   : wuyw
|. Instrument : Instrument 1                  Location :   -
ection Date   : 5/5/2010 6:28:16 PM
|. Method     : C:\CHEM32\1\METHODS\METHOD1.M
t changed     : 5/5/2010 5:48:09 PM by wuyw
                (modified after loading)
lysis Method  : C:\CHEM32\1\METHODS\METHOD1.M
t changed     : 5/5/2010 8:26:06 PM by wuyw
                (modified after loading)
ple Info      : AS-H(new), 1mL/min, Hex/IPA=70/30, 220nm, left, 59bar
```

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

ted By               :      Signal
tiplier              :      1.0000
ution                :      1.0000
 Multiplier & Dilution Factor with ISTDs


nal 1: VWD1 A, Wavelength=220 nm

k RetTime Type  Width     Area      Height     Area
  [min]         [min]  mAU   *s    [mAU   ]     %
-|-------|----|-------|----------|----------|--------|
1  11.210 VV    0.4226 6.26712e4  2434.80176  48.2361
2  12.797 VB    0.4969 6.72547e4  2224.51611  51.7639

als :                  1.29926e5  4659.31787
```

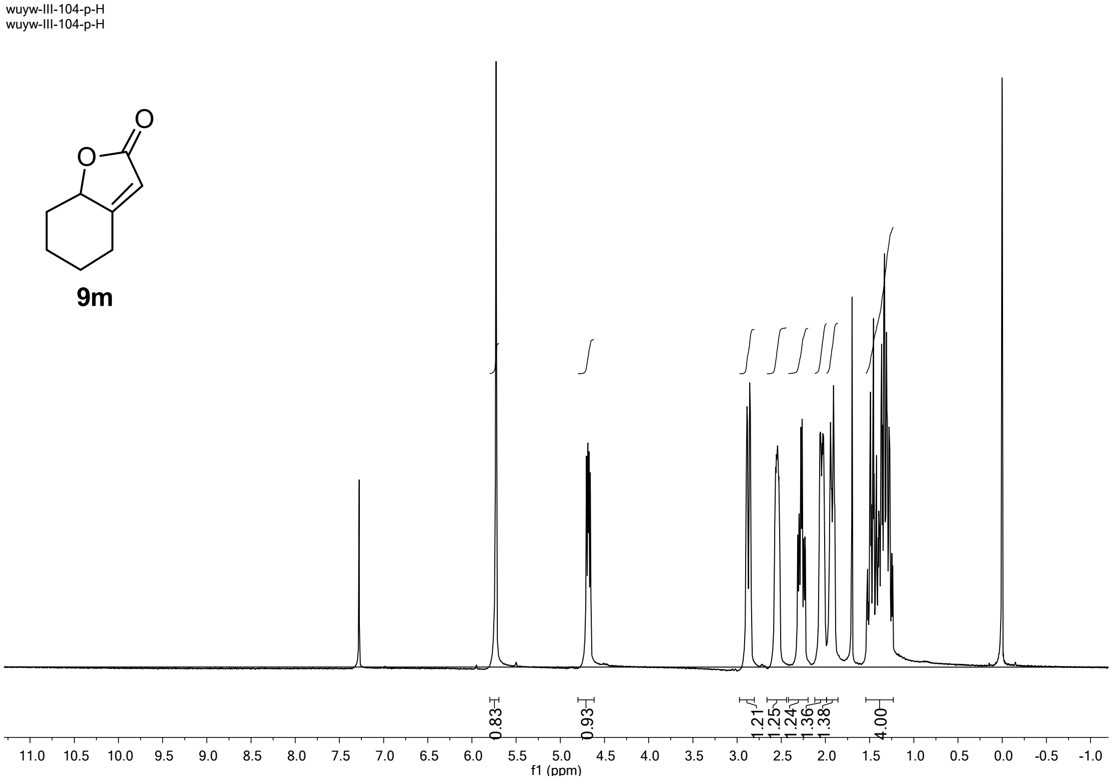


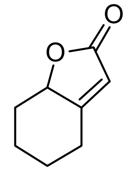
9l, 81% ee from
10 mol% QD-**7**
catalyzed reaction.



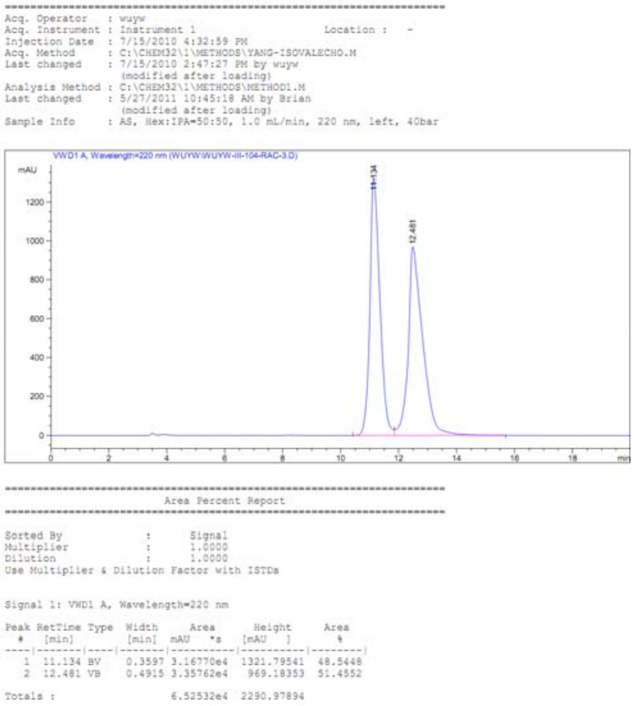
```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-35-2-NEW-1.D
 Sample Name: wuyw-III-35-2-new

==================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                Location :   -
Injection Date  : 5/5/2010 10:17:24 PM
Acq. Method     : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/5/2010 10:19:20 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/21/2010 5:18:03 PM by Brian
                  (modified after loading)
Sample Info     : AS-H(new), 1mL/min, Hex/IPA=70/30, 220nm, left, 59bar
```

```
==================================================================
                     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 Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  11.668 MM    0.2766 4259.79590  256.67853   9.6980
   2  13.050 BB    0.4033 3.96647e4  1573.30017  90.3020

Totals :                  4.39245e4  1829.97870

==================================================================
                     *** End of Report ***



Instrument 1 5/21/2010 5:18:14 PM Brian                        Page
```



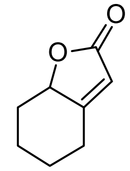


Racemic **9m**

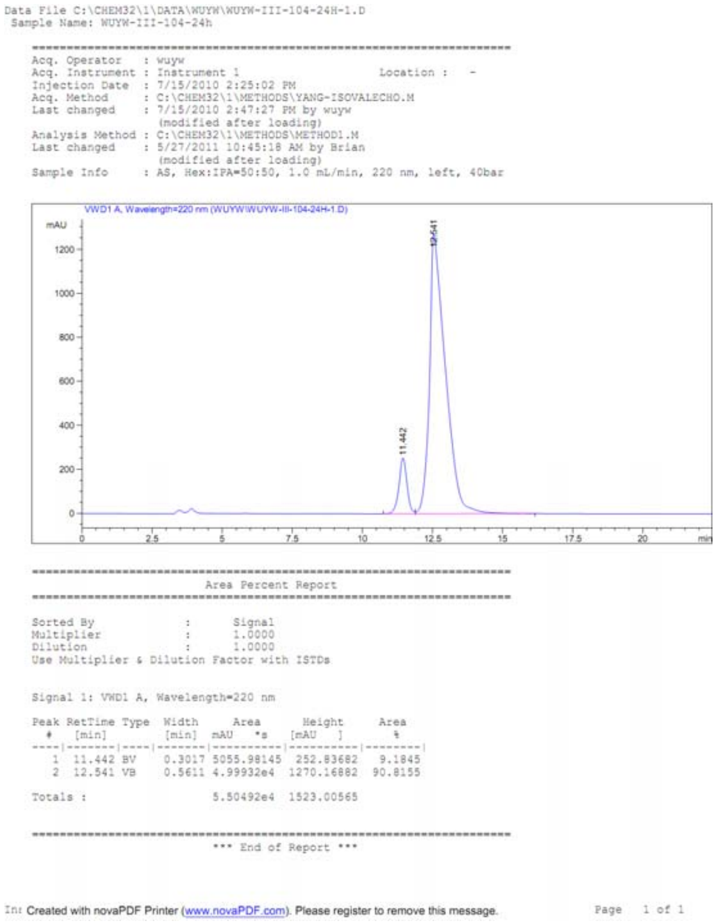


```
=====================================================================
Acq. Operator   : wuyw
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/15/2010 4:32:59 PM
Acq. Method     : C:\CHEM32\1\METHODS\YANG-ISOVALECHO.M
Last changed    : 7/15/2010 2:47:27 PM by wuyw
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
Last changed    : 5/27/2011 10:45:18 AM by Brian
                  (modified after loading)
Sample Info     : AS, Hex:IPA=50:50, 1.0 mL/min, 220 nm, left, 40bar
```

```
=====================================================================
                         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 Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.134 BV    0.3597 3.16770e4 1321.79541 48.5448
   2  12.481 VB    0.4915 3.35762e4  969.18353 51.4552

Totals :                  6.52532e4 2290.97894
```



9m, 82% ee from
10 mol% QD-**7**
catalyzed reaction



```
Data File C:\CHEM32\1\DATA\WUYW\WUYW-III-104-24H-1.D
 Sample Name: WUYW-III-104-24h

    =====================================================================
    Acq. Operator   : wuyw
    Acq. Instrument : Instrument 1                    Location :   -
    Injection Date  : 7/15/2010 2:25:02 PM
    Acq. Method     : C:\CHEM32\1\METHODS\YANG-ISOVALECHO.M
    Last changed    : 7/15/2010 2:47:27 PM by wuyw
                      (modified after loading)
    Analysis Method : C:\CHEM32\1\METHODS\METHOD1.M
    Last changed    : 5/27/2011 10:45:18 AM by Brian
                      (modified after loading)
    Sample Info     : AS, Hex:IPA=50:50, 1.0 mL/min, 220 nm, left, 40bar
```

```
    =====================================================================
                         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 Type  Width     Area      Height     Area
      #   [min]        [min]  mAU   *s   [mAU   ]      %
    ----|-------|----|-------|----------|----------|--------|
       1  11.442 BV    0.3017 5055.98145  252.83682   9.1845
       2  12.541 VB    0.5611 4.99932e4  1270.16882  90.8155

    Totals :                  5.50492e4  1523.00565


    =====================================================================
                          *** End of Report ***
```

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