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Stereocontrolled Creation of Adjacent Quaternary and Tertiary Stereocenters via a Catalytic, Diastereoselective and Enantioselective Conjugate Addition

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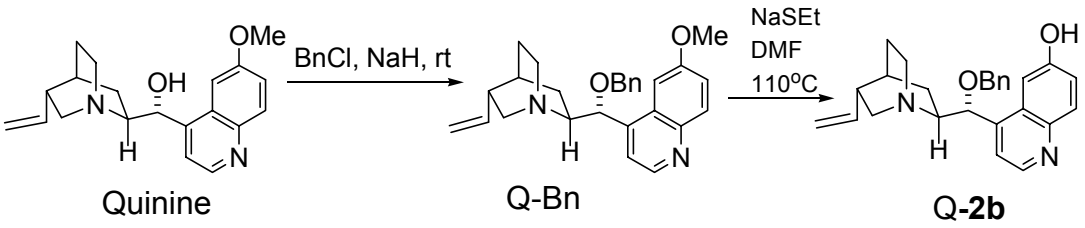
General Information. ^{1}H and ^{13}C NMR spectra were recorded on a Varian instrument (400 MHz and 100 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz), intergration. 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 mass spectra for all the new compounds done by either 20 eV, CH_4/CI or NH_3/CI were recorded on a Hewlett-Packard 5989A GC/MS, and exact mass spectra on a VG 7070 high resolution mass spectrometer. Specific rotations were measured on a Jasco Digital Polarimeter. High pressure liquid chromatography (HPLC) analysis was performed on a Hewlett-Packard 1100 Series instrument equipped with a quaternary pump, using a Daicel Chiralcel OJ, OD Column (250 x 4.6 mm) or Chiralpak AD Column (250 x 4.6 mm). UV detection was monitored at 220 nm or at 215 nm.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-249709(**5Ba**), CCDC-249710(**5Dd**), CCDC-249711(**5De**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ. UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Materials: All the Michael donors **3** are commercially available and used without further purification. Nitroalkenes **4a-c** were purchased from Aldrich Inc. and used without further purifications. Nitroalkenes **4d-f** were prepared according to literature procedures.[1]

Preparatios of catalysts:

1. Preparation of Q-**2b:**

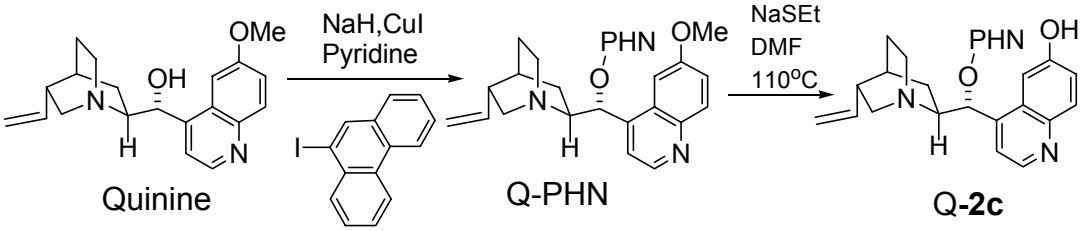


To a solution of Quinine (4.0 g, 12.4 mmol) in DMF (40 mL, freshly distilled from the suspension of CaH_2 in DMF) under nitrogen atmosphere, NaH (1.36 g, 57 % suspension in mineral oil, 32.3 mmol) was added and the resulted mixture was stirred at room temperature for 2 h. Then BnCl (1.56 mL, 13.6 mmol) was added dropwise via a syringe over 10 minutes. The resulting mixture was stirred overnight. After the starting material was completely consumed, brine was added carefully (40 mL) and the resulting mixture was extracted with ethyl acetate (200 mL). The organic phase was washed with H_2O (5 x 100 mL), brine (100 mL) and dried over Na_2SO_4. The solvent was removed in *vacuo* to afford a light yellow oil (5.1 g, 99%). This crude product (Q-Bn) was used for next reaction without further purification.

Under N_2 atmosphere, a suspension of Q-Bn (5.1 g, 12.3 mmol) and NaSEt (4.2g, 50.0 mmol) in dry DMF (75 ml, freshly distilled from the suspension of CaH_2 in DMF) was stirred at 110 °C for 9 hours until a TLC analysis showed that Q-Bn was completely consumed. The reaction mixture was cooled to room temperature, then mixed with sat. NH_4Cl (80 ml) and H_2O (60 ml). The resulting mixture was adjusted to pH = 2 by conc. HCl, washed by ethyl acetate (2×100 mL) and adjusted to pH = 8 by conc. ammonium hydroxide. The resulting mixture was extracted with ethyl acetate (2 × 150 mL). The combined organic phase was dried over Na_2SO_4, and concentrated in *vacuo*. The residue was washed by CH_2Cl_2 (2×30 mL) and dissolved in HCl (2 N, 150 mL). The resulted

solution was washed by ethyl acetate (50 mL) and adjusted to pH = 7 by conc. ammonium hydroxide. The aqueous phase was extracted by ethyl acetate (300 mL). The combined organic phase was dried quickly over Na_2SO_4, and concentrated to afford Q-**2b** as a white powder (3.764g, 77%). $[\alpha]_D^{25}$ = -78.9 (*c*, 0.98 EtOH); ^{1}H NMR (400 MHz, DMSO) 10.03 (br, 1H), 8.63 (d, *J* = 4.4 Hz, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.70-7.15 (m, 8H), 5.92-5.77 (m, 1H), 5.14-4.82 (m, 3H), 4.34 (d, *J* = 11.6 Hz, 1H), 4.27 (d, *J* = 11.6 Hz, 1H), 3.30-2.94 (m , 2H), 2.88-2.70 (m, 1H), 2.50-2.10 (m, 3H), 1.94-1.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 146.6, 144.3, 143.4, 142.3, 138.1, 131.3, 128.2, 127.7, 127.55, 127.49, 121.4, 114.2, 104.7, 70.5, 59.9, 56.0, 54.9, 41.7, 39.4, 27.4, 27.3, 24.6; IR (KBr) ν 3395, 3063, 3033, 2953, 2908, 2863, 2753, 2686, 2613, 2539, 1906, 1638, 1613, 1591, 1509, 1499, 1463, 1401, 1355, 1331, 1280, 1241, 1215, 1132, 1100, 1030, 1014, 921, 853, 814, 751, 702 cm^{-1}; HRMS (ESI) m/z calcd for ($C_{26}H_{29}N_2O_2$+H^+): 401.2229, found: 401.2228.

2. Preparation of Q-**2c**:[2]

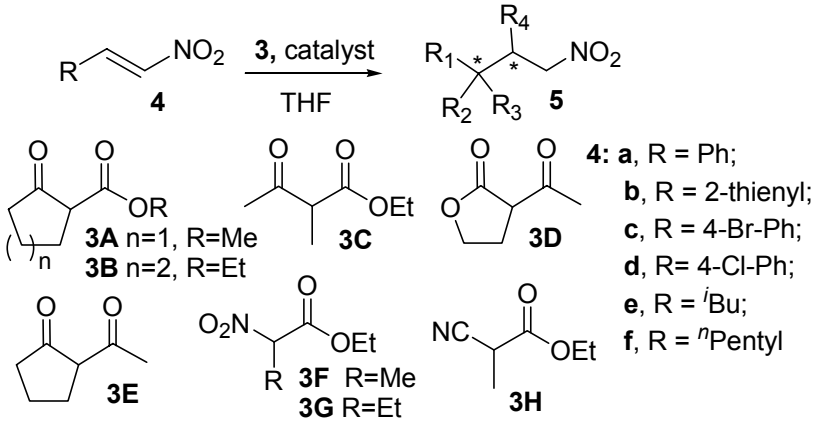


To a three neck round bottom flask (250 mL) charged with quinine (5.0 g) in DMSO (60 ml, freshly distilled from the suspension of CaH_2 in DMSO) was added NaH (0.7g, 60% in mineral oil) in small portion to form an orange solution. Pyridine (2.6 mL), CuI (3.0 g) and 9-I-PHN (4.8 g) were added. The resulting mixture was heated in an oil bath (120 ^oC) for 70 h. The reaction mixture was cooled to room temperature, afterwhich CH_2Cl_2 (40 ml) and H_2O (40 ml) and Et_2O (20 ml) were added. To the resulting reaction mixture, ethylenediaminetetraacetate disodium salt dihydrate (8.5g) and aqueous ammonia solution (6ml) were added. Air was bubbled through to agitate the resulting reaction mixture for 1 h. The brown organic phase was collected and the blue aqueous layer was extracted with CH_2Cl_2 (2 x 20 ml). The combined organic phase was washed with aqueous NH_4OH (5%, 3 x 20 ml,) and the brown solution was dried over Na_2SO_4 and concentrated. The residue was subjected to column

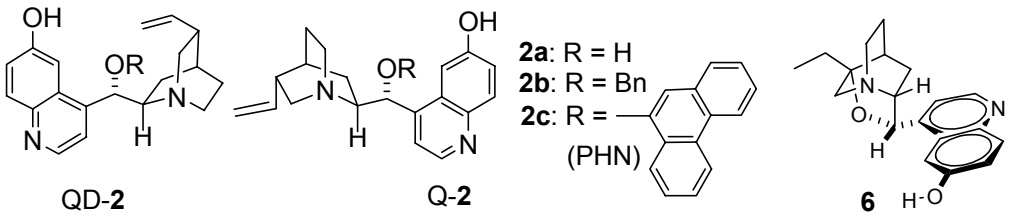
chromatography (SiO_2, CH_2Cl_2 : CH_3OH = 100:1) to funish Q-PHN as a light yellow solid (3.3 g, 43% yield).

To a solution of Q-PHN (3.3g) in DMF (60 ml, freshly distilled from the suspension of CaH_2 in DMF)) was added NaSEt (3g). The resulting mixture was heated at 110°C for 6 hrs and cooled to room temperature. Saturated NH_4Cl solution (40 ml) and water (50 ml) was added sequentially. The resulting mixture was extracted with EtOAc (3 x 200 mL). The combined organic phase was washed with brine (3 x 100 mL), dried over Na_2SO_4, and concentrated. The residue was subjected to column chromatography (SiO_2, CH_2Cl_2 : CH_3OH = 50 :1) to afford Q-**2c** as a yellow solid (1.8 g, 56% yield). $[\alpha]_D^{25}$ = + 371.1 (*c*, 0.64 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) 8.69-8.62 (m, 2H), 8.61 (br, 1H), 8.51 (d, *J* = 5.2 Hz, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.77-7.71 (m, 2H), 7.41 (d, *J* = 4.4 Hz, 1H), 7.29-7.26 (m, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.59 (s, 1H), 6.49 (d, 8.0 Hz, 1H), 6.29 (s, 1H), 5.79-5.70 (m, 1H), 5.30 (s, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.97 (d, *J* = 10.4 Hz, 1H), 3.70-3.62 (m ,1H), 3.49 (t, *J* = 9.2Hz, 1H), 3.33-3.27 (m, 1H), 2.90-2.85 (m, 1H), 2.58-2.53 (m, 1H), 2.47 (br, 1H), 2.60-2.20 (m, 1H), 2.10 (br, 1H), 1.82-1.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.3, 146.8, 143.8, 142.2, 140.6, 131.9, 131.6, 127.4, 127.2, 127.0, 126.7, 126.5, 126.1, 124.6, 123.4, 122.9, 121.9, 121.8, 117.4, 115.2, 106.5, 105.1, 76.4, 59.3, 56.4, 43.3, 39.3, 27.8, 27.3, 20.4; IR (neat) ν 3500-2500, 3073, 2942, 1688, 1622, 1598, 1510, 1453, 1398, 1309, 1231, 1116 cm^{-1}; HRMS (ESI) m/z calcd. for($C_{33}H_{30}N_2O_2$+H^+): 487.2386, found: 487.2378.

General procedure for asymmetric Michael addition of 3A-H to nitroalkenes 4a-f:



Catalysts



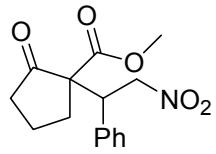
For asymmetric conjugate additions generating **5Aa, 5Ba, 5Bb, 5Bc, 5Ea,** 0.4 mmol of **3A, 3B** and **3E** (2.0 equiv.) and 0.2 mmol of **4a-c** were used; for reactions generating **5Ca,** 0.8 mmol of **3C** (4 equiv.) and 0.2mmol of **4a** were used; for other reactions, 0.2 mmol of **3** and 0.4 mmol of **4** were used. Yields were calculated based on the limiting reagent. The choice of using either a donor or acceptor as the limiting reagent is based on how readily the product (**5**) can be separated from the excessive starting materials (**3** or **4**). Changing the ratio of 3 and 4 has no impact on both the diastereoselectivity and enantioselectivity of the asymmetric conjugate addition.

When catalyst Q-**2b** was used, it is first suspended in THF. The resulting suspension was subjected to ultrasound for 10-15 min. and became a milky mixture. To this solution, the starting materials were added according to the procedure described below.

Procedure: At the temperature specified in tables 1 and 2 to a solution of the limiting reagent (**3** or **4,** 0.2 mmol) and the chiral catalyst (Q-**2,** QD-**2** or **6,** 10-20 mol %.) in THF (0.2 mL) was added the other reagent (**4** or **3,** 2 or 4 eq.). The resulting mixture was kept at the temperature until the limiting reagent is consumed. The reaction mixture was then passed through a plug of silica gel for the removal of the catalyst. The plug of silica gel was eluted with ether or ethyl acetate (2-3 mL). The combined filtrate was concentrated in *vacuo* and the residue was subjected to purification by flash chromatography on silica gel.

Data for the products 5

Q-**2b** (10 mol %) catalyzed reaction was run in THF at -60 °C for 48 h to furnish the crude product [dr = 95:5,

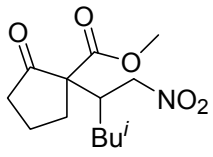


5Aa

determined by integration of one set of ^{1}H NMR signal (δ_{major} 5.16-5.12 ppm, δ_{minor} 5.27-5.21 ppm)]. The crude product was purified by flash chromatography (hexane: ethyl acetate = 12:1) to give adduct **5Aa** as a colorless oil in 94% yield (dr = 95:5) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 80:20, 1.00 mL/min, λ = 220 nm, t (major) = 11.0 min, t (minor) = 17.0 min]. $[\alpha]_D^{25}$ = + 36.5 (*c*, 0.84 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 5H), 5.14 (dd, *J* = 4.0 Hz, 13.6 Hz, 1H), 4.99 (dd, *J* = 11.2 Hz, 2.4 Hz, 1H), 4.05 (dd, *J* = 3.6 Hz, 14.4 Hz, 1H), 3.73 (s, 3H), 2.38-2.28 (m, 2H), 2.04-1.85 (m, 3H), 1.82-1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 169.8, 135.2, 129.2, 128.8, 128.3, 76.4, 62.4, 53.0, 46.1, 37.9, 31.0, 19.3; IR (neat) ν 2957, 1718, 1543, 1496, 1229 cm^{-1}; HRMS (CI) m/z calcd for ($C_{15}H_{17}NO_5$ + H^+): 292.1185, found: 292.1193.

QD-**2c** (10 mol%) catalyzed reaction was run at -60 °C for 48 h to furnish the crude product (dr = 94:6) and was purified by flash chromatography to give adduct **5Aa** in 97% yield (dr = 94:6) and 99% ee (major diasteromer).

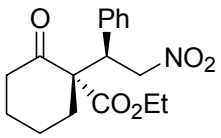
6 (10 mol%) catalyzed reaction was run at -60 °C for 36 h to furnish the crude product (dr = 97:3) and was purified by flash chromatography to give adduct **5Aa** in 97% yield (dr = 97:3) and 98% ee (major diasteromer).



5Ae

Q-**2b** (10 mol %) catalyzed reaction was run in THF at -60 °C for 96 h to furnish the crude product [dr > 98:2, determined by integration of one set of ^{1}H NMR signal (δ_{major} 4.87-4.82 ppm, δ_{minor} 4.55-4.51 ppm, the minor peak can not be detected by ^{1}H NMR)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 15:1) to give adduct **5Ae** as a colorless oil in 87 % yield (dr > 98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 95:5, 0.8 mL/min, λ = 215 nm, t (major) = 11.0 min, t (minor) = 16.6 min]. $[\alpha]_D^{25}$ = + 82.5 (*c*, 0.84 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (dd, *J* = 6.0 Hz, 14.4 Hz, 1H), 4.29 (dd, *J* = 4.4 Hz, 14.4 Hz, 1H), 3.67 (s, 3H), 2.92-2.86 (m, 1H), 2.61-2.55 (m, 1H), 2.46-2.37 (m, 1H), 2.33-2.24 (m, 1H), 2.04-1.88 (m, 3H), 1.56-1.50 (m, 1H), 1.42 (ddd, *J* = 3.6 Hz, 10.4 Hz, 14.0 Hz, 1H), 0.97 (ddd, *J* = 2.4 Hz, 10.4 Hz, 12.8 Hz, 1H), 0.88 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)

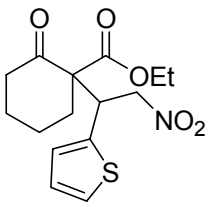
δ 213.2, 169.9, 76.6, 62.9, 52.7, 39.4, 38.4, 38.3, 31.0, 25.6, 23.7, 21.1, 19.4; IR (neat) ν 2959, 1750, 1722, 1557, 1435, 1380, 1230, 1164, 1230 cm^{-1}; HRMS (CI) m/z calcd for ($C_{13}H_{21}NO_5$ + H^+): 272.1498, found: 272.1497.



5Ba

Q-**2a** (10mol %) catalyzed reaction was run in THF at -20 °C for 72 h to furnish the crude product [dr > 98:2, determined by integration of one set of ^{1}H NMR signal (δ_{major} 5.06-5.02 ppm, δ_{minor} 5.17-5.11 ppm, the minor peak can not be detected by ^{1}H NMR)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 10:1) to give adduct **5Ba** as a white solid in 93 % yield (dr > 98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 95:5, 0.9 mL/min, λ = 220 nm, t (major) = 12.3 min, t (minor) = 17.0 min]. $[\alpha]_D^{25}$ = - 91.5 (*c*, 1.02 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.12 (m, 5H), 5.04 (dd, *J* = 3.2 Hz, 13.2 Hz, 1H), 4.77 (dd, *J* = 13.2 Hz, 1.6 Hz, 1H), 4.18 (qd, *J* = 1.6 Hz, 7.2 Hz, 2H), 3.97 (dd, *J* = 3.2 Hz, 10.8 Hz, 1H), 2.52-2.39 (m, 2H), 2.08-1.97 (m, 2H), 1.71-1.55 (m, 3H), 1.48-1.40 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 169.6, 135.3, 129.4, 128.4, 128.1, 77.5, 62.9, 61.9, 47.7, 41.4, 37.0, 27.9, 22.3, 13.9; IR (neat) ν 3032, 2943, 2869, 1712, 1553, 1453, 1378, 1308, 1235 cm^{-1}; HRMS (CI) m/z calcd for ($C_{17}H_{21}NO_5$ + H^+): 320.1498, found: 320.1502.

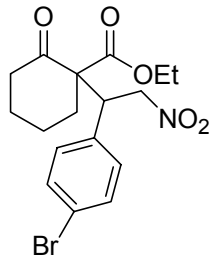
The relative configuration of 5Ba was determined by X-ray crystallography of (-)-5Ba.



5Bb

Q-**2a** (10 mol %) catalyzed reaction was run in THF at -20 °C for 74 h to furnish the crude product [dr > 98:2, determined by integration of one set of ^{1}H NMR signal (δ_{major} 4.88-4.85 ppm, δ_{minor} 5.14-5.08 ppm, the minor peak can not be detected by ^{1}H NMR)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 10:1) to give adduct **5Bb** as a colorless oil in 91 % yield (dr > 98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 95:5, 0.9 mL/min, λ = 220 nm, t (major) = 14.9 min, t (minor) = 24.6 min]. $[\alpha]_D^{25}$ = - 69.0 (*c*, 1.06 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 4.8 Hz, 1H), 6.89-6.85 (m, 2H), 4.86 (dd, *J* = 3.2 Hz, 13.6 Hz, 1H), 4.77 (dd, *J* = 10.4 Hz, 1H), 4.31 (dd, *J* = 4.0 Hz, 10.4 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 2.52 (m, 2H), 2.32-2.28 (m, 1H), 2.01-

1.97 (m, 1H), 1.79-1.77 (m, 1H), 1.69-1.56 (m, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 169.6, 137.7, 128.4, 126.5, 126.1, 78.7, 63.7, 62.1, 43.3, 41.0, 36.1, 27.5, 22.1, 13.9; IR (neat) ν 2942, 1718, 1702, 1559, 1543, 1524, 1437, 1376, 1232 cm^{-1}; HRMS (CI) m/z calcd for ($C_{15}H_{19}NO_5S$ + H^+): 326.1055, found: 326.1058.

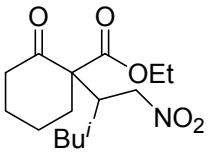


5Bc

Q**-2a** (10 mol %) catalyzed reaction was run in THF at -20 °C for 74 h to furnish the crude product [dr > 98:2, determined by integration of one set of ^{1}H NMR signal (δ_{major} 5.01-4.97 ppm, δ_{minor} 5.16-5.10 ppm, the minor peak can not be detected by ^{1}H NMR)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 12:1) to give adduct **5Bc** as a colorless oil in 95 % yield (dr > 98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 90:10, 0.8 mL/min, λ = 220 nm, t (major) = 11.4 min, t (minor) = 18.6 min]. $[\alpha]_D^{25}$ = - 74.1 (*c*, 0.56 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 4.98 (dd, *J* = 3.2 Hz, 14.0 Hz, 1H), 4.71 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 4.21-4.13 (m, 2H), 3.92 (dd, *J* = 3.2 Hz, 11.6 Hz, 1H), 2.50-2.39 (m, 2H), 2.10-2.05 (m, 1H), 2.02-1.96 (m, 1H), 1.72-1.65 (m, 1H), 1.63-1.50 (m, 2H), 1.46-1.39 (m, 1H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 169.5, 134.5, 131.5, 131.2, 122.3, 76.7, 62.7, 62.0, 47.2, 41.3, 37.0, 27.7, 22.3, 13.9; IR (neat) ν 2942, 1716, 1557, 1490, 1436, 1377, 1307, 1234, 1198, 1012 cm^{-1}; HRMS (CI) m/z calcd for ($C_{17}H_{20}BrNO_5$ + H^+): 398.0603, found: 398.0604.

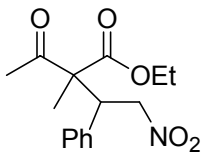
QD**-2a** (10 mol%) catalyzed reaction was run at -20 °C for 72 h to furnish the crude product (dr > 98:2) and was purified by flash chromatography to give adduct **5Bc** in 96% yield (dr > 98:2) and 99% ee (major diasteromer).

6 (10 mol%) catalyzed reaction was run at -20 °C for 60 h to furnish the crude product (dr > 98:2) and was purified by flash chromatography to give adduct **5Bc** in 97% yield (dr > 98:2) and 98% ee (major diasteromer).



5Be

Q-**2c** (10 mol %) catalyzed reaction was run in THF at 23 °C for 96 h to furnish the crude product [dr > 98:2, determined by integration of one set of ^{1}H NMR signal (δ_{major} 4.55-4.50 ppm, δ_{minor} 4.62-4.57 ppm, the minor peak can not be detected by ^{1}H NMR)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 20:1) to give to give adduct **5Be** as a colorless oil in 83 % yield (dr >98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 90:10, 0.8 mL/min, λ = 215 nm, t (major) = 11.0 min, t (minor) = 19.2 min]. $[\alpha]_D^{25}$ = - 33.7 (*c*, 0.92 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (dd, *J* = 4.8 Hz, 14.0 Hz, 1H), 4.30 (dd, *J* = 4.8 Hz, 14.8 Hz, 1H), 4.22 (ddd, *J* = 2.4 Hz, 7.2 Hz, 14.0 Hz, 2H), 2.94 (m, 1H), 2.59 (m, 3H), 2.03 (m, 1H), 1.83 (m, 1H), 1.70-1.61(m, 3H), 1.58-1.51 (m, 1H), 1.43 (ddd, *J* = 4.0 Hz, 10.4 Hz, 14.0 Hz, 1H), 1.30 (t, *J* = 1.30 Hz, 3H), 1.16 (ddd, *J* = 2.4 Hz, 9.6 Hz, 13.6 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 170.9, 77.9, 64.4, 61.8, 41.1, 39.9, 38.8, 33.9, 27.1, 25.9, 23.7, 22.2, 21.2, 14.0; IR (neat) ν 2957, 2896, 1713, 1554, 1465, 1439, 1379, 1235, 1208, 1137, 1020 cm^{-1}; HRMS (CI) m/z calcd for ($C_{15}H_{25}NO_5$ + H^+): 300.1811, found: 300.1811.

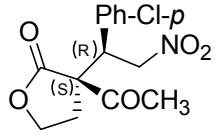


5Ca

Q-**2c** (15 mol %) catalyzed reaction was run in THF at -20 °C for 63 h to furnish the crude product [dr = 91:9, determined by integration of one set of ^{1}H NMR signal (δ_{major} 2.17 ppm, δ_{minor} 2.12 ppm)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 13:1) to give to give adduct **5Ca** as a colorless oil in 73 % yield (pure diastereomer) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 90:10, 0.9 mL/min, λ = 220 nm, t (major) = 10.3 min, t (minor) = 26.6 min]. $[\alpha]_D^{25}$ = - 69.9 (*c*, 0.93 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.27 (m, 3H0, 7.14-7.12 (m, 2H), 4.97 (dd, *J* = 10.4 Hz, 13.2 Hz, 1H), 4.89 (dd, *J* = 3.6 Hz, 13.2Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.14 (dd, *J* = 4.0 Hz, 10.4 Hz, 1H), 2.17 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 171.2, 135.3, 128.9, 128.7, 128.3, 77.5, 62.4, 62.1, 47.7, 26.4, 20.0, 13.9; IR (neat) ν 2986, 1717, 1557, 1457, 1378, 1236 cm^{-1}; HRMS (CI) m/z calcd for ($C_{15}H_{19}NO_5$ + H^+): 294.1341, found: 294.1343.

QD-**2c** (10 mol%) catalyzed reaction was run at -20 °C for 60 h to furnish the crude product (dr = 82:18) and was purified by flash chromatography to give adduct **5Ca** in 70 % yield (pure diastereomer) and 99 % ee (major diastereomer).

6 (10 mol%) catalyzed reaction was run at -20 °C for 64 h to furnish the crude product (dr = 89:11) and was purified by flash chromatography to give adduct **5Ca** in 75% yield (pure diastereomer) and 96% ee (major diastereomer).



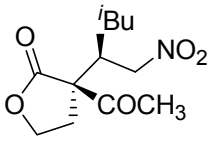
(-)-5Dd

Q-**2b** (10 mol %) catalyzed reaction was run in THF at -60 °C for 44 h to furnish the crude product [dr = 98:2, determined by integration of one set of ^{1}H NMR signal (δ_{major} 2.31 ppm, δ_{minor} 2.43 ppm)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 6:1) to give to give adduct **(-)-5Dd** as a white solid in 87 % yield (dr = 98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 60:40, 1.0 mL/min, λ = 220 nm, t (major) = 10.3 min, t (minor) = 20.0 min]. $[\alpha]_D^{25}$ = - 23.5 (*c*, 1.18 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dt, *J* = 8.4 Hz, 1.6 Hz, 2H), 7.20 (dt, *J* = 8.8 Hz, 1.6 Hz, 2H), 5.00 (dd, *J* = 11.6 Hz, 13.6 Hz, 1H), 4.70 (dd, *J* = 3.2 Hz, 13.6 Hz, 1H), 4.29 (dd, *J* = 3.2 Hz, 11.6 Hz, 1H), 4.10 (dt, *J* = 6.0 Hz, 9.2 Hz, 1H), 3.47 (dt, *J* = 6.0 Hz, 9.2 Hz, 1H), 2.55 (ddd, *J* = 6.0 Hz, 8.8 Hz, 14.0 Hz, 1H), 2.31 (s, 3H), 2.20 (ddd, *J* = 6.0 Hz, 8.8 Hz, 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 175.0, 135.2, 132.7, 130.0, 129.6, 76.2, 66.2, 62.8, 45.6, 29.8, 26.5 ; IR (neat) ν 2994, 2923, 1755, 1716, 1555, 1494, 1434, 1417, 1378, 1175 cm^{-1}; HRMS (CI) m/z calcd for ($C_{14}H_{14}ClNO_5$ + H^+): 312.0639, found: 312.0630.

The absolute configuration of (-)-5Dd was determined by X-ray crystallography of (-) -5Dd.

QD-**2c** (10 mol%) catalyzed reaction was run at -60 °C for 40 h to furnish the crude product (dr = 97:3) and was purified by flash chromatography to give adduct **(+)-5Dd** in 92% yield (dr = 97:3) and 98 % ee (major diastereomer).

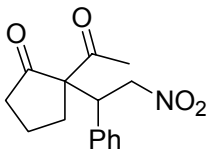
6 (10 mol%) catalyzed reaction was run at -60 °C for 36 h to furnish the crude product (dr = 97:3) and was purified by flash chromatography to give adduct **(+)-5Dd** in 92% yield (dr = 97:3) and 98% ee (major diastereomer).



5De

Q-**2c** (10 mol %) catalyzed reaction was run in THF at -60 °C for 48 h to furnish the crude product [dr = 42 : 1, determined by integration of one set of ^{1}H NMR signal (δ_{major} 2.37 ppm, δ_{minor} 2.40 ppm)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 10:1) to give adduct **5De** as a white solid in 82 % yield (dr = 98:2) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 90:10, 0.8 mL/min, λ = 215 nm, t (major) = 20.4 min, t (minor) = 51.0 min]. $[\alpha]_D^{25}$ = + 80.9 (*c*, 0.92 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (dd, *J* = 4.4 Hz, 13.6 Hz, 1H), 4.38 (dd, *J* = 6.4 Hz, 1H), 4.33 (dt, *J* = 2.0 Hz, 9.2 Hz, 1H), 4.12, (dt, *J* = 7.6 Hz, 9.6 Hz, 1H), 3.29-3.22 (m, 1H), 2.78 (ddd, *J* = 2.4 Hz, 7.2 Hz, 13.2 Hz, 1H), 2.35 (s, 3H), 1.99(td, *J* = 9.6 Hz, 12.8 Hz, 1H), 1.56-1.50 (m, 1H), 1.26 (ddd, *J* = 4.4 Hz, 11.2 Hz, 14.8 Hz, 1H), 0.96 (ddd, *J* = 2.8 Hz, 10.8 Hz, 14.0 Hz, 1H), 0.89 (d, *J* = 6.0 Hz, 3H), 0.87 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 173.8, 76.7, 66.4, 65.1, 39.0, 37.2, 26.2, 25.4, 25.1, 23.6, 21.1; IR (neat) ν 2958, 2930, 1758, 1715, 1560, 1448, 1380, 1223, 1159, 1022 cm^{-1}; HRMS (CI) m/z calcd for ($C_{12}H_{19}NO_5$ + H^+): 258.1341, found: 258.1341.

The relative configuration of 5De was determined by X-ray crystallography of (+)-5De.

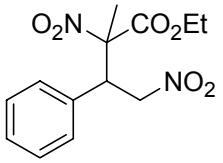


5Ea

Q-**2b** (10 mol %) catalyzed reaction was run in THF at -60 °C for 48 h to furnish the crude product [dr = 86:14, determined by integration of one set of ^{1}H NMR signal (δ_{major} 4.39-4.35 ppm, δ_{minor} 4.28-4.24 ppm)]. Crude product was purified by flash chromatography (hexane: ethyl acetate = 12:1) to give adduct **5Ea** as a white solid (pure diastereomer) in 76 % yield (pure diastereomer) and 99% ee (major diastereomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 80:20, 1.0 mL/min, λ = 220 nm, t (major) = 12.6 min, t (minor) = 53.3 min]. $[\alpha]_D^{25}$ = - 43.3 (*c*, 1.11 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.22 (m, 5H), 4.84 (dd, *J* = 11.6 Hz, 13.2 Hz, 1H), 4.48 (dd, *J* = 4.4 Hz, 14.0 Hz, 1H), 4.36 (dd, *J* = 3.6 Hz, 11.6 Hz, 1H), 2.57-2.51 (m, 1H), 2.30 (s, 3H), 2.21-2.12 (m, 1H), 1.99-1.91 (m, 1H), 1.76-1.64 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.1, 202.7, 134.2, 129.4, 128.8, 128.4, 75.5, 71.1, 46.3, 38.6, 27.2, 26.6, 19.4 ; IR (neat) ν3033, 2971, 1740, 1702, 1554, 1378, 1140 cm^{-1}; HRMS (CI) m/z calcd for ($C_{15}H_{17}NO_4$ + H^+): 276.12136, found: 276.1238.

QD-**2c** (10 mol%) catalyzed reaction was run at -60 °C for 48 h to furnish the crude product (dr = 88:12) and was purified by flash chromatography to give adduct **5Ea** in 70% yield (pure diastereomer) and 98 % ee (major diastereomer).

6 (10 mol%) catalyzed reaction was run at -60 °C for 48 h to furnish the crude product (dr = 90:10) and was purified by flash chromatography to give adduct **5Ea** in 79% yield (pure diastereomer) and 96% ee (major diastereomer).

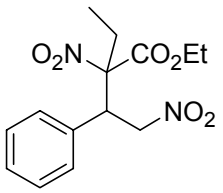


5Fa

Q-**2a** (10 mol%) catalyzed reaction was run in THF at –20 °C for 2.5 days to furnish the crude product [dr = 92:8, determined by ^{1}H NMR peaks at 5.04-5.17 ppm and 4.96-5.00 ppm]. Pure major diastereomer (-)-**5Fa** was obtained by flash chromatography (hexane : ethyl acetate = 15 :1-10:1) as white solid in 78% yield and 92% ee [determined by HPLC, Chiralcel OD, hexane: isopropanol = 80: 20, 1.00 mL/min, λ = 220 nm, t (major) = 7.9 min, t (minor) = 18.8 min]. $[\alpha]_D^{25}$ = -50.2 (*c* 0.93, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.6 Hz, 3H), 1.65 (s, 3H), 4.33 (q, *J* = 6.8 Hz, 2H), 4.41 (dd, *J* = 3.6, 10.4 Hz, 1H), 5.07 (dd, *J* = 10.4, 14.0 Hz, 1H), 5.14 (dd, *J* = 3.6, 14.0 Hz, 1H), 7.12-7.15 (m, 2H), 7.35-7.37 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.74, 21.88, 48.65, 63.80, 77.00, 93.78, 128.88, 128.29, 129.34, 132.39, 166.57; IR (neat) ν 1753, 1561, 1549 cm^{-1}; HRMS (CI/MH^+) Calcd for $C_{13}H_{17}N_2O_6$: 297.1084, found 297.1087.

QD-**2a** (10 mol%) catalyzed reaction was run in THF at –20 °C for 2.5 days to furnish the crude product (dr = 89:11). Major diastereomer (+)-**5Fa** was obtained by flash chromatography as a white solid in 74% yield and 89% ee.

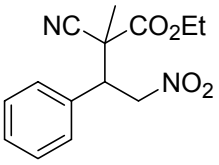
6 (10 mol%) catalyzed reaction was run in THF at –20 °C for 2.5 days to furnish the crude product (dr = 95:5). Major diastereomer (+)-**5Fa** was obtained by flash chromatography as a white solid in 74% yield and 88% ee.



5Ga

Q-**2a** (20 mol%) catalyzed reaction was run in THF at –50 °C for 6 days to furnish crude product [dr = 95:5, determined by ^{1}H NMR peaks at 4.58-4.62 ppm (minor) and 5.17-5.21 ppm (major)]. Pure product was obtained by flash chromatography (hexane : ethyl acetate = 20:1-15:1) as a white solid mixture of two

diastereomers (dr = 95:5) in 77% yield and 96% ee (major isomer) [determined by HPLC, Chiralcel OJ, hexane: isopropanol = 80: 20, 1.00 mL/min, λ = 220 nm, t (major) = 27.3 min, t (minor) = 31.5 min]. After recrystalization in Et_2O, pure diastereomer (-)-**5Ga** was obtained in 50 % yield and more than 99% ee. $[\alpha]_D^{25}$ = -68.1 (*c* 0.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, *J* = 8.0 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.76-1.85 (m, 1H), 2.04-2.13 (m, 1H), 4.33-4.40 (m, 2H), 4.43 (dd, *J* = 3.2, 10.8 Hz, 1H), 4.97 (dd, *J* = 10.4, 13.2 Hz, 1H), 7.08-7.10 (m, 2H), 7.31-7.35 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 8.45, 13.89, 27.79, 46.74, 63.57, 77.72, 97.46, 128.52, 129.30, 129.33, 132.51, 165.65; IR (neat) ν 1753, 1560, 1552 cm^{-1}; HRMS (CI/MH^+) Calcd for $C_{14}H_{19}N_2O_6$: 311.1246, found 311.1243.



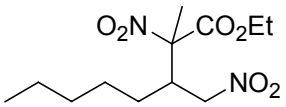
5Ha

Q-**2b** (20 mol%) catalyzed reaction was run in THF at −50 °C for 6 days to furnish the crude product [dr > 98:2, determined by ^1H NMR peaks at 4.82-4.86 ppm and 4.98-5.04 ppm]. Pure major diastereomer (-)-**5Ha** was obtained by flash chromatography (hexane: ethyl acetate = 10:1-8:1) as colorless oil in 78% yield and 99% ee [determined by HPLC, Chiralcel OD, hexane: isopropanol = 80: 20, 1.00 mL/min, λ = 220 nm, t (major) = 32.5 min, t (minor) = 21.5 min]. $[\alpha]_D^{25}$ = -38.0 (*c* 2.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.2 Hz, 3H), 1.38 (s, 3H), 4.02 (dd, *J* = 5.2, 10.4 Hz, 1H), 4.27-4.35 (m, 2H), 4.79 (dd, *J* = 4.8, 13.2 Hz, 1H), 4.98 (dd, *J* = 10.0, 13.6 Hz, 1H), 7.37 (brs, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.86, 22.84, 46.58, 48.34, 63.84, 76.44, 117.81, 128.69, 129.21, 129.31, 133.04, 168.14; IR (neat) ν 1739, 1556 cm^{-1}; HRMS (CI/MH^+) Calcd for $C_{14}H_{17}N_2O_4$: 277.1197, found 277.1188.

QD-**2a** (10 mol%) catalyzed reaction was run in THF at −20 °C for 2.5 days to furnish the crude product (dr = 86:14). Major diastereomer (+)-**5Ha** was obtained by flash chromatography as colorless oil in 76% yield and 95% ee.

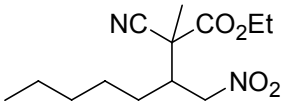
6 (10 mol%) catalyzed reaction was run in THF at −20 °C for 2.5 days to furnish the crude product (dr = 86:14). Major diastereomer (+)-**5Ha** was obtained by flash chromatography as colorless oil in 74% yield and 88% ee.

Q-**2a** (10 mol%) catalyzed reaction was run in THF at −20 °C for 3.5 days to furnish crude product [dr = 93:7, determined by ^1H NMR peaks 3.40 ppm (minor), 3.20-3.25 ppm



5Ff

(major)]. Pure major diastereomer (+)-**5Ff** was obtained by flash chromatography (hexane : ethyl acetate = 50 :1-20:1) as a colorless oil in 78% yield and 92% ee [determined by HPLC, Chiralcel OD, hexane: isopropanol = 99: 1, 1.00 mL/min, λ = 220 nm, t (major) = 31.6 min, t (minor) = 53.2 min]. $[\alpha]_D^{25}$ = +19.3 (*c* 2.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.24-1.42 (m, 10 H), 1.55-1.61 (m, 1H), 1.86 (s, 3H), 3.20-3.25 (m, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.46 (dd, *J* = 6.4, 14.8 Hz, 1H), 4.77 (dd, *J* = 3.6, 14.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 13.68, 13.82, 21.02, 22.23, 26.63, 29.34, 31.49, 42.47, 63.57, 77.00, 94.69, 166.47; IR (neat) ν 1751, 1560 cm^{-1}; HRMS (CI/MH^+) Calcd for $C_{12}H_{23}N_2O_6$: 291.1561, found 291.1556.



5Hf

Q-**2a** (10 mol%) catalyzed reaction was run in THF at −20 °C for 3.5 days to furnish crude product [dr = 93:7, determined by ^{1}H NMR peaks at 2.93-2.96 ppm (minor) and 2.82-2.88 ppm (major)]. Pure product **5Hf** was obtained by flash chromatography (hexane : ethyl acetate = 50:1-30:1) as a colorless oil mixture of two diastereomers (dr = 93:7) in 76% yield and 98% ee (major isomer) [determined by HPLC, Chiralcel OD, hexane: isopropanol = 99: 1, 0.50 mL/min, λ = 220 nm, t (major) = 45.8 min, t (minor) = 66.2 min]. $[\alpha]_D^{25}$ = +17.3 (*c* 1.81, $CHCl_3$); ^{1}H NMR of major diastereomer (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 6.0 Hz, 3H), 1.26-1.50 (m, 10H), 1.67 (s, 3H), 1.70-1.76 (m, 1H), 2.82-2.88 (m, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 4.43 (dd, *J* = 6.4, 14.0 Hz, 1H), 4.64 (dd, *J* = 4.8, 14.0 Hz, 1H); ^{13}C NMR of major diastereomer (101 MHz, $CDCl_3$) δ 13.84, 21.64, 22.27, 26.49, 29.33, 31.48, 42.97, 46.87, 63.47, 76.04, 76.68, 118.34, 168.03; IR (neat) ν 1743, 1560 cm^{-1}; HRMS (CI/MH^+) Calcd for $C_{13}H_{23}N_2O_4$: 271.1652, found 271.1658.

Kinetic Data:

The kinetic parameters of this reaction were determined by *in situ* monitoring of the consumption of nitroalkenes (at peak 1522 cm^{-1}) by the use of a ReactIR 1000 instrument. ReactIR 1000 fitted with a 5/8" Dicomp Probe, running software version 2.1a.

Order in nitroalkene (**4a)** was established by using a large excess of methyl 2-oxocyclopentane carboxylate (**3A,** 5 equiv) and 10 mol% Q**-2c.** Plotting in ln[**4a**] versus time gave a straight line (R^2 = 0.9863, Figure A), thus establishing a first-order dependence on Nitroalkene (**4a**).

Order in methyl 2-oxocyclopentane carboxylate (**3A**) was established by using a large excess of nitroalkene (**4a,** 5 equiv) and 10 mol% **Q-2c.** Plotting in ln[**3A**] versus time gave a straight line (R^2 = 0.9952, Figure C), thus establishing a first-order dependence on **3A.**

The reaction order in catalyst was established by determining the kinetic rate constants at various catalyst concentrations. A plot of the rate constants k_{obs} vs the catalyst concentration gave a straight line for Q**-2c** (R^2 = 0.99, Figure F) The reaction displays first-order dependence on catalysts Q**-2c.**

General procedure for kinetic study:

A mixture of nitroalkene (**4a)** (1.0 mmol) and Q**-2c** (2.5-12.5 mol%) in anhydrous THF (1.0 mL) was stirred at –30°C for 5 minutes, and then pre-cooled methyl 2-oxocyclopentane carboxylate (**3A,** 0.65ml, 5eq) was introduced in one portion via a syringe. The resulting reaction mixture was monitored every 2 seconds for 25 minutes.

Figure A. Determination of the order of nitroalkene **(4a)**

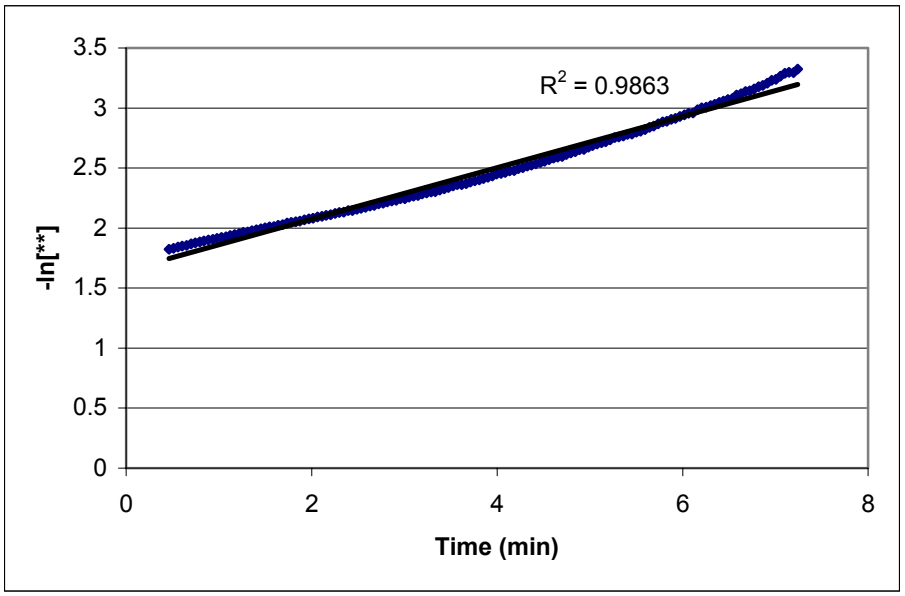


Figure A shows a linear relationship between ln[**4a**] and time indicating the reaction is first order on **4a.**

Figure B. Determination of the order of nitroalkene **(4a)**

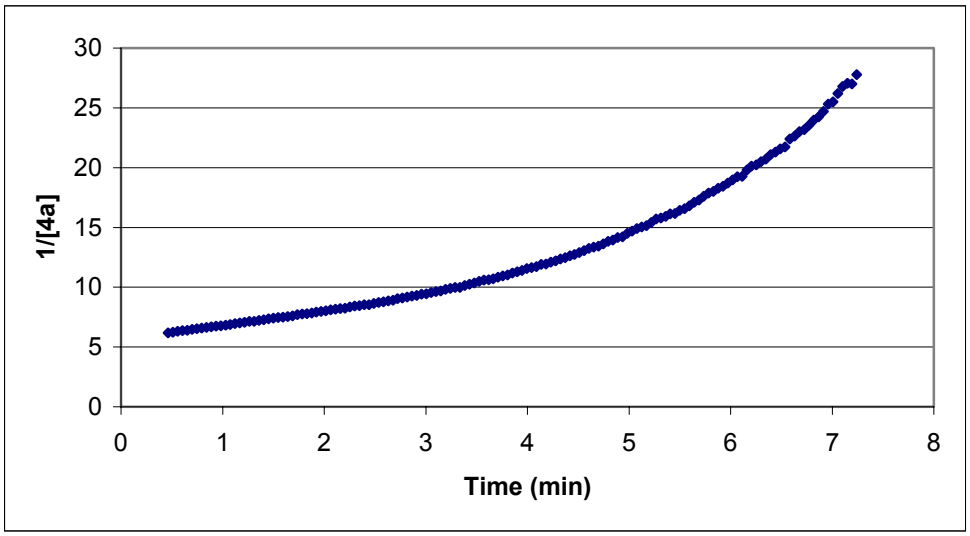


Figure B shows clearly nonlinear relationship between 1/[**4a**] and time indicating the reaction is NOT second order in **4a**

Figure C. Determination of the order of methyl 2-oxocyclopentane carboxylate (**3A**).

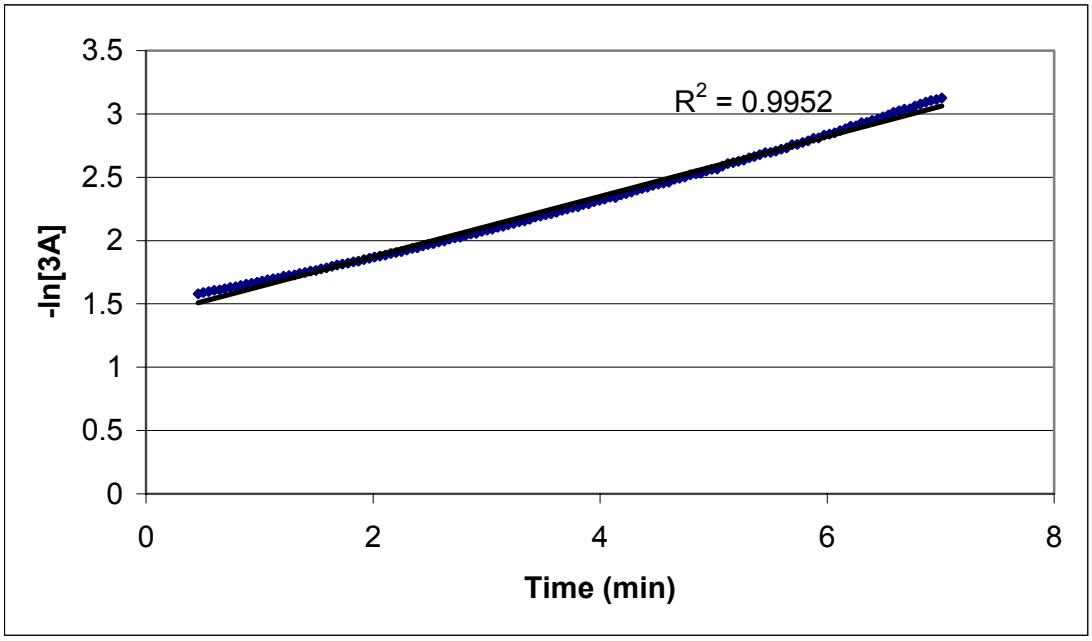


Figure C shows a linear relationship between ln[**3A**] and time indicating the reaction is first order in **3A.**

Figure D. Determination of the order of methyl 2-oxocyclopentane carboxylate (**3A**)

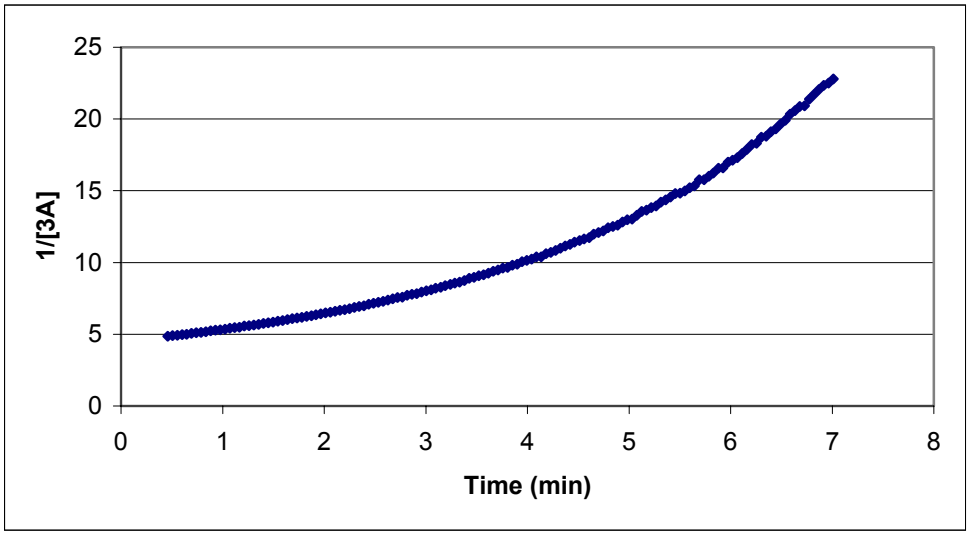
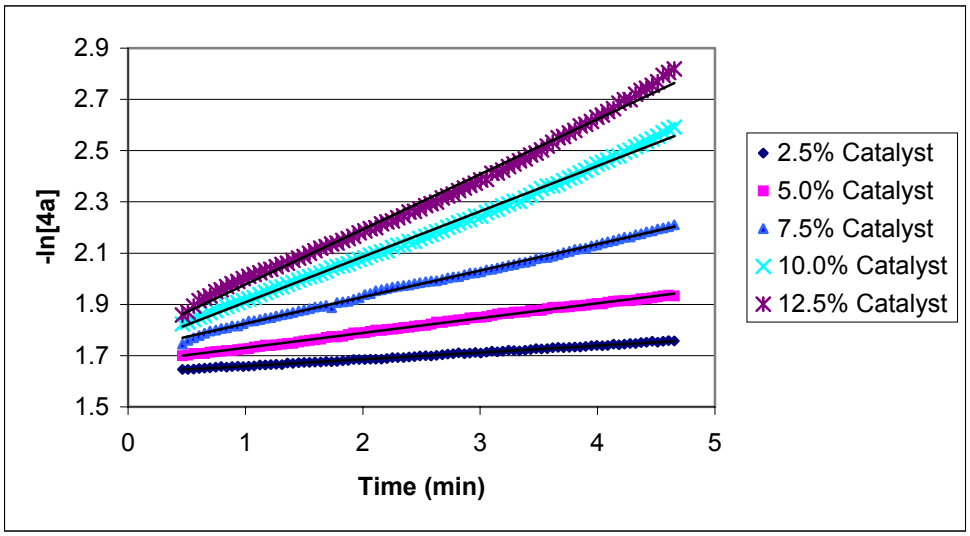


Figure D shows clearly nonlinear relationship between 1/[**3A**] and time indicating the reaction is NOT second order in **3A.**

Figure E. Kinetic profiles for the catalyst Q-**2c**



Catalyst 2.5 mol%	k_{obs} = 0.0268	R^2 = 0.9974
Catalyst 5.0 mol%	k_{obs} = 0.0661	R^2 = 0.9976
Catalyst 7.5 mol%	k_{obs} = 0.1035	R^2 = 0.9978
Catalyst 10.0 mol%	k_{obs} = 0.1775	R^2 = 0.9965
Catalyst 12.5 mol%	k_{obs} = 0.2152	R^2 = 0.9936

Figure F. Kinetic rate constant (k_{obs}) of different concentration of Q-**2c**

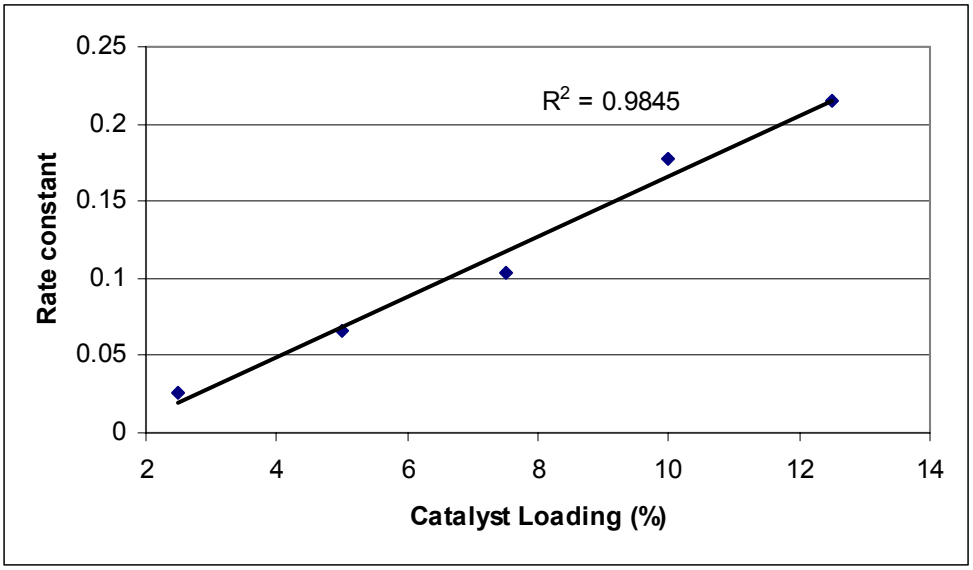
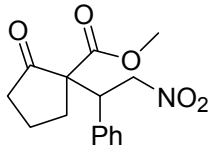
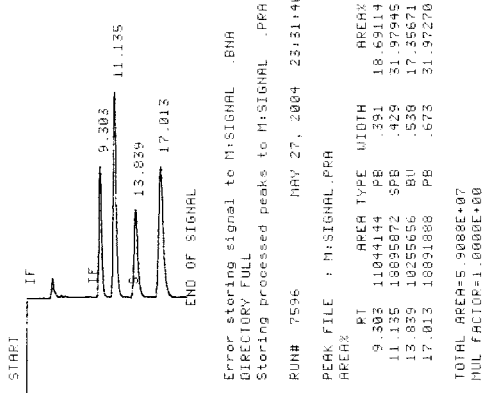


Figure F shows the linear relationship between the kinetic rate constant (k_{obs}) and the concentration of the catalyst, indicating the reaction is first order in catalyst Q-**2c**.

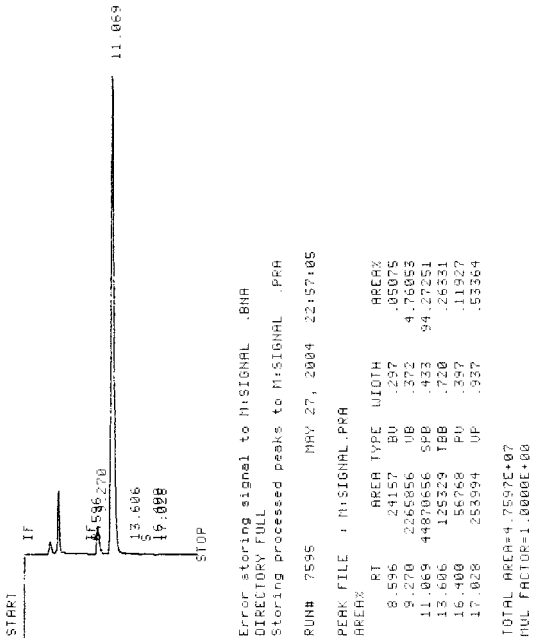
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 80/20, 1.0 mL/min, λ 220 nm



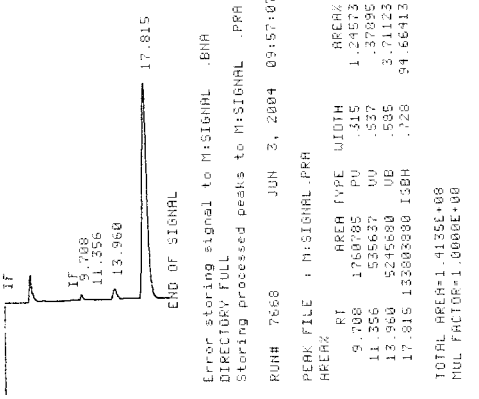
Racemic 5Aa



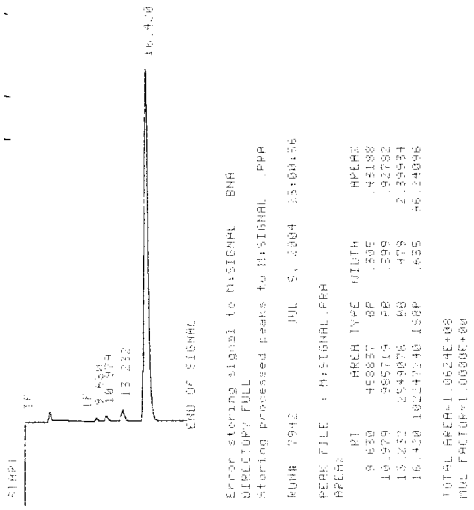
(+)-5Aa 99%ee
Product of **Q-2b**
catalyzed reaction



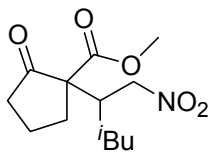
(-)-5Aa 99%ee
Product of **QD-2c**
catalyzed reaction



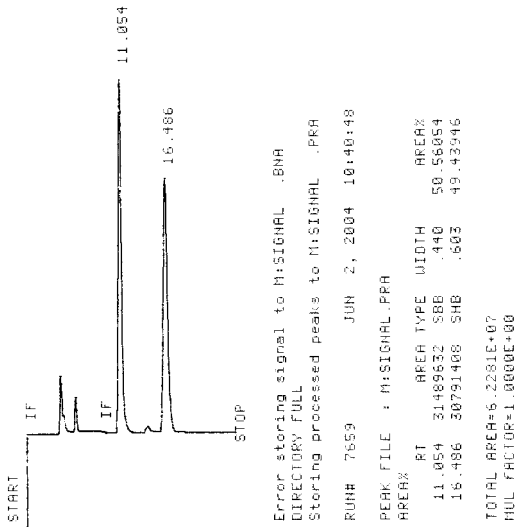
(-)-5Aa 98%ee
Product of **6**
catalyzed reaction



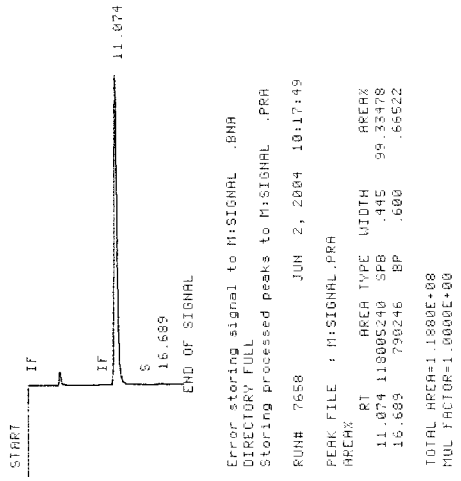
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 95/5, 0.8 mL/min, λ 215 nm



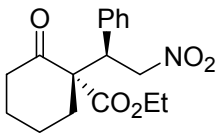
Racemic 5Ae



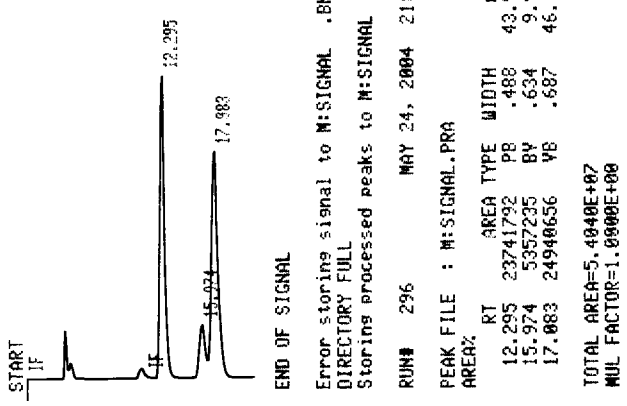
(+)-5Ae 99%ee
Product of **Q-2b**
catalyzed reaction



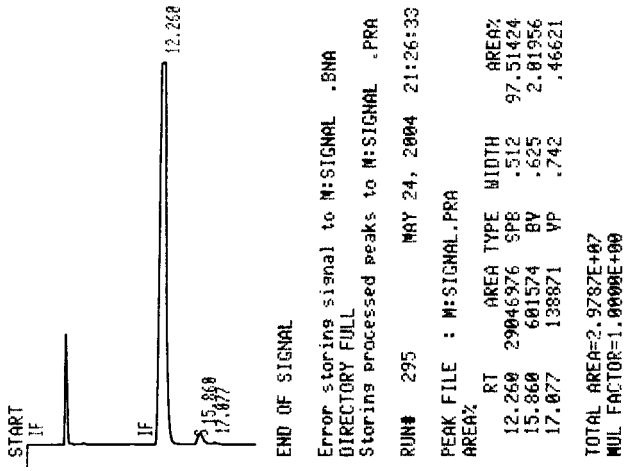
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 95/5 0.9 mL/min, λ 220 nm



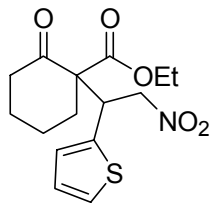
Racemic 5Ba



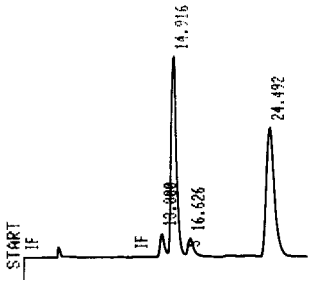
(-)-5Ba 99%ee
Product of **Q-2a**
catalyzed reaction



HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 95/5
0.9 mL/min, λ 220 nm



Racemic 5Bb



END OF SIGNAL

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

RUN# 297 MAY 24, 2004 22:25:21

PEAK FILE : M:SIGNAL.PRA
AREA%

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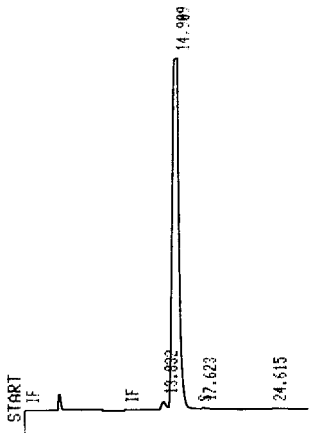
	13.000	8313482	VH	.505	4.61903
	14.916	81865088	SHB	.587	45.48482
	16.626	6873309	BB	.575	3.81886
	24.492	82931520	BB	.923	46.07733

TOTAL AREA=1.7998E+08
MUL FACTOR=1.0000E+00

(-)-5Bb 99%ee
Product of **Q-2a**
catalyzed reaction



STOP

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DIRECTORY FULL
Storing processed peaks to M:SIGNAL .PRA

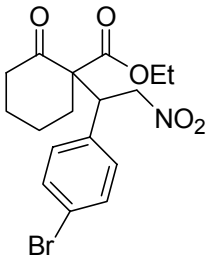
RUN# 298 MAY 24, 2004 22:59:04

PEAK FILE : M:SIGNAL.PRA
AREA%

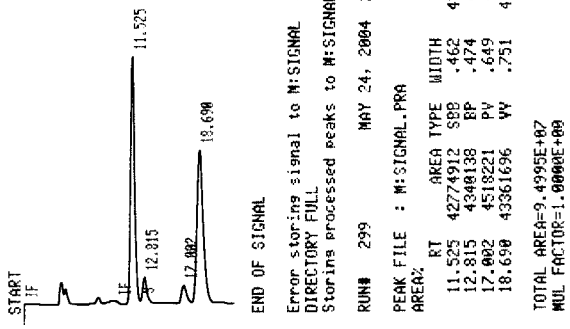
	RT	AREA	TYPE	WIDTH	AREA%
	13.832	1547042	PH	.500	1.40202
	14.909	108189360	SHB	.604	98.04742
	17.623	68795	BB	.223	.06235
	24.615	538726	I BP	1.073	.48822

TOTAL AREA=1.1034E+08
MUL FACTOR=1.0000E+00

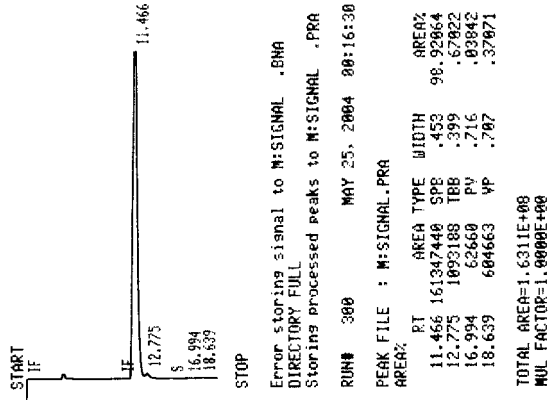
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 90/10 0.8 mL/min, λ 220 nm



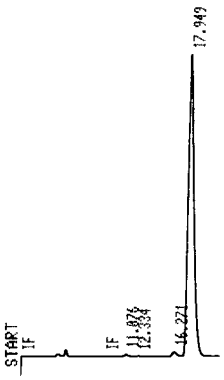
Racemic 5Bc



(-)-5Bc 99%ee
Product of **Q-2a**
catalyzed reaction



(+)-5Bc 99%ee
Product of **QD-2a**
catalyzed reaction



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

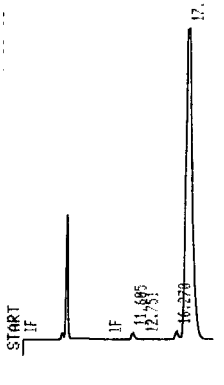
RUN# 426 JUN 3, 2004 22:02:31

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA TYPE	WIDTH	AREA%
	11.876	1590699	BV	.48744
	12.334	335599	VB	.10284
	16.271	4518867	VH	1.38473
	17.949	319889920	ISHH	98.02499

TOTAL AREA=3.2634E+08
MUL FACTOR=1.0000E+00

(+)-5Bc 98%ee
Product of **6**
catalyzed reaction



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

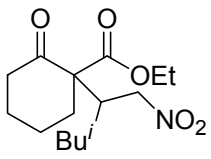
RUN# 732 JUL 6, 2004 09:55:58

PEAK FILE : M:SIGNAL.PRA
AREA%

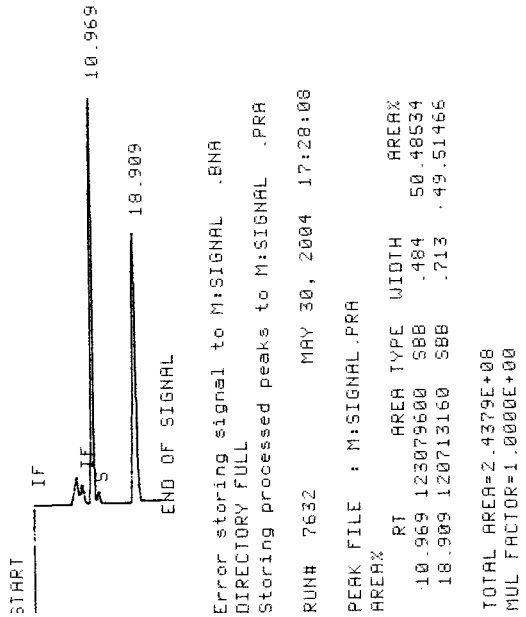
	RT	AREA TYPE	WIDTH	AREA%
	11.685	4462352	PV	.420	1.16290
	12.751	366406	VV	.466	.07985
	16.278	5593968	PH	.428	1.45780
	17.408	373364480	ISHH	.804	97.29946

TOTAL AREA=3.8373E+08
MUL FACTOR=1.0000E+00

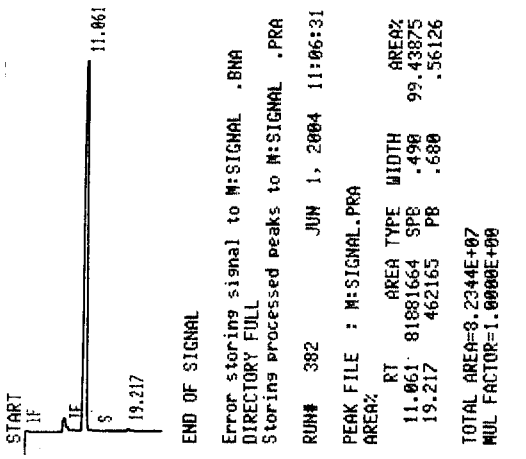
HPLC conditions: Hypersil-Keystone plus Chiralcel OD, Hexane/*iso*-propanol: 90/10 0.8 mL/min, λ 215 nm



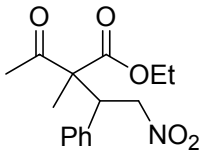
Racemic 5Be



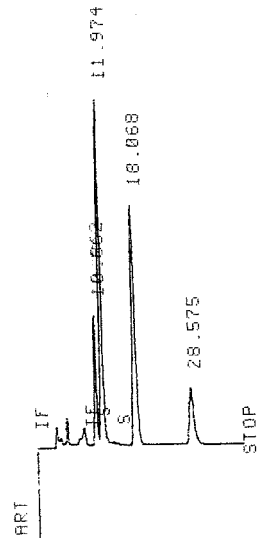
(-)-5Be 99%ee
Product of **Q-2c**
catalyzed reaction



HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 90/10, 0.9mL/min, λ 220 nm



Racemic 5Ca



Error storing signal to M:SIGNAL .BNA
IRECTORY FULL
toring processed peaks to M:SIGNAL .PRA

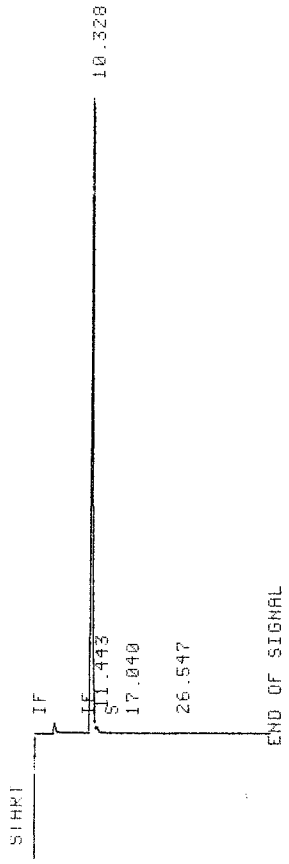
UN# 7801 JUN 16, 2004 16:55:21

EAK FILE : M:SIGNAL.PRA
REA%

	RT	AREA TYPE	WIDTH	AREA%
	10.862	16793440 SBB	.420	12.05329
	11.974	51353920 SPB	.479	36.85866
	18.068	52247552 SPB	.694	37.50005
	28.575	18931712 PB	1.047	13.58800

OTAL AREA=1.3933E+08
UL FACTOR=1.0000E+00

(-)-5Ca 99%ee
Product of **Q-2c**
catalyzed reaction



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

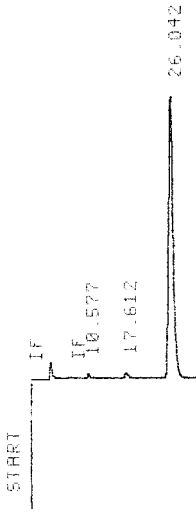
RUN# 7802 JUN 16, 2004 18:06:24

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA TYPE	WIDTH	AREA%
	10.328	171345920 SPB	.427	99.01894
	11.443	669645 TBB	.298	.38698
	17.040	367974 BB	1.360	.21265
	26.547	660053 BF	.914	.38144

TOTAL AREA=1.7304E+08
MUL FACTOR=1.0000E+00

(+)-5Ca 99%ee
Product of **QD-2c**
catalyzed reaction



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

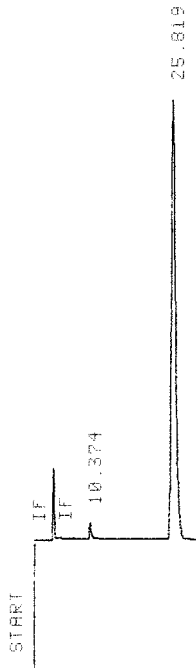
RUN# 8011 JUL 10, 2004 15:22:04

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA TYPE	WIDTH	AREA%
	10.577	638139 BV	.384	.73484
	17.612	1471573 PB	.751	1.69456
	26.042	84731264 BB	.965	97.57059

TOTAL AREA=8.6841E+07
MUL FACTOR=1.0000E+00

(+)-5Ca 96%ee
Product of **6**
catalyzed reaction



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

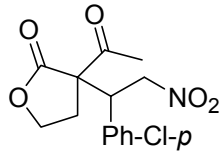
RUN# 7980 JUL 7, 2004 18:35:09

PEAK FILE : M:SIGNAL.PRA
AREA%

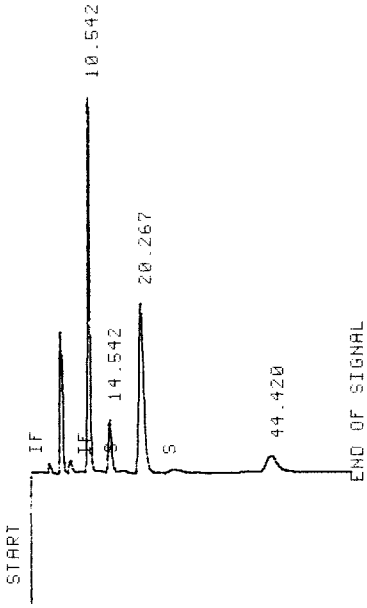
	RT	AREA TYPE	WIDTH	AREA%
	10.374	608563 BV	.455	1.86460
	25.819	32029248 PB	.933	98.13539

TOTAL AREA=3.2638E+07
MUL FACTOR=1.0000E+00

HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 60/40, 1.0 mL/min, λ 220 nm



Racemic 5Dd



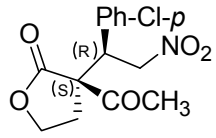
Error storing signal to M:SIGNAL .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL .PRA

RUN# 7599 MAY 28, 2004 09:49:02

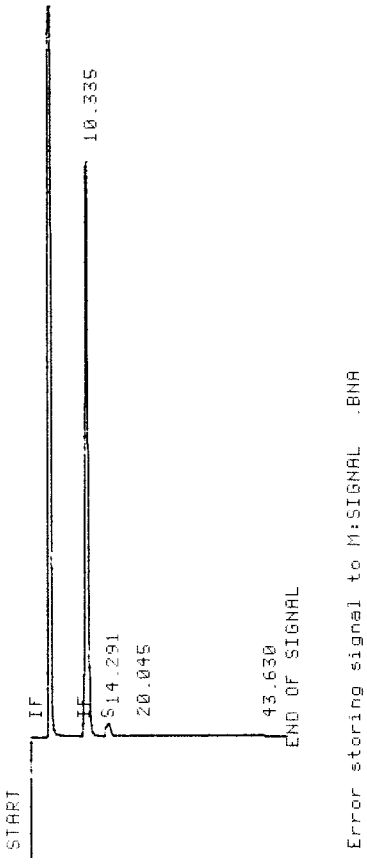
PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA TYPE	WIDTH	AREA%
	10.542	56277152 SBB	.482	41.35301
	14.542	11919288 BV	.707	8.75841
	20.267	56916320 SPB	1.067	41.82267
	44.420	10976872 BB	2.144	8.06591

TOTAL AREA=1.3609E+08
MUL FACTOR=1.0000E+00



(-)-5Dd 99%ee
Product of **Q-2b**
catalyzed reaction



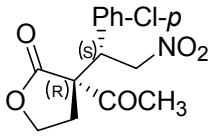
Error storing signal to M:SIGNAL .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL .PRA

RUN# 7597 MAY 28, 2004 00:03:13

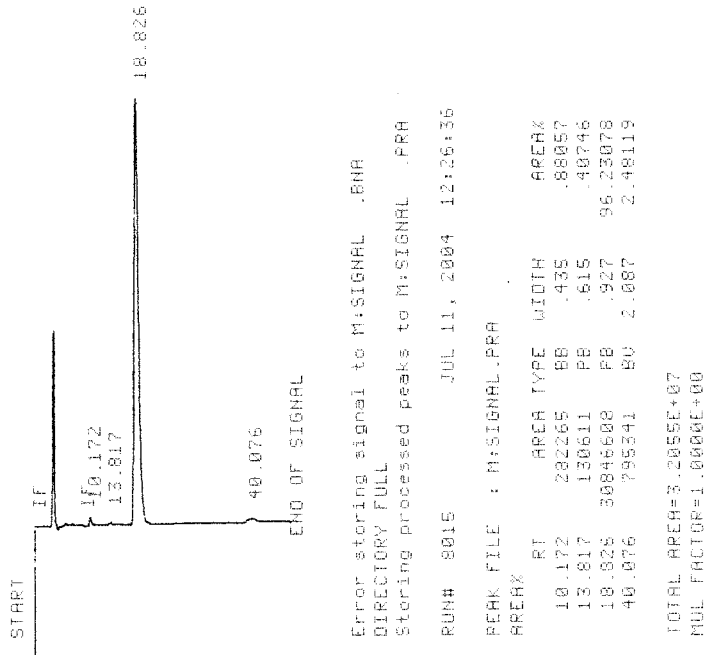
PEAK FILE : M:SIGNAL.PRA
AREA%

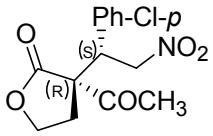
	RT	AREA TYPE	WIDTH	AREA%
	10.335	223744640 SBB	.615	96.15098
	14.291	6394707 BB	.776	2.74803
	20.045	1492207 BB	1.045	.64125
	43.630	1069909 I PP	2.242	.45978

TOTAL AREA=2.3270E+08
MUL FACTOR=1.0000E+00

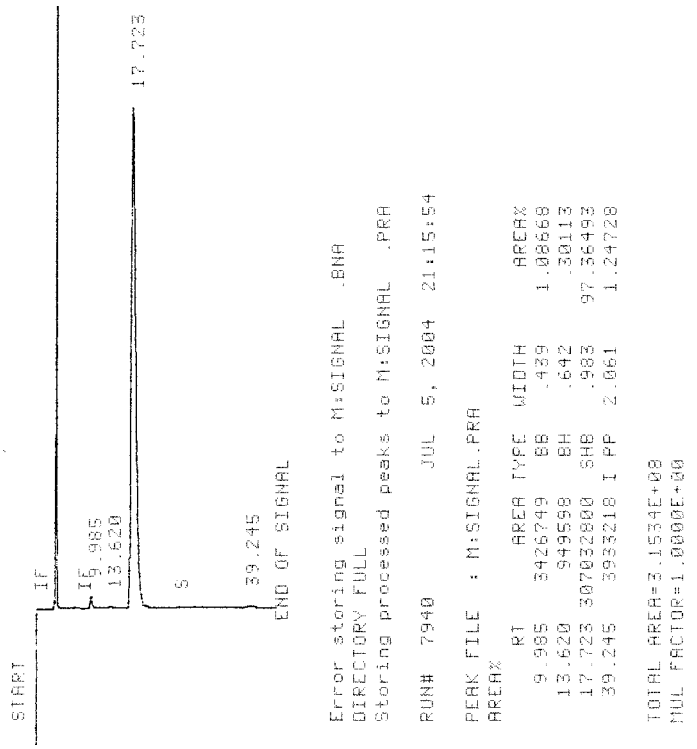


(+)-5Dd 98%ee
Product of **QD-2c**
catalyzed reaction

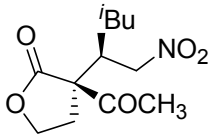




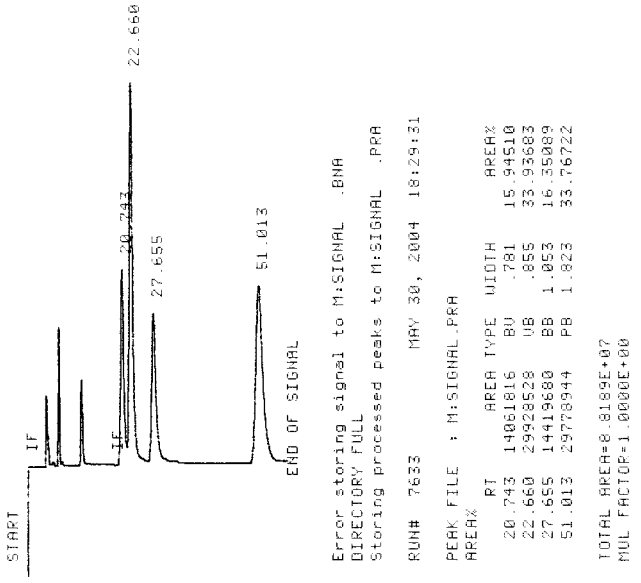
(+)-5Dd 98%ee
Product of **6**
catalyzed reaction



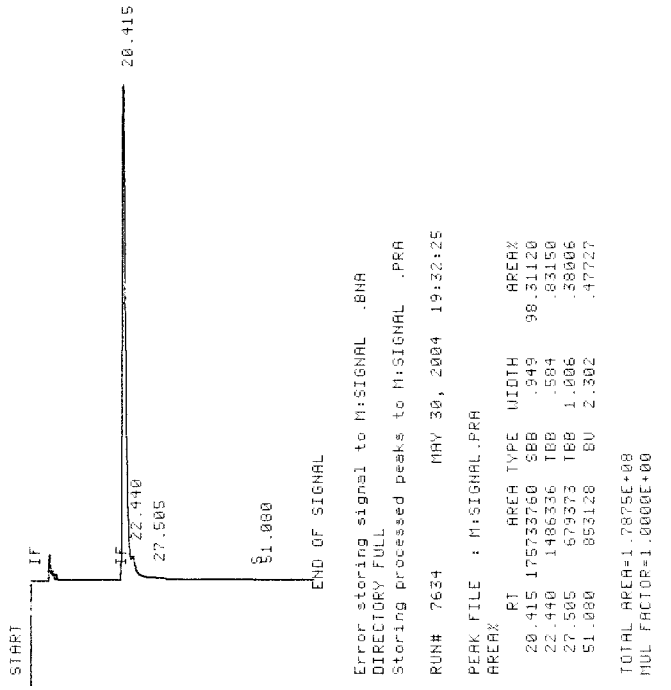
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 90/10, 0.8 mL/min, λ 215 nm



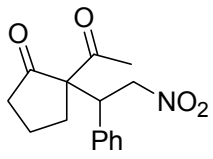
Racemic 5De



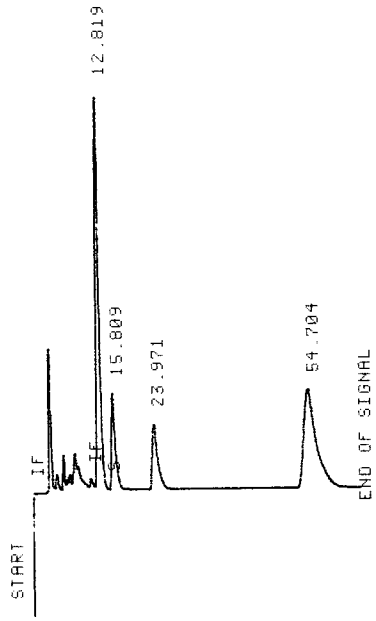
(+)-5De 99%ee
Product of **Q-2c**
catalyzed reaction



HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 80/20, 1.0 mL/min, λ 220 nm



Racemic 5Ea



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

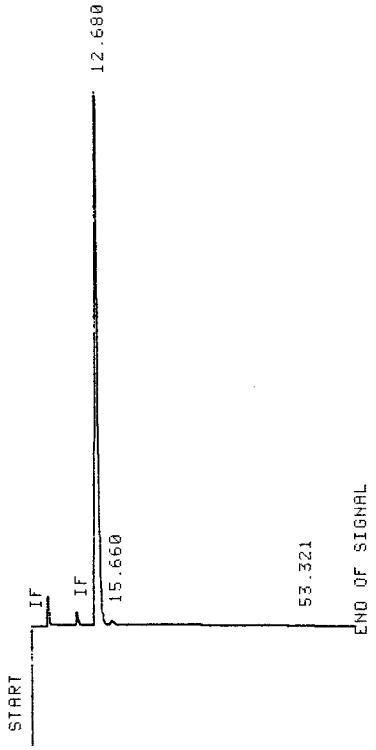
RUN# 7752 JUN 12, 2004 10:07:57

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA	TYPE	WIDTH	AREA%
	12.819	46416160	SPB	.705	38.29846
	15.809	13645768	BB	.843	11.25926
	23.971	13812768	PB	1.252	11.39706
	54.704	47321216	PB	2.838	39.04523

TOTAL AREA=1.2120E+08
MUL FACTOR=1.0000E+00

(-)-5Ea 99%ee
Product of **Q-2b**
catalyzed reaction



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

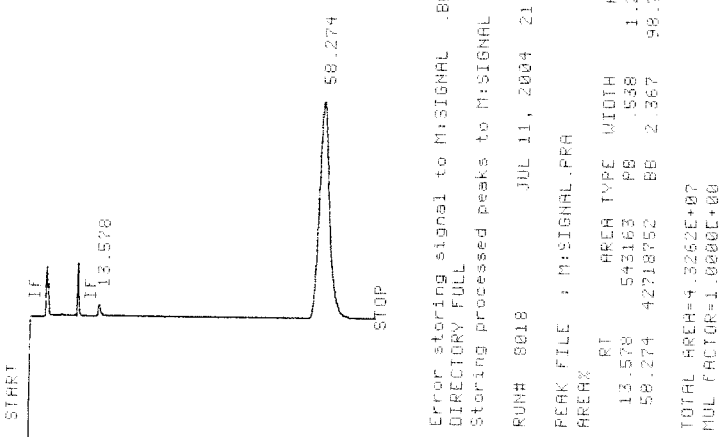
RUN# 7749 JUN 11, 2004 21:51:42

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA	TYPE	WIDTH	AREA%
	12.680	30141216	BB	.679	98.27693
	15.660	302233	BP	.821	.98545
	53.321	226235	BV	2.431	.73765

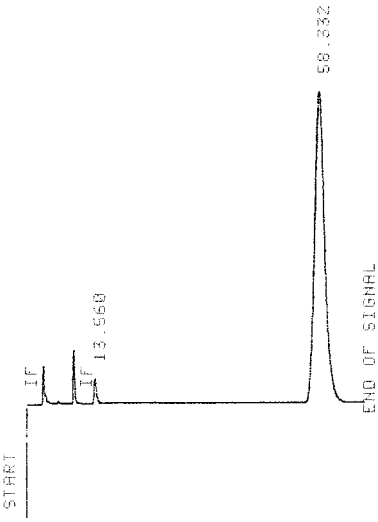
TOTAL AREA=3.0670E+07
MUL FACTOR=1.0000E+00

(+)-5Ea 98%ee
Product of **QD-2c**
catalyzed reaction



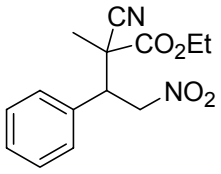

```
Error storing signal to M:SIGNAL  .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL  .PRA

RUN#  8018          JUL 11, 2004  21:15:24

PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT      AREA TYPE  WIDTH      AREA%
  13.578    543163  BB     .538    1.25552
  58.274  42718752  BB    2.367   98.74448

TOTAL AREA=4.32682E+07
MUL FACTOR=1.0000E+00
```

(+)-5Ea 96%ee
Product of **6**
catalyzed reaction

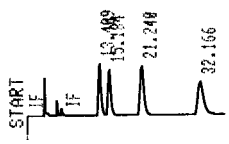



```
Error storing signal to M:SIGNAL  .BNA
DIRECTORY FULL
Storing processed peaks to M:SIGNAL  .PRA

RUN#  8017          JUL 11, 2004  20:01:10

PEAK FILE  : M:SIGNAL.PRA
AREA%
      RT      AREA TYPE  WIDTH      AREA%
  13.560   2279270  BB     .545    1.80797
  58.332 123788720  BB    2.375   98.19203

TOTAL AREA=1.2607E+08
MUL FACTOR=1.0000E+00
```

HPLC conditions: Chiralcel OD, hexane:isopropanol = 80:20, 1 mL/min, λ = 220 nm



Racemic **5Ha**



Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q86EB426.PRO
DIRECTORY FULL

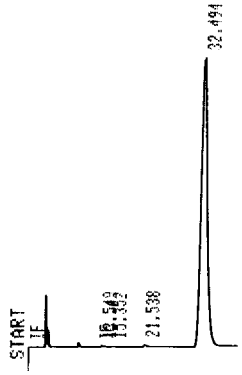
RUN# 316 MAY 26, 2004 10:00:06

SIGNAL FILE: M:SIGNAL.BNC
AREA%:

RT	AREA TYPE	WIDTH	AREA%
13.409	4524410 PV	.530	19.95902
15.184	4513229 VB	.598	19.90970
21.240	6803165 PB	.836	30.01154
32.166	6827693 PB	1.261	30.11975

TOTAL AREA=2.2668E+07
MUL FACTOR=1.0000E+00

(-)-**5Ha** 99% ee
Product of Q-**2b** catalyzed reaction at −50 °C



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

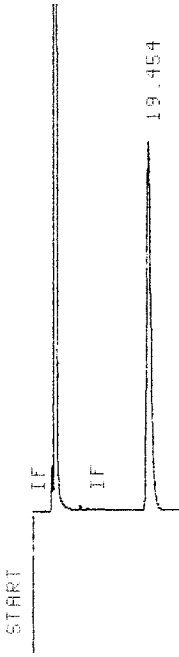
RUN# 317 MAY 26, 2004 10:44:23

PEAK FILE : M:SIGNAL.PRA
AREA%:

RT	AREA TYPE	WIDTH	AREA%
13.549	93892 BP	.486	.15178
15.352	71398 PV	.628	.11542
21.538	272128 PV	.853	.43991
32.494	61422016 PB	1.293	99.29286

TOTAL AREA=6.1859E+07
MUL FACTOR=1.0000E+00

(+)-**5Ha** 95% ee
Product of QD-**2a**
catalyzed reaction
at –20 °C



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

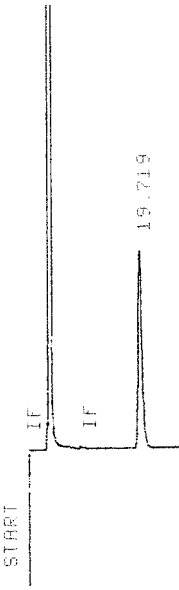
RUN# 7996 JUL 9, 2004 09:18:12

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA	TYPE	WIDTH	AREA%
	19.454	21216544	PB	.811	97.34275
	29.145	579174	PB	1.129	2.65728

TOTAL AREA=2.17966E+07

(+)-**5Ha** 88% ee
Product of **6**
catalyzed reaction
at –20 °C



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

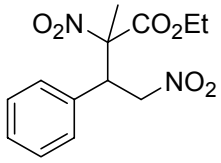
RUN# 7997 JUL 9, 2004 09:59:42

PEAK FILE : M:SIGNAL.PRA
AREA%

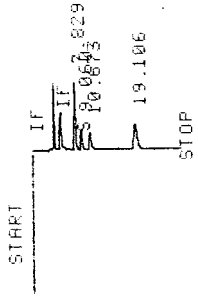
	RT	AREA	TYPE	WIDTH	AREA%
	19.719	23602304	PB	.798	93.98653
	29.810	1510127	BB	1.190	6.01347

TOTAL AREA=2.51132E+07
MUL FACTOR=1.00000E+00

HPLC conditions: Chiralcel OD, hexane:isopropanol = 80:20, 1 mL/min, λ = 220 nm



Racemic **5Fa**



Closing signal file M:SIGNAL .BNC
Storing processed peaks to M:Q84BC613.PRO
DIRECTORY FULL

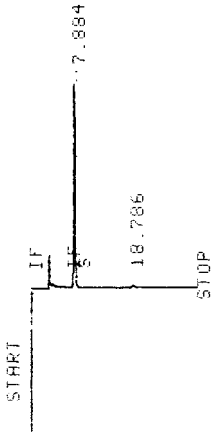
RUN# 7282 APR 30, 2004 22:07:14

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE : M?Q84BC613.PRO
AREA%

	RT	AREA TYPE	WIDTH	AREA%
	7.829	12210216 SPB	.291	36.45294
	9.060	4521082 BB	.353	13.49744
	10.673	4520458 PB	.412	13.49558
	19.106	12244072 PB	.748	36.55403

TOTAL AREA=3.3496E+07
MUL FACTOR=1.0000E+00

(-)-**5Fa** 92% ee
Product of Q-**2a** catalyzed reaction at –20 °C



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

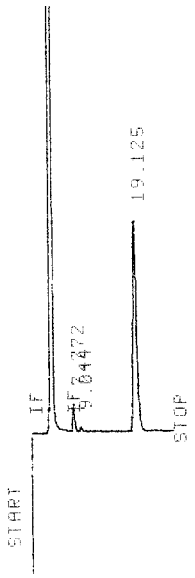
RUN# 7512 MAY 20, 2004 19:49:48

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA TYPE	WIDTH	AREA%
	7.884	17008208 SPB	.272	96.08525
	18.786	696217 BB	.718	3.91476

TOTAL AREA=1.7784E+07
MUL FACTOR=1.0000E+00

(+)-**5Fa** 89% ee
Product of QD-**2a**
catalyzed reaction
at –20 °C



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

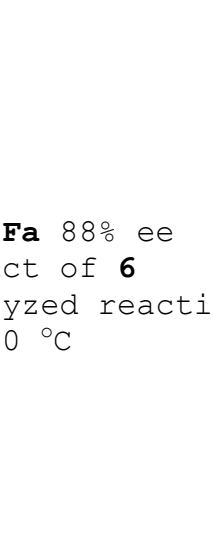
RUN# 7993 JUL 8, 2004 10:31:36

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA	TYPE	WIDTH	AREA%
	7.772	1477184	BP	.356	5.61585
	9.044	256059	PP	.414	.97347
	19.125	24570592	PB	.756	93.41072

TOTAL AREA=2.6304E+07
MUL FACTOR=1.0000E+00

(+)-**5Fa** 88% ee
Product of **6**
catalyzed reaction
at –20 °C



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

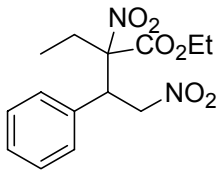
RUN# 7995 JUL 9, 2004 08:46:31

PEAK FILE : M:SIGNAL.PRA
AREA%

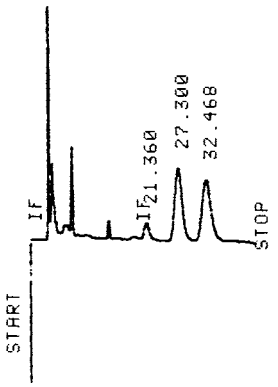
	RT	AREA	TYPE	WIDTH	AREA%
	7.889	4744125	BV	.307	5.32082
	9.099	304776	VB	.350	.40607
	10.822	274474	BV	.439	.36569
	20.015	69732096	SPB	.794	92.90746

TOTAL AREA=7.5055E+07
MUL FACTOR=1.0000E+00

HPLC conditions: Chiralcel OJ, hexane:isopropanol = 80:20, 1 mL/min, λ = 220 nm



Racemic **5Ga**



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

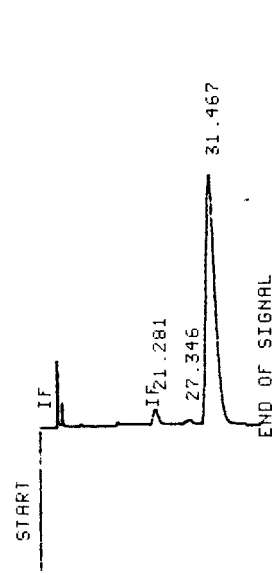
RUN# 7562 MAY 26, 2004 13:40:32

PEAK FILE : M:SIGNAL.PRA
AREA%

	RT	AREA	TYPE	WIDTH	AREA%
	21.360	1446144	BP	1.126	7.20570
	27.300	9094419	PU	1.595	45.31472
	32.468	9528896	VB	1.942	47.47960

TOTAL AREA=2.0069E+07
MUL FACTOR=1.0000E+00

(-)-**5Ga** 96% ee
Product of Q-**2a** catalyzed reaction at −50 °C



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

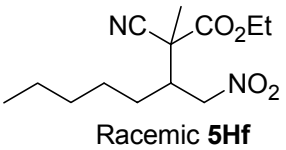
RUN# 7563 MAY 26, 2004 14:58:55

PEAK FILE : M:SIGNAL.PRA
AREA%

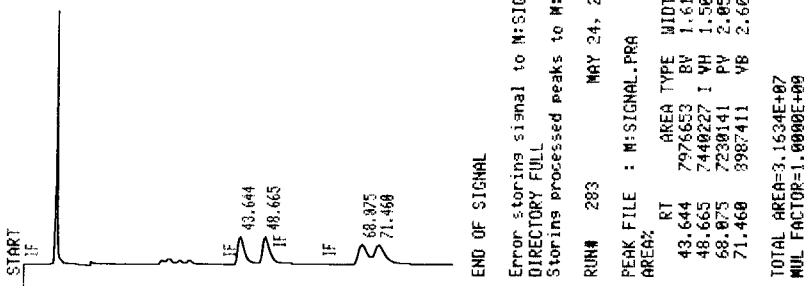
	RT	AREA	TYPE	WIDTH	AREA%
	21.281	5764525	BB	1.133	3.62269
	27.346	2912734	VV	1.531	1.83050
	31.467	150445520	VB	1.959	94.54682

TOTAL AREA=1.5912E+08
MUL FACTOR=1.0000E+00

HPLC conditions: Chiralcel OD, hexane:isopropanol = 99:1, 0.5 mL/min, λ = 220 nm



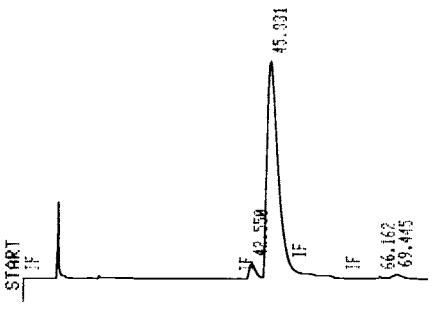
Racemic **5Hf**




```
END OF SIGNAL

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

RUN#  283       MAY 24, 2004  11:27:00

PEAK FILE  : M:SIGNAL.PRA
AREA%:
      RT      AREA TYPE  WIDTH     AREA%
   43.644   7976653  BV  1.617  25.21510
   48.665   7440227 I VH  1.586  23.51940
   68.875   7230141   PV  2.058  22.85529
   71.468   3987411   VB  2.603  28.41022

TOTAL AREA=3.1634E+07
MUL FACTOR=1.0000E+00
```

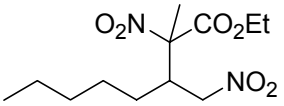
(+)-**5Hf** 98% ee

Product of Q-**2a** catalyzed reaction at −20 °C

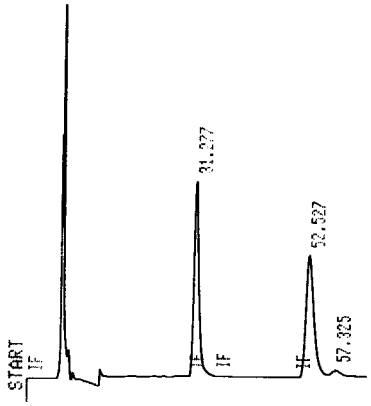



```
STOP

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

RUN#  282       MAY 24, 2004  09:27:48

PEAK FILE  : M:SIGNAL.PRA
AREA%:
      RT      AREA TYPE  WIDTH     AREA%
   42.550  14829480  EH  1.441   3.96508
   45.831  348013000 ISHH  2.435  93.05238
   66.162   2864775   BV  1.893   .76598
   69.445   8290032 I VP  2.514   2.21657

TOTAL AREA=3.7400E+08
MUL FACTOR=1.0000E+00
```

HPLC conditions: Chiralcel OD, hexane:isopropanol = 99:1, 0.5 mL/min, λ = 220 nm



Racemic **5Ff**



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

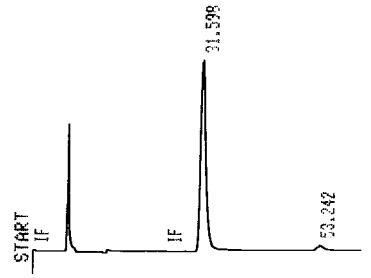
RUN# 285 MAY 24, 2004 14:55:22

PEAK FILE : M:SIGNAL.PRA
AREA%:

	RT	AREA	TYPE	WIDTH	AREA%
	31.277	8325837	BB	1.047	47.49232
	52.527	8503603	BV	1.705	48.50635
	57.325	701474	VV	2.368	4.00136

TOTAL AREA=1.7531E+07
MUL FACTOR=1.0000E+00

(+)-**5Ff** 92% ee
Product of Q-**2a** catalyzed reaction at −20 °C



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

RUN# 284 MAY 24, 2004 13:09:53

PEAK FILE : M:SIGNAL.PRA
AREA%:

	RT	AREA	TYPE	WIDTH	AREA%
	31.598	34163392	PB	1.091	95.95414
	53.242	1440495	VV	1.762	4.04586

TOTAL AREA=3.5604E+07
MUL FACTOR=1.0000E+00

X-Ray Structure Determination. Single crystals of **5Ba**, **5Dd** and **5De** (prepared using catalysts Q-**2** as described in this supporting information**)** suitable for X-ray diffraction measurements were obtained by recrystallization from hexane/Ethyl Acetate, hexane/Ethyl Acetate, and hexane/Ethyl Acetate, respectively. Crystals were mounted in a glass capillary, in order to avoid previously-observed decomposition upon irradiation in air. Data collection was carried out at room temperature (low temperature apparatus was not available) on a CAD-4 Turbo diffractometer equipped with MoKα radiation (**5Ba**), or a CAD-4-U diffractometer equipped with CuKα radiation (**5Dd** and **5De**)[3]. The structures were solved by direct methods (SIR92).[4] Full-matrix least squares refinement was carried out using the Oxford University *Crystals for Windows* system.[5,6] All ordered nonhydrogen atoms were refined by using anisotropic displacement parameters. Disorder of the methyl moiety in the ethyl group of **5Ba** was resolved and refined, with a major component occupancy of 0.55(5). Hydrogen atoms were fixed at calculated geometric positions and updated after each round of least-squares cycles. For **5Dd** (Figure 1), the absolute configuration was established using anomalous scattering, with a Flack parameter value of 0.001(65). For **5De** (Figure 2) and **5Ba** (Figure 3), the relative configurations of the two chiral centers were unambiguously established. These results automatically establish that **5De** and **5Ba** prepared by using catalysts QD-**2** have the same relative configuration as illustrated in Figure 2 and Figure 3. These results also establish that the absolute configuration of 1,4-adduct **5Dd** prepared by using catalysts QD-**2** has the absolute configuration that is opposite to that illustrated in Figure 1.

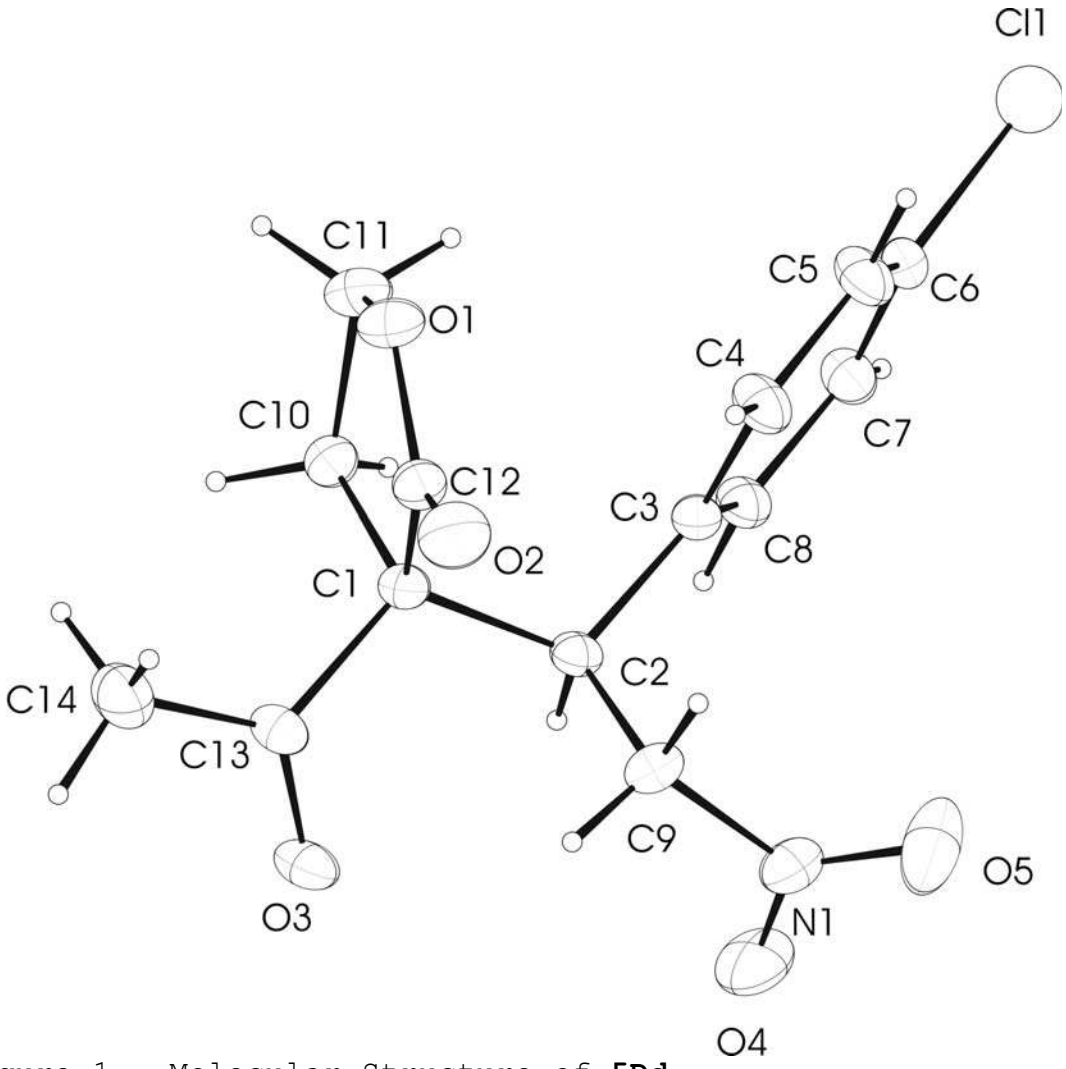


Figure 1. Molecular Structure of **5Dd**

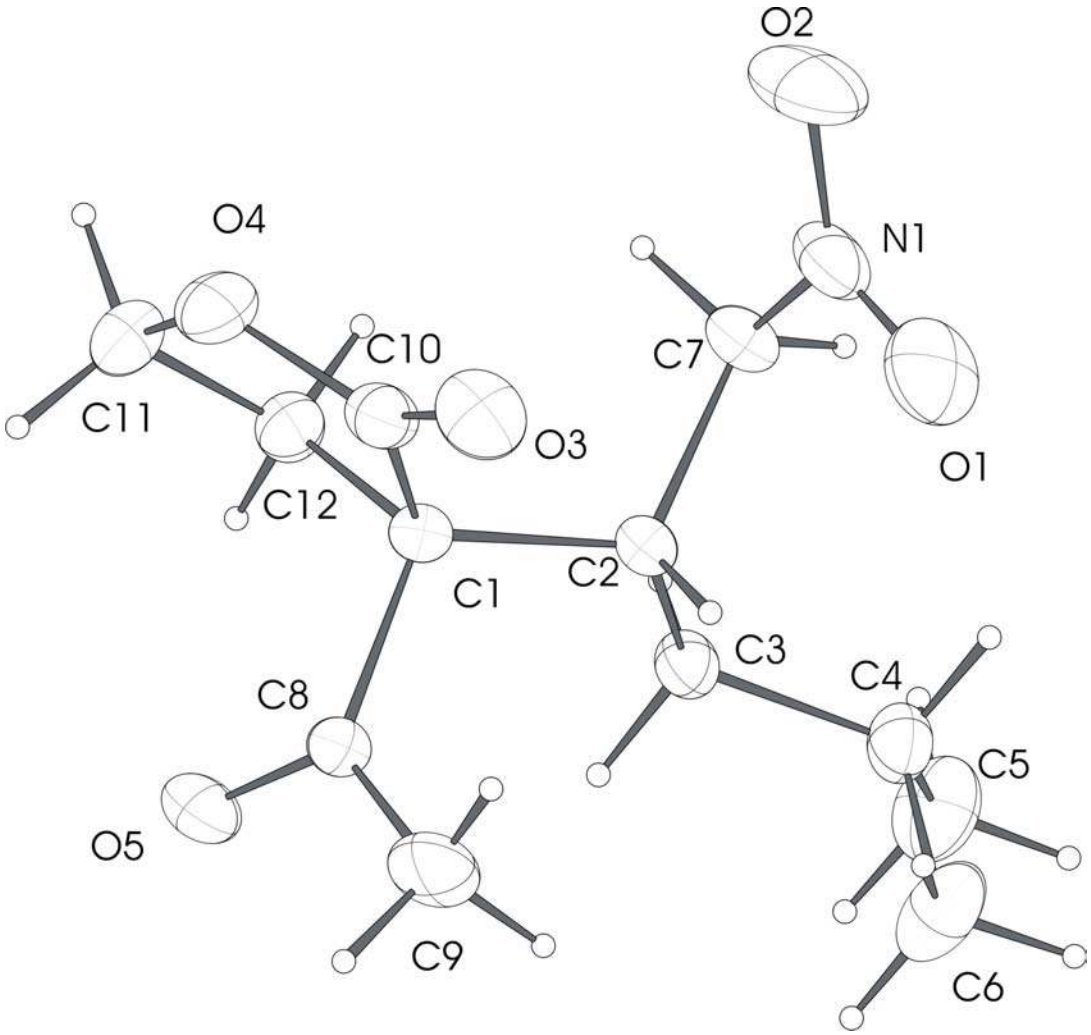


Figure 2. Molecular Structure of **5De**

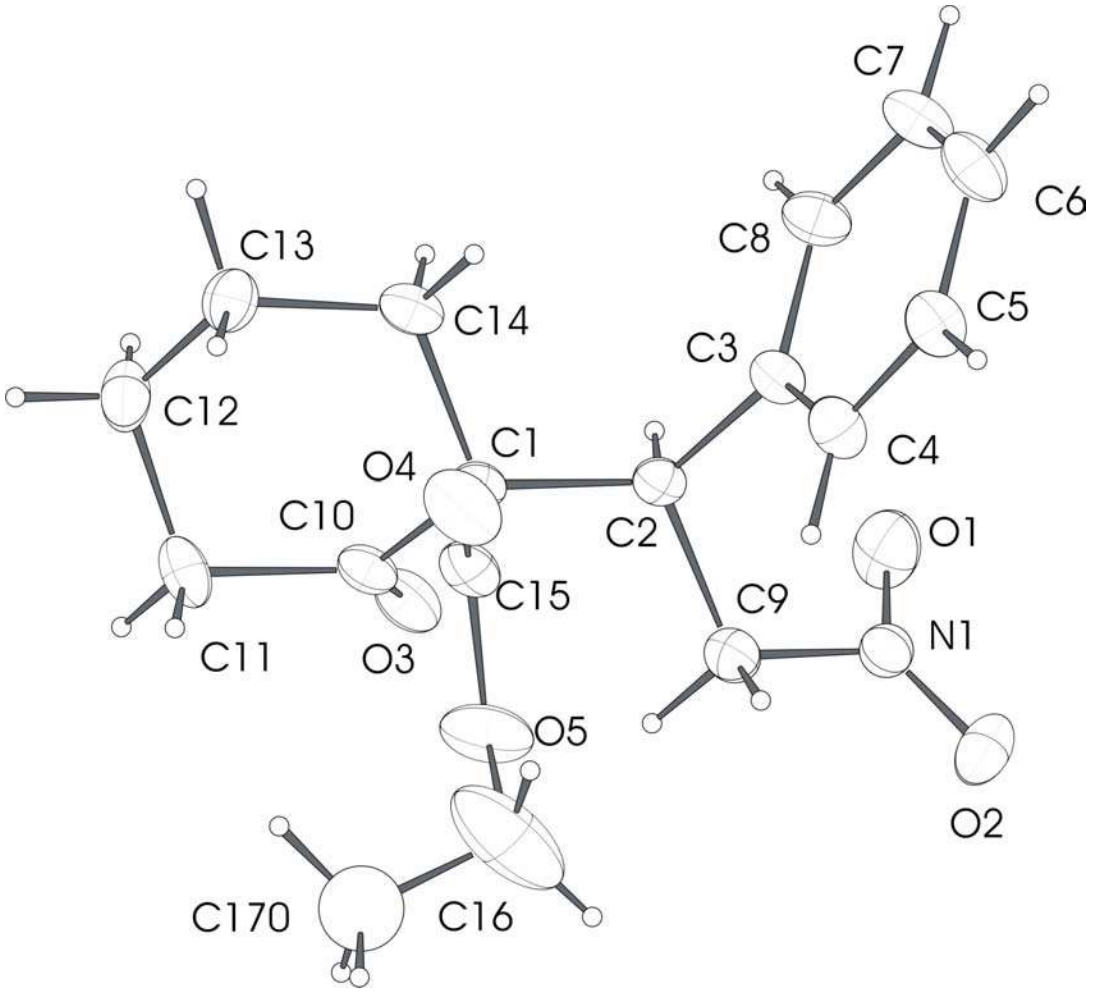


Figure 3. Molecular Structure of **5Ba**

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