Supporting Information

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

Hongming Li, Yi Wang, Liang Tang, Fanghui Wu, Xiaofeng Liu, Chengyun Guo, Bruce M. Foxman and Li Deng*

Department of Chemistry
Brandeis University
Waltham, Massachusetts 02454-9110

*To whom correspondence should be addressed

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), integation. 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

Preparations 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 CaH₂ 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 H₂O (5 x 100 mL), brine (100 mL) and dried over Na₂SO₄. 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 N₂ 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 CaH₂ 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. NH₄Cl (80 ml) and H₂O (60 ml). The resulting mixture was adjusted to pH = 2 by conc. HCl, washed by ethyl acetate (2x100 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 Na₂SO₄, and concentrated in vacuo. The residue was washed by CH₂Cl₂ (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$_2$SO$_4$, 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$_3$) $\delta$ 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) v 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$_2$O$_2$+H$^+$): 401.2229, found: 401.2228.

2. Preparation of Q-2c:

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 °C) for 70 h. The reaction mixture was cooled to room temperature, afterwhich CH$_2$Cl$_2$ (40 ml) and H$_2$O (40 ml) and Et$_2$O (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$_2$Cl$_2$ (2 x 20 ml). The combined organic phase was washed with aqueous NH$_4$OH (5%, 3 x 20 ml), and the brown solution was dried over Na$_2$SO$_4$ and concentrated. The residue was subjected to column
chromatography (SiO₂, CH₂Cl₂ : CH₃OH = 100:1) to furnish 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 CaH₂ in DMF) was added NaSEt (3g). The resulting mixture was heated at 110°C for 6 hrs and cooled to room temperature. Saturated NH₄Cl 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 Na₂SO₄, and concentrated. The residue was subjected to column chromatography (SiO₂, CH₂Cl₂ : CH₃OH = 50 :1) to afford Q-2c as a yellow solid (1.8 g, 56% yield). 

[α]D²⁵ = + 371.1 (c, 0.64 CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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(C₃₃H₃₀N₂O₂⁺H⁺): 487.2386, found: 487.2378.

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

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  R\rightarrow^{\text{NO2}}\rightarrow^{\text{4, catalyst THF}}\rightarrow^{\text{R4}}\rightarrow^{\text{5, NO2}}\rightarrow^{\text{R3}}\rightarrow^{\text{R2}}\rightarrow^{\text{R1}}\rightarrow^{\text{R}}
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4: a, R = Ph;
b, R = 2-thienyl;
c, R = 4-Br-Ph;
d, R = 4-Cl-Ph;
e, R = iBu;
f, R = nPentyl
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 0.2 mmol 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,
determined by integration of one set of $^1$H NMR signal ($\delta_{\text{major}}$ 5.16-5.12 ppm, $\delta_{\text{minor}}$ 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, $\lambda$ = 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$_3$) $\delta$ 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$_3$) $\delta$ 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) v 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 oC 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 diastereomer).

6 (10 mol%) catalyzed reaction was run at -60 oC 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 diastereomer).

Q-2b (10 mol%) catalyzed reaction was run in THF at -60 oC for 96 h to furnish the crude product [dr > 98:2, determined by integration of one set of $^1$H NMR signal ($\delta_{\text{major}}$ 4.87-4.82 ppm, $\delta_{\text{minor}}$ 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, $\lambda$ = 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$_3$) $\delta$ 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$_3$)
\[ \delta 213.2, 169.9, 76.6, 62.9, 52.7, 39.4, 38.4, 38.3, 31.0, 25.6, 23.7, 21.1, 19.4; \text{IR (neat)} \ \nu 2959, 1750, 1722, 1557, 1435, 1380, 1230, 1164, 1230 \text{ cm}^{-1}; \text{HRMS (CI)} \ m/z \text{ calcd for } (C_{13}H_{21}NO_{5} + H^+) : 272.1498, \text{ found: 272.1497.} \]

Q-2a (10mol %) catalyzed reaction was run in THF at -20 °C for 72 h to furnish the crude product [\( \text{dr} > 98:2 \), determined by integration of one set of \( ^1H \) NMR signal (\( \delta_{\text{major}} 5.06-5.02 \text{ ppm, } \delta_{\text{minor}} 5.17-5.11 \text{ ppm, the minor peak can not be detected by } ^1H \text{ NMR) } ]. \text{ Crude product was purified by flash chromatography (hexane: ethyl acetate = 10:1) to give adduct } 5Ba \text{ 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, } \lambda = 220 \text{ nm, } t \text{ (major) = 12.3 min, } t \text{ (minor) = 17.0 min]. } [\alpha]_D^{25} = -91.5 \ (c, 1.02 \text{ CHCl}_3); ^1H \text{ NMR (400 MHz, CDCl}_3) \ \delta 7.25-7.12 \text{ (m, 5H), 5.04 (dd, } J = 3.2 \text{ Hz, 13.2 Hz, 1H), 4.77 (dd, } J = 13.2 \text{ Hz, 1.6 Hz, 1H), 4.18 (qd, } J = 1.6 \text{ Hz, 7.2 Hz, 2H), 3.97 (dd, } J = 3.2 \text{ 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 \text{ Hz, 3H); ^13C \text{ NMR (100 MHz, CDCl}_3) \ \delta 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; \text{IR (neat)} \ \nu 3032, 2943, 2869, 1712, 1553, 1453, 1378, 1308, 1235 \text{ cm}^{-1}; \text{HRMS (CI)} \ m/z \text{ calcd for } (C_{17}H_{21}NO_{5} + H^+) : 320.1498, \text{ found: 320.1502.} \]

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

Q-2a (10 mol %) catalyzed reaction was run in THF at -20 °C for 74 h to furnish the crude product [\( \text{dr} > 98:2 \), determined by integration of one set of \( ^1H \) NMR signal (\( \delta_{\text{major}} 4.88-4.85 \text{ ppm, } \delta_{\text{minor}} 5.14-5.08 \text{ ppm, the minor peak can not be detected by } ^1H \text{ NMR) } ]. \text{ Crude product was purified by flash chromatography (hexane: ethyl acetate = 10:1) to give adduct } 5Bb \text{ 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, } \lambda = 220 \text{ nm, } t \text{ (major) = 14.9 min, } t \text{ (minor) = 24.6 min]. } [\alpha]_D^{25} = -69.0 \ (c, 1.06 \text{ CHCl}_3); ^1H \text{ NMR (400 MHz, CDCl}_3) \ \delta 7.20 (d, } J = 4.8 \text{ Hz, 1H), 6.89-6.85 (m, 2H), 4.86 (dd, } J = 3.2 \text{ Hz, 13.6 Hz, 1H), 4.77 (dd, } J = 10.4 \text{ Hz, 1H), 4.31 (dd, } J = 4.0 \text{ Hz, 10.4 Hz, 1H), 4.17 (q, } J = 7.2 \text{ 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$_3$) $\delta$ 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) $\nu$ 2942, 1718, 1702, 1559, 1543, 1524, 1437, 1376, 1232 cm$^{-1}$; HRMS (CI) m/z calcd for (C$_{15}$H$_{19}$NO$_5$S + H$^+$): 326.1055, found: 326.1058.

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 ($\delta_{\text{major}}$ 5.01-4.97 ppm, $\delta_{\text{minor}}$ 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, $\lambda$ = 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$_3$) $\delta$ 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$_3$) $\delta$ 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) $\nu$ 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 diastereomer).

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 diastereomer).
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 ($\delta_{\text{major}}$ 4.55-4.50 ppm, $\delta_{\text{minor}}$ 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, $\lambda$ = 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$_3$) $\delta$ 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$_3$) $\delta$ 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.

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 ($\delta_{\text{major}}$ 2.17 ppm, $\delta_{\text{minor}}$ 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, $\lambda$ = 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$_3$) $\delta$ 7.33-7.27 (m, 3H), 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$_3$) $\delta$ 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).

QD-2c (10 mol %) catalyzed reaction was run at -60 °C for 44 h to furnish the crude product [dr = 98:2, determined by integration of one set of ¹H 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 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]. [α]D²⁵ = -23.5 (c, 1.18 CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 (Cl) m/z calcd for (C₁₄H₁₂ClNO₅ + 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).
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 ¹H NMR signal (δmajor 2.37 ppm, δminor 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]. [α]D²⁵ = + 80.9 (c, 0.92 CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 (C₁₂H₁₉NO₅ + H⁺): 258.1341, found: 258.1341.

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

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 ¹H NMR signal (δmajor 4.39-4.35 ppm, δminor 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]. [α]D²⁵ = - 43.3 (c, 1.11 CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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) ν 3033, 2971, 1740, 1702, 1554, 1378, 1140 cm⁻¹; HRMS (CI) m/z calcd for (C₁₅H₁₇NO₄ + H⁺): 276.12136, found: 276.1238.

5De

5Ea

O

5Ea

O

O

5De

COCH₃

Ph

NO₂

Bu

NO₂
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).

Q-D-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 ¹H 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]. [α]D²⁵ = -50.2 (c 0.93, CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 C₁₃H₁₇N₂O₆: 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.

Q-D-2a (20 mol%) catalyzed reaction was run in THF at -50 °C for 6 days to furnish crude product [dr = 95:5, determined by ¹H 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 recrystallization in Et₂O, pure diastereomer (-)-5Ga was obtained in 50 % yield and more than 99% ee. [α]D²⁵ = -68.1 (c 0.88, CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 C₁₄H₁₉N₂O₆: 311.1246, found 311.1243.

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]. [α]D²⁵ = -38.0 (c 2.10, CHCl₃); ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) 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 C₁₄H₁₇N₂O₄: 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
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]. [α]$_D^{25}$ = +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$_2$O$_6$: 291.1561, found 291.1556.

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]. [α]$_D^{25}$ = +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, 10 H), 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$_2$O$_4$: 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 (R² = 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 (R² = 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 (R² = 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

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Figure F. Kinetic rate constant ($k_{\text{obs}}$) of different concentration of $Q^{-2c}$.

Figure F shows the linear relationship between the kinetic rate constant ($k_{\text{obs}}$) 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

(+)−5Aa 99% ee
Product of Q-2b catalyzed reaction
(-)-5Aa 98%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

(+) 5Ae 99% ee
catalyzed reaction

Product of Q-2b

Racemic 5Ae

Product of Q-2b catalyzed reaction
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 95/5
0.9 mL/min, λ 220 nm

(-)-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

(-)-5Bb 99%ee
Product of Q-2a
catalyzed reaction
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 90/10
0.8 mL/min, λ 220 nm

[Chemical structure of Racemic 5Bc]

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

(+)-5Bc (99% ee)

Product of 6 catalyzed reaction

(+)-5Bc (99% ee)
HPLC conditions: Hypersil-Keystone plus Chiralcel OD, Hexane/iso-propanol: 90/10 0.8 mL/min, λ 215 nm

(−)-5Be synthesized via a catalyzed reaction

Product of Q-2c

Racemic 5Be

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Racemic 5Ca

(-)-5Ca 99% ee
Product of Q-2c catalyzed reaction
(+)-5Ca 96% ee
Product of QD-2c catalyzed reaction

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

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Product of Q-2b catalyzed reaction

Racemic 5Dd

(−)-5Dd 99% ee

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

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

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(+)-5De 99% ee

Product of Q-2c catalyzed reaction

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TOTAL AREA=1.7875E+08
MUL FACTOR=1.0000E+00

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RUN# 7633 MAY 30, 2004 10:19:31
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<td>UB</td>
<td>0.95</td>
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<td>BB</td>
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<td>51.013</td>
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<td>PA</td>
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TOTAL AREA=8.8199E+07
MUL FACTOR=1.0000E+00
HPLC conditions: Chiralcel OD, Hexane/iso-propanol: 80/20, 1.0 mL/min, λ 220 nm

Racemic 5Ea

(-)-5Ea 99% ee
Product of Q-2b catalyzed reaction
HPLC conditions: Chiralcel OD, hexane:isopropanol = 80:20, 1 mL/min, λ = 220 nm

(-)-5Ha 99% ee
Product of Q-2b catalyzed reaction at -50 °C
(+)-5Ha 95% ee
Product of QD-2a
catalyzed reaction
at -20 °C

(+)-5Ha 88% ee
Product of 6
catalyzed reaction
at -20 °C
HPLC conditions: Chiralcel OD, hexane:isopropanol = 80:20, 1 mL/min, λ = 220 nm

(-)-5Fa 92% ee
Product of Q-2a catalyzed reaction at -20 °C
(+)-5Fa 89% ee
Product of QD-2a
catalyzed reaction
at -20 °C

(+)-5Fa 88% ee
Product of 6
catalyzed reaction
at -20 °C
HPLC conditions: Chiralcel OJ, hexane:isopropanol = 80:20, 1 mL/min, λ = 220 nm

(-)-5Ga 96% ee
Product of Q-2a catalyzed reaction at -50 °C
HPLC conditions: Chiralcel OD, hexane:isopropanol = 99:1,
0.5 mL/min, \( \lambda = 220 \) nm

(+)-5Hf

Product of Q-2a catalyzed reaction at -20 °C
98% ee

Racemic 5Hf

END OF SIGNAL

START

RUN#: 203      MAY 24, 2004  11:27:00
PEAK FILE: M: SIGNAL .PRA
AREAS:
RT  AREA  TYPE  WIDTH  AREA%
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48.665  7449227  LV  1.586  23.5194
60.875  7389141  LV  2.058  22.9529
71.460  3907411  BV  3.643  20.4162
TOTAL AREA=3,163AE+07
MUL FACTOR=1.00000E+00
(+)-5Ff, 92% ee
Product of Q-2a catalyzed reaction at -20°C

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

Racemic 5Ff

NO2
O2N
CO2Et

STOP

Error storing signal to M:STAIN?? BNA
DIRECTORY FULL
Storing processed peaks to M:STAIN?? PRA
RUN# 284 MAY 24, 2004 10:09:53
PEAK FILE : M:STAIN?? PRA
AREA:
RT   AREA   TYPE   WIDTH   AREA:
31.599 34162392  PB  1.601 95.95414
53.242 1448495   VV  1.762 1.84589
TOTAL AREA=5.5684E+07
MUL FACTOR=1.0000E+00

STOP

Error storing signal to M:STAIN?? BNA
DIRECTORY FULL
Storing processed peaks to M:STAIN?? PRA
RUN# 285 MAY 24, 2004 14:55:22
PEAK FILE : M:STAIN?? PRA
AREA:
RT   AREA   TYPE   WIDTH   AREA:
31.277 8325932  BD  1.847 47.49232
52.527 8563603  BV  1.785 48.59635
57.325 761474   VV  2.368 4.00136
TOTAL AREA=1.7531E+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)\. The structures were solved by direct methods (SIR92). Full-matrix least squares refinement was carried out using the Oxford University Crystals for Windows system. 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
References:


