



Supporting Information

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## ***Supporting Information for***

### **Organocatalytic Asymmetric Formal [3+2] Cycloaddition Reaction of Isocyanoesters to Nitroolefins Leading to Highly Optically Active Dihydropyrroles**

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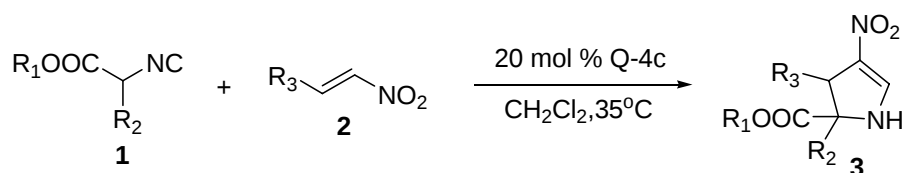
**General Information:** NMR spectra were recorded on a Bruker-400 MHz spectrometer. HRMS (Bio TOF Q) spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Optical rotations were measured on Perkin-Elmer 241 MC polarimeter. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak AD, kromasil columns were purchased from Daicel Chemical Industries, LTD. Solvents for the column chromatography were distilled before use.

All isocyanoesters were prepared according to literature procedures.<sup>1</sup> The preparation of nitroolefins was based on the literature.<sup>2</sup>

#### **General procedure for the preparation of racemic standards:**

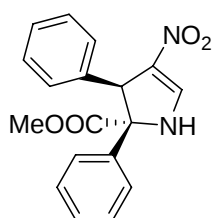
To a solution of a nitroalkene (0.1 mmol) and AgOCOCH<sub>3</sub> (0.01 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added an isocyanoester (0.15 mmol). The reaction mixture was stirred at room temperature until the reaction underwent completely. After removal of the solvent, the residue was purified through column chromatography.

#### **General procedure for the cycloaddition reactions of isocyanoesters to nitroalkenes catalyzed by**

**Q-4c:**

To a solution of a nitroalkene **2** (0.3 mmol) and **Q-4c** (0.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL) was added an isocyanoester **1** (0.45 mmol). The reaction mixture was heated to 35 °C and stirred at this temperature for 1 to 3 days. After removal of the solvent, the residue was purified through column chromatography on a silica gel to yield pure product **3**.

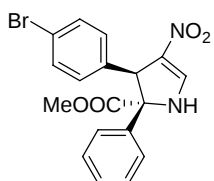
**(2R,3R)-methyl 4-nitro-2,3-diphenyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-(3a):** yield 68%;



>19/1 dr;  $[\alpha]_D^{20} = +468.5$  (c 0.4, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.10-8.11 (d,  $J = 3.56$  Hz, 1H), 7.05-7.09 (m, 5H), 6.97-6.99 (m, 3H), 6.91-6.92 (m, 2H), 6.05 (brs, 1H), 5.36 (s, 1H), 3.83 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.78, 145.50, 135.40, 134.54, 129.16, 128.77, 128.21, 128.06, 127.84, 127.36, 126.31, 53.91, 53.00; IR (KBr)  $\nu$  3226, 1738, 1564, 1429, 1373, 1221, 1176, 1137,

1048, 919, 801, 739, 699 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>) requires  $m/z$  324.1110, found  $m/z$  324.1113. The enantiomeric excess is 97% determined by HPLC (Daicel Chirapak kromasil, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 28.379 (major),  $t_R$  = 31.008 (minor).

**(2R,3R)-methyl 3-(4-bromophenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-**



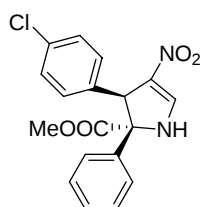
**(3b):** yield 74%; >20/1 dr;  $[\alpha]_D^{20} = +499.5$  (c 0.3, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.08-8.10 (m, 1H), 7.08-7.14 (m, 7H), 6.79-6.82 (d,  $J = 8.4$  Hz, 3H), 5.95 (brs, 1H), 5.33 (s, 1H), 3.84 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.48, 145.60, 134.67, 134.25, 131.20, 130.43, 128.58, 128.50, 126.15, 121.37,

79.753, 53.99, 52.48; IR (KBr)  $\nu$  3226, 1738, 1564, 1491, 1429, 1373, 1221, 1177, 1132, 1048, 1003, 918, 857, 828, 795, 744, 694 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>18</sub>H<sub>15</sub>BrN<sub>2</sub>O<sub>4</sub>) requires  $m/z$  402.0215, found  $m/z$  402.0213. The enantiomeric excess is 96% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 80/ 20, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 6.534 (major),  $t_R$  = 9.070 (minor).

**(-)-3b** This product was obtained in 52% yield and 96% ee (> 20:1 dr) from a reaction catalyzed by **QD-4c** (20 mol%) at 35 °C for 29 h.

**(2R,3R)-methyl**

**3-(4-chlorophenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**



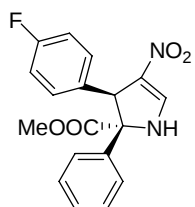
**(+)-(3c):** yield 75%; 8/1 dr;  $[\alpha]_D^{20} = +511.4$  (c 0.5, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.09-8.11 (d,  $J = 3.36$  Hz, 1H), 7.05-7.26 (m, 5H), 6.96-6.98 (d,  $J = 8.48$  Hz, 2H), 6.85-6.88 (d,  $J = 8.4$  Hz, 2H), 6.01 (brs, 1H), 5.34 (s, 1H), 3.84 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.50, 145.49, 134.28, 133.19, 131.33, 130.43, 130.08, 128.75, 128.56, 128.48, 128.26, 127.51, 126.79, 126.16, 53.99,

52.41; IR (KBr)  $\nu$  3253, 1743, 1564, 1491, 1373, 1227, 1176, 1131, 1014, 907, 733, 694 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>18</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>4</sub>) requires m/z 358.0720, found m/z 358.0717. The enantiomeric excess is 91% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 80/ 20, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R = 6.739$  (major),  $t_R = 8.598$  (minor).

**(-)-3c** This product was obtained in 65% yield and 98% ee (> 20:1 dr) from a reaction catalyzed by **QD-4c** (20 mol %) at 35 °C for 30 h.

**(2R,3R)-methyl**

**3-(4-fluorophenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**

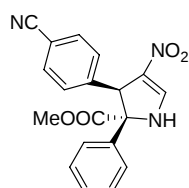


**(+)-(3d):** yield 61%; 14/1 dr;  $[\alpha]_D^{20} = +318.4$  (c 0.3, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.10-8.12 (d,  $J = 3.54$  Hz, 1H), 7.06-7.11 (m, 5H), 6.87-6.91 (m, 2H), 6.65-6.70 (m, 2H), 6.11 (brs, 1H), 5.35 (s, 1H), 3.83 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.53, 163.16, 160.71, 145.80, 134.42, 131.38, 130.33, 130.25, 128.68, 128.41, 128.38, 127.95, 126.18, 115.06, 79.87, 53.92, 52.31; IR (KBr)  $\nu$

3231, 1738, 1564, 1507, 1373, 1378, 1221, 1053, 923, 839, 755, 694 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>18</sub>H<sub>15</sub>FN<sub>2</sub>O<sub>4</sub>) requires m/z 342.1016, found m/z 342.1010. The enantiomeric excess is 96% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R = 15.489$  (major),  $t_R = 19.113$  (minor).

**(2R,3R)-methyl**

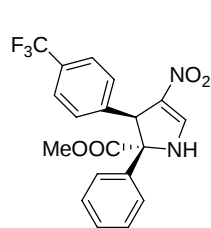
**3-(4-cyanophenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**



**(+)-(3e):** yield 82%; 10/1 dr;  $[\alpha]_D^{20} = +500.6$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.15 (s, 1H), 7.26-7.29 (m, 2H), 7.02-7.12 (m, 7H), 6.26 (brs, 1H), 5.43 (s, 1H), 3.84 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 171.97, 146.30, 141.38, 134.00, 131.80, 129.58, 128.78, 128.60, 125.98, 118.64, 111.10,

54.08, 52.91; IR (KBr)  $\nu$  3259, 2237, 1744, 1575, 1379, 1221, 1053, 924, 863, 755, 694  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_4$ ) requires  $m/z$  349.1063, found  $m/z$  349.1071. The enantiomeric excess is 95% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 38.700 (major),  $t_R$  = 44.232 (minor).

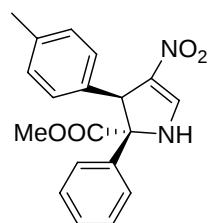
**(2R,3R)-methyl 4-nitro-2-phenyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-pyrrole-2-**



**carboxylate (+)- (3f):** yield 68%; 10/1 dr;  $[\alpha]_D^{20}$  = +520.5 (c 1.1,  $\text{CHCl}_3$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.13-8.15 (d,  $J$  = 3.53 Hz, 1H), 7.25-7.26 (m, 2H), 7.03-7.09 (m, 7H), 6.12 (brs, 1H), 5.43 (s, 1H), 3.84 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 172.25, 146.01, 139.76, 134.11, 129.143, 128.61, 128.48, 126.05, 124.98, 124.94, 79.87, 54.02, 52.73; IR (KBr)  $\nu$  3259, 1737, 1564,

1328, 1227, 1059, 1014, 907, 739, 694  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N}_2\text{O}_4$ ) requires  $m/z$  392.0984, found  $m/z$  392.0987. The enantiomeric excess is 98% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 80/ 20, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 5.388 (major),  $t_R$  = 6.636 (minor).

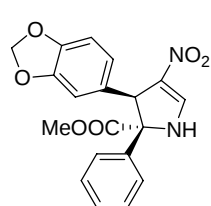
**(2R,3R)-methyl 4-nitro-2-phenyl-3-p-tolyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-(3g):** yield



59%; 8/1 dr;  $[\alpha]_D^{20}$  = +408.0 (c 0.3,  $\text{CHCl}_3$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.07-8.09 (d,  $J$  = 3.56 Hz, 1H), 7.05-7.11 (m, 5H), 6.79-6.83 (m, 4H), 6.03 (brs, 1H), 5.31 (brs, 1H), 3.82 (s, 3H), 2.12 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 172.91, 145.41, 136.91, 134.62, 132.28, 128.98, 128.78, 128.60, 128.19, 126.33, 79.96, 53.87, 52.67, 21.06; IR (KBr)  $\nu$  3226, 1738, 1569, 1429, 1367, 1221,

1176, 1132, 1048, 924, 828, 790, 761, 694  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_4$ ) requires  $m/z$  338.1267, found  $m/z$  338.1272. The enantiomeric excess is 96% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 15.573 (major),  $t_R$  = 20.017 (minor).

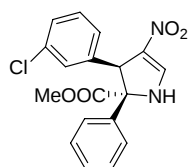
**(2R,3R)-methyl 3-(benzo[d][1,3]dioxol-5-yl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-**



**carboxylate (+)- (3h):** yield 60%; 4/1 dr;  $[\alpha]_D^{20}$  = +61.4 (c 0.4,  $\text{CHCl}_3$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.06-8.07 (d,  $J$  = 3.52 Hz, 1H), 7.13 (s, 5H), 6.46 (s, 2H), 6.38 (s, 1H), 5.92 (brs, 1H), 5.77 (s, 2H), 3.84 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 145.24, 128.38, 128.31, 126.28, 107.88, 100.91, 53.92, 52.76; IR

(KBr)  $\nu$  3226, 1744, 1581, 1491, 1446, 1367, 1238, 1171, 1036, 930, 806, 750, 694  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_6$ ) requires  $m/z$  368.1008, found  $m/z$  368.1001. The enantiomeric excess is 91% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 85/15, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 19.168 (minor),  $t_R$  = 23.826 (major).

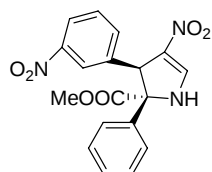
**(2R,3R)-methyl 3-(3-chlorophenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**



**(+)-(3i):** yield 69%; 11/1 dr;  $[\alpha]_D^{20}$  = +385.1 (c 0.6,  $\text{CHCl}_3$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.10-8.12 (m, 1H), 7.06-7.12 (m, 5H), 6.83-6.94 (m, 4H), 6.08 (brs, 1H), 5.33 (s, 1H), 3.84 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 172.36, 145.93, 137.67, 134.19, 133.96, 129.90, 129.28, 128.84, 128.54, 128.40, 127.55, 127.02,

126.75, 126.52, 126.13, 79.92, 54.00, 52.62; IR (KBr)  $\nu$  3226, 1743, 1575, 1435, 1373, 1227, 1183, 1143, 1087, 1053, 930, 879, 801, 750, 700  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{18}\text{H}_{15}\text{ClN}_2\text{O}_4$ ) requires  $m/z$  358.0720, found  $m/z$  358.0718. The enantiomeric excess is 97% determined by HPLC (Daicel Chirapak kromasil, hexane/ isopropanol= 80/ 20, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 12.679 (major),  $t_R$  = 13.841 (minor).

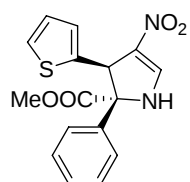
**(2R,3R)-methyl 4-nitro-3-(3-nitrophenyl)-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-(3j):**



yield 61%; 7/1 dr;  $[\alpha]_D^{20}$  = +466.3 (c 0.8,  $\text{CHCl}_3$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.18-8.20 (d,  $J$  = 2.75 Hz, 1H), 7.82-7.86 (m, 1H), 7.76 (s, 1H), 7.29 (s, 1H), 7.16-7.21 (m, 1H), 7.06-7.08 (m, 4H), 6.32 (brs, 1H), 5.50 (s, 1H), 3.86 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 171.94, 147.86, 146.48, 138.18, 134.99,

134.03, 129.09, 128.97, 128.74, 128.69, 125.96, 123.67, 122.44, 79.80, 54.13, 52.62; IR (KBr)  $\nu$  3314, 1743, 1564, 1530, 1424, 1356, 1227, 1171, 1131, 912, 806, 733, 694  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_6$ ) requires  $m/z$  369.0961, found  $m/z$  369.0965. The enantiomeric excess is >99% determined by HPLC (Daicel Chirapak kromasil, hexane/ isopropanol= 80/ 20, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 17.782 (major),  $t_R$  = 19.533 (minor).

**(2R,3R)-methyl 4-nitro-2-phenyl-3-(thiophen-2-yl)-2,3-dihydro-1H-pyrrole-2-carboxylate**

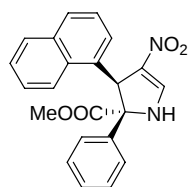


**(+)-(3k):** yield 63%; 8/1 dr;  $[\alpha]_D^{20}$  = +514.5 (c 0.4,  $\text{CHCl}_3$ );  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.05-8.07 (d,  $J$  = 3.60 Hz, 1H), 7.13-7.20 (m, 5H), 6.91-6.93 (m, 1H), 6.63-6.65 (m, 2H), 6.14 (brs, 1H), 5.62 (s, 1H), 3.83 (s, 3H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 172.37, 145.52, 138.68, 133.93, 128.59, 128.32, 127.12, 126.61,

126.62, 125.22, 53.96, 48.45; IR (KBr)  $\nu$  3241, 1743, 1569, 1429, 1367, 1221, 1160, 1131, 1047, 929, 856, 801, 755, 721, 688, 632  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ ) requires  $m/z$  330.0674, found  $m/z$  330.0679. The enantiomeric excess is 98% determined by HPLC (Daicel

Chirapak kromasil, hexane/ isopropanol= 85/15, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 25.167 (minor),  $t_R$  = 28.808 (major).

**(2R,3R)-methyl 3-(naphthalen-1-yl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**

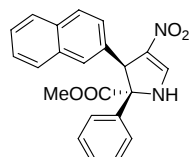


**(+)-(3l):** yield 86%; 8/1 dr;  $[\alpha]_D^{20}$  = +197.7 (c 0.9, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.39-8.42 (d,  $J$  = 8.52 Hz, 1H), 8.15-8.17 (d,  $J$  = 3.08 Hz, 1H), 7.60 (s, 1H), 7.35-7.50 (m, 3H), 7.11-7.14 (m, 1H), 7.01-7.02 (d,  $J$  = 1.16 Hz, 1H), 6.90-6.93 (m, 2H), 6.70-6.77 (m, 3H), 6.31 (s, 1H), 6.15 (brs, 1H), 3.86 (s, 3H); <sup>13</sup>C-NMR

(CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.90 164.68, 163.34, 145.99, 134.08, 133.65, 131.77, 128.45, 128.16, 127.76, 127.37, 126.52, 126.32, 126.13, 125.97, 125.38, 125.21, 124.72, 123.85, 80.37, 53.92, 47.30; IR (KBr)  $\nu$  3332, 1743, 1681, 1586, 1507, 1362, 1227, 1041, 918, 874, 768, 694 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>) requires  $m/z$  374.1267, found  $m/z$  374.1262. The enantiomeric excess is 97% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 85/15, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 7.863 (major),  $t_R$  = 10.583 (minor).

**(-)-3l** This product was obtained in 79% yield and 96% ee (> 20:1 dr) from a reaction catalyzed by **QD-4c** (20 mol%) at 35 °C for 28 h.

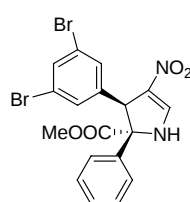
**(2R,3R)-methyl 3-(naphthalen-2-yl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**



**(+)-(3m):** yield 66%; 5/1 dr;  $[\alpha]_D^{20}$  = +662.8 (c 0.3, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.15-8.17 (d,  $J$  = 3.50 Hz, 1H), 7.64-7.66 (m, 2H), 7.50 (s, 1H), 7.32-7.41 (m, 3H), 7.10-7.13 (m, 2H), 6.92-6.96 (m, 4H), 6.15 (brs, 1H), 5.53 (s, 1H), 3.83 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.74, 145.94, 134.40,

133.06, 132.98, 132.59, 130.54, 128.24, 128.16, 127.82, 127.75, 127.49, 126.91, 126.21, 125.83, 125.74, 80.01, 53.91, 53.10; IR (KBr)  $\nu$  3236, 1732, 1558, 1367, 1221, 1171, 1137, 1047, 923, 823, 750, 694 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>) requires  $m/z$  374.1267, found  $m/z$  374.1261. The enantiomeric excess is 95% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 20.114 (major),  $t_R$  = 25.257 (minor).

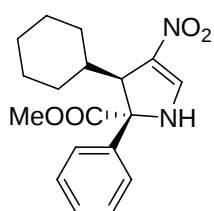
**(2R,3R)-methyl 3-(3,5-dibromophenyl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**



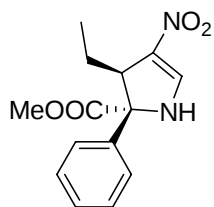
**(+)-(3n):** yield 66%; 7/1 dr;  $[\alpha]_D^{20}$  = +460.4 (c 0.6, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.11-8.13 (m, 1H), 7.15-7.26 (m, 3H), 7.05-7.09 (m, 2H), 6.98 (s, 1H), 6.10 (brs, 1H), 5.28 (s, 1H), 3.86 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$

(ppm) 172.97, 146.13, 139.66, 133.86, 132.98, 130.58, 128.91, 128.56, 125.96, 122.53, 79.99, 54.10, 52.32; IR (KBr)  $\nu$  3248, 1743, 1553, 1435, 1227, 1171, 1131, 1053, 907, 862, 806, 744, 694, 643  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{18}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}_4$ ) requires  $m/z$  483.9279, found  $m/z$  483.9286. The enantiomeric excess is 98% determined by HPLC (Daicel Chirapak kromasil, hexane/ isopropanol= 80: 20, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 20.318 (major),  $t_R$  = 23.024 (minor).

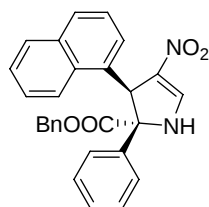
**(2R,3R)-methyl 3-cyclohexyl-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-(3o):** yield 52%; 8/1 dr;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 7.91-7.93 (d,  $J$  = 3.64 Hz, 1H), 7.31-7.48 (m, 5H), 5.799 (brs, 1H), 4.05-4.06 (d,  $J$  = 2.12 Hz, 1H), 3.75 (s, 3H), 0.81-1.6 (m, 11H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 173.64, 146.44, 134.04, 131.07, 128.82, 127.21, 126.63, 81.25, 57.28, 53.77, 50.882, 39.41, 33.48, 27.76, 27.34, 26.16, 25.94; IR (KBr)  $\nu$  3309, 2928, 2849, 1743, 1564, 1362, 1210, 1165, 795, 739, 694  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{18}\text{H}_{22}\text{N}_2\text{O}_4$ ) requires  $m/z$  330.1580, found  $m/z$  330.15776. The enantiomeric excess is 93% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 95:5, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 22.254 (major),  $t_R$  = 27.635 (minor).



**(2R,3R)-methyl 3-ethyl-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-(3p):** yield 52%; 10/1 dr;  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 7.89-7.90 (d,  $J$  = 1.27 Hz, 1H), 7.37-7.89 (m, 5H), 5.77 (brs, 1H), 4.15-4.18 (m, 1H), 3.78 (s, 3H), 1.36-1.58 (m, 2H), 0.46-0.51 (t, 3H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 173.31, 145.65, 134.17, 128.84, 128.78, 128.58, 126.47, 126.03, 79.43, 53.70, 46.74, 20.50, 9.87; The enantiomeric excess is 97% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90: 10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 10.957 (major),  $t_R$  = 15.697 (minor).

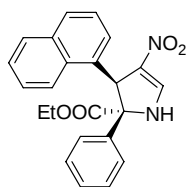


**(2R,3R)-benzyl 3-(naphthalen-1-yl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate (+)-(3q):** yield 73%; 20/1 dr;  $[\alpha]_D^{20}$  = +220.5 (c 0.9,  $\text{CHCl}_3$ );  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm) 8.34-8.37 (d,  $J$  = 8.45 Hz, 1H), 8.09 (s, 1H), 7.26-7.58 (m, 9H), 6.99-7.11 (m, 2H), 6.83-6.86 (m, 2H), 6.65-6.75 (m, 3H), 6.32 (s, 1H), 6.20 (brs, 1H), 5.21-5.32 (m, 2H);  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm) 172.13, 146.20, 134.56, 134.01, 133.59, 132.27, 131.87, 128.89, 128.80, 128.51, 128.42, 128.09, 128.01, 127.28, 126.12, 125.90, 125.33, 125.24, 124.71, 123.85, 80.33, 68.827, 47.294; IR (KBr)  $\nu$  3214, 1733, 1575, 1373, 1205, 1126, 1025, 918, 755, 700  $\text{cm}^{-1}$ ; HRMS: exact mass calcd for ( $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}_4$ ) requires  $m/z$  450.1580, found  $m/z$  450.1586. The enantiomeric excess is 97% determined



by HPLC (Daicel Chirapak kromasil, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R = 21.463$  (major),  $t_R = 23.775$  (minor).

**(2R,3R)-ethyl 3-(naphthalen-1-yl)-4-nitro-2-phenyl-2,3-dihydro-1H-pyrrole-2-carboxylate**

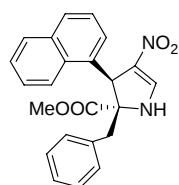


**(+)-(3r):** yield 85%; 8/1 dr;  $[\alpha]_D^{20} = +204.6$  (c 0.5, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.41-8.44 (d,  $J = 8.55$  Hz, 1H), 8.14-8.16 (d,  $J = 3.61$  Hz, 1H), 7.35-7.60 (m, 4H), 6.88-7.13 (m, 4H), 6.68-6.77 (m, 3H), 6.34 (brs, 1H), 6.31 (s, 1H), 4.26-4.36 (m, 2H), 1.17-1.28 (m, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.28, 146.44,

134.20, 133.62, 132.31, 131.98, 129.16, 128.43, 128.06, 127.97, 127.28, 126.09, 125.89, 125.34, 125.23, 124.72, 123.87, 80.31, 63.24, 47.26, 14.00; IR (KBr)  $\nu$  3298, 1732, 1580, 1520, 1452, 1373, 1221, 1030, 913, 857, 773, 739, 700 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>) requires  $m/z$  388.1423, found  $m/z$  388.1417. The enantiomeric excess is 92% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R = 12.104$  (major),  $t_R = 17.000$  (minor).

**(-)-3r** This product was obtained in 78% yield and 91% ee (> 20:1 dr) from a reaction catalyzed by QD-4c (20 mol%) at 35 °C for 31 h.

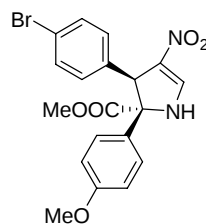
**(2R,3R)-methyl 2-benzyl-3-(naphthalen-1-yl)-4-nitro-2,3-dihydro-1H-pyrrole-2-carboxylate**



**(+)-(3s):** yield 64%; 5/1 dr; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.58-8.61 (d,  $J = 8.60$  Hz, 1H), 8.07-8.09 (d,  $J = 3.68$  Hz, 1H), 7.83-7.92 (m, 2H), 7.46-7.69 (m, 3H), 7.30-7.33 (m, 1H), 7.16-7.18 (m, 3H), 6.84-6.87 (m, 2H), 5.75 (s, 1H), 5.32 (brs, 1H), 3.83 (s 3H), 2.83-2.86 (d,  $J = 13.6$  Hz, 1H), 2.22-2.26 (d,  $J = 13.6$  Hz, 1H); <sup>13</sup>C-NMR

(CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 174.34, 147.08, 134.44, 134.28, 132.90, 130.52, 129.77, 129.60, 129.33, 129.11, 129.01, 128.84, 128.63, 127.70, 126.99, 126.00, 125.55, 125.03, 123.71, 77.06, 53.33, 47.57, 40.08; IR (KBr)  $\nu$  3370, 1744, 1586, 1508, 1440, 1373, 1227, 1048, 874, 783, 744, 694 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>23</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>) requires  $m/z$  388.1423, found  $m/z$  388.1414. The enantiomeric excess is 90% determined by HPLC (Daicel Chirapak kromasil, hexane/ isopropanol= 90/10, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R = 18.295$  (major),  $t_R = 30.672$  (minor).

**(2R,3R)-methyl 3-(4-bromophenyl)-2-(4-methoxyphenyl)-4-nitro-2,3-dihydro-1H-pyrrole-2-carboxylate**

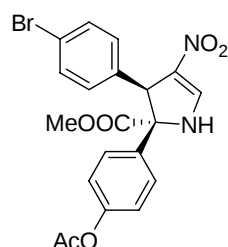


**(+)-(3t):** yield 60%; >20/1 dr; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 8.10 (s, 1H), 7.13-7.16 (d,  $J = 8.52$  Hz, 2H), 6.94-6.98 (m, 2H), 6.79-6.82 (d,  $J = 8.34$  Hz, 2H), 6.62-6.63 (m, 2H), 6.21 (brs, 1H), 5.28 (s, 1H), 3.81 (s, 3H), 3.69 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 172.64, 159.49, 146.12, 134.89, 131.21, 130.43, 129.91, 127.44, 126.18, 121.30, 113.82, 79.44, 55.29, 53.87, 52.41; IR

(KBr)  $\nu$  3236, 1743, 1564, 1508, 1412, 1367, 1255, 1227, 1176, 1137, 1037, 913, 829, 801, 767 cm<sup>-1</sup>;

HRMS: exact mass calcd for (C<sub>19</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>5</sub>) requires m/z 432.0321, found m/z 432.0318. The enantiomeric excess is 97% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 70/ 30, flow rate 1.0 mL/min): *Major*-diastereomer, *t<sub>R</sub>* = 5.595 (major), *t<sub>R</sub>* = 7.211 (minor).

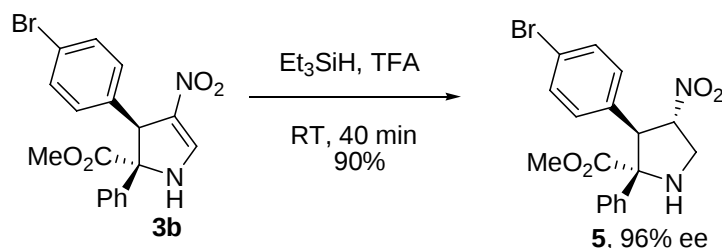
**(2R,3R)-methyl 2-(4-acetoxyphenyl)-3-(4-bromophenyl)-4-nitro-2,3-dihydro-1H-pyrrole-2-**



**carboxylate (+)- (3u):** yield 99%; 6/1 dr; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 8.04 (s, 1H), 7.05-7.15 (m, 4H), 6.77-6.85 (m, 4H), 5.28 (s, 1H), 3.78 (s, 3H), 2.23 (s, 3H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm) 172.22, 169.24, 150.48, 147.11, 146.73, 134.69, 131.92, 131.47, 131.27, 130.37, 129.43, 127.49, 126.81, 122.27, 121.52, 101.55, 79.53, 55.89, 53.92, 21.11; IR (KBr) ν 3236, 1749, 1575, 1435,

1373, 1221, 1003, 912, 862, 778 cm<sup>-1</sup>; HRMS: exact mass calcd for (C<sub>20</sub>H<sub>17</sub>BrN<sub>2</sub>O<sub>6</sub>) requires m/z 460.0270, found m/z 460.0275. The enantiomeric excess is 90% determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 90:10, flow rate 1.0 mL/min): *Major*-diastereomer, *t<sub>R</sub>* = 36.487 (major), *t<sub>R</sub>* = 48.395 (minor).

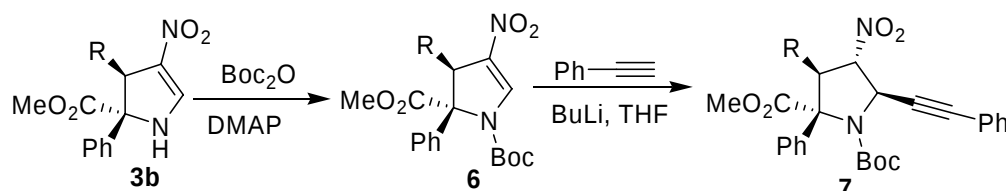
**Diastereoselective reduction of 3b**



To a suspension of **3b** (48.6 mg, 0.12 mmol) in trifluoroacetic acid (1.0 mL) was added triethylsilane (0.24 mL, 1.5 mmol) in one portion and the resulting mixture was stirred at room temperature for 40 minutes. When the reaction was completed, saturated aqueous NaHCO<sub>3</sub> was added and the resulting mixture was extracted with EtOAc. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was purified through flash chromatography on silica gel to give the product (43.6 mg, 90% yield); [α]<sub>D</sub><sup>20</sup> = +27.2 (c 0.9, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) δ (ppm) 7.17-7.26 (m, 4H), 7.07-7.09 (m, 3H), 6.90-6.92 (m, 2H), 5.00-5.05 (m, 1H), 4.82-4.84 (d, *J* = 3.96 Hz, 1H), 3.88-3.91 (m, 1H), 3.77 (s, 3H), 3.72-3.76 (m, 1H), 3.15 (brs, 1H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz) δ (ppm) 144.63, 137.45, 137.22, 131.38, 130.94, 128.04, 127.72, 126.75, 121.42, 91.02, 75.71, 55.92, 53.48, 48.89; IR (KBr) ν 3353, 2956, 1737, 1553, 1496, 1362, 1227, 1081, 1014, 828, 733, 699 cm<sup>-1</sup>; The enantiomeric excess is 96%, determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 85/15, flow rate 1.0 mL/min): *Major*-diastereomer, *t<sub>R</sub>* =

10.504 (major),  $t_R$  = 12.059 (minor). After recrystallized from a solvent mixture of *iso*-propanol and hexane (*i*-PrOH/ hexane= 1/ 3) by slow evaporation, a single crystal was obtained with >99% ee.

### Conversion of (+)-(3b) to 7.<sup>3</sup>

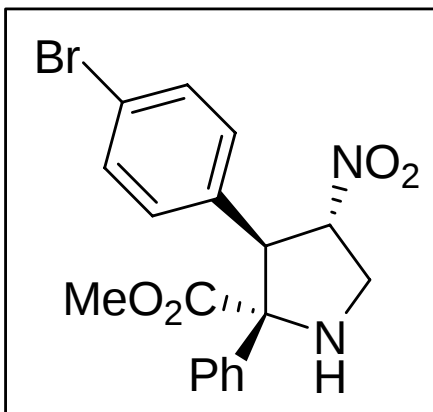
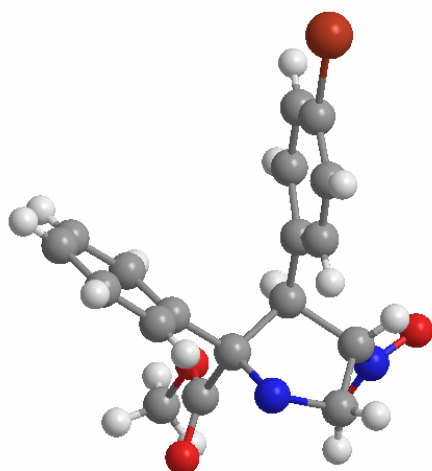


To a mixture of **3b** (30mg, 0.074mmol) and (Boc)<sub>2</sub>O (0.17mL, 0.74mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added DMAP (9mg, 0.074mmol), the resulting reaction mixture was stirred at room temperature for 10 min. Then solvent was removed under reduced pressure and the residue was purified by flash chromatography to give the product **6** (26mg, 70%). *n*BuLi (0.17 mL, 0.5 mmol, 2.81M in hexanes) was added to a solution of phenylacetylene (0.066 mL, 0.6 mmol) in THF (1.0 mL) at –78 °C, and then the mixture was stirred at 0 °C for 3 h. A solution of **6** (20 mg, 0.04 mmol) in THF (0.5 mL) was added dropwise to the mixture at –78 °C. After the mixture had been stirred at this temperature for 12h, the reaction was quenched with a saturated aqueous NH<sub>4</sub>Cl solution (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine and dried with anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by flash chromatography to give **7** (18 mg, 75%).  $[\alpha]_D^{20}$  = –26.5 (c 0.2, CHCl<sub>3</sub>); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  (ppm) 7.33–7.54 (m, 7H), 7.15–7.25 (m, 3H), 6.99 (m, 2H), 6.59–6.61 (d, *J* = 8.4 Hz 1H), 5.50–5.53 (d, *J* = 8.2 Hz, 1H), 5.15–5.21 (m, 1H), 4.75–4.79 (d, *J* = 12.2 Hz, 1H), 3.88 (s, 1H), 1.43–1.62 (m, 9H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  (ppm) 131.95, 131.84, 130.83, 129.65, 129.22, 129.17, 128.61, 128.36, 127.27, 123.51, 89.52, 82.52, 53.35, 28.25; The enantiomeric excess is 96%, determined by HPLC (Daicel Chirapak AD, hexane/ isopropanol= 97/3, flow rate 1.0 mL/min): *Major*-diastereomer,  $t_R$  = 6.624 (minor),  $t_R$  = 10.518 (major).

### References:

- (1) R. S. Bon, C. Hong, M. J. Bouma, R. F. Schmitz, F. Kanter; M. Lutz, A. L Spek, R. Orru, *Org. Lett.* **2003**, 5, 3759–3762.
- (2) (a) S. E. Denmark, L. R. Marcin, *J. Org. Chem.* **1993**, 58, 3850–3856. (b) V. J. Bulbule, G. K. Jnaneshwara, R. R. Deshmukh, H. B. Borate, V. H. Deshpande, *Synthetic Commun.* **2001**, 31, 3623–3626.
- (3) Dong, L.; Xu, Y.-J.; Yuan, W. –C.; Cui, X.; Cun, L. –F.; Gong, L. –Z.; *Eur. J. Org. Chem.* **2006**, 4.93–4105

# X-ray single crystal data for 5



|                      |                                                                 |
|----------------------|-----------------------------------------------------------------|
| Chemical formula     | C <sub>18</sub> H <sub>17</sub> BrN <sub>2</sub> O <sub>4</sub> |
| Formula weight       | 404.24                                                          |
| Space group          | P2(1)                                                           |
| Z                    | 2                                                               |
| a, Å                 | 8.540(4)                                                        |
| b, Å                 | 6.264(3)                                                        |
| c, Å                 | 17.396(9)                                                       |
| α, °                 | 90.00                                                           |
| β, °                 | 103.400(15)                                                     |
| γ, °                 | 90.00                                                           |
| V, Å <sup>3</sup>    | 905.2(8)                                                        |
| T, K                 | 273(2)                                                          |
| ρ, g/cm <sup>3</sup> | 1.483                                                           |

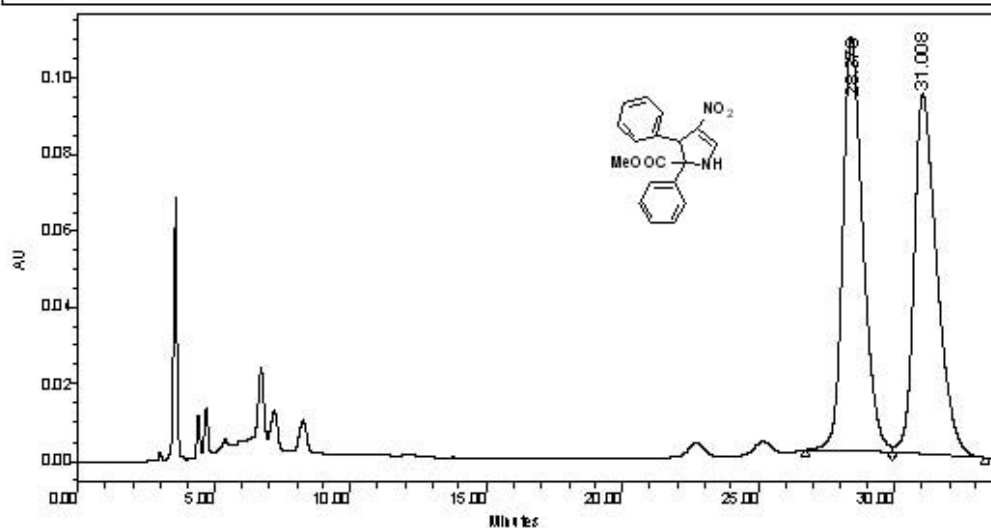
USTC

Project Name: xuemx  
Reported by User: System

Breeze

# SAMPLE INFORMATION

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| Sample Name:      | go-O-K-10%    | Acquired By:     | System                |
| Sample Type:      | Unknown       | Date Acquired:   | 9/25/2007 11:25:11 AM |
| Vial:             | 1             | Acq. Method:     | xmx10%                |
| Injection #:      | 1             | Date Processed:  | 11/17/2007 2:38:48 PM |
| Injection Volume: | 20.00 ul      | Channel Name:    | 2487 Channel 1        |
| Run Time:         | 60.00 Minutes | Sample Set Name: |                       |



|   | RT<br>(min) | Area<br>(AU*sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|------------------|--------|----------------|----------|
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| 2 | 31.008      | 5492526          | 49.63  | 94175          | 46.49    |

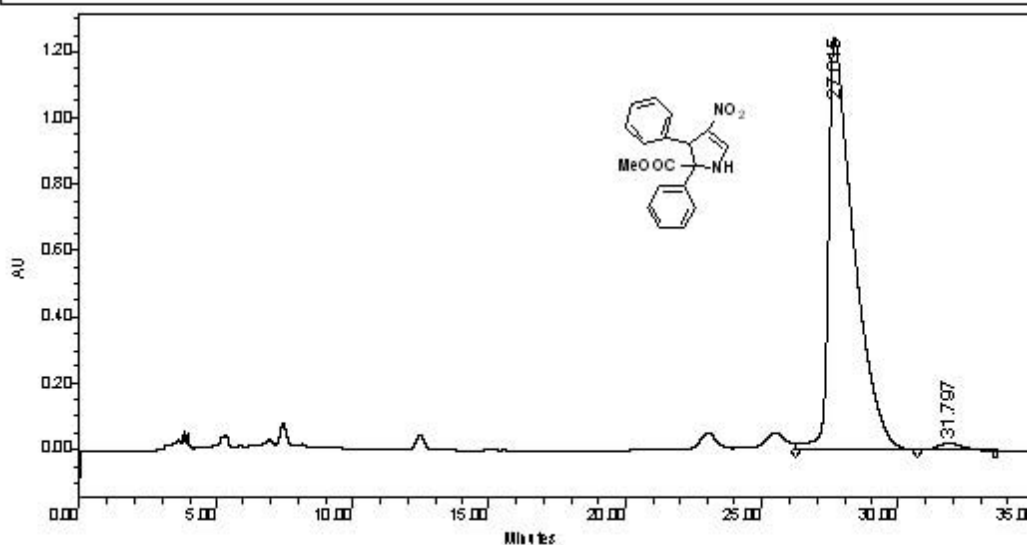
USTC

Project Name: xuemx  
Reported by User: System

Breeze

# SAMPLE INFORMATION

|                   |                |                  |                       |
|-------------------|----------------|------------------|-----------------------|
| Sample Name:      | go-200710114.  | Acquired By:     | System                |
| Sample Type:      | Unknown        | Date Acquired:   | 10/12/2007 5:21:10 PM |
| Vial:             | 1              | Acq. Method:     | xmx10%                |
| Injection #:      | 1              | Date Processed:  | 11/17/2007 2:37:34 PM |
| Injection Volume: | 20.00 ul       | Channel Name:    | 2487 Channel 1        |
| Run Time:         | 100.00 Minutes | Sample Set Name: |                       |



|   | RT<br>(min) | Area<br>(AU*sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|------------------|--------|----------------|----------|
| 1 | 27.615      | 79918993         | 98.24  | 1245169        | 98.27    |
| 2 | 31.797      | 1430465          | 1.76   | 21973          | 1.73     |

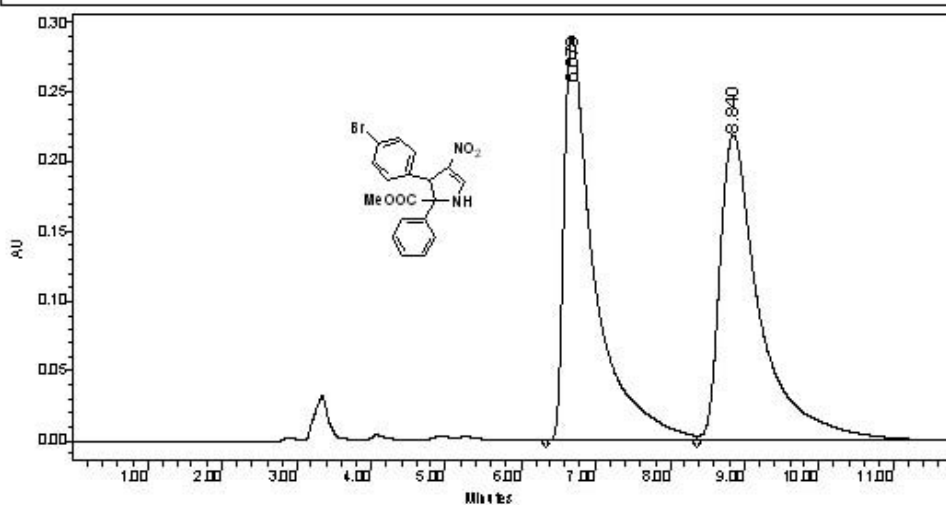
USTC

Project Name: gqx  
Reported by User: System

Breeze

# SAMPLE INFORMATION

|                   |                          |                  |                       |
|-------------------|--------------------------|------------------|-----------------------|
| Sample Name:      | go-0710162-2- dl AD- 20% | Acquired By:     | System                |
| Sample Type:      | Unknown                  | Date Acquired:   | 10/19/2007 4:09:35 PM |
| Vial:             | 1                        | Acq. Method:     | gqx20%                |
| Injection #:      | 1                        | Date Processed:  | 11/16/2007 2:13:56 PM |
| Injection Volume: | 20.00 ul                 | Channel Name:    | 2487 Channel 1        |
| Run Time:         | 100.00 Minutes           | Sample Set Name: |                       |



|   | RT<br>(min) | Area<br>( $\mu$ sec) | % Area | Height<br>( $\mu$ ) | % Height |
|---|-------------|----------------------|--------|---------------------|----------|
| 1 | 6.678       | 8243301              | 50.22  | 290661              | 57.03    |
| 2 | 8.840       | 8169874              | 49.78  | 219014              | 42.97    |

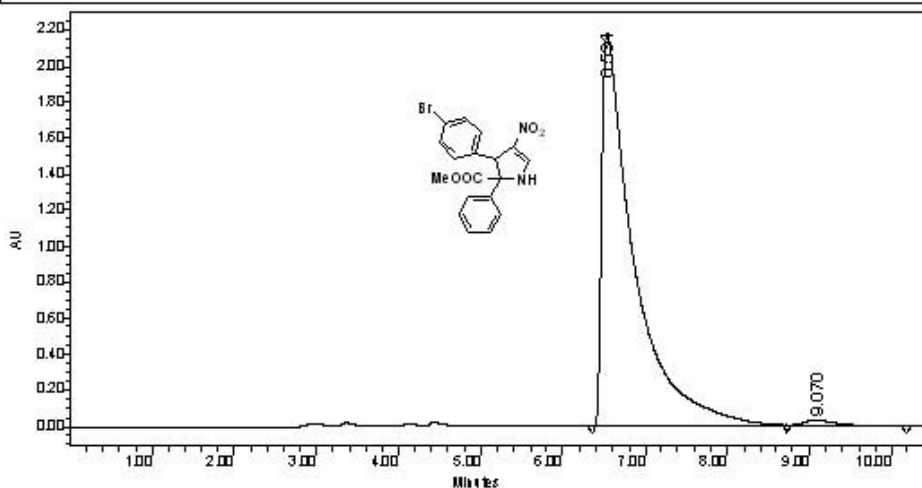
USTC

Project Name: gqx  
Reported by User: System

*Breeze*

# SAMPLE INFORMATION

|                   |                  |                  |                       |
|-------------------|------------------|------------------|-----------------------|
| Sample Name:      | gc-071017 AD-20% | Acquired By:     | System                |
| Sample Type:      | Unknown          | Date Acquired:   | 10/19/2007 7:17:01 PM |
| Vial:             | 1                | Acq. Method:     | gqx20%                |
| Injection #:      | 1                | Date Processed:  | 11/16/2007 2:12:46 PM |
| Injection Volume: | 20.00 ul         | Channel Name:    | 2487 Channel 1        |
| Run Time:         | 100.00 Minutes   | Sample Set Name: |                       |



|   | RT<br>(min) | Area<br>( $10^6$ sec) | % Area | Height<br>(AU) | %<br>Height |
|---|-------------|-----------------------|--------|----------------|-------------|
| 1 | 6.534       | 59578859              | 98.18  | 2185716        | 98.46       |
| 2 | 9.070       | 1104315               | 1.82   | 34359          | 1.55        |

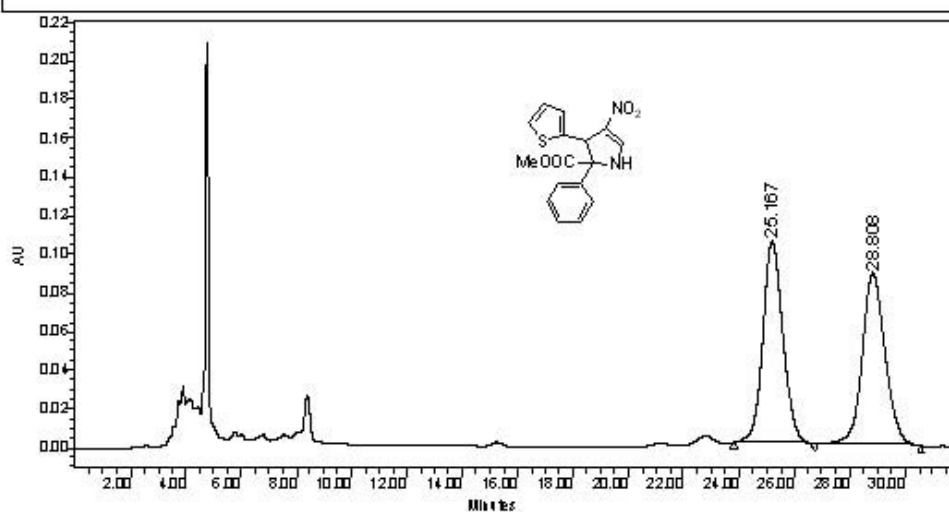
USTC

Project Name: gqx  
Reported by User: System

Breeze

# SAMPLE INFORMATION

|                   |                          |                  |                       |
|-------------------|--------------------------|------------------|-----------------------|
| Sample Name:      | go-200710217--DL-Km-15%- | Acquired By:     | System                |
| Sample Type:      | Unknown                  | Date Acquired:   | 10/28/2007 7:32:13 PM |
| Vial:             | 1                        | Acq. Method:     | gqx15 %               |
| Injection #:      | 1                        | Date Processed:  | 10/28/2007 8:05:03 PM |
| Injection Volume: | 20.00 ul                 | Channel Name:    | 2487 Channel 1        |
| Run Time:         | 100.00 Minutes           | Sample Set Name: |                       |



|   | RT<br>(min) | Area<br>( $10^6$ sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|-----------------------|--------|----------------|----------|
| 1 | 25.167      | 5280927               | 50.85  | 104479         | 54.05    |
| 2 | 28.808      | 5105364               | 49.15  | 88824          | 45.95    |

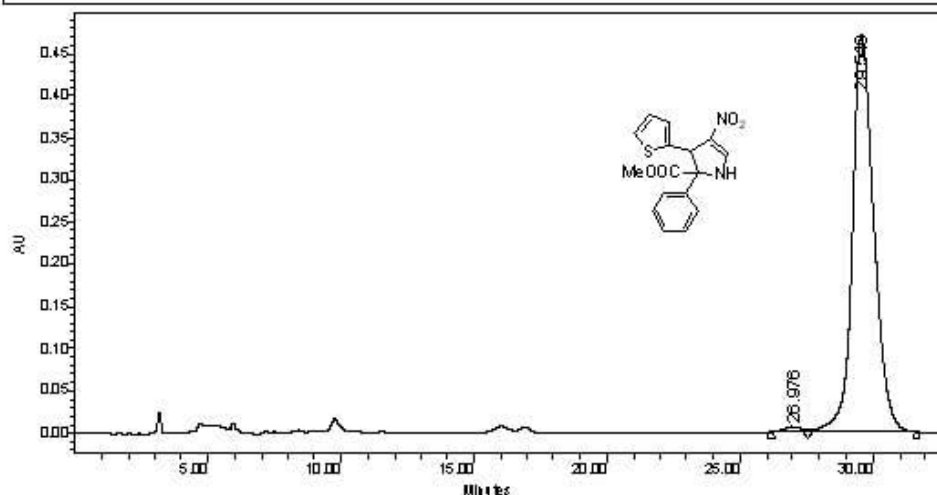
USTC

Project Name: gqx  
Reported by User: System

1/Breeze

# SAMPLE INFORMATION

|                   |                |                  |                        |
|-------------------|----------------|------------------|------------------------|
| Sample Name:      | go-200710213   | Acquired By:     | System                 |
| Sample Type:      | Unknown        | Date Acquired:   | 10/31/2007 12:38:01 PM |
| Vial:             | 1              | Acq. Method:     | gqx15 %                |
| Injection #:      | 1              | Date Processed:  | 11/16/2007 2:52:40 PM  |
| Injection Volume: | 20.00 ul       | Channel Name:    | 2487 Channel 1         |
| Run Time:         | 100.00 Minutes | Sample Set Name: |                        |



|   | RT<br>(min) | Area<br>(AU*sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|------------------|--------|----------------|----------|
| 1 | 26.976      | 297449           | 1.11   | 6302           | 1.32     |
| 2 | 29.540      | 26438005         | 98.89  | 471448         | 98.68    |

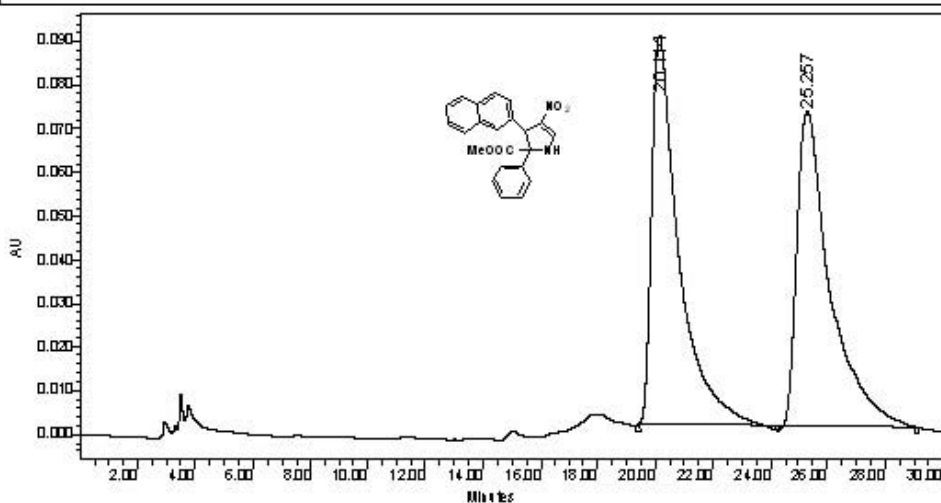
USTC

Project Name: gqx  
Reported by User: System

*Breeze*

# SAMPLE INFORMATION

|                   |                        |                  |                        |
|-------------------|------------------------|------------------|------------------------|
| Sample Name:      | go-200710233-DL-AD-10% | Acquired By:     | System                 |
| Sample Type:      | Unknown                | Date Acquired:   | 10/24/2007 10:59:28 AM |
| Vial:             | 1                      | Acq. Method:     | gqx10%                 |
| Injection #:      | 1                      | Date Processed:  | 11/16/2007 3:01:07 PM  |
| Injection Volume: | 20.00 ul               | Channel Name:    | 2487 Channel 1         |
| Run Time:         | 100.00 Minutes         | Sample Set Name: |                        |



|   | RT<br>(min) | Area<br>( $\mu$ sec) | % Area | Height<br>( $\mu$ ) | %<br>Height |
|---|-------------|----------------------|--------|---------------------|-------------|
| 1 | 20.114      | 5866595              | 50.40  | 89311               | 55.34       |
| 2 | 25.257      | 5774193              | 49.60  | 72069               | 44.66       |

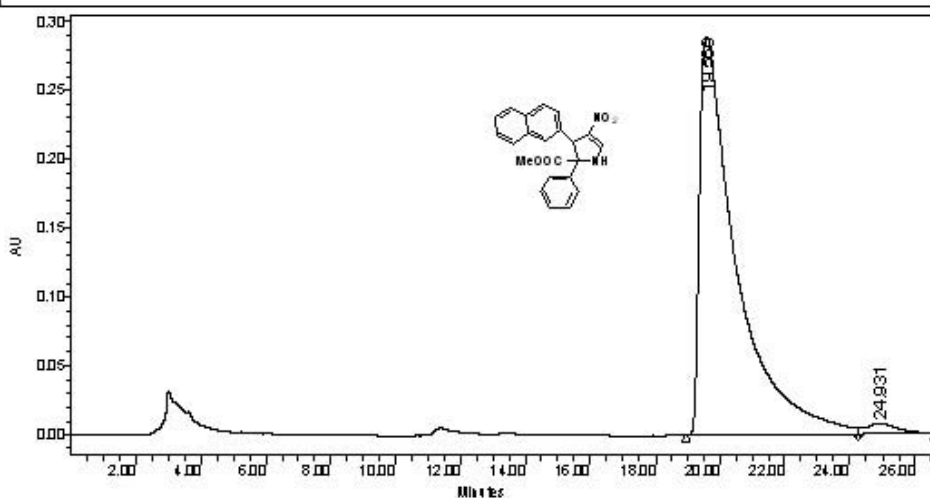
USTC

Project Name: gqx  
Reported by User: System

*1/Breeze*

# SAMPLE INFORMATION

|                   |                |                  |                        |
|-------------------|----------------|------------------|------------------------|
| Sample Name:      | go-20071020224 | Acquired By:     | System                 |
| Sample Type:      | Unknown        | Date Acquired:   | 10/30/2007 10:04:20 AM |
| Vial:             | 1              | Acq. Method:     | gqx10%                 |
| Injection #:      | 2              | Date Processed:  | 10/30/2007 10:31:43 AM |
| Injection Volume: | 20.00 ul       | Channel Name:    | 2487 Channel 1         |
| Run Time:         | 100.00 Minutes | Sample Set Name: |                        |



|   | RT<br>(min) | Area<br>(AU*sec) | % Area | Height<br>(AU) | %<br>Height |
|---|-------------|------------------|--------|----------------|-------------|
| 1 | 19.566      | 22815655         | 97.73  | 289347         | 97.48       |
| 2 | 24.931      | 530680           | 2.27   | 7494           | 2.52        |

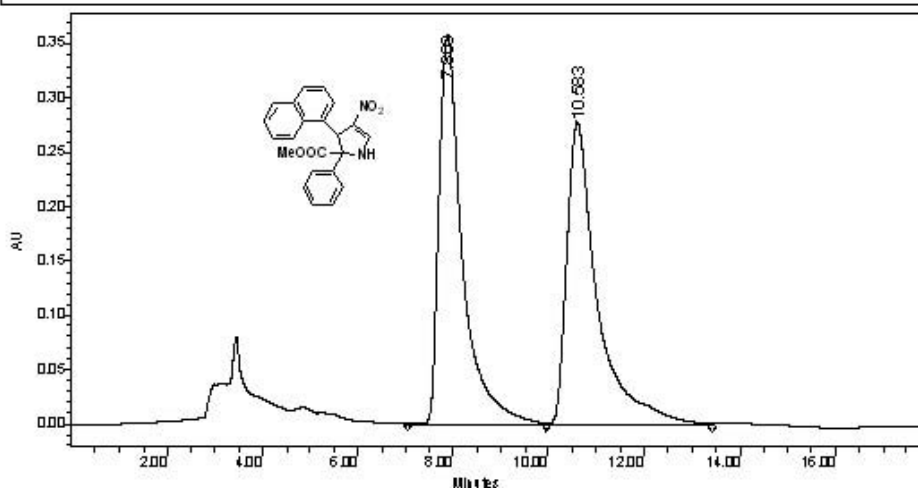
USTC

Project Name: gq×  
Reported by User: System

*Breeze*

# SAMPLE INFORMATION

|                   |                         |                  |                        |
|-------------------|-------------------------|------------------|------------------------|
| Sample Name:      | gc-200710232-DL-AD- 15% | Acquired By:     | System                 |
| Sample Type:      | Unknown                 | Date Acquired:   | 10/24/2007 9:44:27 AM  |
| Vial:             | 1                       | Acq. Method:     | gq×15%                 |
| Injection #:      | 2                       | Date Processed:  | 10/24/2007 10:02:50 AM |
| Injection Volume: | 20.00 ul                | Channel Name:    | 2487 Channel 1         |
| Run Time:         | 100.00 Minutes          | Sample Set Name: |                        |



|   | RT<br>(min) | Area<br>(AU <sup>2</sup> sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|-------------------------------|--------|----------------|----------|
| 1 | 7.863       | 12325142                      | 49.75  | 359656         | 56.33    |
| 2 | 10.583      | 12450146                      | 50.25  | 278769         | 43.67    |

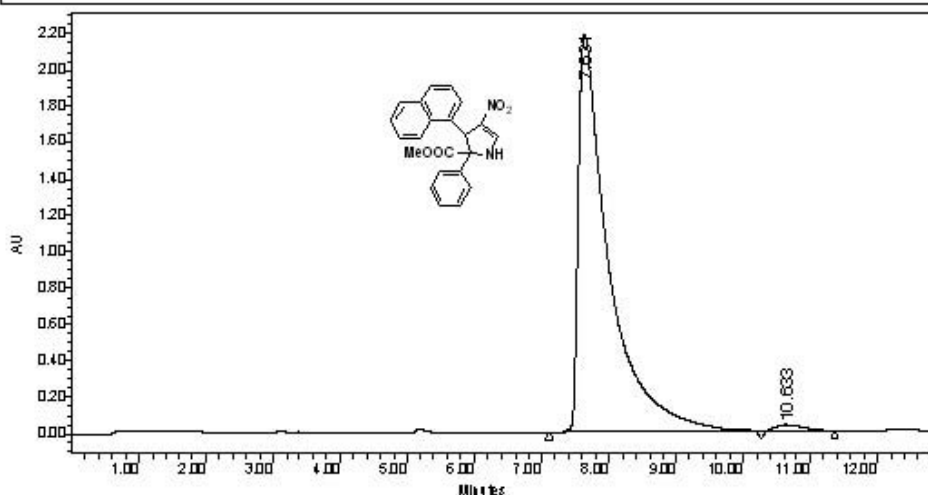
USTC

Project Name: gqx  
Reported by User: System

1/Breeze

# SAMPLE INFORMATION

|                   |                |                  |                       |
|-------------------|----------------|------------------|-----------------------|
| Sample Name:      | go-200710223   | Acquired By:     | System                |
| Sample Type:      | Unknown        | Date Acquired:   | 10/30/2007 7:40:22 AM |
| Vial:             | 1              | Acq. Method:     | gqx15 %               |
| Injection #:      | 1              | Date Processed:  | 10/30/2007 7:54:46 AM |
| Injection Volume: | 20.00 ul       | Channel Name:    | 2487 Channel 1        |
| Run Time:         | 100.00 Minutes | Sample Set Name: |                       |



|   | RT<br>(min) | Area<br>(AU*sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|------------------|--------|----------------|----------|
| 1 | 7.631       | 69463526         | 98.34  | 2192447        | 98.31    |
| 2 | 10.633      | 1172829          | 1.66   | 37711          | 1.69     |

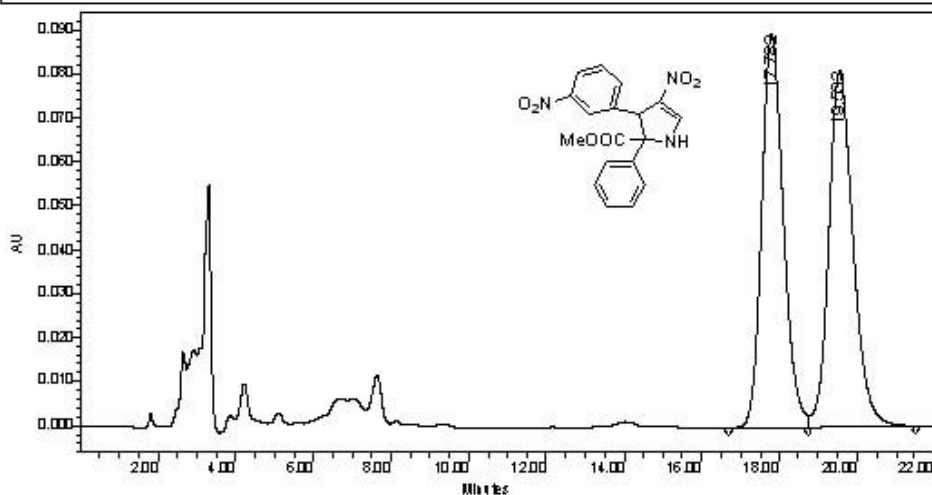
USTC

Project Name: gqx  
Reported by User: System

11/16/2007

# SAMPLE INFORMATION

|                   |                     |                  |                      |
|-------------------|---------------------|------------------|----------------------|
| Sample Name:      | go-200710216-repeat | Acquired By:     | System               |
| Sample Type:      | Unknown             | Date Acquired:   | 11/1/2007 8:02:39 AM |
| Vial:             | 1                   | Acq. Method:     | gqx20%               |
| Injection #:      | 3                   | Date Processed:  | 11/1/2007 8:25:49 AM |
| Injection Volume: | 20.00 ul            | Channel Name:    | 2487 Channel 1       |
| Run Time:         | 100.00 Minutes      | Sample Set Name: |                      |



|   | RT<br>(min) | Area<br>( $\mu$ s $\cdot$ sec) | % Area | Height<br>( $\mu$ ) | %<br>Height |
|---|-------------|--------------------------------|--------|---------------------|-------------|
| 1 | 17.782      | 3489303                        | 49.62  | 89802               | 52.47       |
| 2 | 19.533      | 3542851                        | 50.38  | 81338               | 47.53       |

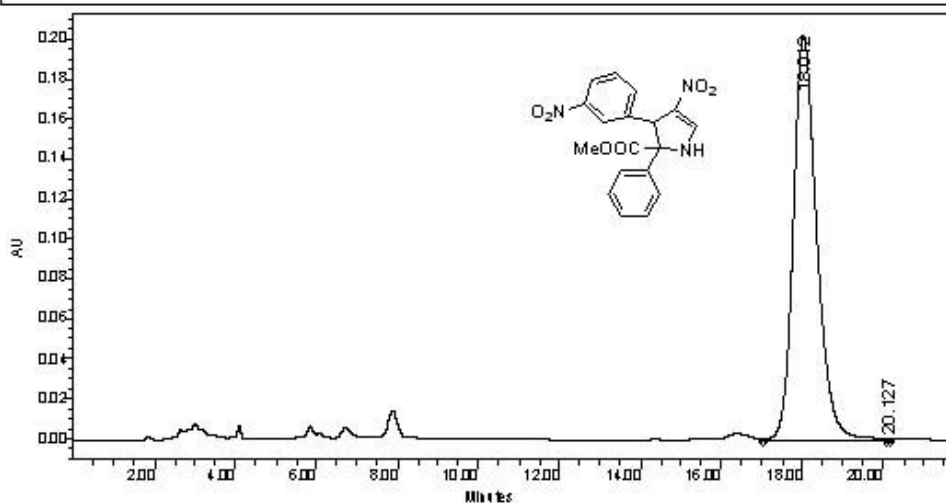
USTC

Project Name: gqx  
Reported by User: System

*Breeze*

# SAMPLE INFORMATION

|                   |                     |                  |                      |
|-------------------|---------------------|------------------|----------------------|
| Sample Name:      | go-200710212-repeat | Acquired By:     | System               |
| Sample Type:      | Unknown             | Date Acquired:   | 11/1/2007 8:25:32 AM |
| Vial:             | 1                   | Acq. Method:     | gqx20%               |
| Injection #:      | 4                   | Date Processed:  | 11/1/2007 8:48:36 AM |
| Injection Volume: | 20.00 ul            | Channel Name:    | 2487 Channel 1       |
| Run Time:         | 100.00 Minutes      | Sample Set Name: |                      |



|   | RT<br>(min) | Area<br>(AU*sec) | % Area | Height<br>(AU) | % Height |
|---|-------------|------------------|--------|----------------|----------|
| 1 | 18.012      | 8079875          | 99.95  | 202272         | 99.52    |
| 2 | 20.127      | 3905             | 0.05   | 977            | 0.48     |

