SURPORTING INFORMATION

Diastereoselectivity-switchable and Enantioselective 1,3-Dipolar Cycloaddition of Nitrones to Alkylidene Malonates

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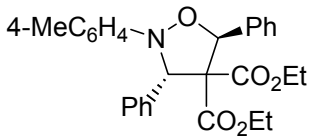
General information: All reactions were carried out under dry notrogen atmosphere. All of the solvents were purified according to the standard method before use. Isopropyl acetate was distilled over well-activated anhydrous $CaSO_4$. All of the nitrones [1] and alkylidene malonates [2] were synthesized according to the literature. MS 4Å was powdered and activated before use. All glassware was flame dried and cooled under a steam of dry nitrogen before use.

I. 1,3-Dipolar cycloaddations to *exo* adducts

General procedures for cycloaddition between nitrones and alkylidene malonates to give *exo* products. A mixture of $Co(ClO_4)_2 \cdot 6(H_2O)$ (4.6 mg, 0.013 mmol, 5 mol%) and ligand **1** (3.1 mg, 0.0087 mmol, 3.3 mol%) in the mixture of toluene and isopropyl acetate (1.5 mL) was stirred at 50℃ for 4 hours under N_2 atmosphere. After cooling to room temperature, the pale amaranth solution was added into a reaction tube with powdered MS 4Å (250 mg). To this mixture was added the solution of alkylidene malonate (0.3 mmol) in the mixture of toluene and isopropyl acetate (1 mL). After stirring for 0.5 h at 0℃, nitrone (0.25 mmol) was added. The resulting suspension was stirred for 20 hours at 0℃. Then 0.5 mL of TMEDA was added and stirred for additional 10 min. After the reaction was completed (monitored by TLC), the reacting mixture was filtrated through silica gel and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure to give crude product, which was used to determine the diastereomer ratio by ^1H NMR. The residue was purified by flash chromatography (silica gel, petroleum ester/ethyl acetate) to afford the pure product. The *ee* was determined by HPLC analysis using a chiral column (Chiralcel

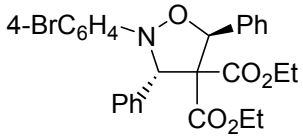
AD column with hexane/^{i}PrOH as eluent).

Table 1, Entry 1: Diethyl *trans*-3,5-diphenyl-2-(*p*-methylphenyl)-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/7, v/v) was used as the solvent]. Yield: 106.7 mg (93%); Exo/endo: >99/1; ee%: 91% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 14.76 min, t_r (major) = 19.63 min). $[\alpha]_D^{20}$ = +39.8° (c 1.00, Ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.42 (m, 4H), 7.26-7.20 (m, 6H), 6.98-6.91 (m, 4H), 6.16 (s, 1H), 5.38 (s, 1H), 3.74-3.65 (m, 2H), 3.27-3.19 (m, 2H), 2.16 (s, 3H), 0.67 (t, *J* = 7.8 Hz, 3H), 0.59 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.29, 167.89, 146.68 (d), 137.75, 135.69, 133.78, 129.37, 129.19, 128.76, 128.61, 128.32, 127.47, 119.22, 83.51, 75.96, 74.06, 61.82, 61.54, 20.05, 13.56, 13.48; LRMS-EI (m/e): 459(M^+, 100.0), 105(100.0); IR(KBr), 3063, 1734, 1612, 1260 cm^{-1}; Anal. Calcd for $C_{28}H_{29}NO_5$: C, 73.18%; H, 6.36%; N, 3.05%; Found: C, 72.91%, H, 6.41%, N, 3.07%; White solid, mp 104-105℃.

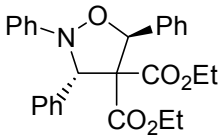
Table 1, Entry 2: Diethyl 2-(*p*-bromophenyl)-*trans*-3,5-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure (isopropyl acetate was used as the solvent). Yield: 99.8 mg (76%); Exo/endo: >99/1; ee%: 95% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 15.43 min, t_r (major) = 21.45 min). $[\alpha]_D^{20}$ = +31.9° (c 1.00, Ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.19 (m, 12H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.14 (s, 1H), 5.35 (s, 1H), 3.77-3.67 (m, 2H), 3.30-3.22(m, 2H), 0.71 (t, *J* = 7.5 Hz, 3H), 0.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.74, 167.15, 148.06, 137.22, 134.85, 131.39, 128.77, 128.60, 128.59, 128.49, 128.08, 127.01, 119.24, 116.02, 83.03, 75.24, 74.49, 61.67, 61.33, 13.25, 13.13; LRMS-EI (m/e): 525 [M^+(^{81}Br), 96.7], 523 [M^+(^{79}Br), 100.0] 169 (98.1);

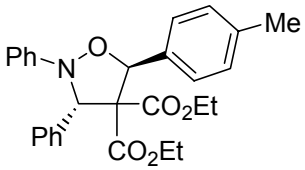
IR(KBr), 3063, 1730, 1590, 1489, 1263 cm^{-1}; Anal. Calcd for $C_{27}H_{26}BrNO_5$: C, 61.84%; H, 5.00%; N, 2.67%; Br, 15.24%; Found: C, 61.54%, H, 5.04%, N, 2.60%, Br, 15.30%; White solid, mp 135-136℃.

Table 1, Entry 3: (3,5 *trans*) Diethyl 2,3,5-triphenyl-4,4-isoxazolidine-dicarboxylate:



Prepared according to general procedure (isopropyl acetate was used as the solvent). Yield: 104.2 mg (94%); Exo/endo: >99/1; ee%: 91% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 12.86 min, t_r (major) = 16.07min). $[\alpha]_D^{20}$ = +51.6° (c 1.12, Ethyl acetate). When isopropyl acetate/toluene (1/8, v/v) was used as the solvent. Yield: 104.5 mg (94%); Exo/endo: >97/3; ee%: 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56-7.49 (m, 4H), 7.34-7.17 (m, 8H), 7.09-6.94 (m, 3H), 6.23 (s, 1H), 5.47 (s, 1H), 3.83-3.73 (m, 2H), 3.36-3.28 (m, 2H), 0.78 (t, *J* = 7.2 Hz, 3H), 0.67 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.82, 167.35, 148.95, 137.58, 135.17, 128.83, 128.43, 128.33, 127.99, 127.06, 123.33, 117.86, 82.99, 75.28, 74.62, 61.51, 61.21, 13.22, 13.11; LRMS-EI (m/e): 445(M^+, 42.1), 91(100.0); IR(KBr), 3067, 1730, 1598, 1257 cm^{-1}; Anal. Calcd for $C_{27}H_{27}NO_5$: C, 72.79%; H, 6.11%; N, 3.14%; Found: C, 72.62%, H, 6.08%, N, 3.36%. White solid, mp 109-110℃.

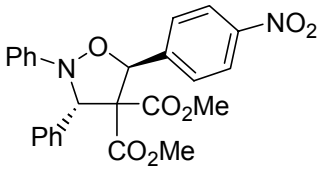
Table 1, Entry 4: (3,5 *trans*) Diethyl 5-(*p*-methlyphenyl)-2,3-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/10, v/v) was used as the solvent]. Yield: 109.3 mg (95%); Exo/endo: >95/5; ee%: 92% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 14.30 min, t_r (major) = 20.10 min). $[\alpha]_D^{20}$ = +51.1° (c 1.00, Ethyl acetate) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.33-6.92 (m, 12H), 6.12 (s, 1H), 5.39 (s, 1H), 3.78-3.66 (m, 2H), 3.35-3.21 (m, 2H), 2.27 (s, 3H), 0.71(t, *J* = 7.2 Hz, 3H), 0.62 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.92, 167.39, 149.05, 138.19, 137.70,

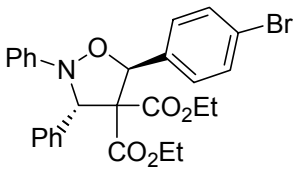
132.07, 128.84, 128.64, 128.43, 128.34, 127.00, 123.23, 117.78, 82.97, 75.25, 74.55, 61.52, 61.17, 21.12, 13.22, 13.08; LRMS-EI (m/e): 459 (M^+, 23.4),91 (100.0); IR(KBr), 3059, 1727, 1597, 1491, 1247 cm^{-1}; Anal. Calcd for $C_{27}H_{29}NO_5$: C, 73.18%; H, 6.36%; N, 3.05%; Found: C, 73.03%, H, 6.39%, N, 2.93%; White solid, mp: 123-124℃.

Table 1, Entry 5: (3,5 *trans*) Dimethyl 5-(*p*-nitrophenyl)-2,3-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/10, v/v) was used as the solvent]. Yield: 107.7 mg (93%); Exo/endo: >97/3; ee%: 94% (determined by HPLC analysis: Chiralcel AD, 20/80 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 20.00 min, t_r (major) = 30.28 min). $[\alpha]_D^{20}$ = +43.9° (c 1.00, Ethyl acetate).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.66 (d, *J* = 8.7 Hz, 2H), 7.48 (m, 2H), 7.30 (m, 3H), 7.20 (m, 2H), 7.01 (m, 3H), 6.25 (s, 1H), 5.44 (s, 1H), 3.10 (s, 3H), 3.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.64, 167.47, 148.44, 147.92, 142.31, 136.92, 128.74, 128.67, 128.56, 127.93, 123.86, 123.22, 117.86, 81.85, 75.30, 74.96, 52.54, 52.25; LRMS-EI (m/e): 462 (M^+, 42.1), 91 (100.0); IR(KBr), 3076, 1730, 1600, 1526, 1349, 1222 cm^{-1}; Anal. Calcd for $C_{25}H_{22}N_2O_7$; C, 64.93%; H, 4.80%; N, 6.06%; Found: C, 64.96%, H, 4.72%, N, 5.90%; Pale yellow solid, mp 155-157℃.

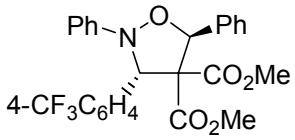
Table 1, Entry 6: (3,5 *trans*) Diethyl 5-(*p*-bromophenyl)-2,3-diphenyl-4,4-isoxazolidine dicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/7, v/v) was used as the solvent]. Yield: 129.5 mg (99%); Exo/endo: >96/4; ee%: 95% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 13.89 min, t_r (major) = 17.34 min). $[\alpha]_D^{20}$ = +52.5° (c 1.02, Ethyl acetate) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-6.91 (m, 14H), 6.11 (s, 1H),

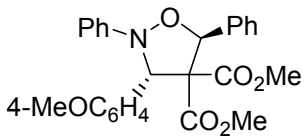
5.39 (s, 1H), 3.78-3.65 (m, 2H), 3.38-3.20 (m, 2H), 0.71-0.63 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.59, 167.22, 148.75, 137.37, 134.20, 131.11, 128.80, 128.74, 128.48, 128.44, 128.38, 123.45, 122.45, 117.77, 82.26, 75.21, 74.41, 61.70, 61.34, 13.21, 13.16; LRMS-EI (m/e): 525 [M^+(^{81}Br), 31.0], 523 [M^+(^{79}Br), 29.7], 332(96.6), 330(100.0); IR(KBr), 3065, 1724, 1598, 1490, 1250 cm^{-1}; Anal. Calcd for $C_{27}H_{26}BrNO_5$: C, 61.84%; H, 5.00%; N, 2.67%, Br, 15.24%; Found: C, 61.75%, H, 5.24%, N, 2.52%, Br, 15.63%; White solid, mp 123-124℃.

Table 1, Entry 7: (3,5 *trans*) Dimethyl 3-(*p*-triflorophenyl)-2,5-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/2, v/v) was used as the solvent]. Yield: 121.3 mg (100%), oil; Exo/endo: >92/8; ee%: 98% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (major) = 16.33 min, t_r (minor) = 18.80 min). $[\alpha]_D^{20}$ = +39.2° (c 1.02, Ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63-7.54 (m, 4H), 7.43-7.40 (m, 2H), 7.29-7.27 (m, 3H), 7.19-7.14 (m, 2H), 7.00-6.97 (m, 3H), 6.19 (s, 1H), 5.50 (s, 1H), 3.04 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.97, 167.43, 148.32, 141.58, 134.65, 130.60 (q, J_{C-F} = 32.3Hz), 129.11, 128.75, 128.67, 128.17, 126.92, 125.30 (q, J_{C-F} = 3.75Hz), 124.02, 123.87 (q, J_{C-F} = 272.35Hz), 118.28, 83.17, 75.08, 74.59, 52.42, 51.98; LRMS-EI (m/e): 485 (M^+, 44.7), 91(100.0); IR(KBr), 3065, 1733, 1619, 1326, 1127 cm^{-1}; HRMS-ESI (m/z): Calcd for $C_{26}H_{22}F_3NO_5$; 485.1450; Found: 485.1426.

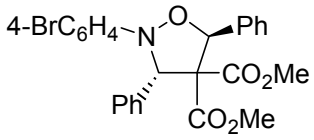
Table 1, Entry 8: (3,5 *trans*) Dimethyl 3-(*p*-methoxylphenyl)-2,5-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/10, v/v) was used as the solvent]. Yield: 104.8 mg (94%), thick oil; Exo/endo: >95/5; ee%: 96% (determined by HPLC analysis: Chiralcel AD, 20/80 ^{i}PrOH/hexanes, 0.1 mL/min, 238

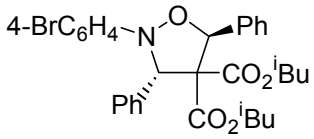
nm; t_r (major) = 82.46 min, t_r (minor) = 88.92 min). $[\alpha]_D^{20}$ = +35.5° (c 1.40, Ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-6.78 (m, 12H), 6.82 (d, *J* = 6.0 Hz, 2H), 6.12 (s, 1H), 5.34 (s, 1H), 3.70 (s, 3H), 3. 05 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.24, 167.81, 159.52, 148.95, 134.96, 129.78, 129.25, 128.54, 128.46, 128.06, 126.83, 123.30, 117.73, 113.71, 82.82, 74.86, 74.80, 55.14, 52.23, 52.03; LRMS-EI (m/e): 447 (M^+, 47.4), 91 (100.0); IR(KBr), 3050, 1731, 1610, 1512, 1250 cm^{-1}; HRMS-ESI (m/z): Calcd for $C_{26}H_{25}NO_6$: 447.17659 ; Found: 447.17239.

Table 1, Entry 9: (3,5 *trans*) Dimethyl 2-(*p*-bromophenyl)-3,5-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure [isopropyl acetate/toluene (1/10, v/v) was used as the solvent]. Yield: 114.5 mg (92%), oil; Exo/endo: >99/1; ee%: 98% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 17.27 min, t_r (major) = 20.51 min). $[\alpha]_D^{20}$ = +28.7° (c 1.03, Ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.31 (m, 12H), 6.97-6.94 (d, *J* = 9.3 Hz, 2H), 6.22 (s, 1H), 5.43 (s, 1H), 3.12 (s, 3H), 3.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.10, 167.53, 147.99, 137.08, 134.60, 131.45, 128.74, 128.67, 128.58, 128.55, 128.17, 126.85, 119.21, 116.10, 83.01, 75.25, 74.89, 52.40, 52.02; LRMS-EI (m/e): 497 [M^+(^{81}Br), 7.2], 495 [M^+(^{79}Br), 7.1], 84(100.0); IR(KBr), 3067, 1734, 1588, 1487, 1260 cm^{-1}; HRMS-ESI (m/z): Calcd for $C_{25}H_{22}BrNO_5$: 495.06813; Found: 495.06800.

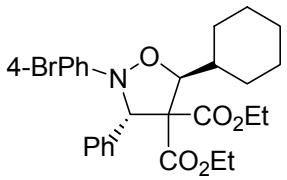
Table 1, Entry 10: (3,5 *trans*) Diisobutyl 2-(*p*-bromophenyl)-3,5-diphenyl-4,4-isoxazolidinedicarboxylates :



Prepared according to general procedure [isopropyl acetate/toluene (1/10, v/v) was used as the solvent]. Yield: 138.0 mg (95%); Exo/endo: >99/1; ee%: 96% (determined by HPLC analysis: Chiralcel AD, 5/95 ^{i}PrOH/hexanes, 0.4 mL/min, 238 nm; t_r (minor) = 14.58 min, t_r (major) = 18.58 min). $[\alpha]_D^{20}$ = +31.3° (c 1.03, Ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.28 (m, 12H), 6.96-6.92 (m, 2H), 6.23 (d, *J* = 3.0 Hz, 1H),

5.45 (d, J = 3.0 Hz, 1H), 3.64-3.52 (m, 2H), 3.03-2.87(m, 2H), 1.43-1.22 (m, 2H), 0.69-0.64 (m, 6H), 0.60-0.51 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 167.90, 167.28, 148.10, 137.21, 134.81, 131.41, 128.81, 128.70, 128.60, 128.22, 127.10, 119.28, 116.09, 83.20, 75.50, 74.66, 72.02, 71.67, 27.01, 26.86, 19.06, 18.89, 18.86, 18.63; LRMS-EI (m/e): 582 [M^+(^{81}Br), 40.0], 580 [M^+(^{79}Br), 38.7], 175(100.0); IR(KBr), 3066, 1729, 1587, 1487, 1246 cm^{-1}; Anal. Calcd for $C_{31}H_{34}BrNO_5$: C, 64.14%; H, 5.90%; N, 2.41%; Found: C, 64.09%, H, 5.81%, N, 2.29%; White solid, mp 129-130 ℃

Table 1, Entry 11: (3,5 *trans*) Diethyl 2-(*p*-bromophenyl)-5-cyclohexyl-3-phenyl-4,4- isoxazolidinedicarboxylates:



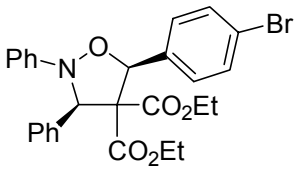
Prepared according to general procedure (isopropyl acetate was used as the solvent). Yield: 120.6 mg (91%); Exo/endo: >90/10; ee%: 89% (determined by HPLC analysis: Chiralcel AD, 4/100 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (minor) = 13.46 min, t_r (major) = 19.03 min). $[\alpha]_D^{20}$ = +38.0° (c 1.08, Ethyl acetate).. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.21-7.08 (m, 5H), 6.65-6.61 (m, 2H), 5.12 (s, 1H), 4.61 (d, J = 8.4 Hz, 1H), 4.16-4.04 (m, 2H), 3.56-3.51(m, 1H), 3.23-3.17(m, 1H), 1.90-1.45 (m, 6H), 1.17-1.04 (m, 8H), 0.72 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.57, 166.92, 148.68, 137.74, 131.29, 128.84, 128.54, 128.33, 117.67, 114.90, 85.00, 76.05, 71.36, 62.03, 61.17, 38.66, 30.28, 29.83, 26.17, 25.91, 25.85, 13.93, 13.36; LRMS-EI (m/e): 531 [M^+(^{81}Br), 50.3], 529 [M^+(^{79}Br), 49.5], 171(97.4), 169(100.0); IR(KBr), 1730, 1487, 1256 cm^{-1}; Anal. Calcd for $C_{27}H_{31}BrNO_5$: C, 61.13%; H, 6.08%; N, 2.64%; Found: C, 61.36%, H, 6.05%, N, 2.50%; White solid, mp 129-130℃

II. 1,3-Dipolar cycloaddations to *endo* adducts

General procedures for cycloaddition between nitrones and alkylidene malonates gave *endo* products catalyzed by Co(II)/TOX. A mixture of $Co(ClO_4)_2 \cdot 6(H_2O)$ (4.6

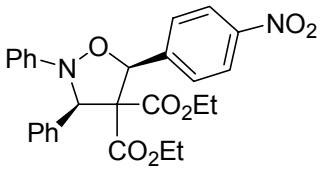
mg, 0.013 mmol, 5 mol%) and TOX (3.1 mg, 0.0087 mmol, 3.3 mol%) in the appropriate solvent (1.5 mL) was stirred at 30℃ for 4 hours under N_2 atmosphere. To the pale amaranth solution was added flame-activated MS 4Å powder 250 mg and alkylidene malonate in the mixture of toluene and isopropyl acetate (1 mL). After stirring for 0.5 h at -40℃, nitrone was added. The resulting suspension was stirred for the appropriate time at -40℃. After the reaction was completed (monitored by TLC), 1.0 mL of TMEDA was added. After stirring for additional 30 min at –40℃, the resulting mixture was filtrated through silica gel (eluted with ethyl acetate). The filtrate was concentrated under reduced pressure to give crude product. The ratio of diastereoisomers was determined by ^{1}H NMR. The residue was purified by flash chromatography (silica gel, petroleum ester/ethyl acetate) to afford the desired product. The *ee* was determined by chiral HPLC**.**

Table 2, Entry 1: (3,5 *cis*) Diethyl 2,3-diphenyl-5-(4-bromo-phenyl)-4,4-isoxazolidinedicarboxylates:



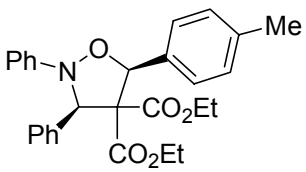
Prepared according to general procedure. [Toluene/isopropyl acetate (v/v, 3/1) was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.2/1; carried out at –40 ℃ for 24hr.] Pale oil. Yield: 115.4 mg (88%); Endo/exo: 95/5; ee%: 80% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; tr (major) = 11.74 min, tr (minor) = 16.57 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 7.5 Hz, 2H), 7.57-7.24 (m, 9H), 7.01-6.96 (m, 3H), 5.78 (s, 1H), 5.61 (s, 1H), 4.33 (q, J = 7.2 Hz, 2H), 3.37 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H), 0.64 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.89, 165.36, 150.89, 138.10, 133.10, 130.78, 129.58, 129.22, 128.11, 127.79, 127.49, 122.51, 121.93, 113.60, 83.59, 76.22, 75.38, 62.66, 61.37, 13.91, 13.10; LRMS-EI (m/e): 525 [M^+(^{81}Br), 17.67], 523 [M^+(^{79}Br), 18.24], 197 (37.86), 196 (49.14), 91 (100.00); IR(KBr), 3422, 2983, 2922, 1733, 1597, 1488, 1373, 1228, 1012, 756, 697 cm^{-1}; $[\alpha]_D^{20}$ = +14.6° (c 1.23, CHCl3, 80% ee); HRMS-ESI (m/z): $[M+Na]^+$ Calcd for $C_{27}H_{26}BrNO_5Na$, 546.0886566; Found: 546.0905550.

Table 2, Entry 2: (3,5 *cis*) Diethyl 2,3-diphenyl-5-(4-nitro-phenyl)-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure. [Toluene/isopropyl acetate (v/v, 3/1) was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.0/1.5; carried out at –50 ℃ for 44hr.] Pale oil. Yield: 121.4 mg (99%); Endo/exo: >90/10; ee%: 83% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.8 mL/min, 238 nm; t_r (major) = 12.61 min, t_r (minor) = 19.85 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 9.0 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 6.9 Hz, 2H), 7.38-7.25 (m, 5H), 7.04-6.99 (m, 3H), 5.87 (s, 1H), 5.73 (s, 1H), 4.37 (q, *J* = 7.5 Hz, 2H), 3.31 (q, *J* = 7.2, 2H), 1.35 (t, *J* = 6.9 Hz, 3H), 0.60 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.70, 165.08, 150.23, 147.62, 141.98, 137.62, 129.26, 128.60, 128.15, 127.95, 127.51, 122.74, 122.30, 113.84, 83.00, 76.08, 75.57, 62.92, 61.49, 13.89, 13.04; LRMS-EI (m/e): 490 [M^+, 12.99], 196 (34.01), 91 (100.00); IR(KBr), 3063, 2983, 2937, 1737, 1599, 1524, 1489, 1348, 1229, 853, 756, 698 cm^{-1}; $[\alpha]_D^{20}$ = -13.9° (c 1.10, $CHCl_3$, 85.4% ee); HRMS-ESI (m/z): $[M+Na]^+$ Calcd for $C_{27}H_{26}N_2O_7Na$, 513.1632223; Found: 513.1624550.

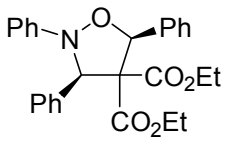
Table 2, Entry 3: (3,5 *cis*) Diethyl 2,3-diphenyl-5-(4-methyl-phenyl)-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure. [Toluene/isopropyl acetate (v/v, 8/1) was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.2; carried out at –40 □ for 88hr.] Pale oil. Yield: 114 mg (99%); Endo/exo: 86/14; ee%: 88% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.8 mL/min, 238 nm; t_r (major) = 7.56 min, t_r (minor) = 9.81 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.37-7.22 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.11-6.94 (m, 3H), 5.76 (s, 1H), 5.63 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 3.44-3.33 (m, 2H), 2.33 (s, 3H), 1.31 (t, *J* = 7.5 Hz, 3H), 0.65 (t, *J* = 6.9 Hz, 3H); ^{13}C

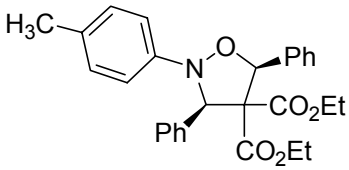
NMR (75 MHz, $CDCl_3$): 169.02, 165.60, 151.27, 138.41, 138.19, 130.64, 129.12, 128.31, 128.03, 127.84, 127.62, 127.49, 121.64, 113.50, 84.30, 76.28, 75.39, 62.43, 61.16, 21.15, 13.87, 13.06; LRMS-EI (m/e): 459 [M^+, 12.85], 197 (22.17), 196 (35.24), 91 (100.00); IR(KBr), 2982, 2932, 1733, 1598, 1488, 1374, 1228, 1064, 756, 698 cm^{-1}; $[\alpha]_D^{20}$ = +11.6° (c 1.00, $CHCl_3$, 88% ee); HRMS-ESI (m/z): $[M+Na]^+$ Calcd for $C_{28}H_{29}NO_5Na$, 482.1937941; Found: 482.1920700.

Table 2, Entry 4: (3,5 *cis*) Diethyl 2,3,5-triphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure. [Toluene/isopropyl acetate (v/v, 16/1) was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 2.0/1; carried out at –40 □ for 72hr.] Pale oil. Yield: 90.2 mg (81%); Endo/exo: 89/11; ee%: 93% (determined by HPLC analysis: Chiralcel AD, 20/80 ^{i}PrOH/hexanes, 0.6 mL/min, 238 nm; t_r (major) = 7.75 min, t_r (minor) = 9.13 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 6.3 Hz, 2H), 7.27 (m, 8H), 6.96 (m, 3H), 5.78 (s, 1H), 5.69 (s, 1H), 4.33 (q, *J* = 7.5 Hz, 2H), 3.34 (m, 2H), 1.32 (t, *J* = 7.5 Hz, 3H), 0.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 169.06, 165.59, 151.07, 138.34, 133.95, 129.16, 128.36, 128.04, 127.75, 127.65, 127.64, 127.49, 121.75, 113.56, 84.17, 76.27, 75.48, 62.51, 61.21, 13.88, 13.02; LRMS(EI): 445 [M^+, 23.58], 91 (100.00); IR(KBr), 3063, 1732, 1599, 1489, 1229 cm^{-1}; $[\alpha]_D^{20}$ = +0.9° (c 1.07, $CHCl_3$, 93% ee); HRMS-ESI (m/z): $[M+H]^+$ Calcd for $C_{27}H_{28}NO_5$, 446.1961994; Found:446.1952420.

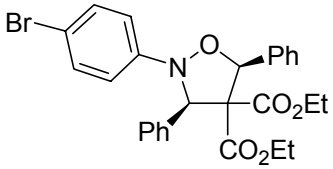
Table 2, Entry 5: (3,5 *cis*) Diethyl 2-(p-methyl-phenyl)-3,5-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure. [Toluene/isopropyl acetate (v/v, 4/1) was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.2/1; carried out at –40 □ for 90hr.] Pale oil. Yield: 88.3 mg (77%); Endo/exo: 86/14; ee%: 87% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (major) = 12.47 min, t_r (minor) = 19.09

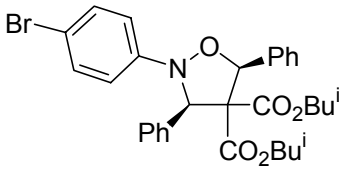
min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (m, 4H), 7.30 (m, 7H), 6.98 (m, 3H), 5.78 (s, 1H), 5.69 (s, 1H), 4.33 (q, *J* = 7.5 Hz, 2H), 3.38-3.318(m, 2H), 1.32 (t, *J* = 7.5 Hz, 3H), 0.61 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 169.06, 165.52, 151.23, 137.30, 135.12, 134.02, 129.11, 128.69, 128.35, 127.76, 127.63, 127.53, 121.68, 113.61, 84.14, 76.25, 75.30, 73.62, 62.42, 61.16, 21.10, 13.87, 13.04; LRMS-EI (m/e): 459 [M^+, 28.19], 211 (44.05), 210 (71.84), 91 (100.00); IR(KBr), 3063, 1732, 1599, 1489, 1229 cm^{-1}; $[\alpha]_D^{20}$ = -4.3° (c 1.33, $CHCl_3$, 87% ee); HRMS-ESI (m/z): $[M+Na]^+$ Calcd for $C_{28}H_{29}NO_5Na$, 482.1937941; Found: 482.1929350.

Table 2, Entry 6: (3,5 *cis*) Diethyl 2-(p-bromo-phenyl)-3,5-diphenyl-4,4-Isoxazolidinedicarboxylates:



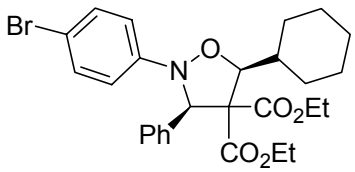
Prepared according to general procedure. [Isopropyl acetate was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.0/1.5; carried out at –50 □ for 200hr.] Pale oil. Yield: 35.5 mg (27%); Endo/exo: 87/13; ee%: 90% (determined by HPLC analysis: Chiralcel AD, 10/90 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (major) = 12.49 min, t_r (minor) = 15.64 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.6 Hz, 2H), 7.64 (m, 2H), 7.39-7.26 (m, 8H), 6.92-6.89 (m, 2H), 5.71 (s, 1H), 5.65 (s, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 3.38-3.32 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.62 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.91, 165.31, 150.15, 137.82, 133.66, 131.99, 128.50, 128.12, 127.84, 127.75, 127.69, 127.49, 115.39, 114.20, 84.31, 76.22, 75.37, 62.63, 61.26, 13.89, 13.03; LRMS-EI (m/e): 525 [$M(^{81}Br)^+$, 30.99], 523 [$M(^{79}Br)^+$, 31.96], 171 (92.62), 169 (100.00), 90 (35.20), 77 (44.24); IR(KBr), 1733, 1584, 1484, 1231 cm^{-1}; $[\alpha]_D^{20}$ = -6.0° (c 1.08, $CHCl_3$, 90% ee); HRMS-ESI (m/z): $[M+Na]^+$ Calcd for $C_{27}H_{26}BrNO_5Na$, 546.0886566; Found: 546.0897220.

Table 2, Entry 7: (3,5 *cis*) Diisobutyl 2-(p-bromo-phenyl)-2,5-diphenyl-4,4-isoxazolidinedicarboxylates:



Prepared according to general procedure. [Toluene/isopropyl acetate (v/v, 3/1) was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.0/1.5; carried out at –40 □ for 72hr.] Pale oil. Yield: 54.33 mg (38%); Endo/exo: 88/12; ee%: > 94% (determined by HPLC analysis: Chiralcel AD, 1.5/100 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (major) = 13.08 min, t_r (minor) = 15.96 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.62 (m, 4H), 7.38-7.25 (m, 8H), 6.91 (m, 2H), 5.68 (s, 1H), 5.65 (s, 1H), 4.06-4.04 (m, 2H), 3.14-3.00 (m, 2H), 2.00 (m, 1H), 1.25-1.18 (m, 1H), 0.92 (d, *J* = 3.0 Hz, 3H), 0.91 (d, *J* = 3.0 Hz, 3H), 0.52 (d, *J* = 4.2 Hz, 3H), 0.49 (d, *J* = 3.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 169.03, 165.08, 150.21, 137.71, 133.62, 131.99, 128.51, 128.17, 127.85, 127.79, 127.71, 127.53, 115.37, 114.20, 84.43, 76.43, 75.37, 72.81, 71.44, 27.60, 26.82, 19.19, 19.10, 18.79, 18.75; LRMS-EI (m/e): 581 [M^+(^{81}Br), 26.44], 579 [M^+(^{79}Br), 26.98], 171 (95.92), 169 (100.00), 105 (47.70); IR(KBr), 3064, 2961, 2929, 2874, 1732, 1586, 1485, 1240 cm^{-1}; $[\alpha]_D^{20}$ = -13.0° (c 1.14, $CHCl_3$, 92% ee); HRMS-ESI (m/z): $[M+Na]^+$ Calcd for $C_{31}H_{34}BrNO_5Na$, 602.1512569; Found: 602.1497920.

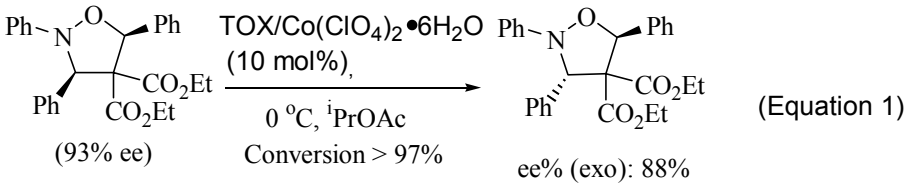
Table 2, Entry 8: (3,5 *cis*) Diethyl2-(p-bromo-phenyl)-3-phenyl-5-cyclohexyl-4,4-isoxazolidinedicarboxylats:



Prepared according to general procedure. [Isopropyl acetate was used as the solvent; alkylidene malonate/nitrone (mol/mol) = 1.2/1; carried out at –50 □ for 5hr.] Pale oil. Yield: 127.5 mg (99%); Endo/exo: 86/14; ee%: 71% (determined by HPLC analysis: Chiralcel AD, 4/100 ^{i}PrOH/hexanes, 0.5 mL/min, 238 nm; t_r (major) = 15.26 min, t_r (minor) = 28.23 min). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.35-7.24 (m, 5H), 6.82 (d, J = 8.2 Hz, 2H), 5.64 (s, 1H), 4.32-4.20 (m, 2H), 4.17 (d, *J* = 8.7 Hz, 1H), 3.74-3.62 (m, 2H), 2.28 (m, 1H), 2.08 (m, 1H), 1.81 (m, 1H), 1.67 (m, 3H), 1.35-1.13 (m, 8H), 0.92 (t, *J* = 7.2, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 169.12, 166.19, 150.05, 137.97, 131.90, 128.09, 127.78, 127.44, 115.22, 113.79, 88.00, 76.53, 73.07, 62.40, 61.37, 38.14, 31.20, 30.01,

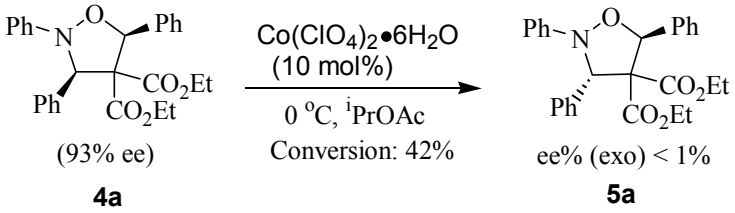
26.15, 25.98, 25.75, 13.88, 13.50; LRMS-EI (m/e): 531 [M^+(^{81}Br), 14.00], 529 [M^+(^{79}Br), 13.77], 171 (95.99), 169 (100.00), 105 (19.59); IR(KBr), 3063, 2980, 2930, 2853, 1735, 1586, 1485, 1451, 1248, 1214, 1053, 1003, 822, 734, 699 cm^{-1}; $[\alpha]_D^{20}$ = -36.4° (c 0.75, $CHCl_3$, 71% ee); HRMS-ESI (m/z): $[M+H]^+$ Calcd for $C_{27}H_{33}BrNO_5Na$, 530.1536622; Found: 530.1531930.

III. Mechanistic investigation



(Equation 1)

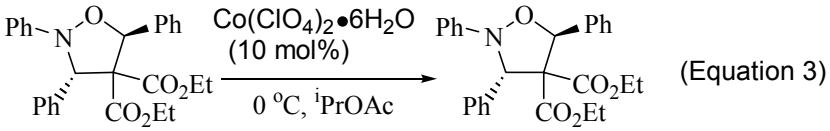
Procedure for enantioselective isomerization from 4a to 5a catalyzed by $Co(ClO_4)_2·6(H_2O)$/TOX (Equation 1). A mixture of $Co(ClO_4)_2·6(H_2O)$ (4.7 mg, 0.013 mmol, 10 mol%) and TOX (3.3 mg, 0.008 mmol, 6.7 mol%) in 1.3 ml of *i*-PrOAc was stirred at 50℃ for 4 hours under N_2 atmosphere. After cooling to room temperature, the pale amaranth solution was added into a reaction tube with **4a** (58 mg, 0.13 mmol, 93% ee) and powdered MS 4Å (130 mg). The resulting suspension was stirred for 19 hours at 0 ℃ and 0.5 mL of Et_3N was added. After being stirred for additional 10 min, the resulting mixture was filtrated through silica gel (eluted with ethyl acetate). The filtrate was concentrated under reduced pressure to give crude *trans*-product. ^{1}H NMR showed that the ratio of **5a** to **4a** was 97/3. The residue was purified by flash chromatography (silica gel, petroleum ester/ethyl acetate) to afford the *trans*-product (52.8 mg, 91%); 91 % ee**.**



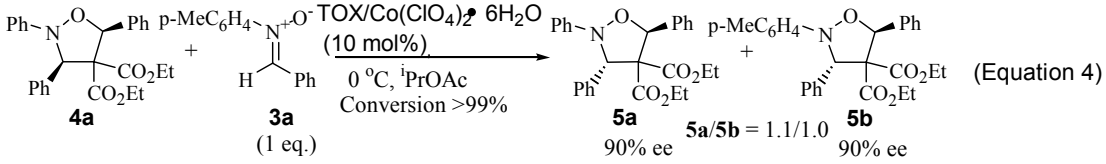
(Equation 2)

Procedure for isomerization from 4a to racemic 5a catalyzed by

$Co(ClO_4)_2·6(H_2O)$ (Equation 2). To a reaction tube was added i-PrOAc (1.3 ml), $Co(ClO_4)_2·6(H_2O)$ (4.7 mg, 0.013 mmol, 10 mol%), **4a** (58 mg, 0.13 mmol, >93% ee) and powdered MS 4Å (130 mg). The resulting suspension was stirred for 16.5 hours at 0 ℃. Then 0.5 mL of Et_3N was added. After being stirred for additional 10 min, the resulting mixture was filtrated through silica gel (eluted with ethyl acetate). The filtrate was concentrated under reduced pressure to give crude products (trans/cis = 1/1.4, by ^1H NMR). The residue was purified by flash chromatography (silica gel, petroleum ester/ethyl acetate) to afford the *trans*-product (15.8 mg, 27%, <1% ee, by chiral HPLC) and *cis*-product (20.0 mg, 35%, 5% ee, by chiral HPLC).



Procedure for isomerization from 5a to racemic 4a catalyzed by $Co(ClO_4)_2·6(H_2O)$ (Equation 3). To a reaction tube was added i-PrOAc (1.3 ml), $Co(ClO_4)_2·6(H_2O)$ (1.7 mg, 0.0048 mmol, 20 mol%), **5a** (10.8 mg, 0.024 mmol, 91.4%ee) and powdered MS 4Å (30 mg). The resulting suspension was stirred for 20 hours at 0 ℃. Then 0.5 mL of TMEDA was added. After being stirred for additional 10 min, the reacting mixture was filtrated through silica gel (eluted with ethyl acetate). The filtrate was concentrated under reduced pressure to give crude products (ee: 90.5 %, by chiral HPLC).



Procedures for isomerization and cross-cycloaddition from 4a to racemic 5a and 5b catalyzed by $Co(ClO_4)_2·6(H_2O)$/TOX. A mixture of $Co(ClO_4)_2·6(H_2O)$ (4.7 mg, 0.013 mmol, 10 mol%) and TOX (3.3 mg, 0.0087 mmol, 6.7 mol%) in 1.3 ml of *i*-PrOAc was stirred at 50℃ for 4 hours under N_2 atmosphere. After cooling to room temperature, the pale amaranth solution was added into a reaction tube with **4a** (58

mg, 0.13 mmol, racemer), **3a** (27.4 mg, 0.13 mmol, 1eq.) and powdered MS 4Å (130 mg). The resulting suspension was stirred for 16 hours at 0 ℃. Then 0.5 mL of TMEDA was added. After being stirred for additional 10 min, the reacting mixture was filtrated through silica gel (eluted with ethyl acetate). The filtrate was concentrated under reduced pressure to give crude products (**5a**/**5b**/**4a** = 1.1/1/0.1, by ^{1}H NMR; 90.0% ee for **5a,** 90.0% ee for **5b,** by chiral HPLC).

IV. Determination of absolute configuration

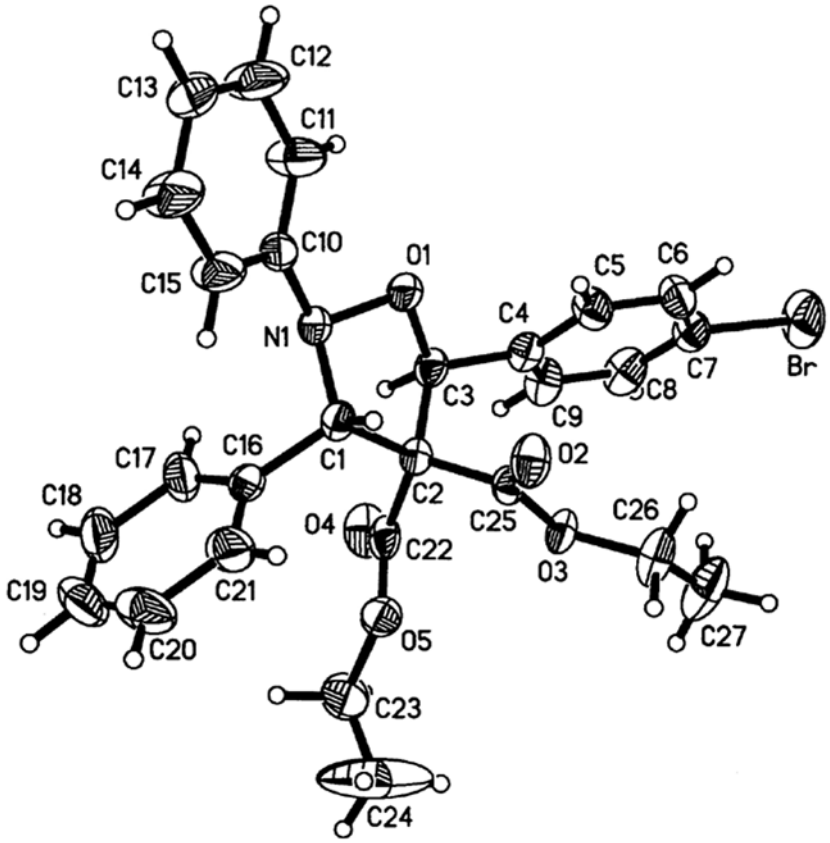


Figure 1. **The crystal structure of (3,5 *trans*) Diethyl 5-(*p*-bromophenyl)-2,3-diphenyl-4,4-isoxazolidinedicarboxylate (100% ee)**

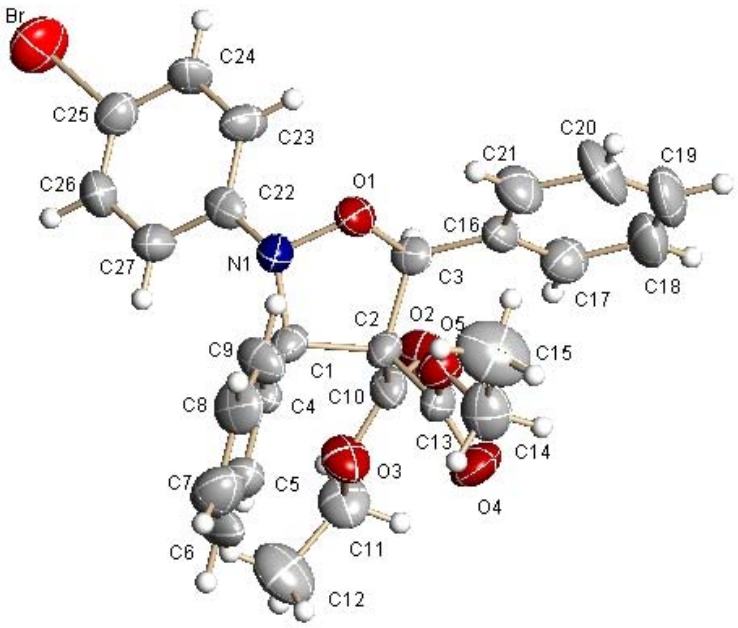


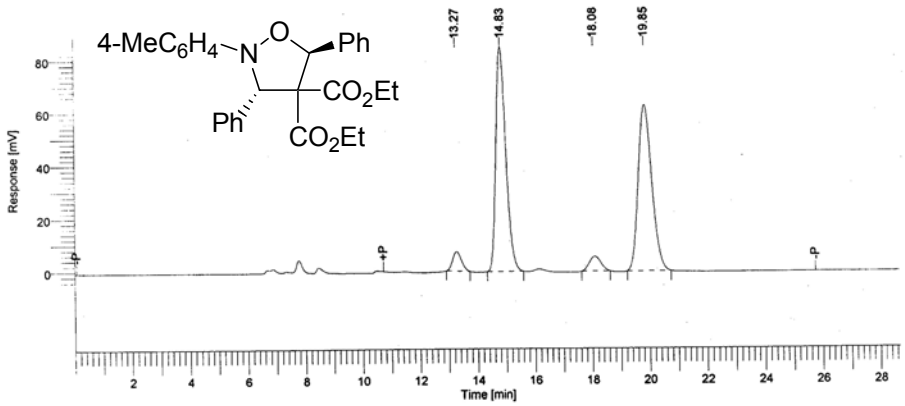
Figure 2. **The crystal structure of (3,5 *cis*) Diethyl 2-(*p*-bromophenyl)-3,5-diphenyl-4,4-isoxazolidinedicarboxylate**

References

(1) (a) Patrick, T. B.; Schield, J. A.; Kirchner, D. G. *J. Org. Chem.* **1974**, *39*(12), 1758. (b) Beissel, T.; Powers, R. E.; Parac, T. N.; Raymond, K. N. *J. Am. Chem. Soc*. **1999**, *121*, 4200. (c) Mallesha, H.; Kumar, K. R. R.; Mantelingu, K.; Rangappa, K. S. *Synthesis* **2001**, 1459.

(2) Cheung, J.; Field, L. D.; Regaglia, F.; Sternhell, S. *Aust. J. Chem.* **1995**, *48*, 1707.

V. Chiral HPLC analysis

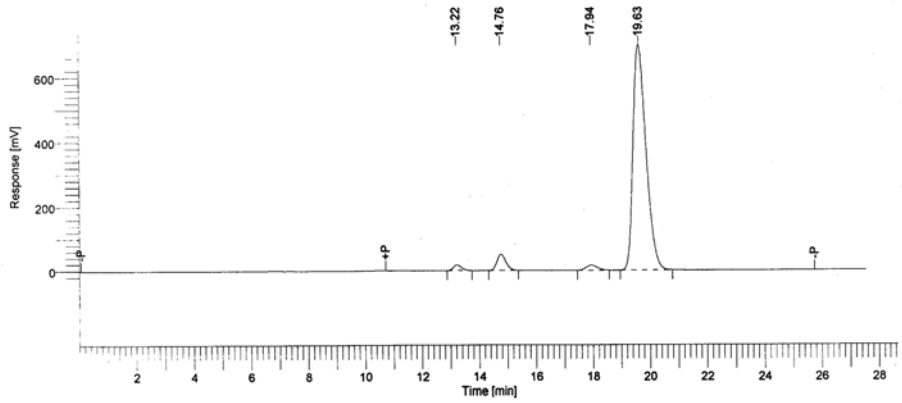


report

hzz-14-44-r2-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.271	299923.60	14079.22	3.51
2		14.834	3988893.18	164598.36	46.64
3		18.081	298530.99	10631.16	3.49
4		19.853	3964670.70	121526.65	46.36
			8552018.47	310835.39	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20
Racemate sample: h-14-44-r2-rac, File: h-14-44-r2

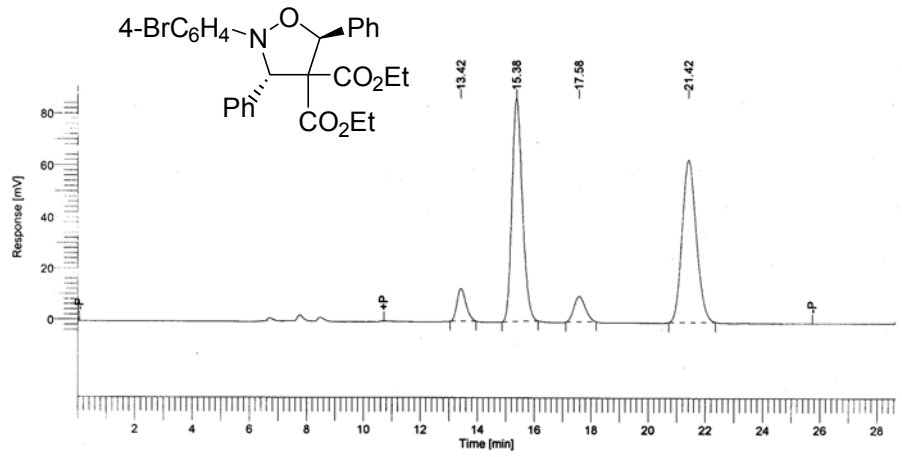


report

hzz-14-44-r2

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.215	664960.94	33992.44	1.44
2		14.760	2111868.25	96936.74	4.57
3		17.942	821525.59	30276.36	1.78
4		19.625	42644858.54	1.35e+06	92.22
			46243213.32	1.51e+06	100.00

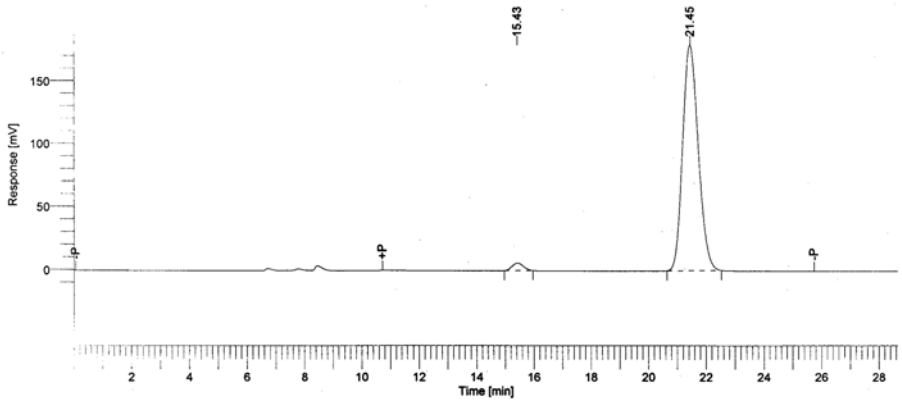
Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20
Racemate sample: h-14-44-r2-rac, File: h-14-44-r2



report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.425	539867.88	24819.30	5.63
2		15.384	4261122.90	167468.62	44.44
3		17.580	535398.24	19318.22	5.58
4		21.420	4251385.86	121931.30	44.34
			9587774.87	333537.44	100.00

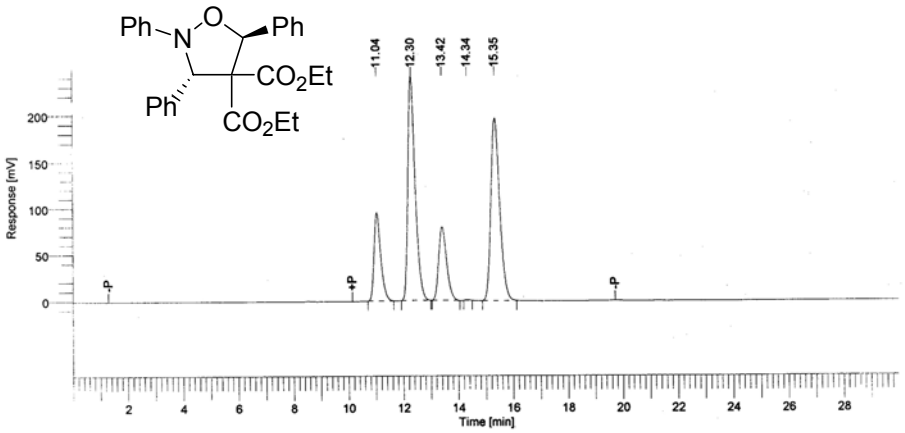
Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20
Racemate sample: h-14-51-rac, File: h-14-51



report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		15.429	309513.15	11304.46	2.31
2		21.448	13104133.44	347335.19	97.69
			13413646.60	358639.65	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20
Racemate sample: h-14-51-rac, File: h-14-51

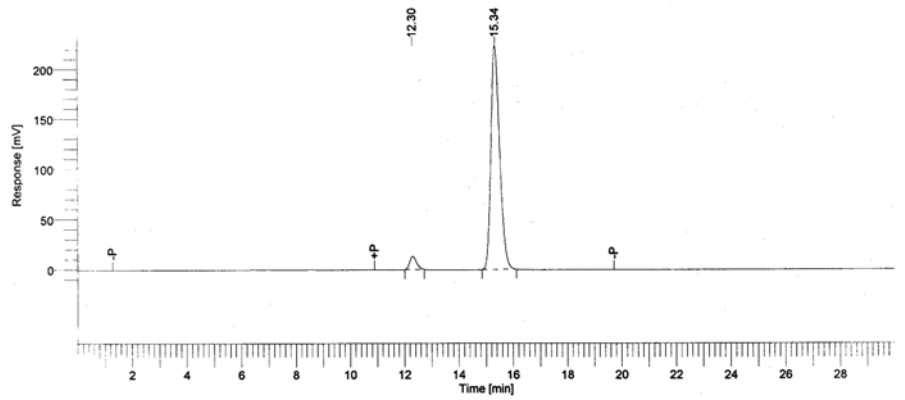


report

Hzz-14-10-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.037	3113608.69	185204.30	13.29
2		12.302	8618167.80	467770.57	36.80
3		13.416	3074233.11	153697.30	13.13
4		14.337	12283.86	1127.29	0.05
5		15.347	8601983.28	380521.77	36.73
			23420276.74	1.19e+06	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

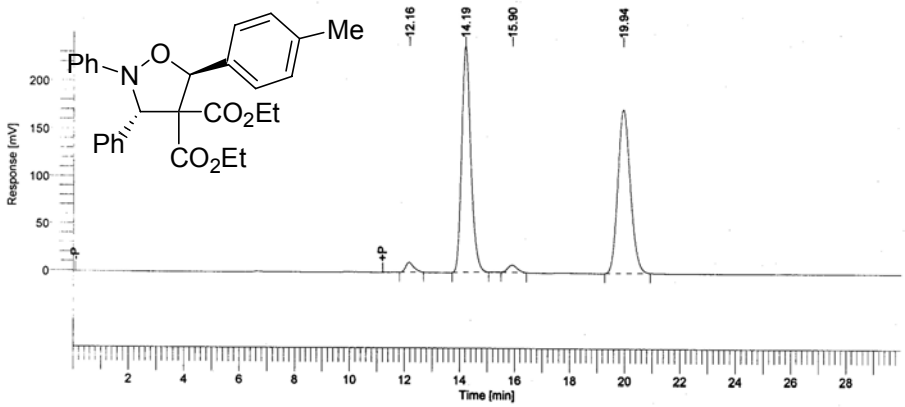


report

Hzz-14-10-r2

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.302	448346.45	25567.89	4.38
2		15.342	9789242.73	433949.25	95.62
			10237589.18	459517.14	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

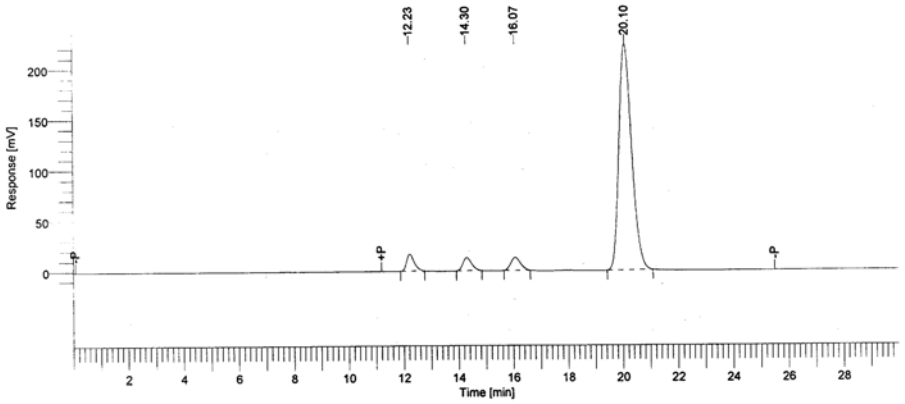


report

Hzz-14-94-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.165	400694.22	19831.38	1.84
2		14.189	10530607.77	460559.13	48.28
3		15.904	348399.59	14701.56	1.60
4		19.936	10533433.19	333513.79	48.29
			21813134.77	828605.86	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

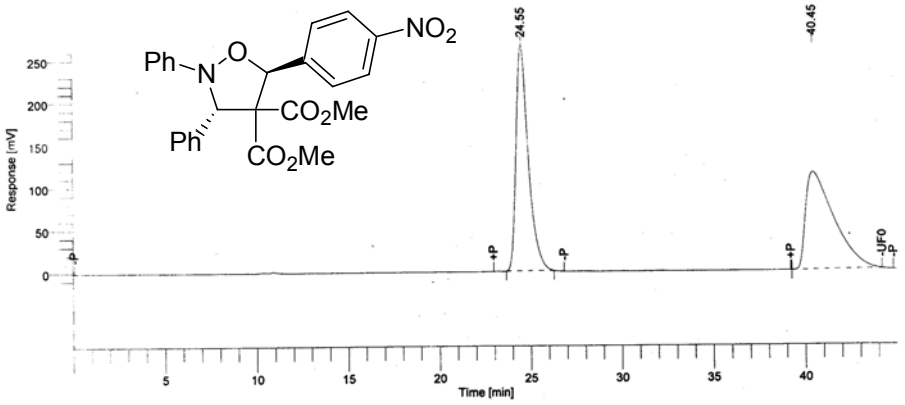


report

Hzz-14-94

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.230	645236.96	32810.66	4.08
2		14.303	566414.29	25536.64	3.59
3		16.075	614751.84	24949.50	3.89
4		20.096	13970743.34	433659.40	88.44
			15797146.43	516956.21	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

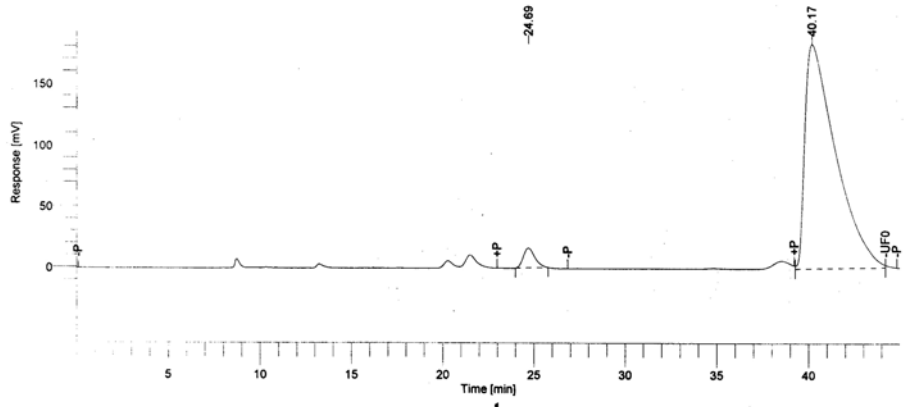


report

Hzz-15-85-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		24.553	24026171.88	515276.89	50.19
2		40.453	23843162.01	222224.87	49.81
			47869333.89	737501.76	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 80/20, Flow rate = 0.5 ml/min, Temperature = 20

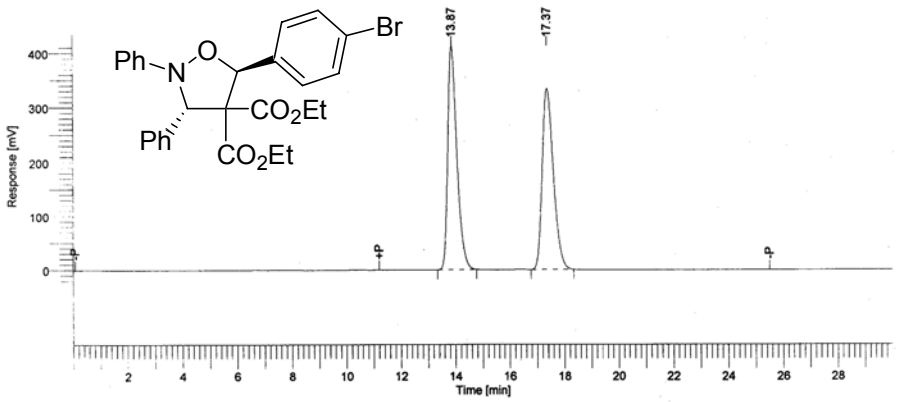


report

Hzz-15-85

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		24.693	1366844.27	31275.28	3.19
2		40.175	41503971.75	353890.70	96.81
			42870816.02	385165.99	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 80/20, Flow rate = 0.5 ml/min, Temperature = 20

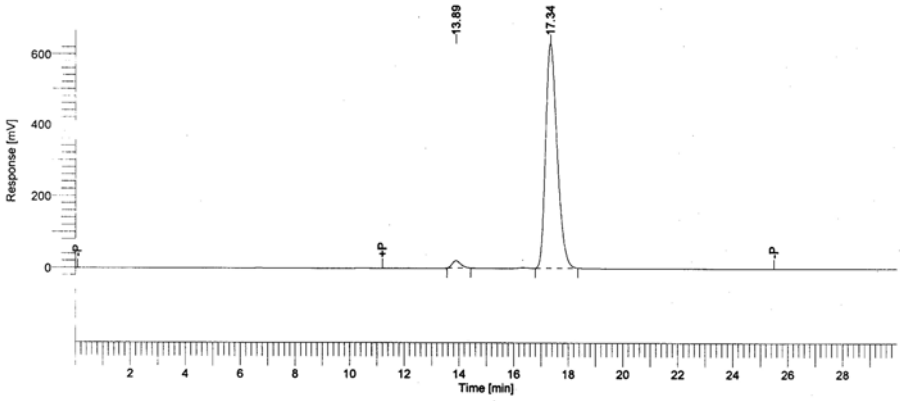


report

Hzz-14-77-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.873	18499080.02	799452.06	50.03
2		17.372	18480220.30	646212.13	49.97
			36979300.32	1.45e+06	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

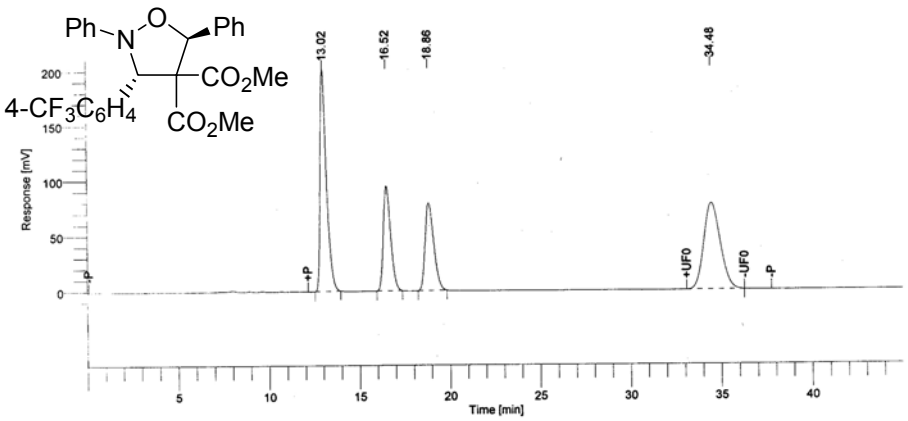


report

Hzz-14-77

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.886	873097.71	40505.95	2.39
2		17.338	35606694.91	1.22e+06	97.61
			36479792.62	1.26e+06	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

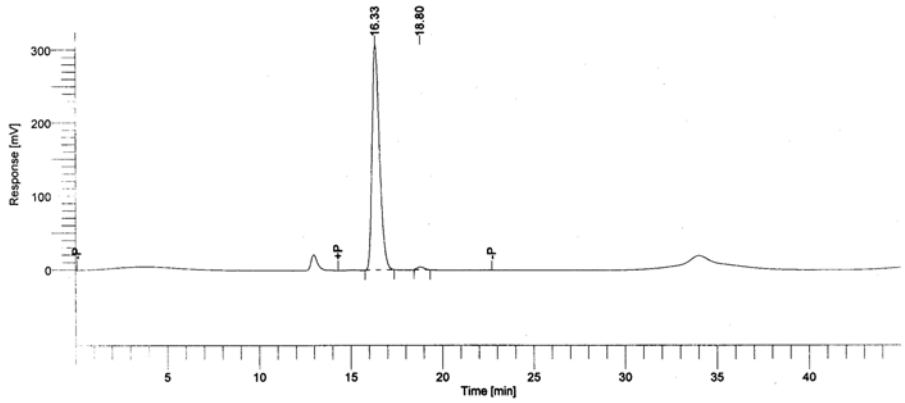


report

Hzz-15-26-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.023	9494939.11	391038.85	32.48
2		16.517	5154172.22	183604.91	17.63
3		18.858	5113622.76	153577.59	17.49
4		34.478	9474131.52	150985.52	32.40
			29236865.61	879206.87	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

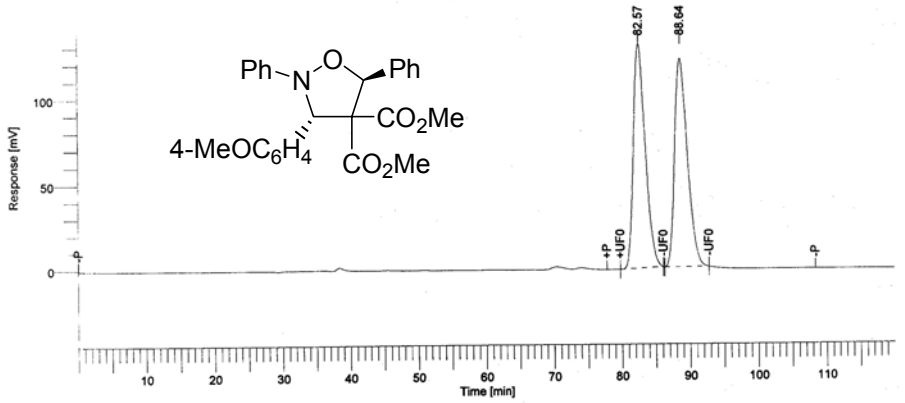


report

Hzz-15-26

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		16.332	16789117.65	595976.94	98.86
2		18.797	193514.76	7135.43	1.14
			16982632.41	603112.37	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20

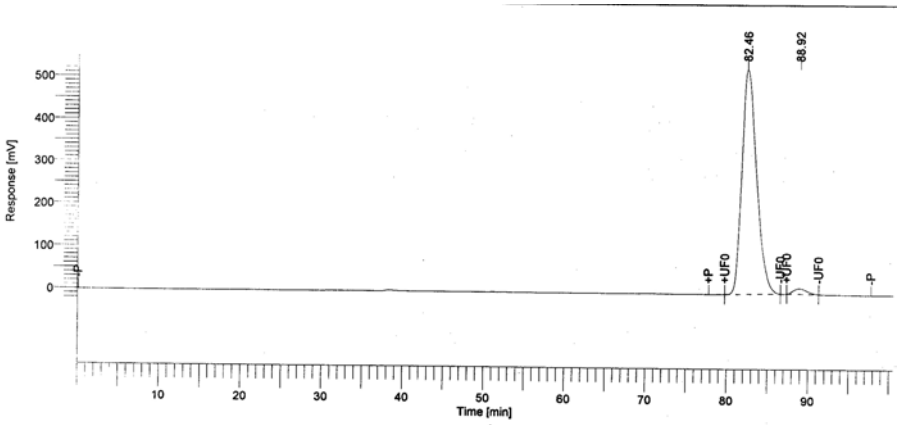


report

Hzz-15-2-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		82.573	31225872.80	256488.32	50.16
2		88.642	31028342.03	238615.23	49.84
			62254214.83	495103.55	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 80/20, Flow rate = 0.1 ml/min, Temperature = 20

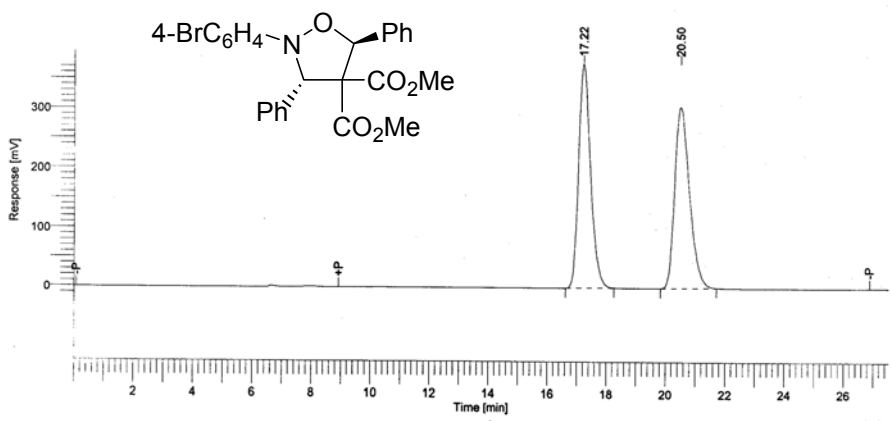


report

Hzz-15-2

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		82.458	1.27e+08	1.02e+06	97.80
2		88.920	2866037.28	25184.51	2.20
			1.30e+08	1.05e+06	100.00

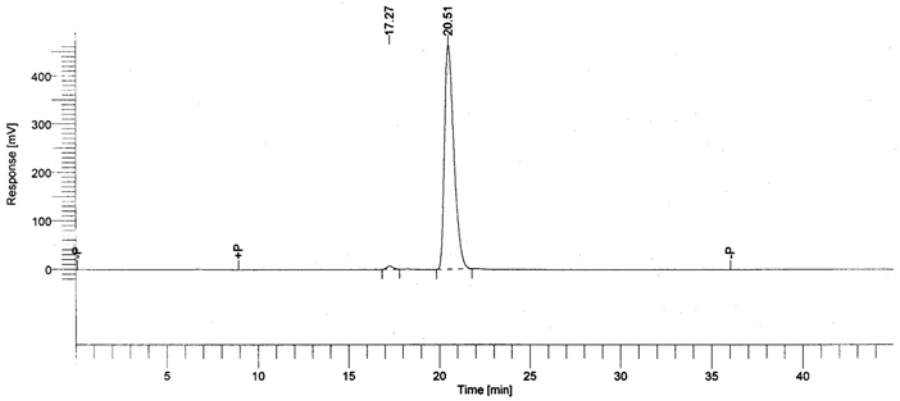
Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 80/20, Flow rate = 0.1 ml/min, Temperature = 20



report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		17.220	20785136.86	729056.54	50.10
2		20.502	20698223.95	590425.27	49.90
			41483360.81	1.32e+06	100.00

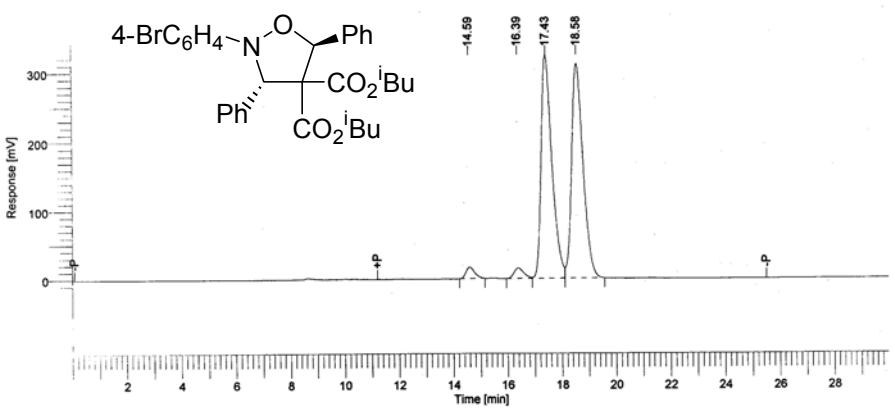
Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20
Racemate sample: h-14-75-rac, File: h-14-75



report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		17.268	345075.25	13330.23	1.06
2		20.508	32299769.07	901486.17	98.94
			32644844.32	914816.40	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 90/10, Flow rate = 0.5 ml/min, Temperature = 20
Racemate sample: h-14-75-rac, File: h-14-75

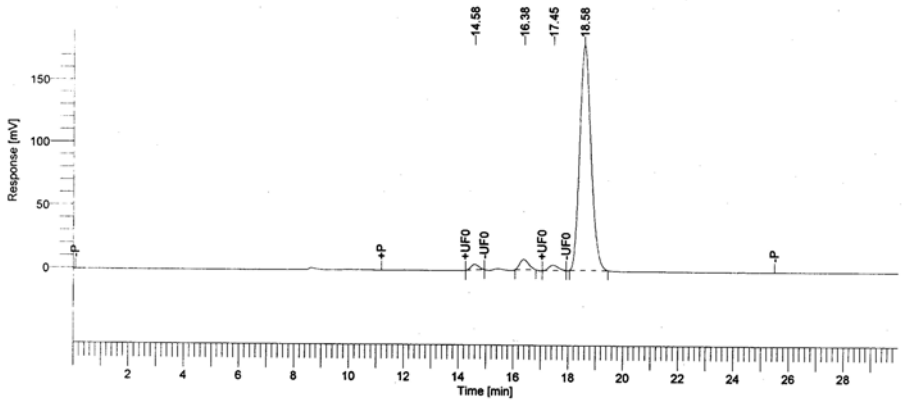


report

Hzz-14-74-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		14.593	725805.38	32308.92	1.99
2		16.388	741663.27	29372.81	2.03
3		17.434	17411420.16	627597.97	47.72
4		18.576	17607593.56	602558.69	48.26
			36486482.36	1.29e+06	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 95/5, Flow rate = 0.4 ml/min, Temperature = 20

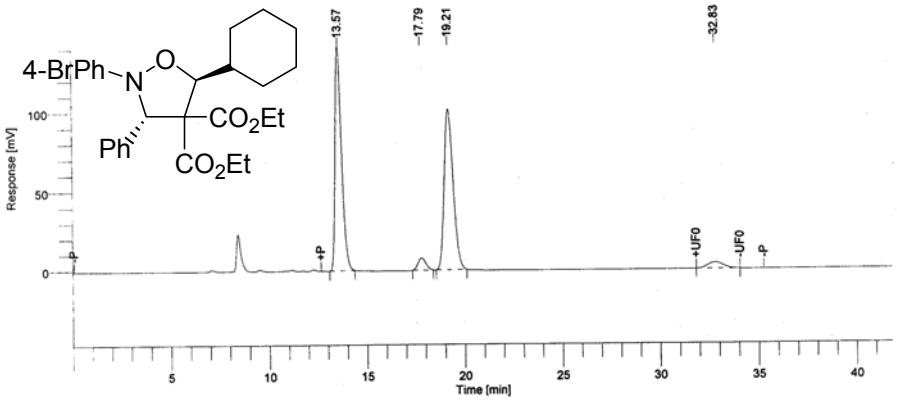


report

Hzz-14-74

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		14.580	176412.24	8990.52	1.65
2		16.383	357272.95	16022.97	3.34
3		17.448	210350.94	8767.97	1.97
4		18.583	9959793.63	348254.17	93.05
			10703829.76	382035.64	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 95/5, Flow rate = 0.4 ml/min, Temperature = 20

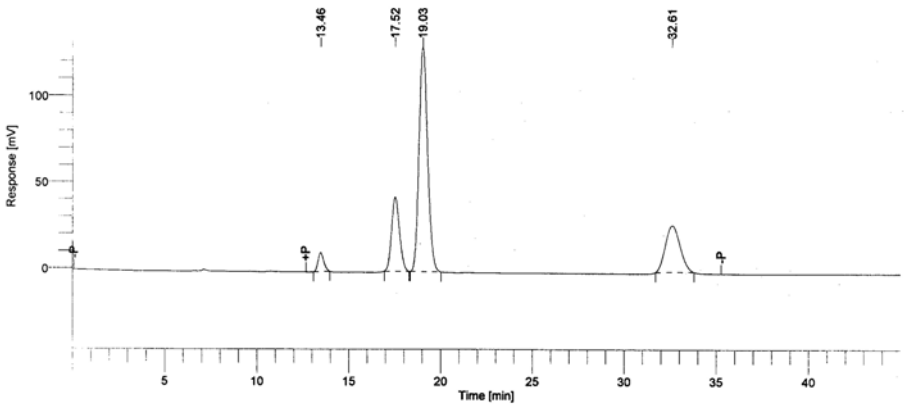


report

Hzz-15-18-rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.571	6346372.36	275841.89	46.96
2		17.794	428004.94	15248.43	3.17
3		19.207	6308899.36	196908.75	46.69
4		32.827	429948.98	7754.40	3.18
			13513225.64	495753.48	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 100/4, Flow rate = 0.5 ml/min, Temperature = 20

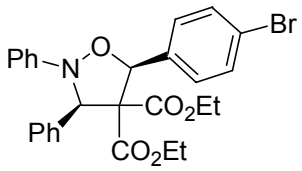


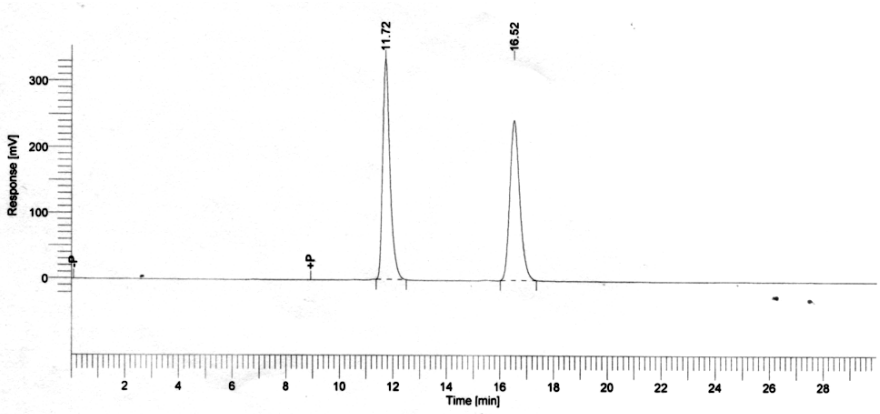
report

Hzz-15-18

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.461	457960.99	21073.11	3.27
2		17.521	2492099.18	83019.28	17.77
3		19.034	8207664.72	251898.02	58.52
4		32.614	2867132.07	52113.01	20.44
			14024856.96	408103.43	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH = 100/4, Flow rate = 0.5 ml/min, Temperature = 20



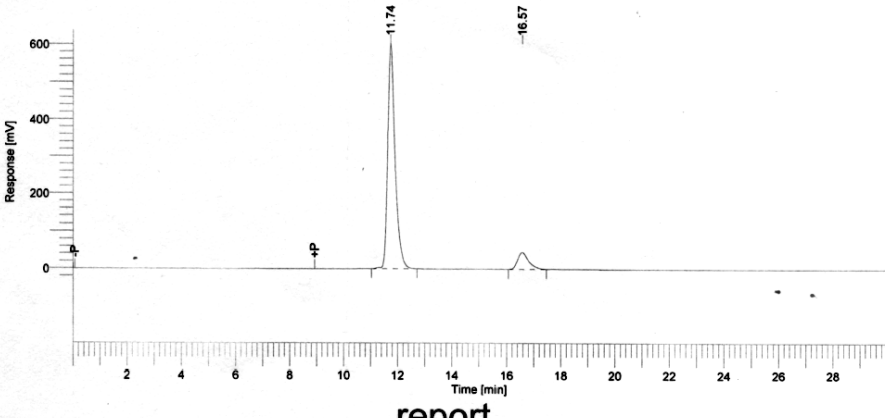


report

kyb-1-39rac

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.720	12330512.84	650688.15	50.01
2		16.520	12324764.33	475692.49	49.99
			24655277.17	1.13e+06	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH =90/10, Flow rate = 0.5 ml/min, Temperature = 20

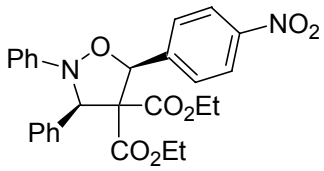


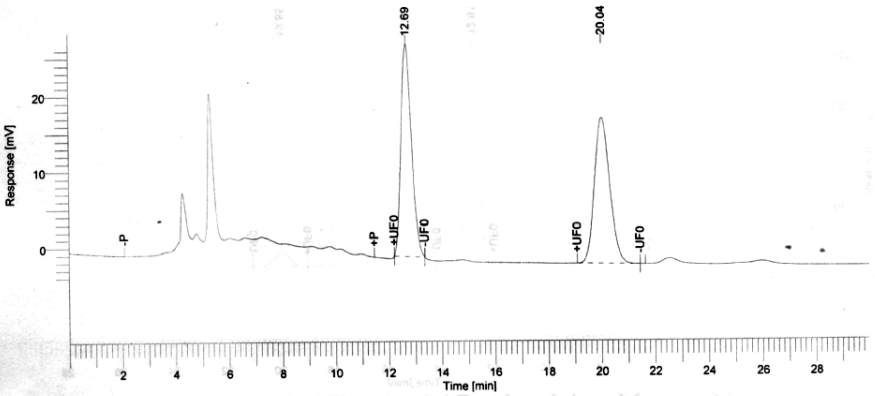
report

kyb-1-39-1

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.737	22448128.16	1.17e+06	90.16
2		16.575	2449929.06	87330.72	9.84
			24898057.22	1.26e+06	100.00

Method: AD Column, Wave length = 238 nm, n-Hexane/i-PrOH =90/10, Flow rate = 0.5 ml/min, Temperature = 20



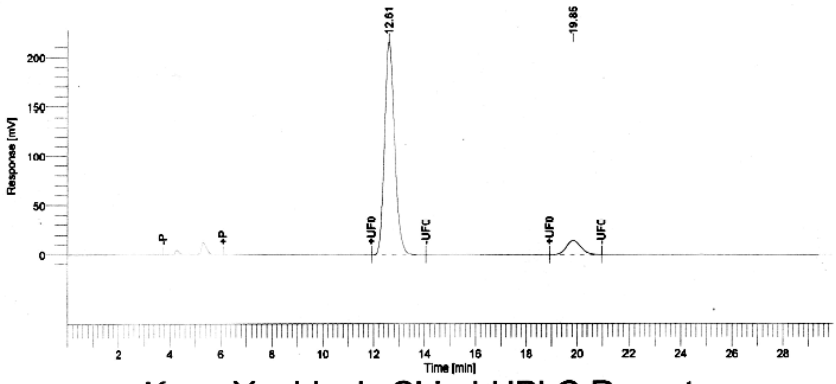


Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.692	1489447.15	54426.87	50.06
2		20.038	1485862.75	37295.29	49.94
			2975309.90	91722.16	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.8 ml/min, Temperature = 20

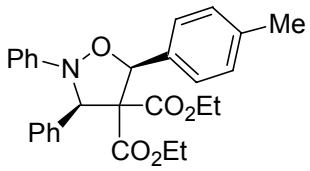


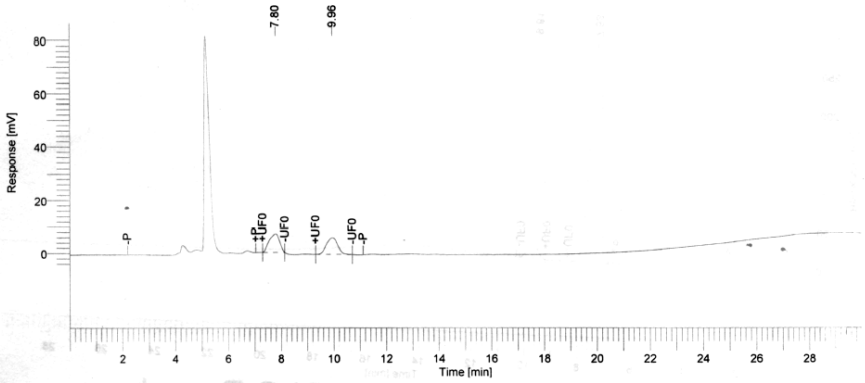
Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.607	11536248.48	419855.86	91.38
2		19.847	1088772.16	27955.79	8.62
			12625020.64	447811.65	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.8 ml/min, Temperature = 20



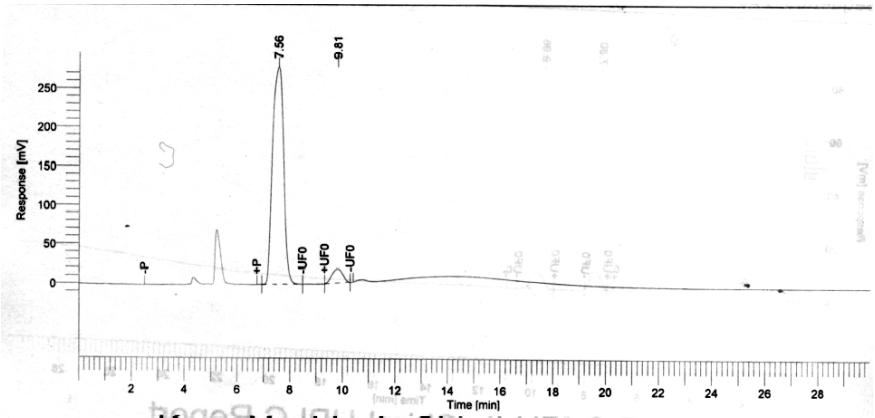


Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.800	369990.30	13649.39	50.05
2		9.962	369299.53	12343.10	49.95
			739289.83	25992.49	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.8 ml/min, Temperature = 20

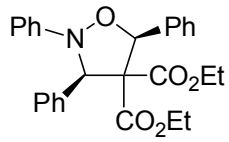


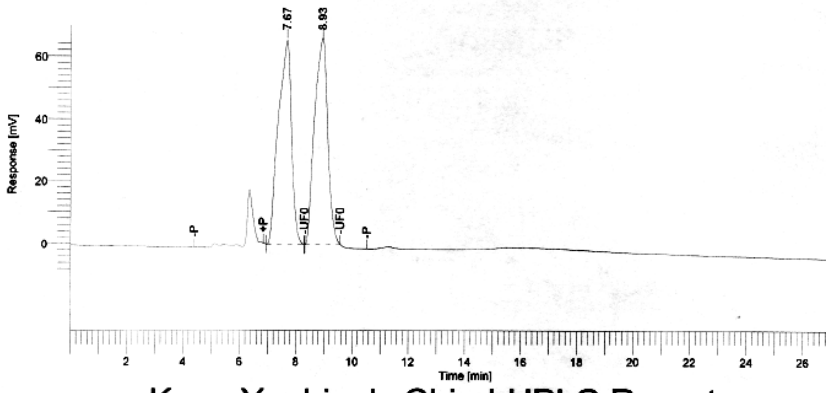
Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.558	15785869.23	542665.93	94.04
2		9.808	999706.97	34631.64	5.96
			16785576.20	577297.57	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.8 ml/min, Temperature = 20



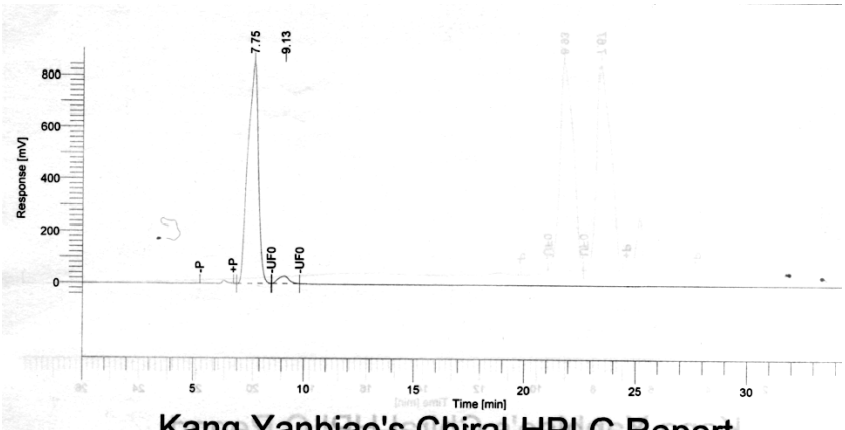


Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.667	4129631.48	126719.88	49.79
2		8.933	4164220.02	128084.46	50.21
			8293851.51	254804.34	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=20/80, Flow rate = 0.6 ml/min, Temperature = 20

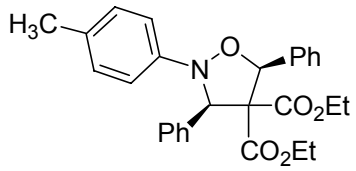


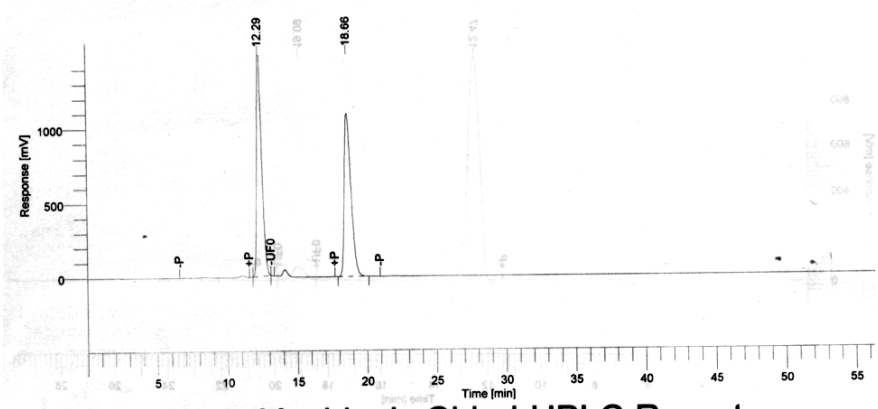
Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.747	54534770.70	1654193.58	96.65
2		9.128	1888226.34	56770.14	3.35
			56422997.04	1710963.72	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=20/80, Flow rate = 0.6 ml/min, Temperature = 20



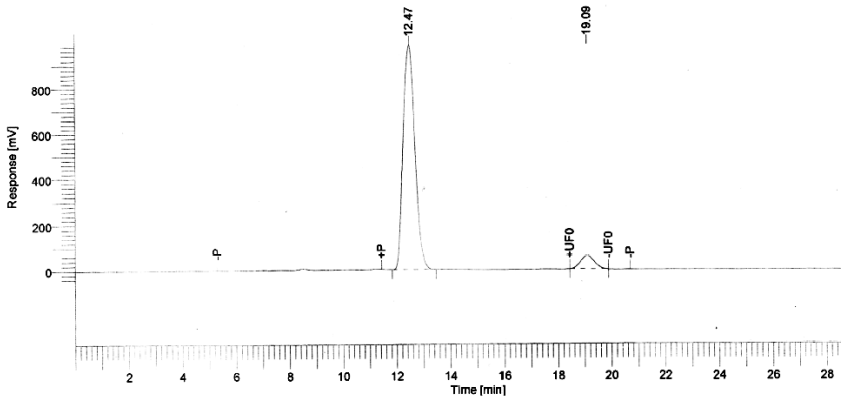


Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.292	73059296.62	2894042.72	50.10
2		18.663	72781358.28	2132133.07	49.90
			145840654.90	5026175.79	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.8 ml/min, Temperature = 20

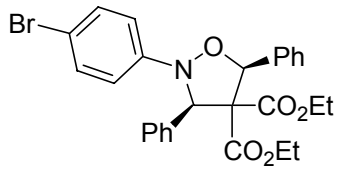


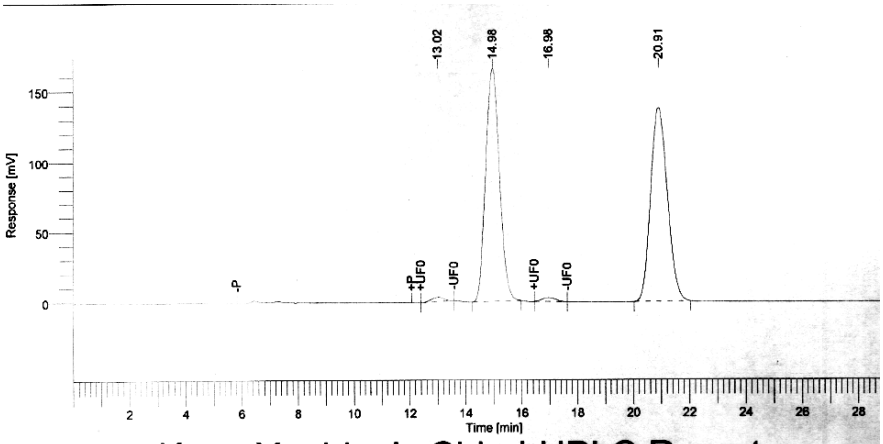
Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.475	58914064.51	1909179.27	93.72
2		19.090	3949992.34	110146.67	6.28
			62864056.85	2019325.94	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.8 ml/min, Temperature = 20

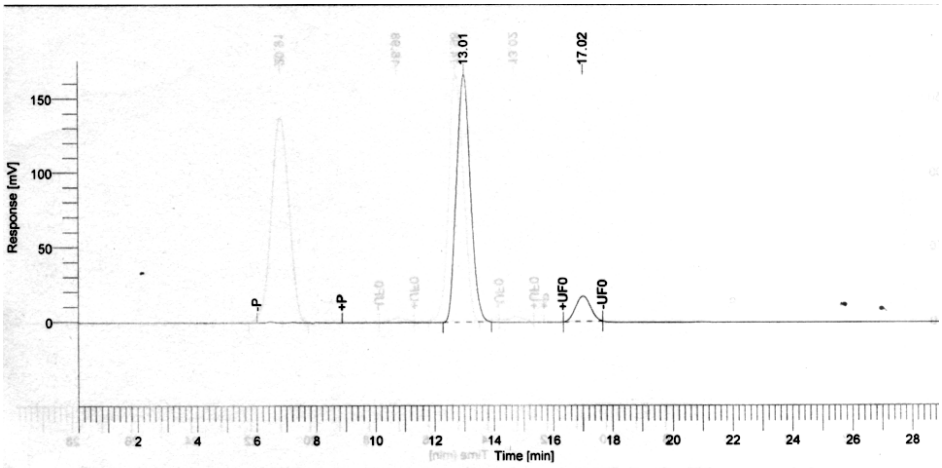




Kang Yanbiao's Chiral-HPLC Report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.020	177569.38	5952.61	0.79
2		14.982	11092175.44	321674.27	49.25
3		16.980	179572.83	5407.97	0.80
4		20.914	11070644.82	268003.17	49.16
			22519962.47	601038.01	100.00

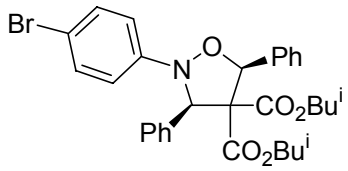
Method: AD Column, Wave length = 254 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.5 ml/min, Temperature = 20

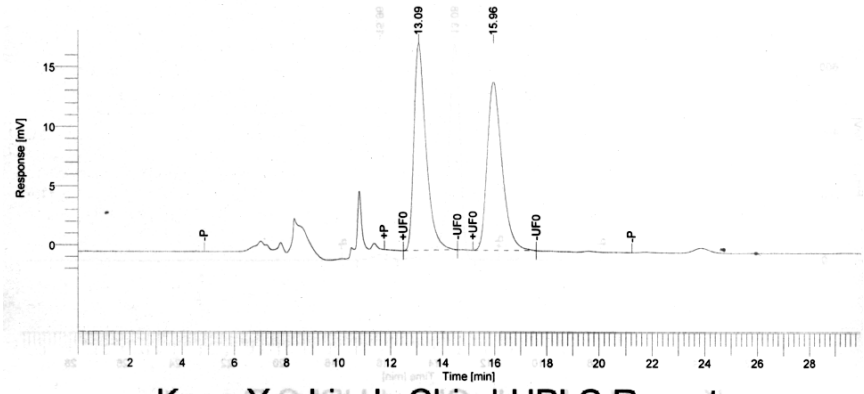


Kang Yanbiao's Chiral-HPLC Report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.013	10641418.31	322986.33	90.01
2		17.023	1180992.42	33486.05	9.99
			11822410.74	356472.37	100.00

Method: AD Column, Wave length = 254 nm, iPrOH/n-Hexane=10/90, Flow rate = 0.5 ml/min, Temperature = 20



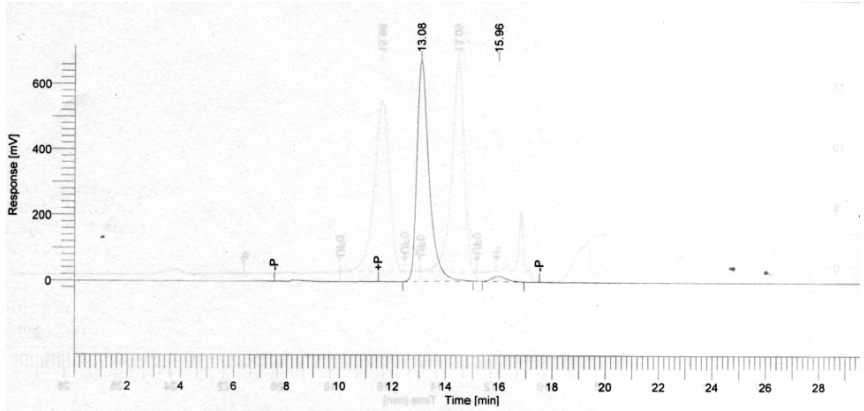


Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.087	1096079.00	33914.04	50.01
2		15.960	1095463.05	27521.59	49.99
			2191542.05	61435.63	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=1.5/100, Flow rate = 0.5 ml/min, Temperature = 20

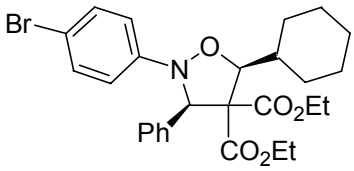


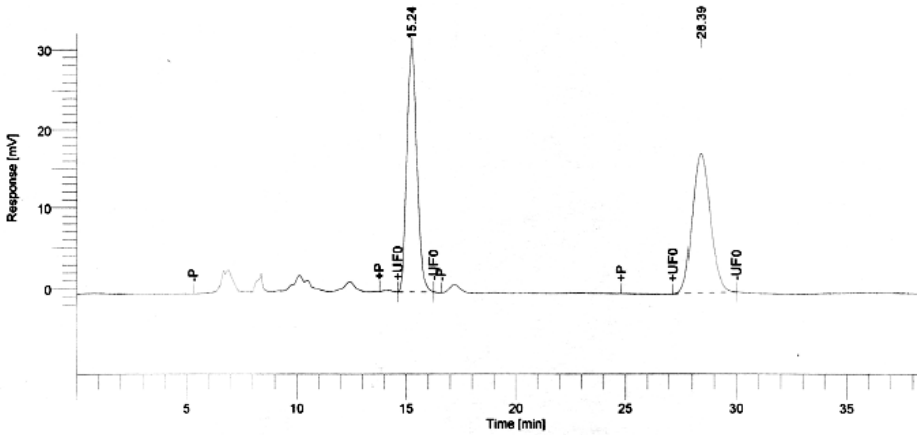
Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.081	42060649.84	1317210.62	97.22
2		15.959	1202558.59	31985.58	2.78
			43263208.44	1349196.20	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=1.5/100, Flow rate = 0.5 ml/min, Temperature = 20

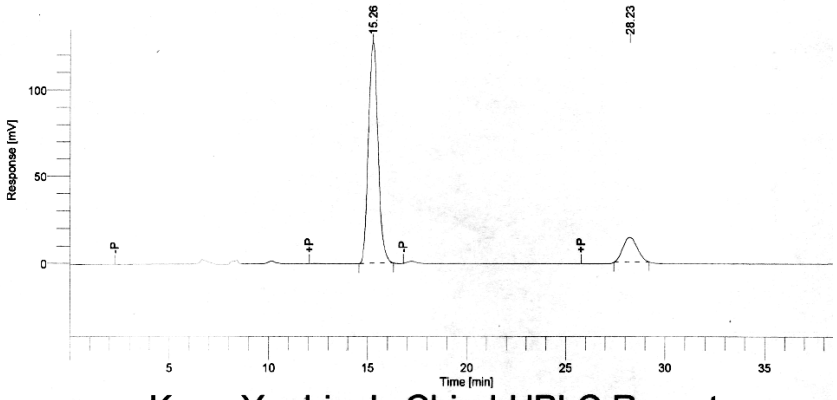




Kang Yanbiao's Chiral-HPLC Report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		15.240	19136774.34	59516.84	50.28
2		28.392	1892141.31	34110.65	49.72
			3805815.65	93627.49	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=4/100, Flow rate = 0.5 ml/min, Temperature = 20



Kang Yanbiao's Chiral-HPLC Report

Cis-Oxazolidine Product

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		15.262	8335714.90	247374.84	85.62
2		28.232	1399941.55	28102.84	14.38
			9735656.45	275477.68	100.00

Method: AD Column, Wave length = 238 nm, iPrOH/n-Hexane=4/100, Flow rate = 0.5 ml/min, Temperature = 20