



Supporting Information

© Wiley-VCH 2007

69451 Weinheim, Germany

# Highly Enantioselective and Diastereoselective Cycloaddition of Cyclopropanes with Nitrones and Its Application in the Kinetic Resolution of 2-Substituted Cyclopropane-1,1-dicarboxylates

Yan-Biao Kang, Xiu-Li Sun, and Yong Tang\*

*The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai, 200032, China.. E-mail: tangy@mail.sioc.ac.cn*

## Table of Contents

|   |         |
|---|---------|
| Experimental Procedures and Spectral Data | S1-S8   |
| NMR Spectra                               | S9-S24  |
| HPLC Spectra                              | S25-S31 |

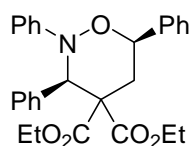
## General information.

All reactions were carried out under dry nitrogen atmosphere. Dimethoxyl ethane (DME) was distilled over calcium hydride prior to use. Activated molecular sieves powder 4 Å (MS 4 Å) was dried at 250 °C in vacuum before use. All of the nitrones<sup>1</sup> and 2-substituted cyclopropane-1,1-dicarboxylates<sup>2</sup> were synthesized according to the literature. All glassware was oven-dried, assembled hot, and cooled under a stream of dry nitrogen before use.

<sup>1</sup>H NMR was recorded on a Varian Mercury-300 (300 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using residual CDCl<sub>3</sub> (7.26 ppm) as an internal standard. <sup>13</sup>C NMR was recorded on a Varian Mercury-300 (75 MHz) spectrometers using proton decoupling. Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of CDCl<sub>3</sub> (77 ppm) as an internal standard.

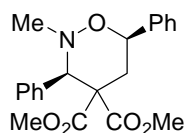
## Typical procedure for the enantioselective [3 + 3] cycloadditions.

A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.040 mmol) and trisoxazoline (0.044 mmol) in dimethoxyethane (1 mL) was stirred at 50 °C for 2 hours under nitrogen. The mixture was cooled to room temperature and then was transferred to cyclopropane diester (0.44 mmol) *via* a syringe. To the resulting solution was added activated molecular sieves 4 Å (100 mg). The mixture was stirred at -30 °C for 30 minutes and then nitrone (0.20 mmol) was added. After the reaction was complete (monitored by TLC), the mixture was passed rapidly through a glass funnel with a thin layer (20 mm) of silica gel (300-400 mesh), washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography.



(cis)-diethyl 2-phenyl-3,6-diphenyl-[1,2]oxazinane-4,4-dicarboxylate

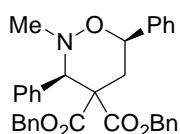
Analytical data: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.61-7.55 (m, 4H), 7.49-7.39 (m, 3H), 7.20-7.09 (m, 7H), 6.83-6.80 (m, 1H), 5.79 (s, 1H), 5.04 (dd, *J* = 3.3, 14.4 Hz, 1H), 4.39 (dd, *J* = 7.2, 14.4 Hz, 2H), 3.91 (m, 2H), 2.88-2.81 (m, 2H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 169.56, 167.88, 148.57, 139.56, 134.95, 130.56, 128.60, 128.48, 128.23, 127.98, 127.85, 126.38, 121.48, 115.71, 78.81, 65.74, 62.32, 61.79, 59.29, 31.81, 14.15, 13.68; IR (thin film, cm<sup>-1</sup>) 2978, 1737, 1586, 1492, 1446, 1255, 1231, 747, 692; Anal. Calcd for C<sub>28</sub>H<sub>29</sub>NO<sub>5</sub>: C, 73.18%; H, 6.36%; N, 3.05%; Found: C, 72.92%, H, 6.42%, N, 3.13%; LRMS-EI (*m/e*): 459 (*M*<sup>+</sup>, 4.5), 198(100.0). The ees listed in table 1 were determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 90/10 as eluent, 254 nm.



(cis)-dimethyl 2-methyl-3,6-diphenyl-[1,2]oxazinane-4,4-dicarboxylate

-30°C, 3 days, 82% yield for *cis*-isomer, dr = 13/1, 90% ee. 43% conversion of cyclopropane (by  $^1\text{H}$  NMR). Analytical data <sup>3,4</sup>:

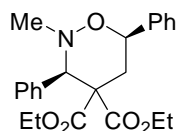
**$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.31 (m, 10H), 4.89 (dd,  $J$  = 2.8 Hz, 11.6 Hz, 1H), 4.85 (s, 1H), 3.89 (s, 3H), 3.39 (s, 3H), 2.78-2.60 (s, 2H), 2.54 (s, 3H);  $[\alpha]_{\text{D}}^{25}$  = +160.8° (c 1.0,  $\text{CHCl}_3$ , 90% ee.). 90% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 90/10 as eluent, 254 nm,  $t_{\text{R}1}$  = 6.10 min (minor),  $t_{\text{R}2}$  = 9.94 min (major). The absolute configuration for the cycloadducts has not been established and positive polar rotation was given, which was accorded with that of literature (+154.7°, same conditions).<sup>3</sup>



(cis)-dibenzyl 2-methyl-3,6-diphenyl-[1,2]oxazinane-4,4-dicarboxylate

-40°C, 4 days, 62% yield for *cis*-isomer, dr = 10/1, 97% ee. 41% conversion of cyclopropane (by  $^1\text{H}$  NMR). Analytical data:

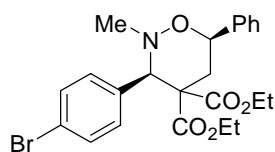
**$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (d,  $J$  = 6.6 Hz, 2H), 7.43-7.22 (m, 16H), 7.04-7.01 (m, 2H), 5.30 (s, 2H), 4.90 (dd,  $J$  = 3.4 Hz, 11.2 Hz, 1H), 4.86 (s, 1H), 4.77-4.65 (m, 2H), 2.79-2.63 (m, 2H), 2.52 (s, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.51, 167.69, 135.44, 134.75, 131.02, 128.55, 128.44, 128.35, 128.25, 128.20, 128.16, 128.05, 126.31, 77.98, 67.73 (2C), 67.26, 59.41, 43.31, 31.23. **IR** (thin film,  $\text{cm}^{-1}$ ) 3032, 2957, 2885, 1741, 1496, 1454, 1257, 1098, 749, 698; **Anal.** Calcd. For  $\text{C}_{33}\text{H}_{31}\text{NO}_5$ : C, 75.99; H, 5.99; N, 2.69. Found: C, 75.66; H, 6.14; N, 2.66. **LRMS-ESI**: 522 ( $\text{M} + \text{H}^+$ , 100).  $[\alpha]_{\text{D}}^{25}$  = +127.6° (c 1.0,  $\text{CHCl}_3$ , 97% ee.), 97% ee was determined by HPLC analysis using a Chiralpak OD-H column with hexane/*i*-PrOH 90/10 as eluent, 1 mL/min, 254 nm,  $t_{\text{R}1}$  = 5.79 min (major),  $t_{\text{R}2}$  = 6.81 min (minor).



(cis)-diethyl 2-methyl-3,6-diphenyl-[1,2]oxazinane-4,4-dicarboxylate

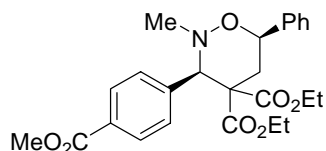
-30°C, 4 days, 88% yield for *cis*-isomer, dr = 11/1, 95% ee. 48% conversion of cyclopropane (by  $^1\text{H}$  NMR). Analytical data:

**$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.30 (m, 10H), 4.89 (dd,  $J$  = 3.3 Hz, 11.7 Hz, 1H), 4.84 (s, 1H), 4.40-4.33 (m, 2H), 3.92-3.72 (m, 2H), 2.78-2.60 (m, 2H), 2.53 (s, 3H), 1.33 (t,  $J$  = 7.2 Hz, 3H), 0.97 (t,  $J$  = 7.2 Hz, 3H);  **$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ )  $\delta$  169.71, 167.97, 140.14, 134.59, 131.02, 128.47, 128.09, 127.96, 127.88, 126.25, 77.88, 67.73, 61.99, 61.49, 59.02, 43.26, 31.07, 14.02, 13.55. **IR** (thin film,  $\text{cm}^{-1}$ ) 3029, 2984, 2885, 1738, 1494, 1453, 1366, 1253, 1099, 753, 700; **Anal.** Calcd. For  $\text{C}_{23}\text{H}_{27}\text{NO}_5$ : C, 69.50; H, 6.85; N, 3.52. Found: C, 69.48; H, 7.09; N, 3.46. **LRMS-ESI**: 398 ( $\text{M} + \text{H}^+$ , 100).  $[\alpha]_{\text{D}}^{25}$  = +160.3° (c 1.0,  $\text{CHCl}_3$ , 95% ee.), 95% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 90/10 as eluent, 1 mL/min, 254 nm,  $t_{\text{R}1}$  = 6.48 min (minor),  $t_{\text{R}2}$  = 7.94 min (major).



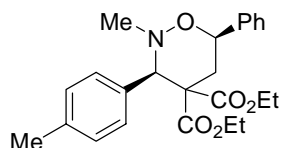
(cis)-diethyl 3-(4-bromophenyl)-2-methyl-6-phenyl-[1,2]oxazinane-4,4-dicarboxylate

-30°C, 4 days, 85% yield for *cis*-isomer, dr = 12/1, 97% ee. 45% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.53-7.34 (m, 9H), 4.90 (t, *J* = 7.4 Hz, 1H), 4.82 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.97-3.76 (m, 2H), 2.66-2.64 (m, 2H), 2.51 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.48, 167.86, 139.93, 133.73, 132.66, 131.12, 128.57, 128.09, 126.22, 122.48, 77.87, 67.11, 62.17, 61.70, 58.93, 43.26, 30.93, 14.05, 13.68. **IR** (thin film, cm<sup>-1</sup>) 2983, 2960, 2884, 1738, 1486, 1253, 1183, 1011, 968, 755, 698; **LRMS-ESI**: 476 (M + H<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>23</sub>H<sub>27</sub>BrNO<sub>5</sub><sup>+</sup> is 476.1067: observed: 476.1076; [α]<sub>D</sub><sup>25</sup> = +156.7° (c 1.0, CHCl<sub>3</sub>, 97% ee.), 97% ee was determined by HPLC analysis using a Chiralcel OD-H column with hexane/*i*-PrOH 50/1 as eluent, 1 mL/min, 254 nm, t<sub>R1</sub> = 5.49 min (major), t<sub>R2</sub> = 6.87 min (minor).



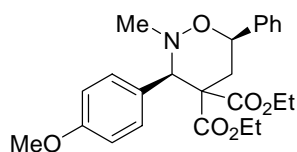
(*cis*)-diethyl 3-(4-(methoxycarbonyl)phenyl)-2-methyl-6-phenyl-[1,2]oxazinane-4,4-dicarboxylate

-30°C, 4 days, 97% yield, dr = 11/1, 97% ee. 46% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.48-7.32 (m, 5H), 4.95-4.90 (m, 1H), 4.91 (s, 1H), 4.41-4.34 (m, 2H), 3.93-3.73 (m, 2H), 3.90 (s, 3H), 2.74-2.63 (m, 2H), 2.52 (s, 3H), 1.33 (t, *J* = 6.9 Hz, 3H), 0.99 (t, *J* = 6.9 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.42, 167.76, 166.72, 140.06, 131.06, 129.82, 129.08, 128.56, 128.08, 126.21, 109.68, 77.92, 67.48, 62.18, 61.67, 58.93, 52.06, 43.27, 31.08, 14.03, 13.63. **IR** (thin film, cm<sup>-1</sup>) 2984, 2956, 2885, 1725, 1436, 1279, 1186, 1105, 699; **LRMS-ESI**: 456 (M + H<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>25</sub>H<sub>30</sub>BrNO<sub>7</sub><sup>+</sup> is 456.2017: observed: 456.2024; [α]<sub>D</sub><sup>25</sup> = +144.1° (c 1.0, CHCl<sub>3</sub>, 97% ee.), 97% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 90/10 as eluent, 1 mL/min, 254 nm, t<sub>R1</sub> = 8.53 min (minor), t<sub>R2</sub> = 11.44 min (major).



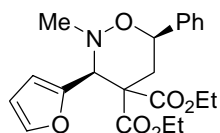
(*cis*)-diethyl 2-methyl-6-phenyl-3-*p*-tolyl-[1,2]oxazinane-4,4-dicarboxylate

-30°C, 4 days, 80% yield for *cis*-isomer, dr = 12/1, 96% ee. 41% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.51-7.33 (m, 7H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.90 (dd, *J* = 3.0 Hz, 12.0 Hz, 1H), 4.81 (s, 1H), 4.36 (q, *J* = 6.9 Hz, 1H), 3.95-3.73 (m, 2H), 2.77-2.53 (m, 2H), 2.52 (s, 3H), 2.32 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.81, 168.06, 140.14, 137.73, 131.41, 130.91, 128.63, 128.49, 127.96, 126.31, 77.92, 67.47, 61.96, 61.47, 59.09, 43.25, 31.08, 21.03, 14.04, 13.62. **IR** (thin film, cm<sup>-1</sup>) 2982, 2885, 1739, 1254, 1181, 1098, 698; **LRMS-ESI**: 412 (M + H<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>24</sub>H<sub>30</sub>BrNO<sub>5</sub><sup>+</sup> is 412.2118: observed: 412.2123; [α]<sub>D</sub><sup>25</sup> = +157.7° (c 1.0, CHCl<sub>3</sub>, 96% ee.), 96% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 90/10 as eluent, 1 mL/min, 254 nm, t<sub>R1</sub> = 6.60 min (minor), t<sub>R2</sub> = 9.67 min (major).



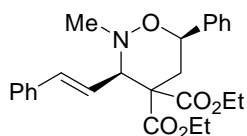
(*cis*)-diethyl 3-(4-methoxyphenyl)-2-methyl-6-phenyl-[1,2]oxazinane-4,4-dicarboxylate

-30°C, 4 days, 92% yield for *cis*-isomer, dr = 13/1, 90% ee. 47% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.55-7.31 (m, 7H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.90 (dd, *J* = 3.0 Hz, 11.6 Hz, 1H), 4.80 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 1H), 3.96-3.80 (m, 2H), 3.79 (s, 3H), 2.84-2.59 (m, 2H), 2.51 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.84, 168.09, 159.30, 140.24, 132.24, 128.51, 127.98, 126.29, 113.24, 77.90, 67.08, 61.99, 61.49, 59.14, 55.06, 43.22, 31.04, 14.05, 13.70. **IR** (thin film, cm<sup>-1</sup>) 2983, 2885, 1738, 1511, 1252, 1180, 699; **LRMS-ESI**: 428 (M + H<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>24</sub>H<sub>30</sub>BrNO<sub>5</sub><sup>+</sup> is 428.2068; observed: 428.2078; [α]<sub>D</sub><sup>25</sup> = +150.9° (c 1.0, CHCl<sub>3</sub>, 90% ee.), 90% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 19/1 as eluent, 1 mL/min, 254 nm, t<sub>R1</sub> = 12.66 min (minor), t<sub>R2</sub> = 16.15 min (major).



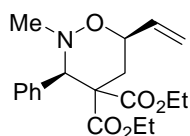
(*cis*)-diethyl 3-(furan-2-yl)-2-methyl-6-phenyl-[1,2]oxazinan-4,4-dicarboxylate

-30°C, 4 days, 99% yield, dr = 13/1, 93% ee. 45% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.45-7.25 (m, 6H), 6.49 (d, *J* = 3.3 Hz, 1H), 6.38 (t, *J* = 1.5 Hz, 1H), 4.98 (s, 1H), 4.93 (dd, *J* = 2.8 Hz, 11.2 Hz, 1H), 4.40-4.30 (m, 2H), 4.09-3.92 (m, 2H), 2.70-2.53 (m, 2H), 2.51 (s, 3H), 1.33 (t, *J* = 7.0 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 168.94, 167.78, 148.5, 142.14, 140.10, 128.42, 127.99, 126.42, 111.51, 110.15, 78.11, 62.11, 62.08, 61.64, 58.04, 42.97, 32.16, 14.00, 13.70. **IR** (thin film, cm<sup>-1</sup>) 2982, 2884, 1738, 1257, 1187, 1099, 1016, 754, 700; **LRMS-ESI**: 388 (M + H<sup>+</sup>, 100). **Anal.** Calcd. For C<sub>21</sub>H<sub>25</sub>NO<sub>6</sub>: C, 65.10; H, 6.50; N, 3.61. Found: C, 64.85; H, 6.64; N, 3.44. [α]<sub>D</sub><sup>25</sup> = +130.6° (c 1.0, CHCl<sub>3</sub>, 93% ee.), 93% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 50/1 as eluent, 1 mL/min, 254 nm, t<sub>R1</sub> = 12.80 min (minor), t<sub>R2</sub> = 15.74 min (major).



(*cis,E*)-diethyl 2-methyl-6-phenyl-3-styryl-[1,2]oxazinan-4,4-dicarboxylate

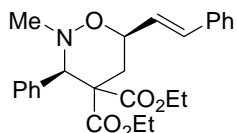
-30°C, 3 days, 76% yield for *cis*-isomer, dr = 4/1, 92% ee. 47% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.45-7.24 (m, 10H), 6.69-6.50 (m, 2H), 4.89 (dd, *J* = 2.4 Hz, 12.0 Hz, 1H), 4.38-4.30 (m, 3H), 4.12-4.04 (m, 2H), 2.64 (s, 3H), 2.64-2.59 (m, 1H), 2.40 (dd, *J* = 12.0 Hz, 14.4 Hz, 1H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.24, 168.19, 140.02, 137.44, 136.19, 128.54, 128.43, 128.04, 127.99, 126.54, 126.38, 120.96, 78.19, 67.15, 61.86, 61.72, 59.01, 43.15, 31.86, 14.04. **IR** (thin film, cm<sup>-1</sup>) 2981, 2883, 1737, 1450, 697; **LRMS-ESI**: 424 (M + H<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>25</sub>H<sub>30</sub>NO<sub>5</sub><sup>+</sup> is 424.2118; observed: 424.2127; [α]<sub>D</sub><sup>25</sup> = +239.3° (c 1.0, CHCl<sub>3</sub>, 92% ee.), 92% ee was determined by HPLC analysis using a Chiralcel OD-H column with hexane/*i*-PrOH 30/1 as eluent, 1 mL/min, 254 nm, t<sub>R1</sub> = 4.86 min (major), t<sub>R2</sub> = 5.53 min (minor).



(*cis*)-diethyl 2-methyl-3-phenyl-6-vinyl-[1,2]oxazinan-4,4-dicarboxylate

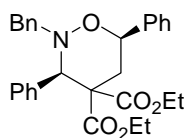
-40°C, 3 days, 88% yield for *cis*-isomer, dr = 6/1, 80% ee. 46% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data <sup>4</sup>:

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.54-7.51 (m, 2H), 7.30-7.27 (m, 3H), 6.04-5.93 (m, 1H), 5.39 (d, *J* = 17.1 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 4.74 (s, 1H), 4.40-4.29 (m, 3H), 3.91-3.71 (m, 2H), 2.46-2.43 (m, 5H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +155.2 (c 1.0, CHCl<sub>3</sub>, 80% ee.), 80% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 50/1 as eluent, 1 mL/min, 254 nm, *t*<sub>R1</sub> = 6.89 min (major), *t*<sub>R2</sub> = 9.59 min (minor).



(*cis,E*)-diethyl 2-methyl-3-phenyl-6-styryl-[1,2]oxazinane-4,4-dicarboxylate

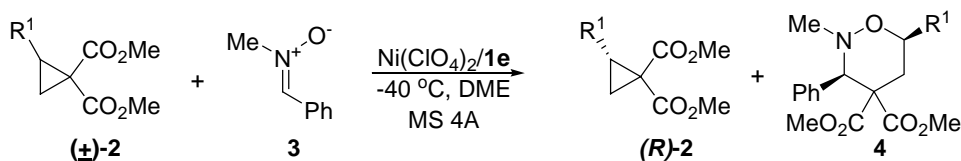
-40°C, 5 hrs, 84% yield, dr = 5/1, 80% ee. 41% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.56-7.26 (m, 10H), 6.72 (d, *J* = 15.9 Hz, 1H), 6.34 (dd, *J* = 5.8 Hz, 15.8 Hz, 1H), 4.78 (s, 1H), 4.57-4.55 (m, 1H), 4.35 (q, *J* = 6.9 Hz, 2H), 3.93-3.72 (m, 2H), 2.62-2.50 (m, 2H), 2.50 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.77, 168.11, 136.49, 134.72, 132.16, 131.15, 128.54, 128.17, 127.92, 127.89, 127.74, 126.60, 76.29, 68.02, 62.07, 61.56, 58.73, 43.34, 30.12, 14.08, 13.64. **IR** (thin film, cm<sup>-1</sup>) 2981, 2885, 1738, 1252, 701; **LRMS-ESI**: 424 (*M* + *H*<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>25</sub>H<sub>30</sub>NO<sub>5</sub><sup>+</sup> is 424.2118; observed: 424.2118; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +121.9° (c 1.0, CHCl<sub>3</sub>, 80% ee.), 80% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 19/1 as eluent, 1 mL/min, 254 nm, *t*<sub>R1</sub> = 7.61 min (major), *t*<sub>R2</sub> = 8.40 min (minor).



(*cis*)-diethyl 2-benzyl-3,6-diphenyl-[1,2]oxazinane-4,4-dicarboxylate

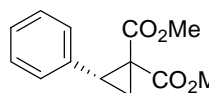
-30°C, 5 days, 74% yield for *cis*-isomer, dr = 11/1, 93% ee. 48% conversion of cyclopropane (by <sup>1</sup>H NMR). Analytical data: **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.60-7.24 (m, 15H), 4.96 (t, *J* = 7.2 Hz, 1H), 4.90 (s, 1H), 4.42-4.25 (m, 2H), 3.92 (d, *J* = 13.8 Hz, 1H), 3.90-3.70 (m, 2H), 3.64 (d, *J* = 13.8 Hz, 1H), 2.74 (s, 1H), 2.71 (s, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 169.53, 168.09, 140.21, 136.92, 134.89, 131.28, 128.79, 128.35, 128.10, 127.92, 127.88, 127.74, 126.97, 126.09, 77.70, 65.70, 61.92, 61.44, 59.38, 59.28, 31.26, 14.05, 13.54. **IR** (thin film, cm<sup>-1</sup>) 3062, 3030, 2981, 2937, 1739, 1453, 1253, 1199, 755, 699; **LRMS-ESI**: 474 (*M* + *H*<sup>+</sup>, 100). **HRMS-ESI** calcd. for C<sub>29</sub>H<sub>32</sub>NO<sub>5</sub><sup>+</sup> is 474.2275; observed: 474.2266; [ $\alpha$ ]<sub>D</sub><sup>25</sup> = +113.3° (c 1.0, CHCl<sub>3</sub>, 93% ee.), 93% ee was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 30/1 as eluent, 1 mL/min, 254 nm, *t*<sub>R1</sub> = 8.27 min (minor), *t*<sub>R2</sub> = 11.19 min (major). When this reaction scale was enlarged by 2 times, the results are similar as above: cyclopropane/nitrone = 0.88 mmol/0.40 mmol, -30°C, 7 days, 83% yield for *cis*-isomer, dr = 10/1, 94% ee, 49% conversion of cyclopropane (by <sup>1</sup>H NMR).

## General procedure for kinetic resolution of cyclopropane-1,1-diester.

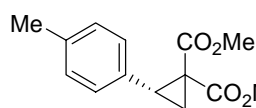


A mixture of Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.040 mmol) and trisoxazoline **1e** (0.044 mmol) in dimethoxyl ethane (1 mL) was stirred at 50 °C for 2 hours under nitrogen. The mixture was cooled to room temperature and then was transferred to cyclopropane diester (0.44 mmol) *via* a syringe. To the resulting solution was added activated molecular sieves 4Å (100 mg). The mixture

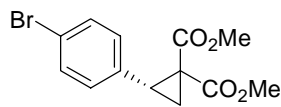
was stirred at -30°C for 30 minutes and then nitron (0.23 mmol) was added. After the conversion of ( $\pm$ ) **2** was higher than 50% (monitored by  $^1\text{H}$  NMR), the mixture was passed rapidly through a glass funnel with a thin layer (20 mm) of silica gel (300-400 mesh), washed with  $\text{CH}_2\text{Cl}_2$  (50 mL). The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography. The absolute configuration for recovered cyclopropanes was assigned *R* by comparing its polar rotation with that reported in the reference.<sup>5</sup>



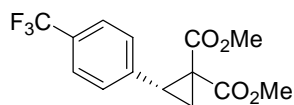
(*R*)-dimethyl 2-phenylcyclopropane-1,1-dicarboxylate.<sup>5</sup> Cyclopropane/nitron = 0.40 mmol/0.40 mmol, at -40 °C, 30 hours, 55 % conversion of cyclopropane by  $^1\text{H}$  NMR. Recovered yield: 43%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.30-7.17 (m, 5H), 3.78 (s, 3H), 3.35 (s, 3H), 3.23 (t,  $J$  = 8.7 Hz, 1H), 2.20 (dd,  $J$  = 5.1 Hz, 8.1 Hz, 1H), 1.74 (dd,  $J$  = 5.1 Hz, 9.3 Hz, 1H).  $[\alpha]_{\text{D}}^{25}$  = +131.9 ( $c$  1.0, PhH), 91% ee determined by HPLC analysis using a Chiralcel OD-H with hexane/*i*-PrOH = 50/1 v/v, 1.0 mL/min, 254 nm,  $t_{\text{R}1}$  = 7.70 min (minor),  $t_{\text{R}2}$  = 8.14 min (major).



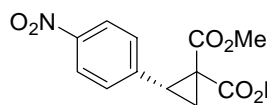
(*R*)-dimethyl 2-*p*-tolylcyclopropane-1,1-dicarboxylate.<sup>5</sup> Cyclopropane/nitron = 0.4 mmol/0.25 mmol, at -40 °C, 48 hours, 50 % conversion of cyclopropane by  $^1\text{H}$  NMR. Recovered yield: 49%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.07 (s, 4H), 3.78 (s, 3H), 3.38 (s, 3H), 3.19 (t,  $J$  = 8.6 Hz, 1H), 2.30 (s, 3H), 2.17 (dd,  $J$  = 5.1 Hz, 8.1 Hz, 1H), 1.72 (dd,  $J$  = 5.1 Hz, 9.3 Hz, 1H).  $[\alpha]_{\text{D}}^{25}$  = +119.3° ( $c$  1.0, PhH), 96% ee determined by HPLC analysis using a Chiralcel OD-H with hexane/*i*-PrOH = 500/3 v/v, 0.6 mL/min, 254 nm,  $t_{\text{R}1}$  = 18.63 min (minor),  $t_{\text{R}2}$  = 19.86 min (major).



(*R*)-dimethyl 2-(4-bromophenyl)cyclopropane-1,1-dicarboxylate.<sup>5</sup> Cyclopropane/nitron = 0.4 mmol/0.23 mmol, at -30 °C, 67 hours, 51 % conversion of cyclopropane by  $^1\text{H}$  NMR. Recovered yield: 49%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.40 (d,  $J$  = 8.4 Hz, 2H), 7.07 (d,  $J$  = 7.8 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 3H), 3.16 (t,  $J$  = 8.7 Hz, 1H), 2.15 (dd,  $J$  = 5.1 Hz, 8.0 Hz, 1H), 1.74 (dd,  $J$  = 5.1 Hz, 9.3 Hz, 1H).  $[\alpha]_{\text{D}}^{25}$  = +90.1° ( $c$  1.0, PhH), 95% ee determined by HPLC analysis using a Chiralcel AD-H with hexane/*i*-PrOH = 50/1 v/v, 0.8 mL/min, 254 nm,  $t_{\text{R}1}$  = 12.02 min (minor),  $t_{\text{R}2}$  = 13.46 min (major).

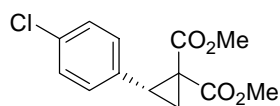


(*R*)-dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate.<sup>5</sup> Cyclopropane/nitron = 0.4 mmol/0.23 mmol, at 0 °C, 168 hours, 50 % conversion of cyclopropane by  $^1\text{H}$  NMR. Recovered yield: 49%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  7.54 (d,  $J$  = 8.1 Hz, 2H), 7.31 (d,  $J$  = 8.1 Hz, 2H), 3.81 (s, 3H), 3.39 (s, 3H), 3.26 (t,  $J$  = 8.7 Hz, 1H), 2.21 (dd,  $J$  = 5.4 Hz, 8.2 Hz, 1H), 1.79 (dd,  $J$  = 5.4 Hz, 9.6 Hz, 1H).  $[\alpha]_{\text{D}}^{25}$  = +44.5° ( $c$  1.0, PhH), 96% ee determined by HPLC analysis using a Chiralcel AD-H with hexane/*i*-PrOH = 50/1 v/v, 0.8 mL/min, 238 nm,  $t_{\text{R}1}$  = 7.91 min (minor),  $t_{\text{R}2}$  = 9.32 min (major).

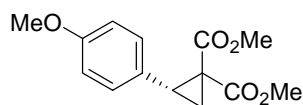


(*R*)-dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate.<sup>6</sup> Cyclopropane/nitron = 0.4 mmol/0.23 mmol, at 0 °C, 96 hours, 53 % conversion of cyclopropane by  $^1\text{H}$  NMR. Recovered yield: 45%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$  8.14 (d,  $J$  = 9.0 Hz, 2H), 7.36 (d,  $J$  = 8.4 Hz, 2H), 3.81 (s, 3H), 3.41 (s, 3H), 3.28 (t,  $J$  = 8.7 Hz, 1H), 2.22 (dd,  $J$  = 5.4 Hz, 7.7 Hz, 1H), 1.83 (dd,  $J$  = 5.4 Hz, 9.3 Hz, 1H).  $[\alpha]_{\text{D}}^{25}$  = +100.5° ( $c$  1.0, PhH), 97% ee determined by HPLC analysis

using a Chiralcel AD-H with hexane/*i*-PrOH = 90/10 v/v, 0.7 mL/min, 254 nm,  $t_{R1}$  = 11.82 min (minor),  $t_{R2}$  = 14.63 min (major).

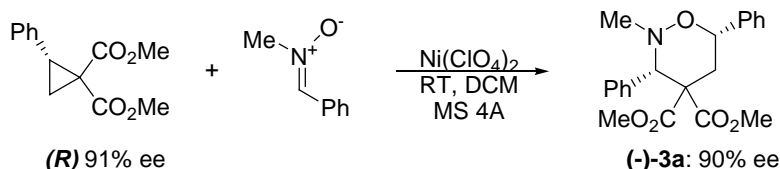


(*R*)-dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate.<sup>5</sup> Cyclopropane/nitrone = 0.4 mmol/0.23 mmol, -30 °C, 72 hours, 50 % conversion of cyclopropane by <sup>1</sup>H NMR. Recovered yield: 49%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.24 (d,  $J$  = 6.9 Hz, 2H), 7.13 (d,  $J$  = 8.4 Hz, 2H), 3.79 (s, 3H), 3.41 (s, 3H), 3.19 (t,  $J$  = 8.4 Hz, 1H), 2.16 (dd,  $J$  = 5.1 Hz, 8.0 Hz, 1H), 1.75 (dd,  $J$  = 5.1 Hz, 9.6 Hz, 1H).  $[\alpha]_D^{25}$  = +95.8° (*c* 1.0, PhH), 94% ee estimated on the basis of HPLC analysis using a chiral column: Diacel Chiralcel AD-H with hexane/*i*-PrOH = 50/1 v/v, 0.8 mL/min, 254 nm,  $t_{R1}$  = 10.79 min (minor),  $t_{R2}$  = 12.31 min (major).

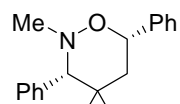


(*R*)-dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate.<sup>7</sup> Cyclopropane/nitrone = 0.4 mmol/0.23 mmol, at -30°C, 48 hours, 57 % conversion of cyclopropane by <sup>1</sup>H NMR. Recovered yield: 40%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.10 (d,  $J$  = 8.4 Hz, 2H), 6.79 (d,  $J$  = 8.7 Hz, 2H), 3.77 (s, 3H), 3.76 (s, 3H), 3.38 (s, 3H), 3.17 (t,  $J$  = 8.6 Hz, 1H), 2.14 (dd,  $J$  = 5.1 Hz, 8.0 Hz, 1H), 1.71 (dd,  $J$  = 5.1 Hz, 9.3 Hz, 1H).  $[\alpha]_D^{25}$  = +56.4° (*c* 1.0, PhH), 92% ee estimated on the basis of HPLC analysis using a chiral column: Diacel Chiralpak AD-H with hexane/*i*-PrOH = 20/1 v/v, 1.0 mL/min, 254 nm,  $t_{R1}$  = 9.26 min (minor),  $t_{R2}$  = 10.24 min (major).

## Procedure for cycloaddition of nitrone with (*R*)-dimethyl 2-phenyl cyclopropane-1,1-dicarboxylate.



A mixture of (*R*)-dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (91% ee, 0.1 mmol), nitrone (0.12 mmol), MS 4Å (100 mg) and Ni(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.01 mmol, absence of ligand) in dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was stirred at room temperature for 48 hours under nitrogen. After the reaction was complete (monitored by TLC), the mixture was passed rapidly through a glass funnel with a thin layer (20 mm) of silica gel (300-400 mesh), washed with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The filtrate was concentrated under reduced pressure and the residue (used for the determination of the diastereomer ratio by <sup>1</sup>H NMR) was purified by flash chromatography. The *ee* was determined by HPLC analysis using a Chiralpak AD-H column with hexane/*i*-PrOH 20/1 as eluent, 254 nm,  $t_{R1}$  = 13.19 min (major),  $t_{R2}$  = 24.19 min (minor).



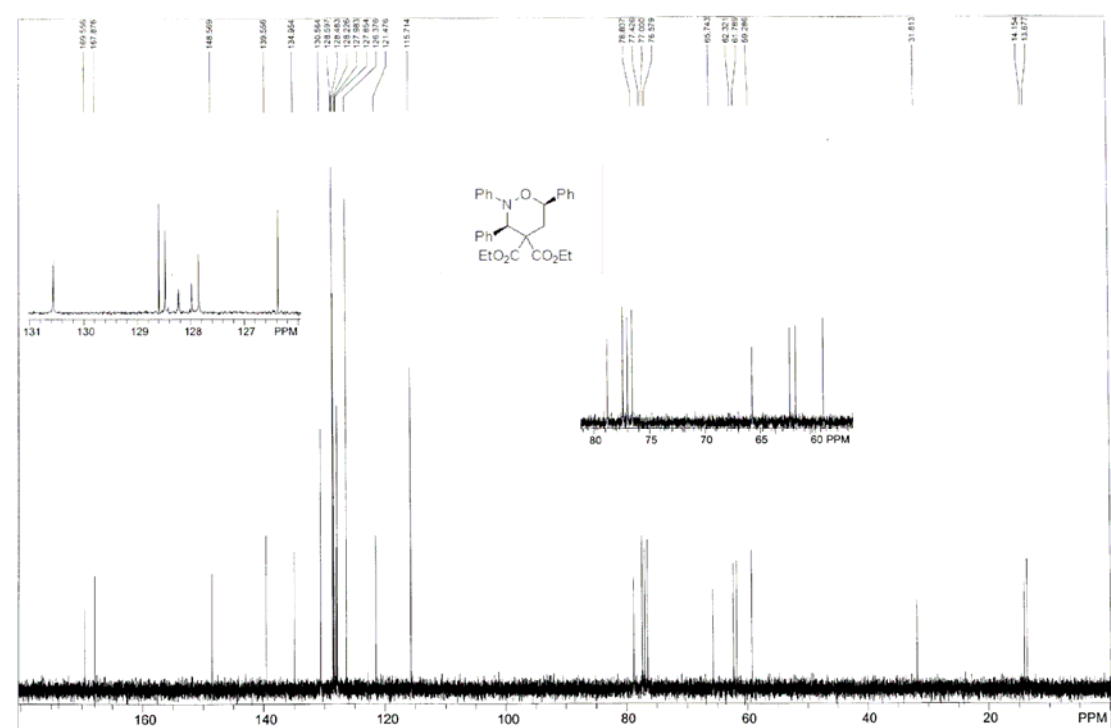
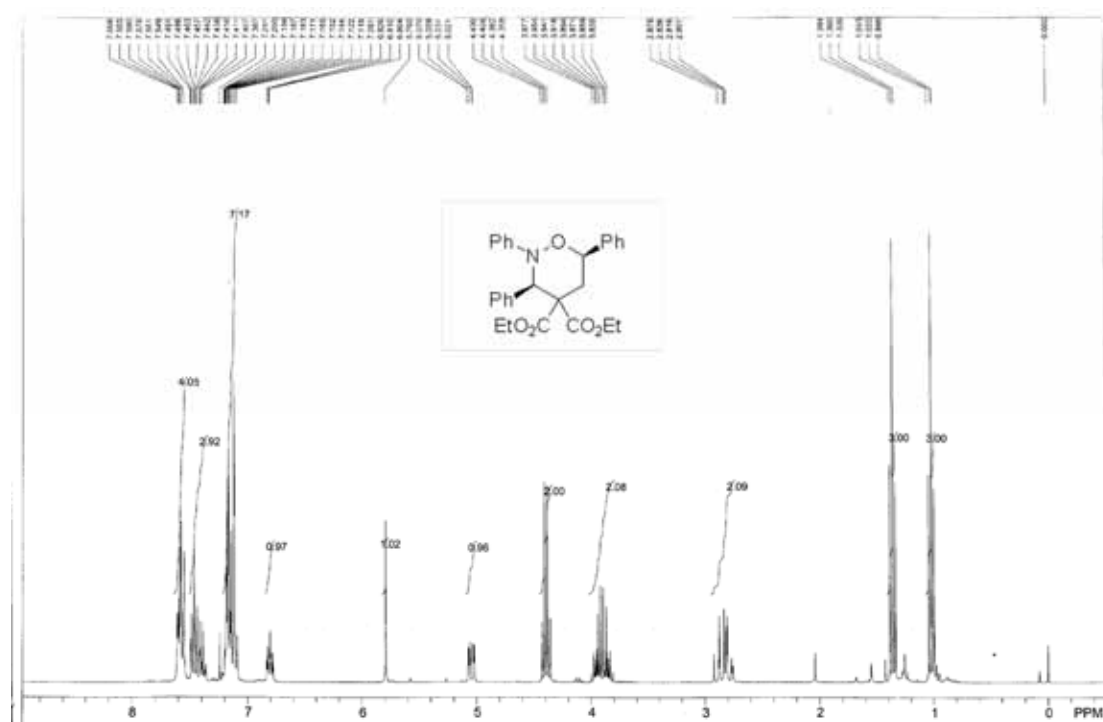
(3*S*, 6*S*)-dimethyl 2-methyl-3,6-diphenylmorpholine-4,4-dicarboxylate. Room temperature, 48 hours, dr > 99/1, 83% yield, 90% ee,  $[\alpha]_D^{25}$  = -152.9° (CHCl<sub>3</sub>, *c* 1.0, 90% ee).

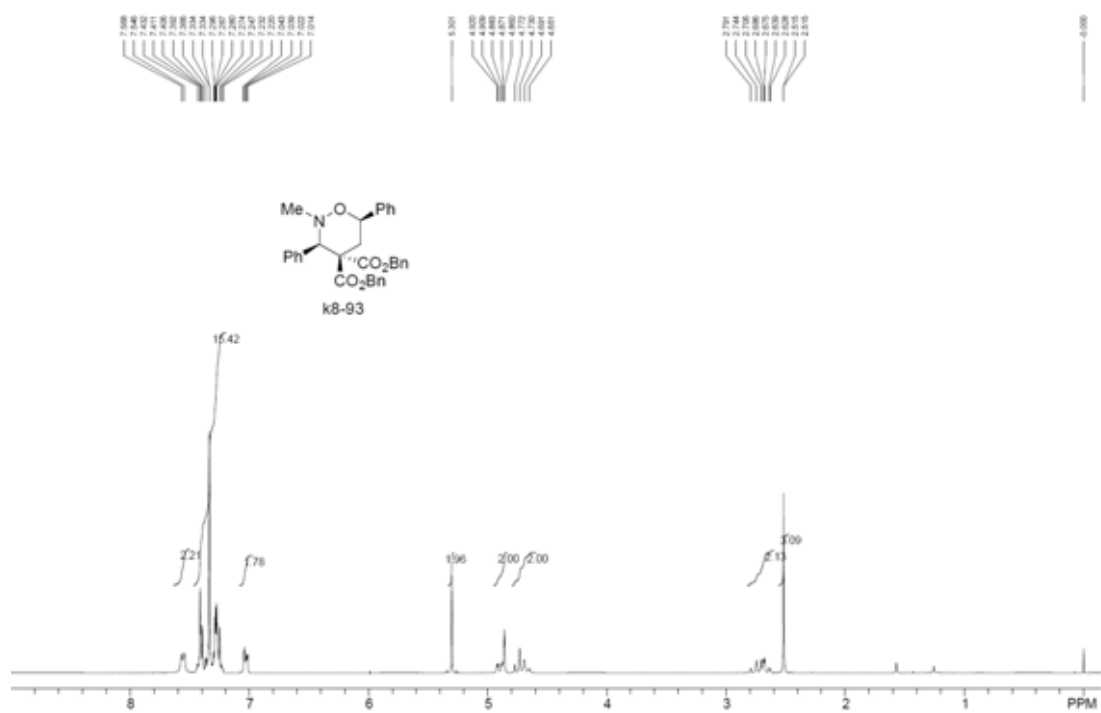
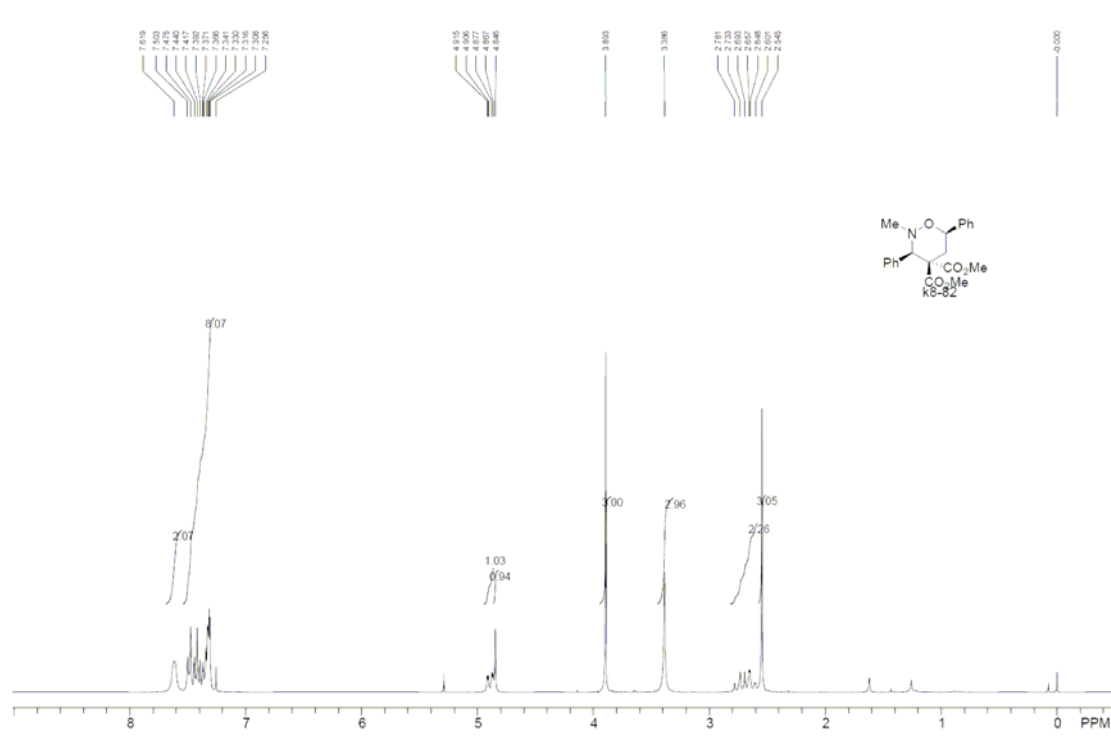
## References

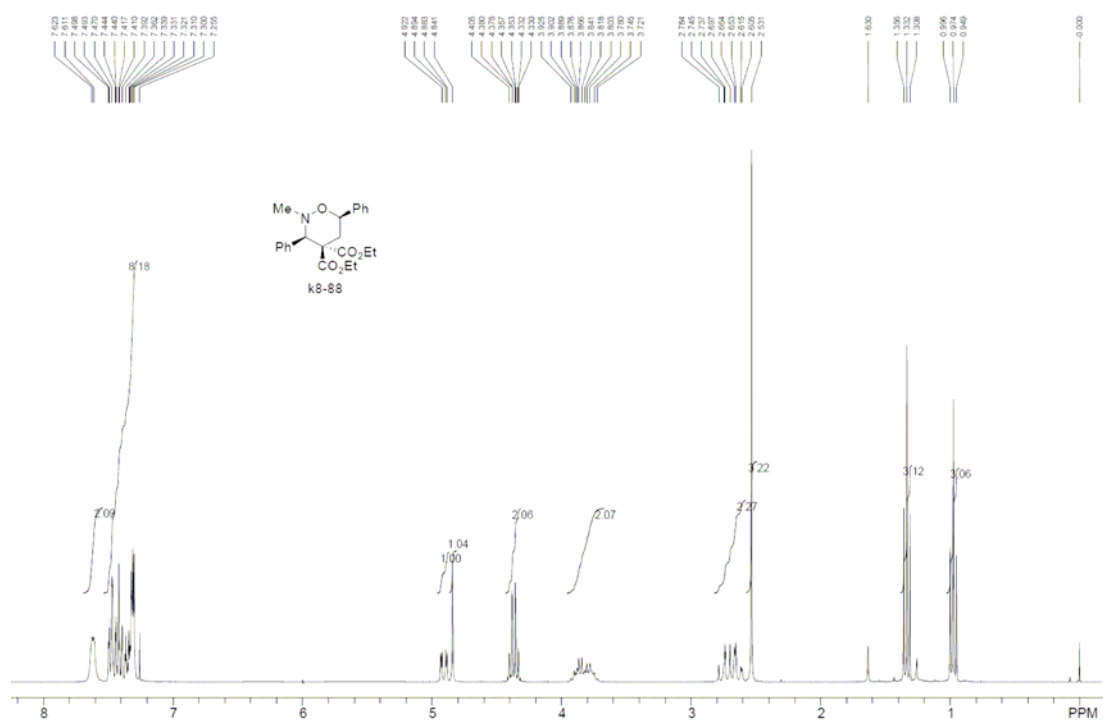
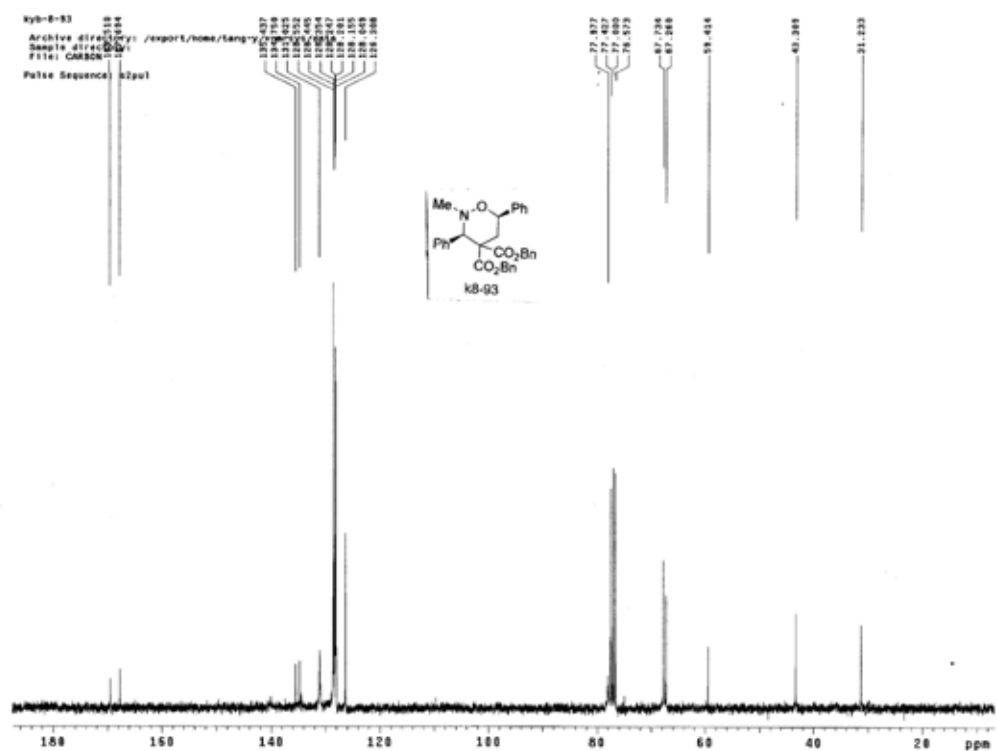
- [1] T. B. Patrick, J. A. Schield, Kirchner, D. G. *J. Org. Chem.* **1974**, 39, 1758.
- [2] E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.*, **1965**, 87, 1353.
- [3] M. P. Sibi, Z. Ma, C. P. Jasperse, *J. Am. Chem. Soc.* **2005**, 127, 5764.

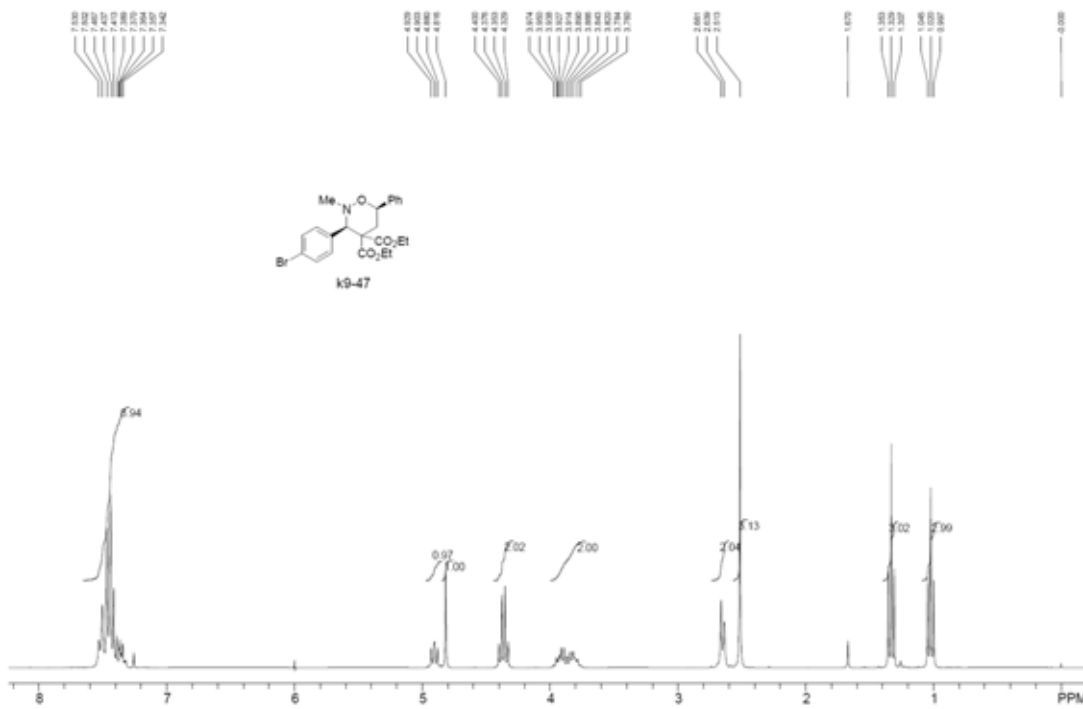
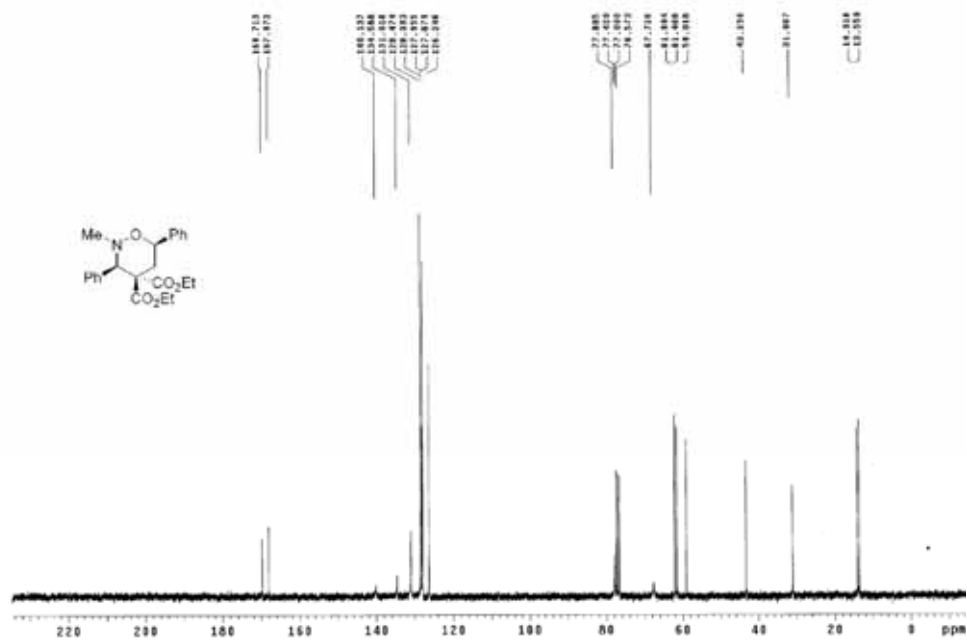
- [4] I. S. Young, M. A. Kerr, *Angew. Chem. Int. Ed.* **2003**, *42*, 3023-3026.
- [5] P. Müller, A. Ghanem, *Org. Lett.* **2004**, *6*, 4347-4350.
- [6] a) J. Martelli, R. Gree, *Chem. Commun.* **1980**, 355-356; b) M. Sato, H. Hisamichi, C. Kaneto, N. Suzaki, T. Furuya, N. Inukai, *Tetrohedron Lett.* **1989**, *30*, 5281-5184.
- [7] H. M. L. Davies, S. A. Panaro, *Tetrahedron* **2000**, *56*, 4871-4880.

# NMR spectra.

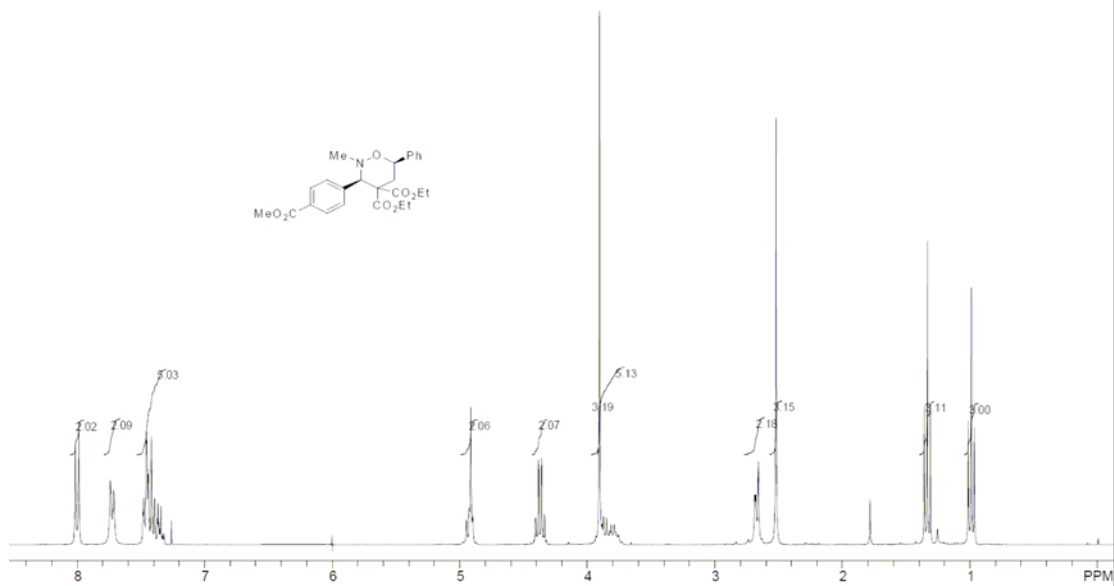
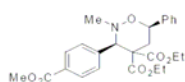
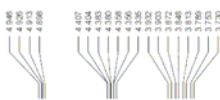
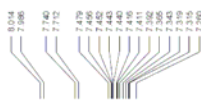
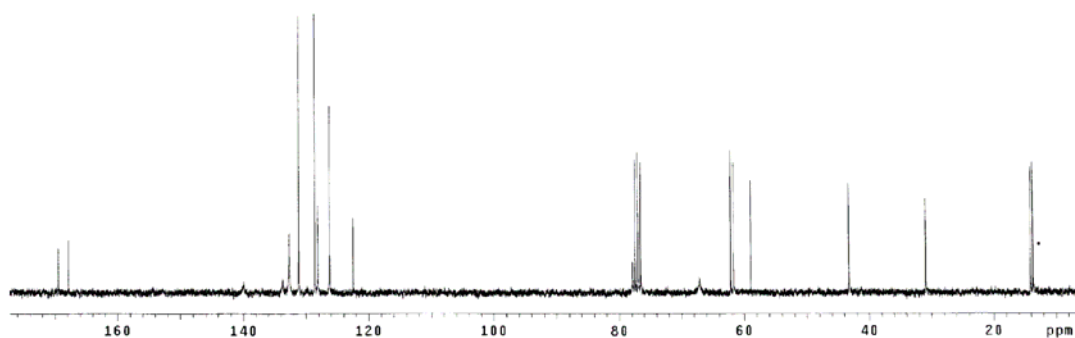
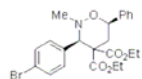
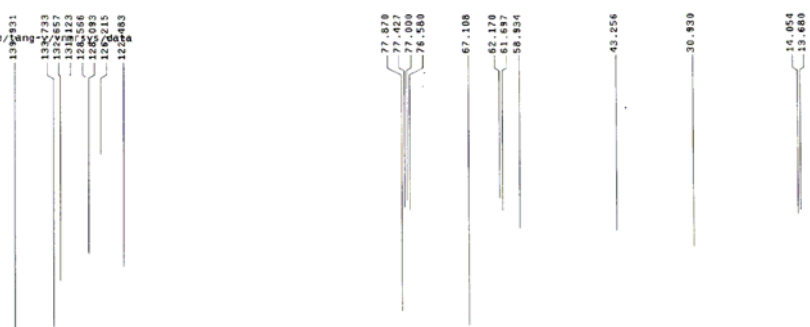




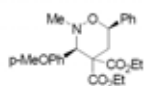
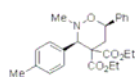




k5-42cc  
 8-40  
 Archive directory: /export/home/lang-2/data  
 Sample directory: /  
 Pulse Sequence: s2pu1

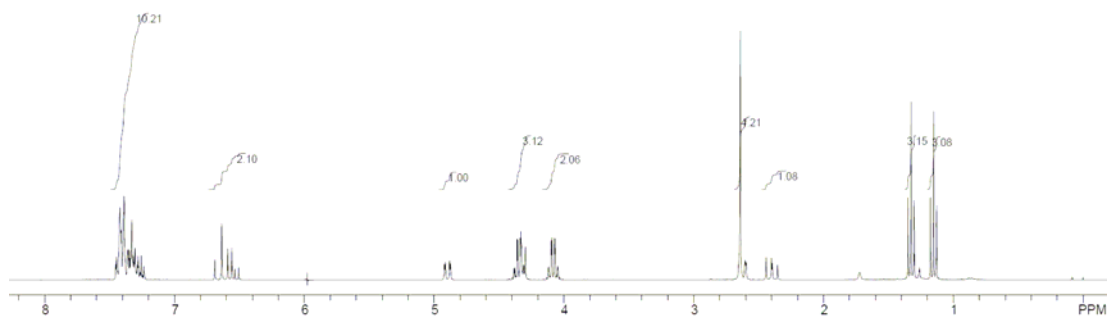
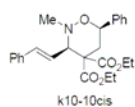
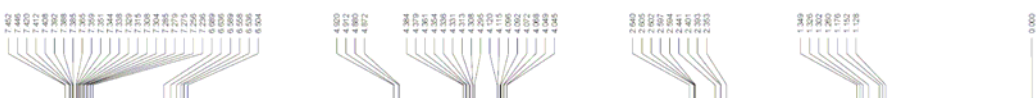
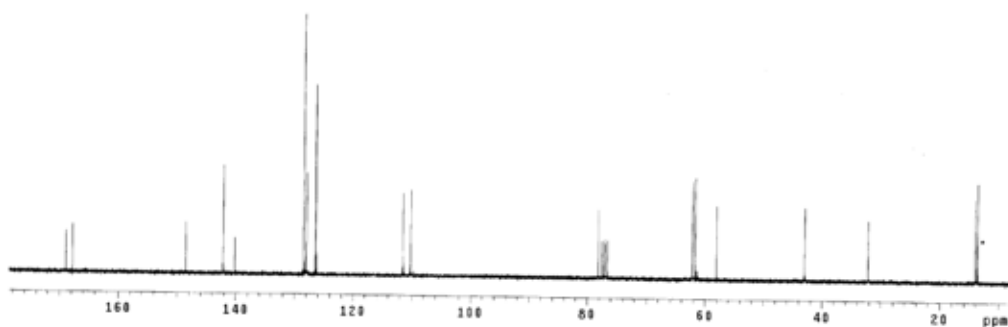
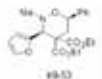




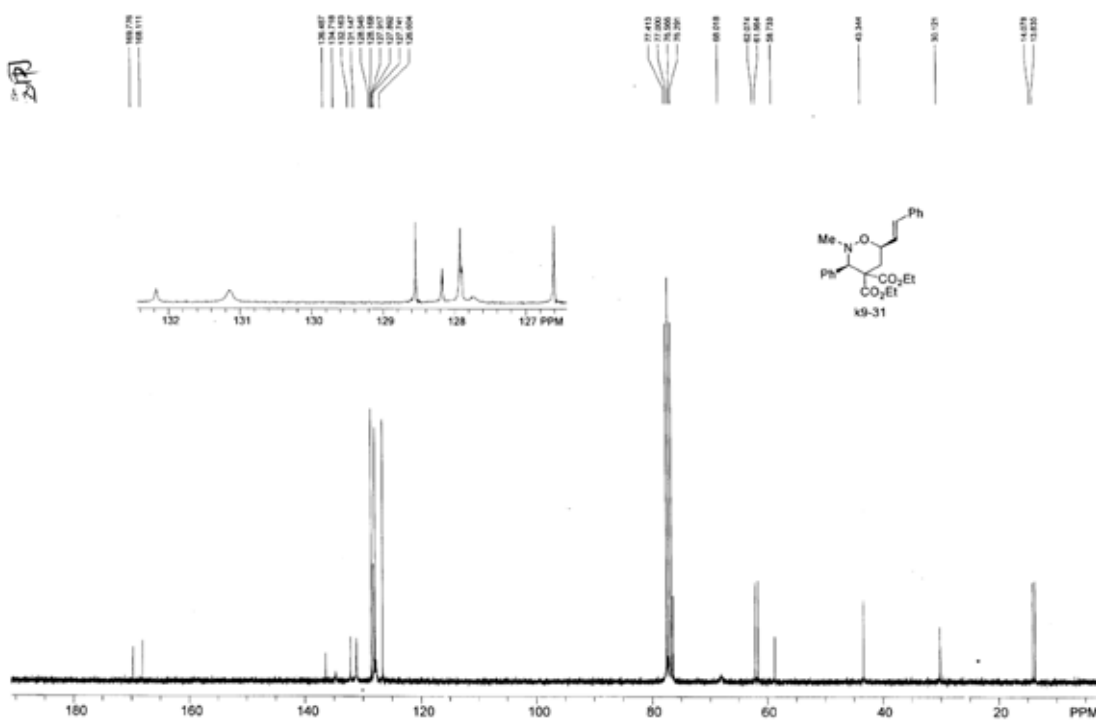
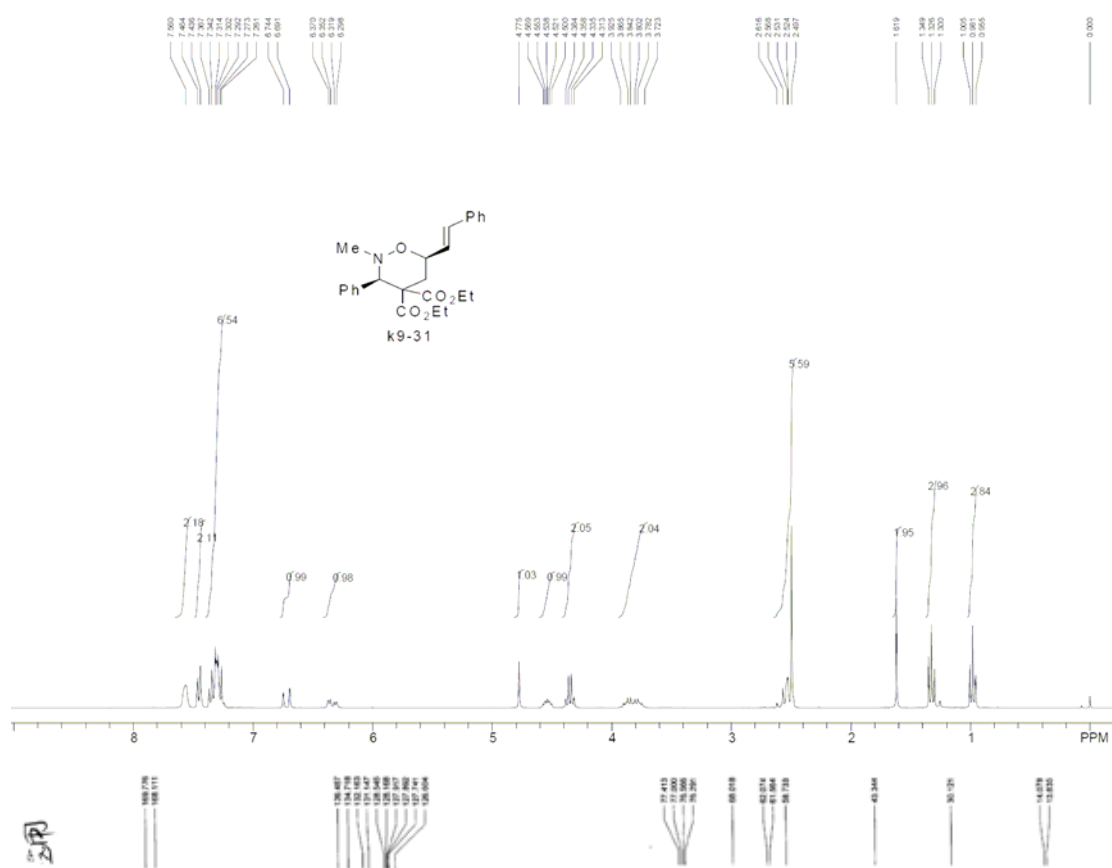


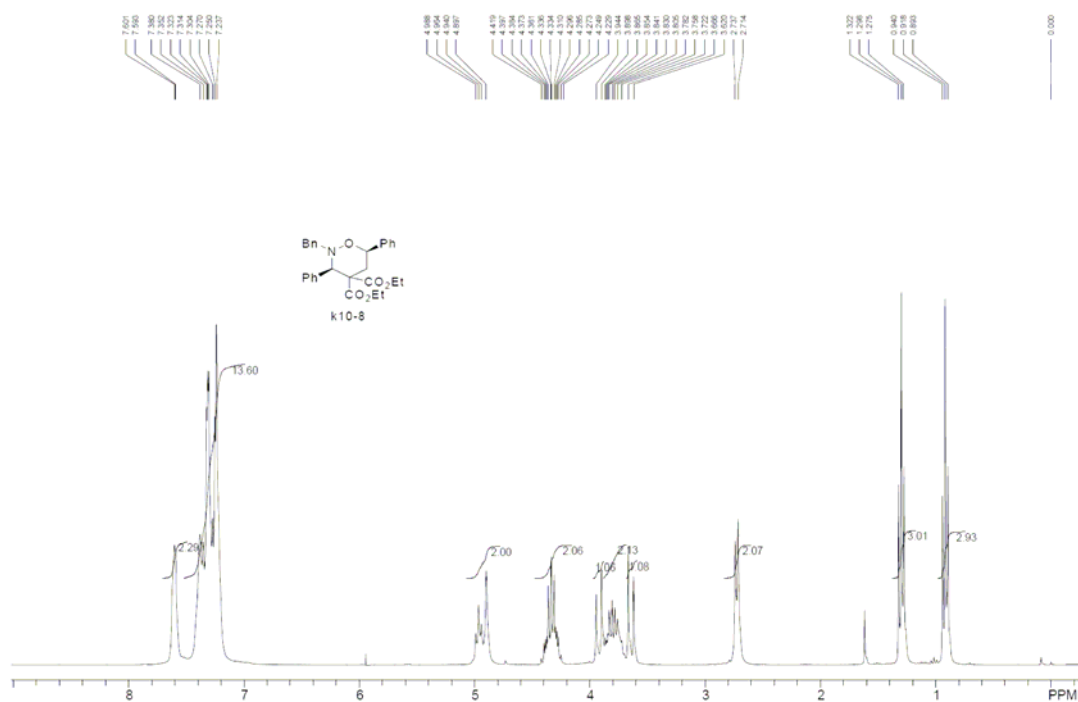


49-5301  
 Archive directory: /export/home/...  
 Sample directory: /...  
 File: 49-5301  
 Pulse Sequence: zgpg30





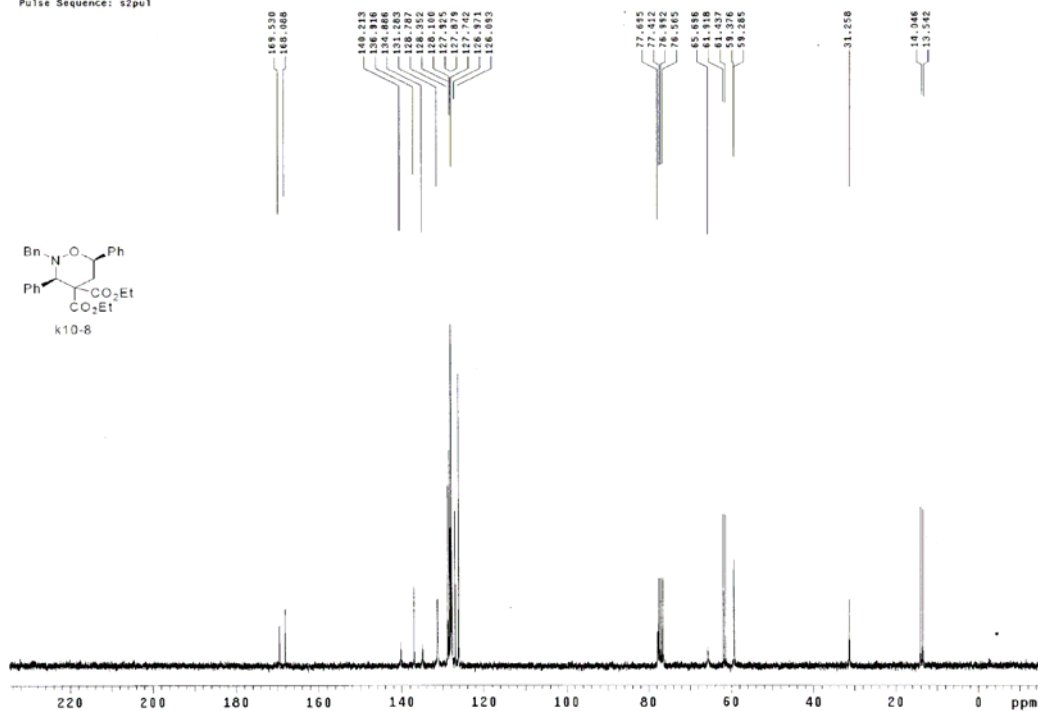




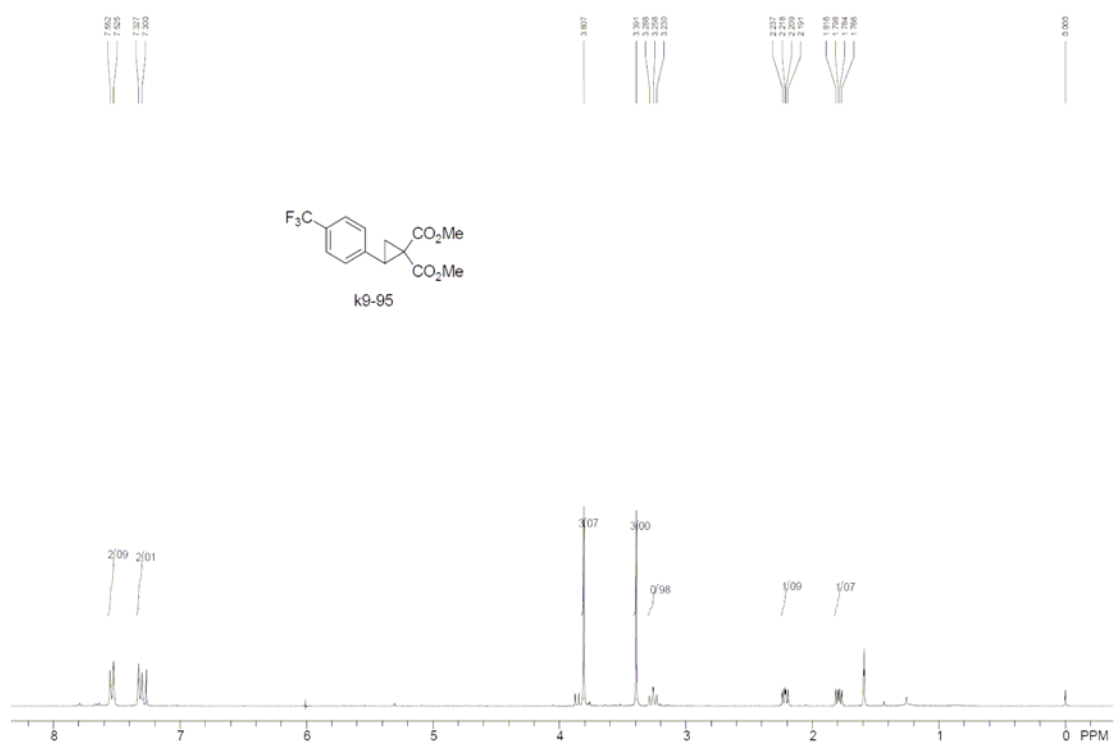
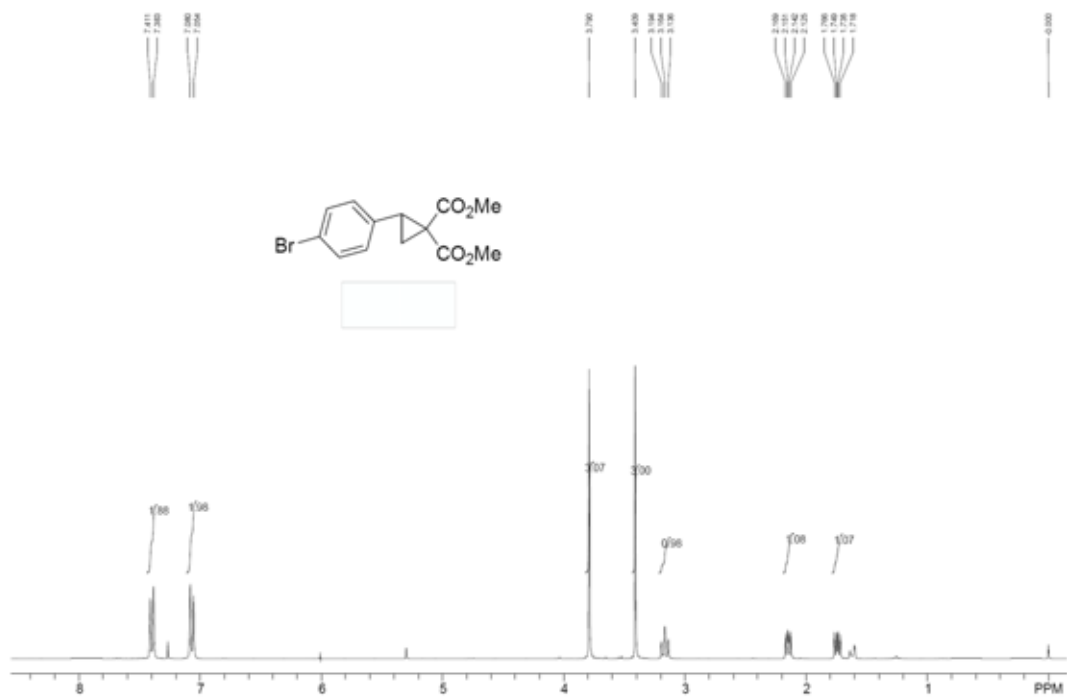
k10-8c

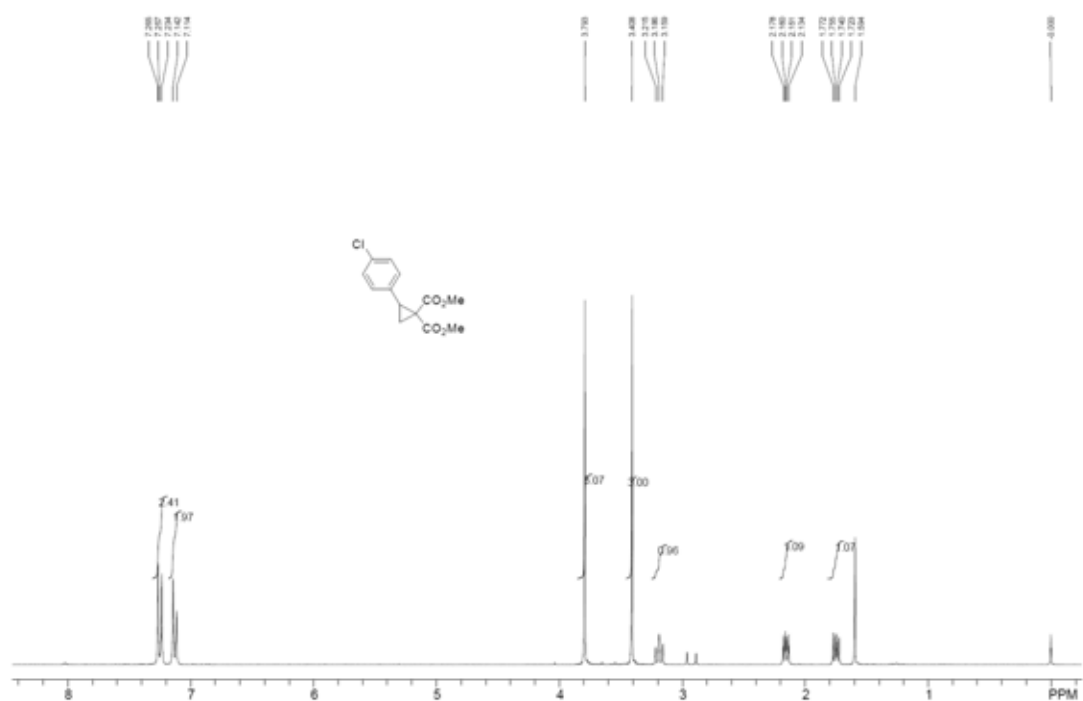
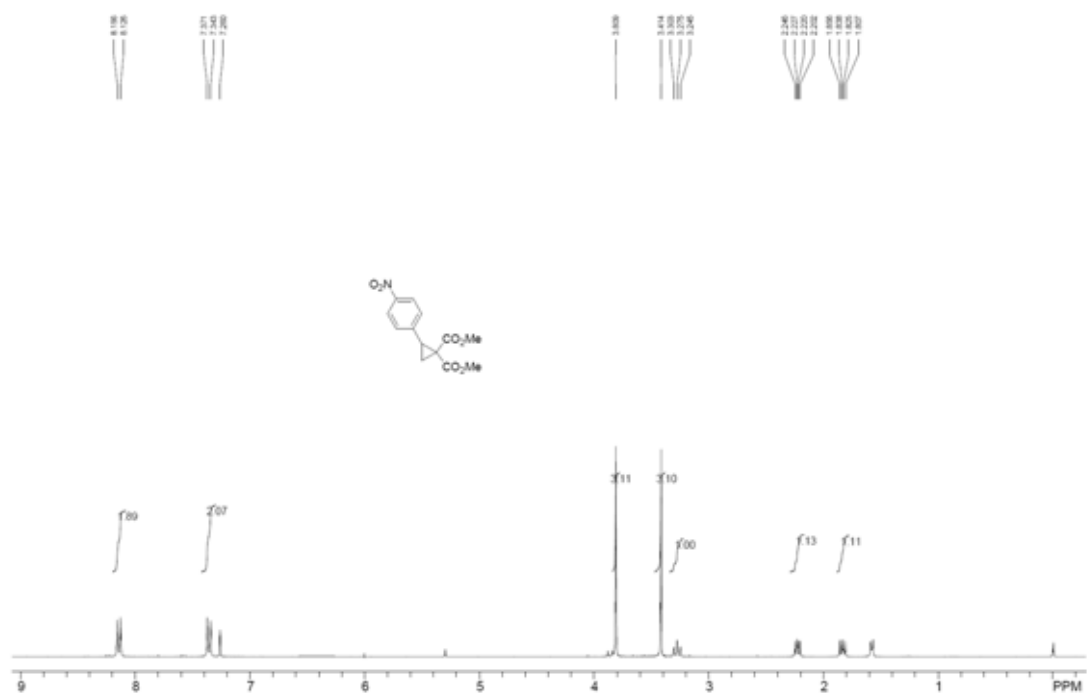
Archive directory: /export/home/tang-y/vnmrsys/data  
Sample directory:  
File: CARBON

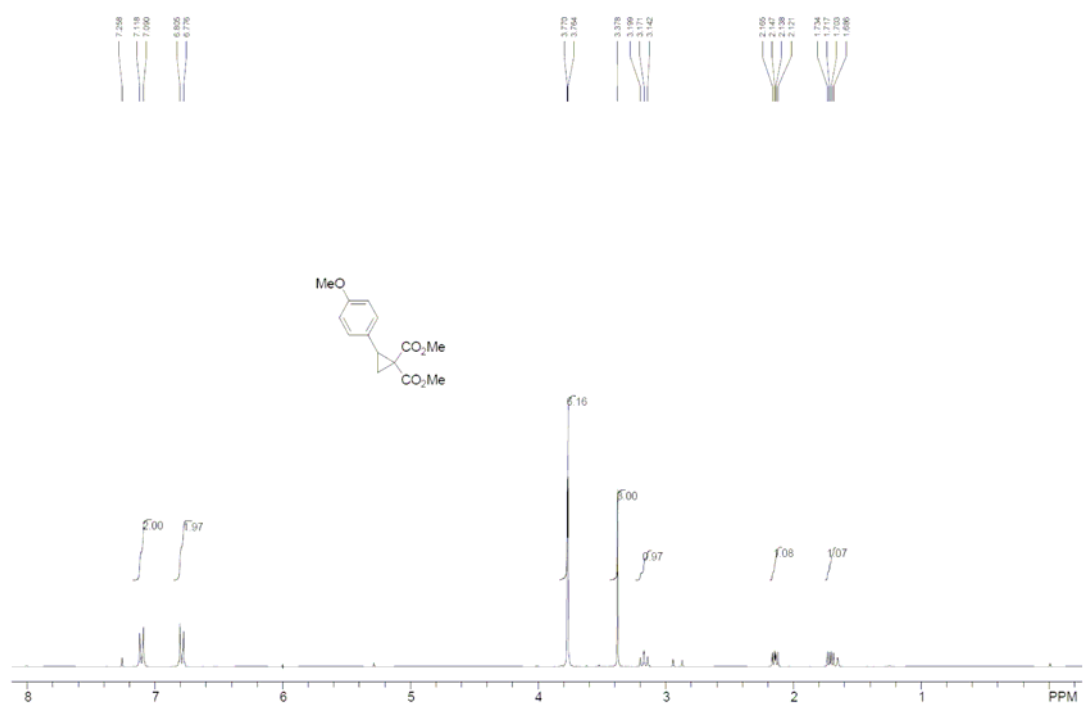
Pulse Sequence: s2pu1



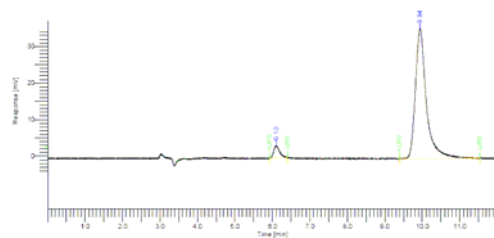
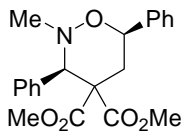








HPLC analytical spectra.



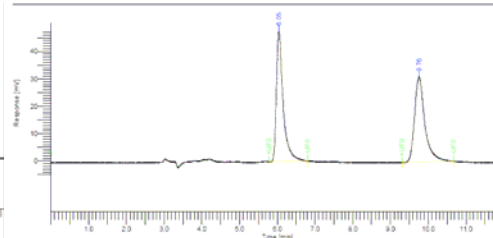
Yan-Biao, Kang

03-78

| Peak #                       | Time (min) | Area (mVsec) | Height (mV) | Area Norm. Area (%) |
|------------------------------|------------|--------------|-------------|---------------------|
| 1                            | 6.10       | 3542.2487    | 599.8317    | 4.80                |
| 2                            | 9.94       | 72981.4842   | 2.564e+04   | 95.20               |
| 797263.7136 3.885e+04 100.00 |            |              |             |                     |

Chromatogram: AD-1 Column, Hs30PCH 0010; Flow rate = 1.0 mL/min; 254 nm; 20 deg

Chiralcel AD-H Column, Hexa:IPCH 90:10, Flow rate = 1.0 mL/min, 254 nm, 20 deg.

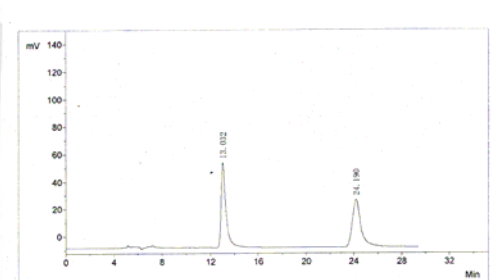
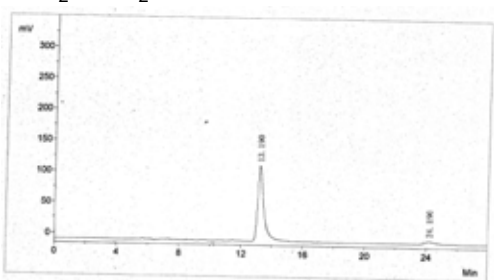
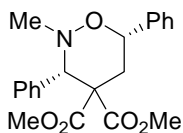


Yan-Biao, Kang

| 49-7590   |            |                             |             |          |                |
|-----------|------------|-----------------------------|-------------|----------|----------------|
| Peak #    | Time [min] | Area [x10 <sup>4</sup> sec] | Height [mV] | Area [%] | Norm. Area [%] |
| 1         | 6.05       | 597339.7462                 | 4.765e+04   | 50.18    | 50.18          |
| 2         | 9.78       | 593107.5342                 | 3.115e+04   | 49.82    | 49.82          |
| 1.190e+09 |            |                             |             |          |                |
| 7.885e+04 |            |                             |             |          |                |
| 100.00    |            |                             |             |          |                |

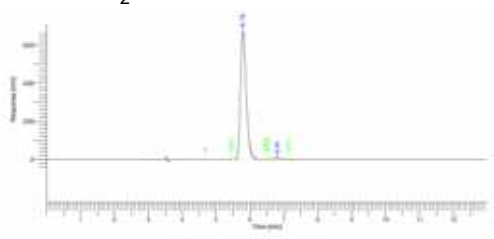
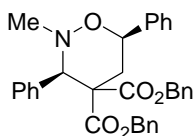
Chromatogram Column: HPLC/PC/CH 5015 Flow rate: 1.0 mL/min 124 min 32 deg

Chiralcel AD-H Column, Hexa:IPCH 90:10, Flow rate = 1.0 mL/min, 254 nm, 20 deg.



| 序号  | 峰号 | 组份名     | 保留时间   | 峰高       | 峰面积       | 面积百分比(%) |
|-----|----|---------|--------|----------|-----------|----------|
| 1   | 1  | Unknown | 13.190 | 130239.0 | 3332866.6 | 95.0569  |
| 2   | 2  | Unknown | 24.190 | 4097.2   | 173313.9  | 4.9431   |
| 合计: |    |         |        | 124336.2 | 3506180.5 | 100.0000 |

| 序号  | 峰号 | 组份名     | 保留时间   | 峰高      | 峰面积       | 面积百分比(%) |
|-----|----|---------|--------|---------|-----------|----------|
| 1   | 1  | Unknown | 13.032 | 61906.5 | 1737116.4 | 50.0476  |
| 2   | 2  | Unknown | 24.190 | 34699.4 | 1733813.1 | 49.9524  |
| 合计: |    |         |        | 96606.0 | 3470929.4 | 100.0000 |

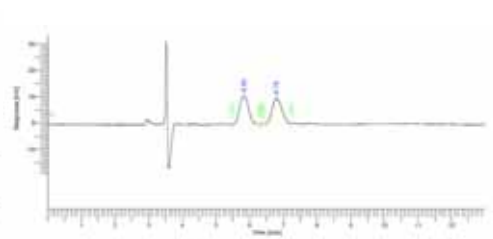


Yan-Biao, Kang

| Peak 1 of 2: 6.10 min, 4.76 min |      |            |                 |       |
|---------------------------------|------|------------|-----------------|-------|
| Peak Time                       | Area | Height     | Area Norm. Area |       |
| #                               | (mV) | (mV)       | (%)             | (%)   |
| 1                               | 6.10 | 3542.2487  | 599.8317        | 4.80  |
| 2                               | 9.94 | 72981.4842 | 2.564e+04       | 95.20 |
| 797263.7136                     |      |            |                 |       |
| 3.885e+04                       |      |            |                 |       |
| 100.00                          |      |            |                 |       |

Chromatogram 1: 6.10 min, 9.94 min, 10.00 min, 10.10 min, 10.20 min, 10.30 min, 10.40 min, 10.50 min, 10.60 min, 10.70 min, 10.80 min, 10.90 min, 11.00 min, 11.10 min, 11.20 min, 11.30 min, 11.40 min, 11.50 min, 11.60 min, 11.70 min, 11.80 min, 11.90 min, 12.00 min, 12.10 min, 12.20 min, 12.30 min, 12.40 min, 12.50 min, 12.60 min, 12.70 min, 12.80 min, 12.90 min, 13.00 min, 13.10 min, 13.20 min, 13.30 min, 13.40 min, 13.50 min, 13.60 min, 13.70 min, 13.80 min, 13.90 min, 14.00 min, 14.10 min, 14.20 min, 14.30 min, 14.40 min, 14.50 min, 14.60 min, 14.70 min, 14.80 min, 14.90 min, 15.00 min, 15.10 min, 15.20 min, 15.30 min, 15.40 min, 15.50 min, 15.60 min, 15.70 min, 15.80 min, 15.90 min, 16.00 min, 16.10 min, 16.20 min, 16.30 min, 16.40 min, 16.50 min, 16.60 min, 16.70 min, 16.80 min, 16.90 min, 17.00 min, 17.10 min, 17.20 min, 17.30 min, 17.40 min, 17.50 min, 17.60 min, 17.70 min, 17.80 min, 17.90 min, 18.00 min, 18.10 min, 18.20 min, 18.30 min, 18.40 min, 18.50 min, 18.60 min, 18.70 min, 18.80 min, 18.90 min, 19.00 min, 19.10 min, 19.20 min, 19.30 min, 19.40 min, 19.50 min, 19.60 min, 19.70 min, 19.80 min, 19.90 min, 20.00 min, 20.10 min, 20.20 min, 20.30 min, 20.40 min, 20.50 min, 20.60 min, 20.70 min, 20.80 min, 20.90 min, 21.00 min, 21.10 min, 21.20 min, 21.30 min, 21.40 min, 21.50 min, 21.60 min, 21.70 min, 21.80 min, 21.90 min, 22.00 min, 22.10 min, 22.20 min, 22.30 min, 22.40 min, 22.50 min, 22.60 min, 22.70 min, 22.80 min, 22.90 min, 23.00 min, 23.10 min, 23.20 min, 23.30 min, 23.40 min, 23.50 min, 23.60 min, 23.70 min, 23.80 min, 23.90 min, 24.00 min, 24.10 min, 24.20 min, 24.30 min, 24.40 min, 24.50 min, 24.60 min, 24.70 min, 24.80 min, 24.90 min, 25.00 min, 25.10 min, 25.20 min, 25.30 min, 25.40 min, 25.50 min, 25.60 min, 25.70 min, 25.80 min, 25.90 min, 26.00 min, 26.10 min, 26.20 min, 26.30 min, 26.40 min, 26.50 min, 26.60 min, 26.70 min, 26.80 min, 26.90 min, 27.00 min, 27.10 min, 27.20 min, 27.30 min, 27.40 min, 27.50 min, 27.60 min, 27.70 min, 27.80 min, 27.90 min, 28.00 min, 28.10 min, 28.20 min, 28.30 min, 28.40 min, 28.50 min, 28.60 min, 28.70 min, 28.80 min, 28.90 min, 29.00 min, 29.10 min, 29.20 min, 29.30 min, 29.40 min, 29.50 min, 29.60 min, 29.70 min, 29.80 min, 29.90 min, 30.00 min, 30.10 min, 30.20 min, 30.30 min, 30.40 min, 30.50 min, 30.60 min, 30.70 min, 30.80 min, 30.90 min, 31.00 min, 31.10 min, 31.20 min, 31.30 min, 31.40 min, 31.50 min, 31.60 min, 31.70 min, 31.80 min, 31.90 min, 32.00 min, 32.10 min, 32.20 min, 32.30 min, 32.40 min, 32.50 min, 32.60 min, 32.70 min, 32.80 min, 32.90 min, 33.00 min, 33.10 min, 33.20 min, 33.30 min, 33.40 min, 33.50 min, 33.60 min, 33.70 min, 33.80 min, 33.90 min, 34.00 min, 34.10 min, 34.20 min, 34.30 min, 34.40 min, 34.50 min, 34.60 min, 34.70 min, 34.80 min, 34.90 min, 35.00 min, 35.10 min, 35.20 min, 35.30 min, 35.40 min, 35.50 min, 35.60 min, 35.70 min, 35.80 min, 35.90 min, 36.00 min, 36.10 min, 36.20 min, 36.30 min, 36.40 min, 36.50 min, 36.60 min, 36.70 min, 36.80 min, 36.90 min, 37.00 min, 37.10 min, 37.20 min, 37.30 min, 37.40 min, 37.50 min, 37.60 min, 37.70 min, 37.80 min, 37.90 min, 38.00 min, 38.10 min, 38.20 min, 38.30 min, 38.40 min, 38.50 min, 38.60 min, 38.70 min, 38.80 min, 38.90 min, 39.00 min, 39.10 min, 39.20 min, 39.30 min, 39.40 min, 39.50 min, 39.60 min, 39.70 min, 39.80 min, 39.90 min, 40.00 min, 40.10 min, 40.20 min, 40.30 min, 40.40 min, 40.50 min, 40.60 min, 40.70 min, 40.80 min, 40.90 min, 41.00 min, 41.10 min, 41.20 min, 41.30 min, 41.40 min, 41.50 min, 41.60 min, 41.70 min, 41.80 min, 41.90 min, 42.00 min, 42.10 min, 42.20 min, 42.30 min, 42.40 min, 42.50 min, 42.60 min, 42.70 min, 42.80 min, 42.90 min, 43.00 min, 43.10 min, 43.20 min, 43.30 min, 43.40 min, 43.50 min, 43.60 min, 43.70 min, 43.80 min, 43.90 min, 44.00 min, 44.10 min, 44.20 min, 44.30 min, 44.40 min, 44.50 min, 44.60 min, 44.70 min, 44.80 min, 44.90 min, 45.00 min, 45.10 min, 45.20 min, 45.30 min, 45.40 min, 45.50 min, 45.60 min, 45.70 min, 45.80 min, 45.90 min, 46.00 min, 46.10 min, 46.20 min, 46.30 min, 46.40 min, 46.50 min, 46.60 min, 46.70 min, 46.80 min, 46.90 min, 47.00 min, 47.10 min, 47.20 min, 47.30 min, 47.40 min, 47.50 min, 47.60 min, 47.70 min, 47.80 min, 47.90 min, 48.00 min, 48.10 min, 48.20 min, 48.30 min, 48.40 min, 48.50 min, 48.60 min, 48.70 min, 48.80 min, 48.90 min, 49.00 min, 49.10 min, 49.20 min, 49.30 min, 49.40 min, 49.50 min, 49.60 min, 49.70 min, 49.80 min, 49.90 min, 50.00 min, 50.10 min, 50.20 min, 50.30 min, 50.40 min, 50.50 min, 50.60 min, 50.70 min, 50.80 min, 50.90 min, 51.00 min, 51.10 min, 51.20 min, 51.30 min, 51.40 min, 51.50 min, 51.60 min, 51.70 min, 51.80 min, 51.90 min, 52.00 min, 52.10 min, 52.20 min, 52.30 min, 52.40 min, 52.50 min, 52.60 min, 52.70 min, 52.80 min, 52.90 min, 53.00 min, 53.10 min, 53.20 min, 53.30 min, 53.40 min, 53.50 min, 53.60 min, 53.70 min, 53.80 min, 53.90 min, 54.00 min, 54.10 min, 54.20 min, 54.30 min, 54.40 min, 54.50 min, 54.60 min, 54.70 min, 54.80 min, 54.90 min, 55.00 min, 55.10 min, 55.20 min, 55.30 min, 55.40 min, 55.50 min, 55.60 min, 55.70 min, 55.80 min, 55.90 min, 56.00 min, 56.10 min, 56.20 min, 56.30 min, 56.40 min, 56.50 min, 56.60 min, 56.70 min, 56.80 min, 56.90 min, 57.00 min, 57.10 min, 57.20 min, 57.30 min, 57.40 min, 57.50 min, 57.60 min, 57.70 min, 57.80 min, 57.90 min, 58.00 min, 58.10 min, 58.20 min, 58.30 min, 58.40 min, 58.50 min, 58.60 min, 58.70 min, 58.80 min, 58.90 min, 59.00 min, 59.10 min, 59.20 min, 59.30 min, 59.40 min, 59.50 min, 59.60 min, 59.70 min, 59.80 min, 59.90 min, 60.00 min, 60.10 min, 60.20 min, 60.30 min, 60.40 min, 60.50 min, 60.60 min, 60.70 min, 60.80 min, 60.90 min, 61.00 min, 61.10 min, 61.20 min, 61.30 min, 61.40 min, 61.50 min, 61.60 min, 61.70 min, 61.80 min, 61.90 min, 62.00 min, 62.10 min, 62.20 min, 62.30 min, 62.40 min, 62.50 min, 62.60 min, 62.70 min, 62.80 min, 62.90 min, 63.00 min, 63.10 min, 63.20 min, 63.30 min, 63.40 min, 63.50 min, 63.60 min, 63.70 min, 63.80 min, 63.90 min, 64.00 min, 64.10 min, 64.20 min, 64.30 min, 64.40 min, 64.50 min, 64.60 min, 64.70 min, 64.80 min, 64.90 min, 65.00 min, 65.10 min, 65.20 min, 65.30 min, 65.40 min, 65.50 min, 65.60 min, 65.70 min, 65.80 min, 65.90 min, 66.00 min, 66.10 min, 66.20 min, 66.30 min, 66.40 min, 66.50 min, 66.60 min, 66.70 min, 66.80 min, 66.90 min, 67.00 min, 67.10 min, 67.20 min, 67.30 min, 67.40 min, 67.50 min, 67.60 min, 67.70 min, 67.80 min, 67.90 min, 68.00 min, 68.10 min, 68.20 min, 68.30 min, 68.40 min, 68.50 min, 68.60 min, 68.70 min, 68.80 min, 68.90 min, 69.00 min, 69.10 min, 69.20 min, 69.30 min, 69.40 min, 69.50 min, 69.60 min, 69.70 min, 69.80 min, 69.90 min, 70.00 min, 70.10 min, 70.20 min, 70.30 min, 70.40 min, 70.50 min, 70.60 min, 70.70 min, 70.80 min, 70.90 min, 71.00 min, 71.10 min, 71.20 min, 71.30 min, 71.40 min, 71.50 min, 71.60 min, 71.70 min, 71.80 min, 71.90 min, 72.00 min, 72.10 min, 72.20 min, 72.30 min, 72.40 min, 72.50 min, 72.60 min, 72.70 min, 72.80 min, 72.90 min, 73.00 min, 73.10 min, 73.20 min, 73.30 min, 73.40 min, 73.50 min, 73.60 min, 73.70 min, 73.80 min, 73.90 min, 74.00 min, 74.10 min, 74.20 min, 74.30 min, 74.40 min, 74.50 min, 74.60 min, 74.70 min, 74.80 min, 74.90 min, 75.00 min, 75.10 min, 75.20 min, 75.30 min, 75.40 min, 75.50 min, 75.60 min, 75.70 min, 75.80 min, 75.90 min, 76.00 min, 76.10 min, 76.20 min, 76.30 min, 76.40 min, 76.50 min, 76.60 min, 76.70 min, 76.80 min, 76.90 min, 77.00 min, 77.10 min, 77.20 min, 77.30 min, 77.40 min, 77.50 min, 77.60 min, 77.70 min, 77.80 min, 77.90 min, 78.00 min, 78.10 min, 78.20 min, 78.30 min, 78.40 min, 78.50 min, 78.60 min, 78.70 min, 78.80 min, 78.90 min, 79.00 min, 79.10 min, 79.20 min, 79.30 min, 79.40 min, 79.50 min, 79.60 min, 79.70 min, 79.80 min, 79.90 min, 80.00 min, 80.10 min, 80.20 min, 80.30 min, 80.40 min, 80.50 min, 80.60 min, 80.70 min, 80.80 min, 80.90 min, 81.00 min, 81.10 min, 81.20 min, 81.30 min, 81.40 min, 81.50 min, 81.60 min, 81.70 min, 81.80 min, 81.90 min, 82.00 min, 82.10 min, 82.20 min, 82.30 min, 82.40 min, 82.50 min, 82.60 min, 82.70 min, 82.80 min, 82.90 min, 83.00 min, 83.10 min, 83.20 min, 83.30 min, 83.40 min, 83.50 min, 83.60 min, 83.70 min, 83.80 min, 83.90 min, 84.00 min, 84.10 min, 84.20 min, 84.30 min, 84.40 min, 84.50 min, 84.60 min, 84.70 min, 84.80 min, 84.90 min, 85.00 min, 85.10 min, 85.20 min, 85.30 min, 85.40 min, 85.50 min, 85.60 min, 85.70 min, 85.80 min, 85.90 min, 86.00 min, 86.10 min, 86.20 min, 86.30 min, 86.40 min, 86.50 min, 86.60 min, 86.70 min, 86.80 min, 86.90 min, 87.00 min, 87.10 min, 87.20 min, 87.30 min, 87.40 min, 87.50 min, 87.60 min, 87.70 min, 87.80 min, 87.90 min, 88.00 min, 88.10 min, 88.20 min, 88.30 min, 88.40 min, 88.50 min, 88.60 min, 88.70 min, 88.80 min, 88.90 min, 89.00 min, 89.10 min, 89.20 min, 89.30 min, 89.40 min, 89.50 min, 89.60 min, 89.70 min, 89.80 min, 89.90 min, 90.00 min, 90.10 min, 90.20 min, 90.30 min, 90.40 min, 90.50 min, 90.60 min, 90.70 min, 90.80 min, 90.90 min, 91.00 min, 91.10 min, 91.20 min, 91.30 min, 91.40 min, 91.50 min, 91.60 min, 91.70 min, 91.80 min, 91.90 min, 92.00 min, 92.10 min, 92.20 min, 92.30 min, 92.40 min, 92.50 min, 92.60 min, 92.70 min, 92.80 min, 92.90 min, 93.00 min, 93.10 min, 93.20 min, 93.30 min, 93.40 min, 93.50 min, 93.60 min, 93.70 min, 93.80 min, 93.90 min, 94.00 min, 94.10 min, 94.20 min, 94.30 min, 94.40 min, 94.50 min, 94.60 min, 94.70 min, 94.80 min, 94.90 min, 95.00 min, 95.10 min, 95.20 min, 95.30 min, 95.40 min, 95.50 min, 95.60 min, 95.70 min, 95.80 min, 95.90 min, 96.00 min, 96.10 min, 96.20 min, 96.30 min, 96.40 min, 96.50 min, 96.60 min, 96.70 min, 96.80 min, 96.90 min, 97.00 min, 97.10 min, 97.20 min, 97.30 min, 97.40 min, 97.50 min, 97.60 min, 97.70 min, 97.80 min, 97.90 min, 98.00 min, 98.10 min, 98.20 min, 98.30 min, 98.40 min, 98.50 min, 98.60 min, 98.70 min, 98.80 min, 98.90 min, 99.00 min, 99.10 min, 99.20 min, 99.30 min, 99.40 min, 99.50 min, 99.60 min, 99.70 min, 99.80 min, 99.90 min, 100.00 min, 100.10 min, 100.20 min, 100.30 min, 100.40 min, 100.50 min, 100.60 min, 100.70 min, 100.80 min, 100.90 min, 101.00 min, 101.10 min, 101.20 min, 101.30 min, 101.40 min, 101.50 min, 101.60 min, 101.70 min, 101.80 min, 101.90 min, 102.00 min, 102.10 min, 102.20 min, 102.30 min, 102.40 min, 102.50 min, 102.60 min, 102.70 min, 102.80 min, 102.90 min, 103.00 min, 103.10 min, 103.20 min, 103.30 min, 103.40 min, 103.50 min, 103.60 min, 103.70 min, 103.80 min, 103.90 min, 104.00 min, 104.10 min, 104.20 min, 104.30 min, 104.40 min, 104.50 min, 104.60 min, 104.70 min, 104.80 min, 104.90 min, 105.00 min, 105.10 min, 105.20 min, 105.30 min, 105.40 min, 105.50 min, 105.60 min, 105.70 min, 105.80 min, 105.90 min, 106.00 min, 106.10 min, 106.20 min, 106.30 min, 106.40 min, 106.50 min, 106.60 min, 106.70 min, 106.80 min, 106.90 min, 107.00 min, 107.10 min, 107.20 min, 107.30 min, 107.40 min, 107.50 min, 107.60 min, 107.70 min, 107.80 min, 107.90 min, 108.00 min, 108.10 min, 108.20 min, 108.30 min, 108.40 min, 108.50 min, 108.60 min, 108.70 min, 108.80 min, 108.90 min, 109.00 min, 109.10 min, 109.20 min, 109.30 min, 109.40 min, 109.50 min, 109.60 min, 109.70 min, 109.80 min, 109.90 min, 110.00 min, 110.10 min, 110.20 min, 110.30 min, 110.40 min, 110.50 min, 110.60 min, 110.70 min, 110.80 min, 110.90 min, 111.00 min, 111.10 min, 111.20 min, 111.30 min, 111.40 min, 111.50 min, 111.60 min, 111.70 min, 111.80 min, 111.90 min, 112.00 min, 112.10 min, 112.20 min, 112.30 min, 112.40 min, 112.50 min, 112.60 min, 112.70 min, 112.80 min, 112.90 min, 113.00 min, 113.10 min, 113.20 min, 113.30 min, 113.40 min, 113.50 min, 113.60 min, 113.70 min, 113.80 min, 113.90 min, 114.00 min, 114.10 min, 114.20 min, 114.30 min, 114.40 min, 114.50 min, 114.60 min, 114.70 min, 114.80 min, 114.90 min, 115.00 min, 115.10 min, 115.20 min, 115.30 min, 115.40 min, 115.50 min, 115.60 min, 115.70 min, 115.80 min, 115.90 min, 116.00 min, 116.10 min, 116.20 min, 116.30 min, 116.40 min, 116.50 min, 116.60 min, 116.70 min, 116.80 min, 116.90 min, 117.00 min, 117.10 min, 117.20 min, 117.30 min, 117.40 min, 117.50 min, 117.60 min, 117.70 min, 117.80 min, 117.90 min, 118.00 min, 118.10 min, 118.20 min, 118.30 min, 118.40 min, 118.50 min, 118.60 min, 118.70 min, 118.80 min, 118.90 min, 119.00 min, 119.10 min, 119.20 min, 119.30 min, 119.40 min, 119.50 min, 119.60 min, 119.70 min, 119.80 min, 119.90 min, 120.00 min, 120.10 min, 120.20 min, 120.30 min, 120.40 min, 120.50 min, 120.60 min, 120.70 min, 120.80 min, 120.90 min, 121.00 min, 121.10 min, 121.20 min, 121.30 min, 121.40 min, 121.50 min, 121.60 min, 121.70 min, 121.80 min, 121.90 min, 122.00 min, 122.10 min, 122.20 min, 122.30 min, 122.40 min, 122.50 min, 122.60 min, 122.70 min, 122.80 min, 122.90 min, 123.00 min, 123.10 min, 123.20 min, 123.30 min, 123.40 min, 123.50 min, 123.60 min, 123.70 min, 123.80 min, 123.90 min, 124.00 min, 124.10 min, 124.20 min, 124.30 min, 124.40 min, 124.50 min, 124.60 min, 124.70 min, 124.80 min, 124.90 min, 125.00 min, 125.10 min, 125.20 min, 125.30 min, 125.40 min, 125.50 min, 125.60 min, 125.70 min, 125.80 min, 125.90 min, 126.00 min, 126.10 min, 126.20 min, 126.30 min, 126.40 min, 126.50 min, 126.60 min, 126.70 min, 126.80 min, 126.90 min, 127.00 min, 127.10 min, 127.20 min, 127.30 min, 127.40 min, 127.50 min, 127.60 min, 127.70 min, 127.80 min, 127.90 min, 128.00 min, 128.10 min, 128.20 min, 128.30 min, 128.40 min, 128.50 min, 128.60 min, 128.70 min, 128.80 min, 128.90 min, 129.00 min, 129.10 min, 129.20 min, 129.30 min, 129.40 min, 129.50 min, 129.60 min, 129.70 min, 129.80 min, 129.90 min, 130.00 min, 130.10 min, 130.20 min, 130.30 min, 130.40 min, 130.50 min, 130.60 min, 130.70 min, 130.80 min, 130.90 min, 131.00 min, 131.10 min, 131.20 min, 131.30 min, 131.40 min, 131.50 min, 131.60 min, 131.70 min, 131.80 min, 131.90 min, 132.00 min, 132.10 min, 132.20 min, 132.30 min, 132.40 min, 132.50 min, 132.60 min, 132.70 min, 132.80 min, 132.90 min, 133.00 min, 133.10 min, 133.20 min, 133.30 min, 133.40 min, 133.50 min, 133.60 min, 133.70 min, 133.80 min, 133.90 min, 134.00 min, 134.10 min, 134.20 min, 134.30 min, 134.40 min, 134.50 min, 134.60 min, 134.70 min, 134.80 min, 134.90 min, 135.00 min, 135.10 min, 135.20 min, 135.30 min, 135.40 min, 135.50 min, 135.60 min, 135.70 min, 135.80 min, 135.90 min, 136.00 min, 136.10 min, 136.20 min, 136.30 min, 136.40 min, 136.50 min, 136.60 min, 136.70 min, 136.80 min, 136.90 min, 137.00 min, 137.10 min, 137.20 min, 137.30 min, 137.40 min, 137.50 min, 137.60 min, 137.70 min, 137.80 min, 137.90 min, 138.00 min, 138.10 min, 138.20 min, 138.30 min, 138.40 min, 138.50 min, 138.60 min, 138.70 min, 138.80 min, 138.90 min, 139.00 min, 139.10 min, 139.20 min, 139.30 min, 139.40 min, 139.50 min, 139.60 min, 139.70 min, 139.80 min, 139.90 min, 140.00 min, 140.10 min, 140.20 min, 140.30 min, 140.40 min, 140.50 min, 140.60 min, 140.70 min, 140.80 min, 140.90 min, 141.00 min, 141.10 min, 141.20 min, 141.30 min, 141.40 min, 141.50 min, 141.60 min, 141.70 min, 141.80 min, 141.90 min, 142.00 min, 142.10 min, 142.20 min, 142.30 min, 142.40 min, 142.50 min, 142.60 min, 142.70 min, 142.80 min, 142.90 min, 143.00 min, 143.10 min, 143.20 min, 143.30 min, 143.40 min, 143.50 min, 143.60 min, 143.70 min, 143.80 min, 143.90 min, 144.00 min, 144.10 min, 144.20 min, 144.30 min, 144.40 min, 144.50 min, 144.60 min, 144.70 min, 144.80 min, 144.90 min, 145.00 min, 145.10 min, 145.20 min, 145.30 min, 145.40 min, 145.50 min, 145.60 min, 145.70 min, 145.80 min, 145.90 min, 146.00 min, 146.10 min, 146.20 min, 146.30 min, 146.40 min, 146.50 min, 146.60 min, 146.70 min, 146.80 min, 146.90 min, 147.00 min, 147.10 min, 147.20 min, 147.30 min, 147.40 min, 147.50 min, 147.60 min, 147.70 min, 147.80 min, 147.90 min, 148.00 min, 148.10 min, 148.20 min, 148.30 min, 148.40 min, 148.50 min, 148.60 min, 148.70 min, 148.80 min, 148.90 min, 149.00 min, 149.10 min, 149.20 min, 149.30 min, 149.40 min, 149.50 min, 149.60 min, 149.70 min, 149.80 min, 149.90 min, 150.00 min, 150.10 min, 150.20 min, 150.30 min, 150.40 min, 150.50 min, 150.60 min, 150.70 min, 150.80 min, 150.90 min, 151.00 min, 151.10 min, 151.20 min, 151.30 min, 151.40 min, 151.50 min, 151.60 min, 151.70 min, 151.80 min, 151.90 min, 152.00 min, 152.10 min, 152.20 min, 152.30 min, 152.40 min, 152.50 min, 152.60 min, 152.70 min, 152.80 min, 152.90 min, 153.00 min, 153.10 min, 153.20 min, 153.30 min, 153.40 min, 153.50 min, 153.60 min, 153.70 min, 153.80 min, 153.90 min, 154.00 min, 154.10 min,

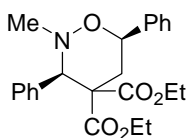
Chiralcel AD-H Column, Hexa:IPCH 90:10, Flow rate = 1.0 mL/min, 254 nm, 20 deg.

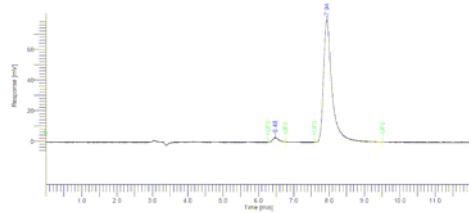


Yan-Biao, Kang

|                          |       |             |           |       |        |      |
|--------------------------|-------|-------------|-----------|-------|--------|------|
| Agilent 8460, 12/10/2010 |       |             |           |       |        |      |
| Peak                     | Time  | Area        | Height    | Area  | Height | Area |
| #                        | (min) | (mV)        | (mV)      | (%)   | (%)    | (%)  |
| 1                        | 6.02  | 597339.7462 | 4.765e+04 | 50.18 |        |      |
| 2                        | 9.78  | 593107.5342 | 3.115e+04 | 49.82 |        |      |
| Total Area: 1.190e+09    |       |             |           |       |        |      |
| Total Height: 7.885e+04  |       |             |           |       |        |      |
| 100.00                   |       |             |           |       |        |      |

Chiralcel AD-H Column, Hexa:IPCH 90:10, Flow rate = 1.0 mL/min, 254 nm, 20 deg.

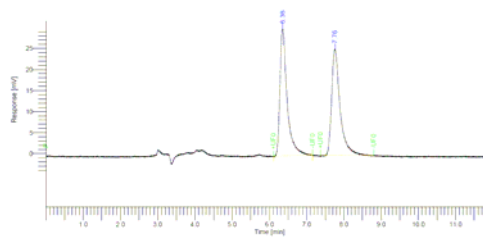




Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|--------|------------|-------------|---------------|----------|------------|
| 1      | 8.45       | 33531.5581  | 2564.6363     | 2.40     | 2.40       |
| 2      | 7.34       | 1.3421e+05  | 1.5732e+04    | 100.00   | 100.00     |

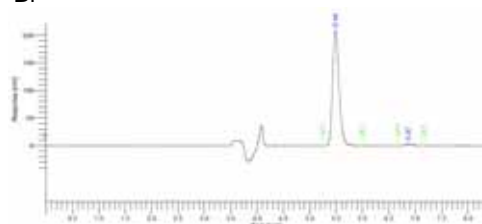
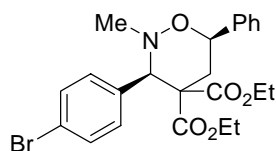
Chromat AD-H Column, HPLC-PCH 99-10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|--------|------------|-------------|---------------|----------|------------|
| 1      | 6.30       | 481909.1586 | 2.0224e+04    | 90.30    | 90.30      |
| 2      | 7.70       | 385962.8829 | 2.3314e+04    | 49.70    | 49.70      |

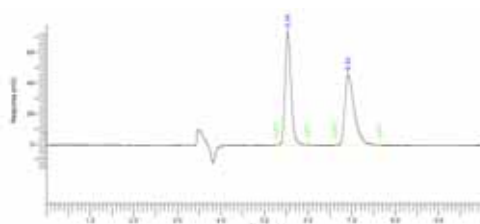
Chromat AD-H Column, HPLC-PCH 99-10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|--------|------------|-------------|---------------|----------|------------|
| 1      | 8.45       | 1.3421e+05  | 1.5732e+04    | 100.00   | 100.00     |
| 2      | 7.34       | 1.3421e+05  | 1.5732e+04    | 100.00   | 100.00     |

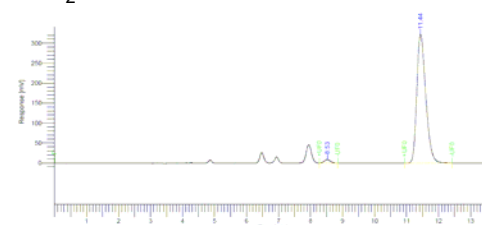
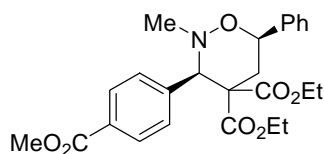
Chromat AD-H Column, HPLC-PCH 99-10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|--------|------------|-------------|---------------|----------|------------|
| 1      | 6.30       | 481909.1586 | 2.0224e+04    | 90.30    | 90.30      |
| 2      | 7.70       | 385962.8829 | 2.3314e+04    | 49.70    | 49.70      |

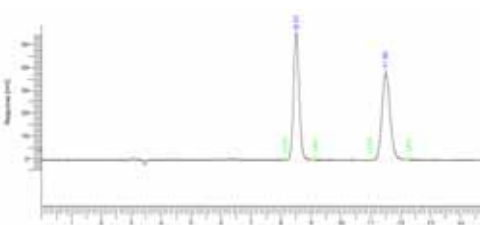
Chromat AD-H Column, HPLC-PCH 99-10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|--------|------------|-------------|---------------|----------|------------|
| 1      | 8.53       | 10014.2095  | 871.9217      | 1.73     | 1.73       |
| 2      | 7.34       | 4.2044e+05  | 3.2294e+04    | 98.27    | 98.27      |

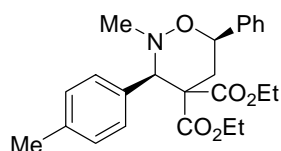
Chromat AD-H Column, HPLC-PCH 99-10, Flow rate = 1.0 mL/min, 254 nm, 20 deg

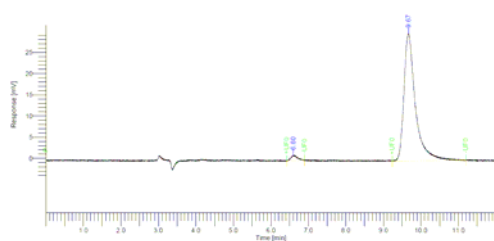


Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|--------|------------|-------------|---------------|----------|------------|
| 1      | 6.30       | 10014.2095  | 871.9217      | 1.73     | 1.73       |
| 2      | 7.34       | 4.2044e+05  | 3.2294e+04    | 98.27    | 98.27      |

Chromat AD-H Column, HPLC-PCH 99-10, Flow rate = 1.0 mL/min, 254 nm, 20 deg

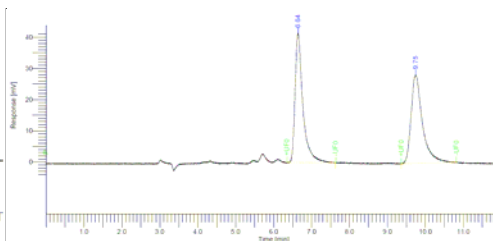




Yan-Biao, Kang

| Peak #                       | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|------------------------------|------------|-------------|---------------|----------|------------|
| 1                            | 9.67       | 14850.4967  | 1277.1745     | 2.25     | 2.25       |
| 2                            | 9.67       | 430157.7470 | 3.553e+04     | 97.75    | 97.75      |
| 650818.1423 3.141e+04 100.00 |            |             |               |          |            |

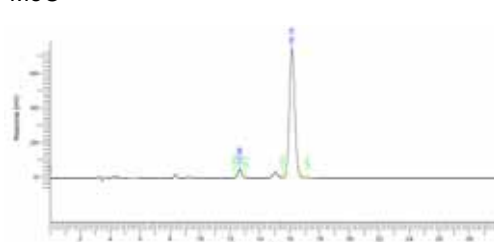
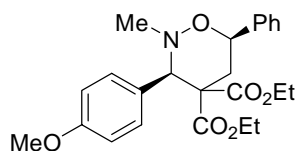
Chiralcel AD-H Column, Hexa-PICN 90/10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak #                      | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|-----------------------------|------------|-------------|---------------|----------|------------|
| 1                           | 6.84       | 101920.6915 | 4.139e+04     | 50.29    | 50.29      |
| 2                           | 9.75       | 100020.9353 | 2.975e+04     | 49.71    | 49.71      |
| 1.1770e+06 6.976e+04 100.00 |            |             |               |          |            |

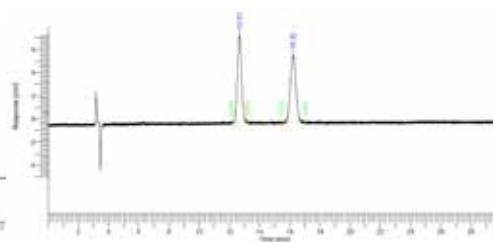
Chiralcel AD-H Column, Hexa-PICN 90/10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak #                       | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|------------------------------|------------|-------------|---------------|----------|------------|
| 1                            | 12.91      | 100000.0000 | 1000.0000     | 49.75    | 49.75      |
| 2                            | 13.27      | 100000.0000 | 1000.0000     | 49.75    | 49.75      |
| 1.0000e+06 1.0000e+06 100.00 |            |             |               |          |            |

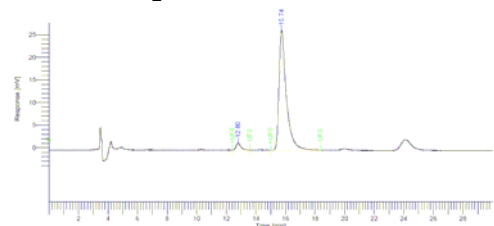
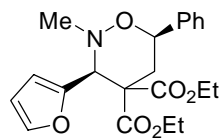
Chiralcel AD-H Column, Hexa-PICN 90/10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak #                       | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|------------------------------|------------|-------------|---------------|----------|------------|
| 1                            | 12.91      | 100000.0000 | 1000.0000     | 49.75    | 49.75      |
| 2                            | 13.27      | 100000.0000 | 1000.0000     | 49.75    | 49.75      |
| 1.0000e+06 1.0000e+06 100.00 |            |             |               |          |            |

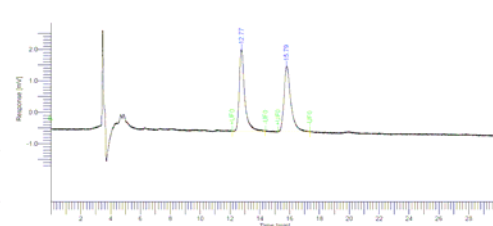
Chiralcel AD-H Column, Hexa-PICN 90/10, Flow rate = 1.0 mL/min, 254 nm, 20 deg



Yan-Biao, Kang

| Peak #                       | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|------------------------------|------------|-------------|---------------|----------|------------|
| 1                            | 12.83      | 34347.1420  | 1573.6200     | 3.66     | 3.66       |
| 2                            | 13.74      | 919773.3387 | 2.5500e+04    | 96.34    | 96.34      |
| 954720.4817 2.868e+04 100.00 |            |             |               |          |            |

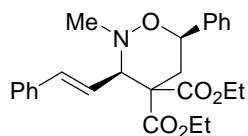
Chiralcel AD-H Column, Hexa-PICN 90/10, Flow rate = 1.0 mL/min, 254 nm, 20 deg

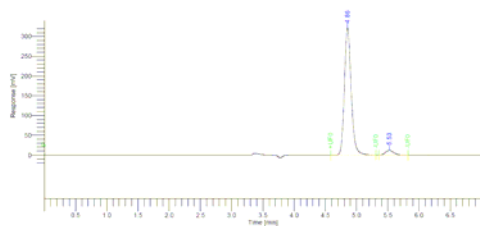


Yan-Biao, Kang

| Peak #                       | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Height [%] |
|------------------------------|------------|-------------|---------------|----------|------------|
| 1                            | 12.77      | 66208.1181  | 2625.4197     | 49.69    | 49.69      |
| 2                            | 13.79      | 66412.8889  | 2604.4799     | 50.32    | 50.32      |
| 132610.9969 6636.4996 100.00 |            |             |               |          |            |

Chiralcel AD-H Column, Hexa-PICN 90/10, Flow rate = 1.0 mL/min, 254 nm, 20 deg

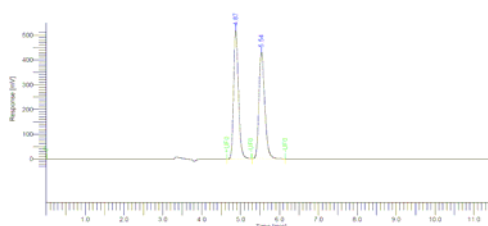




Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 4.86       | 2.432e+05   | 3.217e+05     | 95.76    | 95.76          |
| 2      | 5.50       | 1.0779e+04  | 1.168e+04     | 4.24     | 4.24           |
|        |            | 2.5410e+05  | 3.334e+05     | 100.00   | 100.00         |

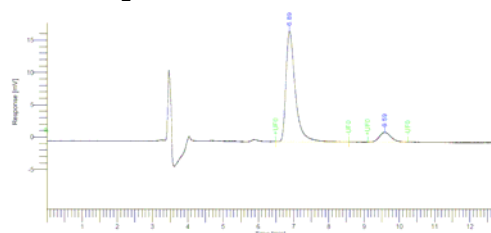
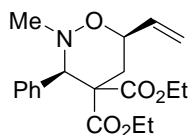
Chiralcel OD-H Column, Hexu-PrOH 50:1, Flow rate = 1.0 mL/min, 254 nm, 27 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 4.87       | 4.4764e+05  | 5.189e+05     | 99.91    | 99.91          |
| 2      | 5.54       | 4.4923e+03  | 4.237e+03     | 1.00     | 1.00           |
|        |            | 9.3707e+05  | 9.486e+05     | 100.00   | 100.00         |

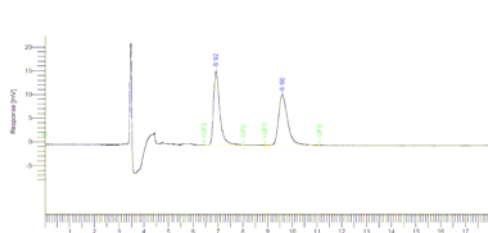
Chiralcel OD-H Column, Hexu-PrOH 50:1, Flow rate = 1.0 mL/min, 254 nm, 27 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 6.89       | 9.1261e+05  | 1.714e+04     | 92.16    | 92.16          |
| 2      | 9.59       | 3.4154e+03  | 1.024e+04     | 9.84     | 9.84           |
|        |            | 5.6836e+05  | 1.655e+04     | 100.00   | 100.00         |

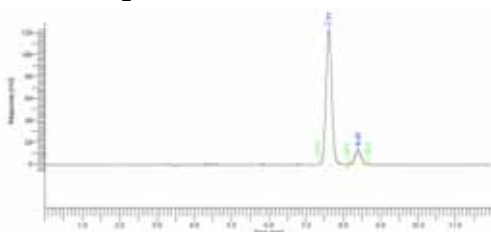
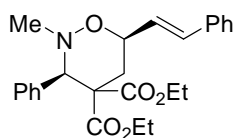
Chiralcel AD-H Column, Hexu-PrOH 50:1, Flow rate = 1.0 mL/min, 254 nm, 27 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 6.92       | 2.0913e+05  | 1.590e+04     | 92.04    | 92.04          |
| 2      | 9.60       | 2.0407e+03  | 1.059e+04     | 89.96    | 89.96          |
|        |            | 1.3377e+04  | 2.670e+04     | 100.00   | 100.00         |

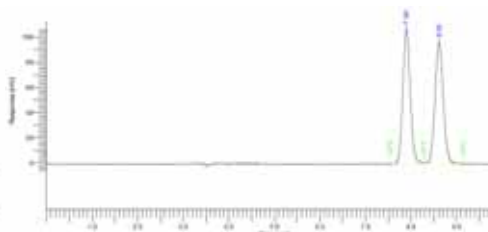
Chiralcel AD-H Column, Hexu-PrOH 50:1, Flow rate = 1.0 mL/min, 254 nm, 27 deg



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 7.14       | 1.4959e+05  | 1.240e+04     | 92.01    | 92.01          |
| 2      | 9.69       | 1.0205e+03  | 1.020e+04     | 6.00     | 6.00           |
|        |            | 1.6424e+05  | 1.332e+04     | 100.00   | 100.00         |

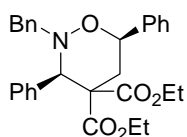
Chiralcel AD-H Column, Hexu-PrOH 50:1, Flow rate = 1.0 mL/min, 254 nm, 27 deg

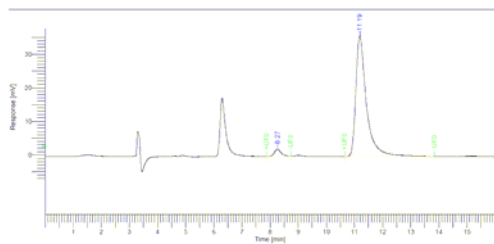


Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 7.14       | 1.1055e+05  | 1.240e+04     | 92.00    | 92.00          |
| 2      | 7.16       | 1.0205e+03  | 1.020e+04     | 6.00     | 6.00           |
|        |            | 1.1055e+05  | 1.240e+04     | 100.00   | 100.00         |

Chiralcel AD-H Column, Hexu-PrOH 50:1, Flow rate = 1.0 mL/min, 254 nm, 27 deg

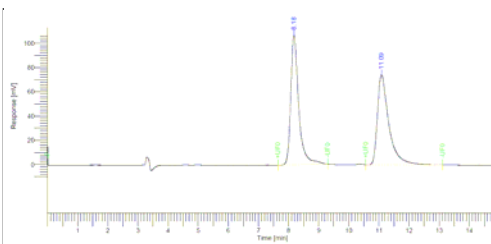




Yan-Biao, Kang

| Peak # | Time [min] | Area [μV*sec] | Height [μV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 8.27       | 14729.9572    | 2114.2054   | 3.53     | 3.53           |
| 2      | 11.19      | 340688.5320   | 3.500e+05   | 96.47    | 96.47          |
|        |            | 963688.4959   | 3.402e+05   | 100.00   | 100.00         |

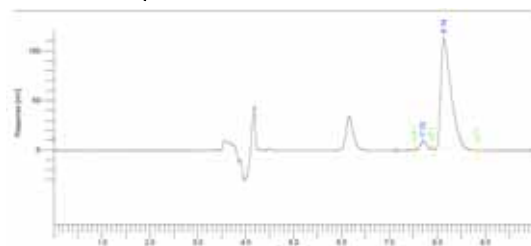
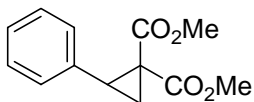
Chiralcel AD-H Column; Hexi-PrOH; 30°C; Flow rate = 1.0 mL/min; 254 nm; 27 deg.



Yan-Biao, Kang

| Peak # | Time [min] | Area [μV*sec] | Height [μV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 8.18       | 1.9591e+05    | 3.003e+05   | 50.06    | 50.06          |
| 2      | 11.18      | 1.9568e+05    | 7.420e+04   | 49.94    | 49.94          |
|        |            | 3.9159e+05    | 1.010e+05   | 100.00   | 100.00         |

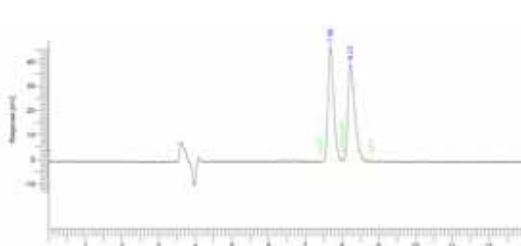
Chiralcel AD-H Column; Hexi-PrOH; 30°C; Flow rate = 1.0 mL/min; 254 nm; 27 deg.



Yan-Biao, Kang

| Peak # | Time [min] | Area [μV*sec] | Height [μV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 1.10       | 6.04677e+08   | 8553.1098   | 4.85     | 4.85           |
| 2      | 1.14       | 1.0917e+09    | 1.125e+05   | 95.15    | 95.15          |
|        |            | 1.7725e+09    | 1.228e+05   | 100.00   | 100.00         |

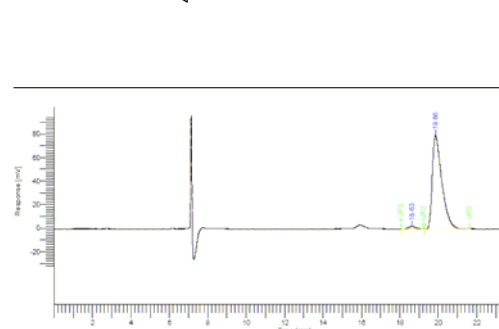
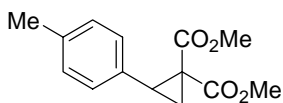
Chiralcel OD-H Column; Hexi-PrOH; 50°C; Flow rate = 1.0 mL/min; 254 nm; 20 deg.



Yan-Biao, Kang

| Peak # | Time [min] | Area [μV*sec] | Height [μV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 1.08       | 8827145.8953  | 4.848e+04   | 48.77    | 48.77          |
| 2      | 1.23       | 8827316.4858  | 3.927e+04   | 50.23    | 50.23          |
|        |            | 1.0101e+08    | 8.578e+04   | 100.00   | 100.00         |

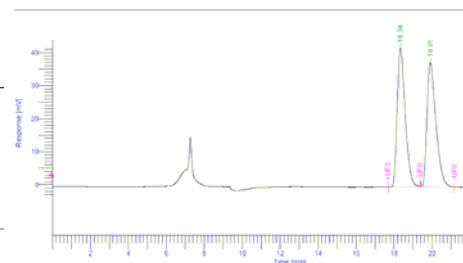
Chiralcel OD-H Column; Hexi-PrOH; 50°C; Flow rate = 1.0 mL/min; 254 nm; 20 deg.



Yan-Biao, Kang

| Peak # | Time [min] | Area [μV*sec] | Height [μV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 18.03      | 23384.6695    | 2051.8942   | 1.92     | 1.92           |
| 2      | 19.09      | 2.7202e+06    | 7.995e+04   | 98.08    | 98.08          |
|        |            | 2.7735e+06    | 8.157e+04   | 100.00   | 100.00         |

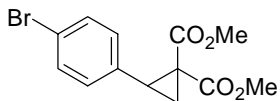
Chiralcel OD-H Column; Hexi-PrOH; 100/0.6; Flow rate = 0.6 mL/min; 254 nm; 29 deg.

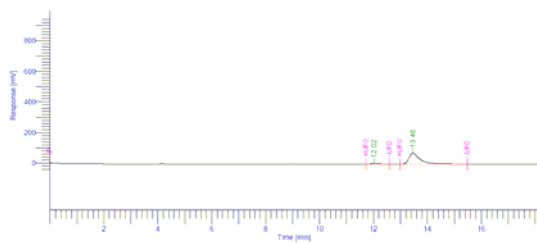


Yan-Biao, Kang

| Peak # | Time [min] | Area [μV*sec] | Height [μV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 18.34      | 1.2244e+06    | 4.197e+04   | 50.03    | 50.03          |
| 2      | 19.91      | 1.2230e+06    | 3.744e+04   | 49.97    | 49.97          |
|        |            | 2.4474e+06    | 7.941e+04   | 100.00   | 100.00         |

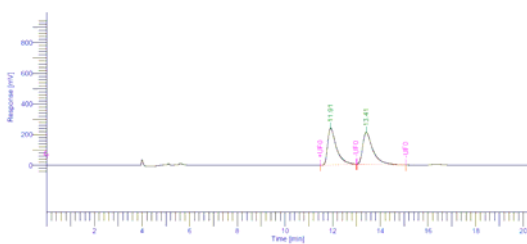
Chiralcel OD-H Column; Hexi-PrOH; 100/0.6; Flow rate = 0.6 mL/min; 254 nm; 29 deg.





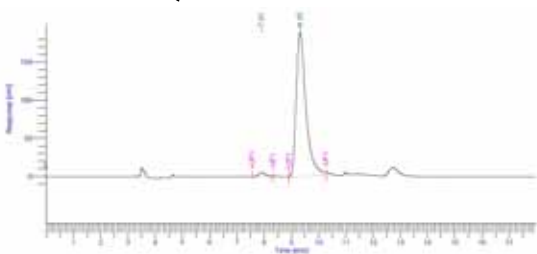
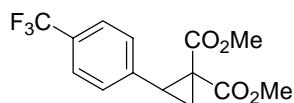
| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 12.02      | 52688.7728    | 2468.9031   | 2.49     | 2.49           |
| 2      | 13.46      | 2.0603e+06    | 7.120e+04   | 97.51    | 97.51          |
|        |            | 2.1129e+06    | 7.367e+04   | 100.00   | 100.00         |

kyb-11-30cp: Chiralcel AD-H Column; Hex/i-PrOH:50/1; Flow rate = 0.8 mL/min; 254 nm; 25 deg.



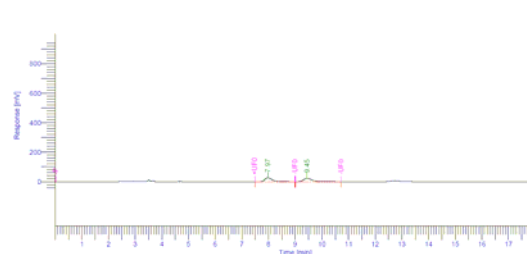
| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 11.91      | 6.1334e+06    | 2.409e+05   | 49.95    | 49.95          |
| 2      | 13.41      | 6.1468e+06    | 2.096e+05   | 50.05    | 50.05          |
|        |            | 1.2280e+07    | 4.505e+05   | 100.00   | 100.00         |

kyb-11-30cp: Chiralcel AD-H Column; Hex/i-PrOH:50/1; Flow rate = 0.8 mL/min; 254 nm; 25 deg.



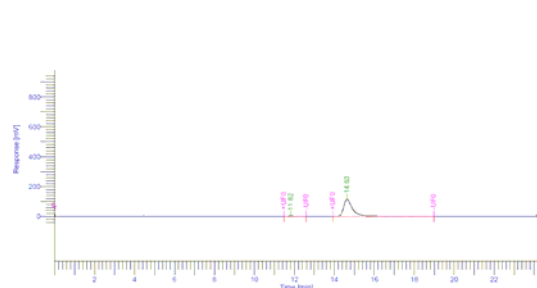
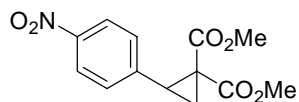
| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 7.91       | 87894.0226    | 4968.2339   | 1.82     | 1.82           |
| 2      | 9.32       | 4.7507e+06    | 1.896e+05   | 98.18    | 98.18          |
|        |            | 4.8386e+06    | 1.945e+05   | 100.00   | 100.00         |

kyb-11-57cp: Chiralcel AD-H Column; Hex/i-PrOH:50/1; Flow rate = 0.8 mL/min; 254 nm; 25 deg.



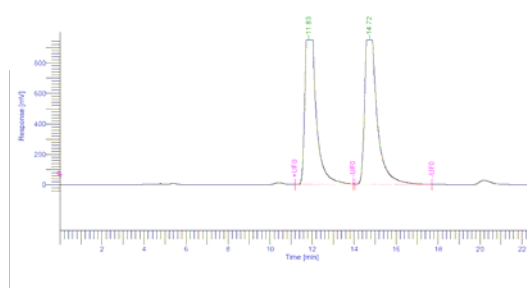
| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 7.97       | 559364.1501   | 2.769e+04   | 50.42    | 50.42          |
| 2      | 9.45       | 549164.8655   | 2.299e+04   | 49.58    | 49.58          |
|        |            | 1.1075e+06    | 5.068e+04   | 100.00   | 100.00         |

kyb-11-57cp-rac: Chiralcel AD-H Column; Hex/i-PrOH:50/1; Flow rate = 0.8 mL/min; 238 nm; 25 deg.



| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 11.82      | 46966.4987    | 2369.9022   | 1.31     | 1.31           |
| 2      | 14.63      | 3.7483e+06    | 1.162e+05   | 98.69    | 98.69          |
|        |            | 3.7961e+06    | 1.185e+05   | 100.00   | 100.00         |

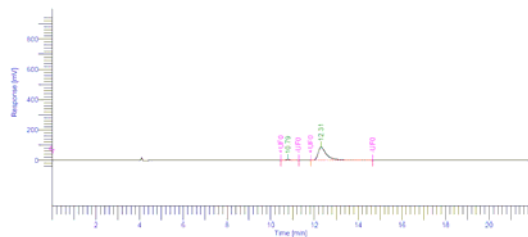
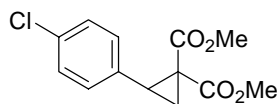
kyb-11-56cp: Chiralcel AD-H Column; Hex/i-PrOH:90/10; Flow rate = 0.7 mL/min; 254 nm; 25 deg.



| Peak # | Time [min] | Area [uV*sec] | Height [uV] | Area [%] | Norm. Area [%] |
|--------|------------|---------------|-------------|----------|----------------|
| 1      | 11.83      | 4.3186e+07    | 1.488e+06   | 49.99    | 49.99          |
| 2      | 14.72      | 4.3207e+07    | 1.226e+06   | 50.01    | 50.01          |
|        |            | 8.6393e+07    | 2.714e+06   | 100.00   | 100.00         |

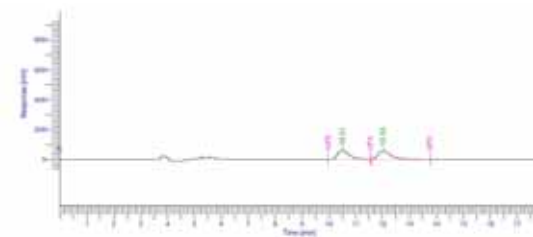
Warning -- Signal level out-of-range in peak

kyb-11-56cp-rac: Chiralcel AD-H Column; Hex/i-PrOH:90/10; Flow rate = 0.7 mL/min; 254 nm; 25 deg.



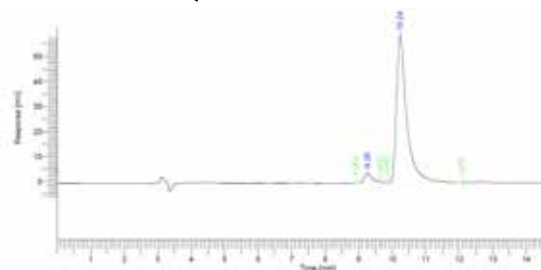
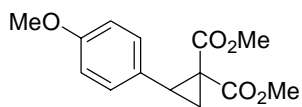
| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 10.79      | 75681.1503  | 3900.5453     | 3.09     | 3.09           |
| 2      | 12.31      | 2.3735e+06  | 8.646e+04     | 96.91    | 96.91          |
|        |            | 2.4492e+06  | 9.036e+04     | 100.00   | 100.00         |

kyb-11-29p: Chiralcel AD-H Column; Hex:i-PrOH:50/1; Flow rate = 0.8 mL/min; 254 nm; 25 deg.



| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 10.81      | 1.7525e+06  | 5.974e+04     | 49.79    | 49.79          |
| 2      | 12.03      | 1.7864e+06  | 5.447e+04     | 50.21    | 50.21          |
|        |            | 3.5389e+06  | 1.142e+05     | 100.00   | 100.00         |

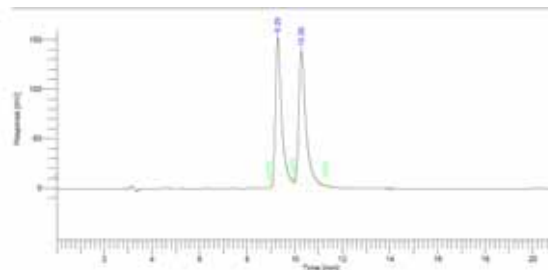
kyb-11-29p-rac: Chiralcel AD-H Column; Hex:i-PrOH:50/1; Flow rate = 0.8 mL/min; 254 nm; 25 deg.



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 9.26       | 84530.5505  | 3488.4881     | 4.22     | 4.22           |
| 2      | 10.24      | 1.9402e+06  | 8.520e+04     | 95.78    | 95.78          |
|        |            | 1.9995e+06  | 8.170e+04     | 100.00   | 100.00         |

Chiralcel AD-H Column; Hex:i-PrOH: 20/1; Flow rate = 1.0 mL/min; 254 nm; 20 deg.



Yan-Biao, Kang

| Peak # | Time [min] | Area [a.u.] | Height [a.u.] | Area [%] | Norm. Area [%] |
|--------|------------|-------------|---------------|----------|----------------|
| 1      | 9.29       | 2.8842e+06  | 1.490e+05     | 49.79    | 49.79          |
| 2      | 10.29      | 2.7504e+06  | 1.322e+05     | 50.21    | 50.21          |
|        |            | 5.6346e+06  | 2.810e+05     | 100.00   | 100.00         |

Chiralcel AD-H Column; Hex:i-PrOH: 20/1; Flow rate = 1.0 mL/min; 254 nm; 20 deg.