## SUPPORTING INFORMATION

# *trans*-Directing Ability of the Amide Group: Enabling the Enantiocontrol in the Synthesis of 1,1-Dicarboxy Cyclopropanes. Reaction Development, Scope, and Synthetic Applications

**David Marcoux, Sébastien R. Goudreau and André B. Charette***

*Département de Chimie, Université de Montréal, P.O. Box 6128, Station Downtown, Québec, Canada H3C 3J7*

**General**: All non-aqueous reactions were run under an inert atmosphere (nitrogen or argon) with rigid exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds.[1] All glassware was stored in the oven and/or was flamedried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, $CH_2Cl_2$, benzene, DMF, $CH_3CN$, toluene, hexane, methanol) on a dried system, by distillation over calcium hydride ($Et_3N$, $ClCH_2CH_2Cl$, pyridine, diisopropylamine, isopropanol) or by distillation over sodium/benzophenone (DME). Analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, iodine, or aqueous potassium permanganate. Flash column chromatography was performed using 230-400 mesh silica of the indicated solvent system according to standard technique.[2] Melting points were obtained on a melting point apparatus and are uncorrected. Infrared spectra were taken on a FTIR and are reported in reciprocal centimeters ($cm^{-1}$). Nuclear magnetic resonance spectra ($^1H$, $^{13}C$, DEPT 135, COSY, HMQC, NOESY) were recorded either on a 300, 400, or 700 MHz spectrometer. Chemical shifts for $^1H$ NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, δ 7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, and integration. Chemical shifts for $^{13}C$ NMR spectra are recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (77.23 ppm) as the internal standard. All spectra were obtained with complete proton decoupling. When ambiguous, proton and carbon assignments were established using COSY, HMQC and DEPT experiments. Optical rotations were determined with a polarimeter at 589 or 546 nm. Data are reported as follows: $[\alpha]_\lambda^{temp}$, concentration (*c* in g/100 mL), and solvent. Analytical gas chromatography was carried out with a splitless mode capillary injector and a flame ionization dectector or with a system equipped with an EI mass detector. Unless otherwise noted, the injector and detector temperatures were set to 250 °C and hydrogen was used as the carrier gas (63 psi). Data are reported as follows: column type, oven temperature, carrier pressure, and retention time ($t_r$). Analytical gas chromatography was carried with a splitless mode capillary injector and a flame ionization. Unless otherwise noted, the injector and detector temperatures were set to 250 ˚C and hydrogen was used as the carrier gas (63 psi). Data are reported as follows: (column type, column length, intial temperature, initial time, rate, final temperature, final time: retention time ($t_r$)). Analytical SFC were performed on SFC and Data are reported as follows: column type, eluent, flow rate, and retention time ($t_r$).

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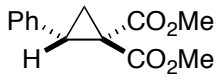
[1] Shriver, D. F.; Drezdzon, M. A. The Manipulation of Air-Sensitive Compounds; 2nd ed.; Wiley: New York, 1986.

[2] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

**Reagents:** Unless otherwise stated, commercial reagents were used without purification. Copper salts, silver salts and bisoxazoline ligands **L1**, **L2**, **L4**, **L5**, and ligand **L9** were commercially available. Bisoxazoline ligands **L3**,[3] **L6**,[4] **L7**,[3] **L8**,[5] and Iodonium ylides[6] were synthesized according to a previously reported procedure. $Rh_2(Oct)_4$, $Rh_2$(*R*-MEPY)$_4$, $Rh_2$(*S*-DOSP)$_4$ were bought. $Rh_2$(*S*-NTV)$_4$,[7] $Rh_2$(*S*-NTTL)$_4$,[7] $Rh_2$(*S*-PTV)$_4$,[8] $Rh_2$(*S*,*S*-DPTIC)$_3$OAc,[9] and $Rh_2$(*S*-PTTL)$_4$[8] were prepared according literature procedure. Alkenes **3** are commercially available and were used without purification.

**General procedure for the enantioselective cyclopropanation of styrene with iodonium ylides:** Cyclopropanes **4a-e** were prepared according to the following general procedure.

In a 10 mL $\mu$-wave tube in a glove box were added CuCl (1.0 mg, 0.010 mmol), $AgSbF_6$ (4.1 mg, 0.012 mmol) and the ligand (0.020 mmol). The flask was covered with a rubber septum, taken out of the glove box and put under argon. Toluene (2.0 mL) was then added and the mixture was stirred for 1 h. The mixture was cooled at 0 °C (cryostat), styrene (286 $\mu$L, 2.50 mmol) was added, the septum was then removed, the iodonium ylide (0.500 mmol) was added in one portion and the septum was put back quickly. Reaction mixture was stirred for 18 h at 0 °C. The resulting solution was filtered on a pad of silica gel, eluting with $Et_2O$. The filtrate was then concentrated and purified by chromatography on silica gel.




**4a**

**Dimethyl (2*S*)-2-phenylcyclopropane-1,1-dicarboxylate (4a).** Purified by chromatography on silica gel (10% EtOAc/hexane) to yield a colorless oil. Yield: 88%, enantiomeric excess (75% ee) was determined by GC analysis (β-dex, 30 m, 130 °C isotherm, $t_r$ (major) 41 min, $t_r$ (minor) 42 min) and on the diol **S1** after reduction of **4a**; $R_f$ 0.53 (20% EtOAc/hexane); $[\alpha]_D^{20}$= –101 (*c* 1.52, $CHCl_3$), lit: +131 (c 1.40, $CHCl_3$, >99% ee)[6]; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (m, 5H), 3.77 (s, 3H), 3.34 (s, 3H), 3.23 (t app, *J* = 8.6 Hz, 1H), 2.19 (dd, *J* = 8.0 Hz, *J* = 5.2 Hz, 1H), 1.73 (dd, *J* = 9.2 Hz, *J* = 5.2 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.9, 134.5, 128.3 (2C), 128.0 (2C), 127.3, 52.6, 52.0, 37.1, 32.4, 19.0; IR (neat) 2953, 1726, 1436, 1332, 1277, 1217, 1130 cm$^{-1}$. The spectral data were consistent with that previously reported.[6]

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[3] Itagaki, M.; Masumoto, K.; Yamamoto, Y. *J. Org. Chem.* **2005**, *70*, 3292-3295.

[4] Garcia, J. I.; Mayoral, J. A.; Pires, E.; Villalba, I. *Tetrahedron: Asymmetry* **2006**, *17*, 2270-2275.

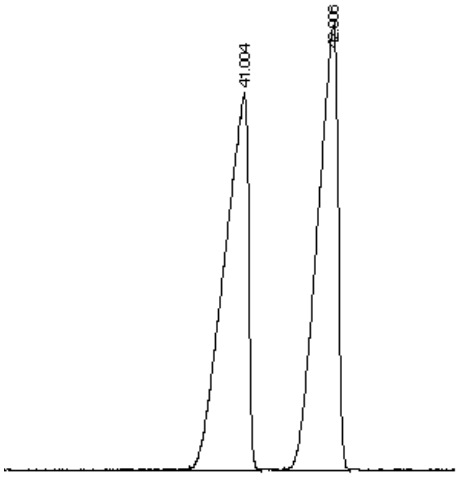
[5] Barrett, I. M.; Breeden, S. W. *Tetrahedron: Asymmetry* **2004**, *15*, 3015-3017.

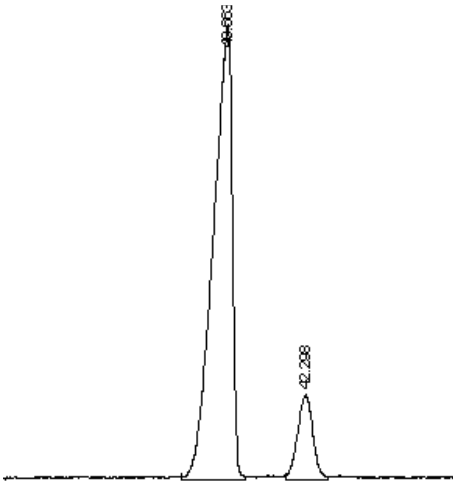
[6] Perreault, C.; Goudreau, S. R.; Zimmer, L. E.; Charette, A. B. *Org. Lett.* **2008**, *10*, 689-692.

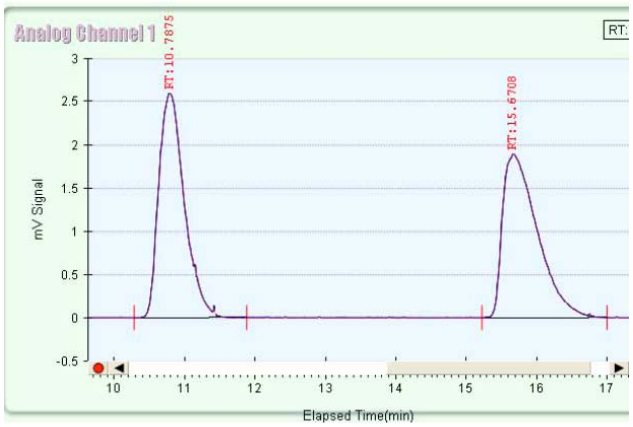
[7] Müller, P.; Allenbach, Y.; Robert, E. *Tetrahedron: Asymmetry* **2003,** *14*, 779.

[8] Watanabe, N.; Ogawa, T.; Ohtake, Y.; Ikegami, S.; Hashimoto, S. *Synlett.* **1996**, 85.

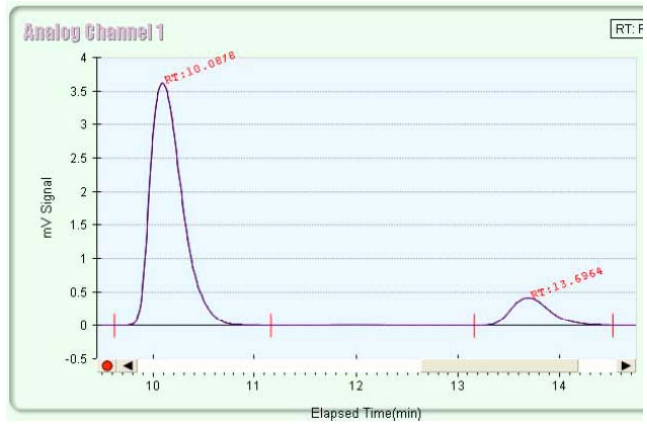
[9] Lou, Y.; Horikawa, M.; Klosher, R. A.; Hawryluk, N. A.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 8916.



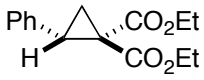




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 50.2083 | 65.0621 | 10.7875 min |
| Peak2 | 49.7917 | 64.5223 | 15.6708 min |



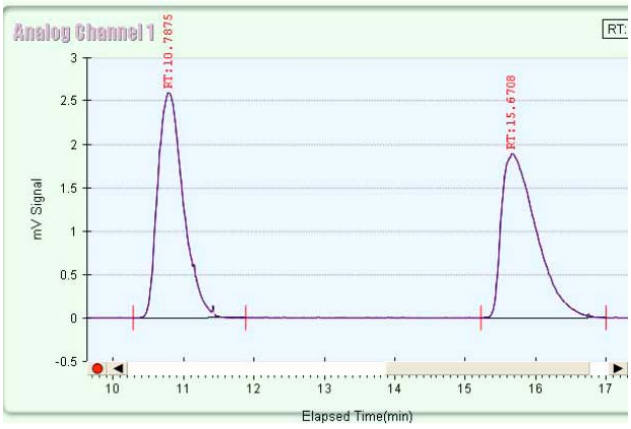

| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 87.5724 | 78.1152 | 10.0878 min |
| Peak2 | 12.4276 | 11.0856 | 13.6964 min |



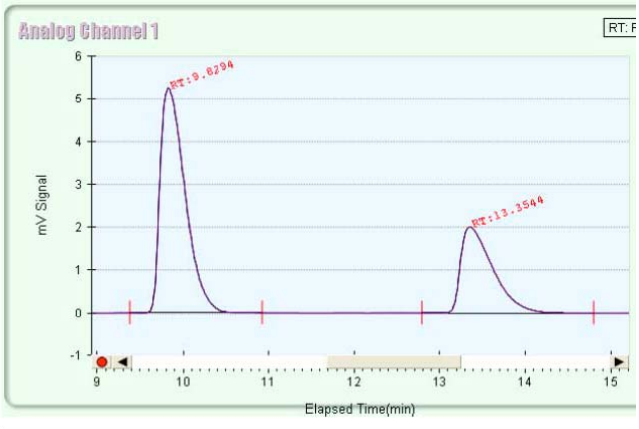

**4b**

**Diethyl (2*S*)-2-phenylcyclopropane-1,1-dicarboxylate (4b).** Purified by chromatography on silica gel (5% EtOAc/hexane) to yield a colorless oil. Yield: 23%, enantiomeric excess (34% ee) was determined on the diol **S1** after reduction of **4b**; $R_f$ 0.34 (10% EtOAc/hexane); $[\alpha]_D^{20}$= –45 (c 1.13, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29-7.19 (m, 5H), 4.32-4.18 (m, 2H), 3.85 (qd, *J* = 7.2 Hz, *J* = 0.4 Hz, 2H), 3.22 (t app, *J* = 8.6 Hz, 1H), 2.18 (dd, *J* = 8.0 Hz, *J* = 5.2 Hz, 1H), 1.71 (dd, *J* = 9.2 Hz, *J* = 5.2 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.9, 166.6, 134.6, 128.5 (2C), 128.1 (2C), 127.3, 61.7, 61.1, 37.4, 32.1, 18.7, 14.1, 13.6; IR (neat) 2982, 1720, 1321, 1273, 1213, 1188, 1129 cm$^{-1}$. The spectral data were consistent with that previously reported.[10]

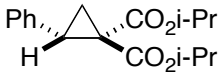
[10] Watanabe, S.; Nakayama, I.; Kataoka, T. *Eur. J. Org. Chem.* **2005**, 1493.




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 50.2083 | 65.0621 | 10.7875 min |
| Peak2 | 49.7917 | 64.5223 | 15.6708 min |

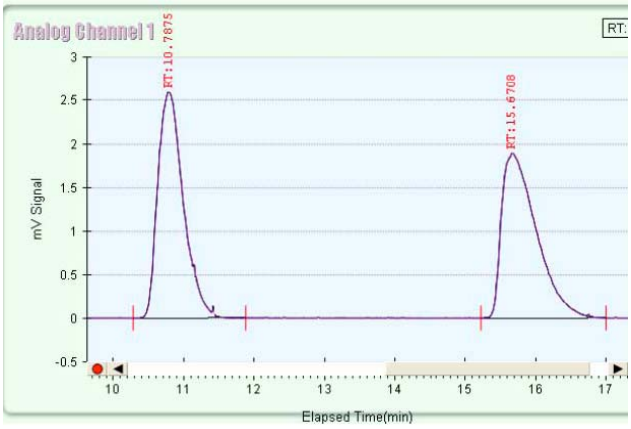



| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 67.1354 | 104.9506 | 9.8294 min |
| Peak2 | 32.8646 | 51.3762 | 13.3544 min |

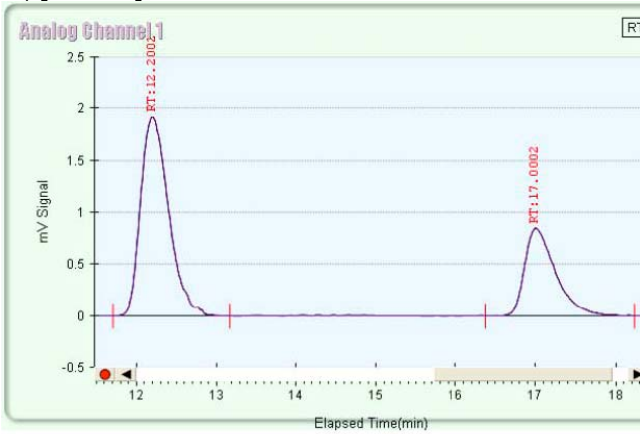



**4c**

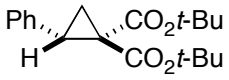
**Diisopropyl (2*S*)-2-phenylcyclopropane-1,1-dicarboxylate (4c).** Purified by chromatography on silica gel (5% EtOAc/hexane) to yield a colorless oil. Yield: 41%, enantiomeric excess (35% ee) was determined on the diol **S1** after reduction of **4c**; $R_f$ 0.38 (10% EtOAc/hexane); $[\alpha]_D^{20}$= –41 (*c* 1.68, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.28-7.17 (m, 5H), 5.09 (sp, *J* = 6.3 Hz, 1H), 4.72 (sp, *J* = 6.3 Hz, 1H), 3.10 (t app, *J* = 8.6 Hz, 1H), 2.13 (dd, *J* = 8.0 Hz, *J* = 5.2 Hz, 1H), 1.64 (dd, *J* = 9.2 Hz, *J* = 5.2 Hz, 1H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.3 Hz, 3H), 1.05 (d, *J* = 6.3 Hz, 3H), 0.68 (d, *J* = 6.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.5, 166.2, 134.7, 128.5 (2C), 128.0 (2C), 127.1, 69.2, 68.5, 37.8, 31.7, 21.7, 21.6, 21.2, 21.0, 18.3; IR (neat) 2980, 2937, 1717, 1374, 1315, 1275, 1215, 1099 $cm^{-1}$; HRMS (ESI) calcd for $C_{17}H_{22}O_4$ $[M+Na]^+$: 313.1410, found 313.1413.




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 50.2083 | 65.0621 | 10.7875 min |
| Peak2 | 49.7917 | 64.5223 | 15.6708 min |

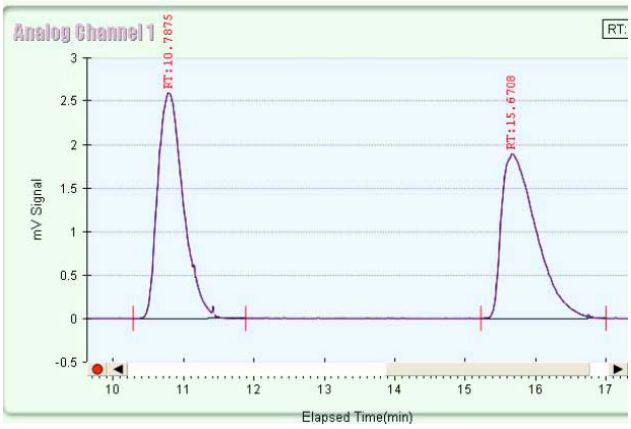



| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 67.2478 | 46.3694 | 12.2002 min |
| Peak2 | 32.7522 | 22.5836 | 17.0002 min |

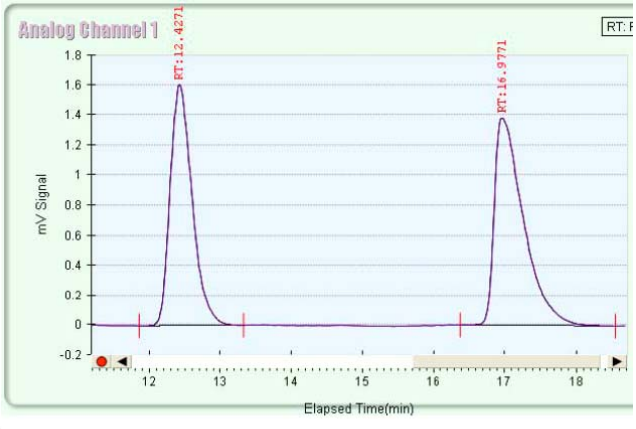



**4d**

**Di-*tert*-butyl (2*S*)-2-phenylcyclopropane-1,1-dicarboxylate (4d).** Purified by chromatography on silica gel (5% EtOAc/hexane) to yield a white solid. Yield: 77%, enantiomeric excess (7% ee) was determined on the diol **S1** after reduction of **4d**; mp 101-103 °C; $R_f$ 0.47 (10% EtOAc/hexane); $[\alpha]_D^{20}$= +4 (*c* 1.29, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.29-7.18 (m, 5H), 3.10 (t app, *J* = 8.6 Hz, 1H), 2.03 (dd, *J* = 7.8 Hz, *J* = 5.0 Hz, 1H), 1.53 (dd, *J* = 9.0 Hz, *J* = 5.0 Hz, 1H), 1.51 (s, 9H), 1.10 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.2, 165.8, 134.9, 128.7 (2C), 127.9 (2C), 126.9, 81.6, 80.8, 39.2, 30.8, 28.0 (3C), 27.4 (3C), 17.6; IR (neat) 2977, 2932, 1715, 1367, 1333, 1289, 1165, 1126 cm$^{-1}$. The spectral data were consistent with that previously reported.[11]




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 50.2083 | 65.0621 | 10.7875 min |
| Peak2 | 49.7917 | 64.5223 | 15.6708 min |




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 46.7139 | 34.1612 | 12.4271 min |
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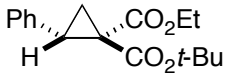
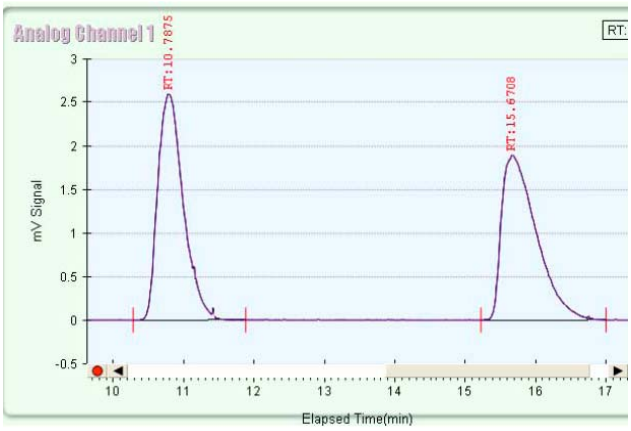


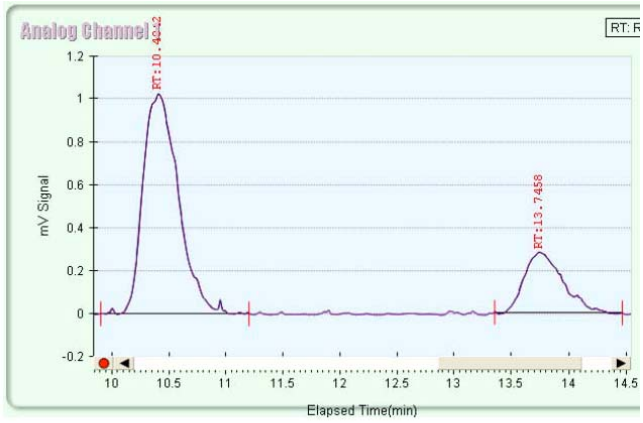

**4e**

**1-*tert*-Butyl 1-ethyl (1*S*,2*S*)-2-phenylcyclopropane-1,1-dicarboxylate (4e).** Purified by chromatography on silica gel (5% EtOAc/hexane) to yield a colorless oil. Yield: 60%, diastereomeric ratio (85:15) was determined by $^1$H NMR analysis of the crude mixture, enantiomeric excess (54% ee) was determined on the diol **S1** after reduction of **4e**; $R_f$ 0.43 (10% EtOAc/hexane); $[\alpha]_D^{20}$= –58 (*c* 1.42, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.31-7.18 (m, 5H), 3.94-3.77 (m, 2H), 3.15 (t, *J* = 8.6 Hz, 1H), 2.11 (dd, *J* = 7.9 Hz, *J* = 5.1 Hz, 1H), 1.64 (dd, *J* = 9.2 Hz, *J* = 5.1 Hz, 1H), 1.51 (s, 9H), 0.91 (t, *J* = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.9, 134.9, 128.4 (2C), 128.0 (2C), 127.0, 81.9, 60.8, 38.4, 31.3, 27.9 (3C), 18.2, 13.7; IR (neat) 2979, 2934, 1716, 1368, 1288, 1165, 1126 cm$^{-1}$; HRMS (ESI) calcd for $C_{17}H_{22}O_4$ $[M+Na]^+$: 313.1410, found 313.1411.

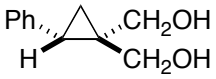
[11] Doyle, M. P.; Hu, W. *ARKIVOC* **2003**, *7*, 15.




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 50.2083 | 65.0621 | 10.7875 min |
| Peak2 | 49.7917 | 64.5223 | 15.6708 min |




| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| Peak1 | 76.8197 | 21.8793 | 10.4042 min |
| Peak2 | 23.1803 | 6.6021 | 13.7458 min |

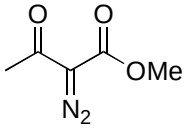



**S1**

**[(2*R*)-2-phenylcyclopropane-1,1-diyl]dimethanol (S1).** In a dry 10 mL flask under argon was added 1,1-cyclopropane diesters (~0.40 mmol) and $CH_2Cl_2$ (2.0 mL). The reaction mixture was cooled at 0 °C and $LiAlH_4$ (1 equiv) was added. The mixture was then stirred at room temperature for 30 min, quenched with $Na_2SO_4 \cdot nH_2O$, filtered on silica gel, eluted with diethyl ether, and concentrated under reduce pressure to yield a white solid. Yields: > 90%, enantiomeric excess was determined by SFC analysis (Chiralpak AD-H 25 cm, 10% MeOH, 3 mL/min, 40 °C, 20 psi, $t_r$ (major) 11 min, $t_r$ (minor) 14 min) (see the corresponding 1,1-cyclopropane diester **4a-e**). mp 78 °C; $R_f$ 0.31 (70% EtOAc/hexane); $[\alpha]_D^{20} = -4$ (*c* 2.16, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 3.77 (d, *J* = 11 Hz, 1H), 3.71 (d, *J* = 11 Hz, 1H), 3.54 (d, *J* = 11 Hz, 1H), 3.39 (d, *J* = 11 Hz, 1H), 3.01 (br, 1H), 2.26 (dd, *J* = 8.4, 6.1 Hz, 1H), 2.16 (br, 1H), 1.09 (t, *J* = 5.8 Hz, 1H), 0.97 (dd, *J* = 8.5, 5.4 Hz, 1H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 137.6, 128.8 (2C), 128.3 (2C), 126.4, 69.9, 65.2, 30.7, 26.7, 12.9; IR (neat) 3347, 2928, 1603, 1497, 1455, 1019 $cm^{-1}$. HRMS (ESI) calcd for $C_{11}H_{14}O_2$ $[M+Na]^+$: 201.0886, found 201.0885.

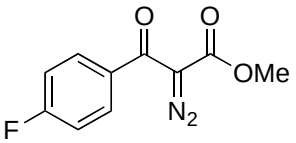
**All diazo reagents were synthesized according literature procedure.** [12,13]

*Although we have not experienced any problem in the handling of these compounds (sulfonyl azide and the α-amide-α-diazocarboxylate derivatives), extreme care should be taken when manipulating them due to their explosive nature.*

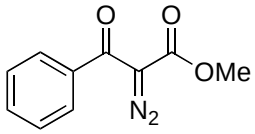



[12] Müller, P.; Ghanem, A. *Org. Lett.* **2004**, *6*, 4347.

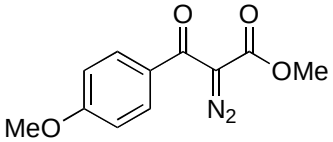
**Methyl 2-diazo-3-oxobutanoate (7a).** All physical data were identical to those reported.[12]



**Methyl 2-diazo-3-oxo-3-(4-flurophenyl)propanoate (7b).** The product was isolated as a yellow liquid. Yield: 79%, $R_f$ 0.81 (100% DCM); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.81-7.69 (m, 2H), 7.23-7.07 (m, 2H), 3.83 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 185.6, 165.4 (d, $J$ = 187.5 Hz, 1C), 161.6, 132.0 (d, $J$ = 180.1 Hz, 1C), 131.4 (d, $J$ = 7.5 Hz, 2C), 115.2 (d, $J$ = 18.8 Hz, 2C), 55.7, 52.6; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -107.38; IR (film) 3054, 2954, 2133, 1725, 1602, 1436, 1309, 1257 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{10}H_7N_2O_3F_1$ $[M+Na]^+$: 245.0333, found 245.0328.

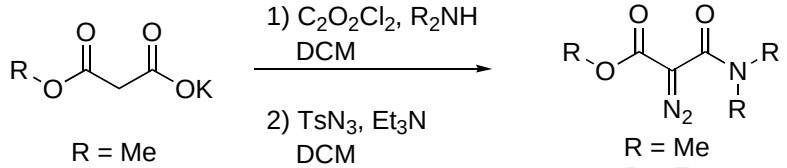


**Methyl 2-diazo-3-oxo-3-phenylpropanoate (7c).** The product was isolated as a yellow liquid. Yield: 91%, $R_f$ 0.75 (100% DCM); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.67-7.61 (m, 2H), 7.55-7.51 (m, 1H), 7.46-7.40 (m, 2H), 3.79 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 186.9, 161.6, 137.1, 132.5, 128.5 (2C), 128.1 (2C), 76.0, 52.5; IR (film) 3054, 2954, 2120, 1715, 1690, 1437, 1400, 1163 cm$^{-1}$.



**Methyl 2-diazo-3-oxo-3-(4-methoxyphenyl)propanoate (7d).** The product was isolated as a yellow liquid. Yield: 89%, $R_f$ 0.67 (100% DCM); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 6.95-6.93 (m, 2H), 3.89 (s, 3H), 3.83 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 184.8, 162.8, 161.4, 130.7 (2C), 128.9, 112.8 (2C), 76.3, 51.9; IR (film) 3024, 2956, 2133, 1724, 1628, 1600, 1436, 1321 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{11}H_{10}N_2O_4$ $[M+Na]^+$: 257.0533, found 257.0526.

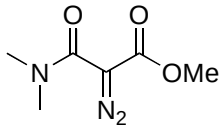
**General procedure for the synthesis of diazo reagents 8.** The diazo reagents have been prepared according to a known literature procedure.[13]



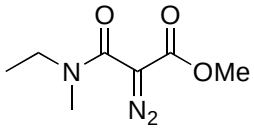

The corresponding potassium carboxylate salt[13] (25 mmol, 1.00 equiv) was suspended in DCM (50 mL) at 0 °C under a positive pressure of Ar. Oxalyl chloride (2.53 mL, 30 mmol, 1.20 equiv) was next added dropwise over 5 min followed by the addition of DMF (5-10

[13] Box, V. G. S.; Marinovic, N.; Yiannikouros, G. P. *Heterocycles* **1991**, *32*, 245.

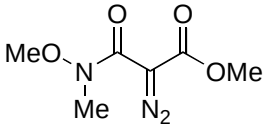
drops). The resulting solution was stirred for 1 h at 0 °C then at 25 °C for 1 h. The solvent was removed under reduced pressure and the solid was rinsed with 50 mL of DCM which was also removed under reduced pressure. The solid was dissolved in 50 mL of DCM and the corresponding amine (50 mmol, 2.00 equiv) was added dropwise at 0 °C. The reddish mixture was stirred for 1 h at 0 °C, then at 25 °C for 1 h. 10% HCl (50 mL) was added and the organic phase was separated, dried over $MgSO_4$, filtered through Celite®, and concentrated under vacuum to afford quantitatively the corresponding β-amide-ester. To this β-amide-ester acetonitrile (50 mL), triethylamine (4.15 mL, 30 mmol, 1.20 equiv), and tosyl azide[14] (5.92 g, 30 mmol, 1.20 equiv) were added. The mixture was stirred at 25 °C for 16 h. Following evaporation of the solvent, the product was suspended in diethyl ether and filtered. The filtrate was washed twice with 3N NaOH and once with brine, then dried over $MgSO_4$ filtered trough Celite®, and concentrated under vacuum. The yellow residue was purified by flash chromatography on silica gel using hexane/ethyl acetate (3:1). Triflic azide[15] can also be used as a diazo transfer agent instead of tosyl azide. 3N Aqueous KOH can also be used as a base instead of $Et_3N$.



**Methyl 2-diazo-3-(dimethylamino)-3-oxopropanoate (8a).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 80%, $R_f$ 0.56 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 2.98 (s, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 163.5, 162.4, 61.2, 53.0, 38.7 (2C); IR (film) 2954, 2122, 1720, 1638, 1437, 1400, 1163 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_6H_9N_3O_3$ $[M+H]^+$: 172.0722, found 172.0716.



**Methyl 2-diazo-3-(ethyl(methyl)amino)-3-oxopropanoate (8c).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 90%, $R_f$ 0.70 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.43 (q, $J$ = 7.1 Hz, 2H), 2.98 (s, 3H), 1.21 (t, $J$ = 7.1 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 163.7, 161.9, 54.3, 53.0, 45.2, 36.0, 13.4; IR (film) 2954, 2122, 1740, 1639, 1437, 1398, 1163 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_7H_{11}N_3O_3$ $[M+Na]^+$: 208.0693, found 208.0684.



**Methyl 2-diazo-3-(methoxy(methyl)amino)-3-oxopropanoate (8d).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 61%, $R_f$ 0.56 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 2.98 (s, 3H), 2.54 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 163.5, 162.4, 61.2, 53.0, 38.7, 16.2; IR (film) 2954, 2122, 1720, 1638, 1437, 1400, 1163 $cm^{-1}$.

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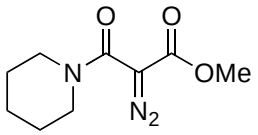
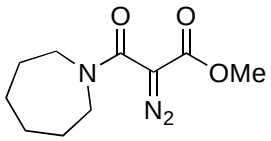
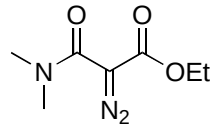
[14] Regitz, M.; Hocker, J.; Liedhegener, A. *Org. Synth.* **1973**, *5*, 179.
[15] Charette, A. B.; Wurz, R. P.; Ollevier, T. *J. Org. Chem.* **2000**, *65*, 9252.



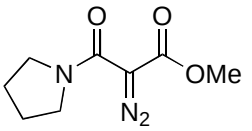
**Methyl 2-diazo-3-oxo-3-(piperidin-1-yl)propanoate (8e).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 78%, $R_f$ 0.73 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.49-3.43 (m, 4H), 1.62-1.55 (m, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 162.8, 160.2, 66.3, 52.2, 46.9 (2C), 25.8 (2C), 24.4; IR (film) 2940, 2858, 2129, 1692, 1625, 1425, 1302, 1103, 732 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_9H_{13}N_3O_3$ $[M+Na]^+$: 234.0849, found 234.0844.



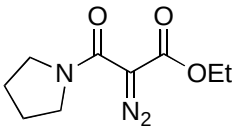
**Methyl 3-(azepan-1-yl)-2-diazo-3-oxopropanoate (8f).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 60%, $R_f$ 0.81 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.51-3.47 (m, 4H), 1.81-1.76 (m, 4H), 1.59-1.53 (m, 4H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 163.1, 161.1, 66.0, 52.3, 49.2 (2C), 48.9 (2C), 28.2 (2C); IR (film) 2927, 2855, 2122, 1710, 1617, 1422, 1305, 1095 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{10}H_{15}N_3O_3$ $[M+Na]^+$: 248.1006, found 248.0996.



**Ethyl 2-diazo-3-(dimethylamino)-3-oxopropanoate (8g)**. Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 85%, $R_f$ 0.60 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 4.27 (q, $J$ = 7.1 Hz, 2H), 3.02 (s, 6H), 1.32 (t, $J$ = 7.1 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 163.1, 162.5, 62.2, 54.3, 38.6(2C), 15.3; IR (film) 2954, 2122, 1740, 1639, 1437, 1398, 1163 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_7H_{11}N_3O_3$ $[M+Na]^+$: 208.0693, found 208.0689.

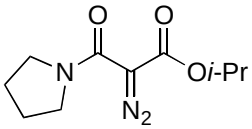


**Methyl 2-diazo-3-oxo-3-(pyrrolidin-1-yl)propanoate (8h).** Prepared according to the general procedure. The product was isolated as a yellow liquid that solidified upon standing at 0 °C. Yield: 96%. The physical data was identical as those reported in the literature.[13]

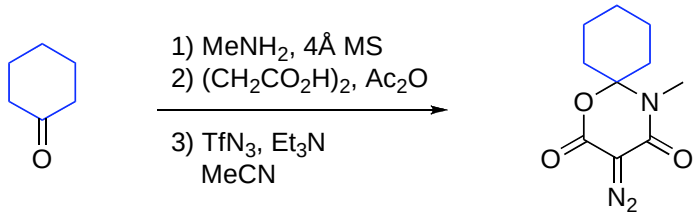


**Ethyl 2-diazo-3-(ethyl(methyl)amino)-3-oxopropanoate (8i).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 80%, $R_f$ 0.67 (100% $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 4.33 (q, $J$ = 7.1 Hz, 2H), 3.52-3.47 (m, 4H), 1.88-1.83

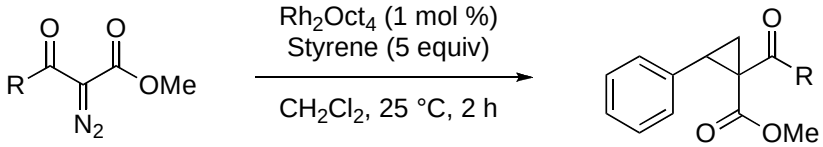
(m, 4H), 1.21 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 162.1, 159.7, 66.9, 61.2, 47.9, 47.8, 25.9, 24.5, 14.4; IR (film) 2976, 2878, 2123, 1711, 1622, 1413, 1297, 1103 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_9H_{13}N_3O_3$ [M+Na]$^+$: 234.0849, found 234.0843.




**Isopropyl 2-diazo-3-(ethyl(methyl)amino)-3-oxopropanoate (8j).** Prepared according to the general procedure. The product was isolated as a yellow liquid. Yield: 78%, $R_f$ 0.70 (100% $Et_2O$); $^1$H NMR (300 MHz, $CDCl_3$) δ 5.08 (s, $J$ = 6.3 Hz, 1H), 3.52-3.47 (m, 4H), 1.88-1.83 (m, 4H),1.25 (t, $J$ = 6.3 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 161.8, 159.7, 69.1, 67.1, 47.9, 47.8, 25.6, 25.5, 22.0 (2C); IR (film) 2979, 2878, 2126, 1704, 1621, 1415, 1286, 1099, 915 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{10}H_{15}N_3O_3$ [M+Na]$^+$: 248.1006, found 248.1002.

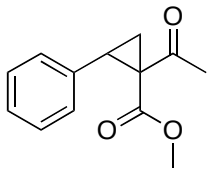



**3-Diazo-5-methyl-1-oxa-5-azaspiro[5.5]undecane-2,4-dione (8b).** A 25 mL sealed tube was charged with cyclohexanone (1.0 mL, 10 mmol, 1.0 equiv), 2 M $MeNH_2$ in THF (5.5 mL, 11 mmol, 1.1 equiv), activated 4Å MS (2.5 g), and a stirring bar. The tube was sealed and the resulting slurry was heated at 40 °C for two days. The reaction was cooled to 25 °C and the MS was removed by filtration throught Celite®. Concentration under reduced pressure afforded the corresponding *N*-Me imine. This imine was dissolved with acetic anhydride (7 mL, 75 mmol, 7.5 equiv) and stirred at 25 °C. Malonic acid (1.04 g, 10 mmol, 1.0 equiv) was added and the mixture was stirred for 24 h. Excess acetic anhydride was removed under high vacuum (0.1 mm Hg) for 16 h. Purification on silica gel ($Et_2O$/EtOAc 1:1) afforded the crude Meldrum acid's derived product. This crude product was engage in the diazo transfert reaction described in the general procedure for the synthesis of diazo reagents to afford the title compounds as a yellow solid. Yield: 21%, $R_f$ 0.78 (100% $Et_2O$); $^1$H NMR (300 MHz, $CDCl_3$) δ 2.96 (s, 3H), 2.10-2.02 (m, 2H), 1.80-1.66 (m, 8H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 160.5, 159.1, 93.7, 66.5, 34.3 (2C), 28.0, 24.3, 21.7 (2C); IR (film) 2938, 2864, 2144, 1722, 1658, 1393 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{10}H_{13}N_3O_3$ [M+H]$^+$: 224.1022, found 224.1030.

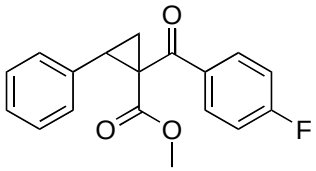



**General procedure for the synthesis of racemic cyclopropanes.** A 10-mL microwave vial was charged with $Rh_2(Oct)_4$ (3.1 mg, 0.004 mmol, 2 mol %) and a magnetic stir bar. The tube was sealed with a Teflon septum and purged with argon. DCM (1 mL) and the corresponding alkene (1.00 mmol, 5.00 equiv) were then added and the reaction was

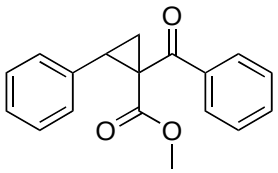
stirred at 25 °C. The diazo reagent (0.20 mmol, 1.00 equiv) dissolved in 1 mL of DCM was added to the reaction mixture over a period of 10 h using a syringe pump at 25 °C. After complete addition, the resulting mixture was stirred for an additional 6 h. The solvent was then removed under reduced pressure and the residue was purified by flash chromatography (100% hexane to 100% $Et_2O$) or by preparative TLC using 100% $Et_2O$.



**Methyl 1-acetyl-2-phenylcyclopropane carboxylate (9a).** Prepared according to the general procedure. All physical datas were identical to those reported.[12]



**Methyl 1-(4-fluorobenzoyl)-2-phenylcyclopropane carboxylate (9b).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 75%; mp: 105-108 °C; $R_f$ 0.84 (100%, DCM); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.03-7.94 (m, 2H), 7.34-7.23 (m, 5H), 7.20-7.12 (m, 2H), 3.56 (t app, *J* = 8.4 Hz, 1H), 3.28 (s, 3H), 2.46 (dd, *J* = 4.3 Hz, *J* = 9.1 Hz, 1H), 1.69 (dd, *J* = 4.9 Hz, *J* = 9.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 193.1, 169.0, 165.4 (d, *J* = 187.5 Hz, 1C), 134.9, 133.4 (d, *J* = 3.8 Hz, 1C), 131.1 (d, *J* = 9.8 Hz, 2C), 129.2 (2C), 128.3 (2C), 127.5, 115.7 (d, *J* = 21.9 Hz, 2C), 52.5, 42.3, 30.9, 20.1; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -106.41; IR (film) 3030, 2951, 1734, 1678, 1598, 1315, 1277 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{15}O_3F_1$ $[M+H]^+$: 299.1078, found 299.1078.



**Methyl 1-benzoyl-2-phenylcyclopropane carboxylate (9c).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 65%; mp: 97-99 °C; $R_f$ 0.78 (100%, DCM); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.59-7.56 (m, 1H), 7.51-7.46 (m, 2H), 7.35-7.25 (m, 5H), 3.60 (t app, *J* = 8.4 Hz, 1H), 3.26 (s, 3H), 2.47 (dd, *J* = 4.8 Hz, *J* = 8.4 Hz, 1H), 1.71 (dd, *J* = 4.8 Hz, *J* = 8.4 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 195.3, 169.8, 162.4, 137.9, 135.7, 133.8, 129.9 (2C), 129.4 (2C), 129.1 (2C), 129.0 (2C), 128.1, 56.2, 53.1, 43.1, 31.5, 20.9; IR (film) 3030, 2951, 1732, 1598, 1449, 1314, 1148 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{16}O_3$ $[M+H]^+$: 281.1172, found 281.1182.

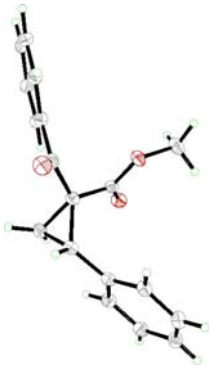


**Table 1.** Crystal data and structure refinement for C18 H16 O3.

| | |
|---|---|
| Identification code | cha187 |
| Empirical formula | C18 H16 O3 |
| Formula weight | 280.31 |
| Temperature | 100K |
| Wavelength | 1.54178 Å |
| Crystal system | Monoclinic |
| Space group | P21/n |
| Unit cell dimensions | a = 14.1950(2) Å $\alpha = 90^\circ$<br>b = 5.9546(1) Å $\beta = 95.036(1)^\circ$<br>c = 17.0522(3) Å $\gamma = 90^\circ$ |
| Volume | 1435.78(4)Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.297 g/cm$^3$ |
| Absorption coefficient | 0.708 mm$^{-1}$ |
| F(000) | 592 |
| Crystal size | 0.10 x 0.06 x 0.03 mm |
| Theta range for data collection | 3.89 to 67.83° |
| Index ranges | $-14 \le h \le 15$, $-7 \le k \le 7$, $-20 \le \ell \le 20$ |
| Reflections collected | 22947 |
| Independent reflections | 2484 [$R_{int}$ = 0.041] |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9790 and 0.7492 |

| | |
|---|---|
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 2484 / 0 / 191 |
| Goodness-of-fit on $F^2$ | 1.033 |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0355, $wR_2$ = 0.0977 |
| R indices (all data) | $R_1$ = 0.0410, $wR_2$ = 0.1010 |
| Largest diff. peak and hole | 0.176 and -0.185 e/Å$^3$ |

**Table 2.** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ x $10^3$) for C18 H16 O3.

$U_{eq}$ is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 2038(1) | 706(2) | 9918(1) | 31(1) |
| C(2) | 1900(1) | 1743(2) | 9093(1) | 34(1) |
| C(3) | 1691(1) | 3098(2) | 9792(1) | 37(1) |
| O(11) | 750(1) | -1883(2) | 9691(1) | 42(1) |
| C(11) | 1309(1) | -943(2) | 10165(1) | 33(1) |
| C(12) | 1283(1) | -1280(2) | 11032(1) | 34(1) |
| C(13) | 1664(1) | 303(2) | 11574(1) | 36(1) |
| C(14) | 1628(1) | -30(2) | 12375(1) | 42(1) |
| C(15) | 1226(1) | -1967(3) | 12642(1) | 45(1) |
| C(16) | 857(1) | -3555(2) | 12110(1) | 45(1) |
| C(17) | 869(1) | -3214(2) | 11309(1) | 40(1) |
| C(18) | 3034(1) | 330(2) | 10230(1) | 30(1) |
| O(18) | 3617(1) | 1766(1) | 10397(1) | 37(1) |
| O(19) | 3214(1) | -1880(1) | 10277(1) | 35(1) |
| C(19) | 4174(1) | -2502(2) | 10553(1) | 46(1) |
| C(21) | 2727(1) | 2240(2) | 8636(1) | 32(1) |
| C(22) | 2998(1) | 654(2) | 8097(1) | 35(1) |
| C(23) | 3717(1) | 1108(2) | 7626(1) | 38(1) |
| C(24) | 4193(1) | 3149(2) | 7685(1) | 38(1) |
| C(25) | 3941(1) | 4718(2) | 8228(1) | 38(1) |
| C(26) | 3212(1) | 4268(2) | 8696(1) | 36(1) |

**Table 3.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for C18 H16 O3.

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H(2) | 1327 | 1197 | 8766 | 41 |
| H(3A) | 1020 | 3413 | 9865 | 44 |
| H(3B) | 2134 | 4327 | 9959 | 44 |
| H(13) | 1952 | 1623 | 11392 | 44 |
| H(14) | 1878 | 1070 | 12740 | 50 |
| H(15) | 1202 | -2206 | 13190 | 54 |
| H(16) | 592 | -4897 | 12297 | 54 |
| H(17) | 595 | -4296 | 10948 | 48 |
| H(19A) | 4608 | -1979 | 10176 | 69 |
| H(19B) | 4218 | -4140 | 10602 | 69 |
| H(19C) | 4344 | -1810 | 11067 | 69 |
| H(22) | 2684 | -755 | 8054 | 42 |
| H(23) | 3888 | 16 | 7258 | 46 |
| H(24) | 4684 | 3463 | 7357 | 45 |
| H(25) | 4268 | 6108 | 8281 | 45 |
| H(26) | 3042 | 5364 | 9063 | 43 |

**Table 4.** Anisotropic parameters ($Å^2$ x $10^3$) for C18 H16 O3.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$$

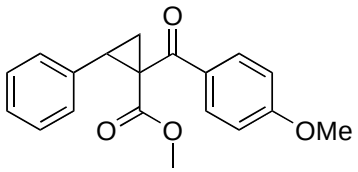
| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 33(1) | 28(1) | 32(1) | 1(1) | 2(1) | 2(1) |
| C(2) | 35(1) | 32(1) | 34(1) | 4(1) | -1(1) | 3(1) |
| C(3) | 37(1) | 30(1) | 44(1) | 2(1) | 6(1) | 5(1) |
| O(11) | 40(1) | 39(1) | 48(1) | -3(1) | -1(1) | -5(1) |
| C(11) | 30(1) | 29(1) | 42(1) | 0(1) | 3(1) | 3(1) |
| C(12) | 28(1) | 35(1) | 41(1) | 4(1) | 6(1) | 3(1) |
| C(13) | 34(1) | 36(1) | 40(1) | 4(1) | 8(1) | 1(1) |
| C(14) | 36(1) | 51(1) | 39(1) | 2(1) | 7(1) | 5(1) |
| C(15) | 36(1) | 57(1) | 44(1) | 14(1) | 11(1) | 10(1) |
| C(16) | 36(1) | 44(1) | 58(1) | 18(1) | 15(1) | 3(1) |
| C(17) | 31(1) | 37(1) | 54(1) | 3(1) | 8(1) | 2(1) |
| C(18) | 35(1) | 29(1) | 27(1) | 1(1) | 4(1) | 0(1) |
| O(18) | 37(1) | 33(1) | 41(1) | 0(1) | -1(1) | -5(1) |
| O(19) | 32(1) | 28(1) | 45(1) | 2(1) | -2(1) | 3(1) |
| C(19) | 34(1) | 38(1) | 64(1) | 4(1) | -6(1) | 6(1) |
| C(21) | 32(1) | 32(1) | 30(1) | 4(1) | -3(1) | 3(1) |
| C(22) | 32(1) | 31(1) | 42(1) | -1(1) | -1(1) | 1(1) |
| C(23) | 33(1) | 38(1) | 44(1) | -6(1) | 2(1) | 3(1) |
| C(24) | 29(1) | 41(1) | 43(1) | 3(1) | 2(1) | 2(1) |
| C(25) | 38(1) | 31(1) | 44(1) | 3(1) | -2(1) | -2(1) |
| C(26) | 41(1) | 33(1) | 34(1) | 0(1) | -1(1) | 2(1) |

**Table 5.** Bond lengths [Å] and angles [°] for C18 H16 O3

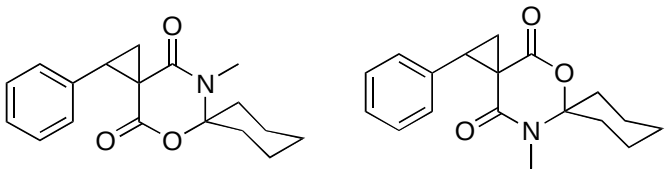
| | | | |
|---|---|---|---|
| C(1)-C(18) | 1.4832(18) | C(3)-C(2)-C(21) | 122.04(11) |
| C(1)-C(11) | 1.5119(18) | C(3)-C(2)-C(1) | 60.13(8) |
| C(1)-C(3) | 1.5160(17) | C(21)-C(2)-C(1) | 121.07(11) |
| C(1)-C(2) | 1.5342(16) | C(2)-C(3)-C(1) | 61.34(8) |
| C(2)-C(3) | 1.4911(18) | O(11)-C(11)-C(12) | 121.53(12) |
| C(2)-C(21) | 1.4948(19) | O(11)-C(11)-C(1) | 122.41(11) |
| O(11)-C(11) | 1.2172(16) | C(12)-C(11)-C(1) | 116.01(11) |
| C(11)-C(12) | 1.4953(17) | C(17)-C(12)-C(13) | 118.90(12) |
| C(12)-C(17) | 1.3947(19) | C(17)-C(12)-C(11) | 119.60(12) |
| C(12)-C(13) | 1.3960(19) | C(13)-C(12)-C(11) | 121.50(12) |
| C(13)-C(14) | 1.3864(18) | C(14)-C(13)-C(12) | 120.69(13) |
| C(14)-C(15) | 1.381(2) | C(15)-C(14)-C(13) | 119.73(14) |
| C(15)-C(16) | 1.381(2) | C(16)-C(15)-C(14) | 119.99(13) |
| C(16)-C(17) | 1.382(2) | C(15)-C(16)-C(17) | 120.75(13) |
| C(18)-O(18) | 1.2071(15) | C(16)-C(17)-C(12) | 119.91(14) |
| C(18)-O(19) | 1.3415(14) | O(18)-C(18)-O(19) | 123.83(12) |
| O(19)-C(19) | 1.4494(16) | O(18)-C(18)-C(1) | 126.21(11) |
| C(21)-C(26) | 1.3897(18) | O(19)-C(18)-C(1) | 109.92(10) |
| C(21)-C(22) | 1.3944(18) | C(18)-O(19)-C(19) | 116.09(10) |
| C(22)-C(23) | 1.380(2) | C(26)-C(21)-C(22) | 118.30(12) |
| C(23)-C(24) | 1.3896(19) | C(26)-C(21)-C(2) | 122.71(12) |
| C(24)-C(25) | 1.3847(19) | C(22)-C(21)-C(2) | 118.92(12) |
| C(25)-C(26) | 1.385(2) | C(23)-C(22)-C(21) | 120.71(12) |
| | | C(22)-C(23)-C(24) | 120.62(12) |
| C(18)-C(1)-C(11) | 117.12(10) | C(25)-C(24)-C(23) | 119.06(13) |
| C(18)-C(1)-C(3) | 118.66(11) | C(24)-C(25)-C(26) | 120.28(12) |
| C(11)-C(1)-C(3) | 115.38(11) | C(25)-C(26)-C(21) | 121.02(12) |
| C(18)-C(1)-C(2) | 115.48(11) | | |
| C(11)-C(1)-C(2) | 118.80(11) | | |
| C(3)-C(1)-C(2) | 58.53(8) | | |

**Table 6.** Torsion angles [°] for C18 H16 O3.

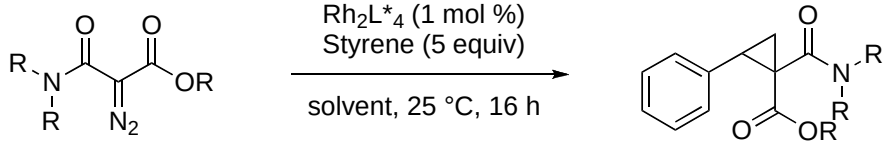
| | |
|---|---|
| C(18)-C(1)-C(2)-C(3) | -109.34(12) |
| C(11)-C(1)-C(2)-C(3) | 103.71(13) |
| C(18)-C(1)-C(2)-C(21) | 2.27(16) |
| C(11)-C(1)-C(2)-C(21) | -144.68(12) |
| C(3)-C(1)-C(2)-C(21) | 111.61(14) |
| C(21)-C(2)-C(3)-C(1) | -110.03(13) |
| C(18)-C(1)-C(3)-C(2) | 103.91(13) |
| C(11)-C(1)-C(3)-C(2) | -109.55(12) |
| C(18)-C(1)-C(11)-O(11) | -128.67(13) |
| C(3)-C(1)-C(11)-O(11) | 84.26(15) |
| C(2)-C(1)-C(11)-O(11) | 17.75(18) |
| C(18)-C(1)-C(11)-C(12) | 54.06(15) |
| C(3)-C(1)-C(11)-C(12) | -93.01(13) |
| C(2)-C(1)-C(11)-C(12) | -159.52(11) |
| O(11)-C(11)-C(12)-C(17) | 22.96(19) |
| C(1)-C(11)-C(12)-C(17) | -159.74(12) |
| O(11)-C(11)-C(12)-C(13) | -156.93(13) |
| C(1)-C(11)-C(12)-C(13) | 20.37(18) |
| C(17)-C(12)-C(13)-C(14) | -0.4(2) |
| C(11)-C(12)-C(13)-C(14) | 179.51(12) |
| C(12)-C(13)-C(14)-C(15) | 1.2(2) |
| C(13)-C(14)-C(15)-C(16) | -0.4(2) |
| C(14)-C(15)-C(16)-C(17) | -1.2(2) |
| C(15)-C(16)-C(17)-C(12) | 2.0(2) |
| C(13)-C(12)-C(17)-C(16) | -1.2(2) |
| C(11)-C(12)-C(17)-C(16) | 178.89(12) |
| C(11)-C(1)-C(18)-O(18) | -146.32(12) |
| C(3)-C(1)-C(18)-O(18) | -0.35(18) |
| C(2)-C(1)-C(18)-O(18) | 66.16(16) |
| C(11)-C(1)-C(18)-O(19) | 36.01(14) |
| C(3)-C(1)-C(18)-O(19) | -178.02(10) |
| C(2)-C(1)-C(18)-O(19) | -111.51(11) |
| O(18)-C(18)-O(19)-C(19) | 0.53(17) |
| C(1)-C(18)-O(19)-C(19) | 178.27(10) |
| C(3)-C(2)-C(21)-C(26) | -16.51(18) |
| C(1)-C(2)-C(21)-C(26) | -88.52(15) |
| C(3)-C(2)-C(21)-C(22) | 166.74(11) |
| C(1)-C(2)-C(21)-C(22) | 94.74(14) |
| C(26)-C(21)-C(22)-C(23) | -1.21(18) |
| C(2)-C(21)-C(22)-C(23) | 175.68(11) |
| C(21)-C(22)-C(23)-C(24) | 0.67(19) |
| C(22)-C(23)-C(24)-C(25) | 0.51(19) |
| C(23)-C(24)-C(25)-C(26) | -1.13(19) |
| C(24)-C(25)-C(26)-C(21) | 0.58(19) |
| C(22)-C(21)-C(26)-C(25) | 0.59(18) |
| C(2)-C(21)-C(26)-C(25) | -176.18(11) |



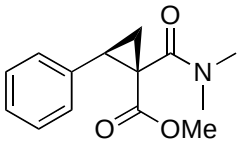
**Methyl 1-(4-methoxybenzoyl)-2-phenylcyclopropane carboxylate (9d).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 69%; mp: 124-127 °C; $R_f$ 0.70 (100%, DCM); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.33-7.27 (m, 5H), 6.97-6.94 (m, 2H), 3.88 (s, 3H), 3.52 (t app, *J* = 8.2 Hz, 1H), 3.28 (s, 3H), 2.43 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 1.64 (dd, *J* = 4.9 Hz, *J* = 9.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 192.8, 169.4, 163.7, 135.2, 130.9 (2C), 129.8, 129.3 (2C), 128.3 (2C), 127.4, 114.0 (2C), 55.7, 52.5, 42.2, 30.5, 19.7; IR (film) 3010, 2951, 2841, 1732, 1670, 1600, 1259 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{19}H_{18}O_4$ $[M+H]^+$: 311.1278, found 311.1274.



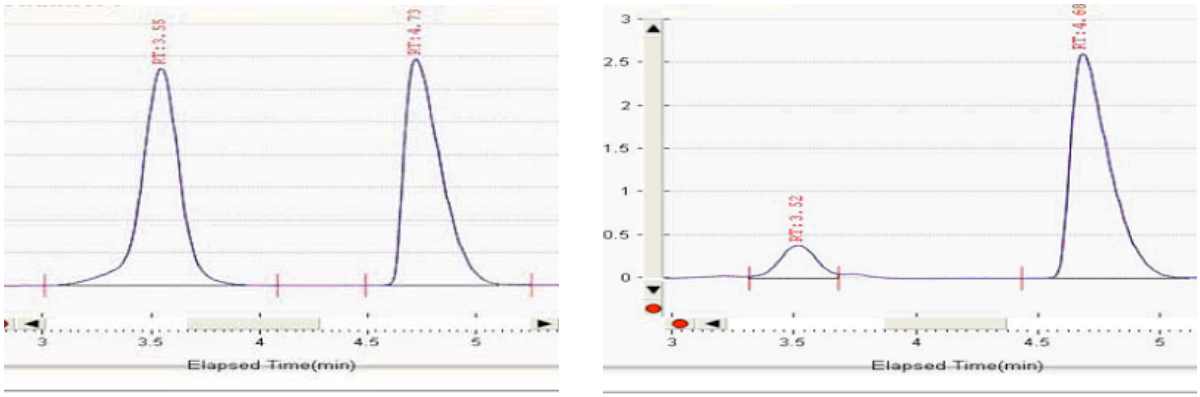
**(6,6-Cyclohexyl)7-trimethyl-1-phenyl-5-oxa-7-azaspiro[2.5]octane-4,8-dione (10b).** Prepared according to the general procedure. The product was isolated as a white solid (*cis*) and colorless oil (*trans*). Yield: 51%; mp: 124-127 °C; $R_f$ 0.78 (Major), 0.70 (Minor) (100%, $Et_2O$); $^1$H NMR (300 MHz, $CDCl_3$) δ (Major) 7.32-7.26 (m, 5H), 3.19 (t app, *J* = 8.8 Hz, 1H), 2.87 (s, 3H), 2.68 (dd, *J* = 4.4 Hz, *J* = 8.9 Hz, 1H), 2.31 (dd, *J* = 4.4 Hz, *J* = 9.5 Hz, 1H), 2.16-2.00 (m, 2H), 1.97-1.74 (m, 6H), 1.67-1.50 (m, 2H), (Minor) 7.32-7.26 (m, 5H), 3.14 (t app, *J* = 9.2 Hz, 1H), 3.07 (s, 3H), 2.52-2.43 (m, 2H), 2.13-1.67 (m, 10H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ (Major) 169.9, 164.0, 133.1, 129.7 (2C), 128.3 (2C), 128.0, 91.8, 41.7, 36.2, 35.4, 34.6, 28.4, 24.5, 22.2, 21.7, 21.1, (Minor) 168.0, 165.6, 132.9, 129.4 (2C), 128.3 (2C), 128.1, 91.7, 41.5, 36.0, 35.4, 35.1, 30.5, 28.6, 24.4, 21.6, 20.7; IR (film) 2936, 2862, 2841, 1742, 1659, 1392, 1120 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{21}N_1O_3$ $[M+H]^+$: 300.1594, found 300.1594.




**General procedure for the optimization (Table 2).** A 10-mL microwave vial was charged with $Rh_2(L^*)_4$ (0.002 mmol, 1 mol %) and a magnetic stir bar. The tube was sealed with a Teflon septum and purged with argon. DCM (1 mL) and styrene (132 µL, 1.00 mmol, 5.00 equiv) were then added. The diazo compound (0.20 mmol, 1.00 equiv) dissolved in 1 mL of DCM was added to the reaction mixture over a period of 10 h using a syringe pump at 25 °C. After complete addition, the resulting mixture was stirred for an additional 6 h at 25 °C. The reaction mixture was put directly on a silica gel column and eluted with a gradient of 100% hexane to 100% $Et_2O$. In cases where the rhodium dimer is complexed to the product, the green mixture was dissolved in DCM and poly(4-vinylpyridine) (≈ 20 mg) was added. The color of the mixture turned from green to red and was then filtered through Celite® to afford a rhodium-free product following concentration under reduced pressure.

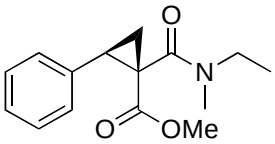


**Methyl 1-(dimethylcarbamoyl)-2-phenylcyclopropanecarboxylate (10a).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 71%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 27.2 min, $t_r$ (major) 27.9 min), enantiomeric excess (75% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*PrOH, 3 mL/min, 25 °C, 200 psi, $t_r$ (minor) 3.6 min, $t_r$ (major) 4.7 min); $R_f$ 0.44 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +13 (*c* 1.00, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.29-7.16 (m, 5H), 3.39 (s, 3H), 3.25 (app. t, *J* = 8.4 Hz, 1H), 3.02 (s, 3H), 2.99 (s, 3H), 2.19 (dd, *J* = 5.0 Hz, *J* = 8.2 Hz, 1H), 1.52 (dd, *J* = 5.0 Hz, *J* = 9.2 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 169.4, 168.9, 136.0, 129.9 (2C), 128.8 (2C), 127.9, 53.1, 38.5, 37.9, 36.7, 33.0, 18.9; IR (film) 3039, 3008, 2946, 2884, 1715, 1638, 1511, 1434, 1334, 1135 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{14}H_{17}N_1O_3$ $[M+H]^+$: 248.1281, found 248.1284.



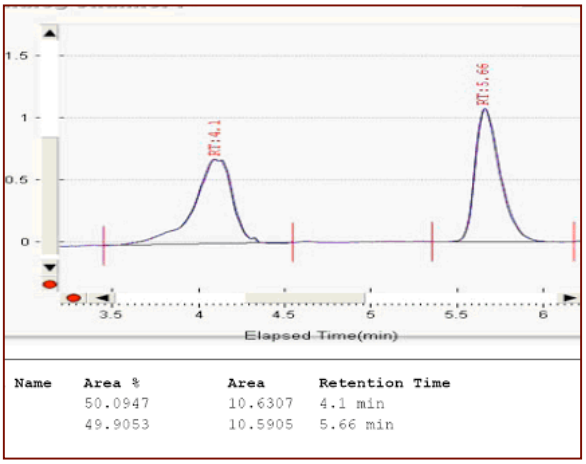

| Area % | Area | Retention Time |
|---|---|---|
| 50.3831 | 39.9397 | 3.55 min |
| 49.6169 | 39.3322 | 4.73 min |

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 12.3685 | 3.9549 | 3.52 min |
| | 87.6315 | 28.0208 | 4.68 min |

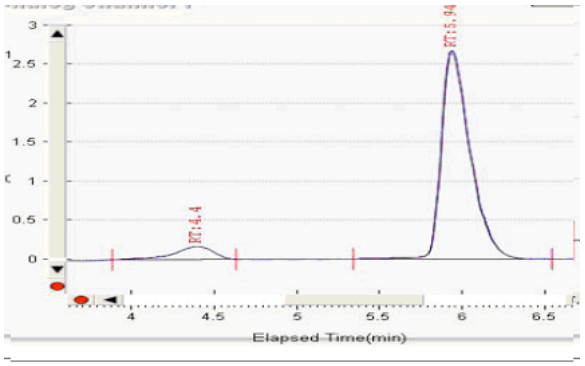


**Methyl 1-(ethyl(methyl)carbamoyl)-2-phenylcyclopropanecarboxylate (10c).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 35%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 28.2 min, $t_r$ (major) 28.5 min), enantiomeric excess (85% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*PrOH, 3 mL/min, 25 °C, 150 psi, $t_r$ (minor) 4.4 min, $t_r$ (major) 5.9 min); $R_f$ 0.67 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +120 (*c* 1.83, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.33-7.22 (m, 5H), 3.57-3.53 (m, 1H), 3.46-3.41 (m, 4H, 1.5:1 rotamer), 3.33-3.27 (m, 1H), 3.04 and 2.99 (2 x s, 3H, 1.5:1 rotamer), 2.26-2.22 (m, 1H), 1.59-1.54 (m, 1H), 1.21-1.15 (m, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ major rotamer: 169.3, 167.1, 134.8, 128.7(2C), 127.6(2C), 126.7, 51.9, 42.6, 34.0, 31.8, 17.7, 11.4; minor rotamer: 167.3, 134.8, 128.6 (2C), 127.6 (2C), 51.8, 43.6, 37.3, 32.2, 17.3, 12.5; IR (film) 3039,

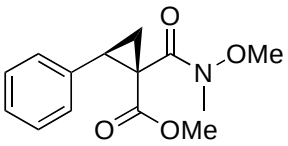
3008, 2946, 2884, 1715, 1638, 1511, 1434, 1334, 1135 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{15}H_{19}N_1O_3$ $[M+Na]^+$: 284.1257, found 284.1250.



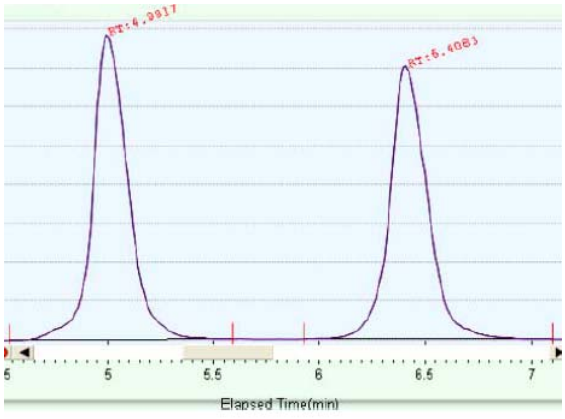

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.0947 | 10.6307 | 4.1 min |
| | 49.9053 | 10.5905 | 5.66 min |



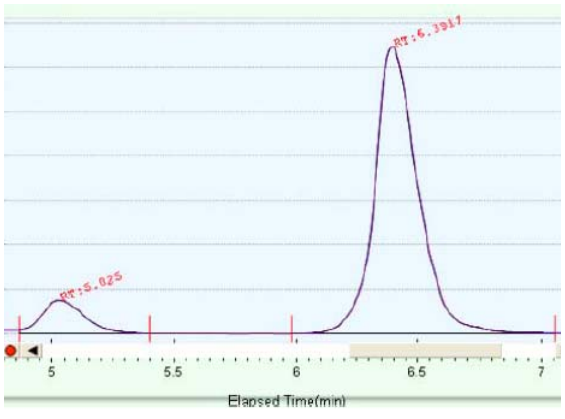

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 7.7685 | 2.7114 | 4.4 min |
| | 92.2315 | 32.1913 | 5.94 min |



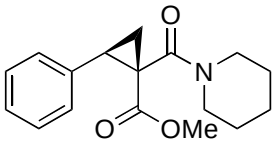

**Methyl 1-(methoxy(methyl)carbamoyl)-2-phenylcyclopropanecarboxylate (10d).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 24%, diastereomeric ratio (> 30:1) was determined by $^1$NMR analysis of the crude mixture, enantiomeric excess (80% ee) was determined by SFC analysis on chiral phase (Whlek-O 25 cm, 7% *i*PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 5.0 min, $t_r$ (major) 6.4 min); mp 89-91 °c; $R_f$ 0.53 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +150 (*c* 0.95, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.29-7.21 (m, 5H), 3.69 (s, 3H), 3.37 (s, 3H), 3.34 (app. t, *J* = 8.3 Hz, 1H), 3.29 (s, 3H), 2.22 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 1.50 (dd, *J* = 5.0 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 167.8, 167.7, 135.2, 139.2 (2C), 128.2 (2C), 127.2, 61.6, 52.2, 36.9, 33.4, 29.0, 17.5; IR (film) 3039, 2949, 1728, 1652, 1432, 1320, 1149 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{14}H_{17}N_1O_4$ $[M+H]^+$: 264.1230, found 264.1226.



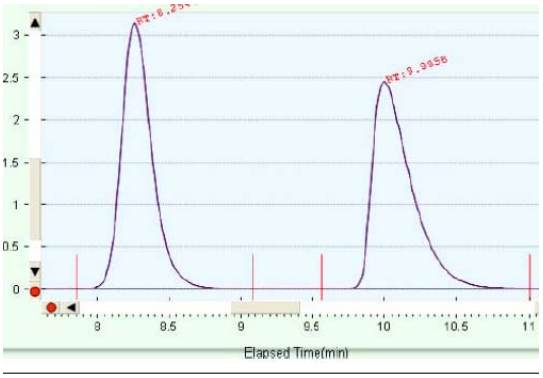

| Area % | Area | Retention Time |
|---|---|---|
| 51.1428 | 45.1822 | 4.9917 min |
| 48.8572 | 43.1629 | 6.4083 min |



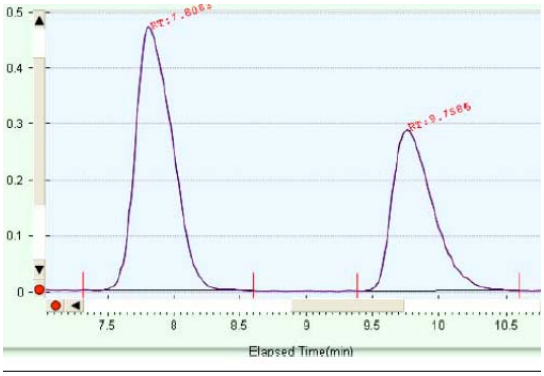

| Area % | Area | Retention Time |
|---|---|---|
| 10.1106 | 8.935 | 5.025 min |
| 89.8894 | 79.4376 | 6.3917 min |



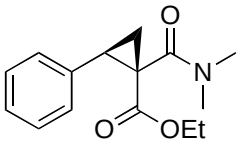

***cis*-Methyl 2-phenyl-1-(piperidine-1-carbonyl)cyclopropanecarboxylate (10e).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 29%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture, enantiomeric excess (19% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*PrOH, 3 mL/min, 30 °C, 150 psi, $t_r$ (minor) 4.6 min, $t_r$ (major) 5.7 min); $R_f$ 0.64 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +11 (*c* 1.58, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.26-7.18 (m, 5H), 3.58-3.40 (m, 4H), 3.39 (s, 3H), 3.18 (app. t, *J* = 8.4 Hz, 1H), 2.16 (dd, *J* = 5.0 Hz, *J* = 8.2 Hz, 1H), 1.63-1.52 (m, 7H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 168.8, 166.6, 135.3, 129.2 (2C), 128.1 (2C), 127.2, 52.3, 46.8, 43.6, 37.7, 32.1, 26.0, 25.5, 24.7, 18.0; IR (film) 3039, 3008, 2946, 2884, 1715, 1638, 1511, 1434, 1334, 1135 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{21}N_1O_3$ $[M+H]^+$: 288.1600, found 288.1605.



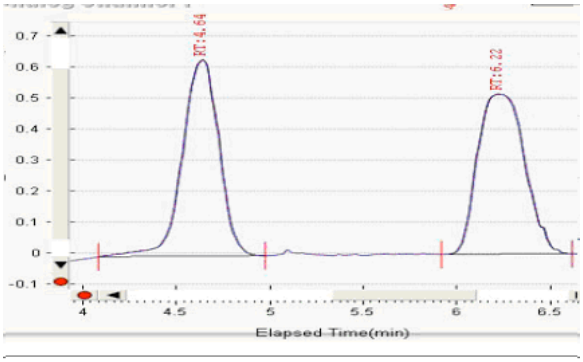

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.1483 | 46.0375 | 8.2544 min |
| | 49.8517 | 45.7653 | 9.9958 min |



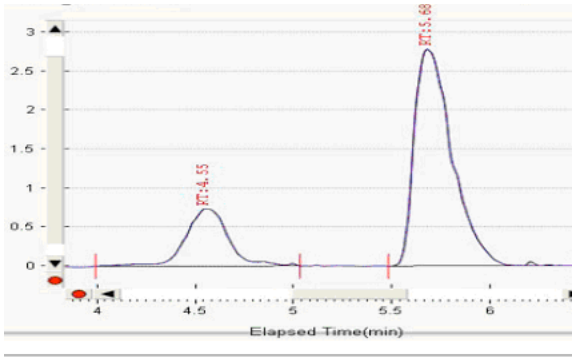

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| 1 | 59.6492 | 8.9885 | 7.8083 min |
| 2 | 40.3508 | 6.0804 | 9.7586 min |



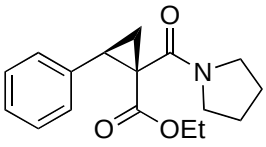

**Ethyl 1-(dimethylcarbamoyl)-2-phenylcyclopropanecarboxylate (10g).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 45%, diastereomeric ratio (50:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 28.2 min, $t_r$ (major) 28.5 min), enantiomeric excess (54% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*PrOH, 3 mL/min, 30 °C, 150 psi, $t_r$ (minor) 4.6 min, $t_r$ (major) 5.7 min); $R_f$ 0.53 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +15 (*c* 0.98, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 3.96-3.82 (m, 2H), 3.31 (app. t, *J* = 8.6 Hz, 1H), 3.09 (s, 3H), 3.04 (s, 3H), 2.24 (dd, *J* = 5.0 Hz, *J* = 8.1 Hz, 1H), 1.54 (dd, *J* = 5.0 Hz, *J* = 9.2 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 169.0, 168.9, 136.0, 130.0 (2C), 128.8 (2C), 127.8, 62.0, 38.4, 37.9, 36.7, 32.8, 18.6, 14.8; IR (film) 3039, 3008, 2946, 2884, 1715, 1638, 1511, 1434, 1334, 1135 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{15}H_{19}N_1O_3$ $[M+Na]^+$: 284.1257, found 284.1250.



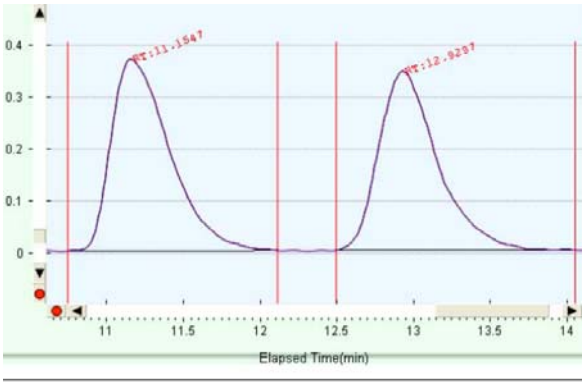

| k Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 48.9566 | 8.4428 | 4.64 min |
| | 51.0434 | 8.8027 | 6.22 min |



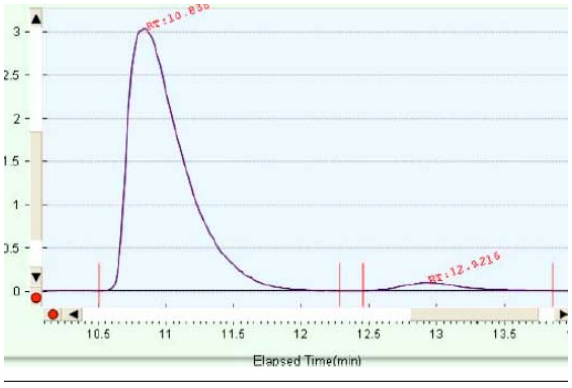

| c Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 22.9752 | 10.9919 | 4.55 min |
| | 77.0248 | 36.8507 | 5.68 min |



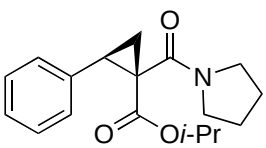
**Ethyl 2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10i).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 45%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture, enantiomeric excess (94% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*PrOH, 3 mL/min, 30 °C, 150 psi, $t_r$ (major) 10.8 min, $t_r$ (minor) 12.9 min); $R_f$ 0.39 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +100 (*c* 1.08, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.32-7.21 (m, 5H), 3.96-3.72 (m, 2H), 3.64-3.48 (m, 3H), 3.42-3.28 (m, 2H), 2.19 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 2.01-1.78 (m, 4H), 1.52 (dd, *J* = 4.9 Hz, *J* = 9.1 Hz, 1H), 0.89 (t, *J* = 7.5 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.3, 166.6, 135.5, 129.4 (2C), 128.1 (2C), 127.1, 61.3, 46.7, 46.6, 38.8, 31.4, 26.3, 24.4, 17.6, 14.1; IR (film) 2973, 2875, 1724, 1637, 1426, 1310, 1142 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{21}N_1O_3$ $[M+H]^+$: 288.1594, found 288.1603.




| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 51.4776 | 9.6513 | 11.1547 min |
| | 48.5224 | 9.0972 | 12.9297 min |

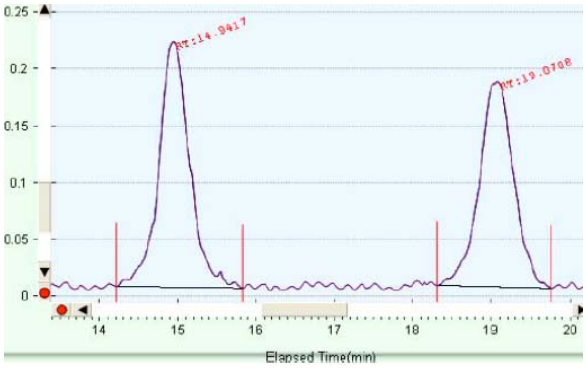



| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 97.0026 | 85.3714 | 10.838 min |
| | 2.9974 | 2.638 | 12.9216 min |

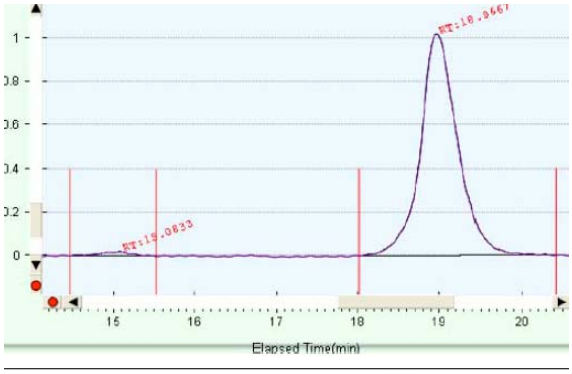


**Isopropyl 2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10j).** Prepared according to the general procedure. The product was isolated as a colorless oil.

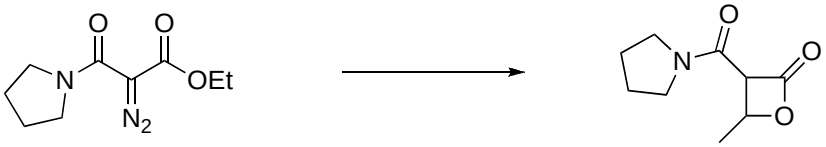
Yield: 19%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture, enantiomeric excess (97% ee) was determined by SFC analysis on chiral phase (Whelk-O 25 cm, 7% *i*PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 15.1 min, $t_r$ (major) 19.0 min); $R_f$ 0.42 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +123 (*c* 1.02, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H), 4.70 (sex, *J* = 6.3 Hz, 1H), 3.64-3.48 (m, 3H), 3.42-3.28 (m, 2H), 2.20 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 2.01-1.78 (m, 4H), 1.50 (dd, *J* = 4.9 Hz, *J* = 9.1 Hz, 1H), 0.92 (dd, *J* = 6.3 Hz, *J* = 7.6 Hz, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 167.8, 166.8, 135.6, 129.5 (2C), 128.1 (2C), 127.1, 68.8, 46.7, 46.5, 38.9, 31.2, 26.3, 24.4, 21.8, 21.4, 13.4; IR (film) 2976, 2875, 1708, 1642, 1427, 1308, 1105 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{23}N_1O_3$ $[M+H]^+$: 302.1751, found 302.1754.



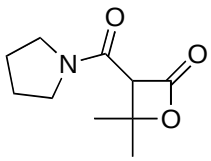

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 52.2475 | 5.9056 | 14.9417 min |
| | 47.7525 | 5.3975 | 19.0708 min |




| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 1.757 | 0.5766 | 15.0833 min |
| | 98.243 | 32.2406 | 18.9667 min |

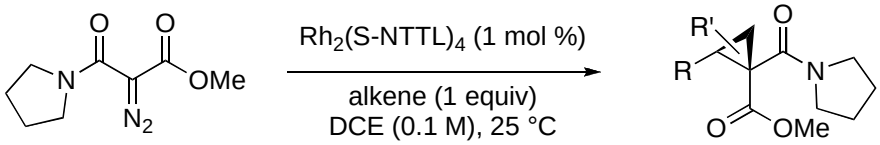



**4-Methyl-3-(pyrrolidine-1-carbonyl)oxetan-2-one (11b).** Prepared according to the general procedure without the use of styrene. The product was isolated as white solid. Yield: 44%, mp 38-40 °C; $R_f$ 0.13 (100%, $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ (Major) 4.35-4.29 (m, 1H), 4.20 (d, *J* = 7.8 Hz, 1H), 3.54-3.45 (m, 3H), 3.43-3.20 (m, 1H), 1.99-1.82 (m, 4H), 1.64 (d, *J* = 8.4 Hz, 3H), (Minor) 4.45-4.39 (m, 1H), 4.08 (d, *J* = 7.8 Hz, 1H), 3.54-3.45 (m, 3H), 3.43-3.20 (m, 1H), 1.99-1.82 (m, 4H), 1.44 (d, *J* = 8.4 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ (Major) 164.3, 162.2, 80.1, 63.4, 47.5, 46.4, 28.8, 25.3, 23.7, (Minor) 161.2, 160.3, 80.9, 64.0, 49.9, 45.2, 26.4, 22.3, 20.1; IR (film) 2944, 2880, 1718, 1635, 1510, 1435 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_9H_{13}N_1O_3$ $[M+H]^+$: 183.0895, found 183.0895.

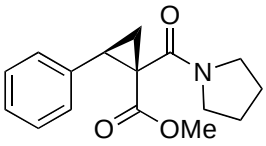



**4,4-Dimethyl-3-(pyrrolidine-1-carbonyl)oxetan-2-one (11c).** Prepared according to the general procedure without the use of styrene. The product was isolated as white solid. Yield: 75%, mp 45-47 °C; $R_f$ 0.11 (100%, $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 4.27 (s, 1H),

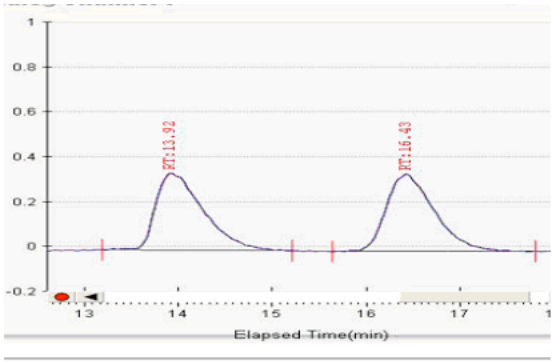
3.56-3.45 (m, 3H), 3.43-3.20 (m, 1H), 1.99-1.82 (m, 4H), 1.68 (s, 3H), 1.62 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 164.4, 162.2, 79.5, 63.4, 47.1, 46.2, 28.3, 26.3, 24.4, 22.9; IR (film) 2946, 2884, 1715, 1638, 1511, 1434, 1334, 1135 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{10}H_{15}N_1O_3$ [M+Na]$^+$: 220.0944, found 220.0934.



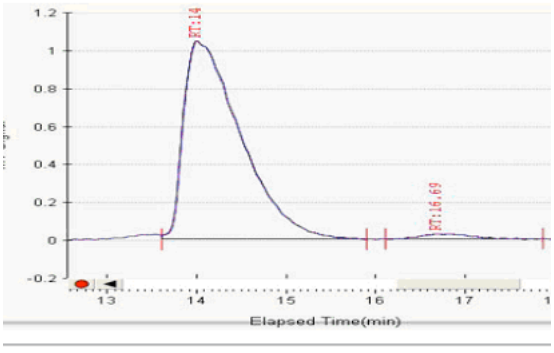

**General procedure of the optimized condition for the synthesis of enantioenriched cyclopropanes (Table 3).** A 10-mL microwave tube was charged with $Rh_2$(*S*-NTTL)$_4$ (2.9 mg, 0.002 mmol, 1 mol%) and a magnetic stir bar. The tube was sealed with a Teflon septum and purged with argon. DCE (1 mL) and the corresponding alkene (0.20 mmol, 1.00 equiv) were then added. The diazo compound (0.60 mmol, 3.00 equiv) dissolved in 1 mL of DCE was added to the reaction mixture over a period of 10 h using a syringe pump at 25 °C. Following complete addition, the resulting mixture was stirred for an additional 6 h at 25 °C. After complete consumption of the diazo reagent, the reaction mixture was put directly on a silica gel column and eluted with 100% hexane to 100% $Et_2O$. In cases where the rhodium dimer is complexed to the product, the green mixture was dissolved in DCM and poly(4-vinylpyridine) (≈ 20 mg) was added. The color of the mixture turned from green to red and the mixture was then filtered through Celite® to afford a rhodium-free product following concentration under reduced pressure.



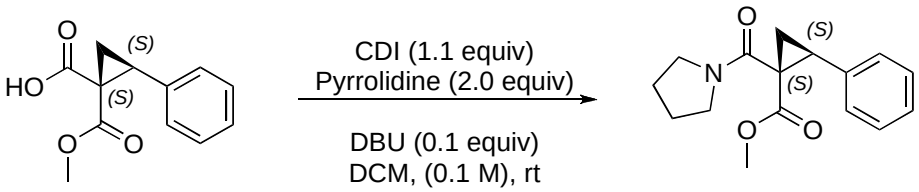

**(1*R*,2*R*)-Methyl 2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10h).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 79%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 32.3 min, $t_r$ (major) 33.3 min), enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 4% *i*PrOH, 5 mL/min, 30 °C, 200 psi, $t_r$ (major) 13.9 min, $t_r$ (minor) 16.8 min,); m.p. 73-75 °C; $R_f$ 0.35 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +113 (*c* 1.18, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.30-7.22 (m, 5H), 3.78-3.50 (m, 3H), 3.42 (s, 3H), 3.41-3.27 (m, 2H), 2.21 (dd, *J* = 4.7 Hz, *J* = 7.9 Hz, 1H), 2.01-1.87 (m, 4H), 1.53 (dd, *J* = 4.7 Hz, *J* = 9.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.5, 135.4, 129.2 (2C), 128.1 (2C), 127.2, 52.4, 46.6, 46.5, 38.8, 31.5, 26.2, 24.3, 17.8; IR (film) 3039, 3008, 2946, 2884, 1715, 1638, 1511, 1434, 1334, 1135 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{19}N_1O_3$ [M+H]$^+$: 274.1438, found 274.1437.




| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.6525 | 11.9117 | 13.92 min |
| | 50.3475 | 12.0784 | 16.43 min |




| k Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 98.0352 | 45.9839 | 14 min |
| | 1.9648 | 0.9216 | 16.69 min |




**13** 96% ee
$[\alpha]_D$ = -113 (*c* 1.2, PhH)
$[\alpha]_D$ = -146 (*c* 1.1, PhH)[1]

*ent*-**10h** 96% ee
$[\alpha]_D$ = -120 (*c* 0.7, $CHCl_3$)
$[\alpha]_D$ = +113 (*c* 1.2, $CHCl_3$, 96% ee)[2]

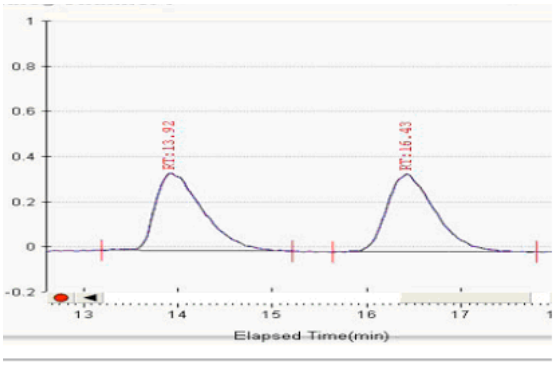
[1] Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.

[2] Sample made by direct cyclopropanation.

**(1*S*,2*S*)-Methyl 2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate.** Acid **13**[16] (100 mg, 0.45 mmol, 1.00 equiv) was added to a 25-mL oven dried round bottom flask. A stirring bar was added and the flask was purged with argon. CDI (89 mg, 0.55 mmol, 1.20 equiv) was added in one portion and the mixture was stirred for 1 h at 25 °C. DBU (10 µL, 0.05 mmol, 0.1 equiv) and pyrrolidine (75 µL, 0.90 mmol, 2.00 equiv) were added and the reaction was followed by TLC. After reaction completion, DCM (10 mL) was added, washed twice with 10% HCl, twice with 3N KOH, and once with brine. The organic phase was dried using $MgSO_4$, filtered over Celite®, and concentrated under reduced pressure. The $^1$H NMR spectrum was identical to that obtained formed from the asymmetric cyclopropanation. The $[\alpha]_D^{20}$ = -120° (*c* 0.70, $CHCl_3$) and the SFC spectra demonstrated that the cyclopropane formed using $Rh_2$(*S*-NTTL)$_4$ had the opposite absolute configuration.

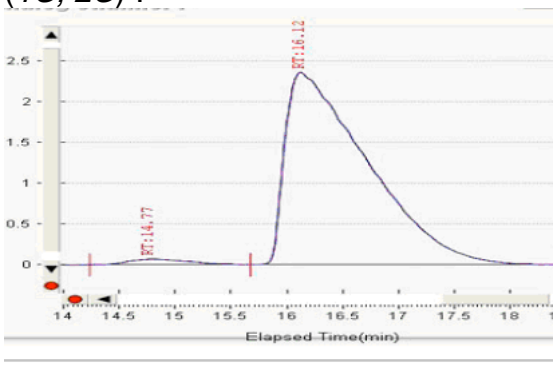
[16] Perreault, C.; Goudreau, S. R.; Zimmer, L. E.; Charette, A. B. *Org. Lett.* **2008**, *10*, 689.

Rac :



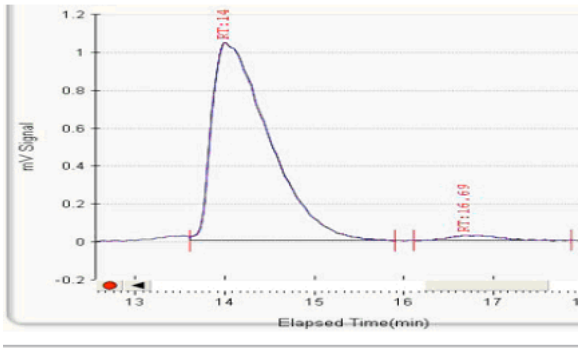

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.6525 | 11.9117 | 13.92 min |
| | 50.3475 | 12.0784 | 16.43 min |

(*1S, 2S*) :

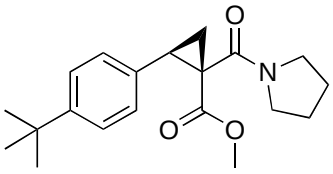



| : Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.1733 | 2.6764 | 14.77 min |
| | 97.8267 | 120.472 | 16.12 min |

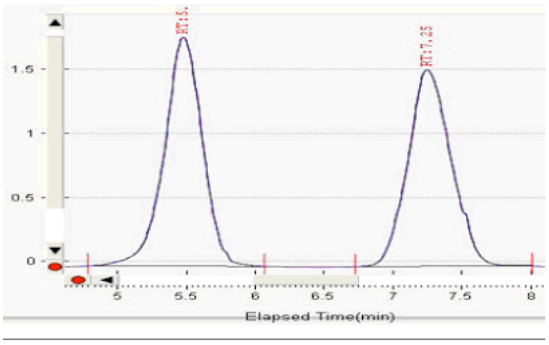
Synthetic



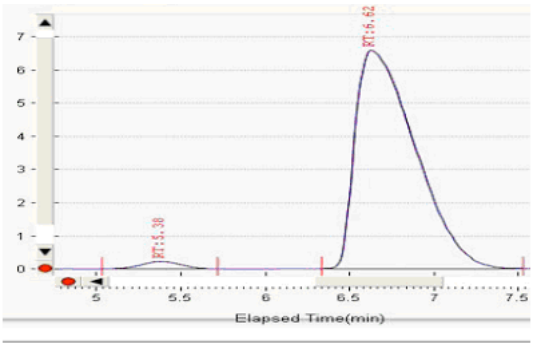

| Peak Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 98.0352 | 45.9839 | 14 min |
| | 1.9648 | 0.9216 | 16.69 min |



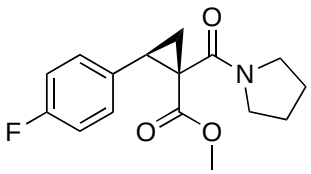
**Methyl 2-(4-*tert*-butylphenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10k).** Prepared according to the general procedure. The product was isolated as a white solide. Yield: 89%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 37.3 min, $t_r$ (major) 38.7 min), enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 200 psi, $t_r$ (minor) 5.4 min, $t_r$ (major) 6.6 min); m.p. 78-80 °C; $R_f$ 0.36 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +124 (*c* 0.35, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 6.4 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 3.71-3.54 (m, 3H), 3.42 (s, 3H), 3.38-3.28 (m, 2H), 2.19 (dd, *J* = 4.9 Hz, *J* = 8.1 Hz, 1H), 2.01-1.85 (m, 4H), 1.54 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1H), 1.31 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.6, 150.0, 132.3, 128.9 (2C), 125.0 (2C), 52.3, 46.7, 46.6, 38.8, 34.6, 31.5 (3C), 31.3, 26.3, 24.4, 17.9; IR (film) 3038, 3009, 2956, 2879, 1729, 1644, 1432, 1319, 1139 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{20}H_{27}N_1O_3$ $[M+H]^+$: 330.2064, found 330.2062.



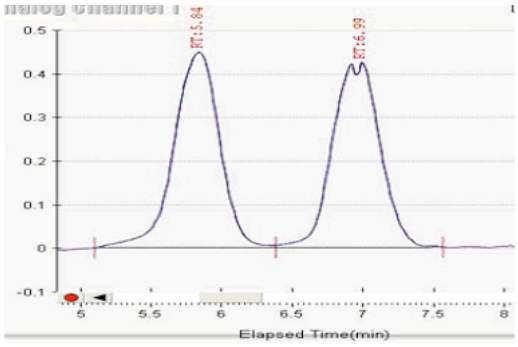

| k Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.7428 | 34.0487 | 5.48 min |
| | 49.2572 | 33.0518 | 7.25 min |



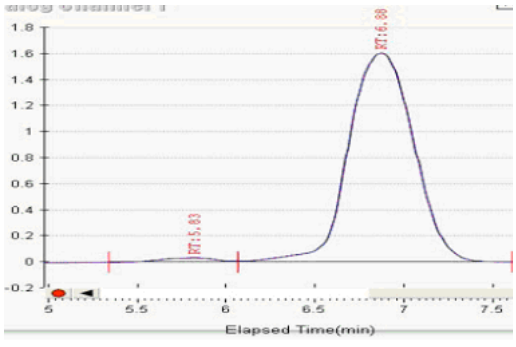

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.2031 | 3.5972 | 5.38 min |
| | 97.7969 | 159.6822 | 6.62 min |



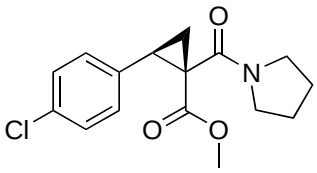

**Methyl 2-(4-fluorophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10l).** Prepared according to the general procedure. The product was isolated as white solid. Yield: 77%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 34.4 min, $t_r$ (major) 35.5 min), enantiomeric excess (97% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 4% MeOH, 3 mL/min, 40 °C, 210 psi, $t_r$ (minor) 5.8 min, $t_r$ (major) 6.9 min); m.p. 68-72 °C; $R_f$ 0.36 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +79 (*c* 1.12, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 6.98 (t, *J* = 8.7 Hz, 2H), 3.53-3.49 (m, 3H), 3.45 (s, 3H), 3.37-3.28 (m, 2H), 2.17 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 2.03-1.87 (m, 4H), 1.54 (dd, *J* = 4.9 Hz, *J* = 9.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 169.3, 166.9, 162.7 (d, *J* = 243.9 Hz, 1C), 131.8 (d, *J* = 3.2 Hz, 1C), 131.5 (d, *J* = 8.1 Hz, 2C), 115.7 (d, *J* = 21.3 Hz, 2C), 53.1, 47.3, 47.2, 39.5, 31.4, 26.9, 25.0, 18.6; $^{19}$F NMR (282 MHz, $CDCl_3$) δ -116.95; IR (film) 3050, 3012, 2953, 2878, 1728, 1632, 1513, 1434, 1316, 1145 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}N_1O_3F_1$ [M+Na]$^+$: 314.1163, found 314.1162.



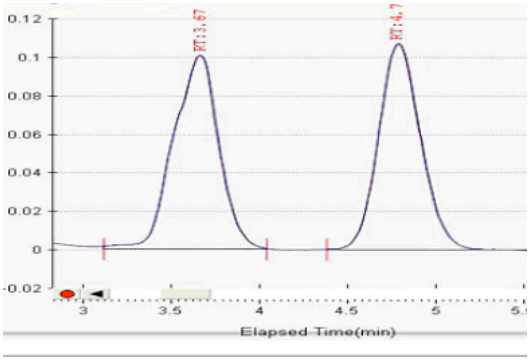

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.4054 | 9.932 | 5.84 min |
| | 49.5946 | 9.7723 | 6.99 min |



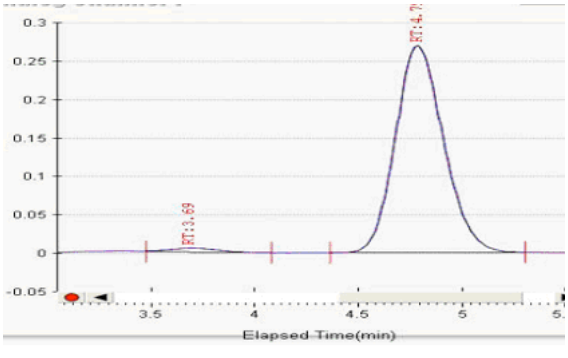

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 1.5928 | 0.6504 | 5.83 min |
| | 98.4072 | 40.1865 | 6.88 min |



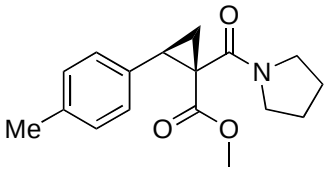

**Methyl 2-(4-chlorophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10m).** Prepared according to the general procedure. The product was isolated as white solid. Yield: 81%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 36.0 min, $t_r$ (major) 36.6 min), enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralcel OD-H 25 cm, 10% MeOH, 2 mL/min, 30 °C, 150 psi, $t_r$ (minor) 3.7 min, $t_r$ (major) 4.8 min); m.p. 72-75 °C; $R_f$ 0.36 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +88 (*c* 1.08, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.27-7.19 (m, 4H), 3.62-3.49 (m, 3H), 3.45 (s, 3H), 3.33-3.24 (m, 2H), 2.16 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 2.00-1.86 (m, 4H), 1.54 (dd, *J* = 5.0 Hz, *J* = 9.0 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 168.6, 166.2, 134.0, 133.1, 130.6 (2C), 128.4 (2C), 52.6, 46.7, 46.6, 39.0, 30.9, 26.3, 24.3, 17.9; IR (film) 3050, 3010, 2951, 2876, 1727, 1635, 1427, 1314, 1143 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}N_1O_3Cl_1$ $[M+H]^+$: 308.1048, found 308.1048.




| Name | Peak Number | Area % | Area | Retention |
|---|---|---|---|---|
| | 1 | 50.3148 | 1.7816 | 3.67 min |
| | 2 | 49.6852 | 1.7593 | 4.79 min |

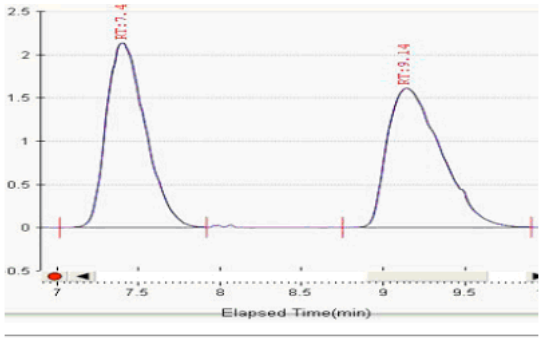



| Name | Peak Number | Area % | Area | Retention Tim |
|---|---|---|---|---|
| | 1 | 1.8572 | 0.0808 | 3.69 min |
| | 2 | 98.1428 | 4.2714 | 4.79 min |

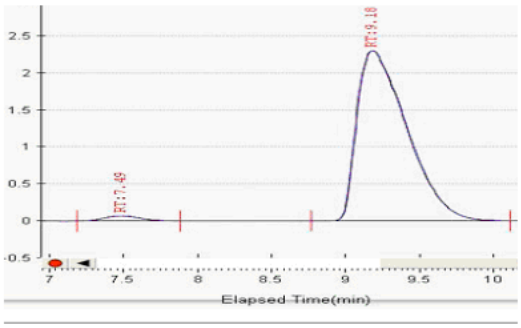



**Methyl 1-(pyrrolidine-1-carbonyl)-2-p-tolylcyclopropanecarboxylate (10n).** Prepared according to the general procedure. The product was isolated as white solid. Yield: 82%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 33.8 min, $t_r$ (major) 35.2 min), enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 200 psi, $t_r$ (minor) 7.5 min, $t_r$ (major) 9.2 min); m.p. 72-74 °C; $R_f$ 0.35 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +85 (*c* 0.83, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 3.68-3.49 (m, 3H), 3.45 (s, 3H), 3.38-3.28 (m, 2H), 2.33 (s, 3H), 2.18 (dd, *J* = 4.9 Hz, *J* = 8.1 Hz, 1H), 2.03-1.87 (m, 4H), 1.54 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 168.8, 166.6, 136.7, 132.3, 129.1 (2C), 128.9 (2C), 52.4, 46.7, 46.6, 38.8, 31.3, 26.3, 24.3, 21.3, 17.8; IR

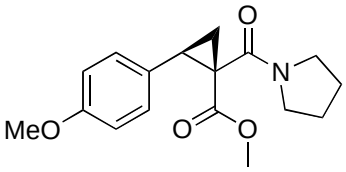
(film) 3050, 3010, 2951, 2876, 1731, 1641, 1429, 1317, 1144 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{21}N_1O_3$ $[M+H]^+$: 288.1594, found 288.1593.



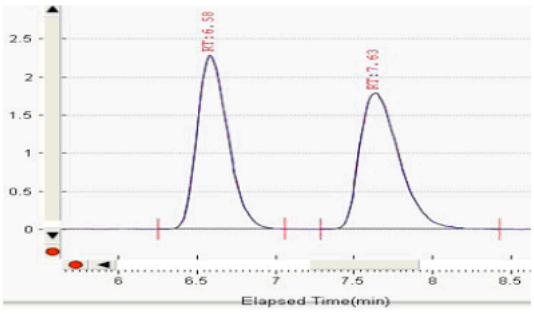

| ame | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.0125 | 34.93 | 7.4 min |
| | 50.9875 | 36.3376 | 9.14 min |



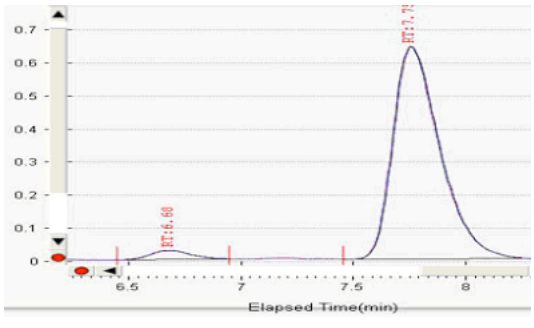

| lame | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.0279 | 1.0982 | 7.49 min |
| | 97.9721 | 53.0579 | 9.18 min |



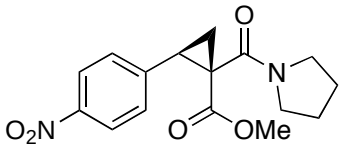

**Methyl 2-(4-methoxyphenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10o).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 92%, diastereomeric ratio (50:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 36.5 min, $t_r$ (major) 37.9 min), enantiomeric excess (93% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 10% *i*PrOH, 3 mL/min, 25 °C, 200 psi, $t_r$ (minor) 6.7 min, $t_r$ (major) 7.8 min); m.p. 78-81 °C; $R_f$ 0.28 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +70 (*c* 0.98, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 3H), 3.76-3.48 (m, 3H), 3.43 (s, 3H), 3.32-3.25 (m, 2H), 2.14 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 2.03-1.82 (m, 4H), 1.51 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 168.8, 166.6, 158.7, 130.3 (2C), 127.4, 113.6 (2C), 55.3, 52.4, 46.6, 46.5, 38.8, 31.0, 26.3, 24.3, 18.0 ; IR (film) 3050, 3010, 2952, 2877, 1729, 1638, 1516, 1429, 1316, 1248, 1143 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{21}N_1O_4$ $[M+Na]^+$: 326.1363, found 326.1359.



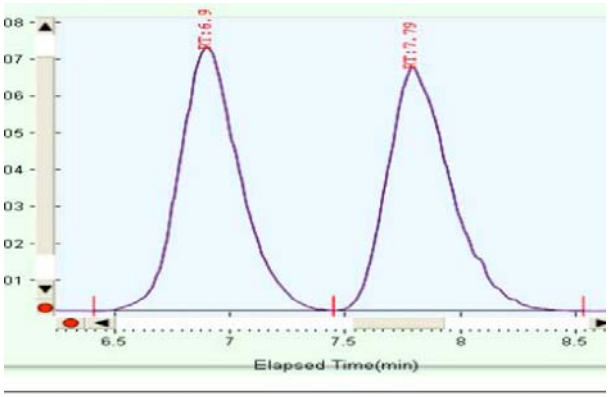

| k Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.7173 | 30.3839 | 6.58 min |
| | 50.2827 | 30.7295 | 7.63 min |



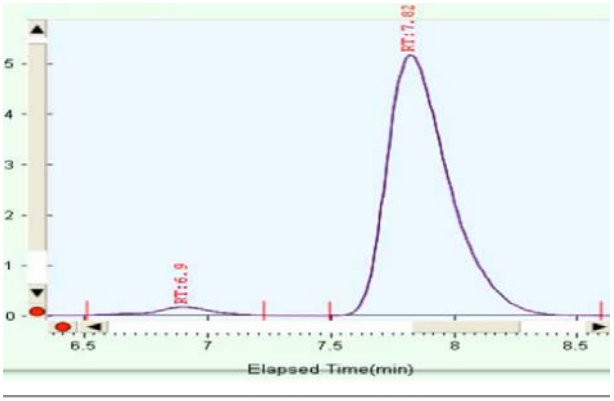

| k Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 3.4287 | 0.3258 | 6.68 min |
| | 96.5713 | 9.1772 | 7.75 min |



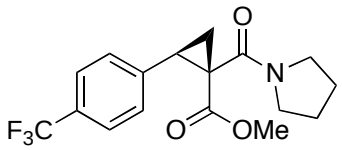
**Methyl 2-(4-nitrophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10p).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 31%, diastereomeric ratio (> 30:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (95% ee) was determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 210 psi, $t_r$ (minor) 6.9 min, $t_r$ (major) 7.8 min); $R_f$ 0.25 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +99 (*c* 1.22, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 3.63-3.49 (m, 3H), 3.47-3.38 (m, 4H), 3.31-3.20 (m, 1H), 2.26 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 1H), 2.07-1.84 (m, 4H), 1.64 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.3, 147.8, 144.0, 130.8 (2C), 124.0 (2C), 53.4, 47.4, 47.2, 40.2, 31.7, 26.9, 25.0, 18.8; IR (film) 3050, 3010, 2951, 2876, 1731, 1641, 1521, 1429, 1317, 1144, 870 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}N_2O_5$ $[M+H]^+$: 319.1289, found 319.1289.




| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 50.6054 | 1.2955 | 6.9 min |
| | 2 | 49.3946 | 1.2645 | 7.79 min |

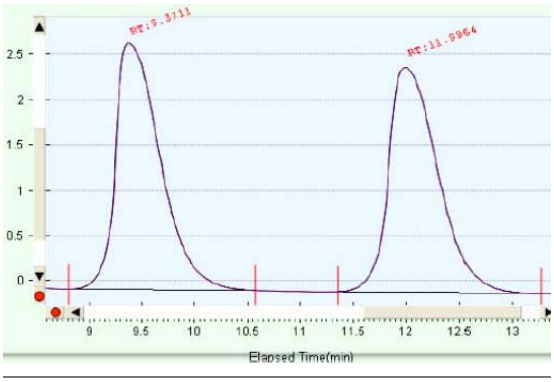



| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 2.756 | 0.2548 | 6.9 min |
| | 2 | 97.244 | 8.9895 | 7.82 min |

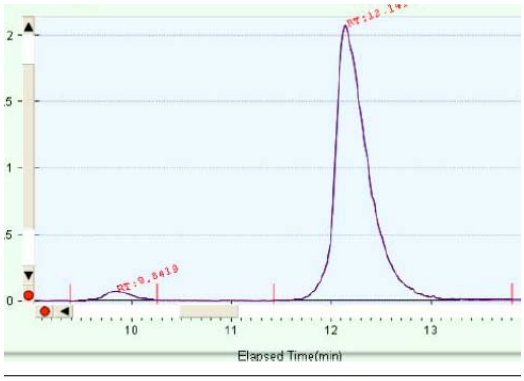


**Methyl 1-(pyrrolidine-1-carbonyl)-2-(4-(trifluoromethyl)phenyl)cyclopropanecarboxylate (10q).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 55%, diastereomeric ratio (> 30:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (95% ee) was determined by SFC analysis on chiral phase (Whelk-O 25 cm, 7% *i*-PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 9.8 min, $t_r$ (major) 12.1 min); $R_f$ 0.42 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +79 (*c* 1.91, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.51-7.47 (m, 2H), 7.38-7.34 (m, 2H), 3.54-3.49 (m, 3H), 3.47-3.38 (m, 4H), 3.31-3.20 (m, 1H), 2.19 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 1.93-1.84 (m, 4H), 1.54 (dd, *J* = 5.0 Hz, *J* = 9.1 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.4, 166.0, 139.7, 129.6 (2C), 126.3 (q, *J* = , 1C), 125.0 (m, 1C), 122.6 (2C), 52.6, 46.7, 46.5, 39.2, 31.1, 26.3, 24.3, 17.9; IR (film)

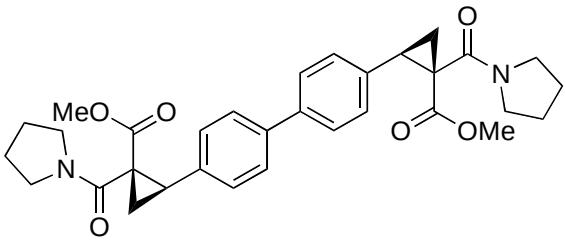
2954, 2878, 1730, 1640, 1433, 1324, 1116, 1068 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{18}N_1O_3F_3$ $[M+H]^+$: 342.1312, found 342.1319.



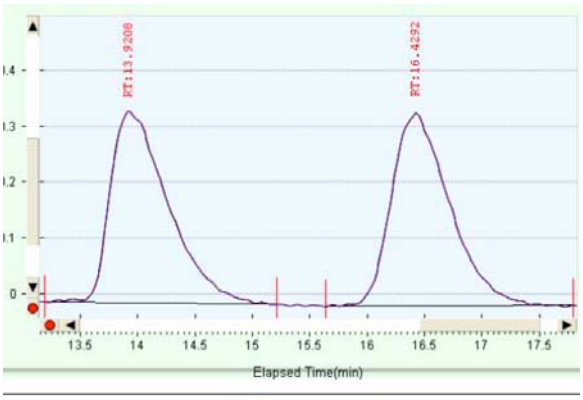

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| 1 | 50.07 | 80.1845 | 9.3711 min |
| 2 | 49.93 | 79.9602 | 11.9964 min |



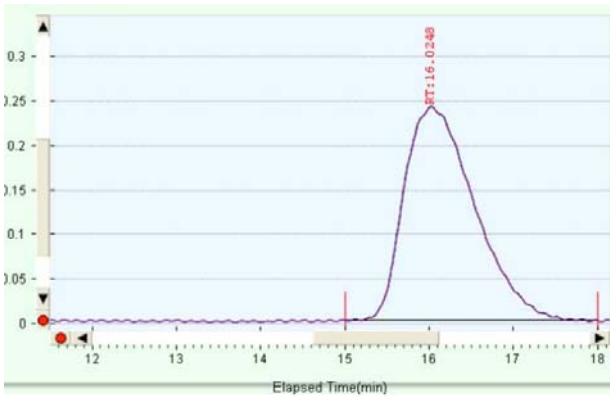

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.6258 | 1.2544 | 9.8419 min |
| | 97.3742 | 46.5186 | 12.1419 min |



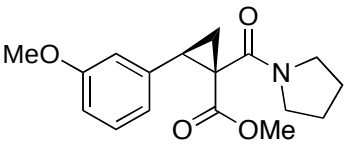

**Dimethyl 2,2'-(biphenyl-4,4'-diyl)bis((pyrrolidine-1-carbonyl)cyclopropanecarboxylate) (10r).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 62%, diastereomeric ratio (25:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (>99% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 20% MeOH, 3 mL/min, 30 °C, 210 psi, $t_r$ (minor) 13.9 min, $t_r$ (major) 16.4 min); mp 194-197 °C; $R_f$ 0.35 (100%, EtOAc); $[\alpha]_D^{20}$ = +209 (*c* 1.03, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.2 Hz, 4H), 3.54-3.49 (m, 6H), 3.47-3.34 (m, 8H), 3.31-3.19 (m, 2H), 2.23 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 2H), 2.06-1.87 (m, 8H), 1.54 (dd, *J* = 5.0 Hz, *J* = 9.1 Hz, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.7 (2C), 166.5 (2C), 139.5 (2C), 134.5 (2C), 129.7 (4C), 126.7 (4C), 52.5 (2C), 46.7 (2C), 46.6 (2C), 39.1 (2C), 31.4 (2C), 26.3 (2C), 24.4 (2C), 18.0 (2C); IR (film) 3044, 2952, 2877, 1727, 1629, 1433, 1312, 1144, 908 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{32}H_{36}N_2O_6$ $[M+H]^+$: 545.2646, found 545.2642.



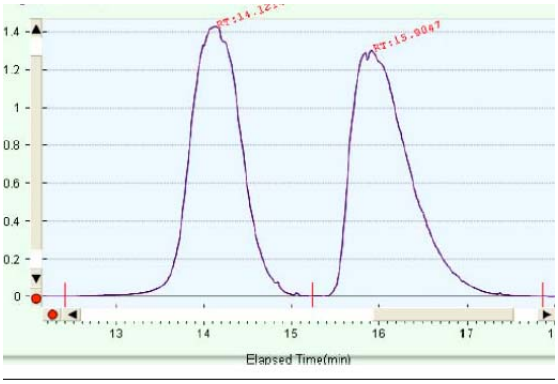

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.6589 | 11.9609 | 13.9208 min |
| | 50.3411 | 12.1252 | 16.4292 min |



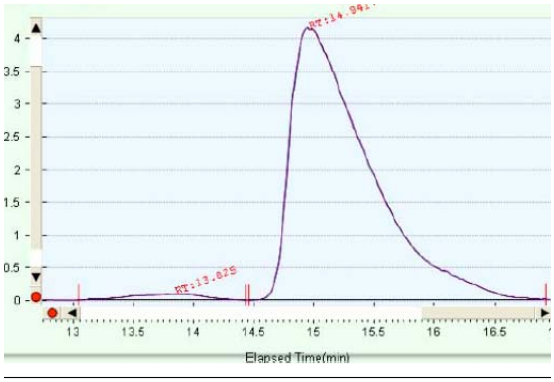

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 100 | 13.9298 | 16.0248 min |



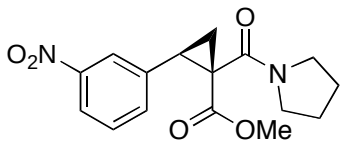

**Methyl 2-(3-methoxyphenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10s).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 78%, diastereomeric ratio (> 30:1) was determined by $^{1}$H NMR of the crude mixture, enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 13.8 min, $t_r$ (major) 14.9 min); $R_f$ 0.34 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +73 (*c* 1.54, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.18-7.13 (m, 1H), 6,85-6.80 (m, 2H), 6.76-6.72 (m, 1H), 3.75 (s, 3H), 3.54-3.49 (m, 3H), 3.41 (s, 3H), 3.31-3.218 (m, 2H), 2.13 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 1H), 1.94-1.84 (m, 4H), 1.44 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.5, 159.5, 137.2, 129.2, 121.6, 114.8, 113.1, 55.4, 52.5, 46.7, 46.6, 38.9, 31.6, 26.3, 24.4, 18.0; IR (film) 2951, 2876, 1730, 1638, 1429, 1315, 1143, 1046 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{21}N_1O_4$ $[M+H]^+$: 304.1543, found 304.1551.



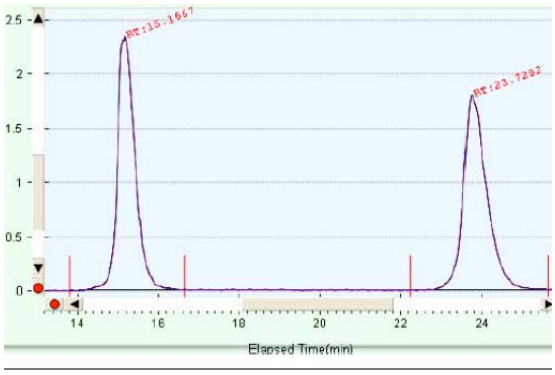

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.2747 | 58.0176 | 14.1214 min |
| | 50.7253 | 59.7257 | 15.9047 min |



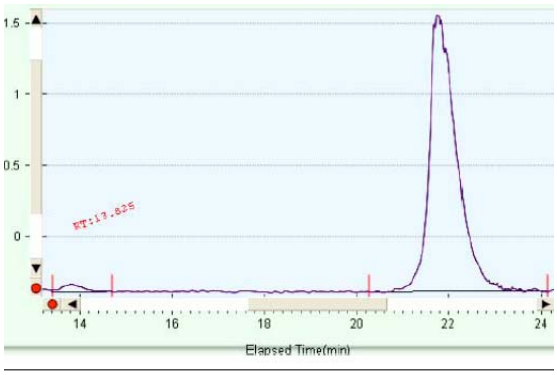

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.0616 | 3.9367 | 13.825 min |
| | 97.9384 | 187.0116 | 14.9417 min |



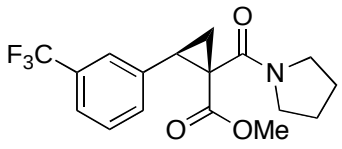
**Methyl 2-(3-nitrophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10t).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 51%, diastereomeric ratio (> 30:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Whelk-O 25 cm, 5% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 13.8 min, $t_r$ (major) 21.8 min); $R_f$ 0.21 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +42 (*c* 2.38, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.13 (s, 1H), 8.10 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 8.8 Hz, 1H), 3.57-3.43 (m, 3H), 3.42 (s, 3H), 3.38 (t app, *J* = 8.0 Hz, 1H), 3.31-3.20 (m, 1H), 2.21 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 1.97-1.84 (m, 4H), 1.61 (dd, *J* = 5.0 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.4, 165.7, 148.2, 137.9, 135.7, 129.1, 124.2, 122.4, 52.8, 46.8, 46.5, 39.1, 30.8, 26.3, 24.3, 18.1; IR (film) 2953, 2877, 1728, 1640, 1529, 1432, 1349, 1147 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}N_2O_5$ [M+H]$^+$: 319.1289, found 319.1297.



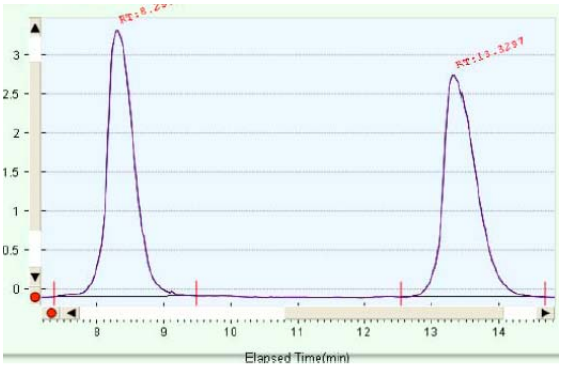

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.2544 | 70.9477 | 15.1667 min |
| | 49.7456 | 70.2295 | 23.7292 min |



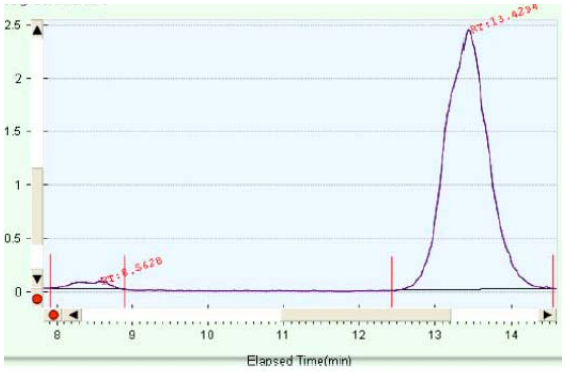

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 1.8425 | 1.4981 | 13.825 min |
| | 98.1575 | 79.8065 | 21.75 min |



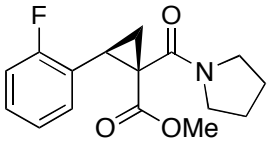

**Methyl 1-(pyrrolidine-1-carbonyl)-2-(3-(trifluoromethyl)phenyl)cyclopropanecarboxlate (10u).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 49%, diastereomeric ratio (> 30:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (95% ee) was determined by SFC analysis on chiral phase (Whelk-O 25 cm, 7% *i*-PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 8.6 min, $t_r$ (major) 13.4 min); $R_f$ 0.25 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +70 (*c* 0.83, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46-7.43 (m, 2H), 7.38-7.34 (m, 1H), 3.57-3.46 (m, 3H), 3.42-3.36 (m, 4H), 3.31-3.24 (m, 1H), 2.17 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 1H), 1.97-1.86 (m, 4H), 1.52 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.4, 166.0, 136.7, 132.7, 130.7 (q, *J* = Hz, 1C), 128.6, 126.1, 124.0, 122.4, 52.5, 46.7, 46.5, 39.0, 30.9, 26.2, 24.3, 17.8; $^{19}$F NMR (182 MHz, $CDCl_3$) δ -117.0. IR (film) 2953, 2878, 1730, 1640, 1429, 1326, 1122 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{18}N_1O_3F_3$ [M+H]$^+$: 342.1312, found 342.1319.



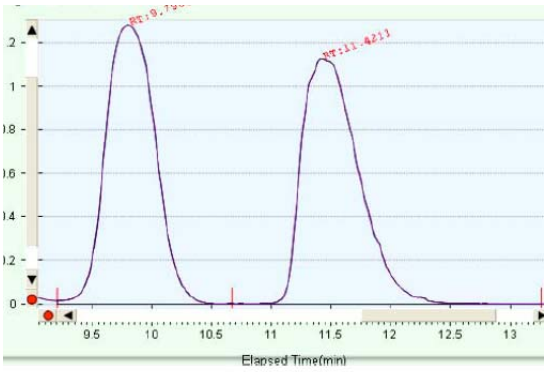

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.5212 | 95.9456 | 8.2961 min |
| | 49.4788 | 93.9658 | 13.3297 min |



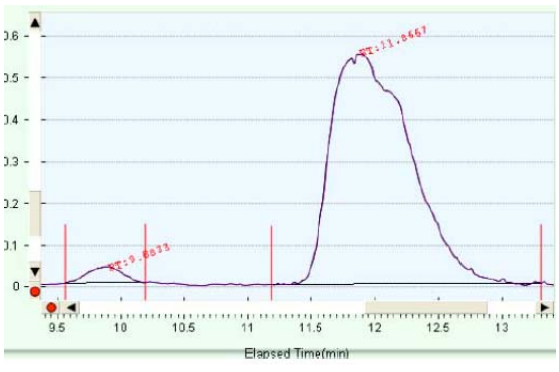

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.4144 | 2.3108 | 8.5628 min |
| | 97.5856 | 93.4002 | 13.4294 min |



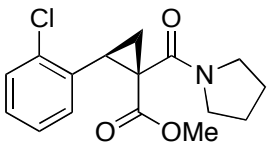

**Methyl 2-(2-fluorophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10v).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a white solid. Yield: 43%, diastereomeric ratio (> 30:1) was determined by $^{1}$H NMR of the crude mixture, enantiomeric excess (94% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 9.8 min, $t_r$ (major) 11.4 min); $R_f$ 0.35 (100%, $Et_2O$); mp 88-91 °C; $[\alpha]_D^{20}$ = +121 (*c* 0.74, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.24-7.16 (m, 2H), 7.06-6.95 (m, 2H), 3.60-3.45 (m, 3H), 3.44 (s, 3H), 3.43-3.38 (m, 1H), 3.22 (t app, *J* = 8.8 Hz, 1H), 2.13 (dd, *J* = 5.0 Hz, *J* = 8.1 Hz, 1H), 1.97-1.87 (m, 4H), 1.63 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 169.0, 166.2, 162.0 (d, *J* = 1C), 130.8 (d, *J* = 1C), 129.0 (d, *J* = 1C), 123.6 (d, *J* = 1C), 122.8 (d, *J* = 1C), 115.2 (d, *J* = 1C), 52.5, 46.7, 46.4, 37.9, 26.3, 26.2, 24.3, 18.3; IR (film) 2952, 2876, 1727, 1637, 1428, 1319, 1145 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}N_1O_3F_1$ $[M+H]^+$: 292.1344, found 292.1349.



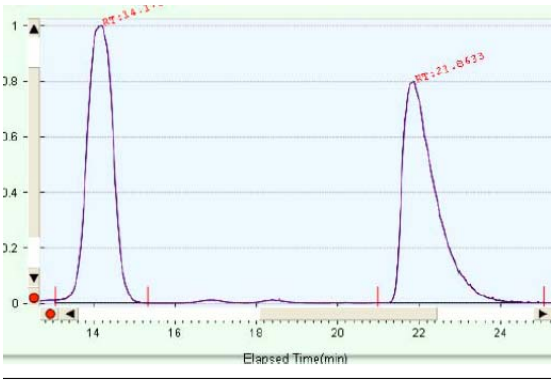

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.7962 | 37.0409 | 9.7964 min |
| | 50.2038 | 37.3441 | 11.4211 min |



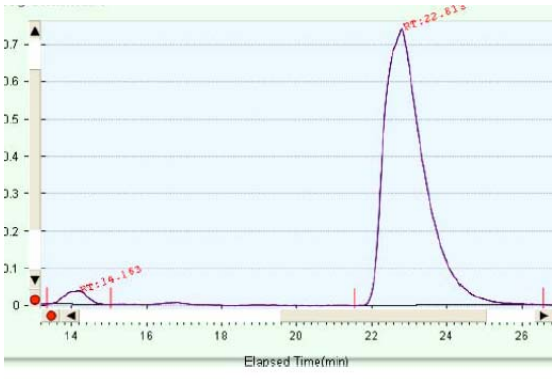

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.9677 | 0.7314 | 9.8833 min |
| | 97.0323 | 23.9134 | 11.8667 min |



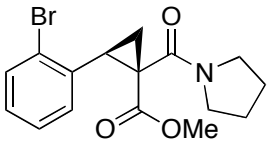
**Methyl 2-(2-chlorophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10w).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a white solid. Yield: 35%, diastereomeric ratio (> 30:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (94% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% *i*-PrOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 14.1 min, $t_r$ (major) 22.8 min); $R_f$ 0.35 (100%, $Et_2O$); mp 96-98 °C; $[\alpha]_D^{20}$ = +49 (*c* 1.00, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.37-7.33 (m, 1H), 7.23-7.19 (m, 3H), 3.88-3.54 (m, 3H), 3.52-3.45 (m, 4H), 3.32-3.28 (m, 1H), 2.21 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 1H), 2.01-1.85 (m, 4H), 1.60 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.1, 136.2, 133.8, 130.6, 129.4, 128.6, 126.3, 52.5, 46.7, 46.4, 38.1, 30.4, 26.3, 24.3, 18.5; IR (film) 2951, 2877, 1728, 1642, 1432, 1317, 1148 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}N_1O_3Cl_1$ $[M+H]^+$: 308.1048, found 308.1054.



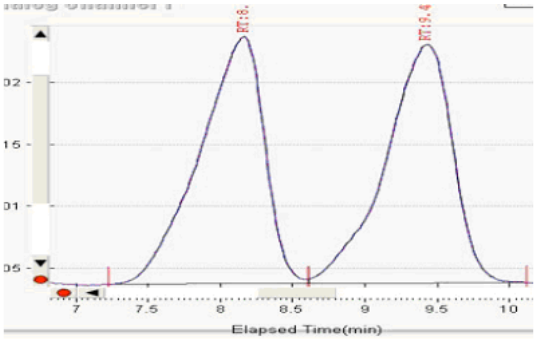

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.819 | 44.0666 | 14.1714 min |
| | 50.181 | 44.3868 | 21.8633 min |



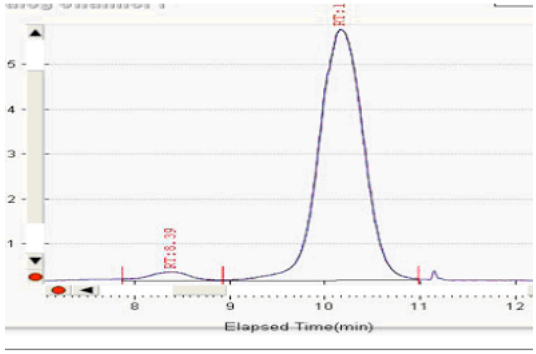

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.6119 | 1.4525 | 14.163 min |
| | 97.3881 | 54.1582 | 22.813 min |



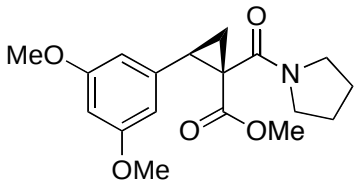

**Methyl 2-(2-bromophenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10x).** Prepared according to the general procedure at 50 °C instead of 25 °C. The product was isolated as a colorless oil. Yield: 24% (85% brsm), diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 36.2 min, $t_r$ (major) 37.3 min), enantiomeric excess (94% ee) was determined by SFC analysis on chiral phase (Chiralpak AS-H 25 cm, 10% *i*PrOH, 2 mL/min, 25 °C, 150 psi, $t_r$ (minor) 8.4 min, $t_r$ (major) 10.2 min); $R_f$ 0.32 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +73 (*c* 0.35, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 1.1 Hz, *J* = 7.9 Hz, 1H), 7.29-7.20 (m, 2H), 7.15-7.09 (m, 1H), 3.66-3.52 (m, 3H), 3.50-3.43 (m, 4H), 3.33-3.24 (m, 1H), 2.20 (dd, *J* = 4.8 Hz, *J* = 8.1 Hz, 1H), 2.04-1.82 (m, 4H), 1.59 (dd, *J* = 4.8 Hz, *J* = 8.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.0, 135.5, 132.5, 130.8, 128.9, 126.9, 126.4, 52.5, 46.7, 46.4, 38.3, 32.7, 26.3, 24.3, 18.9; IR (film) 3050, 3010, 2950, 2877, 1731, 1639, 1413, 1297, 1148 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{18}Br_1N_1O_3$ $[M+H]^+$: 351.0470, found 351.0475.



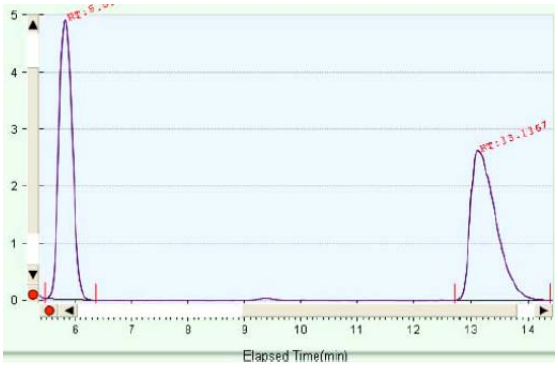

| Name | Peak Number | Area % | Area | Retention Ti |
|---|---|---|---|---|
| | 1 | 49.8707 | 0.6137 | 8.17 min |
| | 2 | 50.1293 | 0.6169 | 9.43 min |



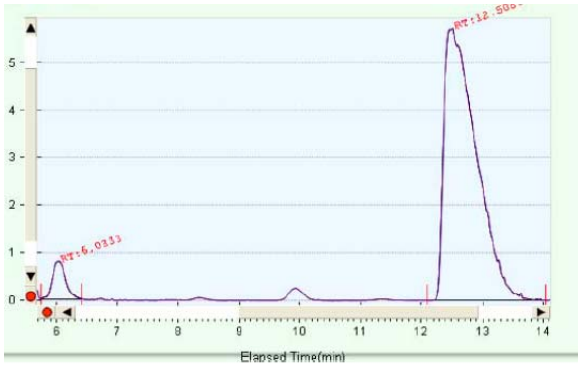

| Name | Peak Number | Area % | Area | Retention Tim |
|---|---|---|---|---|
| | 1 | 3.1704 | 0.0593 | 8.39 min |
| | 2 | 96.8296 | 1.81 | 10.17 min |



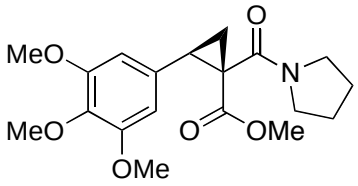

**Methyl 2-(3,5-dimethoxyphenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10y).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 54%, diastereomeric ratio (22:1) was determined by $^{1}$H NMR of the crude mixture, enantiomeric excess (90% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 7% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 6.0 min, $t_r$ (major) 12.5 min); $R_f$ 0.22 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +89 (*c* 1.11, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) δ 6.41 (dd, *J* = 8.8 Hz, *J* = 1.1 Hz, 2H), 6.29 (t, *J* = 8.8 Hz, 1H), 3.72 (s, 6H), 3.60-3.44 (m, 3H), 3.44 (s, 3H), 3.33-3.19 (m, 2H), 2.10 (dd, *J* = 5.0 Hz, *J* = 8.0 Hz, 1H), 2.07-1.84 (m, 4H), 1.44 (dd, *J* = 5.0 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.4, 160.5 (2C), 138.0, 107.2 (2C), 99.6, 55.5 (2C), 52.5, 46.7, 46.5, 38.8, 31.6, 26.2, 24.3, 18.0; IR (film) 2951, 2877, 2840, 1729, 1636, 1594, 1425, 1425, 1310, 1203, 1151 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{23}N_1O_5$ $[M+H]^+$: 334.1649, found 334.1660.



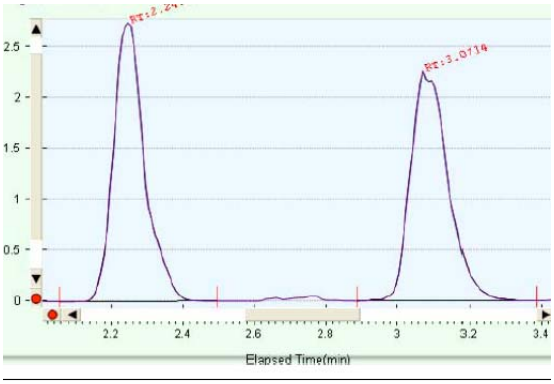

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.3768 | 79.4908 | 5.8333 min |
| | 50.6232 | 81.4974 | 13.1167 min |



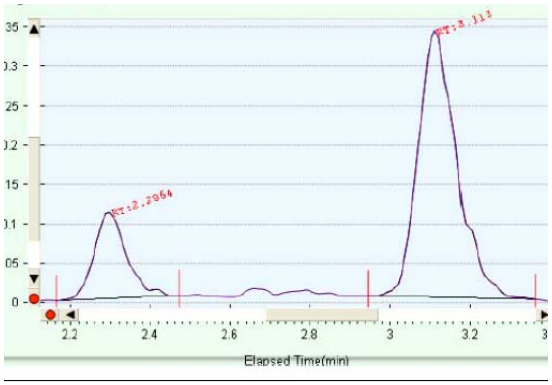

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 5.3419 | 11.5576 | 6.0333 min |
| | 94.6581 | 204.801 | 12.5083 min |



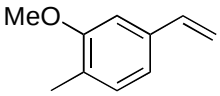

**Methyl 1-(pyrrolidine-1-carbonyl)-2-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (10z).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a colorless oil. Yield: 29%, diastereomeric ratio (24:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (59% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 15% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 2.3 min, $t_r$ (major) 3.1 min); $R_f$ 0.21 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +47 (*c* 1.12, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 6.45 (s, 2H), 3.78 (s, 6H), 3.75 (s, 3H), 3.60-3.43 (m, 3H), 3.42 (s, 3H), 3.42 (t app, *J* = 8.8 Hz, 1H), 3.38-3.24 (m, 1H), 2.10 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 1H), 1.92-1.84 (m, 4H), 1.42 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.6, 166.4, 153.1 (2C), 137.1, 131.3, 106.1 (2C), 61.0, 56.4 (2C), 52.5, 46.7, 46.4, 38.9, 31.6, 26.2, 24.3, 18.0; IR (film) 3050, 3010, 2951, 2876, 1731, 1641, 1521, 1429, 1317, 1144, 870 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{19}H_{25}N_1O_6$ $[M+H]^+$: 363.1760, found 363.1764.




| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.3917 | 16.3643 | 2.2464 min |
| | 49.6083 | 16.1099 | 3.0714 min |

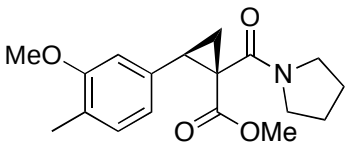



| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 21.2512 | 0.6002 | 2.2964 min |
| | 78.7488 | 2.2243 | 3.113 min |

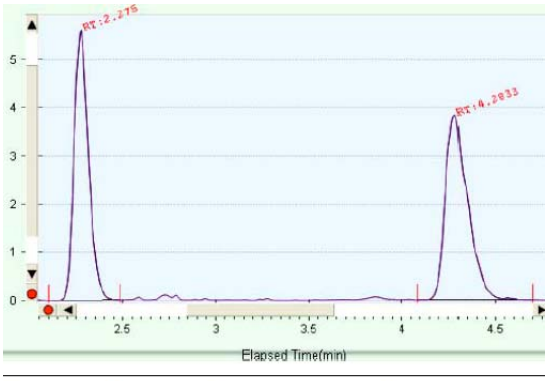



**2-Methoxy-1-methyl-4-vinylbenzene (3aa).** A 500 mL round bottom flask was charged with a magnetic stir bar, $Ph_3MeI$ (13.6 g, 33.7 mmol, 1.1 equiv), and THF (300 mL) under Ar. NaHMDS (5.9 g, 32.1 mmol, 1.05 equiv) was then added portion wised at 25 °C and the reaction mixture is stirred for 1 h at this temperature while the color becomes yellow. To this yellow suspension was assed the corresponding aldehyde (4.6 g, 30.6 mmol, 1.0 equiv) drop wised over a period of 5 min while the yellow color disappeared. One hour latter, the solvent was removed under reduced pressure and the thick oil was portioned between water and pentane. The organic layer was isolated, dried over $MgSO_4$, filtered throught Celite®, and concentrated under reduced pressure. Flash chromatography afforded the title compound (3.6 g). Yield: 80%; $R_f$ 0.80 (100%, Hexanes); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 9.1 Hz, 1H), 6.87 (s, 1H), 6.67 (dd, *J* = 10.8 Hz, *J* = 17.6 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 3.84 (s,

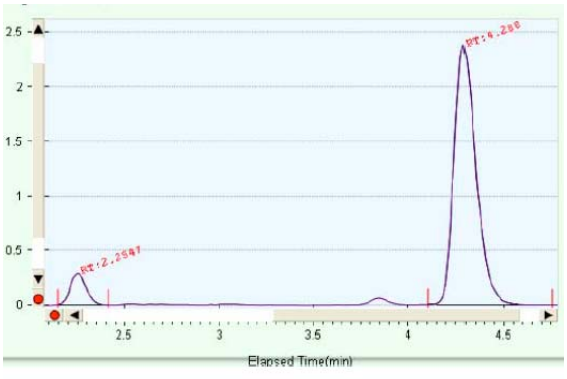
3H), 2.19 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 158.0, 137.2, 136.8, 130.8, 126.8, 118.8, 113.1, 107.6, 55.4, 16.3; IR (film) 3050, 3010, 2951, 2876 cm$^{-1}$.



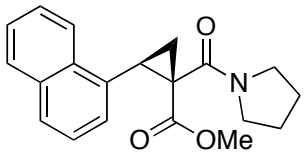

**Methyl 2-(3-methoxy-4-methylphenyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10aa).** Prepared according to the general procedure with a reaction temperature of 50 °C. The product was isolated as a white solid. Yield: 64%, diastereomeric ratio (25:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (81% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 15% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 2.3 min, $t_r$ (major) 4.3 min); mp 105-108 °C; $R_f$ 0.29 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +49 (*c* 2.00, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.8 Hz, 1H), 6.76-6.70 (m, 2H), 3.77 (s, 3H), 3.61-3.48 (m, 3H), 3.48 (s, 3H), 3.36-3.19 (m, 2H), 2.18-2.10 (m, 4H), 1.97-1.80 (m, 4H), 1.44 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.6, 157.5, 134.2, 130.2, 125.5, 120.8, 111.1, 55.4, 52.5, 46.6, 46.5, 38.8, 31.6, 26.2, 24.3, 18.0, 16.1; IR (film) 3050, 3010, 2951, 2876, 1731, 1641, 1521, 1429, 1317, 1144, 870 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{23}N_1O_4$ $[M+H]^+$: 318.1700, found 318.1700.




| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.1443 | 29.838 | 2.275 min |
| | 50.8557 | 30.8771 | 4.2833 min |

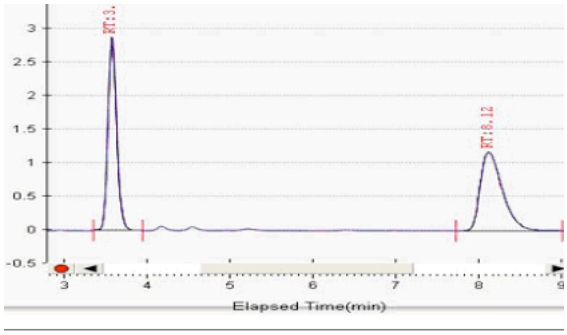



| Name | Area % | Area | Retention Time |
|---|---|---|---|
| 1 | 8.1601 | 1.6057 | 2.2547 min |
| 2 | 91.8399 | 18.0713 | 4.288 min |

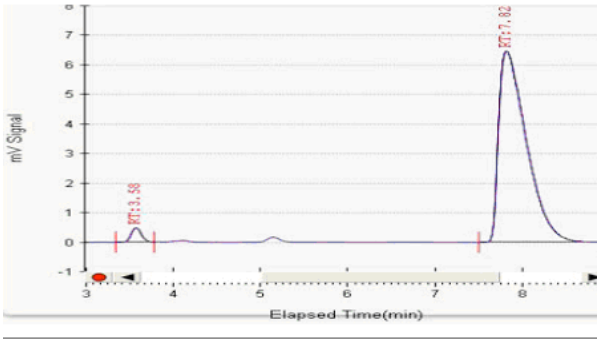



**Methyl 2-(naphthalen-1-yl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10ab).** Prepared according to the general procedure. The product was isolated as a white foam. Yield: 86%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 37.7 min, $t_r$ (major) 38.2 min), enantiomeric excess (95% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 15% MeOH, 3 mL/min, 30 °C, 200 psi, $t_r$ (minor) 3.6 min, $t_r$ (major) 7.8 min); m.p. 83-85 °C; $R_f$ 0.39 (100%, $Et_2O$); $[\alpha]_D^{20}$ = -28 (*c* 1.67, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.60 (t, *J* = 1.4 Hz, 1H), 7.50-7.28 (m, 3H), 3.77 (app. t, *J* = 8.5 Hz, 1H), 3.65-3.53 (m, 3H), 3.27-3.22 (m, 1H), 3.11 (s, 3H), 2.42 (dd, *J* = 4.7 Hz, *J* = 8.1 Hz,

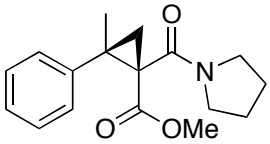
1H), 2.03-1.89 (m, 4H), 1.64 (dd, $J$ = 4.7 Hz, $J$ = 8.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.7, 166.8, 133.5, 133.3, 132.0, 128.2, 128.0, 126.5, 126.4, 126.0, 125.3, 125.1, 52.2, 46.6, 46.3, 38.3, 30.3, 26.2, 24.4, 17.9; IR (film) 3050, 3010, 2951, 2875, 1733, 1639, 1429, 1315, 1140 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{20}H_{21}N_1O_3$ [M+H]$^+$: 324.1594, found 324.1597.



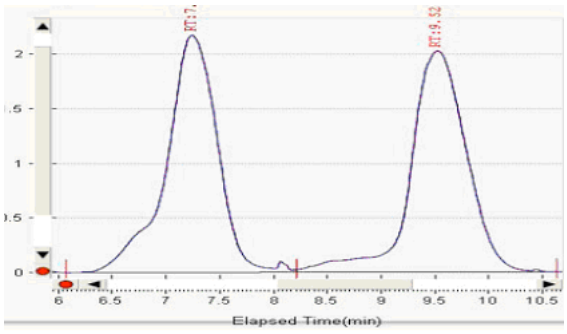

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.0946 | 20.8595 | 3.58 min |
| | 50.9054 | 21.6289 | 8.12 min |



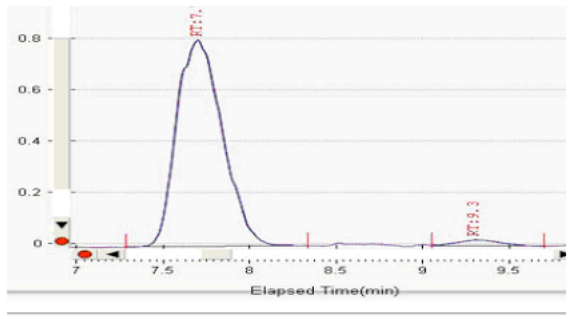

| eak Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 2.6185 | 3.7792 | 3.58 min |
| | 97.3815 | 140.5478 | 7.82 min |



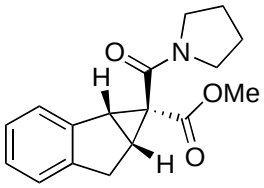

**Methyl 2-methyl-2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10ac).** Prepared according to the general procedure. The product was isolated as a colorless oil after purification by HPLC prep. Yield: 63%, diastereomeric ratio (>20:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (95% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 210 psi, $t_r$ (major) 7.7 min, $t_r$ (minor) 9.3 min); $R_f$ 0.33 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +90 ($c$ 0.85, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.34-7.23 (m, 5H), 3.76-3.72 (m, 1H), 3.64-3.59 (m, 3H), 3.42 (s, 3H), 2.16 (d, $J$ = 4.6 Hz, 1H), 2.05-1.96 (m, 4H), 1.66 (d, $J$ = 4.6, 1H), 1.49 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 170.1, 166.5, 142.6, 129.1 (2C), 129.1 (2C), 127.9, 52.9, 48.1, 47.2, 42.1, 38.9, 27.1, 26.5, 26.3, 25.0; IR (film) 3038, 3009, 2956, 2879, 1729, 1644, 1432, 1319, 1139 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{21}N_1O_3$ [M+H]$^+$: 288.1594, found 288.1593.



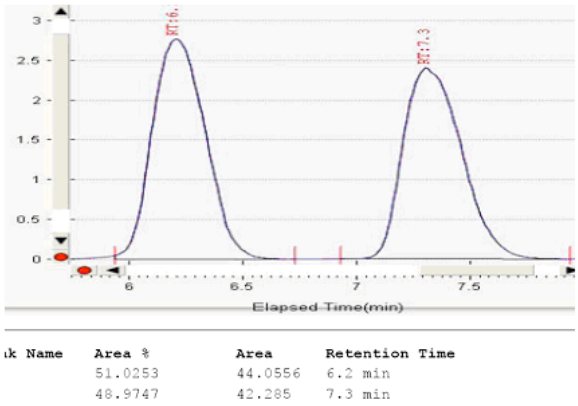

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.7931 | 71.8008 | 7.24 min |
| | 50.2069 | 72.3975 | 9.52 min |

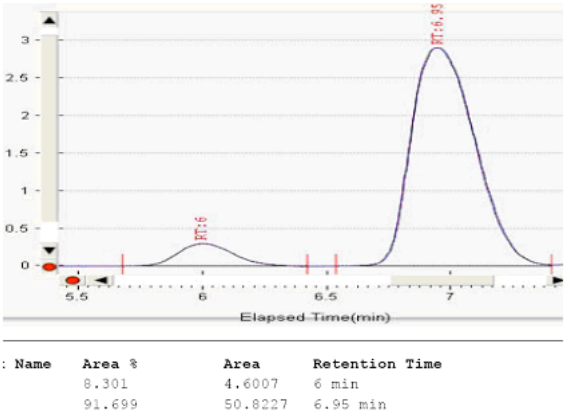


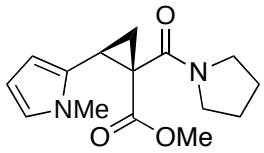

| k Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 97.4229 | 14.5616 | 7.7 min |
| | 2.5771 | 0.3852 | 9.3 min |




**Methyl-1-(pyrrolidine-1-carbonyl)-1, 1a, 6, 6a-tetrahydrocyclopropana[*a*]indene-1-carboxylate (10ad).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 51%, diastereomeric ratio (> 30:1) was determined by GC/MS analysis of the crude mixture (30 m x 0.25 mm, 5 °C/min from 40 °C to 270 °C, 63 psi $H_2$, $t_r$ (minor) 37.8 min, $t_r$ (major) 38.5 min), enantiomeric excess (84% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 200 psi, $t_r$ (minor) 6.0 min, $t_r$ (major) 7.0 min); m.p. 71-73 °C; $R_f$ 0.37 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +43 (*c* 0.53, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.40-7.37 (m, 1H), 7.18-7.12 (m, 3H), 3.71-3.60 (m, 1H), 3.60-3.46 (m, 4H), 3.43-3.24 (m, 5H), 2.50 (t, *J* = 6.5 Hz, 1H), 2.01-1.86 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.2, 166.8, 145.5, 139.8, 127.8, 127.1, 125.9, 124.7, 52.7, 47.5, 47.4, 40.6, 38.9, 34.0, 31.4, 27.0, 24.9; IR (film) 3050, 3010, 2950, 2877, 1731, 1639, 1413, 1297, 1148 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{19}N_1O_3$ $[M+Na]^+$: 308.1257, found 308.1258.

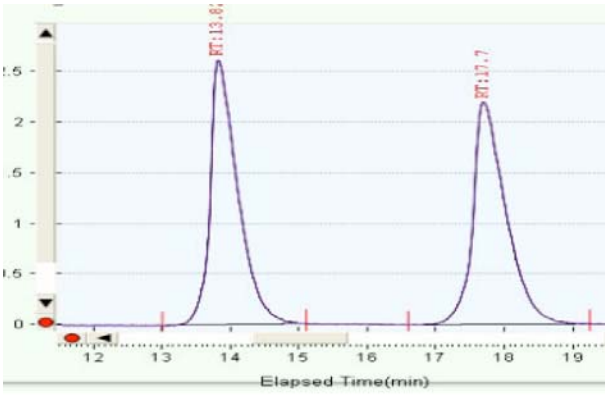


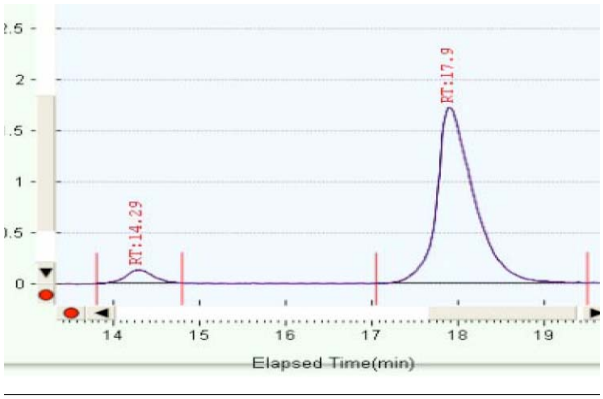




**Methyl 2-(1-methyl-1*H*-pyrrol-2-yl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10ae).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 31%, diastereomeric ratio (> 30:1) was determined by $^1$H NMR analysis of the crude mixture, enantiomeric excess (90% ee) was determined by SFC analysis on chiral phase (R,R-Welko 25 cm, 7% MeOH, 3 mL/min, 40 °C, 160 psi, $t_r$ (minor) 14.3 min, $t_r$ (major) 17.9 min); $R_f$ 0.37 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +97 (*c* 0.93, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 6.56 (t, *J* = 2.2 Hz, 1H), 6.10-6.00 (m, 1H), 5.95-5.90 (m, 1H), 3.68 (s, 3H), 3.64-3.49 (m, 3H), 3.48 (s, 3H), 3.28-3.15 (m, 2H), 2.16 (dd, *J* = 4.7 Hz, *J* = 7.8 Hz, 1H), 2.02-1.86 (m, 4H), 1.50 (dd, *J* = 4.7 Hz, *J* = 9.2 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.4, 166.3, 127.4, 122.5, 108.0, 106.7, 52.5, 46.6, 46.3, 38.2, 33.8, 26.2, 24.3, 23.9, 17.7; IR (film) 2951, 2876, 1723, 1635, 1430, 1313,

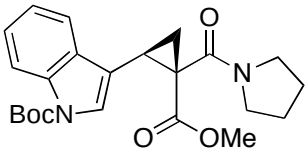
1295, 1142 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{15}H_{20}N_2O_3$ $[M+H]^+$: 277.1558, found 277.1547.



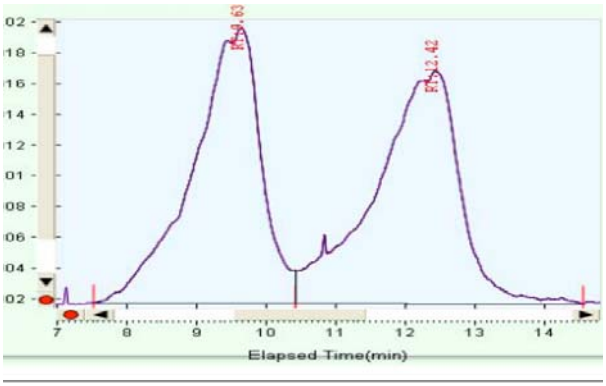

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.8203 | 73.1042 | 13.82 min |
| | 50.1797 | 73.6315 | 17.7 min |



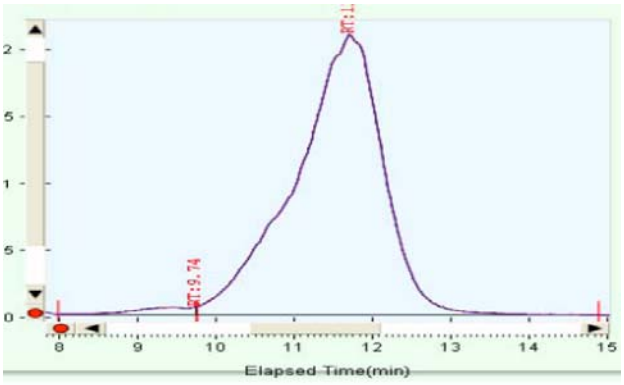

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 5.2956 | 2.8706 | 14.29 min |
| | 94.7044 | 51.3369 | 17.9 min |



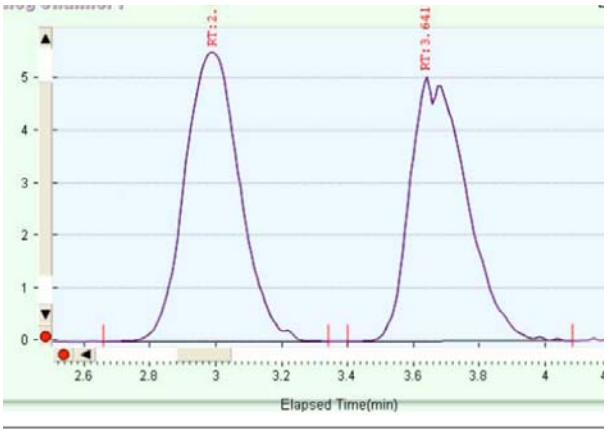

***tert*-Butyl 3-(2-(methoxycarbonyl)-2-(pyrrolidine-1-carbonyl)cyclopropyl)-1*H*-indole-1-carboxylate (10af).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 54%, diastereomeric ratio (1.2:1) was determined by $^1H$ NMR of the crude mixture, enantiomeric excess (96 and 88% ee) was determined by SFC analysis on chiral phase ((Major) Chiralcel AS-H 25 cm, 5% MeOH, 3 mL/min, 35 °C, 150 psi, $t_r$ (minor) 9.7 min, $t_r$ (major) 11.7 min, (Minor) Chiralcel OB-H 25 cm, 5% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (minor) 3.0 min, $t_r$ (major) 3.8 min); mp 165-168 °C; $R_f$ 0.15 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +28 (*c* 0.90, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) δ (Major) 8.08 (bs, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.43 (bs, 1H), 7.33-7.22 (m, 2H), 3.67-3.51 (m, 3H), 3.37 (s, 3H), 3.34-3.22 (m, 2H), 2.16 (dd, *J* = 4.6 Hz, *J* = 8.0 Hz, 1H), 2.07-1.84 (m, 4H), 1.68 (s, 9H), 1.58 (dd, *J* = 4.6 Hz, *J* = 9.0 Hz, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ (Major) 171.3, 168.8, 166.5, 130.8, 124.6, 122.7, 119.8, 116.1, 115.2, 83.7, 66.0, 53.6, 46.6, 46.4, 37.6, 28.4 (3C), 26.2, 35.5, 22.8, 18.1; IR (film) 2975, 2877, 1725, 1631, 1451, 1371, 1309, 1179 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{23}H_{28}N_2O_5$ $[M+H]^+$: 413.2071, found 413.2078.



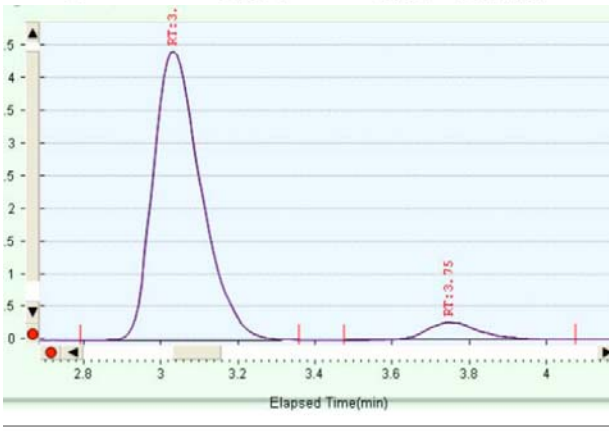

| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 48.6239 | 1.2225 | 9.63 min |
| | 2 | 51.3761 | 1.2917 | 12.42 min |



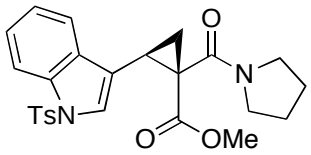

| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 1.6783 | 0.2755 | 9.74 min |
| | 2 | 98.3217 | 16.139 | 11.7 min |



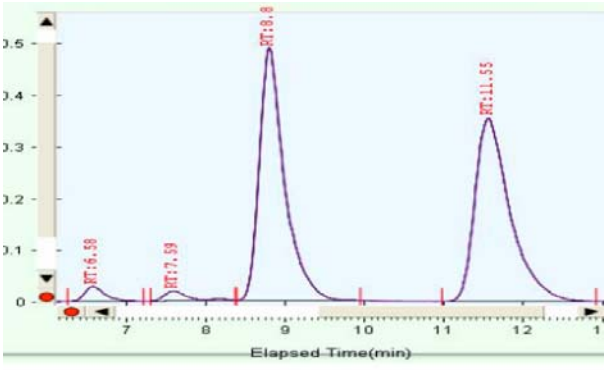

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| 1 | 51.4634 | 63.1948 | 2.9917 min |
| 2 | 48.5366 | 59.6009 | 3.6417 min |



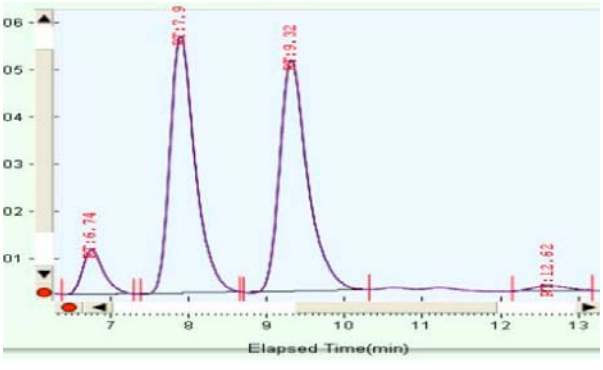

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 93.7715 | 37.6938 | 3.0333 min |
| | 6.2285 | 2.5037 | 3.75 min |



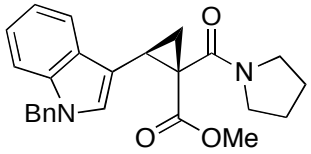

**Methyl 1-(pyrrolidine-1-carbonyl)-2-(1-tosyl-1*H*-indol-3-yl)cyclopropanecarboxylate (10ag).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 58%, diastereomeric ratio (1.2:1) was determined by $^{1}$H NMR of the crude mixture, enantiomeric excess (95 and 83% ee) was determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 10% MeOH, 3 mL/min, 30 °C, 150 psi, $t_r$ (minor-*trans*) 6.7 min, $t_r$ (major-*trans*) 7.9 min, $t_r$ (major-*cis*) 9.3 min, $t_r$ (minor-*cis*) 12.6 min); mp 125-127 °C; $R_f$ 0.25 (100%, EtOAc); mp 180-183 °C; $[\alpha]_D^{20}$ = –26 (*c* 2.95, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) δ (Major+Minor) 8.05-8.00 (m, 1H), 7.89-7.85 (m, 1H), 7.78-7.65 (m, 5H), 7.63-7.55 (m, 1H), 7.35-7.09 (m, 10H), 3.74 (s, 3.74), 3.58-3.47 (m, 4H), 3.24-3.09 (m, 3H), 3.12 (s, 3H), 3.07-2.91 (m, 2H), 2.61-2.50 (m, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.16-2.04 (m, 2H), 1.96-1.84 (m, 4H), 1.81 (dd, *J* = 5.1 Hz, *J* = 8.1 Hz, 1H), 1.53 (dd, *J* = 5.1 Hz, *J* = 9.2 Hz, 1H), 1.45-1.33 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.1, 168.3, 166.2, 163.3, 135.4, 135.3, 135.1, 135.0, 131.3, 130.9, 130.0 (2C), 129.9 (2C), 127.1 (2C), 127.0 (2C), 125.7, 125.1, 125.0, 123.5, 123.4, 121.9, 120.3, 118.9, 118.0, 117.3, 113.9, 113.6, 53.6, 52.9, 52.3, 46.6, 46.4, 46.3, 45.8, 39.6, 38.2, 30.5, 26.2, 25.3, 24.3, 23.7, 23.0, 22.4, 21.7, 21.1, 17.9; IR (film) 3050, 3010, 2951, 2876, 1731, 1641, 1600, 1521, 1429, 1317, 1144, 870 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{25}H_{26}N_2O_5S_1$ $[M+H]^+$: 467.1634, found 467.1635.



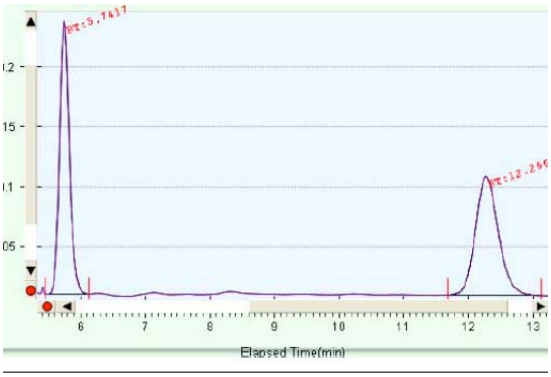

| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 2.2255 | 0.4974 | 6.58 min |
| | 2 | 1.7332 | 0.3873 | 7.59 min |
| | 3 | 47.7862 | 10.6792 | 8.8 min |
| | 4 | 48.255 | 10.7839 | 11.55 min |



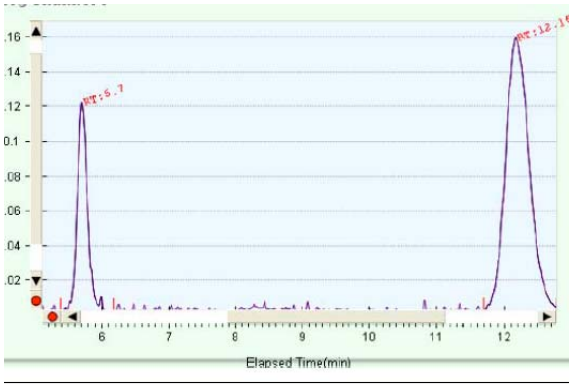

| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 6.5626 | 0.1723 | 6.74 min |
| | 2 | 46.1848 | 1.2125 | 7.9 min |
| | 3 | 46.0704 | 1.2095 | 9.32 min |
| | 4 | 1.1821 | 0.031 | 12.62 min |



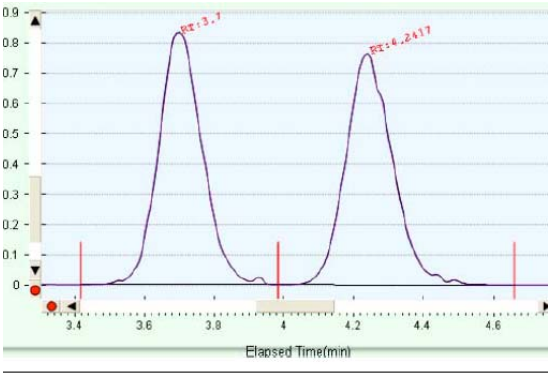

**Methyl 2-(1-benzyl-1*H*-indol-3-yl)-1-(pyrrolidine-1-carbonyl) cyclopropanecarboxylate (10ah).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 88%, diastereomeric ratio (1.5:1) was determined by $^{1}$H NMR of the crude mixture, enantiomeric excess (50 and 41% ee) was determined by SFC analysis on chiral phase (Major: Chiralpak AD-H 25 cm, 20% MeOH, 3 mL/min, 35 °C, 150 psi, $t_r$ (minor) 5.7 min, $t_r$ (major) 12.2 min; Minor: Chiralpak AD-H 25 cm, 20% MeOH, 3 mL/min, 35 °C, 150 psi, $t_r$ (minor) 3.7 min, $t_r$ (major) 4.2 min); $R_f$ 0.25 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +39 (*c* 1.25, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) δ (Major) 7.80 (d, *J* = 8.8 Hz, 1H), 7.78-6.93 (m, 9H), 5.29-5.23 (m, 2H), 3.61-3.3.52 (m, 3H), 3.39 (t app, *J* = 8.7 Hz, 1H), 3.30-3.20 (m, 4H), 2.08 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 1.95-1.83 (m, 4H), 1.57 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1H), (Minor) 7.77 (d, *J* = 8.8 Hz, 1H), 7.48-7.07 (m, 8H), 6.84 (s, 1H), 5.24 (dd, *J* = 4.5 Hz, *J* = 9.2, 2H), 3.79 (s, 3H), 3.40 (t app, *J* = 8.9 Hz, 1H), 3.33-3.14 (m, 2H), 3.08-2.94 (m, 1H), 2.77-2.70 (m, 1H), 2.14 (dd, *J* = 4.9 Hz, *J* = 8.0 Hz, 1H), 1.88 (dd, *J* = 4.9 Hz, *J* = 9.2 Hz, 1H), 1.57-1.35 (m, 3H), 0.52-0.37 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ (Major) 169.0, 166.9, 137.9, 136.6, 129.0, 128.9 (2C), 127.7, 127.3, 126.9 (2C), 122.0, 119.8, 119.5, 110.2, 109.7, 52.3, 50.1, 46.6, 46.5, 38.4, 26.2, 24.4, 23.7, 18.6; IR (film) 2949, 2874, 1726, 1630, 1432, 1308, 1145, 732 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{25}H_{26}N_2O_3$ $[M+H]^+$: 403.2016, found 403.2031.



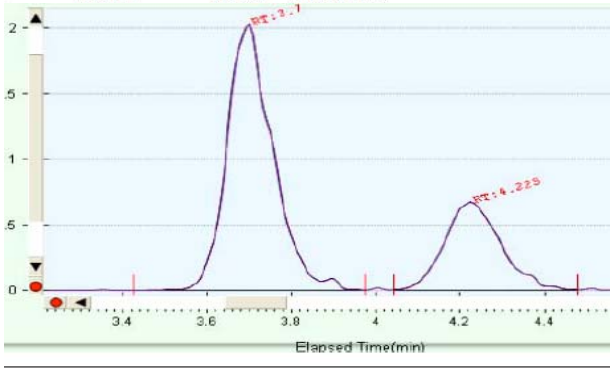

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.6451 | 2.4017 | 5.7417 min |
| | 50.3549 | 2.436 | 12.2667 min |



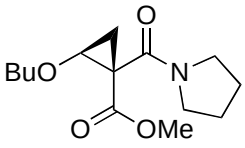

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 24.8575 | 1.2902 | 5.7 min |
| | 75.1425 | 3.9002 | 12.1669 min |



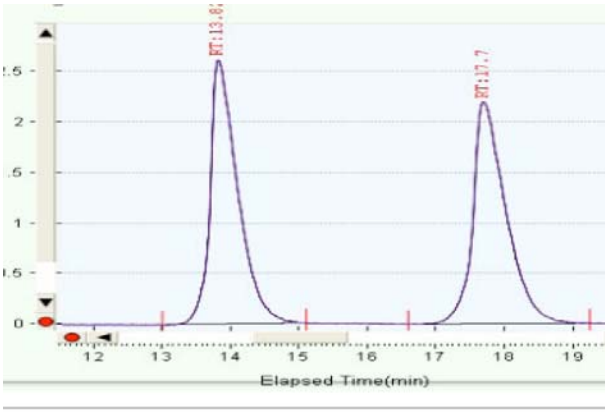

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.6399 | 7.2193 | 3.7 min |
| | 49.3601 | 7.0368 | 4.2417 min |



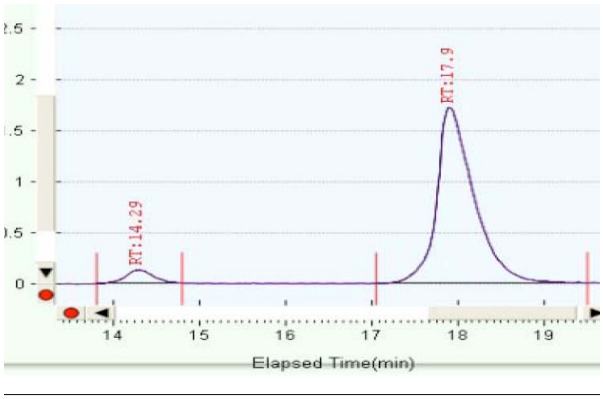

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 71.3597 | 15.1707 | 3.7 min |
| | 28.6403 | 6.0888 | 4.225 min |



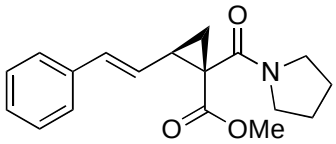

**Methyl 2-butoxy-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10ai).** Prepared according to the general procedure using the alkene with a 10-fold excess. The product was isolated as a colorless oil. Yield: 70%, diastereomeric ratio (89:11) was determined by $^1$H NMR analysis of the crude mixture, enantiomeric excess (89% ee) was determined by SFC analysis on chiral phase (R,R-Welko 25 cm, 7% MeOH, 3 mL/min, 40 °C, 160 psi, $t_r$ (minor) 10.3 min, $t_r$ (major) 15.7 min); $R_f$ 0.38 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +64 (*c* 0.91, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 4.09 (dd, *J* = 5.4 Hz, *J* = 7.0 Hz, 1H), 3.76 (s, 3H), 3.65-3.60 (m, 1H), 3.56-3.42 (m, 3H), 3.26-3.23 (m, 1H), 2.06 (app t, *J* = 5.4 Hz, 1H), 1.97-1.86 (m, 4H), 1.58-1.51 (m, 2H), 1.37-1.22 (m, 4 H), 0.90 (t, *J* = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 168.0, 165.8, 71.5, 64.1, 52.7, 46.4, 46.2, 37.1, 31.6, 26.1, 24.3, 20.3, 19.4, 14.0; IR (film) 2955, 2873, 1732, 1634, 1433, 1307, 1147 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{14}H_{23}N_1O_4$ $[M+H]^+$: 270.1700, found 270.1703.



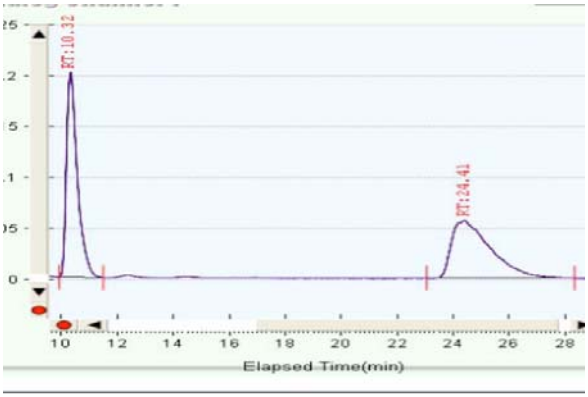

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.8203 | 73.1042 | 13.82 min |
| | 50.1797 | 73.6315 | 17.7 min |



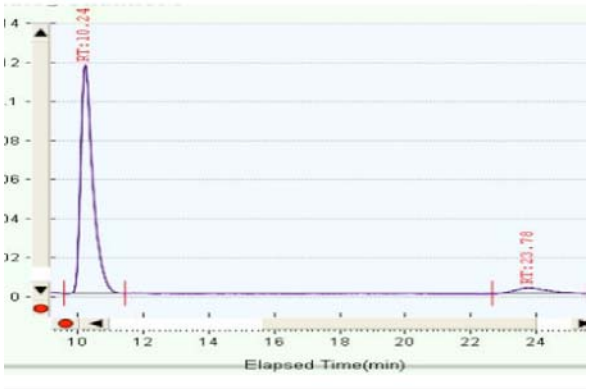

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 5.2956 | 2.8706 | 14.29 min |
| | 94.7044 | 51.3369 | 17.9 min |



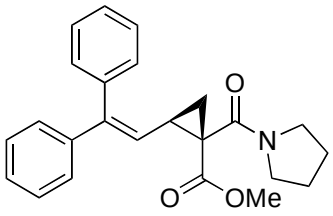
**Methyl 1-(pyrrolidine-1-carbonyl)-2-styrylcyclopropanecarboxylate (10aj).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 77%, diastereomeric ratio (9:1) was determined by $^{1}$H NMR analysis of the crude mixture, enantiomeric excess (87% ee) was determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 150 psi, $t_r$ (major) 10.2 min, $t_r$ (minor) 23.8 min); $R_f$ 0.48 (100%, $Et_2O$); m.p. 72-75 °C; $[\alpha]_D^{20}$ = +116 (*c* 0.58, $CHCl_3$); $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.39-7.23 (m, 5H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 9.3 Hz, *J* = 15.9 Hz, 1H), 3.75 (s, 3H), 3.54-3.50 (m, 3H), 3.41-3.37 (m, 1H), 2.62 (app. q, *J* = 9.3 Hz, *J* = 15.6 Hz, 1H), 1.97-1.91 (m, 4H), 1.84 (dd, *J* = 4.8 Hz, *J* = 7.5 Hz, 1H), 1.68 (dd, *J* = 4.8 Hz, *J* = 9.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 169.8, 166.4, 137.2, 133.3, 128.7 (2C), 127.6, 126.3 (2C), 125.7, 52.8, 46.8, 46.5, 37.8, 31.7, 26.2, 24.4, 21.5; IR (film) 3024, 2959, 2874, 1726, 1633, 1416, 1312, 1139 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{21}N_1O_3$ $[M+H]^+$: 300.1594, found 300.1596.



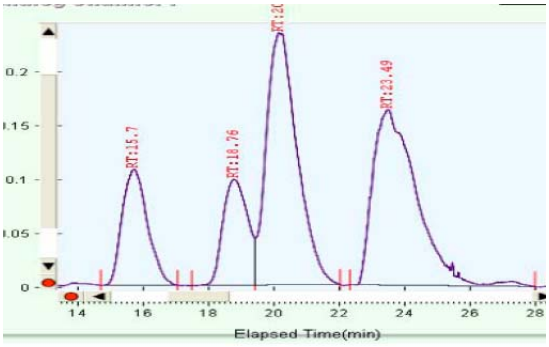

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.8265 | 5.3771 | 10.32 min |
| | 50.1735 | 5.4146 | 24.41 min |



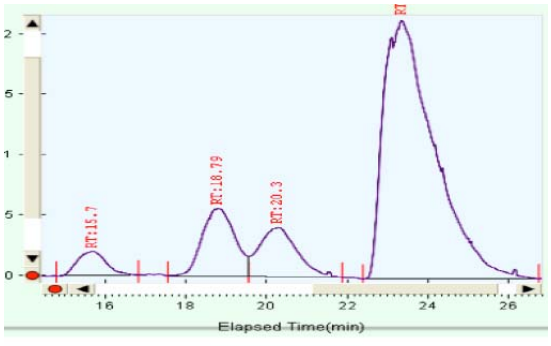

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 93.5577 | 3.0038 | 10.24 min |
| | 6.4423 | 0.2068 | 23.78 min |



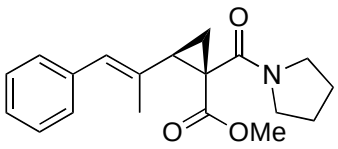
**Methyl 2-(2,2-diphenylvinyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10ak).** Prepared according to the general procedure. The product was isolated as a white solid. Yield: 90%, diastereomeric ratio (6:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (75 and 53% ee) was determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 7% *i*-PrOH, 2 mL/min, 35 °C, 150 psi, $t_r$ (minor *trans*) 15.7 min, $t_r$ (major *trans*) 18.8 min, $t_r$ (minor *cis*) 20.3 min, $t_r$ (major *cis*) 23.4 min); mp 115-118 °C; $R_f$ 0.45 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +44 (*c* 1.83, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ (Major) 7.51-7.21 (m, 10H), 6.13 (d, *J* = 13.1 Hz, 1H), 3.79 (s, 3H), 3.42-3.31 (m, 3H), 3.20-3.09 (m, 1H), 2.64-2.53 (m, 1H), 1.97-1.63 (m, 6H), (Minor) 7.51-7.21 (m, 10H), 5.44 (d, *J* = 13.1 Hz, 1H), 3.69 (s, 3H), 3.45-3.34 (m, 3H), 3.34-3.19 (m, 1H), 2.81-2.70 (m, 1H), 1.97-1.63 (m, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ (Major+Minor) 171.6, 171.5, 170.6, 167.0, 145.7, 145.6, 142.9, 142.7, 140.2, 140.0, 131.1 (2C), 130.7, 139.4, 129.2 (2C), 129.1, 128.9 (2C), 128.4, 128.4, 128.3, 128.2 (2C), 128.1, 128.0, 126.1, 125.2, 53.5, 53.4, 47.3, 47.2, 47.1, 47.0, 38.7, 38.4, 29.9, 29.2, 26.9, 26.7, 26.9, 26.7, 25.1, 24.9, 23.7, 23.1; IR (film) 3057, 3010, 2952, 2877, 1726, 1639 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{24}H_{25}N_1O_3$ $[M+H]^+$: 376.1907, found 376.1919.




| Name | Peak Number | Area % | Area | Retention Tim |
|---|---|---|---|---|
| | 1 | 13.8946 | 5.7446 | 15.7 min |
| | 2 | 12.3537 | 5.1075 | 18.76 min |
| | 3 | 37.0967 | 15.3372 | 20.14 min |
| | 4 | 36.6551 | 15.1546 | 23.49 min |

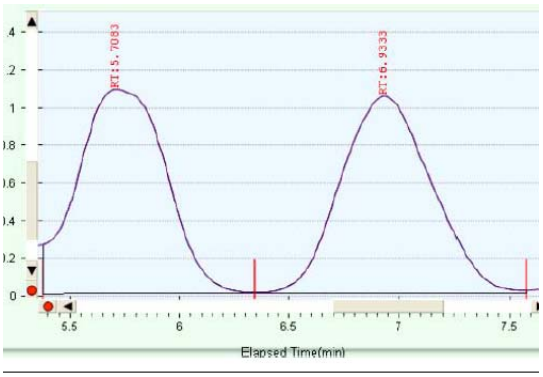



| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 3.8052 | 0.9656 | 15.7 min |
| | 2 | 12.3656 | 3.138 | 18.79 min |
| | 3 | 10.3804 | 2.6342 | 20.3 min |
| | 4 | 73.4489 | 18.6388 | 23.35 min |

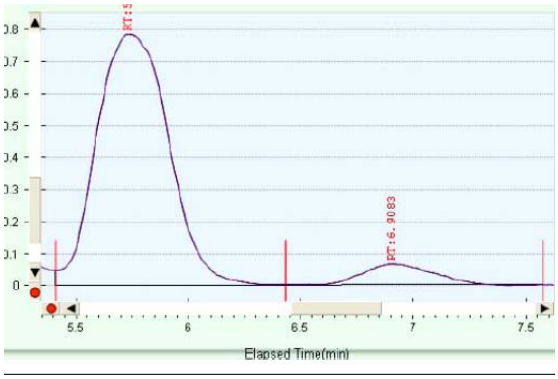


**Methyl 2-((*E*)-1-phenylprop-1-en-2-yl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10al).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 73%, diastereomeric ratio (14:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (85% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 3% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (major) 5.7 min, $t_r$ (minor) 6.9 min); $R_f$ 0.33 (100%, $Et_2O$); $[\alpha]_D^{20}$ = –83 (*c* 1.08, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.35-7.12 (m, 5H), 6.36 (s, 1H),3.63 (s, 3H), 3.60-3.39 (m, 3H), 3.29-3.17 (m, 1H), 2.85 (t app, *J* = 9.2 Hz, 1H), 2.03 (dd, *J* = 4.8

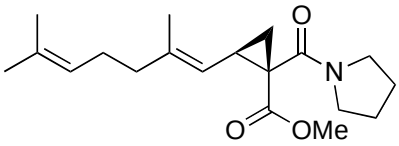
Hz, $J$ = 8.1 Hz, 1H), 1.96-1.78 (m, 7H), 1.32 (dd, $J$ = 4.8 Hz, $J$ = 8.7 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 169.1, 166.6, 137.9, 132.4, 129.0 (2C), 128.5, 128.3 (2C), 126.5, 52.6, 46.7, 46.4, 37.8, 35.7, 30.5, 26.3, 24.3, 18.6; IR (film) 3057, 3010, 2952, 2877, 1726, 1639 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{19}H_{23}N_1O_3$ [M+H]$^+$: 314.1756, found 314.1760.



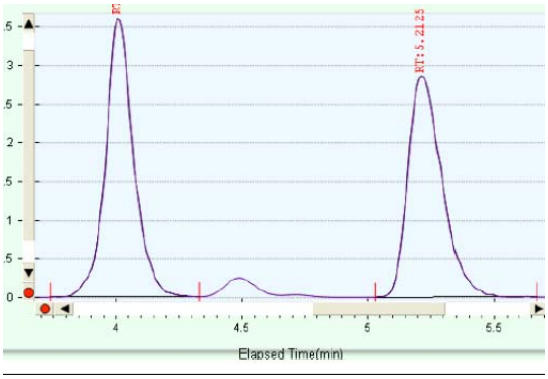

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.3918 | 30.2537 | 5.7083 min |
| | 49.6082 | 29.7833 | 6.9333 min |



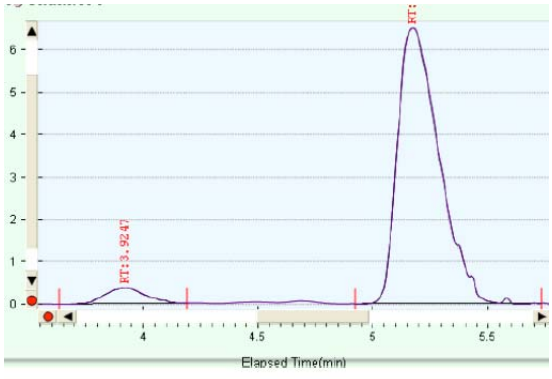

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 92.4334 | 17.312 | 5.7333 min |
| | 7.5666 | 1.4172 | 6.9083 min |



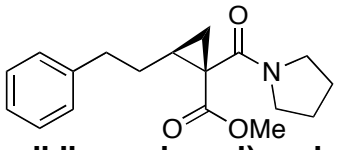

**Methyl 2-((*E*)-2,6-dimethylhepta-1,5-dienyl)-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (10am).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 45%, diastereomeric ratio (22:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (90% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 5% MeOH, 10 mL/min, 40 °C, 150 psi, $t_r$ (minor) 3.9 min, $t_r$ (major) 5.2 min); $R_f$ 0.54 (100%, $Et_2O$); $[\alpha]_D^{20}$ = –32 (*c* 2.70, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 5.05-5.00 (m, 2H), 3.67 (s, 3H), 3.53-3.39 (m, 3H), 3.29-3.15 (m, 1H), 2.52-2.50 (m, 1H), 2.10-1.76 (m, 8H), 1.74 (s, 3H), 1.67-1.60 (m, 4H), 1.56 (s, 3H), 1.43 (dd, $J$ = 4.5 Hz, $J$ = 9.0 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 169.9, 166.8, 140.7, 131.6, 124.1, 119.7, 52.4, 46.5, 46.3, 39.7, 37.6, 27.1, 26.7, 26.1, 25.8, 24.3, 21.1, 17.8, 16.8; IR (film) 2970, 2890, 1729, 1643, 1434, 1310, 1138, 911 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{19}H_{29}N_1O_3$ [M+H]$^+$: 320.2223, found 320.2220.



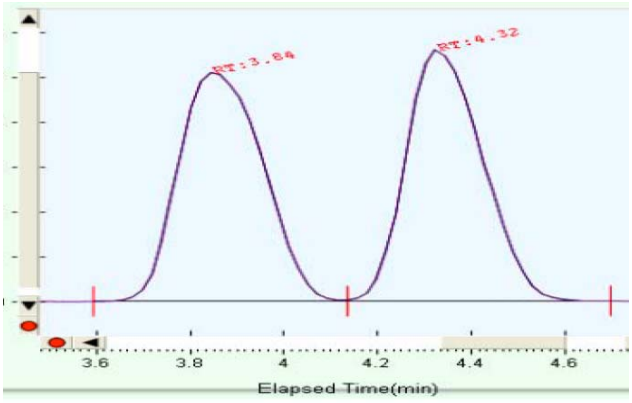

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 51.1639 | 27.6245 | 4.0042 min |
| | 48.8361 | 26.3677 | 5.2125 min |



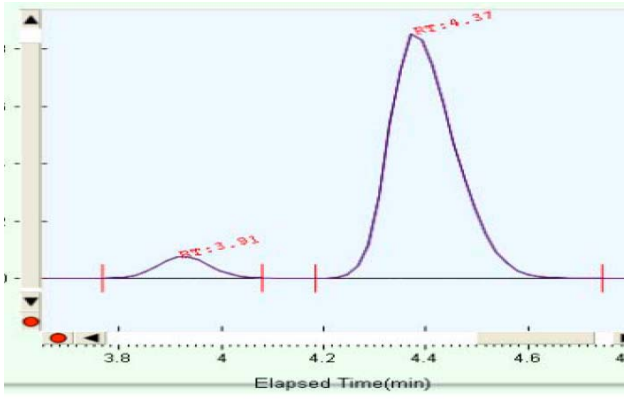

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 5.1643 | 4.4053 | 3.9247 min |
| | 94.8357 | 80.8976 | 5.175 min |



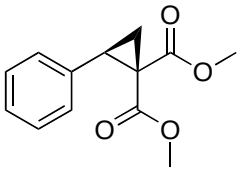
**Methyl 2-phenethyl-1-(pyrrolidinecarbonyl)cyclopropanecarboxylate (12).** Cyclopropane **10aj** (20 mg, 0.067 mmol) was solubilized in EtOAc (4 mL). $Pd(OH)_2/C$ (4.7 mg, 0.007 mmol, 10 mol%) was added and the system was purged with $H_{2(g)}$ with stirring. The suspension was stirred for 20 min under a $H_2$ atmosphere ($H_2$ balloon). The reaction mixture was then filtered through a silica gel pad and eluted with $Et_2O$ (20 mL). **12** was obtained as a colorless oil after flash chromatography on silica gel using hexane:$Et_2O$ 1:1. Yield: 94%, enantiomeric excess (87% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 10 cm, 10% *i*PrOH, 3 mL/min, 40 °C, 100 psi, $t_r$ (minor) 3.9 min, $t_r$ (major) 4.4 min); $R_f$ 0.48 (100%, $Et_2O$); $[a]_D^{20}$ = +46 (*c* 0.98, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) d 7.31-7.16 (m, 5H), 3.73 (s, 3H), 3.54-3.44 (m, 3H), 3.24-3.21 (m, 1H), 2.76-2.67 (m, 2H), 2.00-1.79 (m, 7H), 1.44 (dd, *J* = 4.5 Hz, *J* = 7.2 Hz, 1H), 1.26 (dd, *J* = 4.5 Hz, *J* = 8.7 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.2, 167.8, 142.5, 129.4 (2C), 129.2 (2C), 126.7, 53.3, 47.1, 47.0, 36.3, 36.2, 30.1, 28.6, 26.8, 25.0, 21.1; IR (film) 3025, 2951, 2874, 1724, 1638, 1426, 1312, 1146 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{18}H_{23}N_1O_3$ $[M+H]^+$: 302.1751, found 302.1761.




| umber | Area | Area % | Retention Time |
|---|---|---|---|
| | 6.1856 | 50.1452 | 3.84 min |
| | 6.1498 | 49.8548 | 4.32 min |

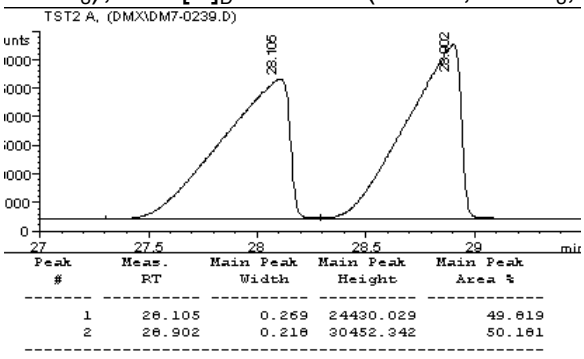



| umber | Area | Area % | Retention Time |
|---|---|---|---|
| | 0.5169 | 6.4802 | 3.91 min |
| | 7.4597 | 93.5198 | 4.37 min |

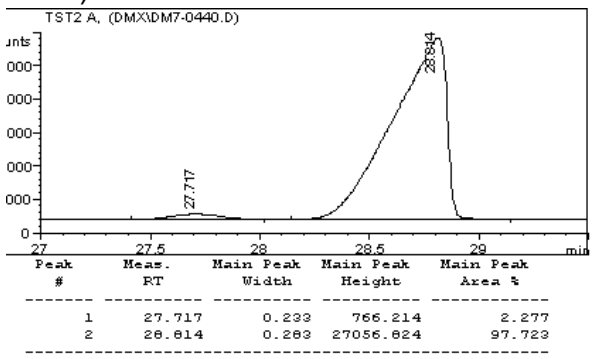


**Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (4a).** A 10-mL round bottom flask was charged with a magnetic stir bar, cyclopropane **10h** (50 mg, 0.18 mmol, 1.00 equiv) and THF (2 mL). To the solution was added water (24 µL, 1.25 mmol, 7.50 equiv) and *t*-BuOK (403 mg, 3.60 mmol, 20.00 equiv). The slurry was vigourously stirred at 70 °C for 35 h, then cooled to 25 °C, diluted with THF (5 mL), and $Me_2SO_4$ (380 µL, 3.96 mmol, 22.00 equiv) was added. The slurry was then vigorously stirred for 2 h at 25 °C then diluted with DCM (20 mL). The organic phase was washed twice with 10% aqueous HCl, dried with $MgSO_4$, filtered on Celite®, and concentrated under vacuum. The title compound was then obtained following flash chromatography on silica gel using hexane to hexane:EtOAc

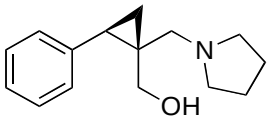
90:10. Isolated as a colorless oil. Yield: 75%, enantiomeric excess (95.4% ee) was determined by GC analysis on chiral phase (β-dextrine 30 m x 0.25 mm, 0.5 °C/min from 130 °C to 200 °C, 63 psi $H_2$, $t_r$ (minor) 27.7 min, $t_r$ (major) 28.8 min); $[\alpha]_D^{20}$ = +115 (*c* 0.48, $CHCl_3$); lit:[16] $[\alpha]_D^{20}$ = 130° (*c* 1.40, $CHCl_3$, 99% ee).



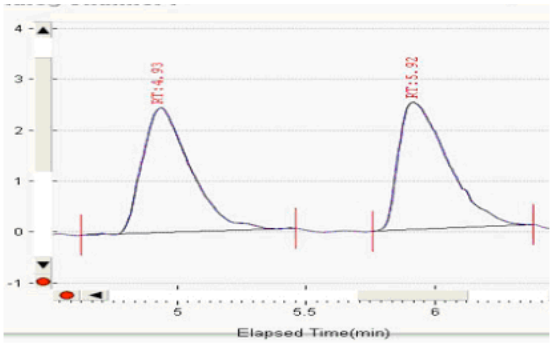

| Peak # | Meas. RT | Main Peak Width | Main Peak Height | Main Peak Area % |
|---|---|---|---|---|
| 1 | 28.105 | 0.269 | 24430.029 | 49.819 |
| 2 | 28.902 | 0.218 | 30452.342 | 50.181 |

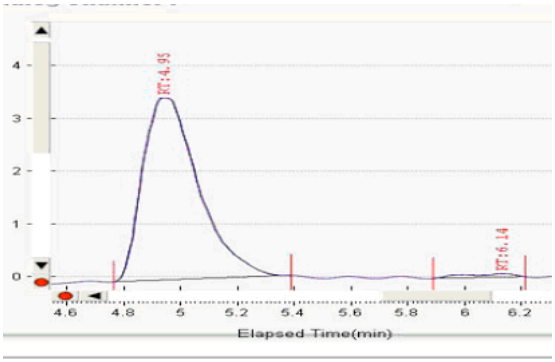



| Peak # | Meas. RT | Main Peak Width | Main Peak Height | Main Peak Area % |
|---|---|---|---|---|
| 1 | 27.717 | 0.233 | 766.214 | 2.277 |
| 2 | 28.814 | 0.283 | 27056.824 | 97.723 |

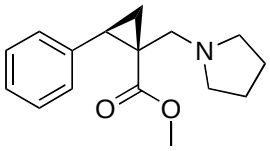



**(2-Phenyl-1-(pyrrolidin-1-ylmethyl)cyclopropyl)methanol (14).** A dried 10-mL round bottom flask was charged with a magnetic stir bar, cyclopropane **10h** (50 mg, 0.18 mmol, 1.00 equiv) and THF (2 mL). The solution was cooled to 0 °C and LAH (28 mg, 0.74 mmol, 4.00 equiv) was added in one portion. The slurry was stirred for 15 min at 0 °C then at 25 °C for 15 min. Unreacted LAH was then quenched with an excess of $Na_2SO_4 \cdot 10H_2O$ and stirred at 25 °C for 30 min prior to filtration through Celite® which was rinced with $Et_2O$. The solvent was then removed under reduced pressure. The resulting solid was dissolved in DCM and extracted twice with 5 mL of 10% aqueous HCl. The combined aqueous layers were made basic with 20 mL of 3M KOH and extracted twice with 10 mL of DCM. The combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum to afford the title compound as a white solid. Yield: 89%, diastereomeric ratio (>20:1) was determined by $^1$H NMR analysis, enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 10% *i*PrOH+0.2%$Et_3N$, 3 mL/min, 30 °C, 150 psi, $t_r$ (major) 4.9 min, $t_r$ (minor) 5.9 min); mp: 85-87 °C; $[\alpha]_D^{20}$ = +52 (*c* 1.25, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.33-7.19 (m, 5H), 5.77 (s(br), 1H), 3.45 (dd, *J* = 11.4 Hz, *J* = 18.8, 2H), 2.86-2.7 (m, 6H), 2.09 (dd, *J* = 6.2 Hz, *J* = 8.5, 1H), 1.87-1.28 (m, 4H), 1.04 (app. t, *J* = 5.5 Hz, 1H), 0.85 (dd, *J* = 5.2 Hz, *J* = 8.6 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 138.3, 129.2 (2C), 128.3 (2C), 126.4, 67.4, 66.0, 55.0(2C), 27.7, 26.5, 23.6(2C), 14.2; IR (film) 3110 (br), 3050, 3010, 2945, 2876, 1144, 721 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{15}H_{21}N_1O_1$ $[M+H]^+$: 232.1696, found 232.1698.

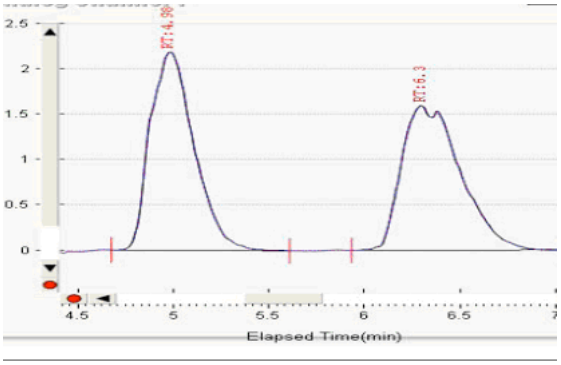


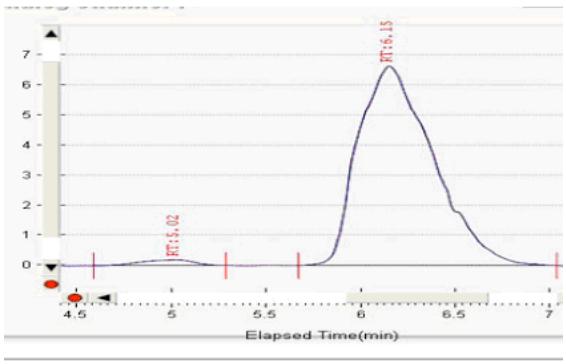

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 98.2113 | 46.0937 | 4.95 min |
| | 1.7887 | 0.8395 | 6.14 min |



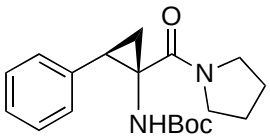
**Methyl 2-phenyl-1-(pyrrolidin-1-ylmethyl)cyclopropanecarboxylate (15)**. A dried 10-mL round bottom flask was charged with a magnetic stir bar, cyclopropane **10h** (50 mg, 0.18 mmol, 1.00 equiv) and THF (2 mL). The mixture was purged with argon and 1 M $BH_3$ (540 µL, 0.54 mmol, 3.00 equiv) was added in one portion at 0 °C and the mixture was refluxed for 1 h then cooled to 25 °C, 10% $H_2SO_4$ in MeOH (1 mL) was added and the mixture was heated under reflux for 1 h. The solvent was then removed under vacuum. The resulting solid was dissolved in DCM and extracted twice with 5 mL of 10% HCl. The combined aqueous layer was made basic with 20 mL of 3M KOH and extracted twice with 10 mL of DCM. The combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. The title compound was obtained after flash chromatography on silica gel using DCM/MeOH 95:5. Yield: 49%, diastereomeric ratio (>20:1) was determined by $^1$H NMR analysis, enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 5% MeOH+0.1%$Et_3N$, 3 mL/min, 35 °C, 150 psi, $t_r$ (minor) 5.0 min, $t_r$ (major) 6.2 min); $R_f$: 0.19 (DCM/MeOH, 90/10); mp: 53-55 °C; $[\alpha]_D^{20}$ = +37 (*c* 0.82, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.29-7.20 (m, 5H), 3.80 (d, *J* = 12.4 Hz, 1H), 3.29 (s, 3H), 2.71-2.64 (m(br), 2H), 2.62-2.55 (m(br), 2H), 2.38 (app. t, *J* = 7.6 Hz, 1H), 2.11-2.04 (m, 2H), 1.82-1.79 (m(br), 4H), 1.32-1.28 (m(br), 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.9, 136.9, 129.0 (2C), 128.2 (2C), 126.8, 61.1, 54.8 (2C), 51.7, 33.7, 30.5, 23.7 (2C), 16.7; IR (film) 3050, 2950, 2788, 1729, 1446, 1157 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{22}N_1O_2$ $[M+H]^+$: 260.1645, found 260.1639.



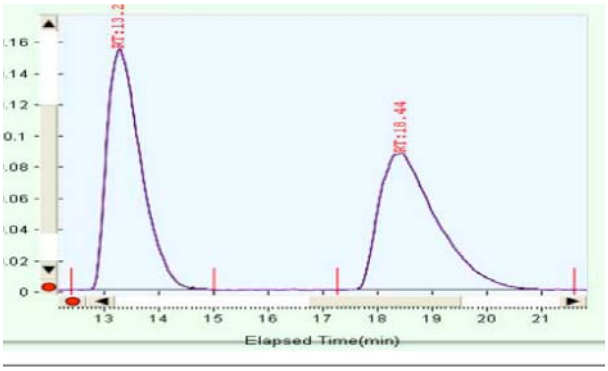

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.5383 | 34.3921 | 4.98 min |
| | 49.4617 | 33.6594 | 6.3 min |



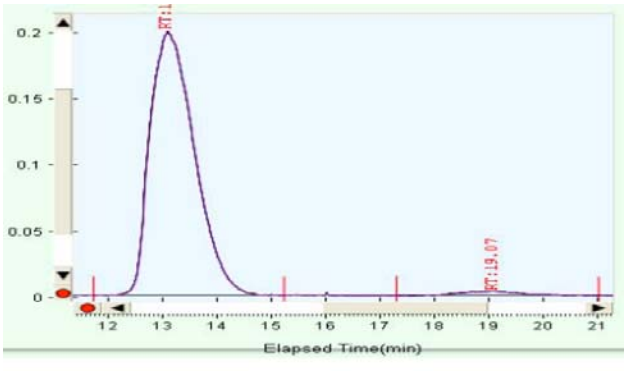

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 1.952 | 3.5947 | 5.02 min |
| | 98.048 | 180.5575 | 6.15 min |




***tert*-Butyl 2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropylcarbamate (16)**. A 10-mL microwave vial was charged with **10h** (106.5 mg, 0.39 mmol, 1.00 equiv), a magnetic stir bar, *i*-PrOH (2 mL, 0.2 M), and 1N aqueous LiOH (585 $\mu$L, 1.5 equiv). The tube was sealed with a Teflon septum and heated to 120 °C under $\mu$-wave irradiation for 30 min. Acid/base extraction afforded the corresponding acid. The acid was transferred in a 10 mL round bottom flask. To this flask was added a magnetic stir bar, dry hexanes (4 mL), $NEt_3$ (61 $\mu$L, 0.44 mmol, 1.13 equiv), *t*-BuOH (361 $\mu$L, 3.9 mmol, 10.00 equiv), and diphenylphosphoryl azide (92 $\mu$L, 0.43 mmol, 1.10 equiv). The mixture was heated under reflux for 18 h under argon followed by the addition of di-*tert*-butyl dicarbonate (127 $\mu$L, 0.59 mmol, 1.50 equiv). The mixture was refluxed for a further 2 h. The reaction was then cooled to room temperature, and the solvent was removed under reduced pressure. The resulting oil was partitioned with water and DCM. The layers were separated and the aqueous layer was extracted twice with DCM (2x5 mL). The combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. The title compound was obtained after flash chromatography on silica gel using 100% EtOAc as a white solid. Yield: 64%, diastereomeric ratio (>20:1) was determined by $^1$H NMR analysis, enantiomeric excess (96% ee) was determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 5% *i*-PrOH, 3 mL/min, 35 °C, 150 psi, $t_r$ (major) 13.3 min, $t_r$ (minor) 18.4 min); mp 89-92 °C; $R_f$ = 0.45 (100% EtOAc); mp 122-125 °C; $[a]_D^{20}$ = –30 (*c* 1.00, $CHCl_3$); $^1$H NMR (700 MHz, $CDCl_3$) $\delta$ (3:2 rotamer mixture, data of the major rotamer are reported) 7.36 (t, *J* = 7 Hz, 2H), 7.30 (t, *J* = 7 Hz, 1H), 7.21 (d, *J* = 7Hz, 2H), 4.68 (bs, 1H), 3.67-3.52 (m, 4H), 2.88 (t, *J* = 9.1 Hz, 1H), 2.25-2.20 (m, 1H), 1.97-1.80 (m, 4H), 1.78 (s, 9H), 1.45 (t, *J* = 7.4 Hz, 1H); $^{13}$C NMR (175 MHz, $CDCl_3$) $\delta$ 169.2, 156.7, 134.8, 128.9 (4C), 127.4, 83.5, 47.8, 47.3, 41.3, 31.4, 28.4 (3C), 27.0; IR (film) 3274(br), 2952, 2878, 1713, 1614, 1522, 1436, 1256, 1088 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{19}H_{26}N_2O_3$ $[M+H]^+$: 331.2016, found 331.2016.




| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 50.8033 | 6.6694 | 13.28 min |
| | 2 | 49.1967 | 6.4585 | 18.44 min |




| ık Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 98.2851 | 11.3182 | 13.08 min |
| | 2 | 1.7149 | 0.1975 | 19.07 min |

This product can be crystallized from $Et_2O$ for X-Ray analysis:

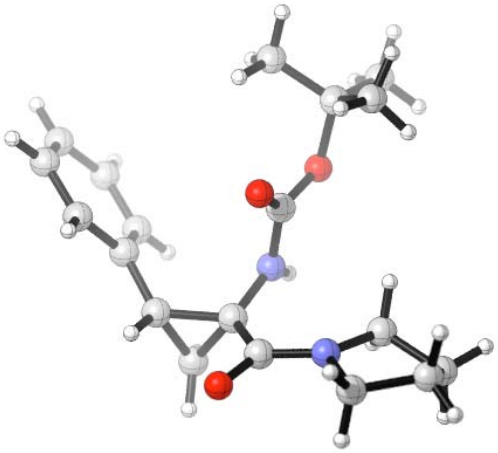


**Table 1.** Crystal data and structure refinement for C19 H26 N2 O3.

| | |
|---|---|
| Identification code | cha193 |
| Empirical formula | C19 H26 N2 O3 |
| Formula weight | 330.42 |
| Temperature | 150K |
| Wavelength | 1.54178 Å |
| Crystal system | Orthorhombic |
| Space group | Pna21 |
| Unit cell dimensions | a = 11.1535(6) Å α = 90°<br>b = 15.5488(8) Å β = 90°<br>c = 10.3661(6) Å γ = 90° |
| Volume | 1797.73(17)Å$^3$ |

| | |
|---|---|
| Z | 4 |
| Density (calculated) | 1.221 g/cm$^3$ |
| Absorption coefficient | 0.664 mm$^{-1}$ |
| F(000) | 712 |
| Crystal size | 0.30 x 0.10 x 0.08 mm |
| Theta range for data collection | 4.88 to 67.49° |
| Index ranges | $-9 \leq h \leq 13$, $-18 \leq k \leq 18$, $-12 \leq \ell \leq 12$ |
| Reflections collected | 6801 |
| Independent reflections | 3225 [$R_{int}$ = 0.052] |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9483 and 0.8871 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3225 / 1 / 220 |
| Goodness-of-fit on $F^2$ | 1.056 |
| Final R indices [I>2sigma(I)] | $R_1$ = 0.0295, $wR_2$ = 0.0820 |
| R indices (all data) | $R_1$ = 0.0296, $wR_2$ = 0.0820 |
| Absolute structure parameter | 0.07(15) |
| Largest diff. peak and hole | 0.168 and -0.159 e/Å$^3$ |

**Table 2.** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$ x $10^3$) for C19 H26 N2 O3.

$U_{eq}$ is defined as one third of the trace of the orthogonalized Uij tensor.

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 9696(1) | 7958(1) | 7999(1) | 27(1) |
| C(2) | 9932(1) | 8073(1) | 9448(1) | 31(1) |
| C(3) | 9857(1) | 7192(1) | 8876(1) | 32(1) |
| O(11) | 11764(1) | 8244(1) | 7624(1) | 34(1) |
| C(11) | 10754(1) | 8145(1) | 7133(1) | 28(1) |
| N(11) | 10607(1) | 8193(1) | 5850(1) | 32(1) |
| C(12) | 9568(1) | 7934(1) | 5062(1) | 37(1) |
| C(13) | 10121(2) | 7748(1) | 3747(2) | 42(1) |
| C(14) | 11149(2) | 8387(1) | 3678(2) | 45(1) |
| C(15) | 11663(1) | 8366(1) | 5033(2) | 41(1) |
| N(16) | 8513(1) | 8112(1) | 7544(1) | 27(1) |
| C(17) | 8138(1) | 8928(1) | 7334(1) | 27(1) |
| O(17) | 8747(1) | 9564(1) | 7479(1) | 37(1) |
| O(18) | 6985(1) | 8907(1) | 6904(1) | 34(1) |
| C(19) | 6356(1) | 9706(1) | 6637(2) | 38(1) |
| C(191) | 6148(2) | 10184(1) | 7895(2) | 56(1) |
| C(192) | 5157(2) | 9381(1) | 6104(2) | 52(1) |
| C(193) | 7005(2) | 10242(1) | 5641(2) | 64(1) |
| C(21) | 8998(1) | 8430(1) | 10321(1) | 30(1) |
| C(22) | 9263(1) | 9165(1) | 11034(1) | 36(1) |
| C(23) | 8448(2) | 9507(1) | 11896(2) | 43(1) |
| C(24) | 7327(1) | 9124(1) | 12050(2) | 44(1) |
| C(25) | 7043(1) | 8403(1) | 11335(2) | 41(1) |
| C(26) | 7868(1) | 8057(1) | 10483(2) | 35(1) |

**Table 3.** Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2\ x\ 10^3$) for C19 H26 N2 O3.

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| H(2) | 10766 | 8262 | 9659 | 37 |
| H(3A) | 9139 | 6843 | 9078 | 39 |
| H(3B) | 10610 | 6860 | 8797 | 39 |
| H(12A) | 8970 | 8403 | 5007 | 44 |
| H(12B) | 9177 | 7414 | 5421 | 44 |
| H(13A) | 10417 | 7149 | 3695 | 51 |
| H(13B) | 9536 | 7848 | 3044 | 51 |
| H(14A) | 10857 | 8969 | 3454 | 53 |
| H(14B) | 11754 | 8206 | 3034 | 53 |
| H(15A) | 12269 | 7905 | 5122 | 50 |
| H(15B) | 12035 | 8924 | 5260 | 50 |
| H(16) | 8025 | 7678 | 7399 | 32 |
| H(19A) | 6922 | 10318 | 8295 | 83 |
| H(19B) | 5676 | 9823 | 8480 | 83 |
| H(19C) | 5713 | 10719 | 7721 | 83 |
| H(19D) | 4759 | 9023 | 6754 | 78 |
| H(19E) | 5300 | 9039 | 5324 | 78 |
| H(19F) | 4644 | 9873 | 5891 | 78 |
| H(19G) | 7238 | 9876 | 4913 | 95 |
| H(19H) | 7724 | 10495 | 6029 | 95 |
| H(19I) | 6475 | 10701 | 5334 | 95 |
| H(22) | 10019 | 9437 | 10925 | 44 |
| H(23) | 8651 | 10004 | 12384 | 51 |
| H(24) | 6764 | 9357 | 12642 | 53 |
| H(25) | 6277 | 8143 | 11428 | 50 |
| H(26) | 7662 | 7558 | 10001 | 42 |

**Table 4.** Anisotropic parameters ($Å^2$ x $10^3$) for C19 H26 N2 O3.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2 [ h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12} ]$$

| | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| C(1) | 25(1) | 26(1) | 31(1) | 2(1) | -2(1) | 0(1) |
| C(2) | 27(1) | 34(1) | 31(1) | 3(1) | -4(1) | 2(1) |
| C(3) | 34(1) | 30(1) | 33(1) | 6(1) | 1(1) | 5(1) |
| O(11) | 25(1) | 35(1) | 41(1) | 3(1) | -2(1) | 1(1) |
| C(11) | 25(1) | 25(1) | 35(1) | 2(1) | 1(1) | 3(1) |
| N(11) | 27(1) | 37(1) | 33(1) | 4(1) | 3(1) | 1(1) |
| C(12) | 33(1) | 45(1) | 33(1) | 2(1) | -2(1) | 0(1) |
| C(13) | 49(1) | 46(1) | 32(1) | 1(1) | 2(1) | -2(1) |
| C(14) | 53(1) | 45(1) | 36(1) | 4(1) | 10(1) | -2(1) |
| C(15) | 34(1) | 49(1) | 41(1) | 6(1) | 10(1) | -2(1) |
| N(16) | 24(1) | 27(1) | 30(1) | 2(1) | -2(1) | -3(1) |
| C(17) | 27(1) | 30(1) | 26(1) | 3(1) | 1(1) | 0(1) |
| O(17) | 34(1) | 29(1) | 47(1) | 3(1) | -1(1) | -2(1) |
| O(18) | 30(1) | 32(1) | 40(1) | 2(1) | -6(1) | 4(1) |
| C(19) | 39(1) | 33(1) | 42(1) | 2(1) | -5(1) | 12(1) |
| C(191) | 49(1) | 54(1) | 64(1) | -20(1) | -2(1) | 8(1) |
| C(192) | 49(1) | 50(1) | 57(1) | -5(1) | -19(1) | 13(1) |
| C(193) | 70(1) | 59(1) | 61(1) | 25(1) | -8(1) | 8(1) |
| C(21) | 31(1) | 33(1) | 26(1) | 4(1) | -5(1) | 3(1) |
| C(22) | 37(1) | 35(1) | 37(1) | 1(1) | -3(1) | -3(1) |
| C(23) | 51(1) | 37(1) | 41(1) | -6(1) | -2(1) | 2(1) |
| C(24) | 44(1) | 54(1) | 34(1) | -4(1) | 3(1) | 6(1) |
| C(25) | 35(1) | 56(1) | 33(1) | -1(1) | 2(1) | -4(1) |
| C(26) | 36(1) | 40(1) | 30(1) | -3(1) | -1(1) | -6(1) |

**Table 5.** Bond lengths [Å] and angles [°] for C19 H26 N2 O3

| | | | |
|---|---|---|---|
| C(1)-N(16) | 1.4215(16) | C(21)-C(2)-C(1) | 121.26(11) |
| C(1)-C(3) | 1.5079(17) | C(3)-C(2)-C(1) | 59.67(8) |
| C(1)-C(11) | 1.5113(18) | C(2)-C(3)-C(1) | 61.50(9) |
| C(1)-C(2) | 1.5352(19) | O(11)-C(11)-N(11) | 120.57(12) |
| C(2)-C(21) | 1.4871(19) | O(11)-C(11)-C(1) | 119.16(12) |
| C(2)-C(3) | 1.4948(19) | N(11)-C(11)-C(1) | 120.27(12) |
| O(11)-C(11) | 1.2459(16) | C(11)-N(11)-C(12) | 129.06(12) |
| C(11)-N(11) | 1.3419(18) | C(11)-N(11)-C(15) | 118.80(12) |
| N(11)-C(12) | 1.4745(18) | C(12)-N(11)-C(15) | 111.06(11) |
| N(11)-C(15) | 1.4750(18) | N(11)-C(12)-C(13) | 103.22(11) |
| C(12)-C(13) | 1.524(2) | C(14)-C(13)-C(12) | 102.98(12) |
| C(13)-C(14) | 1.518(2) | C(13)-C(14)-C(15) | 103.14(12) |
| C(14)-C(15) | 1.518(2) | N(11)-C(15)-C(14) | 103.54(12) |
| N(16)-C(17) | 1.3530(16) | C(17)-N(16)-C(1) | 119.93(10) |
| C(17)-O(17) | 1.2101(15) | O(17)-C(17)-N(16) | 124.94(11) |
| C(17)-O(18) | 1.3610(15) | O(17)-C(17)-O(18) | 126.23(11) |
| O(18)-C(19) | 1.4537(16) | N(16)-C(17)-O(18) | 108.8(1) |
| C(19)-C(193) | 1.512(3) | C(17)-O(18)-C(19) | 119.87(10) |
| C(19)-C(191) | 1.519(2) | O(18)-C(19)-C(193) | 111.68(13) |
| C(19)-C(192) | 1.533(2) | O(18)-C(19)-C(191) | 109.18(13) |
| C(21)-C(22) | 1.394(2) | C(193)-C(19)-C(191) | 112.94(15) |
| C(21)-C(26) | 1.3983(19) | O(18)-C(19)-C(192) | 102.01(11) |
| C(22)-C(23) | 1.381(2) | C(193)-C(19)-C(192) | 110.70(15) |
| C(23)-C(24) | 1.393(2) | C(191)-C(19)-C(192) | 109.77(14) |
| C(24)-C(25) | 1.381(2) | C(22)-C(21)-C(26) | 117.88(13) |
| C(25)-C(26) | 1.385(2) | C(22)-C(21)-C(2) | 118.73(12) |
| | | C(26)-C(21)-C(2) | 123.38(12) |
| N(16)-C(1)-C(3) | 116.37(11) | C(23)-C(22)-C(21) | 121.32(14) |
| N(16)-C(1)-C(11) | 119.68(11) | C(22)-C(23)-C(24) | 120.00(14) |
| C(3)-C(1)-C(11) | 114.66(10) | C(25)-C(24)-C(23) | 119.44(14) |
| N(16)-C(1)-C(2) | 117.65(11) | C(24)-C(25)-C(26) | 120.37(14) |
| C(3)-C(1)-C(2) | 58.83(9) | C(25)-C(26)-C(21) | 120.97(13) |
| C(11)-C(1)-C(2) | 115.09(11) | | |
| C(21)-C(2)-C(3) | 122.93(12) | | |

**Table 6.** Torsion angles [°] for C19 H26 N2 O3.

| | |
|---|---|
| N(16)-C(1)-C(2)-C(21) | -6.82(18) |
| C(3)-C(1)-C(2)-C(21) | -112.43(14) |
| C(11)-C(1)-C(2)-C(21) | 142.78(12) |
| N(16)-C(1)-C(2)-C(3) | 105.61(13) |
| C(11)-C(1)-C(2)-C(3) | -104.78(11) |
| C(21)-C(2)-C(3)-C(1) | 109.71(13) |
| N(16)-C(1)-C(3)-C(2) | -107.79(13) |
| C(11)-C(1)-C(3)-C(2) | 105.52(12) |
| N(16)-C(1)-C(11)-O(11) | 160.01(11) |
| C(3)-C(1)-C(11)-O(11) | -54.49(15) |
| C(2)-C(1)-C(11)-O(11) | 11.06(16) |
| N(16)-C(1)-C(11)-N(11) | -21.01(17) |
| C(3)-C(1)-C(11)-N(11) | 124.50(13) |
| C(2)-C(1)-C(11)-N(11) | -169.95(11) |
| O(11)-C(11)-N(11)-C(12) | 166.71(12) |
| C(1)-C(11)-N(11)-C(12) | -12.3(2) |
| O(11)-C(11)-N(11)-C(15) | -0.26(19) |
| C(1)-C(11)-N(11)-C(15) | -179.22(11) |
| C(11)-N(11)-C(12)-C(13) | -154.59(13) |
| C(15)-N(11)-C(12)-C(13) | 13.19(15) |
| N(11)-C(12)-C(13)-C(14) | -32.79(15) |
| C(12)-C(13)-C(14)-C(15) | 40.44(15) |
| C(11)-N(11)-C(15)-C(14) | -179.05(12) |
| C(12)-N(11)-C(15)-C(14) | 11.76(15) |
| C(13)-C(14)-C(15)-N(11) | -32.03(15) |
| C(3)-C(1)-N(16)-C(17) | 147.09(12) |
| C(11)-C(1)-N(16)-C(17) | -67.98(16) |
| C(2)-C(1)-N(16)-C(17) | 80.19(15) |
| C(1)-N(16)-C(17)-O(17) | 1.6(2) |
| C(1)-N(16)-C(17)-O(18) | 179.93(11) |
| O(17)-C(17)-O(18)-C(19) | -3.33(19) |
| N(16)-C(17)-O(18)-C(19) | 178.35(11) |
| C(17)-O(18)-C(19)-C(193) | 58.07(18) |
| C(17)-O(18)-C(19)-C(191) | -67.55(17) |
| C(17)-O(18)-C(19)-C(192) | 176.34(12) |
| C(3)-C(2)-C(21)-C(22) | 165.66(12) |
| C(1)-C(2)-C(21)-C(22) | -122.43(13) |
| C(3)-C(2)-C(21)-C(26) | -13.3(2) |
| C(1)-C(2)-C(21)-C(26) | 58.61(18) |
| C(26)-C(21)-C(22)-C(23) | 1.4(2) |
| C(2)-C(21)-C(22)-C(23) | -177.60(13) |
| C(21)-C(22)-C(23)-C(24) | -1.1(2) |
| C(22)-C(23)-C(24)-C(25) | 0.0(2) |
| C(23)-C(24)-C(25)-C(26) | 0.7(2) |
| C(24)-C(25)-C(26)-C(21) | -0.4(2) |
| C(22)-C(21)-C(26)-C(25) | -0.7(2) |
| C(2)-C(21)-C(26)-C(25) | 178.31(13) |

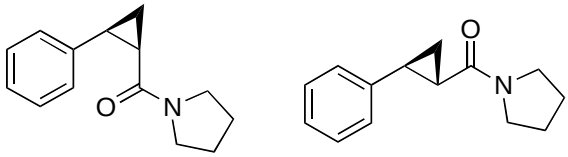
**Table 7.** Bond lengths [Å] and angles [°] related to the hydrogen bonding for C19 H26 N2 O3.

| D-H | ..A | d(D-H) | d(H..A) | d(D..A) | <DHA |
|---|---|---|---|---|---|
| N(16)-H(16) | O(11)#1 | 0.88 | 2.02 | 2.8731(13) | 162.6 |

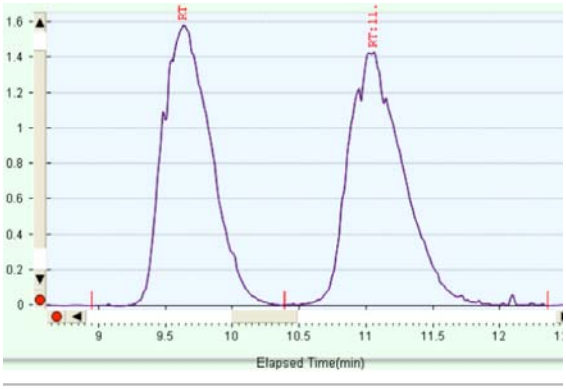
Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,z

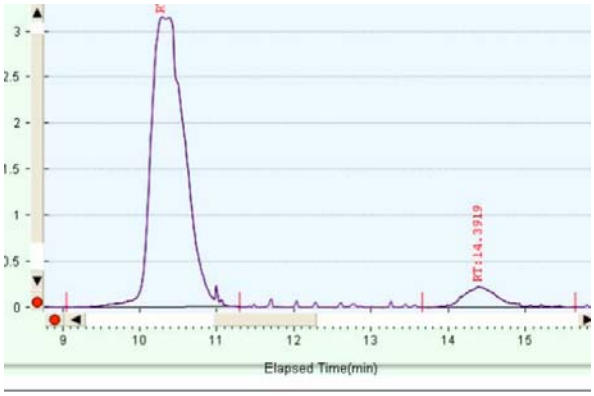
**General procedure for decarboxylation reaction.** A 10-mL microwave vial was charged with the desired amide-ester (1.0 equiv), a magnetic stir bar, *i*-PrOH (0.2 M), and 1N aqueous LiOH (1.5 equiv). The tube was sealed with a Teflon septum and heated to 120 °C under $\mu$-wave irradiation for 30 min. The reaction medium was acidified to pH 3-4 with concentrated acetic acid and heated to 180 °C under $\mu$-wave irradiation for an additional 30 min. The solvent was then removed under reduced pressure. The resulting slurry was partitioned between DCM and water. The organic phase was collected and the aqueous layer was back extracted twice with DCM. The organic layers were combined and washed once with aqueous 3N KOH. The DCM solution was dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. Flash chromatography on silica gel afforded the desired amide (Hexane/EtOAc 80/20).



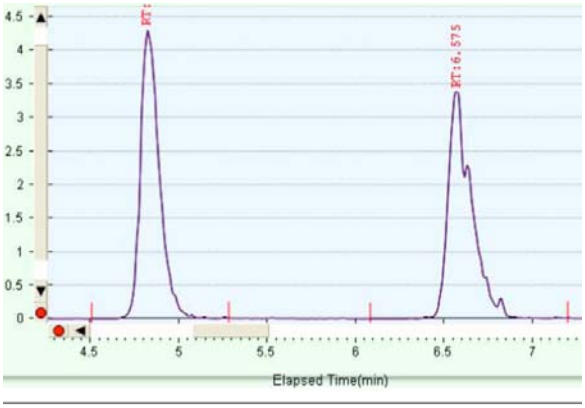

**(2-Phenylcyclopropyl)(pyrrolidin-1-yl)methanone (17).** Prepared according to the general procedure. The product was isolated as a colorless oil. Yield: 76%, diastereomeric ratio (6:1) was determined by $^1$H NMR of the crude mixture, enantiomeric excess (88 and 88% ee) was determined by SFC analysis on chiral phase (Major: Chiralpak AD-H 25 cm, 5% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (major) 10.3 min, $t_r$ (minor) 14.4 min, Minor: Chiralpak AD-H 25 cm, 10% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (major) 4.6 min, $t_r$ (minor) 6.2 min); $R_f$ 0.34 (major), 0.31 (minor) (100%, $Et_2O$); $[\alpha]_D^{20}$ = (Major) +141 (*c* 1.56, $CHCl_3$), (Minor) +60 (*c* 2.86, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (minor) 7.34-7.28 (m, 2H), 7.24-7.7.21 (m, 1H), 7.16-7.13 (m, 2H), 3.66-3.55 (m, 2H), 3.55-3.48 (m, 2H), 2.57-2.51 (m, 1H), 2.05-1.93 (m, 2H), 1.92-1.86 (m, 3H), 1.70-1.67 (m, 1H), 1.33-1.27 (m, 1H), (major) 7.31-7.23 (m, 2H), 7.17-7.14 (m, 3H), 3.53-3.45 (m, 2H), 3.43-3.38 (m, 1H), 3.13-3.05 (m, 1H), 3.52-3.45 (m, 1H), 2.17-2.11 (m, 1H), 1.95-1.83 (m, 2H), 1.79-1.60 (m, 3H), 1.25-1.19 (m, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ (minor) 170.7, 141.4, 128.6 (2C), 126.3 (2C), 126.2, 46.8, 46.3, 26.2, 25.7, 24.9, 24.6, 16.7, (major) 167.6, 137.6, 128.1, 128.0 (2C), 126.3 (2C), 46.5, 45.7, 26.1, 24.9, 24.5, 23.9, 10.3; IR (film) 2972, 2873, 1634, 1446, 1192, 870 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{14}H_{17}N_1O_1$ $[M+H]^+$: 216.1388, found 216.1383.



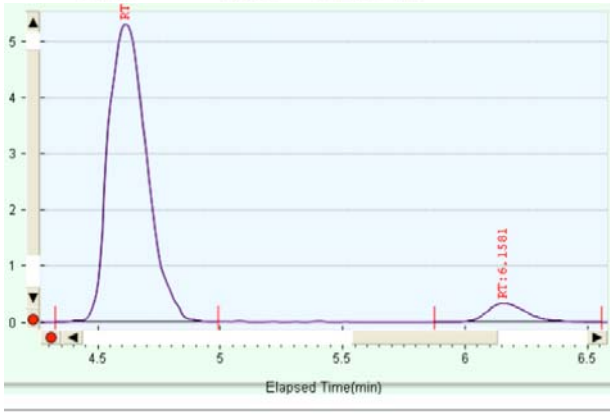

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.2704 | 39.5587 | 9.6417 min |
| | 50.7296 | 40.7303 | 11.0583 min |



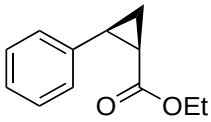

| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 93.3536 | 95.4011 | 10.2836 min |
| | 6.6464 | 6.7921 | 14.3919 min |




| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 50.5147 | 31.4628 | 4.825 min |
| | 49.4853 | 30.8216 | 6.575 min |

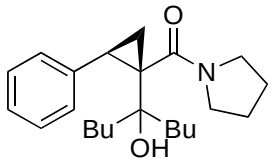



| Name | Area % | Area | Retention Time |
|---|---|---|---|
| | 93.9596 | 57.1996 | 4.6167 min |
| | 6.0404 | 3.6772 | 6.1581 min |

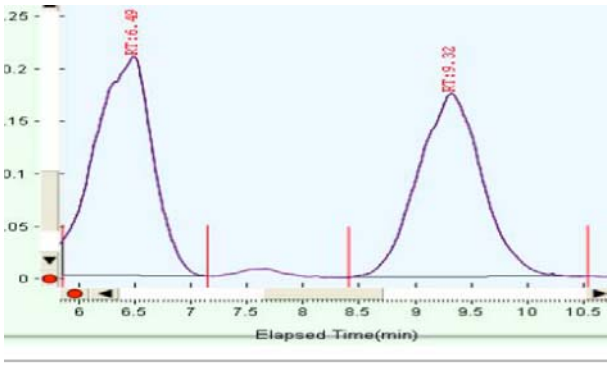



**Ethyl 2-phenylcyclopropanecarboxylate (19)**. A dried 10-mL round bottom flask was charged with a magnetic stir bar, cyclopropane ±*cis*-**17** (30 mg, 0.14 mmol, 1.00 equiv) and DCM (2 mL). The solution was cooled to -40 °C (MeCN/dry ice) and stirred for 5 min. $Tf_2O$ (28 $\mu$L, 0.17 mmol, 1.2 equiv) was added dropwised and the solution was stirred for 30 min. Pyridine (34 $\mu$L, 0.42 mmol, 3.0 equiv) was then added dropwised and the flask was warmed to 25 °C. The reaction mixture was stirred at this temperature for 2 h while the color changed from pale yellow to red. The flask was cooled to 0 °C and EtOH (3 mL) was added. The reaction was allowed to warm to 25 °C overnight (16 h), and was then quenched with saturated aqueous $NaHCO_3$. The biphasic mixture was extracted with DCM (5x3 mL) and the combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. The title compound was obtained following flash chromatography on silica gel (hexane/EtOAc 90/10). Yield: 85%, diastereomeric ratio (>20:1) was determined by $^1$H NMR analysis. The physical data are identical to those of the commercially available product.

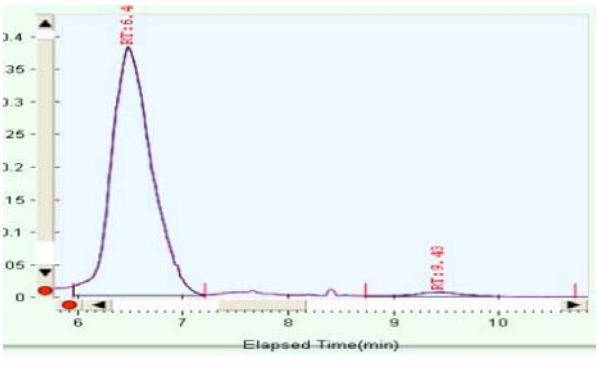
**General procedure for the reaction with $Bu_2CuLi_2CN$:** A dried round bottom flask was charged with a magnetic stir bar, CuCN (1.2 equiv) and $Et_2O$ (0.2 M). The mixture was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. 1.5 M *n*-BuLi in hexanes (2.4 equiv) was added and the flask was immediately removed from the -78 °C bath and placed in a water bath at 25 °C. After stirring for 5 min (yellow solution), the temperature was lowered to -78 °C (dry ice/acetone) and the desired cyclopropane (1.0 equiv) in solution in $Et_2O$/DCM (1/1 mL) was added drop wised. The resulting solution was stirred at this temperature for 10 min and then warmed to 25 °C. After 20 min at 25 °C, the color changed from brown to black. The reaction was then quenched with saturated $NH_4Cl$ (20 mL) and stirred for 1 h. The two phases were separated and the aqueous phase was washed with DCM (15 mL). The combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. Flash chromatography afforded the desired product.



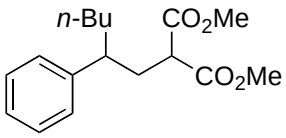

**((1*S*,2*R*)-1-(5-hydroxynonan-5-yl)-2-phenylcyclopropyl)(pyrrolidin-1-yl)methanone (18)**. The general procedure for the reaction with $Bu_2CuLi_2CN$ was followed to afford the title compound as a colorless oil. The reaction was performed with CuCN (2.4 equiv) and BuLi (4.8 equiv). Yield: 77%, enantiomeric excesses (96% ee) were determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 5% MeOH, 3 mL/min, 30 °C, 225 psi, $t_r$ (minor) 11.7 min, $t_r$ (major) 17.4 min and $t_r$ (major) 6.5 min, $t_r$ (minor) 9.4 min); $R_f$ 0.34 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +29 (*c* 2.12, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44-7.40 (m, 2H), 7.31-7.25 (m, 3H), 3.90-3.54 (bs, 2H), 3.52-3.45 (bs, 2H), 2.38 (t app, *J* = 9.0 Hz, 1H), 1.93-1.78 (m, 5H), 1.51-1.15 (m, 12H), 0.79 (t, *J* = 6.8 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 172.3, 137.5, 130.1 (2C), 128.6 (2C), 126.9, 76.6, 48.8, 47.1, 41.7, 39.8, 37.9, 27.5, 26.1, 25.9, 23.5 (2C), 14.3, 14.2, 13.7; IR (film) 3392, 2955, 2871, 1606, 1424, 911, 733 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{23}H_{35}N_1O_2$ $[M+H]^+$: 358.2741, found 358.2732.



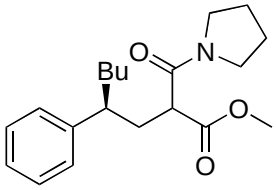

| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 51.9064 | 7.48 | 6.49 min |
| | 2 | 48.0936 | 6.9305 | 9.32 min |




| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 97.9242 | 10.0935 | 6.48 min |
| | 2 | 2.0758 | 0.214 | 9.43 min |

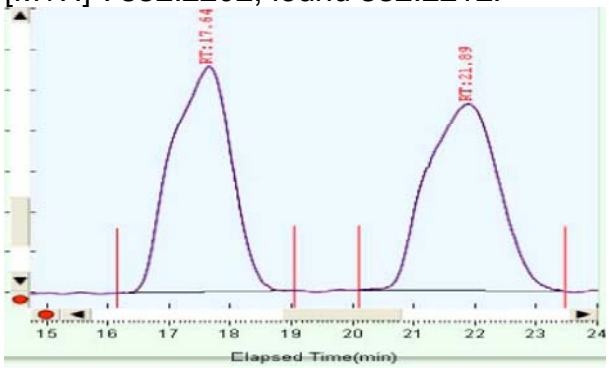



**Dimethyl (2-phenylhexyl)malonate (20).** The crude oil was purified by chromatography on silica gel (10% EtOAc/hexane) to yield 129 mg (88% yield) of a colorless oil: $R_f$ 0.40 (20% EtOAc/hexane); RMN $^1$H (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 2H), 3.73 (s, 3H), 3.59 (s, 3H), 3.16 (dd, *J* = 10.2, 5.0 Hz, 1H), 2.56-2.48 (m, 1H), 2.38-2.31 (m, 1H), 2.16-2.08 (m, 1H), 1.71-1.55 (m, 2H), 1.29-1.08 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H); RMN $^{13}$C (100 MHz, $CDCl_3$) δ 169.7, 143.5, 128.3, 127.5, 126.3, 52.2, 49.6, 43.6, 36.5, 35.5, 29.4, 22.4, 13.7; IR (film) ν 2954, 2929, 2858, 1751, 1733, 1435, 1226, 1200, 1150, 701. HRMS (ESI) calcd for $C_{17}H_{24}O_4$ $[M+H]^+$: 293.1747, found 293.1746.

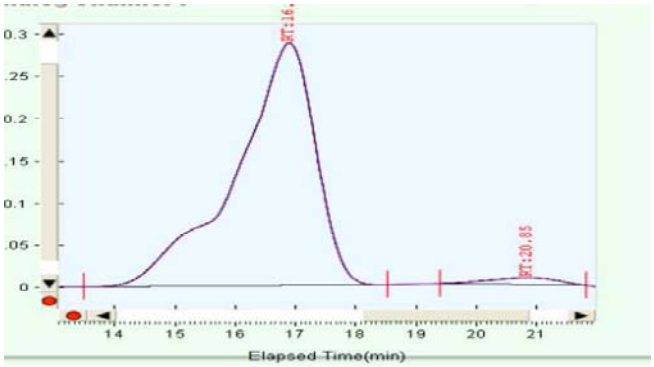



**Methyl 4-phenyl-2-(pyrrolidine-1-carbonyl)octanoate (21)**. A dried 50-mL round bottom flask was charged with a magnetic stir bar, CuCN (108 mg, 1.2 mmol, 6 equiv) and $Et_2O$ (12 mL). The mixture was cooled to -78 °C and stirred for 5 min. 1.5 M *n*-BuLi in hexanes (666 µL, 1.00 mmol, 5.00 equiv) was added and the flask was immediately removed from the -78 °C bath and placed in a water bath at 25 °C. After stirring for 5 min (all the CuCN was dissolved), the temperature was lowered to -78 °C (dry ice/acetone) and cyclopropane **8b** (50 mg, 0.18 mmol, 1.00 equiv) in $Et_2O$ (2 mL) was added drop wised. The resulting solution was stirred at this temperature for 10 min and then warmed to 25 °C. After 20 min at 25 °C, the color changed from brown to black. The reaction was then quenched with saturated $NH_4Cl$ (20 mL) and stirred for 1 h. The two phases were separated and the aqueous phase was washed with DCM (15 mL). The combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under

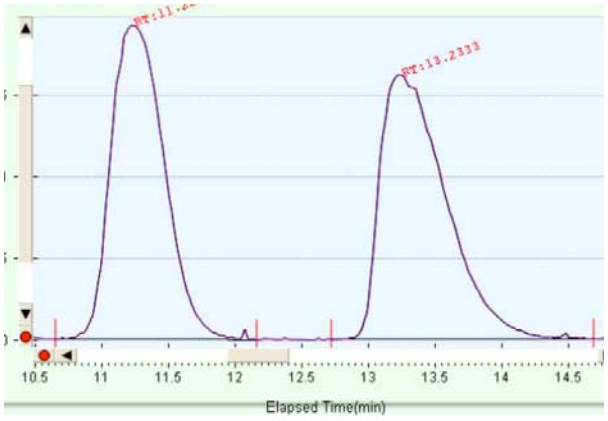
vacuum. The titled compound was then obtained after flash chromatography on silica gel using hexane to hexane:$Et_2O$ 50:50. Isolated as a colorless oil. Yield: 70% (combined yield), diastereomeric ratio (1:1) was determined by $^1H$ NMR analysis, enantiomeric excesses (96.0% and 95.4% ee) were determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 3% MeOH, 3 mL/min, 30 °C, 225 psi, $t_r$ (minor1) 11.9 min, $t_r$ (major1) 14.0 min and $t_r$ (major2) 16.9 min, $t_r$ (minor2) 20.9 min); $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.33-7.27 (m, 4H), 7.24-7.18 (m, 2H), 7.14 (d, $J$ = 7.2 Hz, 2H), 7.10 (d, $J$ = 7.2 Hz, 2H), 3.74 (s, 3H), 3.65 (s, 3H), 3.54-3.50 (m, 2H), 3,41-3.35 (m, 1H), 3.33-3.26 (m, 1H), 3.21-3.10 (m, 3H), 2.61-2.46 (m, 4H), 2.10-1.99 (m, 1H), 1.97-1.89 (m, 1H), 1.86-1.73 (m, 8H), 1.70-1.54 (m, 4H), 1.38-1.25 (m, 10H), 0.87-0,79 (m, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 170.5, 170.3, 167.2, 166.4, 144.4, 144.3, 128.4 (2C), 128.3 (2C), 127.7 (2C), 127.5 (2C), 126.2, 52.1, 48.8, 48.0, 46.3, 46.2, 45.8, 45.7, 44.2, 43.1, 37.4, 36.6, 35.8, 35.0, 30.2, 29.6, 29.5, 29.5, 25.7, 25.6, 24.2, 24.0, 22.3, 22.5, 13.8; IR (film) 3050, 2954, 2927, 2872, 1745, 1646, 1434, 1161 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{20}H_{29}N_1O_3$ $[M+H]^+$: 332.2202, found 332.2212.



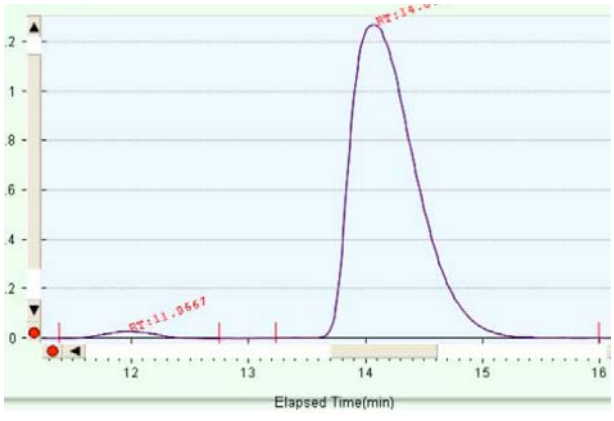

| me | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 49.9337 | 3.7624 | 17.64 min |
| | 2 | 50.0663 | 3.7724 | 21.89 min |




| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 97.5738 | 26.1243 | 16.89 min |
| | 2 | 2.4262 | 0.6496 | 20.85 min |



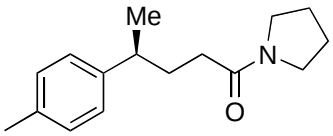

| ame | Area % | Area | Retention Time |
|---|---|---|---|
| | 49.1101 | 53.4788 | 11.225 min |
| | 50.8899 | 55.4169 | 13.2333 min |



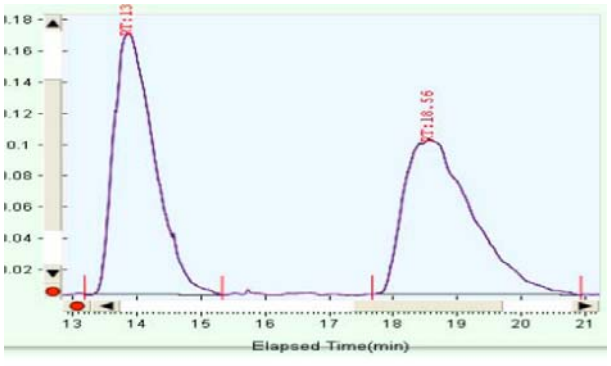

| lame | Area % | Area | Retention Time |
|---|---|---|---|
| | 1.8093 | 0.896 | 11.9667 min |
| | 98.1907 | 48.6257 | 14.0667 min |

**General procedure for the MeCuLiCN/decarboxylation sequence:** A dried round bottom flask was charged with a magnetic stir bar, CuCN (8.0 equiv) and $Et_2O$ (0.2 M).

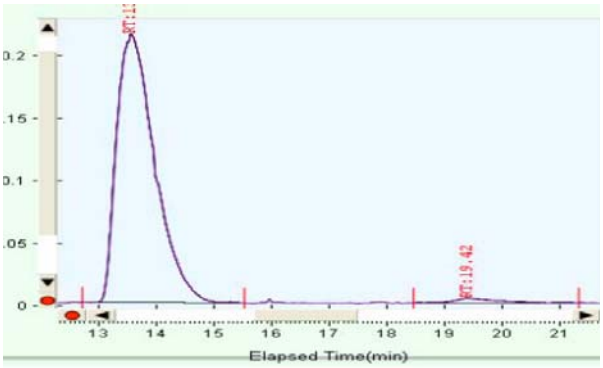
The mixture was cooled to -78 °C (dry ice/acetone) and stirred for 5 min. 1.5 M MeLi in $Et_2O$ (7.0 equiv) was added and the flask was immediately removed from the -78 °C bath and placed in a water bath at 25 °C. After stirring for 5 min (yellow precipitate), the temperature was lowered to -78 °C (dry ice/acetone) and the desired cyclopropane (1.0 equiv) in solution in $Et_2O$/DCM (1/1 mL) was added dropwise. The resulting solution was stirred at this temperature for 10 min and then warmed to 25 °C. The flask was then equipped of a room-temperature condenser and heated to 60 °C for 16 h. The temperature was lowered to room-temperature and the black solid was partitioned between saturated $NH_4Cl$ (20 mL) $Et_2O$ (5 mL). The resulting mixture was stirred for 1 h. The two layers were separated and the aqueous layer was washed with DCM (15 mL). The combined organic layers were dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. The crude product was then submitted to the general procedure for decarboxylation reaction. Flash chromatography afforded the desired amide.



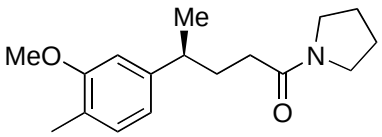

**1-(Pyrrolidin-1-yl)-4-*p*-tolylpentan-1-one (22)**. The general procedure for the MeCuLiCN/decarboxylation sequence was followed using **10h**. Isolated a a brownish solid. Yield: 68%, enantiomeric excesses (96% ee) were determined by SFC analysis on chiral phase (Chiralpak OD-H 25 cm, 5% MeOH, 3 mL/min, 40 °C, 150 psi, $t_r$ (major) 13.9 min, $t_r$ (minor) 18.6 min); mp 80-84 °C; $R_f$ 0.30 (100%, $Et_2O$); $[\alpha]_D^{20}$ = +39 (*c* 1.00, $CHCl_3$); $^1$H NMR (300 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 8.4 Hz, *J* = 10.8 Hz, 4H), 3.44 (td, *J* = 2.6 Hz, *J* = 6.8 Hz, 2H), 3.22 (td, *J* = 2.3 Hz, *J* = 6.7 Hz, 2H), 2.68-2.78 (m, 1H), 2.43 (s, 3H), 2.20-1.79 (m, 8H), 1.27 (d, *J* = 6.9 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 171.8, 143.9, 135.6, 129.2 (2C), 127.1 (2C), 46.6, 45.7, 39.4, 33.2, 33.0, 26.2, 24.6, 22.9, 21.2; IR (film) 3050, 2955, 2873, 1627, 1444, 1256, 909, 730 cm$^{-1}$; HRMS (ES, Pos) Calcd for $C_{16}H_{23}N_1O_1$ $[M+H]^+$: 246.1852, found 246.1851.




| : Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 49.9337 | 7.3519 | 13.86 min |
| | 2 | 50.0663 | 7.3714 | 18.56 min |

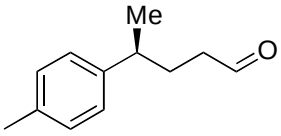



| Name | Peak Number | Area % | Area | Retention Time |
|---|---|---|---|---|
| | 1 | 98.0627 | 9.8088 | 13.57 min |
| | 2 | 1.9373 | 0.1938 | 19.42 min |

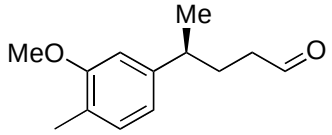



**4-(3-Methoxy-4-methylphenyl)-1-(pyrrolidin-1-yl)pentan-1-one (24)**. The general procedure for the MeCuLiCN/decarboxylation sequence was followed using *rac*-**10aa**. Isolated as a brownish oil. Yield: 65%; $R_f$ 0.38 (100%, $Et_2O$); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 7.00 (d, $J$ = 7.5 Hz, 1H), 6.66 (d, $J$ = 7.5 Hz, 1H), 6.63 (s, 1H), 3.78 (s, 3H), 3.42-3.36 (m, 2H), 3.22-3.14 (m, 2H), 2.72-2.60 (m, 1H), 2.14 (s, 3H), 2.12-1.65 (m, 8H), 1.22 (d, $J$ = 7.2 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 171.7, 157.8, 145.9, 130.5, 124.2, 118.8, 108.9, 60.5, 45.6, 45.7, 39.8, 33.1, 32.9, 26.2, 24.5, 22.9, 14.1; IR (film) 3050, 2955, 2873, 1627, 1444, 1256, 909, 730 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{17}H_{25}N_1O_2$ $[M+H]^+$: 276.1958, found 276.1964.

**General procedure for the reduction with $LiAlH(OEt)_3$:** A 10-mL dried round bottom flask was charged with a magnetic stir bar, LAH (1.1 equiv), $Et_2O$ (0.2 M) and cooled to 0 °C. To the stirred solution was added EtOH (3.3 equiv) in $Et_2O$ (1.0 M) over 2 h using a syringe pump. In a second 10-mL dried round bottom flask was charged with a magnetic stir bar, the corresponding amide (1.0 equiv), $Et_2O$ (0.2 M) and cooled to 0 °C. To this solution was added the $LiAlH(OEt)_3$ over a period of 15 min. The flask containing the aluminum reagent was rinsed with $Et_2O$ and added to the amide solution over 5 min. The mixture was stirred at 0 °C for 1 h. Aqueous 10% HCl (2 mL) was added and the biphasic mixture was stirred for 30 min. The layer were separated and the aqueous layer was extracted twice with DCM (2x2 mL) and twice with $Et_2O$ (2x2 mL). The organic layers were combined, dried with $MgSO_4$, filtered over Celite®, and concentrated under vacuum. Flash chromatography afforded the desired aldehyde.




**4-*p*-Tolylpentanal (23)**. The general procedure for the reduction with $LiAlH(OEt)_3$. Isolated as a colorless oil. Yield: 55-67%; $R_f$ 0.51 (10%, $Et_2O$/Hexanes); $[\alpha]_D^{20}$ = +35 (*c* 0.7, $CHCl_3$); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 9.69 (t, $J$ = 1.5 Hz, 1H), 7.09 (dd, $J$ = 8.0 Hz, $J$ = 17.6 Hz, 4H), 2.75-2.63 (m, 1H), 2.33 (s, 3H), 2.37-2.30 (m, 2H), 1.97-1.83 (m, 2H), 1.27 (d, $J$ = 6.9 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 202.7, 143.2, 136.0, 129.4 (2C), 127.1 (2C), 42.5, 39.1, 30.6, 22.6, 21.2; IR (film) 3043, 2956, 2923, 2854, 1726, 1456, 1376 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{12}H_{16}O_1$ $[M+H]^+$: 177.1274, found 177.1274.



**4-(3-Methoxy-4-methylphenyl)pentanal (25)**. The general procedure for the reduction with $LiAlH(OEt)_3$. Isolated as a colorless oil. Yield: 41-54%; $R_f$ 0.43 (10%, $Et_2O$/Hexanes); $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 9.67 (t, $J$ = 1.1 Hz, 1H), 7.03 (d, $J$ = 7.6 Hz, 1H), 6.64 (d, $J$ = 7.6 Hz, 1H), 6.60 (s, 1H), 3.80 (s, 3H), 2.69-2.61 (m, 1H), 2.36-2.27 (m, 2H), 2.16 (s, 3H), 1.93-1.82 (m, 2H), 1.24 (d, $J$ =7.0 Hz, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 202.8, 158.0, 145.2, 130.8, 124.7, 118.8, 109.0, 55.5, 42.5, 39.6, 30.6, 22.7, 16.1; IR (film) 3050, 2979, 2850, 2252, 1703, 1627, 1452, 907 $cm^{-1}$; HRMS (ES, Pos) Calcd for $C_{13}H_{19}O_2$ $[M+H]^+$: 207.1380, found 207.1388.