Asymmetric construction of trifluoromethylated pyrrolidines via
Cu(I)-catalyzed 1,3-dipolar cycloaddition of azomethine ylides with
4,4,4-trifluoroacrotonates

Qing-Hua Li, Min-Chao Tong, Jun Li, Hai-Yan Tao, and Chun-Jiang Wang*

College of Chemistry and Molecular Sciences, Wuhan University, 430072, China

E-mail: cjwang@whu.edu.cn

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General Remarks.

$^1$H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer in CDCl$_3$. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quartet, m = multiple or unresolved, brs = broad single, coupling constant(s) in Hz, integration). $^{13}$C NMR spectra were recorded on a VARIAN Mercury 75 or VARIAN Mercury 150 MHz spectrometer in CDCl$_3$. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Diastereomeric ratios were determined from crude $^1$H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralcel AD-H column, a chiralpak AS-H column with hexane and $i$-PrOH as solvents. Ligands L3-L7 were prepared according to the literature procedure reported by us.$^1$ trans and cis-4,4,4-Trifluorocrotonates were prepared according to the literature procedure.$^2$ The racemic adducts were obtained by using AgOAc/PPh$_3$ as the catalyst. The absolute configuration of (2$R$,3$S$,4$R$,5$S$)-6cg and (2$R$,3$S$,4$S$,5$S$)-7cg achieved by Cu(CH$_3$CN)$_4$BF$_4$/($S$)-TF-Biphos L7 was determined unequivocally according to the X-ray diffraction analysis, and those of other adducts were deduced on the basis of these results.

General Procedure for racemic 1,3-Dipolar Cycloaddition of Azomethine Ylides with trans or cis-4,4,4-Trifluorocrotonates Catalyzed by AgOAc/PPh$_3$ Complex

Under argon atmosphere, PPh$_3$ (6.6 mg, 0.0253 mmol) and AgOAc (3.8 mg, 0.023 mmol) were dissolved in 2 mL DCM, and stirred at room temperature for about 1h. Then, imine substrate (0.35 mmol), Et$_3$N (0.03 mmol) and trans or cis-4,4,4-Trifluorocrotonates (0.23 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the organic solvent was removed and the residue was purified by column chromatography to give the cycloaddition product, which was used as the racemic sample for the chiral HPLC analysis.
General Procedure for Asymmetric 1,3-Dipolar Cycloaddition of Azomethine Ylides with trans or cis-4,4,4-Trifluorocrotonates Catalyzed by Cu(CH₃CN)₄BF₄ /[S]-TF-BiphamPhos Complex

Under argon atmosphere ([S]-TF-BiphamPhos L7 (6.1 mg, 0.0076 mmol) and Cu(CH₃CN)₄BF₄ (2.1 mg, 0.0069 mmol) were dissolved in 2 mL DCM, and stirred at room temperature for about 1h. Then, imine substrate (0.35 mmol), Et₃N (0.03 mmol) and trans or cis-4,4,4-Trifluorocrotonates (0.23 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the mixture was filtered through celite and the filtrate was concentrated to dryness. The product purified by column chromatography to give the corresponding cycloaddition product, which was then directly analyzed by chiral HPLC to determine the enantiomeric excess.

![Image](image.png)

(3aa)

(2R,3R,4R,5S)-4-ethyl 2-methyl 5-phenyl-3-(trifluoromethyl)pyrrolidine-2,4-di-carboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. m.p. 57 °C; [α]_{D}^{25} = -30.7 (c 0.88, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.24 (m, 5H), 4.55 (d, J = 7.8 Hz, 1H), 3.99 (d, J = 6.3 Hz, 1H), 3.78 (s, 3H), 3.70-3.60 (m, 1H), 3.56-3.48 (m, 2H); 3.33-3.30 (m, 1H); 2.87 (brs, 1H), 0.68 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, TMS, 75 MHz) δ 171.17, 170.87, 136.73, 128.49, 128.30, 126.69, 126.32 (q, J_CF = 270.4Hz), 65.82, 61.00, 60.40, 52.79, 50.89, 50.11 (q, J_CF = 27.2Hz), 13.36; IR (KBr) ν 3683, 3622, 3021, 2975, 2400, 1731, 1516, 1426, 1215, 1045, 929, 756 cm⁻¹. The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 5.64 and 6.68 min.
(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-phenyl-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 82% yield. m.p. 85 °C; [α]$_D^{25}$ = -29.0 (c 1.0, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 7.27-7.20 (m, 5H), 4.51 (d, $J = 7.5$ Hz, 1H), 3.95 (d, $J = 6.6$ Hz, 1H), 3.78 (s, 3H), 3.48-3.41 (m, 1H), 3.29-3.26 (m, 1H); 2.77 (brs, 1H), 0.93 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 150 MHz) δ 171.18, 169.91, 136.82, 128.18, 127.70, 126.97, 126.40 (q, $J_{CF} = 277.2$ Hz), 81.63, 65.51, 60.45, 52.73, 51.31, 50.91 (q, $J_{CF} = 28.4$ Hz), 27.26; IR (KBr) ν 3684, 3622, 3019, 2977, 2439, 1746, 1715, 1520, 1477, 1370, 1216, 1046, 929, 849, 754, 744, 669 cm$^{-1}$. HRMS: calcd. for C$_{18}$H$_{22}$F$_3$NO$_4$: 373.1501, found. 373.1502. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralcel AS-H, $i$-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t$_r$ = 5.84 and 7.81 min.

(3bb)

(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-p-tolyl-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 72% yield. m.p. 82 °C; [α]$_D^{25}$ = -52.1 (c 0.36, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 7.24-7.13 (m, 4H), 4.60 (d, $J = 6.9$ Hz, 1H), 4.08 (d, $J = 6.9$ Hz, 1H), 3.87 (s, 3H), 3.52-3.47 (m, 1H), 3.36-3.34 (m, 1H), 2.33 (s, 3H), 1.04 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 171.21, 170.00, 137.44, 133.71, 128.84, 126.87, 126.42 (q, $J_{CF} = 277.2$ Hz), 81.66, 65.42, 60.54, 52.78, 51.46, 51.03 (q, $J_{CF} = 27.2$ Hz),
27.35, 20.98; IR (KBr) ν 3684, 3621, 3019, 2898, 2400, 1744, 1521, 1423, 1216, 1045, 929, 776 cm\(^{-1}\). HRMS: calcd. for C\(_{19}\)H\(_{24}\)F\(_3\)NO\(_4\): 387.1657, found. 387.1655 The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralcel AS-H, \(i\)-propanol/hexane = 2/98, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 4.17\) and 4.78 min.

(3bc)

\((2R,3R,4R,5S)-4\text{-}\text{tert-}\text{butyl} 2\text{-methyl} 5\text{-}o\text{-tolyl}3\text{-}(\text{trifluoromethyl})\text{pyrrolidine}-2,4\text{-}\text{dicarboxylate}\)

The title compound was prepared according to the general procedure as described above in 87% yield. m.p. 73 °C; [\(\alpha\)]\(^{25}\)_D = -68.9 (c 0.65, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta\) 7.40-7.37 (m, 1H), 7.22-7.18 (m, 3H), 4.69 (d, \(J = 7.5\) Hz, 1H), 4.06 (d, \(J = 6.9\) Hz, 1H), 3.88 (s, 3H), 3.67-3.60 (m, 1H), 3.45-3.41 (m, 1H), 2.38 (s, 3H), 0.96 (s, 9H); \(^1^3\)C NMR (CDCl\(_3\), TMS, 75 MHz) \(\delta\) 171.24, 170.04, 137.79, 136.66, 128.45, 128.16, 127.58, 126.46 (q, \(J_{CF} = 276.7\) Hz), 124.10, 81.60, 65.63, 60.56, 52.78, 51.41, 51.00 (q, \(J_{CF} = 27.2\) Hz), 27.34, 21.30; IR (KBr) ν 3684, 3620, 3019, 2977, 2400, 1746, 1521, 1423, 1221, 1046, 929, 782, 751, 669 cm\(^{-1}\). HRMS: calcd. for C\(_{19}\)H\(_{24}\)F\(_3\)NO\(_4\): 387.1657, found. 387.1659. The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralcel AS-H, \(i\)-propanol/hexane = 2/98, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 5.40\) and 7.44 min.

(3bd)
(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-m-tolyl-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 88% yield. m.p. 82 °C; [α]$_D^{25}$ = -31.2 (c 0.80, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 7.26-7.08 (m, 4H), 4.59 (d, J = 7.2 Hz, 1H), 4.07 (d, J = 6.3 Hz, 1H), 3.87 (s, 3H), 3.54-3.47 (m, 1H), 3.37-3.33 (m, 1H), 2.34 (s, 3H), 1.03 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) 171.21, 170.02, 137.78, 136.61, 128.45, 128.16, 127.55, 126.37 (q, J$_{CF}$ = 267.8 Hz), 124.07, 81.60, 65.61, 60.52, 52.78, 51.38, 50.97 (q, J$_{CF}$ = 26.1 Hz), 27.32, 21.30; IR (KBr) ν 3685, 3624, 3017, 2977, 2400, 1735, 1519, 1420, 1215, 1046, 929, 753 cm$^{-1}$. HRMS: calcd. for C$_{19}$H$_{24}$F$_3$NO$_4$: 387.1657, found. 387.1656. The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); ti = 5.36 and 6.83 min.

(3be)

(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-(4-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 88% yield. m.p. 74 °C; [α]$_D^{25}$ = -32.3 (c 0.85, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) δ 7.29-7.26 (d, J = 7.8 Hz, 2H), 6.89-6.86 (d, J = 8.1 Hz, 2H), 4.57 (d, J = 7.2 Hz, 1H), 4.05 (d, J = 6.3 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.52 (m, 1H), 3.35-3.32 (m, 1H), 1.06 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) δ 171.21, 170.01, 159.26, 128.91, 128.14, 126.73 (q, J$_{CF}$ = 268.8 Hz), 113.64, 81.67, 65.08, 60.43, 55.30, 52.79, 51.41, 50.91 (q, J$_{CF}$ = 27.2 Hz), 27.41; IR (KBr) ν 3684, 3622, 3019, 1745, 1715, 1424, 1216, 1046, 929, 754, 731, 669 cm$^{-1}$. HRMS: calcd. for C$_{19}$H$_{24}$F$_3$NO$_5$: 403.1607, found. 403.1610 The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralcel AS-H,
*i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 5.58$ and 6.50 min.

$\text{(3bf)}$

(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-(2-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 74% yield. m.p. 80 $^\circ$C; $[\alpha]_{D}^{25} = -79.0$ (c 0.88, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ 7.31-7.26 (m, 2H), 6.96-6.86 (m, 2H), 4.67 (d, $J = 7.2$ Hz, 1H), 4.02 (d, $J = 6.9$ Hz, 1H), 3.87 (s, 3H), 3.61-3.58 (m, 1H), 3.50 (m, 1H), 0.97 (s, 9H); $^13$C NMR (CDCl$_3$, TMS, 75 MHz) 171.31, 170.51, 156.96, 128.77, 126.59 (q, $J_{CF} = 277.1$ Hz), 126.30, 125.17, 120.32, 109.76, 81.10, 61.44, 60.28, 55.16, 52.72, 51.03 (q, $J_{CF} = 27.2$ Hz), 49.48, 27.30; IR (KBr) v 3683, 3621, 3019, 2977, 1731, 1521, 1423, 1216, 1046, 929, 770, 629 cm$^{-1}$. HRMS: calcd. for C$_{19}$H$_{24}$F$_3$NO$_5$: 403.1607, found. 403.1609 The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (Chiralcel AS-H, *i*-propanol/hexane = 2/98, flow rate 1.0 mL/min, $\lambda = 220$ nm); $t_r = 6.27$ and 8.60 min.

$\text{(3bg)}$

(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-(4-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 76% yield. m.p. 71 $^\circ$C; $[\alpha]_{D}^{25} = -32.9$ (c 0.76, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ 7.32 (m, 4H), 4.60 (d, $J = 6.0$ Hz, 1H), 4.08 (d, $J = 6.0$ Hz, 1H), 3.87 (s, 3H), 3.54 (m, 1H), 3.34 (m, 1H); 1.06 (s, 9H); $^13$C NMR (CDCl$_3$, TMS, 150
MHz) δ 171.06, 169.64, 135.59, 133.59, 128.47, 128.31, 126.33 (q, J_CF = 277.2 Hz), 81.95, 64.78, 60.30, 52.81, 51.10, 50.46 (q, J_CF = 26.9 Hz), 27.37; IR (KBr) ν 3683, 3583, 3020, 2400, 2361, 1744, 1522, 1421, 1216, 1016, 929, 770, 669 cm⁻¹. HRMS: calcd. for C_{18}H_{21}ClF_3NO_4: 407.1111, found. 407.1108 The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 4.91 and 5.72 min.

(3bh)

(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-(2-chlorophenyl)-3-(trifluoromethyl) pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. m.p. 104 °C; [α]_{D}^{25} = -74.7 (c 0.61, CHCl_3); ^1H NMR (CDCl_3, TMS, 300 MHz) δ 7.51-7.24 (m, 4H), 4.79 (d, J = 7.2 Hz, 1H), 4.00 (d, J = 6.3 Hz, 1H), 3.85 (s, 3H), 3.66-3.64 (m, 2H), 0.98 (s, 9H); ^13C NMR (CDCl_3, TMS, 150 MHz) δ 171.03, 169.72, 134.94, 133.90, 129.21, 128.97, 127.62, 126.79, 126.47 (q, J_CF = 277.1 Hz), 81.58, 62.53, 59.62, 52.82, 49.89 (q, J_CF = 25.8 Hz), 48.37, 27.28; IR (KBr) ν 3684, 3622, 3019, 2977, 2400, 1747, 1520, 1423, 1216, 1046, 929, 757, 669 cm⁻¹. HRMS: calcd. for C_{18}H_{21}ClF_3NO_4: 407.1111, found. 407.1110 The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 6.13 and 9.23 min.

(3bi)

(2R,3R,4R,5S)-4-tert-butyl 2-methyl 5-(3-chlorophenyl)-3-(trifluoromethyl)
**pyrrolidine-2,4-dicarboxylate**

The title compound was prepared according to the general procedure as described above in 80% yield. m.p. 115 °C; [α]$_{D}^{25}$ = -68.0 (c 0.25, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ 7.37-7.26 (m, 4H), 4.73 (d, $J$ = 6.0 Hz, 1H), 4.25 (d, $J$ = 6.3 Hz, 1H), 3.91 (s, 3H), 3.55-3.43 (m, 2H), 1.11 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 75 MHz) $\delta$ 170.98, 169.58, 139.15, 134.26, 129.58, 127.97, 127.40, 125.26, 124.53, 82.05, 64.88, 60.31, 52.87, 51.05, 27.39; IR (KBr) ν 3615, 3584, 3019, 2965, 2400, 1747, 1520, 1422, 1216, 1046, 929, 772, 757, 669 cm$^{-1}$. HRMS: calcd. for C$_{18}$H$_{21}$ClF$_3$NO$_4$: 407.1111, found. 407.1114 The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, $\lambda$ = 220 nm); $t_e$ = 6.88 and 9.57 min.

(3bj)

**(2R,3R,4R,5S)-4-**tert**-butyl 2-methyl 5-(4-bromophenyl)-3-(trifluoromethyl) pyrrolidine-2,4-dicarboxylate**

The title compound was prepared according to the general procedure as described above in 83% yield. m.p. 108 °C; [α]$_{D}^{25}$ = -32.9 (c 0.52, CHCl$_3$); $^1$H NMR (CDCl$_3$, TMS, 300 MHz) $\delta$ 7.50-7.47 (m, 2H), 7.28-7.25 (m, 2H), 4.57 (d, $J$ = 7.5 Hz, 1H), 4.06 (d, $J$ = 5.7 Hz, 1H), 3.87 (s, 3H), 3.54 (m, 1H), 3.36-3.34 (m, 1H); 1.07 (s, 9H); $^{13}$C NMR (CDCl$_3$, TMS, 150 MHz) $\delta$ 171.01, 169.59, 136.05, 131.27, 128.82, 126.30 (q, $J_{CF} = 276.0$ Hz), 121.65, 81.99, 64.79, 60.27, 52.85, 51.04, 50.60 (q, $J_{CF} = 27.0$ Hz), 27.37; IR (KBr) ν 36845, 3622, 3019, 2977, 2400, 1745, 1521, 1423, 1216, 1046, 929, 773, 669 cm$^{-1}$. HRMS: calcd. for C$_{18}$H$_{21}$BrF$_3$NO$_4$: 451.0606, found. 451.0611 The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, $\lambda$ = 220 nm); $t_e$ = 5.07 and 6.02 min.
The title compound was prepared according to the general procedure as described above in 90% yield. m.p. 76 °C; [α]^{25}_D = +7.4 (c 0.61, CHCl₃); ^1H NMR (CDCl₃, TMS, 300 MHz) δ 7.33 (m, 1H), 6.32-6.26 (m, 2H), 4.64 (d, J = 7.2 Hz, 1H), 4.02 (d, J = 5.7 Hz, 1H), 3.80-3.75 (m, 4H), 3.41-3.37 (m, 1H), 1.24 (s, 9H); ^13C NMR (CDCl₃, TMS, 150 MHz) 171.73, 168.84, 151.51, 141.96, 126.51 (q, J_{CF} = 277.2 Hz), 110.35, 107.54, 81.88, 60.19, 59.26, 52.84, 50.34, 49.14 (q, J_{CF} = 26.9 Hz), 27.53; IR (KBr) ν 3684, 3621, 3019, 2977, 2400, 1742, 1522, 1423, 1217, 1046, 929, 770, 669 cm⁻¹. HRMS: calcd. for C₁₆H₂₀F₃NO₅: 363.1294, found. 363.1292. The product was analyzed by HPLC to determine the enantiomeric excess: 88% ee (Chiralcel AS-H, i-propanol/hexane = 2/98, flow rate 1.0 mL/min, λ = 220 nm); t_r = 7.41 and 10.39 min.

The title compound was prepared according to the general procedure as described above in 65% yield. m.p. 88 °C; [α]^{25}_D = -22.2 (c 0.35, CHCl₃); ^1H NMR (CDCl₃, TMS, 300 MHz) δ 7.35-7.30 (m, 5H), 4.82 (d, J = 9.0 Hz, 1H), 3.92-3.86 (m, 4H), 3.51-3.46 (m, 1H), 1.60 (s, 3H), 0.99 (s, 9H); ^13C NMR (CDCl₃, TMS, 150 MHz) 173.57, 169.64, 137.90, 128.17, 127.93, 127.75, 126.08 (q, J_{CF} = 277.1 Hz), 81.40, 65.91, 62.66, 52.98, 52.73 (q, J_{CF} = 28.1 Hz), 51.08, 27.25, 19.79; IR (KBr) ν 3684,
3621, 3019, 2977, 2400, 1731, 1522, 1216, 1046, 929, 770, 669 cm\(^{-1}\). HRMS: calcd. for C\(_{19}\)H\(_{24}\)F\(_3\)N\(_4\): 387.1657, found. 387.1654 The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (Chiralcel AS-H, \(i\)-propanol/hexane = 2/98, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 5.66\) and 7.00 min.

\[
\begin{align*}
\text{EtO}_2\text{C}_\alpha & \quad \text{CF}_3 \\
& \quad \text{N} \\
& \quad \text{CO}_2\text{Me}
\end{align*}
\]

(4ca)

(2\(R\),3\(S\),4\(R\),5\(S\))-4-ethyl 2-methyl 5-phenyl-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 87% yield. m.p. 118 \(^{\circ}\)C; \([\alpha]^{25}\text{D} = -44.3\) (c 1.05, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), TMS, 300 MHz) \(\delta 7.36-7.29\) (m, 5H), 4.49 (d, \(J = 3.9\) Hz, 1H), 4.32 (d, \(J = 9.6\) Hz, 1H), 3.84-3.80 (m, 5H), 3.74-3.69 (m, 1H), 3.56-3.52 (m, 1H), 3.25 (brs, 1H), 0.91 (t, \(J = 7.5\) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), TMS, 150 MHz) 169.97, 168.82, 136.11, 128.36, 127.64, 126.18, 125.04 (q, \(J_{CF} = 277.2\) Hz), 64.70, 60.68, 58.56, 52.55, 50.20, 13.51; IR (KBr) \(\nu 3684, 3622, 3019, 2977, 2400, 1750, 1522, 1437, 1216, 1046, 929, 770, 669\) cm\(^{-1}\). HRMS: calcd. for C\(_{16}\)H\(_{18}\)F\(_3\)N\(_4\): 345.1188, found. 345.1192. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee 96:4 dr (Chiralcel AS-H, \(i\)-propanol/hexane = 5/95, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 11.02\) and 35.62 min.

\[
\begin{align*}
\text{EtO}_2\text{C}_\alpha & \quad \text{CF}_3 \\
& \quad \text{N} \\
& \quad \text{CO}_2\text{Me}
\end{align*}
\]

(4ce)

(2\(R\),3\(S\),4\(R\),5\(S\))-4-ethyl 2-methyl 5-(4-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described
above in 82% yield. m.p. 120 °C; \([\alpha]^{25}_D = -34.7\) (c 0.56, CHCl₃); \(^1\)H NMR (CDCl₃, TMS, 300 MHz) \(\delta 7.29-7.26\) (m, 2H), 6.89-6.86 (m, 2H), 4.42 (d, \(J = 4.2\) Hz, 1H), 4.30 (d, \(J = 10.2\) Hz, 1H), 3.88- 3.80 (m, 8H), 3.70-3.61 (m, 1H), 3.50-3.48 (m, 1H), 0.96 (t, \(J = 7.2\) Hz, 3H); \(^13\)C NMR (CDCl₃, TMS, 150 MHz) 169.97, 168.89, 158.87, 128.11, 127.25, 125.03 (q, \(J_{CF} = 277.1\) Hz) 113.59, 64.17, 60.50, 58.46, 55.04, 52.52 (q, \(J_{CF} = 28.1\) Hz), 52.35, 50.18, 13.48; IR (KBr) ν 3684, 3621, 3019, 2976, 2400, 1744, 1518, 1424, 1216, 1045, 929, 758, 669 cm\(^{-1}\). HRMS: calcd. for C\(_{17}\)H\(_{20}\)F\(_3\)NO\(_5\): 375.1294, found. 375.1296. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee >98:2 dr (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 12.54\) and 26.19 min.

\[
\text{(4cg)}
\]

\((2R,3S,4R,5S)-4\text{-ethyl 2-methyl 5-(4-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate}\)

The title compound was prepared according to the general procedure as described above in 78% yield. m.p. 118 °C; \([\alpha]^{25}_D = -36.0\) (c 0.22, CHCl₃); \(^1\)H NMR (CDCl₃, TMS, 300 MHz) \(\delta 7.30-7.18\) (m, 4H), 4.33 (d, \(J = 4.2\) Hz, 1H), 4.19 (d, \(J = 9.9\) Hz, 1H), 3.86-3.71 (m, 5H), 3.63-3.51(m, 1H), 3.47-3.41 (m, 1H), 2.96 (brs, 1H), 0.88 (d, \(J = 7.2\)Hz, 3H); \(^13\)C NMR (CDCl₃, TMS, 150 MHz) 169.84, 168.71, 134.78, 133.57, 128.59, 127.69, 124.95 (q, \(J_{CF} = 277.1\) Hz), 64.17, 60.93, 58.56, 52.72 (q, \(J_{CF} = 27.0\) Hz), 49.95, 13.63; IR (KBr) ν 3681, 3583, 3019, 2400, 1710, 1523, 1421, 1216, 1018, 929, 773, 669 cm\(^{-1}\). HRMS: calcd. for C\(_{16}\)H\(_{17}\)ClF\(_3\)NO\(_4\): 379.0798, found. 379.0794. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee 96:4 dr (Chiralcel AS-H, \(i\)-propanol/hexane = 10/90, flow rate 1.0 mL/min, \(\lambda = 220\) nm); \(t_r = 9.30\) and 17.09 min.
(4cl)

\((2R,3S,4R,5S)-4\text{-ethyl 2-methyl 2-methyl-5-phenyl-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate}\)

The title compound was prepared according to the general procedure as described above in 83\% yield. \([\alpha]_{25}^{29}D = -59.0 \ (c \ 0.10, \text{CHCl}_3); \) \(^1\text{H} \text{NMR (CDCl}_3, \text{TMS, 300 MHz) }\delta 7.35-7.27 \ (m, 5H), 4.55 \ (d, J = 4.8 \ HZ, 1H), 3.84-3.78 \ (m, 5H), 3.54-3.50 \ (m, 1H), 3.23-3.17 \ (m, 1H), 1.69 \ (s, 3H), 0.88 \ (t, J = 6.9 \ HZ, 3H); \) \(^1\text{C} \text{NMR (CDCl}_3, \text{TMS, 75 MHz) }\) 172.46, 168.80, 136.27, 128.31, 127.58, 126.25, 125.18 (q, \(J_{CF} = 278.3 \ \text{Hz}), 65.37, 62.85, 60.69 \ (q, J_{CF} = 26.2 \ \text{Hz}), 52.75, 52.23, 29.61, 29.33, 13.52; \) \(\text{IR (KBr)}\) \(\nu 3684, 3622, 3019, 2977, 2400, 1746, 1522, 1424, 1216, 1046, 929, 773, 669 \ \text{cm}^{-1}. \) \(\text{HRMS: calcd. for C}_{17}\text{H}_{20}\text{F}_3\text{NO}_4: 359.1344, \) found. 359.1342. The product was analyzed by HPLC to determine the enantiomeric excess: 89\% ee >98:2 dr (Chiralcel AS-H, \(\text{i-propanol/hexane} = 2/98, \) flow rate 1.0 \text{mL/min, } \lambda = 220 \text{ nm); } t_r = 7.68 \text{ and } 9.19 \text{ min.}

(5ce)

\((2R,3S,4S,5S)-4\text{-ethyl 2-methyl 5-(4-methoxyphenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate}\)

The title compound was prepared according to the general procedure as described above in 75\% yield. \([\alpha]_{25}^{29}D = +18.0 \ (c \ 0.14, \text{CHCl}_3); \) \(^1\text{H} \text{NMR (CDCl}_3, \text{TMS, 300 MHz) }\delta 7.37 \ (d, J = 8.7 \ \text{Hz, } 2H), 6.90 \ (d, J = 8.4 \ \text{Hz, } 2H), 4.25-4.23 \ (m, 1H), 4.17-4.10 \ (m, 3H), 3.81(s, 3H), 3.80 \ (s, 3H), 3.69-3.60 \ (m, 1H), 3.16-3.10 \ (m, 1H), 2.50 \ (brs, 1H), 1.17 \ (t, J = 7.5 \ \text{Hz, } 3H); \) \(^1\text{C} \text{NMR (CDCl}_3, \text{TMS, 75 MHz) }\) 171.46, 170.48, 159.59, 130.74, 128.09, 125.88 (q, \(J_{CF} = 278.3 \ \text{Hz), 114.11, 66.40, 61.38,\)}

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60.13, 55.16, 52.44, 51.02, 13.93; IR (KBr) ν 3682, 3583, 3020, 2400, 1735, 1518, 1476, 1425, 1216, 929, 758, 669 cm⁻¹. The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee >98:2 dr (Chiralcel AD-H, i-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 23.96 and 33.23 min.

(5cg)

(2R,3S,4S,5S)-4-ethyl 2-methyl 5-(4-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described above in 85% yield. [α]D²⁵ = +17.3 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, TMS, 300 MHz) δ 7.42-7.33 (m, 4H), 4.29 (d, J = 9.0 Hz, 1H), 4.18-4.12 (m, 3H), 3.81 (s, 3H), 3.69-3.60 (m, 1H), 3.14-3.09 (m, 1H), 2.49 (brs, 1H), 1.19 (t, J = 7.5 Hz, 3H); ¹³C NMR (CDCl₃, TMS, 150 MHz) 171.18, 170.41, 137.60, 134.15, 128.92, 128.37, 125.74 (q, JCF = 278.3 Hz), 65.93, 61.61, 60.12, 52.66, 52.55, 50.95 (q, JCF = 26.9 Hz), 13.99; IR (KBr) ν 3681, 3583, 3020, 2400, 2256, 1735, 1523, 1216, 1089, 909, 765, 669 cm⁻¹. The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralcel AS-H, i-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 13.84 and 18.97 min.

(6cg)

(2R,3S,4R,5S)-4-ethyl 2-methyl 1-benzoyl-5-(4-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate

The title compound was prepared according to the general procedure as described
above in 87% yield. m.p. 208 °C; [α]_{D}^{25} = -32.5 (c 1.16, CHCl₃); \textsuperscript{1}H NMR (CDCl₃, TMS, 300 MHz)  \delta  7.48-7.24 (m, 9H), 5.61 (m, 1H), 4.82 (m, 1H), 3.87 (s, 3H), 3.75-3.54 (m, 3H), 3.40 (m, 1H), 0.83 (t, J = 7.2 Hz, 3H); \textsuperscript{13}C NMR (CDCl₃, TMS, 75 MHz) 171.31, 168.39, 167.55, 135.51, 135.21, 133.43, 130.26, 128.66, 128.34, 128.07, 126.47, 123.45 (q, J_{CF} = 277.1 Hz), 64.24, 61.05, 60.29, 52.43, 48.33, 31.16, 13.35; IR (KBr) ν 3683, 3583, 3020, 2400, 1751, 1655, 1523, 1216, 1017, 929, 747, 669 cm\(^{-1}\). The product was analyzed by HPLC to determine the enantiomeric excess: 99% ee (Chiralcel AD-H, i-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 22.67 and 69.76 min.

\begin{center}
(7cg)
\end{center}

\textbf{(2R,3S,4S,5S)-4-ethyl 2-methyl 1-benzoyl-5-(4-chlorophenyl)-3-(trifluoromethyl)pyrrolidine-2,4-dicarboxylate}

The title compound was prepared according to the general procedure as described above in 88% yield. m.p. 160 °C; [α]_{D}^{25} = -15.0 (c 0.20, CHCl₃); \textsuperscript{1}H NMR (CDCl₃, TMS, 300 MHz)  \delta  7.14 (m, 9H), 5.08 (m, 2H), 4.14-4.10 (m, 2H), 3.87 (s, 3H), 3.64-3.49 (m, 2H), 1.13 (t, J = 6.9 Hz, 3H); \textsuperscript{13}C NMR (CDCl₃, TMS, 150 MHz) 170.06, 169.41, 136.92, 134.97, 133.68, 129.92, 128.51, 127.98, 126.45, 123.87(q, J_{CF} = 277.2 Hz), 67.24, 61.91, 59.35, 52.88, 50.17, 47.15, 13.77; IR (KBr) ν 3684, 3586, 3019, 2400, 1724, 1650, 1525, 1216, 1019, 929, 747, 669 cm\(^{-1}\). The product was analyzed by HPLC to determine the enantiomeric excess: 98% ee (Chiralcel AS-H, i-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 220 nm); tᵣ = 16.50 and 26.73 min.
X-ray crystal structures of (2R,3S,4R,5S)-6cg and (2R,3S,4S,5S)-7cg

For (2R,3S,4R,5S)-6cg: CCDC 827404, C_{23}H_{21}ClF_{3}NO_{5}, M_r = 483.86, T = 293 K, Orthorhombic, space group P2_12_12_1, a = 8.6745(12), b = 13.3919(18), c = 19.262(3) Å, V = 2237.6(5) Å³, Z = 4, 12954 reflections measured, 3670 unique (R_int = 0.0353) which were used in all calculations. The final wR2 = 0.0845(all data), Flack χ = 0.08(7).

For (2R,3S,4S,5S)-7cg: CCDC 827405, C_{23}H_{21}ClF_{3}NO_{5}, M_r = 483.86, T = 293 K, Orthorhombic, space group P2_12_12_1, a = 14.7950(17), b = 15.6582(17), c = 20.390(2) Å, V = 4723.6(9) Å³, Z = 8, 26602 reflections measured, 6467 unique (R_int = 0.0422) which were used in all calculations. The final wR2 = 0.0945 (all data), Flack χ = -0.02(6).
Proposed transition states of the *endo*-selectivity for asymmetric 1,3-dipolar cycloaddition of azomethine ylides with *trans* or *cis*-4,4,4-Trifluorocrotonate

Based on the relative and absolute configuration of the cycloadducts, the high *endo*-selectivity observed in the Cu(CH$_3$CN)$_4$BF$_4$/TF-BiphamPhos catalyzed asymmetric 1,3-dipolar cycloaddition reaction of azomethine ylide with *trans* or *cis*-4,4,4-trifluorocrotonate can be rationalized by the proposed tetracoordinated complex$^3$ shown in Figure 3. The *in situ*-formed azomethine ylide is coordinated to the metallic center and oriented in such transition state because of the steric repulsion between the phenyl group in the ylide and the phenyl ring on the phosphorus atom of the chiral ligand. The highly steric congestion imposed by the latter effectively blocks the dipolarophiles (*trans*- or *cis*-4,4,4-trifluorocrotonate) approach from the *Re* (C=N) face of the azomethine ylide and forms the corresponding *endo*-(*2R,3R,4R,5S*) or *endo*-(*2R,3S,4R,5S*) adduct through *Si* face attack. The carbonyl group of the *trans*- or *cis*-4,4,4-trifluorocrotonate could coordinate with the Cu(I) center, which can stabilize the negatively charged oxygen atom in the proposed transition states.$^3$ It could not rule out the possible hydrogen bond interaction between the carbonyl group of dipolarophile 1a and the NH$_2$ group of the chiral (S)-TF-BiphamPhos ligand (L1), which also facilitates stabilizing the proposed transition states.$^{3b,3c}$

![Figure 3. Proposed transition states leading to *endo*-adducts.](image-url)
References


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