SUPPLEMENTARY INFORMATION

Use of Achiral Additives to Increase the Stereoselectivity in Rh(II)-Catalyzed Cyclopropanations

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General experimental procedures.
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. All glassware was stored in the oven and/or was flame-dried prior to use under an inert atmosphere of gas. Anhydrous solvents were obtained either by filtration through drying columns (THF, ether, CH$_2$Cl$_2$, benzene, DMF, CH$_3$CN, toluene, hexane, methanol) on a GlassContour system, by distillation over calcium hydride (Et$_3$N, CICH$_2$CH$_2$Cl, 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 techniques. 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 ($^1$H, $^{13}$C, DEPT 135, COSY, HMQC, NOESY) were recorded either on a 300, 400 or 700 MHz spectrometer. Chemical shifts for $^1$H NMR spectra are recorded in parts per million from tetramethylsilane with the solvent resonance as the internal standard (chloroform, 7.27 ppm). The data is 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. The data is reported as follows: $\left[\alpha\right]_{\text{temp}}^d$, concentration (c in g/100 mL), and solvent. Analytical gas chromatography was carried out on a gas chromatograph equipped with a splitless mode capillary injector and a flame ionization detector or with a GC 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). The data is reported as follows: column type, oven temperature, carrier pressure, and retention time ($t_r$). Analytical SFC were performed and the data is reported as follows: column type, eluent, flow rate, and retention time ($t_r$).
Reagents: \( \text{Rh}_2(\text{oct})_4 \) and \( \text{Rh}_2(\text{S-DOSP})_4 \) were obtained from Aldrich. \( \text{Rh}_2(\text{S-NTTL})_4 \) and \( \text{Rh}_2(\text{S-TCPTTL})_4 \) were prepared according to literature procedure. Diazo reagents 1a-e were prepared according to a literature procedure.

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

### General procedure for the additive study in the stereoselective formation of 3a (Table 1)

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{(1R,2R)-Methyl 2-phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarboxylate (3a).}};
\end{tikzpicture}
\end{center}

A 10-mL microwave tube was charged with \( \text{Rh}_2(\text{S-NTTL})_4 \) (2.9 mg, 0.002 mmol, 1 mol%), the additive, and a magnetic stir bar. The tube was sealed with a Teflon septum and purged with argon. DCE (1 mL) and styrene (115 μL, 1.00 mmol, 5.00 equiv.) were added. The diazo compound 1a (0.20 mmol, 1.00 equiv.) dissolved in 1 mL of DCE was added to the reaction mixture over a period of 10 h using a syringe pump (Chemyx Fusion 200) at 25 °C. Following 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 100% hexane to 100% Et\(_2\)O. The complexed rhodium dimer could be removed by dissolving the green mixture 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\textsuperscript® to afford a rhodium-free product following concentration under reduced pressure. The product was isolated as a white solid. Diastereomeric ratio was determined by GC/MS analysis of the crude mixture (HP-5HS 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 was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 4% iPrOH, 5 mL/min, 30 °C, 200 bar, t\(_r\) (major) 13.9 min, t\(_r\) (minor) 16.8 min.); m.p. 73-75 °C; R, 0.35 (100%, Et\(_2\)O); [\(\alpha\)]\(_D\) \(= 113^\circ \) (c 1.18, CHCl\(_3\)); \(\text{^1}H\text{ NMR (300 MHz, CDCl}_3\) \(d 7.30-7.22 \text{(m, 5H), 3.78-3.50 \text{(m, 3H), 3.42 \text{(s, 3H), 3.41-3.27 \text{(m, 2H), 2.21 \text{(dd, J = 4.7 Hz, J = 7.9 Hz, 1H), 2.01-1.87 \text{(m, 4H), 1.53 \text{(dd, J = 4.7 Hz, J = 9.1 Hz, 1H); \text{^13C NMR (75 MHz, CDCl}_3\) d 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\(_1\)O\(_3\) [M+H]\(^+\) : 274.1438, found 274.1437.}

### General procedure for the additive study in the stereoselective formation of 3b (Table 2)

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\textbf{2-Phenyl-1-(pyrrolidine-1-carbonyl)cyclopropanecarbonitrile (3b).}};
\end{tikzpicture}
\end{center}

A 25-mL round bottom flask was charged with \( \text{Rh}_2(\text{S-NTTL})_4 \) (5.4 mg, 0.004 mmol, 1 mol %), the additive,\(^5\) and a magnetic stir bar. The flask was purged with argon. Toluene (4 mL) and styrene (228 μL, 3\(\mu\)L, 1.00 mmol, 5.00 equiv.) were added. The diazo compound 1a (0.20 mmol, 1.00 equiv.) dissolved in 1 mL of DCE was added to the reaction mixture over a period of 10 h using a syringe pump (Chemyx Fusion 200) at 25 °C. Following 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 100% hexane to 100% Et\(_2\)O. The complexed rhodium dimer could be removed by dissolving the green mixture 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\textsuperscript® to afford a rhodium-free product following concentration under reduced pressure. The product was isolated as a white solid. Diastereomeric ratio was determined by GC/MS analysis of the crude mixture (HP-5HS 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 was determined by SFC analysis on chiral phase (Chiralpak AD-H 25 cm, 4% iPrOH, 5 mL/min, 30 °C, 200 bar, t\(_r\) (major) 13.9 min, t\(_r\) (minor) 16.8 min.); m.p. 73-75 °C; R, 0.35 (100%, Et\(_2\)O); [\(\alpha\)]\(_D\) \(= 113^\circ \) (c 1.18, CHCl\(_3\)); \(\text{^1}H\text{ NMR (300 MHz, CDCl}_3\) \(d 7.30-7.22 \text{(m, 5H), 3.78-3.50 \text{(m, 3H), 3.42 \text{(s, 3H), 3.41-3.27 \text{(m, 2H), 2.21 \text{(dd, J = 4.7 Hz, J = 7.9 Hz, 1H), 2.01-1.87 \text{(m, 4H), 1.53 \text{(dd, J = 4.7 Hz, J = 9.1 Hz, 1H); \text{^13C NMR (75 MHz, CDCl}_3\) d 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\(_1\)O\(_3\) [M+H]\(^+\) : 274.1438, found 274.1437.

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\(^6\) A 1b/TIN\(_2\) (10 mol%) mixture can be stored for more than 4 weeks at 0 °C and used without negative effect on yield or selectivity.
2.00 mmol, 5.00 equiv) were added. The reaction mixture was cooled to −78 °C (acetone/dry ice) and stirred for 15 min. The diazo compound 1b (66.0 mg, 0.40 mmol, 1.00 equiv) dissolved in toluene (2 mL) was added to the reaction mixture over a period of 2 h using a syringe pump (Chemyx Fusion 200). Following complete addition, the resulting mixture was stirred for an additional 4 h at −78 °C. The reaction was warmed to 25 °C over a period of 16 h. After complete consumption of the diazo reagent, trimethoxybenzene (internal standard) was added and the solvent was then removed under reduced pressure. ¹H NMR analysis was performed to record both dr and ¹H NMR yield. Purification on silica gel (hexane:Et₂O 100:0 to 0:100) afforded the corresponding cyclopropane. The complexed rhodium dimer could be removed by dissolving the green mixture 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. The product was isolated as a white solid. Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on a chiral phase (Chiralcel OJ-H 25 cm, 7% i-PrOH, 3 mL/min, 40 °C, 150 bar, tₘ (minor) 9.7 min, tₘ (major) 11.9 min). Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% i-PrOH, 3 mL/min, 40 °C, 150 bar, tₘ (minor) 9.7 min, tₘ (major) 11.9 min); IR (film) 2973, 2880, 2234, 1639, 1416, 1341 cm⁻¹; HRMS (ES, Pos) Calcd for C₁₅H₁₄N₂O₁ [M+H]+: 241.1335, found 241.1338.

General procedure for the additive study in the stereoselective formation of 3c (Table 3)

(4-methoxyphenyl)((1S,2S)-(Z)-1-nitro-2-phenylcyclopropyl)methanone (3c). A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with Rh₂(S-TCPTTL)₄ (3.9 mg, 0.0020 mmol, 1.0 mol %) and the additive, followed by 3 mL of dry Et₂O and styrene (115 μL, 1.00 mmol, 5.00 equiv) at room temperature (20-23°C). The resulting solution was cooled to −50°C using a cryostat ethanol bath and stirred for 15 minutes at that temperature before diazo 1c (44.2 mg, 0.200 mmol, 1.00 equiv) was added in the solid state under air, the flask was capped back with the rubber septum and the resulting heterogeneous solution was stirred for a further 16 hours at −50°C, keeping an Argon line on the flask to minimize water condensation during the reaction. After 16 hours, the resulting milky heterogeneous solution was allowed to slowly warm to room temperature over a period of 2 hours, diluted with 2 mL CH₂Cl₂, and evaporated to dryness. (The dr was determined at this point using ¹H NMR). Purification on silica gel (CH₂Cl₂:hexane 60:40) afforded the corresponding cyclopropane 3c as a mixture of diastereomers, which was submitted to SFC analysis using a chiral stationary phase for ee determination. The pure cis-cyclopropane product could usually be obtained by simple trituration in hexanes, with virtually no loss of yield with respect to the initial cis/trans ratio. On a larger scale, the residue obtained after silica-gel chromatography could be recrystallized using 30% CHCl₃/hexane as solvent to obtain the product as a single stereoisomer (single diastereoisomer, >99%ee) with various yields of recrystallization (always higher than 90%). mp 134-135°C. Diastereomeric ratio was determined by ¹H NMR analysis of the crude mixture, enantiomeric excess was determined by SFC analysis on chiral stationary phase (Chiralcel OJ-H 25 cm, 7% i-PrOH, 3 mL/min, 40 °C, 150 bar, tₘ (minor) 9.7 min, tₘ (major) 11.9
min; mp 134-135 °C; R_f = 0.30 (60/40, CH_2Cl_2/Hexane); [α]_D^20 = -203.7 (c 1.03, CHCl_3); ¹H NMR (400 MHz, CDCl_3): δ 7.92 (d, J = 8.8 Hz, 2H), 7.43-7.29 (m, 5H), 6.99 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.84 (t, J = 9.6 Hz, 1H), 3.02 (dd, J = 6.8, 9.6 Hz, 1H), 1.95 (dd, J = 6.8, 9.6 Hz, 1H); ¹³C NMR (75 MHz, CDCl_3): δ 187.4, 165.1, 132.5, 131.5, 129.8, 129.4, 129.2, 128.3, 115.2, 77.5, 56.4, 32.8, 21.7; IR (neat) 3089, 2940, 2844, 1675 (C=O), 1601, 1532 (NO_2), 1350 (NO_2), 1292, 1265, 1018, 982; HRMS (ES, Pos) Calcd for C_{17}H_{15}NO_4 [M+H]^+: 298.1074, found 298.1068.

**General procedure for the additive study in the stereoselective formation of 3d (Table 4)**

**E-1-Benzoyl-2-phenyl-cyclopropanecarbonitrile (3d).** A flame-dried, round-bottomed 5 mL flask equipped with a corn-shaped magnetic stirring bar and capped with a rubber septum was charged with Rh_2(oct)_4 (2.6 mg, 0.0033 mmol, 0.5 mol %) and the additive, styrene (150 μL, 1.32 mmol, 0.5 mol %) and the additive, styrene (150 μL, 1.32 mmol, 2.00 equiv) was added and the mixture was stirred for 5 minutes at room temperature (20-23°C) before 700 μL of a 0.943 M stock solution of diazo 1d (0.660 mmol) in CH_2Cl_2 was slowly added via syringe pump (Chemyx Fusion 200) over 15 minutes. The resulting mixture was stirred for 2h at room temperature, the internal standard 1,3,5-trimethoxybenzene (11.1 mg, 0.0660 mmol, 0.100 equiv) was added and the reaction was concentrated under vacuum. ¹H NMR was performed in order to determine the NMR yield (using the internal standard) and the dr of the reaction. Purification on silica gel (CH_2Cl_2:hexane 70:30) afforded the corresponding cyclopropane 3d as a mixture of diastereomers. All spectral and analytical data was in accordance with literature values.⁶

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