Dinitrogen Extrusion from Enoldiazo Compounds under Thermal Conditions: Synthesis of Donor-Acceptor Cyclopropenes

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General Information

All reactions were performed in oven-dried (140 °C) glassware. DCM (dichloromethane), DCE (1,2-dichloroethane) and toluene were distilled prior to use and kept over activated 3 Å molecular sieves; CHCl₃ and CDCl₃ were purchased from Sigma Aldrich and used without further treatment. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates; visualization was accomplished with UV light (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (230-400 mesh). ¹H NMR spectra were recorded on an Inova™ (500 MHz) spectrometer, and chemical shifts were reported in ppm. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite; coupling constant(s) in Hz. ¹³C NMR spectra were recorded on an Inova™ (125 MHz) spectrometer with complete proton decoupling. Enantioselectivity was determined on an Agilent 1200 Series HPLC using Daicel Chiralcel OD-H columns. High-resolution mass spectra (HRMS) were performed on a TOF-CS mass spectrometer using CsI as the standard.

Materials

Rh₂(S-NTTL)₄[¹a,¹b] and Rh₂(S-TCTTL)₄[¹c,¹d] were prepared according to literature procedures. The diazoacetoacetamides S-1 were prepared according to the literature procedures.[²] The diazoacetoacetates S-3 were prepared according to the literature procedures.[³] All the other chemicals were obtained from commercial sources and used without further purification.

General Procedures for the Synthesis of Enoldiazoacetamides 1 and Enoldiazoacetates 3

To a 100 mL oven-dried round bottom flask containing a magnetic stirring bar, S-1 or S-3 (2.0 mmol) and Et₃N (1.5 eq, 3.0 mmol, 0.45 mL) in DCM (10 mL) were added TBSOTf (1.1 eq, 2.2 mmol, 0.5 mL) slowly at 0 °C. After the reaction mixture was stirred for 0.5-1
h under these conditions, hexanes (30 mL) were added, followed by saturated aqueous NaHCO₃ (40 mL). The organic phase was separated and washed two more times with saturated aqueous NaHCO₃ (40 mL X 2) and dried with anhydrous Na₂SO₄. After evaporating the solvents, enoldiazo compounds 1 and 3 were purified by flash chromatography (SiO₂ was treated with hexanes with 2% Et₃N for 30 min before use, hexanes 100%).

**N-tert-Butyl-3-(tert-butylidimethylsilyloxy)-N-(4-chlorobenzyl)-2-diazo-3-enamide** (1a). Red solid, 93% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 4.54 (s, 2H), 4.40 (d, J = 2.1 Hz, 1H), 4.16 (d, J = 2.1 Hz, 1H), 1.37 (s, 9H), 0.88 (s, 9H), 0.17 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.07, 143.83, 138.00, 133.01, 128.72, 128.06, 89.09, 58.29, 50.26, 28.81, 25.55, 18.05, -4.80. This compound has been previously reported; the spectroscopic data are identical to those in reference 2a.

**N-tert-Butyl-3-(tert-butylidimethylsilyloxy)-N-(2-chlorobenzyl)-2-diazo-3-enamide** (1b). Red solid, 89% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.31 (comp, 2H), 7.27 – 7.20 (comp, 2H), 4.73 (s, 2H), 4.46 (d, J = 2.1 Hz, 1H), 4.19 (d, J = 2.1 Hz, 1H), 1.41 (s, 9H), 0.87 (s, 9H), 0.18 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.07, 143.97, 136.77, 132.03, 129.67, 128.32, 128.30, 126.68, 89.58, 58.57, 48.47, 28.68, 25.56, 18.05, -4.82. HRMS (ESI) calculated for C₂₁H₃₅ClN₃O₂Si [M+H]⁺: 422.2025; found: 422.2038.

**N-tert-Butyl-3-(tert-butylidimethylsilyloxy)-2-diazo-N-(4-nitrobenzyl)but-3-enamide** (1c). Red solid, 89% yield. ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 4.66 (s, 2H), 4.40 (d, J = 2.2 Hz, 1H), 4.16 (d, J = 2.2 Hz, 1H), 1.40 (s, 9H), 0.86 (s, 9H), 0.16 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 167.21, 147.25, 147.21, 143.55, 127.34, 123.86,
This compound has been previously reported; the spectroscopic data are identical to those in reference 2a.

**N-tert-Butyl-3-(tert-butylidemethylsilyloxy)-2-diazo-N-(4-methoxybenzyl)but-3-enamide (1d).** Red solid, 93% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.14 (d, $J = 7.3$ Hz, 2H), 6.86 (d, $J = 7.3$ Hz, 2H), 4.52 (s, 2H), 4.41 (d, $J = 1.9$ Hz, 1H), 4.15 (d, $J = 1.9$ Hz, 1H), 3.79 (s, 3H), 1.37 (s, 9H), 0.89 (s, 9H), 0.18 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.95, 158.80, 144.06, 131.28, 127.98, 113.93, 88.78, 58.09, 55.19, 50.46, 28.79, 25.57, 18.05, -4.79. This compound has been previously reported; the spectroscopic data are identical to those in reference 2a.

**3-(tert-Butylidemethylsilyloxy)-2-diazo-N,N-dimethylbut-3-enamide (1e).** Red oil, 89% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.42 (d, $J = 3.7$ Hz, 1H), 4.23 (d, $J = 3.7$ Hz, 1H), 2.95 (s, 6H), 0.89 (s, 9H), 0.19 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.81, 143.76, 90.55, 37.39, 25.52, 18.02, -4.85. HRMS (ESI) calculated for C$_{12}$H$_{23}$N$_3$O$_2$SiNa $[M+Na]^+$: 292.1457; found: 292.1469.

**3-(tert-Butylidemethylsilyloxy)-2-diazo-N,N-diisopropylbut-3-enamide (1f).** Red oil, 95% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.36 (d, $J = 2.0$ Hz, 1H), 4.16 (d, $J = 2.0$ Hz, 1H), 3.76 – 3.68 (comp, 2H), 1.30 (d, $J = 6.7$ Hz, 12H), 0.91 (s, 9H), 0.21 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 162.43, 144.58, 89.65, 48.60, 25.58, 20.86, 18.09, -4.80. HRMS (ESI) calculated for C$_{16}$H$_{31}$N$_3$O$_2$SiNa $[M+Na]^+$: 348.2083; found: 348.2072.

**3-(tert-Butylidemethylsilyloxy)-2-diazo-1-(piperidin-1-yl)but-3-en-1-one (1g).** Red oil, 88% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 4.39 (d, $J = 2.1$ Hz, 1H), 4.20 (d, $J = 2.1$ Hz, 1H), 3.42 – 3.40 (comp, 4H), 1.65 – 1.61 (comp, 2H), 1.58 – 1.53 (comp, 4H), 0.90 (s, 9H), 0.20 (s, 6H); $^{13}$C NMR
(125 MHz, CDCl₃) δ 164.00, 144.11, 90.01, 46.45, 25.77, 25.56, 24.51, 18.07, -4.80.


**N-Benzyl-3-(tert-butylidemethylsilyloxy)-2-diazo-N-methylbut-3-enamide (1h).** Red oil, 87% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.31 (comp, 6H), 7.23 – 7.21 (comp, 4H), 6.81 (s, 1H), 4.52 (d, J = 2.1 Hz, 1H), 4.28 (d, J = 2.1 Hz, 1H), 2.80 (s, 3H), 0.93 (s, 9H), 0.24 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 165.36, 143.68, 138.48, 128.72, 128.50, 127.58, 91.17, 63.09, 33.13, 25.62, 18.12, -4.71. HRMS (ESI) calculated for C₂₄H₃₁N₃O₂SiNa [M+Na]^+: 444.2071; found: 444.2071.

**Red oil, 87% yield.**

This compound has been previously reported; the spectroscopic data are identical to those in reference 3h.

**Z-Methyl 3-(tert-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3a).** Red oil, 95% yield. ¹H NMR (500 MHz, CDCl₃) δ 5.27 (q, J = 7.0 Hz, 1H), 3.79 (s, 3H), 1.69 (d, J = 7.0 Hz, 3H), 0.97 (s, 9H), 0.16 (s, 6H). HRMS (ESI) calculated for C₁₈H₂₆N₂O₃SiNa [M+Na]^+: 369.1610; found: 369.1619.

**Z-Benzyl 3-(tert-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3b).** Red oil, 93% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.32 (comp, 5H), 5.29 (q, J = 7.0 Hz, 1H), 5.24 (s, 2H), 1.69 (d, J = 7.0 Hz, 3H), 0.97 (s, 9H), 0.15 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 164.77, 135.94, 132.85, 128.50, 128.16, 128.10, 127.98, 108.20, 77.25, 77.00, 76.75, 66.29, 25.62, 18.17, 11.80, -4.66. HRMS (ESI) calculated for C₁₈H₂₆N₂O₃SiNa [M+Na]^+: 369.1610; found: 369.1619.

**Z-4-Methoxybenzyl 3-(tert-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3c).** Red oil, 90% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.27 (q, J = 7.0 Hz, 1H), 5.17 (s, 2H), 3.81 (s, 3H), 1.67 (d, J = 7.0 Hz,
$^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.93, 159.62, 132.95, 129.98, 128.12, 113.90, 108.14, 66.21, 55.28, 25.66, 18.21, 11.84, -4.62. HRMS (ESI) calculated for C$_{19}$H$_{28}$N$_2$O$_3$SiNa [M+Na]$^+$: 399.1716; found: 399.1708.

$(Z)$-2-Methoxybenzyl 3-(tert-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3d). Red oil, 89% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.32 – 7.28 (comp, 2H), 6.97 – 6.93 (comp, 1H), 6.89 (d, J = 8.5 Hz, 1H), 5.29(s, 1H), 5.30 (q, J = 7.0 Hz, 1H), 3.84 (s, 3H), 1.68 (d, J = 7.0 Hz, 3H), 0.96 (s, 9H), 0.15 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.88, 157.35, 132.94, 129.37, 129.11, 124.33, 120.36, 110.36, 107.99, 61.92, 55.32, 25.65, 18.19, 11.83, -4.66. HRMS (ESI) calculated for C$_{19}$H$_{28}$N$_2$O$_3$SiNa [M+Na]$^+$: 399.1716; found: 399.1719.

$(Z)$-Benzhydryl 3-(tert-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3e). Red oil, 85% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 – 7.26 (comp, 10H), 6.98 (s, 1H), 5.28 (q, J = 7.0 Hz, 1H), 1.68 (d, J = 7.0 Hz, 3H), 0.96 (s, 9H), 0.12 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.01, 140.13, 132.74, 131.27, 130.45, 128.40, 126.94, 108.53, 77.13, 25.64, 18.19, 11.82, -4.66. HRMS (ESI) calculated for C$_{24}$H$_{30}$N$_2$O$_3$SiNa [M+Na]$^+$: 445.1923; found: 445.1941.

$(Z)$-2,6-Dichlorobenzyl 3-(tert-Butyldimethylsilyloxy)-2-diazopent-3-enoate (3f). Red oil, 88% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.33 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 8.0 Hz, 1H), 5.49 (s, 2H), 5.27 (q, J = 7.0 Hz, 1H), 1.66 (d, J = 7.0 Hz, 3H), 0.94 (s, 9H), 0.14 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 164.44, 136.92, 132.72, 131.27, 130.45, 128.40, 108.24, 61.39, 25.62, 18.16, 11.81, -4.70. HRMS (ESI) calculated for C$_{18}$H$_{24}$O$_3$N$_2$SiNaCl$_2$ [M+Na]$^+$: 437.0831; found: 437.0803.

$(Z)$-Methyl 3-(tert-Butyldimethylsilyloxy)-2-diazo-4-phenylbut-3-enoate (3g). Red oil, 91% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, J = 7.5 Hz, 2H), 7.28 (t, J = 7.5 Hz,
TBSO
Ph\n\n\nO
2H), 7.16 (t, J = 7.5 Hz, 1H), 6.40 (s, 1H), 3.86 (s, 3H), 0.97 (s, 9H), -0.07 (s, 6H). This compound has been previously reported; the spectroscopic data are identical to those in reference 3e.

(Z)-Benzyl 3-(tert-Butyldimethylsilyloxy)-2-diazo-4-phenylbut-3-enoate (3h). Red oil, 90% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.51 (comp, 2H), 7.45 – 7.34 (comp, 5H), 7.32 – 7.24 (comp, 2H), 7.17 (m, 1H), 6.42 (s, 1H), 5.31 (s, 2H), 0.97 (s, 9H), -0.05 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 164.29, 136.29, 135.82, 133.76, 129.02, 128.63, 128.33, 128.04, 127.90, 126.15, 111.42, 66.55, 25.75, 18.13, -4.80. HRMS (ESI) calculated for C$_{23}$H$_{28}$O$_3$N$_2$SiNa [M+Na]$^+$: 431.1767; found: 431.1778.

Screening of Reaction Conditions for Preparation of Donor-Acceptor Cyclopropanes

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$^a$ Reactions were performed on a 0.4 mmol scale: 0.4 mmol 1a in 4 mL solvent at indicated temperature. $^b$ The yield of cyclopropene was determined by $^1$H NMR analysis using an internal standard (1,3,5-trimethoxybenzene).
Temperature Effect on Thermal Reactions of 3h

3h (0.4 mmol) at room temperature was added to a 10-mL oven-dried vial containing a magnetic stirring bar and 4 mL 1,2-dichloroethene (DCE), and then the vial was screwed close. The sealed reaction mixture was heated in oil bath at indicated temperature, during which time the diazo compound was converted to the corresponding cyclopropene. The color of the solution changed from orange to light yellow. After removing DCE under reduced pressure, the resulting reaction mixture was analyzed by $^1$H NMR to determine the ratio of 4h and 5h by using an internal standard (1,3,5-trimethoxybenzene).

General Procedure for the Preparation of Donor-Acceptor Cyclopropenes 2 and 4

Enoldiazo compound (0.4 mmol) at room temperature was added to a 10-mL oven-dried vial containing a magnetic stirring bar and 4 mL CHCl$_3$, and then the vial was screwed close. The sealed reaction mixture was heated in oil bath at 50 °C for 3 to 4 hours, during which time the diazo compound was converted to the corresponding cyclopropene. The color of the solution changed from orange to colorless or light yellow. After removing CHCl$_3$ under reduced pressure, the resulting cyclopropenes were characterized directly without further purification.
**N-tert-Butyl-2-(tert-butyldimethylsilyloxy)-N-(4-chlorobenzyl)cycloprop-1-ene carboxamide (2a).** Colorless oil, quantitative. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.24 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.73 (s, 2H), 1.79 (s, 2H), 1.42 (s, 9H), 0.72 (s, 9H), 0.12 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.32, 139.12, 134.59, 132.23, 128.45, 127.28, 72.09, 57.70, 49.07, 28.68, 24.93, 17.94, 17.51, -4.60. HRMS (ESI) calculated for C$_{21}$H$_{33}$ClNO$_2$SiNa [M+Na]$^+$: 416.1789; found: 416.1767.

**N-tert-Butyl-2-(tert-butyldimethylsilyloxy)-N-(2-chlorobenzyl)cycloprop-1-ene carboxamide (2b).** Colorless oil, quantitative. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.30 – 7.25 (comp, 2H), 7.21– 7.12 (comp, 2H), 4.79 (s, 2H), 1.74 (s, 2H), 1.45 (s, 9H), 0.71 (s, 9H), 0.09 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.54, 137.74, 134.83, 131.51, 129.12, 127.64, 127.44, 126.65, 71.84, 57.62, 47.64, 28.50, 25.03, 17.81, 17.52, -4.65. HRMS (ESI) calculated for C$_{21}$H$_{33}$ClNO$_2$SiNa [M+Na]$^+$: 416.1789; found: 416.1771.

**N-tert-Butyl-2-(tert-butyldimethylsilyloxy)-N-(4-nitrobenzyl)cycloprop-1-ene carboxamide (2c).** Colorless oil, 92% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.17 (d, $J = 8.7$ Hz, 2H), 7.39 (d, $J = 8.7$ Hz, 2H), 4.86 (s, 2H), 1.80 (s, 2H), 1.44 (s, 9H), 0.69 (s, 9H), 0.11 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.28, 148.59, 146.89, 135.06, 126.69, 123.72, 71.89, 57.86, 49.39, 28.73, 24.89, 17.88, 17.48, -4.59. HRMS (ESI) calculated for C$_{21}$H$_{33}$N$_2$O$_4$SiNa [M+Na]$^+$: 427.2029; found: 427.2031.

**N-tert-Butyl-2-(tert-butyldimethylsilyloxy)-N-(4-methoxybenzyl)cycloprop-1-ene carboxamide (2d).** Colorless oil, 85% yield. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.09 (d, $J = 8.7$ Hz, 2H), 6.80 (d, $J = 8.7$ Hz, 2H), 4.71 (s, 2H), 3.76 (s, 3H), 1.80 (s, 2H), 1.42 (s, 9H), 0.72 (s, 9H), 0.12 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 162.30, 158.33, 134.26,
132.41, 127.01, 113.73, 72.41, 55.19, 49.01, 28.67, 25.00, 18.11, 17.55, -4.60. HRMS (ESI) calculated for C_{22}H_{35}NO_{3}SiNa [M+Na]^+: 412.2284; found: 412.2291.

2-(tert-Butyldimethylsilyloxy)-N,N-dimethylcycloprop-1-enecarboxamide (2e). Light yellow oil, quantitative. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.09 (s, 3H), 2.93 (s, 3H), 1.84 (s, 2H), 0.91 (s, 9H), 0.26 (s, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 160.40, 135.82, 70.57, 37.16, 34.64, 25.24, 17.81, 17.77, -4.50. HRMS (ESI) calculated for C_{12}H_{23}NO_{2}SiNa [M+Na]^+: 264.1396; found: 264.1377.

2-(tert-Butyldimethylsilyloxy)-N,N-diisopropylcycloprop-1-enecarboxamide (2f). Light yellow oil, quantitative. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 4.38 – 4.33 (comp, 1H), 3.58 – 3.42 (comp, 1H), 1.84 (s, 2H), 1.40 (d, \(J = 6.7\) Hz, 6H), 1.18 (d, \(J = 6.7\) Hz, 6H), 0.94 (s, 9H), 0.27 (s, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.87, 133.62, 71.96, 48.92, 45.38, 25.22, 20.98, 20.59, 17.79, 17.78, -4.43. HRMS (ESI) calculated for C_{16}H_{31}NO_{2}SiNa [M+Na]^+: 320.2022; found: 320.2040.

(2-(tert-Butyldimethylsilyloxy)cycloprop-1-enyl)(piperidin-1-yl)methanone (2g). Light yellow oil, quantitative. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.58 – 3.54 (comp, 4H), 1.86 (s, 2H), 1.63 – 1.51 (comp, 6H), 0.93 (s, 9H), 0.28 (s, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 158.83, 135.00, 70.65, 46.72, 42.57, 26.57, 25.63, 25.24, 24.70, 17.83, 17.81, -4.49. HRMS (ESI) calculated for C_{15}H_{27}NO_{2}SiNa [M+Na]^+: 304.1709; found: 304.1706.

N-Benzhydryl-2-(tert-Butyldimethylsilyloxy)-N-methylcycloprop-1-enecarboxamide (2h). Light yellow oil, quantitative. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.36 – 7.20 (comp, 22H), 6.74 (s, 1H), 2.96 (s, 3H), 2.81 (s, 3H), 1.95 (s, 2H), 1.92 (s, 2H), 0.96 (s, 9H), 0.86 (s, 9H), 0.32 (s, 6H), 0.25 (s, 6H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 161.16, 160.91, 139.36, 139.13, 136.87,
135.89, 128.85, 128.59, 128.38, 128.35, 128.38, 127.47, 127.25, 70.71, 70.42, 64.49, 59.95, 25.30, 25.21, 17.91, 17.78, -4.34, -4.50. HRMS (ESI) calculated for C_{24}H_{31}NO_2SiNa [M+Na]^+: 416.2022; found: 416.2029.

**Methyl 2-(tert-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4a).**

Light yellow oil, quantitative. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 3.73 (s, 3H), 2.33 (q, $J$ = 4.9 Hz, 1H), 1.23 (d, $J$ = 4.9 Hz, 3H), 0.97 (s, 9H), 0.32 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 160.3, 148.6, 77.2, 51.3, 25.3, 19.4, 18.0, -5.1, -5.2. HRMS (ESI) calculated for C$_{12}$H$_{22}$O$_3$SiNa [M+Na]$^+$: 265.1236; found: 265.1237.

**Benzyl 2-(tert-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4b).**

Light yellow oil, quantitative; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 – 7.44 (comp, 5 H), 5.21 (s, 2H), 2.38 (q, $J$ = 4.8 Hz, 1H), 1.27 (d, $J$ = 4.8 Hz, 3H), 0.98 (s, 9H), 0.32 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.7, 148.8, 136.3, 128.4, 128.3, 128.0, 77.3, 65.9, 25.3, 24.4, 19.4, 18.0, -5.1, -5.2. HRMS (ESI) calculated for C$_{18}$H$_{26}$O$_3$SiNa [M+Na]$^+$: 341.1549; found: 341.1550.

**4-Methoxybenzyl 2-(tert-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4c).**

Light yellow oil, quantitative. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J$ = 8.8 Hz, 2H), 6.88 (d, $J$ = 8.8 Hz, 2H), 5.12 (s, 2H), 3.80 (s, 3H), 2.33 (q, $J$ = 4.8 Hz, 1H), 1.23 (d, $J$ = 4.8 Hz, 3H), 0.95 (s, 9H), 0.29 (s, 3H), 0.28 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 159.8, 159.5, 148.5, 130.1, 128.4, 113.8, 77.3, 65.8, 55.3, 25.3, 24.4, 19.4, 17.9, -5.1, -5.2. HRMS (ESI) calculated for C$_{19}$H$_{28}$O$_3$SiNa [M+Na]$^+$: 371.1655; found: 371.1645.

**2-Methoxybenzyl 2-(tert-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4d).**

Light yellow oil, quantitative; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ ppm 7.35 (d, $J$ = 7.4 Hz, 1H), 7.27 – 7.32 (comp, 1H), 6.95 (t, $J$ = 7.4 Hz, 1H), 6.88 (comp, 1H), 5.25 (s, 1H), 5.24
(s, 1H), 3.83 (s, 3H), 2.35 (q, \(J = 4.8\) Hz, 1H), 1.25 (d, \(J = 4.8\) Hz, 3H), 0.95 (s, 9H), 0.28 (s, 3H), 0.28 (s, 3H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.8, 157.4, 148.2, 129.5, 129.3, 124.6, 120.3, 110.3, 77.4, 61.4, 55.3, 25.3, 24.3, 19.4, 17.9, -5.3, -5.3. HRMS (ESI) calculated for \(\text{C}_{19}\text{H}_{28}\text{O}_{3}\text{SiNa} [\text{M}+\text{Na}]^{+}\): 371.1655; found: 371.1648.

**Benzhydryl 2-( tert-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4e).**

Light yellow oil, quantitative. \(^{1}\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.32 – 7.39 (comp, 8H), 7.27 – 7.31 (comp, 2H), 6.96 (s, 1H), 2.39 (q, \(J = 4.8\) Hz, 1H), 1.29 (d, \(J = 4.8\) Hz, 3H), 0.96 (s, 9H), 0.30 (s, 3H), 0.30 (s, 3H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 158.9, 149.1, 140.5, 140.5, 128.4, 128.4, 127.8, 127.4, 127.0, 127.0, 77.3, 76.5, 25.3, 24.4, 19.4, 17.9, -5.1, -5.2. HRMS (ESI) calculated for \(\text{C}_{24}\text{H}_{30}\text{O}_{3}\text{SiNaCl} \cdot 2\text{[M+Na]}^{+}\): 417.1862; found: 417.1843.

**2,6-Dichlorobenzyl 2-( tert-Butyldimethylsilyloxy)-3-methylcycloprop-1-enecarboxylate (4f).** Light yellow oil, quantitative. \(^{1}\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.33 (d, \(J = 7.8\) Hz, 2-H), 7.18 - 7.24 (t, \(J = 7.8\) Hz, 1H), 5.37 - 5.48 (comp, 2H), 2.32 (q, \(J = 4.8\) Hz, 1H), 1.21 (d, \(J = 4.8\) Hz, 3H), 0.92 (s, 9H), 0.22 (s, 3H), 0.21 (s, 3H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.4, 148.7, 137.1, 131.6, 130.3, 128.3, 76.9, 61.0, 25.3, 24.1, 19.2, 17.9, -5.4. HRMS (ESI) calculated for \(\text{C}_{18}\text{H}_{24}\text{O}_{3}\text{SiNaCl}_{2} \cdot \text{[M+Na]}^{+}\): 409.0769; found: 409.0770.

**Methyl 2-( tert-Butyldimethylsilyloxy)-3-phenylcycloprop-1-enecarboxylate (4g).**

Light yellow oil, 71% yield. \(^{1}\text{H}\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.30 – 7.29 (comp, 2H), 7.20 – 7.19 (comp, 3H), 3.75 (s, 3H), 3.41 (s, 1H), 0.95 (s, 9H), 0.30 (s, 3H), 0.25 (s, 3H); \(^{13}\text{C}\) NMR (125 MHz, CDCl\(_3\)) \(\delta\) 159.55, 141.63, 140.93, 128.27, 126.31, 126.01, 71.67, 33.84, 25.29, 17.93, -5.02, -5.14. HRMS (ESI) calculated for \(\text{C}_{17}\text{H}_{24}\text{O}_{3}\text{SiNa} \cdot \text{[M+Na]}^{+}\): 327.1392; found: 327.1379.
Benzyl 2-(tert-Butyldimethylsilyloxy)-3-phenylcycloprop-1-enecarboxylate (4h).

Light yellow oil, 63% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 – 7.30 (comp, 7H), 7.27 – 7.21 (comp, 3H), 5.25 (s, 2H), 3.47 (s, 1H), 0.97 (s, 9H), 0.32 (s, 3H), 0.26 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 158.97, 141.63, 141.25, 136.07, 128.45, 128.26, 128.21, 128.08, 126.30, 126.10, 109.99, 71.82, 66.18, 33.82, 25.30, 17.93, -5.01, -5.13.

HRMS (ESI) calculated for C$_{23}$H$_{28}$O$_3$SiNa $[M+Na]^+$: 403.1705; found: 403.1698.

Methyl 4-(tert-Butyldimethylsilyloxy)-5-phenyl-1H-pyrazole-3-carboxylate (5g).

White solid, 23% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (d, $J$ = 8.3 Hz, 2H), 7.42 – 7.40 (comp, 2H), 7.35 – 7.34 (comp, 1H), 3.92 (s, 3H), 0.97 (s, 9H), -0.11 (s, 6H). Purified by flash chromatography (SiO$_2$, Hexane:EtOAc = 80:20). This compound has been previously reported; the spectroscopic data are identical to those in reference 3e.

Benzyl 4-(tert-Butyldimethylsilyloxy)-5-phenyl-1H-pyrazole-3-carboxylate (5h).

White solid, 33% yield. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 – 7.72 (comp, 2H), 7.48 – 7.31 (comp, 8H), 5.36 (s, 2H), 0.90 (s, 9H), -0.16 (s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 187.91, 159.37, 139.25, 135.26, 131.18, 128.92, 128.62, 128.57, 128.36, 128.07, 127.50, 66.62, 25.53, 18.01, -4.86. HRMS (ESI) calculated for C$_{23}$H$_{28}$O$_3$N$_2$SiNa $[M+Na]^+$: 431.1767; found: 431.1755. Purified by flash chromatography (SiO$_2$, Hexane:EtOAc = 80:20).
Procedures for the Asymmetric Cyclopropanation of Donor–Acceptor Cyclopropene 4a with Styrenes

The catalyst Rh$_2$(S-TCPTTL)$_4$ (1 mol%, 5.4 mg, 0.003 mmol) was dissolved in Et$_2$O (1.0 mL). After addition of styrene (312 mg, 3.0 mmol) or 4-methylstyrene (354 mg, 3.0 mmol) the mixture was cooled to -20 °C or -40°C, and 4a (0.3 mmol) which was generated from Z-3a (81.1 mg, 0.3 mmol) under thermal conditions, in Et$_2$O (1.0 mL) was added dropwise over 30 minutes. After the addition stirring was continued for 6 h. The solvent was evaporated and the residue was characterized by $^1$H NMR spectral analysis to determine the diastereoselectivities. Then the reaction mixture was purified by flash chromatography (SiO$_2$, Hexane:EtOAc = 95:5) to afford 7 as colorless oil.

The same procedure was applied here as the cyclopropanation catalyzed by Rh$_2$(S-TCPTTL)$_4$, except the Rh$_2$(S-TCPTTL)$_4$ was replaced by Rh$_2$(S-NTTL)$_4$. And the solvent was replaced from Et$_2$O to toluene.

Procedures for the Asymmetric Cyclopropanation of Enoldiazoacetate Z-3a with Styrenes
The same procedure was applied here as the cyclopropanation of donor–acceptor cyclopropene 4a with styrenes, except the donor–acceptor cyclopropene 4a was replaced by enoldiazoacetate Z-3a.

(1R,2S)-Methyl 1-[(Z)-1-(tert-Butyldimethylsilyloxy)prop-1-enyl]-2 phenylcyclopropenecarboxylate (7). Following the procedures for the asymmetric cyclopropanation of donor–acceptor cyclopropene 4a with styrenes from 0.3 mmol 4a (74 mg) and styrene 3.0 mol (312 mg). Colorless oil, 93 mg, 90% yield. [α]D = -182° (c = 1.93, CHCl₃, pour 91% ee). 91% ee, HPLC condition for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexanes:IPA = 97:1, tr = 7.2, 7.8 min. 

1H NMR (500 MHz, CDCl₃) δ 7.25 – 7.13 (comp, 3H), 7.08 (comp, 2H), 4.52 (q, J = 6.5 Hz, 1H), 3.72 (s, 3H), 2.89 (dd, J = 9.3, 7.5 Hz, 1H), 1.79 (dd, J = 9.3, 4.7 Hz, 1H), 1.67 (dd, J = 7.5, 4.7 Hz, 1H), 1.41 (d, J = 6.5 Hz, 3H), 0.76 (s, 9H), 0.05 (s, 3H), -0.07 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 174.0, 143.6, 137.1, 127.9, 127.7, 126.3, 126.1, 109.8, 52.2, 38.3, 33.2, 25.6, 22.5, 18.3, 10.8, -4.4, -4.5. The relative and absolute configurations were assigned following the reference 4.

(1R,2S)-Methyl 1-[(Z)-1-(tert-Butyldimethylsilyloxy)prop-1-enyl]-2-p-tolylcyclopropenecarboxylate (8). Following the procedures for the asymmetric cyclopropanation of donor–acceptor cyclopropene 4a with styrenes from 0.3 mmol 4a (74 mg) and 4- methyl styrene 3.0 mol (354 mg). White solid, 92 mg, 86% yield, m.p. 41-43 °C. [α]D = -145° (c = 1.54, CHCl₃, pour 92% ee). 92% ee, HPLC condition for determination of enantiomeric excess: OD-H column, 230 nm, 0.5 mL/min, hexanes:methanol = 99:1, tr = 10.0, 10.8 min. 

1H NMR (500 MHz, CDCl₃) δ 7.02 (d, J = 8.2 Hz, 2H), 6.95 (d, J = 8.2 Hz, 2H), 4.50 (q, J = 6.6 Hz, 1H), 3.71 (s, 3H), 2.85 (dd, J = 9.4, 7.5 Hz, 1H), 2.29 (s, 3H), 1.77 (dd, J = 9.4, 4.6 Hz, 1H), 1.63 (dd, J = 7.5, 4.6 Hz, 1H), 1.41 (d, J = 6.6 Hz, 3H), 0.77 (s, 9H), 0.05 (s, 3H), -0.08 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 174.1, 143.6, 135.9, 134.0, 128.4, 127.8, 109.8, 52.1, 38.1, 33.1, 25.6,
22.4, 20.9, 18.3, 10.9, -4.4, -4.5. The relative and absolute configurations were assigned following reference 4.

References


NMR Spectra of 1, 2, 3, 5, 7 and 8
HPLC Analyses of 7 and 8