Supporting Information

Regioselective and Room-Temperature Carbon-Carbon Bond Activation of Cyclopropanes by Rhodium(II) Porphyrin

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1. General Information

**General Procedures.** All materials were obtained from commercial suppliers and used without further purification unless otherwise specified. Benzene was distilled from sodium under nitrogen. Rh(tmp) in benzene were prepared by photolysis of Rh(tmp)CH\textsubscript{3} according to the literature procedures.\textsuperscript{1} All solutions used were degassed thrice by freeze-thaw-pump cycle and stored in a Teflon screwhead stoppered flask under N\textsubscript{2}.

Thin layer chromatography was performed on Merck pre-coated silica gel 60 F\textsubscript{254} plates. Silica gel (Merck, 230-400 mesh) was used for column chromatography. All reactions were run in Teflon screw capped flask wrapped with aluminum foils to protect from light.

**Physical and Analytical Measurements.** \textsuperscript{1}H NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer and Bruker AV500 (500 MHz) spectrometer. Spectra were referenced internally to the residual proton resonance in CDCl\textsubscript{3} (δ 7.26 ppm) as an internal standard. Coupling constants (J) are reported in hertz (Hz). \textsuperscript{13}C NMR spectra were recorded on Bruker AV400 (100 MHz) spectrometer, Bruker AV500 (126 MHz) spectrometer and Bruker AV700 (176 MHz) spectrometer with reference to CDCl\textsubscript{3} (δ 77.16 ppm) as an internal standard.

High-resolution mass spectrometry (HRMS) was performed on a Bruker Autoflex speed MALDI-TOF instrument using trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix and CH\textsubscript{2}Cl\textsubscript{2} as the solvent.
2. Experimental Procedures

Reaction of Rh(tmp) and Cyclopropyl Phenyl Ketone with the addition of 1 equiv of PPh₃ and 50 equiv of H₂O at 25 °C. Into the benzene solution of Rh²⁺(tmp) (0.00445 mmol), PPh₃ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (0.5 mL) and H₂O (4 µL, 0.222 mmol) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess cyclopropyl phenyl ketone was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane CH₂Cl₂ (1:1) to give the reddish purple solid Rh(tmp)CH₂CH₂CH₂COPh 2a (2.1 mg, 0.00204 mmol, 46% yield). Rf = 0.64 (Hexane: CH₂Cl₂ = 1:1). ¹H NMR (500 MHz, CDCl₃) δ -4.73 (dt, 2 H, 2 J_Rh-H = 2.8 Hz, 3 J_HH = 8.1 Hz), -3.76 (quint, 2 H, J = 8.0 Hz), 0.18 (t, 3 H, J = 7.6 Hz), 1.82 (s, 12 H), 1.92 (s, 12 H), 2.63 (s, 12 H), 6.81 (d, 2 H, J = 7.8 Hz), 7.03 (t, 2 H, J = 7.5 Hz), 7.28 (s, 4 H), 8.50 (s, 8 H). ¹³C NMR (126 MHz, CDCl₃) δ 12.85 (d, ¹J_Rh-C = 28.5 Hz), 21.60, 21.68, 21.84, 23.62, 36.24, 119.74, 127.40, 127.83, 127.85, 128.06, 130.79, 132.34, 135.83, 137.53, 138.51, 139.08, 139.12, 142.69, 197.52. HRMS (MALDI-MS): calcd for [M]⁺ (C₆₆H₆₃N₄Rh) m/z 1030.4051, found m/z 1030.4064.

Optimization of conditions

a. Temperature effect. Into the benzene solution of Rh²⁺(tmp) (0.00445 mmol), PPh₃ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (500 µL) and H₂O (4 µL, 0.222 mmol) were added. The mixture was then stirred under nitrogen at 50 °C for 10 minutes. Excess solvent was removed and the dark red crude product
was then purified by column chromatography on silica gel eluting with hexane / CH$_2$Cl$_2$ (1:1) to give the reddish purple solid of Rh(tmp)CH$_2$CH$_2$CH$_2$COPh 2a. (2.4 mg, 0.00233 mmol, 52% yield).

b. **Substrate loading effect.** Into the benzene solution of Rh$^{II}$(tmp) (0.00445 mmol), PPh$_3$ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (65 µL, 0.465 mmol), H$_2$O (4 µL, 0.222 mmol) and acetone (430 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH$_2$Cl$_2$ (1:1) to give the reddish purple solid of Rh(tmp)CH$_2$CH$_2$CH$_2$COPh 2a (2.2 mg, 0.00213 mmol, 48% yield).

c. **H$_2$O effect.** Into the benzene solution of Rh$^{II}$(tmp) (0.00445 mmol), PPh$_3$ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (65 µL, 0.465 mmol) and acetone (430 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH$_2$Cl$_2$ (1:1) to give the reddish purple solid of Rh(tmp)CH$_2$CH$_2$CH$_2$COPh 2a (2.0 mg, 0.00194 mmol, 44% yield).

d. **PPh$_3$ effect.** The benzene solvent of Rh$^{II}$(tmp) (0.00445 mmol) was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (65 µL, 0.465 mmol) and acetone (430 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica
gel eluting with hexane / CH₂Cl₂ (1:1) to give the reddish purple solid of Rh(tmp)CH₂CH₂CH₂COPh 2a (1.1 mg, 0.00107 mmol, 24% yield).

**e. Solvent effect.** Into the benzene solution of Rh²⁺(tmp) (0.00445 mmol), PPh₃ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (65 µL, 0.465 mmol) and benzene (430 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH₂Cl₂ (1:1) to give the reddish purple solid of Rh(tmp)CH₂CH₂CH₂COPh 2a (2.4 mg, 0.00233 mmol, 52% yield).

**H source investigation.** Into the benzene solution of Rh²⁺(tmp) (0.00445 mmol), PPh₃ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl phenyl ketone (65 µL, 0.465 mmol), D₂O (4.5 µL, 0.225 mmol) and acetone (430 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH₂Cl₂ (1:1) to give the reddish purple solid of Rh(tmp)CH₂CH₂CH₂COPh 2a (1.9 mg, 0.00184 mmol, 41% yield).

**Substrate scope**

**a. Reaction of Rh²⁺(tmp) and cyclopropyl methyl ketone.** Into the benzene solution of Rh²⁺(tmp) (0.00445 mmol), PPh₃ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl
methyl ketone (42 µL, 0.448 mmol) and benzene (460 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH₂Cl₂ (1:1) to give the reddish purple solid of Rh(tmp)CH₂CH₂CH₂COCH₃ 2b (2.2 mg, 0.00227 mmol, 51% yield). Rf = 0.53 (Hexane: CH₂Cl₂ = 1:1). ¹H NMR (400 MHz, CDCl₃) δ -4.89 (m, 2 H), -3.93 (m, 2 H), -0.38 (t, 3 H, J = 7.1 Hz), 0.80 (s, 3 H), 1.88 (s, 24 H), 2.61 (s, 12 H), 7.19 (s, 4 H), 8.48 (s, 8 H). ¹³C NMR (100 MHz, CDCl₃) δ 12.46 (d, J_{Rh-C} = 27.9 Hz), 21.61, 21.67, 21.92, 22.98, 29.92, 41.42, 119.75, 127.87, 130.81, 137.59, 138.46, 138.92, 139.18, 142.68, 206.74. HRMS (MALDI-MS): calcd for [M]⁺ (C₆₁H₆₁N₄ORh) m/z 968.3895, found m/z 968.3873.

b. Reaction of Rh^{II}(tmp) and cyclopropyl cyanide. Into the benzene solution of Rh^{II}(tmp) (0.00445 mmol), PPh₃ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl cyanide (33 µL, 0.448 mmol) and benzene (470 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH₂Cl₂ (1:1) to give the reddish purple solid of Rh(tmp)CH₂CH₂CH₂CN 2c (1.9 mg, 0.00200 mmol, 45% yield). Rf = 0.58 (Hexane: CH₂Cl₂ = 1:1). ¹H NMR (500 MHz, CDCl₃) δ -4.89 (m, 2 H), -3.92 (quint, 2 H, J = 7.6 Hz), -0.56 (t, 3 H, J = 7.2 Hz), 1.88 (s, 24 H), 2.61 (s, 12 H), 7.26 (s, 4 H), 8.51 (s, 8 H). ¹³C NMR (126 MHz, CDCl₃) δ 8.63 (d, J_{Rh-C} = 29.9 Hz), 13.45, 21.61, 21.66, 21.96, 23.31, 117.45, 119.87, 127.93, 127.97, 130.98, 137.71, 138.31, 138.91, 139.11, 142.69. HRMS (MALDI-MS): calcd for [M]⁺ (C₆₀H₅₈N₄Rh) m/z 951.3742, found m/z 951.3782.
c. Reaction of Rh\textsuperscript{II}(tmp) and cyclopropyl benzene. Into the benzene solution of Rh\textsuperscript{II}(tmp) (0.00445 mmol), PPh\textsubscript{3} (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed cyclopropyl benzene (56 µL, 0.445 mmol) and benzene (445 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 2 hours. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH\textsubscript{2}Cl\textsubscript{2} (1:1) to give the reddish purple solid of Rh(tmp)CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Ph\textsuperscript{2} 2d (1.9 mg, 0.00189 mmol, 42% yield). R\textsubscript{f} = 0.87 (Hexane: CH\textsubscript{2}Cl\textsubscript{2} = 1:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) -4.78 (m, 2 H), -3.90 (quint, 2 H, \(J = 7.9\) Hz), =0.14 (t, 3 H, \(J = 7.4\) Hz), 1.76 (s, 12 H), 1.92 (s, 12 H), 2.61 (s, 12 H), 5.51 (d, 2 H, \(J = 7.3\) Hz), 6.61 (t, 2 H, \(J = 7.2\) Hz), 6.70 (t, 1 H, \(J = 7.1\) Hz), 7.24 (s, 4 H), 8.46 (s, 8 H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 14.15 (d, \(J_{Rh-C} = 26.3\) Hz), 21.61, 21.70, 21.83, 33.3, 119.65, 124.74, 127.03, 127.35, 127.82, 130.70, 137.50 138.57, 139.09, 140.36, 142.67. HRMS (MALDI-MS): calcd for [M]\textsuperscript{+} (C\textsubscript{65}H\textsubscript{63}N\textsubscript{4}Rh) \(m/z\) 1002.4102, found \(m/z\) 1002.4025.

d. Reaction of Rh\textsuperscript{II}(tmp) and Ethyl Cyclopropanecarboxylate. Into the benzene solution of Rh\textsuperscript{II}(tmp) (0.00445 mmol), PPh\textsubscript{3} (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed ethyl cyclopropanecarboxylate (55 µL, 0.467 mmol) and benzene (445 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 4 days. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH\textsubscript{2}Cl\textsubscript{2} (1:1) to give the reddish purple solid of Rh(tmp)CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}COOEt 2e (1.7 mg, 0.00170 mmol, 38% yield). R\textsubscript{f} = 0.58 (Hexane: CH\textsubscript{2}Cl\textsubscript{2} = 1:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) -4.89 (m, 2 H), -3.90 (quint, 2 H, \(J = 8.1\) Hz), -0.48 (t, 2 H, \(J = 7.6\) Hz), 0.65 (t, 3
H, J = 7.1 Hz), 1.87 (s, 12 H), 1.89 (s, 12 H), 2.61 (s, 12 H), 3.29 (qua, 2 H, J = 7.1 Hz), 8.48 (s, 8 H). 13C NMR (100 MHz, CDCl3) δ 12.27 (d, $^1J_{Rh-C} = 28.3$ Hz), 13.86, 21.61, 21.68, 21.89, 23.48, 31.76, 59.25, 119.68, 127.84, 127.87, 130.77, 137.54, 138.52, 139.06, 139.14, 142.66, 171.07. HRMS (MALDI-MS): calcd for [M]$^+$ (C$_{62}$H$_{63}$N$_4$O$_2$Rh) m/z 998.4006, found m/z .998.4039.

e. Reaction of Rh$^{II}$(tmp) and Diethyl Cyclopropane – 1, 1 - Dicarboxylate.
Into the benzene solution of Rh$^{II}$(tmp) (0.00445 mmol), PPh$_3$ (1.2 mg, 0.00458 mmol) was added and the reaction mixture was stirred at 25 °C. After 10 minutes, the benzene solvent was removed by vacuum evaporation and then degassed diethyl cyclopropane – 1, 1 – dicarboxylate (72 µL, 0.450 mmol) and benzene (430 µL) were added. The mixture was then stirred under nitrogen at 25 °C for 10 minutes. Excess solvent was removed and the dark red crude product was then purified by column chromatography on silica gel eluting with hexane / CH$_2$Cl$_2$ (1:1) to give the reddish purple solid of Rh(tmp)CH$_2$CH$_2$CH(COOEt)$_2$ 2f (3.2 mg, 0.00299 mmol, 67% yield). Rf = 0.26 (Hexane: CH$_2$Cl$_2$ = 1:1). 1H NMR (400 MHz, CDCl3) δ -4.96 (m, 2 H), -3.68 (quart, 2 H, J = 8.3 Hz), 0.39 (t, 1 H, J = 7.5 Hz), 0.64 (t, 6 H, J = 7.1 Hz), 1.87 (s, 12 H), 1.89 (s, 12 H), 2.61 (s, 12 H), 3.30 (quart, 4 H, J = 7.1 Hz), 8.49 (s, 8 H). 13C NMR (100 MHz, CDCl3) δ 8.83 (d, $^1J_{Rh-C} = 28.5$ Hz), 13.69, 21.61, 21.66, 21.97, 26.59, 49.17, 60.17, 119.69, 127.83, 127.88, 130.81, 137.56, 138.50, 139.11, 139.15, 142.67, 166.93. HRMS (MALDI-MS): calcd for [M]$^+$ (C$_{65}$H$_{67}$N$_4$O$_4$Rh) m/z 1070.4212, found m/z .1070.4195.

**Reaction of Rh(tmp)H and cyclopropyl benzene.** The benzene solvent of Rh(tmp)H (11.5 mg, 0.013 mmol) was removed by vacuum evaporation and then degassed cyclopropyl benzene (165 µL, 1.32 mmol) and benzene (1 mL) were added. The mixture was then stirred under nitrogen at 25 °C for 2 days. Excess solvent was removed and the dark red crude product was then purified by column
chromatography on silica gel eluting with hexane / CH₂Cl₂ (1:1) to give the reddish purple solid of Rh(tmp)CH₂CH₂CH₂Ph² 2d (7.6 mg, 0.00758 mmol, 58% yield).
# 3. List of Spectra

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<td>$^1$H NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COPh 2a</td>
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$^1$H NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COPh 2a

$^{13}$C NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COPh 2a
$^1$H NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COCH$_3$ 2b

$^{13}$C NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COCH$_3$ 2b

S12
$^1$H NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$CN 2c

$^{13}$C NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$CN 2c
$^1$H NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$Ph 2d

$^{13}$C NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$Ph 2d
$^1$H NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COOEt 2e

$^{13}$C NMR of Rh(tmp)CH$_2$CH$_2$CH$_2$COOEt 2e
\(^1\)H NMR of Rh(tmp)CH\(_2\)CH\(_2\)CH(COOEt)\(_2\) 2f

\(^{13}\)C NMR of Rh(tmp)CH\(_2\)CH\(_2\)CH(COOEt)\(_2\) 2f
4. Reference
