Nickel-Catalyzed Intermolecular Alkyne Insertion into Cyclobutanones

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Supporting Information

General. All reactions were carried out with standard Schlenk and glove box techniques under a nitrogen atmosphere. Preparative thin-layer chromatography was performed with silica gel 60 PF₂₅₄ (Merck). ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 2000 (¹H at 300.07 Hz and ¹³C at 75.46 Hz) spectrometer. All NMR data were obtained in CDCl₃. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm. Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.00 ppm. High resolution mass spectra were recorded on a JOEL JMS-SX102A spectrometer. IR spectra were recorded on a Shimadzu FTIR-8100 spectrometer.

Materials. Cyclobutanones **1** were prepared by [2 + 2] cycloaddition of the corresponding olefins with dichloroketene and the subsequent dechlorination with zinc dust in acetic acid.¹ 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) was prepared according to the literature procedure.² Toluene was distilled over sodium–benzophenone ketyl prior to use. All other commercially available chemical resources were used without further purifications.

Nickel-Catalyzed Reactions of Cyclobutanones **1** and Alkynes **2**.

(1) Hyatt, J. A.; Raynolds, P. W. *Org. React.* **1994**, *45*, 159.

(2) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523.

5-Methyl-5-phenyl-2,3-dipropyl-2-cyclohexenone (3a). To a toluene solution (1.0 mL) of Ni(cod)₂ (5.5 mg, 0.02 mmol) and P(*c*-Hex)₃ (11.2 mg, 0.04 mmol) were added **1a** (32.7 mg, 0.20 mmol) and 4-octyne (**2a**, 33 mg, 0.30 mmol). After being stirred for 3 h at 100 °C, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 9:1) to afford **3a** (52.4 mg, 95%): IR (neat) 1663 cm⁻¹; ¹H NMR δ 0.81 (t, *J* = 7.4 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H), 1.19-1.29 (m, 2H), 1.33 (s, 3H), 1.47 (sext, *J* = 7.5 Hz, 2H), 2.12-2.31 (m, 4H), 2.58 (d, *J* = 18.2 Hz, 1H), 2.59 (dd, *J* = 16.2, 1.2 Hz, 1H), 2.80 (d, *J* = 18.2 Hz, 1H), 2.89 (dd, *J* = 16.1, 1.2 Hz, 1H), 7.15-7.20 (m, 1H), 7.27-7.32 (m, 4H); ¹³C NMR δ 14.1, 14.2, 20.8, 22.6, 26.8, 29.0, 36.9, 39.6, 44.0, 49.9, 125.1, 126.1, 128.3, 135.2, 147.1, 155.7, 198.4; HRMS (EI) calcd for C₁₉H₂₆O (M⁺) 270.1984, found 270.1982. Anal. Calcd for C₁₉H₂₆O: C, 84.39; H, 9.69. Found: C, 84.55; H, 9.85.

2,3-Diethyl-5-methyl-5-phenyl-2-cyclohexenone (3b). To a toluene solution (0.5 mL) of Ni(cod)₂ (5.5 mg, 0.02 mmol) and P(*c*-Hex)₃ (11.2 mg, 0.04 mmol) were added **1a** (32.1 mg, 0.20 mmol) and 3-hexyne (**2b**, 24.6 mg, 0.30 mmol). After being stirred for 6 h at 90 °C, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 9:1) to afford **3b** (47.2 mg, 97%): ¹H NMR δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.04 (t, *J* = 7.7 Hz, 3H), 1.33 (s, 3H), 2.17-2.33 (m, 4H), 2.58 (d, *J* = 17.7 Hz, 1H), 2.60 (dd, *J* = 16.1, 1.1 Hz, 1H), 2.79 (d, *J* = 17.7 Hz, 1H), 2.88 (dd, *J* = 16.1, 1.1 Hz, 1H), 7.17-7.21 (m, 1H), 7.27-7.30 (m, 4H); ¹³C NMR δ 12.0, 14.0, 17.9, 27.7, 28.8, 39.5, 43.6, 49.9, 125.1, 126.1, 128.2, 136.0, 147.1, 156.7, 198.4; HRMS (EI) calcd for C₁₇H₂₂O (M⁺) 242.1671, found 242.1670.

5-Methyl-2,3,5-triphenyl-2-cyclohexenone (3c). A toluene solution (0.3 mL) of Ni(cod)₂ (5.5 mg, 0.02 mmol), P(*c*-Hex)₃ (11.2 mg, 0.04 mmol), and **1a** (31.6 mg, 0.20 mmol) was stirred at 110 °C for a few minutes. A toluene solution (0.2 mL) of diphenylacetylene (**2c**,

106.9 mg, 0.60 mmol) was added dropwise via syringe over 2 h. After being stirred for 4 h, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 9:1) to afford **3c** (56.0 mg, 84%): ^1H NMR δ 1.57 (s, 3H), 2.91 (dd, J = 16.1, 0.6 Hz, 1H), 3.15 (d, J = 18.0 Hz, 1H), 3.24 (dd, J = 16.1, 1.7 Hz, 1H), 3.35 (dd, J = 18.0, 1.7 Hz, 1H), 6.83-6.86 (m, 2H), 6.98-7.03 (m, 2H), 7.11-7.19 (m, 6H) 7.24-7.30 (m, 1H) 7.36-7.45 (m, 4H); ^{13}C NMR δ 29.5, 40.3, 46.3, 50.3, 125.4, 126.4, 126.7, 127.4, 127.7, 127.8, 127.9, 128.5, 130.7, 134.9, 137.4, 140.7, 146.3, 155.2, 197.6; HRMS (EI) calcd for $\text{C}_{25}\text{H}_{22}\text{O}$ (M^+) 338.1671, found 338.1671.

2,5-Dimethyl-3,5-diphenyl-2-cyclohexenone (3d) and 3,5-Dimethyl-2,5-diphenyl-2-cyclohexenone (3'd). A toluene solution (0.4 mL) of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.02 mmol), $\text{P}(c\text{-Hex})_3$ (11.2 mg, 0.04 mmol), and **1a** (31.7 mg, 0.20 mmol) was stirred at 110 °C for a few minutes. A toluene solution (0.1 mL) of 1-phenyl-1-propyne (**2d**, 69.6 mg, 0.60 mmol) was added dropwise via syringe over 2 h. After being stirred for 4 h, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 9:1) to afford **3d** (39.2 mg, 72%) and **3'd** (3.2 mg, 6%). **3d**: ^1H NMR δ 1.44 (s, 3H), 1.68 (t, J = 1.8 Hz, 3H), 2.76 (dd, J = 16.1, 1.1 Hz, 1H), 2.92 (ddd, J = 17.7, 1.9, 1.2 Hz, 1H), 3.07 (dd, J = 16.1, 1.5 Hz, 1H), 3.13 (dt, J = 17.7, 1.5 Hz, 1H), 7.14-7.17 (m, 2H), 7.22-7.26 (m, 1H), 7.30-7.43 (m, 7H); ^{13}C NMR δ 12.5, 29.5, 40.3, 46.3, 49.8, 125.2, 126.3, 126.9, 127.8, 128.4, 128.5, 131.6, 141.2, 146.8, 153.8, 199.3; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{20}\text{O}$ (M^+) 276.1514, found 276.1512. **3'd**: ^1H NMR δ 1.45 (s, 3H), 1.82 (s, 3H), 2.76 (d, J = 16.8 Hz, 1H + 1H), 2.97 (d, J = 18.0 Hz, 1H), 3.05 (d, J = 15.9 Hz, 1H), 6.93-6.96 (m, 2H), 7.22-7.35 (m, 8H).

Stereochemical Assignment of 3d and 3'd. The two regioisomers **3d** and **3'd** were subjected to NOE experiments. No NOE between the methyl protons (δ 1.68) and the C4 and C6 methylene protons (δ 2.76, 2.92, 3.07, and 3.13) was observed for **3d**. On the other hand, an NOE between the methyl protons (δ 1.82) and the C4 methylene protons (δ 2.76 and 2.97) was observed for **3'd**.

3-(4-Methoxyphenyl)-2,5-dimethyl-5-phenyl-2-cyclohexenone (3e) and 2-(4-Methoxyphenyl)-3,5-dimethyl-5-phenyl-2-cyclohexenone (3'e). A toluene solution (0.4 mL) of Ni(cod)₂ (5.5 mg, 0.02 mmol), P(*c*-Hex)₃ (11.2 mg, 0.04 mmol), and **1a** (31.3 mg, 0.20 mmol) was stirred at 110 °C for a few minutes. A toluene solution (0.1 mL) of 1-(4-methoxyphenyl)-1-propyne (**2e**, 87.7 mg, 0.60 mmol) was added dropwise via syringe over 2 h. After being stirred for 4 h, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 8:1) to afford **3e** (31.1 mg, 52%) and **3'e** (3.5 mg, 6%). **3e**: ¹H NMR δ 1.43 (s, 3H), 1.71 (t, *J* = 1.8 Hz, 3 H), 2.74 (dd, *J* = 16.1, 0.8 Hz, 1H), 2.90 (ddd, *J* = 17.9, 1.7, 0.8 Hz, 1H), 3.05 (dd, *J* = 16.1, 1.2 Hz, 1H), 3.12 (dt, *J* = 17.9, 1.6 Hz, 1H), 3.83 (s, 3H), 6.90-6.95 (m, 2H), 7.09-7.14 (m, 2H), 7.19-7.24 (m, 1H), 7.32-7.34 (m, 4H); ¹³C NMR δ 12.7, 29.5, 40.2, 46.3, 49.8, 55.3, 113.7, 125.2, 126.2, 128.4, 128.6, 131.3, 133.4, 146.8, 153.5, 159.2, 199.3; HRMS (EI) calcd for C₂₁H₂₂O₂ (M⁺) 306.1620, found 306.1621. **3'e**: ¹H NMR δ 1.44 (s, 3H), 1.84 (s, 3H), 2.75 (d, *J* = 16.5 Hz, 1H + 1H), 2.96 (d, *J* = 18.9 Hz, 1H), 3.04 (dd, *J* = 15.9, 1.2 Hz, 1H), 3.80 (s, 3H), 6.83-6.90 (m, 4H), 7.20-7.27 (m, 1H), 7.30-7.35 (m, 4H); HRMS (EI) calcd for C₂₁H₂₂O₂ (M⁺) 306.1620, found 306.1617.

2,5-Dimethyl-5-phenyl-3-(4-trifluoromethylphenyl)-2-cyclohexenone (3f) and 3,5-Dimethyl-5-phenyl-2-(4-trifluoromethylphenyl)-2-cyclohexenone (3'f). A toluene

solution (0.4 mL) of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.02 mmol), $\text{P}(c\text{-Hex})_3$ (11.2 mg, 0.04 mmol), and **1a** (31.8 mg, 0.20 mmol) was stirred at 110 °C for a few minutes. A toluene solution (0.1 mL) of 1-(4-trifluoromethylphenyl)-1-propyne (**2f**, 110.4 mg, 0.60 mmol) was added dropwise via syringe over 2 h. After being stirred for 4 h, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3f** (40.8 mg, 60%) and **3'f** (3.9 mg, 6%). **3f**: ^1H NMR δ 1.44 (s, 3H), 1.65 (t, $J = 1.8$ Hz, 3H), 2.77 (d, $J = 15.9$ Hz, 1H), 2.90 (dd, $J = 18.2, 2.0$ Hz, 1H), 3.04-3.14 (m, 2H), 7.20-7.28 (m, 3H), 7.30-7.38 (m, 4H), 7.66 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR δ 12.4, 29.6, 40.5, 46.1, 49.7, 123.9 (q, $^1J_{\text{C-F}} = 271.5$ Hz), 125.2, 125.5 (q, $^3J_{\text{C-F}} = 3.8$ Hz), 126.4, 127.3, 128.6, 129.9 (q, $^2J_{\text{C-F}} = 32.4$ Hz), 132.3, 144.7, 146.4, 151.9, 198.8; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{O}$ (M^+) 344.1388, found 344.1386. **3'f**: ^1H NMR δ 1.46 (s, 3H), 1.82 (s, 3H), 2.76 (d, $J = 16.2$ Hz, 1H), 2.78 (d, $J = 18.0$ Hz, 1H), 2.99 (d, $J = 18.0$ Hz, 1H), 3.08 (dd, $J = 16.2, 1.5$ Hz, 1H), 7.06 (d, $J = 8.4$ Hz, 2H), 7.21-7.29 (m, 1H), 7.31-7.40 (m, 4H), 7.58 (dd, $J = 8.4, 0.6$ Hz, 2H); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{O}$ (M^+) 344.1388, found 344.1385.

5,5-Diphenyl-2,3-dipropyl-2-cyclohexenone (3g). To a toluene solution (0.5 mL) of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.02 mmol) and $\text{P}(c\text{-Hex})_3$ (11.2 mg, 0.04 mmol) were added **1b** (44.5 mg, 0.20 mmol) and 4-octyne (**2a**, 33 mg, 0.30 mmol). After being stirred for 3 h at 110 °C, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3g** (60.7 mg, 91%): ^1H NMR δ 0.73 (t, $J = 7.5$ Hz, 3H), 0.88 (t, $J = 7.4$ Hz, 3H), 1.11-1.23 (m, 2H), 1.39-1.51 (m, 2H), 2.16-2.22 (m, 2H), 2.24-2.29 (m, 2H), 3.14 (s, 2H), 3.15 (s, 2H), 7.13-7.19 (m, 6H), 7.22-7.28 (m, 4H); ^{13}C NMR δ 14.0, 14.2, 20.7, 22.4, 26.8, 37.1, 42.6, 47.6, 49.9, 126.2, 126.7, 128.2, 136.3, 146.3, 155.4, 197.7; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{28}\text{O}$ (M^+) 332.2140, found 332.2143.

2-Methyl-3,5,5-triphenyl-2-cyclohexenone (3h) and 3-Methyl-2,5,5-triphenyl-2-cyclohexenone (3'h). A toluene solution (0.1 mL) of Ni(cod)₂ (5.5 mg, 0.02 mmol), P(*c*-Hex)₃ (11.2 mg, 0.04 mmol), and **1b** (44.5 mg, 0.20 mmol) was stirred at 110 °C for a few minutes. A toluene solution (0.1 mL) of 1-phenyl-1-propyne (**2d**, 69.6 mg, 0.60 mmol) was added dropwise via syringe over 2 h. After being stirred for 4 h, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3h** (43.2 mg, 64%) and **3'h** (3.4 mg, 5%). **3h**: ¹H NMR δ 1.66 (s, 3H), 3.34 (s, 2H), 3.46 (s, 2H), 7.12-7.44 (m, 15H); ¹³C NMR δ 12.5, 45.0, 48.3, 49.7, 126.3, 126.6, 126.9, 128.0, 128.4, 132.6, 141.0, 146.1, 153.4, 198.5 [one carbon signal is missing]; HRMS (EI) calcd for C₂₅H₂₂O (M⁺) 338.1671, found 338.1671. **3'h**: ¹H NMR δ 1.87 (s, 3H), 3.27 (s, 2H), 3.33 (s, 2H), 6.85-6.88 (m, 2H), 7.20-7.32 (m, 13H).

5,5-Diethyl-2,3-dipropyl-2-cyclohexenone (3i). To a toluene solution (1 mL) of Ni(cod)₂ (11.0 mg, 0.04 mmol) and P(*c*-Hex)₃ (22.4 mg, 0.08 mmol) were added **1c** (24.4 mg, 0.19 mmol) and 4-octyne (**2a**, 33 mg, 0.30 mmol). After being stirred for 3 h at 110 °C, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3i** (28.1 mg, 61%): ¹H NMR δ 0.77 (t, *J* = 7.4 Hz, 6H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H), 1.25-1.38 (m, 6H), 1.42-1.55 (m, 2H), 2.16-2.25 (m, 8H); ¹³C NMR δ 7.7, 14.3, 14.4, 21.2, 22.8, 26.9, 28.7, 36.9, 37.8, 40.4, 47.8, 134.6, 155.7, 199.5; HRMS (EI) calcd for C₁₆H₂₈O (M⁺) 236.2140, found 236.2143.

5,5-Diethyl-2-methyl-3-phenyl-2-cyclohexenone (3j) and 5,5-Diethyl-3-methyl-2-phenyl-2-cyclohexenone (3'j). A toluene solution (0.4 mL) of Ni(cod)₂ (11.0 mg, 0.04 mmol), P(*c*-Hex)₃ (22.4 mg, 0.08 mmol), and **1c** (24.5 mg, 0.19 mmol) was stirred at 110 °C for a few minutes. A toluene solution (0.1 mL) of 1-phenyl-1-propyne (**2d**, 69.6 mg, 0.60 mmol) was added dropwise via syringe over 2 h. After being stirred for 4 h, the reaction

mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 20:1) to afford **3j** (20.3 mg, 43%) and **3'j** (2.1 mg, 4%). **3j**: ^1H NMR δ 0.83 (t, J = 7.4 Hz, 6H), 1.45 (q, J = 7.5 Hz, 4H), 1.69 (t, J = 2.0 Hz, 3H), 2.39 (s, 2H), 2.49 (d, J = 1.8 Hz, 2H), 7.16-7.19 (m, 2H), 7.32-7.42 (m, 3H); ^{13}C NMR δ 7.8, 12.5, 28.8, 38.4, 43.0, 47.5, 127.0, 127.7, 128.3, 130.9, 141.6, 153.9, 200.3; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{22}\text{O}$ (M^+) 242.1671, found 242.1671. **3'j**: ^1H NMR δ 0.85 (t, J = 7.5 Hz, 6H), 1.46 (q, J = 7.4 Hz, 4H), 1.80 (s, 3H), 2.36 (s, 2H), 2.41 (s, 2H), 7.04-7.07 (m, 2H), 7.25-7.38 (m, 3H).

5-Octyl-2,3-dipropyl-2-cyclohexenone (3k). To a toluene solution (0.5 mL) of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.02 mmol) and $\text{P}(c\text{-Hex})_3$ (11.2 mg, 0.04 mmol) were added **1d** (36.3 mg, 0.20 mmol) and 4-octyne (**2a**, 33 mg, 0.30 mmol). After being stirred for 3 h at 110 $^\circ\text{C}$, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3k** (21.7 mg, 37%) and **6a** (21.3 mg, 37%): ^1H NMR δ 0.85-0.98 (m, 9H), 1.26-1.35 (m, 16H), 1.42-1.54 (m, 2H), 1.96-2.08 (m, 3H), 2.19-2.26 (m, 4H), 2.30-2.37 (m, 1H), 2.47-2.51 (m, 1H); ^{13}C NMR δ 14.1, 14.3, 21.3, 22.7, 22.9, 26.5, 27.1, 29.3, 29.6, 29.7, 31.9, 34.6, 35.9, 37.0, 37.3, 44.5, 135.3, 158.1, 199.6 [one carbon signal is missing]; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{36}\text{O}$ (M^+) 292.2766, found 292.2770.

5-Phenyl-2,3-dipropyl-2-cyclohexenone (3l). A toluene solution (1.5 mL) of **1e** (29.3 mg, 0.20 mmol) and 4-octyne (**2a**, 33 mg, 0.30 mmol) was stirred for 10 minutes at 110 $^\circ\text{C}$. To the stirring solution, a toluene solution (0.5 mL) of $\text{Ni}(\text{cod})_2$ (5.5 mg, 0.02 mmol) and IPr (7.8 mg, 0.02 mmol), which was stirred for 6 h at room temperature in glove box, was added. After being stirred for 18 h at 110 $^\circ\text{C}$, the reaction mixture was concentrated, and the residue was purified by preparative thin-layer chromatography of silica gel (hexane:AcOEt = 10:1) to afford **3l** (31.4 mg, 61%): ^1H NMR δ 0.94 (t, J = 7.5 Hz, 3H), 0.97 (t, J = 7.4 Hz, 3H), 1.32-

1.44 (m, 2H), 1.47-1.60 (m, 2H), 2.23-2.36 (m, 4H), 2.52-2.62 (m, 3H), 2.71 (dd, $J = 16.2$, 4.2 Hz, 1H), 3.17-3.28 (m, 1H), 7.22-7.26 (m, 3H), 7.31-7.37 (m, 2H); ^{13}C NMR δ 14.2, 14.3, 21.1, 22.8, 27.1, 36.8, 38.5, 40.4, 44.6, 126.5, 126.7, 128.5, 135.4, 143.6, 157.6, 198.5; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{O}$ (M^+) 256.1827, found 256.1829.

2-Phenyl-5-propyl-2,5-nonadien-4-one (6b). The title compound was obtained by the reaction with $\text{Ni}(\text{cod})_2\text{-P}(c\text{-Hex})_3$. ^1H NMR δ 0.94 (t, $J = 7.8$ Hz, 3H), 0.96 (t, $J = 7.8$ Hz, 3H), 1.35-1.56 (m, 4H), 2.25 (q, $J = 7.4$ Hz, 2H), 2.33-2.39 (m, 2H), 2.40 (d, $J = 1.2$ Hz, 3H), 6.62 (t, $J = 7.4$ Hz, 1H), 6.78 (d, $J = 1.2$ Hz, 1H), 7.34-7.42 (m, 3H), 7.48-7.52 (m, 2H); ^{13}C NMR δ 14.0, 14.2, 18.4, 22.3, 22.5, 27.8, 31.0, 123.3, 126.2, 128.4, 128.5, 142.8, 143.1, 143.6, 150.5, 194.7; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{O}$ (M^+) 256.1827, found 256.1826.

Stereochemical Assignment of 6b. Divinyketone **6b** was subjected to NOE experiments. No NOE between the vinyl proton (δ 6.78) and the methyl protons (δ 2.40) was observed. On the other hand, an NOE between the vinyl proton (δ 6.78) and the aromatic *ortho* protons (δ 7.48-7.52) was observed.