Supporting Information for:

Copper-Catalyzed Semihydrogenation of Alkynes to (Z)-Alkenes

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General. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard schlenk technique under an argon atmosphere or in a glove box under a nitrogen atmosphere. Medium pressure liquid chromatography (MPLC) was performed using Kanto Chemical silica gel 60 (spherical, 40–50 μm) and Biotage® SNAP Ultra. Analytical thin layer chromatography (TLC) was performed on Merck TLC silica gel 60 F254 (0.25 mm) plates. Visualization was accomplished with UV light (254 nm). The hydrogenation reactions were performed with the autoclave (EYELA, HIP-7506).

Apparatus. Proton and carbon nuclear magnetic resonance spectra ($^1$H, $^{13}$C, and $^{19}$F NMR) were recorded on a JEOL ECS-400 ($^1$H NMR, 400MHz; $^{13}$C NMR 101 MHz; $^{19}$F NMR 376 MHz) spectrometer with solvent resonance as the internal standard ($^1$H NMR, CHCl$_3$ at 7.26 ppm; $^{13}$C NMR, CDCl$_3$ at 77.0 ppm; $^{19}$F NMR, C$_6$F$_6$ at –162 ppm). NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. Medium pressure liquid chromatography (MPLC) was performed with a Shoko Scientific Purif-espoir2 chromatograph. GC analysis was performed on a Shimadzu GC-2014 equipped with a BP1 column (SGE Analytical Science, 0.25 mm x 30 m, pressure = 149.0 kPa, detector = FID, 290 °C) with helium gas as a carrier. High-resolution mass spectra were obtained with Thermo Scientific Exactive (APCI).

Chemicals. Unless otherwise noted, commercially available chemicals were distilled and degassed before use. [(PPh$_3$)CuCl]$_4$, 1d, 1e were prepared according to the literature. PPh$_3$ was purchased from Nacalai Tesque and recrystallized from EtOH before use. The following reagents were purchased from commercial suppliers and used as received: Cu$_2$O (Aldrich), LiOrBu (Aldrich), LiOriPr (Aldrich), 1c (Aldrich), 1h (TCI), CuCl (Strem Chemicals), CuI (Aldrich), CuBr (Nacalai Tesque), CuCN (Nacalai Tesque), CuOAc (Aldrich), anhydrous iPrOH (Nacalai Tesque), iPrOH-d$_8$ (99.5 atom% D) (Wako Pure Chemical Industries), 4-iodobenzoic acid (Acros Organics), PdCl$_2$(PPh$_3$)$_2$ (TCI), N,N-dimethylformamide (Nacalai Tesque) and SOCl$_2$ (Nacalai Tesque). Anhydrous toluene, Et$_2$O, and CH$_2$Cl$_2$ was purchased from Kanto Chemical and degassed by purging vigorously with argon for 30 min and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al. 3

Preparation of 1g.

**steps i and ii:**
A flask was charged with 4-iodobenzoic acid (3.10 g, 12.5 mmol), CH₂Cl₂ (20 mL), SOCl₂ (2.0 mL, 25 mmol), and DMF (4 drops) in this order. Then, the mixture was stirred under reflux for 2 h. After removal of all volatiles, the residue was used in the next step without further purification. To a flask containing crude 1g–1 and Et₂O (10 mL), a suspension of LiO⁻iPr (918 mg, 13.9 mmol) in Et₂O (15 mL) was added dropwise at 0 °C. Then, the resulting mixture was stirred at room temperature for 1 h and then it was poured into NaHCO₃ aq. and extracted with Et₂O. The combined organic layer was washed with H₂O and dried over MgSO₄. After filtration, all of the volatiles were removed in vacuo, and the residue 1g–2 (3.41 g) was used in the next step without further purification.

**step iii:**
A flask was charged with crude 1g–2 (2.09 g), PdCl₂(PPh₃)₂ (300 mg, 0.43 mmol) and CuI (190 mg, 1.01 mmol). The flask was evacuated and refilled with Ar three times, then, to the flask, Et₂O (20 mL), phenylacetylene (1.0 mL, 9.4 mmol) and NEt₃ (3.9 mL, 28 mmol) were added in this order. The mixture was stirred at room temperature for 3 h and then it was poured into NH₄Cl aq. and extracted with Et₂O. The combined organic layer was washed with H₂O and dried over MgSO₄. After filtration, all of the volatiles were removed in vacuo. The product was purified by MPLC (160 g of silica gel, eluent: hexane then hexane/EtOAc = 95/5) and further purified by recrystallization from hexane, 1g was obtained in 36% yield (690 mg, 2.60 mmol) as a yellow solid, R₇ = 0.10 (n-hexane). 'H NMR (CDCl₃, 400 MHz): δ 8.02 (d, J = 8.1 Hz, 2H), 7.60–7.54 (m, 4H), 7.38–7.36 (m, 3H), 5.26 (sept, J = 6.0 Hz, 1H), 1.38 (d, J = 6.0 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃): δ 165.6, 131.7, 131.4, 130.2, 129.4, 128.7, 128.4, 127.7, 122.7, 92.1, 88.7, 68.6, 21.9. HRMS–APCI(+) (m/z): [M+H]⁺ calcld. for C₁₈H₁₇O₂, 265.1223; found, 265.1220.

**General procedure for Table 1.** In a glove box, to a vial, [(PPh₃)CuCl]₄ (7.2 mg, 5.0 μmol), toluene (1.0 mL), LiOrBu (40 mg, 0.50 mmol) and iPrOH (60 mg, 1.0 mmol) were added in this order. After the resulting mixture was stirred for 1 min at room temperature, 1a (160 mg, 1.0 mmol) and toluene (2.0 mL) were added. The vial was placed in an autoclave and the autoclave was taken out of the glove box. N₂ in the autoclave was replaced with H₂ by positive pressure of H₂. Then, the mixture was stirred at 100 °C for 3 h under 5 atm of H₂. After cooling to room temperature, H₂ was released and the mixture was diluted with EtOAc. The conversion was determined by GC analysis with n-tridecane (18 mg, 0.10 mmol) as an internal standard. The resulting solution was filtered through a pad of silica gel and the yields of the products were determined by 'H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.
**General procedure for entries 3–6 in Table 1.** In a glove box, a vial was charged with CuCl (2.0 mg, 0.020 mmol), a phosphine ligand (0.020 mmol) and toluene (1.00 mL), and the resulting solution was stirred for 10 min at room temperature. To this vial, LiOrBu (40 mg, 0.50 mmol) and iPrOH (60 mg, 1.0 mmol) were added in this order. After the resulting mixture was stirred for 1 min at room temperature, 1a (160 mg, 1.0 mmol) and toluene (2.0 mL) were added. The vial was placed in an autoclave and the autoclave was taken out of the glove box. N₂ in the autoclave was replaced with H₂ by positive pressure of H₂. Then, the mixture was stirred at 100 °C for 3 h under 5 atm of H₂. After cooling to room temperature, H₂ was released and the mixture was diluted with EtOAc. The conversion was determined by GC analysis with n-tridecane (18 mg, 0.10 mmol) as an internal standard. The resulting solution was filtered through a pad of silica gel and the yields of the products were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

(Z)-2a. The reaction of 1a followed by purification by MPLC (16 g of silica gel and Biotage® SNAP Ultra 10 g, n-hexane) gave the corresponding products (Z)-2a (130 mg, 0.80 mmol, 80%) as a colorless oil, Rf = 0.67 (n-hexane).¹H NMR (CDCl₃, 400 MHz): δ 7.37–7.22 (m, 5H), 6.43 (d, J = 11.6 Hz, 1H), 5.69 (dt, J = 11.6 Hz, 7.3 Hz, 1H), 2.35 (dq, J = 7.3 Hz, 1.8 Hz, 4H), 1.48–1.33 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H); ¹³C NMR (CDCl₃, 101 MHz): δ 137.8, 133.2, 128.7, 128.68, 128.1, 126.4, 32.2, 28.3, 22.4, 14.0; All the resonances of ¹H and ¹³C NMR spectra were consistent with reported values.³

**General procedure for Table 2.** Similar procedure for Table 1 was employed. The products were purified by MPLC on silica gel to give the corresponding products. In the case of entries 1, 6, 8, and 11, the yields of (Z)-2b, (E)-2b, 3b, (Z)-2g, (Z)-2i, and (Z)-5-dodecene were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

(Z)-2d. The reaction of 1d (180 mg, 1.0 mmol) at 60 °C followed by purification by MPLC (16 g of silica gel and Biotage® SNAP Ultra 10 g, n-hexane) gave the corresponding product (160 mg, 0.91 mmol, 91%) as a mixture of (Z)-2e, (E)-2d, and 3d prepared from (Z)-2d/(E)-2d/3d = 95/5/1 determined by ¹H NMR analysis) as a colorless oil, Rf = 0.53 (hexane).¹H NMR (CDCl₃, 400 MHz): δ 7.28–7.16 (m, 10H), 6.60 (s, 2H); ¹³C NMR (CDCl₃, 101 MHz): δ 137.2, 130.2, 128.8, 128.2, 127.1. All the resonances of ¹H and ¹³C NMR spectra were consistent with reported values.⁸a

(Z)-2e. The reaction of 1e (210 mg, 1.00 mmol) followed by purification by MPLC (16 g of silica gel and Biotage® SNAP Ultra 10 g, n-hexane) gave the corresponding product (208 mg, 0.99 mmol, 99%) as a mixture of (Z)-2e, (E)-2e, and 3e prepared from (Z)-2e/(E)-2e/3e = 98/1/2 determined by ¹H NMR analysis) as a colorless solid, Rf = 0.59 (n-hexane).¹H NMR (CDCl₃, 400 MHz): δ 7.17 (d, J = 8.1 Hz, 4H), 7.04 (d, J = 8.1 Hz, 4H), 6.50 (s, 2H), 2.32 (s, 6H); ¹³C NMR (CDCl₃, 101 MHz): δ 136.7, 134.5, 129.5, 128.8, 128.7, 122.1. All the resonances of ¹H and ¹³C NMR spectra were consistent with reported values.⁹a

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(Z)-2f. The reaction of 1f (214 mg, 1.00 mmol) followed by purification by MPLC (16 g of silica gel and Biotage® SNAP Ultra 10 g, n-hexane) gave the corresponding product (206 mg, 0.95 mmol, 95%) as a mixture of (Z)-2f, (E)-2f, and 3f in a 2f/2f/3f = 99/1/1 determined by 1H NMR analysis) as a colorless solid, Rf = 0.59 (n-hexane). 1H NMR (CDCl3, 400 MHz): δ 7.20–7.16 (m, 4H), 6.94–6.90 (m, 4H), 6.54 (s, 2H); 13C NMR (CDCl3, 101 MHz): δ 161.8 (d, J = 246.3 Hz), 132.9 (d, J = 2.9 Hz), 130.5 (d, J = 7.8 Hz), 129.1, 115.2 (d, J = 22.0 Hz); 19F NMR (CDCl3, 376 MHz): δ –114.7. All the resonances of 1H and 13C spectrum was consistent with reported values.10

(Z)-2g. The reaction of 1g (79 mg, 0.3 mmol) at 80 °C in toluene (0.8 mL) followed by purification by MPLC (16 g of silica gel and Biotage® SNAP Ultra 10 g, n-hexane/EtOAc = 99/1 to 93/7) gave the corresponding products (Z)-2g (42 mg, 0.16 mmol, 52%) as a pale yellow oil, Rf = 0.35 (n-hexane/EtOAc = 95/5). 1H NMR (CDCl3, 400 MHz): δ 7.90 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.25–7.20 (m, 5H), 6.71 (d, J = 12.2 Hz, 1H), 6.61 (d, J = 12.2 Hz, 1H), 5.24 (sept, J = 6.1 Hz, 1H), 1.36 (d, J = 6.1 Hz, 6H); 13C NMR (CDCl3, 101 MHz): δ 165.9, 141.8, 136.7, 132.1, 129.4, 129.31, 129.28, 128.83, 128.74, 128.3, 127.4, 68.3, 21.9. HRMS–APCl (+) (m/z): [M+H]+ calcd. for C18H19O2, 267.1380; found, 267.1375.

(Z)-2h. The reaction of 1h (170 mg, 1.0 mmol) followed by purification by MPLC (16 g of silica gel and Biotage® SNAP Ultra 10 g, n-hexane) gave the corresponding products (Z)-2h (130 mg, 0.76 mmol, 76%) as a colorless oil, Rf = 0.92 (n-hexane). 1H NMR (CDCl3, 400 MHz): δ 5.36 (m, 2H), 2.03 (q, J = 6.4 Hz, 4H), 1.39–1.24 (m, 12H), 0.89 (t, J = 6.9 Hz, 6H); 13C NMR (CDCl3, 101 MHz): δ 129.9, 31.6, 29.5, 27.2, 22.6, 14.1. All the resonances of 1H and 13C NMR spectra were consistent with reported values.11

The procedure for Eq. 1. Similar procedure for Table 1 was employed by using \(^{1}\text{PrOH-}d_8\) instead of \(^{1}\text{PrOH}.\) The yield and deuterium incorporation were determined by \(^1\text{H} \text{NMR analysis (Figure S1 and S2).}

Figure S1.

Figure S2.
C₅H₁₁ + H₂ → [Cu₄(PPh₃)₂](2.0 mol %/Cu) L(OtBu)₅ (50 mol %)

1.0 mmol

[(PPh₃)CuCl]₄ (2.0 mol %/Cu) LiOₜBu (50 mol %)
iPrOH (1.0 mmol)
toluene, 100 °C, 3 h

85% by NMR

<1% by NMR

S10
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\begin{align*}
\text{Et} + \text{H}_2 & \xrightarrow{\text{[PPh}_3\text{CuCl]}_4 (2.0 \text{ mol %/Cu})} \text{Et}_2\text{HCl} \\
\text{LiO} \text{tBu (50 mol %)} & \xrightarrow{\text{iPrOH (1.0 mmol)}} \text{toluene, 100 °C, 3 h} \\
& \xrightarrow{\text{(20 mg, 0.12 mmol)}} \text{Ha} <1\% \text{by NMR}
\end{align*}
\]
(Z)-2h

$C_9H_{11}$

$C_9H_{11}$

$\text{C}_{13}$

$\text{p.p.m.}$

$129.88$  $77.324$  $77.000$  $76.685$  $43.258$  $29.480$  $27.182$  $22.605$  $14.072$