Supporting Information

Direct β -Alkylation of Secondary Alcohols with Primary Alcohols Catalyzed by a Cp*Ir Complex

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Experimental Section:

General: All reactions and manipulations were carried out under an atmosphere of argon by means of standard Schlenk techniques. ^1H - and ^{13}C -NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. Gas chromatography (GC) analyses were performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17). Column chromatography was carried out by using Wako-gel C-200. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Solvents were dried by standard procedures and distilled prior to use. The catalysts $[\text{Cp}^*\text{IrCl}_2]_2$ (Cp^* = pentamethylcyclopentadienyl), $[\text{Cp}^*\text{RhCl}_2]_2$, and $[\text{IrCl}(\text{cod})]_2$ (cod = 1,5-cyclooctadiene) were prepared according to the literature method.¹ The catalyst $\text{Cp}^*\text{IrCl}_2(\text{PPh}_3)$ was prepared by addition of one equivalent (per iridium) of PPh_3 to $[\text{Cp}^*\text{IrCl}_2]_2$ *in situ*. 1-(4-Methoxyphenyl)ethanol (**1c**) and 1-(4-trifluoromethylphenyl)ethanol (**1e**) were prepared by reduction of corresponding ketones with excess (1.5 - 2.0 equiv) NaBH_4 . All other reagents are commercially available and were used as received.

General procedure for the β -alkylation of 1-phenylethanol (1a) with 1-butanol (2a) under various conditions shown in Table 1: Under an atmosphere of argon in a heavy-walled glass reactor, **1a** (3.0 mmol), **2a** (3.6 mmol), catalyst (0.5-1.0%metal), base (3.0 mmol), solvent (0.3 or 3.0 mL), and a Teflon-coated stirring bar (15 mm) were placed. The reactor was sealed, and the mixture was magnetically stirred for 17 h in an oil bath. The yields of 1-phenylhexan-1-ol (**3a**) and 1-phenylhexan-1-one (**4a**) were determined by GC analysis using decane as an internal standard.

General procedure for the β -alkylation of various secondary alcohols with primary alcohols shown in Table 2: Under an atmosphere of argon in a heavy-walled glass reactor, secondary alcohol (3.0 mmol), primary alcohol (3.6 mmol), [Cp*IrCl₂]₂ (1.0-4.0%Ir), base (NaOtBu or NaOH) (3.0 mmol), toluene (0.3 or 3.0 mL), and a Teflon-coated stirring bar (15 mm) were placed. The reactor was sealed, and the mixture was magnetically stirred at 110 °C for 17 h in an oil bath. After evaporation of the solvent, the products were isolated by silica-gel column chromatography (eluent: hexane/ethyl acetate).

Procedure for the α -alkylation of acetophenone with 2a shown in Eq. (3): Under an atmosphere of argon in a heavy-walled glass reactor, acetophenone (3.0 mmol), **2a** (3.0 mmol), [Cp*IrCl₂]₂ (1.0%Ir), NaOH (3.0 mmol), toluene (0.3 mL), and a Teflon-coated stirring bar (15 mm) were placed. The reactor was sealed, and the mixture was magnetically stirred at 110 °C for 17 h in an oil bath. The yield of **4a** was determined by GC analysis using decane as an internal standard.

Procedure for the transfer hydrogenation of benzylideneacetophenone using 2-propanol as a hydrogen donor shown in Eq. (4) and reference (12): Under an atmosphere of argon in a heavy-walled glass reactor, benzylideneacetophenone (3.0 mmol), 2-propanol (3.0 or 15.0 mmol), [Cp*IrCl₂]₂ (1.0%Ir), NaOtBu (3.0 mmol), toluene (3.0 mL), and a Teflon-coated stirring bar (15 mm) were placed. The reactor was sealed, and the mixture was magnetically stirred at 110 °C for 17 h in an oil bath. The yields of **3e** and **4e** were determined by GC analysis using decane as an internal standard.

Spectroscopic and analytical data:

1-Phenylhexan-1-ol^{2,3} (3a): ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.24 (m, 5H), 4.63 (dd, *J* = 7, 6 Hz, 1H), 1.99 (br, 1H), 1.81-1.74 (m, 1H), 1.71-1.65 (m, 1H), 1.43-1.35 (m, 1H), 1.30-1.26 (m, 5H), 0.87 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 144.9, 128.4, 127.4, 125.9, 74.6, 39.0, 31.7, 25.5, 22.5, 14.0.

1-Phenyldecan-1-ol⁴ (3b): ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.24 (m, 5H), 4.64 (dd, *J* = 13, 6 Hz, 1H), 1.92 (brs, 1H), 1.82-1.75 (m, 1H), 1.72-1.65 (m, 1H), 1.45-1.21 (m, 14H), 0.87 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 145.0, 128.4, 127.4, 125.9, 74.7, 39.1, 31.9, 29.5, 29.3, 25.8, 22.7, 14.1.

4-Methyl-1-phenylpentan-1-ol² (3c): ¹H NMR (270 MHz, CDCl₃) δ 7.29-7.16 (m, 5H), 4.46 (t, *J* = 6 Hz, 1H), 2.93 (s, 1H), 1.72-1.57 (m, 2H), 1.56-1.44 (m, 1H), 1.31-1.18 (m, 1H), 1.11-0.97 (m, 1H), 0.84 (d, *J* = 7 Hz, 3H), 0.83 (d, *J* = 7 Hz, 3H). ¹³C NMR (67.8 MHz, CDCl₃) δ 144.7, 128.0, 127.0, 125.7, 74.6, 36.8, 34.8, 27.9, 22.5.

4-Methyl-1-phenylhexan-1-ol² (3d): ¹H NMR (270 MHz, CDCl₃, 1:1 mixture of diastereomers) δ 7.30-7.17 (m, 5H), 4.48 (t, *J* = 7 Hz, 1H), 2.80 (s, 1H), 1.81-1.50 (m, 2H), 1.44-0.94 (m, 5H), 0.84-0.79 (m, 6H). ¹³C NMR (67.8 MHz, CDCl₃, 1:1 mixture of diastereomers) δ 144.8, 144.7, 128.1, 127.1, 127.0, 125.8, 125.7, 74.8, 74.7, 36.6, 36.5, 34.30, 34.26, 32.51, 32.49, 29.3, 19.10, 19.07, 11.4, 11.3.

1,3-Diphenylpropan-1-ol^{2,5} (3e): ¹H NMR (270 MHz, CDCl₃) δ 7.35-7.15 (m, 10H), 4.68 (t, *J* = 6 Hz, 1H), 2.81-2.60 (m, 2H), 2.22-1.96 (m, 2H), 1.88 (s, 1H). ¹³C NMR (67.8 MHz, CDCl₃) δ 144.3, 141.5, 128.1, 128.00, 127.99, 127.1, 125.6, 125.4, 73.3, 40.2, 31.8.

1-Phenyl-3-(*p*-tolyl)propan-1-ol⁶ (3f): ¹H NMR (270 MHz, CDCl₃) δ 7.31-7.23 (m, 5H), 7.06-7.02 (m, 4H), 4.57 (t, *J* = 6 Hz, 1H), 2.70-2.50 (m, 2H), 2.29 (s, 1H), 2.28 (s, 3H), 2.11-1.87 (m, 2H). ¹³C NMR (67.8 MHz, CDCl₃) δ 144.4, 138.5, 135.0, 128.9, 128.2, 128.1, 127.3, 125.8, 73.7, 40.5, 31.5, 21.0.

3-(*p*-Methoxyphenyl)-1-phenylpropan-1-ol⁶ (3g): ¹H NMR (270 MHz, CDCl₃) δ 7.27-7.16 (m, 5H), 7.01 (d, *J* = 9 Hz, 2H), 6.75 (d, *J* = 9 Hz, 2H), 4.53 (t, *J* = 6 Hz, 1H), 3.65 (s, 3H), 2.81 (s, 1H), 2.65-2.45 (m, 2H), 2.07-1.82 (m, 2H). ¹³C NMR (67.8 MHz, CDCl₃) δ 157.3, 144.4, 133.6, 129.0,

128.1, 127.1, 125.7, 113.5, 73.4, 55.0, 40.6, 31.0.

3-(*p*-Chlorophenyl)-1-phenylpropan-1-ol⁵ (3h): ¹H NMR (270 MHz, CDCl₃) δ 7.31-6.98 (m, 9H), 4.52 (dd, *J* = 8, 6 Hz, 1H), 2.68 (brs, 1H), 2.64-2.46 (m, 2H), 2.05-1.81 (m, 2H). ¹³C NMR (67.8 MHz, CDCl₃) δ 144.1, 140.0, 131.2, 129.5, 128.25, 128.18, 127.4, 125.7, 73.4, 40.1, 31.2.

1-Phenyl-3-(*p*-trifluoromethylphenyl)propan-1-ol (3i): ¹H NMR (500 MHz, CDCl₃) δ 7.51-7.19 (m, 9H), 4.64-4.54 (m, 1H), 2.80-2.59 (m, 2H), 2.16 (br, 1H), 2.13-1.89 (m, 2H). ¹³C NMR (125.65 MHz, CDCl₃) δ 145.9, 144.2, 128.7, 128.5, 128.1 (q, *J* = 32 Hz), 127.7, 125.8, 125.2, 124.3 (q, *J* = 271 Hz), 73.6, 40.0, 31.7. Anal. Calcd for C₁₆H₁₅F₃O: C, 68.56; H, 5.39. Found: C, 68.31; H, 5.43.

1,4-Diphenylbutan-1-ol⁷ (3j): ¹H NMR (270 MHz, CDCl₃) δ 7.25-7.03 (m, 10H), 4.45 (brt, *J* = 5 Hz, 1H), 2.75 (s, 1H), 2.51 (t, *J* = 7 Hz, 2H), 1.75-1.44 (m, 4H). ¹³C NMR (67.8 MHz, CDCl₃) δ 144.5, 141.9, 128.1, 128.03, 127.97, 127.1, 125.6, 125.4, 74.0, 38.4, 35.6, 27.4.

1,5-Diphenylpentan-1-ol² (3k): ¹H NMR (270 MHz, CDCl₃) δ 7.25-7.05 (m, 10H), 4.42 (t, *J* = 6 Hz, 1H), 2.88 (s, 1H), 2.49 (t, *J* = 7 Hz, 2H), 1.74-1.11 (m, 6H). ¹³C NMR (67.8 MHz, CDCl₃) δ 144.6, 142.2, 128.04, 127.97, 127.93, 127.0, 125.6, 125.3, 74.0, 38.7, 35.7, 31.2, 25.3.

1-(*p*-Tolyl)hexan-1-ol (3l): ¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, *J* = 8 Hz, 2H), 7.10 (d, *J* = 8 Hz, 2H), 4.52 (t, *J* = 6 Hz, 1H), 2.39 (br, 1H), 2.31 (s, 3H), 1.76-1.68 (m, 1H), 1.65-1.58 (m, 1H), 1.38-1.17 (m, 6H), 0.86 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 142.0, 136.8, 128.9, 125.8, 74.3, 38.9, 31.7, 25.4, 22.5, 21.0, 13.9. Anal. Calcd for C₁₃H₂₀O: C, 81.20; H, 10.48. Found: C, 81.15; H, 10.47.

1-(*p*-Methoxyphenyl)hexan-1-ol (3m): ¹H NMR (500 MHz, CDCl₃) δ 7.19 (d, *J* = 9 Hz, 2H), 6.82 (d, *J* = 9 Hz, 2H), 4.50 (t, *J* = 5 Hz, 1H), 3.74 (s, 3H), 2.72 (br, 1H), 1.76-1.69 (m, 1H), 1.64-1.57 (m, 1H), 1.37-1.16 (m, 6H), 0.86 (t, *J* = 6 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 158.6, 137.1, 127.0, 113.5, 73.9, 55.0, 38.8, 31.6, 25.4, 22.4, 13.9. Anal. Calcd for C₁₃H₂₀O₂: C, 74.96; H, 9.68. Found: C, 74.66; H, 9.68.

1-(*p*-Chlorophenyl)hexan-1-ol (3n): ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.21 (m, 4H), 4.58 (brd, *J* = 6 Hz, 1H), 2.21 (br, 1H), 1.76-1.67 (m, 1H), 1.66-1.59 (m, 1H), 1.39-1.23 (m, 6H), 0.86 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 143.3, 132.9, 128.4, 127.2, 73.9, 39.0, 31.6, 25.3, 22.5, 14.0. Anal. Calcd for C₁₂H₁₇ClO: C, 67.76; H, 8.06; Cl, 16.67. Found: C, 67.89; H, 8.00; Cl, 16.39.

1-(*p*-Trifluoromethylphenyl)hexan-1-ol (3o): ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 8$ Hz, 2H), 7.41 (d, $J = 7$ Hz, 2H), 4.67 (br, 1H), 2.41 (br, 1H), 1.77-1.63 (m, 2H), 1.41-1.23 (m, 6H), 0.87 (t, $J = 7$ Hz, 3H). ^{13}C NMR (125.65 MHz, CDCl_3) δ 148.9, 129.6 (q, $J = 32$ Hz), 126.1, 125.3, 124.2 (q, $J = 272$ Hz), 74.0, 39.1, 31.6, 25.3, 22.5, 13.9. Anal. Calcd for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{O}$: C, 63.40; H, 6.96. Found: C, 63.69; H, 7.01.

1-Phenyloctan-3-ol⁸ (3p): ^1H NMR (270 MHz, CDCl_3) δ 7.31-7.14 (m, 5H), 3.62 (m, 1H), 2.85-2.60 (m, 2H), 1.86-1.65 (m, 2H), 1.48-1.26 (m, 8H), 0.88 (t, $J = 7$ Hz, 3H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 142.1, 128.29, 128.26, 125.7, 71.4, 39.1, 37.6, 32.1, 31.9, 25.4, 22.7, 14.1.

4-Methyl-1-phenylpentan-3-ol⁹ (3q): ^1H NMR (270 MHz, CDCl_3) δ 7.31-7.17 (m, 5H), 3.38 (m, 1H), 2.89-2.79 (m, 1H), 2.70-2.59 (m, 1H), 1.85-1.61 (m, 3H), 1.48 (s, 1H), 0.91 (d, $J = 7$ Hz, 6H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 142.2, 128.3, 128.2, 125.6, 76.1, 36.0, 33.7, 32.5, 18.8, 17.2.

2-Butyl-1,2,3,4-tetrahydronaphthalen-1-ol² (3r, cis isomer): ^1H NMR (270 MHz, CDCl_3) δ 7.34-7.10 (m, 4H), 4.63 (s, 1H), 2.92-2.69 (m, 2H), 1.78-1.33 (m, 10H), 0.94 (t, $J = 7$ Hz, 3H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 138.6, 137.0, 129.9, 129.0, 127.8, 126.0, 70.1, 39.6, 31.3, 29.4, 29.3, 23.1, 14.2.

2-Butyl-1,2,3,4-tetrahydronaphthalen-1-ol² (3r, trans isomer): ^1H NMR (270 MHz, CDCl_3) δ 7.49-7.06 (m, 4H), 4.42 (brs, 1H), 2.77 (t, $J = 7$ Hz, 2H), 2.11-2.00 (m, 1H), 1.79-1.18 (m, 9H), 0.92 (t, $J = 7$ Hz, 3H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 138.7, 136.8, 128.6, 128.4, 127.2, 126.1, 73.4, 41.9, 31.3, 29.3, 27.6, 24.6, 23.1, 14.2.

1-Phenylhexan-1-one^{10,11,12} (4a): ^1H NMR (270 MHz, CDCl_3) δ 7.97-7.93 (m, 2H), 7.55-7.39 (m, 3H), 2.94 (t, $J = 7$ Hz, 2H), 1.79-1.68 (m, 2H), 1.39-1.32 (m, 4H), 0.91 (t, $J = 7$ Hz, 3H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 200.1, 136.9, 132.6, 128.3, 127.8, 38.5, 31.5, 24.0, 22.5, 13.9.

4-Methyl-1-phenylpentan-1-one¹¹ (4c): ^1H NMR (270 MHz, CDCl_3) δ 7.97-7.94 (m, 2H), 7.58-7.42 (m, 3H), 2.96 (t, $J = 7$ Hz, 2H), 1.69-1.58 (m, 3H), 0.95 (d, $J = 6$ Hz, 6H).

4-Methyl-1-phenylhexan-1-one¹³ (4d): ^1H NMR (270 MHz, CDCl_3) δ 7.98-7.94 (m, 2H), 7.58-7.42 (m, 3H), 3.00-2.92 (m, 2H), 1.84-1.71 (m, 1H), 1.61-1.33 (m, 3H), 1.26-1.13 (m, 1H), 0.94-0.87 (m, 6H). ^{13}C NMR (67.8 MHz, CDCl_3) δ 200.5, 136.9, 132.7, 128.4, 127.9, 36.4, 34.2,

31.0, 29.3, 19.1, 11.4.

1,3-diphenylpropan-1-one¹⁰ (4e): ¹H NMR (500 MHz, CDCl₃) δ 7.96 (d, *J* = 7 Hz, 2H), 7.55 (t, *J* = 7 Hz, 1H), 7.45 (t, *J* = 8 Hz, 2H), 7.32-7.19 (m, 5H), 3.31 (t, *J* = 7 Hz, 2H), 3.07 (t, *J* = 8 Hz, 2H). ¹³C NMR (125.65 MHz, CDCl₃) δ 199.2, 141.3, 136.9, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.

1-(*p*-Tolyl)hexan-1-one¹² (4l): ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8 Hz, 2H), 7.24 (d, *J* = 8 Hz, 2H), 2.92 (t, *J* = 8 Hz, 2H), 2.40 (s, 3H), 1.76-1.70 (m, 2H), 1.38-1.34 (m, 4H), 0.91 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 200.2, 143.5, 134.6, 129.1, 128.1, 38.4, 31.5, 24.1, 22.5, 21.5, 13.9.

1-(*p*-Methoxyphenyl)hexan-1-one¹² (4m): ¹H NMR (500 MHz, CDCl₃) δ 7.95-7.92 (m, 2H), 6.94-6.91 (m, 2H), 3.85 (s, 3H), 2.90 (t, *J* = 7 Hz, 2H), 1.75-1.69 (m, 2H), 1.38-1.34 (m, 4H), 0.91 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 199.1, 163.2, 130.2, 130.1, 113.6, 55.3, 38.2, 31.5, 24.2, 22.5, 13.9.

1-(*p*-Chlorophenyl)hexan-1-one (4n): ¹H NMR (500 MHz, CDCl₃) δ 7.90-7.88 (m, 2H), 7.43-7.11 (m, 2H), 2.92 (t, *J* = 7 Hz, 2H), 1.76-1.70 (m, 2H), 1.38-1.34 (m, 4H), 0.91 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 199.2, 139.2, 135.4, 129.4, 128.8, 38.5, 31.4, 23.9, 22.5, 13.9. Anal. Calcd for C₁₂H₁₅ClO: C, 68.40; H, 7.18. Found: C, 67.74; H, 7.22.

3,4-Dihydro-2-butylnaphthalen-1(2H)-one¹⁴ (4r): ¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8 Hz, 1H), 7.44 (t, *J* = 8 Hz, 1H), 7.28 (t, *J* = 7 Hz, 1H), 7.22 (d, *J* = 8 Hz, 1H), 3.01-2.95 (m, 2H), 2.49-2.43 (m, 1H), 2.26-2.20 (m, 1H), 1.97-1.84 (m, 2H), 1.53-1.31 (m, 5H), 0.92 (t, *J* = 7 Hz, 3H). ¹³C NMR (125.65 MHz, CDCl₃) δ 200.5, 143.9, 133.0, 132.4, 128.6, 127.4, 126.4, 47.4, 29.1, 29.0, 28.2, 28.1, 22.8, 13.9.

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^1H and ^{13}C NMR spectra of **3a**

^1H and ^{13}C NMR spectra of **3b**

^1H and ^{13}C NMR spectra of **3c**

^1H and ^{13}C NMR spectra of **3d**

^1H and ^{13}C NMR spectra of **3e**

^1H and ^{13}C NMR spectra of **3f**

^1H and ^{13}C NMR spectra of **3g**

^1H and ^{13}C NMR spectra of **3h**

^1H and ^{13}C NMR spectra of **3i**

^1H and ^{13}C NMR spectra of **3j**

^1H and ^{13}C NMR spectra of **3k**

^1H and ^{13}C NMR spectra of **3I**

^1H and ^{13}C NMR spectra of **3m**

^1H and ^{13}C NMR spectra of **3n**

^1H and ^{13}C NMR spectra of **3o**

^1H and ^{13}C NMR spectra of **3p**

^1H and ^{13}C NMR spectra of **3q**

^1H and ^{13}C NMR spectra of **3r-cis**

^1H and ^{13}C NMR spectra of **3r-trans**

^1H and ^{13}C NMR spectra of **4a**

^1H NMR spectra of **4c**

^1H and ^{13}C NMR spectra of **4d**

^1H and ^{13}C NMR spectra of **4I**

^1H and ^{13}C NMR spectra of **4m**

^1H and ^{13}C NMR spectra of **4n**

^1H and ^{13}C NMR spectra of **4r**