Supporting Information

Cobalt-catalyzed Heck-type Reaction of Alkyl Halides with Styrenes:

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Instrumentation and Materials

^{1}H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous $CoCl_2$ was purchased from Wako Pure Chemicals and was used after removal of water (vide infra). The ligand dpph was purchased from Tokyo Kasei Kogyo.

Experimental Section

The reaction was quite sensitive to water. Commercially available anhydrous $CoCl_2$ may contain some water. Completely anhydrous salt is clear blue, whereas purchased $CoCl_2$ is somewhat reddish-blue. Handling $CoCl_2$ under air as usual also caused low yield. Hence, in each experiment, $CoCl_2$ was dried in a reaction flask carefully under reduced pressure (0.5 torr) by heating with a hair dryer for 2 min immediately before use.

A Typical Procedure for Cobalt-catalyzed Alkylation of Styrene.

Anhydrous cobalt(II) chloride (6.5 mg, 0.050 mmol) was placed in a 25-mL flask and was heated with a hair dryer in vacuo for 2 min. After the color of cobalt salt became blue, dpph (27 mg, 0.060 mmol) and anhydrous ether (1 mL) were sequentially added under argon. The mixture was stirred for about 30 min. A bright blue mixture was obtained. Bromocyclohexane (0.24 g, 1.5 mmol), styrene (0.10 g, 1.0 mmol), and trimethylsilylmethylmagnesium chloride (1.0 M ether solution, 2.5 mL, 2.5 mmol) were successively added dropwise to the reaction mixture at 0 ˚C. While the Grignard reagent was being added, the mixture turned brown. After being stirred for 8 h at 20 ˚C, the reaction mixture was poured into saturated ammonium chloride solution. The products were extracted with ethyl acetate (20 mL × 2). The combined organic layer was dried over Na_2SO_4 and was concentrated. Silica gel column purification (hexane) of the crude product provided **2a** (0.16 g, 0.86 mmol) in 86% yield.

Characterization Data

Spectral data for some compounds (**2a, 2e, 4c, 4f,**[1] **2c,**[2] **2d,**[3] **5**[4]) were found in the literature. Spectral data of **7** is not described here. After Jones oxidation, the corresponding lactone (**7'**) was analyzed.

***(E)-β*-(1-methylheptyl)styrene (2b)**: IR (neat) 3026, 2926, 2855, 1493, 1454, 964, 746, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.20–1.42 (m, 10H), 2.20–2.37 (m, 1H), 6.11 (dd, *J* = 8.0 Hz, 15.9 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 7.16–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.97, 20.56, 22.57, 27.27, 29.37, 31.79, 37.07, 37.18, 126.04, 126.79, 128.00, 128.53, 137.21, 138.12. Found: C, 89.08; H, 11.34%. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18%.

***(E)-β*-methyl-4-chlorostyrene (2f):** IR (neat) 3024, 2914, 2872, 1491, 1448, 1402, 1248, 1092, 1013, 964, 843, 808, 781, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83 (d, *J* = 6.3 Hz, 3H), 6.10–6.25 (m, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 7.15–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 18.32, 126.54, 126.74, 127.09, 128.23, 128.67, 129.98. Found: C, 70.57; H, 6.06%. Calcd for C_9H_9Cl: C, 70.83; H, 5.94%.

***(E)*-β-cyclohexyl-4-methylstyrene (4b)**: IR (neat) 2924, 2851, 1514, 1448, 966, 843, 797 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09–1.84 (m, 10H), 2.00–2.16 (m, 1H), 2.32 (s, 3H), 6.12 (dd, *J* = 15.9 Hz, 6.9 Hz, 1H), 6.31 (d, *J* = 15.9 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.99, 25.98, 26.12, 32.95, 41.06, 125.91, 127.14, 129.22, 135.41, 135.95, 136.47. Found: C, 89.69; H, 9.88%. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06%.

***(E)*-β-cyclohexyl-3-chlorostyrene (4d)**: IR (neat) 2924, 2851, 1595, 1564, 1448, 1477, 1427, 1078, 997, 962, 880, 773, 683 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.85 (m, 10H), 2.05–2.20 (m, 1H), 6.18 (dd, *J* = 15.9 Hz, 6.3 Hz, 1H), 6.28 (d, *J* = 15.9 Hz, 1H), 7.12–7.22 (m, 3H), 7.33 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.89, 26.03, 32.74, 41.05, 124.29, 125.93, 126.15, 126.71, 129.71, 134.49, 138.51, 140.12. Found: C, 76.23; H, 7.62%. Calcd for $C_{14}H_{17}Cl$: C, 76.18; H, 7.76%.

***(E)*-β-cyclohexyl-2-chlorostyrene (4e):** IR (neat) 2924, 2851, 1470, 1443, 1051, 1034, 964, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.90 (m, 10H), 2.10–2.30 (m, 1H), 6.17 (dd, *J* = 15.9 Hz, 6.9Hz, 1H), 6.74 (d, *J* = 15.9 Hz, 1H), 7.10–7.35 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 25.89, 26.06, 32.78, 41.27, 123.72, 126.60, 126.76, 127.82, 129.65, 132.78, 136.21, 139.78. Found: C, 76.46; H, 7.85%. Calcd for $C_{14}H_{17}Cl$: C, 76.18; H, 7.76%.

***(E)*-3-(2-cyclohexylethenyl)-*N*,*N*-dibenzylbenzamide (4h):** IR (nujol) 1645, 1601, 1412, 1258, 1013, 966, 864, 748, 733, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.78 (m, 10H), 2.12–2.22 (m, 1H), 4.41 (s, 2H), 4.72 (s, 2H), 6.07 (dd, *J* = 15.9 Hz, 6.9Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 7.10–7.40 (m, 13H), 7.47 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.88, 26.04, 32.74, 41.04, 46.93, 51.50, 124.31, 124.89, 126.56, 127.11, 127.36, 127.64, 128.60, 128.67, 128.86, 136.42, 138.20, 138.64, 172.49. Found: C, 84.94; H, 7.70%. Calcd for $C_{29}H_{31}NO$: C, 85.05; H, 7.63%.

***tert*-butyl *(E)*-3-(2-cyclohexylethenyl)benzoate (4i)**: IR (neat) 2976, 2926, 2853, 1715, 1448, 1367, 1298, 1256, 1163, 1111, 966, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.08–1.88 (m, 19H), 2.08–2.20 (m, 1H),

6.17 (dd, *J* = 15.9 Hz, 6.6 Hz, 1H), 6.30 (d, *J* = 15.9 Hz, 1H), 7.23 (dd, *J* = 8.1 Hz, 7.5 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 25.92, 26.06, 28.12, 32.80, 41.08, 80.96, 126.60, 126.97, 127.70, 128.37, 129.91, 132.31, 138.04, 138.33, 166.04. HRMS calcd for $C_{19}H_{26}O_2$ (M^+) 286.1933, found 286.1943.

***β*-cinnamyl-*γ*-butyrolactone (7'):** IR (neat) 2909, 2849, 1771, 1599, 1479, 1418, 1379, 1171, 1020, 970, 843, 748, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25–2.45 (m, 3H), 2.60–2.80 (m, 2H), 4.03–4.09 (m, 1H), 4.40–4.46 (m, 1H), 6.10 (dt, *J* = 15.9 Hz, 7.2 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 7.20–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 33.87, 35.17, 36.35, 72.63, 125.72, 126.18, 127.63, 128.67, 133.10, 136.86, 176.97. HRMS calcd for $C_{13}H_{14}O_2$ (M^+) 202.0994, found 202.0990.

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