Supporting Information

Rhodium-Catalyzed Allyl Transfer from Homoallyl Alcohols to Aldehydes via Retro-allylation Followed by Isomerization into Ketones

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Instrumentation and Materials

^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 with tetramethylsilane as an internal standard. ^{19}F NMR spectra were obtained in CDCl_3 with fluorotrichloromethane as an external standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. 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. Xylene and dioxane were dried over slices of sodium. Chloro(1,5-cyclooctadiene)rhodium dimer and PMe_3 (1.0 M toluene solution) were purchased from Aldrich. $\text{P}(\text{tBu})_3$ was obtained from Wako and diluted to prepare 1.0 M hexane solution. PMe_3 and $\text{P}(\text{tBu})_3$ were stored strictly under argon.

Experimental Section

Procedure for Sequential Methallylation-isomerization of 4-Methoxybenzaldehyde (**1d**) (Table 1, entry 4)

[RhCl(cod)]₂ (6 mg, 0.0125 mmol) and Cs₂CO₃ (24 mg, 0.075 mmol) were placed in a reaction flask. Xylene (3.0 mL) and P(^tBu)₃ (1.0 M hexane solution, 0.05 mL, 0.05 mmol) were added dropwise. The suspension was stirred for 10 min at room temperature. A solution of homoallyl alcohol **2a** (170 mg, 1.0 mmol) in xylene (2.0 mL) and 4-methoxybenzaldehyde (**1d**, 69 mg, 0.5 mmol) were then added and the mixture was heated at reflux. After being stirred for 24 h, the resulting mixture was poured into water (10 mL). Extraction with hexane/ethyl acetate (5:1) followed by silica gel column purification afforded 3-methyl-1-(4-methoxyphenyl)-1-butanone (**3d**, 75 mg, 0.39 mmol) in 77% yield.

Procedure for Crotylation of Benzaldehyde (**1a**) (Table 3, entry 1)

[RhCl(cod)]₂ (6 mg, 0.0125 mmol) and Cs₂CO₃ (24 mg, 0.075 mmol) were placed in a reaction flask. Dioxane (3.0 mL) and PMe₃ (1.0 M toluene solution, 0.05 mL, 0.05 mmol) were added dropwise. The suspension was stirred for 10 min at room temperature. A solution of homoallyl alcohol **2b** (170 mg, 1.0 mmol) in dioxane (2.0 mL) and benzaldehyde (**1a**, 53 mg, 0.5 mmol) were then added and the mixture was heated at reflux. After being stirred for 8 h, the resulting mixture was quenched with water (10 mL). Extraction and purification provided 2-methyl-1-phenyl-3-buten-1-ol (**7a**, 48 mg, 0.29 mmol) in 58% yield (*erythro/threo* = 49:51).

Characterization Data.

¹H NMR spectral charts for known compounds and **1f** were attached in the last part. Characterization data for new compounds were shown below.

1-(4-Trifluoromethylphenyl)-3-methyl-1-butanone (3c): IR (neat) 2958, 1684, 1662, 1598, 1448, 1404, 1367, 1277, 1211, 938, 926, 743, 718, 699, 655 cm⁻¹; ¹H NMR (CDCl₃) δ 1.02 (d, *J* = 7.0 Hz, 6H), 2.27–2.35 (m, 1H), 2.87 (d, *J* = 7.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 22.69, 25.00, 47.72, 125.63 (q, *J* = 3.65 Hz, 1C), 128.39, 130.23, 134.04, 139.93, 199.19; ¹⁹F NMR (CDCl₃) δ –63.65. Found: C, 62.85; H, 5.61%. Calcd for C₁₂H₁₃F₃O: C, 62.60; H, 5.69%.

1-(4-Benzoylphenyl)-3-methyl-1-butanone (3f): IR (neat) 2958, 1684, 1662, 1598, 1448, 1404, 1367, 1277, 1211, 938, 926, 743, 718, 699, 655 cm⁻¹; ¹H NMR (CDCl₃) δ 1.03 (d, *J* = 6.5 Hz, 6H), 2.29–2.38 (m, 1H), 2.90 (d, *J* = 6.5 Hz, 2H), 7.52 (tt, *J* = 7.5, 1.5 Hz, 2H), 7.64 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.82 (dt, *J* = 8.0, 1.5 Hz, 2H), 7.87 (dt, *J* = 8.0, 1.5 Hz, 2H), 8.06 (dt, *J* = 8.0, 1.5 Hz, 2H); ¹³C NMR (CDCl₃) δ 22.73, 25.09, 47.82, 127.93, 128.45, 130.04, 130.10, 132.96, 136.91, 139.86, 141.06, 196.03, 199.74. Found: C, 81.05; H, 6.84%. Calcd for C₁₈H₁₈O₂: C, 81.17; H, 6.81%.

1-(4-Methoxycarbonylphenyl)-3-methyl-1-butanone (3g): IR (neat) 3674, 2956, 1722, 1683, 1504, 1436, 1407, 1365, 1279, 1198, 1109, 763, 695 cm⁻¹; ¹H NMR (CDCl₃) δ 1.01 (d, *J* = 6.5 Hz, 6H), 2.27–2.35 (m, 1H), 2.88 (d, *J* = 7.0 Hz, 2H), 3.96 (s, 3H), 8.01 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (CDCl₃) δ 22.72, 25.01, 47.80, 52.46, 127.97, 129.79, 133.63, 140.54, 166.28, 199.72. Found: C, 71.00; H, 7.53%. Calcd for C₁₃H₁₆O₃: C, 70.89; H, 7.32%.

2-Methyl-4-pentadecanone (3h): IR (neat) 2927, 2855, 1717, 1468, 1410, 1367, 1287, 1144, 1040, 721 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 0.92 (d, $J = 6.5$ Hz, 6H), 1.26–1.31 (m, 16H), 1.55–1.59 (m, 2H), 2.15 (septet, $J = 6.5$ Hz, 1H), 2.28 (d, $J = 7.5$ Hz, 2H), 2.37 (t, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 14.12, 18.24, 22.60, 22.68, 23.78, 24.59, 29.25, 29.32, 29.42, 29.47, 29.60, 31.90, 43.38, 51.81, 211.39. Found: C, 79.96; H, 13.52%. Calcd for $\text{C}_{16}\text{H}_{32}\text{O}$: C, 79.93; H, 13.41%.

1-(4-Trifluoromethylphenyl)-2-methyl-1-butanone (4c): IR (neat) 2971, 2937, 2880, 1692, 1463, 1410, 1326, 1268, 1217, 1170, 1132, 1114, 1068, 1017, 974, 857, 592 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.94 (t, $J = 7.5$ Hz, 3H), 1.22 (d, $J = 7.0$ Hz, 3H), 1.48–1.56 (m, 1H), 1.81–1.89 (m, 1H), 3.37–3.44 (m, 1H), 7.75 (d, $J = 8.0$ Hz, 2H), 8.06 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 11.67, 16.49, 26.46, 42.52, 123.62 (q, $J = 272.5$ Hz), 125.68 (q, $J = 3.8$ Hz), 128.53, 134.1 (q, $J = 32.7$ Hz), 139.49, 203.44; ^{19}F NMR (CDCl_3) δ –63.65. Found: C, 62.36; H, 5.39%. Calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}$: C, 62.60; H, 5.69%.

1-(4-Benzoylphenyl)-2-methyl-1-butanone (4f): IR (neat) 2966, 2934, 2876, 1684, 1662, 1598, 1448, 1404, 1277, 1216, 974, 938, 926, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.96 (d, $J = 7.0$ Hz, 3H), 1.24 (d, $J = 7.0$ Hz, 3H), 1.54 (septet, $J = 7.0$ Hz, 1H), 1.87 (septet, $J = 7.0$ Hz, 1H), 3.44 (septet, $J = 7.0$ Hz, 1H), 7.52 (t, $J = 7.5$ Hz, 2H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H), 8.05 (d, $J = 8.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 11.73, 16.58, 26.53, 42.56, 128.07, 128.46, 130.10, 130.11, 132.96, 136.92, 139.42, 141.01, 196.03, 203.99. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81%.

1-(4-Methoxycarbonylphenyl)-2-methyl-1-butanone (4g): IR (neat) 2936, 2877, 1729, 1683, 1572, 1504, 1436, 1407, 1373, 1280, 1215, 1182, 1109, 1006, 956, 870, 826, 788,

722 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.93 (t, $J = 7.5$ Hz, 3H), 1.21 (d, $J = 7.0$ Hz, 3H), 1.47–1.55 (m, 1H), 1.80–1.88 (m, 1H), 3.41 (septet, $J = 7.0$ Hz, 1H), 3.96 (s, 3H), 8.00 (dt, $J = 8.5$, 2.0 Hz, 2H), 8.13 (dt, $J = 8.5$, 2.0 Hz, 2H); ^{13}C NMR (CDCl_3) δ 11.67, 16.52, 26.48, 42.53, 52.44, 128.10, 129.83, 133.55, 140.09, 166.27, 203.98. Found: C, 70.77; H, 7.25%. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3$: C, 70.89; H, 7.32%.

1-(4-Benzoylphenyl)-2-methyl-3-buten-1-ol (7f) (Mixture of *erythro* and *threo* isomers):
IR (neat) 3446, 2973, 2874, 1645, 1599, 1579, 1448, 1413, 1280, 1178, 1150, 1100, 1001, 924, 844, 749, 702 cm^{-1} ; ^1H NMR (CDCl_3) For *erythro* isomer: δ 1.02 (d, $J = 6.5$ Hz, 3H), 2.06 (d, $J = 3.5$ Hz, 1H), 2.65 (septet, $J = 7.0$ Hz, 1H), 4.76 (t, $J = 4.0$ Hz, 1H), 5.10–5.15 (m, 2H), 5.77–5.85 (m, 1H), 7.44–7.47 (m, 2H), 7.48–7.52 (m, 2H), 7.61 (tt, $J = 7.0$, 1.0 Hz, 1H), 7.80–7.82 (m, 4H); For *threo* isomer: δ 0.95 (d, $J = 6.5$ Hz, 3H), 2.28 (d, $J = 2.5$ Hz, 1H), 2.53 (septet, $J = 7.0$ Hz, 1H), 4.48 (dd, $J = 7.5$, 2.5 Hz, 1H), 5.23–5.26 (m, 2H), 5.77–5.85 (m, 1H), 7.44–7.57 (m, 2H), 7.48–7.52 (m, 2H), 7.61 (tt, $J = 7.0$, 1.0 Hz, 1H), 7.80–7.82 (m, 4H); ^{13}C NMR (CDCl_3) For mixture: δ 13.51, 14.12, 16.44, 22.65, 30.95, 31.58, 44.56, 46.41, 76.59, 77.33, 116.23, 117.60, 126.34, 126.74, 128.26, 129.98, 130.01, 130.03, 130.11, 130.33, 132.37, 132.40, 136.54, 136.88, 137.62, 137.65, 139.80, 139.92, 147.05, 147.20, 196.49. Found: C, 81.45; H, 6.88%. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.17; H, 6.81%.

Chart 1. ^1H NMR Spectrum of **3a** (Ito, M.; Kitahara, S.; Ikariya, T. *J. Am. Chem. Soc.* **2005**, *127*, 6172–6173.)

Chart 2. ^1H NMR Spectrum of **3b** (Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 4852–4855.)

Chart 3. ^1H NMR Spectrum of **3d** (Stauffer, S. R.; Coletta, C. J.; Tedesco, R.; Nishiguchi, G.; Carlson, K.; Sun, J.; Katzenellenbogen, B. S.; Katzenellenbogen, J. A. *J. Med. Chem.* **2000**, *43*, 4943–4947.)

Chart 4. ^1H NMR Spectrum of **3e** (Luzzio, F. A.; Fitch, R. W. *Journal für Praktische chemie* **2000**, 342, 498–501.)

Chart 5. ^1H NMR Spectrum of **4a** (Ito, M.; Kitahara, S.; Ikariya, T. *J. Am. Chem. Soc.* 2005, 127, 6172–6173.)

Chart 6. ^1H NMR Spectrum of **4b** (Lee, S. W.; Lee, K.; Seomoon, D.; Kim, S.; Kim, H.; Kim, H.; Shim, E.; Lee, M.; Lee, S.; Kim, M.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 4852–4855.)

Chart 7. ^1H NMR Spectrum of **4d** (Al-Aseer, M. A.; Smith, S. G. *J. Org. Chem.* **1984**, *49*, 2608–2613.)

Chart 8. ^1H NMR Spectrum of **4e** (Al-Aseer, M. A.; Smith, S. G. *J. Org. Chem.* **1984**, *49*, 2608–2613.)

Chart 9. ^1H NMR Spectrum of **4f**

Chart 10. ^1H NMR Spectrum of **7a** (Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, 59, 6620–6628.)

Chart 11. ^1H NMR Spectrum of **7b** (Shibata, I.; Yoshimura, N.; Yabu, M. Baba, A. *Eur. J. Org. Chem.* **2001**, 3207–3211.)

Chart 12. ^1H NMR Spectrum of **7c** (For *syn* isomer, Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **1992**, 114, 2577–2586. For *anti* isomer, Malkov, A. V.; Dufková, L.; Farrugia, L.; Kocovsky, P. *Angew. Chem. Int. Ed.* **2003**, 42, 3674–3677.)

Chart 13. ^1H NMR Spectrum of **7d** (Takahara, J-P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577–2586.)

Chart 14. ^1H NMR Spectrum of **7e** (Takahara, J.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577–2586.)

Chart 15. ^1H NMR Spectrum of **7g** (Takahara, J.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577–2586.)