**Acceleration Effect of Lewis Acid in Allylboration of Aldehydes.
Catalytic, Regiospecific, Diastereospecific, and Enantioselective Synthesis
of Homoallyl Alcohols**

Tatsuo Ishiyama,* Taka-aki Ahiko, and Norio Miyaure*

*Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University,
Sapporo 060-8628, Japan*

Supporting Information

General Methods. All the experiments were carried out under a nitrogen atmosphere. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solutions using a JEOL JNM-A400II spectrometer (400 or 100 MHz) and Me_4Si or residual protiated solvent as an internal standard. Optical rotations were obtained on a Horiba SEPA-300 digital polarimeter. GC analyses were performed on a Hitachi G-3500 instrument equipped with a glass column (OV-101 on Uniport B, 2 m). HPLC analyses were performed on a JASCO 875-UC and a JASCO 880-PU with a chiral stationary phase column (Chiralcel OD-H purchased from Dical Co., Ltd.). Solvents were purified by distillation from appropriate drying agents. Pinacol allylic boronic esters were prepared by the reported procedure.¹ All of other compounds were used as received.

General Procedure for the Lewis Acid-Catalyzed Allylation of Aldehydes with Pinacol Allylic Boronic Esters (Table 1 and eq 3). AlCl_3 or $\text{Sc}(\text{OTf})_3$ (anhydrous) (0.1 mmol) was added to a flask assembled a magnetic stirring bar, a septum inlet, and a condenser. The flask was flushed with nitrogen, charged with toluene (6 mL), and then cooled to $-78\text{ }^\circ\text{C}$. An aldehyde (1.0 mmol) and a pinacol allylic boronic ester (1.1 mmol) were successively added, and the mixture was stirred at $-78\text{ }^\circ\text{C}$ for the period shown in Table 1 and eq 3. The reaction mixture was treated with DIBAH (2.0 mmol) at $-78\text{ }^\circ\text{C}$ for 1 h and 1N HCl (10 mL) at room temperature for 1 h. The product was extracted with ether, washed with water, dried over MgSO_4 , and isolated by column chromatography over silica gel to give an analytically pure sample. These are all known compounds and were directly compared with the authentic samples.

1-[4-(Trifluoromethyl)phenyl]-3-buten-1-ol^{2,3} (entry 1 in Table 1).

The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 2.14 (d, 1 H, J = 3.2 Hz), 2.43-2.58 (m, 2 H), 4.81 (dt, 1 H, J = 7.8 and 4.0 Hz), 5.16-5.17 (m, 1 H), 5.20-5.21 (m, 1 H), 5.74-5.85 (m, 1 H), 7.48 (d, 2 H, J = 8.3 Hz), 7.61 (d, 2 H, J = 8.3 Hz); ^{13}C NMR δ 43.9, 72.5, 119.2, 124.1 (q, J = 261.6 Hz), 125.3 (q, J = 3.7 Hz), 126.1, 129.7 (q, J = 32.3 Hz), 133.7, 147.7.

1-Phenyl-3-buten-1-ol^{2,3} (entry 2 in Table 1). The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 2.04 (d, 1 H, J = 3.2 Hz), 2.46-2.57 (m, 2 H), 4.74 (ddd, 1 H, J = 8.1, 4.8, and 2.9 Hz), 5.13-5.20 (m, 2 H), 5.76-5.87 (m, 1 H), 7.26-7.39 (m, 5 H); ^{13}C NMR δ 43.8, 73.3, 118.4, 125.8, 127.5, 128.4, 134.4, 143.9.

1-(4-Methylphenyl)-3-buten-1-ol⁴ (entry 3 in Table 1). The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 1.99 (d, 1 H, J = 2.2 Hz), 2.34 (s, 3 H), 2.50 (t, 2 H, J = 7.1 Hz), 4.70 (t, 1 H, J = 5.2 Hz), 5.13 (d, 1 H, J = 9.0 Hz), 5.16 (d, 1 H, J = 14.6 Hz), 5.80 (ddt, 1 H, J = 17.3, 10.1, and 7.1 Hz), 7.16 (d, 2 H, J = 8.1 Hz), 7.25 (d, 2 H, J = 8.1 Hz); ^{13}C NMR δ 21.1, 43.8, 73.2, 118.2, 125.8, 129.1, 134.6, 137.2, 140.9.

1-(4-Methoxyphenyl)-3-buten-1-ol^{2,3} (entry 4 in Table 1). The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 1.96 (d, 1 H, J = 2.9 Hz), 2.50 (t, 2 H, J = 6.8 Hz), 3.81 (s, 3 H), 4.69 (dt, 1 H, J = 2.4 and 6.3 Hz), 5.12-5.18 (m, 2 H), 5.80 (ddt, 1 H, J = 17.3, 10.2, and 7.2 Hz), 6.89 (d, 2 H, J = 8.8 Hz), 7.28 (d, 2 H, J = 8.8 Hz); ^{13}C NMR δ 43.8, 55.3, 72.96, 113.8, 118.2, 127.1, 134.6, 136.0, 159.0.

1-Tetradecen-4-ol⁵ (entry 5 in Table 1). The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 0.72-1.06 (m, 3 H), 1.06-1.69 (m, 18 H), 1.83-2.06 (m, 2 H), 2.14 (d, 1 H, J = 6.6 Hz), 3.33-3.74 (m, 1 H), 4.90-5.20 (m, 2 H), 5.47-6.03 (m, 1 H).

1-Cyclohexyl-3-buten-1-ol² (entry 6 in Table 1). The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 0.99-1.89 (m, 12 H), 2.13 (dt, 1 H, J = 14.6 and 8.2 Hz), 2.29-2.38 (m, 1 H), 3.40 (ddd, 1 H, J = 9.2, 5.9, and 3.3 Hz), 5.13 (d, 1 H, J = 10.5 Hz), 5.14 (d, 1 H, J = 15.6 Hz), 5.79-5.89 (m, 1 H); ^{13}C NMR δ 26.1, 26.3, 26.5, 28.1, 29.1, 38.8, 43.0, 74.7, 117.9, 135.4.

(E)-1-Phenyl-1,5-hexadien-3-ol^{2,3} (entry 7 in Table 1). The purity determined by NMR and GC analyses: > 95%; ^1H NMR δ 1.83 (s, 1 H), 2.37-2.50 (m, 2 H), 4.39 (dt, 1 H, J = 5.8 and 6.0 Hz), 5.18-5.23 (m, 2 H), 5.80 (dddd, 1 H, J = 18.1, 10.2, 7.5, and 6.9 Hz), 6.27 (dd, 1 H, J = 15.8 and 6.4 Hz), 6.63 (d, 1 H, J = 16.1 Hz), 7.25-7.28 (m, 1 H), 7.32-7.35 (m, 2 H), 7.39-7.42 (m, 2 H); ^{13}C NMR δ 42.0, 71.7,

118.5, 126.5, 127.6, 128.6, 130.3, 131.5, 134.0, 136.6.

***anti*-2-Methyl-1-phenyl-3-buten-1-ol^{2,3} (eq 3).** The purity determined by NMR and GC analyses: > 95%; ¹H NMR δ 0.87 (d, 3 H, J = 6.8 Hz), 2.14 (d, 1 H, J = 2.7 Hz), 2.48 (ddq, 1 H, J = 7.3, 7.3, and 7.3 Hz), 4.36 (dd, 1 H, J = 7.8 and 2.4 Hz), 5.17-5.23 (m, 2 H), 5.81 (ddd, 1 H, J = 17.2, 10.2, and 8.2 Hz), 7.25-7.40 (m, 5 H); ¹³C NMR δ 16.5, 46.3, 77.8, 116.8, 126.8, 127.6, 128.2, 140.6, 142.4.

***syn*-2-Methyl-1-phenyl-3-buten-1-ol^{2,3} (eq 3).** The purity determined by NMR and GC analyses: > 95%; ¹H NMR δ 1.01 (d, 3 H, J = 6.8 Hz), 1.94 (br s, 1 H), 2.59 (ddq, 1 H, J = 6.6, 6.6, and 6.6 Hz), 4.61 (d, 1 H, J = 5.6 Hz), 5.03-5.08 (m, 2 H), 5.76 (ddd, 1 H, J = 17.3, 10.0, and 7.0 Hz), 7.24-7.36 (m, 5 H); ¹³C NMR δ 13.9, 44.6, 77.2, 115.5, 126.5, 127.4, 128.1, 140.3, 142.5.

Competition Experiments (eq 2). A mixture of AlCl₃ or Sc(OTf)₃ (anhydrous) (0.1 mmol), 4-(trifluoromethyl)benzaldehyde (1.1 mmol), 4-methoxybenzaldehyde (1.1 mmol), and pinacol 2-propenylboronic ester (1.0 mmol) was stirred at -78 °C for 16 h. The resulting mixture was treated with DIBAH (4.0 mmol) at -78 °C for 1 h and then with 1N HCl (20 mL) at room temperature for 1 h. GC analyses revealed the formation of 1-[4-(trifluoromethyl)phenyl]-3-buten-1-ol as the sole product. A similar reaction in the absence of a Lewis acid at room temperature produced a mixture of 1-[4-(trifluoromethyl)phenyl]-3-buten-1-ol and 1-(4-methoxyphenyl)-3-buten-1-ol in a ratio of 81:19.

Enantioselective Reaction (eq 4). A mixture of (*S*)-BINOL (0.1 mmol) and Et₂AlCl (0.1 mmol) was stirred at room temperature for 30 min in toluene (6 mL). To this solution were added benzaldehyde (1.0 mmol) and pinacol (*E*)-2-butenylboronic ester (1.1 mmol) at -78 °C, and the resulting mixture was stirred at -78 °C for 6 h. The reaction mixture was treated with DIBAH (2.0 mmol) at -78 °C for 1 h, and then with 1N HCl (10 mL) at room temperature. The product was isolated by column chromatography over silica gel to give an analytically pure (> 95%) sample in 40% yield. ¹H NMR analyses revealed the formation of an *anti* isomer with 99% isomeric purity. The formation of a *1R,2R* isomer with 51%ee was confirmed by HPLC and optical rotation analyses. A similar reaction with pinacol (*Z*)-2-butenylboronic ester resulted in the formation of a *syn* isomer in 19% yield with 98% isomeric purity and with 8%ee.

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