Supporting Information

Catalytic Enantioselective Allylboration of Ketones

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General: NMR spectra were recorded on a JEOL JNM-LA500 spectrometer, operating at 500 MHz for ¹H NMR, 125.65 MHz for ¹³C NMR, and 160.4 MHz for ¹¹B NMR. Chemical shifts were reported downfield from TMS (= 0) for ¹H NMR. For ¹³C NMR, chemical shifts were reported in the scale relative to the solvent used as an internal reference. ¹¹B NMR was measured using NaBH₄ as an external standard (−61 ppm). Optical rotations were measured on a JASCO P-1010 polarimeter. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM). The enantiomeric excess (ee) was determined by HPLC or GC analysis. HPLC analysis was performed on JASCO HPLC systems consisting of the following: pump, 880-PU or PU-980; detector, 875-UV or UV-970, measured at 254 nm; mobile phase, hexane-2-propanol. GC analysis was performed on Shimadzu GC-14A with Varian Chirasil DEX CB column (0.25 mm x 25 m). In general, reactions were carried out in dry solvents under an argon atmosphere, unless noted otherwise. Normal glassware can be used to conduct the reactions in this manuscript. CuF•3PPh₃•2EtOH was synthesized following the reported procedure.¹ La(O^{*i*}Pr)₃ was purchased from Kojundo Chemical Laboratory Co., Ltd. (Fax: +81-492-84-1351). Pinacol 2-propenylboronic ester (**2a**) was purchased from Lancaster Synthesis Ltd. *E*- and *Z*-Crotylboronates **2b** and **2c** were synthesized following the reported procedures.² (*R,R*)-^{*i*}Pr-DuPHOS was purchased from Strem Chemicals, Inc.

A typical procedure for catalytic allylboration of ketones (CuCl-TBAT catalyst): A mixture of CuCl (2 mg, 0.02 mmol) and TBAT (11 mg, 0.02 mmol) in THF (1 mL) was stirred for 1 h at room temperature, during which the color of suspension turned to yellowish-green. Allylboronate **2a** (0.5 mL, 3.0 mmol) and acetophenone (**1a**: 117 μ L, 1.0 mmol) were added. After the starting material disappeared on TLC (6 h), H₂O was added to quench the reaction. The product was extracted with AcOEt, and the combined organic layer was washed with satd. NaCl aq. The organic layer was dried over Na₂SO₄. Filtration, evaporation, and purification through silica gel column chromatography (AcOEt/hexane = 1/19 to 1/9) gave **3a** in 100% yield.

A typical procedure for catalytic allylboration of ketones (CuF•3PPh₃•2EtOH catalyst): To a solution of CuF•3PPh₃•2EtOH¹ (14 mg, 0.015 mmol) in THF (0.25 mL), ketone **1c** (68 μ L, 0.50 mmol) and allylboronate **2a** (104 μ L, 0.55 mmol) were added at room temperature. After 3 h, H₂O was

Table 1. CuF-Catalyzed Allylboration of Ketones

		CuCl-TBAT (A: 2 mol %) or CuF•3PPh ₃ •2EtOH (B: 1 or 3 mol %)				
		1	2a	THF, rt	3	
entry	ketone	catalyst (mol %)		2a (equiv)	h	3 (%)
1		1a : R ¹ , R ² , R ³ = H		A (2)	3	100
2		1b : R ¹ = CH ₃ , R ² , R ³ = H		B (1)	1.1	100
3		1c : R ¹ , R ³ = H, R ² = CH ₃		B (3)	1.1	98
4		1j : R ¹ , R ² = H, R ³ = CH ₃		B (1)	1.1	100
5		1k	B (3)	1.1	3	98
6		1d	B (3)	1.2	3	83
7		1l	B (3)	1.2	4	98
8		1m	B (1)	1.1	17	81
9		1h	B (3)	1.2	3	75
10		1n	B (3)	1.2	3	91
11		1o	A (2)	3	6	100
12		1p	A (2)	3	17	64

added. Workup and purification as described above gave the product **3c** in 98% yield. Allylation products **3j**,³ **3m**,⁴ **3n**,⁵ **3o**,⁶ **3p**⁵ are known compounds. Data of new compounds other than described in the asymmetric synthesis are as follows.

2-(1-Naphthalenyl)-4-penten-2-ol (3k): ¹H-NMR (CDCl₃) δ 1.78 (s, 3H), 2.33 (s, 1H), 2.79 (dd, *J* = 8.0, 13.7 Hz, 1H), 3.06 (dd, *J* = 6.9, 13.7 Hz, 1H), 5.08 (m, 2H), 5.62 (m, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.45 (m, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz), 7.83 (d, *J* = 8.0 Hz, 1H), 8.72 (d, *J* = 8.6 Hz, 1H); ¹³C-NMR (CDCl₃) δ 29.52, 47.16, 75.18, 119.2, 123.6, 124.7, 125.1, 125.3, 126.8, 128.5, 129.1, 130.7, 133.9, 134.8, 142.1; IR (neat) 3484, 2926, 2837, 1653, 1559, 1542, 1458, 813 cm⁻¹; ESI-MS *m/z* 235 (M + Na⁺); HRMS Calcd for C₁₅H₁₅ (M-OH⁻) 195.1174. Found 195.1154.

A typical procedure for catalytic enantioselective allylboration of ketones: CuF₂•2H₂O (3 mg, 0.022 mmol) and (*R,R*)-*i*-Pr-DuPHOS (18 mg, 0.044 mmol) were refluxed in MeOH (0.7 mL) for 2 h. The solvent was evaporated, and the resulting amorphous was coevaporated with toluene twice. Then La(O^{*i*}Pr)₃ (0.2 M in THF, 0.16 mL, 0.033 mmol) was added, and the solvent was evaporated under vacuum. The resulting yellow solid was dissolved in DMF (0.2 mL), and the mixture was cooled to -40 °C. Allylboronate **2a** (165 μ L, 0.88 mmol) was added, followed by the addition of a substrate ketone (0.73 mmol) in DMF (50 μ L). After 1 h, 10% citric acid aq. was added to quench the reaction. The product was extracted with AcOEt, and the combined organic layer was washed with satd. NaHCO₃ aq. and satd. NaCl aq.. After drying over Na₂SO₄, filtration, evaporation, and purification through silica gel column chromatography gave the allylated product.

(2S)-(-)-2-Phenyl-4-penten-2-ol (3a): Known compound.⁶ HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 20/1, 1.0 ml/min) *t*_R 7.0 min (minor), 8.1 min (major). [α]_D²³ -48.8 (*c* = 0.84, CHCl₃) (82% ee). The absolute configuration was determined based on the comparison of the sign of optical rotation to the reported value.⁶

(-)-2-(4-Methylphenyl)-4-penten-2-ol (3b): Known compound.⁶ HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 20/1, 0.5 ml/min) *t*_R 12.4 min (minor), 15.3 min (major). [α]_D²⁶ -53.1 (*c* = 1.11, CHCl₃) (84% ee).

(-)-2-(3-Methylphenyl)-4-penten-2-ol (3c): Known compound.³ HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 20/1, 1.0 ml/min) *t*_R 5.4 min (minor), 6.0 min (major). [α]_D²⁸ -52.0 (*c* = 1.83, CHCl₃) (83% ee).

(-)-2-Thiophenyl-4-penten-2-ol (3d): ¹H-NMR (CDCl₃) δ 1.53 (s, 3H), 2.18 (s, 1H), 2.49 (dd, *J* = 8.0, 13.7 Hz, 1H), 2.62 (dd, *J* = 6.9, 13.7 Hz, 1H), 5.13 (m, 2H), 5.66 (m, 1H), 7.05 (dd, *J* = 1.8, 5.2 Hz, 1H), 7.14 (dd, *J* = 1.8, 3.0 Hz, 1H), 7.27 (dd, *J* = 3.0, 5.2 Hz, 2H); ¹³C-NMR (CDCl₃) δ 29.41, 48.23, 72.60, 119.3, 119.5, 125.5, 125.8, 133.6, 149.6; IR (neat) 3419, 3076, 2977, 1639, 1414, 788 cm⁻¹; MS *m/z* 151 (M-OH⁻); HRMS Calcd for C₉H₁₁S (M-OH⁻) 151.0581. Found 151.0561. HPLC (DAICEL CHIRALCEL OJ-H, hexane/2-propanol 20/1, 0.5 ml/min) *t*_R 15.1 min (minor), 16.1 min (major). [α]_D²⁶ -47.1 (*c* = 1.17, CHCl₃) (94% ee).

(2S)-(-)-1-Allyl-1,2,3,4-tetrahydronaphthalen-1-ol (3e): Known compound.⁶ HPLC (DAICEL CHIRALCEL OD, hexane/2-propanol 100/1, 1.0 ml/min) *t*_R 22.9 min (minor), 24.8 min (major). [α]_D²⁶ -28.5 (*c* = 1.17, CHCl₃) (84% ee). The absolute configuration was determined based on the comparison of the retention time on chiral HPLC analysis to the reported values.⁶

(-)-2-(1-Cyclohexenyl)-4-penten-2-ol (3f): Known compound.⁷ GC (Varian Chirasil DEX CB, Injector temp. = Detector temp. = 200 °C, Initial temp. = 100 °C for 10 min, Program rate = 1 °C/min, Final temp. = 120 °C) *t*_R 27.4 min (major), 28.7 min (minor). [α]_D²⁵ -35.6 (*c* = 1.40, CHCl₃) (90% ee).

(-)-2,2,3-Trimethyl-5-hexen-3-ol (3g): Known compound.⁸ [α]_D²⁷ -16.5 (*c* = 1.06, CHCl₃) (91% ee). Ee was determined

after conversion to UV active compound **5g** via treatment of **3g** with phenyl isocyanate (20 eq) and CuCl (1 eq) in DMF at room temperature (60~80% yield), and HPLC analysis. HPLC of **5g** (DAICEL CHIRALPAK AS-H + AS-H, hexane/2-propanol 49/1, 0.5 ml/min) t_R 20.2 min (major), 21.7 min (minor). ^1H NMR (CDCl_3) δ 0.61 (s, 9H), 1.52 (s, 3H), 2.67 (dd, $J = 1.4, 7.5$ Hz, 2H), 5.10 (m, 2H), 5.86 (m, 1H), 7.07 (m, 1H), 7.22 (m, 2H), 7.30 (m, 2H), 7.35 (m, 1H), 7.43 (m, 2H), 7.55 (m, 2H), 10.9 (s, 1H); ESI-MS m/z 403 ($\text{M}+\text{Na}^+$).

(-)-1-Allyl-2,2-dimethylcyclohexanol (3h): ^1H -NMR (CDCl_3) δ 0.87 (t, $J = 7.2$ Hz, 1H), 0.93 (s, 3H), 0.96 (s, 3H), 1.25–1.5 (m, 8H), 2.20 (dd, $J = 7.5, 13.8$ Hz, 1H), 2.33 (dd, $J = 7.5, 13.8$ Hz, 1H), 5.10 (m, 2H), 5.88 (m, 1H); ^{13}C -NMR (CDCl_3) δ 14.08, 21.54, 22.03, 22.62, 23.92, 31.56, 32.28, 37.32, 39.86, 74.70, 118.4, 134.7; IR (neat) 3499, 2935, 2862, 1637, 1165 cm^{-1} ; ESI-MS m/z 191 ($\text{M}+\text{Na}^+$); HRMS Calcd for $\text{C}_{11}\text{H}_{19}$ ($\text{M}-\text{OH}$) 151.1487. Found 151.1457; $[\alpha]_D^{22}$ -27.7 ($c = 1.26$, CHCl_3) (84% ee). Ee was determined after conversion to UV active compound **5h** via treatment of **3h** with phenyl isocyanate (20 eq) and CuCl (1 eq) in DMF at room temperature (52% yield), and HPLC analysis. HPLC of **5h** (DAICEL CHIRALPAK AD-H, hexane/2-propanol 20/1, 0.5 ml/min) t_R 23.7 min (major), 26.2 min (minor). ^1H NMR (CDCl_3) δ 0.39 (s, 3H), 0.82 (s, 3H), 0.90 (m, 1H), 1.2–1.4 (m, 5H), 1.5 (m, 1H), 1.67 (m, 1H), 2.45 (m, 1H), 2.65 (dd, $J = 7.5, 15.5$ Hz, 1H), 2.79 (dd, $J = 8.1, 15.5$ Hz, 1H), 5.09–7.07 (m, 1H), 7.23–7.30 (m, 4H), 7.36 (m, 1H), 7.44 (t, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.6$ Hz, 2H), 10.9 (s, 1H).

(3S)-(-)-3-Methyl-1-phenyl-5-hexen-3-ol (3i): Known compound.⁹ HPLC (DAICEL CHIRALCEL OD-H, hexane/2-propanol 49/1, 1.0 ml/min) t_R 13.8 min (minor), 15.2 min (major). $[\alpha]_D^{23}$ -7.3 ($c = 1.2$, CHCl_3) (67% ee). The absolute configuration was determined based on the comparison of the sign of optical rotation to the reported value.⁹

Summary of Catalytic Enantioselective Crotylboration

$\text{R}-\text{C}(=\text{O})\text{Me} + \text{R}^1\text{CH}=\text{CH}-\text{B}(\text{OR}^2)_2$ 1 2b : $\text{R}^1 = \text{CH}_3, \text{R}^2 = \text{H}$ 2c : $\text{R}^1 = \text{H}, \text{R}^2 = \text{CH}_3$		$\xrightarrow[\text{DMF, } -40^\circ\text{C}]{\text{CuF}_2 \cdot 2\text{H}_2\text{O} (3 \text{ mol } \%), \text{ (R,R)-Pr-DuPHOS (6 mol } \%), \text{ La(O}^i\text{Pr)}_3 (4.5 \text{ mol } \%)}$		 $\text{syn: R}^1 = \text{CH}_3, \text{R}^2 = \text{H}$ $\text{anti: R}^1 = \text{H}, \text{R}^2 = \text{CH}_3$		
entry	substrate	crotylboronate (1.2 equiv)	time (h)	yield (%)	dr (syn/anti)	ee (%)
1		2b	1	73	30/70	75/90
2		2c	5	94	84/16	87/74
3		2b	3	80	27/73	90/93
4		2c	4	90	38/62	90/92
5		2b	4	100	34/66	16/85
6		2c	4	100	36/64	21/85

Comparison in dr and ee of the catalytic enantioselective crotylboration of aromatic, α,β -unsaturated, and aliphatic ketones were summarized in the above table. The diastereoselectivity was dependent on the substrate, although enantioselectivity was comparable or higher than the allylation (Table 2 in the text). Crotylcuprate could undergo metallotropic rearrangement when substrate is not highly reactive, and this is probably the reason why the diastereoselectivities are substrate-dependent.

(+)-(2S,3R)-3-Methyl-2-phenyl-4-penten-2-ol (syn): Known compound.¹⁰ ^1H -NMR (CDCl_3) δ 0.87 (d, $J = 7.4$ Hz, 3H), 1.54 (s, 3H), 1.89 (s, 1H), 2.55 (quintet, $J = 7.4$ Hz, 1H), 5.12 (m, 2H), 5.82 (m, 1H), 7.24 (m, 1H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.41 (m, 2H); ^{13}C -NMR (CDCl_3) δ 14.75, 28.49, 48.90, 75.76, 116.3, 125.2, 126.4, 127.9, 139.9, 146.9. HPLC (DAICEL CHIRALPAK AS-H, hexane/2-propanol 99/1, 0.8 ml/min) t_R 7.4 min (minor), 8.1 min (major). $[\alpha]_D^{22}$ +4.4 ($c = 1.09$, CHCl_3) (83% ee).

(-)-(2S,3S)-3-Methyl-2-phenyl-4-penten-2-ol (anti): Known compound.¹⁰ ^1H -NMR (CDCl_3) δ 0.96 (d, $J = 6.9$ Hz, 3H), 1.52 (s, 3H), 1.99 (s, 1H), 2.59 (quintet, $J = 6.9$ Hz, 1H), 5.10 (m, 2H), 5.70 (m, 1H), 7.23 (m, 1H), 7.33 (t, $J = 7.5$ Hz, 2H), 7.42 (m, 2H); ^{13}C -NMR (CDCl_3) δ 14.07,

25.83, 48.73, 75.66, 116.6, 125.4, 126.6, 127.9, 139.9, 147.0. HPLC (DAICEL CHIRALPAK AS-H, hexane/2-propanol 99/1, 0.8 ml/min) t_R 7.5 min (minor), 7.9 min (major). $[\alpha]_D^{22}$ -72.8 ($c = 1.05$, CHCl_3) (85% ee). *Syn* and *anti* diastereomers were separable by medium pressure SiO_2 column (AcOEt/hexane = 1/50 to 1/15).

2-(1-Cyclohexenyl)-3-methyl-4-penten-2-ol: *Syn* and *anti* diastereomers were inseparable. The stereochemistries were temporarily assigned based on the analogy of ^1H NMR pattern (chemical shifts of 3-Me and 3-C-H) to the crotylated products from acetophenone (shown above). **Presumed *syn* product:** ^1H -NMR (CDCl_3) δ 0.91 (d, $J = 7.0$ Hz, 3H), 1.22 (s, 3H), 1.57 (m, overlap with *anti*), 1.94 (m, overlap with *anti*), 2.06 (m, overlap with *anti*), 2.35 (m, 1H), 5.07 (m, 2H), 5.73 (m, 1H), 5.86 (m, 1H). **Presumed *anti* product:** ^1H -NMR (CDCl_3) δ 0.96 (d, $J = 7.0$ Hz, 3H), 1.22 (s, 3H), 1.57 (m, overlap with *syn*), 1.94 (m, overlap with *syn*), 2.06 (m, overlap with *syn*), 2.47 (m, 1H), 5.07 (m, 2H), 5.69 (m, 1H), 5.86 (m, 1H). Four isomers were separable by Chiral GC column (Varian Chirasil DEX CB, Injector temp. = Detector temp. = 200 °C, Initial temp. = 110 °C for 10 min, Program rate = 1 °C/min, Final temp. = 130 °C) t_R 23.3 min (major of *anti*), 24.5 min (major of *syn*), 25.8 min (minor of *anti*), 26.3 min (minor of *syn*).

3,4-Dimethyl-1-phenyl-5-hexen-3-ol (presumed *syn* product): Known compound.¹¹ ^1H -NMR (CDCl_3) δ 1.04 (d, $J = 7.0$ Hz, 3H), 1.17 (s, 3H), 1.78 (m, 2H), 2.33 (dq, $J = 7.0$ Hz, 1H), 2.71 (m, 2H), 5.14 (m, 2H), 5.85 (m, 1H); ^{13}C -NMR (CDCl_3) δ 14.11, 22.64, 28.95, 41.19, 46.60, 72.70, 115.79, 124.82, 127.50, 127.51, 139.24, 141.91; HPLC (DAICEL CHIRALPAK AS-H, hexane/2-propanol 99/1, 1 ml/min) t_R 7.3 min (major), 7.9 min (minor). $[\alpha]_D^{22}$ +10.2 ($c = 0.30$, CHCl_3) (21% ee).

3,4-Dimethyl-1-phenyl-5-hexen-3-ol (presumed *anti* product): Known compound.¹¹ ^1H -NMR (CDCl_3) δ 1.07 (d, $J = 7.0$ Hz, 3H), 1.21 (s, 3H), 1.74 (m, 2H), 2.33 (dq, $J = 7.0$ Hz, 1H), 2.63–2.79 (m, 2H), 5.10 (m, 2H), 5.80 (m, 1H); ^{13}C -NMR (CDCl_3) δ 13.80, 22.98, 28.95, 40.66, 47.39, 72.81, 115.41, 124.85, 127.49, 127.53, 139.38, 141.93; HPLC (DAICEL CHIRALPAK AS-H, hexane/2-propanol 99/1, 1 ml/min) t_R 7.8 min (minor), 8.7 min (major). *Syn* and *anti* diastereomers were separable by medium pressure SiO_2 column (AcOEt/hexane = 1/20 to 1/9).

Determination of absolute and relative configurations of the crotylated products from acetophenone

The relative configurations were determined through comparison to the reported NMR chemical shifts.¹⁰ The absolute configuration was determined through the conversion to the known compound **7**¹² as follows.

The crotylated compound (52 mg, 0.29 mmol) was treated with O_3 in CHCl_3 (1 mL) in an ice bath for 30 min. After the starting material disappeared on TLC, MeOH (1 mL) was added, followed by the addition of NaBH_4 (90 mg, 2.4 mmol). After 30 min, 10% HCl aq. was added, and the product was extracted with CH_2Cl_2 . The combined organic layer was washed with satd. NaHCO_3 aq. and satd. NaCl aq., and dried over Na_2SO_4 . Filtration, evaporation, and partial purification through silica gel column chromatography gave the corresponding alcohol in 32% (from *syn*) and 31% (from *anti*) yield, respectively. **Intermediate diol with *syn* configuration:** ^1H -NMR (CDCl_3) δ 0.80 (d, $J = 7.0$ Hz, 3H), 1.65 (s, 3H), 2.04 (m, 1H), 2.87 (brs, 1H), 3.43 (brs, 1H), 3.54 (dd, $J = 6.3, 11.5$ Hz, 1H), 3.82 (dd, $J = 3.4, 11.5$ Hz, 1H), 7.25 (m, 1H), 7.34 (tlike, $J = 7.7$ Hz, 2H), 7.40 (dlike, $J = 7.7$ Hz, 2H); ^{13}C -NMR (CDCl_3) δ 12.68, 29.18, 44.21, 65.67, 78.10, 125.3, 126.6, 127.9, 146.0. **Intermediate diol with *anti* configuration:** ^1H -NMR (CDCl_3) δ 0.97 (d, $J = 7.5$ Hz, 3H), 1.54 (s, 3H), 2.05 (m, 1H), 2.74 (brs, 1H), 3.37 (brs, 1H), 3.53 (brd, $J = 10.9$ Hz, 1H), 3.60 (dd, $J = 5.8, 10.9$ Hz, 1H), 7.25 (m, 1H), 7.34 (tlike, $J = 7.7$ Hz, 2H), 7.45 (dlike, $J = 7.7$ Hz, 2H); ^{13}C -NMR (CDCl_3) δ 12.26, 25.64, 43.97, 66.21, 78.16, 125.0, 126.7, 128.1, 148.2.

To the diol (15 mg, 0.083 mmol) in pyridine (0.3 mL), TsCl (21 mg, 0.11 mmol) was added in an ice bath, and the mixture was stirred at room temperature for 15 h. H_2O was added, and the product was extracted

with AcOEt. The combined organic layer was washed with 20% CuSO₄ aq., H₂O, and satd. NaCl aq., and dried over Na₂SO₄. Filtration, evaporation, and purification through silica gel column chromatography (AcOEt/hexane = 1/4) gave the product in 79% (from *syn*) and 86% (from *anti*) yield, respectively.

(2*R*,3*S*)-Toluenesulfonic acid 3-hydroxy-2-methyl-3-phenylbutyl ester (6-*syn*): ¹H-NMR (CDCl₃) δ 0.81 (d, *J* = 6.9 Hz, 3H), 1.54 (s, 3H), 1.82 (brs, 1H), 2.17 (m, 1H), 2.45 (s, 3H), 3.81 (dd, *J* = 7.5, 10.1 Hz, 1H), 4.27 (dd, *J* = 4.0, 10.1 Hz, 1H), 7.23 (m, 1H), 7.30 (m, 4H), 7.76 (d, *J* = 8.6 Hz, 2H); ¹³C-NMR (CDCl₃) δ 12.41, 21.63, 28.12, 43.37, 72.40, 75.56, 124.9, 126.9, 127.9, 128.1, 129.8, 132.9, 144.7, 146.1; IR (neat) 3535, 1357, 1175 cm⁻¹; [α]_D²⁴ -9.1 (*c* = 1.1, CHCl₃).

(2*S*,3*S*)-Toluenesulfonic acid 3-hydroxy-2-methyl-3-phenylbutyl ester (6-*anti*): ¹H-NMR (CDCl₃) δ 0.99 (d, *J* = 6.9 Hz, 3H), 1.48 (s, 3H), 1.85 (brs, 1H), 2.17 (m, 1H), 2.43 (s, 3H), 3.82 (dd, *J* = 8.1, 9.8 Hz, 1H), 3.96 (dd, *J* = 3.5, 9.8 Hz, 1H), 7.23 (m, 1H), 7.30 (m, 4H), 7.65 (d, *J* = 8.6 Hz, 2H); ¹³C-NMR (CDCl₃) δ 11.91, 21.60, 27.24, 43.22, 72.80, 75.63, 124.7, 126.9, 127.8, 128.2, 129.7, 132.7, 144.6, 146.7; IR (neat) 3535, 1356, 1175 cm⁻¹; [α]_D²⁴ -43.1 (*c* = 1.2, CHCl₃).

To lithium aluminum hydride (14 mg, 0.36 mmol), a solution of the tosylate (0.066 mmol and 0.072 mmol) in THF (1 mL) was added at room temperature, and the mixture was stirred under reflux for 1 h. H₂O (15 μ L), 15% NaOH aq. (15 μ L), and H₂O (45 μ L) were added successively. Filtration and evaporation gave the product **7** in 100% (from *syn*) and 76% (from *anti*) yield, respectively. Based on comparison of the sign of optical rotation ([α]_D²⁵ -18.7 (*c* = 0.40, CH₂Cl₂) from *syn*, and [α]_D²⁵ -21.1 (*c* = 0.44, CH₂Cl₂) from *anti*) to the reported one,¹¹ the absolute configuration of the tetrasubstituted carbon was determined to be (*S*).

A typical procedure for catalytic enantioselective allylsilylation of ketones

The chiral catalyst was prepared following the general procedure described above from CuF₂·2H₂O (6.2 mg, 0.045 mmol) and (*R,R*)-*i*Pr-DuPHOS (37.7 mg, 0.090 mmol). After azeotropic evaporation with toluene, the catalyst was dissolved in DMF (0.3 mL), and cooled to -40 °C. Allyltrimethoxysilane (76 μ L, 0.45 mmol) and acetophenone (**1a**, 35 μ L, 0.30 mmol) were added, successively. After 12.5 h, 1 M HCl was added. Work up and purification as described above gave **3a** in 83% yield. Ee was determined to be 81% by chiral HPLC analysis.

A typical procedure for catalytic enantioselective allylstannation of ketones

The chiral catalyst was prepared following the general procedure described above from CuF₂·2H₂O (6.2 mg, 0.045 mmol) and (*R,R*)-*i*Pr-DuPHOS (37.7 mg, 0.090 mmol). After azeotropic evaporation with toluene, the catalyst was dissolved in DMF (0.3 mL), and cooled to -40 °C. Acetophenone (**1a**, 35 μ L, 0.30 mmol) and allyltributyltin (0.23 mL, 0.75 mmol) were added, successively. After 23 h, H₂O was added. Work up and purification as described above gave **3a** in 40% yield. Ee was determined to be 81% by chiral HPLC analysis.

¹¹B NMR studies (Chart 1)

(A), (B): To a THF-*d*₈ (500 μ L) solution of CuF·PPh₃·2EtOH (13.2 mg, 13.7 μ mol) in NMR tube, allylboronate **2a** (1 equiv for (A) and 3 equiv for (B)) was added. Then, peaks corresponding to fluoroboronate **9** and borate complex **8** were observed, which strongly suggested that an allylcopper was generated. ¹H NMR did not give any conclusive information.

(C): To a THF-*d*₈ (500 μ L) solution of TBAT (6.7 mg, 12.4 μ mol) in NMR tube, allylboronate **2a** (7 μ L, 3 equiv) was added. The peak corresponding to **8'** was observed.

(D): Authentic sample of **9** was synthesized following a reported procedure.¹³

Chart 1. ¹¹B NMR Studies

Kinetic studies

Initial kinetics was measured in THF-*d*₈ at room temperature by ¹H NMR, observing the decrease of the methyl signal of acetophenone **1a** and increase of the signal of allylic protons of the product **3a**, with various concentrations of CuF·3PPh₃·2EtOH, **1a**, and **2a** (Fig. 1, 3, 5). The order dependency on each component was determined by the slope of log *k* (slope of Fig. 1, 3, 5)-log[component] (Fig. 2, 4, 6).

The Order Dependency on CuF·3PPh₃·2EtOH **B** was found to be 1.4 (**B** : 9-37 mM, **1a** : 1.84 M, **2a** : 2.21 M).

The Order Dependency on Allylboronate **2a** was found to be 1.0 (**2a** : 1.42-2.21 M, **1a** : 1.84 M, **B** : 9 mM).

The Order Dependency on Acetophenone **1a** was found to be 0 (**1a** : 1.84-2.39 M, **2a** : 2.21 M, **B** : 9 mM).

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