Facile Preparation of Allylzinc Species from Allylboronates and Zinc Amide *via* Boron-to-Zinc Exchange Process and their Reactions with Carbonyl Compounds, Imines and Hydrazones Facile Preparation of Allylzinc Species from

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I. General Experimental

Melting points are uncorrected. Nuclear Magnetic Resonance (NMR) spectra were recorded on a JEOL ECX-400, a JEOL ECA-500, or a JEOL ECX-600 spectrometer, operating at 400 MHz, 500 MHz, or 600 MHz for ¹H NMR, 100 MHz, 125 MHz, or 150 MHz for ¹³C NMR and 192 MHz for ¹¹B NMR. Chemical shifts were reported downfield from tetramethylsilane (TMS) or in the scale relative to the corresponding solvent used as an internal reference. Infra Red (IR) spectra were measured using a JASCO FT/IR-4200 spectrometer. Melting points were collected using Yazawa Micro Melting Point BY-1.High Resolution Mass Spectra (HRMS) were recorded using a JEOL JMST100TD (DART) spectrometer. High-performance liquid chromatography was carried out using following apparatuses; SHIMADZU LC-20AB (liquid chromatograph), SHIMADZU SPD-M20A (Photo diode array detector) and DGU-20A₃. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd.

All solvents used were commercially available dry solvents that were further dried and degassed appropriately under an argon atmosphere, and stored over activated molecular sieves in an argon box prior to use. Unless otherwise specified, all ketones, imines and hydrazones (purchased from commercial sources) used in this work were distilled under an argon atmosphere or recrystallized prior to use. Pinacol allylboronate 1a, allylboronate 1b¹ and α -methyl allylboronate 1c² were prepared by reported methods; their analyses are in agreement with the reported data. Zinc bis[bis(trimethylsilyl)amide] (Zn(HMDS)₂)³ was prepared according to a reported procedure, and stored in glove box at -30 °C. Zinc *tert*-butoxide⁴ was prepared *in situ* according to a reported procedure. Chiral ligand L^5 was prepared according to a literature procedure. Zinc chloride was purchased from Wako Pure Chemical Industries, Ltd.; zinc bromide and zinc triflate were purchased from Tokyo Chemical Industry. Co., Ltd (TCI); zinc fluoride hydrate and zinc acetate were purchased from Aldrich Co. Inc. All the zinc sources were stored in glove box at -30^oC or room temperature, respectively. All reactions were carried out under an argon atmosphere in flame-dried glassware. References following the compound names indicate the corresponding literature articles where ¹H and ¹³C NMR data have previously been reported.

II. General Procedure

NMR Experiments for Allylzinc Species:



NMR experiments focused on monitoring the stoichiomeric reaction of allylboronate with $Zn(HMDS)_2$ by ¹H NMR (Chart S1). When pinacol allylboronate **1a** (33.6 mg, 0.200 mmol) was treated with $Zn(HMDS)_2$ (77.2 mg, 0.200 mmol, 1.00 equiv.) in THF- d_8 at 0.4 M at 20 °C, gradual boron-to-zinc processe was observed.

The series of signals that belonged to pinacol allylboronate gradually faded. The newly appeared signals were assigned as the signals of allylzinc species. After 5 h, the allylzinc species was provided in the 66% conversion (based on **1a**; 1,2,4,5-tetramethylbenzene as an internal standard), and after 16 h, the zinc species was obtained in full conversion.







20 °C, 24 h

1a

These results indicated that the first exchange proceeded faster than the second exchange, although an excess of allylboronate increased the second allyl group transfer to zinc, and that the allylzinc amide was formed predominantly. In addition,

we have detected borane-amide species in the reaction system by NMR analysis. The formation of allyl zinc species was also supported by this observation. Chart S2. ¹H NMR experiments using Zn(HMDS)₂ and 1a (1:2)



A Typical Procedure for $Zn(HMDS)_2$ -Catalyzed Allylation with Allylboronates 1b: To a dried septum-capped 10 mL-flask with magnetic stirring bar under an argon atmosphere was added $Zn(HMDS)_2$ (1.2 mg, 0.0030mmol, 0.10mol%). After addition of dry solvent (pentane or THF or co-solvent of both, depending on substrates) (3.0 mL,1.0 M), allylboronate 1b (508 mg, 560 µL, 3.30 mmol) and electrophile 2a-q (3.00 mmol) were added. The mixture was stirred under an argon atmosphere at 20 °C for 36 h. After dilution with ethyl acetate, a saturated aqueous NH₄Cl was added and the phases were separated. The aqueous phase was then extracted with ethyl acetate (15 mL x 3) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (eluent: n-hexane/ethyl acetate = 15:1 to 2:1) to afford the corresponding homoallylic alcohols, amines and hydrazides **3a-q**.

Zn(HMDS)₂-Catalyzed Allylation with α -Methyl-substitued Allylboronates 1c: To a dried septum-capped 10 mL-flask with magnetic stirring bar under an argon atmosphere was added Zn(HMDS)₂ (4.7 mg, 0.012 mmol, 3.0 mol%). After addition of dry pentane (0.40 mL), the solution was cooled to -20 °C. To this solution was added α -methyl-substituted allylboronate 1c (80 mg, 0.44mmol) and acetophenone (2a, 48 mg, 0.40 mmol). The mixture was stirred under an argon atmosphere at -20 °C for 10 h. After dilution with ethyl acetate, a saturated aqueous NH₄Cl was added and the phases were separated. The aqueous phase was then extracted with ethyl acetate (15 mL x 3) and the combined organic layers were dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was purified by preparative TLC (Hexane/AcOEt = 5/1) to give two diastereomers (*syn/anti* = 2:3, total 96% yield). The ¹H NMR spectra were in full agreement with the reported data.⁶ The d.r. was determined by ¹H NMR analysis (Chart S3).



Chart S3.

Asymmetric Allylationof 2i with Allylboronates 1b (Scheme 4)

Zn(HMDS)₂ (7.7 mg, 0.020 mmol) was dissolved in dry toluene (1.0 mL), and then chiral ligand L1 (9.4 mg, 0.024 mmol) was added, and the mixture was stirred at 75 °C, the color of solution gradually changed to red. After stirred for 1 h, the solution was cooled to -20 °C. To the cooled solution was added allylboronate 1b (68 mg, 75 μ L, 0.44 mmol) and α -ketoester 2i (66 mg, 57 μ L, 0.40 mmol), the mixture was stirred at -20 °C for 24 h. The reaction was quenched with saturated aqueous NH₄Cl. The resultant mixture was extracted with ethyl acetate (10 mL x 3), and the combined organic layers were dried over anhydrous Na₂SO₄. The solvents were evaporated *in vacuo*, and the residue was purified by preparative TLC (Hexane/AcOEt = 7/1) to give **3i** (92% yield). The enantiomeric excess of the product was determined by HPLC analysis (92% ee).

Analytical Data for Homoallylic Alcohols, Amines and Hydrazides 3a-q

Homoallylic alcohols, amines and hydrazides 3a-g, 3i-m and 3o are known compounds; obtained analytical data are in agreement with reported data (¹H and ¹³C NMR spectra). Analytical data of homoallylic alcohols, amines and hydrazides are as follows.

2-phenylpent-4-en-2-ol⁷ (**3a**; Table 2, entry 11)



Prepared from acetophenone **1a** according to the general procedure, colorless oil (yield: 95%); ¹H NMR (CDCl₃, 500 MHz) δ: 7.37-7.15 (m, 5H), 5.56-5.50 (m, 1H), 5.06-5.02 (m, 2H), 2.62 (dd, J = 13.8, 5.7 Hz, 1H), 2.44 (dd, J = 9.8, 5.2 Hz, 1H), 2.03 (s, 1H), 1.46 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ: 147.6, 133.6, 128.1, 126.6,

124.7, 119.4, 73.6, 48.4, 29.8.

3-phenylhex-5-en-3-ol⁸ (**3b**; Table 3, entry 1)



Prepared from ketone 1b according to the general procedure, colorless oil (yield: 95%); ¹H NMR (CDCl₃, 500 MHz) δ: 7.39-7.30 (m, 4H), 7.22-7.19 (m, 1H), 5.61-5.53 (m, 1H), 5.13-5.06 (m, 2H), 2.72 (dd, J = 14.3, 6.3 Hz, 1H), 2.51 (dd, J = 13.8, 8.6 Hz, 1H), 2.10 (s, 1H), 1.87-1.79 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ: 145.7, 133.6, 128.0, 126.4, 125.4, 119.4, 76.0, 46.9, 35.2, 7.8.

2-(4-methoxyphenyl)pent-4-en-2-ol⁷ (**3c**; Table 3, entry 2)



Prepared from ketonelcaccording to the general procedure, colorless oil (yield: 99%); ¹H NMR (CDCl₃, 500 MHz) δ: 7.34 (dt, J = 6.9, 3.5 Hz, 2H),6.84 (dt, J = 6.9, 3.5 Hz, 2H), 5.66-5.58 (m, 1H), 5.09-5.05 (m, 2H), 3.74 (s, 3H), 2.62 (dd, J = 13.8, 6.3 Hz, 1H), 2.48 (dd, J = 14.3, 8.0 Hz, 1H), 2.43(s,

1H), 1.49 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ: 158.1, 139.9, 134.0, 126.0, 118.9, 113.4, 73.4, 55.1, 48.6, 29.7.

1-allyl-2,3-dihydro-1*H*-inden-1-ol⁹ (3d; Table 3, entry 3)



Prepared from ketone 1d according to the general procedure, colorless solid (yield: 97%);¹H NMR (CDCl₃, 500 MHz) δ: 7.34-7.33 (m, 1H), 7.27-7.22 (m, 3H), 5.89-5.83 (m, 1H), 5.19-5.14 (m, 2H), 3.01-2.97 (m, 1H), 2.85-2.80 (m, 1H), 2.65 (dd, J = 14.3, 8.0 Hz, 1H), 2.53 (ddd, J = 12.6, 6.9, 5.7 Hz, 1H), 2.36-2.31 (m, 1H),

2.11-2.05 (m, 1H), 2.00 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ: 147.0, 143.0, 133.8, 128.3, 126.7, 124.9, 122.9, 118.8, 82.7, 45.0, 39.7, 29.4.

1,1-diphenylbut-3-en-1-ol⁷ (**3e**; Table 3, entry 4)



Prepared from ketone 1e according to the general procedure, colorless oil (yield: 99%); ¹H NMR (CDCl₃, 500 MHz) δ: 7.46-7.44 (m, 4H), 7.32-7.29 (m, 4H), 7.23-7.20 (m, 2H), 5.69-5.63 (m, 1H), 5.26-5.16 (m, 2H), 3.08-3.06 (m, 2H), 2.55 (s, 1H). ¹³C NMR

(CDCl₃, 125 MHz) δ: 146.5, 133.4, 128.2, 126.9, 126.0, 120.5, 76.9, 46.7.

2-(naphthalen-1-yl)pent-4-en-2-ol⁷ (**3f**; Table 3, entry 5)



Prepared from ketone **1f** according to the general procedure, colorless solid (yield: 92%); ¹H NMR (CDCl₃, 500 MHz) δ : 8.72 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.53-7.34 (m, 4H), 5.66-5.57 (m, 1H), 5.11-5.04 (m, 2H), 3.07 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.80 (dd, *J* = 14.3, 8.0Hz, 1H), 2.36 (s, 1H), 1.76 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ : 142.1,

134.8, 133.9, 130.8, 129.2, 128.5, 126.8, 125.3, 125.1, 124.7, 123.6, 119.1, 75.2, 47.1, 29.5.

2-(thiophen-2-yl)pent-4-en-2-ol⁷ (3g; Table 3, entry 6)



Prepared from ketone **1g** according to the general procedure, colorless oil(yield: 97%); ¹H NMR (CDCl₃, 500 MHz) δ : 7.12 (dd, J = 5.2, 1.2 Hz, 1H), 6.88 (dd, J = 5.2, 3.4 Hz, 1H), 6.84 (dd, J = 3.4, 1.2 Hz, 1H), 5.70-5.62 (m, 1H), 5.11-5.07 (m, 2H), 2.65 (dd, J = 13.7, 6.9 Hz, 1H), 2.51 (dd, J = 14.3, 8.6 Hz, 1H), 2.26 (s, 1H), 1.54

(s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ: 153.0, 133.3, 126.7, 126.7, 123.8, 122.3, 119.7, 72.9, 49.1, 30.3.

9-allyl-9H-fluoren-9-ol(3h; Table 3, entry 7)



Prepared from ketone **1h** according to the general procedure, colorless solid (yield: 99%), mp: 115-117 °C; ¹H NMR (CDCl₃, 500 MHz) δ: 7.52-7.50 (m,2H), 7.38-7.36 (m, 2H), 7.29-7.26(m, 2H), 7.22-7.18 (m, 2H), 5.49-5.40 (m, 1H), 4.86-4.83 (m, 2H), 2.68-2.67 (m, 2H), 2.46 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ: 148.2, 139.3, 132.6, 128.8, 127.7, 123.8, 119.8, 118.6, 81.4, 43.9. **IR** (neat): v

=3945, 3438, 3055, 2986, 1640, 1448, 1423, 1265, 1054, 896, 737cm⁻¹; **HRMS** (DART) calcd. for $C_{16}H_{13}^{+} = [M-OH]^+$: m/z = 205.1017, found: m/z = 205.1013.

Methyl 2-hydroxy-2-phenylpent-4-enoate¹⁰ (3i; Table 3, entry 8)



Prepared from ketone **1i** according to the general procedure, colorless oil (yield: 83%); ¹H NMR (CDCl₃, 500 MHz) δ : 7.60-7.59 (m, 2H), 7.37-7.27 (m, 3H), 5.83-5.75 (m, 1H), 5.19-5.13 (m, 2H), 3.76 (s, 3H), 3.72 (s, 1H), 2.99 (dd, J = 13.8, 7.4 Hz, 1H), 2.79 (dd, J = 14.3, 6.9 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ :

175.1, 141.2, 132.4, 128.3, 127.9, 125.5, 119.4, 78.2, 53.2, 44.2. Asymmetric allylation: The enantiomeric excess was determined by HPLC analysis (Daicel Chiralcel AS-H, Hexane/*i*-PrOH = 30/1, 254 nm, flow rate = 0.5 mL/min, $t_{\rm R}$ = 15.2 min (*S*), $t_{\rm R}$ = 17.4 min (*R*), 92% ee).

3-methyl-1-phenylhex-5-en-3-ol¹¹ (**3j**; Table 3, entry 9)

Prepared from ketone 1j according to the general procedure, colorless oil (yield:



91%);¹H NMR (CDCl₃, 500 MHz) δ: 7.27-7.24 (m, 2H), 7.18-7.14 (m, 3H), 5.91-5.82 (m, 1H), 5.15-5.11 (m, 2H), 2.70-2.66 (m, 2H), 2.28-2.26 (m, 2H), 1.77-1.73 (m, 3H), 1.22 (s, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ: 142.5, 133.9, 128.4, 128.3, 125.7, 118.7, 72.0, 46.4, 43.7, 30.2, 26.7.

4-methyloct-1-en-4-ol¹² (**3**k; Table 3, entry 10)



Prepared from ketone 1k according to the general procedure, colorless oil (vield: 86%); ¹H NMR (CDCl₃, 500 MHz) δ: 5.90-5.82 (m, 1H), 5.14-5.09 (m, 2H), 2.23-2.21 (m, 2H), 1.61 (s, 1H), 1.47-1.44 (m, 2H), 1.32-1.31 (m, 4H), 1.16 (s, 3H), 0.93 (t,

J = 6.9 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz) δ : 134.1, 118.4, 72.1, 46.2, 41.5, 26.6, 26.0, 23.2, 14.0.

1-allylcyclohexanol⁷ (**3I**; Table 3, entry 11)



Prepared from ketone 11 according to the general procedure, colorless oil (yield: 87%);¹H NMR (CDCl₃, 500 MHz) δ: 5.93-5.85 (m, 1H), 5.14-5.08 (m, 2H), 2.22-2.20 (m, 2H), 1.77 (s,1H), 1.65-1.40 (m, 9H), 1.30-1.23 (m, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ: 133.9, 118.5, 71.0, 46.8, 37.4, 25.8, 22.2, 22.1.

4-methoxy-*N*-(1-phenylbut-3-en-1-yl)aniline¹³ (3m; Table 3, entry 12)



Prepared from imine1maccording to the general procedure, pale yellow oil (yield: 98%); ¹H NMR (CDCl₃, 500 MHz) δ: 7.34-7.28 (m, 4H),7.21-7.18 (m, 1H), 6.66 (d, J = 8.6 Hz, 2H),6.44 (d, J = 8.6 Hz, 2H),5.77-5.72 (m, 1H), 5.17-5.10 (m, 2H), 4.30 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.91 (brs, 1H), 3.64 (s, 3H), 2.58 (dt, *J* = 8.0, 5.2 Hz, 1H), 2.48 (dt, J = 8.0, 6.3 Hz, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ : 151.9,

143.8, 141.6, 134.8, 128.5, 126.9, 126.3, 118.2, 114.7, 114.6, 57.9, 55.6, 43.4.

N-benzyl-1,1-diphenylbut-3-en-1-amine (3n; Table 3, entry 13)



Prepared from imine **1n** according to the general procedure, white solid (vield: 82%), mp: 66-68°C;¹H NMR (CDCl₃, 500 MHz) δ: 7.43-7.41 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.24 (m, 2H), 7.20-7.12 (m, 9H), 5.59-5.50 (m, 1H), 5.11-5.00 (m, 2H), 3.44-3.43 (m, 2H), 3.15-3.14 (m, 2H), 1.90 (s, 1H). ¹³C NMR (CDCl₃, 125 MHz) δ: 146.6, 141.0, 133.9, 128.2, 128.2, 128.0, 127.1, 126.7, 126.3, 118.0,

64.3, 46.5, 41.0.**IR** (neat): v = 3061, 3027, 2932, 2845, 1600, 1494, 1447, 1264, 1184, 1072, 1030, 1000, 915, 782,739, 702cm⁻¹; **HRMS** (DART) calcd. for $C_{23}H_{24}N^+$ = $[M+H]^+$: m/z = 314.1909, found: m/z = 314.1905.

N'-(1-phenylhex-5-en-3-yl)benzohydrazide¹⁴ (30; Table 3, entry 14)

Prepared from hydrazine 10 according to the general procedure, pale yellow oil (yield:



95%); ¹H NMR (CDCl₃, 500 MHz) δ : 8.27 (br, 1H), 7.73-7.71 (m, 2H), 7.46-7.14 (m, 8H), 5.89-5.81 (m, 1H), 5.14-5.07 (m, 2H), 4.87 (br, 1H), 3.07 (t,*J* = 6.3 Hz, 1H), 2.71-2.68 (m, 2H), 2.30-2.20 (m, 2H), 1.81-1.70 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ : 167.4, 142.1, 135.1, 132.8, 131.7, 128.6, 128.3, 128.3,

126.9, 125.8, 117.5, 59.1, 37.3, 34.2, 31.8.

N'-(1,1-diphenylbut-3-en-1-yl)benzohydrazide (3p; Table 3, entry 15)



Prepared from hydrazine **1p** according to the general procedure, colorless solid (yield: 95%), mp:143-145 °C; ¹H NMR (CDCl₃, 500 MHz) δ : 7.46-7.16 (m, 16H), 5.83 (br, 1H), 5.74-5.66 (m, 1H), 5.06-4.99 (m, 2H), 3.12-3.11 (m, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ : 165.7, 143.7, 133.5, 132.9, 131.4, 128.5, 128.1, 127.7, 127.0, 126.7, 118.7, 68.3, 41.9. **IR** (neat): v =3265, 3208,

3056, 3030, 1639, 1578, 1549, 1491, 1430, 1326, 1265, 1194, 918, 761, 743cm⁻¹; **HRMS** (DART) calcd. for $C_{23}H_{23}N_2O^+ = [M+H]^+$: m/z = 343.1810, found: m/z = 343.1804.

N'-(1-allylcyclohexyl)benzohydrazide (3q; Table 3, entry 16)



Prepared from hydrazine **1q** according to the general procedure, colorless solid (yield: 95%), mp: 65-67°C; ¹H NMR (CDCl₃, 500 MHz) δ : 7.90 (br, 1H),7.74-7.72 (m, 2H), 7.46-7.34 (m, 3H), 6.02-5.94 (m, 1H), 5.12-5.08 (m, 2H), 4.95 (br, 1H), 2.25-2.23 (m, 2H), 1.64-1.32(m, 10H). ¹³C NMR (CDCl₃, 125 MHz) δ : 167.1, 134.7, 133.0, 131.5, 128.5, 126.9, 117.4, 58.9, 41.2, 33.5, 25.7, 21.9. **IR** (neat): v =3415, 3285, 3061, 2977, 2932,

2858, 1639, 1579, 1544, 1453, 1360, 1312, 1266, 996, 915, 791, 739, 708 cm⁻¹; **HRMS** (DART) calcd. for $C_{16}H_{23}N_2O^+ = [M+H]^+$: m/z = 259.1810, found: m/z = 259.1804.

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SPD-M	20A Ch1 25	4nm					
ヒ ゚ーク#	保持時間	面積	高さ	濃度	単位	マーク	化合物名
1	14.819	429923	27647	49.396		М	
2	17.400	440439	5663	50.604		М	
合計		870362	33309				

Optically active **3i**



ピ- ク#	保持時間	面積	高さ	濃度	単位	マーク	化合物名
1	15.271	176459	11074	3.848		M	
2	17.380	4409171	185106	96.152		M	
合計		4585631	196180				