**(*E*)- α -Substituted γ -Alkoxyallylboronic Esters as New Reagents:
Synthesis and Reactivity Towards Aldehydes**

by

Françoise Possémé, Michael Deligny, François Carreaux, Bertrand Carboni

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General Remarks: Reactions were performed in oven-dried glassware under an argon atmosphere. Tetrahydrofuran (THF) was distilled from deep blue solutions of sodium/benzophenone ketyl prior to use. CH_2Cl_2 was distilled from CaH_2 . All aldehydes were purified by Kugelrohr distillation prior to use. Unless otherwise stated, all reagents were used as received. Most of reactions were monitored by TLC on pre-coated silica plates (Merck 60 F254 0.25 mm). Silica gel 60F254 was used for column flash chromatography. Deactivated silica-gel refers to the silica-gel washed with triethylamine prior to use. Melting points are uncorrected. NMR spectra were recorded in CDCl_3 on a 200 MHz spectrometer operating in the Fourier transform mode. ^1H NMR data are presented as follows: chemical shift, multiplicity, coupling constant, integration. The following abbreviation are used in reporting data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dq, doublet of quartets; dd, doublet of doublets; ddd, doublet of doublets of doublets; m, multiplet. ^{13}C NMR spectra were obtained with broadband proton decoupling. Chemical shifts were recorded relative to the internal tetramethylsilane (TMS) reference signal. Coupling constants (J) are given in Hz. For ^{11}B NMR, the chemical shifts are in ppm relative to $\text{BF}_3 \cdot \text{OEt}_2$. High resolution mass spectrum (HRMS) and microanalysis were performed on instruments from the University of Rennes 1.

General procedure for the preparation of allylboranes (2): To a solution of **1a** (256.2 mg, 1 mmol) in THF (4 mL) was added a solution of the appropriate organometallic reagent (1.5 mmol) at the temperature indicated in the table 2. The mixture was stirred for 45 min at this temperature before the slow addition of boron trifluoride etherate (253 μL , 2 mmol). The mixture was then stirred for additional 25 min at the same temperature. The reaction was quenched by addition of a saturated aqueous solution of sodium hydrogen carbonate (2 mL) and extracted with dichloromethane (3x10mL). The organic layers were combined, washed with brine (10 mL), then dried over anhydrous MgSO_4 . Evaporation of the solvent gave a residue that was purified by flash chromatography (deactivated silica-gel, heptane/ethyl acetate 9:1) to afford pure allylborane **2**. **2b-c** could not be obtained in a pure form due to their instability on silica gel although deactivated.

2-[(2E)-3-ethoxy-1-methylprop-2-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (crude 2b): ^1H NMR (200 MHz, CDCl_3) δ 0.84-1.31 (m, 19H), 3.69 (q, $J = 7.1$ Hz, 2H), 4.83 (dd, $J = 8.3, 12.9$ Hz, 1H), 6.43 (d, $J = 12.9$ Hz, 1H).

2-[(2E)-3-ethoxy-1-phenylprop-2-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (crude 2c): ^1H NMR (200 MHz, CDCl_3) δ 0.85-1.08 (m, 4H), 1.24 (s, 12H), 3.51 (m, 2H), 5.10 (dd, $J = 9.1, 12.9$ Hz, 1H), 6.37 (d, $J = 12.9$ Hz), 7.30-7.50 (m, 5H).

2-{1-[(*E*)-2-ethoxyvinyl]-2-methylbutyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d): colorless oil, yield (174 mg, 65%). ^1H NMR (200 MHz, CDCl_3) δ 0.70-0.87 (m, 6H), 1.12-1.54 (m, 19H), 3.63 (q, $J = 7.1$ Hz, 2H), 4.68 (dd, $J = 9.8, 12.6$ Hz, 1H), 6.09 (dd, $J = 2.0, 12.6$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 11.5, 12.1, 15.1, 18.1, 20.0, 25.1, 28.1, 29.4, 36.5, 36.8, 64.9, 83.3, 103.4, 104.2, 146.3, 146.4. ^{11}B NMR (96 MHz, $\text{CDCl}_3/\text{BF}_3 \cdot \text{OEt}_2$) δ +33.0 ppm. HRMS (EI) calcd for $\text{C}_{15}\text{H}_{29}\text{O}_3\text{B}$ m/z 268.2210, found 268.2208.

2-[(2*E*)-3-ethoxy-1-isopropylprop-2-en-1-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e): colorless oil, yield (137 mg, 54%). ^1H NMR (200 MHz, CDCl_3) δ 0.89 (d, $J = 6.7$ Hz, 3H), 0.92 (d, $J = 6.7$ Hz, 3H), 1.2-1.46 (m, 16H), 1.72 (m, 1H), 3.73 (q, $J = 7.1$ Hz, 2H), 4.69 (dd, $J = 10.3, 12.4$ Hz, 1H), 6.18 (d, $J = 12.4$ Hz, 1H). ^{13}C NMR (50 MHz, CDCl_3) δ 15.1, 21.9, 22.8, 25.0, 25.1, 30.4, 64.9, 83.3, 104.0, 146.4. ^{11}B NMR (96 MHz, $\text{CDCl}_3/\text{BF}_3 \cdot \text{OEt}_2$) δ +32.7 ppm. HRMS (EI) calcd for $\text{C}_{14}\text{H}_{27}\text{O}_3\text{B}$ m/z 254.2053; found 254.2052.

General procedure for the allylboration reactions under thermal conditions (5): A solution of 1 mmol of **2** and 2 mmol of aldehyde in 10 mL of THF was stirred at room temperature under an argon atmosphere. The reaction was monitored by TLC until complete consumption of **2**. After addition of a saturated solution of NH_4Cl , the aqueous layer was extracted twice with CH_2Cl_2 . Combined organic layers were washed with saturated NaCl, dried over anhydrous MgSO_4 , filtered and concentrated under vacuum. The crude product was purified by column chromatography (heptane/ethyl acetate, 9/1) to yield **5** as indicated in Table 3.

(1*S, 2*R**)-2-Ethoxy-1-phenyl-pent-3-en-1-ol ((*Z*)-5b, (*E*)-5b):** colorless oil, yield (103 mg, 50% as an inseparable 74:26 mixture of *Z* and *E* isomers). ^1H NMR (200 MHz, CDCl_3) δ 1.02-1.23 (m, 3H), 1.41 (dd, $J = 1.5, 7.0$ Hz, 2.22H), 1.70 (d, $J = 6.1$ Hz, 0.78H), 2.83 (br s, 1H), 3.37 (dq, 1H), 3.60 (dq, 1H), 3.84 (dd, $J = 4.5, 8.1$ Hz, 0.26H), 4.32 (dd, $J = 4.0, 9.3$ Hz, 0.74H), 4.80 (d, $J = 4.5$ Hz, 0.26H), 4.89 (d, $J = 4.0$ Hz, 0.74H), 5.33 (m, 1H), 5.62 (dq, $J = 6.0, 15.4$ Hz, 0.26H), 5.75 (dq, $J = 6.8, 11.1$ Hz, 0.74H), 7.26-7.42 (m, 5H). ^{13}C NMR (50 MHz, CDCl_3) δ 13.6, 15.1, 15.2, 17.7, 64.3, 66.3, 75.5, 78.2, 84.4, 126.6, 126.7, 126.8, 127.1, 127.2, 127.7, 129.9, 131.1, 140.2, 140.5. HRMS (EI) calcd for $\text{C}_6\text{H}_{11}\text{O}$ m/z ($\text{M}^+ - \text{C}_7\text{H}_7\text{O}$) 99.0810, found 99.0811. Anal. Calcd. For $\text{C}_{13}\text{H}_{18}\text{O}_2$: C 75.69, H 8.80. Found: C 75.74, H 8.83.

(1S*, 2R*)-2-Ethoxy-1,4-diphenyl-but-3-en-1-ol ((Z)-5c, (E)-5c): colorless oil, yield (169 mg, 63% as an inseparable 5:95 mixture of *Z* and *E* isomers). ^1H NMR (200 MHz, CDCl_3) δ 1.14 (t, $J = 7.1$ Hz, 0.15H), 1.27 (t, $J = 6.8$ Hz, 2.85H), 3.48 (dq, $J = 7.1$, 9.3 Hz, 1H), 3.70 (dq, $J = 7.1$, 9.3 Hz, 1H), 4.10 (ddd, $J = 0.8$, 4.3, 7.8 Hz, 0.95H), 4.44 (ddd, $J = 0.8$, 4.3, 9.8 Hz, 0.05H), 4.96 (d, $J = 4.3$ Hz, 1H), 5.70 (dd, $J = 9.8$, 11.9 Hz, 0.05H), 6.13 (dd, $J = 7.8$, 16.2 Hz, 0.95H), 6.52 (dd, $J = 0.8$, 16.2 Hz, 0.95H), 6.82 (dd, $J = 0.8$, 11.9 Hz, 0.05H), 7.31-7.44 (m, 10H). ^{13}C NMR (50 MHz, CDCl_3) δ 15.2, 64.3, 75.8, 84.3, 125.6, 126.0, 126.2, 126.4, 126.7, 126.8, 127.0, 127.1, 127.5, 134.1, 136.4, 140.3. HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{O}$ m/z ($\text{M}^+ - \text{C}_2\text{H}_5\text{O}$) 223.1123, found 223.1120. Anal. Calcd. For $\text{C}_{18}\text{H}_{20}\text{O}_2$: C 80.56, H 7.51. Found: C 80.58, H 7.55.

(1S*, 2R*)-2-Ethoxy-5-methyl-1-phenyl-hex-3-en-1-ol ((Z)-5e, (E)-5e): colorless oil, yield (178 mg, 76% as an inseparable 75:25 mixture of *Z* and *E* isomers). White solid. M.p. 51°C. ^1H NMR (200 MHz, CDCl_3) δ 0.43 (d, $J = 6.5$ Hz, 2.25H), 0.80 (d, $J = 6.8$ Hz, 3H), 0.81 (d, $J = 6.5$ Hz, 0.75H), 1.09 (t, $J = 7.0$ Hz, 0.75H), 1.11 (t, $J = 7.0$ Hz, 2.25H), 2.24 (m, 1H), 2.67 (br s, 1H), 3.27 (m, 1H), 3.50 (m, 1H), 3.72 (dd, $J = 4.3$, 8.1 Hz, 0.25H), 4.16 (dd, $J = 4.0$, 9.6 Hz, 0.75H), 4.72 (d, $J = 4.3$ Hz, 0.25H), 4.78 (d, $J = 4.0$ Hz, 0.75H), 5.12 (dd, $J = 9.6$, 11.1 Hz, 0.75H), 5.19 (dd, $J = 8.1$, 15.6 Hz, 0.25H), 5.33 (dd, $J = 9.7$, 11.1 Hz, 0.75H), 5.39 (dd, $J = 6.6$, 15.6 Hz, 0.25H), 7.15-7.30 (m, 5H). ^{13}C NMR (50 MHz, CDCl_3) δ 14.0, 14.3, 21.1, 21.2, 21.4, 21.9, 26.1, 29.9, 62.8, 74.7, 77.8, 83.5, 121.4, 121.6, 125.7, 125.9, 126.2, 126.3, 126.8, 139.2, 139.5, 142.2, 142.7. HRMS (EI) calcd for $\text{C}_8\text{H}_{15}\text{O}$ m/z ($\text{M}^+ - \text{C}_7\text{H}_7\text{O}$) 127.1123, found 127.1125. Anal. Calcd. For $\text{C}_{15}\text{H}_{22}\text{O}_2$: C 76.88, H 9.46. Found: C 76.87, H 9.53.

(6S*, 7R*)-7-Ethoxy-tridec-8-en-6-ol ((Z)-5f, (E)-5f): colorless oil, yield (172 mg, 71% as an inseparable 71:29 mixture of *Z* and *E* isomers). ^1H NMR (200 MHz, CDCl_3) δ 0.89-0.91 (m, 6H), 1.18 (t, $J = 7.0$ Hz, 3H), 1.30-1.40 (m, 12H), 2.08-2.16 (m, 3H), 3.35 (m, 1H), 3.53-3.65 (m, 2.29H), 4.03 (dd, $J = 4.0$, 9.3 Hz, 0.71H), 5.35 (m, 1H), 5.59 (dt, $J = 7.8$, 11.3 Hz, 1H). The great majority of signals corresponding of the *E*-isomer, **(E)-5f**, are hidden by those of the *Z*-isomer, **(Z)-5f**. ^{13}C NMR (50 MHz, CDCl_3) δ 13.9, 14.0, 15.3, 15.4, 22.2, 22.4, 22.5, 22.6, 25.4, 25.6, 26.7, 31.3, 31.8, 31.9, 32.0, 32.2, 63.5, 63.6, 73.2, 73.3, 77.6, 126.2, 135.9, 136.7. HRMS (EI) calcd for $\text{C}_9\text{H}_{17}\text{O}$ m/z ($\text{M}^+ - \text{C}_6\text{H}_{13}\text{O}$) 141.1279, found 141.1277. Anal. Calcd. For $\text{C}_{15}\text{H}_{30}\text{O}_2$: C 74.32, H 12.47. Found: C 74.48, H 12.53.

General procedure for the tandem reaction (5, 6): To a solution of **1a** (256.2 mg, 1 mmol) in THF (4 mL) was added a solution of the appropriate organolithium reagent (1.5 mmol) at -78°C under an argon atmosphere. The mixture was stirred for 45 min at this temperature before the slow addition of boron trifluoride etherate (253 μ L, 2 mmol). The mixture was then stirred for additional 25 min at the same temperature. Benzaldehyde (200 μ L, 2 mmol) was then added and the mixture was warmed at room temperature. The reaction was monitored by TLC and allowed to stir until complete consumption of **2**. The reaction was quenched by addition of a saturated aqueous solution of sodium hydrogen carbonate (2 mL) and extracted with dichloromethane (3x10mL). The organic layers were combined, washed with brine (10 mL), then dried over anhydrous MgSO_4 . Evaporation of the solvent gave a residue that was purified by flash chromatography (heptane/ethyl acetate 9:1) to give a mixture of compounds **5** and **6** which were inseparable.

(1S*, 2R*)-2-Ethoxy-1-phenyl-pent-3-en-1-ol ((Z)-5b, (E)-5b) and (1S*, 2S*)-2-Ethoxy-1-phenyl-pent-3E-en-1-ol ((E)-6b): colorless oil, yield (150 mg, 73% as an inseparable 34.5:60.5:5 mixture of **5bZ**, **5bE** and **6bE** as indicated in the table 4). The NMR and analytical data of **(Z)-5b** and **(E)-5b** have been previously described. **(E)-6b**: ^1H NMR (200 MHz, CDCl_3) δ 4.52 (d, J = 8.1 Hz, 0.05H) ppm. The other peaks were hidden by those of **5b**.

(1S*, 2R*)-2-Ethoxy-1,4-diphenyl-but-3-en-1-ol ((Z)-5c, (E)-5c) and (1S*, 2S*)-2-Ethoxy-1,4-diphenyl-but-3E-en-1-ol ((E)-6c): colorless oil, yield (134 mg, 50% as an inseparable 2.6: 85.4:12 mixture of **(Z)-5c**, **(E)-5c** and **(E)-6c** as indicated in the table 4). The NMR and analytical data of **(Z)-5c** and **(E)-5c** have been previously described. **(E)-6c**: ^1H NMR (200 MHz, CDCl_3) δ 1.33 (t, J = 7.1 Hz, 0.36H), 3.96 (ddd, J = 1.1, 7.3, 7.8 Hz, 0.12H), 4.66 (d, J = 7.8 Hz, 0.12H), 6.01 (dd, J = 7.3, 16.1 Hz, 0.12H), 6.42 (dd, J = 1.1, 16.1 Hz, 0.12H). The other peaks were hidden by those of **5c**.

(1S*, 2R*)-2-Ethoxy-5-methyl-1-phenyl-hept-3-en-1-ol ((Z)-5d, (E)-5d) and (1S*, 2S*)-2-Ethoxy-5-methyl-1-phenyl-hept-3E-en-1-ol ((E)-6d): colorless oil, yield (122 mg, 49% as an inseparable 26.5: 72.5:1 mixture of **(Z)-5d**, **(E)-5d** and **(E)-6d** as indicated in the table 4). ^1H NMR (200 MHz, CDCl_3) δ 0.36-0.84 (m, 6H), 1.06-1.19 (m, 5H), 1.93 (m, 1H), 2.64 (br s, 1H), 3.26 (m, 1H), 3.48 (m, 1H), 3.73 (ddd, J = 1.8, 4.3, 7.6 Hz, 0.725H), 4.16 (dd, J = 4.2, 9.1 Hz, 0.265H), 4.40 (d, J = 8.1 Hz, 0.01H), 4.73 (d, J = 4.3 Hz, 0.725H), 4.76 (d, J = 4.2 Hz, 0.265H), 5.18 (dd, J = 7.9, 15.9 Hz, 1H), 5.33 (dd, J = 6.5, 15.9 Hz, 1H), 7.13-7.70 (m, 5H). The signals corresponding of the double bond of **(Z)-5d** and **(E)-6d** are hidden by those of **(E)-5d**. ^{13}C NMR (50 MHz, CDCl_3) δ 11.4, 11.6, 11.7, 12.0, 15.2, 15.3, 20.0, 20.1, 20.4, 24.9, 29.3, 29.4, 30.1, 33.9, 34.2, 38.2, 63.7, 63.8, 75.6, 75.7, 78.7, 79.0, 84.5, 123.8, 123.9, 124.1, 126.7, 126.8, 127.2, 127.3, 127.7, 127.8, 140.2, 140.4, 142.1, 142.4, 142.9. HRMS (EI) calcd for $\text{C}_9\text{H}_{17}\text{O}$ m/z (M^+ - $\text{C}_7\text{H}_7\text{O}$) 141.1279, found 141.1276. Anal. Calcd. For $\text{C}_{16}\text{H}_{24}\text{O}_2$: C 77.38, H 9.74. Found: C 77.43, H 9.72.

allylboration without Lewis acid

85.4/2.6/12

allylboration in presence of Lewis acid
(one pot procedure)