Supporting Information

Palladium Pincer-complex Catalyzed Substitution of Vinyl Cyclopropanes, Vinyl Aziridines and Allyl Acetates with Tetrahydroxydiboron. An Efficient Route to Functionalized Allylboronic Acids and Potassium Trifluoro(allyl)borates

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Experimental Procedures and Characterization of the Prepared Compounds

All reactions were conducted under argon atmosphere by employing standard manifold techniques. The $^1$H-NMR and $^{13}$C-NMR spectra were recorded in acetone-$d_6$ (internal standard: 2.05 ppm, $^1$H; 30.60 ppm, $^{13}$C), DMSO-$d_6$ (internal standard: 2.54 ppm, $^1$H; 40.45 ppm, $^{13}$C) and CDCl$_3$ (internal standard: 7.26 ppm, $^1$H; 77.36 ppm, $^{13}$C) solutions at room temperature by Varian 400 spectrometer. Due to quadrupolar relaxation, the carbon attached to the boron atom was not always detected in $^{13}$C-NMR. $^{19}$F-NMR spectra were recorded at either 282.2 or 376.3 MHz, using $\alpha,\alpha,\alpha$–trifluorotoluene as standard.

Palladium pincer-complex 1a was prepared according to the procedure published by Yao and co-workers$^1$ except that the final product was purified by CH$_2$Cl$_2$:ether 20:1 as eluent. The starting materials were prepared according to literature procedures.$^2$–$^6$ Tetrahydroxydiboron (2a) was purchased from Boron Molecular Ltd and were used as received.

**General Procedure.** The corresponding substrate 3-5 (0.15 mmol) was dissolved in DMSO (0.35 ml) followed by addition of tetrahydroxydiboron 2a (0.18 mmol), pincer complex 1a (0.0075 mmol, 5 mol%) and molecular sieves. This reaction mixture was stirred for the allotted temperatures and times listed in Table 1 under Ar atmosphere. The $^1$H-NMR spectrum of the allylboronic acid products 6a-k was determined from the reaction mixture (in DMSO-$d_6$). Thereafter KHF$_2$ (0.9 mmol, 70 mg) in water (0.7 mL) was added to this mixture and the resulting suspension was stirred for 45 minutes at room temperature. The precipitate was separated and the filtrate containing the crude product was evaporated. The solid remaining after evaporation was extracted with acetone and filtered, subsequently the acetone solution was evaporated and the remaining solid was recrystallized from acetone/ether or chloroform/ether.

**Potassium trifluoro[5,5-di(ethoxycarbonyl)-2-pentenyl]borate** (7a). This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6a was determined from the crude mixture. $^1$H NMR (DMSO-$d_6$): 5.58 (dt, 7.6 Hz, 15.1 Hz, 1H), 5.20 (dt, 7.3 Hz, 15.1 Hz, 1H), 4.13 (q, 7.1 Hz, 4H), 3.47 (t, 7.3 Hz, 1H), 2.43 (ps t, 7.3 Hz, 2H), 1.46 (d, 7.6 Hz, 2H), 1.20 (t, 7.1 Hz, 6H). The NMR data for the isolated compound 7a: $^1$H NMR (CDCl$_3$): 5.63 (dt, 7.7 Hz, 15.0 Hz, 1H), 5.12 (dt, 6.8 Hz, 15.0 Hz, 1H), 4.15 (q, 7.1 Hz,
4H), 3.39 (t, 6.8 Hz, 1H), 2.50 (ps t, 6.8 Hz, 2H), 1.23 (t, 7.1 Hz, 6H), 1.11 (br, 2H). $^{13}\text{C NMR (CDCl}_3): 170.1, 136.0, 121.5, 61.7, 52.5, 32.4, 23.5$ (br), 14.3. $^{19}\text{F NMR (CDCl}_3): -141.0$.

[5,5-di(ethoxycarbonyl)-2-pentenyl]-1,3,6,2-dioxazaborocan (8). This compound was prepared according to the above general procedure except that allylboronic acid product 6a was reacted with diethanolamine instead of KHF$_2$. The NMR data for the isolated compound 8: $^1\text{H NMR (acetone-d}_6): 5.67$ (dt, 8.0 Hz, 15.1 Hz, 2H), 5.14 (dt, 7.2 Hz, 15.1 Hz, 1H), 4.14 (q, 7.1 Hz, 4H), 3.82 (m, 2H), 3.67 (m, 2H), 3.35 (t, 7.2 Hz, 1H), 3.19 (m, 2H), 2.81 (m, 2H), 2.46 (ps t, 7.2 Hz, 2H), 1.23 (br p, 2H), 1.22 (t, 7.1 Hz, 6H). $^{13}\text{C NMR (acetone-d}_6): 170.5, 137.6, 123.0, 64.0, 62.3, 54.1, 52.9, 33.7, 26.5$ (br), 15.2.

Potassium trifluoro[5,5-di(phenylsulfonyl)-2-pentenyl]borate (7b). This compound was prepared according to the above general procedure. The $^1\text{H NMR spectrum of allylboronic acid product 6b} was determined from the crude mixture. $^1\text{H NMR (DMSO-d}_6): 7.94$ (d, 7.3 Hz, 4H), 7.78 (t 7.3 Hz, 2H), 7.66 (t, 7.3 Hz, 4H), 5.69 (t, 5.3 Hz, 1H), 5.47 (dt, 7.4 Hz, 15.0 Hz, 1H), 5.10 (dt, 5.3 Hz, 15.0 Hz, 1H), 2.78 (ps t, 5.3 Hz, 2H), 1.39 (d, 7.4 Hz, 2H). The NMR data for the isolated compound 7b: $^1\text{H NMR (acetone-d}_6): 7.98$ (d, 7.5 Hz, 4H), 7.74 (t, 7.5 Hz, 2H), 7.62 (t, 7.5 Hz, 4H), 5.61 (dt, 7.0 Hz, 15.0 Hz, 1H), 5.09 (dt, 6.4 Hz, 15.0 Hz, 1H), 5.09 (t, 6.4 Hz, 1H), 2.81 (ps t, 6.4 Hz, 2H), 1.01 (br, 2H). $^{13}\text{C NMR (acetone-d}_6): 140.6, 140.1, 135.9, 131.1, 130.6, 119.9, 84.2, 30.7, 25.6$ (br). $^{19}\text{F NMR (acetone-d}_6): -140.4$.

Potassium trifluoro(5-methoxycarbonyl-5-phenylsulfonyl-2-pentenyl)borate (7c). This compound was prepared according to the above general procedure. The $^1\text{H NMR spectrum of allylboronic acid product 6c} was determined from the crude mixture. $^1\text{H NMR (DMSO-d}_6): 7.88$ (d, 7.5 Hz, 2H), 7.82 (t, 7.5 Hz, 1H), 7.71 (t, 7.5 Hz, 2H), 5.58 (dt, 7.5 Hz, 15.0 Hz, 1H), 5.11 (dt, 6.7 Hz, 15.0 Hz, 1H), 4.42 (dd, 4.2 Hz, 10.8 Hz, 1H), 3.57 (s, 3H), 2.50 (m, 2H), 1.44 (d, 7.5 Hz, 2H). The NMR data for the isolated compound 7c: $^1\text{H NMR (acetone-d}_6): 7.90$ (d, 7.5 Hz, 2H), 7.79 (t, 7.5 Hz, 1H), 7.68 (t, 7.5 Hz, 2H), 5.66 (dt, 8.1 Hz, 15.1 Hz, 1H), 4.92 (dt, 7.1 Hz, 15.1 Hz, 1H), 4.07 (dd, 4.4 Hz, 11.0 Hz, 1H), 3.60 (s, 3H), 2.55 (m, 2H), 0.98 (br, 2H). $^{13}\text{C NMR (acetone-d}_6): 167.7, 140.8, 139.7, 135.8, 130.8, 118.6, 72.5, 53.7, 32.1, 21.2$ (br). $^{19}\text{F NMR (acetone-d}_6): -140.7$. 
Potassium trifluoro{4-phenyl-4-[(phenylsulfonyl)amino]-2-butenyl}borate (7d). This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6d was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 8.25 (d, 8.2 Hz, 1H), 7.71 (d, 7.4 Hz, 2H), 7.50 (m, 4H), 7.22 (m, 4H), 5.45 (dt, 7.7 Hz, 15.2 Hz, 1H), 5.24 (dd, 8.2 Hz, 15.2 Hz, 1H), 4.79 (ps t, 8.2 Hz, 1H), 1.36 (d, 7.7 Hz, 2H). The NMR data for the isolated compound 7d: $^1$H NMR (acetone-d$_6$): 7.78 (d, 6.9 Hz, 2H), 7.48 (m, 3H), 7.17 (m, 5H), 6.83 (s, 1H), 5.66 (dt, 7.8 Hz, 15.1 Hz, 1H), 5.19 (dd, 7.2 Hz, 15.1 Hz, 1H), 4.84 (d, 7.2 Hz, 1H), 0.99 (br, 2H). $^{13}$C NMR (acetone-d$_6$): 144.0, 143.7, 138.4, 133.4, 130.2, 129.6, 128.7, 128.6, 128.2, 126.5, 62.2, 26.6 (br). $^{19}$F NMR (acetone-d$_6$): -140.5.

Potassium trifluoro{4-bromophenyl-4-[(4-methylphenylsulfonyl)amino]-2-butenyl}borate (7e). This compound was prepared according to the above general procedure except that the crude product (6e) was isolated from the precipitate obtained after addition of the KHF$_2$ solution. The $^1$H NMR spectrum of allylboronic acid product 6e was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 8.18 (d, 7.6 Hz, 1H), 7.56 (d, 8.0 Hz, 2H), 7.40 (d, 8.2 Hz, 2H), 7.26 (d, 8.0 Hz, 2H), 7.14 (d, 8.2 Hz, 2H), 5.45 (dt, 7.8 Hz, 15.2 Hz, 1H), 5.23 (dd, 7.6 Hz, 15.2 Hz, 1H), 4.75 (ps t, 7.6 Hz, 1H), 2.37 (s, 3H), 1.38 (d, 7.8 Hz, 2H). The NMR data for the isolated compound 7e: $^1$H NMR (acetone-d$_6$): 7.62 (d, 8.3 Hz, 2H), 7.33 (d, 8.6 Hz, 2H), 7.25 (d, 8.3 Hz, 2H), 7.19 (d, 8.6 Hz, 2H), 6.78 (d, 7.3 Hz, 1H), 5.59 (dt, 7.4 Hz, 15.1 Hz, 1H), 5.08 (dd, 7.3 Hz, 15.1 Hz, 1H), 4.77 (ps t, 7.3 Hz, 1H), 2.38 (s, 3H) 0.93 (br, 2H). $^{13}$C NMR (acetone-d$_6$): 143.9, 143.3, 140.5, 138.8, 132.3, 130.8, 130.6, 128.5, 125.6, 121.4, 61.4, 26.6 (br), 22.1. $^{19}$F NMR (acetone-d$_6$): -140.4.

Potassium trifluoro(3-phenyl-2-propenyl)borate (7f). This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6f was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 7.35 (d, 7.3 Hz, 2H), 7.30 (t, 7.3 Hz, 2H), 7.18 (t, 7.3 Hz, 1H), 6.42 (dt, 7.7 Hz, 15.9 Hz, 1H), 6.27 (d, 15.9 Hz, 1H), 1.75 (d, 7.7 Hz, 2H). The NMR data for the isolated compound 7f: $^1$H NMR (acetone-d$_6$): 7.26 (d, 7.4 Hz, 2H), 7.19 (t, 7.4 Hz, 2H), 7.04 (t, 7.4 Hz, 1H), 6.50 (dt, 7.9 Hz, 15.8 Hz, 1H), 6.11 (d, 15.8 Hz, 1H), 1.28 (br, 2H). $^{13}$C NMR (acetone-d$_6$): 141.7, 137.3, 129.8, 127.1, 126.7, 126.6, 27.9 (br). $^{19}$F NMR (acetone-d$_6$): -140.4.
Potassium trifluoro(3-methoxyphenyl-2-propenyl)borate (7g). This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6g was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 7.27 (d, 8.5 Hz, 2H), 6.87 (d, 8.5 Hz, 2H), 6.20 (m, 6.1 Hz, 16.0 Hz, 2H), 3.75 (s, 3H), 1.70 (d, 6.1 Hz, 2H). The NMR data for the isolated compound 7g: $^1$H NMR (acetone-d$_6$): 7.18 (d, 8.8 Hz, 2H), 6.78 (d, 8.8 Hz, 2H), 6.33 (dt, 7.8 Hz, 15.8 Hz, 1H), 6.04 (d, 15.8 Hz, 1H), 3.74 (s, 3H), 1.23 (br, 2H). $^{13}$C NMR (acetone-d$_6$): 159.3, 135.1, 134.6, 127.6, 126.4, 115.2, 56.2, 29.3 (br). $^{19}$F NMR (acetone-d$_6$): -140.5.

Potassium trifluoro(4-acetoxy-2-butenyl)borate (7h). This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6h was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 5.87 (dt, 7.8 Hz, 15.4 Hz, 1H), 5.42 (dt, 6.9 Hz, 15.4 Hz, 1H), 4.41 (d, 6.9 Hz, 2H), 2.02 (s, 3H), 1.56 (d, 7.8 Hz, 2H). The NMR data for the isolated compound 7h: $^1$H NMR (acetone-d$_6$): 5.94 (dt, 7.8 Hz, 15.0 Hz, 1H), 5.23 (dt, 6.9 Hz, 15.0 Hz, 1H), 4.38 (d, 6.9 Hz, 2H), 1.95 (s, 3H), 1.08 (br p, 2H). $^{13}$C NMR (acetone-d$_6$): 171.8, 143.4, 120.2, 68.0, 21.8. $^{19}$F NMR (acetone-d$_6$): -140.9.

Potassium trifluoro(3-acetoxy-2-propenyl)borate (7i). This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6i was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 5.47 (m, 2H), 2.10 (s, 3H), 1.44 (d, 8.1 Hz, 2H). The NMR data for the isolated compound 7i: $^1$H NMR (acetone-d$_6$): 6.73 (d, 12.3 Hz, 1H), 5.52 (dt, 8.3 Hz, 12.3 Hz, 1H), 2.01 (s, 3H), 0.94 (br, 2H). $^{13}$C NMR (acetone-d$_6$): 169.9, 133.9, 119.8, 21.4, 19.7 (br). $^{19}$F NMR (acetone-d$_6$): -141.6.

Potassium trifluoro(4-trimethylsilyl-2-butenyl)borate (7j). This compound was prepared according to the above general procedure except that 0.7 ml DMSO was used as solvent. The $^1$H NMR spectrum of allylboronic acid product 6j was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 5.32 (dt, 6.9 Hz, 15.2 Hz, 1H), 5.22 (dt, 7.3 Hz, 15.2 Hz, 1H), 1.46 (d, 6.9 Hz, 2H), 1.37 (d, 7.3 Hz, 2H), -0.01 (s, 9H). The NMR data for the isolated compound 7j: $^1$H NMR (acetone-d$_6$): 5.41 (dt, 7.7 Hz, 14.8 Hz, 1H), 5.02 (dt, 7.8 Hz, 14.8 Hz, 1H), 1.30 (d, 7.8 Hz, 2H), 1.00 (br, 1H), -0.04 (s, 9H). $^{13}$C NMR (acetone-d$_6$): 133.6, 121.2, 23.6, -1.1. $^{19}$F NMR (acetone-d$_6$): -140.9.
**Potassium trifluoro(3-phenyldimethylsilyl-2-propenyl)borate (7k).** This compound was prepared according to the above general procedure. The $^1$H NMR spectrum of allylboronic acid product 6k was determined from the crude mixture. $^1$H NMR (DMSO-d$_6$): 7.52 (m, 2H), 7.38 (m, 3H), 6.27 (dt, 7.5 Hz, 18.6 Hz, 1H), 5.61 (d, 18.6 Hz, 1H), 1.75 (d, 7.5 Hz, 2H), 0.30 (s, 6H). The NMR data for the isolated compound 7k: $^1$H NMR (acetone-d$_6$): 7.54 (m, 2H), 7.30 (m, 3H), 6.41 (dt, 7.7 Hz, 18.3 Hz, 1H), 5.39 (d, 18.3 Hz, 1H), 1.32 (br, 2H), 0.24 (s, 6H). $^{13}$C NMR (acetone-d$_6$): 156.5, 142.3, 135.4, 129.9, 129.1, 121.8, -0.9. $^{19}$F NMR (acetone-d$_6$): -140.3.

References:
BF₃K
NHSO₂Tol
Br
7e
\[
\text{Br} \quad \text{NHSO}_2\text{Tol} \quad \text{BF}_3\text{K}
\]

\text{ppm}
PhMe$_2$Si$\equiv$BF$_3$K

$7k$