SUPPLEMENTAL INFORMATION

Pd Catalyzed Cross-Coupling of Baylis-Hillman Acetate Adducts with 

Bis(Pinacolato)diboron: An Efficient Route to Functionalized Allyl Borates

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S1
General procedure for the preparation of functionalized allyltrifluoroborate potassium salts: To a mixture of Baylis-Hillman acetate adduct 1 (1 mmol) and bis(pinacolato)diboron 2 (1.1 mmol) in 4 mL of THF, was added Pd catalyst (Pd(OAc)$_2$, 5 mol % or Pd$_2$(dba)$_3$, 3 mol %) and the mixture stirred at 50 °C. After completion of the reaction (TLC), the mixture was treated with excess aqueous KHF$_2$ (6 mmol) and allowed to stir for 20 min at room temperature. All solvents were removed under reduced pressure using a rotary evaporator and the resultant solid was washed with acetone (4 X 10 mL), the combined acetone fractions concentrated under reduced pressure, and the residue washed with Et$_2$O (2 X 5 mL) to obtain the final allyltrifluoroborate salt as a solid.

$\text{BF}_3\text{K}$

$\text{OMe}$

$\text{Cl}$

$\text{4a}$

$\text{BF}_3\text{K}$

$\text{OMe}$

$\text{4b}$

$^1$H NMR (d$_6$ DMSO) $\delta$ 7.61 (d, $J = 8$ Hz, 2H), 7.32-7.22 (m, 3H), 7.05 (s, 1H), 3.63 (s, 3H), 1.55 (m, 2H); $^{13}$C NMR (d$_6$ DMSO) $\delta$ 170.6, 138.2, 137.0, 130.2, 129.5, 127.8, 126.9, 51.2; $^{19}$F (d$_6$ DMSO) $\delta$ −134.388. Anal. Caolcd. For C$_{11}$H$_{11}$BF$_3$KO$_2$: C, 46.83; H, 3.98. Found: C, 46.94; H, 3.82.
\(^1\)H NMR (d\(_6\) DMSO) \(\delta\) 7.65 (d, \(J = 8\) Hz, 2H), 7.36 (d, \(J = 8\) Hz, 2H), 7.03 (s, 1H), 3.64 (s, 3H), 1.55 (brs, 2H); \(^{13}\)C NMR (d\(_6\) DMSO) \(\delta\) 170.4, 139.0, 136.0, 131.5, 131.2, 128.9, 127.8, 51.4; \(^{19}\)F (d\(_6\) DMSO) \(\delta\) –134.474. Anal. Calcd. For C\(_{11}\)H\(_{10}\)BClF\(_3\)KO\(_2\): C, 41.70; H, 3.18. Found: C, 41.87; H, 3.08.

\(\text{BF}_3\text{KO} \quad 4c\)

\(^1\)H NMR (d\(_6\) DMSO) \(\delta\) 8.10-7.40 (m, 8H), 3.69 (s, 3H), 1.46 (m, 2H); \(^{13}\)C NMR (d\(_6\) DMSO) \(\delta\) 170.6, 133.4, 132.9, 131.4, 128.4, 127.3, 126.8, 126.0, 125.6, 125.3, 124.0, 51.3; \(^{19}\)F (d\(_6\) DMSO) \(\delta\) –134.581. Anal. Calcd. for C\(_{15}\)H\(_{13}\)BF\(_3\)KO\(_2\): C, 54.24; H, 3.94. Found: C, 54.11; H, 3.92.

\(\text{BF}_3\text{KO} \quad 4d\)

\(^1\)H NMR (d\(_6\) DMSO) \(\delta\) 7.59 (d, \(J = 8\) Hz, 2H), 7.04 (s, 1H), 6.88 (d, \(J = 8\) Hz, 2H), 3.75 (s, 3H), 3.62 (s, 3H), 1.53 (m, 2H); \(^{13}\)C NMR (d\(_6\) DMSO) \(\delta\) 170.7, 158.4, 136.0, 131.0, 130.4, 128.9, 127.8, 51.4; \(^{19}\)F (d\(_6\) DMSO) \(\delta\) –134.474. Anal. Calcd. For C\(_{11}\)H\(_{10}\)BClF\(_3\)KO\(_2\): C, 41.70; H, 3.18. Found: C, 41.87; H, 3.08.
129.7, 113.3, 55.0, 51.2: \(^{19}\)F (d, DMSO) \(\delta -134.356\). Anal. Calcd. for C\(_{12}\)H\(_{13}\)BF\(_3\)KO\(_3\): C, 46.18; H, 4.20. Found: C, 45.92; H, 4.14

\[\text{BF}_3\text{K}O\text{Me}\]

\(^1\)H NMR (d, DMSO) \(\delta 7.50 (d, J = 8 \text{ Hz}, 2\text{H}), 7.11 (d, J = 8 \text{ Hz}, 2\text{H}), 7.01 (s, 1\text{H}), 3.61 (s, 3\text{H}), 2.28 (s, 3\text{H}), 1.52 (m, 2\text{H}); \)\(^{13}\)C NMR (d, DMSO) \(\delta 170.7, 137.3, 136.2, 134.3, 130.3, 129.5, 128.4, 51.2, 20.9; \)\(^{19}\)F (d, DMSO) \(\delta -134.335\). Anal. Calcd. for C\(_{12}\)H\(_{13}\)BF\(_3\)KO\(_2\): C, 48.67; H, 4.42. Found: C, 48.86; H, 4.22.

\[\text{BF}_3\text{KCl}\]

\(^1\)H NMR (d, DMSO) \(\delta 8.03 (dd, J = 8, 1.5 \text{ Hz}, 1\text{H}), 7.44-7.25 (m, 3\text{H}), 7.08 (s, 1\text{H}), 3.65 (s, 3\text{H}), 1.46 (brs, 2\text{H}); \)\(^{13}\)C NMR (d, DMSO) \(\delta 170.4, 140.3, 134.7, 132.9, 131.5, 128.9, 128.8, 126.6, 126.0, 51.5; \)\(^{19}\)F (d, DMSO) \(\delta -134.495\). Anal. Calcd. for C\(_{11}\)H\(_{10}\)BClF\(_3\)KO\(_2\): C, 41.74; H, 3.18. Found: C, 41.82; H, 3.16.
\textsuperscript{1}H NMR (d\textsubscript{6} DMSO) \(\delta\) 7.64 (dd, \(J = 1.9, 0.8\) Hz, 1H), 6.92 (s, 1H), 6.80 (d, \(J = 3.4\) Hz, 1H), 6.51 (dd, \(J = 3.4, 1.9\) Hz, 1H), 3.61 (s, 3H), 1.59 (m, 2H); \textsuperscript{13}C NMR (d\textsubscript{6} DMSO) \(\delta\) 169.6, 152.6, 142.5, 135.9, 119.0, 111.9, 111.6, 51.4; \textsuperscript{19}F (d\textsubscript{6} DMSO) \(\delta\) –134.014. Anal. Calcd. for C\textsubscript{9}H\textsubscript{9}BF\textsubscript{3}KO\textsubscript{3}: C, 39.73; H, 3.33. Found: C, 39.87; H, 3.25.

Allylation reaction using allyltrifluoroborate salt 4a: To a solution of \(p\)-nitrobenzaldehyde (0.5 mmol) and tetra-\(n\)-butylammonium iodide (10 mol \%, 0.05 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (2 mL) was added allyltrifluoroborate salt 4a (0.5 mmol) and water (2 mL). The biphasic reaction mixture was
vigorously stirred at room temperature for 5 hr, the mixture diluted with CH₂Cl₂ (5 mL), and the layers separated. The aqueous layer was extracted with CH₂Cl₂ (3 X 5 mL), the combined extracts dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography to obtain homoallylic alcohol 5a.

General procedure for the preparation of allylboronates 3 followed by allylation: To a mixture of Baylis-Hillman acetate adduct 1 (1 mmol) and bis(pinacolato)diboron 2 (1.1 mmol) in toluene (4 mL) was added 3 mol % of Pd₂(dba)₃ and the mixture stirred at 50 °C under nitrogen. After completion of the reaction (TLC), the reaction mixture was cooled to 0 °C and p-nitrobenzaldehyde (1 mmol) and BF₃·Et₂O (20 mol %) were added. The reaction mixture was allowed to stir at room temperature for 2 days, quenched with aqueous NaHCO₃, and extracted with ether. The combined organic layers were dried (MgSO₄), concentrated under vacuum, and purified by column chromatography to obtain 5.

\[
\text{Ph} \quad \text{O} \quad \text{O}_2N
\]

\[
\text{OMe} \quad \text{5a}
\]

\(^{1}\text{H NMR (CDCl}_3) \delta 8.08 (d, J = 8 \text{ Hz}, 2\text{H}), 7.42 (d, J = 8 \text{ Hz}, 2\text{H}), 7.30-7.20 \text{ (m, 5H), 6.26 (s, 1H), 5.82 (s,1H), 5.39 (m, 1H); 4.21 (d, J = 7 \text{ Hz}, 1\text{H}), 3.58 (s, 3\text{H), 2.69 (brs, 1H); }^{13}\text{C NMR (CDCl}_3) \delta 168.7, 149.6, 147.0, 140.2, 137.3, 129.1, 128.4, 127.5, 123.1, 74.3, 54.5, 51.9. \text{ Anal. Calcd. for C}_{18}\text{H}_{17}\text{NO}_5: C, 66.05; H, 5.23; N, 4.28. Found: C, 66.21, H, 5.14; N, 4.08.\]
$^{1}H$ NMR (CDCl$_3$) $\delta$ 8.16 (d, $J = 8$ Hz, 2H), 7.52 (d, $J = 8$ Hz, 2H), 6.28 (s, 1H), 5.48 (s, 1H), 4.96 (m, 1H); 3.78 (s, 3H), 3.36 (brs, 1H), 2.94 (m, 1H), 1.52-1.0 (m, 14H), 0.86 (t, $J = 7$ Hz, 3H); $^{13}$C NMR (CDCl$_3$) $\delta$ 168.5, 150.2, 147.0, 139.9, 127.7, 127.2, 123.2, 75.4, 52.3, 49.6, 31.7, 29.3, 29.1, 27.2, 26.6, 22.6, 14.0. Anal. Calcd. for C$_{20}$H$_{20}$NO$_5$: C, 66.09; H, 8.04; N, 3.85. Found: C, 66.27; H, 8.12; N, 3.72.
250 MHz $^1$H NMR in DMSO-d$_6$
62.5 MHz $^{13}$C NMR in DMSO-d$_6$
$^{19}$F NMR in DMSO-$d_6$
300 MHz $^1$H NMR in DMSO-$d_6$
75.5 MHz $^{13}$C NMR in DMSO-d$_6$
$^{19}\text{F} \text{NMR in DMSO-d}_6$
300 MHz $^1$H NMR in DMSO-d$_6$
75.5 MHz $^{13}$C NMR in DMSO-d$_6$
$^{19}$F NMR in DMSO-$d_6$
300 MHz $^1$H NMR in DMSO-$d_6$
75.5 MHz $^{13}$C NMR in DMSO-d$_6$
$^{19}$F NMR in DMSO-$d_6$
300 MHz $^1$H NMR in DMSO-d$_6$
$75.5 \text{ MHz } ^{13}\text{C NMR in DMSO-d}_6$
$^{19}\text{F NMR in DMSO-d}_6$
300 MHz $^1$H NMR in DMSO-d$_6$
$75.5 \text{ MHz } ^{13}\text{C NMR in DMSO-d}_6$
$^{19}$F NMR in DMSO-$d_6$
300 MHz $^1$H NMR in DMSO-d$_6$
75.5 MHz $^{13}$C NMR in DMSO-d$_6$
$^{19}$F NMR in DMSO-$d_6$
300 MHz $^1$H NMR in DMSO-d$_6$
75.5 MHz $^{13}$C NMR in DMSO-d$_6$
$^{19}\text{F NMR in DMSO-d}_6$
250 MHz $^1$H NMR in CDCl$_3$
62.5 MHz $^{13}$C NMR in CDCl$_3$
250 MHz $^1$H NMR in CDCl$_3$
62.5 MHz $^{13}$C NMR in CDCl$_3$