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Supporting Information

Boron Trihalide Mediated Haloallylation of Aryl Aldehydes: Reaction and Mechanistic Insight

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General Methods: All reagents were used as received. Column chromatography was performed using silica gel (60 Å, 230–400 mesh, ICN Biomedicals GmbH, Eschwege, Germany). Analytical thin-layer chromatography was performed using 250 μm silica (Analtech, Inc., Newark, DE).

^{1}H NMR and ^{13}C NMR spectra were recorded at 250.13 and 62.89 MHz, respectively. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra were referenced to TMS and measured with respect to the residual protons in the deuterated solvents. Microanalysis was performed by Atlantic Microlab, Inc. Norcross, Georgia.

Typical reaction procedure: Finely ground 4-chlorobenzaldehyde (210 mg, 1.5 mmol), allyltrimethylsilane (256 mg, 2.25 mmol) and dry hexanes (16 mL) were placed in a dry argon-flushed, 50 mL round-bottomed flask equipped with a magnetic stirring bar. The solution was cooled to 0 °C, and boron trichloride (1.65 mmol, 1.65 mL of a 1.0 M CH_2Cl_2 solution) was added via syringe. After completion of the addition, the ice-bath was removed and the resulting solution was allowed to warm to room tempeartuare. The reaction mixture was hydrolyzed with water and extracted

with hexanes. The organic layer was separated, dried over anhydrous $MgSO_4$, the solvent removed under reduced pressure, and the product isolated by flash column chromatography.

Product 5a: Known compound.[1]

Product 5b: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.25-7.38 (m, 2H), 7.00–7.08 (m, 2H), 5.65-5.79 (m, 1H), 5.08-5.15 (m, 2H), 4.86 (t, J = 7.27 Hz, 1H), 2.73-2.86 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 162.5, ($^1J_{CF}$ = 246.5 Hz), 160.5, 137.4, 133.6, 128.8, ($^3J_{CF}$ = 7.7 Hz), 118.4, 115.5, ($^2J_{CF}$ = *21,2 HZ),* 61.3, 44.2. Anal. Calcd for $C_{10}H_{10}ClF$: C, 65.05; H, 5.46. Found: C, 65.48; H, 5.61.

Product 5c: Known compound.[1]

Product 5d: Known compound.[2]

Product 5e: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.14-7.50 (m, 4H), 5.74-5.80 (m, 1H), 5.07-5.17 (m, 3H), 2.81-2.91 (m, 2H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.1, 135.3, 134.2, 130.5, 128.1, 126.5, 118.1, 58.7, 43.0, 19.1. Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.12; H, 7.25. Found: C, 73.54; H, 7.37.

Product 5f: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45-7.61 (m, 3H), 5.67-5.77 (m, 1H), 5.09-5.16 (m, 2H), 4.72-4.77 (m, 1H), 2.73-2.81 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 133.9, 132.9, 129.0, 123.0, 119.1, 60.6, 43.9. HR-MS for $C_{10}H_9Br_2Cl$:321.8760. Found: 321.8757.

Product 5g: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.23-7.37 (m, 4H), 4.97 (dd, J = 7.21, 7.19 Hz, 1H), 4.83 (s, 1H), 4.73 (s, 1H), 2.71-2.83 (m, 2H), 1.69 (s, 3H). ^{13}C NMR

($CDCl_3$): δ 140.7, 140.0, 134.0, 128.7, 128.4, 114.4, 60.3, 47.9, 22.1. Anal. Calcd for $C_{11}H_{12}Cl_2$: C, 61.42; H, 5.62. Found: C, 61.19; H, 5.25.

Product 5h: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.14-7.51 (m, 4H), 5.30 (dd, J = 6.43, 6.41 Hz, 1H), 4.85 (s, 1H), 4.78 (s, 1H), 2.77-2.85 (m, 2H), 2.39 (s, 3H), 1.73 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.2, 139.4, 135.0, 130.5, 128.0, 126.6, 126.5, 114.0, 57.3, 46.7, 22.2, 19.1. HR-MS for $C_{12}H_{15}Cl$: 194.0862. Found: 194.0874.

Product 5i: ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.35 (t, J = 8.08 Hz, 1H), 4.81 (s, 1H), 4.74 (s, 1H), 2.95 (d, J = 8.08 Hz, 2H), 1.73 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 147.0, 143.0, 140.2, 135.7, 120.8, 114.8, 112.7, 48.5, 45.0, 21.8. HR-MS for $C_{11}H_8ClF_5$: 270.0235. Found: 270.0237.

Product 5j: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.35-7.50 (m, 4H), 4.90 (t, J = 7.47 Hz, 1H), 4.72 (s, 1H), 4.62 (s, 1H), 2.60-2.70 (m, 2H), 1.58 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 145.4, 140.5, 130.7, 130.2, 127.4, 126.1, 125.6, 125.5, 114.6, 60.1, 48.0, 22.1. Anal. Calcd for $C_{12}H_{12}ClF_3$: C, 57.96; H, 4.86. Found: C, 58.04; H, 4.91.

Product 5k: Known compound.[2]

Product 5l: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.26-7.34 (m, 4H), 5.06 (t, J = 7.76 Hz, 1H), 4.82 (s, 1H), 4.72 (s, 1H), 2.86-2.97 (m, 2H), 1.68 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.2, 140.3, 134.0, 128.7, 128.6, 114.3, 51.3, 47.9, 22.0. Anal. Calcd for $C_{11}H_{12}BrCl$: C, 50.90; H, 4.66. Found: C, 50.67; H, 4.32.

Product 5m: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.23-7.39 (m, 4H), 5.03 (t, J = 7.72 Hz, 1H), 4.84 (s, 1H), 4.74 (s, 1H), 2.80-3.02 (m, 2H), 1.70 (s, 3H). ^{13}C NMR ($CDCl_3$): δ

143.7, 141.1, 134.3, 129.9, 128.5, 127.5, 125.5, 114.4, 51.1, 47.8, 22.0. HR-MS for $C_{11}H_{12}Br_2$: C, 301.9306. Found: 301.9312.

Product 5n: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45 (d, J = 8.48 Hz, 2H), 7.26 (d, J = 8.48 Hz, 2H), 5.05 (t, J = 7.73 Hz, 1H), 4.82 (s, 1H), 4.72 (s, 1H), 2.81-3.04 (m, 2H), 1.68 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.2, 140.8, 131.8, 129.0, 122.2, 114.4, 51.3, 47.8, 22.0. Anal. Calcd for $C_{11}H_{12}BrCl$: C, 50.90; H, 4.66. Found: C, 51.07; H, 4.73.

References:

[1] H. Mayr, G. Gorath, *J. Am. Chem. Soc.* 1995, **117**, 7862.

[2] T. Oriyama, K.Iwanami, K. Tsukamoto, Y. Ichimura, G. Koga, *Bull. Chem. Soc. Japan.* 1991, **64**, 1410.