

Supporting information

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).

Experimental

Boron trihalide (1.5 mmol), alkyne (1.5 mmol) and dry dichloromethane (8 mL) were combined in a 50 mL flask and stirred for 1 hour under a nitrogen atmosphere. In a separate flask, the allylic alcohol (1.6 mmol) in dry dichloromethane (8 mL) was treated with *n*-butyllithium (1.0 mL of a 1.6 M solution in hexane) at 0°C and stirred at room temperature for 1 hour. The solution was then transferred to the first flask and allowed to stir at room temperature overnight. Water (20 mL) was added and the reaction mixture was extracted with ethyl acetate and dried over anhydrous MgSO₄. The solvents were removed under reduced pressure and the product purified by silica gel column chromatography using hexane as an eluent.

¹H NMR and ¹³C NMR spectra were recorded at 250.13 and 62.89 MHz, respectively. Chemical shifts for ¹H NMR and ¹³C NMR spectra (CDCl₃) were referenced to TMS. Microanalysis was performed by Atlantic Microlab, Inc. Norcross, Georgia.

Product 3a: ¹H NMR (250 MHz, CDCl₃): δ 7.57–7.60 (m, 2H), 7.15–7.37 (m, 13H), 6.34–6.58 (m, 3H), 4.94 (dd, *J* = 8.98 and 8.88 Hz, 1H). ¹³C NMR (CDCl₃): δ 142.1, 137.9,

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137.1, 133.4, 130.9, 130.3, 128.7, 128.5, 128.3, 127.8, 127.4, 126.9, 126.6, 126.3, 48.5.

Anal. Calcd for C₂₃H₁₉Cl: C, 83.50; H, 5.79. Found: C, 83.57; H, 5.65.

Product 3b: ¹H NMR (250 MHz, CDCl₃): δ 7.47–7.51 (m, 2H), 7.11–7.36 (m, 12H), 6.30–6.58 (m, 3H), 4.93 (dd, *J* = 9.03 and 8.98 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (CDCl₃): δ 142.3, 138.6, 137.2, 135.1, 133.5, 130.8, 130.4, 129.0, 128.7, 128.5, 127.8, 127.4, 127.4, 126.7, 126.5, 126.3, 48.4, 21.1. Anal. Calcd for C₂₄H₂₁Cl: C, 83.58; H, 6.14. Found: C, 83.92; H, 6.03.

Product 3c: ¹H NMR (250 MHz, CDCl₃): δ 7.14–7.36 (m, 13H), 6.90–6.97 (m, 1H), 6.32–6.56 (m, 3H), 4.92 (dd, *J* = 8.98 and 8.96 Hz, 1H). ¹³C NMR (CDCl₃): δ 164.6, 160.6, 141.8, 140.0, 136.9, 132.0, 131.1, 129.9, 129.5, 128.8, 128.5, 127.7, 127.5, 126.7, 126.31, 122.1, 115.6, 115.3, 113.9, 113.5, 48.5. Anal. Calcd for C₂₃H₁₈ClF: C, 79.19; H, 5.20. Found: C, 79.37; H, 5.55.

Product 3d: ¹H NMR (250 MHz, CDCl₃): δ 7.16–7.41 (m, 14H), 6.34–6.61 (m, 2H), 6.09 (d, *J* = 9.28 Hz, 1H), 4.92 (dd, *J* = 9.73 and 9.59 Hz, 1H). ¹³C NMR (CDCl₃): δ 141.8, 138.1, 137.2, 133.0, 131.1, 131.0, 130.0, 129.9, 129.8, 129.5, 128.7, 128.5, 127.8, 127.4, 126.8, 126.7, 126.3, 48.1. Anal. Calcd for C₂₃H₁₈Cl₂: C, 75.62; H, 4.97. Found: C, 75.47; H, 4.76.

Product 3e: ¹H NMR (250 MHz, CDCl₃): δ 7.16–7.46 (m, 14H), 6.33–6.57 (m, 3H), 4.91 (dd, *J* = 9.17 and 9.11 Hz, 1H). ¹³C NMR (CDCl₃): δ 141.9, 137.0, 136.8, 132.3, 131.4, 131.0, 129.9, 129.0, 128.8, 128.5, 128.1, 127.7, 127.5, 126.9, 126.3, 122.7, 48.5. Anal. Calcd for C₂₃H₁₈BrCl: C, 67.40; H, 4.43. Found: C, 67.25; H, 4.36.

Product 3f: ¹H NMR (250 MHz, CDCl₃): δ 7.02–7.52 (m, 14H), 6.37–6.63 (m, 3H), 4.95 (dd, *J* = 9.69 and 9.56 Hz, 1H). ¹³C NMR (CDCl₃): δ 162.5, 157.7, 141.9, 137.1, 133.4,

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133.3, 131.0, 130.4, 130.1, 130.0, 128.7, 128.5, 128.1, 127.8, 127.4, 127.1, 126.8, 126.3, 124.0, 116.2, 115.8, 48.5. Anal. Calcd for C₂₃H₁₈ClF: C, 79.19; H, 5.20. Found: C, 79.33; H, 5.17.

Product 3g: δ 7.54–7.59 (m, 2H), 7.21–7.41 (m, 13H), 6.37–6.55 (m, 3H), 4.90 (dd, J = 8.94 and 8.88 Hz, 1H). ¹³C NMR (CDCl₃): δ 141.9, 139.7, 137.1, 132.1, 131.0, 130.0, 128.7, 128.5, 128.3, 127.8, 127.4, 126.8, 126.3, 126.1, 51.3. Anal. Calcd for C₂₃H₁₉Br: C, 73.61; H, 5.10. Found: C, 73.57; H, 5.22.

Product 3h: ¹H NMR (250 MHz, CDCl₃): δ 7.07–7.46 (m, 14H), 6.34–6.59 (m, 3H), 4.88 (dd, J = 8.79 and 8.70 Hz, 1H), 2.31 (s, 3H). ¹³C NMR (CDCl₃): δ 142.0, 138.6, 137.1, 136.9, 131.2, 130.9, 130.1, 128.9, 128.7, 128.5, 127.8, 127.6, 127.4, 126.8, 126.3, 51.3. Anal. Calcd for C₂₄H₂₁Br: C, 74.04; H, 5.44. Found: C, 73.92; H, 5.09.

Product 3i: ¹H NMR (250 MHz, CDCl₃): δ 7.17–7.39 (m, 10H), 6.29–6.53 (m, 2H), 5.88 (d, J = 9.18 Hz, 1H), 4.70 (dd, J = 8.77 and 8.75 Hz, 1H), 2.47–2.52 (m, 2H), 1.47–1.64 (m, 2H), 1.26–1.38 (m, 2H), 0.92 (t, J = 7.24 Hz, 3H). ¹³C NMR (CDCl₃): δ 142.3, 137.2, 130.5, 129.4, 128.6, 128.5, 127.7, 127.3, 126.6, 126.3, 50.4, 41.2, 30.3, 21.6, 13.8. Anal. Calcd for C₂₁H₂₃Br: C, 70.99; H, 6.52. Found: C, 71.31; H, 6.87.

Product 3j: ¹H NMR (250 MHz, CDCl₃): δ 7.18–7.39 (m, 10H), 6.30–6.52 (m, 2H), 5.88 (d, J = 9.30 Hz, 1H), 4.71 (dd, J = 8.68 and 8.70 Hz, 1H), 2.46–2.51 (m, 2H), 1.56–1.61 (m, 2H), 1.16–1.37 (m, 2H), 0.87 (t, J = 7.21 Hz, 3H). ¹³C NMR (CDCl₃): δ 147.4, 142.3, 137.2, 130.5, 129.5, 129.2, 128.6, 128.5, 127.7, 127.3, 126.6, 126.2, 50.3, 41.7, 31.8, 29.3, 28.4, 28.1, 22.7, 14.1. Anal. Calcd for C₂₅H₃₁Br: C, 72.98; H, 7.59. Found: C, 72.68; H, 7.87.

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Product 3k: ^1H NMR (250 MHz, CDCl_3): δ 6.97–7.33 (m, 9H), 6.05–6.23 (m, 3H), 3.68–3.72 (m, 1H), 1.28 (d, $J = 6.73$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 164.6, 160.7, 137.3, 132.1, 131.9, 131.1, 130.9, 129.7, 129.6, 129.2, 128.6, 128.5, 127.6, 127.2, 126.6, 126.1, 122.0, 115.4, 115.0, 113.7, 113.4, 37.4, 19.7. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{ClF}$: C, 75.39; H, 5.62. Found: C, 75.28; H, 5.87.

Product 3l: ^1H NMR (250 MHz, CDCl_3): δ 6.97–7.38 (m, 9H), 6.13–6.25 (m, 3H), 3.63–3.67 (m, 1H), 1.29 (d, $J = 6.84$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 164.4, 160.7, 137.3, 135.6, 131.9, 1129.7, 129.6, 129.3, 128.5, 127.6, 127.3, 126.1, 126.2, 115.4, 115.1, 115.0, 114.6, 40.3, 19.6. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{BrF}$: C, 65.27; H, 4.87. Found: C, 65.38; H, 4.97.

Product 3m: ^1H NMR (250 MHz, CDCl_3): δ 7.15–7.55 (m, 10H), 6.08–6.50 (m, 3H), 3.63–3.70 (m, 1H), 1.28 (d, $J = 6.85$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 139.8, 137.4, 134.5, 132.9, 132.2, 129.4, 18.5, 128.2, 127.6, 127.2, 26.6, 126.2, 124.7, 40.3, 19.7. HRMS for $\text{C}_{18}\text{H}_{17}\text{Br}$: 312.0514. Found: 312.0518.

Product 3n: ^1H NMR (250 MHz, CDCl_3): δ 7.20–7.61 (m, 15H), 6.01–6.74 (m, 5H), 4.67 (dd, $J = 8.97$ and 8.79 Hz, 1H). ^{13}C NMR (CDCl_3): δ 142.1, 137.9, 137.3, 137.1, 134.5, 133.3, 132.0, 131.4, 130.7, 129.5, 128.6, 128.3, 127.7, 127.4, 126.5, 126.3, 48.4. Anal. Calcd for $\text{C}_{25}\text{H}_{21}\text{Cl}$: C, 84.14; H, 5.93. Found: C, 83.92; H, 6.28.

Product 3o: ^1H NMR (250 MHz, CDCl_3): δ 7.23–8.22 (m, 17H), 6.36–6.58 (m, 3H), 5.06 (dd, $J = 8.79$ and 8.71 Hz, 1H). ^{13}C NMR (CDCl_3): δ 144.3, 139.8, 136.7, 133.6, 133.4, 130.4, 128.8, 128.7, 128.5, 128.5, 128.3, 127.8, 127.4, 126.8, 126.6, 126.3, 126.0, 125.7, 125.6, 123.6, 48.9. HRMS for $\text{C}_{27}\text{H}_{21}\text{Cl}$: 380.1332. Found: 380.1337.