Supplementary Information

“Phosphine Catalyzed α -Arylation of Enones and Enals Using Hypervalent Bismuth Reagents: Regiospecific Enolate Arylation via Nucleophilic Catalysis”

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Experimental Section

General. All reactions were run under an atmosphere of argon, unless otherwise indicated. Anhydrous solvents were transferred by an oven-dried syringe. Flasks were oven-dried and cooled under a stream of argon. Dichloromethane was distilled from calcium hydride. Triarylbi-muth dichloride reagents were prepared according to literature procedure¹. All known products exhibited spectral properties consistent with literature reports **1a**,² **1b**,³ **1h**,⁴ **2a**,⁵ **2b**,⁶ **2c**,⁷ **2d**,⁸ **3a**,⁹ **3b**¹⁰ and the E/Z product ratios were determined by proton nuclear magnetic resonance (¹H NMR).

Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates (DC-Fertigplatten Kieselgel 60 F₂₅₄). Preparative column chromatography employing silica gel was performed according to the method of Still.¹¹ Melting points were determined on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1420 spectrometer. High-resolution mass spectra (HRMS) were obtained on a Karatos MS9 and are reported as m/e (relative intensity). Accurate masses are reported for the molecular ion (M+1) or a suitable fragment ion.

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded with a Varian Gemini (300 MHz) spectrometer and a Mercury (400 MHz) spectrometer. Chemical Shifts are reported in delta (δ) units, parts per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded with a Varian Gemini 300 (75.5 MHz) spectrometer and a Mercury 400 (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. ¹³C NMR spectra were routinely run with broadband decoupling.

Representative Procedure for α-Arylation of Enones 1-2 and Enal 3

To a reaction vessel charged with triphenylbismuth dichloride (261 mg, 0.52 mmol, 100 mol%) and 2-cyclohexen-1-one **1** (50 μL, 0.52 mmol, 100 mol%) was added CH₂Cl₂-^tBuOH (9:1 ratio, 0.52 mL, 1M), followed by diisopropylethylamine (90 μL, 0.52 mmol, 100 mol%) and n-tributylphosphine (25 μL, 0.10 mmol, 20 mol%). The reaction mixture was allowed to stir at room temperature until complete consumption of triphenylbismuth dichloride was observed by TLC (2-12 hours), at which point the reaction mixture was evaporated onto SiO₂. Purification by silica gel chromatography hexane/ethyl acetate 9:1 gave **1a** (0.083g, 93%) as a white solid.

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Tris-(4-fluoro-3-methylphenyl)bismuth

^1H NMR (400 MHz, CDCl_3) δ 7.50-7.48 (d, J = 8.20 Hz, 3H), 7.46-7.42 (m, 3H), 7.03-6.99 (2d, J = 7.87, 8.21 Hz 3H), 2.23 (s, 9H)

^{13}C NMR (100 MHz, CDCl_3) δ 161.6 (d, J = 245 Hz), 140.6, 136.8, 136.7, 127.5, (d, J = 16.14 Hz,), 117.7 (d, J = 20.76 Hz), 14.8

FTIR (NaCl): 3019, 2921, 2867, 1564, 1484, 1237, 1119, 804 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{21}\text{H}_{19}\text{F}_3\text{Bi}$ 537.12427 found 537.12382

MP 85-86 °

Tris-(4-fluoro-3-methylphenyl)bismuth dichloride

^1H NMR (400 MHz, CDCl_3) δ 8.34-8.32 (d, $J = 7.53$ Hz, 6H), 7.29-7.25 (m, 3H), 2.36 (s, 9H)

^{13}C NMR (100 MHz, CDCl_3) δ 162.8 (d, $J = 252.14$ Hz) 149.3, 137.2, 133.7, (d, $J = 8.46$ Hz), 129.0 (d, $J = 18$ Hz), 118.1 (d, $J = 23.83$ Hz), 15.0

FTIR (NaCl): 3074, 2958, 1564, 1486, 1384, 1245, 1176, 1123, 812, 735 cm^{-1}

HRMS calculated [M-1] for $\text{C}_{21}\text{H}_{17}\text{F}_3\text{Cl}_2\text{Bi}$ 605.04633 found 605.04595

MP 115-117 $^\circ\text{C}$

1c

¹H NMR (400 MHz, CDCl₃) δ 7.29-7.26 (m, 2H), 7.04-7.00 (m, 3H), 2.60-2.57 (t, J = 6.49 Hz, 2H), 2.55-2.51 (q, J = 5.47 Hz, 2H), 2.13-2.07 (qt, J = 6.5 Hz, 2H)

¹³C NMR (75 MHz, CDCl₃) δ 197.9, 162.3 (d, J = 246.0 Hz), 147.9, 139.3, 132.4, 130.2 (d, 7.68 Hz), 114.8 (d, J = 21.52 Hz), 38.9, 26.5, 22.8

FTIR (NaCl): 3038, 2929, 1672, 1503, 1350, 1214, 1159 cm⁻¹

HRMS calculated [M+1] for C₁₂H₁₂OF 191.08722 found 191.08722

1d

^1H NMR (300 MHz, CDCl_3) δ 7.32-7.29 (A part of AB pattern, $J = 8.70$ Hz, 2H), 7.26-7.23 (B part of AB pattern, $J = 8.96$ Hz, 2H), 7.04-7.01 (t, $J = 8.71$ Hz, 1H), 2.61-2.51 (m, 4H), 2.14-2.06 (q, $J = 6.15$ Hz, 2H)

^{13}C NMR (75.5 MHz, CDCl_3) δ 197.6, 148.2, 139.3, 134.9, 133.5, 129.9, 128.1, 38.9, 26.5, 22.8

FTIR (NaCl): 2940, 2858, 1673, 1482, 1345, 1099, 826, cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{12}\text{OCl}$ 207.05767 found 207.05823

1e

^1H NMR (400 MHz, CDCl_3) δ 7.47-7.45 (A part of AB pattern, $J = 8.55$ Hz, 2H), 7.19-7.17 (B part of AB pattern $J = 8.55$ Hz, 2H), 7.04-7.02 (t, $J = 4.45$ Hz, 1H), 2.60-2.57 (t, $J = 6.5$ Hz, 2H), 2.55-2.51 (q, $J = 5.81$ Hz, 2H), 2.13-1.07 (qt, $J = 6.15$ Hz, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 148.3, 139.3, 135.3, 131.1, 130.3, 121.7, 38.9, 26.5, 22.9

FTIR (NaCl): 2945, 2869, 1667, 1481, 913, 732, 645 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{12}\text{OBr}$ 251.00715 found 251.00785

1f

^1H NMR (400 MHz, CDCl_3) δ 7.32-7.26 (m, 1H), 7.09-7.02 (m, 3H), 7.01-6.96 (td, J = 1.03, 10.28 Hz, 1H), 2.61-2.52 (m, 4H), 2.14-2.07 (qt, J = 6.16 Hz, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 162.4 (d, J = 245.23 Hz), 148.7, 139.2, 138.5 (d, J = 7.69 Hz), 129.4 (d, 8.45 Hz), 124.2, 115.5 (d, J = 21.50 Hz), 114.2 (d, J = 21.53 Hz), 38.9, 26.5, 22.7

FTIR (NaCl): 3055, 2940, 2863, 1667, 1585, 1471, 1422, 1214, 1164, 771 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{12}\text{OF}$ 191.08722 found 191.08696

1g

^1H NMR (300 MHz, CDCl_3) δ 7.26-7.22 (t, $J = 8.21$ Hz, 1H), 7.03-7.01 (t, $J = 8.55$ Hz, 1H), 6.89-6.83 (m, 3H), 3.79 (s, 3H), 2.59-2.56 (t, $J = 6.5$ Hz, 2H), 2.54-2.50 (q, $J = 5.82$ Hz, 2H), 2.12-2.06 (qt, $J = 6.16$ Hz, 2H)

^{13}C NMR (75.5 MHz, CDCl_3) δ 197.8, 159.1, 148.1, 140.1, 137.8, 128.9, 121.0, 114.1, 113.1, 55.1, 39.0, 26.5, 22.8

FTIR (NaCl): 3011, 2836, 1667, 1579, 1481, 1356, 1290, 1050, 782, 689 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{13}\text{H}_{15}\text{O}_2$ 203.10720 found 203.10704

1i

¹H NMR (400 MHz, CDCl₃) δ 7.13-7.11 (d, J = 7.52 Hz, 1H), 7.10-7.06 (m, 1H), 6.99-6.93 (m, 2H), 2.59-2.56 (t, J = 6.5 Hz, 2H), 2.54-2.50 (q, J = 6.16 Hz, 2H), 2.26 (s, 3H), 2.12-2.06 (qt, J = 6.15 Hz, 2H)

¹³C NMR (100 MHz, CDCl₃) δ 197.9, 160.9 (d, J = 245.23 Hz), 147.7, 139.5, 132.2, 131.7 (d, J = 4.61 Hz), 127.5 (d, J = 8.46 Hz), 124.2 (d, J = 17.68 Hz), 114.5 (d, J = 22.29 Hz), 38.9, 26.5, 22.8, 14.5

FTIR (NaCl): 3049, 2929, 2864, 1673, 1498, 1345, 1236, 1121, 809 cm⁻¹

HRMS calculated [M+1] for C₁₃H₁₄OF 205.10287 found 205.10215

2e

^1H NMR (400 MHz, CDCl_3) δ 7.76-7.75 (t, $J = 6.15$ Hz, 1H), 7.52-7.50 (A part of AB pattern, $J = 8.89$ Hz, 2H), 7.43-7.40 (B part of AB pattern $J = 8.89$ Hz, 2H), 2.61-2.60 (m, 2H), 2.52-2.49 (m, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 207.2, 159.2, 142.2, 131.5, 130.4, 128.5, 122.4, 35.6, 26.2

FTIR (NaCl): 3054, 2918, 1699, 1486, 907, 732 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{11}\text{H}_{10}\text{OBr}$ 136.99150 found 236.99146

MP 77-78 $^{\circ}\text{C}$

2f

^1H NMR (400 MHz, CDCl_3) δ 7.87-7.85 (t, $J = 3.08$ Hz, 1H), 7.48-7.45 (m, 2H), 7.35-7.31 (t, $J = 7.86$ Hz, 1H), 7.05-7.00 (t, $J = 8.21$ Hz, 1H), 2.74-2.70 (m, 2H), 2.63-2.60 (m, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 207.1, 162.7, (d, $J = 245.23$ Hz), 159.8, 142.2, 133.6 (d, $J = 8.45$ Hz), 129.9 (d, $J = 8.46$ Hz), 122.6, 115.1 (d, $J = 21.52$ Hz), 114.0 (d, $J = 22.3$ Hz), 35.7, 26.2

FTIR (NaCl): 3046, 2918, 1700, 1585, 1487, 1334, 1192 771 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{11}\text{H}_{10}\text{OF}$ 177.07157 found 177.07215

2g

^1H NMR (400 MHz, CDCl_3) δ 7.83-7.81 (t, $J = 2.9$ Hz, 1H), 7.32-7.22 (m, 3H), 6.91-6.83 (m, 1H), 3.83 (s, 3H), 2.72-2.68 (m, 2H), 2.61-2.58 (m, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 207.4, 159.5, 143.1, 132.9, 129.3, 119.4, 114.0, 112.4, 55.2, 35.8, 26.1

FTIR (NaCl): 3065, 2929, 2830, 1694, 1579, 1481, 1333, 1235, 1044, 781 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{13}\text{O}_2$ 189.09155 found 189.09129

2h

^1H NMR (400 MHz, CDCl_3) δ 7.94-7.91 (m, 2H), 7.60-7.45 (m, 3H), 2.76-2.73 (m, 2H), 2.63-2.61 (m, 2H)

^{13}C NMR (100 MHz, CDCl_3) δ 206.9, 160.1, 142.2, 132.6, 131.2, 130.9, 130.5, 128.9, 125.0 (q, $J = 3.84$ Hz), 123.8 (q, $J = 3.84$ Hz), 35.6, 26.3

FTIR (NaCl): 3071, 2923, 2852, 1694, 1437, 1322, 1109, 1077 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{12}\text{H}_{10}\text{OF}_3$ 227.06837 found 227.06832

2i

¹H NMR (400 MHz, CDCl₃) δ 7.77-7.76 (m, 1H), 7.55-52 (d, J = 1.71 Hz, 1H), 7.50-7.46 (m, 1H), 7.02-6.97 (t, J = 9.24 Hz, 1H), 2.71-2.67 (m, 2H), 2.60-2.57 (m, 2H), 2.29 (s, 3H)

¹³C NMR (100 MHz, CDCl₃) δ 207.6, 161.3, (d, J = 246.76 Hz), 158.4, 142.5, 130.2, 127.4, 126.3, 124.7 (d, J = 17.68 Hz), 115.0 (d, J = 22.29 Hz), 35.7, 26.0, 14.6

FTIR (NaCl): 3076, 2912, 1683, 1503, 1312, 1229, 1109, 831, 781 cm⁻¹

HRMS calculated [M+1] for C₁₂H₁₂OF 191.08722 found 191.08753

M.P 66-68 °C

3c

E/Z (16:1)

^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H), 7.17-7.05 (m, 4H), 6.88-6.83 (q, J = 6.84 Hz, 1H), 2.02-2.00 (d, J = 7.18 Hz, 3H)

^{13}C NMR (100 MHz, CDCl_3) δ 193.4, 162.4 (d, J = 247.53 Hz), 151.6, 144.1, 131.3 (d, J = 8.45 Hz), 128.0, 115.4 (d, J = 21.52 Hz), 15.9

FTIR (NaCl): 3059, 2830, 2704, 1694, 1508, 1224, 841, 732 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{10}\text{H}_{10}\text{OF}$ 165.07157 found 165.07162

3d

E/Z (27:1)

^1H NMR (400 MHz, CDCl_3) δ 9.59 (s, 1H), 7.40 -7.35 (q, J = 7.86 Hz, 1H), 7.07-7.02 (t, J = 8.55 Hz, 1H), 6.96-6.94 (d, J = 7.87 Hz, 1H), 6.09-6.87 (t, J = 7.52 Hz, 1H), 2.02-2.00 (d, J = 7.18 Hz, 3H)

^{13}C NMR (100 MHz, CDCl_3) 192.9, 162.5, (d, J = 246.76 Hz), 151.9, 143.9, 134.3 (d, J = 8.46 Hz), 129.9 (d, J = 8.46 Hz), 125.2, 116.5 (d, J = 21.53 Hz), 114.8 (d, J = 20.75 Hz), 15.9

FTIR (NaCl): , 2825, 2716, 1694, 1574, 1432, 1246, 908, 738 cm^{-1}

HRMS calculated $[\text{M}+1]$ for $\text{C}_{10}\text{H}_{10}\text{OF}$ 165.07157 found 165.07217