

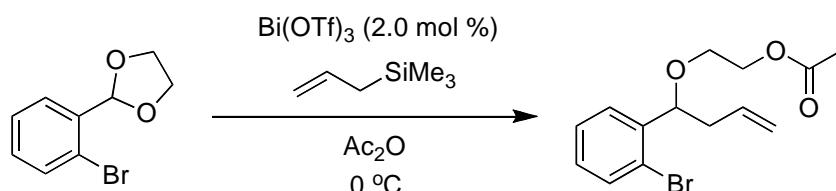
Environmentally-Friendly Organic Synthesis Using Bismuth Compounds. Bismuth Trifluoromethanesulfonate Catalyzed Allylation of Dioxolanes followed by *in situ* Derivatization to Generate Highly Functionalized Esters

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Experimental Procedures (entry numbers refer to Table 1 in manuscript)

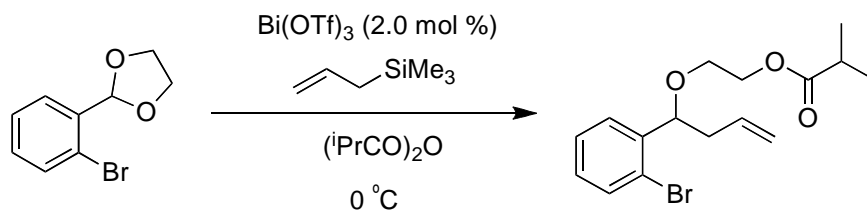
NMR spectra were recorded on a JEOL Eclipse NMR spectrometer at 270 MHz (^1H) or 67.5 MHz (^{13}C) in CDCl_3 as the solvent. The letters s, d, m and t used in describing ^1H NMR spectra refer to singlet, doublet, multiplet and triplet, respectively. Some triplets are characterized as app (apparent). This only refers to their appearance and maybe an oversimplification.

Entry 1a



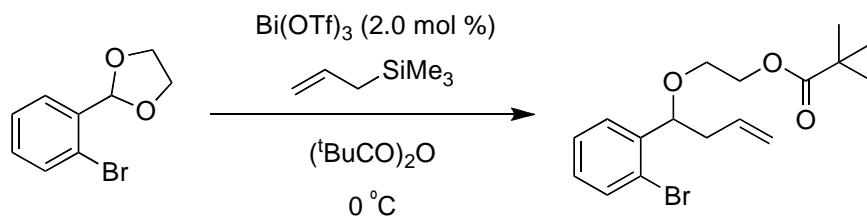
A solution of 2-(2-bromophenyl)-1,3-dioxolane (0.50 g, 2.18 mmol), allyltrimethylsilane (0.59 mL, 0.42 g, 3.71 mmol, 1.7 eq), and acetic anhydride (0.35 mL, 0.38 g, 3.71 mmol, 1.7 eq) was stirred at $0\text{ }^\circ\text{C}$ in a round bottom flask under N_2 as bismuth(III) triflate (0.0286 g, 0.0437 mmol, 2.0 mol %) was added. Reaction progress was monitored by gas chromatography. After 1 h at $0\text{ }^\circ\text{C}$, the reaction mixture was loaded onto 75 g of silica and eluted with EtOAc/heptane (5/95, v/v). Ninety-six fractions (8 mL) were collected. Fractions 41-56 were combined to yield 0.4382 g (62%) of a colorless liquid that was determined to be 99% pure by GC analysis and ^1H & ^{13}C NMR spectroscopy. ^1H NMR: δ 2.04 (s, 3 H), 2.41 (m, 2 H), 3.49-3.52 (m, 2 H), 4.15-4.23 (m, 2 H), 4.75-4.78 (m, 1 H), 4.99-5.08 (m, 2 H), 5.87 (m, 1 H), 7.09 (m, 1 H), 7.30 (dd, 1 H, $J = 7.2\text{ Hz}, 14.6\text{ Hz}$), 7.44-7.49 (m, 2 H). ^{13}C : (13 peaks) δ 170.7, 140.7, 134.2, 132.5, 128.8, 127.5 (2 carbons overlap), 122.8, 117.0, 80.4, 66.9, 63.4, 41.0, 20.8. HRMS: $\text{C}_{14}\text{H}_{17}\text{BrO}_3$, m/e 313.0439 (M+H); $\text{C}_{14}\text{H}_{18}\text{BrO}_3$ calculated 313.0439.

Entry 1b



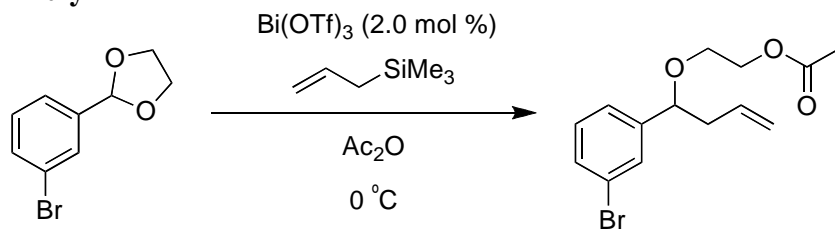
A solution of 2-(2-bromophenyl)-1,3-dioxolane (0.5507 g, 2.19 mmol), allyltrimethylsilane (0.59 mL, 0.42 g, 3.72 mmol, 1.7 eq), and isobutyric anhydride (0.62 mL, 0.59 g, 3.72 mmol, 1.7 eq) was stirred at 0 °C in a flame-dried 3-neck round bottom flask under N₂ as bismuth(III) triflate (0.0297 g, 0.045 mmol, 2.0 mol %) was added. The solution acquired a brown color. Reaction progress was monitored by gas chromatography. After 4 h 30 min, the reaction mixture was loaded onto 70 g of silica gel and eluted with EtOAc/heptane (5/95, v/v). A 100 mL prefraction was collected. Seventy-two fractions (8 ml) were collected. Fractions 38-58 were combined to yield 0.3667 g (47%) of a yellow liquid that was determined to be >97% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 1.18 (d, 6 H), 2.41-2.59 (m, 3 H), 3.52-3.54 (m, 2 H), 4.18-4.21 (m, 2 H), 4.76 (m, 1 H), 5.01-5.09 (m, 2 H), 5.83-5.93 (m, 1 H), 7.12-7.51 (m, 4 H). ¹³C: (14 peaks) δ 176.9, 140.9, 134.4, 132.6, 128.9, 127.6 (two carbons overlap), 122.8, 117.0, 80.5, 67.1, 63.4, 41.1, 33.9, 18.9. HRMS: C₁₆H₂₁BrO₃, *m/e* 341.07519 (M+H); C₁₆H₂₂BrO₃ calculated 341.07523.

Entry 1c



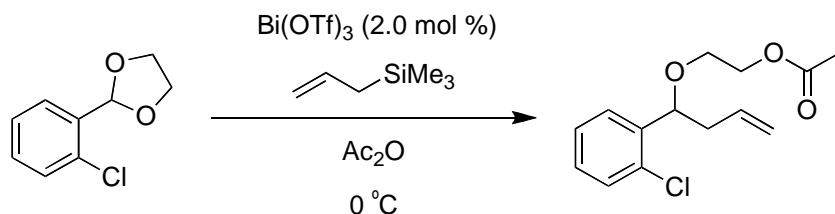
A solution of 2-(2-bromophenyl)-1,3-dioxolane (0.4917 g, 2.15 mmol), allyltrimethylsilane (0.58 mL, 0.42 g, 3.65 mmol, 1.7 eq), and trimethylacetic anhydride (0.74 mL, 0.68 g, 3.65 mmol, 1.7 eq) was stirred at 0 °C in a flame-dried 3-neck round bottom flask under N₂ as bismuth triflate (0.0282 g, 0.043 mmol, 2.0 mol %) was added. The solution became slightly warm. Reaction progress was monitored by gas chromatography. After 2 h 40 min, the reaction mixture was loaded onto 70 g of silica and eluted with EtOAc/heptane (5/95, v/v). Forty-two fractions (8 mL) were collected. Fractions 16-30 were combined to yield 0.4133 g (54%) of a colorless liquid that was determined to be 98% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 1.21 (s, 9 H), 2.34-2.49 (m, 2 H), 3.50-3.59 (m, 2 H), 4.17-4.21 (m, 2 H), 4.73-4.78 (m, 1 H), 5.01-5.11 (m, 2 H), 5.81-5.96 (m, 1 H), 7.09-7.52 (m, 4 H). ¹³C: (14 peaks) δ 178.4, 140.9, 134.4, 132.6, 128.8, 127.6 (two carbons overlap), 122.8, 117.0, 80.5, 67.1, 63.5, 41.1, 38.7, 27.2. HRMS: C₁₇H₂₃BrO₃, *m/e* 355.09119 (M+H); C₁₇H₂₄BrO₃ calculated 355.09088.

Entry 2



A solution of 2-(3-bromophenyl)-1,3-dioxolane (1.0143 g, 4.43 mmol), allyltrimethylsilane (1.20 mL, 0.86 g, 7.53 mmol, 1.7 eq), and acetic anhydride (0.71 mL, 0.77 g, 7.53 mmol, 1.7 eq) was stirred at 0 °C under N₂ in a flame-dried three-neck round bottom flask as bismuth(III) triflate (0.0581 g, 0.0886 mmol, 2.0 mol %) was added. The reaction became warm and turned red. Reaction progress was followed by gas chromatography. After 45 min at 0 °C, aqueous 10 % Na₂CO₃ (20 mL) was added to the reaction mixture, and it was stirred for 15 min. The mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with saturated NaCl (20 mL), dried (Na₂SO₄), and concentrated on a rotary evaporator to yield 0.2521 g of a clear liquid. The crude product was loaded onto 50 g of silica gel and eluted with EtOAc/hexanes (5/95, v/v) for fractions 1-25 (8 ml) and EtOAc/hexanes (10/90, v/v) for fractions 25-72 (8 ml). Seventy-two fractions were collected. Fractions 48-72 were combined to yield 1.02 g (73%) of a clear liquid that was determined to be 98% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 2.05 (s, 3 H), 2.34-2.55 (m, 2 H), 3.47-3.51 (t, 2 H, *J* = 4.9 Hz), 4.15-4.18 (m, 3 H), 4.98-5.04 (m, 2 H), 5.67-5.74 (m, 1 H), 7.17 (m, 2 H), 7.37 (m, 2 H). ¹³C: (14 peaks) δ 170.8, 144.1, 134.0, 130.7, 129.9, 129.5, 125.2, 122.5, 117.3, 81.5, 66.7, 63.4, 42.4, 20.98. HRMS: C₁₄H₁₇BrO₃, *m/e* 313.0440 (M+H); C₁₄H₁₈BrO₃ calculated 313.0439.

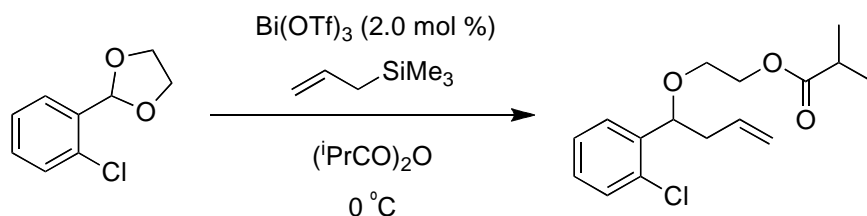
Entry 3a



A solution of 2-(2-chlorophenyl)-1,3-dioxolane (0.5359 g, 2.90 mmol), allyltrimethylsilane (0.78 mL, 1.04 g, 4.93 mmol, 1.7 eq), and acetic anhydride (0.47 mL, 0.93 g, 4.93 mmol, 1.7 eq) was stirred at 0 °C in a flame-dried round bottom flask under N₂ as bismuth(III) triflate (0.0381 g, 0.0581 mmol, 2.0 mol %) was added. Reaction progress was monitored by gas chromatography. After 40 min at 0 °C, the reaction mixture was loaded onto 70 g of silica gel and eluted with EtOAc/heptane (5/95, v/v). Ninety-two fractions (8 mL) were collected. Fractions 49-83 were combined to yield 0.55 g (70 %) of a yellow liquid that was determined to be 98 % pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 2.05 (s, 3 H), 2.42-2.47 (m, 2 H), 3.51-3.54 (m, 2 H), 4.16-4.21 (m, 2 H), 4.80-4.84 (t, 1 H, *J* = 6.2 Hz), 5.01-5.08 (m, 2 H), 5.78-5.93 (m, 1 H), 7.16-7.33 (m, 3 H), 7.46-7.50 (dd, 1 H, *J* = 1.8, 7.5 Hz). ¹³C: (14 peaks) δ 170.8, 139.2,

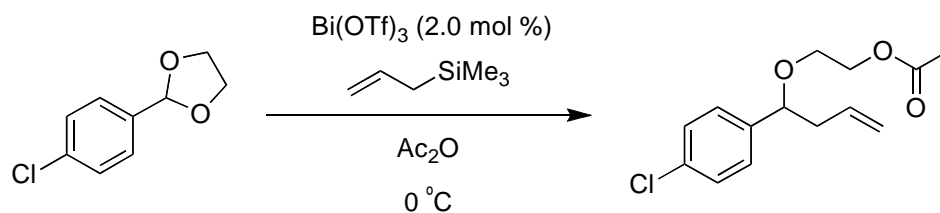
134.3, 132.7, 129.3, 128.5, 127.4, 127.0, 117.0, 78.2, 67.0, 63.5, 40.9, 20.8. HRMS: C₁₄H₁₇ClO₃, *m/e* 269.09432 (M+H); C₁₄H₁₈ClO₃ calculated 269.09445.

Entry 3b



A solution of 2-(2-chlorophenyl)-1,3-dioxolane (0.5354 g, 2.90 mmol), allyltrimethylsilane (0.78 mL, 0.56 g, 4.93 mmol, 1.7 eq), and isobutyric anhydride (0.82 mL, 0.78 g, 4.93 mmol, 1.7 eq) was stirred at 0 °C under N₂ in a flame-dried three-neck round bottom flask as bismuth(III) triflate (0.0381 g, 0.0580 mmol, 2.0 mol %) was added. The reaction mixture became warm and turned pale yellow. Reaction progress was monitored by gas chromatography. After 1 h 15 min at 0 °C, the reaction mixture was loaded onto 60 g of silica gel and eluted with EtOAc/ heptane (5/95, v/v). Sixty fractions (8 mL) were collected. Fractions 29-39 were combined to yield 0.46 g (53%) of a clear liquid that was determined to be 97% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 1.17 (d, 6H, *J* = 7.2 Hz), 2.42-2.55 (m, 3H), 3.52 (m, 2H), 4.19 (t, 2H, *J* = 4.7 Hz), 4.81 (t, 1H, *J* = 6.7 Hz), 5.02 (m, 2H), 5.87 (m, 1H), 7.17-7.47 (m, 4H). ¹³C: (15 peaks) δ 176.8, 139.3, 134.3, 132.6, 129.3, 128.4, 127.3, 126.9, 116.9, 78.1, 67.1, 63.3, 40.9, 33.8, 18.8. HRMS: C₁₆H₂₁ClO₃, *m/e* 297.1259 (M+H); C₁₆H₂₂ClO₃ calculated 297.1258.

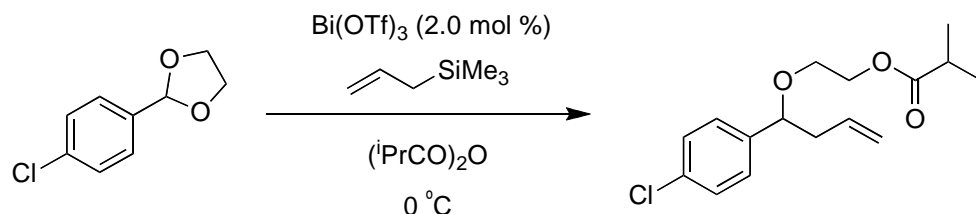
Entry 4a



A solution of 2-(4-chlorophenyl)-1,3-dioxolane (0.5523 g, 2.99 mmol), allyltrimethylsilane (0.81 mL, 0.58 g, 5.09 mmol), and acetic anhydride (0.48 mL, 0.52 g, 5.09 mmol) was stirred at 0 °C in a flame-dried three-neck round bottom flask under N₂ as bismuth(III) triflate (0.0393 g, 0.060 mmol, 2.0 mol %) was added. The reaction mixture became warm and turned yellow. Reaction progress was monitored by gas chromatography. After 40 min at 0 °C, the reaction mixture was loaded onto 60 g of silica and eluted with EtOAc/ heptane (10/90, v/v). Fifty-nine fractions (8 mL) were collected. Fractions 39-59 were combined to yield 0.54 g (67%) of a clear liquid that was determined to be 98% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 2.04 (s, 3H), 2.34-2.57 (m, 2H), 3.47 (t, 2H, *J* = 4.9 Hz), 4.15 (t, 2H, *J* = 5.0 Hz), 4.25 (t, 1H, *J* = 6.5 Hz), 5.01 (app t, 2H, *J* = 5.7 Hz), 5.70 (m, 1H), 7.27 (m, 4H). ¹³C: (12 peaks) δ 170.9, 140.1,

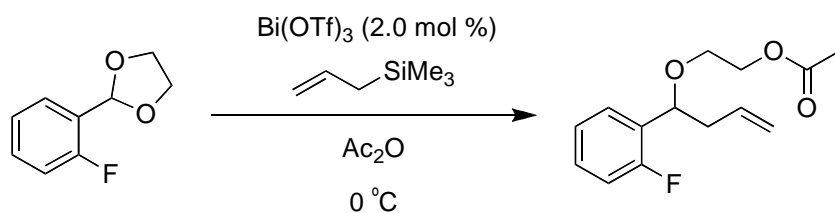
134.1, 133.3, 128.5, 128.0, 117.2, 81.6, 66.5, 63.4, 42.3, 20.8. HRMS: $C_{14}H_{17}ClO_3$, m/e 269.09471 (M+H); $C_{14}H_{18}ClO_3$ calculated 269.09445.

Entry 4b



A solution of 2-(4-chlorophenyl)-1,3-dioxolane (0.5018 g, 2.72 mmol), allyltrimethylsilane (0.73 mL, 0.53 g, 4.62 mmol, 1.7 eq), and isobutyric anhydride (0.77 mL, 0.73 g, 4.62 mmol, 1.7 eq) was stirred at $0\text{ }^\circ\text{C}$ in a flame-dried 3-neck round bottom flask under N_2 as bismuth(III) triflate (0.0362 g, 0.054 mmol, 2.0 mol %) was added. The solution became warm and turned orange-yellow. Reaction progress was monitored by gas chromatography. After 35 min at $0\text{ }^\circ\text{C}$, the reaction mixture was loaded onto 70 g of silica and eluted with EtOAc/ heptane (5/95, v/v). Seventy-two fractions (8 ml) were collected. Fractions 33-50 were combined to yield 0.29 g (36 %) of a colorless liquid that was determined to be >99% pure by GC analysis and 1H & ^{13}C NMR spectroscopy. 1H NMR: δ 1.13-1.16 (dd, 6 H, $J = 1.7, 7.2$ Hz), 2.27-2.59 (m, 3 H), 3.42-3.51 (m, 2 H), 4.14-4.18 (m, 2 H), 4.23-4.28 (m, 1 H), 4.96-5.03 (m, 2 H), 5.64-5.77 (m, 1 H), 7.19-7.30 (m, 4 H). ^{13}C : (13 peaks) δ 176.8, 140.2, 134.1, 133.2, 128.4, 127.9, 117.1, 81.5, 66.6, 63.2, 42.4, 33.8, 18.8. HRMS: $C_{16}H_{21}ClO_3$, m/e 297.1257 (M+H); $C_{16}H_{22}ClO_3$ calculated 297.1258.

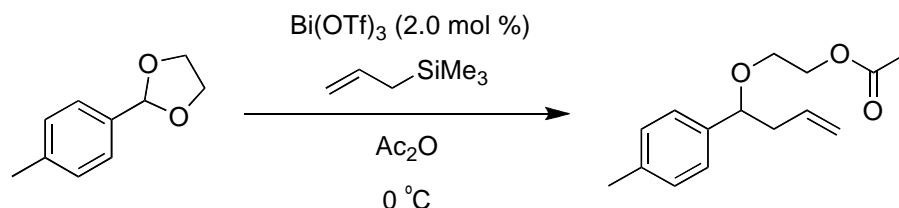
Entry 5



A solution of 2-(2-fluorophenyl)-1,3-dioxolane (0.5420 g, 3.22 mmol), allyltrimethylsilane (0.87 mL, 0.63 g, 5.48 mmol, 1.7 eq), and acetic anhydride (0.52 mL, 0.56 g, 5.48 mmol, 1.7 eq) was stirred at $0\text{ }^\circ\text{C}$ in a flame-dried round bottom flask under N_2 as bismuth(III) triflate (0.0423 g, 0.0645 mmol, 2.0 mol %) was added. Reaction progress was monitored by gas chromatography. After 1 h at $0\text{ }^\circ\text{C}$, the reaction mixture was loaded onto 50 g of silica gel and eluted with EtOAc/heptane (5/95, v/v). Sixty-five fractions (8 mL) were collected. Fractions 23-53 were combined to yield 0.50 g (61 %) of a clear liquid that was determined to be >99% pure by GC analysis and 1H & ^{13}C NMR spectroscopy. 1H NMR: δ 2.04 (s, 3 H), 2.42-2.56 (m, 2 H), 3.51-3.55 (m, 2 H), 4.16-4.19 (m, 2 H), 4.69-4.74 (m, 1 H), 4.98-5.06 (m, 2 H), 5.74-5.84 (m, 1 H), 6.96-7.44 (m, 4 H). ^{13}C : (14 peaks) δ 170.9, 160.4 (d, $J_{13C-F} = 244$ Hz), 134.1, 128.9 (d, $J_{13C-F} = 8.2$ Hz), 128.5 (d, $J_{13C-F} = 13.4$ Hz), 127.6 (d, $J_{13C-F} = 4.1$ Hz), 124.2 (d, $J_{13C-F} = 3.6$ Hz), 117.2,

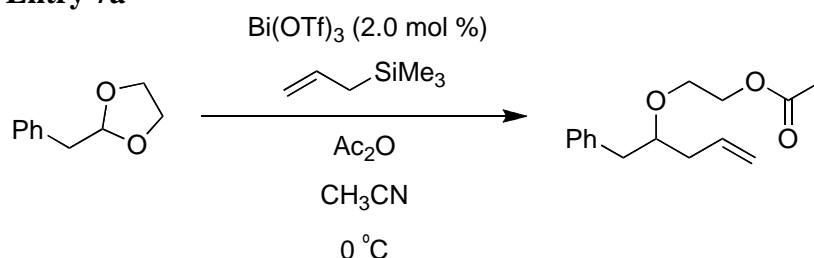
115.3 (d, $J_{13C-F} = 22.2$ Hz), 75.1, 66.9, 63.5, 41.3, 20.8. HRMS: $C_{14}H_{17}FO_3$, m/e 253.1238 (M+H); $C_{14}H_{18}FO_3$ calculated 253.1240.

Entry 6



A solution of 2-*p*-tolyl-1,3-dioxolane (0.9983 g, 6.08 mmol), allyltrimethylsilane (1.64 mL, 1.18 g, 10.34 mmol, 1.7 eq), and acetic anhydride (0.98 mL, 1.05 g, 10.34 mmol, 1.7 eq) was stirred at $0\text{ }^\circ C$ in a flame-dried three-neck round bottom flask under N_2 as bismuth(III) triflate (0.0798 g, 0.12 mmol, 2.0 mol %) was added. The reaction mixture became warm and turned brown. Reaction progress was monitored by gas chromatography. After 1 h at $0\text{ }^\circ C$, aqueous 10 % Na_2CO_3 (30 mL) was added to the reaction mixture, and it was stirred for 30 min. The mixture was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with saturated NaCl (30 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to yield 1.41 g of a brown liquid. The crude product was loaded onto 150 g of silica gel and eluted with EtOAc/heptane (5/95, v/v) for fractions 1-71 (8 mL) and EtOAc/heptane (10/90, v/v) for fractions 72-94 (16 mL). Ninety-four fractions were collected. Fractions 75-94 were combined to yield 0.65 g (43%) of a brownish liquid that was determined to be >99% by GC analysis and 1H & ^{13}C NMR spectroscopy. 1H NMR: δ 2.06 (s, 3H), 2.34-2.62 (m, 5H), 3.46-3.50 (m, 2H), 4.15-4.26 (m, 3H), 4.99-5.07 (m, 2H), 5.72-5.78 (m, 1H), 7.13-7.17 (m, 4H). ^{13}C : (13 peaks) δ 170.9, 138.4, 137.2, 134.7, 129.0, 126.6, 116.7, 82.1, 66.3, 63.5, 42.4, 21.0, 20.8. HRMS: $C_{15}H_{20}O_3$, m/e 247.1338 (M-H); $C_{15}H_{19}O_3$ calculated 247.1334.

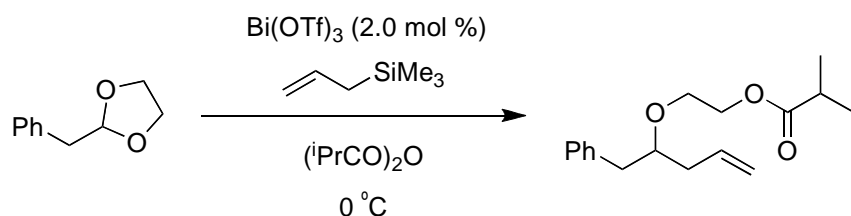
Entry 7a



A solution of phenylacetaldehyde dioxolane (0.500 g, 3.05 mmol), allyltrimethylsilane (0.82 mL, 0.59 g, 5.18 mmol, 1.7 eq), and acetic anhydride (0.49 mL, 0.53 g, 5.18 mmol, 1.7 eq) in anhydrous acetonitrile (10 mL) was stirred at $0\text{ }^\circ C$ in a flame-dried round bottom flask under N_2 as bismuth(III) triflate (0.0400 g, 0.0609 mmol, 2.0 mol %) was added. Reaction progress was monitored by gas chromatography. After 2 h 50 min at $0\text{ }^\circ C$, the solvent was removed on rotary evaporator and aqueous 10% Na_2CO_3 (15 mL) was added to the residue. The reaction mixture was stirred for 15 min and then extracted with EtOAc (2 x 20 mL). The organic layer was washed with saturated NaCl (15 mL), dried (Na_2SO_4), and concentrated on rotary evaporator to

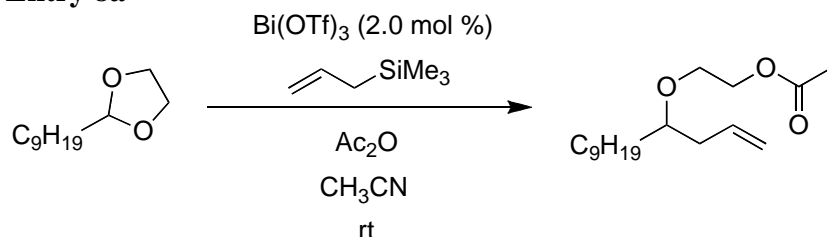
yield 0.7134 g of a yellow liquid. The crude product was loaded on 30 g of silica gel and eluted using EtOAc/hexanes (10/90, v/v). Twenty-seven fractions (8 ml) were collected. Fractions 14-23 were combined to yield 0.5137 g (68%) of a very pale yellow liquid that was determined to be 98% pure by GC analysis and ^1H & ^{13}C NMR spectroscopy. ^1H NMR: δ 2.03 (s, 3H), 2.27 (t, 2H, $J = 5.9$ Hz), 2.78 (m, 2H) 3.47-3.66 (m, 3H) 4.10 (t, 2H, $J = 4.7$ Hz), 5.07 (m, 2H), 5.84 (m, 1H), 7.19-7.30 (m, 5H). ^{13}C : (13 peaks) δ 170.9, 138.7, 134.6, 129.4, 128.1, 126.1, 117.2, 81.0, 67.3, 63.7, 40.5, 38.3, 20.8. HRMS: $\text{C}_{15}\text{H}_{20}\text{O}_3$, m/e 249.1492 (M+H); $\text{C}_{15}\text{H}_{21}\text{O}_3$ calculated 249.1491.

Entry 7b



A solution of phenylacetaldehyde dioxolane (1.0590 g, 6.45 mmol), allyltrimethylsilane (1.74 mL, 1.25 g, 10.96 mmol, 1.7 eq), and isobutyric anhydride (1.82 mL, 1.74 g, 10.96 mmol, 1.7 eq) was stirred at 0°C under N_2 in a flame-dried three neck round bottom flask as bismuth(III) triflate (0.0846 g, 0.1289 mmol, 2.0 mol %) was added. The reaction mixture warmed and turned black. Reaction progress was followed by gas chromatography but the ice bath was not maintained. After 15 h 15 min, aqueous 10% Na_2CO_3 (15 mL) was added to the reaction mixture and it was stirred for 15 min. The mixture was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with saturated NaCl (15 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator to yield 2.227 g of a brown liquid. The crude product was loaded on to 100 g of silica gel and eluted with EtOAc/hexanes (5/95, v/v). One hundred and eleven fractions (8 ml) were collected. Fractions 96-111 were combined to yield 0.70 g (40%) of a yellow liquid that was determined to be >99% pure by GC analysis and ^1H & ^{13}C NMR spectroscopy. ^1H NMR: δ 1.17 (dd, 6H, $J = 0.8$ Hz, 6.9 Hz), 2.26 (t, 2H, $J = 7.2$ Hz), 2.54 (m, 1H), 2.79 (m, 2H), 3.57 (m, 3H), 4.12 (t, 2H, $J = 4.9$ Hz), 5.10 (t, 2H, $J = 3.9$ Hz), 5.88 (m, 1H), 7.23 (m, 5H). ^{13}C : (14 peaks) δ 176.9, 138.7, 134.6, 129.4, 128.1, 126.0, 117.1, 80.8, 67.4, 63.5, 40.4, 38.2, 33.8, 18.8. HRMS: $\text{C}_{17}\text{H}_{24}\text{O}_3$, m/e 277.1801 (M+H); $\text{C}_{17}\text{H}_{25}\text{O}_3$ calculated 277.1804.

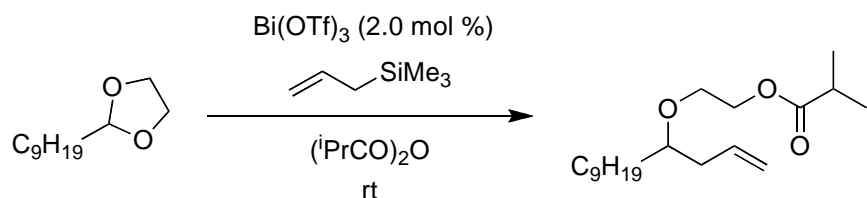
Entry 8a



A solution of 2-nonyl-1,3-dioxolane (1.4990 g, 7.48 mmol), allyltrimethylsilane (2.02 mL, 1.45 g, 12.72 mmol, 1.7 eq), and acetic anhydride (1.20 mL, 1.30 g, 12.72 mmol, 1.7 eq) in anhydrous acetonitrile (30 mL) was stirred at rt in a flame-dried round bottom flask under N_2 as

bismuth(III) triflate (.0991 g, 0.151 mmol, 2.0 mol %) was added. The solution became warm and turned yellow. Reaction progress was monitored by gas chromatography. After 21 h 35 min, the solvent was removed on a rotary evaporator. 10% Na₂CO₃ (40 mL, pH-10 after extraction) was added to the residue and stirred for 20 min. The mixture was extracted with EtOAc (2 x 50 mL). The organic layer was washed with saturated NaCl (45 mL), dried (Na₂SO₄), and concentrated on rotary evaporator to yield 2.06 g of a yellow liquid. The crude product was loaded on to 150 g of silica gel and eluted with EtOAc/hexanes (5/95, v/v). A prefraction of 175 mL was collected, and thirty four fractions (16 ml) were collected. Fractions 20-31 were combined to yield 1.55 g (73 % yield) of a colorless liquid that was determined to be >99% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 0.84 (s, 3 H), 1.22 (s, 14 H), 1.41 (s, 2 H), 2.04 (s, 3 H), 2.22 (t, 2 H, *J* = 5.9 Hz), 3.29 (m, 1 H), 3.62 (m, 2 H), 4.16 (t, 2 H, *J* = 4.9 Hz), 5.03 (m, 2 H), 5.77 (m, 1 H). ¹³C: (17 peaks) δ 170.9, 134.8, 116.7, 79.7, 66.7, 63.9, 38.3, 33.8, 31.8, 29.6, 29.54, 29.47, 29.2, 25.3, 22.6, 20.8, 14.0. HRMS: C₁₇H₃₂O₃, *m/e* 285.2430 (M+H); C₁₇H₃₃O₃ calculated 285.2430.

Entry 8b



A solution of 2-nonyl-1,3-dioxolane (.4998 g, 2.50 mmol), allyltrimethylsilane (0.67 mL, 0.49 g, 4.24 mmol, 1.7 eq), and isobutyric anhydride (0.70 mL, 0.67 g, 4.24 mmol, 1.7 eq) was stirred at rt in a flame-dried round bottom flask under N₂ as bismuth(III) triflate (.0323 g, 0.0492 mmol, 2.0 mol %) was added. The solution warmed and turned brown. Reaction progress was monitored by gas chromatography. After 3 h 35 min, the reaction mixture was filtered on silica gel (14 g) using EtOAc. The crude product was loaded on to 70 g of silica gel and eluted with EtOAc/ heptane (3/97, v/v). A 75 mL prefraction was collected, and 107 fractions (8 ml) were collected. Fractions 51-77 were combined to yield 0.34 g (44%) of a yellow liquid that was determined to be >99% pure by GC analysis and ¹H & ¹³C NMR spectroscopy. ¹H NMR: δ 0.83-0.88 (t, 3 H, *J* = 6.2 Hz), 1.14-1.16 (d, 6 H, *J* = 7.2 Hz), 1.24-1.43 (m, 16 H), 2.21-2.25 (t, 2 H, *J* = 6.2 Hz), 2.50-2.61 (m, 1 H), 3.26-3.32 (m, 1 H), 3.55-3.71 (m, 2 H), 4.15-4.19 (t, 2 H, *J* = 4.7 Hz), 5.00-5.07 (m, 2 H), 5.75-5.85 (m, 1 H). ¹³C: (17 peaks) δ 177.1, 134.9, 116.7, 79.6, 66.9, 63.8, 38.3, 33.9, 31.8, 29.7, 29.6, 29.5, 29.3, 25.3, 22.6, 18.9, 14.1. HRMS: C₁₉H₃₆O₃, *m/e* 313.2745 (M+H); C₁₉H₃₇O₃ calculated 313.2743