Supporting Information for:

Palladium Catalyzed Oxygenation of Unactivated sp^3 C-H Bonds

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Table S1. Yield as a Function of Pd(II) Catalyst in the Acetoxylation of 3-Methyl-2-Butanone *O*-Methyl Oxime

Entry	Catalyst	Yield (GC) ^a
1	Pd(OAc) ₂	72%
2	Pd(Cl) ₂	28%
3	Pd(Br) ₂	53%
4	Pd(I) ₂	54%
5	Pd(TFA) ₂	52%
6	Na ₂ PdCl ₄	16%
7	(BnCN) ₂ Pd(Cl) ₂	29%

^a Yield determined relative to an internal standard (biphenyl) and represents the average of two runs. The error is approximately $\pm 5\%$.

Experimental Section

General Procedures: NMR spectra were obtained on a Varian Inova 500 (499.90 MHz for ¹H; 125.70 MHz for ¹³C) or a Varian Inova 400 (399.96 MHz for ¹H; 100.57 MHz for ¹³C) spectrometer. ¹H NMR chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), and broad resonance (br).

Materials and Methods: Oxime substrates were prepared by reaction of the analogous ketones with MeONH₂•HCl/pyridine.¹ Oximes were obtained as mixtures of *E/Z* isomers when the α -position was mono or disubstituted. The parent ketones of substrates **8** and **15** were prepared by alkylation of the analogous hydrazones followed by hydrolysis with 1 M HCl.² Pyridine **16** was synthesized *via* a CuCN-mediated Grignard reaction between 2-bromopyridine and *t*-butyl magnesium chloride,³ while **17** was prepared by an Fe(acac)₃-catalyzed Grignard reaction between 2-chloropyridine and *i*-propyl magnesium chloride.⁴ All other ketone and pyridine substrates were obtained from commercial sources (Acros, Lancaster, Aldrich) and

used as received. $\text{PhI}(\text{OAc})_2$ and $\text{Pd}(\text{OAc})_2$ were obtained from Acros and Pressure Chemical, respectively, and were used as received. Solvents were obtained from Fisher Chemical and used without further purification. Flash chromatography was performed on EM Science silica gel 60 (0.040–0.063 mm particle size, 230–400 mesh) and thin layer chromatography was performed on Merck TLC plates pre-coated with silica gel 60 F₂₅₄. Control reactions (in the absence of Pd catalyst) were run for each substrate, and generally showed no reaction under our standard conditions.

Pinacolone *O*-methyl oxime (150 mg, 1.16 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (1.70 g, 5.23 mmol, 4.5 equiv), and $\text{Pd}(\text{OAc})_2$ (21 mg, 0.094 mmol, 0.08 equiv) were combined in AcOH (5 mL) and Ac_2O (5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C for 3.5 h. The reaction mixture was evaporated to dryness and then taken up in 3 mL of pyridine. The pyridine suspension was filtered through a short plug of silica, and the silica was washed with copious ethyl acetate to remove the organic products. The resulting solution was concentrated under vacuum to afford a red oil, which was purified by chromatography on silica gel (R_f = 0.28 in 70% hexanes/30% ethyl acetate). The product **3c** was obtained as pale yellow oil (218 mg, 62% yield). ^1H NMR (CDCl_3): δ 4.25 (s, 6H), 3.84 (s, 3H), 2.05 (s, 9H), 1.83 (s, 3H), $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 170.69, 154.34, 62.41, 62.01, 47.50, 20.95, 11.12. Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3$: C, 51.48, H, 6.98, N, 4.62; Found: C, 51.16, H, 7.07, N, 4.80

3-Methyl-2-butanone *O*-methyl oxime (200 mg, 1.74 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (621 mg, 1.91 mmol, 1.1 equiv), and $\text{Pd}(\text{OAc})_2$ (19 mg, 0.087 mmol, 0.05 equiv) were combined in AcOH (7 mL) and Ac_2O (7 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C for 3 h. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (20 mL), and the pentane layer was washed with H_2O (2 x 20 mL), saturated NaHCO_3 (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.3 in 90% hexanes/10% ethyl acetate). The product **9** was obtained as pale yellow oil (222 mg, 74% yield), which was a 6:1 mixture of the oxime *E/Z* isomers. Major Isomer: ^1H NMR (CDCl_3): δ 4.10 (dd, J = 10.9, 7.3 Hz, 1H), 3.99 (dd, J = 10.9, 6.9 Hz, 1H), 3.77 (s, 3H), 2.62 (m, 1H), 1.99 (s, 3H), 1.74 (s, 3H), 1.05 (d, J = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.10, 157.94, 66.24, 61.45, 39.13, 21.05, 14.95, 11.77. Anal. Calcd for $\text{C}_8\text{H}_{15}\text{NO}_3$: C, 55.47, H, 8.73, N, 8.09; Found: C, 55.55, H, 8.57, N, 7.81.

3-Methyl-2-pentanone *O*-methyl oxime (200 mg, 1.55 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (555 mg, 1.71 mmol, 1.1 equiv), and $\text{Pd}(\text{OAc})_2$ (17 mg, 0.078 mmol, 0.05 equiv) were combined in AcOH (6 mL) and Ac_2O (6 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C for 3.5 h. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (20 mL), and the pentane layer was washed with H_2O (2 x 20 mL), saturated NaHCO_3 (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel to afford two oxime (*E/Z*) isomers of the product **10** (major isomer: $R_f = 0.30$; minor isomer: $R_f = 0.21$ in 90% hexanes/10% ethyl acetate). The two isomers were isolated as pale yellow oils (major isomer: 189 mg, 65% yield; minor isomer: 38 mg, 13% yield). Each of the pure isomers was re-subjected to the reaction conditions and the equilibrium mixture (~5:1) was reestablished rapidly in each case (as determined by gas chromatography). Major Isomer: ^1H NMR (CDCl_3): δ 4.07 (pseudo q, $J = 13.9, 7.8, 6.4$ Hz, 2H), 3.79 (s, 3H), 2.45 (m, 1H), 1.99 (s, 3H), 1.72 (s, 3H), 1.45 (m, 2H), 0.84 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.09, 157.09, 65.00, 61.46, 46.03, 22.01, 21.07, 11.48, 11.43. Minor Isomer: ^1H NMR (CDCl_3): 4.16 (dd, $J = 10.9, 5.6$ Hz, 1H), 4.04 (dd, $J = 10.9, 8.3$ Hz, 1H), 3.80, (s, 3H), 3.45 (m, 1H), 2.03, (s, 3H), 1.80 (s, 3H), 1.49 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H). Anal. Calcd for $\text{C}_9\text{H}_{17}\text{NO}_3$ (major isomer): C, 57.73, H, 9.15, N, 7.48; Found: C, 57.71, H, 9.40, N, 7.22.

3-Heptanone *O*-methyl oxime (500 mg, 3.50 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (1.25 g, 3.07 mmol, 1.1 equiv), and $\text{Pd}(\text{OAc})_2$ (78 mg, 0.28 mmol, 0.05 equiv) were combined in AcOH (15 mL) and Ac_2O (15 mL) in a 50 mL round bottom flask and heated at 100°C under nitrogen for 1.5 h. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (80 mL), and the pentane layer was washed with H_2O (2 x 80 mL), saturated NaHCO_3 (2 x 80 mL) and brine (2 x 80 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel to afford two oxime (*E/Z*) isomers of the product **11** (isomer a: $R_f = 0.31$; isomer b: $R_f = 0.25$ in 90% hexanes/10% ethyl acetate). The two isomers were isolated as pale yellow oils (isomer a: 137 mg, 19.5%; isomer b: 137 mg, 19.5%). Each of the pure isomers was re-subjected to the reaction conditions and the equilibrium mixture (~1:1) was reestablished rapidly in each case (as determined by gas chromatography). Isomer a: ^1H NMR (CDCl_3): δ 4.20 (t, $J = 7.0$ Hz, 2H), 3.74 (s, 3H), 2.42 (t, $J = 7.0$ Hz, 2H), 2.24, (m, 2H), 1.99 (s, 3H), 1.38 (m, 2H), 1.28 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.12, 157.84, 61.62, 61.43, 33.27, 28.23, 27.98, 23.01, 21.10, 13.97. Isomer b: ^1H NMR (CDCl_3): δ 4.26 (t, $J = 6.6$ Hz, 2H), 3.76 (s, 3H), 2.56 (t, $J = 6.6$ Hz, 2H), 2.13, (m, 2H), 1.99 (s, 3H), 1.38 (m, 2H), 1.28 (m, 2H) 0.83 (t, $J = 7.3$ Hz, 3H). Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_3$ (mixture of *E/Z* isomers): C, 59.68, H, 9.52, N, 6.96; Found: C, 59.75, H, 9.25, N, 7.26.

2,2-Dimethylcyclopentanone *O*-methyl oxime (100 mg, 0.71 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (253 mg, 0.78 mmol, 1.1 equiv), and $\text{Pd}(\text{OAc})_2$ (8 mg, 0.035 mmol, 0.05 equiv) were combined in AcOH (3 mL) and Ac_2O (3 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 80°C for 5 h. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (20 mL), and the pentane layer was washed with H_2O (2 x 20 mL), saturated NaHCO_3 (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.25 in 90% hexanes/10% ethyl acetate). The product **22** was obtained as a pale yellow oil (86 mg, 61% yield). Unreacted starting material (28 mg, 28% recovered) was also isolated. ^1H NMR (CDCl_3): δ 4.02 (d, J = 11 Hz, 1H), 3.97 (d, J = 11 Hz, 1H), 3.78 (s, 3H), 2.42 (m, 2H), 2.02 (s, 3H), 1.80-1.64 (multiple peaks, 3H), 1.53 (m, 1H), 1.13 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.06, 167.11, 69.32, 61.51, 45.37, 36.16, 27.52, 22.48, 20.99, 20.90. Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{NO}_3$: C, 60.28, H, 8.60, N, 7.03; Found: C, 60.57, H, 8.69, N, 6.90.

Camphor *O*-methyl oxime (170 mg, 0.94 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (611 mg, 1.88 mmol, 2 equiv), and $\text{Pd}(\text{OAc})_2$ (10 mg, 0.047 mmol, 0.05 equiv) were combined in AcOH (4 mL) and Ac_2O (4 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 90°C for 9 h. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (20 mL), and the pentane solution was washed with H_2O (2 x 20 mL), saturated NaHCO_3 (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried over MgSO_4 , filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.3 in 90% hexanes/10% ethyl acetate). The product **23** was obtained as pale yellow oil (165 mg, 75% yield). ^1H NMR (CDCl_3): δ 4.32 (d, J = 12 Hz, 1H), 4.19 (d, J = 12 Hz, 1H), 3.74 (s, 3H), 2.44 (m, 1H), 1.99 (s, 3H), 1.95-1.78 (multiple peaks, 4H), 1.40 (m, 1H), 1.20 (m, 1H), 0.95 (s, 3H), 0.84 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 171.18, 165.94, 61.87, 61.59, 54.17, 48.51, 44.82, 33.49, 28.42, 27.04, 21.12, 20.17, 19.95. Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3$: C, 65.25, H, 8.84, N, 5.85; Found: C, 65.00, H, 8.83, N, 5.87.

2-Methyl-cyclohexanone *O*-methyloxime (200 mg, 1.42 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (691 mg, 2.13 mmol, 1.5 equiv), and $\text{Pd}(\text{OAc})_2$ (16 mg, 0.071 mmol, 0.05 equiv) were combined in AcOH (6 mL) and Ac_2O (6 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was heated at 100°C for 1.5 h. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (20 mL), and the pentane solution was washed with H_2O (2

x 20 mL), saturated NaHCO₃ (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried over MgSO₄, filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel to yield two oxime (E/Z) isomers of the product **24** (major isomer: R_f = 0.27; minor isomer R_f = 0.2 in 90% hexanes/10% ethyl acetate). The two isomers were isolated as pale yellow oils (major isomer: 173 mg, 61% yield; minor isomer: 57 mg, 20% yield). Each of the pure isomers was re-subjected to the reaction conditions and the equilibrium mixture (~3:1) was rapidly reestablished in each case. Major Isomer: ¹H NMR (CDCl₃): δ 4.39 (dd, J = 11.2, 5.9 Hz, 1H), 3.99 (dd, J = 11.2, 8.1 Hz, 1H), 3.74 (s, 3H), 2.76 (m, 1H), 2.46 (m, 1H), 1.96 (m, 2H), 1.99 (s, 3H), 1.67 (m, 2H), 1.40 (multiple peaks, 3H). ¹³C{¹H} NMR (CDCl₃): δ 171.24, 158.86, 64.92, 61.39, 41.21, 30.40, 25.98, 24.30, 24.08, 21.13. Minor Isomer: ¹H NMR (CDCl₃): δ 4.17 (dd, J = 10.8, 7.8 Hz, 1H), 4.06 (dd, J = 10.8, 6.4 Hz, 1H), 3.76 (s, 3H), 3.65 (m, 1H), 2.28 (m, 1H), 2.12 (m, 1H), 1.99 (s, 3H), 1.86 (m, 1H), 1.75 (m, 1H), 1.57-1.33 (multiple peaks, 4H). Anal. Calcd for C₁₀H₁₇NO₃ (mixture of E/Z isomers): C, 60.28, H, 8.60, N, 7.03; Found: C, 59.90, H, 8.91, N, 6.81.

4-*tert*-Butyl-2-methyl-cyclohexanone *O*-methyl oxime (200 mg, 1.01 mmol, 1 equiv), PhI(OAc)₂ (363 mg, 1.12 mmol, 1.1 equiv), and Pd(OAc)₂ (11 mg, 0.051 mmol, 0.05 equiv) were combined in AcOH (4 mL) and Ac₂O (4 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction mixture was heated at 100°C for 5 min. The resulting mixture was filtered through a plug of glass wool and diluted with pentane (20 mL), and the pentane solution was washed with H₂O (2 x 20 mL), saturated NaHCO₃ (2 x 20 mL) and brine (2 x 20 mL). The organic layer was dried over MgSO₄, filtered, and concentrated to afford a yellow oil, which was purified by chromatography on silica gel (R_f = 0.29 in 90% hexanes/10% ethyl acetate). The product **25** was obtained as pale yellow oil (202 mg, 78% yield). ¹H NMR (CDCl₃): δ 4.50 (dd, J = 11.0, 4.4 Hz, 1H), 3.97 (dd, J = 11.0, 8.1 Hz, 1H), 3.75 (s, 3H), 3.27 (m, 1H), 2.39 (m, 1H), 2.08 (m, 1H), 2.02 (s, 3H), 1.86 (m, 1H), 1.55 (m, 1H), 1.24 (m, 1H), 1.09 (m, 1H), 0.94 (m, 1H), 0.83 (s, 9H). ¹³C{¹H} NMR (CDCl₃): δ 174.09, 158.82, 65.20, 61.45, 47.04, 41.63, 32.22, 27.74, 26.98, 24.91, 21.22. Anal. Calcd for C₁₄H₂₅NO₃: C, 65.85, H, 9.87, N, 5.49; Found: C, 65.58, H, 10.10, N, 5.48.

2-*tert*-Butylpyridine (135 mg, 1.00 mmol, 1 equiv), PhI(OAc)₂ (1.03 g, 3.2 mmol, 3.2 equiv), and Pd(OAc)₂ (11 mg, 0.05 mmol, 0.05 equiv) were combined in AcOH (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 h. The reaction was concentrated, and the resulting oil was dissolved in CH₂Cl₂ (50 mL). This solution was washed with 5% pyridine in H₂O (3 x 50 mL) and saturated NaCl (1 x 50 mL), and then dried with MgSO₄ and concentrated *in vacuo*. The resulting oil was sonicated and washed with pentane (5 x 5 mL), and the pentane washes were combined and concentrated under vacuum. The product **26** was obtained as a pale yellow oil (198 mg, 63% yield). ¹H NMR (CDCl₃): δ 8.52

(ddd, $J = 4.7, 1.8, 0.92$ Hz, 1H), 7.62 (td, $J = 7.7, 2.0$ Hz, 1H), 7.23 (dd, 8.0, 0.92 Hz, 1H), 7.15 (ddd, $J = 7.4, 4.8, 1.1$ Hz, 1H), 4.50 (s, 6H), 1.93 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 170.39, 157.89, 149.15, 136.11, 122.18, 121.27, 64.17, 47.76, 20.58. Anal. Calcd $\text{C}_{15}\text{H}_{19}\text{NO}_6$: C, 58.25, H, 6.19, N, 4.53; Found: C, 58.55, H, 6.48, N, 4.26.

2-*i*-Propylpyridine (100 mg, 0.83 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (399 mg, 1.24 mmol, 1.5 equiv), and $\text{Pd}(\text{OAc})_2$ (9 mg, 0.04 mmol, 0.05 equiv) were combined in CH_2Cl_2 (8 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 h. The reaction was diluted with CH_2Cl_2 (40 mL), and this solution was washed with 5% pyridine in H_2O (3 x 50 mL) and saturated NaCl (1 x 50 mL) and was then dried with MgSO_4 and concentrated under vacuum. The resulting oil was chromatographed on silica gel with ($R_f = 0.3$ in 80% hexanes: 20% ethyl acetate). The product **27** was obtained as a yellow oil (68 mg, 42% yield). ^1H NMR (CDCl_3): δ 8.55 (ddd, $J = 5.7, 1.7, 0.9$ Hz, 1H), 7.61 (td, $J = 7.6, 1.7$ Hz, 1H), 7.17-7.12 (multiple peaks, 2H), 4.36 (dd, $J = 10.6, 7.4$ Hz, 1H), 4.27 (dd, $J = 10.6, 7.6$ Hz, 1H), 3.24 (m, 1H), 1.98 (s, 3H), 1.32 (d, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 170.9, 162.38, 149.35, 136.35, 122.14, 121.67, 68.37, 40.96, 20.87, 17.11. Anal. Calcd $\text{C}_{10}\text{H}_{13}\text{NO}_2$: C, 67.02, H, 7.31, N, 7.82; Found: C, 66.86, H, 7.33, N, 6.92.

2-Dimethylaminopyridine (149 μL , 1.2 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (811 mg, 2.52 mmol, 2.1 equiv), and $\text{Pd}(\text{OAc})_2$ (13 mg, 0.06 mmol, 0.05 equiv) were combined in CH_2Cl_2 (10 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 h. The reaction diluted with CH_2Cl_2 (40 mL), and this solution was washed with 5% pyridine in H_2O (3 x 50 mL) and saturated NaCl (1 x 50 mL), and was then dried with MgSO_4 and concentrated *in vacuo*. The resulting oil was sonicated and washed with pentane (5 x 5 mL), and the pentane washes were combined and concentrated under vacuum. The product **28** was obtained as a yellow/brown oil (203 mg, 70% yield). ^1H NMR (CDCl_3): δ 8.29 (ddd, $J = 4.8, 2.0, 1.1$ Hz, 1H), 7.58 (ddd, $J = 8.4, 7.3, 1.8$ Hz, 1H), 6.87-6.84 (multiple peaks, 2H), 5.75 (s, 4H), 2.05 (s, 6H). ^{13}C NMR: δ 171.23, 155.53, 148.12, 138.05, 116.43, 107.77, 74.17, 21.09. Anal. Calcd $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}_4$: C, 55.46, H, 5.92, N, 11.76; Found: C, 55.57, H, 6.15, N, 11.83.

2-Methoxypyridine (173 μL , 1.8 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (638 mg, 1.98 mmol, 1.1 equiv), and $\text{Pd}(\text{OAc})_2$ (21 mg, 0.09 mmol, 0.05 equiv) were combined in CH_2Cl_2 (15 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the mixture was stirred at 100°C for 12 h. The

reaction was concentrated under vacuum and the resulting brown oil was dissolved in ethyl acetate (250 mL) and pyridine (1 mL) and filtered through a plug of silica gel. The resulting solution was concentrated and dried under vacuum. The remaining brown solid was washed and sonicated with hexanes (5 x 10 mL), and the hexanes washes were combined, concentrated, and dried under vacuum. The product **29** was obtained as a yellow oil (201 mg, 66% yield). ^1H NMR (CDCl_3): δ 8.21 (ddd, J = 5.0, 1.9, 0.8 Hz, 1H) 7.63 (ddd, J = 8.3, 7.1, 1.9 Hz, 1H), 6.98 (ddd, 7.1, 5.0, 0.9 Hz, 1H), 6.83 (ddd, 8.2, 0.9, 0.8 Hz, 1H), 6.11 (s, 2H), 2.12 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 170.24, 161.62, 146.84, 139.21, 118.37, 111.41, 81.36, 20.98. Anal. Calcd $\text{C}_8\text{H}_9\text{NO}_3$: C, 57.48, H, 5.43, N, 8.38; Found: C, 57.63, H, 5.53, N, 8.16.

2-Butoxypyridine (92 μL , 1.2 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (425 mg, 1.32 mmol, 1.1 equiv), and $\text{Pd}(\text{OAc})_2$ (13 mg, 0.06 mmol, 0.05 equiv) were combined in CH_2Cl_2 (10 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 100°C for 12 h. The reaction diluted with CH_2Cl_2 (40 mL), and this solution was washed with 10% pyridine in H_2O (3 x 50 mL) and saturated NaCl (1 x 50 mL), and was then dried with MgSO_4 and concentrated *in vacuo*. The resulting oil was sonicated and washed with pentane (5 x 5 mL), and the pentane washes were combined and dried under vacuum. The product **30** was obtained as a yellow oil (110 mg, 44% yield). ^1H NMR (CDCl_3): δ 8.16 (ddd, J = 4.9, 2.0, 0.7 Hz, 1H), 7.59 (ddd, J = 8.2, 7.1, 2.0 Hz, 1H), 7.18 (t, 5.6 Hz, 1H), 6.92 (ddd, J = 7.1, 4.9, 0.9 Hz, 1H), 6.75 (ddd, J = 8.4, 0.91, 0.73 Hz), 2.03 (s, 3H), 1.89 (m, 2H), 1.49 (m, 2H), 0.96 (t, 7.4 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 169.72, 161.83, 147.10, 138.93, 117.96, 111.11, 92.42, 35.86, 21.09, 17.06, 13.82. Anal. Calcd $\text{C}_{11}\text{H}_{15}\text{NO}_3$: C, 63.14, H, 7.23, N, 6.69; Found: C, 63.01, H, 7.22, N, 6.30.

Decalone *O*-methyl oxime (200 mg, 1.11 mmol, 1 equiv), $\text{PhI}(\text{OAc})_2$ (539 mg, 1.66 mmol, 1.5 equiv), and $\text{Pd}(\text{OAc})_2$ (12 mg, 0.055 mmol, 0.05 equiv) were combined in AcOH (5 mL) and Ac_2O (5 mL) in a 20 mL vial. The vial was sealed with a Teflon lined cap, and the reaction was stirred at 80°C for 5 h. The reaction mixture was evaporated to dryness and then taken up in 3 mL of pyridine. The pyridine suspension was filtered through a short plug of silica, and the silica was washed with copious ethyl acetate to remove all of the organic products. The resulting solution was concentrated under vacuum to afford a reddish oil, which was purified by chromatography on silica gel (R_f = 0.3 in 90% hexanes/10% ethyl acetate). The product **31** was obtained as pale yellow crystals (210 mg, 81% yield). ^1H NMR (CDCl_3): δ 5.03 (ddd, J = 10.9, 10.7, 4.8 Hz, 1H), 3.69 (s, 3H), 3.24 (br d, J = 13.1, 1H), 2.0 (m, 1H), 1.93 (s, 3H), 1.91 (d, J = 10.9, 1H), 1.81-0.96 (multiple peaks, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 170.18, 157.54, 70.42, 61.06, 51.70, 43.31, 33.32, 32.97, 31.60, 25.59, 25.38, 23.12, 21.09. Anal. Calcd for $\text{C}_{13}\text{H}_{21}\text{NO}_3$: C, 65.25, H, 8.84, N, 5.85; Found: C, 65.51, H, 8.79, N, 5.77.

The equatorial stereochemistry of the OAc group of **31** was assigned based on standard analysis of the coupling constants of H_α as shown below:

5.03 ppm (ddd, $J = 10.9, 10.7, 4.8$)

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