Supporting Information
For

*Palladium-Catalyzed Cross-Coupling Reactions Between Dihydropyranyliindium
Reagents and Aryl Halides.
Synthesis of C-Aryl Glycols*

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General Procedure for Preparation of Trisdihydropyranyl indium(III) **1**

To a stirred solution of 0.60 ml of dry THF and 3,4-dihydro-2H-pyran (0.273 mL, 3 mmol) was added dropwise a solution of *t*-butyllithium solution (2.1 mL, 3.57 mmol, 1.7 M in pentane) at -78°C under dry N_2 . The resulting yellow suspension was stirred at 0°C for 1 hour whereby a clear yellow solution was obtained. The solution was added at -78°C to a solution of indium(III) chloride (0.221 g, 1 mmol) in dry THF (1.5 ml). The mixture was stirred at this temperature for 30 minutes and was then allowed to warm to room temperature, during which time a white suspension formed. This procedure gives an approximately 0.25 M solution of **1**.

General Procedure for Coupling of Triorganoindiums

Compound **1** was added to a stirring mixture of aryl bromide (0.9- 1.0 mmol) in dry THF (1.5 mL) and palladium catalyst (1- 5 mol %) at reflux. The resulting mixture was refluxed under dry N_2 for 1-2 hours. The progress of the reaction was monitored by TLC and GC/MS. The mixture was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography afforded the coupled product.

Reaction of 4-bromoacetophenone **2a** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 4-bromoacetophenone **2a** (0.179 g, 0.9 mmol) and (PPh₃)₂PdCl₂ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 1 h under dry N₂. The progress of the reaction was monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography (SiO₂, hexane / EtOAc, 20 / 1) gave a **3a** as a colorless oil (65.7 mg, 0.324 mmol, 36.0 % isolated yield).

Data for **3a**:

¹H NMR: (400 MHz, CDCl₃)

7.91 (d, *J* = 8.4 Hz, 2H); 7.62 (d, *J* = 8.4 Hz, 2H); 7.37 (s); 5.51 (t, *J* = 4.2 Hz, 1H); 4.20 (dd, *J* = 5.2, 5.2 Hz, 2H); 2.59 (s, 3H); 2.26 (m, 2H); 1.93 (m, 2H)

¹³C NMR: (100 MHz, CDCl₃)

198.0; 151.3; 141.0; 130.2; 128.7; 124.6; 100.4; 66.9; 26.9; 22.6; 21.4

HRMS: (EI+) calculated for C₁₃H₁₄O₂ 202.0994, found *m/z* = 202.0998

TLC: R_f 0.28 (SiO₂, hexane / EtOAc, 20 / 1)

GC: t_R **3a**, 10.06 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of Ethyl-4-bromobenzoate with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), ethyl-4-bromobenzoate **2b** (0.147 mL, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane / EtOAc, 20 / 1) gave a **3b** as a colorless oil (52 mg, 0.224 mmol, 24.8 % yield).

Data for **3b**:

^1H NMR: (400 MHz, CDCl_3)

7.99 (d, $J = 8.8$ Hz, 2H); 7.61 (d, $J = 8.8$ Hz, 2H); 5.48 (t, $J = 4.2$ Hz, 1H); 4.38 (q, $J = 7.2$ Hz, 2H); 4.19 (t, $J = 5.2$ Hz, 2H); 2.24 (m, 2H); 1.93 (m, 2H); 1.40 (t, $J = 7.2$ Hz, 3H)

^{13}C NMR: (100 MHz, CDCl_3)

166.9; 151.4; 140.7; 129.8; 127.6; 124.4; 100.1; 66.9; 61.2; 22.7; 21.3; 14.7

MS: (EI+) calculated for $\text{C}_{14}\text{H}_{16}\text{O}_3$ 232.1099, found $m/z = 232.1105$

TLC: R_f 0.42 (SiO_2 , hexane / EtOAc, 20 / 1)

GC: t_R **3b**, 11.60 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of Ethyl-3-bromobenzoate **2c** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), ethyl-3-bromobenzoate **2c** (0.160 mL, 1 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Another 2 mol % $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 0.02 mmol) was added and the reaction was refluxed for another hour. Another portion of **1** (2.64 mL, 0.66 mmol, 0.66 equiv) was added and the mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane / EtOAc, 20 / 1) gave **3c** as a yellow oil (25.3 mg, 0.109 mmol, 10.9 % isolated yield).

Data for **3c**:

^1H NMR: (400 MHz, CDCl_3)

8.23 (t, $J = 1.6$ Hz, 1H); 7.95 (d, $J = 5.2$ Hz, 1H); 7.75 (d, $J = 3.2$ Hz, 1H); 7.39 (t, $J = 7.6$ Hz, 1H); 5.44 (t, $J = 4.0$ Hz, 1H); 4.37 (q, $J = 6.8$ Hz, 2H); 4.21 (t, $J = 5.2$ Hz, 2H); 2.24 (m, 2H); 1.94 (m, 2H); 1.40 (t, $J = 7.2$ Hz, 3H)

^{13}C NMR: (100 MHz, CDCl_3)

167.0; 151.1; 136.9; 129.1; 129.0; 128.5; 125.9; 98.6; 66.9; 61.3; 22.7; 21.2; 14.7

MS: (low resolution): calculated for $\text{C}_{14}\text{H}_{16}\text{O}_3$ 232, found $m/z = 232$.

TLC: R_f 0.64 (SiO_2 , hexane / EtOAc, 20 / 1)

GC: t_R **3c**, 14.51 min (HP5890; injector 250°C, column gradient 50°C for 4 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of Ethyl-2-bromobenzoate **2d** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), ethyl-2-bromobenzoate **2d** (0.159 mL, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 3 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS every hour. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane / EtOAc, 20 / 1) gave **3d** as a yellow oil (119.8 mg, 0.515 mmol, 57.2 % isolated yield).

Data for **3d**:

^1H NMR: (400 MHz, CDCl_3)

7.58 (d, $J = 8.0$ Hz, 1H); 7.29- 7.40 (m, 3H); 5.06 (t, $J = 4.0$ Hz, 1H); 4.34 (q, $J = 7.2$ Hz, 2H); 4.08 (dd, $J = 5.6, 5.2$ Hz, 2H); 2.20 (m, 2H); 1.90 (m, 2H); 1.37 (t, $J = 7.2$ Hz, 3H)

^{13}C NMR: (100 MHz, CDCl_3)

169.5; 153.1; 137.1; 132.8; 130.9; 129.1; 128.7; 127.9; 100.5; 67.0; 62.0; 22.6; 21.2; 14.7

MS: (low resolution): calculated for $\text{C}_{14}\text{H}_{16}\text{O}_3$ 232, found $m/z=232$

TLC: R_f 0.50 (SiO_2 , hexane / EtOAc, 10 / 1)

GC: t_R **3d**, 8.11 min (HP5890; injector 250 °C, column gradient 110 °C for 3 min, 25 °C per min to 200 °C, 200 °C for 8 min; 8.4 psi)

Reaction of 1-bromo-4-chlorobenzene **2e** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 1-bromo-4-chlorobenzene **2e** (0.172 g, 0.9 mmol) and (PPh₃)₂PdCl₂ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 1 h under dry N₂. The progress of the reaction was monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography (SiO₂, hexane) gave **3e** as a colorless oil (171.9 mg, 0.882 mmol, 98.0 % yield).

Data for **3e**:

¹H NMR: (400 MHz, CDCl₃)

7.49 (d, *J* = 8.8 Hz, 2H); 7.29 (d, *J* = 8.4 Hz, 2H); 5.34 (t, *J* = 4.2 Hz, 1H); 4.18 (t, *J* = 5.2 Hz, 2H); 2.23 (m, 2H); 1.92 (m, 2H)

¹³C NMR: (100 MHz, CDCl₃)

151.3; 135.1; 133.2; 130.6; 128.6; 126.0; 120.7; 98.2; 66.9; 22.7; 21.2

MS: (low res): calculated for C₁₁H₁₁ClO 194, *m/z* = 195

TLC: R_f 0.68 (SiO₂, hexane)

GC: t_R **3e**, 7.63 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 1-bromo-2-nitrobenzene **2f** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 1-bromo-2-nitrobenzene **2f** (0.202 g, 1 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (21 mg, 0.03 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS after 1 h and 2 h. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) and another 2 mol % $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 0.02 mmol) were added. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane / Et_2O , 20 / 1) gave **3f** as a yellow oil (109 mg, 0.530 mmol, 53.0 % isolated yield).

Data for **3f**:

^1H NMR: (400 MHz, CDCl_3)

7.71 (d, $J = 8.0$ Hz, 1H); 7.53- 7.39 (m, 3H); 5.17 (t, $J = 4.0$ Hz, 1H); 4.06 (t, $J = 5.2$ Hz, 2H); 2.22 (m, 2H); 1.91 (m, 2H).

^{13}C NMR: (100 MHz, CDCl_3)

150.8; 132.5; 132.0; 130.5; 129.2; 124.2; 102.6; 67.4; 55.7; 22.4; 21.1

MS: (EI+) calculated for $\text{C}_{11}\text{H}_{11}\text{NO}_3$ 205.0739, found $m/z = 205.0732$

TLC: R_f 0.43 (SiO_2 , hexane / Et_2O , 30 / 1)

GC: t_R **3f**, 11.97 min (HP5890; injector 250°C, column gradient 50°C for 4 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 2-bromobenzaldehyde **2g** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 2-bromobenzaldehyde **2g** (0.117 mL, 1 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) and another 2 mol % $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 0.02 mmol) were added. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane / EtOAc, 20 / 1) gave **3g** as a yellow oil (44.8 mg, 0.239 mmol, 23.9 % isolated yield).

Data for **3g**:

^1H NMR: (400 MHz, CDCl_3)

10.27 (s, 1H); 7.90 (d, $J = 4.0$ Hz); 7.57-7.41 (m, 3H); 5.01 (t, $J = 4.0$ Hz, 1H); 4.21 (t, $J = 6.0$ Hz, 2H); 2.26 (m, 2H); 1.97 (m, 2H)

^{13}C NMR: (100 MHz, CDCl_3)

192.7; 150.8; 140.9; 134.6; 133.6; 129.4; 128.8; 127.7; 104.8; 67.1; 22.5; 21.3

MS: (EI+) calculated for $\text{C}_{12}\text{H}_{12}\text{O}_2$ 188.0837, found $m/z = 188.0845$

TLC: R_f 0.49 (SiO_2 , hexane / EtOAc, 20 / 1)

GC: t_R **3g**, 8.97 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 1-bromonaphthalene **2h** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 1-bromonaphthalene **2h** (0.125 mL, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (21 mg, 0.03 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) and another 2 mol % $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 0.02 mmol) were added. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane) gave **3h** as a yellow oil.

Data for **3h**:

^1H NMR: (400 MHz, CDCl_3)

8.19 (t, $J = 10.0$ Hz, 1H); 7.83(m, 2H); 7.53-7.42 (m, 4H); 5.06 (t, $J = 4.0$ Hz, 1H); 4.31 (t, $J = 5.2$ Hz, 2H); 2.30 (m, 2H); 2.06 (m, 2H).

^{13}C NMR: (100 MHz, CDCl_3)

129.0; 128.7; 128.5; 128.3; 126.8; 126.3; 126.1; 125.5; 124.8; 102.2; 67.0; 62.9; 22.9; 21.3; 21.1

MS: (low resolution): calculated for $\text{C}_{15}\text{H}_{14}\text{O}$ 210, found $m/z=210$

TLC: R_f 0.44 (SiO_2 , hexane)

GC: t_R **3h**, 10.70 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 4-acetoxylbromobenzene **2l** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (2.64 mL, 0.66 mmol, 0.66 equiv) was added to a refluxing solution of dry THF (1.5 mL), 4-acetoxylbromobenzene **2l** (0.193 g, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (7 mg, 0.01 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography (SiO_2 , hexane / EtOAc, 20 / 1) gave **3l** as a colorless oil (16.9 mg, 0.0773 mmol, 8.6 % isolated yield).

Data for **3l**:

^1H NMR: (400 MHz, CDCl_3)

7.56 (d, $J = 8.8$ Hz, 2H); 7.06 (d, $J = 8.8$ Hz, 2H); 5.31 (t, $J = 4.0$ Hz, 1H); 4.18 (dd, $J = 4.8, 5.0$ Hz, 2H); 2.31 (s, 3H); 2.22 (m, 2H); 1.92 (m, 2H).

^{13}C NMR: (100 MHz, CDCl_3)

178.0; 169.5; 151.5; 134.4; 131.0; 125.8; 121.5; 107.5; 97.8; 66.9; 22.8; 21.5; 21.2

MS: (EI+) calculated for $\text{C}_{13}\text{H}_{14}\text{O}_3$ 218.0943, found $m/z = 218.0945$

TLC: R_f 0.31 (SiO_2 , hexane / EtOAc, 20 / 1)

GC: t_R **3l**, 9.58 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of Iodobenzene **2m** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), iodobenzene **2m** (0.101 mL, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 0.02 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite filter aid. Purification of the residue by column chromatography (SiO_2 , hexane / Et_2O , 15 / 1) gave **3m** as a yellow oil (135.1 mg, 0.842 mmol, 93.5 % yield).

Data for **3m**:

^1H NMR: (400 MHz, CDCl_3)

7.59 (d, $J = 8.0$ Hz, 2H); 7.23-7.40 (m, 3H); 5.38 (t, $J = 4.0$ Hz, 1H); 4.22 (t, $J = 5.2$ Hz, 2H); 2.26 (m, 2H); 1.95 (m, 2H).

^{13}C NMR: (100 MHz, CDCl_3)

152.2; 137.9; 136.7; 130.6; 128.5; 128.1; 124.8; 97.2; 66.9; 22.9; 21.3

MS:

(EI+) calculated for $\text{C}_{11}\text{H}_{12}\text{O}$ 160.0888, found $m/z = 160.0881$

TLC:

R_f 0.65 (SiO_2 , hexane)

GC:

t_R **3m**, 6.33 min (HP5890; injector 250°C, column gradient 110°C for 3 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 4-iodotoluene **2n** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 4-iodotoluene **2n** (0.196 g, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (21 mg, 0.03 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) was added. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography (SiO_2 , hexane / Et_2O , 50 / 1) gave **3n** as a yellow oil (75.4 mg, 0.432 mmol, 48.0 % isolated yield).

Data for **3n**:

^1H NMR: (400 MHz, CDCl_3)

7.45 (d, $J = 8.4$ Hz, 2H); 7.14 (d, $J = 8.0$ Hz, 2H); 5.30 (t, $J = 4.0$ Hz, 1H); 4.19 (t, $J = 5.2$ Hz, 2H); 2.36 (s, 3H); 2.23 (m, 2H); 1.94 (m, 2H)

^{13}C NMR: (100 MHz, CDCl_3)

171.0; 137.8; 133.9; 129.2; 128.7; 124.7; 96.8; 66.8; 32.3; 22.9; 21.3; 14.5

MS: (EI+) calculated for $\text{C}_{12}\text{H}_{14}\text{O}$ 174.1045, found $m/z = 174.1049$

TLC: R_f 0.70 (SiO_2 , hexane / EtOAc , 30 / 1)

GC: t_R **3n**, 10.63 min (HP5890; injector 250°C, column gradient 50°C for 4 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 2-iodotoluene **2o** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 2-iodotoluene **2o** (0.115 mL, 0.9 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (21 mg, 0.03 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) and another 2 mol % $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 0.02 mmol) were added because the reaction was incomplete. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography (SiO_2 , hexane / Et_2O , 50 / 1) gave **3o** as a yellow oil (122.2 mg, 0.700 mmol, 77.8 % yield).

Data for **3o**:

^1H NMR: (400 MHz, CDCl_3)

7.34 (d, $J = 7.6$ Hz, 1H); 7.19-7.24 (m, 3H); 4.89 (t, $J = 3.8$ Hz, 1H); 4.20 (t, $J = 5.2$ Hz, 2H); 2.43 (s, 3H); 2.24 (m, 2H); 1.98 (m, 2H)

^{13}C NMR: (100 MHz, CDCl_3)

154.4; 137.7; 136.9; 130.6; 129.3; 128.5; 125.8; 100.7; 66.7; 22.9; 21.2; 20.6

MS: (low resolution): calculated for $\text{C}_{12}\text{H}_{14}\text{O}$ 174, found $m/z=174$

TLC: R_f 0.63 (SiO_2 , hexane / Et_2O , 50 / 1)

GC: t_R **3o**, 10.09 min (HP5890; injector 250°C, column gradient 50°C for 4 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 4-iodoanisole **2p** with **1**

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 4-iodoanisole **2p** (0.234 mL, 1 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (21 mg, 0.03 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) was added. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. Purification of the residue by column chromatography (SiO_2 , hexane / EtOAc, 40 / 1) gave **3p** as a colorless oil (14.2 mg, 0.075 mmol, 7.45 % isolated yield).

Data for **3p**:

^1H NMR: (400 MHz, CDCl_3)

7.49 (d, $J = 8.8$ Hz, 2H); 6.86 (d, $J = 8.8$ Hz, 2H); 5.22 (t, $J = 4.0$ Hz, 1H); 4.18 (t, $J = 5.2$ Hz, 2H); 3.83 (s, 3H); 2.22 (m, 2H); 1.92 (m, 2H)

^{13}C NMR: (100 MHz, CDCl_3)

159.7; 152.0; 130.7; 129.5; 127.3; 126.1; 113.9; 96.0; 66.9; 55.7; 22.9; 21.3

MS: (EI+) calculated for $\text{C}_{12}\text{H}_{14}\text{O}_2$ 190.0994, found $m/z = 190.1002$

TLC: R_f 0.43 (SiO_2 , hexane / EtOAc, 30 / 1)

GC: t_R **3p**, 11.69 min (HP5890; injector 250°C, column gradient 50°C for 4 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

Reaction of 2-iodoanisole with 1

Following the general procedure, a 0.25 M THF solution of **1** (1.32 mL, 0.33 mmol, 0.33 equiv) was added to a refluxing solution of dry THF (1.5 mL), 2-iodoanisole **2q** (0.130 mL, 1 mmol) and $(\text{PPh}_3)_2\text{PdCl}_2$ (21 mg, 0.03 mmol). The resulting mixture was refluxed for 1 h under dry N_2 . The progress of the reaction was monitored by TLC and GC/MS. Additional **1** (2.64 mL, 0.66 mmol, 0.66 equiv) and another 1 mol % $(\text{PPh}_3)_2\text{PdCl}_2$ (7 mg, 0.01 mmol) were added. The mixture was again refluxed for 1 h and monitored by TLC and GC/MS. The reaction was then quenched by the addition of a few drops of methyl alcohol. The suspension was filtered through a short plug of celite. A few drops of NEt_3 in hexane were added to a silica-gel slurry before loading the column for chromatography. Purification of the residue (SiO_2 , hexane / EtOAc, 40 / 1) gave **3q** as a yellow oil (24.5 mg, 0.129 mmol; 12.9 % isolated yield).

Data for 3q:

^1H NMR: (400 MHz, CDCl_3)

7.48 (m, 1H); 6.94 (m, 3H); 5.41 (t, $J = 4.0$ Hz, 1H); 4.18 (dd, $J = 5.0, 5.2$ Hz, 2H); 2.24 (m, 2H); 1.94 (m, 2H)

^{13}C NMR: (100 MHz, CDCl_3)

156.8; 151.6; 130.6; 129.2; 126.2; 120.8; 111.6; 102.4; 66.8; 56.0; 22.8; 21.4

MS:

(low resolution): calculated for $\text{C}_{12}\text{H}_{14}\text{O}_2$ 190, found $m/z=190$.

TLC:

R_f 0.40 (SiO_2 , hexane / EtOAc, 30 / 1)

GC:

t_R **3q**, 10.96 min (HP5890; injector 250°C, column gradient 50°C for 4 min, 25°C per min to 200°C, 200°C for 8 min; 8.4 psi)

General Procedure for C-Aryl Glycal Synthesis

To a stirred solution of 0.5 ml of dry THF and TIPS glucal **5** (615 mg, 1 mmol) was added dropwise a solution of *tert*-butyllithium (1 mL, 1.67 mmol, 1.7 M in pentane) at -78°C under dry N_2 . The resulting yellow solution was allowed to warm to 0°C and stirred at that temperature for 1.5 hour. The solution was again cooled to -78°C and was added dropwise *via* cannula to a solution of indium(III) chloride (121 mg, 0.55 mmol) in dry THF (0.5 ml) at -78°C . The mixture was stirred at this temperature for 30 minutes and was then allowed to warm to room temperature, during which time a yellow suspension formed.

To this solution was added aryl iodide (1.0-1.5 eq) and $\text{Cl}_2\text{Pd(PPh}_3)_2$ (21 mg, 3 mol%) and a condenser was attached to the reaction, and the mixture was stirred at 70°C for 12 h. At this time tlc analysis indicated the presence of C-aryl glycal. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO_2 , hexanes->100:1 hexanes:ether) afforded pure C-aryl glycal.

Reaction with 2-iodotoluene **2o**

Following the general procedure, 2-iodotoluene **2o** (0.15 ml, 1.1 mmol) was added to the previously prepared THF solution of **5** (R=In(III)) along with $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (21 mg, 3 mol%). A reflux condenser was attached to the reaction, and the mixture was stirred at 70°C for 24 h. At this time tlc analysis indicated the presence of C-aryl glycal **6o**. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO_2 , hexanes) afforded C-aryl glugal **6o** (420 mg, 0.6mmol, 60%).

Data for **6o**:

^1H NMR: (400 MHz, CDCl_3)

7.28-7.14 (m, 4H); 4.94 (dd, $J = 5.6, 1.6$ Hz, 1H); 4.44 (td, $J = 4.8, 2.8$ Hz, 1H); 4.22-4.16 (m, 3H); 4.03 (dd, $J = 11.2, 5.6$ Hz, 1H); 2.44 (s, 1H); 1.10-0.91 (m, 63H)

^{13}C NMR: (100 MHz, CDCl_3)

153.2; 137.5; 130.5; 129.5; 128.7; 126.2; 125.7; 99.7; 82.1; 69.9; 66.8; 62.6; 20.3; 18.6; 18.5; 12.8; 12.4

MS: (FAB+) calculated for $\text{C}_{40}\text{H}_{75}\text{O}_4\text{Si}_3 \text{ Na}$ 703.4973, found $m/z = 703.4996$ (M-H^+)

TLC: R_f 0.17 (SiO_2 , petroleum ether)

IR: 2943, 2866, 1658.0 cm^{-1}

Reaction with 4-iodoacetophenone **2a**

Following the general procedure, 4-iodoacetophenone **2a** (245mg, 1mmol, 1.0 eq) was added to the previously prepared THF solution of **5** (R=In(III)) along with $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (21 mg, 3 mol%). A reflux condenser was attached to the reaction, and the mixture was stirred at 70°C for 24 h. At this time, tlc analysis indicated the presence of C-aryl glycal **6a**. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO_2 , hexanes->100:1 hexanes:ether) afforded C-aryl glucal **6a** (400mg, 0.55mmol, 55% yield).

Data for **6a**:

^1H NMR: (400 MHz, CDCl_3)

7.91 (d, $J = 6.8$ Hz, 2H); 7.74 (d, $J = 6.8$ Hz, 2H); 5.49 (d, $J = 6.4$ Hz, 1H); 4.50 (m, 1H); 4.14-4.20 (m, 3H); 3.87 (dd; $J = 11.6, 6.4$ Hz, 1H); 2.62 (s, 3H); 1.02-1.10 (m, 63H)

^{13}C NMR: (100 MHz, CDCl_3)

198.0; 149.7; 141.0; 137.1; 128.5; 125.7; 99.3; 81.9; 70.4; 66.9; 62.3; 27.0; 18.6-18.3; 12.9; 12.8; 12.4

MS: (FAB+) calculated for $\text{C}_{41}\text{H}_{77}\text{O}_5\text{Si}_3$ 733.5079, found $m/z = 733.5102$ ($\text{M}+\text{H}$)⁺

TLC: R_f 0.53 (SiO_2 , hexane / Et_2O / ethyl acetate, 100 / 1 / 1)

IR: 2975, 2866, 1688, 1651 cm^{-1}

Reaction with methyl-2-iodobenzoate **2d**

Following the general procedure, methyl-2-iodobenzoate **2d** (0.2 ml, 1.4 mmol) was added to the previously prepared THF solution of **5** (R=In(III)) along with $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (21 mg, 3 mol%). A reflux condenser was attached to the reaction, and the mixture was stirred at 70°C for 24 h. At this time tlc analysis indicated the presence of *C*-aryl glycal **6d**. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO_2 , hexanes->100:1 hexanes:ether) afforded pure *C*-aryl glucal **6d** (402 mg, 0.54mmol, 54% yield).

Data for **6d**:

^1H NMR: (400 MHz, CDCl_3)

7.63 (d, $J = 7.2$ Hz, 1H); 7.34-7.50 (m, 3H); 5.03 (d, $J = 5.2$ Hz, 1H); 4.38 (t, $J = 6.8$ Hz, 1H); 4.27 (s, 1H); 4.10-4.23 (m, 3H); 3.83 (s, 3H); 0.97-1.27 (m, 63H)

^{13}C NMR: (100 MHz, CDCl_3)

207.1; 169.4; 151.9; 131.8; 131.0; 130.0; 129.3; 128.6; 99.7; 81.9; 70.0; 67.3; 62.0; 52.4; 31.2; 18.6-18.1; 13.3, 12.4

MS: (FAB+) calculated for $\text{C}_{41}\text{H}_{75}\text{O}_6\text{Si}_3$ 747.4872, found $m/z = 747.4903$ ($\text{M} - \text{H}$)⁺

TLC: R_f 0.34 (SiO_2 , hexane / Et_2O , 100 / 1)

IR: 2943, 2875, 1738, 1662 cm^{-1}

Reaction with 2-iodonaphthalene **2h**

Following the general procedure, 1-iodonaphthalene **2h** (0.2 ml, 1.4 mmol) was added to the previously prepared THF solution of **5** (R=In(III)) along with Cl₂Pd(PPh₃)₂ (21 mg, 3 mol%). A reflux condenser was attached to the reaction, and the mixture was stirred at 70°C for 24 h. At this time tlc analysis indicated the presence of C-aryl glycal **6h**. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO₂, hexanes) afforded C-aryl glugal **6h** (435mg, 0.59mmol, 59% yield).

Data for **6h**:

¹H NMR: (400 MHz, CDCl₃)

7.84 (dd, *J* = 8.0, 4.0 Hz, 2H); 7.53-7.43 (m, 5H); 5.16 (dd, *J* = 3.6, 2.4 Hz, 1H); 4.56 (m, 1H); 4.27-4.16 (m, 4H); 1.07-1.17 (m, 63H)

¹³C NMR: (100 MHz, CDCl₃)

152.7; 143.4; 135.9; 134.0; 132.1; 129.2; 128.3; 127.0; 126.8; 126.3; 126.1; 125.4; 101.1; 82.3; 70.0; 66.9; 18.4; 12.8

MS: (FAB+) calculated for C₄₃H₇₅O₄Si₃ 739.4973, found *m/z* = 739.5015 (M- H)⁺

TLC: R_f 0.32 (SiO₂, hexanes / benzene / ether, 196 / 4 / 1)

IR: 2959, 2840, 1646.4 cm⁻¹

Reaction with 2-iodoanisole **2q**

Following the general procedure, 2-iodoanisole **2q** (0.18 ml, 1.35 mmol) was added to the previously prepared THF solution of **5** (R=In(III)) along with $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (21 mg, 3 mol%). A reflux condenser was attached to the reaction, and the mixture was stirred at 70°C for 24 h. At this time tlc analysis indicated the presence of *C*-aryl glycal. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO_2 , 200:1 hexanes:ether) afforded *C*-aryl glucal **6q** (430 mg, 0.6 mmol, 60% yield).

Data for **6q**:

^1H NMR: (400 MHz, CDCl_3)

7.56 (dd, $J = 7.6, 2.4$ Hz, 1H); 7.26 (td, $J = 6.4, 1.6$ Hz, 1H); 6.95 (t, $J = 7.6$ Hz, 1H); 6.88 (d, $J = 8$ Hz, 1H); 5.49 (m, 1H); 4.42 (m, 1H); 4.18-4.10 (m, 3H); 4.05 (dd, $J = 11.3, 6.4$ Hz, 1H); 3.81 (s, 3H); 1.03-1.11 (m, 63H)

^{13}C NMR: (100 MHz, CDCl_3)

157.6; 148.1; 129.8; 129.3; 120.6; 111.8; 101.6; 81.5; 70.4; 67.3; 62.4; 55.9; 18.6-18.4; 12.9, 12.7

MS: (FAB+) calculated for $\text{C}_{40}\text{H}_{75}\text{O}_5\text{Si}_3$ 719.4922, found $m/z = 719.4909$ ($\text{M} - \text{H}$)⁺

TLC: R_f 0.66 (SiO_2 , hexane / ether, 100 / 1)

IR: 2941, 2865, 1643 cm^{-1}

Reaction with 4-iodoanisole **2p**

Following the general procedure, 4-iodoanisole **2p** (0.18 ml, 1.35 mmol) was added to the previously prepared THF solution of **5** (R=In(III)) along with $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (21 mg, 3 mol%). A reflux condenser was attached to the reaction, and the mixture was stirred at 70°C for 24 h. At this time tlc analysis indicated the presence of *C*-aryl glycal. The cooled reaction mixture was diluted with benzene and a few drops of methanol, and filtered through celite. Concentration *in vacuo* and flash chromatography (SiO_2 , 100:1 hexanes:ether) afforded pure *C*-aryl glucal **6p** (285 mg, 0.4mmol, 40% yield).

Data for **6p**:

^1H NMR: (400 MHz, CDCl_3)

7.58 (dd, $J = 6.8, 2.4$ Hz, 2H); 6.87 (dd, $J = 6.8, 2.4$ Hz, 2H); 5.25 (dd, $J = 5.2, 1.6$ Hz, 1H); 4.45 (m, 1H); 4.20 – 4.06 (m, 3H); 3.91 (dd, $J = 11.0, 6.2$ Hz, 1H); 3.81 (s, 3H); 1.09-1.01 (m, 63 H).

^{13}C NMR: (100 MHz, CDCl_3)

160.0; 150.4; 127.1; 113.7; 95.6; 81.7; 70.6; 67.3; 62.5; 55.6; 18.3; 12.9

MS: (FAB+) calculated for $\text{C}_{40}\text{H}_{75}\text{O}_5\text{Si}_3$ 719.4922, found $m/z = 719.4903$ ($\text{M} - \text{H}$)⁺

TLC: R_f 0.37 (SiO_2 , hexane / ether, 300 / 1)

IR: 2943, 2866, 1650 cm^{-1}

Platinum oxide reduction of **6o**

C-aryl glucal **6o** (109 mg, 0.14 mmol) was dissolved in EtOH (3mL) and PtO₂ (20mg) was added. The system was evacuated and purged with hydrogen gas. After stirring for 30 minutes under an atmosphere of hydrogen, the mixture was filtered through celite and concentrated *in vacuo*, affording 98 mg (90% yield) of 2-deoxy-β-C-aryl glycoside **8**; the crude material was sufficiently pure for analysis.

Data for **8**:

¹H NMR: (400 MHz, CDCl₃)

7.50 (dd, *J*=6.8, 1.6 Hz, 1H); 7.21-7.13 (m, 3H); 4.74 (dd, *J* = 10.8, 2.0 Hz, 1H); 4.14-3.82 (m, 3H); 3.61-3.58 (m, 1H); 2.35 (s, 3H); 1.17-1.07 (m, 63H).

¹³C NMR: (100 MHz, CDCl₃)

140.8; 135.2; 130.4; 127.5; 126.3; 126.0; 83.2; 75.4; 73.2; 72.8; 69.8; 64.6; 62.3; 57.4; 40.5; 18.6; 14.1; 12.8

MS: (FAB+) calculated for C₄₀H₇₈O₄Si₃ Na 729.5106, found *m/z* = 729.5112 (M+Na)⁺

TLC: R_f 0.45 (SiO₂, hexanes)

IR: 2950, 2865 cm⁻¹

Hydroboration/oxidation of 6p

C-aryl glucal **6p** (25 mg, 0.035 mmol) was dissolved in THF (0.1 mL) and $\text{BH}_3 \cdot \text{THF}$ (1.5 M, 0.35 mL, 0.53 mmol) was added dropwise at 0°C . The reaction was stirred at ambient temperature for 24 hours and then 3N NaOH/ 30% H_2O_2 (1:1, 10 mL) was added and the reaction was stirred at room temperature for an additional 24 h. The mixture was diluted with CH_2Cl_2 (25 mL), the organic layer was partitioned and washed successively with 20% NaHSO_3 (25 mL), saturated ammonium chloride (25 mL), water (25 mL), and brine (25 mL). The organic layer was dried over sodium sulfate and concentrated *in vacuo*. Flash chromatography (SiO_2 , 10:1 Hexanes:Ether) afforded pure C-aryl glycoside **9** (10 mg, 39%).

Data for 9:

^1H NMR: (400 MHz, CDCl_3)

7.27 (d, $J = 8.8$ Hz, 2H); 6.87 (d, $J = 8.8$ Hz, 2H); 4.95 (d, $J = 9.5$ Hz, 1H); 4.39 (td, $J = 7.2, 3.6$ Hz, 1H); 4.15 (t, $J = 4.4$ Hz, 1H); 4.04 (m, 1H); 3.87 (d, $J = 6.0$ Hz, 1H); 3.26 (m, 1H); 1.15-1.07 (m, 63H)

^{13}C NMR: (100 MHz, CDCl_3)

159.0; 137.1; 127.3; 114.2; 74.2; 73.4; 66.5; 55.7; 42.8; 18.6-18.3; 13.2; 12.4.

TLC: R_f 0.59 (SiO_2 , hexane / EtOAc, 10 / 1)

IR: 3470, 2925, 2865 cm^{-1}