Mild Palladium-Catalyzed Selective Monoarylation of Nitriles

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Supporting Information

General Methods. Reactions were conducted using standard drybox techniques. All aryl halides, nitriles and bases were purchased from Aldrich Chemical Co. and used without further purification. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on 400 MHz or 500 MHz spectrometers with tetramethylsilane or residual protiated solvent used as a reference and coupling constants reported in hertz (Hz). Chromatographic purifications were performed by flash chromatography using silica gel (200-400 mesh) or an automated chromatography system. The yields of the coupled products included in all tables refer to isolated yields and are the average of two runs. Products that had been reported previously were isolated in greater than 95% purity, as determined by ^1H NMR and capillary gas chromatography (GC). All ^{13}C NMR spectra were proton decoupled. GC analyses were obtained with a DB-1301 narrow bore column suitable for use with a fast temperature ramp (max $120^\circ\text{C}/\text{min}$). Elemental Analyses were performed by Atlantic Microlit Laboratories, Inc., Norcross, Georgia 30071.

Representative procedure for the arylation of silyl-substituted primary nitrile. 4-tert-butyl benzylnitrile (Table 1, entry 1).¹ To a screw-capped vial containing Xantphos (11.6 mg, 0.0200 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol) and 4-bromo-tert-butylbenzene (213 mg, 1.00 mmol) in DMF (1.0 mL) was added trimethylsilylacetonitrile

(136 mg, 1.20 mmol), followed by ZnF_2 (62.0 mg, 0.600 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The heterogeneous reaction mixture was stirred at 90 ° C for 18 h. The crude reaction mixture was then allowed to cool to room temperature and was diluted with Et_2O (50 mL). The resulting solution was washed with H_2O . The organic phase was dried over Na_2SO_4 , filtered, and concentrated at reduced pressure. The residue was then purified by chromatography on silica gel, eluting with hexane/ethyl acetate (95:5) to provide the title compound (150 mg) in 87% yield. ^1H NMR (CDCl_3): δ 7.39 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.70 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (CDCl_3): δ 151.17, 127.73, 127.02, 126.12, 118.17, 34.62, 31.35, 23.14.

Spectral and Analytical Data for Previously Unpublished Compounds in Table 1.

(4-Methoxy-phenyl)-acetonitrile. (Table 1, entry 2).² 4-bromoanisole (187 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 94.1 mg (64%) of (4-methoxy-phenyl)-acetonitrile. ^1H NMR (CDCl_3): δ 7.24 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.68 (s, 2H). ^{13}C NMR (CDCl_3): δ 159.33, 129.11, 121.89, 118.36, 114.51, 55.33, 22.73.

(4-Dimethylamino-phenyl)-acetonitrile (Table 1, entry 3). (4-Bromo-phenyl)-dimethyl-amine (200 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), PhPtBu_2 (8.9 mg, 0.0400 mmol), and ZnF_2 (62.0 mg,

0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 133 mg (83%) of (4-dimethylamino-phenyl)-acetonitrile. ^1H NMR (CDCl_3): δ 7.15 (d, J = 8.8 Hz, 2H), 6.69 (d, J = 8.8 Hz, 2H), 3.62 (s, 2H), 2.94 (s, 6H). ^{13}C NMR (CDCl_3): δ 150.13, 128.62, 118.71, 117.08, 112.68, 40.42, 22.49. Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.91; H, 7.60; N, 17.40.

(3,5-Dimethyl-phenyl)-acetonitrile (Table 1, entry 4). 1-Bromo-3,5-dimethyl-benzene (189 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 108 mg (74%) of (3,5-dimethyl-phenyl)-acetonitrile. ^1H NMR (CDCl_3): δ 6.98 (s, 1H), 6.97 (s, 2H), 3.68 (s, 2H), 2.35 (s, 6H). ^{13}C NMR (CDCl_3): δ 138.92, 129.82, 129.67, 125.78, 118.25, 23.43, 21.26. Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{N}$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.63; H, 7.72; N, 9.43.

(3-[1,3]Dioxolan-2-yl-phenyl)-acetonitrile (Table 1, entry 5). 2-(3-Bromo-phenyl)-[1,3]dioxolane (229 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 148 mg (78%) of (3-[1,3]dioxolan-2-yl-phenyl)-acetonitrile. ^1H NMR (CDCl_3): δ 7.46 (s, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 1H), 5.81 (s, 1H), 4.15-4.10 (m, 2H), 4.09-4.03 (m,

2H), 3.77 (s, 2H). ^{13}C NMR (CDCl_3): δ 139.28, 130.30, 129.41, 128.86, 126.52, 126.14, 117.84, 103.32, 65.56 (two $-\text{O}-\text{CH}_2-$), 23.73. Anal. Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.66; H, 5.79; N, 7.36.

(6-Methoxy-naphthalen-2-yl)-acetonitrile (Table 1, entry 6). 2-Bromo-6-methoxy-naphthalene (237 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 171 mg (87%) of (6-methoxy-naphthalen-2-yl)-acetonitrile. ^1H NMR (CDCl_3): δ 7.72-7.67 (m, 3H), 7.30 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.16 (dd, J = 8.5 Hz, 1.5 Hz, 1H), 7.10 (d, J = 1.5 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 2H). ^{13}C NMR (CDCl_3): δ 158.19, 134.06, 129.28, 128.89, 127.93, 126.77, 126.11, 124.96, 119.73, 118.23, 105.80, 55.44, 23.70. Anal. Calcd for $\text{C}_{13}\text{H}_{11}\text{NO}$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.90; H, 5.54; N, 7.09.

(4-Fluoro-phenyl)-acetonitrile (Table 1, entry 7).² 1-Bromo-4-fluoro-benzene (175 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 107 mg (79%) of (4-fluoro-phenyl)-acetonitrile. ^1H NMR (CDCl_3): δ 7.30 (dd, J = 8.3 Hz, 5.3 Hz, 2H), 7.07 (t, J = 8.3 Hz, 2H), 3.72 (s, 2H). ^{13}C NMR (CDCl_3): δ 162.57 (d, J = 246.7 Hz), 129.81 (d, J = 8.9 Hz), 125.84 (d, J = 3.0 Hz), 117.89, 116.28 (d, J = 20.7 Hz), 23.08.

(4-Trifluoromethyl-phenyl)-acetonitrile (Table 1, entry 8). 1-Bromo-4-trifluoromethyl -benzene (225 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 145 mg (78%) of (4-trifluoromethyl-phenyl)-acetonitrile. ¹H NMR (CDCl₃): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 3.82 (s, 2H). ¹³C NMR (CDCl₃): δ 134.18, 130.58 (q, *J* = 32.8 Hz), 128.61, 126.20 (q, *J* = 4.0 Hz), 123.95 (q, *J* = 273.0 Hz), 117.22, 23.67.

(4-Nitro-phenyl)-acetonitrile (Table 1, entry 9).³ 1-Bromo-4-nitro-benzene (202 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 85/15) to give 110 mg (68%) of (4-nitro-phenyl)-acetonitrile. ¹H NMR (CDCl₃): δ 8.27 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 2H). ¹³C NMR (CDCl₃): δ 148.19, 137.54, 129.41, 124.76, 116.98, 24.01.

(4-Benzoyl-phenyl)-acetonitrile (Table 1, entry 10).⁴ (4-Bromo-phenyl)-phenyl-methanone (261 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 203 mg (92%) of (4-benzoyl-phenyl)-

acetonitrile. ^1H NMR (CDCl_3): δ 7.82 (d, J = 8.0 Hz, 2 H), 7.79 (d, J = 8.0 Hz, 2 H), 7.61 (t, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 8.0 Hz, 2 H), 3.85 (s, 2 H). ^{13}C NMR (CDCl_3): δ 195.75, 137.20, 137.12, 134.47, 132.66, 130.68, 129.90, 128.36, 127.92, 117.33, 23.52.

4-Cyanomethyl-benzoic acid ethyl ester (Table 1, entry 11).⁵ 4-Bromo-benzoic acid ethyl ester (229 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 85/15) to give 159 mg (84%) of 4-cyanomethyl-benzoic acid ethyl ester. ^1H NMR (CDCl_3): δ 8.04 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 4.38 (q, J = 7.2 Hz, 2H), 3.82 (s, 2H), 1.40 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3): δ 165.87, 134.88, 130.35, 130.28, 127.96, 117.31, 61.18, 23.59, 14.29.

(4-Acetyl-phenyl)-acetonitrile (Table 1, entry 12).⁶ 1-(4-Bromo-phenyl)-ethanone (199 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 85/15) to give 124 mg (78%) of (4-acetyl-phenyl)-acetonitrile. ^1H NMR (CDCl_3): δ 7.97 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H), 3.84 (s, 2H), 2.61 (s, 3H). ^{13}C NMR (CDCl_3): δ 197.32, 136.82, 135.06, 129.11, 128.21, 117.17, 26.66, 32.62.

4-Cyanomethyl-benzonitrile (Table 1, entry 13).² 4-Bromo-benzonitrile (182 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 85/15) to give 115 mg (81%) of 4-cyanomethyl-benzonitrile. ¹H NMR (CDCl₃): δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 2H). ¹³C NMR (CDCl₃): δ 135.37, 132.92, 128.86, 118.21, 116.79, 112.23, 23.80.

o-Tolyl-acetonitrile (Table 1, entry 14). 1-Bromo-2-methyl-benzene (171 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), PtBu₃ (8.1 mg, 0.0400 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 109 mg (83%) of o-tolyl-acetonitrile. ¹H NMR (CDCl₃): δ 7.32-7.17 (m, 4H), 3.59 (s, 2H), 2.30 (s, 3H). ¹³C NMR (CDCl₃): δ 136.16, 130.75, 128.68, 128.58, 128.51, 126.83, 117.74, 21.93, 19.40.

(2,4-Dimethyl-phenyl)-acetonitrile (Table 1, entry 15). 1-Bromo-2,4-dimethyl-benzene (185 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), PtBu₃ (8.1 mg, 0.0400 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 106 mg (78%) of (2,4-dimethyl-phenyl)-acetonitrile. ¹H NMR (CDCl₃): δ 7.20 (d, *J* = 8.4 Hz, 1H), 7.01-6.99 (m, 2H), 3.58 (s, 2H), 2.30 (s, 3H), 2.28 (s, 3H). ¹³C NMR (CDCl₃): δ 138.23, 135.90, 131.54, 128.61, 127.39, 125.53,

117.93, 21.54, 21.05, 19.30. Anal. Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.37; H, 7.67; N, 9.68.

(2-Isopropyl-phenyl)-acetonitrile (Table 1, entry 16). 1-Bromo-2-isopropyl-benzene (199 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), $PtBu_3$ (8.1 mg, 0.0400 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 110 mg (69%) of (2-isopropyl-phenyl)-acetonitrile. 1H NMR ($CDCl_3$): δ 7.34-7.32 (m, 3H), 7.21-7.17 (m, 1H), 3.73 (s, 2H), 3.05 (sep, J = 6.8 Hz, 1H), 1.26 (d, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 146.68, 129.21, 128.93, 127.13, 126.56, 126.05, 118.27, 29.43, 23.58, 21.48. Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.03; H, 8.41; N, 8.54.

(2-Cyclohexyl-phenyl)-acetonitrile (Table 1, entry 17). 1-Bromo-2-cyclohexyl-benzene (239 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), $PtBu_3$ (8.1 mg, 0.0400 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 141 mg (71%) of (2-cyclohexyl-phenyl)-acetonitrile. 1H NMR ($CDCl_3$): δ 7.34-7.16 (m, 4H), 3.73 (s, 2H), 2.62-2.57 (m, 1H), 1.88-1.75 (m, 5H), 1.51-1.22 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 146.04, 129.52, 129.10, 127.55, 127.05, 126.80, 118.86, 40.61, 34.29, 27.31, 26.49, 21.86. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.39; H, 8.64; N, 6.95.

(2,6-Dimethyl-phenyl)-acetonitrile (Table 1, entry 18). 2-Bromo-1,3-dimethylbenzene (185 mg, 1.00 mmol), trimethylsilyl acetonitrile (136 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), PtBu₃ (8.1 mg, 0.0400 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 122 mg (84%) of (2,6-dimethyl-phenyl)-acetonitrile. ¹H NMR (CDCl₃): δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 2H), 3.60 (s, 2H), 2.36 (s, 6H). ¹³C NMR (CDCl₃): δ 136.70, 128.67, 128.23, 127.57, 117.36, 20.07, 17.71. Anal. Calcd for C₁₀H₁₁N: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.76; H, 7.66; N, 9.49.

Spectral and Analytical Data for Previously Unpublished Compounds in Table 2.

2-(4-tert-Butyl-phenyl)-propionitrile (Table 2, Entry 1). 1-Bromo-4-tert-butylbenzene (213 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 144 mg (77%) of 2-(4-tert-butyl-phenyl)-propionitrile. ¹H NMR (CDCl₃): δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.86 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.2 Hz, 3H), 1.31 (s, 9H). ¹³C NMR (CDCl₃): δ 151.07, 134.11, 126.46, 126.09, 121.84, 34.60, 31.34, 30.78, 21.43. Anal. Calcd for C₁₃H₁₇N: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.08; H, 9.18; N, 7.45.

2-(4-Methoxy-phenyl)-propionitrile (Table 2, Entry 2). 4-Bromo-anisole (187 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used.

The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 90/10) to give 115 mg (71%) of 2-(4-methoxy-phenyl)-propionitrile. ^1H NMR (CDCl_3): δ 7.26 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 3.84 (q, J = 7.0 Hz, 1H), 3.79 (s, 3H), 1.60 (d, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3): δ 159.41, 129.21, 127.95, 122.00, 114.58, 55.45, 30.54, 21.60. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.76; H, 6.42; N, 6.92.

2-(6-Methoxy-naphthalen-2-yl)-propionitrile (Table 2, Entry 3).⁷ 2-Bromo-6-methoxy -naphthalene (237 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 207 mg (98%) of 2-(6-methoxy-naphthalen-2-yl)-propionitrile. ^1H NMR (CDCl_3): δ 7.74-7.67 (m, 3H), 7.35 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.16 (dd, J = 8.4 Hz, 2.8 Hz, 1H), 7.10 (d, J = 2.0 Hz, 1H), 3.98 (q, J = 7.2 Hz, 1H), 3.89 (s, 3H), 1.67 (d, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3): δ 158.19, 134.11, 132.12, 129.41, 128.86, 128.01, 125.48, 125.04, 121.91, 119.67, 105.77, 55.44, 31.31, 21.52.

2-(4-Benzoyl-phenyl)-propionitrile (Table 2, Entry 4). (4-Bromo-phenyl)-phenyl-methanone (261 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 205 mg (87%) of 2-(4-benzoyl-phenyl)-

propionitrile. ^1H NMR (CDCl_3): δ 7.84-7.48 (m, 9H), 4.01 (q, J = 7.2 Hz, 1H), 1.69 (d, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl_3): δ 196.01, 141.49, 137.55, 137.38, 132.84, 131.02, 130.15, 128.55, 126.91, 121.09, 31.40, 21.44. Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.66; H, 5.48; N, 5.77.

4-(Cyano-methyl-methyl)-benzoic acid ethyl ester (Table 2, Entry 5). 4-Bromo-benzoic acid ethyl ester (229 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 85/15) to give 171 mg (84%) of 4-(cyano-methyl-methyl)-benzoic acid ethyl ester. ^1H NMR (CDCl_3): δ 8.07 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 4.39 (q, J = 7.0 Hz, 2H), 3.97 (q, J = 7.0 Hz, 1H), 1.67 (d, J = 7.0 Hz, 3H), 1.40 (t, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3): δ 165.83, 141.84, 130.34, 130.32, 126.77, 120.97, 61.11, 31.16, 21.23, 14.28. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.76; H, 6.42; N, 6.92.

4-(Cyano-methyl-methyl)-benzonitrile (Table 2, Entry 6). 4-Bromo-benzonitrile (182 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 75/25) to give 182 mg (82%) of 4-(Cyano-methyl-methyl)-benzonitrile. ^1H NMR (CDCl_3): δ 7.72 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 4.00 (q, J = 7.0 Hz, 1H), 1.69 (d, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl_3): δ 142.19, 132.94,

127.68, 120.46, 118.19, 112.09, 31.23, 21.06. Anal. Calcd for $C_{10}H_8N_2$: C, 76.90; H, 5.16; N, 17.94. Found: C, 76.75; H, 5.17; N, 17.89.

2-o-Tolyl-propionitrile (Table 2, Entry 7).⁸ 2-Bromo-toluene (171 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), $PtBu_3$ (8.1 mg, 0.0400 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 103 mg (71%) of 2-o-tolyl-propionitrile. 1H NMR ($CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 1H), 7.27-7.15 (m, 3H), 4.02 (q, J = 7.2 Hz, 1H), 2.34(s, 3H), 1.58 (d, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 135.37, 134.88, 131.08, 128.20, 127.06, 126.77, 121.90, 28.23, 20.11, 19.08.

2-(2-Isopropyl-phenyl)-propionitrile (Table 2, Entry 8). 1-Bromo-2-isopropylbenzene (199 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), $PtBu_3$ (8.1 mg, 0.0400 mmol), and ZnF_2 (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 104 mg (60%) of 2-(2-isopropyl-phenyl)-propionitrile. 1H NMR ($CDCl_3$): δ 7.48 (d, J = 7.6 Hz, 1H), 7.35-7.32 (m, 2H), 7.26-7.24 (m, 1H), 4.30 (q, J = 7.2 Hz, 1H), 3.12 (sep, J = 6.8 Hz, 1H), 1.65 (d, J = 7.2 Hz, 3H), 1.31 (d, J = 6.8 Hz, 3H), 1.30 (d, J = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 145.62, 134.10, 128.67, 127.30, 126.82, 126.33, 122.44, 28.98, 27.81, 24.56, 23.82, 21.59. Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.90; H, 8.76; N, 7.89.

2-(2-Cyclohexyl-phenyl)-propionitrile (Table 2, Entry 9). 1-Bromo-2-cyclohexylbenzene (239 mg, 1.00 mmol), 2-trimethylsilyl-propionitrile (152 mg, 1.20 mmol), Pd₂dba₃ (9.1 mg, 0.010 mmol), PtBu₃ (8.1 mg, 0.0400 mmol), and ZnF₂ (62.0 mg, 0.600 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95/5) to give 136 mg (64%) of 2-(2-Cyclohexyl-phenyl)-propionitrile. ¹H NMR (CDCl₃): δ 7.37 (d, *J* = 8.0 Hz, 1H), 7.22-7.14 (m, 3H), 4.08 (q, *J* = 7.5 Hz, 1H), 2.57-2.54 (m, 1H), 1.82-1.67 (m, 5H), 1.55 (d, *J* = 7.5 Hz, 3H), 1.39-1.32 (m, 5H). ¹³C NMR (CDCl₃): δ 144.75, 134.28, 128.55, 127.37, 127.10, 126.78, 122.43, 40.00, 34.99, 34.24, 27.93, 27.23, 27.19, 26.27, 21.65. Anal. Calcd for C₁₅H₁₉N: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.45; H, 9.12; N, 6.56.

Representative procedure for the arylation of cyclohexanecarbonitrile (Table 3, Entry 1).⁹ To a screw-capped vial containing Xantphos (11.6 mg, 0.0200 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol) and bromobenzene (157 mg, 1.00 mmol) in DMF (1.0 mL) was added trimethylsilylcyclohexanecarbonitrile **5** (217 mg, 1.20 mmol), followed by KF (70.0 mg, 1.20 mmol). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The heterogeneous reaction mixture was stirred at 90 ° C for 24 h. The crude reaction was then allowed to cool to room temperature and was diluted with Et₂O (50 mL). The resulting solution was washed with H₂O. The organic phase was dried over Na₂SO₄, filtered, and concentrated at reduced pressure. The residue was then The crude product was purified by chromatography on silica gel, eluting with hexane/ethyl acetate (95:5) to provide the title compound (125 mg) in 68% yield. ¹H NMR (CDCl₃): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz,

1H), 1.99 (d, J = 11.0 Hz, 2H), 1.77-1.55 (m, 7H), 1.21-1.04 (m, 1H). ^{13}C NMR (CDCl_3): δ 141.59, 129.00, 127.93, 125.70, 122.85, 44.49, 37.50, 25.14, 23.75.

Spectral and Analytical Data for Previously Unpublished Compounds in Table 3.

1-(4-tert-Butyl-phenyl)-cyclohexanecarbonitrile (Table 3, Entry 2). 1-Bromo-4-tert-butyl-benzene (213 mg, 1.00 mmol), trimethylsilylcyclohexanecarbonitrile (217 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and KF (70.0 mg, 1.20 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ ethyl acetate = 95/5) to give 149 mg (62%) of 1-(4-tert-butyl-phenyl)-cyclohexanecarbonitrile. ^1H NMR (CDCl_3): δ 7.41 (s, 4H), 2.14 (d, J = 11.2 Hz, 2H), 1.92-1.68 (m, 7H), 1.39-1.20 (m + s, 1H + 9H). ^{13}C NMR (CDCl_3): δ 150.92, 138.65, 125.95, 125.43, 123.06, 43.96, 37.55, 34.66, 31.46, 25.23, 23.83. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.35; H, 9.61; N, 5.78.

1-(4-Methoxy-phenyl)-cyclohexanecarbonitrile (Table 3, Entry 3). 4-Bromoanisole (187 mg, 1.00 mmol), trimethylsilylcyclohexanecarbonitrile (217 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and KF (70.0 mg, 1.20 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ ethyl acetate = 90/10) to give 165 mg (77%) of 1-(4-methoxy-phenyl)-cyclohexanecarbonitrile. ^1H NMR (CDCl_3): δ 7.39 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 2.13 (d, J = 12.5 Hz, 2H), 1.92-1.65 (m, 7H), 1.34-1.17 (m, 1H). ^{13}C NMR (CDCl_3): δ 159.14, 133.73, 126.80, 123.18, 114.26, 55.44, 43.63, 37.63, 25.13,

23.77. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.32; H, 8.10; N, 6.42.

4-(1-Cyano-cyclohexyl)-benzoic acid ethyl ester (Table 3, Entry 4). 4-Bromo-benzoic acid ethyl ester (229 mg, 1.00 mmol), trimethylsilylcyclohexanecarbonitrile (217 mg, 1.20 mmol), Pd_2dba_3 (9.1 mg, 0.010 mmol), Xantphos (11.6 mg, 0.0200 mmol), and KF (70.0 mg, 1.20 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ ethyl acetate = 85/15) to give 216 mg (84%) of 4-(1-cyano-cyclohexyl)-benzoic acid ethyl ester. 1H NMR ($CDCl_3$): δ 8.06 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 2.16 (d, J = 11.6 Hz, 2H), 1.96-1.71 (m, 7H), 1.40 (t, J = 7.2 Hz, 3H), 1.36-1.20 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 166.16, 146.32, 130.31, 125.84, 122.29, 61.26, 44.77, 37.39, 25.05, 23.66, 14.48. (One aromatic carbon or $-CN$ carbon is missing and may overlap with other carbon peaks). ^{13}C NMR [$(CD_3)_2CO$]: δ 166.77, 140.10, 131.60, 131.34, 127.36, 123.28, 62.18, 45.98, 38.19, 25.96, 24.94, 15.20. Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.80; H, 7.48; N, 5.39.

Representative procedure for the arylation of secondary nitriles. 2-(3,4-Dimethoxyphenyl)-2-isopropyl octanenitrile (Table 4, entry 1). To a screw-capped vial containing $HNiPr_2$ (141 mg, 1.40 mmol) in ether (1.0 mL) was added $n-BuLi$ (0.62 mL, 1.4 mmol). The reaction mixture was allowed to stir at room temperature for 10 min, at which time nitrile **6** (234 mg, 1.40 mmol) in ether (1.0 mL) was added. After stirring at room temperature for 2 h, the volatile materials were removed under vacuum (0.1 torr).

The residue was redissolved in THF (1.0 mL), and the solution was added to another screw-capped vial containing P^tBu_3 (8.0 mg, 0.040 mmol), $Pd_2(dba)_3$ (9.1 mg, 0.010 mmol), $ZnCl_2$ (191 mg, 1.40 mmol) and 4-bromoveratrole (217 mg, 1.00 mmol) in THF (0.5 mL). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred at 23 °C for 12 h. The crude reaction was then allowed to cool to room temperature and was diluted with Et_2O (50 mL). The resulting solution was washed with H_2O . The organic phase was dried over Na_2SO_4 , filtered, and concentrated at reduced pressure. The residue was then purified by chromatography on silica gel, eluting with a 5% gradient of $EtOAc$ in hexane to provide the title compound (203 mg) in 68% yield. 1H NMR ($CDCl_3$): δ 6.90 (dd, $J = 9.0$ Hz, 2.5 Hz, 1H), 6.84 (d, $J = 9.0$ Hz, 1H), 6.83 (d, $J = 2.5$ Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 2.11-2.00 (m, 2H), 1.79-1.71 (m, 1H), 1.39-1.13 (m, 7H), 1.17 (d, $J = 6.5$ Hz, 3H), 0.99-0.88 (m, 1H), 0.82 (t, $J = 7.0$ Hz, 3H), 0.78 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 148.92, 148.17, 130.85, 121.59, 118.73, 111.00, 109.62, 55.99, 55.86, 53.43, 37.86 (big peak with two $-CH_3$ on isopropyl), 31.47, 29.22, 25.48, 22.51, 18.93, 18.58, 13.99. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.16; H, 9.78; N, 4.63.

Spectral and Analytical Data for Previously Unpublished Compounds in Table 4.

2-Isopropyl-2-(4-methoxy-phenyl)-octanenitrile (Table 4, entry 2). $HNiPr_2$ (141 mg, 1.40 mmol), $n-BuLi$ (0.62 mL, 1.4 mmol), nitrile **6** (234 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $Pd_2(dba)_3$ (9.1 mg, 0.010 mmol), $ZnCl_2$ (191 mg, 1.40 mmol), and 4-bromoanisole (217 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 90/10) to give 197 mg (72%)

of 2-isopropyl-2-(4-methoxy-phenyl)-octanenitrile. ^1H NMR (CDCl_3): δ 7.19 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.5$ Hz, 2H), 3.74 (s, 3H), 2.05-1.93 (m, 2H), 1.76-1.65 (m, 1H), 1.33-1.05 (m, 7H), 1.09 (d, $J = 6.6$ Hz, 3H), 0.92-0.79 (m, 1H), 0.75 (t, $J = 7.0$ Hz, 3H), 0.70 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 158.91, 130.44, 127.68, 121.89, 114.09, 55.44, 53.22, 37.98, 37.96, 31.70, 29.44, 25.70, 22.72, 19.04, 18.77, 14.18. Anal. Calcd for $\text{C}_{18}\text{H}_{27}\text{NO}$: C, 79.07; H, 9.95; N, 5.12. Found: C, 79.22; H, 10.06; N, 5.01.

2-(4-Dimethylamino-phenyl)-2-isopropyl-octanenitrile (Table 4, entry 3). HNiPr_2 (141 mg, 1.40 mmol), $n\text{-BuLi}$ (0.62 mL, 1.4 mmol), nitrile **6** (234 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol), ZnCl_2 (191 mg, 1.40 mmol), and (4-bromo-phenyl)-dimethyl-amine (200 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 90/10) to give 197 mg (69%) of 2-(4-dimethylamino-phenyl)-2-isopropyl-octanenitrile. ^1H NMR (CDCl_3): δ 7.11 (d, $J = 9.0$ Hz, 2H), 6.62 (d, $J = 9.0$ Hz, 2H), 2.87 (s, 6H), 2.01-1.92 (m, 2H), 1.74-1.66 (m, 1H), 1.32-1.02 (m, 7H), 1.07 (d, $J = 7.0$ Hz, 3H), 0.98-0.86 (m, 1H), 0.75 (t, $J = 7.0$ Hz, 3H), 0.71 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 149.72, 127.32, 125.79, 122.25, 112.39, 52.91, 40.59, 37.92, 37.80, 31.71, 29.50, 25.71, 22.74, 19.02, 18.76, 14.18. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{N}_2$: C, 79.66; H, 10.56; N, 9.78. Found: C, 79.58; H, 10.67; N, 9.57.

2-(4-tert-Butyl-phenyl)-2-isopropyl-octanenitrile (Table 4, entry 4). HNiPr_2 (141 mg, 1.40 mmol), $n\text{-BuLi}$ (0.62 mL, 1.4 mmol), nitrile **6** (234 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol), ZnCl_2 (191 mg, 1.40 mmol), and 1-

bromo-4-tert-butyl-benzene (213 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 254 mg (85%) of 2-(4-tert-Butyl-phenyl)-2-isopropyl-octanenitrile. ^1H NMR (CDCl_3): δ 7.28 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 2.05-1.90 (m, 2H), 1.78-1.69 (m, 1H), 1.31-1.05 (m, 7H), 1.10 (d, $J = 6.6$ Hz, 3H), 1.25 (s, 9H), 0.95-0.80 (m, 1H), 0.76 (t, $J = 7.0$ Hz, 3H), 0.70 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 150.49, 135.30, 126.28, 125.64, 121.92, 53.52, 37.88, 37.80, 34.66, 31.69, 31.53, 29.50, 25.69, 22.78, 19.14, 18.78, 14.21. Anal. Calcd for $\text{C}_{21}\text{H}_{33}\text{N}$: C, 84.22; H, 11.11; N, 4.68. Found: C, 84.05; H, 11.30; N, 4.80.

2-Isopropyl-2-(6-methoxy-naphthalen-2-yl)-octanenitrile (Table 4, entry 5). HNiPr_2 (141 mg, 1.40 mmol), $n\text{-BuLi}$ (0.62 mL, 1.4 mmol), nitrile **6** (234 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol), ZnCl_2 (191 mg, 1.40 mmol), and 2-bromo-6-methoxy-naphthalene (237 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 262 mg (81%) of 2-isopropyl-2-(6-methoxy-naphthalen-2-yl)-octanenitrile. ^1H NMR (CDCl_3): δ 7.88 (d, $J = 2.0$ Hz, 1H), 7.78 (t, $J = 8.5$ Hz, 2H), 7.35 (dd, $J = 8.5$ Hz, 2.0 Hz, 1H), 7.21 (dd, $J = 8.5$ Hz, 2.5 Hz, 1H), 7.15 (d, $J = 2.5$ Hz, 1H), 3.92 (s, 3H), 2.25-2.14 (m, 2H), 1.96-1.88 (m, 1H), 1.46-1.11 (m, 7H), 1.14 (d, $J = 7.0$ Hz, 3H), 0.98-0.88 (m, 1H), 0.82 (t, $J = 7.0$ Hz, 3H), 0.81 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 158.19, 133.85, 133.50, 129.72, 128.63, 127.65, 126.31, 123.73, 121.71, 119.49, 105.65, 55.48, 54.00, 37.86, 37.69, 31.60, 29.39, 25.78, 22.65, 19.20, 18.75, 14.11. Anal. Calcd for $\text{C}_{22}\text{H}_{29}\text{NO}$: C, 81.69; H, 9.04; N, 4.33. Found: C, 81.33; H, 9.18; N, 4.35.

2-(4-Benzoyl-phenyl)-2-isopropyl-octanenitrile (Table 4, entry 6). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), nitrile **6** (234 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and (4-bromo-phenyl)-phenyl-methanone (261 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 271 mg (78%) of 2-(4-benzoyl-phenyl)-2-isopropyl-octanenitrile. ¹H NMR (CDCl₃): δ 7.79-7.71 (m, 4H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.45-7.39 (m, 4H), 2.15-2.03 (m, 2H), 1.85-1.74 (m, 1H), 1.38-1.02 (m, 7H), 1.15 (d, *J* = 7.0 Hz, 3H), 0.92-0.78 (m, 1H), 0.77 (t, *J* = 7.0 Hz, 3H), 0.74 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃): δ 196.11, 143.37, 137.49, 136.93, 132.77, 130.63, 130.16, 128.53, 126.64, 121.04, 54.23, 37.93, 37.91, 31.59, 29.35, 25.71, 22.67, 19.13, 18.72, 14.13. Anal. Calcd for C₂₄H₂₉NO: C, 82.95; H, 8.41; N, 4.03. Found: C, 82.97; H, 8.64; N, 3.84.

4-(1-Cyano-1-isopropyl-heptyl)-benzoic acid ethyl ester (Table 4, entry 7). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), nitrile **6** (234 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and 4-bromo-benzoic acid ethyl ester (229 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (toluene/CH₂Cl₂ 75/25) to give 148 mg (47%) of 4-(1-cyano-1-isopropyl-heptyl)-benzoic acid ethyl ester. ¹H NMR (CDCl₃): δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.19-2.08 (m, 2H), 1.88-1.76 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.37-1.10 (m, 7H), 1.15 (d, *J* = 6.6 Hz, 3H), 0.95-0.80 (m, 1H), 0.82 (t, *J* = 6.8 Hz, 3H), 0.76 (d, *J* = 6.6 Hz, 3H). ¹³C NMR

(CDCl₃): δ 166.30, 143.75, 130.14, 130.09, 126.70, 121.10, 61.33, 54.28, 38.03, 38.00, 31.64, 29.39, 25.72, 22.70, 19.10, 18.75, 14.56, 14.16. Anal. Calcd for C₂₀H₂₉NO₂: C, 76.15; H, 9.27; N, 4.44. Found: C, 76.01; H, 9.47; N, 4.20.

2-(4-Benzoyl-phenyl)-2-(2-[1,3]dioxolan-2-yl-ethyl)-3-methyl-butyronitrile (Table 4, entry 8). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), nitrile **9** (256 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and (4-bromo-phenyl)-phenyl-methanone (261 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 90/10) to give 312 mg (86%) of 2-(4-benzoyl-phenyl)-2-(2-[1,3]dioxolan-2-yl-ethyl)-3-methyl-butyronitrile. ¹H NMR (CDCl₃): δ 7.86-7.75 (m, 4H), 7.63-7.57 (m, 1H), 7.54-7.45 (m, 4H), 4.82 (t, *J* = 4.6 Hz, 1H), 3.94-3.88 (m, 2H), 3.85-3.78 (m, 2H), 2.33 (td, *J* = 13.0 Hz, 4.0 Hz, 1H), 2.18 (sep, *J* = 6.5 Hz, 1H), 2.04 (td, *J* = 13.0 Hz, 4.0 Hz, 1H), 1.83-1.72 (m, 1H), 1.36-1.24 (m, 1H), 1.23 (d, *J* = 6.5 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (CDCl₃): δ 195.91, 142.63, 137.32, 137.04, 132.72, 130.63, 130.06, 128.46, 126.59, 120.54, 103.45, 65.01, 64.99, 53.65, 37.94, 31.69, 30.10, 19.09, 18.62. Anal. Calcd for C₂₃H₂₅NO₃: C, 76.01; H, 6.93; N, 3.85. Found: C, 76.30; H, 7.14; N, 3.45.

2-(3,4-Dimethoxy-phenyl)-2-(2-[1,3]dioxolan-2-yl-ethyl)-3-methyl-butyronitrile

(Table 4, entry 9). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), nitrile **9** (256 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and 4-bromoveratrole (217 mg, 1.00 mmol) were used. The

crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 90/10) to give 261 mg (82%) of 2-(3,4-dimethoxy-phenyl)-2-(2-[1,3]dioxolan-2-yl-ethyl)-3-methyl-butyronitrile. ^1H NMR (CDCl_3): δ 6.92 (dd, $J = 8.5$ Hz, 2.0 Hz, 1H), 6.85 (d, $J = 2.0$ Hz, 1H), 6.84 (d, $J = 8.5$ Hz, 1H), 4.80 (t, $J = 4.5$ Hz, 1H), 3.93-3.86 (m, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.83-3.77 (m, 2H), 2.25 (td, $J = 13.0$ Hz, 4.5 Hz, 1H), 2.08 (sep, $J = 6.5$ Hz, 1H), 1.92 (td, $J = 13.0$ Hz, 4.5 Hz, 1H), 1.74 (tt, $J = 13.0$ Hz, 4.5 Hz, 1H), 1.32 (td, $J = 13.0$ Hz, 4.5 Hz, 1H), 1.18 (d, $J = 6.5$ Hz, 3H), 0.80 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 149.13, 148.42, 130.30, 121.26, 118.90, 111.25, 109.70, 103.72, 65.00, 64.96, 56.08, 55.99, 53.04, 38.05, 31.83, 30.10, 19.09, 18.64. Anal. Calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_4$: C, 67.69; H, 7.89; N, 4.39. Found: C, 67.41; H, 7.90; N, 4.32.

2-(4-tert-Butyl-phenyl)-2-(2-[1,3]dioxolan-2-yl-ethyl)-3-methyl-butyronitrile (Table 4, entry 10). HNiPr_2 (141 mg, 1.40 mmol), $n\text{-BuLi}$ (0.62 mL, 1.4 mmol), nitrile **9** (256 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol), ZnCl_2 (191 mg, 1.40 mmol), and 1-bromo-4-tert-butyl-benzene (213 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 239 mg (76%) of 2-(4-tert-butyl-phenyl)-2-(2-[1,3]dioxolan-2-yl-ethyl)-3-methyl-butyronitrile. ^1H NMR (CDCl_3): δ 7.28 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.5$ Hz, 2H), 4.73 (t, $J = 4.5$ Hz, 1H), 3.88-3.80 (m, 2H), 3.78-3.70 (m, 2H), 2.18 (td, $J = 13.0$ Hz, 4.0 Hz, 1H), 2.03 (sep, $J = 6.5$ Hz, 1H), 1.89 (td, $J = 13.0$ Hz, 4.0 Hz, 1H), 1.65 (tt, $J = 13.0$ Hz, 4.0 Hz, 1H), 1.31-1.21 (m, 1H), 1.23 (s, 9H), 1.11 (d, $J = 6.5$ Hz, 3H), 0.72 (d, $J = 6.5$ Hz, 3H). ^{13}C NMR (CDCl_3): δ 150.65, 134.67, 126.23, 125.79, 121.38, 103.90, 65.06, 65.02, 53.03, 37.95, 34.62, 31.82, 31.47, 30.20, 19.19, 18.72.

1-(4-Dimethylamino-phenyl)-cyclohexanecarbonitrile (Table 4, entry 12). HNiPr_2 (141 mg, 1.40 mmol), $n\text{-BuLi}$ (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol), ZnCl_2 (191 mg, 1.40 mmol), and 1-bromo-4-dimethylamino-benzene (200 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 90/10) to give 187 mg (82%) of 1-(4-dimethylamino-phenyl)-cyclohexanecarbonitrile. ^1H NMR (CDCl_3): δ 7.25 (d, $J = 9.0$ Hz, 2H), 6.64 (d, $J = 9.0$ Hz, 2H), 2.86 (s, 6H), 2.05 (d, $J = 13.0$ Hz, 2H), 1.79-1.67 (m, 5H), 1.67-1.57 (m, 2H), 1.22-1.12 (m, 1H). ^{13}C NMR (CDCl_3): δ 150.07, 129.20, 126.37, 123.42, 112.63, 43.36, 40.61, 37.63, 25.22, 23.84. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{N}_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.74; H, 8.98; N, 12.03.

1-(6-Methoxy-naphthalen-2-yl)-cyclohexanecarbonitrile (Table 4, entry 14). HNiPr_2 (141 mg, 1.40 mmol), $n\text{-BuLi}$ (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $\text{Pd}_2(\text{dba})_3$ (9.1 mg, 0.010 mmol), ZnCl_2 (191 mg, 1.40 mmol), and 2-bromo-6-methoxy-naphthalene (237 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 214 mg (81%) of 1-(6-Methoxy-naphthalen-2-yl)-cyclohexanecarbonitrile. ^1H NMR (CDCl_3): δ 7.89 (d, $J = 2.0$ Hz, 1H), 7.77 (d, $J = 8.5$ Hz, 1H), 7.76 (d, $J = 8.5$ Hz, 1H), 7.55 (dd, $J = 8.5$ Hz, 2.0 Hz, 1H), 7.20 (d, $J = 8.5$ Hz, 2.5 Hz, 1H), 7.14 (d, $J = 2.5$ Hz, 1H), 3.94 (s, 3H), 2.24 (d, $J = 9.4$ Hz, 2H), 1.98-1.81 (m, 7H), 1.40-1.25 (m, 1H). ^{13}C NMR (CDCl_3): δ 158.23, 136.59, 134.04, 129.74, 128.81,

127.68, 124.30, 124.26, 123.05, 119.55, 105.63, 55.48, 44.41, 37.48, 25.21, 23.82. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.09; H, 7.10; N, 5.23.

4-(1-Cyano-cyclohexyl)-benzonitrile (Table 4, entry 15). $HNiPr_2$ (141 mg, 1.40 mmol), $n-BuLi$ (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $Pd_2(dba)_3$ (9.1 mg, 0.010 mmol), $ZnCl_2$ (191 mg, 1.40 mmol), and 4-bromo-benzonitrile (182 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 75/25) to give 149 mg (71%) of 4-(1-cyano-cyclohexyl)-benzonitrile. 1H NMR ($CDCl_3$): δ 7.71 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 9.0 Hz, 2H), 2.15 (d, J = 12.0 Hz, 2H), 1.95-1.73 (m, 7H), 1.35-1.25 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 146.70, 132.96, 126.80, 121.79, 118.44, 112.23, 44.97, 37.35, 24.99, 23.62. Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.59; H, 6.76; N, 12.88.

1-(4-Benzoyl-phenyl)-cyclohexanecarbonitrile (Table 4, entry 16). $HNiPr_2$ (141 mg, 1.40 mmol), $n-BuLi$ (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu_3 (8.0 mg, 0.040 mmol), $Pd_2(dba)_3$ (9.1 mg, 0.010 mmol), $ZnCl_2$ (191 mg, 1.40 mmol), and (4-bromo-phenyl)-phenyl-methanone (261 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 90/10) to give 217 mg (75%) of 1-(4-benzoyl-phenyl)-cyclohexanecarbonitrile. 1H NMR ($CDCl_3$): δ 7.86-7.79 (m, 4H), 7.66-7.59 (m, 3H), 7.51 (t, J = 8.0 Hz, 2H), 2.20 (d, J = 12.0 Hz, 2H), 1.98-1.76 (m, 7H), 1.40-1.25 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 196.07, 145.89, 137.48, 137.29, 132.79, 130.79, 130.18, 128.54, 125.83, 122.32, 44.77, 37.38,

25.05, 23.67. Anal. Calcd for C₂₀H₁₉NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 82.99; H, 6.71; N, 4.79.

1-o-Tolyl-cyclohexanecarbonitrile (Table 4, entry 18). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and o-bromotoluene (171 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 173 mg (87%) of 1-o-tolyl-cyclohexanecarbonitrile. ¹H NMR (CDCl₃): δ 7.24-7.10 (m, 4H), 2.57 (s, 3H), 2.29 (d, *J* = 13.0 Hz, 2H), 1.90-1.73 (m, 5H), 1.63 (td, *J* = 12.5 Hz, 4.0 Hz, 2H), 1.25-1.10 (m, 1H). ¹³C NMR (CDCl₃): δ 138.56, 136.83, 133.00, 127.94, 126.59, 125.01, 122.45, 41.90, 36.08, 25.33, 23.52, 21.36. Anal. Calcd for C₁₄H₁₇N: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.03; H, 8.64; N, 6.94.

1-(5-tert-Butyl-2-methyl-phenyl)-cyclohexanecarbonitrile (Table 4, entry 19). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and 2-bromo-4-tert-butyl-1-methyl-benzene (227 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 255 mg (91%) of 1-(5-tert-butyl-2-methyl-phenyl)-cyclohexanecarbonitrile. ¹H NMR (CDCl₃): δ 7.38 (d, *J* = 2.0 Hz, 1H), 7.30 (dd, *J* = 7.5 Hz, 2.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 2.66 (s, 3H), 2.43 (d, *J* = 13.0 Hz, 2H), 2.03-1.83 (m, 5H), 1.78 (td, *J* = 13.0 Hz, 4.0 Hz, 2H), 1.38-1.30 (m, 1H), 1.36 (s, 9H). ¹³C

NMR (CDCl₃): δ 149.23, 137.88, 133.55, 132.67, 124.75, 122.48, 121.91, 42.17, 36.02, 34.78, 31.52, 25.28, 23.52, 20.80. Anal. Calcd for C₁₈H₂₅N: C, 84.65; H, 9.87; N, 5.48. Found: C, 84.62; H, 9.96; N, 5.45.

1-Naphthalen-1-yl-cyclohexanecarbonitrile (Table 4, entry 20). HNiPr₂ (141 mg, 1.40 mmol), n-BuLi (0.62 mL, 1.4 mmol), cyclohexanecarbonitrile (153 mg, 1.40 mmol), P^tBu₃ (8.0 mg, 0.040 mmol), Pd₂(dba)₃ (9.1 mg, 0.010 mmol), ZnCl₂ (191 mg, 1.40 mmol), and 1-bromo-naphthalene (207 mg, 1.00 mmol) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 95/5) to give 214 mg (91%) of 1-naphthalen-1-yl-cyclohexanecarbonitrile. ¹H NMR (CDCl₃): δ 8.61 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.63 (ddd, *J* = 8.5 Hz, 7.5 Hz, 1.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 2.69 (d, *J* = 13.0 Hz, 2H), 2.16-2.03 (m, 2H), 2.00-1.89 (m, 3H), 1.84 (td, *J* = 13.0 Hz, 2.7 Hz, 2H), 1.39-1.28 (m, 1H). ¹³C NMR (CDCl₃): δ 136.35, 134.80, 130.41, 129.67, 129.52, 126.22, 125.79, 125.20, 124.72, 123.01, 122.92, 41.42, 36.92, 25.52, 23.57. Anal. Calcd for C₁₇H₁₇N: C, 86.77; H, 7.28; N, 5.95. Found: C, 86.74; H, 7.24; N, 5.97.

2-(2-[1,3]Dioxolan-2-yl-ethyl)-3-methyl-butyronitrile (9, Scheme 3) To LDA (2.32 g, 21.0 mmol) in THF (30 mL) was added nitrile **7** (1.66 g, 20.0 mmol) dropwise at 23 °C. The reaction mixture was allowed to stir at 23 °C for 2 hr. The solution was then cooled to 0 °C and alkyl bromide **8** (2.90 mL, 24.0 mmol) was added dropwise. After stirring at 23 °C for 24 h, the reaction mixture was quenched by adding water (100 mL). The

aqueous solution was extracted by ether (3×50 mL). The combined organic solution was washed with brine, dried over Na_2SO_4 , and concentrated at reduced pressure. The residue was then purified by chromatography on silica gel, eluting with hexane/ethyl acetate (95/5 then 75/25) to provide the title compound (3.10 g) in 85% yield. ^1H NMR (CDCl_3): δ 4.90 (t, $J = 4.5$ Hz, 1H), 4.00-3.90 (m, 2H), 3.90-3.81 (m, 2H), 2.52-2.46 (m, 1H), 1.97-1.81 (m, 2H), 1.80-1.63 (m, 3H), 1.05 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR (CDCl_3): δ 121.11, 103.75, 65.16, 65.11, 37.19, 31.69, 30.27, 24.48, 21.09, 18.81.

Verapamil (1)¹⁰ The mixture of **10** (28.2 mg, 0.0884 mmol), **11** (17.2 mg, 0.0884 mmol), Pd 5 w% in carbon (19.0 mg, 0.00884 mmol), formic acid (0.1 mL), and water (0.1 mL) in ethanol (0.5 mL) was heated at 100 °C for 18 hr. The reaction mixture was cooled to 23 °C, then was added KOH (1M solution) until basic. The aqueous mixture was diluted with water then was extracted by ether (3×50 mL). The combined organic solution was washed with brine, dried over Na_2SO_4 , and concentrated at reduced pressure. The residue was then purified by chromatography on silica gel, eluting with $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{NEt}_3$ (98/2/1) to provide the title compound (33.3 mg) in 83% yield. ^1H NMR (CDCl_3): δ 6.94 (dd, $J = 8.0$ Hz, 2.0 Hz, 1 H), 6.89 (d, $J = 2.0$ Hz, 1 H), 6.84 (d, $J = 8.0$ Hz, 1 H), 6.79 (d, $J = 8.0$ Hz, 1 H), 6.71 (d, $J = 2.0$ Hz, 1 H), 6.68 (dd, $J = 8.0$ Hz, 2.0 Hz, 1 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 3.85 (s, 3 H), 2.70-2.64 (m, 2 H), 2.54-2.50 (m, 2 H), 2.38-2.34 (m, 2 H), 2.18 (s, 3 H), 2.13-2.09 (m, 1 H), 2.07 (sep, $J = 7.0$ Hz, 1H), 1.85-1.81 (m, 1 H), 1.57-1.52 (m, 1 H), 1.21-1.17 (m, 1H), 1.13 (d, $J = 7.0$ Hz, 3H), 0.80 (d, $J = 7.0$ Hz, 3 H). ^{13}C NMR (CDCl_3): δ 149.13, 148.96, 148.39, 147.46, 132.91, 130.77,

121.62, 120.65, 118.81, 112.10, 111.33, 111.18, 109.62, 59.49, 56.94, 56.14, 56.07, 56.04, 56.00, 53.53, 41.98, 38.11, 35.73, 33.18, 23.36, 19.15, 18.79.

Procedure for the stoichiometric reactions of the silylnitriles with isolated arylpalladium halide complexes. To a screw-capped vial was added Palladium complex **13**¹¹ (4.6 mg, 0.010 mmol), trimethylsilylacetonitrile (23.0 mg, 0.200 mmol, 20 equiv), ZnF₂ (21.0 mg, 0.200 mmol, 20 equiv), and dodecane (10 mg) followed by DMF (0.2 mL). The vial was sealed with a cap containing a PTFE septum and removed from the drybox. The reaction mixture was stirred at 90 °C for 0.5 h. The mixture was then cooled to room temperature and analyzed by GC and ³¹P NMR spectroscopy.

Precedure for the synthesis of complex 13.¹² A mixture of Pd(OAc)₂ (112 mg, 0.500 mmol) and PtBu₃ (101 mg, 0.500 mmol) in toluene (5 mL) was heated at 90 °C for 10 min. The mixture was then cooled to room temperature, and the volatile materials were evaporated under vacuum. The residue was dissolved in ether and filtered through Celite. The clear filtrate was then concentrated until solid began to form and was then cooled at -35 °C for 12 h. The supernatant was removed by pipette, and the solid was washed with pentane and dried under vacuum to give complex **13** as white solid (43 mg, 23%). ¹H NMR (CDCl₃): δ 1.88 (s, 3H), 1.50 (d, *J* = 14.0 Hz, 18H), 1.44 (d, *J* = 15.0 Hz, 6H), 1.07 (s, 2H). ³¹P NMR (CDCl₃): δ -8.50.

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