

Electronic Supplementary Information

Iridium-Catalysed Hydrosilylation of Cyclopropanes via Regioselective Carbon–Carbon Bond Cleavage

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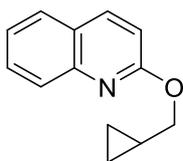
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Table of Contents

1. General Methods	S2
2. Preparation of Cyclopropanes Having Nitrogen-Based Directing Groups	S2
3. General Procedure for Iridium-Catalyzed Hydrosilylation of Cyclopropanes with Silanes	S9
4. References	S15
5. Deuterium-Labeling Experiments	S16
6. ¹ H NMR and ¹³ C-NMR Spectra of Selected Compounds	S17

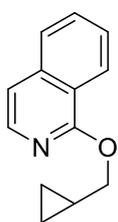
1. General Methods. All reactions were carried out in dry solvent under an argon atmosphere. 1,4-Dioxane was purchased from Wako Pure Chemical Industries, and degassed with an argon gas for 20 min before use. $[\text{IrCl}(\text{cod})]_2$ and Et_3SiH were purchased from Tokyo Chemical Industry. Et_3SiD (97%-*d*) was purchased from Sigma-Aldrich. Unless otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. 2-(Cyclopropylmethoxy)pyridine **1a**,¹ 2-(1-cyclopropylethyl)pyridine **1f**,² 2-cyclopropylquinoline **1j**,³ 2-[1-(naphthalen-2-yl)ethoxy]pyridine **1l**,⁴ and (phoxymethyl)cyclopropane **3**⁵ were prepared according to the reported methods. Column chromatography was performed with silica gel 60N (neutral, 40-50 μm) purchased from Kanto Chemical. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL ECS-400 spectrometer. Proton chemical shifts are reported in ppm based on the solvent resonance resulting from incomplete deuteration (CDCl_3 at 7.26 ppm) as the internal standard. ^{13}C NMR was recorded with complete proton decoupling and the chemical shifts are reported relative to CDCl_3 at 77.00 ppm. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sept: septet, m: multiplet. IR spectra were recorded on a SHIMADZU IRAFFINITY-1 100V J. High-resolution mass spectra (HRMS) was measured with JEOL JMS-700 MStation FAB-MS. Melting points were measured on a Yanaco micromelting point apparatus and are uncorrected.

2. Preparation of Cyclopropanes Having Nitrogen-Based Directing Groups



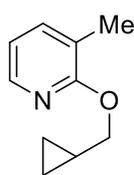
2-(Cyclopropylmethoxy)quinoline (1b): A solution of cyclopropane-methanol (1.05 g, 14.5 mmol) in DMF (26.7 mL) was added NaH (60% oil suspension, 0.59 g, 14.8 mmol) at 0 °C, and the mixture was stirred for 1 h. A solution of 2-chloroquinoline (1.83 g, 11.2 mmol) in DMF (3.0 mL) was added dropwise, and the resultant mixture was stirred at 80 °C for 4 h. The reaction mixture was

quenched with saturated NH_4Cl solution (10 mL), and extracted with EtOAc (20 mL \times 3). The combined organic extracts were dried over MgSO_4 , and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 30 / 1 as the eluent to afford **1b** (2.01 g, 10.1 mmol, 90% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 0.39-0.43 (m, 2H), 0.62-0.67 (m, 2H), 1.30-1.40 (m, 1H), 4.31 (d, $J = 7.2$ Hz, 2H), 6.93 (d, $J = 9.2$ Hz, 1H), 7.36 (dt, $J = 1.2, 7.6$ Hz, 1H), 7.60 (dt, $J = 1.2, 7.6$ Hz, 1H), 7.70 (dd, $J = 1.2, 8.4$ Hz, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.2, 10.1, 70.7, 113.3, 123.8, 125.0, 127.2, 127.4, 129.4, 138.6, 146.6, 162.2. IR (neat / cm^{-1}): 3080, 3005, 2940, 1618, 1605, 1429, 1391, 1310, 1277, 1240, 999, 822. HRMS (FAB $^+$): calcd for $\text{C}_{14}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 200.1075; found. 200.1082.

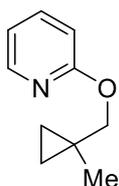


1-(Cyclopropylmethoxy)isoquinoline: Following the procedure for the synthesis of **1b** using cyclopropanemethanol (1.05 g, 14.5 mmol) and 1-chloroisoquinoline (1.83 g, 11.2 mmol), 1.84 g (9.3 mmol, 83% yield) of the title compound was obtained as a colorless oil after purification by flash

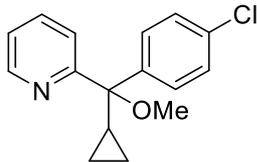
chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.41-0.45 (m, 2H), 0.62-0.67 (m, 2H), 1.37-1.44 (m, 1H), 4.35 (d, $J = 6.8$ Hz, 2H), 7.19 (d, $J = 6.0$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.65 (dt, $J = 1.2, 7.2$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 6.0$ Hz, 1H), 8.32 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.2, 10.1, 70.9, 114.7, 119.9, 124.3, 126.0, 126.4, 130.3, 137.9, 139.7, 160.8. HRMS (FAB $^+$): calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 200.1075; found. 200.1081.



2-(Cyclopropylmethoxy)-3-picoline (1c): Following the procedure for the synthesis of **1b** using cyclopropanemethanol (1.05 g, 14.5 mmol) and 2-chloro-3-picoline (1.43 g, 11.2 mmol), 1.27 g (7.8 mmol, 69% yield) of **1c** was obtained as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.33-0.37 (m, 2H), 0.56-0.60 (m, 2H), 1.25-1.32 (m, 1H), 2.21 (s, 3H), 4.15 (d, $J = 7.2$ Hz, 2H), 6.75 (dd, $J = 4.8, 6.8$ Hz, 1H), 7.37 (dd, $J = 1.2, 6.8$ Hz, 1H), 7.96 (dd, $J = 1.2, 4.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.0, 10.2, 15.9, 70.3, 116.3, 120.8, 138.3, 143.9, 162.3. IR (neat / cm^{-1}): 3080, 3007, 2940, 1595, 1449, 1427, 1395, 1308, 1252, 1003, 783. HRMS (FAB $^+$): calcd for $\text{C}_{10}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 164.1075; found. 164.1081.

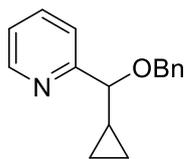


2-[(1-Methylcyclopropyl)methoxy]pyridine (1e): Following the procedure for the synthesis of **1b** using 1-methylcyclopropanemethanol (1.62 g, 18.8 mmol) and 2-chloropyridine (1.64 g, 14.5 mmol), 0.64 g (3.9 mmol, 27% yield) of **1e** was obtained as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.41 (t, $J = 5.0$ Hz, 2H), 0.55 (t, $J = 5.0$ Hz, 2H), 1.22 (s, 3H), 4.07 (s, 2H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.82-6.85 (dd, $J = 5.2, 6.8$ Hz, 1H), 7.56 (dt, $J = 2.0, 8.0$ Hz, 1H), 8.11 (dd, $J = 2.0, 5.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 11.3, 15.4, 21.1, 73.7, 111.2, 116.5, 138.4, 146.7, 164.3. IR (neat / cm^{-1}): 3076, 3003, 2955, 2878, 1603, 1591, 1570, 1474, 1433, 1285, 1271, 779. HRMS (FAB $^+$): calcd for $\text{C}_{10}\text{H}_{14}\text{NO}$ ($[\text{M}+\text{H}]^+$) 164.1075; found. 164.1078.



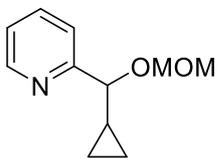
2-[(4-Chlorophenyl)cyclopropylmethoxymethyl]pyridine (1g): A solution of 4-chlorophenyl cyclopropyl ketone (2.71 g, 15.0 mmol) in THF (30 mL) was added THF solution of 2-pyridyl magnesium bromide, which was prepared by the reaction of 2-bromopyridine (2.42 mL, 25.0 mmol),

Mg (668 mg, 27.5 mmol), and a piece of iodine in THF (25 mL), at room temperature. After stirring for 15 h, the reaction mixture was quenched with saturated NH₄Cl solution (20 mL), and extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over MgSO₄, and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent to afford (4-chlorophenyl)cyclopropyl(2-pyridyl)methanol (0.77 g, 3.0 mmol, 20% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 0.34-0.41 (m, 1H), 0.45-0.51 (m, 1H), 0.58-0.68 (m, 2H), 1.58-1.65 (m, 1H), 5.74 (s, 1H), 7.20-7.29 (m, 4H), 7.47-7.50 (m, 2H), 7.66 (dt, *J* = 1.7, 7.7 Hz, 1H), 8.51 (d, *J* = 4.4 Hz, 1H). A solution of (4-chlorophenyl)cyclopropyl(2-pyridyl)methanol (327 mg, 1.3 mmol) in DMF (3.5 mL) and THF (1.0 mL) was added NaH (60% oil suspension, 90.3 mg, 2.3 mmol) at 0 °C, and the mixture was stirred for 1 h. Iodomethane (140 μL, 2.3 mmol) in THF (0.50 mL) was added dropwise, and the resultant mixture was stirred at room temperature for 15 h. The reaction mixture was quenched with saturated NH₄Cl solution (10 mL), and extracted with EtOAc (20 mL × 3). The combined organic extracts were dried over MgSO₄, and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent to afford **1g** (0.31 g, 1.1 mmol, 87% yield) as a colorless solid. mp 58.8-59.8 °C. ¹H NMR (400 MHz, CDCl₃): δ 0.20-0.27 (m, 1H), 0.29-0.35 (m, 1H), 0.54-0.61 (m, 1H), 0.63-0.70 (m, 1H), 1.74-1.81 (m, 1H), 3.24 (s, 3H), 7.13-7.16 (m, 1H), 7.24-7.26 (m, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.54 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.65 (dt, *J* = 2.0, 8.0 Hz, 1H), 8.57 (d, *J* = 4.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 1.7, 3.0, 17.1, 51.1, 84.2, 121.9, 122.6, 127.7, 129.7, 132.9, 136.0, 141.6, 148.4, 162.8. IR (KBr / cm⁻¹): 3009, 2934, 2901, 2824, 1584, 1487, 1076, 1015, 978, 822, 781, 752. HRMS (FAB⁺): calcd for C₁₆H₁₇ClNO ([M+H]⁺) 274.0999; found. 274.1012.



2-[(Benzyloxy)cyclopropylmethyl]pyridine (1h): Following the similar procedure for the synthesis of 2-[cyclopropyl(methoxymethoxy)methyl]pyridine using cyclopropyl(2-pyridinyl)methanol⁶ (597 mg, 4.0 mmol)

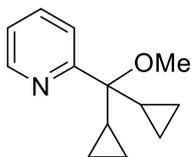
and benzylbromide (523 μ L, 4.4 mmol), 447 mg (1.9 mmol, 47% yield) of **1h** was obtained as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 2 / 1). ¹H NMR (400 MHz, CDCl₃): δ 0.41-0.50 (m, 3H), 0.59-0.64 (m, 1H), 1.22-1.26 (m, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 7.20-7.23 (m, 1H), 7.26-7.33 (m, 5H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.72 (dt, *J* = 1.6, 7.7 Hz, 1H), 8.56-8.58 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 1.8, 3.9, 16.8, 70.9, 85.7, 120.8, 122.5, 127.5, 127.7, 128.3, 136.6, 138.4, 148.9, 162.0. IR (neat / cm⁻¹): 3084, 3028, 3007, 2864, 1589, 1570, 1435, 1329, 1096, 1069, 698. HRMS (FAB⁺): calcd for C₁₆H₁₈NO ([M+H]⁺) 240.1388; found. 240.1377.



2-[Cyclopropyl(methoxymethoxy)methyl]pyridine: A solution of cyclopropyl(2-pyridinyl)methanol⁶ (597 mg, 4.0 mmol) in DMF (9.0 mL) and THF (3.0 mL) was added NaH (60% oil suspension, 178 g,

4.4 mmol) at 0 °C, and the mixture was stirred for 1 h. A solution of 2-chloroquinoline (1.83 g, 11.2 mmol) in DMF (1.0 mL) was added dropwise, and the resultant mixture was stirred at room temperature for 15 h. The reaction mixture was quenched with saturated NH₄Cl solution (10 mL), and extracted with EtOAc (20 mL \times 3). The combined organic extracts were dried over MgSO₄, and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 2 / 1 as the eluent to afford the title compound (0.28 g, 1.5 mmol, 36% yield) as a pale yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 0.39-0.57 (m, 3H), 0.62-0.69 (m, 1H), 1.24-1.30 (m, 1H), 3.36 (s, 3H), 4.11 (d, *J* = 8.4 Hz, 1H), 4.58 (d, *J* = 7.2 Hz, 1H), 4.75 (d, *J* = 7.2 Hz, 1H), 7.18-7.21 (dd, *J* = 4.8, 7.2 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.69

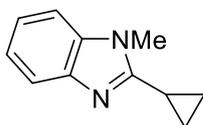
(td, $J = 2.0, 7.6$ Hz, 1H), 8.57-8.58 (d, $J = 4.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 1.9, 4.1, 16.3, 55.5, 82.7, 94.5, 121.1, 122.5, 136.5, 149.1, 161.3. IR (neat / cm^{-1}): 3007, 2887, 1589, 1474, 1435, 1144, 1101, 1040, 920, 750. HRMS (FAB $^+$): calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_2$ ($[\text{M}+\text{H}]^+$) 194.1181; found. 194.1179.



2-[(Dicyclopropyl)methoxymethyl]pyridine (1i): A solution of

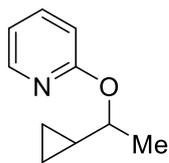
bicyclopropyl ketone (2.20 g, 20.0 mmol) in THF (40 mL) was added THF solution of 2-pyridyl magnesium bromide, which was prepared by the reaction of 2-bromopyridine (2.42 mL, 33.0 mmol), Mg (668 mg, 36.7 mmol), and a small piece of iodine in THF (33 mL), at room temperature. After stirring for 15 h, the reaction mixture was quenched with saturated NH_4Cl solution (20 mL), and extracted with EtOAc (30 mL \times 3). The combined organic extracts were dried over MgSO_4 , and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent to afford dicyclopropyl(2-pyridinyl)methanol (1.14 g, 6.0 mmol, 30% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 0.16-0.23 (m, 2H), 0.31-0.37 (m, 2H), 0.43-0.50 (m, 2H), 0.64-0.70 (m, 2H), 1.14-1.21 (m, 2H), 5.06 (s, 1H), 7.19-7.22 (m, 1H), 7.54 (dd, $J = 0.8, 9.2$ Hz, 1H), 7.65 (dt, $J = 2.0, 8.4$ Hz, 1H), 8.45-8.46 (m, 1H). A solution of dicyclopropyl(2-pyridinyl)methanol (662 mg, 3.5 mmol) in DMF (7.9 mL) and THF (2.6 mL) was added NaH (60% oil suspension, 210 mg, 5.3 mmol) at 0 $^\circ\text{C}$, and the mixture was stirred for 1 h. Iodomethane (327 μL , 5.3 mmol) in THF (0.50 mL) was added dropwise, and the resultant mixture was stirred at room temperature for 15 h. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), and extracted with EtOAc (20 mL \times 3). The combined organic extracts were dried over MgSO_4 , and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 10 / 1 as the eluent to afford **1i** (0.62

g, 3.1 mmol, 87% yield) as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 0.32-0.39 (m, 2H), 0.45-0.51 (m, 2H), 0.57-0.64 (m, 2H), 0.69-0.76 (m, 2H), 1.10-1.17 (m, 2H), 3.31 (s, 3H), 7.13-7.16 (m, 1H), 7.51-7.54 (d, $J = 7.6$ Hz, 1H), 7.65 (dt, $J = 2.0, 7.6$ Hz, 1H), 8.62-8.64 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 0.3, 2.7, 17.0, 50.6, 80.3, 121.6 (two peaks overlapped), 135.7, 148.7, 163.9. IR (neat / cm^{-1}): 3009, 2945, 1587, 1568, 1466, 1429, 1084, 1026, 907, 750. HRMS (FAB $^+$): calcd for $\text{C}_{13}\text{H}_{13}\text{NO}$ ($[\text{M}+\text{H}]^+$) 204.1388; found. 204.1387.



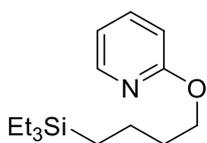
2-Cyclopropyl-1-methyl-1H-benzimidazole (1k): A solution of 2-cyclopropyl-1H-benzimidazole⁷ (0.74 g, 4.7 mmol) in THF (24 mL) was added NaH (60% oil suspension, 0.28 g, 7.0 mmol) at 0 °C, and the

mixture was stirred for 30 min. Iodomethane (0.80 g, 5.6 mmol) was added dropwise, and the resultant mixture was stirred for 15 h. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL), and extracted with EtOAc (20 mL \times 3). The combined organic extracts were dried over MgSO_4 , and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane / EtOAc = 30 / 1 as the eluent to afford **1k** (0.56 g, 3.2 mmol, 70% yield) as a pale yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 1.08-1.13 (m, 2H), 1.21-1.25 (m, 2H), 3.83 (s, 3H), 7.19-7.23 (m, 2H), 7.26-7.29 (m, 1H), 7.63-7.69 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 7.4, 7.9, 29.5, 108.5, 118.8, 121.6, 121.7, 136.0, 142.3, 156.6. IR (neat / cm^{-1}): 3053, 3009, 2943, 1614, 1518, 1456, 1412, 1315, 1283, 1080, 922, 741. HRMS (FAB $^+$): calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2$ ($[\text{M}]^+$) 173.1079; found. 173.1077.



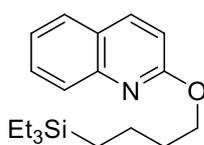
2-(1-Cyclopropylethoxy)pyridine: Following the procedure for the synthesis of **1b** using 1-cyclopropylethanol (1.88 g, 21.8 mmol) and 2-chloropyridine (1.93 g, 16.8 mmol), 2.12 g (13.0 mmol, 76% yield) of the title compound was obtained as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.28-0.33 (m, 1H), 0.40-0.46 (m, 1H), 0.48-0.58 (m, 2H), 1.08-1.17 (m, 1H), 1.39 (d, $J = 6.0$ Hz, 3H), 4.66 (dq, $J = 4.1, 13.4$ Hz, 1H), 6.71 (d, $J = 8.0$ Hz, 1H), 6.79-6.82 (dd, $J = 5.2, 6.8$ Hz, 1H), 7.52-7.56 (dt, $J = 1.6, 8.0$ Hz, 1H), 8.10 (dd, $J = 2.0, 5.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 2.2, 3.5, 16.6, 19.6, 75.2, 111.6, 116.1, 138.4, 146.6, 163.6. IR (neat / cm^{-1}): 3007, 2974, 1591, 1568, 1468, 1429, 1308, 1287, 1271, 1063, 943, 777. HRMS (FAB $^+$): calcd for $\text{C}_{10}\text{H}_{13}\text{NO}$ ($[\text{M}]^+$) 163.0997; found. 163.1004.

3. General Procedure for Iridium-Catalysed Hydrosilylation of Cyclopropanes with Silanes. A flame-dried sealed tube was charged with $[\text{IrCl}(\text{cod})_2]$ (6.7 mg, 0.010 mmol), cyclopropanes (0.20 mmol), silanes (1.0 mmol), diethyl ether or toluene (0.20 or 0.020 mL), and stirred at the temperature specified in the main text for 15 h. The solvent was removed under the reduced pressure, and the residue was subjected to flash column chromatography on silica gel with hexane / EtOAc as the eluent to afford the corresponding alkylsilanes.

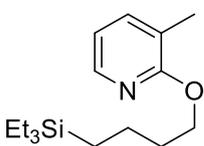


2-[4-(Triethylsilyl)butoxy]pyridine (2a): Following the general procedure using 2-(cyclopropylmethoxy)pyridine **1a** (29.8 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 47.8 mg (0.18 mmol, 90% yield) of the desired product as a yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.52 (q, $J = 8.0$ Hz, 6H), 0.58-0.60 (m, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 1.42-1.50 (m, 2H), 1.80

(quint, $J = 7.2$ Hz, 2H), 4.28 (t, $J = 6.8$ Hz, 2H), 6.72 (d, $J = 7.8$ Hz, 1H), 6.82-6.85 (dd, $J = 4.8, 6.8$ Hz, 1H), 7.53-7.57 (dt, $J = 2.0, 7.8$ Hz, 1H), 8.14 (dd, $J = 1.6, 4.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.4, 11.1, 20.4, 33.1, 65.6, 111.1, 116.4, 138.4, 146.9, 164.1. IR (neat / cm^{-1}): 2951, 2911, 2874, 1595, 1466, 1433, 1287, 1015, 779, 725. HRMS (FAB $^+$): calcd for $\text{C}_{15}\text{H}_{28}\text{NOSi}$ ($[\text{M}+\text{H}]^+$) 266.1940; found. 266.1950.

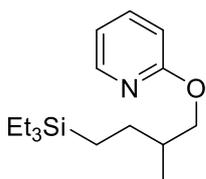


2-[4-(Triethylsilyl)butoxy]quinoline (2b): Following the general procedure using 2-(cyclopropylmethoxy)quinoline **1b** (39.9 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 39.1 mg (0.12 mmol, 62% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.52 (q, $J = 8.0$ Hz, 6H), 0.58-0.63 (m, 2H), 0.93 (t, $J = 8.0$ Hz, 9H), 1.47-1.53 (m, 2H), 1.86 (quint, $J = 6.8$ Hz, 2H), 4.48 (t, $J = 6.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 1H), 7.36 (dt, $J = 1.2, 8.0$ Hz, 1H), 7.58-7.63 (dt, $J = 1.2, 7.2$ Hz, 1H), 7.70 (dd, $J = 1.2, 7.6$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.96 (d, $J = 8.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.5, 11.2, 20.5, 33.0, 65.6, 113.3, 123.8, 125.0, 127.2, 127.4, 129.4, 138.5, 146.7, 162.4. IR (neat / cm^{-1}): 2951, 2911, 2874, 1717, 1699, 1506, 1314, 1277, 822, 754. HRMS (FAB $^+$): calcd for $\text{C}_{19}\text{H}_{29}\text{NOSi}$ ($[\text{M}]^+$) 315.2018; found. 315.2023.



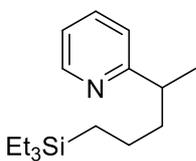
2-[4-(Triethylsilyl)butoxy]-3-picoline (2c): Following the general procedure using 2-(cyclopropylmethoxy)-3-picoline **1c** (32.6 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 41.9 mg (0.15 mmol, 75% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.51 (q, $J = 8.0$ Hz, 6H), 0.56-0.61 (m, 2H), 0.93 (t, $J = 8.0$ Hz, 9H), 1.45-1.53 (m, 2H), 1.77-1.85 (m, 2H), 2.18 (s, 3H), 4.31 (t, $J = 6.4$ Hz, 2H), 6.75 (dd, $J = 5.2, 7.6$ Hz, 1H),

7.35-7.37 (m, 1H), 7.98 (dd, $J = 0.8, 5.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.4, 11.1, 15.9, 20.4, 33.1, 65.3, 116.2, 120.8, 138.2, 144.0, 162.4. IR (neat / cm^{-1}): 2951, 2911, 2874, 1717, 1699, 1684, 1558, 1506, 1420, 725. HRMS (FAB^+): calcd for $\text{C}_{16}\text{H}_{29}\text{NOSi}$ ($[\text{M}]^+$) 279.2018; found. 279.2019.



2-[4-(Triethylsilyl)-2-methylbutoxy]pyridine (2e): Following the general procedure using 2-[(1-methylcyclopropyl)methoxy]pyridine **1e** (32.6 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 50.9

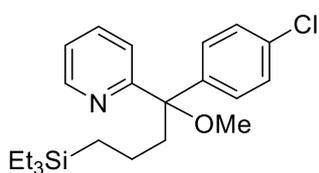
mg (0.18 mmol, 91% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / $\text{EtOAc} = 30 / 1$). ^1H NMR (400 MHz, CDCl_3): δ 0.50 (q, $J = 7.6$ Hz, 6H), 0.51-0.63 (m, 2H), 0.92 (t, $J = 7.6$ Hz, 9H), 1.01 (d, $J = 6.4$ Hz, 3H), 1.19-1.28 (m, 1H), 1.47-1.56 (m, 1H), 1.82-1.90 (m, 1H), 4.07 (dd, $J = 7.0, 10.2$ Hz, 1H), 4.17 (dd, $J = 6.4, 10.0$ Hz, 1H), 6.72 (d, $J = 8.8$ Hz, 1H), 6.81-6.84 (m, 1H), 7.52-7.57 (m, 1H), 8.14 (dd, $J = 2.0, 4.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.2, 7.4, 7.9, 16.6, 27.4, 35.9, 70.4, 111.1, 116.3, 138.4, 146.9, 164.3. IR (neat / cm^{-1}): 2953, 2911, 2874, 1593, 1570, 1433, 1287, 1015, 780, 735. HRMS (FAB^+): calcd for $\text{C}_{16}\text{H}_{30}\text{NOSi}$ ($[\text{M}+\text{H}]^+$) 280.2097; found. 280.2093.



2-[1-(Triethylsilyl)pentan-4-yl]pyridine (2f): Following the general procedure using 2-(1-cyclopropylethyl)pyridine **1f** (29.4 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 36.9 mg (0.14 mmol, 70%

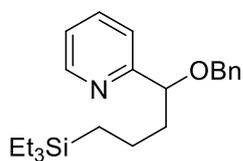
yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / $\text{EtOAc} = 30 / 1$). ^1H NMR (400 MHz, CDCl_3): δ 0.44 (q, $J = 8.0$ Hz, 6H), 0.45-0.52 (m, 8H), 0.87 (t, $J = 8.0$ Hz, 9H), 1.12-1.32 (m, 5H), 1.56-1.63 (m, 1H), 1.72-1.80 (m, 1H), 2.90 (sextet, $J = 7.0$ Hz, 1H), 7.06-7.12 (m, 2H), 7.58 (td, $J = 1.9, 7.6$ Hz, 1H), 8.53 (d, $J = 3.6$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.4, 11.3, 20.7,

21.7, 41.3, 41.5, 120.9, 121.4, 136.2, 149.1, 166.7. IR (neat / cm^{-1}): 2953, 2913, 2874, 1734, 1717, 1699, 1558, 1506, 1456, 746, 725. HRMS (FAB⁺): calcd for $\text{C}_{16}\text{H}_{29}\text{NSi}$ ($[\text{M}]^+$) 263.2069; found. 263.2064.



2-[1-(4-chlorophenyl)-1-methoxy-4-(triethylsilyl)butyl]pyridine (2g): Following the general procedure using 2-[4-chlorophenyl)cyclopropylmethoxymethyl]pyridine **1g**

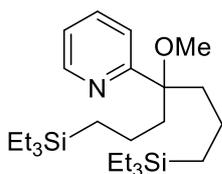
(54.8 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 63.2 mg (0.16 mmol, 81% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 10 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.42 (q, $J = 8.0$, Hz, 6H), 0.48-0.53 (m, 2H), 0.85 (t, $J = 8.0$ Hz, 9H), 0.97-1.05 (m, 1H), 1.06-1.18 (m, 1H), 2.34-2.42 (m, 1H), 2.58-2.66 (m, 1H), 3.13 (s, 3H), 7.08 (dd, $J = 1.2$, 5.2 Hz, 1H), 7.22-7.25 (m, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.62 (dt, $J = 1.6$, 7.8 Hz, 1H), 8.51-8.52 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.4, 11.7, 16.9, 37.8, 50.3, 83.7, 121.2, 121.6, 126.6, 128.1, 132.4, 136.2, 143.3, 148.6, 164.0. IR (neat / cm^{-1}): 2951, 2909, 2874, 1506, 1489, 1456, 1082, 1015, 764, 725. HRMS (FAB⁺): calcd for $\text{C}_{22}\text{H}_{32}\text{ClNOSi}$ ($[\text{M}]^+$) 389.1942; found. 389.1941.



2-[1-(Benzyloxy)-4-(triethylsilyl)butyl]pyridine (2h): Following the general procedure using 2-[(benzyloxy)cyclopropylmethyl]pyridine **1h** (47.9 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided

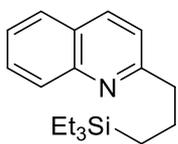
55.5 mg (0.16 mmol, 78% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 2 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.47 (q, $J = 8.0$ Hz, 6H), 0.48-0.53 (m, 2H), 0.89 (t, $J = 8.0$ Hz, 9H), 1.31-1.43 (m, 1H), 1.44-1.56 (m, 1H), 1.71-1.79 (m, 1H), 1.82-1.91 (m, 1H), 4.37 (d, $J = 12.0$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 4.51 (dd, $J = 4.8$, 8.8 Hz, 1H), 7.19 (ddd, $J = 0.8$,

4.8, 7.6 Hz, 1H), 7.26-7.33 (m, 5H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.71 (td, $J = 1.6, 7.6$ Hz, 1H), 8.56-8.57 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.4, 11.2, 20.1, 41.2, 71.3, 82.5, 120.3, 122.2, 127.5, 127.8, 128.3, 136.7, 138.4, 149.0, 163.0. IR (neat / cm^{-1}): 2949, 2911, 2874, 1589, 1472, 1456, 1435, 1099, 748, 731. HRMS (FAB $^+$): calcd for $\text{C}_{22}\text{H}_{33}\text{NOSi}$ ($[\text{M}]^+$) 355.2331; found. 355.2301.



2-(4-Methoxy-1,7-bis(triethylsilyl)heptan-4-yl)pyridine (2i):

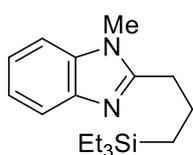
Following the general procedure using 2-[(dicyclopropyl)methoxymethyl]pyridine **1i** (40.7 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 36.6 mg (0.084 mmol, 42% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 10 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.38-0.46 (m, 4H), 0.41 (q, $J = 8.0$ Hz, 12H), 0.84-0.87 (m, 2H), 0.85 (t, $J = 8.0$ Hz, 18H), 1.08-1.19 (m, 2H), 1.92-1.97 (m, 4H), 3.17 (s, 3H), 7.10 (ddd, $J = 1.2, 4.8, 7.4$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.64 (dt, $J = 1.6, 8.0$ Hz, 1H), 8.53-8.56 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.3, 7.4, 11.7, 17.2, 40.1, 49.5, 82.8, 121.2, 121.3, 135.7, 148.4, 164.2. IR (neat / cm^{-1}): 2951, 2911, 2874, 1587, 1468, 1456, 1431, 1238, 1175, 1088, 1016, 760, 729. HRMS (FAB $^+$): calcd for $\text{C}_{25}\text{H}_{49}\text{NOSi}_2$ ($[\text{M}]^+$) 435.3353; found. 435.3358.



2-[3-(Triethylsilyl)propyl]quinoline (2j):

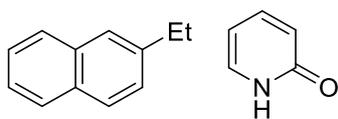
Following the general procedure using 2-cyclopropylquinoline **1j** (33.8 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 40.0 mg (0.14 mmol, 70% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.51 (q, $J = 8.0$ Hz, 6H), 0.62-0.66 (m, 2H), 0.91 (t, $J = 8.0$ Hz, 9H), 1.78-1.86 (m, 2H), 3.00 (t, $J = 7.6$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.68 (t, $J = 8.0$ Hz, 1H), 7.78 (d, $J = 8.0$

Hz, 1H), 8.06 (t, $J = 8.0$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 3.2, 7.4, 11.6, 24.7, 43.4, 121.4, 125.6, 126.7, 127.5, 128.9, 129.3, 136.1, 147.9, 162.9. IR (neat / cm^{-1}): 2951, 2909, 2874, 1601, 1504, 1015, 826, 750, 729. HRMS (FAB^+): calcd for $\text{C}_{18}\text{H}_{27}\text{NSi}$ ($[\text{M}]^+$) 286.1991; found. 286.1972.



2-[3-(Triethylsilyl)propyl]-1-methyl-1H-benzimidazole (2k):

Following the general procedure using 2-cyclopropyl-1-methyl-1H-benzimidazole **1k** (34.4 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 37.5 mg (0.13 mmol, 65% yield) of the desired product as a pale yellow oil after purification by flash chromatography (eluent: hexane / EtOAc = 30 / 1). ^1H NMR (400 MHz, CDCl_3): δ 0.52 (q, $J = 8.0$ Hz, 6H), 0.65-0.70 (m, 2H), 0.92 (t, $J = 8.0$ Hz, 9H), 1.81-1.89 (m, 2H), 2.91 (t, $J = 8.0$ Hz, 2H), 3.73 (s, 3H), 7.21-7.30 (m, 3H), 7.69-7.74 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ -3.2, 7.4, 11.8, 22.6, 29.7, 31.8, 108.8, 119.1, 121.7, 121.9, 135.7, 142.6, 155.3. IR (neat / cm^{-1}): 2951, 2909, 2874, 1508, 1466, 1439, 1398, 1329, 1275, 1234, 1007, 739. HRMS (FAB^+): calcd for $\text{C}_{17}\text{H}_{28}\text{N}_2\text{Si}$ ($[\text{M}]^+$) 288.2022; found. 288.2044.



2-Ethylnaphthalene and 2(1H)-Pyridone: Following the general procedure using 2-[1-(naphthalen-2-yl)ethoxy]-pyridine **11** (49.9 mg, 0.20 mmol) and Et_3SiH (116.3 mg, 1.0 mmol) provided 28.7 mg (0.18 mmol, 92% yield) of 2-ethylnaphthalene as a colorless oil after purification by flash chromatography (eluent: hexane / EtOAc = 99 / 1). ^1H NMR (400 MHz, CDCl_3): δ 1.33 (t, $J = 7.4$ Hz, 3H), 2.82 (q, $J = 7.7$ Hz, 2H), 7.35 (dd, $J = 1.2, 8.4$ Hz, 1H), 7.39-7.46 (m, 3H), 7.63 (s, 1H), 7.76-7.81 (m, 3H). 2(1H)-Pyridone (14.0 mg (0.15 mmol, 74% yield) was also obtained as a colorless solid after purification by flash chromatography (eluent: hexane / EtOAc = 5 / 1). ^1H NMR (400 MHz, CDCl_3): δ 6.26 (t, $J = 6.8$ Hz, 1H), 6.58 (d,

$J = 9.2$ Hz, 1H), 7.34 (dd, $J = 2.0, 6.8$ Hz, 1H), 7.45 (ddd, $J = 2.0, 6.8, 9.2$ Hz, 1H). The analytical data for these compounds match those reported in the literature.^{8,9}

4. References

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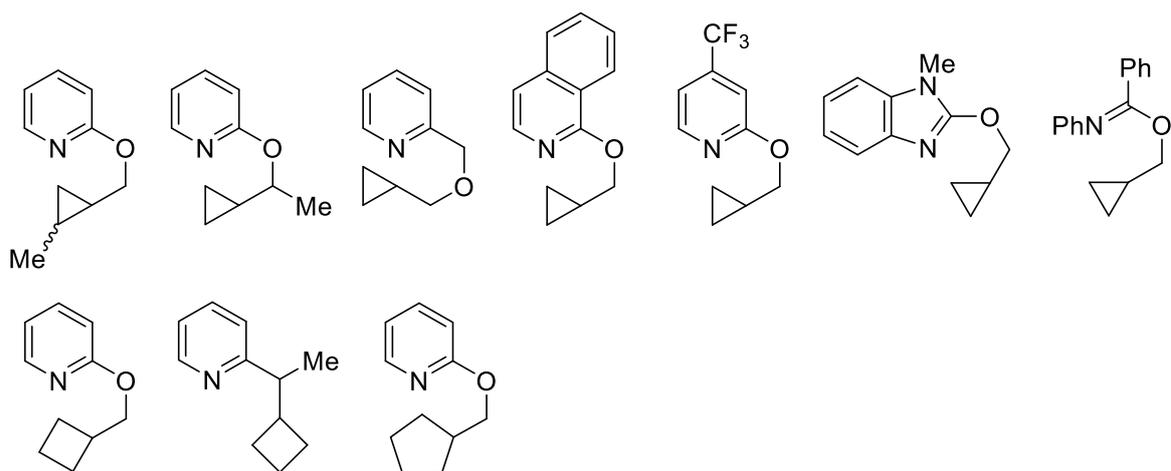


Figure S1. Representative unsuccessful substrates for the current iridium-catalyzed ring-opening hydrosilylation

5. Deuterium-Labeling Experiments

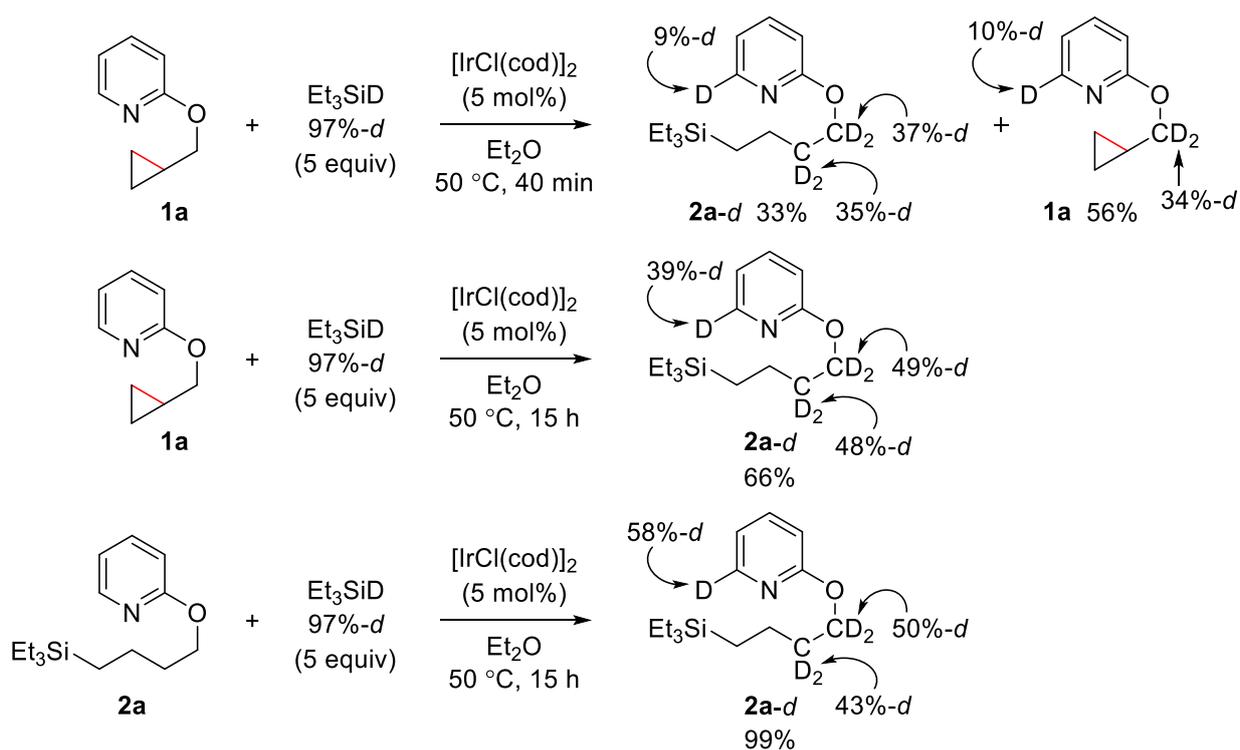


Figure S2. Deuterium-Labeling Experiments with Et_3SiD

6. ^1H NMR and ^{13}C NMR Spectra of New Compounds

