Supporting Information
for DOI: 10.1055/s-0036-1590982
© Georg Thieme Verlag KG Stuttgart · New York 2017
Pincer Ruthenium-Catalyzed Intramolecular Silylation of C(sp²)-H Bonds

Huaquan Fang, Qiaoxing He, Guixia Liu, and Zheng Huang*

State Key Laboratory of Organometallic Chemistry,
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
345 Lingling Road, Shanghai 200032, China

huangzh@sioc.ac.cn

Supporting Information

TABLE OF CONTENTS

1. General Experimental Information ................................................................. S2
2. Preparation of Substrates .................................................................................. S3
3. General Procedure for Intramolecular C(sp²)–H Silylations ............................ S15
4. Hiyama-Denmark Coupling Benzoaxasilole product 3a with Aryl Halides ....... S28
5. References ....................................................................................................... S30
6. NMR Spectra ................................................................................................. S31
1. **General Experimental Information**

a. **Materials**

All manipulations were carried out in an argon-filled glovebox or under an atmosphere of dry argon using standard Schlenk techniques, unless otherwise stated. Triethylamine was purified by distillation over CaH$_2$. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl immediately prior to use. The following chemicals were purchased and used as received: chlorodimethylsilane (Energy Chemical), trichlorosilane (J&K), dichloromethylsilane (Alfa Aesar), Ru$_3$(CO)$_{12}$ (J&K), [Cp$^*$RuCl$_2$]$_2$ (Aladdin), (cod)Ru(2-methylallyl)$_2$ (J&K), Ru(acac)$_3$ (TCI), [RuCl$_2$(p-cymene)]$_2$ (Alfa Aesar). *cis*-Cyclooctene (COE) and *tert*-butylethene (TBE) were purchased from Alfa and distilled from CaH$_2$ prior to use. Chlorodiisopropylsilane[1] (and *tert*-butylmethylchlorosilane[2] were prepared from trichlorosilane and dichloromethylsilane according to a previous reported literature, respectively. ($^{i}$PrPCP)RuH(NBD) (1a) and ($^{i}$PrPOCOP)RuH(NBD) (1b) were prepared according to our previously reported procedures.[3] All other reagents were purchased from commercial sources and used as received, unless specified otherwise.

b. **Methods**

NMR spectra were recorded on Agilent 400 MHz and Varian Mercury 400 MHz spectrometer. $^1$H NMR spectra were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and $^{13}$C NMR spectra were referenced to the solvent resonance. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), integration, coupling constant in hertz (Hz). High resolution mass spectrometer (HRMS) was performed on the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).
2. Preparation of Substrates

Method A:

\[
\text{In a vacuum dried 100 mL Schlenk flask, benzyl alcohol I (10.0 mmol) and triethylamine (20.0 mmol) were dissolved in THF (50 mL) under Ar atmosphere. Then, HClSiMe}_2 (12 mmol) was added at room temperature and the resulting mixture was stirred overnight. After the reaction was complete, the solvent was removed via rotary evaporation. Then, petroleum ether (40 mL) was added. Simple filtration to remove Et}_3\text{N•HCl and concentration in vacuo could give the pure (hydrido)silyl ether product as a colorless liquid.}
\]

Method B:\(^4\)

\[
\text{In a vacuum dried 100 mL Schlenk flask, secondary or primary benzyl alcohol I (10.0 mmol), 4-dimethylaminopyridine (2 mmol), and triethylamine (2.78 mL, 20.0 mmol) were dissolved in THF (50 mL) under Ar atmosphere. Then, HClSiPr}_2 or HClSiMeBu (12 mmol) was added at room temperature and the reaction mixture was stirred overnight at room temperature or 50 °C. After the reaction was complete (monitored by TLC or GC-MS), the reaction mixture was filtered to remove the white precipitate and the solvent was removed via rotary evaporation. Water (20 mL) and MTBE (20 mL) were added, and the mixture was extracted with MTBE (20 mL×3). The combined organic layer was washed with saturated sodium chloride (20 mL), and dried over Na}_2\text{SO}_4. Evaporation of organic solvent afforded a colorless liquid, which was further purified by flash silica column chromatography with petroleum ether as the eluent to give the corresponding (hydrido)silyl ether product as a colorless liquid.}
\]
Spectral data for the (hydrido)silyl ether

\[
\begin{aligned}
  &\text{H} \\
  &\text{SiMe}_2
\end{aligned}
\]

**Dimethyl((2-phenylpropan-2-yl)oxy)silane (2a).** 2-Phenylpropan-2-ol (2.8 mL, 20 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (3.68 g, 95%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.53\) (d, \(J = 8.0\) Hz, 2H), \(7.40\) (t, \(J = 8.0\) Hz, 2H), \(7.30\) (t, \(J = 8.0\) Hz, 1H), \(4.84\) (s, 3H), \(1.70\) (s, 6H), \(0.27\) (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 149.4, 128.1, 126.6, 124.8, 75.6, 31.9, 0.7\).

HRMS (EI+) *calcd.* for C\(_{11}\)H\(_{18}\)OSi ([M\(^+\)]: 194.1127, *found*: 194.1131.

IR \(\nu = 3088.1\) (w), 3062.0 (w), 3029.7 (m), 2975.5 (w), 2931.6 (w), 2116.7 (m), 1253.2 (m), 1168.6 (m), 1027.9 (s), 833.8 (m), 761.4 (s), 696.3 (s).

**Dimethyl((2-(p-tolyl)propan-2-yl)oxy)silane (2b).** 2-(p-Tolyl)propan-2-ol (1.30 g, 8.66 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.62 g, 90%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.41\) (d, \(J = 8.0\) Hz, 2H), \(7.22\) (d, \(J = 8.0\) Hz, 2H), \(4.83\) (m, 1H), \(2.43\) (s, 3H), \(1.70\) (s, 6H), \(0.28\) (d, \(J = 4.0\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 146.5, 136.0, 128.8, 124.8, 75.5, 31.9, 21.1, -0.7\). HRMS (EI+) *calcd.* for C\(_{12}\)H\(_{20}\)OSi ([M\(^+\)]: 208.1283, *found*: 208.1279. IR \(\nu = 2974.8\) (m), 2926.2 (w), 2868.3 (w), 1367.3 (m), 1258.0 (m), 1137.3 (m), 1092.5 (m), 954.4 (m), 909.8 (m), 863.0 (m), 816.8 (s).

((2-[[1,1'-Biphenyl]-4-yl]propan-2-yl)oxy)dimethylsilane (2c).

2-[[1,1'-Biphenyl]-4-yl]propan-2-ol (1.06 g, 5.0 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.34 g, 99%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.67\) (d, \(J = 8.0\) Hz, 2H), \(7.61\) (m, 4H), \(7.49\) (t, \(J = 8.0\) Hz, 2H), \(7.39\) (t, \(J = 8.0\) Hz, 1H), \(4.86\) (m, 1H), \(1.72\) (s, 6H), \(0.29\) (d, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta 148.6, 141.1, 139.4, 128.8, 127.2, 127.2, 126.8, 125.3, 75.5, 31.9, 0.7\). HRMS (EI+) *calcd.* for C\(_{17}\)H\(_{20}\)OSi ([M\(^+\)]:
270.1440, found: 270.1439. IR ν = 3058.0 (w), 3030 (w), 2973.8 (m), 2929.4 (w), 2115.8 (m), 1485.4 (m), 1397.8 (m), 1361.6 (m), 1252.5 (s), 1165.7 (s), 1101.1 (m), 1027.5 (s), 895.1 (s), 834.9 (s), 762.7 (s), 731.5 (m), 695.4 (s).

((2-((4-Methoxyphenyl)propan-2-yl)oxy)dimethylsilane (2d). 2-(4-Methoxyphenyl)propan-2-ol (1.5 g, 9.0 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (2.0 g, 99%). 1H NMR (400 MHz, CDCl3): δ 7.42 (m, 1H), 7.39 (m, 1H), 6.90 (m, 1H), 6.88 (m, 1H), 4.75 (m, 1H), 3.82 (d, 3H), 1.64 (d, J = 4.0 Hz, 6H), 0.20 (t, J = 4.0 Hz, 6H).

13C NMR (101 MHz, CDCl3): δ 158.3, 141.5, 126.0, 113.3, 75.2, 55.3, 31.9, 0.6. HRMS (EI+) calcd. for C12H20O2Si ([M]+): 224.1233, found: 224.1229.

IR ν = 2974.27 (w), 2117.4 (m), 1612.0 (m), 1512.1 (m), 1302.5 (m), 1247.8 (s), 1174.8 (m), 1102.7 (m), 1033.1 (s), 899.1 (s), 831.4 (s), 768.8 (m).

4-(2-((Dimethylsilyl)oxy)propan-2-yl)-N,N-dimethylaniline(2e).

2-(4-(Dimethylamino)phenyl)propan-2-ol (0.85 g, 4.74 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.06 g, 94%). 1H NMR (400 MHz, CDCl3): δ 7.38 (d, J = 12.0 Hz, 2H), 6.77 (d, J = 8.0 Hz, 2H), 4.76 (m, 1H), 2.99 (s, 6H), 1.66 (s, 6H), 0.22 (d, J = 4.0 Hz, 6H). 13C NMR (101 MHz, CDCl3): δ 149.4, 137.2, 125.7, 112.2, 75.2, 40.8, 31.9, 0.6. HRMS (EI+) calcd. for C13H23NOSi ([M]+): 237.1549, found: 237.1552. IR ν = 2972.7 (m), 2927.7 (w), 2116.6 (m), 1741.2 (m), 1613.8 (m), 1521.6 (m), 1352.7 (m), 1251.9 (m), 1164.4 (m), 1028.1 (s), 900.1 (s), 817.9 (m), 765.9 (m).

((2-((4-Fluorophenyl)propan-2-yl)oxy)dimethylsilane (2f). 2-(4-Fluorophenyl)propan-2-ol (1.10 g, 7.14 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.2 g, 99%). 1H NMR (400 MHz, CDCl3): δ 7.41 (m, 1H), 7.38 (m, 1H), 6.83 (m, 1H), 4.75 (m, 1H), 3.83 (d, 3H), 1.63 (d, J = 4.0 Hz, 6H), 0.19 (t, J = 4.0 Hz, 6H).

13C NMR (101 MHz, CDCl3): δ 158.3, 141.5, 126.0, 113.3, 75.2, 55.3, 31.9, 0.6. HRMS (EI+) calcd. for C12H19F3NO2Si ([M]+): 250.0911, found: 250.0909. IR ν = 2972.7 (m), 2927.7 (w), 2116.6 (m), 1741.2 (m), 1613.8 (m), 1521.6 (m), 1352.7 (m), 1251.9 (m), 1164.4 (m), 1028.1 (s), 900.1 (s), 817.9 (m), 765.9 (m).
colorless liquid (1.23 g, 81%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (t, $J = 8.0$ Hz, 2H), 7.01 (t, $J = 8.0$ Hz, 2H), 4.76 (m, 1H), 1.62 (s, 6H), 0.21 (s, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -117.2. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.7, 145.3, 126.5, 114.7, 75.3, 32.0, 0.6. HRMS (EI+) calcd. for C$_{11}$H$_{17}$FOSi ([M]+): 212.1033, found: 212.1030. IR $\nu$ = 2975.8 (w), 2931.4 (w), 2119.3 (m), 1602.1 (m), 1508.1 (s), 1364.2 (m), v1254.6 (m), 1227.6 (s), 1159.2 (s), 1092.7 (m), 1030.0 (m), 899.5 (m), 833.2 (s), 769.2 (m), 553.4 (s), 526.3 (s).

**Dimethyl((2-(4-(trifluoromethyl)phenyl)propan-2-yl)oxy)silane** (2g).

2-(4-(Trifluoromethyl)phenyl)propan-2-ol (0.5 g, 2.45 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (0.52 g, 81%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (m, 4H), 4.83 (m, 1H), 1.66 (d, $J = 4.0$ Hz, 6H), 0.26 (t, $J = 4.0$ Hz, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.4. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 153.7, 128.9, 125.2, 125.1, 124.5, 75.5, 31.7, 0.6. HRMS (EI+) calcd. for C$_{12}$H$_{17}$F$_3$OSi ([M]+): 262.1001, found: 262.0992. IR $\nu$ = 2977.7 (m), 2930.6 (w), 2121.1 (m), 1686.5 (m), 1408.8 (m), 1324.2 (s), 1255.8 (m), 1164.0 (m), 1115.4 (s), 1065.8 (m), 1014.2 (m), 912.7 (m), 838.4 (s), 768.7 (m), 608.5 (m).

**Dimethyl((2-(naphthalen-2-yl)propan-2-yl)oxy)silane** (2h).

2-(Naphthalen-2-yl)propan-2-ol (1.0 g, 5.37 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.25 g, 95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.97 (s, 1H), 7.93 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.70 (dd, $J = 8.0$, 4.0 Hz, 1H), 7.54 (m, 2H), 4.88 (m, 1H), 1.81 (s, 6H), 0.32 (d, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 146.7, 133.2, 132.4, 128.3, 127.8, 127.6, 126.0, 125.7, 124.1, 122.8, 75.7, 31.8, 0.7. HRMS (EI+) calcd. for C$_{16}$H$_{20}$O$_2$Si ([M]+): 244.1283, found: 244.1290. IR $\nu$ = 3057.8 (w), 2974.0 (m), 2929.4 (w), 2116.3 (m), 1381.0 (m), 1251.7 (m), 1157.7 (m), 1024.9 (s), 894.6 (s), 817.1 (s), 767.9 (s).
Dimethyl(2-(m-tolyl)propan-2-yl)oxy)silane (2i). 2-(m-Tolyl)propan-2-ol 2-(Naphthalen-2-yl)propan-2-ol (1.15 g, 7.7 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.42 g, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30 (m, 3H), 7.12 (d, $J = 4.0$ Hz, 1H), 4.83 (m, 1H), 2.44 (d, $J = 4.0$ Hz, 3H), 1.68 (d, $J = 4.0$ Hz, 6H), 0.28 (t, $J = 4.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 149.4, 137.5, 128.0, 127.3, 125.6, 121.9, 75.6, 31.9, 21.8, 0.7. HRMS (EI+) calcd. for C$_{10}$H$_{14}$O ([M - (SiC$_2$H$_6$)]$^+$): 150.1045, found: 150.1041. IR $\nu = 3029.3$ (w), 2975.2 (w), 2925.6 (w), 2864.7 (w), 2118.9 (m), 1607.6 (m), 1456.4 (m), 1363.5 (m), 1253.3 (m), 1168.6 (s), 1033.4 (m), 955.6 (m), 900.7 (s), 825.0 (m), 784.2 (s), 703.8 (s).

((2-(3-Methoxyphenyl)propan-2-yl)oxy)dimethylsilane (2j). 2-(3-Methoxyphenyl)propan-2-ol (1.5 g, 9.14 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.90 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.28 (t, $J = 8.0$ Hz, 1H), 7.09 (s, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 8.0$ Hz, 1H), 4.80 (m, 1H), 1.65 (s, 6H), 0.24 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.5, 151.3, 129.0, 117.2, 111.4, 111.1, 75.5, 55.2, 31.9, 0.6. HRMS (EI+) calcd. for C$_{12}$H$_{20}$O$_2$Si ([M]$^+$): 224.1233, found: 224.1235. IR $\nu = 2975.2$ (w), 2117.2 (m), 1585.2 (m), 1486.0 (m), 1428.7 (m), 1252.6 (m), 1167.49 (m), 1030.8 (s), 896.6 (s), 832.2 (m), 771.4 (m), 734.2 (m).

Dimethyl(2-(o-tolyl)propan-2-yl)oxy)silane (2k). 2-(o-Tolyl)propan-2-ol (1.5 g, 9.14 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.90 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44 (d, $J = 8.0$ Hz, 1H), 7.24 (s, 3H), 4.80 (m, 1H), 2.68 (s, 3H), 1.80 (s, 6H), 0.23 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.6, 136.5, 132.7, 127.0, 125.5, 125.2, 76.6, 31.0, 22.3, 0.4. HRMS (EI+) calcd. for C$_{10}$H$_{14}$O ([M-(SiC$_2$H$_6$)]$^+$): 150.1045, found: 150.1046. IR $\nu = 3060.9$ (w), 2975.2 (m), 2125.4 (m), 1455.3 (m), 1365.1 (m), 1240.8 (m), 1138.0 (m), 1054.8 (m), 949.2 (m), 864.2 (m), 759.0 (s), 726.0 (s).
((2-(2-Methoxyphenyl)propan-2-yl)oxy)dimethylsilane (2l). 2-(2-Methoxyphenyl)propan-2-ol (1.58 g, 9.5 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (2.02 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$): δ 6.68 (m, 1H), 7.29 (m, 1H), 7.02 (m, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 4.93 (m, 1H), 3.88 (s, 3H), 1.78 (d, $J = 4.0$ Hz, 6H), 0.34 (t, $J = 4.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 156.2, 136.9, 127.9, 126.6, 120.4, 111.2, 75.9, 55.1, 29.6, 0.9. HRMS (EI+) calcd. for C$_{12}$H$_{20}$O$_2$Si ([M]$: 224.1233$, found: 224.1226.

IR ν = 2967.9 (m), 2937.9 (w), 2836.8 (w), 2117.2 (m), 1740.5 (m), 1487.1 (m), 1436.1 (m), 1234.5 (s), 1170.3 (m), 1078.2 (m), 1028.6 (s), 895.8 (s), 834.0 (m), 750.6 (s).

((2-(Benzofuran-2-yl)propan-2-yl)oxy)dimethylsilane (2m). 2-(Benzofuran-2-yl)propan-2-ol (1.63 g, 9.25 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (2.03 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.59 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.28 (m, 2H), 6.63 (s, 1H), 4.73 (m, 1H), 1.77 (s, 6H), 0.20 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 162.6, 154.7, 128.4, 124.1, 122.7, 121.1, 111.3, 101.3, 71.7, 29.2, 0.2. HRMS (EI+) calcd. for C$_{13}$H$_{18}$O$_2$Si ([M]$: 234.1076$, found: 234.1069. IR ν = 2981.6 (m), 2935.1 (w), 2122.4 (m), 1454.1 (m), 1364.1 (m), 1252.4 (m), 1163.6 (m), 1082.4 (m), 1028.3 (m), 904.4 (s), 804.9 (m), 743.9 (s), 690.9 (m).

Dimethyl((2-phenylpentan-2-yl)oxy)silane (2n). 2-Phenylpentan-2-ol (1.0 g, 6.09 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.26 g, 93%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.32 (t, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 8.0$ Hz, 1H), 4.78 (m, 1H), 1.79 (t, $J = 8.0$ Hz, 2H), 1.64 (s, 3H), 1.26 (m, 1H), 1.08 (m, 1H), 0.83 (t, $J = 8.0$ Hz, 3H), 0.22 (dd, $J = 8.0$, 4.0 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): δ 148.3, 127.9, 126.3, 125.3, 78.0, 47.5, 29.3, 17.5, 14.4, 0.8, 0.6. HRMS (EI+) calcd. for C$_{13}$H$_{21}$OSi
(2-(4-Fluorophenyl)pentan-2-yl)oxy)silane (2o). 2-(4-Fluorophenyl)pentan-2-ol (1.5 g, 6.24 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.68 g, 84%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 (m, 2H), 7.01 (m, 2H), 4.79 (m, 1H), 1.78 (m, 2H), 1.64 (s, 3H), 1.25 (m, 1H), 1.06 (m, 1H), 0.85 (t, $J = 8.0$ Hz, 3H), 0.22 (dd, $J = 16.0$, 4.0 Hz, 6H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -117.5. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 161.6, 144.0, 126.9, 114.6, 77.7, 47.6, 29.3, 17.4, 14.4, 0.7, 0.6. HRMS (EI+) calcd. for C$_{12}$H$_{16}$FOSi ([M-(CH$_3$)$_3$]+): 225.1111, found: 225.1110.

Dimethyl((3-methyl-2-phenylbutan-2-yl)oxy)silane (2p). 3-Methyl-2-phenylbutan-2-ol (1.5 g, 9.14 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.90 g, 94%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.43 (d, $J = 8.0$ Hz, 2H), 7.36 (m, 2H), 7.28 (m, 1H), 4.80 (m, 1H), 2.00 (m, 1H), 1.68 (d, $J = 4.0$ Hz, 3H), 0.86 (m, 6H), 0.27 (t, $J = 4.0$ Hz, 3H), 0.20 (t, $J = 4.0$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 147.8, 127.7, 126.4, 126.0, 80.2, 40.6, 24.4, 17.7, 17.5, 0.7, 0.6. HRMS (EI+) calcd. for C$_{12}$H$_{16}$OSi ([M-(CH$_3$)$_3$]+): 207.1205, found: 207.1208. IR ν = 2963.1 (m), 2877.1 (w), 2119.2 (m), 1445.9 (m), 1372.2 (m), 1251.6 (m), 1109.4 (m), 1068.2 (s), 969.2 (m), 896.4 (s), 834.8 (m), 798.0 (m), 756.5 (s), 699.0 (s).
(1,1-Diphenylethoxy)dimethylsilane (2q). 1,1-Diphenylethanol (0.99 g, 5.0 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.22 g, 95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.47 (d, $J = 8.0$ Hz, 4H), 7.37 (t, $J = 8.0$ Hz, 4H), 7.29 (t, $J = 8.0$ Hz, 2H), 4.72 (m, 1H), 2.08 (s, 3H), 0.18 (d, $J = 4.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 148.6, 128.0, 126.8, 126.3, 78.9, 30.1, 0.2. HRMS (EI+) calecd. for C$_{16}$H$_{20}$O$_2$Si ([M]$^+$): 256.1282, found: 256.1285.

1H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (m, 4H), 7.30 (m, 1H), 7.24 (m, 3H), 7.02 (dd, $J = 8.0$, 4.0 Hz, 2H), 4.76 (m, 1H), 3.12 (d, $J = 12.0$ Hz, 1H), 3.06 (d, $J = 12.0$ Hz, 1H), 1.73 (s, 3H), 0.22 (dd, $J = 8.0$, 4.0 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 147.8, 137.8, 130.9, 127.9, 127.5, 126.7, 126.2, 125.6, 78.0, 52.5, 17.0, 0.6, 0.5. HRMS (EI+) calecd. for C$_{17}$H$_{21}$OSi ([M-($\text{H}$)]$^+$): 269.1360, found: 269.1360. IR $\nu$ = 3086.4 (w), 3061.6 (w), 3028.0 (w), 2969.1 (s), 2934.3 (s), 2880.4 (w), 2119.5 (m), 1494.4 (m), 1252.3 (m), 1103.4 (m), 1000.0 (m), 900.5 (s), 833.7 (m), 762.4 (m), 697.4 (s).

Dimethyl((3-phenylpentan-3-yl)oxy)silane (2s). 3-Phenylpentan-3-ol (1.0 g, 6.09 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.05 g, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 (m, 4H), 7.22 (t, $J = 8.0$ Hz, 1H), 4.86 (m, 1H), 1.93 (q, $J = 8.0$ Hz, 4H), 0.70 (t, $J = 8.0$ Hz, 6H), 0.28 (d, $J = 4.0$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.7, 127.8, 126.1, 126.0, 81.6, 34.9, 8.2, 0.6. HRMS (EI+) calecd. for C$_{13}$H$_{21}$OSi ([M-($\text{H}$)]$^+$): 221.1362, found: 221.1368. IR $\nu$ = 3088.0 (w), 3061.6 (w), 3028.0 (w), 2969.1 (m), 2934.3 (m), 2880.4 (w), 2116.8 (m), 1450.7 (m), 1252.2 (m), 1159.7 (m), 1062.6 (m), 1021.7 (m), 899.2 (s), 872.3 (m), 753.4 (s), 697.9 (s).
Dimethyl[(1-phenylcyclohexyloxy)silane (2t). 1-Phenylcyclohexanol (0.88 g, 5.0 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (1.13 g, 96%). $^1$H NMR (400 MHz, CDCl₃): δ 7.51 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 8.0 Hz, 2H), 7.28 (t, J = 8.0 Hz, 1H), 4.56 (m, 1H), 2.07 (d, J = 8.0 Hz, 2H), 1.70 (m, 7H), 1.32 (m, 1H), 0.04 (d, J = 4.0 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl₃): δ 148.2, 128.1, 127.0, 125.7, 76.1, 38.7, 25.8, 22.5, 0.4.

HRMS (EI+) calcd. for C_{14}H_{22}O_Si ([M]+): 234.1440, found: 234.1436. IR ν = 3087.8 (w), 3060.7 (w), 3030.3 (w), 2933.7 (w), 2856.8 (w), 2117.2 (m), 1446.6 (m), 1251.2 (m), 1143.3 (m), 1046.8 (m), 1016.0 (m), 901.3 (s), 834.0 (m), 754.8 (m), 696.9 (m).

Dimethyl(trityloxy)silane (2u). Triphenylmethanol (1.3 g, 5.0 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (0.33 g, 21%). $^1$H NMR (400 MHz, CDCl₃): δ 7.54 (m, 6H), 7.34 (m, 9H), 4.55 (m, 1H), 0.08 (d, J = 4.0 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl₃): δ 146.6, 128.4, 127.8, 127.1, 84.9, -0.1. HRMS (EI+) calcd. for C_{21}H_{22}O_Si ([M]+): 318.1440, found: 318.1435. IR ν = 3085.8 (w), 3060.7 (w), 2933.7 (w), 2856.8 (w), 2117.2 (m), 1446.6 (m), 1251.2 (m), 1143.3 (m), 1046.8 (m), 1016.0 (m), 901.3 (s), 834.0 (m), 754.77 (m), 701.4(m).

Dimethyl(1-phenylethoxy)silane (2v). 1-Phenylethanol (1.21 mL, 10 mmol) was subjected to method A to give the corresponding (hydrido)silyl ether as a colorless liquid (0.80 g, 44%). $^1$H NMR (400 MHz, CDCl₃): δ 7.39 (m, 4H), 7.30 (m, 1H), 4.94 (q, J = 12.0, 8.0 Hz, 1H), 4.72 (m, 1H), 1.54 (d, J = 4.0 Hz, 3H), 0.28 (s, 3H), 0.20 (s, 3H). $^{13}$C NMR (101 MHz, CDCl₃): δ 145.8, 128.3, 127.2, 125.6, 72.3, 26.5, -1.0. HRMS (EI+) calcd. for C_{10}H_{16}O_Si ([M]+): 180.0970, found:
180.0972. IR ν = 3065.1 (w), 3030.2 (w), 2972.8 (m), 2928.1 (w), 2876.8 (w), 2111.4 (m), 1252.4 (m), 1092.9 (m), 1029.8 (m), 958.5 (m), 891.0 (m), 834.6 (m), 758.6 (m), 696.5 (m).

**Diisopropyl(1-phenylethoxy)silane (2w).** 1-Phenylethanol (1.2 mL, 10.0 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (1.90 g, 80%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 (m, 4H), 7.26 (t, $J = 8.0$ Hz, 1H), 4.92 (q, $J = 8.0$ Hz, 1H), 4.24 (s, 1H), 1.50 (d, $J = 4.0$ Hz, 3H), 1.10 (t, $J = 4.0$ Hz, 7H), 0.98 (d, $J = 12.0$ Hz, 7H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 146.2, 128.2, 127.0, 125.4, 73.2, 26.6, 17.6, 17.4, 17.4, 17.3, 12.6, 12.5. HRMS (EI+) calcd. for C$_{14}$H$_{24}$O$_2$Si ([M]$^+$): 236.1596, found: 236.1603.

IR ν = 3068.2 (w), 3030.1 (w), 2941.2 (s), 2866.4 (s), 2092.9 (s), 1740.5 (m), 1457.5 (m), 1370.7 (m), 1239.5 (m), 1088.7 (m), 1003.1 (m), 957.0 (m), 833.1 (s), 799.4 (s), 697.2 (m).

**Diisopropyl(1-(2-fluorophenylethoxy)diisopropylsilane (2x).** 1-(2-Fluorophenylethanol (0.35 g, 2.5 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (0.38 g, 60%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.59 (t, $J = 8.0$ Hz, 1H), 7.22 (m, 1H), 7.16 (t, $J = 8.0$ Hz, 1H), 5.26 (q, $J = 8.0$ Hz, 1H), 4.25 (s, 1H), 1.50 (d, $J = 4.0$ Hz, 3H), 1.11 (t, $J = 8.0$ Hz, 7H), 0.99 (d, $J = 8.0$ Hz, 7H). $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -120.4. $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 159.1, 133.2, 128.3, 127.1, 124.1, 114.9, 66.8, 25.4, 17.5, 17.4, 17.3, 12.6, 12.4. HRMS (EI+) calcd. for C$_{14}$H$_{20}$FOSi ([M-(CH$_3$)$_3$]$^+$): 239.1267, found: 239.1265. IR ν = 3064.4 (w), 3024.2 (w), 2938.8 (s), 2864.9 (s), 2090.5 (s), 1743.1 (m), 1458.9 (m), 1373.2 (m), 1235.1 (m), 1085.2 (s), 1013.1 (m), 835.0 (s), 803.8 (s).

**Diisopropyl(1-phenylpropoxy)silane (2y).** 1-Phenylpropan-1-ol (0.69 mL, 5.0 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (0.97 g, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34 (d, $J = 4.0$ Hz, 4H), 7.26 (m, 1H), 4.66 (t, $J = 8.0$ Hz,
1H), 4.21 (s, 1H), 1.80 (m, 2H), 1.11 (t, 6H), 0.92 (m, 11H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 144.7, 128.0, 127.0, 126.2, 78.6, 33.2, 17.7, 17.5, 17.4, 17.3, 12.7, 12.6, 9.8. Spectral data is in agreement with published data.$^{[5]}$

Diisopropyl((1-phenylpentyl)oxy)silane (2z). 1-Phenylpentan-1-ol (0.86 mL, 5.0 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (0.5 g, 36%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.32 (d, $J = 4.0$ Hz, 4H), 7.24 (m, 1H), 4.68 (t, $J = 8.0$ Hz, 1H), 4.17 (s, 1H), 1.78 (m, 1H), 1.69 (m, 1H), 1.30 (m, 5H), 1.07 (t, $J = 8.0$ Hz, 6H), 0.90 (m, 10H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 145.0, 128.0, 127.0, 126.1, 77.4, 40.2, 27.7, 22.7, 17.7, 17.5, 17.4, 17.3, 14.1, 12.6, 12.5. HRMS (EI+) calcd. for C$_{17}$H$_{30}$O$_2$Si ([M]$^+$): 278.2066, found: 278.2070. IR $\nu =$ 2940.4 (m), 2864.4 (m), 2093.0 (m), 1459.6 (m), 1058.4 (m), 1006.2 (m), 839.0 (s), 804.0 (s), 699.2 (m).

(Benzyloxy)diisopropylsilane (2aa). Phenylmethanol (1.03 mL, 10.0 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (0.62 g, 28%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (m, 4H), 7.31 (m, 1H), 4.87 (s, 2H), 4.33 (s, 1H), 1.13 (d, $J = 8.0$ Hz, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 141.0, 128.4, 127.2, 126.5, 67.6, 17.6, 17.5, 12.6. Spectral data is in agreement with published data.$^{[4]}$

(Benzyloxy)(tert-butyl)(methyl)silane (2ab). Phenylmethanol (0.32 mL, 3.05 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (0.5 g, 79%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38 (d, $J = 4.0$ Hz, 4H), 7.32 (m, 1H), 4.85 (s, 2H), 4.46 (m, 1H), 1.04 (d, $J = 4.0$ Hz, 9H), 0.23 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ 140.9, 128.4, 127.2, 126.4, 66.9, 25.8, 18.1, -5.9. HRMS (EI+) calcd. for C$_{17}$H$_{22}$OSi ([M]$^+$): 208.1283, found: 208.1279. IR $\nu = 3031.9$ (w), 2929.0 (m), 2888.6 (w), 2856.8 (m), 2100.9 (m), 1463.1 (m), 1253.9 (m), 1092.3 (m), 858.0 (s), 728.3 (s), 694.4 (m). S13
Diisopropyl((1-phenylcyclohexyl)oxy)silane (2ac). 1-Phenylcyclohexanol (0.88 g, 5 mmol) was subjected to method B to give the corresponding (hydrido)silyl ether as a colorless liquid (1.37 g, 94%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.50 (d, \(J = 8.0\) Hz, 2H), 7.33 (t, \(J = 8.0\) Hz, 2H), 7.24 (t, \(J = 8.0\) Hz, 1H), 4.10 (m, 1H), 2.05 (m, 2H), 1.83 (m, 4H), 1.64 (m, 1H), 1.54 (m, 2H), 1.30 (m, 1H), 0.9 (d, \(J = 12.0, 8.0\) Hz, 12H), 0.72 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \(\delta\) 147.3, 127.9, 127.0, 125.9, 75.0, 38.5, 25.8, 22.6, 17.7, 17.6, 13.0. HRMS (EI+) calcd. for C\(_{18}\)H\(_{30}\)O\(_2\)Si ([M]+): 290.2066, found: 290.2071. IR \(\nu = 2938.8\) (m), 2863.2 (m), 2098.3 (m), 1456.7 (m), 1054.0 (m), 1006.6 (m), 806.2 (m).
3. General Procedure for Intramolecular C(sp²)−H Silylations

General Procedure for the Ru(II)-Catalyzed C-H Silylation of (Hydrido)silyl Ether 2.

To a 5 mL dried Schlenk tube was charged with Ru complex, (hydrido)silyl ether 2 and hydrogen acceptor (TBE or COE, 1 equiv) under Ar atmosphere. Then the flask was sealed tightly with a teflon plug and stirred at 80-120 °C for complete conversion. After that, the reaction mixture was cooled to room temperature. Mesitylene (0.5 equiv) was added as an internal standard, and the yield was determined by ¹H NMR. Then, the crude mixture was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate = 100/1 as eluent) to obtain the benzoxasiloles and silafluorene product.

Silylation of 2v and 2ac.

Spectral data for the products of intramolecular C(sp²)−H silylations

1,1,3,3-Tetramethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3a). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl((2-phenylpropan-2-yl)oxy)silane (97.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (95.0 mg, 99% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 1.58 (s, 6H), 0.42 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 158.0, 134.5, 130.8, 129.8, 126.9, 122.2, 83.5, 32.2, 1.4. Spectral data is in agreement with published data.[⁶]
1,1,3,3,6-pentamethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3b). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl((2-(p-tolyl)propan-2-yl)oxy)silane (104.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (95.6 mg, 93% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.39 (s, 1H), 7.26 (d, \(J = 8.0\) Hz, 1H), 7.16 (d, \(J = 8.0\) Hz, 1H), 2.41 (s, 3H), 1.56 (d, \(J = 4.0\) Hz, 6H), 0.42 (d, \(J = 4.0\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 155.4, 136.4, 134.7, 131.2, 130.9, 122.0, 83.4, 32.3, 21.2, 1.4. HRMS (EI+) calcd. for C\(_{12}\)H\(_{18}\)O\(_2\)Si ([M]+): 206.1124, found: 206.1127. IR ν = 2971.4 (m), 2925.5 (w), 1252.1 (m), 1138.5 (m), 983.1 (s), 903.3 (m), 879.7 (m), 818.9 (s), 788.0 (s), 654.9 (m).

1,1,3,3-tetramethyl-6-phenyl-1,3-dihydrobenzo[c][1,2]oxasilole (3c). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), ((2-([1,1'-Biphenyl]-4-yl)propan-2-yl)oxy)dimethylsilane (135.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (126.6 mg, 94% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.80 (s, 1H), 7.67 (t, \(J = 8.0\) Hz, 3H), 7.49 (t, \(J = 8.0\) Hz, 2H), 7.39 (t, \(J = 8.0\) Hz, 1H), 7.34 (d, \(J = 8.0\) Hz, 1H), 1.64 (s, 6H), 0.49 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 157.2, 141.3, 140.1, 135.4, 129.5, 129.1, 128.9, 127.4, 127.3, 122.6, 83.5, 32.2, 1.4. HRMS (EI+) calcd. for C\(_{13}\)H\(_{20}\)OSi ([M]+): 268.1283, found: 268.1287. IR ν = 3052.2 (w), 2974.0 (m), 2928.2 (w), 2866.6 (w), 1245.6 (m), 1137.8 (m), 1060.8 (m), 983.0 (s), 901.2 (s), 830.5 (s), 787.3 (s), 697.9 (m), 656.1 (m).

6-methoxy-1,1,3,3-tetramethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3d). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol),
((2-(4-methoxyphenyl)propan-2-yl)oxy)dimethylsilane (112.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzosiloxole product was afforded as a colorless liquid (101.9 mg, 92% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.15 (d, J = 8.0 Hz, 1H), 7.03 (s, 1H), 6.98 (dd, J = 8.0, 4.0 Hz, 1H), 3.84 (s, 3H), 1.54 (s, 6H), 0.40 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 158.7, 150.3, 136.1, 123.2, 116.7, 114.2, 83.2, 55.4, 32.3, 1.3. HRMS (EI⁺) calcd. for C₁₂H₁₈O₂Si ([M⁺]): 222.1076. found: 222.1081.

IR ν = 3085.2 (w), 2967.4 (m), 2927.8 (m), 2836.2 (w), 1606.6 (m), 1512.2 (m), 1464.3 (m), 1297.8 (m), 1032.9 (m), 982.4 (m), 828.8 (m), 787.8 (m).

N,N,1,1,3,3-hexamethyl-1,3-dihydrobenzo[c][1,2]oxasilol-6-amine (3e). The general procedure was followed with Ru complex 1b (13.6 mg, 25.0 μmol), 4-(2-((dimethylsilyl)oxy)propan-2-yl)-N,N-dimethylaniline (237.4 mg, 1.0 mmol), and COE (130.0 μL, 1.0 mmol) at 80 °C for 24 h. The benzosiloxole product was afforded as a colorless liquid (187.6 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, J = 8.0 Hz, 1H), 6.86 (m, 2H), 2.99 (s, 6H), 1.54 (s, 6H), 0.41 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 146.4, 135.5, 122.7, 115.2, 113.5, 83.2, 41.0, 32.4, 1.4. HRMS (EI⁺) calcd. for C₁₃H₁₉NOSi ([M⁺]): 235.1392. found: 235.1392. IR ν = 3085.2 (v), 2967.4 (m), 2922.7 (w), 2836.2 (w), 1606.6 (m), 1512.2 (m), 1464.3 (m), 1488.8 (m), 1297.2 (m), 1180.2 (m), 1043.81 (m), 1032.8 (m), 982.4 (m), 880.3 (m), 828.8 (m), 787.8 (m).

6-fluoro-1,1,3,3-tetramethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3f). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), ((2-(4-fluorophenyl)propan-2-yl)oxy)dimethylsilane (106.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzosiloxole product was afforded as a colorless liquid (101.3 mg, 96% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.16 (m, 2H), 7.06 (dt, J = 8.0 Hz, 1H), 1.52 (s, 6H), 0.38 (s, 6H). ¹⁹F NMR (376 MHz, CDCl₃): δ -117.3. ¹³C NMR (101 MHz, CDCl₃) δ 162.2, 153.5, 137.4, 123.8, 117.2, 116.5, 83.3, 32.3, 1.2. HRMS (EI⁺) calcd. for C₁₀H₁₂FOSi
([M-(CH$_3$)$_3$])$^+$): 195.0641, found: 195.0640. IR $\nu$ = 2969.1 (m), 2926.6 (m), 2855.9 (w), 1467.1 (m), 1258.6 (s), 1201.6 (m), 1099.4 (m), 1020.7 (m), 988.0 (s), 899.0 (m), 822.2 (s), 793.7 (s).

$^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -62.2.

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.8, 135.9, 129.2, 127.9, 126.9, 124.6, 122.6, 83.6, 31.9, 1.2.

HRMS (EI$^+$) calcd. for C$_{12}$H$_{15}$F$_3$O$_2$Si ([M]$^+$): 260.0844, found: 260.0842.

IR $\nu$ = 2974.7 (m), 2931.3 (w), 1740.5 (m), 1326.7 (m), 1255.9 (m), 1122.8 (s), 986.6 (s), 903.2 (m), 835.4 (m), 790.8 (s), 658.4 (m).

1,1,3,3-tetramethyl-6-(trifluoromethyl)-1,3-dihydrobenzo[c][1,2]oxasilole (3g). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 $\mu$mol), dimethyl((2-(4-(trifluoromethyl)phenyl)propan-2-yl)oxy)silane (131.2 mg, 0.5 mmol), and COE (65.0 $\mu$L, 0.5 mmol) at 80 $^\circ$C for 24 h. The benzosiloxole product was afforded as a colorless liquid (121.9 mg, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (s, 1H), 7.64 (d, $J$ = 8.0 Hz, 1H), 7.32 (d, $J$ = 8.0 Hz, 1H), 1.55 (s, 6H), 0.41 (s, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.4, 134.4, 134.0, 132.8, 131.6, 128.3, 128.1, 126.7, 125.6, 120.2, 83.6, 32.7, 1.4. HRMS (EI$^+$) calcd. for C$_{15}$H$_{18}$O$_2$Si ([M]$^+$): 242.1127, found: 242.1125. IR $\nu$ = 3051.2 (w), 2969.6 (w), 2925.3 (w), 1248.6 (m), 1152.3 (m), 1002.3 (m), 971.3 (s), 883.8 (s), 818.4 (s), 787.0 (s), 747.0 (s), 653.0 (m).

1,1,3,3-tetramethyl-1,3-dihydronaphtho[2,3-c][1,2]oxasilole (3h). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 $\mu$mol), dimethyl((2-(naphthalen-2-yl)propan-2-yl)oxy)silane (48.9 mg, 0.2 mmol), and COE (26.0 $\mu$L, 0.2 mmol) at 80 $^\circ$C for 24 h. The benzosiloxole product was afforded as a colorless liquid (47.4 mg, 97% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.09 (s, 1H), 7.87 (d, $J$ = 8.0 Hz, 2H), 7.67 (s, 1H), 7.49 (m, 2H), 1.66 (s, 6H), 0.47 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.4, 134.4, 134.0, 132.8, 131.6, 128.3, 128.1, 126.7, 125.6, 120.2, 83.4, 32.7, 1.4. HRMS (EI$^+$) calcd. for C$_{15}$H$_{18}$OSi ([M]$^+$): 242.1127, found: 242.1125. IR $\nu$ = 3051.2 (w), 2969.6 (w), 2925.3 (w), 1248.6 (m), 1152.3 (m), 1002.3 (m), 971.3 (s), 883.8 (s), 818.4 (s), 787.0 (s), 747.0 (s), 653.0 (m).
1,1,3,3,5-pentamethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3i). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl((2-((m-tolyl)propan-2-yl)oxy)silane (41.7 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 80 °C for 24 h. The benzosiloxiane product was afforded as a colorless liquid (28.9 mg, 70% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J$ = 8.0 Hz, 1H), 7.17 (d, $J$ = 8.0 Hz, 1H), 7.08 (s, 1H), 2.43 (s, 3H), 1.58 (s, 6H), 0.41 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 158.5, 139.9, 131.2, 130.8, 128.1, 122.9, 83.4, 32.2, 21.8, 1.4. HRMS (EI+) calcd. for C$_{12}$H$_{18}$O$_2$Si ([M]+): 206.1127, found: 206.1131. IR ν = 3045.0 (w), 2971.5 (m), 2925.4 (w), 2864.5 (w), 1603.7 (m), 1253.0 (m), 1140.8 (m), 982.1 (s), 873.3 (s), 822.9 (s), 785.5 (s), 669.1 (m).

5-methoxy-1,1,3,3-tetramethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3j). The general procedure was followed with Ru complex 1b (13.5 mg, 25.0 μmol), ((2-(3-methoxyphenyl)propan-2-yl)oxy)dimethylsilane (224.4 mg, 1.0 mmol), and COE (130.0 μL, 1.0 mmol) at 80 °C for 24 h. The benzosiloxiane product 3j was afforded as a colorless liquid (103.6 mg, 47% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (t, $J$ = 8.0 Hz, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 6.72 (d, $J$ = 8.0 Hz, 1H), 6.72 (d, $J$ = 8.0 Hz, 1H), 3.83 (s, 3H), 1.55 (s, 6H), 0.42 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.4, 160.3, 132.3, 122.4, 114.9, 107.5, 83.5, 55.2, 32.0, 1.1. HRMS (EI+) calcd. for [C$_{12}$H$_{18}$O$_2$Si]: 222.1076, found: 222.1079. IR ν = 3061.7 (w), 2961.6 (m), 2924.8 (m), 2853.7 (w), 1461.5 (m), 1374.5 (w), 1260.0 (m), 1096.9 (s), 1026.4 (s), 959.9 (m), 864.3 (m), 798.5 (s), 704.9 (w). The benzosiloxiane product 3j was afforded as a colorless liquid (88.5 mg, 40% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (d, $J$ = 8.0 Hz, 1H), 6.88 (dd, $J$ = 8.0, 4.0 Hz, 1H), 6.73 (s, 1H), 3.84 (s, 3H), 1.53 (s, 6H), 0.36 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.5, 160.4, 132.1, 125.7, 113.5, 107.7, 83.3, 55.4, 32.1, 1.6. HRMS (EI+) calcd. for C$_{12}$H$_{18}$O$_2$Si ([M]+): 222.1076, found:
1,1,3,3-tetramethyl-3,4-dihydro-1H-benzo[d][1,2]oxasilole (3k'). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl(2-(o-tolyl)propan-2-yl)oxy)silane (41.7 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 80 °C for 24 h. The benzosiloxole product was afforded as a colorless liquid (20.5 mg, 50% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.27 (m, 1H), 7.14 (m, 3H), 2.15 (s, 2H), 1.60 (s, 6H), 0.15 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 145.7, 134.7, 132.3, 127.1, 125.5, 124.9, 76.2, 31.8, 20.5, 0.6. HRMS (EI+) calcd. for C₁₂H₁₈O₂Si ([M]+): 206.1127, found: 206.1129. IR ν = 3097.1 (w), 3063.5 (w), 3017.7 (w), 2978.2 (m), 2930.5 (w), 1482.2 (m), 1443.8 (m), 1157.5 (m), 1014.8 (s), 839.8 (s), 807.4 (s), 756.4 (s), 633.0 (m).

4-methoxy-1,1,3,3-tetramethyl-1,3-dihydrobenzo[e][1,2]oxasilole (3l). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), ((2-(2-methoxyphenyl)propan-2-yl)oxy)dimethylsilane (44.9 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 100 °C for 24 h. The benzosiloxole product was afforded as a colorless liquid (42.1 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 3.85 (s, 3H), 3.85 (s, 3H), 1.63 (s, 6H), 0.38 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 154.6, 145.0, 137.4, 129.0, 122.7, 112.1, 84.2, 55.1, 29.6, 1.4. HRMS (EI+) calcd. for C₁₂H₁₈O₂Si ([M]+): 222.1076, found: 222.1071. IR ν = 3052.1 (w), 3063.5 (w), 2978.2 (m), 2928.4 (m), 2854.0 (w), 2359.4 (w), 1464.3 (w), 1259.7 (s), 1095.3 (s), 1021.5 (s), 800.4 (s), 730.0 (w).

1,1,3,3-tetramethyl-1,3-dihydro-[1,2]oxasilolo[4,3-b]benzofuran (3m). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol),
((2-(benzofuran-2-yl)propan-2-yl)oxy)dimethylsilane (46.9 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 80 °C for 24 h. The benzosilole product was afforded as a colorless liquid (44.0 mg, 95% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.52 (t, \(J = 8.0\) Hz, 2H), 7.27 (m, 2H), 1.62 (s, 6H), 0.48 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 177.5, 159.5, 129.1, 123.9, 123.1, 122.2, 111.7, 110.2, 76.9, 29.4, 2.0. HRMS (EI+) calcd. for C\(_{13}\)H\(_{16}\)O\(_2\)Si ([M]\(^+\)): 232.0920, found: 232.0923. IR ν = 3051.0 (w), 2970.8 (m), 2931.0 (w), 1539.9 (m), 1451.5 (m), 1250.2 (s), 1098.6 (s), 1009.9 (m), 796.8 (s), 741.5 (s), 675.5 (m).

1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3n). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl(2-phenylpentan-2-yl)oxy)silane (111.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzosilole product was afforded as a colorless liquid (105.5 mg, 96% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.55 (d, \(J = 8.0\) Hz, 1H), 7.41 (t, \(J = 8.0\) Hz, 1H), 7.31 (t, \(J = 8.0\) Hz, 1H), 7.19 (d, \(J = 8.0\) Hz, 1H), 1.84 (m, 2H), 1.53 (s, 3H), 1.37 (m, 1H), 0.95 (m, 1H), 0.86 (t, \(J = 8.0\) Hz, 3H), 0.42 (d, \(J = 8.0\) Hz, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 156.7, 135.5, 130.7, 129.8, 126.8, 122.2, 86.1, 46.0, 31.7, 14.5, 1.7, 0.8. HRMS (EI+) calcd. for C\(_{12}\)H\(_{17}\)O\(_2\)Si ([M-(CH\(_3\))]\(^+\)): 205.1049, found: 205.1051. IR ν = 3059.8 (w), 2960.3 (m), 2931.0 (w), 2908.4 (w), 2872.5 (w), 1250.9 (m), 1132.8 (m), 962.9 (m), 927.4 (m), 825.1 (s), 786.9 (s), 739.2 (s), 651.2 (m).

6-fluoro-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3o). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), ((2-(4-fluorophenyl)pentan-2-yl)oxy)dimethylsilane (120.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzosilole product was afforded as a colorless liquid (112.8 mg, 95% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.14 (dd, \(J = 8.0\), 4.0 Hz, 1H), 7.10 (dd, \(J = 8.0\), 4.0 Hz, 1H), 7.06 (dt, \(J = 8.0\), 4.0 Hz, 1H), 1.78 (m, 2H), 1.47 (s, 3H), 1.33 (m, 1H), 0.92 (m, 1H), 0.82 (t, \(J = 8.0\) Hz, 3H), 0.38 (d, \(J = 8.0\) Hz, 6H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): δ -117.4. \(^{13}\)C NMR (101
MHz, CDCl₃) δ 162.2, 152.2, 138.2, 123.9, 117.2, 116.4, 85.9, 46.1, 31.8, 17.5, 14.5, 1.5, 0.6. HRMS (EI+) *calcld.* for C₁₂H₁₀FOSi ([M-(CH₃)]⁺): 223.0954, *found:* 223.0959. IR ν = 2961.9 (m), 2932.2 (w), 2873.7 (w), 1463.7 (m), 1199.9 (s), 964.2 (s), 929.6 (m), 820.1 (s), 787.7 (s), 650.3 (s).

3-isopropyl-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3p). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl((3-methyl-2-phenylbutan-2-yl)oxy)silane (44.5 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (39.0 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.20 (m, 1H), 1.49 (s, 3H), 1.08 (d, J = 4.0 Hz, 3H), 0.62 (d, J = 8.0 Hz, 3H), 0.42 (s, 3H), 0.37 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.4, 135.6, 130.7, 129.7, 126.8, 122.3, 88.3, 38.1, 29.4, 18.0, 17.2, 1.9, 0.5. HRMS (EI+) *calcld.* for C₁₂H₁₇O⁻Si ([M-(CH₃)]⁺): 205.1049, *found:* 205.1052. IR ν = 3060.2 (w), 2966.5 (m), 2928.0 (w), 1443.4 (m), 1251.9 (m), 120.9 (m), 1026.7 (s), 958.8 (s), 863.7 (m), 825.7 (m), 788.5 (s), 740.4 (m), 653.0 (w).

1,1,3-trimethyl-3-phenyl-1,3-dihydrobenzo[c][1,2]oxasilole (3q). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), (1,1-diphenylethoxy)dimethylsilane (128.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (120.9 mg, 95% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.40 (m, 4H), 7.30 (t, J = 8.0 Hz, 2H), 2.03 (s, 3H), 0.58 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 157.2, 147.4, 134.5, 130.8, 129.9, 128.2, 127.0, 127.0, 125.7, 123.7, 86.4, 31.4, 1.5, 0.9. HRMS (EI+) *calcld.* for C₁₆H₁₇O⁻Si ([M-(H)]⁺): 253.1049, *found:*
253.1045. IR ν = 3059.4 (w), 2998.8 (w), 2929.6 (m), 2856.0 (w), 1442.7 (m), 1250.4 (m), 1134.2 (m), 1074.2 (m), 977.4 (s), 896.9 (s), 820.1 (s), 787.6 (s), 757.6 (m), 654.2 (m).

3,3-diethyl-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3r). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), ((1,2-diphenylpropan-2-yl)oxy)dimethylsilane (135.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (131.3 mg, 98% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (m, 2H), 7.33 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.11 (m, 3H), 6.90 (m, 2H), 3.14 (d, J = 12.0 Hz, 1H), 3.06 (d, J = 12.0 Hz, 1H), 1.59 (s, 3H), 0.30 (s, 3H), 0.14 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.0, 137.6, 135.8, 130.9, 130.7, 129.6, 127.6, 127.0, 126.2, 122.8, 86.1, 50.1, 31.3, 1.7, 0.2. HRMS (EI+) calcd. for C$_{17}$H$_{20}$O$_2$Si ([M]+): 268.1283, found: 268.1285. IR ν = 3059.4 (w), 2968.9 (m), 2933.6 (w), 2878.9 (w), 1745.8 (m), 1251.7 (m), 974.6 (s), 884.4 (m), 834.4 (m), 790.2 (s), 651.3 (m).

3,3-diethyl-1,1-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (3s). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl(3-phenylpentan-3-yl)oxy)silane (111.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (103.7 mg, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 1.90 (m, 2H), 1.82 (m, 2H), 0.70 (t, J = 4.0 Hz, 6H), 0.42 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.4, 136.9, 130.5, 129.8, 126.7, 122.3, 89.5, 35.5, 8.4, 1.1. HRMS (EI+) calcd. for C$_{13}$H$_{19}$O$_2$Si ([M-(H)]+): 219.1205, found: 219.1208. IR ν = 3059.4 (w), 2968.9 (m), 2933.6 (w), 2878.9 (w), 1251.7 (m), 974.6 (s), 884.4 (m), 834.4 (m), 790.2 (s), 651.3 (m).
1,1-dimethyl-1H-spiro[benzo[c][1,2]oxasilole-3,1’-cyclohexane] (3t). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl((1-phenylcyclohexyl)oxy)silane (117.2 mg, 0.5 mmol), and COE (65.0 μL, 0.5 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (109.5 mg, 94% yield). 1H NMR (400 MHz, CDCl₃) δ 7.60 (dd, J = 8.0, 4.0 Hz, 1H), 7.45 (m, 1H), 7.34 (m, 1H), 7.28 (dd, J = 8.0, 4.0 Hz, 1H), 1.88 (m, 5H), 1.68 (t, J = 16.0 Hz, 4H), 1.37 (m, 1H), 0.44 (s, 6H). 13C NMR (101 MHz, CDCl₃) δ 158.5, 135.3, 130.9, 129.6, 126.9, 122.3, 84.8, 40.3, 25.7, 22.5, 16.6. HRMS (EI+) calcd. for C₁₄H₂₀O₄Si ([M]+): 232.1283, found: 232.1282.

IR ν = 3058.2 (w), 2974.2 (m), 2929.2 (w), 1493.2 (m), 1442.2 (m), 1249.5 (w), 947.8 (s), 823.2 (s), 787.0 (m), 741.6 (s), 697.7 (s), 621.4 (m).

1,1-dimethyl-3,3-diphenyl-1,3-dihydrobenzo[c][1,2]oxasilole (3u). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), dimethyl(trityloxy)silane (63.7 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 80 °C for 24 h. The benzoxasilole product was afforded as a colorless liquid (64.4 mg, 94% yield). 1H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.0 Hz, 1H), 7.32 (m, 13H), 0.5 (s, 6H). 13C NMR (101 MHz, CDCl₃) δ 154.4, 147.2, 136.0, 130.8, 129.5, 127.9, 127.7, 127.3, 127.2, 126.1, 91.1, 0.8. HRMS (EI+) calcd. for C₂₁H₂₃O₄Si ([M]+): 316.1283, found: 316.1282. IR ν = 3052.7 (w), 2974.2 (m), 2929.2 (w), 1493.2 (m), 1442.2 (m), 1249.5 (w), 947.8 (s), 823.2 (s), 787.0 (m), 741.6 (s), 697.7 (s), 621.4 (m).

1,1-diisopropyl-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (3w). The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), diisopropyl(1-phenylethoxy)silane (47.2 mg,
0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 120 °C for 12 h. The benzosilole product was afforded as a colorless liquid (42.5 mg, 91% yield). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.54 (d, J = 4.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 1H), 5.33 (q, J = 8.0 Hz, 1H), 1.52 (d, J = 4.0 Hz, 3H), 1.24 (m, 2H), 1.03 (m, 12H), 0.97 (d, J = 8.0 Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 155.3, 132.1, 131.7, 129.7, 126.7, 122.2, 78.4, 25.0, 17.5, 17.4, 17.1, 17.0, 13.3, 12.6. HRMS (EI+) calcd. for C\(_{14}\)H\(_{12}\)O\(_{3}\)Si ([M]+): 234.1440, found: 234.1447. IR ν = 3060.7 (w), 2944.7 (m), 2864.3 (m), 1743.3 (m), 1456.0 (s), 1245.4 (m), 1080.8 (s), 1019.7 (m), 922.5 (s), 878.1 (s), 802.6 (m), 751.4 (m), 710.5 (m), 669.7 (m).

![Chemical structure](image)

**4-fluoro-1,1-diisopropyl-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (3x).** The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), (1-(2-fluorophenyl)ethoxy)diisopropylsilane (50.8 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 120 °C for 12 h. The benzosilole product was afforded as a colorless liquid (46.5 mg, 92% yield). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.28 (m, 2H), 7.03 (m, 1H), 5.47 (q, J = 12.0, 4.0 Hz, 1H), 1.57 (d, J = 8.0 Hz, 3H), 1.18 (m, 2H), 1.06 (dd, J = 8.0, 4.0 Hz, 6H), 0.96 (dd, J = 8.0, 4.0 Hz, 6H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) δ -118.3. \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 158.2, 141.1, 136.2, 129.4, 127.6, 116.6, 76.2, 23.8, 17.4, 17.3, 17.0, 17.0, 13.2, 12.6. HRMS (EI+) calcd. for C\(_{14}\)H\(_{12}\)FOSi ([M]+): 252.1346, found: 252.1340. IR ν = 2945.9 (m), 2866.9 (m), 1458.4 (m), 1273.9 (m), 1084.9 (m), 927.9 (m), 882.9 (m), 794.9 (m), 677.2 (s).

![Chemical structure](image)

**3-ethyl-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (3y).** The general procedure was followed with Ru complex 1b (2.7 mg, 5.0 μmol), diisopropyl(1-phenylpropoxy)silane (50.0 mg, 0.2 mmol), and COE (26.0 μL, 0.2 mmol) at 120 °C for 12 h. The benzosilole product was afforded as a colorless liquid (43.6 mg, 88% yield). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) δ 7.56 (d, J = 4.0 Hz, 1H), 7.41 (t, J = 4.0 Hz, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 5.16 (m, 1H), 2.01 (m, 1H), 1.63 (m, 1H), 1.23 (m, 2H), 1.06 (m, 12H), 0.97 (d, J = 8.0 Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) δ 158.2, 141.1, 136.2, 129.4, 127.6, 116.6, 76.2, 23.8, 17.4, 17.3, 17.0, 17.0, 13.2, 12.6. HRMS (EI+) calcd. for C\(_{14}\)H\(_{12}\)OSi ([M]+): 252.1346, found: 252.1340. IR ν = 2945.9 (m), 2866.9 (m), 1458.4 (m), 1273.9 (m), 1084.9 (m), 927.9 (m), 882.9 (m), 794.9 (m), 677.2 (s).
MHz, CDCl$_3$) δ 154.1, 132.4, 132.0, 129.4, 126.6, 122.2, 83.2, 31.8, 17.5, 17.4, 17.1, 17.0, 13.3, 12.8, 10.0. HRMS (EI+) calcd. for C$_{15}$H$_{24}$O$_5$Si ([M]$^+$): 248.1596, found: 248.1594. IR ν = 3060.4 (w), 2942.5 (m), 2864.2 (m), 1742.1 (m), 1457.2 (m), 1373.3 (m), 1239.8 (m), 1085.0 (m), 982.4 (m), 744.0 (m), 664.8 (m).

3-butyl-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (3z). The general procedure was followed with Ru complex 1b (6.8 mg, 12.5 μmol), diisopropyl((1-phenylpentyl)oxy)silane (55.7 mg, 0.2 mmol), and TBE (25.8 μL, 0.2 mmol) at 120 °C for 12 h. The benzoxasilole product was afforded as a colorless liquid (51.8 mg, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J = 8.0$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.30 (t, $J = 8.0$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 5.22 (m, 1H), 1.96 (m, 1H), 1.62 (m, 2H), 1.44 (m, 2H), 1.26 (m, 2H), 1.11 (t, $J = 8.0$ Hz, 6H), 1.05 (d, $J = 8.0$ Hz, 3H), 0.98 (m, 6H), 0.86 (m, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.5, 132.2, 132.0, 129.4, 126.6, 122.1, 82.1, 39.0, 22.8, 17.5, 17.4, 17.1, 17.0, 14.1, 13.3, 12.8. Spectral data is in agreement with published data.[6]

1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (3aa). The general procedure was followed with Ru complex 1b (5.4 mg, 10.0 μmol), (benzyloxy)diisopropylsilane (44.5 mg, 0.2 mmol), and TBE (25.8 μL, 0.2 mmol) at 120 °C for 12 h. The benzoxasilole product was afforded as a colorless liquid (39.0 mg, 88% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.28 (t, $J = 8.0$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 1H), 5.15 (s, 2H), 1.24 (m, 2H), 1.02 (m, 12H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.8, 132.2, 131.7, 129.5, 126.6, 121.5, 121.5, 125.8, 17.0, 13.1. Spectral data is in agreement with published data.[7]

1-(tert-butyl)-1-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (3ab). The general procedure was followed with Ru complex 1b (4.1 mg, 7.5 μmol), (benzyloxy)(tert-butyl)(methyl)silane (62.6 mg,
0.3 mmol), and COE (39.0 μL, 0.3 mmol) at 120 °C for 12 h. The benzoxasilole product was afforded as a colorless liquid (58.2 mg, 94% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J = 8.0$ Hz, 1H), 7.38 (t, $J = 8.0$ Hz, 1H), 7.28 (t, $J = 8.0$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 5.14 (m, 2H), 0.96 (s, 9H), 0.37 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.3, 133.3, 131.8, 129.6, 126.8, 121.6, 72.1, 25.5, 19.3, 4.8. HRMS (EI+) calcd. for C$_{12}$H$_{18}$O$_2$Si ([M]+): 206.1127, found: 206.1124. IR ν = 3059.0 (w), 2953.3 (m), 2928.8 (m), 2855.9 (m), 2118.6 (w), 1466.0 (m), 1254.5 (m), 1048.7 (m), 1024.7 (m), 900.6 (s), 827.7 (s), 791.6 (s), 631.1 (w).
4. **Hiyama-Denmark Coupling 3a with Aryl Halides**

![Hiyama-Denmark Coupling Reaction Diagram](image.png)

**General Procedure for Hiyama-Denmark Coupling 3a with Ph-I**

In an argon-filled glovebox, a 5 mL dried Schlenk tube was charged with Pd(OAc)$_2$ (3.4 mg, 15.0 µmol, 5 mol%), PPh$_3$ (8.6 mg, 33.0 µmol, 11.0 mol%), CH$_3$ONa (81.0 mg, 1.5 mmol) and $p$-xylene (1 mL). Then, benzoxasilole 3a (57.8 mg, 0.3 mmol) and Ph-I (67.2 µL, 0.60 mmol) were added. The tube was sealed tightly with a teflon plug under Ar atmosphere. The reaction mixture was stirred at room temperature for 1 h, and subsequently heated at 80 °C for 12 h. Then the reaction mixture was cooled to room temperature, and MeOH (1.5 mL) and 10% NaOH (2 mL) were added with vigorously stirring at 50 °C for 48 h. The resulting solution was extracted with EtOAc and washed with brine (15 mL), dried over anhydrous Na$_2$SO$_4$. After filtration and evaporation of the solvent, the crude mixture was purified by flash column chromatography (silica gel, ethyl acetate:petroleum ether = 1: 50) to obtain the desired product 4a as a white solid (49.5 mg, 78%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.67 (d, $J$ = 8.0 Hz, 1H), 7.38 (m, 6H), 7.26 (t, $J$ = 8.0 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 1.89 (s, 1H), 1.49 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.2, 143.9, 140.0, 132.2, 129.6, 127.9, 127.5, 127.2, 125.9, 74.2, 32.7. Spectral data is in agreement with published data.[8]

**General Procedure for Hiyama-Denmark Coupling 3a with Ph-Br**

In an argon-filled glovebox, a 5 mL dried Schlenk tube was charged with Pd(OAc)$_2$ (3.4 mg, 15.0 µmol, 5 mol%), PPh$_3$ (8.6 mg, 33.0 µmol, 11.0 mol%), CH$_3$ONa (81.0 mg, 1.5 mmol) and $p$-xylene (1 mL). Then, benzoxasilole 3a (57.8 mg, 0.3 mmol) and Ph-Br (63.2 µL, 0.60 mmol) were added. The tube was sealed tightly with a teflon plug under Ar atmosphere. The reaction mixture was stirred at room temperature for 1 h, and subsequently heated at 80 °C for 12 h. Then the reaction mixture was cooled to room temperature, and MeOH (1.5 mL) and 10% NaOH (2 mL) were added with vigorously stirring at 50 °C for 48 h. The resulting solution was extracted with EtOAc and washed with brine (15 mL), dried over anhydrous Na$_2$SO$_4$. After filtration and
evaporation of the solvent, the crude mixture was purified by flash column chromatography (silica
gel, ethyl acetate:petroleum ether = 1: 50) to obtain the desired product 4a as a white solid (46.6
mg, 73%).
5. References


6. NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) of 2a

$^1$C NMR (101 MHz, CDCl$_3$) of 2a
$^1$H NMR (400 MHz, CDCl$_3$) of 2b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2b
$^1$H NMR (400 MHz, CDCl$_3$) of 2c

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2c
$^1$H NMR (400 MHz, CDCl$_3$) of 2d

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2d
$^1$H NMR (400 MHz, CDCl$_3$) of 2e

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2e
$^1$H NMR (400 MHz, CDCl$_3$) of 2f

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2f
$^{19}$F NMR (376 MHz, CDCl$_3$) of 2f

$^1$H NMR (400 MHz, CDCl$_3$) of 2g
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2g

$^{19}$F NMR (376 MHz, CDCl$_3$) of 2g
$\text{H NMR (400 MHz, CDCl}_3\text{) of 2h}$

$\text{13C NMR (101 MHz, CDCl}_3\text{) of 2h}$
$^1$H NMR (400 MHz, CDCl$_3$) of 2i

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2i
$^1$H NMR (400 MHz, CDCl$_3$) of 2j

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2j
$^1$H NMR (400 MHz, CDCl$_3$) of 2k

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2k
$^1$H NMR (400 MHz, CDCl$_3$) of 2l

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2l
$^1$H NMR (400 MHz, CDCl$_3$) of 2m

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2m
$^1$H NMR (400 MHz, CDCl$_3$) of $2n$

$^{13}$C NMR (101 MHz, CDCl$_3$) of $2n$
$^1\text{H NMR (400 MHz, CDCl}_3\text{) of 2o}$

$^{13}\text{C NMR (101 MHz, CDCl}_3\text{) of 2o}$
$^{19}$F NMR (376 MHz, CDCl$_3$) of 2o

$^1$H NMR (400 MHz, CDCl$_3$) of 2p
\[ ^{13}\text{C} \text{NMR (101 MHz, CDCl}_3 \text{) of } 2p \]

\[ ^1\text{H} \text{NMR (400 MHz, CDCl}_3 \text{) of } 2q \]
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2q

$^1$H NMR (400 MHz, CDCl$_3$) of 2r
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2r

$^1$H NMR (400 MHz, CDCl$_3$) of 2s
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2s

$^1$H NMR (400 MHz, CDCl$_3$) of 2t
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2t

$^1$H NMR (400 MHz, CDCl$_3$) of 2u
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2u

$^1$H NMR (400 MHz, CDCl$_3$) of 2v
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2v

$^1$H NMR (400 MHz, CDCl$_3$) of 2w
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2w

$^1$H NMR (400 MHz, CDCl$_3$) of 2x
$^{13}$C NMR (101 MHz, CDCl$_3$) of 2x

$^{19}$F NMR (376 MHz, CDCl$_3$) of 2x
$^1$H NMR (400 MHz, CDCl$_3$) of 2y

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2y
$^1$H NMR (400 MHz, CDCl$_3$) of 2z

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2z
$^1$H NMR (400 MHz, CDCl$_3$) of 2aa

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2aa
$^1$H NMR (400 MHz, CDCl$_3$) of 2ab

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2ab
$^1$H NMR (400 MHz, CDCl$_3$) of 2ac

$^{13}$C NMR (101 MHz, CDCl$_3$) of 2ac
$^1$H NMR (400 MHz, CDCl$_3$) of 3a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3a
$^1$H NMR (400 MHz, CDCl$_3$) of 3b

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3b
$^1$H NMR (400 MHz, CDCl$_3$) of 3c

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3c
$^1$H NMR (400 MHz, CDCl$_3$) of 3d

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3d
$^1$H NMR (400 MHz, CDCl$_3$) of 3e

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3e
$^1H$ NMR (400 MHz, CDCl$_3$) of 3f

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 3f
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{) of 3f}$

$^{1}\text{H NMR (400 MHz, CDCl}_3\text{) of 3g}$
\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) of 3g

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) of 3g
$^1$H NMR (400 MHz, CDCl$_3$) of 3h

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3h
$^1$H NMR (400 MHz, CDCl$_3$) of 3i

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3i
$\text{H NMR (400 MHz, CDCl}_3\text{)}$ of $3j$

$\text{C NMR (101 MHz, CDCl}_3\text{)}$ of $3j$
$^1$H NMR (400 MHz, CDCl$_3$) of 3j' 

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3j'
$^1$H NMR (400 MHz, CDCl$_3$) of 3k™

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3k™
$^1$H NMR (400 MHz, CDCl$_3$) of 3l

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3l
$^1$H NMR (400 MHz, CDCl$_3$) of 3m

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3m
$^1$H NMR (400 MHz, CDCl$_3$) of 3n

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3n
$^1$H NMR (400 MHz, CDCl$_3$) of 3o

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3o
$^{19}$F NMR (376 MHz, CDCl$_3$) of 3o

$^1$H NMR (400 MHz, CDCl$_3$) of 3p
$^1$H NMR (400 MHz, CDCl$_3$) of 3q

$^1$H NMR (400 MHz, CDCl$_3$) of 3q

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3p
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3q

$^1$H NMR (400 MHz, CDCl$_3$) of 3r
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3r

$^1$H NMR (400 MHz, CDCl$_3$) of 3s
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3s

$^1$H NMR (400 MHz, CDCl$_3$) of 3t
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3t

$^1$H NMR (400 MHz, CDCl$_3$) of 3u
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3u

$^1$H NMR (400 MHz, CDCl$_3$) of 3w
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3w

$^1$H NMR (400 MHz, CDCl$_3$) of 3x
$^{13}$C NMR (101 MHz, CDCl$_3$) of 3x

$^{19}$F NMR (376 MHz, CDCl$_3$) of 3x
$^{1}H$ NMR (400 MHz, CDCl$_3$) of 3y

$^{13}C$ NMR (101 MHz, CDCl$_3$) of 3y
$^1$H NMR (400 MHz, CDCl$_3$) of 3z

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3z
$^1$H NMR (400 MHz, CDCl$_3$) of 3aa

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3aa
$^1$H NMR (400 MHz, CDCl$_3$) of 3ab

$^{13}$C NMR (101 MHz, CDCl$_3$) of 3ab
$^1$H NMR (400 MHz, CDCl$_3$) of 4a

$^{13}$C NMR (101 MHz, CDCl$_3$) of 4a