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Modular Approach to Reductive C_{sp2}–H and C_{sp3}–H Silylation of Carboxylic Acid Derivatives through Single-Pot, Sequential Transition Metal Catalysis

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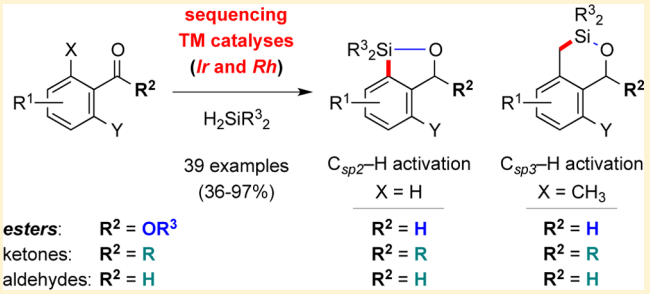
Supporting Information

ABSTRACT: We report a modular approach to catalytic reductive C_{sp2}–H and C_{sp3}–H silylation of carboxylic acid derivatives encompassing esters, ketones, and aldehydes. Choice of either an Ir(I)/Rh(I) or Rh(I)/Rh(I) sequence leads to either exhaustive reductive ester or reductive ketone/aldehyde silylation, respectively. Notably, a catalyst-controlled direct formation of doubly reduced silyl ethers is presented, specifically via Ir-catalyzed exhaustive hydrosilylation. The resulting silyl ethers undergo C_{sp2}–H and benzylic C_{sp3}–H silylation in a single vessel.



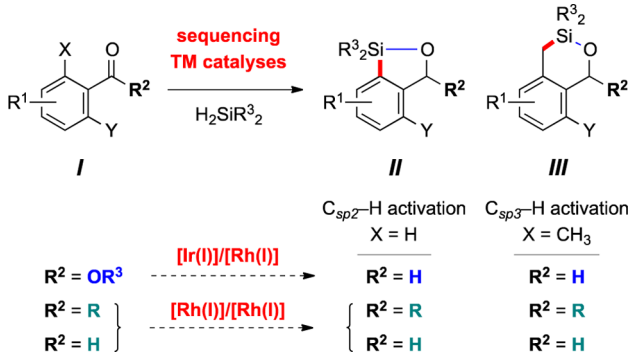
INTRODUCTION

Strategies for transition metal (TM)-catalyzed C–H activation and silylation have emerged as important tools for selective synthesis of functionalized aryl silanes.[1] Because organosilanes are generally environmentally benign, they are widely utilized for biological applications,[2] drug discovery,[3] and synthesis of advanced functional materials.[4] Particularly, cyclic silyl ethers, such as benzoxasiloles and benzoxasilines, have been utilized for complex molecule synthesis.[5] They are also extensively exploited as cross-coupling partners for silicon-based cross-coupling tactics, such as Hiyama–Denmark aryl/alkenyl cross-coupling[5a,6] or Pd- and Cu-catalyzed alkyl/aryl/alkenyl cross-coupling using benzoxasilole transfer agents,[7] through putative cyclic penta-coordinate silicate complexes. Thus, several developments to metal-catalyzed C_{sp2}–H and C_{sp3}–H silylations have been made.[8−16] Hartwig has recently demonstrated methods for in situ introduction of silyl groups into molecules followed by annulation of dialkylhydridosilyl intermediates. For instance, highly efficient Ir-catalyzed reductive C_{sp2}–H and C_{sp3}–H silylation introducing a dialkylhydridosilyl group through Ir-catalyzed hydrosilylation of aldehydes and ketones as well as dehydrogenative silylation of alcohols and challenging amines have been developed.[8f,9a,f] However, sequential dehydrogenative silylation via catalytic exhaustive hydrosilylation of easily accessible aromatic esters[17−19] followed by C–H silylation for direct synthesis of benzoxasiloles and benzoxasilines has not been reported to date. In addition, primary alcohol-derived dialkylhydridosilyl ether-directed, Rh-catalyzed dehydrogenative C_{sp3}–H silylation has not been described in the literature. Herein, we report a modular approach for catalytic reductive C_{sp2}–H and C_{sp3}–H silylation of diverse carboxylic acid derivatives, including esters, ketones, and aldehydes.

RESULTS AND DISCUSSION

We envision the development of a modular method for catalytic dehydrogenative C–H silylation of aromatic carboxylic acid derivatives through a single-pot, sequential transition metal-mediated reductive silylation directed by dialkylhydridosilyl ethers generated in situ (Scheme 1). We recently demonstrated

Scheme 1. Modular Approach for Catalytic Reductive C_{sp2}–H and C_{sp3}–H Silylation of Carboxylic Acid Derivatives Providing Direct Access to Benzoxasiloles and Benzoxasilines



the synthesis of aryl *o*-formyl silanols via reductive arene *o*-silanolization of aromatic esters.[20] During the study, we recognized that the judicious choice of transition metals and supporting ligands for hydrosilylation of carboxylic acid derivatives,[17−19] as well as C–H silylation, significantly impacted the overall efficiency of the single-pot sequence. Because of the importance of a sequential transition metal-catalyzed reaction in

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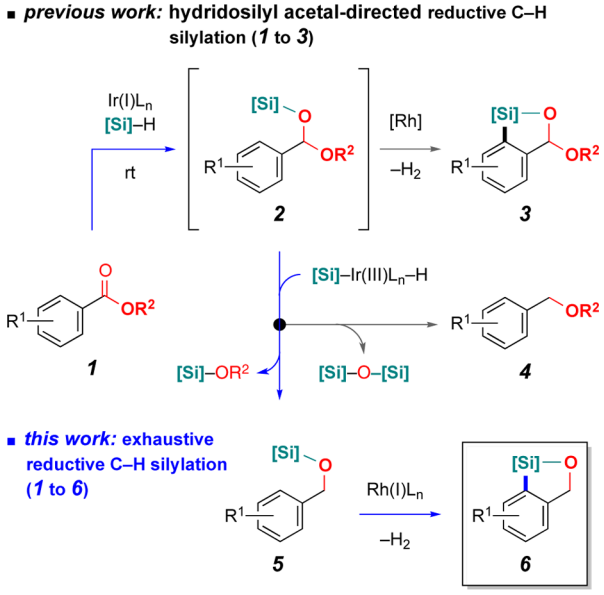
the reductive arene *o*-C−H silylation of aromatic carboxylic acid derivatives, we planned to explore an Ir(I)/Rh(I)-mediated catalytic cascade for esters and a Rh(I)/Rh(I)-mediated catalytic sequence for ketones and aldehydes, which would directly provide corresponding cyclic silyl ethers.

In our previous report examining controlled Ir-catalyzed ester hydrosilylation of esters (**1**) to afford silyl acetals (**2**),[18a,20] we found the formation of doubly reduced cyclic silyl ethers (**5**) as minor byproducts, which were only observed when arenes possessing electron-donating groups, such as an amino group or unprotected indole, were used (Scheme 2). Under these reaction

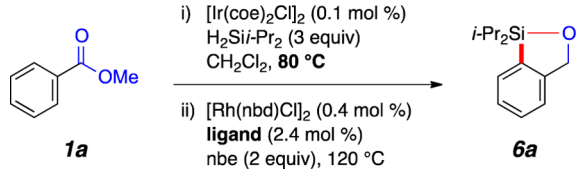
Scheme 2. Controlled Access to Either Cyclic Silyl Acetals (3) or Cyclic Silyl Ethers (5) from Aromatic Esters (6)



conditions, doubly reduced silyl ether intermediates (**5**) were first produced, which underwent subsequent C−H silylation to yield benzoxasiloles (**6**). We speculated that facile departure of the alkoxy group likely generates silyl oxocarbenium intermediates while producing silyl ethers ([Si]-OR^2), which were further reduced in the presence of external dialkyl silanes and metal.[21] We also considered an alternative route for the formation of undesired doubly reduced ethers (**4**) via a competing pathway (**2** to **4**), namely, the elimination of siloxanes ([Si]-O-[Si]) followed by metal hydride reduction of the resulting oxocarbenium intermediates.[21] Our approach requires suitable catalytic conditions favoring selective access to silyl ether intermediates (**5**) over doubly reduced ethers (**4**) in the catalytic cascade, which ultimately leads to single-pot, exhaustive, reductive arene *o*-silylation.

As mentioned earlier, we observed the formation of exhaustively reduced silyl ethers (**5**) from arenes holding electron-donating groups (e.g., *p*-dimethylamino group) in our previous study.[20] We first sought a general protocol for a single-pot, exhaustive, reductive silylation of aromatic esters by sequencing two transition metals (Ir and Rh) regardless of electronic differences of arenes or the impedance of silyl ether (**4**) formation. To this end, we found that simply warming the reaction permits exhaustive reductive silylation of the esters (**1**) to occur via direct formation of hydridosilyl ether intermediates (**5**).[19d−g] Diisopropylsilane was a particularly effective silylating agent due to the superior stability of the resulting silyl ethers (**6**) (comparatively, silyl ethers derived from diethylsilane were considerably unstable under the reaction conditions). In addition, we examined various monodentate phosphine (Table 1, entries 1−7) and phosphite (entries 8−9) ligands to discover

Table 1. Evaluation of Ligands for Sequential, Exhaustive, Reductive Arene *o*-C−H Silylation[a]



entry	ligand (deg)[b]	conv. (%)[c]	**2a** yield (%)[d]
1	PPh_3	100	97
2	P(*o*-tol)$_3$	100	10
3	P(2-furyl)$_3$	100	91
4	P(4-MeOPh)$_3$	100	99
5	P(*t*-Bu)$_3$	100	10
6	PCy_3	100	45
7	RuPhos	100	75
8	P(OEt)$_3$	100	63
9	P(OPh)$_3$	100	64
10	dppm (72°)	100	42
11	dppe (85°)	100	47
12	dppp (91°)	100	80
13	dppb (98°)	100	90
14	BINAP (92°)	100	71
15	Xantphos (107°)	100	72

[a]Conditions: (i) **1a** (0.2 mmol) in CH_2Cl_2 (3.3 M), (ii) THF (1 M). Nbd = norbornadiene; nbe = norbornene; RuPhos = 2-dicyclohexylphosphino-2′,6′-diisopropoxybiphenyl; dppm = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; XantPhos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene. [b]The listed bite angles are from ref 22. [c]Determined by GC/MS analysis and ^{1}H NMR spectroscopy utilizing an internal standard (CH_2Br_2). [d]Determined by ^{1}H NMR spectroscopy.

conditions for efficient Rh-catalyzed exhaustive reductive arene *o*-silylation, as Takai and we reported that monodentate phosphines effect Rh-catalyzed C−H silylation.[10e,20] As seen in Table 1, electron donating and sterically less hindered monodentate phosphine P(4-MeOPh)$_3$ serves as the most effective ligand (99% yield, entry 4) for arene *o*-C−H silylation of aromatic esters. Notably, the Rh-catalyzed C−H silylation [0.4 mol % of Rh/(4-MeOPh)$_3$P, 120 °C] was completed within 30 min.[8f] Other monodentate alkyl phosphines (entries 5−7) and phosphites (entries 8−9) resulted in lower yields. With the exception of BINAP and Xantphos (entries 14−15), bisphosphine ligands with larger ligand bite angles generally increased product yields (entries 10−15).[22]

Upon the reaction conditions being optimized, the scope of the exhaustive, reductive C−H silylation of aromatic esters was explored and is shown in Table 2. Both electron-rich and -deficient aromatic esters underwent exhaustive reductive arene *o*-silylation to afford benzoxasiloles (**6a−j**) in good yields. Furan, unprotected indole, silyl blocking group (TBS), and trisubstituted alkene within **6k−n** tolerated the reaction conditions well. We observed complete regioselectivity within naphthoates (**6o−p**), where the C−H silylation of 1-naphthoate only provided naphthoxasilole **6o** via selective activation of kinetically

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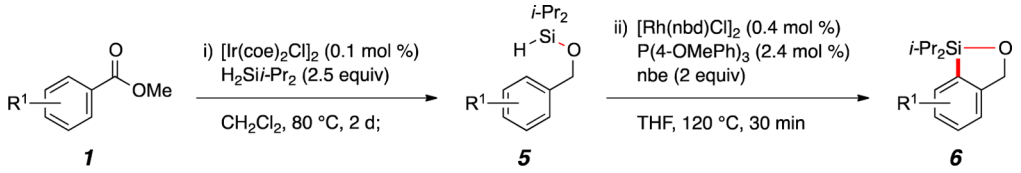
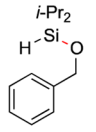
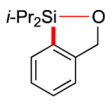
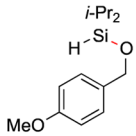
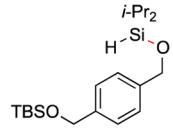
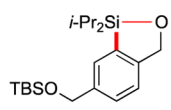
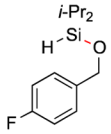
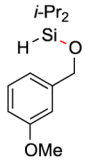
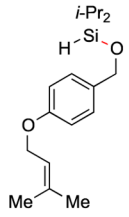
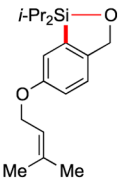
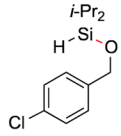
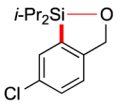
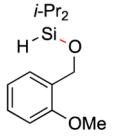
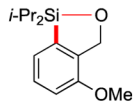
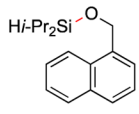
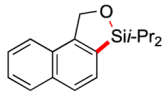
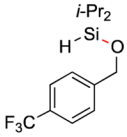
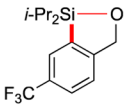
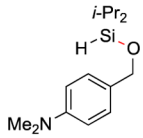
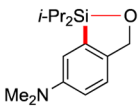
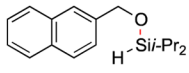
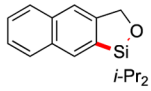
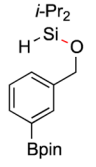
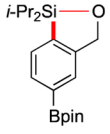
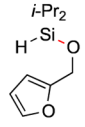
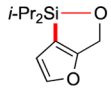
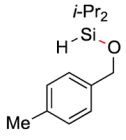
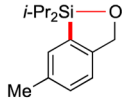
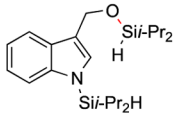
Table 2. Substrate Scope of Aromatic Esters for Sequential, Exhaustive, Reductive Arene *o*-C−H Silylation[a]



silyl ether	product	silyl ether	product	silyl ether	product
 **5a** 97%[b]	 **6a** 91%[c]	 **5g** 98%[b]	 **6g** 95%[c]	 **5m** 94%[b]	 **6m** 90%[c]
 **5b** 84%[b,d]	 **6b** 72%[c]	 **5h** 90%[b]	 **6h** 84%[c]	 **5n** 76%[b]	 **6n** 70%[c]
 **5c** 88%[b]	 **6c** 82%[c]	 **5i** 93%[b]	 **6i** 90%[c]	 **5o** 81%[b,e,f]	 **6o** 75%[c,g]
 **5d** 80%[b,e,f]	 **6d** 71%[c]	 **5j** 99%[b]	 **6j** 96%[c]	 **5p** 85%[b,d]	 **6p** 80%[c]
 **5e** 93%[b,d,f]	 **6e** 88%[c,g]	 **5k** 87%[b]	 **6k** 52%[c,g,h]		
 **5f** 96%[b]	 **6f** 92%[c]	 **5l** 99%[b,i]	 **6l** 97%[c]		

[a]Conditions: (i) **1** (0.5 mmol) in CH_2Cl_2 (3.3 M), (ii) THF (1 M). TBS = *t*-Butyldimethylsilyl; pin = pinacolato. [b]Determined by ^1H NMR spectroscopy utilizing an internal standard (CH_2Br_2). [c]Yields of **6**. [d]Reaction at 80 °C for 4 d. [e]Reaction at 80 °C for 7 d. [f]0.5 mol % of $[Ir(coe)_2Cl]_2$. [g]1 mol % of $[Rh(nbd)Cl]_2$ and 6 mol % of P(4-MeOPh)$_3$. [h]Reaction at 100 °C for 1 h. [i]3.5 equiv of H_2Si*i*-Pr_2 was used.

acidic hydrogen at C2. In addition, 2-naphthoate yielded **6p** as the sole product, but the reasons behind the observed regioselectivity are currently unclear.

Previously, Hartwig reported efficient sequential hydrosilylation of aromatic aldehydes and ketones employing $[Ir(cod)OMe]_2$ and arene *o*-C−H silylation using $[Ir(cod)OMe]_2$/phen.[8f] We examined whether the developed catalytic system of rhodium(I) with monodentate phosphine ligand for reductive arene *o*-C−H silylation of esters was also applicable for reductive arene silylation of aromatic ketones (**7**, Table 3). In these cases, we were able to achieve ketone hydrosilylation[23] and arene *o*-C−H silylation using a single loading of Rh catalyst [i.e., Rh/(4-MeOPh)$_3$P] and lower the catalyst loading to 0.2 mol %. The C−H silylation step required the supporting ligand (4-MeOPh)$_3$P for efficient annulation. On the basis of the brief optimization, we probed the scope of arene *o*-C−H silylation with aromatic ketones (**7**). Various para-substituted methyl ketones provided desired benzoxasiloles **8b−f** with good yields. Substrates **7g−h** possessing meta substituents (i.e., trifluoromethyl, internal alkyne) afforded benzoxasiloles **8g−h** as the sole

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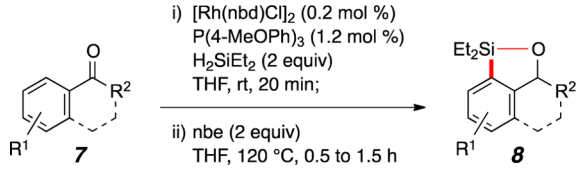
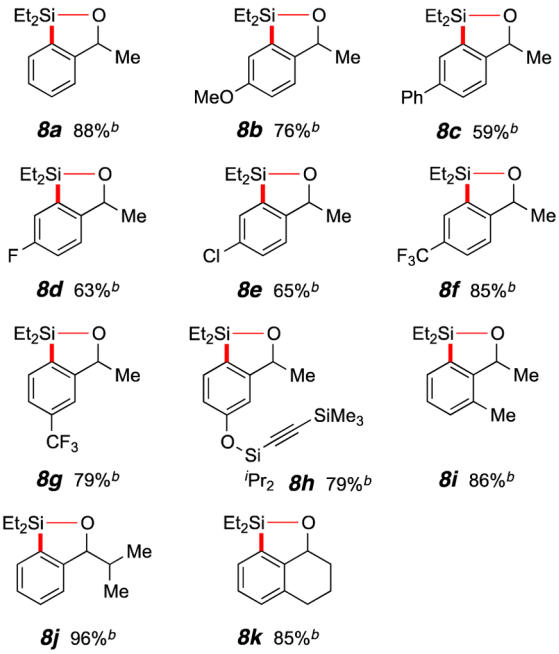
Table 3. Substrate Scope of Ketones for Sequential, Reductive Arene *o*-C−H Silylation[a]



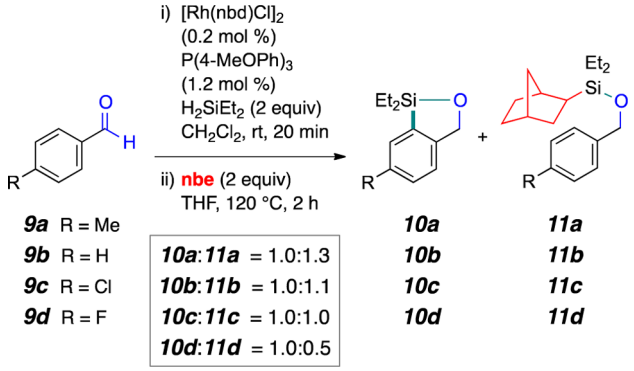


[a]Conditions: (i) 7 (1.0 mmol) in THF (1 M), (ii) THF (1 M). [b]Yields of 8.

products with complete site-selectivity favoring functionalization in less hindered C−H bonds. The more sterically congested ortho-substituted ketone **7j** also gave desired product **8j** with good yield. Sterically hindered isopropyl ketone **7j** was examined and yielded **8j** in excellent yield. Finally, cyclic ketone, 1-tetralone **7k** provided tetrahydronaphthoxasilole **8k** in 85% yield.

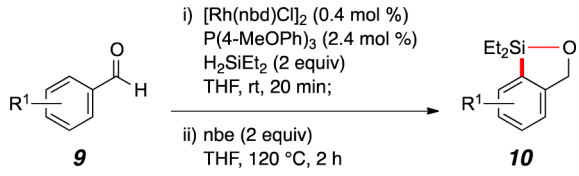
Next, we investigated the scope of arene *o*-C−H silylation with aromatic aldehydes (**9**). Under identical reaction conditions to the C−H silylation of ketones, we encountered inefficient cyclization in which a significant amount of alkene hydrosilylation adducts (**11**) were produced through the reaction between hydridosilyl ether and norbornene (i.e., a hydrogen acceptor) (Scheme 3). Notably, the tendency of the hydrosilylation correlates well to the electronic nature of the substituents on arenes. For instance, an electron-donating group (e.g., Me) in **9a** afforded more hydrosilylation adduct **11a** (**10a**:**11a** = 1.0:1.3). However, electron-withdrawing substituents, such as Cl and F, reduced the competitive hydrosilylation process, favoring the formation of benzoxasiloles (**10c**:**11c** = 1.0:1.0 and **10d**:**11d** = 1.0:0.5, respectively). We did not observe this behavior in the cases of reductive arene C−H silylation of aromatic ketones and exhaustive reductive arene C−H silylation of aromatic esters. These results indicate that the relative rate of cyclization of aldehyde-derived hydridosilyl ethers is slower than that of the ketone-derived hydridosilyl ethers, as well as that of the diisopropylhydridosilyl ethers bearing larger substituents. Thus, the slower the rate of C−H silylation, the greater the impact of competitive hydrosilylation, resulting in

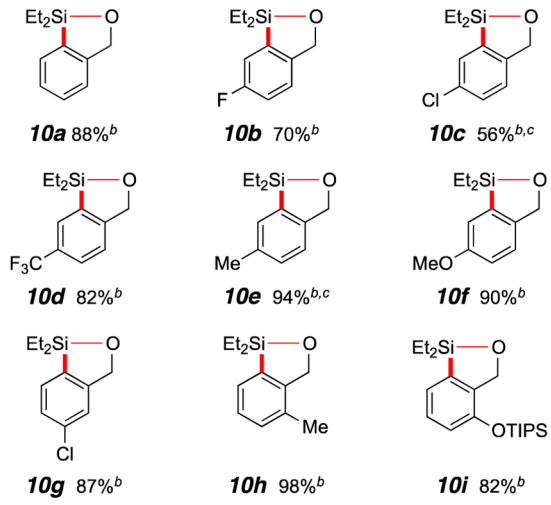
Scheme 3. Competition of C−H Silylation and Alkene Hydrosilylation



lower yields.[8f,9f] In addition, these outcomes also imply that norbornene likely resides on a Rh coordination sphere despite the fact that norbornene is commonly employed and understood as an efficient hydrogen scavenger.[24,25] When the annulation via C−H activation is not facile, the alkene hydrosilylation competes with the C−H silylation. To achieve efficient C−H silylation of aromatic aldehydes, an additional Rh catalyst (0.4−0.6 mol % relative to 0.2 mol % for ketones) was required (Table 4). Under

Table 4. Substrate Scope of Aldehydes for Sequential Reductive Silylation[a]





[a]Conditions: (i) **9** (1.0 mmol) in THF (1.0 M), (ii) THF (1. M). TIPS = triisopropylsilyl. [b]Yields of **10**. [c]0.6 mol % of $[Rh(nbd)Cl]_2$ and 3.6 mol % of $P(4\text{-}MeOPh)_3$.

the reaction conditions, several ortho-, meta-, and para-substituted aromatic aldehydes (**9**) provided corresponding benzoxasiloles **10a**−**h**. Sterically hindered TIPS-protected salicylic aldehyde **9i** also afforded desired product **10i** with good yield.

Lastly, Rh-catalyzed reductive benzylic C_{sp3}−H silylation reactions of esters, ketones, and aldehydes were studied under

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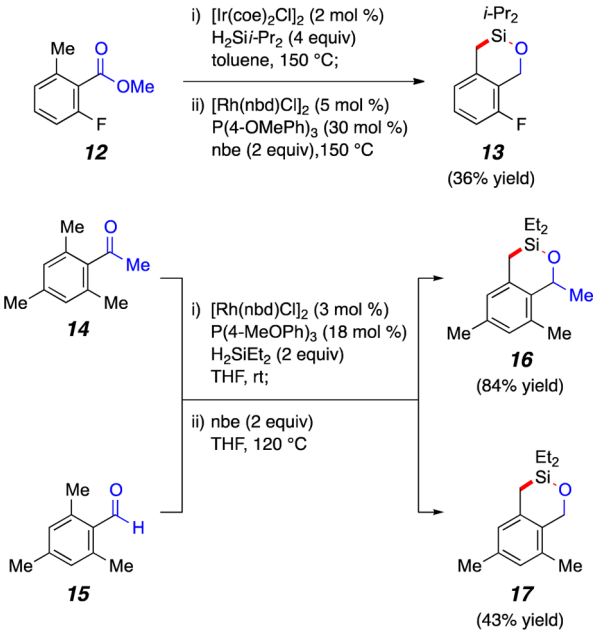
the developed catalytic reaction conditions (Scheme 4). There have been several reports of catalytic dehydrogenative benzylic

Scheme 4. Sequential, Exhaustive, Reductive Benzylic C_{sp3}–H Silylation of Aromatic Esters, Ketones, and Aldehydes



C_{sp3}–H silylation.[9a,f,c,11] For instance, Hartwig demonstrated highly efficient Ir-catalyzed C_{sp3}–H silylation directed by dialkylhydridosilyl ethers derived from tertiary alcohols. Although dialkylhydridosilyl ethers derived from secondary alcohols, which specifically hold substituents β to the hydroxyl groups, were also used for Ir-catalyzed C_{sp3}–H silylation, no example of primary alcohol-derived dialkylhydridosilyl ether-directed dehydrogenative C_{sp3}–H silylation has been reported. When ester **12** was subjected to the catalytic reaction conditions, sequential Ir- and Rh-catalyzed exhaustive, reductive C_{sp3}–H silylation indeed afforded benzoxasiline **13** in modest yield (36%), primarily due to competitive alkene hydrosilylation between the primary alcohol-derived hydridosilyl ether and norbornene (C–H silylation:hydrosilylation = 1:1.5). C_{sp3}–H silylation of aldehyde **15** provided benzoxasiline **17** with modest yield (43%), similar to those observed in esters, and Rh-catalyzed reductive C_{sp3}–H silylation of ketone **14** provided benzoxasiline **16** with good yield (84%) through relatively fast cyclization of the ketone-derived silyl ether.

CONCLUSION

In summary, we have developed a modular catalytic reductive C–H silylation of carboxylic acid derivatives via selective C_{sp2}–H and C_{sp3}–H activation to provide benzoxasiloles and benzoxasilines. A relay of Ir/Rh or Rh/Rh catalytic systems permits C–H silylation for esters, ketones, and aldehydes. Exhaustive, reductive arene *o*-C–H silylation of esters requires sequential Ir (0.1 mol %) and Rh/(4-MeOPh)$_3$P (0.4 mol %) catalytic conditions. Whereas reductive arene *o*-C–H silylation of ketones afforded diverse benzoxasiloles with good yields using Rh/(4-MeOPh)$_3$P (0.2 mol %), the reductive arene silylation of aldehydes was hindered due to competitive alkene hydrosilylation of norbornene. This was resolved by employing 0.4–0.6 mol % of Rh/(4-MeOPh)$_3$P. Finally, we examined reductive benzylic C_{sp3}–H silylation of esters, ketones, and aldehydes to provide benzoxasilines using either the Ir(I)/Rh(I) or Rh(I)/Rh(I) catalytic sequence.

EXPERIMENTAL SECTION

General Experimental Information. Reactions requiring anhydrous conditions were performed under an atmosphere of nitrogen or argon in flame- or oven-dried glassware. Anhydrous toluene and dichloromethane (DCM) were distilled from CaH_2. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone. Triethylamine and pyridine were distilled from KOH. DMF and DMSO were stored over 4 Å molecular sieves. All other solvents and reagents from commercial sources were used as received. NMR spectra were recorded on a 500 or 300 MHz NMR spectrometer. ^{1}H NMR chemical shifts are referenced to chloroform (7.26 ppm) and DMSO-d_6 (2.50 ppm). ^{13}C NMR chemical shifts are referenced to $^{13}CDCl_3$ (77.23 ppm) and DMSO-d_6 (39.52 ppm). The following abbreviations are used to describe multiplets: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), m (multiplet), nfom (nonfirst-order multiplet), and br (broad). The following format was used to report peaks: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment (e.g., CH_aH_b). ^{1}H NMR and ^{13}C NMR were processed with the iNMR software program. Infrared (IR) spectra were recorded using neat (for liquid compound) or a thin film from a concentrated DCM solution. Absorptions are reported in cm^{-1}. Only the most intense and/or diagnostic peaks are reported. MPLC refers to medium pressure liquid chromatography (25–200 psi) using hand-packed columns of silica gel (20–45 μm, spherical, 70 Å pore size), an HPLC pump, and a differential refractive index detector. High-resolution mass spectra (HRMS) were recorded in electrospray ionization time-of-flight (ESI-TOF) mode. Samples were introduced as solutions in a mixed solution of methanol and methylene chloride (DCM). GC-MS experiments using electron impact ionization (EI) were performed at 70 eV using a mass-selective detector. The method used is noted parenthetically: 5029017 refers to 2 min @ 50 °C – 20 °C/min – 3 min @ 290 °C. Analytical TLC experiments were performed on an F254 plate with 250 μm thickness. Detection was performed by UV light or potassium phosphomolybdic acid, permanganate, and *p*-anisaldehyde staining.

General Procedure for Ir-Catalyzed Exhaustive Reductive Ester Silylation—Preparation of Hydridodiisopropylsilyl Ethers (5). [Ir(coe)$_2$Cl]$_2$ (0.5 mg, 0.1 mol %) and ester **1** (0.5 mmol) were dissolved with CH_2Cl_2 (0.15 mL, 3.3 M). Diisopropylsilane (0.24 mL, 144 mg, 1.25 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at 80 °C and stirred for 2 d unless otherwise noted in Table 2. The volatiles were removed in vacuo to afford the hydridodiisopropylsilyl ethers (**5**), which were directly used for subsequent reactions without further purification. The yield of **5** was determined by ^{1}H NMR spectroscopy by the addition of CH_2Br_2 (0.5 mmol) as an internal standard after the volatiles were removed in vacuo.

General Procedure for Rh-Catalyzed Arene *o*-C–H Silylation of Hydridodiisopropylsilyl Ethers—Preparation of Benzoxasilole (6). [Rh(nbd)Cl]$_2$ (0.9 mg, 0.4 mol %), tris(4-methoxyphenyl)-phosphine (4.2 mg, 2.4 mol %), norbornene (94 mg, 2 mmol), and THF (0.25 mL, 2 M) were added to the crude mixture of silyl ethers (**5**) (0.5 mmol). The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 30 min. The reaction progress was monitored by GC-MS spectrometry. The reaction was cooled to room temperature. The volatiles were removed in vacuo, and the crude mixture was purified by MPLC to afford benzoxasilole **6** (hexanes/EtOAc = 40:1, 7 mL/min, 6–10 min).

*1,1-Diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (**6a**).* Yield (91%, 100.1 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (d, J = 7.2 Hz, 1H), 7.39 (dd, J = 7.7, 7.5 Hz, 1H), 7.28 (dd, J = 7.5, 7.2 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 5.14 (s, 2H), 1.24 (septet, J = 7.4 Hz, 2H), 1.03 (d, J = 7.4 Hz, 6H), 1.01 (d, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 151.0, 132.3, 131.9, 129.7, 126.7, 121.7, 72.7, 17.2,

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13.3; IR (neat) 3001 (w), 2942 (m), 1463 (s), 1225 (s), 1044 (s), 1030 (s), 879 (s) cm^{-1}; TLC R_f = 0.6 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.389 min, *m/z* 221 [$(M + H)^+$, 5], 220 (M^+, 18), 219 [$(M - H)^+$, 100], 177 [$(M - {}^iPr)^+$, 2]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{13}H_{21}OSi]^+$ 221.1356, found 221.1338.

*6-Fluoro-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (**6b**).* Yield (72%, 85.6 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21 [dd, J = 7.8 (J^3_{F-H}), 2.5 Hz, 1H], 7.18 [dd, J = 8.4, 4.6 (J^4_{F-H}) Hz, 1H], 7.07 [dd, J = 8.4, 8.4 (J^3_{F-H}), 2.5 Hz, 1H], 5.10 (s, 2H), 1.23 (septet, J = 7.4 Hz, 2H), 1.02 (d, J = 7.4 Hz, 6H), 1.00 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 162.2 (d, J^1_{F-C} = 249 Hz), 146.2 (d, J^4_{F-C} = 1.8 Hz), 134.8 (d, J^3_{F-C} = 4.9 Hz), 123.2 (d, J^3_{F-C} = 8.2 Hz), 118.0 (d, J^2_{F-C} = 20.4 Hz), 117.14 (d, J^2_{F-C} = 22.9 Hz), 72.3, 17.10, 17.08, 13.2; IR (neat) 2943 (w), 1461 (s), 1255 (s), 1124 (s), 632 (s) cm^{-1}; TLC R_f = 0.6 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.924 min, *m/z* 237 [$(M - H)^+$, 100], 195 [$(M - {}^iPr)^+$, 28], 107 (55); HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{13}H_{20}FOSi]^+$ 239.1262, found 239.1247.

*6-Chloro-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (**6c**).* Yield (82%, 104.1 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (d, J = 2.1 Hz, 1H), 7.35 (dd, J = 8.2, 2.1 Hz, 1H), 7.15 (d, J = 8.2 Hz, 1H), 5.09 (s, 2H), 1.23 (septet, J = 7.4 Hz, 2H), 1.02 (d, J = 7.4 Hz, 6H), 1.00 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.2, 134.8, 133.1, 131.8, 129.9, 123.1, 72.3, 17.1 (2), 13.2; IR (neat) 2943 (w), 1461 (m), 1046 (s), 879 (s), 782 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.097 min, *m/z* 255 [(M + 2-H)$^+$, 33], 253 [$(M - H)^+$, 100], 213 [$(M + 2\text{-}{}^iPr)^+$, 10], 211 [$(M - {}^iPr)^+$, 30]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{13}H_{20}ClOSi]^+$ 255.0966, found 255.0949.

*1,1-Diisopropyl-6-(trifluoromethyl)-1,3-dihydrobenzo[c][1,2]-oxasilole (**6d**).* Yield (71%, 102.2 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.80 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 5.17 (s, 2H), 1.26 (septet, J = 7.4 Hz, 2H), 1.02 (d, J = 7.4 Hz, 6H), 1.01 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 154.8, 133.4, 129.4 (q, J^2_{F-C} = 32.3 Hz), 128.9 (q, J^3_{F-C} = 3.9 Hz), 126.8 (q, J^3_{F-C} = 3.5 Hz), 124.7 (q, J^1_{F-C} = 272.2 Hz), 122.1, 72.4, 17.06, 17.04, 13.1; IR (neat) 2945 (w), 1463 (w), 1324 (s), 1123 (s), 1077 (s), 785 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.610 min, *m/z* 287 [$(M - H)^+$, 8], 269 [$(M - F)^+$, 100], 245 [$(M - {}^iPr)^+$, 2]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{14}H_{20}F_3OSi]^+$ 289.1230, found 289.1239.

*1,1-Diisopropyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-dihydrobenzo[c][1,2]oxasilole (**6e**).* Yield (88%, 152.2 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.72 (d, J = 7.2 Hz, 1H), 7.69 (s, 1H), 7.59 (d, J = 7.2 Hz, 1H), 5.14 (s, 2H), 1.35 (s, 12H), 1.23 (septet, J = 7.4 Hz, 2H), 1.01 (d, J = 7.4 Hz, 6H), 0.99 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.3, 135.8, 132.8 (2), 131.7, 127.8, 84.1, 72.6, 25.1, 17.18, 17.16, 13.3; IR (neat) 2978 (w), 2942 (w), 1381 (s), 1213 (s), 1093 (s), 1047 (s), 672 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.871 min, *m/z* 346 (M^+, 30), 345 [$(M - H)^+$, 100], 303 [$(M - {}^iPr)^+$, 48]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{19}H_{32}BO_3Si]^+$ 347.2208, found 347.2226.

*1,1-Diisopropyl-6-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**6f**).* Yield (92%, 107.6 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (s, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 5.12 (s, 2H), 2.39 (s, 3H), 1.24 (septet, J = 7.4 Hz, 2H), 1.04 (d, J = 7.4 Hz, 6H), 1.02 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 148.1, 136.0, 132.6, 132.0, 130.8, 121.4, 72.5, 21.4, 17.2 (2), 13.3; IR (neat) 2955 (w), 1685 (s), 1200 (m), 1039 (s), 1003 (s), 707 (s) cm^{-1}; TLC R_f = 0.55 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.440 min, *m/z* 234 (M^+, 20), 233 [$(M - H)^+$, 100], 191 [$(M - {}^iPr)^+$, 30]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{14}H_{23}OSi]^+$ 235.1513, found 235.1502.

*1,1-Diisopropyl-6-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole (**6g**).* Yield (95%, 118.7 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.14 (d, J = 8.3 Hz, 1H), 7.05 (d, J = 2.5 Hz, 1H), 6.95 (dd, J = 8.3, 2.5 Hz, 1H), 5.08 (s, 2H), 3.83 (s, 3H), 1.23 (septet, J = 7.4 Hz, 2H), 1.03 (d, J = 7.4 Hz, 6H), 1.01 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 158.6, 143.0, 133.6, 122.6, 116.32, 116.23, 72.3, 55.6, 17.18, 17.14, 13.2; IR (neat) 2942 (w), 1463 (s), 1224 (s), 1039 (s), 1044 (s), 879 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.328 min, *m/z* 250 (M^+, 70), 249 [$(M - H)^+$, 100], 207 [$(M - {}^iPr)^+$, 91]; HRMS (ESI/TOF) calcd for [M + Na]$^+$ [$C_{14}H_{22}NaO_2Si]^+$ 273.1281, found 273.1264.

*1,1-Diisopropyl-5-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole (**6h**).* Yield (84%, 105.1 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, J = 8.0 Hz, 1H), 6.83 (dd, J = 8.0, 2.3 Hz, 1H), 6.75 (d, J = 2.3 Hz, 1H), 5.09 (s, 2H), 3.82 (s, 3H), 1.23 (septet, J = 7.4 Hz, 2H), 1.01 (d, J = 7.4 Hz, 6H), 0.99 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 161.5, 153.3, 133.4, 122.7, 114.0, 106.4, 72.5, 55.3, 17.2 (2), 13.3; IR (neat) 2941 (w), 1597 (m), 1462 (m), 1238 (s), 1049 (s), 1044 (s), 781 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.513 min, *m/z* 250 (M^+, 30), 249 [$(M - H)^+$, 100], 207 [$(M - {}^iPr)^+$, 61]; HRMS (ESI/TOF) calcd for [M + Na]$^+$ [$C_{14}H_{22}NaO_2Si]^+$ 273.1281, found 273.1275.

*1,1-Diisopropyl-4-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole (**6i**).* Yield (90%, 112.5 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (dd, J = 7.9, 7.1 Hz, 1H), 7.15 (d, J = 7.1 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 5.13 (s, 2H), 3.83 (s, 3H), 1.24 (septet, J = 7.4 Hz, 2H), 1.04 (d, J = 7.4 Hz, 6H), 1.02 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 154.4, 139.0, 133.8, 128.5, 123.9, 110.6, 70.5, 54.9, 17.2 (2), 13.2; IR (neat) 2941 (w), 1568 (m), 1464 (m), 1255 (s), 1036 (s), 744 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.377 min, *m/z* 250 (M^+, 37), 249 [$(M - H)^+$, 100], 207 [$(M - {}^iPr)^+$, 32]; HRMS (ESI/TOF) calcd for [M + Na]$^+$ [$C_{14}H_{22}NaO_2Si]^+$ 273.1281, found 273.1269.

*1,1-Diisopropyl-N,N-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilol-6-amine (**6j**).* Yield (96%, 126.2 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.11 (d, J = 8.4 Hz, 1H), 6.90 (d, J = 2.5 Hz, 1H), 6.85 (dd, J = 8.4, 2.5 Hz, 1H), 5.08 (s, 2H), 2.97 (s, 6H), 1.23 (septet, J = 7.4 Hz, 2H), 1.05 (d, J = 7.4 Hz, 6H), 1.02 (d, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.7, 139.3, 132.8, 122.1, 115.48, 115.39, 72.3, 41.3, 17.29, 17.23, 13.3; IR (neat) 2941 (w), 1684 (m), 1487 (m), 1341 (m), 1171 (s), 1040 (s), 783 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 11.168 min, *m/z* 264 [$(M + H)^+$, 42], 263 (M^+, 100), 262 [$(M - H)^+$, 39], 220 [$(M - {}^iPr)^+$, 60]; HRMS (ESI/TOF) calcd for [M + Na]$^+$ [$C_{15}H_{25}NNaOSi]^+$ 286.1598, found 286.1605.

*1,1-Diisopropyl-1,3-dihydrofuro[3,2-c][1,2]oxasilole (**6k**).* Yield (52%, 54.6 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (d, J = 1.7 Hz, 1H), 6.36 (d, J = 1.7 Hz, 1H), 4.83 (s, 2H), 1.13 (septet, J = 7.2 Hz, 2H), 1.00 (d, J = 7.2 Hz, 6H), 0.99 (d, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 169.1, 146.3, 111.7, 111.5, 65.1, 17.15, 17.00, 13.4; IR (neat) 2944 (w), 1462 (m), 1133 (s), 1051 (s), 881 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.135 min, *m/z* 210 (M^+, 7), 209 [$(M - H)^+$, 37], 167 [$(M - {}^iPr)^+$, 4], 141 (100); HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{11}H_{19}O_2Si]^+$ 211.1149, found 211.1137.

*8-(Diisopropylsilyl)-1,1-diisopropyl-3,8-dihydro-1H-[1,2]oxasilolo-[3,4-b]indole (**6l**).* Yield (97%, 180.9 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 8.3 Hz, 1H), 7.23 (dd, J = 8.3, 7.1 Hz, 1H), 7.15 (dd, J = 7.8, 7.1 Hz, 1H), 5.22 (s, 2H), 4.58 (t, J = 4.3 Hz, 1H), 1.13 (septet of d, J = 7.4, 4.3 Hz, 2H), 1.32 (septet, J = 7.5 Hz, 2H), 1.21 (d, J = 7.4 Hz, 6H), 1.13 (d, J = 7.4 Hz, 6H), 1.06 (d, J = 7.5 Hz, 6H), 1.01 (d, J = 7.5 Hz, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 147.6, 142.7, 138.3, 126.7, 122.7, 120.0, 119.5, 113.6, 66.4, 18.8, 18.4, 17.6, 17.4, 13.8, 12.8; IR (neat) 2942 (m), 2142 (w), 1501 (m), 1277 (s), 1034 (s), 739 (s) cm^{-1}; TLC R_f = 0.6 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 13.885 min, *m/z* 374 [$(M + H)^+$, 100], 373 (M^+, 50), 330 [$(M - {}^iPr)^+$, 21], 258 [$(M - Si{}^iPr_2H)^+$, 7]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{21}H_{36}NOSi_2]^+$ 374.2330, found 374.2314.

*6-[{(tert-Butyldimethylsilyl)oxy}methyl]-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (**6m**).* Yield (90%, 163.8 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J = 1.6 Hz, 1H), 7.35 (dd, J = 7.9, 1.6 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 5.12 (s, 2H), 4.78 (s, 2H), 1.23 (septet, J = 7.4 Hz, 2H), 1.02 (d, J = 7.4 Hz, 6H), 0.99 (d, J = 7.4 Hz, 6H), 0.93 (s, 9H), 0.09 (s, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.8, 139.8, 131.9, 130.0, 128.1, 121.5, 72.6, 65.3, 26.2, 18.6, 17.2 (2), 13.3, −5.0; IR (neat) 2943 (w), 1462 (m), 1253 (s), 1087 (s), 1046 (s), 835 (s) cm^{-1}; TLC R_f = 0.55 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.347 min, *m/z* 365 [$(M + H)^+$, 29], 364 (M^+, 100),

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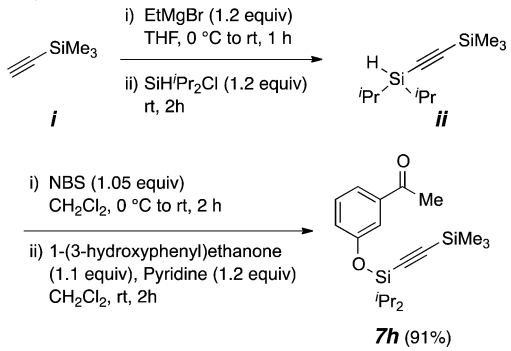
321 [(M − ^{i}Pr)$^+$, 7], 307[(M − ^{t}Bu)$^+$, 21]; HRMS (ESI/TOF) calcd for [M + Na]$^+$ [$C_{20}H_{36}NaO_2Si_2$]$^+$ 387.2146, found 387.2129.

*1,1-Diisopropyl-6-((3-methylbut-2-en-1-yl)oxy)-1,3-dihydrobenzo[c][1,2]oxasilole (**6n**).* **6n** contains double bond migration byproduct (1,1-disubstituted alkene **6n′**). The ratio of the two compounds (**6n**:**6n′**) is approximately 1:0.08. Combined yield (70%, 106.3 mg); clear oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 2.5 Hz, 1H), 6.97 (dd, J = 8.4, 2.5 Hz, 1H), 5.51 (tp, J = 6.8, 1.4 Hz, 1H), 5.08 (s, 2H), 4.86 (app s, 0.08H, **6n′**), 4.82 (app s, 0.08H, **6n′**), 4.54 (d, J = 6.8 Hz, 2H), 4.10 (t, J = 6.8 Hz, 0.16H, **6n′**), 2.52 (t, J = 6.8 Hz, 0.16H, **6n′**), 1.82 (s, 0.24H, **6n′**), 1.80 (s, 3H), 1.76 (s, 3H), 1.22 (septet, J = 7.3 Hz, 2H), 1.02 (d, J = 7.3 Hz, 6H), 1.00 (d, J = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz) only for **6n** δ 157.9, 142.9, 138.4, 133.5, 122.5, 120.0, 117.4, 116.9, 72.3, 65.1, 26.1, 18.4, 17.2 (2), 13.3; IR (neat) 2941 (w), 1597 (w), 1563 (w), 1462 (m), 1216 (s), 1045 (s), 880 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.186 min, m/z 304 (M$^+$, 26), 303 [(M − H)$^+$, 100], 236 [(M − isoprenyl)$^+$, 59]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{18}H_{29}O_2Si$]$^+$ 305.1931, found 305.1929.

*3,3-Diisopropyl-1,3-dihydronaphtho[2,1-c][1,2]oxasilole (**6o**).* Yield (75%, 101.3 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95−7.90 (m, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.74−7.69 (m, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.58−7.51 (m, 2H), 5.61 (s, 2H), 1.31 (septet, J = 7.5 Hz, 2H), 1.07 (d, J = 7.5 Hz, 6H), 1.05 (d, J = 7.5 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 148.5, 134.2, 129.5, 128.8, 128.14, 128.09, 127.3, 126.7, 126.4, 123.2, 72.1, 17.28, 17.23, 13.4; IR (neat) 2941 (w), 1508 (w), 1461 (m), 1070 (s), 1025 (s), 880 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.286 min, m/z 270 (M$^+$, 72), 269 [(M − H)$^+$, 100], 227 [(M − ^{i}Pr)$^+$, 15]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{17}H_{23}OSi$]$^+$ 271.1513, found 271.1502.

*1,1-Diisopropyl-1,3-dihydronaphtho[2,3-c][1,2]oxasilole (**6p**).* Yield (80%, 108.2 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.11 (s, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.68 (s, 1H), 7.51 (ddd, J = 7.8, 6.8, 1.5 Hz, 1H), 7.47 (ddd, J = 7.8, 6.8, 1.5 Hz, 1H), 5.33 (s, 2H), 1.32 (septet, J = 7.4 Hz, 2H), 1.09 (d, J = 7.4 Hz, 6H), 1.05 (d, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 147.0, 134.5, 133.0, 132.9, 131.1, 128.5, 128.0, 126.8, 125.6, 119.5, 77.3, 17.2 (2), 13.3; IR (neat) 2941 (w), 1487 (m), 1462 (m), 1051 (s), 1010 (s), 743 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.282 min, m/z 270 (M$^+$, 59), 269 [(M − H)$^+$, 100], 227 [(M − ^{i}Pr)$^+$, 30]; HRMS (ESI/TOF) calcd for [M + Na]$^+$ [$C_{17}H_{22}NaOSi$]$^+$ 293.1332, found 293.1322.

Synthesis of 1-[3-({Diisopropyl[(trimethylsilyl)ethynyl]silyl}-oxy)phenyl]ethanone (7h).



7h (91%)

Trimethylsilylacetylene (**i**) (1.4 mL, 10 mmol) was dissolved in THF (10 mL, 1 M), and the solution was kept at 0 °C with an ice bath. Ethylmagnesium bromide (4 mL, 3.0 M in Et_2O, 12 mmol) was added to the mixture. The reaction mixture was warmed to rt and stirred for 1h. Chlorodiisopropylsilane (2.0 mL, 1.77 g, 12 mmol) was added to the reaction mixture, and the mixture was stirred for 2 h at rt. The reaction was quenched with aqueous saturated NH_4Cl (20 mL), and the mixture was extracted with diethyl ether (30 mL × 3). The combined organic phase was washed with water and brine and dried over anhydrous sodium sulfate. The volatiles were removed in vacuo to afford the crude disilane (**ii**), which was directly used for the subsequent reaction without further purification. Disilane (**ii**) (636 mg, 3 mmol) was dissolved by CH_2Cl_2 (10 mL, 0.3 M), and the solution was kept at 0 °C with an ice bath. NBS (552 mg, 3.1 mmol) was added in one portion. After being stirred for 5 min at 0 °C, the reaction mixture was warmed to rt and stirred for 2 h. Pyridine (0.31 mL, 3.6 mmol) and 1-(3-hydroxyphenyl)-ethanone (449 mg, 3.3 mmol) in CH_2Cl_2 (3 mL) were added to the reaction mixture. The mixture was stirred for 2 h at rt. The volatiles were removed in vacuo, and the residue was dissolved with pentane and filtered through a pad of Celite. The volatiles were removed in vacuo, and the crude mixture was purified by MPLC to afford ketone **7h** (0.94 g, 91%) (hexanes/EtOAc = 60:1, 7 mL/min, 7 min).

7h: clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.65 (app t, J = 2.0 Hz, 1H), 7.56 (ddd, J = 7.5, 1.5, 1.5 Hz, 1H), 7.32 (dd, J = 8.1, 7.5 Hz, 1H), 7.24 (ddd, J = 8.1, 2.5, 1.5 Hz, 1H), 2.57 (s, 3H), 1.17−1.11 (m, 2H), 1.09 (d, J = 6.2 Hz, 6H), 1.08 (d, J = 6.2 Hz, 6H), 0.18 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 197.9, 155.9, 138.5, 129.4, 124.9, 121.7, 119.7, 118.7, 107.2, 26.8, 17.21, 17.07, 13.1, 0.2; IR (neat) 2947 (w), 2107 (w), 1688 (s), 1464 (w), 1278 (s), 1250 (s), 841 (s), 784 (s), 686 (s) cm^{-1}; TLC R_f = 0.6 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 11.710 min, m/z 347 [(M + H)$^+$, 51], 346 (M$^+$, 49), 345 [(M − H)$^+$, 27], 331 [(M − Me)$^+$, 100], 345 [(M − ^{i}Pr)$^+$, 8]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{19}H_{31}O_2Si_2$]$^+$ 347.1857, found 347.1839.

General Procedure for Rh-Catalyzed Sequential, Reductive Arene *o*-C−H Silylation of Aromatic Ketones (8). [Rh(nbd)Cl]$_2$ (0.9 mg, 0.2 mol %), tris(4-methoxyphenyl)phosphine (4.3 mg, 1.2 mol %), and ketone **7** (1 mmol) were dissolved in THF (1 mL, 1 M). Diethylsilane (0.28 mL, 173 mg, 2 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at rt and stirred for 20 min. The volatiles were removed in vacuo to afford the crude hydridodiethylsilyl ethers, which were directly used for subsequent reactions without further purification. Norbornene (188 mg, 2 mmol) and THF (1 mL, 1 M) were added to the crude silyl ether reaction mixture. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 0.5−1.5 h. The reaction progress was monitored by GC-MS spectrometry. The reaction was cooled to room temperature. The volatiles were removed in vacuo, and the crude mixture was purified by MPLC to afford benzoxasilole **8** (hexanes/EtOAc = 60:1, 7 mL/min, 10−15 min).

*1,1-Diethyl-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8a**).* Yield (88%, 181.2 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (d, J = 7.2 Hz, 1H), 7.40 (dd, J = 7.6, 7.6 Hz, 1H), 7.29 (dd, J = 7.2, 7.2 Hz, 1H), 7.22 (d, J = 7.6 Hz, 1H), 5.34 (q, J = 6.5 Hz, 1H), 1.51 (d, J = 6.5 Hz, 3H), 0.98−0.92 (m, 6H), 0.90−0.74 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 155.2, 133.1, 131.6, 129.8, 126.9, 122.3, 78.3, 25.3, 7.36, 7.25, 6.88, 6.65; IR (neat) 3059 (w), 2956 (w), 1261 (m), 1082 (s), 1019 (s), 922 (s), 711 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.294 min, m/z 207 [(M + H)$^+$, 42], 206 (M$^+$, 22), 205 [(M − H)$^+$, 77], 191 [(M − Me)$^+$, 100]; HRMS (ESI/TOF) calcd for [M + H]$^+$ [$C_{12}H_{19}OSi$]$^+$ 207.1200, found 207.1182.

*1,1-Diethyl-6-methoxy-3-methyl-1,3-dihydrobenzo[c][1,2]-oxasilole (**8b**).* Yield (76%, 179.4 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 6.96 (dd, J = 8.4, 2.5, Hz, 1H), 5.30 (q, J = 6.4 Hz, 1H), 3.83 (s, 3H), 1.48 (d, J = 6.4 Hz, 3H), 0.98−0.92 (m, 6H), 0.90−0.74 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 158.8, 147.4, 134.8, 123.3, 116.5, 115.3, 78.0, 55.6, 25.5, 7.32, 7.23, 6.89, 6.66; IR (neat) 3058 (w), 2956 (w), 1465 (m), 1266 (m), 1223 (s), 1080 (s), 922 (s), 692 (s) cm^{-1}; TLC R_f = 0.3 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.817 min, m/z 237 [(M + H)$^+$, 17], 236 (M$^+$, 28), 235 [(M − H)$^+$, 59], 220 [(M − H − Me)$^+$, 100]; HRMS (ESI/TOF) calcd for [M + K]$^+$ [$C_{13}H_{20}KO_2Si$]$^+$ 275.0864, found 275.0875.

*1,1-Diethyl-3-methyl-6-phenyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8c**).* Yield (59%, 166.4 mg); clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.74 (d, J = 1.6 Hz, 1H), 7.64 (dd, J = 8.0, 1.6 Hz, 1H), 7.62−7.60 (m, 2H), 7.46 (app t, J = 7.7 Hz, 2H), 7.36 (dddd, J = 7.4, 7.4, 1.3, 1.3 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 5.39 (q, J = 6.4 Hz, 1H), 1.56 (d, J = 6.4 Hz, 1H), 1.02−0.96 (m, 6H), 0.94−0.79 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 154.3, 141.5, 140.1, 134.0, 130.2, 129.1, 129.0, 127.5, 127.4, 122.7, 78.2, 25.4, 7.39, 7.28, 6.94, 6.72; IR (neat) 3059 (w), 2956 (w), 1675 (m), 1460 (m), 1070 (s), 1004 (s), 922 (s), 764 (s)

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cm^{-1}; TLC R_f = 0.35 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.529 min, *m/z* 283 [$(M + H)^+$, 29], 282 (M^+, 58), 281 [$(M - H)^+$, 100], 267 [$(M - Me)^+$, 65]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{18}H_{23}OSi]^+$ 283.1513, found 283.1501.

1,1-Diethyl-6-fluoro-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8d**). Yield (63%, 141.2 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.17 [dd, J = 7.8 (J^3_{F-H}), 2.5 Hz, 1H], 7.16 [dd, J = 8.8, 4.6 (J^4_{F-H}) Hz, 1H], 7.07 [ddd, J = 8.8, 8.5 (J^3_{F-H}), 2.5 Hz, 1H], 5.30 (q, J = 6.4 Hz, 1H), 1.49 (d, J = 6.4 Hz, 3H), 0.97−0.91 (m, 6H), 0.90−0.74 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 162.2 (d, J^1_{F-C} = 246 Hz), 150.6 (d, J^4_{F-C} = 2.1 Hz), 135.9 (d, J^3_{F-C} = 4.8 Hz), 123.9 (d, J^3_{F-C} = 8.2 Hz), 117.24 (d, J^2_{F-C} = 19.3 Hz), 117.19 (d, J^2_{F-C} = 22.8 Hz), 78.0, 25.5, 7.25, 7.16, 6.82, 6.58; IR (neat) 2958 (w), 1575 (w), 1464 (m), 1318 (s), 1258 (s), 1149 (s), 925 (s), 725 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.264 min, *m/z* 225 [$(M + H)^+$, 34], 224 (M^+, 14), 223 [$(M - H)^+$, 51], 209 [$(M - Me)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{12}H_{18}FOSi]^+$ 225.1105, found 225.1116.

6-Chloro-1,1-diethyl-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8e**). Yield (65%, 156.1 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, J = 2.1 Hz, 1H), 7.35 (dd, J = 8.2, 2.1 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 5.30 (q, J = 6.5 Hz, 1H), 1.48 (d, J = 6.5 Hz, 3H), 0.99−0.91 (m, 6H), 0.90−0.74 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 153.5, 135.9, 133.2, 131.1, 130.0, 123.8, 78.0, 25.3, 7.26, 7.17, 6.83, 6.59; IR (neat) 2957 (w), 1455 (m), 1317 (m), 1136 (s), 1060 (s), 923 (s), 722 (s) cm^{-1}; TLC R_f = 0.4 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.505 min, *m/z* 243 [$(M + 2 + H)^+$, 13], 241 [$(M + H)^+$, 40], 227 [$(M + 2 - Me)^+$, 37], 209 [$(M - Me)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{12}H_{18}ClOSi]^+$ 241.0810, found 241.0819.

1,1-Diethyl-3-methyl-6-(trifluoromethyl)-1,3-dihydrobenzo[c][1,2]oxasilole (**8f**). Yield (85%, 232.9 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.78 (s, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 5.37 (q, J = 6.5 Hz, 1H), 1.52 (d, J = 6.5 Hz, 3H), 0.98−0.91 (m, 6H), 0.93−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 158.9, 134.5, 129.5 (q, J^2_{F-C} = 32.1 Hz), 128.4 (q, J^3_{F-C} = 3.6 Hz), 126.9 (q, J^3_{F-C} = 3.6 Hz), 124.7 (q, J^1_{F-C} = 272.2 Hz), 122.7, 78.2, 25.1, 7.22, 7.14, 6.78, 6.56; IR (neat) 2960 (w), 1324 (m), 1261 (m), 1121 (s), 1077 (s), 925 (s), 729 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.057 min, *m/z* 275 [$(M + H)^+$, 100], 274 (M^+, 41), 273 [$(M - H)^+$, 70], 259 [$(M - Me)^+$, 42]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{13}H_{18}F_3OSi]^+$ 275.1074, found 275.1081.

1,1-Diethyl-3-methyl-5-(trifluoromethyl)-1,3-dihydrobenzo[c][1,2]oxasilole (**8g**). Yield (79%, 216.5 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.66 (d, J = 7.5 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 7.45 (s, 1H), 5.37 (q, J = 6.5 Hz, 1H), 1.53 (d, J = 6.5 Hz, 3H), 0.98−0.91 (m, 6H), 0.90−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 155.6, 138.1, 132.13, 132.05 (q, J^2_{F-C} = 32 Hz), 124.5 (q, J^1_{F-C} = 273.1 Hz), 123.8 (q, J^3_{F-C} = 3.6 Hz), 119.0 (q, J^3_{F-C} = 3.7 Hz), 78.2, 25.1, 7.19, 7.10, 6.78, 6.55; IR (neat) 2959 (w), 1688 (w), 1370 (m), 1124 (m), 1087 (s), 719 (s) cm^{-1}; TLC R_f = 0.5 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.007 min, *m/z* 275 [$(M + H)^+$, 78], 274 (M^+, 27), 273 [$(M - H)^+$, 100], 259 [$(M - Me)^+$, 30], 255 [$(M - F)^+$, 54]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{13}H_{18}F_3OSi]^+$ 275.1074, found 275.1089.

5-([Diisopropyl{(trimethylsilyl)ethynyl}silyl]oxy)-1,1-diethyl-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8h**). Yield (79%, 340.8 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.37 (d, J = 7.9 Hz, 1H), 6.97 (dd, J = 7.9, 2.0 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 5.25 (q, J = 6.5 Hz, 1H,), 1.47 (d, J = 6.5 Hz, 3H), 1.15−1.04 (m, 14H), 0.96−0.91 (m, 6H), 0.86−0.71 (m, 4H), 0.18 (s, 9H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 157.5, 157.2, 132.4, 124.8, 119.4, 118.3, 113.6, 107.8, 78.0, 25.3, 17.30, 17.26, 17.20 (2), 13.26, 13.24, 7.51, 7.42, 6.91, 6.69, −0.08; IR (neat) 2956 (w), 1596 (w), 1463 (w), 1276 (s), 1250 (s), 1004 (s), 918 (s), 763 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.703 min, *m/z* 433 [$(M + H)^+$, 53], 432 (M^+, 100), 418 [$(M + H - Me)^+$, 33]; HRMS (ESI/TOF) calcd for $[M + Na]^+$ $[C_{23}H_{40}NaO_2Si_3]^+$ 455.2228, found 455.2233.

1,1-Diethyl-3,4-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8i**). Yield (86%, 189.2 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.40 (d, J = 7.0 Hz, 1H), 7.23 (app t, J = 7.2 Hz, 1H), 7.18 (d, J = 7.3 Hz, 1H), 5.41 (q, J = 6.3 Hz, 1H), 2.31 (s, 3H), 1.49 (d, J = 6.3 Hz, 3H), 1.03 (t, J = 7.5 Hz, 3H), 0.91 (t, J = 7.5 Hz, 3H), 0.89−0.74 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 153.4, 133.2, 131.9, 131.7, 129.3, 127.3, 77.9, 24.4, 19.5, 7.81, 7.19, 7.05, 6.63; IR (neat) 2956 (w), 1458 (w), 1018 (s), 943 (s), 871 (s), 744 (s) cm^{-1}; TLC R_f = 0.55 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.076 min, *m/z* 221 [$(M + H)^+$, 23], 220 (M^+, 10), 219 [$(M - H)^+$, 31], 205 [$(M - Me)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{13}H_{21}OSi]^+$ 221.1356, found 221.1343.

1,1-Diethyl-3-isopropyl-1,3-dihydrobenzo[c][1,2]oxasilole (**8j**). Yield (96%, 224.6 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.56 (d, J = 7.2 Hz, 1H), 7.40 (ddd, J = 7.2, 7.2, 1.3 Hz, 1H), 7.29 (dddd, J = 7.2, 7.2, 1.3, 0.9 Hz, 1H), 7.29 (dq, J = 7.7, 0.9 Hz, 1H), 5.15 (d, J = 2.7 Hz, 1H), 2.13 (qqd, J = 6.8, 6.8, 2.7 Hz, 1H), 1.19 (d, J = 6.8 Hz, 3H), 1.08 (t, J = 8 Hz, 3H), 0.93−0.77 (m, 7H), 0.63 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 153.1, 134.8, 131.6, 129.7, 126.8, 122.5, 86.69, 34.66, 20.48, 15.21, 7.26, 7.09, 6.98, 6.66; IR (neat) 2957 (w), 1678 (m), 1459 (w), 1231 (m), 1014 (s), 732 (s) cm^{-1}; TLC R_f = 0.6 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.131 min, *m/z* 235 [$(M + H)^+$, 4], 234 (M^+, 3), 233 [$(M - H)^+$, 15], 191 [$(M - {}^iPr)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{14}H_{23}OSi]^+$ 235.1513, found 235.1501.

2,2-Diethyl-6,7,8,8a-tetrahydro-2H-naphtho[1,8-cd][1,2]oxasilole (**8k**). Yield (85%, 197.1 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.39 (d, J = 7.4 Hz, 1H), 7.24 (dd, J = 7.2, 7.2 Hz, 1H), 7.14 (app d, J = 7.2 Hz, 1H), 4.96 (dd, J = 11.4, 5.0 Hz, 1H), 2.85 (ddd, J = 17.2, 7.7, 3.0 Hz, 1H), 2.73 (ddd, J = 17.2, 9.7, 7.4 Hz, 1H), 2.35 (dddd, J = 12.0, 5.0, 4.3, 4.3 Hz, 1H), 2.02 (ddddd, J = 14.0, 7.4, 4.6, 4.3, 3.0 Hz, 1H), 1.89 (ddddd, J = 14.0, 12.0, 9.7, 7.7, 4.3 Hz, 1H), 1.47 (dddd, J = 12.0, 12.0, 11.4, 4.6 Hz, 1H), 1.04 (t, J = 7.5 Hz, 3H), 0.96−0.75 (m, 7H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.1, 134.0, 133.1, 129.7, 129.1, 127.6 78.8, 31.5, 26.8, 20.7, 6.93, 6.84, 6.79, 6.62; IR (neat) 2951 (w), 1459 (w), 1059 (m), 1006 (s), 724 (s) cm^{-1}; TLC R_f = 0.35 in 20:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.336 min, *m/z* 233 [$(M + H)^+$, 19], 232 (M^+, 100), 233 [$(M - H)^+$, 15], 206 [$(M - H - Me)^+$, 4]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{14}H_{21}OSi]^+$ 233.1356, found 233.1343.

General Procedure for Rh-Catalyzed Sequential, Reductive Arene *o*-C−H Silylation of Aromatic Aldehydes (10). $[Rh(nbd)Cl]_2$ (1.8 mg, 0.4 mol %), *tris*(4-methoxyphenyl)phosphine (8.6 mg, 2.4 mol %), and aldehyde **9** (1 mmol) were dissolved in THF (1 mL, 1 M). Diethylsilane (0.28 mL, 173 mg, 2 mmol) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at rt and stirred for 20 min. The volatiles were removed in vacuo to afford the crude hydridodiethylsilyl ethers, which were directly used for subsequent reactions without further purification. Norbornene (188 mg, 2 mmol) and THF (1 mL, 1 M) were added to the crude reaction mixture of silyl ether. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 2 h. The reaction progress was monitored by GC/MS spectrometry. The reaction was cooled to room temperature. The volatiles were removed in vacuo, and the crude mixture was purified by MPLC to afford benzoxasilole **10** (hexanes/EtOAc = 80:1, 7 mL/min, 7−12 min).

1,1-Diethyl-1,3-dihydrobenzo[c][1,2]oxasilole1,1-diethyl-1,3-dihydrobenzo[c][1,2]oxasilole (**10a**). Yield (88%, 168.9 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J = 7.2 Hz, 1H), 7.39 (dd, J = 7.7, 7.7 Hz, 1H), 7.30 (dd, J = 7.2, 7.2 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 5.16 (s, 2H), 0.97−0.94 (m, 6H), 0.91−0.78 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.7, 133.3, 131.8, 129.7, 126.9, 121.8, 72.3, 7.15, 6.63; IR (neat) 3003 (w), 2956 (w), 1262 (s), 722 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.197 min, *m/z* 193 [$(M + H)^+$, 12], 192 (M^+, 20), 191 [$(M - H)^+$, 67], 179 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{11}H_{17}OSi]^+$ 193.1043, found 193.1032.

1,1-Diethyl-6-fluoro-1,3-dihydrobenzo[c][1,2]oxasilole (**10b**). Yield (70%, 147.1 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.21 [dd, J = 7.8 (J^3_{F-H}), 2.5 Hz, 1H], 7.19 [dd, J = 8.3, 4.5 (J^4_{F-H}) Hz, 1H], 7.08 [dd, J = 8.8 (J^3_{F-H}), 8.3, 2.5 Hz, 1H], 5.11 (s, 2H), 0.97−0.93 (m, 6H), 0.90−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 162.3 (d, J^1_{F-C} = 246 Hz), 145.9 (d, J^4_{F-C} = 2.3 Hz), 136.0 (d, J^3_{F-C} = 5.3 Hz),

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123.3 (d, J^3_{F-C} = 7.2 Hz), 117.47 (d, J^2_{F-C} = 20.3 Hz), 117.17 (d, J^2_{F-C} = 22.8 Hz), 71.9, 7.07, 6.54; IR (neat) 2957 (w), 1461 (w), 1211 (s), 1050 (s), 785 (s), 706 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.181 min, *m/z* 209 [$(M - H)^+$, 85], 181 [$(M - Et)^+$, 10], 109 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{11}H_{16}FOSi]^+$ 211.0949, found 211.0957.

*6-Chloro-1,1-diethyl-1,3-dihydrobenzo[c][1,2]oxasilole (**10c**).* Yield (56%, 125.4 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 5.11 (s, 2H), 0.97−0.92 (m, 6H), 0.90−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 148.8, 136.0, 133.1, 131.3, 129.9, 123.2, 71.9, 7.06, 6.54; IR (neat) 2956 (w), 1454 (w), 1094 (s), 1049 (s), 765 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.461 min, *m/z* 227 [$(M + 2 + H)^+$, 21], 225 [$(M + H)^+$, 60], 197 [$(M - Et)^+$, 2], 89 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{11}H_{16}ClOSi]^+$ 227.0653, found 227.0640.

*1,1-Diethyl-6-(trifluoromethyl)-1,3-dihydrobenzo[c][1,2]oxasilole (**10d**).* Yield (82%, 213.2 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.81 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 5.18 (s, 2H), 0.98−0.93 (m, 6H), 0.93−0.80 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 154.5, 134.6, 129.5 (q, J^2_{F-C} = 32.2 Hz), 128.5 (q, J^3_{F-C} = 3.9 Hz), 126.8 (q, J^3_{F-C} = 3.6 Hz), 124.7 (q, J^1_{F-C} = 272.5 Hz), 122.2, 72.1, 7.05, 6.52; IR (neat) 2955 (w), 1460 (w), 1325 (m), 1261 (s), 1131 (s), 1078 (s), 725 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 7.953 min, *m/z* 261 [$(M + H)^+$, 2], 260 (M^+, 1), 225 [$(M - H)^+$, 7], 241 [$(M - F)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{12}H_{16}F_3OSi]^+$ 261.0917, found 261.0928.

*1,1-Diethyl-6-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**10e**).* Yield (94%, 193.6 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.38 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 5.12 (s, 2H), 2.38 (s, 3H), 0.98−0.94 (m, 6H), 0.90−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 147.8, 136.3, 133.4, 132.1, 130.8, 121.5, 72.2, 21.4, 7.16, 6.65; IR (neat) 2955 (w), 1461 (w), 1267 (s), 1046 (s), 794 (s), 729 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.813 min, *m/z* 207 [$(M + H)^+$, 100], 205 [$(M - H)^+$, 90], 179 [$(M - Et)^+$, 20]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{12}H_{19}OSi]^+$ 207.1200, found 207.1213.

*1,1-Diethyl-6-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole (**10f**).* Yield (90%, 199.8 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.15 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.96 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.10 (s, 2H), 3.84 (s, 3H), 0.97−0.93 (m, 6H), 0.90−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 158.8, 142.7, 134.9, 122.7, 116.6, 115.5, 72.0, 55.6, 7.13, 6.64; IR (neat) 3002 (w), 2954 (w), 1464 (w), 1224 (s), 1047 (s), 1030 (s), 790 (s), 705 (s) cm^{-1}; TLC R_f = 0.55 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.761 min, *m/z* 223 [$(M + H)^+$, 26], 222 (M^+, 84), 221 [$(M - H)^+$, 100], 193[$(M - Et)^+$, 43]; HRMS (ESI/TOF) calcd for $[M + Na]^+$ $[C_{12}H_{18}NaO_2Si]^+$ 245.0968, found 245.0981.

*5-Chloro-1,1-diethyl-1,3-dihydrobenzo[c][1,2]oxasilole (**10g**).* Yield (87%, 194.8 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.27 (ddq, *J* = 7.7, 1.8, 0.8 Hz, 1H), 7.23 (dq, *J* = 1.8, 0.8 Hz, 1H), 5.11 (s, 2H), 0.94 (t, *J* = 7.6 Hz, 6H), 0.90−0.78 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 152.8, 136.3, 132.9, 131.6, 127.4, 122.1, 71.8, 7.11, 6.57; IR (neat) 2956 (w), 1586 (w), 1457 (w), 1189 (s), 1054 (s), 790 (s), 729 (s) cm^{-1}; TLC R_f = 0.6 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.462 min, *m/z* 227 [$(M + 2 + H)^+$, 21], 225 [$(M + H)^+$, 60], 197 [$(M - Et)^+$, 2], 89 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{11}H_{16}ClOSi]^+$ 227.0653, found 227.0641.

*1,1-Diethyl-4-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (**10h**).* Yield (98%, 201.9 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.41 (d, *J* = 7.2 Hz, 1H), 7.24 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 5.10 (s, 2H), 2.22 (s, 3H), 0.98−0.94 (m, 6H), 0.90−0.77 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 149.1, 132.9, 131.7, 130.9, 129.1, 127.5, 71.7, 18.3, 7.23, 6.64; IR (neat) 2955 (w), 1457 (m), 1047 (s), 720 (s) cm^{-1}; TLC R_f = 0.65 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 8.943 min, *m/z* 207 [$(M + H)^+$, 100], 206 (M^+, 17), 205 [$(M - H)^+$, 42]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{12}H_{19}OSi]^+$ 207.1200, found 207.1208.

*1,1-Diethyl-4-[(triisopropylsilyl)oxy]-1,3-dihydrobenzo[c][1,2]-oxasilole (**10i**).* Yield (82%, 298.5 mg); clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.18 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.12 (d, *J* = 7.1 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 5.15 (s, 2H), 1.28 (septet, *J* = 7.3 Hz, 3H), 1.10 (d, *J* = 7.3 Hz, 18H), 0.97−0.93 (m, 6H), 0.89−0.76 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 150.9, 141.0, 135.4, 128.5, 123.9, 119.0, 70.8, 18.2, 13.1, 7.24, 6.60; IR (neat) 2946 (w), 1566 (w), 1459 (w), 1265 (s), 1047 (s), 759 (s) cm^{-1}; TLC R_f = 0.7 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 13.002 min, *m/z* 365 [$(M + H)^+$, 3], 364 (M^+, 9), 363 [$(M - H)^+$, 13], 322 [$(M + H - {}^iPr)^+$, 13]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{20}H_{37}O_2Si_2]^+$ 365.2327, found 365.2308.

*Bicyclo[2.2.1]heptan-2-yldiethyl[(4-methylbenzyl)oxy]silane (**11a**).* Clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.73 (s, 2H), 2.36 (s, 3H), 2.31 (br s, 1H), 2.27 (br s, 1H), 1.62−1.53 (m, 3H), 1.38 (dddd, *J* = 11.6, 9.8, 2.2, 0.8 Hz, 1H), 1.30 (dddd, *J* = 9.3, 4.0, 2.2, 2.2 Hz, 1H), 1.26−1.21 (nfom, 2H), 1.17 (dddd, *J* = 9.4, 3.9, 1.7, 1.7 Hz, 1H), 1.01 (t, *J* = 7.9 Hz, 6H), 0.74 (ddd, *J* = 9.4, 7.3, 1.3 Hz, 1H), 0.73−0.57(m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 141.73, 128.4, 127.0, 126.2, 65.0, 38.4, 37.7, 36.9, 34.3, 32.3, 29.1, 27.6, 21.3, 7.3 (2), 4.37, 4.27; IR (neat) 3007 (w), 2947 (w), 1456 (w), 1083 (s), 1007 (s), 749 (s), 721 (s) cm^{-1}; TLC R_f = 0.7 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.532 min, *m/z* 301 [$(M - H)^+$, 4], 273 [$(M - Et)^+$, 20], 207 [$(M - norbornyl)^+$, 3], 105 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{19}H_{31}OSi]^+$ 303.2139, found 303.2124.

*(Benzyloxy)(bicyclo[2.2.1]heptan-2-yl)diethylsilane (**11b**).* Clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.37−7.32 (nfom, 4H), 7.27−7.22 (m, 1H), 4.76 (s, 2H), 2.29 (br s, 1H), 2.26 (br s, 1H), 1.60−1.51 (m, 3H), 1.39 (dddd, *J* = 10.8, 9.9, 2.3, 0.7 Hz, 1H), 1.31 (dddd, *J* = 9.4, 3.9, 1.9, 1.9 Hz, 1H), 1.24−1.20 (m, 2H), 1.15 (dddd, *J* = 9.4, 3.8, 1.7, 1.7 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 6H), 0.76 (ddd, *J* = 9.4, 7.2, 1.7 Hz, 1H), 0.72−0.60 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 138.7, 136.6, 129.1, 126.3, 65.0, 38.4, 37.7, 36.9, 34.4, 32.3, 29.1, 27.6, 7.31 (2), 4.38, 4.28; IR (neat) 3029 (w), 2947 (w), 1454 (w), 1093 (s), 1067 (s), 1006 (s), 724 (s), 694 (s) cm^{-1}; TLC R_f = 0.7 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.059 min, *m/z* 287 [$(M - H)^+$, 1], 259 [$(M - Et)^+$, 1], 193 [$(M - norbornyl)^+$, 20], 91 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{18}H_{29}OSi]^+$ 289.1982, found 289.1967.

*Bicyclo[2.2.1]heptan-2-yldiethyl[(4-chlorobenzyl)oxy]silane (**11c**).* Clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.30 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.71 (s, 2H), 2.28−2.24 (m, 2H), 1.58−1.51 (m, 3H), 1.38 (ddd, *J* = 11.9, 10.0, 2.2 Hz, 1H), 1.28 (dddd, *J* = 9.4, 3.9, 2.0, 2.0 Hz, 1H), 1.23 (dd, *J* = 6.0, 2.2 Hz, 1H), 1.20 (dd, *J* = 6.2, 2.2 Hz, 1H), 1.15 (dddd, *J* = 9.4, 3.6, 1.7, 1.7 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 6H), 0.75 (ddd, *J* = 9.4, 7.6, 1.6 Hz, 1H), 0.71−0.58 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 140.24, 132.7, 128.5, 127.6, 64.4, 38.4, 37.7, 36.9, 34.3, 32.2, 29.1, 27.6, 7.28 (2), 4.34, 4.24; IR (neat) 2948 (w), 1490 (m), 1275 (m), 1084 (s), 1027 (s), 808 (s), 722 (s) cm^{-1}; TLC R_f = 0.7 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 13.079 min, *m/z* 323[$(M + 2 - H)^+$, 37], 321 [$(M - H)^+$, 100], 293 [$(M - Et)^+$, 14], 227 [$(M - norbornyl)^+$, 16]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{18}H_{28}ClOSi]^+$ 323.1592, found 323.1578.

*Bicyclo[2.2.1]heptan-2-yldiethyl[(4-fluorobenzyl)oxy]silane (**11d**).* Clear oil; ^1H NMR ($CDCl_3$, 500 MHz) δ 7.29 [dd, *J* = 8.7, 5.6 (J^4_{F-H}) Hz, 1H], 7.01 [dd, *J* = 8.7, 8.7 (J^3_{F-H}) Hz, 1H], 4.71 (s, 2H), 2.28−2.24 (m, 2H), 1.58−1.51 (m, 3H), 1.38 (ddd, *J* = 11.9, 10.0, 2.3 Hz, 1H), 1.29 (dddd, *J* = 9.4, 3.8, 2.0, 2.0 Hz, 1H), 1.23 (dd, *J* = 6.0, 2.5 Hz, 1H), 1.20 (dd, *J* = 6.3, 3.0 Hz, 1H), 1.15 (dddd, *J* = 9.4, 3.7, 1.7, 1.7 Hz, 1H), 0.98 (t, *J* = 7.9 Hz, 6H), 0.75 (ddd, *J* = 9.4, 7.6, 1.6 Hz, 1H), 0.71−0.58 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 162.1 (d, J^1_{F-C} = 243.7 Hz), 137.4 (d, J^4_{F-C} = 3.5 Hz), 127.9 (d, J^3_{F-C} = 7.2 Hz), 115.2 (d, J^2_{F-C} = 20.7 Hz), 64.4, 38.4, 37.7, 36.9, 34.3, 32.3, 29.1, 27.6, 7.28 (2), 4.35, 4.25; IR (neat) 2948 (w), 1604 (m), 1509 (s), 1221 (m), 1101 (s), 1082 (s), 751 (s), 721 (s) cm^{-1}; TLC R_f = 0.7 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 12.007 min, *m/z* 305 [$(M - H)^+$, 8], 277 [$(M - Et)^+$, 2], 207 [$(M - norbornyl)^+$, 6], 109 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{19}H_{31}O_2Si]^+$ 319.2088, found 319.2085.

Procedure for Benzylic C_{sp3}−H Silylation of Ester via Exhaustive, Reductive Silylation (13). $[Ir(coe)_2Cl]_2$ (3.6 mg, 2 mol %) and ester **12** (0.2 mmol) were dissolved with toluene (0.2 mL, 1

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M). Diisopropylsilane (0.16 mL, 96 mg, 0.8 mmol) was added to the mixture in one portion. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was kept at 150 °C and stirred for 2 d. The volatiles were removed in vacuo to afford the corresponding crude hydridodiisopropylsilyl ether, which was directly used for subsequent reactions without further purification. $[Rh(nbd)Cl]_2$ (4.6 mg, 5 mol %), tris(4-methoxyphenyl)phosphine (21.1 mg, 30 mol %), norbornene (37.6 mg, 0.4 mmol), and THF (0.5 mL, 0.4 M) were added to the hydridodiisopropylsilyl ether. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 150 °C for 10 h. The reaction progress was monitored by GC-MS spectrometry. The reaction was cooled to rt. The volatiles were removed in vacuo, and the crude mixture was purified by HPLC (hexanes/EtOAc = 80:1, 4 mL/min, 19 min) to afford oxasiline **13** (18.1 mg, 36% yield) as a colorless liquid.

*8-Fluoro-3,3-dipropyl-3,4-dihydro-1H-benzo[d][1,2]oxasiline (**13**).* Clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13 [ddd, J = 7.9, 7.9, 5.8 (J^4_{F-H}) Hz, 1H], 6.95 [d, J = 7.9 Hz, 1H], 6.83 [dd, J = 9.0 (J^3_{F-H}), 7.9 Hz, 1H], 4.95 [d, J = 1.2 (J^4_{F-H}) Hz, 2H], 2.09 (s, 2H), 1.03−0.97 (m, 2H), 0.94 (d, J = 6.7 Hz, 6H), 0.93 (d, J = 6.7 Hz, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 159.1 (d, J^1_{F-C} = 247 Hz), 139.8 (d, J^3_{F-C} = 4.5 Hz), 128.7 (d, J^3_{F-C} = 9.1 Hz), 126.06 (d, J^2_{F-C} = 22.4 Hz), 126.04 (d, J^4_{F-C} = 2.4 Hz), 111.9 (d, J^2_{F-C} = 22.7 Hz), 59.2 (d, J^3_{F-C} = 7.0 Hz), 17.4, 17.2, 13.54, 13.09; IR (neat) 2942 (w), 1616 (m), 1462 (s), 1239 (s), 1054 (s), 1022 (s), 785 (s) cm^{-1}; TLC R_f = 0.4 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 9.915 min, m/z 253 [$(M + H)^+$, 18], 252 (M^+, 14), 251 [$(M - H)^+$, 44], 233 [$(M - F)^+$, 4], 209 [$(M - {}^i$Pr$)^+$, 40], 122 (100); HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{14}H_{22}FOSi]^+$ 253.1418, found 253.1406.

Procedure for Benzylic C_{sp3}−H Silylation of Ketone and Aldehyde via Rh-Catalyzed Reductive Silylation (16 and 17). Ketone **14** or aldehyde **15** (0.5 mmol), $[Rh(nbd)Cl]_2$ (6.9 mg, 3 mol %), and tris(4-methoxyphenyl)phosphine (19.0 mg, 18 mol %) were dissolved with THF (1 mL, 0.5 M). Diethylsilane (0.14 mL, 86 mg, 1 mmol) was added to the crude mixture slowly. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred for 2 h at rt. The reaction progress was monitored by GC-MS spectrometry. The volatiles were removed in vacuo to afford the corresponding crude silyl ethers, which were directly used for subsequent reactions without further purification. Norbornene (94 mg, 1 mmol) and THF (1 mL, 0.5 M) were added to the crude silyl ethers. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was stirred at 120 °C for 4 h. The reaction was cooled to rt. The volatiles were removed in vacuo, and the crude mixture was purified by MPLC to afford **16** (104.1 mg, 84% yield, hexanes/EtOAc = 80:1, 7 mL/min, 13 min) and **17** (50.3 mg, 43% yield, hexanes/EtOAc = 80:1, 6 mL/min, 11 min).

*3,3-Diethyl-1,6,8-trimethyl-3,4-dihydro-1H-benzo[d][1,2]oxasiline (**16**).* Clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.82 (s, 1H), 6.78 (s, 1H), 5.12 (q, J = 6.7 Hz, 1H), 2.26 (s, 3H), 2.24 (s, 3H), 2.15 (d, J = 15.6 Hz, 1H), 1.94 (d, J = 15.6 Hz, 1H), 1.43 (d, J = 6.7 Hz, 1H), 1.07 (t, J = 7.9 Hz, 3H), 0.75 (t, J = 7.9 Hz, 3H), 0.80−0.67 (m, 2H), 0.47−0.39 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 137.9, 136.4, 134.7, 133.6, 130.6, 128.5, 70.1, 23.8, 21.0, 19.5, 16.1, 7.3, 6.80, 6.73, 6.5; IR (neat) 2952 (w), 1457 (m), 1152 (m), 1077 (s), 1009 (s), 748 (s), 729 (s) cm^{-1}; TLC R_f = 0.4 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.274 min, m/z 249 [$(M + H)^+$, 16], 248 (M^+, 9), 247 [$(M - H)^+$, 32], 233 [$(M - Me)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + Na]^+$ $[C_{15}H_{24}NaOSi]^+$ 271.1489, found 271.1496.

*3,3-Diethyl-6,8-dimethyl-3,4-dihydro-1H-benzo[d][1,2]oxasiline (**17**).* Clear oil; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.84 (s, 1H), 6.79 (s, 1H), 4.87 (s, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 2.03 (s, 2H), 0.92 (t, J = 7.9 Hz, 6H), 0.63−0.58 (m, 4H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 136.9, 136.7, 134.3, 134.0, 129.3, 128.1, 62.6, 21.2, 19.4, 16.6, 6.7, 6.2; IR (neat) 2953 (w), 1603 (m), 1458 (m), 1146 (m), 1005 (s), 750 (s), 711 (s) cm^{-1}; TLC R_f = 0.5 in 40:1 hexanes:EtOAc; GC-MS (5029017) t_R = 10.337 min, m/z 235 [$(M + H)^+$, 23], 234 (M^+, 20), 233 [$(M - H)^+$, 91], 219 [$(M - Me)^+$, 35], 205 [$(M - Et)^+$, 100]; HRMS (ESI/TOF) calcd for $[M + H]^+$ $[C_{14}H_{23}OSi]^+$ 235.1513, found 235.1502.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic characterization data for the preparation of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) For selected reviews of C−H functionalization, see: (a) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439−2463. (b) Brookhart, M.; Green, M. L. H.; Parkin, G. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 6908−6914. (c) Seregin, I. V.; Gevorgyan, V. *Chem. Soc. Rev.* **2007**, *36*, 1173−1193. (d) Ackermann, L.; Vicente, R.; Kapdi, A. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 9792−9826. (e) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074−1086. (f) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147−1169. (g) Gutekunst, W. R.; Baran, P. S. *Chem. Soc. Rev.* **2011**, *40*, 1976−1991. (h) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885−1898. (i) Yamaguchi, J.; Yamaguchi, A. D.; Itami, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 8960−9009.

(2) (a) Sieburth, S. McN.; Nittoli, T.; Mutahi, A. M.; Guo, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 812−814. (b) Mutahi, M. wa; Nittoli, T.; Guo, L.; Sieburth, S. McN. *J. Am. Chem. Soc.* **2002**, *124*, 7363−7375. (c) Sieburth, S. McN.; Chen, C.-A. *Eur. J. Org. Chem.* **2006**, 311−322. (d) Nielsen, L.; Skrydstrup, T. *J. Am. Chem. Soc.* **2008**, *130*, 13145−13151.

(3) (a) Showell, G. A.; Mills, J. S. *Drug Discovery Today* **2003**, *8*, 551−556. (b) Gately, S.; West, R. *Drug Dev. Res.* **2007**, *68*, 156−163. (c) Franz, A. K. *Curr. Opin. Drug Discovery Dev.* **2007**, *10*, 654−671. (d) Frantz, A. K.; Wilson, S. O. *J. Med. Chem.* **2013**, *56*, 388−405.

(4) (a) Rochow, E. G. *Silicon and Silicones*; Springer-Verlag: New York, 1987. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410. (c) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205−2236. (d) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974−11975.

(5) (a) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375−1408. (b) Denmark, S. E.; Baird, J. D. *Chem.—Eur. J.* **2006**, *12*, 4954−4963.

(6) (a) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*; de Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, Germany, 2004; Vol. *1*, pp 163−216. (b) Denmark, S. E.; Regens, C. S. *Acc. Chem. Res.* **2008**, *41*, 1486−1499. (c) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893−4901.

(7) (a) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952−6953. (b) Nakao, Y.; Chen, J. S.; Tanaka, M.; Hiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 11694−11695. (c) Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 4447−4450. (d) Smith, A. B., III.; Hoye, A. T.; Martinez-Solorio, D.; Kim, W.-S.; Tong, R. *J. Am. Chem. Soc.* **2012**, *134*, 4533−4536. (e) Tsubouchi, A.; Muramatsu, D.; Takeda, T. *Angew. Chem., Int. Ed.* **2013**, *52*, 12719−12722.

(8) For Ir-catalyzed C_{sp2}−H silylations, see: (a) Gustavson, W. A.; Epstein, P. S.; Curtis, M. D. *Organometallics* **1982**, *1*, 884−885.

DOI: 10.1021/acs.joc.5b00564
J. Org. Chem. 2015, 80, 4661−4671

(b) Ishiyama, T.; Sato, K.; Nishio, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 5346−5348. (c) Ishiyama, T.; Sato, K.; Nishio, Y.; Saiki, T.; Miyaura, N. *Chem. Commun.* **2005**, 5065−5067. (d) Saiki, T.; Nishio, Y.; Ishiyama, T.; Miyaura, N. *Organometallics* **2006**, *25*, 6068−6073. (e) Lu, B.; Falck, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 7508−7510. (f) Simmons, E. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 17092−17095. (g) Hartwig, J. F. *Acc. Chem. Res.* **2012**, *45*, 864−873. (h) Kuznetsov, A.; Gevorgyan, V. *Org. Lett.* **2012**, *14*, 914−917. (i) Kuznetsov, A.; Onishi, Y.; Inamoto, Y.; Gevorgyan, V. *Org. Lett.* **2013**, *15*, 2498−2501.

(9) For Ir-catalyzed C_{sp3}−H silylations, see: (a) Simmons, E. M.; Hartwig, J. F. *Nature* **2012**, *483*, 70−73. (b) Frihed, T. G.; Heuckendorff, M.; Pedersen, C. M.; Bols, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 12285−12288. (c) Mita, T.; Michigami, K.; Sato, Y. *Org. Lett.* **2012**, *14*, 3462−3465. (d) Mita, T.; Michigami, K.; Sato, Y. *Chem.—Asian J.* **2013**, *8*, 2970. (e) Ghavtadze, N.; Melkonyan, F. S.; Gulevich, A. V.; Huang, C.; Gevorgyan, V. *Nat. Chem.* **2014**, *6*, 122−125. (f) Li, B.; Driess, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 6586−6589. (g) Li, Q.; Driess, M.; Hartwig, J. F. *Angew. Chem., Int. Ed.* **2014**, *53*, 8471−8474.

(10) For Rh-catalyzed C_{sp2}−H silylations, see: (a) Sakakura, T.; Tokunaga, Y.; Sodeyama, T.; Tanaka, M. *Chem. Lett.* **1987**, 2375−2378. (b) Djurovich, P. I.; Dolich, A. R.; Berry, D. H. *J. Chem. Soc., Chem. Commun.* **1994**, 1897−1898. (c) Ezbiansky, K.; Djurovich, P. I.; LaForest, M.; Sinning, D. J.; Zayes, R.; Berry, D. H. *Organometallics* **1998**, *17*, 1455−1457. (d) Tobisu, M.; Ano, Y.; Chatani, N. *Chem.—Asian J.* **2008**, *3*, 1585−1591. (e) Ureshino, T.; Yoshida, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324−14326. (f) Tobisu, M.; Hasegawa, J.; Kita, Y.; Kinuta, H.; Chatani, N. *Chem. Commun.* **2012**, 11437−11439. (g) Kuninobu, Y.; Yamauchi, K.; Tamura, N.; Seiki, T.; Takai, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 1520−1522. (h) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853−857.

(11) For Rh-catalyzed C_{sp3}−H silylations, see: Kuninobu, Y.; Nakahara, T.; Takeshima, H.; Takai, K. *Org. Lett.* **2013**, *15*, 426−428.

(12) For Ni-catalyzed dehydrogenative silylations, see: (a) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135−4139. (b) Naka, A.; Lee, K. K.; Yoshizawa, K.; Yamabe, T.; Ishikawa, M. *Organometallics* **1999**, *18*, 4524−4529.

(13) For Pt-catalyzed dehydrogenative silylations, see: (a) Uchimaru, Y.; El, S.; Ahmed Mouneer, M.; Tanaka, M. *Organometallics* **1993**, *12*, 2065−2069. (b) Ishikawa, M.; Naka, A.; Ohshita, J. *Organometallics* **1993**, *12*, 4987−4992. (c) Williams, N. A.; Uchimaru, Y.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1129−1230. (d) Tsukada, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5022−5023. (e) Murata, M.; Fukuyama, N.; Wada, J.-i; Watanabe, S.; Masuda, Y. *Chem. Lett.* **2007**, *36*, 910−911.

(14) For Ru-catalyzed dehydrogenative silylations, see: (a) Kakiuchi, F.; Matsumoto, M.; Sonoda, M.; Fukuyama, T.; Chatani, N.; Murai, S.; Furukawa, N.; Seki, Y. *Chem. Lett.* **2000**, 750−751. (b) Kakiuchi, F.; Igi, K.; Matsumoto, M.; Chatani, N.; Murai, S. *Chem. Lett.* **2001**, 422−423. (c) Kakiuchi, F.; Igi, K.; Matsumoto, M.; Hayamizu, T.; Chatani, N.; Murai, S. *Chem. Lett.* **2002**, 396−396. (d) Kakiuchi, F.; Matsumoto, M.; Tsuchiya, K.; Igi, K.; Hayamizu, T.; Chatani, N.; Murai, S. *J. Organomet. Chem.* **2003**, *686*, 134−144. (e) Kakiuchi, F.; Tsuchiya, K.; Matsumoto, M.; Mizushima, E.; Chatani, N. *J. Am. Chem. Soc.* **2004**, *126*, 12792−12793. (f) Ihara, H.; Suginome, M. *J. Am. Chem. Soc.* **2009**, *131*, 7502−7503. (g) Sakurai, T.; Matsuoka, Y.; Hanataka, T.; Fukuyama, N.; Namikoshi, T.; Watanabe, S.; Murata, M. *Chem. Lett.* **2012**, *41*, 374−376. (h) Klare, H. F. T.; Oestreich, M.; Ito, J.-i.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312−3315. (i) Reference 9c.

(15) For Sc-catalyzed dehydrogenative silylations, see: (a) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 643−656. (b) Oyamada, J.; Nishiura, M.; Hou, Z. *Angew. Chem., Int. Ed.* **2011**, *50*, 10720−10723.

(16) For Pd-catalyzed dehydrogenative silylations, see: (a) Xiao, Q.; Meng, X.; Kanai, M.; Kuninobu, Y. *Angew. Chem., Int. Ed.* **2014**, *53*, 3168−3172. (b) Kanyiva, K. S.; Kuninobu, Y.; Kanai, M. *Org. Lett.* **2014**, *16*, 1968−1971.

(17) For reviews of hydrosilylation, see: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, UK, 1989; Chapter 29. (b) Marciniec, B.; Maciejewski, H.; Pietraszuk, C.; Pawluc, P. In *Hydrosilylation: A Comprehensive Review on Recent Advances*; Marciniec, B., Ed.; Springer: Berlin, 2009; Vol. *1*, Chapter 9−10.

(18) For controlled ester hydrosilylation to aldehydes, see: (a) Cheng, C.; Brookhart, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 9422−9424. (b) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440−9441. (c) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090−3098. (d) Igarashi, M.; Mizuno, R.; Fuchikami, T. *Tetrahedron Lett.* **2001**, *42*, 2149−2151. (e) Nakanishi, J.; Tatamidani, H.; Fukumoto, Y.; Chatani, N. *Synlett* **2006**, 869−872.

(19) For esters hydrosilylation to alcohols and ethers, see: (a) Tsurugi, J.; Nakao, R.; Fukumoto, T. *J. Am. Chem. Soc.* **1969**, *91*, 4587−4588. (b) Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 5093−5095. (c) Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 3751−3753. (d) Mao, Z.; Gregg, B. T.; Cutler, A. R. *J. Am. Chem. Soc.* **1995**, *117*, 10139−10140. (e) Mimoun, H. *J. Org. Chem.* **1999**, *64*, 2582−2589. (f) Ohta, T.; Kamiya, M.; Nobutomo, M.; Kusui, K.; Furukawa, I. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1856−1861. (g) Fernandes, A. C.; Romão, C. C. *J. Mol. Catal. A: Chem.* **2006**, *253*, 96−98. (h) Matsubara, K.; Iura, T.; Maki, T.; Nagashima, H. *J. Org. Chem.* **2002**, *67*, 4985−4988. (i) Sakai, N.; Moriya, T.; Konakahara, T. *J. Org. Chem.* **2007**, *72*, 5920−5922.

(20) Hua, Y.; Asgari, P.; Dakarapu, U. S.; Jeon, J. *Chem. Commun.* **2015**, 3778−3781.

(21) Maeda, K.; Shinokubo, H.; Oshima, K. *J. Org. Chem.* **1997**, *62*, 6429−6431.

(22) Dierkes, P. J.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **1999**, 1519−1530.

(23) For the recent examples of hydrosilylation of ketones and aldehydes, see: (a) Ison, E. A.; Trivedi, E. R.; Corbin, R. A.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2005**, *127*, 15374−15375. (b) Du, G.; Abu-Omar, M. M. *Organometallics* **2006**, *25*, 4920−4923. (c) Shaikh, N. S.; Junge, K.; Beller, M. *Org. Lett.* **2007**, *9*, 5429−5432. (d) Du, G.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 5180−5187. (e) Rendler, S.; Oestreich, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 5997−6000. (f) Rendler, S.; Oestreich, M. In *Modern Reduction Methods*; Andersson, P. G., Munslow, I. J., Eds.; Wiley: Weinheim, Germany, 2008; pp 183−207. (g) Hog, D. T.; Oestreich, M. *Eur. J. Org. Chem.* **2009**, 5047−5056. (h) Yang, J.; Tilley, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 10186−10188. (i) Park, S.; Brookhart, M. *Organometallics* **2010**, *29*, 6057−6064. (j) Müther, K.; Oestreich, M. *Chem. Commun.* **2011**, 334−336. (k) Bhattacharya, P.; Krause, J. A.; Guan, H. *Organometallics* **2011**, *30*, 4720−4729. (l) Riener, K.; Högerl, M. P.; Gigler, P.; Kühn, F. E. *ACS Catal.* **2012**, *2*, 613−621.

(24) (a) Catellani, M.; Fagnola, M. C. *Angew. Chem., Int. Ed.* **1994**, *33*, 2421−2422. (b) Catellani, M.; Frignani, F.; Rangoni, A. *Angew. Chem., Int. Ed.* **1997**, *36*, 119−122. (c) Catellani, M.; Mealli, C.; Motti, E.; Paoli, P.; Perez-Carreno, E.; Pregosin, P. S. *J. Am. Chem. Soc.* **2002**, *124*, 4336−4346. (d) Catellani, M.; Motti, E.; Della Ca', N. *Acc. Chem. Res.* **2008**, *41*, 1512−1522 and references therein. (e) Larock, R. C.; Johnson, P. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1368−1370. (f) Albrecht, K.; Reiser, O.; Weber, M.; Knieriem, B.; de Meijere, A. *Tetrahedron* **1994**, *50*, 383−401. (g) Martins, A.; Mariampillai, B.; Lautens, M. *Top. Curr. Chem.* **2010**, *292*, 1−33.

(25) (a) Oguma, K.; Miura, M.; Satoh, T.; Nomura, M. *J. Am. Chem. Soc.* **2000**, *122*, 10464−10465. (b) Lu, B.; Falck, J. R. *J. Org. Chem.* **2010**, *75*, 1701−1705. (c) Hua, Y.; Nguyen, H. H.; Scaggs, W. R.; Jeon, J. *Org. Lett.* **2013**, *15*, 3412−3415. (d) Chen, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 12064−12072. (e) Hua, Y.; Nguyen, H. H.; Trog, G.; Berlin, A. S.; Jeon, J. *Eur. J. Org. Chem.* **2014**, 5890−5895.

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