Supporting Information for KOt-Bu-Catalyzed Dehydrogenative C–H Silylation of Heteroaromatics: A Combined Experimental and Computational Mechanistic Study

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Materials and Methods

Unless otherwise stated, reactions were performed in a nitrogen-filled glovebox or in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Reaction progress was monitored by thin-layer chromatography (TLC), GC or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, p-anisaldehyde, or KMnO₄ staining. Silicycle SiliaFlash® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ¹H NMR spectra were recorded on Varian Inova 500 MHz or Bruker 400 MHz spectrometers and are reported relative to residual CHCl₃ (δ 7.26 ppm), C₆H₆ (δ 7.16 ppm), or THF (δ 3.58, 1.72 ppm). ¹³C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) or Bruker 400 MHz spectrometers (100 MHz) and are reported relative to CHCl₃ (δ 77.16 ppm). Data for ¹H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ¹³C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm⁻¹). GC-FID analyses were obtained on an Agilent 6850N gas chromatograph equipped with a HP-1 100% dimethylpolysiloxane capillary column (Agilent). GC-MS analyses were obtained on an Agilent 6850 gas chromatograph equipped with a HP-5 (5%-phenyl)-methylpolysiloxane capillary column (Agilent). High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI⁺), atmospheric pressure chemical ionization (APCI⁺), or mixed ionization mode (MM: ESI-APCI⁺), or obtained from Caltech mass spectrometry laboratory. FT-ATR IR measurements were carried out on a Thermo Scientific Nicolet

iS 5 FT-IR spectrometer equipped with an iD5 ATR accessory. ReactIR measurements were carried out on a Mettler-Toledo ReactIR ic10 using a K4 conduit with a Sentinel high-pressure probe and SIComp window. Electron paramagnetic resonance (EPR) spectra were acquired on a X-band Bruker EMX spectrometer. An Omnical SuperCRC or Insight CPR 220 reaction calorimeter were used to monitor heatflow.

Triethyl silane (99%, Sure/Seal™) and KOt-Bu (sublimed grade, 99.99% trace metals basis) were purchased from Aldrich and used directly. KOH was pulverized and dried in a desiccator over P$_2$O$_5$ under vacuum for 24 h prior to use. Di-tert-butyl hyponitrite was synthesized according to literature procedure.\textsuperscript{2} Other reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated.

**Computational details**

All the calculations were carried out with Gaussian 09.\textsuperscript{3} Geometry optimization and energy calculations were performed with the B3LYP method\textsuperscript{4} using the 6-31G(d) basis set\textsuperscript{5} for all atom. Frequency analysis verified that the stationary points were minima or first-order saddle points. Single point energies were calculated at the M06-2X\textsuperscript{6}/6-311+G(d,p) level with solvent effects (solvent = THF) modeled using the CPCM\textsuperscript{7}

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solvation model. Gibbs free energies in THF at 298.15 K were calculated by adding the thermochemical quantities derived from the B3LYP frequency calculation to the M06-2X solution-phase electronic potential energy. Computed structures are illustrated using CYLVIEW.  

**Calculated energies and free energy profiles for selected substrates**

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**Figure S1.**

Calculated energetics of formation of pentacoordinate silicates their IR spectra of Si-H bonds. The distances of Si-H are shown in angstrom.

**Figure S2.**

Free energy profile for generation of silyl radical with oxygen.

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8 Legault, C. Y. CYLView, 1.0b; Universite´ de Sherbrooke, Canada, 2009; http://www.cylview.org.
Figure S3.
Transition structures of hydrogen abstraction by tetrameric (KOT-Bu)$_4$ and (NaOt-Bu)$_4$.

Figure S4.
Free energy profile for C–H silylation of 1-methylpyrrole at C2 and C3 positions. Hydrogen atom is abstracted by tetrameric (KOT-Bu)$_4$. Gibbs free energies, including THF solvation, are shown in kcal/mol.
Free energy profile for C–H silylation of furan at C2 and C3 positions. Hydrogen atom is abstracted by tetrameric (KOT-Bu)$_4$. Gibbs free energies, including THF solvation, are shown in kcal/mol.

Figure S5.

Figure S6.
Free energy profile for C–H silylation of thiophene at C2 and C3 positions. Hydrogen atom is abstracted by tetrameric (KOT-Bu)₄. Gibbs free energies, including THF solvation, are shown in kcal/mol.

**Figure S7.**

Free energy profile for C–H silylation of 1-methylpyrrole at C2 and C3 positions. Hydrogen atom is abstracted by pentacoordinate silicate anion. Gibbs free energies, including THF solvation, are shown in kcal/mol.
Free energy profile for C–H silylation of furan at C2 and C3 positions. Hydrogen atom is abstracted by pentacoordinate silicate anion. Gibbs free energies, including THF solvation, are shown in kcal/mol.

**Figure S8.**

**Figure S9.**
Free energy profile for C–H silylation of furan at C2 and C3 positions. Hydrogen atom is abstracted by pentacoordinate silicate anion. Gibbs free energies, including THF solvation, are shown in kcal/mol.

**1H NMR concentration dependence of silylation product 2 in CDCl3.**

Isolated 1-Methyl-2-(triethylsilyl)-1H-indole was dissolved in CDCl3 at the indicated concentration an 1H NMR spectra were acquired, as shown in Figure S10. This demonstrated the anticipated variation for the product signal under reaction or analytical conditions.
General method for the screening of base catalysts and kinetic profile:

![General method](image)

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### Table 1

In a nitrogen-filled glove box, 1-methylindole (0.5 mmol, 1 equiv), triethylsilane (1.5 mmol, 3 equiv), the indicated base (0.1 mmol, 20 mol%), and THF (5 mL) were added to a 1 dram vial equipped with a magnetic stirring bar. At the indicated time, aliquots were removed using a glass capillary tube, diluted with Et₂O, and analyzed using GC-FID to determine regioselectivity and yield. GC conversion is reported as product (C2- and C3-silylation) divided by product and starting material. For further base screening, see the Supporting Information of our initial disclosure.⁹

### Procedure for time course reaction monitoring by in situ ¹H NMR

In a nitrogen-filled glove box, a stock solution containing KOr-Bu (60.5 mg, 0.539 mmol) and 1,2,5-trimethoxybenzene (if used, 45.4 mg, 0.267 mmol) is prepared in THF-D₈ (2.7 ml). Continuing in the glove box, a J-Young gas-tight NMR tube is then charged

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⁹ Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. Nature 2015, 518, 80–84
with 1-methylindole (32.8 mg, 0.25 mmol, 1 equiv), Et₃SiH (0.75 mmol, 3 equiv), and 0.25 mL of stock solution. The tube is tightly capped with the corresponding Teflon plug, removed from the glove box, placed in the bore of the NMR, and heated to 45 ºC. ¹H NMR spectra were acquired in “array” mode, with a spectrum taken approximately every 3 minutes for the length of experiment. The data was processed using MestReNova and peak integrations were normalized to 1,2,5-trimethoxybenzene (if used). Data is displayed using the MestReNova “stack” function with the axis to the right corresponding to NMR scan number, Scheme 3.

![Figure S11](image)

**Figure S11**

A study was conducted following the procedure for time course reaction monitoring by ¹H NMR (using internal standard) while varying indole [1], from 0.25–0.76 mmol (0.5–1.5 equiv). We observed an initial burst phase of product formation, unfortunately due to the induction period we had difficulty assigning an initial rate for this phase but all trials appear to have a similar rate during the burst phase. The length of the burst phase (i.e. product formed) appears to be related to indole [1]. Interestingly, after the burst phase the slope of all 4 plots appear to be consistent, indicating the reaction may not depend on [1]. This work helped us to understand the reaction occurred in the following 3 regimes;
induction, burst, and sustained reaction periods. Note: induction period was deducted for each experiment.

Procedure for time course reaction monitoring by GC analysis of reaction aliquots

In a nitrogen-filled glove box, 1 dram vials with magnetic stirring bars were charged with the indicated base (0.1 mmol, 20 mol%, as noted in Figure 2, RbOH supplied as unknown hydrate from Strem and used as received), 1-methylindole (65.6 mg, 0.5 mmol, 1 equiv), triethylsilane (174.4 mg, 1.5 mmol, 3 equiv) and THF (0.5 mL, 1M) then sealed with a PTFE-lined screw-cap and heated to 45 °C while stirring. At the indicated time points, an aliquot was removed with a clean, dry glass capillary tube, diluted with Et₂O, and analyzed by GC-FID. Conversion is reported as the percent of both C2- and C3-silylation products divided by products and starting material. Regioselectivity (i.e. C2- to C3-silylation ratios, Table S1) were also obtained at each time point.
Table S1

Procedure for regioselectivity and reversibility of silylation experimentation

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<th>Time (h)</th>
<th>Conversion</th>
<th>C2:C3 ratio (x:1)</th>
<th>Base</th>
<th>Time (h)</th>
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Table 2

In a nitrogen-filled glove box, 1 dram vials were charged with KOt-Bu (0.1 mmol, 20 mol), 1-methylindole (65.6 mg, 0.5 mmol, 1 equiv), triethylsilane (174.4 mg, 1.5 mmol, 3 equiv) and THF if used (0.5 mL, 1M) then sealed with a PTFE-lined screw-cap and heated to the indicated temperature. After the indicated reaction time, the crude reaction mixture was diluted with Et2O, or a small aliquot was removed by glass capillary tube, and analyzed by GC-FID.
Scheme 2

Reversibility (a, b)

In a nitrogen-filled glove box, 1 dram vials with a magnetic stir bar were charged with a mixture of 2 and 3 (24.2 mg, 0.1 mmol, 1 equiv, ratio of 2:3 determined by GC-FID), KOt-Bu (2.4 mg, 0.02 mmol, 20 mol%), Et$_3$Si–H (49 µL, 3 mmol, 3 equiv), and THF (0.1 mL, 1 M). The reactions were heated to 100 °C and stirred for the indicated time, after which they were quenched with Et$_2$O and analyzed by GC (See general method for KOt-Bu-catalyzed silylation for further details).

Cross-over experiment (c)

In a nitrogen-filled glove box, 1 dram vials with a magnetic stir bar were charged with 2 (122.7 mg, 0.5 mmol, 1 equiv), KOt-Bu (11.2 mg, 0.1 mmol, 20 mol%), EtMe$_2$Si–H (44 mg, 0.5 mmol, 1 equiv), and THF (0.5 mL, 1 M). The reaction was heated to 45 °C and stirred for the indicated time, then quenched with Et$_2$O (ca. 1mL), concentrated in vacuo, and analyzed by $^1$H NMR. Product ratio assigned by correlation to known products. Note, product ratio of 2:3 outside of $^1$H NMR detection.
General procedure of gas collection by eudiometry:

![Diagram of eudiometer apparatus]

Figure S12.

The eudiometer apparatus used for measuring H₂ gas evolution in the KOt-Bu-catalyzed cross-dehydrogenative silylation reactions. Note that a Schlenk round-bottom flask with a Teflon valve was used instead of the two neck round bottom flask and ground glass stopcock as depicted above.

In a nitrogen-filled glove box, KOt-Bu (114 mg, 1 mmol, 20 mol%), 1-methylindole (656.4 mmol, 1 equiv), and THF (5 mL) were added to a 25 mL Schlenk flask equipped with a magnetic stirring bar, followed by silane (2.4 mL, 15 mmol, 3 equiv). The flask was sealed and removed from the glove box and placed in a preheated oil bath (45 °C). After stirring at 800 rpm for 15 min for equilibration, the side neck of the Schlenk flask was quickly connected to the gas collection set up (see figure S12). The reactions was stirred for another 20 min (at which point the apparatus was set to volume = 0 mL), the gas volume was recorded over 4 h. For experiment 1, 80 mL of H₂ gas was collected, and the conversion by ¹H NMR based on silylation product 2 was 72%. For experiment 2: 77 mL of H₂ gas was collected, and the conversion by ¹H NMR based on silylation product 2 was 73%. The gas was confirmed by ¹H NMR as H₂ by transferring to a J-Young gastight NMR tube with 0.6 mL of liquid N2 froze C₆D₆. A control experiment with Et₃SiH (2.4 mL) in THF (5 mL) heated to 45 °C in the identical reaction setup resulted in no gas formation in 10 h.
Procedure for silylation reaction in the presence of TEMPO.

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Table S2

General Conditions

In a nitrogen-filled glove box, 1 dram vials with magnetic stirring bars were charged with the KOt-Bu (0.1 mmol, 20 mol%), 1-methylindole (65.6 mg, 0.5 mmol, 1 equiv), triethylsilane (174.4 mg, 1.5mmol, 3 equiv), 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 3 or 6 mol% if used), and THF (0.5 mL, 1M) then sealed with a PTFE-lined screw-cap and heated to 45 °C while stirring. At the indicated time points, an aliquot was removed with a clean, dry glass capillary tube, diluted with Et₂O, and analyzed by GC-FID. Conversion is reported as the percent of both C2- and C3-silylation products.
divided by products and starting material. Despite our efforts, we were not able to observe the TEMPO–SiEt₃ adduct by GC-MS from above experiments.

Following the general procedure above, but using 1 equiv of TEMPO resulted in no product formation. After 52 h the TEMPO–SiEt₃ (TEMPO–TES) adduct was observed by GC-MS and after 91 h the ratio of TEMPO:TEMPO–TES was 40:60. A control experiment conducted in the exact same manner but excluding indole 1 (i.e. TEMPO, KOt-Bu, ET₃SiH, and THF) also resulted in the detection of TEMPO–TES after 52 h. At 91 h, the ratio of TEMPO:TEMPO–TES was 34:66. No TEMPO adduct was observed when NaOt-Bu was in this same control reaction after 9 days.
Effect of additives on the silylation reaction

Table S3

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1 dram vials with magnetic stirring bars were charged with the KOt-Bu (0.1 mmol, 20 mol%), 1-methylindole (65.6 mg, 0.5 mmol, 1 equiv), triethylsilane (174.4 mg, 1.5 mmol, 3 equiv), additive, and THF (0.5 mL, 1M) then sealed with a PTFE-lined screw-cap and heated to 45 °C while stirring. At the indicated time points, an aliquot was removed with a clean, dry glass capillary tube, diluted with Et₂O, and analyzed by GC-FID. Conversion is reported as the percent of both C2- and C3-silylation products divided by products and starting material. All additives increased the length of the induction period and result in lower yields overall. For the impact additional additives have on the silylation of benzothiophene, see the Supplementary Information of our initial disclosure.⁹
Procedure for reactions using chemical generation of tert-butoxyl radical

![Diagram of reaction]

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Table 4

*Note-sufficient precautions should be taken with all peroxide reagents.*

In a nitrogen-filled glove box, 1 dram vials with magnetic stirring bars were charged with peroxide source \([t\text{-BuO–}Ot\text{-Bu}\ (\text{DTBP}) \text{ or } t\text{-BuO–}N\text{=N–}Ot\text{-Bu}\ (\text{TBHN})]\), KOt-Bu (if used, 0.1 mmol, 20 mol%), 1-methylindole (65.6 mg, 0.5 mmol, 1 equiv), triethylsilane (174.4 mg, 1.5mmol, 3 equiv), and THF (0.5 mL, 1M) then sealed with a PTFE-lined screw-cap, and heated indicated temperature while stirring (heating at 135 °C conducted in a fume hood outside of the glove box). At the indicated time points, an aliquot was removed with a clean, dry glass capillary tube, diluted with Et₂O, and analyzed by GC-MS. A number of unidentified impurities were produced along with 10% 2 in entry 3.
Procedure for reaction time course using ReactIR.

A representative ReactIR spectrum showing the growth of the new Si–H peak assigned to the pentacoordinate species, followed by injection of substrate and immediate product formation. Time axis is shown in the format “hh:mm:ss”.

The glass reaction vessel for use with the ReactIR Sentinel high-pressure probe and a magnetic stirring bar were oven dried, fitted with the PTFE adapter, and brought into a nitrogen-filled glove box, or cooled under a flow of argon and standard air-free technique is used for all additions. KOt-Bu (0.8 mmol, 20 mol%), 1-methylindole (1.05 g, 8 mmol, 1 equiv), triethylsilane (13.89 mL, 24 mmol, 3 equiv), additive, and THF (8 mL, 1M) were added to reaction vessel, which was fitted to the ReactIR probe and heated to 45 ºC while stirring under argon. The spectrum was recorded over the course of the reaction and data was analyzed using the ReactIR software.

An analogous experiment was performed whereby the indole 1 is not added until the new peak attributed to the pentacoordinate silicate is seen. Indole 1 is then added via syringe and the reaction immediately proceeds with no induction period.
General procedure of ATR-FTIR measurement:

![Diagram of ATR-FTIR measurement process]

In a nitrogen-filled glove box, base (0.1 mmol), Et₃SiH (80 µL, 0.5 mmol, 5 equiv), and THF (0.5 mL) were added to a 1 dram scintillation vial equipped with a magnetic stirring bar. The vial was sealed and the mixture stirred at 45 ºC for the indicated time as shown in Table S4. The vial was transferred to another nitrogen-filled glove box with an ATR-FTIR and a few drops of this mixture placed on the ATR crystal. After waiting for 5 minutes to evaporate all the volatiles (i.e. THF and silanes), the IR spectrum of the residue was recorded. No new Si–H stretch was observed with bases which did not catalyze the silylation reaction (e.g. NaO₄t-Bu, Mg(Ot-Bu)₂, or LiO₄t-Bu) as these did not form the requisite pentacoordinate complex.

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<td>36</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>KOt-Bu</td>
<td>Et₂SiD</td>
<td>12</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>11</td>
<td>KOt-Bu</td>
<td>Et₂SiH (2.5 equiv) + Et₂SiD (2.5 equiv)</td>
<td>12</td>
<td>2029</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>Mg(Ot-Bu)₂</td>
<td>Et₂SiH</td>
<td>36</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>13</td>
<td>LiO₄t-Bu</td>
<td>Et₂SiH</td>
<td>36</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

*a* The mixture was stirred for the indicated time before IR spectrum was measured. *b* Frequency of Si–H bond stretching. *c* Frequency shift of observed pentacoordinated species from Et₃Si–H.
Procedure for kinetic isotope effect

**Parallel reactions:**

1. 
   \[
   \text{KOt-Bu (20 mol\%)} \quad \text{Et}_3\text{SiH (3 equiv)} \quad \text{THF-}D_8 \quad 45^\circ \text{C} \quad \frac{k_H}{k_D} = 9.3-11.8
   \]

2. 
   \[
   \text{KOt-Bu (20 mol\%)} \quad \text{Et}_3\text{Si-D} \quad (3 \text{ equiv}) \quad \text{THF-}D_8 \quad 45^\circ \text{C} \quad \frac{k_H}{k_D} = 4.6-7.1
   \]

**Scheme 5a**

The general procedure for reaction monitoring by $^1$H NMR was used, with 1,2,5-trimethoxybenzene as the internal standard. A KIE value was obtained using the initial rates method, each experiment was conducted in duplicate.

**Parallel reactions:**

1. 
   \[
   \text{KOt-Bu (20 mol\%)} \quad \text{Et}_3\text{SiH (3 equiv)} \quad \text{THF-}D_8 \quad 45^\circ \text{C} \quad \frac{k_H}{k_D} = 2.5-2.8
   \]

2. 
   \[
   \text{KOt-Bu (20 mol\%)} \quad \text{Et}_3\text{Si-D} \quad (3 \text{ equiv}) \quad \text{THF-}D_8 \quad 45^\circ \text{C} \quad \frac{k_H}{k_D} = 2.5-2.8
   \]

**Scheme 5b**

The general procedure for reaction monitoring by $^1$H NMR was used, without the use of internal standard and using 0.5 equiv of both [CD$_3$]-1 and [D]-1. The KIE value was obtained using the initial rate of product ([CD$_3$]-2 or 2) formation, as these reactions were reversible and reached comparable product yields at later time points. The experiment was conducted in duplicate.

**Procedure for the acquisition of electron paramagnetic resonance (EPR) spectra.**

In a nitrogen-filled glove box, KOt-Bu (11.2 mg, 0.1 mmol), Et$_3$SiH (81 µL, 0.5 mmol, 5 equiv), and THF (0.5 mL) were added to a 1 dram scintillation vial equipped with a magnetic stirring bar. The vial was sealed and the mixture stirred at 45 °C for 5 h. The
reaction mixture was then transferred into an EPR tube, fitted with a plastic cap, taped with parafilm, removed from the glove box, and quickly frozen in liquid nitrogen. The sample was kept at 77 °K and the EPR spectrum was acquired at 77 °K. A signal at approximately $g=2.007$ was observed, further investigations to identify radical intermediates spectroscopically is currently an active area of this project (see page S52 for the spectrum).

**Procedure for reaction calorimetry**
A number of experiments were conducted to probe the thermodynamics of the silylation reaction. We observed no detectible heatflow during these experiments. We previously had concerns relating to the scalability of the silylation reaction, given the rapid formation of product, but were pleased to find reaction exotherm should not be an issue.

![Figure S15](image)

A calorimeter screw cap vial is flame dried and cooled in a vacuum desiccator with the corresponding cap and septum. KOT-Bu (112.2 mg, 1 mmol, 20 mol%) is quickly weighed into the vial, which is then evacuated and refilled with argon 3 times. Et$_3$SiH (2.4 mL, 15 mmol, 3 equiv) and indole 1 (655.8 mg, 5 mmol, 1 equiv) are added using standard air-free technique. The sample was held at 40 °C overnight with no heatflow detected or silylation product 2 detected by GC or TLC. The temperature was then ramped up to 45 °C, a rapid heat flow corresponding to the sample heating was seen but no further heatflow was observed despite the observed of product upon workup.
Figure S16

Heatflow, All Vials

Figure S17

Vial 2-8 GC Data
A second trial was performed with 8 identical vials in parallel. The calorimeter can detect the temperature change due to minute changes in pressure (i.e. using a syringe and needle to remove an aliquot for a GC sample) as seen in figure S16. Therefore one vial was not sampled until the endpoint (Figure S18), while an additional vial was sampled at each time point (i.e. vial 2 at first time point, then vial 2 and 3 at the second time point, etc.). All vials had comparable conversion upon workup (52–60% C2-silylation product 2)

8 calorimeter screw cap vials with the corresponding cap and septum were flame dried and allowed to cool under vacuum, then refilled with argon. Indole 1 (524.7 mg, 4 mmol, 1 equiv), Et₃SiH (1.92 mL, 12 mmol, 3 equiv) and THF (3.2 mL) are added using standard air-free technique. The reactions are equilibrated at 45 °C using an argon filled balloon and then the reaction is initiated using 1M solution of KOt-Bu (0.8 mL, 0.8 mmol, 20 mol%, equilibrated to 45 °C in plugged syringe). Interestingly, an initial negative heat of mixing is observed. Based on the GC data and variance in the heat flow we observed, we estimate the heat of reaction to be ±1 kcal(mol)⁻¹ or less.
General procedure for KOt-Bu-catalyzed silylation and characterization data of new compounds.

![General procedure](image)

Figure S19

In a nitrogen-filled glove box, KOt-Bu (11.2 mg, 0.1 mmol, 20 mol%), indole (0.5 mmol, 1 equiv), and THF (0.5 mL, if indicated, see the details below) were added to a 1 dram scintillation vial equipped with a magnetic stirring bar, followed by silane (1.5 mmol, 3 equiv). Then the vial was sealed and the mixture was stirred at 45 °C for the indicated time. The vial was removed from the glove box, diluted with diethyl ether (2 mL) and concentrated under reduced pressure. The regioselectivity (C2 silylation product to C3 silylation product: C2:C3) was determined by $^1$H NMR or GC analysis of the crude mixture. The residue was purified by silica gel flash chromatography to give the desired product.

![Figure S20](image)

Figure S20

The general procedure was followed. The reaction was performed with KOt-Bu (6.7 mg, 0.06 mmol, 20 mol%), 3-cyclopropyl-1-methyl-1H-indole 8 (51.3 mg, 0.3 mmol, 1 equiv), Et$_2$SiH$_2$ (79.2 mg, 0.9 mmol, 3 equiv), and 0.3 mL of THF at 45 °C for 10 days. Three products shown above, along with some unidentified impurity, were isolated by silica gel flash chromatography (3% CH$_2$Cl$_2$ in hexanes). Unreacted starting material 8 was recovered in 30% yield (15.4 mg). Analytic pure compounds 9 (3.9 mg, 5% yield), 10 (8.8 mg, 8% yield), and 11 (1.9 mg, 3% yield) were purified by preparative HPLC (ACE 5 C18, 250 x 21 2mm id column; gradient, 30→80% MeCN in H$_2$O in 3 min, then 80→100% MeCN in H$_2$O in 7 min, followed by 100% MeCN; flow rate = 10 mL/min; l = 230 nm.).
1,1-Diethyl-9-methyl-2,3,4,9-tetrahydro-1H-silino[2,3-b]indole 9: \( R_f = 0.5 \) (10% CH\(_2\)Cl\(_2\) in hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.55 (dt, \( J = 7.9 \), 1.0 Hz, 1H), 7.29 (dt, \( J = 8.3 \), 0.9 Hz, 1H), 7.22 (ddd, \( J = 8.2 \), 6.9, 1.2 Hz, 1H), 7.07 (ddd, \( J = 7.9 \), 6.8, 1.1 Hz, 1H), 3.78 (s, 3H), 2.91 – 2.80 (m, 2H), 2.07 – 1.95 (m, 2H), 1.05 – 0.90 (m, 8H), 0.90 – 0.78 (m, 4H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 139.4, 133.6, 128.3, 127.4, 122.2, 118.8, 118.3, 108.9, 33.1, 25.2, 23.0, 8.9, 7.9, 6.0. IR (Neat Film NaCl) 2951, 2909, 2872, 1504, 1455, 1361, 1336, 1307, 1234, 1165, 1138, 1011, 920, 806, 761 cm\(^{-1}\); HRMS (FAB+) calc’ed for C\(_{16}\)H\(_{23}\)NSi \([M]^+\): 257.1600, found: 257.1601.

4-(Diethylsilyl)-1,1-diethyl-9-methyl-2,3,4,9-tetrahydro-1H-silino[2,3-b]indole 10: \( R_f = 0.5 \) (10% CH\(_2\)Cl\(_2\) in hexanes); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.48 (dt, \( J = 7.9 \), 1.0 Hz, 1H), 7.26 (dt, \( J = 8.2 \), 1.0 Hz, 1H), 7.19 (ddd, \( J = 8.2 \), 6.8, 1.2 Hz, 1H), 7.02 (ddd, \( J = 7.9 \), 6.8, 1.1 Hz, 1H), 3.82 – 3.79 (m, 1H), 3.77 (s, 3H), 2.84 – 2.81 (m, 1H), 2.36 – 2.30 (m, 1H), 2.07 – 1.98 (m, 1H), 1.06 – 0.91 (m, 11H), 0.91 – 0.76 (m, 7H), 0.75 – 0.65 (m, 2H), 0.62 – 0.44 (m, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 139.4, 132.1, 130.0, 127.9, 122.1, 119.5, 117.9, 108.8, 33.1, 25.8, 22.3, 8.63, 8.61, 8.11, 8.09, 7.2, 6.7, 6.1, 3.4, 2.8. IR (Neat Film NaCl) 2953, 2910, 2873, 2100, 1495, 1455, 1414, 1361, 1321, 1262, 1234, 1164, 1135, 1080, 1013, 968, 809, 761 cm\(^{-1}\); HRMS (FAB+) calc’ed for C\(_{20}\)H\(_{33}\)NSi\(_2\) \([M]^+\): 343.2152, found: 343.2140.
3-(1,3-Bis(diethylsilyl)propyl)-1-methyl-1H-indole 11: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.56 (dt, $J = 7.9$, 1.0 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.19 (ddd, $J = 8.2$, 6.9, 1.1 Hz, 1H), 7.06 (ddd, $J = 7.9$, 6.9, 1.1 Hz, 1H), 6.72 (s, 1H), 3.79 – 3.76 (m, 1H), 3.76 (s, 3H), 3.61 (hept, $J = 3.1$ Hz, 1H), 2.46 – 2.34 (m, 1H), 1.97 – 1.77 (m, 2H), 0.98 (t, $J = 7.9$ Hz, 3H), 0.95 – 0.91 (m, 6H), 0.89 (t, $J = 7.9$ Hz, 3H), 0.81 – 0.74 (m, 1H), 0.69 – 0.41 (m, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 137.0, 128.6, 125.3, 121.3, 119.6, 118.2, 116.4, 109.1, 32.8, 27.0, 25.3, 10.8, 8.6, 8.6, 8.4, 8.4, 2.9, 2.9, 2.4, 2.1. IR (Neat Film NaCl) 2952, 2932, 2910, 2872, 2094, 1469, 1414, 1372, 1325, 2235, 1012, 970, 810, 736 cm$^{-1}$; HRMS (FAB+) calc’d for C$_{20}$H$_{35}$NSi$_2$ [M]$^+$: 345.2308, found: 345.2314.
Possible mechanism for the formation of compounds 9, 10, 11

Figure S21 describes a possible route to the formation of 9, 10, and 11 through an initial hydrogen atom transfer reaction to substrate 8. We envision this is possible since the silylation reaction was shown to be reversible, a process which is thought to occur by hydrogen atom transfer (HAT), likely of a pentacoordinate silicate species, to indole 2.
In the case of cyclopropyl-substituted indole 8, the cyclopropane ring opening is faster than reverse HAT. Figure S21b describes an analogous process but with addition of a silicon radical as compared to a hydrogen radical. The low yield may be explained by a number of radical termination processes limiting reaction rate. A number of these proposed radical intermediates would be high energy and likely to decompose or react in other manners, contributing to the low overall mass balance.

4-cyclopropyl-1-methyl-2-(triethylsilyl)-1H-indol 12: The general procedure was followed. The reaction was performed with KOt-Bu (6.7 mg, 0.06 mmol, 20 mol%), N-Methyl-4-(cyclopropyl)-indole S1 (51.3 mg, 0.3 mmol, 1 equiv), Et3SiH (146 µL, 0.9 mmol, 3 equiv), and 0.3 mL of THF at 45 °C for 48 h. The desired product 12 (54.7 mg, 64% yield) was purified by silica gel flash chromatography (5→10% CH2Cl2 in hexanes) as yellow oil. Rf = 0.4 (10% CH2Cl2 in hexanes); 1H NMR (400 MHz, Chloroform-d) δ 7.20 – 7.12 (m, 2H), 6.91 (s, 1H), 6.74 – 6.65 (m, 1H), 3.85 (s, 3H), 2.31 (ttd, J = 8.5, 5.2, 0.6 Hz, 1H), 1.10 – 1.01 (m, 11H), 1.00 – 0.92 (m, 6H), 0.91 – 0.86 (m, 2H); 13C NMR (101 MHz, Chloroform-d) δ 140.05, 137.59, 136.03, 128.59, 122.24, 113.88, 111.28, 106.59, 33.23, 13.06, 8.14, 7.70, 4.16; IR (Neat Film NaCl) 3080, 3051, 3002, 2953, 2909, 2874, 1581, 1503, 1454, 1441, 1415, 1370, 1351, 1323, 1277, 1237, 1171, 1137, 1070, 1017, 977, 885, 841, 787, 769, 745, 734, 700, 679 cm⁻¹; HRMS (MM+) calc’d for C18H27NSi [M+H]+: 286.1986 found: 286.1997.
3-(Cyclopropylmethyl)-2-(diethylsilyl)-1-methyl-1H-indole 13: The general procedure was followed. The reaction was performed with KOt-Bu (4.5 mg, 0.04 mmol, 20 mol%), N-Methyl-3-(cyclopropylmethyl)-indole S2 (37.0 mg, 0.2 mmol, 1 equiv), Et₂SiH₂ (78 µL, 0.6 mmol, 3 equiv), and 0.2 mL of THF at 45 °C for 5 days. The desired product 13 (17.2 mg, 32% yield) was purified by silica gel flash chromatography (2.5% CH₂Cl₂ in hexanes) as colorless oil. Rᵢ = 0.5 (10% CH₂Cl₂ in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.67 (dt, J = 7.9, 1.0 Hz, 1H), 7.31 (dt, J = 8.2, 0.9 Hz, 1H), 7.26 (ddd, J = 8.2, 6.8, 1.1 Hz, 1H), 7.10 (ddd, J = 7.9, 6.8, 1.0 Hz, 1H), 4.54 – 4.46 (m, 1H), 3.83 (s, 3H), 2.86 (d, J = 6.4 Hz, 2H), 1.10 – 1.02 (m, 7H), 1.03 – 0.87 (m, 4H), 0.53 – 0.43 (m, 2H), 0.33 – 0.22 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.9, 132.3, 128.6, 127.0, 122.3, 119.7, 118.6, 109.1, 32.9, 30.3, 13.3, 8.9, 5.2, 4.8. IR (Neat Film NaCl) 3073, 2999, 2931, 2909, 2872, 2131, 1503, 1457, 1424, 1355, 1319, 1292, 1246, 1228, 1167, 1139, 1087, 1013, 975, 836, 809 cm⁻¹; HRMS (MM⁺) calc’d for C₁₇H₂₆NSi [M+H]⁺: 272.1829, found: 272.1823.

1-Benzyl-5-methoxy-2-(triethylsilyl)-1H-indole 14: The general procedure was followed. The reaction was performed with KOt-Bu (4.6 mg, 0.04 mmol, 20 mol%), 1-(cyclopropylmethyl)-1H-indole S3 (34.2 mg, 0.2 mmol, 1 equiv), Et₂SiH₂ (78 µL, 0.9 mmol, 3 equiv), and 0.2 mL of THF at 45 °C for 96 h. C2:C3 > 20:1. The desired product 14 (29.7 mg, 58% yield) was purified by silica gel flash chromatography (gradient, 2→3.3% CH₂Cl₂ in hexanes) as colorless oil. Rᵢ = 0.5 (10% CH₂Cl₂ in hexanes); ¹H NMR (500 MHz, CDCl₃) δ 7.64 (dt, J = 7.9, 1.0 Hz, 1H), 7.42 (dq, J = 8.3, 0.9 Hz, 1H), 7.26 – 7.18 (m, 1H), 7.10 (ddd, J = 7.9, 6.9, 1.0 Hz, 1H), 6.77 (d, J = 0.9 Hz, 1H), 4.47 (p, J = 3.3 Hz, 1H), 4.17 (d, J = 6.4 Hz, 2H), 1.33 – 1.24 (m, 1H), 1.14 – 1.05
Stereochemical course of the KOt-Bu-catalyzed C–H silylation of benzo[b]thiophene.

1-(Benzo[b]thiophen-2-yl)-1-hexylsilolane 19: In a nitrogen-filled glove box, KOt-Bu (4.5 mg, 0.04 mmol, 20 mol%) and benzo[b]thiophene 18 (26.8 mg, 0.20 mmol, 1.0 equiv) were added to an oven-dried scintillation vial equipped with a magnetic stirring bar, followed by deuterium-labeled 1-hexylsilolane 17 (51.4 mg, 0.30 mmol, 1.5 equiv) and THF (0.2 mL). The vial was sealed and the mixture was stirred at 25 °C for 48 h. The vial was removed from the glove box, and the reaction mixture was passed through a short plug of silica gel, eluting with diethyl ether. The residue was purified by flash chromatography on silica gel (100% n-pentane) to give the desired product 19 (51.7 mg, 85%, C2:C3 > 20:1) as a colorless oil. Rf = 0.7 (100% n-pentane). 1H NMR (700 MHz, CD6D6): δ 7.68 – 7.65 (m, 2H), 7.41 (s, 1H), 7.18 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.08 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 1.78 – 1.70 (m, 2H), 1.68 – 1.60 (m, 2H), 1.47 – 1.41 (m, 2H), 1.36 – 1.31 (m, 2H), 1.31 – 1.21 (m, 4H), 1.03 – 0.96 (m, 2H), 0.94 – 0.90 (m, 2H), 0.89 (t, J = 7.3 Hz, 3H), 0.86 – 0.79 (m, 2H). The analytical data are in accordance with those reported.10

10 Fallon, T.; Oestreich, M. Angew. Chem., Int. Ed. 2015, 54, 12488–12491
Synthesis of 3-3-(cyclopropylmethyl)-1-methyl-1H-indole (S2):

To a stirring solution of indole (1.17 g, 10 mmol) in CH$_2$Cl$_2$ (20 mL) was added SnCl$_4$ (1.44 mL, 12 mmol) in a single portion via syringe at 0 °C. The solution was allowed to warm to room temperature and stirred for 30 min, then cyclopropanecarbonyl chloride (10 mmol) was added in small portions to the suspension by syringe, followed by nitromethane (15 mL). The reaction mixture was stirred at 25 ºC for 2 h, after which ice-water (30 mL) was slowly added. The mixture was then filtered, extracted with ethyl acetate (50 mL), dried over Na$_2$SO$_4$, and concentrated at reduced pressure to give the product S4 as a yellow solid, which was used directly for next step.\footnote{Ottoni, O; Neder, A de V. F.; Dias, A. K. B; Cruz, R. P. A.; A.; Aquino, L. B. Org. Lett. 2001, 3, 1005–1007.}

To a solution of crude S4 in Et$_2$O (50 mL) was added LiAlH$_4$ (0.69 g, 20 mmol) in small portions, and the mixture refluxed overnight. The reaction was cooled to 0 °C, diluted with Et$_2$O (40 mL), and quenched with water (0.76 mL)/15% NaOH aqueous (0.76 mL)/water (2.28 mL). The mixture was stirred for 1 h, dried over Na$_2$SO$_4$, concentrated at reduced pressure, and purified by silica gel flash chromatography (10% Et$_2$O in hexanes) to give 3-(cyclopropylmethyl)-1H-indole S5 (0.63 g, 3.7 mmol) as a yellow oil.

To a dried flask with NaH (60% dispersion in oil, 178 mg, 4.4 mmol) and THF (15 mL) was added the THF (15 mL) solution of S5 (630 mg, 3.7 mmol) dropwise by syringe at 0 ºC. After the mixture was stirred at 0 ºC for 30 min, MeI (0.35 mL, 5.6 mmol) was added slowly. This mixture was stirred overnight, quenched with aqueous NH$_4$Cl, extracted with Et$_2$O (30 mL x 3), and dried over Na$_2$SO$_4$. The solvents were removed under
reduced pressure and the crude mixture was purified by silica gel flash chromatography (10% CH₂Cl₂ in hexanes) to give 3-(cyclopropylmethyl)-1-methyl-1H-indole S2 (0.59 g, 32% yield over three steps) as a colorless oil. \( R_f = 0.4 \) (10% CH₂Cl₂ in hexanes); \(^1\)H NMR (400 MHz, Chloroform-d) \( \delta 7.70 \) (dt, \( J = 7.9, 1.1 \) Hz, 1H), 7.37 (dt, \( J = 8.3, 1.0 \) Hz, 1H), 7.31 (m, \( J = 6.9, 1.1 \) Hz, 1H), 7.19 (ddd, \( J = 8.0, 6.9, 1.2 \) Hz, 1H), 7.01 (s, 1H), 3.82 (s, 3H), 2.77 (d, \( J = 6.7 \) Hz, 2H), 1.18 (ttt, \( J = 8.0, 6.7, 4.9 \) Hz, 1H), 0.66 – 0.59 (m, 2H), 0.39 – 0.26 (m, 2H); \(^{13}\)C NMR (101 MHz, Chloroform-d) \( \delta 137.12, 128.13, 126.26, 121.52, 119.24, 118.66, 115.12, 109.20, 32.67, 30.03, 11.50, 5.03 \). IR (Neat Film NaCl) 3073, 3054, 2999, 2905, 2837, 1615, 1552, 1483, 1472, 1423, 1371, 1355, 1327, 1293, 1253, 1235, 1201, 1156, 1129, 1057, 1013, 975, 929, 884, 828, 803, 737 cm\(^{-1}\); HRMS (MM: ESI-APCI+) calc’d for C\(_{13}\)H\(_{15}\)N [M+H]\(^+\): 186.1277, found: 186.1277.

To a 20 mL microwave vial was added Pd(dppf)Cl\(_2\) (367 mg, 0.5 mmol, 5 mol%), lithium hydroxide mono-hydrate (1.26 g, 30 mmol, 3 equiv), 4-bromo-l-methyl-lH-indole (2.10 g, 10 mmol), and cyclopropylboronic acid (1.03 g, 12 mmol, 1.2 equiv), followed by dioxane (10 mL) and degassed H\(_2\)O (2.5 mL). The vial is purged with N\(_2\) for 15 min, then heated to 150 °C for 30 minutes in a Biotage Initiator 2.5 microwave reactor under normal absorption mode. The vial was cooled and the solution concentrated under reduced pressure, diluted with ethyl acetate (100 mL), washed with saturated sodium bicarbonate (50 mL) then brine (50 mL), dried over Na\(_2\)SO\(_4\), and concentrated under reduced pressure. The crude mixture was purified by silica gel flash chromatography (2→10% CH₂Cl₂ in hexanes) to give 4-cyclopropyl-1-methyl-1H-indole S6 (1.39 g, 81% yield) as a white solid. \( R_f = 0.2 \) (10% CH₂Cl₂ in hexanes); \(^1\)H NMR (400 MHz, Chloroform-d) \( \delta 7.20 – 7.13 \) (m, 2H), 7.07 (d, \( J = 3.1 \) Hz, 1H), 6.79 – 6.70 (m, 1H), 6.67 (d, \( J = 3.1 \) Hz, 1H), 3.80 (s, 3H), 2.26 (tt, \( J = 8.5, 5.2 \) Hz, 1H), 1.08 – 0.95 (m, 1H), 0.92 – 0.80 (m, 1H). \(^{13}\)C NMR (101 MHz, Chloroform-d) \( \delta 136.52, 136.17, 128.64, 128.53, 128.33, 121.84, 114.59, 106.83, 99.40, 33.09, 13.20, 7.76 \). IR (Neat Film NaCl) 3002, 2945, 1581, 1498, 1458, 1418, 1336, 1291, 1252, 1154, 1088, 1034, 961, 811, 786, 746,
715 cm⁻¹; HRMS (MM: ESI-APCI⁺) calc’d for C₁₂H₁₃N [M+H]⁺: 172.1121, found: 172.1120.

**Synthesis of 3-cyclopropyl-1-methyl-1H-indole 8**

(cyclopropylethynyl)trimethylsilane **S7**: Synthesis was conducted by a slight modification of the reported procedure.¹² To a stirring solution of cyclopropylacetylene (1.44 g, 21.8 mmol, 1 equiv) in dry THF (7 mL) at -78 °C was added n-BuLi (8.95 mL of 2.5 M in THF, 22.4 mmol, 1.03 equiv) dropwise via syringe. The solution was allowed to stir for 30 minutes at -78 °C, after which TMS–Cl (freshly distilled from CaH₂, 2.90 mL, 22.8 mmol, 1.04 equiv) was added dropwise and the solution was stirred at -78 °C for 1 hour. The reaction was then allowed to warm to room temperature, diluted with diethyl ether, and filtered through a pad of Na₂SO₄ layered on silica gel, eluting 1:4 Et₂O : pentane. The filtrate was concentrated in vacuo and then carried on crude.

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3-cyclopropyl-2-(trimethylsilyl)-1H-indole S8 and 3-cyclopropyl-1H-indole S9 were synthesized following known procedure using S7 and 2-iodoaniline.13

3-cyclopropyl-1-methyl-1H-indole 8: To a round-bottom flask equipped with a magnetic stirring bar was added NaH (60 % dispersion in mineral oil, 155 mg, 3.9 mmol, 1.4 equiv) and S9 (440 mg, 2.8 mmol, 1 equiv). The flask was placed in an ice bath and THF was added while stirring. The reaction was stirred at 0 ºC for 45 minutes and then at 23 ºC for 15 minutes. The reaction was again placed in an ice bath and Me–I (250 µL, 4 mmol, 1.4 equiv) was added dropwise. This mixture was stirred overnight, quenched with aqueous NH₄Cl, extracted with Et₂O (30 mL x 3), and dried over Na₂SO₄. The solvents were removed under reduced pressure and the crude mixture was purified by silica gel flash chromatography (5→10% CH₂Cl₂ in hexanes) to give 3-cyclopropyl-1-methyl-1H-indole 8 (398 mg, 83% yield) Rf = 0.35 (10% CH₂Cl₂ in hexanes) ¹H NMR (400 MHz, Chloroform-d) δ 7.74 (dt, J = 7.9, 0.9 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.20 (m, 1H), 7.12 (t, J = 8.0 Hz, 1H), 6.76 (s, 1H), 3.72 (s, 3H), 2.11 – 1.87 (m, 1H), 0.92 – 0.85 (m, 2H), 0.71 – 0.56 (m, 2H).¹³C NMR (101 MHz, Chloroform-d) δ 137.14, 128.59, 125.43, 121.73, 119.36, 118.74, 117.74, 109.25, 32.69, 6.19.; HRMS (MM: ESI-APCI+) calc’d for C₁₂H₁₃N [M+H]⁺: 172.1121, found: 172.1119.

FTIR Spectra:

Pure KOt-Bu:
Pure Et$_3$SiH:

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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

KOt-Bu + Et₃SiH (5 equiv) → THF → 45 °C → 2 h → volatiles evaporation (Et₃SiH and THF removal) → IR spectra measurement

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Page 1/1
KOEt + Et₃SiH (5 equiv) → THF → 45 °C 2 h → volatiles evaporation → IR spectra measurement

(Et₃SiH and THF removal)

Instrument type and/or accessory: BRUKER

C:\Users\Peters Group\Documents\USERS\wbl-bms\wbl-X-255-D-KOEt-10/7/2015.web\C:\Users\Peters Group\Documents\USERS\wbl-bms\wbl-X-255-D-KOEt-10/7/2015.web-X-255-D-KOEt-0.web-X-255-D-KOEt-0.web-X-255-D-KOEt-0 webpage.jpg

Transmittance [%] 00 10 20 30 40 50 60 70 80 90 100

Wavenumber cm⁻¹ 3500 3000 2500 2000 1500 1000 500

70 75 80 85 90 95 100

939.36 707.67 660.21 500 457 439 1041.98 1008.71 991.46 959.43 721.95

2945.80 2905.47 2868.31 2804.26 2015.79 1459.02 1416.41 1378.12 1223.80 1115.81
KOMe + Et₃SiH (5 equiv) THF 45 °C 7 h \[\text{volatiles evaporation (Et₃SiH and THF removal)}\]

IR spectra measurement

\[\begin{align*}
2953.36 & \quad 2908.24 & \quad 2875.64 & \quad 2805.29 \\
2053.52 & \quad 1458.91 & \quad 1414.14 & \quad 1378.84 \\
1236.69 & \quad 1070.33 & \quad 1004.36 & \quad 959.22 \\
942.96 & \quad 726.60 & \quad & \\
\end{align*}\]

Instrument type and / or accessory

10/8/2015
KOTMS + $\text{Et}_3\text{SiH}$ (5 equiv) $\xrightarrow{\text{THF}}$ 45 °C 7 h $\xrightarrow{\text{volatiles evaporation}}$ (Et$_3$SiH and THF removal) $\xrightarrow{\text{IR spectra measurement}}$

IR spectra measurement:

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Instrument type and/or accessory:

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10/7/2015
Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

RbOH•xH₂O + Et₃SiH (5 equiv) → THF → 45 °C 7 h → volatiles evaporation (Et₃SiH and THF removal) → IR spectra measurement

IR spectra:

Wavenumber cm⁻¹:

- 3602
- 3599
- 3598
- 3560
- 3500
- 2908.06
- 2875.88
- 2804.38
- 2052.18
- 1458.67
- 1413.85
- 1378.58
- 1236.73
- 1067.83
- 1003.42
- 959.16
- 943.33
- 726.14
- 688.57
- 579.82
- 500

Instrument type and/or accessory:

C:X-255.E-KOMe

Page 1/1
Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

CsOH·H₂O + Et₃SiH
(5 equiv) → THF
45 °C
7 h →

IR spectra measurement

volatiles evaporation
(Et₃SiH and THF removal)

CsOH•H₂O + Et₃SiH
(5 equiv) → THF
45 °C
7 h →

IR spectra measurement

volatiles evaporation
(Et₃SiH and THF removal)

CsOH•H₂O + Et₃SiH
(5 equiv) → THF
45 °C
7 h →

IR spectra measurement

volatiles evaporation
(Et₃SiH and THF removal)

CsOH•H₂O + Et₃SiH
(5 equiv) → THF
45 °C
7 h →

IR spectra measurement

volatiles evaporation
(Et₃SiH and THF removal)
Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

\[
\text{NaOt-Bu} + \text{Et}_2\text{SiH (5 equiv)} \quad \xrightarrow{\text{THF}} \quad 45^\circ\text{C} \quad 36\text{ h} \quad \text{volutiles evaporation} \quad (\text{Et}_2\text{SiH and THF removal}) \quad \text{IR spectra measurement}
\]

\[\text{IR spectra measurement}\]

\[
\begin{align*}
\text{C}:\text{Users}\text{/Peters Group Documents USERS/\text{wbl-bms/}wbl-X-255-Na-36h.0 & wbl-X-255-Na-36h}\text{ wbl-X-255-Na-36h}}} \\
\text{Instrument type and or accessory} \\
\text{Page 1/1}
\end{align*}
\]
Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

KOt-Bu  Et₃SiD  THF-D₈  45 °C  12 h  volatiles evaporation  IR spectra measurement

Et₁K₁══Et₁SiO₁-K₁THF-D₈  KOt-Bu  Et₃SiD  THF-D₈  45 °C  12 h  volatiles evaporation  IR spectra measurement

IR spectra measurement

2941.63  2868.07  2805.89  1460.76  1417.67  1363.82  1337.77  1199.20  1074.01  1008.51  993.54  962.32  863.38  822.93  761.32  722.70  706.72  658.55  481.81  436.38  411.28

Wavenumber cm⁻¹

Transmittance [%]
KO-t-Bu + Et₃SiD (2.5 equiv) + Et₃SiH (2.5 equiv) → THF-D₈ 45 °C 12 h → IR spectra measurement
volatiles evaporation (Et₃SiD and THF-D₈ removal) → IR spectra measurement

KO-t-Bu + Et₃SiD (2.5 equiv) + Et₃SiH (2.5 equiv) → THF-D₈ 45 °C 12 h → volatiles evaporation (Et₃SiD and THF-D₈ removal) → IR spectra measurement

KO-t-Bu + Et₃SiD (2.5 equiv) + Et₃SiH (2.5 equiv) → THF-D₈ 45 °C 12 h → volatiles evaporation (Et₃SiD and THF-D₈ removal) → IR spectra measurement

KO-t-Bu + Et₃SiD (2.5 equiv) + Et₃SiH (2.5 equiv) → THF-D₈ 45 °C 12 h → volatiles evaporation (Et₃SiD and THF-D₈ removal) → IR spectra measurement
Note - small peak at 2101 cm$^{-1}$ due to residual Et$_3$SiH
EPR Spectrum

EPR Spectra of Et₃SiH and KO-Bu
$^1$H NMR and $^{13}$C NMR Spectra

$^1$H NMR (400 MHz, CDCl$_3$) of compound 9.
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 9.
COSY (400 MHz, CDCl$_3$) of compound 9.
HSQC (400 MHz, CDCl₃) of compound 9.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 10.
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound 10.
COSY (400 MHz, CDCl₃) of compound 10.
Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

HSQC (400 MHz, CDCl₃) of compound 10.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 11.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 11.
COSY (500 MHz, CDCl$_3$) of compound 11.
HSQC (500 MHz, CDCl₃) of compound 11.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 12.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 12.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 13.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 13.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 14.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 14.
$^1$H NMR (400 MHz, CDCl$_3$) of compound 8.
$^{13}$C NMR (101 MHz, CDCl$_3$) of compound 8.
$^1$H NMR (400 MHz, CDCl$_3$) of headspace gas for Figure 3.
Figure 22. $^1$H and $^2$H NMR spectra of deuterium-labeled 1-hexylsilolane.

Figure 23. $^1$H and $^2$H NMR spectra of 1-(benzo[b]thiophen-2-yl)-1-hexylsilolane: scrambling of the configuration at the silicon atom.
Figure 24. $^1$H and $^2$H NMR spectra of 1-(benzo[b]thiophen-2-yl)-1-hexylsilolane: scrambling of the configuration at the silicon atom.

Zero-point correction (ZPE), thermal correction to energy ($\Delta E$), thermal correction to enthalpy ($\Delta H$), thermal correction to Gibbs free energy ($\Delta G$), energies (E), enthalpies (H), and Gibbs free energies (G) (in Hartree) of the structures calculated at the M062X/6-31G(d,p)-CPCM(THF)//B3LYP/6-31G(d) level of theory. The radical species were calculated at the UM062X/6-311+G(d,p)-CPCM(THF)//UB3LYP/6-31G(d) level of theory.

Table S1.

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Supporting Information for Liu, Schuman, Toutou, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz
Cartesian coordinates of the structures

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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

\[ \text{NaOtBu} \]

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\text{H} & 0.77266300 \quad -1.74741100 \quad 1.28993500 \\
\text{H} & 2.24227800 \quad -0.74372100 \quad 1.32061800 \\
\text{H} & 0.77029800 \quad -0.20292800 \quad 2.16258500 \\
\text{H} & 2.24687000 \quad -0.76732400 \quad -1.30104300 \\
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\end{align*}

\[ \text{[NaOtBu]}_2 \]

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\[ \text{[NaOtBu]}_3 \]

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\text{O} & 2.05954600 \quad -0.76137900 \quad -0.03349500 \\
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\text{C} & 0.03590500 \quad 3.11875700 \quad 0.23915600 \\
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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

$\text{NaOO}$

O  1.04416800  0.20075100  0.00000000
O  0.00000000  1.06326600  0.00000000
Na -0.75939500  -0.91928500  0.00000000

$[\text{NaOtBu}]\text{NaOO}$

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O  -2.97506000  0.01925700  -0.68027200
C  1.73345000  -0.00684500  0.00004400
C  2.28180200  -0.72616400  -1.25311000
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H  1.87722400  -0.20818600  2.16348900
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Na  -1.23087400  1.37739400  0.00077600
Na  -1.28291400  -1.40311000  0.00083100

$[\text{NaOtBu}]_3\text{NaOO}$ (C-3)

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C  3.26107500  -0.00190900  -0.56984500
C  -1.00053400  4.07525000  -0.09153500
H  -0.00947000  4.14498100  -0.56122200
H  -1.57002500  4.96841300  -0.37854400
H  -0.87158100  4.09757800  0.99945400
C  -3.08415100  2.68890500  0.15665500
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H  -3.59814100  1.76408500  -0.14021600
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H  -2.37500100  1.83477800  -2.36797400
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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

\[ \text{[KoBu]} \cdot \text{HSiMe}_3 \]

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Si -2.68538600  -0.36189000  0.00058400
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O  1.13393500  0.30749900  -0.00092900
C  2.15257400  -0.62244700  -0.00023700
C  3.53301800  0.08313100  -0.08140100
H  4.38128600  -0.61581100  -0.08703500
H  3.58417600  0.68720000  -0.99750900
H  3.65415500  0.75690300  0.77975900
C  2.11156400  -1.46610300  1.29958200
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H  2.81725300  -2.32963200  -1.26065600
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Si  0.60092900  -0.03309900  0.04461900
H  -0.66502200  0.02705000  -1.14457700
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O  -2.55790400  -0.22909390  -0.25608000

HOOP
O  0.05589000  -0.61174300  0.00000000
Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

O  0.05589000  0.72018700  0.00000000
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[tBuOSiMe$_3$]$^-$

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C  -1.29880500 -1.70152100  -0.98909400
H  -2.12215200 -2.36271100  -0.68224700
C  -2.16147300  0.00037100  1.73191600
H  -2.80117500  0.87967200  1.89304900
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H  -2.80286100  0.87930600  1.89231500
C  -1.52596800  0.00002200  0.08760900
H  -1.15631400  0.88347000  1.85710800
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H  1.77236300 -2.16339100  0.28292700
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[tBuOSiMe$_3$]K$^+$

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C -1.74114200 -0.01080600  0.07912600
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H -1.12613900 -1.00937700  1.90855600
H -2.90052700 -1.02951600  1.66570100
C -1.86593400  1.84049900  0.73995400
C -2.85934000 -0.16379900  0.97636900
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### Supporting Information for Liu, Schuman, Yang, Tountov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

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Supporting Information for Liu, Schuman, Yang, Toutou, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

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Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

TS-24

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## Supporting Information for Liu, Schuman, Yang, Toutov, Liang, Klare, Nesnas, Oestreich, Blackmond, Virgil, Banerjee, Zare, Grubbs, Houk, and Stoltz

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