Supplementary Information for

Catalytic Hydrogen Atom Transfer from Hydrosilanes to Vinylarenes by Alkali Metal Lewis Base Catalyst for Hydrosilylation and Polymerization

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• Supplementary Methods

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 CaH₂. Anhydrous tetrahydrofuran (THF) and diethyl ether (Et₂O) 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. ¹H NMR chemical shifts are referenced to chloroform (7.26 ppm) and DMSO-d₆ (2.50 ppm). ¹³C NMR chemical shifts are referenced to ¹³CDCl₃ (77.23 ppm) and DMSO-d₆ (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]. ¹H NMR assignments are indicated by structure environment (e.g., CH₃H). ¹H NMR and ¹³C 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 atmospheric-pressure chemical ionization and time-of-flight (APCI/TOF) mode. Samples were introduced as solutions in a mixed solution of methanol and DCM. GC/MS data were recorded on a Varian 450-GC/Varian 240-MS System and Shimadzu GCMS-QP2010 SE. GC-MS experiments using electron impact ionization (EI) were performed at 70 eV using a mass-selective detector. Analytical TLC experiments were performed on an F254 plate with 250 μm thickness. Detection was performed by UV light or potassium phosphomolybdic acid, potassium permanganate, and p-anisaldehyde staining. Gel permeation chromatography (GPC) analyses were conducted on a TOSOH HLC-8320 system with THF as eluent at 1 mL min⁻¹ flow rate. The system was calibrated against linear polystyrene standards in THF. X-band (9 GHz) electron paramagnetic resonance (EPR) spectra were recorded on a Bruker (Billerica, MA) EMX Plus spectrometer equipped with a bimodal resonator (Bruker model 4116DM). A modulation frequency and amplitude of 100 kHz and 0.1 mT was used for all EPR measurements. All experimental data used for spin-quantification were collected under non-saturating conditions. EPR spectra were calculated by diagonalization of the general spin Hamiltonian for a single electron wavefunction using the software SpinCount (ver. 6.0.6325.21642), written by Professor M. P. Hendrich at Carnegie Mellon University. Nuclear hyperfine interactions (A) are treated with second order perturbation theory. The simulations were generated with consideration of all intensity factors, both theoretical and experimental, to allow for determination of species concentration. The only unknown factor relating the spin concentration to signal intensity was an instrumental factor that is specific to the microwave detection system. However, this was determined by a spin standard, Cu(EDTA), prepared from a copper atomic absorption standard solution purchased from Sigma-Aldrich.
Supplementary Discussion

I) Optimization Studies.

A) Survey of Silanes

Styrene 1a (0.2 mmol, 28 µL), silane (3.5 equiv) were added to a 4 mL flame-dried vial. KO\textsuperscript{t}Bu (40 µL, 1 M in THF, 20 mol %) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 24 h at 23 °C or 80 °C.

**Supplementary Table 1. Survey of silanes**

| entry | H–[Si] | 1a (%)\textsuperscript{a} | 2a (%)\textsuperscript{a} | 3a\textsuperscript{d} | 4a (%)\textsuperscript{a} |
|-------|--------|----------------|----------------|----------------|----------------|
| 1     | O(SiMe\textsubscript{2}H\textsubscript{2}) | 0 | 91 | nd | 5 |
| 2     | NH(SiMe\textsubscript{2}H\textsubscript{2}) | 100 | 0 | nd | 0 |
| 3     | HSiMe(OTMS)\textsubscript{2} | 50 | 28 | yes | 1 |
| 4     | HSiEt\textsubscript{3} | 75 | 1 | yes | 12 |
| 5     | HSiPh\textsubscript{3} | 60 | 12 | yes | 0 |
| 6     | HSi(OEt)\textsubscript{3} | 60 | 20 | yes | 0 |
| 7     | H\textsubscript{2}SiEt\textsubscript{2} | 0 | 96 (97)\textsuperscript{c} | nd | 4(3)\textsuperscript{c} |
| 8     | H\textsubscript{2}SiPr\textsubscript{2} | 0 | 28 | yes | 2 |
| 9     | H\textsubscript{2}SiPh\textsubscript{2} | 0 | 48 | yes | 2 |
| 10    | H\textsubscript{2}SiMePh | 25 | 68\textsuperscript{b} | yes | 3 |
| 11\textsuperscript{d} | H\textsubscript{3}SiPh | 0 | 34 | yes | 2 |
| 12    | Me\textsubscript{3}Si–SiMe\textsubscript{3} | 100 | 0 | 0 | 0 |

\textsuperscript{a}Determined by \textsuperscript{1}H NMR spectroscopy using mesitylene as internal standard. \textsuperscript{b}A diasteromeric mixture of 2a (1:1 \textit{dr}) was formed. \textsuperscript{c}Reaction at 23 °C for 24 h. \textsuperscript{d}Besides monosilylation product 2a a diasteromeric mixture of the disilylation product 2ab\textsubscript{bis} were produced.

The silane screening showed that smaller and electron-donating hydrosilanes are generally better for the hydrosilylation and required >2 equiv for higher conversion.
B) Survey of Lewis Base

Styrene 1a (0.2 mmol, 28 µL) and diethylsilane (90 µL, 3.5 equiv) were added to a 4 mL flame-dried vial. Lewis base (20 mol %) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 24 h at 23 °C or 80 °C.

**Supplementary Table 2. Survey of metal Lewis base**

| entry | base            | 1a (%)<sup>a</sup> | 2a (%)<sup>a</sup> | 3a<sup>a</sup> | 4a (%)<sup>a</sup> |
|-------|----------------|--------------------|--------------------|---------------|-------------------|
| 1     | LiOH           | 100                | 0                  | -             | 0                 |
| 2     | NaOH           | 95                 | 2                  | -             | 3                 |
| 3     | KOH            | 0                  | 93                 | -             | 5                 |
| 4     | RbOH           | 0                  | 0 (43)<sup>b</sup> | -             | 100 (12)<sup>b</sup> |
| 5     | CsOH           | 0                  | 35                 | -             | 64                |
| 6     | Mg(OH)<sub>2</sub> | 100                | 0                  | -             | 0                 |
| 7     | Ca(OH)<sub>2</sub> | 0                  | 0                  | -             | 0                 |
| 8     | Sr(OH)<sub>2</sub> | 100                | 0                  | -             | 0                 |
| 9     | Ba(OH)<sub>2</sub> | 0                  | 10                 | Yes           | 19                |
| 10<sup>b</sup> | La(O<sup>i</sup>Pr)<sub>3</sub> | 87                 | 5                  | -             | 4                 |
| 11<sup>b</sup> | Yb(O<sup>i</sup>Pr)<sub>3</sub> | 15                 | 27                 | -             | 53                |
| 12    | KOEt           | 0                  | 91                 | -             | 7                 |
| 13    | KO'Bu          | 0                  | 97                 | -             | 3                 |
| 14    | KOSiMe<sub>3</sub> | 0                  | 95                 | -             | 5                 |
| 15    | KN(SiMe<sub>3</sub>)<sub>2</sub> | 0                   | 71                 | -             | 28                |
| 16    | K enolate<sup>c</sup> | 0                   | 81                 | -             | 5                 |
| 17    | KH             | 0                  | 87                 | -             | 7                 |
| 18    |KF             | 100                | 0                  | -             | 0                 |
| 19    | KCN            | 100                | 0                  | -             | 0                 |
| 20    | K              | 0                  | 10                 | -             | 18                |
| 21    | LiOSiMe<sub>3</sub> | 96                 | 2                  | -             | 2                 |
| 22    | NaOSiMe<sub>3</sub> | 100                | 0                  | -             | 0                 |
| 23    | NaO'Bu         | 79                 | 7                  | -             | 2                 |
| 24    | NaOEt          | 95                 | 0                  | -             | 1                 |
| 25    | NaH            | 78                 | 7                  | -             | 1                 |
| 26    | Na             | 5                  | 5                  | -             | 6                 |
| 27<sup>d</sup> | TBAF         | 6.5                | 6.2                | Yes           | 6.7               |
| 28    | 18.crown.6/KO'Bu | 0                   | 0                  | Yes           | 0                 |

<sup>a</sup>Determined by <sup>1</sup>H NMR spectroscopy using mesitylene as internal standard. <sup>b</sup>Reaction at 23 °C for 24 h. <sup>c</sup>Potassium 4-ethoxy-4-oxobut-2-en-2-olate. <sup>d</sup>After 168 h at 100 °C.
Supplementary Figure 1. Impact of cations using metal hydroxide (MOH) for branch-selective Markovnikov olefin silylation. Yields of hydrosilylation product 2a with MOH (20 mol %) are indicated.

*Additional important, insightful references for base-mediated reactions between hydrosilanes and alkynes. 5-9

Supplementary Figure 2. Branch-selective, Markovnikov olefin hydrosilylation with bulky potassium alkoxy Lewis bases.

tert-Amyl alcohol (0.2 mmol) or L-menthol (0.2 mmol), excess potassium and THF (0.1 mL, 2 M) were added to a vial. The reaction mixture was heated at 80 °C for 2 h. The solution was transferred to another vial via syringe. 4-Methoxystyrene 1a (28 µL, 0.2 mmol), H₂SiEt₂ (90 µL, 3.5 equiv), and THF (0.1 mL, 2M) were added to the vial. The reaction mixture was heated at 80 °C for 2 h. The yield of 2a, based on ¹H NMR spectroscopy using an internal standard was 91% and 87% for tert-amyl alcohol and L-menthol, respectively, based on ¹H NMR spectroscopy using an internal standard. These results imply that other potassium tertiary alkoioxides and bulky secondary alkoixides can serve as an effective Lewis base for the branch-selective, Markovnikov olefin hydrosilylation.
Screening of Lewis base shows the effectiveness of widely-used oxyanions, amide, enolate, and hydride on hydrosilylation of vinylarenes, but not carbanion and fluoride. The LBCI-HAT was generally efficient when the pKa of the corresponding acid of Lewis base was >ca. 11 (e.g., β-keto ester potassium anion entry 16). Among them, KO'Bu was found to be the most effective Lewis base catalyst. Counter cations played a crucial role in promoting and controlling the reaction pathways; while larger alkali metals (i.e., K⁺, Rb⁺, Cs⁺) promote the reaction, small cations (i.e., Li⁺ and Na⁺) were unable to or inefficiently catalyze the reaction (Supplementary Figure 1).

C) Survey of KO'Bu Loading Percentage

Styrene 1a (0.2 mmol, 28 µL), diethylsilane (90 µL, 3.5 equiv), and KO'Bu (X mol %) were dissolved in C₆D₆ (0.1 mL), THF (0.3 mL) and internal standard mesitylene (28 µL, 0.2 mmol) were placed in a Norell® pressure NMR tube and heated at 80 °C for 24 h.

Supplementary Table 3. Survey of KO'Bu loading

| entry | KO'Bu (mol %) | Time (h) | Conv. (%)ᵃ | 2a (%)ᵃ |
|-------|--------------|----------|------------|---------|
| 1     | 1            | 40       | 100        | 70      |
| 2     | 2            | 24       | 100        | 78      |
| 3     | 5            | 10       | 100        | 81      |
| 4     | 10           | 6        | 100        | 91      |
| 5     | 20           | 0.5      | 100        | 96      |

ᵃDetermined by ¹H NMR spectroscopy using mesitylene as internal standard.

KO'Bu was shown to be most effective Lewis base catalyst, and the catalyst loading can be lowered down to 1 mol%. However, the highest efficiency was achieved with 20 mol% KO'Bu.

D) Survey of Solvent

Styrene 1a (0.2 mmol, 28 µL) and diethylsilane (90 µL, 3.5 equiv) were dissolved with solvent (0.2 mL, 1M) in a 4 mL flame-dried vial. KO'Bu (40 µL, 1 M in THF, 20 mol %) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 10 h at 80 °C.
We found that solvent is indeed not necessary which fits well with the perspective of development of a sustainable chemical process. If needed, non-polar solvents that have Snyder polarity index < ca. 5 were generally better with higher concentration >1 M. as shown in Supplementary Table 4. Choice of temperature (23 °C to 120 °C) was dependent on substrates (steric and electronics).

E) Control Experiments in the Absence of KO'Bu

4-Methoxystyrene (1a, 28 µL, 0.2 mmol) and diethylsilane (90 µL, 3.5 equiv) were placed in a flame-dried vial. The septum on the vial was replaced by a screw cap with a Teflon liner. The mixture was stirred at 80 °C for 1 d. No desired product was observed. The reaction mixture was warmed to 120 °C and stirred for 2 d. No desired product 2a was observed and 1a was cleanly recovered.
F) Effects of the Order of Addition of Reagents and Catalyst

Supplementary Figure 4. Effects of the order of addition of reagents and catalyst. Olefin–Lewis base–silane.

KO\textsuperscript{t}Bu (40 µL, 1 M in THF, 20 mol %) or KH (2 mg, 20 mol %) and styrene (1a or 1e, 0.2 mmol) were placed in a flame-dried vial. The septum on the vial was replaced by a screw cap with a Teflon liner and the mixture was heated at 80 °C. [Note: THF (0.2 mL, 1M) was used when KH was used as Lewis base.] After being stirred for 2 d, styrenes were cleanly recovered and no obvious polymerization was observed. Then diethylsilane (90 µL, 3.5 equiv) was added to the reaction mixture which was stirred for 16 h at rt (with KO\textsuperscript{t}Bu) or for 3 h at 80 °C (with KH), to produce the corresponding hydrosilylation products 2a (87% yield, 100% conversion with KO\textsuperscript{t}Bu; 81%, 100% conversion with KH) based on \textsuperscript{1}H NMR spectroscopy using an internal standard or styrene polymer 3e with 100% conversion with KO\textsuperscript{t}Bu or KH.

Supplementary Figure 5. Effects of the order of addition of reagents and catalyst. Lewis base–silane–olefin.

KO\textsuperscript{t}Bu (40 µL, 1 M in THF, 20 mol %) and diethylsilane (90 µL, 0.7 mmol) were placed in a flame-dried vial. The septum on the vial was replaced by a screw cap with a Teflon liner. The mixture was stirred at rt for 3 h. 4-methoxystyrene 1a (28 µL, 0.2 mmol) was added into the solution. The reaction mixture was heated at 80 °C for 2 h to afford 2a (94% yield) based on \textsuperscript{1}H NMR spectroscopy using an internal standard.
Supplementary Figure 6. Effects of the order of addition of reagents and catalyst. Lewis Base–silane–heating–olefin.

KO'Bu (0.2 mL, 1 M in THF, 100 mol %) and diethylsilane (90 µL, 0.7 mmol) were placed in a flame-dried vial. The septum on the vial was replaced by a screw cap with a Teflon liner. The mixture was stirred at 80 °C for 3 h, and 1a (28 µL, 0.2 mmol) was added into the solution. The reaction mixture was heated at 80 °C for 2 h. The reaction resulted in a complex mixture and no desired product 2a was observed.

During a series of experiments in Supplementary Figure 4-6, no obvious color change of the reaction mixture from a combination of KO'Bu/diethylsilane, KO'Bu/vinylarene (i.e., 1a), or vinylarene/diethylsilane was observed in a wide range of temperatures (23 °C to 120 °C). However, as soon as the three components (i.e., vinylarene, KO'Bu and diethylsilane) were all present in the solution, yellow, brown, or intense red color appeared, depending upon the nature of vinylarenes and the reaction concentrations. The color change may suggest that the reaction might involve anion or radical-mediated processes.

Supplementary Figure 7. Reaction color change at various stages of olefin hydrosilylation. a, Mixture of diethylsilane and vinylarene (e.g., 4-methoxystyrene). b, Color changes to red after addition of KO'Bu. c, Discharge of color after exposure to air.

To summarize, the reaction is insensitive to the order of addition of reagent and catalyst. However, the premature heating of the reaction mixture of Lewis base and hydrosilane, prior to the addition of olefin, did not produce the hydrosilylation product, likely due to the consumption of the Lewis base and some of the hydrosilane by formation of silaketal (See Figure 5a, and 5b, and Supplementary Figure 14-15).
G) Control Reactions with KO'Bu of Different Grades from Various Vendors

Supplementary Table 5. Study on conversion of styrene 1a with various vendors of KO'Bu monitored by NMR spectroscopy

| entry | KO'Bu         | Vendor    | 0.5h | 1h  | 1.2h | 4h  | 8h  | 18h | 28h | 84h | 120h |
|-------|---------------|-----------|------|-----|------|-----|-----|-----|-----|-----|------|
| 1     | 98% in THF    | Acros     | 67   | 100 |      |     |     |     |     |     |      |
|       | 99.99%        |           |      |     |      |     |     |     |     |     |      |
| 2     | solid         | Aldrich   | 32   | 63  | 69   | 88  | 100 |     |     |     |      |
|       | (sublimated)  |           |      |     |      |     |     |     |     |     |      |
| 3     | 98% in solid  | Aldrich   | 1    | 3   | 6    | 12  | 25  | 47  | 64  | 94  | 100  |
| 4     | 95% in solid  | Aldrich   | 0    | 0   | 0    | 0   | 2   | 9   | 16  | 50  | 60   |

4-Methoxystyrene 1a (28 µL, 0.2 mmol), H₂SiEt₂ (90 µL, 3.5 equiv), C₆D₆ (0.1 mL), THF (0.2 mL, 1 M) and internal standard mesitylene (28 µL, 0.2 mmol) were placed in a Norell® pressure NMR tube. Then, KO'Bu (20 mol %) from various sources was added to the NMR tubes. The NMR tubes were kept at rt and the conversion was monitored by ¹H NMR spectroscopy over time. Different purities of KO'Bu gave different kinetic profiles. For example, KO'Bu (98%, 1 M in THF), sublimated (99.99%), 98% in solid and 95% in solid completed the olefin hydrosilylation in 1 h, 8 h, 120 h and 200 h, respectively (Supplementary Supplementary Table 5). However, the overall yield and selectivity were virtually identical.

H) Doping experiments with various transition metals

Supplementary Figure 8. Effects of transition metal additives.

To address the question as to whether this reaction is simply mediated by trace metals, many transition-metals were examined in the absence of KO'Bu.

a) No reaction occurred with transition metals such as Sc(OTf)₃, Ti(O'Pr)₄, V₂O₅, Cr(acac)₃, MnO₂, FeSO₄•7H₂O, FeCl₃•6H₂O, Co(acac)₂, CuBr, CuI, ZnCl₂•4H₂O, RuCl₃•6H₂O at rt or elevated temperatures for 24 h.

b) Other metal salts such as Pd, Rh, Ir, and Pt exhibited slow conversion with poor site selectivity. For instance, i) Pd(OAc)₂ [at 80 °C for 24 h, 28% conversion, 2a(α):4a:2a'(β)=19:1:9], ii) [Rh(nbd)Cl]₂ [at 80 °C for 24 h, 18% conversion,
2a(α):4a:2a'(β)=4:7:7, iii) [Ir(coe)2Cl]2 (at 80 °C for 24 h, 19% conversion, only 4a), and iv) Pt(dvds)2 [at 80 °C for 24 h, 33% conversion, 2a(α):4a:2a'(β)=13:5:15].

c) While NiCl2•6H2O provided the full conversion (rt, 17 h) favoring the Markovnikov product [2a(α):2a'(β) = 3.3:1], Ni(OAc)2•4H2O [the full conversion (rt, 36 h)] produced the anti-Markovnikov product as major [2a(α):2a'(β) = 1:1.5].

In summary, a trace amount of transition metals unlikely catalyzes the proposed highly branch-selective, Markovnikov hydrosilylation.

II) Preliminary Studies on Catalytic Reaction Mechanism on LBCI-HAT

A) Investigation of Mechanism Involving Hydrogen Atom Transfer (HAT)

(a) Effect of Additives

Styrene 1a (0.2 mmol, 28 µL), diethylsilane (90 µL, 3.5 equiv), and an additive were added to a 4 mL flame-dried vial. KO’Bu (40 µL, 1 M in THF, 20 mol %) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 18 h at 80 °C.

Supplementary Table 6. Effect of additives

| Entry | additive (equiv) | 1a (%)a | 2a (%)a | 4a (%)a |
|-------|-----------------|---------|---------|---------|
| 1     | H2O (0.1)       | 0       | 91      | 9       |
| 2     | H2O (2.0)       | 0       | 74      | 10      |
| 3     | H2O (4.0)       | 35      | 18      | 13      |
| 4     | BHT (0.1)       | 97      | 0       | 3       |
| 5     | BHT (0.2)       | 100     | 0       | 0       |
| 6     | O2 (2.2 mL, 0.5)| 84      | 0       | 0       |
| 7     | TEMPO (0.1)     | 0       | 90      | 4       |
| 8     | TEMPO (0.2)     | 0       | 84      | 5       |
| 9     | TEMPO (0.5)     | 0       | 65      | 6       |
| 10    | TEMPO (1)       | 0       | 34      | 6       |
| 11b   | TEMPO (2)       | 0       | 0       | 6       |
| 12    | Galvinoxyl (0.2)| 70      | 20      | 6       |
| 13    | Galvinoxyl (1)  | 80      | 0       | 0       |
| 14    | in dark         | 0       | 95      | 3       |

aDetermined by 1H NMR spectroscopy using mesitylene as internal standard. bThe adduct produced from the reaction of TEMPO and 4-methoxystyrene was observed (47% isolation yield). For details, see Supplementary Figure 9) Additives were examined in this reaction. A proton donor such as H2O did not shut down the reaction, but it lowered the yield. But a radical scavenger such as 2,6-di-tert-
butyl-4-methylphenol (0.1 and 0.2 equiv) completely shut down the reaction. O$_2$ (0.5 equiv) also prevented the reaction. The reaction was shut down completely when TEMPO (2 equiv) or galvinoxyl radical (1 equiv) was used. In case of TEMPO, 5b (49%; for details, see Supplementary Figure 9) was obtained, which indicates a formation of benzylic radical intermediate. The addition of galvinoxyl radical resulted in formation of 6 (40%) which presumably signifies formation of hydrogen atom radical (Supplementary Figure 9). Of note, in the absence of Lewis base we did not observe any reactivity of TEMPO or galvinoxyl with substrate (1a) or hydrosilane, and we also did not observe any reaction between Lewis base and TEMPO or galvinoxyl.

Supplementary Figure 9. Additions of TEMPO and galvinoxyl radicals.

2,2,6,6-Tetramethyl-1-[1-(o-tolyl)ethoxy]piperidine (5b)

**Yield:** 0.4 mmol scale, 135 mg, 49%. (White solid, Melting point: 56-59 °C).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.44 (d, $J = 7.7$ Hz, 1H, Ar-H), 7.21 (dd, $J = 7.7, 7.3$ Hz, 1H, Ar-H), 7.13 (dd, $J = 7.5, 7.3$ Hz, 1H, Ar-H), 7.09 (d, $J = 7.5$ Hz, 1H, Ar-H), 5.00 [q, $J = 6.6$ Hz, 1H, Ar-CH(OR)Me], 2.33 (s, 3H, Ar-CH$_3$), 1.45 [d, $J = 6.6$ Hz, 3H, CH(OR)CH$_3$], 1.33 [br s, 3H, ONC(CH$_3$)$_2$], 1.19 [br s, 3H, ONC(CH$_3$)$_2$], 1.03 [br s, 3H, ONC(CH$_3$)$_2$], and 0.71 [br s, 3H, ONC(CH$_3$)$_2$].

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 144.9, 133.8, 130.1, 126.51, 126.48, 126.1, 80.6, 59.9, 59.6, 40.5 (2), 34.8, 33.6, 23.1, 20.61, 20.46, 19.5, and 17.4.

**IR (neat):** 2953 (s), 2870 (s), 1707 (s), 1462 (m), 1361 (m), 1062 (s), and 758 (s) cm$^{-1}$.

**TLC:** $R_f = 0.5$ in 20:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{19}$H$_{30}$NO)$^+$: 276.2322. Found: 276.2315.

2,6-Di-tert-butyl-4-(3,5-di-tert-butyl-4-hydroxybenzylidene)cyclohexa-2,5-dienone (6)
Yield: 0.4 mmol scale, 67 mg, 40%. (Yellow solid, Melting point: 156-158 °C).

Yellow solids

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta 7.61 (d, J = 2.3 Hz, 1\text{H}, \text{Ar-H}), 7.36 [s, 2\text{H}, \text{C}'(\text{Bu})\text{CH}], 7.17 (s, 1\text{H}, \text{Ar-CH=C}), 7.01 (d, J = 2.3 Hz, 1\text{H}, \text{Ar-H}), 5.56 (s, 1\text{H}, \text{OH}), 1.48 [s, 18\text{H}, (\text{CH}_3)\_2], 1.334 [s, 9\text{H}, (\text{CH}_3)\_3], \) and 1.327 [s, 9\text{H}, (\text{CH}_3)\_3].

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta 186.7, 155.7, 149.0, 147.1, 144.7, 136.6, 135.9, 130.1, 128.39, 128.36, 127.8, 35.7, 35.2, 34.6, 30.5, 29.88, \) and 29.74.

IR (neat): 3629 (m), 2954 (m), 2868 (m), 1632 (m), 1610 (s), 1551 (s), 1435 (s), 1359 (s), 1213 (s), 887 (s), and 502 (m) cm\(^{-1}\).

TLC: \(R_f = 0.5\) in 20:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H\(^+\))\(^+\) (C\(_{29}\)H\(_{43}\)O\(_2\))\(^+\): 423.3258. Found: 423.3246.

(b) Studies on Potassium Cation-\(\pi\) Interaction

To investigate the interaction of K\(^+\) and \(\pi\) system which is likely essential for the homolytic cleavage of Si–H bond within pentavalent silicate for the LBCI-HAT, the following experiments were carried out. We hypothesized that the reduction of TEMPO radical can be utilized as an indicator of HAT. 1) The first experiment performed was whether the HAT occurs in the absence of \(\pi\) system. A solution of TEMPO radical (0.2 mmol, 31 mg, 1 equiv) in THF (0.2 mL, 1 M) was added to a flame-dried vial under nitrogen atmosphere. Then, H\(_2\)SiEt\(_2\) (3.5 equiv) and KO\(_t\)Bu (20 mol %) were added to the mixture (Supplementary Figure 10a). 2) The second experiment was carried out in presence of vinylarene 1a (0.2 mmol, 27 \(\mu\)L) (Supplementary Figure 10b). 3) In the third experiment, 18-crown-6 (20 mol%) was added to a mixture of KO\(_t\)Bu, H\(_2\)SiEt\(_2\), and TEMPO (Supplementary Figure 10c). As a control, the third experiment was repeated in the absence of 18-crown-6, where reduced TEMPO was not observed.

The TEMPO free radical (retention time = 3.78 min) and its reduced form (H-TEMPO, retention time = 3.67 min) are easily distinguishable on GC-MS spectrometry. In the studies, the formation of the reduced TEMPO in the absence of styrene was generally negligible (Supplementary Figure 10a). However, the presence of vinylarene 1a in the reaction triggered the formation of the reduced TEMPO (Supplementary Figure 10b). The most noticeable result (Supplementary Figure 10c) was that more reduced TEMPO was observed vis-à-vis Supplementary Figure 10b, when 18-crown-6 was added in the absence of 1a. We presume that the stronger interaction of K\(^+\) with the crown ether (cf., vinylarene) allows more facile HAT under the reaction conditions. These series of experiments suggest that the LBCI-HAT is essentially associated with the cation-\(\pi\) or cation-n interaction.

During the experiments, H\(_2\) evolution was observed in the beginning phase of the reaction.\(^{11}\) These results are consistent with the previous report of KO\(_t\)Bu-catalyzed cross-dehydrogenative heteroarene C–H silylation, which shares virtually identical reaction parameters with the LBCI-HAT.\(^{11}\) In the report, the initial H\(_2\) formation is related to minor quantity of water.\(^{12}\) Therefore, with supports of the NMR spectroscopic experiments
concerning the LB-mediated silane ligand exchange in Figure 5a and 5b (see main text), the reaction between metal hydride and residual water in the reaction can be responsible for the production of H₂ in the beginning phase of the LBCI-HAT. Alternatively, the generation of H₂ and silylpotassium species can also be possible within the coordination sphere of hypercoordinate silicon species. Further efforts toward elucidating the dehydrogenation mechanism are currently underway.

Supplementary Figure 10. Hydrogen atom trapping experiments for elucidating potassium cation-π interaction in the LBCI-HAT, monitored by GC-MS spectrometry. a, The reaction of H₂SiEt₂ with KO'Bu in the presence of TEMPO radical. b, The reaction of H₂SiEt₂ and KO'Bu with 4-methoxystyrene in the presence of TEMPO radical. c, The reaction of H₂SiEt₂ and KO'Bu with 18-crown-6 in the presence of TEMPO radical.

(c) Mechanism Involving Silyl Radicals

While the radical polymerization of styrenes has been well established, we added several radical initiators to our reaction conditions in the absence of KO'Bu. Radical initiators such as di-tert-butyl peroxide, benzoyl peroxide (BPO), AIBN, triethylborane with O₂, and potassium were examined, which led to the polymerization of styrene as the major product and a trace amount of the desired compound 2a.
Supplementary Figure 11. Survey of different radical initiators for generation of silyl radicals

These series of the reactions (Supplementary Figures 7-11 and Supplementary Table 5-6) indicate that our catalytic hydrosilylation with KO'Bu and hydrosilane involves a radical process, either HAT or silyl radical transfer to alkene. We speculate that HAT (Galvinoxy trapped hydrogen atom, see Supplementary Figure 9) first and likely produces benzylic radical with vinylarene (see the TEMPO experiment, see Supplementary Figure 9), and a subsequent silyl group transfer. Because the silyl radical transfer mechanism should exclusively lead to the formation of anti-Markovnikov hydrosilylation product. In addition, when the free radical polymerization experiment was designed to produce silyl radical which can reacts with vinylarene, we did not observe either Markovnikov or anti-Markovnikov hydrosilylation products. The result suggested that the silyl radical transfer is unlikely responsible for the initial stage of our transition metal-free hydrosilylation involving the Lewis base-catalyzed, complexation-induced hydrogen atom transfer (LBCI-HAT) to olefins, which leads to the formation of the Markovnikov hydrosilylation product.

B) Radical Clock Experiments

When 1c was treated with diethylsilane and KO'Bu at 80 °C, the cyclopropyl ring was opened to form the rearranged product 7c-Et in 81% isolation yield, indicating a benzylic radical was, indeed, involved in the reaction. When HMe₂SiOSiMe₂H (TMDSO) was used, the non-rearranged benzylic radical was kinetically trapped to afford 2c-Me (15% isolation yield) along with the rearranged adduct 7c-Me (80% isolation yield). The occurrence of the rearrangement adduct is indicative of the presence of the benzylic radical species, produced through a preceding HAT to the β-position of styrene. A control experiment with β-cyclopropyl styrene 1d clearly demonstrated the preceding HAT occurs at β-position 2d-Et and 2d-Me. (Supplementary Figure 12)
Supplementary Figure 12. Radical clock experiments and LBCI-HAT with alkyl-substituted alkenes.

(E)-Diethyl(4-phenylpent-3-en-1-yl)silane (7c-Et)

Yield: 0.2 mmol scale, 38 mg, 81%.

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.41-7.38 (d, $J = 8.0$ Hz, 2H, Ar-H), 7.34-7.31 (dd, $J = 8.0$, 7.4 Hz, 2H, Ar-H), 7.23 (dd, $J = 7.4$, 7.4 Hz, 1H, Ar-H), 5.83 [tq, $J = 7.1$, 1.3 Hz, 1H, C(Me)CH$_2$], 3.74 (triplet of pent, $J = 3.2$, 3.2 Hz, 1H, Si-H), 2.29 [td, $J = 7.1$, 7.1 Hz, 2H, C(Me)=CHCH$_2$CH$_2$], 2.05 [app s, 3H, Ar-C(CH$_3$)$_3$], 1.03 [t, $J = 7.9$ Hz, 6H, Si(CH$_2$CH$_3$)$_2$], 0.83-0.78 [nfom, 2H, CH$_2$(SiEt$_3$H)], and 0.65 [qd, $J = 7.9$, 3.2 Hz, 4H, Si(CH$_2$CH$_3$)$_3$].

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 144.2, 133.7, 131.2, 128.3, 126.6, 125.8, 24.0, 15.9, 11.0, 8.4, and 3.1.

IR (neat): 2955 (m), 2173(w), 1720 (m), 1447 (w), 1253 (s), 1027 (s), and 699 (s) cm$^{-1}$.

TLC: $R_f$ = 0.6 in hexanes.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{15}$H$_{25}$Si)$^+$: 223.1720. Found: 223.1732.
(E)-Dimethyl(4-phenylpent-3-en-1-yl)silane (7c-Me)

Yield: 0.2 mmol scale, 33 mg, 80%.

$^1$H NMR (500 MHz): $\delta$ 7.38 (ddd, $J = 7.0$, 1.4, 1.4 Hz, 2H, Ar-$H$), 7.31 (app t, $J = 7.3$ Hz, 2H, Ar-$H$), 7.21 (ddd, $J = 7.2$, 7.2, 1.4, 1.4 Hz, 1H, Ar-$H$), 5.81 [tq, $J = 7.1$, 1.3 Hz, 1H, Ar-C(Me)C$_2$H], 3.92 (triplet of septet, $J = 3.6$, 3.6 Hz, 1H, Si-$H$), 2.27 (dt, $J = 7.1$, 7.1 Hz, 2H, C=CHC$_2$H$_2$), 2.03 (app s, 3H, Ar-CC$_3$H$_3$), 0.80-0.75 [nfom, 2H, C$_2$H$_2$(SiMe$_2$H)], and 0.12 [d, $J = 3.6$ Hz, 6H, Si(CH$_3$)$_2$].

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 144.2, 133.7, 131.1, 128.4, 126.6, 125.8, 23.7, 15.9, 14.5, and –4.1.

IR (neat): 2953 (m), 2176 (w), 1722 (w), 1447 (w), 1255 (s), 1027 (s), and 701 (s) cm$^{-1}$.

TLC: $R_f = 0.6$ in hexanes.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{13}$H$_{21}$Si)$^+$: 205.1407. Found: 205.1410.

(1-Cyclopropyl-1-phenylethyl)dimethylsilane (2c-Me)

Yield: 0.2 mmol scale, 6 mg, 15%.

$^1$H NMR (500 MHz): $\delta$ 7.37-7.25 (m, 5H, Ar-$H$), 3.96 (septet, $J = 3.5$ Hz, 1H, Si-$H$), 1.89 (app t, $J = 7.2$ Hz, 1H, cyclopropyl-$H$), 1.78 (dddd, $J = 14.3$, 11.8, 7.2, 5.1 Hz, 1H, cyclopropyl-$H$), 1.62 (dddd, $J = 14.3$, 11.9, 7.2, 5.1 Hz, 1H, cyclopropyl-$H$), 1.46 [s, 3H, C(Si)CH$_3$], 0.93 (dddd, $J = 14.5$, 11.9, 5.1, 3.0 Hz, 1H, cyclopropyl-$H$), 0.80 (dddd, $J = 14.5$, 11.8, 5.1, 3.0 Hz, 1H), and 0.15 [d, $J = 3.5$ Hz, 6H, Si(CH$_3$)$_2$].

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 143.5, 128.9, 128.6, 127.2, 40.2, 38.4, 20.8, 19.7, 13.6, and –4.3.

IR (neat): 2872 (m), 2109 (m), 1598 (m), 1247 (s), 1165 (w), 1031 (m), 871 (s), 836 (s), and 516 (m) cm$^{-1}$.

TLC: $R_f = 0.6$ in hexanes.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{13}$H$_{21}$Si)$^+$: 205.1417 Found: 205.1426.

(2-Cyclopropyl-1-phenylethyl)diethylsilane (2d-Et)

Yield: 195 mg, 87%. (colorless liquid).
\[ ^1H \text{NMR} \ (\text{CDCl}_3, \ 500 \text{ MHz}): \delta \ 7.26-7.22 \ (m, \ 2H, \ Ar-H), \ 7.14-7.08 \ (m, \ 3H, \ Ar-H), \ 3.67 \ (ddddd, \ J = 3.5, 3.5, 3.5, 3.5, 3.5 \text{ Hz}, \ 1H, \ Si-H), \ 2.37 \ [ddd, \ J = 10.8, 4.5, 3.5 \text{ Hz}, \ 1H, \ C(Si)HCH_2], \ 2.05 \ [ddd, \ J = 14.1, 10.8, 5.2 \text{ Hz}, \ 1H, \ C(Si)HCH_aH_b], \ 1.33 \ [ddd, \ J = 14.1, 8.4, 4.5 \text{ Hz}, \ 1H, \ C(Si)HCH_aH_b], \ 0.96 \ (dd, \ J = 8.0, 8.0, 3H, \ SiCH_2CH_3), \ 0.87 \ (dd, \ J = 8.0, 8.0, 3H, \ SiCH_2CH_3), \ 0.67 \ [dddd, \ J = 13.2, 10.0, 8.4, 5.2 \text{ Hz}, \ 1H, \ C(Si)CHCH_2H], \ 0.64-0.53 \ [m, \ 2H, \ Si(CH_aH_bCH_3)], \ 0.50 \ [dqd, \ J = 14.9, 8.0, 3.5 \text{ Hz}, \ 1H, \ Si(CH_aH_bCH_3)], \ 0.44 \ [dqd, \ J = 14.9, 8.0, 3.5 \text{ Hz}, \ 1H, \ Si(CH_aH_bCH_3)], 0.38-0.31 \ (nfom, \ 2H, \ cyclopropyl-H), \ 0.06-0.04 \ (m, \ 2H, \ cyclopropyl-H). \]

\[ ^{13}C \text{NMR} \ (\text{CDCl}_3, \ 125 \text{ MHz}): \delta \ 144.4, 128.4, 128.1, 124.7, 36.8, 33.6, 11.2, 8.4, 5.3, 4.7, 2.1, \text{ and } 1.7. \]

IR (neat): 2953 (m), 2874 (m), 2098 (m), 1599 (w), 1490 (w), 1234 (s), 1011 (s), 808 (s), 697 (s) and 522 (m) cm\(^{-1}\).

TLC: \( R_f = 0.9 \) in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)\(^+\) \((C_{15}H_{25}Si)\): 233.1720. Found: 233.1715.

(2-Cyclopropyl-1-phenylethyl)dimethylsilane (2d-Me)

Yield: 78\%. (colorless liquid).

\[ ^1H \text{NMR} \ (\text{CDCl}_3, \ 500 \text{ MHz}): \delta \ 7.26-7.23 \ (m, \ 2H, \ Ar-H), \ 7.12-7.08 \ (m, \ 3H, \ Ar-H), \ 3.87 \ (qqd, \ J = 3.7, 3.7, 2.9 \text{ Hz}, \ 1H, \ Si-H), \ 2.28 \ [ddd, \ J = 10.4, 4.9, 2.9 \text{ Hz}, \ 1H, \ C(Si)HCH_2], \ 2.01 \ [ddd, \ J = 14.1, 10.4, 5.2 \text{ Hz}, \ 1H, \ C(Si)HCH_aH_b], \ 1.36 \ (ddd, \ J = 14.1, 8.2, 4.9 \text{ Hz}, \ 1H, \ C(Si)HCH_aH_b), \ 0.69 \ [dddd, \ J = 13.1, 8.2, 8.2, 5.2 \text{ Hz}, \ 1H, \ C(Si)CHCH_2CH], \ 0.39-0.31 \ (m, \ 2H, \ cyclopropyl-H), \ 0.04-0.01 \ (m, \ 2H, \ cyclopropyl-H), \ 0.02 \ (d, \ J = 3.7 \text{ Hz}, \ 3H, \ SiCH_3), \ \text{and} \ -0.04 \ (d, \ J = 3.7 \text{ Hz}, \ 3H, \ SiCH_3). \]

\[ ^{13}C \text{NMR} \ (\text{CDCl}_3, \ 125 \text{ MHz}): \delta \ 144.2, 128.39, 128.0, 124.7, 36.3, 35.6, 11.2, 5.2, 4.8, -5.2, \text{ and } -5.7. \]

IR (neat): 3075 (w), 2999 (w), 2905 (w), 2109 (m), 1599 (w), 1449 (w), 1248 (m), 1014 (m), 873 (s) and 697 (s) cm\(^{-1}\).

TLC: \( R_f = 0.6 \) in hexanes.

HRMS (APCI/TOF): Calcd for (M+H)\(^+\) \((C_{13}H_{21}Si)\): 205.1407. Found: 205.1420.
C) NMR Studies

(a) Procedure for preparation of potassium L-mentholate and the corresponding \(^1\)H NMR study

Supplementary Figure 13.

In a flame dried vial, L-menthol (39.1 mg, 0.25 mmol) was dissolved in C\(_6\)D\(_6\) (0.6 ml). Potassium metal (ca. 40 mg, ca. 1 mmol) was added at 0 °C. The septum on the vial was replaced by a screw cap with a Teflon liner, and the mixture was heated to 80 °C for 3 h. The solution was transferred to a Norell\(^{10}\) pressure NMR tube. Reaction progress was monitored by \(^1\)H NMR spectroscopy.

(b) Procedure for preparation of L-menthylsilane and the corresponding \(^1\)H NMR study

Supplementary Figure 14.
L-Menthol (781 mg, 5 mmol) and \([\text{Rh(COD)Cl}]_2\) (5.0 mg, 0.5 mol%) were dissolved in THF (0.5 M). \(\text{H}_2\text{SiEt}_2\) was slowly added at 0 °C, the mixture was warmed to rt. After completion of the alcoholysis, the volatiles were removed in vacuo and compound 9 was kept at −20 °C. A Norell® pressure NMR tube was purged with N\(_2\), and menthysilane 9 (150 µL, 0.5 mmol) and \(\text{C}_6\text{D}_6\) (0.6 ml) were added. The NMR tube was cooled to 0 °C and KH (4 mg, 0.1 mmol) was added. The mixture was warmed to rt, and the reaction progress was monitored by \(^1\text{H}\) NMR spectroscopy.

(c) Procedure for examining the reversibility of silaketal 10 to identify a Lewis base catalyst consuming route by \(^1\text{H}\) NMR spectroscopy

Supplementary Figure 15.

A Norell® pressure NMR tube was purged with \(\text{N}_2\) and silaketal 10 (80 mg, 0.2 mmol) and \(\text{C}_6\text{D}_6\) (0.6 mL) were added. The NMR tube was cooled to 0 °C and KH (4 mg, 0.1 mmol) was added. The mixture was warmed to rt, then 80 °C. The reaction progress was monitored by \(^1\text{H}\) NMR spectroscopy.

Diethyl bis[(\(\text{IR},2\text{S},5\text{R}\))-2-isopropyl-5-methylocyclohexyl]oxy]silane (10)

\(^1\text{H}\) NMR (CDCl\(_3\), 500 MHz): \(\delta\) 3.66 [ddd, \(J = 10.2, 10.2, 4.3\) Hz, 2H], 2.53 (dddd, \(J = 14.1, 7.0, 7.0, 2.6\) Hz, 2H), 2.20-2.15 (m, 2H), 1.57-1.52 (m, 4H), 1.35-1.26 (m, 4H), 1.26-1.19 (m, 2H), 1.19-1.13 (dd, \(J = 8.0, 8.0\) Hz, 6H), 0.99 (d, \(J = 7.1\) Hz, 6H), 0.91 (d, \(J = 6.4\) Hz, 6H), 0.89 (d, \(J = 6.9\) Hz, 6H), 0.92-0.86 (m, 2H), and 0.82-0.70 (m, 6H).

\(^{13}\text{C}\) NMR (CDCl\(_3\), 125 MHz): \(\delta\) 72.8, 50.6, 46.2, 34.9, 32.0, 25.6, 23.2, 22.6, 21.6, 16.2, 7.3, and 6.2.

\textbf{IR (neat):} 2953 (s), 2870 (m), 1455 (m), 1430 (w), 1236 (w), 1099 (s), 1081 (s), 1000 (s), 730 (s) and 419 (w) cm\(^{-1}\).

\textbf{TLC:} \(R_f = 0.9\) in 80:1 hexanes:EtOAc.

\textbf{HRMS (APCI/TOF):} Calcd for (M+H\(^+\))(\(\text{C}_{24}\text{H}_{49}\text{O}_2\text{Si}\))\(^+\): 397.3496. Found: 397.3516.
(d) Detection of intermediates reaction with TMDSO

Potassium mentholate was prepared same as part (a) and was transferred to a Norell® pressure NMR tube. Tetramethyldisiloxane (1 equiv) was added to the tube. After heating the mixture to 80 °C for 30 min, formation of H₂SiMe₂ was observed by ¹H NMR spectroscopy.

Supplementary Figure 16. Formation of dimethylsilane via reaction between TMSDO and KO'Bu.

D) EPR Spectroscopy

EPR spectroscopy was utilized in an attempt to directly detect radical intermediates in HAT reactions. However, due to the remarkably short lifetime of silyl and carbon-centered radicals at ambient temperature, it is frequently not possible to accumulate sufficient concentrations of radical species for EPR detection and/or characterization. Consequently, the absence of EPR signals in HAT reactions are not sufficient strong evidence to rule out a radical mechanism. To circumvent the kinetic masking of radical intermediates in HAT reactions radical trapping agents 2,6-di-tert-butyl-4-(4-hydroxy-2,5-di-tert-butylphenyl)-methyl]phenol (6H₂) and galvinoxyl [2,6-di-tert-butyl-4-(3,5-di-tert-butyl-4-hydroxybenzylidene)cyclohexa-2,5-dienone] (6) were added to reactions in the reduced form. In these experiments, solutions containing 4-methoxystyrene 1a (14 µL, 0.1 mmol), H₂SiEt₂ (45 µL, 3.5 equiv), and galvinoxyl-H (6) (10 mol %) in THF (0.4 mL) were added to a N₂-purged, 4 mm quartz EPR tube (Wilmad-Labglass p/n 707-SQ-250M). Baseline measurements were made to ensure that no radical species were present in the starting reagents prior to initiating the reaction by addition of KO'Bu (20 µL, 1 M in THF, 20 mol %) via a 50 mL Hamilton gastight syringe. Following initiation of HAT reactions, the EPR spectrometer was quickly re-tuned and spectra were collected at selected time points to monitor the progress of the reaction.

As shown in Supplementary Figure 17a (trace 1), data collected in the absence of 6H₂ or 6 exhibit no discernible features either before or after initiation of reaction. By contrast,
reactions carried out in the presence of either $\textbf{6H}_2$ and $\textbf{6}$ yielded a variety of paramagnetic species which exhibit time dependent accumulation and decay. For instance, following initiation of HAT in the presence of $\textbf{6H}_2$, EPR data was collected at time points ranging from 2 to 20 minutes. Trace 2 (Supplementary Figure 17a) collected 2 minutes after addition of KO'Bu exhibited broad features which cannot be attributed to any single radical species. This spectrum is likely the result of several unresolved signals overlapping and thus cannot be assigned. However, within 10 minutes a triplet centered at an isotropic g-value ($g_{iso}$) of 2.005 (Supplementary Figure 17a trace 3) is observed which can be attributed to a single radical species. The differential area (1:2:1) observed for the satellite features relative to the central resonance arises from degenerate doublets produced when coupled to 2 equivalent nuclei [$^1\text{H}$] with $I = 1/2$ nuclear spin. The observed spectrum can be simulated ($\textit{Sim}1$, dashed line), assuming a single radical coupled to 2 equivalent protons with an isotropic hyperfine coupling ($A_{iso}$) of 4.5 MHz (0.16 mT). Spin quantification of $\textit{Sim}1$ indicates that the concentration of this species is 1.1 ± 0.1 µM. The observed $g$-value, hyperfine splitting pattern, and magnitude of $A_{iso}$ are all consistent with the $\textbf{6H}_2$-radical ($\textbf{6H}_2^\bullet$) shown in Supplementary Figure 17a. This experiment verifies that $\textbf{6H}_2$ can serve as a source of hydrogen atoms in HAT reactions. Moreover, the accumulation and subsequent decay of radical-trapped species is consistent with the radical mechanism involving LBCI-HAT.

If the radical trap $\textbf{6H}_2$ is indeed serving as a H-atom donor in HAT reactions, the observed EPR spectra should be unique to this specific spin trap. Thus, reactions using a different spin trap should yield spectroscopically distinct features. To validate this assertion a second radical trap ($\textbf{6}$, reduced galvinoxyl) was used in equivalent experiments. As before, no signals were observed in reactions in the absence of reduced galvinoxyl $\textbf{6}$ or prior to imitating the reaction by addition of KO'Bu (20 µL, 1 M in THF, 20 mol %). However, following initiation of the LBCI-HAT reaction the complex spectra shown in trace 6 (Supplementary Figure 17b) was observed at 2 minutes. The spectrum is primarily comprised of two distinct radical signals. First, an extended multiline pattern can be observed ranging from 1.997 to 2.012. This broad signal becomes the dominant species in spectra collected at 5 and 10 minutes (Supplementary Figure 17b, trace 7 and 8, respectively) before ultimately decaying. A clean spectrum of the second radical species can be obtained by subtraction of the 10 minute spectrum from trace 6, resulting in the difference spectrum (trace, [6-7]) shown in Supplementary Figure 17b.

Before discussing the assignment of these two radical species, it is instructive to first consider the signal obtained for samples of $\textbf{6}^\bullet$. Shown in Supplementary Figure 17b (trace 5) is the EPR signal for $\textbf{6}^\bullet$ prepared under identical solvent conditions as HAT reactions to avoid the possibility of solvent dependent perturbations to $g$- and $A$-values. This signal is essentially a doublet of multiplets. Simulations of the $\textbf{6}^\bullet$ ($\textit{Sim}5$, dashed line) can be produced assuming coupling to inequivalent sets of protons. Strong coupling [$A_{iso} = 16.7$ MHz (0.59 mT)] to a single proton located at the $\alpha$-carbon (Supplementary Figure 17b) provides the initial separation of multiplets. The two sets of multiline (5-line) is attributed additional hyperfine coupling [$A_{iso} = 3.7$ MHz (0.13 mT)] to four equivalent protons located at carbon atoms C2’, C6’, C3, and C5 of $\textbf{6}^\bullet$ biphenyl ring.
Supplementary Figure 17. X-band EPR spectra of LBCI-HAT reactions carried out in the presence of 6H2 and 6. a, Panel a, trace 1 illustrates the observed EPR spectra of LBCI-HAT performed in the absence of 6H2. Reactions carried out in the presence of 0.01 mmol 6H2 exhibited multiple paramagnetic species which vary with time. Spectra 2, 3, and 4 were collected after 2, 10, and 20 minutes after initiation of reaction. At 10 minutes a single radical species was observed which ultimately decayed by 20 minutes. b, Panel b, represents equivalent reactions carried out using 6 as a spin trap for the LBCI-HAT. Multiple radical species were observed within the first 2 minutes of the reaction (trace 6). Spectra collected at 5 and 10 minutes (trace 7 and 8, respectively) predominately show one radical species with 2-sets of inequivalent 1H-hyperfine coupling patterns. For comparison, the EPR spectrum of the 6-radical (6*) is shown in trace 5. Instrumental conditions: temperature, 293 K; microwave frequency, 9.641 GHz; microwave power, 200 μW; modulation amplitude, 0.1 mT. Simulation parameters: Sim1, giso = 2.0054; I1, 1/2; #I1, (2); Aiso = 4.5 MHz (0.16 mT); σB = 0.01 mT. Sim5, giso = 2.0054; I1, 1/2; #I1, (1); Aiso = 16.7 MHz (0.59 mT); I2, 1/2; #I1, (4); Aiso = 3.7 MHz (0.13 mT); σB, 0.01 mT. Sim6a, giso = 2.0035; I1, 1/2; #I1, (1); Aiso = 32.8 MHz (1.17 mT); I2, 1/2; #I1, (5); Aiso = 8.3 MHz (0.29 mT); σB, 0.01 mT. Sim6b, giso = 2.0047; I1, 1/2; #I1, (4); Aiso = 3.8 MHz (0.13 mT); I2, 1/2; #I1, (1); Aiso = 3.9 MHz (0.14 mT); σB, 0.01 mT.

As expected, the magnitude of this set of four protons couplings are similar in magnitude to what is observed for the equivalent set of protons [C2' and C6'] for 6H2* [Aiso = 4.5 MHz (0.16 mT)]. Additional satellite features can be observed from very weak dipolar coupling [Aiso ~ 1.6 MHz] to the tert-butyl groups; however, these have been neglected for simplicity. The observed g-values and hyperfine coupling constants reported here are consistent with published values for 6*.16, 20 Therefore, unlike reactions carried out in the presence of 6H2, the reduced galvinoxyl 6 appears to produce a unique radical signal distinct from the known spectrum of the 6*, suggesting a modified radical derivative of 6 was produced instead.
Supplementary Figure 18. Expanded X-band EPR difference spectra [6–7] of LBCI-HAT reactions carried out in the presence of reduced galvinoxyl 6. Subtraction of the 10 minute spectra (Supplementary Figure 17b, trace 7) from trace 6 results in the difference spectra [6–7] shown. Instrumental conditions: temperature, 293 K; microwave frequency, 9.641 GHz; microwave power, 200 µW; modulation amplitude, 0.1 mT. Simulation parameters: Sim6b, $g_{iso} = 2.0047$; $I_1$, 1/2; #$I_1$, (4); $A_{iso} = 3.8$ MHz (0.13 mT); $I_2$, 3/2; #$I_1$, (1); $A_{iso} = 3.9$ MHz (0.14 mT); $\sigma_B$, 0.01 mT. Sim6c, $g_{iso} = 2.0047$; $I_1$, 1/2; #$I_1$, (7); $\sigma_B$, 0.01 mT.

The identity of this paramagnetic species produced in HAT reactions is not precisely known; however, some arguments can be made based on their spectroscopic properties and similarity to 6*. For instance, the broad multiline signal shown in trace 7 and 8 has many features which are quite similar to the 6*: the species observed is also a doublet of multiplets. As shown Supplementary Figure 17b (simulation Sim6a), an accurate match in both hyperfine splitting and intensity of multiplets can be obtained. The apparent deviation of Sim6a from the experimental data shown in trace 7 is due to a distortion within the baseline. This appears to be the result of contributions of an additional broad feature near $g \sim 2.003$. Regardless, the position ($g$-value) for each hyperfine transition within the spin-envelope is accurately reproduced assuming a strong coupling to a single proton [$A_{iso} = 32.8$ MHz (1.17 mT)] with weaker coupling to a set of 5 equivalent protons [$A_{iso} = 8.3$ MHz (0.29 mT)]. Integration of this signal in trace 7 accounts for 2.2 ± 0.4 µM. Beyond the obvious inclusion of an addition proton coupling at 8.3 MHz, both sets of hyperfine couplings increase by almost exactly 2-fold relative to couplings observed for 6*. The fact that both sets of hyperfine features shift by a scalar quantity suggests that this observed transient species is from a modified form of 6*.

Assignment of the remaining short-lived species represented by the difference spectra in trace [6–7] (Supplementary Figure 17b) is slightly more complicated. To first order, an 8-line signal can be produced by assuming radical coupling to 7 equivalent [$^1$H, $I = 1/2$] nuclei. However, similar to what was observed for trace 3, the resulting area for each satellite band should follow a predictable pattern due to the degeneracy of doublets produced by coupling to multiple equivalent $I = 1/2$ nuclei. $^1,^2$ To illustrate, a simulation
assuming coupling \(A_{iso} = 3.8\) MHz (0.13 mT) to 7 equivalent protons is shown Supplementary Figure 18 (simulation \textit{Sim6c}). Of note is the maximal intensity of the central resonance observed at \(g = 2.005\) with decreasing area and intensity to either side of the central features. However, the central four doublets observed for the [6-7] difference spectrum are nearly equivalent in area. The only explanation for this behavior is that the observed hyperfine coupling involves a nucleus with a larger nuclear magnetic spin (\(I > 1/2\)). In this instance, the central quartet is consistent with a \(I = 3/2\) nucleus. Given the proposed mechanism for radical initiated HAT shown in Figure 2 (main text), \(39K (I = 3/2)\) is a reasonable choice due to its high natural abundance (93.3%) and the absence of any other quadrupole nuclei in the reaction mixtures. As shown in Supplementary Figure 18, simulations assuming hyperfine coupling to one \(39K\) nucleus \([A_{iso} = 3.8\) MHz (0.13 mT)] and three equivalent \(^1H\) \([A_{iso} = 3.9\) MHz (0.14 mT)] match both hyperfine splitting and transition intensities observed in the [6-7] difference spectrum. Least square \((\chi^2)\) analysis of spectral fits indicates a near 2-fold better agreement with the [6-7] difference spectrum for simulation \textit{Sim6b} as compared to \textit{Sim6c}. While satellite features from the minority \(^{41}K (I = 3/2)\) isotope (6.7%) could not be resolved, the 3.8 MHz (0.13 mT) hyperfine splitting is well within the range reported for organometallic radicals exhibiting coupling to \(^{39}K\).\(^{21-23}\) Spin quantification of this signal represents \(1.3 \pm 0.3\) \(\mu M\).

It should be pointed out that the nearly equivalent magnitude observed for the four equivalent \(I_1 = 1/2\) and single \(I_2 = 3/2\) hyperfine terms [3.8 versus 3.9 MHz], suggests the possibility that rather than including four equivalent protons an additional \(^{39}K\) nucleus might be responsible for the splitting instead. Indeed, nearly equivalent fits can be obtained assuming radical coupling to two equivalent \(^{39}K\) nuclei \((I = 3/2)\) both with \([A_{iso} = 3.8\) MHz (0.13 mT)] rather than four \(^1H\) nuclei. At this time, these two possibilities cannot be unambiguously differentiated but the former solution seems more likely as it is difficult to formulate a radical species not adjacent to at least one proton.

The aforementioned experiments using radical trapping reagents are consistent with the proposed radical mechanism involving LBCI-HAT. However, direct evidence of radical formation in the absence of spin-trapping reagents was not observed under ambient temperatures. Therefore, rapid freeze-quench samples were prepared for HAT reactions for analysis by cryogenic (4-50 K) EPR spectroscopy. These experiments have the benefit of interrogating reaction speciation at shorter time intervals (1-30 seconds) while simultaneously increasing instrumental sensitivity. Freeze-quench EPR samples were prepared by from parallel reactions. For each sample, an oven dried 4 mm quartz EPR tube (Wilmad-Labglass p/n 707-SQ-250M) was equipped with septum and purged with N\(_2\) gas. Subsequently, 4-methoxystyrene 1a (7 \(\mu L\), 0.05 mmol), and H\(_2\)SiEt\(_2\) (23 \(\mu L\), 3 equiv, 0.45 mmol) were dissolved in a binary mixture of diisopropyl ether and isopentane [3:1 (v/v)] to obtain a final 1a concentration of 0.25 M. This solvent mixture was selected based on its ability to form a frozen glass and its compatibility with reaction components.\(^{24}\) Reactions were initiated by addition of KO'Bu (40 \(\mu L\), 40 mol %, 1 M in THF) to the tubes using a Hamilton gas-tight syringe equipped with a 6-inch needle. Samples were freeze-quenched at selected time points by immersion in a liquid N\(_2\) cooled acetone bath. Cryogenic X-band EPR spectra were collected using a Bruker (Billerica, MA) EMX Plus spectrometer equipped with a bimodal resonator (Bruker model 4116DM). Low-temperature measurements (4 - 50 K) were made using an Oxford ESR900 cryostat and an Oxford ITC 503 temperature controller.
As an additional control, baseline samples of individual reaction components 1a (Supplementary Figure 19, trace 9), H₂SiEt₂, and KO'Bu were prepared within the binary solvent mixture and analyzed by EPR under identical conditions to ensure that any paramagnetic species observed in rapid-quench samples were not introduced by base components of the HAT reaction. As shown in Supplementary Figure 19, (trace 10), two radical species can be observed with average \( g \)-values (\( g_{\text{ave}} \)) of 2.006 and 1.993 in samples quenched within 5 seconds. At first glance this spectrum appears much like a doublet split by 2.2 mT (62 MHz). However, the higher field resonance at \( g_{\text{ave}} = 1.993 \) is absent in samples quenched at 10 and 30 seconds, indicating this species decays more rapidly than the low-field (\( g_{\text{ave}}, 2.006 \)) species. Moreover, the intrinsic line width (\( \sigma_B \)) of the \( g_{\text{ave}} = 1.993 \) (\( \sigma_B, 0.9 \) mT) resonance is 3-fold higher than observed for the \( g_{\text{ave}} = 2.002 \) (\( \sigma_B, 0.3 \) mT) signal, indicating that these resonances are attributed to chemically distinct entities. At longer time points, the \( g_{\text{ave}} = 2.006 \) species accumulates, reaching maximum intensity near 10-minutes (Supplementary Figure 19, trace 11). This signal exhibits a triplet hyperfine splitting with a 1:2:1 intensity pattern indicating that the radical is strongly coupled \( [A_{\text{iso}} = 38 \text{ MHz (1.4 mT)}] \) to 2-equivalent \( (I = 1/2) \) \(^1\)H-nuclei. The concentration of this species observed at 10-min (8.4 \( \mu \)M) was determined by quantitative simulation (Supplementary Figure 19, Sim 11). However, by 30-minutes (Supplementary Figure 19, trace 12) this species decreases to 1.6 \( \mu \)M. Collectively, these experiments demonstrate the formation of at least (2) distinct radical species in HAT reactions in the absence of spin-trapping reagents. Further, the \( g_{\text{ave}} = 2.006 \) species persists at a steady-state concentration throughout the time course of the reaction (~45 minutes).

Supplementary Figure 19. 50 K X-band EPR spectra of freeze-quenched HAT reactions performed in the absence of spin-trapping reagents. Baseline spectra for 1a in the [diisopropyl ether: isopentane] binary solvent was collected (trace 9) to confirm the absence of any trace paramagnetic species in the individual reaction components. Equivalent samples were prepared for H₂SiEt₂ and KO'Bu and analyzed by cryogenic X-band EPR. For brevity, only the baseline spectra for 1a is shown as no radical species were observed in any individual reaction component. Trace 10 - 12 represent freeze-quenched HAT reactions collected at 5-sec, 10-min, and 30-min, respectively. Instrumental
conditions: temperature, 50 K; microwave frequency, 9.645 GHz; microwave power, 6 μW; modulation amplitude, 0.3 mT. Quantitation of $g_{ave} = 1.993$ and 2.006 species at 5-seconds was determined to be 17 μM and 3 μM, respectively. While the $g_{ave} = 1.993$ signal is not present in samples collected at 10 and 30-seconds, the intensity of the $g_{ave} = 2.006$ signal remains largely invariant. The concentration of the $g_{ave} = 2.006$ signal at later time points (10-, 20-, and 30-minutes) was measured at 8.4, 5.5, and 1.6 μM, respectively. Simulation parameters: Sim11, $g_{x,y,z} = 2.0042, 2.0072, 2.0057$; $I_1, 1/2$; #I1, (2); $A_{x,y,z} = 10, 18, 38$ MHz; $\sigma_B$, 0.03 mT.

One caveat of with cryogenic measurements of frozen solutions is that the spectral line width is much broader due to unresolved $g$- and $A$-anisotropy. In solution, these quantities are time-averaged by molecular motion and therefore the observed spectra appear isotropic in both $g$- and $A$-values. By contrast, frozen spectra yield a ‘powder pattern’ as all possible molecular orientations are trapped. The resulting spectrum is then comprised of a weighted sum of resonances along each principal molecular axis. The resulting anisotropy makes it difficult to resolve weaker hyperfine interactions contributing to the increased line width. Therefore, additional experiments are needed to verify if the observed species represents a Si- or C-centered radical, only that it is strongly coupled to 2-equivalent $^1$H-protons, suggesting direct bonding to the atom with unpaired electron density.

E) Additional Control Experiments

A series of experiment were carried out to detect or capture the anionic intermediates such as benzylic anions or silyl anions (Supplementary Figure 20). To detect formation of benzylic radical, we first tried a reaction with substrate S1 bearing leaving groups (Cl, OTs, OMs), which is capable of 5-exo-tet type ring closure. Additionally, to investigate a possibility of silyl anions generation, a mixture of styrene 1f and the epoxide S3 was subjected to $\text{H}_2\text{SiEt}_2$ and KO'Bu. However, none of the expected products (i.e., benzylic anions or silyl anions) were observed, suggesting that a formation of nucleophilic benzyl or silyl anions is unlikely.

**Supplementary Figure 20. Investigation on mechanisms involving anionic species.**
The 6-exo-trig Radical cyclization reaction to form carbocycle S6 was investigated (Supplementary Figure 21). However, hydrosilane selectively reacted with aryl-substituted alkene and the allyl group within 2ac remained intact, where the cyclized adduct S6 was not observed. This result suggests that the LBCI-HAT likely does not produce a benzylic free radical. Rather, we propose that the unusual radical-radical cross-coupling arose from the transient, yet effective stabilization of the silyl radial anions within an intimate radical-radical anion pair cage, can be achievable by incoming alkali metal Lewis base. Namely, the “protected radicals” masked with alkali metal Lewis base would perhaps dictate the reaction with stable yet transient, benzylic radicals, by protecting the radical center from potential radical-mediated downstream reactions (e.g., hydrogen abstraction, self-termination dimerization, disproportionation, and polymerization with abundant olefins), which ultimately leads to the hydrosilylation product.

Supplementary Figure 21. Radical-mediated cyclization reactions. An intimate radical-radical anion pair cage.

{1[2-(Allyloxy)phenyl]ethyl}dimethylsilane (2ac)

Yield: 183 mg, 83%. (colorless liquid).

H NMR (CDCl₃, 500 MHz): δ 7.09 (dd, J = 7.5, 1.7 Hz, 1H, Ar-H), 7.06 (ddd, J = 8.0, 7.5, 1.7 Hz, 1H, Ar-H), 6.92 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H, Ar-H), 6.80 (dd, J = 8.0, 1.2 Hz, 1H, Ar-H), 6.08 (dddd, J = 17.2, 10.6, 5.1, 5.1 Hz, 1H, CH=CH₂), 5.43 (dddd, J = 17.2, 1.6, 1.6, 1.6 Hz, 1H, CH=CH(data)), 5.27 (dddd, J = 10.6, 1.6, 1.6, 1.6 Hz, 1H, CH=CH(data)), 4.53 (dddd, J = 13.0, 5.1, 1.6, 1.6 Hz, 1H, OCH₃H₃CH=CH₂), 4.49 (dddd,
\[ J = 13.0, 5.1, 1.6, 1.6 \text{ Hz}, 1H, \text{OCH}_2\text{H}_2\text{CH} = \text{CH}_2 \], 3.80 (qqd, \( J = 3.6, 3.6, 2.7 \text{ Hz}, 1H, \text{Si}-H \)), 2.82 [qd, \( J = 7.6, 2.7 \text{ Hz}, 1H, \text{C(Si)HCH}_3 \)], 1.36 [d, \( J = 7.6 \text{ Hz}, 3H, \text{C(Si)HCH}_3 \)], 0.03 (d, \( J = 3.6 \text{ Hz}, 3H, \text{SiCH}_3 \)), and –0.03 (d, \( J = 3.6 \text{ Hz}, 3H, \text{SiCH}_3 \)).

\textbf{13C NMR (CDCl}_3_, 125 MHz):} \( \delta 155.3, 134.8, 133.9, 126.9, 125.2, 120.9, 117.1, 111.2, 68.8, 19.5, 15.2, \quad –5.3, \) and \( –5.5 \).

\textbf{IR (neat):} 2960 (m), 2925 (m), 2853 (m), 2099 (m), 1735 (w), 1489 (w), 1259 (s), 1088 (s), 1019 (s), 799 (s), 700 (w) and 396 (m) cm\(^{-1}\).

\textbf{TLC:} \( R_f = 0.8 \) in 80:1 hexanes:EtOAc.

\textbf{HRMS (APCI/TOF):} Calcd for \((\text{M} + \text{H})^+ (\text{C}_{13}\text{H}_{21}\text{OSi})^+: 221.1356. \) Found: 221.1364.

\textbf{F) Computational Details}

Geometry optimizations were performed with the M06-2X functional \(^{26}\) along with the 6-311++G(2d,2p) basis set, calculated using the Gaussian suite of programs (version G09) \(^{27}\). To elucidate the origin of the hydrogen atom transfer (HAT) and hydride transfer pathways, single-point energy calculations were performed using multistate density functional theory (MSDFT) \(^{28-30}\) with a modified version of the GAMESS-US program \(^{31}, 32\). In MSDFT, we constructed a set of valence bond (VB) states, corresponding to elementary electron, proton, hydrogen atom, and hydride transfer processes (Supplementary Figure 23). The adiabatic ground and excited state potential energy surfaces (PES) for the styrene silylation and polymerization reactions were obtained from configuration interaction among these VB states.

In particular, the formal transfer of a net hydrogen atom to produce a free radical intermediate (\( \Psi_{2b} \)) may be characterized by the admixture of proton-coupled electron transfer (PCET) and hydrogen atom transfer (HAT) mechanisms (yellow area in Supplementary Figure 23). In case of PCET, the reaction can take place via a concerted pathway, or via stepwise sequences either with an initial ET followed by PT (\( \Psi_{1b} \rightarrow \Psi_{2b} \)) or with a PT first followed by ET (\( \Psi_{2a} \rightarrow \Psi_{2b} \)). HAT and concerted PCET are distinguished by strong and weak electronic coupling, respectively, and they are often associated with adiabatic and non-adiabatic processes. The spectrum of HAT and PCET mechanisms to yield the free radical species can be represented by the three valence bond states in Supplementary Figure 23, which along with the reactant state (\( \Psi_{1a} \)) and hydride transfer state (\( \Psi_{3b} \)) form the basis configurational states to fully characterize the mechanisms for the styrene silylation and polymerization reactions.

We studied the following three reactions (Supplementary Data 1):

\begin{align*}
\text{Reaction 1:} & \quad \text{Me}_2\text{H}_2\text{SiOMe}(-) + \text{PhCHCH}_2 \\
\text{Reaction 2:} & \quad \text{Me}_2\text{H}_2\text{SiOMe}(-) + \text{PhCHCH}_2/\text{K}(+) \\
\text{Reaction 3:} & \quad \text{Me}_2\text{H}_2\text{SiH}(-) + \text{PhCHCH}_2/\text{K}(+)
\end{align*}
We focused on the key reaction step to yield the reaction intermediate, and the potential energy profiles for the hydrogen transfer with and without the presence of K⁺ are shown in Supplementary Figure 22. We have also computed the reaction profile for a smaller model, in which the methoxy substituent is replaced by a hydride ion (Reaction 3). Since the relative energies are within 3 kcal/mol of reaction 2, it is not illustrated for clarity. The energy barrier from the pentavalent silyl anion and styrene complex is 16.3 kcal/mol for the parent system (reaction 1), which is nearly identical for Reaction 2 at 16.3 kcal/mol when K⁺ is included. The reaction-product intermediate is predicted to be exothermic by -18.4 and -26.5 kcal/mol, respectively. The nature of this intermediate was then characterized by analysis of structural weights of the VB states that contribute to the total wave function, which are given in Supplementary Supplementary Table 7.

|                   | W(S₀)         | W(S₁)         |
|-------------------|---------------|---------------|
|                   | ΔE  | RS | BR | HT | ΔE  | RS | BR | HT |
| **Reaction 1**    |     |    |    |    |     |    |    |    |
| RC1               |  0.0 | 0.59 | 0.61 | -0.20 | 98.5 | 0.00 | 1.00 | 0.00 |
| TS1               | 16.3 | 0.26 | 0.57 | 0.17 | 131.5 | 0.27 | 0.66 | 0.07 |
| PI1               | -18.4 | -0.02 | 0.28 | 0.74 |  76.1 | 0.00 | 1.00 | 0.00 |
| **Reaction 2**    |     |    |    |    |     |    |    |    |
| RC3               |  0.0 | 0.67 | 0.23 | 0.13 |  99.4 | 0.01 | 0.99 | 0.00 |
| TS3               | 16.3 | 0.27 | 0.46 | 0.27 | 104.9 | 0.27 | 0.66 | 0.07 |
| PI3               | -26.5 | -0.03 | 0.28 | 0.75 |  24.2 | 0.00 | 1.00 | 0.00 |
| **Reaction 3**    |     |    |    |    |     |    |    |    |
| RC2               |  0.0 | 0.68 | 0.34 | 0.00 |  91.3 | 0.04 | 0.96 | 0.00 |
| TS2               | 13.9 | 0.36 | 0.44 | 0.20 | 112.9 | 0.24 | 0.72 | 0.04 |
| PI2               | -30.5 | 0.05 | 0.30 | 0.75 |  21.2 | 0.00 | 1.00 | 0.00 |

**Supplementary Table 7.** Computed relative energies (kcal/mol) and structural weights (W) for the reactant complex (RC), transition state (TS), and product intermediate (PI) in the singlet ground state (S₀) and excited state (S₁). Structural weights are given in terms of the silyl anionic reactant state (RS), the biradical state due to a net hydrogen atom transfer (BR), and the hydride transfer product (HT). In all cases, the singlet excited state corresponds to an open shell biradical residing on the silyl reagent [(LB)HMe₂Si]⁻ and on the hydrogen atom transfer adduct [CH₃CHPh]⁺, respectively. There is negligible (< 1 kcal/mol) energy difference with the triplet biradical state, except at the transition state geometry where strong correlation of all state functions is found with an S-T splitting as large as 37 kcal/mol.
Supplementary Figure 22. The key reaction step to yield the reaction intermediate, and the potential energy profiles for the hydrogen transfer with and without the presence of K⁺.

ψ₁a : [(LB)HR₂Si-H]⁻[Sty]
ψ₁b : [(LB)HR₂Si]²⁺[H-Sty]⁺
ψ₂a : [(LB)HR₂Si-H]⁺[Sty]⁺
ψ₂b : [(LB)HR₂Si]⁻[H-Sty]⁺

Supplementary Figure 23. Valence bond (VB) states, corresponding to elementary electron, proton, hydrogen atom, and hydride transfer processes.

ψ₁a : [HMe₂(MeO)Si-H]⁻[StyK]⁺ + [KHMe₂(MeO)Si-H][Sty]
ψ₁b : [HMe₂(MeO)Si]²⁺[H-StyK]²⁺ + [KHMe₂(MeO)Si]⁻[H-Sty]⁺
ψ₂a : [HMe₂(MeO)Si-H]²⁻•[StyK]⁺(↑)
[KHMe₂(MeO)Si-H]⁺•[Sty]⁺(↑) + [KHMe₂(MeO)Si-H]⁺•[Sty]⁺(↑)
ψ₂b : [(LB)HR₂Si][H-Sty]⁻
H⁺↑
ψ₁a : [(LB)HR₂Si-H]⁻[Sty]
ψ₁b : [(LB)HR₂Si]²⁻[H-Sty]⁺
ψ₂a : [(LB)HR₂Si-H]⁺[Sty]⁺(↑±±↑)
ψ₂b : [(LB)HR₂Si]⁻[H-Sty]⁺(↑±±↑)
Computed total energies (hartree) for the ground and excited states from multistate density functional calculations.

| Reaction 1 | MeO- without K+ |
|------------|-----------------|
| S0         | -794.6338651 -794.6078672 -794.6631733 |
| T1         | -794.4770261 -794.4836606 -794.5132154 |
| S1         | -794.476972 -794.4242607 -794.5126446 |

| Reaction 2 | MeO- with K+ |
|------------|--------------|
| S0         | -1394.328956 -1394.302931 -1394.371194 |
| T1         | -1394.174641 -1394.102527 -1394.291305 |
| S1         | -1394.170512 -1394.161845 -1394.290333 |

| Reaction 3 | H- with K+ |
|------------|------------|
| S0         | -1279.878142 -1279.855977 -1279.926674 |
| T1         | -1279.743976 -1279.731787 -1279.845634 |
| S1         | -1279.732678 -1279.698231 -1279.844338 |

G) Hammett Plot Analysis

The effect of \textit{para}-Substituents on the rate of the reaction was investigated. To overcome the issue of polymerization which usually happens with the electron withdrawing substrates, we selected 5 mostly electro reach arenes  for this study.

An oven dried Norell\textsuperscript{19} pressure NMR tube was purged with nitrogen and charged with vinyl arene (0.1 mmol), H\textsubscript{2}SiEt\textsubscript{2} (50 \textmu L, 0.4 mmol) and C\textsubscript{6}D\textsubscript{6} (0.45 mL), along with TMS as internal standard. A Solution of KOT\textsubscript{Bu} in THF (0.02 mmol, 20\textmu L) was added to the tube and it was immediately capped, and \textsuperscript{1}H-NMR spectra was obtained over period of 30 minutes with 2-minute time intervals.

After obtaining rate constants of early yields (<15%), Log(k/K\textsubscript{0}) was plotted against the corresponding \(\sigma\) or \(\sigma^*\) values. The \(\sigma\) and \(\sigma^*\) values were taken from J.E. Leffler and E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley, 1963 (Dover reprint) and C. Hansch, A. Leo, and R. W. Taft, \textit{Chem. Rev.} 1991, 91, 165-195.
Supplementary Figure 24. Hammett plots using $\sigma$ and $\sigma^*$ values. *sigma value of NEt$_2$ was used.

The observed rho value ($\rho = 1.15$ and $\rho = 1.99$) suggests decline of reactivity with more electron rich systems, which implies possibility of presence of partial negative charge in the RDS. This may be an indication of the proposed radical anion intermediates in the catalytic cycle of LBC1-HAT.

H) Kinetic Isotope Effect (KIE) Studies

To have a better understanding of the reaction mechanism and the corresponding intermediates, we designed the following KIE studies.
Supplementary Figure 25. KIE studies.

(a) Parallel KIE experiment

An oven dried Norell® pressure NMR tube was purged with nitrogen and charged with vinyl arene (0.1 mmol), $\text{H}_2\text{SiPh}_2$ or $\text{D}_2\text{SiPh}_2$ (55 µL, 0.3 mmol) and $\text{C}_6\text{D}_6$ (0.45 mL), along with TMS as internal standard. A solution of KOTBu in THF (0.02 mmol, 20 µL) was added to the tube and it was immediately capped, and $^1$H-NMR spectra was obtained over period of 15 minutes with 1-minute time intervals. The observed yields were plotted against time where the rate constants for both, normal substrate and the deuterium labeled substrate were determined from the slope of the lines.

Supplementary Figure 26. Parallel KIE study of the hydrosilylation reaction. The experiment was done in triplicates, and the error bars were calculated based on the standard deviation of the measurements.

$$KIE = \frac{k_H}{k_D} = \frac{0.5}{0.219} = 2.28$$
(b) *Intermolecular competition KIE experiment*

An oven dried Norell® pressure NMR tube was purged with nitrogen and charged with vinyl arene (0.1 mmol), H₂SiPh₂ (27 μL, 0.15 mmol), D₂SiPh₂ (27 μL, 0.15 mmol) and C₆D₆ (0.45 mL), along with TMS as internal standard. A Solution of KOTBu in THF (0.02 mmol, 20 μL) was added to the tube and it was immediately capped and ¹H-NMR spectra was obtained (yield < 5%).

\[ KIE = \frac{k_H}{k_D} = \frac{8}{3.4} = 2.35 \]

The observed primary KIE value in both experiments, implies that the rate determining step probably involves homolytic cleavage of Si-H bond.

[1-(4-Methoxyphenyl)ethyl-2-d]diphenylsilane-d (2a-Ph-d₂)

![Structure](image)

**Yield:** 0.2 mmol, 46 mg, 73%.

¹H NMR (CDCl₃, 500 MHz): δ 7.56-7.52 (m, 2H, Ar-H), 7.45-7.34 (m, 6H, Ar-H), 7.32-7.28 (m, 2H, Ar-H), 6.95 (d, J = 8.7 Hz, 2H, Ar-H), 6.77 (d, J = 8.7 Hz, 2H, Ar-H), 3.79 (s, 3H, OCH₃), 2.78 [dd, J = 7.5, 7.5 Hz, 1H, C(Si)HCH₂D], and 1.44 [d, J = 7.5 Hz, 2H, C(Si)HCH₂D].

¹³C NMR (CDCl₃, 125 MHz): δ 157.3, 136.62, 136.48, 135.89, 135.77, 133.3, 129.85, 129.73, 128.7, 128.10, 127.92, 113.8, 55.4, 25.8, and 16.7 (t, ¹J_D-C = 19.4 Hz).

IR (neat): 3068 (m), 2974 (w), 1610 (m), 1441 (m), 1245 (s), 11179 (m), 1113 (s), 1053 (s), 828 (w), 700 (s), and 515 (m) cm⁻¹.

TLC: Rf = 0.2 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)+ (C₂₁H₂₁D₂OSi)+: 321.1638. Found: 321.1643.

III) General Procedure for Transition Metal-Free, Branch-Selective Markovnikov Hydrosilylation and Polymerization.

A) Hydrosilylation Procedure and Characterization:

(a) **Condition A:**

Alkene 1 (1 mmol) and diethylsilane (1.3 mL, 10 mmol) were added to a flame-dried vial. KO'Bu (20 mol %; either 22 mg of solid KO'Bu or 0.2 mL, 1 M in THF) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 48 h at rt. The volatiles were removed *in vacuo* to afford the silanes 2, which were purified by MPLC (hexanes, 3 mL/min, retention time 3-8 min).
(b) Condition B:

Alkene 1 (1 mmol) and diethylsilane (0.45 mL, 3.5 mmol) were added to a flame-dried vial. KO’Bu (20 mol %; either 22 mg of solid KO’Bu or 0.2 mL, 1 M in THF) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 3-12 h at 80 °C. The volatiles were removed \textit{in vacuo} to afford the silanes 2, which were purified by MPLC (hexanes, 3 mL/min, retention time 3-8 min).

(c) Condition C:

Alkene 1 (1 mmol) and diethylsilane (0.65 mL, 5 mmol) or tetramethyldisiloxane (0.88 mL, 5 mmol) were added to a flame-dried vial. KO’Bu (22 mg of solid KO’Bu or 0.2 mL, 1 M in THF, 20 mol %) was added to the mixture. The septum on the vial was replaced by a screw cap with a Teflon liner. The reaction mixture was stirred for 24 h at 120 °C. The volatiles were removed \textit{in vacuo} to afford the silanes 2, which were purified by MPLC (hexanes, 3 mL/min, retention time 3-8 min).

\[ \text{[1-(4-Methoxyphenyl)ethyl]dimethylsilane (2a-Me)} \]

Yield: 176 mg, 91% (colorless liquid).
\(^1\)H NMR (CDCl$_3$, 500 MHz): δ 7.00 (d, \( J = 8.7 \) Hz, 2H, Ar-H), 6.82 (d, \( J = 8.7 \) Hz, 2H, Ar-H), 3.81 (qqd, \( J = 3.6, 3.6, 2.8 \) Hz, 1H, Si-H), 3.78 (s, 3H, OCH$_3$), 2.20 [qd, \( J = 7.5, 2.8 \) Hz, 1H, C(Si)HCH$_3$], 1.36 [d, \( J = 7.5 \) Hz, 3H, C(Si)HCH$_3$], 0.02 (d, \( J = 3.6 \) Hz, 3H, SiHCH$_3$), and –0.02 (d, \( J = 3.6 \) Hz, 3H, SiHCH$_3$).
\(^{13}\)C NMR (CDCl$_3$, 125 MHz): δ 157.0, 137.7, 127.9, 113.9, 55.4, 26.8, 15.9, –5.67, and –5.78.

IR (neat): 2954 (m), 2869 (w), 2108 (m), 1609 (m), 1508 (s), 1241 (s), 1177 (m), 1036 (s), 829 (s) and 528 (m) cm$^{-1}$.

TLC: \( R_f = 0.3 \) in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{11}$H$_{19}$OSi)$^+$: 195.1200. Found: 195.1221.

Diethyl[1-(4-methoxyphenyl)ethyl]silane (2a-Et)

Yield: 204 mg, 92% (colorless liquid).
\(^1\)H NMR (CDCl$_3$, 500 MHz): δ 7.04 (d, \( J = 8.7 \) Hz, 2H, Ar-H), 6.83 (d, \( J = 8.7 \) Hz, 2H, Ar-H), 3.79 (s, 3H, OCH$_3$), 3.65 (dddd, \( J = 3.1, 3.1, 3.1, 3.1 \) Hz, 1H, Si-H), 2.31 [qd, \( J = 7.6, 3.2 \) Hz, 1H, C(Si)HCH$_3$], 1.40 [d, \( J = 7.6 \) Hz, 3H, C(Si)HCH$_3$], 0.98 (dd, \( J = 7.9, 3.2 \) Hz, 3H, SiH$_2$CH$_3$).
7.9 Hz, 3H, SiCH₂CH₃), 0.91 (dd, J = 7.9, 7.9 Hz, 3H, SiCH₂CH₃), 0.64-0.58 (m, 2H, SiCH₂CH₃), and 0.56-0.47 (m, 2H, SiCH₂CH₃).

¹³C NMR (CDCl₃, 125 MHz): δ 157.0, 138.0, 128.0, 113.9, 55.4, 24.8, 16.6, 8.44, 8.41, 1.75, and 1.73.

IR (neat): 2951 (m), 2872 (w), 2094 (m), 1610 (m), 1508 (s), 1457 (m), 1242 (s), 1177 (m), 1039 (s), 1012 (s), 795 (s), 694 (m) and 528 (m) cm⁻¹.

TLC: Rf = 0.5 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)+ (C₁₃H₂₃OSi)+: 223.1513. Found: 223.1520.

[1-(4-Methoxyphenyl)ethyl]diphenylsilane (2a-Ph)

Yield: 153 mg, 78%. (White solid, Melting point: 47-50 ºC).

¹H NMR (CDCl₃, 500 MHz): δ 7.57-7.54 (m, 2H, Ar-H), 7.46-7.35 (m, 6H, Ar-H), 7.32-7.29 (m, 2H, Ar-H), 6.96 (d, J = 8.7 Hz, 2H, Ar-H), 6.78 (d, J = 8.7 Hz, 2H, Ar-H), 4.86 (d, J = 3.4 Hz, 1H, Si-H), 3.79 (s, 3H, OCH₃), 2.80 [qd, J = 7.5, 3.4 Hz, 1H, C(Si)HC₃H₃], and 1.47 [d, J = 7.7 Hz, 3H, C(Si)HC₃H₃].

¹³C NMR (CDCl₃, 125 MHz): δ 157.30, 136.48, 135.90, 135.78, 133.40, 133.36, 129.85, 129.73, 128.74, 128.10, 127.92, 113.83, 55.41, 25.99, and 17.05.

IR (neat): 3067 (m), 2998 (w), 2116 (m), 1608 (m), 1507 (s), 1427 (m), 1242 (s), 1177 (m), 1036 (m), 830 (s), 795 (s), 695 (m) and 484 (m) cm⁻¹.

TLC: Rf = 0.2 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)+ (C₂₁H₂₃OSi)+: 319.1513. Found: 319.1515.

Diisopropyl[1-(4-methoxyphenyl)ethyl]silane (2a-iPr)

Yield: 58 mg, 28%. (colorless liquid).

¹H NMR (CDCl₃, 500 MHz): δ 7.09-7.06 (m, 2H, Ar-H), 6.83-6.80 (m, 2H, Ar-H), 3.79 (s, 3H, OCH₃), 3.52-3.51 (m, 1H, Si-H), 2.40 [qd, J = 7.6, 3.8 Hz, 1H, C(Si)HC₃H₃], 1.42 [d, J = 7.6 Hz, 3H, C(Si)HC₃H₃], 1.09-1.04 [m, 8H, SiCH(CH₃)₂], 0.97-0.94 [m, J = 3.5 Hz, 3H, SiCH(CH₃)₂], and 0.90-0.86 [m, 3H, SiCH(CH₃)₂].

¹³C NMR (CDCl₃, 125 MHz): δ 157.0, 138.4, 128.3, 113.9, 55.4, 23.9, 19.58, 19.44 (2), 19.1, 17.7, 10.61, and 10.56.

IR (neat): 2941 (m), 2863 (m), 2089 (m), 1610 (w), 1508 (s), 1460 (m), 1242 (s), 1177 (m), 1039 (s), 1004 (s), 829 (s), 795 (s) and 539 (m) cm⁻¹.

TLC: Rf = 0.5 in 80:1 hexanes:EtOAc.

38
HRMS (APCI/TOF): Calcd for (M+H)\(^+\) (C\(_{16}\)H\(_{27}\)OSi): 251.1826. Found: 251.1835.

[1-(4-Methoxyphenyl)ethyl](methyl)(phenyl)silane (2a-MePh)

Yield: 174 mg, 68%. (colorless liquid). 1:1 dr

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.43-7.41 (m, 1H, Ar-H), 7.39-7.35 (m, 2H, Ar-H), 7.34-7.29 (m, 2H, Ar-H), 6.95-6.91 (m, 2H, Ar-H), 6.80-6.76 (m, 2H, Ar-H), 4.32 (qd, \(J = 3.7, 2.4\) Hz, 0.5H, Si-H), 4.29 (qd, \(J = 3.7, 3.3\) Hz, 0.5H, Si-H), 3.78 (s, 1.5H, OCH\(_3\)), 3.78 (s, 1.5H, OCH\(_3\)), 2.45 [qd, \(J = 7.5, 2.4\) Hz, 0.5H, C(Si)CH\(_3\)], 2.38 [qd, \(J = 7.5, 3.3\) Hz, 0.5H, C(Si)CH\(_3\)], 1.36 [d, \(J = 2.5\) Hz, 1.5H, C(Si)HCH\(_3\)], 1.34 (d, \(J = 2.5\) Hz, 1.5H, C(Si)HCH\(_3\)], 0.28 (d, \(J = 3.7\) Hz, 1.5H, SiCH\(_3\)), and 0.21 (d, \(J = 3.7\) Hz, 3H, SiC\(_3\)).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 157.06, 157.03, 136.89, 136.75, 135.3, 134.94, 134.89, 129.46, 129.45, 128.8, 128.13, 128.11, 127.80, 127.75, 113.75, 113.70, 55.3, 26.7, 26.4, 16.3, 15.6, –7.0, and –7.9.

IR (neat): 3067 (w), 2998 (w), 2953 (m), 2112 (m), 1609 (m), 1507 (s), 1460 (m), 1242 (s), 1195 (m), 1037 (m), 871 (s), 826 (s), 718 (m) and 698 (s) cm\(^{-1}\).

TLC: \(R_f = 0.2\) in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)\(^+\) (C\(_{16}\)H\(_{21}\)Si): 257.1356. Found: 257.1360.

Diethyl[1-(o-toly)ethyl]silane (2b)

Yield: 124 mg, 60%. (colorless liquid).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.17-7.11 (ddd, \(J = 7.8, 7.8, 1.5\) Hz, 1H, Ar-H), 7.15-7.10 (m, 2H, Ar-H), 7.03-7.00 (m, 1H, Ar-H), 3.65 (dddd, \(J = 3.1, 3.1, 3.1, 3.1\) Hz, 1H, Si-H), 2.55 (qd, \(J = 7.4, 3.1\) Hz, 1H, C(Si)HCH\(_3\)], 2.29 (s, 3H, Ar-CH\(_3\)], 1.40 [d, \(J = 7.4\) Hz, 3H, C(Si)HCH\(_3\)], 0.96 (dd, \(J = 8.0, 8.0\) Hz, 3H, SiCH\(_2\)CH\(_3\)], 0.92 (dd, \(J = 8.0, 8.0\) Hz, 3H, SiCH\(_2\)CH\(_3\)], 0.66-0.61 (m, 2H, SiCH\(_2\)CH\(_3\)], and 0.58-0.50 (m, 2H, SiCH\(_2\)CH\(_3\)].

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 144.62, 134.75, 130.25, 126.44, 126.26, 124.45, 21.11, 20.40, 16.56, 8.54, 8.47, 2.21, and 1.58

IR (neat): 2952 (m), 2873 (m), 2101 (m), 1486 (m), 1458 (m), 1184 (w), 1010 (m), 970 (m), 801 (s), 763 (s), 725 (s), and 445 (w) cm\(^{-1}\).

TLC: \(R_f = 0.8\) in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)\(^+\) (C\(_{16}\)H\(_{21}\)OSi): 257.1356. Found: 257.1360.
Diethyl(1-phenylethyl)silane (2f)

Yield: 146 mg, 76%. (colorless liquid).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.27-7.24 (m, 2H, Ar-H), 7.11-7.08 (m, 3H, Ar-H), 3.64 (dddddd, \(J = 3.1, 3.1, 3.1, 3.1, 3.1\) Hz, 1H, Si-H), 2.36 [qd, \(J = 7.5, 3.1\) Hz, 1H, C(Si)HCH\(_3\)], 1.41 [d, \(J = 7.5\) Hz, 3H, C(Si)HCH\(_3\)], 0.96 (dd, \(J = 7.9, 7.9\) Hz, 3H, SiCH\(_2\)CH\(_3\)), 0.89 (dd, \(J = 7.9, 7.9\) Hz, 3H, SiCH\(_2\)CH\(_3\)), 0.62-0.57 (m, 2H, SiC\(_2\)HCH\(_3\)), and 0.54-0.48 (m, 2H, SiC\(_2\)HCH\(_3\)).

\(^13\)C NMR (125 MHz): \(\delta\) 146.1, 128.4, 127.2, 124.7, 26.0, 16.2, 8.14, 8.13, and 1.7 (2).

IR (neat): 2951 (m), 2872 (w), 2904 (m), 1610 (m), 1508 (s), 1458 (m), 1243 (s), 1177 (m), 1039 (s), 1012 (s), 697 (m), 830 (s), 795 (s) and 533 (m) cm\(^{-1}\).

TLC: \(R_f = 0.6\) in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H\(^+\))\((C_{12}H_{21}Si)\): 193.1407. Found: 193.1398.

[1-(2-Methoxyphenyl)ethyl]dimethylsilane (2g)

Yield: 171 mg, 88%. (colorless liquid).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta\) 7.09 (dddd, \(J = 8.1, 7.5, 1.1\) Hz, 1H, Ar-H), 7.08 (dd, \(J = 7.5, 1.0\) Hz, 1H, Ar-H), 6.91 (dddd, \(J = 7.5, 7.5, 1.1\) Hz, 1H, Ar-H), 6.82 (dd, \(J = 8.1, 1.0\) Hz, 1H, Ar-H), 3.79 (s, 3H, Ar-OCH\(_3\)), 3.78 (qqd, \(J = 3.7, 3.7, 2.7\) Hz, 1H, Si-H), 2.74 [qd, \(J = 7.6, 2.7\) Hz, 1H, C(Si)HCH\(_3\)], 1.34 [d, \(J = 7.6\) Hz, 3H, C(Si)HCH\(_3\)], 0.02 (d, \(J = 3.7\) Hz, 3H, SiCH\(_3\)), and –0.04 (d, \(J = 3.7\) Hz, 3H, SiCH\(_3\)).

\(^13\)C NMR (CDCl\(_3\), 125 MHz): \(\delta\) 156.4, 134.5, 126.9, 125.3, 120.7, 110.0, 55.3, 19.5, 15.2, –5.3, and –5.6.

IR (neat): 2997 (m), 2872 (m), 2092 (m), 1597 (w), 1497 (s), 1234 (s), 1114 (m), 1011 (m), 971 (m), 762 (s), 743 (s), and 462 (w) cm\(^{-1}\).

TLC: \(R_f = 0.6\) in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H\(^+\))\((C_{11}H_{19}OSi)\): 195.1200. Found: 195.1194

Diethyl[1-(2-methoxyphenyl)ethyl]silane (2h)

Yield: 111 mg, 50%. (colorless liquid).
**1H NMR** (CDCl$_3$, 500 MHz): $\delta$ 7.11 (dd, $J = 7.7, 1.7$ Hz, 1H, Ar-H), 7.09 (ddd, $J = 8.1, 7.4, 1.7$ Hz, 1H, Ar-H), 6.91 (ddd, $J = 7.7, 7.4, 1.1$ Hz, 1H, Ar-H), 6.81 (dd, $J = 8.1, 1.1$ Hz, 1H, Ar-H), 3.80 (s, 3H, OCH$_3$), 3.59 (dddd, $J = 3.0, 3.0, 3.0, 3.0$ Hz, 1H, Si-H), 2.81 [qd, $J = 7.6, 2.9$ Hz, 1H, C(Si)HCH$_3$], 1.38 [d, $J = 7.6$ Hz, 3H, C(Si)HC$_3$H], 0.98 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.88 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.64 - 0.59 (m, 2H, SiCH$_2$), and 0.50 - 0.44 (m, 2H, SiCH$_2$CH$_3$).

**13C NMR** (CDCl$_3$, 125 MHz): $\delta$ 156.3, 134.9, 127.1, 125.3, 120.8, 109.9, 55.2, 17.8, 15.9, 8.48, 8.44, 2.2, and 2.0.

**IR (neat):** 2996 (m), 2872 (m), 2091 (m), 1596 (w), 1488 (s), 1236 (s), 1114 (m), 1010 (m), 971 (m), 799 (s), 762 (s), 745 (s), and 460 (w) cm$^{-1}$.

**TLC:** $R_f = 0.6$ in 20:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{13}$H$_{23}$OS)$^+$: 223.1513. Found: 223.1519.

**Dimethyl[1-(m-tolyl)ethyl]silane (2i)**

![Dimethyl[1-(m-tolyl)ethyl]silane (2i)](image)

**Yield:** 162 mg, 91%. (colorless liquid).

**1H NMR** (CDCl$_3$, 500 MHz): $\delta$ 7.17 (dd, $J = 7.5, 7.5$ Hz, 1H, Ar-H), 6.95 (d, $J = 7.5$ Hz, 1H, Ar-H), 6.92 (s, 1H, Ar-H), 6.91 (d, $J = 7.5$ Hz, 1H, Ar-H), 3.86 (qqd, $J = 3.6, 3.6, 2.8$ Hz, 1H, Si-H), 2.35 (s, 3H, Ar-C$_3$H$_3$), 2.25 [qd, $J = 7.5, 2.8$ Hz, 1H, C(Si)HCH$_3$], 1.41 [d, $J = 7.5$ Hz, 3H, C(Si)HCH$_3$], 0.06 (d, $J = 3.6$ Hz, 3H, SiCH$_3$), and 0.02 (d, $J = 3.6$ Hz, 3H, SiCH$_3$).

**13C NMR** (CDCl$_3$, 125 MHz): $\delta$ 145.7, 137.8, 128.3, 127.9, 125.5, 124.2, 27.8, 21.7, 15.6, -5.68, and -5.73.

**IR (neat):** 2956 (w), 2869 (w), 2108 (m), 1604 (w), 1487 (w), 1248 (m), 1023 (w), 871 (s), 834 (s), 699 (s) and 432 (w) cm$^{-1}$.

**TLC:** $R_f = 0.7$ in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{11}$H$_{19}$Si)$^+$: 179.1251. Found: 179.1244.

**Diethyl[1-(m-tolyl)ethyl]silane (2j)**

![Diethyl[1-(m-tolyl)ethyl]silane (2j)](image)

**Yield:** 39 mg, 19%. (colorless liquid).

**1H NMR** (CDCl$_3$, 500 MHz): $\delta$ 7.14 (dd, $J = 7.6, 7.6$ Hz, 1H, Ar-H), 6.92-6.88 (m, 3H, Ar-H), 3.63 (ddddd, $J = 3.1, 3.1, 3.1, 3.1$ Hz, 1H, Si-H), 2.32 (s, 3H, Ar-CH$_3$), 2.31 (qd, $J = 7.5, 3.1$ Hz, 1H, C(Si)HCH$_3$), 1.39 (d, $J = 7.5$ Hz, 3H C(Si)HCH$_3$), 0.96 (dd, $J =$
8.0, 8.0 Hz, 3H, SiCH$_2$H$_3$), 0.89 (dd, $J = 8.0, 8.0$ Hz, 3H, SiCH$_2$CH$_3$), 0.61-0.57 (m, 2H, SiCH$_2$CH$_3$), and 0.53-0.46 (m, 2H, SiCH$_2$CH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 146.0, 137.9, 128.3, 128.0, 125.5, 124.3, 25.8, 21.7, 16.3, 8.43, 8.40, 1.78, and 1.75.

IR (neat): 2956 (w), 2869 (w), 2108 (m), 1486 (w), 1246 (m), 872 (s), 834 (s), 700 (s) and 431 (w) cm$^{-1}$.

TLC: $R_f$ = 0.7 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{13}$H$_{23}$Si)$^+$: 207.1564. Found: 207.1550.

[1-(3-Methoxyphenyl)ethyl]dimethylsilane (2k)

Yield: 126 mg, 65%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.17 (dd, $J = 7.5, 7.5$ Hz, 1H, Ar-H), 6.62-7.00 (m, 3H, Ar-H), 3.86 (qqd, $J = 3.6, 3.6, 2.8$ Hz, 1H, Si-H), 3.79 (s, 3H, Ar-OCH$_3$), 2.25 [qd, $J = 7.5, 2.8$ Hz, 1H, C(Si)HCH$_3$], 1.39 [d, $J = 7.5$ Hz, 3H, C(Si)HC$_3$H], 0.06 (d, $J = 3.6$ Hz, 3H, SiCH$_3$), and 0.01 (d, $J = 3.6$ Hz, 3H, SiCH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 158.7, 147.3, 128.9, 119.5, 112.9, 109.3, 55.1, 27.9, 15.5, –5.71, and –5.75.

IR (neat): 2956 (m), 2870 (w), 2110 (m), 1486 (m), 1249 (m), 1013 (m), 875 (s), 834 (m), 697 (s) and 457 (w) cm$^{-1}$.

TLC: $R_f$ = 0.4 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{11}$H$_{19}$OSi)$^+$: 195.1200. Found: 195.1210.

Diethyl[1-(p-tolyl)ethyl]silane (2l)

Yield: 185 mg, 90%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.09 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.02 (d, $J = 8.1$ Hz, 2H, Ar-H), 3.66 (dddd, $J = 3.1, 3.1, 3.1, 3.1$ Hz, 1H, Si-H), 2.34 [qd, $J = 7.5, 3.1$ Hz, 1H, C(Si)HCH$_3$], 2.33 (s, 3H, Ar-CH$_3$), 1.42 (d, $J = 7.5$ Hz, 3H, C(Si)HCH$_3$), 0.99 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$H$_3$), 0.92 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$H$_3$), 0.68-0.59 (m, 2H, SiCH$_2$H$_3$), and 0.58-0.46 (m, 2H, SiCH$_2$H$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 142.9, 134.0, 129.1, 127.1, 25.4, 21.1, 16.4, 8.4 (2), and 1.7 (2).

IR (neat): 2953 (m), 2873 (m), 2098 (m), 1510 (m), 1457 (m), 1236 (w), 1196 (w), 1047 (m), 1004 (s), 795 (s), 707 (m) and 523 (m) cm$^{-1}$.
TLC: R<sub>f</sub> = 0.7 in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)<sup>+</sup> (C<sub>13</sub>H<sub>23</sub>Si)<sup>+</sup>: 207.1564. Found: 207.1559.

**Diethyl[1-(4-isobutylphenyl)ethyl]silane (2m)**

Yield: 149 mg, 60%. (colorless liquid).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ 7.04 (d, J = 8.4 Hz, 2H, Ar-H), 7.02 (d, J = 8.4 Hz, 2H, Ar-H), 3.65 (dddd, J = 3.1, 3.1, 3.1, 3.1 Hz, 1H, Si-H), 2.44 (app d, J = 7.2 Hz, 2H, CH<sub>2</sub>CHMe<sub>2</sub>), 2.34 [qd, J = 7.5, 3.1 Hz, 1H, C(Si)HCH<sub>3</sub>], 1.85 (ddqq, J = 7.2, 7.2, 6.6, 6.6 Hz, 1H, CH<sub>2</sub>CHMe<sub>2</sub>), 1.41 [d, J = 7.5 Hz, 3H, C(Si)HC<sub>3</sub>H<sub>3</sub>], 1.36 [s, 9H, C(CH<sub>3</sub>)<sub>3</sub>], 0.96 (dd, J = 8.0, 8.0 Hz, 3H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.91 [d, J = 6.6 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>], 0.89 (dd, J = 8.0, 8.0 Hz, 3H, SiCH<sub>2</sub>CH<sub>3</sub>), 0.63-0.58 (m, 2H, SiC<sub>2</sub>CH<sub>3</sub>), and 0.55-0.47 (m, 2H, SiC<sub>2</sub>CH<sub>3</sub>).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 142.8, 137.9, 129.1, 126.8, 45.2, 30.5, 27.4, 22.6 (2), 15.6, 1.18, 1.09, -5.65, and -5.74.

**IR (neat):** 2955 (m), 2867 (w), 2109 (m), 1513 (w), 1268 (m), 125.2, 31.7, 27.2, 15.5, and –5.74.

TLC: R<sub>f</sub> = 0.7 in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)<sup>+</sup> (C<sub>14</sub>H<sub>25</sub>Si)<sup>+</sup>: 221.2033. Found: 221.2025.

**{1-[4-(tert-Butyl)phenyl]ethyl}dimethylsilane (2n)**

Yield: 176 mg, 91% (colorless liquid).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ 7.32 (d, J = 8.4 Hz, 2H, Ar-H), 7.06 (d, J = 8.4 Hz, 2H, Ar-H), 3.89 (qqd, J = 3.6, 3.6, 2.8 Hz, 1H, Si-H), 2.29 [qd, J = 7.5, 2.7 Hz, 1H, C(Si)HCH<sub>3</sub>], 1.43 [d, J = 7.5 Hz, 3H, C(Si)H<sub>3</sub>CH<sub>3</sub>], 1.36 [s, 9H, C(CH<sub>3</sub>)<sub>3</sub>], 0.89 (dd, J = 3.6 Hz, 3H, Si<sub>2</sub>CH<sub>3</sub>), and 0.05 (d, J = 3.6 Hz, 3H, SiHCH<sub>3</sub>).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 125 MHz): δ 147.3, 142.4, 126.7, 125.2, 34.4, 31.7, 27.2, 15.5, and –5.7 (2).

**IR (neat):** 2953 (m), 2862 (w), 2107 (m), 1505 (s), 1240 (s), 1175 (m), 1036 (m), 831 (s) and 527 (m) cm<sup>-1</sup>.

TLC: R<sub>f</sub> = 0.6 in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)<sup>+</sup> (C<sub>14</sub>H<sub>25</sub>Si)<sup>+</sup>: 221.1720. Found: 221.1708.
{1-[4-(tert-Butyl)phenyl]ethyl}diethylsilane (2o)

Yield: 208 mg, 84%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.27 (d, $J = 8.1$ Hz, 2H, Ar-H), 7.03 (d, $J = 8.1$ Hz, 2H, Ar-H), 3.63 (dddd, $J = 3.1$, 3.1, 3.1, 3.1 Hz, 1H, Si-H), 2.33 [qd, $J = 7.5$, 3.1 Hz, 1H, C(Si)HCH$_3$], 1.40 [s, $J = 9H$, CCH$_3$], 1.31 [s, 9H, CCH$_3$], 0.96 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.66-0.57 (m, 2H, SiCH$_2$CH$_3$), and 0.56-0.47 (m, 2H, SiCH$_2$CH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 147.3, 142.8, 126.8, 125.3, 34.4, 31.7, 25.2, 16.2, 8.44, 8.40, 1.77, and 1.74.

IR (neat): 2956 (m), 2869 (w), 2109 (m), 1513 (w), 1459 (w), 1362 (w), 1268 (m), 1008 (w), 873 (s), 832 (s) and 558 (m) cm$^{-1}$.

TLC: R$_f$ = 0.7 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{16}$H$_{29}$Si)$^+$: 249.2033. Found: 249.2025.

4-[1-(Diethylsilyl)ethyl]-N,N-dimethylaniline (2p)

Yield: 219 mg, 93%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.01 (d, $J = 8.6$ Hz, 2H, Ar-H), 6.71 (d, $J = 8.6$ Hz, 2H, Ar-H), 3.64 (ddddd, $J = 3.1$, 3.1, 3.1, 3.1 Hz, 1H, Si-H), 2.91 [s, $J = 6H$, ArN(CH$_3$)$_2$], 2.26 [qd, $J = 7.6$, 3.1 Hz, 1H, C(Si)HCH$_3$], 1.38 [d, $J = 7.6$ Hz, 3H, C(Si)HCH$_3$], 0.98 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.92 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.64-0.57 (m, 2H, SiCH$_2$H$_3$CH$_3$), 0.53 (dqd, $J = 11.5$, 7.9, 3.5 Hz, 1H, SiCH$_2$H$_3$CH$_3$), and 0.49 (dqd, $J = 11.5$, 7.9, 3.5 Hz, 1H, SiCH$_2$H$_3$CH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 148.4, 134.2, 127.8, 113.4, 41.2, 24.5, 16.6, 8.5 (2), 1.84, and 1.79.

IR (neat): 2951 (m), 2871 (m), 2092 (m), 1614 (m), 1515 (s), 1455 (m), 1340 (m), 1224 (m), 1131 (w), 1012 (m), 805 (s), 717 (m) and 538 (m) cm$^{-1}$.

TLC: R$_f$ = 0.3 in 20:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{14}$H$_{26}$NSi)$^+$: 236.1829. Found: 236.1835.
Diethyl[1-(4-fluorophenyl)ethyl]silane (2q)

Yield: 151 mg, 72%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.04 [dd, $J = 8.7, 5.3(3J_{F-H})$ Hz, 2H, Ar-$H$], 6.94 [dd, $J = 8.7, 8.7(3J_{F-H})$ Hz, 2H, Ar-$H$], 3.62 [ddddd, $J = 3.1, 3.1, 3.1, 3.1, 3.1$ Hz, 1H, Si-$H$], 2.33 [qd, $J = 7.5, 3.1$ Hz, 1H, C(Si)HCH$_3$], 1.38 [d, $J = 7.5$ Hz, 3H, C(Si)HCH$_3$], 0.95 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.88 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.59 (td, $J = 7.9, 3.1$ Hz, 2H, SiC$_2$H$_3$), and 0.49 (td, $J = 7.9, 3.1$ Hz, 2H, SiC$_2$H$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 160.63 (d, $1J_{F-C} = 242.2$ Hz), 141.65 (d, $4J_{F-C} = 3.7$ Hz), 128.29 (d, $3J_{F-C} = 7.2$ Hz), 115.14 (d, $2J_{F-C} = 21.3$ Hz), 25.2, 16.5, 8.39, 8.36, 1.70, and 1.67.

IR (neat): 2959 (m), 2871 (w), 2164 (m), 1603 (w), 1456 (w), 1258 (m), 1224 (m), 1158 (w), 1015 (s), 875 (s), 832 (s) 797 (s) and 523 (m) cm$^{-1}$.

TLC: $R_f$ = 0.7 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{12}$H$_{20}$FSi)$^+$: 211.1313. Found: 211.1321.

[1-(2,4-Dimethylphenyl)ethyl]dimethylsilane (2r)

Yield: 146 mg, 76%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.03-7.00 (m, 2H, Ar-$H$), 6.98 (s, 1H, Ar-$H$), 3.88 (qqd, $J = 3.6, 3.6, 2.7$ Hz, 1H, Si-$H$), 2.47 [qd, $J = 7.4, 2.7$ Hz, 1H, C(Si)HCH$_3$], 2.31 (s, 3H, Ar-$CH_3$), 2.28 (s, 3H, Ar-$CH_3$), 1.39 (d, $J = 7.4$ Hz, 3H, C(Si)HCH$_3$), 0.07 (d, $J = 3.6$ Hz, 3H, SiCH$_3$), and 0.06 (d, $J = 3.6$ Hz, 3H, SiCH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 141.1, 134.7, 133.7, 131.1, 126.9, 126.1, 22.3, 21.0, 20.4, 16.0, −5.2, and −5.9.

IR (neat): 2960 (m), 2872 (w), 2090 (w), 1513 (w), 1411 (w), 1257 (s), 1015 (s), 910 (m), 789 (s), 701 (m), 701 (m), and 562 (w) cm$^{-1}$.

TLC: $R_f$ = 0.8 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{12}$H$_{21}$Si)$^+$: 193.1407. Found: 193.1420.

Diethyl(1-phenylpropyl)silane (2s)

Yield: 192 mg, 93%. (colorless liquid).
$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.25 (app t, $J = 7.3$ Hz, 2H, Ar-$H$), 7.11 (t, $J = 7.3$ Hz, 1H, Ar-$H$), 7.08 (d, $J = 7.3$ Hz, 2H, Ar-$H$), 3.68 (dddd, $J = 3.1, 3.1, 3.1, 3.1$ Hz, 1H, Si-$H$), 2.11 [ddd, $J = 9.4, 5.8, 3.1$ Hz, 1H, C(Si)HCH$_2$], 1.91-1.79 [nfom, 2H, C(Si)HCH$_2$CH$_3$], 0.97 [dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$], 0.90 [t, $J = 7.1$ Hz, 3H, C(Si)HCH$_2$CH$_3$], 0.88 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.63-0.57 (m, 2H, SiCH$_2$CH$_3$), and 0.54-0.42 (m, 2H, SiCH$_2$CH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 144.0, 128.4, 128.0, 124.7, 35.3, 24.3, 14.4, 8.46, 8.45, 2.1, and 1.7.

IR (neat): 2947 (m), 2866 (w), 2092 (m), 1610 (m), 1177 (m), 1043 (s), 1013 (s), 696 (m), 830 (s), 799 (s) and 523 (m) cm$^{-1}$.

TLC: $R_f = 0$. 8 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{13}$H$_{23}$Si)$^+$: 207.1564. Found: 207.1576.

Diethyl[1-(o-tolyl)propyl]silane (2t)

**Yield:** 207 mg, 94%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 7.14-7.09 (m, 3H, Ar-$H$), 7.01 (ddd, $J = 7.3, 7.3, 1.6$ Hz, 1H, Ar-$H$), 3.65 (dddd, $J = 3.3, 3.3, 3.3, 3.3$ Hz, 1H, Si-$H$), 2.36 [ddd, $J = 10.8, 5.3, 3.3$ Hz, 1H, C(Si)HCH$_2$], 2.28 (s, 3H, Ar-$CH_3$), 1.88 [qdd, $J = 12.0, 7.2, 5.3$ Hz, 1H, C(Si)HC$_2$H$_5$], 1.82 [ddq, $J = 12.0, 10.8, 7.2$ Hz, 1H, C(Si)HCH$_2$CH$_3$], 0.96 [dd, $J = 7.9, 7.9$ Hz, 3H, C(Si)HCH$_2$CH$_3$], 0.89 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.85 (dd, $J = 7.2, 7.2$ Hz, 3H, SiCH$_2$CH$_3$), 0.65-0.62 (m, 2H, SiCH$_2$CH$_3$), and 0.53-0.49 (m, 2H, SiCH$_2$CH$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 142.5, 135.8, 130.3, 126.7, 126.2, 124.4, 29.9, 24.8, 20.7, 14.3, 8.61, 8.53, 2.13, and 2.07.

IR (neat): 2953 (m), 2872 (m), 2099 (m), 1601 (m), 1507 (s), 1486 (m), 1459 (m), 1233 (w), 1008 (s), 969 (m), 807 (s) and 446 (m) cm$^{-1}$.

TLC: $R_f = 0.8$ in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{14}$H$_{25}$Si)$^+$: 221.1720. Found: 221.1709.

Diethyl[1-(4-methoxyphenyl)propyl]silane (2u)

**Yield:** 217 mg, 92%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ 6.98 (d, $J = 8.7$ Hz, 2H, Ar-$H$), 6.81 (d, $J = 8.7$ Hz, 2H, Ar-$H$), 3.78 (s, 3H, ArOCH$_3$), 3.65 (dddd, $J = 3.3, 3.3, 3.3, 3.3$ Hz, 1H, Si-$H$), 2.02
[ddd, $J = 11.0$, 4.4, 3.3 Hz, 1H, C(Si)HCH$_2$], 1.82 [dqd, $J = 14.1$, 7.2, 4.4 Hz, 1H, C(Si)HCH$_2$H$_3$], 1.76 [ddq, $J = 14.1$, 11.0, 7.2 Hz, 1H, C(Si)HCH$_2$H$_3$], 0.96 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.873 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.865 (dd, $J = 7.2$, 7.2 Hz, 3H, CHCH$_2$CH$_3$), 0.62-0.55 (m, 2H, SiHC$_2$H$_3$), 0.50 (dqd, $J = 14.9$, 7.9, 3.3 Hz, 1H, SiHC$_2$H$_3$), and 0.43 (dqd, $J = 14.9$, 7.9, 3.3 Hz, 1H, SiHC$_2$H$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 157.0, 135.8, 128.8, 113.9, 55.4, 34.1, 24.5, 14.3, 8.5, 2.1, and 1.7.

IR (neat): 2953 (m), 2872 (m), 2094 (m), 1609 (s), 1507 (s), 1246 (s), 1177 (m), 1038 (m), 1009 (m), 832 (s), 802 (s) and 532 (m) cm$^{-1}$.

TLC: $R_f$ = 0.5 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{14}$H$_{25}$OSi)$^+$: 237.1669. Found: 237.1677.

(1,2-Diphenylethyl)diethylsilane (2v)

![Structure](image)

**Yield:** 247 mg, 92%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): δ 7.28-7.22 (m, 4H, Ar-H), 7.18-7.12 (m, 6H, Ar-H), 3.84 (dddd, $J = 3.2$, 3.2, 3.2, 3.2 Hz, 1H), 3.21 [nfom, 2H, C(Si)HC$_2$Ph], 2.64 [dd, $J = 7.8$, 7.8, 3.2 Hz, 1H, C(Si)HCH$_2$], 1.05 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.95 (dd, $J = 7.9$, 7.9 Hz, 3H, SiCH$_2$CH$_3$), 0.76-0.65 (m, 2H, SiCH$_2$CH$_3$), 0.60 (dqd, $J = 15.1$, 7.9, 3.2 Hz, 1H, SiCH$_2$H$_3$), and 0.54 (dqd, $J = 15.1$, 7.9, 3.2 Hz, 1H, SiCH$_2$H$_3$).

$^{13}$C NMR (CDCl$_3$, 125 MHz): δ 143.3, 142.1, 128.7, 128.42, 128.23, 128.16, 125.9, 124.9, 37.5, 34.9, 8.4 (2), 2.1, and 1.8.

IR (neat): 3025 (w), 2953 (m), 2873 (m), 2099 (m), 1507 (s), 1493 (m), 1451 (m), 1007 (m), 810 (s), 788 (s), 694 (s) and 521 (m) cm$^{-1}$.

TLC: $R_f$ = 0.6 in 80:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)$^+$ (C$_{18}$H$_{25}$Si)$^+$: 269.1720. Found: 269.1724.

Dimethyl(1-phenylcyclohexyl)silane (2w)

![Structure](image)

**Yield:** 148 mg, 71%. (colorless liquid).

$^1$H NMR (CDCl$_3$, 500 MHz): δ 7.32-7.28 (m, 2H, Ar-H), 7.23-7.21 (m, 2H, Ar-H), 7.11-7.08 (dddd, $J = 7.2$, 7.2, 1.3, 1.3 Hz, 1H, Ar-H), 3.66 (qq, $J = 3.6$, 3.6 Hz, 1H, Si-H), 2.37-2.22 (nfom, 2H, alkyl-H), 1.73-1.67 (m, 2H, alkyl-H), 1.58-1.54 (m, 1H, alkyl-H), 1.51-1.34 (m, 5H, alkyl-H), and −0.11 [d, $J = 3.6$ Hz, 6H, Si(CH$_3$)$_2$].
**13C NMR** (CDCl$_3$, 125 MHz): δ 144.4, 128.4, 127.2, 124.0, 32.6, 31.4, 27.3, 21.7, and –7.0.

**IR (neat):** 2928 (s), 2872 (m), 2107 (m), 1598 (m), 1491 (m), 1247 (s), 1170 (w), 1029 (m), 1009 (m), 870 (s), 837 (s), 659 (s), and 516 (m) cm$^{-1}$.

**TLC:** $R_f = 0.9$ in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{14}$H$_{23}$Si)$^+$: 219.1564. Found: 219.1566.

**Bis{4-[1-(diethylsilyl)ethyl]phenoxy}methane (2x)**

![Chemical Structure](image)

**Yield:** 0.2 mmol scale, 80 mg, 93%. 1:1 $dr$

**1H NMR** (CDCl$_3$,500 MHz): δ 7.04-6.98 (m, 8H, Ar-$H$), 5.65 (s, 2H, OCH$_2$O), 3.62 (dddd, $J = 3.1, 3.1, 3.1, 3.1$ Hz, 2H, Si-$H$), 2.30 [qd, $J = 7.6, 3.1$ Hz, 2H, C(Si)HCH$_3$], 1.37 [d, $J = 7.6$ Hz, 6H, C(Si)HCH$_3$], 0.95 (dd, $J = 7.9, 7.9$ Hz, 6H, SiCH$_2$CH$_3$), 0.89 (dd, $J = 7.9, 7.9$ Hz, 6H, SiCH$_2$CH$_3$), and 0.59-0.47 [m, 8H, Si(C$_3$H$_2$)CH$_3$].

**13C NMR** (CDCl$_3$, 125 MHz): δ 154.6, 140.0, 128.1, 116.7, 92.1, 77.5, 77.2, 77.0, 25.0, 16.5, 8.44, 8.41, 1.74, and 1.72.

**IR (neat):** 2951 (m), 2909 (w), 2872 (m), 2095 (w), 1607 (w), 1504 (s), 1376 (w), 1206 (s), 1001 (s), 897 (s) and 794 (s) cm$^{-1}$.

**TLC:** $R_f = 0.5$ in hexanes.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{25}$H$_{41}$O$_2$Si$_2$)$^+$: 429.2640. Found: 429.2652.

**5-[1-(Diethylsilyl)ethyl]-1-methyl-1H-indole (2y)**

![Chemical Structure](image)

**Yield:** 0.2 mmol scale, 33 mg, 68%.

**1H NMR** (500 MHz): δ 7.36 [d, $J = 1.7$ Hz, 1H, C(4)$H$], 7.23 [d, $J = 8.4$ Hz, 1H, C(7)$H$], 7.02 [dd, $J = 8.4, 1.7$ Hz, 1H, C(6)$H$], 7.01 [d, $J = 2.9$ Hz, 1H, C(2)$H$], 6.41 [d, $J = 2.9$ Hz, 1H, C(3)$H$], 3.77 (s, 3H, NCH$_3$), 3.70 (dddd, $J = 3.1, 3.1, 3.1, 3.1$ Hz, 1H, Si-$H$), 2.44 [qd, $J = 7.6, 3.2$ Hz, 1H, C(Si)HCH$_3$], 1.48 [d, $J = 7.6$ Hz, 3H, C(Si)HCH$_3$], 0.99 (dd, $J = 7.8, 7.8$ Hz, 3H, SiCH$_2$CH$_3$), 0.87 (dd, $J = 7.8, 7.8$ Hz, 3H, SiCH$_2$CH$_3$), 0.65-0.60 (m, 2H, SiCH$_2$CH$_3$), and 0.59-0.45 (m, 2H, SiCH$_2$CH$_3$).

**13C NMR** (CDCl$_3$, 125 MHz): δ 136.8, 135.0, 128.96, 128.88, 122.0, 118.5, 109.0, 100.5, 33.0, 25.5, 17.2, 8.53, 8.50, 1.89, and 1.85.

**IR (neat):** 2950 (m), 2871 (m), 2091 (m), 1512 (m), 1486 (s), 1245 (m), 1179 (w), 1008 (m), 874 (s), 803 (s) and 711 (m) cm$^{-1}$.

**TLC:** $R_f = 0.2$ in 80:1 hexanes:EtOAc.
HRMS (APCI/TOF): Calcd for (M+H)\(^+\) \((C_{18}H_{24}NSi)^{+}\): 246.1673. Found: 246.1669

**2-(Diethylsilyl)-5-[1-(diethylsilyl)ethyl]-1-methyl-1H-indole (2aa)**

![Chemical structure](image)

**Yield:** 0.2 mmol scale, 31 mg, 47%. (with 5% mono-hydrosilylation product 2x).

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta 7.33 \text{ (d, } J = 1.8 \text{ Hz, 1H)}, \ 7.22 \text{ [d, } J = 8.5 \text{ Hz, 1H}, \ C(7)H], \ 7.01 \text{ [dd, } J = 8.5, 1.8 \text{ Hz, 1H}, \ C(6)H], \ 6.67 \text{ [app s, 1H, } C(3)H], \ 4.41 \text{ [dddd, } J = 3.3, 3.3, 3.3, 3.3 \text{ Hz, 1H, } C(2)Si-H], \ 3.82 \text{ (s, 3H, NCH\(_3\))}, \ 3.69 \text{ [dddddd, } J = 3.1, 3.1, 3.1, 3.1, 3.1, 3.1 \text{ Hz, 1H, } C(5)CHC(Si-H)], \ 2.42 \text{ [qd, } J = 7.6, 3.1 \text{ Hz, 1H, } C(Si)HCH\(_3\)], \ 1.46 \text{ (d, } J = 7.8 \text{ Hz, 3H, } C(Si)HCH\(_3\)], \ 1.07 \text{ [app t, } J = 7.9 \text{ Hz, 6H, } Si(CH\(_2\)CH\(_3\))], \ 0.99 \text{ (dd, } J = 7.9, 7.9 \text{ Hz, 3H, } SiCH\(_2\)CH\(_3\)), \ 0.95-0.87 \text{ [m, 4H, } Si(CH\(_2\)CH\(_3\))], \ 0.91 \text{ (dd, } J = 7.9, 7.9 \text{ Hz, 3H, } SiCH\(_2\)CH\(_3\)), \ 0.65-0.57 \text{ (m, 2H, } SiCH\(_2\)CH\(_3\)), \text{ and 0.57-0.44 (m, 2H, } SiCH\(_2\)CH\(_3\)).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta 138.5, 136.8, 136.5, 129.0, 122.7, 118.11, 112.2, 109.0, 32.9, 25.5, 17.2, 8.54, 8.51, 8.49 (2), 3.7 (2), 1.86, \text{ and 1.84.}

**IR (neat):** 2950 (m), 2871 (m), 2092 (m), 1512 (m), 1486 (m), 1234 (m), 1008 (m), 803 (s) and 711 (s) cm\(^{-1}\).

**TLC:** \(R_f\) = 0.8 in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)\(^+\) \((C_{19}H_{34}NSi\_2)^{+}\): 332.2224. Found: 332.2211

**{1-[2-(Diethylsilyl)]benzofuran-5-yl}ethyl]diethylsilane (2ab)**

![Chemical structure](image)

**Yield:** 0.2 mmol scale, 22 mg, 35%.

\(^1\)H NMR (CDCl\(_3\), 500 MHz): \(\delta 7.38 \text{ [d, } J = 8.5 \text{ Hz, 1H, } C(7)H], \ 7.28 \text{ [dd, } J = 1.9, 0.9 \text{ Hz, 1H, } C(4)H], \ 7.03 \text{ [dd, } J = 8.5, 1.9 \text{ Hz, 1H, } C(6)H], \ 6.99 \text{ [d, } J = 0.9 \text{ Hz, 1H, } C(3)H], \ 4.29 \text{ [ddddd, } J = 3.3, 3.3, 3.3, 3.3 \text{ Hz, 1H, } C(2)Si-H], \ 3.66 \text{ [dddddd, } J = 3.1, 3.1, 3.1, 3.1, 3.1 \text{ Hz, 1H, } C(5)CHC(Si-H)], \ 2.43 \text{ [qd, } J = 7.6, 3.1 \text{ Hz, 1H, } C(Si)HCH\(_3\)], \ 1.44 \text{ [d, } J = 7.6 \text{ Hz, 3H, } C(Si)HCH\(_3\)], \ 1.08 \text{ [dd, } J = 7.9, 7.9 \text{ Hz, 6H, } Si(CH\(_2\)CH\(_3\))], \ 0.97 \text{ (dd, } J = 7.9, 7.9 \text{ Hz, 3H, } SiCH\(_2\)CH\(_3\)), \ 0.95-0.88 \text{ [m, 4H, } Si(CH\(_2\)CH\(_3\))], \ 0.90-0.87 \text{ (dd, } J = 7.9, 7.9 \text{ Hz, 3H, } SiCH\(_2\)CH\(_3\)), \ 0.63-0.58 \text{ (m, 2H, } SiCH\(_2\)CH\(_3\)), \text{ and 0.54-0.46 (m, 2H, } SiCH\(_2\)CH\(_3\)).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz): \(\delta 159.2, 156.5, 140.3, 128.2, 124.5, 118.6, 118.4, 111.0, 25.6, 17.1, 8.47, 8.44, 8.2 (2), 2.9 (2), \text{ and 1.8 (2).}

**IR (neat):** 2953 (m), 2873 (m), 2117 (m), 1528 (w), 1455 (m), 1225 (m), 1007 (m), 791 (s), 713 (s), and 451 (m) cm\(^{-1}\).

**TLC:** \(R_f\) = 0.8 in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)\(^+\) \((C_{18}H_{31}OSi\_2)^{+}\): 319.1908. Found: 319.1900.
{1[2-(Allyloxy)phenyl]ethyl}dimethylsilane (2ac)

\[
\begin{array}{c}
\text{SiMe}_3H \\
\text{O} \\
\text{SiMe}_3H
\end{array}
\]

**Yield:** 183 mg, 83%. (colorless liquid).

**\(^1\)H NMR** (CDCl\(_3\), 500 MHz): \(\delta 7.09\) (dd, \(J = 7.5, 1.7\) Hz, 1H, Ar-\(H\)), 7.06 (ddd, \(J = 8.0, 7.5, 1.7\) Hz, 1H, Ar-H), 6.92 (ddd, \(J = 7.5, 7.5, 1.2\) Hz, 1H, Ar-H), 6.80 (dd, \(J = 8.0, 1.2\) Hz, 1H, Ar-H), 6.08 (ddd, \(J = 17.2, 10.6, 5.1\) Hz, 1H, CH=CH\(_2\)), 5.43 (ddd, \(J = 17.2, 1.6, 1.6\) Hz, 1H, CH=CH\(_{3\alpha\beta}\), trans), 5.27 (ddd, \(J = 10.6, 1.6, 1.6, 1.6\) Hz, 1H, CH=CH\(_{3\alpha\beta}\), cis), 5.27 (ddd, \(J = 10.6, 1.6, 1.6, 1.6\) Hz, 1H, CH=CH\(_{3\alpha\beta}\), cis), 4.53 (dddd, \(J = 13.0, 5.1, 1.6, 1.6\) Hz, 1H, OCH\(_3\)), 4.49 (dddd, \(J = 13.0, 5.1, 1.6, 1.6\) Hz, 1H, OCH\(_3\)), 3.80 (qqd, \(J = 3.6, 3.6, 2.7\) Hz, 1H, Si-H), 2.82 (qd, \(J = 7.6, 2.7\) Hz, 1H, C(Si)CH\(_3\)), 1.36 (d, \(J = 7.6\) Hz, 3H, C(Si)CH\(_3\)), 0.03 (d, \(J = 3.6\) Hz, 3H, SiCH\(_3\)).

**\(^{13}\)C NMR** (CDCl\(_3\), 125 MHz): \(\delta 155.3, 134.8, 133.9, 126.9, 125.2, 120.9, 117.1, 111.2, 68.8, 19.5, 15.2, \)–5.3, and –5.5.

**IR** (neat): 2960 (m), 2925 (m), 2853 (m), 2099 (m), 1735 (w), 1489 (w), 1259 (s), 1088 (s), 1019 (s), 799 (s), 700 (w) and 396 (m) cm\(^{-1}\).

**TLC:** \(R_f = 0.8\) in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H\(^+\))\(^{(\text{C}_{13}\text{H}_{21}\text{OSi})}\): 221.1356. Found: 221.1364.

1,1-Dimethyl-2-phenyl-2,3-dihydro-1\(H\)-benzo[b]silole (2ad)

\[
\begin{array}{c}
\text{Me} \\
\text{Me} \\
\text{SiMe}_3H \\
\text{SiMe}_3H
\end{array}
\]

**Yield:** 0.2 mmol scale, 30 mg, 64%.

**\(^1\)H NMR** (CDCl\(_3\), 500 MHz): \(\delta 7.54\) (d, \(J = 7.2\) Hz, 1H, Ar-H), 7.38 (ddd, \(J = 7.6, 7.6, 1.3\) Hz, 1H, Ar-H), 7.35 (d, \(J = 7.4\) Hz, 1H, Ar-H), 7.28-7.23 (m, 3H, Ar-H), 7.13-7.08 (m, 3H, Ar-H), 5.35 (d, \(J = 16.5, 8.3\) Hz, 1H, C(\(\phi\))HCH\(_{3\alpha\beta}\)), 3.40 (dd, \(J = 16.5, 7.5\) Hz, 1H, C(\(\phi\))HCH\(_{3\alpha\beta}\)), 2.85 (dd, \(J = 8.3, 7.5\) Hz, 1H, C(\(\phi\))HCH\(_{3\alpha\beta}\)), 0.41 (s, 3H, SiCH\(_3\)), and –0.00 (s, 3H, SiCH\(_3\)).

**\(^{13}\)C NMR** (CDCl\(_3\), 125 MHz): \(\delta 151.8, 144.7, 138.8, 132.6, 129.9, 128.6, 126.7, 126.3, 125.7, 124.5, 39.5, 35.7, -1.8, and –3.8.

**IR** (neat): 3056 (m), 3021 (w), 2995 (w), 2904 (m), 1600 (s), 1493 (s), 1246 (s), 896 (s), 698 (s), and 472 (m) cm\(^{-1}\).

**TLC:** \(R_f = 0.6\) in 100:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H\(^+\))\(^{(\text{C}_{16}\text{H}_{19}\text{Si})}\): 239.1251. Found: 239.1265.
**tert-Butyl[(13S)-3-[1-(diethylsilyl)ethyl]-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl]oxy]dimethylsilane (2ae)**

**Yield:** 0.1 mmol scale, 36 mg, 74%. 1:1 dr

**1H NMR (CDCl3, 500 MHz):** δ 7.18 [d, J = 8.0 Hz, 0.5H, C(1)H], 7.17 [d, J = 8.0 Hz, 0.5H, C(1)H], 6.89 [dd, J = 8.0, 1.8 Hz, 1H, C(2)H], 6.88 [dd, J = 8.0, 1.8 Hz, 1H, C(2)H], 6.81 [d, J = 1.8 Hz, 1H, C(4)H], 6.80 [d, J = 1.8 Hz, 1H, C(4)H], 3.68-3.62 [m, 1H, C(17)H], 3.65-3.61 (m, 1H, Si-H), 2.89-2.77 (m, 2H, alkyl-H), 2.34-2.29 (m, 1H, alkyl-H), 2.28 [qd, J = 7.5, 3.3 Hz, 1H, C(Si)HCH3], 2.20 (ddd, J = 11.3, 11.3, 4.1 Hz, 1H, alkyl-H), 1.98-1.83 (m, 3H, alkyl-H), 1.70-1.62 (m, 1H, alkyl-H), 1.53-1.44 (m, 3H, alkyl-H), 1.39 [d, J = 7.5 Hz, 3H, C(Si)HCH3], 1.38-1.30 (m, 2H, alkyl-H), 1.23-1.11 (m, 2H, alkyl-H), 1.00-0.95 [m, 6H, Si(CH2CH3)2], 0.91 [s, 9H, OSi(CH2CH3)2], 0.75 [s, 3H, C(18)H3], 0.66-0.59 (m, 2H, SiCH2CH3), 0.57-0.50 (m, 2H, SiCH2CH3), 0.05 (s, 3H, OSiCH3), and 0.04 (s, 3H, OSiCH3).

**13C NMR (CDCl3, 125 MHz):** δ 143.0, 136.82, 136.67, 136.59, 127.9, 127.5, 125.39, 125.33, 124.8, 124.4, 82.0, 50.0, 44.6, 43.8, 39.0, 37.4, 31.2, 29.94, 29.88, 27.6, 26.4, 26.1, 25.26, 25.19, 23.5, 18.3, 16.3, 11.6, 8.5, 1.78, 1.70, –4.2, and –4.6.

**IR (neat):** 2953 (m), 2856 (m), 2101 (m), 1497 (w), 1460 (m), 1249 (m), 1092 (w), 1006 (m), 833 (s), 811 (s) and 721 (s) cm⁻¹.

**TLC:** Rf = 0.7 in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calced for (M+H)+ (C30H53OSi2): 485.3629. Found: 485.3640.

**{1-[(R)-2,8-Dimethyl-2-[(4R,8R)-4,8,12-trimethyltridecyl]chroman-6-yl]ethyl}diethylsilane (2af)**

**Yield:** 0.1 mmol scale, 31 mg, 62%. 1:1 dr

**1H NMR (CDCl3, 500 MHz):** δ 6.67 (d, J = 2.4 Hz, 1H, Ar-H), 6.59 (d, J = 2.4 Hz, 1H, Ar-H), 3.59 (dddd, J = 3.1, 3.1, 3.1, 3.1 Hz, 1H, Si-H), 2.76-2.64 (m, 2H, Ar-CH2CH2), 2.17 [qd, J = 7.6, 3.1 Hz, 1H, C(Si)HCH3], 2.12 (s, 3H, Ar-CH3), 1.78-1.71 (m, 2H Ar-CH2CH2), 1.56 [s, 3H, C(CH3)], 1.35-1.33 [d, J = 7.6 Hz, 3H, C(Si)HCH3], 1.24-0.91 [m, 22H, alkyl-H, and Si(CH2CH3)2], 0.88-0.84 (m, 17H, alkyl-H), 0.62-0.55 (m, 2H, SiCH2CH3), and 0.52-0.48 (m, 2H, SiCH2CH3).
$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 150.1, 149.5, 135.9, 127.37, 127.29, 125.88, 125.78, 125.23, 125.15, 120.3, 77.5, 77.2, 77.0, 75.8, 40.55, 40.41, 39.6, 37.68, 37.66, 37.51, 33.03, 32.93, 31.64, 31.57, 28.2, 25.0, 24.67, 24.63, 24.51, 24.39, 22.94, 22.85, 22.66, 22.64, 21.2, 19.98, 19.88, 16.6, 16.4, 8.49, 8.47, 1.85, and 1.82.

**IR (neat):** 2925 (m), 2867 (m), 2102 (m), 1472 (m), 1420 (s), 1206 (s), 1142 (s), 980 (m), 874 (m) and 610 (m) cm$^{-1}$.

**TLC:** $R_f = 0.7$ in hexanes.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{33}$H$_{61}$OSi)$^+$: 501.4486. Found: 501.4492.

$(E)$-(1-{4-[(3,7-Dimethylocta-2,6-dien-1-yl)oxy]phenyl}ethyl)diethylsilane (2ag)

![Chemical Structure](image)

**Yield:** 0.1 mmol scale, 21 mg, 60%.

$^1$H NMR (CDCl$_3$,500 MHz): $\delta$ 7.00 (d, $J = 8.7$ Hz, 2H, Ar-H), 6.82 (d, $J = 8.7$ Hz, 2H, Ar-H), 5.49 (ddq, $J = 6.6, 6.6, 1.3$ Hz, 1H, OCH$_2$CH=C), 5.10 (ddqq, $J = 7.2, 7.2, 1.3, 1.3$ Hz, 1H, CH$_2$CH$_2$CH=C), 4.50 (d, $J = 6.6$ Hz, 2H OCH$_2$CH=C), 3.62 (dddd, $J = 3.1, 3.1, 3.1, 3.1$ Hz, 1H, Si-H), 2.28 [qd, $J = 7.6, 3.1$ Hz, 1H C(Si)HCH$_3$], 2.14-2.06 (m, 4H, CH$_2$CH$_2$CH=C), 1.72 [s, 3H C=C(CH$_3$)], 1.68 [s, 3H C=C(CH$_3$)], 1.61 [s, 3H, C=C(CH$_3$)], 1.37 [d, $J = 7.6$ Hz, 3H, C(Si)HCH$_3$], 0.95 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), 0.88 (dd, $J = 7.9, 7.9$ Hz, 3H, SiCH$_2$CH$_3$), and 0.61-0.42 [m, 4H, Si(CH$_2$CH$_3$)$_2$].

$^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ 156.4, 141.1, 138.0, 132.0, 128.0, 124.1, 120.0, 114.8, 65.1, 39.8, 26.5, 25.9, 24.8, 17.9, 16.9, 16.6, 8.45, 8.43, 1.79, and 1.76.

**IR (neat):** 2952 (m), 2872 (m), 2095 (m), 1608 (w), 1506 (s), 1455 (m), 1377 (m), 1233 (s), 1113 (m), 1006 (s) and 807 (s) cm$^{-1}$.

**TLC:** $R_f = 0.6$ in 80:1 hexanes:EtOAc.

**HRMS (APCI/TOF):** Calcd for (M+H)$^+$ (C$_{33}$H$_{61}$OSi)$^+$: 345.2608. Found: 345.2615.

(4S)-tert-Butyl 4-{4-[1-(diethylsilyl)ethyl]benzyl}-2,2-dimethyloxazolidine-3-carboxylate (2ah)

![Chemical Structure](image)

**Yield:** 0.1 mmol scale, 31 mg, 78%. 1:2.1 $dr$

$^1$H NMR (CDCl$_3$,500 MHz): $\delta$ 7.17-6.97 (m, 4H, Ar-H), 4.09-4.07 [m, 0.55 H, CHN(Boc)], 3.98-3.89 (m, 0.55 H, CHN(Boc)), 3.77 (app s, 2H, CH$_2$CHN), 3.61 (br s, 1H, Si-H), 3.14 (d, $J = 13.4$ Hz, 0.45 H, CHCH$_2$O), 3.05 (d, $J = 13.4$ Hz, 0.55 H, CHCH$_2$O), 2.68-2.55 (m, 1H, CHCH$_2$H$_2$O), 1.63-1.42 [br s, 1H, C(Si)HCH$_3$], 1.63-1.45 [m, 15H,
OC(CH₃)₃ and OC(CH₃)₂N], 1.38 [d, J = 7.5 Hz, 3H, C(Si)HCH₃], 1.00-0.80 [m, 6H, Si(CH₂CH₃)₂], and 0.63-0.43 [m, 4H Si(CH₂CH₃)₂].

¹³C NMR (CDCl₃, 125 MHz): δ 151.98, 151.97, 144.40, 144.29, 134.7, 133.8, 129.42, 129.33, 127.41, 127.24, 94.2, 80.3, 79.9, 77.5, 77.2, 77.0, 66.34, 66.21, 59.48, 59.42, 39.4, 38.31, 38.27, 31.2, 28.82, 28.72, 28.57, 27.7, 27.1, 25.59, 25.56, 24.8, 23.5, 16.2, 8.41, 8.37, 1.77, and 1.73.

IR (neat): 2953 (m), 2873 (m), 2098 (m), 1697 (s), 1506 (w), 1385 (s), 1074 (m), 802 (s), and 540 (m) cm⁻¹.

TLC: Rₚ = 0.5 in 20:1 hexanes:EtOAc.

HRMS (APCI/TOF): Calcd for (M+H)⁺ (C₂₃H₄₀NO₃Si)⁺: 406.2772. Found: 406.2760.

B) Polymerization Procedure and Characterization:

(a) Condition A: (Electron-poor arenes)

Styrene 1e (0.2 mmol) and diethylsilane (3 equiv) were dissolved in THF (1 M). KO'Bu (20 mol %) was added to the mixture. Once the polymerization was completed, the polymer was precipitated by addition of methanol to the reaction mixture. After filtration, white solids were washed with cold methanol to provide polystyrenes.

Mn  Mw  Mz  PDI

3e  27600  73000  190000  2.64

Supplementary Figure 27. GPC chromatogram of polystyrene 3d.
Supplementary Figure 28. IR Spectrum of polystyrene 3e.

(b) *Condition B: (Electron-neutral and -rich arenes)*

Styrene 1a (0.2 mmol), 18-crown-6 (10 mol %), and diethylsilane (3 equiv) were dissolved in THF (1 M). KO'Bu (20 mol %) was added to the mixture which immediately turned dark brown. Once the polymerization was completed, the polymer was precipitated by addition of methanol to the reaction mixture. After filtration, white solids were washed with cold methanol to obtain polystyrene 3a.

![Supplementary Figure 28. IR Spectrum of polystyrene 3e.](image)

| Wavenumber cm⁻¹ | Transmittance [%] |
|-----------------|-------------------|
| 2985.13         | 100               |
| 2933.77         | 90                |
| 2986.64         | 80                |
| 2941.05         | 70                |
| 1608.95         | 60                |
| 1608.95         | 50                |
| 1608.95         | 40                |
| 1608.95         | 30                |
| 1608.95         | 20                |
| 1608.95         | 10                |
| 1608.95         | 0                 |

**Supplementary Figure 29. GPC chromatogram of polystyrene 3a.**

\[
\begin{array}{cccc}
3a & Mn & Mw & Mz & PDI \\
10400 & 15200 & 21000 & 1.46 \\
\end{array}
\]
IV) NMR Spectra

![NMR Spectra Image]

2a-Me
$2a^{-Pr}$
2d-Et
2d-Me

Chemical structure:

![Chemical structure image with ppm scale]

ppm scale from 0 to 200
2k
2ad
2ad
SiEt₂H

2ag
$2a$-Ph-d$_2$
$\text{Me} \quad \text{SiEt}_2\text{H}$

$7\text{c-Et}$
7c-Me
10
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