**Supporting Information**

**Experimental details:**

1.) **Ligand Synthesis**

**General**

All manipulations of air- and/or moisture sensitive materials were performed under argon using a dual vacuum/argon line and standard Schlenk techniques. THF was purified and degassed using the manual solvent purification system Pure Solve (Innovative Technology). All other solvents (diethyl ether (Roth), acetonitrile (Roth), cyclohexane (Roth)) and chemicals (indene (97%, Aldrich), n-BuLi (1.6 M in hexanes, Aldrich), 1,2-epoxy-9-decene (96%, Aldrich), triphenylphosphine (99%, Aldrich), imidazole (99%, Aldrich), iodine (Fluka)) were used without further purification.

$^1$H and $^{13}$C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer at 499.82 MHz and 125.69 MHz, respectively. Chemical shifts are listed in delta ($\delta$/ppm) employing the residual protio solvent resonance as internal standard ($\delta = 7.24$ ppm in $^1$H spectra and 77.0 ppm in $^{13}$C spectra for CHCl$_3$).
Preparation of 1-(1H-inden-3-yl)dec-9-en-2-ol (III)

In a 2-neck round bottom flask purged with argon 1 mL (0.996 g, 97%, 8.34 mmol) of indene (I) was dissolved in 10 mL anh. THF. The flask was cooled to -78ºC (liquid nitrogen/methanol bath). Once cool, 5.37 mL (= 8.59 mmol) of n-BuLi (1.6 M in hexanes) was carefully added with a syringe, turning the solution dark brown. The reaction was warmed to room temperature (r.t.), and then cooled back to -78ºC. 2.04 mL (= 1.72 g, 11.15 mmol, 1.33 mol equ.) of 1,2-epoxy-9-decene (II) were added via syringe. The reaction mixture was allowed to warm to r.t. and stirred overnight. Next morning the solution was dark brown. For workup, the reaction was quenched with aqueous sat. NH₄Cl yielding a clear, orange aqueous phase, and a dark red organic phase. The layers were separated, and the aqueous phase was extracted with diethyl ether. The combined organic phases were collected, dried over Na₂SO₄, filtered, and reduced in vacuo. A column separation was performed using 10:1 cyclohexane/diethyl ether (Cy/Et₂O), which yielded the pure target compound as a yellow oil.

Yield: = 51.6%

R_f-value (III) 0.56 (Cy/Et₂O 1:1)
$^1$H: δ (CDCl$_3$) 7.40 (1H, d, J=7.32, H4), 7.30 (1H, d, J=7.32 Hz, H7), 7.23 (1H, t, J=7.32 Hz, H6), 7.15 (1H, t, J=7.32, H5), 6.73 (1H, bs, H2), 5.72 (1H, m, H16), 4.94-4.91 (1H, d, J=17.1 Hz, H17), 4.86 (1H, d, J=10.25 Hz, H17'), 3.86 (1H, bs, H9), 3.30 (2H, bs, H1), 2.74 (1H, dd, J=14.5, 2 Hz, H8a), 2.59-2.54 (1H, m, H8b), 1.99-1.95 (2H, q, J=6.84 Hz, H15) 1.64 (1H, s) 1.5-1.42 (3H, m), 1.35-1.26 (7H, m) (H10-H14)

$^{13}$C: δ (CDCl$_3$) 145.2 (3a) 144.7 (7a), 141.4 (3), 139.4 (16) 130.9 (2), 126.6 (5), 125.1 (6), 124.1 (7), 119.4 (4), 114.5 (17), 70.2 (9), 38.2 (8), 37.4 (1), 36.5 (10), 34.0 (15), 29.8 (14), 29.4 (13), 29.1 (12), 26.0 (11)

**Preparation of 3-[2-((1H-inden-3-yl)dec-9-enyl]-1H-indene (1)**

In a round bottom flask, 0.965 g (3.57 mmol) of III was dissolved in 20 mL diethyl ether abs. and 8 mL acetonitrile. At room temperature, 1.030 g (3.93 mmol, 1.1 mol equ.) of triphenylphosphine was added, as well as 0.486 g (7.14 mmol, 2 mol equ.) of imidazole.

After complete solvation, 0.906 g (3.57 mmol) of iodine was slowly added to the reaction. Initial addition of the iodine turned the solution orange, and later to bright yellow with a white precipitate. The reaction was allowed to stir at r.t. for approximately
1 hour. When the TLC showed that no starting material was left (Cy/Et₂O 10:1), approximately 100 mL of diethyl ether were added and the solution was filtered over Celite to remove the white solid. The organic layer was washed 2 times with sat. NaHCO₃ and once with brine, then dried over Na₂SO₄, filtered, and collected under vacuum to yield a yellow oil. Column chromatography was performed using pure cyclohexane. The appropriate fractions were reduced in vacuo to approximately 10 mL were left, and then were added immediately via cannula to the lithiated indene. The iodide is very unstable, therefore it must be used immediately, and neither the yield of this reaction was determined nor the NMR of IV was collected.

The lithiated indene was prepared by addition of 2.23 mL n-BuLi (1.6 M in hexanes, 3.57 mmol) to 0.414 mL (= 0.414 g, 3.57 mmol) indene I in 10 mL THF abs. at -78°C. Addition of IV turned the solution of the lithiated indene to deep red. The reaction mixture was allowed to warm very slowly to r.t., and was stirred for 18 hrs. The TLC (Cy) indicated presence of product, with a small amount of starting material. For workup, THF was added, followed by aq. sat. NH₄Cl. The layers were separated, and the aqueous layer was extracted twice with diethyl ether. The combined organic layers were dried over Na₂SO₄, filtered, and collected in vacuo. Column chromatography was performed using cyclohexane as the eluent to yield I as a yellow oil.

**Yield:** 37.8%

**Rₜ-value** (I) 0.44 (Cy)
$^1$H: δ (CDCl₃) 7.40 (1H, d, J=7.32 Hz) 7.36 (2H, d, J=7.81 Hz) 7.29 (1H, d, J=7.32 Hz) 7.21 (2H, t, J=7.32 Hz), 7.13 (2H, m) (aromatic Hs); 6.14 (1H, s, H2), 6.07 (1H, s, H2’), 5.70 (1H, m, H16), 4.90 (1H, d, J=17.1 Hz, H17a), 4.84 (1H, d, J=10.25 Hz, H17b), 3.24 (1H, s, H1), 3.20 (1H, s, H1’), 3.10 (1H, t, J=6.84, H8) 2.87 (1H, m, H9a), 2.80 (1H, m, H9b), 1.91 (2H, q, J=7.32 Hz, H15), 1.66 (2H, m, H14) 1.24-1.16 (8H, m, H10-H13)

$^{13}$C: δ (CDCl₃) 148.2 (3), 146.0 (3a), 145.5 (7a), 145.1(3a’), 144.7 (7a’), 143.1 (3’), 139.5 (16), 129.4 (2), 127.9 (2’), 126.2, 126.1, 124.7, 124.1, 123.9 (5-7, 5'-7’), 119.6, 119.2 (4,4’), 114.3 (17), 38.0, 37.9 (8, 9), 37.1, 37.0 (1, 1’) 34.0, 33.0, 29.9, 29.3, 29.1, 27.5 (10-15)
2.) Metalation

a.) via lithium salt

In a Schlenk tube 0.31 g (0.84 mmol) of 3-[2-(1H-inden-3-yl)dec-9-enyl]-1H-indene (1) were dissolved in 20 mL anh. Et₂O and reduced under vacuum for 10 minutes. After cooling to 0°C, 1 mL (1.6 mmol, 1.9 mol equ.) of n-BuLi (1.6 M in hexanes) was added. The mixture was stirred for 1 hr at 0°C and then over night at r.t. After 18 hrs a sample of the lithium salt was taken for NMR (Figure 1). At r.t. 98 mg (0.42 mmol) of ZrCl₄ were added to the yellow lithium salt of the ligand, leading to color change to a deeper shade of yellow. After stirring at r.t. overnight, the solvent was removed, the residue dissolved in 20 mL CH₂Cl₂ and filtered over Celite. The filtrate was reduced in vacuo giving 0.37 g (7.0 mmol) of a pale orange solid (NMR in C₆D₆ see Figure 2).

Yield: 0.37 g (7.0 mmol) 83.3%

C/H Analysis: Calculated: C: 63.61H: 5.72 Found: C: 62.32/62.28, H: 5.86/5.82
Figure 1 $^1$H NMR spectrum of the dilithium salt of 1 in C$_6$D$_6$
Figure 2 $^1$H NMR spectrum of 2 in C$_6$D$_6$ (Synthesis with BuLi and ZrCl$_4$)
b.) via potassium salt

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\begin{align*}
\text{(1) } (n=3) & \quad \text{1.) } KH \\
& \quad \text{2.) } \text{ZrCl}_4 \cdot 2\text{THF} \\
\text{rac-(2)} & \quad + \\
\text{meso-(2)} & \quad \text{(only one isomer shown)}
\end{align*}
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**General Remarks:** All manipulations of air- and/or moisture-sensitive materials were carried out under inert atmosphere using a dual vacuum/argon line and standard Schlenk techniques. All solvents for synthesis and NMR characterization were thoroughly dehydrated and deoxygenated under nitrogen by refluxing over a suitable drying agent (pentane [Lancaster], petroleum ether [Fluka], diethyl ether [Fluka], toluene [Fluka] and THF [Fluka] over K; C₆D₅N [Cambridge Isotopes] over KOH; CD₂Cl₂ [Cambridge Isotopes], CH₂Cl₂ [Fluka], and CDCl₃ [Fluka] over CaH₂) followed by distillation and storage under argon in Young's ampoules. Solvents and solutions were transferred, using a positive pressure of argon, through stainless-steel cannulae (diameter 0.5-2.0 mm) and mixtures were filtered in a similar way using modified cannulae, which could be fitted with glass-fiber filter disks (Whatman GFC).

Zirconium (IV) chloride tetrahydrofuran complex was prepared from ZrCl₄ (Strem) according to literature procedure. (Manzer, L. E. *Inorg. Synth.* 1982, 21, 135-137)

¹H (200.13 MHz) and ¹³C (50.32 MHz) NMR spectra were recorded at room temperature with a Bruker AC200 spectrometer. Spectra were referenced internally using the residual protio solvent resonance relative to tetramethylsilane (δ = 0).
Synthesis of the dipotassium salt 1a:

A solution of 0.288 g of the ligand 1 (0.78 mmol) in THF (20 mL) was added dropwise to a stirred and cooled (0°C) suspension of 0.123 g of KH (3 mmol; Aldrich, 35% in ligroin, weighted 0.35 g in a Schlenk, degassed, washed three times with anhydrous pentane, and dried under vacuum) in THF (20 mL). The suspension slowly turned to a dark purple color. The cooling bath was removed and the suspension was allowed to stir overnight at room temperature. The solution was separated from KH in excess by cannula filtration and the solvent removed under high vacuum to leave a dark purple solid (0.330 g, 95 % yield). About 20 mg were used to record an NMR spectrum in pyridine d5 (Figure 3).

Figure 3 ¹H NMR spectrum of the dipotassium salt 1a in pyridine d5
Metalation of 1a – Synthesis of 2:

![Diagram showing the reaction of 1a with ZrCl4·2THF to form rac- and meso-(2).](image)

A solution of 0.311 g of 1a (0.70 mmol) in diethyl ether (20 mL) and a solution of 0.26 g of ZrCl4·2THF (0.70 mmol) in diethyl ether (20 mL) were added simultaneously to 10 mL of diethyl ether in a third Schlenk. The resulting suspension was brick red. The suspension was stirred for 18 hrs, filtered, and the solvent was removed under vacuum, avoiding heating as much as possible. A sticky solid was obtained. It seemed to be composed of two compounds: a yellow solid and a red sticky glue. The solids (0.356 g = 0.673 mmol = 96.2 % yield) were dissolved in dichloromethane, and then the complex was precipitated with petroleum ether. A light-brown solid (complex 2a, about 240 mg) was obtained, and the concentrated yellow solution gave another sticky solid (complex 2b, about 120 mg).

NMR spectra (recorded in CDCl3) of these two fractions were taken separately. Due to splitted signals in the spectra, we believe that the samples contain different amounts of the rac/meso isomers. The expanded 1H NMR spectrum (Figure 5) indicates that complex 2a contains a 50:50 ratio of rac/meso plus small amounts of starting material. Complex 2b (Figure 7) includes a larger amount of the rac isomer (the signals in Figure 7 which
are marked with + indicate a higher amount of rac in the spectra than in the spectra of complex 2a)

$^1$H: δ (CDCl$_3$) 8.00-6.94 (9H, m, Indenyl and Cp), 6.94-5.96 (3H, m, Cp), 5.94-5.61 (1H, m, H16), 5.11-4.79 (2H, m, H17), 4.51-2.73 (3H, m, H8, H9), 2.18-1.61 (4H, m, H15, H14), 1.54-0.98 (8H, m, H10-H13)

Figure 4 $^1$H NMR spectrum of complex 2a in CDCl$_3$
Figure 5 Expanded $^1$H NMR spectrum of complex 2a in CDCl$_3$.

Figure 6 $^1$H NMR spectrum of complex 2b in CDCl$_3$. 
Figure 7 Expanded $^1$H NMR spectrum of complex 2b in CDCl$_3$. The signals marked with + indicate a higher amount of $rac$ (~ 6.3 ppm) and a higher amount of starting ligand (6.0 and 6.1 ppm) in this spectrum than in the spectrum of complex 2a.

Figure 8 $^{13}$C NMR spectrum of complex 2a in CDCl$_3$. 
Figure 9 $^{13}$C NMR spectrum of complex 2b in CDCl$_3$. 
Figure 10 FTIR spectra of the pure compounds (green: ligand 1, blue: complex 2a, red: complex 2b). The FTIR spectra were collected with an ATR unit (Pike MIRacle with ZnSe crystal) with a Bruker Tensor 37, resolution: 4 cm⁻¹, 16 scans, 4000-600cm⁻¹.
3.) Immobilization

Sample preparation

Low n-doped Si(111) substrates (n-doped, \( \rho \sim 10 \ \Omega \text{cm} \)) were cleaned using the standard cleaning procedure (RCA) to remove the organic and metallic contaminants: the silicon samples were first immersed in a solution of deionized water (DIW, 18.2 M\( \Omega \text{cm} \)): \( \text{H}_2\text{O}_2: \text{NH}_4\text{OH} \) (4:1:1) and then in a solution of DIW: \( \text{H}_2\text{O}_2: \text{HCl} \) (4:1:1). In both cases, the reaction was performed at 80\( ^\circ \text{C} \) for 10 min, and the Si samples were thoroughly rinsed with DIW after each step. The hydrogen termination is obtained by a rapid etch (30 sec) of the \( \text{SiO}_2 \) layer in HF (10-20\%) followed by a 2:30 min dip in concentrated (40\% vol) \( \text{NH}_4\text{F(aq)} \). After this treatment, atomically flat hydrogen-terminated silicon (111) (H/Si) surfaces was obtained.

The H/Si(111) sample were then introduced in a \( \text{N}_2 \)-purged glovebox. Prior to the reaction, the glass tube in which the reaction took place was filled with anhydrous chlorobenzene and was heated to 120\( ^\circ \text{C} \) for a few hours. Then the tube was filled with fresh anhydrous chlorobenzene. For thermal hydrosilylation, the solvent was heated to 120\( ^\circ \text{C} \) and when the temperature was reached, few mg of ligand and the H/Si sample were introduced in the tube and left for reaction for 2hr. The temperature was monitored by a thermocouple placed between the hot plate and the tube. For UV irradiation, the sample was immersed in a beaker in a solution of anhydrous chlorobenzene (~ 20 mL) with ligand 1 or the complexes 2a and 2b (few mg) at room temperature, and was irradiated with UV-light (254 nm) for 2 hours on each side in a \( \text{N}_2 \)-purged environment (the sample is turned over for irradiation of the other side at half-time, the irradiation was carried out directly on the chlorobenzene solution, i.e., not through the glass of the
beaker). When the reaction was complete in either case, the sample was rinsed thoroughly in anhydrous chlorobenzene and was immersed into a sealed vial of anhydrous chlorobenzene, before being removed from the N$_2$-purged glovebox. The functionalized silicon sample was finally sonicated for 5 minutes in anhydrous chlorobenzene.

**Infrared spectroscopy**

After the chemical step, the silicon samples were placed into an N$_2$-purged compartment of an infrared interferometer (Nexus 670, Nicolet 6700) within two minutes. All spectra were recorded between 450 and 4000 cm$^{-1}$ (4 cm$^{-1}$ spectral resolution) mainly in transmission with an incident IR beam angle of 74° off normal (i.e., Brewster angle for silicon). The spectrometer is equipped either with a room temperature thermoelectric (DTGS) detector or a liquid N$_2$ cooled-down Mercury Cadmium Telluride (MCT-B) detector. The silicon oxide surface and the H-terminated silicon surfaces were used as a reference to determine the absorbance of the hydrosilylated surfaces. In some cases we used an ATR accessory (Single Reflection Smart performer, Thermo Electron). In this case the functionalized Si sample was put on a germanium ATR plate (2 mm thick) and a uniform pressure was applied on the sample: the depth of penetration of the IR beam into the powder sample was about 1 μm. The IR signal was recorded through a N$_2$ cooled-down detector (MCT/B) over the range 400-4000 cm$^{-1}$ with 4 cm$^{-1}$ resolution. For each spectrum, 1000 scans were collected.