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# The first example of nickel-catalyzed silyl-Heck reactions: direct activation of silyl triflates without iodide additives

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## ABSTRACT

For the first time, nickel-catalyzed silyl-Heck reactions are reported. Using simple phosphine-supported nickel catalysts, direct activation of silyl triflates has been achieved. These results contrast earlier palladium-catalyzed systems, which require iodide additives to activate silyl-triflates. These nickel-based catalysts exhibit good functional group tolerance in the preparation of vinyl silanes, and unlike earlier systems, allows for the incorporation of trialkylsilanes larger than Me<sub>3</sub>Si.

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# 1. Introduction

Unsaturated organosilanes are potent nucleophiles and highly useful intermediates in organic synthesis.<sup>1</sup> Recently, we have established the silyl-Heck reaction as a novel route to access both allyl and vinyl silanes.<sup>2,3</sup> This general method allows for the direct silylation of terminal alkenes using silyl halides and transition metal catalysts, in a reaction that we believe is analogous to classical Heck arylation (Fig. 1).<sup>4</sup>

Our previous work has focused exclusively on the use of palladium-based catalysts in this transformation.<sup>2a,b</sup> In these processes, we have found that the use of iodosilanes is required. These can either be used directly or prepared in situ from silyl chlorides, bromides, or triflates, and simple iodide salts.<sup>5</sup> Significantly, even



L<sub>n</sub>MHX

the most reactive silyl triflate, trimethylsilyl triflate, fails to undergo reaction under palladium-catalyzed conditions without added iodide. Silicon–oxygen bonds are known to be very strong, we attribute this to the reluctance of palladium to insert into the Si–OTf bond.<sup>6</sup>

An active interest in our group is developing a catalyst capable of engaging silyl halides other than iodosilanes in silyl-Heck type reactions. This interest is fueled by the recognition that iodosilanes are potent Lewis acids, and thus have attenuated functional group compatibility. In addition, access to silyl iodides is limited, with only Me<sub>3</sub>Sil being commercially available. In contrast, a much wider variety of silyl chlorides and triflates can be purchased or readily prepared, making methods that can directly utilize these reagents attractive to develop.<sup>7</sup>

In cross-coupling chemistry of carbon electrophiles, nickel catalysts have proven adept at the activation of strong carbonheteroatom bonds (such as aryl ethers and carboxylates), particularly in comparison to palladium catalysts.<sup>8</sup> Despite the fact that silyl bromides and iodides have been shown to oxidatively add to a variety of late transition metal complexes, to our knowledge such reactions involving nickel compounds have not been described.<sup>3a-e,9</sup> Based upon the precedent with strong C–X bonds, we decided to investigate silyl-Heck type reactions with nickelbased catalysts.<sup>10</sup>

Herein, we report the first examples of nickel-catalyzed silyl-Heck type reactions. We show that unlike in palladium-catalyzed reactions, these nickel-catalyzed reactions are able to utilize silyl triflate electrophiles without the need for iodide additives. Using this system, a variety of styrene derivatives and related terminal alkenes lacking allylic hydrogen atoms can be successfully transformed into *E*-vinyl silanes. As significantly, for the first time, this nickel-based catalyst system allows for the direct preparation of





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vinyl trialkylsilanes from trialkylsilyl electrophiles larger than trimethylsilane. We believe that this new catalytic system not only provides promise for developing general base-metal catalysts for this class of reaction, but also greatly expands the types of unsaturated organosilanes that can be accessed using the silyl-Heck reaction.

# 2. Results and discussion

To begin our investigation of nickel-catalyzed silyl-Heck reactions, we studied the reaction of 4-tert-butyl styrene with trimethylsilyl triflate (Me<sub>3</sub>SiOTf) without iodide additives (Table 1). Consistent with our previous observations, palladium-based catalysts provided only trace yield of desired vinyl silane **1** (entry 1). In our hands, this outcome is not improved by variation of either palladium pre-catalyst, nature of phosphine ligand, metal:ligand ratio, solvent, or temperature (not shown). In contrast, a modest screen of catalysts derived from Ni(COD)<sub>2</sub> and phosphine ligands revealed a significantly different outcome. Whereas catalysts employing triaryl phosphines (entries 2 and 3) or mixed arylalkyl phosphines (entries 4 and 5) were ineffective, moderately bulky trialkyl phosphines provided highly active catalysts (entries 6–10). Interestingly, however, there seems to be a steric limit with regard to ligand size; the very bulky <sup>t</sup>Bu<sub>3</sub>P was ineffective (entry 11). Further optimization revealed that a highly effective catalyst was obtained using <sup>t</sup>BuPCy<sub>2</sub> and Ni(COD)<sub>2</sub> when a 1.5:1 ligand:metal ratio was employed (entry 13).

#### Table 1

Identification of nickel-based catalyst			
	10 mol % pre-ca ligand 3 equiv Me <sub>3</sub> SiO	talyst	SiMe <sub>3</sub>
<sup>t</sup> Bu	$Et_3N$ , dioxane, 75	°C, 24 h /Bu	1
Entry	Pre-catalyst	Ligand (mol %)	Yield 1
1	(COD)Pd(CH <sub>2</sub> TMS) <sub>2</sub>	$^{t}$ BuPPh <sub>2</sub> (30)	0%
2	Ni(COD) <sub>2</sub>	PPh <sub>3</sub> (30)	0%
3	Ni(COD) <sub>2</sub>	P(o-tol) <sub>3</sub> (30)	0%
4	Ni(COD) <sub>2</sub>	$^{t}BuPPh_{2}(30)$	12%
5	Ni(COD) <sub>2</sub>	$Cy_2PPh$ (30)	11%
6	Ni(COD) <sub>2</sub>	${}^{n}\text{Bu}_{3}\text{P}(30)$	69%
7	Ni(COD) <sub>2</sub>	PCy <sub>3</sub> (30)	57%
8	Ni(COD) <sub>2</sub>	PCyp <sub>3</sub> (30)	65%
9	Ni(COD) <sub>2</sub>	$^{t}BuPCy_{2}(30)$	71%
10	Ni(COD) <sub>2</sub>	<sup>t</sup> Bu <sub>2</sub> PCy (30)	55%
11	Ni(COD) <sub>2</sub>	<sup>t</sup> Bu <sub>3</sub> P (30)	7%
12	Ni(COD) <sub>2</sub>	$^{t}BuPCy_{2}(20)$	85%
13	Ni(COD) <sub>2</sub>	$^{t}$ BuPCy <sub>2</sub> (15)	90%

Using these optimized conditions, we studied the scope of the nickel-catalyzed silyl-Heck reaction (Table 2). A variety of styrenyl alkenes participate in the reaction. On preparative scale (1 mmol), vinyl silane 1 was isolated in 82% yield. Likewise, unsubstituted styrene could be silvlated in 89% isolated vield under these conditions (2). A variety of ethereal substrates were also tolerated, including those with both electron-donating para-methoxy (3) and electron-withdrawing meta-methoxy groups (4) in good yield (71% and 76%, respectively). Silyl ethers (5) and dioxoles (6) were also well tolerated. Aromatic fluorides proved amiable to the reaction conditions; fluorinated vinyl styrene 7 was isolated in 66% yield. Unfortunately, larger aromatic halogens were not compatible with the silvlation conditions. For example, the use of 4-chlorostyrene as substrate led to a complex mixture of products without detectable formation of desired vinyl styrene 8. Also problematic were highly electron-deficient or electron-rich styrenes. For example, the

#### Table 2

Substrate scope with respect to styrene



<sup>a</sup> Isolated yields. All reactions run at 0.5 M concentration. <sup>b</sup> 30 mol % Cyp<sub>3</sub>P used in place of <sup>f</sup>BuPCy<sub>2</sub>.

formation of ester 9 was not observed, and dimethylamino product 10 was formed in low yield. Strained rings, such as benzocyclobutane (11), and steric bulk on the aromatic group ortho to the alkene (12), however, were well tolerated. Some heterocyclic substrates could also be silylated using this protocol. For example, silylation of *N*-vinyl carbazole led to vinyl silane **13** in high yield.<sup>11</sup> However, in other cases, such as in the formation of benzofuran 14, yields proved to be suboptimal. Finally, more complex vinyl silanes, such as pinacol borane 15 and estradiol-derived 16, could also be accessed using the nickel-catalyzed protocol. In the case of 15, tricyclopentylphosphine (Cyp<sub>3</sub>P) proved to be a slightly more effective ligand than <sup>t</sup>BuPCy<sub>2</sub>, demonstrating that some ligand optimization might prove necessary in order to maximize vinyl silane yield.<sup>12</sup> Overall, while these yields are slightly lower and scope is somewhat more limited than our previously reported palladiumcatalyzed silvl-Heck protocol involving Me<sub>3</sub>Sil, we believe that this reaction enjoys sufficient substrate scope to make it a synthetically viable alternative, particularly given the advantages of using a nonprecious metal, nickel-based catalyst and a silyl triflate as the silylating reagent.

As mentioned above, silyl triflates are much more abundant than silyl iodides. We therefore wanted to investigate the scope of the transformation with respect to the silyl triflate. We deemed this to be a significant goal as vinyl silanes bearing groups other than trimethylsilyl exhibit improved reactivity in a variety of transformations. In particular, vinyl benzyl silanes are highly effective in Hiyama cross-coupling,<sup>13</sup> and those bearing aromatic functionality on silicon are faster in both acylation and oxidation reactions.<sup>14</sup> The expansion of the silyl-Heck reaction to include these silanes would allow direct preparation of these products from alkenes.

Initial investigations using  ${}^{t}BuPCy_{2}$  and the above-optimized conditions revealed that silyl triflates larger than trimethylsilyl triflate do participate in the reaction. However, we rapidly identified the use of  $Cy_{3}P$  with a ligand:metal ratio of 3:1 as an alternative catalyst that provided generally higher yields with larger silanes.

Scope studies using 4-*tert*-butyl styrene and this latter catalyst system are outlined in Table 3. Dimethylsilyl triflates containing one primary alkyl group, such as <sup>n</sup>BuMe<sub>2</sub>SiOTf or BnMe<sub>2</sub>SiOTf participate well under these conditions (**17** and **18**), providing similar yields to Me<sub>3</sub>SiOTf. One secondary substituent, such as in <sup>i</sup>PrMe<sub>2</sub>SiOTf, can also be tolerated without loss of yield (**19**). However, a tertiary silyl substituent proved to be beyond the steric limit under these conditions; using Cy<sub>3</sub>P as ligand, none of desired vinyl silane **20** was observed using <sup>i</sup>BuMe<sub>2</sub>SiOTf (TBSOTf). However, switching to the smaller ligand <sup>n</sup>Bu<sub>3</sub>P and using elevated temperatures did allow for the formation of **20**. Despite the modest yield, this transformation is remarkable as it presumably involves oxidative addition at a silicon center that bears a fully substitued adjacent center (akin to a neopentylic carbon center). Silyl triflates bearing aromatic groups are also good substrates for the nickel-

#### Table 3



<sup>a</sup> Isolated yields. Unless otherwise noted, all reactions run at 0.5 M concentration. <sup>b</sup> 40% <sup>n</sup>Bu<sub>3</sub>P in place of PCy<sub>3</sub>,105 °C, 1.0 M concentration. catalyzed silyl-Heck reaction. Both phenyldimethyl and diphenylmethyl vinyl silanes can be prepared in good yield in this way (**21** and **22**). Finally, triethylsilyl triflate also participates in the reaction; **23** was prepared in 65% yield. However, triisopropylsilyl triflate appears to be too large (even under forcing conditions). As the previously developed palladium-catalyzed reaction only tolerates Me<sub>3</sub>Sil (used directly or generated in situ), these results greatly expand the types of electrophilic trialkylsilanes that can participate in the silyl-Heck reaction.

In the case of reactions using larger silyl triflates (described in Table 3), the major byproduct is alkene **25** (Fig. 2). We hypothesize that this styrene dimer arises via a metal hydride-mediated Heck-type pathway.<sup>15</sup> Minor amounts of similar dimers are also observed as byproducts in reactions using Me<sub>3</sub>SiOTf (Table 1); however, formation of these dimers is less significant. These results suggest that the dimerization pathway becomes more competitive with increasing steric bulk of the silyl triflate, likely due to the difficulty of oxidative addition.



Fig. 2. Major byproduct from silyl-Heck reactions of larger silyl triflates.

# 3. Conclusions

For the first time, we have demonstrated a nickel-catalyzed silyl-Heck reaction, the first demonstration of a first-row transition metal catalyst in this type of reaction. We have shown that simple phosphine-supported nickel-based catalysts are not only capable of silylating styrene derivatives, but are also capable of promoting the reaction with silyl triflate reagents without the need for in situ generation of silyl iodides. Moreover, good substrate scope with respect to the alkene has been observed. More importantly, for the first time electrophilic trialkylsilanes bearing alkyl groups larger than methyl have been shown to participate in Heck-like reactions. These results provide promising leads for the further development of silyl-Heck reactions using inexpensive catalysts and silylating reagents.

# 4. Experimental section

#### 4.1. General experimental details

Dioxane, tetrahydrofuran, and dichloromethane were dried on alumina according to published procedures.<sup>16</sup> Triethylamine was distilled from CaH<sub>2</sub> and then sparged with nitrogen. 2-Dimethylaminoethanol was distilled under vacuum from anhydrous potassium carbonate and sparged with nitrogen. Trifluoromethanesulfonic acid (TfOH) was distilled under vacuum and stored under nitrogen in a Teflon-sealed vessel. Trimethylsilyl-, triethylsilyl- (Oakwood Chemical), tert-butyldimethylsilyl- (Combi-Blocks), and tri-iso-propylsilyl- (Gelest) trifluoromethanesulfonate were distilled under vacuum and degassed prior to use. All hot glassware was oven dried for a minimum of 4 h or flame-dried under vacuum prior to use. All other substrates and reagents were purchased in highest analytical purity from commercial suppliers. Liquid substrates were sparged with nitrogen before use, and all others were used as received. Column chromatography was performed with 5–20  $\mu m$  or 40–63  $\mu m$  silica gel (Silicycle) with the reported in parentheses. Analytical eluent thin-laver

chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with KMnO<sub>4</sub>.

## 4.2. Instrumentation

NMR spectra were obtained on a Bruker AV400 MHz FT-NMR spectrometer equipped with a Bruker CryoPlatform (400 MHz <sup>1</sup>H, 101 MHz <sup>13</sup>C, and 376 MHz <sup>19</sup>F) or on a Bruker AVIII 600 MHz FT-NMR spectrometer (600 MHz <sup>1</sup>H, 151 MHz <sup>13</sup>C), in the indicated deutero-solvent and were recorded at ambient temperatures. Chemical shifts are reported in parts per million. <sup>1</sup>H NMR were calibrated using the residual protio-solvent as a standard. <sup>13</sup>C NMR spectra are calibrated using the deutero-solvent as a standard and were recorded using the attached proton test.<sup>17</sup> <sup>19</sup>F spectra are referenced to an external FCCl<sub>3</sub> sample. IR spectra were recorded on a Nicolet Magna 560 FTIR spectrometer as thin films. GC–MS data was collected using an Agilent 6850 series GC and 5973 MS detector. High resolution MS was attained on a Waters GCT Premier spectrometer using electron impact ionization (EI).

#### 4.3. General procedures

4.3.1. General procedure A. Reactions of alkenes with trimethylsilyl trifluoromethanesulfonate: in a glovebox (N<sub>2</sub> atmosphere), dicyclohexyl-tert-butylphosphine (15 mol %) and Ni(COD)<sub>2</sub> (10 mol %) were added to a two dram vial equipped with a stirbar. Solid alkenes were also added at this time. Dioxane and triethylamine (5 equiv) were then added sequentially, followed by liquid alkene (1 equiv) if applicable. The vial was sealed with a Teflon-lined septum cap and removed from the glovebox. The reaction mixture was stirred at room temperature until homogeneous. Trimethylsilyl trifluoromethanesulfonate (3 equiv) was then added via syringe at room temperature with stirring. The vessel was then heated in an oil bath at 75 °C with stirring for 24 h. The reaction was removed from the oil bath and cooled to room temperature. The reaction vessel was then opened to air, and brine and diethyl ether or hexanes were added. The brine layer was removed, and the organic layer was washed twice with brine. The combined aqueous layers were back-extracted twice with diethyl ether or hexanes. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The product was purified using flash silica chromatography, eluting with the indicated solvent noted in parenthesis.

4.3.2. General procedure B. Reactions of larger silvl triflates: in a glovebox (N<sub>2</sub> atmosphere), tricyclohexylphosphine (30 mol %) and Ni(COD)<sub>2</sub> (10 mol %) were added to a two dram vial equipped with a stirbar. Dioxane, triethylamine (5 equiv), and 1-tert-butyl-4vinylbenzene (1 equiv) were then added, sequentially. The vial was sealed with a Teflon-lined septum cap and removed from the glovebox. The reaction mixture was stirred at room temperature until homogeneous. The appropriate silyl trifluoromethanesulfonate reagent (3 equiv) was then added via syringe at room temperature with stirring. The vessel was then heated in an oil bath at 75 °C with stirring for 24 h, after which time N,N-dimethyl ethanolamine (3 equiv) was added via syringe with stirring at 75 °C. The vessel was stirred at 75 °C for approximately 1 min before stirring at room temperature for approximately 15 min. The reaction vessel was then opened to air, and hexanes and HCl (1 M aqueous) were added. The HCl layer was removed, and the organic layer was washed twice with HCl (1 M aqueous). The combined aqueous layers were back-extracted with hexanes. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated in vacuo. The product was purified using flash silica chromatography, eluting with the indicated solvent noted in parenthesis.

## 4.4. Characterization data

4.4.1. (*E*)-(4-(*tert-Butyl*)*styryl*)*trimethylsilane* (**1**). Following general procedure A: 1-*tert*-butyl-4-vinylbenzene (183 µL, 1 mmol), <sup>1</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 190 mg of **1** (82%) of a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J*=8.7 Hz, 2H), 7.35 (d, *J*=8.7 Hz, 2H), 6.85 (d, *J*=19.1 Hz, 1H), 6.42 (d, *J*=19.1 Hz, 1H), 1.31 (s, 9H), 0.14 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 143.4, 135.8, 128.6, 126.2, 125.6, 34.7, 31.4, -1.0; FTIR (cm<sup>-1</sup>): 2957, 1248, 986, 868, 838. HRMS (EI) *m/z*, calcd for [C<sub>15</sub>H<sub>24</sub>Si]: 232.1647; found: 232.1668.

4.4.2. (*E*)-*Trimethyl(styryl)silane* (**2**). Following general procedure A: styrene (115 µL, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 158 mg of **2** (89%) of a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 (d, *J*=7.0 Hz, 2H), 7.33 (t, *J*=7.4 Hz, 2H), 7.25 (t, *J*=7.2 Hz, 1H), 6.88 (d, *J*=19.2 Hz, 1H), 6.48 (d, *J*=19.1 Hz, 4H), 0.16 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  143.7, 138.5, 129.7, 128.7, 128.1, 126.5, -1.1; FTIR (cm<sup>-1</sup>) 2955, 1247, 988, 866, 843. HRMS (EI) *m/z*, calcd for [C<sub>11</sub>H<sub>16</sub>Si]: 176.1021; found: 176.1048.

4.4.3. (*E*)-(4-*Methoxystyryl*)*trimethylsilane* (**3**). Following general procedure A: 4-vinyl-anisole (134  $\mu$ L, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700  $\mu$ L, 5 mmol), and Me<sub>3</sub>SiOTf (540  $\mu$ L, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 146 mg of **3** (71%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J*=8.8 Hz, 2H), 6.91–6.75 (m, 3H), 6.31 (d, *J*=19.1 Hz, 1H), 3.81 (s, 3H), 0.14 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.6, 143.1, 131.5, 127.7, 126.8, 114.0, 55.5, -1.0; FTIR (cm<sup>-1</sup>) 2958, 1608, 1510, 1251, 1033, 993, 835, 798. HRMS (EI) *m/z*, calcd for [C<sub>12</sub>H<sub>18</sub>OSi]: 206.1127; found: 206.1140.

4.4.4. (*E*)-(3-*Methoxystyryl*)*trimethylsilane* (**4**). Following general procedure A: 3-vinyl-anisole (139  $\mu$ L, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700  $\mu$ L, 5 mmol), and Me<sub>3</sub>SiOTf (540  $\mu$ L, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (5% Et<sub>2</sub>O:hexanes) and concentrated in vacuo to yield 159 mg of **4** (77%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.27 (t, *J*=7.8 Hz, 1H), 7.06 (d, *J*=7.7 Hz, 1H), 7.01 (t, *J*=2.0 Hz, 1H), 6.87 (d, *J*=19.2 Hz, 1H), 6.83 (dd, *J*=2.7, 0.8 Hz, 1H), 6.50 (d, *J*=19.1 Hz, 1H), 3.86 (s, 3H), 0.18 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.9, 143.5, 139.9, 130.0, 129.6, 119.2, 114.0, 111.3, 55.5, -1.1; FTIR (cm<sup>-1</sup>) 2954, 1263, 865, 838. HRMS (EI) *m*/*z*, calcd for [C<sub>12</sub>H<sub>18</sub>OSi]: 206.1127; found: 206.1148.

4.4.5. (*E*)-tert-Butyldimethyl(3-(2-(trimethylsilyl)vinyl)phenoxy)silane (*5*). Following general procedure A: tert-butyldimethyl(3-vinylphenoxy)silane<sup>18</sup> (234 mg, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700  $\mu$ L, 5 mmol), and Me<sub>3</sub>SiOTf (540  $\mu$ L, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 236 mg of **5** (77%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.18

(t, *J*=7.8 Hz, 1H), 7.04 (d, *J*=7.7 Hz, 1H), 6.91 (t, *J*=2.1 Hz, 6H), 6.80 (d, *J*=19.1 Hz, 1H), 6.73 (dd, *J*=8.0, 2.3 Hz, 1H), 6.43 (d, *J*=19.1 Hz, 1H), 0.99 (s, 9H), 0.20 (s, 6H), 0.15 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 143.5, 140.0, 129.7, 129.5, 119.9, 119.8, 118.0, 25.9, 18.4, -1.1, -4.2; FTIR (cm<sup>-1</sup>) 2956, 2859, 1575, 1280, 985, 838. HRMS (EI) *m/z*, calcd for [C<sub>17</sub>H<sub>30</sub>OSi<sub>2</sub>]: 306.1835; found: 306.1819.

4.4.6. (*E*)-(2-(*Benzo*[*d*][1,3]*dioxo*1-5-*y*1)*viny*1)*trimethylsilane* (**6**). Following general procedure A: 5-vinylbenzo[*d*][1,3]*dioxo*1<sup>8</sup> (148 mg, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (hexanes) and concentrated in vacuo to yield 127 mg of **6** (57%) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.00 (d, *J*=1.8 Hz, 1H), 6.86 (dd, *J*=8.0, 1.7 Hz, 1H), 6.80–6.74 (m, 2H), 6.27 (d, *J*=19.1 Hz, 1H), 5.95 (s, 2H), 0.14 (s, 9H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  148.2, 147.6, 143.1, 133.4, 127.4, 121.5, 108.3, 105.6, 101.2, -1.0; FTIR (cm<sup>-1</sup>) 2954, 2895, 1489, 1248, 866, 839. HRMS (EI) *m/z*, calcd for [C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>Si]: 220.0920; found: 220.0933.

4.4.7. (*E*)-(4-*Fluorostyryl*)*trimethylsilane* (**7**). Following general procedure A: 4-fluorostyrene (119 µL, 1 mmol), <sup>*t*</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (hexanes) and concentrated in vacuo to yield 128 mg of **8** (66%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (ddt, *J*=8.3, 5.4, 2.5 Hz, 2H), 7.01 (app tt, *J*=8.5, 1.9 Hz, 2H), 6.82 (d, *J*=19.1 Hz, 1H), 6.38 (d, *J*=19.1 Hz, 1H), 0.15 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.7 (d, *J*=247.3 Hz), 142.4 (s), 134.7 (s), 129.4 (d, *J*=2.2 Hz), 128.0 (d, *J*=8.0 Hz), 115.5 (d, *J*=21.5 Hz), -1.1 (s); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -114.2; FTIR (cm<sup>-1</sup>) 2956, 1507, 1248, 836. HRMS (EI) *m/z*, calcd for [C<sub>11</sub>H<sub>15</sub>FSi]: 194.0927; found: 194.0945.

4.4.8. (E)-(2-(Bicyclo[4.2.0]octa-1(6),2,4-trien-3-yl)vinyl)trimethylsilane (**11**). Following general procedure A: 4vinylbenzocyclobutene (130 mg, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)2 (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 157 mg of **11** (78%) as a colorless oil. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ) δ 7.24 (d, *J*=10.1 Hz, 1H), 7.18 (s, 1H), 7.00 (d, *J*=7.5 Hz, 1H), 6.85 (d, *J*=19.1 Hz, 1H), 6.38 (d, *J*=19.1 Hz, 1H), 3.16 (s, 4H), 0.14 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  146.2, 146.1, 144.7, 137.5, 127.8, 126.1, 122.7, 120.0, 29.6, 29.4, -1.0; FTIR (cm<sup>-1</sup>) 2955, 2930, 1247, 985, 866, 837. HRMS (EI) *m*/*z*, calcd for [C<sub>13</sub>H<sub>18</sub>Si]: 202.1178; found: 202.1194.

4.4.9. (*E*)-(2,4-*Dimethylstyryl*)*trimethylsilane* (**12**). Following general procedure A: 2,4-dimethystyrene (146 µL, 1 mmol), <sup>1</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (hexanes) and concentrated in vacuo to yield 126 mg of **12** (62%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.43 (d, *J*=7.9 Hz, 1H), 7.10 (d, *J*=19.0 Hz, 1H), 6.99 (d, *J*=8.4 Hz, 1H), 6.96 (s, 1H), 6.33 (d, *J*=19.0 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 0.16 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  141.2, 137.6, 135.3, 134.9, 131.2, 130.2, 127.0, 125.3, 21.3, 19.7, -1.0; FTIR (cm<sup>-1</sup>) 2954, 1247, 987, 868, 842. HRMS (EI) *m/z*, calcd for [C<sub>13</sub>H<sub>20</sub>Si]: 204.1334; found: 204.1350.

4.4.10. (*E*)-9-(2-(*Trimethylsilyl*)*vinyl*)-9*H*-carbazole (**13**). Following general procedure A: *N*-vinyl carbazole (193 mg, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700  $\mu$ L, 5 mmol), and Me<sub>3</sub>SiOTf (540  $\mu$ L, 3 mmol) were reacted in dioxane

(2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 248 mg of **13** (93%) as a white solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, *J*=7.8 Hz, 2H), 7.72 (d, *J*=8.3 Hz, 2H), 7.48 (ddd, *J*=8.3, 7.2, 1.3 Hz, 2H), 7.38–7.27 (m, 3H), 6.04 (d, *J*=17.2 Hz, 1H), 0.27 (s, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.4, 133.6, 126.3, 124.2, 120.8, 120.4, 113.5, 110.9, 77.2, –0.6; FTIR (cm<sup>-1</sup>) 2953, 1610, 1447, 834, 751, 721. HRMS (EI) *m*/*z*, calcd for [C<sub>17</sub>H<sub>19</sub>NSi]: 265.1287; found: 265.1262.

4.4.11. (*E*)-Trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) styryl)silane (**15**). Following a modification to general procedure A: 4-pinacolatoboryl styrene<sup>19</sup> (230 mg, 1 mmol), tricyclopentyl-phosphine (72 mg, 0.3 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (3–15% CH<sub>2</sub>Cl<sub>2</sub>:hexanes) and concentrated in vacuo to yield 123 mg of **15** (41%) as a white solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (d, *J*=8.0 Hz, 2H), 7.43 (d, *J*=8.0 Hz, 2H), 6.88 (d, *J*=19.1 Hz, 1H), 6.55 (d, *J*=19.1 Hz, 1H), 1.35 (s, 12H), 0.16 (s, 9H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  143.7, 141.1, 135.2, 131.1, 125.8, 83.9, 25.0, -1.1 (the carbon attached to boron was not observed); FTIR (cm<sup>-1</sup>) 2953, 1607, 1358, 1141, 1090, 869. HRMS (EI) *m/z*, calcd for [C<sub>17</sub>H<sub>27</sub>BO<sub>2</sub>Si]: 302.1873; found: 302.1893.

4.4.12. tert-Butyldimethyl(((8R,9S,13S,14S,17S)-13-methyl-3-((E)-2-(trimethylsilyl)vinyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)silane (16). Following general procedure A: tert-butyldimethyl(((8R,9S,13S,14S,17S)-13-methyl-3vinyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)silane<sup>2b</sup> (396 mg, 1 mmol), <sup>t</sup>BuPCy<sub>2</sub> (38 mg, 0.15 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and Me<sub>3</sub>SiOTf (540 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 283 mg of **16** (60%) as a white foam. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.25–7.18 (m, 2H), 7.15 (s, 1H), 6.82 (d, J=19.1 Hz, 1H), 6.40 (d, J=19.2 Hz, 1H), 3.64 (t, J=8.2 Hz, 1H), 2.98–2.73 (m, 2H), 2.30 (dt, *J*=12.8, 3.0 Hz, 1H), 2.21 (td, *J*=11.5, 11.0, 3.9 Hz, 1H), 2.08–1.79 (m, 3H), 1.76-1.59 (m, 1H), 1.59-1.09 (m, 7H), 0.89 (s, 9H), 0.74 (s, 3H), 0.14 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.6, 140.7, 137.0, 135.9, 128.5, 127.0, 125.7, 123.7, 81.9, 49.9, 44.7, 43.7, 38.8, 37.3, 31.1, 29.7, 27.4, 26.4, 26.0, 23.4, 18.3, 11.5, -1.0, -4.3, -4.6; FTIR (cm<sup>-1</sup>) 2926, 1248, 1095, 866, 836. HRMS (EI) *m*/*z*, calcd for [C<sub>29</sub>H<sub>48</sub>OSi<sub>2</sub>]: 468.3244; found: 468.3259.

4.4.13. (*E*)-Butyl(4-(tert-butyl)styryl)dimethylsilane (**17**). Following general procedure B: 1-tert-butyl-4-vinylbenzene (183 µL, 1 mmol), Cy<sub>3</sub>P (84 mg, 0.3 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and *n*-butyldimethylsilyl trifluoromethanesulfonate<sup>7b</sup> (790 mg, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (300 µL, 3 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 165 mg of **17** (60%) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.38 (d, *J*=8.4 Hz, 2H), 7.35 (d, *J*=8.5 Hz, 2H), 6.85 (d, *J*=19.2 Hz, 1H), 6.41 (d, *J*=19.1 Hz, 1H), 1.35–1.28 (m, 13H), 0.88 (t, *J*=6.8 Hz, 3H), 0.64–0.59 (m, 2H), 0.12 (s, 6H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 143.8, 135.9, 127.8, 126.2, 125.6, 34.8, 31.5, 26.7, 26.3, 15.6, 14.0, –2.8; FTIR (cm<sup>-1</sup>) 2956, 1982, 986, 837. HRMS (EI) *m/z*, calcd for [C<sub>18</sub>H<sub>30</sub>Si]: 274.2117; found: 274.2092.

4.4.14. (E)-Benzyl(4-(tert-butyl)styryl)dimethylsilane (**18**). Following general procedure B: 1-tert-butyl-4-vinylbenzene (183  $\mu$ L, 1 mmol), Cy<sub>3</sub>P (84 mg, 0.3 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700  $\mu$ L, 5 mmol), and benzyldimethylsilyl trifluoromethanesulfonate<sup>7a</sup> (895 mg, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (300  $\mu$ L, 3 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (0–5% CH<sub>2</sub>Cl<sub>2</sub>:hexanes) and concentrated in vacuo to yield 206 mg of **18** (67%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36 (app s, 4H), 7.22 (t, *J*=7.6 Hz, 2H), 7.08 (t, *J*=7.4 Hz, 1H), 7.03 (app d, *J*=7.3 Hz, 2H), 6.84 (d, *J*=19.2 Hz, 1H), 6.38 (d, *J*=19.2 Hz, 1H), 2.21 (s, 2H), 1.33 (s, 9H), 0.13 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.4, 144.6, 140.1, 135.7, 128.4, 128.3, 126.4, 126.2, 125.6, 124.1, 34.8, 31.4, 26.3, -3.2; FTIR (cm<sup>-1</sup>) 2961, 1493, 832, 698. HRMS (EI) *m*/*z*, calcd for [C<sub>21</sub>H<sub>28</sub>Si]: 308.1960; found: 308.1950.

4.4.15. (*E*)-(4-(tert-Butyl)styryl)(isopropyl)dimethylsilane (**19**). Following general procedure B: 1-tert-butyl-4-vinylbenzene (183 µL, 1 mmol), Cy<sub>3</sub>P (84 mg, 0.3 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and isopropyldimethylsilyl trifluoromethanesulfonate<sup>7a</sup> (750 mg, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (300 µL, 3 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 157 mg of **19** (60%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d, *J*=8.6 Hz, 2H), 7.36 (d, *J*=8.4 Hz, 2H), 6.86 (d, *J*=19.2 Hz, 1H), 6.41 (d, *J*=19.2 Hz, 1H), 1.32 (s, 9H), 0.98 (d, *J*=7.1 Hz, 6H), 0.93–0.80 (m, 1H), 0.10 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 144.4, 135.9, 126.4, 126.2, 125.6, 34.7, 31.4, 17.8, 14.0, –5.1; FTIR (cm<sup>-1</sup>) 2955, 2863, 1267, 987, 839. HRMS (EI) *m/z*, calcd for [C<sub>17</sub>H<sub>28</sub>Si]: 260.1960; found: 260.1968.

4.4.16. (*E*)-tert-Butyl(4-(tert-butyl)styryl)dimethylsilane (**20**). Following a modification of general procedure B: 1-tert-butyl-4-vinylbenzene (183 µL, 1 mmol), <sup>n</sup>Bu<sub>3</sub>P (81 mg, 0.4 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and tertbutyldimethylsilyl trifluoromethanesulfonate (690 µL, 3 mmol) were reacted in dioxane (1 mL) at 105 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (300 µL, 3 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (hexanes) and concentrated in vacuo to yield 86 mg of **20** (31%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 (d, *J*=8.6 Hz, 2H), 7.36 (d, *J*=8.5 Hz, 2H), 6.87 (d, *J*=19.2 Hz, 1H), 6.43 (d, *J*=19.1 Hz, 1H), 1.32 (s, 9H), 0.91 (s, 9H), 0.11 (s, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 144.7, 135.9, 126.2, 125.8, 125.6, 34.8, 31.4, 26.6, 17.0, -5.9; FTIR (cm<sup>-1</sup>) 2954, 2856, 1247, 987, 828. HRMS (EI) *m/z*, calcd for [C<sub>18</sub>H<sub>30</sub>Si]: 274.2117; found: 274.2103.

4.4.17. (*E*)-(4-(*tert-Butyl*)*styryl*)(*phenyl*)*dimethylsilane* (**21**). Following general procedure B: 1-*tert*-butyl-4-vinylbenzene (183 µL, 1 mmol), Cy<sub>3</sub>P (84 mg, 0.3 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and phenyldimethylsilyl trifluoromethanesulfonate<sup>7c</sup> (850 mg, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (300 µL, 3 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 205 mg of **21** (70%) as a colorless oil. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  7.58–7.55 (m, 2H), 7.39 (d, *J*=8.4 Hz, 4H), 7.37–7.33 (m, 5H), 6.93 (d, *J*=19.1 Hz, 1H), 6.54 (d, *J*=19.2 Hz, 1H), 1.32 (s, 9H), 0.42 (s, 6H); <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>)  $\delta$  151.5, 145.3, 138.9, 135.6, 134.1, 129.1, 127.9, 126.4, 126.2, 125.6, 34.8, 31.4, –2.3; FTIR (cm<sup>-1</sup>) 2960, 1247, 1112, 841, 821, 729, 698. HRMS (EI) *m/z*, calcd for [C<sub>20</sub>H<sub>26</sub>Si]: 294.1804; found: 294.1788.

4.4.18. (*E*)-(4-(*tert-Butyl*)*styryl*)(*methyl*)*diphenylsilane* (**22**). Following general procedure B: 1-*tert*-butyl-4-vinylbenzene (137  $\mu$ L, 0.75 mmol), Cy<sub>3</sub>P (63 mg, 0.225 mmol), Ni(COD)<sub>2</sub> (20.6 mg, 0.075 mmol), Et<sub>3</sub>N (529  $\mu$ L, 3.75 mmol), and diphenylmethylsilyl trifluoromethanesulfonate<sup>7c</sup> (780 mg, 2.25 mmol) were reacted in dioxane (1.5 mL) at 75 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (225 µL, 2.25 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (2%–10% CH<sub>2</sub>Cl<sub>2</sub>:hexanes) and concentrated in vacuo to yield 198 mg of **22** (74%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (dd, *J*=7.5, 1.8 Hz, 4H), 7.47–7.33 (m, 10H), 6.97 (d, *J*=19.1 Hz, 1H), 6.73 (d, *J*=19.0 Hz, 1H), 1.33 (s, 9H), 0.72 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.7, 147.1, 136.7, 135.5, 135.1, 129.4, 128.0, 126.5, 125.6, 123.9, 34.8, 31.4, –3.5; FTIR (cm<sup>-1</sup>) 2961, 1427, 1111, 800, 699. HRMS (EI) *m*/*z*, calcd for [C<sub>25</sub>H<sub>28</sub>Si]: 356.1960; found: 356.1955.

4.4.19. (*E*)-(4-(*tert-Butyl*)*styryl*)*triethylsilane* (**23**). Following general procedure B: 1-*tert*-butyl-4-vinylbenzene (183 µL, 1 mmol), Cy<sub>3</sub>P (84 mg, 0.3 mmol), Ni(COD)<sub>2</sub> (27.5 mg, 0.1 mmol), Et<sub>3</sub>N (700 µL, 5 mmol), and triethylsilyl trifluoromethanesulfonate (680 µL, 3 mmol) were reacted in dioxane (2 mL) at 75 °C for 24 h. *N*,*N*-Dimethyl ethanolamine (300 µL, 3 mmol) was added after reaction. The product was purified by flash chromatography on silica gel (petroleum ether) and concentrated in vacuo to yield 178 mg of **23** (65%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d, *J*=8.6 Hz, 2H), 7.36 (d, *J*=8.6 Hz, 2H), 6.88 (d, *J*=19.3 Hz, 1H), 6.38 (d, *J*=19.3 Hz, 1H), 1.32 (s, 9H), 0.98 (t, *J*=7.9 Hz, 9H), 0.65 (q, *J*=7.9 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.2, 144.7, 135.9, 126.1, 125.6, 125.0, 34.7, 31.4, 7.6, 3.7; FTIR (cm<sup>-1</sup>) 2954, 2874, 987, 788, 731. HRMS (EI) *m/z*, calcd for [C<sub>18</sub>H<sub>30</sub>Si]: 274.2117; found: 274.2093.

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#### Supplementary data

Supplementary data associated with this article (NMR spectra of products) can be found in the online version. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.03.021.

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