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# Palladium Catalyzed Coupling Reactions for the Functionalization of Si Surfaces: Superior Stability of Alkenyl Monolayers

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## Abstract

Palladium catalyzed Suzuki, Heck and Sonogashira coupling reactions were studied as reaction protocols for organic modification of Si surfaces. These synthetically useful protocols allow for surface modification of alkene, alkyne and halide terminated surfaces. Surface oxidation and metal contamination was assessed by X-ray photoelectron spectroscopy. The nature of the primary passivation layer was an important factor in the oxidation resistance of the Si surface during the secondary functionalization. Specifically, the use of alkynes as the primary functionalization layer gave superior stability compared to alkene analogues. The ability to utilize Pd catalyzed coupling chemistries on Si surfaces opens great versatility for potential molecular and nanoscale electronics and sensing/biosensing applications.

## Introduction

There has been intense study into the formation and properties of organically modified oxide-free Si surfaces[1, 2]. In particular, for the preparation of densely packed alkyl and alkene monolayers to produce stable oxidation resistance Si surfaces. In addition to chemical and electrical passivation for improved device performance[3, 4], there are emerging applications of Si surfaces modified with more diverse organic species. Grafting polar molecules onto the surface can introduce a net surface dipole, which potentially allows the electronic properties of a material to be modified[5-9]. Electronic tuning of Si surfaces by molecular modification has considerable advantages for nanoscale devices in which high surface area to volume ratios result in surface dominated transport properties[10]. The use of organic-Si hybrid systems in sensing devices is another developing application and such devices require the immobilization of a wide range of molecules, *e.g.* biomolecules and target receptor ligands.[11-13] Direct modification of surfaces with large or bulky molecules can often result in low surface coverage, due to steric effects and poor oxidation resistance, and so multistep reactions can be used to introduce groups of interest.[14]

Several strategies have been devised to create organic functional layers via multistep processes through coupling reactions and ‘click’ chemistries. One of the most well-known click reactions is the 1, 3-Husigen cycloaddition, which couples an azide with a terminal alkyne[12, 15]. The reaction is typically carried out in the presence of a copper catalyst but metal-free click reactions have also been reported[16]. Carbodiimide coupling reagents and succinimide[13, 17-19] based activated esters are used in conjugating carboxylic acids with amines and thiols. Thiol-ene[20] and thiol-yne[21] coupling of thiols with alkenes and alkynes, respectively, has also been reported. Development of coupling chemistries and click reactions allows for the design and formation of tailor-made organic-Si interfaces. These reactions also allows for the introduction of functional groups that may otherwise competitively react with the H-Si surface, *e.g.* amino groups[22].

Transition metal mediated catalytic processes are used extensively in organic synthesis and in particular, palladium (Pd) is a prominent catalyst central to many carbon-carbon bond forming reactions.[23] While Pd catalyzed reactions offer considerable diversity in the design of organic molecules, implementation of such chemistry on Si surfaces is challenging. Many coupling reactions are favoured by aqueous basic conditions and these environments are not compatible with Si surfaces. Furthermore, reagents such as the metal catalyst may lead to surface contamination, which can be detrimental to device applications. Sonogashira coupling has been reported on Si(111) surfaces[24-26], however, the ability of these reactions to produce oxide-free, non-contaminated surfaces was not fully evaluated. Plass *et al.*[27] investigated Heck coupling and ruthenium catalyzed olefin cross-metathesis on allyl terminated Si(111) substrates and found that olefin metathesis gave higher coupling efficiencies and less surface oxidation compared to the Heck reaction. Puniredd and co-workers[28] also observed Pd contamination under Heck coupling conditions. Recently, O'Leary *et al.*[29] used Heck coupling to attach a variety of olefins to surface bound thienyl groups. Direct functionalization of H-terminated Si and Ge surfaces was demonstrated using Pd mediated reactions without metal contamination or surface oxidation, illustrating the potential for further development of Pd catalyzed reactions as a method for organic modification of semiconductor surfaces.[30]

In this report we compare a variety of Pd catalyzed cross coupling protocols, namely Suzuki, Heck and Sonogashira reactions for the formation of organically modified Si(100) and Si(111) surfaces. Si substrates bound with alkyl and alkenyl primary passivation layers are first prepared. We investigate how the nature of the primary functionalization layer influences the stability of the Si surface upon exposure to the coupling reaction conditions.

## Experimental

### Reagents

Single-side polished p-type Si(100) wafers, thickness 500 µm ± 25, resistivity 10-20 Ω cm and n-type Si(111) wafers, thickness 475 ± 25 µm, resistivity 700-1300 Ω cm. All chemicals unless otherwise stated were purchased from Sigma Aldrich. Functionalization reactions were carried out under an Ar atmosphere. Glassware was cleaned with aqua regia, dried overnight at 120 °C and cooled under an inert atmosphere before use. Mesitylene was pre-dried with $CaCl_2$ and distilled from $CaH_2$ under reduced pressure. *N*, *N*-Dimethylformamide (DMF) was dried overnight by stirring in anhydrous barium oxide. The solution was decanted onto alumina powder heated overnight at 550 °C, followed by distillation under reduced pressure onto 4 Å molecular sieves and stored in a $N_2$ filled glovebox. Anhydrous, inhibitor-free tetrahydrofuran (THF) was obtained from Alfa Aesar, packaged under Ar. The Pd catalysts were prepared as stock solutions in freshly purified dichloromethane (DCM) which was washed with water, dried with $CaCl_2$ and distilled from $P_2O_5$. Solvents used for rinsing and sonication of substrates – acetone, DCM, anhydrous toluene, anhydrous ethanol (EtOH) and anhydrous methanol (MeOH) were used as received from Sigma Aldrich. Purification of 4-bromostyrene and 4-chlorostyrene was achieved by distillation under reduced pressure. Octadiene was distilled twice from sodium borohydride ($NaBH_4$) under Ar. Nonadiyne was distilled from $NaBH_4$ under vacuum. Triethylamine ($Et_3N$) was distilled from $CaH_2$. The boronic acids were recrystallized from anhydrous solvents and dried under vacuum overnight. Anhydrous potassium carbonate ($K_2CO_3$) was further dried by heating under vacuum for 36 h prior to use. The Pd catalysts tetrakis(triphenylphosphine)palladium

($Pd(PPh_3)_4$), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$), 1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II)•DCM ($Pd(dppf)Cl_2$.DCM) and bis(triphenylphosphine)palladium dichloride, ($Pd(PPh_3)_2Cl_2$) were used as received.

### Surface Modification of Si Substrates

*H-terminated Si substrates.* The Si substrates were pre-cleaned by sonication in chloroform, acetone and MeOH. The wafers were cleaned by the standard piranha cleaning process using a 3:1 $H_2SO_4$:$H_2O_2$ solution at 90 °C for 30 min. The substrates were rinsed copiously with Milli-Q water (18 MΩ cm). Hydride termination of Si(100) wafers was achieved using 2.5 % aqueous HF solution for 2 min.[31] Hydride termination of Si(111) was achieved by immersion in 2.5 % HF for 1 min, followed by immersion into deoxygenated 40 % HF for 15 min. The substrates were briefly rinsed with 1 % HF to removed physisorbed $NH_4Si$ species and then rinsed with DI water and dried in a stream of Ar. The substrates were immediately transferred into a Schlenk flask, evacuated and flushed several times with Ar before hydrosilyation.

*Hydrosilylation.* Hydride terminated Si surfaces were functionalized using standard hydrosilylation chemistry.[1] Si substrates were functionalized with 4-bromostryrene or 4-chlorostyrene by UV ($h\nu$ = 254 nm) initiated hydrosilylation. The substrates were immersed in the neat styrene, previously degassed by several freeze-pump-thaw cycles, for 2 h under an Ar atmosphere. Attachment of bromophenylacetylene (Br-PA), was achieved through thermally induced hydrosilylation by refluxing the Si-H substrates in a 0.1 M solution in mesitylene for 3 h. Thermal initiated hydrosilylation of Si(111) surfaces was carried out by refluxing in a 25 % v/v solution of 1,7-octadiene or 1,8-nonadiyne in mesitylene for 3 h.

After the hydrosilylation reactions, the substrates were rinsed in toluene and further cleaned by sonication in toluene (×2), DCM, rinsed with EtOH and dried under Ar.

*Suzuki Cross Coupling.* In the glovebox, 0.1 mmol of boronic acid, 2 equivalents of base, $Et_3N$ or finely powdered anhydrous $K_2CO_3$ and the aryl halide functionalized Si substrate were added to a round bottom flask. The Suzuki reaction was evaluated using the traditional catalyst $Pd(PPh_3)_4$ and a second catalyst $Pd_2(dba)_3$ with the addition of a phosphine ligand tri-*tert*-butylphosphine ($Pt\text{-}Bu_3$) in a ratio of 1:2. The reaction flask was equipped with a condenser, sealed and removed from the glovebox. The solution was sonicated for several minutes to aid the dissolution of the reagents and transferred onto the Schlenk line where the solution was heated overnight (18 h). Coupling to aryl chlorides was investigated using $Pd(dppf)Cl_2$.DCM in THF at 70 °C for 24 h. After the reaction, the substrates were washed thoroughly with THF. The substrates were cleaned by sonication in the THF, DCM, and EtOH, followed by drying under a stream of Ar.

*Heck Arylation*. Heck reaction was carried out using 0.1 mmol 3,4-difluoroiodobenzene and the catalyst $Pd_2(dba)_3$.DCM (5 mol%), $PPh_3$ (10 mol%) and 4 equivalents of $Et_3N$ base in THF solvent. Two Heck arylation procedures were investigated. In the Heck type 1 procedure, all the reagents and the diene functionalized Si substrate were added to the reaction vessel initially and heated to 60 °C for 18 h. A modified Heck arylation procedure (Heck type 2) whereby the aryl iodide, the catalyst and $PPh_3$ ligand in THF were reacted separately for 4 h at 60 °C and then injected via cannula into a second reaction flask containing the functionalized Si substrate, the base and additional solvent heated to 60 °C. The reaction proceeded for a further 12 h. After the reaction the substrates were rinsed in THF followed by sonication in THF, DCM, EtOH and dried under a stream of Ar.

*Alkyl Borane Conversion.* Octadiene functionalized Si(111) substrates were immersed in a 0.5 M solution of 9-borabicyclo[3.3.1]nonane **(**9-BBN) in THF, previously degassed with Ar, for 18 h at room temperature in the glovebox. After the reaction, the substrates were rinsed thoroughly with THF in the glovebox, followed by immediate *B*-alkyl Suzuki coupling.

*B-Alkyl Suzuki Coupling.* 0.1 mmol of 3,4-difluoroiodobenzene, Pd(dppf)$Cl_2$**.**DCM (3 mol%) the solvent (THF or THF:DMF mix) and 3 equivalents of $K_2CO_3$, were added to the reaction flask containing an alkylborane terminated Si substrate. The reaction flask was briefly sonicated and heated to 60 °C for 18 h. After the reaction, the substrates rinsed in THF followed by sonication in THF, DCM, EtOH and MeOH.

*Sonogashira Coupling.* 0.1 mmol 4-iodobenzotrifluoride, $Pd(PPh_3)_2Cl_2$ (5 mol %) and 2 equivalents of CuI, and $Et_3N$ were added to the reaction vessel. The diyne functionalized Si substrate was immersed in the solution and heated at 50 °C for 6 h. The substrates rinsed in THF followed by sonication in THF, DCM, EtOH and dried under a stream of Ar.

**Characterization and Instrumentation**

*X-Ray Photoelectron Spectroscopy (XPS).* XPS spectra were collected on a KRATOS-AXIS-165 using a monochromatic Al Kα line (1486.6 eV) as the X-ray source. All spectra were collected at a take-off angle ($\Theta$) of 30° to the surface normal. Spectra are referenced to the C 1s peak at a binding energy of 284.6 eV. The high resolution core level scans were fitted with Voigt profiles. The degree of surface oxidation was calculated as an equivalent fractional monolayer, estimated using the Si and $SiO_x$ peak intensities described by Lewis *et al.* [32, 33]. The relative intensity ratio ($\chi$) for oxidized to bulk Si was determined from equation 1:

$$\chi = \frac{n_{Si}^{surf}}{n_{Si} l_{Si} - n_{Si}^{surf}} \qquad (1)$$

where $n_{Si}$ is the atomic number density of Si atoms ($5 \times 10^{22}$ atoms $cm^{-2}$), $n_{Si,surf}$ is the Si surface atom density, which is $6.78 \times 10^{14}$ atoms $cm^{-2}$ and $7.83 \times 10^{14}$ atoms $cm^{-2}$ for Si(100) and Si(111) surfaces, respectively. The escape depth ($l_{Si}$) was determined by $l_{Si} = \lambda_{Si} \sin\phi$, where $\lambda_{Si} = 1.6$ nm[34] and $\phi$ is the take-off angle from the sample surface used in the XPS collection. The observed oxidized to bulk Si 2p ratios were divided by $\chi$ to estimate the fraction of oxidized surface atoms. The limit of detection for the $SiO_x$ sublayer in the XPS measurement under the collection conditions was estimated to be 0.07 monolayer.

The thickness of the organic monolayers was estimated using the substrate-overlayer model described in equation 2:[32, 35]

$$d_{ov} = Ln\left(\frac{I_{ov}}{I_{Si}} \cdot \frac{\rho_{Si}}{\rho_{ov}} \cdot \frac{SF_{Si}}{SF_{ov}} + 1\right)\lambda Sin\phi \qquad (2)$$

where, $I_{Si}$ and $I_{ov}$ are the integral intensities of the Si and overlayer peak, $SF_{Si}$ and $SF_{ov}$ are the relative sensitivity factors for the Si 2p peak and the overlayer peak. Here, $SF_{Si}$ was taken to be 0.82, while $SF_{ov}$ for C 1s = 1, Br 3d = 2.84 and F 1s = 4.43. $\rho_{Si}$ and $\rho_{ov}$ are the atomic number densities of the Si substrate and the atom of interest in the molecular overlayer; $5 \times 10^{22}$ atoms $cm^{-3}$ for Si, $3.04 \times 10^{22}$ atoms $cm^{-3}$ for Br and $5.28 \times 10^{22}$ atoms $cm^{-3}$ for F. Calculations based on equation 2 assume the escape depth ($\lambda$) of photoelectrons excited from the overlayer and the Si substrate to be equal, *i.e.* $\lambda_{Si} \approx \lambda_{ov} = \lambda$, taken to be 2.6 nm.[34]

*Attenuated-Total-Reflection Infrared Spectroscopy (ATR-IR).* ATR-IR spectra were collected on a Nicolet 6700 Infrared Spectrometer equipped with a VariGATR (Harrick Scientific) and a liquid $N_2$ cooled MgCdTe (MCT) detector. The Si wafers were mounted on a clean germanium ATR crystal and spectra were collected under p-polarization at a grazing angle of 65 °, using 1000 cumulative scans with a resolution of 2 $cm^{-1}$. A freshly prepared H-terminated Si wafer was used as a reference and a liner baseline correction was applied to the spectra.

*Ellipsometry.* Ellipsometric thickness measurements were carried out on a J. A Woollam M2000 instrument at an angle of incidence of 70°. The thicknesses of the monolayers were determined with a planar three layer; ambient, overlayer and substrate model, with assumed refractive indices of 1.00 and 1.45 for ambient and the overlayer, respectively.[36] The reported values are the average of at least 6 measurements on the substrate.

*Water contact angle.* Static water contact angle measurements were recorded using a Dataphysics OCA 20 Wetting Angle System. A minimum of 6 deionised water droplets of 2.5 µL were dispensed on each substrate.

## Results and Discussion

### *Suzuki Coupling on Si(100)*

The formation of conjugated phenyl groups such as styrene molecules, on semiconductor surfaces has attracted much interest due to their potential for unique electrical properties owing to the $\pi$-$\pi$ interactions of the adjacent phenyl rings.[37-39] The ability to tune the structural properties of such monolayers through chemical modification is therefore highly advantageous. Suzuki-Miyaura coupling involves reaction of an aryl boronic acid and aryl halide catalyzed by a Pd(0) species. Suzuki coupling of aryl bromides can often take place under similar reaction conditions to the more reactive aryl iodides, which provides a greater versatility due to the broad range of commercially available aryl bromide precursors. Furthermore, successful cross coupling in solution has been achieved using extremely low catalyst concentrations, *e.g.* $10^{-4}$ mol% Pd,[40] which is beneficial for avoiding possible surface contamination.

To investigate the Suzuki coupling protocol as a strategy for chemical modification on Si surfaces, Si(100) substrates were first functionalized with bromostyrene (Br-Sty) and bromophenylacetylene (Br-PA), as depicted in reaction scheme 1. Thermally initiated hydrosilylation with Br-Sty was found to form multilayers as indicated by ellipsometry, which varied from 5-20 nm. In contrast, UV hydrosilylation was found to be effective for producing a styrene monolayer, with an ellipsometry value of 0.95 ± 0.2 nm, slightly higher than the 0.85 nm observed for Br-Sty on Si(111).[41]

**Scheme 1.** Suzuki coupling of bromostyrene and bromophenylacetylene functionalized Si surfaces.

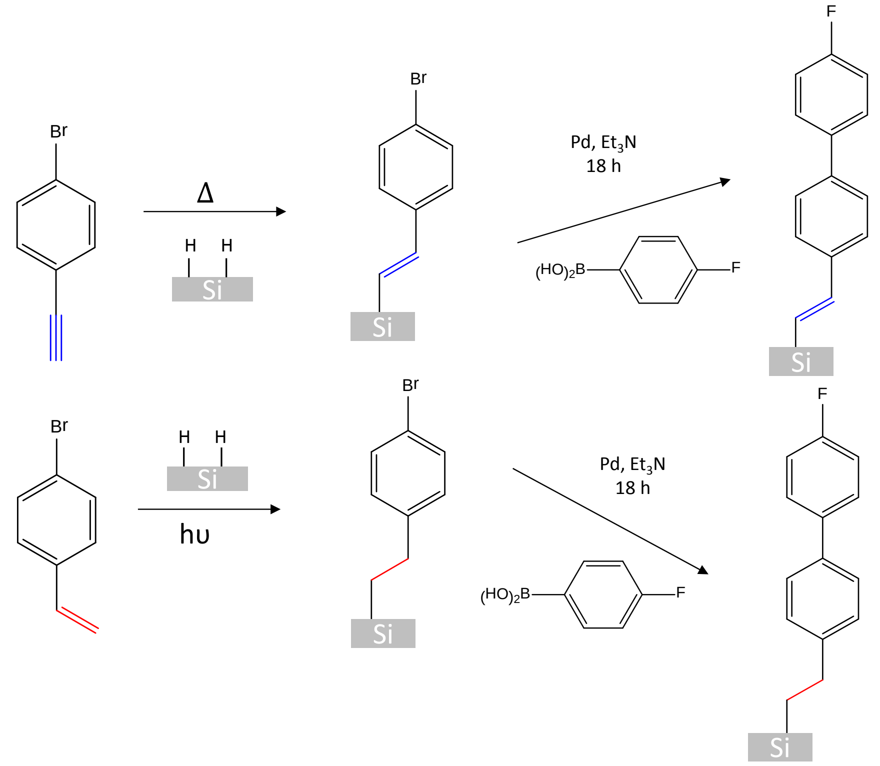


Figure 1 displays the Br 3d core level spectra for Br-Sty and Br-PA functionalized Si substrates. Both spectra exhibit one Br 3d doublet at a binding of 70.4 eV (Br $3d_{3/2}$) and 71.5 eV (Br $3d_{5/2}$), which can be assigned to the C-Br bond.[26] Mixed monolayers, in which the Si surface reacts with the double bond and the terminal Br have been reported with alkyl bromides[42]. Reaction of Br-PA and Br-Sty at the terminal Br group would give rise to an additional doublet in the Br 3d spectra at a binding energy 69.3 and 70.3 eV, due to Br-Si bonds. The absence of such peaks in figure 1 indicate that both Br-Sty and Br-PA react exclusively through the double or triple bond, which is also in agreement with functionalization of Si(100) and Si(111) under UHV conditions.[43] The attachment modes of Br-Sty and Br-PA are important as Suzuki coupling reacts through the -Br functional group and so the -Br group must be persevered at the top of the monolayer.

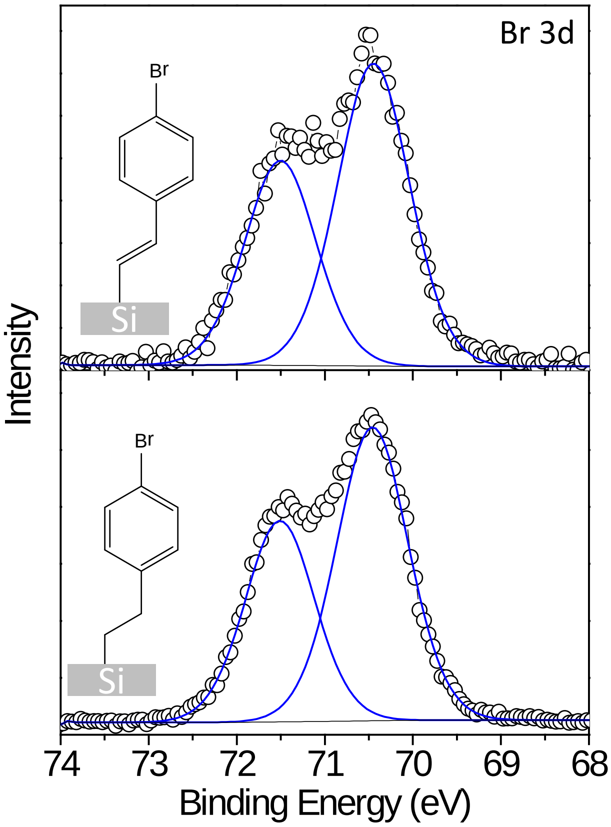


**Figure 1.** Br 3d core level spectra of H-terminated Si(100) after functionalization with Br-PA and Br-Sty.

Figure 2 (a) and (b) illustrate the Si 2p core level spectra for Br-PA and Br-Sty before (blue spectra) and after (red spectra) the Suzuki coupling reaction with fluorophenylboronic acid (F-PhB$(OH)_2$). Initial functionalization of the surface with Br-PA and Br-Sty leaves the surface oxide-free as indicated by the absence of oxide-associated peaks at a binding energy of ~103 eV. The degree of surface oxidation experienced during the coupling conditions is dependent on the nature of the primary functionalization layer. Suzuki coupling on Br-PA functionalized surfaces results in a near-oxide free surface. A small increase in surface oxidation is observed, constituting about 0.2 ± 0.1 of a monolayer[33], however the presence of such a small amount of oxide has been shown not to negatively influence electrical properties.[44] In contrast to Br-PA, a greater degree of surface oxidization is experienced on Br-Sty functionalized surfaces accounting for 0.6 ± 0.1 of a monolayer.

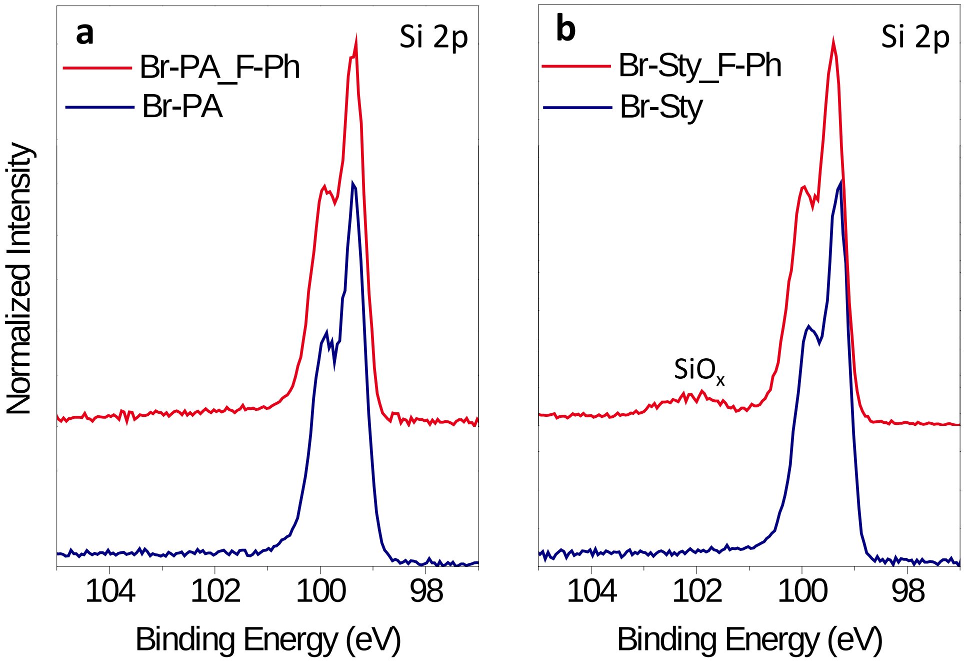


**Figure 2**. Si 2p core level spectra of (a) Br-PA and (b) Br-Sty, before (blue spectra) and after (red spectra) Pd catalyzed coupling reaction.

Figure 3 (a) and (b) illustrates the C 1s spectra of Br-PA and Br-Sty functionalized surfaces after Suzuki coupling. Both C 1s spectra display a peak at a binding energy of 288.6 eV, which is not present before coupling (Supporting Information, Figure S1) and can be assigned to the presence of an aromatic fluoride group (=C-F)[45]. The functionalized Br-Sty spectrum displays a C-O peak at a binding energy of 286.4 eV, attributed to surface oxidation, *i.e.* Si-O-C. A weak C-O peak is also present in the Br-PA spectra, which may be due to adsorbed solvent molecules (THF) incorporated into the functionalization layer or the presence of adventitious hydrocarbons.[46] Successful Suzuki coupling is also indicated in figure 3 (c) and (d), showing the core level F 1s spectra after reaction located at a binding energy of 687.4 eV, which is typical of a fluorocarbon.[47].

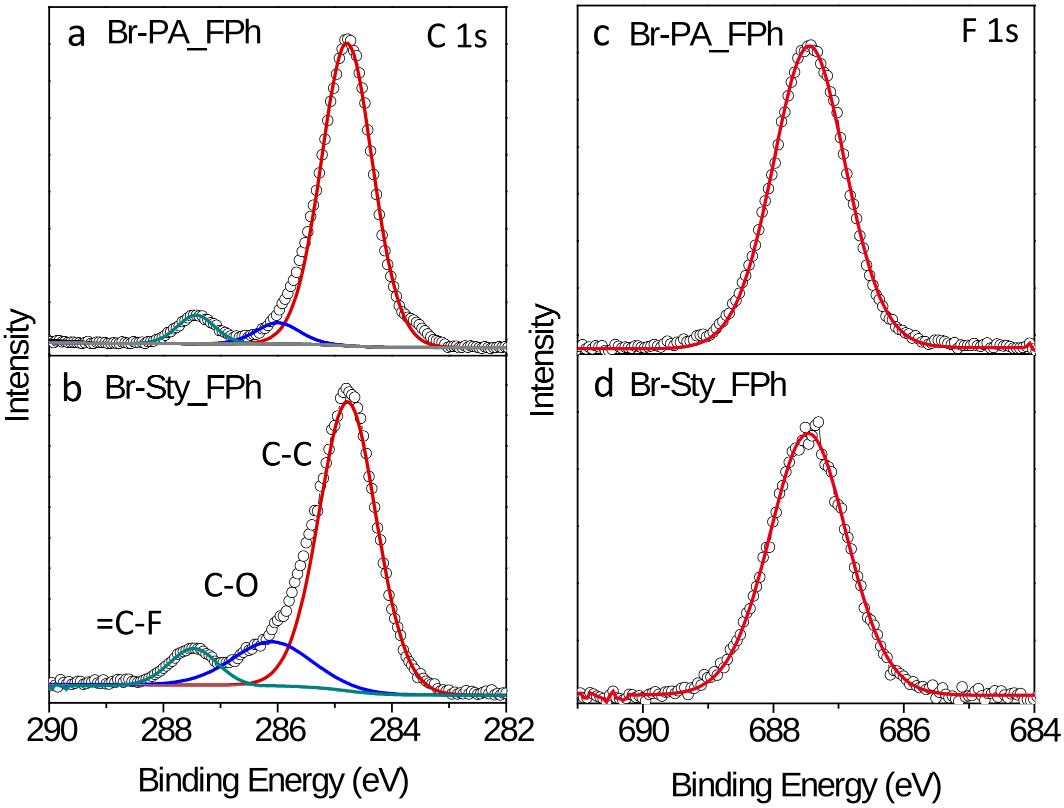


**Figure 3.** (a) and (b) C 1s core level spectra and (c) and (d) F 1s core level spectra of Br-PA and Br-Sty functionalized Si(100) coupled to F-PhB$(OH)_2$.

The XPS analysis indicates that the coupling reactions successfully occur on both Br-PA and Br-Sty functionalized surfaces, however the Br-PA surface displays superior stability towards surface oxidization under the reaction conditions. Experimental[36, 46, 48, 49] and theoretical[50] studies on Si(111) and Si(100)[51] surfaces have demonstrated that Si bound to $sp^2$ hybridized carbon atoms (Si-C=C) exhibit increased stability compared to $sp^3$ hybridized carbons (Si-C-C). The enhanced stability of alkenyl monolayers is attributed to the increased packing density of the alkenyl monolayers and the π-π interactions between adjacent molecules[49, 52-54]. The XPS results in this study are indicative of a similar stabilising affect experienced for Si surfaces functionalized with vinyl and acetylene aryl groups. Consequently, the use of a Si-

C=C primary passivation layer is more robust and resistant to oxidation than a Si-C-C passivation layer, under Suzuki coupling conditions.

The survey spectra of the Suzuki coupled Br-PA substrate, in figure 4 shows the absence of peaks corresponding to Pd, with the Pd 3d doublet typically found at a binding energy of 335 eV.[55] Pd contamination was found to be dependent on the catalyst concentration due to precipitation of Pd. When using catalyst concentrations greater than 0.1 mM, a dark precipitate was observed during the reaction due to the formation of Pd nanoparticles, which resulted in surface Pd contamination (Supporting Information, Figure S2). No boron was detected at a binding energy of ~190 eV, indicating successful reaction of the boronic acid group. The absence of a B associated peak also demonstrates that the F peaks do not arise from adsorption of the aryl groups on the surface but by chemical attachment, although it should be noted that B has a low photoionisation cross section. Residual uncoupled Br species can be seen in the survey spectra. The percentage conversion for Br-PA modified Si surfaces estimated from the integral intensities of the Br 3d and F 1s spectra, varied depending on the reaction conditions, as described in table 1. Comparison of the two catalysts investigated show that they both give rise to successful coupling, but $Pd(dba)_2$ in the presence of a phosphine ligand $P(t\text{-Bu})_3$ resulted in higher coupling conversion. The yield for $Pd(dba)_2$ was 72% compared to 34% for the same concentration of $Pd(PPh_3)_4$. $Pd(dba)_2$ could also be used at lower catalyst concentrations obtaining good conversion (51% at 0.05 mM). The use of bulky electron rich phosphines activate the aryl halide for oxidative addition and facilitate the reaction at lower Pd concentrations. A control sample which contained the reagents without the addition of the Pd catalyst (entry 7, Table 1) did not give rise to a F peak in the survey spectra.

The reaction was also found to be solvent dependent with successful coupling in THF but not in toluene. Solvent dependency is often observed in Pd coupling reactions as the polarity of the solvent can influence the nature of the catalytically active species.[56] Suzuki coupling to aryl chlorides was also investigated using Si functionalized with chlorostyrene. The high resolution Cl 2p spectrum (Supporting Information, Figure S3) indicates one Cl environment attributable to the C-Cl bond at a binding energy of 200.6 and 202.2 eV, illustrating that the reactivity of chlorostyrene toward Si-H, is consistent with that of bromostyrene and bromophenylacetylene with selective reaction taking place via hydrosilyation and no reactivity at the halide group. The survey spectra in Figure 4(c) after coupling to F-PhB(OH)$_2$ confirms the presence of Cl remaining on the surface and the absence of a F 1s peak, indicating that surface bound aryl chlorides are not active towards cross coupling under the reaction conditions studied here.

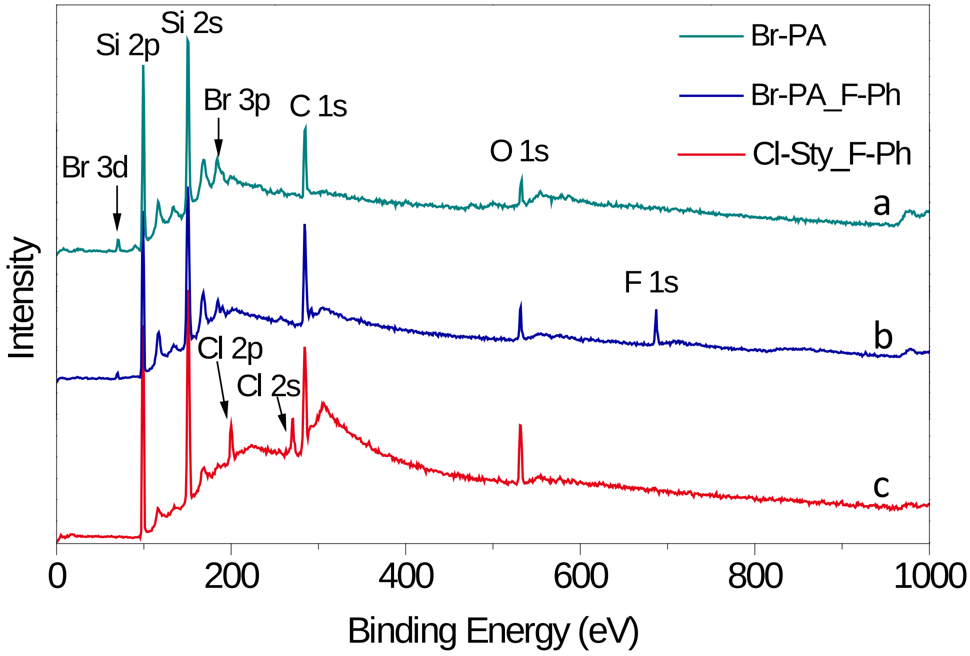


**Figure 4.** XPS survey spectra of (a) Br-PA functionalized Si, (b) Br-PA functionalized Si after cross coupling reaction with F-PhB(OH)$_2$ catalyzed by Pd(PPh$_3$)$_4$ and (c) Cl-Sty functionalized Si after cross coupling with F-PhB(OH)$_2$ using (Pd(dppf)Cl$_2$.DCM.

**Table 1.** Reaction conditions investigated for Suzuki coupling on Br-PA functionalized Si surfaces.

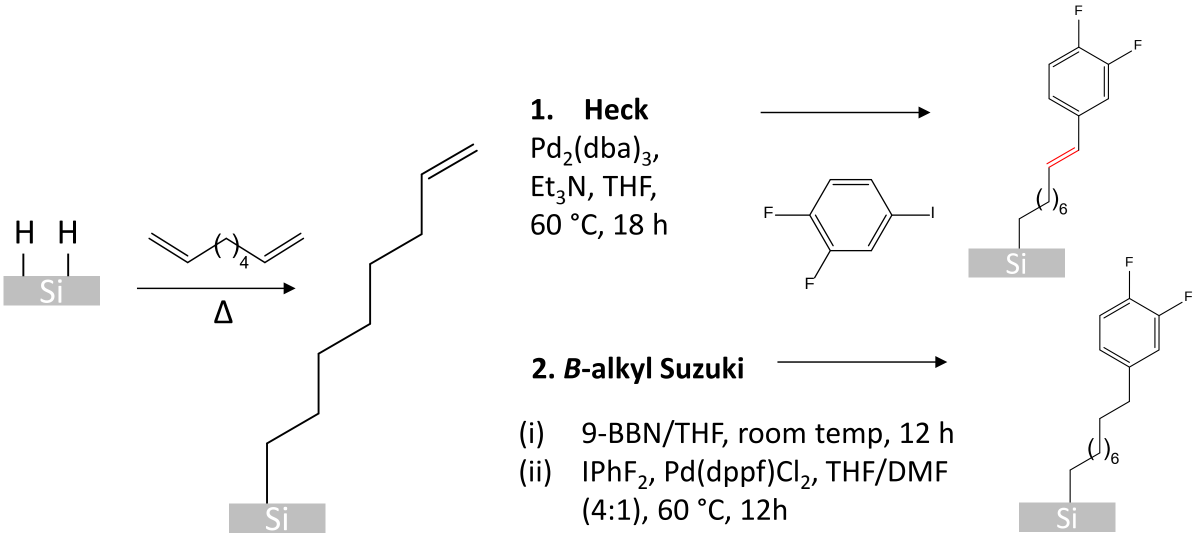
| **Entry** | **Catalyst** | **Concentration mM** | **Solvent** | **Temperature ° C** | **% Conversion** [a] |
|---|---|---|---|---|---|
| 1 | $Pd(PPh_3)_4$ | 0.1 | THF | 60 | 34 |
| 2 | $Pd(PPh_3)_4$ | 0.05 | THF | 60 | 14 |
| 3 | $Pd(PPh_3)_4$ | 0.1 | Toluene | 100 | - [b] |
| 4 | $Pd(dba)_2 + P(tBu)_3$ | 0.1 | THF | 60 | 72 |
| 5 | $Pd(dba)_2 + P(tBu)_3$ | 0.05 | THF | 60 | 51 |
| 6 | $Pd(dba)_2 + P(tBu)_3$ | 0.05 | THF | 20 | < 10 |
| 7 | No catalyst | - | THF | 60 | - [b] |

[a] Based on corrected integral intensities of the Br 3d and F 1s core level spectra**.** [b] No coupling observed. When the low yield Suzuki reactions were left for longer times, little or no improvement was obtained in the coupling yields (it is also unlikely that repetitive functionalization would lead to increased yields).

## Heck Arylation

The formation of straight chain alkyl and alkene monolayers are often utilized as Si passivation layers as they produce a robust interface with good stability.[33] The ability to carry out coupling reactions on these primary functionalization layers is therefore an advantageous strategy for surface modification. Two coupling protocols are investigated for the attachment to terminal alkenes, namely Heck arylation and *B*-alkyl Suzuki coupling, which are illustrated in Scheme 2.

**Scheme 2.** Pd catalyzed Heck and *B*-alkyl Suzuki coupling reactions on alkene terminated Si(111) surfaces.



The Heck arylation reaction has been reported for attaching aryl halides to terminal alkenes but was shown to result in Pd contamination and surface oxidation.[27, 28] We further investigated the Heck strategy by modifying literature procedures. We used a longer alkene primary functionalization layer and the catalyst was used with the addition of a phosphine ligand. Two reaction procedures for the Heck arylation were investigated; Heck type 1 involved the addition of all the reagents and the Si substrate into the reaction vessel initially. Heck type 2 procedure involved addition of the all the reagents except for the Si substrate to the reaction vessel initially. These reagents *i.e.* the catalyst, phosphine, aryl iodide and base were reacted separately in THF for 4 h and then injected into a second vessel containing the Si substrate pre-heated in THF to 60 °C. The purpose of separating the reaction into two parts lies in the mechanism of Heck arylation. The first mechanistic step in the Heck reaction is oxidative addition of the aryl halide to the Pd(0) catalyst and this can be the rate determining step.[57] The alkene, which is attached to the Si surface, is not involved in the oxidative addition step of the mechanism. Consequently, in the Heck type 2 procedure, the oxidative addition product, which is illustrated in figure 5 (b), is formed separately and then introduced into the Si surface. The alkene then undergoes insertion into the oxidative addition product and continues through the remaining steps of the Heck mechanism. To investigate the reaction efficiency of the two approaches, a Si(111) surface was initially functionalized using a diene. The IR spectrum of Si surfaces after modification with 1,7-octadiene (Supporting Information, Figure S4) indicated the preservation of the terminal double bond, due to the presence of the C=C stretching vibration at 1660 $cm^{-1}$. The C-H asymmetric and symmetric stretches are observed at 2924.7 $cm^{-1}$ and 2852.4 $cm^{-1}$, respectively. The C-H stretching vibrations are lower than parent diene (2928.5 $cm^{-1}$, 2854.8 $cm^{-1}$) suggesting some degree of conformational order in the monolayer, but highly ordered monolayers are generally associated with peak frequencies less than 2918 $cm^{-1}$ and 2949 $cm^{-1}$ for the symmetric and asymmetric stretches, respectively. [32] The functionalized Si substrates displayed good hydrophobicity with a water contact angle of 104 ± 5°.

Figure 5 (a) compares the C 1s spectra for octadiene-functionalized Si(111) and after Heck arylation using type 1 and type 2 procedure. Successful coupling is indicated by the presence of a peak at 288.9 eV, which can be assigned to the difluorinated aryl group.[58] The Heck 2 procedure gave rise to lower surface oxidation (0.18 ± 0.1 monolayer) compared to the Heck type 1 (0.55 ± 0.2 monolayer) as illustrated in the Si 2p spectra in figure 5 (c). The presence of F but the absence of I (I 3d $E_B$ ~620 eV) in the survey spectrum (Supporting Information Figure S5) indicates that the aryl group is chemically attached to the surface and present as adsorbed species.

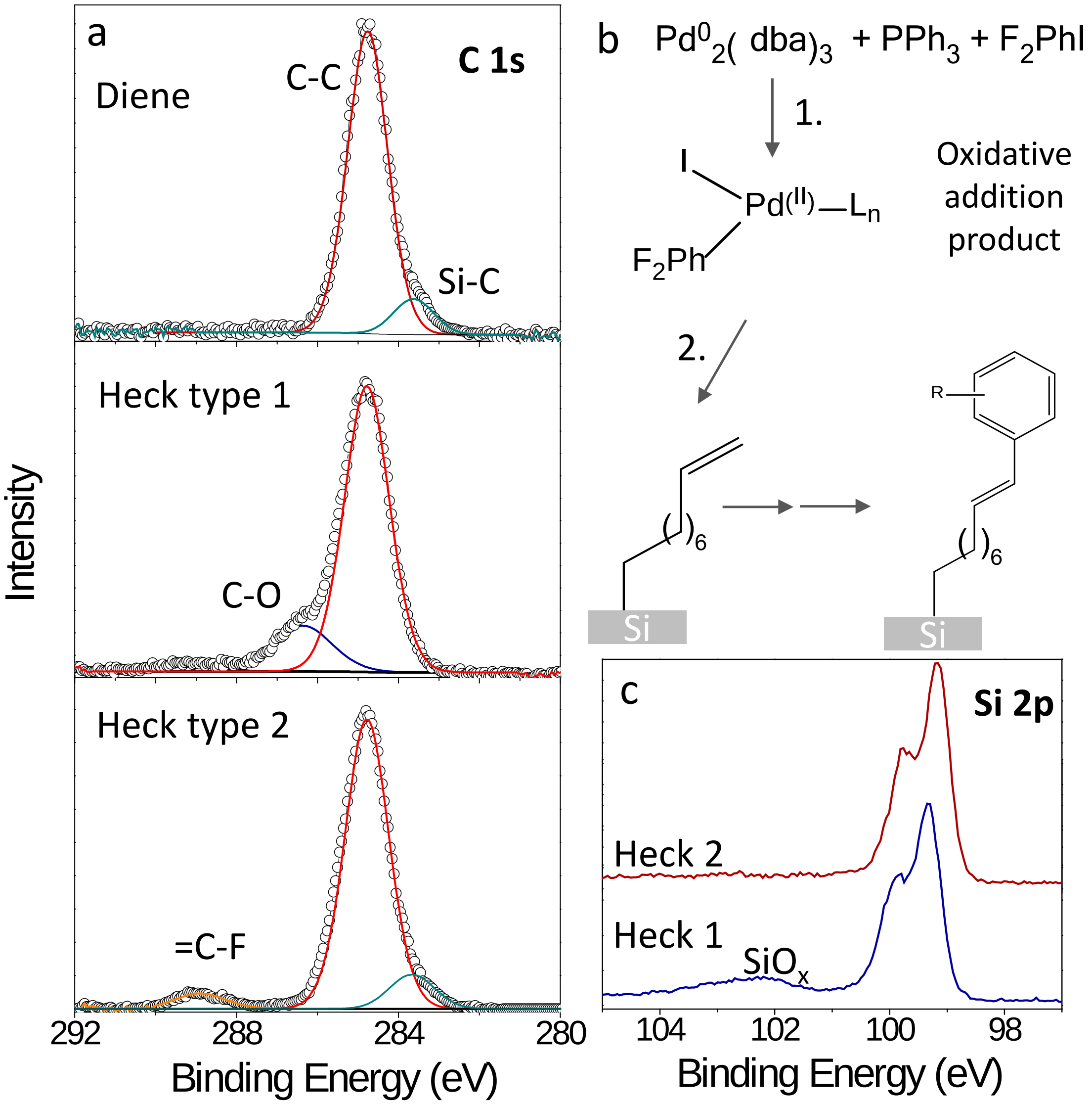


**Figure 5.** (a) C 1s core level spectra of octadiene functionalized Si and after Heck arylation by Heck 1 procedure and Heck 2 procedure. (b) Reaction scheme for Heck arylation showing the oxidative addition step. L represents the ligands dba and PPh$_3$.

The procedure in which the Heck reaction was carried out also influenced the degree of Pd contamination on the surface. Functionalization using the Heck Type 1 reaction Pd gave rise to surface contamination as shown in the survey spectrum (Supporting Information Figure. S5). It is worth noting that in comparison to Suzuki coupling, whereby Pd contamination could be avoided by using low Pd concentrations to avoid precipitation, we were unable to achieve Pd-free surfaces catalyzed under the Heck Type 1 procedure. In contrast, Pd contamination was not observed using the Heck Type 2 procedure, as demonstrated by the absence of Pd associated peaks at ~335 eV in the survey spectrum (Supporting Information, Figure S5.) The non-specific adsorption of the oxidative addition complex may be lower relative to the parent catalyst.[29] The presence of the phosphine ligands is solution may also influence adsorption behaviour of the Pd species.

Considering the lack of Pd contamination observed when using the Suzuki protocol we also investigated *B*-alkyl Suzuki coupling on alkene terminated surfaces. The terminal diene was converted to an alkyl borane by hydroboration with 9-BBN, which was then coupled to I-Ph-$CF_3$, as shown in Scheme 2. This procedure produces a similar functionalization layer to Heck arylation but without the preservation of the terminal double bond. The reaction showed a strong solvent dependence. *B*-alkyl Suzuki coupling was successful in THF:DMF (4:1) but yielded low surface coverage, ~10 % of a monolayer. No coupling was observed when the reaction was carried out in THF alone. In solution chemistry, the nature of the base with alkylboranes is known to be solvent dependent with weak bases favoured by DMF. Changing the reaction solvent to 100 % DMF at 100 °C, resulted in coupling as indicated by the appearance of the F 1s peak and the absence of I associated peaks in the XPS survey spectra (Supporting Information, Figure S6). However, the use of DMF and the higher reaction temperatures led to degradation of the diene functionalization layer resulting in Si oxidation (> 1 monolayer) as shown in figure 6 (a). Low amounts of Pd and base contamination were also observed (Supporting Information, Figures S7 & S8) illustrating the importance of a robust primary functionalization layer. DMF has been used in other Si functionalization reactions[13, 28] and so the low degree of oxidation resistance under the coupling conditions here may originate from the low degree of conformational ordering in the diene functionalization layer, which is consistent with the IR analysis.[44]

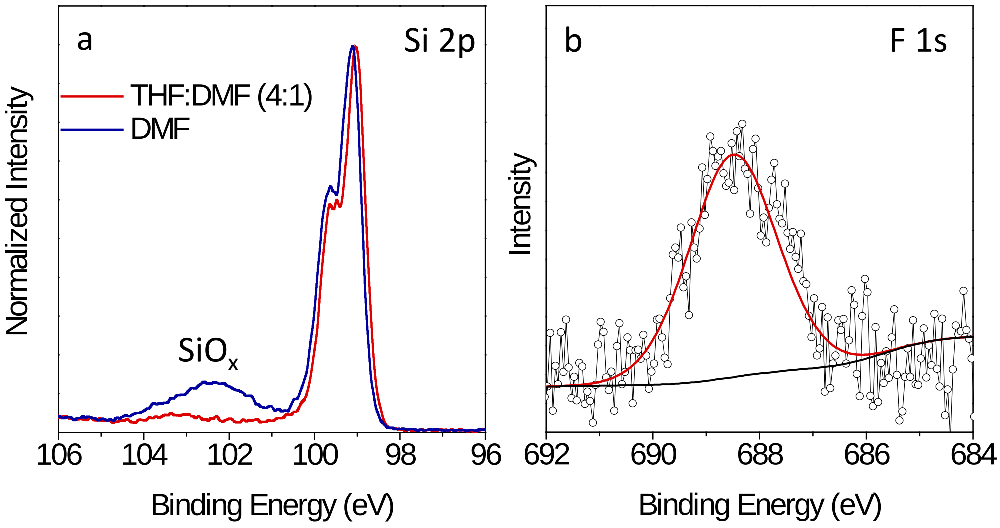
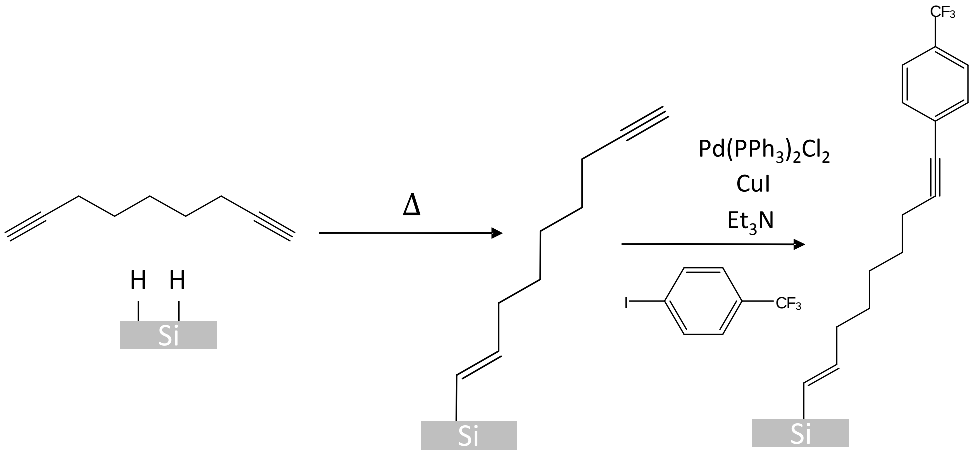


**Figure 6.** (a) Si 2p core level spectra of *B*-alkyl Suzuki coupling in DMF and THF:DMF (4:1). (b) F 1s spectrum after *B*-alkyl Suzuki coupling in THF:DMF.

### Sonogashira Coupling

The Sonogashira reaction involves coupling of an alkyne group and aryl or vinyl halide. Compared to other coupling protocols the Sonogashira reaction can usually take place under milder conditions due to the greater reactivity of the carbon triple bond. However, unlike Suzuki and Heck reactions, Sonogashira coupling usually requires the presence of a copper (I) co-catalyst so metal contamination needs to be evaluated. Sonogashira coupling to surface bound aryl iodide groups has been reported previously, however Si surface oxidation was not evaluated by XPS[24, 25]. Assessment of the Si 2p core level spectrum is important because as we have shown, successful coupling can proceed without the perseveration of an oxide-free surface, depending on the nature of the primary passivation layer. Sonogashira coupling protocol of aryl iodides to surface bound alkyne groups was investigated on Si(111) as depicted in reaction Scheme 3.

**Scheme 3.** Sonogashira coupling on alkyne functionalized Si(111).



Si(111) surfaces were functionalized with 1,8 nonadiyne by thermal hydrosilylation. The substrates displayed water contact angles of 88° ± 2°, which is in excellent agreement with literature reports.[21] Figure 7 (a) compares the C 1s core level spectra of nonadiyne modified Si before and after coupling to I-Ph-$CF_3$ using Sonogashira coupling conditions. Successful coupling is indicated by the presence of a peak at 293 eV, characteristic of the -$CF_3$ functional group.[47] Contributions from the C≡C and C-Si peaks could not be resolved in the C 1s spectra but assuming 50 % diyne coverage[59], the estimated reaction yield based on the F 1s and Si 2p peak intensity[32] is ~60 %. Sonogashira coupling resulted in higher conversions than the Heck and *B*-alkyl Suzuki coupling of diene-terminated Si surfaces. The higher reactivity and linear nature of the triple bond may reduce steric hindrance during the reaction, facilitating higher conversions. Furthermore, confirmation of the reaction was given by the presence of an F 1s peak and the absence of I peaks in the survey spectrum (figure 7 (b)). The survey spectra also confirm the absence of metal contamination with the absence of the Pd 3d and Cu 2p peaks (Cu 2p $E_B$ ~920 eV), at least to the detection limit of the instrument

(0.1 atomic %). The Si 2p core level spectra shown in figure 7 (c) shows excellent stability of the surface with no associated oxide peaks.

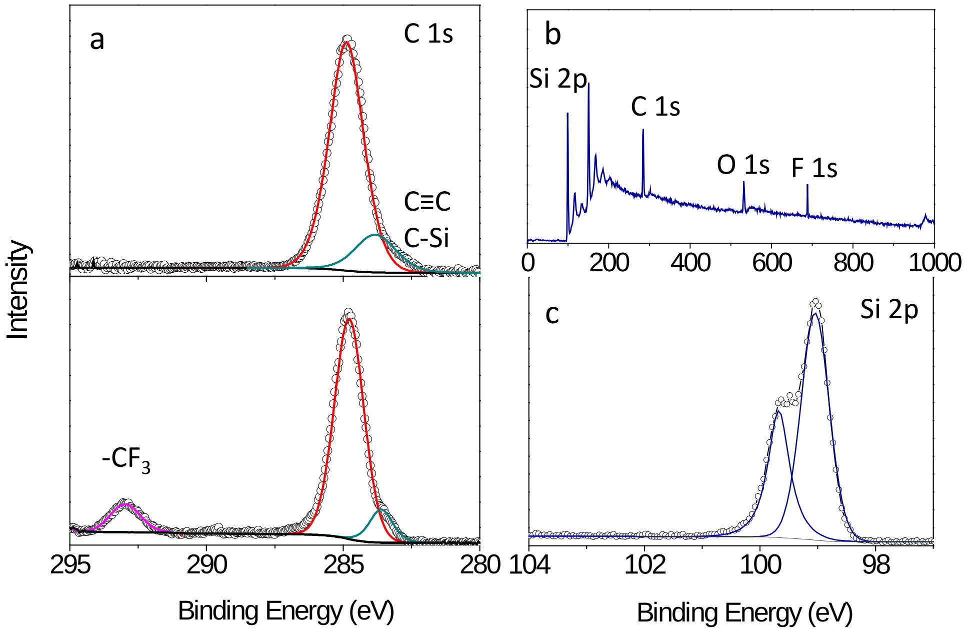


**Figure 7.** (a) C 1s spectra of nonadiyne functionalized Si(111) before and after Sonogashira coupling to I-Ph-$CF_3$. (b) Survey spectrum and (c) Si 2p spectrum of Si substrate after Sonogashira reaction.

## Conclusions

Application of Pd catalysed Heck, Suzuki and Sonogashira coupling protocols were investigated as surface modification strategies for Si substrates. All reaction protocols were found to successfully occur on organically modified Si surfaces. For Suzuki and Sonogashira coupling Pd contamination was not problematic provided that the concentration was low to limit Pd nanoparticle formation. Surface oxidation was found to depend on the nature of the primary organic functionalization layer. Functionalization layers attached using an alkyne functional group resulted in less surface oxidation during the coupling reaction compared to using similar molecules attached through an alkene group. This observation is consistent with reports demonstrating that the incorporation of $sp^2$-bound carbon species to surface Si increases the stability of the monolayer and the work in this study further illustrates that stability of the primary passivation layer is key importance for subsequent surface modification reactions.

In addition to having a robust primary monolayer, carrying out the oxidative addition of the aryl halide to the Pd catalyst *ex-situ* and then introducing the Si surface is beneficial in reducing the reaction time and lowering the degree of surface oxidation and Pd contamination during Heck arylation of modified Si surfaces. This strategy would be highly advantageous for the attachment of unactivated substrates or sterically hindered substrates that would be slow to undergo oxidative addition. While relatively simple organic molecules were utilized in this study, there is considerable scope for expansion to more complex molecules as a wide variety of commercial precursors available for coupling reactions and tolerate to a range of functional groups. The ability to employ such diverse chemistry on Si surfaces has considerable potential for applications that require selective functionalization.

## Acknowledgements

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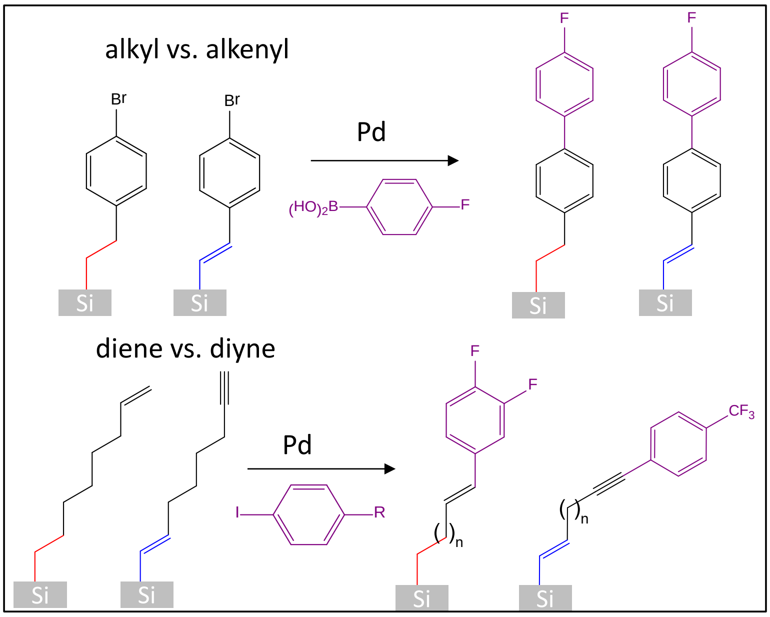
## TOC Graphic


alkyl vs. alkenyl
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Br
Pd
(HO)2B
F
F
F
Si
Si
Si
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diene vs. diyne
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