20-6-2014

Bu4N(+) Alkoxide-Initiated/Autocatalytic Addition Reactions with Organotrimethylsilanes.

Manas Das
Royal College of Surgeons in Ireland

Donal F. O’Shea
Royal College of Surgeons in Ireland

Citation

This Article is brought to you for free and open access by the Department of Pharmaceutical and Medicinal Chemistry at e-publications@RCSI. It has been accepted for inclusion in Pharmaceutical and Medicinal Chemistry Articles by an authorized administrator of e-publications@RCSI. For more information, please contact epubs@rcsi.ie.
Bu₄N⁺-Alkoxide Initiated / Autocatalytic Addition Reactions with Organotrimethylsilanes

Manas Das and Donal F. O’Shea*

*Department of Pharmaceutical and Medicinal Chemistry, Royal College of Surgeons in Ireland, 123 St. Stephen’s Green, Dublin 2; School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland.

Email: donalfoshea@rcsi.ie

Graphical Abstract

Abstract

The use of Me₃SiO⁻/Bu₄N⁺ as a general activation of organotrimethylsilanes for addition reactions has been established. The broad scope of the method offers trimethylsilanes (including acetate, allyl, propargyl, benzyl, dithiane, heteroaryl and aryl derivatives) as bench stable organometallics which can be readily utilized as carbanion equivalents for synthesis. Reactions are achieved at r.t. with no specialised precautions required that are common place for other organometallics.
INTRODUCTION

The research literature on organometallic reagent addition to an electrophilic carbon is nothing short of vast. The common conceptual purpose of generating an organometallic reagent is the formation of a nucleophilic carbon via an electronically polarized carbon-metal bond. A consequence of using the more reactive organometallics of Li, Mg, Zn, Cu, Ti, Ni or Pd is that they can rarely be isolated or stored, leading to individualized reaction conditions for their generation and in situ reaction. An idealized collection of organometallic reagents evoke the seemingly two incompatible features of bench stability and high reactivity. Silicon organometallics, as their corresponding organotrimethylsilanes, could provide this ideal but significant challenges exist in identifying mild conditions that can unlock the carbanion reactivity of organotrimethylsilanes, in a general manner, without using toxic activators or forcing conditions.

The primary attraction of using silicon as the metallic component is the inherent bench stability of organosilanes due to the relatively low bond polarization of the C-Si bond. The synthetic use of organotrimethylsilanes was first established by the pioneering work of Sakurai and others in which it was shown that fluoride could promote the addition reactions of allyl, alkynyl, cyano and trifluoromethyl silanes. Numerous reports have expanded on these earlier publications but the means of activation is most often a fluoride source. In this report we illustrate the first general addition method applicable for the widest range of bench-stable trimethylsilane substrates. The universal reaction conditions are mild, user-friendly, can be carried out at room temperature and do not rely on the use of fluoride. Our approach to achieving this was guided by mechanistic studies of the fluoride promoted addition of allyl and, in our own work, benzyltrimethylsilanes to carbonyls (Scheme 1). These studies have indicated the reaction
pathway is a fluoride initiated formation of hypervalent silicon species 2 which provides a carbanion equivalent which upon carbonyl addition produces an alkoxide 3 and trimethylsilylfluoride.

Scheme 1. Analysis of Trimethylsilane Addition Reactions

The reaction pathway then enters an autocatalytic cycle in which the alkoxide 3 reacts with the starting organotrimethylsilane to generate another hypervalent silicon species 4 thereby propagating the reaction and producing product 5. If the role of fluoride is solely to initiate the reaction, with an alkoxide controlled autocatalytic cycle driving the reaction to completion, then it would be plausible to expect that fluoride could be replaced with a suitable alkoxide. This would result in a reaction sequence that is initiated by one alkoxide and then autocatalytic turnover achieved by the in situ produced alkoxide. With this analysis in mind an investigation into alternative Lewis base (LB) activation of organo-trimethylsilanes was undertaken (Scheme 1). As the most common synthetically utilized organometallics have functional groups such as
acetate, allyl, propargyl, benzyl,\textsuperscript{6} dithiane, heteroaryl and aryl, the substituted trimethylsilanes \textbf{6-13} were selected to evaluate the new method (Figure 1).

\textbf{Figure 1.} Trimethylsilyl organometallic reagents.

\textbf{Results and Discussions}

We have previously reported that the fluoride mediated addition of (3-methoxybenzyl)trimethylsilane \textbf{9c} to benzaldehyde in THF at reflux gave the alcohol \textbf{14a} in good yields (Table 1, entry 1).\textsuperscript{4a} This reaction was chosen to develop a new non-fluoride activation method with an initial screen of the three different Lewis bases \textit{t}BuOK, EtOK and Me\textsubscript{3}SiOK carried out. Alkoxides were chosen to encompass their alcohol pKa range of 17, 16 and 12.7 respectively.\textsuperscript{7} Using the identical conditions but replacing fluoride with an alkoxide failed to produce \textbf{14a} even after prolonged reaction times (entries 2-4). An initial interpretation of the failure of any of the alkoxides to mediate the reaction could lead to the conclusion that the autocatalytic cycle as proposed in Scheme 1 is not in operation. But a critical remaining factor which differs from the fluoride and alkoxide reaction conditions is the role of the cationic counter ion. For the fluoride reagents used the counter ion was a \textit{t}Bu\textsubscript{4}N\textsuperscript{+} salt (entry 1), whereas inorganic potassium salts were employed for the unsuccessfully attempted alkoxides mediated reactions (entries 2-4). To fully replicate the counter cation conditions without the need to pre-synthesize alkoxide \textit{t}Bu\textsubscript{4}N\textsuperscript{+} salts, an \textit{in situ} exchange was devised using inexpensive \textit{t}Bu\textsubscript{4}NCl.\textsuperscript{8} Repeating the three reactions with 10 mol\% of alkoxide and \textit{t}Bu\textsubscript{4}NCl we were delighted to obtain
the product in good yields for each alkoxide after 2-3 h reflux (entries 5-7). Remarkably, selecting Me$_3$SiOK, as the weakest base of the three, the reaction was complete at room temperature after 2 h providing 14a in 80% yield when Bu$_4$NCl was included (entry 8).

Table 1. Screening and Optimization of Conditions$^a$

<table>
<thead>
<tr>
<th>entry</th>
<th>silane</th>
<th>LB</th>
<th>mol %</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>14 (% yield)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>![SiMe$_3$]</td>
<td>TBA$^{b,c}$</td>
<td>5</td>
<td>Δ</td>
<td>3</td>
<td>14a (82)</td>
</tr>
<tr>
<td>2</td>
<td>9c</td>
<td>Me$_3$SiOK</td>
<td>10</td>
<td>Δ</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>9c</td>
<td>EtOK</td>
<td>10</td>
<td>Δ</td>
<td>12</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>9c</td>
<td>tBuOK</td>
<td>10</td>
<td>Δ</td>
<td>3</td>
<td>14a (70)</td>
</tr>
<tr>
<td>5</td>
<td>9c</td>
<td>tBuOK/ Bu$_4$NCl</td>
<td>10</td>
<td>Δ</td>
<td>3</td>
<td>14a (74)</td>
</tr>
<tr>
<td>6</td>
<td>9c</td>
<td>EtOK/ Bu$_4$NCl</td>
<td>10</td>
<td>Δ</td>
<td>3</td>
<td>14a (78)</td>
</tr>
<tr>
<td>7</td>
<td>9c</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>Δ</td>
<td>2</td>
<td>14a (78)</td>
</tr>
<tr>
<td>8</td>
<td>9c</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>rt</td>
<td>2</td>
<td>14a (80)</td>
</tr>
<tr>
<td>9</td>
<td>![SiMe$_3$Cl]</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>0°C</td>
<td>0.5</td>
<td>14b (83)$^d$</td>
</tr>
<tr>
<td>10</td>
<td>![SiMe$_3$]</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>rt</td>
<td>2</td>
<td>14c (88)</td>
</tr>
<tr>
<td>11</td>
<td>![SiMe$_3$]</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>0°C</td>
<td>1</td>
<td>14d (59)$^e$</td>
</tr>
<tr>
<td>12</td>
<td>![SiMe$_3$]</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>rt</td>
<td>2</td>
<td>14e (87)</td>
</tr>
<tr>
<td>13</td>
<td>![SiMe$_3$]</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>rt</td>
<td>5</td>
<td>14f (78)$^f$</td>
</tr>
<tr>
<td>14</td>
<td>![SiMe$_3$]</td>
<td>Me$_3$SiOK/ Bu$_4$NCl</td>
<td>10</td>
<td>rt</td>
<td>5</td>
<td>14g (86)</td>
</tr>
</tbody>
</table>

$^a$Trimethylsilanes 0.6 mmol, aldehydes 0.5 mmol. $^b$Tetrabutylammonium triphenyldifluorosilicate (TBAT). $^c$A similar result was obtained for TBAF, see reference 4a. $^d$Trimethylsilane 0.5 mmol and aldehyde 0.6 mmol. $^e$Mixture of propargyl and allene alcohols isolated. $^f$Trimethylsilane 1.0 mmol and aldehyde 0.5 mmol.
To illustrate the generality of the Bu$_4$N$^+$ effect, the reactions of trimethylsilanes of ethyl acetate 6, allyl 7a, propargyl 8, dithiane 10, heteroaryl 12, and aryl 13b with benzaldehyde were carried out. In each case, the reactions were successful at either rt or 0 °C, with the products 14b-g obtained in good to excellent yields (Table 1, entries 9-14). The exciting potential of this approach can be gauged by the wide range of organotrimethylsilanes undergoing addition reactions under one set of conditions. Of specific note is the ester functional group tolerance of 6 which is often sensitive to organometallic reactions and the aromatic derivative 13b often considered too unreactive to effectively participate in addition reactions.

To probe the practicality of Me$_3$SiO$^-$/Bu$_4$N$^+$ mediated addition reactions, a side by side comparison with fluoride activation was carried out for 15 reactions with various trimethylsilanes and carbonyls (Table 2). The allyl 7a, b, propargyl 8, benzyl 9a-e, dithianyl 10 and benzothiazole 11 derivatives were all successful with rt or 0 °C Me$_3$SiO$^-$/Bu$_4$N$^+$ activation providing products 15a-j with no major differential from fluoride under reflux. A significant difference emerged with the reactions of furan 12 and aryl derivatives 13b-e. Results showed that rt Me$_3$SiO$^-$/Bu$_4$N$^+$ conditions were successful in each case giving the products 15k-o in good yields, contrasting with fluoride (at reflux) for which reactions either failed or gave product in low yields (Table 2).
A more detailed comparison of the two silicon activating conditions was carried out for the reaction of $\textit{9c}$ and $\textit{13b}$ with benzaldehyde to generate $\textit{14a}$ and $\textit{14g}$ respectively. Reactions were monitored for product formation over time using HPLC. It was revealing to see that the $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ mediated reactions gave over 90% conversion to $\textit{14a}$ within 1 h whereas fluoride has only reached approx 40% conversion at this time point (Figure 2, top graph). It
would be expected that the participation of the arylsilane 13b in an addition reaction would be more challenging yet the Me₃SiO⁻/Bu₄N⁺ conditions gave complete conversion within 5 h whereas at that time point only a trace of product could be detected when fluoride was used to promote the reaction (Figure 2, bottom graph). Collectively these results illustrate that Me₃SiO⁻/Bu₄N⁺ is superior to fluoride at obtaining carbanion reactivity from organotrimethylsilanes. This could be attributed to the nucleophilicity of the trimethylsilyl oxide being significantly enhanced as its ammonium salt with respect to an inorganic counter-ion.

**Figure 2.** Relative percentage formation of 14a (top) and 14g (bottom) using fluoride (red) and Me₃SiO⁻/Bu₄N⁺ (green) from the reaction of benzaldehyde with 9c and 13b respectively.
Next, the electrophile scope was explored utilizing Me$_3$SiO$^-$/Bu$_4$N$^+$ as silicon activating conditions. Encouragingly, diversely substituted aromatic, heteroaromatic, $\alpha,\beta$-unsaturated and aliphatic aldehydes, ketones and imines all underwent addition reactions with the eleven different trimethylsilanes tested giving the corresponding alcohol and amine products $16a$-$t$ (Table 3).

**Table 3.** Me$_3$SiO$^-$/Bu$_4$N$^+$ promoted addition to carbonyls and imines with various trimethylsilanes.$^a$

\[
\begin{align*}
R^1\text{-SiMe}_3 + R^2\text{X} & \rightarrow R^1\text{X} + \text{NMe}_2 \\
16a, 16b, 16c, 16d, 16e, 16f, 16g, 16h, 16i, 16j, 16k, 16l, 16m, 16n, 16o, 16p, 16q, 16r, 16s, 16t
\end{align*}
\]
Due to their synthetic importance, yet rarity of use in addition reactions, specific attention was given to the aryl-Si(Me)\textsubscript{3} derivatives 12 and 13a-e (Table 4).\textsuperscript{9} In the case of the furan 12 and the \(\sigma\)-substituted aryl derivatives 12b, c 10 mol\% of Me\textsubscript{3}SiO\textsuperscript{-}/Bu\textsubscript{4}N\textsuperscript{+} was sufficient to progress the reaction to completion, giving products 17a-j in good to excellent yields. For the \(p\)-substituted arenes 13d, e a catalytic amount of Me\textsubscript{3}SiO\textsuperscript{-}/Bu\textsubscript{4}N\textsuperscript{+} proved insufficient for the reaction to reach completion though increasing the amount of Me\textsubscript{3}SiO\textsuperscript{-}/Bu\textsubscript{4}N\textsuperscript{+} to 1.5 equiv gave the diaryl-alcohols 17k, l in yields of 68 and 64\% respectively. A plausible rationale for this experimental observation is the failure of the autocatalytic cycle in these examples due to the nature of di-aryl alkoxide that is generated \textit{in situ}. But as the activating reagents Me\textsubscript{3}SiOK and Bu\textsubscript{4}NCl are inexpensive, non-toxic and easily separated from products, their use in greater than catalytic quantities when necessary is not considered a significant drawback. Of the series examined, the only derivative that failed under these conditions was phenyltrimethylsilane 13a which denotes the current reactivity limit of the method. Investigations remain ongoing to devise conditions to further progress the reactivity limit of our method to promote reactions with substrates such as 13a which have, as would be expected, the lowest reactivity.
Table 4. Aryl and heteroaryl addition to carbonyls.\textsuperscript{a}

\begin{align*}
\text{Ar-SiMe$_3$} & + R\text{CHO} \rightarrow \text{R-OH} \\
12, 13a-e & \rightarrow 17a-I
\end{align*}

\begin{align*}
\text{Ph} & \quad \text{17a, 82\%} \\
\text{Br} & \quad \text{17b, 83\%} \\
\text{Cl} & \quad \text{17c, 87\%} \\
\text{Cl} & \quad \text{17d, 86\%} \\
\text{OH} & \quad \text{17e, 84\%} \\
\text{Cl} & \quad \text{17f, 81\%} \\
\text{OH} & \quad \text{17g, 86\%} \\
\text{OH} & \quad \text{17h, 83\%} \\
\text{CF$_3$} & \quad \text{17i, 72\%} \\
\text{CF$_3$} & \quad \text{17j, 88\%} \\
\text{Cl} & \quad \text{17k, 68\%} \\
\text{Br} & \quad \text{17l, 64\%}
\end{align*}

\textsuperscript{a}Trimethylsilanes 0.6 mmol, aldehydes 0.5 mmol. \textsuperscript{b}Worked up with water.

\textsuperscript{c}Trimethylsilanes 0.75 mmol, aldehydes 0.25 mmol, Me$_3$SiOK/Bu$_4$NCl 0.375 mmol. \textsuperscript{d}Trimethylsilanes 0.375 mmol, aldehydes 0.25 mmol, Me$_3$SiOK/Bu$_4$NCl 0.375 mmol.

\textbf{Conclusion}

In summary, a new Lewis base activation of organotrimethylsilanes utilizing Me$_3$SiO$^-$/Bu$_4$N$^+$ has been developed, with the key to its success lying in use of a Bu$_4$N$^+$ cation, which is superior to fluoride in promoting trimethylsilane addition reactions. Once initiated, reactions proceed to completion via an autocatalytic cycle involving the \textit{in situ} formed alkoxide. For reactions where the autocatalytic cycle is not effective, stoichiometric amounts of activators can be used. Taken together, these results indicate that use of bench stable trimethylsilyl organometallics, many of which are already commercially available, may become increasingly attractive to the wider...
community of synthetic chemists. Investigations into a general asymmetric approach to using organotrimethylsilanes is on-going. A further expansion of the concepts presented in this paper for Peterson olefination reactions is underway and will be reported in due course.

**Experimental Section**

**General Information.** All reactions involving air-sensitive reagents were performed under nitrogen either in oven- or flame-dried glassware using syringe-septum cap technique. All solvents were purified and degassed before use. 2,2,6,6-Tetramethylpiperidine TMP(H) was distilled from CaH₂ prior to use. THF was purified under nitrogen over Na/benzophenone ketyl. BuLi was purchased as a 2.5 M solution in hexanes. The exact concentration of the BuLi was determined by titration with diphenylacetic acid in THF prior to use. KOrBu was purchased as a 1.0 M solution in THF. Tetrabutylammonium difluorotriphenylsilicate (TBAT) was used as received. Pre-weighed amounts of Me₃SiOK and Bu₄NCl were stored in desiccator utilizing P₂O₅ as a desiccant and used immediately upon removal from the desiccator. Aldehydes were purified by distillation or silica gel chromatography prior to use. Chromatographic separations were carried out under pressure on Merck silica gel 60 or Aluminium oxide 60 using flash-column techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates with UV light (254 nm) as visualizing agent. ¹H, ¹³C NMR spectra were recorded at room temperature on a 400 MHz spectrometer. HRMS measurements acquired with a TOF mass analyzer. Yield refers to isolated yield after column chromatography.

Compounds 6, 7a, 7b, 8, 9a, 10, 11 and 13a are commercially available.
Compounds 9b-e\(^{4a}\), 12\(^{10}\), 13b\(^{11}\), 13d\(^{11}\) and 13e\(^{12}\) are prepared according to the literature procedures.

**Trimethyl(2-(trifluoromethyl)phenyl)silane, 13c.\(^{13}\)** A solution of 1-bromo-2-(trifluoromethyl)benzene (1.8 g, 8 mmol) in THF (80 mL) at -78 °C was treated dropwise with s-BuLi (1.3 M, 9.2 mL, 12 mmol) under a N\(_2\) atmosphere. The reaction mixture was stirred for 1 h at -78 °C and chlorotrimethylsilane (1.6 mL, 12 mmol) was added. The reaction mixture was stirred for a further 1 h at -78 °C and then slowly warmed to rt. The solvent removed under reduced pressure, aq HCl (2 M, 40 mL) was added to the residue and extracted with diethyl ether (50 x 3 mL). The organic layers were combined, washed with brine (50 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane (100%) afforded 13c as a colorless oil (1.43 g, 82%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.74 – 7.66 (m, 2H), 7.53 – 7.42 (m, 2H), 0.34 (s, 9H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta\) 138.5, 136.0, 135.0 (q, \(J = 31.0\) Hz), 130.8 (q, \(J = 1.2\) Hz), 129.1, 126.1 (q, \(J = 5.4\) Hz), 125.1 (q, \(J = 273.2\) Hz), 0.4 (q, \(J = 2.6\) Hz) ppm.

**2-(3-Methoxyphenyl)-1-phenylethanol, 14a.\(^{4a}\)**

Addition of 9c to benzaldehyde using tBuOK/Bu\(_4\)NCl in THF.

A solution of (3-methoxybenzyl)trimethylsilane, 9c (116 mg, 0.6 mmol), benzaldehyde (51 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\(_4\)NCl (14 mg, 0.05 mmol) and tBuOK (50 \(\mu\)L, 0.05 mmol, 1M in THF) under N\(_2\) and the resulting solution was stirred at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to
dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 14a as a colorless oil (80 mg, 70%).

Addition of 9c to benzaldehyde using EtOK/But4NCl in THF.

A solution of (3-methoxybenzyl)trimethylsilane, 9c (116 mg, 0.6 mmol), benzaldehyde (51 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried But4NCl (14 mg, 0.05 mmol) and EtOK (4 mg, 0.05 mmol) under N2 and the resulting solution was stirred at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL). Organic layer were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 14a as a colorless oil (84 mg, 74%).

Addition of 9c to benzaldehyde using Me3SiOK/But4NCl in THF.

A solution of (3-methoxybenzyl)trimethylsilane, 9c (116 mg, 0.6 mmol) and benzaldehyde (51 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried But4NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N2 at rt for 2 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL). Organic layer were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 14a as a colorless oil (91 mg, 80%).

1H NMR (400 MHz, CDCl3): δ 7.38 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 7.22 (t, J = 7.9 Hz, 1H), 6.82 – 6.76 (m, 2H), 6.72 (s, 1H), 4.90 (dd, J = 8.3, 4.8 Hz, 1H), 3.77 (s, 3H, OCH3), 3.06 – 2.92 (m, 2H), 1.98 (s, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ 159.7, 143.7, 139.5, 129.5,
Ethyl 3-hydroxy-3-phenylpropanoate, 14b. A solution of ethyl 2-(trimethylsilyl)acetate, 6 (92 μL, 0.50 mmol) and benzaldehyde (61 μL, 0.6 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N₂ at 0 °C for 30 min and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 14b as a colorless oil (81 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ 7.41 – 7.25 (m, 5H), 5.13 (dd, J = 8.7, 4.1 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 2.80 – 2.67 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 172.5, 142.6, 128.7, 127.9, 125.8, 70.5, 61.0, 43.5, 14.3 ppm. HRMS–ESI [M+Na]⁺: 217.0836, C₁₁H₁₄O₃Na requires 217.0814.

1-Phenylbut-3-en-1-ol, 14c. A solution of allyltrimethylsilane, 7a (96 μL, 0.6 mmol) and benzaldehyde (51 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N₂ at rt for 2 h. 2 M HCl (10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL), the organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 14c as a colorless oil (65 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ 7.38 – 7.24 (m, 5H), 5.87 – 5.75 (m, 1H), 5.21 – 5.11 (m, 2H), 4.74 (dd, J = 7.3,
5.7 Hz, 1H), 2.59 – 2.44 (m, 2H), 2.04 (bs, 1H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 144.0, 134.6, 128.5, 127.7, 125.9, 118.6, 73.4, 44.0 ppm. MS–ESI [M–H]: 147.06, \(\text{C}_{10}\text{H}_{11}\text{O}\) requires 147.08.

**1-Phenylbuta-2,3-dien-1-ol, 14d-(1) (major) and 1-phenylbut-3-yn-1-ol, 14d-(2) (minor).\(^{16}\)**

A solution of trimethyl(prop-2-yn-1-yl)silane, 8 (67 mg, 0.60 mmol) and benzaldehyde (51 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\(_4\)NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under \(\text{N}_2\) at 0 °C for 1 h. Solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded a mixture (70:30) of products 14d-(1,2) as a colorless oil (43 mg, 59%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.44 – 7.27 (m, 5H), 5.45 (q, \(J = 6.5\) Hz, 0.7H), 5.31 – 5.25 (m, 0.7H), 4.98 – 4.91 (m, 1.4H), 4.88 (t, \(J = 6.3\) Hz, 0.3H), 2.65 (dd, \(J = 6.5, 2.6\) Hz, 0.6H), 2.41 (br s, 0.3H), 2.39 (s, 0.3H), 2.18 (brs, 0.7H), 2.08 (t, \(J = 2.6\) Hz, 0.3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 207.2, 143.0, 142.6, 128.7, 128.6, 128.1, 128.0, 126.2, 125.9, 95.3, 80.8, 78.4, 72.5, 72.1, 71.1, 29.6 ppm. MS–ESI [M–H]: 145.04, \(\text{C}_{10}\text{H}_{11}\text{O}\) requires 145.07.

Note: Isolation of mixtures of buta-2,3-dien-1-ols and but-3-yn-1-ols from fluoride mediated addition reactions of trimethyl(prop-2-yn-1-yl)silane has been previously reported.\(^{16}\)

**1,3-Dithian-2-yl)(phenyl)methanol, 14e.\(^{17}\)** A solution of (1,3-dithian-2-yl)trimethylsilane, 10 (116 mg, 0.6 mmol) and benzaldehyde (51 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was
treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N$_2$ at rt for 2 h and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layer were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded the product 14e as a colorless solid, mp 59–61 °C (98 mg, 87%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.45 – 7.30 (m, 5H), 4.92 (d, $J = 7.5$, 1H), 4.08 (d, $J = 7.5$ Hz, 1H), 3.01 – 2.89 (m, 3H), 2.78 – 2.68 (m, 2H), 2.13 – 1.91 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.3, 128.6, 128.4, 127.0, 74.9, 52.9, 28.3, 27.7, 25.5 ppm. HRMS–ESI [M+Na]$^+$: 249.0381, C$_{11}$H$_{14}$ONaS$_2$ requires 249.0384.

**Furan-2-yl(phenyl)methanol, 14f.$^{18}$** A solution of furan-2-yltrimethylsilane, 12 (140 mg, 1.0 mmol) and benzaldehyde (51 $\mu$L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N$_2$ at rt for 5 h and 0.2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layer were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded the product 14f as a yellow oil (68 mg, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.46 – 7.29 (m, 6H), 6.31 (dd, $J = 3.2$, 1.8 Hz, 1H), 6.11 (dt, $J = 3.2$, 0.7 Hz, 1H), 5.83 (s, 1H), 2.39 (bs, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 156.1, 142.7, 140.9, 128.6, 128.2, 126.7, 110.4, 107.6, 70.3 ppm. HRMS–EI [M]$^+$: 174.0679, C$_{11}$H$_{10}$O$_2$ requires 174.0681.
(2-Chlorophenyl)(phenyl)methanol, 14g.\textsuperscript{19} A solution of (2-chlorophenyl)trimethylsilane, 13b (111 mg, 0.6 mmol) and benzaldehyde (51 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried \(\text{Bu}_4\text{NCl}\) (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under \(\text{N}_2\) at rt for 5 h and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 14g as a colorless oil (94 mg, 86%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.60 (dd, \(J = 7.7, 1.6\) Hz, 1H), 7.43 – 7.18 (m, 8H), 6.22 (d, \(J = 3.1\) Hz, 1H), 2.43 – 2.35 (m, 1H) ppm. \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 142.4, 141.1, 132.7, 129.7, 128.9, 128.6, 128.2, 127.9, 127.2, 127.0, 72.8 ppm. MS–ESI [(M+H–H\(_2\)O)]\(^{+}\): 201.05, \(\text{C}_{13}\text{H}_{10}\text{Cl}\) requires 201.04.

2-Phenylpent-4-en-2-ol, 15a.\textsuperscript{20}

Addition of 7a to acetophenone using TBAT in THF at reflux.

A solution of allyltrimethylsilane 7a (114 mg, 1.0 mmol) and acetophenone (59 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol), the resulting solution was stirred under \(\text{N}_2\) at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15a as a colorless oil (72 mg, 89%).

Addition of 7a to acetophenone using \(\text{Me}_3\text{SiOK/}\text{Bu}_4\text{NCl}\) in THF at reflux.
A solution of allyltrimethylsilane, 7a (114 mg, 1.0 mmol) and acetophenone (59 µL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N₂ at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layer were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15a as a colorless oil (62 mg, 77%).

1H NMR (400 MHz, CDCl₃): δ 7.47 – 7.41 (m, 2H), 7.38 – 7.31 (m, 2H), 7.27 – 7.21 (m, 1H), 5.69 – 5.56 (m, 1H), 5.18 – 5.08 (m, 2H), 2.69 (dd, J = 13.7, 6.4 Hz, 1H), 2.50 (dd, J = 13.7, 8.3 Hz, 1H), 2.04 (bs, 1H), 1.55 (s, 3H) ppm. 13C NMR (100 MHz, CDCl₃): δ 147.8, 133.8, 128.3, 126.8, 124.9, 119.6, 73.8, 48.6, 30.1 ppm. MS – ESI [M+H]⁺: 163.11, C₁₁H₁₅O requires 163.10.

1-(3,4-Dimethoxyphenyl)-3-methylbut-3-en-1-ol, 15b.

Addition of 7b to 3,4-dimethoxybenzaldehyde using TBAT in THF at reflux.

A solution of trimethyl(2-methylallyl)silane, 7b (102 µL, 0.60 mmol) and 3,4-dimethoxybenzaldehyde (83 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27.0 mg, 0.05 mmol) and the resulting solution was stirred under N₂ at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 15b as a colorless solid (97 mg, 87%).
Addition of 7b to 3,4-dimethoxybenzaldehyde using Me₃SiOK/Bu₄NCl in THF at rt.

A solution of trimethyl(2-methylallyl)silane, 7b (102 µL, 0.60 mmol) and 3,4-dimethoxybenzaldehyde (83 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N₂ at rt for 3 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 15b as a colorless solid, mp 72–74 °C (93 mg, 84%).

¹H NMR (400 MHz, CDCl₃): δ 6.95 (d, J = 1.7 Hz, 1H), 6.90 (dd, J = 8.2, 1.7 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 4.93 (s, 1H), 4.86 (s, 1H), 4.77 (dd, J = 8.7, 4.8 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.49 – 2.36 (m, 2H), 1.80 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 149.2, 148.5, 142.6, 136.9, 118.1, 114.1, 111.1, 109.1, 71.4, 56.1, 56.0, 48.4, 22.5 ppm. IR (neat): 4320, 1592, 1508 cm⁻¹. HRMS−ESI [M+Na]⁺: 245.1157, C₁₃H₁₈O₃Na requires 245.1154.

1-(4-Methoxyphenyl)buta-2,3-dien-1-ol, 15c-1 (major) and 1-(4-Methoxyphenyl)but-3-yn-1-ol, 15c-2 (minor).¹⁶

Addition of 8 to p-anisaldehyde using TBAT in THF at rt.

A solution of trimethyl(prop-2-yn-1-yl)silane, 8 (75 µL, 0.50 mmol) and p-anisaldehyde (73 µL, 0.6 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27.0 mg, 0.05 mmol) and the resulting solution was stirred under N₂ at rt for 30 min. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (15 x 3 mL), organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and
concentrated to dryness. Purification by silica gel chromatography eluting with petroleum ether/ethyl acetate (90:10) yielded a mixture (84:16) of products 15c-(1,2) as a yellow oil (78 mg, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38 – 7.27 (m, 2H), 6.95 – 6.83 (m, 2H), 5.47 – 5.39 (m, 0.84H), 5.26 – 5.19 (m, 0.84H), 4.97 – 4.87 (m, 1.68H), 4.86 – 4.79 (m, 0.16H), 3.82 – 3.78 (m, 3H), 2.65 – 2.60 (m, 0.32H), 2.38 (s, 0.16H), 2.16 (s, 0.84H), 2.08 – 2.05 (m, 0.16H) ppm.

Addition of 8 to $\rho$-anisaldehyde using Me$_3$SiOK/Bu$_4$NCl in THF at 0 °C. A solution of trimethyl(prop-2-yn-1-yl)silane, 8 (75 $\mu$L, 0.50 mmol) and 4-bromobenzaldehyde (73 $\mu$L, 0.60 mmol) in anhydrous THF (2.0 mL) was treated dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N$_2$ at 0 °C for 15 min. Solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), the organic layers were combined and washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with petroleum ether/ethyl acetate (90:10) yielded a mixture (93:7) of products 15c-(1,2) as a yellow oil (72 mg, 82%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38 – 7.28 (m, 2H), 6.94 – 6.84 (m, 2H), 5.47 – 5.39 (m, 0.93H), 5.26 – 5.19 (m, 0.93H), 4.97 – 4.87 (m, 1.86H), 4.86 – 4.79 (m, 0.07H), 3.82 – 3.77 (m, 3H), 2.65 – 2.60 (m, 0.14H), 2.17 – 2.12 (m, 0.93H), 2.08 – 2.05 (m, 0.07H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 207.1, 159.5, 159.4, 135.2, 134.8, 127.6, 127.2, 114.0, 113.9, 95.4, 81.0, 78.3, 72.1, 71.7, 71.0, 55.5, 55.4, 29.5 ppm. HRMS–ESI [M+H]$^+$: 177.0924, C$_{11}$H$_{13}$O$_2$ requires 177.0916.

Note: Isolation of mixtures of buta-2,3-dien-1-ols and but-3-yn-1-ols from fluoride mediated addition reactions of trimethyl(prop-2-yn-1-yl)silane has been previously reported.$^{17}$
1-Benzylcyclohexanol, 15d.\textsuperscript{4a}

Addition of 9a to cyclohexanone using TBAT in THF at rt.

A solution of benzyltrimethylsilane, 9a (164 mg, 1.0 mmol) and cyclohexanone (52 µL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (54 mg, 0.10 mmol) and the resulting solution was stirred under N\textsubscript{2} at rt for 12 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). The organic layers were combined, washed with brine (10 mL), dried over sodium sulfate, and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15d as a colorless solid (69 mg, 71%).

Addition of 9a to cyclohexanone using Me\textsubscript{3}SiOK/Bu\textsubscript{4}NCl in THF at rt.

A solution of benzyltrimethylsilane, 9a (164 mg, 1.0 mmol) and cyclohexanone (52 µL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\textsubscript{4}NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) and the resulting solution was stirred under N\textsubscript{2} at rt for 5 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (10 x 3 mL), the organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15d as a colorless solid, mp 41–43 °C (59 mg, 62%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.34 – 7.18 (m, 5H), 2.75 (s, 2H), 1.65 – 1.38 (m, 10H), 1.25 (brs, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 137.1, 130.6, 128.1, 126.4, 71.1, 48.7, 37.3, 25.8, 22.1 ppm. HRMS–EI [M]\textsuperscript{+}: 190.1361, C\textsubscript{13}H\textsubscript{18}O requires 190.1358.

2-(2-Methoxyphenyl)-1-m-tolylethanol, 15e.\textsuperscript{4a}
Addition of 9b to m-tolualdehyde using TBAT in THF at reflux.

A solution of (2-methoxybenzyl)trimethylsilane, 9b (117 mg, 0.60 mmol) and m-tolualdehyde (60 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27.0 mg, 0.05 mmol) and the resulting solution was stirred under N₂ at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (10 x 3 mL), the organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15e as a colorless solid (74 mg, 61%).

Addition of 9b to m-tolualdehyde using Me₃SiOK/Bu₄NCl in THF at rt.

A solution of (2-methoxybenzyl)trimethylsilane, 9b (117 mg, 0.60 mmol) and m-tolualdehyde (60 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) the resulting solution was stirred under N₂ at rt for 3 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15e as a colorless solid, mp 51–53 °C (77 mg, 63%).

¹H NMR (400 MHz, CDCl₃): δ 7.27 – 7.15 (m, 4H), 7.13 – 7.09 (m, 2H), 6.93 – 6.86 (m, 2H), 4.98 – 4.88 (m, 1H), 3.86 (s, 1H), 3.14 – 3.07 (m, 1H), 3.01 – 2.92 (m, 1H), 2.48 (s, 1H), 2.36 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 157.7, 144.7, 138.0, 131.6, 128.3, 128.1 (2 x C), 126.9, 126.5, 123.0, 120.9, 110.6, 74.4, 55.5, 41.3, 21.6 ppm. HRMS–ESI [M+Na]⁺: 265.1196, C₁₆H₁₈O₂Na requires 265.1204.
2-(3-Bromophenyl)-1-(3-methoxyphenyl)propan-2-ol, 15f.

Addition of 9c to 3'-bromoacetophenone using TBAT in THF at reflux.

A solution of (3-methoxybenzyl)trimethylsilane, 9c (194 mg, 1.0 mmol) and 3'-bromoacetophenone (64 µL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) under N\textsubscript{2} and the resulting solution was stirred at 70 ºC for 4 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (10 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15f as a yellow oil (138 mg, 85%).

Addition of 9c to 3'-bromoacetophenone using Me\textsubscript{3}SiOK/Bu\textsubscript{4}NCl in THF at reflux.

A solution of (3-methoxybenzyl)trimethylsilane, 9c (194 mg, 1.0 mmol) and 3'-bromoacetophenone (64 µL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\textsubscript{4}NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N\textsubscript{2} and the resulting solution was stirred at reflux for 5 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (10 x 3 mL), organic layers combined, washed with water (10 mL), brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane:ethyl acetate (96:4) yielded 15f as a yellow oil (117 mg, 73%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.58 (s, 1H), 7.38 (d, \textit{J} = 7.9 Hz, 1H), 7.31 (d, \textit{J} = 7.9 Hz, 1H), 7.23 – 7.12 (m, 2H), 6.77 (d, \textit{J} = 7.8 Hz, 1H), 6.62 (d, \textit{J} = 7.8 Hz, 1H), 6.50 (s, 1H), 3.70 (s, 3H), 3.08 (d, \textit{J} = 13.2 Hz, 1H), 2.97 (d, \textit{J} = 13.2 Hz, 1H), 1.92 (s, 1H), 1.54 (s, 3H) ppm. \textsuperscript{13}C NMR
(100 MHz, CDCl$_3$): $\delta$ 159.4, 150.0, 137.6, 129.6, 129.2, 128.4, 123.7, 122.9, 122.4, 115.9, 112.6, 74.1, 55.1, 50.3, 29.4 ppm. IR (neat): 3490, 2952, 1585 cm$^{-1}$. HRMS–ESI [M+Na]$^+$: 343.0324, C$_{16}$H$_{17}$O$_2$NaBr requires 343.0310.

4-(2-Hydroxy-2-(5-methylfuran-2-yl)ethy1)-N,N-diisopropylbenzamide, 15g.

Addition of 9d to 5-methylfurfural using TBAT in THF at reflux.

A solution of N,N-diisopropyl-4-((trimethylsilyl)methyl)benzamide, 9d (175 mg, 0.60 mmol) and 5-methylfurfural (50 μL, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) under N$_2$ and the resulting solution was stirred at 70 °C for 2 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 15g as a yellow oil (114 mg, 70%).

Addition of 9d to 5-methylfurfural using Me$_3$SiOK/Bu$_4$NCl in THF at rt.

A solution of N,N-diisopropyl-4-((trimethylsilyl)methyl)benzamide, 9d (175 mg, 0.60 mmol) and 5-methylfurfural (50 μL, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N$_2$ at rt for 3 h. The solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 15g as yellow oil (112 mg, 68%).
^1^H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) 7.24 – 7.16 (m, 4H), 6.07 (d, \( J = 3.1 \) Hz, 1H), 5.89 – 5.86 (m, 1H), 4.81 (dd, \( J = 7.9, 5.5 \) Hz, 1H), 3.68 (brs, 2H), 3.19 – 3.05 (m, 2H), 2.75 (s, 1H), 2.29 (s, 3H), 1.31 (s, 12H) ppm. ^13^C NMR (100 MHz, CDCl\textsubscript{3}): \( \delta \) 171.1, 153.9, 151.6, 138.6, 136.9, 129.5, 125.7, 107.2, 106.0, 68.5, 42.0, 20.7, 13.5 ppm. IR (neat): 3308, 2943, 1710, 1599 cm\textsuperscript{-1}. HRMS–ESI [M+H]^+: 330.2078, C\textsubscript{20}H\textsubscript{28}O\textsubscript{3}N requires 330.2069.

\( (E)\)-1-(4-Bromophenyl)-4-phenylbut-3-en-2-ol, 15h.\textsuperscript{4a}

Addition of \( \textbf{9e} \) to \textit{trans}-cinnamaldehyde using TBAT in THF at reflux.

A solution of (4-bromobenzyl)trimethylsilane, \( \textbf{9e} \) (146 mg, 0.60 mmol) and \textit{trans}-cinnamaldehyde (63 \( \mu \)L, 0.50 mmol)) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) under N\textsubscript{2} and the resulting solution was stirred at reflux for 4 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded \textbf{15h} as a colorless solid (108 mg, 71%).

Addition of \( \textbf{9e} \) to \textit{trans}-cinnamaldehyde using Me\textsubscript{3}SiOK/Bu\textsubscript{4}NCl in THF at rt.

A solution of (4-bromobenzyl)trimethylsilane, \( \textbf{9e} \) (146 mg, 0.60 mmol) and \textit{trans}-cinnamaldehyde (65 \( \mu \)L, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\textsubscript{4}NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N\textsubscript{2} at rt for 3 h. The solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel
chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 15h as a colorless solid, mp 80–82 °C, (106 mg, 70%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.44 (d, $J = 7.1$ Hz, 2H), 7.39 – 7.21 (m, 5H), 7.13 (d, $J = 7.1$ Hz, 2H), 6.57 (d, $J = 16.0$ Hz, 1H), 6.24 (dd, $J = 16.0$, 6.4 Hz, 1H), 4.54 – 4.45 (m, 1H), 2.95 – 2.80 (m, 2H), 1.71 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 136.7, 136.4, 131.5, 131.3, 131.1, 130.8, 128.6, 127.8, 126.5, 120.5, 73.3, 43.4 ppm. HRMS – ESI [M–H]$^-$: 301.0215, C$_{16}$H$_{14}$OBr requires 301.0228.

(E)-1-(1,3-Dithian-2-yl)-3-phenylprop-2-en-1-ol, 15i.

Addition of 10 to trans-cinamaldehyde using TBAT in THF at reflux.

A solution of (1,3-dithian-2-yl)trimethylsilane, 10 (116 mg, 0.6 mmol) and trans-cinamaldehyde (63 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) and the resulting solution was stirred under N$_2$ at reflux for 3 h. The solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15i as a colorless solid (104 mg, 82%).

Addition of 10 to trans-cinamaldehyde using Me$_3$SiOK/Bu$_4$NCl in THF at rt.

A solution of (1,3-dithian-2-yl)trimethylsilane, 10 (116 mg, 0.6 mmol) and trans-cinamaldehyde (63 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N$_2$ at rt for 3 h. The solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL),
dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15i as a colorless solid, mp 58–60 °C (110 mg, 87%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.45 – 7.38 \text{ (m, 2H)}, 7.35 – 7.21 \text{ (m, 3H)}, 6.74 \text{ (d, } J = 15.8 \text{ Hz, 1H}), 6.35 \text{ (dd, } J = 15.8, 6.5 \text{ Hz, 1H}), 4.59 – 7.52 \text{ (m, 1H)}, 4.02 \text{ (d, } J = 6.8 \text{ Hz, 1H}), 3.00 – 2.91 \text{ (m, 2H)}, 2.82 – 2.72 \text{ (m, 2H)}, 2.67 \text{ (d, } J = 3.7 \text{ Hz, 1H}), 2.15 – 1.92 \text{ (m, 2H)} \text{ ppm.} \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta 136.4, 132.9, 128.7, 128.0, 126.8, 73.4, 52.2, 28.4, 28.1, 25.7 \text{ ppm. IR (neat): 3434, 2938, 2883, 1494 cm}^{-1}. \text{ HRMS–ESI [M+Na]}^{\dagger}: 275.0538, \text{ C}_{13}\text{H}_{16}\text{ONaS}_{2} \text{ requires 275.0540.}

**Benzothiazol-2-yl(phenyl)methanol, 15j.**

Addition of 11 to benzaldehyde using TBAT in THF at rt.

A solution of 2-(trimethylsilyl)benzothiazole, 11 (124 mg, 0.6 mmol) and benzaldehyde (51 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) the resulting solution was stirred under N\(_2\) at rt for 3 h. Solvent removed under reduced pressure and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 15j as a colorless solid (98 mg, 81%).

Addition of 11 to benzaldehyde using Me\(_3\)SiOK/Bu\(_4\)NCl in THF at 0 °C.

A solution of 2-(trimethylsilyl)benzothiazole, 11 (124 mg, 0.6 mmol) and benzaldehyde (51 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\(_4\)NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N\(_2\) at 0 °C for 3 h. The solvent was removed under reduced pressure and 1 M HCl (10 mL) added. The residue was
extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL),
dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography
eluting with cyclohexane/ethyl acetate (90:10) yielded 15j as a colorless solid, mp 108–110 °C
(90 mg, 75%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.99 (d, $J = 8.1$ Hz, 1H), 7.84 (dd, $J = 8.1$, 1H), 7.57 – 7.50 (m,
2H), 7.46 (t, $J = 7.7$ Hz, 1H), 7.42 – 7.31 (m, 4H), 6.15 (s, 1H), 3.84 (s, 1H) ppm. $^{13}$C NMR (100
MHz, CDCl$_3$): $\delta$ 174.8, 152.7, 141.1, 135.5, 129.0, 128.9, 126.9, 126.3, 125.3, 123.3, 121.9, 74.6
ppm. IR (neat): 3161, 2924, 2715, 1501 cm$^{-1}$. HRMS–ESI [M+Na]$^+$: 264.0448, C$_{14}$H$_{11}$NONaS
requires 264.0459.

[(3,4-Dimethoxyphenyl)(furan-2-yl)methoxy]trimethylsilane, 15k.

Addition of 12 to 3,4-dimethoxybenzaldehyde using TBAT in THF at reflux.

A solution of furan-2-yltrimethylsilane, 12 (140 mg, 1.0 mmol) and 3,4-dimethoxybenzaldehyde
(83 mg, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol)
under N$_2$ and the resulting solution was stirred at reflux for 4 h. The reaction mixture was cooled
to rt, solvent removed under reduced pressure and 10 mL water was added. The residue was
extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL),
dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography
eluting with cyclohexane/ethyl acetate (95:5) yielded 15k as a colorless oil (64 mg, 42%).

Addition of 12 to 3,4-dimethoxybenzaldehyde using Me$_3$SiOK/Bu$_4$NCl in THF at rt.

A solution of furan-2-yltrimethylsilane, 12 (140 mg, 1.0 mmol) and 3,4-dimethoxybenzaldehyde
(83 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05
mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N$_2$ at rt for 5
h. Water (10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). The organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15k as a colorless oil (116 mg, 76%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.35 (s, 1H), 6.98 (d, $J = 1.9$ Hz, 1H), 6.92 (dd, $J = 8.2$, 1.9 Hz, 1H), 6.83 (d, $J = 8.2$ Hz, 1H), 6.28 (dd, $J = 3.2$, 1.9 Hz, 1H), 6.06 (d, $J = 3.2$ Hz, 1H), 5.73 (s, 1H), 3.88 – 3.86 (m, 6H), 0.11 (s, 9H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.9, 148.94, 148.6, 142.3, 134.5, 118.9, 110.8, 110.2, 109.9, 107.1, 70.2, 56.02, 55.98, 0.1 ppm. IR (neat): 2938, 1515, 1459 cm$^{-1}$. HRMS–EI [M]$^+$: 306.1281, C$_{16}$H$_{22}$O$_4$Si requires 306.1287.

[2-Chlorophenyl](mesityl)methanol, 15l.

Addition of 13b to mesitaldehyde using TBAT in THF at reflux.

A solution of (2-chlorophenyl)trimethylsilane, 13b (111 mg, 0.6 mmol) and mesitaldehyde (74 μL, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) under N$_2$ and the resulting solution was stirred at reflux for 6 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15l as a colorless solid (11 mg, 8%).

Addition of 13b to mesitaldehyde using Me$_3$SiOK/Bu$_4$NCl in THF at rt.

A solution of (2-chlorophenyl)trimethylsilane, 13b (111 mg, 0.6 mmol) and mesitaldehyde (74 μL, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N$_2$ and the resulting solution was stirred at rt for 5 h. The
solvent was removed under reduced pressure and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15l as a colorless solid, mp 91–93 °C (103 mg, 79%).

1H NMR (400 MHz, CDCl3): δ 7.47 – 7.41 (m, 1H), 7.38 – 7.32 (m, 1H), 7.25 – 7.18 (m, 2H), 6.85 (s, 2H), 6.38 (d, J = 3.7 Hz, 1H), 2.38 (d, J = 3.7 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 6H) ppm.

13C NMR (100 MHz, CDCl3): δ 140.0, 137.3, 137.2, 134.0, 134.2, 133.2, 130.3, 129.9, 129.2, 128.7, 126.6, 70.6, 21.2, 21.0 ppm. IR (neat): 3448, 2917, 1438 cm⁻¹. HRMS–ESI [M+Na]⁺: 283.0854, C16H17ONaCl requires 283.0866.

(4-Fluorophenyl)(2-(trifluoromethyl)phenyl)methanol, 15m.

Addition of 13c to 4-fluorobenzaldehyde using TBAT in THF at reflux.

A solution of trimethyl(2-(trifluoromethyl)phenyl)silane, 13c (131 mg, 0.6 mmol) and 4-fluorobenzaldehyde (62 mg, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with TBAT (27 mg, 0.05 mmol) under N₂ and the resulting solution was stirred at reflux for 6 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15m as a colorless oil, (12 mg, 9%).

Addition of 13c to 4-fluorobenzaldehyde using Me₃SiOK/Bu₄NCl in THF at rt.
A solution of trimethyl(2-(trifluoromethyl)phenyl)silane, 13c (131 mg, 0.6 mmol) and 4-fluorobenzaldehyde (62 mg, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N₂ and the resulting solution was stirred at rt for 5 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15m as a colorless oil (108 mg, 80%).

¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.05 – 6.98 (m, 2H), 6.29 (s, 1H), 2.20 (bs, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 162.3 (d, J = 246.1 Hz), 142.4, 138.6 (d, J = 3.2 Hz), 132.6 (q, J = 1.1 Hz), 129.5, 128.3 (d, J = 8.1 Hz), 128.0, 127.7 (q, J = 30.3 Hz), 125.8 (q, J = 5.8 Hz), 124.5 (q, J = 274.0 Hz), 115.4 (d, J = 21.5 Hz), 70.4 (q, J = 2.4 Hz) ppm. IR (neat): 3267, 1508 cm⁻¹. HRMS – ESI [M–H]⁻: 269.0584, C₁₄H₉OF₄ requires 269.0590.

(4-Chlorophenyl)(4-(dimethylamino)phenyl)methanol, 15n.

Addition of 13d to 4-(dimethylamino)benzaldehyde using Me₃SiOK/Bu₄NCl in THF at 0 °C.

A solution of (4-chlorophenyl)trimethylsilane, 13d (70 mg, 0.375 mmol) and 4-(dimethylamino)benzaldehyde (37 mg, 0.25 mmol) in anhydrous THF (1.0 mL) was treated with dried Bu₄NCl (104 mg, 0.375 mmol) and TMSOK (48 mg, 0.375 mmol) the resulting solution was stirred under N₂ at °C for 5 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) added, the residue stirred for 30 min and neutralized with saturated aq NaHCO₃ solution. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined,
washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminum oxide chromatography eluting with petroleum ether/ethyl acetate (80:20) yielded the product 15n as a colorless solid, mp 79-81 °C (43 mg, 66%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.35 – 7.26 (m, 4H), 7.17 (d, $J = 8.7$ Hz, 2H), 6.68 (d, $J = 8.8$ Hz, 2H), 5.74 (s, 1H), 2.93 (s, 6H), 2.1 (brs, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 150.4, 142.9, 132.9, 131.6, 128.5, 127.9, 127.8, 112.6, 75.5, 40.7 ppm. IR (neat): 3273, 2883, 1515 cm$^{-1}$. HRMS–ESI [M+H]$^+$: 262.1006, C$_{15}$H$_{17}$NOCl requires 262.0999.

(4-Bromophenyl)(naphthalen-2-yl)methanol, 15o.

Addition of 13e to 2-napthaldehyde using Me$_3$SiOK/Bu$_4$NCl in THF at 0 °C.

A solution of (4-bromophenyl)trimethylsilane, 13e (86 mg, 0.375 mmol) and 2-napthaldehyde (39 mg, 0.25 mmol) in anhydrous THF (1.0 mL) was treated with dried Bu$_4$NCl (104 mg, 0.375 mmol) and TMSOK (48 mg, 0.375 mmol) and the resulting solution was stirred under N$_2$ at 0 °C for 5 h. Solvent was removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layer washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 15o as a colorless solid, mp 73–75 °C (53 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.88 – 7.78 (m, 4H), 7.53 – 7.44 (m, 4H), 7.39 (dd, $J = 8.5$, 1.7 Hz, 1H), 7.30 (d, $J = 8.5$ Hz, 2H), 5.96 (s, 1H), 2.35 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.7, 140.8, 133.4, 133.1, 131.7, 128.7, 128.5, 128.2, 127.8, 126.5, 126.3, 125.3, 124.7, 121.7, 75.9 ppm. IR (neat): 3308, 2911, 1480 cm$^{-1}$. HRMS–EI [M]$: 312.0155$, C$_{17}$H$_{13}$OBr requires 312.0150.
Methyl 4-(3-ethoxy-1-hydroxy-3-oxopropyl)benzoate, 16a. A solution of 2-(trimethylsilyl)acetate, 6 (92 µL, 0.5 mmol) and methyl 4-formylbenzoate (99 mg, 0.60 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N₂ at 0 °C for 15 min. 1 M HCl (10 mL) was added, the residue extracted with diethyl ether (15 x 3 mL), organic layers combined and washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (80:20) yielded 16a as a colorless oil (100 mg, 79%). ¹H NMR (400 MHz, CDCl₃): δ 8.01 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 5.18 (t, J = 6.3 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.51 (bs, 1H), 2.72 (d, J = 6.3 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 172.3, 167.0, 147.7, 130.0, 129.7, 125.7, 70.0, 61.2, 52.2, 43.2, 14.3 ppm. HRMS−ESI [M+Na]⁺: 275.0882, C₁₃H₁₆O₅Na requires 275.0895.

Ethyl-3-(4-(dimethylamino)phenyl)-3-hydroxypropanoate, 16b. A solution of 2-(trimethylsilyl)acetate, 6 (92 µL, 0.5 mmol) and methyl 4-(dimethylamino)benzaldehyde (90 mg, 0.60 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), the resulting solution was stirred under N₂ at 0 °C for 30 min and 1 M HCl (10 mL) was added, neutralized with saturated NaHCO₃ solution. The residue was extracted with diethyl ether (15 x 3 mL), organic layer was washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 16b as a yellow oil (72 mg, 61%). ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, J = 8.7 Hz, 2H), 6.72 (d, J = 8.7 Hz, 2H), 5.05 (dd, J = 9.4, 3.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.94 (s, 6H), 2.78 (dd, J = 16.1, 9.4 Hz,
1H), 2.67 (dd, $J = 16.1, 3.6$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 172.7, 150.5, 130.5, 126.8, 112.7, 70.4, 60.9, 43.4, 40.8, 14.3 ppm. IR (neat): 3385, 2932, 1696, 1592 cm$^{-1}$. HRMS–ESI [M+Na]$^+$: 260.1266, C$_{13}$H$_{19}$NO$_3$Na requires 260.1263.

(E)-1-Phenylhexa-1,5-dien-3-ol, 16c.$^{23}$ A solution of allyltrimethylsilane, 7a (96 µL, 0.6 mmol) and trans-cinnamaldehyde (63 µL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N$_2$ at rt for 3 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), the organic layer washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16c as a yellow oil (63 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.38 (d, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 2H), 7.27 – 7.20 (m, 1H), 6.61 (d, $J = 15.9$ Hz, 1H), 6.24 (dd, $J = 15.9, 6.3$ Hz, 1H), 5.93 – 5.79 (m, 1H), 5.22 – 5.14 (m, 2H), 4.36 (dd, $J = 12.4, 6.3$ Hz, 1H), 2.49 – 2.33 (m, 2H), 1.79 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 136.8, 134.2, 131.7, 130.5, 128.7, 127.8, 126.6, 118.7, 71.8, 42.2 ppm. MS–ESI [M–H]$^-$: 173.13, C$_{12}$H$_{13}$O requires 173.09.

N-(1-(4-Methoxyphenyl)but-3-enyl)aniline, 16d.$^{24}$ A solution of allyltrimethylsilane, 7a (114 mg, 1.0 mmol) and (E)-N-(4-methoxybenzylidene)aniline (106 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) the resulting solution was stirred under N$_2$ at rt for 4 h. Solvent removed under reduced pressure, water (10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to
dryness. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (98:2) yielded 16d as a colorless oil (92 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30 – 7.23 (m, 2H), 7.11 – 7.03 (m, 2H), 6.85 (d, $J = 7.8$ Hz, 1H), 6.63 (t, $J = 7.3$ Hz, 1H), 6.49 (d, $J = 7.8$ Hz, 1H), 5.82 – 5.69 (m, 1H), 5.21 – 5.09 (m, 2H), 4.33 (t, $J = 6.4$ Hz, 1H), 4.11 (bs, 1H), 3.78 (s, 3H), 2.62 – 2.42 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.7, 147.5, 135.7, 134.9, 129.2, 127.5, 118.3, 117.4, 114.1, 113.6, 56.7, 55.4, 43.5 ppm. HRMS – ESI [M+H]$^+$: 254.1541, C$_{17}$H$_{20}$NO requires 254.1545.

3-Methyl-1-ferrocenylbut-3-en-1-ol, 16e. A solution of trimethyl(2-methylallyl)silane, 7b (102 $\mu$L, 0.6 mmol) and ferrocenealdehyde (107 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N$_2$ at rt for 3 h. Solvent removed under reduced pressure, 2 M HCl (10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 16e as a yellow oil (68 mg, 50%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 4.87 (s, 1H), 4.81 (s, 1H), 4.55 – 4.48 (m, 1H), 4.27 (s, 1H), 4.23 – 4.07 (m, 8H), 2.40 (d, $J = 6.9$ Hz, 2H), 2.03 (d, $J = 2.6$ Hz, 1H), 1.79 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.9, 113.3, 93.6, 68.5, 68.1, 67.9, 67.6, 67.0, 65.8, 47.0, 22.7 ppm. IR (neat): 3455, 3078, 2925, 1647 cm$^{-1}$. HRMS – EI [M]$^+$: 270.0699, C$_{15}$H$_{18}$OFe requires 270.0707.

N-(3-Methyl-1-phenylbut-3-en-1-yl)aniline, 16f. A solution of trimethyl(2-methylallyl)silane, 7b (170 $\mu$L, 1.0 mmol) and (E)-N-benzylideneaniline (91 mg, 0.5 mmol) in anhydrous THF (2.0
mL) was treated with dried Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) the resulting solution was stirred under N₂ at rt for 4 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminum oxide chromatography eluting with petroleum ether/dichloromethane (92:8) yielded 16f as a colorless oil (85 mg, 72%). ¹H NMR (400 MHz, CDCl₃): δ 7.39 (dd, J = 8.0, 0.9 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.25 – 7.20 (m, 1H), 7.10 – 7.03 (m, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.7 Hz, 2H), 4.91 (s, 1H), 4.86 (s, 1H), 4.38 (dd, J = 10.2, 4.5 Hz, 1H), 4.13 (br s, 1H), 2.51 (dd, J = 14.3, 4.0 Hz, 1H), 2.39 (dd, J = 14.3, 10.2 Hz, 1H), 1.75 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 144.5, 142.6, 129.1, 128.8, 127.1, 126.2, 117.5, 114.2, 113.6, 55.7, 48.3, 21.8 ppm. HRMS – ESI [M+H]⁺: 238.1607, C₁₇H₂₀N requires 238.1596.

1-(4-Chlorophenyl)buta-2,3-dien-1-ol 16g-(1) (major) and 1-(4-chlorophenyl)but-3-yn-1-ol 16g-(2) (minor).¹⁶

A solution of trimethyl(prop-2-yn-1-yl)silane, 8 (67 mg, 0.60 mmol) and 4-chlorobenzaldehyde (70 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N₂ at 0 °C for 3 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded a mixture (70:30) of products 16g-(1,2) as a yellow oil (53 mg, 59%). ¹H NMR (400 MHz, CDCl₃): δ 7.36 – 7.30 (m,
4H), 5.40 (q, J = 6.5 Hz, 0.7H), 5.28 – 5.23 (m, 1H), 4.98 – 4.89 (m, 1.4H), 4.86 (t, J = 6.3 Hz, 0.3H), 2.64 – 2.60 (m, 0.6H), 2.42 (br s, 0.3H), 2.18 (br s, 0.7H), 2.08 (t, J = 2.6 Hz, 0.3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.3, 141.4, 141.0, 133.8, 133.6, 128.8, 128.7, 127.6, 127.3, 95.1, 80.3, 78.6, 71.8, 71.5, 71.4, 29.6 ppm. HRMS – ESI [M–H]$^–$: 179.0271, C$_{10}$H$_8$OCl requires 179.0264.

Note: Isolation of mixtures of buta-2,3-dien-1-ols and but-3-yn-1-ols from fluoride mediated addition reactions of trimethyl(prop-2-yn-1-yl)silanes has been previously reported.$^{16}$

1-(Furan-2-yl)-2-phenylethanol, 16h.$^{26}$ A solution of benzyltrimethylsilane, 9a (99 mg, 0.60 mmol) and furfural (42 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N$_2$ at rt for 3 h. The solvent was removed under reduced pressure, 1 M HCl (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16h as a colorless oil (78 mg, 83%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.40 (s, 1H), 7.33 – 7.15 (m, 5H), 6.34 – 6.30 (m, 1H), 6.23 – 6.19 (m, 1H), 4.94 – 4.88 (m, 1H), 3.19 (dd, J = 13.6, 5.4 Hz, 1H), 3.11 (dd, J = 13.6, 8.1 Hz, 1H), 1.99 (bs, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.9, 142.1, 137.5, 129.5, 128.6, 126.8, 110.4, 106.5, 68.9, 42.3 ppm. HRMS – ESI [M+Na]$^+$: 211.0740, C$_{12}$H$_{12}$O$_2$Na requires 211.0735.

$^N$-(2-Phenyl-1-(pyridin-4-yl)ethyl)aniline, 16i. A solution of benzyltrimethylsilane, 9a (164 mg, 1.0 mmol) and $^N$-phenyl-1-(4-pyridyl)methanimine, (91 mg, 0.5 mmol) in anhydrous THF
was treated with dried Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) and the resulting solution was stirred under N₂ at rt for 5 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue extracted with diethylether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminium oxide chromatography eluting with cyclohexane:ethylacetate (95:5) yielded 16i as a colorless solid, mp 92–94 °C (100 mg, 73%). ¹H NMR (400 MHz, CDCl₃): δ 8.54 – 8.49 (m, 2H), 7.32 – 7.19 (m, 5H), 7.12 – 7.02 (m, 4H), 6.66 (t, J = 7.3 Hz, 1H), 6.40 (d, J = 7.5 Hz, 2H), 4.61 – 4.53 (m, 1H), 4.15 (bs, 1H), 3.15 – 2.97 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 152.6, 150.0, 146.6, 136.6, 129.2, 129.1, 128.7, 127.1, 121.7, 118.1, 58.4, 44.4 ppm. IR (neat): 3259, 3015, 1599 cm⁻¹. HRMS – ESI [M+H]+: 275.1540, C₁₉H₁₉N₂ requires 275.1548.

1-(4-Chlorophenyl)-2-(2-methoxyphenyl)ethanol, 16j.⁴a A solution of (2-methoxybenzyl)trimethylsilane, 9b (117 mg, 0.60 mmol) and 4-chlorobenzaldehyde (70 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) and the resulting solution was stirred under N₂ at rt for 3 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with water (10 mL), brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 16j as a colorless solid, mp 62–64 °C, (66 mg, 50%). ¹H NMR (400 MHz, CDCl₃): δ 7.31 – 7.20 (m, 5H), 7.03 (d, J = 7.5 Hz, 1H), 6.91 – 6.85 (m, 2H), 4.97 – 4.90 (m, 1H), 3.84 (s, 3H), 3.09 (dd, J = 13.6, 4.1 Hz, 1H), 2.93 (dd, J = 13.6, 8.4 Hz, 1H), 2.60 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 157.7,
143.1, 132.9, 131.7, 128.4, 128.3, 127.3, 126.2, 120.9, 110.6, 73.8, 55.5, 41.3 ppm. HRMS–ESI [M+Na]^+: 285.0660, C_{15}H_{15}O_{2}ClNa requires 285.0658.

4-Methoxy-N-(2-(2-methoxyphenyl)-1-phenylethyl)aniline, 16k. A solution of (2-methoxybenzyl)trimethylsilane, 9b (194 mg, 1.0 mmol) and (E)-N-(4-methoxyphenyl)-1-phenylmethanimine (106 mg, 0.5 mmol) in anhydrous THF was treated with dried Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) under N₂ and was stirred at rt for 5 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue extracted with diethylether (15 x 3 mL). Combined organic layers was washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminium oxide chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16k as a colorless oil (74 mg, 44%). ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, J = 7.4 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.25 – 7.15 (m, 2H), 7.02 (dd, J = 7.3, 1.3 Hz, 1H), 6.89 – 6.81 (m, 2H), 6.63 (d, J = 8.8 Hz, 2H), 6.38 (d, J = 8.8 Hz, 2H), 4.48 (dd, J = 8.7, 5.0 Hz, 1H), 3.87 (s, 3H), 3.65 (s, 3H), 3.12 – 2.98 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 157.7, 151.9, 144.4, 131.1, 128.6, 128.1, 127.0, 127.0, 126.6, 120.8, 114.8, 114.6, 110.6, 60.2, 55.9, 55.4, 40.1 ppm. HRMS–ESI [M+Na]^+: 356.1616, C_{22}H_{23}NO_{2}Na requires 356.1626.

2-(3-Methoxyphenyl)-1-(4-methoxyphenyl)ethanol, 16l.²⁷ A solution of (3-methoxybenzyl)trimethylsilane, 9c (117 mg, 0.60 mmol) and p-anisaldehyde (61 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N₂ at rt for 3 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) added and the residue extracted with diethyl
ether (15 x 3 mL). Combined organic layers were washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (92:8) yielded 16l as a colorless oil (93 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.30 – 7.24 (m, 2H), 7.21 (t, $J$ = 7.9 Hz, 1H), 6.88 (d, $J$ = 8.7 Hz, 2H), 6.81 – 6.75 (m, 2H), 6.73 (s, 1H), 4.85 (dd, $J$ = 7.7, 5.6 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.03 – 2.92 (m, 2H), 1.91 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.7, 159.1, 139.7, 136.0, 129.4, 127.1, 121.8, 115.1, 113.8, 112.1, 74.8, 55.3, 55.1, 46.1 ppm. HRMS – ESI [M+Na]$^+$: 281.1140, C$_{16}$H$_{18}$O$_3$Na requires 281.1154.

**$N$-((1-(4-Fluorophenyl)-2-(3-methoxyphenyl)ethyl)aniline, 16m.** A solution of (3-methoxybenzyl)trimethylsilane, 9c (194 mg, 1.0 mmol) and ($E$)-$N$-(4-fluorobenzylidene)aniline, (99 mg, 0.5 mmol) in anhydrous THF was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N$_2$ and was stirred at rt for 5 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue extracted with diethylether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminium oxide chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16m as a yellow oil (118 mg, 73%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.31 – 7.25 (m, 2H), 7.20 (t, $J$ = 7.9 Hz, 1H), 7.06 (t, $J$ = 7.5 Hz, 2H), 6.99 (t, $J$ = 8.2 Hz, 2H), 6.77 (dd, $J$ = 8.2, 2.0 Hz, 1H), 6.71 (d, $J$ = 7.5 Hz, 1H), 6.67 – 6.60 (m, 2H), 6.44 (d, $J$ = 8.1 Hz, 2H), 4.59 – 4.53 (m, 1H), 4.13 (s, 1H), 3.74 (s, 3H), 3.06 (dd, $J$ = 13.8, 5.9 Hz, 1H), 2.98 (dd, $J$ = 13.8, 7.9 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 162.0 (d, $J$ = 244.7 Hz), 159.8, 147.2, 139.1 (d, $J$ = 3.0 Hz), 139.0, 129.7, 129.2, 128.1 (d, $J$ = 7.9 Hz), 121.7, 117.8,
115.5 (d, $J = 21.4$ Hz), 115.1, 113.8, 112.4, 58.7, 55.3, 45.4 ppm. IR (neat): 3406, 2925, 1501, cm$^{-1}$. HRMS–EI [M]$^+$: 321.1525, C$_{21}$H$_{20}$NO requires 321.1529.

**4-(2-(4-Fluorophenyl)-2-hydroxyethyl)-N,N-diisopropylbenzamide, 16n.** A solution of N,N-diisopropyl-4-((trimethylsilyl)methyl)benzamide, 9d (175 mg, 0.60 mmol) and p-fluorobenzaldehyde (54 μL, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution stirred under N$_2$ at rt for 3 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with water (10 mL), brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 16n as a colorless solid, mp 125–127 °C (146 mg, 85%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.32 – 7.13 (m, 6H), 7.04 – 6.97 (m, 2H), 4.87 (t, $J = 6.6$ Hz, 1H), 3.69 (brs, 2H), 3.00 (d, $J = 6.6$ Hz, 2H), 2.11 (s, 1H), 1.31 (brs, 12H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 170.9, 162.2 (d, $J =$ 245.7 Hz), 139.4 (d, $J =$ 3.1 Hz), 138.4, 137.3, 129.5, 127.5 (d, $J =$ 8.1 Hz), 125.9, 115.2 (d, $J =$ 21.4 Hz), 74.5, 45.9, 20.7 ppm. IR (neat): 3353, 2975, 1600, 1504 cm$^{-1}$. HRMS–ESI [M+H]$^+$: 344.2019, C$_{21}$H$_{27}$O$_2$NF requires 344.2026.

**((E))-N,N-Diisopropyl-4-(4-phenyl-2-(phenylamino)but-3-enyl)benzamide, 16o.** A solution of N,N-diisopropyl-4-((trimethylsilyl)methyl)benzamide, 9d (291 mg, 1.0 mmol) and (E)-N-3-diphenylprop-2-en-1-imine (104 mg, 0.5 mmol) in anhydrous THF was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N$_2$ and was stirred at rt for 5 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue
extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminium oxide chromatography eluting with pentane/dichloromethane (92:8) yielded 16o as a colorless solid, mp 130–132 °C (152 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.33 – 7.18 (m, 9H), 7.14 (t, $J = 7.7$ Hz, 2H), 6.69 (t, $J = 7.3$ Hz, 1H), 6.63 (d, $J = 7.9$ Hz, 2H), 6.52 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9$, 6.0 Hz, 1H), 4.30 (q, $J = 6.3$ Hz, 1H), 3.80 (s, 1H), 3.61 (brs, 2H), 3.02 (d, $J = 6.5$ Hz, 2H), 1.35 (brs, 12H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 171.0, 147.3, 138.4, 137.4, 136.9, 131.1, 130.7, 129.7, 129.3, 128.6, 127.6, 126.5, 126.0, 117.8, 113.8, 56.4, 42.2, 20.9 ppm. IR (neat): 3315, 2938, 1606, 1494 cm$^{-1}$. HRMS−ESI [M+H]$^+$: 427.2751, C$_{29}$H$_{35}$N$_2$O requires 427.2749.

1-(4-Bromophenyl)-3,3-dimethylbutan-2-ol, 16p. A solution of (4-bromobenzyl)trimethylsilane, 9e (243 mg, 1.0 mmol) and pivalaldehyde (55 μL, 0.5 mmol) in anhydrous THF (2 mL) was treated with dried Bu$_4$NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) and the resulting solution was stirred under N$_2$ at rt for 6 h. The solvent was removed under reduced pressure, 2 M HCl (10 mL) added and the residue extracted with ethyl acetate (10 x 3 mL). The organic layers were combined, washed with water (10 mL), brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16p as a colorless solid, mp 48–50 °C (102 mg, 79%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.43 (d, $J = 8.3$ Hz, 2H), 7.12 (d, $J = 8.3$ Hz, 2H), 3.39 (d, $J = 10.7$ Hz, 1H), 2.84 (dd, $J = 13.7$, 1.6 Hz, 1H), 2.44 (dd, $J = 13.7$, 10.7 Hz, 1H), 0.99 (s, 9H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 139.2, 131.7, 131.2, 120.2, 80.7, 37.9, 35.1, 25.9
ppm. IR (neat): 3455, 2952, 1480 cm\(^{-1}\). HRMS–ESI [M+Na]\(^+\): 279.0365, C\(_{12}\)H\(_{17}\)BrONa requires 279.0360.

\(N\)-(2-(4-Bromophenyl)-1-phenylethyl)-4-methoxyaniline, 16q.\) A solution of (4-bromobenzyl)trimethylsilane, 9e (243 mg, 1.0 mmol) and (E)-\(N\)-(4-methoxyphenyl)-1-phenylmethanimine (106 mg, 0.5 mmol) in anhydrous THF was treated with dried Bu\(_4\)NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) under N\(_2\) and was stirred at rt for 5 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue extracted with diethylether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by aluminum oxide chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16q as a yellow oil (82 mg, 43%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.37 (d, \(J = 8.3\) Hz, 2H), 7.32 – 7.20 (m, 5H), 6.95 (d, \(J = 8.3\) Hz, 2H), 6.65 (d, \(J = 8.9\) Hz, 2H), 6.42 (d, \(J = 8.9\) Hz, 2H), 4.51 – 4.45 (m, 1H), 3.67 (s, 3H), 3.07 – 2.95 (m, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 152.3, 143.2, 141.36, 136.9, 131.6, 131.1, 128.7, 127.3, 126.6, 120.7, 115.0, 114.8, 60.0, 55.8, 44.5 ppm. IR (neat): 3399, 2925, 1508 cm\(^{-1}\). HRMS–ESI [M+H]\(^+\): 382.0814, C\(_{21}\)H\(_{21}\)NOBr requires 382.0807.

\(1\)-(3-Bromophenyl)-1-(1,3-dithian-2-yl)ethanol, 16r.\) A solution of (1,3-dithian-2-yl)trimethylsilane, 10 (192 mg, 1.0 mmol) and \(m\)-bromoacetophenone (63 \(\mu\)L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\(_4\)NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) the resulting solution was stirred under N\(_2\) at reflux for 3 h. The reaction mixture was cooled to rt, solvent removed under reduced pressure, 2 M HCl (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with
water (10 mL), brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 16r as a yellow oil (104 mg, 65%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.7 (s, 1H), 7.50 – 7.36 (m, 2H), 7.23 (t, $J = 7.9$ Hz, 1H), 4.40 (s, 1H), 2.89 (s, 1H), 2.88 – 2.73 (m, 4H), 2.11 – 1.98 (m, 1H), 1.91 – 1.75 (m, 1H), 1.71 (s, 3H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.1, 130.7, 129.6, 128.9, 124.3, 122.6, 76.4, 59.7, 30.4, 30.2, 27.5, 25.4 ppm. IR (neat): 3441, 2889, 1563 cm$^{-1}$. HRMS–ESI [M+Na]$^+$: 340.9655, C$_{12}$H$_{15}$BrOS$_2$Na requires 340.9645.

$N$-((1,3-Dithian-2-yl)(4-methoxyphenyl)methyl)aniline, 16s. A solution of (1,3-dithian-2-yl)trimethylsilane, 10 (192 mg, 1.0 mmol) and (E)-$N$-(4-methoxybenzylidene)aniline (106 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol) the resulting solution was stirred under N$_2$ at 0°C for 4 h. The solvent was removed under reduced pressure, water (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (97:3) yielded 16s as a yellow oil (113 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.37 – 7.31 (m, 2H), 7.12 – 7.05 (m, 2H), 6.88 (d, $J = 7.8$ Hz, 2H), 6.66 (t, $J = 7.3$ Hz, 1H), 6.52 (d, $J = 7.8$ Hz, 1H), 4.71 (s, 1H), 4.63 (s, 1H), 4.47 – 4.43 (m, 1H), 3.79 (s, 1H), 2.95 – 2.73 (m, 4H), 2.14 – 2.05 (m, 1H), 1.93 – 1.80 (m, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.3, 147.0, 131.7, 129.2, 128.4, 117.8, 114.0, 113.7, 61.4, 55.3, 54.8, 30.8, 30.6, 25.9 ppm. IR (neat): 3385, 2903, 1501 cm$^{-1}$. HRMS–ESI [M+H]$^+$: 332.1135, C$_{18}$H$_{22}$NOS$_2$ requires 332.1143.
Benzothiazol-2-yl(4-bromophenyl)methanol, 16t. A solution of 2-(trimethylsilyl)benzothiazole, 11 (124 mg, 0.6 mmol) and 4-bromobenzaldehyde (93 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.025 mmol) and the resulting solution was stirred under N₂ at 0 °C for 3 h. Solvent was removed under reduced pressure, 1 M HCl (10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 16t as a colorless oil (114 mg, 71%). ¹H NMR (400 MHz, CDCl₃): δ 7.96 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 7.9 Hz, 1H), 7.54 – 7.32 (m, 6H), 6.11 (s, 1H), 4.21 (br s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 174.4, 152.6, 140.0, 135.3, 132.1, 128.5, 126.4, 125.5, 123.2, 122.9, 122.0, 73.8 ppm. HRMS-ESI [M+Na]⁺: 341.9561, C₁₄H₁₀BrNONaS requires 341.9564.

(Furan-2-yl(4-(phenoxymethyl)phenyl)methoxy)trimethylsilane, 17a. A solution of furan-2-yltrimethylsilane, 12 (140 mg, 1.0 mmol) and 4-(phenoxymethyl)benzaldehyde (106 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N₂ at rt for 5 h. Water (10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with petroleum ether/ethyl acetate (97:3) yielded 17a as a colorless oil (145 mg, 82%). ¹H NMR (400 MHz, CDCl₃): δ 7.45 – 7.28 (m, 8H), 6.95 (d, J = 8.6 Hz, 2H), 6.27 (dd, J = 3.1, 1.8 Hz, 1H), 6.06 (dd, J = 3.1, 0.6 Hz, 1H), 5.73 (s, 1H), 5.05 (s, 2H), 0.10 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.4, 157.0, 142.2,
137.2, 134.4, 128.7, 128.1, 127.8, 127.6, 114.6, 110.2, 107.1, 70.2, 70.0, 0.1 ppm. IR (neat): 2952, 1606, 1508 cm⁻¹. HRMS – ESI [M+Na]⁺: 375.1399, C_{21}H_{24}O_3NaSi requires 375.1392.

(4-Bromophenyl)(furan-2-yl) methanol, 17b. A solution of furan-2-yltrimethylsilane, 12 (140 mg, 1.0 mmol) and 4-bromobenzaldehyde (93 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N₂ at rt for 5 h. HCl (0.1 M, 10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17b as a colorless oil (105 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ 7.50 (d, J = 8.4 Hz, 2H), 7.41 – 7.38 (m, 1H), 7.32 (d, J = 8.4 Hz, 2H), 6.32 (dd, J = 3.2, 1.9 Hz, 1H), 6.12 (d, J = 3.2 Hz, 1H), 5.80 (s, 1H), 2.40 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 155.5, 142.9, 139.9, 131.7, 128.4, 122.1, 110.5, 107.8, 69.6 ppm. IR (neat): 3427, 2917, 1703, 1487 cm⁻¹. HRMS – EI [M]⁺: 251.9791, C_{11}H_{9}BrO₂ requires 251.9786.

(2-Chlorophenyl)(naphthalen-2-yl)methanol, 17c. A solution of (2-chlorophenyl)trimethylsilane, 13b (111 mg, 0.6 mmol) and 2-napthaldehyde (78 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution stirred under N₂ at rt for 5 h. HCl (2 M, 10 mL) was added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17c as a
(2-Chlorophenyl)(4-fluorophenyl)methanol, 17d. A solution of (2-chlorophenyl)trimethylsilane, 13b (111 mg, 0.6 mmol) and 4-fluorobenzaldehyde (62 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N$_2$ at rt for 5 h. HCl (2 M, 10 mL) was added and the residue was extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17d as a colorless oil (102 mg, 86%). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.59 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.38 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 7.05 – 6.98 (m, 2H), 6.20 (d, $J = 2.9$ Hz, 1H), 2.35 (d, $J = 3.6$ Hz, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): δ 162.2 (d, $J = 246.2$ Hz), 157.1, 140.8, 137.9 (d, $J = 3.2$ Hz), 129.6, 128.9, 128.6 (d, $J = 8.2$ Hz), 127.8, 127.1, 115.3 (d, $J = 21.4$ Hz), 72.0 ppm. HRMS–ESI [M–H]$^-$: 235.0326, C$_{13}$H$_9$ClFO requires 235.0326.

1-(2-Chlorophenyl)-2,2-dimethylpropan-1-ol, 17e. A solution of (2-chlorophenyl)trimethylsilane, 13b (140 mg, 0.75 mmol) and pivalaldehyde (28 µL, 0.25 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (104 mg, 0.375 mmol) and TMSOK
(48 mg, 0.375 mmol) and the resulting solution was stirred under N\textsubscript{2} at 0 °C for 5 h. Solvent was removed under reduced pressure, HCl (2 M, 10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (96:4) yielded 17e as a colorless oil (42 mg, 84%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.55 (dd, \textit{J} = 7.8, 1.7 Hz, 1H), 7.32 (dd, \textit{J} = 7.8, 1.3 Hz, 1H), 7.27 (td, \textit{J} = 7.6, 1.3 Hz, 1H), 7.21 – 7.16 (m, 1H), 5.03 (d, \textit{J} = 3.0 Hz, 1H), 1.86 (d, \textit{J} = 3.0 Hz, 1H), 0.98 (s, 9H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 140.1, 129.6, 129.4, 128.5, 126.4, 123.3, 76.8, 37.1, 25.9 ppm. HRMS−EI [M]\textsuperscript{+}: 198.0807, C\textsubscript{11}H\textsubscript{15}ClO requires 198.0811.

\textit{(E)}-1-(2-Chlorophenyl)-3-phenylprop-2-en-1-ol, 17f. A solution of (2-chlorophenyl)trimethylsilane, 13b (111 mg, 0.6 mmol) and trans-cinnamaldehyde (66 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu\textsubscript{4}NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) and the resulting solution was stirred under N\textsubscript{2} at rt for 5 h. HCl (2 M, 10 mL) was added and the residue was extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17f as a yellow oil (99 mg, 81%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.61 (dd, \textit{J} = 7.7, 1.7 Hz, 1H), 7.40 – 7.26 (m, 6H), 7.25 – 7.19 (m, 2H), 6.72 (d, \textit{J} = 15.9 Hz, 1H), 6.34 (dd, \textit{J} = 15.9, 6.2 Hz, 1H), 5.80 (d, \textit{J} = 6.2 Hz, 1H), 2.18 (s, 1H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 140.2, 136.6, 132.5, 131.1, 129.8, 129.7, 129.0, 128.7, 128.0, 127.8, 127.41, 126.8, 71.5 ppm. IR (neat): 3399, 3022, 2917, 1655 cm\textsuperscript{-1}. HRMS−EI [M]\textsuperscript{+}: 244.0667, C\textsubscript{15}H\textsubscript{13}ClO requires 244.0655.
Naphthalen-2-yl(2-(trifluoromethyl)phenyl)methanol, 17g. A solution of trimethyl(2-(trifluoromethyl)phenyl)silane, 13c (131 mg, 0.6 mmol) and 2-naphthaldehyde (78 mg, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N₂ and the resulting solution was stirred at rt for 5 h. Solvent removed under reduced pressure, HCl (2 M, 10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (92:8) yielded 17g as a colorless oil (130 mg, 86%). ¹H NMR (400 MHz, CDCl₃): δ 7.93 (s, 1H), 7.87 – 7.76 (m, 3H), 7.70 (d, J = 7.9 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.56 – 7.45 (m, 3H), 7.43 – 7.36 (m, 2H), 6.49 (d, J = 3.5 Hz, 1H), 2.44 (d, J = 3.5 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 142.4, 140.2, 133.3, 132.9, 132.5 (q, J = 1.1), 130.0, 128.3, 127.9 (q, J = 30.3 Hz), 128.0, 127.8, 126.4, 126.2, 125.7 (q, J = 5.8 Hz), 125.0, 124.8, 124.6 (q, J = 274 Hz), 71.0 (q, J = 2.4 Hz) ppm. IR (neat): 3259, 3050, 1305 cm⁻¹. HRMS–EI [M]⁺: 302.0904, C₁₈H₁₃F₃O requires 302.0918.

Phenyl(2-(trifluoromethyl)phenyl)methanol, 17h.³¹ A solution of trimethyl(2-(trifluoromethyl)phenyl)silane, 13c (131 mg, 0.6 mmol) and benzaldehyde (51 µL, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N₂ and the resulting solution was stirred at rt for 5 h. Solvent was removed under reduced pressure, HCl (2 M, 10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (92:8) yielded 17h as a colorless oil (105 mg, 83%). ¹H NMR (400
MHz, CDCl$_3$): $\delta$ 7.69 – 7.61 (m, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.41 – 7.23 (m, 6H), 6.31 (s, 1H), 2.36 (s, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 142.7, 142.3, 132.3 (q, $J = 1.1$ Hz), 129.5, 128.4, 127.7, 127.6 (q, $J = 30.2$ Hz), 127.5, 126.4, 125.5 (q, $J = 5.8$ Hz), 124.4 (q, $J = 274.4$ Hz), 70.8 (q, $J = 2.4$ Hz) ppm. MS–ESI [(M+H–H$_2$O)]: 235.08, C$_{14}$H$_{10}$F$_3$ requires 235.07.

**Mesityl(2-(trifluoromethyl)phenyl)methanol, 17i.** A solution of trimethyl(2-(trifluoromethyl)phenyl)silane, 13c (131 mg, 0.6 mmol) and mesitaldehyde (74 $\mu$L, 0.50 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N$_2$ and the resulting solution was stirred at rt for 5 h. Solvent was removed under reduced pressure HCl (2 M, 10 mL) added and the residue was extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17i as a colorless oil (106 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 – 7.71 (m, 1H), 7.47 – 7.36 (m, 3H), 6.87 (s, 2H), 6.59 (d, $J = 4.5$ Hz, 1H), 2.29 (s, 3H), 2.27 – 2.23 (m, 7H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 140.7, 137.4, 137.0, 134.7, 132.0 (q, $J = 1.1$ Hz), 130.4, 129.5, 128.5 (q, $J = 30.3$ Hz), 127.9, 127.1 (q, $J = 6.1$ Hz), 124.9 (q, $J = 274$ Hz), 70.2, 21.5, 21.0 ppm. HRMS–ESI [M–H]$: 293.1147, C$_{17}$H$_{16}$F$_3$O requires 293.1153.

**2,2-Dimethyl-1-(2-(trifluoromethyl)phenyl)propan-1-ol, 17j.**$^{9b}$ A solution of trimethyl(2-(trifluoromethyl)phenyl)silane, 13c (164 mg, 0.75 mmol) and pivalaldehyde (28 $\mu$L, 0.25 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (104 mg, 0.375 mmol) and TMSOK (48 mg, 0.375 mmol) and the resulting solution was stirred under N$_2$ at 0 °C for 5 h. Solvent was
removed under reduced pressure, HCl (2 M, 10 mL) added, and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17j as a colorless oil (51 mg, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.8 (d, $J = 7.9$ Hz, 1H), 7.63 (d, $J = 7.9$ Hz, 1H), 7.55 (t, $J = 7.6$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 1H), 4.92 (s, 1H), 1.93 (s, 1H), 0.98 (s, 9H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 141.7, 131.4 (q, $J = 1.1$ Hz), 129.6, 128.5 (q, $J = 29.6$ Hz), 127.6, 125.8 (q, $J = 6.0$ Hz), 124.6 (q, $J = 274.1$ Hz), 75.8 (q, $J = 2.4$ Hz), 36.5, 26.6 ppm. HRMS – EI [M]$^+$: 232.1082, C$_{12}$H$_{15}$F$_3$O requires 232.1075.

(4-Chlorophenyl)(3-methoxyphenyl)methanol, 17k.\textsuperscript{32} A solution of (4-chlorophenyl)trimethylsilane, 13d (70 mg, 0.375 mmol) and m-anisaldehyde (34 mg, 0.25 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu$_4$NCl (104 mg, 0.375 mmol) and TMSOK (48 mg, 0.375 mmol) and the resulting solution was stirred under N$_2$ at 0 °C for 5 h. Solvent removed under reduced pressure and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 x 3 mL), organic layers combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (90:10) yielded 17k as a colorless oil (42 mg, 68%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.34 – 7.22 (m, 5H), 6.94 – 6.89 (m, 2H), 6.81 (dd, $J = 8.0$, 2.0 Hz, 1H), 5.78 (s, 1H), 3.78 (s, 3H), 2.26 (bs, 1H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.0, 145.2, 142.2, 133.5, 129.8, 128.7, 128.0, 119.0, 113.3, 112.3, 75.7, 55.4, 29.8 ppm. HRMS – ESI [M–H]$^-$: 247.0530, C$_{14}$H$_{12}$O$_2$Cl requires 247.0526.
(4-Bromophenyl)(phenyl)methanol, 17l.18 A solution of (4-bromophenyl)trimethylsilane, 13e (86 mg, 0.375 mmol) and benzaldehyde (26 µL, 0.25 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu4NCl (104 mg, 0.375 mmol) and TMSOK (48 mg, 0.375 mmol) and the resulting solution was stirred under N2 at 0 °C for 5 h. Solvent was removed under reduced pressure, HCl (2 M, 10 mL) added and the residue extracted with diethyl ether (15 x 3 mL). Organic layers were combined, washed with brine (10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with cyclohexane/ethyl acetate (95:5) yielded 17l as a colorless solid, mp 44–46 °C (42 mg, 64%). 1H NMR (400 MHz, CDCl3): δ 7.45 (d, J = 8.5 Hz, 2H), 7.35 – 7.22 (m, 7H), 5.78 (s, 1H), 2.27 (bs, 1H) ppm. 13C NMR (100 MHz, CDCl3): δ 143.5, 142.8, 131.7, 128.8, 128.3, 128.0, 126.7, 121.6, 75.8 ppm. HRMS–ESI [M–H]: 260.9906, C13H10OBr requires 260.9915.

Acknowledgment We thank the European Research Association ERA-Chemistry and the Irish Research Council (IRC) for financial support.

Supporting Information: 1H and 13C spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org/

References


8. Each alkoxide and TMSOK was fully soluble in THF at the concentration used. At higher concentrations the cation exchange could be seen to occur with a visible precipitation of KCl.


