

Bu₄N⁺ Alkoxide-Initiated/Autocatalytic Addition Reactions with Organotrimethylsilanes

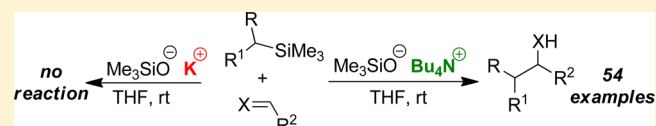
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S Supporting Information

ABSTRACT: The use of Me₃SiO⁻/Bu₄N⁺ as a general activator 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 that can be readily utilized as carbanion equivalents for synthesis. Reactions are achieved at rt without the requirement of specialized precautions that are commonplace for other organometallics.

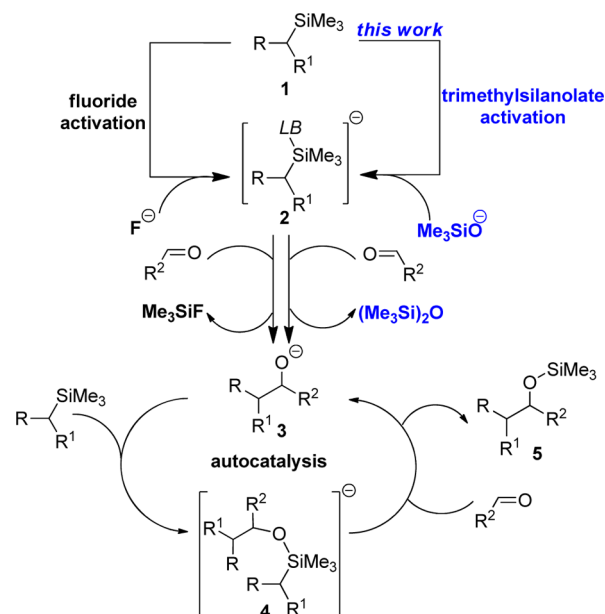


INTRODUCTION

The research literature on organometallic reagent addition to an electrophilic carbon is nothing short of vast.¹ 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, and 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 evokes 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, which showed that fluoride could promote the addition reactions of allyl-, alkynyl-, cyano- and trifluoromethylsilanes.² Numerous reports have expanded on these earlier publications, but the means of activation is most often a fluoride source.³ 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 and 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 **1** to carbonyls (Scheme 1).⁴ These studies have indicated that the reaction pathway is a fluoride-initiated formation of hypervalent silicon species **2**, which provides a carbanion equivalent that upon

Scheme 1. Analysis of Trimethylsilane Addition Reactions



carbonyl addition produces an alkoxide **3** and trimethylsilyl fluoride.

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, while an alkoxide-controlled autocatalytic cycle drives 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

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sequence that is initiated by one alkoxide and then autocatalytic turnover is achieved by the in situ-produced alkoxide. With this analysis in mind, an investigation into alternative Lewis base (LB) activation of organotrimethylsilanes was undertaken (Scheme 1).⁵ As the most common synthetically utilized organometallics have functional groups such as acetate, allyl, propargyl, benzyl,⁶ dithiane, heteroaryl, and aryl, the substituted trimethylsilanes **6–13** (Figure 1) were selected for evaluation of the new method.

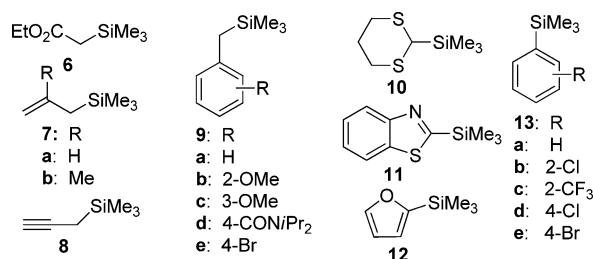


Figure 1. Trimethylsilyl organometallic reagents.

RESULTS AND DISCUSSION

We have previously reported that the fluoride-mediated addition of (3-methoxybenzyl)trimethylsilane (**9c**) to benzaldehyde in THF at reflux gave alcohol **14a** in good yield (Table 1, entry 1).^{4a}

Table 1. Screening and Optimization of Conditions^a

R-SiMe ₃ + PhCHO		(i) Lewis base, THF temp		(ii) H ₃ O ⁺		14a-g
silane	LB	mol %	temp	time (h)	14 (% yield)	
1	9c	TBAT ^{b,c}	5	Δ	3	14a (82)
2	9c	Me ₃ SiOK	10	Δ	12	–
3	9c	EtOK	10	Δ	12	–
4	9c	<i>t</i> BuOK	10	Δ	12	–
5	9c	<i>t</i> BuOK/Bu ₄ NCl	10	Δ	3	14a (70)
6	9c	EtOK/Bu ₄ NCl	10	Δ	3	14a (74)
7	9c	Me ₃ SiOK/Bu ₄ NCl	10	Δ	2	14a (78)
8	9c	Me ₃ SiOK/Bu ₄ NCl	10	rt	2	14a (80)
9	6	Me ₃ SiOK/Bu ₄ NCl	10	0 °C	0.5	14b (83) ^d
10	7a	Me ₃ SiOK/Bu ₄ NCl	10	rt	2	14c (88)
11	8	Me ₃ SiOK/Bu ₄ NCl	10	0 °C	1	14d (59) ^e
12	10	Me ₃ SiOK/Bu ₄ NCl	10	rt	2	14e (87)
13	12	Me ₃ SiOK/Bu ₄ NCl	10	rt	5	14f (78) ^f
14	13b	Me ₃ SiOK/Bu ₄ NCl	10	rt	5	14g (86)

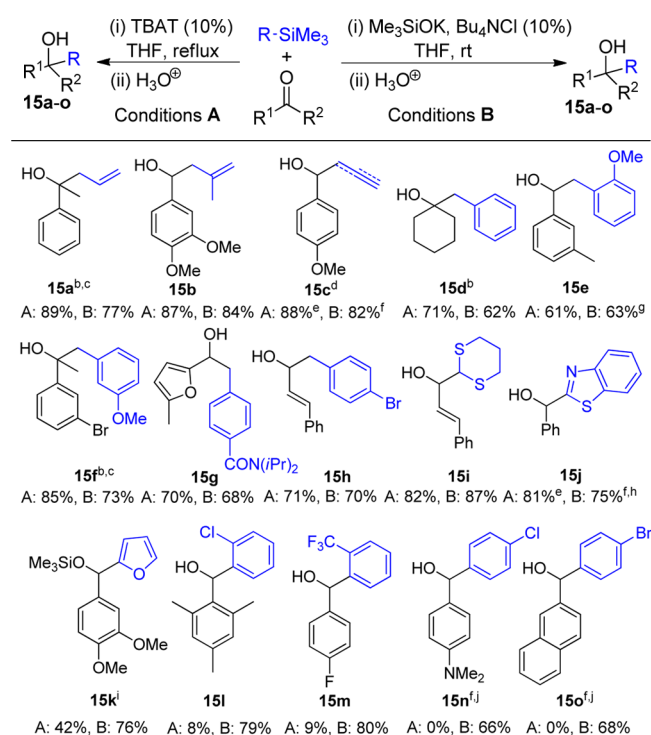
^aTrimethylsilane (0.6 mmol) and aldehyde (0.5 mmol), unless otherwise noted. ^bTBAT = tetrabutylammonium triphenyldifluorosilicate. ^cA similar result was obtained with TBAF (see ref 4a). ^dTrimethylsilane (0.5 mmol) and aldehyde (0.6 mmol). ^eA mixture of propargyl and allenyl alcohols was isolated. ^fTrimethylsilane (1.0 mmol) and aldehyde (0.5 mmol).

This reaction was chosen for the development of a new non-fluoride activation method, and an initial screen of the three different Lewis bases *t*BuOK, EtOK, and Me₃SiOK was carried out. These alkoxides were chosen to encompass the alcohol pK_a range of 17, 16, and 12.7 respectively.⁷ Using the identical conditions but replacing fluoride with an alkoxide failed to produce **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 that differs in the fluoride and alkoxide reaction conditions is the role of the counteranion. For the fluoride reagents used, the counterion was a Bu₄N⁺ salt (entry 1), whereas inorganic potassium salts were employed for the unsuccessfully attempted alkoxide-mediated reactions (entries 2–4). To fully replicate the counteranion conditions without the need to presynthesize Bu₄N⁺ alkoxide salts, an in situ exchange was devised using inexpensive Bu₄NCl.⁸ Repeating the three reactions with 10 mol % alkoxide and Bu₄NCl, we were delighted to obtain the product for each alkoxide in good yield after 2–3 h of reflux (entries 5–7). Remarkably, with Me₃SiOK, the weakest base of the three, the reaction was complete at room temperature after 2 h, providing **14a** in 80% yield when Bu₄NCl was included (entry 8).

To illustrate the generality of the Bu₄N⁺ effect, the reactions of trimethylsilanes bearing ethyl acetate (**6**), allyl (**7a**), propargyl (**8**), dithiane (**10**), heteroaryl (**12**), and aryl (**13b**) groups with benzaldehyde were carried out. In each case, the reaction was successful at either rt or 0 °C, and the corresponding product **14b–g** was obtained in good to excellent yield (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

Table 2. Comparison of Me₃SiO⁻/Bu₄N⁺- and Fluoride-Mediated Additions^a



^aTrimethylsilane (0.6 mmol) and aldehyde (0.5 mmol), unless otherwise noted. ^bTrimethylsilane (1.0 mmol) and aldehyde (0.5 mmol). ^cThe reaction was performed at reflux with Me₃SiOK/Bu₄NCl. ^dA mixture of propargyl and allenyl alcohols was isolated. ^eThe reaction was performed at rt. ^fThe reaction was performed at 0 °C. ^gMe₃SiOK/Bu₄NCl (20 mol %) was used. ^hMe₃SiOK/Bu₄NCl (5 mol %) was used. ⁱWorked up with water. ^jTrimethylsilane (0.375 mmol), aldehyde (0.25 mmol), and Me₃SiOK/Bu₄NCl (0.375 mmol).

tolerance of the ester functional group of **6**, which is often sensitive to organometallic reactions, and the aromatic derivative **13b**, which is often considered too unreactive to effectively participate in addition reactions.

To probe the practicality of $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ -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** and **7b**), propargyl (**8**), benzyl (**9a–e**), dithianyl (**10**), and benzothiazole (**11**) derivatives were all successful with $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ activation at rt or 0 °C, 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**. The results showed that the rt $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ conditions were successful in each case, giving the products **15k–o** in good yields, in contrast to fluoride (at reflux), for which the reactions either failed or gave the products in low yields (Table 2).

A more detailed comparison of the two silicon-activating conditions was carried out for the reactions of **9c** and **13b** with benzaldehyde to generate **14a** and **14g**, respectively. The 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 **14a** within 1 h, whereas fluoride reached only approximately 40% conversion at this time point (Figure 2, top graph). It would be expected that the participation of arylsilane **13b** in an addition reaction would be more challenging, yet the $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ 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 $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ is superior to fluoride at obtaining carbanion reactivity from organotrimethylsilanes. This could be attributed to a significant enhancement of the nucleophilicity of the trimethylsilyl oxide as the ammonium salt with respect to an inorganic counteranion.

Next, the electrophile scope was explored utilizing the $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ silicon-activating conditions. Encouragingly, diversely substituted aromatic, heteroaromatic, α,β -unsaturated, and aliphatic aldehydes, ketones, and imines all underwent addition reactions with the 11 different trimethylsilanes tested to give the corresponding alcohol and amine products **16a–t** (Table 3).

Because of their synthetic importance yet rarity of use in addition reactions, specific attention was given to the aryl-Si(Me)₃ derivatives **12** and **13a–e** (Table 4).⁹ In the case of furan

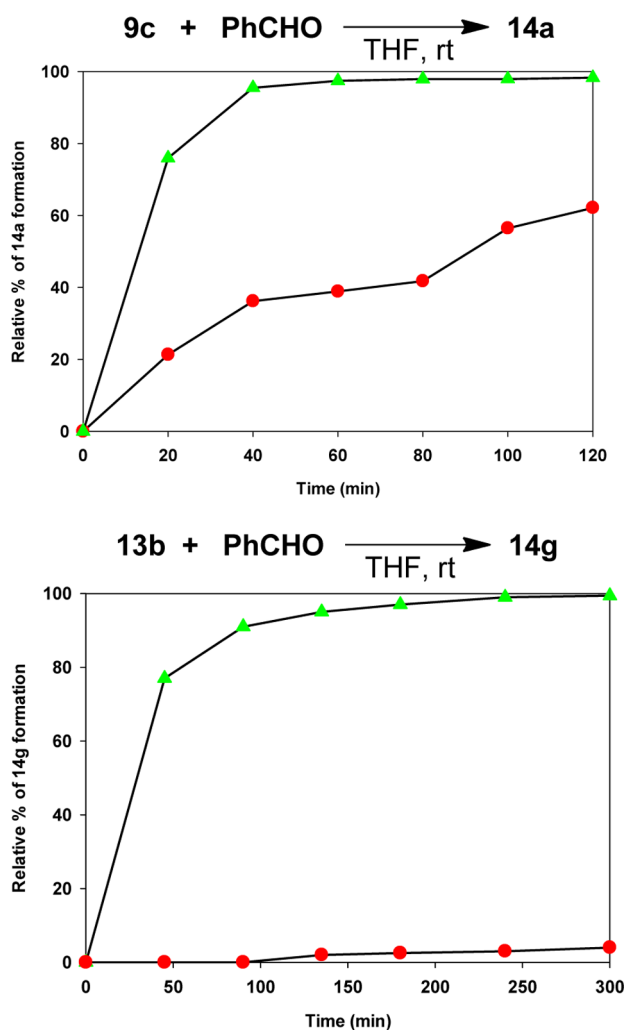
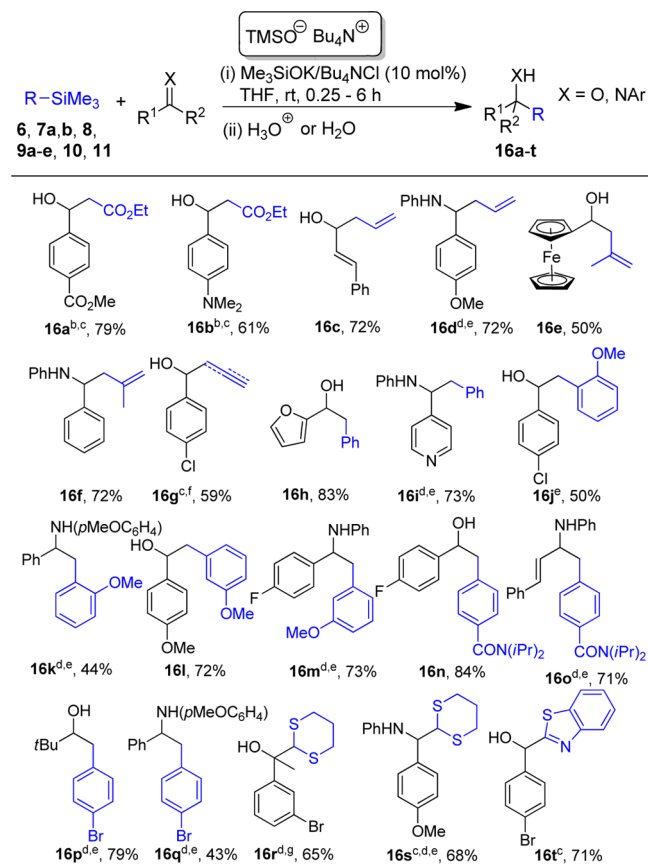


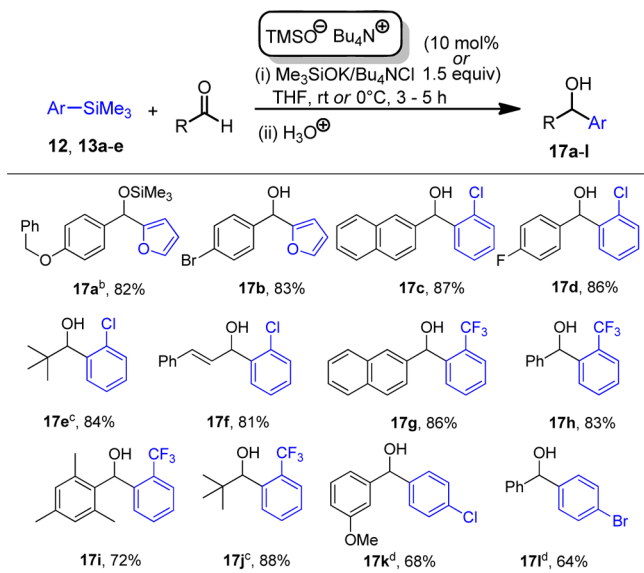
Figure 2. Relative percentage formation of (top) **14a** and (bottom) **14g** using fluoride (red) or $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ (green) in the reactions of benzaldehyde with **9c** and **13b**, respectively.

Table 3. $\text{Me}_3\text{SiO}^-/\text{Bu}_4\text{N}^+$ -Promoted Addition to Carbonyls and Imines with Various Trimethylsilanes^a



^aTrimethylsilane (0.6 mmol) and aldehyde (0.5 mmol), unless otherwise noted. ^bTrimethylsilane (0.5 mmol) and aldehyde (0.6 mmol). ^cThe reaction was performed at 0 °C. ^dTrimethylsilane (1.0 mmol) and electrophile (0.5 mmol). ^e $\text{Me}_3\text{SiOK}/\text{Bu}_4\text{NCl}$ (20 mol %) was used. ^fA mixture of propargyl and allenyl alcohols was isolated. ^gThe reaction was performed at reflux.

Table 4. Aryl and Heteroaryl Addition to Carbonyls^a



^aTrimethylsilane (0.6 mmol) and aldehyde (0.5 mmol), unless otherwise noted. ^bWorked up with water. ^cTrimethylsilane (0.75 mmol), aldehyde (0.25 mmol), and Me_3SiOK/Bu_4NCl (0.375 mmol). ^dTrimethylsilane (0.375 mmol), aldehyde (0.25 mmol), Me_3SiOK/Bu_4NCl (0.375 mmol).

12 and the *ortho*-substituted aryl derivatives **13b** and **13c**, 10 mol % Me_3SiO^-/Bu_4N^+ was sufficient for the reaction to reach completion, giving products **17a–j** in good to excellent yields. For the *para*-substituted arenes **13d** and **13e**, a catalytic amount of Me_3SiO^-/Bu_4N^+ proved insufficient for the reaction to reach completion, though increasing the amount of Me_3SiO^-/Bu_4N^+ to 1.5 equiv gave the diaryl alcohols **17k** and **17l** in yields of 68 and 64% respectively. A plausible rationale for this experimental observation is the failure of the autocatalytic cycle in these examples because of the nature of the diaryl alkoxide that is generated in situ. But as the activating reagents Me_3SiOK and Bu_4NCl are inexpensive, nontoxic, and easily separated from the 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 extend the reactivity limit of our method to promote reactions with substrates such as **13a**, which have, as would be expected, the lowest reactivity.

CONCLUSION

In summary, a new Lewis base activation of organotrimethylsilanes utilizing Me_3SiO^-/Bu_4N^+ has been developed, with the key to its success lying in the use of the Bu_4N^+ cation, which is superior to fluoride in promoting trimethylsilane addition reactions. Once initiated, reactions proceed to completion via an autocatalytic cycle involving the in situ-formed alkoxide. For reactions where the autocatalytic cycle is not effective, a stoichiometric amount of the activator can be used. Taken together, these results indicate that the 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 ongoing. 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 of the reactions involving air-sensitive reagents were performed under nitrogen either in oven- or flame-dried glassware using syringe–septum cap technique. All of the solvents were purified and degassed before use. 2,2,6,6-Tetramethylpiperidine TMP-(H) was distilled from CaH_2 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. $KOtBu$ was purchased as a 1.0 M solution in THF. Tetrabutylammonium difluorotriphenylsilicate (TBAT) was used as received. Preweighed amounts of Me_3SiOK and Bu_4NCl were stored in a desiccator utilizing P_2O_5 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 aluminum 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 the visualizing agent. 1H and ^{13}C NMR spectra were recorded at room temperature on a 400 MHz spectrometer. HRMS measurements were acquired with a TOF mass analyzer. Isolated yields after column chromatography are reported. 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 were 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 $-78^\circ C$ 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 $-78^\circ C$, and chlorotrimethylsilane (1.6 mL, 12 mmol) was added. The reaction mixture was stirred for a further 1 h at $-78^\circ C$ and then slowly warmed to rt. The solvent was removed under reduced pressure, and aq HCl (2 M, 40 mL) was added. The residue was extracted with diethyl ether (50×3 mL), and 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%). 1H NMR (400 MHz, $CDCl_3$): δ 7.74–7.66 (m, 2H), 7.53–7.42 (m, 2H), 0.34 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 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 $tBuOK/Bu_4NCl$ in THF. A solution of (3-methoxybenzyl)trimethylsilane (**9c**) (116 mg, 0.6 mmol) and benzaldehyde (51 μ L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (14 mg, 0.05 mmol) and $tBuOK$ (50 μ L, 0.05 mmol, 1 M in THF) under N_2 , and the resulting solution was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 **14a** as a colorless oil (80 mg, 70%).

Addition of **9c** to Benzaldehyde Using $EtOK/Bu_4NCl$ in THF. A solution of (3-methoxybenzyl)trimethylsilane (**9c**) (116 mg, 0.6 mmol) and benzaldehyde (51 μ L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (14 mg, 0.05 mmol) and $EtOK$ (4 mg, 0.05 mmol) under N_2 , and the resulting solution was stirred at reflux for 3 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 **14a** as a colorless oil (84 mg, 74%).

Addition of 9c to Benzaldehyde Using $\text{Me}_3\text{SiOK}/\text{Bu}_4\text{NCl}$ 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 Bu_4NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), and the resulting solution was stirred under N_2 at rt for 2 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 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 **14a** as a colorless oil (91 mg, 80%).

$^1\text{H NMR}$ (400 MHz, CDCl_3): 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, OCH_3), 3.06–2.92 (m, 2H), 1.98 (s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 159.7, 143.7, 139.5, 129.5, 128.4, 127.6, 125.9, 121.8, 115.0, 112.1, 75.2, 55.1, 46.2 ppm. HRMS-ESI [$\text{M} + \text{Na}$] $^+$: 251.1039, $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Na}$ requires 251.1048.

Ethyl 3-Hydroxy-3-phenylpropanoate (14b).¹⁴ 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 Bu_4NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol). The resulting solution was stirred under N_2 at 0 $^\circ\text{C}$ for 30 min, and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (90:10) yielded **14b** as a colorless oil (81 mg, 83%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 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. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.5, 142.6, 128.7, 127.9, 125.8, 70.5, 61.0, 43.5, 14.3 ppm. HRMS-ESI [$\text{M} + \text{Na}$] $^+$: 217.0836, $\text{C}_{11}\text{H}_{14}\text{O}_3\text{Na}$ requires 217.0814.

1-Phenylbut-3-en-1-ol (14c).¹⁵ 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 Bu_4NCl (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 \times 3 mL), and 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%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 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 (br s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 144.0, 134.6, 128.5, 127.7, 125.9, 118.6, 73.4, 44.0 ppm. MS-ESI [$\text{M} - \text{H}$] $^-$: 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 μL , 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), and the resulting solution was stirred under N_2 at 0 $^\circ\text{C}$ for 1 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 a 70:30 mixture of products **14d**-(1,2) as a colorless oil (43 mg, 59%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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 (br s, 0.7H), 2.08 (t, $J = 2.6$ Hz, 0.3H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 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 [$\text{M} - \text{H}$] $^-$: 145.04, $\text{C}_{10}\text{H}_{11}\text{O}$ requires 145.07.

Note: the 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 μL , 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (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 \times 3 mL), and 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 (90:10) yielded the product **14e** as a colorless solid (98 mg, 87%, mp 59–61 $^\circ\text{C}$). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 140.3, 128.6, 128.4, 127.0, 74.9, 52.9, 28.3, 27.7, 25.5 ppm. HRMS-ESI [$\text{M} + \text{Na}$] $^+$: 249.0381, $\text{C}_{11}\text{H}_{14}\text{ONaS}_2$ 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 μL , 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (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 \times 3 mL), and 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 the product **14f** as a yellow oil (68 mg, 78%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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 (br s, 1H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 156.1, 142.7, 140.9, 128.6, 128.2, 126.7, 110.4, 107.6, 70.3 ppm. HRMS-EI [M] $^+$: 174.0679, $\text{C}_{11}\text{H}_{10}\text{O}_2$ requires 174.0681.

(2-Chlorophenyl)(phenyl)methanol (14g).¹⁹ A solution of (2-chlorophenyl)trimethylsilane (**13b**) (111 mg, 0.6 mmol) and benzaldehyde (51 μL , 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (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 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **14g** as a colorless oil (94 mg, 86%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 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 [($\text{M} + \text{H}$) - H_2O] $^+$: 201.05, $\text{C}_{13}\text{H}_{10}\text{ClO}$ requires 201.04.

2-Phenylpent-4-en-2-ol (15a).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 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 reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **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 Bu_4NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol), and the resulting solution was stirred under N_2 at reflux for 3 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **15a** as a colorless oil (62 mg, 77%).

$^1\text{H NMR}$ (400 MHz, CDCl_3): 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 (br s,

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 and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 (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), and the resulting solution was stirred under N₂ at rt for 3 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 (90:10) yielded **15b** as a colorless solid (93 mg, 84%, mp 72–74 °C).

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): 3420, 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]. *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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (15 × 3 mL), and 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 petroleum ether/ethyl acetate (90:10) yielded an 84:16 mixture of products **15c**-(1,2) as a yellow oil (78 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ 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 p-Anisaldehyde Using Me₃SiOK/Bu₄NCl in THF at 0 °C. A solution of trimethyl(prop-2-yn-1-yl)silane (**8**) (75 μL, 0.50 mmol) and 4-bromobenzaldehyde (73 μL, 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), and the resulting solution was stirred under N₂ at 0 °C for 15 min. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 petroleum ether/ethyl acetate (90:10) yielded a 93:7 mixture of products **15c**-(1,2) as a yellow oil (72 mg, 82%).

¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₁H₁₃O₂ requires 177.0916.

Note: the 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). *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 N₂ at rt for 12 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 Me₃SiOK/Bu₄NCl 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 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, and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (10 × 3 mL), and 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 (59 mg, 62%, mp 41–43 °C).

¹H NMR (400 MHz, CDCl₃): δ 7.34–7.18 (m, 5H), 2.75 (s, 2H), 1.65–1.38 (m, 10H), 1.25 (br s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 137.1, 130.6, 128.1, 126.4, 71.1, 48.7, 37.3, 25.8, 22.1 ppm. HRMS-EI [M]⁺: 190.1361, C₁₃H₁₈O requires 190.1358.

2-(2-Methoxyphenyl)-1-m-tolylethanol (15e). *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 and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (10 × 3 mL), and 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 **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), and the resulting solution was stirred under N₂ at rt for 3 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 **15e** as a colorless solid (77 mg, 63%, mp 51–53 °C).

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 × 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 N₂, and the resulting solution was stirred at 70 °C for 4 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (10 × 3 mL), and 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 **15f** as a yellow oil (138 mg, 85%).

Addition of 9c to 3'-Bromoacetophenone Using Me₃SiOK/Bu₄NCl in THF at Reflux. A solution of (3-methoxybenzyl)trimethylsilane (**9c**) (194 mg, 1.0 mmol) and 3'-bromoacetophenone (64 μ L, 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) under N₂, and the resulting solution was stirred at reflux for 5 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (10 \times 3 mL), and the organic layers were combined, washed with water (10 mL) and 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%).

¹H NMR (400 MHz, CDCl₃): δ 7.58 (s, 1H), 7.38 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 7.23–7.12 (m, 2H), 6.77 (d, J = 7.8 Hz, 1H), 6.62 (d, J = 7.8 Hz, 1H), 6.50 (s, 1H), 3.70 (s, 3H), 3.08 (d, J = 13.2 Hz, 1H), 2.97 (d, J = 13.2 Hz, 1H), 1.92 (s, 1H), 1.54 (s, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 159.4, 150.0, 137.6, 129.7, 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, C₁₆H₁₇O₂NaBr requires 343.0310.

4-(2-Hydroxy-2-(5-methylfuran-2-yl)ethyl)-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 μ L, 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 rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (90:10) yielded **15g** as a yellow oil (114 mg, 70%).

Addition of 9d to 5-Methylfurfural Using Me₃SiOK/Bu₄NCl in THF at rt. A solution of N,N-diisopropyl-4-((trimethylsilyl)methyl)benzamide (**9d**) (175 mg, 0.60 mmol) and 5-methylfurfural (50 μ L, 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), the resulting solution was stirred under N₂ at rt for 3 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (90:10) yielded **15g** as a yellow oil (112 mg, 68%).

¹H NMR (400 MHz, CDCl₃): δ 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 (br s, 2H), 3.19–3.05 (m, 2H), 2.75 (s, 1H), 2.29 (s, 3H), 1.31 (s, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 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⁻¹. HRMS-ESI [M + H]⁺: 330.2078, C₂₀H₂₈O₃N requires 330.2069.

(E)-1-(4-Bromophenyl)-4-phenylbut-3-en-2-ol (15h). **Addition of 9e to trans-Cinnamaldehyde Using TBAT in THF at Reflux.** A solution of (4-bromobenzyl)trimethylsilane (**9e**) (146 mg, 0.60 mmol) and trans-cinnamaldehyde (63 μ L, 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 4 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **15h** as a colorless solid (108 mg, 71%).

Addition of 9e to trans-Cinnamaldehyde Using Me₃SiOK/Bu₄NCl in THF at rt. A solution of (4-bromobenzyl)trimethylsilane (**9e**) (146 mg, 0.60 mmol) and trans-cinnamaldehyde (65 μ L, 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), and the resulting solution was stirred under N₂ at rt for 3 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **15h** as a colorless solid (106 mg, 70%, mp 80–82 °C).

¹H NMR (400 MHz, CDCl₃): 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. ¹³C NMR (100 MHz, CDCl₃): 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, C₁₆H₁₄OBr requires 301.0228.

(E)-1-(1,3-Dithian-2-yl)-3-phenylprop-2-en-1-ol (15i). **Addition of 10 to trans-Cinnamaldehyde Using TBAT in THF at Reflux.** A solution of (1,3-dithian-2-yl)trimethylsilane (**10**) (116 mg, 0.6 mmol) and trans-cinnamaldehyde (63 μ L, 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 N₂ at reflux for 3 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **15i** as a colorless solid (104 mg, 82%).

Addition of 10 to trans-Cinnamaldehyde Using Me₃SiOK/Bu₄NCl in THF at rt. A solution of (1,3-dithian-2-yl)trimethylsilane (**10**) (116 mg, 0.6 mmol) and trans-cinnamaldehyde (63 μ L, 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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 **15i** as a colorless solid (110 mg, 87%, mp 58–60 °C).

¹H NMR (400 MHz, CDCl₃): δ 7.45–7.38 (m, 2H), 7.35–7.21 (m, 3H), 6.74 (d, J = 15.8 Hz, 1H), 6.35 (dd, J = 15.8, 6.5 Hz, 1H), 4.59–7.52 (m, 1H), 4.02 (d, J = 6.8 Hz, 1H), 3.00–2.91 (m, 2H), 2.82–2.72 (m, 2H), 2.67 (d, J = 3.7 Hz, 1H), 2.15–1.92 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 136.4, 132.9, 128.7, 128.0, 126.8, 73.4, 52.2, 28.4, 28.1, 25.7 ppm. IR (neat): 3434, 2938, 2883, 1494 cm⁻¹. HRMS-ESI [M + Na]⁺: 275.0538, C₁₃H₁₆ONaS₂ 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 μ L, 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 N₂ at rt for 3 h. The solvent was removed under reduced pressure, and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (90:10) yielded **15j** as a colorless solid (98 mg, 81%).

Addition of 11 to Benzaldehyde Using Me₃SiOK/Bu₄NCl in THF at 0 °C. A solution of 2-(trimethylsilyl)benzothiazole (**11**) (124 mg, 0.6 mmol) and benzaldehyde (51 μ L, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu₄NCl (7 mg, 0.025 mmol) and TMSOK (3.5 mg, 0.025 mmol), and the resulting solution was stirred under N₂ at 0 °C for 3 h. The solvent was removed under reduced pressure, and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (90:10) yielded **15j** as a colorless solid (90 mg, 75%, mp 108–110 °C).

¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.1 Hz, 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₄H₁₁NONaS 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 N₂, and the resulting solution was stirred at reflux for 4 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 10 mL of water was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 (64 mg, 42%).

Addition of 12 to 3,4-Dimethoxybenzaldehyde Using Me₃SiOK/Bu₄NCl 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 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 was extracted with diethyl ether (15 × 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%).

¹H NMR (400 MHz, CDCl₃): 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. ¹³C NMR (100 MHz, CDCl₃): 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, C₁₆H₂₂O₄Si requires 306.1287.

(2-Chlorophenyl)(mesityl)methanol (15l).²¹ Addition of **13b** to Mesityldehyde Using TBAT in THF at Reflux. A solution of (2-chlorophenyl)trimethylsilane (**13b**) (111 mg, 0.6 mmol) and mesityldehyde (74 μL, 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 and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 **15l** as a colorless solid (11 mg, 8%).

Addition of 13b to Mesityldehyde Using Me₃SiOK/Bu₄NCl in THF at rt. A solution of (2-chlorophenyl)trimethylsilane (**13b**) (111 mg, 0.6 mmol) and mesityldehyde (74 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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 **15l** as a colorless solid (103 mg, 79%, mp 91–93 °C).

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, 137.5, 137.3, 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 and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 **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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 **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 (br s, 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, C₁₁H₉OF₄ requires 269.0590.

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

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), and the resulting solution was stirred under N₂ at 0 °C for 5 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The resulting mixture was stirred for 30 min and neutralized with saturated aq NaHCO₃ solution. The residue was extracted with diethyl ether (15 × 3 mL), and the 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/ethyl acetate (80:20) yielded the product **15n** as a colorless solid (43 mg, 66%, mp 79–81 °C). ¹H NMR (400 MHz, CDCl₃): δ 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 (br s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₅H₁₇NOCl requires 262.0999.

(4-Bromophenyl)(naphthalen-2-yl)methanol (15o). A solution of (4-bromophenyl)trimethylsilane (**13e**) (86 mg, 0.375 mmol) and 2-naphthaldehyde (39 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), and the resulting solution was stirred under N₂ at 0 °C for 5 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 **15o** as a colorless solid (53 mg, 68%, mp 73–75 °C). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, 1490, 1480 cm⁻¹. HRMS-EI [M]⁺: 312.0155, C₁₇H₁₃OBr requires 312.0150.

Methyl 4-(3-Ethoxy-1-hydroxy-3-oxopropyl)benzoate (16a).²² A solution of ethyl 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 Bu_4NCl (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, and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 (80:20) yielded **16a** as a colorless oil (100 mg, 79%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 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 (br s, 1H), 2.72 (d, $J = 6.3$ Hz, 2H), 1.25 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 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 [$\text{M} + \text{Na}$] $^+$: 275.0882, $\text{C}_{13}\text{H}_{16}\text{O}_3\text{Na}$ requires 275.0895.

Ethyl 3-(4-(Dimethylamino)phenyl)-3-hydroxypropanoate (16b). A solution of ethyl 2-(trimethylsilyl)acetate (**6**) (92 μL , 0.5 mmol) and 4-(dimethylamino)benzaldehyde (90 mg, 0.60 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol). The resulting solution was stirred under N_2 at 0°C for 30 min, and 1 M HCl (10 mL) was added. The resulting mixture was neutralized with saturated NaHCO_3 solution. The residue was extracted with diethyl ether (15×3 mL), and the 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 (90:10) yielded **16b** as a yellow oil (72 mg, 61%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 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. $^{13}\text{C NMR}$ (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 [$\text{M} + \text{Na}$] $^+$: 260.1266, $\text{C}_{13}\text{H}_{19}\text{NO}_3\text{Na}$ 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_4NCl (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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 **16c** as a yellow oil (63 mg, 72%). $^1\text{H NMR}$ (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. $^{13}\text{C NMR}$ (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 [$\text{M} - \text{H}$] $^-$: 173.13, $\text{C}_{12}\text{H}_{13}\text{O}$ 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_4NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol), and the resulting solution was stirred under N_2 at rt for 4 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and the 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, 72%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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 (br s, 1H), 3.78 (s, 3H), 2.62–2.42 (m, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 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 [$\text{M} + \text{H}$] $^+$: 254.1541, $\text{C}_{17}\text{H}_{20}\text{NO}$ requires 254.1545.

3-Methyl-1-ferrocenylbut-3-en-1-ol (16e). A solution of trimethyl(2-methylallyl)silane (**7b**) (102 μL , 0.6 mmol) and ferrocenealdehyde (107 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 **16e** as a yellow oil (68 mg, 50%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 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. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 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-ESI [M] $^+$: 270.0699, $\text{C}_{15}\text{H}_{18}\text{OFe}$ requires 270.0707.

N-(3-Methyl-1-phenylbut-3-en-1-yl)aniline (16f).²⁵ A solution of trimethyl(2-methylallyl)silane (**7b**) (170 μL , 1.0 mmol) and (*E*)-*N*-benzylideneaniline (91 mg, 0.5 mmol) in anhydrous THF (2.0 mL) was treated with dried Bu_4NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol), and the resulting solution was stirred under N_2 at rt for 4 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and the 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%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 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. $^{13}\text{C NMR}$ (100 MHz, CDCl_3): 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 [$\text{M} + \text{H}$] $^+$: 238.1607, $\text{C}_{17}\text{H}_{20}\text{N}$ 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 Bu_4NCl (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 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 a 70:30 mixture of products **16g-(1,2)** as a yellow oil (53 mg, 59%). $^1\text{H NMR}$ (400 MHz, CDCl_3): 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. $^{13}\text{C NMR}$ (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 [$\text{M} - \text{H}$] $^-$: 179.0271, $\text{C}_{10}\text{H}_8\text{OCl}$ requires 179.0264.

Note: the 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_4NCl (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. The solvent was removed under reduced pressure, and 1 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15×3 mL), and 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 **16h** as a colorless oil (78 mg, 83%). $^1\text{H NMR}$ (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 (br s, 1H) ppm. $^{13}\text{C NMR}$ (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 [$\text{M} + \text{Na}$] $^+$: 211.0740, $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Na}$ 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, and water (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the 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 (95:5) yielded **16i** as a colorless solid (100 mg, 73%, mp 92–94 °C). 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 (br s, 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, 113.6, 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, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the organic layers were combined, washed with water (10 mL) and 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 (66 mg, 50%, mp 62–64 °C). 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, C₁₅H₁₅O₂ClNa 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 the resulting mixture was stirred at rt for 5 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the 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 **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, 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, C₂₂H₂₃NO₂Na 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, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 (92:8) yielded **16l** as a colorless oil (93 mg, 72%). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₆H₁₈O₃Na 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 Bu₄NCl (14 mg, 0.05 mmol) and TMSOK (7 mg, 0.05 mmol) under N₂, and the resulting mixture was stirred at rt for 5 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the 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 **16m** as a yellow oil (118 mg, 73%). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₂₁H₂₀NOF 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 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, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the organic layers were combined, washed with water (10 mL) and 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 (145 mg, 84%, mp 125–127 °C). ¹H NMR (400 MHz, CDCl₃): δ 7.32–7.13 (m, 6H), 7.04–6.97 (m, 2H), 4.87 (t, *J* = 6.6 Hz, 1H), 3.69 (br s, 2H), 3.00 (d, *J* = 6.6 Hz, 2H), 2.11 (s, 1H), 1.31 (br s, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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, C₂₁H₂₇O₂NF 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 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. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the organic layers were combined, washed with brine (10 mL), dried over sodium sulfate, and concentrated to dryness. Purification by aluminum oxide chromatography eluting with pentane/dichloromethane (92:8) yielded **16o** as a colorless solid (152 mg, 71%, mp 130–132 °C). ¹H NMR (400 MHz, CDCl₃): 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 (br s, 2H), 3.02 (d, *J* = 6.5 Hz, 2H), 1.35 (br s, 12H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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, C₂₉H₃₅N₂O 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 Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol), and the resulting solution was stirred under N₂ at rt for 6 h. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) added. The residue was extracted with ethyl acetate (10 × 3 mL), and the organic layers were combined, washed with water (10 mL) and 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 (102 mg, 79%, mp 48–50 °C). ¹H NMR (400 MHz, CDCl₃): 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. ¹³C NMR (100 MHz, CDCl₃): 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, C₁₂H₁₇BrONa 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-phenyl-methanimine (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 the resulting mixture was stirred at rt for 5 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the 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%). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₂₁H₂₁NOBr 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 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 reflux for 3 h. The reaction mixture was cooled to rt and the solvent removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and the organic layers were combined, washed with water (10 mL) and 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%). ¹H NMR (400 MHz, CDCl₃): 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. ¹³C NMR (100 MHz, CDCl₃): 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, C₁₂H₁₅BrOS₂Na 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 Bu₄NCl (28 mg, 0.1 mmol) and TMSOK (13 mg, 0.1 mmol), and the resulting solution was stirred under N₂ at 0 °C for 4 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 (97:3) yielded **16s** as a yellow oil (113 mg, 68%). ¹H NMR (400 MHz, CDCl₃): 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. ¹³C NMR (100 MHz, CDCl₃): 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, C₁₈H₂₂NO₂S₂ requires 332.1143.

Benzothiazol-2-yl(4-bromophenyl)methanol (16t).²⁸ 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. The solvent was removed under reduced pressure, and 1 M HCl (10

mL) was added. The residue was extracted with diethyl ether (15 × 3 mL), and 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 (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, C₁₄H₁₀BrNONaSi requires 341.9564.

(Furan-2-yl(4-(phenoxy)methyl)phenyl)methoxy)trimethylsilane (17a). A solution of furan-2-yltrimethylsilane (**12**) (140 mg, 1.0 mmol) and 4-(phenoxy)methylbenzaldehyde (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 was extracted with diethyl ether (15 × 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 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, C₂₁H₂₄O₃NaSi 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 was extracted with diethyl ether (15 × 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 **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, C₁₁H₉BrO₂ requires 251.9786.

(2-Chlorophenyl)(naphthalen-2-yl)methanol (17c).²⁹ A solution of (2-chlorophenyl)trimethylsilane (**13b**) (111 mg, 0.6 mmol) and 2-naphthaldehyde (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 was stirred under N₂ at rt for 5 h. HCl (2 M, 10 mL) was added, and the residue was extracted with diethyl ether (15 × 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 **17c** as a colorless oil (118 mg, 87%). ¹H NMR (400 MHz, CDCl₃): δ 7.88 (s, 1H), 7.84–7.78 (m, 3H), 7.62 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50–7.43 (m, 3H), 7.36 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.30 (td, *J* = 7.6, 1.4 Hz, 1H), 7.26–7.20 (m, 1H), 6.40 (d, *J* = 3.8 Hz, 1H), 2.45 (d, *J* = 3.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 141.0, 139.7, 133.4, 133.1, 132.8, 129.8, 129.0, 128.5, 128.4, 128.3, 127.8, 127.3, 126.3, 126.2, 125.8, 125.0, 72.9 ppm. HRMS-ESI [*M* + Na]⁺: 291.0546, C₁₇H₁₃ONaCl requires 291.0553.

(2-Chlorophenyl)(4-fluorophenyl)methanol (17d).³⁰ 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 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 (2 M, 10 mL) was added, and the residue was extracted with diethyl ether (15 × 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 **17d** as a colorless oil (102 mg, 86%). ¹H NMR

(400 MHz, CDCl₃): 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. ¹³C NMR (100 MHz, CDCl₃): 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, C₁₃H₉ClFO 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 μ L, 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. The solvent was removed under reduced pressure, and HCl (2 M, 10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 17e as a colorless oil (42 mg, 84%). ¹H NMR (400 MHz, CDCl₃): δ 7.55 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.32 (dd, $J = 7.8, 1.3$ Hz, 1H), 7.27 (td, $J = 7.6, 1.3$ Hz, 1H), 7.21–7.16 (m, 1H), 5.03 (d, $J = 3.0$ Hz, 1H), 1.86 (d, $J = 3.0$ Hz, 1H), 0.98 (s, 9H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 140.1, 129.6, 129.4, 128.5, 126.4, 123.3, 76.8, 37.1, 25.9 ppm. HRMS-EI [M]⁺: 198.0807, C₁₁H₁₅ClO requires 198.0811.

(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 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 (2 M, 10 mL) was added, and the residue was extracted with diethyl ether (15 \times 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 17f as a yellow oil (99 mg, 81%). ¹H NMR (400 MHz, CDCl₃): δ 7.61 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.40–7.26 (m, 6H), 7.25–7.19 (m, 2H), 6.72 (d, $J = 15.9$ Hz, 1H), 6.34 (dd, $J = 15.9, 6.2$ Hz, 1H), 5.80 (d, $J = 6.2$ Hz, 1H), 2.18 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): 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^{–1}. HRMS-EI [M]⁺: 244.0667, C₁₅H₁₃ClO 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. The solvent was removed under reduced pressure, and HCl (2 M, 10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (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, $J = 1.1$ Hz), 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 μ L, 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. The solvent was removed under reduced pressure, and HCl (2 M, 10 mL) added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (92:8) yielded 17h as a colorless oil (105 mg, 83%). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ

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) – H₂O]⁺: 235.08, C₁₄H₁₀F₃ 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 μ L, 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. The solvent was removed under reduced pressure, and HCl (2 M, 10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 17i as a colorless oil (106 mg, 72%). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₇H₁₆F₃O 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 μ L, 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. The solvent was removed under reduced pressure, and HCl (2 M, 10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 17j as a colorless oil (51 mg, 88%). ¹H NMR (400 MHz, CDCl₃): δ 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. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₂H₁₅F₃O requires 232.1075.

(4-Chlorophenyl)(3-methoxyphenyl)methanol (17k).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 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. The solvent was removed under reduced pressure, and 2 M HCl (10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 (90:10) yielded 17k as a colorless oil (42 mg, 68%). ¹H NMR (400 MHz, CDCl₃): δ 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 (br s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 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, C₁₄H₁₂O₂Cl requires 247.0526.

(4-Bromophenyl)(phenyl)methanol (17l).¹⁸ A solution of (4-bromophenyl)trimethylsilane (13e) (86 mg, 0.375 mmol) and benzaldehyde (26 μ L, 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. The solvent was removed under reduced pressure, and HCl (2 M, 10 mL) was added. The residue was extracted with diethyl ether (15 \times 3 mL), and 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 17l as a colorless solid (42 mg, 64%, mp 44–46 °C). 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 (br s, 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.

■ ASSOCIATED CONTENT

S 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>.

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Notes

The authors declare no competing financial interest.

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