JOC The Journal of Organic Chemistry

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Phase-Transfer Catalyzed *O*-Silyl Ether Deprotection Mediated by a Cyclopropenium Cation

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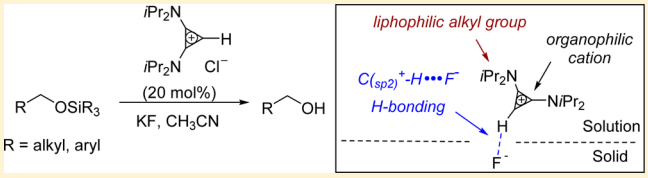
Supporting Information

ABSTRACT: The use of a cyclopropenium cation as a phase-transfer catalyst for *O*-silyl ether deprotection is reported. Mechanistic insight into this deprotection methodology derived by linear free-energy relationships (LFER), quantum theory of atoms in molecules (QTAIM), and density functional theory (DFT) calculations are also provided.



INTRODUCTION

Protecting groups have a rich chemical history dating back to the late-18th century as attested for by their use in Nobel laureate Emil Fischer's syntheses of glucose, fructose, and mannose.[1] Since this formative beginning, protecting groups have become an essential part of the synthetic chemist's toolbox, and today find use in nearly every branch of chemical synthesis. Owing to this fact, an array of protecting groups exist today with *O*-silyl ethers being one of the most utilized, due to stability under various conditions, ease of installation and removal, functional group compatibility, and the commercial availability of countless silane precursors.

The use of *O*-silyl ether protecting groups, however, is not without drawbacks. This is particularly evident with respect to deprotection and product purification.[2] For instance, the use of TBAF (*tert*-butylammonium fluoride), a widely employed source of so-called "naked F^-"[3] for mediating silyl deprotection, is associated with several shortcomings, such as it (1) undergoes Hoffman E_2-elimation at temperatures between 40 and 77 °C (2 Torr),[4] (2) has a poor fluoride to total reagent mass ratio (F^- = 7.3% of total mass of NBu_4F), (3) is hydroscopic, and (4) stoichiometric or greater amounts are usually employed in practice. Making matters worse, the isolation of water-soluble products, such as sugars from TBAF and its byproducts is often challenging as standard workup protocols call for an aqueous acid/base wash. To address these shortcomings various desilylation procedures have been introduced,[5] yet owing to inherit limitations there remains a need for innovation. Relevant in this respect would be the advancement of more robust and operationally simple approaches that were catalytic.

Intrigued by this prospect we envisioned using a cyclopropenium cation as a phase-transfer catalyst (PTC) for *O*-silyl ether deprotection. Notably, the advancement of this technology would build upon a rich history and revitalized interest in bis(dialkylamino)cyclopropenium, while having the advantages of PTC protocols. That is, being simple to perform, amenable to both large and small-scale synthetic protocols, and utilizes mild reaction conditions, as well as, the frequent use of inexpensive reagents and solvents.[6]

As such, in building upon our recent development and use of a N-centered cyclopropenium (**1**) and proton sponge analogue DACN-2H$^+$ (**2**-2H$^+$) as phase-transfer catalyst for fluorination and/or benzylation[7] we were intrigued by the prospect of using an alkali halide, such as KF and a catalytic amount of cyclopropenium **3**·X^- (X^- = BF_4^-, Cl^-, etc.) as a reaction platform for mediating *O*-silyl ether deprotection under biphasic (solid/solution) conditions (Figure 1). To this end,

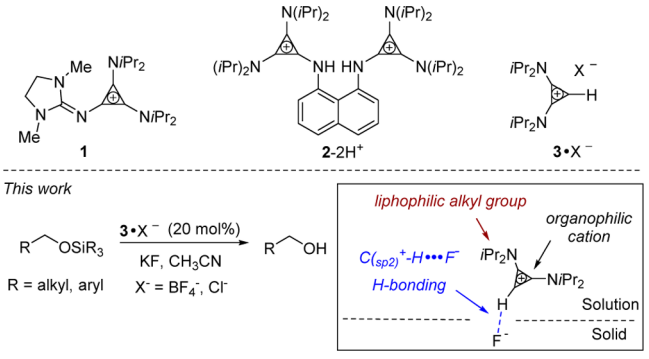


Figure 1. Envisioned use of a cyclopropenium (**3**·X^-) as a phase-transfer catalysts for *O*-silyl ether deprotection.

the ability of **3**·X^- to function as a phase-transfer catalyst was projected to arise from a discrete set of functionalities, which could be subdivided into (1) liphophilic alkyl groups, (2) a π-polarizable aromatic cyclopropenium cation with organophilic character, and (3) a cyclopropenium $C(sp^2)$–H moiety capable of shuttling F^- into solution via $C_{(sp2)}^+$–H···F^- H-bonding. Accordingly, reported here is the use of cyclopropenium **3**·Cl^- as a PTC for *O*-silyl ether deprotection.[8] Catalytic conditions, operational simplicity, and ease of removal of the fluoride

Received: November 16, 2016
Published: December 9, 2016

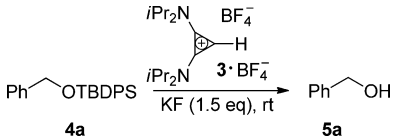
DOI: 10.1021/acs.joc.6b02733
J. Org. Chem. 2017, 82, 709–714

source by simple filtration, typify evident strengths of this novel methodology.

RESULTS AND DISCUSSION

Initial efforts in this study focused on the reaction of substrate **4a** (1 equiv), catalyst **3**·BF_4^- (10−20 mol%), and solid KF (1.5 equiv) as an easy to handle, inexpensive, latent source of nucleophilic fluoride in dichloromethane (DCM). To our disappointment, only unreacted starting material was obtained under these conditions (Table 1, entries 1 and 2). Reasoning

Table 1. Desilylation of Substrate 4a under Various Reaction Conditions



4a 5a

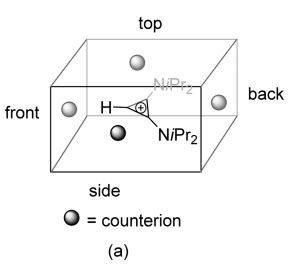
entry	solvent	catalyst (mol%)	time (h)	yield[a] (%)
1 **4a**	DCM	**3**·BF_4^- (10)	19	
2 **4a**	DCM	**3**·BF_4^- (20)	19	
3 **4a**	CH_3CN	**3**·BF_4^- (10)	19	20
4 **4a**	CH_3CN	**3**·BF_4^- (20)	19	38
5 **4a**	CH_3CN		19	4.8

[a]Isolated yields.

this lack of reactivity stemmed, in part, from the poor solubility of KF and/or a putative *in situ* derived species **3**·F^- in DCM, the desilylation of **4a** was performed in CH_3CN. To our delight, the formation of alcohol **5a** was observed in CH_3CN, albeit in low isolated yield (Table 1, entry 3). The loading of **3**·BF_4^- was then increased, manifesting in *circa* a 2-fold improvement in the yield of **5a** (Table 1, entry 4), while a control reaction performed in the absence of **3**·BF_4^- resulted in a negligible yield of **5a** (Table 1, entry 5).

While the ability of **3**·BF_4^- to act as a phase-transfer catalyst for desilylation was encouraging, improvement was needed in terms of yield. Suspecting that the conversion of **3**·BF_4^- to a reactive entity **3**·F^- capable of mediating desilylation was the root of the problem, density functional theory (DFT) calculations were performed at the wB97XD/6-311+G(d,p) (Def2TZV fitting set) level with solvent accounted for using the (IEFPCM) implicit solvation model (CH_3CN, ε = 37.5) to gain insight into this assumption. More specifically, the relative energies of ion pairs **3**·X^- (X^- = Br^-, Cl^-, BF_4^-, $CF_3SO_3^-$, ClO_4^-) vs **3**·F^- were computed using the lowest energy structures generated by optimization of several starting geometries, wherein, the counterion was placed in one of four quadrants (i.e., top, front, back, and side quadrants) at a 4 Å distance from the ring of bis(diisopropylamino)cyclopenium (BACI) **3**, Figure 2a.[9] As seen from Figure 2b, there was an energetic preference for the counterions Cl^-, and F^- to reside in front of the cation, while BF_4^-, Br^-, and $CF_3SO_3^-$ were on top and ClO_4^- was in back. Materializing further was the finding that the conversion of **3**·BF_4^- to **3**·F^- was the least favored counterion exchange process, in terms of ΔE, whereas the conversion of **3**·Cl^- to **3**·F^- was the most favorable (eq 1 and Figure 2b).

Armed with this insight, catalyst **3**·Cl^- (20 mol%), **4a** (1 equiv), and KF (1.5 equiv) were reacted in CH_3CN at ambient temperature to afford the corresponding alcohol in 89% yield (Table 2, entry 1). Having identified **3**·Cl^- as an optimum



(a)

3·X^- + KF ⇌ **3**·F^- + KX eq. 1

X^-	ΔE	favored position of conterion
Cl^-	0.9	front
Br^-	1.7	top
$CF_3SO_3^-$	3.1	top
ClO_4^-	3.5	back
BF_4^-	3.9	top
F^-	---	front

(b)

Figure 2. (a) Schematic of counterion X^- relative to **3**. (b) Calculated ΔE values of eq 1 and favored positioning of counterion X^- with respect to **3**.

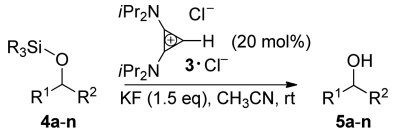
catalyst for desilylation the substrate scope of this methodology was probed. Commencing with the deprotection of trimethylsilyl (TMS) protected **4b** and **4c**, the rapid removal of 1°- and 2°-benzyl alcohols **5b** and **5c** was observed (Table 2, entry 2−3). In comparison, TMS-*O*-protected **4d** was slow to react, forming 3°-benzyl alcohol **5d** in 89% after 17 h (Table 2, entry 4). The lack of reactivity in this case, most likely, arising from the bulky $PhC(Me)_2O$-moiety, which in being isostructural with a neo-pentyl group, adversely affected reactivity at the Si-atom of **4d**.

On the other hand, substrate **4e** underwent rapid desilylation in only 0.5 h to afford **5e** in 95% (Table 2, entry 5). The desilylation of TMS-*O*-protected natural products camphor **4f** and quinine **4g** were then investigated, resulting in **5f** and **5g** in high yields of 92% and 94% (Table 2, entries 6 and 7). Next, to explore the influence of silyl-group size on the rate of desilylation, acid and base sensitive TES protected furanyl **4h** was examined, resulting in the **5h** in 91% (Table 2, entry 8). In contrast, TES protected benzoin **4i** underwent desilylation in a shorter timespan (Table 2, entry 9). The desilylation of aryl protected **4j** and **4k** having a bulky *tert*-butyldimethylsilyl (TBS) group were then carried out to afford **5j** and **5k** in 1 and 0.5 h in high yields, whereas TBS protected benzyl alcohol **4l** required an extended reaction time to obtain **5l** in 90% yield (Table 2, entries 10, 11, and 12). Notably, as attested for by substrates **5j** and **5l**, both aldehyde and iodo functionalities were compatible with the reaction conditions. Finally, switching to the use of a large steric hindering *tert*-butyldiphenylsilyl (TBDPS) protecting group the desilyation of phenol protected **4m**, **4n**, and **4o** was studied. The desylilation of protected phenol **4m** having a resonance donating and inductively electron withdrawing *ortho*-bromo substituted occurred in 15 h with 94% yield (Table 2, entry 13). Meanwhile, *ortho*- and *meta*-methyl substituted protected phenols **4n** provided a lower product yield of 60%, while, **4o** reacted more rapidly to afford **5o** in 85% yield (Table 2, entry 14 and 15).

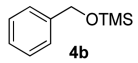
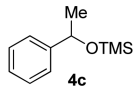
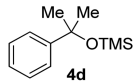
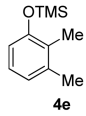
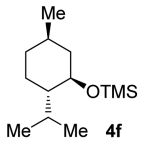
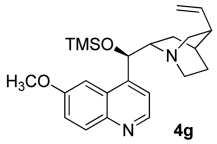
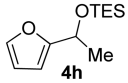
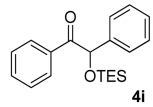
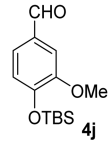
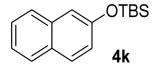
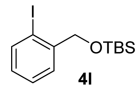
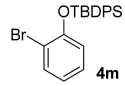
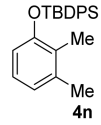
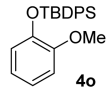
As for the mechanism of these reactions, the trends in Table 2 suggest that both the silyl group (region 1) and substructure R_1 (region 2) have an impact on the rate of desilylation (Figure 3a). While the rate dependency arising from the silyl group (region 1) can be accounted for by known relative hydrolysis rates of *O*-silyl ethers in basic media (e.g., k_{rel} = TMS (1) < TES (10−100) < TBS ∼ TBDPS (20 000) < TIPS (100 000))[10] the effect of the substrate (R_1) substructure (region 2), especially in terms of electronics, is less obvious. As such, to better understand the impact of substrate based (R_1) electronics on the rate of desilylation the linear free-energy relationship (LFER) derived from activated, unactivated and deactivated *para*-substituted *tert*-butyldimethylsilyl protected

DOI: 10.1021/acs.joc.6b02733
J. Org. Chem. 2017, 82, 709−714

Table 2. Deprotection of Substrates 4a−o Using Catalyst[a] 3·Cl⁻



SiR_3 = TMS, TES, TBS, TBDPS

Entry	Substrate	Time (h)	Yield (%)[b]
1	**4a**	19	89
2	 **4b**	0.1	96
3	 **4c**	0.3	95
4	 **4d**	17	89
5	 **4e**	0.5	95
6	 **4f**	11	92
7	 **4g**	6	94
8	 **4h**	4	91
9	 **4i**	6	90
10	 **4j**	1	95
11	 **4k**	0.5	95
12	 **4l**	16	90
13	 **4m**	15	94
14	 **4n**	15	60
15	 **4o**	6	85

[a]All reactions were carried out with 0.2 mmol of the substrate, catalyst **3**·Cl⁻ (20 mol%), and KF (1.5 equiv) in acetonitrile at room temperature. [b]Isolated yields.

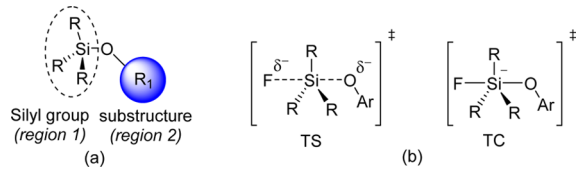


Figure 3. (a) Generalized example of a silyl ether compound. (b) Transition complex (TC) and S_n2−type transition state (TS).

phenols **4p−w** was explored, providing the Hammett plot depicted in Figure 4. To this end, the positive ρ (rho) value (ρ = 0.22) of this Hammett plot is consistent with a modest degree of (δ^-)-charge build-up in the rate determining transition state of these desilylation reactions, thus suggesting the possible formation of a short-lived five-coordinate siliconate conforming to a transition complex (TC) or a reaction mechanism involving a S_n2−type transition state (TS) (Figure 3b). Notably, the former scenario involving a TC would in all likelihood evolve on a single- or triple-well potential energy surface (PES), while the latter would occur on a double-well PES.[11]

Irrespective of whether a short-lived TC or S_n2-type transition state (TS) is involved in these reactions, the question remains what catalytic F^- entity prompts their formation. While numerous off-cycle equilibria leading to inactive catalyst resting states, in principle, might exist under the reaction conditions for

DOI: 10.1021/acs.joc.6b02733
J. Org. Chem. 2017, 82, 709−714

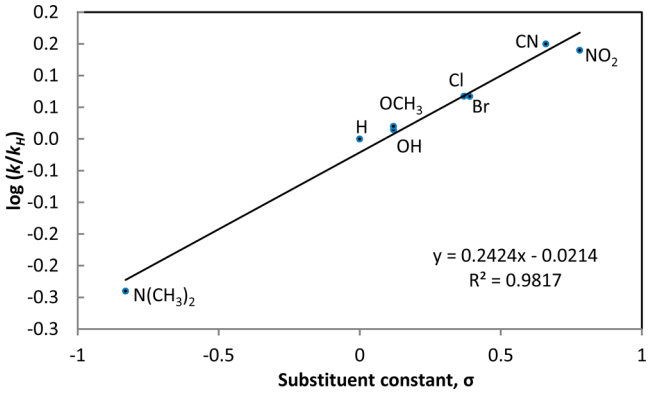
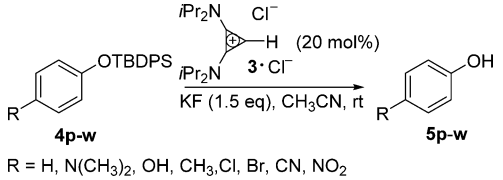


Figure 4. Hammett plot derived from the desilylation of 4-substituted *tert*-butyldimethylsilyl phenols at rt. over 6 h.

desilylation reported *vide supra*, it is suggested that a solution-phase species conforming to **3**·F^- triggers the formation of the aforesaid TC or TS structures.[12] Considering F^- is the smallest anion (ionic radius = 1.33 Å)[13] and a powerful Brønsted base with a strong propensity to form extremely strong H-bonds (H−F BDE = 136 kcal/mol) the catalytic role, for instance, of **3**·F^- in these desilylations is reasonable, given the formation of **3**·F^- would be driven by the creation of a favorable $C_{(sp2)}{}^+$−H···F^- H-bond. Notably, this $C_{(sp2)}{}^+$−H···F^- interaction, which in the lexicon of Gilli[14] typifies a heteronuclear negative/positive charge assisted H-bond [(∓)CAHB], would benefit from both ionic and "partial covalent" character with the later arising from a margin degree of charge transfer H-bonding. To gain insight into this $C_{(sp2)}{}^+$−H···F^- interaction, natural bond order (NBO) analysis, quantum theory of atoms in molecules (QTAIM), NBO charge populations were calculated. To this end, the closed-shell (ionic) character of the $C_{(sp2)}{}^+$−H···F^- H-bond of 1·F^- was supported by a (+3, −1) bond critical point (BCP) residing near the atomic basin of fluoride with density ρ = 0.080 au and Laplacian value $\nabla^2\rho_{bcp}$ = 0.055 au.[15] In addition, the computed NBO charges of the hydrogen (0.337 e) and fluoride (−0.804 e) were consistent with an ionic interaction. The shared nature of this H-bond, on the other hand, was uncovered by NBO analysis, which revealed a substantial donor−acceptor $\eta_{F^-} \rightarrow \sigma^*_{(H-C)}$ component amounting to 78.07 kcal/mol.



On the basis of the above results a plausible catalytic cycle supported by DFT calculations is offered in Figure 5. Counterion exchange between **3**·Cl^- and KF to generate the active catalyst **3**·F^- initiates the cycle, where after precomplex **6** forms in the presence of substrate **4b**. At that stage, low barrier ($\Delta G^{\ddagger}$ = −2.63 kcal mol^{-1}) fluoride addition transition state **TS1** arises. Salient features of this transition state include a Si···F^- bond forming distance of 2.65 Å and a F^- stabilizing H-bond network originating from a $C_{(sp2)}{}^+$−H···F^- interaction (distance =1.45 Å) and two C−H···F^- contacts involving H_1 and H_2 that measured 2.41 and 2.52 Å. An intrinsic reaction coordinate (IRC) calculation revealed that pentavalent silicate transition complex **TC** was the direct product of **TS1**. Finally, Si···O bond cleavage (distance = 2.65 Å) accompanied by $C_{(sp2)}{}^+$−H···$^{-\delta}$OPh H-bond stabilization of the developing phenoxy occurs via rate determining transition state **TS2** ($\Delta G^{\ddagger}$ = 11.07 kcal/mol) resulting in the exergonic formation of 7, TMS−F, and catalyst turnover.

To recap, the use of a cyclopropenium as a phase-transfer catalyst for *O*-silyl ether deprotection was reported. The origin of this reactivity was investigated by LFER analysis and DFT calculations, which revealed the remarkable finding that cyclopropeniums offer promise as a catalytic platform for shuttling fluoride into solution via $C_{(sp2)}{}^+$−H···F^- H-bonding. No doubt, the potential of this H-bonding motif as a means for attenuating fluoride basicity and nucleophilicity will be applicable to other modes of catalysis.

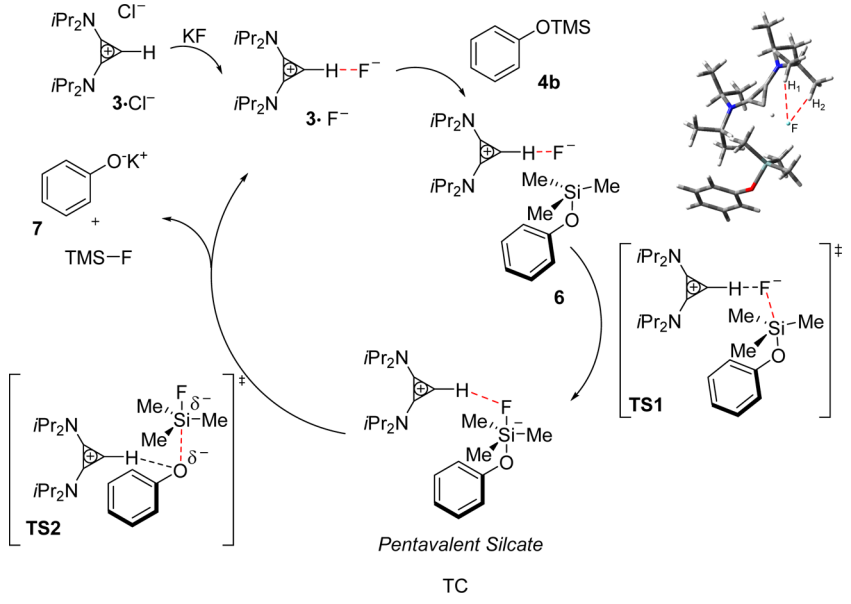


Figure 5. Proposed **3**·Cl^- catalyzed cycle for *O*-silyl ether deprotection.

DOI: 10.1021/acs.joc.6b02733
J. Org. Chem. 2017, 82, 709−714

EXPERIMENTAL SECTION

General Information. Materials were obtained from commercial suppliers and were used without further purification. All reactions were performed under an inert atmosphere. Reactions were monitored by thin layer chromatography (TLC) using TLC silica gel 60 F254. Flash column chromatography was performed over Silicycle ultrapure silica gel (230−400 mesh). NMR spectra were obtained with a 300 or 400 MHz spectrometer (^{1}H 300 MHz, ^{1}H 400 MHz, ^{13}C 75.5 MHz, and ^{13}C 150.9 MHz) in $CDCl_3$ or CD_3CN. The chemical shifts are reported as δ values (ppm) relative to tetramethylsilane. Mass analyzer magnetic-electrostatic sector used for the HRMS measurments.

General Procedure for Silyl Protection of Alcohols 5a−w. *General Procedure*[16] *for Preparation of Trimethylsilyl Ether (**4b−g**).* To a solution of benzyl alcohol (1.0 g, 9.2 mmol) in THF (5 mL) was added triethylamine (2.6 mL, 18.4 mmol) and trimethylsilyl chloride (1.4 mL, 11.04 mmol). The suspension was stirred for 5 h at room temperature. Subsequently, water (5 mL) was added, and the organic layer was separated. The aqueous layer was washed with ethyl acetate (5 mL) three times. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under high vacuum. The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate, 10:1) to yield **4b** (1.5 g, 92% yield).

General Procedure[17] *for Preparation of Triethylsilyl Ether (**4h−i**).* To a stirred solution of benzoin (212.2 mg, 1 mmol) and imidazole (204.2 mg, 3 mmol) in DMF (2 mL) at 5 °C was added dropwise triethylsilyl chloride (0.33 mL, 2 mmol). The reaction mixture was allowed to warm to room temperature over 1 h and then stirred for 10 h. Subsequently, water (2 mL) was added and the resulting mixture was extracted with diethyl ether (5 mL) three times. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under high vacuum. The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate, 10:1) to yield **4i** (293.8 mg, 90% yield).

General Procedure[18] *for Preparation of tert-Butyldiphenylsilyl Ether (**4a, 4m−w**).* *tert*-Butyldiphenylsilyl chloride (1.4 mL, 5.5 mmol) was added dropwise to a stirred solution of benzyl alcohol (540.7 mg, 5 mmol) and imidazole (749.1 mg, 11 mmol) in DMF (2 mL) at room temperature. The reaction mixture was stirred for 10 h. Subsequently, water (2 mL) was added and the resulting mixture was extracted with diethyl ether (5 mL) three times. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under high vacuum. The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate, 10:1) to yield **4a** (1.6 g, 94% yield).

General Procedure[19] *for Preparation of Ether (**4j−l**).* To a stirred solution of 2-iodobenzyl alcohol (585.1 mg, 2.5 mmol) and imidazole (374 mg, 5.5 mmol) in DMF (2 mL) at room temperature was added dropwise *tert*-butyldimethylsilyl chloride (414.5 mL, 2.7 mmol). The reaction mixture was stirred for 10 h. Subsequently, water (2 mL) was added and the resulting mixture was extracted with diethyl ether (5 mL) three times. Combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under high vacuum. The crude product was purified by column chromatography on silica gel (hexanes:ethyl acetate, 10:1) to yield **4l** (801.1 mg, 92% yield).

*Benzyloxy-tert-butyldiphenylsilane (**4a**).* Registry number 139706-45-9. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92−7.98 (m, 4H), 7.44−7.61 (m,1H), 5.04 (s, 2H), 1.37 (s, 9H).

*(Benzyloxy)trimethylsilane (**4b**).* Registry number 14642-79-6.

*Trimethyl(1-phenylethoxy)silane (**4c**).*[20] (1.6 g, 92% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.44 (m, 5H), 4.94 (q, J = 6.4 Hz, 1H), 1.52 (d, J = 6.4 Hz, 3H), 0.16 (s, 9H).

*Trimethyl((2-phenylpropan-2-yl)oxy)silane (**4d**).*[20] (1.8 g, 92% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.52 (m, 2H), 7.34−7.39 (m, 2H), 7.23−7.29 (m, 1H), 1.64 (s, 6H), 0.16 (s, 9H).

*(2,3-Dimethylphenoxy)triethylsilane (**4e**).* (1.7 g, 94% yield), Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.11 (s, 1H), 7.01 (d, J = 8.1 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 0.43 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 151.4, 132.0, 130.5, 128.6, 127.1, 118.9, 20.6, 16.6, 0.5. HRMS (EI): m/z calcd for $C_{11}H_{18}OSi$ (M+): 194.1127; found: 194.1120.

*(((1R,2S,5R)-2-Isopropyl-5-methylcyclohexyl)oxy)trimethylsilane (**4f**).*[21] (1.9 g, 90% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.41 (td, J = 10.3, 4.4 Hz, 1 H), 2.16 (dsept, J = 7.0, 2.4 Hz, 1H), 1.84−1.90 (m, 1 H), 1.58−1.68 (m, 2 H), 1.31−1.47 (m, 1 H), 1.00−1.20 (m, 3 H), 0.96 (d, J = 7.0 Hz, 6 H), 0.75 (m, 3H), 0.82−0.87 (m, 1H), 0.14 (s, 9).

*(2S)-2-((R)-(6-Methoxyquinolin-4-yl)((trimethylsilyl)oxy)methyl)-5-vinylquinuclidine (**4g**).*[22] (3.3 g, 91% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (d, J = 4.32 Hz, 1H), 8.04 (d, J = 9.24 Hz, 1H), 7.45−7.55 (m, 1H), 7.39 (dd, J = 8.34, 2.61 Hz, 2H), 5.62−6.80 (br, 1H), 4.87−5.00 (m, 2H), 3.96−4.06 (m, 3H), 3.36−3.69 (m, 1H), 2.92−3.30 (m, 2H), 2.49−2.86 (m, 1H), 2.17−2.49 (m, 1H), 1.74−1.83 (m, 4H), 1.47−1.62 (br, 1H), 1.26−1.29 (br, 1H), 0.84−0.97 (br, 1H), 0.085 (s, 9H).

*Triethyl(1-(furan-2-yl)ethoxy)silane (**4h**).*[23] (208.3 mg, 92% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.32 (m, 1H), 6.27- 6.329 (m, 1H), 6.15 (d, J = 3.24 Hz, 1H), 4.85 (q, J = 19.5, 6.5 Hz, 1H), 1.47 (d, J = 6.50 Hz, 3H), 0.92 (t, J = 8.01 Hz, 9H), 0.46−0.62 (m, 6H).

*1,2-Diphenyl-2-triethylsilyloxyethanone (**4i**).*[24] ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02−8.05 (m, 2H), 7.53−7.56 (m, 2H), 7.45−7.49 (m, 1H), 7.33−7.39 (m, 4H), 7.27−7.29 (m, 1H), 5.80 (s, 1H), 0.91 (t, J = 8.0 Hz, 9H), 0.62−0.67 (m, 6H).

*4-(tert-Butyldimethylsilyloxy)-3-methoxybenzaldehyde (**4j**).*[25] (619.4 g, 93% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.84 (s, 1H), 7.34−7.40 (m, 2H), 6.65 (d, J = 7.95 Hz, 1H), 3.86 (s, 3H), 1.00 (s, 9H), 0.19 (s, 6H).

*tert-Butyldimethyl(naphthalen-2-yloxy)silane (**4K**).*[26] (587.9 g, 91% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88−7.95 (m, 3H), 7.57−7.62 (m, 1H), 7.48−7.53 (m, 1H), 7.40−7.46 (m, 1H), 7.27−7.31 (m, 1H), 1.24−1.27 (m, 9H), 0.46−0.48 (m, 6H).

*tert-Butyl(2-iodobenzyl)oxy)dimethylsilane (**4l**).*[27] ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (dd, J = 7.8, 0.99 Hz, 1H), 7.54 (d, J = 7.59 Hz, 1H), 7.39 (dt, J = 7.62, 0.66 Hz, 1H), 7.00 (dt, J = 7.92, 1.02 Hz, 1H), 4.65 (s, 2H), 0.99 (s, 9H), 0.16 (s, 6H).

*(2-Bromophenoxy)(tert-butyl)diphenylsilane (**4m**).*[28] (2.1 g, 92% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73−7.76 (m, 4H), 7.52−7.55 (m, 1H), 7.41−7.47 (m, 6H), 6.82−6.87 (m, 1H), 6.70−6.75 (m, 1H), 6.47 (dd, J = 7.92, 1.2 Hz, 1H), 1.15 (s, 9 H).

*tert-Butyl(2,3-dimethylphenoxy)diphenylsilane (**4n**).* (1.8 g, 90% yield), Viscus oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72−7.74 (m, 4 H), 7.34−7.43 (m, 6 H), 6.95−7.00 (m, 1 H), 6.56 (d, J = 8.07 Hz, 1 H), 6.31 (d, J = 8.16 Hz, 1 H), 2.37 (s, 3 H), 2.19 (s, 3 H), 1.11 (s, 9 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 151.5, 135.5, 133.2, 131.5, 129.9, 127.9, 127.8, 126.7, 118.2, 30.9, 26.7, 20.5, 19.7, 17.1. HRMS (EI): m/z calcd for $C_{24}H_{28}OSi$ (M+): 360.1909; found: 360.1895.

*tert-Butyl(2-methoxyphenoxy)diphenylsilane (**4o**).*[29] (1.8 g, 92% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (m, 4 H), 7.31−7.43 (m, 6 H), 6.74 (m, 4 H), 3.56 (s, 3 H), 1.11 (s, 9 H).

*tert-Butyl(phenoxy)diphenylsilane (**4p**).* (1.7 g, 92% yield), Viscus oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73−7.61 (m, 4H) 7.36−7.48 (m, 6H), 7.09−7.14 (m, 2H), 6.86−6.93 (m, 1H), 6.78 (d, J = 7.71 Hz, 2H), 1.13 (s, 9 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 155.7, 151.5, 153.6, 133.1, 131.6, 129.9, 129.3, 127.8, 126.8, 121.1, 119.8, 118.2, 26.6, 19.5. HRMS (EI): m/z calcd for $C_{22}H_{24}OSi$ (M+): 332.1596; found: 332.1602.

*4-tert-Butyldiphenylsilyloxy-N,N-dimethylaniline (**4q**).* (1.9 g, 90% yield), light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74−7.77 (m, 4H) 7.35−7.47 (m, 6H), 6.70−6.73 (m, 2H), 6.54−6.60 (m, 2H), 2.83 (s, 6H), 1.12 (s, 9 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 147.6, 145.6, 135.6, 135.5, 134.9, 133.5, 129.8, 129.8, 129.6, 127.7, 119.9, 114.6, 41.7, 26.7, 19.5. HRMS (EI): m/z calcd for $C_{24}H_{29}NOSi$ (M+): 375.2018; found: 375.2018.

*4-tert-Butyldiphenylsilyloxyphenol (**4r**).*[30] (1.7 g, 91% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74−7.77 (m, 4 H), 7.37−7.49 (m, 6 H), 6.65−6.70 (m, 2 H), 6.55−6.61 (m, 2 H), 4.55 (br, 1 H), 1.14 (s, 9 H).

DOI: 10.1021/acs.joc.6b02733
J. Org. Chem. 2017, 82, 709−714

*tert-Butyl-4-methoxyphenoxydiphenylsilane (**4s**).*[30] (1.8 g, 90% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73−7.76 (m, 4 H) 7.36−7.48 (m, 6 H), 6.64−6.74 (m, 4 H), 3.72 (s, 3 H), 1.13 (s, 9 H).

*tert-Butyl-4-chlorophenoxy-diphenylsilane (**4t**).*[31] (1.8 g, 93% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70−7.73 (m, 4H), 7.37−7.46 (m, 6H), 7.04−7.07 (m, 2H), 6.69−6.71 (m, 2H), 1.12 (s, 9H).

*4-Bromophenoxy-tert-butyl-diphenylsilane (**4u**).*[32] (2.1 g, 92% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71 (dd, J = 7.86, 1.47 Hz, 4H), 7.37−7.46 (m, 6H), 7.20 (m, 2H), 6.64−6.67 (m, 2H), 1.11 (s, 9H).

*4-tert-Butyl-diphenylsilyloxybenzonitrile (**4v**).*[33] (1.8 g, 91% yield), ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67−7.69 (m, 4H), 7.43−7.44 (m, 2H), 7.39−7.41 (m, 6H), 6.78−6.81 (m, 2H), 1.11 (s, 9H).

*tert-Butyl(4-nitrophenoxy)diphenylsilane (**4w**).* (1.9 g, 91% yield), White solid. MP = 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (dd, J = 9.15, 2.15 Hz, 2 H), 7.74−7.77 (m, 4 H), 7.42−7.52 (m, 6 H), 6.86 (d, J = 9.12 Hz, 2 H), 1.18 (s, 9 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 161.4, 141.9, 135.4, 131.5, 130.5, 128.1, 125.7, 120.0, 26.4, 19.4. HRMS (EI): m/z calcd for $C_{22}H_{23}NO_3Si$ (M+): 377.1447; found: 377.1427.

Procedure for Deprotection of Alcohol and Phenols 4a−w. An RBF was charged with reported[8a,34] cyclopropenium chloride (**3**·Cl^-) (11 mg, 0.04 mmol), and KF (17.4 mg, 0.3 mmol). Subsequently, a solution of (benzyloxy)(*tert*-butyl)diphenylsilane **4a** (69.3 mg, 0.2 mmol) in acetonitrile (1 mL) was added. The resulting mixture was stirred for 19 h, after which, the solvent was removed and the residue dissolved in diethyl ether. The resulting suspension was filtered and the filtrate concentrated followed by flash chromatography purification (hexanes to ethyl acetate = 10:1) to provide product benzyl alcohol as a colorless oil (19.2 mg, 89% yield).

Hammett correlation. A series of separate reactions were performed in which a solution of a respective 4-*R*-*tert*-butyl-(benzyloxy)diphenylsilane (R = NO_2, CN, Br, Cl, OH, OMe, NMe_2) (0.2 mmol) substrate in acetonitrile (1 mL) was added to catalyst **3**·Cl^- (11 mg, 0.04 mmol) and KF (17.4 mg, 0.3 mmol) and stirred at room temperature. Each reaction was monitored (30 min intervals up to 6 h) by ^{1}H NMR spectroscopy using 2-bromomesitylene (19.9 mg, 0.1 mmol) as an internal standard. The K_x was estimated from a first-order plot of log [product] vs reaction time rather than log [*tert*-butyl(benzyloxy)diphenylsilane] vs reaction time.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02733.

Spectroscopic data for all starting compounds, and computational details (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding of this research.

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DOI: 10.1021/acs.joc.6b02733
J. Org. Chem. 2017, 82, 709−714