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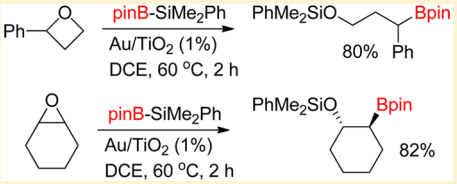
Gold-Nanoparticle-Catalyzed Silaboration of Oxetanes and Unactivated Epoxides

Eleni Vasilikogiannaki, Anastasia Louka, and Manolis Stratakis*

Department of Chemistry, University of Crete, 71003 Voutes, Iraklion, Greece

Supporting Information

ABSTRACT: Supported gold nanoparticles catalyze the unprecedented insertion of a silylborane into the C−O bond of oxetanes and unactivated epoxides, forming γ- or β-silyloxy boronates in good to excellent yields. In the silaboration process the boron moiety is acting as a nucleophile and the silyl as an electrophile. No external additives or ligands are required, while the catalytic system is recyclable and reusable.



INTRODUCTION

Boronate esters are valuable building blocks in modern organic chemistry, widely used in transition-metal-catalyzed cross-coupling reactions.[1] The classical procedures for the synthesis of boronates include[2] reaction of organometallic compounds with alkoxyboranes, metal-catalyzed hydroboration of alkenes, borylation of alkanes/arenes via C−H activation, conjugated alkenes in a Michael fashion, alkyl/aryl halides, π systems, etc. One of the main protocols for the synthesis of boronates is the addition of silylboranes and primarily the readily available $PhMe_2SiBpin$ (pin = pinacolato) on unsaturated substrates under catalytic conditions.[3] Typically, noble metals such as Pd(0) and Pt(0) activate the σ Si−B bond via redox catalysis followed by addition on π bonds.

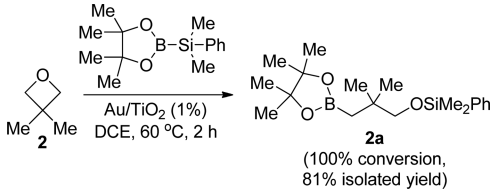
We have recently shown that supported Au nanoparticles (Au NPs) on TiO_2 catalyze the cis addition of $PhMe_2SiBpin$ to alkynes under mild conditions, forming in good yields 1,2-vinyl silyl boronates with abnormal regioselectivity.[4] The facile activation of silylborane by Au NPs spurred us to examine new potential applications of silaboration to other functionalities such as oxetanes and epoxides. The inspiration toward this goal was motivated by the fact that upon studying the Au-catalyzed silaboration of alkynes[4] we had observed that tetrahydrofuran (THF) is a poor solvent, and analysis of the reaction mixture revealed that, apart from alkyne silaboration, the partial addition of $PhMe_2SiBpin$ on the cyclic ether formed the linear silyloxy boronate $PhMe_2SiOCH_2CH_2CH_2CH_2Bpin$ (**1a**) as a minor side product. In a separate experiment we found that, on mixing $PhMe_2SiBpin$ with Au/TiO_2 in THF (**1**) as solvent (60 °C, 2 h), the adduct **1a** was isolated in 52% yield. Of course, the utility of this addition reaction is low, as one of the reactants (THF) is the reaction solvent. We anticipated, however, that more strained cyclic ethers, such as epoxides and oxetanes,[5] might undergo smoother addition by $PhMe_2SiBpin$, forming silyloxy and indirectly hydroxy boronates.

Silyloxy boronates are a class of compounds with scarce synthetic protocols. The enantioselective synthesis of α-silyloxy boronates has been reported via borylation of carbonyl compounds followed by protection of hydroxyl with silyl chloride,[6] while some γ- and δ-silyloxy boronates have been employed as starting materials for cross-coupling reactions, but their synthesis arose via diboration of alkenyl alcohols.[7] With regard to hydroxyl-substituted boronates, the α-hydroxy derivatives can be easily synthesized primarily via borylation of carbonyl compounds,[8] and there have been a few recent reports on the synthesis of β-[9] and γ-hydroxy boronates,[10] but the concept of these approaches is different from ours. A similarity might be the fact that in the synthesis of γ-hydroxy boronates[10] epoxides are used as starting materials, which undergo regioselective Cu-catalyzed coupling with a *gem*-diborylmethane.

RESULTS AND DISCUSSION

Initially we focused on oxetanes, with commercially available 3,3-dimethyloxetane (**2**) being examined as a representative substrate using Au/TiO_2 (1 mol %) as catalyst. To our delight, reaction of oxetane **2** (1 equiv) with $PhMe_2SiBpin$ (1.5 equiv) in dry 1,2-dichloroethane (DCE) as solvent at 60 °C afforded after 2 h the adduct **2a** in 81% isolated yield, with no other products being formed (Scheme 1). To the best of our knowledge, this is the first example in the literature of the silaboration of ethers and essentially constitutes a new method for the synthesis of functionalized boronates. The studies of process optimization are discussed below and summarized in Table S1 in the Supporting Information. When Au/TiO_2 was

Scheme 1. Silaboration of 2,2-Dimethyloxetane (2) by $PhMe_2Si$-Bpin Catalyzed by Au/TiO_2



2a
(100% conversion,
81% isolated yield)

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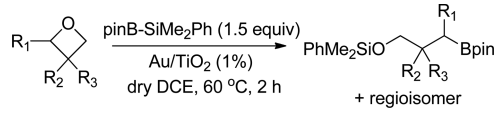
used as catalyst, after 2 h the consumption of oxetane **2** was 100%; in the case of other supported Au catalysts[11] such as Au/Al_2O_3 and Au/ZnO (also 1 mol %) the conversion yields on the same time scale were moderate. Thus, we focused on Au/TiO_2. As per solvent suitability, apart from DCE, hexane and ethyl acetate are also appropriate but require extra time (~3 h) to drive the reaction to completion. We also tested several catalysts which are known to activate $PhMe_2SiBpin$ under homogeneous conditions toward addition reactions to π systems such as $Pd(PPh_3)_4$, $Pt(PPh_3)_4$, and $(\eta^3\text{-}C_3H_5)Pd(PPh_3)Cl$,[12,13] but none were effective[14] to catalyze oxetane silaboration. In addition, soluble ionic gold catalysts such as $AuCl_3$, AuCl, $Ph_3PAuNTf_2$, and (acetonitrile)[(2-biphenyl)-di-*tert*-butylphosphine]gold(I) hexafluoroantimonate were tested,[14] but no silaboration product was seen in any case, other than unidentified mixtures of products (Table S1). The Au NPs are recyclable and reusable without significant loss of their activity after five consecutive runs (Table S2 in the Supporting Information). Recycling was performed by filtration of the catalyst after each run, washing with solvent, and drying at 100 °C for 1 h. In blank experiments, the support (TiO_2) is completely inefficient, indicative that Au nanoparticles are the catalytic sites.

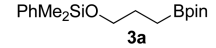
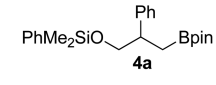
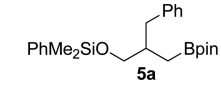
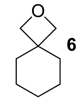
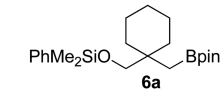
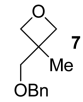
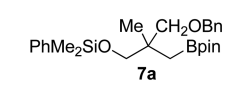
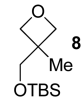
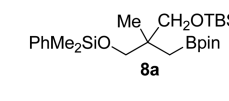
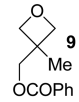
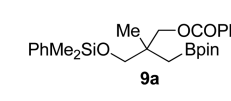
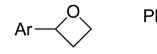
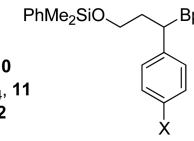
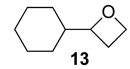
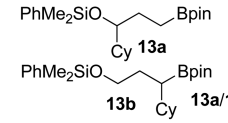
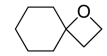
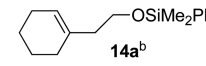
The highly encouraging reaction outcome among $PhMe_2SiBpin$ and oxetane **2** prompted us to examine the scope and limitations of this unprecedented transformation. A series of substituted oxetanes (and parent oxetane as well) smoothly undergo this addition reaction in good to excellent yields (Table 1). 3-Substituted oxetanes are excellent substrates for this purpose, cleanly forming γ-silyloxy boronates. 2,2-Disubstituted oxetanes seem to be unsuitable substrates, as they preferentially undergo isomerization under the reaction conditions (also in the absence of silylborane) primarily into homoallylic alcohols, a process that is more likely similar to the isomerization of substituted epoxides into allylic alcohols catalyzed by gold nanoparticles.[15] For instance, in the attempted silaboration of oxetane **14**, the silyl ether of the corresponding homoallylic alcohol **14a** was mainly formed. It is reasonable that isomerization to homoallylic alcohol is taking place followed by alcoholysis of $PhMe_2SiBpin$. Notably, 2-aryl oxetanes **10**–**12** provide a highly regioselective silaboration, with the boryl group attached exclusively at the benzylic position (products **10a**–**12a**). In contrast, the regioselectivity in the case of 2-cyclohexyloxetane **13** is inferior (**13a**/**13b** = 35/65), while the overall yield is much lower due to the partial competing destructive isomerization of reacting oxetane, just as in the case of **14**.

Following the determination of the suitability of oxetanes in their facile ring-opening silaboration, we focused on epoxides. In general, under catalysis by Au nanoparticles, epoxides are known to undergo either deoxygenation in the presence of a suitable reducing agent[16] or fixation with CO_2.[17] In addition, suitably substituted epoxides have been previously shown by our group to undergo Au-nanoparticle-catalyzed isomerization into allylic alcohols.[15]

Thus, *gem*-disubstituted or tri-/tetrasubstituted epoxides isomerize, while 1,2-disubstituted or monosubstituted epoxides are unreactive as a consequence of the requirement for development of a profound partial carbocationic character in the proposed six-membered-ring concerted transition state of isomerization. We chose cyclohexene oxide (**15**) as a suitable substrate to study, as it does not undergo any isomerization to allylic alcohol by Au NPs. To our delight, in the reaction of **15**

Table 1. Silaboration of Oxetanes by $PhMe_2Si$-Bpin Catalyzed by Au/TiO_2



reactant	product(s)	isolated yield (%)
 **3**	 **3a**	44
 **4**	 **4a**	83
 **5**	 **5a**	74
 **6**	 **6a**	83
 **7**	 **7a**	81
 **8**	 **8a**	78
 **9**	 **9a**	61
 Ar = phenyl, **10** Ar = *p*-F-C_6H_4, **11** Ar = *p*-tolyl, **12**		X = H, **10a** 80 X = F, **11a** 69 X = Me, **12a** 64
 **13**	 **13a** / **13b**	37 **13a**/**13b** = 35/65[a]
 **14**	 **14a**[b]	79

[a]The product ratio was determined by GC and ^{1}H NMR of the crude reaction mixture. [b]Product **14a** results from isomerization of oxetane **14** into a homoallylic alcohol catalyzed by Au nanoparticles.

with 1.5 equiv of $PhMe_2SiBpin$ in dry DCE (1 mol % of Au/TiO_2), after 2 h at 60 °C the epoxide had been completely consumed and the adduct **15a** (Table 2) was seen as the only product in the crude ^{1}H NMR spectrum. The relative stereochemistry of **15a** was assigned as trans, given that deprotection to the corresponding boryl alcohol (**15a′**) with KF in methanol and treatment of **15a′** with $NaBO_3{\cdot}4H_2O$ afforded *trans*-1,2-cyclohexanediol (Scheme 2). Again, as in the case of oxetanes, Au/TiO_2 was proven to be a superior catalyst relative to Au/Al_2O_3 or Au/ZnO, while no reaction was seen in the absence of Au NPs or under homogeneous Pd(0) or Pt(0) catalysis. As noted earlier, the scope and limitations of this transformation were somehow limited (Table 2). Epoxides that have the tendency to isomerize to allylic alcohols in the presence of Au/TiO_2 do not form any silaboration adduct. In

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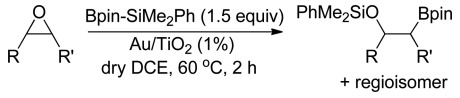
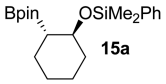
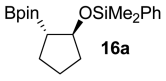
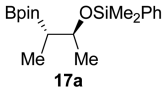
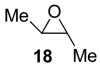
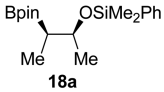
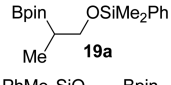
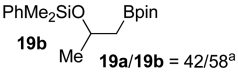
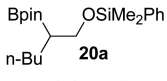
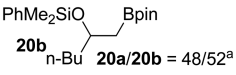
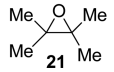
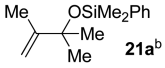
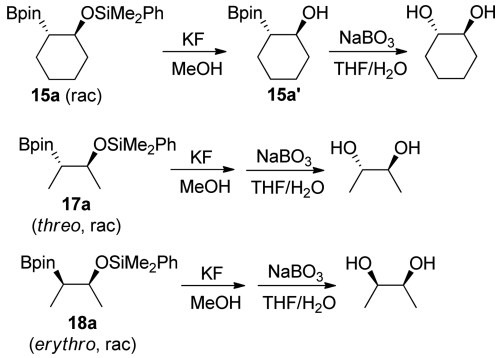
Table 2. Silaboration of Unactivated Epoxides by $PhMe_2Si$-Bpin Catalyzed by Au/TiO_2



reactant	product(s)	isolated yield (%)
 **15**	 **15a**	82
 **16**	 **16a**	78
 **17**	 **17a** (threo/erythro = 9/1)[a]	82
 **18**	 **18a** (erythro/threo = 85/15)[a]	78
 **19**	 **19a**  **19b** **19a/19b** = 42/58[a]	83
 **20**	 **20a**  **20b** **20a/20b** = 48/52[a]	80
 **21**	 **21a**[b]	77

[a]The product ratio was determined by GC and ^{1}H NMR of the crude reaction mixture. [b]Product **21a** results from isomerization of epoxide **21** into a allylic alcohol catalyzed by Au nanoparticles.[15]

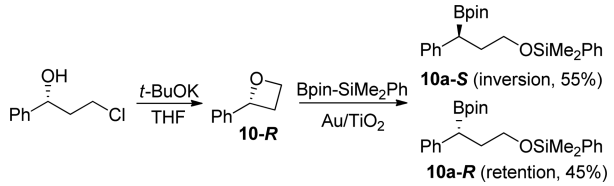
Scheme 2. Proof of Relative Stereochemistry of Silaboration Adducts



the case of **21**, for example, the dimethylphenylsilyl ether of the corresponding allylic alcohol **21a** was formed, just as oxetane **14** behaves. Aryl epoxides such as styrene oxide are also unsuitable, as they quickly isomerize in the presence of Au/TiO_2. Thus, we examined only the unactivated mono- or 1,2-disubstituted epoxides. Cyclopentene oxide (**16**) also works perfectly, providing a single trans adduct (**16a**). Notably, *cis*-2-butene oxide (**17**) affords a mixture of threo and erythro adducts in the relative ratio ~90/10, while in the case of isomeric *trans*-2-butene oxide (**18**) a relative threo/erythro ratio of ~15/85 was seen. The relative stereochemistry of the above addition products was established after deprotection/treatment with $NaBO_3{\cdot}4H_2O$ and comparison of the resulting 2,3-butanediols with authentic samples (Scheme 2). Monosubstituted epoxides **19** and **20** afford two regioisomeric products in a relative ratio of 1/1, a selectivity resembling that of the 2-monosubstituted cyclohexyloxetane **13**.

Before discussing the possible reaction mechanism and the origins of regioselectivity, we present in Scheme 3 the

Scheme 3. Stereochemistry in the Silaboration of Optically Pure Oxetane 10-*R*



stereochemical outcome of silaboration of optically active (*R*)-2-phenyloxetane (**10-*R***), prepared by treatment of (*R*)-3-chloro-1-phenylpropan-1-ol with *t*-BuOK.[18] The silaboration product of **10-*R*** was deprotected and treated with $NaBO_3{\cdot}4H_2O$ to yield 1-phenylpropane-1,3-diol. Through analysis by chiral HPLC, it was found that the diol exists as a mixture of enantiomers in a relative *S*/*R* ratio of 55/45 (Figure S19 in the Supporting Information), which implies that in this specific case almost complete racemization occurs. Note that oxetane **10-*R*** does not undergo racemization during the progress of the reaction, as was proven by chiral HPLC analysis. Partial epimerization has been also reported in the reaction of **10-*R*** with triarylborates,[19] a reaction proceeding via a profound carbocationic character at the benzylic position.

The Au-catalyzed silaboration reaction has the following characteristics that are helpful in the mechanistic discussion. (a) It could be seen as nucleophilic substitution of the cyclic ether by the postulated intermediate $PhMe_2Si$-Au_n-Bpin,[4,20] with the boron moiety attached to carbon and dimethylphenylsilyl to oxygen. We emphasize herein that, in the examples of Cu(I)-[21] or Rh(I)-catalyzed[22] silaboration of oxygen-containing substances (carbonyl compounds, CO_2) known so far, the silyl group acts as the nucleophile, in contrast to our results where the boryl group is acting as the nucleophile. (b) Aryl-substituted oxetanes **10**–**12** provide a single regioisomer with the boron moiety attached at the benzylic position. In cyclohexyl analogue **13**, however, the regioselectivity is lower, with boron primarily attached at the more hindered (secondary) position. (c) Optically active 2-phenyloxetane **10-*R*** provides an almost nonstereospecific reaction (Scheme 3, inversion/retention 55/45). (d) Similarly to 2-monosubstituted oxetane **13**, in the case of monosubstituted epoxides **19** and **20**, no substantial regioselectivity is observed, with the boron moiety attached on both sides (hindered and unhindered) in a relative ratio of ~1/1. (e) In addition, *cis*-epoxide **17** and *trans*-epoxide **18** mainly yield threo and erythro adducts, respectively, but the reaction is not stereospecific. Overall, these stereo-

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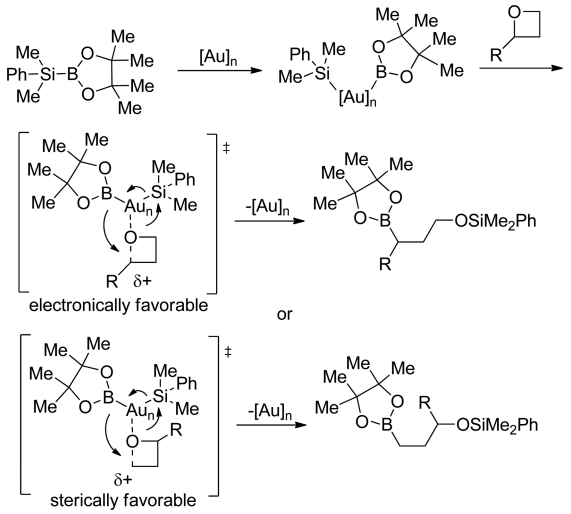
chemical results (a−e) rule out a typical S_N2-type addition mode, which in monosubstituted epoxides should have formed one regioisomer, and imply that a partial positive charge is developing on the carbon atom bonded to the ether oxygen. Thus, the regioselectivity pattern in oxetane **13** or monosubstituted epoxides **19** and **20** is a balance among electronic and steric factors. The partial positive charge becomes more profound in 2-aryl-substitued oxetanes, where it is stabilized through resonance, and the stereochemical outcome resembles that of an S_N1 reaction, where complete racemization is rarely seen. In the case of isomeric epoxides **17** and **18**, the partial positive charge is less apparent relative to oxetanes **10**−**12**; thus, the selectivity is higher. These conclusions are depicted in the proposed mechanism applied to a 2-substituted oxetane, shown in Scheme 4. A completely analogous mechanism could

Scheme 4. Proposed Mechanism of Au-Nanoparticle-Catalyzed Silaboration of a 2-Substituted Oxetane



be drawn for epoxides. Marginal mechanistic analogies could be seen in the metal-free borylative ring opening of vinyl epoxides, which generates hydroxyl-functionalized allylic boronates via an S_N2' mechanism,[23] in the Pd-catalyzed ring-opening borylation of 2-arylaziridines,[24] in the Cu(I)-catalyzed borylation of cyclic sulfamidates,[25] and in the catalytic borylative opening of propargyl epoxides and oxetanes[26] with pinB-Bpin.

CONCLUSIONS

In summary, we present an unprecedented reaction, the silaboration of strained ethers (oxetanes and epoxides) to form γ- and β-silyloxy boronates using as catalysts recyclable supported Au nanoparticles free of any ligands or external additives. Our mechanistic analysis suggests that, in the transition state of addition, a profound partial positive charge is developing on the carbon atom linked to the ether oxygen. The current reactivity mode and catalytic application of Au nanoparticles provide new and unique features of supported Au nanoparticles in the catalysis of organic transformations.[27]

EXPERIMENTAL SECTION

Synthesis of Substrates. All epoxides used were commercially available. Oxetanes **2** and **3** are commercially available, while **4**−**6** were prepared by successive treatment of the corresponding 1,3-diols with *n*-BuLi (1 equiv)/TsCl and then *n*-BuLi (1 equiv) in THF.[28]

*3-Phenyloxetane (**4**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42−7.27 (m, 5H, *Ph*), 5.08 (dd, $^2J_{HH}$ = 8.0, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 4.79 (dd, $^2J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2), 4.24 (tt, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, *benzylic*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.5 (*Ph*), 128.7 (2C, *Ph*), 127.0 (*Ph*), 126.8 (2C, *Ph*), 78.9 (2C, C−O), 40.3 (*C-Ph*).

*3-Benzyloxetane (**5**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *Ph*), 7.21 (t, $^3J_{HH}$ = 8.0 Hz, 1H, *Ph*), 7.12 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *Ph*), 4.79 (dd, $^2J_{HH}$ = 8.0, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2), 4.48 (dd, $^2J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2), 3.30 (m, 1H, *CH*), 3.22 (d, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2-*Ph*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.4 (*Ph*), 128.6 (2C, *Ph*), 128.3 (2C, *Ph*), 126.3 (*Ph*), 77.2 (2C, C−O), 39.6 (*tertiary C*), 36.1 (*C-Ph*).

*2-Oxaspiro[3.5]nonane (**6**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.35 (s, 4H, CH_2-*O*), 1.74−1.68 (m, 4H, *cyclohexyl*), 1.42−1.32 (m, 6H, *cyclohexyl*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.6 (2C, C−O), 40.3 (*quaternary C*), 35.5 (2C, *cyclohexyl*), 25.3 (*cyclohexyl*), 22.9 (2C, *cyclohexyl*).

Oxetanes **7**−**9** were prepared by derivatization[29] of commercially available (3-methyloxetan-3-yl)methanol.

*3-((Benzyloxy)methyl)-3-methyloxetane (**7**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.27 (m, 5H, *Ph*), 4.58 (s, 2H, OCH_2Ph), 4.52 (d, $^2J_{HH}$ = 6.0 Hz, 2H, CH_2-*O*), 4.37 (d, $^2J_{HH}$ = 6.0 Hz, 2H, CH_2-*O*), 3.53 (s, 2H, CH_2OBn), 1.34 (s, 3H, *Me*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3 (*Ph*), 128.4 (2C, *Ph*), 127.6 (*Ph*), 127.5 (2C, *Ph*), 80.1 (2C, C−O *oxetane*), 75.3 (C−O), 73.3 (C−O), 39.8 (*quaternary C*), 21.4 (*Me*).

*tert-Butyldimethyl((3-methyloxetan-3-yl)methoxy)silane (**8**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.48 (d, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2-*O*), 4.31 (d, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2-*O*), 3.62 (s, 2H, CH_2OTBS), 1.26 (s, 3H, *Me*), 0.90 (s, 9H, *t-Bu*), 0.06 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 79.7 (2C, C−O *oxetane*), 68.1 (*C-OTBS*), 40.9 (*quaternary*), 25.8 (3C, *t-Bu*), 20.9 (*Me*), 18.3 (*t-Bu*), −5.5 (2C, $SiMe_2$).

*(3-Methyloxetan-3-yl)methyl Benzoate (**9**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 1.5 Hz, 2H, *Ph*), 7.58−7.55 (m, 1H, *Ph*), 7.45−7.43 (m, 2H, *Ph*), 4.64 (d, $^2J_{HH}$ = 6.0 Hz, 2H, CH_2-*O*), 4.45 (d, $^2J_{HH}$ = 6.0 Hz, 2H, CH_2-*O*), 4.39 (s, 2H, CH_2−*OCOPh*), 1.42 (s, 3H, *Me*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5 (C═O), 133.1 (*Ph*), 129.8 (*Ph*), 129.6 (2C, *Ph*), 128.4 (2C, *Ph*), 79.5 (2C, C−O *oxetane*), 68.9 (C−O), 39.3 (*quaternary C*), 21.2 (*Me*).

Oxetanes **10**−**15** were prepared using the Corey−Chaykovsky reaction of an aldehyde or ketone with trimethylsulfoxonium iodide in the presence of *t*-BuOK in *t*-BuOH as solvent.[29]

*2-Phenyloxetane (**10**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47−7.45 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *Ph*), 7.40 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *Ph*), 7.31 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *Ph*), 5.83 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *benzylic C−H*), 4.87−4.82 (m, 1H, CH_2-*O*), 4.69−4.65 (m, 1H, CH_2-*O*), 3.07−3.00 (m, 1H, CH_2), 2.72−2.65 (m, 1H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.5 (*Ph*), 128.4 (2C, *Ph*), 127.8 (*Ph*), 125.2 (2C, *Ph*), 82.9 (*O−C−Ph*), 68.2 (C−O), 30.7 (*aliphatic*).

*2-(4-Fluorophenyl)oxetane (**11**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43−7.40 (m, 2H, *Ar*), 7.09−7.05 (m, 2H, *Ar*), 5.78 (t, *J* = 7.5 Hz, 1H, *benzylic C−H*), 4.84−4.80 (m, 1H, CH_2-*O*), 4.66−4.62 (m, 1H, CH_2-*O*), 3.04−2.98 (m, 1H, CH_2), 2.67−2.60 (m, 1H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.3 (d, $^1J_{CF}$ = 244.5 Hz, *Ar*), 139.3 (d, $^4J_{CF}$ = 3.0 Hz, *Ar*), 127.1 (d, $^3J_{CF}$ = 8.0 Hz, 2C, *Ar*), 115.3 (d, $^2J_{CF}$ = 21.5 Hz, 2C, *Ar*), 82.3 (*O−C−Ar*), 68.0 (C−O), 30.8 (*aliphatic*).

*2-(p-Tolyl)oxetane (**12**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *Ar*), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, 2H, *Ar*), 5.82 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *benzylic C−H*), 4.87−4.82 (m, 1H, CH_2-*O*), 4.70−4.66 (m, 1H, CH_2-*O*), 3.06−2.99 (m, 1H, CH_2), 2.74−2.66 (m, 1H, CH_2), 2.41 (s, 3H, *Me*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.4 (*Ar*), 137.3 (*Ar*), 129.0 (2C, *Ar*), 125.2 (2C, *Ar*), 82.7 (*O−C−Ar*), 67.9 (C−O), 30.6 (*aliphatic*), 21.0 (*Me*).

*2-Cyclohexyloxetane (**13**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.64−4.58 (m, 1H, *tertiary CH−O*), 4.47−4.39 (m, 2H, CH_2-*O*), 2.56−2.50 (m, 1H, *oxetane* CH_2), 2.39−2.32 (m, 1H, *oxetane* CH_2), 1.87−1.83 (m, 1H, *cyclohexyl*), 1.75−1.55 (m, 5H, *cyclohexyl*), 1.27−1.08 (m, 3H, *cyclohexyl*), 0.90−0.77 (m, 2H, *cyclohexyl*). ^{13}C NMR (125 MHz,

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$CDCl_3$): δ 86.6 (*tertiary C−O*), 68.0 (*secondary C−O*), 44.6 (*tertiary C*), 27.4, 26.4, 26.0, 25.6, 25.6, 25.4 (*all secondary C*).

*1-Oxaspiro[3.5]nonane (**14**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.47 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *CH_2-O*), 2.30 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *oxetane CH_2*), 1.83−1.80 (m, 2H, *cyclohexyl*), 1.69−1.59 (m, 4H, *cyclohexyl*), 1.39−1.23 (m, 4H, *cyclohexyl*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 86.5 (*quaternary C−O*), 64.7 (*secondary C−O*), 38.6 (2C), 32.3, 25.0, 22.4 (2C).

General Procedure for the Au/TiO_2-Catalyzed Silaboration of Oxetanes or Epoxides. In a vial containing the oxetane or epoxide (0.2 mmol), $PhMe_2SiBpin$ (0.3 mmol), and 1 mL of dry DCE was placed 40 mg of Au/TiO_2 (1.0 mol % in Au). After 2 h at 60 °C the starting material was typically consumed. The slurry was filtered with the aid of dichloromethane under a low pressure through a short pad of silica gel or Celite, and the filtrate was evaporated to afford the silaboration products, which were purified by flash column chromatography.

Characterization of Silaboration Products and Byproducts. *Dimethyl(phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-butoxy)silane (**1a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62−7.56 (m, 2H, *Ph*), 7.40−7.33 (m, 3H, *Ph*), 3.58 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *CH_2-O*), 1.57−1.52 (m, 2H, *CH_2−C-O*), 1.45−1.39 (m, 2H, *CH_2−C-B*), 1.23 (s, 12H, *Me Bpin*), 0.76 (t, *J* = 7.5 Hz, 2H, *CH_2-Bpin*), 0.36 (s, 6H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1 (*Ph*), 133.5 (2C, *Ph*), 129.5 (*Ph*), 127.8 (2C, *Ph*), 82.9 (2C, *quaternary Bpin*), 63.0 (*C−O*), 35.2 (*aliphatic*), 24.8 (4C, *Me Bpin*), 20.2 (*aliphatic*), −1.7 (2C, *$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{18}H_{31}BO_3Si$ + H, 335.2208; found, 335.2208.

*(2,2-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propoxy)dimethyl(phenyl)silane (**2a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.57 (m, 2H, *Ph*), 7.39−7.34 (m, 3H, *Ph*), 3.29 (s, 2H, *CH_2-O*), 1.23 (s, 12H, *Me Bpin*), 0.94 (s, 6H, *Me*), 0.79 (s, 2H, *CH_2-Bpin*), 0.34 (s, 6H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6 (*Ph*), 133.5 (2C, *Ph*), 129.3 (*Ph*), 127.7 (2C, *Ph*), 82.7 (2C, *quaternary Bpin*), 73.6 (*C−O*), 34.4 (*tertiary*), 26.0 (2C, *Me*), 24.9 (4C, *Me Bpin*), −1.7 (2C, *$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{19}H_{33}BO_3Si$ + H, 349.2365; found, 349.2363.

*Dimethyl(phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (**3a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58−7.56 (m, 2H, *Ph*), 7.40−7.34 (m, 3H, *Ph*), 3.56 (t, $^3J_{HH}$ = 7.0 Hz, 2H, *CH_2-O*), 1.69−1.63 (m, 2H, *CH_2−C-O*), 1.22 (s, 12H, *Me Bpin*), 0.77 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *CH_2-Bpin*), 0.37 (s, 6H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1 (*Ph*), 133.5 (2C, *Ph*), 129.4 (*Ph*), 127.7 (2C, *Ph*), 82.9 (2C, *quaternary Bpin*), 64.9 (*C−O*), 27.0 (*aliphatic*), 24.8 (4C, *Me Bpin*), −1.7 (2C, *$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{17}H_{29}BO_3Si$ + H, 321.2052; found, 321.2053.

*Dimethyl(phenyl)(2-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (**4a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51−7.48 (m, 2H, *Ph*), 7.41−7.32 (m, 3H, *Ph*), 7.27−7.16 (m, 5H, *Ph*), 3.69 (dd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, *CH_2-O*), 3.63 (dd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *CH_2-O*), 3.11−3.06 (m, 1H, *CH-Ph*), 1.34 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, *CH_2-Bpin*), 1.10 (dd, $^2J_{HH}$ = 15.5 Hz, $^3J_{HH}$ = 9.0 Hz, 1H, *CH_2-Bpin*), 1.10 (s, 6H, *Me Bpin*), 1.07 (s, 6H, *Me Bpin*), 0.29 (s, 3H, *$SiMe_2$*), 0.28 (s, 3H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3 (*Ph*), 138.0 (*Ph*), 133.4 (2C, *Ph*), 129.4 (*Ph*), 128.0 (2C, *Ph*), 127.9 (2C, *Ph*), 127.7 (2C, *Ph*), 126.1 (*Ph*), 82.9 (2C, *quaternary Bpin*), 69.5 (*C−O*), 43.8 (*C-Ph*), 24.6 (2C, *Me Bpin*), 24.5 (2C, *Me Bpin*), −1.8 (*$SiMe_2$*), −1.9 (*$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{23}H_{33}BO_3Si$ + H, 397.2365; found, 397.2362.

*(2-Benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propoxy)dimethyl(phenyl)silane (**5a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59−7.56 (m, 2H, *Ph*), 7.41−7.35 (m, 3H, *Ph*), 7.26−7.14 (m, 5H, *Ph*), 3.50 (dd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 5.0 Hz, 1H, *CH_2-O*), 3.42 (dd, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, *CH_2-O*), 2.79 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, *CH_2-Ph*), 2.50 (dd, $^2J_{HH}$ = 13.5 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, *CH_2-Ph*), 2.11−2.05 (m, 1H, *CH-Bn*), 1.20 (s, 6H, *Me Bpin*), 1.20 (s, 6H, *Me Bpin*), 0.78 (d, $^3J_{HH}$ = 7.0 Hz, 2H, *CH_2-Bpin*), 0.36 (s, 3H, *$SiMe_2$*), 0.36 (s, 3H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.0 (*Ph*), 138.3 (*Ph*), 133.5 (2C, *Ph*), 129.5 (2C, *Ph*), 129.4 (*Ph*), 128.0 (2C, *Ph*), 127.7 (2C, *Ph*), 125.6 (*Ph*), 82.9 (2C, *quaternary Bpin*), 66.7 (*C−O*), 39.5 (*C-Ph*), 38.9 (*C-Bn*), 24.9 (2C, *Me Bpin*), 24.8 (2C, *Me Bpin*), −1.7 (*$SiMe_2$*), −1.8 (*$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{24}H_{35}BO_3Si$ + H, 411.2521; found, 411.2520.

*Dimethyl(phenyl)((1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclohexyl)methoxy)silane (**6a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61−7.58 (m, 2H, *Ph*), 7.40−7.34 (m, 3H, *Ph*), 3.46 (s, 2H, *CH_2-O*), 1.47−1.27 (m, 10H, *cyclohexyl*), 1.21 (s, 12H, *Me Bpin*), 0.90 (s, 2H, *CH_2-Bpin*), 0.35 (s, 6H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8 (*Ph*), 133.5 (2C, *Ph*), 129.2 (*Ph*), 127.6 (2C, *Ph*), 82.5 (2C, *quaternary Bpin*), 70.3 (*C−O*), 37.1 (*quaternary cyclohexyl*), 34.2 (2C, *cyclohexyl*), 26.4 (*cyclohexyl*), 24.8 (4C, *Me Bpin*), 21.9 (2C, (*cyclohexyl*), −1.7 (2C, *$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{22}H_{37}BO_3Si$ + H, 389.2678; found, 389.2682.

*(3-(Benzyloxy)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)propoxy)dimethyl(phenyl)silane (**7a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59−7.57 (m, 2H, *Ph*), 7.40−7.25 (m, 8H, *Ph*), 4.50 (s, 2H, *O−CH_2-Ph*), 3.52 (d, $^2J_{HH}$ = 9.5 Hz, 1H, *CH_2-OSi*), 3.47 (d, $^2J_{HH}$ = 9.5 Hz, 1H, *CH_2-OSi*), 3.32 (s, 2H, *CH_2-OBn*), 1.21 (s, 12H, *Me Bpin*), 0.98 (s, 3H, *Me*), 0.88 (d, $^2J_{HH}$ = 15.0 Hz, 1H, *CH_2-Bpin*), 0.82 (d, $^2J_{HH}$ = 15.0 Hz, 1H, *CH_2-Bpin*), 0.36 (s, 3H, *$SiMe_2$*), 0.35 (s, 3H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.2 (*Ph*), 138.6 (*Ph*), 133.5 (2C, *Ph*), 129.3 (*Ph*), 128.1 (2C, *Ph*), 127.6 (2C, *Ph*), 127.3 (2C, *Ph*), 127.1 (*Ph*), 82.7 (2C, *quaternary Bpin*), 75.7 (*C−O*), 73.0 (*C−O*), 68.6 (*C−O*), 38.6 (*quaternary*), 24.8 (2C, *Me Bpin*), 24.8 (2C, *Me Bpin*), 21.2 (Me), −1.7 (*$SiMe_2$*), −1.8 (*$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{26}H_{39}BO_4Si$ + H, 455.2783; found, 455.2781.

*2,5,8,8,9,9-Hexamethyl-2-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,7-dioxa-2,8-disiladecane (**8a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58−7.56 (m, 2H, *Ph*), 7.40−7.32 (m, 3H, *Ph*), 3.43−3.37 (m, 4H, *CH_2-OTBS* + *CH_2-OSiMe_2Ph*), 1.21 (s, 12H, *Me Bpin*), 0.88 (s, 9H, *t-Bu*), 0.87 (s, 3H, *Me*), 0.77 (s, 2H, *CH_2-Bpin*), 0.33 (s, 3H, *$SiMe_2$*), 0.33 (s, 3H, *$SiMe_2$*), 0.02 (s, 6H, *$SiMe_2$ of TBS*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.8 (*Ph*), 133.5 (2C, *Ph*), 129.2 (*Ph*), 127.6 (2C, *Ph*), 82.6 (2C, *quaternary Bpin*), 67.8 (*C−O*), 67.8 (*C−O*), 39.1 (*quaternary*), 26.0 (3C, *t-Bu*), 24.8 (2C, *Me Bpin*), 20.4 (*Me*), 18.3 (*quaternary t-Bu*), −1.7 (*$SiMe_2$*), −1.7 (*$SiMe_2$*), −5.5 (2C, (*$SiMe_2$ of TBS*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{25}H_{47}BO_4Si_2$ + H, 479.3179; found, 479.3175.

*3-((Dimethyl(phenyl)silyl)oxy)-2-methyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)propyl Benzoate (**9a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01−7.99 (m, 2H, *Ph*), 7.56−7.54 (m, 3H, *Ph*), 7.42 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *Ph*), 7.34−7.27 (m, 3H, *Ph*), 4.24 (d, $^2J_{HH}$ = 10.5 Hz, 1H, *CH_2−OCOPh*), 4.21 (d, $^2J_{HH}$ = 10.5 Hz, 1H, *CH_2−OCOPh*), 3.55 (d, $^2J_{HH}$ = 10.0 Hz, 1H, *CH_2-OSi*), 3.49 (d, $^2J_{HH}$ = 10.0 Hz, 1H, *CH_2-OSi*), 1.21 (s, 12H, *Me Bpin*), 1.05 (s, 3H, *Me*), 0.96 (d, $^2J_{HH}$ = 15.0 Hz, 1H, *CH_2-Bpin*), 0.92 (d, $^2J_{HH}$ = 15.0 Hz, 1H, *CH_2-Bpin*), 0.34 (s, 3H, *$SiMe_2$*), 0.33 (s, 3H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5 (*C = O*), 138.0 (*Ph*), 133.4 (2C, *Ph*), 132.6 (*Ph*), 130.6 (*Ph*), 129.5 (2C, *Ph*), 129.4 (*Ph*), 128.2 (2C, *Ph*), 127.7 (2C, *Ph*), 83.0 (2C, *quaternary Bpin*), 69.7 (*C−O*), 68.2 (*C−O*), 37.7 (*quaternary*), 24.8 (2C, *Me Bpin*), 24.8 (2C, *Me Bpin*), 20.9 (*Me*), −1.9 (*$SiMe_2$*), −1.9 (*$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{26}H_{37}BO_5Si$ + H, 469.2576; found, 469.2576.

*Dimethyl(phenyl)(3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (**10a**).* ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56−7.54 (m, 2H, *Ph*), 7.40−7.34 (m, 3H, *Ph*), 7.22 (t, $^3J_{HH}$ = 7.5 Hz, 2H, *Ph*), 7.16 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *Ph*), 7.12 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *Ph*), 3.59−3.50 (m, 2H, *CH_2-O*), 2.45 (t, $^3J_{HH}$ = 8.0 Hz, 1H, *benzylic*), 2.15−2.08 (m, 1H, *CH_2-C-OSi*), 1.93−1.86 (m, 1H, *CH_2-C-OSi*), 1.17 (s, 6H, *Me Bpin*), 1.15 (s, 6H, *Me Bpin*), 0.34 (s, 6H, *$SiMe_2$*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6 (*Ph*), 138.1 (*Ph*), 133.5 (2C, *Ph*), 129.4 (*Ph*), 128.4 (2C, *Ph*), 128.2 (2C, *Ph*), 127.8 (2C, *Ph*), 125.1 (*Ph*), 83.3 (2C, *quaternary Bpin*), 62.1 (*C−O*), 35.0 (*secondary*), 24.6 (2C, *Me Bpin*), 24.5 (2C, *Me Bpin*), −1.8 (*$SiMe_2$*), −1.8 (*$SiMe_2$*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{23}H_{33}BO_3Si$ + H, 397.2365; found, 397.2365.

*(3-(4-Fluorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)dimethyl(phenyl)silane (**11a**).* ^{1}H NMR (500 MHz,

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$CDCl_3$): δ 7.5−7.53 (m, 2H, *Ar*), 7.40−7.34 (m, 3H, *Ar*), 7.11−7.09 (m, 2H, *Ar*), 6.91 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HF}$ = 8.5 Hz, 2H, *Ar*), 3.56−3.48 (m, 2H, CH_2-*O*), 2.44 (t, $^3J_{HH}$ = 8.0 Hz, 1H, *benzylic*), 2.11−2.04 (m, 1H, CH_2-*C-OSi*), 1.87−1.80 (m, 1H, CH_2-*C-OSi*), 1.17 (s, 6H, *Me Bpin*), 1.15 (s, 6H, *Me Bpin*), 0.34 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9 (d, $^1J_{CF}$ = 241.0 Hz, *Ar*), 138.2 (d, $^4J_{CF}$ = 3.0 Hz, *Ar*), 137.9 (*Ar*), 133.4 (2C, *Ar*), 129.6 (d, $^3J_{CF}$ = 8.0 Hz, 2C, *Ar*), 129.5 (*Ar*), 127.8 (2C, *Ar*), 114.9 (d, $^2J_{CF}$ = 21.0 Hz, 2C, *Ar*), 83.3 (2C, *quaternary Bpin*), 61.8 (*C*−*O*), 35.0 (*secondary*), 24.6 (2C, *Me Bpin*), 24.5 (2C, *Me Bpin*), −1.8 (2C, $SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{23}H_{32}BFO_3Si$ + H, 415.2271; found, 415.2271.

Dimethyl(phenyl)(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)propoxy)silane (**12a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56−7.54 (m, 2H, *Ar*), 7.40−7.34 (m, 3H, *Ar*), 7.05 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *Ar*), 7.03 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *Ar*), 3.59−3.48 (m, 2H, CH_2-*O*), 2.40 (t, $^3J_{HH}$ = 8.0 Hz, 1H, *benzylic*), 2.29 (s, 3H, *Me*), 2.10−2.05 (m, 1H, CH_2-*C-OSi*), 1.90−1.81 (m, 1H, CH_2-*C-OSi*), 1.17 (s, 6H, *Me Bpin*), 1.14 (s, 6H, *Me Bpin*), 0.34 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.5 (*Ar*), 138.1 (*Ar*), 134.4 (*Ar*), 133.5 (2C, *Ar*), 129.4 (*Ar*), 129.0 (2C, *Ar*), 128.3 (2C, *Ar*), 127.7 (2C, *Ar*), 83.2 (2C, *quaternary Bpin*), 62.2 (*C*−*O*), 35.2 (*secondary*), 24.6 (2C, *Me Bpin*), 24.5 (2C, *Me Bpin*), 21.0 (*Me*), −1.7 ($SiMe_2$), −1.8 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{24}H_{35}BO_3Si$ + H, 411.2521; found, 411.2520.

(1-Cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propoxy)dimethyl(phenyl)silane (**13a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H, *Ph*), 7.39−7.33 (m, 3H, *Ph*), 3.43−3.39 (m, 1H, *CH*−*OSi*), 1.73−0.80 (m, 15H, *aliphatic*), 1.23 (s, 12H, *Me Bpin*), 0.37 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0 (*Ph*), 133.6 (2C, *Ph*), 129.2 (*Ph*), 127.6 (2C, *Ph*), 82.8 (2C, *quaternary Bpin*), 78.7 (*C*−*O*), 42.6, 29.7, 28.9, 28.2, 27.5, 26.5, 26.5, 24.8 (2C, *Me Bpin*), 24.8 (2C, *Me Bpin*), −0.7 ($SiMe_2$), −0.8 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{23}H_{39}BO_3Si$ + H, 403.2834; found, 403.2835.

(3-Cyclohexyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-propoxy)dimethyl(phenyl)silane (**13b**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59−7.56 (m, 2H, *Ph*), 7.40−7.34 (m, 3H, *Ph*), 3.61−3.56 (m, 1H, CH_2-*O*), 3.53−3.47 (m, 1H, CH_2-*O*), 1.73−0.80 (m, 14H, *aliphatic*), 1.19 (s, 6H, *Me Bpin*), 1.18 (s, 6H, *Me Bpin*), 0.37 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1 (*Ph*), 133.5 (2C, *Ph*), 129.4 (*Ph*), 127.7 (2C, *Ph*), 82.8 (2C, *quaternary Bpin*), 63.4 (*C*−*O*), 39.5, 32.7, 32.3, 31.7, 26.8, 26.7, 26.7, 25.0 (2C, *Me Bpin*), 24.7 (2C, *Me Bpin*), −1.7 ($SiMe_2$), −1.7 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{23}H_{39}BO_3Si$ + H, 403.2834; found, 403.2835.

(2-(Cyclohex-1-en-1-yl)ethoxy)dimethyl(phenyl)silane (**14a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H, *Ph*), 7.41−7.36 (m, 3H, *Ph*), 5.41 (br t, 1H, *olefinic C*−*H*) 3.66 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2-*O*), 2.19 (t, $^3J_{HH}$ = 7.0 Hz, 1H, CH_2−*C-O*), 1.99−1.95 (m, 2H, *allylic*), 1.91−1.87 (m, 2H, *allylic*), 1.62−1.52 (m, 4H, *aliphatic*), 0.39 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.0 (*Ph*), 134.6 (*olefinic*), 133.5 (2C, *Ph*), 129.5 (*Ph*), 127.8 (2C, *Ph*), 122.8 (*olefinic*), 62.3 (*C*−*O*), 41.2, 28.7, 25.2, 22.9, 22.3, −1.7 (2C $SiMe_2$).

trans-Dimethyl(phenyl)((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)oxy)silane (**15a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63−7.61 (m, 2H, *Ph*), 7.37−7.32 (m, 3H, *Ph*), 3.84−3.79 (m, 1H, *CH*−*OSi*), 1.77−1.74 (m, 2H, *aliphatic*), 1.68−1.66 (m, 1H, *aliphatic*), 1.53−1.49 (m, 1H, *aliphatic*), 1.31−1.11 (m, 5H, *aliphatic* + *CH-Bpin*), 1.23 (s, 6H, *Me Bpin*), 1.22 (s, 6H, *Me Bpin*), 0.39 (s, 3H, $SiMe_2$), 0.37 (s, 3H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.4 (*Ph*), 133.5 (2C, *Ph*), 129.1 (*Ph*), 127.5 (2C, *Ph*), 82.8 (2C, *quaternary Bpin*), 73.0 (*C*−*O*), 36.3 (*aliphatic*), 26.1 (*aliphatic*), 25.9 (*aliphatic*), 24.9 (2C, *Me Bpin*), 24.6 (2C, *Me Bpin*), 24.4 (*aliphatic*), −0.4 (2C, $SiMe_2$), −0.7 (2C, $SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{20}H_{33}BO_3Si$ + H, 361.2365; found, 361.2365.

trans-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-cyclohexanol (**15a′**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.58−3.53 (m, 1H, *CH*−*O*), 2.65 (br s, 1H, −OH), 1.98−1.94 (m, 1H, *aliphatic*), 1.84−1.79 (m, 1H, *aliphatic*), 1.78−1.74 (m, 1H, *aliphatic*), 1.62−1.57 (m, 1H, *aliphatic*), 1.24 (s, 12H, *Me Bpin*), 1.26−1.06 (m, 4H, *aliphatic*), 0.94−0.90 (m, 1H, *CH-Bpin*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 83.3 (2C, *quaternary Bpin*), 71.7 (*C*−*OH*), 35.3 (*aliphatic*), 26.2 (*aliphatic*), 26.1 (*aliphatic*), 24.8 (*aliphatic*), 24.7 (4C, *Me Bpin*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{12}H_{23}BO_3$ + H, 227.1813; found, 227.1814.

trans-Dimethyl(phenyl)((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentyl)oxy)silane (**16a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H, *Ph*), 7.39−7.33 (m, 3H, *Ph*), 4.37−4.34 (m, 1H, *CH*−*OSi*), 1.95−1.88 (m, 1H, *aliphatic*), 1.75−1.33 (m, 6H, *aliphatic* + *CH-Bpin*), 1.21 (s, 6H, *Me Bpin*), 1.21 (s, 6H, *Me Bpin*), 0.38 (s, 3H, $SiMe_2$), 0.37 (s, 3H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9 (*Ph*), 133.5 (2C, *Ph*), 129.2 (*Ph*), 127.6 (2C, *Ph*), 82.9 (2C, *quaternary Bpin*), 76.9 (*C*−*O*), 36.7 (*aliphatic*), 26.4 (*aliphatic*), 24.7 (4C, *Me Bpin*), 24.2 (*aliphatic*), −0.9 (2C, $SiMe_2$), −1.1 (2C, $SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{19}H_{31}BO_3Si$ + H, 347.2208; found, 347.2206.

trans-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-cyclopentanol (**16a′**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.29−4.25 (m, 1H, *CH*−*O*), 1.95−1.89 (m, 1H, *aliphatic*), 1.86−1.81 (m, 1H, *aliphatic*), 1.78−1.71 (m, 1H, *aliphatic*), 1.60−1.52 (m, 3H, *aliphatic*), 1.26−1.22 (m, 1H, *CH-Bpin*), 1.24 (s, 12H, *Me Bpin*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 83.2 (2C, *quaternary Bpin*), 76.4 (*C*−*O*), 35.7 (*aliphatic*), 25.7 (*aliphatic*), 24.8 (2C, *Me Bpin*), 24.7 (2C, *Me Bpin*), 23.5 (*aliphatic*). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{11}H_{21}BO_3$ + H, 213.1657; found, 213.1657.

threo-Dimethyl(phenyl)((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)oxy)silane (**17a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63−7.61 (m, 2H, *Ph*), 7.37−7.34 (m, 3H, *Ph*), 4.03−3.98 (m, 1H, *CH*−*OSi*), 1.24−1.20 (m, 1H, *CH-Bpin*), 1.23 (s, 6H, *Me Bpin*), 1.22 (s, 6H, *Me Bpin*), 1.14 (d, $^3J_{HH}$ = 6.0 Hz, 3H, *Me*), 0.97 (d, $^3J_{HH}$ = 7.5 Hz, 3H, *Me*), 0.38 (s, 3H, $SiMe_2$), 0.36 (s, 3H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1 (*Ph*), 133.5 (2C, *Ph*), 129.2 (*Ph*), 127.6 (2C, *Ph*), 82.8 (2C, *quaternary Bpin*), 71.7 (*C*−*O*), 24.9 (2C, *Me Bpin*), 24.6 (2C, *Me Bpin*), 22.2 (*Me*), 11.0 (*Me*), −0.7 ($SiMe_2$), −0.9 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{18}H_{31}BO_3Si$ + H, 335.2208; found, 335.2208.

threo-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (**17a′**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.78−3.72 (m, 1H, *CH*−*O*), 2.35 (br s, 1H, −OH), 1.25 (s, 12H, *Me Bpin*), 1.20 (d, $^3J_{HH}$ = 6.0 Hz, 3H, *Me*), 1.16−1.11 (m, 1H, *CH-Bpin*) 1.00 (d, $^3J_{HH}$ = 7.5 Hz, 3H, *Me*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 83.3 (2C, *quaternary Bpin*), 71.0 (*C*−*O*), 24.8 (2C, *Me Bpin*), 24.6 (2C, *Me Bpin*), 22.7 (*Me*), 12.2 (*Me*). MS (EI): 182 ($M^+ - H_2O$, < 1%), 83 (8%), 59 (17%), 45 (100%).

erythro-Dimethyl(phenyl)((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)oxy)silane (**18b**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62−7.60 (m, 2H, *Ph*), 7.37−7.34 (m, 3H, *Ph*), 3.90−3.85 (m, 1H, *CH*−*OSi*), 1.22 (s, 6H, *Me Bpin*), 1.21 (s, 6H, *Me Bpin*), 1.13 (d, $^3J_{HH}$ = 6.0 Hz, 3H, *Me*), 0.97 (d, $^3J_{HH}$ = 7.5 Hz, 3H, *Me*), 0.90−0.85 (m, 1H, *CH-Bpin*), 0.38 (s, 3H, $SiMe_2$), 0.37 (s, 3H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9 (*Ph*), 133.6 (2C, *Ph*), 129.3 (*Ph*), 127.6 (2C, *Ph*), 82.8 (2C, *quaternary Bpin*), 71.3 (*C*−*O*), 24.7 (2C, *Me Bpin*), 24.5 (2C, *Me Bpin*), 23.7 (*Me*), 12.3 (*Me*), −0.8 ($SiMe_2$), −1.0 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{18}H_{31}BO_3Si$ + H, 335.2208; found, 335.2208.

erythro-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-ol (**18b′**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87−3.82 (m, 1H, *CH*−*O*), 1.80 (bs, 1H, −OH), 1.26−1.22 (m, 1H, *CH-Bpin*), 1.25 (s, 12H, *Me Bpin*), 1.18 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *Me*), 0.99 (d, $^3J_{HH}$ = 7.5 Hz, 3H, *Me*). ^{13}C NMR (125 MHz, $CDCl_3$): δ 83.3 (2C, *quaternary Bpin*), 70.0 (*C*−*O*), 24.7 (2C, *Me Bpin*), 24.7 (2C, *Me Bpin*), 21.7 (*Me*), 10.8 (*Me*). MS (EI): 182 ($M^+ - H_2O$, < 1%), 83 (6%), 59 (20%), 45 (100%).

Dimethyl(phenyl)(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propoxy)silane (**19a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.58 (m, 2H, *Ph*), 7.40−7.34 (m, 3H, *Ph*), 3.70 (dd, $^2J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2-*OSi*), 3.60 (dd, $^2J_{HH}$ = 9.5 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2-*OSi*), 1.36−1.30 (m, 1H, *CH-Bpin*), 1.23 (s, 12H, *Me Bpin*), 0.98 (d, $^3J_{HH}$ = 7.5 Hz, 3H, *Me*), 0.35 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4 (*Ph*), 133.5 (2C, *Ph*), 129.3 (*Ph*), 127.7 (2C, *Ph*), 83.0 (2C, *quaternary Bpin*), 66.0 (*C*−*O*), 24.7 (2C, *Me Bpin*), 24.7

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(2C, *Me Bpin*), 12.1 (*Me*), −1.7 ($SiMe_2$), −1.7 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{17}H_{29}BO_3Si$ + H, 321.2052; found, 321.2051.

Dimethyl(phenyl)((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)oxy)silane (**19b**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H, *Ph*), 7.39−7.33 (m, 3H, *Ph*), 4.18−4.11 (m, 1H, *CH−OSi*), 1.22 (s, 6H, *Me Bpin*), 1.21 (s, 6H, *Me Bpin*), 1.17 (d, $^3J_{HH}$ = 6.0 Hz, 3H, *Me*), 1.15 (dd, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 5.5 Hz, 1H, CH_2-*Bpin*), 1.09 (dd, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2-*Bpin*), 0.38 (s, 3H, $SiMe_2$), 0.37 (s, 3H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9 (*Ph*), 133.5 (2C, *Ph*), 129.3 (*Ph*), 127.6 (2C, *Ph*), 83.0 (2C, *quaternary Bpin*), 66.8 (*C−O*), 25.8 (*Me*), 24.9 (2C, *Me Bpin*), 24.6 (2C, *Me Bpin*), −0.9 ($SiMe_2$), −1.0 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{17}H_{29}BO_3Si$ + H, 321.2052; found, 321.2051.

Dimethyl(phenyl)((2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)silane (**20a**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.58−7.56 (m, 2H, *Ph*), 7.37−7.34 (m, 3H, *Ph*), 3.69−3.64 (m, 2H, CH_2-*OSi*), 1.46−1.20 (m, 7H, *aliphatic* + *CH-Bpin*), 1.23 (s, 12H, *Me Bpin*), 0.86 (t, $^3J_{HH}$ = 7.0 Hz, 3H, *Me*), 0.34 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4 (*Ph*), 133.5 (2C, *Ph*), 129.3 (*Ph*), 127.7 (2C, *Ph*), 82.9 (2C, *quaternary Bpin*), 64.5 (*C−O*), 31.2 (*aliphatic*), 27.1 (*aliphatic*), 24.8 (2C, *Me Bpin*), 24.7 (2C, *Me Bpin*), 23.0 (*aliphatic*), 14.1 (*Me*), −1.7 ($SiMe_2$), −1.7 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{20}H_{35}BO_3Si$ + H, 363.2521; found, 363.2521.

Dimethyl(phenyl)((1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)oxy)silane (**20b**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.61−7.59 (m, 2H, *Ph*), 7.37−7.32 (m, 3H, *Ph*), 4.01−3.96 (m, 1H, *CH−OSi*), 1.50−1.39 (m, 2H, *aliphatic*), 1.35−1.20 (m, 4H, *aliphatic*), 1.21 (s, 6H, *Me Bpin*), 1.20 (s, 6H, *Me Bpin*), 1.11 (dd, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 8.0 Hz, 1H, CH_2-*Bpin*), 1.07 (dd, $^2J_{HH}$ = 15.0 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH_2-*Bpin*), 0.84 (t, $^3J_{HH}$ = 7.0 Hz, 3H, *Me*), 0.38 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0 (*Ph*), 133.6 (2C, *Ph*), 129.2 (*Ph*), 127.6 (2C, *Ph*), 82.9 (2C, *quaternary Bpin*), 70.5 (*C−O*), 39.0 (*aliphatic*), 27.8 (*aliphatic*), 24.9 (2C, *Me Bpin*), 24.6 (2C, *Me Bpin*), 22.6 (*aliphatic*), 14.0 (*Me*), −0.8 ($SiMe_2$), −0.9 ($SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{20}H_{35}BO_3Si$ + H, 363.2521; found, 363.2521.

((2,3-Dimethylbut-3-en-2-yl)oxy)dimethyl(phenyl)silane (**21a**). ^1H NMR (500 MHz, $CDCl_3$): δ 7.65−7.62 (m, 2H, *Ph*), 7.39−7.35 (m, 3H, *Ph*), 4.98 (dq, $^2J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, *olefinic C−H*), 4.75 (dq, $^2J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, *olefinic C−H*), 1.81 (dd, $^4J_{HH}$ = 1.5 Hz, $^4J_{HH}$ = 1.0 Hz, 3H, *allylic Me*), 1.37 (s, 6H, *Me*), 0.40 (s, 6H, $SiMe_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0 (*olefinic*), 140.3 (*Ph*), 133.3 (2C, *Ph*), 129.1 (*Ph*), 127.6 (2C, *Ph*), 108.6 (*olefinic*), 76.3 (*C−O*), 29.6 (2C, *Me*), 19.0 (*allylic Me*), 1.2 (2C, $SiMe_2$). HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{14}H_{22}OSi$ + H, 235.1513; found, 235.1511.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00465.

^1H and ^{13}C NMR spectra of all products (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for M.S.: stratakis@uoc.gr.

Notes

The authors declare no competing financial interest.

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Formation of $PhMe_2Si$-Au_n-Bpin could be envisioned via oxidative insertion[30] of Au(I) species into a Si−B bond, and such species are well established to exist on Au NPs supported on metal oxide surfaces.[31] On the other hand, oxidative insertion of single Au(0) atoms, as a parallel to Pd(0) catalysis, should generate Au(II) species, which is unlikely to occur. As these assumptions are unclear, theoretical calculations are in progress to examine the role of Au NPs (e.g. oxidation state of Au) in the activation of σ heteroatom bonds, including silylboranes. It should be stated that, in general, reaction mechanisms involving catalysis by Au and other metal NPs are little understood so far, not only regarding the oxidation state of the metal but also the crucial role of surface support and leaching issues, while different pathways possibly include single or multiple catalytic species.[27,32]

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