JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Synthesis of Formylsilanes through Oxidative Cleavage of α-Silyl Glycols

Henrik von Wachenfeldt and Daniel Strand*

Centre for Analysis and Synthesis, Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden

Supporting Information

ABSTRACT: A convenient method for the synthesis and isolation of highly reactive formylsilanes by oxidative cleavage of α-silyl glycols is presented. The mild conditions provide an entry to acid- and heat-sensitive members of this theoretically intriguing class of compounds. The utility of the method is demonstrated through the isolation and subsequent diastereoselective derivatization of *t*-BuMe$_2$- and *t*-BuPh$_2$-formylsilanes, previously not reported in isolated form.

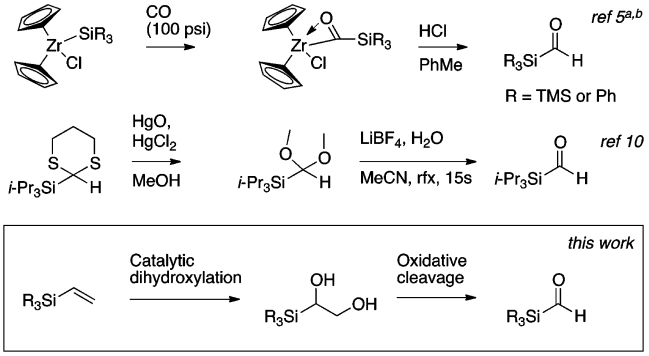
The simplest acylsilanes,[1] formylsilanes, are a class of highly reactive species that are in principle synthetically equivalent to prostereogenic formaldehyde.[2] While higher acylsilanes are frequently employed in synthesis,[3] applications of formylsilanes are surprisingly rare. This paucity is likely a reflection of their challenging synthesis and very high inherent reactivity. When exposed to limited amounts of oxygen, formylsilanes rapidly rearrange to the correponding silanols with loss of carbon dioxide,[4] and exposure to the atmosphere has been reported to cause spontaneous ignition.[5] To advance the chemistry of these potentially useful compounds, general, mild, and operationally convenient procedures that enable isolation of the products are of particular interest.

In a pioneering study, Swern oxidation of trimethylsilylmethanol was used to generate Me$_3$-formylsilane, which was trapped in situ by reactions with Wittig ylides to produce vinylsilanes.[6a,7] This procedure was later extended also to reactions with hydrazines and organometallics.[6b] More recently, (1,3-dioxolan-2-yl)silanes[8] and benzotriazol(1-yl)carbazol(9-yl)-silylmethane derivatives[9] have been used in transacetalization reactions with hydrazines and the latter also to generate the electrophile in an aldol condensation.

For more elaborate applications of formylsilanes in synthesis, preparative scale access to such compounds in isolated form is likely a prerequisite. To this end, only two procedures are currently available (Scheme 1): (i) insertion of carbon monoxide into the Zr−Si bond of TMS$_3$Si− and Ph$_3$Si−Zr complexes to generate the corresponding η^2-complexes, which upon exposure to HCl produces the thermally stable Ph$_3$- and (Me$_3$Si)$_3$-formylsilanes,[5a,b] and (ii) hydrolysis of (dimethoxymethyl)-triisopropylsilane under carefully controlled conditions to form *i*-Pr$_3$-formylsilane.[10] Importantly, the *i*-Pr$_3$-formylsilane was in the latter work shown to participate in highly diastereoselective Wittig and aldol reactions.

The potential of using formylsilanes, and by extension their imine derivatives, as homologues to their nonenolizable aliphatic counterparts in multicomponent reactions,[11] together with the operational drawbacks of current procedures (high-pressure carbon monoxide and strong acid or elevated temperature and stochiometric use of mercury) prompted us to investigate alternative methods for their prepration. Herein

Scheme 1. Preparative Synthesis of Formylsilanes



we present an operationally simple procedure for the syntheses of formylsilanes by oxidative cleavage of readily available α-silyl glycols.[12] On a 3 mmol scale, the formylsilane products were obtained in good isolated yields with homogenities adequate for synthetic applications as demonstrated by diastereoselective aldol and HWE reactions.

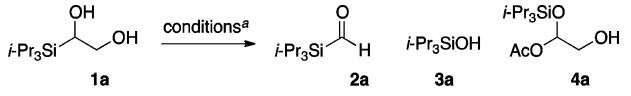
The principal byproducts of the reaction, formaldehyde and sodium iodate, are water soluble and can thus be conveniently removed by partitioning the reaction mixture against pentane under an inert atmosphere. The mild conditions (i.e., neutral pH and ambient temperature) enabled the synthesis of *t*-BuMe$_2$-formylsilane and *t*-BuPh$_2$-formylsilane, previously not reported in isolated form.

The possibility of using oxidative diol cleavage for formylsilane synthesis was first evaluated by a screening of standard conditions and reagents using α-silyl glycol **1a**[13] as the substrate (Table 1). NaIO$_4$ in a mixture of acetonitrile and water (2:1) gave complete consumption of the starting materials within one hour, and the desired formylsilane **2a** was formed in 61% yield along with minor amounts of the corresponding silanol **3a**.[14] Longer reaction times, use of excess NaIO$_4$, or a more concentrated reaction mixture under

Received: September 25, 2013
Published: November 1, 2013

   dx.doi.org/10.1021/jo402123j | J. Org. Chem. 2013, 78, 12268−12273

Table 1. Reagents and Conditions for Oxidative Cleavage of α-Silyl Glycol 1a[a]



1a 2a 3a 4a

entry	oxidant (equiv)	solvent	time	yield (%)[b] 2a; 3a; 4a
1[b]	$NaIO_4$ (1.0)	MeCN/H_2O (2:1)	30 min	49; 5; 0
2[b]	$NaIO_4$ (1.0)	MeCN/H_2O (2:1)	1 h	61; 8; 0
3[b]	$NaIO_4$ (1.0)	MeCN/H_2O (2:1)	2 h	60; 13; 0
4[b]	$NaIO_4$/silica (1.0)	DCM	22 h	1; 10; 0
5[b]	$NaIO_4$ (1.0)	EtOAc/H_2O (2:1)	22 h	3; 33; 0
6[b]	H_5IO_6 (1.2)	THF	10 min	0; 67; 0
7[c]	PIDA (1.2)	DCM	10 min	0; 0; 38
8[c]	$Pb(OAc)_4$ (1.2)	MeCN	10 min	0; 0; 69
9[c]	$Mn(OAc)_3$ (4.0)	MeCN	5 h	0; 0; 37

[a]General conditions: Diol **2a** (0.1 mmol), organic solvent (1 mL), water (0.5 mL), rt. [b]Yield determined by ^{13}C NMR using triisopropylsilane as internal standard. [c]Yield determined by ^1H NMR using mesitylene as internal standard.

otherwise identical conditions gave lower yields due to increased overoxidation.

Silica-supported $NaIO_4$,[15] or a two-phase solvent system (EtOAc/water), gave very slow conversion and only trace amounts of product. Periodic acid gave a fast consumption of the starting material, even at 0 °C, but no formylsilane formation was detected. Oxidants like PIDA,[16] $Pb(OAc)_4$,[17] and $Mn(OAc)_3$[18] did not give detectible amounts of product **2a**; instead acyl-silyl acetal **4a**, formed via a radical Brook rearrangement,[19] was obtained (yields are unoptimized).[20] The formation of **4a** with hypervalent iodine and $Mn(OAc)_3$ is noteworthy as these reagents have potential as less toxic alternatives to $Pb(OAc)_4$ for the generation of α-silyloxy carbon radicals in this context.

The successful cleavage of diol **1a** with $NaIO_4$ prompted an investigation of the scalability and substrate scope of these conditions. Multigram preparation of α-silyl glycols **1a–c** for this study was performed via a two-step procedure starting with a partial hydrogenation of alkynylsilanes **5a–c** with Lindlar catalyst.[21] Upjohn-dihydroxylation of the resulting vinylsilanes **6a–c**[22] then gave the corresponding α-silyl glycols **1a–c** in good yields over two steps. In contrast, the attempted dihydroxylation of (TMS_3Si)-vinylsilane **6d** gave only a complex mixture with OsO_4/NMO. The desired α-(TMS_3Si)-glycol **1d** could, however, be efficiently formed by dihydroxylation with AD-mix β (Scheme 2).[23,24]

When conducting the cleavage of α-silyl glycol **1a** on a preparative scale (3 mmol), the reaction was complete in just 20 min, enabling the isolation of formylsilane **2a** in good yield together with only trace amounts of silanol (5%) (Table 2). The same conditions translated well also to the synthesis and isolation of the new *t*-$BuPh_2$- and *t*-$BuMe_2$-formylsilanes **2b** and **2c**. Access to these compounds is particularly attractive, as nucleophilic addition to *t*-$BuMe_2$-formylsilane (**2b**) constitutes an entry to α-(*t*-$BuMe_2Si$)-alcohols, a motif previously exploited as a chiral primary alcohol equivalent,[25] and derivatives carrying a *t*-$BuPh_2$-group have added value as a masked hydroxyl group.[26] Partial evaporation of the semi-

Scheme 2. Synthesis of α-Silyl Glycols 1a–d

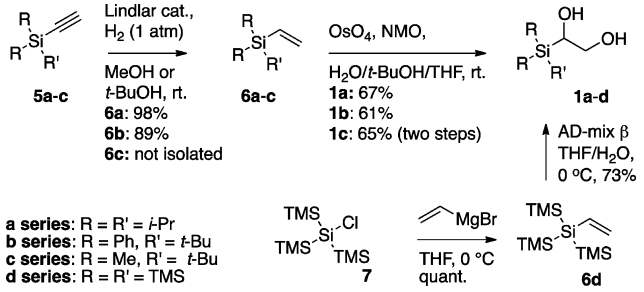
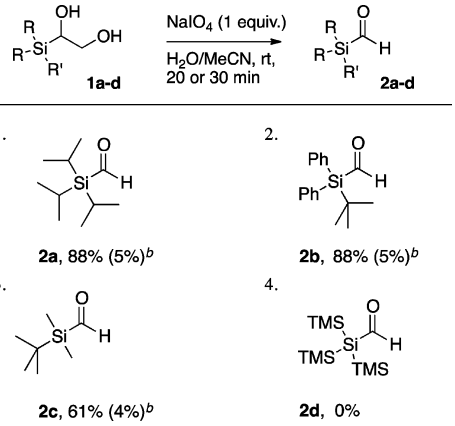


Table 2. Preparative Synthesis of Formylsilanes 2a–c[a]



[a]Isolated yields are corrected for silanol content. [b]Mol % of silanol in isolated product (^1H NMR).

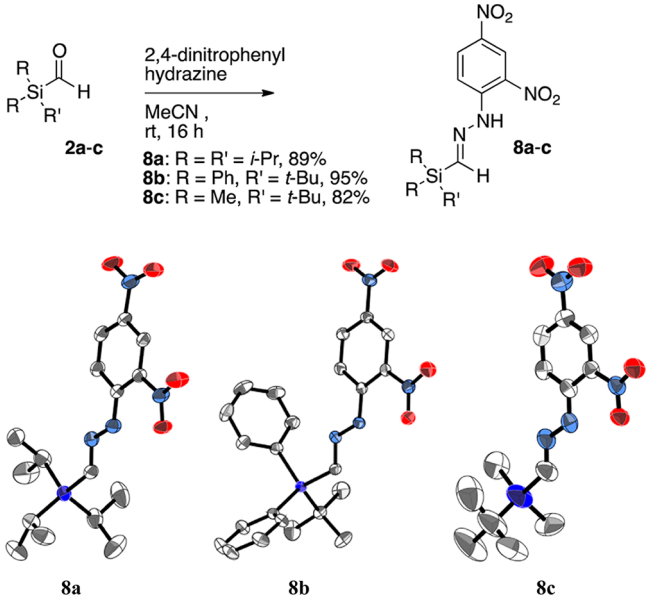
volatile product and silanol during solvent removal accounts for the somewhat reduced isolated yield in Table 2, entry 3. In contrast to diols **1a–c**, cleavage of α-(TMS_3Si)-glycol (**1d**) gave only unspecific decomposition. This result is attributed, at least in part, to the propensity of TMS_3-silanes to be oxidized at the Si–Si bond.[27]

In agreement with the literature data for known formylsilanes, *t*-$BuPh_2$-formylsilane (**2b**) and *t*-$BuMe_2$-formylsilane (**2c**) display properties characteristic of a highly polarized C=O bond (**2b**: ^{13}C NMR δ = 243 (CO) ppm, IR ν_{CO} = 1650 cm^{-1}; **2c**: ^{13}C NMR δ = 246 (CO) ppm, IR ν_{CO} = 1648 cm^{-1}). Molecular ions of the fragile structures were not detected by MS-ESI. For analytical purposes, the isolated formylsilanes were instead converted into their corresponding known 2,4-dinitrophenylhydrazones **8a–c** (Scheme 3).[8,9] Noteworthy in this context is the essentially quantitative formation of *t*-$BuPh_2$-derivative **8b** from **2b**. Recrystallization of the hydrazones from MeOH gave single crystals from which the solid-state structures were solved by X-ray crystallography.[28] In agreement with the apparent stability of these compounds, virtually no elongation of the C=N bonds (1.27–1.28 Å) were found compared to that of related hydrazone derivatives of aliphatic aldehydes (typically ranging from 1.25 to 1.26 Å).[29]

The usefulness of the title conditions to provide formylsilanes for applications in synthesis was investigated by subjecting *i*-Pr-formylsilane (**2a**) to the known *syn*-selective aldol reaction with a *Z*-enolate of propiophenone.[30] The yield and selectivity of this reaction (64%; *syn*:*anti* > 98:2) followed that previously reported for this substrate (65%, *syn*:*anti* > 97:3).[10a] Formylsilanes **2b** and **2c** were also investigated as substrates in this reaction and were both found to give the

dx.doi.org/10.1021/jo402123j | J. Org. Chem. 2013, 78, 12268–12273

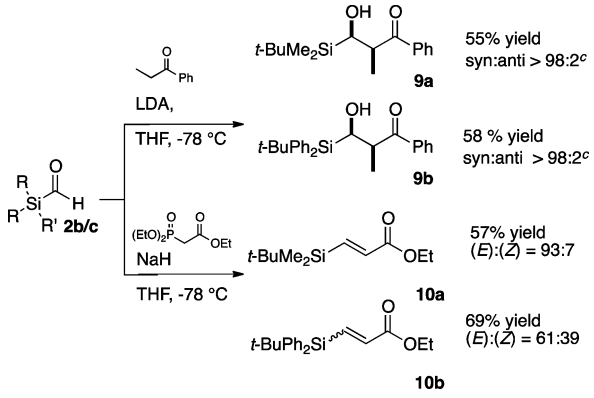
Scheme 3. Synthesis and Crystal Structures of Hydrazones 8a–c[a]



[a]Thermal ellipsoid plots at 30% probability; hydrogen atoms are omitted for clarity.

corresponding aldols with complete diastereoselectivities and moderate isolated yields (Scheme 4). The propensity of the *t*-BuPh$_2$ group to migrate after addition of the enolate leading to a reduced yield could be suppressed by quenching the reaction immediately after addition of the enolate. The library of available transformations for formylsilanes was also expanded to include *E*-selective olefinations by reacting silanes **2b** and **2c** under Horner–Wadsworth–Emmons (HWE) conditions.[31] In this reaction *t*-BuMe$_2$ formylsilane (**2c**) gave a good geometric selectivty (*E*:*Z* = 93:7), whereas *t*-BuPh$_2$-formylsilane (**2b**) gave only a fair selectity (*E*:*Z* = 61:39) but a higher isolated yield.

Scheme 4. Diastereoselective Derivatization of Formylsilanes 2b and 2c[a,b]



[a]Isolated yields. [b]The selectivities were quantified by ^{1}H NMR spectroscopy of the crude reaction mixtures. [c]No minor diastereomer detected. The relative configuration was assigned by analogy: see ref 10a and references therein.

In conclusion, an operationally convenient procedure for the synthesis of formylsilanes by oxidative cleavage of readily available α-silyl glycols with NaIO$_4$ is described. The conditions enable access to formylsilanes in isolated form with good to moderate isolated yields. The mildness of the protocol is highlighted by synthesis, isolation, and characterization of the sensitive *t*-BuMe$_2$- and *t*-BuPh$_2$-formylsilanes **2b** and **2c**. The formylsilane products derived from this procedure were shown to efficiently participate in diastereoselective aldol and HWE reactions with up to excellent levels of diastereoselectivity. Studies on expanding this methodology as well as investigations of the properties and applications of these potentially very useful compounds in synthesis are currently under way.

EXPERIMENTAL SECTION

Optimization Study for Oxidative Cleavage of α-Silyl Glycol 1a. For details, see Table 1. To a vial charged with oxidant and a magnetic stir-bar (for entries 1–3 and 5, dissolved in degassed water, 0.5 mL) was added a solution of α-silyl glycol **1a** (21.8 mg, 0.1 mmol) in the solvent indicated (1 mL, degassed). The resulting mixture was stirred for the time and temperature indicated, after which pentane (3 mL, degassed) and water (3 mL, degassed) were added sequentially. The aqueous layer was removed by syringe, and the organic layer was concentrated under reduced pressure and then backfilled with nitrogen. The yields were determined by quantitative ^{13}C NMR[32] for entries 1–6 and ^{1}H NMR for entries 7–9 using triisopropylsilane and mesitylene, respectively, as internal standard.

2-Hydroxy-1-((triisopropylsilyl)oxy)ethyl acetate (4a). The NMR sample used in Table 1 entry 7 was concentrated and purified by silica-gel chromatography eluting with EtOAc/petroleum ether (0–20% EtOAc) to yield acyl-silyl acetal **4a** (8.3 mg, 30%) as a clear oil, >95% pure by NMR spectroscopy and a single spot by TLC: R_f = 0.53 in 1:3 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 6.31 (t, *J* = 4.7 Hz, 1H), 3.57 (t, *J* = 5.3 Hz, 2H), 1.68 (s, 3H), 1.52 (t, *J* = 6.3 Hz, 1H), 1.12–1.04 (m, 21H) ppm; ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 169.8, 92.4, 65.7, 20.9, 18.1, 18.0, 12.5 ppm; IR (CHCl$_3$ film) 3020 (m), 2948 (w), 2869 (m), 1734 (s), 1464 (m), 1375 (m) cm^{-1}; HRMS-ESI (*m*/*z*) [M + K]$^+$ calcd for C$_{13}$H$_{28}$KO$_4$Si, 315.1400, found 315.1394.

General Procedure for the Oxidative Cleavage of α-Silyl Glycols 1a–c. To a gently stirred solution of diol (1 equiv) in MeCN (10 mL/mmol diol, degassed) was added NaIO$_4$ (1 equiv) dissolved in water (5 mL/mmol diol, degassed) under a nitrogen atmosphere. Within a few minutes the mixture turned yellow, and a white precipitate started to form. After stirring for a total of 20 min (**1a**) or 30 min (**1b** and **1c**), pentane (20 mL/mmol diol, degassed) and water (10 mL/mmol diol, degassed) were added sequentially. The aqueous layer was removed by syringe, and the remaining organic layer was concentrated in the reaction vessel under reduced pressure (house vacuum 20 mbar), after which it was backfilled with nitrogen to leave the corresponding formylsilanes as yellow oils (**2a**,**b**) or a yellow amorphous solid (**2c**).

*Formyltriisopropylsilane (**2a**).*[10a] Scale: 3.0 mmol of diol **1a**. Yield: 556 mg, 88% (5% silanol), isolated as a yellow oil; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 12.07 (s, 1H), 1.09–1.05 (m, 3H), 0.99 (d, *J* = 6.5 Hz, 18H) ppm; ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 246.7, 18.5, 10.4 ppm; IR (CHCl$_3$ film) 1647 (ν_{CO}) cm^{-1}.

*Formyl-tert-butyldiphenylsilane (**2b**).* Scale: 3.0 mmol of diol **1b**. Yield: 743 mg, 88% (5% silanol), isolated as a yellow oil; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 12.14 (s, 1H), 7.62–7.53 (m, 4H), 7.16–7.09 (m, 6H), 1.09 (s, 9H) ppm; ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 242.5, 136.5, 131.1, 130.4, 128.5, 27.4, 18.9 ppm; IR (CHCl$_3$ film) 1650 (ν_{CO}) cm^{-1}.

*Formyl-tert-butyldimethylsilane (**2c**).* Scale: 5.0 mmol of diol **1c**. Yield: 459 mg, 61% (4% silanol), isolated as a yellow amorphous solid; ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 11.89 (s, 1H), 0.81 (s, 9H), −0.08 (s, 6H) ppm; ^{13}C NMR (101 MHz, C$_6$D$_6$) δ 245.7, 26.4, 16.9, −8.8 ppm; IR (CHCl$_3$ film) 1648 (ν_{CO}) cm^{-1}.

General Procedure for the Hydrazone Formation. To 2,4-dinitrophenylhydrazine (1.48 g, 5.0 mmol, 33% in H$_2$O) was added formylsilane (3.05–4.10 mmol) in MeCN (50 mL, degassed) under a

dx.doi.org/10.1021/jo402123j | J. Org. Chem. 2013, 78, 12268–12273

nitrogen atmosphere. The resulting mixture was stirred at ambient temperature for 20 h, and then concentrated, suspended in $CHCl_3$ (50 mL), and filtered. The filtrate was concentrated and purified by silica-gel chromatography eluting with EtOAc/petroleum ether (0−10% EtOAc) to yield the corresponding hydrazones **8a**−**c**.

*(E)-1-(2,4-Dinitrophenyl)-2-((triisopropylsilyl)methylene)-hydrazine (**8a**).*[9,10a] Scale: 3.34 mmol of formylsilane **2a**. Yield: 1.19 g, 89%, isolated as a yellow solid, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.74 in 1:10 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 9.14 (d, J = 2.6 Hz, 1H), 8.34 (ddd, J = 9.6, 2.6, 0.6 Hz, 1H), 7.99 (d, J = 9.6 Hz, 1H), 7.82 (d, J = 1.1 Hz, 1H), 1.35−1.25 (m, 3H), 1.15 (d, J = 7.2 Hz, 18H) ppm; IR ($CHCl_3$ film) 3301 (m), 3021 (m), 2867 (m), 1618 (s), 1595 (m), 1517 (m), 1338 (s), 1317 (s) cm^{-1}; mp 112.1−112.5 °C (recrystallized from warm MeOH by slow cooling).

*(E)-1-((tert-Butyldiphenylsilyl)methylene)-2-(2,4-dinitrophenyl)-hydrazine (**8b**).*[9] Scale: 4.10 mmol of formylsilane **2b**. Yield: 1.75 g, 95%, isolated as a yellow solid, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.34 in 1:10 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 9.14 (d, J = 2.5 Hz, 1H), 8.33 (dd, J = 9.5, 2.0 Hz, 1H), 8.10 (d, J = 1.1 Hz, 1H), 7.95 (d, J = 9.5 Hz, 1H), 7.74−7.64 (m, 4H), 7.51−7.36 (m, 6H), 1.22 (s, 9H) ppm; IR ($CHCl_3$ film) 3300 (m), 3019 (m), 2861 (w), 1618 (s), 1596 (m), 1515 (m), 1339 (s), 1317 (s) cm^{-1}; mp 128.2−128.5 °C (recrystallized from warm MeOH by slow cooling).

*(E)-1-((tert-Butyldimethylsilyl)methylene)-2-(2,4-dinitrophenyl)-hydrazine (**8c**).*[9] Scale: 3.05 mmol of formylsilane **2c**. Yield: 809 mg, 82%, isolated as a yellow solid, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.50 in 1:10 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.09 (s, 1H), 9.13 (d, J = 2.6 Hz, 1H), 8.33 (ddd, J = 9.6, 2.6, 0.7 Hz, 1H), 8.01 (d, J = 9.6 Hz, 1H), 7.82 (d, J = 1.1 Hz, 1H), 1.00 (s, 9H), 0.23 (s, 6H) ppm; IR ($CHCl_3$ film) 3302 (m), 3020 (m), 2862 (w), 1618 (s), 1595 (m), 1517 (m), 1338 (s), 1317 (s) cm^{-1}; mp 135.1−136.9 °C (recrystallized from warm MeOH by slow cooling).

General Procedure for the Partial Hydrogenation to Alkenes 6a,b. To a stirred solution of silylacetylene (1.0 equiv) and quinoline (0.05 equiv) in methanol (0.8 M) was added Lindlar catalyst (5% Pd on $CaCO_3$ poisoned with lead, 0.3%), under a nitrogen atmosphere. The atmosphere was changed to H_2 (H_2 from a balloon) and purged three times. Upon complete consumption of the alkyne (TLC control), the mixture was filtered trough a plug of Celite and concentrated. The crude mixture was redissolved in petroleum ether, filtered trough a plug of silica, and concentrated to yield the corresponding vinyl silanes **6a,b**.

*Triisopropyl(vinyl)silane (**6a**).*[33] Yield: 98%, isolated as a clear oil, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.96 in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10−5.98 (m, 2H), 5.71 (dd, J = 17.5, 7.1 Hz, 1H), 1.07−1.02 (m, 21H) ppm.

*tert-Butyldiphenyl(vinyl)silane (**6b**).*[34] Yield: 89%, isolated as a clear oil, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.48 in petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.62 (m, 4H), 7.45−7.36 (m, 6H), 6.60 (dd, J = 20.3, 14.8 Hz, 1H), 6.30 (dd, J = 14.8, 3.8 Hz, 1H), 5.74 (dd, J = 20.3, 3.8 Hz, 1H), 1.12 (s, 9H) ppm.

General Procedure for Dihydroxylation of Vinyl Silanes 6a,b. To a stirred solution of alkene (1.0 equiv) and NMO (2.0 equiv) in *t*-BuOH, THF, and water (ratio 1.0:1.4:1.0, 0.6 M) was added OsO_4 (0.005 equiv, 2.5% in *t*-BuOH) under a nitrogen atmosphere. After stirring at ambient temperature for 26 h, the reaction was quenched by addition of Na_2SO_3 (0.3 g/mmol alkene), and the resulting mixture was stirred for an additional 30 min. The reaction was then extracted with petroleum ether (4 mL/mmol alkene), washed with water (2 × 4 mL/mmol alkene), and concentrated under reduced pressure. The resulting crude product was dissolved in Et_2O (2 mL/mmol alkene), filtered trough a plug of silica, and concentrated. Crystallization from pentane (0.5 M) at −78 °C gave the corresponding diols **1a,b**. The mother liquor was concentrated and purified by silica-gel chromatography, eluting with EtOAc/petroleum ether (0−25% EtOAc), to increase the yield.

*1-(Triisopropylsilyl)ethane-1,2-diol (**1a**).*[13] Yield: 67% (60% from crystallization and 7% from chromatography), isolated as a white solid, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.36 in 1:3 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96−3.74 (m, 3H), 2.01 (bs, 2H), 1.19−1.06 (m, 21H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 66.6, 66.0, 19.1, 19.0, 10.7 ppm; IR ($CHCl_3$ film) 3364 (s, br), 2943 (s), 2866 (s), 1434 (m), 1050 (m), 882 (m) cm^{-1}; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{11}H_{26}NaO_2Si$, 241.1600, found 241.1599; mp 52.5−52.8 °C (recrystallized from pentane at −78 °C).

*1-(tert-Butyldiphenylsilyl)ethane-1,2-diol (**1b**).* Yield: 61% (20% from crystallization and 41% from chromatography), isolated as a white solid, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.32 in 1:3 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75−7.69 (m, 2H), 7.69−7.62 (m, 2H), 7.47−7.30 (m, 6H), 4.23 (dd, J = 10.5, 3.1 Hz, 1H), 3.83−3.63 (m, 2H), 2.09 (bs, 2H), 1.16 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.6, 136.3, 133.2, 132.8, 129.71, 129.69, 128.0, 66.4, 65.7, 28.4, 18.5 ppm. The spectra contain a signal overlap in the aromatic region; IR ($CHCl_3$ film) 3376 (s, br), 3072 (w), 3013 (w) 2859 (m), 1427 (m), 1105 (m), 1053 (m), 882 (m) cm^{-1}; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_{18}H_{24}NaO_2Si$, 323.1443, found 323.1444; mp 86.6−87.1 °C (recrystallized from pentane at −78 °C).

*1-(tert-Butyldimethylsilyl)ethane-1,2-diol (**1c**).* To a stirred solution of *tert*-butyldimethylsilylacetylene (4.94 g, 35.2 mmol, 1 equiv) and quinoline (207 μL, 1.76 mmol, 5%) in *t*-BuOH (35.2 mL) was added Lindlar catalyst (5% Pd on $CaCO_3$ poisoned with lead, 225 mg, 0.105 mmol, 3%), under a nitrogen atmosphere. The atmosphere was changed to H_2 (purged three times using H_2 from a balloon). After 3 h the mixture was filtered trough a plug of Celite. *t*-BuOH (17.6 mL), water (17.6 mL), NMO (50% in water, 14.6 mL, 70.4 mmol, 2 equiv), and OsO_4 (2.5% in *t*-BuOH, 1.78 mL, 0.176 mmol, 0.5%) were added. After stirring at ambient temperature for 1 h the reaction was quenched by addition of Na_2SO_3 (10 g) and stirred for additionally 30 min. The mixture was diluted with water (200 mL), extracted with *tert*-butyl methylether (2 × 200 mL), and concentrated. Purification by silica-gel chromatography eluting with EtOAc/petroleum ether (0−25% EtOAc) yielded diol **1c** (4.02 g, 65%) as a white solid, >95% pure by NMR spectroscopy and a single spot by TLC: R_f = 0.18 in 1:3 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83−3.68 (m, 2H), 3.63 (dd, J = 9.4, 3.2 Hz, 1H), 2.05 (s, 2H), 0.94 (s, 9H), 0.05 (s, 3H), −0.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 66.1, 66.0, 27.0, 16.8, −7.4, −8.0 ppm; IR ($CHCl_3$ film) 3377 (s, br), 2954 (m), 2858 (m), 1464 (m), 1057 (m) cm^{-1}; HRMS-ESI (m/z) $[M + Na]^+$ calcd for $C_8H_{20}NaO_2Si$, 199.1130, found 199.1136; mp 65.8−66.3 °C (from EtOAc:petroleum ether).

*Tri(trimethylsilyl)(vinyl)silane (**6d**).*[35] To chlorotris(trimethylsilyl)-silane (8.39 g, 30 mmol) was added vinyl magnesium bromide (0.7 M in THF, 64.3 mL, 45 mmol) at 0 °C under a nitrogen atmosphere. The resulting mixture was stirred for 20 min and then quenched by addition of NH_4Cl (aq., sat.). The resulting mixture was diluted with water (50 mL) and extracted with CH_2Cl_2 (×2). The organic layer was dried using a phaseseparator and concentrated to yield alkene **6d** (8.27 g, 100%) as a white waxy solid, >95% pure by NMR spectroscopy and a single spot by TLC: R_f = 0.91 in 1:10 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (dd, J = 19.8, 14.0 Hz, 1H), 5.93 (dd, J = 14.0, 3.8 Hz, 1H), 5.66 (dd, J = 19.8, 3.8 Hz, 1H), 0.17 (s, 27H) ppm.

*(Tri(trimethylsilyl)silyl)ethane-1,2-diol (**1d**).* To a solution of $K_3Fe(CN)_6$ (0.98 g, 3.0 mmol), K_2CO_3 (0.41 g, 3.0 mmol), and $(DHQD)_2$-PHAL (78 mg, 0.1 mmol) in *t*-BuOH:water 1:1 (14 mL) was added $K_2OsO_2(OH)_2$ (7.4 mg, 0.02 mmol). The resulting yellow mixture was cooled to 0 °C (some precipitation was observed). Vinyl silane **6d** (250 mg, 0.91 mmol) was added in one portion dissolved in *t*-BuOH (1.5 mL) followed by addition of water (1.5 mL). The resulting mixture was stirred at 0 °C for 20 h and then quenched by addition of Na_2SO_3 (0.5 g) followed by stirring for an additional 30 min. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and concentrated under reduced pressure.

dx.doi.org/10.1021/jo402123j | J. Org. Chem. 2013, 78, 12268−12273

Purification by silica-gel chromatography, eluting with EtOAc/petroleum ether (3.13−12.5% EtOAc), yielded diol **1d** (204 mg, 73%) as a white solid, >95% pure by NMR spectroscopy and a single spot by TLC: $[\alpha]_D^{25}$ +7.9 (c = 0.7, CH_2Cl_2); R_f = 0.59 in 1:3 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06−3.95 (m, 1H), 3.81−3.68 (m, 2H), 2.01 (bs, 1H), 1.76 (bs, 1H), 0.21 (app. d, J = 2.6 Hz, 27H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 68.5, 67.1, 1.7 ppm; IR ($CHCl_3$ film) 3401 (s, br), 2949 (m), 2893 (m), 1397 (m), 1059 (m) cm^{-1}; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{11}H_{32}NaO_2Si_4$, 331.1377, found 331.1376; mp 102.0−103.5 °C (from EtOAc:petroleum ether).

General Procedure for Aldol Reaction with Formylsilanes. To a stirred solution of diisopropylamine (2 equiv) in THF (0.2 M) was added *n*-BuLi (1.6 M in hexanes, 1.5 equiv) at −78 °C under a nitrogen atmosphere. The temperature was raised to 0 °C over 20 min and then reduced back to −78 °C. Propiophenone (1.5 equiv) was added dropwise over 1 min, and the resulting mixture was stirred for 20 min. The resulting enolate solution was then transferred by cannula to a solution of freshly prepared formylsilane (1 equiv, corrected for silanol) in THF (0.2 M) at −78 °C. After complete consumption of the formylsilane (5 s for **2a,b** and 2 h for **2c**) the reaction was quenched by addition of AcOH (10% v/v, in MeOH) or NH_4Cl (aq. sat.), diluted with water (50 mL/mmol formylsilane), extracted with Et_2O (2 × 50 mL/mmol formylsilane), dried with Na_2SO_4, filtered, and concentrated. Purification of the crude product by silica-gel chromatography, eluting with EtOAc/petroleum ether (0−10% EtOAc), yielded the aldol adduct.

(2R,3R*)-3-(tert-Butyldimethylsilyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (**9a**).* Yield: 55%, isolated as a clear oil, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.24 in 1:20 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.90 (m, 2H), 7.62−7.56 (m, 1H), 7.52−7.46 (m, 2H), 4.01 (dd, J = 3.3, 1.9 Hz, 1H), 3.57 (qd, J = 7.2, 1.9 Hz, 1H), 2.84 (d, J = 3.4 Hz, 1H), 1.32 (d, J = 7.2 Hz, 3H), 0.96 (s, 9H), 0.15 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.4, 135.8, 133.5, 129.0, 128.6, 63.3, 42.6, 26.9, 16.9, 12.9, −6.5, −7.2 ppm; IR ($CHCl_3$ film) 3516 (m, br), 2952 (m), 2928 (m), 1666 (s), 1449 (m), 972 (m) cm^{-1}; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{16}H_{26}NaO_2Si$, 301.1600, found 301.1598.

(2R,3R*)-3-(tert-Butyldiphenylsilyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (**9b**).* Yield: 58%, isolated as a white solid, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.59 in 1:10 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, C_6D_6) δ 8.13−8.07 (m, 2H), 7.75−7.69 (m, 2H), 7.59−7.55 (m, 2H), 7.24−7.13 (m, 6H), 7.03−6.98 (m, 1H), 6.93−6.87 (m, 2H), 4.70 (dd, J = 2.8, 1.5 Hz, 1H), 3.60 (d, J = 2.8 Hz, 1H), 3.39 (qd, J = 7.2, 1.3 Hz, 1H), 1.22 (s, 9H), 1.19 (d, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, C_6D_6) δ 206.4, 137.7, 136.6, 135.9, 134.7, 134.2, 133.2, 129.74, 129.72, 128.8, 128.7, 128.3, 127.8, 65.8, 41.7, 28.6, 18.8, 13.5 ppm; IR ($CHCl_3$ film) 3510 (w, br), 3017 (m), 2951 (m), 2862 (m), 1665 (s), 1428 (m), 1106 (m) cm^{-1}; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{26}H_{30}NaO_2Si$, 425.1913, found 425.1913; mp 105.8−107.7 °C (from EtOAc:petroleum ether).

(2R,3R*)-3-(triisopropylsilyl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (**11**).*[10a] Yield: 64%, isolated as a clear oil, >95% pure by NMR spectroscopy and a single spot by TLC; R_f = 0.60 in 1:10 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.91 (m, 2H), 7.62−7.56 (m, 1H), 7.53−7.46 (m, 2H), 4.18 (dd, J = 3.1, 1.5 Hz, 1H), 3.65 (qd, J = 7.2, 1.4 Hz, 1H), 2.93 (d, J = 3.3 Hz, 1H), 1.40 (d, J = 7.2 Hz, 3H), 1.27−1.19 (m, 3H), 1.18−1.11 (m, 18H) ppm.

General Procedure for HWE Olefination of Formylsilanes. To a stirred solution of triethyl phosphonoacetate (2.0 equiv) in THF (0.3 M) was added NaH (60% in mineral oil, 1.5 equiv), under a nitrogen atmosphere, at 0 °C. After stirring for 30 min, the mixture was cooled to −78 °C and transferred by cannula to a solution of formylsilane (1.0 equiv) in THF (0.3 M). After stirring at −78 °C for 2 h, the reaction was quenched by addition of NH_4Cl (aq., sat.). The resulting mixture was poured onto water, extracted with *tert*-butyl methylether (2 × 60 mL/mmol), dried ($MgSO_4$), filtered, and concentrated. Purification by silica-gel chromatography, eluting with EtOAc/petroleum ether (5% EtOAc), yielded the vinyl silane.

*(E)- and (Z)-Ethyl 3-(tert-butyldimethylsilyl)acrylate (**10a**).* Yield: 57%, (*E*):(*Z*) = 93:7, isolated as a clear oil, >95% pure by NMR spectroscopy and two spots by TLC; R_f major = 0.54; minor = 0.51 in 1:20 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ (*E*-isomer) 7.27 (d, J = 18.9 Hz, 1H), 6.26 (d, J = 18.9 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 6H) ppm. (*Z*-isomer) 6.59 (d, J = 14.9 Hz, 1H), 6.54 (d, J = 14.9 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 0.92 (s, 9H), 0.17 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ (*E*-isomer) 165.8, 147.4, 135.2, 60.5, 26.4, 16.5, 14.3, −6.5 ppm; IR ($CHCl_3$ film) 2954 (m), 29.24 (s), 2855 (m), 1721 (m), 1463 (m), 997 (m) cm^{-1}; HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{11}H_{23}O_2Si$, 215.1467, found 215.1472.

*(E)- and (Z)-Ethyl 3-(tert-butyldiphenylsilyl)acrylate (**10b**).* Yield: 69%, (*E*):(*Z*) = 61:39, isolated as a clear oil, >95% pure by NMR spectroscopy and two spots by TLC; R_f major = 0.43; minor = 0.41 in 1:20 EtOAc:petroleum ether; ^{1}H NMR (400 MHz, $CDCl_3$) δ (*E*)-isomer 7.68 (d, J = 18.8 Hz, 1H), 7.60−7.54 (m, 4H), 7.45−7.30 (m, 6H), 6.23 (d, J = 18.8 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.11 (s, 9H) ppm; (*Z*)-isomer 7.70−7.66 (m, 4H), 7.45−7.30 (m, 6H), 6.94 (d, J = 14.9 Hz, 1H), 6.89 (d, J = 14.9 Hz, 1H), 3.40 (q, J = 7.1 Hz, 2H), 0.99 (s, 9H), 0.58 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ (*E*)-isomer 165.8, 143.8, 138.8, 136.4, 133.1, 129.8, 128.0, 60.9, 27.8, 18.5, 14.4 ppm; (*Z*)-isomer 166.1, 142.1, 140.7, 135.5, 133.9, 129.1, 127.6, 60.1, 27.3, 18.5, 13.5 ppm; IR ($CHCl_3$ film) 2959 (m), 2929 (m), 2858 (m), 1720 (s), 1427 (m), 999 (m) cm^{-1}; HRMS-ESI (m/z) [M + Na]$^+$ calcd for $C_{21}H_{26}NaO_2Si$, 361.1600, found 361.1599.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra, X-ray diffraction structures, and crystallographic data for compounds **8a−c** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: daniel.strand@chem.lu.se.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Swedish Research Council and the Royal Physiographical Society for financial support.

■ REFERENCES

(1) For reviews of the chemistry of acyl and formylsilanes, see: (a) Patroci'nio, A. F.; Moran, P. J. S. *J. Braz. Chem. Soc.* **2001**, *12*, 7−31. (b) Cirillo, P. F.; Panek, J. S. *Org. Prep. Proced. Int.* **1992**, *24*, 553−582. (c) Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147−195.

(2) For synthesis and characterization of related formylphosphanes, see: Amsallem, D.; Gornitzka, H.; Baceiredo, A.; Bertrand, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 2201−2203.

(3) For recent representative examples, see: (a) Ito, K.; Tamashima, H.; Iwasawa, N.; Kusama, H. *J. Am. Chem. Soc.* **2011**, *133*, 3716−3719. (b) Schmink, J. R.; Krska, S. W. *J. Am. Chem. Soc.* **2011**, *133*, 19574−19577. (c) Tarr, J. C.; Johnson, J. S. *J. Org. Chem.* **2010**, *75*, 3317−3325. (d) Mi, Y.; Schreiber, J. V.; Corey, E. J. *J. Am. Chem. Soc.* **2002**, *124*, 11290−11291. (e) Chen, M.-J.; Tsai, Y.-M. *Tetrahedron* **2011**, *67*, 1564−1574. (f) Sasaki, M.; Oyamada, K.; Takeda, K. *J. Org. Chem.* **2010**, *75*, 3941−3943.

(4) Trammer, M.; Sander, W.; Patyk, A. *J. Am. Chem. Soc.* **1993**, *115*, 11775−11783.

(5) (a) Elsner, F. H.; Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* **1988**, *110*, 313−314. (b) Woo, H. G.; Freeman, W. P.; Tilley, T. D. *Organometallics* **1992**, *11*, 2198−2205.
(6) (a) Ireland, R. E.; Norbeck, D. W. *J. Org. Chem.* **1985**, *50*, 2198−2200. (b) Linderman, R. J.; Suhr, Y. *J. Org. Chem.* **1988**, *53*, 1569−1572.
(7) This procedure was also used for isolation of Me_3-formylsilane by cold trap distillation followed by preparative GC. See reference 4.
(8) Silverman, R. B.; Lu, X.; Banik, G. M. *J. Org. Chem.* **1992**, *57*, 6617−6622.
(9) Katritzky, A. R.; Yang, Z.; Hong, Q. *J. Org. Chem.* **1994**, *59*, 5097−5099.
(10) (a) Soderquist, J. A.; Miranda, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 10078−10079. (b) Soderquist, J. A.; Miranda, E. I. *Tetrahedron Lett.* **1993**, *34*, 4905−4908.
(11) For examples, see: (a) Peshkov, V. A.; Pereshivkoa, O. P.; Eycken, E. v. d. *Chem. Soc. Rev.* **2012**, *41*, 3790−3807. (b) Wachenfeldt, H. v.; Röse, P.; Paulsen, F.; Loganathan, N.; Strand, D. *Chem.—Eur. J.* **2013**, *19*, 7982−7988. (c) Torssell, S.; Kienle, M.; Somfai, P. *Angew. Chem., Int. Ed.* **2005**, *44*, 3096−3099.
(12) An unsuccessful attempt to generate formylsilanes through ozonolysis of vinylsilanes has been reported: Sommer, L. H.; Bailey, D. L.; Goldbeg, G. M.; Buck, C. E.; Bye, T. S.; Evans, F. J.; Whitmore, F. C. *J. Am. Chem. Soc.* **1954**, *76*, 1613−1618.
(13) For enantioselective synthesis of **1a**, see reference 23b.
(14) The amount of silanol was determined by quantitative ^{13}C NMR, a method which likely overestimates the actual amount of silanol formed in the reaction due to the difficulties of rigorous exclusion of air during the workup and analysis process.
(15) Gupta, D. N.; Hodge, P.; Davies, J. E. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2970−2973.
(16) Nicolaou, K. C.; Adsool, V. A.; Hale, C. R. H. *Org. Lett.* **2010**, *12*, 1552−1555.
(17) Wolf, F. J.; Weijlard, J. *Org. Synth.* **1955**, *35*, 18.
(18) Lena, J. I. C.; Ferreira, M. R. R.; Hernando, J. I. M.; Altinel, E.; Arseniyadis, S. *Tetrahedron Lett.* **2001**, *42*, 3179−3182.
(19) Moser, W. H. *Tetrahedron* **2001**, *57*, 2065−2084.
(20) For $Pb(OAc)_4$-promoted formation of acyl-silyl acetals from α-silyl alcohols, see: (a) Paredes, M. A.; Alonso, R. *Tetrahedron Lett.* **1999**, *40*, 3973−3976. (b) Paredes, M. D.; Alonso, R. *J. Org. Chem.* **2000**, *65*, 2292−2304.
(21) For alternative synthesis of vinylsilanes, see: (a) Barberot, A.; Cuadradot, P.; Fleming, I.; M. Gonzalezt, A. M.; Pulido, F. J.; Sanchez, A. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1525−1532. (b) Kakiya, H.; Shinokubo, H.; Oshima, K. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2139−2147. (c) Soderquist, J. A.; Isaac Rivera, I.; Negron, A. *J. Org. Chem.* **1989**, *54*, 4051−4055.
(22) For an example of Upjohn dihydroxylation of a *t*-$BuMe_2Si$ vinylsilane, see: Cunico, R. F. *Tetrahedron Lett.* **1986**, *27*, 4269−4272.
(23) (a) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483−2547. (b) Soderquist, J. A.; Rane, A. M.; López, C. J. *Tetrahedron Lett.* **1993**, *34*, 1893−1896.
(24) The e.r. of the product was not quantified.
(25) Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668−3670.
(26) For lead references, see: Knölker, H.-J.; Jones, P. G.; Wanzl, G. *Synlett* **1998**, 613−616 and referenecs therein.
(27) Chatgilialoglu, C.; Guarini, A.; Guerrini, A.; Seconi, G. *J. Org. Chem.* **1992**, *57*, 2207−2208.
(28) A single-crystal X-ray structure of a tosylhydrazone of **2a** was reported in reference 10a.
(29) Literature values for selected 2,4-dinitrohydrazones: Mase, N.; Thayumanavan, R.; Tanaka, F.; Barbas, C. F. *Org. Lett.* **2004**, *6*, 2527−2530 (CSD-REFCOD: DAGKUS) 1.25 Å. Li, J.; Lowary, T. L.; McDonald, R. *Acta Crystallogr.* **2008**, *E64*, o459−o460 (CSD-REFCOD: GISYEN) 1.26 Å. Marek, R.; Potacek, M.; Marek, J.; De Groot, A.; Dommisse, R. *Monatsh. Chem.* **1995**, *126*, 1151−1160 (CSD-REFCOD: HITNED) 1.25 Å. Marsh, R. E. *Acta Crystallogr.* **2005**, *B61*, 359 (CSD-REFCOD: HITNED01) 1.26 Å.
(30) The utility of α-silyl alcoxyderivatives in synthesis was recently highlighted by the use of α-silyl-silylethers in sp^3−sp^3 cross coupling reactions: Brekan, J. A.; Chernyak, D.; White, K. L.; Scheidt, K. A. *Chem. Sci.* **2012**, *3*, 1205−12010.
(31) Wadsworth, W. S., Jr. *Org. React.* **1977**, *25*, 73−253.
(32) The relaxation delay was set to 11 s ($>5 \times T_1$) for all quantitative ^{13}C NMR. T_1 was calculated from an inversion recovery experiment using triisopropylsilane, triisopropylsilanol and α-silyl glycol **1a**.
(33) Usanov, D. L.; Yamamoto, H. *Org. Lett.* **2012**, *14*, 414−417.
(34) Gerstenberger, B. S.; Konopelski, J. P. *J. Org. Chem.* **2005**, *70*, 1467−1470.
(35) Zhang, S.; Ezhova, M. B.; Conlin, R. T. *Organometallics* **1995**, *14*, 1471−1477.