JOC The Journal of Organic Chemistry

Featured Article

pubs.acs.org/joc

Ir-Catalyzed Regio- and Stereoselective Hydrosilylation of Internal Thioalkynes: A Combined Experimental and Computational Study

Li-Juan Song,[†,∥] Shengtao Ding,[‡,∥] Yong Wang,[§] Xinhao Zhang,[*,†] Yun-Dong Wu,[*,†] and Jianwei Sun[*,‡]

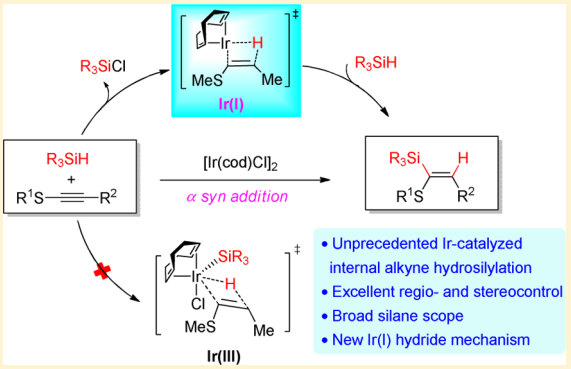
[†]Lab of Computational Chemistry and Drug Design, Laboratory of Chemical Genomics, Peking University Shenzhen Graduate School, Shenzhen 518055, China

[‡]Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

[§]HKUST Shenzhen Research Institute, Shenzhen 518057, China

Supporting Information

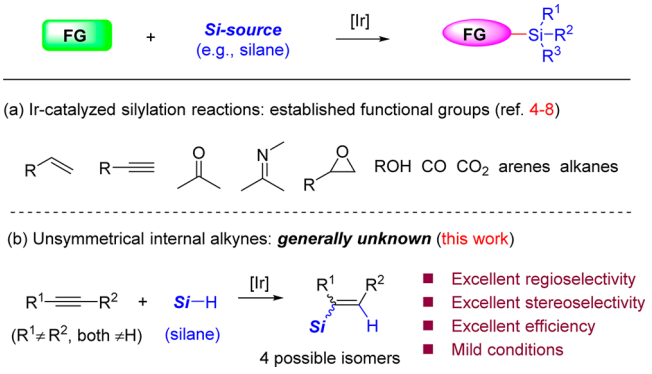
ABSTRACT: Iridium complexes are known catalysts for a range of silylation reactions. However, the exploitation for selective hydrosilylation of unsymmetrical internal alkynes has been limitedly known. Described here is a new example of this type. Specifically, $[(cod)IrCl]_2$ catalyzes the efficient and mild hydrosilylation of thioalkynes by various silanes with excellent regio- and stereoselectivity. DFT studies suggested a new mechanism involving Ir(I) hydride as the key intermediate.



INTRODUCTION

Efficient and atom-economic introduction of a silyl group to an organic molecule (silylation reaction) represents one of the most useful reactions, owing to the wide utility of organosilane compounds, a family of nontoxic stable metalloid species with demonstrated application in industry.[1−3] Consequently, over the past few decades, a wide range of metal-catalyzed silylation reactions have been developed.[1c,d] In these reactions, iridium complexes proved to be particularly versatile, presumably due to their exceptional capability in silane Si−H bond activation.[2] Notably, silylations of a wide variety of functional groups, including olefins, terminal alkynes, carbonyls, imines, epoxides, alcohols, CO, CO_2, arenes, and even alkanes, have been well-documented with Ir catalysis in the context of various reaction types (Scheme 1a).[4−8] Among these reactions, alkyne hydrosilylation is of particular significance as it provides the most atom-economic and straightforward access to the valuable vinylsilane compounds from readily available chemical feedstock.[3,8] However, these reactions are often plagued by the challenges in regio- and stereocontrol, particularly for unsymmetrical internal alkynes in an intermolecular fashion where four isomers can be possibly formed.[3] Successful examples reported so far have been largely limited to alkynes with a highly polarized and electron-deficient triple bond[9] or bearing an internal directing group[10] or intramolecular hydrosilylations.[11] Morever, recent reports on hydrosilylation of unsymmetrical internal alkynes have been mainly based on ruthenium,[9a,11f,12] platinum,[9c,d,g,10e] and some other metal complexes.[13] Despite the well-known exceptional catalytic ability of iridium complexes in silylation reactions, their exploitation for regio- and stereoselective hydrosilylation of unsymmetrical internal alkynes has remained limitedly known to date.[14] In this context, here we report another example of this type with excellent selectivity and broad scope under mild conditions (Scheme 1b).

Scheme 1. Introduction to Iridium-Catalyzed Silylation Reactions

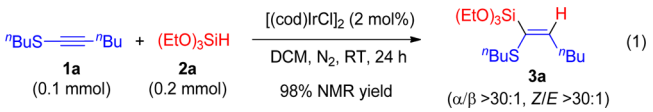


Received: April 15, 2016
Published: May 27, 2016

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164

RESULTS AND DISCUSSION

In continuation of our efforts in the studies of electron-rich alkynes[15] and hydrosilylation reactions,[16] we employed thioalkyne **1a** as the representative substrate. Triethoxysilane **2a** was used as the silane source in view of the proved superiority of trialkoxysilyl groups (vs trialkylsilyl) for transmetalation in Hiyama cross-coupling reactions and for their wide utilities in material science.[17] A range of Ir(I) complexes bearing different ligand systems, including a cationic complex, were evaluated for the reaction between **1a** and **2a**. While the majority of them did not show any catalytic activity, $[(cod)IrCl]_2$ could catalyze the desired hydrosilylation at room temperature with exceptional efficiency and excellent α *syn* selectivity (eq 1; see the SI for more details). It is



noteworthy that the previously established Pt, Co, and Ru catalysts proved to be either catalytically inactive or significantly less selective for the same transformation,[16b] thereby highlighting the complementary capability of the present iridium-based catalytic system.

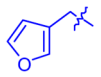
The established protocol is general in substrates. A wide range of different thioalkynes smoothly participated in the intermolecular hydrosilylation reaction (Table 1). The mild conditions can tolerate a diverse set of functional groups, such as ethers, acetals (THPO), silyl-protected alcohols, and even free alcohols. Electron-donating and withdrawing substituents do not significantly affect the reactivity and selectivity (entries 14−17). A heterocycle can also be incorporated into the vinylsilane product (entry 18).

Various electronically and sterically distinct silanes are all suitable reaction partners, providing the desired α *syn* addition products with high efficiency and selectivity (Table 2). It is worth mentioning that such a broad silane scope is noteworthy when directly compared with the precedented cases in which high selectivity was only achieved with limited silanes.[16b,18] Notably, the use of excess silane is partly due to the self-decomposition of silane (e.g., formation of disilane) in the presence of the iridium catalyst. The excellent efficiency, selectivity, generality, and mild conditions may lead to potential applications.

To demonstrate the utility of the Ir-catalyzed hydrosilylation process, we carried out derivatizations of the stereodefined multisubstituted vinylsilane products. For example, the silyl group in the product can be easily removed in the presence of AgF and MeOH, affording the vinyl sulfide **5** with excellent *Z*-selectivity (eq 2). The vinylsilane can also undergo efficient Hiyama cross-coupling to form the vinyl sulfide **6** with retention of the olefin configuration (eq 3). Notably, synthesis of these stereodefined (*Z*)-vinyl sulfides with high selectivity has not been so straightforward using conventional strategies.[19] Finally, the efficient hydrosilylation protocol can be coupled with oxidation in a one-pot process to generate the vinyl sulfone **7** with retained double-bond configuration (eq 4).

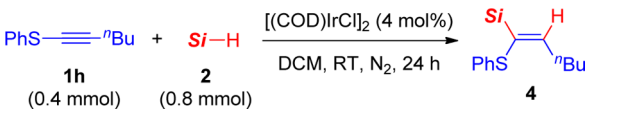
To understand the mechanism, including the origin of the exceptional regio- and stereoselectivity, density functional theory (DFT) studies were carried out.[20] The most straightforward mechanism leading to *syn*-hydrosilylation of alkynes and alkenes is the Chalk−Harrod mechanism,[21] which involves oxidative addition of the silane followed by hydrometalation of the alkyne and reductive elimination. However, the calculated barrier for this Ir(III) pathway is rather high (**A-TS-1a** with 31.2 kcal/mol, Figure S1 in the SI), although the

Table 1. Scope of Thioalkynes

entry	R^1	R^2	product	yield	α/β^a	Z/E^a
1	^{n}Bu	^{n}Bu	**3a**	85%	>30:1	>30:1
2	^{n}Bu		**3b**	87%	12:1	>30:1
3[d,e]	^{n}Bu	$(CH_2)_2$OTHP	**3c**	88%	>30:1	>30:1
4[c,e]	^{n}Bu	$(CH_2)_2$OTBS	**3d**	52%	16:1	>30:1
5[b]	Me	^{n}Bu	**3e**	76%	>30:1	>30:1
6	^{i}Pr	^{n}Bu	**3f**	71%	20:1	>30:1
7[c,d,e]	Bn	^{n}Bu	**3g**	75%	>30:1	>30:1
8	Ph	^{n}Bu	**3h**	85%	12:1	>30:1
9[c,e]	Ph	^{n}Octyl	**3i**	60%	12:1	>30:1
10	Ph		**3j**	89%	25:1	>30:1
11	Ph	$(CH_2)_2$OTHP	**3k**	81%	>30:1	>30:1
12[d,e]	Ph	$(CH_2)_2$OTBS	**3l**	65%	>30:1	>30:1
13	Ph	$(CH_2)_2$OH	**3m**	60%	11:1	>20:1
14[c]	(*p*-Me)C_6H_4	^{n}Bu	**3n**	77%	>30:1	>30:1
15[c]	(*p*-MeO)C_6H_4	^{n}Bu	**3o**	71%	>30:1	>30:1
16[e]	(*p*-Cl)C_6H_4	^{n}Bu	**3p**	73%	>30:1	>30:1
17[c,e]	(*p*-NO_2)C_6H_4	^{n}Bu	**3q**	80%	25:1	>30:1
18[c,e]		^{n}Bu	**3r**	66%	25:1	>30:1

[a]Determined from ^{1}H NMR spectra of the crude product on the basis of the vinylic proton signal in the product. [b]Run with MeCN as solvent. [c]Run at 40 °C. [d]Run with 4.0 equiv of **2a**. [e]Run with 4 mol % of the catalyst.

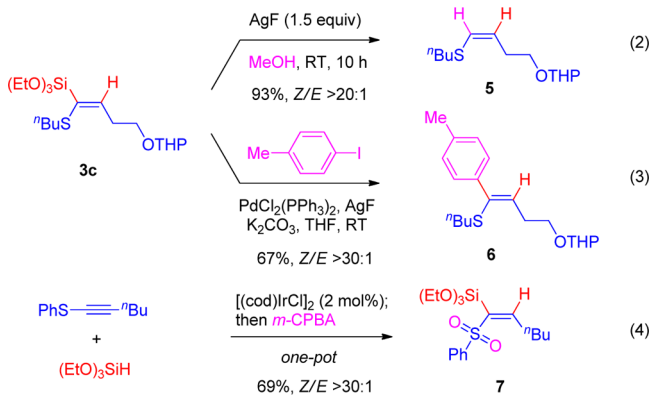
Table 2. Silane Scope



entry	silane	product	yield (%)	α/β^a	Z/E^a
1[b]	$HSi(OMe)_3$ (**2b**)	**4a**	84	>30:1	>30:1
2	$HSi(OEt)_2Me$ (**2c**)	**4b**	40	12:1	>30:1
3	$HSiClMe_2$ (**2d**)	**4c′**[c]	72	>30:1	>30:1
4	$HSi(OTMS)_2Me$ (**2e**)	**4d**	67	>30:1	>30:1
5	$HSi(OTMS)_3$ (**2f**)	**4e**	69	>30:1	>30:1
6	$HSiMe_2Ph$ (**2g**)	**4f′**[d]	53	12:1	>30:1
7	$HSiMe_2Bn$ (**2h**)	**4g′**[d]	78	25:1	>30:1

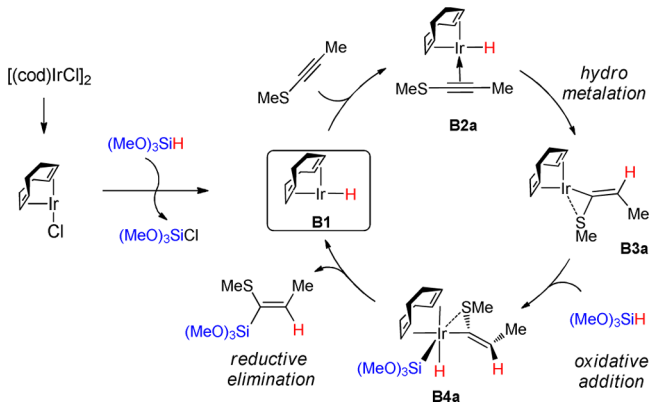
[a]Determined from ^{1}H NMR spectra of the crude product on the basis of the vinylic proton signal in the product. [b]Run at 40 °C. [c]The reaction was quenched with Et_3N and MeOH, and the methyl silyl ether was obtained as product. [d]To simplify purification, the product was in situ oxidized by *m*-CPBA to the sulfone.

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164



regioselectivity was consistent.[22] The high barrier suggested that other mechanisms should be explored. An alternative mechanism involving silylmetalation of the Ir(III) species was also conceived, but the calculated barrier was even higher (**A-TS′-1b** with 47.7 kcal/mol, Figure S1).[8c,22] An important finding is that alkyne coordination to the iridium(III) hydride is not favored. Thus, other plausible pathways to provide sufficient vacant sites for substrate coordination should be considered. To this end, release of a small molecule (e.g., R_3SiCl) from the precatalyst was postulated.[23] Specifically, as shown in Scheme 2, the Ir(I) hydride mechanism was

Scheme 2. Proposed Ir(I) Hydride Mechanism



proposed, which involves (1) release of $Si(OMe)_3Cl$ to furnish the Ir(I) hydride **B1**, (2) hydrometalation to form **B3a**, (3) silane oxidative addition to generate **B4a**, and (4) reductive elimination to obtain the final product.

The potential energy surface is depicted in Figure 1. Initially, the Ir(I) hydride (**B1**) can be generated from Ir(I) chloride (**I1**) via a metathesis transition state **B-TS1** with an energy barrier of 27.1 kcal/mol. Alternatively, formation of the Ir(I) silyl complex via **B-TS1′** (Figure S2) was found to be unfeasible.[22] It is worth noting that although Ir(III) hydride has been extensively reported (e.g., in hydrogenation),[24] low-coordinate Ir(I) hydride remains limitedly known.[25] Recently, the X-ray structure of a four-coordinate iridium(I) hydride has been reported.[26] As expected, the coordination of alkyne with the newly formed Ir(I) hydride (**B1**) is much stronger than that with the Ir(III) complex, and consequently, it facilitates the subsequent hydrometalation (**B-TS2a/b**) to form σ-vinyl complexes (**B3a/b**). Formation of the stable intermediate **B3a** is thermodynamically more favorable with sulfur chelation to the iridium center (Ir--S distance of 2.70 Å), which maintains a distorted square geometry.[27a] Oxidative addition of a second silane to the metal center via **B-TS3a** and **B-TS3b** is facile, leading to Ir(III) intermediates **B4a** and **B4b**, respectively. Following the oxidative addition step, reductive elimination of the Ir(III) σ-vinyl complex **B4a** gives the hydrosilylation product **B5a**.[27b] Substrate exchange liberates the product vinylsilane and regenerates the active Ir(I) hydride complex **B2a** to close the catalytic cycle. Overall, regioselectivity is controlled by the alkyne insertion step. The preference of **B-TS2a** over **B-TS2b** (3.3 kcal/mol) agrees with the experimental results. This regioselectivity is dictated by the polarization of the triple bond (see Figure S5 for geometries and Scheme S3 for the Hirshfeld charge distribution).

CONCLUSIONS

In summary, despite the proven versatility of iridium complexes for various silylation reactions, hydrosilylations of unsymmetrical internal alkynes have remained limitedly known to date. Here we have demonstrated the first selective example of this type, thereby expanding the portfolio of iridium-catalyzed silylation reactions. With the proper choice of catalyst, a range of internal thioalkynes participated in the efficient intermolecular hydrosilylation with a diverse set of silanes to furnish the corresponding multisubstituted vinylsilanes with excellent α regio- and *syn* stereoselectivity. The mild conditions combined with a broad silane scope make this process an important complement to the previously established protocols. The vinylsilane products proved to be useful precursors to a range of stereodefined vinyl sulfides and vinyl sulfones whose previous synthesis has not been so straightforward. Computational investigations provided important insights into the reaction mechanism. Unlike the classic Chalk−Harrod mechanism using Ir(III) hydride as the key intermediate, it was found that a new mechanism involving an Ir(I) hydride intermediate is most consistent with the observed mild conditions and excellent stereo- and regiocontrol. These results are expected to shed light on future development of new iridium-catalyzed processes and alkyne hydrofunctionalization reactions.

EXPERIMENTAL SECTION

General Procedure. In a glovebox, to an oven-dried 5 mL vial was added the alkyne (0.40 mmol), the silane (0.80 mmol), $[(cod)IrCl]_2$ (5.4 mg, 8.0 μmol), and DCM (3.0 mL). The vial was capped and removed from the glovebox. The reaction mixture was stirred at room temperature for 24 h and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 0 → 50% Et_2O in hexanes) to give the desired product.

*(Z)-(1-(Butylthio)hex-1-enyl)triethoxysilane (**3a**).* Compound **3a** was prepared as a pale yellow oil from **1a** (0.40 mmol, 68.1 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 85% yield (113.0 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (t, J = 6.8 Hz, 1 H), 3.84 (q, J = 7.2 Hz, 6 H), 2.82 (t, J = 7.2 Hz, 2 H), 2.34 (q, J = 7.2 Hz, 2 H), 1.55−1.49 (m, 2 H), 1.42−1.30 (m, 6 H), 1.23 (t, J = 7.2 Hz, 9 H), 0.90−0.86 (m, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.6, 127.3, 58.7, 32.6, 32.2, 30.9, 30.1, 22.4, 21.9, 18.1, 13.9, 13.7; IR (thin film) 2961, 1699, 1576, 1465, 1390 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{16}H_{33}O_3SSi$ $(M - H)^+$ 333.1920, found 333.1926.

*(Z)-(1-(Butylthio)-2-cyclopropylvinyl)triethoxysilane (**3b**).* Compound **3b** was prepared as a pale yellow oil from **1b** (0.40 mmol, 61.7 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 87% yield (110.9 mg, α/β = 12:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (d, J = 9.6 Hz, 1 H), 3.86 (q, J = 6.8 Hz, 6 H), 2.84 (t, J = 7.2 Hz, 2 H), 2.25−2.17 (m, 1 H), 1.64−1.55

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164

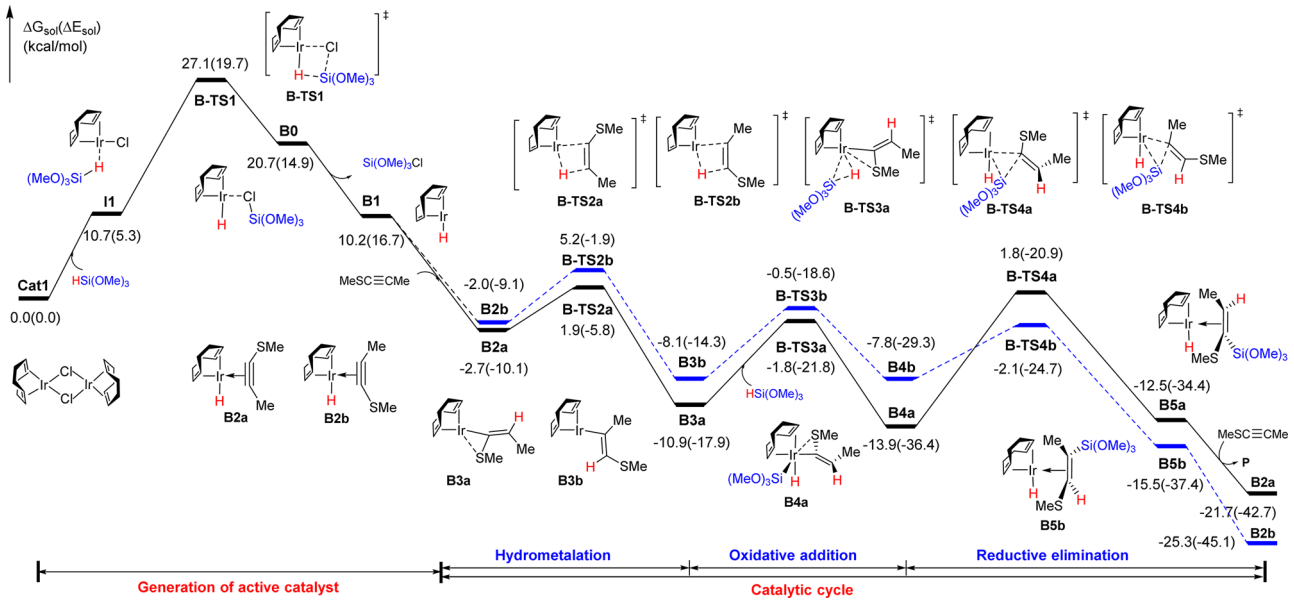


Figure 1. Energy profile of Ir(I) hydride mechanism in solvent. The relative free energies and electronic energies (in parentheses) are given in kcal/mol.

(m, 2 H), 1.49−1.38 (m, 2 H), 1.25 (t, J = 6.8 Hz, 9 H), 0.95−0.88 (m, 5 H), 0.57−0.51 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.5, 123.6, 58.7, 33.4, 32.1, 21.9, 18.1, 13.6, 13.2, 8.1; IR (thin film) 2973, 1779, 1586, 1390, 1081 cm^{-1}; HRMS m/z (CI) calcd for $C_{15}H_{29}O_3SSi$ $(M - H)^+$ 317.1607, found 317.1609.

*(Z)-(1-(Butylthio)-4-(tetrahydro-2H-pyran-2-yloxy)but-1-enyl)-triethoxysilane (**3c**).* Compound **3c** was prepared as a pale yellow oil from **1c** (0.40 mmol, 97.0 mg) and the silane **2a** (0.80 mmol, 132.0 mg), according to the General Procedure in 88% yield (142.6 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.48 (t, J = 6.8 Hz, 1 H), 4.65 (t, J = 3.2 Hz, 1 H), 3.90−3.78 (m, 8 H), 3.53−3.46 (m, 2 H), 2.86 (t, J = 7.2 Hz, 2 H), 2.70−2.62 (m, 2 H), 1.86−1.36 (m, 10 H), 1.26 (t, J = 6.8 Hz, 9 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 129.6, 98.4, 65.9, 61.9, 58.8, 32.6, 32.2, 30.9, 30.6, 25.5, 21.9, 19.3, 18.1, 13.7; IR (thin film) 2928, 1696, 1576, 1390, 1033 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{19}H_{38}O_5SSi$ $(M)^+$ 406.2209, found 406.2215.

*(Z)-8-(Butylthio)-9,9-diethoxy-2,2,3,3-tetramethyl-4,10-dioxa-3,9-disiladodec-7-ene (**3d**).* Compound **3d** was prepared as a pale yellow oil from **1d** (0.40 mmol, 109.0 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 52% yield (90.4 mg, α/β = 16:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (t, J = 6.8 Hz, 1 H), 3.86 (q, J = 7.2 Hz, 6 H), 3.69 (t, J = 6.8 Hz, 2 H), 2.84 (t, J = 7.2 Hz, 2 H), 2.57 (q, J = 6.8 Hz, 2 H), 1.58−1.49 (m, 2 H), 1.45−1.36 (m, 2 H), 1.23 (t, J = 7.2 Hz, 9 H), 0.91−0.86 (m, 12 H), 0.05 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.5, 129.2, 62.0, 58.7, 34.0, 32.6, 32.2, 25.9, 21.9, 18.3, 18.1, 13.7, −5.3; IR (thin film) 2929, 1780, 1555, 1472, 1255 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{20}H_{45}O_4SSi_2$ $(M + H)^+$ 437.2577, found 437.2571.

*(Z)-Triethoxy(1-(methylthio)hex-1-enyl)silane (**3e**).* Compound **3e** was prepared as a pale yellow oil from **1e** (0.40 mmol, 51.3 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 76% yield (89.4 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (t, J = 6.8 Hz, 1 H), 3.85 (q, J = 7.2 Hz, 6 H), 2.35 (s, 3 H), 2.30 (q, J = 7.2 Hz, 2 H), 1.44−1.30 (m, 4 H), 1.23 (t, J = 7.2 Hz, 9 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.3, 128.3, 58.7, 30.8, 30.0, 22.4, 18.1, 16.1, 13.9; IR (thin film) 2926, 1780, 1647, 1437, 1102 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{13}H_{28}O_3SSi$ $(M - H)^+$ 291.1450, found 291.1456.

*(Z)-Triethoxy(1-(isopropylthio)hex-1-enyl)silane (**3f**).* Compound **3f** was prepared as a pale yellow oil from **1f** (0.40 mmol, 62.5 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 71% yield (91.2 mg, α/β = 20:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (t, J = 6.8 Hz, 1 H), 3.86 (q, J = 7.2 Hz, 6 H), 3.47−3.39 (m, 1 H), 2.40 (q, J = 7.2 Hz, 2 H), 1.43−1.31 (m, 4 H), 1.26−1.21(m, 15 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.4, 126.9, 58.7, 36.6, 30.9, 30.1, 23.9, 22.4, 18.1, 13.9; IR (thin film) 2973, 1581, 1443, 1390, 1103 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{15}H_{31}O_3SSi$ $(M - H)^+$ 319.1763, found 319.1776.

*(Z)-(1-(Benzylthio)hex-1-enyl)triethoxysilane (**3g**).* Compound **3g** was prepared as a pale yellow oil from **1g** (0.40 mmol, 81.7 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 75% yield (110.4 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.28 (m, 4 H), 7.25−7.21 (m, 1 H), 6.49 (t, J = 6.8 Hz, 1 H), 4.08 (s, 2 H), 3.92 (q, J = 6.8 Hz, 6 H), 2.25 (q, J = 7.2 Hz, 2 H), 1.33−1.26 (m, 13 H), 0.88 (t, J = 6.8 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.5, 138.7, 129.0, 128.2, 126.7, 126.6, 58.8, 37.7, 30.7, 30.0, 22.4, 18.2, 13.9; IR (thin film) 2974, 1700, 1585, 1495, 1080 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{19}H_{31}O_3SSi$ $(M - H)^+$ 367.1763, found 367.1765.

*(Z)-Triethoxy(1-(phenylthio)hex-1-enyl)silane (**3h**).* Compound **3h** was prepared as a pale yellow oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 85% yield (120.9 mg, α/β = 12:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.26 (m, 2 H), 7.24−7.19 (m, 2 H), 7.13−7.08 (m, 1 H), 6.89 (t, J = 6.8 Hz, 1 H), 3.73 (q, J = 7.2 Hz, 6 H), 2.42 (q, J = 7.2 Hz, 2 H), 1.43−1.31 (m, 4 H), 1.13 (t, J = 7.2 Hz, 9 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.4, 137.1, 128.5, 128.4, 125.3, 124.9, 58.8, 30.7, 30.4, 22.4, 18.0, 13.9; IR (thin film) 2973, 1646, 1586, 1478, 1082 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{18}H_{29}O_3SSi$ $(M - H)^+$ 353.1607, found 353.1613.

*(Z)-Triethoxy(1-(phenylthio)dec-1-enyl)silane (**3i**).* Compound **3i** was prepared as a pale yellow oil from **1i** (0.40 mmol, 98.6 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 60% yield (98.4 mg, α/β = 12:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.21 (m, 4 H), 7.15−7.10 (m, 1 H), 6.91 (t, J = 6.8 Hz, 1 H), 3.75 (q, J = 6.8 Hz, 6 H), 2.44 (q, J = 7.2 Hz, 2 H), 1.47−1.43 (m, 2 H), 1.35−1.20 (m, 10 H), 1.15 (t, J = 6.8 Hz, 9 H), 0.90 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 137.1, 128.5, 128.4, 125.3, 124.8, 58.8, 31.8, 30.6, 29.34, 29.33, 29.2, 28.6, 22.6, 18.1, 14.1; IR (thin film) 2926, 1585, 1478, 1390, 1082 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{22}H_{38}O_3SSi$ $(M)^+$ 410.2311, found 410.2313.

*(Z)-(2-Cyclopropyl-1-(phenylthio)vinyl)triethoxysilane (**3j**).* Compound **3j** was prepared as a pale yellow oil from **1j** (0.40 mmol, 69.7

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164

mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 89% yield (120.4 mg, α/β = 25:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2 H), 7.25−7.20 (m, 2 H), 7.11−7.07 (m, 1 H), 6.25 (d, J = 10.0 Hz, 1 H), 3.74 (q, J = 6.8 Hz, 6 H), 2.26−2.16 (m, 1 H), 1.22 (t, J = 6.8 Hz, 9 H), 0.91−0.85 (m, 2 H), 0.65−0.61 (m, 2 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.7, 137.4, 128.4, 127.7, 124.9, 120.0, 58.8, 18.0, 13.8, 8.4; IR (thin film) 2974, 1867, 1586, 1478, 1390 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{17}H_{25}O_3SSi$ (M − H)$^+$ 337.1294, found 337.1296.

*(Z)-Triethoxy(1-(phenylthio)-4-(tetrahydro-2H-pyran-2-yloxy)-but-1-enyl)silane (**3k**).* Compound **3k** was prepared as a pale yellow oil from **1k** (0.40 mmol, 105.0 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 81% yield (138.0 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.27 (m, 2 H), 7.25−7.20 (m, 2 H), 7.16−7.10 (m, 1 H), 6.97 (t, J = 6.8 Hz, 1 H), 4.63 (t, J = 3.2 Hz, 1 H), 3.88−3.82 (m, 2 H), 3.74 (q, J = 6.8 Hz, 6 H), 3.54−3.48 (m, 2 H), 2.77−2.72 (m, 2 H), 1.85−1.50 (m, 6 H), 1.14 (t, J = 6.8 Hz, 9 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.4, 136.7, 128.8, 128.4, 127.1, 125.4, 98.4, 65.7, 61.9, 58.8, 31.2, 30.5, 25.4, 19.2, 18.0; IR (thin film) 2973, 1645, 1478, 1390, 1080 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{21}H_{33}O_5SSi$ (M − H)$^+$ 425.1818, found 425.1821.

*(Z)-9,9-Diethoxy-2,2,3,3-tetramethyl-8-(phenylthio)-4,10-dioxa-3,9-disiladodec-7-ene (**3l**).* Compound **3l** was prepared as a pale yellow oil from **1l** (0.40 mmol, 117.0 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 65% yield (119.0 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.21 (m, 4 H), 7.16−7.11 (m, 1 H), 7.00 (t, J = 6.8 Hz, 1 H), 3.77−3.72 (m, 8 H), 2.67 (q, J = 6.8 Hz, 2 H), 1.15 (t, J = 6.8 Hz, 9 H), 0.92 (s, 9 H), 0.07 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.9, 136.8, 128.7, 128.4, 126.8, 125.4, 61.8, 58.8, 34.2, 25.9, 18.3, 18.0, −5.4; IR (thin film) 2928, 2869, 1584, 1477, 1256 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{22}H_{39}O_4SSi_2$ (M − H)$^+$ 455.2108, found 455.2107.

*(Z)-4-(Phenylthio)-4-(triethoxysilyl)but-3-en-1-ol (**3m**).* Compound **3m** was prepared as a pale yellow oil from **1m** (0.40 mmol, 71.3 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 60% yield (82.2 mg, α/β = 11:1, Z/E > 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.21 (m, 4 H), 7.17−7.12 (m, 1 H), 6.94 (t, J = 6.8 Hz, 1 H), 3.78−3.72 (m, 8 H), 2.75−2.68 (m, 2 H), 1.15 (t, J = 6.8 Hz, 9 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.3, 136.5, 128.9, 128.5, 128.3, 125.6, 61.5, 58.9, 34.2, 18.0; IR (thin film) 3494, 2975, 1733, 1584, 1478 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{16}H_{26}O_4SSi$ (M)$^+$ 342.1321, found 342.1338.

*(Z)-Triethoxy(1-(p-tolylthio)hex-1-enyl)silane (**3n**).* Compound **3n** was prepared as a pale yellow oil from **1n** (0.40 mmol, 81.7 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 77% yield (113.7 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 2 H), 7.04 (d, J = 8.0 Hz, 2 H), 6.83 (t, J = 6.8 Hz, 1 H), 3.73 (q, J = 6.8 Hz, 6 H), 2.43 (q, J = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.45−1.40 (m, 4 H), 1.14 (t, J = 6.8 Hz, 9 H), 0.89 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.2, 135.2, 133.2, 129.1 (2 C), 125.6, 58.7, 30.7, 30.3, 22.4, 20.9, 18.0, 13.8; IR (thin film) 2957, 1792, 1647, 1492, 1083 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{19}H_{31}O_3SSi$ (M − H)$^+$ 367.1763, found 367.1761.

*(Z)-Triethoxy(1-(4-methoxyphenylthio)hex-1-enyl)silane (**3o**).* Compound **3o** was prepared as a pale yellow oil from **1o** (0.40 mmol, 88.1 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 71% yield (108.6 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.0 Hz, 2 H), 6.79 (d, J = 8.0 Hz, 2 H), 6.70 (t, J = 6.8 Hz, 1 H), 3.76 (s, 3 H), 3.69 (q, J = 6.8 Hz, 6 H), 2.43 (q, J = 7.2 Hz, 2 H), 1.44−1.30 (m, 4 H), 1.14 (t, J = 6.8 Hz, 9 H), 0.89 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 154.2, 132.0, 127.0, 126.9, 114.0, 58.6, 55.2, 30.8, 30.2, 22.4, 18.0, 13.9; IR (thin film) 2958, 1724, 1593, 1494, 1246 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{19}H_{31}O_4SSi$ (M − H)$^+$ 383.1713, found 383.1713.

*(Z)-(1-(4-Chlorophenylthio)hex-1-enyl)triethoxysilane (**3p**).* Compound **3p** was prepared as a pale yellow oil from **1p** (0.40 mmol, 89.9 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 73% yield (112.9 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−1.15 (m, 4 H), 6.88 (t, J = 6.8 Hz, 1 H), 3.73 (q, J = 6.8 Hz, 6 H), 2.40 (q, J = 7.2 Hz, 2 H), 1.45−1.26 (m, 4 H), 1.13 (t, J = 6.8 Hz, 9 H), 0.88 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.6, 135.7, 131.1, 129.7, 128.4, 124.8, 58.8, 30.7, 30.3, 22.4, 18.0, 13.8; IR (thin film) 2958, 1715, 1574, 1475, 1390 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{18}H_{28}ClO_3SSi$ (M − H)$^+$ 387.1217, found 387.1221.

*(Z)-Triethoxy(1-(4-nitrophenylthio)hex-1-enyl)silane (**3q**).* Compound **3q** was prepared as a pale yellow oil from **1q** (0.40 mmol, 94.1 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 80% yield (127.4 mg, α/β = 25:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.03 (m, 2 H), 7.31−7.27 (m, 2 H), 7.07 (t, J = 6.8 Hz, 1 H), 3.76 (q, J = 6.8 Hz, 6 H), 2.38 (q, J = 7.2 Hz, 2 H), 1.44−1.26 (m, 4 H), 1.13 (t, J = 6.8 Hz, 9 H), 0.86 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 148.0, 144.8, 126.5, 123.5, 122.6, 59.0, 30.53, 30.46, 22.3, 18.0, 13.8; IR (thin film) 2958, 1645, 1578, 1510, 1337 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{18}H_{29}NO_5SSi$ (M)$^+$ 399.1536, found 399.1541.

*(Z)-Triethoxy(1-(furan-3-ylmethylthio)hex-1-enyl)silane (**3r**).* Compound **3r** was prepared as a pale yellow oil from **1r** (0.40 mmol, 77.7 mg) and the silane **2a** (0.80 mmol, 132.0 mg) according to the General Procedure in 66% yield (94.2 mg, α/β = 25:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 0.8 Hz, 1 H), 6.53 (t, J = 6.8 Hz, 1 H), 6.30−6.27 (m, 1 H), 6.16−6.14 (m, 1 H), 4.07 (s, 2 H), 3.90 (q, J = 6.8 Hz, 6 H), 2.25 (q, J = 7.2 Hz, 2 H), 1.34−1.25 (m, 13 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.9, 152.1, 141.7, 125.8, 110.3, 107.3, 58.9, 30.8, 30.0, 29.9, 22.4, 18.1, 13.9; IR (thin film) 2973, 1736, 1590, 1503, 1391 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{17}H_{29}O_4SSi$ (M − H)$^+$ 357.1556, found 357.1560.

*(Z)-Trimethoxy(1-(phenylthio)hex-1-enyl)silane (**4a**).* Compound **4a** was prepared as a pale yellow oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2b** (0.80 mmol, 97.8 mg) according to the General Procedure in 84% yield (94.1 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.24 (m, 4 H), 7.18−7.15 (m, 1 H), 6.88 (t, J = 6.8 Hz, 1 H), 3.47 (s, 9 H), 2.47 (q, J = 7.2 Hz, 2 H), 1.48−1.32 (m, 4 H), 0.92 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.7, 136.6, 128.8, 128.5, 125.6, 124.0, 50.8, 30.7, 30.3, 22.4, 13.9; IR (thin film) 2957, 1645, 1477, 1297, 1080 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{15}H_{24}OSSi$ (M)$^+$ 280.1317, found 280.1316.

*(Z)-Diethoxy(methyl)(1-(phenylthio)hex-1-enyl)silane (**4b**).* Compound **4b** was prepared as a pale yellow oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2c** (0.80 mmol, 107.4 mg) according to the General Procedure in 40% yield (52.4 mg, α/β = 12:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.20 (m, 4 H), 7.17−7.11 (m, 1 H), 6.87 (t, J = 6.8 Hz, 1 H), 3.74 (q, J = 7.2 Hz, 4 H), 2.46 (q, J = 7.2 Hz, 2 H), 1.48−1.30 (m, 4 H), 1.18 (t, J = 7.2 Hz, 6 H), 0.92 (t, J = 7.2 Hz, 3 H), 0.04 (s, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 155.9, 137.2, 128.51, 128.45, 128.3, 125.3, 58.5, 30.8, 30.4, 22.4, 18.2, 13.9, −4.7; IR (thin film) 2966, 1645, 1585, 1478, 1257 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{17}H_{27}O_2SSi$ (M − H)$^+$ 323.1501, found 323.1511.

*(Z)-Methoxydimethyl(1-(phenylthio)hex-1-enyl)silane (**4c′**).* Compound **4c′** was prepared as a pale yellow oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2d** (0.80 mmol, 75.7 mg) according to the General Procedure (after workup with Et_3N and MeOH) in 72% yield (81.2 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.21 (m, 4 H), 7.16−7.12 (m, 1 H), 6.75 (t, J = 6.8 Hz, 1 H), 3.42 (s, 3 H), 2.47 (q, J = 7.2 Hz, 2 H), 1.48−1.32 (m, 4 H), 0.92 (t, J = 7.2 Hz, 3 H), 0.12 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.7, 137.3, 131.0, 128.6, 128.2, 125.3, 50.6, 30.9, 30.5, 22.4, 13.9, −2.4; IR (thin film) 2959, 1648, 1585, 1477, 1252 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{15}H_{23}OSSi$ (M − H)$^+$ 279.1239, found 279.1248.

*(Z)-1,1,1,3,5,5,5-Heptamethyl-3-(1-(phenylthio)hex-1-en-1-yl)-trisiloxane (**4d**).* Compound **4d** was prepared as a pale yellow oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2e** (0.80 mmol, 178.0 mg) according to the General Procedure in 67% yield (110.4 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.19 (m, 4

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164

H), 7.13−7.08 (m, 1 H), 6.80 (t, J = 6.8 Hz, 1 H), 2.42 (q, J = 7.2 Hz, 2 H), 1.47−1.30 (m, 4 H), 0.92 (t, J = 7.2 Hz, 3 H), 0.09 (s, 18 H), 0.03 (s, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 154.9, 138.1, 130.7, 128.5, 127.4, 124.7, 30.8, 30.3, 22.4, 13.9, 1.7, −0.5; IR (thin film) 2958, 1586, 1478, 1254, 1068 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{19}H_{35}O_2SSi_3$ $(M - H)^+$ 411.1666, found 411.1668.

*(Z)-1,1,1,5,5,5-Hexamethyl-3-(1-(phenylthio)hex-1-en-1-yl)-3-((trimethylsilyl)oxy)trisiloxane (**4e**).* Compound **4e** was prepared as a pale yellow oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2f** (0.80 mmol, 237.1 mg) according to the General Procedure in 69% yield (134.2 mg, α/β > 30:1, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.16 (m, 4 H), 7.11−7.05 (m, 1 H), 6.85 (t, J = 6.8 Hz, 1 H), 2.41 (q, J = 7.2 Hz, 2 H), 1.45−1.28 (m, 4 H), 0.90 (t, J = 7.2 Hz, 3 H), 0.07 (s, 27 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.7, 138.4, 128.4, 127.2, 126.9, 124.3, 30.8, 30.2, 22.4, 13.9, 1.6; IR (thin film) 2959, 1587, 1477, 1255, 1067 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{21}H_{42}O_3SSi_4$ $(M)^+$ 486.1932, found 486.1918.

*(Z)-Dimethyl(phenyl)(1-(phenylsulfonyl)hex-1-en-1-yl)silane (**4f′**).* Compound **4f′** was prepared as a colorless oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2g** (0.80 mmol, 297.4 mg) in 53% yield (75.9 mg, α/β = 12:1, Z/E > 30:1) according to the General Procedure, except that the reaction mixture was treated with m-CPBA (3.0 equiv) and stirred at room temperature for 3 h before workup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.50 (m, 5 H), 7.45−7.37 (m, 5 H), 6.42 (t, J = 6.8 Hz, 1 H), 2.43 (q, J = 7.2 Hz, 2 H), 1.18−1.13 (m, 4 H), 0.79 (t, J = 6.4 Hz, 3 H), 0.65 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.2, 145.7, 143.2, 136.2, 134.5, 132.5, 129.6, 128.7, 127.9, 127.1, 30.6, 30.3, 22.3, 13.7, −1.9; IR (thin film) 2959, 1589, 1447, 1296, 1142 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{20}H_{26}O_2SSi$ $(M)^+$ 358.1423, found 358.1432.

*(Z)-Benzyldimethyl(1-(phenylsulfonyl)hex-1-enyl)silane (**4g′**).* Compound **4g′** was prepared as a colorless oil from **1h** (0.40 mmol, 76.1 mg) and the silane **2h** (0.80 mmol, 120.2 mg) in 78% yield (116.1 mg, α/β = 25:1, Z/E > 30:1) according to the General Procedure, except that the reaction mixture was treated with m-CPBA (3.0 equiv) and stirred at room temperature for 3 h before workup: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.89 (m, 2 H), 7.61−7.51 (m, 3 H), 7.28−7.21 (m, 2 H), 7.14−7.08 (m, 3 H), 6.43 (t, J = 7.2 Hz, 1 H), 2.50 (s, 2 H), 2.46−2.40 (m, 2 H),1.20−1.15 (m, 4 H), 0.81 (t, J = 7.2 Hz, 3 H), 0.26 (s, 6 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.7, 144.8, 143.5, 138.9, 132.7, 128.9, 128.6, 128.1, 126.9, 124.3, 30.6, 30.3, 25.6, 22.2, 13.7, −2.6; IR (thin film) 2958, 1770, 1594, 1448, 1295 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{21}H_{28}O_2SSiNa$ $(M + Na)^+$ 395.1477, found 395.1462.

*(Z)-2-(4-(Butylthio)but-3-enyloxy)tetrahydro-2H-pyran (**5**).* Under N_2, to an oven-dried 5 mL vial were added **3c** (81.3 mg, 0.20 mmol), AgF (38.0 mg, 0.30 mmol), and MeOH (2.0 mL). The mixture was stirred at room temperature for 10 h and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 2% Et_2O in hexanes) to give the desired product **5** as a colorless oil (45.4 mg, 93%, Z/E > 20:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (d, J = 8.8 Hz, 1 H), 5.62 (dt, J = 7.2 and 8.8 Hz, 1 H), 4.64−4.61 (m, 1 H), 3.89−3.75 (m, 2 H), 3.54−3.45 (m, 2 H), 2.68 (t, J = 7.2 Hz, 2 H), 2.48−2.42 (m, 2 H), 1.89−1.39 (m, 10 H), 0.93 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 127.0, 125.4, 98.5, 66.2, 62.2, 33.6, 32.4, 30.7, 29.7, 25.5, 21.7, 19.5, 13.6; IR (thin film) 2953, 1609, 1465, 1352, 1033 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{13}H_{23}O_2S$ $(M - H)^+$ 243.1419, found 243.1423.

*(Z)-2-(4-(Butylthio)-4-p-tolylbut-3-enyloxy)tetrahydro-2H-pyran (**6**).* Under N_2, to an oven-dried 5 mL vial were added **3c** (81.3 mg, 0.20 mmol), 1-iodo-4-methylbenzene (87.2 mg, 0.40 mmol), $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol), AgF (50.7 mg, 0.40 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), and THF (2.0 mL). The reaction mixture was stirred at room temperature for 10 h and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 2% Et_2O in hexanes) to give the desired product **6** as a colorless oil (44.6 mg, 67%, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 8.0 Hz, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 6.01 (t, J = 7.2 Hz, 1 H), 4.68−4.65 (m, 1 H), 3.91−3.81 (m, 2 H), 3.57−3.50 (m, 2 H), 2.82−2.76 (m, 2 H), 2.40−2.35 (m, 5 H), 1.90−1.51 (m, 6 H), 1.42−1.26 (m, 4 H), 0.82 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 137.7, 137.5, 137.2, 130.9, 128.9, 127.8, 98.5, 66.6, 62.1, 31.8, 31.7, 31.1, 30.7, 25.5, 21.5, 21.1, 19.4, 13.6; IR (thin film) 2955, 1506, 1455, 1351, 1033 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{20}H_{29}O_2S$ $(M - H)^+$ 333.1889, found 333.1890.

*(Z)-Triethoxy(1-(phenylsulfonyl)hex-1-enyl)silane (**7**).* Under N_2, to an oven-dried 5 mL vial were added 1-(phenylsulphenyl)hexyne (38.1 mg, 0.20 mmol), triethoxysilane (74 μL, 0.40 mmol), $[Ir(COD)Cl]_2$ (2.7 mg, 4.0 μmol), and DCM (2.0 mL). The vial was capped and removed from the glovebox. The reaction mixture was stirred at room temperature for 13 h, and then m-CPBA (103.6 mg, 0.60 mmol) was added in one portion. The reaction mixture was stirred for 3 h under air and then concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: 5% Et_2O in hexanes) to give the desired product **7** as a colorless oil (53.0 mg, 69%, Z/E > 30:1): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.00 (m, 2 H), 7.60−7.54 (m, 1 H), 7.53−7.47 (m, 2 H), 6.94 (t, J = 7.6 Hz, 1 H), 3.95 (q, J = 7.2 Hz, 6 H), 2.55−2.48 (m, 2 H), 1.27 (t, J = 7.2 Hz, 9 H), 1.25−1.19 (m, 4 H), 0.81 (t, J = 7.2 Hz, 3 H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.7, 143.1, 139.5, 132.6, 128.6, 127.4, 59.4, 30.2 (2 C), 22.3, 18.0, 13.7; IR (thin film) 2975, 1595, 1447, 1304, 1149 cm^{-1}; HRMS m/z (CI, TOF) calcd for $C_{18}H_{29}O_5SSi$ $(M - H)^+$ 385.1505, found 385.1505.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00854.

Experimental and computational details; computational and characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

* E-mail: zhangxh@pkusz.edu.cn.
* E-mail: wuyd@pkusz.edu.cn.
* E-mail: sunjw@ust.hk.

Author Contributions

‖L.-J.S. and S.D. contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support was provided by the National Natural Science Foundation of China (21133002, 21232001, 21302006, 21490570, 21490572), Hong Kong RGC (604513, 16304714), the Shenzhen STIC (KQTD201103, JCYJ20140509093817689), and Nanshan (KC2014ZDZJ0026A). We thank Prof. Lung Wa Chung for his insightful discussion. We thank Dr. Taokai Zheng for the cover design.

■ REFERENCES

(1) (a) Ojima, I.; Li, Z.; Zhu, J. In *The Chemistry of Organosilicon Compounds*; Rappoport, S., Apeloig, Y., Eds.; Wiley: New York, 1998. (b) Langkopf, E.; Schinzer, D. *Chem. Rev.* **1995**, *95*, 1375−1408. (c) Marciniec, B.; Pietraszuk, C. *Top. Organomet. Chem.* **2004**, *11*, 197−248. (d) Corey, J. Y. *Chem. Rev.* **2011**, *111*, 863−1071.

(2) For reviews on iridium-catalyzed silylation reactions, see: (a) Marciniec, B.; Kownacki, I. *Iridium Complexes in Organic Synthesis*; Wiley−VCH, 2009; p 345. (b) Malacea, R.; Poli, R.; Manoury, E. *Coord. Chem. Rev.* **2010**, *254*, 729−752.

(3) Reviews and highlights on alkyne hydrosilylations: (a) Brunner, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2749−2750. (b) Trost, B. M.; Ball, Z. T. *Synthesis* **2005**, *2005*, 853−887. (c) Marciniec, B.; Maciejewski,

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164

H.; Pietraszuk, C.; Pawluc, P. In *Hydrosilylation: A Comprehensive Review on Recent Advances*; Marciniec, B., Ed.; Springer: Berlin, 2009; Vol. *1*, Chapters 2 and 3. (d) Lim, D. S. W.; Anderson, E. A. *Synthesis* **2012**, *44*, 983−1010. (e) Zhou, H.; Moberg, C. *Org. Lett.* **2013**, *15*, 1444−1447.

(4) Selected reviews and recent examples of Ir-catalyzed silylation of olefins, arenes, and alkanes: (a) Hesp, K. D.; Wechsler, D.; Cipot, J.; Myers, A.; McDonald, R.; Ferguson, M. J.; Schatte, G.; Stradiotto, M. *Organometallics* **2007**, *26*, 5430−5437. (b) Lu, B.; Falck, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 7508−7510. (c) McBee, J. L.; Escalada, J.; Tilley, T. D. *J. Am. Chem. Soc.* **2009**, *131*, 12703−12713. (d) Simmons, E. M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 17092−17096. (e) Simmons, E. M.; Hartwig, J. F. *Nature* **2012**, *483*, 70−73. (f) Cheng, C.; Hartwig, J. F. *Chem. Rev.* **2015**, *115*, 8946−8975. (g) Wakaki, T.; Kanai, M.; Kuninobu, Y. *Org. Lett.* **2015**, *17*, 1758−1761.

(5) Selected recent examples of Ir-catalyzed carbonyl, imine, and epoxide silylation as well as the related cascade reactions: (a) Frölander, A.; Moberg, C. *Org. Lett.* **2007**, *9*, 1371−1374. (b) Voutchkova, A. M.; Gnanamgari, D.; Jakobsche, C. E.; Butler, C.; Miller, S. J.; Parr, J.; Crabtree, R. H. *J. Organomet. Chem.* **2008**, *693*, 1815−1821. (c) Li, B.-J.; Shi, Z.-J. *Chem. Sci.* **2011**, *2*, 488−493. (d) Park, S.; Brookhart, M. *Chem. Commun.* **2011**, *47*, 3643−3645. (e) Iali, W.; La Paglia, F.; Le Goff, X. F.; Sredojevic, D.; Pfeffer, M.; Djukic, J.-P. *Chem. Commun.* **2012**, *48*, 10310−10312. (f) Cheng, C.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 11304−11307. (g) Shinohara, K.; Kawabata, S.; Nakamura, H.; Manabe, Y.; Sakaguchi, S. *Eur. J. Org. Chem.* **2014**, *2014*, 5532−5539. (h) Hua, Y.; Asgari, P. U.; Dakarapu, S.; Jeon, J. *Chem. Commun.* **2015**, *51*, 3778−3781.

(6) Selected examples involving CO and CO_2: (a) Kownacki, I.; Marciniec, B.; Szubert, K.; Kubicki, M. *Organometallics* **2005**, *24*, 6179−6183. (b) Chatani, N.; Ikeda, S.; Ohe, K.; Murai, S. *J. Am. Chem. Soc.* **1992**, *114*, 9710−9711. (c) Park, S.; Bézier, D.; Brookhart, M. *J. Am. Chem. Soc.* **2012**, *134*, 11404−11407. (d) Lalrempuia, R.; Iglesias, M.; Polo, V.; Sanz Miguel, P. J.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. *Angew. Chem., Int. Ed.* **2012**, *51*, 12824−12827.

(7) Selected examples of silylation of alcohols, water, and ethers: (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527−2535. (b) Lee, Y.; Seomoon, D.; Kim, S.; Han, H.; Chang, S.; Lee, P. H. *J. Org. Chem.* **2004**, *69*, 1741−1743. (c) Chung, M. K.; Schlaf, M. *J. Am. Chem. Soc.* **2005**, *127*, 18085−18092. (d) McLaughlin, M. P.; Adduci, L. L.; Becker, J. J.; Gagné, M. R. *J. Am. Chem. Soc.* **2013**, *135*, 1225−1227. (e) Aliaga-Lavrijsen, M.; Iglesias, M.; Cebollada, A.; Garcés, K.; García, N.; Sanz Miguel, P. J.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Organometallics* **2015**, *34*, 2378−2385.

(8) Selected examples of Ir-catalyzed alkyne hydrosilylations (all terminal alkynes): (a) Apple, D. C.; Brady, K. A.; Chance, J. M.; Heard, N. E.; Nile, T. A. *J. Mol. Catal.* **1985**, *29*, 55−64. (b) Fernandez, M. J.; Oro, L. A.; Manzano, B. R. *J. Mol. Catal.* **1988**, *45*, 7−15. (c) Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984−7989. (d) Miyake, Y.; Isomura, E.; Iyoda, M. *Chem. Lett.* **2006**, *35*, 836−837. (e) Zanardi, A.; Peris, E.; Mata, J. A. *New J. Chem.* **2008**, *32*, 120−126. (f) Iglesias, M.; Pérez-Nicolás, M.; Miguel, P. J. S.; Polo, V.; Fernández-Alvarez, F. J.; Pérez-Torrente, J. J.; Oro, L. A. *Chem. Commun.* **2012**, *48*, 9480−9482. See also refs 2 and 3 for more examples.

(9) (a) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2004**, *126*, 13942−13944. (b) Hamze, A.; Provot, O.; Alami, M.; Brion, J.-D. *Org. Lett.* **2005**, *7*, 5625−5628. (c) Rooke, D. A.; Ferreira, E. M. *J. Am. Chem. Soc.* **2010**, *132*, 11926−11928. (d) Rooke, D. A.; Ferreira, E. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 3225−3230. (e) Sumida, Y.; Kato, T.; Yoshida, S.; Hosoya, T. *Org. Lett.* **2012**, *14*, 1552−1555. (f) Huang, K.-H.; Isobe, M. *Eur. J. Org. Chem.* **2014**, *2014*, 4733−4740 and references cited therein. (g) Rooke, D. A.; Menard, Z. A.; Ferreira, E. M. *Tetrahedron* **2014**, *70*, 4232−4244.

(10) (a) Stork, G.; Jung, M. E.; Colvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684−3686. (b) Kahle, K.; Murphy, P. J.; Scott, J.; Tamagni, R. *J. Chem. Soc., Perkin Trans. 1* **1997**, 997−999. (c) Humilière, D.; Thorimbert, S.; Malacria, M. *Synlett* **1998**, *1998*, 1255−1257. (d) Trost, B. M.; Ball, Z. T.; Jöge, T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3415−3418. (e) Kawasaki, Y.; Ishikawa, Y.; Igawa, K.; Tomooka, K. *J. Am. Chem. Soc.* **2011**, *133*, 20712−20715. (f) McLaughlin, M. G.; Cook, M. J. *Chem. Commun.* **2011**, *47*, 11104−11106.

(11) (a) Marshall, J. A.; Yanik, M. M. *Org. Lett.* **2000**, *2*, 2173−2175. (b) Sudo, T.; Asao, N.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 8919−8923. (c) Denmark, S. E.; Pan, W. *Org. Lett.* **2001**, *3*, 61−64. (d) Denmark, S. E.; Pan, W. *Org. Lett.* **2002**, *4*, 4163−4166. (e) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 30−32. (f) Denmark, S. E.; Pan, W. *Org. Lett.* **2003**, *5*, 1119−1122.

(12) Selected examples of selective hydrosilylation of Ru-catalyzed internal alkynes: (a) Na, Y.; Chang, S. *Org. Lett.* **2000**, *2*, 1887−1889. (b) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2001**, *123*, 12726−12727. (c) Trost, B. M.; Ball, Z. T.; Jõge, T. *J. Am. Chem. Soc.* **2002**, *124*, 7922−7923. (d) Chung, L. W.; Wu, Y.-D.; Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2003**, *125*, 11578−11582. (e) Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17644−17655. (f) Rummelt, S. M.; Radkowski, K.; Rosca, D.-A.; Furstner, A. *J. Am. Chem. Soc.* **2015**, *137*, 5506−5519.

(13) Representative examples of Ti-, Ni-, Fe-, and Co-catalyzed selective hydrosilylation of internal alkynes: (a) Takahashi, T.; Bao, F.; Gao, G.; Ogasawara, M. *Org. Lett.* **2003**, *5*, 3479−3481. (b) Chaulagain, M. R.; Mahandru, G. M.; Montgomery, J. *Tetrahedron* **2006**, *62*, 7560. (c) Belger, C.; Plietker, B. *Chem. Commun.* **2012**, *48*, 5419−5421. (d) Yong, L.; Kirleis, K.; Butenschön, H. *Adv. Synth. Catal.* **2006**, *348*, 833−836. (e) Sun, J.; Deng, L. *ACS Catal.* **2016**, *6*, 290−300.

(14) We are aware of only one single example of Ir-catalyzed hydrosilylation of unsymmetrical internal alkynes, which employed a relatively high temperature and gave low selectivity and efficiency Field, L. D.; Ward, A. J. *J. Organomet. Chem.* **2003**, *681*, 91−97.

(15) (a) Zhao, W.; Wang, Z.; Sun, J. *Angew. Chem., Int. Ed.* **2012**, *51*, 6209−6213. (b) Zhao, W.; Li, Z.; Sun, J. *J. Am. Chem. Soc.* **2013**, *135*, 4680−4683. (c) Ding, S.; Jia, G.; Sun, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 1877−1880. (d) Zhao, W.; Qian, H.; Li, Z.; Sun, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 10005−10008.

(16) (a) Ding, S.; Song, L.-J.; Chung, L. W.; Zhang, X.; Sun, J.; Wu, Y.-D. *J. Am. Chem. Soc.* **2013**, *135*, 13835−13842. (b) Our recent Ru-catalyzed hydrosilylation of thioalkynes works well only with the bulky and expensive silane $(TMSO)_3SiH$, which invokes atom-economy issue for application: Ding, S.; Song, L.-J.; Wang, Y.; Zhang, X.; Chung, L. W.; Wu, Y.-D.; Sun, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 5632−5635.

(17) (a) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley−VCH: Weinheim, 1998; p 421. (b) Denmark, S. E.; Sweis, R. F. In *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; de Meijere, A., Diederich, F., Eds.; Wiley−VCH: Weinheim, 2004; p 163. (c) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893−4901.

(18) Pt and Co complexes have also been known to catalyze hydrosilylation of thioalkynes, but only two silanes (Et_3SiH and $PhMe_2SiH$) were demonstrated and relatively high temperature (>60 °C) was typically required: (a) Herunsalee, A.; Isobe, M.; Fukuda, Y.; Goto, T. *Synlett* **1990**, *1990*, 701−703. (b) Adachi, M.; Yamauchi, E.; Komada, T.; Isobe, M. *Synlett* **2009**, *2009*, 1157−1161. (c) Isobe, M.; Niyomchon, S.; Cheng, C.-Y.; Hasakunpaisarn, A. *Tetrahedron Lett.* **2011**, *52*, 1847−1850. (d) Huang, K.-H.; Isobe, M. *Eur. J. Org. Chem.* **2014**, *2014*, 4733−4740 and references cited therein.

(19) Regio- and stereoselective hydrothiolations of alkynes remain challenging. For some reviews, see: (a) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596−1636. (b) Castarlenas, R.; Di Giuseppe, A.; Perez-Torrente, J. J.; Oro, L. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 211−222.

(20) Some recent DFT studies on reaction mechanism of hydrosilylation: (a) Wu, Y.; Karttunen, V. A.; Parker, S.; Genest, A.; Rösch, N. *Organometallics* **2013**, *32*, 2363−2372. (b) Gu, P.; Wang, Q.; Wang, Y.; Wei, H. *Organometallics* **2013**, *32*, 47−51. (c) Zhang, X.-H.; Chung, L. W.; Lin, Z.; Wu, Y.-D. *J. Org. Chem.* **2008**, *73*, 820−829. (d) Sridevi, V. S.; Fan, W. Y.; Leong, W. K. *Organometallics* **2007**, *26*, 1157−1160. (e) Chung, L. W.; Lee, H. G.; Lin, Z.; Wu, Y.-D. *J. Org.*

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164

Chem. **2006**, *71*, 6000−6009. (f) Tuttle, T.; Wang, D.; Thiel, W.; Köhler, J.; Hofmann, M.; Weis, J. *Organometallics* **2006**, *25*, 4504−4513. (g) Beddie, C.; Hall, M. B. *J. Am. Chem. Soc.* **2004**, *126*, 13564−13565.

(21) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16−21. (b) Ananikov, V. P.; Beletskaya, I. P. In *Hydrofunctionalization*; Ananikov, P. V., Tanaka, M., Eds.; Springer: Berlin, 2013; Vol *43*, pp 1−20.

(22) See the SI for more calculation details.

(23) It is worth noting that the formation of the corresponding chlorosilane was observed by GC/MS in our experiments. For previous examples on reductive elimination of R_3SiCl by others, see: (a) Roy, A. K.; Taylor, R. B. *J. Am. Chem. Soc.* **2002**, *124*, 9510−9524. (b) Karshtedt, D.; Bell, A. T.; Tilley, T. D. *Organometallics* **2006**, *25*, 4471−4482.

(24) For selected reports on Ir(III) hydride, see: (a) Albertin, G.; Antoniutti, S.; Castro, J.; Garcia-Fontán, S.; Gurabardhi, E. *J. Organomet. Chem.* **2006**, *691*, 1012−1024. (b) Klei, S. R.; Golden, J. T.; Burger, P.; Bergman, R. G. *J. Mol. Catal. A: Chem.* **2002**, *189*, 79−94. (c) Li, X.; Vogel, T.; Incarvito, C. D.; Crabtree, R. H. *Organometallics* **2005**, *24*, 62−76. (d) Sperger, T.; Sanhueza, I. A.; Kalvet, I.; Schoenebeck, F. *Chem. Rev.* **2015**, *115*, 9532−9586. (e) Polo, V.; Al-Saadi, A. A.; Oro, L. A. *Organometallics* **2014**, *33*, 5156−5163. (f) Li, S.; Zhu, S.-F.; Xie, J.-H.; Song, S.; Zhang, C.-M.; Zhou, Q.-L. *J. Am. Chem. Soc.* **2010**, *132*, 1172−1179. (g) Roseblade, S. J.; Pfaltz, A. *C. R. Chim.* **2007**, *10*, 178−187. (h) Verendel, J. J.; Pàmies, O.; Dièguez, M.; Andersson, P. G. *Chem. Rev.* **2014**, *114*, 2130−2169.

(25) For examples of (cod)Ir(I) hydride complexes, see: (a) Millard, M. D.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 8921−8923. (b) Handgraaf, J.-W.; Reek, J. N. H.; Meijer, E. J. *Organometallics* **2003**, *22*, 3150−3157. (c) Hesp, K. D.; Tobisch, S.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132*, 413−426. (d) Jiménez, M. V.; Fernández-Tornos, J.; Pérez-Torrente, J. J.; Modrego, F. J.; Winterle, S.; Cunchillos, C.; Lahoz, F. J.; Oro, L. A. *Organometallics* **2011**, *30*, 5493−5508.

(26) Millard, M. D.; Moore, C. E.; Rheingold, A. L.; Figueroa, J. S. *J. Am. Chem. Soc.* **2010**, *132*, 8921−8923.

(27) (a) Isomerization to an anti intermediate was considered. However, optimization of the 3-membered metallacycle converged to **B3a** or **B3b**. (b) Side reactions to yield vinyl sulfide via hydride migration (**B-TS4a′** and **B-TS4b′**) are also found to be unfavorable due to steric effects; see Figure S3.

DOI: 10.1021/acs.joc.6b00854
J. Org. Chem. 2016, 81, 6157−6164