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[1,2]- and [1,4]-Wittig rearrangements of α-alkoxysilanes: effect of substitutions at both the migrating benzylic carbon and the terminal sp^2 carbon of the allyl moiety

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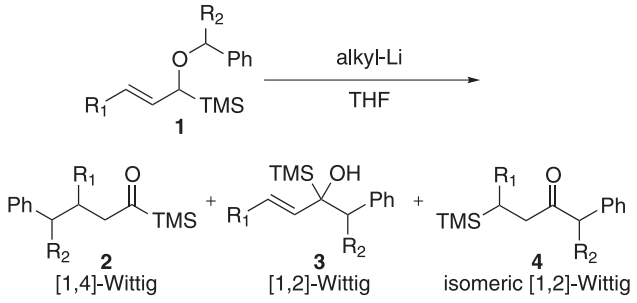
ABSTRACT

Substituted α-alkoxysilanes can be deprotonated by alkyllithium bases and made to undergo Wittig rearrangements to afford the [1,4]- and [1,2]-rearranged products in varying ratios. Substitution at the benzylic migrating carbon and/or at the allylic carbon of the allyl moiety impacts the rearrangement reaction, influencing the reactivity as well as the [1,4]-/[1,2]-selectivity. Diastereomeric α-alkoxysilanes show different reactivities with the *syn* diastereomer being the more reactive isomer.

1. Introduction

The isomerizations of ethers under basic conditions to the corresponding alcohols are known as Wittig rearrangements and can proceed via two main pathways: a stepwise [1,2]-migration involving a radical/radical-anion species[1] or via a concerted symmetry-allowed [2,3]-shift.[2] In addition, during the reorganization of allylic ethers [1,4]-Wittig rearrangements can compete with the [1,2]-migration and give rise to carbonyl compounds.[3] Despite its potential to construct adjacent stereocenters, transfer chirality, or obtain stereodefined enolates that could be used in subsequent transformations, very few examples where [1,4]-Wittig rearrangements predominate over [1,2]-pathways exist in the literature.[4] Furthermore, although some experiments support a stepwise [1,4]-Wittig process, the involvement of a concerted mechanism has not been discarded.[5]

In an earlier communication,[6a] we showed that unsubstituted α-alkoxysilane **1** (R_1=R_2=H) rearranged exclusively via the [1,4]-pathway at low temperatures to give acylsilane **2** in 80% yield (Scheme 1). We observed that the [1,2]-pathway became competitive with increasing temperature, leading to a gradual erosion in [1,4]-selectivity and producing mixtures of **2** and the isomeric [1,2]-Wittig product **4**, with the [1,4]-/[1,2]-ratio reaching 2:1 at room temperature.[6,7] Following this report, we questioned whether a high [1,4]-/[1,2]-selectivity could be retained if we made structural changes in our model substrate **1** (e.g., where R_1 and/or $R_2 \neq H$).



Ref 6a: R_1 = R_2 = H; conditions: *sec*-BuLi (1.5 equiv), THF, –78 °C, 30 min; yield of **2**: 80%, **3** and **4** not observed

Scheme 1. [1,4]-/[1,2]-Wittig rearrangements of α-alkoxysilanes.

Nakai and co-workers previously showed that the scope and limitations of the [1,2]-Wittig rearrangement are determined principally by the migratory aptitude of the alkyl group

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(primary<secondary<tertiary=allyl<benzyl) thus following increasing radical stability.[1] In cases of limited radical stability of the migrating group, carbanion-stabilizing groups similarly facilitate [1,2]-migrations.[1] In contrast, the yield of [1,4]-Wittig products has been reported to be relatively insensitive to substitution at the α- or γ-position of the allylic moiety,[3] although Schlosser observed that [1,4]-/[1,2]-selectivity is diminished with increasing alkyl substitution about the migrating carbon.[8] In the context of these previous findings, we set out to systematically investigate the introduction of alkyl substitution at the benzylic carbon and/or terminal allylic carbon of α-alkoxysilanes so as to gain insight into the steric and stereochemical factors that might control the course of Wittig rearrangements of α-alkoxysilanes.[9]

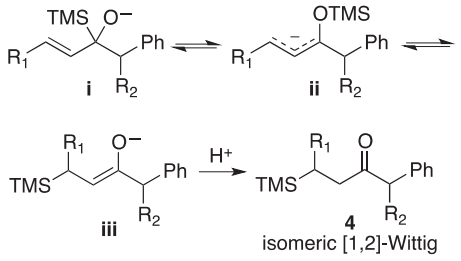
2. Results and discussion

We initially studied the effect of alkyl substituents at the terminal sp^2 carbon of the allyl moiety (R_1=alkyl, R_2=H in **1**, Scheme 1). Compounds **5**, **8**, and **11**, possessing a methyl, *n*-hexyl, and *t*-butyl at the terminal olefin carbon, respectively, were prepared from the corresponding α-(trimethylsilyl)-γ-alkyl allyl alcohols by acid-catalyzed O-alkylation with benzyl trichloroacetimidate.[10]

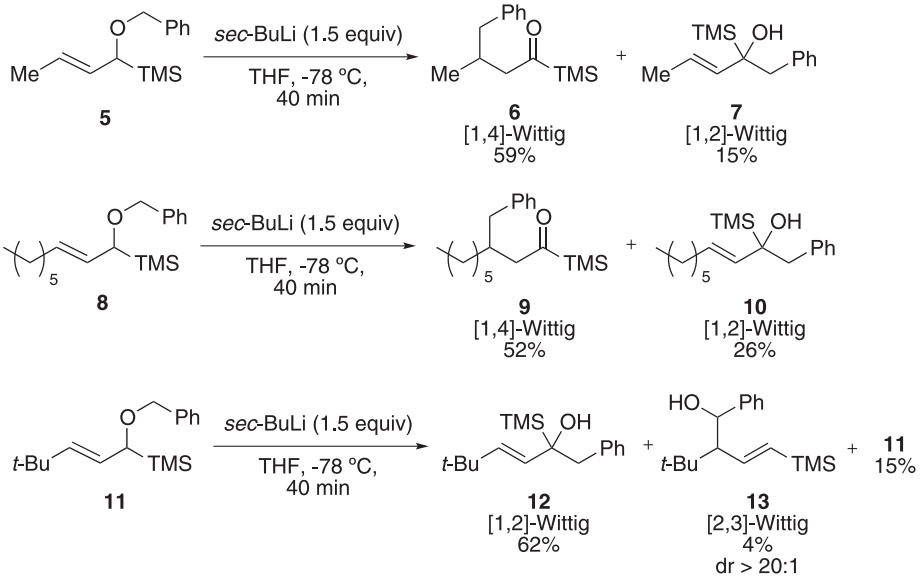
Subjection of methyl-substituted compound **5** to our previously developed conditions (*sec*-BuLi, THF, −78 °C)[6] afforded 74% overall yield of a 4:1 ratio of acylsilane **6** and alcohol **7** resulting from [1,4]- and [1,2]-Wittig rearrangements, respectively (Scheme 2). The effect on the rate of deprotonation/rearrangement was negligible, consistent with the fact that the site of deprotonation is at a relatively remote position with respect to the alkyl substituent. The observed erosion of the [1,4]-/[1,2]-selectivity with substitution at the terminal allylic position is in apparent contrast with literature reports.[3] A longer alkyl chain at the γ-position in compound **8** led to a lower ratio (2:1) of [1,4]-/[1,2]-Wittig products **9** and **10** in 78% overall yield. This trend reached a maximum point in the case of compound **11** in which the bulky *t*-butyl group completely inhibited the [1,4]-Wittig shift (Scheme 2). Allylic deprotonation of **11** preceeded [1,2]-Wittig rearrangement to give alcohol **12**, in addition, benzylic deprotonation was competitive and allowed a [2,3]-sigmatropic shift to afford alcohol **13** as a single diastereomer. Thus, bulkier alkyl groups at the γ-carbon appear to lower the reactivity toward deprotonation at the allylic position, allowing competitive benzylic deprotonation. In fact, **11** underwent incomplete conversion in the same period of time that compounds **5** and **8** were completely consumed. In addition, increasing steric hindrance increases the selectivity in favor of the [1,2]-Wittig product. This could be interpreted as an increasingly prohibitive [1,4]-recombination of the radical and radical-anion fragments, but also as the difficulty of the α-(benzyloxy)allyllithium species to adopt an optimum conformation for a concerted [1,4]-shift. Although the inverse relationship between steric demand of the γ-alkyl group and the [1,4]-/[1,2]-selectivity is consistent with both stepwise and concerted mechanisms for the [1,4]-migration, at this point it is difficult to predict which mechanism would be more susceptible to such steric effects.

Based on our earlier observations 6,7 in which only the isomeric [1,2]-product was isolated (**4** instead of **3**, Scheme 1) we were surprised to find that the rearrangement of **5**, **8** and **11** gave the direct [1,2]-Wittig producs (alcohols **7**, **10** and **12** Scheme 2) and none of the corresponding isomeric [1,2]-products. The isomerization of the [1,2]-Wittig alkoxides (**i**, Scheme 3) is likely to take place via Brook rearrangement to homoenolate **ii** followed by a [1,4]-Retro-Brook migration to enolate **iii**. As pointed out elsewere 11 such net carbon-to-carbon 1,3-silyl migrations are generally substrate-dependent, sensitive to steric and electronic factors, and favored at higher temperatures. We have evidence, however, that in our case this isomerization may, in part, also be an artifact of work-up and in certain cases can be minimized (vide infra).

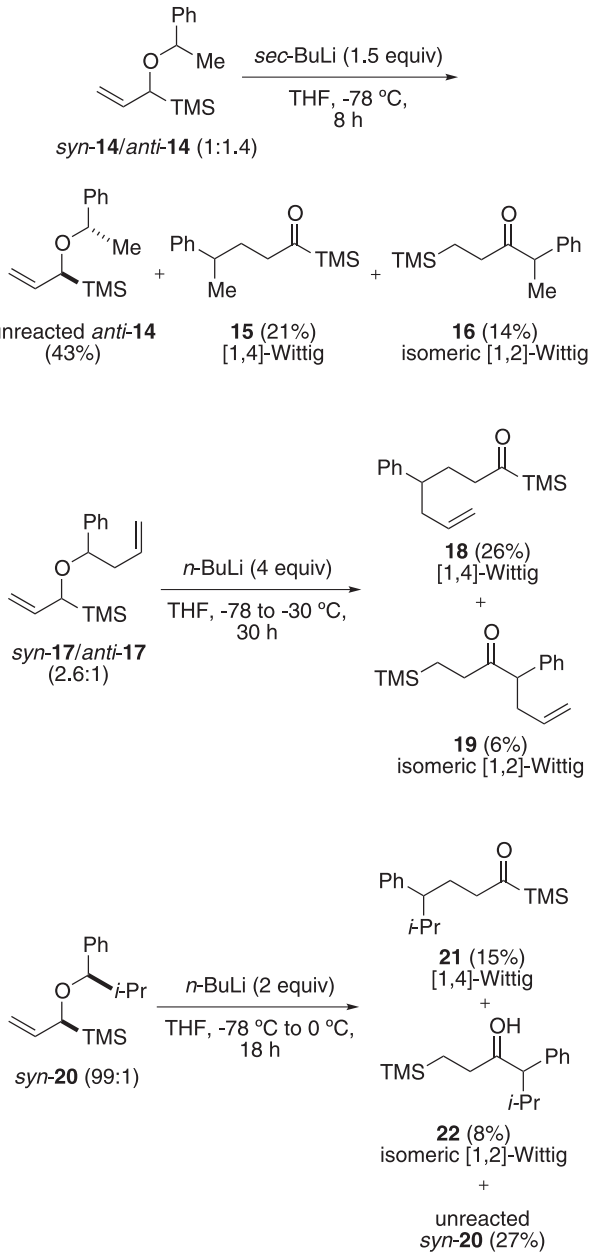
We continued our studies by analyzing the influence of substituents at the migrating (benzylic) carbon, a structural change



Scheme 3. Plausible mechanism for the isomerization of the [1,2]-Wittig alkoxide **i** to enolate **iii**.



Scheme 2. Effect of alkyl substitution at the terminal sp^2 carbon of the allyl moiety.



Scheme 4. Wittig rearrangements of α-alkoxysilanes **14**, **17**, and *syn*-**20** bearing a substituent (methyl, 2-propenyl, and *iso*-propyl, respectively) at the benzylic carbon.

that inherently led to diastereomeric substrates. Our simplest models, α-(trimethylsilyl)allyl ethers *syn*-**14** and *anti*-**14** bearing a methyl group at the benzylic position, were not separable by column chromatograph on silica gel, thus a 1:1.4 mixture of *syn*-**14**/*anti*-**14** was employed (Scheme 4). Employing such a mixture did not constitute a problem since it was possible to monitor the reaction by ^{1}H NMR. Under our standard reaction conditions we found that the more reactive diastereomer (*syn*-**14**) was consumed within 8 h whereas the 'less reactive' diastereomer *anti*-**14** was recovered in 43%. The [1,4]- and isomeric [1,2]-products (**15** and **16**, respectively) were obtained in a ratio of 1.5:1 and in a combined 35% yield. It was observed that allowing the reaction to proceed overnight resulted in an increased overall yield of **15** and **16** (46%) and basically the same [1,4]-/[1,2]-ratio (1.7:1) with a corresponding decrease in the recovery of the 'less reactive' *anti*-**14** (26%). The near complete erosion of the [1,4]-/[1,2]-selectivity (>99:1 in compound **1**)[6] is in agreement with the detrimental effect of substituents at the migrating carbon in the [1,4]-/[1,2]-selectivity observed by Schlosser.[8b]

The marked difference in the reactivity of diastereomers *syn*-**14** and *anti*-**14** points to the determinant role of relative stereochemistry, and more specifically the steric environment around the allylic proton (α to silicon) in allowing the key deprotonation step to take place prior to rearrangement.[12] The relative ability of the *syn* and *anti* diastereomers to adopt an optimum conformation for deprotonation might be responsible for the observed difference in reactivity. We propose that the allylic C–H bond should be perpendicular to the olefin and therefore aligned with the π system. At the same time, antiperiplanar alignment of the allylic C–H bond to the cleaving C–O would allow weakening of the C–H bond. The phenyl group would take the less crowded and furthest position, maximizing conjugation by aligning with the C–O bond and thus leading to the pseudo-eclipsed conformers shown in Fig. 1. These proposed conformational requirements pose a more severe steric interaction in *anti*-**14**, the less reactive diastereomer, in which the pseudo-eclipsing methyl and TMS groups collide. On the other hand, in *syn*-**14** the TMS group is pseudo-eclipsed with H_b and a less unfavorable steric interaction between the benzylic methyl and vinyl groups is possible. Alternatively, positioning the benzylic H_b proton in an 'eclipsed' alignment with the TMS groups in both *anti*-**14** and *syn*-**14** would lead to a more unfavorable steric interaction in *anti*-**14** (Ph vs vinyl) than in *syn*-**14** (Me vs vinyl).

Our conformational analysis is consistent with the fact that increasing the steric demand of the substituent at the benzylic position (methyl in **14**) dramatically reduced deprotonation rate. The diastereomeric 2-propenyl (**17**) and the isopropyl (**20**) analogs were unreactive under standard reaction conditions (*sec*-BuLi, THF, −78 °C, 24 h). In these two cases the use of a less bulky base (*n*-BuLi) was necessary to effect a reaction. A mixture of *syn*-**17**/*anti*-**17** (2.6:1) required 30 h for complete reaction at −30 °C, yielding acylsilane **18** and ketone **19** in a 4.3:1 ratio. The seemingly higher [1,4]-/[1,2]-selectivity is clouded by the reaction also affording a complex mixture of alkylated and otherwise unidentified byproducts. A temperature of 0 °C was necessary for the isopropyl substituted *syn*-**20** to undergo deprotonation and rearrangement to give the [1,4]- and isomeric [1,2]-products **21** and **22**, in 23% yield (1.8:1 ratio), along with 27% of unreacted *syn*-**20**.

We also studied the behavior of diastereomeric ethers **23**, containing a *para* methyl group on the aromatic ring (Scheme 5).[9] This weakly electron-donating group barely influenced the [1,4]-/[1,2]-selectivity, relative to the unsubstituted analogs **14** (2:1 vs 1.5:1, respectively), providing [1,4]-product **24** and [1,2]-product **25** in 40% overall yield. However, a significant amount of diastereomeric dibenzyl dimer **26** was isolated from the reaction mixture, suggesting that (1) the stepwise mechanism is the major pathway in the rearrangements of **23**, and (2) that the

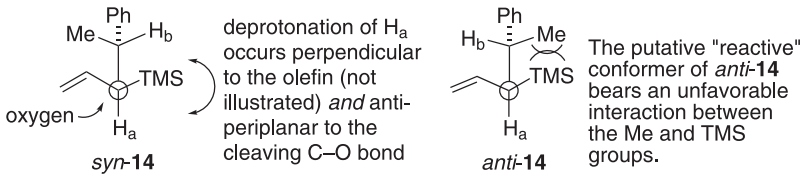
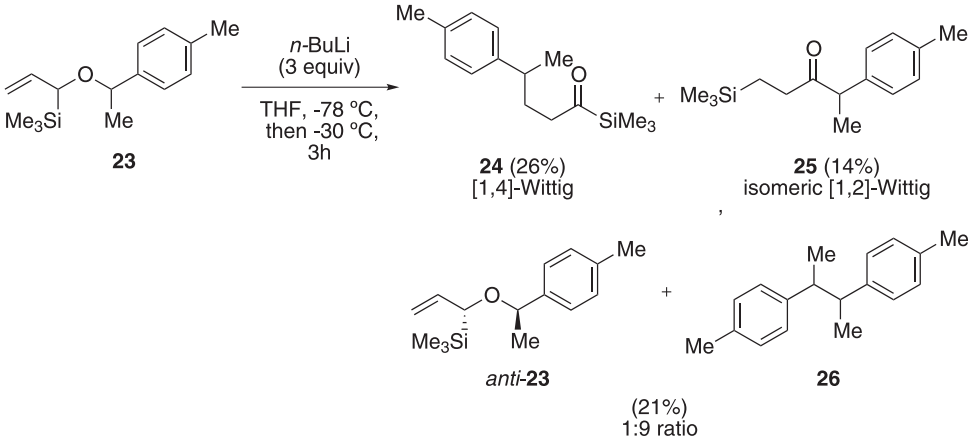


Fig. 1. Proposed relevant conformers for allylic deprotonation in *syn*-**14** and *anti*-**14**.



Scheme 5. Wittig rearrangements of diastereomeric **23** having an electron-rich migrating (benzylic) group.

expected benzyl radical stabilization by the *para* methyl group prevents radical/radical-anion recombination within the solvent cage,[13] allowing benzyl radicals to escape and dimerize.

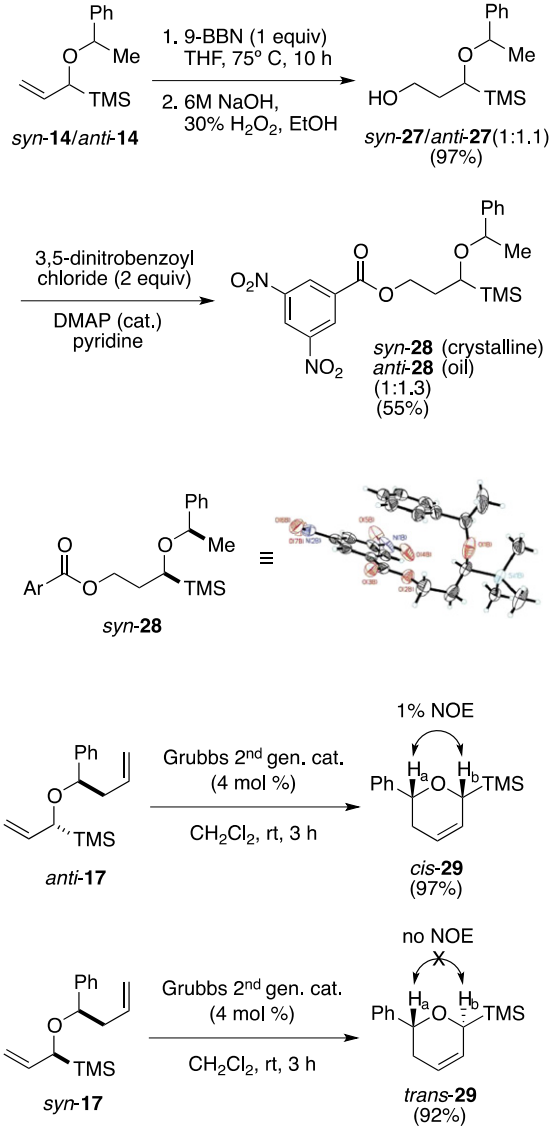
It is important to mention that we have consistently observed that *syn* diastereomers (general structure **1**, $R_2 \neq H$, Scheme 1) are more reactive than the corresponding *anti* isomers in *all* cases. The relative stereochemistry of diastereomers *syn*-**14**/*anti*-**14** and *syn*-**17**/*anti*-**17** was determined as shown in Scheme 5.[14] Derivatization of *syn*-**14**/*anti*-**14** to the 3,5-dinitrobenzoyl esters *syn*-**28**/*anti*-**28** and crystallization of *syn*-**28** allowed the determination of its crystal structure.[15] On the other hand, ring-closing metathesis of *syn*-**17** and *anti*-**17** followed by NOE studies of the corresponding products *trans*-**29** and *cis*-**29** led to the assignment of relative stereochemistry in *syn*-**17** and *anti*-**17** (Scheme 6).

Finally, we studied the behavior of substrates bearing substitution at both the migrating carbon and the terminal allylic carbon. These experiments gave us the opportunity to evaluate the effect of olefin geometry not only on the reactivity and selectivity of the rearrangements, but also on the stereochemistry of the bond reorganization.

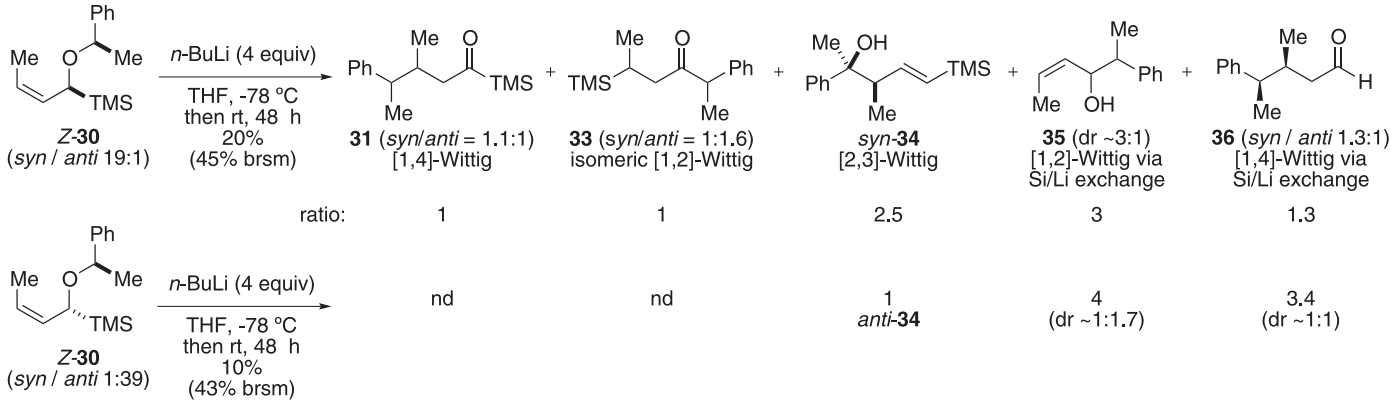
Compounds **30** were synthesized as geometrically pure *Z* or *E* isomers, however, while the *Z* diastereomers (*syn Z*-**30** and *anti Z*-**30**)[16] could be largely separated by column chromatography (dr>19:1), the *E* diastereomers proved very difficult to separate and therefore were used as a diastereomeric mixture (*E*-**30**).

In theory, clean deprotonation of **30** (*E* or *Z*) followed by rearrangement should afford pairs of diastereomeric [1,4]- and [1,2]-products (**31** and **32**, respectively). As described above, further isomerization of the [1,2]-products via silyl migration could also lead to another pair of diastereomeric ketones (**33**). In practice, *syn* and *anti Z*-**30** were very unreactive when treated with *n*-BuLi or other bases[17] at low temperature, and even at room temperature these diastereomers reacted sluggishly. Reaction of *syn Z*-**30** (Scheme 7) with *n*-BuLi led to almost 50% conversion and ~20% yield of a complex mixture of products. Careful examination and separation of these mixtures revealed that compound **33** was accompanied by [2,3]-Wittig (**34**),[18] diastereomeric [1,2]- and [1,4]-Wittig products lacking the trimethylsilyl group (**35** and **36**, respectively) and alkylated products (not shown). The actual [1,2]-Wittig product (**32**, Scheme 8) was not observed.

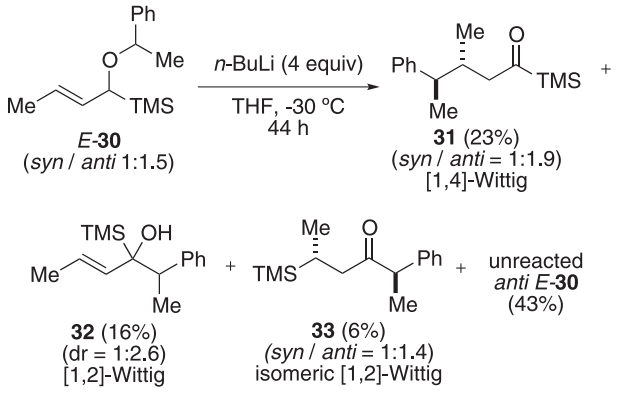
Although it was not possible to obtain exact ratios of products or diastereomers from either ^{1}H NMR or HPLC of crude reaction mixtures, the products could be partially purified allowing their approximate ratios to be determined.[19] The [2,3]-Wittig rearrangement of *syn Z*-**30** proceeded through a standard transition structure[2a] to give *syn*-**34** as a single diastereomer,[18] on the other hand all other products from [1,4]- and [1,2]-migrations were obtained in low diastereomeric ratios (ranging from 1:1 to ~3:1). Isolation of the [2,3]-Wittig product is diagnostic of competitive deprotonation at the



Scheme 6. Determination of relative stereochemistry of *syn*-**14**/*anti*-**14** and *syn*-**17**/*anti*-**17**.



Scheme 7. Substitution at the migrating carbon and terminal sp^2 carbon, *Z* isomers.



Scheme 8. Substitution at the migrating carbon and terminal sp^2 carbon, *E* isomers.

benzylic position, rather than α to silicon, likely as a consequence of the relatively high temperature required for the desired reaction to occur. The elevated temperature may allow these substrates to overcome an unfavorable conformation for deprotonation of the allylic hydrogen due to the minimization of A(1,3)-strain.[20]

As expected, *anti Z*-**30** was less reactive under the same reaction conditions. Here, the starting material was recovered in 77% and only a total ~10% yield of products **34**–**36** was obtained (Scheme 7). The absence of compounds **31**–**33** suggests that deprotonation α to silicon is inhibited due to severe steric crowding. [2,3]-Wittig rearrangement of *anti Z*-**30** proceeded stereospecifically[2a] to give only *anti*-**34**.[21] Compounds **35** and **36**, likely to be formed via a silicon/lithium exchange[7] followed by [1,2]- and [1,4]-Wittig rearrangement, respectively, were obtained again in low diastereomeric ratios. Interestingly, the [1,2]-product **35** showed an inverse diastereoselection in comparison to that observed in the rearrangement of *syn Z*-**30**.

Changing the geometry of the olefin had a pronounced effect (Scheme 8). In line with our previous discussion, the reactivity toward initial deprotonation was dominated by the relative configuration at the α and α′ positions of the ethers, as illustrated by the rearrangement of *E*-**30** (*syn*/*anti*=1:1.5). For example, *syn E*-**30** was completely consumed by *n*-BuLi at low temperature, while its diastereomer *anti E*-**30** was mostly recovered (Scheme 8). Quenching the reaction at −30 °C led to the isolation of the [1,4]-Wittig product (**31**) in 23% yield and with low diastereoselectivity,[22] accompanied by the isomeric [1,2]-product (**33**) also in low yield. Interestingly, quenching the reaction at lower temperature allowed the isolation of the direct [1,2]-Wittig product **32**,[23] which in our previous room temperature experiments (Scheme 7) had undergone silicon migration and rearrangement to **33**. This was evidenced in an experiment run at 0 °C for 52 h and quenched at −78 °C, which gave the [1,4]- and [1,2]-Wittig products **31** and **32** in 30% yield (1:1 ratio) with only traces of the isomeric [1,2]-product **33**. Thus, in certain cases, quenching the reaction at low temperature significantly reduces silyl migration.

The relative stereochemistry of diastereomeric acylsilane **31** was determined by oxidation to the corresponding carboxylic acid.[22,23] The relative stereochemistry of diastereomeric alcohol **32** was not determined. Attempts to derivatize **32** to the corresponding 3,5-dinitrobenzoyl ester failed presumably due to the congested nature of the tertiary alcohol. The relative stereochemistry in isomeric [1,2]-Wittig product (**33**) was determined as shown in Scheme 9. Compound **33** (dr=1.4:1) was reduced to the corresponding alcohol **39** as a mixture of only three diastereomers. Partial separation of the diastereomers of **39** led to a mixture with a ratio 10:2:1. Benzoylation of this mixture with 3,5-dinitrobenzoyl chloride in pyridine gave **40** as a mixture of diastereomers. Recrystallization from CH_2Cl_2/hexanes gave a single diastereomer and its relative stereochemistry was determined by X-ray. Hydrolysis (NaOH) and oxidation (DMP) of this single isomer (**40**) gave *anti*-**33**, which matched spectroscopically with the major diastereomer in the initial diastereomeric mixture of **33**.

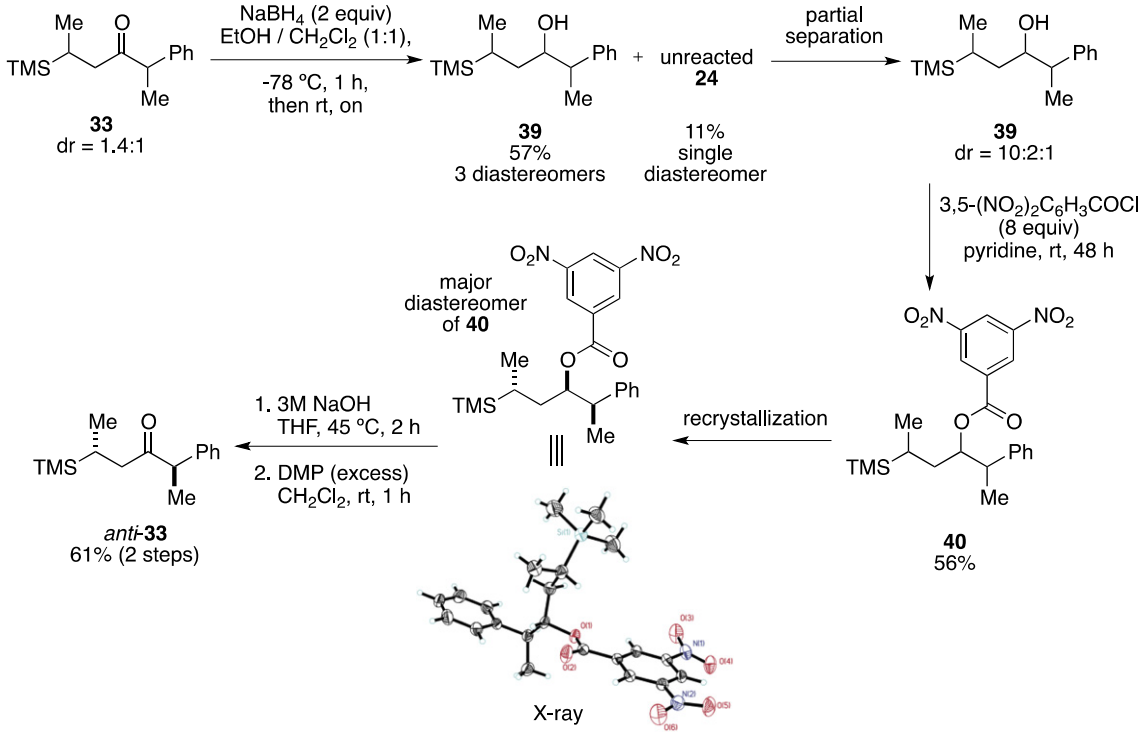
3. Conclusions

In conclusion, we have shown that substitution at the migrating carbon impacts the Wittig rearrangement of α-alkoxysilanes, decreasing reactivity toward deprotonation and eroding the [1,4]-/[1,2]-selectivity. Similarly, substitutions at the terminal carbon of the allyl moiety alone or in combination with substitution at the migrating carbon also lowers the [1,4]-/[1,2]-selectivity, especially where substitution comes in the form of *Z*-olefins. Increasingly bulkier substituents at the terminal allylic position gradually decrease the [1,4]-/[1,2]-selectivity, leading to complete inhibition of the [1,4]-pathway in the bulkier case (*t*-butyl). The reactivity in these diastereomeric substrates heavily depends on their relative stereochemistry, *syn* or *anti*, the former being more reactive in all cases. Taken together these results show the beneficial effect of silyl groups on reactivity (by lowering the acidity of allylic hydrogens) is countered by the steric congestion afforded upon substitution at the benzylic or allylic (or both) positions, which presumably prevents the access of optimal conformation for the key deprotonation step.

4. Experimental section

4.1. General considerations

All reactions were run under nitrogen in previously flame-dried flasks or disposable vials. THF was freshly distilled from sodium



Scheme 9. Determination of the relative stereochemistry of **33** by derivatization to the crystalline ester **40** (major diastereomer) followed by the reverse transformations to *anti*-**33**.

benzophenone ketyl. Dichloromethane was distilled from calcium hydride. Cyclohexane and hexane were used without further purification. Ultrapure silica gel 60 (230–400 mesh ASTM) from Silicycle was used for flash column chromatography. Melting points are not corrected.

Nuclear Magnetic Resonance spectra were recorded on 300 MHz, 500 MHz, and 600 MHz Varian instruments using $CDCl_3$ as solvent and referenced to 7.24 ppm (residual proton). IR was recorded on a Perkin–Elmer instrument. High Resolution Mass Spectrometry spectra were recorded at the Michigan State University Mass Spectrometry Facility using a Waters Qtof Ultima (ESI) and JEOL AX 505H (EI/CI) instruments.

4.2. Preparation of α-alkoxysilanes—general procedure A

Trichloroacetimidate of the appropriate alcohol (prepared according to literature procedure)[10] (2.0 equiv) was added to a stirred solution of the requisite α-(trimethylsilyl)allyl alcohol[11d] (1.0 equiv) in cyclohexane or hexane (0.2 M) at room temperature. A solution of TMSOTf (0.055 equiv) in cyclohexane or hexane (usually 0.1 mL/1.0 mL cyclohexane) or, alternatively, $BF_3{\cdot}OEt_2$ in dry diethyl ether, was then added dropwise. White precipitate formed upon addition of the Lewis acid. The reaction mixture was stirred at room temperature until completion as judged by ^1H NMR (typically overnight) and filtered through a plug of Celite. The precipitate was then washed with pentane or hexane (precipitate is soluble in ether) and the filtrate diluted with ether. The diluted filtrate was subsequently washed with $NaHCO_3$ (aq satd) (twice), 1 M HCl (twice), and lastly with brine (twice). The organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated to furnish the crude product. Purification by column chromatography on silica gel (0–2% EtOAc in hexane gradient) afforded the pure product.

4.2.1. Preparation of ***5****.* Applying general procedure A to 6.75 g (46.86 mmol) of (*E*)-1-(trimethylsilyl)but-2-en-1-ol, 17.75 g (70.29 mmol) of trichloroacetimidate of benzyl alcohol, and $BF_3{\cdot}OEt_2$ (0.65 mL, 5.15 mmol) in cyclohexane afforded 2.11 g (34%) of **5** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.55–5.39 (m, 2H), 4.69–4.65 (d, J=12.4 Hz, 1H), 4.37–4.28 (d, J=12.4 Hz, 1H), 3.52–3.50 (d, J=7.1 Hz, 1H), 1.74–1.72 (d, J=4.7 Hz, 3H), 0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 129.7, 128.0 (2C), 127.5 (2C), 127.0, 125.1, 75.1, 71.3, 18.0, −3.7. HRMS (CI) m/z 252.1775 [$(M+NH_4)^+$; calcd for $C_{14}H_{22}OSi$, 252.1784].

4.2.2. Preparation of compound ***8****.* Compound **8** was prepared by alkylation of (*E*)-1-(trimethylsilyl)non-2-en-1-ol. Preparation of (*E*)-1-(trimethylsilyl)non-2-en-1-ol: To a solution of (*E*)-2-nonen-1-ol (800 mg, 5.62 mmol, 1 equiv) in THF (15 mL) at −78 °C was added *n*-BuLi (1.6 M in hexanes, 3.9 mL, 6.19 mmol, 1.1 equiv) slowly. After 30 min, TMSCl (0.79 mL, 6.19 mmol, 1.1 equiv) was added and the mixture stirred at room temperature for 1 h. The reaction mixture was cooled down to −78 °C and *t*-BuLi (3.97 mL, 6.74 mmol, 1.2 equiv) was added dropwise (within 15 min). The reaction was monitored by ^1H NMR. After 8 h the reaction was quenched by quickly adding $NH_4Cl_{(sat)}$ (7 mL). The mixture was diluted with Et_2O (20 mL) and the aqueous phase was extracted with Et_2O (3×10 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated to give 1.1 (91%, crude yield) of almost pure (*E*)-1-(trimethylsilyl)non-2-en-1-ol as a yellowish oil. ^1H NMR (500 MHz, $CDCl_3$) δ 5.56 (ddt, J=1.0, 6.5, 15.0 Hz, 1H), 5.46 (m, 1H), 3.88 (dt, J=1.5, 7.0 Hz, 1H), 2.01 (q, J=7.0 Hz, 2H), 1.35–1.25 (m, 8H), 0.86 (t, J=7.0 Hz, 3H), 0.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 131.2, 127.8, 68.4, 32.5, 31.7, 29.7, 28.8, 22.7, 14.1, 1.3, −4.2. IR (neat) 3416, 2928, 1248, 841 cm^{-1}. HRMS (EI) m/z 196.1647 [$(M-H_2O)^+$; calcd for $C_{12}H_{24}Si$, 196.1647].

Alkylation of (*E*)-1-(trimethylsilyl)non-2-en-1-ol: Applying general procedure A to (*E*)-1-(trimethylsilyl)non-2-en-1-ol (300 mg, 1.4 mmol, 1 equiv) and trichloroacetimidate of benzyl alcohol (671 mg, 2.5 mmol, 1.8 equiv) in 10:1 hexane/CH_2Cl_2 (8 mL) with TMSOTf (38 μL, 0.21 mmol, 0.15 equiv) for 2.5 h afforded 134 mg (31%) of **8** as a colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30

(m, 4H), 7.24 (m, 1H), 5.43 (m, 2H), 4.66 (d, J=12.5 Hz, 1H), 4.30 (d, J=12.0 Hz, 1H), 3.50 (d, J=8.0 Hz, 1H), 2.04 (q, J=7.0 Hz, 2H), 1.38–1.24 (m, 8H), 0.88 (t, J=8.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.5, 130.9, 128.6, 128.1, 127.6, 127.1, 75.1, 71.3, 32.5, 31.7, 29.6, 28.8, 22.7, 14.1, −3.9. IR (film) 3030, 2957, 1246, 841 cm^{-1}. HRMS (EI) m/z 289.1985 [$(M-CH_3)^+$; calcd for $C_{18}H_{29}OSi$, 289.1988].

*4.2.3. Preparation of compound **11**.* Compound **11** was prepared by alkylation of (*E*)-4,4-dimethyl-1-(trimethylsilyl)pent-2-en-1-ol. Preparation of (*E*)-4,4-dimethyl-1-(trimethylsilyl)pent-2-en-1-ol: To a solution of (*E*)-4,4-dimethyl-2-penten-1-ol (700 mg, 6.13 mmol, 1 equiv) in THF (17.5 mL) at −78 °C was added *n*-BuLi (1.6 M in hexanes, 2.7 mL, 6.74 mmol, 1.1 equiv) slowly. After 30 min, TMSCl (0.86 mL, 6.74 mmol, 1.1 equiv) was added and the mixture stirred at room temperature for 1 h. The reaction mixture was cooled down at −78 °C and *t*-BuLi (9 mL, 15.3 mmol, 2.5 equiv) was added dropwise (within 25 min). The reaction was transferred to a cold bath at −30 °C and monitored by ^{1}H NMR. After 6 h the reaction was quenched by quickly adding $NH_4Cl_{(sat)}$ (10 mL). The mixture was diluted with Et_2O (20 mL) and the aqueous phase was extracted with Et_2O (3×10 mL). Combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography (5% EtOAc in hexanes) to give 790 (69%) of **11** as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.49 (m, 2H), 3.90 (dd, J=1.0, 3.5 Hz, 1H), 1.0 (s, 9H), 0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.6, 125.9, 68.4, 32.8, 29.8, −4.2. IR (film) 3406, 2959, 1248, 843 cm^{-1}. HRMS (EI) m/z 168.1334 [$(M-H_2O)^+$; calcd for $C_{10}H_{20}Si$, 168.1334].

Alkylation of (*E*)-4,4-dimethyl-1-(trimethylsilyl)pent-2-en-1-ol: Applying general procedure A to (*E*)-4,4-dimethyl-1-(trimethylsilyl)pent-2-en-1-ol (350 mg, 1.88 mmol, 1 equiv) and trichloroacetimidate of benzyl alcohol (900 mg, 3.38 mmol, 1.8 equiv) in 10:1 hexane/CH_2Cl_2 (10 mL) with TMSOTf (51 μL, 0.282 mmol, 0.15 equiv) for 2.5 h afforded 245 mg (49%) of **11** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (m, 4H), 7.24 (m, 1H), 5.49 (dd, J=1.0, 15.5 Hz, 1H), 5.31 (dd, J=6.5, 16.0 Hz, 1H), 4.64 (d, J=12.5 Hz, 1H), 4.30 (d, J=12.5 Hz, 1H), 3.51 (dd, J=1.0, 8.5 Hz, 1H), 1.01 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 139.5, 128.1, 127.7, 127.1, 123.2, 75.2, 71.3, 29.8, −3.9. IR (film) 3026, 2959, 1246, 841 cm^{-1}. HRMS (EI) m/z 185.1353 [$(M+Bn)^+$; calcd for $C_{10}H_{21}OSi$, 185.1362].

*4.2.4. Preparation of compounds **14**.* Applying general procedure A to 4.01 g (30.82 mmol) of α-hydroxysilane 1-(trimethylsilyl)-prop-2-en-1-ol, 17.25 g (58.57 mmol) of the trichloroacetimidate of 2-methyl-1-phenylpropan-1-ol, and 0.38 g (1.70 mmol) of TMSOTf, and stirring the reaction overnight afforded 5.7 g (79%) of **14** as a 1:1 mixture of diastereomers. IR (neat) 2972, 2928, 2899, 1628, 1493, 1452, 1248 cm^{-1}. Mixture of *syn*-**14**/*anti*-**14**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.10 (m, 10H), 5.83–5.68 (m, 2H), 5.06–4.87 (m, 4H), 4.56–4.46 (m, 2H), 3.82–3.80 (dt, J=6.9, 1.4 Hz, 1H), 3.43–3.41 (dt, J=6.9, 1.4 Hz, 1H), 1.39 (d, J=6.6 Hz, 3H), 1.35 (d, J=6.6 Hz, 3H), 0.06 (s, 9H), 0.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 144.2, 137.6, 128.4, 128.0, 127.9, 127.1, 126.7, 126.6, 125.8, 112.1, 111.7, 76.0, 75.6, 74.1, 73.2, 24.8, 22.3, −3.7, −3.8. HRMS (EI) m/z 234.1434 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440]. *anti*-**14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.21 (m, 5H), 5.82–5.70 (m, 1H), 5.05–4.95 (m, 2H), 4.56–4.49 (q, J=6.6, Hz, 1H), 3.43–3.40 (dt, J=7.1, 1.3 Hz, 1H), 1.39 (d, J=6.6 Hz, 3H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, CDCl3) δ 144.4, 137.8, 128.2, 127.2, 126.8, 112.2, 75.7, 73.3, 24.6, −3.9. HRMS (EI) m/z 234.1428 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*4.2.5. Preparation of compound **20**.* Applying general procedure A to 0.88 g of 1-(trimethylsilyl)-prop-2-en-1-ol (6.73 mmol), 3.96 g of the trichloroacetimidate of 1-phenylbutan-1-ol (13.45 mmol, 2 equiv), and 0.07 mL of TMSOTf (0.4 mmol, 0.055 equiv) overnight afforded 1.32 g of **20** (75%) as a 1:1 mixture of diastereomers after column chromatography (0–2% EtOAc gradient). IR (neat) 1628 cm^{-1}.

anti-**20**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.19 (m, 5H), 5.77–5.70 (m, 1H), 5.03–4.92 (dd, J=10.6, 17.2 Hz, 2H), 4.07–4.06 (d, J=7.5 Hz, 1H), 3.39–3.37 (d, J=8.0 Hz, 1H), 1.91–1.85 (m, 1H), 1.01–1.00 (d, J=6.6 Hz, 3H), 0.72–0.70 (d, J=7.1 Hz, 3H), −0.01 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 138.0, 128.1 (2C), 127.8, 127.1 (2C), 113.1, 84.7, 72.6, 35.0, 19.2, 19.0, −4.0. HRMS (APCI) m/z 263.1821 [$(M+H)^+$; calcd for $C_{16}H_{27}OSi$, 263.1831].

syn-**20**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.17 (m, 5H), 5.64–5.53 (m, 1H), 4.89–4.72 (dd, J=10.7, 16.7 Hz, 2H), 4.01–3.99 (d, J=6.9 Hz, 1H), 3.72–3.68 (d, J=7.4 Hz, 1H), 1.99–1.89 (m, 1H), 0.93–0.91 (d, J=6.9 Hz, 3H), 0.77–0.74 (d, J=6.9 Hz, 3H), 0.05 (s, 9H), 0.08 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 138.2, 127.4 (2C), 127.3 (2C), 126.5, 111.4, 87.5, 76.6, 34.5, 18.7 (2C), −3.5. HRMS (APCI) m/z 263.1821 [$(M)^+$; calcd for $C_{16}H_{27}OSi$, 263.1831].

*4.2.6. Preparation of **23**.* Applying general procedure A to 1 g (7.68 mmol) of 1-(trimethylsilyl)-prop-2-en-1-ol, 3 g (10.75 mmol) of the trichloroacetimidate of 4-methylbenzyl alcohol and TMSOTf (35 μL, 0.19 mmol) in hexane afforded 1.7 g (95%) of diastereomeric **23** as a colorless oil. Mixture of *syn*-**23**/*anti*-**23** (1:1) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J=8.5 Hz, 2H), 7.15–7.09 (m, 6H), 5.73 (m, 2H), 5.01–4.94 (m, 3H), 4.88 (dt, J=11.0 Hz, 1H), 4.48 (q, J=6.5 Hz, 1H), 4.45 (d, J=6.5 Hz, 1H), 3.78 (dt, J=1.5, 6.5 Hz, 1H), 3.40 (dt, J=1.5, 7.0 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 1.35 (d, J=6.5 Hz, 3H), 1.32 (d, J=6.5 Hz, 3H), 0.03 (s, 9H), −0.05 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.5, 141.3, 137.84, 137.81, 136.7, 136.3, 128.8 (2C), 128.7 (2C), 126.7 (2C), 125.9 (2C), 112.1, 111.6, 75.9, 75.4, 74.1, 73.1, 24.7, 22.2, 21.13, 21.09, −3.0, −4.0. IR (film) 3050, 2972, 1248, 841 cm^{-1}. HRMS (EI) m/z 248.1597 [(M^+); calcd for $C_{15}H_{24}OSi$, 248.1596].

*4.2.7. Preparation of compound E-**30**.* Applying general procedure A to 3.6 g of (*E*)-1-(trimethylsilyl)but-2-en-1-ol (24.98 mmol),[11d] 13.32 g of the trichloroacetimidate of phenethyl alcohol (49.5 mmol, 2 equiv) and 0.47 mL of $BF_3\cdot OEt_2$ (3.74 mmol, 0.15 equiv) afforded 3.07 g of *E*-**30** (39%).

E-**30** (mixture of diastereomers *anti*/*syn* 0.58:0.42): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5H), 5.42–5.31 (m, 2H), 4.52 (q, J=6.5 Hz, 0.58H), 4.49 (q, J=6.0 Hz, 0.42H), 3.69 (d, J=7.0 Hz, 0.42H), 3.29 (d, J=7.0 Hz, 0.58H), 1.71 (d, J=5.5 Hz, 1.74H), 1.61 (d, J=6.0 Hz, 1.26H), 1.35 (d, J=6.5 Hz, 1.74H), 1.32 (d, J=6.0 Hz, 1.26H), 0.03 (s, 3.78H), −0.05 (s, 5.22H). ^{13}C NMR (125 MHz, $CDCl_3$) *anti E*-**30**: δ 144.6, 130.2, 128.1 (2C), 127.0, 126.8 (2C), 124.6, 75.0, 72.4, 24.7, 17.9, −3.9. *syn E*-**30**: δ 145.8, 130.4, 127.9 (2C), 126.6, 125.9 (2C), 124.0, 75.2, 73.2, 22.0, 17.8, −3.8. HRMS (CI) m/z 248.1591 [$(M)^+$; calcd for $C_{15}H_{24}OSi$, 248.1596].

*4.2.8. Preparation of compound Z-**30**.* Following the general procedure A to 3.49 g of 1-(trimethylsilyl)but-2-yn-1-ol (24.53 mmol) and 13.1 g of the trichloroacetimidate of *sec*-phenethyl alcohol (49.06 mmol, 2 equiv) in cyclohexane (140 mL) at 0 °C was added 0.46 mL of $BF_3\cdot OEt_2$ (3.68 mmol, 0.15 equiv). After 1 h the reaction was stopped, worked up according to the general procedure A followed by column chromatography (8% DCM in hexanes) to afford 5 g (83%) of diastereomeric alkyne **37** as a colorless oil (diastereomers partially separated). Alkyne reduction: To a solution of 1.435 g of **37** (5.82 mmol, dr=1:1) in hexanes (210 mL) was added Et_3N (2.6 mL, 2.5 mL/mmol **37**) and Lindlar's catalyst (38.8 mg, 37.5 mg/mmol **37**). The flask was flushed with hydrogen and a hydrogen balloon attached. The mixture was vigorously stirred and the reaction monitored by NMR (about 4 h). The reaction mixture was partially concentrated, filtered through a plug of Celite, and fully concentrated. Column chromatography (10% DCM in hexanes) afforded 900 mg (62%) of *Z*-**30**. Note: Pure alkyne **37** decomposes

relatively quickly after isolation and its decomposition products appear to poison the catalyst and hamper reduction thus requiring addition of more catalyst. Samples of **37** stored at −20 °C slowly decomposed turning yellow, such samples in hexanes were filtered through a short silica gel plug and rinsed with more hexanes. After concentration clean **37** was immediately submitted to the reduction reaction. IR (neat) 2963, 2203, 1248, 1082, 843 cm^{-1}. HRMS (EI) *m*/*z* 246.1444 [$(M)^+$; calcd for $C_{15}H_{22}OSi$, 246.1440].

anti-**37**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.37–7.23 (m, 5H), 4.79 (q, *J*=6.5 Hz, 1H), 3.43 (q, *J*=2.5 Hz, 1H), 1.88 (d, *J*=2.5 Hz, 3H), 1.40 (d, *J*=7.0 Hz, 3H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 128.3 (2C), 127.3, 126.8 (2C), 82.7, 77.6, 76.3, 60.5, 24.4, 3.9, −4.0.

syn-**37**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J*=7.5 Hz, 2H), 7.30 (m, 2H), 7.21 (tt, *J*=1.5, 7.5 Hz, 1H), 4.71 (q, *J*=6.5 Hz, 1H), 3.88 (q, *J*=2.5 Hz, 1H), 1.78 (d, *J*=2.5 Hz, 3H), 1.36 (d, *J*=6.5 Hz, 3H), 0.12 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 128.0 (2C), 126.8, 126.1 (2C), 83.1, 77.6, 76.1, 61.0, 21.4, 3.8, −3.8.

anti Z-**30**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J*=7.0 Hz, 2H), 7.23 (m, 3H), 5.50 (ddq, *J*=1.0, 7.0, 11.0 Hz, 1H), 5.39 (ddq, *J*=1.5, 10.5, 11.0 Hz, 1H), 4.44 (q, *J*=6.5 Hz, 1H), 3.67 (d, *J*=10.5 Hz, 1H), 1.35 (ddd, *J*=0.5, 2.0, 7.0 Hz, 3H), 1.34 (d, *J*=6.5 Hz, 3H), −0.03 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6, 130.5, 128.1 (2C), 127.1, 126.9 (2C), 124.4, 75.6, 67.4, 24.6, 13.4, −3.9. HRMS (ESI) *m*/*z* 249.1663 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675].

syn Z-**30**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.26 (m, 4H), 7.20 (m, 1H), 5.43–5.32 (m, 2H), 4.45 (q, *J*=6.5 Hz, 1H), 4.13 (d, *J*=9.5 Hz, 1H), 1.51 (m, 3H), 1.34 (d, *J*=6.5 Hz, 3H), 0.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.6, 130.9, 127.9 (2C), 126.7, 126.0 (2C), 123.2, 75.8, 68.4, 22.0, 13.5, −3.8. HRMS (ESI) *m*/*z* 249.1675 [$(M+H)^+$; calcd for $C_{15}H_{25}OSi$, 249.1675].

*4.2.9. Preparation of compound **17**.* Compound **17** was prepared following a procedure reported in literature.[24] Allyltrimethylsilane 1-(trimethylsilyl)prop-2-en-1-ol (1.26 g, 11.0 mmol, 1.75 mL), benzaldehyde (1.67 g, 11.0 mmol, 1.12 mL), and TMSOTf (0.36 mL, 2.0 mmol, 0.44 g) were successively added to a stirred cold (−78 °C) solution of α-(trimethylsilyl)allyl trimethysilyl ether (2.0 g, 10.0 mmol) in CH_2Cl_2 (100 mL). The reaction was stirred for 70 min and then quenched with $NaHCO_3$ (aq satd). The aqueous phase was extracted with CH_2Cl_2 (100 mL×4), and the combined organic layers were washed with $NaHCO_3$ (100 mL×2), brine (100 mL×2), and then dried ($MgSO_4$). Filtration and concentration afforded the crude product as a 1:2.56 mixture of diastereomers. After silica gel chromatography 1.96 g (7.58 mmol) of the pure products were obtained in a combined yield of 77%. The pair of diastereomers is separable by column chromatography on silica gel (5% and 10% CH_2Cl_2 in hexanes).

anti-**17**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 5.88–5.69 (m, 2H), 5.05–4.95 (m, 4H), 4.46–4.42 (dd, *J*=7.7, 5.8 Hz, 1H), 3.44–3.42 (d, *J*=7.4 Hz, 1H), 2.59–2.49 (quint, *J*=7.7 Hz, 1H), 2.39–2.30 (quint, *J*=6.86, 1H), −0.01 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.5, 137.7, 135.4, 128.1 (2C), 127.4 (3C), 116.3, 112.9, 79.3, 73.0, 43.03, −4.0. HRMS (CI) *m*/*z* 261.1664 [$(M+H)^+$; calcd for $C_{16}H_{24}OSi$, 261.1675.

syn-**17**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.30–7.20 (m, 5H), 5.79–5.60 (m, 2H), 5.01–4.80 (m, 4H), 4.39–4.35 (t, *J*=6.2 Hz, 1H), 3.82–3.78 (dt, *J*=7.1, 1.3 Hz, 1H), 2.54–2.40 (m, 2H), 0.05 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.6, 137.9, 134.9, 127.8 (2C), 126.9, 126.6 (2C), 116.8, 111.9, 81.1, 75.8, 41.5, −3.7. HRMS (CI) *m*/*z* 261.1681 [$(M+H)^+$; calcd for $C_{16}H_{24}OSi$, 261.1675].

4.3. Wittig rearrangements of α-alkoxysilanes—general procedure B

A solution of α-alkoxysilane (1.0 equiv) in freshly distilled THF (0.06–0.07 M) was cooled to the desired temperature under nitrogen. The required amount of *s*-BuLi (1.5–4.0 equiv, 1.3 M in cyclohexane) or *n*-BuLi (1.6 M in hexanes) was added dropwise via syringe. The reaction mixture was stirred at the reaction temperature for the desired length of time, then quenched with saturated aqueous NH_4Cl and diluted with ether. Phases separated and the organic phase was washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and concentrated. Silica gel chromatography (0–2% EtOAc in hexane gradient) afforded the rearranged products usually as light oils.

*4.3.1. Wittig rearrangements of compound **5**.* Applying the general procedure B to 141 mg (0.60 mmol) of **5** and 0.69 mL (0.90 mmol) of *s*-BuLi (1.3 M in cyclohexane) at −78 °C for 30 min, after purification by column chromatography on silica gel, afforded 106 mg (75%) of a 4:1 mixture of both [1,4]- and [1,2]-rearrangement products **6** (a light yellow oil) and **7** as a colorless oil.

Compound **6**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.17 (m, 5H), 2.61–2.50 (m, 2H), 2.47–2.30 (m, 3H), 0.84–0.81 (d, *J*=6.6 Hz, 3H), −0.13 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 248.6, 140.6, 129.2 (2C), 128.2 (2C), 125.9, 54.9, 43.3, 29.6, 19.9, −3.3. IR (neat) 1709 cm^{-1}. HRMS (EI) *m*/*z* 233.1355 [$(M-H)^+$; calcd for $C_{14}H_{21}OSi$, 233.1362].

Compound **7**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.26–7.10 (m, 5H), 5.60–5.56 (dq, *J*=15.4, 1.6 Hz, 1H), 5.19–5.12 (apparent dq, *J*=15.4, 6.6 Hz, 1H), 2.86 (d, *J*=7.7 Hz, 1H), 2.81 (d, *J*=7.7 Hz, 1H), 1.64–1.62 (dd, *J*=6.6, 1.6 Hz, 3H), 0.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.2, 135.4, 130.6 (2C), 127.9 (2C), 126.3, 121.62, 70.4, 43.1, 17.8, −4.2. IR (neat) 3432 cm^{-1}. HRMS (EI) *m*/*z* 234.1435 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*4.3.2. Wittig rearrangements of compound **8**.* Applying the general procedure B to compound **8** (62 mg, 0.204 mmol, 1 equiv) and *sec*-BuLi (1.4 M in cyclohexane, 0.22 mL, 1.5 equiv) at −78 °C for 40 min, after purification by silica gel column chromatography (3% EtOAc in hexanes), afforded 48.4 mg (78%) of a 2:1 mixture of both [1,4]- and [1,2]-rearrangement products **9** and **10** as colorless oils. An analytically pure sample of **9** could be obtained by subsequent silica gel column chromatography (3% EtOAc in hexanes).

Compound **9**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (m, 2H), 7.15 (m, 1H), 7.11 (m, 2H), 2.58 (dd, A of ABX system, *J*=6.5, 13.5 Hz, 1H), 2.49 (d, *J*=6.5 Hz, 2H), 2.42 (dd, B of ABX system, *J*=7.0, 13.5 Hz, 1H), 2.29 (m, 1H), 1.23 (m, 10H), 0.85 (t, *J*=7.5 Hz, 3H), 0.12 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 248.7, 140.7, 129.3 (2C), 128.2 (2C), 125.8, 52.5, 40.5, 34.1, 33.9, 31.8, 29.5, 26.8, 22.6, 14.1, −3.2. IR (film) 3026, 2926, 1643, 1456, 1250, 844 cm^{-1}. HRMS (EE) *m*/*z* 304.2242 [$(M)^+$; calcd for $C_{19}H_{32}OSi$, 304.2222].

Mixture of **9** and **10** (1.8:1): ^1H NMR (500 MHz, $CDCl_3$) δ 7.23–7.11 (m, 14H), 5.55 (dt, *J*=1.0, 15.5 Hz, 1H), 5.13 (dt, *J*=7.0, 15.5 Hz, 1H), 2.87 (d, *J*=13.0 Hz, 1H), 2.81 (d, *J*=13.5 Hz, 1H), 2.58 (dd, *J*=7.0, 13.5 Hz, 1.8H), 2.49 (d, *J*=6.5 Hz, 3.6H), 2.42 (dd, *J*=7.0, 13.5 Hz, 1.8H), 2.29 (m, 1.8H), 1.97 (m, 2H), 1.21 (m, 26H), 0.85 (m, 8.4H), 0.12 (s, 16.2H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) signals corresponding to **9** δ 248.7, 140.7, 129.3 (2C), 128.2 (2C), 125.8, 52.5, 40.5, 34.1, 33.9, 31.8, 29.5, 26.8, 22.6, 14.1, −3.2. Signals corresponding to **10** δ 136.2, 134.3, 130.6 (2C), 127.8 (2C), 127.3, 126.3, 70.3, 43.1, 32.5, 31.7, 29.7, 28.7, 22.6, 14.0, −4.2. IR (film) 3534, 3028, 2957, 1745, 1643, 1248, 843 cm^{-1}. HRMS for **10** (EI) *m*/*z* 286.2150 [$(M-H_2O)^+$; calcd for $C_{19}H_{30}Si$, 286.2117].

*4.3.3. Wittig rearrangements of compound **11**.* Applying the general procedure B to compound **11** (91 mg, 0.329 mmol, 1 equiv) and *sec*-BuLi (1.4 M in cyclohexane, 0.35 mL, 1.5 equiv) at −78 °C for 40 min, after purification by silica gel column chromatography (3% EtOAc in hexanes), afforded 56.2 mg (62%) of [1,2]-product **12**, 3.7 mg (4%) of [2,3]-product **13**, and 14 mg of unreacted **11** (15%) as colorless oils.

Compound **12**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (m, 2H), 7.17 (m, 1H), 7.10 (m, 2H), 5.46 (d, *J*=16.0 Hz, 1H), 5.14 (d, *J*=16.0 Hz, 1H),

2.88 (d, J=13.5 Hz, 1H), 2.83 (d, J=13.0 Hz, 1H), 0.92 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 136.1, 130.6 (2C), 129.2, 127.7 (2C), 126.3, 70.0, 43.1, 32.8, 29.9, −4.2. IR (film) 3534, 3028, 2959, 1248, 843 cm^{-1}. HRMS (EI) m/z 258.1820 [$(M-H_2O)^+$; calcd for $C_{17}H_{26}Si$, 258.1804].

Compound **13**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (m, 2H), 7.19 (m, 3H), 6.11 (dd, J=10.0, 18.5 Hz, 1H), 5.25 (dd, J=0.5, 18.0 Hz, 1H), 5.03 (t, J=3.0 Hz, 1H), 1.93 (dd, J=2.5, 9.0 Hz, 1H), 1.70 (d, J=3.5 Hz, 1H), 0.97 (s, 9H), 0.00 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.3, 142.1, 136.3, 127.8 (2C), 126.9 (2C), 126.2, 73.6, 65.0, 33.0, 28.9, −1.2. IR (film) 3422, 2955, 1246, 837 cm^{-1}. HRMS (EI) m/z 258.1791 [$(M-H_2O)^+$; calcd for $C_{17}H_{26}Si$, 258.1804].

*4.3.4. Wittig rearrangements of compound **14**.* Applying general procedure B to 360 mg (1.53 mmol) of **14** and 1.8 mL (2.30 mmol) of *s*-BuLi (1.3 M in cyclohexane) at −78 °C overnight, afforded 162 mg (46%) of a 1.68:1 mixture of **15** and **16** as a colorless oil.

Compound **15**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.12 (m, 5H), 2.67–2.57 (m, 1H), 2.54–2.41 (m, 1H), 1.89–1.67 (m, 2H), 1.24–1.21 (d, J=7.1 Hz, 3H), 0.11 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 248.2, 146.6, 128.4, 127.0, 126.0, 46.4, 39.3, 30.2, 22.4, −3.2. IR (neat) 1643 cm^{-1}. HRMS (EI) m/z 233.1358 [$(M-H)^+$; calcd for $C_{14}H_{21}OSi$, 233.1362].

Compound **16**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5H), 3.82–3.75 (q, J=6.9 Hz, 1H), 2.34–2.28 (m, 2H), 1.38 (d, J=6.9 Hz, 3H), 0.77–0.55 (m, 2H), −0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.8, 140.8, 128.8 (2C), 127.8 (2C), 127.0, 52.3, 35.6, 17.7, 10.3, −1.9. IR (neat) 1717, 1601 cm^{-1}. HRMS (CI) m/z 234.1466 [$(M)^+$; calcd for $C_{14}H_{22}OSi$, 234.1440].

*4.3.5. Wittig rearrangements of compound **17**.* Applying general procedure B to 165 mg (0.638 mmol) of **17** and 1.6 mL of *n*-BuLi (2.55 mmol, 4 equiv, 1.6 M in hexanes) at −78 °C, allowing the reaction to warm to −30 °C and stirring at this temperature for about 48 h, after purification by column chromatography on silica gel afforded 45 mg (32%) of a 4.53:1 mixture of **18** and **19** as light yellow oils. Note: the reported yield is based on 2.64:1 diastereomeric ratio of *anti*/*syn* **17**.

Compound **18**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.16 (m, 5H), 5.78–5.60 (m, 1H), 5.00–4.89 (m, 2H), 2.58–2.52 (m, 1H), 2.50–2.45 (m, 1H), 2.39–2.31 (m, 3H), 2.00–1.93 (m, 1H), 1.72–1.64 (m, 1H), 0.09 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.1, 144.4, 136.8, 128.4 (2C), 127.7 (2C), 126.2, 116.0, 46.1, 45.1, 41.4, 27.9, −3.2. IR (neat) 1717, 1643 cm^{-1}. HRMS (EI) m/z 260.1595 [$(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

Compound **19**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.08 (m, 5H), 5.68–5.60 (m, 1H), 5.00–4.91 (m, 2H), 3.72 (t, J=7.4 Hz, 1H), 2.81–2.75 (m, 1H), 2.45–2.39 (m, 1H), 2.31 (m, 2H), 0.74–0.68 (m, 1H), 0.62–0.56 (m, 1H), −0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 138.6, 135.9, 128.8 (2C), 128.2 (2C), 127.2, 116.6, 58.1, 36.7, 36.5, 10.1, −1.9. IR (neat) 1716, 1643 cm^{-1}. HRMS (EI) m/z 260.1593 [$(M)^+$; calcd for $C_{16}H_{24}OSi$, 260.1596].

*4.3.6. Wittig rearrangements of compound **20**.* Applying general procedure B to 69.5 mg of *syn*-**20** (0.265 mmol) and 0.33 mL of *n*-BuLi (0.5296 mmol, 2 equiv) in THF (3.3 mL) at −78 °C and then at 0 °C for 17 h afforded a mixture (15.8 mg) of **21** and **22** in a combined 23% yield as colorless oil along with 18.6 mg of unreacted *syn*-**20**. Column chromatography was performed with 3% EtOAc in hexanes.

Compound **21**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.03 (m, 5H), 2.39–2.35 (m, 1H), 2.30–2.24 (m, 1H), 2.20–2.15 (m, 1H), 2.08–2.02 (m, 1H), 1.80–1.73 (m, 1H), 1.71–1.63 (m, 1H), 0.94 (d, J=6.8 Hz, 3H), 0.68 (d, J=6.8 Hz, 3H), 0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 248.6, 143.8, 128.4 (2C), 128.1 (2C), 126.0, 52.4, 33.7, 25.2, 20.9, 15.3, −3.3. IR (neat) 1719, 1643 cm^{-1}. HRMS (APCI) m/z 263.1840 [$(M+H)^+$; calcd for $C_{16}H_{27}OSi$, 263.1831].

Compound **22**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.20 (m, 5H), 3.30 (d, J=10.2 Hz, 1H), 2.42–2.25 (m, 3H), 0.94 (d, J=6.3 Hz, 3H), 0.74–0.67 (m, 1H), 0.63 (d, J=6.8 Hz, 3H), 0.61–0.54 (m, 1H), −0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 211.7, 138.4, 128.7 (2C), 128.6 (2C), 127.0, 66.4, 37.8, 30.7, 21.7, 20.4, 9.9, −1.9. IR (neat) 1715 cm^{-1}. HRMS (CI) m/z 262.1755 [$(M)^+$; calcd for $C_{16}H_{26}OSi$, 262.1753].

*4.3.7. Wittig rearrangements of compound **23**.* Applying the general procedure B to compound **23** (*anti*/*syn*=1:1) (66 mg, 0.282 mmol, 1 equiv) and *n*-BuLi (1.6 M in cyclohexane, 0.53 mL, 3 equiv) at −78 °C and then at −30 °C for 3 h, after purification by silica gel column chromatography (3% EtOAc in hexanes), afforded 16.3 mg (26%) of **24**, 10.2 mg (14%) of **25** as colorless oils, and 7.5 mg of a mixture of *anti*-**23** and **26** (1:9 ratio). An analytical sample of **26** was obtained by column chromatography eluting with hexanes.

Compound **24**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.08 (d, J=7.8 Hz, 2H), 7.02 (d, J=8.4 Hz, 2H), 2.59 (m, 1H), 2.51 (ddd, A of ABX system, J=6.0, 9.0, 16.8 Hz, 1H), 2.41 (ddd, B of ABX system, J=6.0, 9.0, 17.4 Hz, 1H), 2.30 (s, 3H), 1.80 (m, 1H), 1.72 (m, 1H), 1.20 (d, J=6.6 Hz, 3H), 0.12 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 248.2, 143.6, 135.5, 129.1 (2C), 126.9 (2C), 46.5, 38.9, 30.3, 22.5, 21.0, −3.2. IR (film) 2959, 1643, 1250, 844 cm^{-1}. HRMS (EI) m/z 248.1595 [$(M)^+$; calcd for $C_{15}H_{24}OSi$, 248.1596].

Compound **25**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (d, J=8.0 Hz, 2H), 7.08 (d, J=8.5 Hz, 2H), 3.74 (q, J=7.0 Hz, 1H), 2.30 (m, 6H), 1.35 (d, J=7.0 Hz, 3H), 0.71 (ddd, A of ABX system, J=6.5, 10.0, 15.0 Hz, 1H), 0.60 (ddd, B of ABX system, J=6.5, 9.0, 14.0 Hz, 1H), 0.11 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.0, 137.9, 136.7, 129.5 (2C), 127.7 (2C), 51.9, 35.5, 21.0, 17.7, 10.4, −1.9. IR (film) 2955, 1716, 1456, 1250, 837 cm^{-1}. HRMS (EI) m/z 233.1363 [$(M-CH_3)^+$; calcd for $C_{14}H_{21}OSi$, 233.1362].

Compound **26**: (1:0.7 mixture of diastereomers) ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (m, 8H), 6.97 (d, J=8.0 Hz, 2.8H), 6.91 (d, J=8.5 Hz, 2.8H), 2.90 (m, 1.4H), 2.72 (m, 2H), 2.32 (s, 6H), 2.25 (s, 4.2H), 1.20 (m, 4.2H), 0.98 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 142.8, 135.4, 135.0, 128.9, 128.5, 127.7, 127.5, 46.8, 45.8, 21.2, 21.0, 20.9, 17.8. IR (film) 3021, 2961, 1514, 1452, 817 cm^{-1}. HRMS (EI) m/z 238.1724 [$(M)^+$; calcd for $C_{18}H_{22}$, 238.1722].

*4.3.8. Wittig rearrangements of anti/syn E-**30**.* Applying representative procedure B to 235 mg (0.946 mmol) of *E*-**30** (*anti*/*syn*=1.5:1) and 2.36 mL of *n*-BuLi (3.78 mmol, 4 equiv, 1.6 M in hexanes) in THF (12 mL) at −30 °C for 44 h. After purification by column chromatography on silica gel (30% CH_2Cl_2 in hexanes) 101 mg of *anti E*-**30** (43%), 10.1 mg of **32** (16%), and 72 mg of a mixture of **31** (23%, *anti*/*syn*=1.9:1) and **33** (6%, *anti*/*syn*=1.44:1) were obtained. Analytical samples of **31** and **33** were obtained by subsequent column chromatography of the mixture (30% CH_2Cl_2 in hexanes).

Compound **31** (mixture of diastereomers *anti*-**31**/*syn*-**31**, 0.65:0.35 ratio): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.24 (m, 2H), 7.18–7.12 (m, 3H), 2.64 (m, 0.65H), 2.61 (m, 0.65H), 2.52 (m, 0.35H), 2.46 (m, 0.35H), 2.38–2.26 (m, 2H), 1.21 (d, J=6.6 Hz, 1.05H), 1.20 (d, J=7.2 Hz, 1.95H), 0.84 (d, J=6.6 Hz, 1.05H), 0.70 (d, J=6.6 Hz, 1.95H), 0.14 (s, 5.85H), 0.08 (s, 3.15H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer (*anti*-**31**): δ 248.6, 145.4, 128.1 (2C), 127.9 (2C), 126.0, 53.0, 44.6, 33.5, 18.2, 18.04, −3.16. Minor diastereomer (*syn*-**31**): δ 248.7, 146.3, 128.2 (2C), 127.6 (2C), 126.0, 54.0, 45.0, 33.8, 18.05, 17.4, −3.25. IR (neat) 1643 cm^{-1}. HRMS (ESI) m/z 249.1665 [$(M+H^+)$; calcd for $C_{15}H_{25}OSi$, 249.1675].

Compound **32** (mixture of diastereomers, 0.88:0.12 ratio, relative stereochemistry not assigned): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26–7.14 (m, 5H), 5.72 (dd, J=1.2, 15.6 Hz, 0.12H), 5.59 (dd, J=1.2, 15.6 Hz, 0.88H), 5.28 (dq, J=6.6, 15.6 Hz, 0.12H), 5.12 (dq, J=6.6, 15.6 Hz, 0.88H), 3.04 (q, J=7.2 Hz, 0.88H), 3.00 (q, J=7.2 Hz, 0.12H), 1.71 (dd, J=1.8, 6.6 Hz, 0.36H), 1.61 (dd, J=1.2, 6.6 Hz, 2.64H), 1.32 (d, J=7.2 Hz, 2.64H), 1.27 (d, J=7.2 Hz, 0.36H), 1.03 (s, 0.12H), 1.02 (s,

0.88H), −0.03 (s, 7.92H), −0.09 (s, 1.08H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer: δ 142.8, 135.1, 128.9 (2C), 127.8 (2C), 126.3, 120.8, 73.6, 46.8, 17.8, 16.4, −2.5. Minor diastereomer: δ 143.0, 133.5, 129.2 (2C), 127.9 (2C), 126.6, 122.0, 73.4, 46.9, 18.0, 16.5, −3.0. HRMS (CI) *m*/*z* 249.1666 [(M+H)$^+$; calcd for $C_{15}H_{24}OSi$, 249.1675].

Compound **33** (mixture of diastereomers, *anti*-**33**/*syn*-**33**, 0.55:0.45) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.24–7.20 (m, 3H), 3.78 (q, *J*=7.2 Hz, 0.55H), 3.71 (q, *J*=7.2 Hz, 0.45H), 2.36 (m, 0.45H), 2.33 (m, 0.55H), 2.14 (dd, *J*=10.2, 16.8 Hz, 0.45H), 2.08 (dd, *J*=10.8, 16.2 Hz, 0.55H), 1.38 (d, *J*=6.6 Hz, 1.35H), 1.37 (d, *J*=7.2 Hz, 1.65H), 1.18 (m, 0.55H), 1.13 (m, 0.45H), 0.82 (d, *J*=7.8 Hz, 1.35H), 0.69 (d, *J*=7.2 Hz, 1.65H), −0.118 (s, 4.95H), −0.160 (s, 4.05H). ^{13}C NMR (151 MHz, $CDCl_3$) major diastereomer (*anti*-**33**): δ 210.8, 140.6, 128.8 (2C), 127.91 (2C), 127.05, 52.2, 43.3, 17.6, 15.3, 14.1, −3.55. Minor diastereomer (*syn*-**33**): δ 211.4, 128.7 (2C), 127.89 (2C), 127.03, 53.6, 43.5, 17.4, 15.5, 14.7, −3.54. IR (neat) 1718 cm^{-1}. HRMS (ESI) *m*/*z* 249.1667 [(M+H$^+$); calcd for $C_{15}H_{25}OSi$, 249.1675].

*4.3.9. Wittig rearrangement of compound syn Z-**30**.* Following the general procedure B to 253.8 mg of *syn Z*-**30** (1.02 mmol) in 10.5 mL of THF at −78 °C was added 2.56 mL of *n*-BuLi (4.086 mmol, 4 equiv, 1.6 M in hexanes), the cold bath was removed and the reaction stirred at room temperature for 48 h. After work up and column chromatography (gradient of 2–10% EtOAc in hexanes, then 50% EtOAc in hexanes) afforded 142.1 mg of *syn Z*-**30** (56%, dr=18:1), 11.1 mg of a 1:1 mixture of **31** (*syn*/*anti*=1.1:1) and **33** (*syn*/*anti*=1:1.6), 15.6 mg of **34** (6%, single diastereomer), 13 mg of **35** (7%, dr=3:1), and 5.4 mg of **36** (3%, *syn*/*anti*=1.3:1).

Compound **34** (tentatively assigned as *syn*-**34**):[17] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 2H), 7.31 (m, 2H), 7.21 (tt, *J*=1.5, 7.5 Hz, 1H), 5.97 (dd, *J*=8.0, 19.0 Hz, 1H), 5.70 (dd, *J*=1.0, 19.0 Hz, 1H), 2.52 (m, 1H), 1.85 (s, 1H), 1.50 (s, 3H), 0.84 (d, *J*=6.5 Hz, 1H), 0.04 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.8, 147.0, 132.4, 127.8 (2C), 126.4, 125.2 (2C), 75.9, 51.4, 28.3, 14.5, −1.2. IR (neat) 3474 cm^{-1}. HRMS (ESI) *m*/*z* 249.1680 [(M+H)$^+$; calcd for $C_{15}H_{25}OSi$, 249.1675].

Compound **35** (mixture of diastereomers, 0.63:0.37 ratio): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 3H), 7.19 (m, 2H), 5.68 (m, 0.37H), 5.49 (m, 0.63H), 5.40 (m, 0.37H), 5.31 (m, 0.63H), 4.51 (m, 1H), 1.66 (ddd, *J*=0.5, 2.0, 7.0 Hz, 1.11H), 1.53 (ddd, *J*=0.5, 1.5, 6.5 Hz, 1.89H), 1.43 (s, 1H), 1.33 (dd, *J*=0.5, 7.0 Hz, 1.89H), 1.21 (dd, *J*=0.5, 7.5 Hz, 1.11H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.28, 143.26, 131.33, 131.30, 128.6, 128.2, 128.1, 128.1, 127.7, 126.9, 126.7, 126.4, 71.7, 71.5, 46.6, 45.9, 17.5, 16.0, 13.5, 13.2. IR (neat) 3397 cm^{-1}.

Compound **36** (mixture of diastereomers 1:1 ratio): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (m, 1H) 9.57 (m, 1H), 7.28 (m, 4H), 7.18 (m, 2H), 7.14 (m, 4H), 2.67 (m, 1H), 2.56 (m, 1H), 2.49 (ddd, *J*=1.0, 4.5, 16.0 Hz, 1H), 2.33–2.26 (m, 3H), 2.17 (ddd, *J*=3.0, 9.0, 16.0 Hz, 1H), 2.07 (ddd, *J*=2.5, 8.5, 16.0 Hz, 1H), 1.26 (d, *J*=2.5 Hz, 3H), 1.25 (d, *J*=2.5 Hz, 3H), 0.99 (d, *J*=6.5 Hz, 3H), 0.85 (d, *J*=6.5 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.8, 202.5, 145.7, 144.8, 128.4, 128.2, 127.8, 127.5, 126.3, 126.2, 49.5, 48.3, 45.1, 44.5, 34.6, 34.4, 18.4, 18.03, 17.98, 17.6. IR (neat) 1724 cm^{-1}. Diastereomers **36** are known compounds and have spectral data in accord with those previously reported.[20b]

4.4. Preparation of diastereomeric 27

A 100 mL round-bottomed flask equipped with a magnetic stir bar and a N_2 line was charged with 9-BBN (0.5 M solution in THF, 2.04 mL, 1.02 mmol) and substrate **14** (671 mg, 2.85 mmol) was then added as a THF solution (0.57 M). The reaction was refluxed at an oil bath temperature of 90 °C, for 10 h. The reaction mixture was cooled to 55–65 °C and ethanol (2.0 mL), NaOH (6 M, 0.5 mL), and H_2O_2 (30% w/w, 1.0 mL) were added. The reaction was stirred at 55–65 °C for 1 h and cooled to room temperature. The aqueous phase was saturated with K_2CO_3, phases were separated, the organic phase was dried over anhydrous magnesium sulfate, and concentrated to afford the crude product. Purification by silica gel (EtOAc 0–10% in hexanes) gave 702 mg of pure *syn*-**27**/*anti*-**27** in 97% yield. IR (neat) 3370 cm^{-1}.

anti-**27**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.23 (m, 5H), 4.56 (q, *J*=6.5 Hz, 1H), 3.86 (m, 1H), 3.78 (m, 1H), 3.23 (t, *J*=5.0 Hz, 1H), 2.75 (m, 1H), 2.20–2.13 (m, 1H), 1.63 (m, 1H), 1.42 (d, *J*=6.5 Hz, 3H), −0.06 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 128.2 (2C), 127.5, 126.8 (2C), 76.4, 70.1, 62.4, 31.7, 23.7, −2.8. HRMS (EI) *m*/*z* 253.1618 [(M+H)$^+$; calcd for $C_{14}H_{25}O_2Si$, 253.1624].

syn-**27**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 4H), 7.29 (m, 1H), 4.36 (q, *J*=6.5 Hz, 1H), 3.54–3.45 (m, 2H), 3.26 (dd, *J*=4.5, 9.5 Hz, 1H), 1.81 (m, 1H), 1.67–1.60 (m, 2H), 1.42 (d, *J*=6.5 Hz, 3H), 0.09 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 128.5 (2C), 127.8, 126.8 (2C), 77.9, 69.1, 61.3, 33.8, 23.6, −2.5. HRMS (EI) *m*/*z* 253.1627 [(M+H)$^+$; calcd for $C_{14}H_{25}O_2Si$, 253.1624].

4.5. Preparation of ester *syn*-28

A mixture of the substrate alcohol obtained by 9-BBN oxidation of reactive *syn*-**27** (201 mg, 0.80 mmol) and 3,5-dinitrobenzoyl chloride (366 mg, 1.59 mmol) in pyridine as solvent, was heated to reflux for 52–55 h. Then the solvent was removed under reduced pressure and the crude product purified by chromatography on silica gel (hexanes/EtOAc 0–10%) to afford 194 mg, 55% of the expected ester *syn*-**28** as a solid. Recrystallization from a 1:1 EtOH/hexane mixed solvent afforded product as colorless crystals mp 74.5–75.5 °C. IR (neat) 1728, 1630 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.17 (t, *J*=2.2 Hz, 1H), 8.88 (d, *J*=2.2 Hz, 2H), 7.29–6.99 (m, 5H), 4.36–4.29 (m, 2H), 4.18–4.10 (m, 1H), 3.25–3.20 (dd, *J*=8.0, 6.0 Hz, 1H), 1.90–1.83 (m, 2H), 1.41 (d, *J*=6.3 Hz, 3H), 0.15 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 162.2, 148.4, 143.9, 134.0, 129.2, 128.2, 127.4, 126.7, 122.1, 78.1, 66.7, 64.4, 30.6, 23.6, −2.7. HRMS (ESI) *m*/*z* 447.1599 [(M+H)$^+$; calcd for $C_{21}H_{27}N_2O_7Si$, 447.1587].

4.6. Preparation of *cis*-29 and *trans*-29

To a solution of unreactive (*anti*) **17** (167 mg, 0.641 mmol) in CH_2Cl_2 (10 mL, ~0.7 M) was added Grubbs second-generation catalyst (4 mol %, 21.4 mg, 0.025 mmol) and the solution was stirred under nitrogen at room temperature for 3 h. The reaction mixture was concentrated and purified by column chromatography (10% CH_2Cl_2 in hexanes) to afford 144 mg of *cis*-**29** (97%).

cis-**29**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.22 (m, 5H), 5.82–5.78 (m, 2H), 4.38 (dd, *J*=3.5, 10 Hz, 1H), 4.17–4.15 (m, 1H), 2.26–2.12 (m, 2H), 0.08 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 128.10 (2C), 128.06, 126.9, 125.6 (2C), 121.1, 75.3, 71.6, 34.2, −4.0. HRMS (CI) *m*/*z* 261.1681 [(M+H$^+$) calcd for $C_{16}H_{24}OSi$, 261.1675]. The relative stereochemistry of *cis*-**29** was assigned based on positive NOESY signals between protons at 4.15 ppm and 2.26–2.12 ppm.

Following the same procedure for the reactive (*syn*) **17** (184 mg, 0.707 mmol) and Grubbs second-generation catalyst (4 mol %, 24 mg, 0.028 mmol) in CH_2Cl_2 for 3 h, followed by column chromatography (30% CH_2Cl_2 in hexanes) afforded 151 mg (92%) of *trans*-**29**.

trans-**29**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.24 (m, 5H), 5.83–5.76 (m, 2H), 4.72 (t, *J*=5.5 Hz, 1H), 4.01 (m, 1H), 2.41–2.38 (m, 2H), 0.09 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 128.5 (2C), 128.4, 127.5, 126.9 (2C), 120.3, 72.6, 70.4, 30.4, −2.7. HRMS (CI) *m*/*z* 261.1664 [(M+H$^+$) calcd for $C_{16}H_{24}OSi$, 261.1675]. The relative stereochemistry of *trans*-**29** was confirmed based on negative NOESY signals between protons at 4.72 ppm and 4.01 ppm.

4.7. Preparation of compound 38

The [1,4]-Wittig product **31** from the Wittig rearrangement of α-alkoxysilane of *E*-**30** (217 mg, 0.87 mmol) was dissolved in THF

(0.24 M, 3.6 mL), and 3 N NaOH (0.83 mL/mmol starting material, 0.72 mL) added. The mixture was heated to 35–40 °C, and then oxidized by dropwise addition of 30% H_2O_2 (0.42 mL/mmol starting material, 0.36 mL), while maintaining the reaction temperature below 50 °C for 2 h. The aqueous phase was cooled to 0 °C, and acidified to pH of 1–2 with 6 M HCl. The resulting aqueous material was extracted with ether (5×20 mL), and the ether solution dried with anhydrous $MgSO_4$. Filtration and concentration afforded 158 mg (94% yield) of diastereomeric **38** as a thick colorless oil. Purification by column chromatography on silica gel (hexane/EtOAc 0–10%) afforded **38** as a 2.8:1 mixture of diastereomers (ratio by ^{1}H NMR). IR (neat) 3100–2500 (br), 2967, 1707, 1495, 1452, 1412, 1290 cm^{-1}.

Major, *anti*-**38**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.49 (br s, 1H), 7.31–7.18 (m, 5H), 2.72–2.65 (quint, J=7.1 Hz, 1H), 2.53–2.48 (dd, J=14.8, 4.4 Hz, 1H), 2.28–2.18 (m, 1H), 2.14–2.09 (dd, J=15.1, 9.1 Hz, 1H), 1.28–1.26 (d, J=7.1 Hz, 3H), 0.88 (d, J=6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 144.8, 128.2, 127.6, 126.2, 44.4, 38.9, 36.2, 18.3, 17.5.

Minor, *syn*-**38**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.49 (br s, 1H), 7.33–7.18 (m, 5H), 2.63–2.56 (quint, J=7.1 Hz, 1H), 2.35–2.31 (apparent dd, J=15.4, 4.4 Hz, 1H), 2.28–2.18 (m, 1H), 2.04–1.99 (dd, J=14.8, 9.3 Hz, 1H), 1.27–1.24 (d, J=7.1 Hz, 3H), 1.04 (d, J=6.6 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.8, 145.7, 128.2, 127.5, 126.1, 44.7, 39.8, 36.4, 18.3, 17.2. *anti*-**38** and *syn*-**38** are known compounds and have spectral data in accord with those previously reported.[19]

4.8. Assignment of relative stereochemistry for compound 33

*4.8.1. Preparation of **39**.* To a cold (−78 °C) solution of **33** (50 mg, 0.20 mmol, dr=1.4:1) in 1:1 CH_2Cl_2/EtOH (3 mL) was added a suspension of $NaBH_4$ (15.2 mg, 2 equiv) in EtOH (0.8 mL). After 1 h the temperature was slowly raised to rt and the reaction stirred overnight. The reaction mixture was then treated with H_2O (2 mL) and diluted with diethyl ether. The aqueous phase was washed with diethyl ether (×2). Combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated. Column chromatography (5% EtOAc in hexanes) gave 28.5 mg (57%) of **39** in two fractions of different diastereomeric ratio along with 5.2 mg (11%) of unreacted **33**.

Compounds **39** (major diastereomer): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.20 (m, 3H), 3.80 (m, 1H), 2.72 (quint, J=6.6 Hz, 1H), 1.42 (m, 1H), 1.31 (d, J=7.2 Hz, 3H), 1.29 (d, J=4.8 Hz, 1H), 1.07 (m, 1H), 0.84 (s, 3H), 0.82 (m, 1H), −0.10 (m, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.8, 128.4 (2C), 127.7 (2C), 126.3, 73.0, 46.4, 36.3, 15.9, 15.0, 13.1, −3.6. IR (neat) 3423, 2955, 1456, 1248, 839 cm^{-1}. HRMS (ESI) m/z 232.1651 [(M−OH)$^+$; calcd for $C_{15}H_{24}Si$, 232.1647].

*4.8.2. Preparation of **40**.* One fraction of **39** (15.6 mg, 0.063 mmol, dr=10:2:1) was dissolved in pyridine (1 mL) and 3,5-dinitrobenzoyl chloride (flakes were crushed prior to addition) was added in one portion. After 48 h the mixture was diluted with diethyl ether (15 mL) and washed with 1 M HCl (2 mL×3), H_2O, brine, dried over $MgSO_4$, and concentrated. Partial separation of the diastereomers (two fractions) by column chromatography (4% EtOAc in hexanes) gave 24.4 mg (56%) of **40** as a solid. Recrystallization of one fraction from CH_2Cl_2/hexanes gave a single diastereomer of **40** whose relative stereochemistry was determined by X-ray crystallography.

Compound **40** (major diastereomer): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.22 (t, J=2.0 Hz, 1H), 9.13 (d, J=2.0 Hz, 2H), 7.30 (t, J=7.5 Hz, 2H), 7.22 (m, 3H), 5.86 (m, 1H), 3.09 (m, 1H), 1.75 (ddd, J=2.5, 10.0, 13.0 Hz, 1H), 1.32 (d, J=7.0 Hz, 3H), 1.26 (ddd, J=2.5, 12.0, 14.5 Hz, 1H), 0.87 (d, J=7.5 Hz, 3H), 0.47 (m, 1H), −0.14 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4, 148.8 (2C), 142.7, 134.3, 129.4 (2C), 128.7 (2C), 127.7 (2C), 127.0, 122.3, 79.4, 44.5, 34.2, 17.7, 15.4, 13.5, −3.7. Mp 139–140 °C. IR (neat) 3107, 2957, 1726, 1545, 1348, 1278, 1170 cm^{-1}.

*4.8.3. Preparation of anti-**33** from recrystallized **40**.* To a solution of **40** (4.4 mg, 0.010 mmol, dr>95:5) in THF (1 mL) was added 3 M NaOH (0.5 mL) and the mixture stirred for 2 h in an oil bath at 45 °C. Then, the reaction mixture was diluted with diethyl ether (10 mL). The aqueous phase was washed with diethyl ether (2 mL×2). Combined organic extracts were washed with H_2O, brine, dried over $MgSO_4$, and concentrated. Pasteur pipette chromatography (5% EtOAc in hexanes) gave 1.5 mg (61%) of **39** as a single diastereomer. This alcohol (1.5 mg) was dissolved in dry CH_2Cl_2 (0.5 mL) and DMP (0.3 M in CH_2Cl_2, 0.25 mL, excess) was added at room temperature. After 1 h the reaction mixture was concentrated, suspended in 5% EtOAc in hexanes, and filtered through a plug of silica to give ~1.5 mg (ca. 100%) of *anti*-**33**.

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Supplementary data

Supplementary data: Copies of ^{1}H and ^{13}C NMR for compounds **5**–**40** and X-ray structural data of compounds *syn*-**28** and **40**. The crystal structures of *syn*-**28** and **40** were deposited in the Cambridge Crystallographic Data Centre and allocated deposition numbers CCDC 886782 and 886781, respectively. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.10.091.

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15. Notice that although crystalline *syn*-**28** was obtained from a mixture of diastereomers *syn*-**28**/*anti*-**28**, independent derivatization of the 'less reactive' *anti*-**14** following the sequence in Scheme 6 led to a clear oil spectroscopically identical to the non-crystalline ester *anti*-**28** obtained from the mixture of diastereomers *syn*-**28**/*anti*-**28** depicted in Scheme 6.
16. *syn Z*-**30** and *anti Z*-**30** were prepared by semihydrogenation of the corresponding alkynes *syn*/*anti*-**37**. See Experimental section

17. *sec*-BuLi led to lower conversion. No improvement was observed with *n*-BuLi/TMEDA. The 'super' basic mixture of *n*-BuLi/potassium *tert*-butoxide led to complete desilylation of *Z*-**30** followed by rearrangement in low yields, significant amounts of alkylated products were also observed.
18. The relative stereochemistry of this diastereomer was assigned tentatively as *syn*-**34** by comparison with the ^{1}H NMR of the *syn* and *anti* desilylated analogs Wada, R.; Oisaki, K.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2004**, *126*, 8910–8911 Attempts to protodesilylate the [2,3]-Wittig product *syn*-**34** with TBAF or TFA failed.
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