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# Domino Alkene-Isomerization–Claisen Rearrangement Strategy to Substituted Allylsilanes

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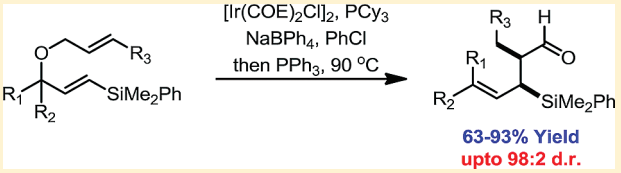
Supporting Information

**ABSTRACT:** A one-pot isomerization–Claisen protocol has been developed for the synthesis of highly substituted allylsilanes. Monosilylated divinyl ethers can be isomerized using a cationic iridium(I) catalyst followed by a thermal Claisen rearrangement to provide the allylsilanes in excellent yields and diastereoselectivities.

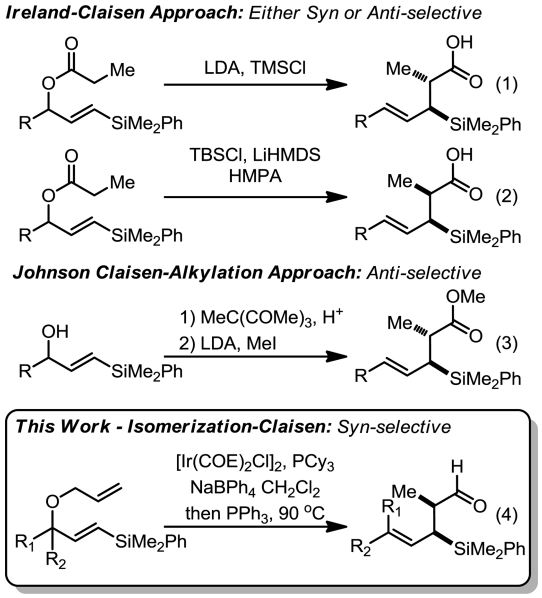



Allylsilanes bearing stereogenic centers at the carbon–silicon bond have been shown to be very versatile synthetic intermediates in organic synthesis.[1] They have been utilized in many stereospecific and stereoselective reactions including Sakurai allylations,[2] oxidations,[3] aminations,[4] tetrahydrofuran and cyclopentane annulations,[5] cyclopropanations,[6] and protodesilylations[7] and as traceless stereodirecting groups for boron aldol reactions.[8] They have also been impressively demonstrated in the arena of total synthesis, with many polyketide-derived natural product syntheses benefiting from these flexible intermediates.[9]

We recently reported a new method for the hydrosilylation of propargylic alcohols which works especially well for sterically encumbered tertiary alcohols.[10] We wanted to use these compounds to synthesize highly substituted allylsilanes via a Claisen rearrangement strategy. Panek reported the conversion of secondary hydrosilylated alcohols to chiral allylsilanes using both Johnson[11] and Ireland–Claisen[12] rearrangements forming two contiguous stereogenic centers in the process. When the Ireland–Claisen approach is used the diastereoselctivity can be directed by controlling the enol ether geometry to provide either *syn* or the *anti* isomer selectively, generally in good diastereoselctivities (eqs 1 and 2). Alternatively, the product of the Johnson–Claisen approach can undergo base-mediated α-alkylation with alkyl halides with the *anti* diastereomer being favored (eq 3).[13]

Our stategy was to perform an isomerization–Claisen reaction of a monosilylated bis-allylic ether to provide products complementary to those previously reported (eq 4).[14] This approach would afford highly substituted chiral allylsilanes as the *syn* diastereoisomer at the aldehyde oxidation level. The major advantages of this are the mild, neutral reaction conditions and the tolerance of tertiary-substituted allyl ethers which generate trisubstituted alkenes on the allylsilane moiety. Herein we report a simple procedure for the synthesis of allylsilanes with high diastereoselectivity, predominately as the *syn* diastereoisomer.

We began investigating whether we could isomerize the allyl ethers to the corresponding vinyl ether using basic conditions (Table 1). All attempts at performing this were unsuccessful with extensive decompsition observed. Several isomerization–Claisen rearrangements have been reported using a variety of transition-metal catalysts, including ruthenium and iridium.[15] An isomerization–Claisen reaction has been reported previously using a similar substrate and $(Ph_3P)_3RuCl_2$ as the catalyst; however, this required very high temperature (190 °C) and led to a near 1:1 mixture of diastereomers.[16] We began investigating the use of these catalysts and found that the combination of Grubbs' first-generation metathesis




catalyst and ethyl vinyl ether (which forms an isomerization catalyst in situ) gave good reactivity; however, the resulting product was a 58:42 mix of diastereoisomers.[17] Similarly, the combination of $[Ir(COD)Cl]_2$ and $Cs_2CO_3$ gave good reactivity and a 55:45 mix of diastereoisomers.[18] Both these conditions use elevated temperatures (ca. 100 °C) for the isomerization, which leads to significant epimerization of the resulting aldehyde center.

Nelson found a powerful solution to this problem by using a highly active cationic Ir(I) catalyst, which performs the isomerization at ambient temperature.[19] Following isomerization, $PPh_3$ is added which sequesters the Ir catalyst and negates its Lewis acidic properties.[20] Gratifyingly, when this procedure was used, the isomerization–Claisen product could be isolated in 95:5 dr. A minor modification of the solvent from $CH_2Cl_2$ to PhCl was required as dichloromethane was not high enough boiling to perform the Claisen rearrangement efficiently. The use of 1,2-dichloroethane, the other solvent used by Nelson, resulted in a very slow isomerization reaction. However, when

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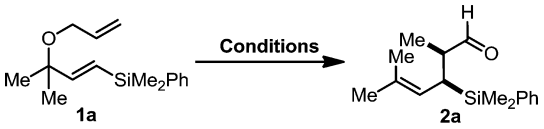
**Table 1. Optimization Studies**



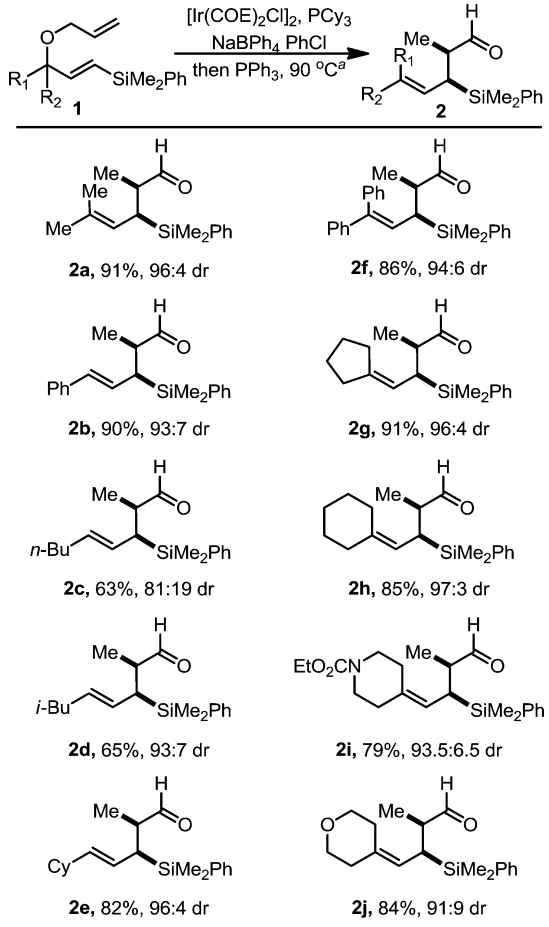

| entry | conditions | yield[a] (%) | dr[b] |
|---|---|---|---|
| 1 | *t*-BuOK, toluene, 90 °C | dec | |
| 2[c] | Grubbs I, $EtOCHCH_2$, toluene, 100 °C | 87 | 58:42 |
| 3[d] | $[Ir(COD)Cl]_2$, $CS_2CO_3$, toluene, 90 °C | 73 | 53:47 |
| 4[e] | $[Ir(COE)_2Cl]_2$, $PCy_3$, $NaBPh_4$, $CH_2Cl_2$/acetone (20:1) then $PPh_3$, 40 °C | 45 | 95:5 |
| 5[e] | $[Ir(COE)_2Cl]_2$, $PCy_3$, $NaBPh_4$, $(CH_2Cl)_2$/acetone (20:1) then $PPh_3$, 80 °C | 20 | 95:5 |
| **6**[e] | **$[Ir(COE)_2Cl]_2$, $PCy_3$, $NaBPh_4$, PhCl/acetone (20:1) then $PPh_3$, 90 °C** | **91** | **95:5** |

[a]Isolated yield. [b]Determined by $^1H$ NMR. [c]5 mol %. [d]2 mol % dimer. [e]1 mol % of dimer, 6 mol % of $PCy_3$, 2 mol % of $NaBPh_4$ then 6 mol % of $PPh_3$.

chlorobenzene was used, a fast isomerization occurred. This, coupled with its high boiling point, allowed a thermal Claisen rearrangement to take place at 90 °C to provide a yield of 91% in a 95:5 diastereomeric ratio.

We began to examine the scope of the reaction (Table 2) and discovered allyl ethers derived from secondary alcohols worked with both aryl and alkyl substituents tolerated. The phenyl substituent gave excellent yields and diastereoselectivities of the requisite allylsilane **2b**. Alkyl substituents gave the corresponding allylsilane **2c**–**e** in moderate yields and diasteroselectivities. The isomerization of these substrates

**Table 2. Substrate Scope**

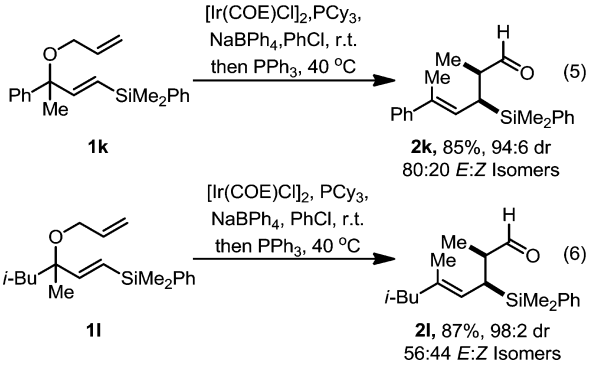



[a]Conditions: 1 mol % of $[Ir(COE)Cl]_2$, 6 mol % of $PCy_3$, 2 mol % of $NaBPh_4$, PhCl/acetone (20:1), rt, 0.75–35 h, then 6 mol % of $PPh_3$, 90 C, 0.75–35 h. For full details, see the Experimental Section.

generally occurs within 1 h; however, the Claisen rearrangement is slower to occur. The lower diastereoselectivity observed is due to the prolonged reaction times thus allowing the aldehyde product to epimerize. The use of a more bulky cyclohexyl substituent accelerates the Claisen rearrangement and provides allylsilane **2e** in good yield and excellent dr.

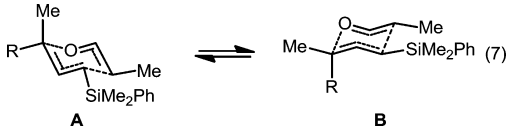
We next investigated the tertiary alcohol derived substrates. As was mentioned previously, the dimethyl derivative could be converted to the allylsilane in excellent yields and diastereoselctivities. Similarly, the diphenyl **2f** and cycloalkyl **2g,h** substrates performed the Claisen rearrangement very quickly, though the isomerization was slow, to provide the corresponding allylsilanes **2f**–**h**. Once again, in excellent yields and diastereoselectivities were obtained. The isomerization does not appear to be adversely effected by basic heteroatoms with good yields and diastereoselectivities being obtained for the carbamate protected piperidine **2i** and pyran **2j**.

Unsymmetrical tertiary allylic ethers were also examined to see whether we could control *E*/*Z* isomers in the corresponding allylsilane. We examined the phenyl methyl substrate **1k**, and under standard conditions we observed a 93% yield; however, the allylsilane **2k** was produced as a 55:45 mixture of *E*/*Z* isomers (eq 5). We discovered




that by performing the Claisen rearrangement we could improve this ratio to 80:20 with excellent diastereoselectivity.[21] We next turned our attention to the methyl isobutyl derivative **1l**, which gave an excellent yield of **2l** as a 52:48 mix of *E*/*Z* isomers at 90 °C. Lowering the temperature to 40 °C did not alter this ratio significantly with a 56:44 ratio being observed (eq 6).

These findings are consistent with a chair-type transition state which correlate to the substituent *A* values (eq 7). There is a large difference in *A* values between phenyl and methyl (Ph = 3.1; Me =





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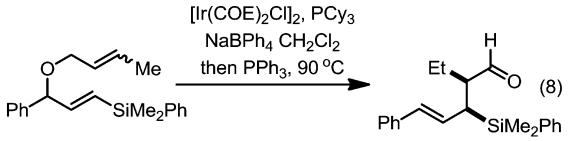
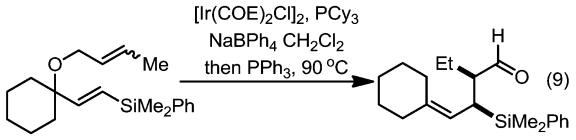
1.8), which would account for increased selectivity at lower temperatures, as conformation **A** will be more favored than **B**, whereas the difference between isobutyl and methyl is very small (*i*-Bu = 2.1; Me = 1.8), and therefore, very little selectivity is observed.[22]

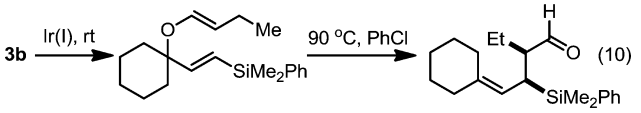
We also investigated substitution on the allylic ether. The crotylation reaction of the allylic alcohol with crotyl bromide provides the corresponding crotyl products as a mixture of geometric isomers (75:25 secondary phenyl and 85:15 for the tertiary cyclohexyl substrates) (eqs 8 and 9). When these were subjected to the standard reaction conditions described previously, they underwent the isomer-




**3a**, *75:25 E/Z isomers* **4a**, 51%, 97:3 dr




**3b**, *85:15 E/Z isomers* **4b**, 93%, 97:3 dr




**5**, 95%, *E only* **4b**, 94%, 97:3 dr

ization and subsequent Claisen rearrangement to provide the $\alpha$-ethyl products. The phenyl substrate **3a** afforded the ethyl product **4a** in 51% yield as a 97:3 mixture of diastereomers and the cyclohexyl derivative **3b** performs excellently to give the ethyl product **4b** in 93% yield and 97:3 dr.

Both of these reactions take a mixture of *E*/*Z* isomers and during the isomerzation procedure convert them to a single *E* isomer in the vinyl ether intermediate. This can then undergo the rearrangement with near complete stereocontrol. To prove this, we performed the isomerization and isolated the vinyl ether **5** which was formed exclusively as the *E* isomer. Furthermore, the pure *E* vinyl ether was subjected to the rearrangement conditions and we obtained the same diastereoselectivity (eq 10), which further supports the fact that the diastereoselectivity is entirely derived from the Claisen rearrangement of the geometrically pure vinyl ether.

In conclusion, we have developed a rapid and reliable method for the synthesis of highly substituted chiral allylsilanes containing two contiguous stereogenic centers based on the isomerization−Claisen work developed by Nelson. We have demonstrated the formation of trisubstituted alkenes and the use of internal allylic ethers. Our approach gives the *syn*-isomer and is complementary to approaches developed by others. The use of these compounds in synthesis is currently being explored.

## EXPERIMENTAL SECTION

**General Procedure A: Formation of Allyl Ethers.** To a solution of vinylsilane alcohols[10] in DMF (0.08 M) cooled to 0 °C was added NaH (2 equiv, 60% unwashed) in one portion followed by allyl bromide (2 equiv). The mixture was stirred for 1 h, quenched with water, extracted with EtOAc (3 × 25 mL), washed with water (25 mL) and brine (50 mL), and dried over $MgSO_4$ to afford the requisite allyl ether following column chromatography (9:1 hexane−EtOAc).

**(*E*)-(3-(Allyloxy)-3-methylbut-1-en-1-yl)dimethyl(phenyl)-silane (1a).** Alcohol (1.91 g, 8.67 mmol) was used to afford **1a** (2.03 g, 90%) as a colorless oil: $R_f$ (9:1 hexane−ethyl acetate) = 0.91; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 3069, 1646, 1111,1084, 993, 731, 488 ; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.54−7.48 (2H, m), 7.37−7.32 (3H, m), 6.11 (1H, d, *J* = 19.1 Hz), 5.91 (1H, d, *J* = 19.1 Hz), 5.96−5.84 (1H, m), 5.25 (1H, dd, *J* = 17.3, 1.7 Hz), 5.11 (1H, dd, *J* = 10.3, 1.7 Hz), 3.83 (2H, dt, *J* = 5.5, 1.7 Hz), 1.29 (6H, s), 0.35 (6H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 153.1, 138.7, 136.0, 133.8, 128.9, 127.7, 126.2, 115.8, 76.5, 64.2, 25.9, −2.5; HRMS (ES+) calcd for $C_{16}H_{27}NOSi$ [M + $NH_3$] 278.1940, found 278.1945.

**Synthesis of (*E*)-(3-(Allyloxy)-3-phenylprop-1-en-1-yl)-dimethyl(phenyl)silane (1b).** Alcohol (200 mg, 0.746 mmol) was used to afford **1b** (161 mg, 70%) as a colorless oil: $R_f$ (9:1 hexane−ethyl acetate) = 0.80; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2900, 1522, 1400, 999, 767 565, 490; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.57−7.52 (2H, m), 7.42−7.30 (8H, m), 6.26 (1H, ddd, *J* = 18.8, 5.8, 1.7 Hz), 6.12 (1H, d, *J* = 18.8 Hz), 6.05−5.94 (1H, m), 5.33 (1H, ddt, *J* = 17.3, 3.0, 3.0 Hz), 5.23 (1H, ddt, *J* = 10.5, 2.8, 2.8 Hz), 4.89 (1H, d, *J* = 5.8 Hz), 4.03 (1H, m), 0.39 (3H, d, *J* = 1.5 Hz), 0.38 (3H, d, *J* = 1.5 Hz) $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.6, 140.8, 138.5, 134.8, 133.8, 129.2, 128.9, 128.4, 127.7, 127.6, 127.1, 116.9, 83.7, 69.3, −2.6, −2.7; HRMS (EI+) calcd for $C_{19}H_{21}OSi$ [M − $CH_3$]$^+$ 293.1374, found 293.1362.

**(*E*)-(3-(Allyloxy)-5-methylhex-1-en-1-yl)dimethyl(phenyl)-silane (1d).** Alcohol (213 mg, 0.869 mmol) was used to afford **1d** (200 mg, 80%) as a colorless oil: $R_f$ (9:1 hexane−ethyl acetate) = 0.74; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2955, 1616, 1427, 1248, 1082, 920, 842, 782, 698, 467; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.56−7.51 (2H, m), 7.40−7.34 (3H, m), 5.99−5.88 (3H, m), 5.27 (1H, dq, *J* = 17.1, 1.5 Hz), 5.18 (1H, dq, *J* = 10.3, 1.5 Hz), 5.07 (1H, ddt, *J* = 12.8, 5.3, 1.5 Hz), 3.87−3.79 (2H, m), 1.84−1.73 (1H, m), 1.61−1.53 (1H, m), 1.36−1.27 (2H, m), 0.93 (6H, dd, *J* = 6.7, 0.6 Hz), 0.38 (3H, s), 0.37 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 148.9, 138.6, 135.2, 133.8, 129.7, 129.0, 127.8, 116.6, 80.8, 69.4, 44.5, 24.4, 23.0, 22.5, −2.5, −2.6; HRMS (EI+) calcd for $C_{18}H_{28}OSi$ [M]$^+$ 288.1909, found 288.1905.

**(*E*)-(3-(Allyloxy)-3,3-diphenylprop-1-en-1-yl)dimethyl-(phenyl)silane (1f).** Alcohol (472 mg, 1.37 mmol) was used to afford **1f** (405 mg, 77%) as a waxy yellow solid: $R_f$ (9:1 hexane−ethyl acetate) = 0.85; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2956, 2955, 1646, 1446, 1247, 1114, 842, 469; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.48−7.44 (2H, m), 7.38−7.20 (13H, m), 6.64 (1H, d, *J* = 18.8 Hz), 6.08 (1H, d, *J* = 18.8 Hz), 5.99−5.88 (1H, m), 5.36 (1H, dd, *J* = 17.3, 1.6 Hz), 5.14 (1H, dd, *J* = 10.5, 1.6 Hz), 3.74 (2H, dt, *J* = 5.1, 1.6 Hz), 0.35 (6H, s); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 149.2, 143.9, 138.7, 135.3, 133.8, 129.0, 128.5, 127.9, 127.9, 127.8, 127.0, 115.4, 85.2, 65.0, −2.4; HRMS (ES+) calcd for $C_{19}H_{36}NO_6Si$ [M + $NH_3$]$^+$ 402.2312, found 402.2305.

**(*E*)-Ethyl 4-(allyloxy)-4-(2-(dimethyl(phenyl)silyl)vinyl)-piperidine-1-carboxylate (1i).** Alcohol (205 mg, 0.616 mmol) was used to afford **1i** (200 mg, 87%) as a colorless oil (chromatography eluent: 1:1 hexane−EtOAc): $R_f$ (1:1 hexane−ethyl acetate) = 0.39; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2925, 1700, 1428, 1236, 1063, 898, 826; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.52−7.46 (2H, m), 7.38−7.31 (3H, m), 6.02 (1H, d, *J* = 19.1 Hz), 5.95 (1H, d, *J* = 19.1 Hz), 5.95−5.84 (1H, m), 5.26 (1H, dd, *J* = 17.1, 1.5 Hz), 5.12 (1H, dd, *J* = 10.5, 1.5 Hz), 4.12 (2H, q, *J* = 7.0 Hz), 3.94−3.81 (2H, br), 3.79 (2H, d, *J* = 5.5 Hz), 3.30−3.14 (2H, br m), 1.86−1.75 (2H, br m) 1.65−1.55 (2H, br m) 1.25 (3H, t, *J* = 7.0 Hz), 0.35 (6H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 155.6, 150.8, 138.3, 135.4, 133.8, 129.1, 128.8, 127.9, 116.0, 75.3, 63.3, 61.2, 39.7, 14.7, −2.6; HRMS (EI+) calcd for $C_{21}H_{31}NO_3Si$ [M]$^+$ 373.2073, found 373.2113.

**(*E*)-(3-(Allyloxy)-3-phenylbut-1-en-1-yl)dimethyl(phenyl)-silane (1k).** Alcohol (403 mg, 1.43 mmol) was used to afford **1k** (424 mg, 92%) as a pale yellow oil: $R_f$ (9:1 hexane−ethyl acetate) = 0.87; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2955, 2855, 1646, 1446, 1248, 1114, 995, 919, 791, 469; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.53−7.49 (2H, m), 7.45−7.40 (2H, m), 7.37−7.32 (5H, m), 7.29−7.23 (1H, m), 6.30 (1H, d, *J* = 18.8 Hz), 6.08 (1H, d, *J* = 18.8 Hz), 6.00−5.90 (1H, m), 5.32 (1H, dq, *J* = 17.2, 1.8 Hz), 5.14 (1H, dq, *J* = 10.3, 1.8 Hz), 3.90−3.78 (2H, m), 1.64 (3H, s), 0.36 (6H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 151.7, 144.6, 138.7, 135.7, 133.8, 129.0, 128.1, 127.8, 127.0, 126.6, 126.3, 115.7, 80.4, 64.3, 24.7, −2.5, −2.5; HRMS (EI+) calcd for $C_{20}H_{23}OSi$ [M − $CH_3$]$^+$ 307.1505, found 307.1518.

**(*E*)-3-((*E*)-But-2-en-1-yloxy)-3-phenylprop-1-en-1-yl)-dimethyl(phenyl)silane (3a).** Alcohol (272 mg, 1.015 mmol) was used to afford **3a** (256 mg, 78%, 75:25 *E*/*Z* isomers) as a colorless oil (using crotyl bromide): $R_f$ (9:1 hexane−ethyl acetate) = 0.78; IR $\nu_{max}$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(thin film)/cm$^{-1}$ 3067, 2956, 1377, 1248, 1113, 731, 524; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.50−7.46 (2H, m), 7.38−7.28 (8H, m), 6.21 (minor, 0.25H, dd, $J$ = 13.1, 5.8 Hz), 6.20 (major, 0.75H, dd, $J$ = 18.7, 5.8 Hz), 6.03 (minor, 0.25H, dd, $J$ = 18.6, 1.2 Hz), 6.02 (major, 0.75H, dd, $J$ = 18.6, 1.2 Hz), 5.73−5.56 (2H, m), 4.82 (1H, dd, $J$ = 5.8, 1.2 Hz), 3.91−3.87 (2H, m), 1.70 (major, 2.25H, dq, $J$ = 6.0, 1.0 Hz), 1.57 (minor, 0.75H, dq, $J$ = 6.0, 1.0 Hz) 0.33 (minor, 0.75H, s), 0.33 (major, 2.25H, s), 0.32 (minor, 0.75H, s), 0.31 (major, 2.25H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 147.9, 141.0, 138.6, 133.8, 129.5 129.1, 129.0, 128.4, 127.7, 127.6, 127.6, 127.2, 127.0, 83.6, 69.2, 17.8, −2.6, −2.6; HRMS (ES+) calcd for $C_{21}H_{30}NOSi$ $[M + NH_4]^+$ 340.2097, found 340.2097.

**((*E*)-2-(1-((*E*)-But-2-en-1-yloxy)cyclohexyl)vinyl)dimethyl-(phenyl)silane (3b).** Alcohol (306 mg, 1.13 mmol) was used to afford **3b** (272 mg, 74%, 85:15 *E*/*Z* isomers) as a colorless oil (using crotyl bromide): $R_f$ (9:1 hexane−ethyl acetate) = 0.81; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2956, 1600, 1499, 1144, 953, 800, 479; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.59−7.53 (2H, m), 7.41−7.37 (3H, m), 6.08 (minor, 0.15H, d, $J$ = 19.3 Hz), 6.07 (major, 0.85H, d, $J$ = 19.3 Hz), 5.98 (minor, 0.15H, d, $J$ = 19.3 Hz), 5.97 (major, 0.85H, d, $J$ = 19.3 Hz), 5.76−5.57 (2H, m),3.88−3.86 (minor, 0.15H, m), 3.76−3.73 (major, 0.85H, m), 1.85−1.76 (2H, m), 1.74 (3H, dd, $J$ = 6.0, 1.0 Hz), 1.70−1.62 (4H, m), 1.57−1.46 (4H, m), 0.39 (6H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.8, 138.8, 133.7, 128.9, 128.7, 128.1, 127.7, 76.8, 62.6, 57.2, 34.3, 26.7, 21.9, 17.8, −2.5; HRMS (ES+) calcd for $C_{20}H_{34}NOSi$ $[M + NH_4]^+$ 332.2410, found 332.2410.

**General Procedure B: Isomerization−Claisen Reaction.** Chlorobis(cyclooctene)iridium(I) dimer (1 mol %), tricyclohexylphosphine (6 mol %), and sodium tetraphenylborate (2 mol %) were measured into a flask and purged with argon. A 20:1 mixture of chlorobenzene−acetone (0.7 M) was added and the resulting yellow solution stirred at room temperature for 5 min followed by addition of the allyl ether **1**. The mixture was stirred until completion as judged by TLC, after which triphenylphosphine (6 mol %) was added and stirred at room temperature for 10 min. The flask was then fitted with a reflux condenser and heated to 90 °C. The reaction was concentrated and chromatographed to afford the requisite aldehyde.

**(2*S*,3*S*)-3-(Dimethyl(phenyl)silyl)-2,5-dimethylhex-4-enal (2a).** The title compound was prepared from **1a** (155 mg, 0.60 mmol). Isomerization was complete in 6 h, and heating for 8 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (141 mg, 86%, 96:4 dr) as a colorless oil: $R_f$ ($CH_2Cl_2$) = 0.45; IR: $\nu_{max}$ (thin film)/cm$^{-1}$ 2925, 1628, 1427, 1251, 1115, 828, 700 ; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.46 (1H, d, $J$ = 2.8 Hz), 7.52−7.46 (2H, m), 7.36−7.31 (3H, m), 4.97 (1H, ddq, $J$ = 11.8, 1.2, 1.2 Hz), 2.42 (1H, qdd, $J$ = 7.0, 7.0, 2.8 Hz), 2.18 (1H, dd, $J$ = 11.8, 7.0 Hz), 1.69 (3H, d, $J$ = 1.2 Hz), 1.46 (3H, d, $J$ = 1.2 Hz), 0.97 (3H, d, $J$ = 7.0 Hz), 0.34 (3H, s), 0.30 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 205.4, 138.0, 133.8, 132.1, 129.1, 127.7, 121.7, 47.6, 31.4, 25.8, 18.0, 14.3, −2.9, −3.9; HRMS (EI+) calcd for $C_{16}H_{24}OSi$ $[M]^+$ 260.1596, found 260.1598.

**(2*S*,3*S*,*E*)-3-(Dimethyl(phenyl)silyl)-2-methyl-5-phenylpent-4-enal (2b).** The title compound was prepared from **1b** (mg, 0.166 mmol). Isomerization was complete in 45 min, and heating for 1.5 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (46 mg, 90%, 93:7 dr) as a pale yellow oil: $R_f$ (1:1 DCM−hexane) = 0.45; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2898, 1710,1422, 753, 710, 454; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.58 (1H, d, $J$ = 2.3 Hz), 7.67−7.49 (2H, m), 7.42−7.35 (3H, m), 7.32−7.25 (4H, m), 7.23−7.18 (1H, m), 6.27 (1H, d, $J$ = 15.8 Hz), 6.10 (1H, dd, $J$ = 15.8, 10.3 Hz), 2.63 (1H, qd, $J$ = 7.0 2.3 Hz), 2.27 (1H, ddd, $J$ = 10.3, 6.5, 0.5 Hz), 1.09 (3H, d, $J$ = 7.0 Hz), 0.43 (3H, s), 0.40 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 204.9, 137.5, 137.3, 134.0, 130.4, 129.4, 128.5, 128.4, 127.9, 126.9, 125.9, 47.1, 36.7, 14.6, −2.8, −3.6; HRMS (EI+) calcd for $C_{20}H_{23}OSi$ $[M - H]^+$ 307.1518, found 307.1511.

**(2*S*,3*S*,*E*)-3-(Dimethyl(phenyl)silyl)-2-methylnon-4-enal (2c).** The title compound was prepared from **1c** (100 mg, 0.347 mmol). Isomerization was complete in 3 h, and heating for 27 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (63 mg, 63%, 81:19 dr) as a yellow oil: $R_f$ (1:1 DCM−hexane) = 0.61; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2900, 1650, 1147, 900, 865, 735, 444; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.50 (1H, d, $J$ = 2.5 Hz), 7.53−7.47 (2, m), 7.37−7.33 (3H, m), 5.38−5.19 (2H, m), 2.48 (1H, qd, $J$ = 7.0, 2.5 Hz), 1.35−1.24 (6H, m), 1.00 (3H, d, $J$ = 7.0 Hz), 0.89 (3H, t, $J$ = 7.0 Hz), 0.36 (3H, s), 0.34 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 205.4, 137.8, 133.9, 132.1, 129.1, 128.0, 127.1, 47.0, 35.6, 32.4, 22.1, 14.4, 13.9, −2.9, −3.8; HRMS (EI+) calcd for $C_{18}H_{28}OSi$ $[M]^+$ 288.1909, found 288.1915.

**(2*S*,3*S*,*E*)-3-(Dimethyl(phenyl)silyl)-2,7-dimethyloct-4-enal (2d).** The title compound was prepared from **1d** (150 mg, 0.521 mmol). Isomerization was complete in 3 h, and heating for 28 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (97 mg, 63%, 97:3 dr) as a colorless oil: $R_f$ (1:1 DCM−hexane) = 0.6; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2955, 1699, 1111, 850, 753, 700; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.50 (1H, d, $J$ = 2.5 Hz), 7.53−7.47 (2H, m), 7.38−7.31 (3H, m), 5.36−5.20 (2H, m), 2.48 (1H, qd, $J$ = 7.0, 2.5 Hz), 1.98 (1H, dd, $J$ = 9.0, 7.0 Hz), 1.87 (2H, td, $J$ = 6.3, 1.2 Hz), 1.61−1.50 (1H, m), 0.98 (3H, d, $J$ = 7.0 Hz), 0.85 (3H, d, $J$ = 3.0 Hz), 0.84 (3H, d, $J$ = 3.0 Hz), 0.35 (3H, s), 0.35 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 205.4, 137.8, 133.9, 130.8, 129.1, 128.2, 127.8, 47.0, 42.2, 35.7, 28.6, 22.3, 22.2, 14.4, −2.8, −3.8; HRMS (EI+) calcd for $C_{18}H_{28}OSi$ $[M]^+$ 288.1909, found 288.1922.

**(2*S*,3*S*,*E*)-5-Cyclohexyl-3-(dimethyl(phenyl)silyl)-2-methylpent-4-enal (2e).** The title compound was prepared from **1e** (129 mg, 0.412 mmol). Isomerization was complete in 1 h, and heating for 35 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (106 mg, 82%, 96:4 dr) as a colorless oil: $R_f$ (1:1 DCM−hexane) = 0.53; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2936, 1700, 1115, 838, 721, 465; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.48 (1H, d, $J$ = 2.5 Hz), 7.54−7.46 (2H, m), 7.40−7.31 (3H, m), 5.29−5.16 (2H, m), 2.46 (1H, qd, $J$ = 7.0, 2.5 Hz), 1.93 (1H, dd, $J$ = 7.2, 2.0 Hz), 1.75−1.59 (5H, m), 1.31−1.00 (6H, m), 0.95 (3H, d, $J$ = 7.0 Hz), 0.34 (3H, s), 0.32 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 205.5, 138.0, 137.8, 134.0, 129.1, 127.8, 124.6, 47.0, 41.0, 35.5, 33.3, 26.1, 26.0, 14.4, −2.9, −3.7; HRMS (EI+) calcd for $C_{19}H_{27}OSi$ $[M - CH_3]^+$ 299.1831, found 299.1841.

**(2*S*,3*S*)-3-(Dimethyl(phenyl)silyl)-2-methyl-5,5-diphenylpent-4-enal (2f).** The title compound was prepared from **1f** (93 mg, 0.242 mmol). Isomerization was complete in 2.5 h and heating for 2 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (80 mg, 86%, 94:6 dr) as a colorless oil which solidified upon standing in the freezer for 3 days: $R_f$ (1:1 DCM−hexane) = 0.39; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2957, 1722. 1660, 1597, 1446, 1250, 1112, 764 ; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.59 (1H, d, $J$ = 2.5 Hz), 7.44−7.39 (2H, m), 7.36−7.26 (6H, m), 7.25−7.16 (3H, m), 7.15−7.10 (2H, m), 6.98−6.94 (2H, m), 6.00 (1H, d, $J$ = 12.4 Hz), 2.55 (1H, qdd, $J$ = 6.8, 6.8, 2.5 Hz), 2.32 (1H, dd, $J$ = 12.4, 6.8 Hz), 1.03 (3H, d, $J$ = 6.8 Hz), 0.39 (3H, s), 0.33 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 204.8, 142.6, 142.0, 139.8, 137.4, 134.0, 129.9, 129.3, 128.3, 128.1, 127.9, 127.1, 127.0, 126.9, 126.9, 47.9, 33.0, 14.4, −2.5, −3.3; HRMS (EI+) calcd for $C_{26}H_{27}OSi$ $[M - H]^+$ 383.1831, found 383.1829.

**(2*S*,3*S*)-4-Cyclopentylidene-3-(dimethyl(phenyl)silyl)-2-methylbutanal (2g).** The title compound was prepared from **1g** (64 mg, 0.224 mmol). Isomerization was complete in 2.5 h, and heating for 11 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (58 mg, 91%, 96:4 dr) as a colorless oil: $R_f$ (1:1 DCM−hexane) = 0.55; IR $\nu_{max}$ (thin film)/cm$^{-1}$ 2957, 1716, 1427, 1115, 832, 700; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.46 (1H, d, $J$ = 2.4 Hz), 7.52−7.48 (2H, m), 7.36−7.31 (3H, m), 5.10 (1H, dt, $J$ = 11.5, 2.3 Hz), 2.42 (1H, qdd, $J$ = 6.8, 6.8, 2.4 Hz), 2.25−2.15 (2H, m), 2.10−2.00 (1H, m), 2.03 (1H, dd, $J$ = 11.5, 6.8 Hz), 1.90−1.78 (1H, m), 1.62−1.47 (4H, m), 0.98 (3H, d, $J$ = 6.8 Hz), 0.36 (3H, s), 0.31 (3H, s);$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 205.6, 114.3, 138.1, 133.9, 127.7, 129.0. 127.7,


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117.2, 47.7, 33.7, 33.2, 29.2, 26.3, 26.2, 14.4, −3.0, −3.8; HRMS (EI+) calcd for $C_{18}H_{26}OSi$ $[M]^+$ 286.1753, found 286.1730.

**(2*S*,3*S*)-4-Cyclohexylidene-3-(dimethyl(phenyl)silyl)-2-methylbutanal (2h).** The title compound was prepared from **1h** (164 mg, 0.58 mmol). Isomerization was complete in 4 h, and heating for 5 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (141 mg, 86%, 97:3 dr) as a colorless oil: $R_f$ (1:1 DCM−hexane) = 0.43; IR $\nu_{max}$ (thin film)/$cm^{-1}$ 2930, 1642, 1380, 1259, 1051, 749; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.47 (1H, d, $J$ = 2.5 Hz), 7.53−7.46 (2H, m), 7.36−7.31 (3H, m), 4.91 (1H, d, $J$ = 11.8 Hz), 2.43 (1H, qdd, $J$ = 7.0, 7.0, 2.5 Hz), 2.23 (1H, dd, $J$ = 11.8, 7.0 Hz), 2.11−2.03 (3H, m), 1.96−1.88 (1H, m), 1.56−1.25 (6H, m), 0.97 (3H, d, $J$ = 7.0 Hz), 0.35 (3H, s), 0.31 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 205.6, 140.4, 138.0, 133.9, 129.0, 127.7, 118.3, 47.6, 37.4, 30.2, 28.9, 28.6, 27.4, 26.8, 14.3, −2.9, −3.8; HRMS (EI+) calcd for $C_{18}H_{25}OSi$ $[M - CH_3]^+$ 285.1675, found 285.1685.

**Ethyl 4-((2*S*,3*S*)-2-(Dimethyl(phenyl)silyl)-3-methyl-4-oxobutylidene)piperidine-1-carboxylate (2i).** The title compound was prepared from **1i** (104 mg, 0.279 mmol). Isomerization was complete in 24 h, and heating for 15 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (82 mg, 79%, 93.5:6.5 dr) as a colorless oil: $R_f$ (1:1 EtOAc−hexane = 0.8; IR $\nu_{max}$ (thin film)/$cm^{-1}$ 1700, 1614, 1428. 1236, 1063, 898, 826; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.50 (1H, $J$ = 2.5 Hz), 7.50−7.45 (2H, m), 7.40−7.35 (3H, m), 5.07 (1H, d, $J$ = 11.9 Hz), 4.12 (2H, q, $J$ = 7.0 Hz), 3.39−3.21 (3H, m), 3.14−3.01 (1H, m), 2.49 (1H, td, $J$ = 7.0, 2.5 Hz), 2.22 (1H, dd, $J$ = 11.9, 7.0 Hz), 2.15−2.04 (3H, m), 1.97−1.88 (1H, m), 1.25 (3H, t, $J$ = 7.0 Hz), 1.02 (3H, d, $J$ = 7.0 H) 0.36 (3H, s), 0.31 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 204.9, 155.4, 137.6, 135.4, 133.8, 129.3, 127.8, 121.4, 61.2, 47.5, 45.6, 44.2, 30.5, 14.7, 14.3, −3.3, −3.4; HRMS (EI+) calcd for $C_{20}H_{28}O_3NSi$ $[M - CH_3]^+$ 358.1838, found 358.1841.

**(2*S*,3*S*)-4-(Dihydro-2*H*-pyran-4(3*H*)-ylidene)-3-(dimethyl(phenyl)silyl)-2-methylbutanal (2j).** The title compound was prepared from **1j** (38 mg, 0.126 mmol). Isomerization was complete in 2.5 h, and heating for 5 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (32 mg, 84%, 91:9 dr) as a yellow oil: $R_f$ = 0.15; IR $\nu_{max}$ (thin film)/$cm^{-1}$ 3100, 2955, 1600, 1522, 1000, 827, 411; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.52 (1H, d, $J$ = 2.5 Hz), 7.52−7.47 (2H, m), 7.39−7.33 (3H, m), 5.04 (1H, d, $J$ = 11.8 Hz), 3.65−3.47 (3H, m), 3.34 (1H, ddd, $J$ = 10.9, 6.8, 4.1 Hz), 2.5 (1H, td, $J$ = 6.8, 2.5 Hz), 2.22 (1H, dd, $J$ = 11.8, 6.8 Hz), 2.20−2.10 (3H, m), 2.00 (1H, qdd, $J$ = 7.0, 4.1, 1.0 Hz), 1.03 (3H, d, $J$ = 7.0 Hz), 0.38 (3H, s), 0.35 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 205.0, 137.7, 135.0, 133.9, 129.3, 127.8, 120.4, 69.6, 68.3, 47.5, 37.2, 30.3, 29.9, 14.4, −3.2, −3.4 ; HRMS (EI+) calcd for $C_{17}H_{24}O_2Si$ $[M - CH_3]^+$ 288.1546, found 288.1542.

**(2*S*,3*S*,*E*)-3-(Dimethyl(phenyl)silyl)-2-methyl-5-phenylhex-4-enal (2k).** The title compound was prepared from **1k** (115 mg, 0.356 mmol mmol). Isomerization was complete in 1.5 h and heating at 40 °C for 2 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (98 mg, 85%, 94:6 dr, 80:20 *E*/*Z* isomers) as a colorless oil: $R_f$ (1:1 DCM−hexane) = 0.45; IR $\nu_{max}$ (thin film)/$cm^{-}$ 2961, 1722, 1380, 1025, 823, 699, 471 ; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.55 (major, 0.8H, d, $J$ = 2.5 Hz), 9.48 (minor, 0.2H, d, $J$ = 2.5 Hz) 7.55−7.50 (major, 1.6H, m), 7.41−7.28 (6H, m), 7.25−7.17 (2H, m), 6.94−6.90 (minor, 0.4H, m), 5.62 (minor, 0.8H, qd, $J$ = 12.0, 1.4 Hz),5.34 (0.2H, qd, $J$ = 12.0, 1.4 Hz), 2.57 (1H, qd, $J$ = 7.0, 2.5 Hz), 2.42 (1H, dd, $J$ = 12.0, 7.0 Hz), 2.00 (minor, 0.6H, d, $J$ = 1.4 Hz), 1.85 (major, 2.4H, d, $J$ = 1.4 Hz), 1.05 (major, 2.6H, d, $J$ = 7.0 Hz), 0.94 (minor, 0.6H, d, $J$ = 7.0 Hz), 0.42 (major, 2.4H, s), 0.37 (major, 2.4H, s), 0.33 (minor, 0.6H, s), 0.28 (minor, 0.6H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 205.3 (minor), 205.0 (major), 143.9 (major), 142.0 (minor), 137.7 (minor), 135.2 (major), 134.0 (minor), 133.9 (major), 129.3 (major), 129.2 (minor), 128.2 (major), 128.2 (minor),127.9 (major), 127.8 (major), 127.8 (minor),126.6 (major),126.4 (minor), 126.1 (major), 125.8 (minor), 125.7 (major), 124.3 (minor), 47.8 (major), 47.8 (minor), 32.8 (major), 31.5 (minor), 16.3 (major), 14.5 (major), 14.3 (minor), 11.7 (minor),-2.6 (minor), −2.8 (major), −3.5 (minor),-3.6 (major); HRMS (EI+) calcd for $C_{21}H_{30}NOSi$ 340.2097, found 340.2093.

**(2*S*,3*S*,*E*)-3-(Dimethyl(phenyl)silyl)-2,5,7-trimethyloct-4-enal (2l).** The title compound was prepared from **1l** (157 mg, 0.520 mmol). Isomerization was complete in 45 min, and heating at 40 °C for 5 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (137 mg, 87%, 98: 2 dr, 56:44 *E*/*Z* isomers) as a pale yellow oil: $R_f$ (1:1 DCM−hexane) = 0.43; IR $\nu_{max}$ (thin film)/$cm^{-1}$ 2977, 1700. 1662, 1177, 764, 477; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.51 (major, 0.56H, d, $J$ = 2.6 Hz), 9.50 (minor, 0.44H, d, $J$ = 2.6 Hz), 7.55−7.50 (2H, m), 7.41−7.33 (3H, m), 5.08 (minor, 0.44H, dq, $J$ = 11.8, 1.0 Hz), 4.99 (major, 0.56H, dq, $J$ = 11.8, 1.2 Hz), 2.50−2.40 (1H, m), 2.29 (minor, 0.44, dd, $J$ = 11.8, 7.2 Hz), 2.24 (major, 0.56H, dd, $J$ = 11.8, 7.2 Hz), 1.92−1.70 (3H, m), 0.99 (3H, d, $J$ = 6.8 Hz), 0.91−0.80 (6H, m), 0.37 (major, 1.68H, s), 0.36 (minor, 1.32H, s), 0.34 (major, 1.68H, s), 0.33 (minor, 1.32H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 205.5 (minor), 205.4 (major), 138.0 (minor), 135.4 (major), 135.3 (minor), 133.9 (minor), 133.9 (major), 129.1 (minor), 129.1 (major), 127.9 (major), 127.8 (minor), 123.3 (minor), 122.9 (major), 49.8, 47.9 (minor), 47.7 (major), 41.2, 31.6 (minor), 31.4 (major), 30.8, 26.3 (minor), 26.2 (major), 23.7 (major), 23.3 (minor), 22.6 (minor), 22.5 (major), 22.4 (major), 22.0 (minor), 16.3, 14.4 (major), 14.4 (minor), 14.1, −2.7 (minor), −2.8 (major), −3.8 (minor), −3.8 (major); HRMS (EI+) calcd for $C_{19}H_{30}OSiNa$ $[M + Na]^+$ 325.1964, found 325.1966.

**(2*S*,3*S*,*E*)-3-(Dimethyl(phenyl)silyl)-2-ethyl-5-phenylpent-4-enal (4a).** The title compound was prepared from a 75:25 (*E*/*Z*) mixture of **3a** (60 mg, 0.184 mmol). Isomerization was complete in 36 h, and heating for 6 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (31 mg, 51%, 97:3 dr) as a yellow oil: $R_f$ (1:1 DCM−hexane) = 0.53 ; IR $\nu_{max}$ (thin film)/$cm^{-1}$ 2825, 1721, 1427, 1112, 831, 735; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.54 (1H, d, $J$ = 3.3 Hz), 7.52−7.49 (2H, m), 7.39−7.33 (3H, m), 7.31−7.25 (4H, m), 7.22−7.17 (1H, m), 6.23 (1H, d, $J$ = 15.8 Hz), 6.08 (1H, dd, $J$ = 15.8, 10.5 Hz), 2.41−2.33 (1H, m), 2.25 (1 H, dd, $J$ = 10.5, 6.3 Hz), 1.73−1.59 (1H, m), 1.50−1.39 (1H, m), 0.83 (3H, t, $J$ = 7.4 Hz), 0.40 (3H, s), 0.38 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 205.0, 137.6, 137.3, 134.0, 130.5, 129.3, 128.5, 128.0, 127.9, 126.9, 125.9, 54.1, 34.9, 30.0, 22.3, 11.7, −3.0, −3.7; HRMS (ES+) calcd for $C_{21}H_{26}OSiNa$ $[M + Na]^+$ 345.1651, found 345.1652.

**(2*S*,3*S*)-4-Cyclohexylidene-3-(dimethyl(phenyl)silyl)-2-ethylbutanal (4b).** The title compound was prepared from a 85:15 (*E*/*Z*) mixture of **3b** (128 mg, 0.431 mmol). Isomerization was complete in 1.5 h, and heating for 1 h achieved the Claisen rearrangement. Purification was performed using chromatography (1:1 $CH_2Cl_2$−hexane) to afford the title compound (119 mg, 93%, 97:3 dr) as a colorless oil: $R_f$ (1:1 DCM−hexane) = 0.56 ; IR $\nu_{max}$ (thin film)/$cm^{-1}$2929, 1709, 1427, 1115, 830, 700, 471; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.46 (1H, d, $J$ = 3.5 Hz), 7.53−7.47 (2H, m), 7.38−7.32 (3H, m), 4.90 (1H, d, $J$ = 11.8 Hz), 2.31 (1H, dd, $J$ = 11.8, 6.3 Hz), 2.26−2.20 (1H, m), 1.92 (2H, qd, $J$ = 7.2, 5.0 Hz), 1.64−1.26 (10H, m), 0.79 (3H, t, $J$ = 7.2 Hz), 0.36 (3H, s), 0.32 (3H, s); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ 205.6, 140.3, 138.0, 133.9, 129.1, 127.7, 117.9, 54.7, 37.5, 28.3, 27.5, 26.9, 22.0, 11.7, −3.1, −3.8; HRMS (ES+) calcd for $C_{20}H_{34}NOSi$ $[M + NH_4]^+$ 332.2410, found 332.2420.

## ■ ASSOCIATED CONTENT

### Supporting Information

$^1H$ and $^{13}C$ NMR spectra of all reported compounds. This material is available free of charge via the Internet at http://pubs.acs.org.


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