Titanium Tetrachloride-Induced Three-Component Coupling Reaction of α-Haloacylsilane, Allylsilane, and Carbonyl Compound

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There has been considerable interest in the chemistry of acylsilanes[1] and many procedures have been developed for the preparation of many functionalized acylsilanes.[2] Only a few reports, however, have been published for the synthesis of α-haloacylsilanes.[3] Recently we have reported a facile approach to α-haloacylsilanes based on the rearrangement of α-haloepoxysilane and their use for triethylborane-mediated Reformatsky type reaction giving *β*-hydroxyacylsilane.[4] Here we describe another application of α-haloacylsilanes to organic synthesis. Treatment of an α-chloroacylsilane with titanium tetrachloride in the presence of allylsilane[5] afforded a *β*,*γ*-unsaturated ketone[6] or α-silyl-*β*′,*γ*′-unsaturated ketone[7] in good yield.

Treatment of a dichloromethane solution of α-chloroacylsilane **1a** (R′ = Me, 0.23 g, 1.0 mmol) and allyltrimethylsilane (0.16 mL, 1.0 mmol) with titanium tetrachloride[8] (1.0 M dichloromethane solution, 2.0 mL, 2.0 mmol)at −78 °C for 30 min gave 1-undecen-4-one **2** (0.16 g) in 98% yield. The use of α-chloroacylsilane **1b** (R′ = Ph) in place of **1a** also gave **2** in 76% yield, while **1c** (R′ = *t*-Bu) afforded 5-(*tert*-butyldimethylsilyl)-1-undecen-4-one (**3a**) (0.22 g)[9] in 78% yield upon treatment with $TiCl_4$ in the presence of allyltrimethylsilane (Scheme 1). Whereas the trimethylsilyl and dimethylphenylsilyl groups of the acylsilane moiety have been lost completely under the reaction conditions, the *tert*-butyldimethylsilyl group remained on the products.

The partial isomerization of the product **2** into the α,*β*-unsaturated ketone took place after prolonged stirring of the reaction mixture at −78 °C. For instance, stirring a mixture of **1a,** titanium tetrachloride, and allyltrimethylsilane at −78 °C for 3 h provided 2-undecen-4-one (25%) in addition to **2** (73%). Coexistence of α-halogen with acylsilane moiety was essential for the formation of *β*,*γ*-unsaturated ketone. In fact, treatment of acylsilane (n-$C_6H_{13}CH_2C(O)SiMe_2Ph$) or α-chloroaldehyde ($n$-$C_5H_{11}CHClCHO$) with $TiCl_4$ in the presence of allyltrimethylsilane afforded homoallylic alcohol (n-$C_6H_{13}CH_2C(OH)SiMe_2PhCH_2CH{=}CH_2$) or chlorohydrin ($n$-$C_5H_{11}CHClCH(OH)CH_2CH{=}CH_2$) in 85% or 95% yield, respectively.[10]

Crotyldimethylphenylsilane, cinnamyldimethylphenylsilane, methallyldimethylphenylsilane, and prenyldimethylphenylsilane reacted at the *γ*-position exclusively to provide the corresponding α-(*tert*-butyldimethylsilyl)-*β*',*γ*'-unsaturated ketones **3b**, **3c**, **3d**, **3e** in 52%, 50%, 66%, and 33% yields, respectively upon treatment with $TiCl_4$ in the presence of **1c** (Scheme 2). The reaction of **1c** with 2,4-pentadienyldimethylphenylsilane afforded 7-(*tert*-butyldimethylsilyl)-1,3-tridecadien-6-one (**3f**) exclusively in 63% yield.[11]

On the basis of these findings, we are tempted to assume the following reaction mechanism (Scheme 3). The chloro substituent coordinates titanium to give a carbonium ion[12] at the α position of the acylsilane which is stabilized by a silicon atom. Participation of silicon atom might produce a cationic intermediate **4** in which the silicon bridges[13−15] both the carbonyl carbon and the neighboring carbon atom. Nucleophilic attack of allyl-

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(5) Allylation with allylmetals: (a) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 5198. (b) Sato, T.; Matsumoto, K.; Abe, T.; Kuwajima, I. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2167. (c) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (d) Yanagisawa, A.; Habaue, S.; Yamamoto, H. *Tetrahedron* **1992**, *48*, 1969.

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(8) The use of $BF_3{\cdot}OEt_2$ and TMSOTf as Lewis acids resulted in a recovery of **1a**, and no allylation product was detected in the reaction mixture.

(9) $TiCl_4$ was added at 0 °C instead of −78 °C, and the resulting mixture was stirred for 30 min at 25 °C. The reaction at −78 °C gave **3** (53%) along with the recovered starting acylsilane **1c** (39%).

(10) (a) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295. (b) Hayashi, T.; Kabeta, K.; Hamachi, I.; Kumada, M. *Ibid.* **1983**, *24*, 2865.

(11) The reaction of 1-propynyltrimethylsilane with **1c** provided 5-(*tert*-butyldimethylsilyl)-2-undecyn-4-one (**3g**) in 33% yield.

(12) Treatment of α-iodoacylsilane (n-$C_6H_{13}CHIC(O)SiMe_2$-*t*-Bu) with silver tetrafluoroborate in the presence of allyltrimethylsilane also provided **3a** in 67% yield. In this case, the use of iodide was critical for the successful reaction. The reaction of **1c** with $AgBF_4$ in the presence of allyltrimethylsilane resulted in complete recovery of starting material **1c**.

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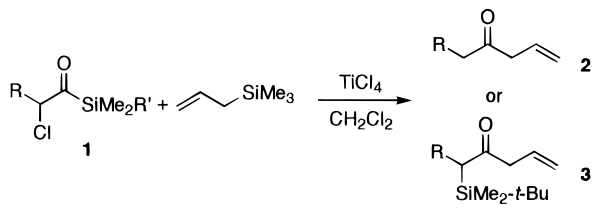
(14) The possibility of ketene formation was suggested by a reviewer. The reaction of α-chloroacylsilane **1c** with $TiCl_4$ in the presence of PhCH=N-*n*-Pr did not give any lactam. Thus we assume that ketene is not an intermediate. In contrast, the reaction with a fluoride source might proceed via ketene intermediate, since treatment of α-chloroacylsilane with n-Bu_4NF in the presence of alcohol (R′OH) afforded ester RCH_2COOR' in 76% (R′ = $PhCH_2$) or 75% (R′ = $CH_2{=}CHCH_2$) yield.

(15) The following crossover experiment was performed. Treatment of a 1:1 mixture of **1** (R = n-C_3H_7, R′ = *t*-Bu) and **1b** (R = n-C_6H_{13}, R′ = Ph) with $TiCl_4$ in the presence of allyltrimethylsilane provided only two products, n-$C_3H_7CH(SiMe_2$-*t*-$Bu)COCH_2CH{=}CH_2$ and n-$C_6H_{13}CH_2COCH_2CH{=}CH_2$ which suggested that the silane remained attached to the carbon skeleton throughout the reaction.

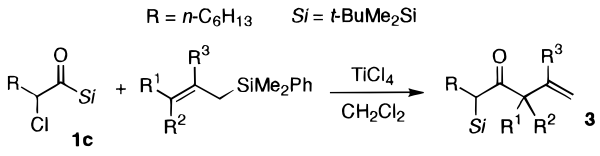
S0022-3263(96)00233-2 CCC: $12.00

Scheme 1



R = *n*-C_6H_{13} **1a**: R' = Me **1b**: R' = Ph **1c**: R' = *t*-Bu

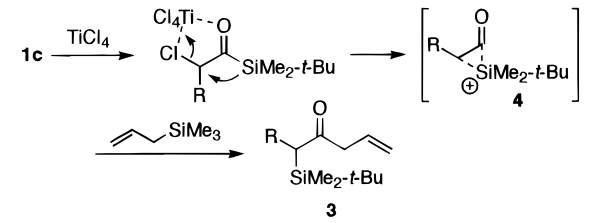
Scheme 2



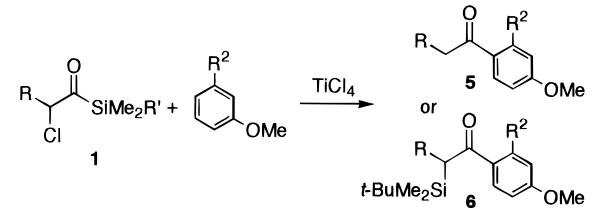
R = *n*-C_6H_{13} *Si* = *t*-$BuMe_2Si$

$R^1 = CH_3$	$R^2 = R^3 = H$	**3b**: 52%
$R^1 = Ph$	$R^2 = R^3 = H$	**3c**: 50%
$R^1 = R^2 = H$	$R^3 = CH_3$	**3d**: 66%
$R^1 = R^2 = CH_3$	$R^3 = H$	**3e**: 33%

Scheme 3



Scheme 4



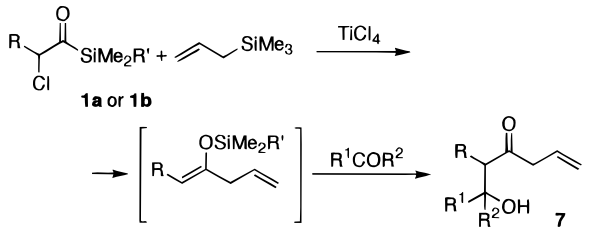
R = *n*-C_3H_7	R^1 = Me	R^2 = H	**5a**: 77%
R = *n*-C_3H_7	R^1 = *t*-Bu	R^2 = H	**6a**: 66%
R = *n*-C_6H_{13}	R^1 = Me	R^2 = OMe	**5b**: 84%
R = *n*-C_3H_7	R^1 = *t*-Bu	R^2 = OMe	**6b**: 87%

silane on the carbonyl carbon affords β,γ-unsaturated ketone **3** which is apparently produced by migration of silyl group[16] to adjacent carbon followed by allylation.

The intermediary acyl cation equivalent **4** has been expected to react with electron-rich aromatic compounds such as methoxybenzene or *m*-dimethoxybenzene via Friedel−Crafts type reaction. This was indeed the case, and an addition of these aromatic compounds instead of allylsilane gave the corresponding acylated products (Scheme 4). Trimethylsilyl group was lost under the reaction conditions and *tert*-butyldimethylsilyl group remained on the products as in the case of the reaction with allylsilane. Thiophene could be used as a trapping reagent of acyl cation to give the corresponding adduct in moderate yield (46%) upon treatment with **1a** and $TiCl_4$. The use of furan instead of methoxybenzene furnished only poor yield of Friedel−Crafts type adduct (<4%).

The loss of the trimethylsilyl and dimethylphenylsilyl groups during the reaction might be attributed to a facile transformation[17,18] of the α-silyl ketone to the corresponding silyl enol ether under the reaction conditions, which then collapsed to β,γ-unsaturated ketone or heptyl 2,4-dimethoxyphenyl ketone upon aqueous workup. Thus, it was anticipated that the sequential treatment of **1a** or **1b** with allyltrimethylsilane in the presence of $TiCl_4$ followed by carbonyl compounds would provide three-component coupling products. The representative results which realized this expectation are shown below (Scheme 5). For instance, an addition of acetaldehyde to the reaction mixture derived from **1a** and allyltrimethylsilane gave aldol type product **7a** in 70% yield, and therefore, α-chloroacylsilane **1a** or **1b** can be regarded as a synthon of $^-C^-C^+(=O)$.

Scheme 5



α-chloroacylsilane	electrophile	product
1a	CH_3CHO	**7a**: 70% (*e*/*t* = 80/20)*
1a	PhCHO	**7b**: 58% (*e*/*t* = 77/23)
1a	CH_3COCH_3	**7c**: 83%
1a	$CH_3CH(OCH_3)_2$	**7d**: 61% (*e*/*t* = 50/50)
1b	CH_3COCH_3	**7c**: 81%
1b	$CH_3CH(OCH_3)_2$	**7d**: 60% (*e*/*t* = 50/50)

* *e* = erythro *t* = threo

In summary, a simple procedure has been devised for the preparation of an α-silylacyl cation equivalent. Additionally, a convenient and efficient three component coupling reaction of α-chloroacylsilane, allyltrimethylsilane and carbonyl compound has been achieved which further enhances the synthetic utility of α-haloacylsilanes.

Experimental Section

Preparation of α-Chloroacylsilanes. 2-Chloro-1-(trimethylsilyl)-1-octanone (**1a**), 2-Chloro-1-(dimethylphenylsilyl)-1-octanone (**1b**), 2-chloro-1-(*tert*-butyldimethylsilyl)-1-octanone (**1c**), and 2-chloro-1-(*tert*-butyldimethylsilyl)-1-pentanone (**1d**) were prepared according to the reported procedure.[4] 1-(Dimethylphenylsilyl)-1-octanone was produced following the literature.[2a] The physical data are as follows.

1-(Dimethylphenylsilyl)-1-octanone: 1.2 g, 80% yield; Bp 113 °C (0.5 Torr); IR (neat) 2954, 2924, 2852, 1643, 1429, 1250, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.48 (s, 6H), 0.85 (t, *J* = 6.8 Hz, 3H), 1.06−1.34 (m, 8H), 1.43 (m, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 7.34−7.46 (m, 3H), 7.52−7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −4.76, 14.02, 22.13, 22.53, 29.03, 29.12, 31.59, 48.84, 128.13, 129.84, 133.98, 134.63, 246.78. Found: C, 73.23; H, 10.14%. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.98%.

(16) 1,2-Silyl migration: (a) Bideau, F. L.; Gilloir, F.; Nilsson, Y.; Anbert, C.; Malacria, M. *Tetrahedron Lett.* **1995**, *36*, 1641. (b) Knölker, H-J.; Graf, R.; *Synlett* **1994**, 131. (c) Monti, H.; Audran, G.; Monti, J.-P.; Leandri, G. *Synlett* **1994**, 403. (d) Knölker, H.-J.; Foitzik, N.; Goesmann, H.; Graf, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1081. (e) Sato, T.; Otera, J.; Nozaki, H. *J. Org. Chem.* **1990**, *55*, 6116.

(17) β-Ketosilanes have been known to undergo a facile thermal rearrangement to silyl enol ethers. Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. See also ref 7e and 7f.

(18) Aldol reaction of β-ketosilane with aldehyde in the presence of a Lewis acid have been reported. Kuwajima, I.; Inoue, T.; Sato, T. *Tetrahedron Lett.* **1978**, 4887.

2-Chloro-1-(trimethylsilyl)-1-octanone (1a).[3a] Diisobutylaluminum hydride (18.7 mL, 105 mmol) was added dropwise to a solution of 1-(trimethylsilyl)-1-octyne (17.3 g, 95 mmol) in ether (95 mL) at 25 °C under argon atmosphere. The mixture was heated at reflux for 3 h. The resulting solution was cooled to −15 °C (dry ice−ethylene glycol) and *N*-chlorosuccinimide (14.0 g, 105 mmol) was added portionwise. Exothermic reaction took place. After completion of the addition, the mixture was warmed to 25 °C and stirred for 30 min. Then the mixture was poured into ice-cold 1 M HCl. Extraction with hexane followed by purification by silica gel column (hexane) chromatography gave *(E)*-1-(trimethylsilyl)-1-chloro-1-octene (18.5 g, 85 mmol). *m*-Chloroperoxybenzoic acid (19.4 g, 80% purity, 90 mmol) was added to a solution of *(E)*-1-(trimethylsilyl)-1-chloro-1-octene (18.5 g) in dichloromethane (100 mL) at 25 °C, and the resulting mixture was stirred for 8 h. The mixture was poured into saturated $NaHCO_3$ and extracted with hexane (60 mL × 3). Concentration of the dried combined organic layers followed by silica gel column chromatography afforded α-chloroepoxysilane (17.3 g, 74 mmol) in 78% overall yield from 1-(trimethylsilyl)-1-octyne. A catalytic amount of zinc chloride (3 g, 22 mmol) was added to a solution of α-chloroepoxysilane (17.3 g, 74 mmol) in ether (50 mL) at 0 °C and the mixture was stirred at 25 °C for 1 h. Extractive workup (EtOAc−H_2O) followed by purification by silica gel column chromatography provided the title compound (16.6 g, 71 mmol) in 96% yield.

2-Chloro-1-(dimethylphenylsilyl)-1-octanone (1b): 15.3 g, 53% overall yield; Bp 137 °C (0.5 Torr); IR (neat) 2952, 2926, 2856, 1652, 1466, 1429, 1251, 1111, 838, 820, 784, 734, 699, 646 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 3H), 0.59 (s, 3H), 0.85 (t, J = 6.9 Hz, 3H), 1.00−1.39 (m, 8H), 1.61 (m, 1H), 1.80 (m, 1H), 4.29 (dd, J = 5.4, 8.7 Hz, 1H), 7.36−7.48 (m, 3H), 7.56−7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.66, −3.60, 13.95, 22.42, 25.77, 28.56, 31.41, 31.74, 68.28, 128.14, 130.07, 134.03, 134.18, 235.25. Found: C, 65.02; H, 8.82%. Calcd for $C_{16}H_{26}OSiCl$: C, 64.73; H, 8.49%.

2-Chloro-1-(*tert*-butyldimethylsilyl)-1-octanone (1c): 20 g, 65% overall yield; Bp 98 °C (0.5 Torr); IR (neat) 2952, 2926, 2856, 1652, 1465, 1251, 839, 824, 778 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 3H), 0.26 (s, 3H), 0.86 (t, J = 6.7 Hz, 3H), 0.93 (s, 9H), 1.17−1.51 (m, 8H), 1.67 (m, 1H), 1.87 (m, 1H), 4.31 (dd, J = 5.4, 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −5.88, 14.00, 16.97, 22.49, 26.05, 26.46, 28.74, 31.26, 31.51, 67.12, 236.30. Found: C, 61.00; H, 10.82%. Calcd for $C_{14}H_{29}OSiCl$: C, 60.72; H, 10.56%.

2-Chloro-1-(*tert*-butyldimethylsilyl)-1-pentanone (1d): 15 g, 60% overall yield; Bp 45 °C (0.5 Torr); IR (neat) 2954, 2930, 2854, 1651, 1465, 1365, 1252, 839, 823, 811, 779, 679 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.26 (s, 3H), 0.28 (s, 3H), 0.939 (t, J = 7.4 Hz, 3H), 0.943 (s, 9H), 1.28−1.56 (m, 2H), 1.69 (m, 1H), 1.85 (m, 1H), 4.34 (dd, J = 5.3, 8.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −5.90, −5.86, 13.51, 16.96, 19.36, 26.46, 33.23, 66.79, 236.26. Found: C, 56.29; H, 10.06%. Calcd for $C_{11}H_{23}OSiCl$: C, 56.26; H, 9.87%.

General Procedure for the Reaction of 1 and Allyltrimethylsilane in the Presence of $TiCl_4$. The reaction of **1a** with allyltrimethylsilane is representative. Under an argon atmosphere, a dichloromethane solution of $TiCl_4$ (1.0 M, 2.0 mL, 2.0 mmol) was added dropwise to a solution of α-chloroacylsilane **1a** (0.24 g, 1.0 mmol) and allyltrimethylsilane (0.16 mL, 1.0 mmol) in dichloromethane (5 mL) at −78 °C. After being stirred for 30 min at the same temperature, the mixture was poured into saturated aqueous NaCl. Extraction with EtOAc (20 mL × 3) followed by purification by silica-gel column chromatography afforded 1-undecen-4-one (**2**, 165 mg) in 98% yield: Bp 110 °C (13 Torr); IR (neat) 2954, 2924, 2852, 1718, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3H), 1.12−1.47 (m, 8H), 1.57 (m, 2H), 2.42 (t, J = 7.5 Hz, 2H), 3.16 (d, J = 6.6 Hz, 2H), 5.13 (dd, J = 1.2, 17.1 Hz, 1H), 5.17 (dd, J = 1.2, 10.2 Hz, 1H), 5.92 (ddt, J = 10.2, 17.1, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.92, 22.48, 23.59, 28.95, 29.04, 31.56, 42.31, 47.65, 118.72, 130.84, 209.26. Found: C, 78.23; H, 12.09%. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98%.

5-(*tert*-Butyldimethylsilyl)-1-undecen-4-one (3a): 0.22 g, 78% yield; Bp 112 °C (0.5 Torr); IR (neat) 2954, 2926, 2856, 1693, 1466, 1252, 834, 823, 807, 771 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.04 (s, 3H), 0.03 (s, 3H), 0.85 (t, J = 6.8 Hz, 3H), 0.92 (s, 9H), 1.02−1.46 (m, 9H), 1.97 (m, 1H), 2.51 (dd, J = 2.1, 12.0 Hz, 1H), 3.05 (dd, J = 6.9, 16.2 Hz, 1H), 3.14 (dd, J = 6.9, 16.2, Hz, 1H), 5.09 (dd, J = 1.5, 17.1 Hz, 1H), 5.15 (dd, J = 1.5, 10.2 Hz, 1H), 5.91 (ddt, J = 10.2, 17.1, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −7.17, −5.83, 14.02, 17.82, 22.58, 26.81, 28.38, 29.16, 30.90, 31.64, 44.68, 49.89, 118.26, 131.23, 210.55. Found: C, 72.19; H, 12.42%. Calcd for $C_{17}H_{34}OSi$: C, 72.27; H, 12.13%.

5-(*tert*-Butyldimethylsilyl)-3-methyl-1-undecen-4-one (3b): 0.15 g, 52% yield; Bp 108 °C (0.5 Torr); IR (neat) 2952, 2926, 2854, 1694, 1466, 1257, 1135, 915, 839, 822, 769 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.05 (s, 3H), 0.02 (s, 3H), 0.85 (t, J = 6.9 Hz, 3H, major), 0.86 (t, J = 6.9 Hz, 3H, minor), 0.93 (s, 9H, minor), 0.94 (s, 9H, major), 1.08−1.43 (m, 12H, including, 1.12 (d, J = 6.6 Hz, 3H, major), 1.18 (d, J = 7.2 Hz, 3H, minor)), 1.99 (m, 1H), 2.61 (dd, J = 1.8, 11.7 Hz, 1H, minor), 2.73 (dd, J = 1.8, 11.7 Hz, 1H, major), 3.10 (m, 1H), 5.00−5.23 (m, 2H), 5.59 (ddd, J = 8.7, 9.9, 17.4 Hz, 1H, major), 6.02 (ddd, J = 8.1, 10.5, 17.1 Hz, minor); ^{13}C NMR ($CDCl_3$) δ −7.24, −7.18, −5.99, −5.22, 14.04, 14.83, 17.59, 17.91, 22.61, 26.79, 26.90, 28.33, 28.57, 29.21, 29.31, 30.77, 31.15, 31.69, 42.96, 43.73, 52.28, 53.50, 115.33, 117.23, 137.90, 138.18, 212.08, 213.94. Found: C, 72.98; H, 12.09%. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.23%.

5-(*tert*-Butyldimethylsilyl)-3-phenyl-1-undecen-4-one (3c): 0.18 g, 50% yield; Bp 150 °C (0.5 Torr); IR (neat) 2952, 2926, 2854, 1692, 1466, 1455, 1253, 1132, 1079, 914, 823, 806, 699 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.13 (s, 3H, minor), 0.02 (s, 3H, minor), 0.05 (s, 6H, major), {0.74−1.55 (m, 13H) including 0.77 (t, J = 7.2 Hz, 3H, major), 0.86 (t, J = 6.9 Hz, minor), 0.92 (s, 9H, minor), 0.96 (s, 9H, major)}, 1.93 (m, 1H), 2.56 (dd, J = 1.8, 11.7 Hz, 1H, major), 2.78 (dd, J = 2.1, 11.7 Hz, 1H, minor), 4.19 (d, J = 7.8 Hz, 1H, major), 4.29 (d, J = 9.3 Hz, 1H, minor), 4.94−5.25 (m, 2H), 6.02 (ddd, J = 9.3, 9.6, 16.8 Hz, 1H, minor), 6.40 (ddd, J = 7.8, 10.2, 17.1 Hz, major), 7.20−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −7.17, −7.05, −5.22, 13.99, 14.05, 17.90, 17.95, 22.38, 22.60, 26.83, 26.86, 27.82, 28.60, 28.96, 29.23, 29.49, 30.98, 31.57, 31.67, 43.44, 43.80, 64.82, 65.16, 116.43, 117.82, 126.92, 127.31, 128.34, 128.61, 128.73, 128.79, 128.86, 136.96, 137.69, 209.42, 209.83. Found: C, 76.98; H, 10.65%. Calcd for $C_{23}H_{38}OSi$: C, 77.03; H, 10.68%.

5-(*tert*-Butyldimethylsilyl)-2-methyl-1-undecen-4-one (3d): 0.20 g, 66% yield; Bp 104 °C (0.5 Torr); IR (neat) 2952, 2926, 2854, 1691, 1466, 1252, 890, 833, 823, 808, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.01 (s, 3H), 0.04 (s, 3H), 0.86 (t, J = 6.8 Hz, 3H), 0.93 (s, 9H), 0.99−1.43 (m, 9H), 1.76 (s, 3H), 1.96 (m, 1H), 2.59 (dd, J = 1.8, 11.7 Hz, 1H), 3.00 (d, J = 14.4 Hz, 1H), 3.09 (d, J = 14.4 Hz, 1H), 4.78 (s, 1H), 4.91 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −7.17, −5.67, 14.03, 17.88, 22.58, 22.72, 26.81, 28.29, 29.16, 30.73, 31.67, 43.97, 54.41, 114.71, 139.47, 210.10. Found: C, 72.64; H, 12.16%. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.23%.

5-(*tert*-Butyldimethylsilyl)-3,3-dimethyl-1-undecen-4-one (3e): 0.10 g, 33% yield; Bp 118 °C (0.5 Torr); IR (neat) 2954, 2926, 2854, 1683, 1466, 1254, 1137, 1067, 1006, 916, 841, 822, 810, 788, 769, 687 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.10 (s, 3H), 0.03 (s, 3H), 0.86 (t, J = 6.8 Hz, 3H), 0.92 (s, 9H), 1.16−1.49 (m, 15H, including 1.18 (s, 3H), 1.21 (s, 3H)), 1.90 (m, 1H), 2.90 (dd, J = 1.8, 11.7 Hz, 1H), 5.10−5.18 (m, 2H), 6.00 (dd, J = 10.5, 17.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −6.91, −4.45, 14.05, 18.26, 22.60, 23.47, 24.40, 27.09, 29.34, 31.07, 31.43, 31.69, 38.06, 51.20, 113.81, 143.59, 216.72. Found: C, 73.29; H, 12.53%. Calcd for $C_{19}H_{38}OSi$: C, 73.48; H, 12.33%.

7-(*tert*-Butyldimethylsilyl)-1,3-tridecadien-6-one (3f): 0.19 g, 63% yield; Bp 118 °C (0.5 Torr); IR (neat) 2952, 2926, 2854, 1693, 1466, 1252, 1087, 1003, 835, 824, 805, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.04 (s, 3H), 0.03 (s, 3H), 0.85 (t, J = 6.9 Hz, 3H), 0.93 (s, 9H), 1.10−1.46 (m, 9H), 1.97 (m, 1H), 2.52 (dd, J = 2.1, 11.7 Hz, 1H), 3.08 (dd, J = 7.2, 16.5 Hz, 1H), 3.18 (dd, J = 7.2, 16.5 Hz, 1H), 5.04 (d, J = 9.9 Hz, 1H), 5.14 (d, J = 16.8 Hz, 1H), 5.79 (dt, J = 15.3, 7.2 Hz, 1H), 6.09 (dd, J = 10.2, 15.3 Hz, 1H), 6.34 (ddd, J = 9.9, 10.2, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −7.32, −5.93, 13.94, 17.72, 22.50, 26.71, 28.36, 29.06, 30.81, 31.58, 44.61, 48.61, 116.47, 126.74, 134.32, 136.73, 210.61. Found: C, 73.99; H, 11.83%. Calcd for $C_{19}H_{36}OSi$: C, 73.95; H, 11.76%.

5-(*tert*-Butyldimethylsilyl)-2-undecyn-4-one (3g): 92 mg, 33% yield; Bp 120 °C (0.5 Torr); IR (neat) 2952, 2926, 2854, 2216, 1651, 1467, 1252, 1167, 838, 825, 810, 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.06 (s, 3H), 0.07 (s, 3H), 0.87 (t, J = 6.6 Hz, 3H), 0.93 (s, 9H), 1.14−1.52 (m, 9H), 2.00 (s, 1H), 2.08 (m, 1H), 2.54 (dd, J = 1.8, 11.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −6.82, −6.38, 3.95, 14.03, 17.96, 22.54, 26.75, 28.00, 29.05, 30.76, 31.58, 48.69, 81.30, 88.97, 190.68. Found: C, 72.53; H, 11.41%. Calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50%.

4-(Dimethylphenylsilyl)-1-undecen-4-ol: 0.26 g, 85% yield; Bp 127 °C (0.5 Torr); IR (neat) 2926, 2852, 1429, 1248, 1112, 914, 831, 812, 772, 734, 701, 648 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.38 (s, 3H), 0.39 (s, 3H), 0.88 (t, J = 6.8 Hz, 3H), 1.11 (bs, 1H), 1.15−1.35 (m, 10H), 1.52 (m, 2H), 2.33 (d, J = 7.2 Hz, 2H), 5.03−5.12 (m, 2H), 5.79 (ddt, J = 10.2, 16.8, 7.2 Hz, 1H), 7.33−7.42 (m, 3H), 7.56−7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −4.52, −4.45, 14.03, 22.58, 23.46, 29.12, 30.28, 31.74, 37.78, 41.58, 68.14, 118.44, 127.73, 129.18, 133.80, 134.59, 137.05. Found: C, 75.03; H, 10.72%. Calcd for $C_{19}H_{32}OSi$: C, 74.93; H, 10.59%.

1-(4-Methoxyphenyl)-1-pentanone (5a): 0.15 g, 77% yield; Bp 113 °C (0.5 Torr); IR (neat) 2956, 1679, 1602, 1577, 1510, 1460, 1311, 1259, 1213, 1171, 1031, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 3H), 1.40 (tq, J = 7.8, 7.4 Hz, 2H), 1.70 (tt, J = 7.5, 7.8 Hz, 2H), 2.91 (d, J = 7.5 Hz, 2H), 3.87 (s, 3H), 6.93 (d, J = 9.0 Hz, 2H), 7.94 (d, J = 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.91, 22.50, 26.70, 37.99, 55.42, 113.64, 130.19, 130.32, 163.30, 199.30. Found: C, 74.84; H, 8.58%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

2-(*tert*-Butyldimethylsilyl)-1-(4-methoxyphenyl)-1-pentanone (6a): 0.20 g, 66% yield; Bp 145 °C (0.5 Torr); IR (neat) 2928, 2854, 1651, 1602, 1509, 1464, 1260, 1246, 1209, 1171, 835, 824 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.26 (s, 3H), 0.03 (s, 3H), 0.85 (t, J = 7.2 Hz, 3H), 0.90 (s, 9H), 1.10−1.43 (m, 2H), 1.53 (m, 1H), 2.21 (m, 1H), 3.37 (dd, J = 2.1, 11.7 Hz, 1H), 3.85 (s, 3H), 6.91 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −7.27, −5.83, 14.04, 18.12, 24.04, 27.02, 31.19, 38.15, 55.36, 113.54, 130.19, 132.81, 162.92, 202.25. Found: C, 70.60; H, 10.11%. Calcd for $C_{18}H_{30}O_2Si$: C, 70.53; H, 9.86%.

1-(2,4-Dimethoxyphenyl)-1-octanone (5b): 0.22 g, 84% yield; Bp 140 °C (0.5 Torr); IR (neat) 2926, 2852, 1665, 1602, 1576, 1465, 1293, 1262, 1212, 1163, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.8 Hz, 3H), 1.20−1.39 (m, 8H), 1.85 (tt, J = 7.5, 7.5 Hz, 2H), 2.91 (t, J = 7.5 Hz, 2H), 3.84 (s, 3H), 3.87 (s, 3H), 6.45 (d, J = 2.4 Hz, 1H), 6.51 (dd, J = 2.4, 8.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.94, 22.50, 24.50, 29.09, 29.35, 31.64, 43.57, 55.35, 55.41, 98.37, 104.98, 121.51, 132.64, 160.68, 164.25, 201.22. Found: C, 72.92; H, 9.24%. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15%.

1-(2,4-Dimethoxyphenyl)-2-(*tert*-butyldimethylsilyl)-1-pentanone (6b): 0.29 g, 87% yield; Bp 154 °C (0.5 Torr); IR (neat) 2954, 2928, 1644, 1602, 1465, 1255, 1212, 1162, 1135, 1028, 823 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.23 (s, 3H), −0.03 (s, 3H), 0.87 (s, 9H), 0.88 (t, J = 6.8 Hz, 3H), 1.16−1.53 (m, 3H), 2.23 (m, 1H), 3.80 (dd, J = 1.2, 9.6 Hz, 1H), 3.84 (s, 3H), 3.85 (s, 3H), 6.43 (d, J = 2.4 Hz, 1H), 6.50 (dd, J = 2.4, 8.7 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −7.13, −5.75, 14.10, 18.06, 23.82, 27.03, 31.22, 43.08, 55.27, 55.40, 98.54, 104.75, 124.00, 132.94, 159.86, 163.53, 203.25. Found: C, 67.74; H, 9.73%. Calcd for $C_{19}H_{32}O_3Si$: C, 67.81; H, 9.58%.

1-Thienyl-1-pentanone: 77 mg, 46% yield; Bp 122 °C (13 Torr); IR (neat) 2956, 2930, 2868, 1661, 1519, 1417, 1266, 1209, 856, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.2 Hz, 3H), 1.41 (tq, J = 7.5, 7.2 Hz, 2H), 1.73 (tt, J = 7.5, 7.5 Hz, 2H), 2.90 (t, J = 7.5 Hz, 2H), 7.12 (m, 1H), 7.62 (m, 1H), 7.71 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.76, 22.35, 26.78, 39.08, 128.10, 131.73, 133.39, 144.64, 193.76. Found: C, 64.05; H, 7.15%. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19%.

General Procedure for Three-Component Coupling Reaction. The reaction of **1a**, allyltrimethylsilane, and acetaldehyde was representative. $TiCl_4$ (2.0 mmol) was added to a dichloromethane solution of **1a** (1.0 mmol) and allyltrimethylsilane (1.0 mmol) at −78 °C. After being stirred for 15 min, acetaldehyde (44 mg, 0.06 mL, 1.0 mmol) was added to the reaction mixture and the whole was stirred for another 25 min at −78 °C. The resulting mixture was poured into saturated aqueous NaCl. Extractive workup followed by purification by silica-gel column chromatography gave 5-(1-hydroxyethyl)-1-undecen-4-one (**7a**, 149 mg) in 70% yield: Bp 158 °C (13 Torr); IR (neat) 3404, 2954, 2924, 2854, 1707, 1459, 1378, 1143, 1109, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.6 Hz, 3H), 1.13−1.35 (m, 10H, including, 0.16 (d, J = 6.3 Hz, 3H, *erythro*) 0.20 (d, J = 6.6 Hz, 3H, *threo*)), 1.48−1.76 (m, 3H), 2.25 (bs, 1H, *erythro*), 2.42 (bs, 1H, *threo*), 2.54−2.65 (m, 1H, mainly, 2.62, ddd, J = 4.5, 4.8, 9.2 Hz, *erythro*), 3.21 (dq, J = 6.9, 17.1 Hz, 1H), 3.29 (dd, J = 6.9, 17.1 Hz, 1H), 3.93 (m, 1H, *threo*), 3.96 (dq, J = 4.8, 6.3 Hz, 1H, *erythro*), 5.09−5.21 (m, 2H), 5.83−5.97 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 20.47, 21.68, 22.46, 26.85, 27.16, 27.87, 29.10, 29.34, 29.45, 31.49, 49.06, 49.21, 57.32, 58.05, 67.89, 68.56, 119.04, 119.08, 130.24, 213.32. Found: C, 73.46; H, 11.44%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

***erythro*-5-(1-Hydroxy-1-phenylmethyl)-1-undecen-4-one (7b):** 0.16 g, 58% combined yield (*erythro* and *threo* isomers); Bp 153 °C (0.5 Torr); IR (neat) 3396, 2952, 2924, 2854, 1710, 1455, 1053, 918, 763, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.9 Hz, 3H), 1.05−1.33 (m, 8H), 1.57−1.83 (m, 2H), 2.67 (bs, 1H), 2.84−3.08 (m, 3H), 4.84 (d, J = 6.0 Hz, 1H), 4.98 (dd, J = 1.5, 17.1 Hz, 1H), 5.12 (dd, J = 1.5, 10.2 Hz, 1H), 5.43 (dddd, J = 7.1, 7.1, 10.2, 17.1 Hz, 1H), 7.24−7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.90, 22.42, 27.33, 27.65, 29.36, 31.43, 49.46, 58.62, 74.21, 119.12, 126.23, 127.82, 128.51, 129.93, 142.01, 212.94. Found: C, 78.83; H, 9.70%. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55%.

***threo*-5-(1-Hydroxy-1-phenylmethyl)-1-undecen-4-one (7b):** Bp 153 °C (0.5 Torr); IR (neat) 3448, 2952, 2924, 2854, 1711, 1455, 916, 764, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (t, J = 6.8 Hz, 3H), 1.00−1.24 (m, 8H), 1.42−1.56 (m, 2H), 2.73 (bs, 1H), 2.85 (ddd, J = 4.8, 7.5, 9.1 Hz, 1H), 3.00 (m, 1H), 3.08 (m, 1H), 4.67 (d, J = 7.5 Hz, 1H), 4.95 (dd, J = 1.5, 17.1 Hz, 1H), 5.05 (dd, J = 1.5, 10.2 Hz, 1H), 5.75 (dddd, J = 6.9, 6.9, 10.2, 17.1 Hz, 1H), 7.15−7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 13.85, 22.35, 27.09, 29.14, 29.39, 31.36, 49.80, 57.98, 75.76, 118.92, 126.28, 127.95, 128.58, 130.09, 142.61, 213.86. Found: C, 78.58; H, 9.35%. Calcd for $C_{18}H_{26}O_2$: C, 78.79; H, 9.55%.

5-(1-Hydroxy-1-methylethyl)-1-undecen-4-one (7c): 0.19 g, 83% yield; Bp 94 °C (0.5 Torr); IR (neat) 3436, 2954, 2926, 2854, 1703, 1467, 1378, 1152, 918 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 6.3 Hz, 3H), 1.13−1.36 (m, 14H, including 1.19 (s, 3H) and 1.21 (s, 3H)), 1.47−1.80 (m, 2H), 2.64 (dd, J = 3.3, 10.8 Hz, 1H), 2.69 (bs, 1H), 3.23 (dd, J = 6.9, 17.5 Hz, 1H), 3.33 (dd, J = 6.9, 17.5 Hz, 1H), 5.13 (dd, J = 3.0, 17.1 Hz, 1H), 5.20 (dd, J = 3.0, 10.2 Hz, 1H), 5.91 (dddd, J = 6.9, 6.9, 10.2, 17.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.92, 22.47, 26.86, 28.26, 28.32, 29.49, 29.60, 31.49, 51.35, 59.96, 72.04, 119.05, 130.15, 215.59. Found: C, 74.16; H, 11.83%. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58%.

***erythro*-5-(1-Methoxyethyl)-1-undecen-4-one (7d):** 0.14 g, 61% combined yield (*erythro* and *threo* isomers); R_f 0.50 (hex/AcOEt = 10/1); Bp 90 °C (0.5 Torr); IR (neat) 2924, 2854, 1712, 1459, 1379, 1143, 1116, 1096, 917 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.04 (d, J = 6.3 Hz, 3H), 1.09−1.34 (m, 8H), 1.43 (m, 1H), 1.65 (m, 1H), 2.76 (ddd, J = 4.2, 6.3, 9.8 Hz, 1H), 3.17 (dd, J = 7.2, 17.1 Hz, 1H), 3.31 (dd, J = 7.2, 17.1 Hz, 1H), 3.32 (s, 3H), 3.39 (dq, J = 6.3, 6.3 Hz, 1H), 5.10 (dd, J = 1.5, 17.4 Hz, 1H), 5.15 (dd, J = 1.5, 10.5 Hz, 1H), 5.90 (ddt, J = 10.5, 17.4, 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 16.05, 22.45, 27.55, 28.38, 29.35, 31.51, 49.53, 56.42, 78.06, 118.56, 130.76, 211.19. Found: C, 74.54; H, 11.79%. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58%.

***threo*-5-(1-Methoxyethyl)-1-undecen-4-one (7d):** R_f 0.46 (hex/AcOEt = 10/1); Bp 90 °C (0.5 Torr); IR (neat) 2924, 2854, 2820, 1717, 1465, 1379, 1145, 1116, 1095, 992, 915 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 6.8 Hz, 3H), 1.08−1.39 (m, 12H, including 1.21 (d, J = 6.3 Hz, 3H)), 1.55 (m, 1H), 2.60 (ddd, J = 3.6, 8.8, 10.6 Hz, 1H), 3.16 (dd, J = 6.9, 17.4 Hz, 1H), 3.23 (s, 3H), 3.27 (dd, J = 6.9, 17.4 Hz, 1H), 3.41 (dq, J = 8.8, 6.3 Hz, 1H), 5.10 (dd, J = 1.5, 17.1 Hz, 1H), 5.16 (dd, J = 1.5, 10.5 Hz, 1H), 5.93 (ddt, J = 10.5, 17.1, 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 16.46, 22.45, 27.34, 28.29, 29.37, 31.47, 49.30, 56.52, 58.05, 78.91, 118.39, 130.91, 212.20. Found: C, 74.30; H, 11.75%. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58%.

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