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Fluoride-Promoted Rearrangement of Organo Silicon Compounds: A New Synthesis of 2-(Arylmethyl)aldehydes from 1-Alkynes

Laura Antonella Aronica, Patrizio Raffa, Anna Maria Caporusso, and Piero Salvadori*

Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, Via Risorgimento 35, 56126 Pisa, Italy

psalva@dcci.unipi.it

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A new approach to 2-(arylmethyl)aldehydes **4** based upon a 1,2-anionotropic rearrangement of an aryl group is presented. The synthetic sequence begins with a silylformylation reaction of terminal acetylenes **5** with aryl and heteroaryl silanes **6**, followed by treatment of the products **(*Z*)-1** with TBAF. The optimization of the experimental conditions of the fluoride-promoted step is described, together with the synthetic potentialities of the process. A plausible mechanism of the rearrangement reaction is reported that suggests the addition of the fluoride ion to the arylsilicon moiety of β-silylalkenals **(*Z*)-1** and the consequent migration of the aryl group to the adjacent carbon atom. Both aryl and heteroaryl substituents can rearrange without any loss of configuration. Bromo-functionalized substrates undergo an intramolecular reaction that affords exclusively carbacyclobenzyl aldehydes, further enhancing the high synthetic value of this method.

Introduction

Silicon has received the attention of chemists for many years because of its low cost, abundance, and nontoxic properties. In particular, the use of organosilicon compounds to synthetic laboratory and large-scale applications has been growing intensively, due to their relatively high stability and their ability to induce chemo-, regio-, and stereoselective transformation when combined with appropriate catalysts. For instance, the transition-metal-mediated hydrosilylation[1] and, more recently, the rhodium-mediated silylformylation reactions[2] are among the suitable methods used to functionalize carbon−carbon multiple bonds.

During our studies on the silylformylation of terminal acetylenes[3] with dimethylphenylsilane, we investigated the synthetic potentialities of (*Z*)-2-(dimethylphenylsilylmethylene)hexanal **(*Z*)-1aa**. While the isomerization, the reduction, and the Wittig transformation of this compound can be easily performed,[3,4] all the attempts to achieve the protodesilylation reaction surprisingly failed[5] (Scheme 1). KF/MeOH and TBAF/MeOH were completely ineffective, and the reaction with BF_3−acetic acid complex generated a mixture of (*E*)-2-(dimethylphenylsilylmethylene)hexanal **(*E*)-1aa** and 2-benzylhexanal **4aa**. Complete isomerization of **(*Z*)-1aa** to **(*E*)-1aa** resulted when paratoluensulfinic acid was used.

On the other hand, we observed that when (*Z*)-2-(dimethylphenylsilylmethylene)hexanal **(*Z*)-1aa** was reacted with a fluoride source such as tetrabutylammonium fluoride (TBAF) in a polar aprotic solvent[5] (THF, DMSO, CH_3CN) 2-benzylhexanal **4aa** was exclusively formed (Scheme 1). This appeared very promising from the synthetic point of view. The reaction seemed to involve an anionotropic 1,2-migration of a phenyl group from the silicon atom to the adjacent carbon atom of the α,β-unsaturated aldehyde **(*Z*)-1aa**. To our knowledge, only Fleming[6] described a similar phenyl transposition from Si to the β position of a polysilylated enone system. As a matter of fact, while silicon migrations from carbon to oxygen (Brook rearrangements) are well-known processes,[7] the shift of a carbon (especially aryl groups) from silicon to an adjacent carbon atom is more recent and usually occurs in acylsilanes[8] and in molecules character-

* Corresponding author.

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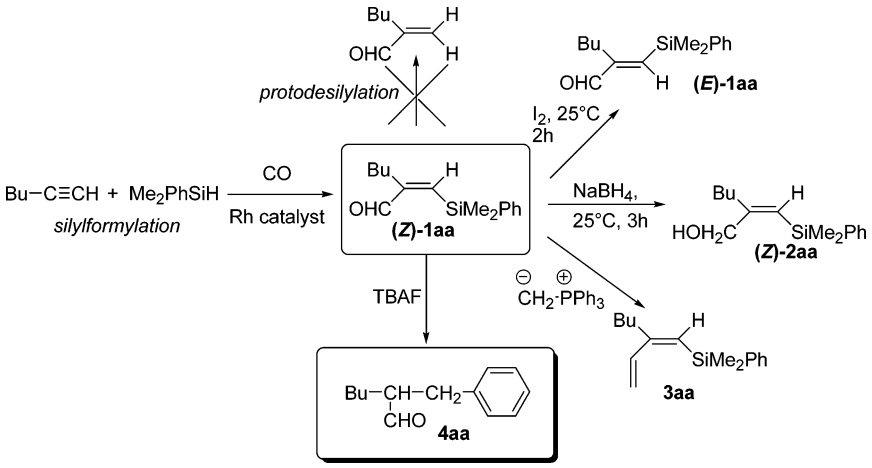
SCHEME 1



ized by the presence of a good leaving group such as halide and triflate.[9]

Here, we report the optimization and the extension of this fluoride mediated reaction to several β-silylalkenals **(*Z*)-1**, which can represent a novel route to the preparation of a large variety of 2-arylmethyl and 2-heteroarylmethyl aldehydes from 1-alkynes, usually obtained through complex synthetic pathways.[10]

Results and Discussion

Alkynes **5a**−**f** and arylsilanes **6a**−**f** (Table 1) were chosen as precursors for the synthesis of the β-silylalkenals **(*Z*)-1**, having different steric and electronic features.

Except for the commercially available 1-hexyne (**5a**) and bromoalkynes **5e**,**f**, acetylenes **5b**−**d** were prepared from the corresponding bromoallenes through a well-known procedure.[11] The synthesis of arylsilanes was performed by reacting excess Me_2ClSiH with ArMgBr, according to the method described by Hiyama and coworkers[12] (Scheme 2). Both aromatic and heteroaromatic silanes were obtained with good to excellent yields (61−85%).

The β-silylalkenals **(*Z*)-1** were then prepared by silylformylation[2] of equimolar amounts of the corresponding acetylenes **5** and the appropriate aryldimethylsilane **6**, as reported in Table 1. The reactions were performed at room temperature, in a stainless steel autoclave, and required a catalytic (0.1mol %) amount of $Rh_4(CO)_{12}$ with respect to the silane.

Both aromatic and heteroaromatic silanes **6a**−**f** were successfully reacted, affording the silylformylation products **(*Z*)-1** with good yields and complete regio- and stereoselectivity. As we previously reported,[3] the silylformylation process was markedly affected by the structure of the reagents: linear β-silylalkenals **(*Z*)-1aa** and **(*Z*)-1fa** were obtained with excellent yields under mild experimental conditions (10 atm of CO, Table 1, entries 1 and 11), while higher CO pressure (25−50 atm) and longer reaction times were required when the steric hindrance of both the alkynes and the hydrosilanes increased (Table 1, entries 2−5 and 8).

To optimize the reaction of fluoride-mediated rearrangement, preliminary experiments were performed using (*Z*)-2-(dimethylphenylsilylmethylene)hexanal **(*Z*)-1aa** as model compound (Table 2). All the reactions were carried out in tetrahydrofuran since a polar aprotic solvent was necessary to achieve the fluoride ion coordination to the silicon atom of the β-silylalkenal.[5] Indeed, in the presence of a polar protic solvent such as methanol, no reaction occurred, probably due to the strong hydrogen bonds between MeO−H and F^- that could generate a shield effect around the fluoride ion. On the other hand, when a solution of **(*Z*)-1aa** in THF was treated with an equimolar amount of TBAF at room temperature, the complete consumption of the β-silylalkenal and the formation of the corresponding 2-benzylhexanal **4aa** was observed immediately after the addition of tetrabutylammonium fluoride (1 M in THF) to **(*Z*)-1aa** and hydrolyzation with water. According to this method (A, Table 2, entry 1), the desired product **4aa** was obtained with good but not excellent yield after purification on silica gel column. The lack of purified product (60% yield vs 100% conversion) could be possibly ascribed to the mild acid experimental conditions that could favor the formation of high weighted polycondensated products, detected by GC analysis. With the aim of minimizing the extent of byproducts, hydrolysis with a pH 7 buffer (KH_2PO_4/

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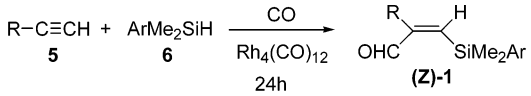
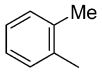
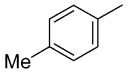
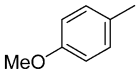
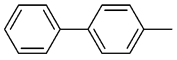
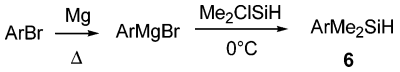
TABLE 1. Silylformylation of 1-Alkynes 5[a]



Entry	5		6		P_{CO} (atm)	Yield(%)[b] (*Z*)-1	
1	*n*-Bu	**a**	Ph	**a**	10	95	**aa**
2	Me Me−CH	**b**	Ph	**a**	10	55	**ba**
3[c]	Et Me−CH	**c**	Ph	**a**	25	60	**ca**
4	Ph Me−CH	**d**	Ph	**a**	50	62	**da**
5	*n*-Bu	**a**		**b**	30	56	**ab**
6	*n*-Bu	**a**		**c**	30	73	**ac**
7	*n*-Bu	**a**		**d**	30	77	**ad**
8	*n*-Bu	**a**		**e**	45	55	**ae**
9	*n*-Bu	**a**		**f**	30	85	**af**
10	$Br(CH_2)_2$	**e**	Ph	**a**	35	62	**ea**
11	$Br(CH_2)_4$	**f**	Ph	**a**	10	87	**fa**

[a] Reaction performed in a stainless steel autoclave, with 3 mmol of silane **6** and 3 mmol of 1-alkyne **5**, in 3 mL of toluene, at room temperature. [b] Yields of purified products. [c] Reaction time: 48 h.

SCHEME 2



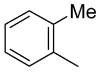
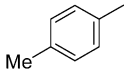
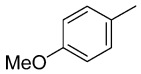
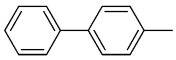
NaOH) was carried out. Yet, no increase of the product amount was observed, even operating at low temperature (methods B and C, Table 2). A remarkable improvement of the yield (78%) was achieved by performing a reverse addition of the *β*-silylalkenal to a solution of excess TBAF in THF (method E). The same result was obtained when this methodology was extended to different *β*-silylaldehydes such as *o*-tolyl-, *p*-tolyl-, and even thienyldimethylsilylalkenal, confirming the large applicability and the high synthetic potentialities of the rearrangement process.

In all cases, the yields of the corresponding 3-arylaldehydes **4** were clearly enhanced (Table 2, entries 5, 7, 9, and 13 vs entries 1, 6, 8, and 12). The excess tetrabutylammonium solution, which contains 5% water, probably favors the fast hydrolysis of enol silyl ethers **9** and **10**, reasonably formed during the process, speeding up the formation of aldehyde **4** (Scheme 3). Indeed, the proposed mechanism involves the addition of fluoride to silicon yielding a pentacoordinate Si atom **7**, aryl-1,2-anionotropic rearrangement to the adjacent carbon atom with formation of enolate **8**, and its possible cyclization and final removal of enol silyl ether **10** by water or excess fluoride itself (Scheme 3).

While all attempts to isolate enol silyl ethers **9** and **10** were unsuccessful, the presence of enolate **8** as intermediate of the reaction was confirmed by the results obtained performing the reaction with the bromo-substituted aldehydes **(*Z*)-1ea** and **(*Z*)-1fa** (Scheme 4). Surprisingly, not only the cyclopentyl but even the cyclopropyl derivatives were easily formed, indicating an intramolecular nucleophilic attack of the carbanion to the $Br-CH_2$ bond. The cyclization process was so favored (82−90% yields of the purified product) that the experimental conditions did not need to be optimized in these cases.

The described results demonstrate that no protodesilylation process may occur when a *β*-silylalkenal is treated with a fluoride source that is under the common

TABLE 2. TBAF-Induced Anionotropic Rearrangement of β-Silylalkenal

Entry	R	Ar	(*Z*)-1	Reaction Conditions	Yield[a]	4
1	*n*-Bu	Ph	**aa**	A[b]	60	**aa**
2	*n*-Bu	Ph	**aa**	B[c]	55	**aa**
3	*n*-Bu	Ph	**aa**	C[d]	45	**aa**
4	*n*-Bu	Ph	**aa**	D[e]	55	**aa**
5	*n*-Bu	Ph	**aa**	E[f]	78	**aa**
6	*n*-Bu		**ab**	A	51	**ab**
7	*n*-Bu		**ab**	E	61	**ab**
8	*n*-Bu		**ac**	A	35	**ac**
9	*n*-Bu		**ac**	E	63	**ac**
10	*n*-Bu		**ad**	A	35	**ad**
11	*n*-Bu		**ae**	E	54	**ae**
12	*n*-Bu		**af**	A	25	**af**
13	*n*-Bu		**af**	E	58	**af**
14[g]	Me−CH(Me)	Ph	**ba**	A	46	**ba**
15[g]	Me−CH(Et)	Ph	**ca**	A	71	**ca**[h]
16[g]	Me−CH(Ph)	Ph	**da**	A	60	**da**[h]

[a] Yields of purified products. [b] Method A: 1 mL of TBAF (1 M in THF) was added to 1 mmol of aldehyde in 10 mL of THF at room temperature and then hydrolyzed immediately with water. [c] Method B: 1 mL of TBAF (1 M in THF) was added to 1 mmol of aldehyde in 10 mL of THF at room temperature and then hydrolyzed immediately with KH_2PO_4−NaOH (pH 7). [d] Method C: 1 mL of TBAF (1 M in THF) was added to 1 mmol of aldehyde in 10 mL of THF at 0 °C and then hydrolyzed immediately with KH_2PO_4−NaOH (pH 7). [e] Method D: 1 mmol of aldehyde was added to 1 mL of TBAF (1 M in THF) dissolved in 10 mL at room temperature and then hydrolyzed immediately with water. [f] Method E: 1 mmol of aldehyde was added to 2.5 mL of TBAF (1 M in THF) dissolved in 10 mL at room temperature and then hydrolyzed immediately with water. [g] Reactions performed in DMSO. [h] A diastereoisomeric (50:50) mixture was obtained.

protodesilylation conditions.[13] On the other hand, the transformation of the β-silylalkenals into the corresponding α,β-unsaturated aldehydes would represent an alternative preparation of these important molecules with respect to the direct hydroformylation of alkynes, which usually suffers from a lack of regio-, chemo-, and stereoselectivity.[14] On the contrary, an easy three-step sequence of reduction,[15] protodesilylation,[16] and reoxidation[17] can afford the desired aldehydes, as described in Scheme 5 for (*Z*)-2-(dimethylphenylsilylmethylene)hexanal **(*Z*)-1aa**.

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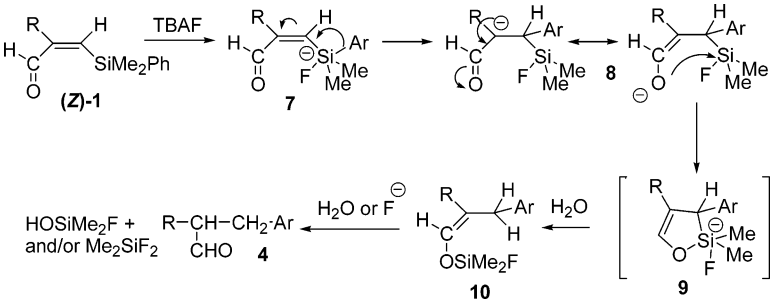
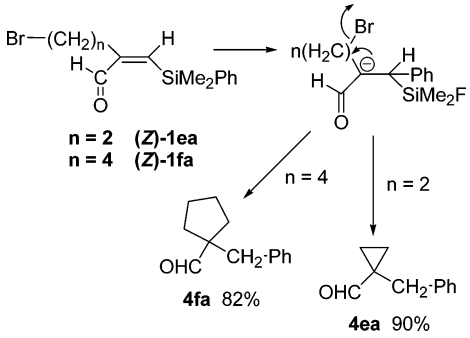
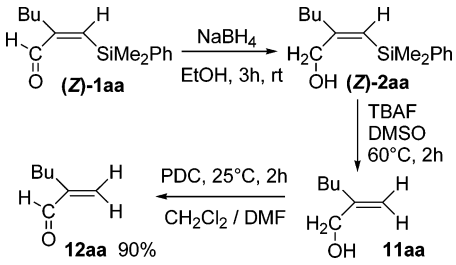
SCHEME 3



SCHEME 4



SCHEME 5



The three reactions were performed under mild experimental conditions, and the crude products were employed in the next step without any further purification, affording aldehyde **12aa** with a 90% total yield from **(*Z*)-1aa**.

The protodesilylation process of the allylic alcohol **(*Z*)-2aa** was easily performed, since the presence of the OH in the β position to the silyl moiety promotes the removal of the silicon group (beta effect).[14,6] The subsequent oxidation[17] with pyridinium dichromate (PDC) yielded the desired unsaturated aldehyde **12aa** quantitatively.

Conclusions

This paper describes a new synthetic pathway to 2-(arylmethyl)aldehydes from terminal acetylenes consisting of a two-step silylformylation−aryl migration sequence. The aryl anionotropic rearrangement, which represents the key step of the method, was optimized. During the rearrangement process, the original configuration of the Ar group on the silicon atom (*o*-tolyl, *p*-tolyl, 1-thienyl, ...) was maintained and the migratory aptitudes of the aryl and heteroaryl moiety appeared to be greater than that of methyl. Considering that the anionotropic migration can be successfully extended to a large variety of β-silylalkenal characterized by different steric and electronic features, the method can easily afford 2-(arylmethyl)aldehydes and related derivatives, useful building blocks for organic synthesis[18] and important industrial substrates.[19] It is noteworthy that when the reaction was performed with a bromo-functionalized β-silylalkenal an unexpected intramolecular process occurred and carbacyclobenzyl aldehydes were obtained with excellent yields.

Experimental Section

General Remarks. All solvents were reagent-grade materials purified by standard methods. Tetrahydrofuran and toluene were distilled from sodium immediately before use. Dimethylphenylsilane and 1-hexyne were distilled and stored over molecular sieves. Bromoalkynes **5e**,**f** were used without purification. $Rh_4(CO)_{12}$[20] was prepared and purified as previously reported. 3-Methyl-1-butyne **5b**, 3-methyl-1-pentyne **5c**, and 3-phenyl-1-butyne **5d** were synthesized from the corresponding bromoallenes according to literature methods.[11] (*o*-Methylphenyl)dimethylsilane[21] **6b**, (*p*-methylphenyl)dimethylsilane[12] **6c**, (*p*-methoxyphenyl)dimethylsilane[12] **6d**, biphenyl-4-yl-dimethylsilane[22] **6e**, and dimethylthiophen-2-ylsilane[23] **6f** were generated from the corresponding Grignard reagents according to the method described by Hiyama and co-workers.[12]

GLC analyses were performed with a DB1 capillary column (30 m × 0.52 mm, 5 micron) using He as the carrier gas and a flame ionization detector (FID). Column chromatography was performed on silica gel 60 (230−400 mesh).

General Procedure for the Rhodium-Catalyzed Silylformylation of 1-Alkynes 5a−f with silanes 6a−f. Carbonylation reactions were run in a 25 mL stainless steel autoclave fitted with a Teflon inner crucible and a stirring bar. In a typical run, 3 mmol of silane, 3 mmol of the required

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1-alkyne, 3 mL of toluene, and a 0.1 mmol % of $Rh_4(CO)_{12}$ were put, under CO atmosphere, in a Pyrex Schlenk tube. This solution was introduced in the autoclave, previously placed under vacuum (0.1 mmHg), by a steel siphon. The reactor was pressurized with carbon monoxide and the mixture was stirred at room temperature for 24 h, unless otherwise specified. After removal of excess CO (fume hood), the reaction mixture was diluted with pentane, filtered (Celite), and concentrated by bulb-to-bulb distillation (1 mmHg). The residue was purified by column chromatography on silica gel using pentane/EtOAc (95/5) as eluent, affording the pure aldehydes **(*Z*)-1aa**−**fa** (Table 1).

Spectral data of **(*Z*)-1aa**, **(*Z*)-1ba**, **(*Z*)-1ca**, and **(*Z*)-1da** perfectly agreed with literature.[3]

2-[(Dimethyl-*o*-tolylsilyl)methylene]hexanal (*Z*)-1ab: colorless oil; IR (neat) 3048, 2952, 2741, 1683, 1589, 1448, 1252 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.52 (s, 6H), 0.89 (t, J = 7.2 Hz, 3H), 0.24−1.42 (m, 4H), 2.27 (dt, J = 7.3, 0.9 Hz, 2H), 2.36 (s, 3H), 6.98 (t, J = 0.9 Hz, 1H), 7.24−7.44 (m. 3H), 7.57 (dd, J = 7.3, 1.5 Hz, 1H), 9.97 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 0.4, 13.9, 22.4, 23.3, 30.6, 31.4, 125.3, 129.9, 130.1, 134.1, 136.4, 143.2, 150.2, 156.6, 193.3; GC−MS (EI) *m*/*z* (rel int) 245 (M^+ − 15), 203 (35), 169 (15), 151(18), 140 (20), 127 (33), 91 (12), 75 (35), 61 (33), 43 (100). Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.73; H, 9.26.

2-[(Dimethyl-*p*-tolylsilyl)methylene]hexanal (*Z*)-1ac: colorless oil; IR (neat) 3052, 2941, 2733, 1684, 1590, 1458, 1250, 1106 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.53 (s, 6H), 0.95 (t, J = 6.9 Hz, 3H), 1.32−1.52 (m, 4H), 2.35 (t, J = 7.8 Hz, 2H), 2.38 (s, 3H), 6.97 (s, 1H), 7.22 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 9.82 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 0.02, 13.9, 21.5, 22.5, 30.7, 31.6, 129.0, 133.6, 134.4, 139.4, 149.2, 157.1, 193.3; GC−MS (EI) *m*/*z* (rel int) 245 (M^+-15), 217 (11), 203 (70), 149(32), 127 (38), 119 (15), 105 (16), 91 (15), 75 (25), 61 (34), 43 (100). Anal. Calcd for $C_{16}H_{24}OSi$: C, 73.79; H, 9.29. Found: C, 73.76; H, 9.29.

2-[(4-Methoxyphenyl)dimethylsilylmethylene]hexanal (*Z*)-1ad: colorless oil; IR (neat) 3009, 2956, 2847, 2737, 1682, 1594, 1503, 1464, 1279, 1249, 1112 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.48 (s, 6H), 0.90 (t, J = 7.3 Hz, 3H), 1.26−1.44 (m, 4H), 2.29 (t, J = 7.2 Hz, 2H), 3.80 (s, 3H), 6.89−6.93 (m, 3H), 7.43 (d, J = 8.4 Hz, 2H), 9.77 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 0.1, 13.9, 22.4, 30.6, 31.5, 55.0, 114.0, 128.8, 135.0, 149.4, 157.0, 160.7, 193.4; GC−MS (EI) *m*/*z* (rel int) 276 (M^+), 161 (42), 219 (100), 165 (40), 159 (43), 135 (21), 127 (50), 91 (24), 75 (43), 59 (66). Anal. Calcd for $C_{16}H_{24}O_2Si$: C, 69.51; H, 8.75. Found: C, 69.48; H, 8.72.

2-[(Biphenyl-4-yldimethylsilanyl)methylene]hexanal (*Z*)-1ae: colorless oil; IR (neat) 3066, 3026, 2957, 2738, 1682, 1597, 1428, 1254 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.57 (s, 6H), 0.95 (t, J = 6.9 Hz, 3H), 1.28−1.56 (m, 4H), 2.37 (t, J = 7.0 Hz, 2H), 6.99 (s,1H), 7.35−7.50 (m. 4H), 7.60−7.65 (m, 5H), 9.98 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ −0.1, 13.9, 22.4, 30.5, 31.55, 126.8, 127.1, 127.5, 128.7, 134.0, 136.6, 140.7, 142.2, 148.8, 157.2, 193.2; GC−MS (EI) *m*/*z* (rel int) 322 (M^+), 307 (60), 265 (75), 211 (29), 205 (30), 195 (34); 181 (26), 181 (26), 169 (67), 153 (29), 127 (100), 105 (22), 75 (75). Anal. Calcd for $C_{21}H_{26}OSi$: C, 78.21; H, 8.13. Found: C, 78.22; H, 8.10.

2-[(Dimethylthiophene-2-ylsilanyl)methylene]hexanal (*Z*)-1af: colorless oil; IR (neat) 3075, 2956, 2929, 2859, 2735, 1686, 1585, 1466, 1406, 1253, 1214 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.54 (s, 6H), 0.90 (t, J = 7.3 Hz, 3H), 1.26−1.44 (m, 4H), 2.30 (t, J = 7.2 Hz, 2H), 6.88 (s, 1H), 7.18 (dd, J = 3.3, 4.5 Hz, 1H), 7.29 (dd, J = 0.6, 3.3 Hz, 1H), 7.62 (dd, J = 0.6, 4.5 Hz, 1H) 9.82 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 1.1, 13.9, 22.0, 30.5, 31.6, 128.4, 131.5, 135.1, 137.5, 147.9, 175.4, 193.1; GC−MS (EI) *m*/*z* (rel int) 252 (M^+), 237 (56), 195 (100), 177 (19), 135 (26), 111 (13), 98 (14), 75 (20). Anal. Calcd for $C_{13}H_{20}OSSi$: C, 61.85; H, 7.99. Found: C, 61.83; H, 7.96.

4-Bromo-2-[(dimethylphenylsilyl)methylene]butanal (*Z*)-1ea: colorless oil; IR (neat) 3067, 2954, 2808, 1687, 1594, 1428, 1250, 1106 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.54 (s, 6H), 2.78 (t, J = 7.6 Hz, 2H), 3.25 (t, J = 7.6 Hz, 2H), 6.96 (s, 1H), 7.34−7.43 (m, 3H), 7.49−7.56 (m, 2H), 9.41 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ −1.7, 30.0, 32.0, 128.2, 129.7, 133.7, 136.3, 153.4, 154.8, 194.8; GC−MS (EI) *m*/*z* (rel int) 297 (M^+), 295 (M^+), 283 (8), 281 (12), 203 (62), 210 (8), 189 (81), 141 (86), 135 (100), 129 (66), 105 (46), 91 (28), 77 (55). Anal. Calcd for $C_{13}H_{17}BrOSi$: C, 52.53; H, 5.76; Br, 26.88. Found: C, 52.51; H, 5.73; Br, 26.85.

6-Bromo-2-[(dimethylphenylsilyl)methylene]hexanal (*Z*)-1fa: colorless oil; IR (neat) 3063, 2957, 2736, 1686, 1589, 1455, 1428, 1251 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.51 (s, 6H), 1.50−1.68 (m, 2H), 1.78−1.94 (m, 2H), 2.32 (t, J = 8.1 Hz, 2H), 3.39 (t, J = 6.6 Hz, 2H), 6.96 (s, 1H), 7.33−7.43 (m, 3H), 7.45−7.55 (m, 2H), 9.76 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ −0.1, 26.9, 30.9, 32.3, 33.3, 128.2, 129.5, 133.5, 137.8, 149.6, 156.2, 193.0; GC−MS (EI) *m*/*z* (rel int) 311 (M^+ − 15), 309 (M^+ − 15), 249, (15), 247 (16), 203 (43), 187 (97), 167 (28), 139 (64), 129 (100), 105 (64), 91 (81), 75 (50), 43 (58). Anal. Calcd for $C_{15}H_{21}BrOSi$: C, 55.38; H, 6.51; Br, 24.56. Found: C, 55.34; H, 6.53; Br, 24.59.

General Procedures for the TBAF-Promoted Rearrangements of (Z)-1: Method A. To a solution of 1 mmol of **(Z)-1** in 10 mL of THF was added, at room temperature, 1 mL of TBAF (1 M in THF). The reaction mixture was hydrolyzed with water and extracted with Et_2O, and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using hexane/EtOAc (90/10) as eluent. **Method B.** To a solution of 1 mmol of **(*Z*)-1** in 10 mL of THF was added, at room temperature, 1 mL of TBAF (1 M in THF). The reaction mixture was hydrolyzed with KH_2PO_4−NaOH (pH 7) and submitted to the usual workup (method A). **Method C.** Identical to method B, except for the experimental temperature (0 °C). **Method D.** One millimole of aldehyde was added to 1 mL of TBAF (1 M in THF) dissolved in 10 mL of THF, at room temperature, hydrolyzed immediately after with water, and extracted with Et_2O, and the organic layers were dried over Na_2SO_4. After concentration under vacuum, the crude product was purified by column chromatography on silica gel using hexane/EtOAc (90/10) as eluent. **Method E.** Identical to method D, except for the quantity of TBAF (2.5 mL).

2-Benzylhexanal 4aa perfectly agreed with the literature.[4]

2-(2-Methylbenzyl)hexanal, 4ab: colorless oil; IR (neat) 2956, 2930, 2716, 1726, 1464 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J = 6.6 Hz, 3H), 1.20−1.38 (m, 2H), 1.40−1.78 (m, 4H); 2.31 (s, 3H), 2.52−2.6 (m, 1H), 2.69 (dd, J = 6.6, 13.3 Hz, 1H), 2.97 (dd, J = 6.6, 13.3 Hz, 1H), 7.10−7.14 (m, 4H), 9.53 (d, J = 2.6, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.8, 19.4, 22.7, 28.7, 29.1, 32.4, 52.1, 125.9, 126.4, 126.5, 130.4, 136.0, 137.1, 204.6; GC−MS (EI) *m*/*z* (rel int) 147 (M^+-57), 129 (21), 105 (100), 91 (18), 77 (10). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.28; H, 9.91.

2-(4-Methylbenzyl)hexanal, 4ac: colorless oil; IR (neat) 2956, 2932, 2712, 1725, 1513, 1248 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.6 Hz, 3H), 1.23−1.35 (m, 2H), 1.42−1.53 (m, 2H), 1.58−1.70 (m, 2H), 2.31 (s, 3H), 2.52−2.64 (m, 1H), 2.67 (dd, J = 6.6, 13.6 Hz, 1H), 2.94 (dd, J = 6.6, 13.6 Hz, 1H), 7.04 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H) 9.64 (d, J = 2.4, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.8, 20.9, 22.7, 28.2, 29.0, 34.6, 53.4, 128.8, 129.1, 135.7, 135.8, 204.8; GC−MS (EI) *m*/*z* (rel int) 204 (M^+), 147 (30), 91(17), 77 (12). Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.28; H, 9.85.

2-(4-Methoxybenzyl)hexanal, 4ad: colorless oil; IR (neat) 2956, 2932, 2712, 1725, 1513, 1248 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, J = 6.6 Hz, 3H), 1.21−1.33 (m, 2H), 1.39−1.50 (m, 2H); 1.55−1.65 (m, 2H), 2.49−2.58 (m, 1H), 2.65 (dd, J = 7.5, 14.2 Hz, 1H), 2.89 (dd, J = 7.5, 14.2 Hz, 1H), 3.75 (s, 3H), 6.79 (d, J = 8.7 Hz, 2H), 7.05 (d, J = 8.7 Hz, 2H) 9.62 (d, J = 2.7, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.8, 22.7, 28.3, 29.1, 34.2, 53.6, 55.2, 113.9, 129.9, 130.8, 158.1, 205.0; GC−

MS (EI) *m/z* (rel int) 221 ($M^+ + 1$) 163 (4), 121 (100), 91 (5), 77 (5), 41 (13). Anal. Calcd for $C_{13}H_{18}O_2$: C, 76.33; H, 9.15. Found: C, 76.31; H, 9.18.

2-Biphenyl-4-ylmethylhexanal 4ae: colorless oil; IR (neat) 2956, 2929, 2710, 1724, 1487, 1261 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, J = 7.0 Hz, 3H), 1.28−1.82 (m, 6H), 2.58−2.72 (m, 1H), 2.78 (dd, J = 6.6, 13.5 Hz, 1H), 3.05 (dd, J = 6.6, 13.5 Hz, 1H), 7.23−7.63 (m, 9H) 9.70 (d, J = 2.6, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.8, 22.6, 28.3, 29.0, 34.5, 53.3, 126.9, 127.10, 127.13, 128.7, 129.3, 137.9, 139.2, 140.7, 204.6; GC−MS (EI) *m/z* (rel int) 266 (M^+), 209 (9), 167 (100), 152 (12), 115 (4). Anal. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.69; H, 8.35.

2-Thiophene-2-ylmethylhexanal, 4af: colorless oil; IR (neat) 3103, 3067, 2958, 2911, 2859, 2714, 1726, 1456 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.6 Hz, 3H), 1.24−1.38 (m, 2H), 1.46−1.60 (m, 2H); 1.62−1.74,(m, 2H), 2.56−2.66 (m, 1H), 2.95 (dd, J = 6.3, 15.0 Hz, 1H), 3.18 (dd, J = 6.3, 15 Hz, 1H), 6.76−6.78 (m, 1H), 6.89 (dd, J = 3.3, 5.1 Hz, 1H) 7.11 (dd, J = 1.2, 5.1 Hz, 1H) 9.66 (d, J = 2.4, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.8, 22.7, 28.2, 28.8, 28.9, 53.4, 123.8, 125.6, 126.9, 141.3, 204.1; GC−MS (EI) *m/z* (rel int) 196 (M^+), 139 (17), 111 (13), 97 (100), 84 (27). Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.31; H, 8.26.

2-Benzyl-3-methylbutanal 4ba: colorless oil; IR (neat) 2717, 1949, 1877, 1804, 1724 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.04 (d, J = 7 Hz, 6H), 2.06 (m, 1H), 2.45−2.56 (m, 1H), 2.75 (dd, J = 14.0, 2.7 Hz, 1H), 2.99 (dd, J = 14.0, 9.2 Hz, 1H), 7.10−7.32 (m, 5H), 9.68 (d, J = 2.6 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 19.7, 19.9, 28.2, 31.9, 59.6, 126.1, 128.4, 128.8, 139.6, 204.9; GC−MS (EI) *m/z* (rel int) 133 ($M^+ - 43$), 105 (9), 91 (50), 65 (11), 56 (20), 52 (21), 43 (42), 41 (92), 39 (100). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.75; H, 9.18.

2-Benzyl-3-methylpentanal 4ca (diastereoisomeric mixture, 50:50): colorless oil; IR (neat) 2719, 1945, 1879, 1802, 1724, 1705 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.83−1.04 (m, 12H), 1.2−2.0 (m, 6H), 2.56−3.10 (m, 6H), 7.1−7.3 (m, 10H); 9.66 (d, J = 2.3 Hz, 1H), 9.72 (d, J = 2.3 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 11.7 and 11.8, 16.0 and 16.2, 27.0, 30.6 and 32.2, 34.5 and 35.3, 58.0 and 58.2, 126.1 and 126.2, 128.3 and 128.4, 128.7 and 128.8, 139.6 and 139.9, 204.7 and 205.1; GC−MS (EI) *m/z* (rel int) (1 diastereoisomer), 133 ($M^+ - 57$), 115 (10), 91 (55), 77 (3), 65 (6), 56 (29), 43 (29), 41 (100); GC−MS (EI) *m/z* (rel int) (1 diastereoisomer) 133 ($M^+ - 57$), 105 (8), 91 (66), 65 (8), 56 (13), 43 (35), 41 (100), 39 (79). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.03; H, 9.55.

2-Benzyl-3-phenylbutanal 4da (diastereoisomeric mixture, 50:50): colorless oil; IR (neat) 2721, 1945, 1877, 1792, 1724 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.31 (d, J = 6.9 Hz, 3H), 1.39 (d, J = 6.9, 3H), 2.55−3.31 (m, 8H), 7.00−7.40 (m, 20H), 9.57 (d, J = 3 Hz, 1H), 9.65 (d, J = 3 Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 18.2 and 19.4, 32.4 and 34.3, 39.9 and 40.1, 59.6 and 59.9, 126.3 and 126.3, 126.9, 127.5 and 127.7, 128.5 and 128.6, 128.7 and 128.9, 136.8 and 139.2, 143.8, 204.2 and 204.7; GC−MS (EI) *m/z* (rel int) (1 diastereoisomer), 220 ($M^+ - 18$), 147 (10), 133 (80), 115 (10), 105 (100), 91 (54), 77 (16), 65 (11), 51 (15); GC−MS (EI) *m/z* (rel int) (1 diastereoisomer), 220 ($M^+ - 18$), 147 (23), 133 (75), 115 (9), 105 (100), 91 (62), 77 (19), 65 (12), 51 (15). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.66; H, 7.63.

1-Benzylcyclopropanecarbaldehyde, 4ea: colorless oil; IR (neat) 2919, 2728, 2080, 1947, 1879, 1708, 1495 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.06−1.12 (m, 2H), 1.25−1.31 (m, 2H), 3.12 (s, 2H); 7.27−7.42 (m, 5H), 8.87 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 12.7, 32.6, 34.9, 126.2, 128.2, 129.3, 138.6, 201.3; GC−MS (EI) *m/z* (rel int) 160 (M^+), 159 (28), 142 (39), 129 (52), 103 (16), 91 (100), 77 829), 65 (33), 51 (17). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.41; H, 7.52.

1-Benzylcyclopentanecarbaldehyde, 4fa: colorless oil; IR (neat) 2721, 1948, 1877, 1809, 1720.cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.48−1.68 (m, 6H), 1.85−1.95 (m, 2H), 2.91 (s, 2H), 7.09−7.27 (m, 5H), 9.56 (s, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 24.8, 32.3, 41.1, 59.1, 126.4, 128.2, 129.8, 137.9, 205.0; GC−MS (EI) *m/z* (rel int) 188 (M^+), 91(100), 41 (16), 39 (19). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.91; H, 8.53.

Synthesis of 2-Methylenehexanal 12aa. To a solution of 2 mmol of **(*Z*)-1aa** in 10 mL of absolute EtOH, cooled at 0 °C, were added 3 mmol of $NaBH_4$. The suspension was stirred at room temperature for 3 h, hydrolyzed with water and extracted with dichloromethane. The organic layers were dried over Na_2SO_4 and then concentrated under vacuum. The crude 2-[(dimethylphenylsilyl)methylene]hexan-1-ol **(*Z*)-2aa** was dissolved in 10 mL of DMSO and treated with 2 mL of TBAF (1 M in THF). The solution was heated at 60 °C for 2 h, hydrolyzed (H_2O), and extracted with Et_2O. The organic fractions were dried over Na_2SO_4 and evaporated in vacuo, and the crude 2-methylenehexan-1-ol **11aa** was added to a solution of PDC (6 mmol in 10 mL of DMF and 10 mL of CH_2Cl_2). The solution was stirred for 2 h, hydrolyzed with water, and extracted with pentane. The organic layers were dried (Na_2SO_4), and the solvent was removed under vacuum. The crude 2-methylenehexanal **12aa** was purified by column chromatography on silica gel using hexane/EtOAc (95/5) as eluent affording 0.20 g (1.8 mmol, 90%) of pure aldehyde.

2-[(Dimethylphenylsilyl)methylene]hexan-1-ol (*Z*)-2aa: colorless oil; IR (neat) 3354; 1614; 1427; 1248 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.36 (s, 6H), 0.91 (t, J = 7.0 Hz, 3H), 1.03 (s, 1H), 1.22−1.52 (m, 4H), 2.50 (t, J = 7.0 Hz, 2H), 3.97 (s, 2H), 5.55 (s, 1H), 7.32−7.35 (m, 3H), 7.45−7.55 (m, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 0.5, 13.9, 22.5, 30.4, 36.9, 65.2, 124.2, 127.9, 128.9, 133.5, 140.3, 159.0; GC−MS (EI) *m/z* (rel int) 233 (M^+-15), 215 (9), 171 (9), 145 (16), 155 (25), 137 (71), 135 (86), 121 (17), 105 (19), 91 (12), 75 (100), 61 (29), 43 (48). Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.52; H, 9.74. Found: C, 72.50; H, 9.77.

2-Methylenehexan-1-ol 11aa:[24] colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, J = 6.9 Hz, 3H), 1.23−1.50 (m, 4H), 2.10 (t, J = 8.0 Hz, 2H), 4.05 (s, 2H), 4.80−4.88 (m, 1H), 4.92−5.00 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 13.9, 22.5, 30.0, 32.7, 66.9, 109.0, 149.3.

2-Methylenehexanal 12aa:[25] colorless oil; ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, J = 6.9 Hz, 3H), 1.26−1.52 (m, 4H), 2.25 (t, J = 6.8 Hz, 2H), 5.98 (s, 1H), 6.24 (s, 1H), 9.54 (s, 1H).

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