JOC The Journal of Organic Chemistry

Article

Chemoselective Nucleophilic Functionalizations of Aromatic Aldehydes and Acetals via Pyridinium Salt Intermediates

Takahiro Kawajiri, Maho Kato, Hiroki Nakata, Ryota Goto, Shin-yo Aibara, Reiya Ohta, Hiromichi Fujioka, Hironao Sajiki, and Yoshinari Sawama

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02965 • Publication Date (Web): 12 Feb 2019

Chemoselective Nucleophilic Functionalizations of Aromatic Aldehydes and Acetals via Pyridinium Salt Intermediates

Takahiro Kawajiri,[a] Maho Kato,[a] Hiroki Nakata,[a] Ryota Goto,[a] Shin-yo Aibara,[a] Reiya Ohta,[b] Hiromichi Fujioka,[b] Hironao Sajiki*[a] and Yoshinari Sawama*[a]

[a] Laboratory of Organic Chemistry, Gifu Pharmaceutical University, 1-25-4, Daigaku-nishi, Gifu, 501-1196, Japan

[b] Graduate School of Pharmaceutical Sciences, Osaka University, 1-6, Yamada-oka, Suita, Osaka, 565-0871, Japan

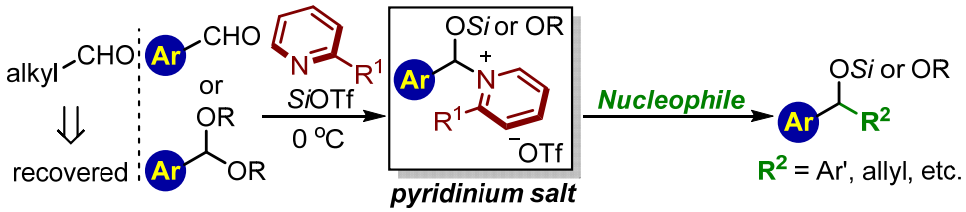
Phone/Fax: (+81)-58-230-8109; email: sawama@gifu-pu.ac.jp, sajiki@gifu-pu.ac.jp

CORRESPONDING AUTHOR

Yoshinari Sawama and Hironao Sajiki

*E-mail: sawama@gifu-pu.ac.jp; sajiki@gifu-pu.ac.jp

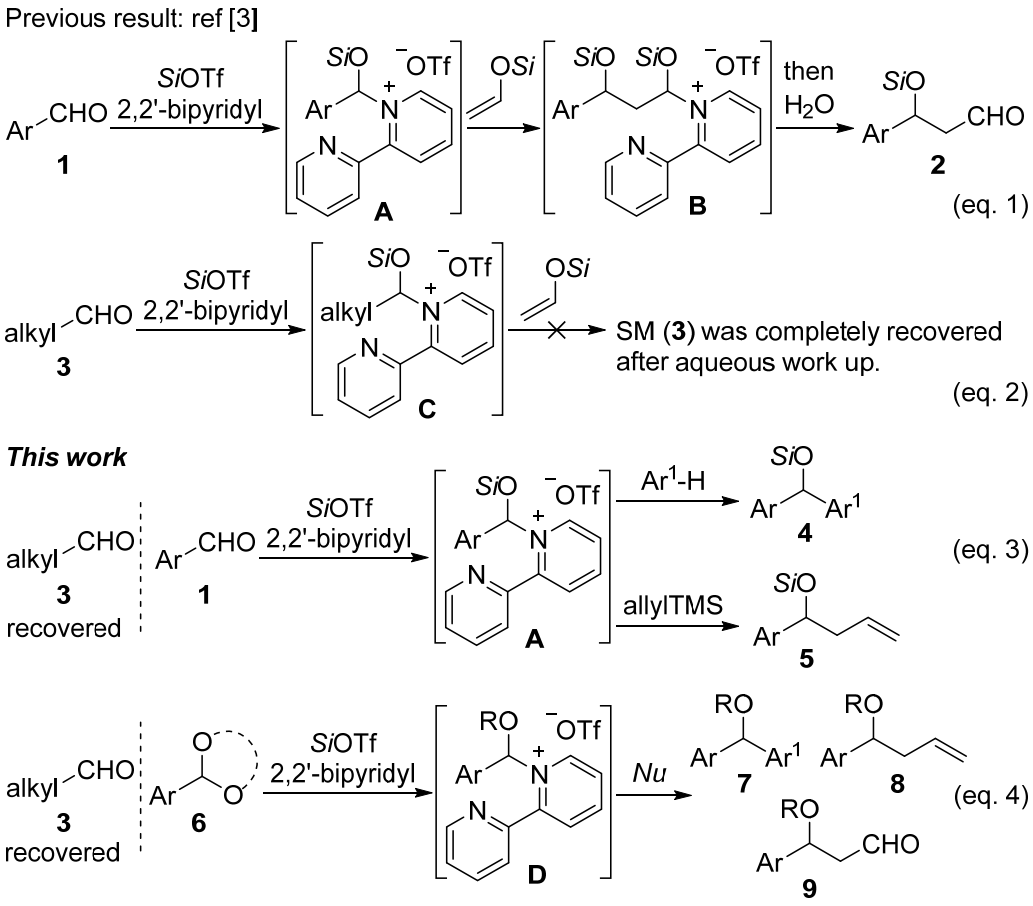
ABSTRACT



The development of a novel chemoselective functionalization can diversify the strategy for synthesizing the target molecules. The perfect chemoselectivity between aromatic and aliphatic aldehydes is difficult to be achieved by the previous methods. The aromatic aldehyde-selective nucleophilic addition in the presence of aliphatic aldehydes was newly accomplished. Namely, the aromatic aldehyde-selective nucleophilic addition using arenes and allyl silanes proceeded in the presence of trialkylsilyl triflate and 2,2'-bipyridyl, while the aliphatic aldehydes completely remained unchanged. The reactive pyridinium-type salt intermediate derived from an aromatic aldehyde chemoselectively underwent the nucleophilic substitution. Moreover, the aromatic acetals as the protected aldehydes could be directly transformed into similar pyridinium salt intermediates, which reacted with various nucleophiles coexisting with the aliphatic aldehydes.

INTRODUCTION

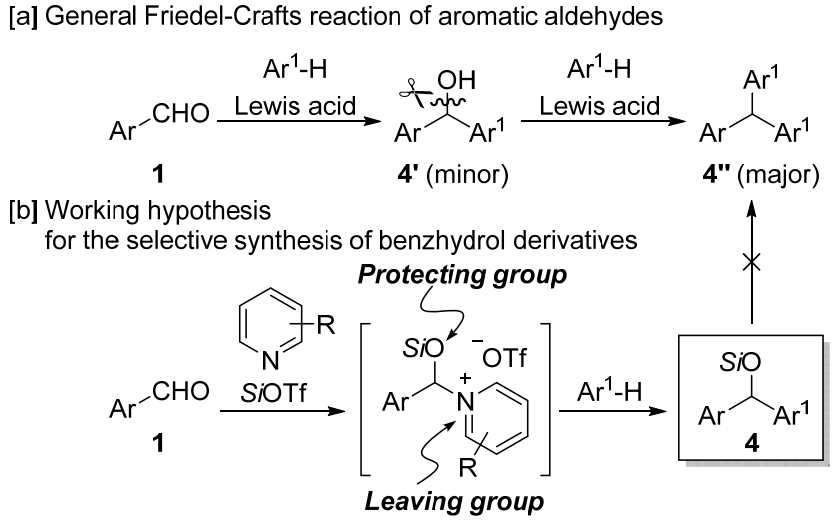
The chemoselective reaction is important to effectively construct target molecules.[1,2] Aldehydes are widely utilized as reactive electrophiles in organic synthesis. However, the development of a perfectly chemoselective reaction distinguishing aromatic from aliphatic aldehydes is still difficult and challenging. We recently reported the chemoselective Mukaiyama aldol reaction of aromatic aldehydes with a silyl enol ether derived from acetaldehyde in the presence of trialkylsilyl triflate (*Si*OTf) and 2,2'-bipyridyl (Scheme 1, eqs. 1 and 2).[3] Both aromatic and aliphatic aldehydes (**1** and **3**) are smoothly transformed into the corresponding pyridinium salt intermediates (**A** and **C**) in the presence of *Si*OTf and 2,2'-bipyridyl. The pyridinium salt intermediate (**A**) derived from **1** easily reacts with silyl enol ethers due to the preferential elimination of the pyridinium moiety on the benzylic carbon and the steric repulsion between the aromatic ring (Ar) and pyridine ring, while the non-benzylic pyridinium salt **C** derived from **3** is inert under the started reaction conditions and **3** was quantitatively reproduced after an aqueous work-up. Namely, the aliphatic aldehyde **3** is masked and protected from the nucleophilic attack by the silyl enol ether as the pyridinium salt **C**. The reaction of **A** with a silyl enol ether derived from acetaldehyde produces the aliphatic aldehyde (**2**)-derived pyridinium salt intermediate **B**, which is inert towards the nucleophilic attack by the silyl enol ether and the *β*-siloxy aldehyde derivative (**2**) is produced after the aqueous work-up. We newly demonstrate the chemoselective nucleophilic addition using arene as a nucleophile via the corresponding pyridinium salt intermediate (**A**) (**3**; eq. 3).



Scheme 1. Outline of the chemoselective nucleophilic functionalizations via pyridinium-type salts.

The Lewis acid-catalyzed Friedel-Crafts reaction is valuable from the viewpoint of atom economy, because arene nucleophiles can be directly utilized without any preliminary functionalization.[4-6] The benzhydrol derivatives (**4'**) can be constructed by the nucleophilic addition of an arene nucleophile (Ar^1-H) to an aromatic aldehyde (**1**). However, the selective synthesis of **4'** from **1** as a substrate under Lewis acid-mediated Friedel-Crafts reaction conditions is still challenging (Scheme 2[a]), because the hydroxyl group of **4'** is easily eliminated to form the benzylic cation species stabilized by both aromatic rings (Ar and Ar^1), and the over-substitution of **4'** by Ar^1-H smoothly proceeds to generate the triarylmethane (**4"**).[7] Although the addition of the catalytic amount of pyridine was reported to suppress the over-substitution under $AlBr_3$-mediated reaction conditions, the selectivity was still inadequate and the yields of the desired **4'** were not very high.[8] Our research hypothesis for the selective preparation of the benzhydrol derivative (silylated benzhydrol; **4**) from **1** is shown in Scheme 2[b]. If the pyridinium

salt intermediate (like **A** in Scheme 1) also undergoes the nucleophilic substitution by arenes, the silyl-protected benzhydrol (**4**) can be generated and the undesirable over-substitution is avoidable due to the reduction of the leaving-group ability of the corresponding siloxy group.[9]



Scheme 2. [a] Friedel-Crafts reaction between arenes and aromatic aldehydes.

[b] Our strategy for the synthesis of the benzhydrol derivatives.

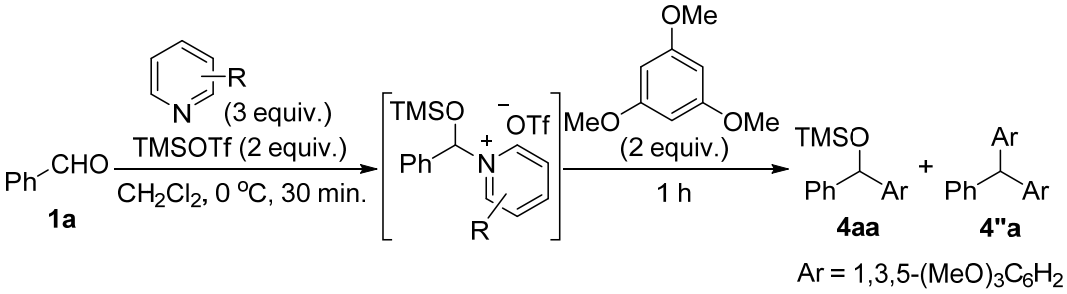
We have additionally demonstrated the nucleophilic addition using allylsilane derivatives as nucleophiles via the reactive salt **A** in the presence of **3** (Scheme 1. eq. 3). Moreover, the aromatic acetals (**6**) as protected aromatic aldehydes could be selectively transformed to **7**-**9** via the corresponding pyridinium salt intermediate (**D**) in the presence of **3** (Scheme 1. eq. 4).

RESULTS AND DISCUSSION

The reaction of the pyridinium salt (like **A** in Scheme 1) with an arene nucleophile was initially investigated using various pyridine derivatives (3 equiv.) in the presence of benzaldehyde (**1a**), 1,3,5-trimethoxybenzene (2 equiv.) and trimethylsilyl triflate (TMSOTf: 2 equiv.) in CH_2Cl_2 at 0 °C (Table 1). The reaction without a pyridine derivative gave the undesired triarylmethane derivative (**4"a**) as the sole product in 94% yield, and the desired benzyl silyl ether (**4aa**) was not detected (entry 1). On the other hand, the desired reaction using 1,3,5-trimethoxybenzene never proceeded after the preliminary treatment of **1a** with pyridine, *N*,*N*-dimethyl-4-aminopyridine (DMAP) or 2-picoline in the presence of

TMSOTf, and **1a** was recovered after the aqueous work-up (entries 2-4). The 2,6-lutidine and 2,4,6-collidine-derived salts could be transformed into the desired **4aa** in moderate yields (46 and 34%, respectively; entries 5 and 6). The use of 2-phenylpyridine caused the generation of the triarylmethane derivative (**4"a**) as a by-product together with **4aa** and the recovered **1a** (entry 7). 2,2'-Bipyridyl was a good additive to give **4aa** in 78% yield (entry 8), while 2,4'-bipyridyl led to the complete recovery of **1a** (entry 9). The effect of 2,2'-bipylidyl was unclear.

Table 1. Effect of pyridine derivatives.

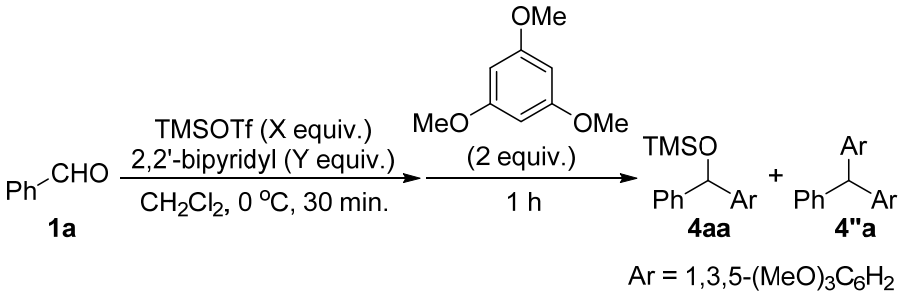


entry	pyridine derivative	yield [%][a]		
		1a	**4aa**	**4"a**
1	—	0	0	94
2	pyridine	77	0	0
3	DMAP	85	0	0
4	2-picoline	84	0	0
5	2,6-lutidine	47	46	0
6	2,4,6-collidine	51	34	0
7	2-phenylpyridine	58	15	15
8	2,2'-bipyridyl	17[b]	78[b]	0
9	2,4'-bipyridyl	95	0	0

[a] The yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as the internal standard. [b] Isolated yield.

The ratio and use of TMSOTf and 2,2'-bipyridyl strongly influenced the reaction efficiency (Table 2). While the desired reaction could proceed in the presence of TMSOTf (2 equiv.) and 2,2'-bipyridyl (3 equiv.) (Table 1, entry 8: Table 2, entry 1), the reduced use of both reagents by half significantly decreased the yield of **4aa** (entry 2). The use of an equal or excess amount of TMSOTf *vs*. the use of 2,2'-bipyridyl caused the formation of the undesired **4"a** (entries 3-5).

Table 2. Ratio effect of TMSOTf and 2,2'-bipyridyl.



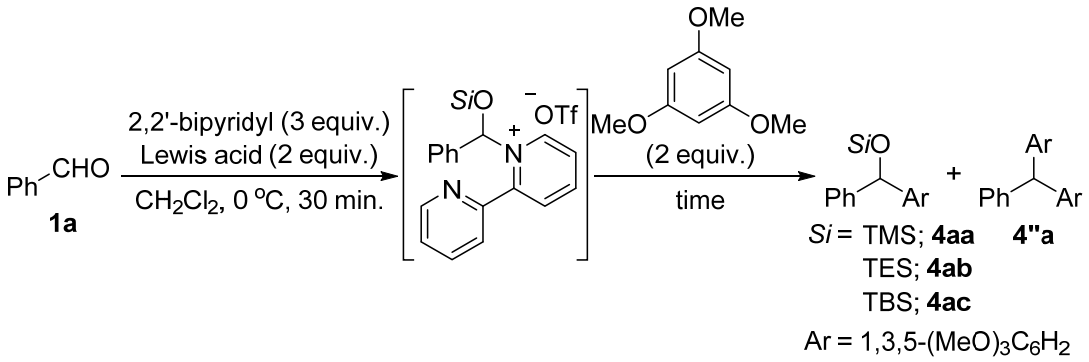
entry	X (equiv.)	Y (equiv.)	yield [%][a]		
			1a	**4aa**	**4"a**
1	2	3	17[b]	78[b]	0
2	1	1.5	90	10	0
3	0.2	—	39	0	50
4	2	2	13	0	67
5	3	2	0	59	35

[a] The yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as the internal standard. [b] Isolated yield.

The effect of other Lewis acids was next examined (Table 3). The use of triethylsilyl triflate (TESOTf) or *tert*-buthyldimethylsilyl triflate (TBSOTf) instead of TMSOTf significantly improved the reaction efficiencies to produce **4ab** (*Si* = TES) or **4ac** (*Si* = TBS) in 92% or 91% yield (entries 2 and 3).

While the formation of the key pyridinium salt intermediates could be detected by the combined use of *Si*OTf and the pyridine derivative (entries 1-3; the spectra were attached in Supporting Information), the less Lewis acidic TMSCl and TMSBr were inactive as a catalyst to generate the pyridinium salt as well as the arene adduct (entries 4 and 5). When stopping the reaction using TESTf or TBSOTf in 3 min., it was obvious that the reaction using TBSOTf was faster than that using TESOTf (entries 6 *vs.* 7). The present reaction could be accelerated by the steric repulsion between the silyl moiety and the 2,2'-bipyridyl.

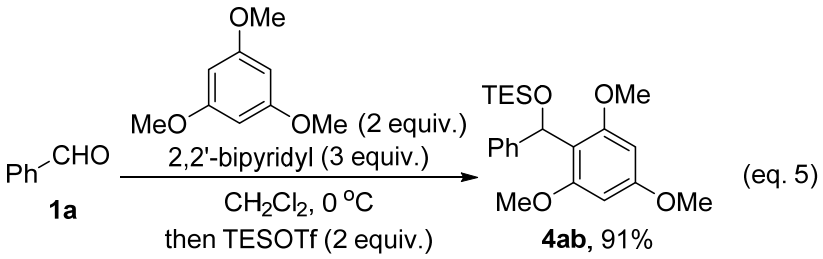
Table 3. Effect of Lewis acid.



entry	Lewis acid	time	yield [%][a]		
			1a	**4a**	**4"a**
1	TMSOTf	1 h	17	**4aa**: 78	0
2	TESOTf	1 h	0	**4ab**: 92	0
3	TBSOTf	1 h	0	**4ac**: 91	0
4	TMSCl	1 h	83[b]	0	0
5	TMSBr	1 h	85[b]	0	0
6	TESOTf	3 min	24[b]	**4ab**: 70[b]	0
7	TBSOTf	3 min	8[b]	**4ac**: 90[b]	0

[a] Isolated yield. [b] The yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as the internal standard.

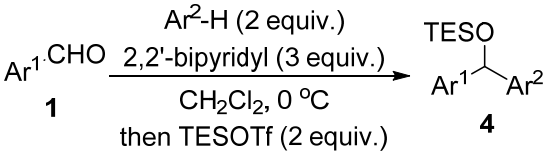
The preliminary formation process of the pyridinium salt by the stepwise addition of 2,2'-bipyridyl, TESOTf, prior to the addition of 1,3,5-trimethoxybenzene (Table 3, entry 2) is not required, and the direct addition of TESOTf to the mixture of **1a**, 2,2'-bipyridyl, 1,3,5-trimethoxybenzene, also gave **4ab** in excellent yield (eq. 5).

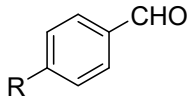
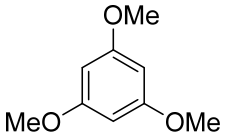
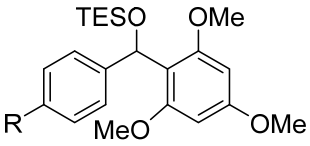
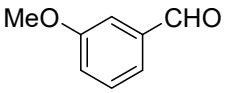
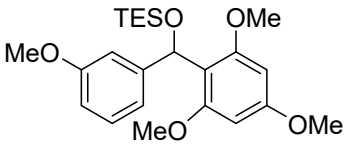
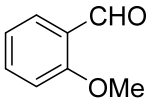
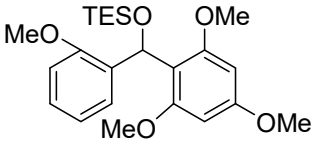
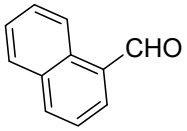
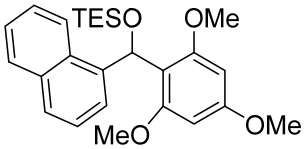
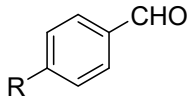
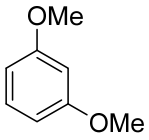
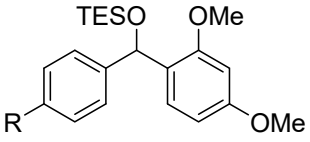


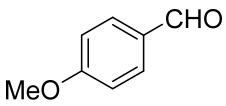
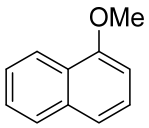
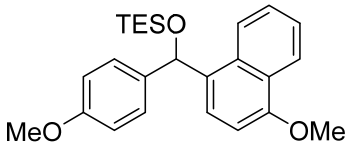
(eq. 5)

Various aromatic aldehydes (**1**) and arene nuclephiles were applicable to the present reaction (Table 4). Benzaldehyde derivatives (**1b**-**1i**) bearing OMe, NO_2, Cl, Br, Ph, CO_2t-Bu, OTBS or OAc at the 4-position of the aromatic ring could react with 1,3,5-trimethoxybenzene under the optimal reaction conditions shown by eq. 5 to afford the corresponding benzhydrol silyl ether derivatives (**4b**-**4i**) in good to excellent yields (entries 1-8). Benzaldehydes (**1j** and **1k**) bearing a methoxy group at the 3 and 2-positions and 1-naphthaldehyde (**1l**) were effectively converted to the corresponding silyl ether products (**4j**-**4l**) in good yields (entries 9-11). 1,3-Dimethoxybenzene as a nucleophile could also be applied to the reactions of **1a**, **1b** and **1d** to give the silyl ethers (**4m**-**4o**) in moderate to good yields (entries 12-14). The reaction using 1-methoxynaphthalene gave the corresponding **4p** (entry 14). The reaction using indole-3-carboxaldehyde, furfural or pyrrole-2-carbaldehyde as a substrate with 1,3,5-trimethoxybenzene gave complex mixture. When using heteroarenes such as indole, *N*-methylindole, furan and *N*-methylpyrrole as nucleophiles, the reactions of **1b** gave complex mixtures.

Table 4. Scope of aromatic aldehydes and arene nucleophiles.



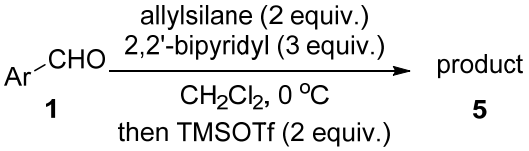
entry	substrate	Ar^2-H	product
			
1	**1b**, R = OMe		**4b**, 95% (30 min.)
2	**1c**, R = NO_2		**4c**, 71% (24 h)
3	**1d**, R = Cl		**4d**, 84% (24 h)
4	**1e**, R = Br		**4e**, 93% (2 h)
5	**1f**, R = Ph		**4f**, 90% (2 h)
6	**1g**, R = CO_2t-Bu		**4g**, 68% (24 h)
7	**1h**, R = OTBS		**4h**, 65% (6 h)
8	**1i**, R = OAc		**4i**, 90% (1 h)
9	 **1j**		 **4j**, 86% (24 h)
10	 **1k**		 **4k**, 87% (2 h)
11	 **1l**		 **4l**, 70% (2 h)
			

12[a]	**1a**, R = H		**4m**, 81% (24 h)
13[a]	**1b**, R = OMe		**4n**, 45% (24 h)
14[a]	**1d**, R = Cl		**4o**, 45% (24 h)
15	 **1b**		 **4p**, 32% (24 h)

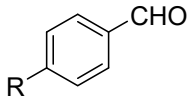
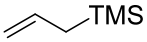
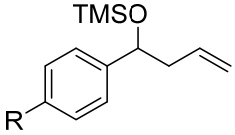
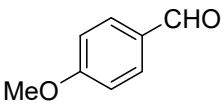
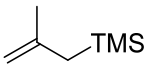
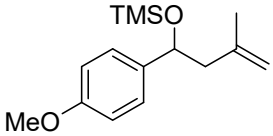
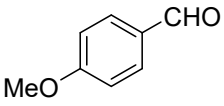
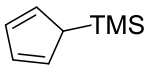
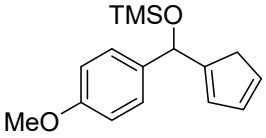
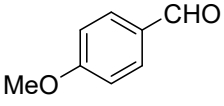
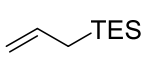
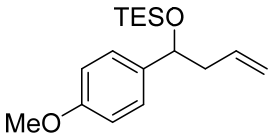
[a] 10 equiv. of arene were used.

The pyridinium salt intermediates derived from aromatic aldehydes could also react with allylsilanes as nucleophiles (Table 5). Various aromatic aldehydes (**1a**-**1f**, **1h**, **1i** and **1m**) bearing an electron-donating or electron-withdrawing group at the 4-position of each aromatic ring could be used to produce the corresponding homoallyl silyl ethers (**5a**-**5f**, **5h**, **5i** and **5m**) in good to excellent yields (entries 1-9). Trimethyl(2-methylallyl)silane was also used to give the desired **5n** (entry 10). Furthermore, the reaction with 5-trimethylsilyl-1,3-cyclopentadiene and **1b** smoothly proceeded to produce **5o** as a consequence of the olefin isomerization (entry 11). Allyltriethylsilane also effectively reacted with the pyridinium salt intermediate to produce the desired silyl ether (**5bb**) in excellent yield (entry 12). The heteroaromatic aldehyde such as indole-3-carboxaldehyde or furfural were not applicable in the reaction with allyltrimethylsilane to give a complex mixture, respectively.

Table 5. Scope of aromatic aldehydes and allylsilanes.

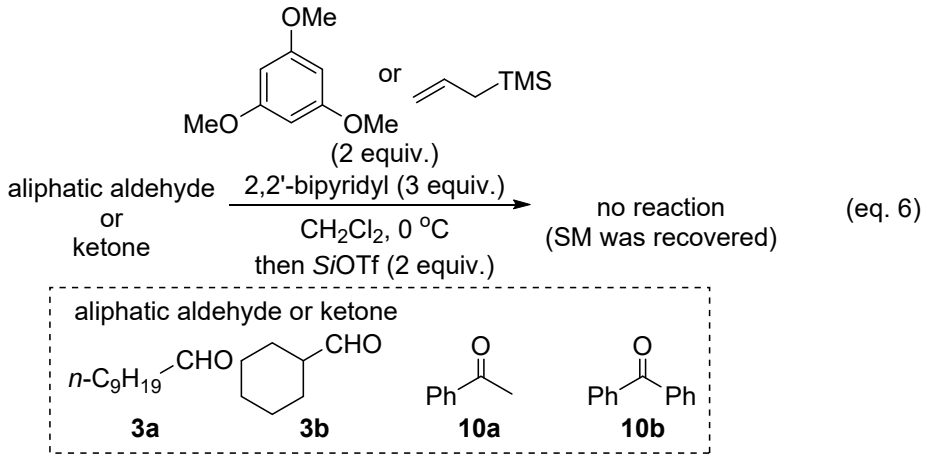


entry	substrate	allylsilane	product

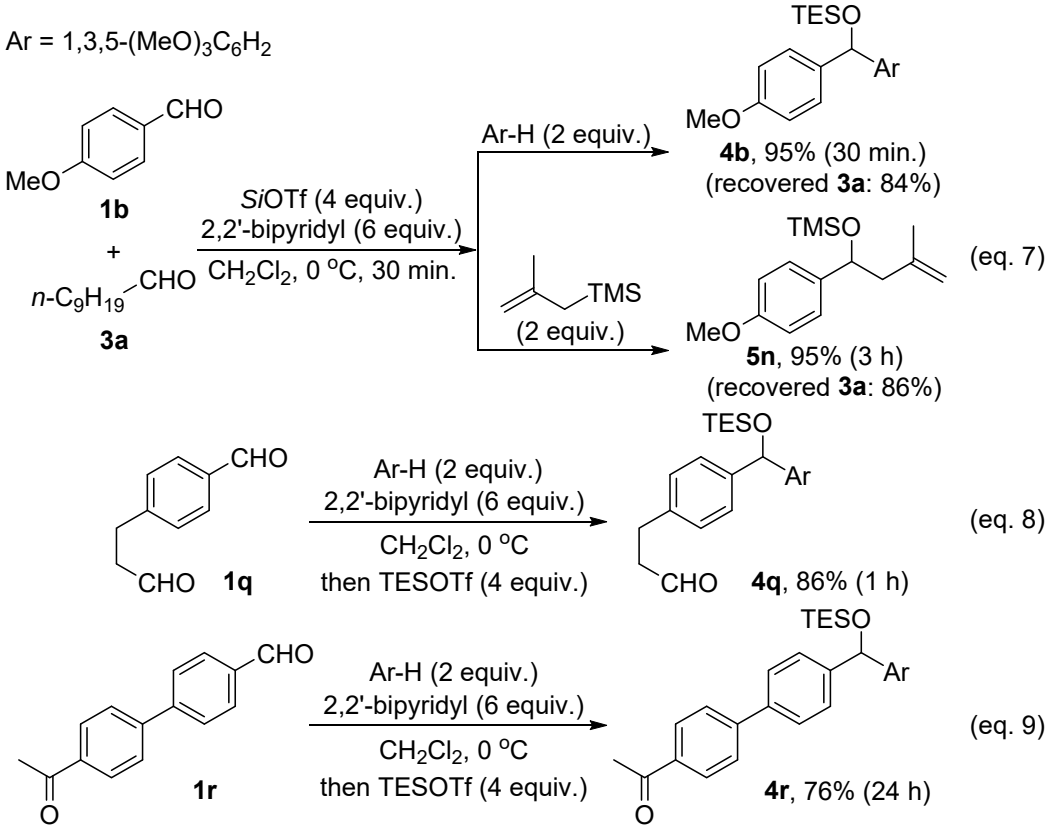
			
1	**1a**, R = H		**5a**, 89% (24 h)
2	**1b**, R = OMe		**5ba**, 82% (24 h)
3	**1c**, R = NO_2		**5c**, 78% (24 h)
4	**1d**, R = Cl		**5d**, 98% (24 h)
5	**1e**, R = Br		**5e**, 65% (24 h)
6	**1f**, R = Ph		**5f**, 63% (24 h)
7	**1h**, R = OTBS		**5h**, 72% (24 h)
8	**1i**, R = OAc		**5i**, 53% (24 h)
9	**1m**, R = CO_2Me		**5m**, 89% (24 h)
10	 **1b**		 **5n**, 99% (3 h)
11	 **1b**		 **5o**, 74% (3 h)
12	 **1b**		 **5bb**, 98% (24 h)

It is noteworthy that aliphatic aldehydes (**3a** and **3b**) and ketones (**10a** and **10b**) were inert under the present reaction conditions using arenes and allylsilanes as nucleophiles and the substrates were

completely recovered (eq. 6). While aliphatic aldehydes (**3a** and **3b**) were converted to the less reactive pyridinium salt intermediates in the presence of *Si*OTf and 2,2'-bipyridyl, ketones (**10a** and **10b**) could not be transformed into any of the pyridinium salt intermediates. (When using arene nucleophile, TESOTf was used as *Si*OTf. When using allylTMS, TMSOTf was used as *Si*OTf.) Therefore, the aromatic aldehyde-selective nucleophilic additions of arenes and allylTMS derivatives were accomplished in the presence of the aliphatic aldehyde or ketone. When using a 1:1 mixture of an aromatic aldehyde (**1b**) and an aliphatic aldehyde (**3a**) as substrates, the nucleophilic attack of 1,3,5-trimethoxybenzene chemoselectively occurred at **1b** to give **4b** in 95% yield and 84% of **3a** was recovered (eq. 7, top). The present chemoselectivity was similarly observed in the allylation with trimethyl(2-methylallyl)silane as a nucleophile (eq. 7, bottom). Furthermore, the substrate (**1q**) bearing aromatic and aliphatic aldehydes within the same molecule was efficiently transformed into the corresponding silyl ether (**4q**) as a result of the chemoselective reaction at the aromatic aldehyde (eq. 8). The chemoselective reaction of **1r**, having aromatic aldehyde and aromatic ketone, with 1,3,5-trimethoxybenzene was also successfully accomplished to produce **4r** with the ketone moiety intact (eq. 9). The side products, such as the silyl enol ether derivative and adduct to the ketone, were not observed.

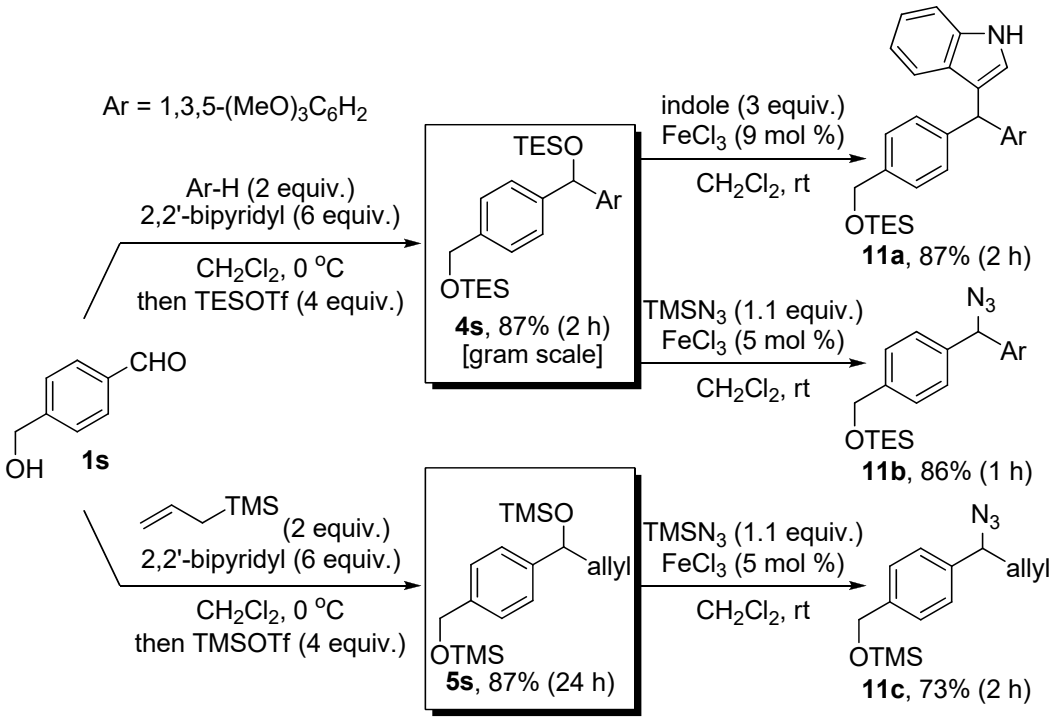


Aromatic aldehyde-selective nucleophilic addition of arene and allylsilane



The resulting secondary benzyl silyl ether functional groups in the products (**4** and **5**) were chemoselectively transformed into the newly functionalized products (**11**) via the $FeCl_3$-catalyzed nucleophilc substitution accompanied by the elimination of the siloxy group (Scheme 3).[10] 4-Hydroxymethylbenzaldehyde **1s** underwent the present nucleophilic addition of an arene to produce **4s** bearing both primary and secondary benzyl silyl ether moieties within the molecule on a gram scale. The secondary siloxy group of **4s** could be chemoselectively transformed into the indolyl group by the

$FeCl_3$-catalyzed nucleophilic substitution to give the corresponding triarylmethane products (**11a**) possessing three different aromatic nuclei, which is a useful basic skeleton for pharmaceuticals and functional materials.[11] The $FeCl_3$-catalyzed azidation of **4s** by the use of $TMSN_3$ also proceeded to give the corresponding **11b** in 86% yield. Furthermore, the chemoselective azidation of **5s**, which was the allylated product, could be successfully performed to produce **11c** in 73% yield.

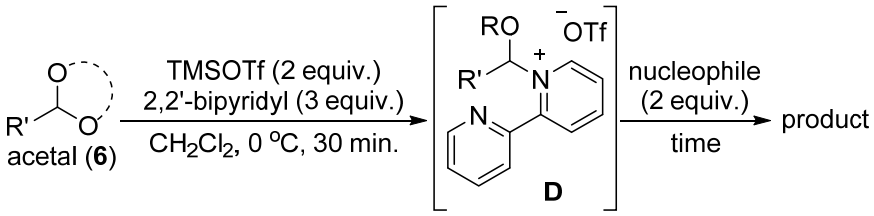


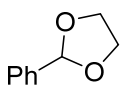
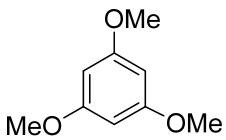
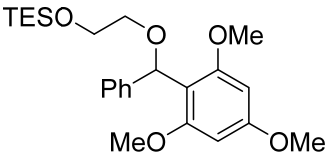
Scheme 3. Further chemoselective functionalizations of the obtained benzyl silyl ethers.

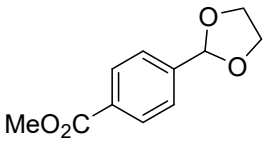
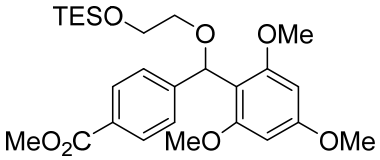
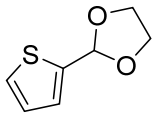
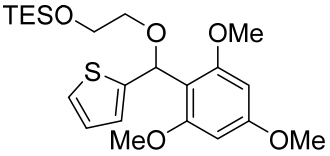
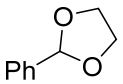
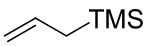
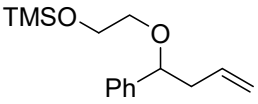
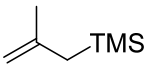
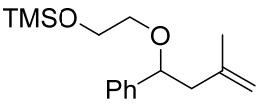
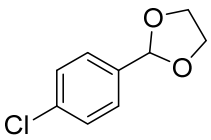
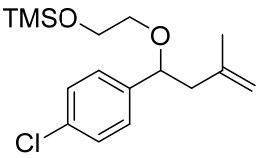
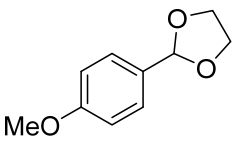
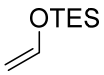
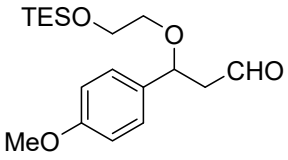
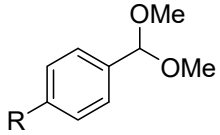
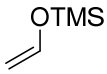
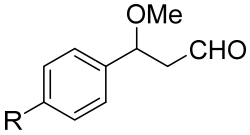
Acetals are generally and frequently utilized as protecting groups of aldehydes and the direct functionalizations without the deprotection steps were sometimes powerful tools to effectively synthesize the target molecules.[12,13] Although the reactivities of the pyridinium salt intermediates derived from acetals, *Si*OTf and adequate pyridine derivatives have already been reported,[13] the reaction with arenes, allylsilanes or silyl enol ethers derived from acetaldehyde as nucleophiles have never been reported in the literature. The reaction with the pyridinium salt (**D**) derived from benzaldehyde ethylene

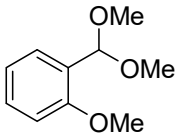
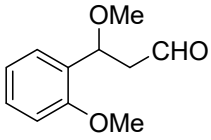
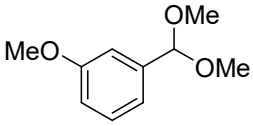
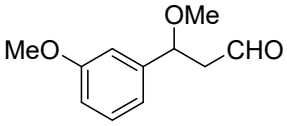
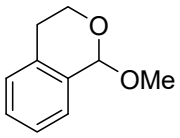
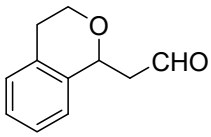
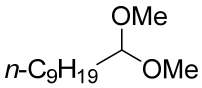
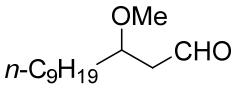
glycol acetal derivatives (**6a** and **6b**), TESOTf and 2,2'-bipyridyl could react with 1,3,5-trimethoxybenzene to produce the desired ethylene glycol asymmetric ether products (**7a** and **7b**) (Table 6, entries 1 and 2). 2-(Thiophen-2-yl)-1,3-dioxolane (**6c**) was also converted into the corresponding silyl ether (**7c**) in moderate yield (entry 3). Pyridinium salt (**D**) derived from **6a** or **6d** could react with allylsilanes to produce the desired homoallylalchol derivatives (**8a**, **8b** and **8c**) in excellent yields (entries 4-6). Acetal **6e** was effectively transformed into the *β*-alkoxy aldehyde (**9e**) via the Mukaiyama aldol reaction using TES enol ether derived from acetaldehyde as a nucleophile after an aqueous work-up (entry 7: see also eq. 1). Various aromatic aldehyde dimethyl acetals (**6f-6n**) possessing electron-donating or electron–withdrawing groups on the aromatic ring were applicable for the Mukaiyama aldol reaction using the TMS enol ether (entries 8-16). The cyclic mixed acetal (**6o**) resulting from isochroman was smoothly converted to the corresponding product (**9o**) by the selective elimination of the methoxy group (entry 17). Decanal dimethyl acetal (**6p**) as an aliphatic acetal was also transformed into **9p** in a moderate yield after 24 h (entry 18). On the other hand, 2-nonyl-1,3-dioxolane as an aliphatic acetal did not react with 1,3,5-trimethoxybenzene or allyltrimethylsilane to give a mixture of the unchanged aliphatic acetal and deprotected aldehyde (see Supporting Information).

Table 6. Nucleophilic functionalization of acetals.



entry	acetal	nucleophile	product
1	 **6a**		 **7a**, 90% (1 h)[a]

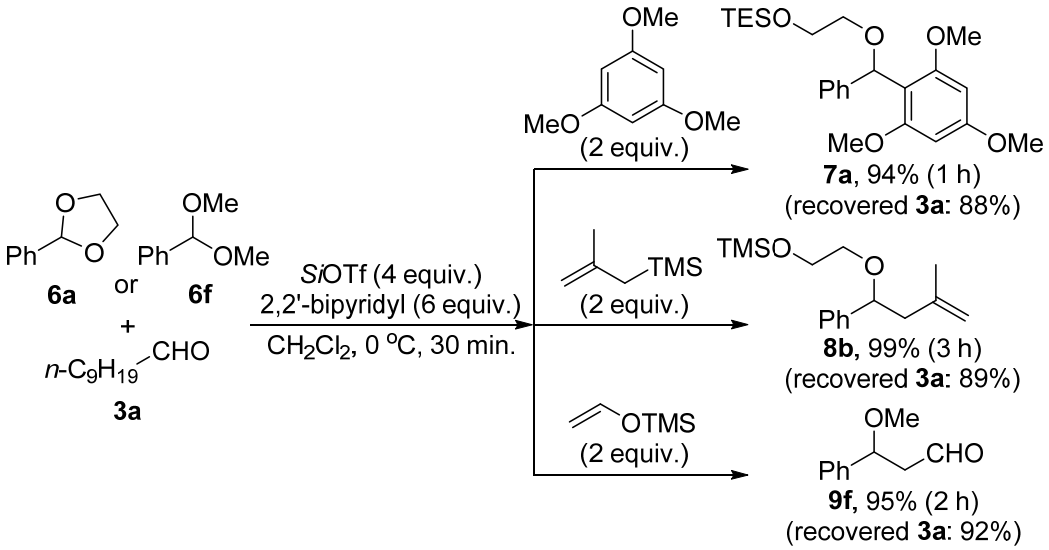
2	 **6b**		 **7b**, 43% (2 h)[a]
3	 **6c**		 **7c**, 63% (2 h)[a]
4	 **6a**		 **8a**, 83% (24 h)
5			 **8b**, 99% (3 h)
6	 **6d**		 **8c**, 96% (24 h)
7	 **6e**		 **9e**, 84% (24 h)[a]
			
8	**6f**, R = H		**9f**, 94% (2 h)[b]
9	**6g**, R = OMe		**9g**, 71% (2 h)[b, c]
10	**6h**, R = NO_2		**9h**, quant. (6 h)[c]

11	**6i**, R = CO_2Me	**9i**, quant. (2 h)
12	**6j**, R = Cl	**9j**, 90% (1 h)
13	**6k**, R = Br	**9k**, 88% (2 h)
14	**6l**, R = OTBS	**9l**, 84% (6 h)[b]
15	 **6m**	 **9m**, quant. (2 h)[b]
16	 **6n**	 **9n**, quant. (2 h)
17	 **6o**	 **9o**, 84% (24 h)
18	 **6p**	 **9p**, 53% (24 h)

[a] TESOTf was used instead of TMSOTf. [b] 1 equiv. of TMSOTf and 1.5 equiv. of 2,2'-bipyridyl were used. [c] The product was contaminated by trace amounts of inseparable by-products including 2,2'-bipyridyl and α,β-unsaturated aldehyde.

These reactions could be realized as the chemoselective transformation of acetals, which are generally utilized as the protected form of aldehydes, in the presence of aliphatic aldehydes (Scheme 4). For the 1 : 1 mixture of an aromatic acetal **6a** and an aliphatic aldehyde **3a** under *Si*OTf and 2,2'-bipyridyl conditions, the nucleophilic attack of 1,3,5-trimethoxybenzene or trimethyl(2-methylallyl)silane into the pyridinium salt intermediate derived from **6a** gave the desired products **7a** or

8b, respectively, while **3a** was completely recovered. The chemoselective reaction between the TMS vinyl ether and benzaldehyde dimethyl acetal (**6f**) coexisting with an aliphatic aldehyde (**3a**) could be similarly accomplished to give the desired aldol adduct (**9f**).



Scheme 4. Chemoselective functionalization of aromatic acetal.

CONCLUSION

We have developed the aromatic aldehyde and acetal-selective nucleophilic functionalization methods via the pyridinium salt intermediates mediated by a silyl triflate and 2,2'-bipyridyl in the presence of the aliphatic aldehyde. Arenes, allylsilanes and silyl enol ethers derived from acetaldehyde could be used as nucleophiles to give the corresponding benzyl silyl ether products. The present chemoselective C-C bond formations are useful to formulate novel synthetic strategies of the target molecules.

EXPERIMENTAL SECTION

1. General Information

All reactions were performed in an oven-dried glassware under argon. Unless otherwise noted, substrates and anhydrous solvents were purchased from commercial sources and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (63–210 μm spherical, neutral). ^{1}H and ^{13}C $\{^{1}H\}$ NMR spectra

were recorded at room temperature in $CDCl_3$ or CD_2Cl_2 as a solvent and internal standard (^1H NMR: δ = 7.26; ^{13}C {^1H} NMR: δ = 77.0 for $CDCl_3$; ^1H NMR: δ = 5.32; ^{13}C NMR: δ = 53.5 for CD_2Cl_2) with tetramethylsilane as an additional internal standard. ESI high resolution mass spectra (HRMS) were measured IT-TOF mass spectrometer.

2. Procedures to prepare the substrates and their spectroscopic data.

2-1. Preparation of 4-(*tert*-butyldimethylsilyloxy)benzaldehyde (1h)[14a]

To a solution of 4-hydroxybenzaldehyde (2.40 g, 19.6 mmol) in anhydrous DMF (30 mL) were added imidazole (2.0 g, 29.3 mmol) and TBSCl (4.5 g, 29.8 mmol) at 0 °C under argon. After stirring for 22 h at room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (20 mL) and extracted with mixture of hexane and AcOEt (Hex/EtOAc = 4/1, 20 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 15/1) to give **1h** (3.99 g, 16.9 mmol, 86% yield). Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.79 (d, 2H, *J* = 8.6 Hz), 6.94 (d, 2H, *J* = 8.6 Hz), 1.00 (s, 9H), 0.25 (s, 6H). Spectroscopic date of ^1H NMR was identical to that of reference 14a.

2-2. Preparation of 4-formylphenyl acetate (1i)[14b]

To a solution of 4-hydroxybenzaldehyde (610.6 mg, 5 mmol) in pyridine (5 mL) were added Ac_2O (510.5 mg, 10 mmol) and DMAP (30.5 mg, 0.25 mmol) at room temperature under argon. After stirring for 20 h, the reaction mixture was quenched with H_2O (5 mL) and extracted with Et_2O (10 mL × 3). The combined organic layers were washed with sat. $CuSO_4$ aq. (40 mL), dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to give **1i** (450.2 mg, 2.49 mmol, 49% yield). Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.28 (d, 2H, *J* = 8.0 Hz), 2.34 (s, 3H). Spectroscopic date of ^1H NMR was identical to that of reference 14b.

2-3. Preparation of *tert*-butyl-4-formylbenzoate (1g)[14c]

To a solution of 4-formylbenzoic acid (1.0 g, 6.7 mmol) in *t*-BuOH (20 mL) were added $(Boc)_2O$ (1754.3 mg, 8.0 mmol) and DMAP (491.1 mg, 4.0 mmol). After stirring for 24 h at room temperature, the reaction mixture was quenched with H_2O (30 mL) and extracted with Et_2O (30 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give **1g** (1063.9 mg, 5.14 mmol, 77% yield). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 8.13 (d, 2H, *J* = 7.6 Hz), 7.93 (d, 2H, *J* = 7.6 Hz), 1.62 (s, 9H). Spectroscopic date of ^1H NMR was identical to that of reference 14c.

2-4. Preparation of 4-(3-oxopropyl)benzaldehyde (1q)

The reaction scheme is depicted in the Supporting Information.

Step 1: To a solution of 4-bromobenzaldehyde (**1e**: 1.85 g, 10.0 mmol) in anhydrous DMF (50 mL) were added acrylic aldehyde (0.8 mL, 12.0 mmol), tetrabutyl-anmonium chloride (5.6 mL, 20.6 mmol), $NaHCO_3$ (1.26 g, 15.0 mmol) and $Pd(OAc)_2$ (22.4 mg, 0.10 mmol) under argon. After stirring for 40 h at 80 °C, the reaction mixture was passed through a celite pad. The filtrate was extracted with AcOEt (30 mL ×3) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to give (*E*)-4-(3-oxoprop-1-en-1-yl)benzaldehyde (861 mg, 5.4 mmol, 54% yield). Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.06 (s, 1H), 9.77 (d, 1H, *J* = 7.5 Hz), 7.95 (d, 2H, *J* = 8.3 Hz), 7.73 (d, 2H, *J* = 8.3 Hz), 7.53 (d, 1H, *J* = 16.0 Hz), 6.81 (dd, 1H, *J* = 16.0, 7.5 Hz). Spectroscopic date of ^{1}H NMR was identical to that of the reference 14d.

Step 2 was carried out according to reference 14e: To a solution of a (*E*)-4-(3-oxoprop-1-en-1-yl)benzaldehyde (32.0 mg, 0.2 mmol) in methanol (1 mL) was added Pd/C(Ph_2S) (2.1 mg, 0.002 mmol) at 0 °C under H_2. After stirring for 3 h, the reaction mixture was passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C(Ph_2S). The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give 4-(3,3-dimethoxypropyl)benzaldehyde (24.9 mg). Then, to this compound in CH_3CN (0.5 mL) was added 1N HCl (1 mL) at room temperature. After stirring for 42 h, the reaction mixture was extracted with CH_2Cl_2 (10 mL × 2) and the combined organic layers were dried over Na_2SO_4, and concentrated to give 4-(3-oxopropyl)benzaldehyde (**1q**; 16.7 mg, 0.10 mmol, 49%). Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$); δ 9.98 (s, 1H), 9.84 (s, 1H), 7.82 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 3.04 (t, 2H, *J* = 7.5 Hz), 2.85 (t, 2H, *J* = 7.5 Hz). Spectroscopic date of 1H NMR was identical to that of the reference 14f.

2-5. Preparation of 4'-acetyl-(1,1'-biphenyl)-4-carbaldehyde (1r)

This step was carried out according to reference 14g: To a solution of 4-bromobenzaldehyde (0.93 g, 5 mmol) in H_2O (10 mL) and *i*-PrOH (10 mL) was added 4-acetylphenylboronic acid (0.90 g, 5.5 mmol), 10% Pd/HP20 (26.5 mg, 0.025 mmol, 0.5 mol%) and $Na_3PO_4 \cdot 12H_2O$ (6.65 g, 17.5 mmol). The reaction mixture was stirred at room temperature for 30 h and then passed through a celite pat to remove the catalyst. The filtrate was extracted with AcOEt (30 mL ×3) and the combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hex/EtOAc = 5/1) to give 4'-acetyl-(1,1'-

biphenyl)-4-carbaldehyde (**1r**: 1.11 g, 4.95 mmol, 99%). Colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.08 (d, 2H, *J* = 8.4 Hz), 8.00 (d, 2H, *J* = 8.4 Hz), 7.80 (d, 2H, *J* = 8.4 Hz), 7.74 (d, 2H, *J* = 8.4 Hz), 2.66 (s, 3H). Spectroscopic date of ^{1}H NMR was identical to that of the reference 14h.

2-6. Preparation of 4-(hydroxymethyl)benzaldehyde (1s)[14i]

To a solution of terephthalaldehyde (1.28 g, 9.5 mmol) in THF (20 mL) and EtOH (15 mL) was added $NaBH_4$ (85 mg, 2.4 mmol) at 0 °C. After stirring for 24 h at room temperature, the reaction mixture was concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give **1s** (873 mg, 6.4 mmol, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 4.81 (d, 2H). Spectroscopic date of ^{1}H NMR was identical to that of the reference 14i.

2-7. Preparation of benzaldehyde ethylene glycol acetal derivatives (6b-6e)

To a solution of benzaldehyde derivative (5 mmol) and triethyl orthoformate (0.9 mL, 5.5 mmol) in ethylene glycol (1.1 mL, 20 mmol) was added tetrabutylammonium tribromide (24.1 mg, 0.05 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After adiquate time, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (1 mL) and extracted with Et_2O (10 mL × 2). The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding acetal (**6**).

methyl 4-(1,3-dioxolan-2-yl)benzoate (6b)[12b]

When using methyl 4-formylbenzoate (**1m**; 985 mg, 6 mmol), methyl 4-(1,3-dioxolan-2-yl)benzoate (**6b**; 599 mg, 2.9 mmol) was obtained in 48% yield for 48 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, 2H, *J* = 8.4 Hz), 7.56 (d, 2H, *J* = 8.4 Hz), 5.86 (s, 1H), 4.15—4.10 (m, 2H), 4.09–4.04 (m, 2H), 3.92 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 12b.

2-(thiophen-2-yl)-1,3-dioxolane (6c)[15a]

When using thiophene-2-carbaldehyde (673 mg, 6 mmol), 2-(thiophen-2-yl)-1,3-dioxolane (**6c**; 337 mg, 2.2 mmol) was obtained in 36% yield for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 1H, *J* = 5.0 Hz), 7.17 (d, 1H, *J* = 3.7 Hz), 7.00 (dd, 1H, *J* = 5.0, 3.7 Hz), 6.13 (s, 1H), 4.18—4.10 (m, 2H), 4.07–3.99 (m, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15a.

2-(4-chlorophenyl)-1,3-dioxolane (6d)[12b]

When using 4-chlorobenzaldehyde (**1d**; 422 mg, 3 mmol), 2-(4-chlorophenyl)-1,3-dioxolane (**6d**; 443 mg, 2.4 mmol) was obtained in 80% yield for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, 2H, *J* = 8.2 Hz), 7.35 (d, 2H,

J = 8.2 Hz), 5.79 (s, 1H), 4.14—4.08 (m, 2H), 4.08–4.02 (m, 2H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 12b.

2-(4-methoxyphenyl)-1,3-dioxolane (6e)[15a]

When using 4-methoxybenzaldehyde (**1b**; 0.6 mL, 5 mmol), 2-(4-methoxyphenyl)-1,3-dioxolane (**6e**; 829.9 mg, 4.6 mmol) was obtained in 92% yield for 9 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, 2H, *J* = 8.4 Hz), 6.91 (d, 2H, *J* = 8.4 Hz), 5.76 (s, 1H), 4.15—4.12 (m, 2H), 4.04–4.00 (m, 2H), 3.81 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15a.

2-8. Preparation of dimethyl acetals (6g-n)[15a]

To a solution of aldehyde (5 mmol) in MeOH (5 mL) was added trimethyl orthoformate (5.5 mmol) at room temperature under argon. After stirring for adequate time, the mixture was quenched by the addition of sat. $NaHCO_3$ aq. (10 mL). The mixture was extracted with ethyl acetate (25 mL x 2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding dimethyl acetal.

1-(Dimethoxymethyl)-4-methoxybenzene (6g)[15b]

When using 4-methoxybenzaldehyde (**1b**; 0.6 mL, 5 mmol), 1-(dimethoxymethyl)-4-methoxybenzene (**6g**; 414.7 mg, 2.3 mmol) was obtained in 46% yield for 20 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37—7.36 (m, 2H), 6.91—6.89 (m, 2H), 5.35 (s, 1H), 3.81 (s, 3H), 3.31 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15b.

1-(Dimethoxymethyl)-4-nitrobenzene (6h)[15c]

When using 4-nitrobenzaldehyde (**1c**; 755.6 mg, 5 mmol), 1-(dimethoxymethyl)-4-nitrobenzene (**6h**; 970.8 mg, 4.9 mmol) was obtained in 98% yield for 3 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, *J* = 11.0 Hz, 2H), 7.64 (d, 2H, *J* = 11.0 Hz), 5.48 (s, 1H), 3.34 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15c.

Methyl 4-(dimethoxymethyl)benzoate (6i)[15a]

When using 4-methoxycarbonylbenzaldehyde (820.8 mg, 5 mmol), methyl 4-(dimethoxymethyl)benzoate (**6i**; 817.7 mg, 3.9 mmol) was obtained in 78% yield for 1.5 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, 2H, *J* = 8.5 Hz), 7.53 (d, 2H, *J* = 8.5 Hz), 5.44 (s, 1H), 3.92 (s, 3H), 3.33 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15a.

1-Chloro-4-(dimethoxymethyl)benzene (6j)[15b]

When using 4-chlorobenzaldehyde (**1d**; 421.7 mg, 3 mmol), 1-chloro-4-(dimethoxymethyl)benzene (**6j**; 515.7 mg, 2.8 mmol) was obtained in 92% yield for 24 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, *J* = 8.5 Hz), 7.34 (d, 2H, *J* = 8.5 Hz), 5.37 (s, 1H), 3.31 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15b.

1-Bromo-4-(dimethoxymethyl)benzene (6k)[15b]

When using 4-bromobenzaldehyde (**1e**; 555.1 mg, 3 mmol), 1-bromo-4-(dimethoxymethyl)benzene (**6k**; 682.7 mg, 2.95 mmol) was obtained in 98% yield for 24 h. ^{1}H NMR (500 MHz, CDCl3): δ 7.50 (d, 2H, *J* = 8.8 Hz), 7.33 (d, 2H, *J* = 8.8 Hz), 5.36 (s, 1H), 3.31 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15b.

***tert*-Butyl(4-(dimethoxymethyl)phenoxy)dimethylsilane (6l)[15d]**

When using 4-((*tert*-butyldimethylsilyl)oxy)benzaldehyde (**1g**; 0.4 mL, 2.5 mmol), *tert*-butyl(4-(dimethoxymethyl)phenoxy)dimethylsilane (**6l**; 80.5 mg, 0.3 mmol) was obtained in 11% yield for 16 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, 2H, *J* = 8.5 Hz), 6.83 (d, 2H, *J* = 8.5 Hz), 5.33 (s, 1H), 3.31 (s, 6H), 0.98 (s, 9H), 0.19 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15d.

1-(Dimethoxymethyl)-2-methoxybenzene (6m)[15e]

When using 2-methoxybenzaldehyde (0.4 mL, 3 mmol), 1-(dimethoxymethyl)-2-methoxybenzene (**6m**; 687.4 mg, 3 mmol) was obtained in quantitative yield for 1 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, 1H, *J* = 7.5, 2.0 Hz), 7.32—7.29 (m, 1H), 6.97 (t, 1H, *J* = 7.5 Hz), 6.90 (d, 1H, *J* = 8.0 Hz), 5.68 (s, 1H), 3.85 (s, 3H), 3.36 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15e.

1-(Dimethoxymethyl)-3-methoxybenzene (6n)[15f]

When using 3-methoxybenzaldehyde (0.4 mL, 3 mmol), 1-(dimethoxymethyl)-3-methoxybenzene (**6n**; 668.1 mg, 3 mmol) was obtained in quantitative yield for 1 h. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (t, 1H, *J* = 7.8 Hz), 7.04—7.01 (m, 2H), 6.87 (dd, 1H, *J* = 7.8, 2.3 Hz), 5.36 (s, 1H), 3.82 (s, 3H), 3.34 (s, 6H). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15f.

2-9. Preparation of 1-methoxyisochroman (6o)[15g]

To a solution of DDQ (1.34 g, 6.0 mmol) in CH_2Cl_2 (50 mL) were added MeOH (280 μL, 6.0 mmol) and isochroman (650 μL, 5.0 mmol). The mixture was stirred at room temperature for 24 h, quenched with of sat. $NaHCO_3$ aq. (50 mL) and filtered through celite pad. The aqueous layer was extracted with CH_2Cl_2 (60 mL x 2) and concentrated in vacuo. The crude mixture was purified by flash chromatography with silica-gel

(EtOAc/hexane 1/7, 3% Et_3N) to afford 1-methoxyisochroman (**6o**; 660 mg, 4.0 mmol, 80 % yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25—7.23 (m, 3H), 7.16—7.12 (m, 1H), 5.46 (s, 1H), 4.13 (dt, 1H, *J* = 11.0, 3.5 Hz), 3.93—3.89 (m, 1H), 3.55 (s, 3H), 3.08—2.97 (m, 1H), 2.63 (dd, 1H, *J* = 15.5, 1.8 Hz). Spectroscopic data of ^{1}H NMR was identical to that of the reference 15g.

2-10. Preparation of 1,1-dimethoxydecane (6p)

To a solution of decanal (**3a**: 0.78 g, 5 mmol) in anhydrous methanol (0.8 mL, 20 mmol) was added palladium acetate (112.3 mg, 0.5 mmol). After stirring for 48 h at room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (1mL). The solution was extracted with Et_2O (20 mL × 2), the combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 10/1) to give 1,1-dimethoxy decane (**6p**; 0.83 g, 4.1 mmol, 82%).^{1}H NMR (500 MHz, $CDCl_3$): δ 4.35 (t, 1H, *J* = 6.0 Hz), 3.31 (s, 6H), 1.60—1.55 (m, 2H), 1.30—1.27 (m, 14H), 0.88 (t, 3H, *J* = 6.0 Hz). Spectroscopic data of ^{1}H NMR was identical to that of the reference 13b.

2-11. Preparation of triethylsilyl vinyl ethers[16a]

2.6 M Hexane solution of *n*-butyllithium (15 mL, 39.0 mmol) was mixed with anhydrous THF (25 mL) at 0 °C under argon. After stirring for 5 h at room temperature, triethylsilyl chloride (30.0 mmol) was added to the reaction mixture at 0 °C, and reaction mixture was stirred for 24 h at room temperature under argon. The reaction mixture was concentrated under reduced pressure. The residue was treated with water (30 mL) at 0 °C, and the aqueous layers were extracted with diethylether (20 mL × 3). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (Hex/Et_3N = 100/1) to give triethylsilyl vinyl ether (2.4 g, 15.3 mmol, 51% yield).^{1}H NMR (500 MHz, $CDCl_3$); δ 6.45 (dd, 1H, *J* = 13.1, 5.9 Hz), 4.44 (d, 1H, *J* = 13.1 Hz), 4.11 (d, 1H, *J* = 5.9 Hz), 0.98 (t, 9H, *J* = 8.0 Hz), 0.68 (q, 6H, *J* = 8.0 Hz). Spectroscopic date of ^{1}H NMR was identical to that of the reference 16b.

3. General procedures in key reactions.

Typical procedure A (Tables 1, 2 and 3)

To solution of benzaldehyde (**1a**: 0.15 mmol) in CH_2Cl_2 (0.75 mL) were added pyridine derivative (0.45 mmol) and *Si*OTf (0.30 mmol) at 0 °C and the reaction mixture was stirred for 30 min. Then 1,3,5-trimethoxybenzene (0.30 mmol) was added to the reaction mixture at 0 °C. After stirring for 1 hour, the mixture was quenched with

sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2 (5 mL x 2). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by silica-gel column chromatography to give the silylated benzhydrols **4**.

Typical procedure B (Tables 4 and 5; eqs. 5, 8 and 9; Scheme 3, first step)

To the mixture of aromatic aldehyde (**1**: 0.15 mmol), 2,2'-bipyridyl (0.45 mmol) and arene or allylsilane (0.30 mmol) in CH_2Cl_2 (0.75 mL) was added *Si*OTf (0.30 mmol) at 0 °C. After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2 (5 mL x 2). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by silica-gel column chromatography to give the silylated product **4** or **5**.

Typical procedure C (Table 6)

To solution of acetal (**6**: 0.15 mmol) in CH_2Cl_2 (0.75 mL) were added 2,2'-bipyridyl (0.45 mmol) and *Si*OTf (0.30 mmol) at 0 °C and the reaction mixture was stirred for 30 min. Then nucleophile (1,3,5-trimethoxybenzene, allylsilane or silyl enol ether; 0.30 mmol) was added to the reaction mixture at 0 °C. After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2 (5 mL x 2). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by silica-gel column chromatography to give the product **7**, **8** or **9**.

Typical procedure D (Scheme 3, second step)

$TMSN_3$ (0.165 mmol) or indole (0.45 mmol) and $FeCl_3$ (0.015 mmol) were added to a solution of the silyl ether derivative (**4s** or **5s**: 0.15 mmol) in CH_2Cl_2 (0.75 mL) at room temperature. After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. and the mixture was extracted with CH_2Cl_2 (5 mL x 2). The combined organic layers were dried over Na_2SO_4, concentrated in vacuo and purified by silica-gel column chromatography to give the product **11**.

4. Spectroscopic data of the products.

Trimethyl(phenyl(2,4,6-trimethoxyphenyl)methoxy)silane (4aa) in Table 1, entry 8.

Benzaldehyde (**1a**: 15.7 mg, 0.15 mmol), 2,2'-bipyridyl (70.0 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (50.0 mg, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure A and trimethyl(phenyl(2,4,6-trimethoxyphenyl)methoxy)silane (**4aa**: 43.2 mg, 0.12 mmol) was obtained in 78% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2956, 2838, 1591, 1492, 1455, 1417, 1333, 1223, 1203, 1149, 1118, 1084, 1055; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, 2H, *J* = 7.8 Hz), 7.23 (t, 2H, *J* = 7.8 Hz), 7.13 (t, 1H, *J* = 7.8 Hz), 6.42 (s, 1H), 6.11 (s,

2H), 3.80 (s, 3H), 3.67 (s, 6H), 0.05 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.7, 159.4, 145.5, 127.3, 125.5, 125.4, 113.6, 91.3, 66.5, 55.8, 55.2, -0.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{26}O_4SiNa$ 369.1493; Found 369.1506.

Triethyl(phenyl(2,4,6-trimethoxyphenyl)methoxy)silane (4ab) in Table 3, entry 2.

Benzaldehyde (**1a**: 16.6 mg, 0.17 mmol), 2,2'-bipyridyl (73.1 mg, 0.47 mmol), 1,3,5-trimethoxybenzene (52.5 mg, 0.31 mmol) and TESOTf (71 μL, 0.31 mmol) were used according to the typical procedure A and triethyl(phenyl(2,4,6-trimethoxyphenyl)methoxy)silane (**4ab**: 56.6 mg, 0.14 mmol) was obtained in 92% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2875, 2837, 1591, 1492, 1455, 1333, 1223, 1202, 1149, 1118, 1084; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 2H, J = 7.4 Hz), 7.22 (t, 2H, J = 7.4 Hz), 7.11 (t, 1H, J = 7.4 Hz), 6.42 (s, 1H), 6.09 (s, 2H), 3.79 (s, 3H), 3.67 (s, 6H), 0.87 (t, 9H, J = 8.0 Hz), 0.54 (q, 6H, J = 8.0 Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.6, 159.4, 146.0, 127.2, 125.4, 125.3, 114.4, 91.4, 66.4, 55.8, 55.2, 6.8, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{32}O_4SiNa$ 411.1962; Found 411.1982.

***tert*-Butyldimethyl(phenyl(2,4,6-trimethoxyphenyl)methoxy)silane (4ac) in Table 3, entry 3.**

Benzaldehyde (**1a**: 15.7 mg, 0.15 mmol), 2,2'-bipyridyl (69.3 mg, 0.44 mmol), 1,3,5-trimethoxybenzene (49.8 mg, 0.30 mmol) and TBSOTf (68 μL, 0.30 mmol) were used according to the typical procedure A and *tert*-butyldimethyl(phenyl(2,4,6-trimethoxyphenyl)methoxy)silane (**4ac**: 56.1 mg, 0.14 mmol) was obtained in 91% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless solid; M. p. 63.1—64.7 °C; IR (ATR) cm^{-1}: 2954, 2929, 2854, 1590, 1492, 1457, 1334, 1223, 1202, 1184, 1150, 1118, 1085; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, 2H, J = 7.4 Hz), 7.22 (t, 2H, J = 7.4 Hz), 7.11 (t, 1H, J = 7.4 Hz), 6.41 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.69 (s, 6H), 0.90 (s, 9H), 0.03 (s, 3H), -0.19 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.6, 159.3, 146.0, 127.2, 125.4, 125.3, 114.4, 91.2, 66.6, 55.7, 55.2, 25.9, 18.3, -5.1, -5.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{32}O_4SiNa$ 411.1962; Found 411.1980.

Triethyl((4-methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (4b) in Table 4, entry 1.

4-Methoxybenzaldehyde (**1b**: 21.1 mg, 0.15 mmol), 2,2'-bipyridyl (72.6 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (52.1 mg, 0.31 mmol) and TESOTf (73 μL, 0.31 mmol) were used according to the typical procedure B and triethyl((4-methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (**4b**: 59.6 mg, 0.14 mmol) was obtained in 95% yield after 30 min stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2951, 2874, 1589, 1508, 1457, 1415, 1298, 1223, 1203, 1149,

1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, 2H, *J* = 8.8 Hz), 6.77 (d, 2H, *J* = 8.8 Hz), 6.38 (s, 1H), 6.09 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.69 (s, 3H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.53 (q, 6H, *J* = 8.0 Hz); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.5, 159.3, 157.5, 138.1, 126.5, 114.5, 112.7, 91.4, 66.2, 55.8, 55.2, 6.8, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{34}O_5SiNa$ 441.2068; Found 441.2061.

Triethyl((4-nitrophenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (4c) in Table 4, entry 2.

4-Nitrobenzaldehyde (**1c**: 22.4 mg, 0.15 mmol), 2,2'-bipyridyl (69.3 mg, 0.44 mmol), 1,3,5-trimethoxybenzene (49.8 mg, 0.30 mmol) and TESOTf (67 μL, 0.30 mmol) were used according to the typical procedure B and triethyl((4-nitrophenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (**4c**: 46.1 mg, 0.11 mmol) was obtained in 71% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2875, 2839, 1593, 1517, 1458, 1416, 1343, 1224, 1204, 1151, 1121, 1056; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, 2H, *J* = 8.2 Hz), 7.52 (d, 2H, *J* = 8.2 Hz), 6.44 (s, 1H), 6.08 (s, 2H), 3.80 (s, 3H), 3.68 (s, 6H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.54 (q, 6H, *J* = 8.0 Hz); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.3, 159.2, 154.4, 146.0, 126.2, 122.6, 112.9, 91.1, 66.1, 55.6, 55.3, 6.7, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{31}NO_6SiNa$ 456.1813; Found 456.1813.

((4-Chlorophenyl)(2,4,6-trimethoxyphenyl)methoxy)triethylsilane (4d) in Table 4, entry 3.

4-Chlorobenzaldehyde (**1d**: 22.3 mg, 0.16 mmol), 2,2'-bipyridyl (74.5 mg, 0.48 mmol), 1,3,5-trimethoxybenzene (53.5 mg, 0.32 mmol) and TESOTf (72 μL, 0.32 mmol) were used according to the typical procedure B and ((4-chlorophenyl)(2,4,6-trimethoxyphenyl)methoxy)triethylsilane (**4d**: 56.6 mg, 0.13 mmol) was obtained in 84% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/CH_2Cl_2 = 1/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2874, 2837, 1591, 1488, 1457, 1415, 1335, 1223, 1150, 1116, 1055; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, 2H, *J* = 8.0 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 6.36 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.68 (s, 6H), 0.86 (t, 9H, *J* = 7.5 Hz), 0.57—0.48 (m, 6H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 160.8, 159.2, 144.6, 130.8, 127.2, 126.9, 113.7, 91.1, 65.9, 55.7, 55.2, 6.8, 4.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{31}O_4SiClNa$ 445.1572; Found 445.1577.

((4-Bromophenyl)(2,4,6-trimethoxyphenyl)methoxy)triethylsilane (4e) in Table 4, entry 4.

4-Bromobenzaldehyde (**1e**: 27.8 mg, 0.15 mmol), 2,2'-bipyridyl (71.8 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (52.2 mg, 0.30 mmol) and TESOTf (68 μL, 0.30 mmol) were used according to the typical procedure B and ((4-bromophenyl)(2,4,6-trimethoxyphenyl)methoxy)triethylsilane (**4e**: 56.1 mg, 0.14 mmol) was obtained in 93% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1). Colorless oil; IR

(ATR) cm^{-1}: 2952, 2874, 1590, 1483, 1455, 1416, 1223, 1203, 1150, 1119, 1055, 1007; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, 2H, *J* = 8.6 Hz), 7.25 (d, 2H, *J* = 8.6 Hz), 6.35 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.68 (s, 6H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.57—0.49 (m, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.8, 159.2, 145.2, 130.1, 127.3, 119.0, 113.6, 91.1, 65.9, 55.7, 55.2, 6.7, 4.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{31}O_4SiBrNa$ 489.1067; Found 489.1060.

([1,1'-Biphenyl]-4-yl(2,4,6-trimethoxyphenyl)methoxy)triethylsilane (4f) in Table 4, entry 5.

4-Phenylbenzaldehyde (**1f**: 36.6 mg, 0.20 mmol), 2,2'-bipyridyl (94.0 mg, 0.60 mmol), 1,3,5-trimethoxybenzene (67.8 mg, 0.40 mmol) and TESOTf (90 μL, 0.40 mmol) were used according to the typical procedure B and ([1,1'-biphenyl]-4-yl(2,4,6-trimethoxyphenyl)methoxy)triethylsilane (**4f**: 83.5 mg, 0.18 mmol) was obtained in 90% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2874, 1591, 1487, 1456, 1224, 1204, 1151, 1120, 1056, 1006; ^1H NMR (500 MHz, $CDCl_3$): δ 7.59—7.57 (m, 2H), 7.48—7.39 (m, 6H), 7.29 (t, 1H, *J* = 7.5 Hz), 6.47 (s, 1H), 6.11 (s, 2H), 3.81 (s, 3H), 3.70 (s, 6H), 0.89 (t, 9H, *J* = 7.5 Hz), 0.60—0.52 (m, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.7, 159.4, 145.1, 141.5, 138.2, 128.6, 127.0, 126.7, 126.0, 125.9, 114.1, 91.3, 66.3, 55.8, 55.2, 6.8, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{36}O_4SiNa$ 487.2275; Found 487.2302.

***tert*-butyl 4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)benzoate (4g) in Table 4, entry 6.**

tert-Butyl 4-formylbenzoate (**1g**: 30.8 mg, 0.15 mmol), 2,2'-bipyridyl (69.8 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (50.1 mg, 0.30 mmol) and TESOTf (67 μL, 0.30 mmol) were used according to the typical procedure B and *tert*-butyl 4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)benzoate (**4g**: 49.8 mg, 0.10 mmol) was obtained in 68% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm^{-1}: 2954, 2875, 1708, 1592, 1456, 1414, 1366, 1287, 1224, 1203, 1151, 1056; ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J* = 8.4 Hz), 7.41 (d, 2H, *J* = 8.4 Hz), 6.72 (s, 1H), 6.07 (s, 2H), 3.79 (s, 3H), 3.67 (s, 6H), 1.57 (s, 9H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.54 (q, *J* = 8.0 Hz, 6H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 166.2, 160.9, 159.3, 151.3, 129.2, 128.4, 125.2, 113.9, 91.3, 80.3, 66.3, 55.7, 55.2, 28.2, 6.7, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{40}O_6SiNa$ 511.2486; Found 511.2468.

***tert*-butyldimethyl(4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)phenoxy)silane (4h) in Table 4, entry 7.**

4-((*tert*-Butyldimethylsilyl)oxy)benzaldehyde (**1h**: 36.6 mg, 0.15 mmol), 2,2'-bipyridyl (72.6 mg, 0.47 mmol), 1,3,5-trimethoxybenzene (52.1 mg, 0.31 mmol) and TESOTf (70 μL, 0.31 mmol) were used according to the

typical procedure B and *tert*-butyldimethyl(4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)phenoxy)silane (**4h**: 50.5 mg, 0.98 mmol) was obtained in 65% yield after 6 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2875, 1603, 1505, 1460, 1415, 1250, 1203, 1119, 1056; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, 2H, *J* = 8.4 Hz), 6.69 (d, 2H, *J* = 8.4 Hz), 6.36 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.66 (s, 6H), 0.69 (s, 9H), 0.86 (t, 9H, *J* = 7.6 Hz), 0.53 (q, 6H, *J* = 7.6 Hz), 0.15 (s, 6H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 160.6, 159.4, 153.3, 138.7, 126.4, 118.8, 114.5, 91.3, 66.2, 55.7, 55.2, 25.7, 18.2, 6.8, 4.7, -4.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{46}O_5Si_2Na$ 541.2776; Found 541.2755.

4-(((Triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)phenyl acetate (4i) in Table 4, entry 8.

4-Acetyloxybenzaldehyde (**1i**: 24.6 mg, 0.15 mmol), 2,2'-bipyridyl (71.0 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (50.5 mg, 0.30 mmol) and TESOTf (68 μL, 0.30 mmol) were used according to the typical procedure B and 4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)phenyl acetate (**4i**: 63.3 mg, 0.14 mmol) was obtained in 90% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2875, 1753, 1591, 1504, 1457, 1417, 1368, 1203, 1151, 1119, 1056, 1008; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, 2H, *J* = 8.4 Hz), 6.93 (d, 2H, *J* = 8.4 Hz), 6.40 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.67 (s, 6H), 2.25 (s, 3H), 0.86 (t, 9H, *J* = 8.0 Hz), 0.58—0.49 (m, 6H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 169.6, 160.8, 159.3, 148.5, 143.6, 126.4, 120.1, 114.0, 91.3, 66.1, 55.7, 55.2, 21.4, 6.7, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{34}O_6SiNa$ 469.2017; Found 469.2016.

Triethyl((3-methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (4j) in Table 4, entry 9.

3-Methoxybenzaldehyde (**1j**: 20.7 mg, 0.15 mmol), 2,2'-bipyridyl (71.2 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (51.1 mg, 0.30 mmol) and TESOTf (69 μL, 0.30 mmol) were used according to the typical procedure B and triethyl((3-methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (**4j**: 53.9 mg, 0.13 mmol) was obtained in 86% yield after 30 min stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2951, 2874, 2835, 1588, 1455, 1415, 1278, 1222, 1203, 1147, 1117, 1042; ^1H NMR (500 MHz, $CDCl_3$): δ 7.12 (t, 1H, *J* = 8.0 Hz), 7.06 (s, 1H), 6.87 (d, 1H, *J* = 8.0 Hz), 6.67 (d, 1H, *J* = 8.0 Hz), 6.39 (s, 1H), 6.08 (s, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.67 (s, 6H), 0.87 (t, 9H, *J* = 7.5 Hz), 0.58—0.50 (m, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.6, 159.3, 158.9, 147.1, 128.1, 117.9, 114.1, 111.4, 110.7, 91.2, 66.2, 55.8, 55.2, 55.1, 6.8, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{34}O_5SiNa$ 441.2068; Found 441.2089.

Triethyl((2-methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (4k) in Table 4, entry 10.

2-Methoxybenzaldehyde (**1k**: 21.7 mg, 0.16 mmol), 2,2'-bipyridyl (74.5 mg, 0.48 mmol), 1,3,5-trimethoxybenzene (53.5 mg, 0.32 mmol) and TESOTf (72 μL, 0.32 mmol) were used according to the typical procedure B and triethyl((2-methoxyphenyl)(2,4,6-trimethoxyphenyl)methoxy)silane (**4k**: 54.6 mg, 0.12 mmol) was obtained in 87% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2951, 2874, 2835, 1590, 1458, 1238, 1224, 1149, 1120, 1048; ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, 1H, *J* = 7.6 Hz), 7.11 (t, 1H, *J* = 7.6 Hz), 6.94 (t, 1H, *J* = 7.6 Hz), 6.71 (d, 1H, *J* = 7.6 Hz), 6.51 (s, 1H), 6.06 (s, 2H), 3.77 (s, 3H), 3.67 (s, 6H), 3.59 (s, 3H), 0.86 (t, 9H, *J* = 8.0 Hz), 0.54 (q, 6H, *J* = 8.0 Hz); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 160.2, 159.3, 155.9, 133.9, 128.6, 126.5, 119.5, 114.4, 110.3, 91.6, 62.9, 55.9, 55.6, 55.1, 6.8, 4.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{34}O_5SiNa$ 441.2068; Found 441.2066.

Triethyl(naphthalen-1-yl(2,4,6-trimethoxyphenyl)methoxy)silane (4l) in Table 4, entry 11.

1-Naphthylaldehyde (**1l**: 23.2 mg, 0.15 mmol), 2,2'-bipyridyl (69.8 mg, 0.45 mmol), 1,3,5-trimethoxybenzene (50.1 mg, 0.30 mmol) and TESOTf (67 μL, 0.30 mmol) were used according to the typical procedure B and triethyl(naphthalen-1-yl(2,4,6-trimethoxyphenyl)methoxy)silane (**4l**: 46.0 mg, 0.11 mmol) was obtained in 70% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2874, 2836, 1589, 1456, 1415, 1333, 1223, 1203, 1185, 1149, 1059; ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, 1H, *J* = 7.0 Hz), 7.95 (d, 1H, *J* = 8.0 Hz), 7.78 (d, 1H, *J* = 7.5 Hz), 7.68 (d, 1H, *J* = 8.0 Hz), 7.50 (t, 1H, *J* = 8.0 Hz), 7.33—7.29 (m, 2H), 6.36 (s, 1H), 6.08 (s, 2H), 3.73 (s, 3H), 3.67 (s, 6H), 0.88 (t, 9H, *J* = 7.5 Hz), 0.58 (q, 6H, *J* = 7.5 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.6, 159.2, 140.7, 133.2, 130.3, 128.4, 126.2, 125.1, 125.0, 124.8, 124.3, 123.6, 113.8, 91.4, 64.7, 55.6, 55.0, 6.8, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{34}O_4SiNa$ 461.2119; Found 461.2136.

((2,4-Dimethoxyphenyl)(phenyl)methoxy)triethylsilane (4m) in Table 4, entry 12.

Benzaldehyde (**1a**: 15.8 mg, 0.15 mmol), 2,2'-bipyridyl (71.0 mg, 0.45 mmol), 1,3-dimethoxybenzene (195 μL, 1.5 mmol) and TESOTf (68 μL, 0.30 mmol) were used according to the typical procedure B and ((2,4-dimethoxyphenyl)(phenyl)methoxy)triethylsilane (**4m**: 30.5 mg, 0.12 mmol) was obtained in 81% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 12/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2875, 1611, 1589, 1504, 1455, 1415, 1284, 1255, 1206, 1155, 1118, 1081, 1060, 1039, 1004; ^1H NMR (500 MHz, $CDCl_3$): δ 7.39—7.37 (m, 3H), 7.26—7.23 (m, 2H), 7.16 (t, 1H, *J* = 7.5 Hz), 6.46 (dd, 1H, *J* = 8.3, 2.9 Hz), 6.39 (d, 1H, *J* = 2.9 Hz), 6.14 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.55 (q, 6H, *J* = 8.0

Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.7, 156.6, 145.6, 128.0, 127.8, 126.6, 126.4, 126.2, 104.4, 97.9, 69.2, 55.3, 6.8, 4.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{30}O_3SiNa$ 381.1856; Found 381.1864.

((2,4-Dimethoxyphenyl)(4-methoxyphenyl)methoxy)triethylsilane (4n) in Table 4, entry 13.

4-Methoxybenzaldehyde (**1b**: 23.6 mg, 0.173 mmol), 2,2'-bipyridyl (81.1 mg, 0.52 mmol), 1,3-dimethoxybenzene (227 μL, 1.7 mmol) and TESOTf (78 μL, 0.35 mmol) were used according to the typical procedure B and ((2,4-dimethoxyphenyl)(phenyl)methoxy)triethylsilane (**4n**: 34.0 mg, 0.08 mmol) was obtained in 45% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2875, 2837, 1590, 1483, 1456, 1416, 1366, 1223, 1203, 1150, 1007; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 1H, *J* = 8.6 Hz), 7.27 (d, 2H, *J* = 8.6 Hz), 6.78 (d, 2H, *J* = 8.6 Hz), 6.46 (d, 1H, *J* = 8.6 Hz), 6.37 (s, 1H), 6.07 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 0.86 (t, 9H, *J* = 8.0 Hz), 0.54 (q, 6H, *J* = 8.0 Hz); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.7, 158.2, 156.5, 138.0, 127.7, 127.4, 126.9, 113.2, 104.4, 98.0, 68.9, 55.3, 55.2, 6.8, 4.8; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{32}O_4Si$ 389.2143; Found 389.2171.

((4-Chlorophenyl)(2,4-dimethoxyphenyl)methoxy)triethylsilane (4o) in Table 4, entry 14.

4-Chlorobenzaldehyde (**1d**: 21.0 mg, 0.15 mmol), 2,2'-bipyridyl (70.0 mg, 0.45 mmol), 1,3-dimethoxybenzene (195 μL, 1.5 mmol) and TESOTf (68 μL, 0.30 mmol) were used according to the typical procedure B and ((4-chlorophenyl)(2,4-dimethoxyphenyl)methoxy)triethylsilane (**4o**: 16.2 mg, 0.07 mmol) was obtained in 45% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2954, 2875, 1611, 1589, 1504, 1488, 1462, 1414, 1299, 1255, 1206, 1156, 1118, 1067, 1038, 1012; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, 1H, *J* = 8.0 Hz), 7.31 (d, 2H, *J* = 8.6 Hz), 7.21 (d, 2H, *J* = 8.6 Hz), 6.46 (dd, 1H, *J* = 8.0, 2.9 Hz), 6.39 (d, 1H, *J* = 2.9 Hz), 6.08 (s, 1H), 3.78 (s, 3H), 3.78 (s, 3H), 0.86 (t, 9H, *J* = 8.0 Hz), 0.55 (q, 6H, *J* = 8.0 Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.9, 156.5, 144.3, 132.0, 127.9, 127.7, 127.5, 126.1, 104.4, 98.0, 68.7, 55.3, 6.7, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{29}O_3SiClNa$ 415.1467; Found 415.1467.

Triethyl((4-methoxynaphthalen-1-yl)(4-methoxyphenyl)methoxy)silane (4p) in Table 4, entry 15.

4-Methoxybenzaldehyde (**1b**: 19.5 mg, 0.14 mmol), 2,2'-bipyridyl (67.0 mg, 0.43 mmol), 1-methoxynaphthalene (41.5 μg, 0.30 mmol) and TESOTf (65 μL, 0.29 mmol) were used according to the typical procedure B and triethyl((4-methoxynaphthalen-1-yl)(4-methoxyphenyl)methoxy)silane (**4p**: 19.6 mg, 0.05 mmol) was obtained in 32% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1).

Colorless oil; IR (ATR) cm^{-1}: 2953, 2874, 1584, 1509, 1461, 1391, 1301, 1240, 1171, 1158, 1093, 1069, 1033, 1005; ^1H NMR (500 MHz, $CDCl_3$): δ 8.27—8.25 (m, 1H), 7.98 (dd, 1H, *J* = 7.7, 1.7 Hz), 7.64 (d, 1H, *J* = 8.0 Hz), 7.41—7.35 (m, 2H), 7.27 (d, 2H, *J* = 8.0 Hz), 6.82 (d, 1H, *J* = 8.0 Hz), 6.77 (d, 2H, *J* = 8.0 Hz), 6.27 (s, 1H), 4.02 (s, 3H), 3.74 (s, 3H), 0.86 (t, 9H, *J* = 8.0 Hz), 0.62—0.50 (m, 6H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 158.3, 155.0, 137.3, 132.2, 131.3, 127.7, 126.0, 125.9, 125.0, 124.6, 124.5, 122.3, 113.4, 102.3, 74.4, 55.4, 55.2, 6.8, 4.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{32}O_3SiNa$ 431.2013; Found 431.2038.

3-(4-(((Triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)phenyl)propanal (4q) in eq. 8.

4-(3-Oxopropyl)benzaldehyde (**1q**: 21.7 mg, 0.13 mmol), 2,2'-bipyridyl (121.8 mg, 0.78 mmol), 1,3,5-trimethoxybenzene (48.2 mg, 0.26 mmol) and TESOTf (118 μL, 0.52 mmol) were used according to the typical procedure B and 3-(4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)phenyl)propanal (**4q**: 49.6 mg, 0.11 mmol) was obtained in 86% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 3/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2874, 1723, 1590, 1455, 1437, 1415, 1224, 1203, 1171, 1149, 1118, 1055, 1004; ^1H NMR (500 MHz, $CDCl_3$): δ 9.80 (t, 1H, *J* = 1.7 Hz), 7.30 (d, 2H, *J* = 7.9 Hz), 7.05 (d, 2H, *J* = 7.9 Hz), 6.40 (s, 1H) 6.10 (s, 2H), 3.80 (s, 3H), 3.69 (s, 6H), 2.91 (t, 2H, *J* = 8.0 Hz), 2.74 (dt, 2H, *J* = 8.0, 1.7 Hz), 0.87 (t, 9H, *J* = 8.0 Hz), 0.58—0.50 (m, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 202.1, 160.6, 159.3, 143.9, 137.1, 127.1, 125.7, 114.1, 91.3, 66.3, 55.8, 55.2, 45.3, 27.8, 6.8, 4.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{36}O_5SiNa$ 467.2224; Found 467.2241.

1-(4'-(((Triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)-[1,1'-biphenyl]-4-yl)ethanone (4r) in eq. 9.

4'-Acetyl-[1,1'-biphenyl]-4-carbaldehyde (**1r**: 32.4 mg, 0.15 mmol), 2,2'-bipyridyl (140.1 mg, 0.90 mmol), 1,3,5-trimethoxybenzene (51.0 mg, 0.30 mmol) and TESOTf (135 μL, 0.60 mmol) were used according to the typical procedure B and 1-(4'-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)-[1,1'-biphenyl]-4-yl)ethanone (**4r**: 55.2 mg, 0.11 mmol) was obtained in 76% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2954, 2875, 1679, 1602, 1493, 1456, 1417, 1359, 1267, 1224, 1203, 1150, 1116; ^1H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, 2H, *J* = 8.5 Hz), 7.67 (d, 2H, *J* = 8.5 Hz), 7.52 (d, 2H, *J* = 8.5 Hz), 7.47 (d, 2H, *J* = 8.5 Hz), 6.47 (s, 1H), 6.11 (s, 2H), 3.80 (s, 3H), 3.71 (s, 6H), 2.62 (s, 3H), 0.89 (t, 9H, *J* = 8.0 Hz), 0.59—0.53 (m, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 197.8, 160.7, 159.3, 146.4, 146.1, 136.8, 135.3, 128.8, 126.9, 126.1, 126.1, 113.9, 91.3, 66.2, 55.8, 55.2, 26.6, 6.8, 4.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{38}O_5SiNa$ 529.2381; Found 529.2392.

Triethyl((4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)benzyl)oxy)silane (4s) in Scheme 3.

4-(Hydroxymethyl)benzaldehyde (**1s**: 1.00 g, 7.3 mmol), 2,2'-bipyridyl (6.8 g, 41.8 mmol), 1,3,5-trimethoxybenzene (2.5 g, 14.6 mmol) and TESOTf (6.6 mL, 29.2 mmol) were used according to the typical procedure B and triethyl((4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)benzyl)oxy)silane (**4s**: 3.4 g, 6.4 mmol) was obtained in 87% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2875, 1591, 1456, 1415, 1224, 1204, 1151, 1120, 1057, 1004; ^1H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, 2H, *J* = 8.0 Hz), 7.19 (d, 2H, *J* = 8.0 Hz), 6.40 (s, 1H), 6.08 (s, 2H), 4.68 (s, 2H), 3.79 (s, 3H), 3.67 (s, 6H), 0.95 (t, 9H, *J* = 8.0 Hz), 0.87 (t, 9H, *J* = 8.0 Hz), 0.62 (q, 6H, *J* = 8.0 Hz), 0.57—0.50 (m, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 160.6, 159.3, 144.8, 138.2, 125.4, 125.3, 114.4, 91.2, 66.3, 64.9, 55.7, 55.2, 6.8, 6.8, 4.6, 4.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{29}H_{48}O_5Si_2Na$ 555.2933; Found 555.2939.

Trimethyl((1-phenylbut-3-en-1-yl)oxy)silane (5a) in Table 5, entry 1.

Benzaldehyde (**1a**: 109.2 mg, 1.0 mmol), 2,2'-bipyridyl (438.3 mg, 3.0 mmol), allyltrimethylsilane (298 μL, 2.0 mmol) and TMSOTf (438 μL, 2.0 mmol) were used according to the typical procedure B and trimethyl((1-phenylbut-3-en-1-yl)oxy)silane (**5a**: 201.3 mg, 0.89 mmol) was obtained in 89% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 3077, 3029, 2957, 1641, 1493, 1453, 1363, 1306, 1250, 1198, 1086, 1067, 1011; ^1H NMR (500 MHz, $CDCl_3$): δ 7.33—7.30 (m, 4H), 7.25—7.22 (m, 1H), 5.81—5.73 (m, 1H), 5.05—5.00 (m, 2H), 4.66 (dd, 1H, *J* = 5.2, 2.3 Hz), 2.51—2.49 (m, 1H), 2.43—2.37 (m, 1H), 0.04 (s, 9H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 144.8, 135.3, 128.0, 127.0, 125.9, 116.8, 74.8, 45.1, 0.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{20}OSiNa$ 243.1176; Found 243.1203.

((1-(4-Methoxyphenyl)but-3-en-1-yl)oxy)trimethylsilane (5ba) in Table 5, entry 2.

4-Methoxybenzaldehyde (**1b**: 20.0 mg, 0.15 mmol), 2,2'-bipyridyl (68.9 mg, 0.44 mmol), allyltrimethylsilane (47 μL, 0.30 mmol) and TMSOTf (53 μL, 0.30 mmol) were used according to the typical procedure B and ((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)trimethylsilane (**5ba**: 30.1 mg, 0.12 mmol) was obtained in 82% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2933, 2905, 2834, 1640, 1510, 1462, 1350, 1299, 1171, 1104, 1071, 1033; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, 2H, *J* = 8.8 Hz), 6.85 (d, 2H, *J* = 8.8 Hz), 5.81—5.70 (m, 1H), 5.05—5.00 (m, 2H), 4.62 (t, 1H, *J* = 7.2 Hz), 3.80 (s, 3H), 2.51—2.44 (m, 1H), 2.42—2.35 (m, 1H), 0.04 (s, 9H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 158.6,

137.0, 135.4, 127.1, 116.7, 113.4, 74.5, 55.2, 45.1, 0.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{22}O_2SiNa$ 273.1281; Found 273.1307.

Trimethyl((1-(4-nitrophenyl)but-3-en-1-yl)oxy)silane (5c) in Table 5, entry 3.

4-Nitrobenzaldehyde (**1c**: 22.7 mg, 0.15 mmol), 2,2'-bipyridyl (72.1 mg, 0.45 mmol), allyltrimethylsilane (49 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and trimethyl((1-(4-nitrophenyl)but-3-en-1-yl)oxy)silane (**5c**: 31.3 mg, 0.12 mmol) was obtained in 78% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 3078, 2957, 1641, 1606, 1520, 1433, 1345, 1316, 1293, 1251, 1195, 1085, 1012; ^1H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, 2H, *J* = 8.5 Hz), 7.48 (d, 2H, *J* = 8.5 Hz), 5.76—5.69 (m, 1H), 5.05—5.00 (m, 2H), 4.79 (t, 1H, *J* = 6.5 Hz), 2.49—2.39 (m, 2H), 0.07 (s, 9H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 152.3, 147.0, 133.9, 126.6, 123.5, 117.9, 73.8, 44.8, 0.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}NO_3Si$ 266.1207; Found 266.1223.

((1-(4-Chlorophenyl)but-3-en-1-yl)oxy)trimethylsilane (5d) in Table 5, entry 4.

4-Chlorobenzaldehyde (**1d**: 23.9 mg, 0.15 mmol), 2,2'-bipyridyl (72.0 mg, 0.45 mmol), allyltrimethylsilane (49 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and ((1-(4-chlorophenyl)but-3-en-1-yl)oxy)trimethylsilane (**5d**: 42.5 mg, 0.15 mmol) was obtained in 98% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2933, 2905, 2834, 1640, 1510, 1462, 1350, 1299, 1171, 1104, 1071, 1033; ^1H NMR (500 MHz, $CDCl_3$): δ 7.28 (d, 2H, *J* = 8.5 Hz), 7.23 (d, 2H, *J* = 8.5 Hz), 5.76—5.70 (m, 1H), 5.03—5.00 (m, 2H), 4.64 (dd, 1H, *J* = 5.2, 2.3 Hz), 2.45—2.41 (m, 1H), 2.38—2.34 (m, 1H), 0.04 (s, 9H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 143.4, 134.8, 132.6, 128.2, 127.2, 117.2, 74.1, 45.0, 0.1; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}OSiCl$ 255.0966; Found 255.0957.

((1-(4-Bromophenyl)but-3-en-1-yl)oxy)trimethylsilane (5e) in Table 5, entry 5.

4-Bromobenzaldehyde (**1e**: 37.2 mg, 0.20 mmol), 2,2'-bipyridyl (93.8 mg, 0.60 mmol), allyltrimethylsilane 64 μL, 0.40 mmol) and TMSOTf (73 μL, 0.40 mmol) were used according to the typical procedure B and ((1-(4-chlorophenyl)but-3-en-1-yl)oxy)trimethylsilane (**5e**: 38.8 mg, 0.82 mmol) was obtained in 65% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2956, 1641, 1592, 1487, 1404, 1251, 1072, 1009; ^1H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, 2H, *J* = 8.0 Hz), 7.18 (d, 2H, *J* = 8.0 Hz), 5.77—5.69 (m, 1H), 5.04—5.00 (m, 2H), 4.62 (dd, 1H, *J* = 7.2, 5.2 Hz), 2.46—2.40 (m, 1H),

2.38—2.33 (m, 1H), 0.04 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.9, 134.7, 131.2, 127.6, 120.7, 117.2, 74.1, 45.0, 0.1; Anal. Calcd for $C_{13}H_{19}OSiBr$: C, 52.17; H, 6.40; N, 0.00. Found: C, 51.95; H, 6.39; N, 0.00.

((1-([1,1'-Biphenyl]-4-yl)but-3-en-1-yl)oxy)trimethylsilane (5f) in Table 5, entry 6.

4-Phenylbenzaldehyde (**1f**: 36.6 mg, 0.20 mmol), 2,2'-bipyridyl (93.5 mg, 0.60 mmol), allyltrimethylsilane (64 μL, 0.40 mmol) and TMSOTf (73 μL, 0.40 mmol) were used according to the typical procedure B and ((1-(4-chlorophenyl)but-3-en-1-yl)oxy)trimethylsilane (**5f**: 37.2 mg, 0.80 mmol) was obtained in 63% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2956, 1486, 1250, 1077, 1007; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, 2H, *J* = 8.0 Hz), 7.56 (d, 2H, *J* = 8.0 Hz), 7.44 (dd, 2H, *J* = 8.0, 7.5 Hz), 7.39 (d, 2H, *J* = 8.0 Hz), 7.34 (t, 1H, *J* = 7.5 Hz), 5.85—5.77 (m, 1H), 5.09—5.03 (m, 2H), 4.73 (dd, 1H, *J* = 7.5, 5.7 Hz), 2.55—2.49 (m, 1H), 2.48—2.42 (m, 1H), 0.08 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.9, 141.0, 139.8, 135.2, 128.7, 127.1, 127.0, 126.8, 126.3, 116.9, 74.6, 45.1, 0.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{24}OSiNa$ 319.1489; Found 319.1492.

***tert*-Butyldimethyl(4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)phenoxy)silane (5h) in Table 5, entry 7.**

4-((*tert*-Butyldimethylsilyl)oxy)benzaldehyde (**1h**: 35.5 mg, 0.15 mmol), 2,2'-bipyridyl (70.4 mg, 0.45 mmol), allyltrimethylsilane (48 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and *tert*-butyldimethyl(4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)phenoxy)silane (**5h**: 40.0 mg, 0.12 mmol) was obtained in 78% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2957, 2859, 1608, 1509, 1473, 1252, 1082; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (d, 2H, *J* = 8.5 Hz), 6.78 (d, 2H, *J* = 8.5 Hz), 5.77—5.71 (m, 1H), 5.03—5.00 (m, 2H), 4.60—4.58 (m, 1H), 2.49—2.44 (m, 1H), 2.39—2.35 (m, 1H), 0.98 (s, 9H), 0.18 (s, 6H), 0.04 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 154.6, 137.6, 135.5, 127.0, 119.6, 116.6, 74.6, 45.0, 25.7, 0.1, -4.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{34}O_2Si_2Na$ 373.1990; Found 373.1983.

4-(1-((Trimethylsilyl)oxy)but-3-en-1-yl)phenyl acetate (5i) in Table 5, entry 8.

4-Acetoxybenzaldehyde (**1i**: 24.6 mg, 0.15 mmol), 2,2'-bipyridyl (72.0 mg, 0.45 mmol), allyltrimethylsilane (48 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and 4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)phenyl acetate (**5i**: 24.0 mg, 0.08 mmol) was obtained in 53% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2957, 1770, 1506, 1369, 1251, 1198, 1083, 1012; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (d, 2H, *J* = 8.6 Hz), 7.03 (d 2H, *J* = 8.6 Hz), 5.80—5.71 (m, 1H), 5.05—5.01 (m, 2H), 4.68—4.65 (m, 1H), 2.48—2.42 (m, 1H),

2.41—2.35 (m, 1H), 2.29 (s, 3H), 0.04 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.5, 149.5, 142.4, 135.1, 126.8, 121.0, 117.0, 74.3, 45.1, 21.2, 0.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}O_3SiNa$ 301.1230; Found 301.1231.

Methyl 4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)benzoate (5m) in Table 5, entry 9.

Methyl 4-formylbenzoate (**1m**: 24.7 mg, 0.15 mmol), 2,2'-bipyridyl (70.4 mg, 0.45 mmol), allyltrimethylsilane (48 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and methyl 4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)benzoate (**5m**: 37.0 mg, 0.12 mmol) was obtained in 89% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2954, 1723, 1611, 1435, 1275, 1251, 1175, 1084, 1018; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, 2H, *J* = 8.0 Hz), 7.38 (d, 2H, *J* = 8.0 Hz), 5.77—5.70 (m, 1H), 5.03—5.00 (m, 2H), 4.72 (dd, 1H, *J* = 6.3, 6.3 Hz), 3.91 (s, 3H), 2.49—2.37 (m, 2H), 0.04 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.0, 150.1, 134.6, 129.5, 128.9, 125.8, 117.3, 74.4, 52.0, 44.9, 0.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}O_3SiNa$ 301.1230; Found 301.1240.

((1-(4-Methoxyphenyl)-3-methylbut-3-en-1-yl)oxy)trimethylsilane (5n) in Table 5, entry 10.

4-Methoxybenzaldehyde (**1b**: 21.0 mg, 0.15 mmol), 2,2'-bipyridyl (71.0 mg, 0.45 mmol), trimethyl(2-methylallyl)silane (56 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and ((1-(4-methoxyphenyl)-3-methylbut-3-en-1-yl)oxy)trimethylsilane (**5n**: 40.4 mg, 0.15 mmol) was obtained in 99% yield after 3 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2955, 1723, 1613, 1511, 1246, 1172, 1082; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, 2H, *J* = 8.5 Hz), 6.84 (d, 2H, *J* = 8.5 Hz), 4.76 (s, 1H), 4.72 (dd, 1H, *J* = 8.0, 5.0 Hz), 4.67 (s, 1H), 3.80 (s, 3H), 2.44 (dd, 1H, *J* = 13.0, 6.5 Hz), 2.29 (dd, 1H, *J* = 13.0, 6.5 Hz), 1.71 (s, 3H), 0.08 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.6, 142.7, 137.3, 127.1, 113.1, 112.8, 73.8, 55.2, 49.0, 23.1, 0.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{24}O_2SiNa$ 287.1438; Found 287.1459.

(Cyclopenta-1,3-dien-1-yl(4-methoxyphenyl)methoxy)trimethylsilane (5o) in Table 5, entry 11.

4-Methoxybenzaldehyde (**1b**: 20.2 mg, 0.15 mmol), 2,2'-bipyridyl (70.0 mg, 0.45 mmol), cyclopenta-2,4-dien-1-yltrimethylsilane (49 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure B and (cyclopenta-1,3-dien-1-yl(4-methoxyphenyl)methoxy)trimethylsilane (**5o**: 30.4 mg, 0.12 mmol) was obtained in 74% yield after 3 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2955, 1611, 1510, 1463, 1442, 1363, 1301, 1245, 1170, 1149, 1059, 1036,

1011; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, 2H, *J* = 8.6 Hz), 6.84 (d, 2H, *J* = 8.6 Hz), 6.39 (dd, 1H, *J* = 5.5, 1.7 Hz), 6.32 (dd, 1H, *J* = 5.5, 1.7 Hz), 6.28 (s, 1H), 5.57 (s, 1H), 3.80 (s, 3H), 2.85 (t, 1H, *J* = 1.7 Hz), 0.08 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.5, 152.2, 136.6, 132.6, 131.6, 128.0, 127.3, 113.4, 73.0, 55.2, 40.1, 0.1; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}O_2Si$ 275.1462; Found 275.1439.

((1-(4-Methoxyphenyl)but-3-en-1-yl)oxy)triethylsilane (5bb) in Table 5, entry 12.

4-Methoxybenzaldehyde (**1b**: 20.1 mg, 0.15 mmol), 2,2'-bipyridyl (70.1 mg, 0.45 mmol), allyltriethylsilane (68 μL, 0.30 mmol) and TESOTf (69 μL, 0.30 mmol) were used according to the typical procedure B and ((1-(4-methoxyphenyl)but-3-en-1-yl)oxy)triethylsilane (**5bb**: 46.1 mg, 0.15 mmol) was obtained in 89 % yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2953, 2909, 2875, 1612, 1511, 1459, 1301, 1244, 1171, 1077, 1038, 1004; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, 2H, *J* = 8.6 Hz), 6.84 (d, 2H, *J* = 8.6 Hz), 5.79—5.71 (m, 1H), 5.02—4.98 (m, 2H), 4.63 (t, 1H, *J* = 7.2 Hz), 3.80 (s, 3H), 2.50—2.44 (m, 1H), 2.39—2.34 (m, 1H), 0.87 (t, 9H, *J* = 8.0 Hz), 0.55—0.47 (m, 6H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.6, 137.3, 135.3, 127.0, 116.7, 113.3, 74.4, 55.2, 45.4, 6.8, 4.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{28}O_2SiNa$ 315.1736; Found 315.1751.

Trimethyl((4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)benzyl)oxy)silane (5s) in Scheme 3.

4-(Hydroxymethykl)benzaldehyde (**1s**: 20.4 mg, 0.15 mmol), 2,2'-bipyridyl (140.9 mg, 0.90 mmol), allyltrimethylsilane (48 μL, 0.30 mmol) and TMSOTf (110 μL, 0.60 mmol) were used according to the typical procedure B and trimethyl((4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)benzyl)oxy)silane (**5s**: 29.9 mg, 0.13 mmol) was obtained in 87% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2957, 2900, 1419, 1374, 1250, 1210, 1081, 1016; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27—7.26 (m, 4H), 5.80—5.71 (m, 1H), 5.04—4.99 (m, 2H), 4.68 (s, 2H), 4.66 (dd, 1H, *J* = 10.0, 5.2 Hz), 2.49—2.43 (m, 1H), 2.40—2.35 (m, 1H), 0.15 (s, 9H), 0.03 (s, 9H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 143.8, 139.6, 135.3, 126.4, 125.8, 116.8, 74.7, 64.5, 45.1, 0.1, -0.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{30}O_2Si_2Na$ 345.1677; Found 345.1670.

3-((4-(((Triethylsilyl)oxy)methyl)phenyl)(2,4,6-trimethoxyphenyl)methyl)-*1H*-indole (11a) in Scheme 3.

Triethyl((4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)benzyl)oxy)silane (**4s**: 82.7 mg, 0.16 mmol), $FeCl_3$ (2.1 mg, 0.013 mmol) and indole (54.5 mg, 0.47 mmol) were used according to the typical procedure D and 3-((4-(((Triethylsilyl)oxy)methyl)phenyl)(2,4,6-trimethoxyphenyl)methyl)-*1H*-indole (**11a**: 69.2 mg, 0.13 mmol) was obtained in 87% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc =

5/1). Colorless oil; IR (ATR) cm^{-1}: 3418, 2954, 2875, 1604, 1510, 1492, 1456, 1416, 1337, 1220, 1204, 1149, 1115, 1092, 1010; ^1H NMR (500 MHz, $CDCl_3$): δ 7.89 (brs, 1H), 7.34 (d, 1H, *J* = 8.2 Hz), 7.31 (d, 1H, *J* = 8.2 Hz), 7.20 (d, 2H, *J* = 8.0 Hz), 7.15—7.10 (m, 3H), 6.98 (t, 1H, *J* = 8.2 Hz), 6.86 (d, 1H, *J* = 1.7 Hz), 6.26 (s, 1H), 6.15 (s, 2H), 4.68 (s, 2H), 3.79 (s, 3H), 3.58 (s, 6H), 0.95 (t, 9H, *J* = 8.0 Hz), 0.61 (q, 6H, *J* = 8.0 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 159.7, 159.0, 143.4, 137.7, 136.1, 128.4, 125.6, 123.6, 121.3, 119.8, 118.9, 114.3, 110.7, 91.7, 64.9, 55.8, 55.2, 36.1, 6.8, 4.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{31}H_{39}NO_4SiNa$ 540.2541; Found 540.2536.

((4-(Azido(2,4,6-trimethoxyphenyl)methyl)benzyl)oxy)triethylsilane (11b) in Scheme 3.

Triethyl((4-(((triethylsilyl)oxy)(2,4,6-trimethoxyphenyl)methyl)benzyl)oxy)silane (**4s**: 79.9 mg, 0.15 mmol), $FeCl_3$ (1.4 mg, 0.0075 mmol) and $TMSN_3$ (22 μL, 0.165 mmol) were used according to the typical procedure D and ((4-(azido(2,4,6-trimethoxyphenyl)methyl)benzyl)oxy)triethylsilane (**11b**: 57.2 mg, 0.13 mmol) was obtained in 86% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2954, 2875, 2095, 1590, 1456, 1416, 1335, 1224, 1204, 1150, 1118; ^1H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, 2H, *J* = 8.8 Hz), 7.24 (d, 2H, *J* = 8.8 Hz), 6.30 (s, 1H), 6.14 (s, 2H), 4.70 (s, 2H), 3.81 (s, 3H), 3.71 (s, 6H), 0.96 (t, 9H, *J* = 8.0 Hz), 0.63 (q, 6H, *J* = 8.0 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 161.4, 159.4, 139.5, 138.8, 126.4, 125.8, 107.8, 90.9, 64.5, 58.2, 55.7, 6.7, 4.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{33}N_3O_4SiNa$ 466.2133; Found 466.2127.

((4-(1-Azidobut-3-en-1-yl)benzyl)oxy)trimethylsilane (11c) in Scheme 3.

Trimethyl((4-(1-((trimethylsilyl)oxy)but-3-en-1-yl)benzyl)oxy)silane (**5s**: 48.8 mg, 0.15 mmol), $FeCl_3$ (1.4 mg, 0.0075 mmol) and $TMSN_3$ (22 μL, 0.30 mmol) were used according to the typical procedure D and ((4-(1-azidobut-3-en-1-yl)benzyl)oxy)trimethylsilane (**11c**: 30.0 mg, 0.11 mmol) was obtained in 73% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2957, 2094, 1642, 1513, 1422, 1377, 1250,1086, 1019; ^1H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, 2H, *J* = 8.0 Hz), 7.28 (d, 2H, *J* = 8.0 Hz), 5.78—5.69 (m, 1H), 5.14—5.08 (m, 2H), 4.70 (s, 2H), 4.49 (dd, 1H, *J* = 7.2 , 7.2 Hz), 2.61—2.55 (m, 1H), 2.54—2.48 (m, 1H), 0.16 (s, 9H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 141.1, 137.9, 133.7, 126.9, 126.9, 118.2, 65.6, 64.2, 40.5, -0.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{21}N_3OSiNa$ 298.1346; Found 298.1358.

Triethyl(2-(phenyl(2,4,6-trimethoxyphenyl)methoxy)ethoxy)silane (7a) in Table 6, entry 1.

2-Phenyl-1,3-dioxolane (**6a**: 22.8 mg, 0.15 mmol), 2,2'-bipyridyl (71.2 mg, 0.46 mmol), 1,3,5-trimethoxybenzene (51.1 mg, 0.30 mmol) and TESOTf (69 μL, 0.30 mmol) were used according to the typical procedure C and triethyl(2-(phenyl(2,4,6-trimethoxyphenyl)methoxy)ethoxy)silane (**7a**: 58.9 mg, 0.14 mmol) was obtained in 90% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2955, 2876, 1592, 1493, 1457, 1417, 1326, 1225, 1204, 1150, 1120, 1088, 1006; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, 2H, *J* = 7.3 Hz), 7.24 (t, 2H, *J* = 7.3 Hz), 7.14 (t, 1H, *J* = 7.3 Hz), 6.12 (s, 2H), 6.10 (s, 1H), 3.87—3.76 (m, 2H), 3.80 (s, 3H), 3.68 (s, 6H), 3.65—3.52 (m, 2H), 0.94 (t, 9H, *J* = 7.8 Hz), 0.59 (q, 6H, *J* = 7.8 Hz); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 161.0, 159.9, 143.3, 127.3, 126.0, 125.8, 110.9, 91.3, 74.1, 70.1, 62.1, 55.8, 55.2, 6.7, 4.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{36}O_5SiNa$ 455.2224; Found 455.2229.

Methyl 4-((2-((triethylsilyl)oxy)ethoxy)(2,4,6-trimethoxyphenyl)methyl)benzoate (7b) in Table 6, entry 2.

Methyl 4-(1,3-dioxolan-2-yl)benzoate (**6b**: 42.3 mg, 0.2 mmol), 2,2'-bipyridyl (94.0 mg, 0.60 mmol), 1,3,5-trimethoxybenzene (67.2 mg, 0.40 mmol) and TESOTf (90 μL, 0.40 mmol) were used according to the typical procedure C and methyl 4-((2-((triethylsilyl)oxy)ethoxy)(2,4,6-trimethoxyphenyl)methyl)benzoate (**7b**: 42.2 mg, 0.09 mmol) was obtained in 43% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2876, 1721, 1607, 1457, 1435, 1417, 1276, 1225, 1205, 1151, 1119, 1039, 1018; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, 2H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.4 Hz), 6.12 (s, 1H), 6.10 (s, 2H), 3.85—3.77 (m, 2H), 3.80 (s, 3H), 3.66 (s, 6H), 3.64—3.54 (m, 2H), 0.94 (t, 9H, *J* = 7.8 Hz), 0.59 (q, 6H, *J* = 7.8 Hz); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 167.4, 161.2, 159.8, 149.3, 128.7, 127.5, 125.8, 110.1, 91.1, 73.6, 70.1, 62.1, 55.8, 55.3, 51.9, 6.7, 4.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{38}O_7SiNa$ 513.2309; Found 513.2279.

Triethyl(2-(thiophen-2-yl(2,4,6-trimethoxyphenyl)methoxy)ethoxy)silane (7c) in Table 6, entry 3.

Thiophen-2-carbaldehyde (31.8 mg, 0.20 mmol), 2,2'-bipyridyl (93.7 mg, 0.60 mmol), 1,3,5-trimethoxybenzene (67.2 mg, 0.40 mmol) and TESOTf (90 μL, 0.40 mmol) were used according to the typical procedure C and triethyl(2-(thiophen-2-yl(2,4,6-trimethoxyphenyl)methoxy)ethoxy)silane (**7c**: 55.2 mg, 0.13 mmol) was obtained in 63% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1). Colorless oil; IR (ATR) cm^{-1}: 2952, 2911, 2875, 1604, 1590, 1456, 1417, 1225, 1204, 1148, 1119, 1087, 1039, 1014; ^1H NMR (400 MHz, $CDCl_3$): δ 7.14 (dd, 1H, *J* = 5.0, 1.4 Hz), 6.86 (dd, 1H, *J* = 5.0, 3.7 Hz), 6.82—6.81 (m, 1H), 6.29 (s, 1H), 6.13 (s, 2H), 3.84—3.72 (m, 2H), 3.81 (s, 3H), 3.75 (s, 6H), 3.66—3.50 (m, 2H), 0.93 (t, 9H, *J* = 8.0 Hz), 0.58 (q, 6H, *J* = 8.0 Hz); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ 161.1, 159.8, 146.8, 125.8, 123.9,

123.7, 109.7, 91.1, 71.7, 69.8, 62.0, 55.8, 55.3, 6.7, 4.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{34}O_5SiSNa$ 461.1788; Found 461.1800.

Trimethyl(2-((1-phenylbut-3-en-1-yl)oxy)ethoxy)silane (8a) in Table 6, entry 4.

2-Phenyl-1,3-dioxolane (**6a**: 22.5 mg, 0.15 mmol), 2,2'-bipyridyl (70.8 mg, 0.45 mmol), allyltrimethylsilane (48 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure C and trimethyl(2-((1-phenylbut-3-en-1-yl)oxy)ethoxy)silane (**8a**: 32.9 mg, 0.13 mmol) was obtained in 83% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2956, 2866, 1642, 1493, 1453, 1250, 1097; ^1H NMR (500 MHz, $CDCl_3$): δ 7.35—7.25 (m, 5H), 5.81—5.73 (m, 1H), 5.05—4.98 (m, 2H), 4.31 (t, 1H, *J* = 6.9 Hz), 3.71—3.69 (m, 2H), 3.43—3.34 (m, 2H), 2.62—2.57 (m, 1H), 2.43—2.38 (m, 1H), 0.11 (s, 9H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 142.0, 134.9, 128.3, 127.5, 126.8, 116.8, 82.3, 69.9, 62.0, 12.6, -0.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{24}O_2SiNa$ 287.1438; Found 287.1446.

Trimethyl(2-((3-methyl-1-phenylbut-3-en-1-yl)oxy)ethoxy)silane (8b) in Table 6, entry 5.

2-Phenyl-1,3-dioxolane (**6a**: 22.8 mg, 0.15 mmol), 2,2'-bipyridyl (70.7 mg, 0.45 mmol), trimethyl(2-methylallyl)silane (52 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure C and trimethyl(2-((3-methyl-1-phenylbut-3-en-1-yl)oxy)ethoxy)silane (**8b**: 41.3 mg, 0.15 mmol) was obtained in 99% yield after 3 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 15/1). Colorless oil; IR (ATR) cm^{-1}: 2956, 2866, 1453, 1250, 1135, 1094, 1057, 1027; ^1H NMR (500 MHz, $CDCl_3$): δ 7.35—7.25 (m, 5H), 4.75 (s, 1H), 4.69 (s, 1H), 4.44 (dd, 1H, *J* = 8.0, 5.7 Hz), 3.72—3.65 (m, 2H), 3.42—3.33 (m, 2H), 2.58 (dd, 1H, *J* = 14.0, 8.0 Hz), 2.31 (dd, 1H, *J* = 14.0, 5.7 Hz), 1.73 (s, 3H), 0.10 (s, 9H). ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 142.5, 142.4, 128.2, 127.5, 126.7, 112.6, 81.4, 69.9, 62.0, 46.5, 23.0, -0.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{26}O_2SiNa$ 301.1594; Found 301.1582.

(2-((1-(4-Chlorophenyl)-3-methylbut-3-en-1-yl)oxy)ethoxy)trimethylsilane (8c) in Table 6, entry 6.

2-(4-Chlorophenyl)-1,3-dioxolane (**6d**: 27.8 mg, 0.15 mmol), 2,2'-bipyridyl (70.6 mg, 0.45 mmol), trimethyl(2-methylallyl)silane (52 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure C and trimethyl(2-((3-methyl-1-phenylbut-3-en-1-yl)oxy)ethoxy)silane (**8c**: 44.9 mg, 0.15 mmol) was obtained in 96 % yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 20/1). Colorless oil; IR (ATR) cm^{-1}: 2956, 2866, 1489, 1410, 1374, 1250, 1135, 1088, 1062, 1014; ^1H NMR (500

MHz, $CDCl_3$): δ 7.30 (d, 2H, *J* = 8.5 Hz), 7.23 (d, 2H, *J* = 8.5 Hz), 4.75—4.74 (m, 1H), 4.65—4.64 (m, 1H), 4.43—4.40 (m, 1H), 3.70—3.67 (m, 2H), 3.37—3.34 (m, 2H), 2.55 (dd, 1H, *J* = 14.2, 7.8 Hz), 2.27 (dd, 1H, *J* = 14.2, 6.0 Hz), 1.71 (s, 3H), 0.11 (s, 9H). ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ: 142.0, 140.9, 133.1, 128.4, 128.1, 112.9, 80.8, 70.0, 61.9, 46.4, 22.9, -0.5. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{25}O_2SiClNa$ 335.1215; Found 335.1205.

3-(4-Methoxyphenyl)-3-(2-((triethylsilyl)oxy)ethoxy)propanal (9e) in Table 6, entry 7.

2-(4-Methoxyphenyl)-1,3-dioxolane (**6e**: 27.0 mg, 0.15 mmol), 2,2'-bipyridyl (70.3 mg, 0.45 mmol), triethyl(vinyloxy)silane (33 μL, 0.30 mmol) and TESOTf (68 μL, 0.30 mmol) were used according to the typical procedure C and 3-(4-methoxyphenyl)-3-(2-((triethylsilyl)oxy)ethoxy)propanal (**9e**: 42.8 mg, 0.13 mmol) was obtained in 84% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm^{-1}: 2954, 2911, 2875, 2836, 2729, 1726, 1612, 1586, 1512, 1460, 1414, 1351, 1297, 1249, 1174, 1096, 1035, 1016; ^1H NMR (500 MHz, $CDCl_3$): δ 9.79 (dd, 1H, *J* = 2.5, 1.5 Hz), 7.26 (d, 2H, *J* = 8.5 Hz), 6.89 (d, 2H, *J* = 8.5 Hz), 4.82 (dd, 1H, *J* = 9.0, 4.5 Hz), 3.81 (s, 3H), 3.72—3.70 (m, 1H), 3.42—3.36 (m, 2H), 2.90 (ddd, 1H, *J* = 16.5, 9.0, 1.5 Hz), 2.61 (ddd, 1H, *J* = 16.5, 4.5, 2.5 Hz,), 0.94 (t, 9H, *J* = 8.0 Hz), 0.59 (q, 6H, *J* = 8.0 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 201.1, 159.4, 132.7, 127.8, 114.0, 76.9, 70.0, 62.2, 55.3, 51.7, 6.7, 4.3. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{30}O_4SiNa$ 361.1806; Found 361.1819.

3-Methoxy-3-phenylpropanal (9f) in Table 6, entry 8.

(Dimethoxymethyl)benzene (**6f**: 24.0 mg, 0.15 mmol), 2,2'-bipyridyl (35.1 mg, 0.225 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (28 μL, 0.15 mmol) were used according to the typical procedure C and 3-methoxy-3-phenylpropanal (**9f**: 18.1 mg, 0.15 mmol) was obtained in 94% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). ^1H NMR (500 MHz, $CDCl_3$): δ 9.80 (dd, 1H, *J* = 2.3, 1.8 Hz), 7.39—7.30 (m, 5H), 4.69 (dd, 1H, *J* = 8.5, 4.0 Hz), 3.23 (s, 3H), 2.91 (ddd, 1H, *J* = 16.5, 8.5, 2.3 Hz), 2.64 (ddd, 1H, *J* = 16.5, 4.0, 1.8 Hz). Spectroscopic data of ^1H NMR was identical to that of the reference 17.

3-Methoxy-3-(4-methoxyphenyl)propanal (9g) in Table 6, entry 9.

1-(Dimethoxymethyl)-4-methoxybenzene (**6g**: 54.7 mg, 0.30 mmol), 2,2'-bipyridyl (70.3 mg, 0.45 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (54 μL, 0.30 mmol) were used according to the typical procedure C and the mixture of 3-methoxy-3-(4-methoxyphenyl)propanal (**9g**; 71% yield), (*E*)-3-(4-methoxyphenyl)acrylaldehyde and 2,2'-bipyridyl (total; 40.6 mg) was obtained after 3 h stirring and purification

by silica-gel column chromatography (Hex/EtOAc = 5/1). Yellow oil; IR (ATR) cm^{-1}: 2935, 2904, 2837, 2731, 1722, 1671, 1601, 1572, 1511, 1462, 1443, 1425, 1393, 1353, 1300, 1247, 1174, 1126, 1101, 1070, 1029; ^1H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.5, 1.5 Hz), 7.25 (d, 2H, *J* = 8.5 Hz), 6.91 (d, 2H, *J* = 8.5 Hz), 4.64 (dd, 1H, *J* = 8.8, 4.5 Hz,), 3.81 (s, 3H), 3.20 (s, 3H), 2.90 (ddd, 1H, *J* = 16.5, 8.8, 2.5 Hz), 2.63 (ddd, 1H, *J* = 16.5, 4.5, 1.5 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 200.8, 159.4, 132.2, 127.8, 114.0, 78.1, 56.4, 55.3, 51.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}O_3Na$ 217.0835; Found 217.0849.

3-Methoxy-3-(4-nitrophenyl)propanal (9h) in Table 6, entry 10.

1-(Dimethoxymethyl)-4-nitrobenzene (**6h**: 29.6 mg, 0.15 mmol), 2,2'-bipyridyl (70.2 mg, 0.45 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (54 μL, 0.30 mmol) were used according to the typical procedure C and the mixture of 3-methoxy-3-(4-nitrophenyl)propanal (**9h**: quantitative yield) and 2,2'-bipyridyl (total; 93.0 mg) was obtained after 6 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 2/1). Yellow solid; M.p. 64–70 °C; IR (ATR) cm^{-1}: 3079, 2934, 2828, 2730, 1722, 1682, 1601, 1519, 1455, 1396, 1344, 1293, 1228, 1180, 1104, 1071, 1052, 1013; ^1H NMR (500 MHz, $CDCl_3$): δ 9.79 (dd, 1H, *J* = 1.8, 1.0 Hz), 8.25 (d, 2H, *J* = 8.8 Hz), 7.53 (d, 2H, *J* = 8.8 Hz), 4.83 (dd, 1H, *J* = 8.5, 4.5 Hz), 3.28 (s, 3H), 2.95 (ddd, 1H, *J* = 17.5, 8.5, 1.8 Hz), 2.67 (ddd, 1H, *J* = 17.5, 4.5, 1.0 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 199.1, 148.1, 147.7, 127.3, 124.0, 77.6, 57.2, 51.3; HRMS (ESI-TOF) m/z: $[M+H-OCH_3]^+$ Calcd for $C_9H_9NO_3$ 179.0577; Found 179.0575.

Methyl 4-(1-methoxy-3-oxopropyl)benzoate (9i) in Table 6, entry 11.

Methyl 4-(dimethoxymethyl)benzoate (**6i**: 31.5 mg, 0.15 mmol), 2,2'-bipyridyl (35.1 mg, 0.225 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (28 μL, 0.15 mmol) were used according to the typical procedure C and methyl 4-(1-methoxy-3-oxopropyl)benzoate (**9i**: 92.5 mg, 0.15 mmol) was obtained in quantitative yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Yellow solid; M.p. 51–56 °C; IR (ATR) cm^{-1}: 2925, 2850, 2731, 1719, 1161, 1578, 1436, 1414, 1348, 1278, 1177, 1103; ^1H NMR (500 MHz, $CDCl_3$): δ 9.79 (s, 1H), 8.05 (d, 2H, *J* = 8.3 Hz), 7.41 (d, 2H, *J* = 8.3 Hz), 4.76 (dd, 1H, *J* = 9.0, 4.3 Hz), 3.92 (s, 3H), 3.25 (s, 3H), 2.94—2.88 (m, 1H), 2.66—2.62 (m, 1H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 200.0, 166.8, 145.7, 130.2, 130, 126.5, 78.2, 57.1, 52.2, 51.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{14}O_4Na$ 245.0784; Found 245.0792.

3-(4-Chlorophenyl)-3-methoxypropanal (9j) in Table 6, entry 12.

1-(Dimethoxymethyl)-4-methoxybenzene (**6j**: 28.0 mg, 0.15 mmol), 2,2'-bipyridyl (35.1 mg, 0.225 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (28 μL, 0.15 mmol) were used according to the typical procedure C and 3-(4-Chlorophenyl)-3-methoxypropanal (**9j**: 25.2 mg, 0.14 mmol) was obtained in 90% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 7/1). Colorless oil; IR (ATR) cm^{-1}: 2828, 2253, 1724, 1491, 1408, 1091, 1015; ^1H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.0, 1.8 Hz), 7.35 (d, 2H, *J* = 8.8 Hz), 7.27 (d, 2H, *J* = 8.8 Hz), 4.68 (dd, 1H, *J* = 8.8, 4.5 Hz), 3.22 (s, 3H), 2.89 (ddd, 1H, *J* = 16.5, 8.8, 2.0 Hz), 2.62 (ddd, 1H, *J* = 16.5, 4.5, 1.8 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 200.1, 139.0, 133.9, 128.9, 127.9, 77.9, 56.8, 51.5; ESI-HRMS m/z: 221.0322 ($[M+Na]^+$); Calcd for $C_{10}H_{11}O_2ClNa$: 221.0340.

3-(4-Bromophenyl)-3-methoxypropanal (9k) in Table 6, entry 13.

1-(Dimethoxymethyl)-4-methoxybenzene (**6k**: 34.7 mg, 0.15 mmol), 2,2'-bipyridyl (70.3 mg, 0.45 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (54 μL, 0.30 mmol) were used according to the typical procedure C and 3-(4-Bromophenyl)-3-methoxypropanal (**9k**: 32.1 mg, 0.14 mmol) was obtained in 88% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 7/1). Colorless solid; M.p. 145—149; IR (ATR) cm^{-1}: 2988, 2932, 2896, 2824, 2725, 1724, 1591, 1486, 1404, 1344, 1297, 1228, 1180, 1102, 1071, 1010; ^1H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.0, 1.8 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 7.21 (d, 2H, *J* = 8.5 Hz), 4.66 (dd, 1H, *J* = 9.0 Hz, 4.0 Hz), 3.22 (s, 3H), 2.89 (ddd, 1H, *J* = 16.5, 9.0, 2.0 Hz), 2.62 (ddd, 1H, *J* = 16.5, 4.0, 1.8 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 200.0, 139.5, 131.9, 128.2, 122.0, 77.9, 56.8, 51.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{11}O_2BrNa$ 264.9835; Found 264.9858.

3-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-methoxypropanal (9l) in Table 6, entry 14.

1-(Dimethoxymethyl)-4-methoxybenzene (**6l**: 42.4 mg, 0.15 mmol), 2,2'-bipyridyl (35.1 mg, 0.225 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (28 μL, 0.15 mmol) were used according to the typical procedure C and 3-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-methoxypropanal (**9l**: 36.9 mg, 0.13 mmol) was obtained in 84% yield after 6 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Yellow oil; IR (ATR) cm^{-1}: 2930, 2858, 1725, 1607, 1509, 1471, 1391, 1362, 1255, 1168, 1100, 1071, 1010; ^1H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.5, 2.0 Hz), 7.18 (d, 2H, *J* = 9.0 Hz), 6.83 (d, 2H, *J* = 9.0 Hz), 4.62 (dd, 1H, *J* = 8.5, 4.5 Hz), 3.20 (s, 3H), 2.89 (ddd, 1H, *J* = 16.5, 8.5, 2.5 Hz), 2.62 (ddd, 1H, *J* = 16.5, 4.5, 2.0 Hz), 0.98 (s, 9H), 0.20 (s, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 200.9, 132.8, 127.7, 120.2, 99.9, 78.2, 56.4, 51.6, 25.6, 18.2, -4.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{26}O_3SiNa$ 317.1543; Found 317.1551.

3-Methoxy-3-(2-methoxyphenyl)propanal (9m) in Table 6, entry 15.

1-(Dimethoxymethyl)-2-methoxybenzene (**6m**: 27.3 mg, 0.15 mmol), 2,2'-bipyridyl (35.1 mg, 0.225 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (28 μL, 0.15 mmol) were used according to the typical procedure C and 3-methoxy-3-(2-methoxyphenyl)propanal (**9m**: 32.0 mg, 0.15 mmol) was obtained in quantitative yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 7/1). Yellow oil; IR (ATR) cm^{-1}: 2936, 2827, 2725, 1722, 1601, 1589, 1489, 1462, 1438, 1398, 1355, 1283, 1238, 1181, 1161, 1100, 1066, 1048, 1026; ^1H NMR (500 MHz, $CDCl_3$): δ 9.81 (dd, 1H, *J* = 3.0, 2.0 Hz), 7.38 (dd, 1H, *J* = 7.5, 2.0 Hz), 7.30—7.26 (m, 1H), 7.01 (t, 1H, *J* = 7.5 Hz), 6.89 (d, 1H, *J* = 8.0 Hz), 5.12 (dd, 1H, *J* = 8.5, 4.0 Hz), 3.83 (s, 3H), 3.30 (s, 3H), 2.74 (ddd, 1H, *J* = 16.0, 8.5, 3.0 Hz), 2.68 (ddd, 1H, *J* = 16.0, 4.0, 2.0 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 201.5, 156.5, 128.7, 128.3, 126.3, 120.8, 110.3, 72.9, 57.1, 55.2, 50.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{14}O_3Na$ 217.0835; Found 217.0839.

3-Methoxy-3-(3-methoxyphenyl)propanal (9n) in Table 6, entry 16.

1-(Dimethoxymethyl)-4-methoxybenzene (**6n**: 27.3 mg, 0.15 mmol) , 2,2'-bipyridyl (70.3 mg, 0.45 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure C and 3-methoxy-3-(3-methoxyphenyl)propanal (**9n**: 29.7 mg, 0.15 mmol) was obtained in quantitative yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1). Colorless oil; IR (ATR) cm^{-1}: 2937, 2826, 2727, 1722, 1600, 1586, 1487, 1455, 1434, 1398, 1346, 1316, 1286, 1262, 1181, 1154, 1104, 1066, 1040; ^1H NMR (500 MHz, $CDCl_3$): δ 9.79 (dd, 1H, *J* = 2.5, 1.5 Hz), 7.29 (t, 1H, *J* = 8.5 Hz), 6.91—6.88 (m, 2H), 6.86—6.84 (m, 1H), 4.67 (dd, 1H, *J* = 9.0, 4.0 Hz), 3.82 (s, 3H), 3.25 (s, 3H), 2.89 (ddd, 1H, *J* = 16.0, 9.0, 2.5 Hz), 2.64 (ddd, 1H, *J* = 16.0, 4.0, 1.5 Hz); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$): δ 200.6, 160.0, 142.1, 129.8, 118.8, 113.5, 111.8, 78.5, 56.8, 55.2, 51.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{26}O_3SiNa$ 317.1543; Found 317.1551.

2-(Isochroman-1-yl)acetaldehyde (9o) in Table 6, entry 17.

1-Methoxyisochroman (**6o**: 24.6 mg, 0.15 mmol), 2,2'-bipyridyl (70.4 mg, 0.45 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (55 μL, 0.30 mmol) were used according to the typical procedure C and 2-(isochroman-1-yl)acetaldehyde (**9o**: 22.2 mg, 0.12 mmol) was obtained in 84% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 6/1). Colorless oil; IR (ATR) cm^{-1}: 2928, 2853, 1721, 1492, 1453, 1426, 1376, 1340, 1281, 1246, 1192, 1160, 1105, 1036; ^1H NMR (500 MHz, $CDCl_3$): δ 9.81 (dd, 1H, *J* = 2.9, 2.3 Hz), 7.22—7.18 (m, 2H), 7.16—7.13 (m, 1H), 7.05—7.02 (m, 1H), 5.30 (dd, 1H, *J* = 6.6, 5.2

Hz), 4.18—4.14 (m, 1H), 3.84—3.79 (m, 1H), 3.07—3.01 (m, 1H), 2.95—2.86 (m, 2H), 2.71 (dt, 1H, *J* = 16.6, 2.9 Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 201.4, 136.3, 133.9, 129.2, 126.8, 126.5, 124.4, 71.7, 63.8, 49.4, 28.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{12}O_2Na$ 199.0730; Found 199.0746.

3-Methoxydodecanal (9p) in Table 6, entry 18.

1-(Dimethoxymethyl)-4-methoxybenzene (**6p**: 30.3 mg, 0.15 mmol) , 2,2'-bipyridyl (70.3 mg, 0.45 mmol), trimethyl(vinyloxy)silane (44 μL, 0.30 mmol) and TMSOTf (54 μL, 0.30 mmol) were used according to the typical procedure C and 3-methoxydodecanal (**9p**: 17.2 mg, 0.08 mmol) was obtained in 53% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 7/1). Colorless oil; IR (ATR) cm^{-1}: 2991, 2926, 2855, 2724, 1725, 1614, 1587, 1514, 1495, 1463, 1380, 1302, 1248, 1197, 1163, 1100, 1036, 1019; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.81 (dd, 1H, *J* = 3.0, 2.0 Hz), 3.73—3.68 (m, 1H), 3.35 (s, 3H), 2.60 (ddd, 1H, *J* = 16.3, 7.5, 3.0 Hz), 2.52 (ddd, 1H, *J* = 16.3, 5.0, 2.0Hz), 1.61—1.59 (m, 1H), 1.52—1.47 (m, 1H), 1.35—1.23 (m, 14H), 0.88 (t, 3H, *J* = 7.0 Hz); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ 201.8, 76.3, 56.8, 48.0, 33.8, 31.9, 29.6, 29.5, 29.5, 29.3, 25.0, 22.7, 14.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{26}O_2Na$ 237.1825; Found 237.1823.

ASSOCIATED CONTENT

Supporting Information

Detailed optimizations and spectroscopic data of products are described.

ACKNOWLEDGMENTS

This study was partially supported by a Grant-in-Aid for JSPS Research Fellows from the Japan Society for the Promotion of Science (JSPS, Number: 17J08551 for T. K.) and Grant-in-Aid for Scientific Research (C) from the Japan Society for the Promotion of Science (JSPS: 16K08169 for Y. S.).

REFERENCES

(1) Cernak, T.; Dykstra, K. D.; Tyagarajan, S.; Vachal, P. and Krska, S. W.; The Medicinal Chemist's Toolbox for Late Stage Functionalization of Drug-Like Molecules, *Chem. Soc. Rev.* **2016**, *45*, 546–576.

(2) (a) Baran, P. S.; Maimone, T. J. and Richter, J. M.; Total Synthesis of Marine Natural Products without Using Protecting Groups, *Nature* **2007**, *446*, 404–408; (b) Shenvi, R. A.; O'Malley, D. P. and Baran, P. S.; Chemoselectivity: The Mother of Invention in Total Synthesis, *Acc. Chem. Res.*, **2009**, *42*, 530–541; (c) Yan, M.; Lo, J. C.; Edwards, J. T. and Baran, P. S.; Radicals: Reactive Intermediates with Translational Potential, *J. Am. Chem. Soc.*, **2016**, *138*, 12692–12714; (d) Wei, X.-F.; Shimizu, Y. and Kanai, M.; An Expeditious Synthesis of Sialic Acid Derivatives by Copper(I)-Catalyzed Stereodivergent Propargylation of Unprotected Aldoses, *ACS Cent. Sci.*, **2016**, *2*, 21–26.

(3) Kawajiri, T.; Ohta, R.; Fujioka, H.; Sajiki, H. and Sawama, Y.; Aromatic Aldehyde-Selective Aldol Addition with Aldehyde-Derived Silyl Enol Ethers, *Chem. Commun.*, **2018**, *54*, 374–377.

(4) Friedel, C.; and Crafts, J. M.; Organic Chemistry, *J. Chem. Soc.*, **1877**, *32*, 725–791.

(5) (a) Olah, G. A.; *Friedel-Crafts Chemistry*, Wiley, New York, **1973**; (b) Bandini, M.; Melloni, A. and Ronchi, A. U.; New Catalytic Approaches in the Stereoselective Friedel-Crafts Alkylation Reaction, *Angew. Chem. Int. Ed.*, **2004**, *43*, 550–556; (c) Rueping, M. and Nachtsheim, B. J.; A Review of New Developments in the Friedel-Crafts Alkylation – From Green Chemistry to Asymmetric Catalysis, *Beilstein J. Org. Chem.*, **2010**, *6*, 6–29; (d) Sunke, R.; Nallapati, S. B.; Kumar, J. S.; Kumar, K. S. and Pal, M.; Use of $AlCl_3$ in Friedel-Crafts Arylation Type Reactions and Beyond: An Overview on the Development of Unique Methodologies Leading to *N*-Heteroarenes, *Org. Biomol. Chem.*, **2017**, *15*, 4042–4057.

(6) (a) Thirupathi, P. and Kim, S. S.; Friedel-Crafts Arylation Reactions of *N*-Sulfonyl Aldimines or Sulfonamidesulfones with Electron-Rich Arenes Catalyzed by $FeCl_3 \cdot 6H_2O$: Synthesis of Triarylmethanes and Bis-heteroarylarylmethanes, *J. Org. Chem.*, **2010**, *75*, 5240–5249; (b) Kaya, U.; Chauhan, P.; Mahajan, S.; Deckers, K.; Valkonen, A.; Rissanen, K. and Enders, D.; Squaramide-Catalyzed Asymmetric aza–Friedel–Crafts/*N*,*O*-Acetalization Domino Reactions between 2-Naphthols and Pyrazolinone Ketimines, *Angew. Chem. Int. Ed.*, **2017**, *56*, 15358–15362.

(7) Gomes, R. F. A.; Coelho, J. A. S.; Frade, R. F. M.; Trindade, A. F. and Afonso, C. A. M.; Synthesis of Symmetric Bis(*N*-alkylaniline)triarylmethanes via Friedel-Crafts-Catalyzed Reaction between Secondary Anilines and Aldehydes, *J. Org. Chem.*, **2015**, *80*, 10404–10411.

(8) Harikrishnan, A.; Selvakumar, J.; Gnanamani, E.; Bhattacharya, S. and Ramanathan, R.; Friedel-Crafts Hydroxyalkylation through Activation of a Carbonyl Group Using $AlBr_3$: An Easy Access to Pyridyl Aryl/Heteroaryl Carbinols, *New J. Chem.*, **2013**, *37*, 563–567.

(9) Wuts, P. G. M. in *Greene's Protective Groups in Organic Synthesis*, *5th ed.*, Wiley, Hoboken, NJ, **2014**.

(10) (a) Sawama, Y.; Nagata, S.; Yabe, Y.; Morita, K.; Monguchi, Y. and Sajiki, H.; Iron-Catalyzed Chemoselective Azidation of Benzylic Silyl Ethers, *Chem. Eur. J.*, **2012**, *18*, 16608–16611; (b) Sawama, Y.; Shishido, Y.; Yanase, T.; Kawamoto, K.; Goto, R.; Monguchi, Y. and Sajiki, H.; Efficient Generation of *ortho*-Naphthoquinone Methides from 1,4-Epoxy-1,4-dihydronaphthalenes and Their Annulation with Allyl Silanes, *Angew. Chem. Int. Ed.*, **2013**, *52*, 1515–1519; (c) Sawama, Y.; Shishido, Y.; Kawajiri, T.; Goto, R.; Monguchi, Y. and Sajiki, H.; Iron-Catalyzed Friedel-Crafts Benzylation with Benzyl TMS Ethers at Room Temperature, *Chem. Eur. J.*, **2014**, *20*, 510–516; (d) Sawama, Y.; Goto, R.; Nagata, S.; Shishido, Y.; Monguchi, Y. and Sajiki, H.; Chemoselective and Direct Functionalization of Methyl Benzyl Ethers and Unsymmetrical Dibenzyl Ethers Using Iron Trichloride, *Chem. Eur. J.*, **2014**, *20*, 2631–2636; (e) Sawama, Y.; Asai, S.; Kawajiri, T.; Monguchi, Y. and Sajiki, H.; Biaryl Synthesis by Ring-Opening Friedel-Crafts Arylation of 1,4-Epoxy-1,4-dihydronaphthalenes Catalyzed by Iron Trichloride, *Chem. Eur. J.*, **2015**, *21*, 2222–2229; (f) Sawama, Y.; Kawajiri, T.; Asai, S.; Yasukawa, N.; Shishido, Y.; Monguchi, Y. and Sajiki, H.; Biarylmethane and Fused Heterocyclic Arene Synthesis via in Situ Generated *o*- and/or *p*-Naphthoquinone Methides, *J. Org. Chem.*, **2015**, *80*, 5556–5565; (g) Sawama, Y. in *New Horizons of Process Chemistry -Scalable Reactions and Technologies-*, (Eds.; Tomioka, K.; Shioiri, T. and Sajiki, H.), Springer Nature, **2017**, 51–63.

(11) (a) Mondal, S. and Panda, G.; Synthetic Methodologies of Achiral Diarylmethanols, Diaryl and Triarylmethanes (TRAMs) and Medicinal Properties of Diaryl and Triarylmethanes – An Overview, *RSC. Adv.*, **2014**, *4*, 28317–28358; (b) Nambo, M.; Ariki, Z. T.; Gonzalez, D. C.-; Beattie, D. D. and Crudden, C. M.; Arylative Desulfonation of Diarylmethyl Phenyl Sulfone with Arenes Catalyzed by Scandium Triflate, *Org. Lett.*, **2016**, *18*, 2339–2342; (c) Ruengsangtongkul, S.; Taprasert, P.; Siriona, U. and Jaratjaroonphong, J.; Facile Synthesis of Nonsymmetrical Heteroaryl-Substituted Triarylmethanes via The $FeCl_3 \cdot 6H_2O$-Catalyzed Two-Step Friedel-Crafts-Type Reaction, *Org. Biomol. Chem.*, **2016**, *14*, 8493–8502.

(12) (a) Zerth, H. M.; Laonard, N. M. and Mohan, R. S.; Synthesis of Homoallyl Ethers via Allylation of Acetals in Ionic Liquids Catalyzed by Trimethylsilyl Trifluoromethanesulfonate, *Org. Lett.*, **2003**, *5*, 55–57; (b) Yasukawa, N.; Asai, S.; Kato, M.; Monguchi, Y.; Sajiki, H. and Sawama, Y.; Palladium on Carbon-Catalyzed Chemoselective Oxygen Oxidation of Aromatic Acetals, *Org. Lett.*, **2016**, *18*, 5604–5607; (c) Yasukawa, N.; Kanie, T.; Kuwata, M.; Monguchi, Y.; Sajiki, H. and Sawama, Y.; Palladium on Carbon-Catalyzed Benzylic Methoxylation for Synthesis of Mixed Acetals and Orthoesters, *Chem. Eur. J.*, **2017**, *18*, 5604–5607.

(13) (a) Fujioka, H.; Sawama, Y.; Murata, N.; Okitsu, T.; Kubo, O.; Matsuda, S. and Kita, Y.; Unexpected Highly Chemoselective Deprotection of the Acetals from Aldehydes and Not Ketones: TESOTf-2,6-Lutidine Combination, *J. Am. Chem. Soc.*, **2004**, *126*, 11800–11801; (b) Fujioka, H.; Okitsu, T.; Sawama, Y.; Murata, N.; Li, R. and Kita, Y.; Reaction of the Acetals with TESOTf-Base Combination; Speculation of the Intermediates and Efficient Mixed Acetal Formation, *J. Am. Chem. Soc.*, **2006**, *128*, 5930–5938; (c) Fujioka, H.; Okitsu, T.; Ohnaka, T.; Li, R.; Kubo, O.; Okamoto, K. Sawama, Y. and Kita, Y.; Organic Chemistry Using Weakly Electrophilic Salts: Efficient Formation of *O*,*O*-Mixed, *O*,*S*- and *N*,*O*-Acetals, *J. Org. Chem.*, **2007**, *72*, 7898–7902; (d) Fujioka, H.; Okitsu, T.; Ohnaka, T.; Sawama, Y.; Kubo, O.; Okamoto, K. and Kita, Y.; Reaction of Tetrahydropyranyl Ethers with Triethylsilyl Trifluoromethanesulfonate-2,4,6-Collidine Combination: Speculation on the Intermediate,

Efficient Deprotection, and Application to Efficient Ring-Closing Metathesis as a Tether, *Adv*. *Synth*. *Catal*., **2007**, *349*, 636-646; (e) Fujioka, H.; Kubo, O.; Senami, K.; Okamoto, K.; Okitsu, T. and Kita, Y.; Organic Chemistry Using Weakly Electrophilic Salts: The Reaction with Nitrogen Nucleophiles, *Heterocycles* **2009**, *79*, 1113-1120; (f) Fujioka, H.; Yahata, K.; Hamada, T.; Kubo, O.; Okitsu, T.; Sawama, Y.; Ohnaka, T.; Maegawa, T. and Kita, Y.; Reaction of Acetals with Various Carbon Nucleophiles under Non-Acidic Conditions: C-C Bond Formation via a Pyridinium-Type Salt, *Chem*. *Asian J*., **2012**, *7*, 367–373.

(14) (a) Keilitz, J.; Newman, S. G. and Lautens, M.; Enantioselective Rh-Catalyzed Domino Transformations of Alkynylcyclohexadienones with Organoboron Reagents, *Org*. *Lett*., **2013**, *15*, 1148; (b) Wang, G.–Z.; Li, X.–L.; Dai, J.–J. and Xu, H.–J.; AIBN-Catalyzed Oxidative Cleavage of *gem*-Disubstituted Alkenes with O_2 as an Oxidant, *J*. *Org*. *Chem*. **2014**, *79*, 7220; (c) Nepomnyashchii, A. B.; Pistner, A. J.; Bard, A. J. and Rosenthal, J.; Synthesis, Photophysics, Electrochemistry and Electrogenerated Chemiluminescence of PEG-Modified BODIPY Dyes in Organic and Aqueous Solutions, *J*. *Phys*. *Chem*. *C*, **2013**, *117*, 5599; (d) Battistuzzi, G.; Cacchi, S. and Fabrizi, G.; An Efficient Palladium-Catalyzed Synthesis of Cinnamaldehydes from Acrolein Diethyl Acetal and Aryl Iodides and Bromides, *Org*. *Let*., **2003**, *5*, 777; (e) Mori, A.; Miyakawa, Y.; Ohashi, E.; Haga, T.; Maegawa, T. and Sajiki, H.; Pd/C-Catalyzed Chemoselective Hydrogenation in the Presence of Diphenylsulfide, *Org*. *Lett*., **2006**, *8*, 3279; (f) Chen, M.; Wang, J.; Chai, Z.; You, C. and Lei. A.; C-X (X=Br, I) Bond-Tolerant Aerobic Oxidative Cross-Coupling: A Strategy to Selectively Construct *β*-Aryl Ketones and Aldehydes, *Adv*. *Synth*. *Catal*. **2012**, *354*, 341; (g) Monguchi, Y.; Fujita, Y.; Endo, K.; Takao, S.; Yoshimura, M.; Takagi, Y.; Maegawa, T. and Sajiki, H.; A highly Active Heterogeneous Palladium Catalyst Supported on a Synthetic Adsorbent, *Chem*. *Eur*. *J*. **2009**, *15*, 834; (h) Edwards, G. A.; Trafford, M. A.; Hamilton, A. E.; Buxton, A. M.; Bardeaux, M. C. and Chalker, J. M.; Melamine and Melamine-Formaldehyde Polymers as Ligands for Palladium and Application to Suzuki-Miyaura Cross-Coupling Reactions in Sustainable Solvents, *J*. *Org*. *Chem*. **2014**, *79*, 2094; (i) Chatterjee, S. and

Ramakrishnan, S.; A Novel Photodegradable Hyperbranched Polymeric Photoresist, *Chem. Commun*., **2013**, *49*, 11041.

(15) (a) R.; Haque, S. J. and Patel, B. K.; Tetrabutylammonium Tribromide (TBATB) as an Efficient Generator of HBr for an Efficient Chemoselective Reagent for Acetalization of Carbonyl Compounds Gopinath, *J. Org. Chem*., **2002**, *67*, 5842; (b) Yi, H.; Niu, L.; Wang, S.; Liu, T.; Singh, A. K. and Lei, A.; Visible-Light-Induced Acetalization of Aldehydes with Alcohols, *Org. Lett*., **2017**, *19*, 122; (c) Mahon, C. S.; Fascione, M. A.; Sakonsinsiri, C.; McAllister, T. E.; Turnbull, W. B. and Fulton, D. A.; Templating Carbohydrate-Functionalised Polymer-Scaffolded Dynamic Combinatorial Libraries with Lectins, *Org. Biomol. Chem*., **2015**, *13*, 2756; (d) Shimada, K.; Kaburagi, Y. and Fukuyama, T.; Total Synthesis of Leustroducsin B, *J. Am. Chem. Soc*., **2003**, *125*, 4048; (e) Tsukada, H.; Mukaeda, Y. and Hosokawa, S.; *syn*-Selective Kobayashi Aldol Reaction Using Acetals, *Org. Lett*., **2013**, *15*, 678; (f) Qin, L.; Wang, P.; Zhang, Y.; Ren, Z.; Zhang, X. and Da, C.–S.; Direct Asymmetric Friedel-Crafts Reaction of Naphthols with Acetals Catalyzed by Chiral Brønsted Acids, *Synlett*, **2016**, *27*, 571; (g) Maity, P.; Srinivas, H. D. and Watson, M. P.; Copper-Catalyzed Enantioselective Additions to Oxocarbenium Ions: Alkynylation of Isochroman Acetals, *J. Am. Chem. Soc*., **2011**, *133*, 17142.

(16) (a) Jung, M. E. and Blum, R. B.; Generation of the Enolate of Acetaldehyde from Non-Carbonyl Substances and its C-Alkylation, *O*-Acylation and *O*-Silylation, *Tetrahedron Lett*., **1977**, *43*, 3791; (b) Nguyen, T. Q.; Chai, W.; Gu, J.; Cook, K.; Kim, E.; Goets, S.; Farni, Z.; Chepuru, M.; Cox, M.; Nguyen, P.; Raja, H.; Magistrado, P.; Michael, F.; Oelschlaeger, P. and Buynak, J. D.; Triethysilyl Enol Ethers in the Synthesis of Carbapenem Precursors, *Tetrahedron Lett*., **2015**, *56*, 3385;

(17) Roda, G.; Riva, S. and Danieli, B.; Almond Oxynitrilase-Catalyzed Transformation of Aldehydes is Strongly Influenced by Naphthyl and Alkoxy Substituents, *Tetrahedron Asymmetry*, **1999**, *10*, 3939.