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The reaction of acetal-type protective groups in combination with TMSOTf and 2,2′-bipyridyl; mild and chemoselective deprotection and direct conversion to other protective groups

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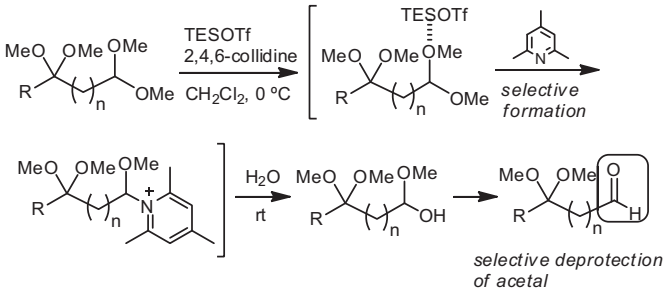
ABSTRACT

A mild and chemoselective deprotection method of various acetal-type protective groups, such as MOM, MEM, BOM, and SEM ethers, has been developed. The combination of TMSOTf and 2,2′-bipyridyl was very effective for the deprotection, and the reaction proceeded via the formation of pyridinium intermediates, which were hydrolyzed to the corresponding alcohols in good to high yields. The features of this method are mild (almost neutral) reaction conditions and the tolerability of acid-sensitive functional groups. This method is also applicable for the direct conversion of MOM ether to BOM or SEM ether using the appropriate alcohols instead of H_2O.

1. Introduction

The protection of functional groups is fundamental in organic syntheses, especially when constructing complex molecules. A number of protective groups have been developed to date since appropriate choice of them is the key for the success of total synthesis. Deprotection is also important and must be conducted under mild reaction conditions in order to avoid any side reactions with sensitive functional groups as well as racemization or epimerization of stereo center because the protective groups are often cleaved at late stage in the synthesis.[1] Many protective groups for the hydroxy group have been developed,[2] and the acetal-type protective groups are one of the most popular groups and recognized as very useful. Acetal is known to be stable not only under strongly basic to neutral conditions but also to the strong nucleophiles including organometallic and hydride reducing reagents. Various acetal-type protective groups, such as the methoxymethyl (MOM), tetrahydropyranyl (THP), and methoxyethoxymethyl (MEM) ethers, are widely used in organic syntheses. In addition, these groups can be used as directing groups by their chelating ability. The deprotection of these acetal-type protective groups is generally performed under mildly acidic conditions. However, rather strongly acidic conditions are sometimes required to cleave them depending on the substrates and undesirable side reactions of other functional groups occur due to the acidity of the reagents. Therefore, a milder deprotection method is necessary and has been desired.

We have recently developed a novel chemoselective deprotection of dimethylacetals using triethylsilyl triflate (TESOTf)/2,4,6-collidine that allows the ketals to remain intact (Scheme 1).[3] The reaction conditions are mild and the reaction proceeded via the selective formation of the collidinium intermediates, which are susceptible to hydrolysis to give the hemiacetal. The chemoselectivity toward the acetals arises from the selective coordination of TESOTf to the less hindered acetal oxygen. Many acid-labile functional groups, such as trityl ether and TBS ether are tolerable in this reaction.



Scheme 1. Chemoselective deprotection of acetal in the presence of a ketal.

As an extension of this method, we developed the mild deprotection of THP ethers in combination with TESOTf/2,4,6-collidine[4]

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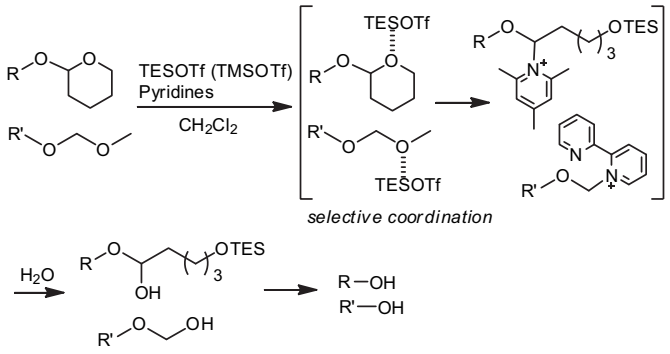
as well as the MOM ethers in combination with TMSOTf (or TESOTf)/2,2′-bipyridyl.[5] In these reactions, we rationalized that the silyl triflate also selectively coordinated to the less hindered oxygen to form the pyridinium salt by attack of the pyridine derivative. Sequential hydrolysis led to the deprotected alcohol via the hemiacetal (Scheme 2).



Scheme 2. Mild deprotection of the THP and MOM ethers.

We were next interested in the deprotection of other acetal-type protective groups, i.e., MEM, benzyloxymethyl (BOM) and trimethylsilylethoxymethyl (SEM) ethers, which have more bulky substituents than the THP and MOM ethers.

In this paper, we report the mild and efficient deprotection of acetal-type protective groups, such as the MEM, BOM and SEM ethers including the MOM ether, and the investigation of the reaction mechanism in detail. Further application to the direct conversion of MOM ethers to other protective groups is also described.

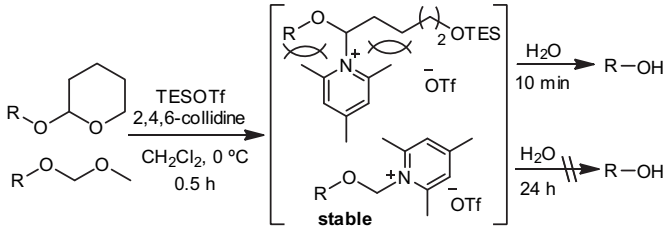
2. Results and discussion

2.1. Deprotection of MOM ethers

The deprotection of the MOM ether is usually performed under acidic conditions using protic acids,[6] Lewis acids,[7] Lewis acid-thiol,[8] boron halides,[9] and other reagents[10] in protic or aprotic media. However, some methods cause undesirable side reactions of other functional groups due to the acidity of the reagents. Therefore, a few methods for the deprotection of the MOM ether with acid-labile functional groups have been reported,[11] but they require a high reaction temperature or limit the generality of the substrates.

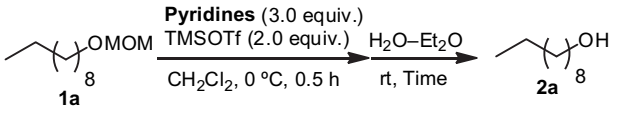
We first attempted our deprotection method of the THP ether (TESOTf and 2,4,6-collidine) to the deprotection of the MOM ether, but only the stable collidinium salt was obtained even after a 24 h-treatment with H_2O (Scheme 3).

These results are attributed to the steric hindrance around the acetal carbons. The structures of the pyridines may play an important role in the formation of the pyridinium salt intermediates and hydrolysis. We then investigated the effect of the pyridines using *n*-decylmethoxymethyl ether (**1a**) with TMSOTf (Table 1).[12] The reaction of 2,6-lutidine and **1a** followed by H_2O treatment gave a trace amount of the deprotected alcohol (**2a**) and the corresponding lutidinium salt as the major product (entry 2). The more bulky 2,6-di-*tert*-butylpyridine and 2,6-dichloropyridine afforded a trace amount of **2a**, while the starting material **1a** and byproduct[13] were mainly obtained (entries 3 and 4). The deprotection effectively proceeded to give the corresponding alcohol (**2a**) in 77% yield when 2-chloropyridine was used (entry 5). Surprisingly, the results of the deprotection with the similar 2-substituted pyridine, 2-phenylpyridine, and 2,2′-bipyridyl, were quite different. The reaction with 2,2′-bipyridyl was completed within 6 h and **2a** was obtained in 85%, but 2-phenylpyridine gave **2a** in 75% yield even after 72 h (entries 6 and 7). 4,4-Bipyridyl formed the corresponding pyridinium salt at rt but successive hydrolysis did not occurred (entry 8).



Scheme 3. The reaction of the THP and MOM ethers with TESOTf and 2,4,6-collidine.

Table 1
Effect of pyridines[a]



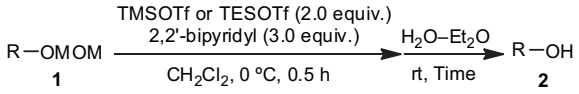
Entry	Pyridines	Time [h]	Yield [%]
1	2,4,6-Collidine	24	Trace[b]
2	2,6-Lutidine	24	Trace[b]
3	2,6-Di-*tert*-butylpyridine	24	Trace[b]
4	2,6-Dichloropyridine	24	3
5	2-Chloropyridine	24	77
6	2-Phenylpyridine	72	75
7	2,2′-Bipyridyl	6	83
8	4,4′-Bipyridyl	24	Trace[b,c]

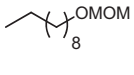
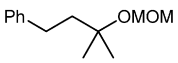
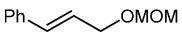
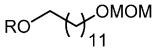
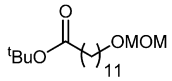
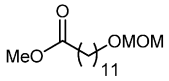
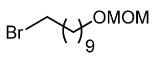
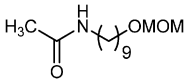
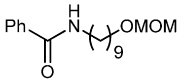
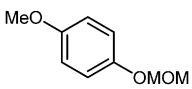
[a] Reaction conditions: **1a** (1.0 equiv), TMSOTf (2.0 equiv) and the pyridine (3.0 equiv) in CH_2Cl_2 (0.2 M) were stirred at 0 °C for 0.5 h, then H_2O and Et_2O were added and stirred at rt.
[b] Formation of the pyridinium salt was detected by TLC analysis.
[c] Pyridinium salt was formed at rt for 1 h.

We employed the combination of TMSOTf (or TESOTf) and 2,2′-bipyridyl as the optimized conditions and next examined the deprotection of diverse MOM ethers (Table 2).

MOM-protected aliphatic primary, secondary, and tertiary alcohols were easily deprotected under the stated conditions and the corresponding alcohols were obtained in high yields (Table 2, entries 1–6). The use of both TMSOTf and TESOTf gave almost similar results in these cases. However, in the case of the MOM ether of the allyl alcohol **1d**, TMSOTf was more effective (entries 7 and 8). Other hydroxy protecting groups, such as the acetyl, benzoyl, and benzyl groups, were tolerated under the stated conditions (entries 9–14). It is noteworthy that the selective deprotection of the MOM ether could be achieved in the presence of acid-sensitive TBS ether, trityl ether and *tert*-butyl ester (entries 15–19), while the reaction of the MOM ether containing a *tert*-butyl ester resulted in a slight decrease of the yield (74%).[14] These results indicated that the reaction conditions are nearly neutral. Some conventional deprotection methods under acidic conditions are known to cause undesirable side reactions with acid-sensitive functionalities due to their acidity.[7c,d,15] The presence of a methyl ester, halogen, and amide did not affect the reaction although the additional TMSOTf and 2,2′-bipyridyl were necessary in the case of the amide (entries 20–23). The aromatic MOM ether, interestingly, is less reactive under the stated conditions (entries 24 and 25) and no pyridinium intermediate was formed at all for the combination of TESOTf and

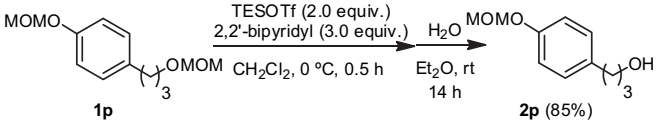
Table 2
Deprotection of the MOM ether by TMSOTf (TESOTf)/2,2′-bipyridyl[a]



Entry	Substrate	Silyl triflate	Time [h]	Yield [%]
1	 (**1a**)	TMSOTf	6	85 (**2a**)
2		TESOTf	6	90 (**2a**)
3	 (**1b**)	TMSOTf	2	91 (**2b**)
4		TESOTf	2	81 (**2b**)
5	 (**1c**)	TMSOTf	1	99 (**2c**)
6		TESOTf	2	92 (**2c**)
7	 (**1d**)	TMSOTf	10	81 (**2d**)
8		TESOTf	7	55 (**2d**)
9		TMSOTf	5	89 (**2e**)
10	(R = Ac) (**1e**)	TESOTf	5	91 (**2e**)
11	(R=Bz) (**1f**)	TMSOTf	5	93 (**2f**)
12		TESOTf	5	86 (**2f**)
13	(R=Bn) (**1g**)	TMSOTf	5	86 (**2g**)
14		TESOTf	5	87 (**2g**)
15	(R=TBS) (**1h**)	TMSOTf	5	88 (**2h**)
16		TESOTf	4	91 (**2h**)
17	(R=Tr) (**1i**)	TMSOTf	4	92 (**2i**)
18[b]		TESOTf	2.5	82 (**2i**)
19	 (**1j**)	TMSOTf	8	74 (**2j**)
20	 (**1k**)	TMSOTf	7	96 (**2k**)
21	 (**1l**)	TMSOTf	7	88 (**2l**)
22[c]	 (**1m**)	TMSOTf	9	86 (**2m**)
23[c]	 (**1n**)	TMSOTf	6	94 (**2n**)
24	 (**1o**)	TMSOTf	24	19 (**2o**)
25		TESOTf	24	n.r.[d]

[a] Reaction conditions: **1** (1.0 equiv), TMSOTf (2.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) were stirred at 0 °C for 0.5 h, then H_2O and Et_2O were added and stirred at rt.
[b] The reaction was conducted in CH_2Cl_2 (0.5 M).
[c] TMSOTf (4.0 equiv) and 6.0 equiv of 2,2′-bipyridyl were used.
[d] No pyridinium salt was formed.

2,2′-bipyridyl (entry 25). Conventional methods could simultaneously cleave both the aliphatic and phenolic MOM ethers,[7c,d,10d,e] and also the preferential cleavage of the phenolic MOM ether to that of the aliphatic one was reported in some methods.[10c,d] Our results then led us to examine the opposite chemoselective deprotection between the aliphatic and aromatic MOM ethers. As a result, the aliphatic MOM ether was preferentially cleaved in the presence of the aromatic one to give the mono-MOM protected alcohol (**2p**) in high yield (Scheme 4).

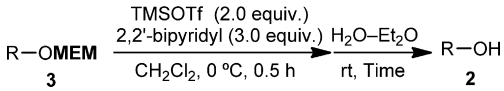


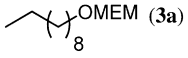
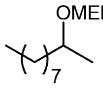
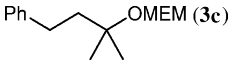
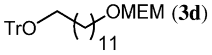
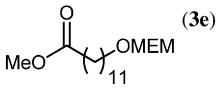
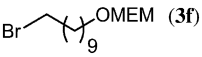
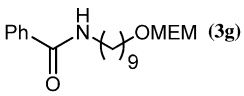
Scheme 4. Selective deprotection of the aliphatic MOM ether in the presence of the phenolic MOM ether.

2.2. Deprotection of MEM ethers

To expand the utility of our method, we investigated the deprotection of various acetal-type protective groups. The MEM group, a similar protective group to MOM, is also widely utilized and its deprotection is usually conducted under acidic conditions.[6d,9b,c,10b,16] We next applied our method to the deprotection of the MEM ethers (Table 3). The reaction proceeded without any reaction time increase to give the corresponding alcohols in high yields. Other functional groups, such as the trityl ether, ester, halogen, and amide, are tolerable under the stated conditions without any loss of the functional group (entries 4–7).

Table 3
The deprotection of the MEM ether by TMSOTf/2,2′-bipyridyl[a]



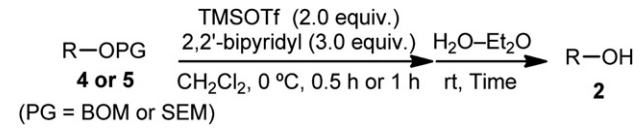
Entry	Substrate	Time [h]	Yield [%]
1	 (**3a**)	6	90 (**2a**)
2	 (**3b**)	3	88 (**2b**)
3	 (**3c**)	1	91 (**2c**)
4	 (**3d**)	5	87 (**2i**)
5	 (**3e**)	6	92 (**2k**)
6	 (**3f**)	5	95 (**2l**)
7[b]	 (**3g**)	6	96 (**2n**)

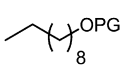
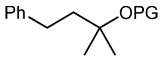
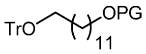
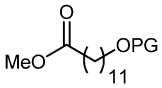
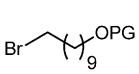
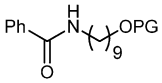
[a] Reaction conditions: **3** (1.0 equiv), TMSOTf (2.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) were stirred at 0 °C for 0.5 h, then H_2O and Et_2O were added and stirred at rt.
[b] TMSOTf (4.0 equiv) and 6.0 equiv of 2,2′-bipyridyl were used.

2.3. Deprotection of BOM and SEM ethers

For further application to other acetal-type protective groups, we chose the BOM and SEM ethers. Various deprotection methods for the BOM[17] and SEM[8b,17d,18] ethers have already been developed. The BOM ethers can be cleaved by reduction with a metal or hydrogenolysis[17a–i] as well as by protic or Lewis acids.[17j–p] The SEM ethers are also cleaved under acidic conditions,[8b,18a–j] and another effective method is exposure to fluoride species.[18k–t] Although these cleavage methods are well-established, some require rather harsh conditions. Therefore, it is worthwhile to develop another mild method for their deprotection. We were also interested in the deprotection of these ethers bearing bulky substituents because a Lewis acid coordinates to the less hindered acetal oxygen, which seems to be important in our method. We found that the TMSOTf and 2,2′-bipyridyl conditions were effective for the cleavage of the BOM and SEM ethers (Table 4). Both ethers could be removed within 6 h to afford the corresponding alcohols in good yields, while an additional 0.5 h stirring was necessary for the complete formation of the pyridinium salt in the case of the BOM ethers. Other functional groups including the acid-labile trityl group survived under these

Table 4
The deprotection of the BOM and SEM ethers by TMSOTf/2,2′-bipyridyl[a]



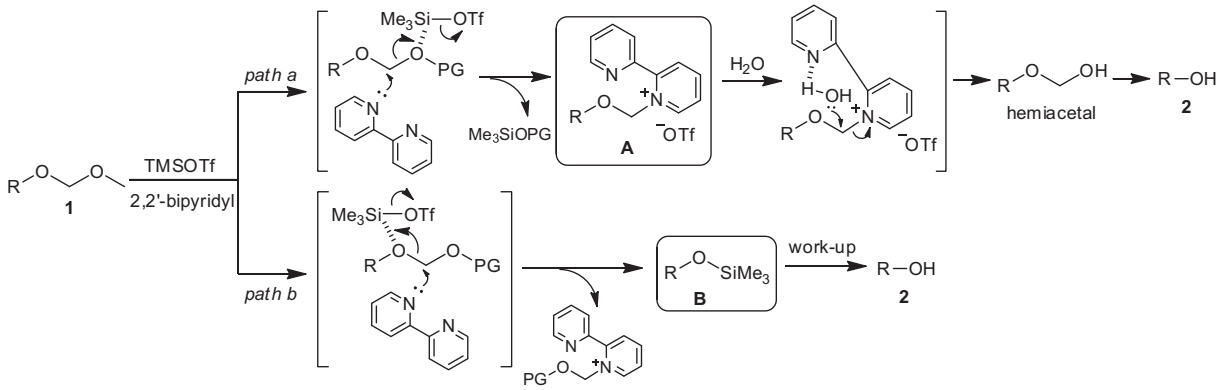
Entry	Substrate	Protecting group (PG)	Time [h]	Yield [%]
1		BOM (**4a**)	6	85 (**1a**)
2		SEM (**5a**)	4	92 (**1a**)
3		BOM (**4b**)	3	82 (**2b**)
4		SEM (**5b**)	2	84 (**2b**)
5		BOM (**4c**)	1	88 (**2c**)
6		SEM (**5c**)	1	87 (**2c**)
7		BOM (**4d**)	3	84 (**2i**)
8		SEM (**5d**)	3	89 (**2i**)
9		BOM (**4e**)	4	95 (**2k**)
10		SEM (**5e**)	3	95 (**2k**)
11		BOM (**4f**)	5	88 (**2l**)
12		SEM (**5f**)	4	92 (**2l**)
13[b]		BOM (**4g**)	5	90 (**2n**)
14[b]		SEM (**5g**)	4	90 (**2n**)

[a] Reaction conditions: **4** or **5** (1.0 equiv), TMSOTf (2.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) were stirred at 0 °C for 1 h (BOM ether **4**) or 0.5 h (SEM ether **5**), then H_2O and Et_2O were added and stirred at rt.
[b] TMSOTf (4.0 equiv) and 6.0 equiv of 2,2′-bipyridyl were used.

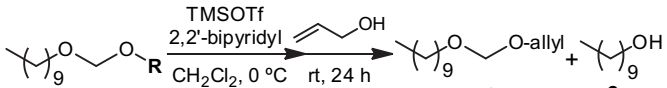
conditions (entries 7–14). This method will provide a new and complementary deprotection of these protective groups.

2.4. Presumable reaction mechanism of deprotection of various acetal-type protective groups

The presumable reaction mechanism is shown in Scheme 5. First, TMSOTf coordinated the less hindered acetal oxygen,[19] then 2,2′-bipyridyl attacked the activated acetal carbon affording the pyridinium intermediate. In the case of the BOM and SEM ethers, the coordination manner may be different since they have bulky substituents compared to the MOM and MEM ethers. Therefore, two reaction pathways (paths a and b) are possible for the reaction of TMSOTf and 2,2′-bipyridyl and different intermediates, **A** and **B**, could be generated. The reaction of **A** with H_2O would give the hemiacetal, which leads to the deprotected alcohol **2**. The TMS-protected alcohol **B** is also deprotected during the work-up giving **2** as a result. To reveal the major reaction pathway of each protective group, we carried out the substitution reaction of the pyridinium intermediates generated from the MOM, MEM, BOM, and SEM ethers with allyl alcohol as the nucleophile under TMSOTf and 2,2′-bipyridyl conditions (Scheme 6).[3b,4a,20] The coordination manner



Scheme 5. Presumed reaction mechanism for deprotection of acetal-type protective groups by TMSOTf and 2,2′-bipyridyl.



R = CH_3	(MOM)	76%	7%
$CH_3OCH_2CH_2$	(MEM)	78%	10%
Bn	(BOM)	72%	20%
$TMSCH_2CH_2$	(SEM)	40%	49%

Scheme 6. The substitution reaction of acetal-type ethers with allyl alcohol in combination with TMSOTf and 2,2′-bipyridyl.

could be estimated by comparison with the yields of the substituted product (allyloxymethyl ether) **6** and deprotected alcohol **2a** derived from TMS-protected alcohol during the reaction.

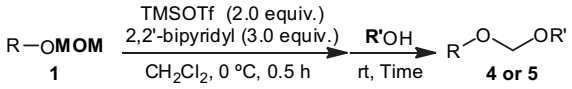
As expected, the reaction of the MOM and MEM ethers gave **6** as the main product and a small amount of the free alcohol **2a**.[21] A similar tendency was observed in the case of the BOM ether although the phenyl ring of the BOM ether seems to be more bulky than the other side substituent. The SEM ether afforded the comparable mixture of **6** and **2a** (4:4.9). Consequently, the deprotection proceeded in both pathways, but path a is the major one except for the SEM ether.

On the other hand, the bulkiness of the pyridine derivative plays a very important role in this reaction. The less bulky 2,6-lutidine and 2,4,6-collidine could form the pyridinium intermediates, but no hydrolysis occurred (Table 1, entries 1 and 2). The more bulky 2,6-di-*tert*-butylpyridine did not give the corresponding pyridinium intermediate at all and 2,6-dichloropyridine led to undesirable side reactions (Table 1, entries 3 and 4). The successful deprotection was achieved by using the 2-substituted pyridines (Table 1, entries 5–7). It is of interest that the substituents at the 2-position on pyridine ring significantly affected the reaction rate. The pyridinium intermediate was formed within 0.5 h in each case, but the hydrolysis is much different. 2,2′-Bipyridyl is the most effective for the hydrolysis affording **2** in 6 h, while 2-chloropyridine and 2-phenylpyridine yielded **2** in 24 h and 72 h, respectively. It should be noted that 2,2′-bipyridyl and 2-phenylpyridine showed very different reactivity regardless of their similar structure. We presumed that the hydrogen bond between H_2O and the nitrogen on the pyridine ring may help to bring the H_2O close to the acetal carbon and make the nucleophilic attack by H_2O easier, although the electronic effect could not be excluded.

2.5. Direct conversion of MOM ethers to BOM and SEM ethers

As a further extension of this method, we next examined the one-pot conversion of the MOM ether to other acetal-type protective groups by the nucleophilic substitution using the appropriate alcohol to the pyridinium salt. A direct conversion of one protective group to another one should be a convenient and useful method in syntheses. A few methods for the direct conversion of the acetal-type protective group were reported. Magnus and co-worker reported the direct conversion of the methylthiomethyl ether to cyanomethyl ether with ZnI_2 and TMSCN.[22a] Corey and co-workers also reported the conversion of the MEM ether to *i*-propylthioether with $(i\text{-PrS})_2BBr$ and to cyanomethyl ether with Et_2AlCN,[16d] respectively. The reaction of acetal-type protective groups including MOM and MEM ethers with Me_2BBr were reported by Guindon and co-workers[22b,c] and gave rise to the bromo methyl ethers as reactive intermediates. Successive treatment with alcohols, thiols, and cyanide to give the corresponding substituted ethers. However, some of these reactions must be conducted at −78 °C. In our case, the MOM ether was readily converted to the pyridinium salt at 0 °C and the substitution of the salt with the allyl alcohol gave the desired product in 76% yield within 24 h at rt (Scheme 6). We then performed the direct conversion of the MOM ether using the appropriate alcohols, such as benzyl alcohol and trimethylsilylethanol, to the BOM and SEM ethers in a one-pot procedure. The successful conversion was achieved using an excess amount of R′OH (5.0 equiv) instead of H_2O to give the BOM and SEM ethers in good yields (Table 5). No significant improvement in the yield and reaction time was observed by increasing R′OH (10 equiv) (entry 2). Another functional group within a molecule can be tolerated under these

Table 5
The direct conversion of the MOM ether into other acetal-type protective groups[a]



Entry	Substrate	R′	Product	Time [h]	Yield [%]
1	**1a**	Bn	**4a**	22	80
2[b]		Bn	**4a**	22	81
3		$TMS(CH_2)_2$	**5a**	5	80
4	**1b**	Bn	**4b**	6	76
5		$TMS(CH_2)_2$	**5b**	3	82
6	**1c**	Bn	**4c**	4	79
7		$TMS(CH_2)_2$	**5c**	1	77
8	**1i**	Bn	**4d**	20	73
9		$TMS(CH_2)_2$	**5d**	6	78
10	**1k**	Bn	**4e**	14	77
11		$TMS(CH_2)_2$	**5e**	6	84
12	**1l**	Bn	**4f**	24	86
13		$TMS(CH_2)_2$	**5f**	6	75
14[c]	**1n**	Bn	**4g**	13	82
15[c]		$TMS(CH_2)_2$	**5g**	7	84

[a] Reaction conditions: **1** (1.0 equiv), TMSOTf (2.0 equiv), 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C for 0.5 h, then R′OH (5.0 equiv) were added and stirred at rt.
[b] BnOH (10 equiv) was used.
[c] TMSOTf (4.0 equiv) and 6.0 equiv of 2,2′-bipyridyl were used.

conditions. A small amount of the MOM ether was regenerated during the reaction in each case, which resulted in a decreased yield since CH_3OH re-attacked the generated pyridinium salt.

3. Conclusion

We have developed a novel and efficient deprotection method of various acetal-type protective groups, such as the MOM, MEM, BOM, and SEM ethers. This method has wide applicability of the substrates having acid-sensitive groups, esters, halogens, and amides, which indicated that our conditions are very mild and almost neutral in contrast to the previous methods (strong acidic conditions).[6–10,16,17j–p,18a–j] The one-pot conversion to the BOM and SEM ethers from the MOM ethers is facile and efficient replacement of the protective group. We believe that the present method would be useful and enhance the utility of the MOM ethers in organic syntheses, and will also be employed as an alternative in synthetic strategies.

4. Experimental section

4.1. General

Melting point (mp) was measured by Büchi B-545. Infrared spectra (IR) were recorded by Shimadzu FTIR 8400 using a diffuse reflectance measurement of samples dispersed in KBr powder. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA 500, JNM-ECS 400, JNM-AL 300 JMN-EX 270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in parts per million (δ), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br s=broad singlet) and coupling constant (Hz). Mass spectra were obtained on a Shimadzu GC–MS-QP 5000 instrument with ionization voltages of 70 eV. Column chromatography and TLC were carried out on Merck Silica gel 60 (230–400 mesh), Kanto kagaku Silica gel 60 N (40–50 μm, spherical, neutral), and Merck silica gel F_{254} plates (0.25 mm), respectively. The commercially available reagents were used without further purification. Alcohols **2a**–**d**, **2l**, and **2o** are commercially available.

4.2. Preparation of MOM ethers 1

*4.2.1. Preparation of **1a**–**d**, **1k**, **1o**, and **1p**[10b].* A solution of an alcohol (1 equiv), MOMCl (1.5–1.8 equiv), ^{i}Pr$_2$NEt (3–3.6 equiv), and DMAP (0.1 equiv) in dry CH_2Cl_2 (0.2–0.5 M) was stirred at 0 °C to rt under N_2. After disappearance of the alcohol on TLC, the mixture was evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography to give a MOM/ether. **1a**,[10b] **1b**,[23] **1c**,[24] **1d**,[25] **1o**,[26] and **1p**[27] are known compounds.

*4.2.1.1. Compound **1k**.* According to the general procedure, treatment of methyl 1-hydroxydodecanoate **2k**[28] (1.51 g, 6.56 mmol) with MOMCl (0.99 mL, 13.1 mmol), ^{i}Pr$_2$NEt (3.3 mL, 19.7 mmol), and DMAP (80.6 mg, 0.66 mmol) gave **1k** (1.68 g, 93%). Eluent; *n*-hexane/AcOEt (15/1). Colorless oil; IR (KBr): 2929, 1730, 1217, 912, 770 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27–1.36 (m, 14H), 1.56–1.65 (m, 4H), 2.30 (t, *J*=7.5 Hz, 2H), 3.36 (s, 3H), 3.52 (t, *J*=7.0 Hz, 2H), 3.67 (s, 3H), 4.62 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.0, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 34.1, 51.4, 55.1, 67.9, 96.4, 174.3 ppm; HRMS (FAB): calcd for $C_{15}H_{31}O_4$ $[M+H]^+$ 275.2222, found 275.2204.

*4.2.2. Preparation of MOM ether **1e**–**i**.* MOM ethers **1e**–**i** were prepared from 12-methoxymethoxydodecanol.[29]

*4.2.2.1. Compound **1e**.* (R=Ac); a solution of 12-methoxymethoxydodecanol (309 mg, 1.25 mmol), Ac_2O (0.21 mL, 2.25 mmol), ^{i}Pr$_2$NEt (0.78 mL, 4.51 mmol), and DMAP (14.6 mg, 0.120 mmol) in dry CH_2Cl_2 (6.3 mL) was stirred at rt under N_2 for 1 h. The reaction mixture was evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography (*n*-hexane/AcOEt=12/1) to give **1e** (352 mg, 97%). Colorless oil, IR (KBr): 2926, 2855, 1742, 1468, 1238 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.27 (br s, 16H), 1.53–1.64 (m, 4H), 2.05 (s, 3H), 3.36 (s, 3H), 3.52 (t, *J*=6.5 Hz, 2H), 4.05 (t, *J*=6.8 Hz, 2H), 4.62 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7, 25.7, 26.0, 28.4, 29.0, 29.23, 29.28, 29.32, 29.34, 29.4, 29.5, 54.8, 64.3, 67.6, 96.1, 170.8 ppm; HRMS (FAB): calcd for $C_{16}H_{33}O_4$ $[M+H]^+$: 289.2379, found 289.2377.

*4.2.2.2. Compound **1f**.* (R=Bz); a solution of 12-methoxymethoxydodecanol (330 mg, 1.34 mmol), BzCl (0.28 mL, 2.41 mmol), ^{i}Pr$_2$NEt (0.82 mL, 4.82 mmol), and DMAP (16.3 mg, 0.133 mmol) in dry CH_2Cl_2 (6.7 mL) was stirred at rt under N_2 for 17.5 h. The mixture was evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography (*n*-hexane/benzene=1/10 to *n*-hexane/AcOEt=5/1) to give **1f** (440 mg, 94%). Colorless oil, IR (KBr): 2930, 2855, 1713, 1468, 1279 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.28–1.43 (m, 16H), 1.51–1.61 (m, 2H), 1.71–1.82 (m, 2H), 3.36 (s, 3H), 3.52 (t, *J*=6.8 Hz, 2H), 4.31 (t, *J*=6.8 Hz, 2H), 4.62 (s, 2H), 7.40–7.46 (m, 2H), 7.52–7.59 (m, 1H), 8.03–8.07 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9, 26.1, 28.6, 29.2, 29.3, 29.41, 29.45, 29.48, 29.7, 54.9, 65.0, 67.7, 96.3, 128.2, 129.4, 130.4, 132.7, 166.5 ppm; HRMS (FAB): calcd for $C_{21}H_{35}O_4$ $[M+H]^+$: 351.2535, found 351.2528.

*4.2.2.3. Compound **1g**.* (R=Bn); to a solution of 12-methoxymethoxydodecanol (308 mg, 1.25 mmol) in dry THF (3.1 mL), BnBr (0.22 mL, 1.88 mmol), and NaH (76.8 mg, 1.92 mmol) were added successively at rt under N_2 and stirred for 20 h. H_2O was added to the reaction mixture and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography (*n*-hexane/AcOEt=15/1) to give **1g** (364 mg, 86%). Colorless oil, IR (KBr): 2926, 2853, 1454, 1209 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (br s, 16H), 1.56–1.61 (m, 4H), 3.36 (s, 3H), 3.44–3.54 (m, 4H), 4.50 (s, 2H), 4.62 (s, 2H), 7.26–7.35 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.11, 26.14, 29.36, 29.39, 29.5, 29.66, 29.68, 54.9, 67.7, 70.4, 72.7, 96.2, 127.3, 127.5, 128.2, 138.6 ppm; HRMS (FAB): calcd for $C_{21}H_{36}O_3Na$ $[M+Na]^+$: 359.2562, found 359.2563.

4.2.2.4. Compound ***1h***. (R=TBS); a solution of 12-methoxymethoxydodecanol (308 mg, 1.25 mmol), TBSCl (332 mg, 2.21 mmol), $^{i}Pr_2NEt$ (0.78 mL, 4.50 mmol), and DMAP (15.0 mg, 0.123 mmol) in dry CH_2Cl_2 (6.3 mL) was stirred at rt under N_2 for 4 h. The mixture was evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography (*n*-hexane/AcOEt=25/1, neutral) to give **1h** (428 mg, 95%). Colorless oil, IR (KBr): 2856, 2251, 1794, 1470, 1385 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 6H), 0.89 (s, 9H), 1.27 (br s, 16H), 1.47–1.63 (m, 4H), 3.36 (s, 3H), 3.52 (t, *J*=6.8 Hz, 2H), 3.60 (t, *J*=6.8 Hz, 2H), 4.62 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.3, 18.4, 25.8, 26.0, 26.2, 29.4, 29.56, 29.58, 29.61, 29.7, 32.9, 55.1, 63.3, 67.8, 96.3 ppm; HRMS (FAB): calcd for $C_{20}H_{45}O_3Si$ $[M+H]^+$: 361.3138, found 361.3162.

4.2.2.5. Compound ***1i***. (R=Tr); a solution of 12-methoxymethoxydodecanol (232 mg, 0.942 mmol), TrCl (485 mg, 1.74 mmol), $^{i}Pr_2NEt$ (0.60 mL, 3.51 mmol) and TBAI (35.0 mg, 0.095 mmol) in dry CH_2Cl_2 (1.0 mL) was stirred at rt under N_2 for 24 h. The mixture was evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography (*n*-hexane/AcOEt=15/1, neutral) to give **1i** (448 mg, 97%). Colorless oil, IR (KBr): 2926, 2853, 1448, 1217, 1150 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (br s, 16H), 1.54–1.64 (m, 4H), 3.03 (t, *J*=6.6 Hz, 2H), 3.36 (s, 3H), 3.51 (t, *J*=6.6 Hz, 2H), 4.62 (s, 2H), 7.19–7.46 (m, 9H), 7.43–7.46 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.20, 26.24, 29.4, 29.5, 29.56, 29.58, 29.7, 30.0, 55.1, 63.7, 67.8, 86.2, 96.4, 126.7, 127.6, 128.7, 144.5 ppm; HRMS (FAB): calcd for $C_{33}H_{44}O_3$ $[M]^+$: 488.3290, found 488.3290.

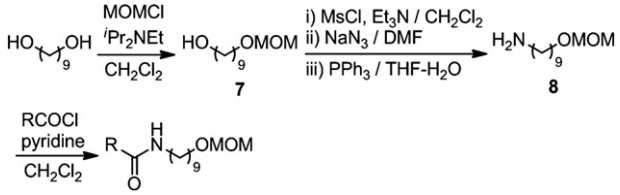
4.2.3. Preparation of MOM ether ***1j***. To a solution of MOM ether **1k** (1.37 g, 5.00 mmol) in MeOH (10 mL) was added 2 M NaOH aq at 0 °C and the mixture was stirred at rt overnight. The reaction mixture was acidified with diluted HCl aq and extracted with AcOEt. The organic layer was dried over Na_2SO_4 and evaporated in vacuo to give the carboxylic acid, which was used without further purification. To a solution of the carboxylic acid in CH_2Cl_2 (15 mL) were added $^{t}BuOH$ (631.5 mg, 8.52 mmol), EDCI (1.63 g, 8.52 mmol), and DMAP (52.5 mg, 0.43 mmol) at 0 °C and the mixture was stirred at rt for 12 h. The reaction mixture was evaporated and H_2O was added to the residue and extracted with AcOEt. The organic layer was washed with satd $NaHCO_3$ aq, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography (*n*-hexane/AcOEt=10/1) to give *tert*-butyl ester **1j** (two steps: 270.6 mg, 17%).

Compound **1j**: Colorless oil; IR (KBr): 2856, 1712, 1219, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.27–1.37 (m, 14H), 1.53 (s, 9H), 1.55–1.62 (m, 4H), 2.20 (t, *J*=7.6 Hz, 2H), 3.36 (s, 3H), 3.52 (t, *J*=7.2 Hz, 2H), 4.62 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.1, 26.2, 28.1, 29.1, 29.2, 29.40, 29.48, 29.52, 29.7, 35.6, 55.0, 67.8, 79.8, 96.3, 173.3 ppm; HRMS (FAB): calcd for $C_{18}H_{37}O_4$ $[M+H]^+$ 317.2692, found 317.2682.

4.2.4. Preparation of MOM ether ***1l***. MOM ether **1l** was prepared according to the procedure of literature.[30] LiBr (189.3 mg, 2.18 mmol) and catalytic amount of TsOH (125.7 mg, 0.73 mmol) were added to a solution of 10-bromo-1-decanol (1.72 g, 7.25 mmol) in dimethoxymethane (15 mL). The reaction mixture was stirred at rt for 5 h, treated with brine, and extracted with hexane. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt=15/1) to give 1-bromo-10-methoxymethoxydecane **1l** (956.8 mg, 47%).

Compound **1l**: Colorless oil; IR (KBr): 2855, 1043, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30–1.44 (m, 12H), 1.56–1.62 (m, 2H), 1.82–1.88 (m, 2H), 3.36 (s, 3H), 3.40 (t, *J*=7.0 Hz, 2H), 3.52 (t, *J*=7.0 Hz, 2H), 4.62 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.2, 28.2, 28.8, 29.37, 29.40, 29.5, 29.8, 32.3, 33.9, 55.1, 67.9, 96.5 ppm. Anal. Calcd for $C_{12}H_{25}BrO_2$: C, 51.25; H, 8.96; Br, 28.41, found: C, 51.39; H, 8.81; Br, 28.08.

4.2.5. Preparation of MOM ethers ***1m*** *and* ***1n***. MOM ethers **1m** and **n** were prepared from 1,9-nonanediol in three steps via 9-methoxymethoxy-1-nonanol **7** and 1-amino-9-methoxymethoxynonane **8**.



4.2.5.1. Synthesis of 9-methoxymethoxy-1-nonanol ***7***. A solution of 1,9-nonanediol (4.01 g, 25.0 mmol), MOMCl (1.88 mL, 25.0 mmol), and $^{i}Pr_2NEt$ (12.8 mL, 75.0 mmol) in dry CH_2Cl_2 (70 mL) was stirred at 0 °C to rt under N_2 for 15 h. After disappearance of diol on TLC, the mixture was added to satd NH_4Cl aq and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt=2/1) to give **7** (2.96 g, 58%).

Compound **7**: Colorless oil; IR (KBr): 3443, 2932, 1385, 1041, 912, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (s, 1H), 1.31–1.36 (m, 10H), 1.55–1.62 (m, 4H), 3.63 (s, 3H), 3.52 (t, *J*=7.0 Hz, 2H), 3.63–3.68 (m, 2H), 4.62 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.6, 26.1, 29.3, 29.4, 29.6, 32.7, 55.0, 62.8, 67.8, 96.3 ppm; HRMS (FAB): calcd for $C_{11}H_{25}O_3$ $[M+H]^+$ 205.1804, found 208.1815.

4.2.5.2. Synthesis of 1-amino-9-methoxymethoxynonane ***8***. To a solution of 9-methoxymethoxy-1-nonanol **7** (2.96 g, 14.5 mmol) in dry CH_2Cl_2 (60 mL) were added Et_3N (2.41 mL, 17.4 mmol) and MsCl (1.35 mL, 17.4 mmol) at 0 °C and the reaction mixture was stirred at rt under N_2 for 30 min. The reaction mixture was then evaporated in vacuo to afford the crude mesylate, which was used for the next reaction without further purification. NaN_3 (2.83 g, 43.5 mmol) was added to the solution of mesylate in DMF (50 mL) at 0 °C and the reaction mixture was stirred at rt for 14 h. The reaction mixture was quenched by H_2O at 0 °C and extracted with Et_2O. The organic phase was dried over Na_2SO_4, filtered through the short column of SiO_2 silica gel, and evaporated in vacuo to afford the crude azide. To the azide in THF (60 mL) and H_2O (5 mL) was added PPh_3 (9.51 g, 36.3 mmol) at 0 °C and the reaction mixture was stirred at rt for 22 h. The mixture was then evaporated in vacuo, and the residue was purified by flash column chromatography (CH_2Cl_2/MeOH=10/1 to CH_2Cl_2/MeOH/Et_3N=100/20/1) to give 1-amino-9-methoxymethoxynonane **8** (2.34 g, 80%; three steps).

Compound **8**: Colorless oil; IR (KBr): 2930, 1581, 1468, 912, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.30–1.45 (m, 14H), 1.55–1.62 (m, 2H), 2.68 (t, *J*=6.8 Hz, 2H), 3.36 (s, 3H), 3.52 (t, *J*=6.8 Hz, 2H), 4.62 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.0, 26.7, 29.2, 29.3, 29.4, 29.6, 33.6, 42.1, 54.9, 67.7, 96.2 ppm; HRMS (FAB): calcd for $C_{11}H_{26}NO_2$ $[M+H]^+$ 204.1964, found 204.1966.

4.2.5.3. Synthesis of ***1m***. Pyridine (391 μL, 4.85 mmol) and AcCl (346 μL, 4.85 mmol) were added to the solution of 1-amino-9-methoxymethoxynonane **8** (657.3 mg, 3.23 mmol) in dry CH_2Cl_2 (25 mL) at 0 °C under N_2. The reaction mixture was stirred at rt for 18 h, treated with 3.5% HCl aq, and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography (*n*-hexane/AcOEt=3/1 to CH_2Cl_2/MeOH=15/1) to give acetamide **1m** (523.3 mg, 66%).

Compound **1m**: Colorless oil; IR (KBr): 3298, 3086, 2928, 1651, 1553, 1292, 914, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.30–1.45 (m, 10H), 1.47–1.51 (m, 2H), 1.55–1.62 (m, 2H), 1.97 (s, 3H), 3.23 (dt, J=12.8, 7.2 Hz, 2H), 3.36 (s, 3H), 3.52 (t, J=6.8 Hz, 2H), 4.62 (s, 2H), 5.48 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.2, 26.1, 26.8, 29.1, 29.2, 29.4, 29.5, 29.6, 39.9, 67.8, 96.3, 170.0 ppm. Anal. Calcd for $C_{13}H_{27}NO_3$: C, 63.64; H, 11.09; N, 5.71, found: C, 63.41; H, 10.90; N, 5.65.

4.2.5.4. Synthesis of ***1n****.* Pyridine (425 μL, 5.27 mmol) and BzCl (607 μL, 5.27 mmol) were added to the solution of 1-amino-9-methoxymethoxynonane **8** (712.7 mg, 3.51 mmol) in dry CH_2Cl_2 (30 mL) at 0 °C under N_2. The reaction mixture was stirred at rt for 18 h, treated with 3.5% HCl aq, and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography using *n*-hexane/AcOEt (5/2) as an eluent to give benzamide **1n** (1.06 g, 98%).

Compound **1n**: Colorless oil; IR (KBr): 3318, 2928, 1643, 1537, 1307, 912, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.32–1.37 (m, 10H), 1.57–1.66 (m, 4H), 3.36 (s, 3H), 3.45 (dt, J=12.8, 7.2 Hz, 2H), 3.51 (t, J=7.2 Hz, 2H), 4.62 (br s, 2H), 7.41–7.44 (m, 2H), 7.47–7.51 (m, 1H), 7.75–7.77 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.9, 26.8, 29.0, 29.1, 29.2, 29.4, 29.5, 39.9, 54.8, 67.6, 96.1, 126.7, 128.1, 130.9, 134.6, 167.4 ppm. Anal. Calcd for $C_{18}H_{29}NO_3$: C, 70.32; H, 9.51; N, 4.56, found: C, 70.49; H, 9.40; N, 4.57.

4.3. Preparation of MEM ether 3

4.3.1. Preparation of MEM ethers ***3a–c****,* ***3e****.* A solution of alcohol **2** (1.0 equiv), MEMCl (2.0 equiv), $^iPr_2NEt$ (3.0 equiv), and DMAP (0.1 equiv) in dry CH_2Cl_2 (0.2–0.5 M) was stirred at 0 °C to rt under N_2. After disappearance of **2** on TLC, satd NH_4Cl aq was added to the mixture and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography to give MEM ether **3**. **3a** is a known compound.[10b]

4.3.1.1. Compound ***3a****[10b].* Treatment of **2a** (791.5 mg, 5.00 mmol) with MEMCl (1.13 mL, 10.0 mmol), $^iPr_2NEt$ (2.55 mL, 15.0 mmol), and DMAP (61.1 mg, 0.500 mmol) gave **3a** (1.04 g, 84%). Eluent; *n*-hexane/AcOEt (4/1).

4.3.1.2. Compound ***3b****.* Treatment of **2b** (791.5 mg, 5.00 mmol) with MEMCl (1.13 mL, 10.0 mmol), $^iPr_2NEt$ (2.55 mL, 15.0 mmol), and DMAP (61.1 mg, 0.500 mmol) gave **3b** (1.17 g, 95%). Eluent; *n*-hexane/AcOEt (10/1).

Colorless oil; IR (KBr): 2926, 1456, 1377, 1043, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=6.8 Hz, 3H), 1.15 (d, J=6.0 Hz, 3H), 1.26–1.55 (m, 14H), 3.40 (s, 3H), 3.56 (t, J=6.0 Hz, 2H), 3.69–3.73 (m, 3H), 4.75 (d, J=19.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.1, 22.6, 25.5, 29.2, 29.5, 29.6, 31.8, 36.9, 58.9, 66.6, 71.7, 73.0, 93.7 ppm. Anal. Calcd for $C_{14}H_{30}O_3$: C, 68.25; H, 12.27, found: C, 68.36; H, 12.07.

4.3.1.3. Compound ***3c****.* Treatment of **2c** (492.7 mg, 3.0 mmol) with MEMCl (0.68 mL, 6.0 mmol), $^iPr_2NEt$ (1.5 mL, 9.0 mmol), and DMAP (36.7 mg, 0.30 mmol) gave **3c** (689.0 mg, 91%). Eluent; *n*-hexane/AcOEt (5/1).

Colorless oil; IR (KBr): 2887, 1219, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.29 (s, 6H), 1.79–1.84 (m, 2H), 2.65–2.69 (m, 2H), 3.38 (s, 3H), 3.54 (t, J=6.0 Hz, 2H), 3.75 (t, J=6.0 Hz, 2H), 4.85 (s, 2H), 7.15–7.29 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.3, 30.3, 43.7, 58.9, 66.6, 71.7, 75.9, 89.9, 125.5, 128.2, 142.6 ppm. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59, found: C, 71.48; H, 9.60.

4.3.1.4. Compound ***3e****.* Treatment of **2k**[8] (1.71 g, 7.42 mmol) with MEMCl (1.68 mL, 14.8 mmol), $^iPr_2NEt$ (3.8 mL, 22.3 mmol), and DMAP (90.4 mg, 0.74 mmol) gave **3e** (2.29 g, 97%). Eluent; n-hexane/AcOEt (15/1 to 5/1).

Colorless oil; IR (KBr): 2928, 1730, 1219, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.27–1.36 (m, 14H), 1.55–1.65 (m, 4H), 2.30 (t, J=7.5 Hz, 2H), 3.34 (s, 3H), 3.53–3.57 (m, 4H), 3.66 (s, 3H), 3.68–3.70 (m, 2H), 4.71 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.0, 26.2, 29.2, 29.3, 29.43, 29.44, 29.5, 29.6, 29.7, 34.1, 51.4, 59.0, 66.7, 68.0, 71.9, 95.5, 174.3 ppm; HRMS (FAB): calcd for $C_{17}H_{35}O_5$ $[M+H]^+$ 319.2484, found 319.2466.

4.3.2. Preparation of MEM ethers ***3d****,* ***3f****, and* ***3g****.* TMSOTf (2.0 equiv) was added dropwise to a solution of MOM ether **1** (1.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C under N_2 and the reaction mixture was stirred for 30 min at 0 °C. After disappearance of **1** on TLC, $MeOCH_2CH_2OH$ (5.0 equiv) was added to the reaction mixture and the resulting solution was stirred at rt. After the reaction was completed, satd $NaHCO_3$ aq was added and the resulting solution was extracted with CH_2Cl_2. The organic layer was washed with 3.5% HCl aq, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography to give MEM ether. For the preparation of **3g**, 6.0 equiv of TMSOTf and 4.0 equiv of 2,2′-bipyridyl were used.

4.3.2.1. Compound ***3d****.* Treatment of **1i** (117.7 mg, 0.241 mmol) with 2,2′-bipyridyl (112.9 mg, 0.723 mmol), TMSOTf (87 μL, 0.482 mmol), and $MeOCH_2CH_2OH$ (95 μL, 1.205 mmol) gave **3d** (101.4 mg, 79%). Eluent; *n*-hexane/AcOEt (12/1).

Colorless oil; IR (KBr): 2926, 912, 742 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.24–1.35 (m, 16H), 1.55–1.63 (m, 4H), 3.04 (t, J=6.5 Hz, 2H), 3.39 (s, 3H), 3.52–3.57 (m, 4H), 3.69 (t, J=5.0 Hz, 2H), 4.70 (s, 2H), 7.20–7.28 (m, 9H), 7.43–7.44 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.0, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.8, 34.1, 51.4, 55.1, 67.9, 96.4, 174.3 ppm; HRMS (FAB): $C_{35}H_{48}O_4Na$ $[M+Na]^+$ 555.3450, found 555.3454.

4.3.2.2. Compound ***3f****.* Treatment of **1l** (68.2 mg, 0.243 mmol) with 2,2′-bipyridyl (113.9 mg, 0.729 mmol), TMSOTf (88 μL, 0.486 mmol), and $MeOCH_2CH_2OH$ (100 μL, 1.215 mmol) gave **3f** (72.9 mg, 92%). Eluent; *n*-hexane/AcOEt (10/1).

Colorless oil; IR (KBr): 2855, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.26–1.36 (m, 10H), 1.39–1.44 (m, 2H), 1.55–1.62 (m, 2H), 1.82–1.88 (m, 2H), 3.396 (s, 3H), 3.402 (t, J=7.0 Hz, 2H), 3.53–3.57 (m, 4H), 3.68–3.70 (m, 2H), 4.71 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.2, 28.2, 28.7, 29.37, 29.40, 29.5, 29.7, 32.9, 34.0, 59.0, 66.7, 68.0, 71.9, 95.5 ppm; HRMS (FAB): calcd for $C_{14}H_{30}O_3Br$ $[M+H]^+$ 325.1378, found 325.1382.

4.3.2.3. Compound ***3g****.* Treatment of **1n** (70.3 mg, 0.229 mmol) with 2,2′-bipyridyl (214.6 mg, 1.374 mmol), TMSOTf (166 μL, 0.916 mmol), and $MeOCH_2CH_2OH$ (90 μL, 1.145 mmol) gave **3g** (68.5 mg, 85%). Eluent; *n*-hexane/AcOEt (3/2).

Colorless oil; IR (KBr): 3333, 3065, 2930, 1643, 1537, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.31–1.37 (m, 10H), 1.55–1.62 (m, 4H), 3.40 (s, 3H), 3.45 (dt, J=13.5, 7.5 Hz, 2H), 3.52–3.58 (m, 4H), 3.69 (t, J=5.0 Hz, 2H), 4.71 (s, 2H), 6.11 (br s, 1H), 7.42–7.44 (m, 2H), 7.48–7.51 (m, 1H), 7.75–7.76 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.1, 26.9, 29.2, 29.3, 29.4, 29.6, 40.1, 59.0, 66.6, 67.9, 71.8, 95.4, 126.8, 128.5, 131.2, 134.8, 167.5 ppm; HRMS (FAB): calcd for $C_{20}H_{34}NO_4$ $[M+H]^+$ 352.2488, found 352.2499.

4.4. Preparation of BOM ethers 4

4.4.1. Preparation of BOM ethers ***4a–c****.* A solution of alcohol **2** (1.0 equiv), BOMCl (2.0 equiv), $^iPr_2NEt$ (3.0 equiv), and DMAP (0.1 equiv) in dry CH_2Cl_2 (0.3–0.5 M) was stirred at 0 °C to rt under N_2. After disappearance of **2** on TLC, the mixture was added satd NH_4Cl aq

and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by flash column chromatography to give BOM ether **4**.

*4.4.1.1. Compound **4a**.* Treatment of **2a** (791.5 mg, 5.0 mmol) with BOMCl (1.37 mL, 10.0 mmol), $^{i}Pr_2NEt$ (2.55 mL, 15.0 mmol), and DMAP (61.1 mg, 0.50 mmol) gave **4a** (1.32 g, 95%). Eluent; *n*-hexane–benzene (5/2).

Colorless oil; IR (KBr): 2942, 1069, 912, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=6.8 Hz, 3H), 1.27–1.38 (m, 14H), 1.56–1.63 (m, 2H), 3.58 (t, J=6.8 Hz), 4.60 (s, 2H), 4.76 (s, 2H), 7.27–7.36 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.6, 26.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 68.0, 69.2, 94.5, 127.6, 127.8, 128.3, 138.0 ppm. Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86, found: C, 77.92; H, 10.75.

*4.4.1.2. Compound **4b**.* Treatment of **2b** (791.5 mg, 5.0 mmol) with BOMCl (1.37 mL, 10.0 mmol), $^{i}Pr_2NEt$ (2.55 mL, 15.0 mmol), and DMAP (61.1 mg, 0.50 mmol) gave **4b** (429.3 mg, 31%). Eluent; *n*-hexane/AcOEt (5/1).

Colorless oil; IR (KBr): 2856, 1379, 1217, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J=6.8 Hz, 3H), 1.18 (d, J=6.4 Hz, 3H), 1.21–1.60 (m, 14H), 3.72–3.80 (m, 1H), 4.62 (dd, J=14.4, 12.0 Hz, 2H), 4.78 (d, J=16.8 Hz), 7.26–7.37 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 20.2, 22.6, 25.6, 29.2, 29.6, 29.7, 31.8, 37.0, 69.2, 73.1, 92.8, 127.5, 127.8, 128.3, 138.0 ppm. Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86, found: C, 77.63; H, 10.77.

*4.4.1.3. Compound **4c**.* Treatment of **2c** (821.2 mg, 5.0 mmol) with BOMCl (1.37 mL, 10.0 mmol), $^{i}Pr_2NEt$ (2.55 mL, 15.0 mmol), and DMAP (61.1 mg, 0.50 mmol) gave **4c** (886.3 mg, 62%). Eluent; *n*-hexane/AcOEt (5/1).

Colorless oil; IR (KBr): 2972, 1219, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 6H), 1.82–1.87 (m, 2H), 2.68–2.72 (m, 2H), 4.66 (s, 2H), 4.89 (s, 2H), 7.15–7.36 (m, 10H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.4, 30.3, 43.8, 69.2, 69.4, 76.0, 77.2, 125.6, 127.4, 127.7, 128.2, 138.1, 142.6 ppm. Anal. Calcd for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51, found: C, 80.47; H, 8.49.

*4.4.2. Preparation of BOM ethers **4d–g**.* TMSOTf (2.0 equiv) was added dropwise to the solution of MOM ether **1** (1.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C under N_2 and the reaction mixture was stirred for 30 min at 0 °C. After disappearance of **1** on TLC, BnOH (5.0 equiv) was added to the reaction mixture and the resulting solution was stirred at rt. After the reaction was completed, satd $NaHCO_3$ aq was added and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography to give BOM ether **4**. For the preparation of **4g**, 6.0 equiv of TMSOTf and 4.0 equiv of 2,2′-bipyridyl were used. Compound **4d** is known compound.[5]

*4.4.2.1. Compound **4d**[5].* Treatment of **2i** (112.0 mg, 0.229 mmol) with 2,2′-bipyridyl (107.2 mg, 0.687 mmol), TMSOTf (83 μL, 0.458 mmol), and BnOH (120 μL, 1.150 mmol) gave **4d** (95.1 mg, 73%). Eluent; *n*-hexane/benzene (1/3).

*4.4.2.2. Compound **4e**.* Treatment of **1k** (58.0 mg, 0.211 mmol) with 2,2′-bipyridyl (98.9 mg, 0.633 mmol), TMSOTf (76 μL, 0.422 mmol), and BnOH (110 μL, 1.055 mmol) gave **4e** (56.8 mg, 77%). Eluent; benzene/Et_2O (150/1).

Colorless oil; IR (KBr): 2926, 1732, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.27–1.37 (m, 14H), 1.57–1.64 (m, 4H), 2.30 (t, J=7.5 Hz, 2H), 3.58 (t, J=6.5 Hz, 2H), 3.67 (s, 3H), 4.60 (s, 2H), 4.76 (s, 2H), 7.27–7.36 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.0, 26.2, 29.2, 29.3, 29.43, 29.45, 29.53, 29.6, 29.8, 34.1, 51.4, 68.2, 69.3, 94.7, 127.6, 127.9, 128.4, 138.1, 174.3 ppm; HRMS (FAB): calcd for $C_{21}H_{35}O_4$ $[M+H]^+$ 351.2535, found 351.2535.

*4.4.2.3. Compound **4f**.* Treatment of **1l** (68.9 mg, 0.245 mmol) with 2,2′-bipyridyl (114.8 mg, 0.735 mmol), TMSOTf (89 μL, 0.490 mmol), and BnOH (130 μL, 1.225 mmol) gave **4f** (84.9 mg, 86%). Eluent; benzene/Et_2O (200/1).

Colorless oil; IR (KBr): 2931, 1217, 912, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.26–1.43 (m, 12H), 1.57–1.63 (m, 2H), 1.82–1.88 (m, 2H), 3.40 (t, J=6.5 Hz, 2H), 3.58 (t, J=6.5 Hz, 2H), 4.60 (s, 2H), 4.75 (s, 2H), 7.25–7.36 (m, 5H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.2, 28.1, 28.7, 29.3, 29.4, 29.7, 32.8, 33.9, 68.1, 69.3, 94.6, 127.6, 127.8, 128.4, 138.0 ppm; HRMS (FAB): calcd for $C_{18}H_{29}O_2{}^{79}BrNa$ $[M+Na]^+$ 379.1249, found 379.1205.

*4.4.2.4. Compound **4g**.* Treatment of **1n** (60.4 mg, 0.196 mmol) with 2,2′-bipyridyl (183.7 mg, 1.176 mmol), TMSOTf (142 μL, 0.784 mmol), and BnOH (102 μL, 0.980 mmol) gave **4g** (61.3 mg, 82%). Eluent; benzene/Et_2O (10/1 to 4/1).

Colorless crystal; mp: 46.1–46.2 °C; IR (KBr): 3331, 3061, 2930, 1643, 1537, 1045, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.25–1.43 (m, 10H), 1.57–1.62 (m, 4H), 3.45 (dt, J=13.5, 6.5 Hz, 2H), 3.58 (t, J=6.5 Hz, 2H), 4.60 (s, 2H), 4.76 (s, 2H), 6.10 (br s, 1H), 7.26–7.51 (m, 8H), 7.75–7.76 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 26.2, 27.0, 29.2, 29.3, 29.5, 29.7, 40.1, 68.1, 69.2, 94.6, 126.8, 127.6, 127.9, 128.4, 128.5, 131.3, 134.9, 138.0, 167.5 ppm; HRMS (FAB): calcd for $C_{24}H_{34}NO_3$ $[M+H]^+$ 384.2539, found 384.2538.

*4.4.3. General procedure: preparation of SEM ethers **5**.* TMSOTf (2.0 equiv) was added dropwise to the solution of MOM ether **1** (1.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C under N_2 and the reaction mixture was stirred for 30 min at the same temperature. After disappearance of **1** on TLC, $TMSCH_2CH_2OH$ (5.0 equiv) was added to the reaction mixture and the resulting solution was stirred at rt. After the reaction was completed, satd $NaHCO_3$ aq was added and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography to give SEM ether **5**. For the preparation of **5g**, 6.0 equiv of TMSOTf and 4.0 equiv of 2,2′-bipyridyl were used. Compound **5d** is a known compound.[5]

*4.4.3.1. Compound **5a**.* According to the general procedure, treatment of **1a** (60.7 mg, 0.300 mmol) with 2,2′-bipyridyl (140.6 mg, 0.900 mmol), TMSOTf (108 μL, 0.600 mmol), and $TMSCH_2CH_2OH$ (214 μL, 1.50 mmol) gave **5a** (69.1 mg, 80%). Eluent; *n*-hexane/benzene (3/1 to 2/1).

Colorless oil; IR (KBr): 2924, 1250, 1061, 914, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.02 (s, 9H), 0.88 (t, J=6.4 Hz, 3H), 0.95 (t, J=8.8 Hz, 2H), 1.27–1.43 (m, 14H), 1.59–1.99 (m, 2H), 3.53 (t, J=6.8 Hz, 2H), 3.61 (t, J=8.8 Hz, 2H), 4.67 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.44, 14.1, 18.1, 22.7, 26.2, 29.3, 29.45, 29.57, 29.61, 29.8, 31.9, 64.9, 67.9, 94.8 ppm; HRMS (FAB): calcd for $C_{16}H_{36}O_2SiNa$ $[M+Na]^+$ 311.2382, found 311.2378.

*4.4.3.2. Compound **5b**.* According to the general procedure, treatment of **1b** (41.9 mg, 0.207 mmol) with 2,2′-bipyridyl (97.0 mg, 0.621 mmol), TMSOTf (75 μL, 0.414 mmol), and $TMSCH_2CH_2OH$ (150 μL, 1.035 mmol) gave **5b** (49.2 mg, 82%). Eluent; benzene/Et_2O (200/1).

Colorless oil; IR (KBr): 2857, 1377, 1259, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.02 (s, 9H), 0.88 (t, J=7.0 Hz, 3H), 0.94 (t, J=10.5 Hz, 2H), 1.15 (d, J=6.0 Hz, 3H), 1.28–1.55 (m, 14H), 3.59–3.69 (m, 3H), 4.69 (d, J=20.5 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.46, 14.1, 18.1, 20.2, 22.6, 25.6, 29.3, 29.6, 29.7, 31.9, 37.1, 64.8, 72.9, 93.0 ppm; HRMS (FAB): calcd for $C_{16}H_{36}O_2SiLi$ $[M+Li]^+$ 295.2645, found 295.2622.

*4.4.3.3. Compound **5c**.* According to the general procedure, treatment of **1c** (62.2 mg, 0.299 mmol) with 2,2′-bipyridyl (140.1 mg, 0.897 mmol), TMSOTf (108 μL, 0.598 mmol), and $TMSCH_2CH_2OH$ (210 μL, 1.495 mmol) gave **5c** (68.0 mg, 77%). Eluent; *n*-hexane/AcOEt (25/1).

Colorless oil; IR (KBr): 2972, 1219, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.02 (s, 9H), 0.94 (t, *J*=8.5 Hz, 2H), 1.29 (s, 6H), 1.80–1.83 (m, 2H), 2.66–2.70 (m, 2H), 3.67 (t, *J*=10.5 Hz, 2H), 4.79 (s, 2H), 7.15–7.29 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.42, 18.2, 26.5, 30.4, 43.8, 64.9, 75.8, 89.3, 125.6, 128.3, 142.8 ppm; HRMS (FAB): calcd for $C_{17}H_{31}O_2Si$ $[M+H]^+$ 295.2093, found 295.2098.

*4.4.3.4. Compound **5d**[5].* According to the general procedure, treatment of **1i** (119.0 mg, 0.242 mmol) with 2,2′-bipyridyl (113.6 mg, 0.728 mmol), TMSOTf (88 μL, 0.484 mmol), and $TMSCH_2CH_2OH$ (170 μL, 1.210 mmol) gave **5d** (108.0 mg, 78%). Eluent; *n*-hexane/benzene (1/3).

*4.4.3.5. Compound **5e**.* According to the general procedure, treatment of **1k** (58.4 mg, 0.213 mmol) with 2,2′-bipyridyl (99.8 mg, 0.639 mmol), TMSOTf (77 μL, 0.426 mmol), and $TMSCH_2CH_2OH$ (150 μL, 1.065 mmol) gave **5e** (64.3 mg, 84%). Eluent; *n*-hexane/AcOEt (20/1).

Colorless oil; IR (KBr): 2930, 1738, 1219, 912, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.02 (m, 9H), 0.94 (t, *J*=8.5 Hz, 2H), 1.27–1.35 (m, 14H), 1.55–1.64 (m, 4H), 2.30 (t, *J*=7.5 Hz, 2H), 3.52 (t, *J*=7.0 Hz, 2H), 3.61 (t, *J*=7.5 Hz, 2H), 3.66 (s, 3H), 4.66 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ −1.4, 18.1, 25.0, 26.2, 29.1, 29.2, 29.41, 29.43, 29.5, 29.6, 29.8, 34.1, 51.4, 64.9, 67.9, 94.8, 174.3 ppm; HRMS (FAB): calcd for $C_{19}H_{40}O_4SiNa$ $[M+Na]^+$ 383.2594, found 383.2589.

*4.4.3.6. Compound **5f**.* According to the general procedure, treatment of **1l** (78.9 mg, 0.280 mmol) with 2,2′-bipyridyl (131.2 mg, 0.840 mmol), TMSOTf (102 μL, 0.560 mmol), and $TMSCH_2CH_2OH$ (200 μL, 1.40 mmol) gave **5f** (77.6 mg, 75%). Eluent; benzene/Et_2O (200/1).

Colorless oil; IR (KBr): 2928, 1217, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.02 (s, 9H), 1.27–1.36 (m, 14H), 1.56–1.65 (m, 2H), 1.82–1.88 (m, 2H), 3.40 (t, *J*=7.0 Hz, 2H), 3.52 (t, *J*=6.5 Hz, 2H), 3.62 (t, *J*=10.5 Hz, 2H), 4.66 (s, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ −1.45, 18.1, 25.0, 26.2, 28.1, 28.7, 29.33, 29.36, 24.44, 29.7, 32.8, 33.8, 64.9, 67.8, 94.8 ppm. Anal. Calcd for $C_{16}H_{35}BrO_2Si$: C, 52.30; H, 9.60; Br, 21.75, found: C, 52.34; H, 9.49; Br, 21.60.

*4.4.3.7. Compound **5g**.* According to the general procedure, the treatment of **1n** (70.1 mg, 0.228 mmol) with 2,2′-bipyridyl (213.7 mg, 1.368 mmol), TMSOTf (165 μL, 0.912 mmol), and $TMSCH_2CH_2OH$ (162 μL, 1.320 mmol) gave **5g** (75.7 mg, 84%) for 7 h. Eluent; *n*-hexane/AcOEt (4/1).

Colorless oil; IR (KBr): 3313, 3063, 2928, 1645, 1524, 1058, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 0.02 (s, 9H), 0.94 (t, *J*=8.5 Hz, 2H), 1.31–1.35 (m, 10H), 1.55–1.64 (m, 4H), 3.44 (dt, *J*=13.0, 7.0 Hz, 2H), 3.52 (t, *J*=6.5 Hz, 2H), 3.61 (t, *J*=8.5 Hz, 2H), 4.66 (s, 2H) 7.41–7.44 (m, 2H), 7.48–7.50 (m, 1H), 7.76–7.77 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ −1.46, 18.1, 26.2, 26.9, 29.2, 29.3, 29.4, 29.6, 29.7, 40.1, 64.9, 67.8, 94.7, 126.8, 128.5, 131.2, 134.8, 167.5 ppm; HRMS (FAB): calcd for $C_{22}H_{40}NO_3Si$ $[M+H]^+$ 394.2777, found 394.2778.

4.5. Deprotection of MOM, MEM, BOM, or SEM ether by TMSOTf (TESOTf)/2,2′-bipyridyl combination

TMSOTf or TESOTf (2.0 equiv) was added dropwise to a solution of MOM, MEM, BOM, or SEM ether (**1**, **3**–**5**) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C under N_2. The reaction mixture was stirred at the same temperature. After checking the disappearance of the starting material on TLC (30 min), H_2O (2 mL/mmol) and Et_2O (2 mL/mmol) were added to the reaction mixture and vigorously stirred. After disappearance of the high polar component was ascertained by TLC, the reaction mixture was extracted with CH_2Cl_2. The organic layer was washed with 3.5% HCl aq twice (for removal of 2,2′-bipyridyl) and with satd $NaHCO_3$ aq. The combined organic layer was dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by flash column chromatography to give an alcohol **2**. Silica gel 60 N (neutral) was used for the purification of substrate having TBS or Tr ethers instead of Merck Silica gel 60. Compounds **2e**[31a], **2f**[4a], **2g**[31b], **2h**[31c], **2i**[31d], **2j**[31e], and **2k**[28] are known compounds.

*4.5.1. Compound **2m**.* Colorless crystal; mp: 55.2–55.3 °C; IR (KBr): 3286, 3094, 1645, 1557, 1296, 912, 743 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.30–1.34 (m, 10H), 1.48–1.50 (m, 2H), 1.54–1.59 (m, 2H), 1.97 (s, 3H), 3.46 (dd, *J*=13.0, 7.0 Hz, 2H), 3.64 (q, *J*=6.5 Hz, 2H), 5.43 (br s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 23.3, 25.6, 26.8, 29.1, 29.2, 29.4, 29.5, 32.7, 39.6, 62.9, 170.1 ppm. Anal. Calcd for $C_{11}H_{23}NO_2$: C, 65.63; H, 11.52; N, 6.96, found: C, 65.27; H, 11.29; N, 6.88.

*4.5.2. Compound **2n**.* Colorless crystal; mp: 78.0–78.1 °C; IR (KBr): 3304, 3061, 1643, 1539, 1310, 912, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.26–1.35 (m, 10H), 1.58–1.65 (m, 4H), 3.46 (dd, *J*=12.0, 6.0 Hz, 2H), 3.64 (t, *J*=6.8 Hz, 2H), 6.10 (br s, 1H), 7.41–7.45 (m, 2H), 7.48–7.51 (m, 1H), 7.75–7.77 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.6, 26.9, 29.1, 29.3, 29.6, 32.7, 40.0, 63.0, 126.8, 128.5, 131.3, 134.8, 167.5 ppm. Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.96; H, 9.57; N, 5.32, found: C, 72.52; H, 9.37; N, 5.34.

4.6. Selective deprotection of aliphatic MOM group in the presence of phenolic MOM group (Scheme 4)

According to the general procedure for deprotection of MOM ethers, treatment of **1p**[27] (39.4 mg, 0.164 mmol) with 2,2′-bipyridyl (76.7 mg, 0.491 mmol) and TESOTf (74 μL, 0.328 mmol) gave **2p**[32] (27.3 mg, 85%). Eluent; *n*-hexane/AcOEt (1/1).

4.7. The substitution reaction of acetal-type ethers with allyl alcohol in the combination with TMSOTf-2,2′-bipyridyl (Scheme 6)

TMSOTf (2.0 equiv) was added dropwise to a solution of MOM-type ether (**1a**, **3a**, **4a**, and **5a**) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C under N_2 and the reaction mixture was stirred for 30 min at 0 °C. After disappearance of MOM-type ether on TLC, allyl alcohol (5.0 equiv) was added to the reaction mixture and the resulting solution was stirred at rt for 24 h. Then, satd $NaHCO_3$ aq was added and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography to give acetal **6** and alcohol **2a**.

Compound **6**: Colorless oil; IR (KBr): 2926, 1468, 1265, 912, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J*=6.8 Hz, 3H), 1.26–1.37 (m, 14H), 1.55–1.62 (m, 2H), 3.54 (t, *J*=6.8 Hz, 2H), 4.08 (dt, *J*=6.0, 1.6 Hz, 2H), 4.70 (s, 2H), 5.18 (dq, *J*=9.6, 3.2, 1.6 Hz, 1H), 5.30 (dq, *J*=17.2, 3.2, 1.6 Hz, 1H), 5.88–5.98 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 26.2, 29.3, 29.4, 29.55, 29.59, 29.7, 31.9, 68.0, 68.2, 94.5, 116.9, 134.4 ppm; Anal. Calcd for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36, found: C, 73.64; H, 12.64.

4.8. General procedure: direct conversion to BOM and SEM ethers from MOM ethers (Table 5)

TMSOTf (2.0 equiv) was added dropwise to a solution of MOM ether **1** (1.0 equiv) and 2,2′-bipyridyl (3.0 equiv) in CH_2Cl_2 (0.2 M) at 0 °C under N_2 and the reaction mixture was stirred for 30 min at 0 °C. After disappearance of **1** on TLC, BnOH or $TMSCH_2CH_2OH$

(5.0 equiv) was added to the reaction mixture and the resulting solution was stirred at rt. After the reaction was completed, satd $NaHCO_3$ aq was added and the resulting solution was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated in vacuo. The residue was purified by column chromatography to give BOM **4** or SEM ether **5**.

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12. We examined the reactions with TMSOTf or TESOTf and both reagents could form the collidinium salt without any differences. We then chose the less expensive TMSOTf for further optimization. The equivalent of reagents and the order of the addition of reagents are important and decrease of reagents led to remaining starting material. We also found that the use of Et_2O with H_2O for hydrolysis gave a better result. Bis(*n*-decyloxy)methane was obtained in the absence of Et_2O as the major byproduct.
13. Bis(*n*-decyloxy)methane was obtained as the byproduct.
14. We attempted the use of TESOTf instead of TMSOTf to improve the reaction, but the yield of **2j** dropped to 47%.
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