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Solvent-modulated Pd/C-catalyzed deprotection of silyl ethers and chemoselective hydrogenation

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Abstract—Recently we have reported undesirable and frequent deprotection of the TBDMS protective group of a variety of hydroxyl functions occurred under neutral and mild hydrogenation conditions using 10% Pd/C in MeOH. The deprotection of silyl ethers is susceptible to significant solvent effect. TBDMS and TES protecting groups were selectively cleaved in the presence of acid-sensitive functional groups such as TIPS ether, TBDPS ether and dimethyl acetal under hydrogenation condition using 10% Pd/C in MeOH. In contrast, chemoselective hydrogenation of reducible functional groups such as acetylene, olefin and benzyl ether, proceeds in the presence of TBDMS or TES ethers in AcOEt or MeCN.

1. Introduction

Hydroxyl groups are partial structures of a number of organic compounds. During oxidation, acylation, halogenation or dehydration reaction of these compounds, the hydroxyl groups must be protected. Silyl ethers are among the most frequently used protective groups for alcohols in organic synthesis,[1] because they can be easily installed in high yield and can withstand a variety of reaction conditions. Although silyl ethers can be easily deprotected by treatment with a fluoride anion,[2] the strongly basic conditions make it inappropriate to apply to base-sensitive substrates.[2] Many alternative and mild methods have been reported for the deprotection of silyl ethers under mild conditions.[1] However, most of these methods suffer from the use of acidic and basic conditions, strong oxidising and reducing reagents and complicated workup.[3] In this context, it is very important to develop a novel, neutral and mild deprotection method of silyl ethers.

On the other hand, Pd/C is one of the most useful heterogeneous hydrogenation catalysts in organic synthesis,[4] because it can be safely handled and removed from the reaction mixture by simple filtration. Although it has been well known that the TBDMS (*tert*-butyldimethylsilyl) ether is inert toward Pd/C-catalyzed hydrogenation conditions,[5] we have recently reported that the TBDMS ethers are easily and frequently cleaved under hydrogenation conditions using Pd/C as a catalyst in MeOH.[6] In a related reaction, we found that the reductive deprotection of the silyl ether under hydrogenation conditions using 10% Pd/C was strongly affected by the solvent. Herein, we report a selective cleavage method of TES and TBDMS ethers under mild and neutral hydrogenation conditions using 10% Pd/C in MeOH, and a selective hydrogenation method of some reducible functionalities in the presence of TES and TBDMS ethers using 10% Pd/C in MeCN or AcOEt.[7]

2. Results and discussion

Our initial studies focused on the solvent effect toward the deprotection of TBDMS ethers under hydrogenation conditions using 10% Pd/C. 1-*tert*-Butyldimethylsilyloxy-3-phenyl-2-propene (**1a**) was hydrogenated with 10% Pd/C (10% of the weight of the substrate (**1a**); 2.3 mol% as Pd metal) for 24 h at room temperature in various solvents (Table 1). While smooth hydrogenation of the olefin function and complete deprotection of the TBDMS protective group of **1a** simultaneously proceeded in MeOH (entry 1), TBDMS cleavage reaction was slightly depressed in EtOH and strongly inhibited in ^{t}BuOH (entries 2 and 3). In spite of the poor water solubility of **1a**, considerable cleavage (77%) of the TBDMS ether was observed (entry 4). As compared with protic solvents, use of aprotic solvents is inconvenient for the deprotection of TBDMS ether (**1a**) under hydrogenation conditions using Pd/C (entries 5–11). Especially in toluene, AcOEt and MeCN, the TBDMS ether was stable and selective hydrogenation of the olefin was achieved (entries 9–11). While no deprotection of the TBDMS group was observed in the absence of hydrogen or 10% Pd/C in MeOH, both

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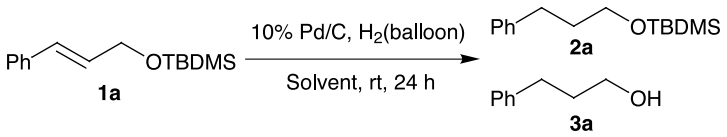
Table 1. Solvent effect toward the deprotection of the TBDMS ether (**1a**) using 10% Pd/C[a]



Entry	Solvent	Relative yield (%)[b]	
		2a	**3a**
1	MeOH[c]	0	100
2	EtOH	34	66
3	^{t}BuOH	92	8
4	H_2O	23	77
5	Hexane	86	14
6	Cyclohexane	89	11
7	DMF	87	13
8	THF	98	2
9	Toluene	100	0
10	EtOAc	100	0
11	MeCN	100	0

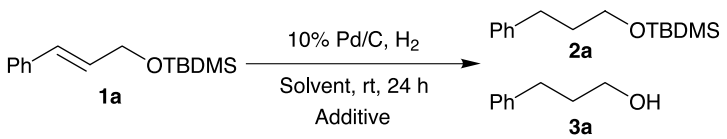
[a] 10% Pd/C was purchased from Aldrich (Aldrich product number 20,569-9).
[b] Determined by ^{1}H NMR.
[c] No reaction was observed under Ar.

hydrogen and Pd/C were essential for the deprotection of the TBDMS group.[8]

The effect of the addition of a small amount of MeOH or H_2O (0.1 mL of MeOH or H_2O/1 mL of EtOAc or MeCN) into the reaction mixture of TBDMS ether (**1a**) under 10% Pd/C-catalyzed hydrogenation conditions in AcOEt or MeCN is summarized in Table 2. The addition of MeOH or H_2O into the reaction mixture did not affect cleavage of the TBDMS ether at all and the olefin of **1a** was reduced selectively to form TBDMS ether (**2a**) in high yield (entries 1, 3 and 4). These data imply that AcOEt or MeCN strongly coordinates with the Pd metal to compete with the reacting substance and decreases the catalyst activity toward the deprotection of the TBDMS ether.[10] When a small amount of H_2O was added into the reaction mixture in AcOEt as a solvent, partial TBDMS deprotection was exceptionally observed for the following reason (entry 2). The reaction mixture of entry 2 separated into two layers (H_2O and AcOEt), and the deprotection of TBDMS progressed in the aqueous layer as well as in Table 1, entry 4. On the other hand, the reaction mixture in MeCN in the presence of a small amount of H_2O consisted of a homogeneous layer (single layer) and, no cleavage of the TBDMS ether was observed (entry 4).

To further explore the solvent effect toward the deprotection of various kinds of silyl ethers, we carried out the Pd/C-catalyzed hydrogenation reaction of TBDMS, TES (triethylsilyl), TPS (triphenylsilyl), TBDPS (*tert*-butyldiphenylsilyl) and TIPS (triisopropylsilyl) ethers in several solvents (Table 3). While TIPS (**1d**) and TBDPS ethers (**1e**) were stable under hydrogenation conditions using Pd/C even in MeOH (entries 4 and 5), TES (**1b**) and TPS ethers (**1c**) were completely deprotected in MeOH as well as the TBDMS ether (**1a**) (entries 1–3). The cleavage of silyl ethers was apparently depressed in aprotic solvents such as THF and EtOAc (entries 6–8 and 11–13) and silyl ethers were nearly stable in MeCN (entries 16–18). Although a small amount of TBDMS deprotection was observed in THF, it was entirely stable in AcOEt and MeCN (compare entries 6 with 11 and 16). In THF and AcOEt, the TES ether (**1b**) was partially cleaved, but it was completely suppressed by the use of MeCN as a solvent (entry 17). On the other

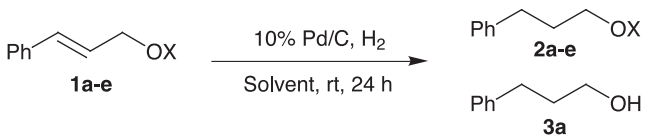
Table 2. Effect of the addition of a small amount of MeOH or H_2O into the reaction mixture of TBDMS ether (**1a**) in AcOEt or MeCN using 10% Pd/C[a] as a catalyst



Entry	Solvent	Additive[b]	Product	Yield (%)[c]
1	EtOAc	MeOH	**2a**	86
2	EtOAc	H_2O	**2a** (26),[d] **3a** (74)[d]	—
3	MeCN	MeOH	**2a**	100
4	MeCN	H_2O	**2a**	75

[a] 10% Pd/C was purchased from Aldrich (Aldrich product number 20,569-9).
[b] 0.1 mL of an additive/1 mL of EtOAc or MeCN.
[c] Isolated yield.
[d] The ratio was determined by ^{1}H NMR.

Table 3. Solvent effect toward the deprotection of various kinds of silyl ethers using 10% Pd/C[a]



Entry	Substrate	X	Solvent	Relative yield (%)[b]	
				2a–e	**3a**
1	**1a**	TBDMS	MeOH	0	100
2	**1b**	TES	MeOH	0	100
3	**1c**	TPS	MeOH	0	100
4	**1d**	TIPS	MeOH	100	0
5	**1e**	TBDPS	MeOH	100	0
6	**1a**	TBDMS	THF	98	2
7	**1b**	TES	THF	63	37
8	**1c**	TPS	THF	62	38
9	**1d**	TIPS	THF	100	0
10	**1e**	TBDPS	THF	100	0
11	**1a**	TBDMS	EtOAc	100	0
12	**1b**	TES	EtOAc	67	33
13	**1c**	TPS	EtOAc	100	0
14	**1d**	TIPS	EtOAc	100	0
15	**1e**	TBDPS	EtOAc	100	0
16	**1a**	TBDMS	MeCN	100	0
17	**1b**	TES	MeCN	100	0
18	**1c**	TPS	MeCN	97	3
19	**1d**	TIPS	MeCN	100	0
20	**1e**	TBDPS	MeCN	100	0

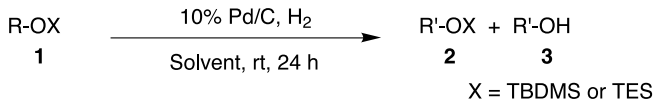
[a] 10% Pd/C was purchased from Aldrich (Aldrich product number 20,569-9).
[b] Determined by ^{1}H NMR.

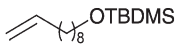
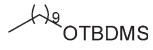
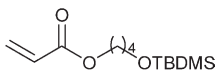
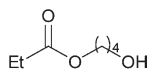
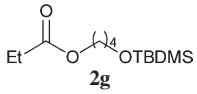
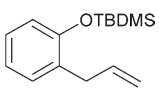
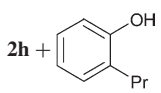
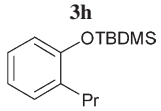
hand, partial TPS deprotection was observed in THF and MeCN while no cleavage of the TPS ether (**1c**) in AcOEt was achieved. Needless to say, TBDPS and TIPS ethers were quite stable under Pd/C-catalyzed hydrogenation condition in aprotic solvents (entries 9, 10, 14, 15, 19 and 20).

Next, we applied the present solvent effect to the chemoselective hydrogenation of some reducible functionalities in the presence of silyl ethers in AcOEt or MeCN and to the mild deprotection method of silyl ethers in MeOH. TBDMS or TES ethers (**1f–m**) possessing olefin or acetylene within a molecule were hydrogenated in MeOH, AcOEt or MeCN (Table 4). The reduction of olefin and the deprotection of the alkyl-*O*-TBDMS ether of **1f** or **1g** simultaneously proceeded to afford the corresponding saturated alcohols (**3f** or **3g**) (entries 1 and 3). However, the cleavage of the TBDMS group of **1h** and **1n–q** was incomplete under the hydrogenation conditions because of steric hindrance or an electronic factor (entry 5 and Fig. 1). In AcOEt olefin and benzyl ether functionalities of **1f–h** were hydrogenated chemoselectively to form the corresponding TBDMS ethers (**2f–h**) (entries 2, 4 and 6).

On the other hand, the TES ethers of primary (**1i** or **j**), secondary (**1k**), tertiary (**1l**) and phenolic (**1m**) alcohols possessing an olefin or acetylene functionality within the molecule were reduced and cleaved smoothly under the hydrogenation conditions in MeOH (entries 7, 9, 11, 13 and 15). On the contrary, during the hydrogenation of an olefin or acetylene functionality, the deprotection of the TES ether of aliphatic alcohols was not observed in MeCN (entries 8, 10, 12 and 14). While the TBDMS protective group of

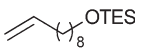
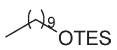
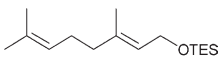
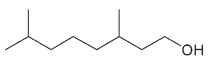
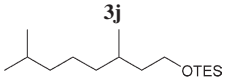
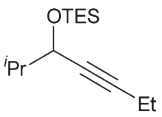
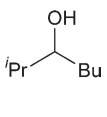
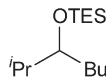
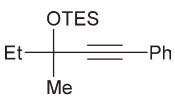
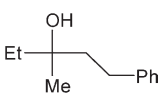
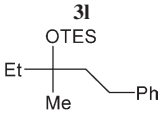
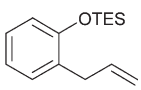
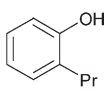
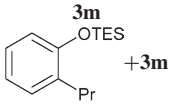
Table 4. Cleavage of the TBDMS or TES ethers and chemoselective hydrogenation using 10% Pd/C[a]



Entry	Substrate	Solvent	**2**:**3**[b]	Product	Yield (%)[c]
1	 **1f**	MeOH	0:100	 **3f**	80
2		AcOEt	100:0	 **2f**	98
3	 **1g**	MeOH	0:100	 **3g**	71
4		AcOEt	100:0	 **2g**	98
5	 **1h**	MeOH	92:8	 **2h** + **3h**	—
6		AcOEt	100:0	 **2h**	100

(*continued on next page*)

Table 4 (*continued*)

Entry	Substrate	Solvent	**2**:**3**[b]	Product	Yield (%)[c]
7	 **1i**	MeOH	0:100	 **3f**	94[d] (67)[e]
8		MeCN	100:0	 **2i**	99
9	 **1j**	MeOH	0:100	 **3j**	92[d] (45)[e]
10		MeCN	100:0	 **2j**	88
11	 **1k**	MeOH	0:100	 **3k**	90[d] (21)[e]
12		MeCN	100:0	 **2k**	93
13	 **1l**	MeOH	0:100	 **3l**	96
14		MeCN	100:0	 **2l**	98
15	 **1m**	MeOH	0:100	 **3m**	83
16		MeCN	3:97	 **2m**	-

[a] 10% Pd/C was purchased from Aldrich (Aldrich product number 20,569-9).
[b] Determined by ^{1}H NMR.
[c] Isolated yield.
[d] Product contaminated with a small amount of TES-OH.
[e] The yield of isolated and analytically pure product is indicated in parentheses. The low isolated yield is due to the volatile nature of the product and difficulty using silica gel column chromatography.

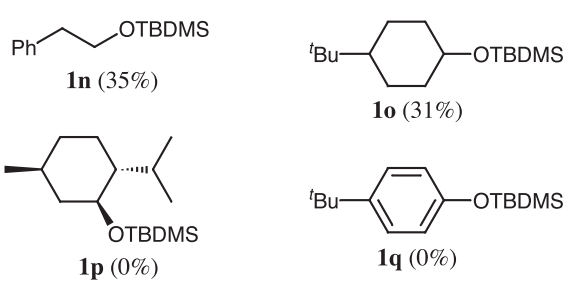
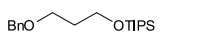
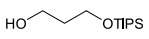
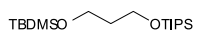
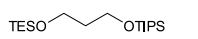
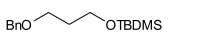
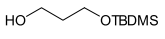
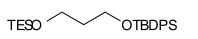
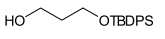
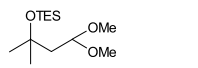
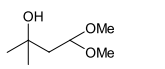


Figure 1. Cleavage of TBDMS ether in MeOH using 10% Pd/C (the ratio of desilylated mother alcohol was indicated in parentheses).

phenolic alcohols (**1h** and **1q**) was quite stable even in MeOH (entry 5 and Fig. 1), the TES protective group of the phenolic alcohol (**1m**) was deprotected easily not only in MeOH but also even in MeCN (entries 15 and 16).

Manipulation of functional groups is a fundamental process in synthetic organic chemistry and, hence, the development of new selective transformations remains of great interest.[11] Since hydroxyl groups are quite general functionalities of organic compounds, the development of a new, selective removal method of a specific protective group of hydroxyl groups among various protective groups is extremely important.[1,12] To examine the scope of our deprotection

Table 5. Selective deprotection under hydrogenation conditions in MeOH using 10% Pd/C[a]

Entry	Substrate	Time (h)	Product	Yield (%)[b]
1	 **1r**	30	 **3r**	86
2	 **1s**	26	**3r**	61
3	 **1t**	10	**3r**	100
4[c]	 **1u**	36	 **3u**	95
5	 **1v**	41	 **3v**	91
6	 **1w**	24	 **3w**	47[d]

[a] 10% Pd/C was purchased from Aldrich (Aldrich product number 20,569-9).
[b] Isolated yield.
[c] This reaction was performed in EtOAc.
[d] The low isolated yield is due to the volatile nature of the product and difficulty using silica gel column chromatography.

method using hydrogenation conditions, we have carried out a selective deprotection of Bn, TBDMS and TES protective groups of alcohols in the presence of other protective groups. The stability of the TIPS and TBDPS groups under the hydrogenation conditions (Table 3, entries 4 and 5) has been exploited for the selective deprotection of benzyl (**1r** and **1u**), TBDMS (**1s**) and TES ethers (**1t** and **1v**) in the presence of TIPS or TBDPS ether within the molecule. The results shown in Table 5 demonstrate that the selective deprotection of benzyl, TBDMS and TES ethers can be successfully carried out in the presence of TIPS or TBDPS ether using 10% Pd/C in MeOH or AcOEt as a solvent (entries 1–5).[12] The present procedure can be also applied to the chemoselective cleavage of a TES ether as distinguished from an acetal-type protective group (**1w**) (entry 6). Accordingly, this method may serve as a useful component to the existing methodologies and find applications in the synthesis of complicated molecules.

3. Conclusion

In summary, the cleavage of TBDMS, TES and TPS ethers under hydrogenation conditions using 10% Pd/C indicates significant solvent effect. While TIPS and TBDPS ethers were quite stable under the hydrogenation conditions in MeOH, THF, AcOEt and MeCN, TBDMS and TES protective groups were readily cleaved in MeOH. Consequently, Pd/C-catalyzed hydrogenation in MeOH can be applied to the convenient and neutral[8] deprotection method of TBDMS and TES protective groups in the presence of other protective groups. In contrast, the TBDMS ether was not deprotected under the hydrogenation conditions in AcOEt and MeCN at all, and the TES ether was stable in MeCN. Thus, chemoselective hydrogenation of reducible functionalities such as olefin, acetylene and benzyl ethers, as distinguished from TBDMS and TES ethers can be achieved using 10% Pd/C-catalyzed hydrogenation conditions in AcOEt or MeCN as a solvent. Since catalytic hydrogenation using Pd/C as a catalyst has found numerous applications in organic synthesis, the present solvent effect is extremely important information for synthetic organic chemists. The present mild and neutral deprotection method of TBDMS and TES protective groups will serve as a useful complement to the existing methodologies.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer, JEOL AL-400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz), or a GL-270 spectrometer (^{1}H: 270 MHz) with tetramethylsilane or residual protiated solvent used as a reference. EI and FAB Mass spectra were taken on a JEOL JMS-SX102A instrument. Elemental analyses were performed by YANACO CHN CORDER MT-5 instrument. Column chromatography was performed using Merck silica gel 60 (230–400 mesh). HPLC grade MeOH and H_2O and anhydrous EtOH were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification. Anhydrous hexane, cyclohexane, DMF, toluene, AcOEt and MeCN were purchased from Kanto Kagaku Co., Ltd. and used without further purification. THF was distilled from sodium benzophenone ketyl immediately prior to use. ^{t}BuOH and CH_2Cl_2 were distilled on CaH_2. 10% Pd/C was purchased from Aldrich (product number: 20,569-9). All other reagents were purchased from commercial sources and used without further purification.

4.2. General procedure for the synthesis of silyl ethers

Method A. To a solution of an alcohol, DMAP (0.01 equiv.), and Et_3N (1.2 equiv.) in CH_2Cl_2 (20 mL) was added silyl chloride (1.1 equiv.). The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with ether (50 mL) and washed with water (50 mL) and brine (50 mL). The organic layer were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

Method B. To a solution of an alcohol and imidazole (1.2 equiv.) in CH_2Cl_2 (20 mL) was added silyl chloride (1.2 equiv.). The reaction mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with ether (50 mL) and washed with water (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel.

4.2.1. 1-*tert*-Butyldimethylsilyloxy-3-phenyl-2-propene (1a).[13] With Method A, cinnamyl alcohol (1.34 g, 10.0 mmol), DMAP (48 mg, 0.40 mmol), Et_3N (1.21 g, 12.0 mmol), and *tert*-butyldimethylsilyl chloride (904 mg, 12.0 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1a**) as a colorless oil (2.20 g, 90%).

^{1}H NMR ($CDCl_3$): δ 7.38–7.20 (m, 5H), 6.59 (d, J=15.9 Hz, 1H), 6.28 (dt, J=4.9, 15.9 Hz, 1H), 4.35 (d, J=4.9 Hz, 2H), 0.94 (s, 9H), 0.11 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 137.1, 129.5, 129.1, 128.4, 127.3, 126.4, 63.9, 26.0, 18.4, −5.2.

4.2.2. 1-Triethylsilyloxy-3-phenyl-2-propene (1b).[14] With Method B, cinnamyl alcohol (671 mg, 5.00 mmol), imidazole (408 mg, 6.00 mmol), and triethylsilyl chloride (904 mg, 1.20 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1b**) as a colorless oil (717 mg, 93%).

^{1}H NMR ($CDCl_3$): δ 7.37 (d, J=7.5 Hz, 2H), 7.30 (t, J=7.5 Hz, 2H), 7.22 (t, J=7.5 Hz, 1H), 6.60 (d, J=16.1 Hz, 1H), 6.29 (dt, J=5.1, 16.1 Hz, 1H), 4.35 (d, J=5.1 Hz, 2H), 0.99 (t, J=7.9 Hz, 9H), 0.66 (q, J=7.9 Hz, 6H).

4.2.3. 1-Triphenylsilyloxy-3-phenyl-2-propene (1c). With Method B, cinnamyl alcohol (671 mg, 5.00 mmol), imidazole (408 mg, 6.00 mmol), and triphenylsilyl chloride (1.77 g, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1c**) as a colorless needles (1.14 g, 58%).

^{1}H NMR ($CDCl_3$): δ 7.67 (dd, J=1.47, 7.82 Hz, 6H), 7.48–7.19 (m, 14H), 6.59 (d, J=15.9 Hz, 1H), 6.29 (dt, J=5.1, 15.9 Hz, 1H), 4.51 (dd, J=1.47, 4.63 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 136.9, 135.4, 134.0, 130.1, 130.1, 128.4, 128.2, 127.9, 127.3, 126.4, 64.5. MS (EI) m/z 392 (M^+, 24%), 314 (22), 260 (22), 259 (100), 236 (23), 199 (45), 181 (22), 117 (16), 115 (15). Anal. Calcd for $C_{27}H_{24}OSi$: C, 82.61; H, 6.16. Found C, 82.49; H, 6.19.

4.2.4. 1-Triisopropylsilyloxy-3-phenyl-2-propene (1d). With Method B, cinnamyl alcohol (671 mg, 5.00 mmol), imidazole (408 mg, 6.00 mmol), and triisopropylsilyl chloride (1.16 g, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1d**) as a colorless oil (1.22 g, 85%).

^{1}H NMR ($CDCl_3$): δ 7.42–7.24 (m, 5H), 6.67 (d, J=15.6 Hz, 1H), 6.34 (dt, J=15.6, 4.9 Hz, 1H), 4.46 (dd, J=4.9, 1.5 Hz, 2H), 1.21–1.12 (m, 3H and 18H). ^{13}C NMR ($CDCl_3$): δ 137.3, 129.4, 129.0, 128.5, 127.2, 126.4, 63.9, 18.0, 12.1. MS (EI) m/z 290.5 (M^+, 20%), 248 (21), 247 (100), 117 (47), 115 (15). HRMS (EI) calcd for $C_{18}H_{30}OSi$ (M^+) 290.2066. Found 290.2057.

4.2.5. 1-*tert*-Butyldiphenylsilyloxy-3-phenyl-2-propene (1e).[15] With Method B, cinnamyl alcohol (335 mg, 2.50 mmol), imidazole (204 mg, 3.00 mmol), and *tert*-butyldiphenylsilyl chloride (825 mg, 3.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1e**) as a colorless oil (799 mg, 86%).

^{1}H NMR ($CDCl_3$): δ 7.71 (dd, J=1.5, 7.8 Hz, 4H), 7.45–7.20 (m, 11H), 6.64 (d, J=15.6 Hz, 1H), 6.28 (dt, J=4.9, 15.6 Hz, 1H), 4.38 (d, J=4.9 Hz, 2H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.2, 135.6, 133.6, 129.7, 129.4, 128.7, 128.5, 127.7, 127.3, 126.4, 64.5, 26.8, 19.3.

4.2.6. 1-*tert*-Butyldimethylsilyloxy-9-decene (1f).[16] With Method A, 9-decen-1-ol (1.56 g, 10.0 mmol), DMAP (48 mg, 0.40 mmol), Et_3N (1.20 g, 12.0 mmol), and *tert*-butyldimethylsilyl chloride (1.66 g, 11.0 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1f**) as a colorless oil (1.81 g, 67%).

^{1}H NMR ($CDCl_3$): δ 5.89–5.73 (m, 1H), 5.30–4.90 (m, 2H), 3.59 (t, J=5.6 Hz, 2H), 2.07–2.00 (m, 2H), 1.53–1.29 (m, 12H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 139.1, 114.1, 63.3, 33.8, 32.9, 29.5, 29.4, 29.1, 29.0, 26.0, 25.8, 18.4, −5.3.

4.2.7. 4-*tert*-Butyldimethylsilyloxy-1-butyl acrylate (1g). With Method A, 4-hydroxybutyl acrylate (2.88 g, 20.0 mmol), DMAP (98 mg, 0.80 mmol), Et_3N (2.23 g, 22.0 mmol), and *tert*-butyldimethylsilyl chloride (3.17g, 21.0 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1g**) as a colorless oil (5.04 g, 98%).

^{1}H NMR ($CDCl_3$): δ 6.40 (dd, J=1.3, 17.5 Hz, 1H), 6.12 (dd, J=1.05, 17.5 Hz, 1H), 4.18 (t, J=6.5 Hz, 2H), 3.65 (t, J=6.5 Hz, 2H), 1.78–1.71 (m, 2H), 1.64–1.57 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.0, 130.2, 128.6, 64.3, 62.4, 29.1, 25.8, 25.2, 18.2, −5.5. MS (EI) m/z 201 ($M^+-C_4H_9$, 10%), 129 (100), 75 (15), 55 (35). HRMS (EI) calcd for $C_9H_{17}O_3Si$ ($M^+-C_4H_9$) 201.0947. Found 201.0939.

4.2.8. 1-*tert*-Butyldimethylsilyloxy-2-(2-propenyl)benzene (1h).[17] With Method B, 2-allylphenol (1.34 g, 10.0 mmol), imidazole (1.36 g, 20.0 mmol), and *tert*-butyldimethylsilyl chloride (1.80 g, 12.0 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1h**) as a colorless oil (1.89 g, 76%).

^{1}H NMR ($CDCl_3$): δ 7.13 (d, J=7.6 Hz, 1H), 7.08 (t, J=7.6 Hz, 1H), 6.89 (t, J=7.6 Hz, 1H), 6.78 (d, J=7.6 Hz, 1H), 6.02–5.92 (m, 1H), 5.05 (s, 1H), 5.02 (d, J=3.9 Hz, 1H), 3.37 (d, J=6.8 Hz, 2H), 1.01 (s, 9H), 0.23 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 153.4, 137.0, 130.7, 130.2, 127.0, 121.1, 118.4, 115.4, 34.4, 25.8, 18.3, −4.1.

4.2.9. 1-Triethylsilyloxy-9-decene (1i). With Method A, 9-decene-1-ol (753 mg, 4.80 mmol), DMAP (110 mg, 0.90 mmol), triethylsilyl chloride (1.00 g, 7.23 mmol) in pyridine (10 mL) used as a solvent instead of CH_2Cl_2. The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1i**) as a colorless oil (1.11 g, 85%).

^{1}H NMR ($CDCl_3$): δ 5.86–5.76 (m, 1H), 4.99 (dd, J=2.0, 17.1 Hz, 1H), 4.92 (dd, J=2.0, 10.3 Hz, 1H), 3.59 (t, J=6.8 Hz, 2H), 2.03 (q, J=7.0 Hz, 2H), 1.55–1.51 (m, 2H), 1.37–1.29 (m, 10H), 0.95 (t, J=8.0 Hz, 9H), 0.60 (q, J=8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 139.2, 114.1, 63.0, 33.8, 32.9, 29.5, 29.4, 29.1, 28.9, 25.8, 6.8, 4.5. MS (EI) m/z 271

($M^+-C_2H_5$), 213 (15%), 103 (100), 75 (33), 57 (15), 55 (14). HRMS (EI) calcd for $C_{16}H_{34}OSi$ ($M^+-C_2H_5$) 241.1975. Found 241.1988.

4.2.10. Geranyl triethylsilyl ether (1j).[18] With Method B, geraniol (771 mg, 5.00 mmol), imidazole (409 mg, 6.00 mmol), and triethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1j**) as a colorless oil (1.07 g, 86%).

^{1}H NMR ($CDCl_3$): δ 5.33 (t, J=6.0 Hz, 1H), 5.10 (t, J=7.3 Hz, 1H), 4.18 (d, J=6.0 Hz, 2H), 2.10 (q, J=7.3 Hz, 2H), 2.01 (t, J=7.3 Hz, 2H), 1.67 (s, 3H), 1.63 (s, 3H), 1.60 (s, 3H), 0.97 (t, J=8.0 Hz, 9H), 0.61 (q, J=8.0 Hz, 6H). HRMS (EI) calcd for $C_{16}H_{32}OSi$ (M^+): 268.2222. Found: 268.2230.

4.2.11. 7-Methyl-5-triethylsilyloxy-3-octyne (1k). With Method B, 2-methyl-5-octyne-4-ol (701 mg, 5.00 mmol), imidazole (408 mg, 6.00 mmol), and triethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1k**) as a colorless oil (1.09 g, 86%).

^{1}H NMR ($CDCl_3$): δ 4.38 (t, J=7.1 Hz, 1H), 2.20 and 2.19 (each q, J=7.4 Hz, 1H), 1.84–1.78 (m, 1H), 1.61–1.43 (m, 2H), 1.12 (t, J=7.4 Hz, 3H), 0.98 (t, J=7.8 Hz, 9H), 0.91 and 0.90 (each d, J=6.6 Hz, 3H), 0.72–0.62 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 85.6, 81.4, 61.4, 48.2, 24.6, 22.7, 22.5, 13.8, 12.4, 6.8, 4.9. MS (EI) *m/z* 225 ($M^+-C_2H_5$, 100%), 197 (35), 171 (18), 141 (20), 111 (36), 103 (21), 75 (19), 44 (24). HRMS (EI) calcd for $C_{15}H_{30}OSi$ ($M^+-C_2H_5$) 225.1634. Found 225.1675.

4.2.12. 1-Phenyl-3-methyl-3-triethylsilyloxy-1-pentyne (1l). With Method B, 1-phenyl-3-methyl-1-pentyne-3-ol (871 mg, 5.00 mmol), imidazole (613 mg, 9.00 mmol), and triethylsilyl chloride (1.36 g, 9.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1l**) as a colorless oil (1.31 g, 91%).

^{1}H NMR ($CDCl_3$): δ 7.41–7.38 (m, 2H), 7.31–7.29 (m, 3H), 1.79–1.68 (m, 2H), 1.55 (s, 3H), 1.04 (t, J=7.3 Hz, 3H), 0.98 (t, J=7.7 Hz, 9H), 0.71 (q, J=7.7 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 131.4, 128.3, 128.0, 123.3, 93.8, 83.5, 70.0, 38.2, 30.5, 9.1, 7.1, 6.1. MS (EI) *m/z* 259 ($M^+-C_2H_5$, 100%), 187 (10), 149 (13), 61 (9), 44 (53). HRMS (EI) calcd for $C_{16}H_{23}OSi$ ($M^+-C_2H_5$) 259.1518. Found 259.1523.

4.2.13. 1-Triethylsilyloxy-2-(2-propenyl)benzene (1m). With Method B, 2-allylphenol (671 mg, 5.00 mmol), imidazole (408 mg, 6.00 mmol), and triethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1m**) as a colorless oil (1.27 g, 85%).

^{1}H NMR ($CDCl_3$): δ 7.12 (d, J=7.6 Hz, 1H), 7.07 (t, J=7.6 Hz, 1H), 6.88 (t, J=7.6 Hz, 1H), 6.78 (d, J=7.6 Hz, 1H), 6.02–5.92 (m, 1H), 5.07–5.02 (m, 2H), 3.37 (d, J=6.4 Hz, 2H), 1.00 (t, J=7.7 Hz, 6H), 0.77 (q, J=7.7 Hz, 9H). ^{13}C NMR ($CDCl_3$): δ 153.5, 137.1, 130.6, 130.0, 127.0, 121.0, 118.2, 115.3, 34.5, 6.7, 5.3. MS (FAB, NBA) *m/z* 249 (M^++H, 10%), 248 (15), 219 (11). HRMS (EI) calcd for $C_{15}H_{24}OSi$ (M^+) 248.1597. Found 248.1623.

4.2.14. 1-*tert*-Butyldimethylsilyloxy-2-phenylethane (1n).[19] With Method B, 2-phenylethan-1-ol (335 mg, 2.50 mmol), imidazole (204 mg, 3.00 mmol), and *tert*-butyldimethyl chloride (825 mg, 3.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1n**) as a colorless oil (799 mg, 86%).

^{1}H NMR ($CDCl_3$): δ 7.67 (dd, J=1.5, 7.8 Hz, 4H), 7.44–7.15 (m, 16H), 3.69 (t, J=6.4 Hz, 2H), 2.72 (t, J=7.8 Hz, 2H), 1.91–1.84 (m, 2H), 1.07 (s, 9H).

4.2.15. 1-*tert*-Butyldimethylsilyloxy-4-*tert*-butylcyclohexane (1o).[15] With Method A, 4-*tert*-butylcyclohexanol (781 mg, 5.00 mmol), DMAP (48 mg, 0.40 mmol), Et_3N (607 mg, 6.00 mmol), and *tert*-butyldimethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1o**) as a colorless oil (718 mg, 53%).

^{1}H NMR ($CDCl_3$): δ 3.51–3.43 (m, 1H), 1.89–1.86 (m, 2H), 1.75–1.72 (m, 2H), 1.29–1.21 (m, 2H), 1.04–0.91 (m, 3H), 0.88 (s, 9H), 0.84 (s, 9H), 0.05 (s, 6H).

4.2.16. (−)-Menthyl *tert*-butyldimethylsilyl ether (1p).[20] With Method A, (−)-menthol (781 mg, 5.00 mmol), DMAP (48 mg, 0.40 mmol), Et_3N (607 mg, 6.00 mmol), and *tert*-butyldimethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1p**) as a colorless oil (639 mg, 47%).

^{1}H NMR ($CDCl_3$): δ 3.37 (dt, J=4.2, 10.3 Hz, 1H), 3.40–3.34 (m, 1H), 2.60–2.18 (m, 1H), 1.86–1.83 (m, 1H), 1.64–1.57 (m, 1H), 1.38–1.32 (m, 1H), 1.58–1.09 (m, 1H), 1.04–0.77 (m, 4H), 0.90 (s, 6H), 0.88 (s, 9H), 0.72 (d, J=6.8 Hz, 3H), 0.06 (s, 3H), 0.05 (s, 3H).

4.2.17. 1-*tert*-Butyldimethylsilyloxy-4-*tert*-butylbenzene (1q).[21] With Method A, 4-*tert*-butylphenol (751 mg, 5.00 mmol), DMAP (48 mg, 0.40 mmol), Et_3N (607 mg, 6.00 mmol), and *tert*-butyldimethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1q**) as a colorless oil (743 mg, 56%).

^{1}H NMR ($CDCl_3$): δ 7.22 and 6.75 (each d, J=8.3 Hz, 4H), 1.28 (s, 9H), 0.97 (s, 9H), 0.19 (s, 6H).

4.2.18. 1-Benzyloxy-3-triisopropylsilyloxypropane (1r). With Method B, 3-benzyloxy-1-propanol (831 mg, 5.00 mmol), imidazole (408 mg, 6.00 mmol), and triisopropylsilyl chloride (1.16 g, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane/ether 10:1) to give the title compound (**1r**) as a colorless oil (1.46 g, 91%).

^{1}H NMR ($CDCl_3$): δ 7.34–7.26 (m, 5H), 4.51 (s, 2H), 3.80 (t, J=6.2 Hz, 2H), 3.60 (t, J=6.2 Hz, 2H), 1.88–1.82 (m, 2H), 1.11–1.00 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 138.7, 128.3, 127.6, 127.4, 73.0, 67.2, 60.2, 33.2, 18.0, 12.0. MS (FAB, NBA) m/z 323 (M^++H, 12%), 91 (100). HRMS (FAB, NBA) calcd for $C_{19}H_{35}O_2Si$ (M^++H) 323.2406. Found 323.24103.

4.2.19. 1-*tert*-Butyldimethylsiyloxy-3-triisopropylsilyloxypropane (1s).[22] After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of 1-benzyloxy-3-triisopropylsilyloxypropane (**1r**) (1.40 g, 5.00 mmol), 10% Pd/C (70.1 mg, 5 wt% of the substrate) in solvent (10 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20 °C) for 24 h. The reaction mixture was filtered using a membrane filter (Millex®-LG, 0.20 μm) and the filtrate was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluting with hexane/ether 5:1) to afford 3-triisopropylsilyloxypropan-1-ol (**3r**) as a colorless oil (1.70 g, 73%). ^{1}H NMR ($CDCl_3$): δ 3.94 (t, J=5.4 Hz, 2H), 3.84 (q, J=5.4 Hz, 2H), 2.76 (t, J=5.4 Hz, OH), 1.83–1.78 (m, 2H), 1.17–1.03 (m, 21H). ^{13}C NMR ($CDCl_3$): δ 63.6, 62.7, 34.2, 17.9, 11.8. MS (FAB, NBA) m/z 233 (M^++H, 60%), 189 (36). HRMS (FAB, NBA) calcd for $C_{12}H_{28}O_2Si$ (M^++H) 233.1937. Found 233.1930. With Method A, **3r** (403 mg, 1.70 mmol), DMAP (37 mg, 0.30 mmol), Et_3N (202 mg, 2.00 mmol), and *tert*-butyldimethylsilyl chloride (301 mg, 3.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1s**) as a colorless oil (449 mg, 67%).

^{1}H NMR ($CDCl_3$): δ 3.76 (t, J=6.1 Hz, 2H), 3.73 (t, J=6.1 Hz, 2H), 1.77–1.71 (m, 2H), 1.13–1.01 (m, 21H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 60.0, 59.8, 36.1, 25.9, 18.3, 12.0, −5.4. MS (FAB, NBA) m/z 347 (M^++H, 21%), 303 (40), 157 (25), 115 (28), 73 (100). HRMS (FAB, NBA) calcd for $C_{18}H_{43}O_2Si_2$ (M^+) 347.2817. Found 347.2802.

4.2.20. 1-Triethylsilyloxy-3-triisopropylsilyloxypropane (1t). With Method A, 3-triisopropylsilyloxypropan-1-ol (**3r**) (465 mg, 2.00 mmol), DMAP (49 mg, 0.40 mmol), Et_3N (243 mg, 2.40 mmol), and triethylsilyl chloride (362 mg, 2.40 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane/ether 10:1) to give the title compound (**1t**) as a colorless oil (603 mg, 87%).

^{1}H NMR ($CDCl_3$): δ 3.77 (t, J=6.2 Hz, 2H), 3.73 (t, J=6.2 Hz, 2H), 1.79–1.73 (m, 2H), 1.11–1.00 (m, 21H), 0.96 (t, J=8.0 Hz, 9H), 0.60 (q, J=8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 60.1, 59.7, 36.2, 18.0, 12.0, 6.8, 4.4. MS (FAB, NBA) m/z 347 (M^++H, 40%), 303 (62), 245 (28), 157 (40), 115 (99), 87 (82), 59 (40). HRMS (FAB, NBA) calcd for $C_{18}H_{43}O_2Si_2$ (M^++H) 347.2802. Found 347.2806.

4.2.21. 3-*tert*-Butyldimethylsilyloxy-1-propyl benzyl ether (1u). With Method A, 3-benzyloxy-1-propanol (831 mg, 5.00 mmol), DMAP (48 mg, 0.40 mmol), Et_3N (607 g, 6.00 mmol), and *tert*-butyldimethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane) to give the title compound (**1u**) as a colorless oil (1.26 g, 90%).

^{1}H NMR ($CDCl_3$): δ 7.34–7.26 (m, 5H), 4.50 (s, 2H), 3.72 (t, J=6.4 Hz, 2H), 3.57 (t, J=6.4 Hz, 2H), 1.82 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 138.6, 128.3, 127.6, 127.4, 72.9, 67.0, 59.9, 33.0, 25.9, 18.3, −5.4. MS (FAB, NBA) m/z 281 (M^++H, 28%), 91 (100), 73 (19). HRMS (FAB, NBA) calcd for $C_{16}H_{29}O_2Si$ (M^++H) 281.1937. Found 281.1933.

4.2.22. 1-*tert*-Butyldiphenylsiyloxy-3-triethylsilyloxypropane (1v). To a solution of 1,3-propandiol (761 mg, 10.0 mmol), diisopropylethylamine (1.29 g, 10.0 mmol) in CH_2Cl_2 (20 mL) was added *tert*-butyldiphenylsilyl chloride (2.75 mg, 10.0 mmol). The reaction mixture was stirred at room temperature for 19 h. The reaction mixture was diluted with ether (50 mL) and washed with saturated NH_4Cl solution (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (eluting with hexane/ether 2:1) to afford 3-*tert*-butyldiphenylsilyloxypropan-1-ol (**3v**)[23] as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.68 (dd, J=1.5, 7.8 Hz, 4H), 7.46–7.38 (m, 6H), 3.87–3.83 (m, 4H), 2.36 (t, J=5.6 Hz, OH), 1.84–1.78 (m, 2H), 1.06 (s, 9H). With Method A, **3v** (944 mg, 3.00 mmol), DMAP (37 mg, 0.3 mmol), imidazole (245 mg, 3.60 mmol) instead of Et_3N, and triethylsilyl chloride (453 mg, 3.60 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane/ether 20:1) to give the title compound (**1v**) as a colorless oil (1.23 g, 96%).

^{1}H NMR ($CDCl_3$): δ 7.67 (dt, J=1.5, 7.8 Hz, 4H), 7.44–7.35 (m, 6H), 3.77–3.73 (m, 4H), 1.81–1.74 (m, 2H), 0.94 (t, J=8.0 Hz, 9H), 0.59 (q, J=8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 135.6, 134.0, 129.5, 127.5, 60.6, 59.6, 35.8, 26.8, 19.2, 6.8, 4.4. MS (FAB, NBA) m/z 429 (M^++H, 10%), 371 (29), 197 (12), 87 (35). Anal. Calcd for $C_{25}H_{40}O_2Si_2$: C, 70.03; H, 9.40. Found C, 70.19; H, 9.77.

4.2.23. 4,4-Dimethoxy-2-methyl-2-triethylsilyloxybutane (1w). With Method A, 4,4-dimethoxy-2-methyl-2-butanol (**3w**) (741 mg, 5.00 mmol), DMAP (61 mg, 0.50 mmol), imidazole (408 mg, 6.00 mmol), and triethylsilyl chloride (904 mg, 6.00 mmol). The crude product was purified by column chromatography on silica gel (eluting with hexane/ether 10:1) to give the title compound (**1w**) as a colorless oil (1.36 g, 91%).

^{1}H NMR ($CDCl_3$): δ 4.60 (t, J=4.9 Hz, 1H), 3.31 (s, 6H), 1.75 (d, J=4.9 Hz, 2H), 1.25 (s, 6H), 0.95 (t, J=7.8 Hz, 9H), 0.58 (q, J=7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 102.6, 72.0, 52.5, 47.3, 30.4, 7.1, 6.7. MS (EI) 175 (85), 117 (100), 89 (23), 75 (40). Anal. Calcd for $C_{13}H_{30}O_3Si$ 1/3H_2O: C, 58.16; H, 11.50. Found C, 82.49; H, 6.19.

4.3. General procedure for solvent effect toward the deprotection of the TBDMS ether (1a) using 10% Pd/C (Table 1)

After two vacuum/H_2 cycles to remove air from the reaction

tube, the stirred mixture of 1-*tert*-butyldimethylsilyloxy-3-phenyl-2-propene (**1a**) (62.0 mg, 0.25 mmol), 10% Pd/C (6.2 mg, 10 wt% of the substrate) in solvent (1 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20 °C) for 24 h. The reaction mixture was filtered using a membrane filter (Millex®-LG, 0.20 μm) and the filtrate was concentrated under reduced pressure to afford a colorless oil. (When using H_2O as a solvent, ether was added to the reaction mixture and filtrated using a membrane filter (Millex®-LG, 0.20 μm). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure to afford the colorless oil. The ratio of the 1-*tert*-butyldimethylsilyloxy-3-phenylpropane (**2a**) (86%, entry 10) and 3-phenyl-1-propanol (**3a**) (88%, entry 1) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$.

4.3.1. 1-*tert*-Butyldimethylsilyloxy-3-phenylpropane (2a).[24] 86% yield as a colorless oil (entry 10). ^{1}H NMR ($CDCl_3$): δ 7.67 (dd, J=1.5, 7.8, 4H), 7.44–7.15 (m, 16H), 3.69 (t, J=6.4 Hz, 2H), 2.72 (t, J=7.8 Hz, 2H), 1.91–1.84 (m, 2H), 1.07 (s, 9H).

4.4. General procedure for effect of the addition of a small amount of MeOH or H_2O into the reaction mixture of TBDMS ether (1a) in AcOEt or MeCN using 10% Pd/C as a catalyst (Table 2)

After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of 1-*tert*-butyldimethylsilyloxy-3-phenyl-2-propene (**1a**) (62.0 mg, 0.25 mmol), 10% Pd/C (6.2 mg, 10 wt% of the substrate) and MeOH or H_2O (0.1 mL) in EtOAc or MeCN (1 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20 °C) for 24 h. The reaction mixture was filtered using a membrane filter (Millex®-LG, 0.20 μm,) and the filtrate was concentrated under reduced pressure to afford the colorless oil. The ratio of the 1-*tert*-butyldimethylsilyloxy-3-phenylpropane (**2a**) and 3-phenyl-1-propanol (**3a**) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$.

4.5. General procedure for solvent effect toward the deprotection of the silyl ethers using 10% Pd/C (Table 3)

After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of a silyl ether (**1a**–**e**) (0.25 mmol), 10% Pd/C (10 wt% of the substrate) in solvent (1 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20 °C) for 24 h. The reaction mixture was filtered using a membrane filter (Millex®-LG, 0.20 μm) and the filtrate was concentrated under reduced pressure to afford the colorless oil. The ratio of the corresponding silyl ether (**2a**–**e**) and 3-phenyl-1-propanol (**3a**) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$.

4.5.1. 1-Triethylsilyloxy-3-phenylpropane (2b).[14] 91% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.29–7.15 (m, 5H), 3.64 (t, J=6.4 Hz, 2H), 2.68 (t, J=7.8 Hz, 2H), 1.89–1.82 (m, 2H), 0.96 (t, J=8.0 Hz, 9H), 0.60 (q, J=8.0 Hz, 6H).

4.5.2. 1-Triphenylsilyloxy-3-phenylpropane (2c). 100% yield as a colorless solid. ^{1}H NMR ($CDCl_3$): δ 7.63 (dd, J=1.6, 8.1 Hz, 6H), 7.46–7.36 (m, 10H), 7.26–7.11 (m, 4H), 3.83 (t, J=6.9 Hz, 2H), 2.71 (t, J=6.9 Hz, 2H), 1.92–1.88 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 142.1, 135.4, 135.2, 134.4, 130.0, 128.5, 128.3, 127.9, 125.7, 63.1, 34.1, 32.1. MS (FAB, NBA) m/z 395 (M^++H, 40%), 317 (25), 259 (40), 199 (30), 118 (30), 91 (35). Anal. Calcd for $C_{27}H_{26}OSi$ 1/10H_2O: C, 81.81; H, 6.66. Found C, 81.87; 6.58.

4.5.3. 1-Triisopropylsilyloxy-3-phenylpropane (2d). 93% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.29–7.17 (m, 5H), 3.71 (t, J=6.1 Hz, 2H), 2.71 (t, J=7.8 Hz, 2H), 1.89–1.82 (m, 2H), 1.12–1.04 (m, 3H and 18H). ^{13}C NMR ($CDCl_3$): δ 142.4, 128.5, 128.2, 125.6, 62.6, 34.7, 32.1, 18.0, 12.0, 11.8. MS (EI) m/z 249 ($M^+-C_3H_7$, 100%). HRMS (EI) calcd for $C_{15}H_{25}OSi$ ($M^+-C_3H_7$) 249.1675. Found 249.1667.

4.5.4. 1-*tert*-Butyldiphenylsilyloxy-3-phenylpropane (2e).[25] 99% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.67 (dd, J=1.5, 7.8 Hz, 4H), 7.44–7.15 (m, 16H), 3.69 (t, J=6.4 Hz, 2H), 2.72 (t, J=7.8 Hz, 2H), 1.91–1.84 (m, 2H), 1.07 (s, 9H).

4.6. General procedure for cleavage of the TBDMS or TES ethers and chemoselective hydrogenation using 10% Pd/C (Table 4)

After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of a silyl ether (**1f**–**n**) (0.25 mmol), 10% Pd/C (10 wt% of the substrate) in MeOH or AcOEt or MeCN (1 mL) was hydrogenated at ambient pressure (balloon) and temperature (ca. 20 °C). The reaction mixture was filtered using a membrane filter (Millex®-LG, 0.20 μm) and the filtrate was concentrated under reduced pressure to afford a colorless oil. The ratio of the corresponding silyl ether (**2f**–**m**) and corresponding alcohol (**3f**-**3m**) was confirmed by ^{1}H NMR of the crude mixture in $CDCl_3$. The crude material was purified by flash column chromatography on silica gel (eluting with hexane/ether 20:1 for **3f**, hexane/ether 10:1 for **3g**, hexane/ether 10:1 for **3k**, hexane/ether 10:1 for **3l**, hexane/ether 20:1 for **3n**) to give **3f** (80%, entry 1), **3f** (67%, entry 7), **3g** (71%), **3k** (21%), **3l** (96%), **3m** (83%) as a colorless oil. ^{1}H NMR were comparable with each authentic sample.

4.6.1. 1-*tert*-Butyldimethylsilyloxydecane (2f).[26] 98% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.59 (t, J=6.6 Hz, 2H), 1.55–1.51 (m, 2H), 1.35–1.26 (m, 14H), 0.89 (s, 9H), 0.88 (t, J=7.3 Hz, 3H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 63.3, 32.9, 31.9, 29.7, 29.6, 29.5, 29.4, 26.0, 25.8, 22.7, 18.4, 14.1, −5.3.

4.6.2. 4-*tert*-Butyldimethylsilyloxybutyl propionate (2g). 98% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 4.09 (t, J=6.3 Hz, 2H), 3.63 (t, J=6.3 Hz, 2H), 2.32 (q, J=7.7 Hz, 2H), 1.61–1.56 (m, 2H), 1.16–1.12 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 174.5, 64.2, 62.6, 29.2, 27.6, 25.9, 25.2, 18.3, 9.2, −5.3. MS (FAB, NBA) m/z 261 (M^++H, 50%), 203 (37), 187 (62), 131 (139), 73 (45), 57 (38). HRMS (FAB, NBA) calcd for $C_{13}H_{29}O_3Si$ (M^++H) 261.1886. Found 261.1886.

4.6.3. 1-*tert*-Butyldimethylsilyloxy-2-propylbenzene (2h). 100% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ

7.12 (d, J=7.6 Hz, 1H), 7.05 (t, J=7.6 Hz, 1H), 6.87 (t, J=7.6 Hz, 1H), 6.77 (d, J=7.6 Hz, 1H), 2.55 (t, J=7.5 Hz, 2H), 1.58 (hex, J=7.5 Hz, 2H), 1.02 (s, 9H), 0.94 (t, J=7.5 Hz, 3H), 0.23 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 153.5, 133.3, 130.2, 126.5, 120.9, 118.3, 32.7, 25.8, 23.3, 18.2, 14.1, −4.2. Anal. Calcd for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46. Found: C, 71.68; H, 10.60.

4.6.4. 1-Triethylsilyloxydecane (2i). 99% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.59 (t, J=6.6 Hz, 2H), 1.54–1.51 (m, 2H), 1.36–1.22 (m, 14H), 0.96 (t, J=7.9 Hz, 9H), 0.89 (t, J=6.8 Hz, 3H), 0.55 (q, J=7.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 63.0, 32.9, 31.9, 29.6, 29.6, 29.5, 29.3, 25.8, 22.7, 14.1, 6.8, 4.4. MS (FAB: NBA) m/z 273 (M^++H, 10%), 271 (8), 243 (25), 214 (42), 115 (22), 103 (20). HRMS (FAB: NBA) calcd for $C_{16}H_{36}OSi$ (M^++H) 273.2614. Found 273.2610.

4.6.5. 3,7-Dimethyl-1-triethylsilyloxyoctane (2j). 88% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.67–3.58 (m, 2H), 1.61–1.48 (m, 4H), 1.37–1.31 (m, 4H), 1.28–1.10 (m, 2H), 0.96 (t, J=7.8 Hz, 9H), 0.88–0.86 (m, 9H), 0.60 (q, J=7.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 61.2, 40.1, 39.3, 37.4, 29.6, 28.0, 24.7, 22.7, 22.6, 19.8, 6.8, 4.5. MS (EI) 243 ($M^+-C_2H_5$, 100), 205 (46), 83 (83), 57 (53). HRMS (EI) calcd for $C_{14}H_{31}OSi$ ($M^+-C_2H_5$) 243.2154. Found 243.2144.

4.6.6. 2-Methyl-4-triethylsilyloxyoctane (2k). 93% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.73–3.67 (m, 1H), 1.72–1.63 (m, 1H), 1.44–1.22 (m, 8H), 0.69 (t, J=7.9 Hz, 9H), 0.89–0.87 (m, 9H), 0.60 (q, J=7.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 70.6, 46.7, 37.5, 27.4, 24.5, 23.2, 22.9, 22.8, 14.1, 7.0, 5.2. MS (EI) 229 ($M^+-C_2H_4$, 99%), 201 (55), 173 (22), 115 (26), 103 (100), 87, (21), 75 (37), 44 (20). MS (EI) m/z 229 ($M^+-C_2H_5$, 99%), 201 (55), 173 (22), 115 (26), 103, (100), 75 (37). HRMS (EI) calcd for $C_{13}H_{29}OSi$ ($M^+-C_2H_5$) 229.1988. Found 229.1981.

4.6.7. 3-Methyl-1-phenyl-3-(triethylsilyl)oxypentane (2l). 98% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 7.30–7.27 (m, 2H), 7.26–7.14 (m, 3H), 2.66–2.60 (m, 2H), 1.75–1.68 (m, 2H), 1.55 (q, J=7.4 Hz, 2H), 1.23 (s, 3H), 0.97 (t, J=7.9 Hz, 9H), 0.88 (t, J=7.4 Hz, 3H), 0.60 (q, J=7.9 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 143.3, 128.3, 125.5, 75.5, 43.7, 34.8, 30.6, 27.2, 8.8, 7.2, 7.0. MS (EI) m/z 263 ($M^+-C_2H_5$, 93%), 187 (33), 160 (13), 131 (10), 115, (20), 103 (100), 91 (23), 75 (26), 44 (14). HRMS (EI) calcd for $C_{16}H_{27}OSi$ ($M^+-C_2H_5$) 263.1831. Found 263.1824.

4.6.8. 1-Triethylsilyloxy-2-propylbenzene (2m).[27] The crude material was purified by flash column chromatography on silica gel (eluting with hexane) to afford **2n** as a colorless oil (3% yield). ^{1}H NMR ($CDCl_3$): δ 7.11 (d, J=7.6 Hz, 1H), 7.04 (t, J=7.6 Hz, 1H), 6.86 (t, J=7.6 Hz, 1H), 6.76 (d, J=7.6 Hz, 1H), 2.56 (t, J=7.6 Hz, 1H), 1.65–1.54 (m, 2H), 1.00 (t, J=7.7 Hz, 9H), 0.94 (t, J=7.6 Hz, 3H), 0.77 (q, J=7.7 Hz, 6H).

4.7. General procedure for selective deprotection under the hydrogenation condition in MeOH using 10% Pd/C (Table 5)

After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of silyl ether (**1r**–**w**) (0.25 mmol), 10% Pd/C (10 wt% of the substrate) in MeOH was hydrogenated at ambient pressure (balloon) and temperature (ca. 20 °C). The reaction mixture was filtered using a membrane filter (Millex®-LG or LH, 0.20 μm, 0.45 μm) and the filtrate was concentrated under reduced pressure to afford a colorless oil. The crude material was purified by flash column chromatography on silica gel (eluting with hexane/ether 5:1 for **3r**, hexane/ether 95:5 for **3v**, hexane/ether 10:1 for **3w**) to give **3r** (86%, entry 1), (61%, entry 2), (100%, entry 3), **3u** (95%), **3v** (91%) and **3w** (47%) as colorless oils. These samples were identified with commercial samples.

4.7.1. 3-*tert*-Butyldimethylsilyloxy-1-propanol (3u).[28] 95% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.84 (t, J=5.6 Hz, 2H), 3.84–3.80 (m, 2H), 2.61 (brs, 1H), 1.81–1.76 (m, 2H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 63.0, 62.5, 34.1, 25.9, 18.2, −5.5.

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