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**ALKYL- AND ARYLATION OF OXACYCLIC ETHERS WITH
TRIETHYLSILYL TRIFLATE—2,4,6-COLLIDINE—GILMAN
REAGENT COMBINATION: REMARKABLE DISCRIMINATION OF
TWO ETHER OXYGENS[†]**

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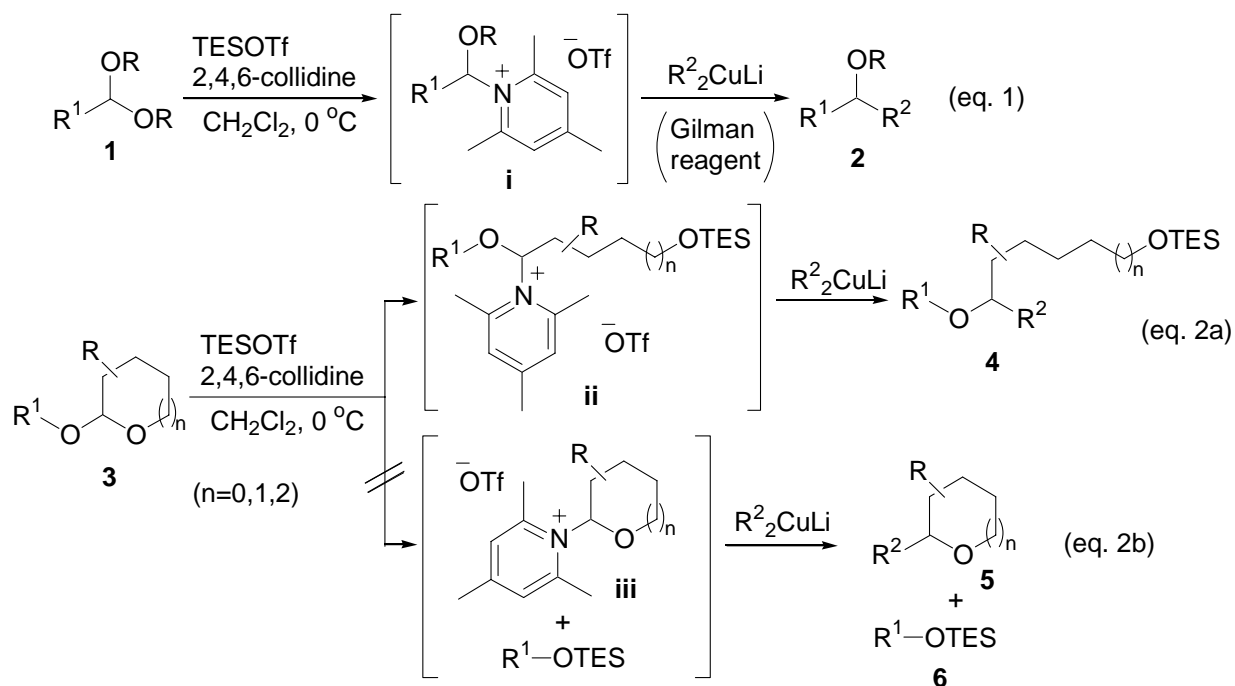
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Abstract – The alkylation reaction of oxacyclic ethers such as THP-ethers, THF-ethers, etc., has been developed. The treatment of oxacyclic ether with TESOTf and 2,4,6-collidine gives the collidinium salt intermediate obtained by the reaction of the cyclic oxygen atom. The addition of Gilman reagent to the mixture gives the alkylated product. The reaction proceeds with high chemoselectivity though there are two different oxygen atoms in the oxacyclic ethers.

C-C bond formation is a fundamental reaction in organic synthesis. Recently, we succeeded in developing new C-C bond formation reactions of acetals with Gilman reagents via the collidinium intermediates **i** obtained from acetals (Scheme 1, eq. 1).¹ We then proposed to apply this reaction to oxacyclic ethers, because they also have acetal structures. However, two oxygen atoms in the oxacyclic ethers are different from each other, whereas the two oxygen atoms in the acetal function of eq. 1 are equivalent. When the reaction proceeds via the intermediate **ii** obtained by the reaction of the cyclic oxygen atom, a single product **4** would be obtained (Scheme 1, eq. 2a). On the other hand, when the reaction proceeds via

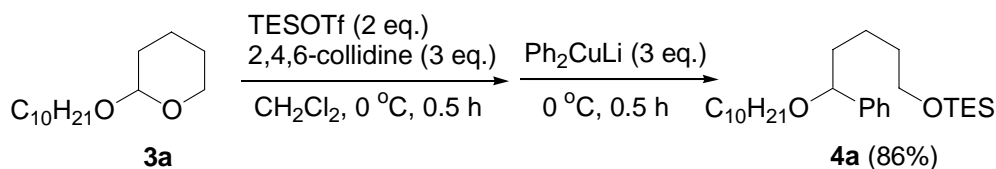
[†]This paper is dedicated to Professor Yoshito Kishi on the occasion of his 70th birthday.

the intermediate **iii** obtained by the reaction of the exo-cyclic oxygen atom, two products **5** and **6** would be obtained (Scheme 1, eq. 2b). We quite recently found that the deprotection of THP-ethers **3** ($n = 1$) with TESOTf—2,4,6-collidine followed by H₂O treatment proceeded via the intermediate **ii** ($n = 1$).² We now found that the reaction of oxacyclic ethers ($n = 0, 1, 2$) with TESOTf—2,4,6-collidine followed by the reaction with Gilman reagents proceeds in a highly chemoselective manner and gives the products via the intermediate **ii** (Scheme 1).



Scheme 1 Highly chemoselective alkylation of the acetals and oxacyclic ethers

Since THP-ethers are the most popular oxacyclic ethers in organic synthesis,³ we first examined the reaction of THP-ethers. Thus, the treatment of the decanol-THP ether **3a** with TESOTf (2.0 equiv.)—2,4,6-collidine (3.0 equiv.) gave the polar compound (TLC check).⁴ The addition of Gilman reagent, lithium diphenylcuprate (3.0 equiv.),⁵ to the mixture afforded the product **4a** in high yield (86%) (Scheme 2). Product **4a** was a compound obtained by the reaction of the cyclic oxygen atom. That is, the reaction proceeds via the intermediate **ii** (Scheme 1, eq. 2a). No formation of the product via the intermediate **iii** (Scheme 1, eq. 2b) was observed. These results showed that the reaction proceeded in a highly chemoselective manner.



Scheme 2. The reaction of decanol-THP ether **3a**

The generality of the reaction, i.e., high chemoselectivity, was observed for the reaction of **3a** and various Gilman reagents (Table 1). For comparison, the result in Scheme 2 is shown in entry 1. Every reaction afforded the products **4b-d** via the intermediates **ii** (Scheme 1, eq. 2a) obtained by the reaction of the cyclic oxygen atom.

Table 1. Alkylation of THP-ether **3a** with various Gilman reagents

Entry	R ²	Product	Yield (%)
1	Ph	4a	86
2	Me	4b	95
3	<i>n</i> -Bu	4c	94
4	TMSCH ₂	4d	82

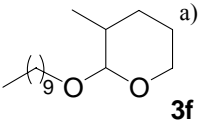
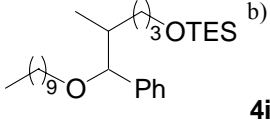
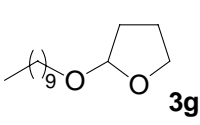
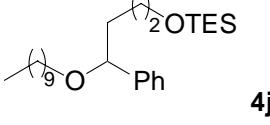
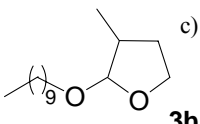
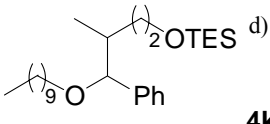
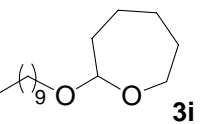
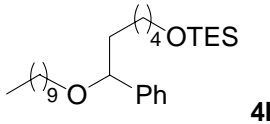
The reactions of various THP-ethers **3a-e**, in which the alcohol units are different from each other, with lithium diphenylcuprate were next examined (Table 2). For THP-ethers **3a-d** from the primary alcohols, every reaction well proceeded to give the desired product in high yield (entries 1-4). The reaction conditions are very mild, and benzyl alcohol and allyl alcohol were used without problems (entries 2 and 4). In the case of THP-ether **3e** from the secondary alcohol, the yield of the desired product decreased (entry 5).

Table 2. Alkylation of tetrahydropyranyl ethers **3a-e** with Ph₂CuLi

Entry	Substrate	Product	Yield (%)
1			86
2	3b : R = PhCH ₂	4e : R = PhCH ₂	86
3	3c : R = Ph(CH ₂) ₃	4f : R = Ph(CH ₂) ₃	81
4	3d : R = Allyl	4g : R = Allyl	79
5			62

Table 3 shows the applicability of other cyclic ethers in this reaction. The reactions of decanol ethers **3f-i** using lithium diphenylcuprate as a carbon nucleophile were examined. The 6-membered oxacyclic ether **3f** having a methyl substituent next to the acetal carbon gave the desired product **4i** in 79% yield (entry 1). Tetrahydrofuranyl ether **3g** afforded the desired product **4j** in high yield (96%) (entry 2). However, the introduction of a methyl group next to the acetal carbon decreased the yield of the product **4k** (entry 3). Furthermore, compound **3i** with a 7-membered oxacyclic ring well proceeded to give the desired compound **4l** in high yield (94%) (entry 4).

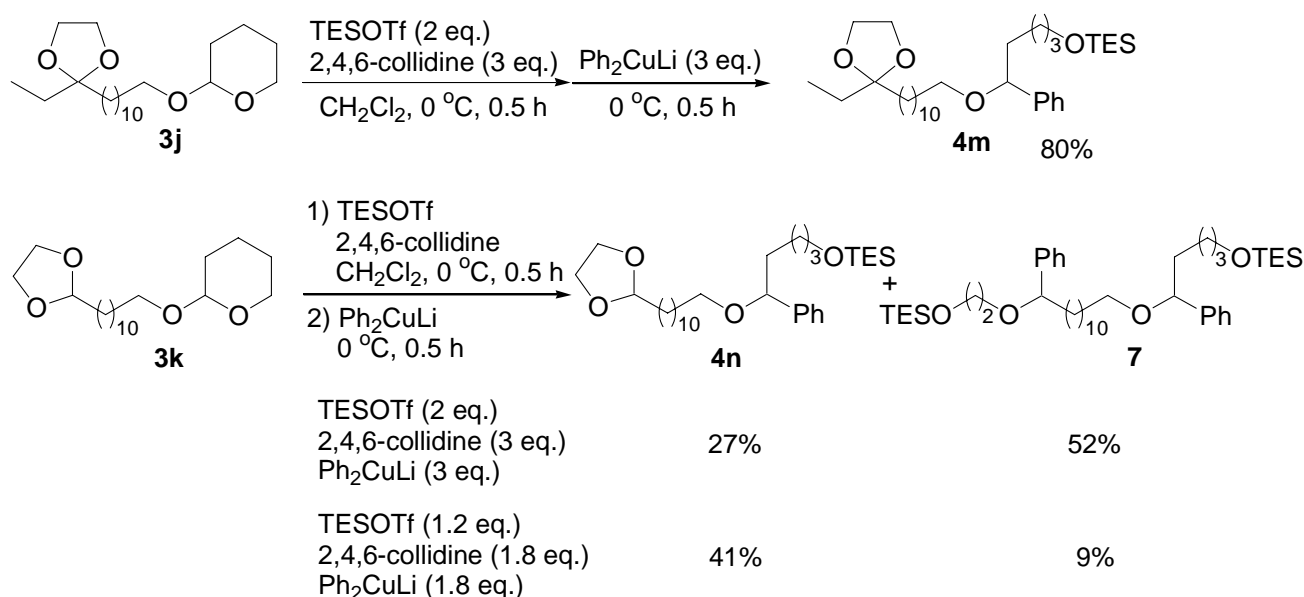
Table 3. Alkylation of Various Oxacyclic Ethers **3f-i** with Ph_2CuLi

Entry	Substrate	Product	Yield (%)
1	 3f	 4i	79
2	 3g	 4j	96
3	 3h	 4k	61
4	 3i	 4l	94

a) 1 to 1 mixture of two diastereomers were used. b) 1 to 1 mixture of two diastereomers were obtained. c) 6 to 1 mixture of two diastereomers were used. d) 2 to 1 mixture of two diastereomers were obtained.

The characteristic feature of this reaction is the high chemoselectivity. This aspect is also obvious from the following reactions (Scheme 3). Thus, compound **3j** having dioxolane ketal and THP-ether units in the molecule afforded the monophenyl product **4m** obtained by the reaction at only the THP-part. This tendency was observed even in compound **3k** having an acetal, not a ketal. Thus, compound **3k** having dioxolane acetal and THP-ether units in the molecule gave the monophenyl product **4n**, obtained by the reaction at only the THP-position, and the diphenyl product **7** obtained by the reaction at the dioxolane

part and THP part. No formation of a monophenyl product, obtained by the reaction at only the dioxolane part, was observed. This phenomenon became clearer when a lower amount of reagent was used. Thus, the treatment of **3k** with TESOTf (1.2 equiv.) and 2,4,6-collidine (1.8 equiv.) followed by the addition of lithium diphenylcuprate (1.8 equiv.) gave **4n** in 41% yield and **7** in 9% yield along with the recovered starting material **3k** (18 %). These results show that the THP-unit reacts much faster than the dioxolane unit, although the dioxolane unit also reacts under the same conditions.¹



Scheme 3. The reactions of the compounds having THP-unit and acetal unit in the molecule

The reaction mechanism is rationalized as follows. First, the formation of the collidinium salts **ii** (Scheme 1, eq. 2a) occurs under the TESOTf—2,4,6-collidine conditions. The reason why the cyclic oxygen atoms predominantly react is not clear at this stage, though the oxacyclic ethers have two different oxygen atoms. The formation of the collidinium salt **ii** is quite easy as shown in Scheme 3, although the dioxolane acetal is also affected under the reaction conditions as previously reported by us.⁶ The nucleophilic substitution of the 2,4,6-collidine substituent by carbon nucleophiles then gives the desired products.

In conclusion, the alkylation reaction of oxacyclic ethers has been developed. This is an extension of the alkylation of acetals.¹ However, it contains several new findings. The reaction proceeds with a high chemoselectivity though there are two different oxygen atoms in the oxacyclic ethers. The reaction proceeds in various oxacyclic ethers. Furthermore, it is noteworthy that the reaction selectively proceeds in the compounds having a dioxolane acetal unit and an oxacyclic ether unit in the molecule.

EXPERIMENTAL

General techniques

The ^1H and ^{13}C NMR spectra were measured by 300 MHz or 270 MHz spectrometers with tetramethylsilane as an internal standard at 20-25 °C. IR spectra were recorded by a diffuse reflectance measurement of samples dispersed in KBr powder. Merck silica gel 60 was used for column chromatography.

General Procedure for Preparation of Oxacyclic Ethers **3a-e**, **3g**, and **3j,k**.

According to a literature,⁷ a solution of alcohol (1 equiv.), pyridinium *p*-toluenesulfonate (PPTS) (0.1 equiv.) and 3,4-dihydro-2*H*-pyran or 2,3-dihydrofuran (1.8-2 equiv.) in dry CH_2Cl_2 (0.1 M) was stirred at rt. After checking disappearance of the alcohol on TLC, the mixture was quenched with saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over Na_2SO_4 , filtered, and evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography to give a THP-ether. **3a**,^{8a} **3b**,^{8b} **3c**,^{8c} **3d**,^{8d} and **3g**^{8e} are known in the literatures.

3e: colorless oil, IR (KBr) 2925, 913, 743 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.88 (3H, t, $J = 6.6$ Hz), 1.10 (3/2H, d, $J = 6.3$ Hz), 1.22 (3/2H, d, $J = 6.3$ Hz), 1.27-1.58 (20H, m), 1.63-1.95 (2H, m), 3.46-3.53 (1H, m), 3.67-3.97 (2H, m), 4.64 (1/2H, t, $J = 3.5$ Hz), 4.71 (1/2H, t, $J = 3.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 19.0, 19.7, 20.0, 21.5, 22.6, 25.4, 25.46, 25.51, 25.8, 29.3, 29.5, 29.56, 29.58, 29.67, 29.70, 31.1, 31.8, 36.4, 37.5, 62.3, 62.8, 71.0, 73.8, 95.4, 98.5; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{33}\text{O}_2$ ($\text{M}^+\text{+H}$) 257.2481, found 257.2489.

3j: colorless oil, IR (KBr) 2925, 1078 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, t, $J = 7.4$ Hz), 1.27-1.43 (16H, m), 1.43-1.87 (12H, m), 3.38 (1H, dt, $J = 9.5, 6.7$ Hz), 3.46-3.53 (1H, m), 3.73 (1H, dt, $J = 9.5, 6.7$ Hz), 3.84-3.90 (1H, m), 3.93 (4H, br s), 4.58 (1H, t, $J = 3.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 8.1, 19.7, 23.8, 25.5, 26.2, 29.5, 29.55, 29.58, 29.7, 29.8, 29.9, 30.8, 36.7, 62.3, 64.9, 67.7, 98.8, 112.1; HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{40}\text{O}_4\text{Na}$ ($\text{M}^+\text{+Na}$) 379.2824, found 379.2826.

3k: colorless oil, IR (KBr) 2926, 912, 743 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 1.21-1.47 (15H, m), 1.49-1.75 (10H, m), 1.74-1.88 (1H, m), 3.38 (1H, dt, $J = 9.6, 6.8$ Hz), 3.46-3.54 (1H, m), 3.73 (1H, dt, $J = 9.6, 6.8$ Hz), 3.82-4.02 (5H, m), 4.58 (1H, t, $J = 3.6$ Hz), 4.84 (1H, t, $J = 4.9$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 19.7, 24.1, 25.5, 26.2, 29.46, 29.47, 29.52, 29.54, 29.7, 30.8, 33.9, 62.3, 64.8, 67.7, 98.8, 104.7; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{36}\text{O}_4\text{Na}$ ($\text{M}^+\text{+Na}$) 351.2511, found 351.2510.

General Procedure for Preparation of Oxacyclic Ethers **3f** and **3h**.

n-BuLi (1.1 equiv.) in hexane was added dropwise to a solution of diisopropylamine (1.1 equiv.) in dry

THF (2.0 M) at 0 °C. After being stirred for 1 h at the same temperature and cooled to -78 °C, δ -valerolactone or γ -butyrolactone was added dropwise to the reaction mixture. After being stirred for 0.5 h at the same temperature, hexamethylphosphoric triamide (HMPA) (1.0 equiv.) was added dropwise to the reaction mixture. After being stirred for 0.5 h at the same temperature, MeI (1.0 equiv.) was added dropwise to the reaction mixture and the mixture was warmed to -40 °C. After checking disappearance of the δ -valerolactone on TLC, the mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4 , filtered, and evaporated in vacuo. DIBAL-H (1.05 equiv.) in hexane was added dropwise to a solution of the crude residue in dry CH_2Cl_2 (0.2 M) at -78 °C. After checking disappearance of the residue on TLC, the mixture was quenched with MeOH and H_2O , filtered with celite, and evaporated in vacuo. A solution of the crude product, pyridinium *p*-toluenesulfonate (PPTS) (0.1 equiv.) and decanol (2.0 equiv.) in dry CH_2Cl_2 (0.2 M) was stirred at rt. After checking disappearance of the crude product on TLC, the mixture was quenched with saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over Na_2SO_4 , filtered, and evaporated in vacuo. The residue was purified by flash SiO_2 column chromatography to give a THP-ether.

3f: colorless oil, IR (KBr) 2928, 913, 742 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.86-0.97 (6H, m), 1.14-1.26 (15H, m), 1.43-1.68 (5H, m), 1.71-1.87 (1H, m), 3.28-3.54 (2H, m), 3.64-3.85 (3/2H, m), 3.92-4.06 (1H, m), 4.51 (1/2H, d, $J = 2.7$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 16.72, 16.74, 22.7, 24.6, 25.5, 26.10, 26.13, 26.2, 29.3, 29.4, 29.57, 29.59, 29.6, 29.7, 29.8, 31.9, 34.9, 35.1, 59.4, 65.0, 67.3, 68.7, 100.3, 106.0; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{33}\text{O}_2$ (M^++H) 257.2481, found 257.2480.

3h: colorless oil, IR (KBr) 2925, 913, 743 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.88 (3H, t, $J = 6.5$ Hz), 1.04 (3H, d, $J = 6.9$ Hz), 1.10-1.39 (15H, m), 1.40-1.57 (2H, m), 2.06-2.26 (2H, m), 3.29-3.39 (1H, m), 3.57-3.70 (1H, m), 3.77-4.00 (2H, m), 4.69 (6/7H, br s), 4.82 (1/7H, d, $J = 4.5$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1, 17.7, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 31.8, 31.9, 39.5, 66.6, 67.5, 109.7; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{30}\text{O}_2\text{Na}$ (M^++Na) 265.2143, found 265.2151.

Preparation of Oxacyclic Ether 3i.

DIBAL-H (9.95 mL, 9.64 mmol) in hexane was added dropwise to a solution of 6-hexanolactone (1.00 g, 8.76 mmol) in dry CH_2Cl_2 (43.8 mL) at -78 °C. After checking disappearance of 6-hexanolactone on TLC, the mixture was quenched with MeOH and H_2O , and filtered with celite, and evaporated in vacuo. A solution of the crude product, pyridinium *p*-toluenesulfonate (PPTS) (75.4 mg, 0.438 mmol) and decanol (3.34 mL, 17.5 mmol) in dry CH_2Cl_2 (29.2 mL) was stirred at rt. After checking disappearance of the crude product on TLC, the mixture was quenched with saturated aqueous NaHCO_3 and extracted with CH_2Cl_2 . The organic layer was washed with brine, dried over Na_2SO_4 , filtered, and evaporated in vacuo.

The residue was purified by flash SiO₂ column chromatography to give a THP-ether **3i** (997 mg, 44%). This reaction is not optimized.

3i: colorless oil, IR (KBr) 2924, 1128, 964 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.88 (3H, t, *J* = 6.6 Hz), 1.26-1.68 (22H, m), 1.81-1.86 (1H, m), 2.01-2.10 (1H, m), 3.36 (1H, dt, *J* = 9.6, 6.8 Hz), 3.49-3.55 (1H, m), 3.68 (1H, dt, *J* = 9.6, 6.8 Hz), 3.76-3.84 (1H, m), 4.69 (1H, t, *J* = 6.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 14.1, 22.65, 22.69, 26.2, 29.3, 29.4, 29.50, 29.54, 29.6, 29.7, 30.7, 31.9, 35.0, 61.5, 67.2, 101.8; HRMS (FAB) calcd for C₁₆H₃₃O₂ (M⁺+H) 257.2481, found 257.2480.

Typical Reaction Procedure: Reaction of THP-ether **3a** and Ph₂CuLi

2,4,6-Collidine (69 μL, 0.522 mmol) and TESOTf (79 μL, 0.348 mmol) were added to a solution of a THP-ether **3a** (42.2 mg, 0.174 mmol) in CH₂Cl₂ (1.74 mL) at 0 °C under N₂. The reaction mixture was stirred at the same temperature. After checking disappearance of **3a** on TLC (0.5 h), Ph₂CuLi (0.522 mmol, 0.4 M diethyl ether solution prepared according to Johnson's method⁹) was added to the reaction mixture and stirred for 0.5 h. Disappearance of the polar component was ascertained by TLC analysis. The reaction mixture was quenched with saturated aqueous NH₄Cl and stirred for more than 10 min at rt. The mixture was extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, filtered, and evaporated in vacuo. The residue was purified by flash SiO₂ column chromatography using hexanes-Et₂O (50/1) to give **4a** (64.9 mg, 86%) as a colorless oil.

4a: colorless oil, IR (KBr) 2928, 1101, 748 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.58 (6H, q, *J* = 7.9 Hz), 0.88 (3H, t, *J* = 6.9 Hz), 0.94 (9H, t, *J* = 7.9 Hz), 1.15-1.32 (16H, m), 1.38-1.67 (5H, m), 1.75-1.87 (1H, m), 3.21 (1H, dt, *J* = 9.0, 6.7 Hz), 3.30 (1H, dt, *J* = 9.0, 6.7 Hz), 3.57 (2H, t, *J* = 6.5 Hz), 4.16 (1H, t, *J* = 6.6 Hz), 7.22-7.35 (5H, m); ¹³C NMR (75 MHz, CDCl₃) δ 4.4, 6.8, 14.1, 22.3, 22.7, 26.2, 29.3, 29.5, 29.56, 29.59, 29.9, 31.9, 32.8, 38.3, 62.8, 68.9, 82.2, 126.5, 127.2, 128.2, 143.3; *Anal.* Calcd for C₂₇H₅₀O₂Si: C, 74.59; H, 11.59. Found: C, 74.79; H, 11.50.

4b: colorless oil, IR (KBr) 2932, 1097, 743 cm⁻¹; ¹H NMR (270 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 7.9 Hz), 0.88 (3H, t, *J* = 6.5 Hz), 0.96 (9H, t, *J* = 7.9 Hz), 1.12 (3H, d, *J* = 6.3 Hz), 1.26-1.49 (16H, m), 1.50-1.62 (6H, m), 3.27-3.37 (2H, m), 3.40-3.51 (1H, m), 3.60 (2H, t, *J* = 6.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 4.4, 6.8, 14.1, 19.7, 21.9, 22.7, 26.2, 29.3, 29.5, 29.58, 29.61, 30.2, 31.9, 32.9, 36.5, 62.9, 68.6, 75.2; HRMS (FAB) calcd for C₂₂H₄₉O₂Si (M⁺+H) 373.3502, found 373.3477.

4c: colorless oil, IR (KBr) 2928, 1097, 743 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.60 (6H, q, *J* = 7.8 Hz), 0.86-0.99 (15H, m), 1.27-1.66 (28H, m), 3.15-3.20 (1H, m), 3.39 (2H, t, *J* = 6.6 Hz), 3.60 (2H, t, *J* = 6.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 4.4, 6.8, 14.1, 21.8, 22.7, 22.9, 26.3, 27.6, 29.3, 29.5, 29.58, 29.60, 29.63, 30.2, 31.9, 33.1, 33.8, 33.9, 62.9, 69.0, 79.4; HRMS (FAB) calcd for C₂₅H₅₅O₂Si (M⁺+H)

415.3971, found 415.3984.

4d: colorless oil, IR (KBr) 2855, 912, 743 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.10 (9H, s), 0.59 (6H, q, $J = 7.9$ Hz), 0.76 (1H, dd, $J = 14.7, 6.9$ Hz), 0.87 (3H, t, $J = 6.8$ Hz), 0.92 (1H, dd, $J = 14.7, 7.2$ Hz), 0.95 (9H, t, $J = 7.9$ Hz), 1.26-1.58 (22H, m), 3.31-3.37 (3H, m), 3.60 (2H, t, $J = 6.8$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ -0.7, 4.4, 6.8, 14.1, 21.6, 22.7, 22.8, 26.3, 29.3, 29.5, 29.58, 29.61, 30.2, 31.9, 33.0, 36.3, 62.9, 68.3, 77.3; *Anal.* Calcd for $\text{C}_{25}\text{H}_{56}\text{O}_2\text{Si}_2$: C, 67.49; H, 12.69. Found: C, 67.53; H, 12.46.

4e: colorless oil, IR (KBr) 912, 743 cm^{-1} ; ^1H NMR (270 MHz, CDCl_3) δ 0.57 (6H, q, $J = 7.9$ Hz), 0.93 (9H, t, $J = 7.9$ Hz), 1.23-1.35 (1H, m), 1.43-1.72 (4H, m), 1.81-1.95 (1H, m), 3.56 (2H, t, $J = 6.4$ Hz), 4.24 (1H, d, $J = 11.9$ Hz), 4.29 (1H, t, $J = 6.6$ Hz), 4.44 (1H, d, $J = 11.9$ Hz), 7.26-7.39 (10H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 4.4, 6.8, 22.2, 32.7, 38.2, 62.7, 70.4, 81.5, 126.8, 127.4, 127.5, 127.7, 128.3, 128.4, 138.6, 142.6; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{37}\text{O}_2\text{Si}$ (M^+H) 385.2563, found 385.2553.

4f: colorless oil, IR (KBr) 2951, 1101, 748 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.57 (6H, q, $J = 7.9$ Hz), 0.94 (9H, t, $J = 7.9$ Hz), 1.12-1.69 (5H, m), 1.77-1.91 (3H, m), 2.58-2.75 (2H, m), 3.24 (1H, dt, $J = 9.3, 6.4$ Hz), 3.34 (1H, dt, $J = 9.3, 6.4$ Hz), 3.58 (2H, t, $J = 6.6$ Hz), 4.17 (1H, dd, $J = 7.8, 5.7$ Hz), 7.13-7.35 (10H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 4.4, 6.8, 22.3, 31.5, 32.5, 32.8, 38.2, 62.8, 68.0, 82.3, 125.7, 126.6, 127.3, 128.2, 128.3, 128.4, 142.1, 143.1; *Anal.* Calcd for $\text{C}_{26}\text{H}_{40}\text{O}_2\text{Si}$: C, 75.67; H, 9.77. Found: C, 75.34; H, 9.73.

4g: colorless oil, IR (KBr) 2953, 1265, 748 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.57 (6H, q, $J = 7.9$ Hz), 0.94 (9H, t, $J = 7.9$ Hz), 1.15-1.70 (5H, m), 1.79-1.91 (1H, m), 3.57 (2H, t, $J = 6.6$ Hz), 3.74 (1H, dd like, $J = 12.7, 6.2$ Hz), 3.90 (1H, dd like, $J = 12.7, 5.1$ Hz), 4.26 (1H, t, $J = 6.6$ Hz), 5.12-5.25 (2H, m), 5.88 (1H, m), 7.24-7.36 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 4.4, 6.7, 22.2, 32.8, 38.1, 62.8, 69.5, 81.5, 116.6, 126.7, 127.4, 128.3, 135.0, 142.6; *Anal.* Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2\text{Si}$: C, 71.80; H, 10.24. Found: C, 71.96; H, 10.21.

4h: colorless oil, IR (KBr) 2928, 1099, 743 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.57 (6H, q, $J = 7.9$ Hz), 0.85-0.99 (14H, m), 1.10 (1H, d, $J = 6.2$ Hz), 1.15-1.35 (15H, m), 1.38-1.62 (6H, m), 1.72-1.84 (1H, m), 3.27-3.59 (1H, m), 3.57 (2H, t, $J = 6.9$ Hz), 4.28 (1H, dd, $J = 7.7, 5.6$ Hz), 7.21-7.35 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 4.4, 6.8, 14.1, 20.9, 22.3, 22.7, 25.2, 29.3, 29.6, 29.7, 29.9, 31.9, 32.8, 35.8, 38.6, 62.8, 73.4, 80.1, 126.6, 127.1, 128.1, 144.2; HRMS (FAB) calcd for $\text{C}_{28}\text{H}_{52}\text{O}_2\text{SiLi}$ (M^+Li) 455.3897, found 455.3890.

4i: colorless oil, IR (KBr) 2855, 913, 743 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.51-0.64 (6H, m), 0.69 (3/2H, d, $J = 6.6$ Hz), 0.80-0.99 (12H+3/2H, m), 1.11-1.35 (15H, m), 1.43-1.75 (6H, m), 3.12-3.33 (2H, m), 3.48-3.61 (2H, m), 3.89 (1/2H, d, $J = 7.5$ Hz), 3.98 (1/2H, d, $J = 6.3$ Hz), 7.22-7.34 (5H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 4.36, 4.40, 6.77, 6.79, 14.1, 15.2, 15.7, 22.7, 26.2, 28.8, 29.2, 29.3, 29.5, 29.59,

29.62, 29.9, 30.3, 30.5, 31.9, 39.4, 39.9, 63.2, 63.4, 69.1, 69.2, 86.1, 86.7, 127.0, 127.1, 127.2, 127.5, 127.89, 127.91, 141.7, 142.0; HRMS (FAB) calcd for $C_{28}H_{52}O_2SiLi$ ($M^+ + Li$) 455.3897, found 455.3925.

4j: colorless oil, IR (KBr) 2926, 1275, 748 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 0.57 (6H, q, $J = 7.9$ Hz), 0.88 (3H, t, $J = 6.6$ Hz), 0.94 (9H, t, $J = 7.9$ Hz), 1.17-1.30 (15H, m), 1.43-1.85 (5H, m), 3.21 (1H, dt, $J = 9.2, 6.7$ Hz), 3.30 (1H, dt, $J = 9.2, 6.7$ Hz), 3.53-3.66 (2H, m), 4.18 (1H, dd, $J = 7.8, 5.1$ Hz), 7.25-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.4, 6.8, 14.1, 22.7, 26.2, 29.27, 29.31, 29.5, 29.56, 29.60, 29.9, 31.9, 34.7, 62.8, 68.9, 82.1, 126.6, 127.2, 128.2, 143.2; *Anal.* Calcd for $C_{26}H_{48}O_2Si$: C, 74.22; H, 11.50. Found: C, 74.30; H, 11.32.

4k: colorless oil, IR (KBr) 2856, 1263, 748 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 0.50-0.62 (6H, m), 0.73 (1H, d, $J = 6.9$ Hz), 0.86-0.98 (14H, m), 1.20-1.39 (15H, m), 1.50-1.65 (8/3H, m), 1.84-1.99 (4/3H, m), 3.13-3.36 (2H, m), 3.50-3.72 (2H, m), 3.92 (1/3H, d, $J = 6.6$ Hz), 4.01 (2/3H, d, $J = 6.0$ Hz), 7.23-7.34 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.39, 4.43, 6.78, 6.80, 14.1, 15.1, 16.3, 22.7, 26.3, 29.3, 29.5, 29.58, 29.62, 29.9, 31.9, 36.0, 36.3, 36.68, 36.71, 61.1, 61.5, 69.1, 69.2, 86.0, 86.8, 127.0, 127.1, 127.3, 127.5, 127.90, 127.94, 141.7, 141.9; HRMS (FAB) calcd for $C_{27}H_{51}O_2Si$ ($M^+ + H$) 435.3658, found 435.3656.

4l: colorless oil, IR (KBr) 2927, 1100, 746 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 0.58 (6H, q, $J = 7.9$ Hz), 0.88 (3H, t, $J = 6.6$ Hz), 0.95 (9H, t, $J = 7.9$ Hz), 1.13-1.66 (23H, m), 1.74-1.86 (1H, m), 3.21 (1H, dt, $J = 9.0, 6.7$ Hz), 3.29 (1H, dt, $J = 9.0, 6.7$ Hz), 3.57 (2H, t, $J = 6.6$ Hz), 4.16 (1H, t, $J = 6.6$ Hz), 7.22-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.4, 6.8, 14.1, 22.7, 25.7, 26.2, 29.3, 29.5, 29.56, 29.60, 29.9, 31.9, 32.8, 38.5, 62.9, 68.9, 82.2, 126.6, 127.2, 128.2, 143.3; HRMS (EI) calcd for $C_{28}H_{52}O_2Si$ (M^+) 448.3736, found 448.3725.

4m: colorless oil, IR (KBr) 2854, 1101, 743 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 0.57 (6H, q, $J = 7.9$ Hz), 0.90 (3H, t, $J = 7.4$ Hz), 0.94 (9H, t, $J = 7.9$ Hz), 1.25-1.40 (17H, m), 1.42-1.70 (10H, m), 1.75-1.87 (1H, m), 3.21 (1H, dt, $J = 9.0, 6.7$ Hz), 3.30 (1H, dt, $J = 9.0, 6.7$ Hz), 3.57 (2H, t, $J = 6.6$ Hz), 3.93 (4H, br s), 4.16 (1H, t, $J = 6.6$ Hz), 7.22-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.4, 6.7, 8.1, 22.2, 23.8, 26.2, 29.4, 29.55, 29.57, 29.59, 29.8, 29.89, 29.93, 32.7, 36.7, 38.2, 62.8, 64.9, 68.9, 82.2, 112.1, 126.5, 127.2, 128.2, 143.3; HRMS (FAB) calcd for $C_{33}H_{60}O_4SiNa$ ($M^+ + Na$) 571.4159, found 571.4193.

4n: colorless oil, IR (KBr) 2930, 912, 743 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 0.58 (6H, q, $J = 8.0$ Hz), 0.94 (9H, t, $J = 8.0$ Hz), 1.24-1.68 (25H, m), 1.75-1.86 (1H, m), 3.21 (1H, dt, $J = 9.0, 6.7$ Hz), 3.30 (1H, dt, $J = 9.0, 6.7$ Hz), 3.57 (2H, t, $J = 6.6$ Hz), 3.80-4.02 (4H, m), 4.16 (1H, dd, $J = 7.5, 5.7$ Hz), 4.84 (1H, t, $J = 4.8$ Hz), 7.20-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.4, 6.8, 22.2, 24.1, 26.2, 29.4, 29.49, 29.52, 29.54, 29.6, 29.9, 32.8, 33.9, 38.3, 62.8, 64.8, 68.9, 82.2, 104.7, 126.6, 127.2, 128.2, 143.3; HRMS (FAB) calcd for $C_{31}H_{56}O_4SiNa$ ($M^+ + Na$) 543.3846, found 543.3851.

7: colorless oil, IR (KBr) 2856, 912, 744 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.53-0.67 (12H, m), 0.94 (9H, t, $J = 7.8$ Hz), 0.95 (9H, t, $J = 7.8$ Hz), 1.22-1.65 (24H, m), 1.76-1.87 (2H, m), 3.17-3.43 (4H, m), 3.57 (2H, t, $J = 6.6$ Hz), 3.67-3.79 (2H, m), 4.16 (1H, t, $J = 6.6$ Hz), 4.24 (1H, t, $J = 6.6$ Hz), 7.23-7.35 (10H, m); ^{13}C NMR (75 MHz, CDCl_3) δ 4.4, 6.8, 22.2, 25.8, 26.2, 29.5, 29.6, 29.9, 32.8, 38.26, 38.33, 62.3, 62.8, 68.9, 70.0, 77.2, 82.2, 82.7, 126.6, 126.7, 127.21, 127.24, 128.2, 143.0, 143.3; HRMS (FAB) calcd for $\text{C}_{43}\text{H}_{76}\text{O}_4\text{Si}_2\text{Li}$ ($\text{M}^+ + \text{Li}$) 719.5442, found 719.5440.

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$\left[\begin{array}{c} \text{R}-\text{O}-\text{C}(\text{CH}_3)_2-\text{CH}_2-\text{N}^+(\text{CH}_2)_4-\text{C}(\text{CH}_3)_2-\text{OTES} \\ | \\ \text{C}_6\text{H}_3(\text{CH}_3)_3 \\ | \\ \text{OTf}^- \\ \text{iv} \end{array} \right]$
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