

Reactions of *gem*-Dibromo Compounds with Trialkylmagnesate Reagents to Yield Alkylated Organomagnesium Compounds**

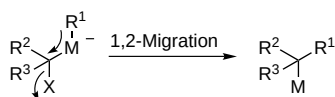
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Abstract: The reaction of *gem*-dibromocyclopropanes **5** with $n\text{Bu}_3\text{MgLi}$ affords butylated cyclopropylmagnesium species that can be trapped with various electrophiles. The reaction of dibromomethylsilanes **12** requires the addition of a catalytic amount of $\text{CuCN} \cdot 2\text{LiCl}$ for smooth migration of the alkyl groups. The resultant α -silylpentylmagnesium compounds **16** react with electrophiles, such as acyl chlorides or α,β -unsaturated ketones to afford α - or γ -silyl ketones, respectively. Treatment of dibromodisilylmethanes with Me_3MgLi yields 1-bromo-1,1-disilylethanes **25** that can be converted into 1,1-disilylethenes **29** by dehydrobromination.

Keywords: ate complexes • carbenoids • Grignard reagents • magnesium • migrations

Introduction

The utility of organometallic ate complexes in organic synthesis is well recognized, and numerous reports have been published on the reaction which makes use of various ate complexes that contain boron, copper, aluminum, zinc, manganese, zirconium, and other metals as the key atoms. Among reactions with ate complexes, the 1,2-migration of a ligand on a metal is a representative reaction pattern of ate-type carbenoids (Scheme 1).^[1, 2] Organometallic ate com-



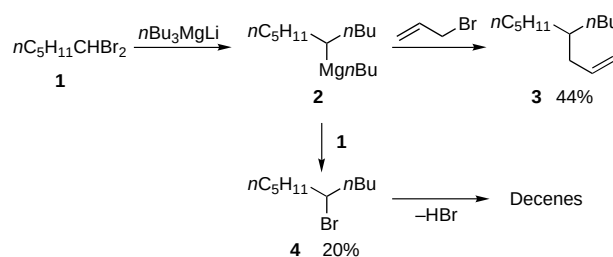
Scheme 1. 1,2-Migration of ate-type carbenoids.

plexes also induce halogen–metal exchange reactions.^[3] The combination of these two reactions enables a variety of transformations starting from *gem*-dihalo compounds.^[4, 5]

We have already reported the halogen–magnesium exchange reaction with magnesium ate complexes.^[6–8] The reaction proceeds at low temperatures of around -78°C , and hence the exchange reaction of *gem*-dibromoalkanes is expected to provide ate-type carbenoid species that would

undergo 1,2-migration of the alkyl group on magnesium to the adjacent carbon to form new organomagnesium reagents.

We started this research with the reaction of 1,1-dibromoalkane. Treatment of 1,1-dibromohexane (**1**) with $n\text{Bu}_3\text{MgLi}$ followed by the addition of allyl bromide as an electrophile yielded 4-butyl-1-nonene (**3**, 44%) as well as 5-bromodecane (**4**, 20%) and decenes (Scheme 2). This result



Scheme 2. Reaction of 1,1-dibromohexane with $n\text{Bu}_3\text{MgLi}$.

indicates that bromine–magnesium exchange and subsequent 1,2-migration of the butyl group affords the secondary alkylmagnesium species **2**. The coupling reaction of **2** with allyl bromide provides **3**. The magnesium compound **2** also abstracts bromine from dibromoalkane to afford **4**.

To eliminate the possibility of these side reactions, we chose *gem*-dibromocyclopropanes and dibromomethylsilanes as substrates and investigated their reactions with magnesate reagents.

Results and Discussion

Reaction of *gem*-dibromocyclopropanes: Cyclopropane derivatives are versatile synthetic intermediates in organic synthesis. Double alkylation of *gem*-dihalocyclopropanes,

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[**] Preliminary accounts have already been published: Ref. [22].

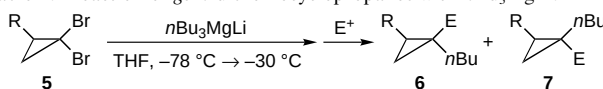
which can be readily prepared by the addition of dihalocarbenes to olefins, provided an expeditious route to a variety of functionalized cyclopropane derivatives. The reaction of *gem*-dibromocyclopropanes with dialkylcuprates,^[5a,b] alkylolithiums,^[5c,d] trialkylzincates,^[5e,f] or trialkylmanganates^[5g,h] have been reported to afford alkylated cyclopropylmetals, which could undergo further reactions with various electrophiles, such as alkyl halides and carbonyl compounds, to furnish double-alkylated cyclopropane derivatives. We have found that a magnesium ate complex (trialkylmagnesate) also effects this type of alkylative metalation.

Treatment of various *gem*-dibromocyclopropanes **5** with $n\text{Bu}_3\text{MgLi}$ at low temperatures followed by the addition of electrophiles afforded the expected products as diastereomeric mixtures (**6** and **7**). The results are summarized in Tables 1 and 2.

Several characteristics of this reaction are noteworthy:

- 1) The reaction should be performed at -78°C to -30°C . Treatment of **5a** with $n\text{Bu}_3\text{MgLi}$ at 0°C gave the desired product in modest yield together with a significant amount

Table 1. Reaction of *gem*-dibromocyclopropanes with $n\text{Bu}_3\text{MgLi}$.

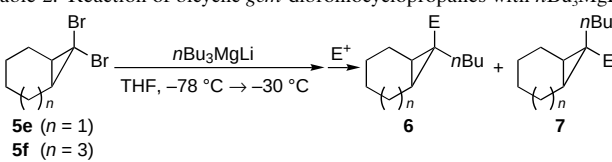


Entry	Substrate	Electrophile	Product	Yield[%]	Ratio 6/7
1	5a	H_3O^+	6a/7a	97	57/43
2		D_2O	6b/7b	97	56/44
3		I_2	6c/7c	80	62/38
4		$\text{CH}_2=\text{CHCH}_2\text{Br}$	6d/7d	65	51/49
5		MeI	6e/7e	74	45/55
6		PhCHO	6f/7f	78	44/56
7	5b	H_3O^+	6g/7g	91	48/52
8	5c	H_3O^+	6h/7h	86	81/19
9		$\text{CH}_2=\text{CHCH}_2\text{Br}^{[a]}$	6i/7i	82	80/20
10	5d	I_2	6j	91	
11		$\text{CH}_2=\text{CHCH}_2\text{Br}^{[a]}$	6k	73	

[a] In the presence of $\text{CuCN} \cdot 2\text{LiCl}$ (30 mol %).

Abstract in Japanese: *gem*-ジブロモシクロプロパン**5**に $n\text{Bu}_3\text{MgLi}$ を作用させると、ブチル基が導入されたシクロプロピルマグネシウム種**11**が生成した。この**11**は種々の求電子剤によって収率良く捕捉することができた。ジブロモメチルシラン**12**との反応では、触媒量の銅塩によってブチル基の転位が促進されることが明らかとなった。生成した α -シリルペンチルマグネシウム種**16**は酸塩化物や α,β -不飽和ケトンで捕捉することにより、 α -及び γ -シリルケトンへと導くことができた。また、ジブロモジシリルメタンと Me_3MgLi の反応では臭素の一つがメチル基に置換された生成物**25**を与えた。**25**は塩基によって脱臭化水素化することにより、1,1-ジシリルエテン**29**へと変換することができた。

Table 2. Reaction of bicyclic *gem*-dibromocyclopropanes with $n\text{Bu}_3\text{MgLi}$.



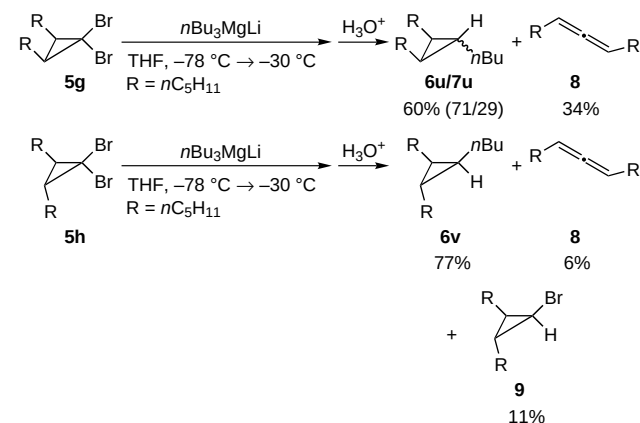
Entry	Substrate	Electrophile	Product	Yield[%]	Ratio 6:7
1	5e	H_3O^+	6l/7l	81	63/37
2		D_2O	6m/7m	82	63/37
3		I_2	6n/7n	91	61/39
4		$\text{CH}_2=\text{CHCH}_2\text{Br}^{[a]}$	6o/7o	89	73/27
5		$\text{PhCOCl}^{[b]}$	6p/7p	88	88/12
6		PhCHO	6q/7q	42 ^[d]	27/73
7	5f	H_3O^+	6r/7r	97	58/42
8		I_2	6s/7s	86	64/36
9		PhCHO	6t/7t	35 ^[e]	6/94
10		$\text{PhCHO}^{[c]}$	6t/7t	43 ^[f]	94/6

[a] In the presence of $\text{CuCN} \cdot 2\text{LiCl}$ (30 mol %). [b] In the presence of $\text{CuCN} \cdot 2\text{LiCl}$ (3.0 equiv). [c] In the presence of $\text{CuCN} \cdot 2\text{LiCl}$ (3.0 equiv) and $\text{BF}_3 \cdot \text{OEt}_2$ (3.0 equiv). [d] The product **6l** was also obtained in 47 % yield. [e] The product **6r** was also obtained in 65 %. [f] The products **6r** and **7r** were also obtained in 47 % yield (45/55).

of 1,2-nonadiene. On the other hand, 1,2-migration of a butyl group did not go to completion at -78°C . Quenching of the reaction mixture at -78°C provided 1-bromo-2-hexylcyclopropane as a major product in addition to the butylated product.

- 2) A variety of electrophiles, such as iodine, allyl bromide, methyl iodide, benzaldehyde, and benzoyl chloride, can be employed. The use of allyl bromide as the electrophile required the coexistence of $\text{CuCN} \cdot 2\text{LiCl}$. Without the assistance of a copper salt, the intermediary tertiary cyclopropylmagnesium failed to react with allyl bromide because of steric hindrance.^[9]
- 3) Stereoselectivities are somewhat lower than those observed in the reactions mediated by cuprates, zincates, or manganates. Interestingly, the reaction of **5e** or **5f** with $n\text{Bu}_3\text{MgLi}$ followed by the addition of benzaldehyde exhibited relatively high *exo* selectivity, although the yield was not satisfactory (vide infra).

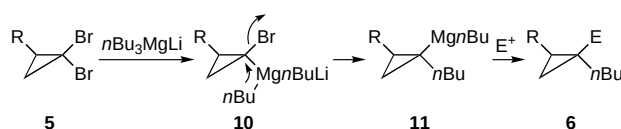
The use of 2,3-dialkyl-1,1-dibromocyclopropanes afforded disappointing results (Scheme 3). Steric hindrance of alkyl



Scheme 3. Reaction of 2,3-dialkyl-1,1-dibromocyclopropanes.

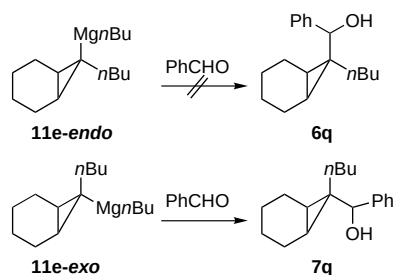
substituents on the cyclopropane ring retards 1,2-migration of the butyl group. In the reaction of **5g** or **5h**, migration of the butyl moiety competed with the formation of allene **8**.

We propose a similar reaction mechanism to the reactions with cuprates, zincates, and manganates (Scheme 4). Firstly, bromine–magnesium exchange occurs predominantly at the less hindered bromine atom to afford **10**. Next, the butyl



Scheme 4. Proposed mechanism of the reaction of *gem*-dibromocyclopropanes with $n\text{Bu}_3\text{MgLi}$.

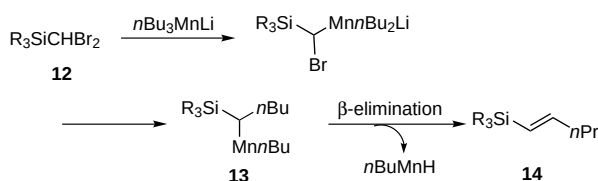
group on magnesium migrates to the adjacent carbon atom with concomitant elimination of the bromide ion and inversion of the configuration on the cyclopropane carbon. The resultant butylated cyclopropylmagnesium species **11** is eventually trapped by an electrophile with retention of configuration. The inverse stereoselectivity and the low yield in trapping with benzaldehyde are attributed to the low reactivity of the major diastereomer **11-endo** (Scheme 5). The



Scheme 5. Difference in the reaction between PhCHO and the *endo* or *exo* isomers of **11e**.

magnesium species **11-endo** fails to react with benzaldehyde and gives **6l** or **6r** after protonation. On the other hand, the other isomer, **11-exo**, is trapped with benzaldehyde to provide the cyclopropylbenzyl alcohol derivative.

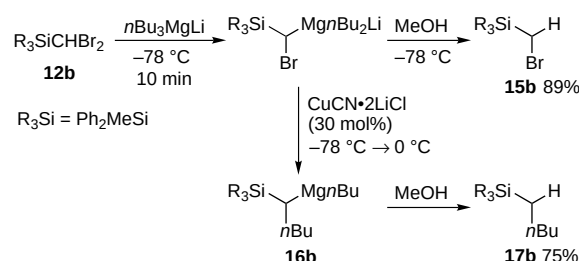
Copper(0)-catalyzed reaction of dibromomethylsilanes: We have previously reported synthesis of 1-alkenylsilanes **14** from dibromomethylsilanes **12**^[10] via manganese carbenoids (Scheme 6).^[5i,j] In this reaction, α -silylalkylmanganese **13** cannot be coupled with electrophiles because of its rapid conversion to alkenylsilane **14** by β -hydride elimination.



Scheme 6. Reaction of dibromomethylsilanes **12** with tributylmanganate.

We then investigated the reaction of dibromomethylsilanes with trialkylmagnesate. The reaction promised to be a facile method for the preparation of α -silylalkylmagnesium species, which are highly useful reagents in organic synthesis.^[11]

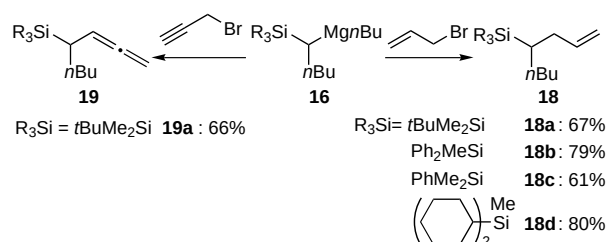
Treatment of dibromomethylsilane **12** with $n\text{Bu}_3\text{MgLi}$ induced clean bromine–magnesium exchange^[6] to provide bromomethylsilane **15** upon quenching with methanol at -78°C (Scheme 7). Warming the reaction mixture to room



Scheme 7. Bromine–magnesium exchange and the subsequent migration of an alkyl group.

temperature before quenching resulted in the migration of the butyl group to yield α -silylpentylmagnesium **16**.^[12] A copper salt proved to facilitate this migration.^[1a] The addition of $\text{CuCN} \cdot 2\text{LiCl}$ (30 mol %) to the reaction mixture induced smooth migration of the butyl group at lower temperatures (-30°C for **12a** and 0°C for **12b**) to afford **16** in good yield. Butyllithium or $n\text{BuMgBr}$ instead of tributylmagnesate also induced metalation and the subsequent butylation. Under these conditions, however, the yields of the desired products were quite low.

The α -silylpentylmagnesium **16** could be trapped with allyl bromide to give **18** in good yield (Scheme 8). The reaction with propargyl bromide furnished exclusively the allenylated product **19**.



Scheme 8. Reaction of α -silylalkylmagnesium compounds **16** with allyl or propargyl bromide.

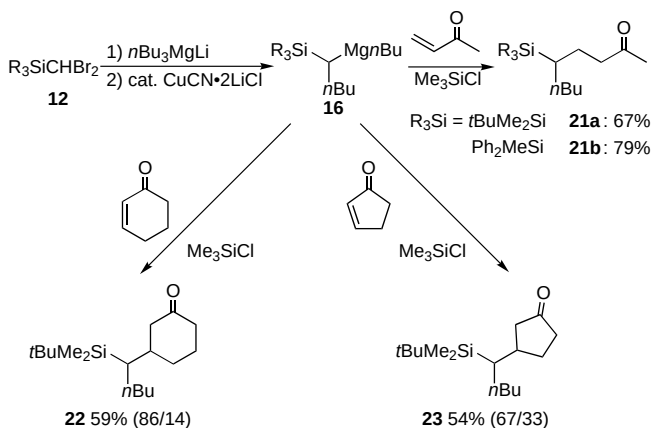
α -Silyl ketones are quite useful intermediates in organic synthesis.^[13] Therefore, we undertook the preparation of α -silyl ketones with this new methodology.^[14] The reaction of α -silylalkylmagnesium compounds **16** with various acyl chlorides was examined.^[15] The results are summarized in Table 3. The addition of acyl chlorides to the resulting solution of **16** furnished the corresponding α -silyl ketones **20** in good yields. 1,3-Dimethyl-2-imidazolidinone (DMI) proved to be an effective additive for the formation of α -silyl ketones. Without the use of DMI, the yield of product decreased (entry 7).

Table 3. Synthesis of α -silyl ketones from dibromomethylsilanes.^[a]

$\text{R}_3\text{SiCHBr}_2 \xrightarrow[2) \text{ cat. CuCN} \cdot 2\text{LiCl}]{1) \text{ R}^1_3\text{MgLi}} \text{R}_3\text{Si} \begin{array}{c} \text{MgR}^1 \\ \\ \text{R}^1 \end{array} \xrightarrow[\text{DMI}]{\text{R}^2\text{COCl}} \text{R}_3\text{Si} \begin{array}{c} \text{O} \\ \\ \text{R}^1 \end{array} \text{R}^2$						
Entry	Substrate	R ₃ Si	R ¹	R ²	Product	Yield [%]
1	12a	<i>t</i> BuMe ₂ Si	<i>n</i> Bu	CH ₃	20a	60
2				<i>c</i> Pr	20b	56
3				Ph	20c	66
4				(<i>E</i>)-CH ₃ CH=CH-	20d	53
5				(<i>E</i>)-PhCH=CH-	20e	51
6	12b	Ph ₂ MeSi	<i>n</i> Bu	CH ₃	20f	63
7			<i>n</i> Pr		20g	49
8 ^[b]			<i>n</i> Pr		20g	74
9 ^[b]			<i>i</i> Pr		20h	63
10 ^[b]			<i>c</i> Pr		20i	69
11 ^[b]			Ph		20j	77
12 ^[b, c]		<i>n</i> C ₆ H ₁₃	<i>n</i> Pr		20k	85
13 ^[c]				Ph	20l	70

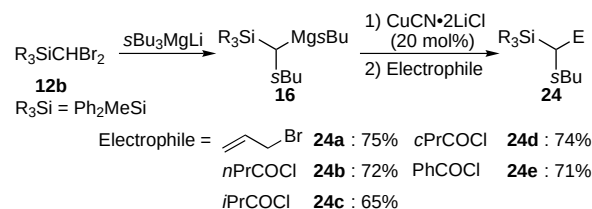
[a] Reaction conditions: Magnesate was prepared from butyllithium (2.0 mmol) and butylmagnesium bromide (1.0 mmol) in THF (5 mL) at 0 °C. Dibromomethylsilanes (1.0 mmol) in THF (2 mL) were introduced at –78 °C. CuCN·2LiCl (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added. [b] DMI (2.0 mmol) was added before introduction of acyl chlorides. [c] Magnesate was prepared from hexyllithium (3.0 mmol) and MgBr₂ (1.0 mmol) in THF (5 mL) at 0 °C.

We also explored the conjugate addition of **16** to α,β -unsaturated ketones (Scheme 9). Addition of methyl vinyl ketone to the solution of **16** provided 5-silyl-2-nonanones **21a** and **21b** in good yields in the presence of Me₃SiCl.^[16] The

Scheme 9. 1,4-Addition of α -silylalkylmagnesium compounds **16** toward enones.

addition of **16** to cyclohexenone or cyclopentenone also furnished the desired silylketones.

In the case of tri(*sec*-butyl)magnesate, which was prepared from *s*BuLi (3.0 equiv) and MgBr₂ (1.0 equiv), the migration of the secondary butyl group afforded the corresponding α -silylalkylmagnesium **16** smoothly without the assistance of a copper catalyst (Scheme 10). However, the addition of CuCN·2LiCl was beneficial for the acylation or allylation step to provide the coupling products **24** in good yields.

Scheme 10. Reaction of dibromomethylsilanes **12** with *s*Bu₃MgLi.

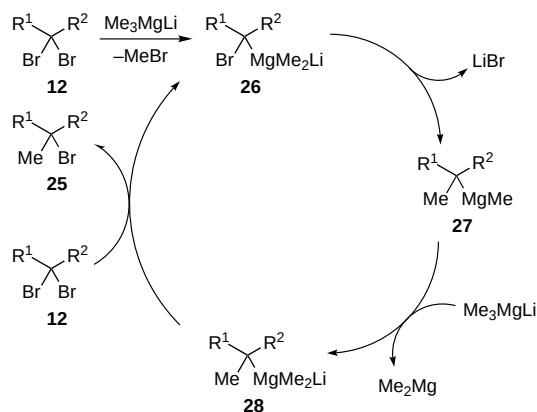
Reaction of dibromomethylsilanes with Me₃MgLi: The reaction of dibromomethylsilane **12b** with Me₃MgLi gave a different result from the reaction of *n*Bu₃MgLi. One of the two bromine atoms was substituted by the methyl group. This monomethylation reaction was successfully applied to dibromodisilylmethanes.^[17] The results are summarized in Table 4.

Table 4. Monomethylation of dibromodisilylmethanes with Me₃MgLi.^[a]

$\text{R}^1 \begin{array}{c} \text{R}^2 \\ \\ \text{Br} \end{array} \text{Br} \xrightarrow[\text{THF, } -78^\circ\text{C, 0.5 h}]{\text{Me}_3\text{MgLi (1.0 equiv)}} \text{R}^1 \begin{array}{c} \text{R}^2 \\ \\ \text{Me} \end{array} \text{Br}$					
Entry	Substrate	R ¹	R ²	Product	Yield [%]
1	12a	Ph ₂ MeSi	H	25a	98
2	12e	Ph ₂ MeSi	Me	25e	89
3	12f	Ph ₂ MeSi	Me ₃ Si	25f	93
4	12g	Et ₃ Si	Et ₃ Si	25g	90
5	12h	<i>t</i> BuMe ₂ Si	Me ₃ Si	25h	82
6	12i	Me ₃ Si	Me ₃ Si	25i	89
7	12j	PhMe ₂ Si	PhMe ₂ Si	25j	80
8	12k	Ph ₂ MeSi	Ph ₂ MeSi	25k	90
9	12l	Ph ₂ MeSi	Et ₃ Ge	25l	93

[a] The substrate **12** (10 mmol) was treated with Me₃MgLi, prepared by mixing MeMgBr (THF solution, 10 mmol) and MeLi (Et₂O solution, 20 mmol), for 0.5 h in THF at –78 °C.

Substrates such as dibromomethylsilane (entry 1), 1,1-dibromoethylsilane (entry 2), and dibromodisilylmethanes (entries 3–8) could be converted into the corresponding monomethylated compounds **25** in good yields, regardless of the bulkiness of silyl substituents. Methylation of germysilyldibromomethane also proceeded in good yield (entry 9). We propose the following mechanism^[18] that involves the formation of the ate-type carbenoid species **26** through a bromine–magnesium exchange reaction (Scheme 11).^[5, 6]



Scheme 11. Plausible mechanism of monomethylation.

The 1,2-migration of one of the methyl groups on magnesium provides **27** with concomitant elimination of the bromide anion. One of methyl groups in Me_3MgLi is transferred to **27** to form the ate complex **28**, which is more reactive than Me_3MgLi for the bromine–magnesium exchange reaction. The complex **28** abstracts the bromine atom from **12** to yield the monobromo compound **25** and the carbenoid **26**.

The resultant monomethylated products were converted into the corresponding 1,1-disilylenes by dehydrobromination.^[19, 20] Treatment of **25** with two equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in DMF at 90 °C for eight hours provided 1,1-disilylenes **29** (Table 5). In each case, the desired product was obtained in good yield.

Table 5. Dehydrobromination of **25** with DBU.^[a]

Entry	Substrate	R ¹	R ²	Product	Yield [%]
1	25f	Ph ₂ MeSi	Me ₃ Si	29f	98
2	25g	Et ₃ Si	Et ₃ Si	29g	98
3	25h	<i>t</i> BuMe ₂ Si	Me ₃ Si	29h	85
4	25i	Me ₃ Si	Me ₃ Si	29i	83
5	25j	PhMe ₂ Si	PhMe ₂ Si	29j	97
6	25k	Ph ₂ MeSi	Ph ₂ MeSi	29k	89
7	25l	Ph ₂ MeSi	Et ₃ Ge	29l	85

[a] A solution of **25** (9.0 mmol) and DBU (18.0 mmol) in DMF (30 mL) was stirred for 8 h at 90 °C.

Conclusion

We have investigated the reactions of *gem*-dibromo compounds with trialkylmagnesate reagents (R_3MgLi). The halogen–magnesium exchange reaction and subsequent 1,2-migration of the alkyl group on magnesium affords the alkylated organomagnesium species in the presence or absence of a copper catalyst. The resultant organomagnesium species can be trapped with a variety of electrophiles. Trimethylmagnesate (Me_3MgLi) shows a different reactivity. The reagent induces monomethylation of dibromomethylsilanes or dibromodisilylmethanes.

Experimental Section

General: ¹H NMR (300 MHz) and ¹³C NMR (75.3 MHz) spectra were recorded on a Varian GEMINI 300 spectrometer in CDCl_3 as a solvent, and chemical shifts were given in δ with tetramethylsilane as an internal standard. IR spectra were determined on a JASCO IR-810 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merck silica gel 60F₂₅₄. Column chromatography was performed on silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone before use. Grignard reagents were prepared from the corresponding alkyl halide and Mg turnings (Nacalai tesque, INC). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aldehydes were distilled and stored under argon.

Synthesis of *gem*-dibromocyclopropanes **5:** Aqueous sodium hydroxide (10 mL, 50 w/w%) was added dropwise to a mixture of an alkene (20 mmol), bromoform (2.6 mL, 30 mmol), benzytriethylammonium chloride (0.1 g), dichloromethane (2 mL), and ethanol (0.08 mL) at 0 °C. After stirring for 24 h, water was added (50 mL). The mixture was extracted with hexane and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by chromatography on a silica gel column gave provided *gem*-dibromocyclopropanes **5**.

1,1-Dibromo-2-hexylcyclopropane (5a**):** R_f = 0.71 (hexane); IR (neat): $\tilde{\nu}$ = 2922, 2852, 1111, 1042, 677 cm^{-1} ; ¹H NMR (CDCl_3): δ = 0.89 (t, J = 6.9 Hz, 3H), 1.18 (dd, J = 6.9, 7.2 Hz, 1H), 1.23–1.67 (m, 11H), 1.73 (dd, J = 6.9, 9.9 Hz, 1H); ¹³C NMR (CDCl_3): δ = 14.1, 22.6, 28.3, 28.5, 29.0, 29.7, 31.5, 31.7, 32.6; elemental analysis calcd (%) for $\text{C}_9\text{H}_{16}\text{Br}_2$: C 38.06, H 5.68; found: C 37.77, H 5.44.

2-(Benzyloxymethyl)-1,1-dibromocyclopropane (5b**):** R_f = 0.42 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 3026, 2856, 1496, 1454, 1372, 1155, 1094, 1029, 735, 696, 680 cm^{-1} ; ¹H NMR (CDCl_3): δ = 1.37 (dd, J = 7.2, 7.5 Hz, 1H), 1.80 (dd, J = 7.2, 10.5 Hz, 1H), 1.89–2.01 (m, 1H), 3.58 (dd, J = 7.2, 10.8 Hz, 1H), 3.63 (dd, J = 5.7, 10.8 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 12.0 Hz, 1H), 7.26–7.40 (m, 5H); ¹³C NMR (CDCl_3): δ = 26.0, 26.6, 30.2, 71.5, 73.0, 127.9, 127.9, 128.5, 138.1; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{12}\text{Br}_2\text{O}$: C 41.28, H 3.78; found: C 41.11, H 3.71.

1,1-Dibromo-2-phenylcyclopropane (5c**):** R_f = 0.41 (hexane); IR (neat): $\tilde{\nu}$ = 1605, 1498, 1452, 1425, 1108, 1040, 766, 734, 696, 679 cm^{-1} ; ¹H NMR (CDCl_3): δ = 2.02 (dd, J = 7.8, 8.4 Hz, 1H), 2.14 (dd, J = 7.8, 10.5 Hz, 1H), 2.97 (dd, J = 8.4, 10.5 Hz, 1H), 7.22–7.30 (m, 2H), 7.30–7.40 (m, 3H); ¹³C NMR (CDCl_3): δ = 27.2, 28.3, 35.9, 127.7, 128.4, 129.0, 136.1; elemental analysis calcd (%) for $\text{C}_9\text{H}_8\text{Br}_2$: C 39.17, H 2.92; found: C 39.02, H 3.03.

1,1-Dibromo-2,2,3,3-tetramethylcyclopropane (5d**):** IR (Nujol): $\tilde{\nu}$ = 1105, 1031, 994, 952, 863, 792, 774 cm^{-1} ; ¹H NMR (CDCl_3): δ = 1.25 (s, 12H); ¹³C NMR (CDCl_3): δ = 21.7, 29.7, 58.9. We were not able to perform an analysis on this compound because of its sublimation.

7,7-Dibromobicyclo[4.1.0]heptane (5e**):** R_f = 0.72 (hexane); IR (neat): $\tilde{\nu}$ = 2936, 2852, 1462, 1444, 1334, 1165, 1020, 729 cm^{-1} ; ¹H NMR (CDCl_3): δ = 1.00–1.25 (m, 2H), 1.30–1.43 (m, 2H), 1.50–1.62 (m, 2H), 1.76–1.90 (m, 2H), 1.92–2.07 (m, 2H); ¹³C NMR (CDCl_3): δ = 20.1, 20.6, 27.0, 40.7; elemental analysis calcd (%) for $\text{C}_7\text{H}_{10}\text{Br}_2$: C 33.11, H 3.97; found: C 33.20, H 3.95.

9,9-Dibromobicyclo[6.1.0]nonane (5f**):** R_f = 0.69 (hexane); IR (neat): $\tilde{\nu}$ = 2920, 2848, 1467, 1164, 1060, 858, 815, 760, 710 cm^{-1} ; ¹H NMR (CDCl_3): δ = 1.07–1.25 (m, 2H), 1.30–1.70 (m, 10H), 2.00–2.10 (m, 2H); ¹³C NMR (CDCl_3): δ = 25.3, 26.3, 27.8, 33.2, 37.0; elemental analysis calcd (%) for $\text{C}_9\text{H}_{14}\text{Br}_2$: C 38.33, H 5.00; found: C 38.28, H 4.83.

cis-1,1-Dibromo-2,3-dipentylcyclopropane (5g**):** R_f = 0.80 (hexane); IR (neat): $\tilde{\nu}$ = 2952, 2922, 2854, 1466, 1379, 716 cm^{-1} ; ¹H NMR (CDCl_3): δ = 0.90 (t, J = 6.9 Hz, 6H), 1.24–1.59 (m, 18H); ¹³C NMR (CDCl_3): δ = 13.9, 22.5, 26.9, 28.1, 31.6, 33.8, 38.3; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{24}\text{Br}_2$: C 45.91, H 7.11; found: C 46.02, H 6.99.

trans-1,1-Dibromo-2,3-dipentylcyclopropane (5h**):** R_f = 0.83 (hexane); IR (neat): $\tilde{\nu}$ = 2952, 2924, 2854, 1466, 1379, 1137, 1046, 722 cm^{-1} ; ¹H NMR (CDCl_3): δ = 0.90 (t, J = 6.9 Hz, 6H), 1.01–1.11 (m, 2H), 1.24–1.52 (m, 14H), 1.52–1.68 (m, 2H); ¹³C NMR (CDCl_3): δ = 13.9, 22.5, 27.9, 31.4, 32.6, 37.0, 39.4; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{24}\text{Br}_2$: C 45.91, H 7.11; found: C 46.01, H 6.84.

General procedure for the reaction of *gem*-dibromocyclopropanes **5 with $n\text{Bu}_3\text{MgLi}$:** Butyllithium (1.5 mL, 1.6 M solution in hexane, 2.4 mmol) was added to a solution of butylmagnesium bromide (1.2 mL, 1.0 M solution in THF, 1.2 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to –78 °C, and a solution of the corresponding **5** (1.0 mmol) in THF (2 mL) was added dropwise. After the reaction mixture was gradually warmed to –30 °C over a period of 2 h, the corresponding electrophile (3.0 mmol) was added. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl . The mixture was extracted with ethyl acetate, and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by chromatography on a silica gel column provided **6** and **7** as diastereomeric mixtures.

Spectral data for **6a**, **7a**, **6e**, **7e**, **6h**, **7h**,^[4b] **6f**, **7f**, **6g**, **7g**, **6l**, **7l**,^[4c] **6c**, **7c**, **6d**, **7d**, **6i**, **7i**, **6o**, **7o**, **6t**, **7t**,^[4g] **6r**, and **7r**^[21] were identical with those reported

in the literature. Alcohols (**6f**, **7f**, **6q**, **7q**, **6t**, and **7t**) were converted into the corresponding ketones by Jones oxidation for data collection.

1-Butyl-1-iodo-2,2,3,3-tetramethylcyclopropane (6j): R_f = 0.83 (hexane); IR (neat): $\tilde{\nu}$ = 2942, 2864, 1460, 1378, 1105, 1005, 935, 828 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.92 (t, J = 7.2 Hz, 3H), 1.05 (s, 6H), 1.23 (s, 6H), 1.32 (tq, J = 7.5, 7.2 Hz, 2H), 1.47–1.60 (m, 2H), 1.74–1.81 (m, 2H); ^{13}C NMR (CDCl_3): δ = 14.1, 16.7, 22.4, 25.8, 28.6, 33.4, 39.0, 49.9. This compound is very sensitive to light or a trace of acid, and we were not able to perform an analysis or mass spectrometry.

1-Allyl-1-butyl-2,2,3,3-tetramethylcyclopropane (6k): R_f = 0.89 (hexane); IR (neat): $\tilde{\nu}$ = 2996, 2924, 2870, 1640, 1468, 1379, 1110, 994, 909 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.87 (t, J = 6.9 Hz, 3H), 0.98 (s, 6H), 0.99 (s, 6H), 1.15–1.36 (m, 6H), 2.13 (d, J = 6.6 Hz, 2H), 4.98 (d, J = 10.2 Hz, 1H), 5.00 (d, J = 17.1 Hz, 1H), 5.71 (ddt, J = 10.2, 17.1, 6.6 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 14.1, 18.6, 18.7, 22.9, 23.3, 27.5, 28.7, 29.1, 32.4, 115.2, 138.4; elemental analysis calcd (%) for $\text{C}_{14}\text{H}_{26}$: C 86.52, H 13.48; found: C 86.50, H 13.78.

endo-7-Butyl-7-iodobicyclo[4.1.0]heptane (6n): R_f = 0.80 (hexane); IR (neat): $\tilde{\nu}$ = 2924, 2852, 1461, 1444, 1378, 1170, 1124, 819 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.66–0.77 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H), 1.12–1.40 (m, 6H), 1.40–1.59 (m, 4H), 1.59–1.67 (m, 2H), 2.02–2.16 (m, 2H); ^{13}C NMR (CDCl_3): δ = 14.1, 20.7, 21.2, 21.9, 23.9, 31.7, 39.3, 47.8; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{19}\text{I}$: C 47.49, H 6.88; found: C 47.27, H 6.90.

exo-7-Butyl-7-iodobicyclo[4.1.0]heptane (7n): R_f = 0.74 (hexane); IR (neat): $\tilde{\nu}$ = 2918, 2854, 1467, 1450, 1378, 1209, 1168, 1112, 1049, 926, 748 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.94 (t, J = 7.2 Hz, 3H), 1.08–1.42 (m, 6H), 1.42–1.60 (m, 8H), 1.76–1.92 (m, 2H); ^{13}C NMR (CDCl_3): δ = 14.1, 18.6, 21.7, 22.3, 24.5, 28.8, 32.4, 35.2; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{19}\text{I}$: C 47.49, H 6.88; found: C 47.20, H 6.86.

endo-7-Benzoyl-7-butylbicyclo[4.1.0]heptane (6p): R_f = 0.61 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2928, 2854, 1674, 1598, 1449, 1354, 1215, 1174, 935, 713, 690 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.78 (t, J = 6.9 Hz, 3H), 0.84–1.00 (m, 2H), 1.06–1.32 (m, 8H), 1.53–1.62 (m, 2H), 1.74–1.94 (m, 4H), 7.41–7.51 (m, 2H), 7.51–7.58 (m, 1H), 8.02–8.08 (m, 2H); ^{13}C NMR (CDCl_3): δ = 13.8, 20.7, 21.3, 21.3, 22.4, 29.4, 35.0, 40.5, 128.5, 129.6, 132.7, 137.1, 201.1; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{O}$: C 84.32, H 9.44; found: C 84.56, H 9.64.

exo-7-Benzoyl-7-butylbicyclo[4.1.0]heptane (7p): R_f = 0.54 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2926, 2856, 1673, 1448, 1270, 1212, 1020, 710 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.73 (t, J = 6.9 Hz, 3H), 1.08–1.22 (m, 4H), 1.24–1.46 (m, 4H), 1.50–1.64 (m, 4H), 1.71–1.80 (m, 2H), 1.96–2.12 (m, 2H), 7.42 (dd, J = 6.6, 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.78 (d, J = 6.6 Hz, 2H); ^{13}C NMR (CDCl_3): δ = 13.7, 18.4, 18.6, 22.0, 22.8, 26.5, 29.4, 37.2, 128.3, 128.4, 131.8, 137.6, 204.5; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{O}$: C 84.32, H 9.44; found: C 84.59, H 9.66.

endo-9-Butyl-9-iodobicyclo[6.1.0]nonane (6s): R_f = 0.86 (hexane); IR (neat): $\tilde{\nu}$ = 2906, 2852, 1466, 1173, 1111, 943, 741 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.18–0.29 (m, 2H), 0.90 (t, J = 7.5 Hz, 3H), 1.10–1.71 (m, 16H), 1.79 (dd, J = 2.1, 13.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ = 14.1, 21.8, 26.7, 27.3, 29.1, 30.0, 31.5, 34.0, 46.9; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{23}\text{I}$: C 50.99, H 7.57; found: C 51.28, H 7.63.

exo-9-Butyl-9-iodobicyclo[6.1.0]nonane (7s): R_f = 0.82 (hexane); IR (neat): $\tilde{\nu}$ = 2920, 2852, 1466, 1178, 1113, 741 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.92 (t, J = 6.9 Hz, 3H), 1.00–1.17 (m, 2H), 1.24–1.64 (m, 16H), 2.06 (dd, J = 1.8, 13.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ = 14.0, 19.1, 21.7, 22.3, 26.0, 28.6, 31.8, 32.7, 34.8; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{23}\text{I}$: C 50.99, H 7.57; found: C 51.02, H 7.39.

1-Butyl-2,3-dipentylcyclopropane (2,3-cis, 6u/7u = 71/29): R_f = 0.85 (hexane); IR (neat): $\tilde{\nu}$ = 2954, 2920, 2852, 1467, 1378, 725 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.02 (tt, J = 5.1, 6.3 Hz, 1H), 0.31–0.43 (m, 2H), 0.79–0.98 (m, 9H), 1.00–1.44 (m, 22H); ^{13}C NMR (CDCl_3): δ = 14.0, 14.1, 17.7, 17.8, 22.5, 22.6, 22.8, 23.1, 23.4, 25.3, 28.1, 28.4, 29.9, 30.0, 31.8, 31.9, 32.1, 32.5, 32.6, 34.2; elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{34}$: C 85.63, H 14.37; found: C 85.64, H 14.61.

r-1-Butyl-2-c-3-t-dipentylcyclopropane (6v): R_f = 0.94 (hexane); IR (neat): $\tilde{\nu}$ = 2954, 2918, 2850, 1467, 1378, 723 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.03 (tt, J = 4.8, 6.6 Hz, 1H), 0.30–0.43 (m, 2H), 0.84–0.94 (m, 9H), 1.02–1.42 (m, 22H); ^{13}C NMR (CDCl_3): δ = 14.0, 14.1, 22.6, 22.6, 23.3, 23.4, 25.4, 28.1,

28.4, 29.3, 29.9, 31.7, 31.8, 32.5, 34.5; elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{34}$: C 85.63, H 14.37; found: C 85.68, H 14.62.

Synthesis of dibromomethylsilanes 12: The solution of LDA (lithium diisopropylamide) was prepared by the slow addition of butyllithium (39 mL, 1.6 M solution in hexane, 62 mmol) to a solution of diisopropylamine (8.8 mL, 63 mmol) in THF (40 mL) at 0 °C. The resulting solution was added to a solution of dibromomethane (4.2 mL, 60 mmol) and trialkylchlorosilane (60 mmol) in THF (50 mL) dropwise at –78 °C. After stirring for 0.5 h at –78 °C, the resulting mixture was poured into 1 M HCl and extracted with hexane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided **12a–d**. Spectral data for **12a**,^[9b] **12b**, and **12d**^[41] were identical with those reported in the literature.

(Dibromomethyl)dimethylphenylsilane (12c): R_f = 0.40 (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu}$ = 2968, 1427, 1252, 1117, 820, 787, 735, 698, 644, 617 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.57 (s, 6H), 5.25 (s, 1H), 7.35–7.50 (m, 3H), 7.60–7.65 (m, 2H); ^{13}C NMR (CDCl_3): δ = –5.0, 35.2, 128.0, 130.3, 133.9, 134.6; elemental analysis calcd (%) for $\text{C}_9\text{H}_{12}\text{Br}_2\text{Si}$: C 35.09, H 3.93; found: C 35.32, H 3.74.

General procedure for the preparation of 1-silylpentylmagnesium species and its reaction with electrophiles: Butyllithium (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to –78 °C, and a solution of **12** (1.0 mmol) in THF (2 mL) was added dropwise. After the mixture was stirred for 10 min, $\text{CuCN} \cdot 2\text{LiCl}$ (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added, and the mixture was allowed to gradually warm to –30 °C over a period of 2 h. Allyl bromide (0.26 mL, 3.0 mmol) was added at –30 °C. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl . The mixture was extracted with hexane, and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography provided **18**.

(Bromomethyl)methylphenylsilane (15b): R_f = 0.37 (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu}$ = 2928, 1428, 1385, 1254, 1115, 999, 804, 765, 733, 696 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.75 (s, 3H), 2.93 (s, 2H), 7.36–7.48 (m, 6H), 7.55–7.60 (m, 4H); ^{13}C NMR (CDCl_3): δ = –5.2, 14.7, 128.1, 130.0, 134.5, 134.7; elemental analysis calcd (%) for $\text{C}_{14}\text{H}_{15}\text{BrSi}$: C 57.73, H 5.19; found: C 57.72, H 5.18.

Methylpentylphenylsilane (17b): R_f = 0.49 (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu}$ = 2918, 1428, 1251, 784, 729, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.55 (s, 3H), 0.85 (t, J = 6.9 Hz, 3H), 1.07 (t, J = 8.0 Hz, 2H), 1.20–1.38 (m, 6H), 7.31–7.40 (m, 6H), 7.49–7.56 (m, 4H); ^{13}C NMR (CDCl_3): δ = –4.6, 13.9, 14.0, 22.1, 23.4, 35.8, 127.8, 129.1, 134.6, 137.7; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{Si}$: C 80.53, H 9.01; found: C 80.44, H 8.85.

4-(tert-Butyldimethylsilyl)-1-octene (18a): R_f = 0.87 (hexane); IR (neat): $\tilde{\nu}$ = 2924, 2854, 1465, 1254, 908, 825, 806, 761 cm^{-1} ; ^1H NMR (CDCl_3): δ = –0.06 (s, 3H), –0.05 (s, 3H), 0.75–0.90 (m, 1H), 0.87 (t, J = 6.9 Hz, 3H), 0.89 (s, 9H), 1.14–1.38 (m, 5H), 1.38–1.52 (m, 1H), 1.97–2.10 (m, 1H), 2.22–2.34 (m, 1H), 4.94 (d, J = 9.9 Hz, 1H), 4.98 (d, J = 16.8 Hz, 1H), 5.78 (ddt, J = 9.9, 16.8, 6.9 Hz, 1H); ^{13}C NMR (CDCl_3): δ = –6.4, –6.3, 14.0, 17.4, 22.3, 22.9, 27.2, 29.1, 31.1, 34.4, 114.8, 139.5; elemental analysis calcd (%) for $\text{C}_{14}\text{H}_{30}\text{Si}$: C 74.25, H 13.35; found: C 74.00, H 13.11.

4-(Methyldiphenylsilyl)-1-octene (18b): R_f = 0.55 (hexane); IR (neat): $\tilde{\nu}$ = 3064, 2920, 2854, 1638, 1428, 1252, 1110, 998, 908, 785, 732, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.59 (s, 3H), 0.80 (t, J = 7.2 Hz, 3H), 1.10–1.62 (m, 7H), 2.01–2.15 (m, 1H), 2.28–2.40 (m, 1H), 4.90 (d, J = 10.2 Hz, 1H), 4.92 (d, J = 17.4 Hz, 1H), 5.75 (ddt, J = 10.2, 17.4, 7.2 Hz, 1H), 7.30–7.40 (m, 6H), 7.48–7.59 (m, 4H); ^{13}C NMR (CDCl_3): δ = –5.3, 13.8, 22.7, 23.5, 28.9, 31.4, 34.2, 115.0, 127.8, 129.1, 134.6, 137.1, 139.2; elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{28}\text{Si}$: C 81.75, H 9.15; found: C 81.74, H 9.20.

4-(Dimethylphenylsilyl)-1-octene (18c): R_f = 0.64 (hexane); IR (neat): $\tilde{\nu}$ = 2920, 2854, 1639, 1428, 1112, 995, 908, 814, 766, 731, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.28 (s, 6H), 0.82 (t, J = 6.9 Hz, 3H), 0.90–0.95 (m, 1H), 1.08–1.48 (m, 6H), 1.96–2.09 (m, 1H), 2.17–2.28 (m, 1H), 4.88–4.98 (m, 2H), 5.73 (ddt, J = 10.2, 17.4, 7.2 Hz, 1H), 7.31–7.38 (m, 3H), 7.47–7.54 (m, 2H); ^{13}C NMR (CDCl_3): δ = –3.8, –3.8, 13.9, 22.8, 25.0, 28.7, 31.1, 34.0, 114.9, 127.7, 128.8, 137.0, 139.2, 139.3; elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{26}\text{Si}$: C 77.97, H 10.63; found: C 77.68, H 10.37.

4-(Dicyclohexylmethylsilyl)-1-octene (18d): R_f = 0.82 (hexane); IR (neat): $\tilde{\nu}$ = 2925, 2848, 1638, 1446, 1249, 1098, 997, 907, 889, 846, 770, 738 cm^{-1} ; ^1H NMR (CDCl_3): δ = -0.13 (s, 3H), 0.72–0.90 (m, 3H), 0.88 (t, J = 6.9 Hz, 3H), 1.06–1.52 (m, 16H), 1.58–1.84 (m, 10H), 1.95–2.07 (m, 1H), 2.21–2.32 (m, 1H), 4.89–8.02 (m, 2H), 5.79 (ddt, J = 9.9, 16.8, 6.9 Hz, 1H); ^{13}C NMR (CDCl_3): δ = -8.7, 14.0, 22.3, 22.6, 22.9, 23.9, 24.0, 27.1, 28.4, 28.4, 28.4, 28.5, 29.8, 31.5, 32.1, 35.0, 114.3, 140.3; elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{40}\text{Si}$: C 78.67, H 12.57; found: C 78.52, H 12.73.

4-(tert-Butyldimethylsilyl)-1,2-octadiene (19a): R_f = 0.80 (hexane); IR (neat): $\tilde{\nu}$ = 2952, 2924, 2854, 1951, 1466, 1362, 1250, 834 cm^{-1} ; ^1H NMR (CDCl_3): δ = -0.06 (s, 3H), -0.06 (s, 3H), 0.88 (t, J = 7.2 Hz, 3H), 0.90 (s, 9H), 1.12–1.58 (m, 7H), 4.63 (d, J = 6.9 Hz, 1H), 4.64 (d, J = 6.6 Hz, 1H), 4.98 (ddd, J = 6.6, 6.9, 9.3 Hz, 1H); ^{13}C NMR (CDCl_3): δ = -7.3, -7.2, 14.0, 17.4, 22.3, 25.9, 27.2, 29.3, 31.6, 74.6, 92.4, 208.7; HRMS (m/z) calcd for $\text{C}_{14}\text{H}_{26}\text{Si}$: 224.1960; found: 224.1955.

Procedure for the synthesis of α -silylketones 20a–l with acyl halide as the electrophile: Butyllithium (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to -78 °C, and a solution of **12** (1.0 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 10 min, $\text{CuCN} \cdot 2\text{LiCl}$ (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added, and the mixture was allowed to warm gradually to 0 °C over a period of 3 h. DMI (0.22 mL, 2.0 mmol) and the corresponding acyl chloride (2.5 mmol) were successively added. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH_4Cl . The mixture was extracted with ethyl acetate and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography gave **20**.

3-(tert-Butyldimethylsilyl)-2-heptanone (20a): R_f = 0.54 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2926, 2856, 1692, 1467, 1353, 1252, 1167, 836, 772 cm^{-1} ; ^1H NMR (CDCl_3): δ = -0.02 (s, 3H), 0.03 (s, 3H), 0.85 (t, J = 7.1 Hz, 3H), 0.92 (s, 9H), 1.04–1.34 (m, 4H), 1.34–1.48 (m, 1H), 1.96–2.03 (m, 1H), 2.07 (s, 3H), 2.47 (dd, J = 1.8, 11.9 Hz, 1H); ^{13}C NMR (CDCl_3): δ = -7.2, -5.2, 13.8, 17.7, 22.4, 26.7, 28.0, 32.0, 33.1, 46.1, 211.2; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{26}\text{SiO}$: C 68.35, H 12.35; found: C 68.17, H 12.55.

2-(tert-Butyldimethylsilyl)-1-cyclopropyl-1-hexanone (20b): R_f = 0.54 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2928, 2856, 1676, 1466, 1378, 1252, 1140, 1071, 836 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.02 (s, 3H), 0.04 (s, 3H), 0.77–0.84 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H), 0.94 (s, 9H), 0.94–1.00 (m, 1H), 1.00–1.08 (m, 1H), 1.08–1.20 (m, 1H), 1.20–1.36 (m, 3H), 1.36–1.49 (m, 1H), 1.82 (tt, J = 4.5, 7.8 Hz, 1H), 1.94–2.09 (m, 1H), 2.62 (dd, J = 2.1, 11.7 Hz, 1H); ^{13}C NMR (CDCl_3): δ = -7.1, -6.0, 10.4, 11.1, 13.8, 17.7, 22.0, 22.4, 26.8, 27.7, 33.1, 46.6, 212.5; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{30}\text{SiO}$: C 70.80, H 11.88; found: C 70.66, H 12.14.

2-(tert-Butyldimethylsilyl)-1-phenyl-1-hexanone (20c): R_f = 0.54 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2928, 2854, 1654, 1597, 1580, 1466, 1447, 1252, 1227, 1003, 833, 731, 688 cm^{-1} ; ^1H NMR (CDCl_3): δ = -0.26 (s, 3H), 0.03 (s, 3H), 0.84 (t, J = 6.9 Hz, 3H), 0.91 (s, 9H), 1.12–1.40 (m, 4H), 1.50–1.65 (m, 1H), 2.16–2.32 (m, 1H), 3.42 (dd, J = 2.1, 11.7 Hz, 1H), 7.44 (dd, J = 6.6, 7.2 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.90 (d, J = 6.6 Hz, 2H); ^{13}C NMR (CDCl_3): δ = -7.4, -5.8, 13.8, 18.1, 25.6, 26.9, 28.7, 33.3, 39.2, 128.1, 128.5, 132.4, 140.0, 203.9; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{30}\text{SiO}$: C 74.42, H 10.41; found: C 74.68, H 10.52.

(E)-5-(tert-Butyldimethylsilyl)-2-nonen-4-one (20d): R_f = 0.48 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2928, 2854, 1679, 1657, 1628, 1466, 1256, 1143, 1065, 969, 822, 770 cm^{-1} ; ^1H NMR (CDCl_3): δ = -0.08 (s, 3H), 0.03 (s, 3H), 0.84 (t, J = 7.2 Hz, 3H), 0.92 (s, 9H), 1.03–1.35 (m, 4H), 1.38–1.51 (m, 1H), 1.87 (dd, J = 1.8, 6.9 Hz, 3H), 1.96–2.11 (m, 1H), 2.61 (dd, J = 2.1, 11.7 Hz, 1H), 6.12 (dq, J = 15.6, 1.8 Hz, 1H), 6.77 (dq, J = 15.6, 6.9 Hz, 1H); ^{13}C NMR (CDCl_3): δ = -7.2, -6.0, 13.8, 17.9, 17.9, 22.5, 26.8, 27.8, 33.0, 43.1, 133.5, 140.4, 202.5; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{30}\text{SiO}$: C 70.80, H 11.88; found: C 71.00, H 11.61.

(E)-4-(tert-Butyldimethylsilyl)-1-phenyl-1-octen-3-one (20e): R_f = 0.44 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2926, 2854, 1673, 1642, 1609, 1466, 1450, 1252, 1138, 1070, 835, 688 cm^{-1} ; ^1H NMR (CDCl_3): δ = -0.22 (s, 3H), 0.08 (s, 3H), 0.85 (t, J = 6.9 Hz, 3H), 0.95 (s, 9H), 1.10–1.39 (m, 4H), 1.49–1.58 (m, 1H), 2.05–2.20 (m, 1H), 2.75 (dd, J = 2.4, 12.0 Hz, 1H), 6.73 (d, J = 15.9 Hz, 1H), 7.36–7.42 (m, 3H), 7.52 (d, J = 15.9 Hz, 1H), 7.52–7.58 (m, 2H); ^{13}C NMR (CDCl_3): δ = -7.0, -5.9, 13.8, 18.0, 22.5, 26.9, 27.9, 33.1,

44.6, 127.8, 128.3, 129.0, 130.2, 135.0, 140.7, 202.2; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{32}\text{SiO}$: C 75.88, H 10.19; found: C 76.17, H 9.90.

3-(Methyldiphenylsilyl)-2-heptanone (20f): R_f = 0.43 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2924, 1687, 1428, 1353, 1255, 1167, 1111, 790, 735, 699 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.64 (s, 3H), 0.81 (t, J = 6.9 Hz, 3H), 1.05–1.34 (m, 4H), 1.34–1.48 (m, 1H), 1.71 (s, 3H), 1.96–2.11 (m, 1H), 2.98 (dd, J = 2.1, 11.4 Hz, 1H), 7.31–7.45 (m, 6H), 7.47–7.53 (m, 2H), 7.55–7.60 (m, 2H); ^{13}C NMR (CDCl_3): δ = -6.4, 13.7, 22.3, 27.3, 32.5, 32.9, 47.7, 128.1, 128.2, 129.8, 129.9, 134.4, 134.8 (2C), 134.9, 210.6; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{26}\text{SiO}$: C 77.36, H 8.44; found: C 77.59, H 8.51.

5-(Methyldiphenylsilyl)-4-nonanone (20g): R_f = 0.53 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2954, 1691, 1429, 1254, 1112, 789 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.64 (s, 3H), 0.64 (t, J = 7.4 Hz, 3H), 0.81 (t, J = 6.9 Hz, 3H), 1.05–1.32 (m, 5H), 1.32–1.52 (m, 2H), 1.80 (ddd, J = 6.0, 8.7, 16.8 Hz, 1H), 1.98 (ddd, J = 6.0, 8.7, 16.8 Hz, 1H), 2.00–2.14 (m, 1H), 2.94 (dd, J = 2.1, 11.7 Hz, 1H), 7.30–7.45 (m, 6H), 7.46–7.53 (m, 2H), 7.55–7.61 (m, 2H); ^{13}C NMR (CDCl_3): δ = -6.5, 13.5, 13.7, 16.8, 22.4, 27.4, 32.9, 46.5, 47.4, 128.0, 128.1, 129.8, 129.8, 134.7, 134.7, 134.8, 135.1, 212.6; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{30}\text{SiO}$: C 78.05, H 8.93; found: C 78.07, H 9.12.

2-Methyl-4-(methyldiphenylsilyl)-3-octanone (20h): R_f = 0.49 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2956, 2924, 1689, 1466, 1428, 1112, 1057, 788, 736, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.58 (d, J = 6.9 Hz, 3H), 0.64 (s, 3H), 0.80 (t, J = 7.2 Hz, 3H), 0.96 (d, J = 6.9 Hz, 3H), 1.00–1.42 (m, 5H), 1.97 (sept, J = 6.9 Hz, 1H), 2.00–2.15 (m, 1H), 3.14 (dd, J = 2.4, 11.7 Hz, 1H), 7.29–7.44 (m, 6H), 7.46–7.52 (m, 2H), 7.54–7.61 (m, 2H); ^{13}C NMR (CDCl_3): δ = -6.5, 13.8, 16.1, 19.0, 22.5, 27.6, 33.1, 42.1, 45.3, 128.0, 128.1, 129.8 (2C), 134.7, 134.8, 134.8, 135.2, 215.9; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{30}\text{SiO}$: C 78.05, H 8.93; found: C 77.86, H 9.19.

1-Cyclopropyl-2-(methyldiphenylsilyl)-1-hexanone (20i): R_f = 0.50 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2926, 2854, 1675, 1429, 1378, 1254, 1112, 792, 736, 721, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.30 (dddd, J = 2.7, 6.6, 7.5, 9.0 Hz, 1H), 0.57–0.68 (m, 1H), 0.64 (s, 3H), 0.71–0.93 (m, 2H), 0.81 (t, J = 7.2 Hz, 3H), 1.08–1.35 (m, 4H), 1.36–1.49 (m, 2H), 1.99–2.14 (m, 1H), 3.13 (dd, J = 2.4, 11.4 Hz, 1H), 7.30–7.45 (m, 6H), 7.50–7.56 (m, 2H), 7.56–7.61 (m, 2H); ^{13}C NMR (CDCl_3): δ = 5.9, 10.5, 11.1, 13.8, 22.3, 22.5, 27.0, 32.9, 48.3, 127.9, 128.0, 129.6, 129.7, 134.8, 134.9, 134.9, 135.2, 211.6; elemental analysis calcd (%) for $\text{C}_{22}\text{H}_{28}\text{SiO}$: C 78.52, H 8.39; found: C 78.23, H 8.49.

2-(Methyldiphenylsilyl)-1-phenyl-1-hexanone (20j): R_f = 0.53 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2922, 2854, 1659, 1447, 1429, 1344, 1255, 1228, 1112, 1002, 790, 732, 697 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.57 (s, 3H), 0.80 (t, J = 7.2 Hz, 3H), 1.16–1.42 (m, 4H), 1.55–1.68 (m, 1H), 2.20–2.36 (m, 1H), 3.86 (dd, J = 2.4, 11.4 Hz, 1H), 7.13–7.20 (m, 2H), 7.20–7.28 (m, 3H), 7.33–7.42 (m, 6H), 7.54–7.60 (m, 2H), 7.64–7.70 (m, 2H); ^{13}C NMR (CDCl_3): δ = -5.7, 13.8, 22.4, 28.2, 33.0, 41.0, 127.7, 128.0, 128.0, 128.1, 129.5, 129.7, 132.0, 134.4, 134.7, 134.8, 134.9, 139.7, 203.3; elemental analysis calcd (%) for $\text{C}_{25}\text{H}_{28}\text{SiO}$: C 80.59, H 7.57; found: C 80.40, H 7.47.

5-(Methyldiphenylsilyl)-4-undecanone (20k): R_f = 0.52 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2928, 2856, 1690, 1464, 1429, 1254, 1111, 791, 737, 700 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.64 (s, 3H), 0.64 (t, J = 7.5 Hz, 3H), 0.83 (t, J = 6.9 Hz, 3H), 1.08–1.32 (m, 9H), 1.32–1.49 (m, 2H), 1.80 (ddd, J = 6.0, 8.7, 16.8 Hz, 1H), 1.97 (ddd, J = 6.0, 8.7, 16.8 Hz, 1H), 2.03–2.15 (m, 1H), 2.94 (dd, J = 2.4, 11.4 Hz, 1H), 7.30–7.44 (m, 6H), 7.46–7.51 (m, 2H), 7.55–7.59 (m, 2H); ^{13}C NMR (CDCl_3): δ = -6.4, 13.5, 13.9, 16.8, 22.5, 27.7, 29.0, 30.7, 31.5, 46.5, 47.4, 128.0, 128.1, 129.8, 129.8, 129.8, 134.7, 134.7, 134.8, 135.1; HRMS (m/z) calcd for $\text{C}_{24}\text{H}_{34}\text{OSi}$ 366.2379; found: 366.2362.

2-(Methyldiphenylsilyl)-1-phenyl-1-octanone (20l): R_f = 0.49 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2926, 2855, 1661, 1429, 1342, 1256, 1217, 1113, 791, 733, 698 cm^{-1} ; ^1H NMR (CDCl_3): δ = 0.55 (s, 3H), 0.80 (t, J = 6.9 Hz, 3H), 1.08–1.40 (m, 8H), 1.52–1.64 (m, 1H), 2.18–2.32 (m, 1H), 3.84 (dd, J = 2.4, 11.4 Hz, 1H), 7.12–7.25 (m, 5H), 7.32–7.42 (m, 6H), 7.53–7.60 (m, 2H), 7.62–7.69 (m, 2H); ^{13}C NMR (CDCl_3): δ = -5.7, 13.9, 22.4, 28.5, 29.0, 30.8, 31.5, 41.1, 127.7, 128.0, 128.1, 129.5, 129.7, 132.0, 134.5, 134.8, 134.9, 139.8, 203.3; elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{32}\text{OSi}$: C 80.95, H 8.05; found: C 80.70, H 8.16.

Procedure for the conjugate addition of α -silylpentylmagnesium to enones: Butyllithium (1.2 mL, 1.6 M solution in hexane, 2.0 mmol) was added to a solution of butylmagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to -78 °C, and a solution of **12**

(1.0 mmol) in THF (2 mL) was added dropwise. The mixture was stirred for 10 min, CuCN · 2LiCl (0.3 mL, 1.0 M solution in THF, 0.3 mmol) was added, and the mixture was allowed to warm gradually to 0 °C over a period of 3 h. Then the mixture was cooled to –78 °C and a mixture of the corresponding enone (4.0 mmol) and chlorotrimethylsilane (0.51 mL, 4.0 mmol) in THF (2 mL) was added. The reaction mixture was gradually warmed to 0 °C and then poured into saturated aqueous NH₄Cl and extracted with ethyl acetate. The organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography provided **21**, **22**, or **23**.

5-(tert-Butyldimethylsilyl)-2-nonanone (21a): R_f = 0.51 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2926, 2854, 1720, 1467, 1362, 1252, 1155, 828, 805, 763 cm^{–1}; ¹H NMR (CDCl₃): δ = –0.06 (s, 6H), 0.65–0.75 (m, 1H), 0.88 (t, J = 7.1 Hz, 3H), 0.89 (s, 9H), 1.15–1.38 (m, 5H), 1.40–1.60 (m, 2H), 1.72–1.86 (m, 1H), 2.13 (s, 3H), 2.40 (ddd, J = 6.0, 10.5, 16.5 Hz, 1H), 2.44 (ddd, J = 6.0, 10.5, 16.5 Hz, 1H); ¹³C NMR (CDCl₃): δ = –6.5, –6.4, 13.9, 17.3, 22.0, 23.0, 24.1, 27.2, 29.3, 29.8, 31.2, 43.3, 209.6; elemental analysis calcd (%) for C₁₅H₃₂SiO: C 70.24, H 12.57; found: C 70.30, H 12.42.

5-(Methyldiphenylsilyl)-2-nonanone (21b): R_f = 0.60 (hexane/ethyl acetate 5:1); IR (neat): $\tilde{\nu}$ = 2920, 2854, 1714, 1428, 1358, 1253, 1109, 785, 735, 719, 699 cm^{–1}; ¹H NMR (CDCl₃): δ = 0.58 (s, 3H), 0.79 (t, J = 7.2 Hz, 3H), 1.08–1.40 (m, 6H), 1.46–1.90 (m, 3H), 1.95 (s, 3H), 2.24 (ddd, J = 6.0, 9.6, 16.5 Hz, 1H), 2.35 (ddd, J = 6.0, 9.6, 16.5 Hz, 1H), 7.30–7.39 (m, 6H), 7.50–7.56 (m, 4H); ¹³C NMR (CDCl₃): δ = –5.7, 13.8, 22.7, 23.1, 23.9, 29.4, 29.6, 31.4, 43.3, 127.9, 127.9, 129.2, 129.2, 134.8, 136.9, 136.9, 209.4; elemental analysis calcd (%) for C₂₂H₃₀SiO: C 78.05, H 8.93; found: C 77.90, H 8.80.

3-[1-(tert-Butyldimethylsilyl)pentyl]-1-cyclohexanone (22, 86:14 mixture of diastereomers): R_f = 0.49 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2928, 2850, 1711, 1462, 1254, 823, 805, 764 cm^{–1}; ¹H NMR (CDCl₃): δ = –0.03 (s, 2.58H), –0.03 (s, 0.42H), 0.01 (s, 0.42H), 0.02 (s, 2.58H), 0.65–0.72 (m, 0.14H), 0.77–0.84 (m, 0.86H), 0.84–0.93 (m, 1.68H), 0.88 (s, 7.74H), 0.89 (t, J = 6.9 Hz, 2.58H), 1.18–1.45 (m, 6H), 1.48–1.78 (m, 3H), 1.94–2.10 (m, 2H), 2.14–2.42 (m, 4H); ¹³C NMR (CDCl₃) (major isomer): δ = –5.8, –5.1, 14.0, 17.3, 23.1, 25.8, 26.7, 27.1, 28.6, 31.7, 34.1, 40.9, 41.2, 46.6, 212.7; elemental analysis calcd (%) for C₁₇H₃₄SiO: C 72.27, H 12.13; found: C 72.16, H 12.16.

3-[1-(tert-Butyldimethylsilyl)pentyl]-1-cyclopentanone (23, 67:33 mixture of diastereomers): R_f = 0.53 (hexane/ethyl acetate 5:1); IR (neat): $\tilde{\nu}$ = 2924, 2854, 1744, 1466, 1252, 1155, 825, 763 cm^{–1}; ¹H NMR (CDCl₃): δ = –0.03 (s, 4.02H), –0.01 (s, 0.99H), 0.00 (s, 0.99H), 0.78–0.96 (m, 4H), 0.91 (s, 9H), 1.16–1.52 (m, 6H), 1.60–2.48 (m, 7H); ¹³C NMR (CDCl₃): δ = –5.8, –5.5, –5.4, –5.0, 13.9, 17.4, 17.5, 23.1, 23.2, 26.4, 26.7, 27.0, 27.2, 27.2, 28.0, 29.6, 33.9, 34.1, 38.9, 38.9, 39.1, 39.1, 43.0, 45.3, 220.1; elemental analysis calcd (%) for C₁₆H₃₂SiO: C 71.57, H 12.01; found: C 71.31, H 12.28.

Procedure for the introduction of a sec-butyl group: sec-Butyllithium (2.0 mL, 1.0 M solution in hexane-cyclohexane, 2.0 mmol) was added to a solution of sec-butyldimagnesium bromide (1.0 mL, 1.0 M solution in THF, 1.0 mmol) in THF (5 mL) at 0 °C, and the mixture was stirred for 10 min. The resulting solution was cooled to –78 °C and a solution of (dibromomethyl)methyldiphenylsilane (**12b**, 370 mg, 1.0 mmol) in THF (2 mL) was added dropwise. The mixture was allowed to warm to ambient temperature gradually. CuCN · 2LiCl (0.2 mL, 1.0 M solution in THF, 0.2 mmol) and the corresponding electrophile (3.0 mmol) were successively added at 0 °C. After stirring for 1 h at 0 °C, the reaction was quenched with saturated aqueous NH₄Cl. The mixture was extracted with hexane and the organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography provided **24**.

5-Methyl-4-(methyldiphenylsilyl)-1-heptene (24a): R_f = 0.46 (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu}$ = 3071, 2959, 1638, 1460, 1427, 1252, 1109, 997, 908, 787, 737, 700 cm^{–1}; ¹H NMR (CDCl₃): δ = 0.64 (s, 1.5H), 0.65 (s, 1.5H), 0.76 (t, J = 7.5 Hz, 1.5H), 0.79 (d, J = 6.6 Hz, 1.5H), 0.82 (t, J = 7.2 Hz, 1.5H), 0.90 (d, J = 7.2 Hz, 1.5H), 1.15–1.33 (m, 2H), 1.51–1.62 (m, 1H), 1.62–1.76 (m, 1H), 2.19–2.36 (m, 2H), 4.83–4.94 (m, 2H), 5.71–5.79 (m, 1H), 7.34–7.38 (m, 6H), 7.50–7.59 (m, 4H); ¹³C NMR (CDCl₃): δ = –4.3, –3.7, 12.3, 12.5, 17.7, 19.2, 28.3, 29.1, 29.8, 30.5, 30.7, 32.3, 35.1, 35.4, 114.4, 114.7, 127.8, 127.9, 129.0, 129.3, 134.3, 134.8, 134.9, 134.9, 137.6, 137.8, 138.2, 140.2, 140.7; HRMS (m/z) calcd for C₂₁H₂₈Si: 308.1960; found: 308.1945.

6-Methyl-5-(methyldiphenylsilyl)-4-octanone (24b, ≈1:1 mixture of two diastereomers): R_f = 0.49 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2961,

2874, 1690, 1464, 1429, 1254, 1111, 1038, 793, 737, 700 cm^{–1}; ¹H NMR (CDCl₃): δ = 0.57 (t, J = 7.5 Hz, 1.5H), 0.60 (t, J = 7.5 Hz, 1.5H), 0.70 (t, J = 7.5 Hz, 1.5H), 0.72 (s, 1.5H), 0.73 (d, J = 6.3 Hz, 1.5H), 0.75 (s, 1.5H), 0.79 (t, J = 7.5 Hz, 1.5H), 0.88 (d, J = 6.3 Hz, 1.5H), 0.85–1.15 (m, 2H), 1.22–1.44 (m, 2H), 1.69 (ddd, J = 5.7, 9.0, 17.4 Hz, 0.5H), 1.75 (ddd, J = 5.7, 9.0, 17.4 Hz, 0.5H), 1.90–2.03 (m, 1H), 2.04–2.16 (m, 0.5H), 2.18–2.31 (m, 0.5H), 2.85 (d, J = 10.8 Hz, 0.5H), 2.87 (d, J = 9.9 Hz, 0.5H), 7.26–7.35 (m, 3H), 7.35–7.41 (m, 3H), 7.47–7.53 (m, 2H), 7.55–7.61 (m, 2H); ¹³C NMR (CDCl₃): δ = –5.4, –5.2, 10.8, 11.4, 13.4, 13.4, 16.1, 16.2, 18.8, 19.1, 29.2, 29.8, 30.0, 35.4, 48.7, 48.9, 52.4, 52.6, 127.9, 128.0, 129.5, 129.5, 129.5, 134.6, 134.7, 135.1, 135.1, 135.5, 135.6, 135.8, 136.0, 213.4, 213.6; elemental analysis calcd (%) for C₂₂H₃₀OSi: C 78.05, H 8.93; found: C 78.30, H 8.94.

2,5-Dimethyl-4-(methyldiphenylsilyl)-3-heptanone (24c, ≈1:1 mixture of two diastereomers): R_f = 0.56 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2966, 1688, 1454, 1429, 1381, 1254, 1109, 1042, 791, 700 cm^{–1}; ¹H NMR (CDCl₃): δ = 0.36 (d, J = 6.6 Hz, 1.5H), 0.38 (d, J = 6.6 Hz, 1.5H), 0.46–0.75 (m, 0.5H), 0.70 (t, J = 7.5 Hz, 1.5H), 0.73 (s, 1.5H), 0.76 (s, 1.5H), 0.76 (d, J = 6.6 Hz, 1.5H), 0.81 (t, J = 7.5 Hz, 1.5H), 0.87 (d, J = 6.6 Hz, 1.5H), 0.96 (d, J = 7.5 Hz, 1.5H), 0.98 (d, J = 7.5 Hz, 1.5H), 1.00–1.26 (m, 0.5H), 1.33–1.53 (m, 1H), 1.84–2.06 (m, 1H), 2.06–2.29 (m, 1H), 3.05 (d, J = 10.5 Hz, 0.5H), 3.08 (d, J = 10.2 Hz, 0.5H), 7.26–7.42 (m, 6H), 7.47–7.53 (m, 2H), 7.57–7.62 (m, 2H); ¹³C NMR (CDCl₃): δ = –5.2, –5.0, 11.4, 11.5, 15.9, 18.6, 18.7, 18.7, 19.4, 29.1, 30.1, 35.1, 35.2, 43.0, 43.1, 51.1, 51.9, 127.9, 128.0, 129.5, 129.5, 129.5, 134.7, 134.7, 135.3, 135.3, 135.5, 136.0, 136.2, 216.2, 216.5; elemental analysis calcd (%) for C₂₂H₃₀OSi: C 78.05, H 8.93; found: C 78.16, H 9.16.

1-Cyclopropyl-3-methyl-2-(methyldiphenylsilyl)-1-pentanone (24d, ≈1:1 mixture of two diastereomers): R_f = 0.44 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2963, 2930, 1674, 1429, 1377, 1254, 1111, 1063, 797, 737, 700 cm^{–1}; ¹H NMR (CDCl₃): δ = 0.16–0.26 (m, 0.5H), 0.24–0.35 (m, 0.5H), 0.50–0.67 (m, 2H), 0.67–0.83 (m, 1H), 0.71 (s, 1.5H), 0.72 (t, J = 7.5 Hz, 1.5H), 0.73 (s, 1.5H), 0.78 (d, J = 6.9 Hz, 1.5H), 0.81 (t, J = 7.5 Hz, 1.5H), 0.92 (d, J = 6.6 Hz, 1.5H), 0.91–1.07 (m, 0.5H), 1.07–1.24 (m, 0.5H), 1.35–1.58 (m, 2H), 1.95–2.15 (m, 0.5H), 2.15–2.32 (m, 0.5H), 3.09 (d, J = 10.8 Hz, 0.5H), 3.11 (d, J = 9.6 Hz, 0.5H), 7.26–7.40 (m, 6H), 7.52–7.58 (m, 2H), 7.58–7.64 (m, 2H); ¹³C NMR (CDCl₃): δ = –4.7, –4.4, 10.1, 10.3, 10.6, 11.2, 11.3, 11.4, 18.9, 19.3, 23.4, 23.4, 29.3, 29.9, 34.8, 35.2, 54.3, 54.7, 127.8, 128.0, 129.4, 129.4, 129.5, 134.8, 134.8, 135.1, 135.2, 135.6, 135.8, 136.0, 212.8, 213.0; elemental analysis calcd (%) for C₂₂H₂₈OSi: C 78.52, H 8.39; found: C 78.34, H 8.51.

3-Methyl-2-(methyldiphenylsilyl)-1-phenyl-1-pentanone (24e, ≈1:1 mixture of two diastereomers): R_f = 0.42 (hexane/ethyl acetate 10:1); IR (neat): $\tilde{\nu}$ = 2963, 2930, 1659, 1429, 1263, 1204, 1111, 789, 735, 718, 698 cm^{–1}; ¹H NMR (CDCl₃): δ = 0.67 (s, 1.5H), 0.71 (s, 1.5H), 0.71 (t, J = 7.4 Hz, 1.5H), 0.78 (t, J = 7.7 Hz, 1.5H), 0.86 (d, J = 6.9 Hz, 1.5H), 0.94 (d, J = 6.6 Hz, 1.5H), 0.98–1.12 (m, 0.5H), 1.12–1.28 (m, 0.5H), 1.41–1.58 (m, 1H), 2.22–2.36 (m, 0.5H), 2.36–2.51 (m, 0.5H), 3.81 (d, J = 10.5 Hz, 0.5H), 3.83 (d, J = 9.9 Hz, 0.5H), 7.12–7.23 (m, 5H), 7.24–7.40 (m, 6H), 7.40–7.48 (m, 2H), 7.52–7.60 (m, 2H); ¹³C NMR (CDCl₃): δ = –4.6, –4.4, 11.0, 11.5, 19.0, 19.5, 29.4, 30.2, 35.8, 36.1, 46.9, 47.1, 127.6, 127.6, 127.9, 128.0, 128.1, 128.1, 129.2, 129.4, 129.4, 131.9, 131.9, 134.7, 134.8, 135.1, 135.1, 135.2, 135.6, 135.8, 140.0, 140.3; HRMS (m/z) calcd for C₂₅H₂₈OSi 372.1909; found: 372.1912.

Preparation of dibromodisilylmethanes

Method A: Butyllithium (2.6 mL, 1.6 M solution in hexane, 4.2 mmol) was added dropwise to a solution of diisopropylamine (0.63 mL, 4.5 mmol) in THF (4 mL) at 0 °C, and the mixture was stirred for 0.5 h. The resulting solution of LDA was cooled to –78 °C, and a solution of a dibromomethylsilane (4.0 mmol) in THF (8 mL) was added dropwise at –78 °C. The mixture was stirred for 0.5 h, and the corresponding trialkylchlorosilane or iodomethane (5.0 mmol) was added. After stirring for 0.5 h at –78 °C, the mixture was poured into 1 M HCl and extracted with hexane. The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification by silica-gel column chromatography provided the corresponding dibromodisilylmethane.

Method B: The solution of LDA (lithium diisopropylamide) was prepared by the slow addition of butyllithium (39 mL, 1.6 M solution in hexane, 62 mmol) to a solution of diisopropylamine (8.8 mL, 63 mmol) in THF (40 mL) at 0 °C. The resulting solution was added to a solution of dibromomethane (4.2 mL, 30 mmol) and trialkylchlorosilane (65 mmol) in

THF dropwise at -78°C . After stirring for 2 h at room temperature, the resulting mixture was poured into 1 M HCl and extracted with hexane. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography or recrystallization provided the corresponding dibromodisilylmethane.

Method C: Butyllithium (25 mL, 1.6 M solution in hexane, 40 mmol) was slowly added to a solution of (chloro)methyldiphenylsilane (8.4 mL, 40 mmol) and carbon tetrabromide (6.63 g, 20 mmol) in THF (50 mL) at -78°C under an argon atmosphere. The cooling bath was removed and the mixture was stirred for 2 h at room temperature. Then, 1 M HCl was added to the reaction mixture and the whole mixture was extracted with chloroform. The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Recrystallization from hexane/ethyl acetate afforded **12k**.

Spectral data for **12f**^[18c] (prepared by method A from **12b** and chlorotrimethylsilane), and **12i**^[18a] (prepared by method B), were identical with those reported in the literature.

1,1-Dibromo-1-(methyldiphenylsilyl)ethane (12e, prepared by method A from 12b and iodomethane): $R_f = 0.31$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 1427, 1256, 1113, 1049, 999, 793, 733, 698\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.90$ (s, 3H), 2.59 (s, 3H), 7.36–7.51 (m, 6H), 7.78–7.84 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -4.6, 37.0, 58.4, 127.9, 130.3, 132.6, 136.0$; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{16}\text{Br}_2\text{Si}$: C 46.90, H 4.20; found: C 47.09, H 4.21.

Dibromobis(triethylsilyl)methane (12g, prepared by method A from dibromomethyltriethylsilane and chlorotriethylsilane): $R_f = 0.74$ (hexane); IR (neat): $\tilde{\nu} = 2955, 2878, 1462, 1414, 1379, 1242, 1009, 818, 743, 679\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.90$ (q, $J = 7.8\text{ Hz}$, 12H), 1.10 (t, $J = 7.8\text{ Hz}$, 18H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 4.8, 8.3, 58.2$; elemental analysis calcd (%) for $\text{C}_{13}\text{H}_{30}\text{Br}_2\text{Si}_2$: C 38.81, H 7.52; found: C 38.63, H 7.62.

Dibromo(tert-butyl)dimethylsilyl(trimethylsilyl)methane (12h, prepared by method A from 12a and chlorotrimethylsilane): $R_f = 0.77$ (hexane); IR (neat): $\tilde{\nu} = 2932, 2860, 1464, 1252, 847, 772, 691\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.26$ (s, 6H), 0.33 (s, 9H), 1.11 (s, 9H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -3.55, -0.58, 20.64, 57.30$; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{24}\text{Br}_2\text{Si}_2$: C 33.34, H 6.71; found: C 33.30, H 6.83.

Dibromobis(dimethylphenylsilyl)methane (12j, prepared by method B): $R_f = 0.61$ (hexane/ethyl acetate 30:1); m.p. 63°C ; IR (Nujol): $\tilde{\nu} = 1427, 1252, 1117, 839, 785, 735, 700, 640\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.33$ (s, 12H), 7.32–7.46 (m, 6H), 7.67 (dd, $J = 1.5, 7.8\text{ Hz}$, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -3.1, 56.0, 127.6, 130.1, 135.2, 135.6$; elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{22}\text{Br}_2\text{Si}_2$: C 46.16, H 5.01; found: C 46.08, H 4.94.

Dibromobis(methyldiphenylsilyl)methane (12k, prepared by method C): m.p. 174°C ; IR (Nujol): $\tilde{\nu} = 1429, 1252, 1103, 814, 789, 719, 700\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.27$ (s, 6H), 7.35 (dd, $J = 7.2, 8.1\text{ Hz}$, 8H), 7.44 (t, $J = 7.2\text{ Hz}$, 4H), 7.79 (d, $J = 8.1\text{ Hz}$, 8H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -2.7, 50.2, 127.6, 130.1, 134.1, 136.5$; elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{26}\text{Br}_2\text{Si}_2$: C 57.25, H 4.63; found: C 56.98, H 4.53.

Dibromo(methyldiphenylsilyl)(triethylgermyl)methane (12l, prepared by method A from 12a and chlorotriethylgermane): $R_f = 0.47$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2950, 2870, 1460, 1427, 1252, 1111, 1014, 813, 696\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.82$ – 0.92 (m, 6H), 0.87 (s, 3H), 0.96–1.04 (m, 9H), 7.37–7.47 (m, 6H), 7.86–7.92 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -2.1, 6.4, 9.2, 53.3, 127.7, 130.0, 134.3, 136.3$; elemental analysis calcd (%) for $\text{C}_{20}\text{H}_{28}\text{Br}_2\text{GeSi}$: C 45.42, H 5.34; found: C 45.14, H 5.22.

Procedure for the monomethylation of dibromodisilylmethanes 12 with Me_3MgLi : A solution of lithium trimethylmagnesate, [prepared by mixing methylmagnesium bromide (10.8 mL, 0.93 M solution in THF, 10 mmol) and methyl lithium (17.5 mL, 1.14 M solution in Et_2O , 20 mmol) in THF (15 mL)] was added to a solution of **12** (10 mmol) in THF (50 mL) at -78°C under an argon atmosphere. After stirring for 0.5 h at -78°C , the mixture was carefully poured into 1 M HCl and extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography or recrystallization provided **25**.

(1-Bromoethyl)methyldiphenylsilane (25a): $R_f = 0.36$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2956, 1428, 1254, 1114, 1006, 790, 731, 697\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.73$ (d, $J = 0.6\text{ Hz}$, 3H), 1.74 (dd, $J = 0.6, 7.5\text{ Hz}$, 3H), 3.86 (q, $J = 7.5\text{ Hz}$, 1H), 7.34–7.47 (m, 6H), 7.55–7.60 (m, 2H), 7.60–

7.66 (m, 2H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -6.3, 20.9, 33.9, 128.0, 128.0, 129.9$ (2C), 134.2, 134.3, 135.1, 135.1; elemental analysis calcd (%) for $\text{C}_{15}\text{H}_{17}\text{BrSi}$: C 59.01, H 5.61; found: C 59.07, H 5.60.

2-Bromo-2-(methyldiphenylsilyl)propane (25e): $R_f = 0.36$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 3071, 2951, 1427, 1254, 1111, 1088, 893, 791, 727, 700\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.78$ (s, 3H), 1.86 (s, 6H), 7.35–7.48 (m, 6H), 7.71–7.77 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -5.1, 31.3, 53.7, 127.9, 129.8, 134.1, 135.7$; elemental analysis calcd (%) for $\text{C}_{16}\text{H}_{19}\text{BrSi}$: C 60.18, H 6.00; found: C 60.23, H 5.96.

1-Bromo-1-(methyldiphenylsilyl)-1-(trimethylsilyl)ethane (25f): $R_f = 0.44$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2955, 1427, 1252, 1109, 964, 841, 802, 736, 721, 700\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = -0.10$ (s, 9H), 0.79 (s, 3H), 1.92 (s, 3H), 7.30–7.48 (m, 6H), 7.72 (dd, $J = 1.8, 7.8\text{ Hz}$, 2H), 7.86 (dd, $J = 1.8, 7.8\text{ Hz}$, 2H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -2.2, -1.8, 23.7, 43.9, 127.5, 127.8, 129.5, 129.6, 135.0, 135.3, 135.8, 136.0$; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{23}\text{BrSi}_2$: C 57.28, H 6.68; found: C 57.53, H 6.67.

1-Bromo-1,1-bis(triethylsilyl)ethane (25g): $R_f = 0.84$ (hexane); IR (neat): $\tilde{\nu} = 2955, 2878, 1462, 1416, 1379, 1242, 1007, 970, 777, 735\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.76$ (q, $J = 8.4\text{ Hz}$, 6H), 0.78 (q, $J = 7.8\text{ Hz}$, 6H), 1.04 (t, $J = 7.8\text{ Hz}$, 9H), 1.04 (t, $J = 8.4\text{ Hz}$, 9H), 1.82 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = 4.0, 8.3, 25.0, 47.2$; elemental analysis calcd (%) for $\text{C}_{14}\text{H}_{33}\text{BrSi}_2$: C 49.82, H 9.86; found: C 49.80, H 9.56.

1-Bromo-1-(tert-butyl)dimethylsilyl-1-(trimethylsilyl)ethane (25h): $R_f = 0.77$ (hexane); IR (neat): $\tilde{\nu} = 2956, 2854, 1467, 1252, 966, 840, 822, 766\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.11$ (s, 3H), 0.17 (s, 3H), 0.15 (s, 9H), 1.02 (s, 9H), 1.85 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -4.3, -4.1, -1.2, 20.1, 24.3, 28.3, 45.9$; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{27}\text{BrSi}_2$: C 44.72, H 9.21; found: C 44.42, H 9.42.

1-Bromo-1,1-bis(trimethylsilyl)ethane (25i): $R_f = 0.72$ (hexane); IR (neat): $\tilde{\nu} = 2955, 1252, 966, 841, 760, 691\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.14$ (s, 18H), 1.71 (s, 3H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -1.6, 23.0, 45.0$; elemental analysis calcd (%) for $\text{C}_8\text{H}_{21}\text{BrSi}_2$: C 37.93, H 8.36; found: C 37.78, H 8.49.

1-Bromo-1,1-bis(dimethylphenylsilyl)ethane (25j): $R_f = 0.46$ (hexane/ethyl acetate 40:1); m.p. 73°C ; IR (Nujol): $\tilde{\nu} = 1587, 1427, 1258, 1111, 966, 827, 783, 739, 702, 671\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.25$ (s, 6H), 0.26 (s, 6H), 1.82 (s, 3H), 7.32–7.44 (m, 6H), 7.59 (dd, $J = 1.8, 7.8\text{ Hz}$, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -3.9, -3.4, 23.5, 44.1, 127.6, 129.5, 135.1, 136.7$; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{23}\text{BrSi}_2$: C 57.28, H 6.68; found: C 57.39, H 6.71.

1-Bromo-1,1-bis(methyldiphenylsilyl)ethane (25k): m.p. 126°C ; IR (Nujol): $\tilde{\nu} = 1429, 1254, 1103, 999, 964, 797, 735, 698\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.23$ (s, 6H), 2.12 (s, 3H), 7.26–7.43 (m, 12H), 7.58 (dd, $J = 1.2, 7.8\text{ Hz}$, 4H), 7.76 (dd, $J = 1.2, 7.8\text{ Hz}$, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -3.4, 24.5, 42.3, 127.6, 127.7, 129.6, 134.8, 135.3, 136.0, 136.3$; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{26}\text{BrSi}_2$: C 67.05, H 5.63; found: C 66.86, H 5.87.

1-Bromo-1-(methyldiphenylsilyl)-1-(triethylgermyl)ethane (25l): $R_f = 0.51$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2948, 2868, 1458, 1428, 1253, 1109, 1014, 791, 734, 698\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.75$ (t, $J = 7.5\text{ Hz}$, 6H), 0.79 (s, 3H), 0.96 (t, $J = 7.5\text{ Hz}$, 9H), 2.03 (s, 3H), 7.30–7.45 (m, 6H), 7.72 (dd, $J = 1.5, 7.8\text{ Hz}$, 2H), 7.85 (dd, $J = 1.5, 7.8\text{ Hz}$, 2H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -2.6, 5.0, 6.5, 9.4, 25.9, 127.5, 127.7, 129.4, 129.6, 135.1, 135.3, 135.7, 136.0$; elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{31}\text{BrGeSi}$: C 54.35, H 6.73; found: C 54.58, H 6.67.

Procedure for the synthesis of 1,1-disilylethenes 29 by dehydrobromination of 1-bromo-1,1-disilylethanes 25: A solution of **25** (9.0 mmol) and DBU (2.7 mL, 18.0 mmol) in DMF (40 mL) was stirred for 8 h at 90°C . The mixture was carefully poured into 1 M HCl and extracted with AcOEt. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica-gel column chromatography or recrystallization provided **29**. Spectral data for **29i** were identical with those reported in the literature.^[19a]

1-(Methyldiphenylsilyl)-1-(trimethylsilyl)ethene (29f): $R_f = 0.52$ (hexane/ethyl acetate 40:1); IR (neat): $\tilde{\nu} = 2957, 1427, 1250, 1113, 972, 839, 789, 737, 723, 700\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = -0.04$ (s, 9H), 0.68 (s, 3H), 6.24 (d, $J = 5.1\text{ Hz}$, 1H), 6.55 (d, $J = 5.1\text{ Hz}$, 1H), 7.30–7.40 (m, 6H), 7.48 (dd, $J = 2.1, 7.5\text{ Hz}$, 4H); $^{13}\text{C NMR}$ (CDCl_3): $\delta = -2.7, -0.4, 127.7, 129.2, 135.3, 136.8, 144.9, 150.8$; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{Si}_2$: C 72.90, H 8.16; found: C 72.86, H 8.06.

1,1-Bis(triethylsilyl)ethene (29g): $R_f = 0.85$ (hexane); IR (neat): $\tilde{\nu} = 2955, 1462, 1416, 1236, 1005, 966, 814, 733\text{ cm}^{-1}$; $^1\text{H NMR}$ (CDCl_3): $\delta = 0.61$ (q,

$J = 7.8$ Hz, 12 H), 0.90 (t, $J = 7.8$ Hz, 18 H), 6.37 (s, 2 H); ^{13}C NMR (CDCl_3): $\delta = 3.5$, 7.2, 143.3, 147.4; HRMS (m/z) calcd for $\text{C}_{14}\text{H}_{32}\text{Si}_2$ 256.2043; found: 256.2034.

1-(tert-Butyldimethylsilyl)-1-(trimethylsilyl)ethene (29h): $R_f = 0.81$ (hexane); IR (neat): $\tilde{\nu} = 2957$, 1472, 1408, 1362, 1248, 1148, 966, 837, 770, 675 cm^{-1} ; ^1H NMR (CDCl_3): $\delta = 0.08$ (s, 6 H), 0.09 (s, 9 H), 0.85 (s, 9 H), 6.34 (d, $J = 4.8$ Hz, 1 H), 6.43 (d, $J = 4.8$ Hz, 1 H); ^{13}C NMR (CDCl_3): $\delta = -4.4$, 0.1, 17.1, 26.9, 142.9, 152.0; elemental analysis calcd (%) for $\text{C}_{11}\text{H}_{26}\text{Si}_2$: C 61.60, H 12.22; found: C 61.39, H 12.48.

1,1-Bis(dimethylphenylsilyl)ethene (29j): $R_f = 0.53$ (hexane/ethyl acetate 80:1); IR (neat): $\tilde{\nu} = 1564$, 1427, 1248, 1111, 968, 841, 781, 729, 700, 640 cm^{-1} ; ^1H NMR (CDCl_3): $\delta = 0.25$ (s, 12 H), 6.41 (s, 2 H), 7.25–7.36 (m, 6 H), 7.38–7.44 (m, 4 H); ^{13}C NMR (CDCl_3): $\delta = -2.0$, 127.7, 128.9, 134.2, 139.0, 144.0, 151.0; elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{Si}_2$: C 72.90, H 8.16; found: C 73.02, H 8.31.

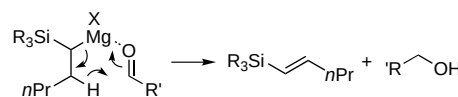
1,1-Bis(methyldiphenylsilyl)ethene (29k): m.p. 123 °C; IR (Nujol): $\tilde{\nu} = 1427$, 1261, 1113, 980, 829, 789, 739, 700 cm^{-1} ; ^1H NMR (CDCl_3): $\delta = 0.34$ (s, 6 H), 6.41 (s, 2 H), 7.18–7.32 (m, 12 H), 7.35 (d, $J = 7.5$ Hz, 8 H); ^{13}C NMR (CDCl_3): $\delta = -2.8$, 127.6, 129.1, 135.1, 136.4, 146.7, 149.6; elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{28}\text{Si}_2$: C 79.94, H 6.71; found: C 79.83, H 6.80.

1-(Methyldiphenylsilyl)-1-(triethylgermyl)ethene (29l): $R_f = 0.49$ (hexane); IR (neat): $\tilde{\nu} = 2948$, 1428, 1251, 1111, 1015, 965, 808, 788, 735, 718, 697 cm^{-1} ; ^1H NMR (CDCl_3): $\delta = 0.66$ (s, 3 H), 0.69 (q, $J = 7.8$ Hz, 6 H), 0.91 (t, $J = 7.8$ Hz, 9 H), 6.29 (d, $J = 4.5$ Hz, 1 H), 6.41 (d, $J = 4.5$ Hz, 1 H), 7.30–7.42 (m, 6 H), 7.45–7.54 (m, 4 H); ^{13}C NMR (CDCl_3): $\delta = -3.0$, 4.6, 8.7, 127.7, 129.2, 135.2, 136.8, 143.8, 149.1; elemental analysis calcd (%) for $\text{C}_{21}\text{H}_{30}\text{GeSi}$: C 65.83, H 7.89; found: C 65.67, H 7.81.

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