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Heterosubstituted cyclopropanation of alkenes with organochromium reagents derived from heterosubstituted dihalomethanes, $CrCl_2$, and tetraalkylethylenediamine

Kazuhiko Takai *, Shota Toshikawa, Atsushi Inoue, Ryo Kokumai, Masato Hirano

Division of Chemistry and Biochemistry, Graduate School of Natural Science and Technology, Okayama University, Tsushima, Okayama 700-8530, Japan

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Abstract

Iodocyclopropanes of *trans* configuration are produced stereoselectively from terminal alkenes by treatment with a reagent derived from iodoform, chromium(II) chloride, and TEEDA (*N*,*N*,*N*′,*N*′-tetraethylethylenediamine) in THF. Similarly, cyclopropylsilanes and cyclopropylboronic esters are obtained by using R_3SiCHI_2, and a combination of $Cl_2CHB(OR)_2$ and LiI instead of iodoform, respectively. The heterocyclopropanation occurs selectively at terminal double bonds, and di- and trisubstituted double bonds in the same molecules remain unchanged. Such functional groups as alcohol, ether, silyl ether, ester, tertiary amine, and amide groups are compatible with the reaction conditions.

Keywords: Chromium(II); Cyclopropane; Cyclopropylsilane

1. Introduction

Heterosubstituted cyclopropanes are useful building blocks for constructing compounds having cyclopropane rings [1–5]. For example, iodocyclopropanes [1,2] and cyclopropylboronic esters [5,7] can be used in Suzuki–Miyaura-type cross-coupling reactions to prepare the cyclopropyl–cyclopropyl and –vinyl carbon skeletons of natural products [6] such as FR-900848 and U-106305. Heterosubstituted cyclopropanes are typically accessed via Simmons–Smith cyclopropanation of the corresponding heterosubstituted olefins [8]. Cyclopropanation with zinc carbenoids, however, suffers from the low reactivity of the olefins due to electron-deficiency by substitution of halogen or boron atoms, or steric hindrance by substitution of trialkylsilyl groups. Therefore, it has been necessary to bring the zinc carbenoid close to the olefinic double bonds using oxygen functional groups [9,10]. An attractive direct-approach to heterosubstituted cyclopropanes is via the heterocyclopropanation of alkenes due of the accessibility of the starting materials [2]. However, this has not been popular due to the lack of appropriate reagents for simple terminal alkenes which satisfy both yield and stereoselective requirements. We have recently discovered the iodocyclopropanation of terminal olefins with a reagent derived from iodoform, chromium(II) chloride, and *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA) [11a]. Also, cyclopropylsilanes [11b] and -boronic esters have been prepared using a reagent derived from R_3SiCHX_2 and $(RO)_2BCHCl_2$ instead of iodoform, respectively. These methods will provide an alternative route to heterosubstituted cyclopropanes.

2. Results and discussion

Iodocyclopropanation [11a]. Treatment of allyl benzyl ether (**1**) with a mixture of iodoform (2 equiv.) and chromium(II) chloride (4 equiv.) in THF at 25 °C for 24 h afforded (2-iodocyclopropyl)methyl benzyl ether (**2**) in 32%

* Corresponding author.
E-mail address: ktakai@cc.okayama-u.ac.jp (K. Takai).

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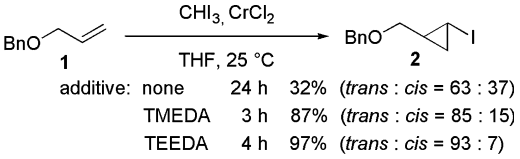
yield along with the recovery of **1** in 64% yield (Eq. (1)). The *trans*/*cis* ratio of the produced cyclopropanes was 63/37. Addition of several amines was examined, and the yields and stereoselectivities of **2** with the amines (4 equiv.) are as follows: Et_3N, 25% (*trans*/*cis* = 70/30); $Me_2NCH_2NMe_2$, 0%; $Me_2N(CH_2)_2NMe_2$ (TMEDA), 87% (85/15); $Me_2N(CH_2)_3NMe_2$, 69% (83/17); $Et_2N(CH_2)_2NEt_2$ (TEEDA), 97% (93/7); *i*-PrMeN$(CH_2)_2$N(*i*-Pr)Me, 19% (71/29); DL-Me_2NCHPhCHPhNMe_2, 61% (82/18), 2,2′-bipyridyl, 13% (64/36). It was found that both TMEDA and TEEDA accelerate the iodocyclopropanation.

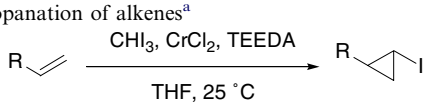


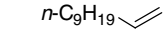
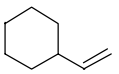
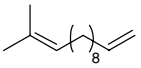
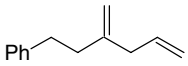
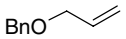
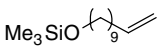
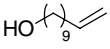
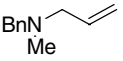
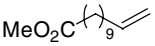
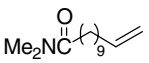
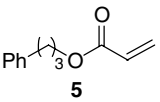
(1)

The results of the iodocyclopropanation of alkenes with iodoform, chromium(II) chloride, and TEEDA are shown in Table 1. It is worth noting that the iodocyclopropanation proceeded smoothly without the presence of a hydroxy or an alkoxy group near the double bond (Table 1, entries 1–4), which is necessary for the cyclopropanation of iodoalkenes mediated with zinc carbenoids [1a]. On the other hand, a steric hindrance around the double bond affected the yield considerably. For example, terminal alkenes afforded the corresponding iodocyclopropanes in 89–96% yields; however, an (*E*)-disubstituted alkene [(*E*)-2-dodecene], a 1,1-disubstituted alkene (2-methyl-1-undecene), and a trisubstituted alkene (2-methyl-2-dodecene) were recovered unchanged after 24 h stirring at 25 °C in 99%, 95% and 97% yields, respectively. The selectivity of the iodocyclopropanation is shown with a substrate having both a terminal and trisubstituted (or 1,1-disubstituted) double bond; **3** and **4** were produced in selective manners, respectively (entries 3 and 4). This reactivity contrasts with that of the Simmons–Smith zinc carbenoid, which reacts faster with more substituted electron-rich alkenes [10]. The iodocyclopropanation reaction proceeded without affecting the following functional groups: benzyl and silyl ethers, tertiary amine, ester, and amide (entries 5, 6, 8–10). It is also worth noting that the reaction proceeded without protecting the hydroxyl group though 3 equiv. of the reagent was required to obtain a high yield (entry 7). Electron-rich dodecyl vinyl ether was recovered in 85% yield after being stirred for 24 h; however, electron-deficient, α,β-unsaturated ester **5** reacted with the reagent to give **6** in 37% yield (entry 11).

The increased reactivity toward olefinic double bonds by addition of TMEDA or TEEDA to the iodoform-chromium(II) chloride reagent is further demonstrated using terminal alkenes having carbonyl groups (Scheme 1). The reagent derived from iodoform and chromium(II) chloride in the absence of diamines reacted only with aldehyde and ketone carbonyl groups, and selective iodoolefination occurred to give iodoalkenes **7** and **8** in 83% and 74% yields, respectively. An ester carbonyl group was inert to the reagent, and **11** was recovered in 94% yield. In contrast,

Table 1
Iodocyclopropanation of alkenes[a]

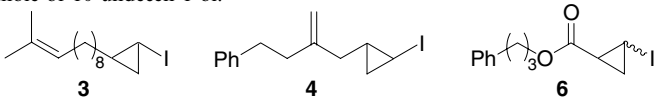


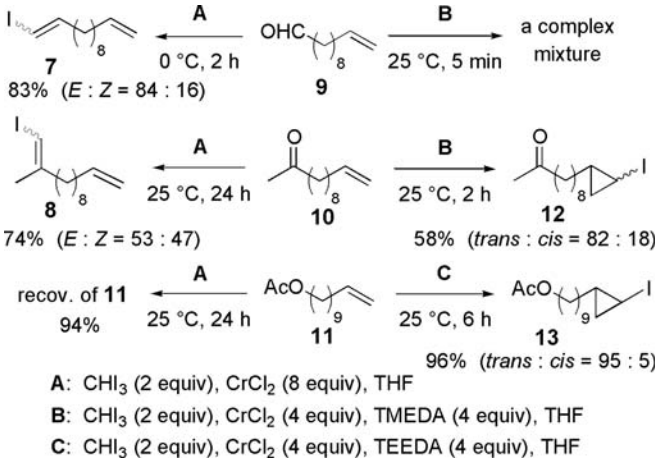
Entry	Alkene	Time (h)	Yield (%)	*trans*/*cis*[b]
1		4	93	95/5
2		16	89	97/3
3		4	90 (**3**)	96/4
4		8	96 (**4**)	96/4
5		4	97	93/7
6		8	97	97/3
7		8	87[c]	95/5
8		8	79	91/9
9		8	91	96/4
10		8	80	98/2
11	 **5**	24	37 (**6**)	78/22

[a] The reactions were conducted on a 1.0-mmol scale. Iodoform (1.5 mol), $CrCl_2$ (4 mol), and TEEDA (4 mol) were used per mole of an alkene.

[b] Isomeric ratios were determined by isolation and/or ^{1}H NMR spectroscopy.

[c] Iodoform (3 mol), $CrCl_2$ (8 mol), and TEEDA (8 mol) were used per mole of 10-undecen-1-ol.


3 **4** **6**



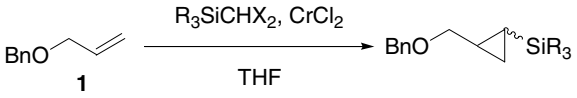
Scheme 1. Comparison of the reactivity in the presence and absence of diamines.

when the diamines were added to the reaction mixture and the amount of chromium(II) chloride reduced to half of the iodoolefination reagent, the product distributions changed markedly. Although the aldehyde **9** gave a complex mixture, the terminal alkenes **10** and **11** were selectively converted to the corresponding iodocyclopropanes **12** and **13** in 58% and 96% yields, respectively. The amount of chromium(II) chloride was not important for this chemoselectivity. For example, treatment of **10** with iodoform (2 equiv.) and chromium(II) chloride (4 equiv.) resulted in iodoolefination but the yield of **8** decreased to 54% (*E*/*Z* = 54/46), and **10** was recovered in 43% yield; **12** was not detected. The dramatic effect on the reactivity of the reagents derived from iodoform and chromium(II) chloride, caused by the addition of the diamines, suggests that different reactive species are generated in the reaction mixture.

Silylcyclopropanation [11b]. Cyclopropylsilanes are useful synthetic intermediates for organic synthesis [3]; however, their use has been quite limited due to the lack of general preparative methods [4]. We examined using Me_3SiCHI_2 instead of iodoform, and found that the reagent derived from Me_3SiCHI_2, chromium(II) chloride, and TMEDA reacted with allyl benzyl ether to give the corresponding cyclopropylsilane. Treatment of allyl benzyl ether (**1**) with the reagent generated in the presence of TMEDA in THF at 25 °C for 6 h gave [(2-benzyloxymethyl)cyclopropyl]trimethylsilane (**14**) in 89% yield (*trans*/*cis* = 69/31) (Table 2, entry 2). Addition of TEEDA was most effective in the case of the iodocyclopropanation, slightly improving the *trans*/*cis* ratio; however, the reaction proceeded sluggishly (entry 3). The reduction rates of Me_3SiCHX_2 (X = halogen) with chromium(II) decreased when the halogen was changed from I to Br and Cl (entries 4 and 7). The problem was solved by adding LiI, which was effective for substitution leading to Me_3SiCHI_2, and raising the reaction temperature (entries 6 and 8). However, the *trans*/*cis* ratio of **14** was still only about 2/1. Next, steric hindrance caused by substitution on the silyl atom was examined. Because only trimethyl-substituted diiodomethylsilane (Me_3SiCHI_2) can be easily prepared in good yield [8d], reactions were conducted with a combination of $R_3SiCHBr_2$ [12] and LiI instead of R_3SiCHI_2. The silylcyclopropanation of allyl benzyl ether proceeded similarly at 50 °C for 6 h with $R_3SiCHBr_2$ in the presence of LiI to give the corresponding cyclopropylsilanes in excellent yields (entries 9–11). The *trans*/*cis* ratio was improved by using the bulky triisopropyl-substituted dibromomethylsilane (entry 11).

The results obtained with several kinds of alkenes are summarized in Table 3. Only terminal double bonds were affected by the reaction; however, a trisubstituted olefin

Table 2
Formation of cyclopropylsilanes from allyl benzyl ether[a]

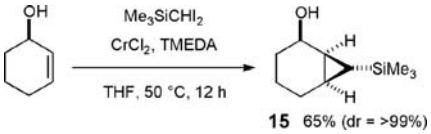


Entry	R_3Si	X	Additive[b]	Temperature (°C)	Time (h)	Yield (%)	*trans*/*cis*
1	Me_3Si (14)	I	None	25	24	16	50/50
2		I	TMEDA	25	6	89[c]	69/31
3		I	TEEDA	25	24	25	73/27
4		Br	TMEDA	25	24	49	64/36
5		Br	TMEDA, LiI	25	24	74[d]	60/40
6		Br	TMEDA, LiI	50	6	89	67/33
7		Cl	TMEDA	50	24	0	–
8		Cl	TMEDA, LiI	85	12	87	64/36
9	$PhMe_2Si$	Br	TMEDA, LiI	50	6	92	67/33
10	Et_3Si	Br	TMEDA, LiI	50	6	96	71/29
11	*i*-Pr_3Si	Br	TMEDA, LiI	50	6	82	87/13

[a] Reaction was conducted on a 1.0 mmol scale. Two mol of R_3SiCHX_2, and 8 mol of $CrCl_2$ were used per mole of allyl benzyl ether.
[b] Eight mole of TMEDA (or TEEDA) and 4 mol of LiI were used per mole of allyl benzyl ether.
[c] See Method A in Section 3.
[d] See Method B in Section 3.

remained unchanged (Table 3, entry 3). In the case of the conjugated diene, silylcyclopropanation occurred only at the terminal olefin, and the stereochemistry of the internal double bond did not change (entry 4).

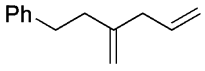
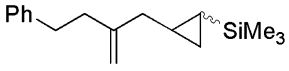
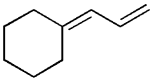
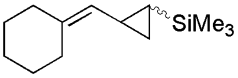
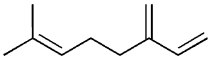
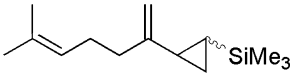
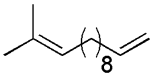
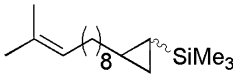
Although oxygen-functionalities near the carbon–carbon double bonds were not necessary to promote this silylcyclopropanation (Table 3, entries 1–4), a hydroxyl group accelerated the reaction markedly. For example, treatment of 2-cyclohexen-1-ol with the reagent derived from Me_3SiCHI_2, chromium(II) chloride, and TMEDA at 50 °C for 12 h afforded cyclopropylsilane **15** in 65% yield as a single stereoisomer (Eq. (2)) [6]. However, the reaction of cyclohexene, a 1,2-disubstituted alkene, did not give the corresponding cyclopropylsilane under the same reaction conditions even in the presence of cyclohexanol as an additive.



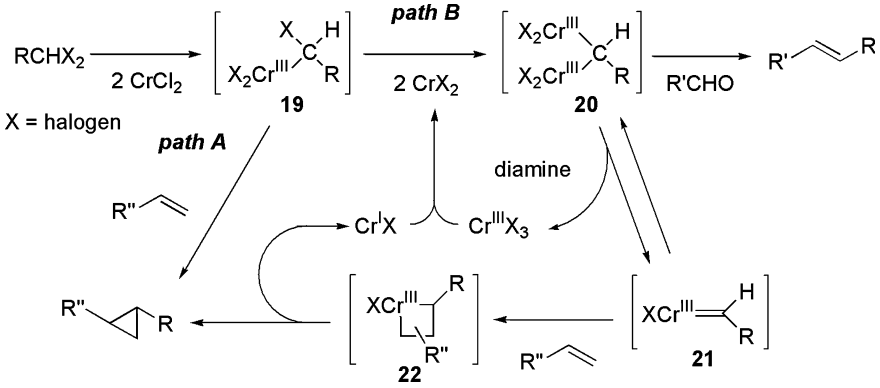
15 65% (dr = >99%) (2)

Borylcyclopropanation [5]. When Me_3SiCHI_2 was replaced by a combination of dichloromethylboronic ester **16** [13] and LiI, allyl benzyl ether was converted to the corresponding boron-substituted cyclopropane **17** in 75% yield although the stereoselectivity was low (Eq. (3)). Because reduction of polyhalogen compounds with chromium(II) increases in the order Cl < Br < I, addition of LiI was indispensable to obtain the product in high yield. A simple alkene having no oxygen functional group, 1-dodecene, was also converted to cyclopropylboronic ester **18** under the same reaction conditions.

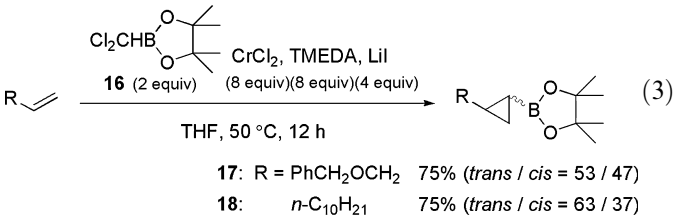
Table 3
Preparation of cyclopropyltrimethylsilanes from terminal alkenes[a]

Entry	Alkene	Time (h)	Product	Yield (%)	*trans*/*cis*
1		24		84	51/49
2		24		81	53/47
3		12		80	78/22
4		12		80	68/32

[a] See Method A in Section 3. Reaction was conducted on a 1.0 mmol scale. Me_3SiCHI_2 (2 mol), $CrCl_2$ (8 mol), and TMEDA (8 mol) were used per mole of an alkene.



Scheme 2. A plausible mechanism.

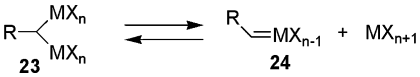


(3)

Proposed reaction mechanism of the heterosubstituted cyclopropanation. Cyclopropanation of alkenes can be accomplished by both metal-carbenoid species and metal–carbene complexes [14]. Thus, there are two possible reaction pathways for the production of iodocyclopropanes (Scheme 2). The active species of path A is the chromium–carbenoid **19**, and that of path B is the chromium–carbene species **21** [15].

One important feature of the reduction of polyhalogen compounds with chromium(II) is that the reduction step from the chromium carbenoid species **19** to geminal dichromium species **20** proceeds smoothly [8,16]. Reduction of iodoform, R_3SiCHI_2, and $(RO)_2BCHI_2$ with 4 equiv. of chromium(II) gives the corresponding geminal dichromium species, which are effective for transformation from aldehydes to iodoolefins [8a], alkenylsilanes [8b], and -boronic esters [8c], of *E*-configuration, respectively. Once chromium carbenoid **19** was reduced with chromium(II) to generate the geminal dichromium species **20**, it could be difficult to regenerate the chromium carbenoid **19** under the reduction conditions. Therefore, we examined the following reactions. The geminal dichromium reagent was generated by stirring iodoform (1.5 equiv.) and chromium(II) chloride (4 equiv.) in THF at 25 °C for 30 min. Formation of the reagent was examined by treatment with 3-phenylpropanal, which gave 1-iodo-4-phenyl-1-butene in 70% yield ($E/Z = 82/18$) after stirring at 25 °C for 30 min [8a]. In contrast, when TMEDA (4 equiv.) was added to the geminal dichromium reagent generated at 25 °C for 1 h, and the mixture was stirred for a further 15 min, treatment of **10** with the new base-added reagent at 25 °C for 2 h gave **12** in 38% yield (*trans*/*cis* = 80/20) along with **8** in 1% yield; the reactant **10** was recovered in 37% yield. The results suggest that the cyclopropanation does not proceed via the carbenoid pathway (path B).

It has been reported that the dimetallic species **23** of early transition metals are postulated in equilibrium with the metal–alkylidene complex **24** and MX_{n+1} (Eq. (4)) [17], and the equilibrium-shift is caused especially by the addition of an appropriate amine [4]. For example, the equilibrium-shift from the Tebbe reagent to a titanocene–methylene complex occurs by addition of pyridine, and the complex reacts with 2-methylpropene [18]. As mentioned earlier (Scheme 1), the reactivity of the species derived from iodoform and chromium(II) chloride changes markedly by addition of TMEDA or TEEDA, and that *trans*-iodocyclopropanes are produced stereoselectively from terminal alkenes by treatment with the base-added reagent system.



(4)

We are tempted to assume that the chromium–alkylidene species **21** could be involved in the cyclopropanation (Scheme 2). Reduction of $RCHI_2$ with 4 equiv. of chromium(II) gives geminal dichromium species **20**. The dichromium species **20** is converted to the chromium–alkylidene complex **21** by treatment with the diamine [17]. A [2+2] addition reaction of **21** with an alkene followed by reductive elimination from the chromacyclobutane **22** produces the heterosubstitutedcyclopropane [19]. The comproportionation of both 1 equiv. of CrX_3 and CrX generating 2 equiv. of CrX_2 could reduce the amount of the required $CrCl_2$.

3. Experimental

Experimental conditions. Dry, oxygen-free tetrahydrofuran (THF) was purchased from Kanto Chemicals, Co. Column chromatography was performed with silica gel (200 mesh). Analytical samples of isomers were collected by recycling preparative HPLC (Japan Analytical Industry, LC-908) using toluene as an eluent. Distillation of small amounts of the products was performed with a Buchi Kugelrohr, and boiling points were indicated by an air bath temperature without correction. FT-IR spectra were obtained on a Nicolet Protege 460 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 instrument. Chemical shifts were expressed in ppm downfield from internal tetramethylsilane using a scale. Low and high resolution EI mass spectra were obtained with a capillary GC interfaced JEOL JMS-GCmate and JMS-700 MStation spectrometers, respectively. Elemental analyses were performed by the staff at the Elemental Analyses Center of Kyoto University.

General procedure for iodocyclopropanation of terminal alkenes. To a mixture of $CrCl_2$ (0.49 g, 4.0 mmol) in dry, oxygen-free THF (5 mL) was added TEEDA (0.85 mL, 4.0 mmol) at 25 °C. The color of the mixture turned from greenish white to purple. After stirring for 15 min at 25 °C, a solution of an alkene (1.0 mmol) in THF (2 mL) was added to the mixture at 25 °C. A solution of iodoform (0.59 g, 1.5 mmol) in THF (3 mL) was added dropwise to the mixture at 25 °C over a period of 5 min. The color of the mixture turned to brown and then black. After stirring for an appropriate time shown in Table 1 at 25 °C, the reaction mixture was poured into aqueous hydrochloric acid (1 M, 15 mL). The mixture was extracted with ether (3×20 mL), and organic extracts were washed with aqueous sodium thiosulfate (2×20 mL), dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel gave the desired iodocyclopropane.

*trans-(2-Iodocyclopropyl)methyl benzyl ether (**2**) [7a]*. IR (neat): 3029, 2856, 1496, 1453, 1253, 1212, 1095, 1077, 1039, 737 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.98-1.02 (m, 2H), 1.49–1.57 (m, 1H), 2.23–2.27 (m, 1H), 3.35 (dd, $J = 10.5$,

6.6 Hz, 1H), 3.44 (dd, $J = 10.5$, 6.3 Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 7.26–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −17.6, 14.6, 22.9, 71.6, 72.6, 127.7, 127.7, 128.4, 138.0.

trans-1-Iodo-2-nonylcyclopropane. B.p. 110 °C (bath temperature, 0.9 Torr); IR (neat): 2955, 2924, 2853, 1465, 1441, 1378, 1216, 1194, 1076, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (ddd, $J = 7.8$, 4.0, 4.0 Hz, 1H), 0.87–0.91 (m, 4H), 1.11–1.19 (m, 1H), 1.24–1.32 (m, 14H), 1.35–1.42 (m, 2H), 2.07 (ddd, $J = 7.8$, 4.0, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −14.6, 14.1, 16.6, 22.7, 23.7, 28.7, 29.3, 29.4, 29.6, 29.6, 31.9, 33.5. Anal. Calc. for $C_{12}H_{23}I$: C, 48.99; H, 7.88. Found: C, 49.27; H, 7.75%.

trans-(2-Iodocyclopropyl)cyclohexane. B.p. 57 °C (bath temperature, 0.6 Torr); IR (neat): 2922, 2851, 1448, 1241, 1208, 1192, 1063, 1035, 936 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.58–0.68 (m, 1H), 0.79–0.88 (m, 2H), 0.98–1.08 (m, 2H), 1.12–1.20 (m, 4H), 1.60–1.74 (m, 4H), 1.78–1.85 (m, 1H), 2.13 (ddd, $J = 7.3$, 4.2, 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −16.4, 15.3, 26.0, 26.0, 26.3, 30.0, 32.0, 32.2, 42.2. Anal. Calc. for $C_9H_{15}I$: C, 43.22; H, 6.04. Found: C, 43.35; H, 5.90%.

*trans-1-Iodo-2-(10-methyl-9-undecenyl)cyclopropane (**3**)*. IR (neat): 2993, 2965, 2853, 1455, 1441, 1376, 1217, 1192, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (ddd, $J = 7.6$, 6.2, 6.1 Hz, 1H), 0.89 (ddd, $J = 9.0$, 6.0, 4.5 Hz, 1H), 1.08–1.19 (m, 1H), 1.24–1.32 (m, 12H), 1.33–1.41 (m, 2H), 1.60 (s, 3H), 1.69 (s, 3H), 1.92–2.00 (m, 2H), 2.07 (ddd, $J = 7.8$, 3.9, 3.9 Hz, 1H), 5.11 (t, $J = 7.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.5, 17.7, 23.7, 25.7, 28.0, 28.7, 29.3, 29.3, 29.5, 29.5, 29.9, 33.5, 124.9, 131.1. Anal. Calc. for $C_{15}H_{27}I$: C, 53.90; H, 8.14. Found: C, 53.98; H, 7.93%.

*trans-[3-(2-Iodocyclopropylmethyl)-3-butenyl]benzene (**4**)*. IR (neat): 3026, 2924, 2857, 1645, 1496, 1453, 1437, 1214, 1189, 1035, 894, 747, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.84 (ddd, $J = 7.8$, 6.1, 6.1 Hz, 1H), 0.96 (ddd, $J = 9.1$, 4.6, 3.1 Hz, 1H), 1.24–1.34 (m, 1H), 1.96 (dd, $J = 15.9$, 7.5 Hz, 1H), 2.04–2.12 (m, 2H), 2.34 (dd, $J = 8.4$, 7.6 Hz, 2H), 2.74 (dd, $J = 8.4$, 7.6 Hz, 2H), 4.82 (s, 1H), 4.89 (s, 1H), 7.15–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.6, 22.0, 26.9, 34.4, 38.0, 40.2, 110.4, 125.8, 128.3, 142.0, 147.4. Anal. Calc. for $C_{14}H_{17}I$: C, 53.86; H, 5.49. Found: C, 53.98; H, 5.51%.

trans-[9-(2-Iodocyclopropyl)nonyloxy]trimethylsilane. IR (neat): 2926, 2854, 1259, 1250, 1097, 873, 841, 747 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.11 (s, 9H), 0.78 (ddd, $J = 7.5$, 6.0, 6.0 Hz, 1H), 0.89 (ddd, $J = 9.0$, 6.0, 4.5 Hz, 1H), 1.10–1.18 (m, 1H), 1.25–1.35 (m, 12H), 1.35–1.42 (m, 2H), 1.48–1.56 (m, 2H), 2.07 (ddd, $J = 7.7$, 4.2, 3.8 Hz, 1H), 3.57 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ −14.7, −0.5, 16.5, 23.7, 25.8, 28.7, 29.3, 29.4, 29.5, 29.5, 32.7, 33.5, 62.7. Anal. Calc. for $C_{15}H_{31}IOSi$: C, 47.11; H, 8.17. Found: C, 47.29; H, 8.31%.

trans-9-(2-Iodocyclopropyl)nonan-1-ol. IR (neat): 3338, 2924, 2853, 1464, 1439, 1218, 1192, 1057, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (ddd, $J = 7.5$, 6.0, 6.0 Hz, 1H), 0.89 (ddd, $J = 9.0$, 6.0, 4.2 Hz, 1H), 1.11–1.18 (m, 1H), 1.19–1.39 (m, 15H), 1.57 (tt, $J = 6.9$, 6.9 Hz, 2H), 2.07 (ddd, $J = 7.7$, 3.9, 3.9 Hz, 1H), 3.64 (q, $J = 6.1$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.5, 23.7, 25.7, 28.7, 29.3, 29.3, 29.4, 29.5, 32.8, 33.5, 63.0. Silylation of the alcohol afforded the above compound.

trans-Benzyl(2-iodocyclopropylmethyl)methylamine. IR (neat): 2788, 1453, 1365, 1216, 1193, 1075, 1039, 1025, 739, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.79 (ddd, $J = 7.7$, 6.2, 6.2 Hz, 1H), 0.93 (ddd, $J = 9.3$, 6.3, 4.5 Hz, 1H), 1.31–1.36 (m, 1H), 2.04–2.13 (m, 2H), 2.24 (s, 3H), 2.48 (dd, $J = 12.9$, 5.7 Hz, 1H), 3.45 (d, $J = 12.9$ Hz, 1H), 3.67 (d, $J = 13.2$ Hz, 1H), 7.19–7.29 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −15.1, 15.3, 21.5, 42.4, 60.6, 62.1, 127.0, 128.3, 129.0,138.9. Anal. Calc. for $C_{12}H_{16}IN$: C, 47.86; H, 5.35. Found: C, 47.88; H, 5.23%.

Methyl trans-10-(2-iodocyclopropyl)decanoate. IR (neat): 2926, 2854, 1740, 1436, 1361, 1196, 1172, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (ddd, $J = 7.5$, 6.0, 6.0 Hz, 1H), 0.89 (ddd, $J = 9.0$, 6.0, 4.2 Hz, 1H), 1.10–1.19 (m, 1H), 1.26–1.33 (m, 12H), 1.35–1.43 (m, 2H), 1.56–1.67 (m, 2H), 2.07 (ddd, $J = 7.8$, 3.9, 3.9 Hz, 1H), 2.30 (t, $J = 7.5$ Hz, 2H), 3.67 (s, 3H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.5, 23.7, 24.9, 26.9, 28.6, 29.1, 29.1, 29.2, 29.3, 33.5, 34.1, 51.4, 174.3. Anal. Calc. for $C_{14}H_{25}IO_2$: C, 47.74; H, 7.15. Found: C, 47.97; H, 6.98%.

N,N-Dimethyl [trans-10-(2-iodocyclopropyl)]decanamide. IR (neat): 3542, 2924, 2853, 1649, 1463, 1397, 1265, 1145, 1034 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (ddd, $J = 7.5$, 6.0, 6.0 Hz, 1H), 0.88 (ddd, $J = 9.0$, 6.0, 4.4 Hz, 1H), 1.10–1.19 (m, 1H), 1.23–1.42 (m, 14H), 1.59–1.66 (m, 2H), 2.07 (ddd, $J = 7.8$, 3.9, 3.9 Hz, 1H), 2.30 (t, $J = 7.6$ Hz, 2H), 2.94 (s, 3H), 3.00 (s, 3H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.5, 23.7, 25.1, 26.9, 28.7, 29.3, 29.3, 29.4, 29.4, 33.4, 33.5, 35.3, 37.3, 173.2. Anal. Calc. for $C_{15}H_{28}INO$: C, 49.32; H, 7.73. Found: C, 49.08; H, 7.48%.

*3-Phenylpropyl trans-2-iodocyclopropanecarboxylate (trans-**6**)*. IR (neat): 3026, 2954, 1726, 1398, 1367, 1229, 1195, 1026 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.30 (ddd, $J = 8.8$, 5.8, 5.8 Hz, 1H), 1.62 (ddd, $J = 8.2$, 5.6, 5.6 Hz, 1H), 1.94–2.02 (m, 3H), 2.70 (t, $J = 7.6$ Hz, 2H), 2.75 (ddd, $J = 8.3$, 5.5, 3.6 Hz, 1H), 4.11 (t, $J = 6.6$ Hz, 2H), 7.18–7.40 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −17.1, 19.7, 24.6, 30.1, 32.1, 64.6, 126.1, 128.4, 128.5, 141.0, 172.0. Anal. Calc. for $C_{13}H_{15}IO_2$: C, 47.29; H, 4.58. Found: C, 47.55; H, 4.57%.

*3-Phenylpropyl cis-2-iodocyclopropanecarboxylate (cis-**6**)*. IR (neat): 3026, 2954, 2926, 1732, 1399, 1371, 1249, 1172 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.39–1.44 (m, 1H), 1.49–1.54 (m, 1H), 1.89 (ddd, $J = 8.7$, 7.4, 7.2 Hz, 1H), 1.97–2.06 (m, 2H), 2.73 (t, $J = 7.8$ Hz, 2H), 2.82 (ddd, $J = 8.8$, 7.3, 7.3 Hz, 1H), 4.15–4.27 (m, 2H), 7.18–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −14.6, 16.4, 19.3, 30.4, 32.2, 64.6, 126.0, 128.4, 128.4, 141.2, 169.9. Anal. Calc. for $C_{13}H_{15}IO_2$: C, 47.29; H, 4.58. Found: C, 47.51; H, 4.56%.

*trans-10-(2-Iodocyclopropyl)-2-decanone (trans-**12**)*. IR (neat): 2925, 2853, 1717, 1437, 1358, 1192, 1163 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.78 (ddd, $J = 7.0$, 6.9, 6.0 Hz, 1H), 0.88 (ddd, $J = 9.0$, 6.0, 4.2 Hz, 1H), 1.10–1.18 (m, 1H), 1.25–1.31 (m, 10H), 1.34–1.39 (m, 2H), 1.54–1.60 (m, 2H), 2.07 (ddd, $J = 7.8$, 3.9, 3.9 Hz, 1H), 2.13 (s, 3H), 2.41 (t, $J = 7.4$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.5, 23.7, 23.8, 28.7, 29.1, 29.2, 29.3, 29.3, 29.9, 33.5, 43.8, 209.4. Anal. Calc. for $C_{13}H_{23}IO$: C, 48.46; H, 7.19. Found: C, 48.74; H, 7.36%.

*cis-10-(2-Iodocyclopropyl)-2-decanone (cis-**12**)*. IR (neat): 2924, 2852, 1717, 1457, 1437, 1361, 1056 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.42–0.52 (m, 2H), 0.81–0.90 (m, 1H), 1.24–1.36 (m, 10H), 1.41–1.52 (m, 2H), 1.53–1.61 (m, 2H), 2.13 (s, 3H), 2.42 (t, $J = 7.5$ Hz, 2H), 2.58–2.65 (m, 1H); ^{13}C NMR ($CDCl_3$): δ −6.1, 15.6, 15.8, 23.8, 28.5, 29.1, 29.3, 29.3, 29.4, 29.8, 35.0, 43.8, 209.4. Anal. Calc. for $C_{13}H_{23}IO$: C, 48.46; H, 7.19. Found: C, 48.56; H, 7.37%.

*trans-9-(2-Iodocyclopropyl)nonyl acetate (**13**)*. IR (neat): 2925, 2854, 1741, 1365, 1240, 1036 cm^{-1}; ^1H NMR ($CDCl^3$): δ 0.77 (ddd, $J = 12.0$, 7.5, 6.0 Hz, 1H), 0.89 (ddd, $J = 9.1$, 5.9, 4.4 Hz, 1H), 1.09–1.17 (m, 1H), 1.21–1.41 (m, 14H), 1.56–1.66 (m, 2H), 2.04 (s, 3H), 2.05–2.08 (m, 1H), 4.04 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ −14.7, 16.5, 21.0, 23.7, 25.9, 28.6, 28.7, 29.2, 29.3, 29.4, 29.4, 33.5, 64.6, 171.2. Anal. Calc. for $C_{14}H_{25}IO_2$: C, 47.74; H, 7.15. Found: C, 48.03; H, 6.93%.

General procedure for silylcyclopropanation of terminal alkenes (Method A). To a greenish gray suspension of $CrCl_2$ (0.98 g, 8.0 mmol) in dry, oxygen-free THF (12 mL) was added TMEDA (0.93 g, 8.0 mmol) at 25 °C and the resulting light blue mixture was stirred at 25 °C for 15 min. A solution of an alkene (1.0 mmol) in THF (2 mL) and a solution of Me_3SiCHI_2 (0.68 g, 2.0 mmol) in THF (3 mL) was added successively to the suspension at 25 °C. The mixture was stirred at 25 °C for an appropriate time shown in Table 3, and the color changed gradually to dark brown while stirring. The mixture was poured into water (10 mL). This mixture was extracted with ether (3×10 mL), and the organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel (hexane) gave the desired silylcyclopropanes. Analytical samples of *trans*- and *cis*-isomers were collected by recycling preparative HPLC.

Method B. A combination of *i*-$Pr_3SiCHBr_2$ (0.66 g, 2.0 mmol) and LiI (0.53 g, 4.0 mmol) was used instead of Me_3SiCHI_2 in Method A.

*[trans-2-(Benzyloxymethyl)cyclopropyl]trimethylsilane (trans-**14**)*. IR (neat): 2954, 2853, 1454, 1248, 1096, 1028, 836, 747, 735, 697, 666 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.50 (ddd, $J = 13.7$, 7.1, 7.1 Hz, 1H), −0.04 (s, 9H), 0.44–0.51 (m, 2H), 0.98–1.03 (m, 1H), 3.24 (dd, $J = 10.1$, 7.1 Hz, 1H), 3.47 (dd, $J = 10.1$, 5.9 Hz, 1H), 4.54 (s, 2H), 7.26–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −2.4, 2.3, 7.5, 14.9, 72.3, 75.9, 127.4, 127.6, 128.3, 138.6. Anal. Calc. for $C_{14}H_{22}Si$: C, 71.73; H, 9.46. Found: C, 71.55; H, 9.46%.

*[cis-2-(Benzyloxymethyl)cyclopropyl]trimethylsilane (cis-**14**)*. IR (neat): 2953, 2855, 1454, 1247, 1090, 1029, 836, 751, 735, 697, 648 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.25 (ddd, $J = 9.5$, 9.5, 7.8 Hz, 1H), −0.01 (s, 9H), 0.20–0.24 (m, 1H), 0.84–0.89 (m, 1H), 1.33–1.43 (m, 1H), 3.32 (dd, $J = 9.7$, 7.8 Hz, 1H), 3.41 (dd, $J = 9.7$, 7.1 Hz, 1H), 4.52 (s, 2H), 7.26–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −0.3, 2.1, 7.8, 16.3, 72.7, 72.9, 127.5, 127.9, 128.3, 138.4. Anal. Calc. for $C_{14}H_{22}Si$: C, 71.73; H, 9.46. Found: C, 71.84; H, 9.68%.

[trans-2-(Benzyloxymethyl)cyclopropyl]dimethylphenylsilane. IR (neat): 2954, 2852, 1427, 1248, 1113, 1098, 832, 814, 773, 732, 699, 667 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.26 (ddd, $J = 9.8$, 6.6, 6.6 Hz, 1H), 0.20 (s, 3H), 0.21 (s, 3H), 0.54–0.57 (m, 2H), 1.06–1.14 (m, 1H), 3.31 (dd, $J = 10.0$, 7.1 Hz, 1H), 3.48 (dd, $J = 10.0$, 6.4 Hz, 1H), 4.52 (s, 2H), 7.27–7.59 (m, 10H); ^{13}C NMR ($CDCl_3$): δ −3.9, −3.8, 1.3, 7.6, 15.1, 72.4, 75.7, 127.4, 127.6, 127.7, 128.3, 128.9, 133.8, 138.6, 138.9. Anal. Calc. for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 77.27; H, 8.16%.

[cis-2-(Benzyloxymethyl)cyclopropyl]dimethylphenylsilane. IR(neat): 2954, 2855, 1427, 1248, 1112, 1091, 833, 815, 773, 733, 699, 666 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.02 (ddd, $J = 9.5$, 9.5, 7.8 Hz, 1H), 0.25 (s, 3H), 0.28 (s, 3H), 0.30–0.34 (m, 1H), 0.94–0.99 (m, 1H), 1.41–1.49 (m, 1H), 3.28 (d, $J = 7.3$ Hz, 2H), 4.44 (s, 2H), 7.28–7.59 (m, 10H); ^{13}C NMR ($CDCl_3$): δ −1.6, 1.4, 8.0, 16.5, 72.6, 76.5, 127.5, 127.7, 127.8, 128.3, 128.8, 133.7, 138.3, 139.8. Anal. Calc. for $C_{19}H_{24}OSi$: C, 76.97; H, 8.16. Found: C, 76.87, H, 8.30%.

[trans-2-(Benzyloxymethyl)cyclopropyl]triethylsilane. IR (neat): 2953, 2874, 1720, 1455, 1098, 1016, 736, 697, 666 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.54 (ddd, $J = 10.2$, 6.8, 6.8 Hz, 1H), 0.44–0.54 (m, 2H), 0.47 (q, $J = 7.9$ Hz, 6H), 0.94 (t, $J = 7.9$ Hz, 9H), 1.03–1.12 (m, 1H), 3.19 (dd, $J = 10.3$, 7.6 Hz, 1H), 3.52 (dd, $J = 10.3$, 5.9 Hz, 1H), 4.54 (s, 2H), 7.26–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −1.4, 2.9, 7.4, 7.5, 14.5, 72.4, 76.1, 127.4, 127.6, 128.3, 138.7. Anal. Calc. for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.57; H, 10.22%.

[cis-2-(Benzyloxymethyl)cyclopropyl]triethylsilane. IR (neat): 2952, 2873, 1455, 1091, 734, 697, 667 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.28 (ddd, $J = 9.8$, 9.8, 8.1 Hz, 1H), 0.21–0.26 (m, 1H), 0.42–0.54 (m, 6H), 0.86–0.96 (m, 10H), 1.33–1.39 (m, 1H), 3.19 (dd, $J = 10.0$, 8.5 Hz, 1H), 3.52 (dd, $J = 10.0$, 6.1 Hz, 1H), 4.52 (s, 2H), 7.26–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$): −1.6, 4.4, 7.5, 7.9, 15.6, 72.6, 73.3, 127.5, 127.8, 128.3, 138.4. Anal. Calc. for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.57; H, 10.45%.

[trans-2-(Benzyloxymethyl)cyclopropyl]triisopropylsilane. IR (neat): 2942, 2865, 1464, 1098, 1075, 882, 734, 696, 666 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.56 (ddd, $J = 6.8$, 6.8, 10.0 Hz, 1H), 0.49–0.53 (m, 1H), 0.64–0.69 (m, 1H), 1.01–1.05 (m, 21H), 1.17–1.25 (m, 1H), 3.12 (dd, $J = 9.8$, 10.0 Hz, 1H), 3.59 (dd, $J = 5.5$, 10.0 Hz, 1H), 4.55 (s,

2H), 7.27–7.52 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −2.9, 8.5, 12.1, 15.6, 19.0, 19.0, 72.7, 73.4, 127.5, 127.9, 128.3, 138.4. Anal. Calc. for $C_{20}H_{34}OSi$: C, 75.40; H, 10.76. Found: C, 75.28; H, 10.77%.

[cis-2-(Benzyloxymethyl)cyclopropyl]triisopropylsilane. IR (neat): 2942, 2865, 1464, 1077, 883, 731, 697, 677 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.28 (ddd, J = 9.0, 9.5, 9.5 Hz 1H), 0.37–0.41 (m, 1H), 0.90–1.04 (m, 22H), 1.34–1.43 (m, 1H), 3.08 (dd, J = 9.5, 9.5 Hz, 1H), 3.70 (dd, J = 5.3, 9.8 Hz, 1H), 4.54 (q, J = 11.9 Hz, 2H), 7.27–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −2.9, 8.2, 11.2, 14.9, 18.8, 72.6, 76.4, 127.4, 127.6, 128.3, 138.6. Anal. Calc. for $C_{20}H_{34}OSi$: C, 75.40; H, 10.76. Found: C, 75.31; H, 10.80%.

Trimethyl[trans-2-(2-phenethyl-2-propenyl)cyclopropyl]-silane. IR (neat): 2953, 1645, 1497, 1454, 1247, 1048, 1032, 882, 747, 698, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.60 (ddd, J = 9.8, 6.8, 6.8 Hz, 1H), −0.07 (s, 9H), 0.34 (ddd, J = 10.5, 3.6, 3.6 Hz, 1H), 0.42 (ddd, J = 7.1, 7.1, 3.6 Hz, 1H), 0.69–0.76 (m, 1H), 1.91 (dd, J = 15.5, 7.1 Hz, 1H), 2.10 (dd, J = 15.5, 6.4 Hz, 1H), 2.36 (t, J = 8.4 Hz, 2H), 2.75 (t, J = 8.4 Hz, 2H), 4,77 (s, 1H), 4,87 (s, 1H), 7.10–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −2.3, 4.5, 8.9, 14.2, 34.4, 38.1, 42.6, 109.0, 125.8, 128.3, 128.3, 142.3, 149.6. Anal. Calc. for $C_{17}H_{26}Si$: C, 79.00; H, 10.14. Found: C, 78.70; H, 10.20%.

Trimethyl[cis-2-(2-phenethyl-2-propenyl)cyclopropyl]-silane. IR (neat): 2952, 1646, 1497, 1455, 1247, 1031, 833, 748, 697, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.32 (ddd, J = 10.2, 10.2, 7.2 Hz, 1H), 0.02 (s, 9H), 0.09–0.13 (m, 1H), 0.80–0.86 (m, 1H), 1.09–1.15 (m, 1H), 1.79 (dd, J = 15.6, 8.8 Hz, 1H), 2.27 (dd, J = 15.6, 5.1 Hz, 1H), 2.37 (t, J = 8.6 Hz, 2H), 2.76 (t, J = 8.6 Hz, 2H), 4,81 (s, 1H), 4,93 (s, 1H), 7.18–7.30 (m, 5H); ^{13}C NMR ($CDCl_3$): δ −0.1, 2.6, 9.1, 15.3, 34.4, 38.2, 38.3, 38.6, 109.2, 125.8, 128.3, 142.3, 149.6. Anal. Calc. for $C_{17}H_{26}Si$: C, 79.00; H, 10.14. Found: C, 79.12; H, 10.18%.

[trans-2-(Cyclohexylidenemethyl)cyclopropyl]trimethylsilane. IR (neat): 2953, 1645, 1497, 1454, 1247, 1048, 1032, 882, 747, 698, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.44 (ddd, J = 10.0, 6.4, 6.4 Hz, 1H), −0.05 (s, 9H), 0.51 (ddd, J = 10.0, 3.9, 3.9 Hz, 1H), 0.59 (ddd, J = 7.3, 7.3, 3.9 Hz, 1H), 1.33–1.40 (m, 1H), 1.46–1.62 (m, 6H), 2.03 (t, J = 5.1 Hz, 2H), 2.20–2.30 (m, 2H), 4,51 (d, 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −2.3, 6.7, 10.8, 13.5, 26.9, 27.7, 28.5, 29.1, 36.8, 126.3, 138.0. Anal. Calc. for $C_{13}H_{24}Si$: C, 74.92; H, 11.61. Found: C, 74.96; H, 11.63%.

[cis-2-(Cyclohexylidenemethyl)cyclopropyl]trimethylsilane. IR (neat): 2927, 2853, 1447, 1247, 833, 751, 689, 648 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.17 (ddd, J = 9.8, 9.8, 7.8 Hz, 1H), 0.00 (s, 9H), 0.31 (ddd, J = 7.8, 4.9, 3.7 Hz, 1H), 0.96 (ddd, J = 9.8, 7.6, 3.4 Hz, 1H), 1.48–1.58 (m, 6H), 1.70–1.75 (m, 1H), 2.03 (t, J = 5.6 Hz, 2H), 2.18–2.31 (m, 2H), 4,68 (d, J = 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −0.5, 5.2, 11.2, 14.2, 26.9, 27.5, 28.4, 28.9, 37.0, 123.7, 139.6; EI MS m/z (%): 208 (M^+, 4), 134 (11), 92 (8), 73 (100). HRMS (EI) m/z calcd. for (M^+) $C_{13}H_{24}Si$ 208.1647, found 208.1646.

[trans-2-(5-Methyl-1-methylene-4-hexenyl)cyclopropyl]-trimethylsilane. IR (neat): 2955, 2927, 1642, 1448, 1248, 835, 751, 690, 667 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.25 (ddd, J = 10.3, 7.5, 7.5 Hz, 1H), −0.04 (s, 9H), 0.53 (ddd, J = 7.5, 7.5, 3.7 Hz, 1H), 0.72 (ddd, J = 10.3, 4.9, 3.7 Hz, 1H), 1.18–1.23 (m, 1H), 1.62 (s, 3H), 1.69 (s, 3H), 2.01 (t, J = 7.7 Hz, 2H), 2.12–2.18 (m, 2H), 4.62 (s, 1H), 4,66 (s, 1H), 5.12 (t, J = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −2.4, 6.4, 9.6, 17.7, 20.5, 25.7, 27.0, 35.6, 105.8, 124.2, 131.5, 151.5. Anal. Calc. for $C_{14}H_{26}Si$: C, 75.59; H, 11.78. Found: C, 75.32; H, 11.81%.

[cis-2-(5-Methyl-1-methylene-4-hexenyl)cyclopropyl]trimethylsilane. IR (neat): 2954, 2927, 1643, 1450, 1249, 835, 753, 689, 666 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.15 (ddd, J = 10.0, 10.0, 7.6 Hz, 1H), −0.03 (s, 9H), −0.07–0.00 (m, 1H), 0.66 (ddd, J = 7.6, 5.6, 3.8 Hz, 1H), 0.83 (ddd, J = 11.2, 7.5, 3.7 Hz, 1H), 1.62 (s, 3H), 1.69 (s, 3H), 2.11–2.27 (m, 4H), 4.68 (s, 1H), 4,74 (s, 1H), 5.14–5.17 (m, 1H); ^{13}C NMR ($CDCl_3$): δ −0.5, 6.0, 6.6, 17.7, 22.0, 25.7, 26.5, 37.8, 108.8, 124.2, 131.6, 148.8; EI MS m/z (%): 222 (M^+, 1), 207 (1), 179 (10), 73 (100), 69 (20). HRMS (EI) m/z calcd. for (M^+) $C_{14}H_{26}Si$ 222.1804, found 222.1811.

[trans-2-(10-Methyl-9-undecenyl)cyclopropyl]trimethylsilane. IR (neat): 2924, 2854, 1456, 1247, 1031, 835, 728, 694, 666 cm^{-1}; ^{1}H NMR($CDCl_3$): δ −0.72 (ddd, J = 9.8, 6.6, 6.6 Hz, 1H), −0.08 (s, 9H), 0.24–0.28 (m, 1H), 0.31–0.35 (m, 1H), 0.52–0.60 (m, 1H), 1.03–1.09 (m, 1H), 1.26–1.42 (m, 13H), 1.60 (s, 3H), 1.69 (s, 3H), 1.93–1.98 (m, 2H), 5.11 (t, J = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −2.3, 1.0, 4.3, 8.8, 15.6, 17.6, 25.7, 28.0, 29.4, 29.5, 29.6, 29.7, 29.9, 36.0, 124.9, 131.1. Anal. Calc. for $C_{18}H_{36}Si$: C, 77.06; H, 12.93. Found: C, 77.01; H, 13.23%.

[cis-2-(10-Methyl-9-undecenyl)cyclopropyl]trimethylsilane. IR (neat): 2925, 2854, 1457, 1247, 834, 728, 694, 667 cm^{-1}; ^{1}H NMR($CDCl_3$): δ −0.44 (ddd, J = 9.8, 9.8, 7.3 Hz, 1H), 0.03 (s, 9H), 0.69–0.74 (m, 1H), 0.89–0.95 (m, 1H), 1.00–1.07 (m, 1H), 1.27–1.49 (m, 14H), 1.60 (s, 3H), 1.68 (s, 3H), 1.93–1.98 (m, 2H), 5.11 (t, J = 7.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −0.1, 2.6, 8.8, 8.9, 15.6, 17.0, 25.7, 28.0, 29.3, 29.6, 29.7, 29.9, 30.4, 32.3, 124.9, 131.1. Anal. Calc. for $C_{18}H_{36}Si$: C, 77.06; H, 12.93. Found: C, 76.89; H, 13.10%.

7-Trimethylsilylbicyclo[4.1.0]heptan-2-ol (***15***). IR (nujol): 1248, 835 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ −0.42 (dd, J = 6.7, 6.7 Hz, 1H), −0.05 (s, 9H), 1.02–1.21 (m, 5H), 1.36–1.45 (m, 2H), 1.58–1.65 (m, 1H), 1.89–1.90 (m, 1H), 4.18 (ddd, J = 8.6, 5.6, 5.6 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ −2.4, 7.0, 17.4, 20.7, 22.5, 23.6, 29.5, 67.6. Elemental analysis was conducted with a trimethylsilyl ether of 7-trimethylsilylbicyclo[4.1.0]heptan-2-ol. Anal. Calc. for $C_{13}H_{28}OSi_2$: C, 60.87; H, 11.00. Found: C, 60.83; H, 10.73%.

Typical procedure for the synthesis of pinacol (2-benzoxy-1-cyclopropyl)boronate (***17***). To a greenish gray suspension of $CrCl_2$ (0.98 g, 8.0 mmol) in dry, oxygen-free THF (12 mL) was added TMEDA (0.93 g, 8.0 mmol) at 25 °C and the resulting light blue mixture was stirred at 25 °C

for 15 min. A solution of allyl benzyl ether (0.15 g, 1.0 mmol) in THF (2 mL) and a solution of pinacol dichloromethylboronic ester (0.42 g, 2.0 mmol) and LiI (0.54 g, 4.0 mmol) in THF (3 mL) was added successively to the suspension at 25 °C. The mixture was stirred at 25 °C for 24 h, and the color changed gradually to dark brown while stirring. The mixture was poured into water (10 mL). This mixture was extracted with ether (3×10 mL), and the organic extracts were dried over anhydrous magnesium sulfate and concentrated. Purification by column chromatography on silica gel (hexane–ethyl acetate, 50:1) gave the desired cyclopropylboronic ester. Analytical samples of *trans*- and *cis*-isomers were collected by recycling preparative HPLC.

*Pinacol (trans-2-benzyloxy-1-cyclopropyl)boronate (trans-**17**)*.IR (neat): 2977, 2930, 2857, 1496, 1455, 1439, 1413, 1390, 1372, 1319, 1223, 1166, 1145, 1092, 857, 736, 697 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.24 (dt, $J = 5.6$, 6.1 Hz, 1H), 0.53–0.57 (m, 1H), 0.75–0.79 (m, 1H), 1.22 (s, 12H), 1.31–1.37 (m, 1H), 3.24 (dd, $J = 10.3$, 7.1 Hz, 1H), 3.46 (dd, $J = 10.3$, 6.1 Hz, 1H), 4.48–4.57 (m, 2H), 7.22–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 9.5, 17.5, 24.6, 24.9, 71.9, 72.5, 83.0, 127.4, 127.7, 128.2. Anal. Calc. for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74. Found: C, 70.84; H, 8.90%.

*Pinacol (cis-2-benzyloxy-1-cyclopropyl)boronate (cis-**17**)*. IR (neat): 2978, 2931, 2857, 1455, 1427, 1389, 1370, 1319, 1216, 1166, 1146, 1098, 858, 737, 698 cm^{-1}; ^1H NMR ($CDCl_3$): δ −008 (ddd, $J = 16.1$, 9.3, 7.1 Hz, 1H), 0.53 (ddd, $J = 6.8$, 5.4, 3.7 Hz, 1H), 0.87 (ddd, $J = 9.0$, 7.8, 3.6 Hz, 1H), 1.19 (s, 12H), 1.38–1.48 (m, 1H), 3.44 (dd, $J = 10.0$, 7.8 Hz, 1H), 3.58 (dd, $J = 10.0$, 7.1 Hz, 1H), 4.49 (d, $J = 11.7$ Hz, 1H), 4.53 (d, $J = 11.7$ Hz, 1H), 7.22–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$): δ 9.6, 17.1, 24.6, 72.3, 74.7, 82.9, 126,9, 127.4, 127.6, 128.2, 128.3. Anal. Calc. for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74. Found: C, 71.14; H, 8.80%.

*Pinacol (trans-2-decyl-1-cyclopropyl)boronate (trans-**18**)*. IR (neat): 2978, 2924, 2854, 1457, 1420, 1388, 1370, 1315, 1217, 1147, 858, 669 cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.45 (ddd, $J = 10.4$, 5.7, 4.7 Hz, 1H), 0.31–0.37 (m, 1H), 0.60–0.66 (m, 1H), 0.82–0.91 (m, 4H), 1.19 (s, 12H), 1.11–1.36 (m, 18H); ^{13}C NMR ($CDCl_3$): δ 11.4, 14.1, 18.3, 22.7, 24.6, 29.3, 29.4, 29.6, 29.7, 31.9, 35.2, 82.7. Anal. Calc. for $C_{19}H_{37}BO_2$: C, 74.02; H, 12.10. Found: C, 73.86; H, 12.26%.

*Pinacol (cis-2-decyl-1-cyclopropyl)boronate (cis-**18**)*. IR (neat): 2978, 2924, 2854, 1457, 1438, 1412, 1389, 1371, 1316, 1218, 1147, 856, 666 cm^{-1}; ^1H NMR ($CDCl_3$): δ −0.10–0.13 (rn. 1H), 0.35–0.42 (m, 1H), 0.72–0.77 (m, 1H), 0.86 (d, $J = 6.8$ Hz, 3H), 0.97-1.15 (m, 1H), 1.11–1.37 (m, 30H). ^{13}C NMR ($CDCl_3$): δ 10.9, 14.1, 18.5, 22.7, 24.5, 24.6, 25.1, 29.4, 29.6, 29.6, 29.7, 29.8, 30.3, 31.1, 31.9, 82.8. Anal. Calc. for $C_{19}H_{37}BO_2$: C, 74.02; H, 12.10. Found: C, 73.83; H, 11.83%.

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