

Carbocyclization Reaction of Malonate Derivatives with Allylsilane Moiety Mediated by $AlCl_3$-*n*-Bu_3N

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Allylsilane bearing malonate moiety underwent intramolecular carbocyclization reaction by means of $AlCl_3$-*n*-Bu_3N to give silyl-substituted cyclopentanes in good yields.

Allylsilane has been extensively employed as an allyl anion equivalent in the Lewis acid mediated addition reaction toward aldehyde, aldimine, and α,β-unsaturated carbonyl compounds.[1] The high reactivity of the allylsilane as a nucleophile is ascribed to the propensity of the silyl group to stabilize a β-silyl carbocation intermediate.[2] Recently, a novel method for the preparation of carbocycles and heterocycles has been developed, wherein nucleophilic attack on the carbon center of the β-silyl carbocation intermediate[3] has been efficiently employed for the formation of a carbon–carbon bond[4,5] as well as a carbon–hetero atom bond.[6,7] We have already reported that the Brønsted acid promoted cyclization of allylsilane bearing hydroxy and *N*-tosyl moieties leading to tetrahydrofuran[8] and pyrolidine,[9] respectively (Scheme 1).[10,11]

We expected that use of carbon nucleophile in place of hetero atom nucleophile would lead to 5-membered carbocycles under the similar reaction conditions and would provide a novel method for the formation of cyclopentanes (Scheme 2).

Results and Discussion

Carbocyclization reaction of allylsilane **1** bearing a malonate moiety as a carbon nucleophile was investigated. At the outset, we studied several Brønsted acid to promote the cyclization reaction (Table 1). *p*-TsOH, which was effective for the cyclization leading to tetrahydrofuran and pyrolidine, turned out to be ineffective to give desilylation product **3** (Entry 1). We found that the use of $AlCl_3$ gave cyclization product **2a** albeit in a low yield (Entry 5).

After screening the reaction conditions, we found that the addition of a tertiary amine had beneficial effect on the yield of **2b** (Table 2). Among the amines used, *n*-Bu_3N gave the best results in terms of the yield (Entry 3).

Because the combination of $AlCl_3$ and *n*-Bu_3N gave the best results, we screened the solvents (Table 3).

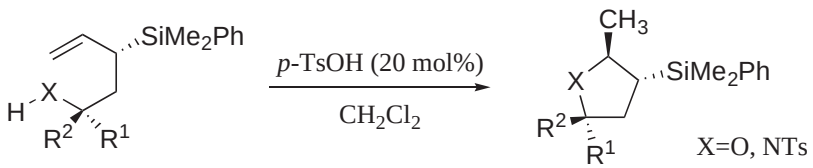
Among the solvents tested, CH_2Cl_2 exhibited the best result (Entry 1), whereas benzene, THF, and hexane were not effective (Entries 4–6). Finally, allylsilanes bearing different silyl moieties were examined as a substrate (Table 4).

The relative stereochemistry of the cyclization products **2** was determined by ^{1}H NMR NOE analysis. NOE data for **2a**, **2b**, and **2d** are shown in Scheme 3.

In order to clarify the reaction mechanism, a labeling experiment was performed (Scheme 4). Treatment of **1b-D** with $AlCl_3$-$(n\text{-}Bu)_3N$ gave cyclization product **2b-D** in a good yield. Deuterium was incorporated in the methyl group. Furthermore, treatment of **1b** with *n*-Bu_3N-$AlCl_3$ under the standard reaction conditions and quenched with D_2O gave **2b**, but no deuterium was incorporated (Scheme 5).

On the basis of experimental data, we propose the following reaction mechanism (Scheme 6). $AlCl_3$ is activated the carbonyl group to facilitate the release of the a methine proton. An ammonium salt then acts as a Brønsted acid to generate β-silyl carbocation intermediate, which is attacked by a carbon nucleophile to give cyclization product **2**. The carboalumination mechanism, shown in Scheme 5, does not seem to be operative.

Preparation of the Substrates. Substrates **1** were readily prepared starting from the corresponding allylsilane (Scheme 7). Treatment of the carbanion that was generated from allylsilane with ethylene oxide gave silyl-substituted bishomoallylic alcohols **4**. The malonate moiety was introduced after transformation of the alcohol to iodide **5** to give **1** in good yields.



Scheme 1.

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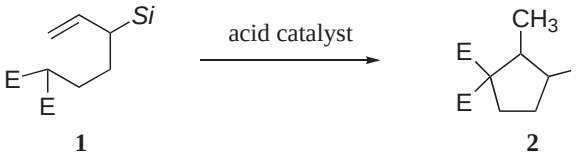


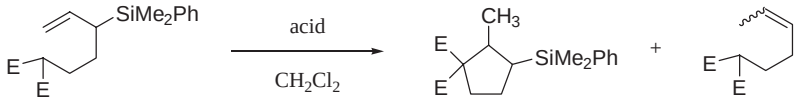
1 **2**

Scheme 2.

Conclusion

We found a novel carbocyclization of malonate moiety in the allylsilane mediated by the combined use of $AlCl_3$-(n-$Bu)_3N$. Silyl-substituted cyclopentanes were obtained in good yields. On the basis of labeling experiments, a reaction mechanism was proposed.

Table 1. Effect of Acid on the Cyclization[a)]

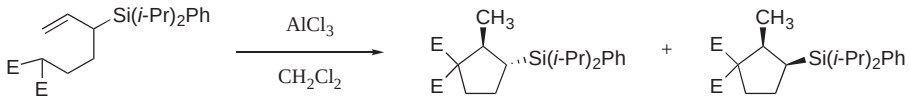


1a; E = CO_2CH_3 **2a** **3**

Entry	Acid	Time	Yield of **2a**/%	Yield of **3**/%	Recovery of **1a**/%
1	*p*-TsOH	2 d	0	96	0
2	CF_3CO_2H	2 d	0	64	19
3	CSA	2 d	0	57	33
4	$SnCl_4$	3 h	0	90	0
5	$AlCl_3$	4 h	11	10	0
6	$GaCl_3$	4 h	0	0	0

a) 1.0 equiv of acid was employed at room temperature.

Table 2. Effect of Base[a)]

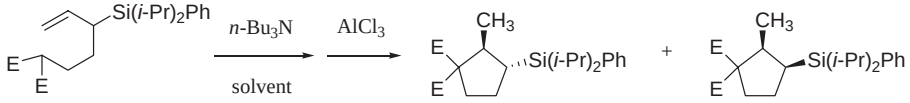


1b **2b-*trans*** **2b-*cis***

Entry	Amine	Yield of **2b-*trans***/%	Yield of **2b-*cis***/%
1	—	21	20
2	Et_3N	44	33
3	n-Bu_3N	55	30
4	2,6-Lutidine	39	30
5	Pyridine	40	30
6[b)]	TMEDA	8	5

a) Compound **1b** was treated with 1.0 equiv of amine for 2 h in CH_2Cl_2 followed by treated with 2.0 equiv of $AlCl_3$ at room temperature for 15 h. b) Compound **1b** was recovered in 71% yield.

Table 3. Influence of Solvent[a)]

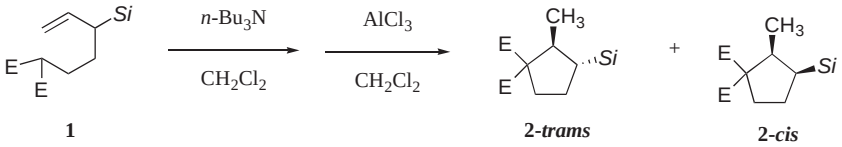


1b **2b-*trans*** **2b-*cis***

Entry	Solvent	Yield of **2b-*trans***/%	Yield of **2b-*cis***/%
1	CH_2Cl_2	55	30
2	$CHCl_3$	49	25
3	$ClCH_2CH_2Cl$	41	35
4	Benzene	39	37
5[b)]	THF	0	0
6[c)]	Hexane	15	16

a) Compound **1b** was treated with 1.0 equiv of n-Bu_3N in the solvent at room temperature for 2 h followed by treated with 2.0 equiv of $AlCl_3$ at room temperature for 15 h. b) Compound **1b** was recovered in 74% yield. c) **3** was obtained in 52% yield.

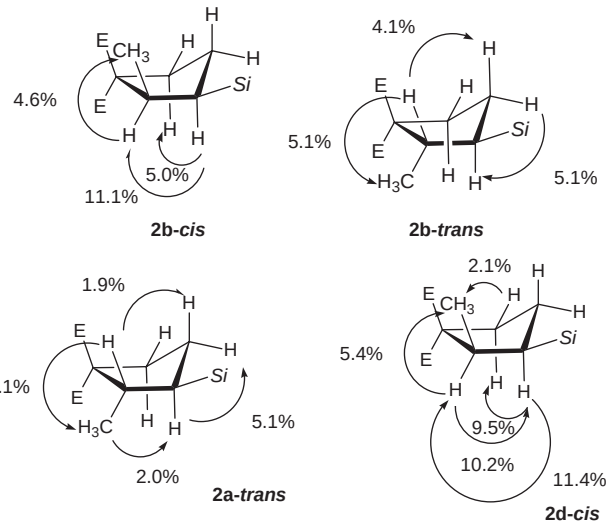
Table 4. Effect of Silyl Substituents[a)]



1 **2-*trams*** **2-*cis***

Entry	Starting material	*Si*	Yield of **2-*trans*** /%	Yield of **2-*cis*** /%
1	**1a**	$SiMe_2Ph$	29	3
2	**1b**	$SiPh(i\text{-}Pr)_2$	55	30
3	**1c**	$Si(i\text{-}Pr)_3$	41	39
4	**1d**	$Si(t\text{-}Bu)_2Ph$	13	57

a) Compound **1** was treated with 1.0 equiv of n-Bu_3N in the solvent at room temperature for 2 h followed by treated with 2.0 equiv of $AlCl_3$ at room temperature for 6–15 h.

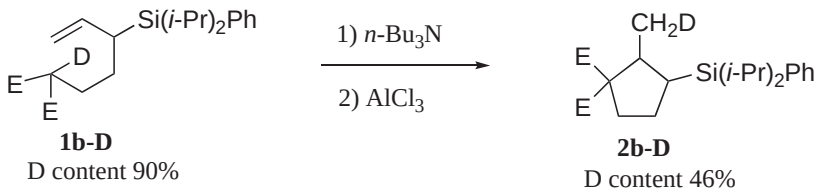


Scheme 3.

Experimental

NMR spectra were measured in $CDCl_3$ on 400 MHz spectrometer (JEOL AL-400) with tetramethylsilane (TMS) as an internal standard. $CDCl_3$ was used as an internal standard for ^{13}C NMR. All reagents were commercially available from Wako Pure Chemical Industries Ltd., Japan.

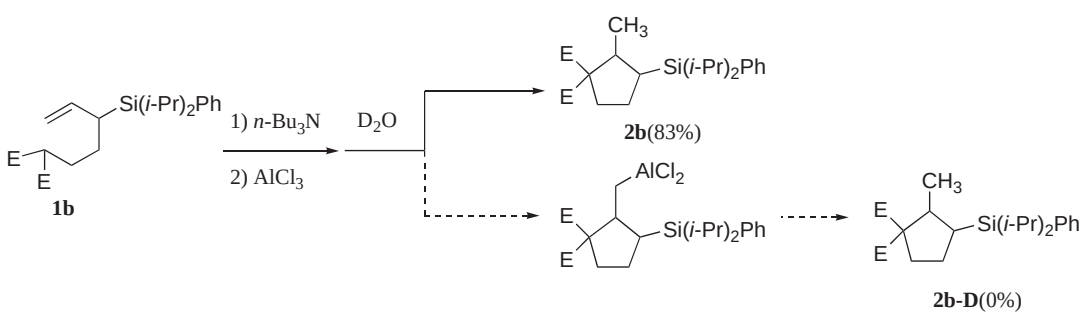
Typical Procedure for the Preparation of 3-(Dimethylphenylsilyl)pent-4-en-1-ol (4a). A hexane solution of n-BuLi (29.1 mL, 45.4 mmol, 1.56 mol L^{-1}) was added to a solution of allyldimethylphenylsilane (4.40 mL, 22.7 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (4.4 mL, 29.5 mmol) in THF (50 mL) at −10 °C. After being stirred for 1 h, the mixture was cooled down to −45 °C. Ethylene oxide, generated by the reaction of 2-chloroethanol (3.0 mL, 45.4 mmol) with powder KOH (12.7 g, 226.3 mmol) in another flask, was added to the reaction mixture to react with allyl anion. After being stirred for another 1 h at −45 °C, the reaction mixture was quenched by addition of 1 mol dm^{-3} HCl solution. The water layer was extracted with EtOAc. The combined organic layer was washed with sat. $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by silica-gel chromatography (hexane/EtOAc = 7/1, v/v) gave **4a** as colorless



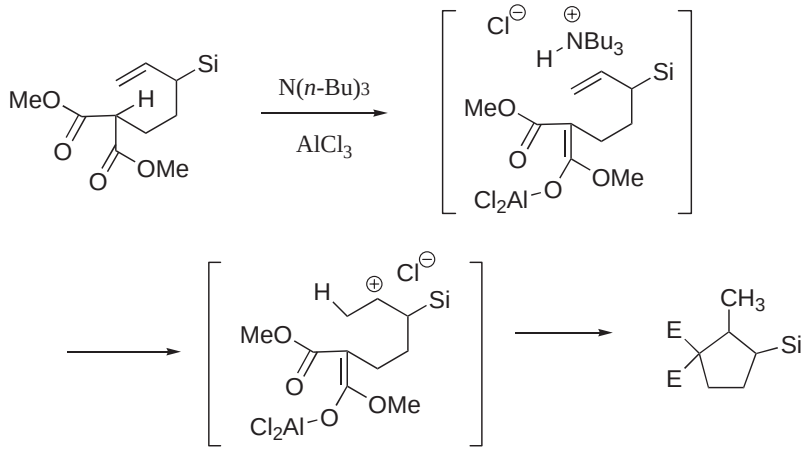
1b-D
D content 90%

2b-D
D content 46%

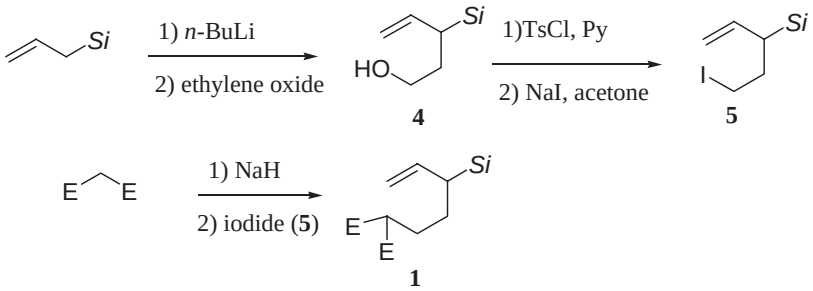
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

oil (3.15 g, 14.3 mmol) in 63% yield.

Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.45 (2H, m), 7.38–7.31 (3H, m), 5.62 (1H, ddd, $J = 17.6$, 10.3, 9.7 Hz), 4.92 (1H, dd, $J = 10.3$, 0.9 Hz), 4.88 (1H, dd, $J = 17.6$, 0.9 Hz), 3.64 (1H, ddd, $J = 10.6$, 9.2, 5.1 Hz), 3.50 (1H, ddd, $J = 10.6$, 7.2, 7.1 Hz), 1.87 (1H, dt, $J = 9.7$, 2.7 Hz), 1.66 (1H, dddd, $J = 11.2$, 9.2, 7.2, 2.7 Hz), 1.62–1.53 (2H, m), 0.28 (3H, s), 0.27 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.2, 133.9, 129.0, 127.6, 113.0, 62.5, 31.4, 31.0, −4.5, −5.4. IR (neat) 3072, 2961, 1732, 1624, 1427, 1250, 1113, 1037, 902, 835, 700 cm^{-1}. MS(EI) m/z (%) = 204(10), 137(100), 119(30), 105(80), 68(80). Found: C, 70.55; H, 9.45%. Calcd for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15%.

3-(Diisopropylphenylsilyl)pent-4-en-1-ol (4b): Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.48 (2H, m), 7.35–7.33 (3H, m), 5.75 (1H, ddd, $J = 17.1$, 10.0, 10.0 Hz), 4.96 (1H, dd, $J = 17.1$, 1.5 Hz), 4.92 (1H, dd, $J = 10.0$, 1.5 Hz), 3.66 (1H, ddd, $J = 10.5$, 7.1, 4.8 Hz), 3.55 (1H, ddd, $J = 10.5$, 7.8, 6.3 Hz), 2.31 (1H, dt, $J = 10.0$, 2.0 Hz), 1.79 (1H, dddd, $J = 14.9$, 7.1, 6.3, 2.0 Hz), 1.67–1.58 (2H, m), 1.51–1.39 (2H, m), 1.14–1.06 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 135.1, 133.7, 128.7, 127.5, 127.3, 113.1, 62.6, 32.0, 27.6, 18.6, 18.5, 18.4, 18.3, 10.8, 10.6. IR (neat) 2963, 2860, 1626, 1427, 1105, 999, 819, 702, 632 cm^{-1}. MS(EI) m/z (%) = 267(30), 199(100), 181(10), 135(100), 105(80). Found: C, 73.98; H, 10.63%. Calcd for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21%.

3-(Triisopropylsilyl)pent-4-en-1-ol (4c): Colorless oil. $R_f = 0.4$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (1H, ddd, $J = 17.1$, 10.3, 10.1 Hz), 4.94 (1H, d, $J = 17.1$ Hz), 4.90 (1H, dd, $J = 10.1$, 1.8 Hz), 3.68 (1H, ddd, $J = 12.1$, 6.0, 5.7 Hz), 3.58 (1H, ddd, $J = 12.1$, 7.1, 5.5 Hz), 2.03 (1H, ddd, $J = 12.2$, 5.5, 2.7 Hz), 1.86–1.75 (1H, m), 1.61–1.54 (2H, m), 1.19–1.06 (21H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 112.6, 62.9, 32.2, 28.3, 19.1, 19.1, 19.0, 11.2. IR (neat) 3011, 2892, 1624, 1464, 1427, 1236, 1107, 1030, 995, 902, 702, 657 cm^{-1}. MS(EI) m/z (%) = 233(30), 191(30), 165(80), 137(100), 121(80), 105(50). Found: C, 69.71; H, 12.32%. Calcd for $C_{14}H_{30}OSi$: C, 69.35; H, 12.47%.

3-(*t*-Butyldiphenylsilyl)pent-4-en-1-ol (4d): Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 7/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (2H, dd, $J = 6.7$, 1.1 Hz), 7.61 (2H, dd, $J = 6.7$, 1.1 Hz), 7.41–7.32 (6H, m), 5.88 (1H, ddd, $J = 17.0$, 10.1, 10.1 Hz), 5.01 (1H, dd, $J = 17.0$, 1.7 Hz), 5.00 (1H, dd, $J = 10.1$, 1.7 Hz), 3.60 (1H, ddd, $J = 10.6$, 6.8, 3.9 Hz), 3.55 (1H, ddd, $J = 10.6$, 8.2, 6.1 Hz), 2.55 (1H, dt, $J = 10.1$, 2.0 Hz), 1.83 (1H, dddd, $J = 12.8$, 8.2, 6.8, 2.0 Hz), 1.51–1.40 (2H, m), 1.09 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 136.5, 136.3, 134.0, 133.4, 129.0, 129.0, 127.4, 127.4, 114.7, 61.9, 32.5, 28.6, 27.8, 19.4. IR (neat) 2963, 2860, 1626, 1427, 1105, 999, 819, 702, 632 cm^{-1}. MS(EI) m/z (%) = 267(30), 199(100), 181(10), 135(100), 105(80). Found: C, 77.67; H, 8.88%. Calcd for $C_{21}H_{28}OSi$: C, 77.72; H, 8.70%.

[1-(2-Iodoethyl)allyl]dimethylphenylsilane (5a). Alcohol **4a** (2.13 g, 9.67 mmol) was added to a solution of tosyl chloride (2.40 g, 12.57 mmol) in pyridine (10 mL) at 0 °C. After being stirred at room temperature overnight, the reaction mixture was quenched by addition of 1 M HCl solution. The water layer was extracted with EtOAc. The combined organic layer was successively washed with 1 mol dm^{-3} HCl solution, sat. $NaHCO_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to dryness. Purification of the crude mixture by silica-gel chromatography gave corresponding tosylate as a colorless oil (2.99 g, 7.99 mmol, 83%). The tosylate (1.47 g, 3.92 mmol)

was added to a solution of sodium iodide (880.5 mg, 5.87 mmol) in acetone (8 mL) at room temperature, and then, the reaction mixture was refluxed for 5 h, was cooled down, and quenched by 5% of sodium sulfite solution. The water layer was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by silica-gel chromatography (hexane/EtOAc = 30/1, v/v) gave **5a** as a colorless oil (1.09 g, 3.29 mmol, 84%).

Colorless oil. $R_f = 0.6$ (hexane/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.46 (2H, m), 7.36–7.32 (3H, m), 5.49 (1H, ddd, $J = 16.3$, 10.3, 9.0 Hz), 4.96 (1H, dd, $J = 10.3$ 1.7 Hz), 4.89 (1H, dd, $J = 16.3$, 1.7 Hz), 3.26 (1H, ddd, $J = 9.3$, 8.4, 3.9 Hz), 2.99 (1H, dt, $J = 9.3$, 8.4 Hz), 1.96–1.83 (3H, m), 0.28 (3H, s), 0.27 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.7, 133.9, 129.1, 127.7, 127.7, 114.2, 35.9, 32.7, 7.8, −4.4, −5.2. IR (neat) 3854, 2963, 2359, 1558, 1427, 1251, 1114, 904, 835, 814 cm^{-1}. MS(EI) m/z (%) = 315(10), 247(80), 203(30), 185(80), 159(70), 143(100), 121(80) 105(100). Found: C, 47.78; H, 5.53%. Calcd for $C_{13}H_{19}ISi$: C, 47.27; H, 5.80%.

[1-(2-Iodoethyl)allyl]diisopropylphenylsilane (5b): Colorless oil. $R_f = 0.6$ (hexane/EtOAc = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.47 (2H, m), 7.36–7.35 (3H, m), 5.58 (1H, ddd, $J = 17.1$, 10.0, 10.0 Hz), 5.01 (1H, dd, $J = 17.1$, 0.9 Hz), 4.98 (1H, dd, $J = 10.0$, 0.9 Hz), 3.33 (1H, ddd, $J = 10.0$, 6.8, 3.7 Hz), 3.07 (1H, dt, $J = 10.0$, 7.9 Hz), 2.32 (1H, dt, $J = 10.0$, 9.3 Hz), 2.00 (1H, ddt, $J = 11.6$, 9.3, 7.9 Hz), 1.86–1.77 (1H, m), 1.50–1.38 (2H, m), 1.13–1.06 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 135.1, 133.4, 128.9, 127.6, 114.5, 32.7, 32.1, 18.6, 18.5, 18.4, 18.3, 10.8, 10.6, 8.5. IR (neat) 2891, 1427, 1107, 997, 883, 781, 702, 655 cm^{-1}. MS(EI) m/z (%) = 343(10), 275(30), 247(50), 233(10), 191(100), 149(80), 135(50), 121(80), 105(80). Found: C, 53.21; H, 7.41%. Calcd for $C_{17}H_{27}ISi$: C, 52.84; H, 7.04%.

[1-(2-Iodoethyl)allyl]triisopropylsilane (5c): Colorless oil. $R_f = 0.6$ (hexane/EtOAc = 30/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (1H, ddd, $J = 17.0$, 10.1, 9.9 Hz), 4.98 (1H, dd, $J = 17.0$, 1.8 Hz), 4.96 (1H, dd, $J = 10.1$, 1.8 Hz), 3.37 (1H, ddd, $J = 9.5$, 7.5, 3.8 Hz), 3.06 (1H, dt, $J = 9.5$, 7.3 Hz), 2.26 (1H, ddd, $J = 9.9$, 6.8, 1.3 Hz), 2.10–1.89 (2H, m), 1.18–0.93 (21H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 114.1, 33.0, 32.9, 18.7, 18.6, 11.1, 8.4. IR (neat) 3005, 2891, 1464, 1385, 1255, 1174, 1064, 1016, 904, 646 cm^{-1}. MS(EI) m/z (%) = 352(10), 309(80), 241(70), 213(50), 185(50), 171(50), 157(30) 111(50). Found: C, 47.01; H, 7.72%. Calcd for $C_{14}H_{29}ISi$: C, 47.72; H, 8.30%.

***t*-Butyl[1-(2-iodoethyl)allyl]diphenylsilane (5d):** Colorless oil. $R_f = 0.6$ (hexane/EtOAc = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.59 (4H, m), 7.42–7.34 (6H, m), 5.64 (1H, ddd, $J = 17.1$, 10.0, 10.0 Hz), 5.07 (1H, dd, $J = 17.1$, 0.9 Hz), 5.06 (1H, dd, $J = 10.0$, 0.9 Hz), 3.28 (1H, ddd, $J = 9.8$, 6.5, 3.8 Hz), 3.07 (1H, ddd, $J = 9.8$, 9.5, 6.3 Hz), 2.56 (1H, dt, $J = 10.0$, 1.8 Hz), 2.06 (1H, dddd, $J = 11.6$, 9.5, 6.5, 2.6 Hz), 1.59 (1H, dddd, $J = 11.6$, 6.3, 3.8, 3.7 Hz), 1.09 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 136.5, 136.4, 133.5, 133.2, 129.2, 129.1, 127.5, 127.4, 116.0, 32.7, 31.8, 28.6, 19.4, 8.4. IR (neat) 2963, 2860, 1626, 1427, 1105, 999, 909, 820, 700, 632, 607, 517, 486 cm^{-1}. MS(EI) m/z (%) = 377(80), 309(100), 221(10), 183(10), 135(80), 105(30). Found: C, 58.34; H, 6.49%. Calcd for $C_{21}H_{27}$-ISi: C, 58.06; H, 6.26%.

Dimethyl 2-[3-(Dimethylphenylsilyl)pent-4-enyl]malonate (1a). Dimethyl malonate (1.1 mL, 9.90 mmol) was added to a suspension of sodium hydride (237.58 mg, 9.90 mmol) in THF (10 mL) at 0 °C. The reaction mixture was allowed to stir at 50 °C for 30 min, and then, a solution of **5a** (1.09 g, 3.30 mmol) in THF (5 mL) was added to the reaction mixture. The reaction mixture was refluxed for 4 h and quenched by 1 mol dm^{-3} HCl solution. The water layer was extracted with EtOAc. The combined organic layer was successively washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by silica-gel chromatography (hexane/EtOAc = 10/1, v/v) gave **1a** as colorless oil (888 mg, 2.65 mmol, 81%).

Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.45 (2H, m), 7.35–7.32 (3H, m), 5.57 (1H, ddd, $J = 17.1$, 10.3, 9.5 Hz), 4.92 (1H, dd, $J = 10.3$, 1.3 Hz), 4.82 (1H, ddd, $J = 17.1$, 1.3, 1.0 Hz), 3.66 (3H, s), 3.65 (3H, s), 3.29 (1H, dd, $J = 8.4$, 6.7 Hz), 2.03 (1H, dddd, $J = 13.9$, 8.3, 5.6, 4.5 Hz), 1.78–1.68 (2H, m), 1.46–1.36 (2H, m), 0.26 (3H, s), 0.25 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 169.5, 138.6, 137.2, 133.9, 128.9, 127.5, 113.2, 52.3, 51.2, 34.0, 28.5, 26.0, −4.5, −5.4. IR (neat) 2957, 1732, 1626, 1437, 1282, 1250, 1159, 1113, 902, 835, 767, 702 cm^{-1}. MS(EI) m/z (%) = 334(50), 279(100), 221(20), 151(100), 113(80). Found: C, 64.93; H, 7.97%. Calcd for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83%.

Dimethyl 2-[3-(Diisopropylphenylsilyl)pent-4-enyl]malonate (1b): Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.44 (2H, m), 7.35–7.32 (3H, m), 5.67 (1H, ddd, $J = 17.6$, 9.8, 9.8 Hz), 4.95 (1H, d, $J = 17.6$ Hz), 4.94 (1H, d, $J = 9.8$ Hz), 3.69 (3H, s), 3.68 (3H, s), 3.33 (1H, t, $J = 7.6$ Hz), 2.15–2.06 (2H, m), 1.76 (1H, ddt, $J = 13.4$, 10.0, 6.7 Hz), 1.59–1.36 (3H, m), 1.31–1.23 (1H, m), 1.11–1.04 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 169.6, 138.9, 135.1, 133.7, 128.7, 127.5, 113.4, 52.3, 51.2, 30.9, 28.8, 26.6, 18.5, 18.5, 18.3, 18.2, 10.8, 10.5. IR (neat) 2946, 1728, 1626, 1437, 1383, 1282, 1157, 1107, 997, 902, 702, 655 cm^{-1}. MS(EI) m/z (%) = 390(10), 347(10), 190(50), 148(100), 135(50), 121(100). Found: C, 67.53; H, 8.90%. Calcd for $C_{22}H_{34}O_4Si$: C, 67.65; H, 8.77%.

Dimethyl 2-[3-(Triisopropylsilyl)pent-4-enyl]malonate (1c): Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (1H, ddd, $J = 18.8$, 6.3, 6.3 Hz), 5.67 (1H, dd, $J = 6.3$, 1.7 Hz), 5.52 (1H, d, $J = 18.8$ Hz), 3.74 (3H, s), 3.73 (3H, s), 3.40 (1H, t, $J = 7.6$ Hz), 2.17 (1H, dt, $J = 8.1$, 6.8 Hz), 2.00 (1H, dt, $J = 8.1$, 7.3 Hz), 1.44 (1H, ddd, $J = 13.2$, 7.6, 6.3 Hz), 1.17–1.10 (2H, m), 1.05–1.03 (21H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 139.8, 133.0, 52.4, 51.2, 28.5, 26.1, 18.8, 18.7, 16.3, 11.0, 10.8. IR (neat) 2892, 1732, 1460, 1437, 1340, 1280, 1197, 1159, 997, 902, 663 cm^{-1}. MS(EI) m/z (%) = 356(10), 313(20), 281(20), 157(80), 115(100), 87(80). Found: C, 64.21; H, 10.51%. Calcd for $C_{19}H_{36}O_4Si$: C, 64.00; H, 10.18%.

Dimethyl 2-[3-(*t*-Butyldiphenylsilyl)pent-4-enyl]malonate (1d): Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (2H, dd, $J = 7.2$, 1.2 Hz), 7.55 (2H, dd, $J = 7.2$, 1.2 Hz), 7.41–7.32 (6H, m), 5.75 (1H, ddd, $J = 17.1$, 10.3, 10.0 Hz), 5.00 (1H, d, $J = 10.3$ Hz), 4.97 (1H, d, $J = 17.1$ Hz), 3.64 (3H, s), 3.63 (3H, s), 3.25 (1H, t, $J = 7.6$ Hz), 2.31 (1H, dt, $J = 10.0$, 0.2 Hz), 2.10–2.00 (1H, m), 1.74 (1H, dddd, $J = 13.2$, 7.3, 6.8, 6.8 Hz), 1.61–1.53 (1H, m), 1.33–1.23 (1H, m), 1.07 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 136.6, 136.29, 134.0, 133.4, 128.8, 128.7, 127.6, 127.1, 115.0, 52.9, 51.7, 31.2, 29.2, 28.1, 27.0, 19.3. IR (neat) 2955, 1732, 1437, 1257, 1105, 906, 720, 702 cm^{-1}. MS(EI) m/z (%) = 438(5), 381(20), 239(20), 197(50), 135(100). Found: C, 71.18; H, 7.99%. Calcd for $C_{26}H_{34}$-O_4Si: C, 71.19; H, 7.81%.

***trans*-Dimethyl 2-Methyl-3-(dimethylphenylsilyl)cyclopentane-1,1-dicarboxylate (2a-*trans*).** *n*-Bu_3N (24 μL, 0.10 mmol)

was added to a solution of **1a** (34.0 mg, 0.10 mmol) in CH_2Cl_2 (0.5 mL) at room temperature. After the mixture was stirred for 2 h, $AlCl_3$ (27.1 mg, 0.20 mmol) was added to the reaction mixture, and the reaction mixture was stirred for 6 h. The reaction was quenched by 1 mol dm^{-3} HCl solution and the water layer was extracted with EtOAc. The combined organic layers were washed with sat. $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. Purification of the crude mixture by silica-gel chromatography (hexane/EtOAc = 10/1, v/v) gave **2a-*trans*** as a colorless oil (9.7 mg, 0.029 mmol, 29%) and **2a-*cis*** as a colorless oil (1.0 mg, 0.003 mmol, 3%).

Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (2H, m), 7.35–7.34 (3H, m), 3.68 (3H, s), 3.68 (3H, s), 2.58 (1H, dq, $J = 11.2$, 6.8 Hz), 2.33 (1H, dt, $J = 13.4$, 7.8 Hz), 2.00–1.84 (2H, m), 1.43 (1H, ddt, $J = 11.8$, 11.8, 8.5 Hz), 1.14 (1H, dt, $J = 12.7$, 8.3 Hz), 0.88 (3H, d, $J = 6.8$ Hz), 0.32 (3H, s), 0.29 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 171.7, 138.3, 133.6, 128.8, 127.6, 65.3, 52.5, 51.9, 43.2, 35.3, 32.9, 27.3, 17.6, −4.0, −4.1 IR(neat) 3071, 2955, 2845, 1726, 1458, 1381, 1251, 1201, 1155, 1111, 1080, 910, 833, 702 cm^{-1}. MS(EI) m/z (%) = 318(5), 278(80), 256(10), 135(100), 113(80). Found: C, 64.83; H, 8.24%. Calcd for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83%.

***cis*-Dimethyl 2-Methyl-3-(dimethylphenylsilyl)cyclopentane-1,1-dicarboxylate (2a-*cis*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.51 (2H, m), 7.34–7.32 (3H, m), 3.68 (3H, s), 3.66 (3H, s), 3.02 (1H, dq, $J = 7.3$, 7.3 Hz), 2.64 (1H, ddd, $J = 14.4$, 9.0, 5.4 Hz), 2.00–1.84 (2H, m), 1.81–1.74 (1H, m), 1.33–1.24 (1H, m), 0.72 (3H, d, $J = 7.3$ Hz), 0.34 (3H, s), 0.28 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 171.7, 138.8, 133.5, 128.7, 127.6, 66.7, 52.5, 52.3, 43.7, 32.4, 32.1, 24.4, 14.9, −2.3, −3.1. IR (neat) 3071, 2955, 2845, 1726, 1458, 1381, 1251, 1201, 1155, 1111, 1080, 910, 833, 702 cm^{-1}. MS(EI) m/z (%) = 318(5), 278(80), 256(10), 135(100), 113(80). Found: C, 64.61; H, 8.14%. Calcd for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83%.

***trans*-Dimethyl 3-Diisopropylphenylsilyl-2-methylcyclopentane-1,1-dicarboxylate (2b-*trans*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.48 (2H, m), 7.34–7.31 (3H, m), 3.71 (3H, s), 3.70 (3H, s), 2.77 (1H, dq, $J = 11.7$, 6.8 Hz), 2.65 (1H, ddd, $J = 13.9$, 9.0, 4.9 Hz), 2.12–2.03 (2H, m), 1.99–1.91 (1H, m), 1.61–1.56 (1H, m), 1.51–1.38 (2H, m), 1.12–1.04 (12H, m), 1.00 (3H, d, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 171.9, 135.8, 135.1, 128.6, 127.3, 65.0, 52.4, 52.2, 43.9, 32.0, 29.6, 27.8, 19.0, 19.0, 18.9, 18.9, 17.1, 11.5, 11.4. IR (neat) 3020, 2401, 1726, 1477, 1220, 1045, 930, 750, 671 cm^{-1}. MS(EI) m/z (%) = 390(30), 346(100), 178(30), 151(50), 121(50), 107(20). Found: C, 67.79; H, 9.03%. Calcd for $C_{22}H_{34}O_4Si$: C, 67.65; H, 8.77%.

***cis*-Dimethyl 3-Diisopropylphenylsilyl-2-methylcyclopentane-1,1-dicarboxylate (2b-*cis*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (2H, m), 7.34–7.31 (3H, m), 3.67 (3H, s), 3.65 (3H, s), 3.13 (1H, dq, $J = 9.2$, 7.3 Hz), 2.37 (1H, ddd, $J = 13.5$, 8.2, 7.1 Hz), 1.99–1.91 (2H, m), 1.83 (1H, ddd, $J = 9.2$, 7.4, 5.2 Hz), 1.67–1.56 (1H, m), 1.33–1.25 (2H, m), 1.20–0.95 (12H, m), 0.61 (3H, d, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 170.9, 135.1, 134.4, 128.5, 127.4, 66.4, 52.2, 51.8, 42.6, 35.4, 28.9, 25.3, 18.6, 18.5, 18.3, 15.2, 12.4, 12.0. IR (neat) 3020, 2401, 1726, 1477, 1220, 1045, 930, 750, 671 cm^{-1}. MS(EI) m/z (%) = 390(30), 346(100), 178(30), 151(50), 121(50), 107(20). Found: C, 67.82; H, 9.01%. Calcd for $C_{22}H_{34}O_4Si$: C, 67.65; H, 8.77%.

***trans*-Dimethyl 2-Methyl-3-triisopropylsilylcyclopentane-1,1-dicarboxylate (2c-*trans*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74 (3H, s), 3.73 (3H, s), 3.10 (1H, dq, $J = 6.5$, 6.3 Hz), 2.09 (1H, ddd, $J = 14.4$, 7.3, 7.1 Hz), 2.01–1.98 (1H, m), 1.83–1.74 (2H, m), 1.57 (3H, d, $J = 6.5$ Hz), 1.46–1.39 (1H, m), 1.20–1.05 (21H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 66.3, 52.3, 42.6, 31.7, 30.1, 26.0, 18.7, 17.7, 16.2, 12.4, 12.3. IR (neat) 3030, 2890, 1726, 1462, 1435, 1271, 1242, 1199, 1159, 1064, 883 cm^{-1}. MS(EI) m/z (%) = 313(100), 281(30), 145(30), 117(50), 89(30), 75(50), 59(30). Found: C, 64.51; H, 10.38%. Calcd for $C_{19}H_{36}O_4Si$: C, 64.00; H, 10.18%.

***cis*-Dimethyl 2-Methyl-3-triisopropylsilylcyclopentane-1,1-dicarboxylate (2c-*cis*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (3H, s), 3.70 (3H, s), 3.40 (1H, dq, $J = 7.3$, 3.4 Hz), 2.66 (1H, ddd, $J = 14.2$, 10.3, 3.9 Hz), 2.30–2.00 (1H, m), 2.18 (1H, dt, $J = 7.6$, 7.0 Hz), 1.95–1.89 (1H, m), 1.30–1.25 (1H, m), 1.31–1.03 (21H, m), 0.85 (3H, d, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 171.0, 66.3, 51.0, 50.9, 42.6, 28.8, 28.3, 25.6, 19.3, 17.7, 15.1, 10.8. IR (neat) 3030, 2890, 1726, 1462, 1435, 1271, 1242, 1199, 1159, 1064, 883 cm^{-1}. MS(EI) m/z (%) = 313(100), 281(30), 145(30), 117(50), 89(30), 75(50), 59(30). Found: C, 64.21; H, 10.31%. Calcd for $C_{19}H_{36}O_4Si$: C, 64.00; H, 10.18%.

***trans*-Dimethyl 3-*t*-Butyldiphenylsilyl-2-methylcyclopentane-1,1-dicarboxylate (2d-*trans*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (2H, dd, $J = 7.6$, 1.5 Hz), 7.59 (2H, dd, $J = 7.6$, 1.5 Hz), 7.34–7.28 (6H, m), 3.72 (3H, s), 3.67 (3H, s), 2.69 (1H, dq, $J = 6.8$, 5.8 Hz), 2.38–2.28 (1H, m), 1.97–1.91 (2H, m), 1.89–1.84 (1H, m), 1.12–1.05 (1H, m), 1.08 (9H, s), 0.78 (3H, d, $J = 6.8$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 171.8, 136.3, 136.2, 134.7, 128.9, 128.8, 127.4, 127.1, 64.7, 52.3, 51.8, 43.9, 35.3, 29.8, 28.8, 28.7, 22.6, 19.1, 17.9. IR (neat) 2955, 1726, 1471, 1242, 1157, 1105, 1078, 702, 607, 503 cm^{-1}. MS(EI) m/z (%) = 438(5), 381(100), 213(80), 183(50), 135(30), 105(20). Found: C, 71.32; H, 8.04%. Calcd for $C_{26}H_{34}O_4Si$: C, 71.19; H, 7.81%.

***cis*-Dimethyl 3-*t*-Butyldiphenylsilyl-2-methylcyclopentane-1,1-dicarboxylate (2d-*cis*):** Colorless oil. $R_f = 0.3$ (hexane/EtOAc = 10/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (2H, dd, $J = 7.4$, 1.8 Hz), 7.55 (2H, dd, $J = 7.4$, 1.8 Hz), 7.40–7.33 (6H, m), 3.75 (3H, s), 3.61 (3H, s), 3.29 (1H, dq, $J = 7.3$, 6.0 Hz), 2.61 (1H, ddd, $J = 13.9$, 10.6, 3.7 Hz), 2.24 (1H, ddd, $J = 13.9$, 7.1, 5.6 Hz), 2.07 (1H, ddd, $J = 13.0$, 9.2, 7.8 Hz), 2.02–1.91 (1H, m), 1.33–1.24 (1H, m), 1.09 (9H, s), 0.48 (3H, d, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 170.6, 136.3, 135.0, 128.8, 128.7, 127.4, 127.1, 66.4, 52.5, 52.2, 43.0, 32.0, 28.6, 28.4, 25.8, 18.8, 14.9. IR (neat) 2955, 1726, 1471, 1242, 1157, 1105, 1078, 702, 607, 503 cm^{-1}. MS(EI) m/z (%) = 438(5), 381(100), 213(80), 183(50), 135(30), 105(20). Found: C, 71.45; H, 8.19%. Calcd for $C_{26}H_{34}O_4Si$: C, 71.19; H, 7.81%.

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