Phosphine-Dependent Selective Cross-Dimerization between Terminal Alkylacetylene and Silylacetylene by Iridium(I) Guanidinate Complex–Phosphine System

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Abstract: The new iridium(I)–guanidinate complex served as an efficient catalyst for phosphine-dependent selective cross-dimerization between silylacetylene and terminal alkyl- or arylacetylene. Especially, in case of cross-dimerization between silylacetylene and alkylacetylene, *E*/*Z* selectivity of resulting enynes could be controlled by changing phosphine.

Key words: alkynes, enynes, coupling, dimerizations, iridium

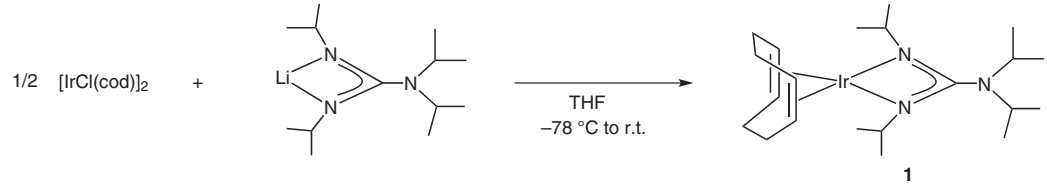
The transition-metal-catalyzed regio- and stereoselective dimerization of alkynes has been received much attentions as a useful method for the synthesis of substituted enynes.[1] Not only homodimerization of terminal alkynes but also cross-dimerization between terminal alkynes and internal alkynes have been reported,[2] while the cross-dimerization between two different terminal alkynes is scarce.[3] A notable success of such a reaction is Ru-[3c] and Rh-catalyzed[3d] head-to-head cross-dimerization between terminal acetylene and silylacetylene, and Pd-catalyzed head-to-tail cross-dimerization between terminal alkylacetylene and triisopropylsilylacetylene.[3e]

Our research group has recently demonstrated that an iridium(I)–pyridine-2-thiolate complex [Ir(SNC_5H_4)(PPh_3)$_2$] catalyzes homodimerization of terminal alkynes in good yield with high *E*-selectivity through activation of a terminal C–H bond of an alkyne.[4] We anticipated that an iridium(I) complex bearing a highly electron-donating anionic chelate ligand would show high catalytic activity toward dimerization of terminal alkynes.

In this report, we describe the preparation of a new iridium(I) complex with a highly electron-donating guanidinate ligand[5] and its application to the first phosphine-dependent selective cross-dimerization between various silylacetylenes and terminal alkylacetylenes as well as arylacetylenes with high regio- and stereoselectivity.

We prepared an iridium(I)–guanidinate complex through the reaction of [IrCl(cod)]$_2$ with a lithium guanidinate (Scheme 1). Iridium(I)–guanidinate complex **1** was isolated in good yield as an orange solid.[6] Although many late-transtion-metal guanidinate complex has been reported,[7] the example of iridium complex bearing a guanidinate ligand is scarce.[8] Especially, a low valent iridium(I)–guanidinate complex, which might be suitable for metal-catalyzed reactions, has not been prepared. In the ^{1}H NMR spectrum of **1**, two kinds of methyl protons were obserbed as doublet at δ = 0.96 and 1.23 ppm, respectively. The structure of complex **1** was also confirmed by X-ray analysis.[9] The complex have square planar geometry around an iridium atom.

To evaluate the catalytic efficiency of complex **1** for dimerization of alkyne, we investigated homodimerization of terminal alkylacetylene and arylacetylene by complex **1** in the presence of phosphine. As shown in Table 1, head-to-head dimerization of 1-octyne (**2a**) proceeded with high *E*-selectivity by **1**–Ph_3P system (entry 1).[10] Straight-chain alkylacetylenes such as 1-octyne (**2a**) hardly dimerize by a previously reported [IrCl(cod)]$_2$–phosphine catalytic system.[1a] In the case of the acetylacetonato complex catalytic system {[Ir(acac)(cod)]–Ph_3P} which bears a less electron-donating anionic ligand than the guanidinate ligand, the dimerization of 1-octyne (**2a**) resulted in low yield (38%, *E*/*Z* = 80:20). From this result, the catalytic reactivity for dimerization of 1-octyne by **1**–Ph_3P system probably derived from electron-donating



Scheme 1

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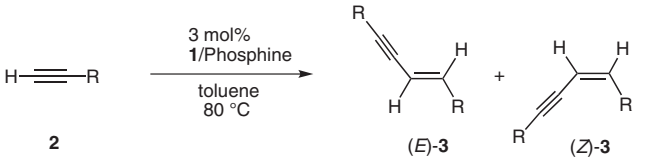
ability of guanidinate ligand. The selectivity of resulting enynes were highly dependent on using phosphine. After screening various phosphines, we found that a *Z*-selective dimerization of **2a** was achieved by the use of diethylphenylphosphine (Et_2PhP) in good yield with high selectivity (entry 2). The dimerization of **2a** catalyzed by **1** with trialkylphosphine such as a triethylphosphine (Et_3P) or tri-*n*-propylphosphine (*n*-Pr_3P) resulted in low *Z*-selectivity.[11] Not only alkylacetylene but also arylacetylene such as phenylacetylene (**2b**) gave head-to-head dimers **3b** in high yields with excellent selectivities (entries 3 and 4).

Table 1 Dimerization of Terminal Alkyne **2** Catalyzed by **1**–Phosphine System



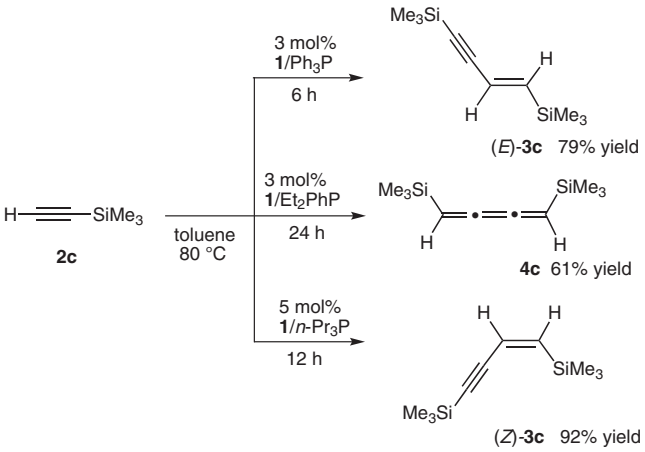
2 (*E*)-**3** (*Z*)-**3**

Entry	**2** (R)	Phosphine	Time (h)	Yield of **3** (%)[a]	*E*/*Z*[b]
1	**2a** (*n*-C_6H_{13})	Ph_3P	6	**3a** (71)	85:15
2	**2a** (*n*-C_6H_{13})	Et_2PhP	24	**3a** (77)	7:93
3	**2b** (Ph)	Ph_3P	6	**3b** (94)	>99:1
4	**2b** (Ph)	Et_2PhP	24	**3b** (92)	0:100

[a] Isolated yield.
[b] Determined by ^1H NMR.

The catalyst system **1**–Ph_3P also catalyzed dimerization of trimethylsilylacetylene (**2c**) leading to enyne in good yield with complete *E*-selectivity (Scheme 2).[10] On the other hand, the reaction of **2c** by **1**–Et_2PhP system afforded a *Z*-butatriene **4c** in a moderate yield. The *Z*-enyne was obtained by **1**–*n*-Pr_3P system in a good yield with complete *Z*-selectivity. Reaction mechanism for homodimerization of alkyne have been demonstrated in various research groups.[1,12] It is known that phosphine ligand containing high electron-donating property such as alkylphosphine favors the formation of *Z*-enyne and *Z*-butatriene rather than that of *E*-enyne because of a formation of vinylidene intermediate.[1f] In our catalytic system, the dimerization reaction probably proceeded with similar reaction mechanism.

We next examined the cross-dimerization between trimethylsilylacetylene (**2c**) and 1-octyne (**2a**) in the presence of a **1**–Ph_3P catalyst. After screening the reaction conditions, we found that cross-dimerization between **2c** and excess **2a** (2 equiv) proceeded to give the corresponding cross-dimer **5a** with complete *E*-selectivity (Table 2, entry 1).[13] Although the homo-dimer (*E*)-**3a** also formed in this reaction,[14] the resulting cross-dimer **5a** could be isolated by silica gel column chromatography in high yield. It should be noted that *Z*-type cross-dimerization between **2c** and **2a** proceeded by **1**–*n*-Pr_3P catalytic system in high yield with complete selectivity (entry 2). It is the first example for phosphine-controlled cross-dimerization reac-



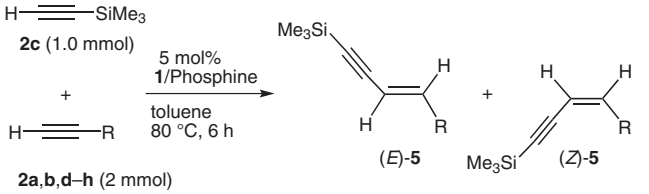
Scheme 2

tion of terminal alkyne. The reaction by **1**–Et_2PhP system resulted in low *Z*-selectivity compared with that by **1**–*n*-Pr_3P system.[15] The cross-dimerization involving branch-chain alkylacetylene **2d** by **1**–Ph_3P or **1**–*n*-Pr_3P also proceeded in good yield with complete *E*- or *Z*-selectivity, respectively (entries 3 and 4). The cross-dimer between **2c** and benzylacetylene (**2e**) also obtained in good yield with excellent or high selectivity (entries 5 and 6). Cyclohexylacetylene (**2f**) also reacted with **2c** to give the corresponding cross-dimer **5f** in good yield with complete *E*- and high *Z*-selectivity, respectively (entries 7 and 8). Not only alkylacetylene but also arylacetylene such as phenylacetylene (**2b**) could participate in the *E*-selective cross-dimerization with good yield and good selectivity (entry 9), however, *Z*-selective dimerization by **1**–*i*-Pr_3P system could not achieved (entry 10). Concerning *E*-selective cross-dimerization between **2c** and other terminal arylacetylene, cross-dimerization between **2c** and 4-tolylacetylene (**2g**) or 4-methoxyphenylacetylene (**2h**) were also achieved in good yield with good to high *E*-selectivity (entries 11 and 12).

In the presence of the **1**–Ph_3P or **1**–*n*-Pr_3P, other silylacetylenes such as triisopropylacetylene and *tert*-butyldimethylsilylacetylene were also reacted with alkylacetylene (Scheme 3).[13] The cross-dimerization between triisopropylsilylacetylene (**2i**) and 1-octyne (**2a**) proceeded to give the corresponding cross-dimer (*E*)-**5i** or (*Z*)-**5i** in high yield with complete stereoselectivity. *tert*-Butyldimethylsilylacetylene (**2j**) also reacted with **2a** to give the corresponding cross-dimer **5j** though yields and selectivities of resulting cross-dimers **5j** are lower than that of **5i**.

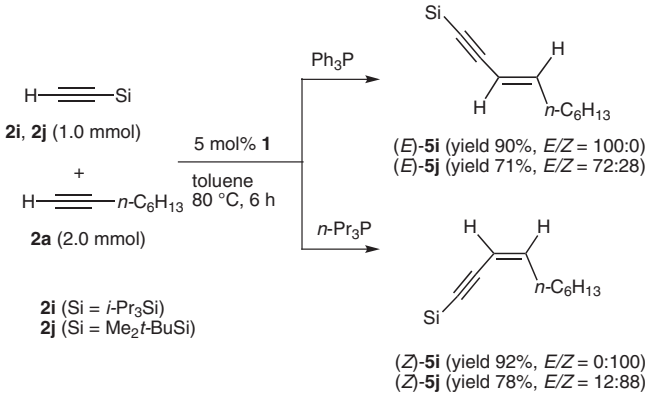
In summary, we demonstrated that an iridium(I)–guanidinate complex–phosphine system is a versatile new catalyst for regio- and stereoselective cross-dimerization between two different terminal alkynes. Especially, in the case of cross-dimerization between silylacetylenes and alkylacetylenes, the *E*/*Z* selectivity of resulting enynes could be controlled by changing phosphines.

Table 2 Cross-Dimerization between Trimethylsilylacetylene (**2c**) and Alkyl- or Arylacetylene **2a**,**b**,**d**–**h** Catalyzed by **1**–Phosphine System



Entry	**2** (R)	Phosphine	Yield of **5** (%)[a]	*E*/*Z*[b]
1	**2a** (n-C_6H_{13})	Ph_3P	**5a** (80)	100:0
2	**2a** (n-C_6H_{13})	n-Pr_3P	**5a** (90)	0:100
3	**2d** [$Me_2CH(CH_2)_2$]	Ph_3P	**5d** (78)	100:0
4	**2d** [$Me_2CH(CH_2)_2$]	n-Pr_3P	**5d** (87)	0:100
5	**2e** ($PhCH_2$)	Ph_3P	**5e** (72)	100:0
6	**2e** ($PhCH_2$)	n-Pr_3P	**5e** (70)	10:90
7	**2f** (Cy)	Ph_3P	**5f** (72)	100:0
8	**2f** (Cy)	n-Pr_3P	**5f** (92)	4:96
9	**2b** (Ph)	Ph_3P	**5b** (72)	88:12
10	**2b** (Ph)	n-Pr_3P	**5b** (60)	87:13
11	**2g** (4-MeC_6H_4)	Ph_3P	**5g** (76)	91:9
12	**2h** (4-$MeOC_6H_4$)	Ph_3P	**5h** (81)	91:9

[a] Isolated yield.
[b] Determined by ^{1}H NMR.



Scheme 3

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(6) **Synthesis of {Ir[(N_2 (*i*-Pr)$_2$CN(*i*-Pr)$_2$](cod)} (1)**
A solution of $[IrCl(cod)]_2$ (281 mg, 0.42 mmol) in THF (5 mL) was cooled to –78 °C, and then a THF solution of Li[(N_2 (*i*-Pr)$_2$CN(*i*-Pr)$_2$], which was prepared by the reaction of the DIC (0.13 mL, 0.84 mmol) with LDA solution (1.8 M in heptane–THF–ethylbenzene solution, 0.48 mL, 0.86 mmol) at –78 °C, was added. The mixture was allowed to warm to r.t. After 4 h, the volatiles were removed under reduced pressure. The residual solid was extracted with toluene and the filtrate was evaporated off under high vacuum to give orange complex **1** (278 mg, 0.53 mmol, 63%). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.96 (d, *J* = 6.4 Hz, 12 H, *i*-PrCH_3), 1.23 (d, *J* = 6.9 Hz, 12 H, *i*-PrCH_3), 1.39 (d, *J* = 7.8 Hz, 4 H, cod), 2.20 (br, 4 H, cod), 3.43 (sept, *J* = 6.9 Hz, 2 H, *i*-PrCH), 3.80 (sept, *J* = 6.4 Hz, 2 H, *i*-PrCH), 4.09 (br, 4 H, cod). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 22.8, 25.0, 32.5, 47.1, 48.6, 58.9 (cod, *i*-Pr), 128.5 (cod), 179.7 (NCN). Anal. Calcd for $C_{21}H_{40}IrN_3$: C, 47.88; H, 7.65; N, 7.98. Found: C, 47.82; H, 7.60; N, 8.00.

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(9) **Crystal Data for 1**
$C_{21}H_{40}IrN_3$, MW = 526.79, monoclinic, $P2_1/n$, a = 20.5195 (4) Å, b = 15.5067 (4) Å, c = 27.6890 (4) Å, β = 102.4145 (16)°, V = 8604.4 (3) $Å_3$, Z = 16, D_{calc} = 1.626 g/cm^3, μ (Mo Kα) = 62.328 cm^{-1}, 84841 measured reflections, 24677 independent (R_{int} = 0.063), 13318 observed [I > 2σ(I)]. $R1$ = 0.0353, $wR2$ = 0.0903 (all data). Atomic coordinates, thermal parameters, bond distances, and angles have been deposited at the Cambridge Crystallographic Data Center. CCDC number: 668977.

(10) **General Procedure for Homodimerization of Terminal Alkynes (Table 1 and Scheme 2)**
The mixture of **1** (16 mg, 0.03 mmol), toluene (3 mL), phosphine (16 mg, 0.06 mmol), and terminal alkyne (1.0 mmol) was charged in a sealed tube under argon atmosphere. After stirring for 6 h at 80 °C, the solvent was removed, and the residue was chromatographed on SiO_2, using hexane or Et_2O–hexane (1:3) as eluent. The solvent was removed to give dimeric product **3** or **4**.

(11) Results of dimerization of 1-octyne(**2a**) catalyzed by **1**–trialkylphosphine system; **1**–Et_3P: yield 60%, *E*/*Z* = 42:58; **1**–*n*-Pr_3P: yield 79%, *E*/*Z* = 40:60

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(13) **General Procedure for Cross-Dimerization of Silylacetylene with Terminal Alkynes (Table 2 and Scheme 3)**
The mixture of **1** (25 mg, 0.05 mmol), toluene (3 mL), phosphine (26 mg, 0.10 mmol), silylacetylene (1.0 mmol), and terminal alkyne (2.0 mmol) was charged in sealed tube under argon atmosphere. After stirring for 6 h at 80 °C, the solvent was removed, and the residue was chromatographed on SiO_2, using hexane as eluent. Homo-dimer was eluted first. Then the eluate containing cross-dimer **5** was obtained. The solvent was removed to give cross-dimer **5** as colorless or pale-yellow oil.
Spectral Data for New Compounds
Product (*E*)-**5d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 (s, 9 H, $SiMe_3$), 0.87 (d, *J* = 7.0 Hz, 6 H, CH_3), 1.20–1.30 (m, 2 H, CH_2), 1.50–1.60 (m, 1 H, CH), 2.00–2.20 (m, 2 H, CH_2), 5.50 (dt, *J* = 15.8, 1.8 Hz, 1 H, CH=CH), 6.21 (dt, *J* = 15.8, 7.0 Hz, 1 H, CH=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 0.0 (s, $SiMe_3$), 22.4, 27.3, 30.9, 37.6 (s, C_6H_{13}), 92.4, 104.2 (s, C=C), 109.4, 146.5 (C=C). HRMS (EI): *m/z* [M – Me]$^+$ calcd for $C_{11}H_{19}Si$: 179.1256; found: 179.1259.
Product (*Z*)-**5d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 (s, 9 H, $SiMe_3$), 0.90 (d, *J* = 6.4 Hz, 6 H, CH_3), 1.20–1.30 (m, 2 H, CH_2), 1.50–1.60 (m, 1 H, CH), 2.30–2.40 (m, 2 H, CH_2), 5.46 (d, *J* = 10.5 Hz, 1 H, CH=CH), 5.95 (dt, *J* = 10.5, 7.6 Hz, 1 H, CH=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 0.0 (s, $SiMe_3$), 22.4, 27.3, 30.9, 37.6 (s, C_6H_{13}), 88.7, 92.4 (s, C=C), 109.4, 146.5 (C=C). HRMS (EI): *m/z* [M – Me]$^+$ calcd for $C_{11}H_{19}Si$: 179.1256; found: 179.1213.
Product (*E*)-**5e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.17 (s, 9 H, $SiMe_3$), 3.43 (d, *J* = 6.9 Hz, 2 H, CH_2), 5.53 (dt, *J* = 15.6, 1.8 Hz, 1 H, CH=CH), 6.35 (dt, *J* = 15.6, 6.9 Hz, 1 H, CH=CH), 7.10–7.40 (m, 5 H, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = –0.1 (s, $SiMe_3$), 39.3 (s, CH_2Ph), 93.5, 103.7 (s, C=C), 111.0, 126.4, 128.5, 128.7, 138.6, 144.2 (S, C=C, Ph). HRMS (EI): *m/z* [M]$^+$calcd for $C_{14}H_{18}Si$: 214.1178; found: 214.1169.
Product (*Z*)-**5e**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, $SiMe_3$), 3.67 (d, *J* = 7.3 Hz, 2 H, CH_2), 5.60 (d, *J* = 11.0 Hz, 1 H, CH=CH), 6.10 (dt, *J* = 10.6, 7.3 Hz, 1 H, CH=CH), 7.10–7.40 (m, 5 H, Ph). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = –0.02 (s, $SiMe_3$), 36.5 (s, CH_2Ph), 99.0, 101.8 (s, C=C), 109.9, 126.2, 128.5, 128.5, 139.7, 143.2 (S, C=C, Ph). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{14}H_{18}Si$: 214.1178; found: 214.1158.
Product (*E*)-**5g**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 (s, 9 H, $SiMe_3$), 2.34 (s, 3 H, CH_3), 6.12 (d, *J* = 16.5 Hz, 1 H, CH=CH), 6.98 (d, *J* = 16.5 Hz, 1 H, CH=CH), 7.10–7.30 (m, 4 H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 0.0 (s, $SiMe_3$), 21.5 (s, CH_3), 96.4, 104.6 (s, C=C), 106.9, 126.2, 129.0, 129.4, 138.9, 142.4 (s, C=C, Ph). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{14}H_{18}Si$: 214.1178; found: 214.1171.
Product (*E*)-**5h**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 9 H, $SiMe_3$), 3.81 (s, 3 H, CH_3, 6.16 (d, *J* = 19.2 Hz, 1 H, CH=CH), 6.48 (d, *J* = 19.2 Hz, 1 H, CH=CH), 6.84 (d, *J* = 9.2 Hz, 2 H, Ar), 7.37 (d, *J* = 9.2 Hz, 2 H, Ar). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = –1.6 (s, $SiMe_3$), 55.2 (s, OCH_3), 88.4, 89.9 (s, C=C), 113.9, 128.4, 132.1, 133.0, 144.7, 159.6 (s, C=C, Ph). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{14}H_{18}OSi$: 230.1127; found: 230.1133.
Product (*E*)-**5i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–2.20 (m, 16 H, C_6H_{13}, *i*-PrCH), 1.07 (br d, 18 H, *i*-$PrCH_3$), 5.52 (dt, *J* = 16.0, 1.4 Hz, 1 H, CH=CH), 6.20 (dt, *J* = 16.0, 6.9 Hz, 1 H, CH=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 11.3, 14.1, 22.6, 28.6, 28.9, 31.7, 33.1 (s, C_6H_{13}, *i*-PrCH), 18.6 (s, *i*-$PrCH_3$), 88.5, 106.1 (s, C=C), 109.8, 145.8 (s, CH=CH). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{19}H_{36}Si$: 292.2586; found: 292.2583.
Product (*Z*)-**5i**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80–2.40 (m, 16 H, C_6H_{13}, *i*-PrCH), 1.09 (br d, 18 H, *i*-$PrCH_3$), 5.50 (d, *J* = 10.5 Hz, 1 H, CH=CH), 6.0 (m, 1 H, CH=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 11.3, 14.1, 22.6, 28.8, 29.0, 30.4, 31.7 (s, C_6H_{13}, *i*-PrCH), 18.6 (s, *i*-$PrCH_3$), 94.6, 103.9 (s, C=C), 109.6, 145.2 (s, CH=CH). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{19}H_{36}Si$: 292.2586; found: 292.2587.
Product (*E*)-**5j**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.11 (s, 6 H, $SiMe_2$), 0.80–2.20 (m, 13 H, C_6H_{13}), 0.94 (s, 9 H, *t*-Bu), 5.50 (d, *J* = 15.8 Hz, 1 H, CH=CH), 6.21 (dt, *J* = 15.8, 7.0 Hz, 1 H, CH=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = –4.6 (s, $SiMe_2$), 14.1, 16.6, 22.6, 28.6, 28.8, 31.6, 33.1 [s, C_6H_{13}, $C(CH_3)_3$], 26.1 [s, $C(CH_3)_3$], 90.6, 104.8 (s, C=C), 109.6, 146.2 (s, CH=CH). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{16}H_{30}Si$: 250.2117; found: 250.2116.
Product (*Z*)-**5j**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.13 (s, 6 H, $SiMe_2$), 0.80–2.40 (m, 13 H, C_6H_{13}), 0.96 (s, 9 H, *t*-Bu), 5.48 (d, *J* = 10.8 Hz, 1 H, CH=CH), 5.96 (dt, *J* = 10.8, 7.4 Hz, 1 H, CH=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = –4.6 (s, $SiMe_2$), 14.1, 16.6, 22.6, 28.7, 28.9, 30.3, 31.6 [s, C_6H_{13}, $C(CH_3)_3$], 26.1 [s, $C(CH_3)_3$], 96.6, 102.8 (s, C=C), 109.2, 145.6 (s, CH=CH). HRMS (EI): *m/z* [M]$^+$ calcd for $C_{16}H_{30}Si$: 250.2117; found: 250.2108.

(14) Formation ratio of (*E*)-**5a**/(*E*)-**3a** = 77:23 (determined by ^{1}H NMR).

(15) Result of cross-dimerization between **2c** and **2a** catalyzed by **1**–Et_2PhP system: yield 88%, *E*/*Z* = 9:91.