ORGANOMETALLICS

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Ligand-Controlled Regiodivergent Hydrosilylation of Conjugated Dienes Catalyzed by Mono(phosphine)palladium(0) Complexes

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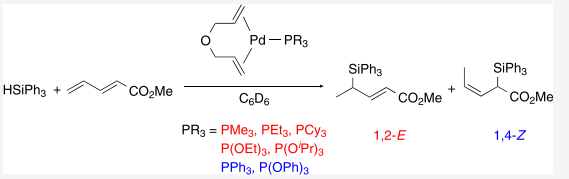
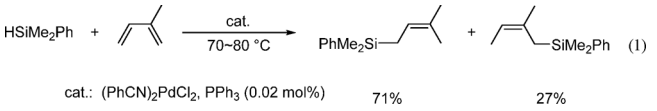
ABSTRACT: Mono(phosphine)palladium(0) complexes, [Pd(η^2:η^2-$C_6H_{10}O$)(PR_3)] (**1**), catalyze hydrosilylation of electron-deficient conjugated dienes with $HSiPh_3$. Hydrosilylation of methyl penta-2,4-dienoate with $HSiPh_3$ catalyzed by [Pd(η^2:η^2-$C_6H_{10}O$)(PR_3)] (R = Me (**1a**), Et (**1b**), OEt (**1d**), O^{i}Pr (**1e**)) proceeds to give the 1,2-*E* product in quantitative yield with exclusive Markovnikov selectivity. In contrast, their triphenylphosphine and -phosphite analogues, [Pd(η^2:η^2-$C_6H_{10}O$)(PR_3)] (R = Ph (**1f**), OPh (**1g**)), mainly produce the 1,4-*Z* product (1,2-*E*/1,4-*Z* = 3/7). The regioselectivity in the hydrosilylation of methyl 2,4-pentadienoate is also controlled by organosilanes. Mechanistic studies suggest that the reaction using a compact and basic mono-phosphorus complex proceeds by the Chalk−Harrod mechanism involving the reductive elimination from an (η^3-allyl)(silyl)palladium(II). A poor electron-donating mono-phosphorus ligand such as $P(OPh)_3$ destabilizes a Pd(II) species and promotes direct reductive elimination to give the 1,4-*Z* product. On the other hand, a compact and electron-donating phosphorus ligand, such as PMe_3, PEt_3, and $P(OMe)_3$, favors to give the more stable (η^3-allyl)(silyl)palladium(II) intermediate by the allyl rotation, followed by reductive elimination to give the 1,2-*E* product.



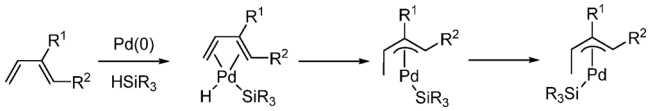
INTRODUCTION

Hydrosilylation is undoubtedly an important reaction in organic synthesis.[1] The main difficulty of this reaction using unsymmetric conjugated dienes is in the control of regio- and stereoselectivities (eq 1).[2,3] The 1,4-selective addition of

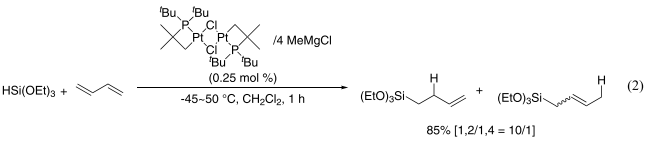


triorganosilanes to conjugated dienes can be achieved with known catalysts. In these catalytic reactions, the formation of an η^3-allyl intermediate is proposed (Scheme 1).

Scheme 1. Mechanism of Hydrosilylation of Conjugated Dienes Catalyzed by Pd(0)



In contrast, the 1,2-selective addition of silanes to conjugated dienes is still rare. Recently, Ritter and co-workers reported a Pt(II) catalyst bearing a cyclometalated phosphine ligand to catalyze the 1,2- and *anti*-Markovnikov-selective hydrosilylation of conjugated diene (eq 2).[4] The key for the 1,2-selective hydrosilylation is believed to be that a hexacoordinate Pt(IV) intermediate with a hemilabile



phosphine ligand prevents the η^4-coordination of a conjugated diene that leads to an η^3-allyl intermediate (Figure 1).

Similarly, the 1,2- and *anti*-Markovnikov-selective hydrosilylation of conjugated dienes catalyzed by an *in situ* generated cobalt catalyst was reported by RajanBabu and co-workers (eq 3).[5] The reaction of [$CoCl_2$($^{i\text{-Pr}}$PDI)] with 2 equiv of

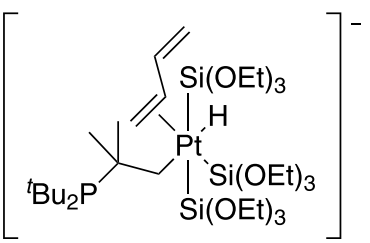


Figure 1. A possible intermediate of hydrosilylation of 1,3-butadiene.

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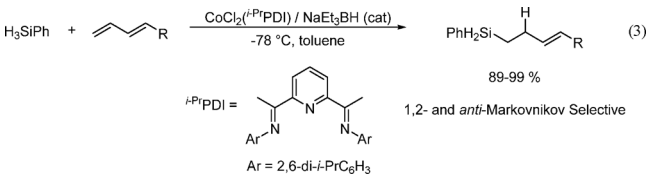
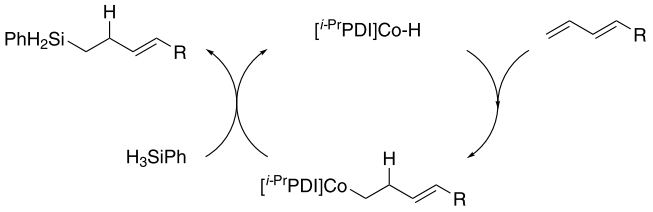


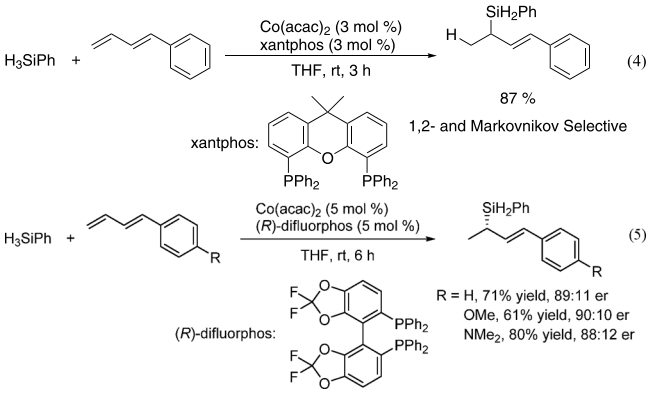
(3)

$NaEt_3BH$ generates an efficient catalyst for selective *anti*-Markovnikov hydrosilylation of the terminal double bond in conjugated dienes. Primary and secondary silanes such as H_3SiPh, H_2SiPh, and $H_2SiMePh$ react with a wide range of terminal dienes without affecting the configuration of the other double bond. The reduction of the $[CoCl_2(^{i\text{-}Pr}PDI)]$ with $NaEt_3BH$ afforded the corresponding cobalt hydride species, $[CoH(^{i\text{-}Pr}PDI)]$, that reacted with the Co center coordinated with a bulky tridentate ligand added to the terminal carbon in a less-hindered double bond of the conjugated diene to give an (η^1-homoallyl)cobalt species (Scheme 2). This cobalt species reacted with the silane to give the linear hydrosilylation product, regenerating the cobalt-hydride.

Scheme 2. Mechanism of Hydrosilylation of Conjugated Dienes Catalyzed by $[CoCl_2(^{i\text{-}Pr}PDI)]/NaEt_3BH$



On the other hand, Ge and co-workers reported the 1,2- and Markovnikov-selective hydrosilylation of conjugated dienes using catalysts generated from $Co(acac)_2$ and a phosphine ligand (eqs 4 and 5).[6] They proposed a hydrometalation pathway with a Co(I)−H formed by the reaction of Co(II) species with hydrosilane for this hydrosilylation of conjugated dienes. In contrast to the $[CoCl_2(^{i\text{-}Pr}PDI)]/NaEt_3BH$ system, the 2,1-addition of Co−H species into conjugated diene forms an allylcobalt intermediate, which reacts with H_3SiPh to give the allylsilane product and regenerate the Co−H species. This regioselectivity of the addition of Co−H species into conjugated diene was controlled by the ligand (Scheme 3).



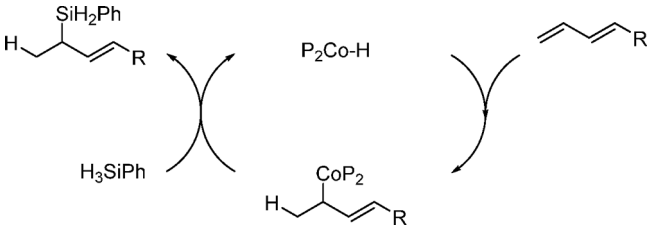
(4)

(5)

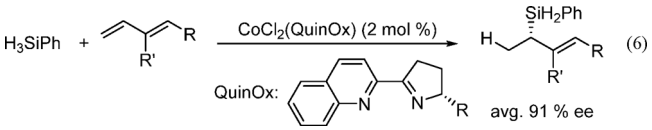
Furthermore, asymmetric hydrosilylation of (*E*)-1-aryl-1,3-diene derivatives catalyzed by the $Co(acac)_2$/(*R*)-difluorphos system was also reported to give chiral allylsilanes (eq 5).

The asymmetric 1,2-Markovnikov hydrosilylation of conjugated dienes catalyzed by a cobalt complex containing a

Scheme 3. Mechanism of Hydrosilylation of Conjugated Dienes Catalyzed by $Co(acac)_2$/Phosphine Ligand



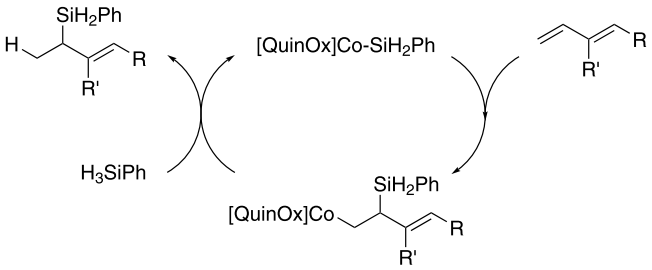
dinitrogen ligand such as a quinolineoxazoline was also reported by Huang and co-workers (eq 6).[7] The catalyst



(6)

system is effective for a wide array of conjugated dienes, including mono- and 1,2-disubstituted dienes with aryl and/or alkyl substituents. From the result of a deuterium-labeling experiment, they suggested that the hydrosilylation most likely proceeded through a modified Chalk−Harrod mechanism involving the 1,2-insertion of a Co−Si bond into the terminal double bond of the diene to form primary Co species for avoiding steric repulsion (Scheme 4). Similarly, the iron

Scheme 4. Mechanism of Hydrosilylation of Conjugated Dienes Catalyzed by $CoCl_2$/QuinOx Ligand



catalysts with 2,9-diaryl-1,10-phenanthroline ligands produced 1,2-addition products of 1-substituted and 1,1-disubstituted buta-1,3-dienes with Markovnikov selectivity.[8]

Palladium-catalyzed hydrosilylation is an important strategy for the synthesis of organosilanes, and recently several progresses of palladium-catalyzed hydrosilylation of various alkenes were reported.[9] On the other hand, although Pd complexes having phosphine ligands have long been known as a catalyst for Markovnikov-selective hydrosilylations,[10] the low catalytic activity has been a problem. Sumida, Hosoya, and co-workers pioneeringly documented efficient hydrosilylations of electron-deficient alkynes by $[Pd(dba)_2]/PCy_3$.[11] We found mono(phosphine)palladium(0) complexes having a diallyl ether ligand to be efficient catalysts for Markovnikov-selective hydrosilylation of electron-deficient alkenes (eq 7).[12]

In the course of our study, we came across that the hydrosilylation of conjugated dienes catalyzed by a mono(phosphine)palladium(0) complex gives the 1,2-*E* and 1,4-*Z* products depending on the phosphorus ligand used and the nature of silanes (eq 8). In this contribution, we disclose regiodivergent hydrosilylation of conjugated diene catalyzed by the mono(phosphine)palladium(0) complexes.[13]

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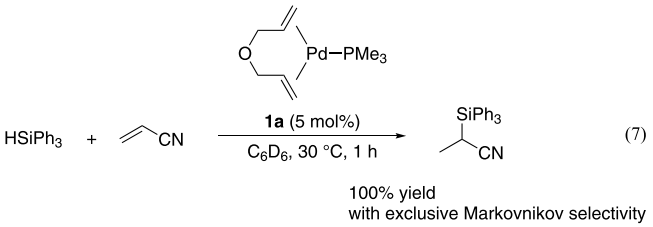
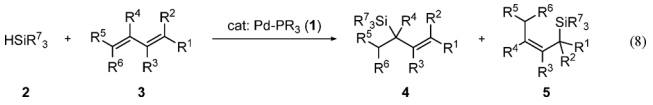




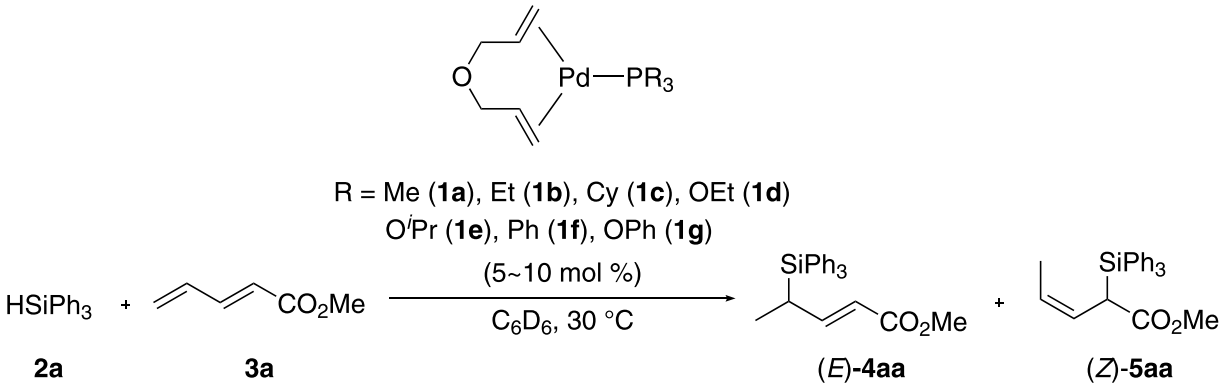
RESULTS AND DISCUSSION

Reaction of Methyl Penta-2,4-dienoate with Triphenylsilane Catalyzed by Mono(phosphine)palladium(0). A series of palladium(0) complexes having a diallyl ether ligand and an ancillary phosphorus ligand (**1**) were screened in hydrosilylation of methyl penta-2,4-dienoate with $HSiPh_3$ (Table 1). The reaction catalyzed by 5 mol % of **1a** (PR_3 = PMe_3) at 30 °C exclusively gave the 1,2-*E* product in quantitative yield with perfect Markovnikov selectivity (Table 1, entry 1). With 10 mol % of **1b**, **1d**, and **1e**, the reaction also proceeded with 1,2-*E* and Markovnikov selectivity in high yield (entries 2, 4, 5). When 5 mol % of **1c** was used, a 78/22 mixture of 1,2-*E*/1,4-*Z* products was obtained (entry 3). Interestingly, the catalysts **1f** and **1g** mainly produced the 1,4-*Z* product (entries 6, 7). The catalyst **1f** (10 mol %) gave preferentially the 1,4-*Z* product in moderate yield. The $P(OPh)_3$ derivative **1g** showed the lower catalytic activity. When the reaction was carried out at 50 °C for 48 h in the presence of 10 mol % of **1g**, the hydrosilylation product was formed in 62% yield.

As an alternative method to form a mono-phosphine complex of Pd(0), we also evaluated the hydrosilylation catalyzed by $[Pd(dba)_2]$ in the presence of 1 equiv of the phosphorus ligand (Table 2). First of all, no catalytic activity was observed in the presence of $[Pd(dba)_2]$ without addition of the phosphorus ligand (entry 1). Hydrosilylation catalyzed by bis(dibenzylideneacetone)palladium(0) with PMe_3 proceeded with similar selectivity as the reaction catalyzed by **1a** (entry 2), although **1a** showed higher catalytic activity than $[Pd(dba)_2]/PMe_3$. With the PPh_3 ligand, the 1,4-*Z* product also dominated as shown in the reaction catalyzed by **1f** (entry 9). According to these results, both catalytic systems probably generate the same active species and the product selectivity depends on the phosphorus ligand used. The reactions with PMe_2Ph, $PMePh_2$, PPh_2Cy, and $P(OMe)_3$ gave 1,2-*E* selective hydrosilylation (entries 4–7). Interestingly, a *para*-substituted triaryl phosphine such as $P(C_6H_4OMe\text{-}4)_3$ and $P(C_6H_4F\text{-}4)_3$ shows 1,2-*E* or 1,4-*Z* selectivity, respectively. The steric property of *para*-substituted triaryl phosphine is similar to that of PPh_3. Therefore, the higher electron-donating property of $P(C_6H_4OMe\text{-}4)_3$ than PPh_3 provided the 1,2-*E* product. In contrast, when an electron-withdrawing triaryl phosphine such as $P(C_6H_4F\text{-}4)_3$ was used, the 1,4-*Z* product was formed in high selectivity. The reaction rate diminished by the addition of 1 equiv of PMe_3 and was completely hampered in the presence of 2 equiv of PMe_3 (Figure 2). These results suggest the active catalyst is a mono(phosphine)palladium complex and this catalysis does not depend on the substrate concentrations.

Scope of Silanes. With these results in hand, we turned our attention to the nature of silanes. We evaluated the electronic effect of silanes on the hydrosilylations products by use of 4-substituted triarylsilanes. Complexes **1a** and **1f** were used as the catalysts in this reaction (Table 3). The regioselectivity in these reactions is highly dependent on the

Table 1. Hydrosilylation of Methyl Penta-2,4-dienoate with Triphenylsilane Catalyzed by [Pd(η^2:η^2-diallyl ether)(PR_3)] (1)[a]



entry	Pd cat (mol %)	time/h	yield/%	selectivity/% (*E*)-**4aa**	selectivity/% (*Z*)-**5aa**
1	**1a** (5)	8	99	100	0
2	**1b** (10)	12	83	100	0
3	**1c** (5)	16	84	78	22
4[b]	**1d** (10)	24	92	100	0
5[b]	**1e** (10)	26	81	100	0
6[b]	**1f** (10)	72	60	28	72
7[b,c]	**1g** (10)	48	62	26	74

[a]Conditions: $[PhSiH]_0$ = 0.1 M, $[methyl\ penta\text{-}2,4\text{-}dienoate]_0$ = 0.1 M, [**1**] = 0.005, 0.010 M, solvent: C_6D_6, temperature: 30 °C. [b][**1**] = 0.010 M. [c]50 °C.

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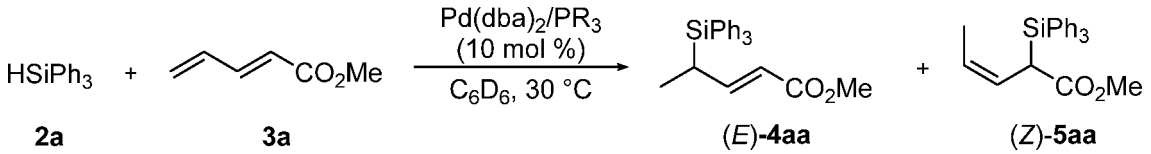
Table 2. Hydrosilylation of Methyl Penta-2,4-dienoate with Triphenylsilane Catalyzed by $Pd(dba)_2$ in the Presence of PR_3[a]



2a 3a (E)-4aa (Z)-5aa

entry	PR_3	time/h	yield/%	selectivity/% (E)-4aa	selectivity/% (Z)-5aa
1	none	48	0		
2	PMe_3	24	79	100	0
3[b]	PMe_3	24	0		
4	PMe_2Ph	21	82	98	2
5	$PMePh_2$	46	84	89	11
6	PPh_2Cy	7	34	78	22
7	$P(OMe)_3$	24	77	100	0
8	$P(C_6H_4OMe\text{-}4)_3$	40	60	77	23
9	PPh_3	63	50	28	72
10	$P(C_6H_4F\text{-}4)_3$	40	32	10	90
11	$P(CH_2Ph)_3$	15	41	18	82

[a]Conditions: $[HSiPh_3]_0$ = 0.10 M, [methyl penta-2,4-dienoate]$_0$ = 0.10 M, $[Pd(dba)_2]$ = 0.005 M, $[PMe_3]$ = 0.005 M, solvent: C_6D_6, temperature: 30 °C. [b]$[Pd(dba)_2]$ = 0 M, $[PMe_3]$ = 0.005 M.

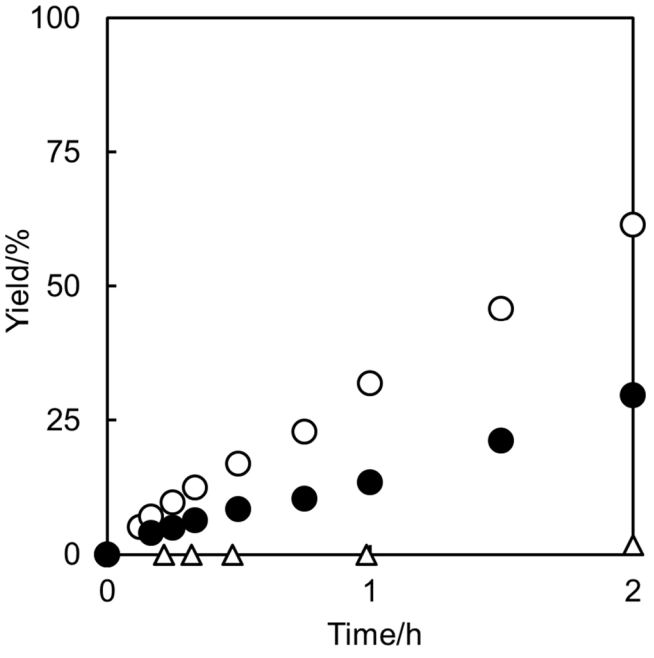


Figure 2. Effect of added PMe_3 on hydrosilylation of methyl penta-2,4-dienoate (3a) with triphenylsilane (2a) catalyzed by the mono(trimethylphosphine)palladium(0) complex [Pd(η^2:η^2-$C_6H_{10}O$)(PMe_3)] (1a): $[PMe_3]$ = 0 (○), 0.0055 (●), 0.010 M (△). Conditions: $[2a]_0$ = 0.10 M, $[3a]_0$ = 0.10 M, [1a] = 0.005 M, solvent: C_6D_6, temperature: 30 °C.

electric property of the triarylsilane. Namely, when $HSi(C_6H_4OMe\text{-}4)_3$ and $HSi(C_6H_4Me\text{-}4)_3$ were treated with methyl penta-2,4-dienoate in the presence of 5 mol % of 1a at 30 °C, 1,2-selective hydrosilylation also took place to give the corresponding 1,2-*E* products (entries 1, 2). However, in the similar reactions using $HSi(C_6H_4Cl\text{-}4)_3$ or $HSi(C_6H_4CF_3\text{-}4)_3$, the 1,2-*E* selectivity was decreased (entries 4, 5). After treatment of $HSi(C_6H_4OMe\text{-}4)_3$ or $HSi(C_6H_4Me\text{-}4)_3$ with methyl penta-2,4-dienoate in the presence of 1f (10 mol %) at 30 °C, a mixture of 1,2-*E* and 1,4-*Z*-allylsilane was formed (entries 6, 7). When the reaction of $HSi(C_6H_4Cl\text{-}4)_3$ or $HSi(C_6H_4CF_3\text{-}4)_3$ with 1f was carried out, the corresponding hydrosilylation product was obtained with completely 1,4-*Z* selectivity (entries 9, 10). These results suggest the electron-rich silanes to favor the 1,2-*E* products, and formation of the 1,4-*Z* product is encouraged by 1f.

Then we also evaluated a series of triorganosilanes in this hydrosilylation. When 1a was used as the catalyst, the 1,2-*E* products were exclusively formed (Table 4, entries 1−4). In contrast, the regioselectivity in these reactions catalyzed by 1f was highly dependent on the structure of the silane. The hydrosilylation reaction using $HSiMePh_2$ and $HSiMe_2Ph$ produced both the 1,2-*E* and 1,4-*Z* products in a roughly 1/1 ratio (entries 5, 6). This suggests that the regioselectivity of the hydrosilylation of methyl 2,4-pentadienoate catalyzed by the mono(phosphine)palladium(0) complex is controlled by the phosphine ligand as well as the silane.

The hydrosilylation of methyl penta-2,4-dienoate with primary and secondary silanes such as phenyl and diphenyl silanes was investigated (Table 5). Similar to triphenyl silane, the hydrosilylation of methyl penta-2,4-dienoate with diphenyl silane (2k) in the presence of 1a or 1f gave the corresponding hydrosilylation products in 1,2-*E* or 1,4-*Z* selective, respectively (entries 1, 3). In contrast, no hydrosilylation product with phenyl silane (2l) was detected and gave unidentified silylated mixtures (entries 2, 4). Note that RajanBabu and co-workers reported the Co-catalyzed reactions of (*E*)-dodeca-1,3-diene with $HSiPh_3$ dominantly gave the reduction product, (*E*)-3-dodecene, and those with H_2SiPh_2 and H_3SiPh gave a 1,2-*E*-*anti*-Markovnikov selective product, (*E*)-1-silyldodec-3-ene.[5] Formation of a silylene species has been reported in the Ru-,[14] Ir-,[15] and Fe-catalyzed[16] hydrosilylation using a primary silane, and the present catalyst may have reacted with a primary silane and changed the course of the reaction.

Scope of Conjugated Dienes. The scope of dienes in the hydrosilylation with $HSiPh_3$ catalyzed by 1 is given in Table 6. The hydrosilylation of methyl (2*E*,4*E*)-hexa-2,4-dienoate proceeded to give the corresponding allylsilane with complete 1,2-*E* selectivity in 90% yield for 19 h in the presence of 1 mol

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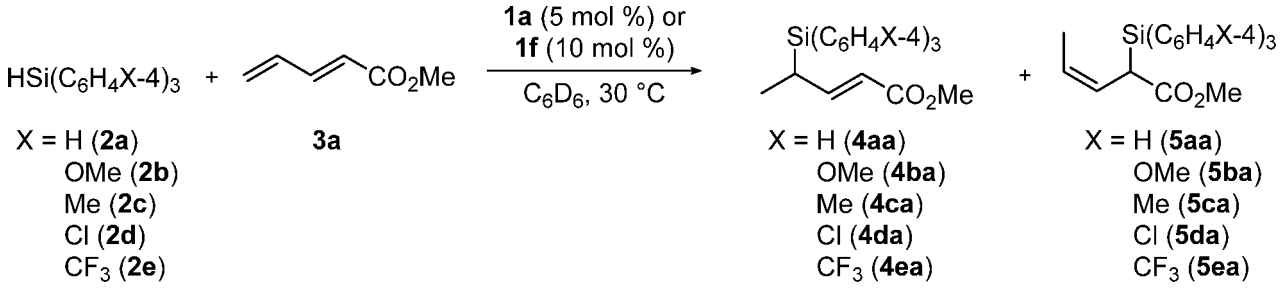
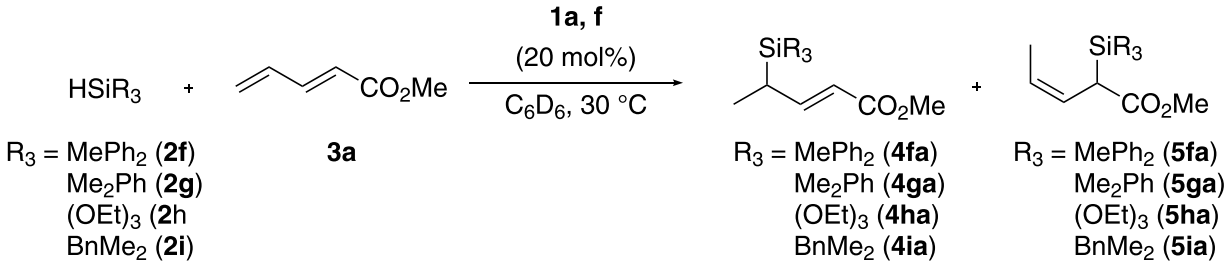
Table 3. Hydrosilylation of Methyl Penta-2,4-dienoate with Triarylsilane Catalyzed by Pd(η^2:η^2-diallyl ether)(PR_3) (R = Me, Ph)[a]



entry	Pd cat. (mol %)	$HSiAr_3$	time/h	yield/%	selectivity/% (E)-4	selectivity/% (Z)-5
1	**1a** (5)	$HSi(C_6H_4OMe\text{-}4)_3$ (**2b**)	22	82	100	0
2	**1a** (5)	$HSi(C_6H_4Me\text{-}4)_3$ (**2c**)	22	100	100	0
3	**1a** (5)	$HSiPh_3$ (**2a**)	8	99	100	0
4	**1a** (5)	$HSi(C_6H_4Cl\text{-}4)_3$ (**2d**)	4	100	96	4
5	**1a** (5)	$HSi(C_6H_4CF_3\text{-}4)_3$ (**2e**)	7	86	82	18
6[b]	**1f** (10)	$HSi(C_6H_4OMe\text{-}4)_3$ (**2b**)	24	42	66	34
7[b]	**1f** (10)	$HSi(C_6H_4Me\text{-}4)_3$ (**2c**)	24	56	50	50
8[b]	**1f** (10)	$HSiPh_3$ (**2a**)	72	60	28	72
9[b]	**1f** (10)	$HSi(C_6H_4Cl\text{-}4)_3$ (**2d**)	4.5	62	0	100
10[b]	**1f** (10)	$HSi(C_6H_4CF_3\text{-}4)_3$ (**2e**)	0.5	97	0	100

[a]Conditions: $[HSi(C_6H_4X\text{-}4)_3]_0$ = 0.10 M, [methyl penta-2,4-dienoate]$_0$ = 0.10 M, [**1a**] = 0.005 M, solvent: C_6D_6, temperature: 30 °C. [b][**1f**] = 0.010 M.

Table 4. Hydrosilylation of Methyl Penta-2,4-dienoate with $HSiR_3$ Catalyzed by Pd(η^2:η^2-diallyl ether)(PR_3) (R = Me, Ph)[a]



entry	Pd cat.	$HSiR_3$	time/h	yield/%	selectivity/% (E)-4	selectivity/% (Z)-5
1	**1a**	$HSiMePh_2$ (**2f**)	24	78	100	0
2	**1a**	$HSiMe_2Ph$ (**2g**)	150	52	100	0
3	**1a**	$HSi(OEt)_3$ (**2h**)	20	83	100	0
4	**1a**	$HSiBnMe_2$ (**2i**)	120	30	100	0
5	**1a**	$HSiEt_3$ (**2j**)	8	62	100	0
6	**1f**	$HSiMePh_2$ (**2f**)	42	27	50	50
7	**1f**	$HSiMe_2Ph$ (**2g**)	42	35	48	52

[a]Conditions: $[HSiR_3]_0$ = 0.10 M, [methyl penta-2,4-dienoate]$_0$ = 0.10 M, [**1**] = 0.020 M, solvent: C_6D_6, temperature: 30 °C.

% of **1a** (entry 2). Similarly, 1,2-*E* selective hydrosilylation of methyl (2*E*)-2-methylpenta-2,4-dienate and ethyl (2*E*)-3-methylpenta-2,4-dienate with $HSiPh_3$ also took place (entries 4, 5). In contrast, 1,4-*Z* selective hydrosilylation took place for methyl (2*E*)-4-methylpenta-2,4-dienate (entry 3). The hydrosilylation of methyl (2*E*,4*E*)-4-methylhexa-2,4-dienoate gave a mixture of methyl (*Z*)-4-methyl-2-(triphenylsilyl)hex-3-enoate and methyl (*E*)-4-methyl-2-(triphenylsilyl)hex-4-enoate (entry 6). No hydrosilylation product was formed in the reaction of methyl (2*E*)-5-methylhexa-2,4-dienoate (entry 7). This result suggests that the reaction proceeds with the prior coordination of the C═C bond to the palladium center. Hydrosilylation of 1-phenyl-1,3-butadiene derivatives with triphenylsilane was also performed (entries 8−17). The reaction of phenylbutadiene catalyzed by **1a** yielded a 4:6 mixture of 1,2-*E* and 1,4-*Z* product (entry 12). The hydrosilylation of 1-(4-nitrophenyl)-1,3-butadiene catalyzed by **1a** proceeded with complete 1,2-*E* selectivity (entry 8). On the other hand, **1f** catalyzed 1,4-*Z* selective hydrosilylation of 1-phenyl-1,3-butadiene derivatives (entries 9, 11, 13, 15, 17). The hydrosilylation of 1,3-butadine, isoprene, and *β*-myrcene catalyzed by **1a** and **1f** took place to give the corresponding hydrosilylation product with 1,4-*Z* selectivity (entries 18−26). In the case of (*E*)-1,3-pentadiene, it is not clear whether the 1,2- or 1,4 product is produced as it is (entry 20). However, as noted in the next section, we concluded that the reaction did

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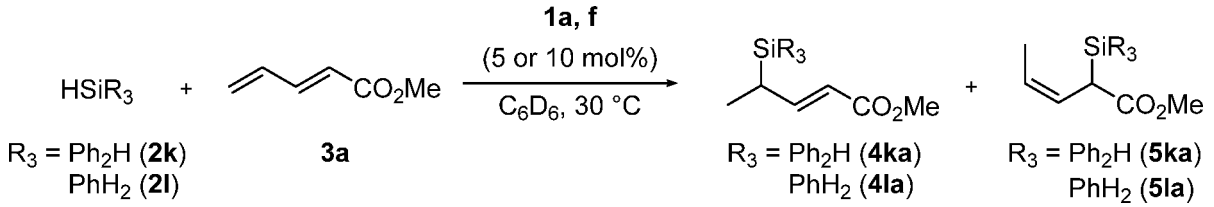
Table 5. Hydrosilylation of Methyl Penta-2,4-dienoate with Phenyl and Diphenyl Silane Catalyzed by Pd(η^2:η^2-diallyl ether)(PR_3) (R = Me, Ph)[a]

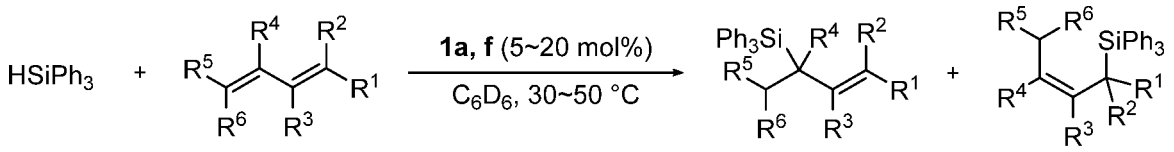


R3 = Ph2H (2k), PhH2 (2l) | 3a | R3 = Ph2H (4ka), PhH2 (4la) | R3 = Ph2H (5ka), PhH2 (5la)

					selectivity/%	
entry	Pd cat. (mol %)	silane	time/h	yield/%	(*E*)-**4**	(*Z*)-**5**
1	**1a** (5)	H_2SiPh_2	2	79	95	5
2	**1a** (5)	H_3SiPh	24	0		
3[b]	**1f** (10)	H_2SiPh_2	3	58	13	87
4[b]	**1f** (10)	H_3SiPh	24	0		

[a]Conditions: $[H_2SiR_2]_0$ = 0.10 M, [methyl penta-2,4-dienoate]$_0$ = 0.10 M, [**1a**] = 0.005 M, solvent: C_6D_6, temperature: 30 °C. [b][**1f**] = 0.010 M.

Table 6. Hydrosilylation of Conjugated Dienes Catalyzed by [Pd(η^2,η^2-diallyl ether)(PMe_3)] (**1**)[a]



2a | **3** | **4a** | **5a**

	diene										selectivity/%	
entry	R^1	R^2	R^3	R^4	R^5	R^6		cat.	time/h	yield/%	(*E*)-**4**	(*Z*)-**5**
1	CO_2Me	H	H	H	H	H	(**3a**)	**1a**	8.3	99	100	0
2	CO_2Me	H	H	H	Me	H	(**3b**)	**1a**	19	90	100	0
3[b]	CO_2Me	H	H	Me	H	H	(**3c**)	**1a**	10	82	0	100
4	CO_2Me	Me	H	H	H	H	(**3d**)	**1a**	75	94	100[c]	0
5	CO_2Et	H	Me	H	H	H	(**3e**)	**1a**	5	86	100	0
6[d,e]	CO_2Me	H	H	Me	Me	H	(**3f**)	**1a**	120	45	0	100
7[b,f]	CO_2Me	H	H	H	Me	Me	(**3g**)	**1a**	120	0		
8[g]	$C_6H_4NO_2$-4	H	H	H	H	H	(**3h**)	**1a**	2	89	100	0
9[f,g]	$C_6H_4NO_2$-4	H	H	H	H	H	(**3h**)	**1f**	24	81	17	83
10[g]	$C_6H_4CF_3$-4	H	H	H	H	H	(**3i**)	**1a**	30	60	50	50[h]
11[g,i]	$C_6H_4CF_3$-4	H	H	H	H	H	(**3i**)	**1f**	35	27	0	100
12[f,g]	Ph	H	H	H	H	H	(**3j**)	**1a**	4	99	40	60
13[f,g]	Ph	H	H	H	H	H	(**3j**)	**1f**	72	19	0	100
14[f,g]	C_6H_4OMe-4	H	H	H	H	H	(**3k**)	**1a**	4.5	97	43	57[j]
15[f,g]	C_6H_4OMe-4	H	H	H	H	H	(**3k**)	**1f**	124	80	0	100
16[f,g]	$C_6H_4NMe_2$-4	H	H	H	H	H	(**3l**)	**1a**	9	51	58	42[k]
17[f,g]	$C_6H_4NMe_2$-4	H	H	H	H	H	(**3l**)	**1f**	72	14	0	100
18[l,m]	H	H	H	H	H	H	(**3m**)	**1a**	0.6	93	9	91
19[l,m]	H	H	H	H	H	H	(**3m**)	**1f**	96	57	7	93
20[f]	Me	H	H	H	H	H	(**3n**)	**1a**	168	70	13	87
21[f,g]	Me	H	H	H	H	H	(**3n**)	**1f**	96	9	0	100
22[f,g]	H	H	Me	H	H	H	(**3o**)	**1a**	2	93	0	100
23[f,g]	H	H	Me	H	H	H	(**3o**)	**1f**	96	7	0	100
24[f,g,n]	Me	H	R	H	H	H	(**3p**)	**1a**	2	94	0	100
25[f,g,n]	Me	H	R	H	H	H	(**3p**)	**1f**	96	12	0	100
26[b,f,g]	Me	Me	H	H	H	H	(**3q**)	**1a**	18	0		

[a]Conditions: $[HSiPh_3]_0$ = 0.1 M, [conjugated diene]$_0$ = 0.1 M, [**1**] = 0.005 M, solvent: C_6D_6, temperature: 30 °C. [b]Temperature: 50 °C. [c]*E*/*Z* = 82/18. [d]$[HSiPh_3]_0$ = 0.3 M. [e]Methyl (*E*)-4-methyl-2-(triphenylsilyl)hex-4-enoate (**6af**) was formed (21%). [f]$[HSiPh_3]_0$ = 0.4 M. [g][**1**] = 0.01 M. [h]*E*/*Z* = 6/94. [i]$[HSiPh_3]_0$ = 0.2 M. [j]*E*/*Z* = 14/86. [k]*E*/*Z* = 24/76. [l]$[HSiPh_3]_0$ = 0.6 M. [m][**1**] = 0.02 M. [n]R = $CH_2CH_2CH{=}CMe_2$.

proceed in a 1,4-*Z* addition manner by use of $DSiPh_3$. No hydrosilylation took place for $CH_2{=}CHCH{=}CMe_2$ (entry 26).

Deuterium-Labeling Experiments in the Hydrosilylation of Dienes by Mono(phosphine)palladium(0) Catalyst. In order to obtain further insight into the reaction mechanism of the catalytic reaction, the reaction with $DSiPh_3$

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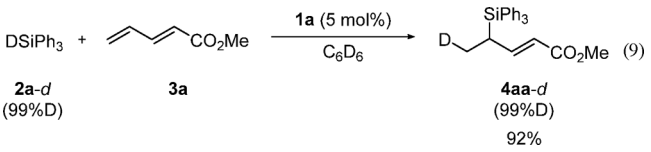
was carried out. At first, the reaction of methyl penta-2,4-dienoate with $DSiPh_3$ (99 atom % D) in the presence of a catalytic amount of Pd(η^2:η^2-diallyl ether)(PMe_3) (**1a**) was carried out. The deuterium atom was exclusively incorporated in the methyl group of the product (eq 9). The reaction



profiles using $HSiPh_3$ and $DSiPh_3$ catalyzed by **1a** are shown in Figure 3. It is worthwhile to note that this process is a zero-

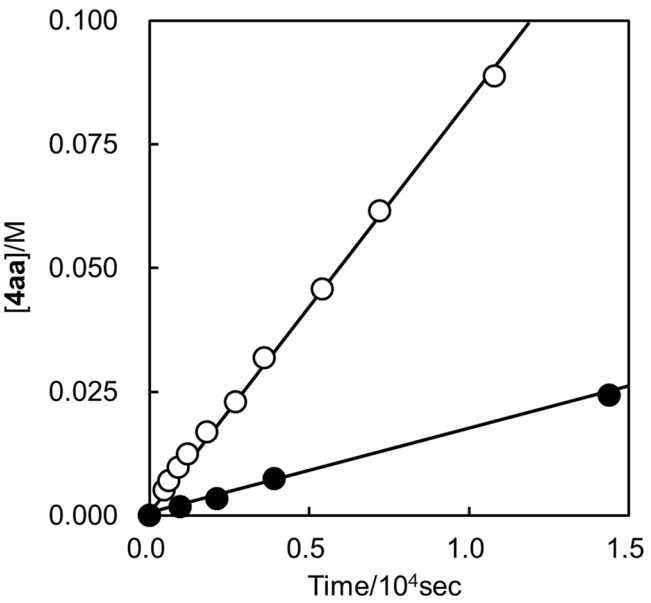
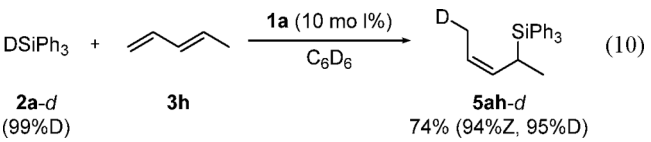


Figure 3. Time−yield curves for hydrosilylation of methyl penta-2,4-dienoate (**3a**) with H(or D)$SiPh_3$ catalyzed by Pd(η^2:η^2-$C_6H_{10}O$)(PMe_3) (**1a**): reaction with $HSiPh_3$ (100% H) (○) or $DSiPh_3$ (99% D) (●). Conditions: $[\mathbf{2a}]_0$ = 0.10 M, $[\mathbf{3a}]_0$ = 0.10 M, [**1a**] = 0.005 M, solvent: C_6D_6, temperature: 30 °C.

order reaction for both silane and diene concentrations. The rates for the reaction of $HSiPh_3$ and $DSiPh_3$ (99% D) were calculated as $(8.42 \pm 0.11) \times 10^{-6}$ M s^{-1} and $(1.87 \pm 0.03) \times 10^{-6}$ M s^{-1}, respectively. The KIE value (k_H/k_D) estimated by using these initial rates based on these independent reactions was 4.51. The KIE is primary and indicates the rate-determining step (rds) in this catalysis to involve the Si−H or Pd−H cleavage step.[17−20] No dependence of the reaction rate on substrate concentrations suggests that the rds is an intramolecular step such as the migratory insertion of the Pd−H bond to the C═C bond.

The reaction of $DSiPh_3$ with 1,3-pentadiene was also carried out (eq 10). Note that only the methyl group in the α-position



of the $SiPh_3$ fragment was deuterated and no incorporation of the D atom was observed in the methyl group in the β-position in the hydrosilylation product. This fact suggests the hydrosilylation being proceeded with 1,4-selectivity.

Possible Catalytic Cycle. The catalytic cycle for hydrosilylation was proposed as shown in Scheme 5. Initially, the reaction of conjugated diene and silane to the mono(phosphine)palladium(0) species (**A**) gave the palladium complex (**B**). In the presence of PMe_3, the active species **A** would give bis(phosphine)palladium(0), which is the resting state in this catalytic system. In the complex **B**, the terminal C═C double bond of *cisoid*-1,3-diene coordinates at the palladium center. Migratory insertion of the Pd−H bond to the terminal C═C bond in the diene takes place via addition to the terminal diene carbon to produce the η^1-allyl complex (**C**). The isotope experiment suggests this step being the turnover-limiting step. The coordination of the substituted C═C bond in **C** results in the formation of the *syn*-η^3-allyl intermediate (**D**) in which the silyl group is located in the cis of the R^3 group and reductive elimination from **D** gives the 1,4-*Z* product. The 1,2-*E* product is produced by reductive elimination from the allyl palladium complex (**E**), which formed by apparent allyl rotation of complex **D**. Three possible pathways for apparent allyl rotation in the η^3-allyl palladium complex have been proposed, *i.e.*, (1) dissociative mechanism, (2) associative mechanism, and (3) sequential η^3-to-η^1 isomerization/C−Pd bond rotation/η^1-to-η^3 isomerization.[21] Probably, a compact and electron-donating phosphine, such as PMe_3, PEt_3, and a compact and weaker electron-withdrawing phosphine, such as $P(OMe)_3$ (cone angle < 140°), can promote allyl rotation by the associative mechanism via formation of an 18e species. Therefore, in these cases, allyl rotation smoothly proceeds to give complex **E**, following reductive elimination to give the 1,2-*E* product. On the other hand, a strong electron-withdrawing phosphorus ligand such as $P(C_6H_4F\text{-}4)_3$ promotes reductive elimination from **D**. As is well-known, sterically bulky phosphines such as $P(CH_2Ph)_3$ and PCy_3 inhibit the allylic rotation and the electron-withdrawing phosphine promotes reductive elimination. Therefore, the hydrosilylation product was formed with 1,4-*Z*-selectivity or lower 1,2-*E*-selectivity.

SUMMARY

There is a long-standing discussion regarding regio- and stereochemistry of hydrosilylation of conjugated dienes. The present study shows isolated mono(trimethylphosphine)-palladium(0) complexes, Pd(η^2:η^2-$C_6H_{10}O$)(PR_3) (**1**), catalyzed hydrosilylation of electron-deficient conjugated dienes with $HSiPh_3$. The hydrosilylation of methyl penta-2,4-dienoate with $HSiPh_3$ by 5 mol % of Pd(η^2:η^2-$C_6H_{10}O$)(PR_3) (R = Me (**1a**), Et (**1b**), OEt (**1d**), O^{i}Pr (**1e**)) proceeds to give the 1,2-*E* product in quantitative yield with perfect Markovnikov selectivity. In contrast, Pd(η^2:η^2-$C_6H_{10}O$)(PR_3) (R = Ph (**1f**), OPh (**1g**)) mainly produced the 1,4-*Z* product (1,2-*E*/1,4-*Z* = 3/7). The regioselectivity of the hydrosilylation of methyl 2,4-pentadienoate catalyzed by the mono(phosphine)-palladium(0) complex is also controlled by the silane. The reaction is proceeding by a Chalk−Harrod mechanism with the reductive elimination of an (η^3-allyl)(silyl)palladium(II). The migratory insertion to the terminal C═C bond in the diene, followed by the coordination of the substituted C═C bond, takes place to produce the η^3-allyl complex. A strong electron-withdrawing phosphine such as $P(OPh)_3$ destabilizes the Pd(II) species and promotes direct reductive elimination to give the 1,4-*Z* product. On the other hand, a compact and

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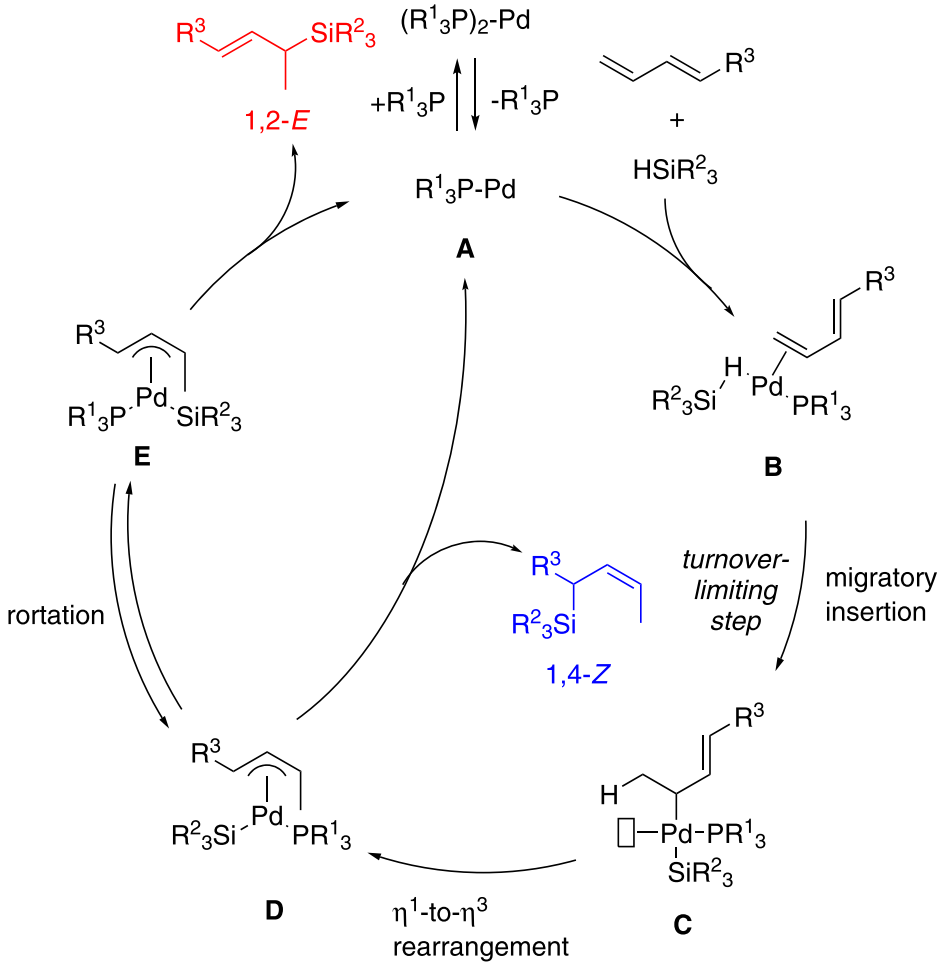
Scheme 5. A Possible Mechanism



electron-donating phosphine, such as PMe_3, PEt_3, and a compact and weaker electron-withdrawing phosphine, such as $P(OMe)_3$, promotes allyl rotation smoothly to give the regioisomeric η^3-allyl complex, following reductive elimination to give the 1,2-*E* product.

EXPERIMENTAL SECTION

All procedures described in this paper were carried out under a nitrogen or argon atmosphere by use of Schlenk and vacuum line techniques. Benzene-d_6 was dried over sodium wire and purified by vacuum distillation prior to use. $HSiPh_3$, $HSiPh_2Me$, $HSiPhMe_2$, $HSiBnMe_2$, $HSi(OEt)_3$, $HSiEt_3$, diallyl ether, and dienes **3a**, **3b**, **3m**, **3n**, **3o**, and **3p** were purchased from TCI or Aldrich. The mono(phosphine)palladium(0) complexes Pd{η^2:η^2-(CH_2=$CHCH_2$)$_2$O}(PR_3) (R = Me (**1a**), Et (**1b**), Cy (**1c**), OEt (**1d**), O^{i}Pr (**1e**), Ph (**1f**), OPh (**1g**)),[20,22] $DSiPh_3$ (**2a**-*d*),[23] $HSiAr_3$ (Ar = C_6H_4OMe-4 (**2b**), C_6H_4Me-4 (**2c**), C_6H_4Cl-4 (**2d**), $C_6H_4CF_3$-4 (**2e**)),[24] and dienes **3c**,[25] **3d**,[26] **3e**,[25] **3f**,[27] **3g**,[25] **3h**,[28] **3i**, **3j**,[29] **3k**,[30] **3l**,[29] and **3q**[31] were prepared by literature procedures with modification. ^{1}H, ^{2}H, and ^{13}C{^{1}H} NMR spectra were measured on a 400 MHz (for ^{1}H) NMR spectrometer. GC and GC-MS were performed on Shimadzu GC-2014 (FID) and Shimadzu GCMS-2010 (EI) instruments, respectively, equipped with a TC-1 column (0.25 mm i.d. × 30 m). HRMS (APCI) analysis was performed on a Bruker Daltonics micrOTOF-QII instrument.

Hydrosilylation of Electron-Deficient Conjugated Dienes Catalyzed by Mono(phosphine)palladium(0) Complexes. As a typical procedure, the hydrosilylation of methyl penta-2,4-dienoate (**2a**) with triphenylsilane (**3a**) is given. (a) In an NMR tube containing 355 μL of C_6D_6 were placed 205 μL of a 0.296 M C_6D_6 solution of $HSiPh_3$ (**2a**) (0.061 mmol), methyl penta-2,4-dienoate (**3a**) (0.067 mmol), and hexamethyldisiloxane (0.0031 mmol). After the addition of a C_6D_6 solution of Pd{η^2:η^2-(CH_2=$CHCH_2$)$_2$O}(PMe_3) (**1a**; 0.0668 M, 45 μL, 0.0030 mmol) to form a 0.1 M solution of $HSiPh_3$ (**2a**) and methyl penta-2,4-dienoate (**3a**), the reaction was monitored by ^{1}H NMR at 30 °C, and the yields were periodically estimated by ^{1}H NMR. The final yield of methyl (*E*)-4-(triphenylsilyl)pent-2-enoate (**4aa**) was 99%. (b) In an NMR tube containing 20.2 mg of $HSiPh_3$ (**2a**) (0.0776 mmol) were placed 400 μL of C_6D_6 and 10.0 μL of methyl penta-2,4-dienoate (**3a**) (0.0866 mmol). To this was added hexamethyldisiloxane (0.4 μL, 0.0006 mmol) as an internal standard. After the addition of a C_6D_6 solution of Pd{η^2:η^2-(CH_2=$CHCH_2$)$_2$O}{P(OPh)$_3$} (**1g**; 0.0345 M, 200 μL, 0.0034 mmol) to form a 0.1 M solution of methyl penta-2,4-dienoate and $HSiPh_3$, the reaction was monitored by ^{1}H NMR at 30 °C, and the yields were periodically estimated by ^{1}H NMR. The final yield of methyl (*E*)-4-(triphenylsilyl)pent-2-enoate (**4aa**) and methyl (*Z*)-2-(triphenylsilyl)pent-3-enoate (**5aa**) were 15% and 42%, respectively. The products were isolated by PTLC (hexane/Et_2O = 5/1) as a colorless powder. **Methyl (*E*)-4-(triphenylsilyl)pent-2-enoate (4aa)**: ^{1}H NMR (C_6D_6, rt): δ 1.15 (d, J_{HH} = 7.0 Hz, 3H, CH_3), 2.55 (dqd, J_{HH} = 7.3, 7.0, 1.6 Hz, 1H, $CH_3CH(SiPh_3)$), 3.35 (s, 3H, CO_2CH_3), 5.82 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.09−7.19 (m, 9H, *m,p-Ph*), 7.54−7.59 (m, 6H, *o-Ph*), 7.59 (dd, J_{HH} = 15.6, 7.3 Hz, 1H, CH=$CHCO_2CH_3$). ^{13}C{^{1}H} NMR (C_6D_6, rt): 13.81 (CH_3), 25.91 ($CHSi$), 50.81 (CO_2CH_3), 118.78 (CH=$CHCO_2CH_3$), 130.02 (aromatic *C*H), 133.24 (ipso-*C*), 136.34 (aromatic *C*H), 152.45 (CH=$CHCO_2CH_3$), 166.68 (CO_2CH_3). ^{1}H NMR ($CDCl_3$, rt): δ 1.29 (d, J_{HH} = 6.9 Hz, 3H, CH_3), 2.82 (dqd, J_{HH} = 7.3, 6.9, 1.7 Hz, 1H, $CH_3CH(SiPh_3)$), 3.65 (s, 3H, CO_2CH_3), 5.61 (dd, J_{HH} = 15.6,

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1.7 Hz, 1H, CH=C*H*CO_2CH_3), 7.30 (dd, J_{HH} = 15.6, 7.3 Hz, 1H, C*H*=$CHCO_2CH_3$), 7.33−7.45 (m, 9H, *m,p-Ph*), 7.48−7.58 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.71 (CH_3), 25.91 (*C*HSi), 51.28 (CO_2CH_3), 118.04 (CH=*C*HCO_2CH_3), 127.97 (*m-C* of $SiPh_3$), 129.80 (*p-C* of $SiPh_3$), 132.73 (*ipso*-C of $SiPh_3$), 135.99 (o-*C* of $SiPh_3$), 152.78 (CH=*C*HCO_2CH_3), 167.23 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{24}H_{24}O_2Si + H^+$: 373.1618 $[M + H]^+$; found: 373.1605. **Methyl (*Z*)-2-(triphenylsilyl)pent-3-enoate (5aa)**: ^1H NMR (C_6D_6, rt): δ 1.25 (dd, J_{HH} = 6.8, 1.8 Hz, 3H, C*H*$_3$), 3.10 (s, 3H, CO_2CH_3), 4.22 (d, J_{HH} = 11.3 Hz, 1H, C*H*($SiPh_3$)(CO_2CH_3)), 5.34 (dq, J_{HH} = 10.7, 6.8 Hz, 1H, CH=C*H*CH_3), 6.18 (tq, J_{HH} = 11.0, 1.8 Hz, 1H, C*H*=$CHCH_3$), 7.10−7.22 (m, 9H, *m,p-Ph*), 7.72−7.85 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 13.01 (CH_3), 37.65 (*C*HSi), 50.81 (CO_2CH_3), 124.74 (CH_3*C*H=CH), 125.48 (CH_3CH=*C*H), 128.34 (*p-C* of $SiPh_3$), 130.15 (*m-C* of $SiPh_3$), 133.11 (*ipso*-C of $SiPh_3$), 136.85 (*o-C* of $SiPh_3$), 172.88 (CO_2CH_3). ^1H NMR ($CDCl_3$, rt): δ 1.37 (dd, J_{HH} = 6.9, 1.9 Hz, 3H, C*H*$_3$), 3.32 (s, 3H, CO_2CH_3), 4.02 (dd, J_{HH} = 11.2, 0.8 Hz, 1H, C*H*($SiPh_3$)-(CO_2CH_3)), 5.45 (dqd, J_{HH} = 10.7, 6.8, 0.8 Hz, 1H, CH=C*H*CH_3), 5.78 (tq, J_{HH} = 11.1, 1.8 Hz, 1H, C*H*=$CHCH_3$), 7.35 (m, 6H, *m*-Ph), 7.42 (m, 3H, *p*-Ph), 7.59 (m, 6H, *o*-Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.00 (CH_3), 37.06 (*C*($SiPh_3$)(CO_2CH_3)), 51.20 (CO_2CH_3), 124.44 (CH_3CH=CH), 124.92 (CH_3CH=*C*H), 127.74 (*m-C* of $SiPh_3$), 129.88 (*p*-C of $SiPh_3$), 132.39 (*ipso-C* of $SiPh_3$), 136.31 (*o-C* of $SiPh_3$), 173.33 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{24}H_{24}O_2Si + H^+$: 373.1618 $[M + H]^+$; found: 373.1620.

*Methyl (E)-4-(Tris(4-methoxyphenyl)silyl)pent-2-enoate (**4ba**).* Yield: 82% (NMR), 71% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.21 (d, J_{HH} = 6.9 Hz, 3H, C*H*$_3$), 2.56 (dtd, J_{HH} = 7.2, 6.9, 1.4 Hz, 1H, C*H*Si($C_6H_4OCH_3$-4)$_3$), 3.23 (s, 9H, $C_6H_4OCH_3$-4), 3.32 (s, 3H, CO_2CH_3), 5.84 (dd, J_{HH} = 15.6, 1.4 Hz, 1H, CH=C*H*CO_2CH_3), 6.76 (m, 6H, $C_6H_4OCH_3$-4), 7.52 (m, 6H, $C_6H_4OCH_3$-4), 7.64 (dd, J_{HH} = 15.6, 7.2 Hz, 1H, C*H*=$CHCO_2CH_3$). ^1H NMR ($CDCl_3$, rt): δ 1.26 (d, J_{HH} = 6.9 Hz, 3H, C*H*$_3$CHSi(C_6H_4O-4)$_3$), 2.71 (dtd, J_{HH} = 7.2, 6.9, 1.6 Hz, 1H, C*H*Si($C_6H_4OCH_3$-4)$_3$), 3.66 (s, 3H, CO_2CH_3), 3.80 (s, 9H, $C_6H_4OCH_3$-4), 5.59 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=C*H*CO_2CH_3), 6.90 (m, 6H, $C_6H_4OCH_3$-4), 7.30 (dd, J_{HH} = 15.6, 7.2 Hz, 1H, C*H*=$CHCO_2CH_3$), 7.42 (m, 6H, $C_6H_4OCH_3$-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.69 (CH_3CHSi), 26.63 (*C*HSi), 51.25 (CO_2CH_3), 55.00 ($C_6H_4OCH_3$-4), 113.67 (3-*C* of $C_6H_4OCH_3$-4), 117.55 (CH=*C*HCO_2CH_3), 124.12 (1-*C* of $C_6H_4OCH_3$-4), 137.44 (2-*C* of $C_6H_4OCH_3$-4), 153.48 (CH=CHCO_2CH_3), 160.77 (4-*C* of $C_6H_4OCH_3$-4), 167.34 (CO_2CH_3). This was characterized by spectroscopic methods. HRMS (APCI): *m/z* calcd for $C_{27}H_{30}O_5Si + H^+$: 463.1935 $[M + H]^+$; found: 463.1924.

*Methyl (Z)-2-(Tris(4-methoxyphenyl)silyl)pent-3-enoate (**5ba**).* Yield: 14% (NMR), 4% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.35 (dd, J_{HH} = 6.6, 1.7 Hz, 3H, C*H*$_3$), 3.19 (s, 3H, CO_2CH_3), 3.28 (s, 9H, $C_6H_4OCH_3$-4), 4.29 (d, J_{HH} = 11.5 Hz, 1H, C*H*(Si($C_6H_4OCH_3$-4)$_3$)(CO_2CH_3)), 5.43 (dq, J_{HH} = 11.2, 6.6 Hz, 1H, CH=C*H*CH_3), 6.29 (tq, J_{HH} = 11.2, 1.7 Hz, 1H, C*H*=$CHCH_3$), 6.86 (m, 6H, $C_6H_4OCH_3$-4), 7.81 (m, 6H, $C_6H_4OCH_3$-4). ^1H NMR ($CDCl_3$. rt): δ 1.34 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, C*H*$_3$), 3.33 (s, 3H, CO_2CH_3), 3.80 (s, 9H, $C_6H_4OCH_3$-4), 3.93 (dd, J_{HH} = 11.3, 0.7 Hz, 1H, C*H*(Si($C_6H_4OCH_3$-4)$_3$)(CO_2CH_3)), 5.42 (dqd, J_{HH} = 10.8, 6.9, 0.7 Hz, 1H, CH=C*H*CH_3), 5.75 (ddq, J_{HH} = 11.3, 10.8, 1.8 Hz, 1H, C*H*=$CHCH_3$), 6.88 (m, 6H, 3-C*H* of $C_6H_4OCH_3$-4), 7.49 (m, 6H, 2-C*H* of $C_6H_4OCH_3$-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.05 (CH_3), 37.54 (*C*HSi)), 51.19 (CO_2CH_3), 54.99 ($C_6H_4OCH_3$-4), 113.41 (3-*C* of $C_6H_4OCH_3$-4), 123.77 (1-*C* of $C_6H_4OCH_3$-4), 124.38 (CH_3CH=CH), 124.81 (CH_3CH=CH), 137.77 (2-*C* of $C_6H_4OCH_3$-4), 160.87 (4-*C* of $C_6H_4OCH_3$-4), 173.59 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{27}H_{30}O_5Si + H^+$: 463.1935 $[M + H]^+$; found: 463.1922.

*Methyl (E)-4-(Tri-p-tolylsilyl)pent-2-enoate (**4ca**).* Yield: 100% (NMR), 78% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.25 (d, J_{HH} = 6.9 Hz, 3H, C*H*$_3$), 2.76 (dtd, J_{HH} = 7.2, 6.9, 1.6 Hz, 1H, C*H*Si($C_6H_4CH_3$-4)$_3$), 2.34 (s, 9H, $C_6H_4CH_3$-4), 3.36 (s, 3H, CO_2CH_3), 5.59 (dd, J_{HH} = 15.7, 1.6 Hz, 1H, CH=C*H*CO_2CH_3), 7.03 (m, 6H, $C_6H_4CH_3$-4), 7.59 (m, 1H, C*H*=$CHCO_2CH_3$), 7.61 (m, 6H, $C_6H_4CH_3$-4). ^1H NMR ($CDCl_3$, rt): δ 1.26 (d, J_{HH} = 6.9 Hz, 3H, C*H*$_3$), 2.76 (dtd, J_{HH} = 7.2, 6.9, 1.7 Hz, 1H, C*H*Si($C_6H_4CH_3$-4)$_3$), 2.34 (s, 3H, $C_6H_4CH_3$-4), 3.65 (s, 3H, CO_2CH_3), 5.59 (dd, J_{HH} = 15.8, 1.7 Hz, 1H, CH=C*H*CO_2CH_3), 7.16 (m, 6H, $C_6H_4CH_3$-4), 7.29 (dd, J_{HH} = 15.8, 7.2 Hz, 1H, C*H*=$CHCO_2CH_3$), 7.40 (m, 6H, $C_6H_4CH_3$-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): 13.70 (CH_3CHSi), 21.53 ($C_6H_4CH_3$-4), 26.19 (*C*HSi), 51.24 (CO_2CH_3), 117.70 (CH=CHCO_2CH_3), 128.76 (3-*C* of $C_6H_4CH_3$-4), 129.47 (1-*C* of $C_6H_4CH_3$-4), 136.00 (2-*C* of $C_6H_4CH_3$-4), 139.61 (4-*C* of $C_6H_4CH_3$-4), 153.31 (CH=CHCO_2CH_3), 167.31 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{27}H_{30}O_2Si + H^+$: 415.2088 $[M + H]^+$; found: 415.2077.

*Methyl (Z)-2-(Tri-p-tolylsilyl)pent-3-enoate (**5ca**).* Yield: 28% (NMR), 28% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.33 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, C*H*$_3$), 2.09 (s, 9H, $C_6H_4CH_3$-4), 3.18 (s, 3H, CO_2CH_3), 4.27 (dd, J_{HH} = 11.3, 0.8 Hz, 1H, C*H*Si($C_6H_4CH_3$-4)$_3$(CO_2CH_3)), 5.38 (dqd, J_{HH} = 10.7, 6.9, 0.8 Hz, 1H, CH=C*H*CH_3), 5.75 (ddq, J_{HH} = 11.3, 10.7, 1.8 Hz, 1H, C*H*=$CHCH_3$), 7.03 (m, 6H, $C_6H_4CH_3$-4), 7.60 (m, 6H, $C_6H_4CH_3$-4). ^1H NMR ($CDCl_3$, rt): δ 1.37 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, C*H*$_3$), 2.35 (s, 3H, $C_6H_4CH_3$-4), 3.33 (s, 3H, CO_2CH_3), 3.97 (d, J_{HH} = 11.6 Hz, 1H, C*H*Si($C_6H_4CH_3$-4)$_3$(CO_2CH_3)), 5.42 (dq, J_{HH} = 10.8, 6.9 Hz, 1H, CH=C*H*CH_3), 5.75 (ddq, J_{HH} = 11.6, 10.8, 1.8 Hz, 1H, C*H*=CHCH_3), 7.15 (m, 6H, $C_6H_4CH_3$-4), 7.462 (m, 6H, $C_6H_4CH_3$-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.06 (CH_3), 21.56 ($C_6H_4CH_3$-4), 37.17 (CHSi)), 51.16 (CO_2CH_3), 123.53 (CH_3CH=CH), 124.71 (CH_3CH=CH), 128.51 (3-*C* of $C_6H_4CH_3$-4), 129.08 (1-C of $C_6H_4CH_3$-4), 136.27 (2-*C* of $C_6H_4CH_3$-4), 139.67 (4-*C* of $C_6H_4CH_3$-4), 173.49 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{27}H_{30}O_2Si + H^+$: 415.2067 $[M + H]^+$; found: 415.2077.

*Methyl (E)-4-(Tris(4-chlorophenyl)silyl)pent-2-enoate (**4da**).* Yield: 96% (NMR), 75% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 0.97 (d, J_{HH} = 7.0 Hz, 3H, C*H*$_3$CHSi(C_6H_4Cl-4)$_3$), 2.75 (dtd, J_{HH} = 7.5, 7.0, 1.7 Hz, 1H, C*H*Si(C_6H_4Cl-4)$_3$), 3.37 (s, 3H, CO_2CH_3), 5.77 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=C*H*CO_2CH_3), 7.18 (dd, J_{HH} = 15.6, 7.5 Hz, 1H, C*H*=$CHCO_2CH_3$), 7.10−7.13 (m, 12H, C_6H_4Cl-4). ^1H NMR ($CDCl_3$, rt): δ 1.26 (d, J_{HH} = 7.0 Hz, 3H, C*H*$_3$CHSi(C_6H_4Cl-4)$_3$), 2.75 (dtd, J_{HH} = 7.3, 7.0, 1.7 Hz, 1H, C*H*Si(C_6H_4Cl-4)$_3$), 3.67 (s, 3H, CO_2CH_3), 5.61 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=C*H*CO_2CH_3), 7.18 (dd, J_{HH} = 15.6, 7.3 Hz, 1H, C*H*=CHCO_2CH_3), 7.33−7.41 (m, 12H, C_6H_4Cl-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): 13.62 (CH_3CHSi), 25.43 (*C*HSi), 51.44 (CO_2CH_3), 118.80 (CH=CHCO_2CH_3), 128.57 (3-*C* of C_6H_4Cl-4), 130.15 (4-*C* of C_6H_4Cl-4), 136.79 (2-*C* of C_6H_4Cl-4), 137.11 (*ipso*-C of C_6H_4Cl-4), 151.36 (CH=CHCO_2CH_3), 166.95 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{24}H_{21}Cl_3O_2Si + H^+$: 475.0449 $[M + H]^+$; found: 475.0428.

*Methyl (Z)-2-(Tris(4-chlorophenyl)silyl)pent-3-enoate (**5da**).* Yield: 62% (NMR), 62% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.16 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, C*H*$_3$), 3.04 (s, 3H, CO_2CH_3), 3.96 (dd, J_{HH} = 11.0, 0.8 Hz, 1H, C*H*(Si(C_6H_4Cl-4)$_3$)(CO_2CH_3)), 5.34 (dqd, J_{HH} = 11.0, 6.9, 0.8 Hz, 1H, CH=C*H*CH_3), 5.85 (tq, J_{HH} = 11.0, 1.8 Hz, 1H, C*H*=$CHCH_3$), 7.15 (m, 6H, C_6H_4Cl-4), 7.38 (m, 6H, C_6H_4Cl-4). ^1H NMR ($CDCl_3$, rt): δ 1.38 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, C*H*$_3$), 3.38 (s, 3H, CO_2CH_3), 3.96 (d, J_{HH} = 11.2 Hz, 1H, C*H*(Si(C_6H_4Cl-4)$_3$)(CO_2CH_3)), 5.49 (dq, J_{HH} = 10.8, 6.9 Hz, 1H, CH=C*H*CH_3), 5.70 (ddq, J_{HH} = 11.2, 10.8, 1.8 Hz, 1H, C*H*=$CHCH_3$), 7.36 (m, 6H, C_6H_4Cl-4), 7.47 (m, 6H, C_6H_4Cl-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.12 (CH_3), 36.61 (*C*HSi)), 51.50 (CO_2CH_3), 123.57 (CH_3CH=*C*H), 125.72 (CH_3*C*H=CH), 128.31 (2-*C* of C_6H_4Cl-4), 129.82 (1-*C* of C_6H_4Cl-4), 136.90 (4-*C* of C_6H_4Cl-4), 137.43 (3-*C* of C_6H_4Cl-4), 172.82 (CO_2CH_3). HRMS (APCI): *m/z* calcd for $C_{24}H_{21}Cl_3O_2Si + H^+$: 475.0449 $[M + H]^+$; found: 475.0444.

*Methyl (E)-4-(Tris(4-(trifluoromethyl)phenyl)silyl)pent-2-enoate (**4ea**).* Yield: 71% (NMR), 46% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 0.94 (d, J_{HH} = 7.1 Hz, 3H, C*H*$_3$CHSi($C_6H_4CF_3$-4)$_3$), 2.34 (dtd, J_{HH} = 7.5, 7.1, 1.6 Hz, 1H, C*H*Si($C_6H_4CF_3$-4)$_3$), 3.37 (s, 3H, CO_2CH_3), 5.72 (dd, J_{HH} = 15.6, 1.6 Hz, 1H, CH=

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$CHCO_2CH_3$), 7.23 (m, 6H, $C_6H_4CF_3$-4), 7.28 (dd, J_{HH} = 15.6, 7.5 Hz, 1H, CH=$CHCO_2CH_3$), 7.34 (m, 6H, $C_6H_4CF_3$-4). ^{1}H NMR ($CDCl_3$, rt): δ 1.31 (d, J_{HH} = 7.0 Hz, 3H, $CH_3CHSi(C_6H_4CF_3\text{-}4)_3$), 2.891 (dtd, J_{HH} = 7.3, 7.0, 1.7 Hz, 1H, $CHSi(C_6H_4CF_3\text{-}4)_3$), 3.67 (s, 3H, CO_2CH_3), 5.67 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.19 (dd, J_{HH} = 15.6, 7.3 Hz, 1H, CH=$CHCO_2CH_3$), 7.62 (m, 6H, $C_6H_4CF_3$-4), 7.65 (m, 6H, $C_6H_4CF_3$-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.61 (CH_3CHSi), 24.83 ($CHSi$), 51.51 (CO_2CH_3), 119.50 (CH=$CHCO_2CH_3$), 123.81 (q, J_{CF} = 272.5 Hz, CF_3), 124.95 (q, J_{CF} = 3.8 Hz, 3-C of $C_6H_4CF_3$-4), 132.41 (q, J_{CF} = 32.6 Hz, 4-C of $C_6H_4CF_3$-4), 136.04 (1-C of $C_6H_4CF_3$-4), 136.12 (2-C of $C_6H_4CF_3$-4), 150.31 (CH=$CHCO_2CH_3$), 166.77 (CO_2CH_3). $^{19}F\{^1H\}$ NMR ($CDCl_3$, rt): δ −63.06. HRMS (APCI): m/z calcd for $C_{27}H_{21}F_9O_2Si$ + H^+: 577.1240 $[M + H]^+$; found: 577.1221.

Methyl (Z)-2-(Tris(4-(trifluoromethyl)phenyl)silyl)pent-3-enoate (***5ea***). Yield: 97% (NMR), 35% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ 1.23 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, CH_3), 3.01 (s, 3H, CO_2CH_3), 3.98 (dd, J_{HH} = 11.2, 0.8 Hz, 1H, $CH(Si(C_6H_4CF_3\text{-}4)_3)(CO_2CH_3)$), 5.34 (dqd, J_{HH} = 10.8, 6.9, 0.8 Hz, 1H, CH=$CHCH_3$), 5.85 (ddq, J_{HH} = 11.2, 10.8, 1.8 Hz, 1H, CH=$CHCH_3$), 7.31 (m, 6H, $C_6H_4CF_3$-4), 7.47 (m, 6H, $C_6H_4CF_3$-4). ^{1}H NMR ($CDCl_3$, rt): δ 1.40 (dd, J_{HH} = 6.8, 1.7 Hz, 3H, CH_3), 3.39 (s, 3H, CO_2CH_3), 4.06 (dd, J_{HH} = 11.2, 0.8 Hz, 1H, $CH(Si(C_6H_4CF_3\text{-}4)_3)(CO_2CH_3)$), 5.55 (dqd, J_{HH} = 10.9, 6.8, 0.8 Hz, 1H, CH=$CHCH_3$), 5.78 (tq, J_{HH} = 10.9, 1.7 Hz, 1H, CH=$CHCH_3$), 7.64 (m, 6H, $C_6H_4CF_3$-4), 7.69 (m, 6H, $C_6H_4CF_3$-4). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.15 (CH_3), 36.16 ($CHSi$)), 51.66 (CO_2CH_3), 123.86 (q, J_{CF} = 272.2 Hz, CF_3), 124.67 (q, J_{CF} = 3.8 Hz, 3-C of $C_6H_4CF_3$-4), 122.95 (CH_3CH=CH), 126.53 (CH_3CH=CH), 132.45 (q, J_{CF} = 32.6 Hz, 4-C of $C_6H_4CF_3$-4), 135.74 (CSi), 136.448 (2-C of $C_6H_4CF_3$-4), 172.45 (CO_2CH_3). ^{19}F NMR ($CDCl_3$, rt): δ −63.06. HRMS (APCI): m/z calcd for $C_{27}H_{21}F_9O_2Si$ + H^+: 577.1240 $[M + H]^+$; found: 577.1238.

Methyl (E)-4-(Methyldiphenylsilyl)pent-2-enoate (***4fa***). Yield: 78% (NMR), 83% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 0.29 (s, 3H, $SiCH_3$), 0.96 (d, J_{HH} = 7.0 Hz, 3H, $CH_3CHSiCH_3Ph_2$), 2.19 (dqd, J_{HH} = 7.5, 7.0, 1.6 Hz, 1H, $CHSiCH_3Ph_2$), 3.40 (s, 3H, CO_2CH_3), 5.78 (dd, J_{HH} = 15.6, 1.6 Hz, 1H, CH=$CHCO_2CH_3$), 7.10−7.19 (m, 6H, *m,p-Ph*), 7.39−7.45 (m, 4H, *o-Ph*), 7.410 (dd, J_{HH} = 15.6, 7.5 Hz, 1H, CH=$CHCO_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ −6.40 (CH_3), 13.11 (CH_3), 26.49 ($CHSi$), 50.80 (CO_2CH_3), 117.98 (CH=$CHCO_2CH_3$), 128.22 (m-C) (overlapped with carbon of C_6D_6), 129.79 (p-C of Ph), 129.84 (p-C of Ph), 134.77 (*ipso*-C of Ph), 134.85 (*ipso*-C of Ph), 135.08 (o-C of Ph), 135.10 (o-C of Ph), 152.27 (CH=$CHCO_2CH_3$), 166.77 (CO_2CH_3). ^{1}H NMR ($CDCl_3$, rt): δ 0.55 (s, 3H, $SiCH_3$), 1.17 (d, J_{HH} = 6.9 Hz, 3H, $CH_3CHSiCH_3Ph_2$), 2.51 (dqd, J_{HH} = 7.3, 6.9, 1.7 Hz, 1H, $CHSiPh_3$), 3.68 (s, 3H, CO_2CH_3), 5.62 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.19 (dd, J_{HH} = 15.6, 7.3 Hz, 1H, = $CHCO_2CH_3$), 7.32−7.43 (m, 6H, *m,p-Ph*), 7.48−7.53 (m, 4H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ −6.44 ($SiCH_3$), 13.08 (CH_3CHSi), 26.55 ($CHSi$), 51.25 (CO_2CH_3), 117.22 (CH=$CHCO_2CH_3$), 127.93 (m-C of Ph), 129.62 (p-C of Ph), 134.45 (o-C of Ph), 134.74 (*ipso*-C of Ph), 153.15 (CH=$CHCO_2CH_3$), 167.31 (CO_2CH_3). This compound was characterized by spectroscopic methods.

Methyl (Z)-2-(Methyldiphenylsilyl)pent-3-enoate (***5fa***). Yield: 14% (NMR). ^{1}H NMR (C_6D_6, rt): δ 0.66 (s, 3H, $SiCH_3$), 1.14 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, CH_3CH=), 3.16 (s, 3H, CO_2CH_3), 3.88 (dd, J_{HH} = 11.1, 0.9 Hz, 1H, $CH(SiPh_2CH_3)(CO_2CH_3)$), 5.30 (dqd, J_{HH} = 10.9, 6.9, 0.9 Hz, 1H, CH_3CH=), 6.06 (ddq, J_{HH} = 11.1, 10.9, 1.8 Hz, 1H, CH=$CHCH_3$), 7.10−7.19 (m, 6H, *m,p-Ph*), 7.42−7.47 (m, 4H, *o-Ph*). ^{1}H NMR ($CDCl_3$, rt): δ 0.66 (s, 3H, $SiCH_3$), 1.27 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, CH_3CH=), 3.39 (s, 3H, CO_2CH_3), 3.88 (dd, J_{HH} = 11.0, 0.8 Hz, 1H, $CH(SiPh_2CH_3)(CO_2CH_3)$), 5.39 (dqd, J_{HH} = 11.0, 6.9, 0.8 Hz, 1H, CH_3CH=), 5.71 (tq, J_{HH} = 11.0, 1.8 Hz, 1H, CH=$CHCH_3$), 7.30−7.41 (m, 6H, *m,p-Ph*), 7.57 (m, 4H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ −5.32 (CH_3Si), 12.97 (CH_3), 37.63 ($CHSiPh_3$), 51.19 (CO_2CH_3), 123.79 (CH_3CH=CH), 124.09 (CH_3CH=CH), 127.73 (m-C of Ph), 129.71 (p-C of Ph), 134.91 (*ipso*-C of Ph), 134.95 (o-C of Ph), 173.35 (CO_2CH_3). This was characterized by spectroscopic methods.

Methyl (E)-4-(Dimethyl(phenyl)silyl)pent-2-enoate (***4ga***). Yield: 52% (NMR), 43% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 0.08 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$), 0.86 (d, J_{HH} = 6.9 Hz, 3H, $CH_3CHSi(CH_3)_2Ph$), 1.72 (dqd, J_{HH} = 7.7, 6.9, 1.7 Hz, 1H, $CHSi(CH_3)_2Ph$), 3.45 (s, 3H, CO_2CH_3), 5.76 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.13−7.19 (m, 3H, *m,p-Ph*), 7.30−7.34 (m, 2H, *o-Ph*), 7.32 (dd, J_{HH} = 15.6, 7.7 Hz, 1H, CH=$CHCO_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ −5.64 (CH_3), −4.90 (CH_3), 12.72 (CH_3CHSi), 28.01 ($CHSi$), 50.81 (CO_2CH_3), 117.27 (CH=$CHCO_2CH_3$), 128.09 (p-C of Ph), 129.60 (m-C of Ph), 134.15 (o-C of Ph), 136.45 (*ipso*-C of Ph), 153.23 (CH=$CHCO_2CH_3$), 166.89 (CO_2CH_3). ^{1}H NMR ($CDCl_3$, rt): δ 0.308 (s, 3H, $SiCH_3$), 0.312 (s, 3H, $SiCH_3$), 1.10 (d, J_{HH} = 6.9 Hz, 3H, $CH_3CHSi(CH_3)_2Ph$), 2.09 (dqd, J_{HH} = 7.5, 6.9, 1.7 Hz, 1H, $CHSi(CH_3)_2Ph$), 3.71 (s, 3H, CO_2CH_3), 5.60 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.14 (dd, J_{HH} = 15.7, 7.5 Hz, 1H, =$CHCO_2CH_3$), 7.33−7.40 (m, 3H, *m,p-Ph*), 7.45−7.50 (m, 2H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ −5.41 ($SiCH_3$), −4.79 ($SiCH_3$), 12.75 (CH_3CHSi), 28.13 ($CHSi$), 51.24 (CO_2CH_3), 116.50 (CH=$CHCO_2CH_3$), 127.83 (m-C of Ph), 129.39 (p-C of Ph), 133.86 (o-C of Ph), 136.32 (*ipso*-C of Ph), 153.69 (CH=$CHCO_2CH_3$), 167.45 (CO_2CH_3). HRMS (APCI): m/z calcd for $C_{14}H_{20}O_2Si$ + H^+: 249.1305 $(M + H)^+$; found: 249.1302.

Methyl (Z)-2-(Dimethyl(phenyl)silyl)pent-3-enoate (***5ga***). Yield: 18% (NMR). ^{1}H NMR ($CDCl_3$, rt): δ 0.37 (s, 6H, $SiCH_3$), 1.31 (dd, J_{HH} = 6.9, 1.7 Hz, 3H, CH_3CH=), 3.38 (d, J_{HH} = 11.0 Hz, 1H, $CH(SiPh_2CH_3)(CO_2CH_3)$), 3.51 (s, 3H, OCH_3), 5.39 (dq, J_{HH} = 11.0, 6.9 Hz, 1H, CH_3CH=), 6.06 (tq, J_{HH} = 11.0, 1.7 Hz, CH=$CHCH_3$), 7.10−7.19 (m, 3H, *m,p-Ph*), 7.45−7.51 (m, 2H, *o-Ph*). This was characterized by spectroscopic methods.

Methyl (E)-4-(Triethoxysilyl)pent-2-enoate (***4ha***). Yield: 83% (NMR). ^{1}H NMR (C_6D_6, rt): δ 1.08 (t, J_{HH} = 7.2 Hz, 3H, CH_3CH_2OSi), 1.17 (d, J_{HH} = 7.2 Hz, 3H, $CH_3CHSi(OCH_2CH_3)_3$), 1.91 (dtd, J_{HH} = 7.5, 7.2, 1.7 Hz, 1H, $CH_3CHSi(OCH_2CH_3)_3$), 3.42 (s, 3H, CO_2CH_3), 3.69 (q, J_{HH} = 7.2 Hz, 1H, CH_3CH_2OSi), 5.98 (dd, J_{HH} = 15.8, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.55 (dd, J_{HH} = 15.8, 7.5 Hz, 1H, CH=$CHCO_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 12.40 (CH_3CHSi), 18.37 (CH_3CH_2O), 24.95 ($CHSi$), 50.82 (CO_2CH_3), 59.05 (CH_3CH_2O), 118.15 (CH=$CHCO_2CH_3$), 151.91 (CH=$CHCO_2CH_3$), 166.89 (CO_2CH_3). This was characterized by spectroscopic methods.

Methyl (E)-4-(Benzyldimethylsilyl)pent-2-enoate (***4ia***). Yield: 30% (NMR). ^{1}H NMR (C_6D_6, rt): δ −0.24 (s, 3H, $SiCH_3$), −0.22 (s, 3H, $SiCH_3$), 0.84 (d, J_{HH} = 7.0 Hz, 3H, CH_3CHSi), 1.54 (dqd, J_{HH} = 7.6, 7.0, 1.6 Hz, 1H, CH_3CHSi), 1.85 (s, 2H, CH_2Ph), 3.47 (s, 3H, OCH_3), 5.78 (dd, J_{HH} = 15.6, 1.6 Hz, 1H, CH=$CHCO_2CH_3$), 6.82 (m, 2H, *o-Ph*), 6.98 (m, 1H, *p-Ph*), 7.10 (m, 2H, *m-Ph*), 7.30 (dd, J_{HH} = 15.6, 7.6 Hz, 1H, CH=$CHCO_2CH_3$). ^{1}H NMR ($CDCl_3$, rt): δ −0.04 (s, 3H, $SiCH_3$), −0.03 (s, 3H, $SiCH_3$), 1.13 (d, J_{HH} = 6.9 Hz, 3H, CH_3CHSi), 1.92 (dqd, J_{HH} = 7.7, 6.9, 1.7 Hz, 1H, CH_3CHSi), 2.11 (s, 2H, CH_2Ph), 3.71 (s, 3H, OCH_3), 5.63 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 6.98 (dm, J_{HH} = 7.0, 2H, *o-Ph*), 7.07 (t, m, J_{HH} = 7.37 Hz, 1H, *p-Ph*), 7.14 (dd, J_{HH} = 15.6, 7.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.20 (t, m, J_{HH} = 7.37−7.73 Hz, 2H, *m-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ −5.43 (CH_3Si), −5.26 (CH_3Si), 12.66 (CH_3CHSi), 23.60 (CH_2Ph), 27.06 ($CHSi$), 51.29 (OCH_3), 116.42 (CH=$CHCO_2CH_3$), 124.27 (p-C of Ph), 128.16 (o or m-C of Ph), 128.32 (o or m-C of Ph), 139.16 (*ipso*-C of Ph), 153.68 (CH=$CHCO_2CH_3$), 167.47 (CO_2CH_3). This was characterized by spectroscopic methods.

Methyl (E)-4-(Triethylsilyl)pent-2-enoate (***4ja***). Yield: 62% (NMR), 48% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 0.39 (q, J_{HH} = 8.0 Hz, 6H, CH_3CH_2Si), 0.89 (t, J_{HH} = 8.0 Hz, 9H, CH_3CH_2Si), 0.91 (d, J_{HH} = 7.0 Hz, 3H, CH_3CHSi), 1.70 (dqd, J_{HH} = 7.6, 7.0, 1.7 Hz, 1H, CH_3CHSi), 3.47 (s, 3H, OCH_3), 5.82 (dd, J_{HH} = 15.6, 1.7 Hz, 1H, CH=$CHCO_2CH_3$), 7.30 (dd, J_{HH} = 15.6, 7.6 Hz, 1H, CH=$CHCO_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 2.29 (CH_3CH_2Si), 7.56 (CH_3CH_2Si), 12.83 (CH_3CHSi), 25.61 (CH_3CHSi), 50.81 (CO_2CH_3), 116.49 (CH=$CHCO_2CH_3$), 154.10

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($CH{=}CHCO_2CH_3$), 167.03 (CO_2CH_3). HRMS (APCI): m/z calcd for $C_{12}H_{24}O_2Si + H^+$: 229.1618 $(M + H)^+$; found: 229.1612.

*Methyl (E)-4-(Diphenylsilyl)pent-2-enoate (**4ka**).* Yield: 79% (NMR). ^1H NMR (C_6D_6, rt): δ 1.02 (d, J_{HH} = 7.0 Hz, 3H, CH_3), 2.20 (dqdd, J_{HH} = 7.5, 7.0, 2.9, 1.6 Hz, 1H, $CH_3CH(SiPh_3)$), 3.38 (s, 3H, CO_2CH_3), 4.85 (d, J_{HH} = 2.9 Hz, 1H, Si*H*), 5.77 (dd, J_{HH} = 15.6, 1.6 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.07−7.18 (m, 6H, *m,p-Ph*), 7.59 (dd, J_{HH} = 15.6, 7.5 Hz, $CH{=}CHCO_2CH_3$), 7.44−7.52 (m, 4H, *o-Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 13.66 (CH_3), 25.27 (*C*HSi), 50.84 (CO_2CH_3), 118.38 ($CH{=}CHCO_2CH_3$), 128.37 (*m-C* of $SiPh_2H$), 128.39 (*m-C* of $SiPh_2H$), 130.24 (*p-C* of $SiPh_2H$), 130.29 (*p-C* of $SiPh_2H$), 131.98 (ipso *C*), 132.17 (ipso *C*), 135.71 (o-*C* of $SiPh_2H$), 135.81 (o-*C* of $SiPh_2H$), 152.07 ($CH{=}CHCO_2CH_3$), 166.65 (CO_2CH_3). This was characterized by spectroscopic methods.

*Methyl (Z)-2-(Diphenylsilyl)pent-3-enoate (**5ka**).* Yield: 50% (NMR). ^1H NMR (C_6D_6, rt): δ 1.19 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, CH_3), 3.20 (s, 3H, CO_2CH_3), 3.92 (dd, J_{HH} = 10.8, 2.9 Hz, 1H, $CH(SiPh_2H)(CO_2CH_3)$), 5.18 (d, J_{HH} = 2.9 Hz, 1H, Si*H*), 5.33 (dqd, J_{HH} = 10.8, 6.9, 1.0 Hz, 1H, $CH{=}CHCH_3$), 6.11 (tqd, 10.8, 1.8, 0.4 Hz, 1H, $CH{=}CHCH_3$), 7.07−7.20 (m, 6H, *m,p-Ph*), 7.63−7.71 (m, 4H, *o-Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 12.98 (CH_3), 36.69 ($CHSiPh_3$), 51.00 (CO_2CH_3), 123.93 ($CH_3CH{=}CH$), 124.91 ($CH_3CH{=}CH$), 128.22 (*m-C* of Ph), 128.24 (*m-C* of Ph), 130.32 (*p-C* of Ph), 130.36 (*p-C* of Ph), 131.96 (*ipso-C* of Ph), 132.17 (*ipso-C* of Ph), 135.92 (*o-C* of Ph), 136.02 (*o-C* of Ph), 172.36 (CO_2CH_3). This was characterized by spectroscopic methods.

*Methyl (E)-4-(Triphenylsilyl)hex-2-enoate (**4ab**).* Yield: 90% (NMR), 64% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 0.78 (t, J_{HH} = 7.5 Hz, 3H, CH_3), 1.47 (dq, J_{HH} = 11.1, 7.5 Hz, 1H, $CHHCH(SiPh_3)$), 1.82 (qd, J_{HH} = 7.5, 2.3 Hz, 1H, $CHHCH(SiPh_3)$), 2.45 (dddd, J_{HH} = 11.1, 9.7, 2.3, 1.2 Hz, 1H, $CH_2CH(SiPh_3)$), 3.33 (s, 3H, CO_2CH_3), 5.81 (dd, J_{HH} = 15.9, 1.2 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.13−7.17 (m, 9H, *m,p-Ph*), 7.31 (dd, J_{HH} = 15.9, 9.7 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.56−7.59 (m, 6H, *o-Ph*). ^1H NMR ($CDCl_3$, rt): δ 0.91 (t, J_{HH} = 7.5 Hz, 3H, CH_3), 1.58 (ddq, J_{HH} = 14.2, 10.0, 7.5 Hz, 1H, $CHHCH(SiPh_3)$), 1.89 (dqd, J_{HH} = 14.2, 7.5, 2.3 Hz, 1H, $CHHCH(SiPh_3)$), 2.59 (ddd, J_{HH} = 10.0, 9.7, 2.3 Hz, 1H, $CH_2CH(SiPh_3)$), 3.65 (s, 3H, CO_2CH_3), 5.63 (dd, J_{HH} = 15.6, 0.9 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.03 (dd, J_{HH} = 15.6, 9.7 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.352 (m, 3H, *m-Ph*), 7.41 (m, 3H, *p-Ph*), 7.52 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 14.52 (CH_3), 22.42 (CH_2), 34.90 (*C*HSi), 51.24 (CO_2CH_3), 119.92 ($CH{=}CHCO_2CH_3$), 127.94 (*m-C* of $SiPh_3$), 129.74 (*p-C* of $SiPh_3$), 132.95 (*ipso-C* of $SiPh_3$), 136.01 (*o-C* of $SiPh_3$), 151.15 ($CH{=}CHCO_2CH_3$), 166.98 (CO_2CH_3). HRMS (APCI): m/z calcd for $C_{25}H_{26}O_2Si + H^+$: 387.1775 $(M + H)^+$; found: 387.1781.

*Methyl 4-Methyl-2-(triphenylsilyl)pent-3-enoate (**5ac**).* Yield: 82% (NMR), 59% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.23 (d, J_{HH} = 1.2 Hz, 3H, CH_3), 1.45 (d, J_{HH} = 1.4 Hz, 3H, CH_3), 3.12 (s, 3H, CO_2CH_3), 4.07 (d, J_{HH} = 11.2 Hz, 1H, $CH{=}CH(SiPh_3)(CO_2CH_3)$), 5.86 (d, J_{HH} = 11.2 Hz, 1H, $(CH_3)_2C{=}CH$), 7.11−7.18 (m, 9H, *m, p-Ph*), 7.53−7.60 (m, 6H, *o-Ph*). ^1H NMR ($CDCl_3$, rt): δ 1.30 (d, J_{HH} = 1.4 Hz, 3H, CH_3), 1.61 (d, J_{HH} = 1.3 Hz, 3H, CH_3), 3.32 (s, 3H, CO_2CH_3), 3.87 (d, J_{HH} = 11.2 Hz, 1H, $CH{=}CH(SiPh_3)(CO_2Me)$), 5.50 (dqq, J_{HH} = 11.2, 1.4, 1.3 Hz, 1H, $(CH_3)_2C{=}CH$), 7.34 (m, 6H, *m-Ph*), 7.41 (m, *p-Ph*, 3H), 7.57 (m, *o-Ph*, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 17.98 (CH_3, *cis* to CHSi), 25.81 (CH_3, *trans* to CHSi), 37.87 ($CH(SiPh_3)(CO_2Me)$), 51.13 (CO_2CH_3), 118.16 ($(CH_3)_2CH{=}CH$), 127.67 (*m-C* of $SiPh_3$), 129.76 (*p-C* of $SiPh_3$), 132.62 (*ipso-C* of $SiPh_3$), 132.95 ($(CH_3)_2CH{=}CH$), 136.29 (*o-C* of $SiPh_3$), 173.70 (CO_2CH_3). HRMS (APCI): m/z calcd for $C_{25}H_{26}O_2Si + H^+$: 387.1775 $(M + H)^+$; found: 387.1786.

*Methyl (E)-2-Methyl-4-(triphenylsilyl)pent-2-enoate ((E)-**4ad**).* Yield: 77% (NMR), 46% (isolated). Colorless oil. ^1H NMR ($CDCl_3$, rt): δ 1.29 (d, J_{HH} = 7.1 Hz, 3H, $CH_3CHSiPh_3$), 1.53 (d, J_{HH} = 1.4 Hz, 3H, $=C(CH_3)$), 2.86 (dq, J_{HH} = 12.0, 7.1 Hz, 1H, $CH_3CH(SiPh_3)$), 3.68 (s, 3H, CO_2CH_3), 6.84 (dq, J_{HH} = 12.0, 1.4 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.32−7.38 (m, 6H, *m -Ph*), 7.38−7.44 (m, 3H, *p-Ph*), 7.51−7.56 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 12.62 (CH_3), 15.75 (CH_3), 25.91 (*C*HSi), 51.63 (CO_2CH_3), 125.10 ($CH{=}CCH_3CO_2CH_3$), 127.86 (*m-C* of $SiPh_3$), 129.66 (*p-C* of $SiPh_3$), 133.10 (*ipso*-C of $SiPh_3$), 136.06 (o-C of $SiPh_3$), 145.46 ($CH{=}CCH_3CO_2CH_3$), 168.69 (CO_2CH_3). This was characterized by spectroscopic methods.

*Methyl (Z)-2-Methyl-4-(triphenylsilyl)pent-2-enoate ((Z)-**4ad**).* Yield: 17% (NMR). ^1H NMR ($CDCl_3$, rt): δ 1.24 (d, J_{HH} = 7.1 Hz, 3H, $CH_3CHSiPh_3$), 1.80 (d, J_{HH} = 1.1 Hz, 3H, $=C(CH_3)$), 3.48 (s, 3H, CO_2CH_3), 4.05 (dq, J_{HH} = 11.8, 7.1 Hz, 1H, $CH_3CH(SiPh_3)$), 6.84 (dq, J_{HH} = 11.8, 1.3 Hz, 1H, $CH{=}CHCO_2CH_3$), 7.30−7.35 (m, 6H, *m -Ph*), 7.35−7.41 (m, 3H, *p-Ph*), 7.49−7.55 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 16.11 (CH_3), 20.94 (CH_3), 22.78 (*C*HSi), 50.90 (CO_2CH_3), 124.30 ($CH{=}CCH_3CO_2CH_3$), 127.68 (*m-C* of $SiPh_3$), 129.41 (*p-C* of $SiPh_3$), 133.54 (*ipso*-C of $SiPh_3$), 136.11 (o-C of $SiPh_3$), 146.97 ($CH{=}CCH_3CO_2CH_3$), 168.27 (CO_2CH_3). This was characterized by spectroscopic methods.

*Ethyl (E)-3-Methyl-4-(triphenylsilyl)pent-2-enoate (**4ae**).* Yield: 86% (NMR), 53% (isolated). Yellow powder. ^1H NMR (C_6D_6, rt): δ 0.98 (t, J_{HH} = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.23 (d, J_{HH} = 7.4 Hz, 3H, $CH_3CHSiPh_3$), 2.19 (d, J_{HH} = 1.2 Hz, 3H, $=C(CH_3)$), 1.55 (qd, J_{HH} = 7.4, 0.6 Hz, 1H, $CH_3CHSiPh_3$), 4.01 (dt, J_{HH} = 10.0, 7.2 Hz, 2H, $CO_2CH_2CH_3$), 5.76 (qd, J_{HH} = 1.2, 0.6 Hz, 1H, $=CH(CO_2CH_2CH_3)$), 7.10−7.20 (m, 9H, *m,p-Ph*), 7.57−7.62 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 14.43 ($CO_2CH_2CH_3$), 15.92 ($CH_3CHSiPh_3$), 20.76 ($=C(CH_3)$), 34.03 ($CH_3CHSiPh_3$), 59.21 ($CO_2CH_2CH_3$), 116.09 ($=CH(CO_2CH_2CH_3)$), 128.17 (*p-C* of $SiPh_3$), 129.94 (*m-C* of $SiPh_3$), 133.68 (*ipso-C* of $SiPh_3$), 136.62 (*o-C* of $SiPh_3$), 163.46 ($=C(CH_3)\{CH(SiPh_3)(CH_3)\}$, 166.53 ($CO_2CH_2CH_3$). HRMS (APCI): m/z calcd for $C_{26}H_{28}O_2Si + H^+$: 401.1931 $(M + H)^+$; found: 401.1916.

*Methyl (Z)-4-Methyl-2-(triphenylsilyl)hex-3-enoate (**5af**).* Yield: 45% (NMR), 25% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 0.69 (dd, J_{HH} = 7.6 Hz, 3H, CH_2CH_3), 1.62 (d, J_{HH} = 1.2 Hz, 3H, CCH_3), 1.654 (dq, J_{HH} = 14.2, 7.6 Hz, 1H, $CHHCH_3$), 1.88 (dqd, J_{HH} = 14.2, 7.6, 0.8 Hz, 1H, $CHHCH_3$), 3.12 (s, 3H, OCH_3), 4.16 (d, J_{HH} = 11.2 Hz, 1H, $CH(SiPh_3)(CO_2CH_3)$), 5.90 (dq, J_{HH} = 11.2, 1.2 Hz, 1H, $=CH$), 7.17 (m, 6H, *m-Ph*), 7.76 (m, 3H, *p-Ph*), 7.80 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 12.17 ($CH_3CH_2C{=}$), 22.81 ($CH_3C{=}$), 25.16 ($CH_3CH_2C{=}$), 37.96 ($CSiPh_3$), 50.87 (OCH_3), 118.88 ($=CH$), 130.08 (*m-C* of Ph), 133.29 (*ipso-C* of Ph), 136.62 (*p-C* of Ph), 136.85 (*o-C* of Ph), 138.33 ($=C$), 173.21 (CO_2CH_3). ^1H NMR ($CDCl_3$, rt): δ 0.74 (dd, J_{HH} = 7.7, 7.5 Hz, 3H, CH_2CH_3), 1.62 (d, J_{HH} = 1.2 Hz, 3H, CCH_3), 1.67 (dq, J_{HH} = 13.7, 7.5 Hz, 1H, $CHHCH_3$), 1.89 (dq, J_{HH} = 13.7, 7.7 Hz, 1H, $CHHCH_3$), 3.32 (s, 3H, OCH_3), 3.91 (d, J_{HH} = 11.2 Hz, 1H, $CH(SiPh_3)(CO_2CH_3)$), 5.47 (d, J_{HH} = 11.2 Hz, 1H, $=CH$), 7.34 (m, 6H, *m-Ph*), 7.41 (m, 3H, *p-Ph*), 7.57 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 11.96 ($CH_3CH_2C{=}$), 22.86 ($CH_3C{=}$), 24.81 ($CH_3CH_2C{=}$), 37.34 ($CSiPh_3$), 51.16 (OCH_3), 117.58 ($=CH$), 127.66 (*m-C* of Ph), 129.77 (*p-C* of Ph), 132.54 (*ipso-C* of Ph), 136.31 (*o-C* of Ph), 138.59 ($=C$), 173.77 (CO_2CH_3). This was characterized by spectroscopic methods.

*Methyl (E)-4-Methyl-2-(triphenylsilyl)hex-4-enoate (**6af**).* Yield: 21% (NMR), 14% (isolated). Colorless powder. ^1H NMR (C_6D_6, rt): δ 1.45 (dq, J_{HH} = 6.7, 1.0 Hz, 3H, $=CHCH_3$), 1.53 (dd, J_{HH} = 1.2, 1.0 Hz, 3H, $=C(CH_2)(CH_3)$), 2.48 (dd, J_{HH} = 14.6, 1.6 Hz, 1H, CHH), 3.04 (dd, J_{HH} = 14.6, 12.2 Hz, 1H, CHH), 3.11 (s, 3H, OCH_3), 3.34 (dd, J_{HH} = 12.2, 1.6 Hz, 1H, $CH(SiPh_3)(CO_2CH_3)$), 5.38 (qq, J_{HH} = 6.7, 1.2 Hz, 1H, $=CHCH_3$), 7.34 (m, 6H, *m-Ph*), 7.41 (m, 3H, *p-Ph*), 7.57 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR (C_6D_6, rt): δ 13.50 ($=CHCH_3$), 15.57 ($=C(CH_2)(CH_3)$), 35.15 ($CH(SiPh_3)$-(CO_2CH_3)), 38.82 ($=C(CH_2)(CH_3)$), 50.73 (OCH_3), 119.48 ($=C(CH_2)(CH_3)$), 130.08 (*m-C* of Ph), 133.29 (*ipso-C* of Ph), 136.62 (*p-C* of Ph), 135.27 ($=C$), 136.85 (*o-C* of Ph), 174.91 (CO_2CH_3). ^1H NMR ($CDCl_3$, rt): δ 1.52 (d, J_{HH} = 6.6 Hz, 3H, $=CHCH_3$), 1.55 (d, J_{HH} = 1.2 Hz, 3H, $=C(CH_2)(CH_3)$), 2.27 (dd, J_{HH} = 14.9, 2.0 Hz, 1H, CHH), 2.65 (dd, J_{HH} = 14.9, 12.1 Hz, 1H, CHH), 3.10 (dd, J_{HH} = 12.1, 2.0 Hz, 1H, $CH(SiPh_3)(CO_2CH_3)$), 3.27 (s, 3H, OCH_3), 5.20 (qq, J_{HH} = 6.6, 1.2 Hz, 1H, $=CH$), 7.34 (m, 6H, *m-Ph*), 7.41 (m, 3H, *p-Ph*), 7.57 (m, 6H, *o-Ph*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, rt): δ 13.39

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(=CHCH$_3$), 15.52 (=C(CH$_2$)(CH$_3$)), 34.62 (CH(SiPh$_3$)-(CO$_2$CH$_3$)), 38.10(=C(CH$_2$)(CH$_3$)), 50.94 (OCH$_3$), 119.11 (=C(CH$_2$)(CH$_3$)), 127.80 (*m-C* of Ph), 129.81 (*p-C* of Ph), 132.58 (*ipso-C* of Ph), 135.14 (=C(CH$_2$)(CH$_3$)), 136.10 (*o-C* of Ph), 175.23 (CO$_2$CH$_3$). HRMS (APCI): *m/z* calcd for $C_{26}H_{28}O_2Si + H^+$: 401.1931 $(M + H)^+$; found: 401.1921.

*(E)-(4-(4-Nitrophenyl)but-3-en-2-yl)triphenylsilane (**4ah**).* Yield: 89% (NMR), 65% (isolated). Yellow powder. ^{1}H NMR (C_6D_6, rt): δ 1.32 (d, J_{HH} = 7.5 Hz, 3H, C*H*$_3$), 2.65 (qui.d, J_{HH} = 7.5, 1.7 Hz, 1H, C*H*(SiPh$_3$)(CO$_2$CH$_3$)), 5.96 (dd, J_{HH} = 16.2, 1.7 Hz, 1H, =C*H*C$_6$H$_4$NO$_2$-4), 6.46 (dd, J_{HH} = 16.2, 7.5 Hz, 1H, C*H*=CH C$_6$H$_4$NO$_2$-4), 6.67 (m, 2H, C$_6$*H*$_4$NO$_2$-4), 7.17−7.21 (m, 9H, *m,p-Ph*), 7.59−7.62 (m, 6H, *o-Ph*), 7.72 (m, 2H, C$_6$*H*$_4$NO$_2$-4). ^{1}H NMR (CDCl$_3$, rt): δ 1.37 (d, J_{HH} = 7.1 Hz, 3H, C*H*$_3$), 2.85 (dq, J_{HH} = 7.5, 7.1 Hz, 1H, C*H*(SiPh$_3$)(CO$_2$CH$_3$)), 6.19 (d J_{HH} = 16.1 Hz, 1H, =C*H*C$_6$H$_4$NO$_2$-4), 6.60 (dd, J_{HH} = 16.1, 7.5 Hz, 1H, C*H*=CH C$_6$H$_4$NO$_2$-4), 7.23 (m, 2H, C$_6$*H*$_4$NO$_2$-4), 7.35 (m, 6H, *m-Ph*), 7.42 (m, 3H, *p-Ph*), 7.55 (m, 6H, *o-Ph*), 8.08 (m, 2H, C$_6$*H*$_4$NO$_2$-4). ^{13}C{^{1}H} NMR (CDCl$_3$, rt): δ 14.39 (CH$_3$CHSiPh$_3$), 25.66 (CH$_3$CHSiPh$_3$), 124.02 (2-*C* of C$_6$H$_4$NO$_2$-4), 125.81 (=CHC$_6$H$_4$NO$_2$-4), 125.92 (3-*C* of C$_6$H$_4$NO$_2$-4), 127.93 (*m-C* of Ph), 129.74 (*p-C* of Ph), 133.20, (*ipso-C* of Ph), 136.04 (*o-C* of Ph), 139.21 (CH=CHC$_6$H$_4$NO$_2$-4), 144.74 (4-*C* of C$_6$H$_4$NO$_2$-4), 146.02 (*ipso-C* of C$_6$H$_4$NO$_2$-4). HRMS (APCI): *m/z* calcd for $C_{28}H_{26}NO_2Si + H^+$: 436.1727 $(M + H)^+$; found: 436.1721.

*(Z)-(1-(4-Nitrophenyl)but-2-en-1-yl)triphenylsilane (**5ah**).* Yield: 31% (NMR), 20% (isolated). Light yellow powder. ^{1}H NMR (C_6D_6, rt): δ 1.37 (dd, J_{HH} = 6.8, 1.8 Hz, 3H, =CHC*H*$_3$), 4.07 (d, J_{HH} = 10.9 Hz, 1H, C*H*(C$_6$H$_4$NO$_2$-4)(SiPh$_3$)), 5.411 (dq, J_{HH} = 10.9, 6.8 Hz, 1H, =C*H*CH$_3$), 5.86 (tq, J_{HH} = 10.9, 1.8 Hz, 1H, C*H*=CHCH$_3$), 6.62 (m, 2H, 3-C*H* of C$_6$*H*$_4$NO$_2$-4), 7.10 (m, 6H, *m-Ph*), 7.17 (m, 3H, *p-Ph*), 7.46 (m, 6H, *o-Ph*), 7.69 (m, 2H, 2-C*H* of C$_6$*H*$_4$NO$_2$-4). ^{13}C{^{1}H} NMR (C$_6$D$_6$, rt): δ 13.17 (*C*H$_3$), 35.84 (*C*HSiPh$_3$), 123.33 (2-*C* of C$_6$H$_4$NO$_2$-4), 125.56 (CH=CHCH$_3$), 128.12 (*m-C* of Ph), 128.82 (CH=CHCH$_3$), 129.22 (3-*C* of C$_6$H$_4$NO$_2$-4), 130.18 (*p*-C ofPh), 133.02 (*ipso*-C of Ph), 136.80 (*o-C* of Ph), 145.97 (4-*C* of C$_6$H$_4$NO$_2$-4), 150.23 (*ipso*-C$_6$H$_4$NO$_2$-4). ^{1}H NMR (CDCl$_3$, rt): δ 1.52 (dd, J_{HH} = 6.9, 1.6 Hz, 3H, =CHC*H*$_3$), 4.24 (d, J_{HH} = 11.0 Hz, 1H, C*H*(C$_6$H$_4$NO$_2$-4)(SiPh$_3$)), 5.57 (dq, J_{HH} = 10.6, 6.9 Hz, 1H, =C*H*CH$_3$), 5.88 (ddq, J_{HH} = 11.0, 10.6, 1.6 Hz, 1H, C*H*=CHCH$_3$), 6.96 (m, 2H, 3-C*H* of C$_6$H$_4$NO$_2$-4), 7.32 (t, J_{HH} = 7.2 Hz, 6H, *m-Ph*), 7.40 (d, J_{HH} = 7.2 Hz, 6H, *o-Ph*), 7.41 (m, 3H, *p*-Ph), 7.93 (m, 2H, 2-C*H* of C$_6$H$_4$NO$_2$-4). ^{13}C{^{1}H} NMR (CDCl$_3$, rt): δ 13.23 (*C*H$_3$), 35.57 (*C*HSiPh$_3$), 123.72 (2-*C* of C$_6$H$_4$NO$_2$-4), 125.80 (CH=CHCH$_3$), 127.82 (*m-C* of Ph), 128.00 (CH=CHCH$_3$), 129.01 (3-*C* of C$_6$H$_4$NO$_2$-4), 129.93 (*p*-C of Ph), 132.34 (*ipso*-C of Ph), 136.40 (*o-C* of Ph), 145.28 (4-*C* of C$_6$H$_4$NO$_2$-4), 150.78 (*ipso-C* of C$_6$H$_4$NO$_2$-4). HRMS (APCI): *m/z* calcd for $C_{28}H_{26}NO_2Si + H^+$: 436.1727 $(M + H)^+$; found: 436.1724.

*(E)-Triphenyl(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)silane (**4ai**).* Yield: 30% (NMR), 12% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 1.36 (d, J_{HH} = 7.2 Hz, 3H, C*H*$_3$), 2.69 (dqd, J_{HH} = 7.6, 7.2, 1.4 Hz, 1H, C*H*(C$_6$H$_4$CF$_3$-4)(SiPh$_3$)), 6.10 (dd, J_{HH} = 15.9, 1.4 Hz, 1H, =C*H*C$_6$H$_4$CF$_3$-4), 6.50 (dd, J_{HH} = 15.9, 7.6 Hz, 1H, C*H*=CHC$_6$H$_4$CF$_3$-4), 6.92 (m, 2H, 3-C*H* of C$_6$H$_4$CF$_3$-4), 7.09−7.21 (m, 9H, *m,p*-Ph), 7.22 (m, 2H, 2-C*H* of C$_6$H$_4$CF$_3$-4), 7.56−7.60 (m, 6H, *o*-Ph). ^{1}H NMR (CDCl$_3$, rt): δ 1.37 (d, J_{HH} = 7.2 Hz, 3H, C*H*$_3$), 2.82 (dq J_{HH} = 7.7, 7.2 Hz, 1H, C*H*(C$_6$H$_4$CF$_3$-4)(SiPh$_3$)), 6.19 (d, J_{HH} = 16.0 Hz, 1H, =C*H*C$_6$H$_4$CF$_3$-4), 6.49 (dd, J_{HH} = 16.0, 7.7 Hz, 1H, C*H*=CHC$_6$H$_4$CF$_3$-4), 7.23 (m, 2H, 3-C*H* of C$_6$H$_4$CF$_3$-4), 7.30−7.45 (m, 9H, *m,p-Ph*), 7.45 (m, 2H, 2-C*H* of C$_6$H$_4$CF$_3$-4), 7.54−7.59 (m, 6H, *o-Ph*). ^{19}F NMR (CDCl$_3$, rt): δ −62.20. HRMS (APCI): *m/z* calcd for $C_{29}H_{26}F_3Si + H^+$: 459.1750 $(M + H)^+$; found: 459.1741.

*(Z)-Triphenyl(1-(4-(trifluoromethyl)phenyl)but-2-en-1-yl)silane (**5ai**).* Yield: 27% (NMR), 13% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 1.41 (dd, J_{HH} = 6.9, 1.8 Hz, 3H, C*H*$_3$CH=), 4.15 (dd, J_{HH} = 10.8, 0.9 Hz, 1H, C*H*(C$_6$*H*$_4$CF$_3$-4)(SiPh$_3$)), 5.44 (dqd, J_{HH} = 10.8, 6.9, 0.9 Hz, 1H, CH$_3$C*H*=), 5.97 (tq, J_{HH} = 10.8, 1.8 Hz, 1H, CH$_3$CH=C*H*), 6.85 (d, J_{HH} = 8.2 Hz, 2H, 2-C*H* of C$_6$H$_4$CF$_3$-4), 7.09−7.21 (m, 9H, *m,p-Ph*), 7.28 (d, J_{HH} = 8.2 Hz, 2H, 3-C*H* of C$_6$H$_4$CF$_3$-4), 7.56−7.60 (m, 6H, *o-Ph*). ^{1}H NMR (CDCl$_3$, rt): δ 1.51 (dd, J_{HH} = 6.9, 1.9 Hz, 3H, C*H*$_3$CH=), 4.17 (d, J_{HH} = 11.2 Hz, 1H, C*H*(C$_6$H$_4$CF$_3$-4)(SiPh$_3$)), 5.52 (dqd, J_{HH} = 10.6, 6.9, 0.9 Hz, 1H, CH$_3$C*H*=), 5.89 (ddq, J_{HH} = 11.2, 10.6, 1.9 Hz, 1H, CH$_3$CH=C*H*), 6.95 (d, J_{HH} = 8.2 Hz, 2H, 2-C*H* of C$_6$H$_4$CF$_3$-4), 7.27−7.35 (m, 6H, *m-Ph*), 7.321 (d, J_{HH} = 8.2 Hz, 2H, 3-C*H* of C$_6$H$_4$CF$_3$-4), 7.37−7.43 (m, 9H, *o,p-Ph*). ^{13}C{^{1}H} NMR (CDCl$_3$, rt): 13.15 (CH$_3$), 35.02 (CH(C$_6$H$_4$CF$_3$-4)(SiPh$_3$)), 124.39 (q, $^1J_{CF}$ = 272 Hz, CF$_3$), 124.85 (CH$_3$CH=), 124.90 (3-*C* of C$_6$H$_4$CF$_3$-4), 127.15 (q, $^2J_{CF}$ = 33 Hz, 4-*C* of C$_6$H$_4$CF$_3$-4), 127.88 (*m-C* of SiPh$_3$), 128.73 (2-*C* of C$_6$H$_4$CF$_3$-4), 129.84 (CH$_3$CH=*C*), 129.7262 (*p-C* of SiPh$_3$), 132.89 (*ipso-C* of SiPh$_3$), 136.48 (*o-C* of SiPh$_3$), 146.55 (1-C of C$_6$H$_4$CF$_3$-4). ^{19}F NMR (CDCl$_3$, rt): −62.01. This was characterized by spectroscopic methods.

*(E)-Triphenyl(4-phenylbut-3-en-2-yl)silane (**4aj**).* Yield: 40% (NMR), 13% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 1.39 (d, J_{HH} = 7.3 Hz, 3H, C*H*$_3$), 2.71 (dqd, J_{HH} = 7.7, 7.3, 1.3 Hz, 1H, C*H*Ph(SiPh$_3$)), 6.29 (dd, J_{HH} = 15.9, 1.3 Hz, 1H, CH=C*H*Ph), 5.53 (tq, J_{HH} = 15.9, 7.7 Hz, 1H, C*H*=CHPh), 7.10−7.21 (m, 14H, *m,p-Ph* in SiPh$_3$ and *Ph*), 7.55−7.62 (m, 6H, *o-Ph* in SiPh$_3$). HRMS (APCI): *m/z* calcd for $C_{28}H_{26}Si + H^+$: 391.1877 $(M + H)^+$; found: 391.1859.

*(Z)-Triphenyl(1-phenylbut-2-en-1-yl)silane (**5aj**).* Yield: 59% (NMR), 45% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ 1.45 (dd, J_{HH} = 6.8, 1.9 Hz, 3H, C*H*$_3$), 4.23 (dd, J_{HH} = 11.3, 0.9 Hz, 1H, C*H*Ph(SiPh$_3$)), 5.44 (dqd, J_{HH} = 10.7, 6.8, 0.9 Hz, 1H, CH=C*H*CH$_3$), 6.11 (ddq, J_{HH} = 11.3, 10.7, 1.9 Hz, 1H, C*H*=CHCH$_3$), 7.10−7.21 (m, 14H, *m,p-Ph* in SiPh$_3$ and *Ph*), 7.55−7.62 (m, 6H, *o-Ph* in SiPh$_3$). ^{1}H NMR (CDCl$_3$, rt): δ 1.50 (dd, J_{HH} = 6.7, 1.7 Hz, 3H, C*H*$_3$), 4.12 (d, J_{HH} = 11.5 Hz, 1H, C*H*Ph(SiPh$_3$)), 5.47 (dq, J_{HH} = 10.7, 6.8 Hz, 1H, CH=C*H*CH$_3$), 5.91 (tq, J_{HH} = 11.0, 1.7 Hz, 1H, C*H*=CHCH$_3$), 6.89 (m, 2H, *o-Ph*), 7.04−7.12 (m, 3H, *m,p-Ph*), 7.29 (m, 6H, *m-Ph* in SiPh$_3$, 6H), 7.35−7.45 (m, 9H, *o,p-Ph* in SiPh$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, rt): δ 13.12 (CH$_3$), 34.83 (CHPh(SiPh$_3$)), 125.01 (*p-C* of Ph), 127.53 (*m-C* of SiPh$_3$), 128.10 (*m-C* of Ph), 128.66 (*o-C* of Ph), 129.45 (*p-C* of SiPh$_3$), 129.87 (CH=CHPh(SiPh$_3$)), 133.54 (*ipso-C* of SiPh$_3$), 136.57 (*o-C* of SiPh$_3$), 142.00 (*ipso-C* of Ph). HRMS (APCI): *m/z* calcd for $C_{28}H_{26}Si + H^+$: 391.1877 $(M + H)^+$; found: 391.1877.

*(E)-(4-(4-Methoxyphenyl)but-3-en-2-yl)triphenylsilane ((E)-**4ak**).* Yield: 42% (NMR), 19% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 1.42 (d, J_{HH} = 7.2 Hz, 3H, C*H*$_3$CH(SiPh$_3$)), 2.72 (dqd, J_{HH} = 7.5, 7.2, 1.2 Hz, 1H, CH$_3$C*H*(SiPh$_3$)), 3.26 (s, 3H, OC*H*$_3$), 6.29 (d, J_{HH} = 16.0 Hz, 1H, CH=CH(C$_6$H$_4$OCH$_3$-4)), 6.42 (dd, J_{HH} = 16.0, 7.5 Hz, 1H, C*H*=CH(C$_6$H$_4$OCH$_3$-4)), 6.67 (m, 2H, 3-C*H* of C$_6$H$_4$OCH$_3$-4), 7.12 (m, 2H, 2-C*H* of C$_6$H$_4$OCH$_3$-4), 7.10−7.21 (m, 9H, *m,p-Ph* in SiPh$_3$), 7.55−7.62 (m, 6H, *o-Ph* in SiPh$_3$). HRMS (APCI): *m/z* calcd for $C_{29}H_{28}OSi + H^+$: 421.1982 $(M + H)^+$; found: 421.1978.

*(Z)-(1-(4-Methoxyphenyl)but-2-en-1-yl)triphenylsilane ((Z)-**5ak**).* Yield: 37% (NMR), 25% (isolated). Colorless oil. ^{1}H NMR (C_6D_6, rt): δ 1.46 (dd, J_{HH} = 6.8, 1.8 Hz, 3H, C*H*$_3$), 3.23 (s, 3H, OC*H*$_3$), 4.20 (d, J_{HH} = 11.3 Hz, 1H, C*H*(C$_6$H$_4$OCH$_3$-4)(SiPh$_3$)), 5.44 (dqd, J_{HH} = 10.3, 6.8, 0.8 Hz, 1H, CH=C*H*CH$_3$), 6.10 (ddq, J_{HH} = 11.3, 10.3, 1.8 Hz, 1H, C*H*=CHCH$_3$), 6.64 (m, 2H, 3-C*H* of C$_6$H$_4$OCH$_3$-4), 6.95 (m, 2H, 2-C*H* of C$_6$H$_4$OCH$_3$-4), 7.10−7.21 (m, 9H, *m,p-Ph* in SiPh$_3$), 7.55−7.62 (m, 6H, *o-Ph* in SiPh$_3$). ^{1}H NMR (CDCl$_3$, rt): δ 1.51 (dd, J_{HH} = 6.7, 1.8 Hz, 1H, CH$_3$CH=CH), 3.74 (s, 3H, OC*H*$_3$), 4.08 (d, J_{HH} = 11.2 Hz, 1H, C*H*(CO$_2$CH$_3$)(SiPh$_3$)), 5.46 (dqd, J_{HH} = 10.7, 6.7, 0.7 Hz, 1H, CH$_3$C*H*=CH), 5.87 (ddq, J_{HH} = 11.2, 10.7, 1.8 Hz, 1H, CH$_3$C*H*=CH), 6.67 (m, 2H, C$_6$*H*$_4$OCH$_3$-4), 6.82 (n, 2H, C$_6$*H*$_4$OCH$_3$-4), 7.31 (m, 6H, *m-Ph*), 7.34 (m, 3H, *p-Ph*), 7.43 (m, 6H, *o-Ph*). HRMS (APCI): *m/z* calcd for $C_{29}H_{28}OSi + H^+$: 421.1982 $(M + H)^+$; found: 421.1899.

*(E)-(1-(4-Methoxyphenyl)but-2-en-1-yl)triphenylsilane ((E)-**5ak**).* Yield: 6% (NMR). ^{1}H NMR (C_6D_6, rt): δ 1.49 (dd, J_{HH} = 6.4, 1.5 Hz, 3H, C*H*$_3$), 3.26 (s, 3H, OC*H*$_3$), 3.88 (d, J_{HH} = 7.7 Hz, 1H, C*H*(C$_6$H$_4$OCH$_3$-4)(SiPh$_3$)), 5.36 (dqd, J_{HH} = 15.2, 6.4, 1.5 Hz, 1H, CH=C*H*CH$_3$), 6.03 (ddq, J_{HH} = 15.2, 7.7, 1.5 Hz, 1H, C*H*=CHCH$_3$), 6.67 (m, 2H, 3-C*H* of C$_6$H$_4$OCH$_3$-4), 6.99 (m, 2H, 2-C*H*

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of $C_6H_4OCH_3$-4), 7.10−7.21 (m, 9H, *m,p-Ph* in $SiPh_3$), 7.55−7.62 (m, 6H, *o-Ph* in $SiPh_3$). This was characterized by spectroscopic methods.

*(E)-N,N-Dimethyl-4-(3-(triphenylsilyl)but-1-en-1-yl)aniline ((E)-**4al**).* Yield: 30% (NMR). ^{1}H NMR (C_6D_6, rt): δ 1.45 (d, J_{HH} = 7.2 Hz, 3H, CH_3), 2.47 (s, 3H, $N(CH_3)_2$), 2.76 (qd, J_{HH} = 7.2, 6.9 Hz, 1H, $CH_3CH(SiPh_3)$), 6.38 (d, J_{HH} = 15.7 Hz, 1H, CH=$CHC_6H_4N(CH_3)_2$-4), 6.45 (dd, J_{HH} = 15.7, 6.9 Hz, 1H, CH=$CHC_6H_4N(CH_3)_2$-4), 6.49 (m, 2H, 3-CH in $C_6H_4N(CH_3)_2$-4), 7.23 (m, 2H, 2-CH in $C_6H_4N(CH_3)_2$-4), 7.16 (m, *m,p*-Ph, 9H), 7.72 (m, *o*-Ph, 6H). HRMS (APCI): *m/z* calcd for $C_{30}H_{31}NSi + H^+$: 434.2299 $(M + H)^+$; found: 434.2295.

*(Z)-N,N-Dimethyl-4-(1-(triphenylsilyl)but-2-en-1-yl)aniline ((Z)-**5al**).* Yield: 16% (NMR), 9% (isolated). Yellow powder. ^{1}H NMR (C_6D_6, rt): δ 1.48 (dd, J_{HH} = 6.8, 1.8 Hz, 3H, CH_3CH=CH), 2.45 (s, 6H, $N(CH_3)_2$), 4.24 (d, J_{HH} = 11.3 Hz, 1H, $CH(C_6H_4N(CH_3)_2$-4)($SiPh_3$)), 5.45 (dqd, J_{HH} = 10.7, 6.8, 0.8 Hz, 1H, CH=$CHCH_3$), 6.15 (ddq, J_{HH} = 11.3, 10.7, 1.8 Hz, 1H, CH=$CHCH_3$), 6.49 (m, 2H, 3-CH in $C_6H_4N(CH_3)_2$-4), 7.04 (m, 2H, 2-CH in $C_6H_4N(CH_3)_2$-4), 7.16 (m, 9H, *m,p*-Ph), 7.67 (m, 6H, *o*-Ph). ^{1}H NMR ($CDCl_3$, rt): δ 1.48 (dd, J_{HH} = 6.9, 1.7 Hz, 3H, CH_3CH=CH), 2.85 (s, 6H, $N(CH_3)_2$), 4.04 (d, J = 11.7 Hz, 1H, $CH(C_6H_4N(CH_3)_2$-4)($SiPh_3$)), 5.41 (dq, J_{HH} = 10.9, 6.9 Hz, 1H, CH_3CH=CH), 5.86 (ddq, J = 11.7, 10.9, 1.7 Hz, 1H, CH_3CH=CH), 6.54 (m, 2H, 3-CH in $C_6H_4N(CH_3)_2$-4), 6.78 (m, 2H, 2-CH in $C_6H_4N(CH_3)_2$-4), 7.29 (m, 6H, *m-Ph*), 7.38 (m, 3H, *p-Ph*), 7.43 (m, 6H, *o-Ph*). ^{13}C{^{1}H} NMR ($CDCl_3$, rt): δ 13.06 (CH_3CH=CH), 33.25 ($CHSiPh_3$), 40.92 ($N(CH_3)_2$), 113.05 (2-*C* in $C_6H_4N(CH_3)_2$-4), 122.85 (CH_3CH=CH), 127.48 (*m-C* of $SiPh_3$), 129.27 (3-*C* in $C_6H_4N(CH_3)_2$-4), 129.30 (*p-C* of $SiPh_3$), 130.05 (1-*C* in $C_6H_4N(CH_3)_2$-4), 130.52 (CH_3CH=CH), 134.10 (*ipso-C* of $SiPh_3$), 136.61 (*o-C* of $SiPh_3$), 148.49 (4-*C* in $C_6H_4N(CH_3)_2$-4). HRMS (APCI): *m/z* calcd for $C_{30}H_{31}NSi + H^+$: 434.2299 $(M + H)^+$; found: 434.2317.

*(E)-N,N-Dimethyl-4-(1-(triphenylsilyl)but-2-en-1-yl)aniline ((E)-**5al**).* Yield: 5% (NMR). ^{1}H NMR (C_6D_6, rt): δ 1.50 (dt, J_{HH} = 6.5, 1.5 Hz, 3H, CH_3), 2.47 (s, 6H, $N(CH_3)_2$), 3.92 (d, J_{HH} = 7.5 Hz, 1H, $CH(C_6H_4N(CH_3)_2$-4)($SiPh_3$)), 5.40 (dqd, J_{HH} = 15.2, 6.5, 1.5 Hz, 1H, CH=$CHCH_3$), 6.09 (ddq, J_{HH} = 15.2, 7.5, 1.5 Hz, 1H, CH=$CHCH_3$), 6.47 (m, 2H, 3-CH in $C_6H_4N(CH_3)_2$-4), 7.07 (m, 2H, 2-CH in $C_6H_4N(CH_3)_2$-4), 7.16 (m, 6H, *m,p-Ph*), 7.64 (m, 6H, *o-Ph*). This was characterized by spectroscopic methods.

*(Z)-But-2-en-1-yltriphenylsilane (**5am**).* Yield: 79% (NMR), 23% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ 1.37 (ddt, J_{HH} = 6.7, 1.8, 0.9 Hz, 3H, CH_3CH=), 2.33 (ddq, J_{HH} = 8.2, 1.6, 0.9 Hz, 2H, =$CHCH_2SiPh_3$), 5.39 (dqt, J_{HH} = 10.7, 6.7, 1.6 Hz, 1H, CH_3CH=), 5.67 (dtq, J_{HH} = 10.7, 8.2, 1.8 Hz, 1H, =$CHCH_2SiPh_3$), 7.13−7.20 (m, 9H, *m,p-Ph*), 7.58−7.62 (m, 6H, *o-Ph*). ^{1}H NMR ($CDCl_3$. rt): δ 1.39 (dm, J_{HH} = 6.7 Hz, 3H, CH_3CH=), 2.33 (dm, J_{HH} = 8.1 Hz, 2H, =$CHCH_2SiPh_3$), 5.38 (dqt, J = 10.5, 6.7, 1.5 Hz, 1H, CH_3CH=), 5.56 (dtq, J = 10.5, 8.1, 1.5 Hz, 1H, =$CHCH_2SiPh_3$), 7.35 (m, 6H, *m-Ph*), 7.40 (m, 3H, *p-Ph*), 7.53 (m, 6H, *o-Ph*). ^{13}C{^{1}H} NMR ($CDCl_3$, rt): 12.65 (CH_3CH=), 14.50 (=$CHCH_2SiPh_3$), 123.46 (CH_3CH=), 124.84 (=$CHCH_2SiPh_3$), 127.77 (*m-C* of Ph), 129.46 (*p-C* of Ph), 134.81 (*ipso-C* of Ph), 135.68 (*o-C* of Ph). This was characterized by spectroscopic methods.

*(Z)-Pent-3-en-2-yltriphenylsilane (**5an**).* Yield: 61% (NMR), 43% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ 1.29 (d, J_{HH} = 7.3 Hz, 3H, $CH(CH_3)(SiPh_3)$), 1.45 (dd, J_{HH} = 6.7, 1.6 Hz, 3H, CH_3CH=), 2.90 (dq, J_{HH} = 11.3, 7.3 Hz, 1H, =$CHCH(CH_3)$-($SiPh_3$)), 5.38 (dq, J_{HH} = 10.7, 6.7 Hz, 1H, CH_3CH=), 5.57 (ddq, J_{HH} = 11.3, 10.7, 1.6 Hz, 1H, =$CHCH(CH_3)$), 7.17 (m, 9H, *m,p-Ph*), 7.68 (m, 6H, *o-Ph*). ^{13}C{^{1}H} NMR (C_6D_6, rt): δ 13.16 (CH_3CH=$CHCH(CH_3)(SiPh_3)$), 16.90 (CH_3CH=$CHCH(CH_3)$-($SiPh_3$)), 19.89 (CH_3CH=$CHCH(CH_3)(SiPh_3)$), 122.39 (CH_3CH=$CHCH(CH_3)(SiPh_3)$), 128.09 (*m-C* of Ph), 129.65 (*p-C* of Ph), 133.34 (CH_3CH=$CHCH(CH_3)(SiPh_3)$), 134.71 (*ipso-C* of Ph), 136.56 (*o-C* of Ph). HRMS (APCI): *m/z* calcd for $C_{23}H_{24}Si + H^+$: 329.1720 $(M + H)^+$; found: 329.1727.

*(Z)-(2-Methylbut-2-en-1-yl)triphenylsilane (**5ao**).* Yield: 93% (NMR), 63% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ 1.28 (dm, J_{HH} = 6.7 Hz, 3H, CH_3CH=$C(CH_3)CH_2SiPh_3$), 1.60 (qd, J_{HH} = 1.4, 1.2 Hz, 3H, CH_3CH=$C(CH_3)CH_2SiPh_3$), 2.39 (s, 2H, CH_3CH=$C(CH_3)CH_2SiPh_3$), 5.10 (qq, J_{HH} = 6.7, 1.2 Hz, 1H, CH_3CH=$C(CH_3)CH_2SiPh_3$), 7.12−7.19 (m, 9H, *m,p-Ph*), 7.59−7.63 (m, 6H, *o-Ph*). ^{1}H NMR ($CDCl_3$, rt): δ 1.18 (dm, J_{HH} = 6.7 Hz, 3H, CH_3CH=$C(CH_3)CH_2SiPh_3$), 1.52 (qd, J_{HH} = 1.4, 1.3 Hz, 3H, CH_3CH=$C(CH_3)CH_2SiPh_3$), 2.36 (s, 2H, CH_3CH=$C(CH_3)$-CH_2SiPh_3), 5.10 (qq, J_{HH} = 6.7, 1.3 Hz, 1H, CH_3CH=$C(CH_3)$-CH_2SiPh), 7.35 (m, *m-Ph*, 6H), 7.411 (m, *p-Ph*, 3H), 7.53 (m, *o-Ph*, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, rt): 13.64 (CH_3CH=$C(CH_3)$-CH_2SiPh_3), 19.75 (CH_3CH=$C(CH_3)CH_2SiPh_3$), 26.44 (CH_3CH=$C(CH_3)CH_2SiPh_3$), 118.31 (CH_3CH=$C(CH_3)$-CH_2SiPh_3), 127.69 (*m-C* of Ph), 129.39 (*p-C* of Ph), 132.41 (CH_3CH=$C(CH_3)CH_2SiPh_3$), 135.05 (*ipso-C* of Ph), 135.80 (*o-C* of Ph). HRMS (APCI): *m/z* calcd for $C_{23}H_{24}Si + H^+$: 329.1720 $(M + H)^+$; found: 329.1707.

*(Z)-(2-Ethylidene-6-methylhept-5-en-1-yl)triphenylsilane (**5ap**).* Yield: 94% (NMR), 85% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ 1.29 (d, J_{HH} = 6.9 Hz, 3H, CH_3CH=), 1.50 (s, 3H, $(CH_3)_2C$=), 1.62 (s, 3H, $(CH_3)_2C$=), 1.99 (t, J_{HH} = 7.7 Hz, 2H, =$CHCH_2CH_2$), 2.15 (td, J_{HH} = 7.7, 6.9 Hz, 2H, =$CHCH_2CH_2$), 2.46 (s, 2H, CH_2SiPh_3), 5.10 (tm, J_{HH} = 6.9 Hz, 1H, $(CH_3)_2C$=CH), 5.25 (q, J_{HH} = 6.9 Hz, 1H, CH_3CH=), 7.13−7.20 (m, 6H, *m,p-Ph*), 7.64 (m, 4H, *o-Ph*). ^{13}C{^{1}H} NMR (C_6D_6, rt): δ 13.94 (CH_3CH=), 17.74 ($(CH_3)_2C$=), 18.27 (CH_2SiPh_3), 25.82 ($(CH_3)_2C$=), 27.27 (=$CHCH_2CH_2$), 39.50 (=$CHCH_2CH_2$), 118.10 (CH_3CH=), 124.91 ($(CH_3)_2C$=CH), 128.08 (*p-C* of Ph), 129.73 (*m-C* of Ph), 130.97 ($(CH_3)_2C$=CH), 135.50 (*ipso-C* of Ph), 136.26 (*o-C* of Ph), 136.57 (CH_3CH=C). This was characterized by spectroscopic methods.

*Methyl (E)-4-(Triphenylsilyl)pent-2-enoate-5-d (**4aa-d**).* Yield: 92% (NMR), 73% (isolated). Colorless powder. ^{1}H NMR (C_6D_6, rt): δ1.14 (dm, J_{HH} = 6.6 Hz, 2H, CH_2D), 2.56 (dt, J_{HH} = 7.5, 6.6 Hz, 1H, $CH_2DCHSiPh_3$), 5.80 (dd, J_{HH} = 15.6, 1.6 Hz, 1H, CH=$CHCO_2CH_3$), 7.14 (m, 6H, *m,p-Ph*), 7.562 (m, 6H, *o-Ph*), 7.57 (dd, J_{HH} = 15.6, 7.5 Hz, 1H, CH=$CHCO_2CH_3$). D NMR (C_6H_6, rt): δ 1.11 (CH_2D). HRMS (APCI): *m/z* calcd for $C_{24}H_{23}DO_2Si + H^+$: 374.1681 $(M + H)^+$; found: 374.1668.

*(Z)-(Pent-3-en-2-yl-5-d)triphenylsilane (**5ah-d**).* Yield: 70% (NMR). ^{1}H NMR (C_6D_6, rt): δ 1.29 (d, J_{HH} = 7.5 Hz, 3H, $CH(CH_3)(SiPh_3)$), 1.42 (ddt, J_{HH} = 6.7, 2.0 Hz, J_{DH} = 2.0 Hz, 2H, CH_2DCH=), 2.89 (dq, J_{HH} = 10.9, 7.5 Hz, 1H, =$CHCH(CH_3)$-($SiPh_3$)), 5.37 (dt, J_{HH} = 10.9, 6.7 Hz, CH_2DCH=), 5.57 (tt, J_{HH} = 10.9, 2.0 Hz, =$CHCH(CH_3)(SiPh_3)$), 7.17 (m, 9H, *m,p-Ph*), 7.68 (m, 6H, *o-Ph*). D NMR (C_6H_6, rt): δ 1.41 (td, J_{DH} = 2.2, 0.9 Hz, CH_2DCH=). This was characterized by spectroscopic methods.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00597.

NMR spectra of hydrosilylation products (PDF)

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