

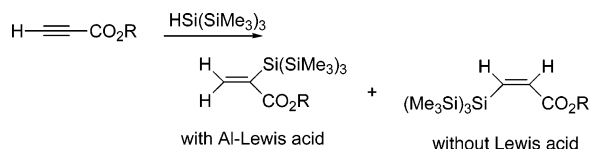
Regioselective Hydrosilylations of Propiolate Esters with Tris(trimethylsilyl)silane

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Lewis acid and substituent dependency on the regioselectivity of hydrosilylation of propiolate esters **1a–c** with tris(trimethylsilyl)silane (**2a**) was found. The reaction of methyl and ethyl propiolate esters and **2a** without Lewis acid and in the presence of EtAlCl₂ and Et₂AlCl gave β -silicon-substituted *Z*-alkenes **3** selectively. On the other hand, reaction in the presence of AlCl₃ in dichloromethane gave α -silicon-substituted alkenes **4**. In the case of trifluoroethyl propiolate ester **1c**, reaction with aluminum chloride-based Lewis acids gave α -silicon-substituted alkenes **4** exclusively. Two competitive mechanisms, free-radical and ionic, are proposed as the source of the complementary regioselectivity displayed in these reactions. A transition state of the radical-forming step was obtained computationally. The reaction of various reactive acetylene substrates and **2a** without Lewis acid and without solvent at room temperature gave β -silicon-substituted *Z*-alkenes **3** selectively.

Introduction

Hydrosilylation of alkynes and alkenes is one of the most effective C–Si bond formation reactions.¹ Lewis acid-promoted hydrosilylation of unactivated alkynes and alkenes has been recently studied;² however, Lewis acid-promoted hydrosilylation of activated or carbonyl group-functionalized alkynes and alkenes has received little attention. We are interested in the synthesis of functionalized organosilicon compounds via an efficient and regioselective hydrosilylation reaction. As a hydrosilane reagent, tris(trimethylsilyl)silane (**2a**) was examined. The hydrosilylation of alkynes and alkenes with **2a** without Lewis acid was previously studied by Chatgililoglu et al.³ This silane has three Si–Si bonds and reaction conditions to retain Si–Si bonds are of mechanistic interest, particularly for the development of model reactions toward the modification of silicon surfaces.⁴ The

transformation of tris(trimethylsilyl)silyl groups to bromine or OH groups has also been demonstrated.^{3a} In addition, the hydrosilylated products, vinyl tris(trimethylsilyl)silanes, are potential substrates for useful cross-coupling reactions,⁵ and a cross-coupling reaction of vinyl tris(trimethylsilyl)silanes has been demonstrated recently.⁶ In this study, we have found Lewis acid dependency and substituent dependency in the regioselective hydrosilylation of propiolate esters.

Results and Discussion

1. Reactions without Lewis Acid and Solvent.

Reactions of the terminal alkyne substrates **1** shown in

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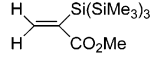
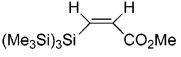
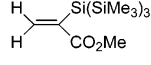
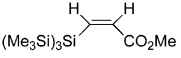
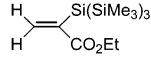
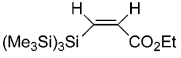
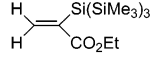
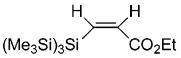
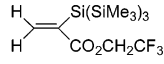
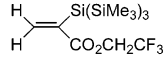
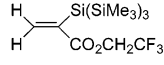
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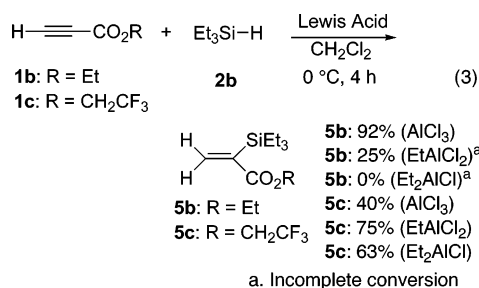
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TABLE 2. Lewis Acid-Promoted Hydrosilylation of Propiolates **1a–c** with **2a** in Eq 2^a

Entry	Substrate	Lewis acid	3 (Yield/%)	4 (Yield/%)
1	1a H—C≡C—CO ₂ Me	AlCl ₃	(0)	4a  (72)
2	1a H—C≡C—CO ₂ Me	EtAlCl ₂	3a  (51)	4a  (15)
3	1a H—C≡C—CO ₂ Me	Et ₂ AlCl	3a  (49) ^b	(0) ^b
4	1b H—C≡C—CO ₂ Et	AlCl ₃	(0)	4b  (62)
5	1b H—C≡C—CO ₂ Et	EtAlCl ₂	3b  (69)	4b  (12)
6	1b H—C≡C—CO ₂ Et	Et ₂ AlCl	3b  (51) ^b	(0) ^b
7	1c H—C≡C—CO ₂ CH ₂ CF ₃	AlCl ₃	(0)	4c  (55)
8	1c H—C≡C—CO ₂ CH ₂ CF ₃	EtAlCl ₂	(0)	4c  (64)
9	1c H—C≡C—CO ₂ CH ₂ CF ₃	Et ₂ AlCl	(0) ^b	4c  (37) ^b

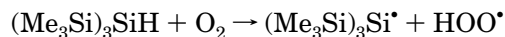
^a Reactions were carried out with **1** (2.0 mmol), **2a** (2.1 mmol), and Lewis acid (2.4 mmol) in CH₂Cl₂ (2 mL) at 0 °C for 4 h. ^b **2a** was incompletely consumed. Starting materials **1a–c** were not detected.

reaction of **1c** and **2b** in the presence of AlCl₃, EtAlCl₂, and Et₂AlCl gave α-silicon adducts **5c** in 40%, 75%, and 63% yields, respectively. In these reactions, formation of β-silicon adducts was not identified. Without Lewis acid in CH₂Cl₂, and using neat conditions, the reaction of **1b,c** and **2b** did not proceed.



3. Reaction Mechanism. The radical mechanism involving **2a** was studied by Chatgililoglu in detail.^{3,7} The reaction pathway to give **3** in eqs 1 and 2 is considered to be a radical process. The radical mechanism is supported by the fact that the reaction of **1b** and **2a** was retarded by addition of a radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol. The radical initiator may be molecular oxygen, as we could not exclude oxygen completely. A key question is concerned with the radical

initiating step. Chatgililoglu suggested that the initiation step for the autoxygenation reaction without radical initiator is the following hydrogen abstraction reaction.^{7d}

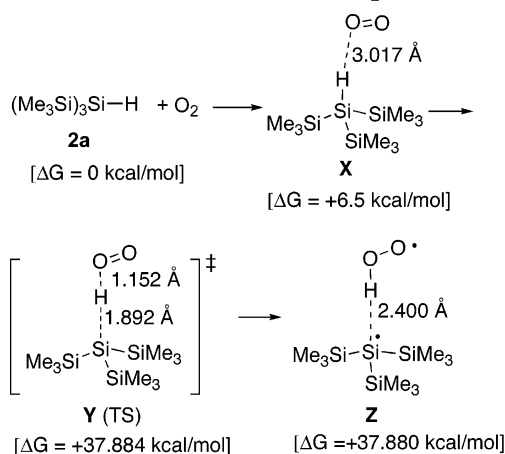


Adventitious in situ oxygen was considered to initiate the radical process in view of relatively weak Si–H bond energy (=84 kcal/mol) for **2a**.¹² To obtain theoretical support, we have examined this process by UB3LYP/6-31G* calculations^{13,14} (Scheme 1). The weakly bound complex of **2a** and a triplet oxygen molecule was calculated as the structure **X** ($\Delta E = -0.84$ kcal/mol and $\Delta G_{298} = +6.5$ kcal/mol). The hydrogen abstraction by molecular oxygen transition state **Y** was obtained ($\Delta E = +30.1$ kcal/mol and $\Delta G_{298} = +37.884$ kcal/mol) (Figure 1). The reaction coordinate vectors show the hydrogen transfer clearly. Then, the resulting intermediate is the structure **Z** ($\Delta E = +28.2$ kcal/mol and $\Delta G_{298} = +37.880$ kcal/mol). Geometries of **X** and **Z** are shown in Figures S1 and S2,

(11) The reaction of **1a** and **2b** with iridium catalyst undergoes cyclotrimerization instead of hydrosilylation. Tanke, R. S.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 7984.

(12) (a) Chatgililoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67. (b) Chatgililoglu, C. *Chem. Rev.* **1995**, *95*, 1229.

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

SCHEME 1. Radical Initiation Step^a

^a ΔG in this scheme is at 273.15 K (25 °C). Geometries of X and Z are in the Supporting Information. That of Y is in Figure 1.

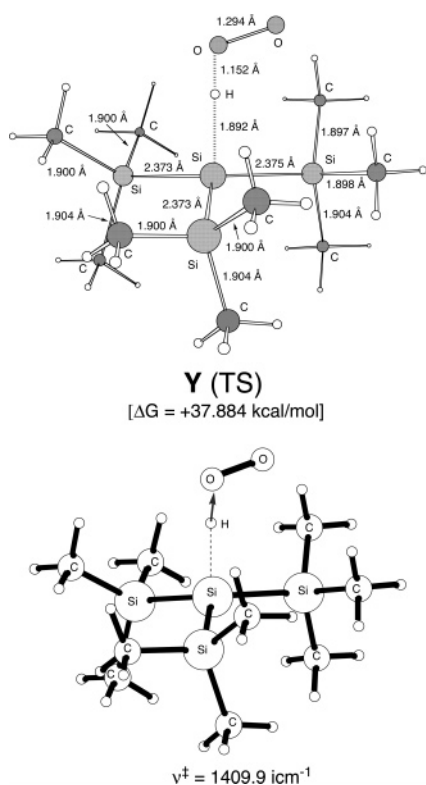
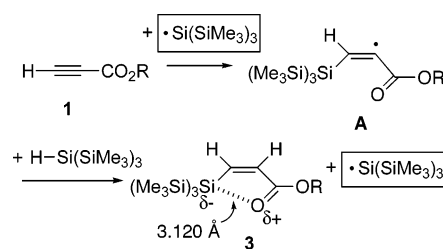


FIGURE 1. UB3LYP/6-31G*-optimized TS structure of Y in Scheme 1 and reaction-coordinate vectors corresponding to the sole imaginary frequency ν[‡]. ΔG is relative to (Me₃Si)₃Si-H and triplet O₂ (T = 298.15 K).

respectively (Supporting Information). The generated (Me₃Si)₃Si· can induce a chain reaction (Scheme 2) to produce the results in Table 1. The activation free energy ΔG[‡] at 343 K (70 °C) was also calculated to compare with the experimental data obtained by Chatgialiloglu et al.^{7d} ΔG[‡]₃₄₃ in this work is 31.8 kcal/mol (relative to the initially formed complex X),¹⁵ which is in good agreement with 29.4 kcal/mol calculated from the kinetic constant of 3.5 × 10⁻⁵ M⁻¹ s⁻¹ at 70 °C.^{7d,16} Thus, the radical initiation step that (Me₃Si)₃Si-H (2a) and O₂ generate the radical (Me₃Si)₃Si· through hydrogen abstraction was clarified by the present theoretical study.

SCHEME 2. Radical Chain Mechanism^a

^a The (Me₃Si)₃Si· radical is consumed by addition to the triple bond and is reproduced to yield the Z olefin. 3.120 Å in 3 was obtained for 3a (Figure S4 in the Supporting Information).

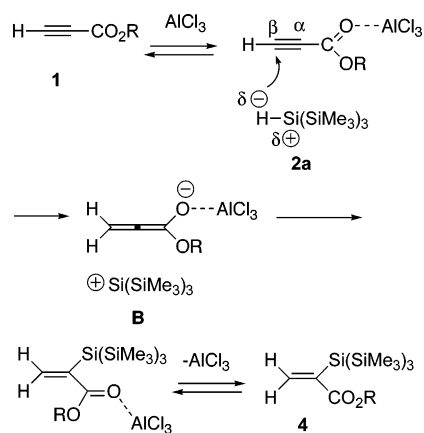
Lewis acid noncoordinated species 1 would proceed with a free-radical mechanism to give β-adducts 3 as shown in Scheme 2. The regiochemistry of addition is explained by the stabilization of the generated radical center by the ester-carbonyl group. The radical intermediate A (R = Me, in Scheme 2) was obtained by UB3LYP/6-31G* optimization and is shown in Figure S3 (Supporting Information). The free energy difference ΔG₂₉₈ of A (R = Me) compared to 1a (R = Me) and tris(trimethylsilyl)silyl radical ((Me₃Si)₃Si·) is -6.1 kcal/mol. The radical adduct A may be stabilized by the CO₂R group through spin delocalization. The radical intermediate from 1-hexyne has no delocalization, therefore the reaction did not proceed in this mild condition. No reactivity toward methyl 2-butynoate can be understood by the steric consideration that the approach of (Me₃Si)₃Si· is disturbed by the methyl group.

The obtained Z-stereochemistry for the products 3 may arise from preferred hydrogen abstraction from the anti side of the silyl group by the steric effect of the bulky tris(trimethylsilyl)silyl group as suggested previously (see A in Figure S3).^{3a} In addition, the Z-product 3a (R = Me) is 8.9 kcal/mol more stable than the corresponding E-isomer. The stability probably arises from (Me₃Si)₃Si...O=COR through-space interaction, which is suggested by the calculated short Si-O distance (3.120 Å) and the accumulated bonding charge distributions between Si and O. The high reactivity of the tris(trimethylsilyl)silyl radical allows propiolate 1 to react as a radical acceptor. The ester and the other substituents in 1 work to stabilize the transient radical intermediate and to control the Z stereochemistry.

(14) MO calculations with Gaussian 98 were made at the Information Processing Center (Nara University of Education). Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) ΔG[‡]₃₄₃ relative to reactants 2a and oxygen is 39.2 kcal/mol. (16) From the Eyring equation, k (L mol⁻¹ s⁻¹) = (kT/h)(RT/P)e^{-ΔG[‡]/RT}, where k = Boltzmann's constant = 1.381 × 10⁻²³ J K⁻¹, h = Planck's constant = 6.626 × 10⁻³⁴ J s, T = 343 K, P = 1 atm, R = gas constant = 0.082 atm L mol⁻¹ K⁻¹ = 1.987 cal mol⁻¹ K⁻¹, and ΔG[‡]₃₄₃ (29.4 kcal/mol) was obtained by using the kinetic constant (k = 3.5 × 10⁻⁵ M⁻¹ s⁻¹).^{7d} See, for example: Sana, M.; Leroy, G.; Villaveces, J. L. *Theor. Chim. Acta (Berlin)* **1984**, *65*, 109.

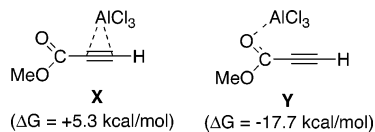
SCHEME 3. Ionic Mechanism



On the other hand, α -adducts **4** seem to be produced via an ionic mechanism as shown in Scheme 3. The negatively charged hydrogen of **2a** attacks the β -carbon of propiolate, where the ester-carbonyl group is complexed with AlCl_3 and the alkyne is highly electrophilic.¹⁷ The nucleophilic attack would give an ion pair intermediate **B**, which leads to α -adducts **4**. The regioselectivity is controlled by the LUMO of the **1a**- AlCl_3 complex where orbital extension at C_β is larger than that of C_α as described later. The ion pair intermediate **B** ($R = \text{Me}$) was obtained by B3LYP/6-31G* optimization with the SCRf solvent effect¹⁸ (CH_2Cl_2 , dielectric constant 8.93) (Figure S5). At the optimization of **B**, **1a**- AlCl_3 complex and tris(trimethylsilyl)silane (**2a**) were set to the C_β - $\text{H}-\text{Si}$ distance of 1.18 Å as an initial structure.¹⁹

In the LUMO of **1b** and the Al-coordinated complexes, the coefficient at β -carbon (-0.49 to -0.55) is larger than that of α -carbon (0.21 to 0.34) by RHF/STO-3G SCRf//B3LYP/6-31G* SCRf. The regiochemistry dependency on aluminum Lewis acids can be explained as follows. When the LUMO levels are lower (**1b**- AlCl_3 0.134 au) and the alkyne is very electrophilic, ionic addition occurs leading to the α -silicon adduct **4**. When the LUMO levels are higher (**1b**- Et_2AlCl_2 0.149 au, **1b**- Et_2AlCl 0.163 au, and **1b** 0.242 au), more reactive tris(trimethylsilyl)silyl radical reacts instead, leading to β -silicon adducts **3**. Because the above-mentioned ΔG_{298} (-6.1 kcal/mol) of the radical intermediate **A** in Scheme 2 toward **1a** and $\cdot\text{Si}(\text{SiMe}_3)_3$ is relatively small, **A** is a transient species. Therefore, the ionic mechanism can take place competitively.²⁰ Thus, the strong Lewis acid AlCl_3 facilitates the ionic mechanism. The reactions of the weaker Lewis acid (Et_2AlCl_2 and Et_2AlCl)-coordinated propiolate complex proceed

(17) The structures of two possible **1a**- AlCl_3 complexes **X** and **Y** were calculated (B3LYP/6-31G*). The π -complex **X** suggested for unactivated alkynes by Yamamoto² is unstable ($\Delta G = +5.3$ kcal/mol) relative to reactants **1a** and AlCl_3 and the σ -complex **Y** is stable ($\Delta G = -17.7$ kcal/mol).



(18) Onsager, L. *J. Am. Chem. Soc.* **1938**, *58*, 1486.

(19) In reality, $^+\text{Si}(\text{SiMe}_3)_3$ in **B** may be surrounded and stabilized by the solvent CH_2Cl_2 .

(20) For the hydride donor ability of **2a**, see: Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060.

with the free-radical mechanism. The exclusive β -adduct formation in the case of the use of a catalytic amount of AlCl_3 can be explained by a higher concentration of **1a** than that of **1a**- AlCl_3 complex under equilibrium, and the noncoordinated species **1a** undergoes the radical addition process.²¹ The reaction of **1b,c** and triethylsilane (**2b**) only gave the α -silicon adducts **5b,c** (eq 3). Apparently, the reaction of hydrosilane **2b** ($\text{Si}-\text{H}$ bond energy for **2b**, 95 kcal/mol)¹² only undergoes the ionic mechanism.²²

In entries 7–9 of Table 2, the CH_2CF_3 esters have afforded only α -adducts regardless of the strength of Al Lewis acids. The α -adduct preference can be explained by the low LUMO energy levels of Al complexes arising from the inductive effect of the CF_3 group.²³

In summary, we have found Lewis acid and substituent dependency on regioselectivity in the hydrosilylation of propiolate esters. The regioselectivity was explained by two competitive mechanisms, free radical and ionic. The radical-initiating step was explicitly demonstrated. The present hydrosilylation is highly selective and clean, and only requires simple operation. The mild neat conditions with reactive alkynes to form a $\text{C}-\text{Si}$ bond also may be suitable to modification of silicon surfaces. Further utility of this regioselective reaction is under investigation.

Experimental Section

Substrates **2a,b**, **1a,b**, and **1d,e** were purchased. **1c** was prepared by the reaction of propionic acid and 2,2,2-trifluoroethanol with BF_3 -etherate according to the literature method.²⁴

2,2,2-Trifluoroethyl propiolate (1c): colorless oil; bp 46–47 °C/65 mmHg; ^1H NMR (400 MHz, CDCl_3) δ 3.05 (s, 3H), 4.56 (q, 2H, $J_{\text{F-H}} = 8.1$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 61.4 (q, $-\text{CH}_2\text{CF}_3$, $J_{\text{F-C}} = 37.4$ Hz), 73.1 ($\text{HC}\equiv\text{C}-$), 77.6 ($\text{HC}\equiv\text{C}-$), 122.4 (q, $-\text{CH}_2\text{CF}_3$, $J_{\text{F-C}} = 277.0$ Hz), 150.9 ($-\text{C}(\text{O})\text{O}-$); ^{19}F NMR (376.3 MHz, CDCl_3) δ -74.2 (t, $J_{\text{F-H}} = 8.3$ Hz).

Typical Hydrosilylation Procedure of Neat Condition (Table 1, entry 1). A mixture of tris(trimethylsilyl)silane (**2a**) (520 mg, 2.1 mmol) and methyl propiolate (**1a**) (168 mg, 2.0 mmol) was stirred at room temperature overnight. The reaction mixture was purified by column chromatography over silica gel eluting with hexanes–ethyl acetate (20:1) to give **3a** (295 mg, 89%).

Typical Hydrosilylation Procedure (Table 2, entry 1). To a mixture of AlCl_3 (320 mg, 2.4 mmol) and dichloromethane (2.0 mL) was added tris(trimethylsilyl)silane (**2a**) (520 mg, 2.1 mmol) at 0 °C. After being stirred for 5 min, methyl propiolate (**1a**) (168 mg, 2.0 mmol) was added to the mixture. The reaction mixture was stirred at 0 °C for 4 h. After the addition of water, the mixture was extracted with ether and the organic phase was dried (MgSO_4) and evaporated in vacuo. The residue

(21) The background reaction of **1a,c** (at 0 °C 4 h without Lewis acid in CD_2Cl_2 , checked by ^1H NMR) proceeded in 37% (for **1a**) and 47% (for **1c**) conversion to give **3a** and **3c**, respectively. Therefore, the radical and ionic processes compete under these reaction conditions. Some inconsistency in isolated yields may arise from the possibilities that the reaction completed after treatment with water or the β -addition reaction is accelerated by weak Lewis acids or catalytic Lewis acid.

(22) We attempted to seek the potential surface of the hydrogen shift, $\text{Et}_3\text{Si}-\text{H} + \text{O}_2 \rightarrow \text{Et}_3\text{Si}\cdot + \text{HOO}\cdot$, which is similar to that of $(\text{Me}_3\text{Si})_3\text{SiH} + \text{O}_2 \rightarrow (\text{Me}_3\text{Si})_3\text{Si}\cdot + \text{HOO}\cdot$. However, the former path could not be found despite many attempts. The radical species $\text{Et}_3\text{Si}\cdot$ would not be generated by the O_2 attack.

(23) Hammett constants of the CF_3 group are $\sigma_m = 0.46$ and $\sigma_p = 0.53$. Exner, O. In *Correlation Analysis in Organic Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10.

(24) Jung, M. E.; Buszek, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 3965.

was purified by column chromatography over silica gel eluting with hexanes–ethyl acetate (20:1) to give **4a** (487 mg, 72%).

Methyl 2-[tris(trimethylsilyl)silyl]propenoate (4a): R_f 0.4 (hexanes–EtOAc = 20:1); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.19 (s, 27H), 3.71 (s, 3H), 5.99 (d, 1H, $J = 2.6$ Hz), 6.66 (d, 1H, $J = 2.6$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.1 ($-\text{Si}(\text{CH}_3)_3$), 51.7 ($-\text{OCH}_3$), 138.9 ($\text{H}_2\text{C}=\text{C}$), 140.0 ($\text{H}_2\text{C}=\text{C}$), 171.0 ($-\text{C}(\text{O})\text{O}-$); IR (neat) 2952, 2896, 1721, 1435, 1246, 837 cm^{-1} ; MS (EI) m/z 317 ($\text{M}^+ - \text{CH}_3$), 259 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3$), 73 ($\text{Si}^+(\text{CH}_3)_3$).

Ethyl 2-(tris(trimethylsilyl)silyl)propenoate (4b): R_f 0.5 (hexanes–EtOAc = 20:1); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.20 (s, 27H), 1.30 (t, 3H, $J = 7.1$ Hz), 4.19 (q, 2H, $J = 7.1$ Hz), 5.98 (d, 1H, $J = 2.6$ Hz), 6.60 (d, 1H, $J = 2.6$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.2 ($-\text{SiCH}_3$), 14.5 ($-\text{OCH}_2\text{CH}_3$), 60.8 ($-\text{OCH}_2\text{CH}_3$), 138.2 ($\text{H}_2\text{C}=\text{C}$), 140.8 ($\text{H}_2\text{C}=\text{C}$), 170.7 ($-\text{C}(\text{O})\text{O}-$); IR (neat) 2957, 2896, 1705, 1401, 1253, 839 cm^{-1} ; MS (EI) m/z 331 ($\text{M}^+ - \text{CH}_3$), 301 ($\text{M}^+ - \text{OC}_2\text{H}_5$), 273 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3$), 73 ($\text{Si}^+(\text{CH}_3)_3$).

2,2,2-Trifluoroethyl 2-[tris(trimethylsilyl)silyl]propenoate (4c): R_f 0.5 (hexanes–EtOAc = 40:1); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.20 (s, 27H), 4.51 (q, 2H, $J_{\text{F-H}} = 8.6$ Hz), 6.14 (d, 1H, $J = 2.2$ Hz), 6.70 (d, 1H, $J = 2.2$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 1.1 ($-\text{SiCH}_3$), 60.5 (q, $J_{\text{C-F}} = 36.6$ Hz, $-\text{OCH}_2\text{CF}_3$), 123.2 (q, $J_{\text{C-F}} = 277.0$ Hz, $-\text{CF}_3$), 139.2 ($\text{H}_2\text{C}=\text{C}$), 140.2 ($\text{H}_2\text{C}=\text{C}$), 168.5 ($-\text{C}(\text{O})\text{O}-$); ^{19}F NMR (376.3 MHz, CDCl_3) δ -74.0 (t, $J_{\text{F-H}} = 8.6$ Hz); IR (neat) 2956, 2897, 1728, 1411, 1286, 1248, 838 cm^{-1} ; MS (EI) m/z 385 ($\text{M}^+ - \text{CH}_3$), 327 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3$), 301 ($\text{M}^+ - \text{OCH}_2\text{CF}_3$), 228 ($\text{M}^+ - \text{Si}(\text{CH}_3)_3 - \text{OCH}_2\text{CF}_3$), 73 ($\text{Si}^+(\text{CH}_3)_3$).

Ethyl 2-(triethylsilyl)propenoate (5b): R_f 0.4 (hexanes–EtOAc = 20:1); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.70 (q, 6H, $J = 7.9$ Hz), 0.92 (t, 9H, $J = 7.9$ Hz), 1.30 (t, 3H, $J = 7.1$ Hz), 4.20 (q, 2H, $J = 7.1$ Hz), 5.97 (d, 1H, $J = 2.9$ Hz), 6.83 (d, 1H, $J = 2.9$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 3.1

($-\text{Si}(\text{CH}_2\text{CH}_3)_3$), 7.4 ($-\text{Si}(\text{CH}_2\text{CH}_3)_3$), 14.3 ($-\text{OCH}_2\text{CH}_3$), 60.5 ($-\text{OCH}_2\text{CH}_3$), 140.3 ($\text{H}_2\text{C}=\text{C}$), 141.6 ($\text{H}_2\text{C}=\text{C}$), 169.8 ($-\text{C}(\text{O})\text{O}-$); IR (neat) 2955, 2911, 2876, 1720, 1464, 1394, 1274, 1222, 1147, 1120, 1007, 974 cm^{-1} ; MS (EI) m/z 199 ($\text{M}^+ - \text{CH}_3$), 185 ($\text{M}^+ - \text{C}_2\text{H}_5$), 169 ($\text{M}^+ - \text{OC}_2\text{H}_5$), 141 ($\text{M}^+ - \text{COOC}_2\text{H}_5$). Anal. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_2\text{Si}$: C, 61.63; H, 10.34. Found: C, 61.35; H, 10.35.

2,2,2-Trifluoroethyl 2-(triethylsilyl)propenoate (5c): R_f 0.65 (hexanes–ether = 10:1); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 0.71 (q, 6H, $J = 7.9$ Hz), 0.93 (t, 9H, $J = 7.9$ Hz), 4.52 (q, 2H, $J = 8.6$ Hz), 6.12 (d, 1H, $J = 2.8$ Hz), 6.95 (d, 1H, $J = 2.8$ Hz); ^{13}C NMR (100.6 MHz, CDCl_3) δ 2.9 ($-\text{SiCH}_2\text{CH}_3$), 7.2 ($-\text{SiCH}_2\text{CH}_3$), 60.5 (q, $-\text{CH}_2\text{CF}_3$, $J_{\text{C-F}} = 35.9$ Hz), 123.2 (q, $-\text{CH}_2\text{CF}_3$, $J_{\text{C-F}} = 277.0$ Hz), 139.9 ($-\text{SiCH}=\text{CH}-\text{C}(\text{O})-$), 142.9 ($-\text{SiCH}=\text{CH}-\text{C}(\text{O})-$), 167.9 ($-\text{COO}-$); ^{19}F NMR (376.3 MHz, CDCl_3) δ -74.0 (t, $J_{\text{F-H}} = 9.1$ Hz); IR (neat) 2958, 2914, 2829, 1733, 1243, 1409, 1285, 1254, 1212, 1170, 1133, 978, 736 cm^{-1} ; MS (EI) m/z 239 ($\text{M}^+ - \text{CH}_2\text{CH}_3$), 115 ($\text{Si}^+(\text{CH}_2\text{CH}_3)_3$). Anal. Calcd for $\text{C}_{11}\text{H}_{19}\text{F}_3\text{O}_2\text{Si}$: C, 49.21; H, 7.14. Found: C, 49.23; H, 7.14.

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Supporting Information Available: General experimental methods and additional spectral data, B3LYP/6-31G*-optimized geometries and Cartesian coordinates and total energy of **X**, **Y**, **Z**, **A**, **3a**, **B**, **1b**, and Al-complexes of **1b**, and copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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