Cationic Palladium Complex-Catalyzed Hydrosilylative Cross-Coupling between Alkynes and Alkenes

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Supporting Information

I. General

All moisture-sensitive manipulations were carried out under an argon atmosphere. All reactions were conducted in a 5 ml screw-capped testing tube. Dichloromethane was used after distillation over phosphorus pentoxide. Absolute ethanol and triethylamine distilled over calcium hydride were used for ethoxylation of chlorosilanes. Hexane was distilled over sodium wire.

$[(\eta^3\text{-C}_3\text{H}_5)\text{Pd}(\text{cod})][\text{PF}_6]$ (**A**) was synthesized according to the literature procedure.¹ PPh_3 was used after recrystallization from ethanol. Triethyl and trimethyl methanetricarboxylates were prepared by the reported procedure.² All other chemicals were purchased from Aldrich, Wako Chemicals, TCI and used as received.

¹ White, D. A. *Inorg. Synth.* **1972**, *13*, 61.

² (a) Padgett, H. C.; Csendes, I. G.; Rapoport, H. *J. Org. Chem.* **1979**, *44*, 3492. (b) Brummond, K. M.; Chen, H.; Sill, P.; You, L. *J. Am. Chem. Soc.* **2002**, *124*, 15186.

II. Preparation of Substrates

The yields have not been optimized.

Monopropargyl malonic ethyl or methyl ester was prepared in reasonable yield by the alkylation of the triethyl or trimethyl sodiomethanetricarboxylate with propargyl bromide or 1-bromo-2-butyne, followed by the cleavage of the corresponding carbonate.²

Diethyl propargylmalonate: bp 112-115 °C/11 Torr. ¹H NMR (270 MHz, CDCl₃, TMS): δ 1.28 (t, J = 7.3 Hz, 6H), 2.02 (t, J = 2.6 Hz, 1H), 2.78 (dd, J = 7.6, 2.6 Hz, 2H), 3.57 (t, J = 7.6 Hz, 1H), 4.233 (q, J = 6.9 Hz, 2H), 4.236 (q, J = 7.3 Hz, 2H).

Dimethyl propargylmalonate: bp 66-67 °C/1.5 Torr. ¹H NMR: 2.03 (t, J = 2.6 Hz, 1H), 2.80 (dd, J = 7.6, 2.6 Hz, 2H), 3.62 (t, J = 7.6 Hz, 1H), 3.78 (s, 6H).

Diethyl (2-butyne-1-yl)malonate : bp 116-118 °C/1 Torr. ¹H NMR: 1.28 (t, J = 7.3 Hz, 6H), 1.75 (t, J = 2.6 Hz, 3H), 2.72 (dq, J = 7.9, 2.6 Hz, 1H), 3.51 (t, J = 7.9 Hz, 1H), 4.22 (q, J = 7.3 Hz, 4H). ¹³C NMR

(67.8 MHz, CDCl₃, TMS): 3.45, 14.0, 18.8, 51.7, 61.6, 74.7, 77.8, 168.2.

Dimethyl (2-butyn-1-yl)malonate : bp 85-87 °C/1.5 Torr. ¹H NMR: 1.75 (t, *J* = 2.6 Hz, 3H), 2.73 (dq, *J* = 7.6, 2.6 Hz, 1H), 3.56 (t, *J* = 7.6 Hz, 1H), 3.77 (s, 6H).

1,6-Heptenyne equivalent: Diethyl allylpropargylmalonate (B):³

Diethyl propargylmalonate (4.1 g, 21 mmol) was treated with NaOEt (1.55 g, 22 mmol) in dry toluene/DMF (1:1, 25 ml) and to the resulting slurry was added allyl bromide (2.5 g, 21 mmol). The whole mixture was heated at 80 °C for 14 h and worked up as usual to afford compound **B** by distillation under reduced pressure, bp 118-120 °C/1 Torr, 2.0 g (41% yield): ¹H NMR: δ 1.26 (t, *J* = 7.3 Hz, 6H), 2.01 (t, *J* = 2.6 Hz, 1H), 2.80 (d, *J* = 2.6 Hz, 2H), 2.81 (br d, *J* = 7.6 Hz, 1H), 4.21 (q, *J* = 7.3 Hz, 4H), 5.14 (dq, *J* = 10.6, 1.0 Hz, 1H), 5.19 (dq, *J* = 17.2, 1.0 Hz, 1H), 5.63 (ddt, *J* = 17.2, 10.6, 7.3 Hz, 1H).

1,6-Heptadiyne equivalent: Dimethyl dipropargylmalonate (C): Prepared by direct dipropargylation of dimethyl sodiomalonate in THF. mp 87-89 °C (hexane-ethanol). *Lit.* 4 mp 85-87 °C.

1,6-Octadiyne equivalent: Dimethyl (2-butyn-1-yl)propargylmalonate (D):³

In the similar manner as above, dimethyl propargylmalonate (6.3 g, 37 mmol) was treated with NaH (1.5 g, 60% dispersion in mineral oil, 37 mmol) in dry THF (45 ml). To the resulting slurry was added 2-butyn-1-yl bromide (4.9 g, 37 mmol) in THF (15 ml) and the reaction mixture was heated with stirring at 50 °C for 6 h, then stood overnight at room temperature. Usual work up and crude product obtained was purified by recrystallization (hexane-ethanol) to afford compound **C** – 6.07 g (74% yield), mp 63-64 °C. ¹H NMR: δ 1.76 (t, *J* = 2.6 Hz, 3H), 2.03 (t, *J* = 2.6 Hz, 1H), 2.93 (q, *J* = 2.6 Hz, 2H), 2.98 (d, *J* = 2.6 Hz, 2H), 3.76 (s, 6H). ¹³C NMR (67.8 MHz, CDCl₃, TMS): δ 3.47, 22.6, 23.0, 53.0, 56.7, 71.5, 72.7, 78.6, 79.3, 169.4.

³ (a) Hicks, F. A.; Kablaoui, N. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5881. (b) Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. *J. Am. Chem. Soc.* **2002**, *124*, 3806.

⁴ Atkinson, R. S.; Grimshire, M. J. *J. Chem. Soc., Perkin Trans. 1* **1986**, 1215.

III. Catalytic Hydrosilylative Cross-Coupling between Alkynes and Alkenes

Procedure for Scheme 1. The procedure is typical for all reactions reported in the text.

Preparation of 1-(Triethoxysilyl)methyl-2-methylene-4,4-bis(ethoxycarbonyl)cyclopentane (1b): Into a 5 ml screw-capped testing tube with a stirring bar under argon were placed a cationic palladium catalyst **A** (5 × 10⁻³ mmol) and the substrate **B** (1.0 mmol). When HSiCl₃ (1 M, 1 ml, 1 mmol) was added to this mixture, an exothermic reaction took place, and the whole reaction mixture was kept at room temperature with stirring for 0.1 h. Since GLC analysis (3 mm x 3 m SE-30 column at programmed heating at 10 °C/min from 100~280 °C) revealed the reaction was complete, the whole mixture was treated with an excess ethanol and triethylamine dissolved in CH₂Cl₂ in a ice-cooled bath for 1 h. Et₃N/HCl salt formed was removed by repeated trituration with cold hexane and filtration through a celite plug, and the filtrates were concentrated by a coolnit evaporator. The residual oil was purified by a bulb-to-bulb distillation under a reduced pressure to give 0.382 g (95% yield) of almost pure product. An analytical sample was collected by a preparative GLC. Spectral data: ¹H NMR: δ 0.60 (dd, *J* = 15.2, 10.6 Hz, 1H), 1.10 (dd, *J* = 15.2, 3.6 Hz, 1H), 1.23 (t, *J* = 6.9 Hz, 9H), 1.24 (t, *J* = 7.3 Hz, 3H), 1.25 (t, *J* = 7.3 Hz, 3H), 1.81 (dd, *J* = 12.4, 11.1 Hz, 1H), 2.62 (centered m, 1H), 2.72 (dd, *J* = 12.0, 7.6 Hz, 1H), 2.90 (dq, *J* = 16.8, 2.0 Hz, 1H), 3.06 (br d, *J* = 16.8 Hz, 1H), 3.83 (q, *J* = 6.9 Hz, 6H), 4.16 (q, *J* = 7.3 Hz, 2H), 4.19 (q, *J* = 7.3 Hz, 2H), 4.86 (q, *J* = 2.3 Hz, 1H), 4.91 (q, *J* = 2.3 Hz, 1H). ¹³C NMR: δ 13.9 (q), 14.3 (t), 18.2 (q), 37.6 (d), 40.0 (t), 41.7 (d), 58.0 (s), 58.3 (t), 61.3 (t),

106.1 (t), 154.1 (s), 171.9 (s), 171.8 (s). Anal. Calcd for C₁₉H₃₄O₇Si: C, 56.69; H, 8.51. Found: 56.28; H, 8.66.

Preparation of (Z)-1-(Triethoxysilyl)methylene-2-methylene-4,4-bis(methoxycarbonyl)cyclopentane(2b): The procedure was the same as described above except the reaction time of 15 h, the product being obtained, after purification by GPC, in an improved yield (0.298 g, 80%, *Z/E* = 98/2), compared with the previous data (56%; *Z/E* = 92/8).⁵

Spectral data: ¹H NMR: δ 1.21 (t, *J* = 6.9 Hz, 1 H), 3.08 (br t, *J* = 2.2 Hz, 2 H), 3.13 (br d, *J* = 1.7 Hz, 2 H), 3.72 (s, 6 H), 3.80 (q, *J* = 6.9 Hz, 6 H), 5.17 (br t, *J* = 2.2 Hz, 1 H), 5.32 (br t, *J* = 2.0 Hz, 1 H), 5.95 (t, *J* = 2.3 Hz, 1 H). ¹³C NMR: δ 18.1 (× 3), 42.1, 45.1, 52.8, 56.9, 58.4 (× 3), 112.0, 112.5, 143.7, 158.3, 171.6. Anal. Calcd for C₁₇H₂₈O₇Si: C, 54.82; H, 7.58. Found: C, 54.56; H, 7.58.

⁵ Uno, T.; Wakayanagi, S.; Sonada, Y.; Yamamoto, K. *Synlett* **2003**, 1997. (Ref. 4i in the text)

Procedure for eq 1. 2-Phenyl-3-(trichlorosilyl)methyl-1-heptene (3a) and 2-Phenyl-4-trichlorosilyl-1-octene (4a): a mixture of phenylacetylene (1 mmol), 1-hexene (3 mmol), and the catalyst A (5 × 10⁻³ mmol) dissolved in dry CH₂Cl₂ (1 ml) was placed in a 5 ml screw-capped test tube under an argon atmosphere. To this solution was added HSiCl₃ (1 M, CH₂Cl₂, 1 ml) and the whole mixture was heated at 50 °C for 1 h. Color change of the reaction mixture may be diagnostic of the end-point of reaction. The chlorosilane cross-coupling products were directly subjected to bulb-to-bulb distillation to give the regioisomeric products 3a and 4a (0.223 g, 70% combined yield), in a ratio 60 : 40 by GLC analysis. They were separated by preparative GLC for the spectral identification. Spectral data for 3a: ¹H NMR: δ 0.85(t, *J* = 7.1 Hz, 3H), 1.2 ~ 1.3 (m, 6H), 1.68 (dd, *J* = 15.5, 6.9 Hz, 1H), 1.78 (dd, *J* = 15.5, 7.3 Hz, 1H), 3.03 (quint, *J* = 7.1 Hz, 1H), 5.12 (s, 1H), 5.29 (d, *J* = 0.7 Hz, 1H), 7.3 ~ 7.4 (aromatic H, 5H). ¹³C NMR: δ 14.0, 22.6, 28.7, 29.8, 31.4, 39.1, 113.6, 126.9, 127.5, 128.3, 141.9, 151.8. Spectral data for 4a: ¹H NMR: δ 0.85(t, *J* = 6.9 Hz, 3H), 1.2 ~ 1.4 (m, 6H), 1.19 (quint, *J* = 6.9 Hz, 1H), 2.55 (ddd, *J* = 14.5, 9.9, 0.7 Hz, 1H), 3.09 (dd, *J* = 14.5, 3.5 Hz, 1H), 5.17 (d, *J* = 0.7 Hz, 1H), 5.36 (d, *J* = 1.3 Hz, 1H), 7.3 ~ 7.4 (aromatic H, 5H). ¹³C NMR: δ 13.8, 22.8, 27.4, 29.9, 34.1, 35.8, 115.4, 126.5, 127.8, 128.5, 139.7, 145.8. Triethoxysilyl compounds **3b** and **4b** were derived from 3a and 4a, respectively, for the analytical purpose. Anal. Calcd. for C₂₀H₃₄O₃Si: C, 68.52; H, 9.78. Found: C, 68.25; H, 9.51.

Procedure for eq 2. (E)-1-Phenyl-3-(triethoxysilyl)methyl-1-heptene (5b): A catalyst system consisting of the palladium complex **A** and PPh₃ (1 equiv) was employed and the reaction of phenylacetylene (1 mmol) and 1-hexene (3 equiv) with HSiCl₃ was conducted at 50 °C for 4 h, in exactly the same manner as above. The product was either distilled directly from the reaction mixture to afford **5a** or isolated as triethoxy derivative, which was substantially a single **5b** (0.203 g, 58% yield). Spectral data for **5b**: ¹H NMR: δ 0.80 (dd, *J* = 15.2, 7.4 Hz, 1H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.87 (dd, *J* = 15.2, 4.3 Hz, 1H), 1.20 (t, *J* = 6.9 Hz, 9H), 1.29 (centered m, 6H), 2.39 (centered m, 1H), 3.80 (q, *J* = 6.9 Hz, 6H), 6.06 (dd, *J* = 15.7, 8.9 Hz, 1H), 6.33 (d, *J* = 15.7 Hz, 1H), 7.15 ~ 7.36 (aromatic H, 5H). ¹³C NMR: δ 14.1, 17.5, 18.3, 22.7, 29.6, 37.6, 38.1, 58.3, 126.0, 126.6, 128.2, 128.4, 137.0, 138.0. Anal. Calcd. for C₂₀H₃₄O₃Si: C, 68.52; H, 9.78. Found: C, 68.56; H, 9.77.

Spectral and Analytical Data for Products listed in Table 1.

Entry 1 & 2: 1-Heptyne/1-Hexene

2-Pentyl-3-(trichlorosilyl)methyl-1-heptene (6a): [α-1]

¹H NMR: δ 0.88 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H), 1.2-1.6 (m, 12H), 1.43 (dd, *J* = 14.2, 6.3 Hz, 1H), 2.00 (t, *J* = 7.4 Hz, 2H), 2.12 (dd, *J* = 14.2, 9.6 Hz, 1H), 2.49 (quint, *J* = 7.1 Hz, 1H), 4.82 (s), 4.86 (s).

2-Pentyl-3-(triethoxysilyl)methyl-1-heptene (6b): [α -1]

^1H NMR: δ 0.81 (dd, $J = 14.4, 7.6$ Hz, 1H), 0.87 (t, $J = 7.3$ Hz, 6H), 0.88 (dd, $J = 14.4, 7.4$ Hz, 1H), 1.15-1.3 (br m, 12H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.95 (dt, $J = 15.2, 7.9$ Hz, 2H), 2.16 (m, 1H), 3.83 (q, $J = 6.9$ Hz, 6H), 4.69 (d, $J = 1.7$ Hz, 1H), 4.74 (s, 1H). ^{13}C NMR: δ 14.09, 14.14, 17.6, 18.3, 22.6, 22.7, 29.5, 29.8, 31.4, 32.5, 37.5, 37.7, 58.2, 128.8, 136.3.

5-(Trichlorosilyl)methyl-6(E)-dodecene (7a): [β -1]

^1H NMR: δ 0.88 (t, $J = 6.6$ Hz, 6H), 1.2-1.4 (m, 12H), 1.45 (dd, $J = 15.2, 9.2$ Hz, 1H), 1.55 (dd, $J = 15.2, 5.3$ Hz, 1H), 1.98 (q, $J = 6.9$ Hz, 2H), 2.32-2.44 (m, 1H), 5.15 (dd, $J = 15.2, 8.9$ Hz, 1H), 5.46 (dd, $J = 15.2, 6.9$ Hz, 1H).

5-(Triethoxysilyl)methyl-6(E)-dodecene (7b): [β -1]

^1H NMR: δ 0.69 (dd, $J = 15.2, 7.3$ Hz, 1H), 0.73 (dd, $J = 15.2, 6.6$ Hz, 1H), 0.87 (t, $J = 6.9$ Hz, 3H), 0.88 (t, $J = 6.6$ Hz, 3H), 1.15-1.30 (m, 12H), 1.22 (t, $J = 6.9$ Hz, 9H), 1.96 (q, $J = 6.9$ Hz, 2H), 2.16 (m, 1H), 3.80 (q, $J = 6.9$ Hz, 6H), 5.23 (ddt, $J = 15.2, 8.6, 0.7$ Hz, 1H), 5.34 (dt, $J = 15.2, 6.4$ Hz, 1H). **Anal.** Calcd for $\text{C}_{19}\text{H}_{40}\text{O}_3\text{Si}$: C, 66.22, H, 11.70. Found: C, 66.51, H, 11.79.

Entry 3 & 4: Methyl propiolate/1-Hexene**Methyl 2-(1-trichlorosilyl-2-hexyl)propenoate (8a) [α -1]**

^1H NMR: δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.15-1.35 (m, 6H), 1.55 (dd, $J = 15.5, 8.1$ Hz, 1H), 1.62 (dd, $J = 15.5, 6.1$ Hz, 1H), 2.62 (m, 1H), 3.76 (s, 3H), 5.64 (br s, 1H), 6.27 (d, $J = 1$ Hz, 1H).

Methyl 2-{1-(triethoxysilyl)-2-hexyl}propenoate (8b): [α -1]

^1H NMR: δ 0.86 (t, $J = 6.9$ Hz, 3H), 0.90 (dd, $J = 8.9, 7.3$ Hz, 1H), 1.04 (dd, $J = 8.9, 6.9$ Hz, 1H), 1.21 (t, $J = 6.9$ Hz, 9H), 1.2-1.3 (m, 6H), 2.78 (quint, $J = 7.2$ Hz, 1H), 3.74 (s, 3H), 3.79 (q, $J = 6.9$ Hz, 6H), 5.54 (brs, 1H), 6.17 (d, $J = 1$ Hz, 1H). ^{13}C NMR: δ 14.1, 16.7, 18.2, 22.7, 29.4, 36.2, 36.3, 51.6, 58.3, 124.0, 145.4, 167.7. IR (neat): 2973.7, 2927.5, 2885.0, 2734.6, 1724.1, 1627.7, 1437.7, 1390.4, 1274.7, 1201.5, 958.5 cm^{-1} . **Anal.** Calcd as $\text{C}_{16}\text{H}_{32}\text{O}_5\text{Si}$: C, 57.79; H, 9.70. Found C, 57.90; H, 9.49.

Methyl 4-(trichlorosilyl)methyl-2(*E*)-octenoate (9a): [β-1]

¹H NMR: δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.27 (centered m, 6H), 1.70 (dd, *J* = 15.5, 6.3 Hz, 1H), 1.91 (dd, *J* = 15.5, 8.9 Hz, 1H), 2.90 (tt, *J* = 8.7, 5.9 Hz, 1H), 3.77 (s, 3H), 5.86 (dd, *J* = 15.5, 0.7 Hz, 1H), 6.75 (dd, *J* = 15.5, 9.2 Hz, 1H).

Methyl 4-(triethoxysilyl)methyl-2(*E*)-octenoate (9b): [β-1]

¹H NMR: δ 0.73 (dd, *J* = 15.2, 6.9 Hz, 1H), 0.80 (dd, *J* = 15.2, 6.9 Hz, 1H), 0.87 (t, *J* = 6.9 Hz, 3H), 1.21 (t, *J* = 6.9 Hz, 9H), 1.2-1.3 (m, 6H), 2.4 (m, 1H), 3.72 (s, 3H), 3.80 (q, *J* = 6.9 Hz, 6H), 5.78 (dd, *J* = 15.5, 1 Hz, 1H), 6.83 (dd, *J* = 15.5, 8.9 Hz, 1H). ¹³C NMR: δ 14.0, 16.5, 18.2, 22.6, 29.4, 36.4, 37.4, 51.4, 58.4, 119.3, 155.1, 167.4. IR (neat): 2973.7, 2927.5, 2885.0, 1726.0, 1654.6, 1435.8, 1269.9, 1104.0, 1081.9, 959.4 cm⁻¹. **Anal.** Calcd as C₁₆H₃₂O₅Si: C, 57.79; H, 9.70. Found C, 57.74; H, 9.40.

Entry 5 & 6: Phenylacetylene/Styrene**2,3-Diphenyl-4-trichlorosilyl-1-butene (10a): [α-1]**

¹H NMR: δ 2.04 (dd, *J* = 15.2, 8.9 Hz, 1H), 2.15 (dd, *J* = 15.2, 6.6 Hz, 1H), 4.27 (ddd, *J* = 8.9, 6.6, 1.0 Hz, 1H), 5.27 (d, *J* = 1.0 Hz, 1H), 5.42 (s, 1H), 7.2-7.4 (aromatic H, 10H). ¹³C NMR: δ 30.8, 45.1, 113.9, 126.9 (× 2), 127.1, 127.5, 128.1 (× 2), 128.2 (× 2), 128.6 (× 2), 141.4, 141.7, 151.3.

2,3-Diphenyl-4-triethoxysilyl-1-butene (10b): [α-1]

¹H NMR: δ 1.12 (t, *J* = 6.9 Hz, 9H), 1.24 (dd, *J* = 15.2, 9.2 Hz, 1H), 1.35 (dd, *J* = 15.2, 5.9 Hz, 1H), 3.63 (q, *J* = 6.9 Hz, 6H), 4.09 (dd, *J* = 8.7, 6.4 Hz, 1H), 5.27 (t, *J* = 1.2 Hz, 1H), 5.33 (s, 1H), 7.1-7.3 (aromatic H, 10H). **Anal.** Calcd for C₂₂H₃₀O₃Si: C, 71.31; H, 8.16. Found: C, 71.31; H, 8.23.

2,4-Diphenyl-4-trichlorosilyl-1-butene (11a): [α-2]

¹H NMR: δ 2.85, (dd, *J* = 11.5, 3.6 Hz, 1H), 3.06 (dd, *J* = 13.9, 11.5 Hz, 1H), 3.42 (dd, *J* = 13.9, 3.6 Hz, 1H), 4.94(s, 1H), 5.13(s, 1H), 7.2-7.4 (aromatic H, 10 H). ¹³C NMR: δ 34.8, 41.0, 115.6, 126.4 (× 2), 127.3, 127.3, 128.5 (× 4), 129.1 (× 2), 135.5, 139.9, 144.9.

2,4-Diphenyl-4-triethoxysilyl-1-butene (11b): [α-2]

¹H NMR: δ 1.14 (t, *J* = 6.9 Hz, 9H), 2.31 (dd, *J* = 11.4, 3.5 Hz, 1H), 2.86, (dd, *J* = 15.3, 11.4 Hz, 1H), 3.22 (dd, *J* = 15.3, 3.5 Hz, 1H), 3.70 (q, *J* = 6.9 Hz, 6H), 4.79 (d, *J* = 0.7 Hz, 1H), 5.05(d, *J* = 1.0 Hz, 1H), 7.2-7.4 (aromatic H, 10 H).

1,3-Diphenyl-4-trichlorosilyl-1(*E*)-butene (12a): [β-1]

^1H NMR: δ 2.03 (dd, $J = 15.2, 7.3$ Hz, 1H), 2.07 (dd, $J = 15.2, 7.9$ Hz, 1H), 3.93 (q, $J = 7.7$ Hz, 1H), 6.32 (dd, $J = 15.8, 7.9$ Hz, 1H), 6.49 (d, $J = 15.8$ Hz, 1H), 7.2- 7.4 (aromatic H, 10H).

1,3-Diphenyl-4-triethoxysilyl-1(*E*)-butene (12b): [β -1]

^1H NMR: δ 1.14₈ (t, $J = 6.9$ Hz, 9H), 1.24 (dd, $J = 15.2, 7.3$ Hz, 2H), 1.28 (dd, $J = 15.2, 7.9$ Hz, 1H), 3.60 (q, $J = 6.9$ Hz, 1H), 3.70 (q, $J = 6.9$ Hz, 6H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.41 (dd, $J = 15.8, 5.6$ Hz, 1H), 7.15-7.35 (aromatic H, 10H). ^{13}C NMR δ 18.2 ($\times 3$), 43.5 ($\times 2$), 58.3 ($\times 3$), 126.2 ($\times 2$), 126.9, 127.5 ($\times 2$), 128.3, 128.4 ($\times 4$), 135.9, 137.7, 146.0.

1,4-Diphenyl-4-triethoxysilyl-1(*E*)-butene (13b): [β -2] could only be separated by column chromatography (Silica gel, hexane-ethyl acetate 2%) from a mixture with **12b**: ^1H NMR: δ 1.15₃ (t, $J = 6.9$ Hz), 2.32 (dd, $J = 10.1, 5.4$ Hz), 2.76 (centered m.), 3.70 (q, $J = 6.9$ Hz), 6.14 (dt, $J = 15.8, 6.8$ Hz), 6.32 (d, $J = 15.5$ Hz), 7.15-7.35 (aromatic H). ^{13}C NMR δ 18.2 ($\times 3$), 33.7, 34.1, 58.8 ($\times 3$), 126.0 ($\times 2$), 126.7, 126.9, 127.9 ($\times 2$), 128.3 ($\times 2$), 128.7 ($\times 2$), 130.2, 130.4, 137.9, 141.4.

Entry 7: Phenylacetylene/3-Hexene

2-Phenyl-3-ethyl-4-trichlorosilyl-1-hexene (14a): [α -]

^1H NMR: δ 0.95 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.1$ Hz, 3H), 1.33 (ddd, $J = 9.2, 4.3, 2.6$ Hz, 1H), 3.17 (dt, $J = 10.6, 2.5$ Hz, 1H), 5.07 (s, 1H), 5.45 (s, 1H) 7.2-7.4 (aromatic H, 5H). Diastereotopic hydrogens (4H) are not resolved. ^{13}C NMR: δ 12.5, 14.5, 17.5, 22.2, 39.5, 44.8, 114.4, 126.7 ($\times 2$), 127.6, 128.5 ($\times 2$), 142.5, 148.0. (a *threo* isomer must be formed)

1-Phenyl-3-ethyl-4-trichlorosilyl-1(*E*)-hexene (15a): [β -]

^1H NMR: δ 0.91 (t, $J = 7.4$ Hz, 3H), 1.09 (t, $J = 7.4$ Hz, 3H), 2.54 (ddt, $J = 9.6, 7.6, 4.6$ Hz, 1H), 6.10 (dd, $J = 15.5, 9.6$ Hz, 1H), 6.43 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR: δ 12.3, 13.5, 19.8, 26.2, 41.7, 44.8, 126.3 ($\times 2$), 127.0, 127.6 ($\times 2$), 131.5, 132.0, 137.2.

Entry 8: 3-Hexyne/allylbenzene

3-{1-Phenyl-3-(trichlorosilyl)prop-2-yl}-3(*E*)-hexene (16a): [(α) -1]

^1H NMR: δ 0.93 (t, $J = 7.6$ Hz, 3H), 0.97 (t, $J = 7.6$ Hz, 3H), 1.52 (dd, $J = 15.5, 5.1$ Hz, 1H), 1.61 (dd, $J = 15.5, 9.1$ Hz, 1H), 1.92 (q, $J = 7.6$ Hz, 2H), 1.98 (quint, $J = 7.3$ Hz, 2H), 2.6 (m, 1H), 5.20 (t, $J = 7.1$ Hz, 1H), 7.1-7.3 (m, aromatic protons, 5H). Benzylic protons hardly be assigned.

4-Ethyl-6-trichlorosilyl-7-phenyl-3(E)-heptene (17a): $[(\alpha)-2]$

^1H NMR: δ 0.83 (t, $J = 7.6$ Hz, 3H), 0.94 (t, $J = 7.6$ Hz, 3H), 1.77 (m, 1H), 1.91 (q, 7.3 Hz, 2H), 1.98 (quint, $J = 7.3$ Hz, 2H), 2.15 (dd, $J = 14.2, 8.9$ Hz, 1H), 2.46 (dd, $J = 14.2, 6.1$ Hz, 1H), 2.73 (dd, $J = 14.2, 7.6$ Hz, 1H), 2.99 (dd, $J = 14.2, 6.1$ Hz, 1H), 5.22 (t, $J = 7.1$ Hz, 1H), 7.1-7.3 (m, aromatic protons, 5H).