

## Electronic Supplementary Information

### Cu-Catalyzed Regioselective Carbomagnesiation of Dienes and Enynes with *sec*- and *tert*-Alkyl Grignard Reagents

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#### Typical Experimental Procedures and Analytical Data of Products.

##### General

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a JEOL JNM-Alice 400 spectrometer (400 MHz and 100 MHz, respectively). Chemical shifts are given in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC Mass analyses (EI) were run using a SATURN GCMS-2000 operating in the electron impact mode (70 eV) equipped with a RTX-5 30MX.25MMX.25U column. The HPLC separation was performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using CHCl<sub>3</sub> as the eluent. Elemental analyses were performed on a Perkin Elmer 240C apparatus. Grignard reagents were used as purchased. NMR yields were determined using dioxane as an internal standard.

##### A Typical Procedure

###### 2,2-Dimethyl-hexadec-4-ene (4)

A solution of *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF was cooled to -78 °C under nitrogen and 1,3-butadiene (22.4 mL, 1.0 mmol) and a catalytic amount of Li<sub>2</sub>CuCl<sub>4</sub> (0.1 M, 0.1 mL, 0.01 mmol) was added to the solution at -78 °C, and the mixture was stirred for 3 h at 25 °C. Then decyl bromide (332.1 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, ca. 2 mL of 1 N HCl(aq) was added to the solution at 0 °C, and the mixture was warmed to 25 °C. A saturated

aqueous  $\text{NH}_4\text{Cl}$  solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over  $\text{MgSO}_4$ , and evaporated to give a pale yellow crude product (87 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 207 mg (82 %) of **4**. IR (neat): 2955, 2924, 2854, 1466, 1364, 1240, 969  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.46-5.33 (m, 2H), 1.99 (q,  $J$  = 6.4 Hz, 2H), 1.85 (d,  $J$  = 6.4 Hz, 2H), 1.34-1.26 (m, 18H), 0.89 (t,  $J$  = 2.8 Hz, 3H), 0.86 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 132.6, 127.0, 47.2, 42.2, 32.8, 32.1, 29.82, 29.79, 29.65, 29.50, 29.41, 29.39, 29.29, 29.4, 22.9, 14.3; MS (EI)  $m/z$  (relative intensity, %) 252 ( $\text{M}^+$ , 3), 196 (12), 111 (4), 97 (6), 83 (6), 69 (7), 57(100), 41(8); HR-MS: calcd for  $\text{C}_{18}\text{H}_{36}$ (M) 252.2817, found 252.2807; elemental analysis: calcd for  $\text{C}_{18}\text{H}_{36}$ : C, 85.63; H, 14.37. found: C, 85.65; H, 14.08.

#### **Tributyl-(5,5-dimethyl-hex-2-enyl)-silane (5)**

A solution of *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF was cooled to  $-78$  °C under nitrogen and 1,3-butadiene (22.4 mL, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added to the solution at  $-78$  °C, and the mixture was stirred for 3 h at  $25$  °C. Then  $\text{Bu}_3\text{SiCl}$  (352.7 mg, 1.5 mmol) was added to the solution at  $0$  °C. After stirring for 1 h at  $25$  °C, similar workup as mentioned above afforded a pale yellow crude product (78 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 226.8 mg (73 %) of **5**. IR (neat): 2955, 1464, 1194, 965, 886, 762  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.38-5.23 (m, 2H), 1.84 (d,  $J$  = 6.4 Hz, 2H), 1.45 (d,  $J$  = 7.6 Hz, 2H), 1.35-1.24 (m, 12H), 0.88 (t,  $J$  = 6.8 Hz, 9H), 0.86 (s, 9H), 0.52 (t,  $J$  = 4.8 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 128.3, 125.6, 47.6, 31.1, 29.4, 27.0, 26.2, 18.7, 14.0, 12.1; MS (EI)  $m/z$  (relative intensity, %) 310 ( $\text{M}^+$ , 2), 253 (3), 199 (69), 143 (100), 101 (32), 87 (27), 59 (26); HR-MS: calcd for  $\text{C}_{20}\text{H}_{42}\text{Si}$ (M) 310.3056, found 310.3061; elemental analysis: calcd for  $\text{C}_{20}\text{H}_{42}\text{Si}$ : C, 77.33; H, 13.63. found: C, 77.38; H, 13.61.

#### **1-[1-(2,2-Dimethyl-propyl)-allyl]-cyclohex-2-enol (6)**

A solution of *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF was cooled to  $-78$  °C under nitrogen and 1,3-butadiene (22.4 mL, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added to the solution at  $-78$  °C, and the mixture was stirred for 3 h at  $25$  °C. Then cyclohexenone (144.6 mg, 1.5 mmol) was added to the solution at  $0$  °C. After stirring for 1 h at  $25$  °C, similar workup as mentioned above afforded a pale yellow crude product (72 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 143.8 mg (69 %) of **6**. IR (neat): 3466, 2952,

1706, 1636, 1475, 1365, 1166, 977  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.97-5.81 (m, 1H), 5.77-5.66 (m, 1H), 5.60-5.45 (m, 1H), 5.22-5.08 (m, 2H), 2.22-2.15 (m, 1H), 2.05-1.96 (m, 2H), 1.79 (s, 1H), 1.67-1.48 (m, 4H), 1.27-1.21 (m, 2H), 0.89 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 140.8, 130.9, 130.1, 117.4, 70.7, 50.5, 42.1, 32.8, 31.1, 30.2, 25.2, 18.7; MS (EI)  $m/z$  (relative intensity, %) 208 ( $\text{M}^+$ , 1), 191 (3), 175 (3), 137 (2), 119 (3), 105 (2), 97 (100), 79 (10), 67 (7), 55 (8), 41 (13); HR-MS: calcd for  $\text{C}_{14}\text{H}_{24}\text{O}$  (M) 208.1827, found 208.1822; elemental analysis: calcd for  $\text{C}_{14}\text{H}_{24}\text{O}$ : C, 80.71; H, 11.61. found: C, 80.65; H, 11.77.

### **2-(2,2-Dimethyl-propyl)-2,3-dimethyl-1-phenyl-but-3-en-1-one (7)**

To a mixture of 2,3-dimethyl-1,3-butadiene (82.5 mg, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then benzoyl chloride (210.9 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (73 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 168.6 mg (69 %) of **7**. IR (neat): 2952, 2360, 1676, 1632, 1446, 1234, 1197, 961, 882, 700  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.90 (d,  $J$  = 6.8 Hz, 2H), 7.44 (t,  $J$  = 7.2 Hz, 1H), 7.34 (t,  $J$  = 7.6 Hz, 2H), 5.15 (s, 1H), 5.04 (s, 1H), 2.57 (d,  $J$  = 14.8 Hz, 2H), 1.89 (d,  $J$  = 14.8 Hz, 1H), 1.73 (s, 9H), 1.48 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 204.6, 149.6, 138.2, 131.4, 128.7, 127.8, 111.7, 56.7, 49.3, 32.0, 24.3, 20.9; MS (EI)  $m/z$  (relative intensity, %) 244 ( $\text{M}^+$ , 5), 188 (18), 170 (13), 106 (12), 105 (100), 77 (23), 57 (18); HR-MS: calcd for  $\text{C}_{17}\text{H}_{24}\text{O}$  (M) 244.1827, found 244.1826; elemental analysis: calcd for  $\text{C}_{17}\text{H}_{24}\text{O}$ : C, 83.55; H, 9.90. found: C, 83.28; H, 9.67.

### **Triethyl-(2,3,5-trimethyl-hept-2-enyl)-silane (9)**

To a mixture of 2,3-dimethyl-1,3-butadiene (82.5 mg, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *sec*-BuMgCl (0.7 M, 2.2 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then  $\text{Et}_3\text{SiCl}$  (226.1 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (85 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 198.5 mg (78 %) of **9**. IR (neat): 2955, 2875, 1461, 1416, 1376, 1238, 1166, 1074, 1016, 774, 738  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.97 (dd,  $J$  = 13.4, 6.2 Hz, 1H), 1.86 (dd,  $J$  = 13.4, 8.3 Hz, 1H), 1.63 (s, 3H), 1.58 (s, 3H), 1.54 (d,  $J$  = 2.7 Hz, 2H), 1.50-1.45 (m, 1H), 1.39-1.32 (m, 1H), 1.15-1.04 (m, 1H), 0.95 (t,  $J$  = 7.8 Hz, 9H), 0.88 (t,  $J$  = 7.3 Hz, 3H), 0.82 (d,  $J$  = 6.6 Hz, 3H), 0.54 (q,  $J$  = 7.8, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 126.8, 124.6, 42.3, 34.5, 30.2, 21.6, 21.1, 19.9, 19.6, 12.3, 8.0, 4.7; MS (EI)  $m/z$  (relative intensity, %) 254 ( $\text{M}^+$ , 13), 225 (1), 197 (5), 183 (1), 169 (2), 155 (1),

139 (1), 127 (1), 115 (100), 87 (65), 73 (2), 59 (16); HR-MS: calcd for C<sub>16</sub>H<sub>34</sub>Si(M) 254.2430, found 254.2423.

#### General Procedure for the Preparation of Enynes

Vinyl bromide (1.0 M, 30 mL, 30 mmol) in THF was added to a solution 1-Alkynes (20 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (280 mg, 0.4 mmol) and CuI (152 mg, 0.8 mmol) in Et<sub>3</sub>N (20 mL) at 25 °C. After stirring for 3 h at 25 °C, 1 N HCl<sub>aq</sub> was added to the solution. A saturated aqueous NH<sub>4</sub>Cl solution (30 mL) was added, and the product was extracted with ether (30 mL). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under vacuum. Purification by column chromatography with hexane afforded the corresponding enynes as an oil.

#### But-3-en-1-ynyl-triisopropyl-silane (21)

Vinyl bromide (1.0 M, 30 mL, 30 mmol) in THF was added to a solution triisopropylsilylacetylene (3.8 g, 20 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (280.5 mg, 0.4 mmol) and CuI (152.3 mg, 0.8 mmol) in Et<sub>3</sub>N (20 mL) at 25 °C. After stirring for 3 h at 25 °C, 1 N HCl<sub>aq</sub> was added to the solution. A saturated aqueous NH<sub>4</sub>Cl solution (30 mL) was added, and the product was extracted with ether (30 mL). The organic layer was dried over MgSO<sub>4</sub>, and concentrated under vacuum. Purification by column chromatography with hexane afforded 3.8 g (92%) of **21**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 5.84 (dd, *J* = 11.2, 17.6 Hz, 1H), 5.68 (dd, *J* = 17.6, 2.4 Hz, 1 H), 5.49 (dd, *J* = 11.1, 2.4 Hz, 1H), 1.09-1.08 (m, 21H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 127.6, 117.5, 105.7, 91.4, 18.6, 11.2; MS (EI) *m/z* (relative intensity, %) 208 (M<sup>+</sup>, 12), 165 (100), 149 (1), 137 (39), 123 (30), 109 (52), 95 (55), 79 (8); HR-MS: calcd for C<sub>13</sub>H<sub>24</sub>Si (M) 208.1647, found 208.1649; elemental analysis: calcd for C<sub>13</sub>H<sub>24</sub>Si: C, 74.92; H, 11.61. found: C, 75.14; H, 11.33

#### (5,5-Dimethyl-1-phenyl-hexa-1,2-dienyl)-triethyl-silane (14)

To a mixture of but-3-en-1-ynyl-benzene (128.2 mg, 1.0 mmol) and a catalytic amount of Li<sub>2</sub>CuCl<sub>4</sub> (0.1 M, 0.1 mL, 0.01 mmol) was added *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then Et<sub>3</sub>SiCl (226.1 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (98 % NMR yield). Purification by HPLC with CHCl<sub>3</sub> as an eluent afforded 285.5 mg (95 %) of **14**. IR (neat): 3053, 2950, 2873, 1924, 1595, 1489, 1444, 1363, 1240, 1006, 756, 734, 704, 695 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.28-7.12 (m, 5H), 5.06 (t, *J* = 8.0 Hz, 1H), 2.00 (d, *J* = 8.0 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 9H), 0.93 (s, 9H), 0.73 (q, *J* = 7.6 Hz, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 209.8, 138.7, 128.1, 127.5, 125.6, 95.4, 83.0, 43.7, 31.2, 29.3, 7.6, 4.2; MS (EI) *m/z*

(relative intensity, %) 300 ( $M^+$ , 4), 272(17), 243(4), 215(5), 187(8), 159(5), 131(9), 115(100), 87(67), 59(18); HR-MS: calcd for  $C_{20}H_{32}Si(M)$  300.2273, found 300.2271; elemental analysis: calcd for  $C_{20}H_{32}Si$ : C, 79.92; H, 10.73. found: C, 80.03; H, 10.61

#### Triethyl-(5-methyl-1-phenyl-hexa-1,2-dienyl)-silane (15)

To a mixture of but-3-en-1-ynyl-benzene (128.2 mg, 1.0 mmol) and a catalytic amount of  $Li_2CuCl_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *i*-PrMgBr (0.6 M, 2.7 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then  $Et_3SiCl$  (226.1 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (83 % NMR yield). Purification by HPLC with  $CHCl_3$  as an eluent afforded 226.4 mg (79 %) of **15**. IR (neat): 3436, 3058, 2956, 2874, 1925, 1706, 1597, 1490, 1465, 1380, 1239, 1005, 910, 827, 734, 696  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.27-7.14 (m, 5H), 5.06 (t,  $J$  = 7.6 Hz, 1H), 1.99 (td,  $J$  = 7.1, 2.3 Hz, 2H), 1.74-1.64 (m, 1H), 0.95 (t,  $J$  = 7.8 Hz, 9H), 0.94 (d,  $J$  = 7.6 Hz, 6H), 0.72 (q,  $J$  = 7.9 Hz, 6H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 209.7, 138.8, 128.3, 127.6, 125.8, 96.0, 84.8, 38.0, 29.0, 22.4, 7.3, 4.1; MS (EI)  $m/z$  (relative intensity, %) 286 ( $M^+$ , 1), 257 (46), 229 (4), 215 (1), 187 (12), 163 (20), 159 (11), 135 (5), 131 (17), 115 (100), 105 (5), 87 (98), 59 (27); HR-MS: calcd for  $C_{19}H_{30}Si(M)$  286.2117, found 286.2108

#### 4-Hexyl-8-methyl-nona-1,4,5-triene (17)

To a mixture of dec-1-en-3-yne (136.5 mg, 1.0 mmol) and a catalytic amount of  $Li_2CuCl_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *i*-PrMgBr (0.6 M, 2.7 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then allyl bromide (181.5 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (73 % NMR yield). Purification by HPLC with  $CHCl_3$  as an eluent afforded 143.3 mg (65 %) of **17**. IR (neat): 3400, 3078, 2956, 2871, 1963, 1724, 1638, 1466, 1382, 1367, 1168, 991, 912, 835, 724  $cm^{-1}$ ;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 5.86-5.76 (m, 1H), 5.06-4.98 (m, 3H), 2.69 (d,  $J$  = 5.9 Hz, 2H), 1.94-1.84 (m, 4H), 1.68-1.58 (m, 1H), 1.40-1.28 (m, 8H), 0.93 (d,  $J$  = 14.6 Hz, 6H), 0.88 (t,  $J$  = 6.8 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 201.8, 136.6, 115.3, 101.8, 90.4, 90.3, 39.0, 37.8, 32.2, 31.8, 29.0, 28.6, 27.6, 22.7, 14.1; MS (EI)  $m/z$  (relative intensity, %) 220 ( $M^+$ , 1), 205 (1), 191 (1), 177 (28), 163 (6), 150 (25), 135 (29), 121 (19), 107 (80), 93 (93), 79 (100), 67 (29), 55 (20); HR-MS: calcd for  $C_{16}H_{28}(M)$  220.2191, found 220.2194

#### **(1-Allyl-5,5-dimethyl-hexa-1,2-dienyl)-trimethyl-silane (19)**

To a mixture of but-3-en-1-ynyl-trimethyl-silane (124.3 mg, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then allyl bromide (181.5 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (99 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 143.3 mg (98 %) of **19**. IR (neat): 4378, 3880, 3326, 2954, 2348, 1936, 1638, 1474, 1388, 1364, 1248, 992, 910, 838, 754, 628  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.80-5.71 (m, 1H), 4.97-4.87 (m, 2H), 4.73-4.69 (m, 1H), 2.65-2.63 (m, 2H), 1.88 (d,  $J$  = 7.8 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 207.3, 137.7, 114.7, 93.3, 82.5, 43.7, 34.5, 31.0, 29.3, -1.3; MS (EI)  $m/z$  (relative intensity, %) 222 ( $\text{M}^+$ , 1), 179 (1), 165 (20), 148 (1), 137 (2), 123 (2), 109 (3), 91 (1), 73 (100), 57 (8); HR-MS: calcd for  $\text{C}_{14}\text{H}_{26}\text{Si}$ (M) 222.1804, found 222.1799.

#### **5-Methyl-3-tributylsilanyl-1-trimethylsilanyl-hept-1-yne (20)**

To a mixture of but-3-en-1-ynyl-trimethyl-silane (124.3 mg, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *sec*-BuMgCl (0.7 M, 2.1 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then  $\text{Bu}_3\text{SiCl}$  (352.3 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (93 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 327.5 mg (86 %) of **20**. IR (neat): 4331, 3592, 2958, 2873, 2596, 2157, 1814, 1464, 1410, 1377, 1248, 1195, 1082, 1000, 964, 873, 841, 759, 733, 656  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.87-1.82 (m, 1H), 1.53-1.48 (m, 1H), 1.37-1.22 (m, 16H), 0.93-0.83 (m, 15H), 0.65-0.60 (m, 6H), 0.12 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 110.3, 83.7, 35.6, 33.3, 30.0, 26.5, 25.7, 17.7, 15.7, 15.1, 13.5, 10.8, -0.01; MS (EI)  $m/z$  (relative intensity, %) 380 ( $\text{M}^+$ , 2), 323 (7), 310 (1), 267 (6), 254 (1), 245 (1), 211 (3), 199 (51), 183 (2), 166 (2), 143 (100), 127 (7), 109 (5), 87 (17), 73 (16), 59 (25); HR-MS: calcd for  $\text{C}_{23}\text{H}_{48}\text{Si}_2$ (M) 380.3295, found 380.3290.

#### **5,5-Dimethyl-3-triethylsilanyl-1-triisopropylsilanyl-hex-1-yne (22)**

To a mixture of but-3-en-1-ynyl-triisopropyl-silane (208.4 mg, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then  $\text{Et}_3\text{SiCl}$  (226.1 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (74 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 258.9 mg (68 %) of **22**.

IR (neat): 4099, 3522, 2953, 2865, 2360, 2151, 1732, 1464, 1416, 1365, 1241, 1103, 1072, 1017, 919, 883, 766, 718, 675, 620  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.85 (d,  $J$  = 11.2 Hz, 1H), 1.46 (t,  $J$  = 11.2 Hz, 1H), 1.31 (d,  $J$  = 14.0 Hz, 1H), 1.05-0.96 (m, 39H), 0.73-0.61 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 113.0, 79.5, 43.3, 32.5, 29.7, 18.6, 13.3, 11.5, 7.6, 2.3; MS (EI)  $m/z$  (relative intensity, %) 380 ( $\text{M}^+$ , 4), 351 (5), 337 (57), 323 (1), 309 (1), 295 (2), 267 (1), 253 (9), 239 (1), 225 (6), 211 (3), 197 (3), 183 (4), 157 (100), 129 (9), 115 (86), 101 (1), 87 (50), 73 (14); HR-MS: calcd for  $\text{C}_{23}\text{H}_{48}\text{Si}_2(\text{M})$  380.3295, found 380.3289; elemental analysis: calcd for  $\text{C}_{23}\text{H}_{48}\text{Si}_2$ : C, 72.54; H, 12.71. found: C, 72.54; H, 12.71.

#### **Triethyl-(1-ethyl-3,5,5-trimethyl-hexa-1,2-dienyl)-silane (24)**

To a mixture of 2-methyl-1-hexen-3-yne (94.2 mg, 1.0 mmol) and a catalytic amount of  $\text{Li}_2\text{CuCl}_4$  (0.1 M, 0.1 mL, 0.01 mmol) was added *tert*-BuMgCl (0.8 M, 1.9 mL, 1.5 mmol) in THF, and the mixture was stirred for 3 h at 25 °C. Then  $\text{Et}_3\text{SiCl}$  (226.1 mg, 1.5 mmol) was added to the solution at 0 °C. After stirring for 1 h at 25 °C, similar workup as mentioned above afforded a pale yellow crude product (85 % NMR yield). Purification by HPLC with  $\text{CHCl}_3$  as an eluent afforded 207.9 mg (78 %) of **24**. IR (neat): 2953, 2910, 2874, 1931, 1476, 1464, 1416, 1362, 1311, 1238, 1200, 1085, 1054, 1008, 973, 924, 733, 703  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.96-1.90 (m, 2H), 1.73 (s, 2H), 1.67 (s, 3H), 1.02 (t,  $J$  = 7.3 Hz, 3H), 0.94 (s, 9H), 0.93 (t,  $J$  = 7.8 Hz, 9H), 0.56 (t,  $J$  = 7.8 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 206.8, 92.4, 91.3, 48.6, 31.2, 29.9, 23.5, 21.8, 14.1, 7.5, 3.3; MS (EI)  $m/z$  (relative intensity, %) 266 ( $\text{M}^+$ , 31), 237 (7), 209 (22), 181 (12), 151 (3), 139 (35), 115 (100), 87 (55), 59 (10), 41 (2); HR-MS: calcd for  $\text{C}_{17}\text{H}_{34}\text{Si}(\text{M})$  266.2430, found 266.2439; elemental analysis: calcd for  $\text{C}_{17}\text{H}_{34}\text{Si}$ : C, 76.61; H, 12.86. found: C, 76.62; H, 13.13.