**Highly Regio- and Stereoselective Acylboration, Acylsilation,
and Acylstannation of Allenes Catalyzed by Phosphine-Free
Palladium-Complexes: An Efficient Route to a New Class of
2-Acylallylmetal Reagents**

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Supporting Information

Spectral data of compounds **4a-t**, **6a-p**, **7a-c**, **9a-d**, **11a-j**, and **12a-c** are shown below.

3-Methyl-1-(4-methylphenyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4a). ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 8.4$ Hz, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 2.40 (s, 3H), 1.92 (s, 2H), 1.80 (s, 3H), 1.55 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.22, 143.33, 135.14, 132.77, 130.82, 129.75, 129.03, 83.30, 24.72, 22.91, 21.64, 20.83; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{27}\text{BO}_3$ (M^+) 314.2053, found 314.2057.

3-Methyl-1-phenyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4b). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 6.8$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 7.2$ Hz, 2H), 1.93 (s, 2H), 1.82 (s, 3H), 1.56 (s, 3H), 1.19 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.38, 137.82, 133.39, 132.51, 130.80, 129.53, 128.27, 83.30, 24.70, 22.94, 20.91; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{26}\text{BO}_3$ ($\text{M}^+ + \text{H}$) 301.1975, found 301.1969.

1-(2-Methoxyphenyl)-3-methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4c). ^1H NMR (400 MHz, CDCl_3) δ 7.52 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.39 - 7.35 (m, 1H), 6.95 - 6.89 (m, 2H), 3.81 (s, 3H), 1.90 (s, 2H), 1.80 (s, 3H), 1.63 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.44, 157.53, 138.55, 133.53, 132.00, 130.56, 130.33, 120.21, 111.59, 83.04, 55.74, 24.73, 22.73, 22.62; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{28}\text{BO}_4$ ($\text{M}^+ + \text{H}$) 331.2081, found 331.2080.

1-(3-Methoxyphenyl)-3-methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4d). ^1H NMR (400 MHz, CDCl_3) δ 7.54 (dd, $J = 8.0, 1.6$ Hz, 1H), 7.50 - 7.49 (m, 1H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.08 - 7.05 (m, 1H), 3.85 (s, 3H), 1.93 (s, 2H), 1.81 (s, 3H), 1.57 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.23, 159.70, 139.16, 133.43, 130.77, 129.27, 122.47, 119.18, 113.34, 83.31, 59.35, 24.70, 22.93, 20.89; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{28}\text{BO}_4$ ($\text{M}^+ + \text{H}$) 331.2081, found 331.2083.

1-(4-Methoxyphenyl)-3-methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4e). ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.8$ Hz, 2H), 6.90 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 3H), 1.92 (s, 2H), 1.80 (s, 3H), 1.56 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.30, 163.28, 131.97, 131.89, 130.71, 130.48, 113.47, 83.27, 55.35, 24.70, 22.77, 20.65; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{28}\text{BO}_4$ ($\text{M}^+ + \text{H}$) 331.2081, found 331.2080.

Methyl

4-{3-methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-butenoyl} benzoate (4f). ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.8$ Hz, 2H), 7.98 (d, $J = 8.8$ Hz, 2H), 3.95 (s, 3H), 1.96 (s, 2H), 1.83 (s, 3H), 1.55 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.65, 166.41, 141.65, 135.11, 133.20, 130.68, 129.53, 129.24, 83.37, 52.29, 24.67, 23.15, 21.15; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{28}\text{BO}_5$ ($\text{M}^+ + \text{H}$) 359.2029, found 359.2029.

3-Methyl-1-(4-nitrophenyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4g). ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 8.8$ Hz, 2H), 8.09 (d, $J = 8.8$ Hz, 2H), 1.96 (s, 2H), 1.85 (s, 3H), 1.55 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.44, 149.92, 143.21, 136.35, 130.50, 130.24, 123.55, 83.51, 24.70, 23.35, 21.30; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{25}\text{BNO}_5$ ($\text{M}^+ + \text{H}$) 346.1826, found 346.1828.

3-Methyl-1-(1-naphthyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4h). ^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 7.2$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.2$ Hz, 1H), 7.43 (t, $J = 8.0$ Hz, 1H), 2.04 (s, 2H), 1.85 (s, 3H), 1.54 (s, 3H), 1.21 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.85, 139.05, 137.25, 133.85, 133.67, 131.67, 130.35, 128.83, 128.13, 127.33, 126.08, 125.85, 124.50, 83.15, 24.67, 13.12, 22.36; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{28}\text{BO}_3$ ($\text{M}^+ + \text{H}$)

351.2131, found 351.2111.

3-Methyl-1-(2-naphthyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4i). ^1H NMR (400 MHz, CDCl_3) δ 8.49 (s, 1H), 8.02 (d, $J = 8.8$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.8$ Hz, 1H), 7.58 - 7.49 (m, 3H), 1.99 (s, 2H), 1.84 (s, 3H), 1.56 (s, 3H), 1.17 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.62, 135.52, 135.13, 133.40, 132.71, 131.85, 130.91, 129.51, 128.18, 128.16, 127.77, 126.40, 124.94, 83.37, 24.76, 23.03, 20.98; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{28}\text{BO}_3$ ($\text{M}^+ + \text{H}$) 351.2131, found 351.2111.

3-Methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-(2-thienyl)-2-buten-1-one (4j). ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 5.2$ Hz, 1H), 7.64 (d, $J = 6.0$ Hz, 1H), 7.09 (dd, $J = 5.2, 6.0$ Hz, 1H), 1.95 (s, 2H), 1.79 (s, 3H), 1.66 (s, 3H), 1.20 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.83, 144.64, 134.50, 134.02, 132.38, 130.68, 127.77, 83.31, 24.64, 22.88, 20.54; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{24}\text{BO}_3\text{S}$ ($\text{M}^+ + \text{H}$) 307.1539, found 307.1526.

1-(5-Isoxazolyl)-3-methyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-buten-1-one (4k). ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 1.6$ Hz, 1H), 6.87 (d, $J = 1.6$ Hz, 1H), 1.96 (s, 2H), 1.83 (s, 3H), 1.70 (s, 3H), 1.17 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 186.79, 167.00, 150.42, 140.19, 130.13, 107.62, 83.52, 24.64, 22.89, 21.79; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{23}\text{BNO}_4$ ($\text{M}^+ + \text{H}$) 292.1720, found 292.1720.

2,6,6-Trimethyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-hepten-4-one (4l). ^1H NMR (400 MHz, CDCl_3) δ 2.47 (s, 2H), 1.82 (s, 3H), 1.77 (s, 2H), 1.71 (s, 3H), 1.24 (s, 12H), 1.02 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.10, 134.29, 133.96, 83.28, 53.41, 31.36, 29.75, 24.75, 22.34, 21.68; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{31}\text{BO}_3$ (M^+) 294.2366, found 294.2362.

2,6-Dimethyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-hept

en-4-one (4m). ^1H NMR (400 MHz, CDCl_3) δ 2.44 (d, $J = 7.2$ Hz, 2H), 2.24 - 2.13 (m, 1H), 1.84 (s, 3H), 1.78 (s, 2H), 1.73 (s, 3H), 1.24 (s, 12H), 0.92 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.72, 135.31, 133.42, 83.28, 50.80, 24.73, 24.65, 22.73, 22.44, 21.96; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{30}\text{BO}_3$ ($\text{M}^+ + \text{H}$) 281.2288, found 281.2270.

4-Methyl-1-phenyl-3-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-3-penten-2-one (4n). ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.19 (m, 5H), 3.88 (s, 2H), 1.86 (s, 2H), 1.78 (s, 3H), 1.73 (s, 3H), 1.27 (s, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ 204.78, 136.29, 134.93, 132.50, 129.63, 128.33, 1263.57, 83.49, 48.37, 24.76, 22.58, 21.82; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{28}\text{BO}_3$ ($\text{M}^+ + \text{H}$) 315.2131, found 315.2131.

(E)-2,2-Dimethyl-5-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-5-decen-4-one (4o). ^1H NMR (400 MHz, CDCl_3) δ 6.56 (t, $J = 7.2$ Hz, 1H), 2.55 (s, 2H), 2.24 (q, $J = 7.2$ Hz, 2H), 1.69 (s, 2H), 1.48 - 1.42 (m, 2H), 1.41 - 1.32 (m, 2H), 1.24 (s, 12H), 0.99 (s, 9H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.67, 142.17, 141.06, 82.87, 47.81, 31.26, 30.80, 30.06, 29.28, 24.72, 22.44, 13.85; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{35}\text{BO}_3$ (M^+) 322.2679, found 322.2680.

(E)-1-(4-Methoxyphenyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-hepten-1-one (4p). ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 6.16 (t, $J = 7.2$ Hz, 1H), 3.83 (s, 3H), 2.23 (q, $J = 7.2$ Hz, 2H), 1.92 (s, 2H), 1.42 - 1.25 (m, 4H), 1.22 (s, 12H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.91, 162.22, 143.80, 138.42, 131.71, 131.16, 113.13, 83.17, 55.35, 30.89, 29.01, 24.75, 22.53, 13.91; HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{31}\text{BO}_4$ 358.2315 (M^+) found 358.2312.

(E)-1-(1-Naphthyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-hepten-1-one (4q). ^1H NMR (400 MHz, CDCl_3) δ 8.04 - 8.02 (m, 1H), 7.89 - 7.83 (m, 2H), 7.49 - 7.41 (m, 4H), 6.27 (t, $J = 7.2$ Hz, 1H), 2.22 (q, $J = 7.2$ Hz, 2H), 2.02 (s,

2H), 1.31 (s, 12H), 1.31 - 1.20 (m, 4H), 0.83 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.44, 149.00, 140.75, 137.78, 133.36, 131.06, 129.43, 127.98, 126.34, 125.99, 125.47, 124.33, 83.26, 30.39, 29.25, 24.81, 22.32, 13.73; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{32}\text{BO}_3$ ($\text{M}^+ + \text{H}$) 379.2444, found 379.2443.

(*E*)-5,5-Dimethyl-1-phenyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-hexen-3-one (4r). ^1H NMR (400 MHz, CDCl_3) δ 7.49 (s, 1 H), 7.44 - 7.26 (m, 5H), 2.71 (s, 2H), 1.97 (s, 2H), 1.25 (s, 12H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.40, 141.60, 138.19, 136.43, 129.44, 128.28, 128.18, 83.02, 48.16, 31.47, 30.09, 24.73; HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{31}\text{BO}_3$ (M^+) 342.2366, found 342.2378.

(*E*)-1-Cyclohexyl-5,5-dimethyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-1-hexen-3-one (4s). ^1H NMR (400 MHz, CDCl_3) δ 6.37 (d, $J = 8.8$ Hz, 1H), 2.54 (s, 2H), 2.40 - 2.29 (m, 1H), 1.71 (s, 2H), 1.80 - 1.64 (m, 4H), 1.23 (s, 12H), 1.40 - 1.12 (m, 6H), 0.99 (s, 9 H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.08, 147.19, 139.04, 82.81, 47.90, 38.61, 31.89, 31.18, 30.09, 25.87, 25.55, 24.72; HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{37}\text{BO}_3$ (M^+) 348.2836, found 348.2854.

(*E*)-4,4-Dimethyl-1-(4-methylphenyl)-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]-2-penten-1-one (4t). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.18 (s, 1H), 2.40 (s, 3H), 2.12 (s, 2H), 1.24 (s, 12H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 200.21, 152.89, 141.60, 137.34, 136.02, 129.86, 128.50, 83.14, 33.52, 30.29, 24.73, 21.48; HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{32}\text{BO}_3$ ($\text{M}^+ + \text{H}$) 343.2444, found 343.2443.

3-Methyl-1-phenyl-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6a). ^1H NMR (300 MHz, CDCl_3): δ 7.85 (d, $J = 7.2$ Hz, 2H), 7.51 (t, $J = 7.2$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 2H), 1.77 (s, 2H), 1.76 (s, 3H), 1.56 (s, 3H), -0.04 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.35, 137.25, 132.69, 132.36, 130.11, 129.38, 128.50, 22.62, 21.82,

20.76, -0.95; HRMS (FAB) calcd for $C_{15}H_{22}OSi$ (M^+) 246.1440, found 246.1438.

1-(4-Methoxyphenyl)-3-methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6b). 1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, $J = 8.8$ Hz, 2H), 6.89 (d, $J = 8.8$ Hz, 2H), 3.83 (s, 3H), 1.75 (s, 2H), 1.73 (s, 3H), 1.54 (s, 3H), -0.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.11, 163.29, 132.40, 131.67, 130.10, 128.83, 113.68, 55.36, 22.54, 21.96, 20.61, -0.91; HRMS (FAB) calcd for $C_{16}H_{24}O_2Si$ (M^+) 276.1546, found 276.1548.

1-(2-Furyl)-3-methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6c). 1H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, $J = 3.6$ Hz, 1H), 7.07 (d, $J = 3.6$ Hz, 1H), 6.49 (t, $J = 3.6$ Hz, 1H), 1.81 (s, 2H), 1.72 (s, 3H), 1.61 (s, 3H), -0.05 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.07, 153.01, 146.53, 131.78, 131.12, 118.74, 112.15, 22.54, 21.67, 21.01, -1.05; HRMS (FAB) calcd for $C_{13}H_{20}O_2Si$ (M^+) 236.1233, found 236.1229.

3-Methyl-1-(4-methylphenyl)-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6d). 1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 2.37 (s, 3H), 1.76 (s, 2H), 1.74 (s, 3H), 1.55 (s, 3H), -0.04 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.12, 143.51, 134.76, 132.59, 129.62, 129.44, 129.30, 22.58, 21.69, 21.60, 20.67, -0.93; HRMS (FAB) calcd for $C_{16}H_{24}OSi$ (M^+) 260.1596, found 260.1596.

3-Methyl-1-(4-nitrophenyl)-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6e). 1H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, $J = 8.8$ Hz, 2H), 7.79 (d, $J = 8.8$ Hz, 2H), 1.80 (s, 3H), 1.77 (s, 2H), 1.58 (s, 3H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 199.19, 150.11, 142.24, 132.60, 131.67, 130.16, 123.67, 22.66, 21.75, 21.11, -0.94; HRMS (FAB) calcd for $C_{15}H_{21}NO_3Si$ (M^+) 291.1291, found 291.1293.

3-Methyl-1-(3-nitrophenyl)-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one

(6f). ^1H NMR (300 MHz, CDCl_3): δ 8.63 (s, 1H), 8.36 (d, $J = 8.0$ Hz, 1H), 8.18 (d, $J = 7.2$ Hz, 1H), 7.65 (t, $J = 8.0$ Hz, 1H), 1.81 (s, 3H), 1.78 (s, 2H), 1.59 (s, 3H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.64, 148.56, 138.27, 134.25, 132.39, 131.54, 129.85, 127.01, 124.20, 22.27, 21.60, 21.03, -0.02; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_3\text{Si}$ (M^+) 291.1291, found 291.1293.

3-Methyl-1-(2-naphthyl)-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6g).

^1H NMR (300 MHz, CDCl_3): δ 8.35 (s, 1H), 7.97 – 7.85 (m, 4H), 7.58 – 7.50 (m, 2H), 1.85 (s, 2H), 1.82 (s, 3H), 1.60 (s, 3H), -0.01 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.36, 135.54, 134.58, 132.72, 132.76, 130.76, 130.11, 129.56, 128.39, 128.22, 127.76, 126.54, 124.96, 22.58, 21.97, 20.73, -0.98; HRMS (FAB) calcd for $\text{C}_{19}\text{H}_{24}\text{OSi}$ (M^+) 296.1596, found 296.1593.

3-Methyl-1-(2-thienyl)-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6h).

^1H NMR (300 MHz, CDCl_3): δ 7.59 (d, $J = 5.6$ Hz, 1H), 7.55 (d, $J = 3.6$ Hz, 1H), 7.05 (t, $J = 3.6$ Hz, 1H), 1.79 (s, 2H), 1.71 (s, 3H), 1.61 (s, 3H), -0.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3): δ 193.51, 144.56, 133.75, 133.32, 132.60, 129.23, 127.69, 22.74, 21.68, 20.50, -1.05; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{20}\text{OSSi}$ (M^+) 252.1004, found 252.1005.

1-(4-Chlorophenyl)-3-methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6i).

^1H NMR (300 MHz, CDCl_3): δ 7.66 (d, $J = 8.0$ Hz, 1H), 7.26 (d, $J = 8.0$ Hz, 1H), 1.62 (s, 5H), 1.42 (s, 3H), -0.17 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 199.87, 139.06, 135.57, 132.04, 130.72, 130.46, 126.84, 22.60, 21.79, 20.75, -0.96; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{21}\text{ClOSi}$ (M^+) 280.1050, found 280.1049.

1-(4-Bromophenyl)-3-methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-buten-1-one (6j).

^1H NMR (300 MHz, CDCl_3): δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.8$ Hz, 2H), 1.75 (s, 5H), 1.54 (s, 3H), -0.04 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.14,

136.01, 132.00, 131.87, 130.89, 130.70, 127.83, 22.68, 21.82, 20.82, -0.95; HRMS (FAB) calcd for $C_{15}H_{21}BrOSi$ (M^+) 324.0545, found 324.0544.

2,6,6-Trimethyl-3-[(1,1,1-trimethylsilyl)methyl]-2-hepten-4-one (6k). 1H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 2H), 1.72 (s, 3H), 1.68 (s, 2H), 1.63 (s, 3H), 1.02 (s, 9H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 206.94, 135.95, 128.74, 53.65, 31.05, 29.71, 21.63, 21.16, 20.22, -0.95; HRMS (FAB) calcd for $C_{14}H_{28}OSi$ (M^+) 240.1909, found 240.1912.

2,2,5-Trimethyl-4-[(1,1,1-trimethylsilyl)methyl]-4-hexen-3-one (6l). 1H NMR (300 MHz, $CDCl_3$): δ 1.58 (s, 2H), 1.57 (s, 3H), 1.52 (s, 3H), 1.15 (s, 9H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 218.19, 134.57, 123.49, 43.63, 28.06, 22.30, 20.61, 19.46, -0.91; HRMS (FAB) calcd for $C_{13}H_{26}OSi$ (M^+) 226.1753, found 226.1751.

2-Methyl-3-[(1,1,1-trimethylsilyl)methyl]-2-octen-4-one (6m). 1H NMR (300 MHz, $CDCl_3$): δ 2.47 (t, $J = 7.6$ Hz, 2H), 1.74 (s, 3H), 1.71 (s, 2H), 1.67 (s, 3H), 1.57 – 1.49 (m, 2H), 1.32 – 1.26 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H), -0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.55, 134.92, 130.03, 41.74, 26.29, 22.47, 22.03, 21.34, 19.99, 13.91, -1.02; HRMS (FAB) calcd for $C_{13}H_{26}OSi$ (M^+) 226.1753, found 226.1755.

(Z)-1-(Butyl)-3-phenyl-2-[(1,1,1-trimethylsilyl)methyl]-2-propen-1-one (6n). 1H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, $J = 8.0$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 6.06 (t, $J = 7.0$ Hz, 1H), 2.37 (s, 3H), 2.17 (q, $J = 7.2$ Hz, 2H), 1.99 (s, 2H), 1.36 – 1.29 (m, 4H), 0.87 (t, $J = 6.8$ Hz, 3H), 0.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.46, 142.66, 141.77, 139.08, 136.13, 129.58, 128.65, 30.98, 29.19, 21.46, 17.47, 17.42, 13.69, -0.95; HRMS (FAB) calcd for $C_{18}H_{28}OSi$ (M^+) 288.1909, found 288.1909.

(Z)-3-Cyclohexyl-1-(4-methylphenyl)-2-[(1,1,1-trimethylsilyl)methyl]-2-propen-1-one (6o). ^1H NMR (300 MHz, CDCl_3): δ 7.53 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 5.88 (d, J = 7.2 Hz, 1H), 2.36 (s, 3H), 2.34 (m, 1H), 1.99 (s, 2H), 1.75 – 1.65 (m, 5H), 1.35 – 1.02 (m, 5H), 0.01 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.63, 147.47, 141.70, 136.73, 136.03, 129.61, 128.56, 38.43, 31.98, 25.79, 25.54, 21.38, 17.17, -1.08; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{30}\text{OSi}$ (M^+) 314.2066, found 314.2065.

(Z)-1-(4-Methylphenyl)-3-phenyl-2-[(1,1,1-trimethylsilyl)methyl]-2-propen-1-one (6p). ^1H NMR (300 MHz, CDCl_3): δ 7.70 (d, J = 8.4 Hz, 2H), 7.41 – 7.18 (m, 7H), 6.99 (s, 1H), 2.42 (s, 3H), 2.38 (s, 2H), 0.05 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 199.11, 142.33, 140.58, 137.90, 136.45, 135.64, 129.84, 129.35, 129.25, 129.10, 121.73, 21.52, 18.49, -0.61; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{24}\text{OSi}$ (M^+) 308.1596, found 308.1593.

(E)-1-(4-methylphenyl)-3-phenyl-2-[(1,1,1-trimethylsilyl)methyl]-2-propen-1-one (6p). ^1H NMR (300 MHz, CDCl_3): δ 7.78 (d, J = 8.0 Hz, 2H), 7.21 – 7.00 (m, 7H), 6.55 (s, 1H), 2.31 (s, 3H), 1.93 (s, 2H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.25, 143.90, 140.04, 136.51, 133.03, 129.67, 129.16, 128.24, 128.10, 127.78, 126.76, 27.54, 21.55, -1.23; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{24}\text{OSi}$ (M^+) 308.1596, found 308.1599.

5-Methyl-2-(1-methylethylidene)-1-phenyl-4-[(1,1,1-trimethylsilyl)methyl]-4-hexen-1-one (7a). ^1H NMR (300 MHz, CDCl_3): δ 7.77 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.37 (t, J = 7.2 Hz, 2H), 3.05 (s, 2H), 1.85 (s, 3H), 1.55 (s, 3H), 1.41 (s, 2H), 1.31 (s, 3H), 1.25 (s, 3H), -0.03 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 202.15, 137.72, 133.86, 132.62, 131.09, 128.98, 128.14, 125.84, 123.66, 35.15, 22.54, 22.33, 21.05, 20.32, 20.03, -0.55; HRMS (FAB) calcd for $\text{C}_{20}\text{H}_{30}\text{OSi}$ (M^+) 314.2066, found

314.2067.

1-(4-Methoxyphenyl)-5-methyl-2-(1-methylethylidene)-4-[(1,1,1-trimethylsilyl)methyl]-4-hexen-1-one (7b). ^1H NMR (300 MHz, CDCl_3): δ 7.76 (d, $J = 8.8$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 3.82 (s, 3H), 3.03 (s, 2H), 1.83 (s, 3H), 1.52 (s, 3H), 1.41 (s, 2H), 1.34 (s, 3H), 1.27 (s, 3H), -0.02 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.84, 163.21, 133.86, 131.34, 130.94, 130.30, 125.99, 123.51, 113.31, 55.32, 35.25, 22.47, 22.40, 21.08, 20.39, 19.96, -0.58; HRMS (FAB) calcd for $\text{C}_{21}\text{H}_{32}\text{O}_2\text{Si}$ (M^+) 344.2172, found 344.2187.

1-(2-Furyl)-5-methyl-2-(1-methylethylidene)-4-[(1,1,1-trimethylsilyl)methyl]-4-hexen-1-one (7c). ^1H NMR (300 MHz, CDCl_3): δ 7.52 (d, $J = 4.0$ Hz, 1H), 6.93 (d, $J = 3.6$ Hz, 1H), 6.43 (dd, $J = 4.0, 3.6$ Hz, 1H), 3.04 (s, 2H), 1.80 (s, 3H), 1.59 (s, 3H), 1.42 (s, 3H), 1.40 (s, 2H), 1.34 (s, 3H), -0.04 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 189.18, 153.49, 146.53, 133.45, 132.40, 125.95, 123.37, 118.75, 112.37, 35.78, 22.84, 22.14, 21.19, 20.25, 20.14, -0.58; HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$ (M^+) 304.1859, found 304.1860.

Phenyl 3-Methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-butenolate (9a). ^1H NMR (300 MHz, CDCl_3): δ 7.37 (t, $J = 8.0$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.09 (d, $J = 8.0$ Hz, 2H), 2.09 (s, 3H), 1.95 (s, 2H), 1.82 (s, 3H), 0.05 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.88, 150.97, 141.62, 129.35, 125.48, 124.35, 121.23, 23.31, 23.11, 20.25, -0.89; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{Si}$ (M^+) 262.1389, found 262.1390.

Benzyl 3-Methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-butenolate (9b). ^1H NMR (300 MHz, CDCl_3): δ 7.39 – 7.27 (m, 5H), 5.12 (s, 2H), 1.95 (s, 3H), 1.81 (s, 2H), 1.71 (s, 3H), 0.06 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 169.83, 138.66, 136.35, 128.55, 128.50, 128.14, 125.07, 66.07, 22.88, 22.72, 20.28, -1.13; HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Si}$ (M^+) 276.1546, found 276.1545.

Butyl 3-Methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-butenate (9c). ^1H NMR (300 MHz, CDCl_3): δ 4.07 (t, $J = 7.0$ Hz, 2H), 1.93 (s, 3H), 1.78 (s, 2H), 1.64 (s, 3H), 1.66 – 1.59 (m, 2H), 1.41 – 1.35 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H), -0.03 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.23, 132.55, 125.33, 63.99, 30.74, 22.76, 22.56, 20.27, 19.35, 13.72, -1.10; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 242.1702, found 242.1702.

Isobutyl 3-Methyl-2-[(1,1,1-trimethylsilyl)methyl]-2-butenate (9d). ^1H NMR (300 MHz, CDCl_3): δ 3.84 (d, $J = 6.4$ Hz, 2H), 1.97 (m, 1H), 1.93 (s, 3H), 1.79 (s, 2H), 1.70 (s, 3H), 0.94 (d, $J = 4.8$ Hz, 6H), -0.03 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.19, 137.54, 125.27, 70.42, 27.67, 22.76, 22.53, 20.19, 19.31, -1.16; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{26}\text{O}_2\text{Si}$ (M^+) 242.1702, found 242.1701.

3-Methyl-1-(4-methylphenyl)-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one (11a). ^1H NMR (300 MHz, CDCl_3): δ 7.66 (d, $J = 8.8$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 2.41 (s, 3H), 1.84 (s, 2H), 1.76 (s, 3H), 1.54 (s, 3H), 1.49 – 1.29 (m, 6H), 1.28 – 1.25 (m, 6H), 0.89 – 0.82 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 201.34, 143.50, 134.79, 134.53, 129.53, 129.23, 124.94, 29.66, 27.35, 22.39, 21.64, 20.10, 14.09, 13.66, 10.16; HRMS (FAB) calcd for $\text{C}_{25}\text{H}_{43}\text{OSn}$ ($\text{M}^+ + \text{H}$) 477.2336, found 477.2340.

3-Methyl-1-(4-phenylacetate)-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one (11b). ^1H NMR (300 MHz, CDCl_3): δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H), 3.92 (s, 3H), 1.81 (s, 2H), 1.75 (s, 3H), 1.50 (s, 3H), 1.47 – 1.40 (m, 6H), 1.32 – 1.22 (m, 6H), 0.90 – 0.81 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.98, 166.43, 140.75, 134.98, 133.23, 130.27, 129.82, 129.14, 52.36, 29.03, 27.34, 22.59, 20.42, 14.11, 13.65, 10.19; HRMS (FAB) calcd for $\text{C}_{26}\text{H}_{43}\text{O}_3\text{Sn}$ ($\text{M}^+ + \text{H}$) 521.2334, found 521.2338.

3-Methyl-1-(4-nitrophenyl)-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one

ne (11c). ^1H NMR (300 MHz, CDCl_3): δ 8.26 (d, $J = 9.1$ Hz, 2H), 8.00 (d, $J = 9.1$ Hz, 2H), 1.81 (s, 2H), 1.79 (s, 3H), 1.52 (s, 3H), 1.48 – 1.39 (m, 6H), 1.38 – 1.19 (m, 6H), 0.96 – 0.82 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 199.56, 150.17, 142.12, 134.31, 130.15, 128.21, 123.87, 29.03, 27.84, 22.69, 20.53, 14.15, 13.66, 10.26; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{40}\text{NO}_3\text{Sn}$ ($\text{M}^+ + \text{H}$) 508.2030, found 508.2041.

3-Methyl-1-(3-nitrophenyl)-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one

ne (11d). ^1H NMR (300 MHz, CDCl_3): δ 8.64 (s, 1H), 8.38 (d, $J = 9.1$ Hz, 1H), 8.19 (d, $J = 7.8$ Hz, 1H), 7.63 (t, $J = 7.9$ Hz, 1H), 1.82 (s, 2H), 1.78 (s, 3H), 1.55 (s, 3H), 1.49 – 1.37 (m, 6H), 1.31 – 1.21 (m, 6H), 0.87 – 0.81 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 198.90, 148.60, 138.72, 134.71, 133.06, 129.81, 127.95, 127.04, 124.23, 29.03, 27.34, 22.64, 20.48, 14.13, 13.65, 10.23; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{40}\text{NO}_3\text{Sn}$ ($\text{M}^+ + \text{H}$) 508.2030, found 508.2035.

3-Methyl-1-(2-thienyl)-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one

(11e). ^1H NMR (300 MHz, CDCl_3): δ 7.61 (d, $J = 3.9$ Hz, 1H), 7.58 (d, $J = 2.7$ Hz, 1H), 7.08 (t, $J = 3.3$ Hz, 1H), 1.86 (s, 2H), 1.72 (s, 3H), 1.61 (s, 3H), 1.46 – 1.37 (m, 6H), 1.29 – 1.22 (m, 6H), 0.86 – 0.81 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 194.06, 144.54, 135.17, 133.92, 133.56, 128.00, 125.27, 29.14, 27.36, 22.75, 20.12, 14.10, 13.67, 10.17; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{39}\text{OSSn}$ ($\text{M}^+ + \text{H}$) 469.1743, found 469.1755.

1-(4-Chlorophenyl)-3-methyl-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one

one (11f). ^1H NMR (300 MHz, CDCl_3): δ 7.80 (d, $J = 6.7$ Hz, 2H), 7.39 (d, $J = 6.7$ Hz, 2H), 1.79 (s, 2H), 1.76 (s, 3H), 1.51 (s, 3H), 1.47 – 1.36 (m, 6H), 1.30 – 1.20 (m, 6H), 0.86 – 0.81 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 200.29, 139.16, 135.46, 134.41, 130.76, 128.87, 126.04, 29.04, 27.34, 22.46, 20.21, 14.08, 13.66, 10.20; HRMS (FAB)

calcd for $C_{24}H_{40}ClOSn$ ($M^+ + H$) 497.1789, found 497.1793.

1-(4-Bromophenyl)-3-methyl-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one (11g). 1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 1.79 (s, 2H), 1.76 (s, 3H), 1.51 (s, 3H), 1.47 – 1.38 (m, 6H), 1.31 – 1.19 (m, 6H), 0.91 – 0.77 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.52, 135.86, 134.33, 131.68, 130.90, 127.91, 126.20, 29.04, 27.36, 22.58, 20.25, 14.05, 13.68, 10.17; HRMS (FAB) calcd for $C_{24}H_{40}BrOSn$ ($M^+ + H$) 541.1284, found 541.1290.

3-Methyl-1-(2-naphthyl)-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-buten-1-one (11h). 1H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.98 – 7.84 (m, 4H), 7.59 – 7.48 (m, 2H), 1.90 (s, 2H), 1.82 (s, 3H), 1.55 (s, 3H), 1.48 – 1.37 (m, 6H), 1.31 – 1.19 (m, 6H), 0.93 – 0.74 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.79, 145.94, 141.71, 136.34, 133.88, 131.33, 130.90, 130.24, 129.14, 128.33, 125.95, 30.26, 29.35, 27.93, 25.54, 13.37, 12.91, 10.15; HRMS (FAB) calcd for $C_{28}H_{42}OSn$ (M^+) 512.2258, found 512.2265.

2,6,6-Trimethyl-3-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-hepten-4-one (11i). 1H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 2H), 1.68 (s, 3H), 1.65 (s, 2H), 1.59 (s, 3H), 1.40 – 1.46 (m, 6H), 1.29 – 1.24 (m, 6H), 0.99 (s, 9H), 0.87 – 0.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.83, 138.56, 125.11, 54.52, 31.18, 29.79, 29.02, 27.42, 21.86, 20.28, 13.69, 12.88, 10.24; HRMS (FAB) calcd for $C_{23}H_{47}OSn$ ($M^+ + H$) 457.2649, found 457.2653.

2,2,5-Trimethyl-4-[(1,1,1-tri-*n*-butylstannyl)methyl]-4-hexen-3-one (11j). 1H NMR (300 MHz, $CDCl_3$): δ 1.66 (s, 2H), 1.55 (s, 3H), 1.51 (s, 3H), 1.42 (m, 6H), 1.26 (m, 6H), 1.16 (s, 9H), 0.80 – 0.88 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 218.41, 136.45, 119.14, 43.59, 28.92, 27.96, 27.32, 22.27, 19.89, 13.60, 13.39, 10.02; HRMS (FAB) calcd for $C_{22}H_{45}OSn$ ($M^+ + H$) 443.2492, found 443.2497.

Phenyl 3-Methyl-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-butenolate (12a). ^1H NMR (300 MHz, CDCl_3): δ 7.39 – 7.17 (m, 3H), 7.05 (d, J = 8.1 Hz, 2H), 2.09 (s, 3H), 2.06 (s, 2H), 1.84 (s, 3H), 1.51 – 1.41 (m, 6H), 1.32 – 1.20 (m, 6H), 0.94 – 0.75 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.66, 150.93, 139.24, 129.33, 126.60, 125.47, 121.78, 28.98, 27.38, 23.11, 22.93, 13.64, 13.27, 8.66; HRMS (FAB) calcd for $\text{C}_{24}\text{H}_{41}\text{O}_2\text{Sn}$ ($\text{M}^+ + \text{H}$) 479.2128, found 479.2135.

Benzyl 3-Methyl-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-butenolate (12b). ^1H NMR (300 MHz, CDCl_3): δ 7.36 – 7.28 (m, 5H), 5.13 (s, 2H), 1.97 (s, 3H), 1.86 (s, 2H), 1.74 (s, 3H), 1.43 – 1.33 (m, 6H), 1.29 – 1.18 (m, 6H), 0.86 – 0.72 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 169.48, 136.34, 136.18, 128.44, 128.06, 127.22, 65.97, 29.04, 27.37, 22.74, 22.58, 13.67, 13.20, 10.00; HRMS (FAB) calcd for $\text{C}_{25}\text{H}_{43}\text{O}_2\text{Sn}$ ($\text{M}^+ + \text{H}$) 493.2285, found 493.2289.

Isobutyl 3-Methyl-2-[(1,1,1-tri-*n*-butylstannyl)methyl]-2-butenolate (12c). ^1H NMR (300 MHz, CDCl_3): δ 3.87 (d, J = 6.6 Hz, 2H), 1.97 (m, 1H), 1.95 (s, 3H), 1.87 (s, 2H), 1.71 (s, 3H), 1.46 – 1.40 (m, 6H), 1.31 – 1.22 (m, 6H), 0.93 (d, J = 5.4 Hz, 6H), 0.87 – 0.81 (m, 15H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.05, 134.79, 127.68, 70.45, 28.98, 27.68, 27.13, 22.72, 22.40, 19.35, 13.67, 13.24, 10.00; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{45}\text{O}_2\text{Sn}$ (MH^+) 459.2441, found 459.2452.

The stereochemistry of 2-acylallylboronates **4o-t** were established by typical ^1H NMR NOE experiments. For example, selective irradiation of the vinylic proton H_a at δ 6.56 in **4o** caused 7.44% enhancement of the signal for the methylene protons H_b at δ 2.55 and no enhancement of the signal for the H_c proton at δ 1.69. Irradiation of the methylene protons H_c at δ 1.69 caused 2.66% enhancement of the signal for the methylene protons H_d at δ 2.24 and no enhancement of the vinylic proton H_a at δ 6.56. These NOE results strongly confirm the stereochemistry of **4o** as (*E*) isomer. Similar

results are obtained for other derivatives of (*E*) **4p-t** and the results are shown below.

Similarly, the stereochemistry of (*Z*) 2-acylallylsilanes **6n** and **6o** was established by ^1H NMR NOE techniques and the results are shown below.

The two stereoisomers (*E*)-**6p** and (*Z*)-**6p** were also distinguished based on the NOE techniques. For example, (*E*)-**6p** exhibits ^1H NMR signals at 1.93 and 6.55 ppm for the methylene (H_a) and the olefin proton (H_b), respectively. Irradiation at H_b signal led to an increase of the H_a intensity by 5.04 %. In contrast, selective irradiation of the olefinic proton H_i at δ 6.99 in (*Z*)-**6p** caused no enhancement of the signal for the methylene protons H_e at δ 2.38. These NOE results unambiguously determined the stereochemistry of these two stereoisomers.