Supporting Information

Copper(I) *tert*-Butoxide-Promoted 1,4 C^{sp2}-to-O Silyl Migration: Generation of Vinyl Copper Equivalents and Their Stereospecific Cross-Coupling with Allylic, Aryl, and Vinylic Halides

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Characterization data for compounds **Z-3b-d**, **E-3e**, **7b**, **7c**, **Z-8b**, **Z-8c**, **Z-11b**, **14b**, **17b-h**, **19b-h**, **21a-c**, **22a**, and **22b**

1. γ -Trimethylsilyl allylic alcohols 3

(Z)-4-Methyl-7-phenyl-5-(trimethylsilyl)hept-4-en-3-ol (Z-3b): IR (neat) 3386, 3086, 3062, 3028, 2962, 1603, 1496, 1454, 1408, 1373, 1250, 1093, 1049, 1030, 999, 960, 899, 835, 748, 698 cm^{-1} ; ^1H NMR δ 0.21 (s, 9H), 0.91 (t, $J = 7.5$ Hz, 3H), 1.34 (bs, 1H), 1.46-1.55 (m, 1H), 1.63-1.72 (m, 1H), 1.68 (s, 3H), 2.35-2.46 (m, 2H), 2.47-2.58 (m, 2H), 4.36 (dd, $J = 7.9, 6.1$ Hz, 1H), 7.17-7.20 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR δ 1.48, 10.5, 11.7, 27.6, 34.4, 36.1, 76.9, 125.8, 128.3, 137.0, 142.2, 149.0. Anal. Calcd for $\text{C}_{17}\text{H}_{28}\text{OSi}$: C, 73.85; H, 10.21. Found: C, 74.05; H, 10.53.

(Z)-5-Methyl-1-phenyl-3-(trimethylsilyl)hex-2-en-1-ol (Z-3c): IR (neat) 3342, 3087, 3064, 3032, 2952, 2870, 1603, 1493, 1454, 1383, 1365, 1327, 1250, 1192, 1169, 1066, 1007, 835, 756, 698 cm^{-1} ; ^1H NMR δ 0.24 (s, 9H), 0.80 (d, $J = 6.4$ Hz, 3H), 0.88 (d, $J = 6.4$ Hz, 3H), 1.58-1.66 (m, 1H), 1.75 (bs, 1H), 1.93 (dd, $J = 12.8, 7.6$ Hz, 1H), 2.08 (dd, $J = 12.8, 7.6$ Hz, 1H), 5.43 (d, $J = 9.5$ Hz, 1H), 6.06 (d, $J = 9.8$ Hz, 1H), 7.20-7.26 (m, 1H), 7.33-7.40 (m, 2H), 7.41-7.44 (m, 2H); ^{13}C NMR δ 0.84, 22.1, 22.6, 28.0, 48.1, 72.7, 125.9, 127.3, 128.4, 143.28, 143.30, 144.4. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{OSi}$: C, 73.22; H, 9.98. Found: C, 73.37; H, 10.22.

(Z)-3-Phenyl-3-(trimethylsilyl)prop-2-en-1-ol (Z-3d): IR (neat) 3338, 3076, 3059, 3024, 2956, 2898, 1680, 1597, 1489, 1442, 1408, 1252, 1113, 1072, 1030, 883, 839, 768, 706 cm^{-1} ; ^1H NMR δ 0.15 (s, 9H), 1.42 (bs, 1H), 4.36 (d, $J = 6.7$ Hz, 2H), 6.24 (t, $J = 6.7$ Hz, 1H), 7.02-7.04 (m, 2H), 7.17-7.21 (m, 1H), 7.25-7.29 (m, 2H); ^{13}C NMR δ 0.68, 62.2, 125.8, 127.1, 127.9, 143.7, 146.1, 146.9. Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{OSi}$: C, 69.85; H, 8.79. Found: C, 69.52; H, 8.98.

(E)-5-Phenyl-3-(trimethylsilyl)pent-2-en-1-ol (E-3e): IR (neat) 3504, 3089, 3068, 3033, 3006, 2968, 2870, 1604, 1496, 1456, 1261, 1250, 1078, 1047, 1003, 835, 744, 698 cm^{-1} ; ^1H NMR δ 0.14 (s,

9H), 0.97 (bs, 1H), 2.43-2.46 (m, 2H), 2.57-2.64 (m, 2H), 4.04 (d, $J = 6.1$ Hz, 2H), 5.93 (t, $J = 6.3$ Hz, 1H), 7.15-7.22 (m, 3H), 7.23- 7.32 (m, 2H); ^{13}C NMR δ -1.27, 32.0, 36.4, 59.4, 126.0, 128.4, 128.6, 139.3, 141.9, 142.8. Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: C, 71.73; H, 9.46. Found: C, 71.99; H, 9.90.

2. β -Trimethylsilyl ketones 7

4-Methyl-7-phenyl-5-phenylthio-5-(trimethylsilyl)heptan-3-one (7b): IR (neat) 3072, 3059, 3024, 3005, 2981, 2970, 2954, 2939, 2900, 2881, 1714, 1601, 1491, 1473, 1456, 1439, 1431, 1412, 1373, 1255, 1248, 1105, 1066, 1026, 976, 883, 850, 806, 752, 702, 692, 683 cm^{-1} ; ^1H NMR δ 0.17 (s, 6.3H), 0.34 (s, 2.7H), 0.93 (t, $J = 7.2$ Hz, 0.9H), 1.03 (t, $J = 7.2$ Hz, 2.1H), 1.32 (d, $J = 7.0$ Hz, 2.1H), 1.38 (d, $J = 7.3$ Hz, 0.9H), 1.75 (dt, $J = 13.7, 4.3$ Hz, 0.3H), 1.88 (dt, $J = 13.4, 4.6$ Hz, 0.3H), 1.95-2.01 (m, 0.7H), 2.13-2.20 (m, 0.7H), 2.23-2.31 (m, 0.3H), 2.46-2.57 (m, 1H), 2.62-2.71 (m, 2H), 2.82 (dt, $J = 13.1, 4.5$ Hz, 0.7H), 3.14-3.20 (m, 1H), 7.09-7.13 (m, 2H), 7.15-7.20 (m, 1H), 7.24-7.37 (m, 5H), 7.54-7.58 (m, 2H); ^{13}C NMR δ 0.69, 1.3, 7.6, 7.8, 15.1, 15.6, 31.7, 33.0, 36.6, 37.0, 37.4, 39.4, 46.8, 47.6, 50.9, 54.2, 125.8, 125.9, 128.2, 128.3, 128.38, 128.43, 128.57, 128.61, 128.7, 128.8, 131.3, 132.2, 136.9, 137.4, 142.1, 142.3, 213.9, 215.0.

5-Methyl-1-phenyl-3-phenylthio-3-(trimethylsilyl)hexan-1-one (7c): IR (neat) 3066, 3032, 2964, 2906, 2873, 2850, 1701, 1599, 1581, 1471, 1450, 1439, 1408, 1387, 1367, 1346, 1250, 1211, 1182, 1026, 1003, 980, 850, 752, 704, 690, 660 cm^{-1} ; ^1H NMR δ 0.27 (s, 9H), 0.97 (d, $J = 6.7$ Hz, 3H), 1.09 (d, $J = 6.7$ Hz, 3H), 1.72 (dd, $J = 14.7, 5.8$ Hz, 1H), 1.83 (dd, $J = 14.7, 5.2$ Hz, 1H), 1.99-2.07 (m, 1H), 3.10 (d, $J = 18.0$ Hz, 1H), 3.29 (d, $J = 17.7$ Hz, 1H), 7.29-7.37 (m, 3H), 7.39-7.43 (m, 2H), 7.50-7.54 (m, 3H), 7.77-7.80 (m, 2H); ^{13}C NMR δ -0.35, 25.3, 25.4, 26.2, 41.6, 45.8, 47.7, 127.8, 128.45, 128.52, 128.7, 131.6, 132.9, 137.5, 137.7, 198.4.

3. β -Trimethylsilyl- α,β -unsaturated ketones 8

(Z)-4-Methyl-7-phenyl-5-(trimethylsilyl)hept-4-en-3-one (Z-8b): IR (neat) 3087, 3066, 3032, 2985, 2956, 2906, 1695, 1604, 1558, 1496, 1456, 1412, 1379, 1348, 1248, 1122, 1080, 1030, 982, 945, 843, 808, 752, 702 cm^{-1} ; ^1H NMR δ 0.17 (s, 9H), 1.10 (t, $J = 7.3$ Hz, 3H), 1.91 (s, 3H), 2.50-2.60 (m, 6H), 7.1-7.3 (m, 5H); ^{13}C NMR δ 0.62, 7.9, 15.4, 33.7, 34.9, 35.2, 126.0, 128.3, 128.4, 141.8, 145.8, 148.9, 206.8. Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{OSi}$: C, 74.39; H, 9.55. Found: C, 74.52; H, 9.66.

(Z)-5-Methyl-1-phenyl-3-(trimethylsilyl)hex-2-en-1-one (Z-8c): IR (neat) 3066, 3030, 2968, 2929, 2906, 2871, 2850, 1662, 1601, 1581, 1568, 1466, 1448, 1385, 1367, 1329, 1246, 1180, 1032, 1018, 850, 779, 752, 702, 679, 652 cm^{-1} ; ^1H NMR δ 0.21 (s, 9H), 0.93 (d, $J = 6.4$ Hz, 6H), 1.75-1.83 (m, 1H), 2.29 (dd, $J = 7.2, 1.2$ Hz, 2H), 7.31 (s, 1H), 7.45-7.49 (m, 2H), 7.52-7.57 (m, 1H), 7.96-7.99 (m, 2H); ^{13}C NMR δ -0.39, 22.5, 27.8, 49.3, 128.4, 128.5, 132.5, 135.9, 138.3, 166.5, 190.8. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.72; H, 9.40.

4. β -Trimethylsilyl- α,β -unsaturated carboxylic acid esters **11**

Ethyl (Z)-5-Phenyl-3-(trimethylsilyl)pent-2-enoate (Z-11b): IR (neat) 3086, 3064, 3028, 2951, 2866, 1720, 1599, 1496, 1454, 1410, 1369, 1338, 1246, 1196, 1090, 1066, 1041, 843, 748, 698, 683 cm^{-1} ; ^1H NMR δ 0.25 (s, 9H), 1.30 (t, $J = 7.0$ Hz, 3H), 2.54-2.58 (m, 2H), 2.67-2.71 (m, 2H), 4.17 (q, $J = 7.0$ Hz, 2H), 6.30 (t, $J = 1.2$ Hz, 1H), 7.16-7.23 (m, 3H), 7.27-7.31 (m, 2H); ^{13}C NMR δ -0.47, 14.3, 36.1, 40.9, 60.1, 126.0, 128.3, 128.4, 130.5, 141.4, 165.2, 166.8. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Si}$: C, 69.52; H, 8.75. Found: C, 69.74; H, 8.91.

5. Cyclic silyl ether **14**

5-Ethyl-2,2,4-trimethyl-3-phenethyl-1-oxa-2-silacyclopent-3-ene (14b): IR (neat) 3066, 3032, 2979, 2941, 2877, 2860, 1454, 1252, 1109, 993, 877, 839, 783, 698 cm^{-1} ; ^1H NMR δ 0.23 (s, 3H),

0.24 (s, 3H), 0.82 (t, $J = 7.3$ Hz, 3H), 1.37-1.45 (m, 1H), 1.52 (s, 3H), 1.72-1.80 (m, 1H), 2.44-2.53 (m, 2H), 2.62-2.73 (m, 2H), 4.49 (s, 1H), 7.17-7.20 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR δ 0.80, 1.39, 8.19, 12.8, 27.8, 29.8, 36.3, 85.7, 125.8, 128.3, 128.4, 133.5, 142.1, 151.9. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{OSi}$: C, 73.79; H, 9.29. Found: C, 73.88; H, 9.58.

6. Allylation products 17

(Z)-2-(6-Phenylhex-1-en-4-ylidene)cyclohexanol (17b): IR(neat) 3356, 3062, 3026, 2931, 2856, 1633, 1603, 1496, 1452, 1404, 1350, 1335, 1255, 1176, 1142, 1120, 1074, 1030, 987, 964, 912, 879, 748, 733, 698 cm^{-1} ; ^1H NMR δ 1.05-1.16 (m, 1H), 1.34 (bs, 1H), 1.36-1.52 (m, 2H), 1.72-1.82 (m, 2H), 1.89-1.95 (m, 1H), 2.07 (dt, $J = 4.0, 13.7$ Hz, 1H), 2.27-2.43 (m, 3H), 2.64 (t, $J = 8.2$ Hz, 2H), 2.84 (dd, $J = 15.4, 5.6$ Hz, 1H), 2.92 (dd, $J = 15.4, 5.6$ Hz, 1H), 4.73 (t, $J = 2.7$ Hz, 1H), 4.98-5.05 (m, 2H), 5.75-5.84 (m, 1H), 7.15-7.20 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR δ 20.0, 25.0, 27.3, 33.8, 34.5, 35.1, 36.1, 66.5, 114.9, 125.8, 128.2, 128.4, 129.9, 136.4, 137.1, 142.0. Anal. Calcd for $\text{C}_{18}\text{H}_{24}\text{O}$: C, 84.32; H, 9.43. Found: C, 84.16; H, 9.78.

(Z)-4,7-Dimethyl-5-phenethylocta-4,7-dien-3-ol (17c): IR (neat) 3394, 3064, 3026, 2964, 2873, 1647, 1603, 1496, 1454, 1375, 1317, 1169, 1093, 1076, 1059, 1030, 999, 960, 889, 744, 698 cm^{-1} ; ^1H NMR δ 0.86 (t, $J = 7.5$ Hz, 3H), 1.36 (bs, 1H), 1.41-1.50 (m, 1H), 1.58-1.67 (m, 1H), 1.63 (s, 3H), 1.71 (s, 3H), 2.25-2.40 (m, 2H), 2.64 (t, $J = 8.1$ Hz, 2H), 2.74 (d, $J = 15.9$ Hz, 1H), 2.88 (d, $J = 15.9$ Hz, 1H), 4.44 (t, $J = 7.0$ Hz, 1H), 4.68 (s, 1H), 4.77 (bm, 1H), 7.15-7.20 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR δ 10.4, 11.3, 22.9, 27.7, 34.5, 35.2, 39.6, 72.5, 111.0, 125.8, 128.26, 128.34, 132.9, 133.3, 142.2, 144.4. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{O}$: C, 83.67; H, 10.14. Found: C, 83.55; H, 10.35.

(Z)-4-Methyl-5-phenethylocta-4,7-dien-3-ol (17d): IR (neat) 3394, 3062, 3028, 3001, 2960, 2873, 1635, 1603, 1496, 1454, 1377, 1319, 1093, 1078, 1053, 1030, 995, 964, 910, 744, 698 cm^{-1} ; ^1H NMR δ 0.86 (t, $J = 7.3$ Hz, 3H), 1.34 (bs, 1H), 1.42-1.50 (m, 1H), 1.58-1.67 (m, 1H), 1.60 (s, 3H), 2.28-2.40 (m, 2H), 2.66 (t, $J = 8.2$ Hz, 2H), 2.83-2.93 (m, 2H), 4.49 (t, $J = 7.0$ Hz, 1H), 4.99-5.07 (m, 2H), 5.73-5.81 (m, 1H), 7.16-7.20 (m, 3H), 7.25-7.29 (m, 2H); ^{13}C NMR δ 10.4, 11.2, 27.7, 34.4, 35.1, 36.1, 72.4, 115.2, 125.8, 128.3, 128.4, 132.7, 132.9, 137.0, 142.1. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}$: C, 83.55; H, 9.90. Found: C, 83.53; H, 10.20.

(Z)-4,8-Dimethyl-5-phenethylnona-4,7-dien-3-ol (17e): IR (neat) 3398, 3086, 3064, 3028, 2968, 2937, 2877, 1604, 1496, 1456, 1377, 1093, 1032, 999, 748, 698 cm^{-1} ; ^1H NMR δ 0.86 (t, $J = 7.5$ Hz, 3H), 1.30 (bs, 1H), 1.43-1.50 (m, 1H), 1.57 (s, 3H), 1.60-1.66 (m, 1H), 1.68 (s, 3H), 1.70 (d, $J = 0.9$ Hz, 3H), 2.25-2.36 (m, 2H), 2.66 (t, $J = 8.0$ Hz, 2H), 2.76-2.87 (m, 2H), 4.53 (t, $J = 7.0$ Hz, 1H), 4.98-5.03 (m, 1H), 7.16-7.22 (m, 3H), 7.23-7.33 (m, 2H); ^{13}C NMR δ 10.4, 11.1, 17.9, 25.8, 27.8, 30.6, 34.4, 35.2, 72.5, 123.2, 125.8, 128.3, 128.4, 131.3, 131.7, 135.1, 142.3. Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}$: C, 83.77; H, 10.36. Found: C, 83.58; H, 10.39.

(Z)-3-(2-Methylpropyl)-1-phenylhexa-2,5-dien-1-ol (17f): IR (neat) 3481, 3089, 3035, 3008, 2981, 2848, 1664, 1637, 1604, 1495, 1466, 1387, 1367, 1333, 1250, 1196, 1169, 1066, 999, 914, 760, 698 cm^{-1} ; ^1H NMR δ 0.83 (d, $J = 6.4$ Hz, 3H), 0.87 (d, $J = 6.4$ Hz, 3H), 1.73-1.82 (m, 1H), 1.87 (bs, 1H), 1.89-1.92 (m, 2H), 2.93 (dd, $J = 6.4, 0.9$ Hz, 2H), 5.04 (ddt, $J = 10.1, 3.4, 1.5$ Hz, 1H), 5.08 (ddt, $J = 17.1, 3.4, 1.5$ Hz, 1H), 5.45-5.51 (m, 2H), 5.78 (ddt, $J = 17.1, 10.1, 6.4$ Hz, 1H), 7.23-7.28 (m, 1H), 7.31-7.40 (m, 4H); ^{13}C NMR δ 22.5, 22.6, 26.0, 35.0, 46.5, 70.3, 115.9, 125.9, 127.3, 128.4, 129.8, 136.0, 139.6, 144.0. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}$: C, 83.43; H, 9.63. Found: C, 83.32; H, 9.81.

(E)-5-Methyl-3-phenylhexa-2,5-dien-1-ol (17g): IR (neat) 3319, 3080, 3028, 2970, 2914, 1649, 1599, 1576, 1495, 1446, 1375, 1225, 1109, 1078, 1051, 1018, 972, 893, 752, 698 cm^{-1} ; ^1H NMR δ 1.57 (bs, 1H), 1.75 (s, 3H), 3.20 (s, 2H), 4.30 (d, $J = 6.7$ Hz, 2H), 4.71-4.73 (m, 1H), 4.76-4.79 (m, 1H), 6.10 (t, $J = 7.0$ Hz, 1H) 7.20-7.36 (m, 3H), 7.39-7.43 (m, 2H); ^{13}C NMR δ 23.0, 38.4, 59.9, 111.3, 126.2, 127.2, 128.2, 128.7, 139.8, 142.2, 143.4. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{O}$: C, 82.94; H, 8.57. Found: C, 82.66; H, 8.70.

(Z)-5-Methyl-3-phenethylhexa-2,5-dien-1-ol (17h): IR (neat) 3340, 3062, 3026, 2933, 1645, 1603, 1496, 1454, 1373, 1271, 1223, 1086, 1003, 891, 744, 698 cm^{-1} ; ^1H NMR δ 1.23 (bs, 1H), 1.69 (s, 3H), 2.31 (m, 2H), 2.71-2.75 (m, 2H), 2.82 (s, 2H), 4.15 (d, $J = 7.0$ Hz, 2H), 4.73 (d, $J = 0.6$ Hz, 1H), 4.79 (s, 1H), 5.59 (t, $J = 7.0$ Hz, 1H), 7.15-7.20 (m, 3H), 7.25-7.30 (m, 2H); ^{13}C NMR δ 22.4, 34.4, 38.6, 39.0, 59.3, 111.6, 125.7, 125.8, 128.28, 128.32, 140.4, 142.0, 143.3. Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 83.29; H, 9.32. Found: C, 83.35; H, 9.59.

7. Arylation products 19

(Z)-2-[1-(3-Methoxyphenyl)-3-phenylpropan-1-ylidene]cyclohexanol (19b): IR (neat) 3431, 3087, 3064, 3032, 3003, 2937, 2862, 1608, 1512, 1496, 1456, 1282, 1246, 1180, 1144, 1109, 1074, 1034, 982, 958, 835, 810, 752, 702 cm^{-1} ; ^1H NMR δ 1.14 (tq, $J = 13.4, 3.9$ Hz, 1H), 1.28 (bs, 1H), 1.37-1.45 (m, 1H), 1.46-1.51 (m, 1H), 1.72-1.82 (m, 3H), 2.19 (dt, $J = 3.9, 13.6$ Hz, 1H), 2.44-2.70 (m, 5H), 3.82 (s, 3H), 4.33 (bs, 1H), 6.88 (d, $J = 8.9$ Hz, 2H), 7.04-7.07 (m, 2H), 7.10-7.17 (m, 3H), 7.22-7.27 (m, 2H); ^{13}C NMR δ 20.1, 25.1, 27.5, 34.1, 34.4, 36.1, 55.2, 68.0, 113.5, 125.7, 128.2, 128.4, 129.7, 134.5, 134.6, 137.0, 141.9, 158.1. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_2$: C, 81.95; H, 8.13. Found: C, 82.23; H, 8.40.

(Z)-2-[1-(3-Nitrophenyl)-3-phenylpropan-1-ylidene]cyclohexanol (19c): IR (neat) 3566, 3446, 3105, 3064, 3028, 2952, 2862, 1601, 1522, 1496, 1456, 1354, 1286, 1255, 1236, 1144, 1109, 1074, 1030, 1014, 984, 862, 810, 760, 725, 702 cm^{-1} ; ^1H NMR δ 1.15-1.31 (m, 2H), 1.38-1.46 (m, 1H), 1.50-1.58 (m, 1H), 1.74-1.88 (m, 3H), 2.26 (dt, $J = 4.2, 13.8$ Hz, 1H), 2.50-2.63 (m, 3H), 2.70 (t, $J = 7.9$ Hz, 2H), 4.18 (bs, 1H), 7.09 (d, $J = 7.0$ Hz, 2H), 7.24-7.32 (m, 5H), 8.20 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR δ 19.9, 25.2, 27.4, 34.42, 34.44, 35.6, 68.0, 123.5, 126.1, 128.4, 129.7, 133.1, 139.2, 141.1, 146.6, 149.8. Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{O}_3\text{N}$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.56; H, 6.77; N, 3.95.

(Z)-4-Methyl-5,7-diphenylhept-4-en-3-ol (19d): IR (neat) 3581, 3406, 3060, 3026, 2960, 2873, 1603, 1574, 1496, 1456, 1377, 1317, 1244, 1203, 1178, 1153, 1093, 1078, 1045, 1030, 1003, 914, 771, 748, 698, 671 cm^{-1} ; ^1H NMR δ 0.73 (t, $J = 7.5$ Hz, 3H), 1.25 (bs, 1H), 1.41-1.56 (m, 2H), 1.70 (s, 3H), 2.53-2.70 (m, 4H), 4.04 (t, $J = 7.2$ Hz, 1H), 7.08-7.21 (m, 5H), 7.23-7.29 (m, 3H), 7.32-7.36 (m, 2H); ^{13}C NMR δ 10.2, 11.0, 27.7, 33.8, 37.0, 73.6, 125.8, 126.4, 128.1, 128.2, 128.4, 128.8, 133.3, 138.3, 142.0, 142.5. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}$: C, 85.67; H, 8.63. Found: C, 85.63; H, 8.84.

(Z)-5-Methyl-1,3-diphenylhex-2-en-1-ol (19e): IR (neat) 3346, 3062, 3032, 2956, 2870, 1653, 1603, 1576, 1495, 1466, 1385, 1367, 1335, 1252, 1169, 1113, 1066, 1030, 916, 775, 737, 698 cm^{-1} ; ^1H NMR δ 0.73 (d, $J = 6.4$ Hz, 3H), 0.77 (d, $J = 6.4$ Hz, 3H), 1.38-1.46 (m, 1H), 1.82 (bs, 1H), 2.17 (dd, $J = 7.2, 0.92$ Hz, 1H), 2.18 (dd, $J = 7.2, 0.92$ Hz, 1H), 5.14 (d, $J = 9.5$ Hz, 1H), 5.70 (d, $J = 9.5$ Hz, 1H), 7.19-7.36 (m, 10H); ^{13}C NMR δ 22.3, 22.4, 25.9, 48.9, 71.2, 126.0, 127.1, 127.4, 128.17, 128.20, 128.5, 129.9, 140.1, 143.3, 143.9. Anal. Calcd for $\text{C}_{19}\text{H}_{22}\text{O}$: C, 85.67; H, 8.32. Found: C, 85.66; H, 8.56.

(Z)-3,5-Diphenylpent-2-en-1-ol (19f): IR (neat) 3346, 3060, 3026, 2925, 1653, 1603, 1576, 1495, 1454, 1442, 1242, 1157, 1082, 1003, 771, 748, 698 cm^{-1} ; ^1H NMR δ 1.35 (bs, 1H), 2.63-2.72 (m, 4H), 4.02 (d, $J = 7.0$ Hz, 2H), 5.67 (tt, $J = 6.9, 1.1$ Hz, 1H), 7.11-7.18 (m, 5H), 7.23-7.31 (m, 3H), 7.33-7.37 (m, 2H); ^{13}C NMR δ 34.4, 40.7, 60.1, 125.8, 126.1, 127.2, 128.17, 128.19, 128.23, 128.4, 139.6, 141.7, 143.7. Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: C, 85.67; H, 7.61. Found: C, 85.78; H, 7.74.

(Z)-3-(3-Methoxyphenyl)-5-phenylpent-2-en-1-ol (19g): IR (neat) 3568, 3087, 3064, 3033, 3005, 2945, 2862, 2839, 1653, 1610, 1576, 1516, 1496, 1456, 1412, 1385, 1292, 1252, 1180, 1113, 1074, 1034, 843, 752, 702 cm^{-1} ; ^1H NMR δ 1.25 (bs, 1H), 2.62-2.70 (m, 4H), 3.82 (s, 3H), 4.05 (d, $J = 6.7$ Hz, 2H), 5.63 (t, $J = 6.9$ Hz, 1H), 6.88-6.91 (m, 2H), 7.08-7.18 (m, 5H), 7.24-7.28 (m, 2H); ^{13}C NMR δ 34.5, 40.8, 55.2, 60.2, 113.6, 125.77, 125.79, 128.2, 128.4, 129.4, 131.8, 141.8, 143.4, 158.8. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2$: C, 80.56; H, 7.52. Found: C, 80.67; H, 7.71.

(Z)-3-(3-Nitrophenyl)-5-phenylpent-2-en-1-ol (19h): IR (neat) 3371, 3064, 3032, 2945, 2862, 1601, 1520, 1496, 1456, 1350, 1111, 1014, 858, 702 cm^{-1} ; ^1H NMR δ 1.41 (bs, 1H), 2.62-2.68 (m, 2H), 2.71-2.76 (m, 2H), 4.01 (d, $J = 6.9$ Hz, 2H), 5.80 (t, $J = 6.9$ Hz, 1H), 7.10-7.12 (m, 2H), 7.17-7.20 (m, 1H), 7.25-7.28 (m, 2H), 7.32-7.35 (m, 2H), 8.21-8.23 (m, 2H); ^{13}C NMR δ 34.3, 40.1, 59.7, 123.5, 126.1, 128.2, 128.3, 128.4, 129.2, 140.9, 141.8, 146.7, 147.0. Anal. Calcd for $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$: C, 72.07; H, 6.05; N, 4.94. Found: C, 72.17; H, 6.17; N, 5.02.

9. Vinylation products 21 and 22

(Z)-1-(5-Phenylpent-1-en-3-ylidene)-2-(trimethylsiloxy)cyclohexane (21a): IR (neat) 3093, 3068, 3033, 2941, 2866, 1628, 1606, 1498, 1475, 1456, 1446, 1437, 1363, 1315, 1252, 1190, 1151, 1126,

1093, 1076, 1045, 1018, 924, 904, 870, 843, 748, 698 cm^{-1} ; ^1H NMR δ 0.08 (s, 9H), 1.12 (tq, $J = 4.0$, 13.1 Hz, 1H), 1.35-1.45 (m, 2H), 1.74-1.80 (m, 1H), 1.82-1.92 (m, 2H), 2.32 (dt, $J = 4.0$, 13.3 Hz, 1H), 2.40 (dt, $J = 3.4$, 13.1 Hz, 1H), 2.50-2.55 (m, 2H), 2.63-2.66 (m, 2H), 5.01 (bs, 1H), 5.10 (dd, $J = 11.0$, 0.6 Hz, 1H), 5.28 (dd, $J = 17.4$, 0.6 Hz, 1H), 6.81 (dd, $J = 17.4$, 11.0 Hz, 1H), 7.17-7.22 (m, 3H), 7.26-7.30 (m, 2H); ^{13}C NMR δ 0.4, 20.3, 26.1, 28.0, 30.0, 35.3, 35.8, 66.2, 112.9, 125.8, 128.3, 128.4, 133.2, 141.9, 142.4. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{OSi}$: C, 76.37; H, 9.61. Found: C, 76.19; H, 9.72.

Mixture of (Z)-1-[(E)-6-Phenylhex-2-en-4-ylidene]-2-(trimethylsiloxy)cyclohexane and (Z)-1-[(Z)-6-Phenylhex-2-en-4-ylidene]-2-(trimethylsiloxy)cyclohexane (21b): IR (neat) 3089, 3068, 3033, 2937, 2864, 1653, 1606, 1506, 1496, 1456, 1437, 1365, 1252, 1192, 1149, 1128, 1086, 1074, 1043, 1016, 958, 924, 904, 870, 841, 748, 717, 698 cm^{-1} ; ^1H NMR δ 0.04 (s, 2.7H), 0.08 (s, 6.3H), 1.04-1.15 (m, 1H), 1.34-1.46 (m, 2H), 1.57 (dd, $J = 6.7$, 1.5 Hz, 0.7H), 1.72-1.91 (m, 5.3H), 2.16-2.68 (m, 6H), 4.55 (bs, 0.3H), 5.00 (bs, 0.7H), 5.62 (dq, $J = 11.0$, 6.7 Hz, 0.3H), 5.75 (dq, $J = 15.6$, 6.7 Hz, 0.7H), 5.87 (δ , $J = 11.0$ Hz, 0.3H), 6.45 (d, $J = 15.6$ Hz, 0.7H), 7.15-7.21 (m, 3H), 7.25-7.30 (m, 2H); ^{13}C NMR δ 0.3, 0.4, 15.0, 18.9, 20.29, 20.34, 25.0, 25.9, 28.06, 28.09, 30.9, 34.4, 34.7, 34.8, 35.4, 35.7, 66.3, 68.5, 124.3, 125.66, 125.73, 126.2, 128.1, 128.2, 128.3, 128.4, 130.4, 138.9, 142.6. Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{OSi}$: C, 76.77; H, 9.82. Found: C, 76.87; H, 9.68.

(1E,3Z)-3-(2-Methylpropyl)-1,5-diphenyl-5-(trimethylsiloxy)penta-1,3-diene (21c): IR (neat) 3084, 3062, 3030, 3005, 2958, 2927, 2904, 2870, 1599, 1495, 1466, 1448, 1385, 1367, 1252, 1200, 1115, 1090, 1070, 1055, 1028, 960, 887, 870, 843, 750, 698 cm^{-1} ; ^1H NMR δ 0.15 (s, 9H), 0.86 (d, $J = 6.6$ Hz, 3H), 0.93 (d, $J = 6.6$ Hz, 3H), 1.85-1.95 (m, 1H), 2.16 (dd, $J = 13.8$, 6.6 Hz, 1H), 2.22 (dd, $J = 13.8$, 6.6 Hz, 1H), 5.53 (d, $J = 8.9$ Hz, 1H), 5.82 (d, $J = 8.9$ Hz, 1H), 6.65 (d, $J = 15.9$ Hz, 1H), 7.21-7.27 (m, 3H), 7.30-7.39 (m, 6H), 7.44 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR δ 0.4, 22.6, 22.9, 27.3, 43.6,

70.0, 124.8, 125.8, 126.4, 126.9, 127.6, 128.3, 128.7, 130.1, 134.6, 135.2, 137.6, 144.2. Anal. Calcd for C₂₄H₃₂OSi: C, 79.06; H, 8.85. Found: C, 79.36; H, 8.87.

(Z)-2-[(E)-1,5-Diphenylpent-1-en-3-ylidene]cyclohexanol (22a): IR (neat) 3446, 3084, 3062, 3028, 2945, 2862, 1603, 1496, 1456, 1435, 1271, 1142, 1090, 1074, 1030, 987, 960, 752, 698 cm⁻¹; ¹H NMR δ 1.11-1.21 (m, 1H), 1.41 (bs, 1H), 1.48-1.55 (m, 2H), 1.77-1.86 (m, 2H), 1.99-2.03 (m, 1H), 2.23 (dt, *J* = 4.2, 13.8 Hz, 1H), 2.51 (d, *J* = 14.0 Hz, 1H), 2.64-2.76 (m, 4H), 5.19 (bs, 1H), 6.67 (d, *J* = 15.9 Hz, 1H), 7.19-7.35 (m, 9H), 7.43-7.45 (m, 2H); ¹³C NMR δ 20.1, 26.1, 27.4, 30.4, 33.9, 35.4, 65.8, 125.3, 126.0, 126.3, 127.3, 128.3, 128.4, 128.60, 128.62, 130.9, 138.0, 140.8, 142.0. Anal. Calcd for C₂₃H₂₆O: C, 86.75; H, 8.23. Found: C, 86.66; H, 8.32.

(2Z,4E)-3-Phenethyl-5-phenylpenta-2,4-dien-1-ol (22b): IR (neat) 3379, 3086, 3064, 3030, 3005, 2941, 2870, 1604, 1496, 1456, 1074, 1030, 1003, 960, 752, 698, 671 cm⁻¹; ¹H NMR δ 1.41 (bs, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.85 (t, *J* = 8.0 Hz, 2H), 4.38 (d, *J* = 7.0 Hz, 2H), 5.60 (t, *J* = 7.0 Hz, 1H), 6.70 (d, *J* = 16.2 Hz, 1H), 7.08 (dd, *J* = 16.3, 0.8 Hz, 1H), 7.17-7.35 (m, 9H), 7.45 (d, *J* = 7.3 Hz, 8H); ¹³C NMR δ 35.1, 35.7, 58.5, 124.0, 126.0, 126.5, 127.8, 128.3, 128.4, 128.6, 128.9, 130.0, 137.2, 138.6, 141.9.

The dienyl alcohol (**22b**) was fully characterized after acetylation with acetyl chloride-pyridine (72%).

(2Z,4E)-3-Phenethyl-5-phenyl-2,4-pentadienyl acetate (Ac-22b): IR(neat) 3087, 3066, 3032, 3005, 2952, 2871, 1747, 1604, 1496, 1456, 1373, 1236, 1097, 1076, 1030, 960, 754, 698 cm⁻¹; ¹H NMR δ 2.08 (s, 3H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.86 (t, *J* = 8.0 Hz, 2H), 4.83 (d, *J* = 7.3 Hz, 2H), 5.55 (t, *J* = 7.3 Hz, 1H), 6.73 (d, *J* = 16.2 Hz, 1H), 7.09 (d, *J* = 16.2 Hz, 1H), 7.20-7.37 (m, 8H), 7.46 (d, *J* =

7.9 Hz, 2H); ^{13}C NMR δ 21.0, 35.1, 35.8, 60.4, 123.3, 123.7, 126.0, 126.6, 127.9, 128.37, 128.40, 128.7, 130.6, 137.1, 140.7, 141.8, 171.0. Anal. Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_2$: C, 82.32; H, 7.24. Found: C, 82.17; H, 7.15.