Supporting Information

The Ru₃(CO)₁₂-Catalyzed Silylation of Benzylic C-H Bonds in Arylpyridines and Arylpyrazoles with Hydrosilanes via C-H Bond Cleavage

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General Information. ¹H NMR and ¹³C NMR were recorded on a JEOL JNM-EX270 spectrometer operating at 270 and 67.5 MHz, respectively. The chemical shift of ¹H NMR and ¹³C NMR signals are quoted relative to internal CHCl₃ (δ = 7.26 and 77.0) or tetramethylsilane (δ = 0.0). ¹H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, c = complex, br = broad), coupling constant (Hz), relative intensity, and interpretation. ¹³C NMR data are reported as follow: chemical shift in ppm (δ). IR spectra were recorded on a Hitachi 270-50 infrared spectrometer. The GCMS analyses were measured on a Shimadzu GCMS QP-5000 gas chromatography mass spectrometer.

Solvents and Materials. Toluene was distilled under nitrogen from CaH₂. Ru₃(CO)₁₂ was prepared by literature method.

General Procedure. The apparatus consisted of a 10-mL two-necked flask equipped with a reflux condenser connected to a nitrogen line, a rubber septum, and a magnetic stirring bar was flame dried under a flow of nitrogen. In the flask were placed the Ru₃(CO)₁₂ (0.06 mmol), 0.5 mL of toluene, arylpyridine (1 mmol), triethylsilane (5 mmol), and norbornene (5 mmol). The resulting mixture was refluxed under nitrogen atmosphere. The progress of the reaction was monitored by a GC analysis. The product was isolated by a silica gel column chromatography.

2-(2-Ethyl-6-methylphenyl)pyridine. (bp = 80 °C/2 mmHg) ¹H NMR (CDCl₃) 1.03 (t, *J* = 7.6 Hz, 3H, CH₂CH₃), 2.02 (s, 3H, CH₃), 2.36 (q, *J* = 7.6 Hz, 2H, CH₂), 7.08-7.16 (m, 2H, ArH), 7.21-7.28 (m, 3H, ArH), 7.75 (td, *J* = 7.6 Hz, 1.6 Hz, 1H, ArH), 8.72 (d, *J* = 4.6 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 15.49, 20.35, 26.57, 121.52, 124.47, 125.74, 127.31, 127.95, 135.66, 135.95, 139.88, 141.73, 149.42, 159.62; IR (neat) 3062 m, 2966 s, 2931 s, 2871 s, 1585 s, 1564 s, 1464 s, 1423 s, 1375 m, 1279 w, 1147 m, 1092 m, 1057 m, 1026 m, 989 m, 789 s, 752 s, 688 w cm⁻¹; MS *m/z* (% relative intensity) 197 (M⁺, 32), 196 (100), 182 (14), 181 (36), 180 (19), 167 (20), 97 (10), 96 (11), 90 (57), 83 (23), 77 (20), 51 (13). Anal. Calcd for C₁₄H₁₅N: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.44; H, 7.75; N, 7.12.

2-(2,6-dimethylphenyl)-4-methoxypyridine. (bp = 120 °C/2 mmHg) ¹H NMR (CDCl₃) 2.06 (s, 6H, CH₃), 3.87 (s, 3H, OCH₃), 6.76 (d, *J* = 2.7 Hz, 1H, ArH), 6.80 (dd, *J* = 5.9 Hz, 2.1 Hz, ArH), 7.08-7.10 (m, 2H, ArH), 7.18 (dd, *J* = 8.6 Hz, 6.2 Hz, 1H, ArH), 8.53 (d, *J* = 5.4 Hz, 1H, ArH);

¹³C NMR (CDCl₃) 20.02, 55.04, 107.90, 110.21, 127.36, 127.71, 135.59, 140.49, 150.82, 161.35, 165.82; IR (neat) 3062 m, 3014 m, 2966 m, 2945 m, 2922 m, 2843 w, 1599 s, 1589 s, 1564 s, 1469 s, 1446 s, 1379 m, 1308 s, 1250 m, 1207 s, 1178 m, 1090 w, 1049 m, 1030 s, 989 m, 876 s, 862 m, 829 m, 771 s, 742 m, 696 w, 652 w, 544 w cm⁻¹; MS *m/z* (% relative intensity) 213 (M⁺, 34), 212 (100), 198 (12), 197 (10), 128 (11), 106 (12), 98 (11), 77 (11), 51 (11). Anal. Calcd for C₁₄H₁₅NO: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.73; H, 7.03; N, 6.68.

2-(2,6-dimethylphenyl)-6-methylpyridine. (bp = 90 °C/3 mmHg) ¹H NMR (CDCl₃) 2.05 (s, 6H, CH₃), 2.61 (s, 3H, CH₃), 7.02 (d, *J* = 7.6 Hz, 1H, ArH), 7.07-7.20 (m, 4H, ArH), 7.64 (t, *J* = 7.6 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 20.18, 24.59, 121.02, 121.22, 127.47, 127.64, 135.70, 136.42, 140.63, 158.19, 159.16; IR (neat) 3062 m, 3020 m, 2954 m, 2922 m, 2858 w, 1579 s, 1456 s, 1375 m, 1292 w, 1232 w, 1157 m, 1091 w, 1064 m, 1033 w, 995 m, 866 w, 800 s, 771 s, 667 w cm⁻¹; MS *m/z* (% relative intensity) 197 (M⁺, 32), 196 (100), 181 (24), 180 (11), 97 (25), 90 (29), 83 (12), 77 (10). Anal. Calcd for C₁₄H₁₅N: C, 85.24; H, 7.66; N, 7.10. Found: C, 84.95; H, 7.54; N, 7.15.

3-Methyl-2-(2-methylnaphthalen-1-yl)pyridine. (mp = 61 °C) ¹H NMR (CDCl₃) 1.98 (s, 3H, CH₃), 2.17 (s, 3H, CH₃), 7.09 (d, *J* = 8.1 Hz, 1H, ArH), 7.26-7.44 (m, 4H, ArH), 7.67 (d, *J* = 7.6 Hz, 1H, ArH), 7.83 (m, 2H, ArH), 8.63 (dd, *J* = 4.6 Hz, 0.8 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 18.41, 19.61, 122.28, 124.72, 124.77, 126.06, 127.76, 127.87, 128.54, 131.77, 131.99, 132.70, 132.97, 135.90, 137.53, 147.29, 158.17; IR (neat) 3049 m, 2951 w, 2920 m, 2860 w, 1622 w, 1583 m, 1566 m, 1508 m, 1442 s, 1379 s, 1336 w, 1250 w, 1217 w, 1182 w, 1107 m, 1063 w, 976 w, 910 w, 866 w, 812 s, 789 s, 744 s, 675 m, 627 m, 580 w cm⁻¹; MS *m/z* (% relative intensity) 233 (M⁺, 34), 232 (48), 219 (18), 218 (100), 217 (27), 216 (20), 115 (43), 108 (68), 102 (11), 96 (10), 94 (10), 63 (11). Anal. Calcd for C₁₇H₁₅N: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.24; H, 6.52; N, 5.95.

1-Methyl-3-(2,4,6-trimethylphenyl)-1H-pyrazole. (mp = 60 °C) ¹H NMR (CDCl₃) 2.11 (s, 6H, CH₃), 2.30 (s, 3H, CH₃), 3.95 (s, 3H, NCH₃), 6.13 (d, *J* = 2.4 Hz, 1H, pyrazolyl-H), 6.90 (s, 2H, ArH), 7.41 (d, *J* = 2.2 Hz, 1H, pyrazolyl-H); ¹³C NMR (CDCl₃) 20.53, 21.10, 38.80, 106.31, 127.80, 130.02, 130.91, 136.96, 137.31, 150.29; MS *m/z* (% relative intensity) 201 (16), 200 (M⁺, 100), 199 (23), 186 (26), 172 (13), 170 (17), 169 (10), 168 (11), 159 (50), 158 (47), 157 (10), 144 (72), 143 (15), 128 (10), 116 (10), 115 (26), 100 (10), 99 (12), 91 (23), 86 (10), 78 (10), 77 (21), 70 (54), 65 (13), 56 (26), 52 (10), 51 (18). HRMS Calcd for C₁₃H₁₆N₂: 200.1313. Found: 200.1312.

2-(2-Methyl-6-triethylsilanylmethylphenyl)pyridine. (bp = 100 °C/2 mmHg) ¹H NMR (CDCl₃) 0.37 (q, *J* = 7.8 Hz, 6H, SiCH₂), 0.72 (t, *J* = 7.8 Hz, 9H, SiCH₂CH₃), 1.94 (s, 2 H, CH₂), 2.01 (s, 3H, CH₃), 6.98 (d, *J* = 7.7 Hz, 2H, ArH), 7.14 (t, *J* = 7.7 Hz, 1H, ArH), 7.21-7.26 (m, 2H, ArH), 7.74 (td, *J* = 7.7 Hz, 1.6 Hz, 1H, ArH), 8.72 (d, *J* = 4.6 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 3.36, 7.12, 18.23, 20.67, 121.45, 125.26, 125.85, 126.79, 127.48, 135.97, 138.70, 139.15, 149.57, 160.07; IR (neat) 2942 s, 2876 s, 1584 s, 1563 m, 1459 s, 1422 s, 1377 w, 1274 w, 1237 m, 1155 m, 1083 w, 1049 w, 1013 s, 964 m, 925 m, 906 m, 786 s, 771 s, 726 s cm⁻¹; MS *m/z* (% relative intensity) 297 (M⁺, 7), 296 (16), 282 (40), 269 (23), 268 (100), 254 (40), 196 (18), 182 (11), 181 (11), 105 (28), 99 (10), 87 (62), 86 (14), 59 (87), 58 (14). Anal. Calcd for C₁₉H₂₇NSi: C, 76.70; H, 9.15; N, 4.71. Found: C, 76.52; H, 9.27; N, 4.85.

2-(2,6-Bis-triethylsilanylmethylphenyl)pyridine. (bp = 130 °C/2 mmHg) ¹H NMR (CDCl₃) 0.35 (q, *J* = 8.1 Hz, 12H, SiCH₂), 0.71 (t, *J* = 7.8 Hz, 18H, SiCH₂CH₃), 1.94 (s, 4 H, CH₂), 6.86 (d, *J* = 7.7 Hz,

2H, ArH), 7.07 (t, $J = 7.7$ Hz, 1H, ArH), 7.21 (ddd, $J = 7.7$ Hz, 4.9 Hz, 1.4 Hz, 1H, pyridyl-H), 7.26 (d, $J = 7.7$ Hz, 1H, ArH), 7.72 (ddd, $J = 7.26$ Hz, 7.6 Hz, 1.6 Hz, 1H, ArH), (d, $J = 4.6$ Hz, 1H, ArH), 8.72 (ddd, 4.9 Hz, 1.9 Hz, 0.8 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 3.34, 7.14, 18.60, 121.32, 125.13, 126.19, 127.22, 135.69, 137.82, 138.99, 149.49, 160.27; IR (neat) 2940 s, 2574 s, 1462 m, 1420 m, 1241 w, 1232 w, 1118 w, 1051 s, 1001 m, 956 m, 845 w, 717 s, 559 w cm^{-1} ; MS m/z (% relative intensity) 412 (M^+ , 8), 383 (18), 382 (53), 282 (15), 266 (18), 254 (14), 115 (12), 87 (67), 59 (100), 58 (14). Anal. Calcd for $\text{C}_{25}\text{H}_{41}\text{NSi}_2$: C, 72.92; H, 10.04; N, 3.40. Found: C, 72.66; H, 9.85; N, 3.55.

2-{2-[(Dimethylphenylsilanyl)methyl]-6-methylphenyl}pyridine. (bp = 140 °C/2 mmHg) ^1H NMR (CDCl_3) 0.12 (s, 6H, SiCH_3), 1.96 (s, 3H, CH_3), 2.13 (s, 2H, CH_2), 6.86-6.92 (m, 2H, ArH), 6.98 (d, $J = 7.6$ Hz, 1H, ArH), 7.10 (t, $J = 7.6$ Hz, 1H, ArH), 7.18 (ddd, $J = 7.6$ Hz, 4.9 Hz, 1.4 Hz, 1H, ArH), 7.23-7.31 (m, 5H, ArH), 7.60 (td, $J = 7.6$ Hz, 1.9 Hz, 1H, ArH), 8.66 (ddd, $J = 4.9$ Hz, 1.9 Hz, 1.1 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) -2.77, 20.64, 22.90, 121.47, 125.20, 126.14, 126.84, 127.50, 127.61, 128.83, 133.58, 135.90, 136.01, 137.77, 139.08, 139.34, 149.47, 159.83; IR (neat) 3066 m, 3018 m, 2954 m, 2897 w, 1583 s, 1564 m, 1462 s, 1425 s, 1248 s, 1159 m, 1113 s, 1026 m, 989 w, 930 m, 835 s, 752 s, 733 s, 700 s, 625 w, 588 w, 563 w, 505 w cm^{-1} ; MS m/z (% relative intensity) 303 (M^+ -15, 18), 302 (65), 227 (21), 226 (100), 182 (15), 181 (14), 180 (12), 167 (12), 136 (15), 135 (100), 107 (22), 105 (15). Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NSi}$: C, 79.44; H, 7.30; N, 4.41. Found: C, 79.25; H, 7.48; N, 4.45.

2-{2,6-Bis-[(dimethylphenylsilanyl)methyl]phenyl}pyridine. (mp = 52 °C) ^1H NMR (CDCl_3) 0.11 (s, 12H, SiCH_3), 2.11 (s, 4H, CH_2), 6.66 (dt, $J = 8.1$ Hz, 1.1 Hz, 1H, ArH), 6.80 (d, $J = 7.6$ Hz, 1H, ArH), 7.05 (t, $J = 7.6$ Hz, 1H, ArH), 7.13 (ddd, $J = 7.6$ Hz, 4.9 Hz, 1.4 Hz, 1H, ArH), 7.23-7.31 (m, 5H, ArH), 7.60 (td, $J = 7.6$ Hz, 1.9 Hz, 1H, ArH), 8.66 (ddd, $J = 7.6$ Hz, 4.9 Hz, 0.9 Hz, 1H, ArH), 7.24-7.35 (m, 10H, ArH), 7.47 (td, $J = 7.6$ Hz, 1.9 Hz, 1H, ArH), 8.64 (ddd, $J = 5.1$ Hz, 1.9 Hz, 0.8 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) -2.73, 23.18, 121.31, 125.40, 125.90, 127.20, 127.59, 128.76, 133.56, 135.53, 138.11, 139.23, 149.29, 159.76; IR (neat) 3000 m, 2946 m, 2894 m, 1580 m, 1447 m, 1422 m, 1243 m, 1148 w, 1107 m, 1019 w, 988 w, 941 s, 817 s, 721 s, 697 s cm^{-1} ; MS m/z (% relative intensity) 436 (M^+ -15, 15), 361 (13), 360 (35), 303 (12), 302 (41), 300 (13), 136 (14), 135 (100), 107 (18). Anal. Calcd for $\text{C}_{29}\text{H}_{33}\text{NSi}_2$: C, 77.10; H, 7.36; N, 3.10. Found: C, 77.10; H, 7.57; N, 3.18.

2-{2-[(*tert*-Butyldimethylsilanyl)methyl]-6-methylphenyl}pyridine. (bp = 115 °C/2.5 mmHg) ^1H NMR (CDCl_3) -0.21 (s, 6H, SiCH_3), 0.71 (s, 9H, CH_3), 1.97 (s, 2H, CH_2), 2.04 (s, 3H, ArCH₃), 6.97-7.02 (m, 2H, ArH), 7.16 (t, $J = 7.6$ Hz, 1H, ArH), 7.21-7.27 (m, 2H, ArH), 7.74 (td, $J = 7.6$ Hz, 1.6 Hz, 1H, ArH), 8.73 (ddd, $J = 4.9$ Hz, 1.9 Hz, 1.1 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) -5.95, 16.62, 18.87, 20.67, 26.15, 121.49, 125.40, 125.90, 126.62, 127.53, 135.91, 136.00, 138.86, 139.22, 149.56, 160.06; IR (neat) 2922 w, 2850 m, 1580 m, 1458 m, 1420 m, 1360 w, 1239 m, 1153 m, 1022 w, 1003 w, 925 w, 809 s, 747 s cm^{-1} ; MS m/z (% relative intensity) 241 (22), 240 (M^+ -57, 100), 181 (11), 112 (11), 73 (46), 59 (15). Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{NSi}$: C, 76.70; H, 9.15; N, 4.71. Found: C, 76.66; H, 9.21; N, 4.77.

2-{2-Methyl-6-[(triphenylsilanyl)methyl]phenyl}pyridine. (mp = 118 °C) ^1H NMR (CDCl_3) 1.89(s, 3H, CH_3), 2.74 (brs, 2H, CH_2), 5.81 (d, $J = 7.6$ Hz, 1H, ArH), 6.84 (dd, $J = 5.9$ Hz, 3.0 Hz, 1H, ArH), 6.97-6.99 (m, 2H, ArH), 7.11-7.48 (m, 17H, ArH), 8.64 (brd, $J = 4.6$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 20.26, 20.50, 121.31, 125.08, 126.39, 126.94, 127.63, 129.41, 129.77, 134.38, 135.16, 135.76, 135.98, 136.56, 139.97, 149.42, 159.56; IR (KBr) 3062 m, 3043 m, 2993 m, 2920 w, 1583 m,

1562 m, 1456 m, 1425 s, 1240 m, 1171 m, 1107 s, 1028 m, 993 w, 931 w, 787 m, 756 s, 737 s, 700 s, 621 w, 594 w, 515 m cm⁻¹; MS *m/z* (% relative intensity) 364 (M⁺-77, 15), 351 (19), 350 (52), 260 (25), 259 (100), 182 (11) 181 (43), 180 (22), 155 (15), 105 (23), 53 (11). Anal. Calcd for C₃₁H₂₇NSi: C, 84.31; H, 6.16; N, 3.17. Found: C, 84.07; H, 6.20; N, 3.09.

2-(2-Ethyl-6-triethylsilanylmethylphenyl)pyridine. (bp = 150 °C/3 mmHg) ¹H NMR (CDCl₃) 0.39 (q, *J* = 7.8 Hz, 6H, SiCH₂), 0.73 (t, *J* = 7.8 Hz, 9H, SiCH₂CH₃), 0.99 (t, *J* = 7.6 Hz, 3 H, CH₃), 1.61 (s, 2H, SiCH₂), 2.32-2.36 (m, 2H, CH₂), 6.98 (d, *J* = 7.8 Hz, 1H, ArH), 7.02 (d, *J* = 7.7 Hz, 1H, ArH), 7.18 (t, *J* = 7.7 Hz, 1H, ArH), 7.21-7.26 (m, 2H, ArH), 7.73 (td, *J* = 7.7 Hz, 1.8 Hz, 1H, ArH), 8.72 (d, *J* = 4.3 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 3.52, 7.12, 15.21, 18.39, 26.76, 121.45, 124.12, 125.47, 126.76, 127.72, 138.75, 138.76, 138.80, 142.15, 149.49, 160.05; IR (neat) 2870 s, 1580 s, 1452 s, 1421 s, 1228 m, 1145 m, 1085 w, 1003 m, 902 w, 723 s cm⁻¹; MS *m/z* (% relative intensity) 311 (M⁺, 3), 283 (25), 282 (100), 254 (15), 196 (15), 87 (51), 59 (80), 58 (13). Anal. Calcd for C₂₀H₂₉NSi: C, 77.11; H, 9.38; N, 4.50. Found: C, 77.11; H, 9.48; N, 4.44.

2-(2-Methyl-6-triethylsilanylphenyl)pyridine. (bp = 120 °C/2 mmHg) ¹H NMR (CDCl₃) 0.36 (q, *J* = 7.8 Hz, 6H, SiCH₂), 0.80 (t, *J* = 7.8 Hz, 9H, SiCH₂CH₃), 2.02 (s, 3 H, CH₃), 7.23-7.31 (m, 4H, ArH), 7.43 (dd, *J* = 6.8 Hz, 2.0 Hz, 1H, ArH), 7.71 (td, *J* = 7.6 Hz, 1.9 Hz, 1H, ArH), 8.67 (ddd, *J* = 5.1 Hz, 2.2 Hz, 1.1 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 3.72, 7.51, 20.45, 122.01, 124.82, 127.09, 130.71, 133.15, 135.26, 135.61, 147.01, 148.98, 161.23; IR (neat) 3055 w, 2952 s, 2908 m, 2873 s, 1587 m, 1562 m, 1462 m, 1412 m, 1377 w, 1277 w, 1238 m, 1192 w, 1147 m, 1097 w, 1053 w, 1005 m, 860 m, 791 m, 773 m, 752 s, 729 s, 706 s, 621 2, 598 w cm⁻¹; MS *m/z* (% relative intensity) 255 (23), 254 (M⁺-29, 100), 196 (40), 29 (33), 98 (10). Anal. Calcd for C₁₈H₂₅NSi: C, 76.26; H, 8.89; N, 4.94. Found: C, 76.26; H, 9.18; N, 4.96.

2-(2-Triethylsilyl-6-triethylsilylmethylphenyl)pyridine. (mp = 38 °C, bp = 150 °C/2 mmHg) ¹H NMR (CDCl₃) 0.32 (q, *J* = 7.8 Hz, 6H, SiCH₂), 0.40 (q, *J* = 7.8 Hz, 6H, SiCH₂), 0.70 (t, *J* = 7.8 Hz, 9H, CH₃), 0.78 (t, *J* = 7.8 Hz, 9H, CH₃), 2.01 (s, 2H, CH₂), 7.13 (dd, *J* = 7.3 Hz, 1.4 Hz, 1H, ArH), 7.19-7.32 (m, 4H, ArH), 7.69 (td, *J* = 7.8 Hz, 1.6 Hz, 1H, ArH), 8.67 (t, *J* = 4.6 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 3.54, 3.85, 7.11, 7.56, 18.24, 121.89, 125.66, 126.72, 129.91, 131.57, 135.33, 135.50, 138.32, 145.55, 148.93, 161.50; IR (KBr) 2952 s, 2908 s, 2873 s, 1587 m, 1562 w, 1460 m, 1414 m, 1377 w, 1277 w, 1238 m, 1194 m, 1155 w, 1005 m, 793 m, 773 m, 729 m cm⁻¹; MS *m/z* (% relative intensity) 370 (12), 369 (35), 368 (M⁺-29, 100), 283 (13), 282 (53), 254 (11), 252 (18), 194 (10), 141 (14), 113 (13), 87 (37), 59 (60). Anal. Calcd for C₂₄H₃₁NSi: C, 72.47; H, 9.88; N, 3.52. Found: C, 72.38; H, 9.70; N, 3.50.

4-Methoxy-2-(2-methyl-6-triethylsilylmethylphenyl)pyridine. (bp = 110 °C/2.5 mmHg) ¹H NMR (CDCl₃) 0.41 (q, *J* = 7.9 Hz, 6H, SiCH₂), 0.74 (q, *J* = 7.9 Hz, 9H, SiCH₂CH₃), 1.94 (s, 2H, CH₂), 2.03 (s, 3H, CH₃), 3.87 (s, 3H, OCH₃), 6.77-6.80 (m, 2H, ArH), 6.97 (d, *J* = 7.6 Hz, 2H, ArH), 7.13 (t, *J* = 7.6 Hz, 1H, ArH), 8.53 (dd, *J* = 4.9 Hz, 1.6 Hz, 1H, ArH); ¹³C NMR (CDCl₃) 3.45, 7.18, 18.25, 20.59, 55.11, 107.91, 111.03, 125.80, 126.75, 127.45, 135.90, 138.65, 139.32, 150.78, 161.62, 165.72; IR (neat) 2952 s, 2910 m, 2873 s, 1728 w, 1589 s, 1564 m, 1466 s, 1306 m, 1244 m, 1209 m, 1159 w, 1028 s, 876 w, 791 m, 773 m, 733 m cm⁻¹; MS *m/z* (% relative intensity) 320 (10), 312 (M⁺-15, 40), 299 (24), 298 (100), 285 (14), 284 (55), 226 (12) 121 (26), 114 (15), 87 (50), 59 (91), 58 (13). Anal. Calcd for C₂₀H₂₉NOSi: C, 73.34; H, 8.92; N, 4.28. Found: C, 73.63; H, 8.82; N, 4.14.

2-(2,6-Bis-triethylsilylmethylphenyl)-4-methoxypyridine. (bp = 140 °C/2 mmHg) ^1H NMR (CDCl_3) 0.38 (q, J = 7.7 Hz, 12H, SiCH_2), 0.73 (q, J = 7.9 Hz, 18H, SiCH_2CH_3), 1.93 (s, 4H, CH_2), 3.86 (s, 3H, OCH_3), 6.74-6.78 (m, 2H, ArH), 6.85 (d, J = 7.8 Hz, 2H, ArH), 7.07 (t, J = 7.8 Hz, 1H, ArH), 8.52 (d, J = 5.4 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 3.48, 7.15, 18.54, 55.06, 107.79, 111.87, 125.03, 127.12, 137.98, 138.87, 150.65, 161.74, 165.53; IR (neat) 2951 s, 2908 s, 2875 s, 1591 s, 1564 s, 1460 s, 1414 m, 1308 m, 1240 m, 1209 m, 1157 m, 1024 s, 966 w, 943 w, 877 w, 862 w, 808 m, 773 s, 727 s cm^{-1} ; MS m/z (% relative intensity) 427 (M^+ -15, 13), 414 (10), 413 (27), 412 (65), 399 (13), 312 (19), 298 (10), 296 (16), 284 (26), 87 (59), 59 (100), 58 (11). Anal. Calcd for $\text{C}_{26}\text{H}_{43}\text{NOSi}_2$: C, 70.68; H, 9.81; N, 3.17. Found: C, 70.67; H, 9.75; N, 3.17.

2-Methyl-6-(2-methyl-6-triethylsilylmethylphenyl)pyridine. (bp = 125 °C/2.3 mmHg) ^1H NMR (CDCl_3) 0.38 (q, J = 7.7 Hz, 6H, CH_2), 0.72 (t, J = 7.7 Hz, 9H, CH_2CH_3), 1.93 (s, 1H, SiCHH), 1.94 (s, 1H, SiCHH), 2.01 (s, 3H, CH_3), 2.60 (s, 3H, CH_3), 6.94-7.14 (m, 5H, ArH), 7.62 (t, J = 7.8 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 3.42, 7.14, 18.21, 20.74, 24.56, 120.90, 122.10, 125.90, 126.88, 127.34, 135.96, 136.25, 138.69, 139.47, 158.17, 159.40; IR (neat) 3060 m, 3018 m, 2951 s, 2908 s, 2873 s, 2730 w, 1776 s, 1458 s, 1415 w, 1375 w, 1292 w, 1240 s, 1157 s, 1088 w, 1059 m, 1014 s, 972 m, 931 w, 791 s, 771 s, 729 s, 648 w cm^{-1} ; MS m/z (% relative intensity) 311 (M^+ , 18), 310 (12), 297 (11), 296 (41), 283 (26), 282 (M^+ -29, 100), 268 (10), 210 (10), 196 (18), 195 (14), 115 (18), 112 (12), 105 (11), 87 (74), 59 (73). Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NSi}$: C, 77.11; H, 9.38; N, 4.50. Found: C, 76.91; H, 9.10; N, 4.70.

3-Methyl-2-(2-methyl-6-triethylsilylmethylphenyl)pyridine. (bp = 110 °C/2.5 mmHg) ^1H NMR (CDCl_3) 0.37-0.46 (m, 6H, CH_2), 0.70-0.76 (m, 9H, CH_2CH_3), 1.57 (d, J = 13.8 Hz, 1H, SiCHH), 1.90 (d, J = 13.8 Hz, 1H, SiCHH), 1.91 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 6.97-7.00 (m, 2H, ArH), 7.13 (t, J = 7.6 Hz, 1H, ArH), 7.16 (dd, J = 7.6 Hz, 5.7 Hz, 1H, ArH), 7.56 (ddd, J = 7.6 Hz, 6.8 Hz, 0.8 Hz, 1H, ArH), 8.54 (dt, J = 5.1 Hz, 0.8 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 3.49, 7.14, 17.80, 18.57, 20.08, 121.90, 125.89, 126.61, 127.23, 131.93, 135.68, 137.43, 138.29, 138.47, 147.10, 159.55; IR (neat) 2870 s, 1570 m, 1447 s, 1414 m, 1235 m, 1150 w, 1007 m, 925 w, 754 s cm^{-1} ; MS m/z (% relative intensity) 311 (M^+ , 21), 296 (18), 283 (23), 282 (79), 268 (63), 194 (10), 181 (13), 113 (31), 105 (11), 87 (52), 59 (100), 58 (16), 57 (10). Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{NSi}$: C, 77.11; H, 9.38; N, 4.50. Found: C, 77.04; H, 9.56; N, 4.53.

2-(2,6-Bis-triethylsilylmethylphenyl)-3-methylpyridine. (bp = 130 °C/2 mmHg) ^1H NMR (CDCl_3) 0.39 (q, J = 7.9 Hz, 12H, SiCH_2), 0.72 (q, J = 7.9 Hz, 18H, SiCH_2CH_3), 1.59 (d, J = 13.8 Hz, 2H, ArSiCHH), 1.91 (d, J = 13.8 Hz, 2H, ArSiCHH), 2.05 (s, 3H, CH_3), 6.87 (d, J = 7.6 Hz, 2H, ArH), 7.08 (t, J = 7.6 Hz, 1H, ArH), 7.14 (dd, J = 7.6 Hz, 4.9 Hz, 1H, ArH), 7.53 (d, J = 7.6 Hz, 1H, ArH), 8.53 (d, J = 4.9 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 3.57, 7.18, 18.25, 18.85, 121.72, 125.03, 126.84, 132.28, 137.11, 137.32, 138.85, 146.92, 159.72; IR (neat) 2872 s, 1571 m, 1452 m, 1414 m, 1232 w, 1150 w, 1006 m, 942 m, 750 s, 717 s cm^{-1} ; MS m/z (% relative intensity) 398 (15), 396 (M^+ -29, 47), 282 (19), 268 (27), 266 (28), 208 (15), 115 (10), 87 (64), 59 (100), 58 (11). Anal. Calcd for $\text{C}_{26}\text{H}_{43}\text{NSi}_2$: C, 73.34; H, 10.18; N, 3.29. Found: C, 73.29; H, 10.23; N, 3.45.

3,3'-Bis-triethylsilylmethyl-[2,2']bipyridyl. (bp = 135 °C/3 mmHg) ^1H NMR (CDCl_3) 0.42 (q, J = 7.9 Hz, 12H, CH_2), 0.74 (t, J = 7.9 Hz, 18H, CH_3), 2.05 (s, 4H, ArCH₂), 7.14 (dd, J = 8.1 Hz, 4.9 Hz, 2H, ArH), 7.44 (dd, J = 7.6 Hz, 1.6 Hz, 2H, ArH), 8.42 (dd, J = 4.8 Hz, 1.6 Hz, 2H, ArH); ^{13}C NMR (CDCl_3) 3.34, 7.12, 17.36, 122.24, 135.00, 137.02, 145.07, 156.28; IR (neat) 3047 m, 2952 s, 2908 s,

2875 s, 1576 w, 1458 m, 1417 s, 1238 m, 1192 m, 1157 m, 1061 w, 1038 m, 1012 s, 970 m, 804 s, 773 s, 727 s, 629 w cm^{-1} ; MS m/z (% relative intensity) 412 (M^+ , 13), 384 (17), 383 (41), 298 (15), 297 (63), 269 (17), 268 (17), 267 (73), 209 (11), 206 (13), 177 (11), 87 (59), 59 (100). Anal. Calcd for $\text{C}_{24}\text{H}_{40}\text{N}_2\text{Si}_2$: C, 69.84; H, 9.77; N, 6.79. Found: C, 69.60; H, 9.86; N, 6.87.

3-Methyl-2-(2-triethylsilanylmethylnaphthalen-1-yl)pyridine. (bp = 150 °C/2 mmHg) ^1H NMR (CDCl_3) 0.35-0.45 (m, 6H, CH_2), 0.70 (t, $J = 7.8$ Hz, 9H, CH_3), 1.78 (d, $J = 13.5$ Hz, 1H, SiCHH), 1.95 (s, 3H, CH_3), 2.07 (d, $J = 13.5$ Hz, 1H, SiCHH), 7.00 (d, $J = 8.1$ Hz, 1H, ArH), 7.19-7.32 (m, 4H, ArH), 7.60 (dd, $J = 7.6$ Hz, 1.1 Hz, 1H, ArH), 7.70 (d, $J = 8.6$ Hz, 1H, ArH), 7.75 (d, $J = 7.8$ Hz, 1H, ArH), 8.58 (dd, $J = 4.9$ Hz, 0.8 Hz, ArH); ^{13}C NMR (CDCl_3) 3.61, 7.18, 18.73, 18.82, 122.22, 124.26, 124.88, 126.14, 127.52, 127.83, 128.28, 131.23, 132.31, 133.09, 133.94, 136.47, 137.63, 147.26, 158.45; IR (neat) 3049 m, 2951 s, 2908 s, 2873 s, 1620 w, 1585 m, 1508 m, 1460 m, 1442 m, 1379 m, 1335 w, 1248 m, 1209 w, 1159 m, 1107 w, 1016 m, 978 m, 928 w, 863 w, 822 s, 789 s, 773 s, 746 s, 733 s, 717 s, 685 w, 625 w cm^{-1} ; MS m/z (% relative intensity) 347 (M^+ , 23), 318 (44), 304 (33), 123 (11), 115 (10), 87 (49), 59 (100), 58 (13), 57 (11). Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{NSi}$: C, 79.48; H, 8.41; N, 4.03. Found: C, 79.28; H, 8.35; N, 4.30.

8-Triethylsilanylmethylquinoline. (bp = 100 °C/2 mmHg) ^1H NMR (CDCl_3) 0.48 (q, $J = 7.7$ Hz, 6H, CH_2), 0.87 (t, $J = 7.7$ Hz, 9H, CH_3), 2.85 (s, 2H, ArCH_2), 7.35 (dd, $J = 8.1$ Hz, 4.3 Hz, 1H, ArH), 7.38-7.42 (m, 2H, ArH), 7.54 (dd, $J = 6.2$ Hz, 3.2 Hz, 1H, ArH), 8.09 (dd, $J = 8.1$ Hz, 2.0 Hz, 1H, ArH), 8.88 (dd, $J = 4.3$ Hz, 1.8 Hz, 1H, ArH); ^{13}C NMR (CDCl_3) 3.50, 7.30, 16.90, 120.65, 123.74, 126.16, 127.78, 128.39, 136.05, 140.82, 146.60, 148.51; IR (neat) 2951 s, 2908 s, 2873 s, 1610 w, 1595 w, 1572 w, 1496 s, 1465 m, 1415 m, 1392 w, 1363 m, 1315 m, 1238 m, 1171 m, 1153 m, 1076 m, 1018 m, 974 m, 877 w, 827 m, 795 s, 775 s, 758 s, 731 s cm^{-1} ; MS m/z (% relative intensity) 242 ($\text{M}^+ - 15$, 22), 229 (20), 228 (100), 170 (31), 169 (14), 87 (28), 86 (18), 85 (14), 59 (34). Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{NSi}$: C, 74.65; H, 9.00; N, 5.44. Found: C, 74.52; H, 9.11; N, 5.43.

3-(2,4-Dimethyl-6-triethylsilanylmethylphenyl)-1-methyl-1H-pyrazole. (bp = 125 °C/3 mmHg) ^1H NMR (CDCl_3) 0.40 (q, $J = 7.8$ Hz, 6H, CH_2), 0.76 (t, $J = 7.8$ Hz, 9H, CH_3), 2.04 (s, 2H, ArCH_2), 2.07 (s, 3H, ArCH_3), 2.27 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 6.11 (d, $J = 1.9$ Hz, 1H, pyrazolyl-H), 6.75-6.77 (m, 2H, ArH), 7.39 (d, $J = 2.2$ Hz, 1H, pyrazolyl-H); ^{13}C NMR (CDCl_3) 3.40, 7.12, 18.60, 20.89, 21.18, 38.75, 107.00, 126.42, 127.12, 129.80, 129.98, 136.64, 137.54, 140.43, 150.76; IR (neat) 2951 s, 2910 s, 2873 s, 1610 m, 1570 w, 1523 m, 1498 m, 1458 m, 1415 m, 1331 w, 1294 w, 1225 m, 1161 m, 1068 m, 1016 m, 970 w, 850 m, 739 s cm^{-1} ; MS m/z (% relative intensity) 314 ($\text{M}^+ - 1$, 5), 299 ($\text{M}^+ - 16$, 17), 286 (25), 285 (100), 271 (32), 227 (14), 213 (11), 115 (16), 114 (14), 107 (16), 87 (66), 86 (13), 59 (87), 58 (12). Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{N}_2\text{Si}$: C, 72.55; H, 9.61; N, 8.91. Found: C, 72.30; H, 9.74; N, 8.90.

1-(2-Methyl-6-triethylsilanylmethylphenyl)-1H-pyrazole. (bp = 115 °C/2 mmHg) ^1H NMR (CDCl_3) 0.45 (q, $J = 7.8$ Hz, 6H, CH_2), 0.79 (t, $J = 7.8$ Hz, 9H, CH_3), 1.81 (s, 2H, ArCH_2), 1.95 (s, 3H, ArCH_3), 6.43 (t, $J = 2.2$ Hz, 1H, pyrazolyl-H), 7.00 (d, $J = 8.1$ Hz, 2H, ArH), 7.18 (t, $J = 7.6$ Hz, 1H, ArH), 7.44 (d, $J = 2.2$ Hz, 1H, pyrazolyl-H), 7.72 (d, $J = 2.2$ Hz, 1H, pyrazolyl-H); ^{13}C NMR (CDCl_3) 3.36, 7.14, 16.62, 17.56, 105.73, 126.27, 127.21, 128.53, 131.03, 136.47, 138.10, 139.27, 139.87; IR (neat) 2952 s, 2910 m, 2875 s, 1595 w, 1516 m, 1468 m, 1415 m, 1392 m, 1317 w, 1242 w, 1159 m, 1080 w, 1043 m, 1018 m, 941 m, 789 s, 773 s, 752 s, 729 s, 629 w cm^{-1} ; MS m/z (% relative intensity) 258 (14), 257 ($\text{M}^+ - 29$, 69), 243 (11), 154 (15), 153 (100), 125 (17), 87 (59), 59 (92), 58

(12), 57 (11). Anal. Calcd for $C_{17}H_{26}N_2Si$: C, 71.27; H, 9.15; N, 9.78. Found: C, 71.13; H, 9.20; N, 9.84.

1-(2,6-Bis-triethylsilylmethylphenyl)-1H-pyrazole. (bp = 130 °C/2 mmHg) ^1H NMR ($CDCl_3$) 0.43 (q, J = 7.8 Hz, 12H, CH_2), 0.78 (t, J = 7.8 Hz, 18H, CH_3), 1.74 (d, J = 1.6 Hz, 4H, $ArCH_2$), 6.42 (t, J = 2.2 Hz, 1H, pyrazolyl-H), 6.87 (d, J = 7.7 Hz, 2H, ArH), 7.12 (t, J = 7.7 Hz, 1H, ArH), 7.43 (d, J = 2.2 Hz, 1H, pyrazolyl-H), 7.70 (d, J = 2.2 Hz, 1H, pyrazolyl-H); ^{13}C NMR ($CDCl_3$) 3.42, 7.17, 16.19, 105.64, 125.33, 128.20, 131.36, 136.90, 139.55, 139.68; IR (neat) 2952 s, 2908 s, 1589 w, 1516 m, 1466 s, 1415 m, 1392 m, 1317 w, 1240 m, 1157 m, 1068 m, 1016 s, 941 m, 806 m, 775 s, 750 s, 729 s cm^{-1} ; MS m/z (% relative intensity) 372 (M^+ -29, 13), 371 (43), 154 (12), 153 (82), 115 (19), 87 (66), 59 (100). Anal. Calcd for $C_{23}H_{40}N_2Si_2$: C, 68.93; H, 10.06; N, 6.99. Found: C, 68.89; H, 10.10; N, 7.00.

(2,4-Dimethyl-6-triethylsilylmethylbenzylidene)piperidin-1-ylamine. ^1H NMR ($CDCl_3$) 0.51 (q, J = 8.10 Hz, 6H, CH_2CH_3), 0.88 (t, J = 8.10 Hz, 9 H, CH_2CH_3), 1.49-1.57 (m, 2H, CH_2), 1.71-1.80 (m, 4H, CH_2), 2.04 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.33 (s, 2H, CH_2), 3.09-3.13 (m, 4H, CH_2N), 6.68 (s, 1H, ArH), 6.72 (s, 1H, ArH), 7.71 (s, 1H, $CH=N$); ^{13}C NMR ($CDCl_3$) 3.62, 7.43, 19.07, 21.14, 21.42, 24.34, 25.25, 52.44, 127.43, 127.97, 129.34, 136.24, 136.56, 139.29; IR (neat) 2937 s, 2873 s, 2857 s, 2804 s, 1607 s, 1590 m, 1559 m, 1465 s, 1452 s, 1415 m, 1376 m, 1359 m, 1290 m, 1270 m, 1260 m, 1243 m, 1217 m, 1162 s, 1121 m, 1078 s, 1017 s, 988 s, 972 s, 946 m, 919 m, 899 m, 850 s, 780 s, 757 s, 733 s, 655 w cm^{-1} ; MS m/z (% relative intensity) 344 (M^+ , 10), 315 (12), 232 (11), 175 (10), 170 (11), 157 (12), 147 (12), 146 (15), 145 (11), 115 (13), 101 (14), 100 (27), 88 (11), 87 (97), 84 (35), 59 (100), 57 (11), 56 (18), 55 (28). Anal. Calcd for $C_{21}H_{36}N_2Si$: C, 73.19; H, 10.53; N, 8.13. Found: C, 73.06; H, 10.55; N, 8.09.

(4-Methyl-2,6-bis(triethylsilylmethyl)benzylidene)piperidin-1-ylamine. ^1H NMR ($CDCl_3$) 0.50 (q, J = 7.56 Hz, 12H, CH_2CH_3), 0.88 (t, J = 7.56 Hz, 18H, CH_2CH_3), 1.53-1.56 (m, 2H, CH_2), 1.72-1.75 (m, 4H, CH_2), 2.20 (s, 3H, CH_3), 2.30 (s, 4H, $SiCH_2$), 3.08-3.13 (m, 4H, NCH_2), 6.57 (s, 2H, ArH), 7.65 (s, 1H, $CH=N$); ^{13}C NMR ($CDCl_3$) 3.68, 7.51, 19.23, 21.31, 24.41, 25.40, 52.33, 126.38, 128.17, 135.97, 136.71, 139.54; IR (neat) 2944 s, 2936 s, 2910 s, 2873 s, 2806 s, 1603 s, 1559 m, 1465 s, 1415 s, 1377 m, 1360 m, 1271 m, 1259 s, 1161 s, 1078 s, 1017 s, 990 s, 977 s, 919 w, 900 w, 855 s, 780 s, 751 s, 729 s cm^{-1} ; MS m/z (% relative intensity) 459 ($M+1^+$, 8), 430 (14), 243 (13), 115 (35), 100 (21), 88 (10), 87 (97), 84 (20), 59 (100), 55 (11). Anal. Calcd for $C_{27}H_{50}N_2Si_2$: C, 70.67; H, 10.98; N, 6.10. Found: C, 70.88; H, 10.77; N, 6.02.