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Supporting Information

Supporting Information

Rhodium-Catalyzed Silylation of Aromatic Carbon-Hydrogen Bonds in 2-Arylpyridines Using Disilane

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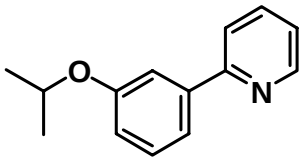
General Information. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer or JEOL JM TC-400/54/ss spectrometer in $CDCl_3$ using $CHCl_3$ as the internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorbance is reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained on a Shimadzu GCMS-QP 5000 or GCMS-QP 2010 instrument with ionization voltages of 70 eV. Elemental analyses were performed by the Elemental Analysis Section of Osaka University. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

Materials. Commercially available materials were used as received unless otherwise noted. Toluene and *o*-xylene were distilled from CaH_2. $[RhCl(cod)]_2$ and benzo[*h*]quinoline were purchased from Wako Chemicals. Hexamethyldisilane was purchased from TCI. 2-phenylpyridine and 4,4-dimethyl-2-phenyl-2-oxazoline was purchased from Aldrich. 2-(2-naphthalenyl)pyridine (CAS 66318-88-5), 9-phenyl-3-(2-pyridinyl)-9*H*-carbazole (CAS 922721-28-6), ethyl 3-(2-pyridinyl)benzoate (CAS 4550-32-7) and 2-(3-cyanophenyl)pyridine (CAS 4350-51-0) were prepared from the Pd-catalyzed cross-coupling reaction of 2-bromopyridine with the corresponding arylboronic acid.[1] *N*,*N*-dimethyl-3-(2-pyridinyl)benzenamine (CAS 917508-46-4) was obtained according to a previously published method.[2] Other substituted 2-arylpyridines were prepared from the Ni-catalyzed cross-coupling reaction of 2-bromopyridine with corresponding arylmagnesium

[1] A. Ford, E. Sinn, S. Woodward, *J. Organomet. Chem.* **1995**, *493*, 215.
[2] D. Kalyani, A. R. Dick, W. Q. Anani, M. S. Sanford, *Tetrahedron* **2006**, *62*, 11483.

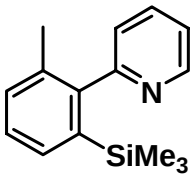
bromides. [3]

2-[(1-Methylethoxy)phenyl]pyridine (24c). R_f 0.19 (hexane/EtOAc = 10/1). Colorless oil. b.p. = 85 ºC (0.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 1.37 (d, *J* = 5.9 Hz, 6H), 4.68 (septet, *J* = 4.68 Hz, 1H), 6.95 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.23-7.26 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.52-7.57 (m, 2H), 7.69-7.78 (m, 2H), 8.68 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 22.19, 69.97, 114.27, 116.66, 119.06, 120.54, 122.05, 129.61, 136.56, 140.73, 149.43, 157.16, 158.20; IR (neat) 3074 w, 2978 s, 2931 m, 1585 s, 1564 s, 1493 w, 1385 m, 1290 s, 1213 s, 1117 s, 995 m, 966 m, 883 m, 771 s, 744 w, 694 m, 640 w, 615 w; MS *m/z* (relative intensity, %) 213 (M^+, 28), 172 (13), 171 (100), 170 (15), 143 (35), 117 (24), 115 (13). Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57; Found: C, 78.63; H, 7.08; N, 6.40.



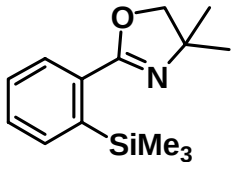
General Procedure for the Rhodium-Catalyzed Silylation of 2-Arylpyridines Using Disilane. To an oven-dried 10-mL two-necked flask, $[RhCl(cod)]_2$ (0.05 mmol), 2-arylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol) and *o*-xylene (0.5 mL) were added under a gentle stream of nitrogen. The mixture was stirred for 15 h at 130 °C under a N_2-atmosphere. The product was isolated by silica gel column chromatography.

2-[2-Methyl-6-(trimethylsilyl)phenyl]pyridine (3). R_f 0.21 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 130 ºC (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ -0.13 (s, 9H), 1.99 (s, 3H), 7.18-7.23 (m, 3H), 7.42 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.65 (td, *J* = 7.6, 2.1 Hz, 1H), 8.61-8.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.20, 20.36, 128.85, 124.89, 127.21, 130.66, 131.97, 135.00, 135.58, 138.36, 146.30, 148.90, 160.91; IR (neat) 3055 m, 2954 m, 2897 m, 1587 m, 1564 m, 1473 m, 1410 m, 1248 m, 1194 w, 1149 m, 1097 w, 1053 w, 1026 w, 993 w, 877 s, 837 s, 791 m, 762 s, 690 w, 623 w, 569 w; MS *m/z* (relative intensity, %) 241 (M^+, 3), 227 (20), 226 (100), 196 (20), 106 (22). Anal. Calcd for $C_{15}H_{19}NSi$: C, 74.63; H, 7.93; N, 5.80; Found: C, 74.39; H, 7.69; N, 5.77.

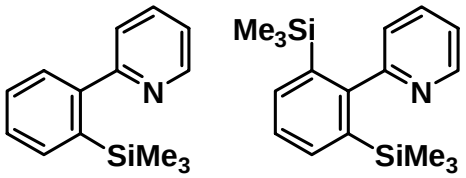


[3] B. M. Holligan, J. C. Jeffery, M. K. Norgett, E. Schatz, M. D. Ward, *J. Chem. Soc., Dalton Trans.* **1992**, 3345.

4,5-dihydro-4,4-dimethyl-2-[2-(trimethylsilyl)phenyl]oxazole (11, CAS 98191-32-7). R_f 0.31 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 80 ºC (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.32 (s, 9H), 1.41 (s, 6H), 4.12 (s, 2H), 7.36-7.45 (m, 2H), 7.63 (dd, *J* = 6.4, 2.6 Hz, 1H), 7.90 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.59, 28.36, 67.42, 79.39, 128.79, 129.85, 130.14, 135.24, 140.39, 164.36; IR (neat) 3057 w, 2968 m, 2895 w, 1657 s, 1462 w, 1435 w, 1352 m, 1309 m, 1282 w, 1246 m, 1213 w, 1190 w, 1128 w, 1095 m, 1059 w, 1041 m, 991 w, 968 w, 926 w, 845 s, 781 w, 733 s, 690 w, 621 w; MS *m/z* (relative intensity, %) 247 (M^+, 16), 233 (20), 232 (100), 178 (14), 161 (19), 160 (57), 119 (19), 109 (14), 91 (24), 75 (24), 73 (16), 55 (26). HRMS Calcd for $C_{14}H_{21}NOSi$: 247.1392; Found: 247.1385.

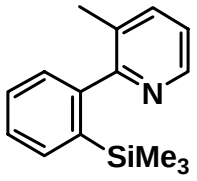


2-[2-(Trimethylsilyl)phenyl]pyridine, 2-[2,6-Bis(trimethylsilyl)phenyl]pyridine (13 as a mixture). R_f 0.23 (hexane/EtOAc = 15/1). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ -0.09 (s, di-silylated product), 0.08 (s, mono-silylated product), 7.24-7.51 (m), 7.63-7.77 (m), 8.64-8.68 (m); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.38, 0.94, 121.85, 122.38, 122.86, 125.56, 126.28, 127.32, 128.46, 128.63, 135.05, 135.30, 135.33, 136.25, 137.99, 139.23, 146.80, 148.27, 148.45, 152.92, 161.16, 162.39; IR (neat) 3049 w, 2952 m, 2897 w, 1587 m, 1562 w, 1475 w, 1427 w, 1390 w, 1248 s, 1147 w, 1124 w, 1099 w, 1051 w, 1022 w, 991 w, 856 s, 839 s, 800 w, 771 w, 752 s, 729 w, 688 w, 621 w, 463 w; MS *m/z* (mono-silylated product, relative intensity, %) 226 (M^+-H, 4), 213 (20), 212 (M^+-Me, 100), 182 (29), 99 (22); MS *m/z* (di-silylated product, relative intensity, %) 298 (M^+-H, 1), 286 (10), 285 (27), 284 (M^+-Me, 100), 268 (13), 126 (15). HRMS Calcd for mono-silylated product, $C_{14}H_{17}NSi$: 227.1130; Found: 227.1104. HRMS Calcd for disilylated product, $C_{17}H_{25}NSi_2$; 299.1526; Found: 299.1486.

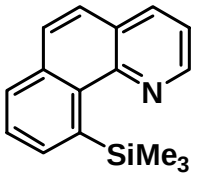


3-Methyl-2-[2-(trimethylsilyl)phenyl]pyridine (15). R_f 0.26 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 130 ºC (1.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ -0.05 (s, 9H), 2.15 (s, 3H), 7.18-7.23 (m, 2H), 7.34-7.41 (m, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.65-7.68 (m, 1H), 8.47 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ -0.09, 19.73, 122.34, 126.79, 128.26, 128.27, 131.41, 134.89,

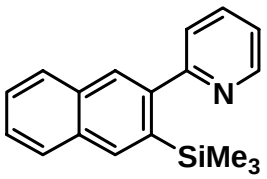
137.54, 138.44, 145.82, 146.43, 160.97; IR (neat) 3051 w, 2952 m, 2897 w, 1583 w, 1570 w, 1458 m, 1442 m, 1419 m, 1250 m, 1126 m, 1092 m, 849 s, 841 s, 795 m, 758 m, 731 m; MS *m/z* (relative intensity, %) 240 (M^+-H, 2), 227 (21), 226 (M^+-Me, 100), 196 (18), 105 (20). Anal. Calcd for $C_{15}H_{19}NSi$: C, 74.63; H, 7.93; N, 5.80; Found: C, 74.51; H, 7.76; N, 5.74.



10-(Trimethylsilyl)benzo[*h*]quinoline (17). R_f 0.40 (hexane/EtOAc = 25/1). White solid. m.p. = 110-111 ºC. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.46 (s, 9H), 7.53 (dd, *J* = 7.8, 4.3 Hz, 1H), 7.67-7.23 (m, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 8.12 (d, *J* = 7.3 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H), 8.90 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 3.31, 121.34, 124.59, 126.52, 127.33, 128.70, 129.18, 133.48, 135.17, 135.70, 135.92, 138.60, 145.40, 146.38; IR (KBr) 3043 w, 3016 w, 2951 m, 2935 m, 2897 w, 1502 w, 1406 m, 1240 s, 1107 m, 933 w, 829 s, 773 m, 746 s, 721 m, 663 m, 619 m; MS *m/z* (relative intensity, %) 250 (M^+-H, 1), 237 (22), 236 (M^+-Me, 100), 206 (38), 111 (29), 110 (13). Anal. Calcd for $C_{16}H_{17}NSi$: C, 76.44; H, 6.82; N, 5.57; Found: C, 76.33; H, 6.77; N, 5.52.

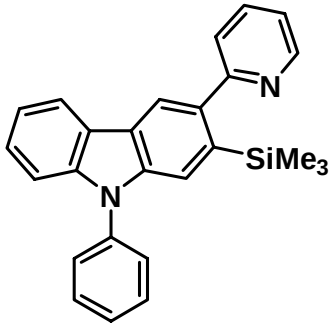


2-[3-(Trimethylsilyl)-2-naphthalenyl]pyridine (19). R_f 0.34 (hexane/EtOAc = 10/1). Colorless oil. b.p. = 130 ºC (0.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.17 (s, 9H), 7.26-7.32 (m, 1H), 7.48-7.54 (m, 2H), 7.64 (d, *J* = 7.6, 1H), 7.79-7.94 (m, 4H), 8.2 (s, 1H), 8.68 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 1.19, 121.83, 122.87, 126.19, 126.62, 127.35, 127.65, 127.83, 132.33, 133.13, 136.35, 136.40, 137.18, 143.48, 148.25, 161.07; IR (neat) 3053 m, 2951 m, 2897 w, 1587 m, 1566 m, 1477 m, 1423 m, 1284 m, 1243 s, 1082 m, 975 m, 889 m, 841 s, 787 m, 769 m, 746 s, 685 w, 476 m; MS *m/z* (relative intensity, %) 263 (23), 262 (M^+-Me, 100), 232 (28), 124 (18), 116 (14). Anal. Calcd for $C_{18}H_{19}NSi$: C, 77.93; H, 6.90; N, 5.05; Found: C, 77.93; H, 6.95; N, 5.10.



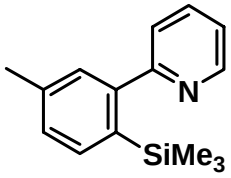
2-[2-(Trimethylsilyl)-1-naphthalenyl]pyridine (21). R_f 0.23 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 150 ºC (2.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.01 (s, 9H), 7.33-7.49 (m, 5H), 7.72-7.91 (m, 4H), 8.79 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.24, 122.30, 125.77, 125.91, 125.99, 126.11, 127.09, 127.71, 130.35, 131.82, 133.50, 135.64, 136.23, 145.00, 149.16, 160.11; IR (neat) 3051 m, 2952 m, 2895 w, 1585 m, 1562 m, 1502 w, 1471 m, 1427 m, 1377 w, 1248 s, 1149 w, 1105 w, 1026 w, 995 w, 876 s, 841 s, 816 s, 783 m, 760 s, 652 w; MS *m/z* (relative intensity, %) 277 (M^+, 2), 263 (23), 262 (100), 232 (31), 124 (15), 116 (11). Anal. Calcd for $C_{18}H_{19}NSi$: C, 77.93; H, 6.90; N, 5.05; Found: C, 77.80; H, 6.85; N, 5.09.

9-Phenyl-3-(2-pyridinyl)-2-(trimethylsilyl)-9*H*-carbazole (23). R_f 0.19 (hexane/EtOAc = 5/1). Yellow solid. m.p. = 116-117 ºC. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.10 (s, 9H), 7.20-7.34 (m, 2H), 7.39-7.52 (m, 3H), 7.59-7.70 (m, 5H), 7.75-7.77 (m, 2H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.27 (s, 1H), 8.65 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 1.37, 108.32, 109.92, 109.96, 116.76, 119.94, 120.41, 120.58, 121.36, 122.93, 123.20, 126.17, 126.88, 127.35, 129.78, 136.27, 136.29, 137.38, 137.43, 140.06, 141.27, 148.13, 161.65; IR (KBr) 3060 w, 3010 w, 2949 m, 2895 w, 1585 s, 1545 w, 1500 s, 1454 s, 1425 s, 1406 m, 1362 m, 1329 m, 1227 s, 1227 s, 1151 w, 1082 w, 837 s, 791 m, 762 s, 744 s, 698 m, 663 m; MS *m/z* (relative intensity, %) 392 (M^+, 2), 378 (32), 377 (100), 347 (11), 189 (18). HRMS Calcd for $C_{26}H_{24}N_2Si$: 392.1709; Found: 392.1713.

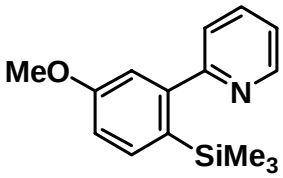


2-[5-Methyl-2-(trimethylsilyl)phenyl]pyridine (25a). R_f 0.32 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 130 °C (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.06 (s, 9H), 2.40 (s, 3H), 7.21-7.29 (m, 3H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.73 (td, *J* = 7.6, 1,6 Hz, 1H), 8.63 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.94, 21.33, 121.78, 122.91, 128.08, 129.41, 135.38, 135.57, 136.08, 138.45, 147.00, 148.33, 161.33; IR (neat) 3051 m, 3012 m, 2952 s, 2897 m, 1587 s, 1568 m, 1475 s, 1425 s, 1248 s, 1149 w, 1099 m, 1051 m, 995 m, 881 s, 839 s, 791 s, 768 s, 748 s,

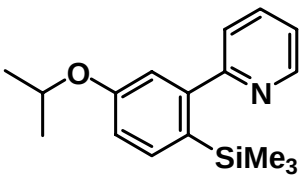
682 m, 648 m, 584 m, 472 m; MS *m/z* (relative intensity, %) 240 (M^+-H, 3), 227 (21), 226 (M^+-Me, 100), 196 (21), 105 (20). HRMS Calcd for $C_{15}H_{19}NSi$: 241.1287; Found: 241.1244.



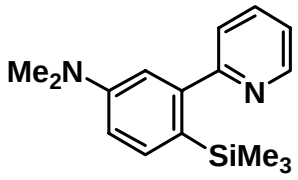
2-[5-Methoxy-2-(trimethylsilyl)phenyl]pyridine (25b). R_f 0.30 (hexane/EtOAc = 5/1). White solid. m.p. = 53-54 ºC. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.05 (s, 9H), 3.85 (s, 3H), 6.95 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 7.24-7.26 (m, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.75 (td, *J* = 7.6, 1.6 Hz, 1H), 8.65 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 1.01, 55.21, 112.86, 114.55, 122.00, 122.92, 130.22, 136.21, 136.77, 148.32, 148.48, 159.84, 160.99; IR (KBr) 3051 w, 3005 m, 2960 s, 2947 s, 2897 m, 2835 m, 1589 s, 1554 s, 1473 s, 1423 s, 1404 m, 1304 s, 1277 s, 1252 s, 1215 s, 1180 m, 1151 m, 1103 s, 1053 m, 1030 s, 879 s, 841 s, 831 s, 793 s, 762 s, 762 s, 754 s, 727 m, 681 m; MS *m/z* (relative intensity, %) 256 (M^+-H, 1), 243 (21), 242 (M^+-Me, 100), 199 (18), 114 (13). Anal. Calcd for $C_{15}H_{19}NOSi$: C, 69.99; H, 7.44; N, 5.44; Found: C, 69.98; H, 7.28; N, 5.42.



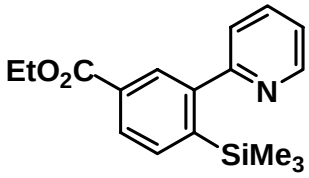
2-[5-(1-Methylethoxy)-2-(trimethylsilyl)phenyl]pyridine (25c). R_f 0.30 (hexane/EtOAc = 10/1). Colorless oil. b.p. = 130 °C (1.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.04 (s, 9H), 1.35 (d, *J* = 5.9 Hz, 6H), 4.62 (septet, *J* = 5.9 Hz, 1H), 6.92 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 7.24-7.29 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.74 (td, *J* = 7.6, 1.6 Hz, 1H), 8.64 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 1.05, 22.19, 69.69, 114.45, 116.44, 121.94, 122.88, 129.92, 136.23, 136.81, 148.24, 148.44, 158.22, 161.05; IR (neat) 3060 m, 2978 s, 2951 s, 2897 m, 1591 s, 1552 m, 1471 s, 1425 s, 1383 s, 1302 s, 1248 s, 1209 s, 1107 s, 1051 m, 1032 m, 995 m, 968 s, 839 s, 793 s, 768 s, 748 s, 685 m, 615 s; MS *m/z* (relative intensity, %) 271 (21), 270 (M^+-Me, 89), 229 (20), 228 (100), 199 (11), 198 (25). HRMS Calcd for $C_{17}H_{23}NOSi$: 285.1549; Found: 286.1636.



***N*,*N*-Dimethyl-3-(2-pyridinyl)-4-(trimethylsilyl)benzenamine (25d).** R_f 0.20 (hexane/EtOAc = 5/1). White solid. m.p. = 109-110 ºC. ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.04 (s, 9H), 3.00 (s, 6H), 6.77-6.81 (m, 2H), 7.24-7.28 (m, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.73 (td, *J* = 7.6, 1.6 Hz, 1H), 8.65 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.99, 40.35, 111.42, 113.05, 121.71, 123.09, 124.47, 135.95, 136.27, 148.10, 148.28, 150.55, 162.09; IR (KBr) 3078 w, 3047 w, 2954 w, 2893 m, 1603 s, 1585 m, 1537 m, 1427 m, 1363 m, 1250 m, 1227 m, 1107 m, 854 s, 835 s, 795 m, 758 m; MS *m/z* (relative intensity, %) 270 (M^+, 1), 256 (22), 255 (100), 239 (36), 127 (22). Anal. Calcd for $C_{16}H_{22}N_2Si$: C, 71.06; H, 8.20; N, 10.36; Found: C, 71.01; H, 8.09; N, 10.34.

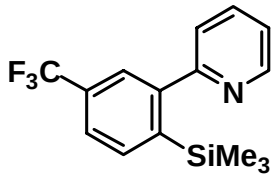


3-(2-Pyridynyl)-4-(trimethylsilyl)benzoic acid ethyl ester (25e). R_f 0.24 (hexane/EtOAc = 10/1). Colorless oil. b.p. = 175 °C (1.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.10 (s, 9H), 1.39 (t, *J* = 7.0 Hz, 3H), 4.39 (q, *J* = 7.0 Hz, 2H), 7.28 (dd, *J* = 6.5, 4.6 Hz 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.73-7.81 (m, 2H), 8.04 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.13 (s, 1H), 8.64 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.80, 14.39, 60.96, 122.16, 122.78, 127.83, 128.92, 130.46, 135.47, 136.40, 145.45, 146.92, 148.29, 160.17, 166.28; IR (neat) 3059 w, 2981 m, 2954 m, 2898 m, 1720 s, 1587 s, 1568 m, 1477 m, 1427 m, 1398 s, 1367 m, 1309 s, 1246 s, 1124 m, 1095 s, 1084 s, 843 s, 795 m, 756 s; MS *m/z* (relative intensity, %) 298 (M^+-H, 3), 285 (24), 284 (M^+-Me, 100), 257 (17), 256 (76), 226 (16), 119 (10), 91 (15). Anal. Calcd for $C_{17}H_{21}NO_2Si$: C, 68.19; H, 7.07; N, 4.68; Found: C, 68.16; H, 6.91; N, 4.70.

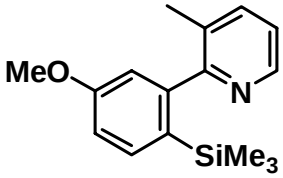


2-[5-(Trifluoromethyl)-2-(trimethylsilyl)phenyl]pyridine (25f). R_f 0.34 (hexane/EtOAc = 20/1). Colorless oil. b.p. = 115 ºC (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.11 (s, 9H), 7.32 (dd, *J* = 7.3, 5.1 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, H), 7.70 (s, 1H), 7.76-7.85 (m, 2H), 8.67 (d, *J* = 4.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.72, 122.46, 122.81, 123.63 (q, *J* = 3.9 Hz), 124.02 (q, *J* = 271.1 Hz), 124.84 (q, *J* = 3.9 Hz), 130.66 (q, *J* = 32.3 Hz), 135.82, 136.54, 144.29, 147.40, 148.51, 159.80; IR (neat) 3066 m, 3020 m, 2954 s, 2898 m, 1589 s, 1570 m, 1477 s, 1400 m, 1400 s, 1338 s, 1281 s, 1252 s, 1171 s, 1128 s, 1066 s, 993 m, 904 s, 854 s, 837 s, 793 s,

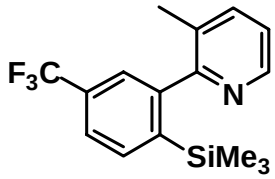
771 s, 748 s, 690 s, 658 m, 621 m, 484 w; MS *m/z* (relative intensity, %) 294 (M^+-H, 4), 281 (21), 280 (M^+-Me, 100), 250 (29), 132 (12). Anal. Calcd for $C_{15}H_{16}F_3NSi$: C, 60.99; H, 5.46; N, 4.74; Found: C, 60.83; H, 5.57; N, 4.72.



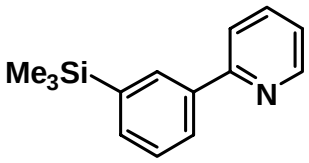
2-[5-Methoxy-2-(trimethylsilyl)phenyl]-3-methylpyridine (27a). R_f 0.17 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 155 °C (3.5 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ -0.08 (s, 9H), 2.16 (s, 3H), 3.81 (s, 3H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.21 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.54-7.59 (m, 2H), 8.47 (d, *J* = 3.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ 0.05, 19.67, 55.17, 112.70, 114.22, 122.50, 129.47, 131.53, 136.44, 137.70, 145.72, 147.79, 159.60, 160.64; IR (KBr) 3066 w, 2958 m, 2898 m, 1597 s, 1581 m, 1556 m, 1462 m, 1427 s, 1302 s, 1248 s, 1213 s, 1174 s, 1117 s, 1097 s, 1059 m, 1034 s, 883 s, 837s, 808 s, 761 m, 748 m, 731 m, 700 w, 683 m, 594 m; MS *m/z* (relative intensity, %) 257 (21), 256 (M^+-Me, 100), 213 (17), 121 (12). Anal. Calcd for $C_{16}H_{21}NOSi$: C, 70.80; H, 7.80; N, 5.16; Found: C, 70.90; H, 7.74; N, 5.17.



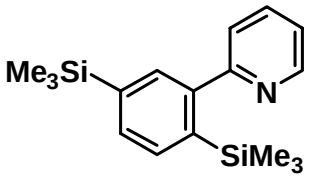
3-Methyl-2-[5-(trifluoromethyl)-2-(trimethylsilyl)phenyl]pyridine (27b). R_f 0.36 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 130 °C (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.02 (s, 9H), 2.15 (s, 3H), 7.22-7.27 (m, 1H), 7.46 (s, 1H), 7.58-7.63 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 8.49 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ -0.29, 16.63, 122.93, 123.31 (q, *J* = 3.9 Hz), 124.00 (q, *J* = 271.1 Hz), 124.88 (q, *J* = 3.9 Hz), 130.38 (q, *J* = 32.3 Hz), 131.44, 135.50, 137.88, 143.78, 146.11, 147.03, 159.59; IR (neat) 3053 w, 2954 m, 2898 m, 1585 m, 1572 m, 1446 m, 1392 s, 1336 s, 1281 s, 1252 s, 1169 s, 1068 s, 1057 s, 860 s, 843 s, 800 s, 791 m, 771 m, 758 m, 737 m, 721 m, 683 m, 633 m; MS *m/z* (relative intensity, %) 308 (M^+-H, 2), 295 (23), 294 (M^+-Me, 100), 264 (21), 139 (10). Anal. Calcd for $C_{16}H_{18}F_3NSi$: C, 62.11; H, 5.86; N, 4.53; Found: C, 61.88; H, 5.90; N, 4.58.

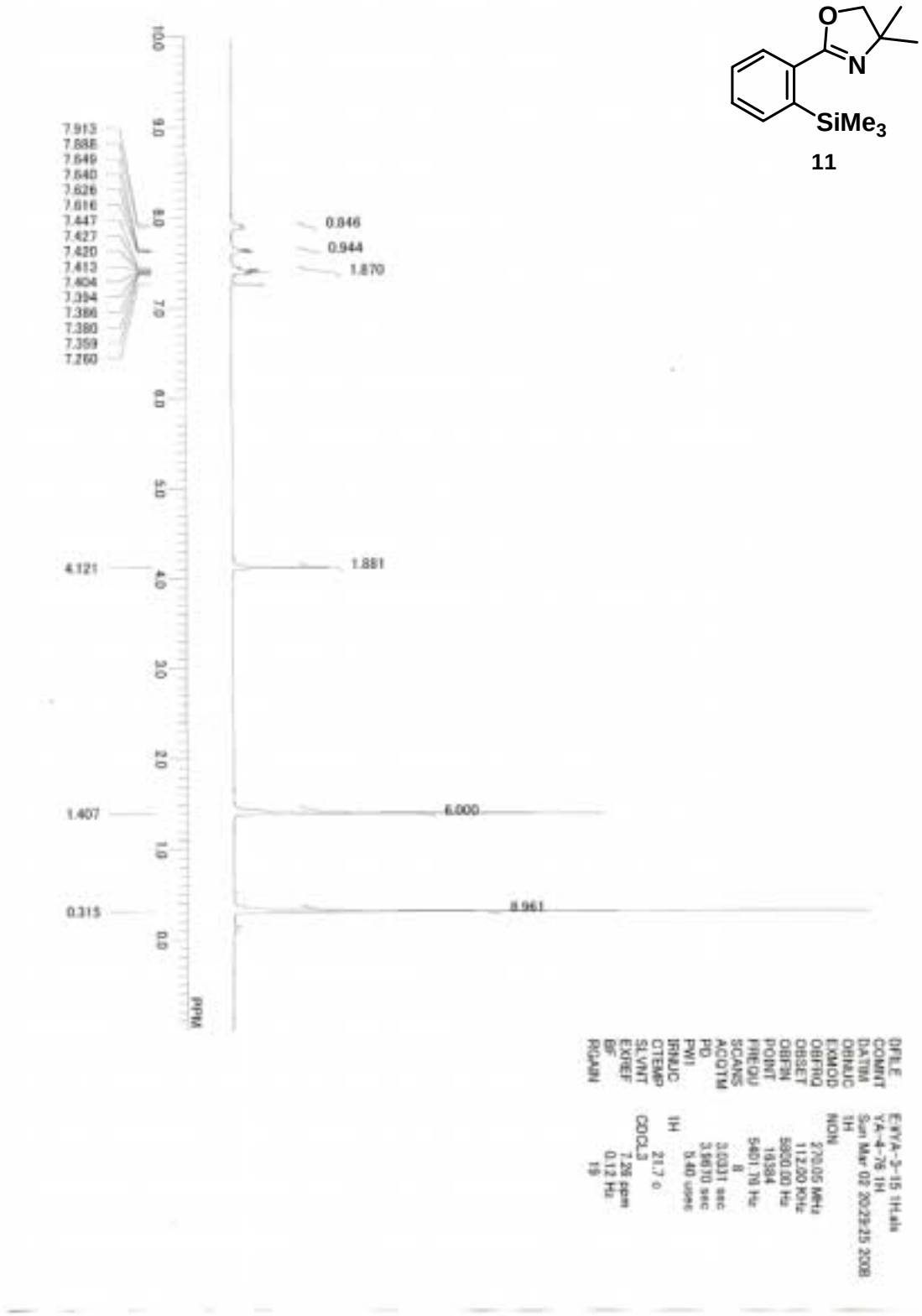


2-[3-(Trimethylsilyl)phenyl]pyridine (29). R_f 0.37 (hexane/EtOAc = 5/1). Colorless oil. b.p. = 110 ºC (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.32 (s, 9H), 7.22-7.26 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.72-7.80 (m, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 8.12 (s, 1H), 8.71 (d, *J* = 4.6 Hz, 1H); ^{13}C NMR (67.80 MHz) δ -0.93, 120.71, 121.89, 127.43, 128.00, 131.69, 133.85, 136.59, 138.54, 140.89, 157.80; IR (neat) 3084 m, 3051 m, 3006 m, 2954 s, 2897 m, 1587 s, 1564 m, 1460 s, 1431 m, 1389 m, 1282 m, 1250 s, 1174 w, 1153 m, 1120 s, 1095 w, 1041 m, 991 w, 858 s, 838 s, 771 s, 754 s, 694 m, 638 w, 620 m; MS *m/z* (relative intensity, %) 227 (M^+, 27), 213 (20), 212 (100), 182 (22). Anal. Calcd for $C_{14}H_{17}NSi$: C, 73.95; H, 7.54; N, 6.16; Found: C, 74.06; H, 7.32; N, 6.36.



2-[2,6-Bis(trimethylsilyl)phenyl]pyridine (30). R_f 0.14 (hexane/EtOAc = 20/1). Colorless oil. b.p. = 120 ºC (2.0 mmHg). ^{1}H NMR ($CDCl_3$, 270.05 MHz) δ 0.07 (s, 9H), 0.29 (s, 9H), 7.26-7.30 (m, 1H), 7.48-7.57 (m, 3H), 7.68-7.79 (m, 2H), 8.65 (d, *J* = 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 67.80 MHz) δ -1.07, 0.79, 121.82, 123.06, 132.24, 133.29, 133.61, 134.46, 136.21, 139.68, 140.98, 148.35, 161.64; IR (neat) 3051 w, 3010 w, 2954 m, 2897 w, 1587 m, 1566 w, 1475 w, 1425 w, 1367 w, 1250 m, 1157 m, 1130 w, 1038 w, 993 w, 841 s, 793 m, 752 m, 694 w, 636 m, 586 w, 480 w, 445 w; MS *m/z* (relative intensity, %) 298 (M^+-H, 2), 286 (10), 285 (28), 284 (M^+-Me, 100), 135 (13). Anal. Calcd for $C_{17}H_{25}NSi_2$: C, 68.16; H, 8.41; N, 4.68; Found: C, 68.43; H, 8.19; N, 4.90.

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7.404
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7.386
7.380
7.359
7.260
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0.944
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6.000
1.407
8.961
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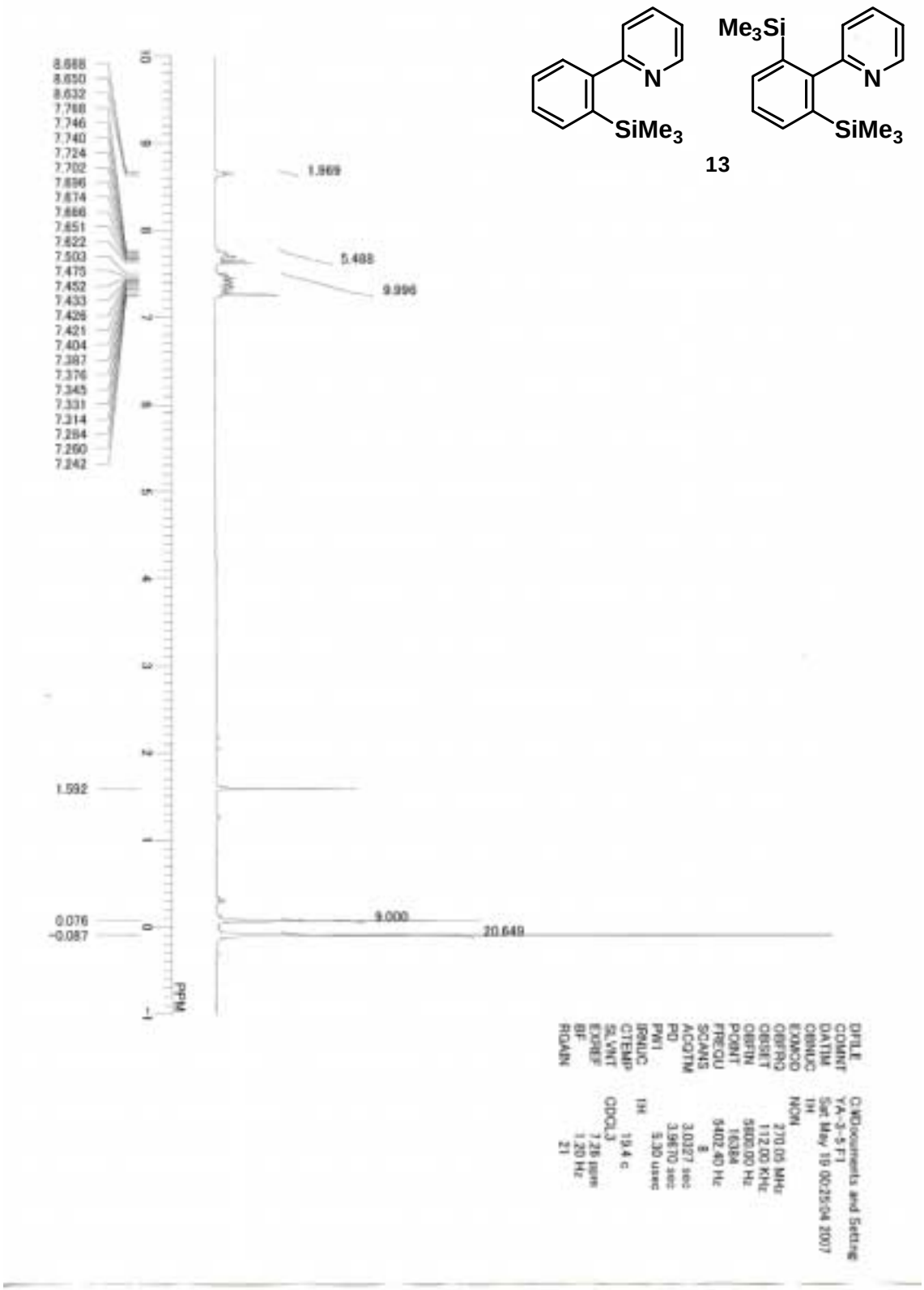
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SiMe3
N
SiMe3
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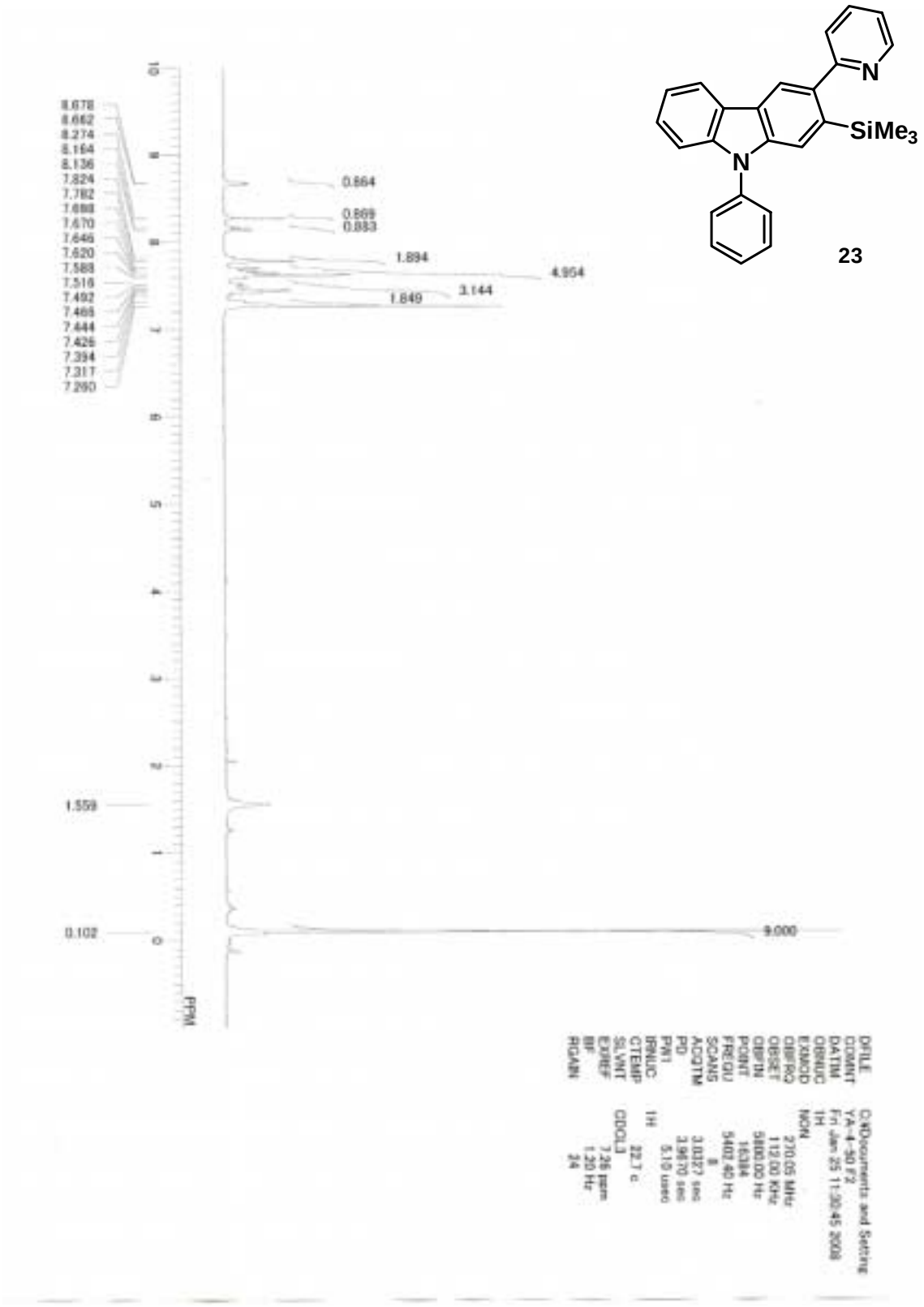
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7.620
7.588
7.516
7.492
7.469
7.444
7.426
7.394
7.317
7.290
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3.144
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9.000
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Fri Jan 25 11:30:45 2008
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113.00 KHz
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22.7 c
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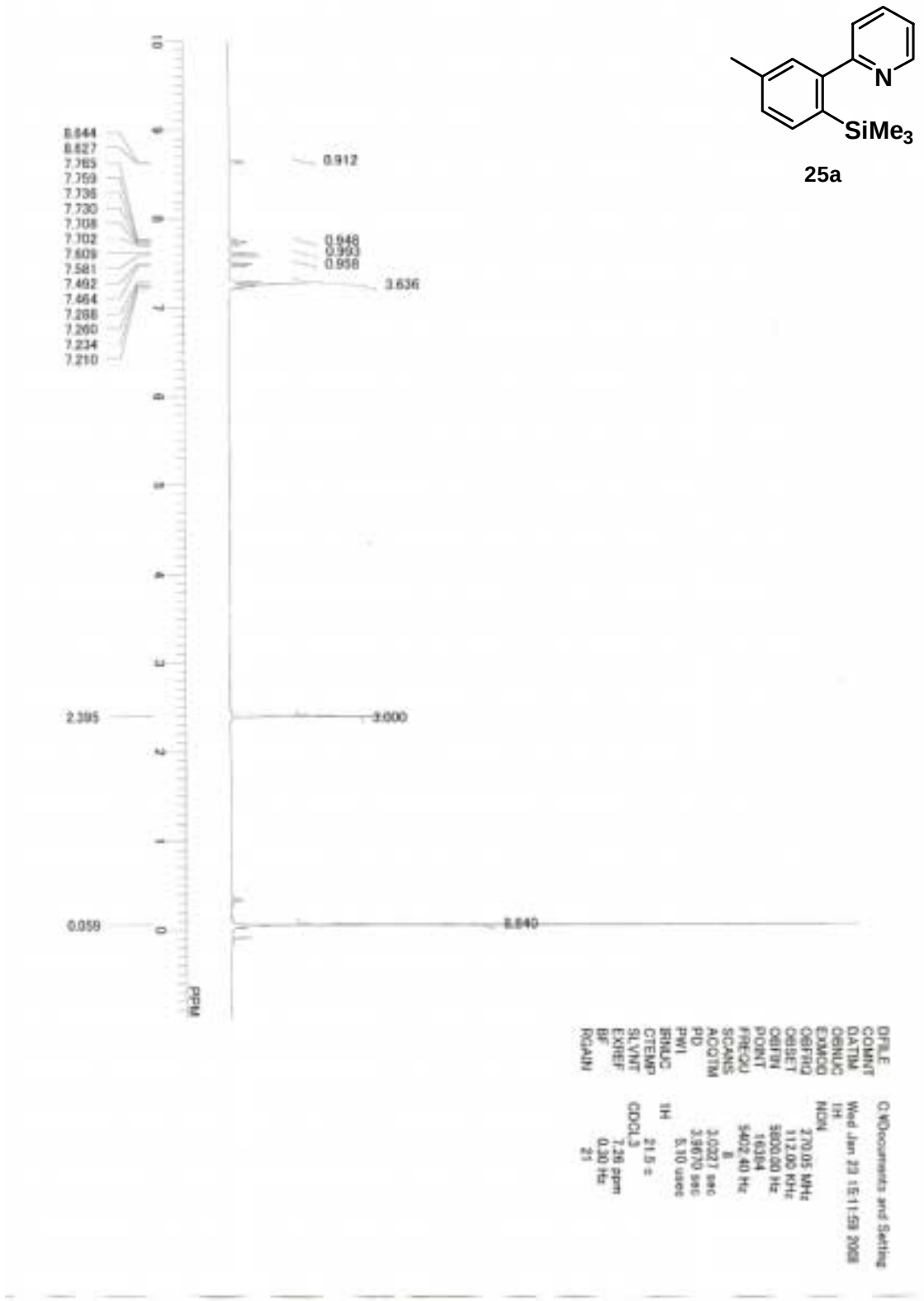
7.26 ppm
1.20 Hz
24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DATIM Wed Jan 23 15:11:59 2008
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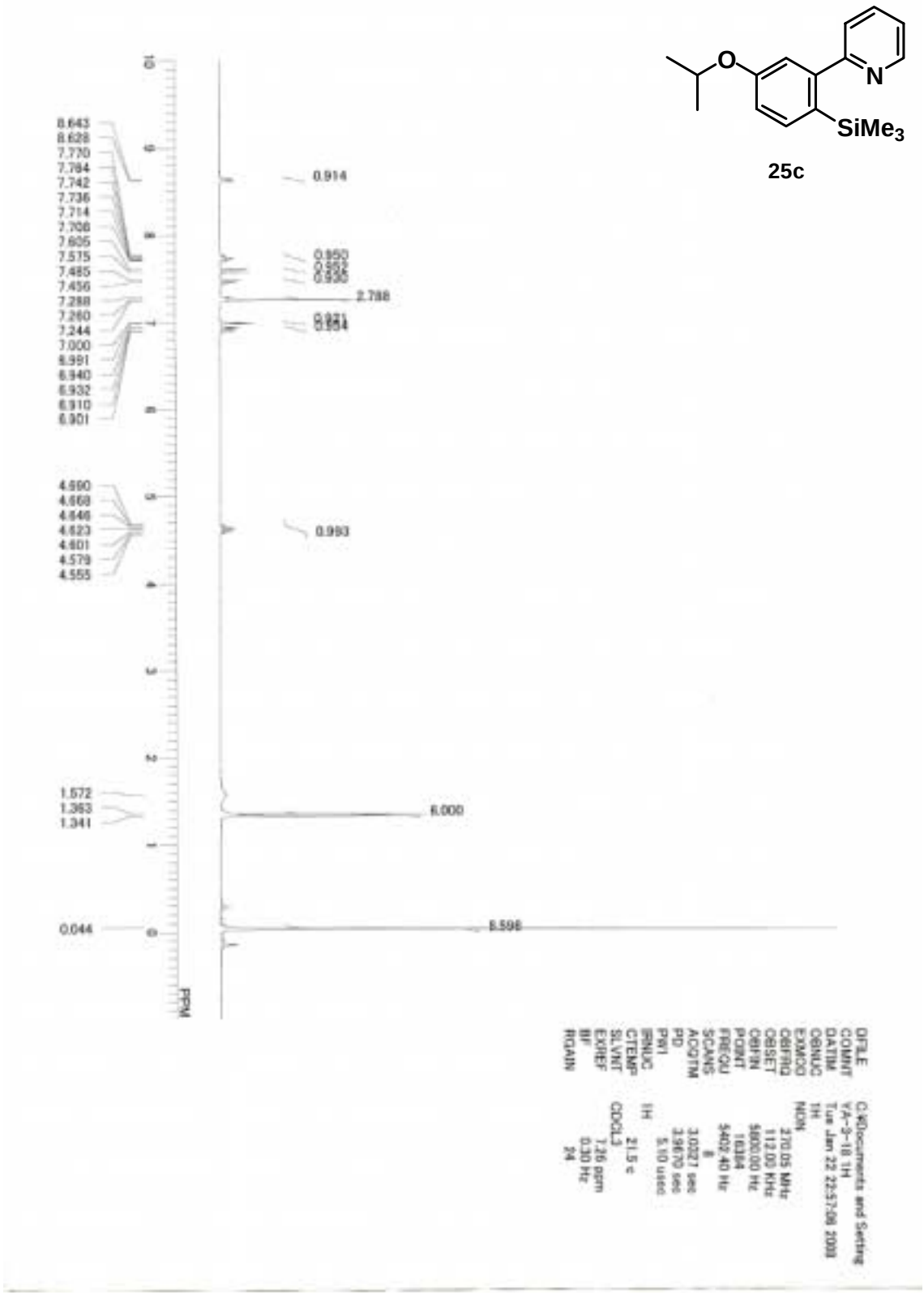
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7.260
7.244
7.000
6.991
6.940
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4.590
4.568
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4.623
4.601
4.579
4.555
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1.363
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SLVNT CDCL3
EXREF 7.26 ppm
BF 0.30 Hz
RGAIN 24

Substituent Effect. To examine the effect of the substituent, the reactions of three 2-phenylpyridine derivatives as shown below were carried out under the same conditions. As a result, the reactivity order is as follows: CF_3>H>OMe.

Kinetic Isotope Effect. To an oven-dried 10-mL two-necked flask, $[RhCl(cod)]_2$ (0.05 mmol), 3-methyl-2-phenylpyridine (1.0 mmol), hexamethyldisilane (2.0 mmol) and *o*-xylene (0.5 mL) were added under a gentle stream of nitrogen. To another oven-dried 10-mL two-necked flask, $[RhCl(cod)]_2$ (0.05 mmol), 3-methyl-2-phenylpyridine-d_5 (1.0 mmol), hexamethyldisilane (2.0 mmol) and *o*-xylene (0.5 mL) were added in the same manner. These two mixtures were stirred for 3 h at 130 °C under a N_2-atmosphere and reaction progress was monitored using GC analysis.