Supporting Information

A Highly Efficient Iridium-Catalyzed Oxidation of Organosilanes to Silanols

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General. All commercial reagents were used without purification, and all solvents were reaction grade. $[\text{IrCl}(\text{C}_8\text{H}_{12})]_2$ was purchased from Strem Co., and used as obtained without further purification. All reaction mixtures were stirred magnetically and were stirred magnetically and were monitored by thin-layer chromatography using Merck silica gel 60 F₂₅₄ precoated glass plates, which were visualized with UV light, and then, developed by using Fluka silica gel 60 (0.040-0.063 mm, 230-400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DPX FT(400 and 250 MHz) spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent (δ 7.24 for ^1H and δ 77.0 for ^{13}C). High-resolution mass spectra were recorded on a VG Autospec Ulpima. Infrared spectra were recorded on a JASCO FT/IR-460 plus FT-IR spectrometer as either a thin film pressed between two sodium chloride plates or as a solid suspended in a potassium bromide disk. Optical rotation of the optically active silane and silanol were measured on Jasco DIP-140 digital polarimeter.

Triethylsilanol : ^1H NMR (400 MHz, CDCl_3) δ 1.45 (bs, 1H), 0.97 (t, J = 7.9 Hz, 9H), 0.59 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 6.59, 5.79; IR (film): 3432 (br), 2096, 1642 cm^{-1} ; HRMS (EI) calcd for $\text{C}_6\text{H}_6\text{OSi}$ 132.0971, found 132.0979.

Triisobutylsilanol : ^1H NMR (400 MHz, CDCl_3) δ 1.88-1.80 (m, 3H), 1.27 (bs, 1H), 0.96 (d, $J = 6.5$ Hz, 18H), 0.61 (d, $J = 6.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 27.0, 26.4, 24.3; IR (film): 3432 (br), 2955, 1650, 1464, 1218 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{28}\text{OSi}$ 216.1910, found 216.1903.

Dimethyloctadecylsilanol : ^1H NMR (400 MHz, CDCl_3) δ 2.07 (bs, 1H), 1.18-1.14(m, 34H), 0.75 (t, $J = 6.7$ Hz, 3H), 0.45 (m, 2H), 0.00 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 34.0, 32.4, 30.2, 30.1, 29.9, 23.7, 23.2, 18.3, 14.6, 0.2; IR (film): 3246 (br), 2919, 2850, 2361, 1464 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{44}\text{OSi}$ 328.3163 found 328.3160.

Dimethylphenylsilanol : ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.52 (m, 2H), 7.50-7.39 (m, 3H), 1.87 (bs, 1H), 0.40 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.11, 133.05, 129.67, 127.93; IR (film): 3332 (br), 2095, 1650, 1464, 1216 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{12}\text{OSi}$ 152.0657 found 152.0650

Diphenylmethylsilanol : ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.39 (m, 4H), 7.21-7.13 (m, 6H), 3.57 (bs, 1H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.7, 133.6, 129.3, 126.8; IR (film): 3398 (br), 2097, 1643, 1427, 1254 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{OSi}$ 214.0814 found 214.0811.

Diphenylsilanediol : ^1H NMR (400 MHz, CDCl_3) δ 7.75-7.73 (m, 4H), 7.48-7.39 (m, 6H), 2.85 (bs, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.9, 131.6, 128.3, 126.7; IR (film): 3432 (br), 2094, 1644 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{Si}$ 216.0606 found 216.0613.

Dimethyl(4-methoxyphenyl)silanol : ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, J = 8.46 Hz, 2H), 6.93 (d, J = 8.44 Hz, 2H), 3.82 (s, 3H), 1.80 (s, 1H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.75, 134.53, 130.06, 113.52, 54.96; IR (film): 3432 (br), 1643, 1248, 1116 cm^{-1} ; HRMS (EI) calcd for $\text{C}_9\text{H}_{14}\text{O}_2\text{Si}$ 182.0763, found 182.0766.

Dimethyl(4-*n*-butylphenyl)silanol : ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, J = 7.82 Hz, 2H), 7.21 (d, J = 7.76 Hz, 2H), 2.61 (t, J = 7.55 Hz, 2H), 1.78 (s, 1H), 1.64-1.56 (m, 2H), 1.40-1.31 (m, 2H), 0.92 (t, J = 7.32 Hz, 3H), 0.39 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.60, 135.74, 133.08, 128.07, 35.67, 33.50, 22.38, 13.92; IR (film): 3432 (br), 2958, 1643, 1251, 1114, cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{20}\text{OSi}$ 208.1284, found 208.1287.

Dimethyl(4-methylbenzyl)silanol : ^1H NMR (400 MHz, CDCl_3) δ 7.04 (d, J = 7.83 Hz, 2H), 6.95 (d, J = 7.90 Hz, 2H), 2.29 (s, 3H), 2.13 (s, 2H), 1.57 (s, 1H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.32, 134.34, 129.84, 128.73, 28.07, 21.58; IR (film):

3302 (br), 2958, 1511, 1251, 838 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{16}\text{OSi}$ 180.0970, found 180.0962.

(E)-Dimethyl(2-phenylethenyl)silanol : ^1H NMR (250 MHz, CDCl_3) δ 7.44-7.23 (m, 5H), 6.95 (d, $J = 19.3$ Hz, 1H), 6.47 (d, $J = 19.2$ Hz, 1H), 2.45 (bs, 1H), 0.35 (s, 6H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 145.6, 138.4, 129.0, 128.8, 128.0, 127.0, 0.54; IR (film): 3264 (br), 2960, 1604, 1253 cm^{-1} .

Dimethyl(5-chloropentynyl)silanol : ^1H NMR (250 MHz, CDCl_3) δ 3.65 (t, $J = 6.3$ Hz, 2H), 2.43 (t, $J = 6.8$ Hz, 3H), 1.98 (m, 2H), 0.28 (s, 6H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 131.5, 110.8, 49.1, 36.7, 22.7, 7.2; IR (film): 3306 (br), 2962, 2177, 1256 cm^{-1} ; MS (EI) 169 (6.1), 167 (14.0), 133 (11.5), 123 (5.7), 95 (6.5), 74 (5.8), 73 (100.0).

Diisopropyl(phenylethynyl)silanol : ^1H NMR (250 MHz, CDCl_3) δ 7.50-7.46 (m, 2H), 7.32-7.26 (m, 3H), 2.26 (bs, 1H), 1.15-1.02 (m, 14H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 132.6, 129.3, 128.7, 123.1, 106.6, 90.2, 17.5, 17.3, 13.7; IR (film): 3360 (br), 2946, 2159, 1463, 1028 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{20}\text{OSi}$ 232.1283, found 232.1281.

Dimethyl(2-thienyl)silanol : ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, $J = 4.6$ Hz, 1H), 7.36 (d, $J = 3.3$ Hz, 1H), 7.21 (m, 1H), 2.10 (bs, 1H), 0.46 (s, 6H); ^{13}C NMR (100 MHz,

CDCl_3) δ 137.6, 133.7, 130.2, 127.2, 1.3; IR (film) 3339 (br), 2962, 1256, 1086 cm^{-1} ;

HRMS (EI) calcd for $\text{C}_6\text{H}_{10}\text{OSi}$ 158.0222, found 158.0218.

Diphenyl(2-thienyl)silanol : ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.67 (m, 5H), 7.46-7.38 (m, 7H), 7.24-7.22 (m, 1H), 2.70 (s, 1H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 137.64, 134.89, 134.75, 134.69, 132.57, 130.37, 128.33, 127.96; IR (film): 3430 (br), 2967, 2143, 1254 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{14}\text{OSSi}$ 282.0535, found 282.0534.

Dimethylquinolin-3-ylsilanol : ^1H NMR (400 MHz, CDCl_3) δ 9.03 (s, 1H), 8.25 (s, 1H), 8.09 (d, J = 8.88 Hz, 1H), 7.74-7.71 (m, 2H), 7.53 (t, J = 7.87 Hz, 1H), 1.80 (bs, 1H), 0.49 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.06, 147.73, 142.47, 132.12, 129.98, 128.55, 127.83, 127.52, 126.49; IR (film): 3425 (br), 1618, 1257, 1058 cm^{-1} ;
HRMS (EI) calcd for $\text{C}_{11}\text{H}_{13}\text{NOSi}$ 203.0767, found 203.0765.

(+/-)-Methyl(α -naphthyl)phenylsilanol : ^1H NMR (250 MHz, CDCl_3) δ 8.14 (m, 1H), 7.97-7.83 (m, 3H), 7.68-7.66 (m, 2H), 7.54-7.40 (m, 6H), 2.41 (bs, 1H), 0.86 (s, 3H); ^{13}C NMR (62.5 MHz, CDCl_3) δ 138.1, 137.2, 135.2, 135.1, 134.4, 133.8, 131.2, 130.3, 129.3, 128.8, 128.4, 126.4, 125.9, 125.4, 0.45.

(-)-Methyl(α -naphthyl)phenylsilanol : ^1H NMR (250 MHz, CDCl_3) δ 8.16 (m, 1H), 7.97-7.83 (m, 3H), 7.68-7.65 (m, 2H), 7.50-7.29 (m, 6H), 2.41 (bs, 1H), 0.85 (s, 3H);

^{13}C NMR (62.5 MHz, CDCl_3) δ 138.1, 137.2, 135.2, 135.1, 134.4, 133.8, 131.2, 130.3, 129.3, 128.8, 128.4, 126.5, 126.0, 125.4, 0.46.