Supporting Information

Rh(I)-Catalyzed Silylation of Aryl and Alkenyl Cyanides Involving Simultaneous Cleavage of C-C and Si-Si Bonds

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General Information. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL JMN-270 spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained on a Horiba FT-700 spectrometer; absorptions are 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 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. Analytical gas chromatography (GC) was carried out on a Shimadzu GC-14A gas chromatography, equipped with a flame ionization detector. Column chromatography was performed with SiO_2 (Merck SilicaGel 60 (230-400 mesh)).

Materials. Dioxane, DMA, and ethylcyclohexane were distilled from CaH_2 . $[\text{RhCl}(\text{cod})]_2$ was purchased from Wako Chemicals and used as received. $[\text{RhCl}(\text{coe})_2]_2$ was purchased from Strem Chemicals and used as received. $[\text{Rh}(\text{OMe})(\text{cod})]_2$ ¹, $[\text{Rh}(\text{cod})_2]\text{BF}_4$ ², 1,1,2,2-Tetramethyl-1,2-dibenzylidisilane [20156-42-7]³, 4-(1,1-dimethylethyl)-1-cyclohexene-1-carbonitrile [7370-14-1]⁴ were prepared according to the literature procedures. 4-Acetyoxybenzonitrile [13031-41-9] was prepared by acetylation of 4-cyanophenol. 4-Cyanobenzoic acid 1,1-dimethylethyl ester [55696-50-9] was prepared by the acid chloride formation, followed by the esterification by *t*-BuOH. 2-(4-Cyanophenyl)-5,5-dimethyl[1,3,2]dioxaborinane [214360-44-8] was prepared by the reaction of 4-cyanophenyl boronic acid with 2,2,-dimethyl-1,3-propanediol.⁵ 1-[(4-Methylphenyl)sulfonyl]-1*H*-Indole-3-carbonitrile [859205-33-7] was prepared by *N*-tosylation of 1*H*-Indole-3-carbonitrile.⁶ Cyanoferrocene [1273-84-3] was prepared by the oxime formation of ferrocenecarbaldehyde and the subsequent dehydration by Ac_2O .⁷

Typical procedure for silylation of aryl and alkenyl cyanides. (Table 2, entry 1) An oven-dried

5 mL screw-capped vial was charged with 2-naphthonitrile (2 mmol), hexamethyldisilane (4 mmol), $[\text{RhCl}(\text{cod})]_2$ (0.1 mmol), and ethylcyclohexane (1 mL) under gentle stream of nitrogen. The vessel was heated in an oil bath at 130 °C for 15 h followed by cooling. The contents were subjected to flash chromatography (hexane) to give 2-(trimethylsilyl)naphthalene (348 mg, 87%) as a colorless oil.

2-(Trimethylsilyl)naphthalene [18052-85-2].

^1H NMR (CDCl_3 , 270 MHz): δ 8.02 (s, 1H), 7.87-7.83 (m, 3H), 7.62 (d, J = 8.4 Hz, 1H), 7.50-7.47 (m, 2H), 0.36 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 137.8, 133.6, 133.5, 132.8, 129.7, 127.9, 127.6, 126.8, 126.1, 125.8, -0.9.

2-(Dimethylphenylsilyl)naphthalene.

Mp 56-58 °C

^1H NMR (CDCl_3 , 270 MHz): δ 8.03 (s, 1H), 7.84-7.81 (m, 3H), 7.61-7.36 (m, 8H), 0.65 (s, 6H) ;

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 138.0, 135.5, 134.7, 134.1, 133.6, 132.7, 130.2, 129.0, 127.9, 127.7, 127.5, 126.9, 126.3, 125.8, -2.2;

IR(neat): 3048 s, 2956 s, 1589 m, 1494 w, 1427 m, 1407 m, 1324 m, 1251 m, 1189 w, 1112 m, 1085 m, 1020 w, 898 w, 856 s, 827 s, 809 s, 775 s, 734 m, 700 s, 661 w, 630 w, 582 w, 503 w, 474 s, 408 m;

MS m/z (% relative intensity): 262(M^+ , 31), 248 (23), 247 (100), 169 (16), 167 (11), 123 (26);

HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{Si}$ 262.1178, found 262.1173.

2-(Dimethylbenzylsilyl)naphthalene.

^1H NMR (CDCl_3 , 270MHz): δ 7.94 (s, 1H), 7.83-7.81 (m, 3H), 7.54-7.48 (m, 3H), 7.21-6.94 (m, 5H), 2.39 (s, 2H), 0.34 (s, 6H);

^{13}C NMR (CDCl_3 , 67.5MHz): δ 139.4, 135.7, 134.2, 133.5, 132.7, 129.8, 128.2, 128.0, 127.9,

127.5, 126.7, 126.2, 125.7, 123.9, 26.2, -3.2;

IR(KBr): 3048 s, 3021 s, 2958 s, 2888 s, 1592 s, 1490 s, 1448 s, 1349 m, 1322 s, 1274 s, 1247 s, 1201 s, 1143 s, 1081 s, 1054 s, 1020 s, 970 m, 948 m, 900 m, 858 s, 815 s, 757 s, 740 s, 696 s, 640 s, 580 m, 478 s;

MS m/z (% relative intensity): 276 (M^+ , 7), 186 (18), 185 (100);

HRMS calcd for $C_{19}H_{20}Si$ 276.1334, found 276.1340.

1-(Trimethylsilyl)naphthalene [18052-80-7].

1H NMR ($CDCl_3$, 270 MHz): δ 8.11 (d, $J = 7.0$ Hz, 1H), 7.88 (d, $J = 3.8$ Hz, 2H), 7.71 (d, $J = 6.8$ Hz, 1H), 7.55-7.43 (m, 3H), 0.49 (s, 9H);

^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 138.0, 136.7, 133.2, 133.0, 129.6, 128.9, 128.0, 125.4, 125.1, 124.9, 0.3.

Trimethyl(4-trifluoromethylphenyl)silane [312-75-4].

1H NMR ($CDCl_3$, 270 MHz): δ 7.62 (m, 4H), 0.31 (s, 9H);

^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 145.3, 133.5, 130.6 (q, $J = 32.0$ Hz), 124.1 (q, $J = 270.9$ Hz), 124.1 (q, $J = 3.7$ Hz), -1.2.

4-(Trimethylsilyl)benzoic acid methyl ester [22515-30-6].

1H NMR ($CDCl_3$, 270 MHz): δ 7.99 (d, $J = 8.1$ Hz, 2H), 7.59 (d, $J = 8.1$ Hz, 2H), 3.92 (s, 3H), 0.29 (s, 9H);

^{13}C NMR ($CDCl_3$, 67.5 MHz): δ 167.1, 146.7, 133.1, 130.1, 128.3, 52.1, -1.2.

4-(Trimethylsilyl)benzoic acid 1,1-dimethylethyl ester [547744-73-0].

^1H NMR (CDCl_3 , 270 MHz): δ 7.96 (d, $J = 7.8$ Hz, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 1.60 (s, 9H), 0.29 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 165.7, 145.9, 132.9, 132.0, 128.2, 80.8, 28.2, -1.1.

4-(Trimethylsilyl)phenol acetate. [18001-11-1].

^1H NMR (CDCl_3 , 270 MHz): δ 7.53 (d, $J = 8.1$ Hz, 2H), 7.07 (d, $J = 8.1$ Hz, 2H), 2.30 (s, 3H), 0.26 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 169.3, 151.1, 137.8, 134.4, 120.7, 21.2, -0.9.

4-Fluorophenyltrimethylsilane [455-17-4].

^1H NMR (CDCl_3 , 270 MHz): δ 7.48 (dd, $J = 6.5, 8.1$ Hz, 2H), 7.04 (dd, $J = 8.6, 8.9$ Hz, 2H), 0.26 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 163.4 (d, $J = 246.6$ Hz), 135.7, 135.0 (d, $J = 7.3$ Hz), 114.7 (d, $J = 19.5$ Hz), -0.9.

(4-Methoxyphenyl)trimethylsilane [877-68-9].

^1H NMR (CDCl_3 , 270 MHz): δ 7.46 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.1$ Hz, 2H), 3.82 (s, 3H), 0.26 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 160.0, 134.5, 131.1, 113.3, 55.0, -0.8.

***N,N*-Dimethyl-4-(trimethylsilyl)aniline [16087-24-4].**

¹H NMR (CDCl₃, 270 MHz): δ 7.41 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 2.96 (s, 6H), 0.24 (s, 9H);

¹³C NMR (CDCl₃, 67.5 MHz): δ 150.7, 134.2, 125.3, 111.8, 40.2, -0.7.

2-(4-Trimethylsilylphenyl)-5,5-dimethyl[1,3,2]dioxaborinane [574755-28-5]

¹H NMR (CDCl₃, 270 MHz): δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 2H), 3.77 (s, 4H), 1.02 (s, 6H), 0.27 (s, 9H);

¹³C NMR (CDCl₃, 67.5 MHz): δ 143.2, 132.8, 132.4, 72.3, 31.9, 21.9, -1.1.

(2-Methylphenyl)trimethylsilane [7450-03-5].

¹H NMR (CDCl₃, 270 MHz): δ 7.46 (d, *J* = 4.1 Hz, 1H), 7.29-7.14 (m, 3H), 2.46 (s, 3H), 0.32 (s, 9H);

¹³C NMR (CDCl₃, 67.5 MHz): δ 143.3, 138.2, 134.1, 129.5, 129.0, 124.7, 23.0, 0.0.

1-[(4-Methylphenyl)sulfonyl]-3-trimethylsilyl-1*H*-indole.

Mp 146-148 °C

¹H NMR (CDCl₃, 270 MHz): δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 7.3

Hz, 1H), 7.51 (s, 1H), 7.32-7.19 (m, 4H), 2.35 (s, 3H), 0.34 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 144.7, 135.7, 135.3, 134.4, 131.3, 129.8, 126.8, 124.1, 122.8, 122.1, 118.0, 113.4, 21.7, -0.6

IR(KBr): 2954 s, 1596 m, 1511 s, 1469 m, 1442 s, 1403 s, 1371 s, 1365 s, 1274 s, 1249 s, 1170 s, 1133 s, 1116 s, 1091 s, 1045 m, 1018 m, 943 s, 838 s, 811 s, 765 s, 748 s, 701 s, 661 s, 586 s, 536 s;

MS m/z (% relative intensity): 344 (31), 343 (M^+ , 100), 329 (28), 328 (79), 197 (20), 181 (35), 173 (23), 158 (19), 156 (25), 149 (31), 145 (21), 139 (24), 132 (14), 131 (19), 130 (22), 117 (15), 115 (13), 105 (17), 92 (10), 91 (72), 90 (13), 89 (14), 84 (10), 77 (21), 76 (10), 75 (95), 73 (27), 65 (40), 64 (10), 63 (12), 59 (32), 58 (34), 53 (14);

HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2\text{Si}$ 343.1062, found 343.1057

3-(Trimethylsilyl)quinoline [65094-39-5].

^1H NMR (CDCl_3 , 270 MHz): δ 8.97 (s, 1H), 8.26 (s, 1H), 8.08 (d, $J = 8.6$ Hz, 1H), 7.80 (d, $J = 7.8$ Hz, 1H), 7.71 (dd, $J = 7.6, 8.1$ Hz, 1H), 7.51 (dd, $J = 7.3, 7.8$ Hz, 1H), 0.39 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 153.7, 148.0, 141.9, 132.6, 129.5, 129.1, 127.6(2C), 126.3, -1.2

(Trimethylsilyl)ferrocene [12215-68-8].

^1H NMR (CDCl_3 , 270 MHz): δ 4.33 (d, $J = 1.6$ Hz, 2H), 4.10 (s, 5H), 4.09 (d, $J = 1.6$ Hz, 2H), 0.22 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 72.7, 72.0, 70.6, 68.1, -0.1.

Trimethyl[(1E)-2-phenylethyl]silane [19372-00-0].

^1H NMR (CDCl_3 , 270 MHz): δ 7.41 (d, $J = 7.5$ Hz, 2H), 7.32-7.19 (m, 3H), 6.85 (d, $J = 19.2$, 1H), 6.45 (d, $J = 19.2$ Hz, 1H), 0.13 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 143.4, 138.2, 129.4, 128.3, 127.8, 126.2, -1.1.

4-*tert*-Buthyl-1-(trimethylsilyl)cyclohexene [63031-67-4].

^1H NMR (CDCl_3 , 270 MHz): δ 6.00 (s, 1H), 2.21-2.05 (m, 3H), 1.84-1.81 (m, 2H), 1.55-1.06 (m, 2H), 0.86 (s, 9H), 0.03 (s, 9H);

^{13}C NMR (CDCl_3 , 67.5 MHz): δ 138.1, 135.8, 44.0, 32.3, 28.6, 28.4, 27.1, 24.3, -2.0.

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