A Novel and Convenient Chemoselective Deprotection Method for Both Silyl and Acetyl Groups on Acidic Hydroxyl Groups Such as Phenol and Carboxylic Acid by Using a Nitrogen Organic Base, 1,1,3,3-Tetramethylguanidine

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Supporting information

General Experimental Procedures. Melting points were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer PARAGON1000 spectrometer. ¹H and ¹³C NMR spectra were measured on JEOL JNM-GX500 spectrometer at 500 and at 125Hz, respectively. ¹H and ¹³C chemical shifts were referenced to the internal deuterated solvent or tetramethylsilane. Mass spectra were recorded on a JEOL JMX 700 mass spectrometer. Optical rotations were measured on JASCO P-1010-GT polarimeter. Flash column chromatography was performed on Merck Kieselgel 60. Thin layer chromatography was performed on Merck Kieselgel 60 F₂₅₄. All phenols, solvents, and reagents were purchased from Aldrich, Tokyo Kasei Co., Ltd., or Hayashi Kasei Co., Ltd. and used without further purification.

Silyl ethers **1-10**, silyl esters **20-22**, and acetates **26** and **28** were prepared from commercially available phenols using the standard procedure (For silyl ethers and silyl esters: TBDMS chloride or TBDPS chloride, imidazole, DMF; For acetates: Ac₂O, pyridine). Acetates **27** was synthesized according to our previous report.¹ Silyl ether **11** was prepared from **19** (Table 4, entry II) using the standard procedure. Silyl ethers **7**² and **8**³ are known compounds and their analytical data were in agreement with literature data. The desilylated products **2**⁴, **12-15**, **23**, and **24** were compared with authentic samples and their analytical data were in perfect agreement with the authentic samples.

Silyl ether **1**

IR (neat) 2956, 2853, 1714, 1634, 1600 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.20 (6H, s), 0.97 (9H, s), 3.77 (3H, s), 6.28 (1H, d, $J = 16.1$ Hz), 6.82 (2H, d, $J = 8.3$ Hz), 7.39 (2H, d, $J = 8.3$ Hz), 7.62 (1H, d, $J = 16.1$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ -4.4, 18.2, 25.6, 51.5, 115.5, 120.5, 127.7, 129.7, 144.6, 157.9, 167.7; HRMS (EI) Calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_3\text{Si}$ $[\text{M}]^+$, 292.1495, Found 292.1468.

Silyl ether 3

IR (KBr) 2960, 2859, 1713, 1637, 1602 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.10 (9H, s), 3.76 (3H, s), 6.23 (1H, d, $J = 16.2$ Hz), 6.75 (2H, d, $J = 8.7$ Hz), 7.27 (2H, d, $J = 8.7$ Hz), 7.35-7.45 (6H, m), 7.56 (1H, d, $J = 16.2$ Hz), 7.70 (4H, dd, $J = 8.1, 1.3$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 19.4, 26.5, 51.5, 115.4, 120.2, 127.5, 127.9, 129.5, 130.1, 132.4, 135.5, 144.6, 157.7, 167.7; HRMS (EI) Calcd. for $\text{C}_{26}\text{H}_{28}\text{O}_3\text{Si}$ $[\text{M}]^+$, 416.1808, Found 416.1825.

Silyl ether 4

IR (neat) 2957, 2858, 1630, 1600, 1508 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.23 (6H, s), 1.01 (9H, s), 7.06 (1H, dd, $J = 8.3, 2.4$ Hz), 7.17 (1H, d, $J = 2.4$ Hz), 7.31 (1H, ddd, $J = 8.2, 6.8, 1.0$ Hz), 7.40 (1H, ddd, $J = 8.2, 6.8, 1.0$ Hz), 7.67 (1H, d, $J = 8.2$ Hz), 7.70 (1H, d, $J = 8.3$ Hz), 7.75 (1H, d, $J = 8.2$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ -4.3, 18.3, 25.7, 114.9, 122.1, 123.7, 126.1, 126.7, 127.6, 129.3, 134.6, 153.5; HRMS (EI) Calcd. for $\text{C}_{16}\text{H}_{22}\text{OSi}$ $[\text{M}]^+$, 258.1440, Found 258.1449.

Silyl ether 5

IR (neat) 2931, 1508, 1235, 923, 830 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.15 (6H, s), 0.96 (9H, s), 3.74 (3H, s), 6.75 (4H, s); ^{13}C NMR (CDCl_3 , 125 MHz) δ -4.5, 18.2, 25.7, 55.6, 114.5, 120.6, 149.4, 154.1; HRMS (EI) Calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{Si}$ $[\text{M}]^+$, 238.1389, Found 238.1376.

Silyl ether 6

IR (neat) 2957, 2859, 1671, 1602, 1255 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.28 (6H, s), 0.99 (9H, s), 2.55 (3H, s), 3.79 (3H, s), 6.35 (1H, d, $J = 2.0$ Hz), 6.52 (1H, dd, $J = 8.8, 2.0$ Hz), 7.69 (1H, d, $J = 8.8$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ -3.9, 18.5, 25.9, 31.3, 55.4, 105.8, 106.8, 123.9, 132.2, 157.0, 163.7, 198.5; HRMS (FAB) Calcd. for $\text{C}_{15}\text{H}_{25}\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$, 281.1573, Found 281.1561.

Silyl ether 9

IR (neat) 2959, 2858, 1509, 1256, 1113 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.03 (9H, s), 1.08 (9H, s), 4.61 (2H, s), 6.71 (2H, d, $J = 8.8$ Hz), 7.02 (2H, d, $J = 8.8$ Hz), 7.30-7.42 (12H, m), 7.63 (4H, dd, $J = 8.1, 1.5$ Hz), 7.71 (4H, dd, $J = 8.1, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 19.3, 19.5, 26.6, 26.9, 65.3, 119.4, 127.1, 127.6, 127.7, 129.6, 129.8, 133.1, 133.5,

133.7, 135.6, 154.5; HRMS (EI) Calcd. for $C_{39}H_{44}O_2Si_2 [M]^+$, 600.2880, Found 600.2879.

Estradiol disilylether (10)

$[\alpha]^{25.9}_D -2.6$ ($c = 1.0$, $CHCl_3$); IR (KBr) 2958, 2857, 1497, 1256, 1113 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 0.86 (3H, s), 1.07 (9H, s), 1.08 (9H, s), 0.91-1.62 (11H, m), 1.70-1.75 (1H, m), 1.80-1.83 (1H, m), 1.97-2.02 (1H, m), 2.09-2.13 (1H, m), 2.57-2.70 (2H, m), 3.68 (3H, t, $J = 8.1$ Hz), 6.46 (1H, dd, $J = 8.7, 2.8$ Hz), 6.50 (1H, d, $J = 2.8$ Hz), 6.93 (1H, d, $J = 8.7$ Hz), 7.33-7.42 (12H, m), 7.65-7.72 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.7, 19.4, 19.5, 23.3, 26.3, 26.6, 27.1, 27.2, 29.5, 30.8, 37.0, 38.7, 43.9, 44.0, 49.3, 82.5, 116.7, 119.5, 125.9, 127.3, 127.4, 127.7, 129.4, 129.5, 129.7, 133.0, 133.3, 134.4, 135.0, 135.5, 136.0, 137.7, 153.1; HRMS (EI) Calcd. for $C_{50}H_{60}O_2Si_2 [M]^+$, 748.4132, Found 748.4117.

Compound 11

$[\alpha]^{23.1}_D -19.5$ ($c = 1.0$, $CHCl_3$); IR (KBr) 2958, 1748, 1511, 1231, 1072 cm^{-1} ; 1H NMR ($CDCl_3$, 270 MHz) δ 0.22 (6H, s), 0.96 (9H, s), 1.99 (3H, s), 2.01 (3H, s), 2.01 (3H, s), 2.02 (3H, s), 2.06 (3H, s), 3.87 (1H, ddd, $J = 10.1, 4.3, 2.2$ Hz), 4.11 (1H, dd, $J = 12.6, 2.2$ Hz), 4.11 (1H, dd, $J = 12.6, 4.3$ Hz), 5.15 (1H, t, $J = 9.5$ Hz), 5.22 (1H, dd, $J = 9.5, 8.1$ Hz), 5.28 (1H, t, $J = 9.5$ Hz), 5.83 (1H, d, $J = 8.1$ Hz), 6.25 (1H, d, $J = 16.0$ Hz), 6.82 (1H, d, $J = 8.8$ Hz), 7.41 (1H, d, $J = 8.8$ Hz), 7.68 (1H, d, $J = 16.0$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -4.4, 18.2, 20.5, 20.7, 25.6, 61.5, 67.9, 70.3, 72.7, 72.8, 91.8, 113.7, 120.6, 127.2, 130.1, 147.2, 158.5, 164.9, 169.3, 169.4, 170.1, 170.6; HRMS (FAB) Calcd. for $C_{29}H_{40}O_{12}SiNa [M+Na]^+$, 631.2187, Found 631.2188.

Silyl ether 16

IR (neat) 3318, 2956, 2858, 1616, 1256 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 0.07 (s, 6H), 0.91 (s, 9H), 4.64 (s, 2H), 4.85 (s, 1H, OH), 6.76 (2H, d, $J = 8.3$ Hz), 7.17 (2H, d, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ -5.2, 18.4, 26.0, 64.7, 115.1, 127.8, 133.6, 154.5; HRMS (EI) Calcd. for $C_{13}H_{22}O_2Si [M]^+$, 238.1389, Found 238.1377.

Silyl ether 17

IR (neat) 3331, 2959, 2858, 1615, 1212 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 1.06 (9H, s), 4.67 (1H, s, OH), 4.68 (2H, s), 6.77 (2H, d, $J = 8.3$ Hz), 7.18 (2H, d, $J = 8.3$ Hz), 7.34-7.42 (6H, m), 7.67 (4H, dd, $J = 8.3, 1.5$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 19.3, 26.9, 65.3, 115.0, 127.7, 129.6, 133.4, 133.7, 135.6, 154.5; HRMS (EI) Calcd. for $C_{23}H_{26}O_2Si [M]^+$, 362.1702, Found 362.1698.

Estradiol 17-monosilylether (18)

$[\alpha]^{27.4}_D -4.4$ ($c = 0.5$, $CHCl_3$); IR (KBr) 3424, 2930, 2857, 1428, 1113 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 0.88 (3H, s), 0.94-1.66 (9H, m), 1.07 (9H, s), 1.76-1.80 (1H, m), 1.84 (1H, dt, $J = 12.6, 3.4$), 2.04 (1H, dt, $J = 11.4, 4.2$ Hz), 2.16-2.21 (1H, m), 2.71-2.82 (2H, m),

3.69 (1H, t, $J = 8.1$ Hz), 4.50 (1H, s, OH), 6.52 (1H, d, $J = 2.5$ Hz), 6.59 (1H, dd, $J = 8.3$, 2.5 Hz), 7.11 (1H, d, $J = 8.3$ Hz), 7.34-7.43 (6H, m), 7.67 (4H, t, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 11.7, 19.4, 23.3, 26.4, 27.1, 29.6, 30.8, 37.0, 38.8, 43.9, 44.0, 49.3, 82.5, 112.6, 115.2, 126.5, 127.4, 129.4, 129.5, 133.0, 134.5, 135.0, 136.0, 138.3, 153.2; HRMS (EI) Calcd. for $\text{C}_{34}\text{H}_{42}\text{O}_2\text{Si}$ $[\text{M}-^t\text{Bu}]^+$, 510.2954, Found 510.2975.

Phenol 19

mp 194-195 °C; $[\alpha]_{\text{D}}^{26.8} -29.8$ ($c = 0.3$, CHCl_3); IR (KBr) 3357, 2942, 1754, 1721, 1228 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 2.02 (3H, s), 2.03 (3H, s), 2.05 (3H, s), 2.08 (3H, s), 3.90 (1H, ddd, $J = 10.0$, 4.4, 2.2 Hz), 4.14 (1H, dd, $J = 12.4$, 2.2 Hz), 4.32 (1H, dd, $J = 12.4$, 4.4 Hz), 5.71 (1H, t, $J = 10.0$ Hz), 5.24 (1H, t, $J = 8.1$ Hz), 5.30 (1H, t, $J = 9.3$ Hz), 5.54 (1H, s, OH), 5.85 (1H, d, $J = 8.1$ Hz), 6.23 (1H, d, $J = 16.9$ Hz), 6.85 (2H, d, $J = 8.5$ Hz), 7.43 (2H, d, $J = 8.5$ Hz), 7.69 (1H, d, $J = 16.1$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 20.6, 20.7, 61.5, 67.9, 70.4, 72.7, 72.8, 91.8, 113.5, 116.0, 126.7, 130.4, 147.2, 158.4, 165.0, 169.5, 170.1, 170.8; HRMS (FAB) Calcd. for $\text{C}_{23}\text{H}_{26}\text{O}_{12}\text{Na}$ $[\text{M}+\text{Na}]^+$, 517.1322, Found 517.1332.

Silyl ester 20

IR (neat) 2959, 2933, 1712, 1288, 1116 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.19 (9H, s), 7.37-7.46 (8H, m), 7.72 (4H, dd, $J = 7.9$, 1.5 Hz), 8.07 (2H, d, $J = 8.6$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 19.4, 26.9, 27.0, 27.1, 127.8, 128.8, 128.9, 129.7, 130.2, 131.6, 131.7, 131.8, 135.3, 139.7, 164.7; HRMS (EI) Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_2\text{ClSi}$ $[\text{M}-^t\text{Bu}]^+$, 337.0452, Found 337.0443.

Silyl ester 21

IR (neat) 2959, 2933, 1713, 1271, 1082 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.14 (9H, s), 2.27 (3H, s), 2.30 (6H, s), 6.83 (2H, s), 7.35-7.44 (6H, m), 7.74 (4H, dd, $J = 7.9$, 1.5 Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 19.3, 20.5, 21.1, 27.1, 127.7, 128.7, 130.1, 131.7, 132.0, 135.6, 135.7, 137.9, 139.2, 169.0; HRMS (EI) Calcd. for $\text{C}_{22}\text{H}_{21}\text{O}_2\text{Si}$ $[\text{M}-^t\text{Bu}]^+$, 345.1311, Found 345.1308.

Silyl ester 22

$[\alpha]_{\text{D}}^{26.7} +22.6$ ($c = 0.8$, CHCl_3); IR (neat) 2931, 2859, 1734, 1241, 1112 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.60 (3H, s), 0.68-1.98 (26H, m), 0.80 (3H, s), 0.93 (3H, d, $J = 6.9$ Hz), 1.04 (9H, s), 1.10 (9H, s), 2.33-2.39 (1H, m), 2.46-2.53 (1H, m), 3.60 (1H, sept, $J = 4.6$ Hz), 7.33-7.43 (12H, m), 7.65-7.68 (8H, m); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0, 18.3, 19.1, 20.8, 23.3, 24.2, 26.4, 26.6, 26.9, 27.0, 27.2, 28.2, 30.8, 31.2, 33.2, 34.5, 35.3, 35.4, 35.8, 36.6, 40.1, 40.3, 42.1, 42.8, 56.1, 56.4, 73.6, 127.4, 127.7, 129.4, 130.0, 132.1, 134.8, 134.9, 135.0, 135.3, 135.8, 173.5; HRMS (EI) Calcd. for $\text{C}_{52}\text{H}_{67}\text{O}_3\text{Si}_2$ $[\text{M}-^t\text{Bu}]^+$, 795.4629,

Found 795.4628.

Silyl ether **25**

$[\alpha]^{27.1}_D +31.4$ ($c = 1.5$, CHCl_3); IR (neat) 2934, 2863, 1708, 1216, 1111 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.62 (3H, s), 0.68-1.94 (26H, m), 0.80 (3H, s), 0.92 (3H, d, $J = 6.1$ Hz), 1.04 (9H, s), 2.22-2.28 (1H, m), 2.36-2.42 (1H, m), 3.61 (1H, sept, $J = 4.6$ Hz), 7.33-7.41 (6H, m), 7.67 (4H, dt, $J = 7.9, 1.2$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0, 18.3, 19.1, 20.8, 23.3, 24.2, 26.4, 27.0, 27.2, 28.2, 30.8, 31.0, 34.5, 35.3, 35.4, 35.8, 36.6, 40.1, 40.3, 42.1, 42.8, 56.0, 56.4, 73.6, 127.4, 129.4, 134.9, 135.0, 135.8, 180.0; HRMS (EI) Calcd. for $\text{C}_{36}\text{H}_{49}\text{O}_3\text{Si}$ $[\text{M}-\text{Bu}]^+$, 557.3451, Found 557.3461.

Acetate **26**

mp 80-81 $^\circ\text{C}$; IR (KBr) 1759, 1713, 1640, 1510, 1233 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 2.31 (3H, s), 3.81 (3H, s), 6.39 (1H, d, $J = 16.0$ Hz), 7.12 (2H, d, $J = 8.9$ Hz), 7.54 (2H, d, $J = 8.9$ Hz), 7.67 (1H, d, $J = 16.0$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 21.1, 51.7, 118.0, 122.1, 129.2, 132.1, 143.7, 152.1, 167.2, 169.1; HRMS (EI) Calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_4$ $[\text{M}]^+$, 220.0736, Found 220.0744.

Estradiol 3,17-diacetate (**28**)⁵

mp 123-124; $[\alpha]^{25.4}_D +43.4$ ($c = 1.0$, CHCl_3); IR (KBr) 2925, 2875, 1765, 1737, 1197 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.81 (3H, s), 1.22-1.58 (7H, m), 1.69-1.76 (1H, m), 1.84-1.89 (2H, m), 2.04 (3H, s), 2.15-2.30 (3H, m), 2.25 (3H, s), 2.83-2.86 (2H, m), 4.67 (1H, t, $J = 8.6$ Hz), 6.77 (1H, d, $J = 2.5$ Hz), 6.82 (1H, dd, $J = 8.5, 2.5$ Hz), 7.25 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0, 21.1, 21.2, 23.3, 26.0, 27.0, 27.6, 29.5, 36.9, 38.2, 42.9, 44.0, 49.9, 82.7, 118.6, 121.5, 126.4, 137.9, 138.2, 148.5, 169.8, 171.2; HRMS (FAB) Calcd. for $\text{C}_{22}\text{H}_{28}\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$, 379.1885, Found 379.1905.

Estradiol 17-monoacetate (**29**)^{5a}

mp 216-217 $^\circ\text{C}$; $[\alpha]^{25.6}_D +44.3$ ($c = 1.0$, CHCl_3); IR (KBr) 3432, 2936, 2870, 1711, 1277 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 0.81 (3H, s), 1.21-1.60 (7H, m), 1.69-1.75 (1H, m), 1.82-1.88 (2H, m), 2.04 (3H, s), 2.13-2.28 (3H, m), 2.75-2.87 (2H, m), 4.67 (1H, t, $J = 8.6$ Hz), 4.67 (1H, s, OH), 6.54 (1H, d, $J = 2.5$ Hz), 6.60 (1H, dd, $J = 8.5, 2.5$ Hz), 7.12 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 12.0, 21.2, 23.2, 26.2, 27.2, 27.6, 29.6, 36.9, 38.6, 42.9, 43.8, 49.8, 82.8, 112.7, 115.2, 126.5, 132.5, 138.2, 153.4, 171.4; HRMS (EI) Calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_3$ $[\text{M}]^+$, 314.1882, Found 314.1882.

Acetate **30**

IR (KBr) 2932, 2858, 1766, 1214, 1112 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.08 (9H, s), 2.28 (3H, s), 4.73 (2H, s), 7.03, (2H, d, $J = 8.3$ Hz), 7.33 (2H, d, $J = 8.3$ Hz), 7.35-7.43 (6H, m), 7.67 (4H, dd, $J = 8.3, 1.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz) δ 19.3, 21.1, 26.8, 65.0, 121.2, 126.9, 127.7, 129.7, 133.4, 134.8, 135.5, 138.6, 149.5, 169.6

; HRMS (FAB) Calcd. for $C_{25}H_{28}O_3SiNa$ $[M+Na]^+$, 427.1705, Found 427.1727.

Acetate **31**

$[\alpha]^{26.2}_D -1.4$ ($c = 0.6$, $CHCl_3$); IR (KBr) 2932, 2857, 1767, 1368, 1208 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 0.87 (3H, s), 0.94-1.01 (2H, m), 1.06 (9H, s), 1.17-1.66 (7H, m), 1.76-1.81 (1H, m), 1.84 (1H, dt, $J = 12.3, 3.4$ Hz), 2.08 (1H, dt, $J = 11.2, 4.4$ Hz), 2.16-2.23 (1H, m), 2.25 (3H, s), 2.75-2.86 (2H, m), 3.69 (1H, t, $J = 8.3$ Hz), 6.74 (1H, d, $J = 2.4$ Hz), 6.80 (1H, dd, $J = 8.3, 2.4$ Hz), 7.22 (1H, s), 7.33-7.43 (6H, m), 7.66 (4H, ddd, $J = 8.3, 6.7, 1.5$ Hz); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.7, 19.3, 21.1, 23.2, 26.2, 26.9, 27.1, 29.5, 30.8, 36.9, 38.4, 43.9, 44.1, 49.3, 82.4, 118.5, 121.4, 126.4, 127.4, 129.4, 129.5, 134.4, 134.9, 136.0, 138.2, 148.3, 169.8; HRMS (FAB) Calcd. for $C_{36}H_{44}O_3SiNa$ $[M+Na]^+$, 575.2957, Found 575.2954.

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Scheme 1. 1H NMR data for silyl ether **17** and **18** and their acetates **30** and **31**

Date : Thu May 16 16:41:58 2002

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 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.70 usec
 OBNUC : 1H
 OBPRO : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 20
 SCANS : 16 times
 SLVNT : CD3CN
 SPINNT : 10 Hz
 TEMP : 23.8 C

2.1482
 1.9598
 1.9544
 1.9500
 1.9451
 1.9397

3.7390

7.6508
 7.6186
 7.5459
 7.5293
 6.9181
 6.9011
 6.4139
 6.3817

solvent : CD₃CN

Date : Wed Jun 5 21:24:22 2002

FileName : ko020406.mmdata
 Comment : 1H S/N
 SliceHistory :
 EXMODE : non

POINT : 32768 points
 SAMPD : 32768 points
 FREQU : 10000.0 Hz
 FILTR : 5000 Hz
 DELAY : 40.0 usec
 DEAT : 57.1 usec
 INTVL : 100.0 usec
 TIMES : 8 times
 DUMMY : 1 times
 PD : 3.7232 sec
 ACQTM : 3276.7998 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.31 Hz
 PM1 : 5.70 usec
 DBNUC : 1H
 DBFQ : 500.00 MHz
 DBSET : 162160.00 Hz
 RGAIN : 21
 SCANS : 8 times
 SLVNT : CD3CN
 SPINNT : 10 Hz
 TEMP : 26.4 C

1H S/N

Date : Tue May 14 20:39:15 2002

FileName : kotmg.mdata
 Comment : 1H S/N
 SliceHistory :
 EXMODE : non

POINT : 32768 points
 SAMPO : 32768 points
 FREQ : 8000.0 Hz
 FILTR : 4000 Hz
 DELAY : 50.0 usec
 DEAT : 72.2 usec
 INVT : 125.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 2.9040 sec
 ACQTM : 4096.0000 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.70 usec
 OBNUC : 1H
 OBERQ : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 17
 SCANS : 16 times
 SLVNT : CD3CN
 SPINNING : 12 Hz
 TEMP : 24.6 C

solvent : CD₃CN

ppm

0

2

4

6

8

Date : Tue May 14 21:24:14 2002
 File Name : kotmgsi30a.rmdata
 Comment : 1H S/N
 Slice History : non
 EXMODE : non
 POINT : 32768 points
 SAMPD : 32768 points
 FREQ : 8000.0 Hz
 FILTR : 4000 Hz
 DELAY : 50.0 usec
 DEAT : 72.2 usec
 INTVL : 125.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 2.9040 sec
 ACQTM : 4096.0000 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.70 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 18
 SCANS : 16 times
 SLVNT : CD3CN
 SPINNING : 11 Hz
 TEMP : 24.8 C

solvent : CD₃CN

TBDMSE

1H S/N

Date : Fri Aug 25 14:13:33 2000

File Name : LoadingFTD.nmdata
 Comment : 1H S/N
 Slice History : non
 EXMODE :

POINT 16384 points
 SAMP 16384 points
 FREQ 8000.0 Hz
 FILTR 4000 Hz
 DELAY 50.0 usec
 DEAD 72.3 usec
 INVT 125.0 usec
 TIMES 16 times
 DUMMY 1 times
 PD 4.9520 sec
 ACQTM 2048.0000 msec
 PREDL 0.010000 msec
 INIWT 1000.0000 msec
 RESOL 0.49 Hz
 PW1 5.50 usec
 OBNUC 1H
 OBFRQ 500.00 MHz
 OBSET 162410.00 Hz
 RGAIN 22
 SCANS 16 times
 SLVNT COCL3
 SPINNING 12 Hz
 TEMP 30.6 C

0.1983
 0.9656
 1.5270
 3.7714
 4.7047
 6.2950
 6.2657
 6.8241
 6.8075
 7.6022
 7.6344
 7.3855
 7.4021
 7.2400

3.10

2.11

2.14

1.00

0.95

ppm

2

4

6

8

1H S/N

Date : Wed Jul 24 13:12:41 2002

Filename : LoadingFID.nmdata
 Comment : 1H S/N
 SliceHistory :
 EXMODE : non

POINT : 32768 points
 SAMPO : 32768 points
 FREQ : 8000.0 Hz
 F1F2 : 4000 Hz
 DELAY : 50.0 usec
 DEACT : 72.2 usec
 INVT : 125.0 usec
 TIMES : 8 times
 DUMMY : 1 times
 PD : 2.9040 sec
 ACQTM : 4096.0000 msec
 PREL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PW1 : 5.70 usec
 OBNUC : 1H
 OBFREQ : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 21
 SCANS : 8 times
 SLVNT : CDCL3
 SPINNING : 12 Hz
 TEMP : 29.4 C

7.7080
 7.7055
 7.6919
 7.6894
 7.5801
 7.5479
 7.4503
 7.4468
 7.4444
 7.4371
 7.4322
 7.4278
 7.4205
 7.4175
 7.4151
 7.3839
 7.3687
 7.3580
 7.3556
 7.3531
 7.2809
 7.2633
 7.2555
 6.7600
 6.7430
 6.2417
 6.2094

4.22
 1.00
 2.03
 4.22
 2.90
 2.16
 1.13

3.7610

1.5469

1.0997

9.17

ppm

1H S/N

Date : Sat Apr 29 11:54:29 2000

FileName : LoadingFID.nmdata
 Comment : 1H S/N
 SliceHistory :
 EXMODE : non

POINT : 16384 points
 SAMPD : 16384 points
 FREQ : 8000.0 Hz
 FILTR : 4000 Hz
 DELAY : 50.0 usec
 DEADT : 72.3 usec
 INVL : 125.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 4.9520 sec
 ACQTM : 2048.0000 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.49 Hz
 PW1 : 5.50 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 21
 SCANS : 16 times
 SLVNT : CDCL3
 SPINNT : 14 Hz
 TEMP : 26.7 C

7.7545
 7.7379
 7.7115
 7.6949
 7.6813
 7.6637
 7.4138
 7.4118
 7.4001
 7.3982
 7.3952
 7.3845
 7.3816
 7.3269
 7.3249
 7.3132
 7.3103
 7.3083
 7.2966
 7.2947
 7.2693
 7.2400
 7.1765
 7.1717
 7.0692
 7.0653
 7.0526
 7.0477

3.84
 1.07
 0.92
 0.96
 1.00

1.0066
 0.2315

0.06

ppm

2

4

6

8

¹H S/N

Date : Sun Jul 7 20:00:56 2002

FileName : .LoadingFID.nmdata
Comment : 1H S/N
SliceHistory :
EXMODE : non

POINT : 32768 points
SAMP0 : 32768 points
FREQU : 8000.0 Hz
FILT0 : 4000 Hz
DELAY : 50.0 usec
DEAD0 : 72.2 usec
INTVL : 125.0 usec
TIMES : 16 times
DUMMY : 1 times
PD : 2.9040 sec
ACQTM : 4096.0000 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 0.24 Hz
PM1 : 5.70 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz
RGAIN : 15
SCANS : 16 times
SLVNT : CDCl3
SPINNING : 12 Hz
TEMP : 28.1 C

0.1495

0.9598

1.5441

3.7397

6.7450

7.2400

2.47

3.42

1.00

1.21

ppm

1H S/N

Date : Sat Apr 29 11:25:48 2000

File Name : .LoadingFID.nmdata
Comment : 1H S/N
Slice History :
EXMODE : non

POINT : 16384 points
SAMPD : 16384 points
FREQU : 8000.0 Hz
FILTR : 4000 Hz
DELAY : 50.0 usec
DEAD : 72.3 usec
INVL : 125.0 usec
TIMES : 16 times
DUMMY : 1 times
PD : 4.9520 sec
ACQTM : 2048.0000 msec
PREDL : 0.01000 msec
ININT : 1000.0000 msec
RESOL : 0.49 Hz
PW1 : 5.50 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162410.00 Hz
RGAIN : 20
SCANS : 16 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 26.5 C

1H S/N

Date : Tue Jun 20 17:13:54 2000
 FileName : LoadingFID.rmd
 Comment : 1H S/N
 SliceHistory : non
 EXMODE : non
 POINT : 16384 points
 SAMPO : 16384 points
 FREQU : 8000.0 Hz
 FILTR : 4000 Hz
 DELAY : 50.0 usec
 DEATH : 72.3 usec
 INVTL : 125.0 usec
 TIMES : 16 times
 DUMMY : 1 times
 PD : 4.9520 sec
 ACQTM : 2048.0000 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.49 Hz
 PW1 : 5.50 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 22
 SCANS : 16 times
 SLVNT : CDCL3
 SPINNING : 12 Hz
 TEMP : 29.3 C

7.7145
7.7125
7.7096
7.7027
7.6988
7.6959
7.6973
7.6354
7.6325
7.6256
7.6217
7.6188
7.4226
7.4196
7.4177
7.4108
7.4050
7.4001
7.3962
7.3933
7.3903
7.3874
7.3816
7.3767
7.3698
7.3669
7.3630
7.3474
7.3357
7.3201
7.3093
7.3064
7.3044
7.2654
7.2400
7.2146
7.0321
7.0145
6.7138
6.6962
4.6129

1H S/N

Date : Sun Jul 21 22:56:10 2002
Filename : .LoadingFID.nmdata
Comment : 1H S/N
SliceHistory :
EXMODE : non

POINT : 32768 points
SAMPD : 32768 points
FREQ : 10000.0 Hz
FILT : 5000 Hz
DEL : 40.0 usec
DEAD : 57.1 usec
INTVL : 100.0 usec
TIMES : 8 times
DUMMY : 1 times
PD : 3.7232 sec
ACQTM : 3276.7998 msec
PREDL : 0.01000 msec
ININT : 1000.0000 msec
RESOL : 0.31 Hz
PM1 : 5.70 usec
OBNUC : 1H
OBFRQ : 500.00 MHz
OBSET : 162160.00 Hz
RGAIN : 20
SCANS : 8 times
SLVNT : CDCL3
SPINNING : 13 Hz
TEMP : 28.2 C

Date : Thu Oct 31 15:19:14 2002

Filename : LoadingFID.mdata
 Comment : 1H S/N
 SliceHistory : non
 EXMODE :

POINT : 32768 points
 SAMPD : 32768 points
 FREQ : 8000.0 Hz
 FILTR : 4000 Hz
 DELAY : 50.0 usec
 DEACT : 72.2 usec
 INVL : 125.0 usec
 TIMES : 16 times
 DUMY : 1 times
 PD : 2.9040 sec
 ACQTM : 4095.0000 msec
 PREDL : 0.010000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.24 Hz
 PM1 : 5.70 usec
 OBNUC : 1H
 OBFRQ : 500.00 MHz
 OBSET : 162410.00 Hz
 RGAIN : 21
 SCANS : 16 times
 SLVNT : CDCl3
 SPINNING : 14 Hz
 TEMP : 29.6 C

ppm

1H S/N

Date : Wed Mar 1 19:22:24 2000

File Name : LoadingFID.nmdata
Comment : 1H S/N
SliceHistory :
EXMODE : non

POINT : 16384 points
SAMPD : 16384 points
FREQ : 8000.0 Hz
FILTR : 4000 Hz
DELAY : 50.0 usec
DEADT : 72.3 usec
INVT : 125.0 usec
TIMES : 16 times
DUMMY : 1 times
PD : 4.9520 sec
ACQTM : 2048.0000 msec
PREDL : 0.01000 msec
ININT : 1000.0000 msec
RESOL : 0.49 Hz
PW1 : 5.50 usec
OBNUC : 1H
OBFG : 500.00 MHz
OBSET : 162410.00 Hz
RGAIN : 17
SCANS : 16 times
SLVNT : COCL3
SPINNING : 12 Hz
TEMP : 25.6 C

5.05

0.9139

0.0714

ppm

1H S/N

Date : Fri Aug 18 20:31:15 2000

File Name : .LoadingFID.nmdata
Comment : 1H S/N
Slice History : non
EXMODE :

POINT : 16384 points
SAMP0 : 16384 points
FREQU : 8000.0 Hz
FILTR : 4000 Hz
DELAY : 50.0 usec
DEADT : 72.3 usec
INTVL : 125.0 usec
TIMES : 14 times
DUMMY : 1 times
PD : 4.9520 sec
ACQTM : 2048.0000 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 0.49 Hz
PW1 : 5.50 usec
1H : 1H
OBNUC : 500.00 MHz
OBFRQ : 162410.00 Hz
OBSET : 23
RGAIN : 23
SCANS : 14 times
SLVNT : COCL3
SPINNT : 10 Hz
TEMP : 30.8 C

7.6774
7.6754
7.6617
7.6588
7.4226
7.4196
7.4167
7.4108
7.4050
7.4001
7.3933
7.3903
7.3874
7.3689
7.3552
7.3542
7.3425
7.3396
7.3376
7.2400
7.1873
7.1707
6.7782
6.7616

4.6803
4.6744

1.5397

1.0623

2.25
3.32
1.00
1.07
1.52

4.44

ppm