Supporting Information For

Facile Rearrangement of O-Silylated Oximes on Reduction with Borane /Boron Trifluoride

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Experimental Section

All experiments were carried out under an atmosphere of dry nitrogen using standard procedures for handling air sensitive compounds. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz in $CDCl_3$ solution using TMS as internal reference, and D_2O for the hydrochloride salts. Mass spectra were measured at 70 eV instrument. Analytical gas chromatography (GC) was performed using a flame ionization detector and a capillary column (25 mm x 0.33 mm bonded 5% phenyl methylsilicone). Commercial grade reagents and solvents were used after standard purification procedures. The silica gel, used for column chromatography was 230-400 mesh. Dry THF and ether was distilled from sodium benzophenone ketyl. Borontrifluoride and dichloromethane was distilled over CaH_2, prior to use.

Representative Procedure for Silylation of Oximes. (E)-*O*-Triisopropylsilyl-1-indanone oxime: To a stirred solution of 1-indanone oxime (2.90 g, 19.8 mmol) and triisopropylsilyl (TPS) chloride (4.23 mL, 3.81g, 19.8 mmol) in CH_2Cl_2 (7 mL) was added dropwise a solution of imidazole (268 g, 39.5 mmol) in CH_2Cl_2 (17 mL) at room temperature. The reaction was left overnight stirring and a GC analysis indicated the complete formation of the product. The white precipitate was removed by filtration and the solution concentrated under vacuum. The crude product was passed through a silica gel pad with hexane; yield 97% (5.8g). The clear oil was fractional distilled under vacuum: yield 80% (4.8 g); bp. 120°C (0.25 mmHg); FT/IR: υ/cm^{-1} 1636 (C=N); ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.13(d, *J* = 7.2 Hz, 18H),1.27 (m, *J* = 7.2 Hz, 3H), 2.93 (m, *J* = 4.0 Hz, 2H), 2.99 (t, *J* = 4.0 Hz, 2H), 7.21 (m, *J* = 7.2, 0.4 Hz, 1H), 7.28 (t,d, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ12.1, 18.1, 26.2, 28.4, 121.6, 125.5, 126.8, 130.0, 136.9, 148.3, 166.4; MS *m/z* 304 (M^+), 218 (M^+- C_6H_{14}), 130 (M^+- $C_9H_{21}SiO$); Anal. Calcd. For $C_{18}H_{29}NOSi$: C 71.23, H 9.63, N 4.61, Found: C 71.47, H 9.86, N 4.57.

(E)-*O*-TIPS-5-methoxy-1-indanone oxime: Purified by column chromatography on silica gel/hexane as a white solid; yield 80% (7.5 g); FT/IR: υ/cm^{-1} 1636 (C=N) ^{1}H-NMR (C_6D_6) δ(ppm) 1.39 (d, *J* = 7.6 Hz, 18H), 1.50 (m, *J* = 7.6 Hz, 3H), 2.58 (t, *J* = 6.0 Hz, 2H), 2.90 (t, *J* = 2.7 Hz, 2H), 3.36 (s, 3H), 7.65 (s, 1H), 6.79 (d,d, J_1 = 6.4, J_2 = 2.1 Hz, 1H), 7.86 (d,d, J_1 = 5.5, J_2 = 6.1 Hz, 1H); ^{13}C-NMR (C_6D_6) δ 12.8, 18.8, 27.3, 28.8, 55.2, 110.4, 114.8, 123.3, 130.1, 151.0, 162.6, 166.7; MS *m/z* 333 (M^+), 290 (M^+- C_3H_7), 248 (M^+- C_6H_{14}), 220 (M^+- $C_6H_{14}Si$); Anal. Calcd. For $C_{19}H_{31}NO_2Si$: C 68.42, H 9.37, N 4.20, Found: C 68.39, H 9.57, N 4.15.

(E)-*O*-TBS-α-tetralone oxime: Purified by column chromatography on silica gel/ hexane:ethylacetate (98:2) as a white solid; yield 78% (11.7 g); FT/IR: υ/cm^{-1} 1614 (C=N); ^{1}H-NMR ($CDCl_3$) δ(ppm) 0.29 (s, 6H), 1.04 (s, 9H), 2.03 (m, *J* = 1.1 Hz, 2H), 2.97 (t,d, J_1 = 5.7, J_2 = 1.1 Hz, 2H), 3.05 (t, *J* = 5.7 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.34 (m, J_1 = 7.5, J_2 = 0.97 Hz, 2H), 7.75 (d, *J* = 5.0 Hz, 1H),: ^{13}C-NMR ($CDCl_3$) δ: -5.1, 18.2, 21.5, 24.1, 26.2, 29.9, 124.3, 126.2, 128.4, 128.9, 131.2, 139.4, 158.0; MS *m/z* 276 (M^++1,), 145 (M^+ -$C_9H_{15}SiO$), 218 (M^+- C_4H_9), 117 (M^+-$C_{10}H_{18}SiO$); Anal. Calcd. For $C_{16}H_{25}NOSi$: C 69.76, H 9.15, N 5.08, Found: C 69.87, H 9.10, N 5.37.

(E)-*O*-TIPS-α-tetralone oxime: Purified by column chromatography on silica gel/ hexane:ethylacetate (9:1); yield 86% (8.1 g); FT/IR: υ/cm^{-1} 2944 (C-H), 1661 (C=N); ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.13 (d, *J* = 7.26 Hz, 18H), 1.29 (m, *J* = 7.3, 3H), 1.82 (m, *J* = 6.3 Hz, 2H), 2.71 (t, *J* = 6.1 Hz, 2H), 2.81 (t, *J* = 6.1Hz, 2H), 7.17 (d, *J* = 5.6 Hz, 1H), 7.19 (m, J_1 = 5.6, J_2 = 1.6 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ 12.0, 18.1, 21.6, 24.0, 30.0, 124.3, 126.2, 128.0, 128.8, 131.4, 139.4, 157.8; MS *m/z* 317 (M^+), 274 (M^+- C_3H_7), 274 (M^+- C_6H_{14}), 186 (M^+- C_9H_{21}), 177 (M^+- $C_9H_{21}Si$), 161(M^+- $OC_9H_{21}Si$); Anal. Calcd. For $C_{19}H_{31}NOSi$: C 71.87, H 9.84, N 4.41, Found: C 71.55, H 10.19, N 4.24.

(E)-*O*-TIPS 6-methoxy-tetralone oxime: Purified by column chromatography on silica gel/ hexano:CH_2Cl_2 (2:1) as a white solid; yield 95% (4.4 g) FT/IR: υ/cm^{-11} 1613 (C=N); ^{1}H-NMR ($CDCl_3$) δ(ppm) 1.12 (d, *J* = 7.3 Hz, 18H), 1.27 (m, *J* = 7.3 Hz, 3H), 1.82 (q, *J* = 6.3 Hz, 2H), 2.70 (t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 3.77 (s, 3H), 7.61 (d, *J* = 2.4 Hz,1H), 6.74 (d,d, J_1 = 2.8, J_2 = 1.2 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H,); ^{13}C-NMR ($CDCl_3$) δ: 12.0, 18.1, 21.7, 23.9, 30.3, 55.1, 112.7, 112.9, 124.3, 125.9, 141.1, 157.5, 160.1; MS *m/z* 347 (M^+), 262 (M^+- C_3H_7), 262 (M^+- C_6H_{14}), 234 (M^+- C_8H_{18}); Anal. Calcd. For $C_{20}H_{33}NO_2Si$: C 69.11, H 9.57, N 4.03, Found: C 68.75, H 9.73, N 4.09.

(E)-*O*-TIPS- 4-chromanone oxime: Purified by column chromatography on silica gel/ hexano as a white solid; yield 99% (9.67 g); FT/IR: υ/cm^{-1} 1611 (C=N); ^{1}H-NMR ($CDCl_3$) δ (ppm) 1.12(d, *J* = 7.2 Hz, 18H), 1.46 (m, *J* = 7.2 Hz, 3H,), 2.76 (t, *J* = 6.2 Hz, 2H), 3.75 (t, *J* = 6.2 Hz, 2H), 6.7 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 7.39 (t,d, J_1 = 6.42Hz, J_2 = 1.6 Hz,1H), 7.31 (d,d, J_1 = 16.4, 1.6 Hz,1H); ^{13}C-NMR ($CDCl_3$) δ: 12.7, 18.6, 24.31, 65.4, 113.4, 119.8, 122.0, 124.9, 131.6, 153.3, 157.5; MS *m/z* 319 (M^+), 276 (M^+- C_3H_7), 234 (M^+- C_6H_{12}), 206 (M^+- C_8H_{15}) 146.2 (M+ - $C_9H_{21}SiO$); Anal. Calcd. For $C_{18}H_{29}NO_2Si$: C 67.66, H 9.15, N 4.38, Found: C 67.96, H 9.55, N 4.38.

(E)-*O*-TBS-4-chromanone oxime: Purified by column chromatography on silica gel/ hexane:ethylacetate (98:2) as a white solid; yield 84% (1.9 g); FT/IR: υ/cm^{-1} 1618 (C=N); ^{1}H-NMR ($CDCl_3$) δ(ppm) 0.14 (s, 6H), 0.87 (s, 9H), 2.87 (t, *J* = 6.2 Hz, 2H), 4.11 (t, *J* = 6.2 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.4, 1H), 7.14 (t,d, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1H), 7.83 (d,d, J_1 = 1.8 Hz, J_2 = 7.4 Hz, 1H); ^{13}C-NMR ($CDCl_3$) δ: -5.1, 18.2, 23.9, 26.1, 6.5.2, 117.5, 119.0, 121.2, 124.3, 130.8, 152.4, 156.4; MS *m/z* 2787 (M^++1), 220 (M^+ - t-Bu), 146 (M^+ - OTBS), 218 (M^+- C_4H_9), 117 (M^+-$C_{10}H_{18}SiO$); Anal. Calcd. For $C_{15}H_{23}NO_2Si$: C 64.94, H 8.36, N 5.05, Found: C 64.89, H 8.41, N 4.90.

Representative Procedures for the Synthesis of Secondary Anilines. 7-methoxy-2,3,4,5-tetrahydro-1H-benzo[b]azepine.[1] To a stirred solution of *O-tert*-butyldimethylsilyl-6-methoxy-1-tetralone oxime (1.7 g, 5.6 mmol) in ether (6 mL) under nitrogen was added via syringe boron trifluoride ethearate (2.1 mL, 16.7 mmol), freshly distilled from CaH_2. Immediately, a solution of borane dimethyl sulfide in THF (5.6 mL, 2M, 11.2 mmol) was added drop wise to the reaction flask at room temperature. The reaction mixture was left stirring for 19 h at room temperature. After cooling at 0 °C, the excess of borane was slowly reacted with distilled water (7 mL). To complete the

[1] Katayama, H.; Maeda, K.; Kaneko, K. *J. Heterocyclic Chem.***1988**, 25, 937-942.

hydrolysis, a solution of hydrochloric acid (10 mL, 6M) was slowly added at low temperature and the reaction mixture was refluxed at 70°C for 1 h. The reaction mixture was extracted with ether (3 x 15 mL), and the aqueous phase was basified (pH >10) with aqueous NaOH (6M), extracted with ether (3 x 20 mL), washed with brine (15 mL), and dried with anhydrous K_2CO_3. The solution was concentrated at reduced pressure (20 mm Hg). The crude product was analyzed by GC/MS (>95% purity) and purified by flash chromatography (dichloromethane) as a yellow oil (0.71 g, 72 %); FTIR (neat) ν cm^{-1}: 3362 (NH); ^{1}H NMR ($CDCl_3$). (δ ppm): 1.65 (m, J_1 = 4.4, J_2 = 1.6, 2H), 1.82 (m, 2H), 2.78 (t, J_1 = 5.6, 2H), 3.01 (m, J_1 = 5.2, 2H), 3.54 (br s, 1H), 3.79 (s, 3H), 6.64 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 6.72 (d, J_1 = 8.4 Hz,1H), 6.75 (d, J_2 = 2.8 Hz, 1H); and ^{13}C NMR: 154.1, 144.0, 135.6, 120.2, 116.3, 111.3, 55.4, 49.3, 36.2, 32.3, 27.0; MS *m/z*: 177 ($M^{\cdot+}$, 100), 162, 148, 117, 106, 91, 77.

Following a similar procedure as above the 7-methoxy-2,3,4,5-tetrahydro-1H-benzo[b]azepine was obtained by the reduction of *O*-triisopropylsilyl-6-methoxy-1-tetralone oxime (1.5 g, 4.3 mmol) in ether (6 mL) with boron trifluoride ethearate (1.2 g, 8.6 mmol), and borane dimethyl sulfide in THF (4.3 mL, 2M, 8.6 mmol) under reflux for 7 h. The crude product (0.64 g, 85%) was treated with gaseous HCl in hexane at rt and the pure hydrochlororide salt was obtained (0.72 g, 93%). Mp. 201-202 ^{o}C (dec) ; ^{1}H NMR (D_2O). (δ ppm): 1.67 (m, J = 5.2, 2H), 2.04 (m, J = 6.4, 2H), 2.82 (m, 2H), 3.30 (t, J = 5.2,2H), 3.72 (s, 3H), 6.78 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 6.84 (d, J_1 = 8.4 Hz, 1H), 7.25 (d, J_2 = 2.8 Hz, 1H); and ^{13}C NMR((D_2O): 159.4, 139.4, 129.0, 124.1, 116.8, 112.2, 55.6, 50.5, 33.1, 27.7, 25.1.

2,3,4,5-Tetrahydro-1H-benzo[b]azepine.[2] Following a similar procedure as above the title compound was obtained by the reduction of *O*-triisopropylsilyl-1-tetralone oxime (1.5 g, 4.7 mmol) in ether (2 mL) with boron trifluoride ethearate (0.67 g, 4.7 mmol), and borane dimethyl sulfide in THF (9.4 mL, 2M, 18.9 mmol) under reflux overnight. The crude product analyzed by GC/MS (0.47 g, 68%, 97% secondary amine and 3% stating material): MS *m/z*: 147 ($M^{\cdot+}$, 100), 132, 130, 119, 106, 91. The reaction was repeated with two equivalents of boron trifluoride and the reaction was completed. The crude product was treated with gaseous HCl n hexane at rt and the pure hydrochlororide salt was obtained (0.93 g, 81%).; ^{1}H NMR (D_2O). (δ ppm): 1.71(m, J = 6.4, 2H), 2.08 (m, J = 6.4, 2H), 2.89 (t, J_1 = 6.4, 2H), 3.6 (t, J_1 = 5.6,2H), 7.2-7.4 (m, 4H); and ^{13}C NMR: 138.3, 135.8, 131.5, 130.1, 127.8, 122.7, 50.3, 32.9, 27.8, 25.1.

1,2,3,4-Tetrahydroquinoline.[3] To a stirred solution of 1-indanone *O*-triisopropylsilyl oxime (1.7 g, 5.6 mmol) in ether (2 mL) under nitrogen was added via syringe freshly distilled boron trifluoride ethearate (0.69 mL, 5.6 mmol). Immediately, a solution of borane dimethyl sulfide in THF (6.6 mL, 2M, 13.6 mmol) was added via syringe. The reaction

[2] Kotera, K.; Miyazaki, S.; Takahashi, H.; Okada, T.; Kitahonoki, K *Tetrahedron* **1968**, *24*, 3681-3696.

[3] (a) Fujita, K.; kitatsuji, C.; Furukawa, S.; Yamaguchi, R. *Tetrahedron Lett.* **2004**, *45*, 3215-3217. (b) Fujita, K.; kitatsuji, C.; Furukawa, S.; Yamaguchi, R. *Organic Lett.* **2002**, *4*, 2691-2694. (c) Maruoka, K.; Miyazaki, T.; Ando, M.; Matsamura, Y. Sakane, S.; Hattori, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 2831-2843.

mixture was refluxed for 24h. The crude product was analyzed by GC and purified by flash chromatography as clear yellow oil: Yield 62 %; MS *m/z*: 133 ($M^{\cdot+}$, 100), 132, 130, 91. ^{1}H NMR ($CDCl_3$) (δ ppm): 1.90 (m, *J* = 5.1, 2H), 2.73 (m, *J* = 6.3, 2H), 3.24 (t, *J* = 5.4, 2H), 3.59 (br s, 2H), 6.42 (d, *J* = 7.8, 1H), 6.58 (t, *J* = 7.2, 1H), 6.93 (m, 2H); and ^{13}C NMR: 144.6, 129.4, 126.6, 121.3, 116.7, 114.0, 41.8, 26.9, 22.0.

The reaction was repeated with two equivalents of boron trifluoride and the reaction was completed. The crude product was treated with gaseous HCl in hexane at rt obtaining the hydrochlororide salt as a white crystalline compound (1.0 g, 98%). Mp 158-162 ^{o}C; ^{1}H NMR (D_2O) (δ ppm): 2.0 (m, *J* = 6.0, 2H), 2.8 (t, 2H), 3.4 (m, 2H), 3.6 (t, 2H), 4.7 (s, 2H), 7.1-7.3 (m, 4H); and ^{13}C NMR: 131, 130, 129.6, 129.2, 127, 122, 42, 24, 19.

***N*-Ethyl-4-methoxyaniline.**[4] To a stirred solution of 4-methoxy-1-indanone *O*-triisopropylsilyl oxime (1.5 g, 5.4 mmol) in ether (2 mL) under nitrogen was added via syringe freshly distilled boron trifluoride ethearate (0.7 mL, 5.4 mmol) and a solution of borane dimethyl sulfide in THF (5.4 mL, 2M, 16.1 mmol). The reaction mixture was refluxed for 2h. Yield (0.56g, 67%, 99% purity, no primary amine); MS *m/z*: 151 ($M^{\cdot+}$, 100), 136, 121. The reaction was repeated with two equivalents of boron trifluoride. The crude product was treated with gaseous HCl in hexane at rt and the pure hydrochlororide salt was obtained in 64% yield. Mp 138-142 ^{o}C; ^{1}H NMR ($CDCl_3$) (δ ppm): 1.33 (t, *J* = 6.0, 3H), 3.27 (m, 2H), 3.74 (s, 3H), 6.83 (d, *J* = 8.4, 2H), 7.50 (d, *J* = 8.4, 2H), 11.2 (br s, 2H); ^{13}C NMR: 159, 127, 124, 114, 55, 48, 11.

2,3,4,5-Tetrahydro-benzo[*b*][1,5]oxazepine[5] To a stirred solution of 4-chromanone *O*-triisopropylsilyl oxime (2.5 g, 7.8 mmol) in ether (2.9 mL) under nitrogen was added via syringe freshly distilled boron trifluoride ethearate (0.97 mL, 7.8 mmol) and a solution of borane dimethyl sulfide in THF (7.8 mL, 2M, 23.5 mmol). The reaction mixture was refluxed for 3h. Yield (0.69 g, 59%, mixture 86% product,7% primary amine, 7% starting material); MS of benzoxazepine *m/z*: 149 ($M^{\cdot+}$, 100), 130, 121,118,91. The reaction was repeated with two equivalents of boron trifluoride. The crude product (61%, 99% purity by GC/MS) was treated with gaseous HCl in hexane at rt and the pure hydrochlororide salt was obtained in 62% yield.; ^{1}H NMR (D_2O) (δ ppm): 2.37 (m, *J* = 4.4, 2H), 3.59 (t, *J* = 5.2, 2H), 4.25 (t, *J* = 4.8, 2H), 7.33 (m, 2H), 7.52 (m, 2H); and ^{13}C NMR: 153.3, 131.5, 129.3, 125.5, 123.7, 123.5, 72.1, 47.9, 28.0.

[4] Ortiz-Marciales, M. Cruz, E.; Alverio, I.; Figueroa, D.; Cordero, J. F.; Morales, J. A.; Dashmana, H.; Burgos, C. *J. Chem. Res.*(M) **1998**, 151-167. Rerick, M. N.; Trottier, C. H.; Daignault, R. A.; Defoe, J. D. In *Tetrahedron Lett.*, **1963**, *10*, 629-634.

[5] Nagarajan, K.; KulKarni, C. L.; Venkateswarlu., A. *Indian J. Chem.* **1974**, *12*, 247-251.