Supporting Information

For

Highly Efficient Chemoselective N-TBS Protection of Anilines under Exceptional Mild Conditions in the Eco-Friendly Solvent 2-Methyltetrahydrofuran.

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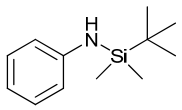
Materials and Instrumentation.

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 spectrometer at room temperature at 250 MHz and at 62.5 MHz respectively, from $CDCl_3$ solutions. The center of the solvent signal was used as an internal standard which was related to TMS with δ 7.26 ppm (^{1}H) and δ 77.0 ppm (^{13}C). Chemical shifts are reported in δ (ppm) referred to ^{1}H (of residual protons) of the deuterated solvents. Spin-spin coupling constants (*J*) are given in Hz. Carbon multiplicities were obtained from DEPT experiments. Whenever necessary, 2D NMR experiments such as HMBC and HMQC were carried out. Melting points were determined with a Buchi SMP-20 apparatus and are uncorrected. IR absorption spectra were recorded on a Perkin-Elmer System 2000 FT-IR spectrophotomer. Elementary microanalyses were carried out in the corresponding 'Centro de Apoyo a la Investigación of the Complutense University, Madrid, using a Leco® CHNS 932 equipment. Column chromatography purifications were conducted on silica gel 60 (40-63 μm). TLC was carried out on aluminum sheets precoated with silica gel $60F_{254}$ (Macherey-Nagel, Merk); the spots were visualized under UV light (λ=254 nm) and/or I_2 was used as revealing system.

General procedure for the Preparation of *N*-tertbutylsilylarylamines 2, 4a-p.

In a dry and argon flushed *Schlenk*-flask, anilines **1** and **3a-p** (1.0 equiv.) were dissolved in dry MeTHF and cooled to 0ºC. MeLi (1.6 M in diethyl ether, 1.05 equiv.) was added dropwise and the resulting mixture was stirred for 5 min. Then, TBDMSCl (1.05 equiv.) dissolved in MeTHF was added dropwise and, the cooling bath was removed. Once the system reached room temperature, stirring was continued for 30 min: then the mixture was filtered over a small pad of Celite to remove the LiCl formed during the reaction. Finally, solvent and volatiles were removed under high vacuum for 1 h.

1-*tert*-butyl-1,1-dimethyl-N-phenylsilanamine (**2**)[1]



By using the aforementioned methodology starting from aniline (**1**) (500 mg, 5.37 mmol), MeLi (1.6 M in Et_2O, 5.64 mmol) and TBDMSCl (848 mg, 5.64 mmol), protected amine **2** was obtained in quantitative yield (1112 mg) as a light brown oil.

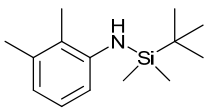
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.26 (s, 6H), 0.97 (s, 9H), 3.31 (bs, 1H), 6.60-6.71 (m, 3H), 7.03-7.18 (m, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.7, 17.5, 26.9, 115.8, 117.3, 128.7, 148.1.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3381, 2961, 1604, 1501, 1301, 898.

Anal. Calcd for $C_{12}H_{21}NSi$. Calcd.: C, 69.50; H, 10.21; N, 6.75. Found: C, 69.19; H, 10.54; N, 7.08.

1-*tert*-butyl-N-(2,3-dimethylphenyl)-1,1-dimethylsilanamine (**4a**)



By using the aforementioned methodology starting from 2,3-dimethylaniline (**3a**) (600 mg, 4.95 mmol), MeLi (1.6 M in Et_2O, 5.20 mmol, 3.25 mL) and TBDMSCl (782 mg, 5.20 mmol), protected amine **4a** was obtained in 95% yield (1107 mg) as a light brown oil.

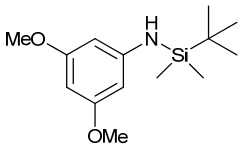
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.36 (s, 6H), 1.08 (s, 9H), 2.17 (s, 3H), 2.37 (s, 3H), 3.35 (bs, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 7.4 Hz, *J* = 8.0 Hz, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.6, 13.4, 18.2, 21.5, 113.9, 120.2, 122.7, 126.2, 137.4, 146.1.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3390, 2973, 1600, 902.

Anal. Calcd for $C_{14}H_{25}NSi$. Calcd.: C, 71.42; H, 10.70; N, 5.95. Found: C, 71.74; H, 10.34; N, 6.19.

1-*tert*-butyl-N-(3,5-dimethoxyphenyl)-1,1-dimethylsilanamine (**4b**)



By using the aforementioned methodology starting from 3,5-dimethoxyaniline (**3b**) (700 mg, 4.57 mmol), MeLi (1.6 M in Et_2O, 4.80 mmol, 3.00 mL) and TBDMSCl (506 mg, 4.80 mmol), protected amine **4b** was obtained in 97% yield (1185 mg) as a light brown oil.

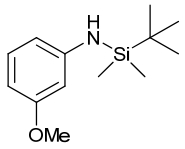
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.81 (s, 9H), 3.20 (bs, 1H), 3.59 (s, 6H), 5.72 (d, *J* = 1.8 Hz, 3H)

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.8, 18.4, 26.8, 55.5, 90.6, 95.9, 150.0, 161.9.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3369, 3082, 2973, 1574; 1475, 1228, 830.

Anal. Calcd for $C_{14}H_{25}NO_2Si$. Calcd.: C, 62.87; H, 9.42; N, 5.24. Found: C, 63.11; H, 9.18; N, 5.01.

1-*tert*-butyl-N-(3-methoxyphenyl)-1,1-dimethylsilanamine (**4c**)



By using the aforementioned methodology starting from 3-methoxyaniline (**3c**) (700 mg, 5.68 mmol), MeLi (1.6 M in Et_2O, 5.96 mmol, 3.73 mL) and TBDMSCl (896 mg, 5.96 mmol), protected amine **4c** was obtained in 95% yield (1281 mg) as a light brown oil.

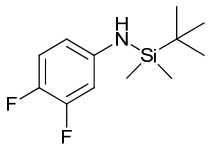
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.35 (s, 6H), 1.06 (s, 9H), 3.45 (bs, 1H), 3.85 (s, 3H), 6.33-6.40 (m, 3H), 7.09-7.17 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.7, 17.8, 26.8, 55.4, 103.1, 103.4, 130.2, 149.5, 161.1.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3382, 3076, 2965, 1574; 1483, 1231, 825.

Anal. Calcd for $C_{13}H_{23}NOSi$. Calcd.: C, 65.77; H, 9.76; N, 5.90. Found: C, 65.98; H, 9.99; N, 5.64.

1-*tert*-butyl-N-(3,4-difluorophenyl)-1,1-dimethylsilanamine (**4d**)



By using the aforementioned methodology starting from 3,4-difluoroaniline (**3d**) (800 mg, 6.20 mmol), MeLi (1.6 M in Et_2O, 6.51 mmol, 4.07 mL) and TBDMSCl (979 mg, 6.51 mmol), protected amine **4d** was obtained in 91% yield (1373 mg) as a light brown oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.82 (s, 9H), 3.15 (bs, 1H), 6.14-6.23 (m, 1H), 6.27-6.38 (m, 1H), 6.68-6.84 (m, 1H).

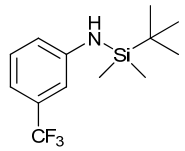
^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -4.0, 18.3, 26.7, 102.5 (d, $^2J_{C,F}$ = 20.7 Hz), 108.9 (dd, $^4J_{C,F}$ = 3.1 Hz, $^4J_{C,F}$ = 5.5 Hz), 118.0 (dd, $^4J_{C,F}$ = 1.9 Hz, $^2J_{C,F}$ = 17.3 Hz), 143.9 (dd, $^3J_{C,F}$ = 14.7 Hz, $^1J_{C,F}$ = 236.0 Hz), 145.1 (dd, $^4J_{C,F}$ = 1.9 Hz, $^3J_{C,F}$ = 8.5 Hz), 151.3 (dd, $^3J_{C,F}$ = 14.7 Hz, $^1J_{C,F}$ = 243.0 Hz).

^{19}F NMR (235 MHz, $CDCl_3$) δ -164.8 (bs).

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3259, 3070, 1630.

Anal. Calcd for $C_{12}H_{19}F_2NSi$. Calcd.: C, 59.22; H, 7.87; N, 5.76. Found: C, 59.48; H, 7.61; N, 5.98.

1-*tert*-butyl-1,1-dimethyl-N-(3-(trifluoromethyl)phenyl)silanamine (**4e**)



By using the aforementioned methodology starting from 3-trifluoromethylaniline (**3e**) (700 mg, 4.34 mmol), MeLi (1.6 M in Et_2O, 4.56 mmol, 2.85 mL) and TBDMSCl (685 mg, 4.56 mmol), protected amine **4e** was obtained in 98% yield (1171 mg) as a light brown oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.35 (s, 6H), 1.06 (s, 9H), 3.59 (bs, 1H), 6.89-6.92 (m, 1H), 6.93-6.99 (m, 2H), 7.04-7.33 (m, 1H).

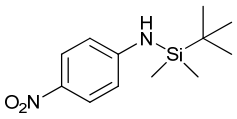
^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -4.0, 18.4, 26.7, 114.3, 120.1 (d, $^2J_{C,F}$ = 31.2 Hz), 124.8 ($^1J_{C,F}$ = 243.0 Hz), 127.1 (d, $^4J_{C,F}$ = 5.5 Hz), 148.9.

^{19}F NMR (235 MHz, $CDCl_3$) δ -63:3 (bs).

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3312, 3074, 1512; 1478.

Anal. Calcd for $C_{13}H_{20}F_3NSi$. Calcd.: C, 56.70; H, 7.32; N, 5.09. Found: C, 56.42; H, 7.65; N, 4.86.

1-tert-butyl-1,1-dimethyl-N-(4-nitrophenyl)silanamine (**4f**)



By using the aforementioned methodology starting from 4-nitroaniline (**3e**) (800 mg, 5.79 mmol), MeLi (1.6 M in Et_2O, 6.08 mmol, 3.80 mL) and TBDMSCl (914 mg, 6.08 mmol), protected amine **4f** was obtained in 94% yield (1374 mg) as a yellow oil.

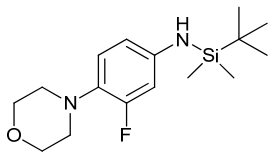
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.31 (s, 6H), 0.98 (s, 9H), 3.75 (bs, 1h), 6.66 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -4.0, 18.4, 26.6, 113.8, 116.0, 126.5, 155.2.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3388, 2989, 1605, 1535, 1509, 1478, 1303, 1189, 1111, 1066, 996.

Anal. Calcd for $C_{12}H_{20}N_2O_2Si$. Calcd.: C, 57.11; H, 7.99; N, 11.10. Found: C, 56.79; H, 7.62; N, 10.80.

1-*tert*-butyl-N-(3-fluoro-4-morpholinophenyl)-1,1-dimethylsilanamine (4g)



By using the aforementioned methodology starting from 3-fluoro-4-morpholinoaniline[2] (**3g**) (700 mg, 4.59 mmol), MeLi (1.6 M in Et_2O, 4.82 mmol, 3.01 mL) and TBDMSCl (725 mg, 4.82 mmol), protected amine **4g** was obtained in 90% yield (1281 mg) as a brown oil.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.81 (s, 9H), 2.83 (dd, J = 4.5 Hz, J = 9.2 Hz, 4H), 3.11 (bs, 1H), 3.72 (dd, J = 4.3 Hz, J = 9.1 Hz, 4H), 6.22-6.33 (m, 2H), 6.59-6.69 (m, 1H).

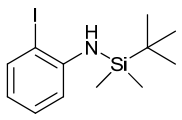
^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.9, 18.4, 26.7, 52.1, 67.6, 105.2 (d, $^2J_{C,F}$ = 26.1 Hz), 112.5 (d, $^4J_{C,F}$ = 4.0 Hz), 120.5 (d, $^4J_{C,F}$ = 4.1 Hz), 131.4 (d, $^3J_{C,F}$ = 9.5 Hz), 144.7 (d, $^3J_{C,F}$ = 10.6 Hz), 156.8 (d, $^1J_{C,F}$ = 245.0 Hz).

^{19}F NMR (235 MHz, $CDCl_3$) δ -166:6 (bs).

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3275, 1649, 1518, 1461, 1116.

Anal. Calcd for $C_{16}H_{27}FN_2OSi$. Calcd.: C, 61.89; H, 8.77; N, 9.02. Found: C, 62.12; H, 8.39; N, 9.33.

1-tert-butyl-N-(2-iodophenyl)-1,1-dimethylsilanamine (4h)



By using the aforementioned methodology starting from 2-iodoaniline (**3h**) (1000 mg, 4.56 mmol), MeLi (1.6 M in Et_2O, 4.79 mmol, 2.99 mL) and TBDMSCl (720 mg, 4.79 mmol), protected amine **4h** was obtained in 97% yield (1474 mg) as a brown oil.

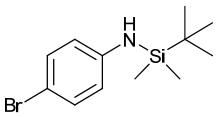
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.36 (s, 6H), 1.09 (s, 9H), 4.04 (bs, 1H), 6.52 (ddd, *J* = 1.4 Hz, *J* = 7.6 Hz, *J* = 8.0 Hz 1H), 6.90 (dd, *J* = 1.4 Hz, *J* = 8.0 Hz, 1H), 7.19 (ddd, *J* = 1.4 Hz, *J* = 7.6 Hz, *J* = 8.0 Hz 1H), 7.74 (dd, *J* = 1.4 Hz, *J* = 8.0 Hz, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm):-3.9, 18.1, 26.7, 90.7, 115.2, 119.5, 129.6, 139.6, 148.3.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3248, 3081, 1526, 1421, 1001.

Anal. Calcd for $C_{12}H_{20}INSi$. Calcd.: C, 43.24; H, 6.05; N, 4.20. Found: C, 42.96; H, 6.21; N, 4.38.

N-(4-bromophenyl)-1-*tert*-butyl-1,1-dimethylsilanamine (4j)[3]



By using the aforementioned methodology starting from 4-bromoaniline (**3j**) (800 mg, 4.65 mmol), MeLi (1.6 M in Et_2O, 4.88 mmol, 3.05 mL) and TBDMSCl (734 mg, 4.88 mmol), protected amine **4j** was obtained in 98% yield (1304 mg) as a yellow oil.

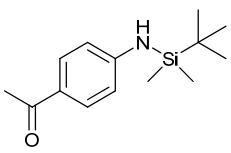
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.81 (s, 9H), 3.20 (bs, 1H), 6.41 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.9, 18.4, 26.7, 109.8, 118.7, 132.3, 147.2.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3309, 3079, 1542, 1462, 1078, 994, 715.

Anal. Calcd for $C_{12}H_{20}BrNSi$. Calcd.: C, 50.34; H, 7.04; N, 4.89. Found: C, 50.59; H, 7.24; N, 4.68.

1-(4-(tert-butyldimethylsilylamino)phenyl)ethanone (4k)[4]



By using the aforementioned methodology starting from 4-acetylaniline (**3k**) (500 mg, 3.70 mmol), MeLi (1.6 M in Et_2O, 3.88 mmol, 2.43 mL) and TBDMSCl (583 mg, 3.88 mmol), protected amine **4k** was obtained in 90% yield (830 mg) as a light brown oil.

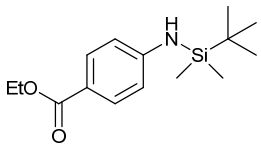
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.79 (s, 9H), 2.30 (s, 3H), 3.55 (bs, 1H), 6.48 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 7.7 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.9, 18.4, 26.4, 26.7, 113.9, 116.2, 127.5, 153.7, 196.8

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3261, 3085, 1746, 1523, 999, 723.

Anal. Calcd for $C_{14}H_{23}NOSi$. Calcd.: C, 67.42; H, 9.29; N, 5.62. Found: C, 67.69; H, 9.02; N, 5.39.

ethyl 4-(*tert*-butyldimethylsilylamino)benzoate (**4l**)



By using the aforementioned methodology starting from 4-ethoxycarbonylaniline (**3l**) (500 mg, 3.03 mmol), MeLi (1.6 M in Et_2O, 3.18 mmol, 1.99 mL) and TBDMSCl (478 mg, 3.18 mmol), protected amine **4l** was obtained in 93% yield (787 mg) as a light brown oil.

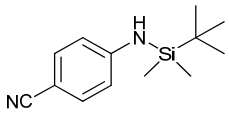
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.79 (s, 9H), 1.18 (t, J = 7.1 Hz, 3H), 3.67 (bs, 1H), 4.14 (q, J = 7.1 Hz, 2H), 6.50 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.9, 14.8, 18.4, 26.7, 60.6, 116.2, 119.7, 131.7, 153.1, 167.2.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3301, 3069, 1703, 1521, 886.

Anal. Calcd for $C_{15}H_{25}NO_2Si$. Calcd.: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.63; H, 8.84; N, 5.19.

4-(*tert*-butyldimethylsilylamino)benzonitrile (**4m**)



By using the aforementioned methodology starting from 4-cyanoaniline (**3m**) (800 mg, 6:77 mmol), MeLi (1.6 M in Et_2O, 7:11 mmol, 4:44 mL) and TBDMSCl (1069 mg, 7:11 mmol), protected amine **4m** was obtained in 98% yield (1542 mg) as a brown oil.

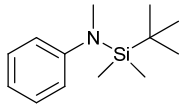
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0:10 (s, 6H), 0.79 (s, 9H), 3.64 (bs, 1H), 6.49 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -4.0, 18.4, 26.6, 100.1, 117.0, 120.7, 133.9, 152.7.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3385, 3075, 2929, 2233, 1612, 1575, 1525, 1340, 1268, 896, 789.

Anal. Calcd for $C_{13}H_{20}N_2Si$. Calcd.: C, 67.19; H, 8.67; N, 12.05. Found: C, 66.93; H, 8.45; N, 12.29.

1-*tert*-butyl-*N*,1,1-trimethyl-N-phenylsilanamine (**4n**)[5]



By using the aforementioned methodology starting from *N*-methylaniline (**3n**) (500 mg, 4.66 mmol), MeLi (1.6 M in Et_2O, 4.90 mmol, 3.06 mL) and TBDMSCl (737 mg, 3.06 mmol), protected amine **4n** was obtained in 91% yield (939 mg) as a light brown oil.

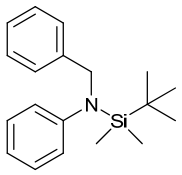
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.09 (s, 6H), 0.75 (s, 9H), 2.96 (s, 3H), 6.66-6.74 (m, 3H), 7.09-7.16 (m, 2H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.9, 18.1, 26.6, 35.2, 116.0, 117.8, 129.2, 149.0.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3080, 1602, 1468, 989, 726.

Anal. Calcd for $C_{13}H_{23}NSi$. Calcd.: C, 70.52; H, 10.47; N, 6.33. Found: C, 70.18; H, 10.71; N, 6.50.

N-benzyl-1-tert-butyl-1,1-dimethyl-N-phenylsilanamine (**4o**)



By using the aforementioned methodology starting from *N*-benzylaniline (**3o**) (500 mg, 2.73 mmol), MeLi (1.6 M in Et_2O, 2.87 mmol, 1.79 mL) and TBDMSCl (431 mg, 2.87 mmol), protected amine **4o** was obtained in 88% yield (715 mg) as a brown oil.

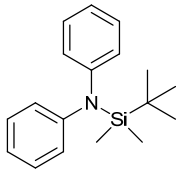
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.29 (s, 6H), 1.02 (s, 9H), 4.28 (s, 2H), 6.80-7,01 (m, 5H), 7.21-7.34 (m, 5H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.8, 18.3, 26.9, 52.9, 113.0, 118.1, 127.3, 127.5, 129.1, 129.7, 138.9, 149.0

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3089, 1605, 995, 731.

Anal. Calcd for $C_{19}H_{27}NSi$. Calcd.: C, 76.70; H, 9.15; N, 4.71. Found: C, 76.87; H, 8.94; N, 4.37.

1-tert-butyl-1,1-dimethyl-N,N-diphenylsilanamine (**4p**)



By using the aforementioned methodology starting from *N*-phenylaniline (**3p**) (500 mg, 2.95 mmol), MeLi (1.6 M in Et_2O, 3.10 mmol, 1.94 mL) and TBDMSCl (466 mg, 3.10 mmol), protected amine **4p** was obtained in 93% yield (778 mg) as a brown oil.

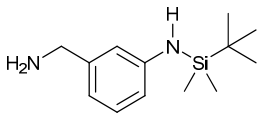
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.29 (s, 6H), 0.86 (s, 9H), 6.88 (d, J = 8.0 Hz, 4H), 7.00 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 7.6 Hz, J = 8.0 Hz, 4H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -4.0, 17.9, 27.1, 120.3, 121.5, 122.8, 124.0, 125.6, 129.2, 129.8, 138.3, 148.4, 148.5.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3085, 3078, 1598, 1523, 969.

Anal. Calcd for $C_{18}H_{25}NSi$. Calcd.: C, 76.26; H, 8.89; N, 4.94. Found: C, 76.43; H, 8.62; N, 4.73.

N-(3-(aminomethyl)phenyl)-1-*tert*-butyl-1,1-dimethylsilanamine (**6**)



To a solution of 3-aminomethylaniline (**5**) (500 mg, 4.09 mmol, 1.00 equiv.) in dry MeTHF (3 mL) cooled at -50°C, MeLi (1.6 M in Et_2O, 4.29 mmol, 2.68 mL) was added dropwise and the resulting mixture was stirred at the same temperature for 5 min. Then TBDMSCl (645 mg, 4.29 mmol) dissolved in dry MeTHF (4 mL) was added dropwise during 10 min and, the solution was stirred at -50°C for 3 hours. Subsequently, the solution was filtered on a small pad of Celite and volatiles were removed under high vacuum for 2 hours. The crude was then purified by LC (alumina grade 3 as the stationary phase, petroleum ether/ethyl acetate 9/1 as the eluent), affording *N*-monoprotected amine **6** in 90% yield (870 mg) as a light brown oil and *N,N*-diprotected amine **7** in 4% yield (57 mg) as a brown oil.

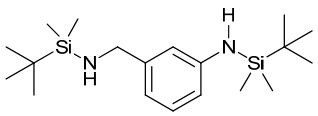
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.10 (s, 6H), 0.92 (s, 9H), 2.25 (bs, 2H), 3.45 (bs, 1H), 3.76 (s, 2H), 6.58-6.71 (m, 3H), 7.09-7.17 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.1, 18.4, 26.1, 46.7, 114.0, 114.2, 117.7, 129.9, 144.6, 147.0.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3452, 3381, 3091, 1601, 1425, 998, 712.

Anal. Calcd for $C_{13}H_{24}N_2Si$. Calcd.: C, 66.04; H, 10.23; N, 11.85. Found: C, 66.28; H, 10.48; N, 11.57.

1-*tert*-butyl-N-(3-(*tert*-butyldimethylsilylamino)benzyl)-1,1-dimethylsilanamine (**7**)



^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 0.08 (s, 6H), 0.10 (s, 6H), 0.90 (s, 9H), 0.93 (s, 9H), 2.36 (bs, 1H), 3.53 (bs, 1H), 3.71 (s, 2H), 6.60-6.69 (m, 3H), 7.11-7.18 (m, 1H).

^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): -3.9, -3.1, 17.8, 18.4, 25.9, 26.2, 46.1, 114.1, 114.2, 117.6, 130.0, 144.5, 148.0.

FT-IR (NaCl) (ν_{max}/cm^{-1}): 3449, 3356, 3082, 1605, 997, 723.

Anal. Calcd for $C_{19}H_{38}N_2Si_2$. Calcd.: C, 65.07; H, 10.92; N, 7.99. Found: C, 64.86; H, 10.76; N, 8.15.

Deprotection of *N*-TBS anilines with the combined system SiO_2 – ethanol – water.

A solution of the *N*-TBS aniline in ethanol was added to a suspension of silica (10 equiv.) in ethanol – water (1:5 v/v) at rt and the stirring was continued for 2h. Then, the suspension was filtered under vacuum and the filtrate was extracted twice with ethyl acetate. The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was removed under vacuum, giving the unprotected aniline.

Aniline (**1**)

Starting from *N*-TBS-aniline (**2**) (311 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**1**) was recovered in quantitative yield (139 mg) as a light yellow oil. The spectroscopic data were identical to the pure commercially available compound.

2,3-dimethylaniline (3a)

Starting from *N*-TBS-2,3-dimethylaniline (**4a**) (353 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3a**) was recovered in quantitative yield (181 mg) as a light yellow oil. The spectroscopic data were identical to the pure commercially available compound.

3,4-difluoroaniline (3d)

Starting from *N*-TBS-3,4-difluoroaniline (**4d**) (365 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3d**)

was recovered in quantitative yield (193 mg) as a light yellow oil. The spectroscopic data were identical to the pure commercially available compound.

3-fluoro-4-morpholinoaniline (3g)

Starting from *N*-TBS-3-fluoro-4-morpholinoaniline (**4g**) (466 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3g**) was recovered in quantitative yield (294 mg) as a light brown solid. The spectroscopic data were identical to the pure commercially available compound.

4-bromoaniline (3j)

Starting from *N*-TBS-4-bromoaniline (**4j**) (429 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3j**) was recovered in quantitative yield (158 mg) as a white solid. The spectroscopic data were identical to the pure commercially available compound.

4-acetylaniline (3k)

Starting from *N*-TBS-4-acetylaniline (**4k**) (374 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3k**) was recovered in quantitative yield (202 mg) as a white solid. The spectroscopic data were identical to the pure commercially available compound.

4-cyanoaniline (3m)

Starting from *N*-TBS-4-cyanoaniline (**4m**) (349 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3m**) was recovered in quantitative yield (177 mg) as a light brown solid. The spectroscopic data were identical to the pure commercially available compound.

***N*-methylaniline (3n)**

Starting from *N*-TBS-*N*-methylaniline (**4n**) (332 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3n**) was recovered in quantitative yield (160 mg) as a light yellow oil. The spectroscopic data were identical to the pure commercially available compound.

***N*-benzylaniline (3o)**

Starting from *N*-TBS-*N*-benzylaniline (**4o**) (446 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3o**) was recovered in quantitative yield (274 mg) as a white solid. The spectroscopic data were identical to the pure commercially available compound.

***N*-phenylaniline (3p)**

Starting from *N*-TBS-*N*-phenylaniline (**4o**) (425 mg, 1.50 mmol) and SiO_2 (901 mg, 15.00 mmol) in EtOH-water (1 mL – 5 mL) by following the above described procedure, aniline (**3p**) was recovered in quantitative yield (253 mg) as a light brown solid. The spectroscopic data were identical to the pure commercially available compound.

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