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SUPPORTING INFORMATION

Title: Catalytic Activation of Silylated Nucleophiles Using *t*Bu-P4 as a Base
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Ref. No.: O200500087

General Comments.

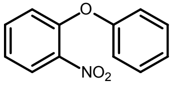
1H-NMR spectra were recorded on a Varian Gemini 2000 using tetramethylsilane as an internal standard. Chemical shifts are expressed in δ (ppm) values, and coupling constants are expressed in herts (Hz). The following abbreviations are used: s = singlet, d = doublet, m = multiplet, t = triplet, brs = broad singlet, dd = double-doublet, dt = double-triplet and ddd = double-doublet-doublet. Mass spectra were recorded on JEOL JMS-DX303 or JEOL JMS-AX500 spectrometer. IR spectra were measured with SensIR ATR FT-IR.

All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under argon atmosphere unless otherwise noted. Flash column chromatography was carried out using Kanto Chemical Silica gel 60N (70-230 mesh). THF were distilled from sodium-benzo phenone ketyl immediately prior to use. Dry DMF was purchased from Kanto Chemical Company and dry DMSO was purchased from Wako Pure Chemical Industries and used as supplied. *tert*-Butyl P4 base, *1.0 M* solution in *n*-hexane was purchased from Fulka Chemie and used as supplied. Silyl ethers were obtained by the usual procedures.[i] Reagents were purchased commercially and used without further purification.

4-Fluorobenzotrifluroride, tetrabutylammonium fluoride, 1.0 *M* solution in THF solution, 1-fluoro- 2-nitrobenzene, phenylethynyltrimethylsilane, 4-fluorobenzonitrile, allyltrimethylsilane, *tert*-butyl dimethylsilyl chloride were purchased from *Aldrich*. 4-(Trimethylsilyl)morpholine, azidotrimethyl silane, ethyl 4-fluorobenzoate, 1-bromo-2-fluorobenzene, 1-fluoro-2-iodobenzene, styrene oxide, 2-*tert*-butylphenol were purchased from *Tokyo Kasei Kogyo*. Benzophenone was purchased from *Nacalai Tesque*. Triethylsilane was purchased from *Acros*. Benzaldehyde was purchased from *Kanto Chemical Company* and distilled under reduced pressure.

Procedures and Characterization:

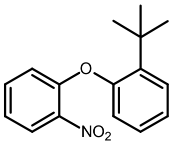
1-Phenoxy-2-nitrobenzene (2a)



A mixture of 1-fluoro-2-nitrobenzene **1** (141 mg, 1.00 mmol), *tert*-butyldimethylphenoxysilane (416 mg, 2.00 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution at ambient temperature and the mixture was stirred for 1 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 204 mg (96%) of compound **2a**.

PMR($CDCl_3$)δ(ppm): 7.00-7.07 (m, 3 H), 7.16-7.26 (m, 2 H), 7.39 (t, 2 H, *J* = 8.1 Hz), 7.50 (ddd, 1 H, *J* = 1.8 Hz, 7.5 Hz, 8.1 Hz), 7.95 (dd, 1 H, *J* = 1.8 Hz, 8.1Hz); MS(EI) *m/z* : 215 (M^+); HRMS : Calcd. for $C_{12}H_9NO_3$: 215.0582: found: 215.0553; IR(neat) : 3068, 3041, 1586, 1522, 1349, 1243 cm^{-1}

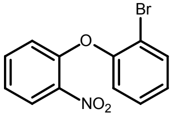
1-(2-*t*-Butylphenoxy)-2-nitrobenzene (2b)



A mixture of 1-fluoro-2-nitrobenzene **1** (141 mg, 1.00 mmol), *tert*-butyldimethyl(2-*tert*-butyl phenoxy)silane (405 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution at ambient temperature and the mixture was stirred for 1 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 271 mg (99%) of compound **2b**.

PMR($CDCl_3$)δ(ppm): 1.41(s, 9 H), 6.82 (dd, 1 H, *J* = 1.8 Hz, 8.1 Hz), 6.91 (d, 1 H, *J* = 8.1 Hz), 7.10 -7.20 (m, 3 H), 7.40-7.49 (m, 2 H), 7.95 (dd, 1 H, *J* = 1.8 Hz, 8.1 Hz); MS(EI) m/z : 271 (M^+); HRMS : Calcd. for $C_{16}H_{17}NO_3$, 271.1208 ; found: 271.1207; IR(neat) : 2956, 2910, 1603, 1574, 1524, 1476, 1439, 1349, 1241, 1189, 1090 cm^{-1}

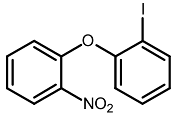
1-(2-Bromophenoxy)-2-nitrobenzene (2c)



A mixture of 1-fluoro-2-nitrobenzene **1** (142 mg, 1.01 mmol), 2-bromophenoxy-*tert*-butyldimethyl silane (429 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution at ambient temperature and the mixture was stirred for 6 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 282 mg (95%) of compound **2c**.

PMR($CDCl_3$)δ(ppm) : 6.85 (d, 1 H, *J* = 8.1 Hz), 7.06 (dd, 1 H, *J* = 1.5 Hz, 8.1 Hz), 7.09-7.15 (m, 1 H), 7.18-7.24 (m, 1 H), 7.31-7.36 (m, 1 H), 7.46-7.53 (m, 1 H), 7.66 (dd, 1 H, *J* = 1.5 Hz, *J* = 8.1 Hz), 8.00 (dd, 1 H, *J* = 1.5 Hz, *J* = 8.1 Hz); MS(EI) m/z : 293 (M^+), 295 (M+2); HRMS : Calcd. for $C_{12}H_8NO_3Br$: 292.9688. found: 292.9668; IR(neat) : 3072, 1605, 1578, 1522, 1466, 1347, 1239, 1162, 1046, 1030 cm^{-1}

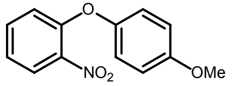
1-(2-Iodophenoxy)-2-nitrobenzene (2d)



A mixture of 1-fluoro-2-nitrobenzene **1** (142 mg, 1.01 mmol), 2-iodophenyl-*tert*-butyldimethylsilyl ether (501 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution at ambient temperature and the mixture was stirred for 8 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 298 mg (87%) of compound **2d**.

PMR($CDCl_3$)δ(ppm): 6.86 (d, 1 H, *J* = 8.1 Hz), 6.93-6.99 (m, 2 H), 7.22 (t, 1 H, *J* = 8.1 Hz), 7.35 (t, 1 H, *J* = 8.1 Hz), 7.50 (t, 1 H, *J* = 8.1 Hz), 7.88 (d, 1 H, *J* = 8.1 Hz), 7.99 (d, 1 H, *J* = 8.1 Hz); MS(EI) m/z : 341 (M^+); HRMS : Calcd. for $C_{12}H_8INO_3$: 340.9547, found: 340.9561; IR(neat) : 3066, 1605, 1522, 1461, 1437, 1345, 1260, 1237, 1019, 886, 841, 741 cm^{-1}

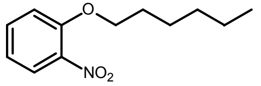
1-(4-Methoxyphenoxy)-2-nitrobenzene (2e)



1-Fluoro-2-nitrobenzene **1** (141 mg, 1.00 mmol), 4-methoxyphenoxy-*tert*-butyldimethylsilyl ether (358 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 1 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% ethyl acetate-hexane) to afford 239 mg (98%) of compound **2e**.

m.p. 73-75°C (lit[ii]. 73-74.5°C); PMR($CDCl_3$)δ(ppm): 3.81 (s, 3 H), 6.88-6.93 (m, 3 H), 7.02 (d, 2H, *J* = 9.3 Hz), 7.09-7.15 (m, 1 H), 7.44 (ddd, 1 H, *J* = 1.7 Hz, *J* = 7.5 Hz, *J* = 8.3 Hz), 7.91 (dd, 1 H, *J* = 1.7 Hz, *J* = 8.3 Hz); MS(EI) m/s: 245 (M^+); HRMS: Calcd. for $C_{13}H_{11}NO_4$: 245.0688, found: 245.0688; IR (crystal) 3101, 3012, 2840, 1600, 1497, 1345, 1229 cm^{-1}

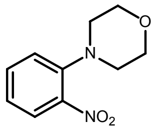
1-(Hexyloxy)-2-nitrobenzene (2f)



A mixture of 1-fluoro-2-nitrobenzene **1** (141 mg, 1.00 mmol), *tert*-butyldimethyl(*n*-hexyloxy)silane (432 mg, 2.00 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 24 h at 100°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (1% AcOEt-hexane) to afford 158 mg (72%) of compound **2f**.

PMR($CDCl_3$)δ(ppm) : 0.91 (t, 3 H, *J* = 6.6 Hz), 1.31-1.36 (m, 4 H), 1.45-1.54 (m, 2 H), 1.83 (quint, 2 H, *J* = 6.6 Hz), 4.10 (t, 2 H, *J* = 6.6 Hz), 7.00 (t, 1 H, *J* = 8.4 Hz), 7.07(d, 1 H, *J* = 8.4 Hz), 7.51(t, 1 H, *J* = 8.4 Hz), 7.82 (d, 1 H, *J* = 8.4 Hz; MS(EI) *m/z* : 223(M^+); HRMS : Calcd. for $C_{12}H_{17}NO_3$: 223.1208, found: 223.1191); IR (neat) : 2931, 2860, 1607, 1522, 1351, 1277, 1254, 908 cm^{-1}

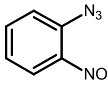
4-(2-Nitrophenyl)morpholine (2g)



A mixture of 1-fluoro-2-nitrobenzene **1** (138 mg, 0.98 mmol), 4-(trimethylsilyl)morpholine (191 mg, 1.20 mmol) and dry DMSO (2 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 12 h at ambient temperature. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with

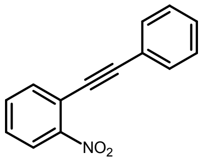
AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (20% AcOEt-hexane) to afford 187 mg (92%) of compound **2g**.
PMR($CDCl_3$)δ(ppm): 3.06 (t, 4 H, *J* = 4.7 Hz), 3.85 (t, 4 H, *J* = 4.7 Hz), 7.09 (dt, 1 H, *J* = 1.2 Hz, 8.0 Hz), 7.15 (dd, 1 H, *J* = 1.2 Hz, 8.0 Hz), 7.51 (dt, 1 H, *J* = 1.5 Hz, 8.0 Hz), 7.77 (dd, 1 H, *J* = 1.5 Hz, 8.0 Hz); MS(EI) *m/z* : 208 (M^+); HRMS : Calcd. for $C_{10}H_{12}N_2O_3$, 208.0848; found: 208.0824; IR (neat) : 2960, 2856, 1603, 1515, 1341, 1229, 1113, 939 cm^{-1}

1-Azido-2-nitrobenzene (2h)



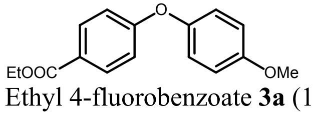
A mixture of 1-fluoro-2-nitrobenzene **1** (71 mg, 0.50 mmol), azidotrimethysilane (115 mg, 1.00 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.05 mL, 0.05 mmol) was added to the solution and the mixture was stirred for 29 h at ambient temperature. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (10% AcOEt-hexane) to afford 78 mg (95%) of compound **2h**.
m.p. 51-52°C (ether-hexane) (lit.[iii] 51-52°C); PMR($CDCl_3$)δ(ppm): 7.27 (ddd, 1 H, *J* = 1.2 Hz, 7.4 Hz, 8.2 Hz), 7.35 (dd, 1 H, *J* = 1.2 Hz, 8.2 Hz), 7.63 (ddd, 1 H, *J* = 1.2 Hz, 7.4 Hz, 8.2 Hz), 7.95 (dd, 1 H, *J* = 1.2 Hz, 8.2 Hz); MS(EI) *m/z* : 164 (M^+); HRMS : Calcd. for $C_6H_4N_4O_2$, 164.0334 ; found: 164.0324; IR (crystral): 3103, 2117, 2092, 1602, 1519, 1314, 1289, 857 cm^{-1}

1-Nitro-2-(2-phenylethynyl)benzene (2i)



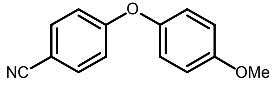
A mixture of 1-fluoro-2-nitrobenzene **1** (71 mg, 0.50 mmol), phenylethynyltrimethylsilane (105 mg, 0.60 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution at -78°C and the reaction was allowed to warm to 10°C gradually for 12h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (20% chloroform-hexane) to afford 46mg (41%) of compound **2i**.
PMR($CDCl_3$)δ(ppm): 7.36-7.42 (m, 3 H), 7.47 (dt, 1 H, *J* = 1.6 Hz, 8.0 Hz), 7.57-7.62 (m, 3 H), 7.72 (dd, 1 H, *J* = 1.6 Hz, 8.0 Hz), 8.09 (dd, 1 H, *J* = 1.6 Hz, 8.0 Hz); MS(EI) *m/z* : 223 (M^+); HRMS : Calcd. for $C_{14}H_9NO_2$, 223.0633 ; found: 223.0605; IR(neat) : 3080, 2925, 2219, 1607, 1520, 1339, 886 cm^{-1}

Ethyl 4-(4-Methoxyphenoxy)benzoate (4a)



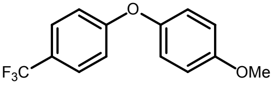
Ethyl 4-fluorobenzoate **3a** (168 mg, 1.00 mmol), 4-methoxyphenoxy-*tert*-butyldimethylsilyl ether (358 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 2 h at 80°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 250 mg (92%) of compound **4a**.
PMR($CDCl_3$)δ(ppm): 1.38 (t, 3 H, *J* = 7.2 Hz), 3.83 (s, 3 H), 4.35 (q, 2 H, *J* = 7.2 Hz), 6.90-6.96 (m, 4 H), 7.02 (d, 2 H, *J* = 9.0 Hz), 7.99 (d, 2 H, *J* = 9.0 Hz); MS(EI) m/s: 272 (M^+); HRMS: Calcd. for $C_{16}H_{16}O_4$: 272.1049, found: 272.1039; IR (neat) 2979, 2933, 2836, 1710, 1600, 1495, 1223, 1160, 1098, 1032 cm^{-1}

4-(4-Methoxyphenoxy)benzonitrile (4b)



4-Fluorobenzonitrile **3b** (121 mg, 1.00 mmol), 4-methoxyphenoxy-*tert*-butyldimethylsilyl ether (358 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 4 h at 100°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 217 mg (92 %) of compound **4b**. m.p. 108-109°C (lit.[iv] 107.5°C); PMR($CDCl_3$)δ(ppm): 3.82 (s, 3 H), 6.92 (d, 2 H, *J* = 9.3 Hz), 6.95 (d, 2 H, *J* = 9.0 Hz), 7.00 (d, 2 H, *J* = 9.3 Hz), 7.57 (d, 2 H, *J* = 9.0 Hz); MS(EI) m/s: 225 (M^+); HRMS: Calcd. for $C_{14}H_{11}NO_2$: 225.0790, found: 225.0754; IR (crystal) 3010, 2985, 2848, 2221, 1609, 1495, 1235, 1030 cm^{-1}

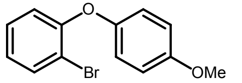
4-Methoxyphenoxy-4-trifluoromethylphenyl ether (4c)



4-Fluorobenzotrifluoride **3c** (164 mg, 1.00 mmol), 4-methoxyphenoxy-*tert*-butyldimethylsilyl ether (358 mg, 1.50 mmol) and dry DMSO (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 10 h at 100°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 261 mg (93 %) of compound **4c**.

PMR($CDCl_3$)δ(ppm): 3.81 (s, 3H), 6.91 (d, 2H, *J* = 9.0 Hz), 6.96-7.02 (m, 4H), 7.53 (d, 2 H, *J* = 9.0 Hz); MS m/s: 268 (M^+); HRMS: Calcd. for $C_{14}H_{11}O_2F_3$: 268.0710, found: 268.0703; IR (neat) 3031, 2962, 2842, 1611, 1501, 1326, 1123, 1102, 1065, 1032 cm^{-1}

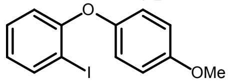
2-(4-Methoxyphenoxy)bromobenzene (4d)



1-Bromo-2-fluorobenzene **3d** (175 mg, 1.00 mmol), 4-methoxyphenoxy-*tert*-butyldimethylsilyl ether (358 mg, 1.50 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 48 h at 100°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 236 mg (85%) of compound **4d**.

PMR($CDCl_3$)δ(ppm): 3.80 (s, 3 H), 6.82 (dd, 1 H, *J* = 1.2 Hz, 8.0 Hz), 6.88 (d, 2 H, *J* = 9.0 Hz), 6.92-6.96 (m, 1 H), 6.95 (d, 2 H, *J* = 9.0 Hz), 7.20 (dt, 1 H, *J* = 1.2 Hz, 8.0 Hz), 7.60 (dd, 1 H, J = 1.2 Hz, 8.0 Hz); MS(EI) m/s: 278 (M^+), 280 $(M+2)^+$; HRMS: Calcd. for $C_{13}H_{11}O_2{}^{79}Br$: 277.9942, found: 277.9916; IR (neat) 3010, 2931, 2836, 1584, 1505, 1233, 1030 cm^{-1}

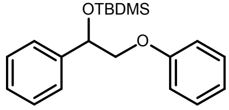
2-(4-Methoxyphenoxy)iodobenzene (4e)



1-Fluoro-2-iodobenzene **3e** (222 mg, 1.00 mmol), 4-methoxyphenoxy-*tert*-butyldimethylsilyl ether (358 mg, 1.50 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 48 h at 100°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with Et_2O. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 138 mg (43%) of compound **4e**.

PMR($CDCl_3$)δ(ppm): 3.80 (s, 3 H), 6.75-6.84 (m, 2 H), 6.88 (d, 2 H, *J* = 9.3 Hz), 6.95 (d, 2 H, *J* = 9.3 Hz), 7.21-7.26 (m, 1 H), 7.83 (dd, 1 H, *J* = 1.5 Hz, 7.8 Hz); MS(EI) *m/z* : 326 (M^+); HRMS : Calcd. for $C_{13}H_{11}O$□I : 325.9802, found: 325.9797; IR(neat) : 2958, 2933, 1735, 1501, 1465, 1227, 1040 cm^{-1}

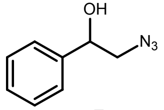
tert-Butyldimethyl(2-phenoxy-1-phenylethoxy)silane (6)



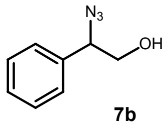
A mixture of styrene oxide **5** (230 mg, 1.91 mmol), *tert*-butyldimethylphenoxysilane (512 mg, 2.46 mmol) and dry DMF (4 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.20 mL, 0.20 mmol) was added to the solution and the mixture was stirred for 2 h at 100°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (10% chloroform-hexane) to afford 567 mg (90 %) of compound **6**.

PMR($CDCl_3$)δ(ppm): 0.03 (s, 3 H), 0.09 (s, 3 H), 0.89 (s, 9 H), 3.85-3.92 (m, 2 H), 4.98 (dd, 1 H, *J* = 5.4 Hz, 8.1 Hz), 6.76-6.87 (m, 3 H), 7.14-7.36 (m, 7 H) ; MS(EI) *m/z* : 271 (M-57 ; *t*-Bu)$^+$; IR (neat) : 2927, 2856, 1600, 1495, 1243, 1117, 974 cm^{-1}

2-Azido-1-phenylethanol (7a), 2-Azido-2-phenylethanol (7b)



7a



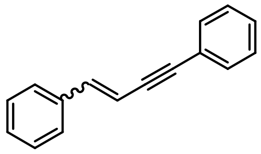
7b

A mixture of styrene oxide **5** (127 mg, 1.05 mmol), azidotrimethylsilane (243 mg, 2.11 mmol) and dry THF (2 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 12 h at 65°C. AcOH (0.5 mL) and H_2O (1 mL) was added and stirred for 8 h at ambient temperature. The reaction mixture was treated with saturated $NaHCO_3$ and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 160 mg (94 %) of the mixture of compound **7a** and **7b**. (**7a** : **7b** = 85 : 15 , The ratios of the two regioisomers were determined by PMR).

7a PMR($CDCl_3$)δ(ppm): 2.32 (d, 1 H, *J* = 3.0 Hz), 3.41-3.47 (m, 2 H), 4.83-4.86 (m, 1 H), 7.26-7.39 (m, 5 H); MS(EI) m/z : 107 (M-56 : CH_2N_3); IR(neat) : 3402, 2921, 2095, 1702, 1453, 1253, 1063 cm^{-1}

7b PMR($CDCl_3$)δ(ppm): 2.00 (bs, 1 H), 3.75 (d, 2 H, *J* = 6.2 Hz), 4.68 (t, 1 H, *J* = 6.2 Hz), 7.25-7.48 (m, 5 H), MS(EI) m/z : 163 (M^+); HRMS : Calcd. for $C_{12}H_{17}NO_3$, 163.0746; found: 163.0745; IR(neat) : 3363, 2927, 2094, 1493, 1455, 1246, 1069, 1038 cm^{-1}

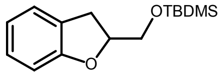
1,4-Diphenyl-but-1-en-3-yne (8)



A mixture of styrene oxide **5** (60 mg, 0.50 mmol), phenylethynyltrimethylsilane (105 mg, 0.60 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.05 mL, 0.05 mmol) was added to the solution in an ice bath and the mixture was stirred for 0.5 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford product compound **8** as a mixture of diastereomers 57mg (55%, E/Z = 4/1).

PMR($CDCl_3$)δ(ppm): 5.92 (d, 0.2 H, *J* = 11.9 Hz), 6.38 (d, 0.8 H, *J* = 16.4 Hz), 6.70 (d, 0.2 H, *J* = 11.9 Hz), 7.05 (d, 0.8 H, *J* = 16.4 Hz), 7.25-7.52 (m, 9.6 H), 7.93 (d, 0.4 H, *J* = 7.8 Hz); MS(EI) *m/z* : 204(M^+); HRMS : Calcd. for $C_{16}H_{12}$, 204.0939 ; found: 204.0923; IR (neat): 3053, 2923, 1592, 1488, 1439, 949 cm^{-1}

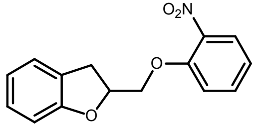
***tert*-Butyl(2,3-dihydrobenzofuran-2-ylmethoxy)dimethylsilane (10)**



A mixture of *tert*-butyldimethyl(2-oxiranylmethylphenoxy)silane **9** (132 mg, 0.50 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.05 mL, 0.05 mmol) was added to the solution in an ice bath and the mixture was stirred for 1 h . The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 115 mg (87%) of compound **10**.

PMR($CDCl_3$)δ(ppm): 0.03 (s, 3 H), 0.08 (s, 3 H), 0.86 (s, 9 H), 3.05 (dd, 1 H, *J* = 6.9 Hz, 15.7 Hz), 3.24 (dd, 1 H, *J* = 9.3 Hz, 15.7 Hz), 3.71-3.86 (m, 2 H), 4.73-4.89 (m, 1 H), 6.76 (dd, 1 H, *J* = 0.8 Hz, 7.8 Hz), 6.81 (dt, 1 H, *J* = 0.8 Hz, 7.8 Hz), 7.05-7.13 (m, 1 H), 7.13-7.18 (m, 1 H); MS(EI) *m/z* : 264 (M^+); HRMS : Calcd. for $C_{15}H_{24}O_2Si$, 264.1546 ; found: 264.1517; IR (neat): 2929, 2856, 1600, 1480, 1233, 1127, 982 cm^{-1}

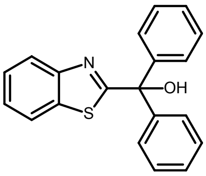
2-(2-Nitrophenoxymethyl)-2,3-dihydrobenzofuran (11)



A mixture of *tert*-butyldimethyl(2-oxiranylmethylphenoxy)silane **9** (132 mg, 0.50 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.05 mL, 0.05 mmol) was added to the solution in an ice bath and the mixture was stirred for 0.75 h . Then 1-

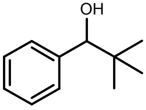
fluoro-2-nitrobenzene **1** (106 mg, 0.75 mmol) was added to the reaction mixture and the mixture was stirred for 32 h at ambient temperature. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 110 mg (81%) of compound **11**.
PMR($CDCl_3$)δ(ppm): 3.23 (dd, 1 H, J = 6.6 Hz, 15.9 Hz), 3.42 (dd, 1 H, J = 9.6 Hz, 15.9 Hz), 4.21 (dd, 1 H, J = 5.4 Hz, 9.8 Hz), 4.36 (dd, 1 H, J = 5.4 Hz, 9.8 Hz), 5.13-5.24 (m, 1 H), 6.79 (d, 1 H, J = 7.7 Hz), 6.88 (t, 1 H, J = 7.7 Hz), 7.03-7.17 (m, 3 H), 7.20 (d, 1 H, J = 7.7 Hz), 7.48-7.56 (m, 1 H), 7.83 (dd, 1 H, J = 1.6 Hz, 7.7 Hz); MS(EI) m/z : 271 (M^+); HRMS : Calcd. for $C_{15}H_{13}NO_4$, 271.0845 ; found: 271.0828; IR(neat) : 3080, 2933, 1605, 1520, 1478, 1347, 1297, 1223, 1015 cm^{-1}

(2-Benzothiazolyl)diphenylmethanol (13)



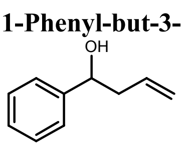
A mixture of 2-trimethylsilylbenzothiazole **12** (62 mg, 0.30 mmol), benzophenone (84 mg, 0.45 mmol) and dry THF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.06 mL, 0.06 mmol) was added to the solution and the mixture was stirred for 1.5 h at -78°C. To the reaction mixture 2*N* NaOH (1.5 mL) and MeOH (1.5 mL) were added and the mixture was stirred for 1 h in an ice bath. The mixture was treated with saturated aq.NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 88 mg (95%) of compound **13**.
m.p. 149.5-150.5°C (ether-hexane) (lit.[v] 149.5-150°C); PMR($CDCl_3$)δ(ppm): 4.44 (s, 1 H), 7.31-7.39 (m, 7 H), 7.45-7.49 (m, 5 H), 7.82 (d, 1 H, J = 8.0 Hz), 8.01 (d, 1 H, J = 8.0 Hz); MS(EI) m/z : 317 (M^+); HRMS : Calcd. for $C_{20}H_{15}NOS$, 317.0874 ; found: 317.0860; IR(crystal) : 3085, 2954, 1492, 1447, 1250, 1069 cm^{-1}

2,2-Dimethyl-1-phenylpropanol (15)



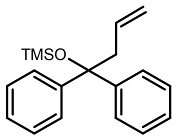
A mixture of phenyltrimethylsilane **14** (47 mg, 0.30 mmol), trimethylacetaldehyde (40 mg, 0.45 mmol) and dry THF (0.5 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.06 mL, 0.06 mmol) was added to the solution and the mixture was stirred for 24 h at ambient temperature. MeOH (1 mL) was added to the reaction mixture and stirred for 1 h. The reaction mixture was treated with saturated NH_4Cl and water and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and afforded the crude material. The yield of compound **15** was 40%, determined by PMR using 1,1,2,2-tetrachloroethane as an internal standard.
PMR($CDCl_3$)δ(ppm): 0.92 (s, 9 H), 1.86 (s, 1 H), 4.39 (s, 1 H), 7.25-7.35 (m, 5 H); MS(EI) m/z : 164 (M^+); IR(neat) : 3488, 2954, 1719, 1465, 1362, 1293, 1046, 1005 cm^{-1}

1-Phenyl-but-3-en-1-ol (16a)



A mixture of benzaldehyde (106 mg, 1.00 mmol), allyltrimethylsilane (137 mg, 1.20 mmol) and dry DMF (2 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 1 h at -78°C and stirred for 3 h at -40°C. AcOH (0.5 mL) and H_2O (1 mL) was added to the reaction mixture and stirred for 2 h. The reaction mixture was treated with saturated $NaHCO_3$ and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (5% AcOEt-hexane) to afford 125 mg (84%) of compound **16a**.
PMR($CDCl_3$)δ(ppm): 2.02 (d, 1 H, J = 3.3 Hz), 2.42-2.59 (m, 2 H), 4.71-4.78 (m, 1 H), 5.04-5.21 (m, 2 H), 5.75-5.99 (m, 1 H), 7.24-7.39 (m, 5 H); MS(EI) m/z : 148 (M^+); IR(neat) : 3365, 3029, 2906, 1640, 1455, 1044, 915 cm^{-1}

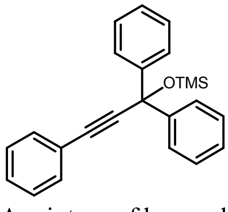
(1,1-Diphenyl-but-3-enyloxy)trimethylsilane (16b)



A mixture of benzophenone (93 mg, 0.50 mmol), allyltrimethylsilane (69 mg, 0.60 mmol) and dry DMF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.05 mL, 0.05 mmol) was added to the solution and the mixture was stirred for 1 h at -78°C and stirred for 1 h at - 40°C. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (10% chloroform-hexane) to afford 134 mg (91%) of compound **16b**.

PMR($CDCl_3$)δ(ppm): 0.09 (s, 9 H), 3.12 (d, 2 H, *J* = 6.6 Hz), 4.90-4.98 (m, 2 H), 5.56-5.70 (m, 1 H), 7.28-7.35 (m, 10 H); MS(EI) m/z : 281 (M-15 ; Me)$^+$, 255 (M-41 ; allyl)$^+$; IR(neat) : 3085, 2954, 1492, 1447, 1250, 1069 cm^{-1}

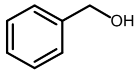
Trimethyl-(1,1,3-triphenylprop-2-ynyloxy)silane (17)



A mixture of benzophenone (1.86 mg, 10.0 mmol), phenylethynyltrimethylsilane (2.10 g, 12.0 mmol) and dry THF (20 mL) was placed in a 100-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.01 mL, 0.01 mmol) was added to the solution in an ice bath and the mixture was stirred for 3 h. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (2% AcOEt-hexane) to afford 3.29 g (92%) of compound **17**.

m.p. 65°C (MeOH) (lit.[vi] 62°C); PMR($CDCl_3$)δ(ppm): 0.15 (s, 9 H), 7.18-7.38 (m, 9H), 7.48-7.54 (m, 2 H), 7.61-7.66 (m, 4H); MS(EI) *m/z* : 356 (M$^+$); HRMS : Calcd. for $C_{24}H_{24}OSi$, 356.1596: found: 356.1601; IR(crystal) : 3083, 2958, 2221, 1488, 1449, 1250, 1061 cm^{-1}

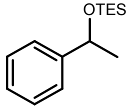
Benzyl alcohol (18a)



A mixture of benzaldehyde (106 mg, 1.00 mmol), triethylsilane (232 mg, 2.00 mmol) and dry THF (2 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution in an ice bath and the mixture was stirred for 0.5 h. AcOH (0.5 mL) and H_2O (1 mL) was added to the reaction mixture and stirred for 2 h. The reaction mixture was treated with saturated $NaHCO_3$ and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (10% AcOEt-hexane → 30% AcOEt-hexane) to afford 94 mg (89%) of compound **18a.**

PMR($CDCl_3$)δ(ppm): 4.70 (s, 2 H), 7.26-7.40 (m, 5 H); MS(EI) m/z : 108 (M$^+$); HRMS : Calcd. for C_7H_8O, 108.0575 ; found: 108.0555; IR(neat) : 3321, 3029, 2871, 1704, 1453, 1208, 1013 cm^{-1}

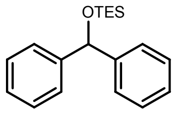
(1-Phenylethoxy)triethylsilane (18b)



A mixture of acetophenone (120 mg, 1.00 mmol), triethylsilane (232 mg, 2.00 mmol) and dry THF (2 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.10 mL, 0.10 mmol) was added to the solution and the mixture was stirred for 23 h at ambient temperature. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (1% AcOEt-hexane) to afford 182 mg (62%) of compound **18b**.

PMR($CDCl_3$)δ(ppm): 0.54 (q, 6 H, *J* = 7.6 Hz), 0.91 (t, 9 H, *J* = 7.6 Hz), 1.42 (d, 3 H, *J* = 6.3 Hz), 4.83 (q, 1 H, *J* = 6.3 Hz), 7.09-7.37 (m, 5 H); MS(EI) m/z : 236 (M$^+$); HRMS : Calcd. for $C_{14}H_{24}OSi$, 236.1596 ; found: 236.1575; IR(neat) : 2954, 2875, 1457, 1237, 1094, 1003, 955 cm^{-1}

Benzhydroxytriethylsilane (18c)



A mixture of benzophenone (97 mg, 0.53 mmol), triethylsilane (116 mg, 1.00 mmol) and dry THF (1 mL) was placed in a 20-mL flask equipped with a magnetic stirring bar under argon atmosphere. *t*Bu-P4 base, *1.0 M* solution in *n*-hexane (0.05 mL, 0.05 mmol) was added to the solution and the mixture was stirred for 23 h at ambient temperature. The mixture was treated with saturated aq. NH_4Cl and H_2O and the mixture was extracted with AcOEt. The extract was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by SiO_2 column chromatography (1% AcOEt-hexane) to afford 114 mg (72%) of compound **18c**.
PMR($CDCl_3$)δ(ppm): 0.46-0.61 (m, 6 H), 0.84-0.97 (m, 9 H), 5.76 (s, 1 H), 7.16-7.38 (m, 10 H); MS(EI) m/z : 298 (M^+); HRMS : Calcd. for $C_{19}H_{26}OSi$, 298.1753 ; found: 298.1768; IR(neat) : 2954, 2875, 1457, 1239, 1065, 1005cm^{-1}

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[i] Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; John Wiley & Sons: New York,1999; Kocienski, P. J. *Protective Groups*; Georg Thieme Verlag: New York, 1994.

[ii] Wassmundt, F. W.; Pedemonte R. P. *J. Org. Chem*. **1995**, *60*, 4991.

[iii] Kauer, J. C.; Carboni, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2633.

[iv] Harington, C. R. *Biochem. J.* **1926**, *20*, 300.

[v] Kress, J. T.; Moore, L.L. *J. Het. Chem*. **1972**, *9*, 1161.

[vi] Komissarova, E. V.; Aleksandrova, E. K.; Stadnichuk, M. D. *Russ. J. Gen. Chem*. **1997**, *67*, 412.