## Supplementary Information

## Biocatalytic Silylation: The Condensation of Phenols and Alcohols with Triethylsilanol.

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**Supplementary Results Page 2**

**GC Calibration Plots for Product Quantification Page 6**

**Synthetic Procedures for the Preparation of Product Standards Page 12**

**Supplementary Results**



**Figure S1.** Graph of percentage conversions of phenols to the corresponding silyl ethers after 72 hours. This graph contains the same data as Figure 1 but grouped by type of substitution. The error bars indicate standard deviations. A one-tailed Student's t-test assuming unequal variance was performed, comparing each enzyme to its control. Comparisons resulting in a *p* < 0.05 were deemed to be significant and marked with \*.

**Table S1.** Percentage conversion, net enzymatic conversion and conversion enhancement for the condensation of aromatic alcohols and triethylsilanol after 72 h. The limit of quantification (LOQ) in all cases were defined as 8 times the standard deviation of the blanks (n = 5), divided by the slope of the calibration curve. All results presented here are within the LOQ, with an estimated instrumental error of ~ 0.1% conversion.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Substrate | Enzymatic reaction conversion (%) | Control reaction conversion (%) | Net enzymatic conversion (%)a | Fold-increase in conversionb |
| Phenol | 88 | 27 | 61 | 3.3 |
| *o*-chlorophenol | 91 | 52 | 40 | 1.8 |
| *m*-chlorophenol | 68 | 41 | 27 | 1.7 |
| *p*-chlorophenol | 39 | 31 | 8 | 1.3 |
| *o*-methylphenol | 34 | 30 | 4 | 1.1 |
| *m*-methylphenol | 28 | 9 | 19 | 3.2 |
| *p*-methylphenol | 31 | 24 | 7 | 1.3 |
| *o*-methoxyphenol | 15 | 4 | 11 | 3.7 |
| *m*-methoxyphenol | 72 | 37 | 35 | 1.9 |
| *p*-methoxyphenol | 75 | 13 | 62 | 5.8 |
| 1-octanol | 0.8 | 0.8 | - | - |
| 1-octanol (after 192 h) | 2.7 | 4.0 | - | - |
| 3-penten-2-ol | 0.3 | 0.7 | - | - |
| *R*-2-octanol | 0.9 | 0.1 | 0.8 | 6.3 |
| *S*-2-octanol | 1.9 | < 0.1 | 1.9 | 38.8 |
| *R*-2-phenylethanol | 2.3 | 0.1 | 2.2 | 25.6 |
| *S*-2-phenylethanol | 3.4 | 0.2 | 3.23 | 20 |

a Net enzymatic conversion calculated as percentage conversion of the enzymatic reaction minus percentage conversion of the control reaction.

b Fold increase calculated as the percentage conversion of the enzymatic reaction divided by the percentage conversion of the control reaction.

**Table S2.** Percentage conversion, net enzymatic conversion, and conversion enhancement for the condensation of *m*-methoxyphenol and triethylsilanol in various solvents after 72 h. The limit of quantification (LOQ) in all cases were defined as 8 times the standard deviation of the blanks (n = 5), divided by the slope of the calibration curve. All results presented here are within the LOQ, with an estimated instrumental error of ~ 0.1% conversion.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Solvent | Normalised polarity, $E\_{T}^{N}$ | Enzymatic Conversion (%) | Control Conversion (%) | Net Enzymatic Conversion (%) | Fold-increase in conversionb |
| Ethyl acetate | 0.228 | 33 | 38 | - | - |
| Tetrahydrofuran | 0.207 | 12 | 15 | - | - |
| 1,4-dioxane | 0.164 | 16 | 17 | - | - |
| Diisopropyl ether | 0.105 | 28 | 27 |  1a | - |
| Toluene | 0.099 | 76 | 36 | 40 | 2.1 |
| *n*-Octane | 0.012 | 74 | 35 | 39 | 2.1 |

a Not statistically significant, see Figure 3.

b Fold increase calculated as the percentage conversion of the enzymatic reaction divided by the percentage conversion of the control reaction.

**Table S3.** Percentage conversion, net enzymatic conversion and conversion enhancement for the condensation of *m*-methoxyphenol and triethylsilanol in various mixtures of 1,4-dioxane and *n*-octane.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| % *v/v* of 1,4-dioxane | Enzymatic Conversion (%) | Control Conversion (%) | Net Enzymatic Conversion (%) | Fold-increase in conversiona |
| 0 | 74 | 35 | 39 | 2.1 |
| 10 | 81 | 52 | 29 | 1.6 |
| 20 | 61 | 49 | 12 | 1.2 |
| 30 | 38 | 41 | - | - |

a Fold increase calculated as the percentage conversion of the enzymatic reaction divided by the percentage conversion of the control reaction.

**GC Calibration Plots for Product Quantification**

**Figure S2.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(phenoxy)silane) in the GCMS trace against concentration.

**Figure S3**. A calibration graph of area under the peak corresponding to silyl ether (triethyl(o-methoxyphenoxy)silane) in the GCMS trace against concentration.

**Figure S4**. A calibration graph of area under the peak corresponding to silyl ether (triethyl(m-methoxyphenoxy)silane) in the GCMS trace against concentration.

**Figure S5**. A calibration graph of area under the peak corresponding to silyl ether (triethyl(p-methoxyphenoxy)silane) in the GCMS trace against concentration.

**Figure S6**. A calibration graph of area under the peak corresponding to silyl ether (triethyl(o-methylphenoxy)silane) in the GCMS trace against concentration.

**Figure S7.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(m-methylphenoxy)silane) in the GCMS trace against concentration.

**Figure S8.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(p-methylphenoxy)silane) in the GCMS trace against concentration.

**Figure S9.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(o-chlorophenoxy)silane) in the GCMS trace against concentration.

**Figure S10.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(m-chlorophenoxy)silane) in the GCMS trace against concentration.

**Figure S11.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(p-chlorophenoxy)silane) in the GCMS trace against concentration .

**Figure S12**. A calibration graph of area under the peak corresponding to silyl ether (triethyl(octyloxy)silane) in the GCMS trace against concentration.

**Figure S13.** A calibration graph of area under the peak corresponding to silyl ether (triethyl(E-pent-3-en-2-yloxy)silane) in the GCMS trace against concentration.

**Synthetic Procedures for the Preparation of Product Standards**

**Triethyl(phenoxy)silane.1** Chlorotriethylsilane (1.2 mL, 7.1 mmol) was added dropwise to a solution of phenol (559 mg, 6.0 mmol) and imidazole (1000 mg, 14.7 mmol) in anhydrous DMF (6 mL). The reaction mixture was stirred at room temperature for 24 h, after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by flash chromatography with silica gel using the eluent noted below to yield the desired compound as a colourless oil (742 mg, 60 %); Rf 0.52 (EtOAc:hexane, 1:30); νmax (liquid)/cm–1 2953 (Ar C-H), 2875 (C-H), 1595 (Ar C=C), 1258, 1002, 972 (SiCH2CH3), 1235 (SiOAr); δH (400 MHz, CDCl3) 0.71 − 0.77 (q, 6H, SiCH2CH3), 0.99 (t, *J* = 8.0 Hz, 9H, SiCH2CH3), 6.84 – 6.87 (dd, *J* = 8.60, 1.0 Hz, 2H), 6.93 – 6.96 (m, 1H, ArH), 7.20 − 7.24 (m, 2H, ArH); MS *m/z* (ES+) 209 (100 %, [M+H]+).

**Triethyl(*o*-chlorophenoxy)silane.2** Chlorotriethylsilane (1.2 mL, 7.1 mmol) was added dropwise to a solution of *o*-chlorophenol (765 mg, 6.0 mmol) and imidazole (1000 mg, 14.7 mmol) in anhydrous DMF (6 mL). The reaction mixture was stirred at room temperature for 24 h, after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by flash chromatography with silica gel using the eluent noted below to yield the desired compound as a colourless oil (560 mg, 38 %); Rf 0.40 (hexane); νmax (liquid)/cm–1 2955 (Ar C-H), 2876 (C-H), 1585 (Ar C=C), 1245, 1004 (SiCH2CH3), 1245 (SiOAr) 745 (C-Cl); δH (400 MHz, CDCl3) 0.75 – 0.81 (q, 6H, SiCH2CH3), 0.99 – 1.03 (t, *J* = 8.0 Hz, 9H, SiCH2CH3), 6.86 – 6.89 (m, 2H, ArH), 7.09 – 7.13 (m, 1H, ArH), 7.32 – 7.34 (dd, *J* = 8.2, 1.8 Hz, 1H, ArH); MS *m/z* (EI+) 242 (100 %, M·+ for 35Cl isotopologue), 244 (35 %, M·+ for 37Cl isotopologue).

**Triethyl(*m*-chlorophenoxy)silane.2** Chlorotriethylsilane (1 mL, 6.0 mmol) was added dropwise to a solution of *m*-chlorophenol (940 μL, 5.8 mmol) and imidazole (800 mg, 11.8 mmol) in anhydrous DMF (5 mL). The reaction mixture was stirred at room temperature for 16 h, after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired compound as a colourless oil (650 mg, 45 %); Rf 0.56 (hexane); νmax (liquid)/cm–1 2956 (Ar C-H), 2910, 1590 (Ar C=C), 1239, 999, 937 (SiCH2CH3), 1239, 973 (SiOAr), 770, 744, 682 (C-Cl);δH (100 MHz, CDCl3) 0.71 – 0.77 (q, 6H, SiCH2CH3), 0.98 – 1.02 (t, *J* = 7.8 Hz, 9H, SiCH2CH3), 6.72 – 6.74 (ddd, *J* = 8.0, 1.6 Hz, 1H, ArH), 6.85 (t, *J* = 2.2 Hz, 1H, ArH), 6.92 – 6.94 (ddd, *J* = 8.0, 1.6 Hz, 1H, ArH), 7.14 (t, *J* = 8.2 Hz, 1H); MS *m/z* (EI+) 242 (100 %, M·+ for 35Cl isotopologue), 244 (35 %, M·+ for 37Cl isotopologue).

**Triethyl(*p*-chlorophenoxy)silane.2** Chlorotriethylsilane (1 mL, 5.8 mmol) was added dropwise to a solution of *m*-chlorophenol (940 μL, 5.8 mmol) and imidazole (800 mg, 11.8 mmol) in anhydrous DMF (5 mL). The reaction mixture was stirred at room temperature for 20 h, after which diethyl ether (60 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired **14** as a colourless oil (710 mg, 49 %); Rf 0.42 (hexane); νmax (liquid)/cm–1 2955 (Ar C-H), 2955, 1592 (Ar C=C), 1259, 1005 (SiCH2CH3), 1259, 1005 (SiOAr), 829, 748 (C-Cl); δH (400 MHz, CDCl3) 0.69 – 0.76 (q, 6H, SiCH2CH3), 0.99 (t, *J* = 8.0 Hz, 9H, SiCH2CH3), 6.76 – 6.78 (m, 2H, ArH), 7.16 – 7.18 (m, 2H, ArH); MS *m/z* (EI+) 242 (100 %, M·+ for 35Cl isotopologue), 244 (35 %, M·+ for 37Cl isotopologue).

**Triethyl(*o*-methylphenoxy)silane.2** Chlorotriethylsilane (1 mL, 6.0 mmol) was added dropwise to a solution of *o*-cresol (643 mg, 6.0 mmol) and imidazole (811 mg, 11.8 mmol) in anhydrous acetonitrile (6 mL). The reaction mixture was stirred at room temperature for 16 h, after which diethyl ether (20 mL) was added and the organic phase washed with H2O (2 × 20 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired product as a colourless oil (438 mg, 33 %); Rf 0.64 (EtOAc:hexane, 9:1); νmax (liquid)/cm–1 2954 (Ar C-H), 2910, 2876 (C-H), 1601 (Ar C=C), 1259, 1002, 915 (SiCH2CH3), 1236, 1002 (SiOAr); δH (400 MHz, CDCl3) 0.73 – 0.79 (m, 6 H, SiCH2CH3) 0.98 – 1.02 (m, *J* = 8.0, 9 H, SiCH2CH3) 2.21 (s, 3 H, ArCH3) 6.76 – 6.78 (m, 1 H, ArH) 6.83 – 6.86 (m, 1 H, ArH) 7.03 – 7.06 (m, 1 H, ArH) 7.11 – 7.13 (dd, *J* = 7.6 Hz, 1 H, ArH); MS *m/z* (ES+) 223 (100 %, [M+H]+).

**Triethyl(*m*-methylphenoxy)silane.2** Chlorotriethylsilane (1 mL, 6.0 mmol) was added dropwise to a solution of *o*-cresol (643 mg, 6.0 mmol) and imidazole (811 mg, 11.8 mmol) in anhydrous acetonitrile (6 mL). The reaction mixture was stirred at room temperature for 16 h, after which diethyl ether (20 mL) was added and the organic phase washed with H2O (2 × 20 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired product as a colourless oil (256 mg, 19 %); Rf 0.64 (EtOAc:hexane, 9:1); νmax (liquid)/cm–1 3031 (Ar C-H), 2954, 2911, 2876 (C-H), 1602 (Ar C=C), 1237, 954 (SiOAr), 1004 (SiCH2CH3); δH (400 MHz, CDCl3) 0.71 – 0.77 (q, 6H, SiCH2CH3) 0.98 – 1.02 (t, 9H, SiCH2CH3) 2.29 (s, 3H, ArCH3) 6.64 – 6.67 (m, 2H, ArH) 6.75 (d, *J* = 7.6 Hz, 1 H, ArH) 7.09 (t, *J* = 7.8 Hz, 1 H, ArH); MS *m/z* (ES+) 223 (100 %, [M+H]+).

**Triethyl(*p*-methylphenoxy)silane.2** Chlorotriethylsilane (1 mL, 6.0 mmol) was added dropwise to a solution of *o*-cresol (643 mg, 6.0 mmol) and imidazole (811 mg, 11.8 mmol) in anhydrous acetonitrile (6 mL). The reaction mixture was stirred at room temperature for 16 h, after which diethyl ether (20 mL) was added and the organic phase washed with H2O (2 × 20 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired compound as a colourless oil (543 mg, 41%); Rf 0.64 (EtOAc:hexane, 9:1); νmax (liquid)/cm–1 2953 (Ar C-H), 2090, 2875 (C-H), 1612 (Ar C=C), 1257, 1002, 942 (SiCH2CH3), 1235, 969 (SiOAr); δH (400 MHz, CDCl3) 0.69 – 0.76 (q, 6H, SiCH2CH3) 0.98 – 1.01 (m, 9H, SiCH2CH3) 2.27 (s, 3H, ArCH3) 6.74 (d, *J* = 8.4 Hz, 2H, ArH) 7.01 (d, *J* = 8.4 Hz, 2H, ArH); MS *m/z* (ES+) 223 (100 %, [M+H]+).

**Triethyl(*o*-methoxyphenoxy)silane.2** Chlorotriethylsilane (1.5 mL, 8.9 mmol) was added dropwise to a solution of *o*-methoxyphenol (990 μL, 8.9 mmol) and imidazole (1200 mg, 17.6 mmol) in anhydrous DMF (9 mL). The reaction mixture was stirred at 80 °C for 72 h, after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired silyl ether as a colourless oil (1529 mg, 72 %); Rf 0.49 (EtOAc:hexane, 1:40); νmax (liquid)/cm–1 2954, 2911, 2876, 2834 (C-H), 1455, 1439 (Ar C=C), 1222, 1005, 974 (SiCH2CH3); δH (400 MHz, CDCl3) 0.69 – 0.76 (q, 6H, *J* = 8.0 Hz, SiCH2CH3) 0.97 – 1.01 (t, 9H, *J* = 8.0 Hz, SiCH2CH3) 3.81 (s, 3H, OCH3) 6.77 – 6.93 (m, 4H, ArH); MS *m/z* (ES+) 239 (100 %, [M+H]+).

**Triethyl(*m*-methoxyphenoxy)silane.2** Chlorotriethylsilane (1.5 mL, 8.9 mmol) was added dropwise to a solution of *m*-methoxyphenol (740 mg, 5.9 mmol) and imidazole (1200 mg, 17.82 mmol) in anhydrous DMF (9 mL). The reaction mixture was stirred at 80 °C for 72 h, after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired silyl ether as a colourless oil (1111 mg, 52 %); Rf 0.56 (EtOAc:hexane, 1:5); νmax (liquid)/cm–1 2955, 2912, 2877, 2834 (C-H), 1451, 1414 (Ar C=C), 1288, 1269, 1239, 973 (SiCH2CH3); δH (400 MHz, CDCl3) 0.72 – 0.78 (m, 6H, SiCH2CH3) 0.99 – 1.03 (m, 9H, SiCH2CH3) 3.78 (s, 3H, OCH3) 6.43 – 6.44 (t, *J* = 2.4 Hz, 1H, ArH) 6.46 – 6.48 (ddd, *J* = 8.0, 2.0, 0.8 Hz 1H, ArH) 6.5 – 6.54 (ddd, *J* = 8.2, 2.4, 0.8 Hz, 1H, ArH) 7.13 (t, *J* = 8.2 Hz, 1H, ArH); MS *m/z* (ES+) 239 (100 %, [M+H]+).

**Triethyl(*p*-methoxyphenoxy)silane.2** Chlorotriethylsilane (1.5 mL, 8.9 mmol) was added dropwise to a solution of *m*-methoxyphenol (740 mg, 5.9 mmol) and imidazole (1200 mg, 17.82 mmol) in anhydrous DMF (9 mL). The reaction mixture was stirred at 80 °C for 72 h, after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired product as a colourless oil (741 mg, 60 %); Rf 0.50 (EtOAc:hexane, 1:5); νmax (liquid)/cm–1 3042 (Ar C-H), 2954, 2911, 2877, 2833 (C-H), 1462, 1441 (Ar C=C), 1294, 1227, 1039 (Ar O-CH3), 1004, 975 (SiCH,CH3); δH (400 MHz, CDCl3) 0.68 – 0.74 (q, 6H, SiCH2CH3) 0.97 – 1.01 (t, 9H, SiCH2CH3) 3.76 (s, 3H, OCH3) 6.74 – 6.79 (m, 4H, ArH); MS *m/z* (ES+) 239 (100 %, [M+H]+).

**Triethyl(octyloxy)silane.3** To a solution of octanol (2.81 mL, 17.8 mmol) and imidazole (857 mg, 12.5 mmol) in anhydrous DMF (12 mL), chlorotriethylsilane (3 mL, 17.8 mmol) was added dropwise. The reaction mixture was stirred under N2 at RT for 36 h, after which diethyl ether (300 mL) was added and the organic phase washed with H2O (2 × 60mL). The organic phase was dried with MgSO4 and condensed under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired product as a colourless oil. (887 mg, 57 %), Rf 0.33 (Hexane/EtOAc, 40:1), νmax (liquid)/cm–1 2953, 2924, 2874, 2855 (C-H), 1237, 1097 (C-O), 1004 (C-H), 976 (SiCH2CH3); δH (400 MHz, CDCl3) 0.57 – 0.62 (q, 6H, SiCH2CH3) 0.86 – 0.90 (m, 3H, octyl CH3) 0.96 (t, *J* = 8.0 Hz, 9H, SiCH2CH3) 1.28 (m, 10 H, octyl CH2) 1.49 – 1.54 (m, 2H, octyl CH2) 3.59 (t, *J* = 6.8 Hz, 2H, CH2O);MS *m/z* (APCI) 245 (100%, [M+H]+).

***rac*-Triethyl(*E-*pent-3-en-2-yloxy)silane.4** Chlorotriethylsilane (195 μL, 1.2 mmol) was added dropwise to a solution of *E*-3-penten-2-ol (90 mg, 1.1 mmol) and pyridine (100 μL, 1.2 mmol) in anhydrous dichloromethane (12 mL) under N2 at 0 °C. The reaction was stirred at RT for 4 h and saturated ammonium chloride (6 mL) was gradually added followed by DCM (30 mL). The organic phase was washed with H2O (15 mL) and saturated aqueous NaCl (10 mL). The organic phase was dried with MgSO4 and condensed under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desiredcompound as a colourless oil (60 mg, 30 %); Rf 0.68 (DCM:pentane, 2:3); νmax (liquid)/cm–1 2876 (C-H), 2954 (C-H), 1674 (C=C), 1081 (C-O), 992 (Si-O); δH (400 MHz, CDCl3) 0.52 (q, *J* = 7.8 Hz, 6H, SiCH2CH3), 0.95 – 0.81 (m, 9H, SiCH2CH3), 1.13 (d, *J* = 6.2 Hz, 3H, CH3CO), 1.59 (dt, *J* = 6.2, 1.0 Hz, 3H, CH3CH=), 4.22 – 4.10 (m, 1H, CHO), 5.57 – 5.34 (m, 2H, CH=); m/z (EI) 200 (17%, M·+), 171 (100%, [M–Et]+).

**(*R*)-triethyl(octan-2-yloxy)silane.5** To a solution of (*R*)-2-octanol (2.8 mL, 17.8 mmol) and imidazole (1224 mg, 18.0 mmol) in anhydrous DMF (12 mL), chlorotriethylsilane (3 mL, 17.8 mmol) was added dropwise. The reaction mixture was stirred under N2 at RT for 36 h after which diethyl ether (300 mL) was added and the organic phase washed with H2O (2 × 60mL). The organic phase was dried with MgSO4 and condensed under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired product as a colourless oil (3180 mg, 73 %); Rf 0.46 (Hexane/EtOAc, 40:1), νmax (liquid)/cm–1 2954, 2925, 2874, 2858 (C-H), 1050 (C-O), 1005 (SiCH2CH3);δH (400 MHz, CDCl3) 0.49 – 0.62 (m, 6H, SiCH2CH3) 0.87 – 0.90 (t, 3H, CH2CH3)0.91 – 0.98 (m, 9H, SiCH2CH3) 1.13 (d, *J* = 6.4 Hz, 3H, CH3CO) 1.27 – 1.31 (m, 10H, CH) 3.75 – 3.79 (m, *J* = 6.0 Hz, 1H, CHO);MS *m/z* (APCI) 245 (100%, [M+H]+).

**(*S*)-triethyl(octan-2-yloxy)silane.6** To a solution of (*S*)-2-octanol (1 mL, 6.3 mmol) and imidazole (2420 mg, 35.5 mmol) in anhydrous DMF (8 mL), chlorotriethylsilane (1 mL, 6.3 mmol) was added dropwise. The reaction mixture was stirred under N2 at RT for 36 h after which diethyl ether (150 mL) was added and the organic phase washed with H2O (2 × 50 mL). The organic phase was dried with MgSO4 and condensed under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired compound as a colourless oil (887 mg, 58%); Rf 0.46 (Hexane/EtOAc, 40:1), νmax (liquid)/cm–1 2955, 2924, 2874, 2858 (C-H), 1052 (C-O), 1005 (SiCH2CH3);δH (400 MHz, CDCl3) 0.49 – 0.62 (m, 6H, SiCH2CH3) 0.87 – 0.90 (t, 3H, CH2CH3) 0.91 – 0.98 (m, 9H, SiCH2CH3) 1.13 (d, *J* = 6.0 Hz, 3H, CH3CO) 1.27 – 1.31 (m, 10H, CH) 3.73 – 3.79 (m, *J* = 6.0 Hz, 1H, CHO);MS *m/z* (APCI) 245 (100%, [M+H]+).

**(*R*)-triethyl-(1-phenylethoxy)silane.6** To a solution (*R*)-1-phenylethan-1-ol (2.14 mL, 17.8 mmol) and imidazole (1000 mg, 14.7 mmol) in anhydrous DMF (6 mL), chlorotriethylsilane (1.2 mL, 7.1 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h, after which diethyl ether (150 mL) was added and the organic phase washed with water (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired compound as a colourless oil (1217 mg, 85.7%); Rf 0.50 (Hexane/EtOAc, 5:1); νmax (liquid)/cm–1 3063, 3027 (Ar C-H), 2952, 2875 (C-H), 1492, 1452 (Ar C=C), 1237, 1002, 959 (SiCH2CH3), 1091, 1031 (C-O);δH (400 MHz, CDCl3) 0.53 – 0.59 (m, 6H, SiCH2CH3) 0.89 – 0.93 (t, 9H, SiCH2CH3) 1.43 (d, *J* = 6.4 Hz, 3H, CH3CO) 4.79 (q, *J* = 6.4 Hz, 1H, CHO) 7.20 − 7.24 (m, 1H, ArH) 7.28 − 7.35 (m, 4H, ArH);MS *m/z* (ES+) 237 (100 %, [M+H]+).

***S*-triethyl(1-phenylethoxy)silane.6** To a solution of (S)-1-phenylethan-1-ol (2.14 mL, 17.8 mmol) and imidazole (1000 mg, 14.87 mmol) in anhydrous DMF (6 mL), chlorotriethylsilane (1.2 mL, 7.14 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h, after which diethyl ether (150 mL) was added and the organic phase washed with water (2 × 60 mL). The organic phase was then dried with MgSO4 and concentrated under reduced pressure. The residue was purified by silica gel using the eluent noted below to yield the desired compound as a colourless oil (1147 mg, 80.8%); Rf 0.50 (Hexane/EtOAc, 5:1); νmax (liquid)/cm–1 3063, 3027 (Ar C-H), 2953, 2875 (C-H), 1492, 1452 (Ar C=C), 1237, 1003, 954 (SiCH2CH3), 1091, 1031 (C-O);δH (400 MHz, CDCl3) 0.53 – 0.59 (m, 6H, SiCH2CH3), 0.89 – 0.93 (t, 9H, SiCH2CH3), 1.43 (d, *J* = 6.4 Hz, 3H, CH3CO) 4.84 – 4.89 (q, *J* = 6.4 Hz, 1H, CHO), 7.20 – 7.24 (m, 1H, ArH) 7.28 – 7.35 (m, 1H, ArH);MS *m/z* (ES+) 237 (100 %, [M+H]+).

**References for SI**

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