Supporting Information

Ruthenium catalyzed selective hydrosilylation of aldehydes

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General Experimental: All catalytic reactions were performed under nitrogen atmosphere. All stoichiometric reactions were performed in nitrogen atmosphere MBraun glove box. Chemicals were purchased from Acros, Sigma-Aldrich, Alfa-aesar, Himedia Chemicals and used without further purification. Dry solvents were prepared according to standard procedures. Ruthenium hydride intermediates [{(η^6 -*p*-cymene)RuCl}₂(μ -H- μ -Cl)] (2) and [(η^6 -*p*-cymene)Ru(H)₂(SiEt₃)₂] (3) were prepared and isolated inside glove box. ¹H, ¹³C spectra were recorded at Bruker AV-400 (¹H: 400 MHz, ¹³C: 100.6 MHz). ¹H and ¹³C {1H} NMR chemical shifts were reported in ppm downfield from tetramethyl silane. Multiplicity is abbreviated as: s, Singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; dq, doublet of quartet; m, multiplate. Assignment of spectra was done based on one dimensional (dept-135) NMR techniques. IR Spectra were recorded in Perkin-Elmer FT-IR Spectrometer. Mass spectra were recorded on Bruker micrOTOF-Q II Spectrometer.

Optimization of Reaction Conditions: At the outset various common and commercially available ruthenium complexes were explored to find out a suitable catalyst for the hydrosilylation of aldehydes using benzaldehyde as a benchmark substrate (Table S1). The initial screen of ruthenium complexes provided encouraging results (Entries 1-3). Although few ruthenium complexes were ineffective for the hydrosilylation of aldehydes (entries 4-6), moderate yields were obtained with complexes containing chloride ligands (entries 7-8). Out of all the complexes studied, the dinuclear Ru(II) complex, $[Ru(p-cymene)Cl_2]_2$ (1) proved to be the optimal catalyst and provided the 95% yield of benzyl(triethylsilyl)ether (entry 9). Upon identifying suitable catalyst for hydrosilylation of aldehydes, the reaction conditions were optimized further with $[Ru(p-cymene)Cl_2]_2$ at different temperatures and catalyst loadings (See, Table S1) and use of various silanes revealed the suitability of triethylsilane (See, Table S3). Despite taking 10h for completion, reaction at room temperature provided 94% yields (Table S2, entry 1); lowering the catalyst load (0.5mol%) and slightly increasing the temperature (50 °C) provided the product in 94% yield after 8h (entry 2). Heating the reaction mixture at 50 °C with 1 mol% catalyst load yielded 95% of product after 3h (entry 3). The reaction also effectively proceeded under solvent less condition and the corresponding silvl ether product was obtained in 94% (entry 4). Further, increase of temperature resulted in decrease of reaction time (2h), however, product yield decreased to 90% (entry 5).

Table S1. Screening of Ruthenium Catalysts.^a

PhCHO + Et₃SiH $\xrightarrow{\text{catalyst (1 mol%)}}$ PhCH₂OSiEt₃

Entry	Ru	Time (h)	Yield (%) ^b
1	RuCl ₃ .3H ₂ O	36	25
2	Ru(CO) ₃ (PPh ₃) ₃	36	52
3	Ru ₃ (CO) ₁₂	24	53
4	$[Ru(CO)_2Cl_2]_n$	36	0
5	Ru(COD)Cl ₂	24	7
6	Ru(acac) ₃	36	9
7	RuCl ₂ (PPh ₃) ₃	36	68
8	RuHCl(CO)(PPh ₃) ₃	11	85
9	[Ru(p-cymene)Cl ₂] ₂	3	95
10	RuH ₂ (CO)(PPh ₃) ₃	10	74

Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013 a) Ruthenium complex (1 mol%), benzaldehyde (1 mmol), triethylsilane (1.3 mmol) and toluene (2 mL) were heated at 50 °C under nitrogen atmosphere. b) Yields of isolated product after column chromatography.

Table S2. Optimization of Reaction Conditions with [Ru(p-cymene)Cl₂].^a

PhCHO + Et₃SiH $\frac{[Ru(p-cymene)Cl_2]_2 (1)}{neat \text{ or toluene}} PhCH_2OSiEt_3$

Entry	1 (mol%)	Temp. (°C)	Time (h)	Yield (%) ^b
1	1	25	10	94
2	0.5	50	8	94
3	1	50	3	95
4 ^c	1	50	3.5	94
5	1	75	2	90

a) [Ru(p-cymene)Cl₂]₂ (1 mol%), benzaldehyde (1 mmol), triethylsilane (1.3 mmol) and toluene (2 mL) were reacted under nitrogen atmosphere. b) Yields of isolated product after column chromatography. c) Reaction carried out under neat conditions.

The next focus turned on towards search for suitable silane. Various hydrosilylation products were obtained upon reaction of benzaldehyde (1 equiv.) with silanes (1.3 equiv.) in the presence of $[Ru(p-cymene)Cl_2]_2$ (1 mol%) (Table S3). Although, the silvl ether formed in all the reactions, the yields were lower than that of hydrosilylation product resulted from triethylsilane (Table S2).

Table S3. Optimization of Silanes.^a

PhCHO + $R_3SiH \xrightarrow{[Ru(p-cymene)Cl_2]_2(1)}{toluene} PhCH_2OSiR_3$						
Entry	Silane	Time (h)	Yield (%) ^b			
1	Ph ₃ SiH	5	60			
2	EtOMe ₂ SiH	3	83			
3	^{<i>i</i>} Pr ₃ SiH	24	38			
4 ^c	Et ₂ SiH ₂	15	72 ^d			
5°	Ph ₂ SiH ₂	15	35 ^e			

a) [Ru(p-cymene)Cl₂]₂ (1 mol%), benzaldehyde (1 mmol), and silane (1.3 mmol) were heated at 50 °C under argon atmosphere and under neat conditions. b) Yields of isolated product after column chromatography. c) Reaction carried out under neat conditions. d) Corresponding bis(benzyloxy)diethylsilane formed in 17% yields. e) Corresponding bis(benzyloxy)diphenylsilane formed in 11% yields.

General Procedure for Catalytic Hydrosilylation of Aldehydes: Aldehyde (1 mmol), triethylsilane (1.3 mmol), [Ru(p-cymene)Cl₂]₂ (1 mol%) [and toluene (2 ml), if aldehyde is in solid form] were taken in a closed flask equipped with a magnetic bar and the reaction mixture was heated at 50 °C. Progress of the reaction was monitored by TLC and ¹H NMR. Upon completion of the reaction, the resulting residue was chromatographed over silica-gel using 2% ethyl acetate/hexane mixture as eluent.

((Triethylsilyloxy)methyl)benzene¹: Colorless liquid. IR (DCM): 2955, 2877, 1455, 1414, 1377, 1240, 1207, 1097, 1069, 1008, 809, 730, 696 cm^{-1.1}H NMR (CDCl₃): δ 7.38-7.25 (m, 5H, 5ArC*H* overlapped with solvent peak), 4.77 (s, 2H, OC*H*₂); 1.02 (t, *J*= 8 Hz, 9H, (SiCH₂C*H*₃)₃), 0.69 (q, *J*= 8 Hz, 6H, (SiC*H*₂CH₃)₃). ¹³C{¹H} NMR (CDCl₃): δ 141.46 (quat-C), 128.34 (CH), 126.96 (CH), 126.35 (CH), 64.86 (OC*H*₂), 6.91 (SiCH₂CH₃), 4.65 (SiCH₂CH₃). MS (ESI) m/z 222.14 (M)⁺. HR/MS: calcd (C₁₃H₂₂OSi)⁺ 222.1440. Found: 222.1434.

4-methyl((triethylsilyloxy)methyl)benzene²: Colorless liquid. IR (DCM): 3023, 2955, 2913, 2877, 1516, 1458, 1415, 1237, 1203, 1073, 1005, 803, 741, 688. cm⁻¹. ¹H NMR (CDCl₃): δ 7.25 (d, *J*= 8 Hz, 2H, ArC*H*), 7.16 (d, *J*= 8 Hz, 2H, ArC*H*), 4.72 (s, 2H, OC*H*₂), 2.36 (s, 3H,C*H*₃), 1.00 (t, *J*= 8 Hz, 9H, (SiCH₂C*H*₃)₃), 0.67 (q, *J*= 8Hz, 6H, (SiC*H*₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 138.44 (quat-*C*), 136.65 (quat-*C*), 129.02 (*C*H), 126.46 (*C*H), 64.78 (OC*H*₂), 21.24 (*C*H₃), 6.92 (SiCH₂CH₃), 4.66 (SiCH₂CH₃).). MS (ESI) m/z 237.16 (M+1)⁺. HR/MS: calcd (C₁₄H₂₅OSi)⁺ 237.1675. Found: 237.1680.

4-methoxy((triethylsilyloxy)methyl)benzene³: Colorless liquid. IR (DCM): 2955, 2910, 2876, 1613, 1513, 1463, 1376, 1310, 1246, 1170, 1088, 1038, 1008, 819, 741 cm^{-1.1}H NMR (CDCl₃): δ 7.28 (d, *J*= 8 Hz, 2H, ArC*H*), 6.89 (d, *J*= 8 Hz, 2H, ArC*H*), 4.69 (s, 2H, OC*H*₂), 3.82 (s, 3H, OC*H*₃), 1.00 (t, *J*= 8 Hz,9H, (SiCH₂C*H*₃)₃), 0.66 (q, *J*= 8 Hz, 6H, SiC*H*₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 158.86 (quat-*C*), 133.59 (quat-*C*), 127.87 (*C*H), 113.76 (*C*H), 64.57 (OC*H*₂), 55.32 (OC*H*₃), 6.89 (SiCH₂CH₃), 4.64 (SiCH₂CH₃). MS (ESI) m/z 252.15 (M)⁺. HR/MS: calcd (C₁₄H₂₄O₂Si)⁺ 252.1546. Found: 252.1541.

3,5-dimethoxy((triethylsilyloxy)methyl)benzene: Colorless liquid. IR (DCM): 2955, 2877, 1599, 1462, 1430, 1240, 1205, 1155, 1065, 1015, 832, 743 cm⁻¹. ¹H NMR (CDCl₃): δ 6.52(s, 1H, ArC*H*), 6.36(s, 1H, ArC*H*), 4.70(s, 2H, OC*H*₂), 3.79(s, 2H, OC*H*₃), 1.00(t, *J*= 2 Hz, 9H, (SiCH₂C*H*₃)₃), 0.67(q, *J*= 2 Hz, 6H, (SiC*H*₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 160.91(*C*H), 144.07(quat-*C*), 104.01(*C*H), 99.13(quat-*C*), 64.75(OC*H*₂), 55.36(OC*H*₃), 6.90(SiCH₂CH₃), 4.63(SiCH₂CH₃).MS (ESI) m/z 283.16 (M+1)⁺. HR/MS: calcd (C₁₅H₂₇O₃Si)⁺ 283.1729. Found 283.1724.

9-((triethylsilyloxy)methyl)anthracene: Yellow solid. IR (DCM): 3053, 2951, 2875, 1623, 1502, 1476, 1454, 1412, 1382, 1345, 1239, 1072, 1009, 897, 868, 851, 822,779, 732 cm⁻¹. ¹H NMR (CDCl₃): δ 8.46(d, *J*= 8Hz,(2+1)H, Overlapped with a singlet, ArCH), 8.03 (d, *J*= 8Hz, 2H, ArCH), 7.58 (t, *J*= 8Hz, 2H, ArCH), 7.50 (t, *J*= 8Hz, 2H, ArCH), 5.69 (s, 2H, OCH₂), 1.04 (t, *J*= 8Hz, 9H, (SiCH₂CH₃)₃), 0.75 (q, *J*= 8Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 131.71 (quat-*C*), 131.55 (quat-*C*), 130.53 (quat-*C*), 129.10 (*C*H), 128 (*C*H), 125.96 (*C*H), 124.96 (*C*H), 124.60 (*C*H), 57.59 (OCH₂), 6.97 (SiCH₂CH₃), 4.72 (SiCH₂CH₃). MS (ESI) m/z 322.14 (M)⁺. HR/MS: calcd (C₁₇H₂₅ClNO₂Si)⁺ 322.1752. Found: 322.1749.

3-bromo((triethylsilyloxy)methyl)benzene: Colorless liquid. IR (DCM): 2956, 2877, 1572, 1458, 1427, 1240, 1198, 1107, 1079, 1009, 814, 771, 744 cm⁻¹. ¹H NMR (CDCl₃): δ 7.51(s, 1H, ArC*H*), 7.38(d, *J*= 8Hz, 1H, ArC*H*), 7.26(d, *J*= 8Hz, 1H, ArC*H*), 7.20(t, *J*= 8Hz, 1H, ArC*H*), 4.72(s, 2H, OC*H*₂), 1.00(t, *J*= 2 Hz, 9H, (SiCH₂CH₃)₃), 0.68(q, *J*= 2 Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 143.87(quat-*C*), 130.09(*C*H), 129.90(*C*H),

Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013 129.29(CH), 124.70(CH), 122.56(quat-C), 64.02(OCH₂), 6.87(SiCH₂CH₃), 4.58(SiCH₂CH₃). MS (ESI) m/z 301.06 (M)⁺.HR/MS: calcd. (C₁₃H₂₂BrOSi)⁺ 301.0625. Found: 301.0618.

> 4-bromo((triethylsilyloxy)methyl)benzene⁴: Crystalline solid. IR (DCM): 2955, 2911, 2876, 1486, 1459, 1406, 1368, 1239, 1203, 1114, 1087, 1010, 798, 744 cm⁻¹. ¹H NMR (CDCl₃): δ 7.45 (d, J=8 Hz ,2H, ArCH),7.21(d, J=8 Hz ,2H, ArCH), 4.68 (s, 2H, OCH₂), 0.97 $(t, J= 8 Hz, 9H, (SiCH_2CH_3)_3), 0.65 (q, J= 8Hz, 6H, (SiCH_2CH_3)_3), {}^{13}C{}^{1}H} NMR(CDCl_3); \delta$ 140.40 (quat-C), 131.30 (quat-C), 127.85 (CH), 120.67 (CH), 64.05 (OCH₂), 6.77 $(SiCH_2CH_3)$, 4.50 $(SiCH_2CH_3)$. MS (ESI) m/z 301.06 $(M+1)^+$. HR/MS: calcd $(C_{13}H_{22}BrOSi)^+$ 301.0623. Found: 301.0620.

> 4-cyano((triethylsilyloxy)methyl)benzene: Colorless liquid. IR (DCM): 2956, 2877, 2229, 1610, 1458, 1414, 1376, 1240, 1207, 1092, 1017, 818, 743, 547 cm⁻¹.¹H NMR (CDCl₃): δ 7.60 (d, J= 8Hz ,2H, ArCH), 7.43 (d, J= 8Hz ,2H, ArCH), 4.77 (s, 2H, OCH₂), 0.97 (t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.65 (q, J= 8Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 146.97 (quat-C), 132.08 (CH), 126.40 (CH), 119.02 (quat-C), 110.62 (quat-C), 63.87 (OCH₂), 6.72 (SiCH₂CH₃), 4.42 (SiCH₂CH₃). MS (ESI) m/z 248.1 (M+1)⁺. HR/MS: calcd. $(C_{14}H_{22}NOSi)^+$ 248.1472. Found: 248.1465.

> 4-nitro((triethylsilyloxy)methyl)benzene: White solid. IR (DCM): 2957, 2878, 1603, 1520, 1345, 1241, 1203, 1099, 1014, 815, 736 cm⁻¹. ¹H NMR (CDCl₃): δ 8.18 (d, J= 8Hz , 2H, ArCH), 7.49 (d, J= 8Hz, 2H, ArCH), 4.82 (s, 2H, OCH₂), 0.98 (t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.67 (q, J=8Hz, 6 H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 149.05 (quat-C), 147.01 (quat-C), 126.36 (CH), 123.51 (CH), 63.71 (OCH₂), 6.71 (SiCH₂CH₃), 4.42 (SiCH₂CH₃). MS (ESI) $m/z268.13 (M+1)^+$.HR/MS: calcd (C₁₃H₂₂NO₃Si)⁺ 268.1369. Found: 268.1363.

> 2-bromo-4-methyl((triethylsilyloxy)methyl)benzene: Colorless liquid. IR (DCM): 2954, 2875, 1606, 1458, 1238, 1207, 1101, 1032, 855, 816, 740 cm⁻¹. ¹H NMR (CDCl₃): δ 7.44(d, J= 8Hz, 1H, ArCH), 7.33(s, 1H, ArCH), 7.13(d, J= 8Hz, 1H, ArCH), 4.72(s, 2H, OCH₂), 2.32(s, 3H, CH₃), 1.00(t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.68(q, J= 8Hz, 6H, (SiCH₂CH₃)₃). $^{13}C{^{1}H}$ NMR(CDCl₃): δ 138.22(quat-C), 137.18(quat-C), 132.51(CH), 128.10(CH), 127.52(CH), 120.93(quat-C), 64.16(OCH₂), 20.68(CH₃), 6.80(SiCH₂CH₃), 4.49(SiCH₂CH₃). MS (ESI) m/z 315.07 (M+1)⁺. HR/MS: calcd. (C₁₃H₂₄BrOSi)⁺ 315.0781. Found: 315.0774.

> 2-bromo-5-methoxy((triethylsilyloxy)methyl)benzene: Faint yellow liquid. IR (DCM): 2924, 2852, 1595, 1471, 1272, 1296, 1238, 1161, 1051, 1015, 916, 857, 804 cm⁻¹.¹H NMR (CDCl₃): δ 7.37(d, J= 8Hz, 1H, ArCH), 7.19(d, J= 4Hz, 1H, ArCH), 6.67(dd, J= 4Hz, 1H, ArCH), 4.72(s, 2H, OCH₂), 3.80(s, 3H, OCH₃), 1.02(t, J= 2 Hz, 9H, (SiCH₂CH₃)₃), 0.70(q, $J= 2Hz, 6H, (SiCH_2CH_3)_3)$. ¹³C{¹H} NMR(CDCl_3): δ 159.33(quat-C), 141.59(quat-C), 132.71(*C*H), 114.12(*C*H), 113.20(*C*H), 111.14(quat-*C*), 64.34(O*C*H₂), 55.52(O*C*H₃), $6.94(\text{SiCH}_2\text{CH}_3)$, $4.63(\text{SiCH}_2\text{CH}_3)$. MS (ESI) m/z 331.07 (M+1)⁺. HR/MS: calcd. $(C_{14}H_{24}BrO_2Si)^+$ 331.0728. Found: 331.0723.

> 2-chloro-6-methoxy((triethylsilyloxy)methyl)quinoline: Colorless liquid .IR(DCM): 2956, 2877, 1623, 1600, 1498, 1457, 1415, 1336, 1228, 1163, 1105, 1040, 910, 828, 745, 727 cm⁻ ¹.¹H NMR (CDCl₃): δ 8.20(s, 1H, ArCH), 7.89(d, J= 8Hz, 1H, ArCH), 7.33(dd, J= 4Hz, 1H, ArCH), 7.09(d, J= 4Hz, 1H, ArCH), 4.87(s, 2H, OCH₂), 3.93(s, 3H, OCH₃), 1.03(t, J= 8Hz, 9H, $(SiCH_2CH_3)_3$, 0.74(q, J= 8Hz, 6H, $(SiCH_2CH_3)_3$). ¹³C{¹H} NMR(CDCl₃): δ 158.25(quat-C), 145.87(quat-C), 142.70(quat-C), 134.25(CH), 133.38(quat-C), 129.65(CH),

Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013 128.75(quat-C), 122.51(CH), 105.33(CH), 61.56(OCH₂), 55.72(OCH₃), 6.94(SiCH₂CH₃), 4.57(SiCH₂CH₃). MS (ESI) m/z 338.13 (M+1)⁺. HR/MS: calcd $(C_{17}H_{25}CINO_2Si)^+$ 338.1343. Found: 338.1338.

> 2-((triethylsilyloxy)methyl)furan: Colorless liquid. IR (DCM): 2956, 2913, 2877, 1455, 1368, 1239, 1206, 1095, 1033, 1016, 955, 793, 743, 699 cm⁻¹. ¹H NMR (CDCl₃): δ 7.37(d, J= 4Hz, 1H, ArCH), 6.31(dd, J= 4Hz, 1H, ArCH), 6.24(t, J= 4Hz, 1H, ArCH), 4.63(s, 2H, OCH₂), 0.96(t, J= 4Hz, 9H, (SiCH₂CH₃)₃), 0.63(q, J= 4Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): § 154.34 (quat-C), 142.23 (CH), 110.32 (CH), 107.52 (CH), 57.81 (OCH₂), 6.76 (SiCH₂CH₃), 4.52 (SiCH₂CH₃). MS (ESI) m/z 212.12 (M)⁺. HR/MS: calcd $(C_{11}H_{20}O_2Si)^+$ 212.1233. Found: 212.1231.

> 2-((triethylsilyloxy)methyl)thiophene: Faint yellow liquid. IR (DCM): 2955, 2876, 1460, 1414, 1379, 1238, 1225, 1176, 1085, 1075, 1008, 829, 802, 742, 697 cm⁻¹.¹H NMR (CDCl₃): δ 7.27(dd, J= 1Hz, 1H, ArCH), 6.99(overlapped, 2H, ArCH), 4.93(s, 2H, OCH₂), 1.04(t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.71 (q, J= 3Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ145.05(quat-C), 126.49(CH), 124.70(CH), 124.07(CH), 60.35(OCH₂), 6.75(SiCH₂CH₃), 4.53(SiCH₂CH₃). MS (ESI) m/z 229.10 (M+1)⁺. HR/MS: calcd $(C_{11}H_{21}OSSi)^+$ 229.1082. Found 229.1077.

> 1,3-bis((triethylsilyloxy)methyl)benzene⁵: Colorless liquid. IR (DCM): 2955, 2877, 1462, 1456, 1415, 1239, 1154, 1104, 1076, 1016, 824, 741 cm⁻¹. ¹H NMR (CDCl₃): δ 7.36-7.23(m, 3H, ArCH), 4.77(s, 2H, OCH₂), 1.02(t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.69(q, J= 8Hz, 6H, $(SiCH_2CH_3)_3).^{13}C{^1H}$ NMR(CDCl₃): δ141.37(*C*H), 128.20(*C*H), 124.97(quat-C), 124.21(CH), 64.85(OCH₂), 6.87(SiCH₂CH₃), 4.62(SiCH₂CH₃). MS (ESI) m/z 367.24 $(M+1)^+$. HR/MS: calcd $(C_{20}H_{39}O_2Si_2)^+$ 367.2488. Found 367.2488.

> ((triethylsilyloxy)butane⁶: Colorless liquid. IR (DCM): 2956, 2877, 1459, 1415, 1238, 1098, 1015, 839, 780, 739 cm⁻¹. ¹H NMR (CDCl₃): δ 3.60(t, J= 6Hz, 2H, OCH₂), 1.53-1.48(m,J= 4Hz, 2H, CH₂), 1.38-1.26 (m, J= 4Hz, 2H, CH₂), 0.96 (t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.91(t, $J=8Hz, 3H, CH_3$, 0.59(q, $J=8Hz, 6H, (SiCH_2CH_3)_3$). ¹³C{1H} NMR(CDCl_3): δ 62.83(OCH₂), 35.22(CH₃), 19.16(CH₂), 14.06(CH₂), 6.91(SiCH₂CH₃), 4.59(SiCH₂CH₃). MS (ESI) m/z 188.16 (M)⁺. HR/MS: calcd $(C_{10}H_{24}OSi)^+$ 188.1596. Found 188.1600.

> ((triethylsilyloxy)decane⁷: Colorless liquid. IR (DCM): 2954, 2926, 1459, 1415, 1238, 1100, 1015, 797, 740 cm⁻¹. ¹H NMR (CDCl₃): δ 3.59(t, J= 8Hz, 2H, OCH₂), 1.51 (m, J= 5Hz, 2H, CH₂), 1.27(overlapped,14H, CH₂) 0.96(t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.88(t, J= 8Hz, 3H, CH₃), 0.59(q, J= 8Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 63.16 (OCH₂), 33.11 (CH₂), 32.02 (CH₂), 29.82 (CH₂), 29.75 (CH₂), 29.65 (CH₂), 29.50 (CH₂), 26.01 (CH₂), 22.85 (CH_2) , 14.24 (CH_3) , 6.91 $(SiCH_2CH_3)$, 4.60 $(SiCH_2CH_3)$. MS (ESI) m/z 273.26 $(M+1)^+$. HR/MS: calcd $(C_{16}H_{36}OSi)^+$ 273.2615. Found 273.2608.

> 1-phenyl-1-((triethylsilyloxy)methyl)methane⁸: Colorless liquid. IR (DCM): 2955, 2875, 1490, 1435, 1235, 1075, 1014, 931, 865, 723 cm⁻¹. ¹H NMR (CDCl₃): δ 7.27(overlapped, 3H, ArCH), 7.19(d, J= 8Hz, 2H, ArCH), 3.80 (t, J= 8Hz, 2H, OCH₂), 2.84 (t, J= 8Hz, 2H, CH₃), 0.93 (t, J=8Hz, 9H, (SiCH₂CH₃)₃), 0.56 (q, J=8Hz, 6H, (SiCH₂CH₃)₃). ¹³C{¹H} NMR(CDCl₃): δ 139.17(quat-*C*), 129.23(*C*H), 128.39(*C*H), 126.28(*C*H), 64.38(O*CH*₂), 39.83(*C*H₃), 6.87(SiCH₂CH₃), 4.54(SiCH₂CH₃). MS (ESI) m/z 237.16 (M+1)⁺. HR/MS: calcd (C₁₄H₂₅OSi)⁺ 237.1675. Found 237.1669.

1-phenyl-1-((triethylsilyloxy)methyl)ethane⁹: Colorless liquid. IR (DCM): 3029, 2956, 2876, 1493, 1454, 1239, 1087, 1015, 830, 743, 699 cm⁻¹. ¹H NMR (CDCl₃): δ 7.32(t, *J*= 8Hz, 2H, ArC*H*), 7.23(t, *J*= 6Hz, 3H, ArC*H*), 3.68(dq, *J*= 48Hz, 2H, OC*H*₂), 2.94(m, *J*= 5Hz, 1H, C*H*), 1.34(d, *J*= 4Hz, 3H, C*H*₃), 0.96 (t, *J*= 8Hz, 9H, (SiCH₂C*H*₃)₃), 0.59 (q, *J*= 8Hz, 6H, (SiC*H*₂CH₃)₃). ¹³C{1H} NMR(CDCl₃): δ 144.66(quat-*C*), 128.34(*C*H), 127.65(*C*H), 126.37(*C*H), 69.13(OC*H*₂), 42.72(*C*H), 17.70(*C*H₃), 6.86(SiCH₂C*H*₃), 4.54(SiC*H*₂CH₃). MS (ESI) m/z 251.18 (M+1)⁺. HR/MS: calcd (C₁₅H₂₇OSi)⁺ 251.1833. Found 251.1826.

Procedure for Intermolecular Chemoselective Catalytic Hydrosilylation: Benzaldehyde (1 mmol), triethylsilane (1 mmol), diphenyl carbonate (1 mmol), $[Ru(p-cymene)Cl_2]_2$ (1, 1 mol%) and toluene (2 ml) were taken in a closed flask equipped with a magnetic bar and the reaction mixture was heated at 50 °C. Progress of the reaction was monitored by TLC and ¹H NMR. Upon completion of the reaction, the resulting residue was chromatographed over silica-gel using 2% ethyl acetate/hexane mixture as eluent. Similar experiment was also performed using acetophenone (1 mmol) as a competing substrate. Both unreacted acetophenone and diphenylcarbonate were quantitatively recovered.



Procedures for Intramolecular Chemoselective Catalytic Hydrosilylation:

2-((triethylsilyloxy)methyl)phenyl acetate:



2-formylphenyl acetate (1 mmol), triethylsilane (1 mmol), [Ru(p-cymene)Cl₂]₂ (1 mol%) and toluene (2 ml) were taken in a closed flask equipped with a magnetic bar and the reaction mixture was heated at 50 °C. Progress of the reaction was monitored by TLC and ¹H NMR. Upon completion of the reaction, the resulting residue was chromatographed over silica-gel using 2% ethyl acetate/hexane mixture as eluent. Colorless liquid. IR (DCM): 2955, 2877, 1767, 1487, 1456, 1369, 1206, 1175, 1079, 1010, 910, 789, 747 cm⁻¹. ¹H NMR (CDCl₃): δ 7.55 (d, J= 4Hz, 1H, ArCH), 7.30-7.22 (m, J= 4Hz, 2H, ArCH), 7.04 (d, J= 8Hz, 1H, ArCH), 4.68(s, 2H, OCH₂), 2.36(s, 3H, CH₃), 0.99(t, J= 8Hz, 9 H, (SiCH₂CH₃)₃), 0.66(q, J= 8Hz, 6H, $(SiCH_2CH_3)_3)$. ¹³C{1H} NMR(CDCl_3): δ 169.15(quat-C), 147.78(quat-C), 133.24(quat-C), 128.03(CH), 127.98(*C*H), 126.11(*C*H), 121.91(*C*H), 59.90(OCH₂), 20.85(CH₃), $6.81(\text{SiCH}_2\text{CH}_3)$, $4.51(\text{SiCH}_2\text{CH}_3)$. MS (ESI) m/z 281.15 (M)⁺. HR/MS: calcd (C₁₅H₂₅O₃Si)⁺ 281.1573. Found 281.1567.

5-((triethylsilyloxy)methyl)furan-2-yl acetate:

(5-formylfuran-2-yl)methyl acetate (1 mmol), triethylsilane (1 mmol), $[Ru(p-cymene)Cl_2]_2$ (1 mol%) and toluene (2 ml) were taken in a closed flask equipped with a magnetic bar and the reaction mixture was heated at 80 °C. Progress of the reaction was monitored by TLC and ¹H NMR. Upon completion of the reaction, the resulting residue was chromatographed over silica-gel using 2% ethyl acetate/hexane mixture as eluent. Colorless liquid. IR (DCM): 2955, 2877, 1741, 1413, 1377, 1237, 1066, 1017, 801, 742 cm⁻¹. ¹H NMR (CDCl₃): $\delta 6.32$ (d, *J*= 2Hz, 1H, ArC*H*), 6.20(d, *J*= 2Hz, 1H, ArC*H*), 5.01(s, 2H, OC*H*₂), 4.61(s, 2H, OC*H*₂), 2.05(s, 3H, C*H*₃), 0.94(t, *J*= 8Hz, 9H, (SiCH₂C*H*₃)₃), 0.61(q, *J*= 8Hz, 6H, (SiC*H*₂C*H*₃)₃). ¹³C {1H} NMR(CDCl₃): δ 170.71(quat-*C*), 155.20(quat-*C*), 149.08(quat-*C*), 111.47(CH), 108.39(CH), 58.31(OC*H*₂), 57.88(OC*H*₂), 20.95(CH₃), 6.73(SiCH₂CH₃), 4.49(SiCH₂CH₃). MS (ESI) m/z 284.14 (M)⁺. HR/MS: calcd (C₁₄H₂₄O₄Si)⁺ 284.1444. Found 284.1440.

1-phenyl-2-(4-(((triethylsilyl)oxy)methyl)phenoxy)ethanone:



4-(2-oxo-2-phenylethoxy)benzaldehyde (1 mmol), triethylsilane (1 mmol), [Ru(pcymene)Cl₂]₂ (1 mol%) and toluene (2 ml) were taken in a closed flask equipped with a magnetic bar and the reaction mixture was cooled to 0 to 5 °C. Progress of the reaction was monitored by TLC and ¹H NMR. Upon completion of the reaction, the resulting residue was chromatographed over silica-gel using 2% ethyl acetate/hexane mixture as eluent (Corresponding product having hydrosilylation over both functional groups was also isolated in 6% yield). Colorless liquid. IR (DCM): 3061, 2925, 2856, 2360, 2340, 1699, 1598, 1507, 1217, 1177, 1086, 977, 823, 756, 689 cm⁻¹ ¹H NMR (CDCl₃): δ 8.00(d, *J*= 8Hz, 2H, ArC*H*), 7.61(t, J= 8Hz, 1H, ArCH), 7.50(t, J= 8Hz, 2H, ArCH), 7.25(d, J= 8Hz, 2H, ArCH), 6.91(d, J= 8Hz, 2H, ArCH), 5.26(s, 2H, OCH₂), 4.66(s, 2H, OCH₂), 0.96(t, J= 8Hz, 9 H, $(silylCH_2CH_3)_3), 0.63(q, J = 8Hz, 6H, (silylCH_2CH_3)_3).$ ¹³C{1H} NMR(CDCl_3): δ 194.80(quat-C), 157.35(quat-C)5, 134.78(quat-C), 134.71(quat-C), 133.98(CH), 128.96(CH), 128.31(CH), 127.93(CH), 114.77(CH), 71.16(OCH₂), 64.39(OCH₂), 6.91(silyl CH₃), 4.63(silyl CH₂). MS (ESI) m/z 357.18. HR/MS: calcd (C₂₁H₂₉O₃Si)⁺ 357.1886. Found 357.1890.

1-(1H-indol-1-yl)(3-(triethylsilyloxy)methyl)ethanone:



1-acetyl-3-formyl indole (1 mmol) (Scheme 1 c), triethylsilane (1 mmol), $[Ru(p-cymene)Cl_2]_2$ (1 mol%) and toluene (2 ml) were taken in a closed flask equipped with a magnetic bar and the reaction mixture was heated at 80 °C. Progress of the reaction was monitored by TLC and ¹H NMR. Upon completion of the reaction, the resulting residue was chromatographed over silica-gel using 4% ethyl acetate/hexane mixture as eluent. Faint

Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013 yellow liquid. IR (DCM):2955, 2876, 1711, 1607, 1451, 1385, 1329, 1220, 1240, 1124, 1090, 1061, 1016, 934, 746 cm⁻¹. ¹H NMR (CDCl₃): δ 8.42(d, *J*= 8Hz, 1H, ArCH), 7.54(d, *J*= 8Hz, 1H ArCH), 7.35(t, J= 8Hz, 2H ArCH), 7.27(t, J= 8Hz, 1H ArCH), 4.88(s, 2H, OCH₂), 2.61(s, 3H, CH₃), 1.00(t, J= 8Hz, 9H, (SiCH₂CH₃)₃), 0.69(q, J= 8Hz, 6H, (SiCH₂CH₃)₃). $^{13}C{^{1}H}$ NMR(CDCl₃): δ 168.67(quat-C), 136.34(quat-C), 129.22(quat-C), 125.46(CH-C), 123.62(*C*H). 123.13(CH), 122.33(CH), 119.29(CH), 116.84(quat-C), 57.71(OCH₂), 24.08(*C*H₃), 6.95 (SiCH₂*C*H₃), 4.59 (Si*C*H₂CH₃). MS (ESI) m/z 304.17 (M+1)⁺. HR/MS: calcd $(C_{17}H_{25}NO_2Si)^+$ 304.1735. Found 304.1727.

In situ NMR studies:



Figure S1. NMR monitoring of the reaction progress: benzyl triethylsilyl ether formation vs. time; benzene-d6 solution of 1 and reactants (mesitylene is added as a reference) was heated at 50 °C



Figure S2: NMR study of the reaction progress shows formation of hydride peaks at different time interval

Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013 Synthesis of Complex [{ $(\eta^6-p-cymene)Ru$ }_2(μ -H- μ -Cl)(Cl)₂](2): To benzene-d6 (1 ml) solution of [Ru(p-cymene)Cl₂]₂ (0.05 mmol) in a vial, triethylsilane (0.2 mmol) was added dropwise and the resulting mixture allowed to stir at room temperature for 30 min. The volume of dark red solution was reduced to one third and slow addition of cold pentane (2 ml) provided dark red precipitate. The solution was decanted and the precipitate was washed with a mixture of pentane and toluene. The resulted dark red complex was dried under vacuum for overnight (28 mg, quantitative yields). ¹H NMR (Benzene-d₆): δ 5.44 (d, J= 8Hz, 2H, ArCH), 5.20 (d, J= 4Hz, 2H, ArCH), 5.14 (d, J= 8Hz, 2H, ArCH), 4.74 (d, J= 4Hz, 2H, ArCH), 2.86 (m, J= 8 Hz, 2H, ^{*i*}PrCH), 1.95 (s, 6H, CH₃), 1.27 (d, J= 8 Hz, 6H, ^{*i*}PrCH₃), 1.18 (d, J=8 Hz, 6H, ^{*i*}PrCH₃), -10.18(s, 1H, RuH). ¹³C{1H} NMR(Benzene-d₆): δ 102.60 (quat-C), 97.64, (quat-C), 86.69 (ArCH), 83.34 (ArCH), 81.75 (ArCH), 81.50 (ArCH), 32.00 (^{*i*}PrCH), 24.05 (CH₃), 22.70 (CH₃), 19.92 (CH₃).

Synthesis of Complex $[(\eta^6-p-cymene)Ru(H)_2(SiEt_3)_2](3)$:



Scheme S1: Synthesis of Intermediate Complex 3 from 1 or 2.

To benzene-d6 (1 ml) solution of either $[Ru(p-cymene)Cl_2]_2(1)$ or $[{(\eta^6-p-cymene)Ru}_2(\mu H-\mu-Cl(Cl)_2$ (0.05 mmol), triethylsilane (0.4 mmol) was added dropwise and the resulting mixture in a sealed vial was heated to 50 °C for 48 h. Then the reaction mixture was cooled to room temperature and solvents are evaporated under reduced pressure. The resulted residue was dissolved in hexane and filtered through celite. The filtrate was dried under high vaccum to obtain a colorless solid (32 mg, 80% yield). IR(C₆D₆): 2016 cm⁻¹. ¹H NMR (Benzene-d₆): δ 5.19(d, J=8 Hz, 2H, ArCH), 5.14(d, J=8 Hz, 2H, ArCH), 2.27(m, J=8 Hz, 1H, ⁱPrCH), 1.84(s, 3H, CH₃), 1.16(t, J=8 Hz, 18H, SiCH₂CH₃), 1.02(d, J=4 Hz, 6H, ⁱPrCH₃), $0.84(q, J=8 Hz, 12H, SiCH_2CH_3)$, -13.52 (s, 2H, RuH). ¹³C{1H} NMR(Benzene-d_6): δ 120.22(quat-C), 107.32(quat-C), 94.36(ArCH), 91.64(ArCH), 32.68(CH₃), 24.68(CH₃), 20.56(^{*i*}Pr*C*H), 14.50(silyl *C*H₃), 9.75(silyl *C*H₂).

Determination of the Molecular Structures of 2 and 3 in the Solid State by X-ray Single Crystal Diffraction: Single crystals of complexes 2 and 3 suitable for X-ray analysis was obtained from solutions of toluene-pentane and hexane, respectively. Crystals suited for single crystal x-ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Bruker SMART D8 goniometer equipped with an APEX CCD detector and with an Incoatec microsource (Mo-K α radiation, $\lambda = 0.71073$ Å, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT+¹⁰ and corrected for absorption with SADABS.¹¹ The structures were solved by direct methods and refined on F^2 with SHELXL-97.¹²

Crystal Data of Complex [{(η^6 -*p*-cymene)RuCl}₂(μ -H- μ -Cl)](2): C₂₀H₂₉Cl₃Ru₂, crystal dimensions: 0.24 x 0.15 x 0.10, *M*=577.92, Orthorhombic with space group Pbca, *a*=13.6640(6), *b*=15.9211(7), *c*= 19.2494(9), $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, *V*=4187.6(3)Å³, *Z*=8, $2\theta_{max} = 61.26$, $\rho_{calcd} = 1.833$ Mg/m³,T= 296(2)K, μ -(Mo_{ko})= 0.71073, min/max transmission factors= 0.6153/0.7461, 72584 Reflections collected, 6414 unique (*R*1= 0.0195), *WR2*=0.0447(all data). Residual electron density max/min=0.626/-0.512 e.Å⁻³. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number CCDC932852.

Crystal Data of Complex $[(\eta^6-p-cymene)Ru(H)_2(SiEt_3)_2](3)$: C₂₂H₄₆Si₂Ru₁, crystal dimensions: 0.12 x 0.08 x 0.05, M=467.84,Monoclinic with space group P21/C, a=16.4631 (15), b=8.7200(8), c=17.7452(16), $\alpha = 90^{\circ}$, $\beta = 102.003^{\circ}(4)$, $\gamma = 90^{\circ}$, $V=2491.8(4)Å^3$, Z=4, $2\theta_{max}=61.22$, $\rho_{calcd}=1.247$ Mg/m³, T= 200(2) K, μ - (Mo_{ko}) = 0.71073, min/max transmission factors= 0.5565/0.7461, 44034 Reflections collected, 7598 unique (R1= 0.0299), WR2 =0.0745 (all data). Residual electron density max/min=1.586/-1.009 e.Å⁻³. The structure has been deposited at the CCDC data center and can be retrieved using the deposit number CCDC971350.

NMR Spectra of Silyl ethers and intermediate complexes:

¹H NMR spectrum of ((Triethylsilyloxy)methyl)benzene:



¹³C NMR spectrum of ((Triethylsilyloxy)methyl)benzene:







¹³C NMR spectrum of 4-methyl((triethylsilyloxy)methyl)benzene:









¹³C NMR spectrum of 3,5-dimethoxy((triethylsilyloxy)methyl)benzene:







¹³C NMR spectrum of 9-((triethylsilyloxy)methyl)anthracene:







¹³C NMR spectrum of 3-bromo((triethylsilyloxy)methyl)benzene:







¹³C NMR spectrum of 4-bromo((triethylsilyloxy)methyl)benzene:



¹H NMR spectrum of 4-cyano((triethylsilyloxy)methyl)benzene:



¹³C NMR spectrum of 4-cyano((triethylsilyloxy)methyl)benzene:



¹H NMR spectrum of 4-nitro((triethylsilyloxy)methyl)benzene:



¹³C NMR spectrum of 4-nitro((triethylsilyloxy)methyl)benzene:







¹³C NMR spectrum of 2-bromo-4-methyl((triethylsilyloxy)methyl)benzene:







¹³C NMR spectrum of 2-bromo-5-methoxy((triethylsilyloxy)methyl)benzene:





¹H NMR spectrum of 2-chloro-6-methoxy((triethylsilyloxy)methyl)quinoline:

¹³C NMR spectrum of 2-chloro-6-methoxy((triethylsilyloxy)methyl)quinoline:







¹³C NMR spectrum of 2-((triethylsilyloxy)methyl)furan:



¹H NMR spectrum of 2-((triethylsilyloxy)methyl)thiophene:



¹³C NMR spectrum of 2-((triethylsilyloxy)methyl)thiophene:



¹H NMR spectrum of 1,3-bis((triethylsilyloxy)methyl)benzene:



¹³C NMR spectrum of 1,3-bis((triethylsilyloxy)methyl)benzene:







¹³C NMR spectrum of ((triethylsilyloxy)butane:



¹H NMR spectrum of ((triethylsilyloxy)decane:



¹³C NMR spectrum of ((triethylsilyloxy)decane:



Electronic Supplementary Material (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2013 ¹H NMR spectrum of 1-phenyl-1-((triethylsilyloxy)methyl)ethane:



¹³C NMR spectrum of 1-phenyl-1-((triethylsilyloxy)methyl)methane:





¹H NMR spectrum of 1-phenyl-1-((triethylsilyloxy)methyl)ethane:

¹³C NMR spectrum of 1-phenyl-1-((triethylsilyloxy)methyl)ethane:







¹³C NMR spectrum of 2-((triethylsilyloxy)methyl)phenyl acetate:







¹³C NMR spectrum of 5-((triethylsilyloxy)methyl)furan-2-yl acetate:







¹³C NMR spectrum of 1-(1H-indol-1-yl)(3-(triethylsilyloxy)methyl)ethanone:





¹³C NMR spectrum of 1-phenyl-2-(4-(((triethylsilyl)oxy)methyl)phenoxy)ethanone:





¹³C NMR spectrum of [{(η^6 -*p*-cymene)RuCl}₂(μ -H- μ -Cl)] **2**:





Expanded ¹H NMR spectrum of $[(\eta^6-p-cymene)Ru(H)_2(SiEt_3)_2]$ 3:







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