Supporting Information for the manuscript

Chemo- and regioselective catalytic reduction of *N*-heterocycles by silane

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Experimental details. All manipulations were carried out using conventional high-vacuum or nitrogen-line Schlenk techniques. NMR spectra were recorded on a Bruker DPX-300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz) and/or Bruker DPX-600 (^{1}H, 600 MHz; ^{13}C, 150.8 MHz) spectrometers at 298 K. All chemicals were purchased from Sigma-Aldrich and Alfa Aesar apart from $HSiMe_2Ph$ which was purchased from Gelest. These reagents were used without further purification. Acetone-d_6 and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories. CD_2Cl_2 was dried over CaH_2 and acetone-d_6 was dried over molecular sieves (3Å). Other solvents were dried by distillation from appropriate drying agents or using Grubbs-type solvent purification system. Complex $[Cp(iPr_3P)Ru(CH_3CN)_2]An$ (**1**) (An = PF_6^- or $B(C_6F_5)_4^-$) was prepared according to literature procedures.[1]

Catalytic hydrosilylation

3-Chloropyridine. The reaction was performed in CH_2Cl_2 (0.6 mL) with 3-chloropyridine (12.4 μL, 0.13 mmol), $HSiMe_2Ph$ (30 μL, 0.19 mmol) and **1-BAF** (0.006 g, 5% mol). Full conversion of the starting chloropyridine was observed after 15 min at ambient temperature to give *N*-silylated 1,4-dihydro-3-chloropyridine.

^{1}H NMR (CH_2Cl_2, D_2O insert): δ 7.50-7.45 (m, 2, Ph), 7.37-7.28 (m, 3, Ph), 6.05 (s, 1, N-C*H*), 5.83 (d, *J*(H-H) = 7.9 Hz, 1, N-C*H*), 4.47 (m, 1, NCH=C*H*), 3.12 (s, 2, CH_2), 0.40 (s, 6,

Si*Me*). ^{1}H-^{13}C HSQC (CH_2Cl_2, D_2O insert, selected data): δ 127.4 (N*C*H=CH), 125.7 (N*C*H=CCl), 99.1 (NCH=*C*H), 30.2 (*C*H_2), -3.3 (Si*Me*). ^{1}H-^{29}Si HSQC (CH_2Cl_2, D_2O insert): δ 3.5

3,5–Lutidine. The reaction was performed in CH_2Cl_2 (0.6 mL) with 3,5–lutidine (15.0 μL, 0.13 mmol), $HSiMe_2Ph$ (30 μL, 0.19 mmol) and **1-BAF** (0.006 g, 5% mol). There was 82% conversion of the starting pyridine after 3 h at ambient temperature.

N-(SiMe$_2$Ph)-1,4-dihydro-3,5-lutidine: ^{1}H NMR (CH_2Cl_2, D_2O insert): δ 7.50-7.45 (m, 2, Ph), 7.37-7.28 (m, 3, Ph), 5.72 (s, 2, NC*H*=C(CH_3)), 2.65 (s, 2, CH_2), 1.46 (s, 6, NCH=C(CH_3)), 0.38 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC (CH_2Cl_2, D_2O insert, selected data): δ 122.7 (N*C*H=C(CH_3), 33.7 (CH_2), 19.9 (NCH=C(*C*H_3)), -3.3 (Si*Me*). ^{1}H-^{29}Si HSQC (CH_2Cl_2, D_2O insert): δ 2.5.

2,6-Lutidine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 2,6-lutidine (5.4 μL, 0.05 mmol) in CD_2Cl_2 was added [Cp*(phen)Ru(CH_3CN)]PF_6 (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

2,4-Lutidine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 2,4-lutidine (5.4 μL, 0.05 mmol) in CD_2Cl_2 was added [Cp*(phen)Ru(CH_3CN)]PF_6 (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

2-Bromopyridine. To a solution of 2-bromopyridine (12.4 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added **1-BAF** (0.006 g, 5% mol). After 3 h at ambient temperature there was 47% conversion of 2-bromopyridine into a mixture of pyridine and *N*-silyl 1,4-dihydropyridine (1:4).

2-Ethylpyridine. To a solution of 2-ethylpyridine (15 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL) was added **1-BAF** (0.006 g, 5% mol). There was no

hydrosilylation of 2-ethylpyridine after 3 h at ambient temperature, only the hydrosilyation of the acetonitrile ligands and slow chlorination of silane by CH_2Cl_2 was observed.

Quinoline.

Method 1. To a mixture of $HSiMe_2Ph$ (338.8.0 μL, 2.20 mmol) and quinoline (260.0 μL, 2.00 mmol) was added $[Cp^*Ru(Phen)(CH_3CN)]PF_6$ (8.4 mg, 0.014 mmol). The reaction was periodically monitored by NMR spectroscopy. 80% conversion was achieved after 5 h at 70ºC. A mixture of *N*-($SiMe_2Ph$)-1,2-dihydroquinoline (3%) and *N*-($SiMe_2Ph$)-1,4-dihydroquinoline (97%) was obtained. Full conversion was achieved overnight. Isolated yield 0.52 g (98 %).

Method 2 (reaction without solvent). To a mixture of quinoline (0.20 mL, 1.7 mmol) and $HSiMe_2Ph$ (0.26 mL, 1.7 mmol) was added **1-BAF** (0.009 g, 0.5% mol). There was 70% conversion of quinoline after 2 h at ambient temperature with formation of a mixture of *N*-($SiMe_2Ph$)-1,2-dihydroquinoline (19%) and *N*-($SiMe_2Ph$)-1,4-dihydroquinoline (81%). The products decomposed slowly (>20 h) with the formation of a complex mixture.

Method 3. Complex $[Cp(iPr_3P)Ru(CH_3CN)_2]BAF$ (0.007 g, 5% mol) was added to a solution of quinoline (15.4 μL, 0.13 mmol) and $HSiMe_2Ph$ (30 μL, 0.19 mmol) in CH_2Cl_2 (0.6 mL). After 30 min at ambient temperature 50 % of the quinoline was converted into a mixture of *N*-($SiMe_2Ph$)-1,2-dihydroquinoline (22%) and *N*-($SiMe_2Ph$)-1,4-dihydroquinoline (78%). The mixture of hydrosilylated quinolines slowly decomposed (after 24 h) with the formation of a complex mixture of products.

Method 4 (reaction with $DSiMe_2Ph$). To a mixture of $DSiMe_2Ph$ (174.3 μL, 1.27 mmol) and quinoline (150.0 μL, 1.27 mmol) was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (5.5 mg, 0.0089 mmol). The reaction was periodically monitored by NMR spectroscopy. After 5 h at 70ºC, 75% of quinoline was converted into *N*-($SiMe_2Ph$)-1,4-dihydroquinoline. The identity of the product was confirmed by ^2H and ^1H-^{13}C HSQC NMR.

N-(SiMe$_2$Ph)-1,4-dihydroquinoline: ^{1}H NMR ($CDCl_3$, selected data): δ 6.29 (d, *J*(H-H) = 7.8 Hz, 1, NC*H*CHCH$_2$), 4.77 (dt, *J*(H-H) = 7.8 Hz and 3.4 Hz, 1, NCHC*H*CH$_2$), 3.51 (d, *J*(H-H) = 3.4 Hz, 2, NCHCHC*H*$_2$), 0.60 (s, 6, Si*Me*). ^{1}H NMR (CH_2Cl_2, D_2O insert, selected data): δ 7.50-7.38 and 7.28-7.18 (m, Ph), 6.84-6.51 (m, 3, NC*H*C*H*C*H*), 6.18 (dt, *J*(H-H) = 7.8 Hz and 1.3 Hz, 1, NC*H*CHCH$_2$), 4.64 (dt, *J*(H-H) = 7.8 Hz and 3.4 Hz, 1, NCHC*H*CH$_2$), 3.35 (d, *J*(H-H) = 3.4 Hz, 2, NCHCHC*H*$_2$), 0.46 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC NMR (CH_2Cl_2, D_2O insert, selected data): δ 130.3 (N*C*HCHCH$_2$), 99.5 (NCH*C*HCH$_2$), 26.3 (NCHCH*C*H$_2$), -1.13 (Si*Me*). ^{1}H-^{13}C HSQC ($CDCl_3$): -0.9 (Si*Me*$_2$Ph), 27.0 (*C*H$_2$), 99.8, 117.6, 121.2, 125.6, 129.2, 130.4 (quin), 127.9, 129.0, 133.1 (SiMe$_2$*Ph*). ^{1}H-^{29}Si HSQC NMR (CH_2Cl_2, D_2O insert): δ 2.5.

Triazine.

Method 1. To a solution of triazine (0.011 g, 0.13 mmol) and $HSiMe_2Ph$ (20 μL, 0.13 mmol) in PhCl (0.6 mL) was added **1-BAF** (0.007 g, 5% mol). A mixture of triazine, mono- and bis(hydrosilylated) triazines was obtained after 30 min at ambient temperature. Addition of a second equivalent of silane resulted in 98% conversion of triazine with formation of the bis(hydrosilylated) product after 3 h at ambient temperature.

Method 2. To a solution of $HSiMe_2Ph$ (15.4 μL, 0.1 mmol) and triazine (8.1 mg, 0.1 mmol) in CD_2Cl_2 was added [Cp*Ru(Phen)(CH_3CN)]PF_6 (3.0 mg, 0.005 mmol). The reaction was periodically monitored by NMR spectroscopy. 90% conversion was achieved after 1.5 h at 70ºC to give monohydrosilylated triazine.

N,N'-(SiMe$_2$Ph)-1,2,3,4-tetrahydrotriazine: ^{1}H NMR (C_6D_6): δ 7.54-7.50 (m, 2, Ph), 7.47 (s, 1, N=C*H*), 7.35-7.28 (m, 2, Ph), 7.26-7.18 (m, 6, Ph), 4.44 (s, 4, C*H*$_2$), 0.24 (s, 6, Si*Me*), 0.09 (s, 6, Si*Me*). ^{13}C NMR (C_6D_6, selected data): δ 147.9 (*C*=N), 59.5 (*C*H$_2$), -2.0 (Si*Me*), -3.3 (Si*Me*). ^{1}H-^{29}Si HSQC (C_6D_6): δ 1.5 and -1.0.

N-(SiMe$_2$Ph)-1,4-tetrahydrotriazine: ^{1}H NMR (CD_2Cl_2): δ 0.62 (s, 6, Si*Me*$_2$Ph), 4.93 (s, 2,

C*H*$_2$), 7.09 (s, 2, C*H*), 7.46-7.49 (m, 3, SiMe$_2$*Ph*), 7.61-7.62 (m, 2, SiMe$_2$*Ph*), ^{1}H-^{13}C HSQC (CD_2Cl_2): δ -2.83 (Si*Me*$_2$Ph), 62.4 (*C*H$_2$), 145.4 (*C*H), 128.4, 133.5, 134.0 (SiMe$_2$*Ph*).

2-Cyano-1,10-Phenanthroline. To a solution of $HSiMe_2Ph$ (3.9 μL, 0.025 mmol) and 2-cyano-1,10-phenanthroline (5.1 mg, 0.025 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (0.8 mg, 0.0013 mmol). The reaction was periodically monitored by NMR spectroscopy. A very little conversion was achieved at 70ºC and a mixture of products was obtained.

Acridine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and acridine (8.9 mg, 0.05 mmol) in CD_2Cl_2 was added $[Cp^*Ru(Phen)(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after 24 h at 70ºC to give hydrosilylated acridine.

N-(SiMe$_2$Ph)-9,10-tetrahydroacridine: ^{1}H NMR (CD_2Cl_2): δ 0.73 (s, 6, Si*Me*$_2$Ph), 4.07 (s, 2, C*H*$_2$), 6.72-6.73 (d, 2, acridine), 6.87-6.89 (t, 2, acridine), 7.10-7.14 (m, 4, acridine), 7.45-7.49 (m, 3, SiMe$_2$*Ph*), 7.67-7.69 (m, 2, SiMe$_2$*Ph*), ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 1.73 (Si*Me*$_2$Ph), 31.4 (*C*H$_2$), 113.2, 120.5, 126.9,128.5 (acridine), 128.1, 129.7, 133.1 (SiMe$_2$*Ph*).

Pyrazine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and pyrazine (4.0 mg, 0.05 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

Isoquinoline. To a mixture of $HSiMe_2Ph$ (200.2 μL, 1.30 mmol) and isoquinoline (130.0 μL, 1.00 mmol) was added $[Cp^*Ru(Phen)(CH_3CN)]PF_6$ (30.0 mg, 0.05 mmol). The reaction was periodically monitored by NMR spectroscopy. 90% conversion was achieved after 9 days at 70ºC.

N-(SiMe$_2$Ph)-1,2-isoquinoline: ^{1}H NMR ($CDCl_3$): δ 7.56-7.59 (m, 2, SiMe$_2$*Ph*), 7.37-7.43 (m, 3, SiMe$_2$*Ph*), 7.09-7.12 (m, 1, quin), 6.98-7.04 (td, 1, quin), 6.84-6.90 (t, 2, quin), 6.38-6.41 (d, 1, quin), 5.53-5.56 (d, 1, quin), 4.28 (s, 2, C*H*$_2$), 0.50 (s, 6, Si*Me*$_2$Ph), ^{1}H-^{13}C HSQC ($CDCl_3$): -2.5 (Si*Me*$_2$Ph), 47.3 (*C*H$_2$), 102.3, 125.3, 125.4, 127.6, 136.3 (quin), 127.9, 129.3, 133.5 (SiMe$_2$*Ph*). Isolated yield 0.25 g (95 %).

7-Chloroquinaldine. To a solution of $HSiMe_2Ph$ (3.9 μL, 0.025 mmol) and 7-chloroquinaldine (4.5 mg, 0.025 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (0.8 mg, 0.0013 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

2-Phenylquinoline. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 2-phenylquinoline (10.3 mg, 0.05 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

7-Methyl-8-nitroquinoline. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 7-Methyl-8-nitroquinoline (9.4 mg, 0.05 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

2-Ethylpyridine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 2-ethylpyridine (5.4 μL, 0.05 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

2-Methylquinoxaline. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 2-methylquinoxaline (7.2 μL, 0.05 mmol) in CD_2Cl_2 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. No reaction was observed at 70ºC.

Hydrosilylation of pyridine in the presence of acetone

Method 1. To a solution of pyridine (0.7 mL, 8.6 mmol) and $HSiMe_2Ph$ (1.5 mL, 9.8 mmol) in acetone (3 mL) was added **1-PF_6** (0.025 g, 0.5% mol). There was 93% conversion of pyridine after 5 min at ambient temperature with the formation of *N*-(CMe_2OSiMe_2Ph)-1,4-dihydropyridine (less than 5% mol of $Me_2CHOSiMe_2Ph$ was also observed in the reaction mixture). Extraction of the product from the reaction mixture with hexane or benzene resulted

in dehydroamination of the product with the formation of 1,4-(C_5H_6NH) and CH_2=C(OSiMe_2Ph)CH_3.

Method 2. To the solution of pyridine (10.0 μL, 0.12 mmol), HSiMe_2Ph (20 μL, 0.13 mmol) and acetone (8.8 μL, 0.12 mmol) in CD_2Cl_2 (0.6 mL) was added **1-PF_6** (0.003 g, 5% mol). After 4 h at ambient temperature 84% of the pyridine was converted into a mixture of silylated 1,4-dihydropyridine and the product of coupling with acetone (1.6:1). After 2 days at ambient temperature the ratio of products changed to 2.3:1 with the formation of free pyridine and ClSiMe_2Ph.

N-(CMe_2OSiMe_2Ph)-1,4-dihydropyridine: ^{1}H NMR (C_6D_6): δ 7.65-7.57 (m, 2, Ph), 7.27-7.17 (m, 3, Ph), 6.08 (d, *J*(H-H) = 8.0 Hz, 2, NC*H*=CHCH_2), 4.45 (dt, *J*(H-H) = 8.0 Hz and 3.3 Hz, 2, NCH=C*H*CH_2), 3.00 (m, 2, NCH=CHC*H_2*), 1.23 (s, 6, OC(C*H_3*)$_2$), 0.42 (s, 6, Si*Me*). ^{1}H NMR (acetone-d_6): δ 7.70-7.60 (m, 2, Ph), 7.40-7.30 (m, 3, Ph), 6.16 (dt, *J*(H-H) = 8.8 Hz and 1.3 Hz, 2, NC*H*=CHCH_2), 4.36 (dt, *J*(H-H) = 8.8 Hz and 3.3 Hz, 2, NCH=C*H*CH_2), 2.87 (m, 2, NCH=CHC*H_2*), 0.43 (s, 6, Si*Me*). ^{1}H-^{13}C HSQC (C_6D_6, selected data): δ 126.9 (N*C*H=CHCH_2), 98.6 (NCH=*C*HCH_2), 29.5 (OC(*C*H_3)$_2$), 0.7 (Si*Me*). ^{1}H-^{29}Si HSQC (acetone-d_6): δ -1.3.

Hydrosilylation of pyridine in the presence of benzaldehyde. To a solution of pyridine (20 μL, 0.25 mmol), HSiMe_2Ph (45 μL, 0.29 mmol) and PhCHO (25 μL, 0.25 mmol) in CD_2Cl_2 (0.6 mL) was added [CpRu(PPr^i_3)(CH_3CN)$_2$]PF_6 (0.004 g, 3% mol). There was 95 % conversion of benzaldehyde with the formation of *N*-(CHPhOSiMe_2Ph)-1,4-dihydripyridine.

N-(CHPhOSiMe_2Ph)-1,4-dihydripyridine: ^{1}H NMR (CD_2Cl_2): δ 7.72 (m, 2, Ph), 7.53-7.32 (m, 8, Ph), 5.78 (d, *J*(H-H) = 8.1 Hz, 2, NC*H*CH), 5.60 (s, 1, OC*H*), 4.44 (dt, *J*(H-H) = 8.1 Hz and 3.2 Hz, 2, NCHC*H*), 2.97 (m, 2, C*H_2*), 0.59 (s, 3, Si*Me*), 0.54 (s, 3, Si*Me*). ^{13}C NMR (CD_2Cl_2): δ 140.9 (Ph), 137.2 (Ph), 133.7 (Ph), 129.8 (N*C*HCH), 128.8 (Ph), 128.1 (Ph),

127.9 (Ph), 127.8 (Ph), 126.4 (Ph), 99.0 (NCH*C*H), 86.0 (O*C*H), 23.0 (*C*H_2), -1.3 (Si*Me*), -1.6 (Si*Me*). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ 7.2.

Hydrosilylation of pyridine in the presence of cinnamaldehyde. To a solution of pyridine (20 μL, 0.25 mmol), $HSiMe_2Ph$ (45 μL, 0.29 mmol) and PhCH=CHCHO (31 μL, 0.25 mmol) in CD_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]PF_6$ (0.004 g, 3% mol). Full conversion of cinnamaldehyde was observed after 30 min at ambient temperature with the formation of *N*-(CH(CH=CHPh)OSiMe_2Ph)-1,4-dihydropyridine.

N-(CH(CH=CHPh)OSiMe$_2$Ph)-1,4-dihydropyridine: ^{1}H NMR (CD_2Cl_2): δ 7.73 (m, 2, Ph), 7.52-7.28 (m, 8, Ph), 6.77 (dd, *J*(H-H) = 15.9 and 1.5 Hz, 1, =C*H*Ph), 6.25 (dd, *J*(H-H) = 15.9 and 4.3 Hz, 1, =C*H*CH), 5.92 (d, *J*(H-H) = 8.3 Hz, 2, NC*H*=CHCH_2), 5.14 (dd, *J*(H-H) = 1.5 and 4.3 Hz, 1, =CHC*H*), 4.50 (dt, *J*(H-H) = 8.3 and 3.1 Hz, 2, NCH=C*H*CH_2), 3.00 (m, 2, NCH=CHCH_2), 0.59 (s, 3, Si*Me*), 0.55 (s, 3, Si*Me*). ^{1}H-^{13}C HSQC (CD_2Cl_2): δ 128.8 (=*C*HPh), 128.6 (N*C*H=CHCH_2), 128.5 (=*C*HCH), 98.8 (NCH=*C*HCH_2), 84.6 (=CH*C*H), 22.6 (NCH=CH*C*H_2), -1.3 (Si*Me*), -1.6 (Si*Me*). ^{1}H-^{29}Si HSQC (CD_2Cl_2): δ 7.0.

The reaction of *N*-(SiMe$_2$Ph)-1,4-dihydropyridine with benzaldehyde. To a solution of *N*-(SiMe$_2$Ph)-1,4-dihydropyridine (20 μL, 0.09 mmol) and PhCHO (9.5 μL, 0.09 mmol) in CH_2Cl_2 (0.6 mL) was added $[CpRu(PPr^i_3)(CH_3CN)_2]$BAF (0.005 g, 5% mol). After 24 h at ambient temperature 100% of the silylated 1,4-dihydropyridine was converted into a mixture of products, containing free pyridine and *N*-(CHPhOSiMe_2Ph)-1,4-dihydripyridine (1:2.1).

The reaction of *N*-(SiMe$_2$Ph)-1,4-dihydropyridine with 4-Br-(C$_6$H$_4$)C(O)Cl. To a solution of *N*-(SiMe$_2$Ph)-1,4-dihydropyridine (30 μL, 0.14 mmol) in C_6D_6 (0.6 mL) was added 4-Br-(C_6H_4)C(O)Cl (0.030 g, 0.14 mmol). The resulting yellow solution was heated at 80ºC for 1 h, which resulted in the formation of the corresponding amide and $ClSiMe_2Ph$.

4-Br-(C$_6$H$_4$)C(O)(NC$_5$H$_6$): ^{1}H NMR (C_6D_6, 70ºC): δ 7.12 (d, *J*(H-H) = 4.2 Hz, 2, C_6H_4), 6.95

(d, *J*(H-H) = 4.2 Hz, 2, C_6H_4), 6.73 (bs, 2, NC_5H_6), 4.59 (bs, 2, NC_5H_6), 2.55 (bs, 2, NC_5H_6).

^1H-^{13}C HSQC (C_6D_6, 70ºC): δ 131.5 (C_6H_4), 129.4 (C_6H_4), 106.6 (*m*-NC_5H_6), 23.1 (*p*-NC_5H_6).

Catalytic hydrogenation by $HSiMe_2Ph$/EtOH

Acridine. To a solution of $HSiMe_2Ph$ (9.24 μL, 0.6 mmol), acridine (8.9 mg, 0.05 mmol) and EtOH (6.9 μL, 0.15 mmol) in Acetone-d_6 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy. Full conversion was achieved after 10 m at room temperature. 1,8-dihydroacridine and $CH_3CH_2OSiMe_2Ph$ were obtained.
1,8-dihydroacridine: ^1H NMR (CD_2Cl_2): δ 7.86 (s, br, 1, NH), 7.08-7.09 (d, 2, acridine), 7.03-7.05 (t, 2, acridine), 6.77-6.80 (m, 4, acridine), 4.02 (s, 2, C*H*$_2$), ^1H-^{13}C HSQC (CD_2Cl_2): δ 31.4 (CH_2), 113.6, 120.1, 126.9,128.5 (acridine).

Pyrazine. To a solution of $HSiMe_2Ph$ (15.4 μL, 0.1 mmol), pyrazine (8.0 mg, 0.1 mmol) and EtOH (13.8 μL, 0.3 mmol) in Acetone-d_6 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (3.0 mg, 0.005 mmol). The reaction was periodically monitored by NMR spectroscopy at room temperature. Cp^* (phen) Ru(pyrazine) complex was obtained.

2,6-Lutidine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol), 2,6-lutidine (5.4 μL, 0.05 mmol) and EtOH (6.9 μL, 0.15 mmol) in Acetone-d_6 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy at room temperature. Formation of $EtOSiMe_2Ph$ and H_2 was observed.

2,4-Lutidine. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol), 2,4-lutidine (5.4 μL, 0.05 mmol) and EtOH (6.9 μL, 0.15 mmol) in Acetone-d_6 was added $[Cp^*(phen)Ru(CH_3CN)]PF_6$ (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy at room temperature. Formation of $EtOSiMe_2Ph$ and H_2 was observed.

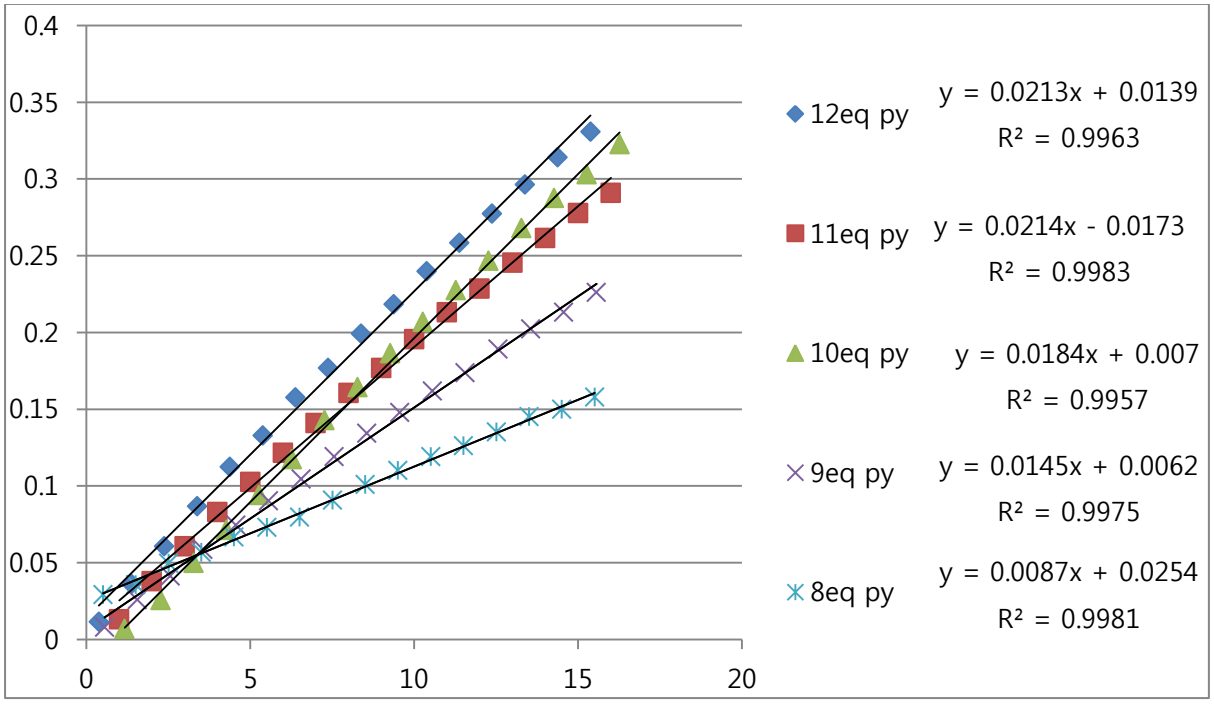
2-Phenylquinoline. To a solution of $HSiMe_2Ph$ (7.7 μL, 0.05 mmol) and 2-phenylquinoline (10.3 mg, 0.05 mmol) and EtOH (6.9 μL, 0.15 mmol) in Acetone-d_6 was added

[Cp^*(phen)Ru(CH_3CN)]PF_6 (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy at room temperature. Formation of $EtOSiMe_2Ph$ and H_2 was observed.

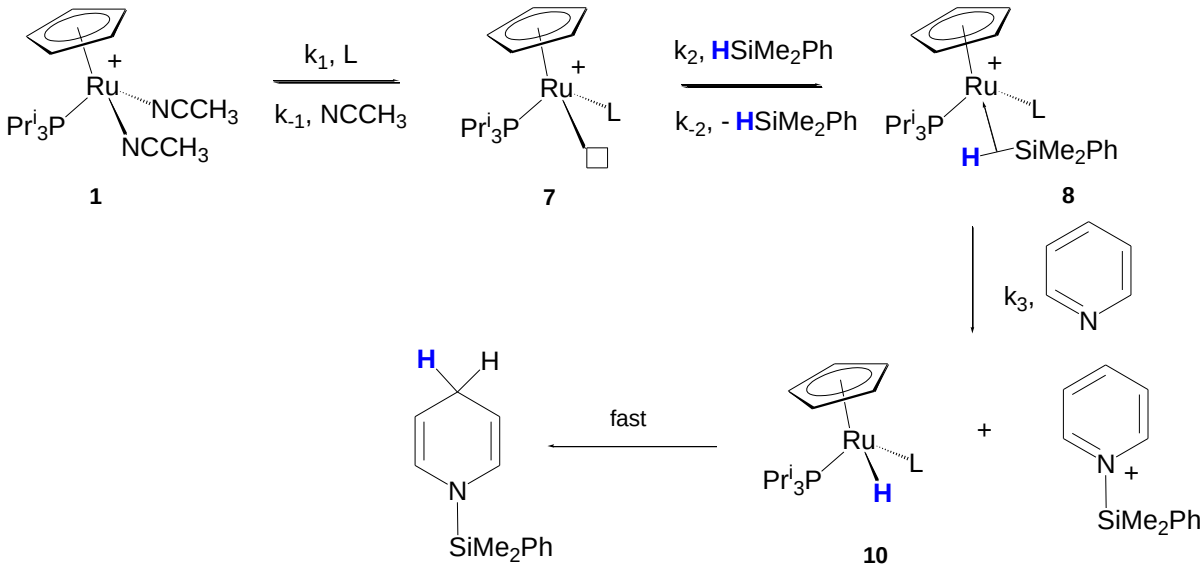
2-Ethylpyridine. To a solution of $HSiMe_2Ph$ (7.7 µL, 0.05 mmol) and 2-ethylpyridine (5.4 µL, 0.05 mmol) and EtOH (6.9 µL, 0.15 mmol) in Acetone-d_6 was added [Cp^*(phen)Ru(CH_3CN)]PF_6 (1.5 mg, 0.0025 mmol). The reaction was periodically monitored by NMR spectroscopy at room temperature. Formation of $EtOSiMe_2Ph$ and H_2 was observed.

Kinetic studies

$HSiMe_2Ph$ (23.7 µL, 0.15 mmol) was added to a frozen solution of [Cp(*i*PrP_3)Ru(CH_3CN)]BAF (0.96 mg, 0.0009 mmol) and pyridine (96.8 – 145.2 µL, 1.20 – 1.80 mmol, (8 – 12 eq.)) in CD_2Cl_2. The reaction was automatically monitored by NMR spectroscopy at room temperature every minute.



The deduction of the rate law.



1 **7** **8** **10**

Assuming a fast equilibrium between **1** and **7** and the steady state condition for **8**,

$$-\frac{d[8]}{dt} = k_2[7] - k_{-2}[8] - k_3[8][pyr] = 0$$

Hence

$$k_2[7] = (k_{-2} + k_3[pyr])[8]$$

$$k_1[1] = k_{-1}[7]$$

$$rate = k_3[8][pyr] = k_3 \frac{k_2[7][HSiMe_2Ph][pyr]}{k_{-1}k_{-2} + k_{-1}k_3[pyr]} = \frac{k_1k_2k_3[1][HSiMe_2Ph][pyr]}{k_{-1}k_{-2} + k_{-1}k_3[pyr]}$$

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1 (a) C. M. Standfest-Hauser, K. Mereiter, R. Schmid , K. Kirchner , *Eur. J. Inorg. Chem.*, **2003**, 1883. (b) A. L. Osipov, D. V. Gutsulyak, L. G. Kuzmina, J. A. K. Howard, D. A. Lemenovskii, G. Suss-Fink, G. I. Nik onov, *J. Organomet. Chem.*, **2007**, *692*, 5081.