Electronic Supplementary Material (ESI) for Dalton Transactions.

Catalytic exploration of NHC-Ag(I)-HMDS complexes for the hydroboration and hydrosilylation of carbonyl compounds

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Supporting Information

Table of Contents

Experimental

General Experimental

Unless specified all reactions and manipulations were carried out under a protective nitrogen atmosphere using either standard Schlenk techniques or an MBraun glove box fitted with a gas purification and recirculation unit. NMR measurements were conducted in either a standard NMR tube or clear/amber J. Youngs tube oven dried and flushed with nitrogen prior to use. NMR spectra were recorded in C_6D_6, $CDCl_3$ or $(CD_3)_2SO$ on a Bruker DRX400 NMR spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei, or Bruker DRX600 NMR spectrometer operating at 600 MHz for proton and 150 MHz for carbon nuclei. NMR data recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) J (Hz), relative integral], where multiplicity is defined: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof, and prefixed br = broad. Solvents were obtained from an MBraun SPS-800 solvent purification system and stored over 4 Å molecular sieves under a nitrogen atmosphere. Pentane was refluxed and dried over Na turnings and stored over 4 Å molecular sieves under nitrogen. All reagents and substrates were purchased commercially from Sigma Aldrich, Oakwood Chemicals, Merck or Alfa-Aesar and used as received without any further purification.

X-ray Crystallography

Crystallographic data for compounds **3** and **4** were collected on the OXFORD XtaLAB Synergy, Dualflex, HyPix diffractometer equipped with an OXFORD Cryosystems 700 Cryostream and cooled to 123(1) K. Data was collected with MoKα radiation (λ = 0.71070 Å) and processed using the CrysAlisPro v 1.171.40.49a software. [1] Each compound was solved and refined using SHELX-2016 utilising the graphical interface Olex2.[2, 3] Refinement was achieved by using the full matrix least-squares technique on F^2, which minimises the function given by (Fo-Fc)2, where Fo and Fc are the observed and calculated structure amplitudes respectively, given that the weight is defined as 4F02/2Fo2. Unless otherwise indicated, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions using a riding model with C- H = 0.95–0.98 Å and Uiso(H) = xUiso(C), x = 1.2 or 1.5 unless otherwise indicated. Selected crystallographic details and refinements are provided in Table S1, page 13. CCDC 2218138 and 2218137 contains the supplementary crystallographic data for these structures. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General catalytic protocol

In a typical procedure, the substrate (0.5 mmol) was added to an amber J. Youngs NMR tube and dissolved in C_6D_6 (0.5 mL) containing 10 mol % of the internal reference standard hexamethylcyclotrisiloxane and the ^1H NMR data recorded. Pinacolborane (0.6 mmol, 90 µL) or diphenylsilane (0.75 mmol, 93 µL) and catalyst **3** or **4** (5 mol %, 1 M, 50 µL) was then added and the reaction monitored by ^1H and/or ^{11}B NMR spectroscopy until completion. For hydrosilylation reactions in some cases, multiple species were obtained, and these are

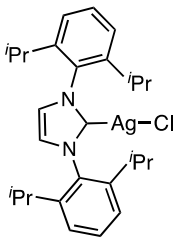
proposed to be due to Ph_2SiH_2 redistribution in solution resulting in various silyl protected alcohol products. In these cases, the reactions were quenched with tetrabutylammonium fluoride (TBAF) and the crude organic product was analysed by ^1H with internal standard to determine the yield of a single alcohol product.

Hydrosilylation reactions work up:

Typical quench reaction for hydrosilylation, substrates for **3** and **4: 2b**, **3b**, **4b, 10b**, **12b** and **6b** for **4**:

On a 1mM scale reaction in C_6D_6 the hydrosilylation reactions were performed in a amber scintillation vial. Each reaction was allowed to stir for the given time in Table **S4** and **S5** in order for conversion to be complete. The reaction mixture was then cooled to 0°C via an ice bath and 1.1 equivalents of TBAF (1.1mL; 1M solution in THF) was added drop wise and allowed to stir warming to room temperature. Next H_2O (10 mL) was added and the product extracted with DCM (3 x 10mL). The combined organics were washed with brine (15mL), dried with $MgSO_4$ and solvent removed *in vacuo.* The crude residue was analysed by ^1H NMR in $CDCl_3$ with 10 mol% internal standard hexamethylcyclotrisiloxane (0.022g, 0.1mM); 10%).

Synthesis of NHC-Ag(I)HMDS pre-catalysts



*Synthesis and characterisation of Ag(IDipp)Cl **1**:*

To a 3 neck 250 mL RBF was added 1,3-bis(2,6-diisopropylphenyl) imidazolium chloride (6.4 g, 15 mmol) and Ag_2O (2.8 g, 12 mmol) in 80 mL of dichloromethane (DCM) and heated to 52˚C in an oil bath and stirred vigorously for 2.5hrs. The suspension was then allowed to cool and filtered at room temperature. The light-yellow filtrate was concentrated in *vacuo* and recrystallised from DCM and then dried to form a colourless crystalline solid 5.5 g (Yield: 70%).[4]

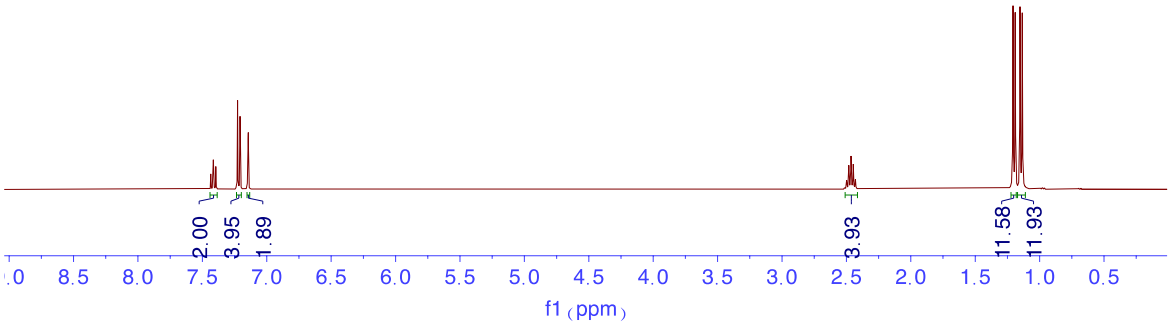


Figure S1: ^1H NMR (400 MHz, $CDCl_3$) 7.49 (m, 2H), 7.31 (m, 4H), 7.22 (s, 2H), 2.54 (septet, J= 1.29 Hz, 4H), 1.29 (d, J= 1.23 Hz, 12H), 1.23 (d, J= 2.5 Hz, 12H) ppm

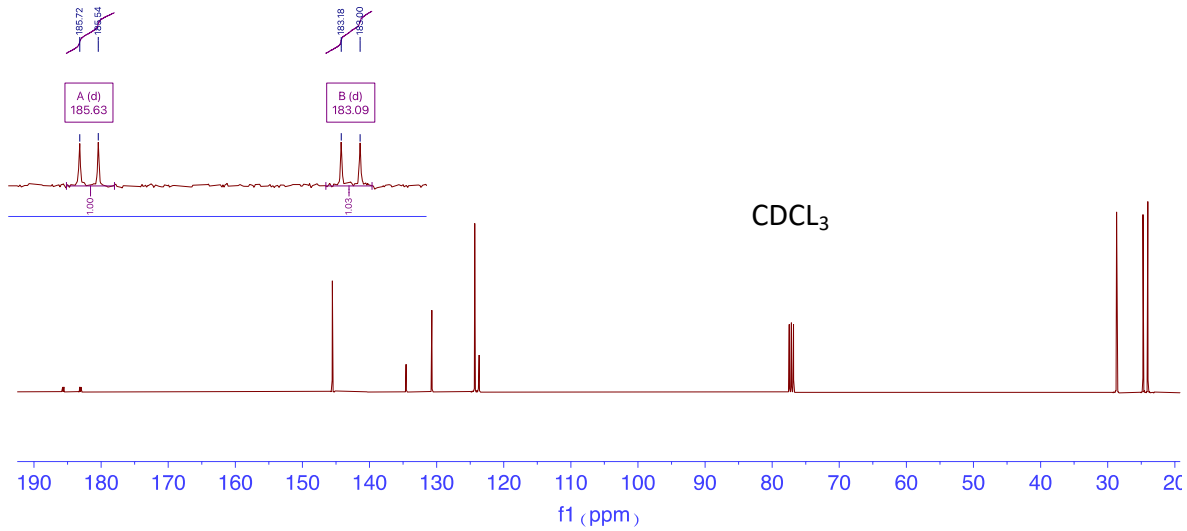
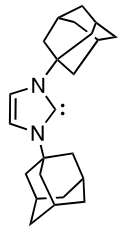


Figure S2: ^{13}C NMR (101 MHz, C_6D_6) 185.6 (d, C^2-Ag), 145.4, 134.4, 130.7, 28.3, 24.6, 23.7 185.7-183.0(d, ^1J $^{107/109}$Ag-^{13}C), 185.5-183.1 (d, ^1J $^{107/109}$Ag-^{13}C) ppm.



*Synthesis and characterisation o 1,3-bis(1-adamantyl)imidazol-2-ylidene **2**:*

Following a modified literature procedure to an oven dried 100 mL J Young's Schlenk Flask was added 1,3-bis(1-adamantyl)imidazolium tetrafluoroborate (10.4 g, 24.5 mmol) and KOtBu (2.87 g, 25.6 mmol) and suspended in 90 mL of dry-tetrahydrofuran (THF). The reaction was left to stir at room temperature for 6 hours. The solution was dried in vacuo and resuspended in 50 mL of Et2O and filtered. The filtrate was then concentrated in vacuo and recrystallised from hexane to form a colourless solid 4.92 g (60%).[5]

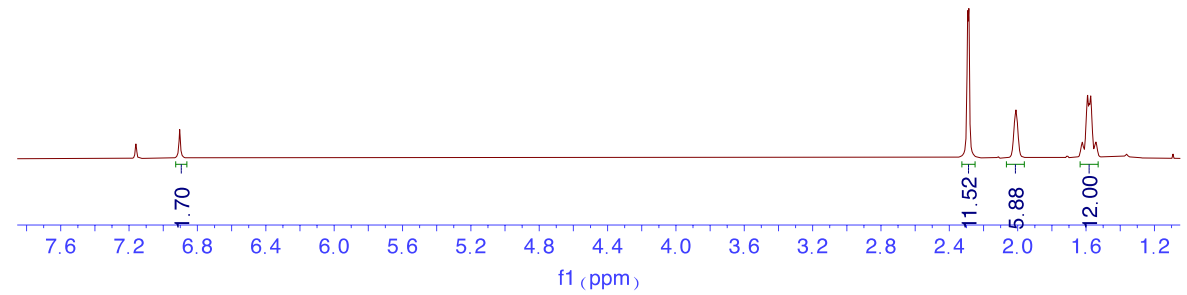


Figure S3: ^{1}H NMR (400 MHz, C_6D_6) 1.57 (m, 12H), 2.00 (s, 6H), 2.29 (s, 12H), 6.90 (s, 2H) ppm

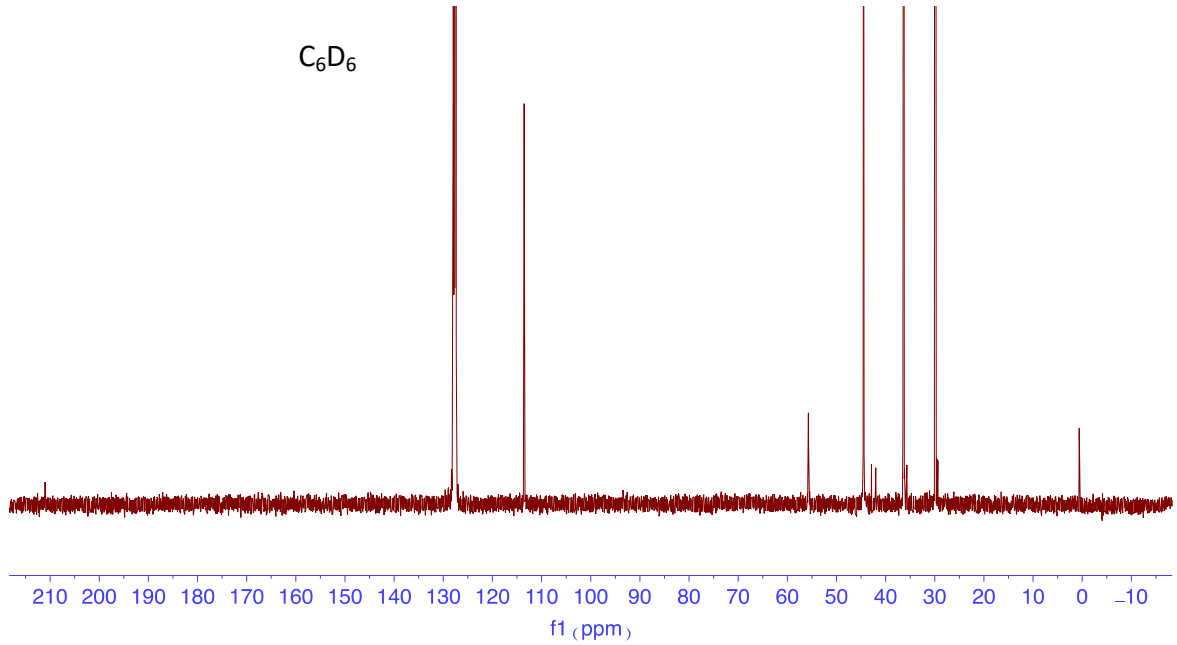
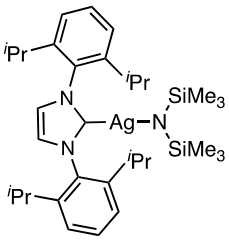


Figure S4: ^{13}C NMR (101 MHz, C_6D_6) 211.5 (s, C_2), 113.9 (dd), 55.8, 44.5, 36.6, 30.4 ppm



Synthesis and characterisation of [Ag(IDipp)HMDS], ***3***

Ag(IDipp)Cl **1** (2.07 g, 4 mmol) was suspended in dry-THF (20 mL). The suspension was cooled to -78˚C (dry ice/acetone bath) and LiHMDS 1M in THF (4.0 mL, 4 mmol) was added dropwise. The resulting clear yellow solution was left to stir overnight warming to room temperature. The reaction was dried *in vacuo* and resuspended in 20 mL of dry pentane. The resulting suspension was left to stir overnight and filtered. The filtrate was dried in vacuo to afford a colourless crystalline solid (0.718g. 40 %). X-ray quality crystals were grown from a concentrated n-hexane solution stored at -30˚C. Elemental analysis calculated for $C_{33}H_{55}AgN_3Si_2$: C, 60.25; H, 8.43; N, 6.39; found: C, 59.44; H, 8.31; N, 6.21.

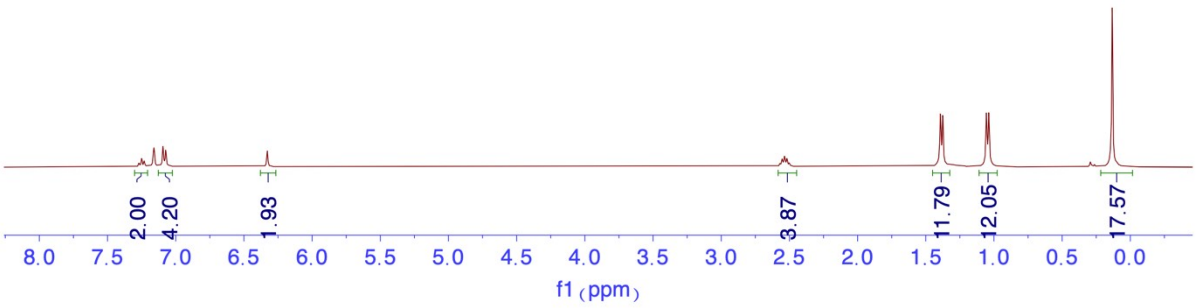


Figure S5: ^{1}H NMR (400 MHz, C_6D_6) 0.13 (s, 18H), 1.04 (d, 12H), 1.39 (d, 12H), 2.53 (septet, 4H), 6.31 (s, 2H), 7.08 (m, 4H), 7.25 (m, 2H) ppm

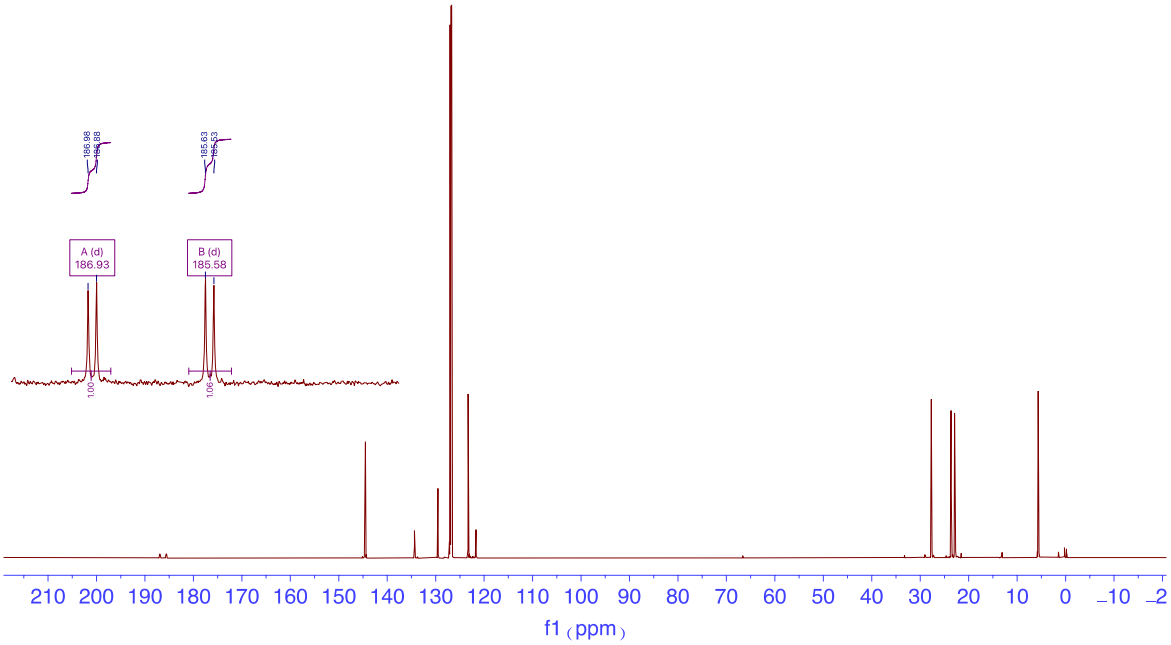


Figure S6: ^{13}C NMR (101 MHz, C_6D_6, 298 K): δ/ppm =6.8, 24.0, 24.8, 28.9, 122.8, 124.5, 130.7, 135.5, 145.6, 188.1-186.7(d, ^{1}J $^{107/109}$Ag-^{13}C), 188.0-186.8 (d, ^{1}J $^{107/109}$Ag-^{13}C) ppm.

Co-crystallisation of [Ag(IDipp)HMDS] **3** and $[(AgHMDS)_4]$ in a 3:1 ratio respectively

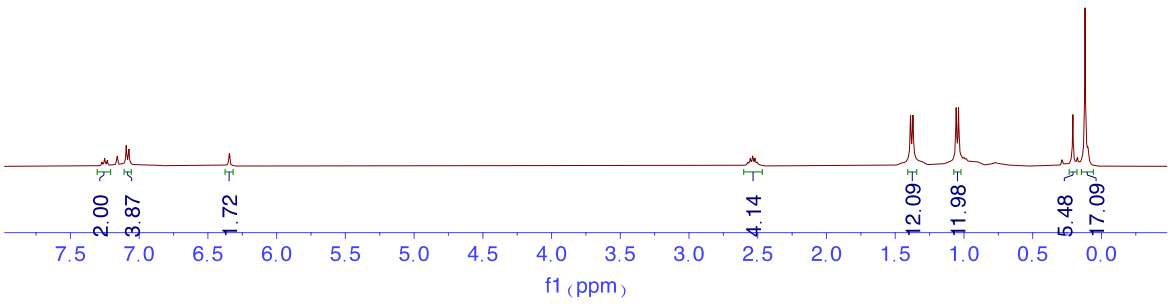
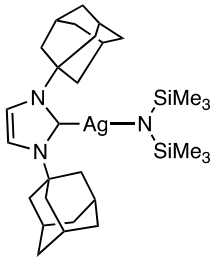


Figure S7: ^{1}H NMR (400 MHz, C_6D_6) [Ag(IDipp)HMDS] **3**: 0.13 (s, 18H), 1.04 (d, 12H), 1.38 (d, 12H), 2.53 (septet, 4H), 6.34 (s, 2H), 7.08 (m, 4H), 7.24 (m, 2H) ppm. $[(AgHMDS)_4]$: 0.20 (s, 6H) ppm.



Synthesis and characterisation of [Ag(IAd)HMDS], ***4***

1,3-Bis(1-adamantyl)imidazol-2-ylidene **2** (1.01 g, 3 mmol) and AgCl (0.43 g, 3 mmol) were suspended in 15 mL of dry-THF. The creamy grey suspension was left to stir overnight, cooled to 0˚C (ice/salt bath) to form **3** *in situ*. Next LiHMDS (1M in THF, 3.1 mL, 3.1 mmol) was added dropwise and left to stir overnight warming to room temperature. The reaction was dried in *vacuo* and the resulting cream solid resuspended in 20 mL of dry toluene. After stirring overnight, the reaction was filtered and the filtrate dried in *vacuo* to afford an off colourless crystalline solid (1.70g, 94%). X-ray quality crystals were grown from a concentrated toluene solution stored at -30˚C. Elemental analysis calculated for $C_{29}H_{51}AgN_3Si_2$: C, 57.50; H, 8.49; N, 6.94; found: C, 57.50; H, 8.49; N, 6.94; C, 57.65; H, 8.83; N, 7.02.

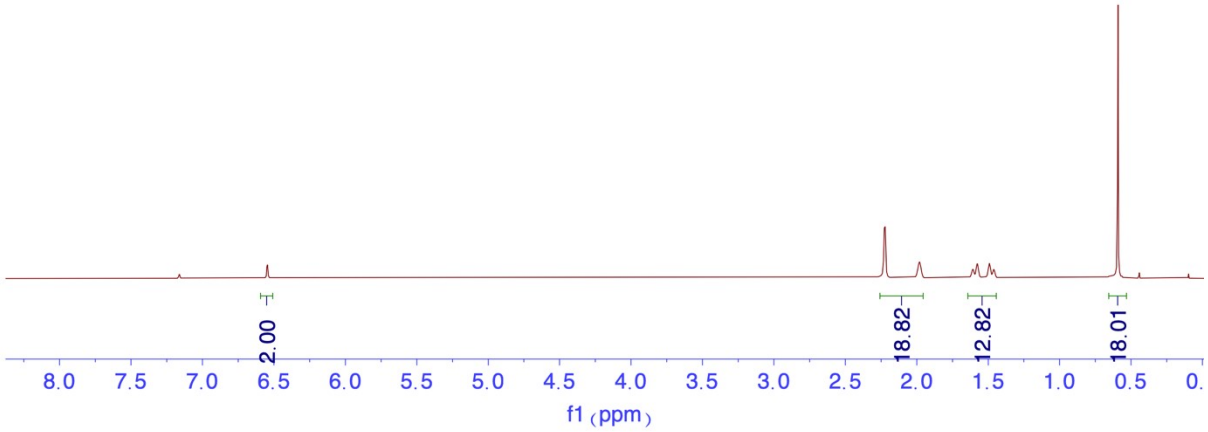


Figure S8: ^{1}H NMR (400 MHz, C_6D_6) 0.60 (s, 18H), 1.47-1.59 (m, 12H), 1.90-2.22 (m, 12H), 6.54 (m, 2H) ppm

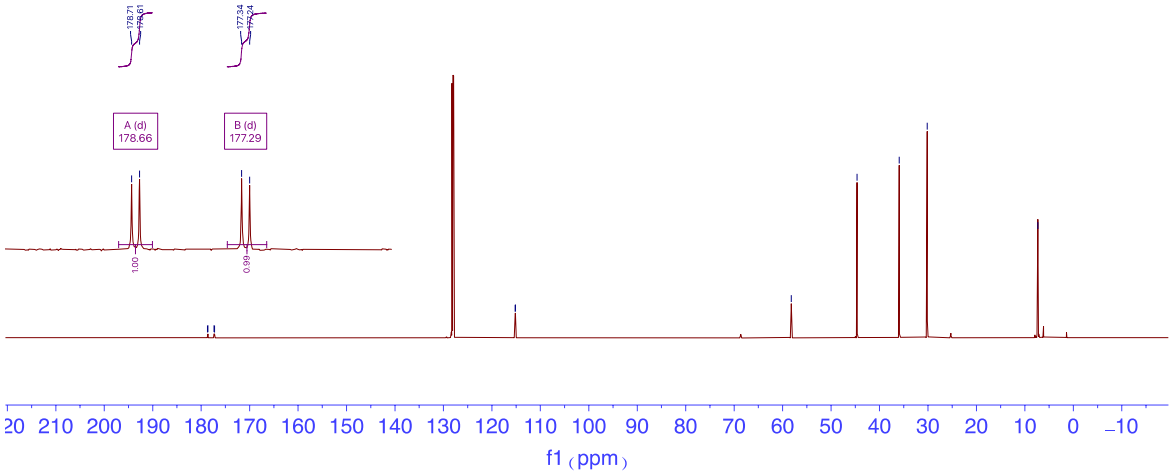


Figure S9: ^{13}C NMR (101 MHz, C_6D_6, 298 K): δ/ppm= 6.9, 29.7, 35.5, 44.2, 57.8, 114.7, 177.5-176.0 (d, ^{1}J $^{107/109}$Ag-^{13}C), 177.4-176.1 (d, ^{1}J $^{107/109}$Ag-^{13}C) ppm.

Light experiments

In a typical procedure a 20 mol% 1M solution of pre-catalyst **3**-**5** was prepared and added to a clear J. Youngs NMR tube and dissolved in 0.5 mL of C_6D_6 containing 10 mol% internal reference standard hexamethylcyclotrisiloxane and monitored by ^{1}H NMR and ^{12}C NMR under standard laboratory conditions

[Ag(IDipp)HMDS] 3:

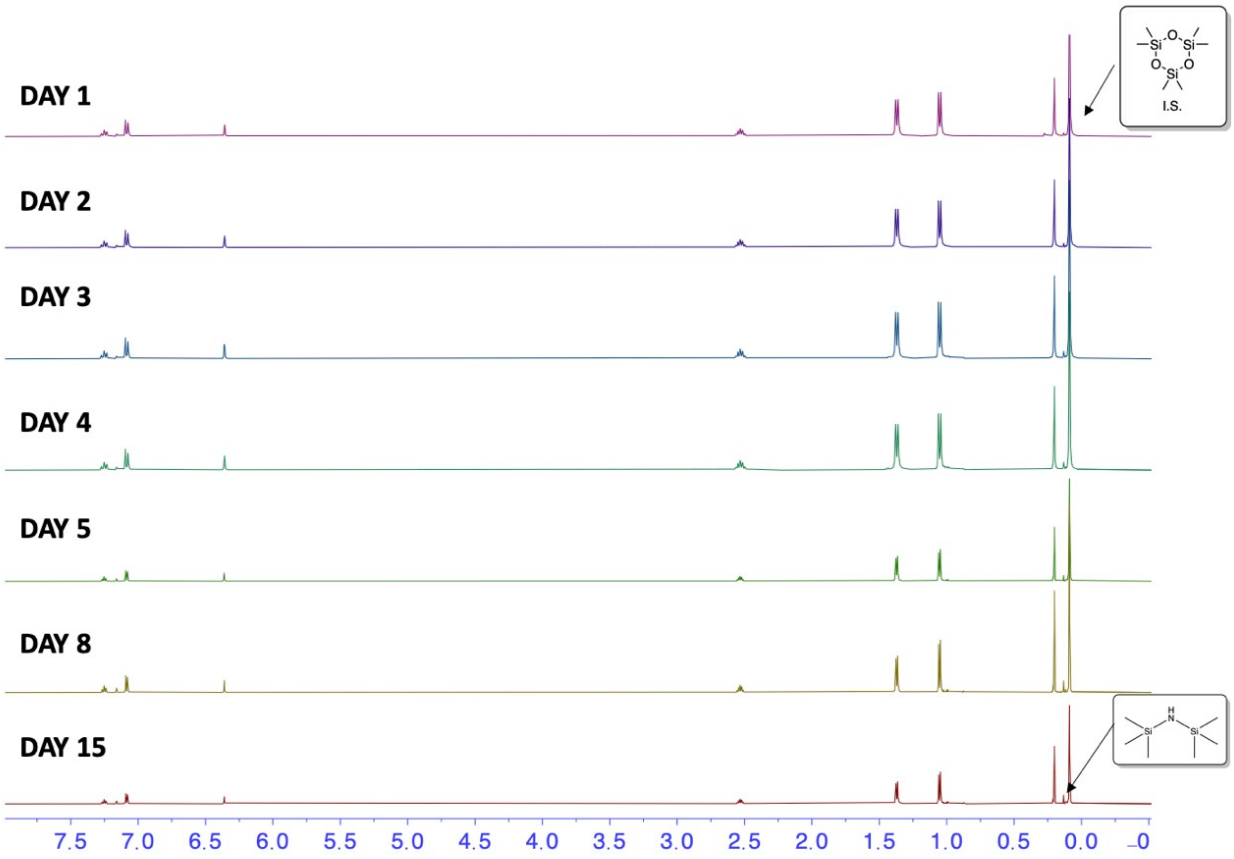


Figure S10. ^{1}H NMR overlay at 300K of 20 mol% [Ag(IDipp)HMDS] **3** in C_6D_6

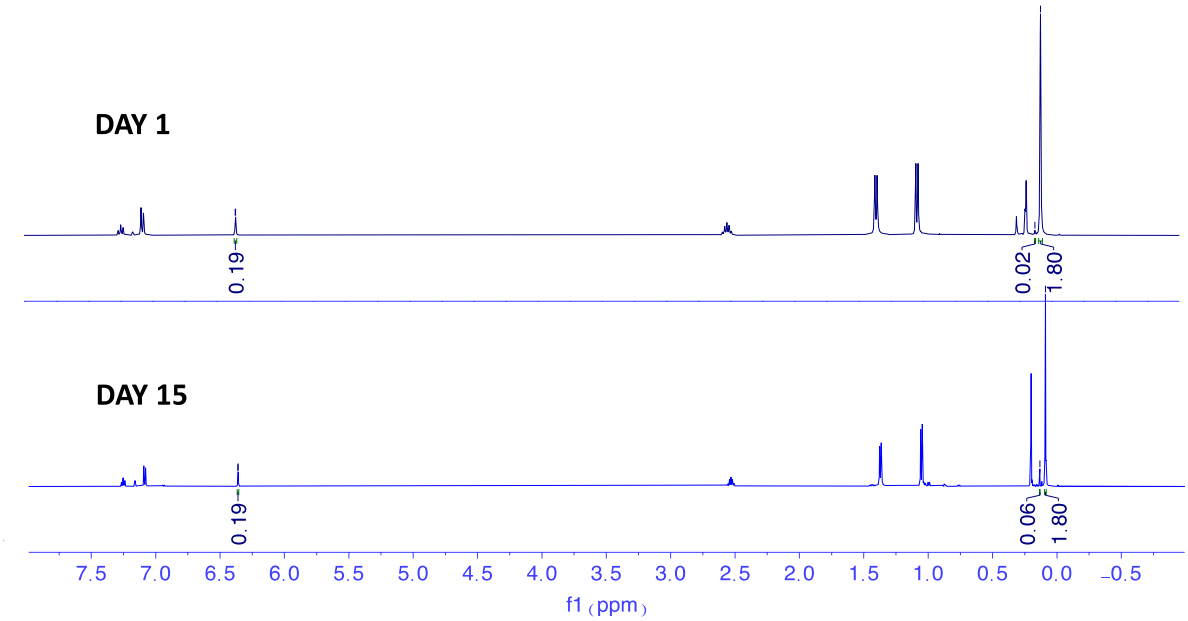


Figure S11. ^{1}H NMR overlay at 300K of 20 mol% [Ag(IDipp)HMDS] **3** in C_6D_6 on day 1 versus day 15 with integrations

[Ag(IAd)HMDS] 4:

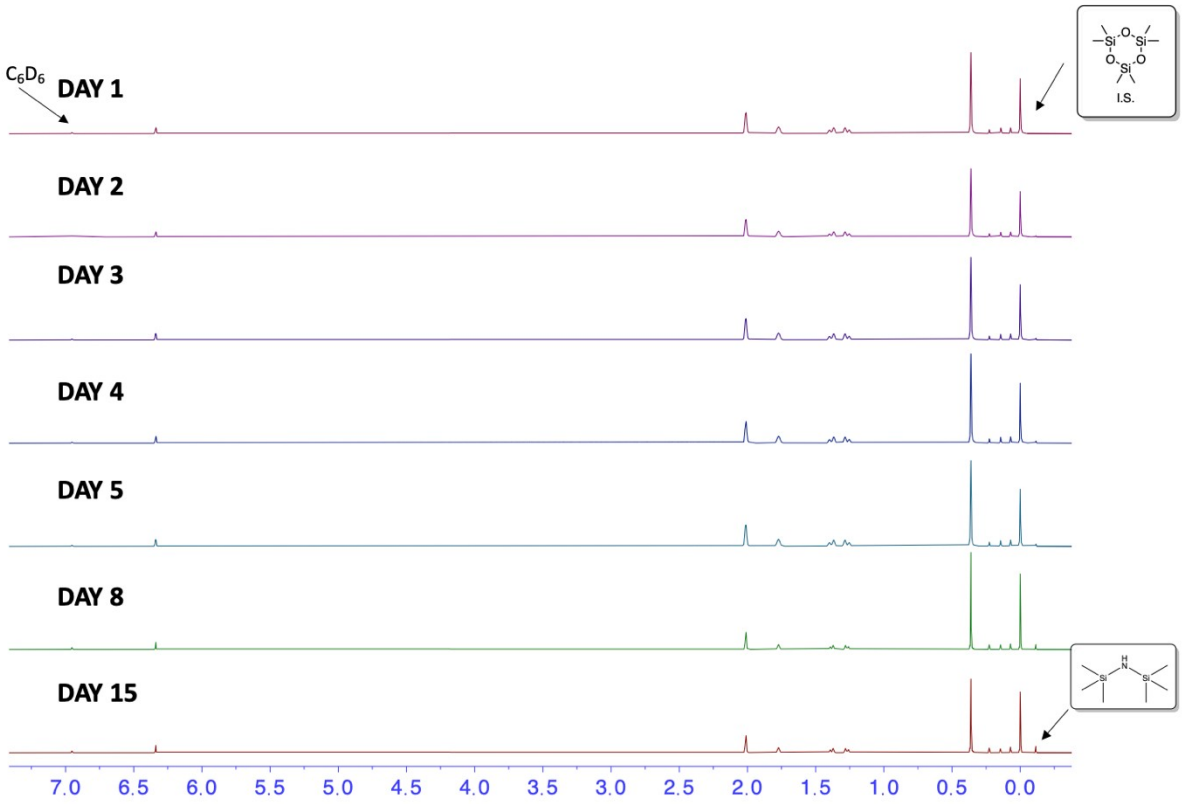


Figure S12. ^{1}H NMR overlay at 300K of 20 mol% [Ag(IAd)HMDS] **4** in C_6D_6

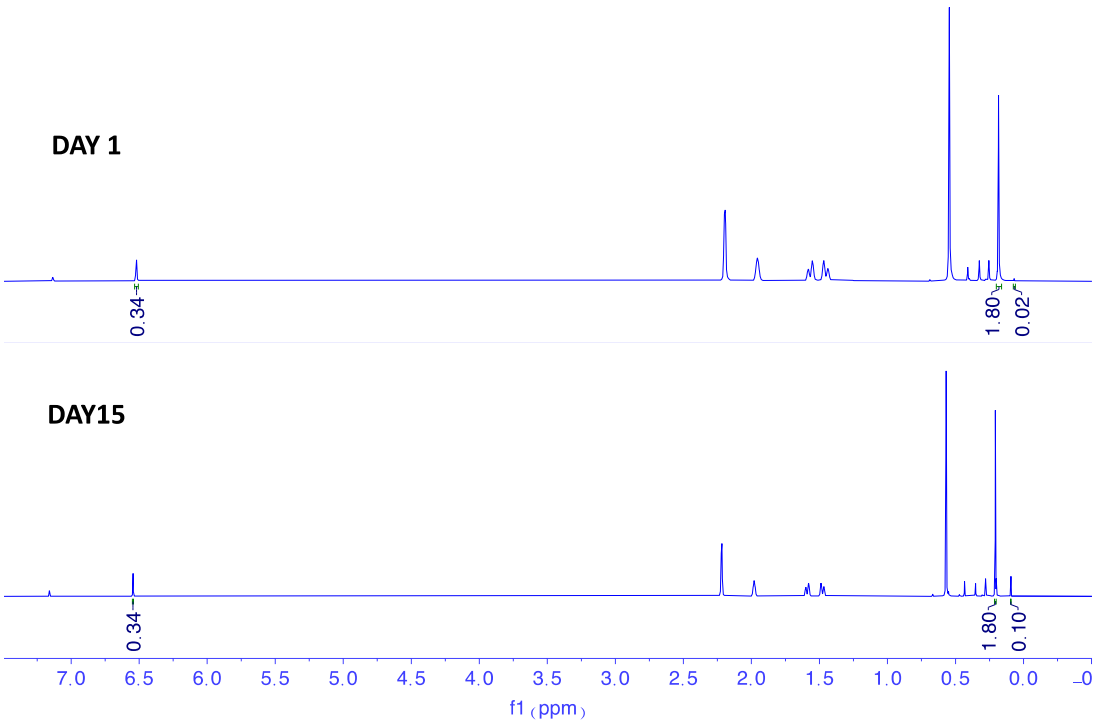


Figure S13. ^{1}H NMR overlay at 300K of 20 mol% [Ag(IAd)HMDS] **4** in C_6D_6 on day 1 versus day 15 with integrations

[Ag(PCy$_3$)HMDS] 5:

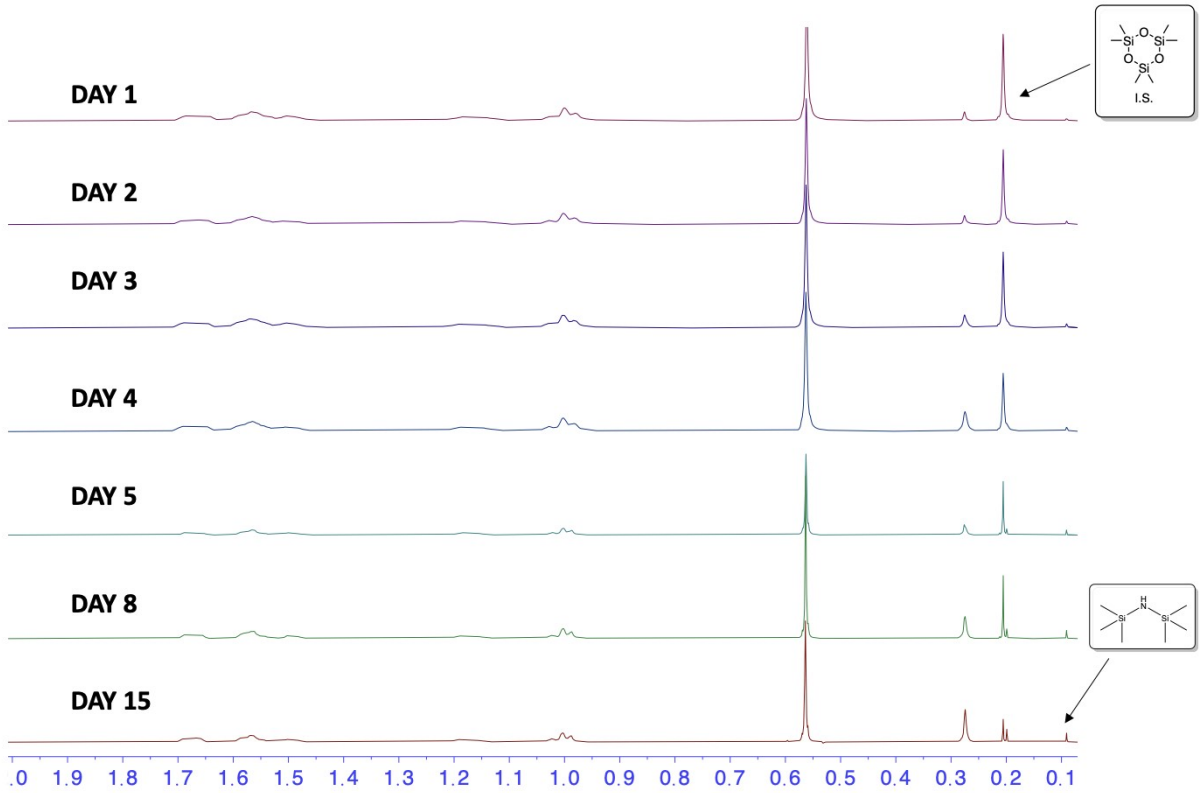


Figure S14. ^{1}H NMR overlay at 300K of 20 mol% [Ag(PCy$_3$)HMDS] **5** in C_6D_6

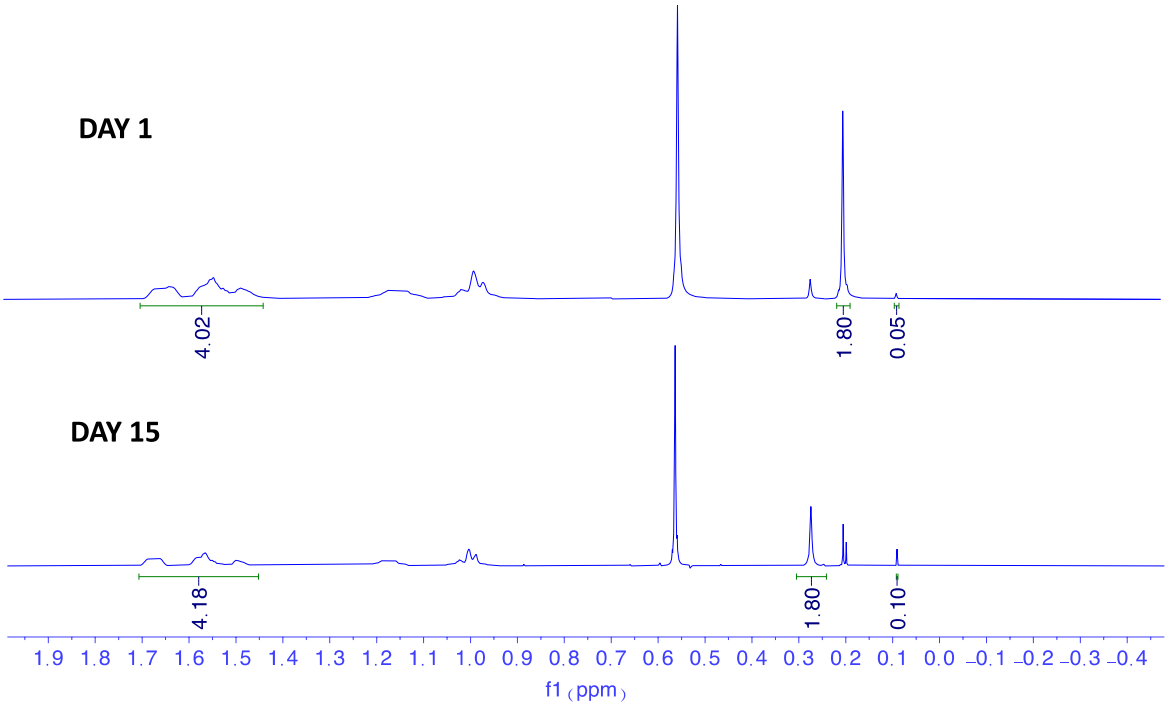


Figure S15. ^{1}H NMR overlay at 300K of 20 mol% [Ag(PCy$_3$)HMDS] **5** in C_6D_6 on day 1 versus day 15 with integrations

X-ray crystallography data

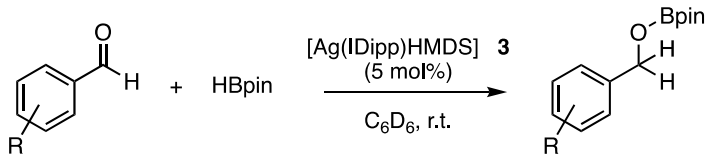
Table S1 Crystallographic data and refinement details for compounds **4** and **5**.

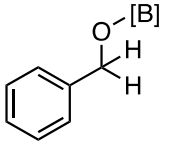
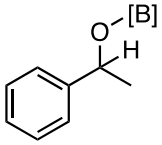
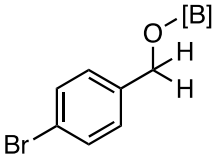
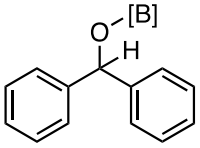
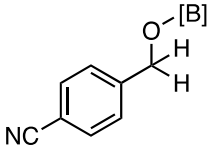
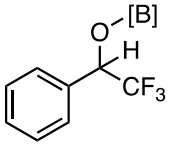
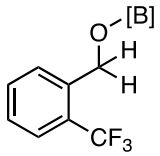
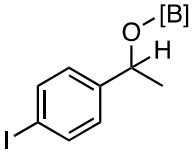
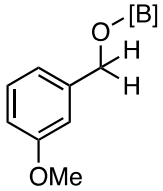
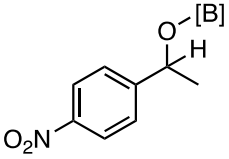
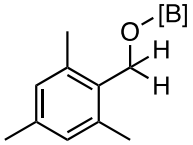
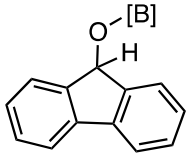
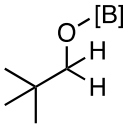
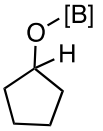
Identification	[(Dipp)AgHMDS] **3**	[(IAd)AgHMDS] **4**
Empirical formula	$C_{33}H_{54}AgN_3Si_2$	$C_{29}H_{50}AgN_3Si_2$
Formula weight	656.84	604.77
Temperature	123.0(3)	123.0(3)
Wavelength	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C2/c
a (Å)	12.9154(4)	20.2489(8)
b (Å)	13.4372(4)	12.2700(5)
c (Å)	21.5913(7)	12.8905(6)
α (°)	90	90
β(°)	104.206(3)	105.751(4)
γ (°)	90	90
Cell volume ($Å^3$)	3632.5(2)	3082.4(2)
Z, calculated density	16	4
Absorption coefficient	1.048 mm^-1	0.753 mm^-1
F(000)	1517.0	1280.0
Crystal size	0.021 x 0.104 x 0.271 mm	0.526 x 0.164 x 0.109 mm
Theta range for data collection	6.676 to 61.41°	6.642 to 56.55°
Limiting indices	-15 ≤ h ≤ 17, -14 ≤ k ≤ 18, -26 ≤ l ≤ 26	-26 ≤ h ≤ 26, -15 ≤ k ≤ 16, -16 ≤ l ≤ 17
Reflections collected / unique	38963/ 9021 [R_{int}= 0.0535]	19847/3815 [R_{int} = 0.0678]
Completeness to theta = 25.244	99.69%	99.73%
Absorption correction	spherical harmonics	spherical harmonics
Max. and min. transmission	1.00000 and 0.53434	1.000 and 0.438
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9021/0/157	3815/0/163
Goodness-of-fit on F^2	1.637	1.068
Final R indices [I>2sigma(I)]	R_1= 0.0811, wR_2= 0.2417	R1 = 0.0396, wR2 = 0.1087
R indices (all data)	R_1= 0.1185 wR_2= 0.2547	R1 = 0.0425, wR2 = 0.1107
Extinction coefficient	n/a	n/a
Largest diff. peak and hole	2.30/-1.42	1.43/-1.36

Catalytic hydroboration using 3

Table S2: Carbonyl hydroboration using HBpin, catalysed by [Ag(IDipp)HMDS]

Table S2. Hydroboration of carbonyls catalysed by **3**

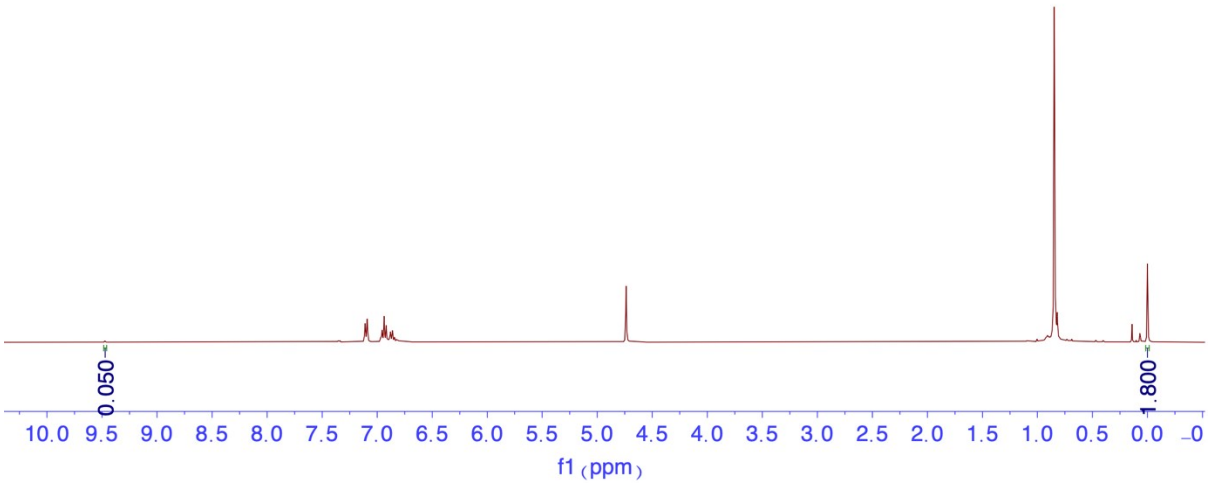


Entry	Product	3	Entry	Product	3
1a		0.5h 95%	**8a**		24h 61%
2a		0.5h 98%	**9a**		1.5h 97%
3a		0.2h 99%	**10a**		0.7h 99%
4a		0.2h 98%	**11a**		6.7h 90%
5a		0.2h 93%	**12a**		2h 75%
6a		1.5h 98%	**13a**		0.7h 90%
7a		0.5h 98%	**14a**		24h 60%

% values indicate % conversion of starting material [a] Reaction conditions: substrate (1 mmol), HBpin (1.5 mmol), 5 mol% [Ag(Dipp)HMDS] (**3**) with 10 mol% internal standard hexamethylcyclotrisiloxane in C_6D_6 at room temperature.

1a, Benzaldehyde

t= 0.5h
c= 95%



Before addition of **3** and HBpin

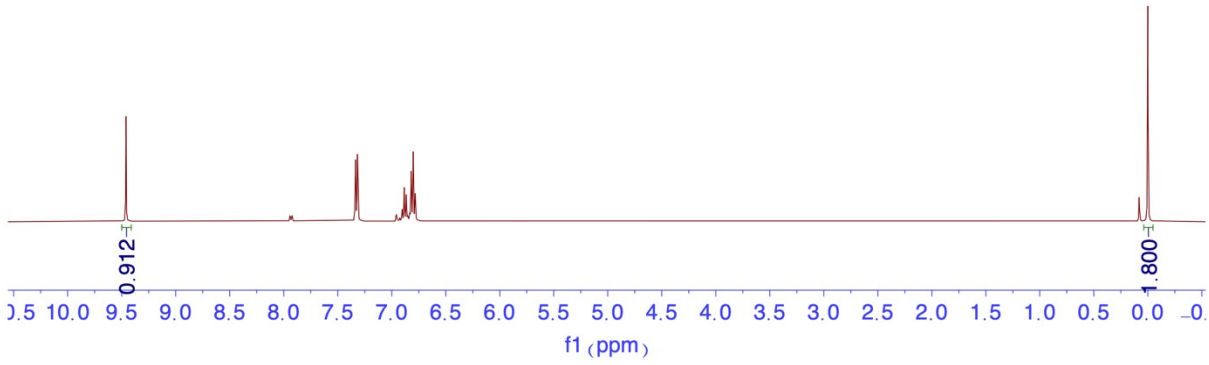


Figure S16 . ^{1}H NMR overlay of catalytic hydroboration of benzaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

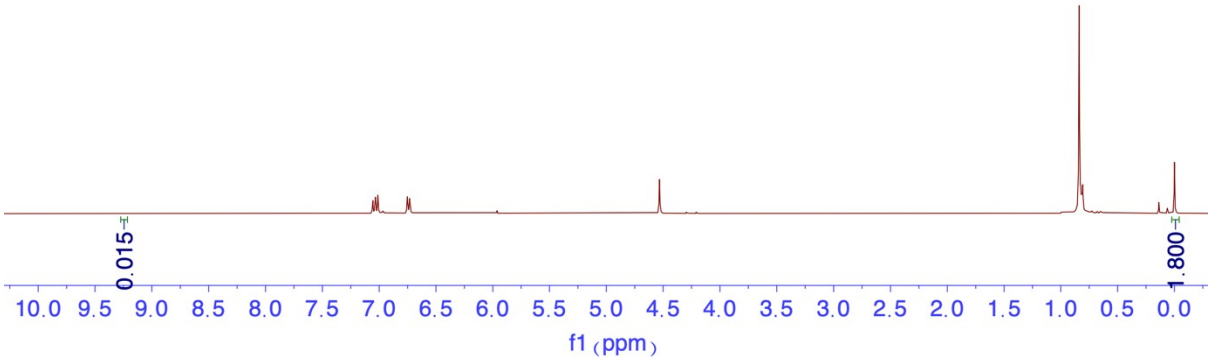
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.30 (2H, d), 7.14 (2H, t), 7.06 (1H, m), 4.92 (2H, s) and 1.05 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 ppm (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 139.2 (quat-C), 128.5, (Ar-C), 127.5 (Ar-C), 127.0 (Ar-C), 82.8 (C of Bpin), 66.8 (C-H) and 24.6 (CH_3 of Bpin) ppm.

2a, 4-Br-Benzaldehyde

t= 0.5h
c=98%



Before addition of **3** and HBpin

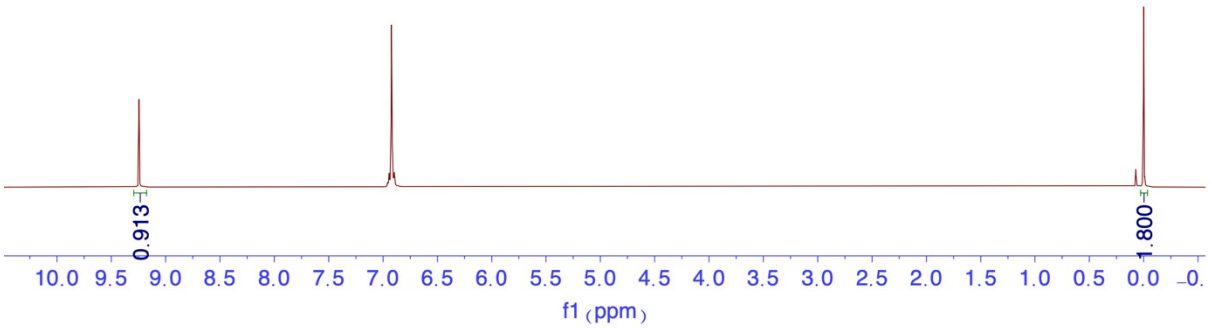


Figure S17. ^{1}H NMR overlay of catalytic hydroboration of 4-Br-Benzaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

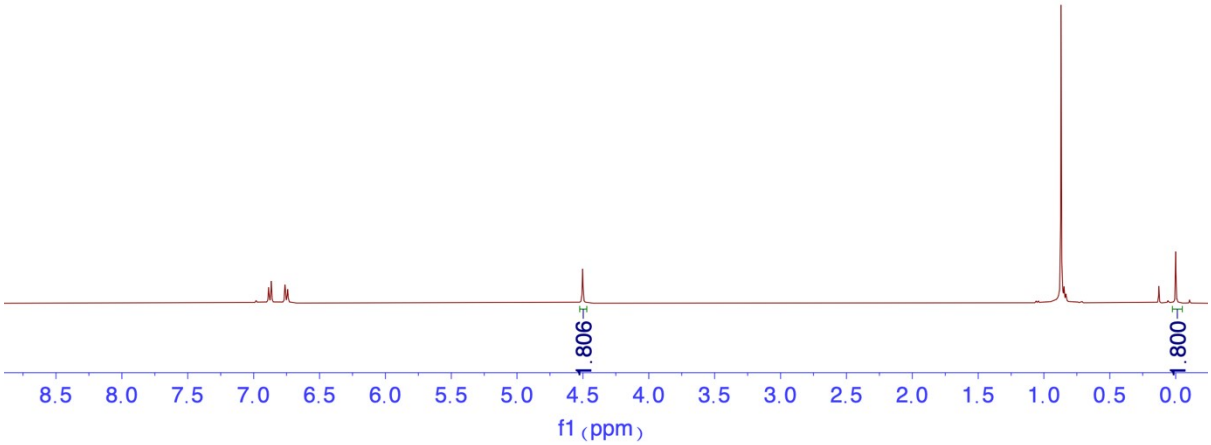
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.02 (2H, t), 8.74 (2H, d), 7.06 (1H, m), 4.52 (2H, s) and 0.83 (12H, s, CH_3 of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 139.1 (quat-C), 131.8 (Ar-C), 121.4 (Ar-C), 82.8 (C of Bpin), 66.0 (O-CH_2), 24.6 (CH_3 of Bpin) ppm.

3a, 4-CN-Benzaldehyde

t= 0.2h
c= 99%



Before addition of **3** and HBpin

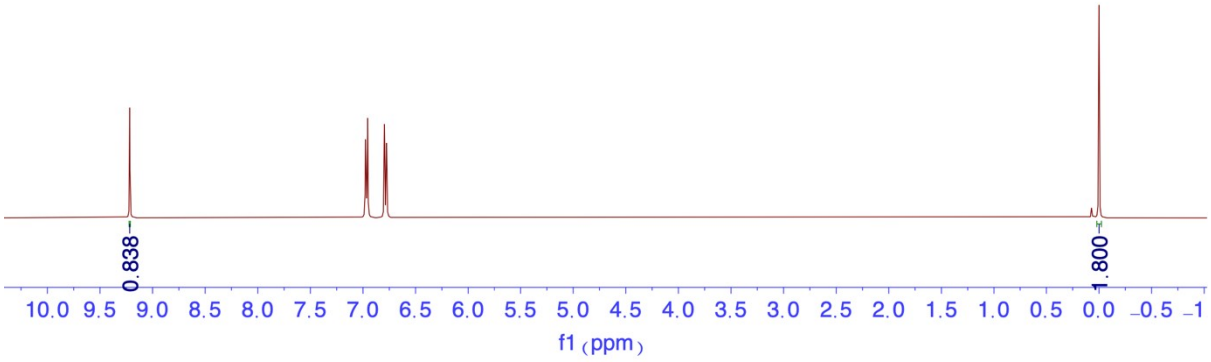


Figure S18. ^{1}H NMR overlay of catalytic hydroboration of 4-CN-Benzaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

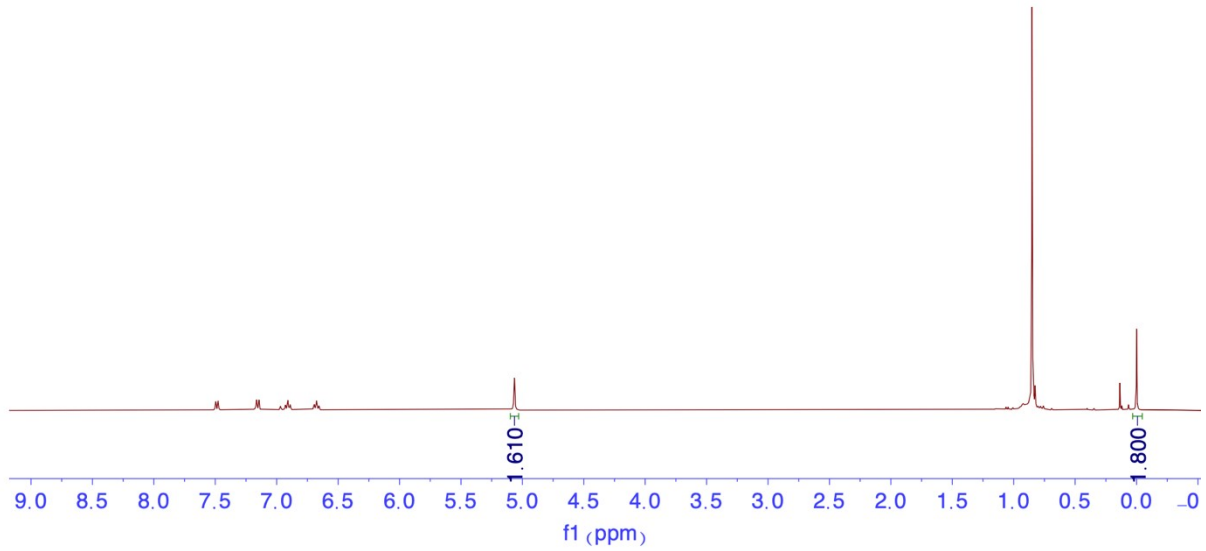
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.05 (2H, d), 6.93 (2H, d), 4.68 (2H, s), 1.04 (12H, s, CH_3-of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 144.6, 132.1, 126.8, 118.8, 111.6, 83.2, 66.2, 24.7 (CH_3-of Bpin) ppm.

4a, 2-CF_3-Benzaldehdye

t=0.2h
c=98%



Before addition of **3** and HBpin

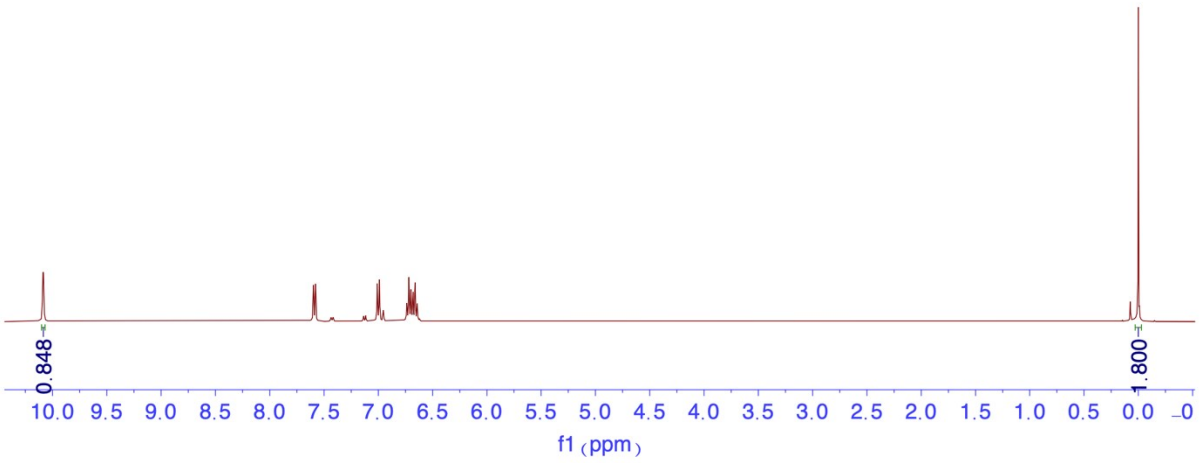


Figure S19. ^{1}H NMR overlay of catalytic hydroboration of 2-CF_3-Benzaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

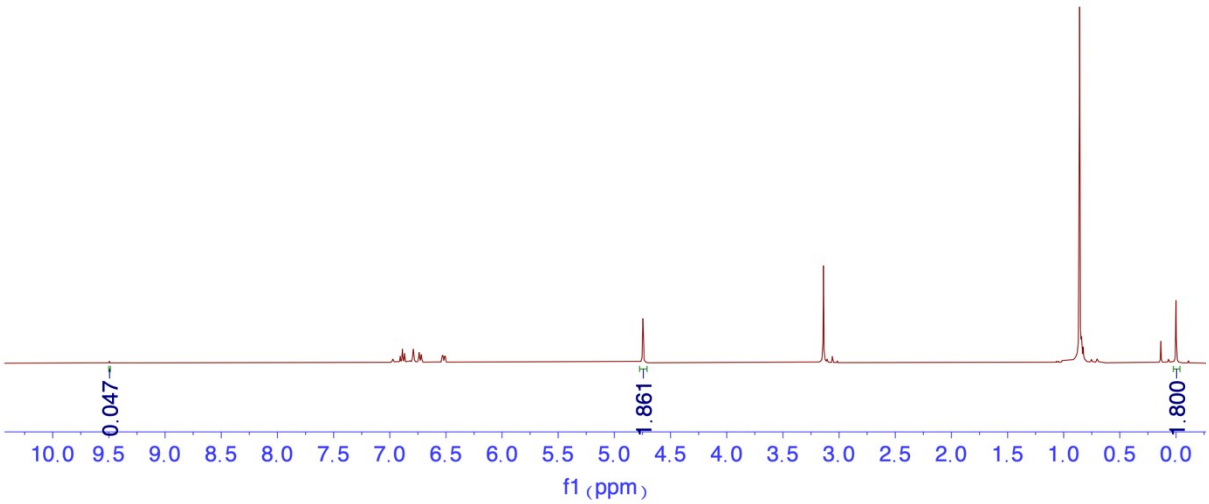
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.48 (1H, d), 7.16 (1H, d), 6.90 (1H, t), 6.67 (1H, t), 5.06 (2H, s), 0.85 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.7 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 138.4, 131.9, 127.1, 126.6, 126.4, 125.7, 123.7, 82.8, 62.7, 24.1 ppm.

5a, 3-OMe-Benzaldehyde

t= 0.2h
c= 93%



Before addition of **3** and HBpin

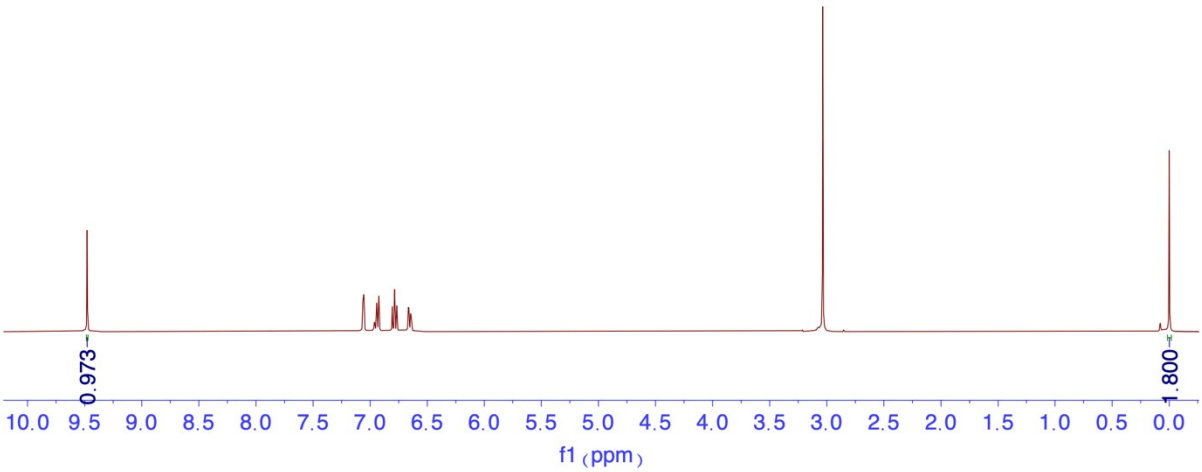


Figure S20. ^{1}H NMR overlay of catalytic hydroboration of 3-OMe-Benzaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

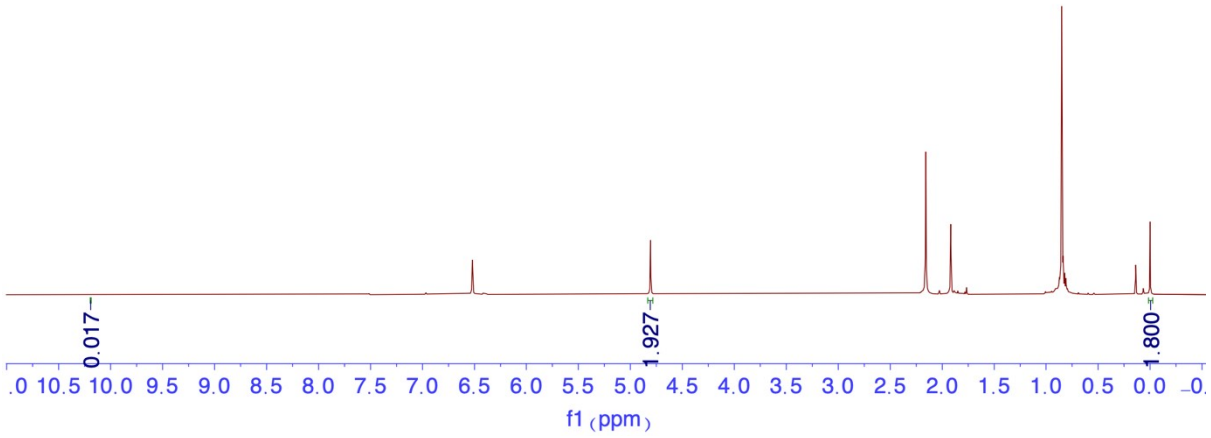
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 6.88 (1H, t), 6.79 (1H, m), 6.72 (1H, d), 6.51 (1H, dd), 4.72 (2H, s), 3.13 (3H, s), 0.85 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 160.3, 141.5, 129.5, 119.0, 113.5, 112.0, 82.6, 66.8, 54.6, 24.4 ppm.

6a, Mesitaldehyde

t= 1.5h
c= 98%



Before addition of **3** and HBpin

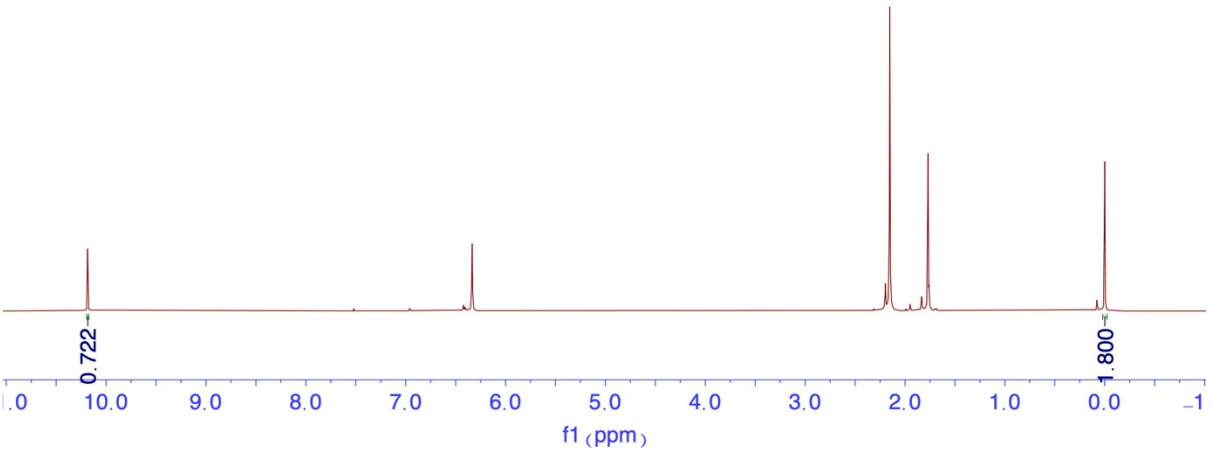


Figure S21. ^{1}H NMR overlay of catalytic hydroboration of mesitaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

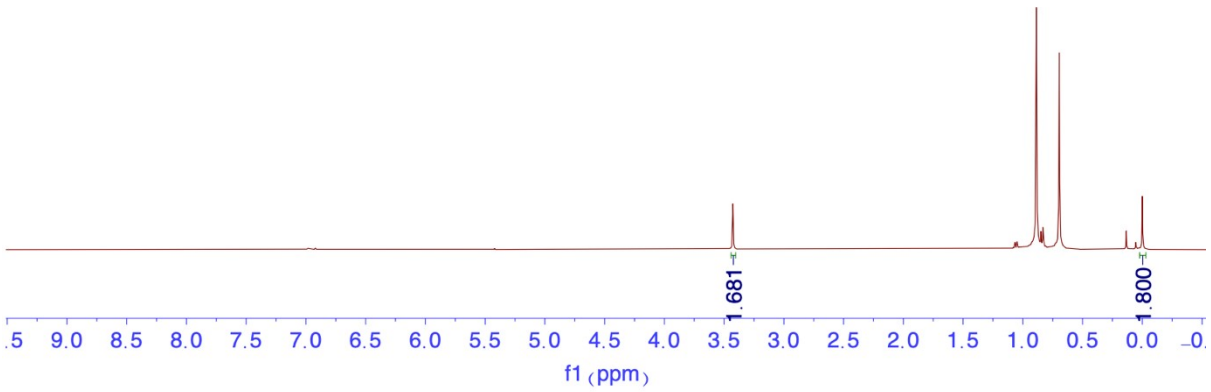
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 6.70 (2H, s), 4.99 (2H, s), 2.34 (6H, s), 2.10 (3H, s), 1.03 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.7 (O-Bpin), 25.6 (HMDS-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 137.7, 132.9, 129.3, 82.3, 61.5, 24.4, 20.8, 19.3 ppm.

7a, *t*Butylaldehyde

t= 0.5h
c=98%



Before addition of **3** and HBpin

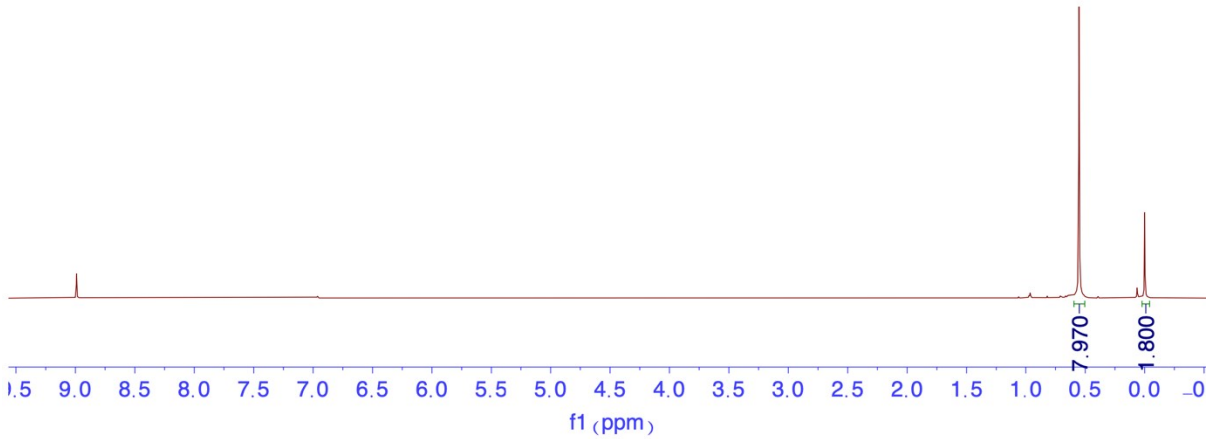


Figure S22. ^{1}H NMR overlay of catalytic hydroboration of *t*Butylaldehyde with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

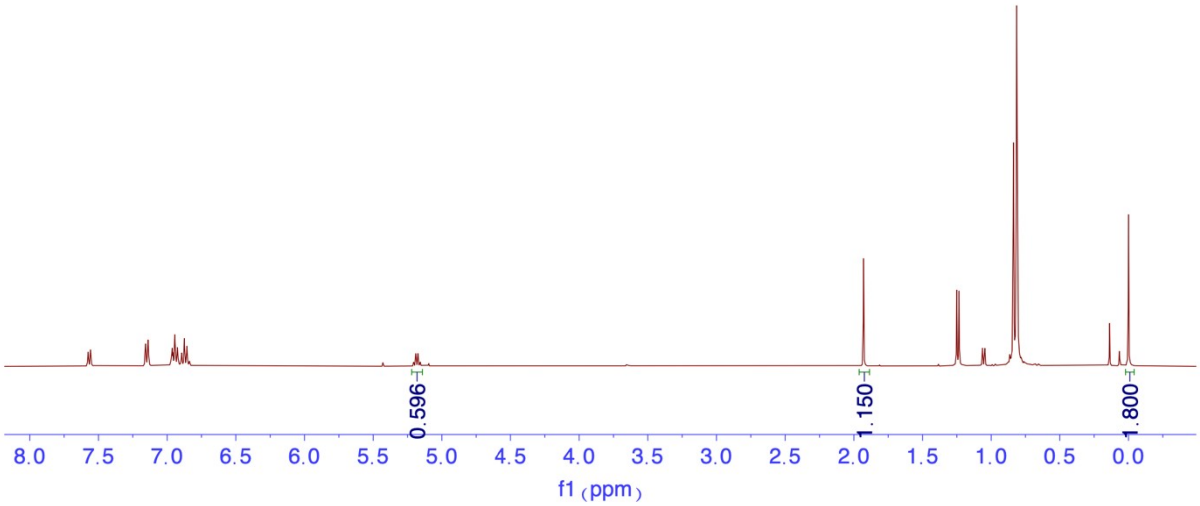
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 3.60 (2H, s), 1.07 (12H, s), 0.87 (9H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.6 (O-Bpin) ppm

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 82.3, 75.0, 32.5, 26.2, 24.5 ppm.

8a, Acetophenone

t= 24h
c= 61%



Before addition of **3** and HBpin

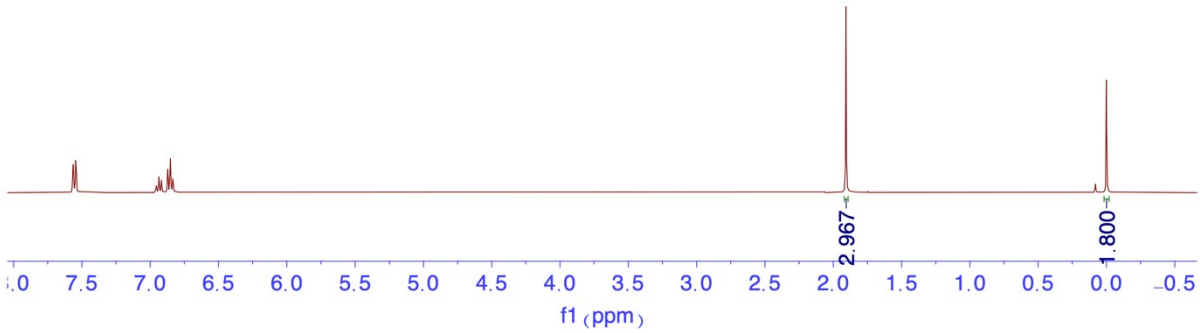


Figure S23. ^{1}H NMR overlay of catalytic hydroboration of acetophenone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

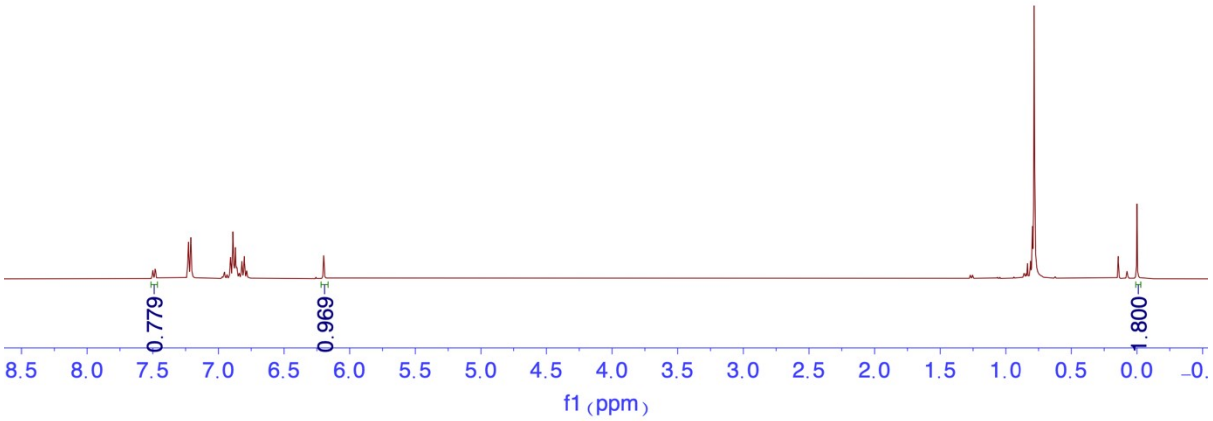
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.56 (1H, d), 7.14 (1H, d), 6.98-6.91 (2H, m), 6.89-6.83 (1H, m), 5.18 (1H, s), 1.24 (3H, s) 0.81 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 145.3, 128.5, 127.3, 125.7, 82.5, 72.8, 24.9 and 24.6 ppm.

9a, Benzophenone

t= 1.5h
c= 97%



Before addition of **3** and HBpin

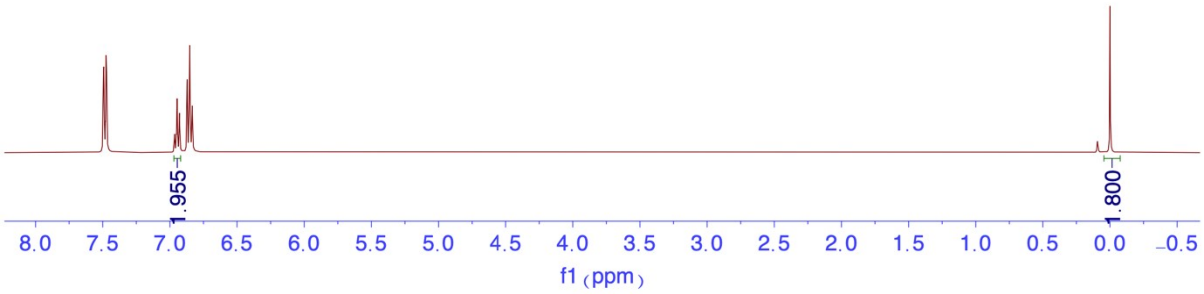


Figure S24. ^{1}H NMR overlay of catalytic hydroboration of benzophenone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

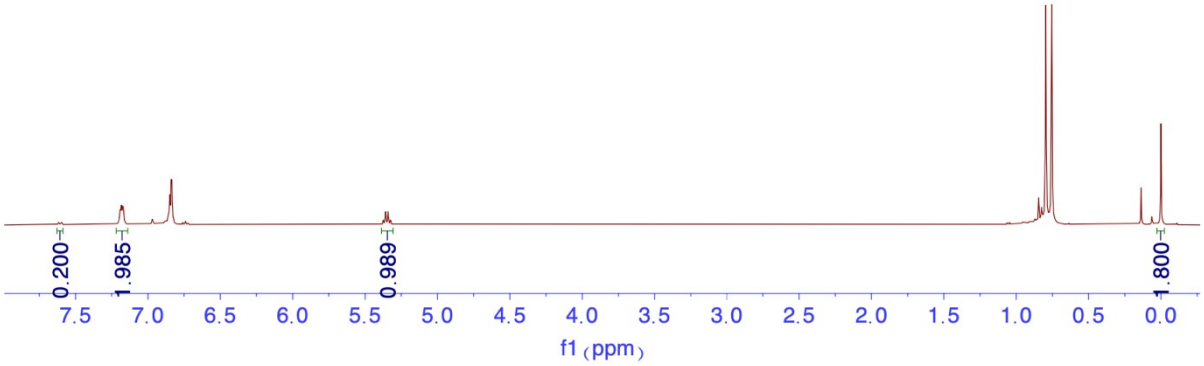
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.42 (4H, d), 7.15 (1H, t), 7.09 (4H, t), 7.01 (2H, tt) and 0.98 (12H, s, C*H*$_3$ of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.8 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 143.8, 128.5, 127.5, 126.9, 82.8, 78.4, 24.3 ppm.

10a, 2,2,2-Trifluroacetophenone

t= 0.7h
c=99%



Before addition of **3** and HBpin

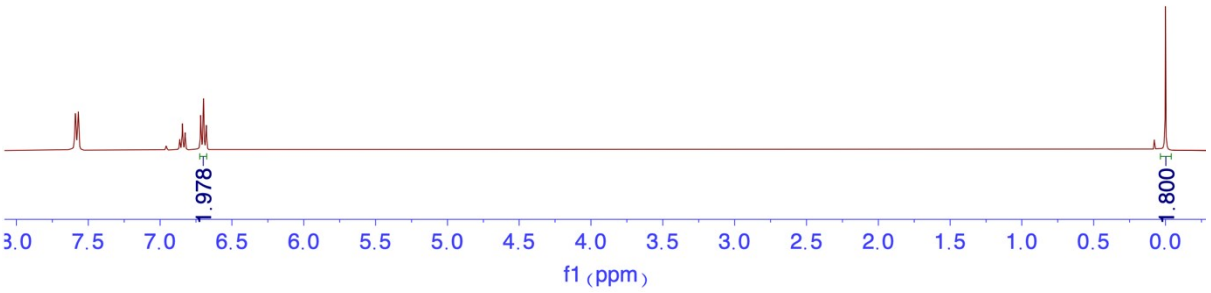


Figure S25. ^{1}H NMR overlay of catalytic hydroboration of 2,2,2-Trifluroacetophenone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

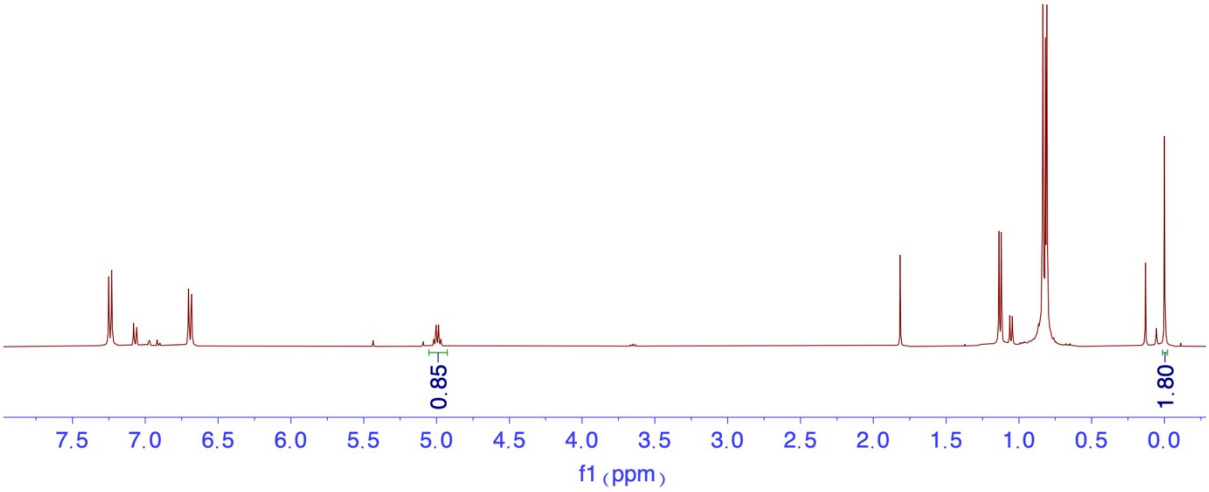
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.37 (2H, m), 7.05-6.98 (3H, m), 5.52 (1H, q), 0.96 (12H, d) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 25.7 (HMDS-Bpin), 22.8 ppm (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 133.9, 129.5, 128.6, 127.9, 83.7, 74.6, 24.4 ppm.

11a, 4-Iodoacetophenone

t= 6.7h
c= 90%



Before addition of **3** and HBpin

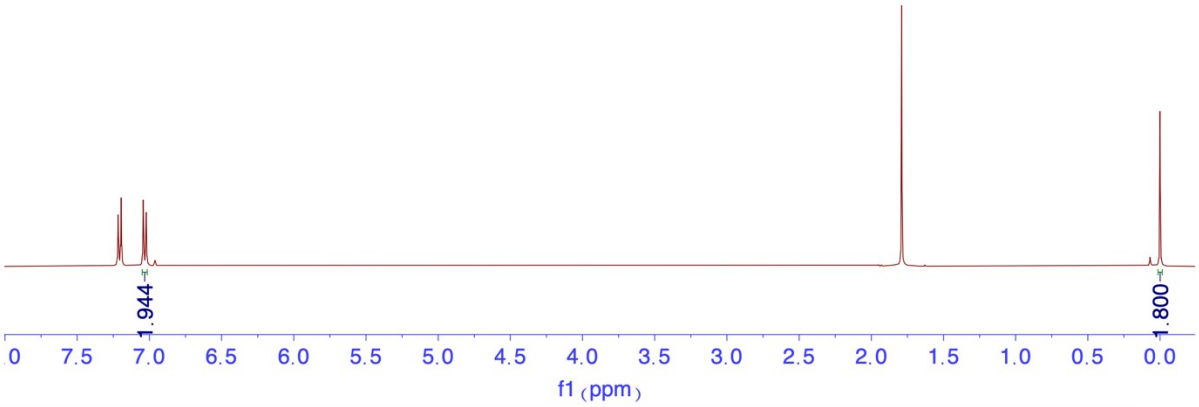


Figure S26. ^{1}H NMR overlay of catalytic hydroboration of 4-Iodoacetophenone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

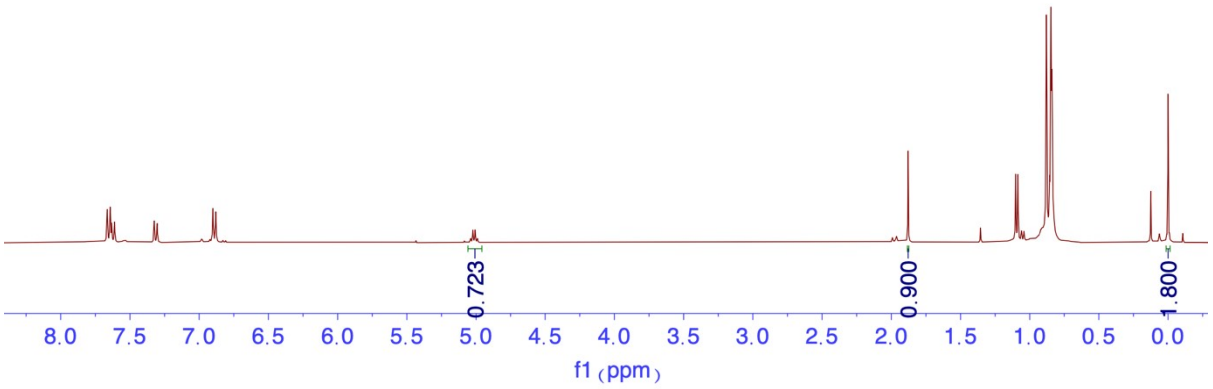
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.23 (2H, d), 6.69 (2H, d), 4.99 (1H, q- OCH), 1.13 (3H, d), 0.81 (12H, d, CH_3 OF Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.8 ppm (O-Bpin),

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 144.8, 137.6, 127.7, 92.7, 82.5, 72.3, 25.5, 24.6 ppm.

12a, 4-NO_2-Acetophenone

t= 2h
c= 75%



Before addition of **3** and HBpin

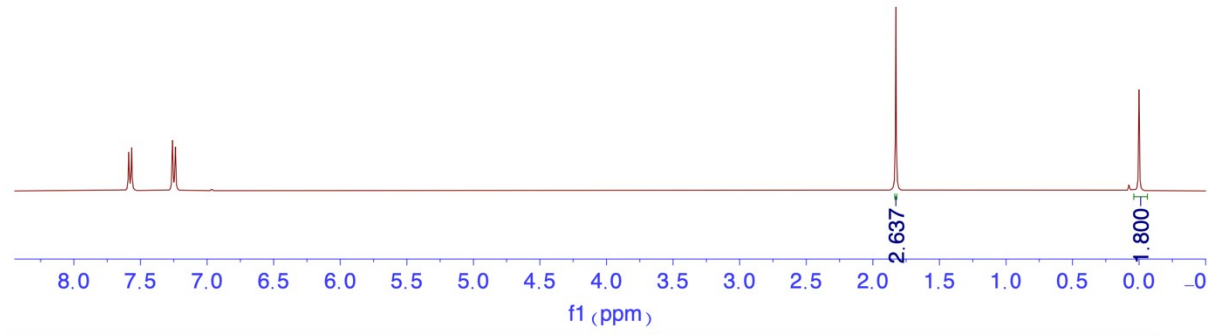


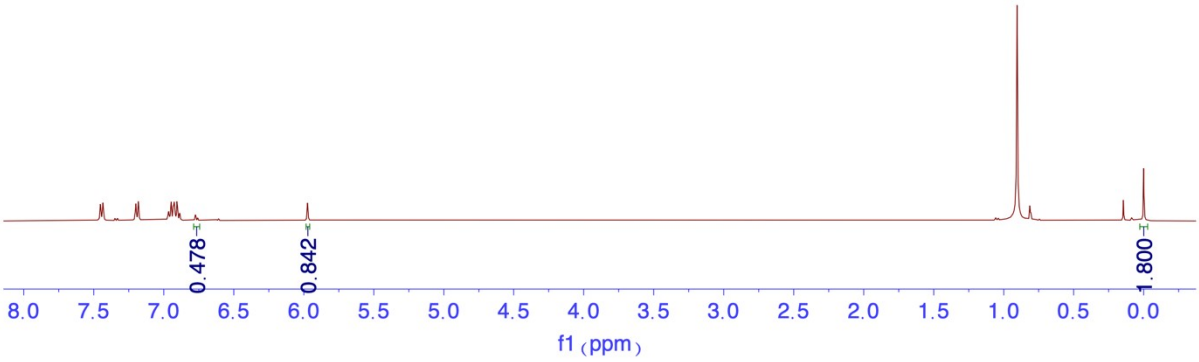
Figure S27. ^{1}H NMR overlay of catalytic hydroboration of 4-NO_2-Acetophenone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.64 (2H, d), 6.88 (2H, d), 4.99 (1H, s, OCH), 1.27 (3H, s), 1.09 (3H, s) and 1.04 (12H, s, C*H*$_3$ of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 (O-Bpin) ppm.

13a, 9-Fluorenone

t= 0.7h
c= 90%



Before addition of **3** and HBpin

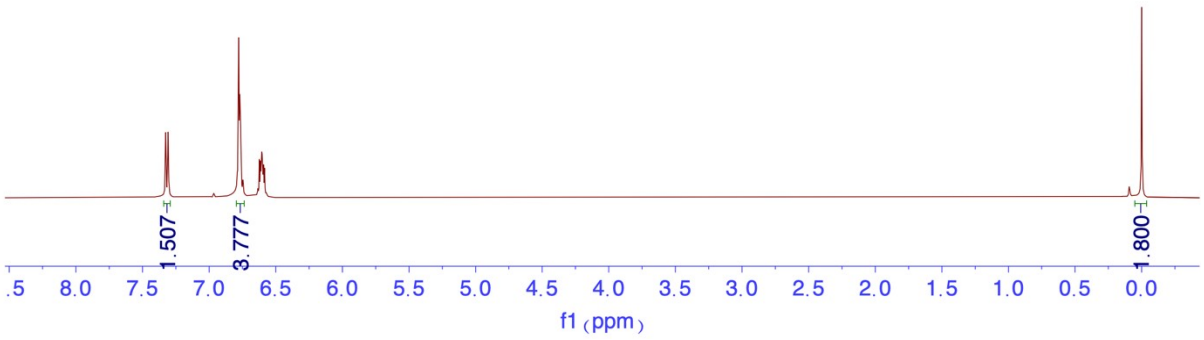


Figure S28. ^{1}H NMR overlay of catalytic hydroboration of 9-Fluorenone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

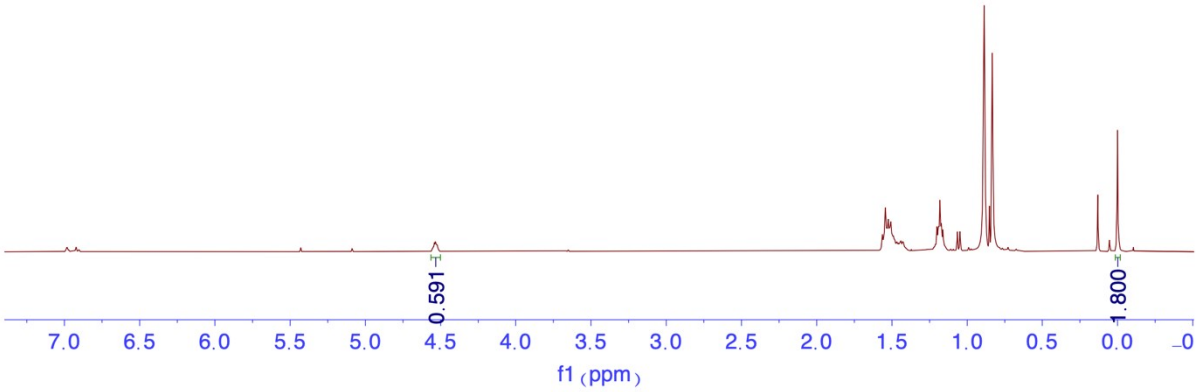
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.44 (2H, d), 7.18 (2H, d), 6.92 (4H, m), 5.97 (1H, s OCH), 0.90 (12H, s, CH_3 of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 23.5 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 145.1, 140.8, 129.1, 127.8, 125.5, 120.2, 83.2, 76.7, 24.8 (Ch_3 of Bpin) ppm.

14a, Cyclopentanone

t=24h
c=60%



Before addition of **3** and HBpin

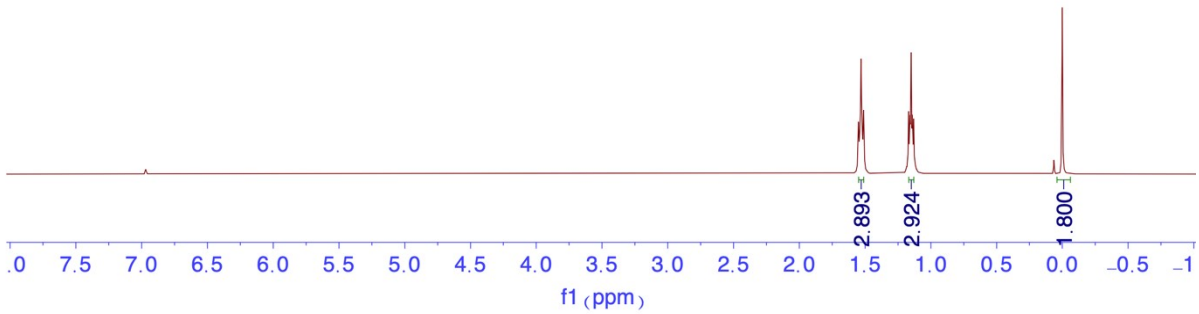


Figure S29. ^{1}H NMR overlay of catalytic hydroboration of cyclopentanone with HBpin using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

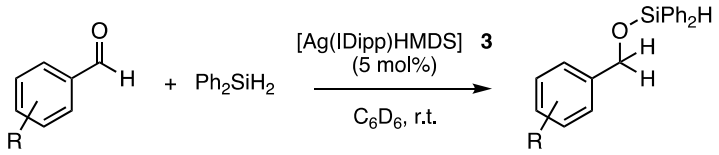
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 4.54 (1H, m), 1.59-1.38 (6H, m), 1.20-1.15 (2H, m), 0.86 (12H, s, CH_3 of Bpin)

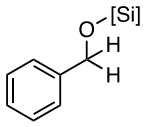
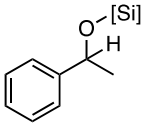
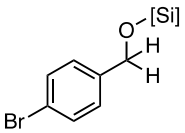
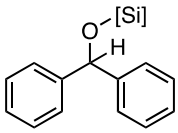
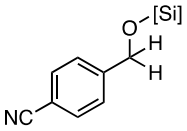
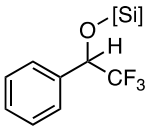
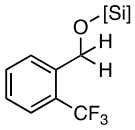
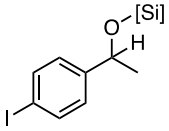
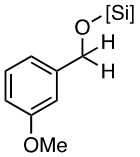
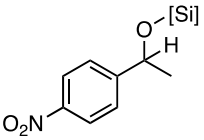
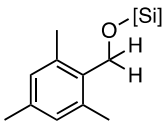
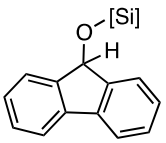
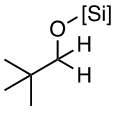
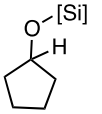
^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 ppm (O-Bpin)

Catalytic hydrosilylation using 3

Table S3: Carbonyl hydrosilylation using Ph_2SiH_2, catalysed by [Ag(IDipp)HMDS]

Table S3. Hydrosilylation of carbonyls catalysed by **3**

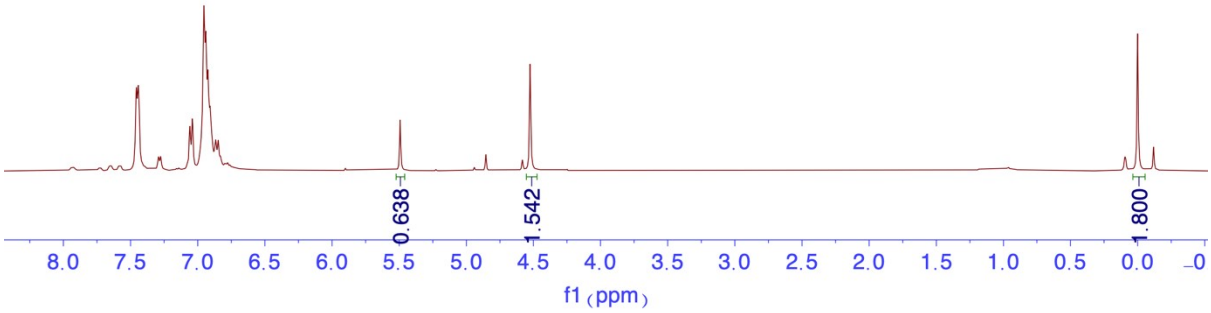


Entry	Product	3	Entry	Product	3
1b		0.5h 95%	**8b**		24h <20%
2b		0.5h 99%[b,c]	**9b**		24h 96%
3b		1h 99% [b,c]	**10b**		1h 99%[b,c]
4b		0.25h 99%[b,c]	**11b**		24h <5%
5b		0.25h 99%	**12b**		2h 84%[b,c]
6b		0.7h 99%	**13b**		0.7h 93%
7b		3h 99%	**14b**		24h <5%

% values indicate % conversion of starting material [a] Reaction conditions: substrate (1 mmol), Ph_2SiH_2 (1.5 mmol), 5 mol% [Ag(Dipp)HMDS] (**3**) with 10 mol% internal standard hexamethylcyclotrisiloxane in C_6D_6 at room temperature. [b] conversion of substrate. [c] yield of corresponding alcohol product after reaction quench in C_6D_6.

1b, Benzaldehyde

t= 0.5h
c= 95%



Before addition of **3** and Ph_2SiH_2

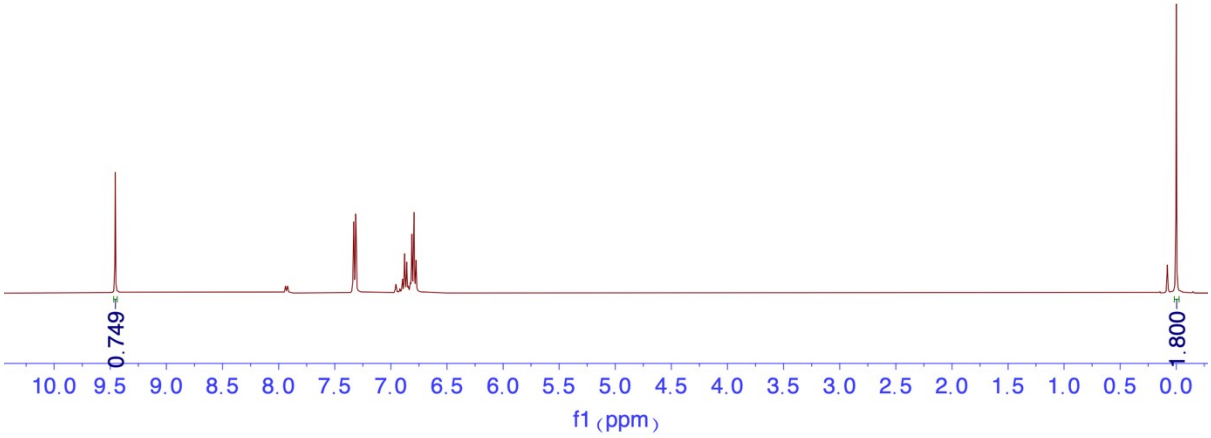


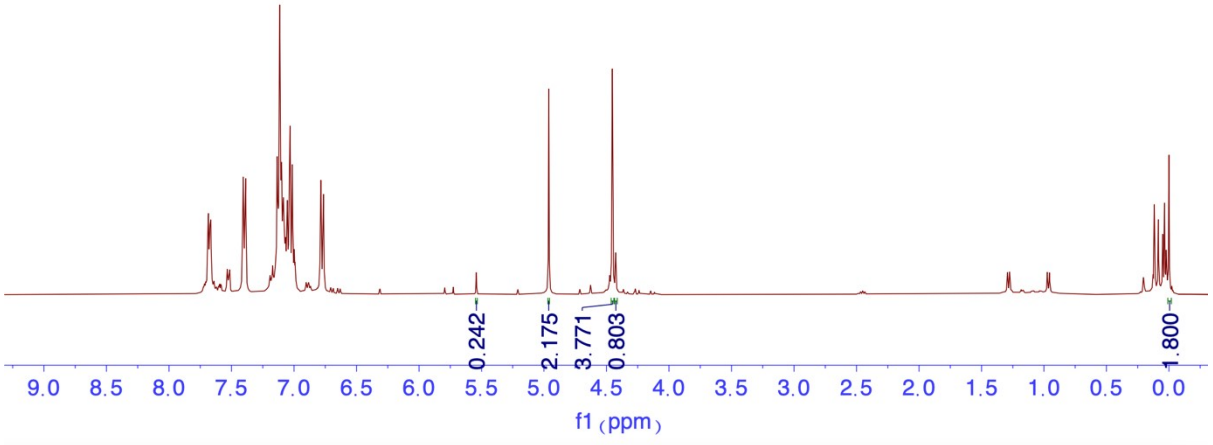
Figure S30. ^{1}H NMR overlay of catalytic hydrosilylation of benzaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.59 – 7.50 (4H, m), 7.15 (2H, m), 7.09 – 6.92 (9H, m), 5.59 (1H, s) and 4.62 (2H, s) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 140.6, 135.1, 134.2, 130.7, 128.6, 128.5, 127.5, 126.9 and 66.9 ppm.

2b, 4-Br-Benzaldehyde

t= 0.5h
c= 99%[b] 97%[c]



Before addition of **3** and Ph_2SiH_2

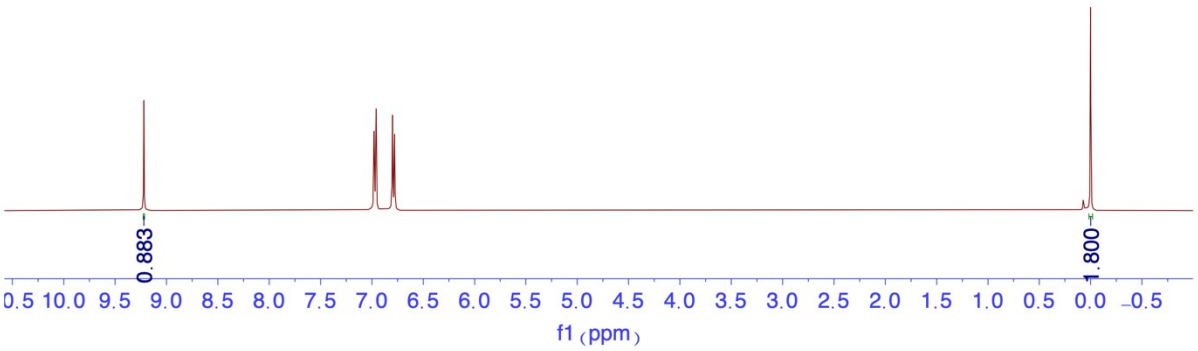


Figure S31. ^{1}H NMR overlay of catalytic hydrosilylation of 4-Br-Benzaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF.

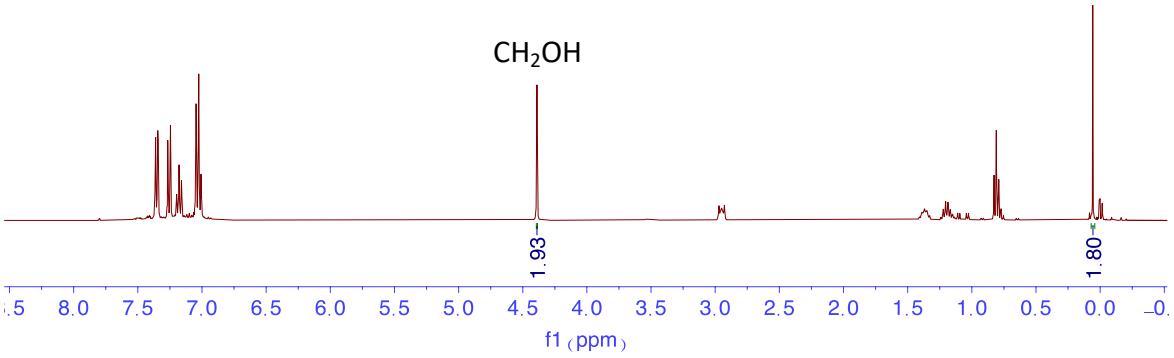
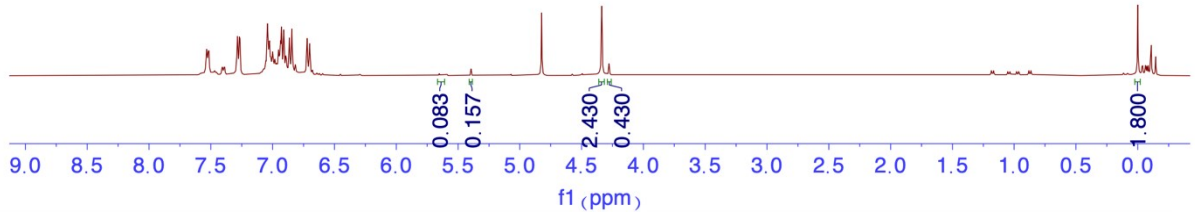


Figure S32. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-Br-benzaldehyde with Ph_2SiH_2 using **3** (5 mol%) in $CDCl_3$ at 300K.

3b, 4-CN-Benzaldehyde

t= 1h
c= 99%[b] 60%[c]



Before addition of **3** and Ph_2SiH_2

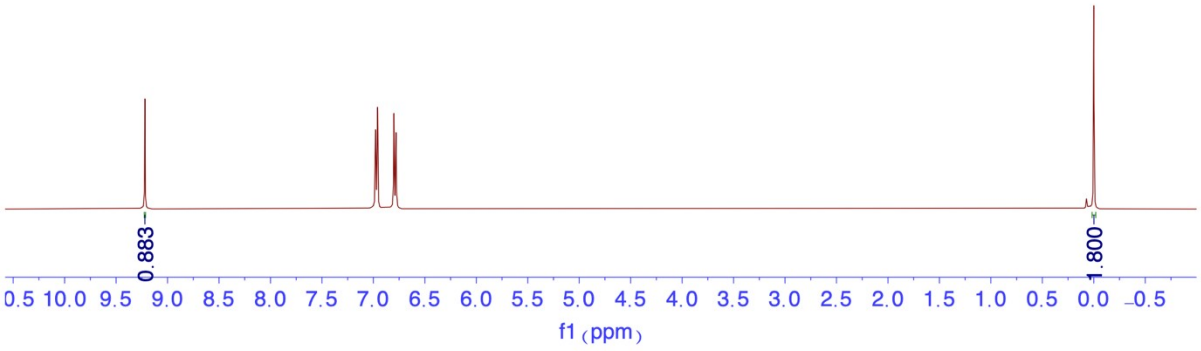


Figure S33. ^{1}H NMR overlay of catalytic hydrosilylation of 4-CN-Benzaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF.

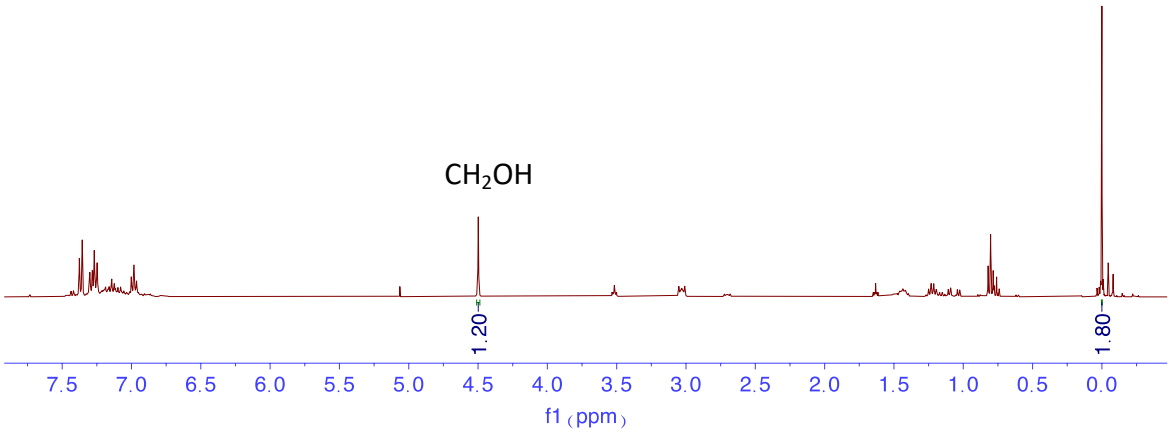
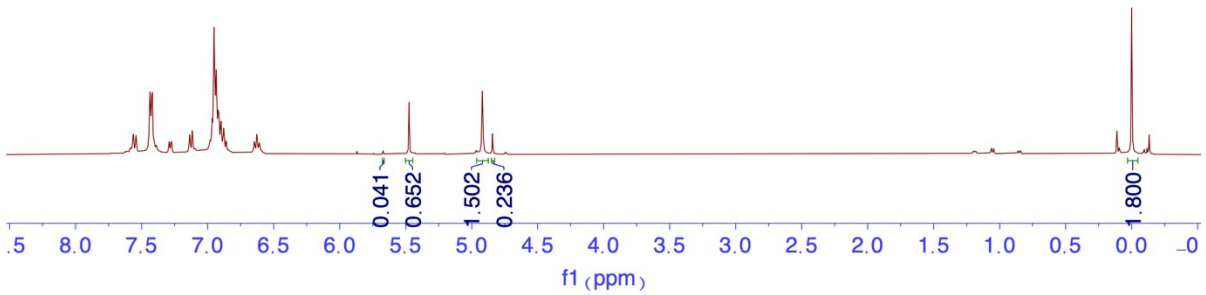


Figure S34. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-CN-benzaldehyde with Ph_2SiH_2 using **3** (5 mol%) in $CDCl_3$ at 300K.

4b, 2-CF_3-Benzaldehdye

t= 0.25h
c=99%[b] 94%[c]



Before addition of **3** and Ph_2SiH_2

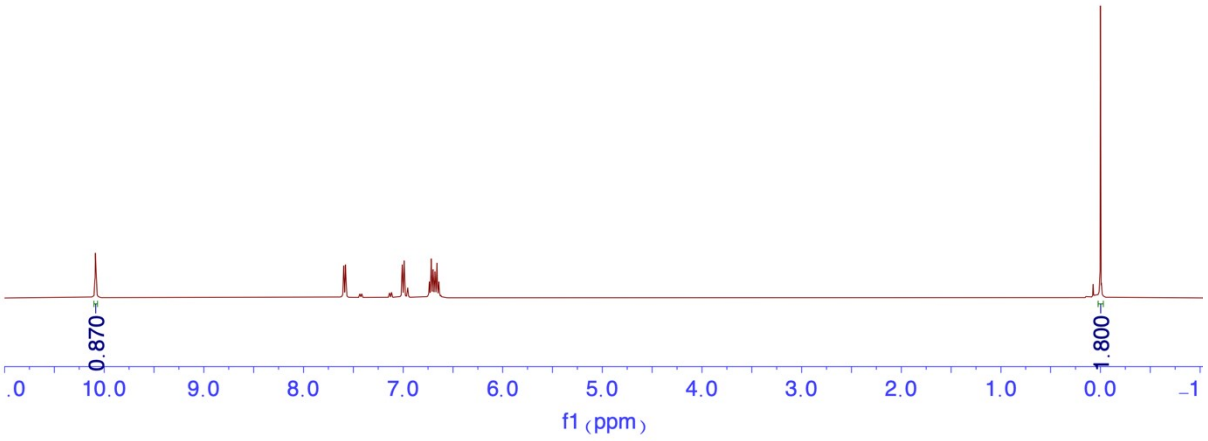


Figure S35. ^1H NMR overlay of catalytic hydrosilylation of 2-CF_3-Benzaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF.

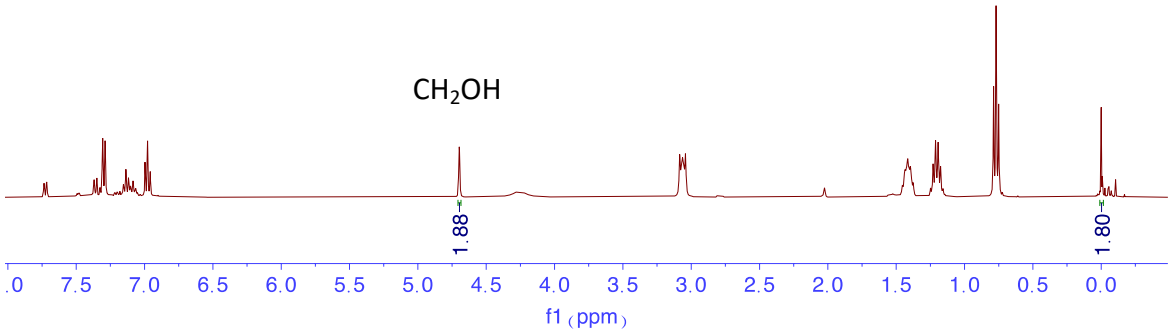
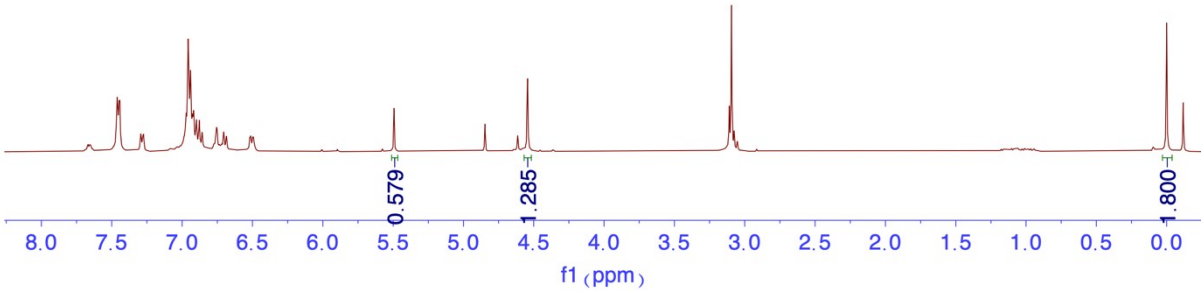


Figure S36. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 2-CF_3-benzaldehyde with Ph_2SiH_2 using **3** (5 mol%) in $CDCl_3$ at 300K.

5b, 3-OMe-Benzaldehyde

t= 0.25h
c= 99%



Before addition of **3** and Ph_2SiH_2

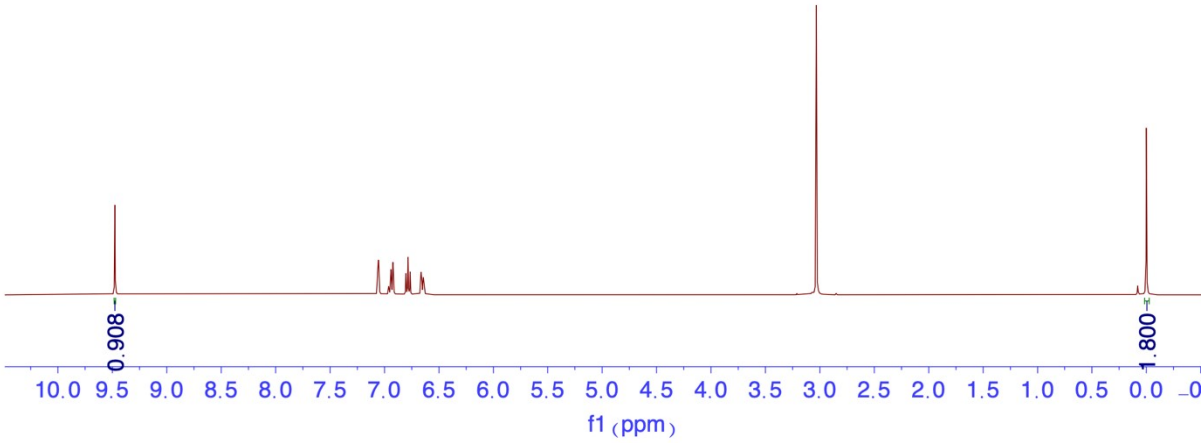


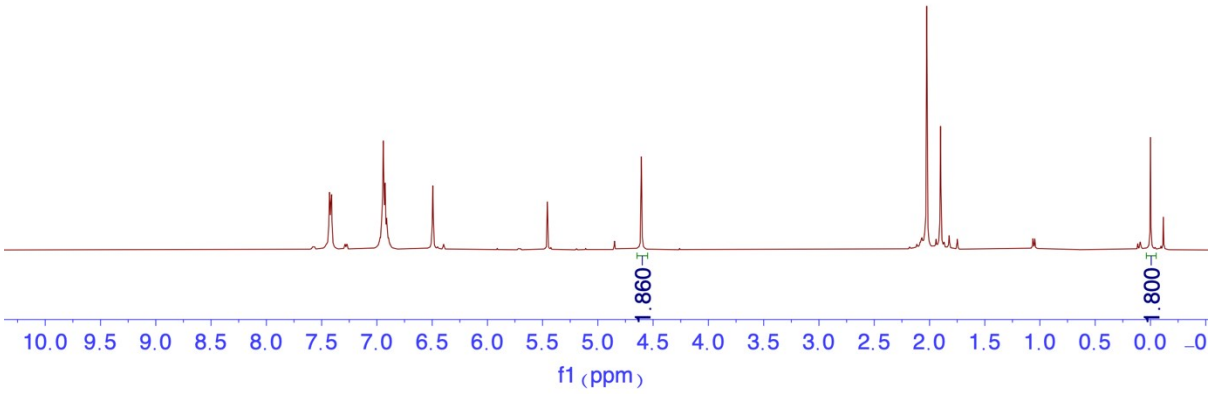
Figure S37. ^{1}H NMR overlay of catalytic hydrosilylation of 3-OMe-Benzaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.49-7.25 (4H, m), 7.02-6.89 (7H, m), 6.75 (1H, br s), 5.46 (1H, s, Si-H), 4.52 (2H, s, CH_2), 3.09 (3H, s, OCH_3),

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 160.2, 142.3, 135.1, 134.2, 130.7, 129.6, 128.4, 119.1, 112.3, 66.7, 54.5

6b, Mesitaldehyde

t= 0.7h
c=99%



Before addition of **3** and Ph_2SiH_2

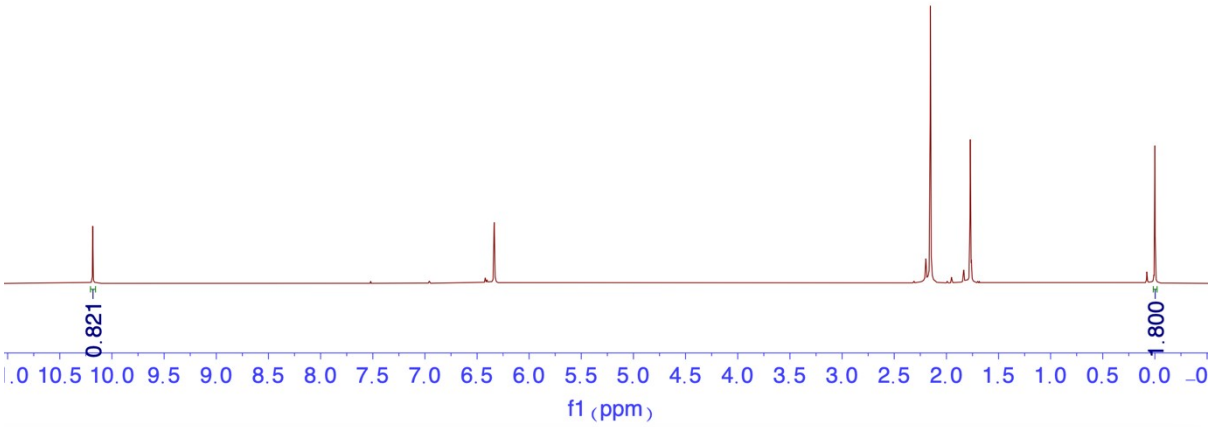


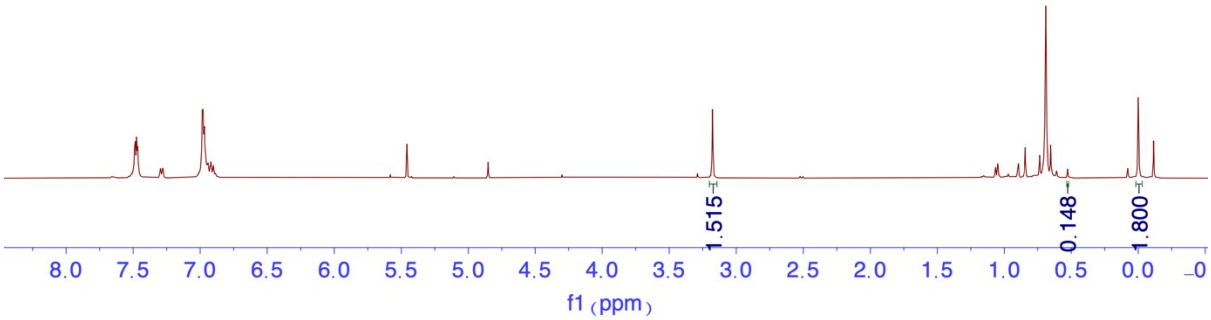
Figure S38. ^{1}H NMR overlay of catalytic hydrosilylation of mesitaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ d 7.45 – 7.39 (4H, m), 6.98 – 6.88 (6H, m), 6.49(2H, s), 5.45 (1H, s, Si-H), 2.02 (6H, s) and 1.90 (3H,s) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 137.6, 137.3,135.0, 134.6, 133.4, 130.5, 129.3, 128.2, 61.4, 21.2 and 19.4 ppm.

7b, *t*Butylaldehyde

t= 3h
c= 99%



Before addition of **3** and Ph_2SiH_2

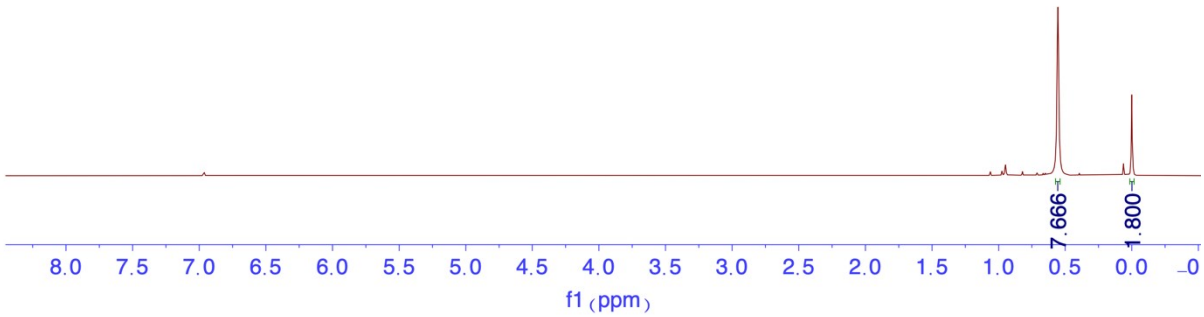
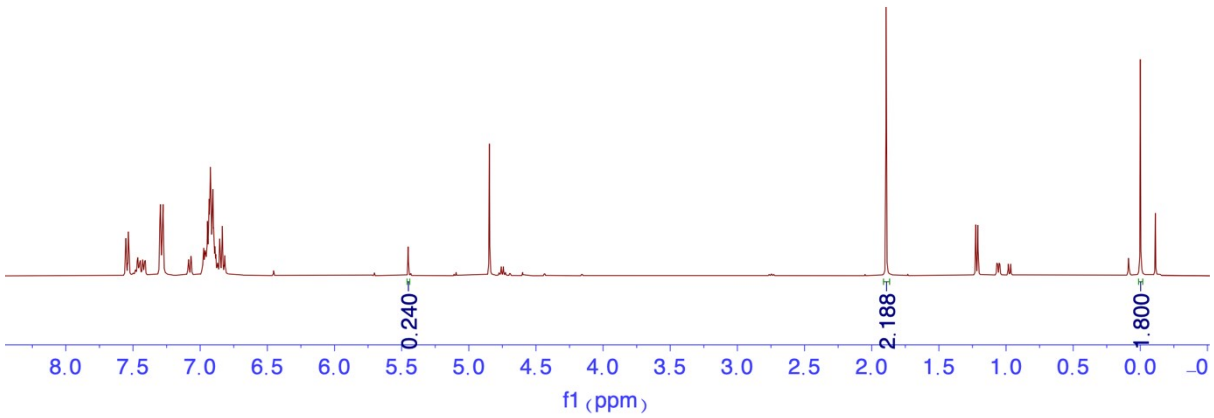


Figure S39. ^{1}H NMR overlay of catalytic hydrosilylation of *t*Butylaldehyde with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.48-7.25 (4H, m), 7.02-6.88 (6H, m), 5.44 (1H, s, SiH), 3.16 (1H,s), 0.68 (9H, s)

8b, Acetophenone

t= 24h,
c=<20%



Before addition of **3** and Ph_2SiH_2

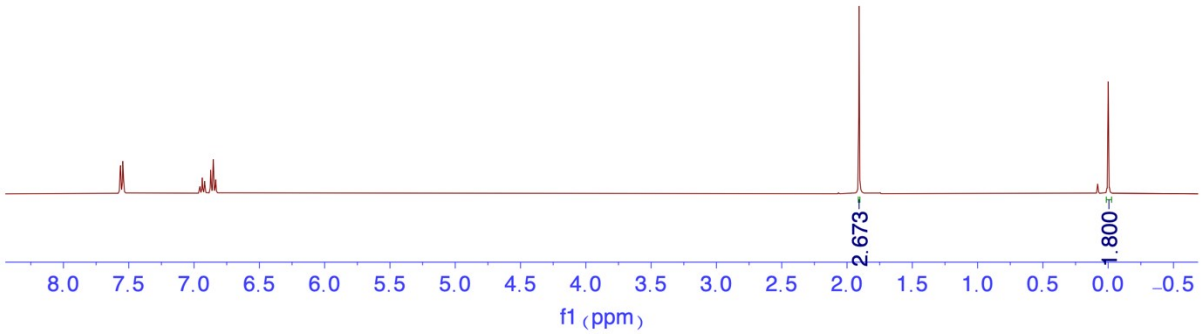
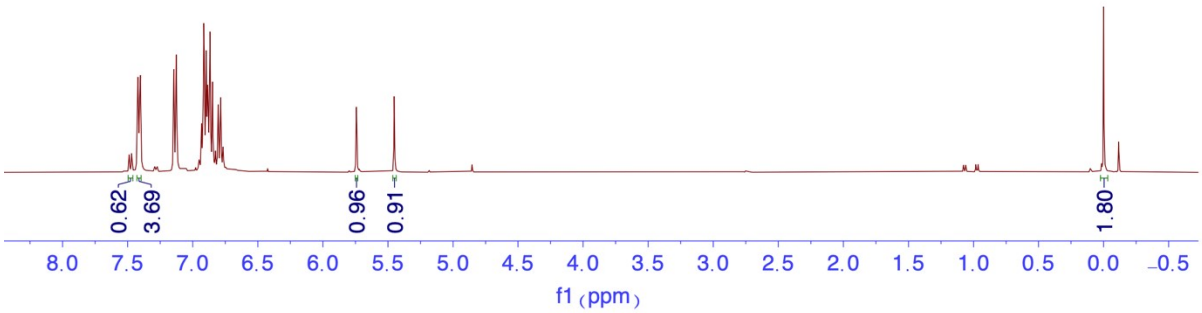


Figure S40. ^1H NMR overlay of catalytic hydrosilylation of acetophenone with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

9b, Benzophenone

t= 24h
c=96%



Before addition of **3** and Ph_2SiH_2

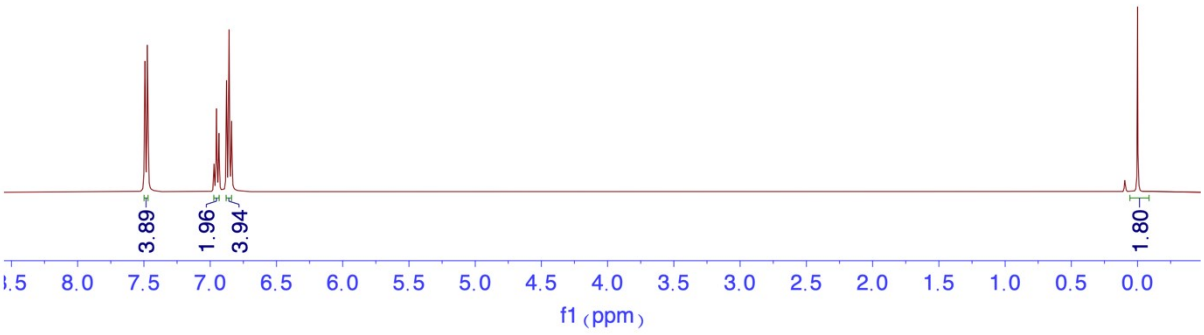
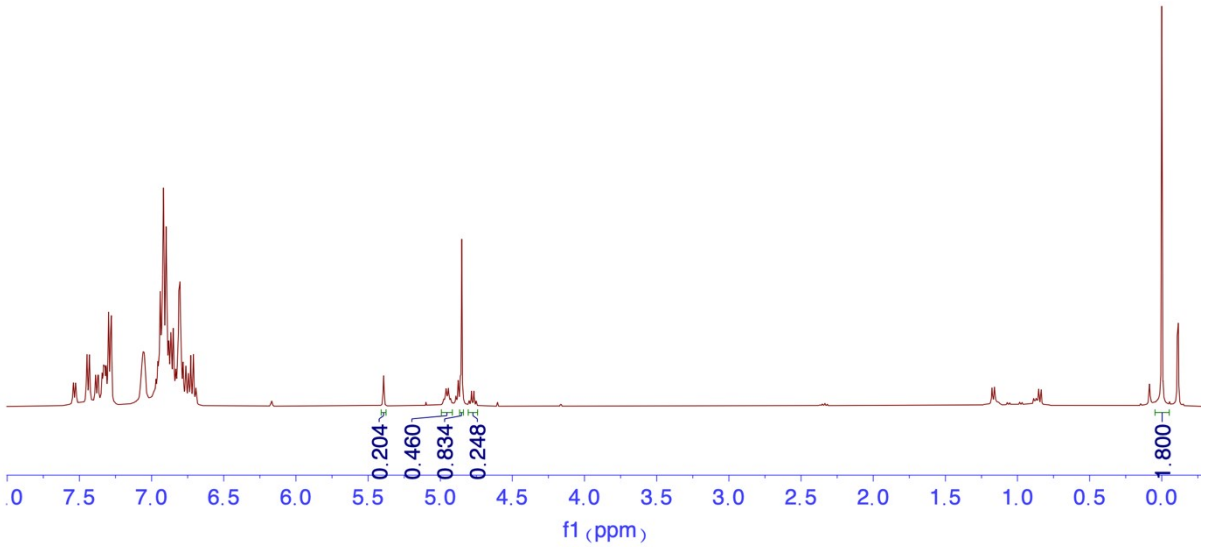


Figure S41. ^{1}H NMR overlay of catalytic hydrosilylation of benzophenone with Ph_2SiH_2using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.41 (4H, d), 7.13 (4H, m), 6.79 (2H, tt), 5.74 (1H, s, SiH), 5.45 (1H, s) ppm.

10b, 2,2,2-Trifluroacetophenone

t= 1h
c= 99%[b], 55%[c]



Before addition of **3** and Ph_2SiH_2

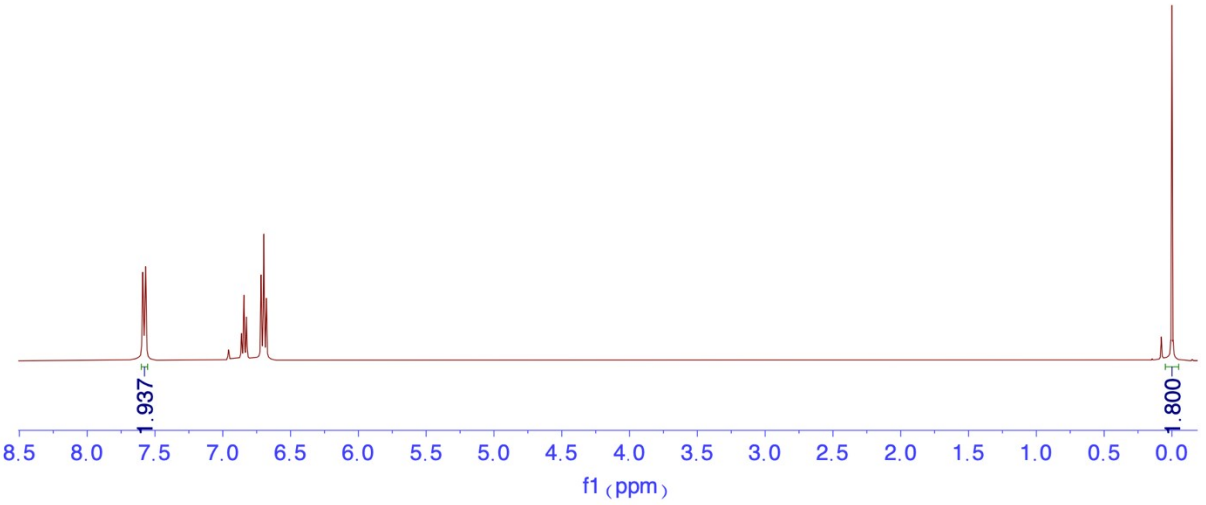


Figure S42. ^{1}H NMR overlay of catalytic hydrosilylation of 2,2,2-Trifluroacetophenone with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF.

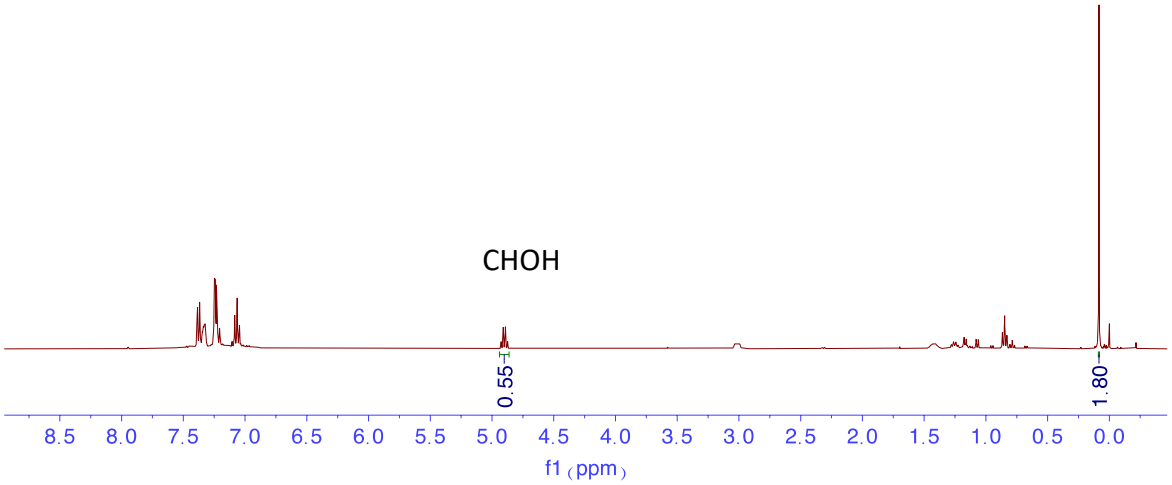
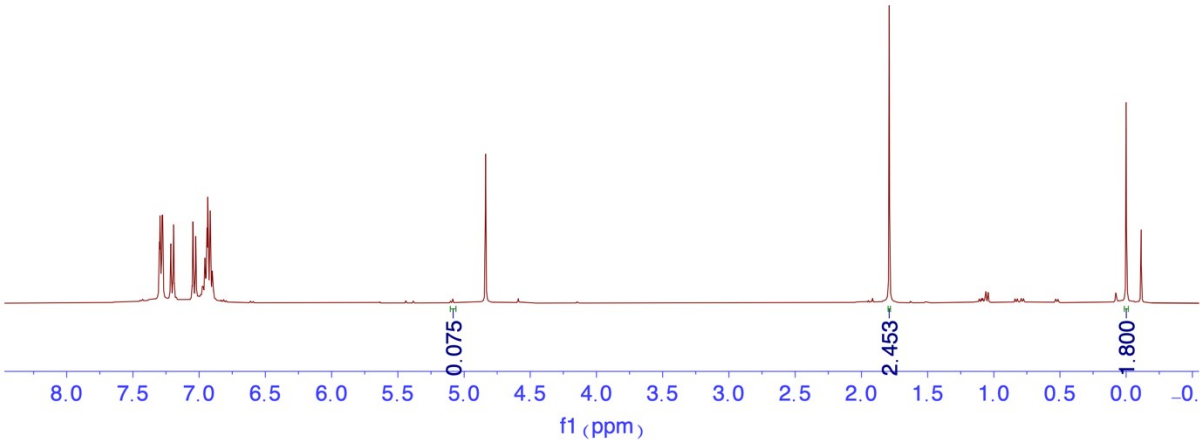


Figure S43. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 2,2,2-trifluroacetophenone with Ph_2SiH_2 using **3** (5 mol%) in $CDCl_3$ at 300K.

11b, 4-Iodoacetophenone

t= ≈24h
c=<5%



Before addition of **3** and Ph_2SiH_2

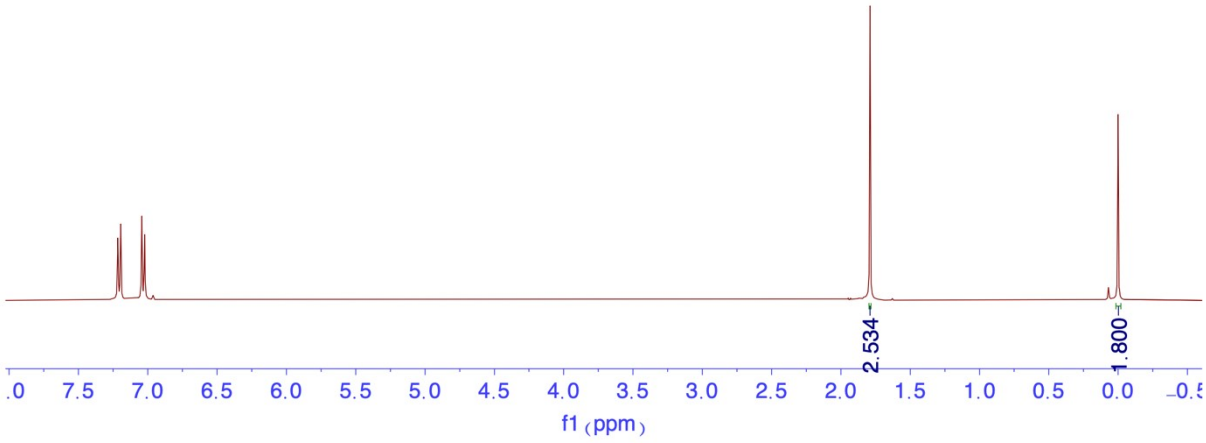
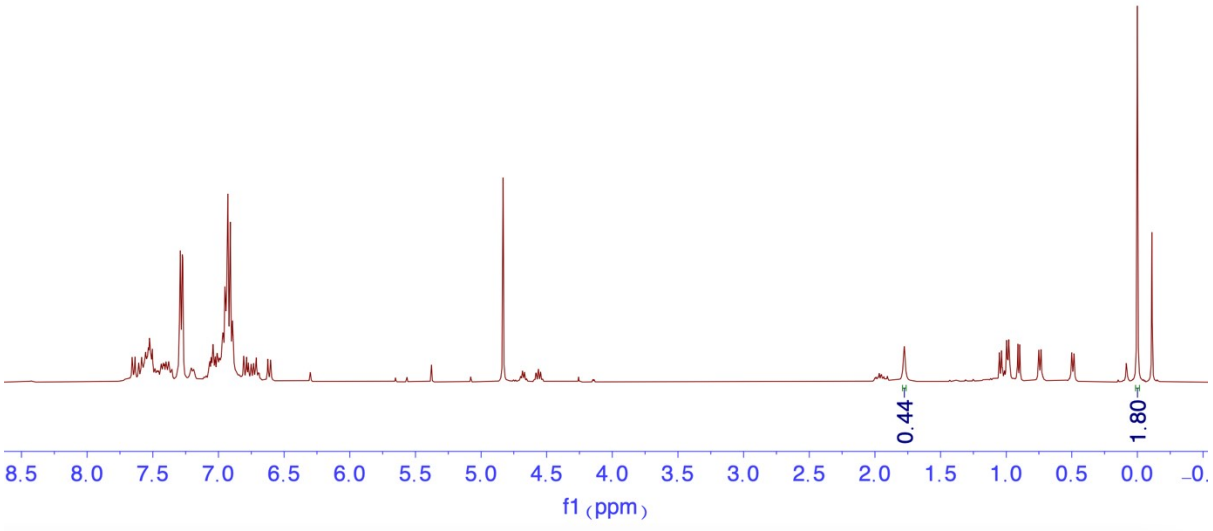


Figure S44. ^1H NMR overlay of catalytic hydrosilylation of 4-Iodoacetophenone with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

12b, 4-NO_2-Acetophenone

t= 2h
c= 84%[b] 68%[c]



Before addition of **3** and Ph_2SiH_2

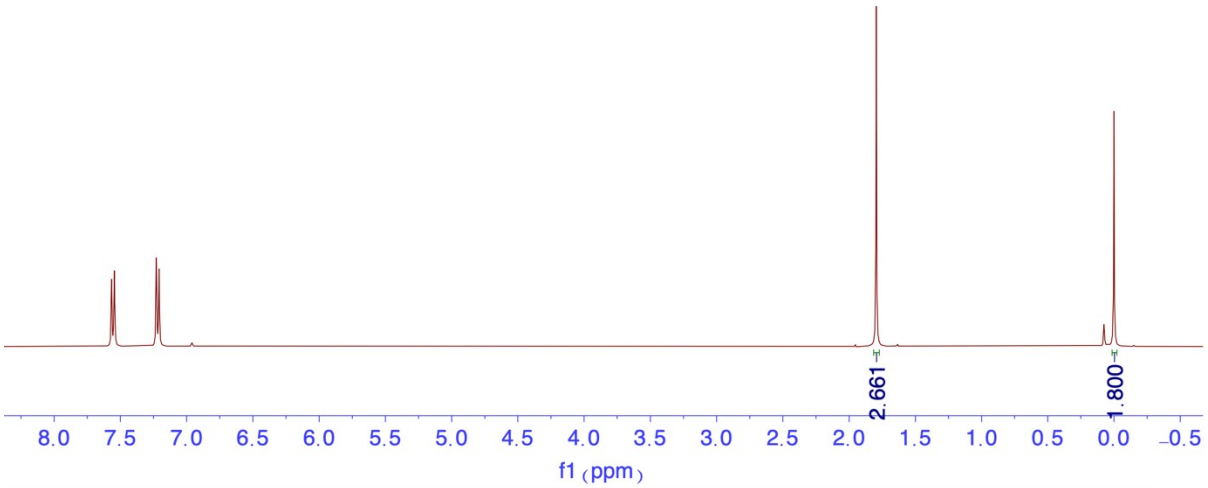


Figure S45. ^{1}H NMR overlay of catalytic hydrosilylation of 4-NO_2-Acetophenone with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

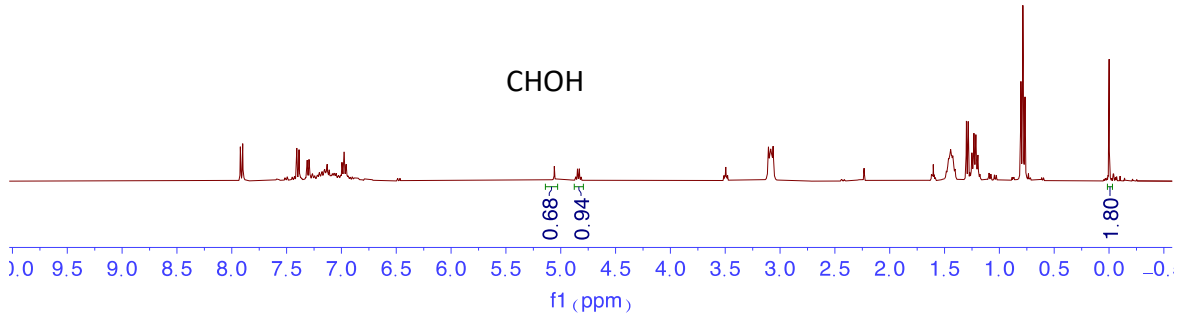
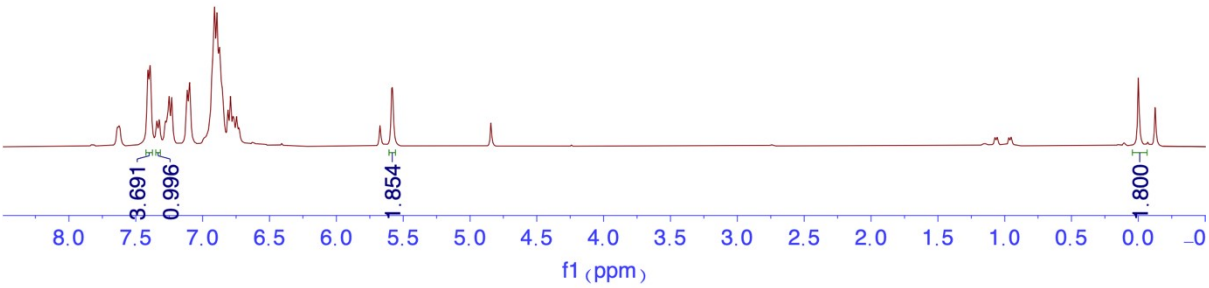


Figure S46. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-NO_2-acetophenone with Ph_2SiH_2 using **3** (5 mol%) in $CDCl_3$ at 300K.

13b, 9-Fluorenone

t= 0.7h
c= 93%



Before addition of **3** and Ph_2SiH_2

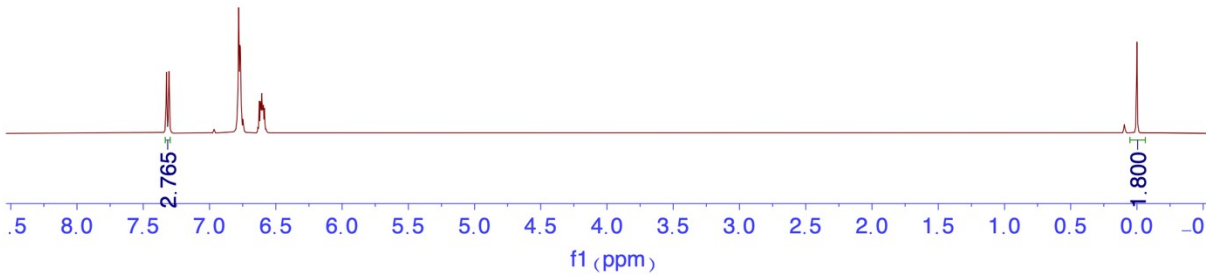


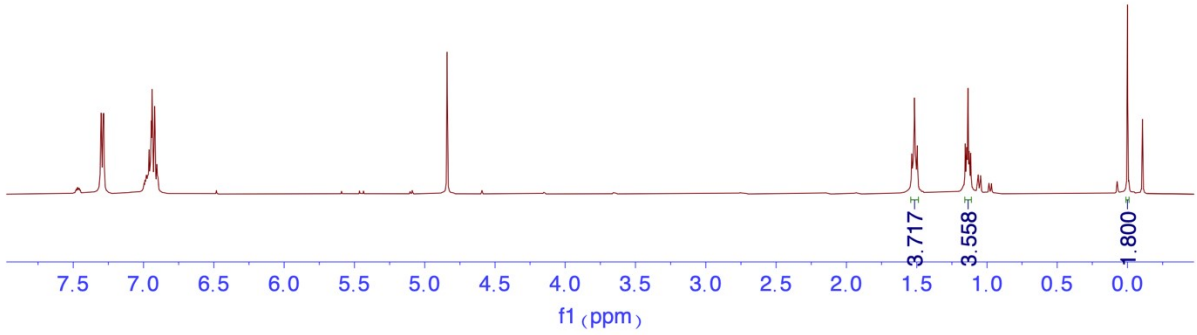
Figure S47. ^{1}H NMR overlay of catalytic hydrosilylation of 9-Fluorenone with Ph_2SiH_2using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.36 (4H, d, Ar-H), 7.24 (4H, d, Ar-H), 7.10 (2H, d, Ar-H), 6.98-6.70 (8H, m, Ar-H), 5.68-5.55 (2H, Si-H and O-CH)

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 140.7, 135.2, 134.6, 130.6, 129.0, 128.9, 125.9, 76.9 (CH_2) ppm

14b, Cyclopentanone

t= 24h
c= <5%



Before addition of **3** and Ph_2SiH_2

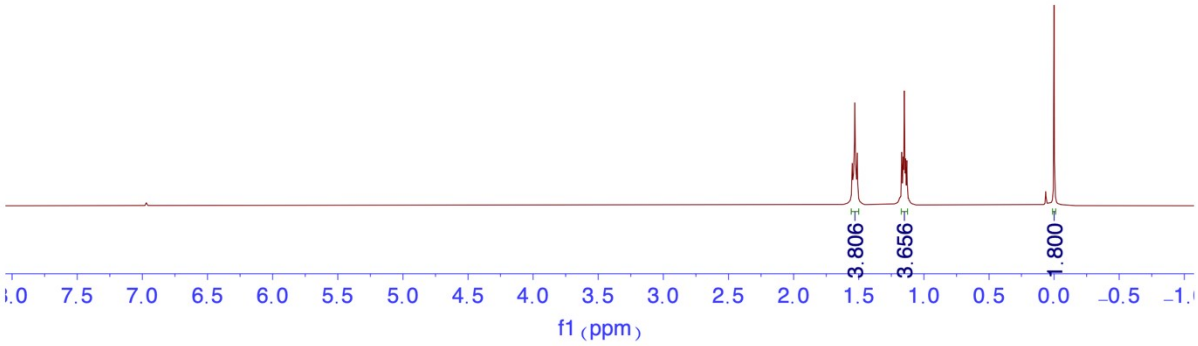
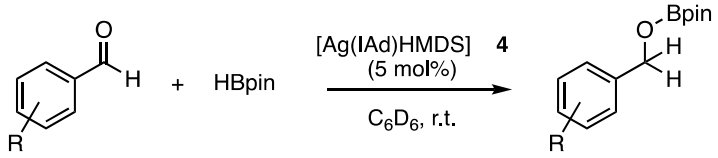


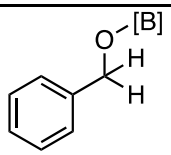
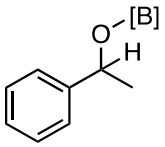
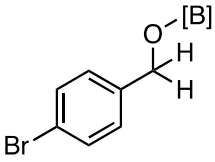
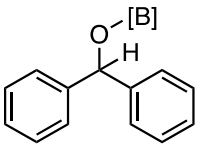
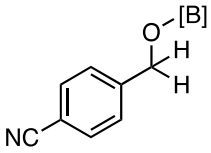
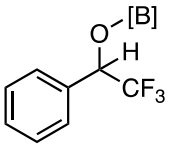
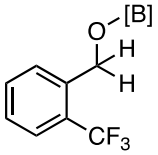
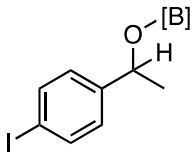
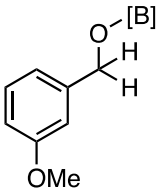
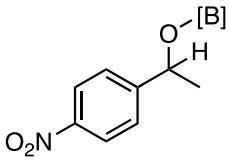
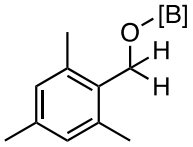
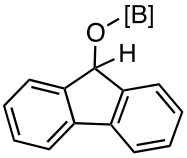
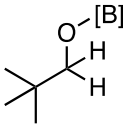
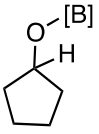
Figure S48. ^1H NMR overlay of catalytic hydrosilylation of cyclopentanone with Ph_2SiH_2 using **[Ag(IDipp)HMDS] 3** (5 mol%) in C_6D_6 at 300K

Catalytic hydroboration using 4

Table S4: Carbonyl hydroboration using HBpin, catalysed by [Ag(IAd)HMDS]

Table S4. Hydroboration of carbonyls catalysed by **4**

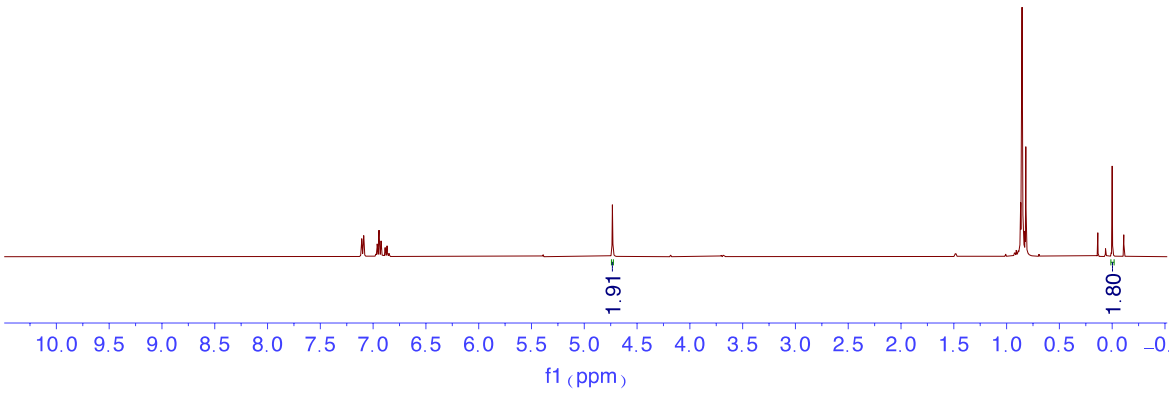


Entry	Product	4	Entry	Product	4
1a		1h 95%	**8a**		24h 50%
2a		0.25h 99%	**9a**		5h 50%
3a		0.25h 99%	**10a**		0.2h 90%
4a		4h 51%	**11a**		24h 80%
5a		6.5h 87%	**12a**		0.7h 99%
6a		24h 90%	**13a**		3.5h 70%
7a		2.5h 98%	**14a**		9h 60%

% values indicate % conversion of starting material [a] Reaction conditions: substrate (1 mmol), HBpin (1.5 mmol), 5 mol% [Ag(IAd)HMDS] (**4**) with 10 mol% internal standard hexamethylcyclotrisiloxane in C_6D_6 at room temperature.

1a, Benzaldehyde

t= 1h
c= 95%



Before addition of **4** and HBpin

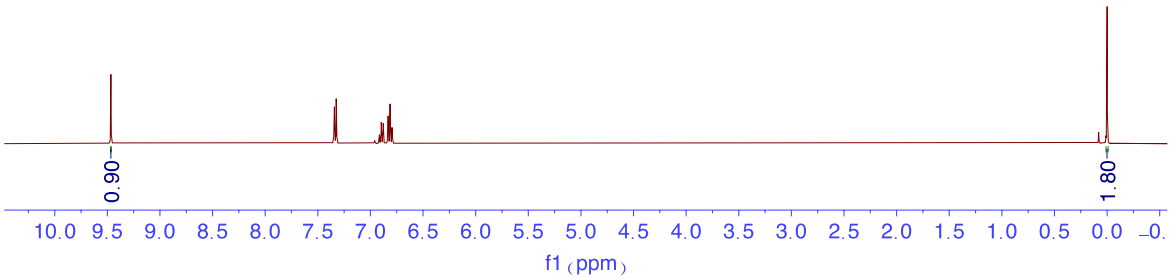


Figure S49. ^{1}H NMR overlay of catalytic hydroboration of benzaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

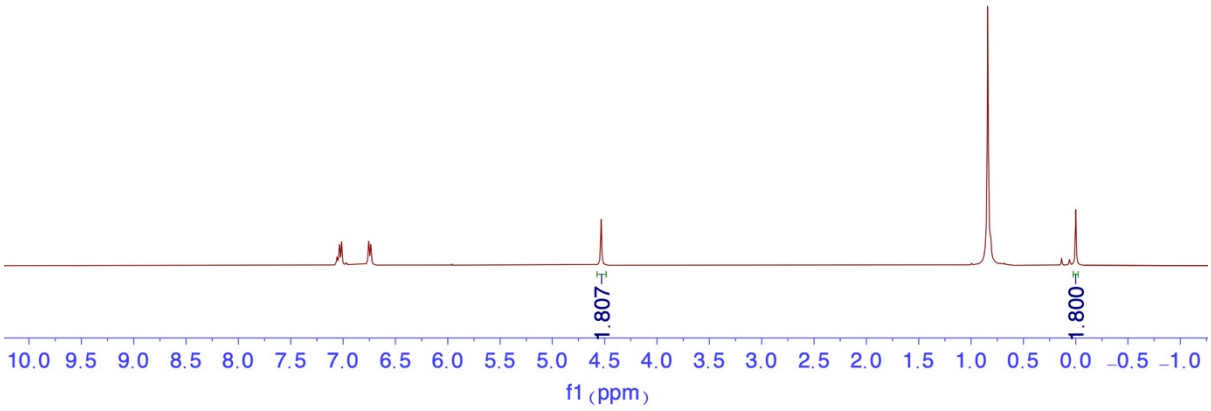
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.31 (2H, d), 7.16 (2H, t), 7.08 (1H, m), 4.94 (2H, s) and 1.07 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.9 ppm (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 139.0 (quat-C), 127.6, (Ar-C), 126.6 (Ar-C), 126.1 (Ar-C), 82.0 (C of Bpin), 65.9 (C-H) and 23.9 (CH_3 of Bpin) ppm.

2a, 4-Br-Benzaldehyde

t= 0.25h
c= 99%



Before addition of **4** and HBpin

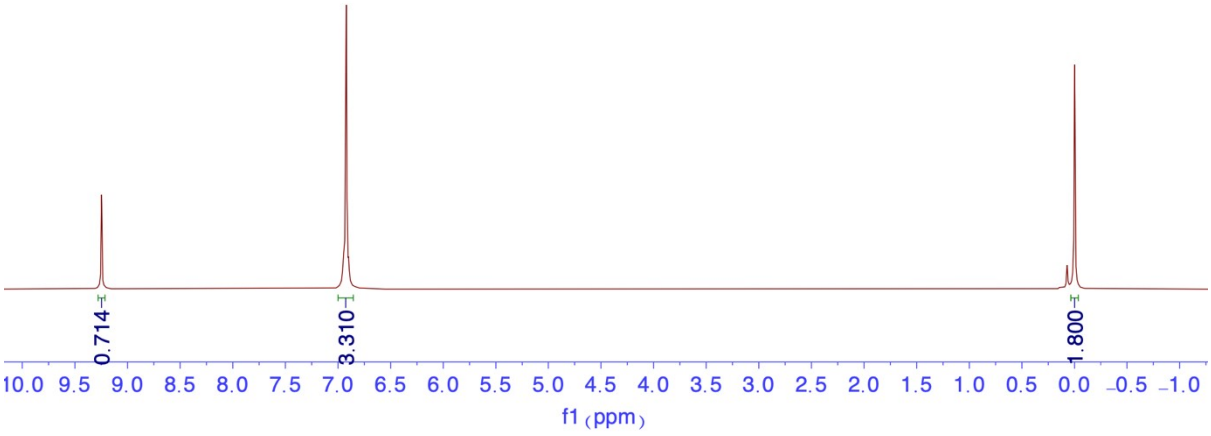


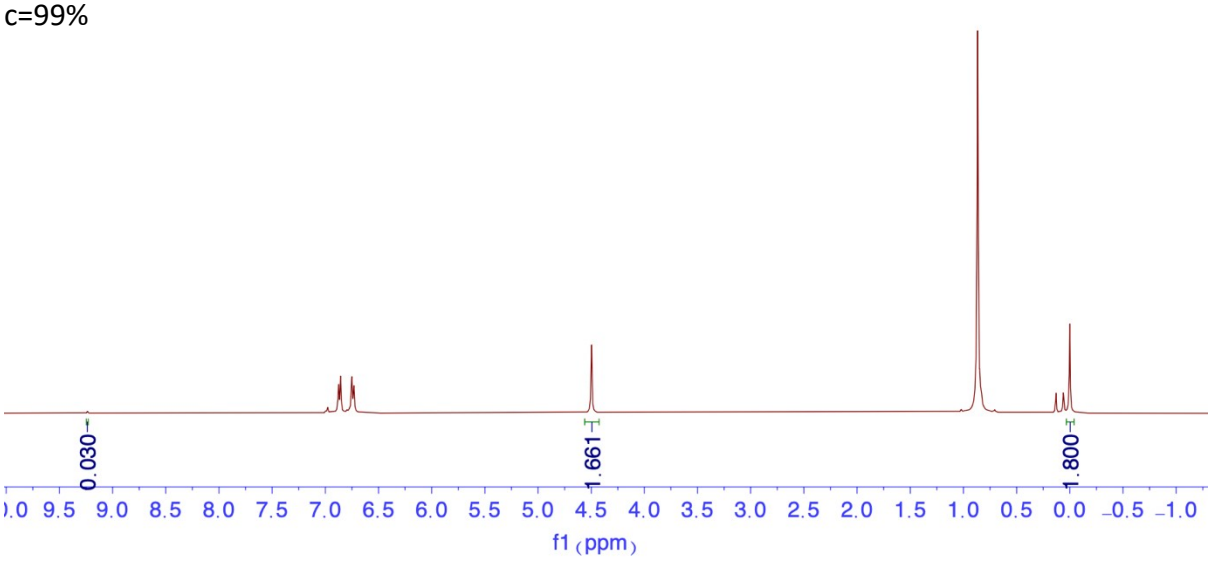
Figure S50. ^{1}H NMR overlay of catalytic hydroboration of 4-Br-Benzaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.05 (2H, t), 6.74 (2H, d), 7.06 (1H, m), 4.51 (2H, s) and 0.84 (12H, s, CH_3 of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.6 ppm (O-Bpin)

3a, 4-CN-Benzaldehyde

t= 0.25h
c=99%



Before addition of **4** and HBpin

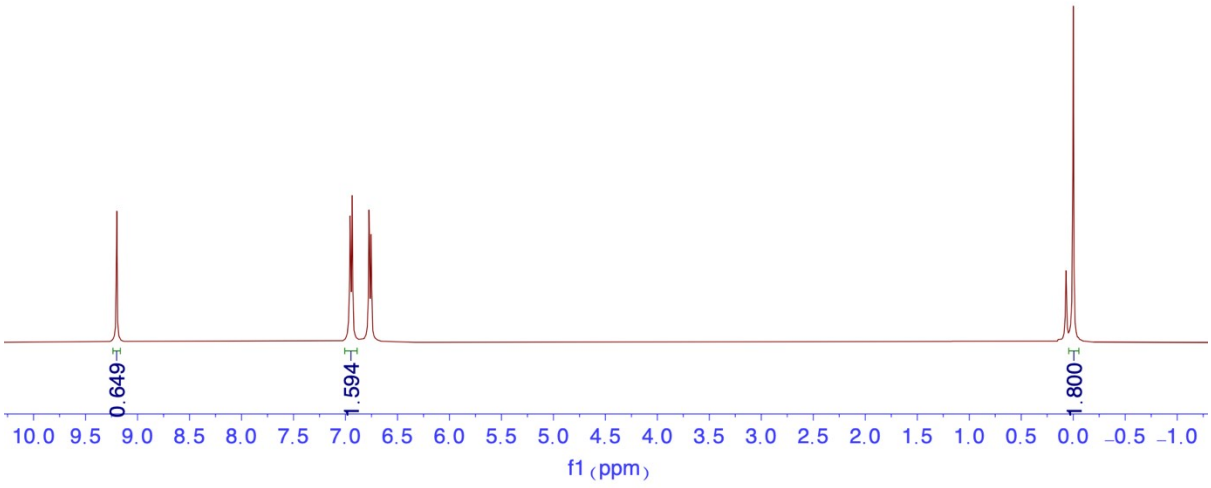


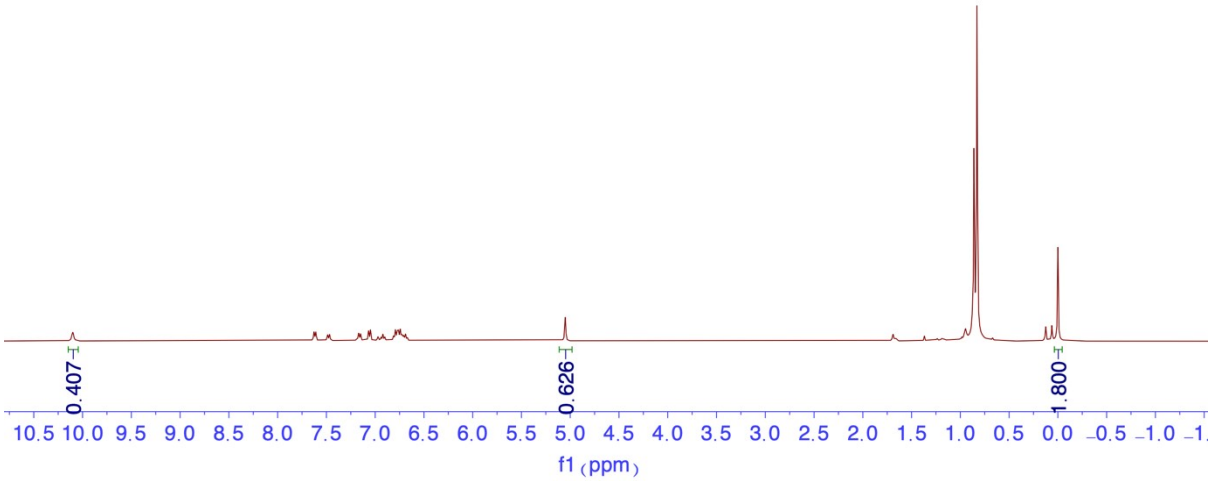
Figure S51. ^{1}H NMR overlay of catalytic hydroboration of 4-CN-Benzaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 6.85 (2H, d), 6.75 (2H, d), 4.50 (2H, s), 0.85 (12H, s, CH_3-of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.6 ppm (O-Bpin)

4a, 2-CF_3-Benzaldehdye

t= 4h
c= 51%



Before addition of **4** and HBpin

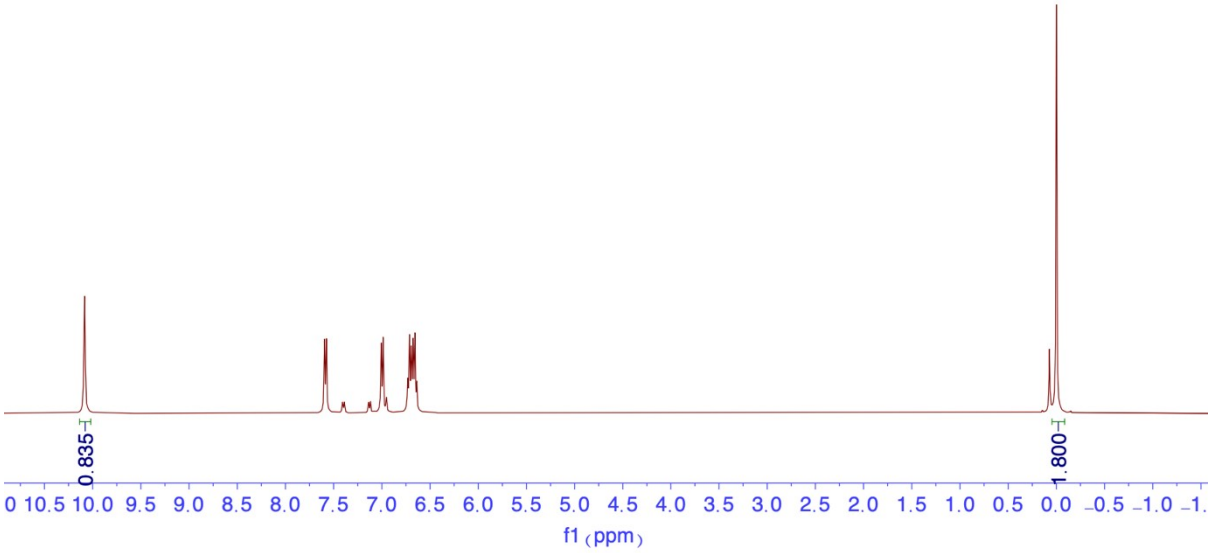


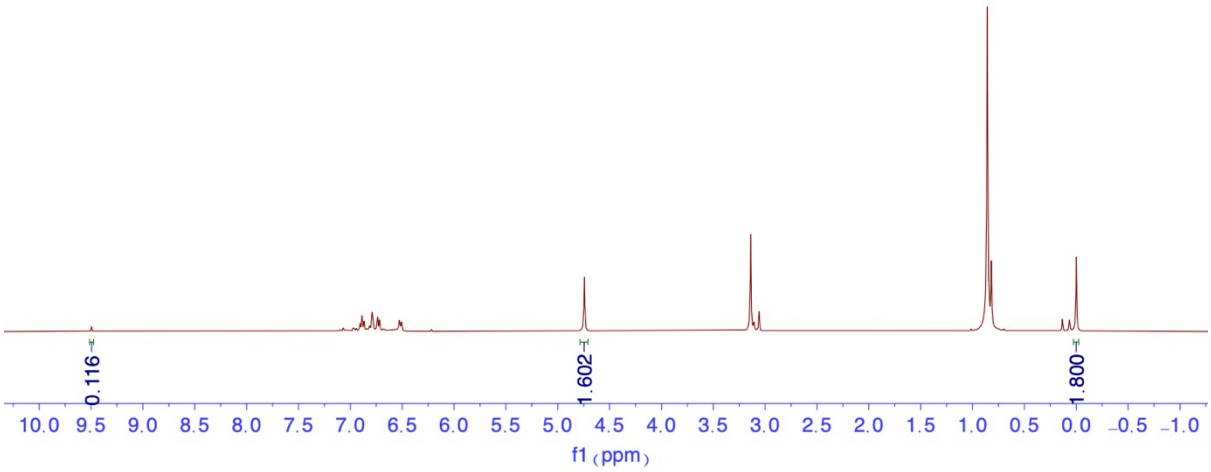
Figure S52. ^{1}H NMR overlay of catalytic hydroboration of 2-CF_3-Benzaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.64-7.46 (1H, m), 7.20-7.02 (1H, m), 6.93 (1H, t), 6.75 (1H, t), 5.05 (2H, s), 0.82 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.6 (O-Bpin) ppm

5a, 3-OMe-Benzaldehyde

t= 6.5h
c= 87%



Before addition of **4** and HBpin

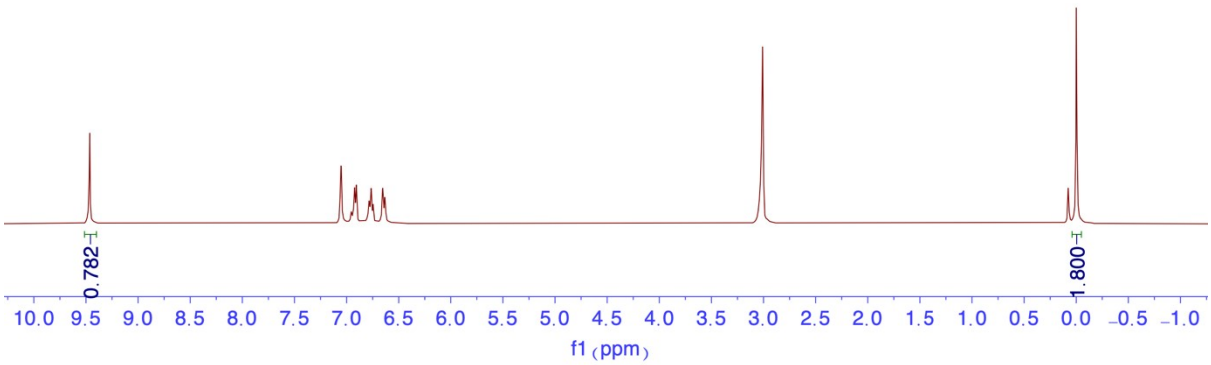


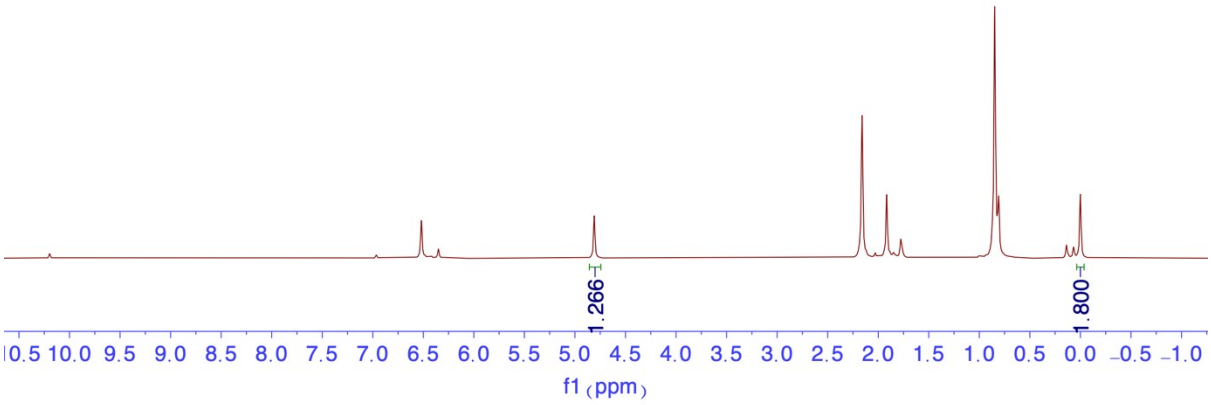
Figure S53. ^{1}H NMR overlay of catalytic hydroboration of 3-OMe-Benzaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 6.89 (1H, t), 6.78 (1H, m), 6.72 (1H, d), 6.51 (1H, dd), 4.52 (2H, s), 3.05 (3H, s), 0.85 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 ppm (O-Bpin)

6a, Mesitaldehyde

t= 24h
c= 90%



Before addition of **4** and HBpin

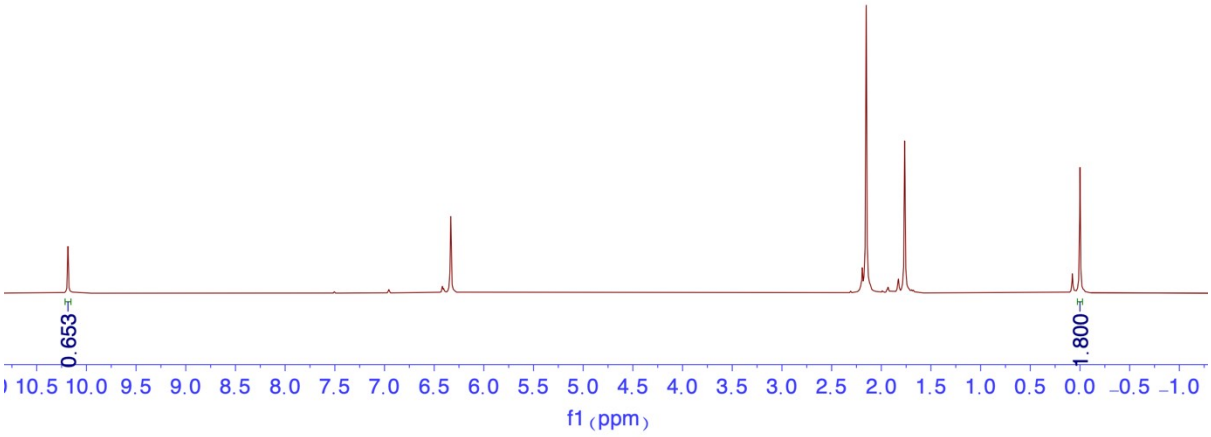


Figure S54. ^{1}H NMR overlay of catalytic hydroboration of mesitaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

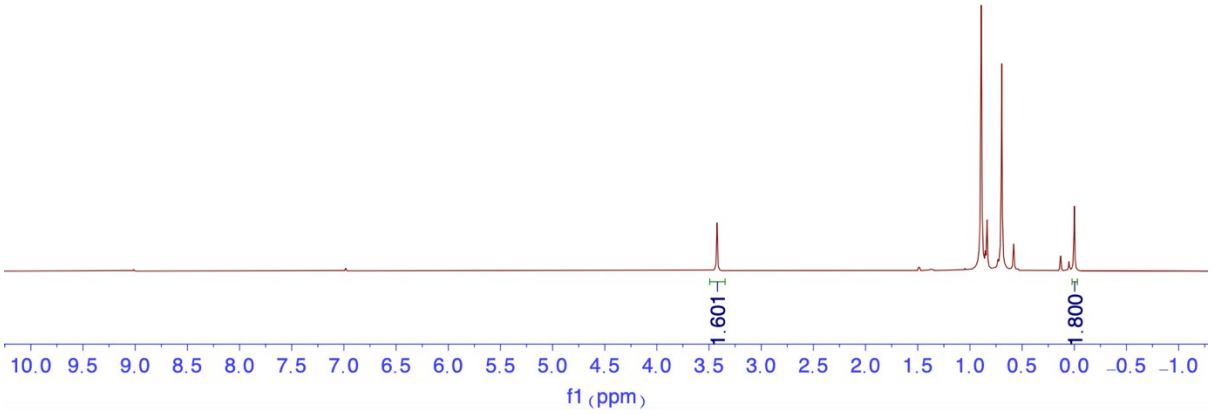
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 6.52 (2H, s), 4.81 (2H, s), 2.15 (6H, s), 1.91 (3H, s), 0.87 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.6 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 137.7, 132.7, 129.3, 82.5, 61.5, 24.5, 20.8, 19.4 ppm.

7a, *t*Butylaldehyde

t=2.5h
c=98%



Before addition of **4** and HBpin

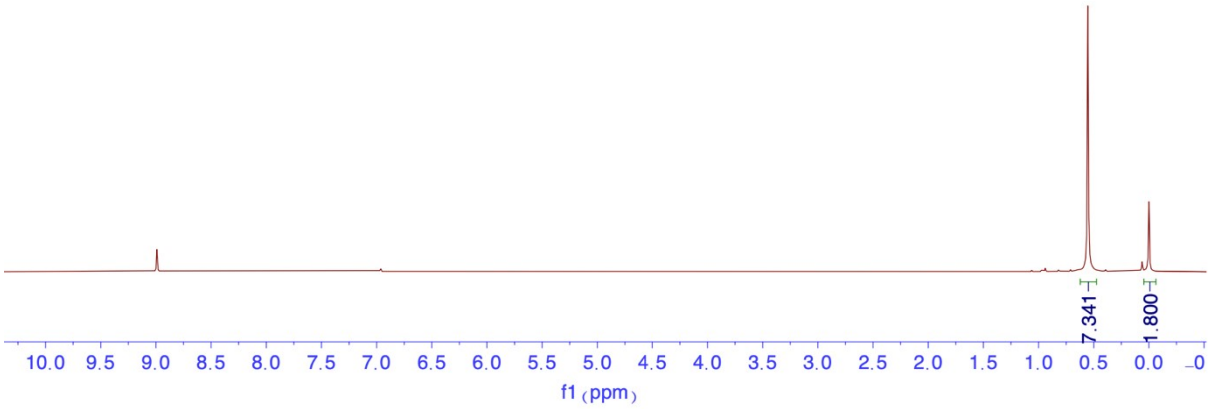


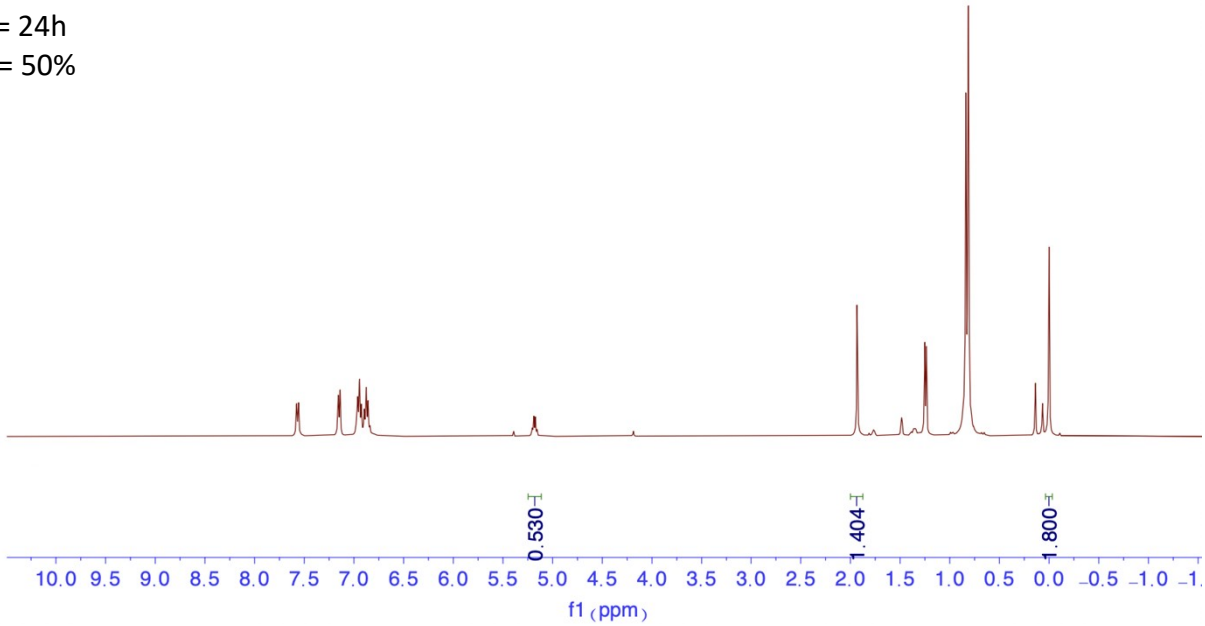
Figure S55. ^{1}H NMR overlay of catalytic hydroboration of *t*Butylaldehyde with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 3.59 (2H, s), 1.04 (12H, s), 0.82 (9H, s) ppm

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.6 ppm (O-Bpin) ppm

8a, Acetophenone

t= 24h
c= 50%



Before addition of **4** and HBpin

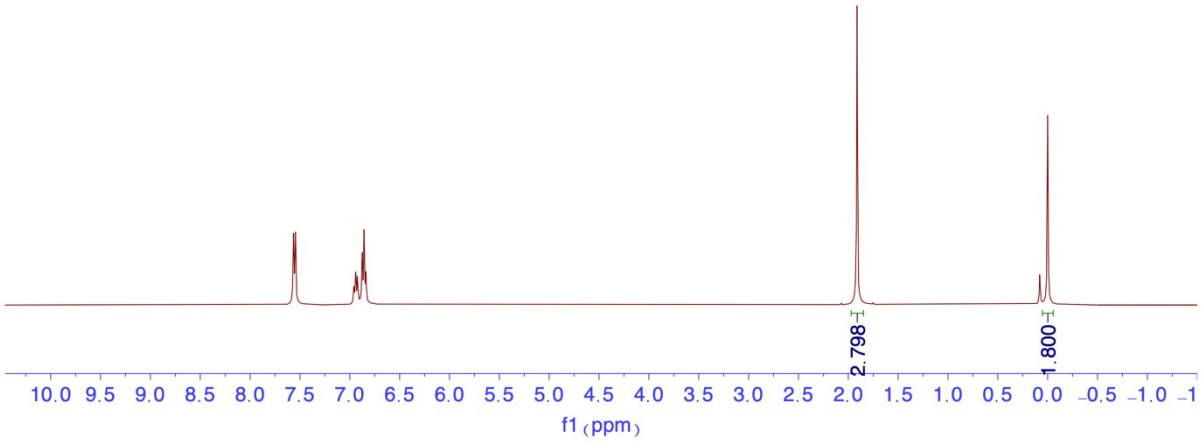


Figure S56. ^{1}H NMR overlay of catalytic hydroboration of acetophenone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

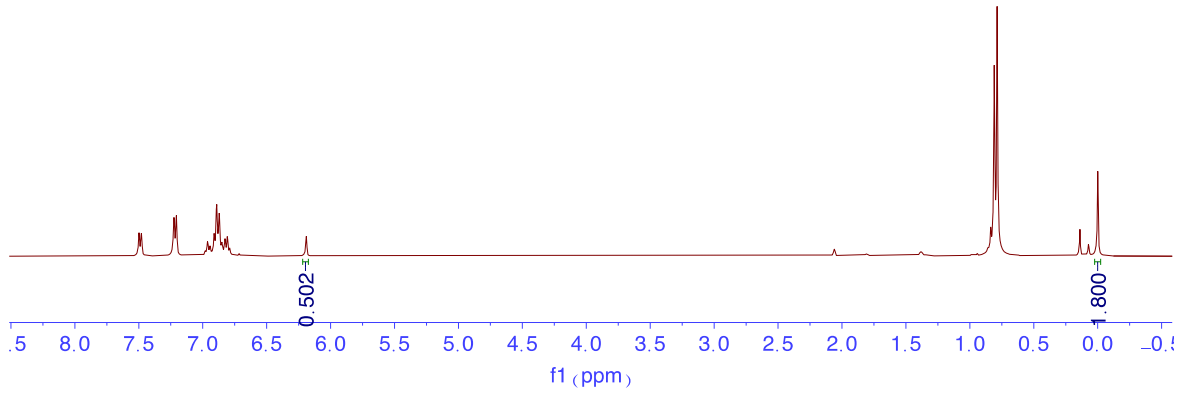
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.56 (1H, d), 7.15 (1H, d), 6.98-6.81 (2H, m), 6.90-6.84 (1H, m), 5.18 (1H, q), 1.21 (3H, s) 0.81 (12H, s) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 144.4, 128.5, 127.3, 125.6, 82.5, 72.7, 24.9 and 24.6 ppm.

9a, Benzophenone

t= 5h,
c= 50%



Before addition of **4** and HBpin

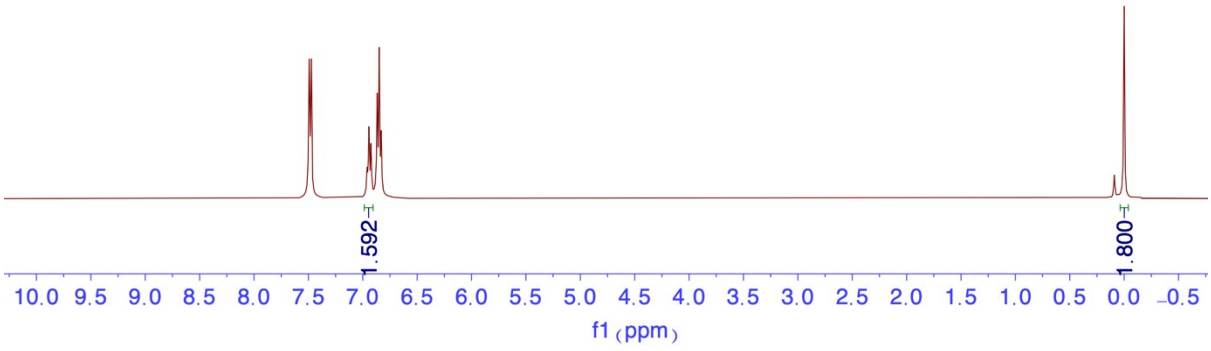


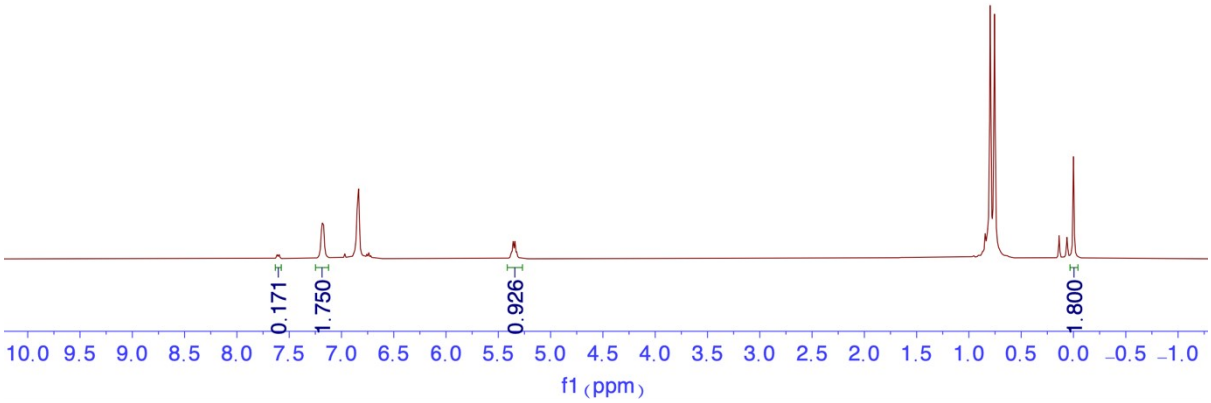
Figure S57. ^{1}H NMR overlay of catalytic hydroboration of benzophenone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.49 (1H, d), 7.15 (2H, t), 7.95 (4H, t), 6.89 (4H,t) and 0.98 (12H, s, C*H*$_3$ of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.8 (O-Bpin) ppm.

10a, 2,2,2-Trifluroacetophenone

t= 0.2h
c= 90%



Before addition of **4** and HBpin

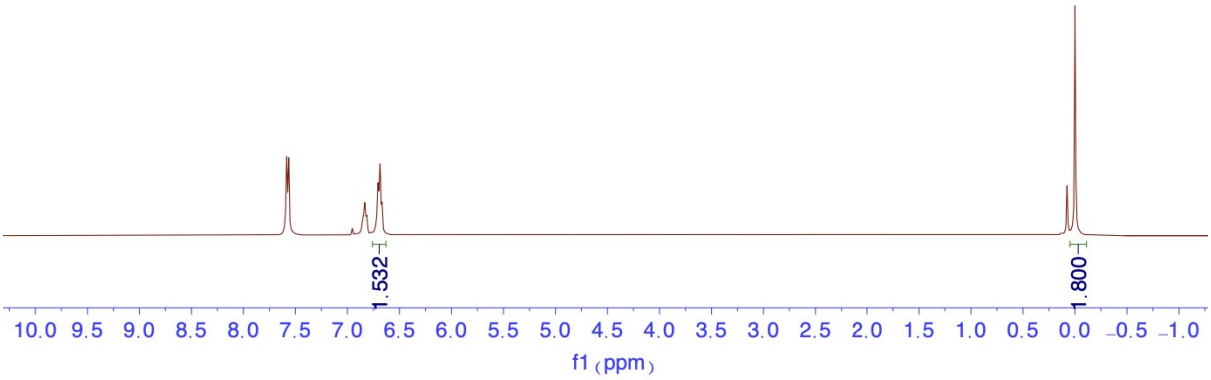


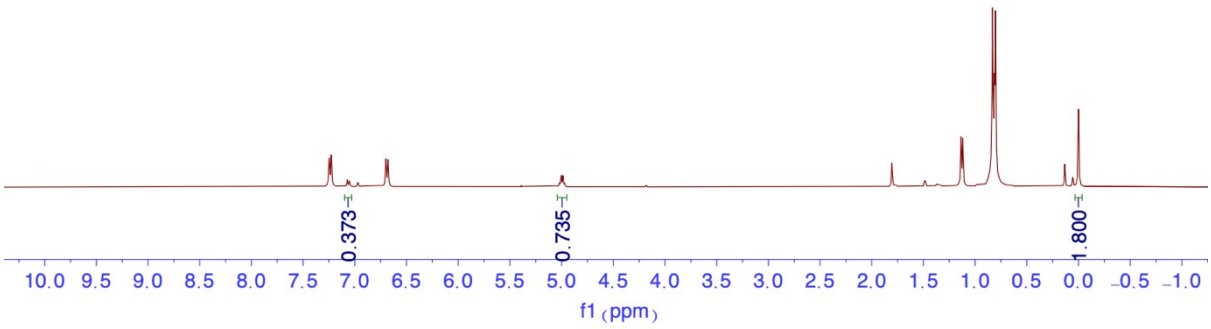
Figure S58. ^{1}H NMR overlay of catalytic hydroboration of 2,2,2-Trifluroacetophenone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.16 (2H, m), 6.94-6.75 (3H, m), 5.34 (1H, q), 0.78 (12H, d) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.9 (HMDS-Bpin) ppm

11a, 4-Iodoacetophenone

t= 24h
c= 80%



Before addition of **4** and HBpin

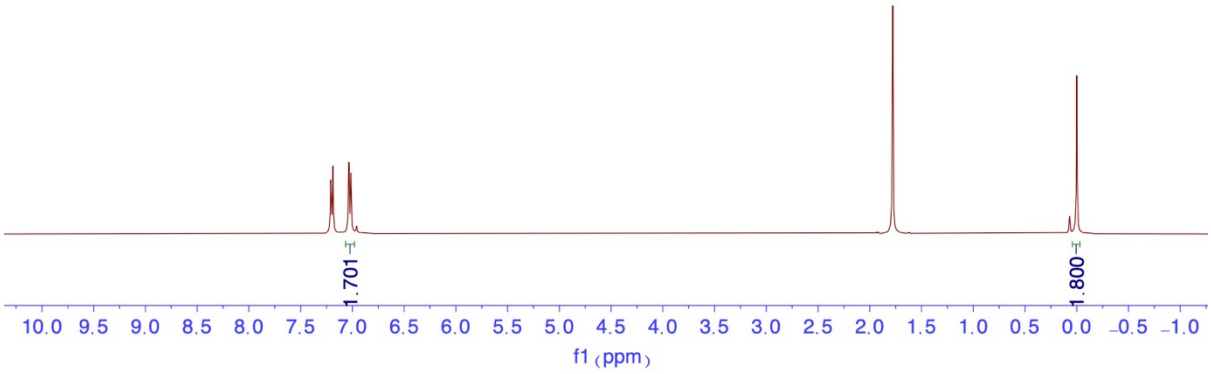


Figure S59. ^{1}H NMR overlay of catalytic hydroboration of 4-Iodoacetophenone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

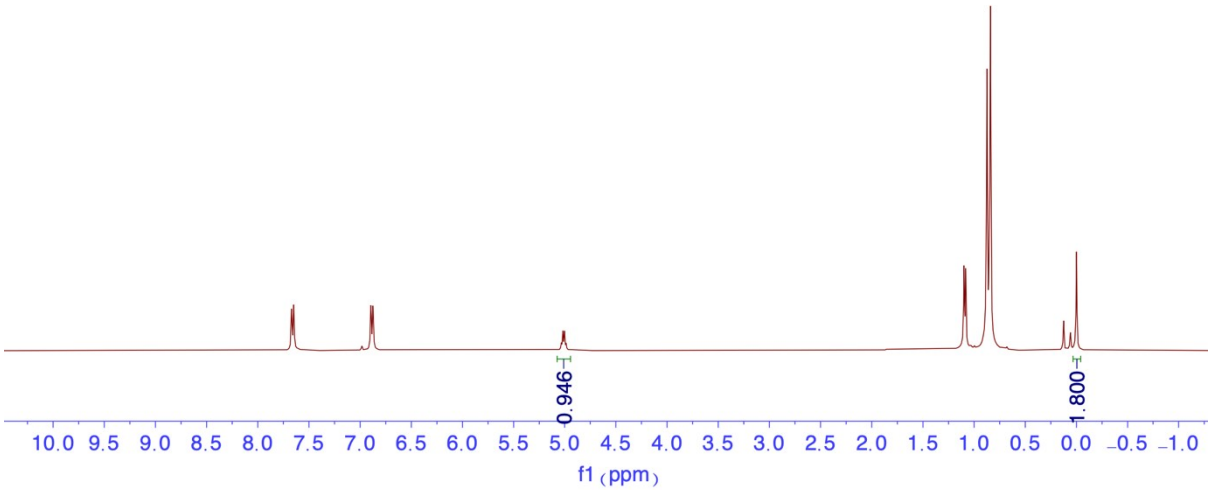
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.23 (2H, d), 6.68 (2H, d), 4.99 (1H, q- OCH), 1.12 (3H, d), 0.81 (12H, d, CH_3 of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.2 ppm (O-Bpin) ppm.

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 143.9, 137.6, 127.6, 92.7, 82.5, 72.3, 25.5, 24.6 ppm.

12a, 4-NO_2-Acetophenone

t= 0.7h
c= 99%



Before addition of **4** and HBpin

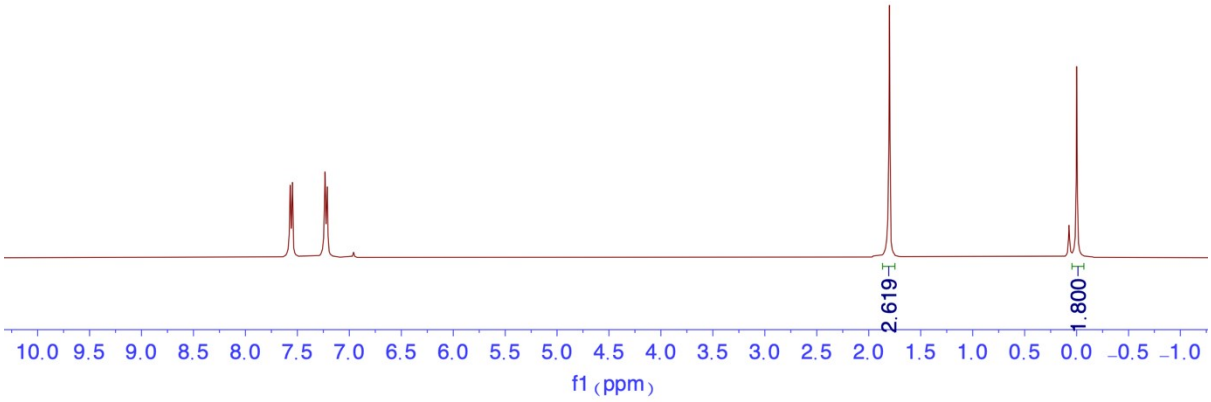


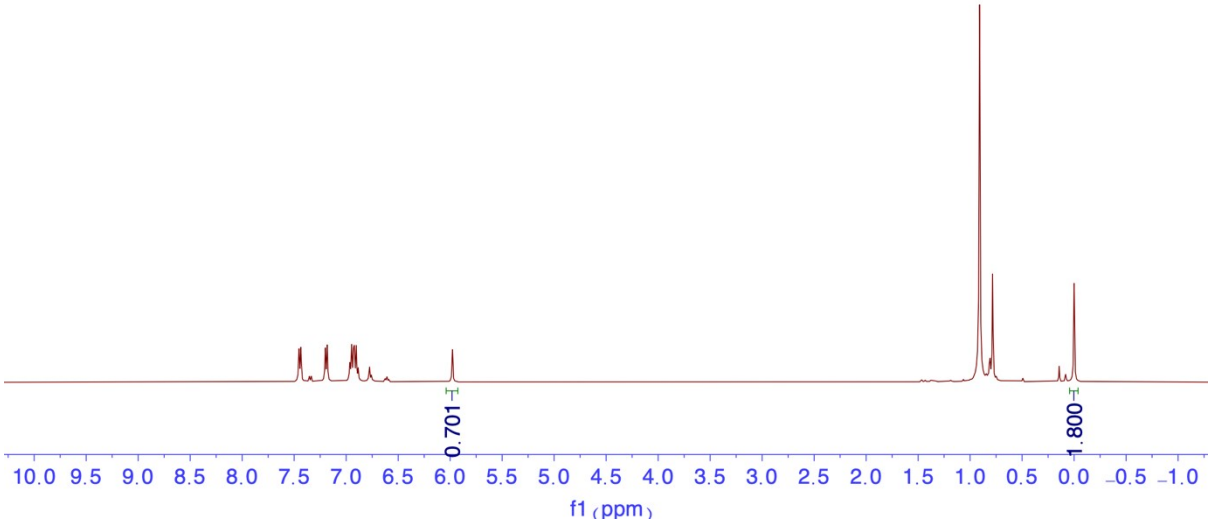
Figure S60. ^{1}H NMR overlay of catalytic hydroboration of 4-NO_2-Acetophenone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.66 (2H, d), 6.88 (2H, d), 5.00 (1H, s, OCH), 1.07 (3H, s), and 0.85 (12H, s, C*H*$_3$ of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.9 (O-Bpin) ppm.

13a, 9-Fluorenone

t= 3.5h
c= 70%



Before addition of **4** and HBpin

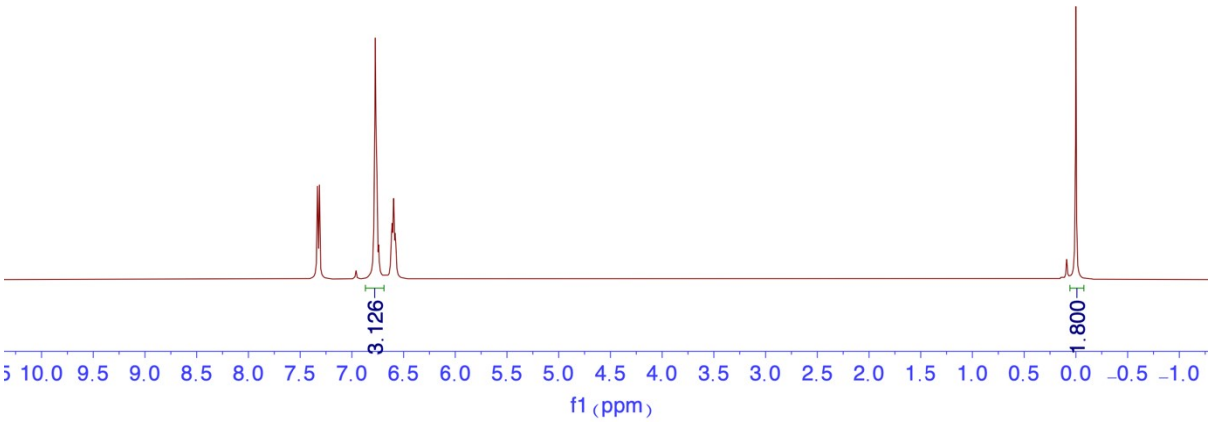


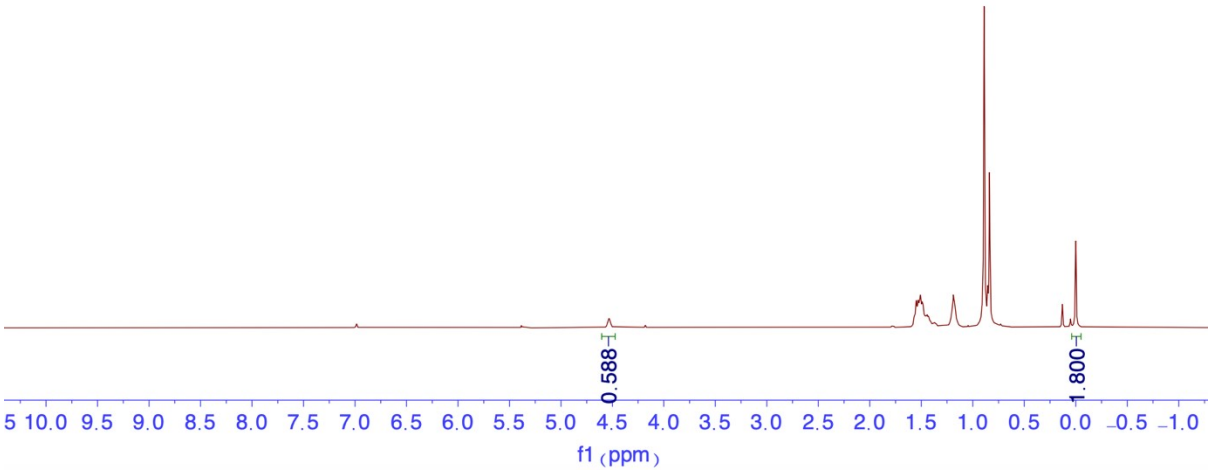
Figure S61. ^{1}H NMR overlay of catalytic hydroboration of 9-Fluorenone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.45 (2H, d), 7.19 (2H, d), 6.92 (4H, m), 5.97 (1H, s OCH), 0.90 (12H, s, CH_3 of Bpin) ppm.

^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.9 (O-Bpin) ppm.

14a, Cyclopentanone

t= 9h
c= 60%



Before addition of **4** and HBpin

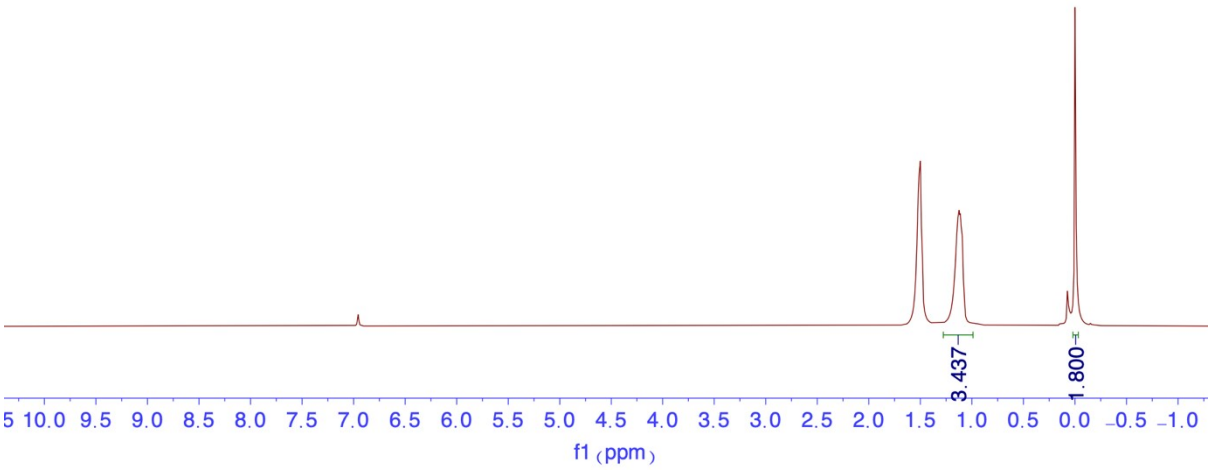


Figure S62. ^{1}H NMR overlay of catalytic hydroboration of cyclopentanone with HBpin using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

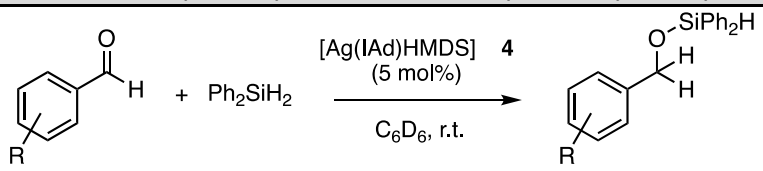
^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 4.69 (1H, m), 1.74-1.51 (6H, m), 1.39-1.33 (2H, m), 0. (12H, s, CH_3 of Bpin)

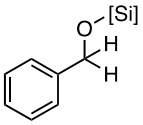
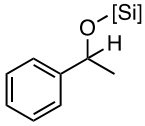
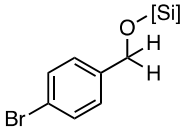
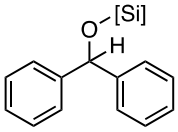
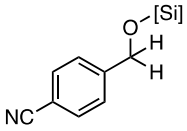
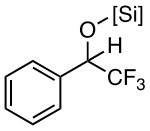
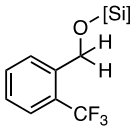
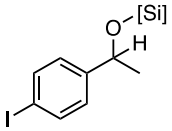
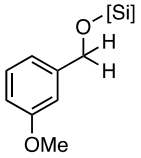
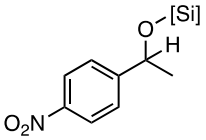
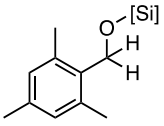
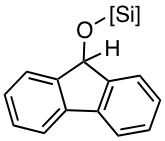
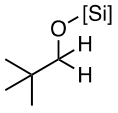
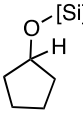
^{11}B (128.38 MHz, C_6D_6, 300K) δ 22.5 ppm (O-Bpin)

Catalytic hydrosilylation using 4

Table S5: Carbonyl hydrosilylation using Ph_2SiH_2, catalysed by [Ag(IAd)HMDS]

Table S5. Hydrosilylation of carbonyls catalysed by **4**

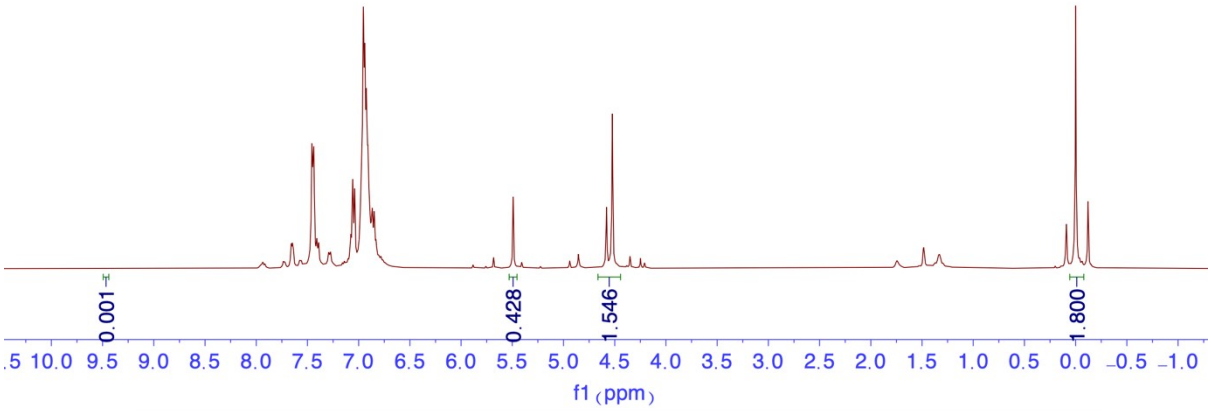


Entry	Product	4	Entry	Product	4
1b		1h 99%	**8b**		24h <5%
2b		0.5h 99%[b,c]	**9b**		24h <5%
3b		0.25h 99%[b,c]	**10b**		0.5h 99%[b,c]
4b		0.5h 99%[b,c]	**11b**		18h <5%
5b		3.5h 74%	**12b**		1.5h 99%[b,c]
6b		24h 99%[b,c]	**13b**		0.5h 80%
7b		8.5h 40%	**14b**		24h <5%

% values indicate % conversion of starting material [a] Reaction conditions: substrate (1 mmol), Ph_2SiH_2 or HBpin (1.5 mmol), 5 mol% [Ag(IAd)HMDS] (**4**) with 10 mol% internal standard hexamethylcyclotrisiloxane in C_6D_6 at room temperature. [b] conversion of substrate. [c] yield of corresponding alcohol product after reaction quench in C_6D_6.

1b, Benzaldehyde

t= 1h
c= 99%



Before addition of **4** and Ph_2SiH_2

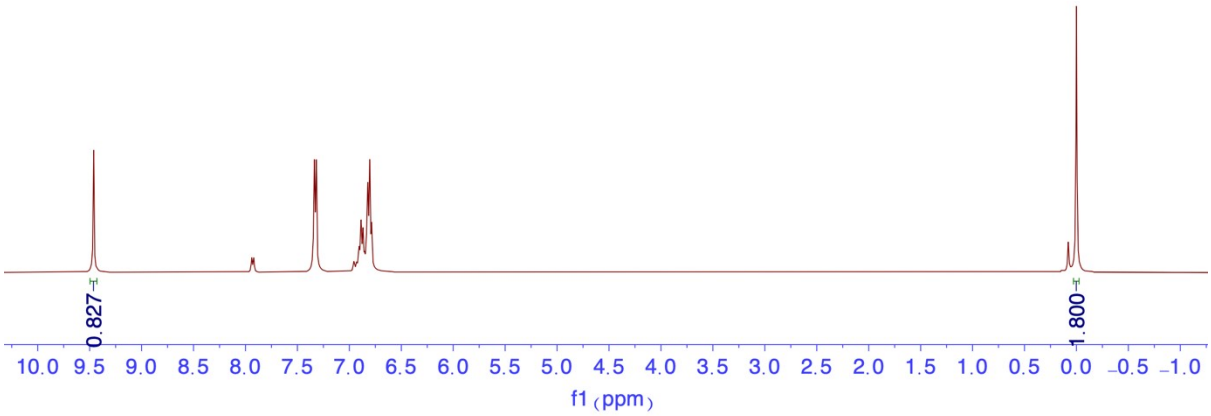
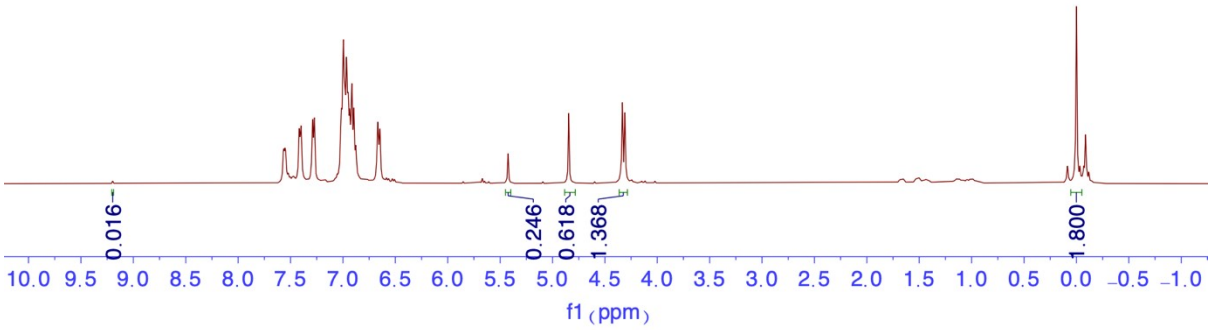


Figure S63. ^{1}H NMR overlay of catalytic hydrosilylation of benzaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.63 – 7.28 (4H, m), 7.05 (2H, m), 6.99 – 6.92 (9H, m), 5.49 (1H, s, SiH) and 4.53 (2H, s) ppm.

2b, 4-Br-Benzaldehyde

t= 0.5h
c= 99%[b] 65[c]



Before addition of **4** and Ph_2SiH_2

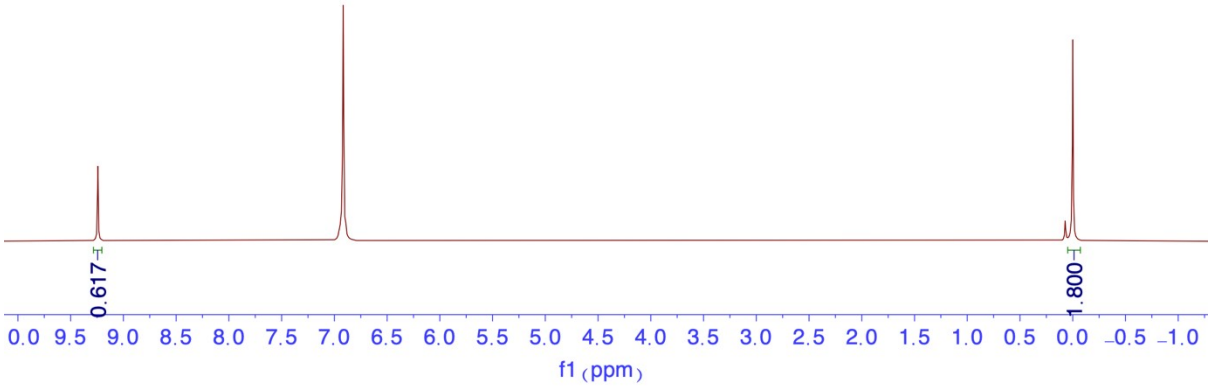


Figure S64. ^{1}H NMR overlay of catalytic hydrosilylation of 4-Br-Benzaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

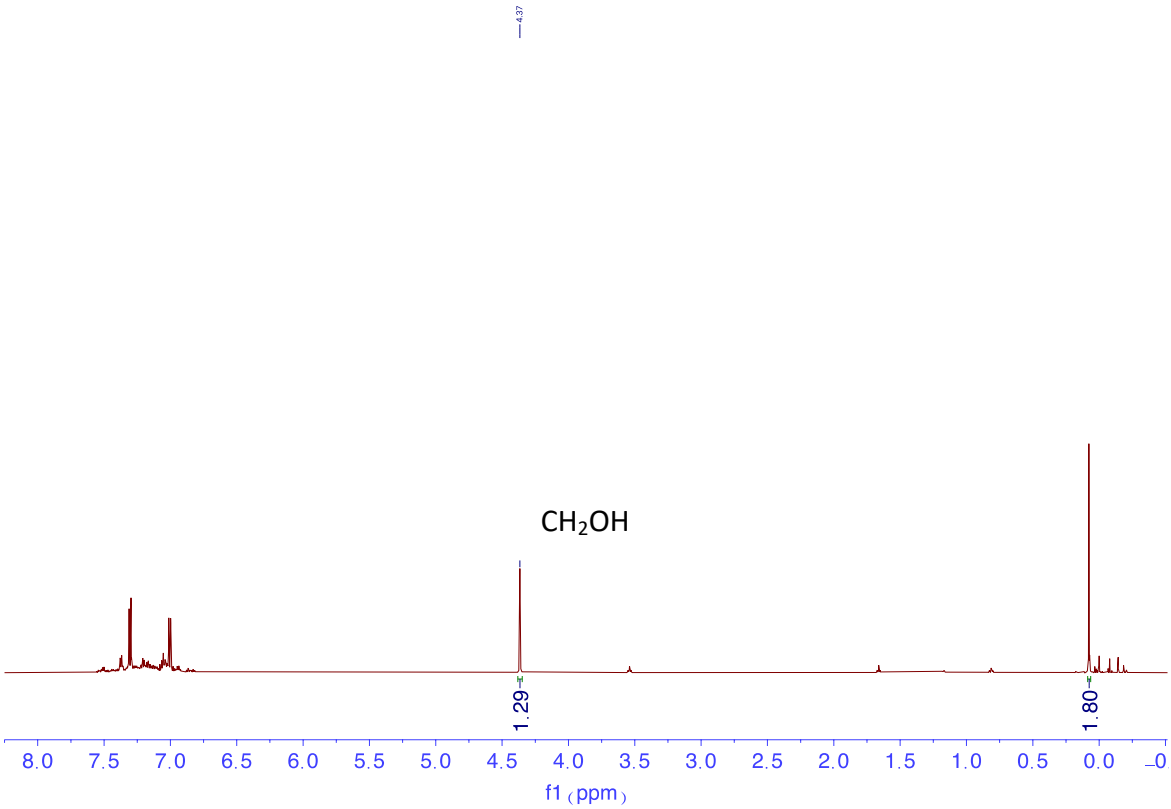
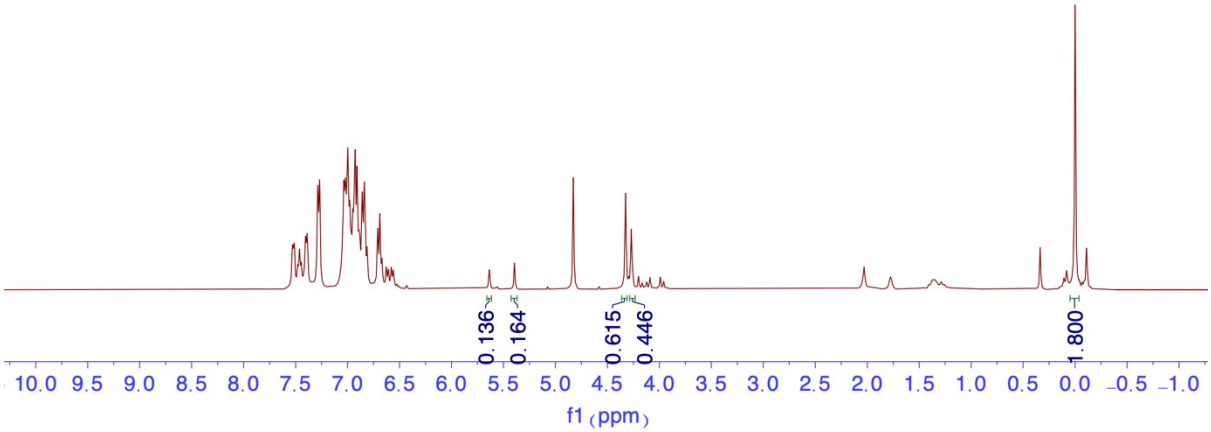


Figure S65. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-Br-benzaldehyde with Ph_2SiH_2 using **4** (5 mol%) in $CDCl_3$ at 300K.

3b, 4-CN-Benzaldehyde

t= 0.25h
c= 99%[b] 93[c]



Before addition of **4** and Ph_2SiH_2

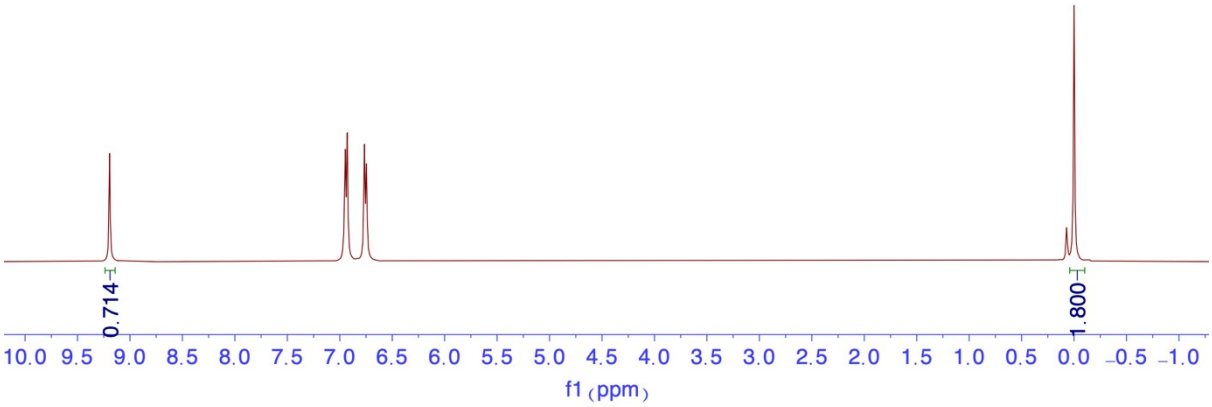


Figure S66. ^1H NMR overlay of catalytic hydrosilylation of 4-CN-Benzaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

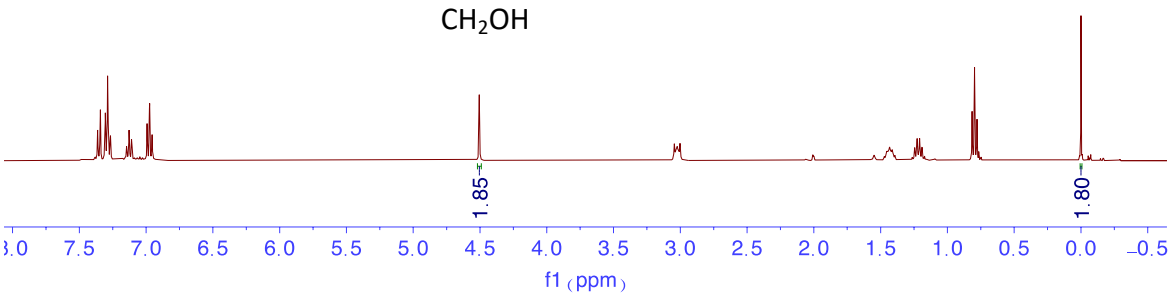
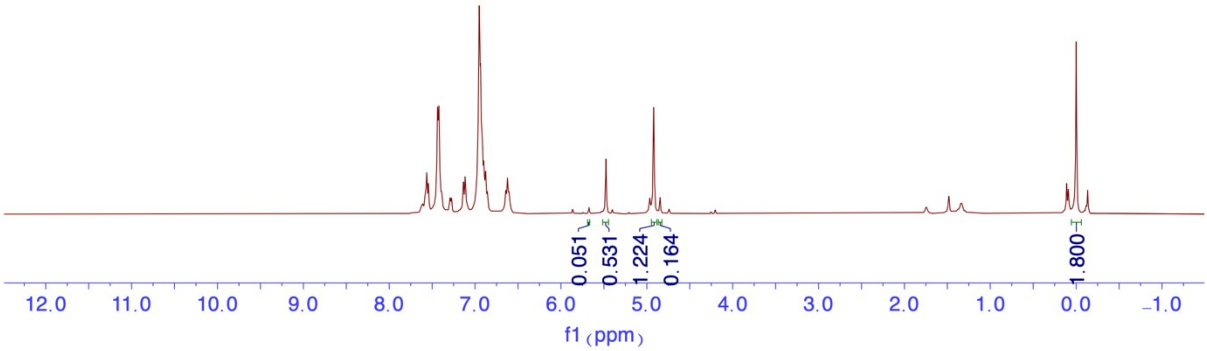


Figure S67. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-CN-benzaldehyde with Ph_2SiH_2 using **4** (5 mol%) in $CDCl_3$ at 300K.

4b, 2-CF_3-Benzaldehdye

t= 0.5h
c= 99%[b] 87[c]



Before addition of **4** and Ph_2SiH_2

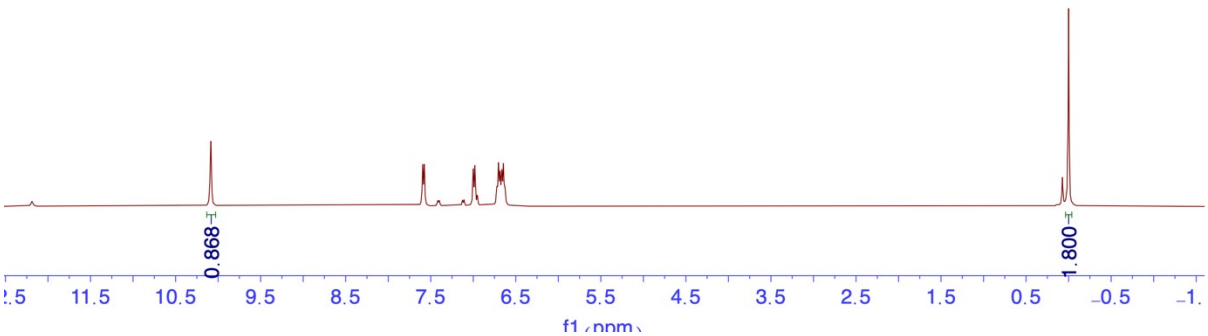


Figure S68. ^{1}H NMR overlay of catalytic hydrosilylation of 2-CF_3-Benzaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

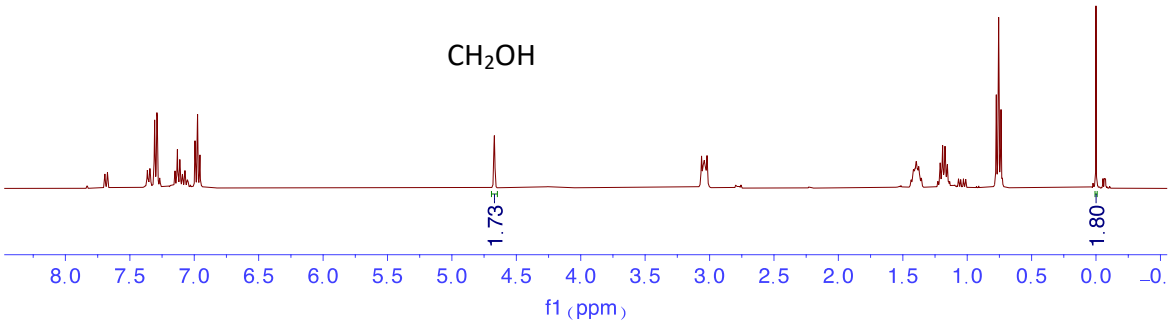
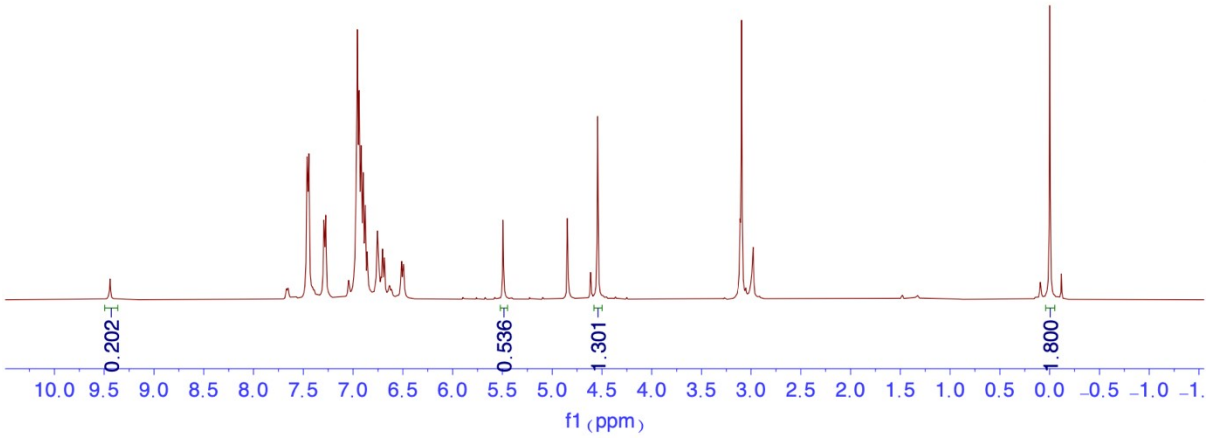


Figure S69. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-CF_3-benzaldehyde with Ph_2SiH_2 using **4** (5 mol%) in $CDCl_3$ at 300K.

5b, 3-OMe-Benzaldehyde

t= 3.5h
c= 74%



Before addition of **4** and Ph_2SiH_2

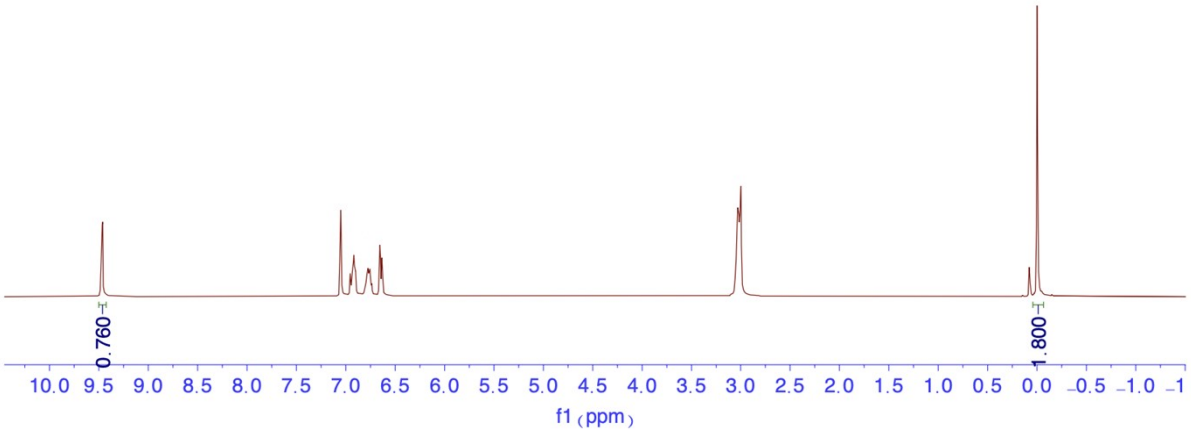


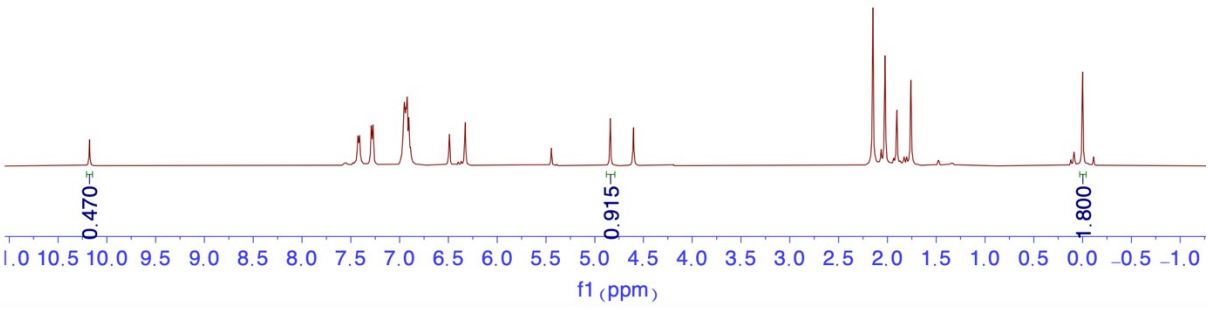
Figure S70. ^{1}H NMR overlay of catalytic hydrosilylation of 3-OMe-Benzaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.49-7.24 (4H, m), 7.02-6.83 (7H, m), 6.75 (1H, br s), 5.47 (1H, s, Si-H), 4.54 (2H, s, CH_2), 3.08 (3H, s, OCH_3),

^{13}C NMR (100.62 MHz, C_6D_6, 300K) δ 160.2, 142.3, 136.0, 135.1, 130.6, 129.6, 128.4, 119.1, 113.3, 66.6, 54.5

6b, Mesitaldehyde

t= 24h
c= 99%[b] 81%[c]



Before addition of **4** and Ph_2SiH_2

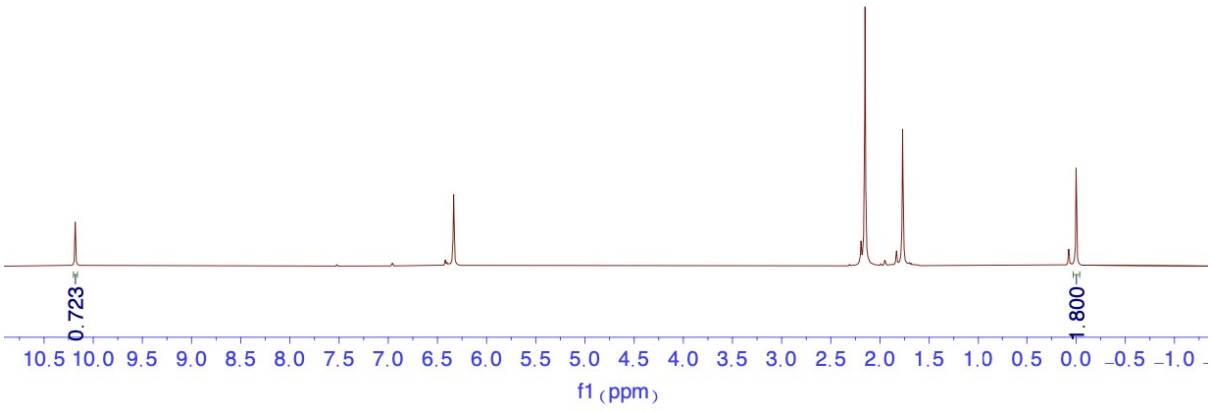


Figure S71. ^1H NMR overlay of catalytic hydrosilylation of mesitaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

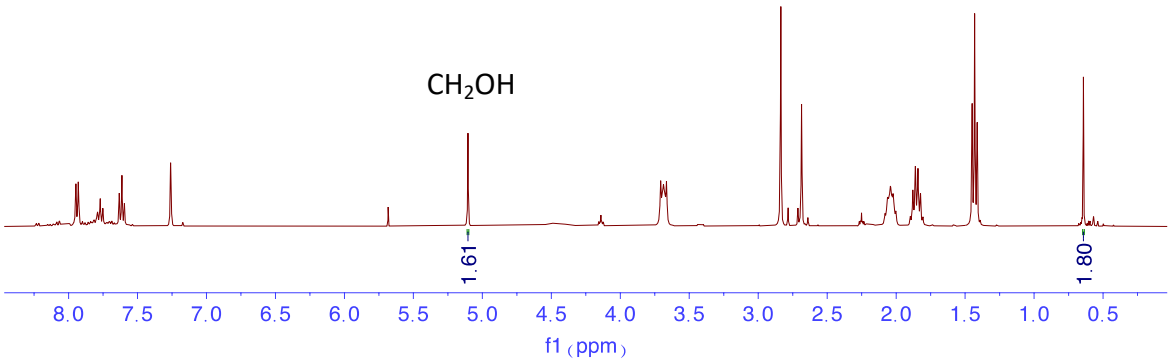
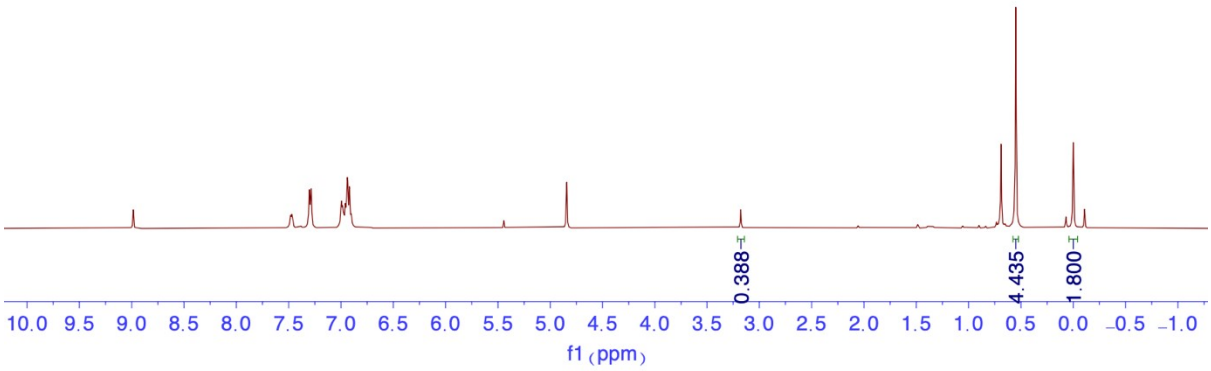


Figure S72. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of mesitaldehyde with Ph_2SiH_2 using **4** (5 mol%) in $CDCl_3$ at 300K.

7b, *t*Butylaldehyde

t= 8.5h
c= 40%,



Before addition of **4** and Ph_2SiH_2

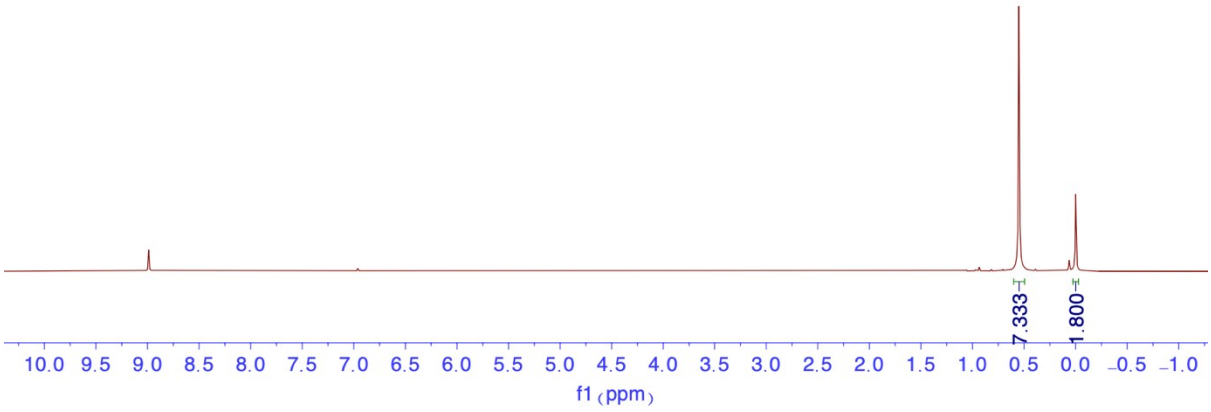
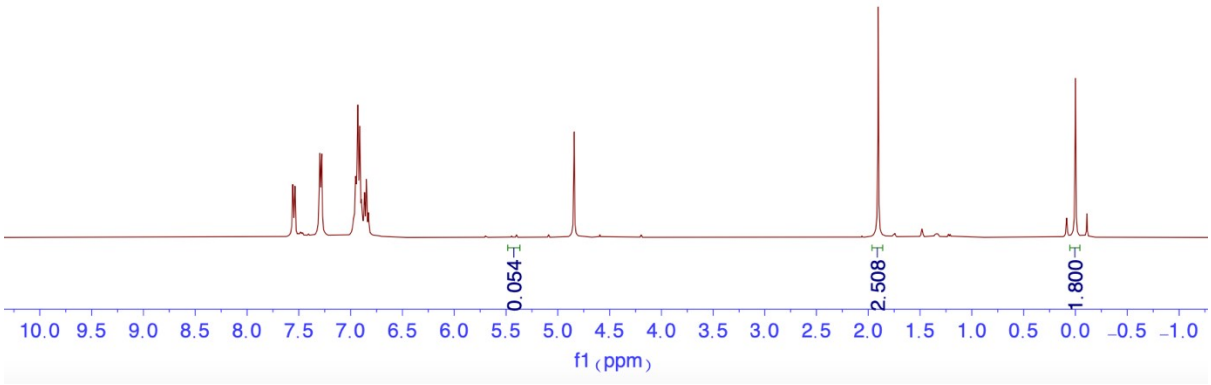


Figure S73. ^{1}H NMR overlay of catalytic hydrosilylation of *t*Butylaldehyde with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.51-7.21 (4H, m), 7.02-6.81 (6H, m), 4.84 (1H, s, SiH), 3.16 (1H,s), 0.63 (9H, s)

8b, Acetophenone

t= 24h,
c= <5%



Before addition of **4** and Ph_2SiH_2

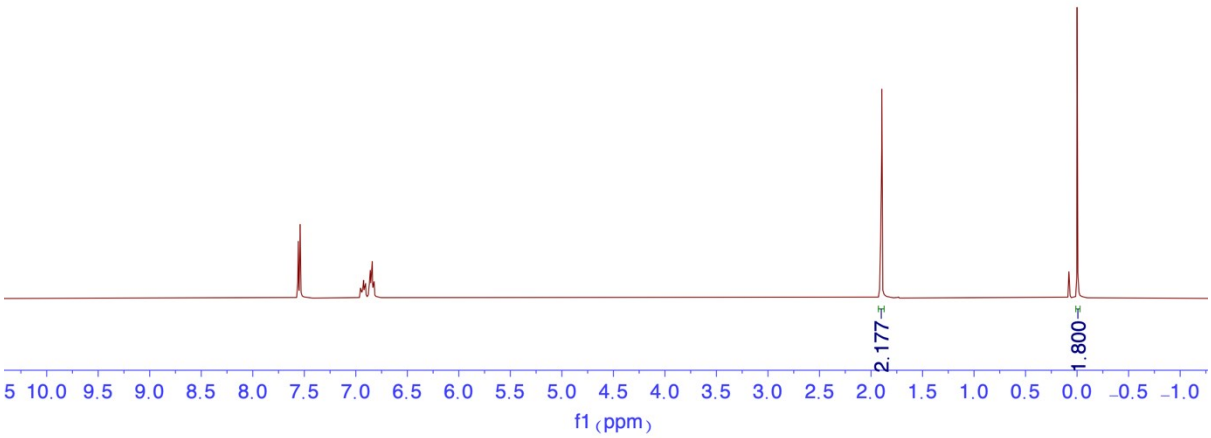
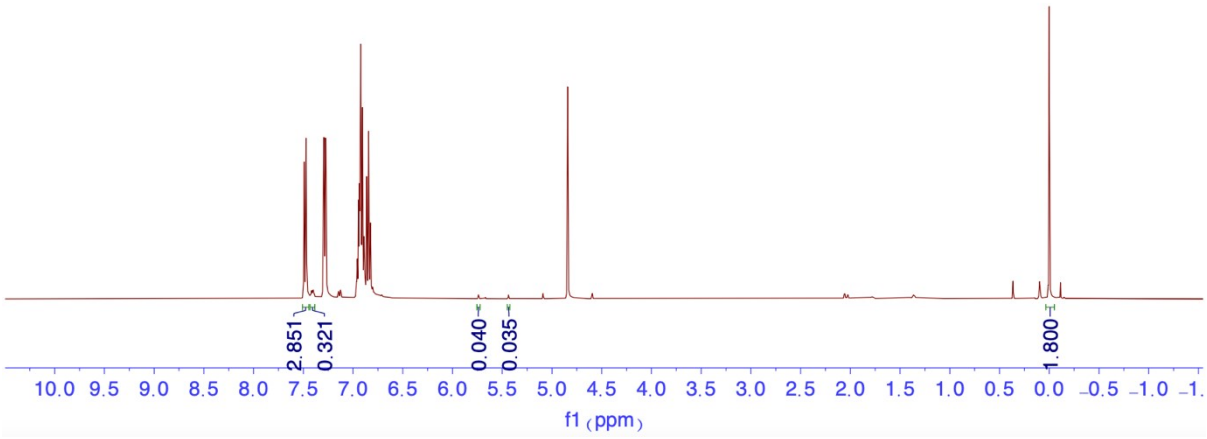


Figure S74. ^1H NMR overlay of catalytic hydrosilylation of acetophenone with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

9b, Benzophenone

t= 24h
c=<5%



Before addition of **4** and Ph_2SiH_2

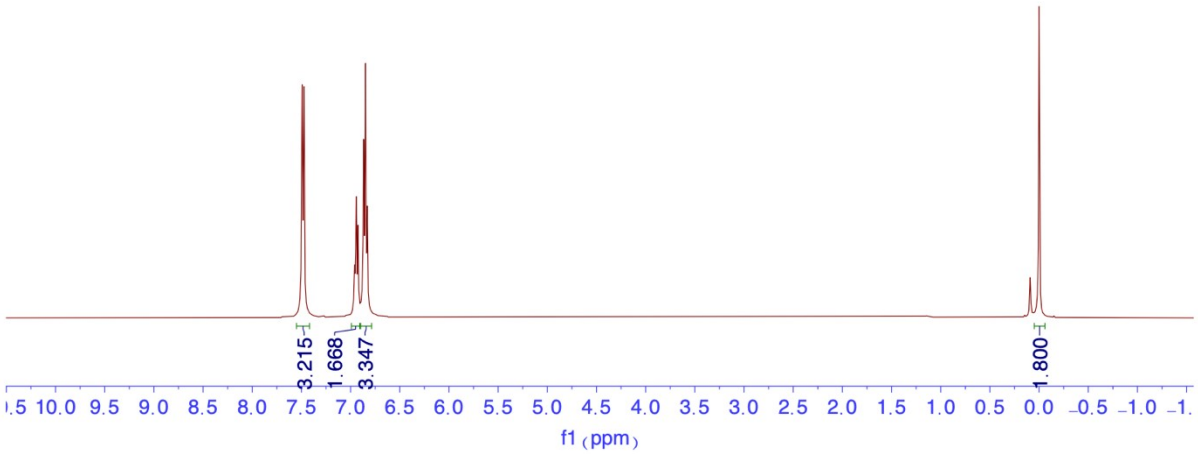
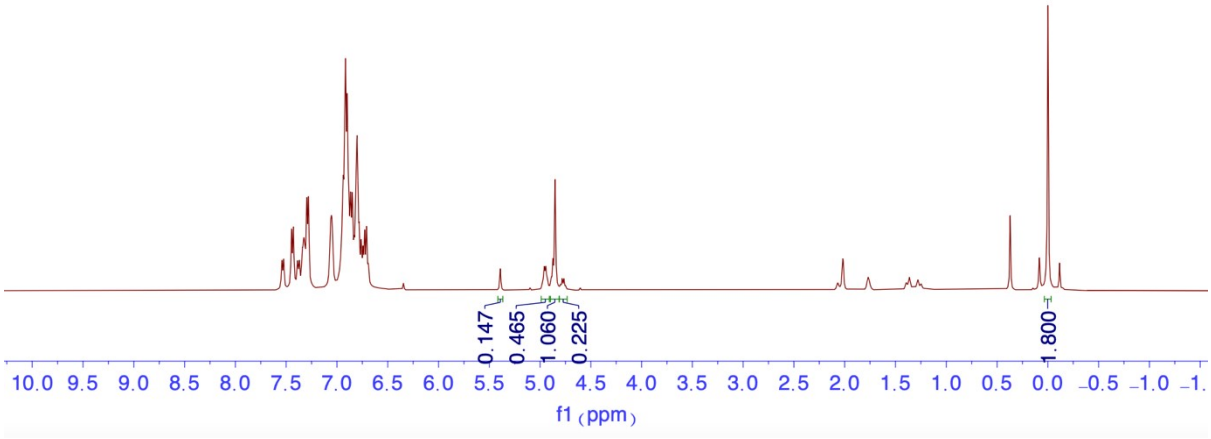


Figure S75. ^{1}H NMR overlay of catalytic hydrosilylation of benzophenone with Ph_2SiH_2using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

10b, 2,2,2-Trifluroacetophenone

t= 0.5 h
c= 99%[b] 69%[c]



Before addition of **4** and Ph_2SiH_2

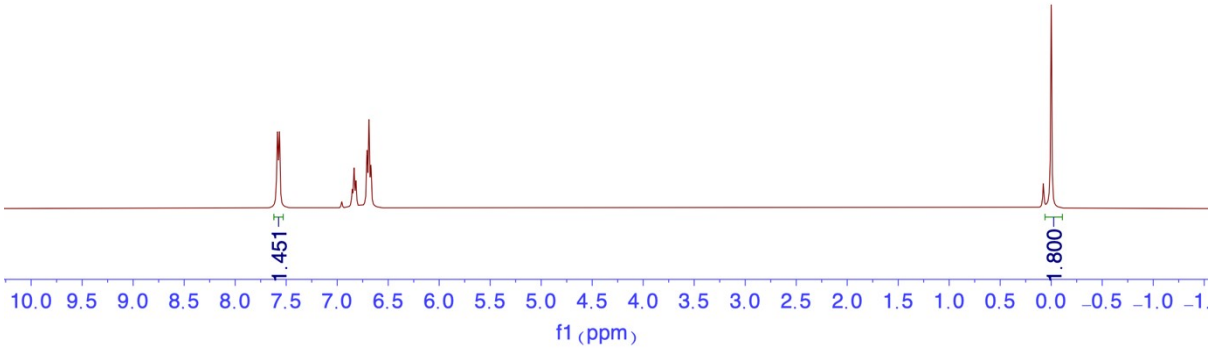


Figure S76. ^1H NMR overlay of catalytic hydrosilylation of 2,2,2-Trifluroacetophenone with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

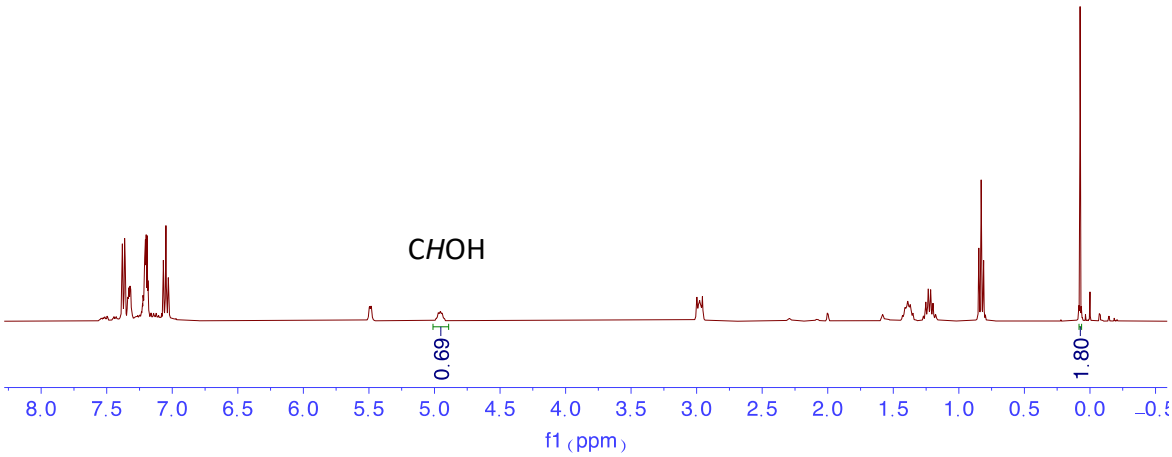
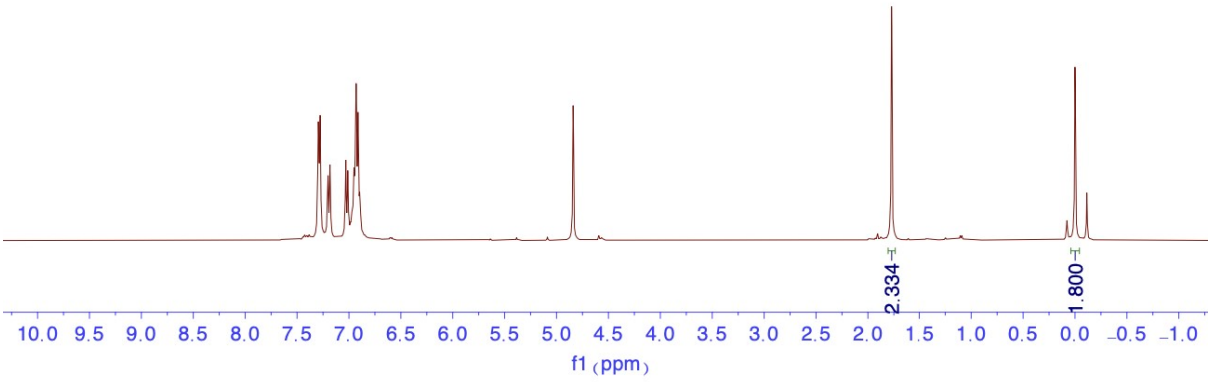


Figure S77. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 2,2,2-trifluroacetophenone with Ph_2SiH_2 using **4** (5 mol%) in $CDCl_3$ at 300K.

11b, 4-Iodoacetophenone

t= 18h
c=<5%



Before addition of **4** and Ph_2SiH_2

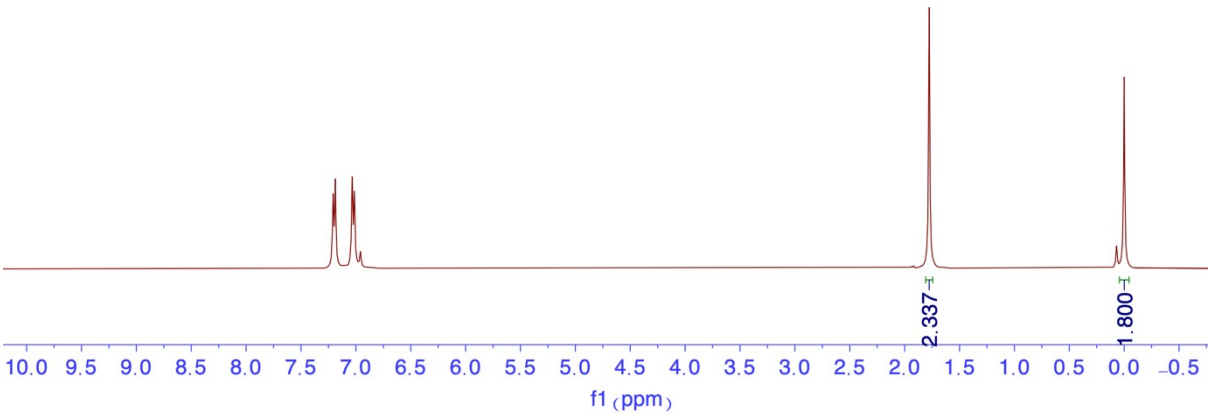
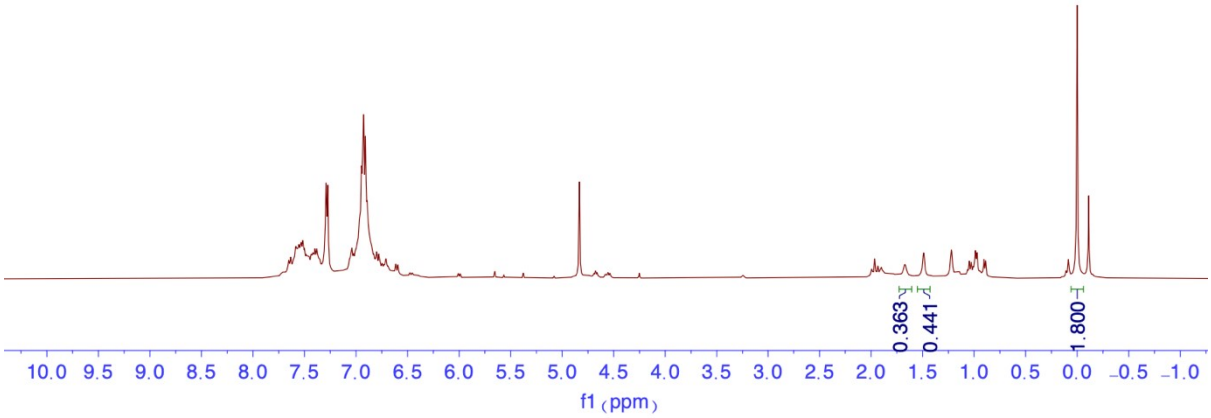


Figure S78. ^1H NMR overlay of catalytic hydrosilylation of 4-Iodoacetophenone with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

12b, 4-NO_2-Acetophenone

t= 1.5h
c= 99%[b] 48%[c]



Before addition of **4** and Ph_2SiH_2

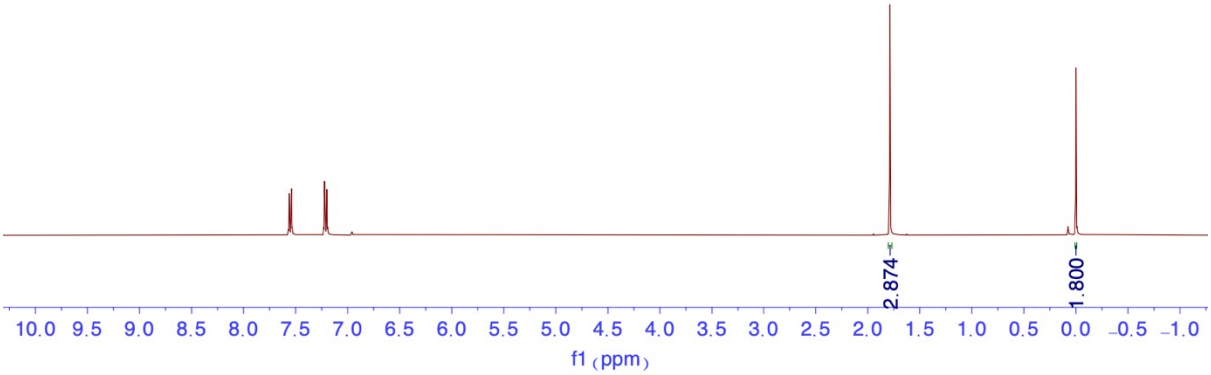


Figure S79. ^{1}H NMR overlay of catalytic hydrosilylation of 4-NO_2-Acetophenone with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Mixture of products - reaction quenched with TBAF

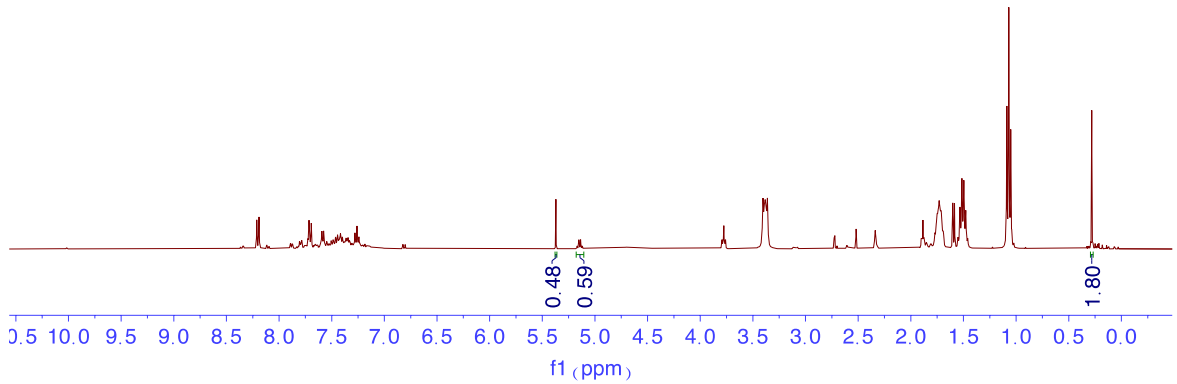
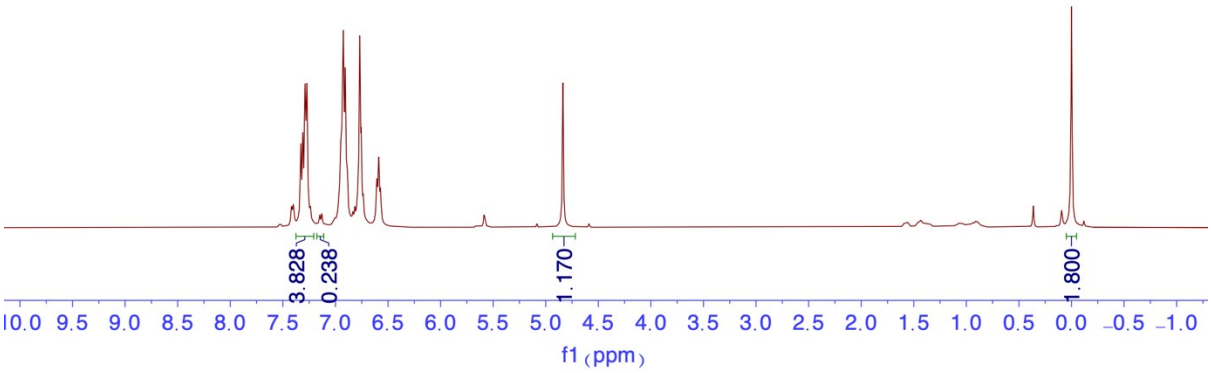


Figure S80. ^{1}H NMR of organic product following a quench of the catalytic hydrosilylation reaction of 4-NO_2-acetophenone with Ph_2SiH_2 using **4** (5 mol%) in $CDCl_3$ at 300K.

13b, 9-Fluorenone

t= 0.5h
c= 80%



Before addition of **4** and Ph_2SiH_2

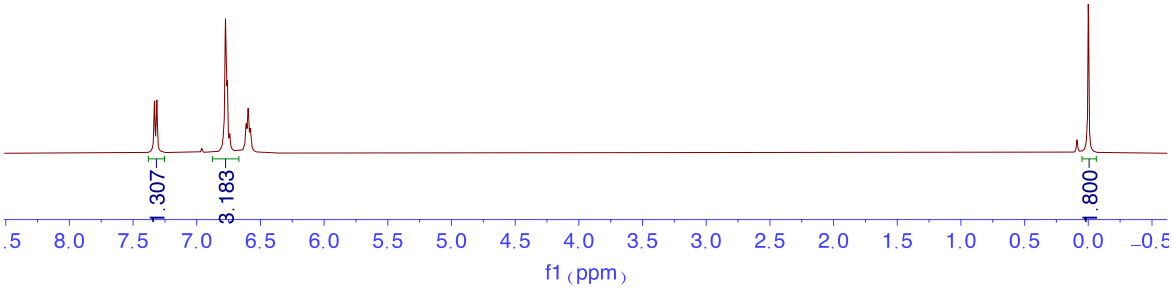
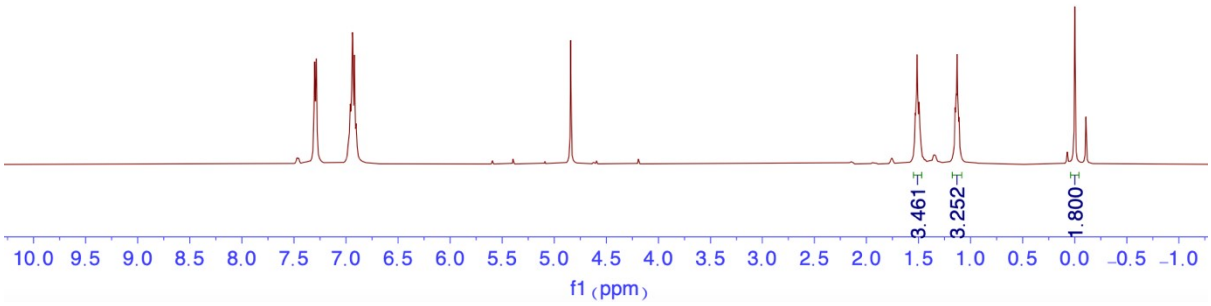


Figure S81. ^{1}H NMR overlay of catalytic hydrosilylation of 9-Fluorenone with Ph_2SiH_2using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

^{1}H NMR (400.1 MHz, C_6D_6, 300K) δ 7.50-7.15 (6H, overlapping-Ar-H), 6.84 (9H, d, overlapping- Ar-H), 6.6 (2H, d, Ar-H), 5.68-5.55 (2H, Si-H and O-CH)

14b, Cyclopentanone

t= 22h
c= <5%



Before addition of **4** and Ph_2SiH_2

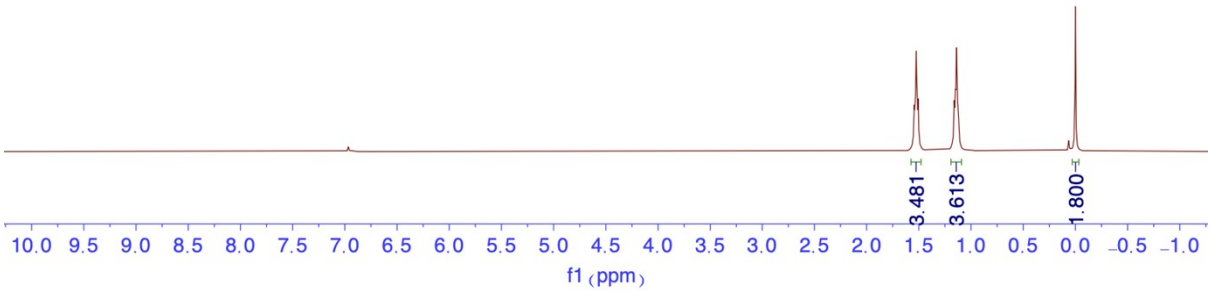


Figure S82. ^1H NMR overlay of catalytic hydrosilylation of cyclopentanone with Ph_2SiH_2 using **[Ag(IAd)HMDS] 4** (5 mol%) in C_6D_6 at 300K

Proposed catalytic cycle

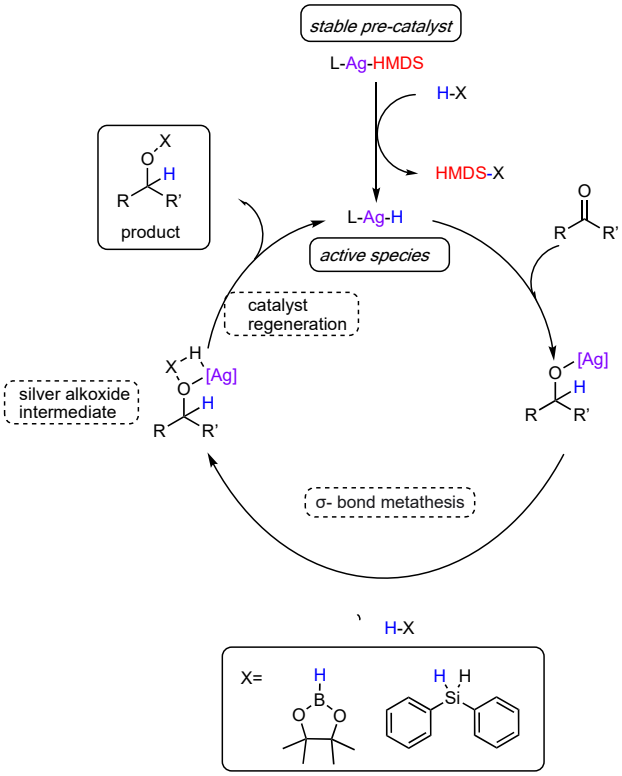


Figure S83. Proposed catalytic mechanism for the hydrofunctionalisation of carbonyls mediated by a silver(I) hydride intermediate

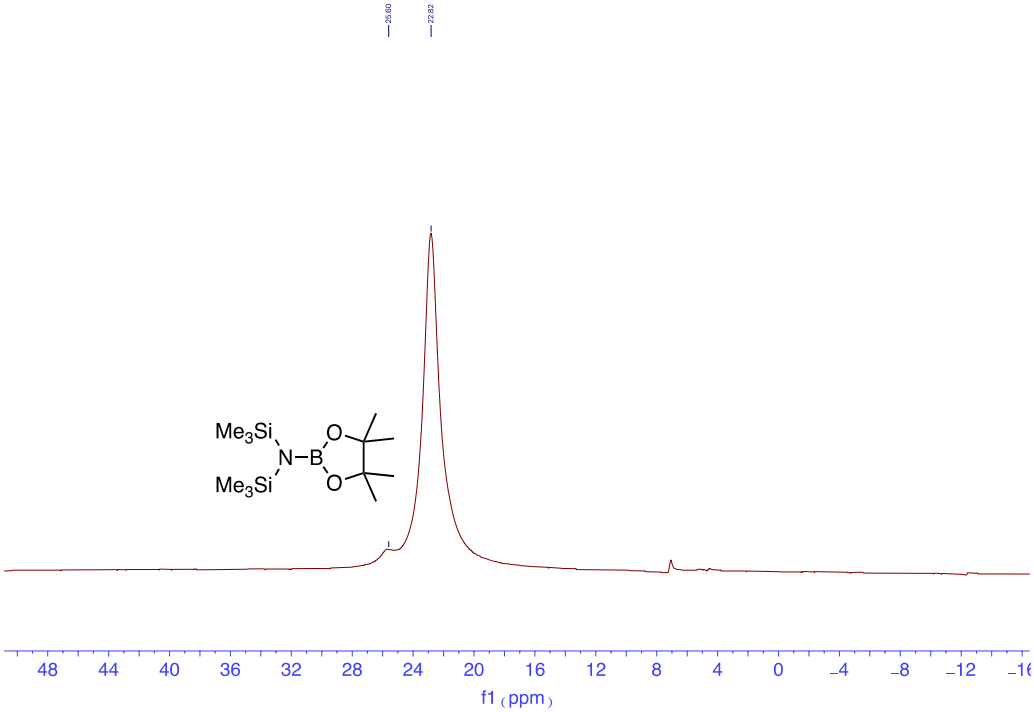


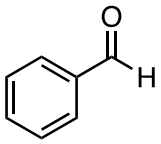
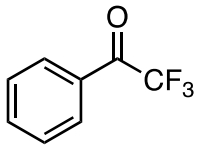
Figure S84. Proposed catalytic mechanism for the hydrofunctionalisation of carbonyls mediated by a silver(I) hydride intermediate

Reusability studies of pre-catalyst 3

General catalytic protocol for reusability study

In a typical procedure, the substrate benzaldehyde or 2,2,2-trifluoroacetophenone (0.5 mmol) was added to an amber J. Youngs NMR tube and dissolved in C_6D_6 (0.5 mL) containing 10 mol % of the internal reference standard hexamethylcyclotrisiloxane and the ^1H NMR data recorded. Pinacolborane (0.6 mmol, 90 µL) or diphenylsilane (0.75 mmol, 93 µL) and lead pre-catalyst **3** (5 mol %, 1 M, 50 µL) was then added and the reaction monitored by ^1H NMR spectroscopy until completion and recorded as cycle 1. For cycles 2-5 an extra equivalent of substrate (0.5 mmol) and pinacolborane (0.6 mmol, 90 µL) or diphenylsilane (0.75 mmol, 93 µL) was added for each cycle, and percent (%) conversions were monitored ^1H NMR spectroscopy until completion, these values are recorded in table S6.

Table S6. Reusability study of lead pre-catalyst [Ag(IDipp)HMDS] **3**

Substrate	Cycle	Hydroboration	Hydrosilylation
	**1**	0.2h, 99%	0.25h, 95%
	2	0.2h, 99%	0.25h, 95%
	3	0.2h, 99%	0.8h, 98%
	4	0.25h, 99%	0.7h, 96%
	5	0.5h, 99%	2h, 93%
	**1**	0.2h, 97%	0.2h, 93%
	2	0.2h, 97%	0.3h, 95%
	3	0.2h, 98%	0.5h, 99%
	4	0.6h, 94%	0.5h, 90%
	5	0.5h, 99%	0.5h, 89%

Five reusability cycles of pre-catalyst (**3**) for the hydroboration and hydrosilylation of benzaldehyde and 2,2,2-trifluroacetophenone. % values indicate % conversions of starting material. Reaction conditions: substrate (1 mmol), Ph_2SiH_2 or HBpin (1.5mmol), 5 mol% [Ag(IDipp)HMDS] (**3**) with 10 mol% internal standard hexamethylcyclotrisiloxane in C_6D_6 at room temperature.

Hydroboration reusability cycles

Benzaldehyde

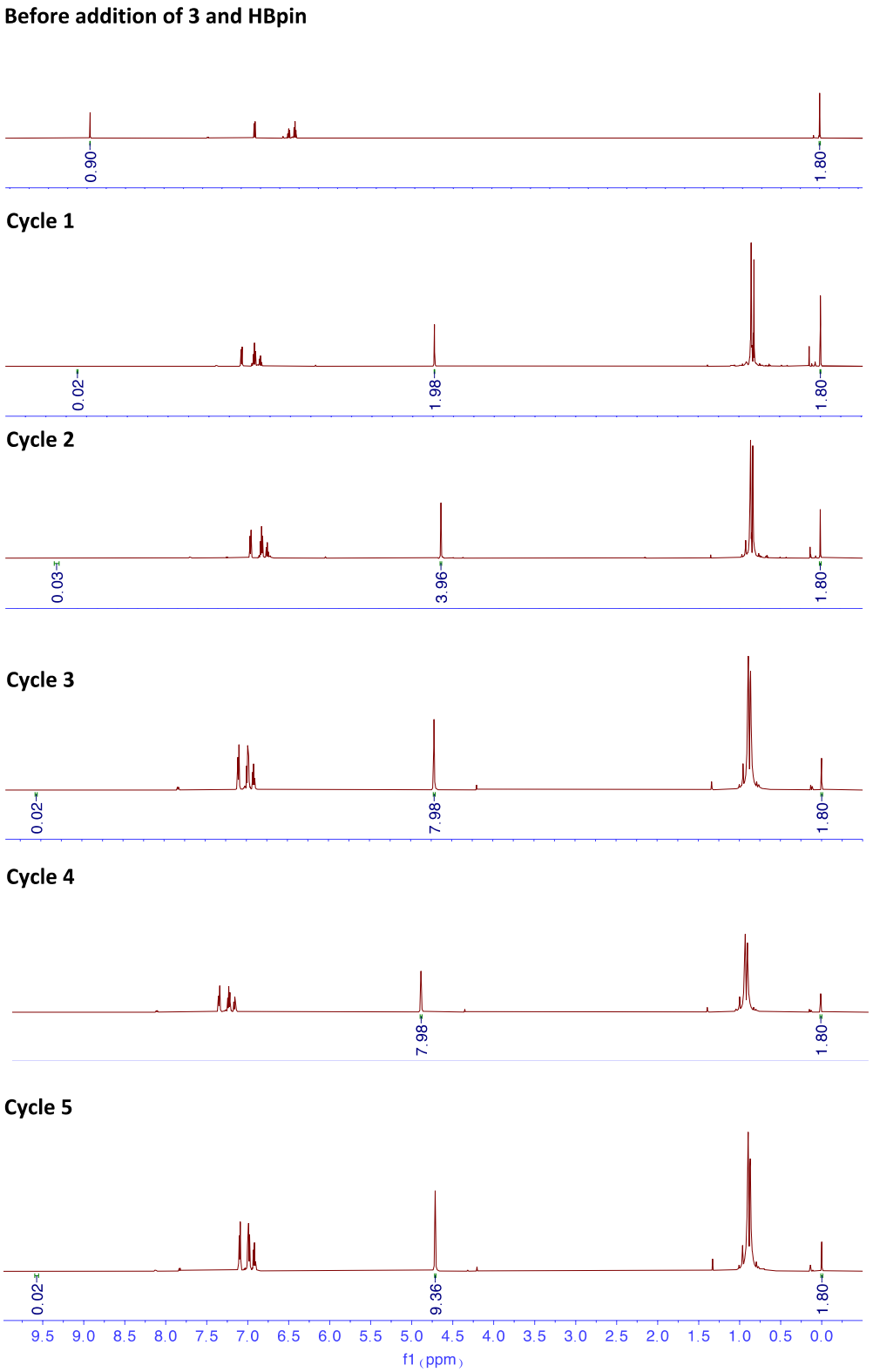


Figure S85. ^{1}H NMR in C_6D_6 with 10% mol IS overlay at 300K of five reusability cycles using **3** for the hydroboration of benzaldehyde

2,2,2-trifluoroacetophenone

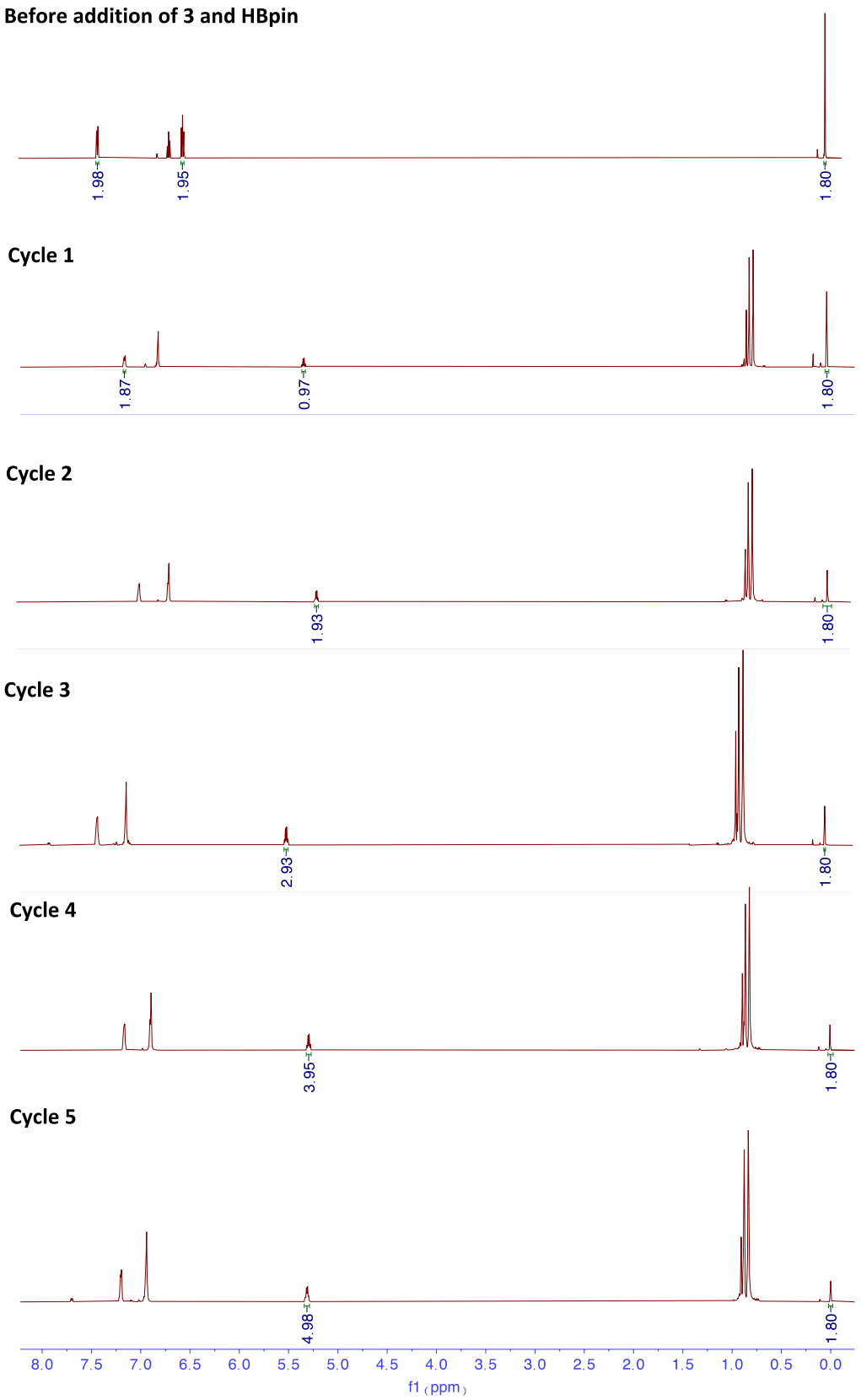


Figure S86. ^{1}H NMR in C_6D_6 with 10% mol IS overlay at 300K of five reusability cycles using **3** for the hydroboration 2,2,2-trifluoroacetophenone

Hydrosilylation reusability cycles

Benzaldehyde

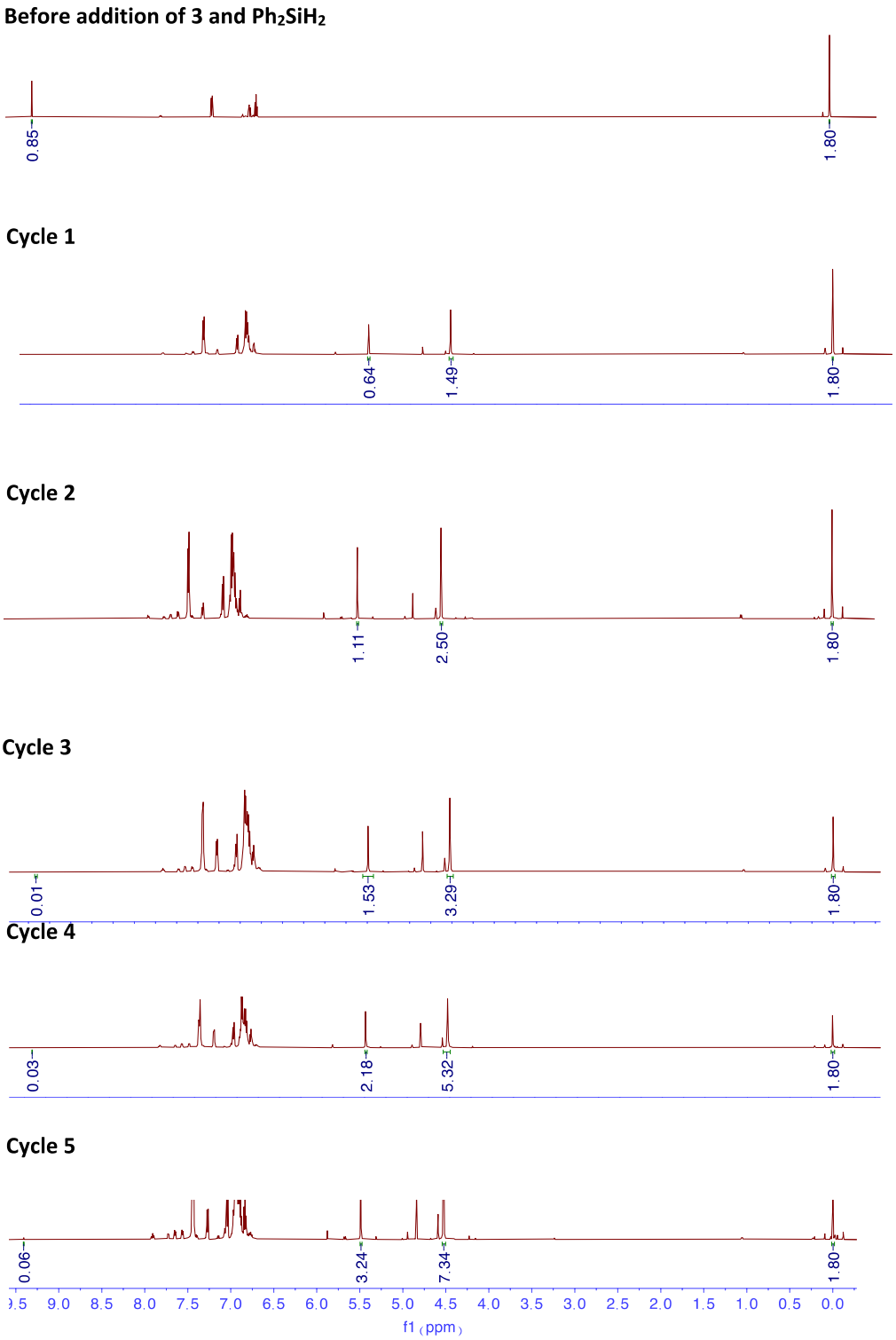


Figure S87. ^1H NMR in C_6D_6 with 10% mol IS overlay at 300K of five reusability cycles using **3** for the hydrosilylation of benzaldehyde

2,2,2-trifluoroacetophenone

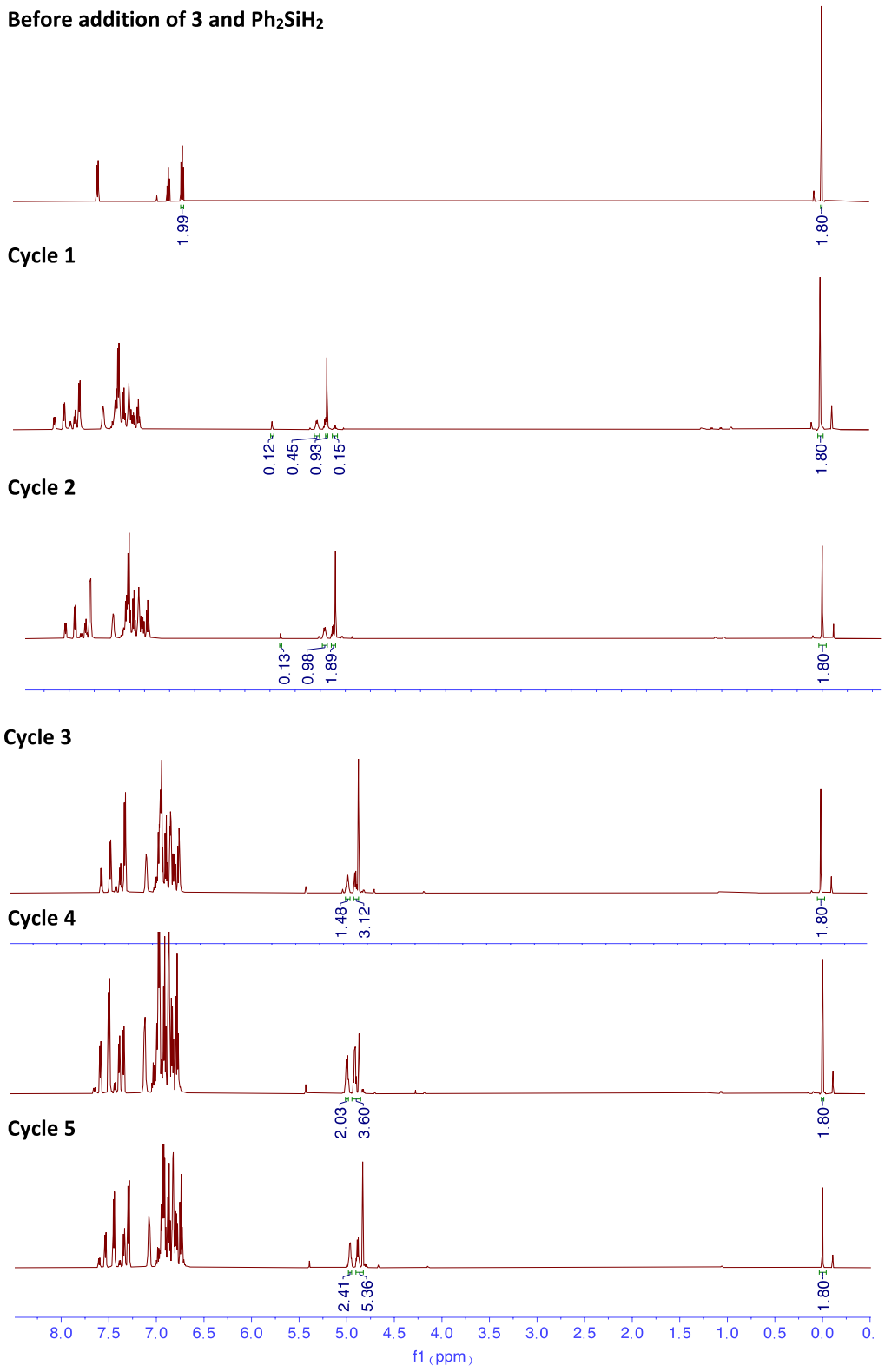


Figure S88. ^1H NMR in C_6D_6 with 10% mol IS overlay at 300K of five reusability cycles using **3** for the hydrosilylation 2,2,2-trifluoroacetophenone

Isolation of alcohol product from reusability study

The NMR reusability study solutions (see above), at the end of the five cycles was cooled to 0°C via an ice bath and 1.1 equivalents of TBAF (1.1mL; 1M solution in THF) was added drop wise and allowed to stir warming to room temperature. Next H_2O (10 mL) was added, and the product extracted with Et_2O (3 x 10mL). The combined organics were washed with brine (15mL), saturated $NaHCO_3$ and NH_4Cl (5 x 5mL) to remove residual TBAF and further dried with $MgSO_4$. Solvent was removed *in vacuo.* For model substrate benzaldehyde the isolated product resulting from the hydroboration was collected as a pale-yellow oil (0.099 g, yield: 37%) Figure S89 and for the hydrosilylation as a pale-yellow oil (0.222 g, yield: 82%) figure S90.

Following the same procedure for substrate 2,2,2-trifluoroacetophenone, lead to difficulties in pure isolationof the corresponding alcohol product, with residual TBAF remaining, even after attempted purification via column chromatography, or washing with NH_4Cl and or $NaHCO_3$ multiple times.

Benzaldehyde, HBpin:

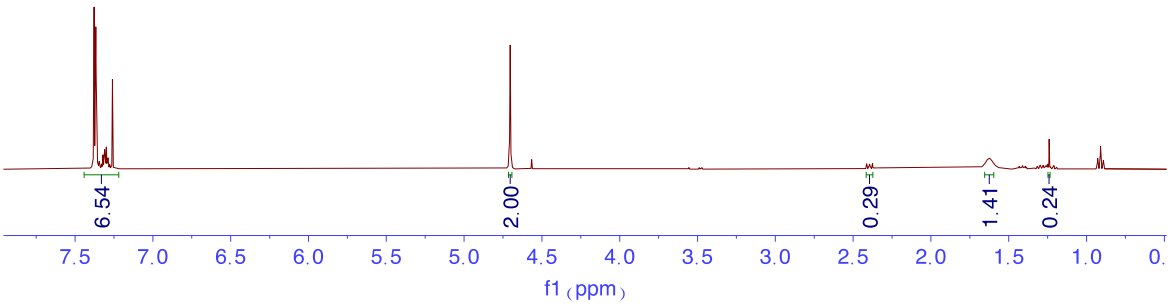


Figure S89. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.22-7.40 (m, 6H), 4.70 (s, 2H), 1.62 (s, 1H) ppm.

Benzaldehyde, Ph_2SiH_2:

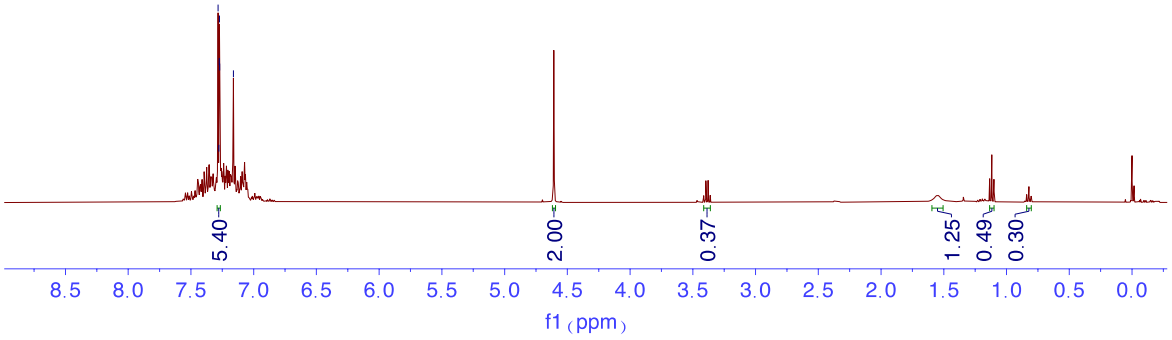


Figure S90. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.08-7.42 (m, 6H), 4.60 (s, 2H) , 1.57 (s, 1H, OH) ppm.

2D steric mapping

Percent buried volume (%V_{Bur})

The percent buried volume (%V_{Bur}) and topographical steric maps presented herein were calculated via the SambVca 2.1 web tool. [6, 7] The radius of the sphere around the silver metal centre was set to 3.5 Å, whereas for the atoms we adopted the Bondi radii scaled by 1.17, and a mesh spacing of 0.10 Å was used to scan the sphere for buried voxels.[6, 7]

[Ag(IDipp)HMDS] 3

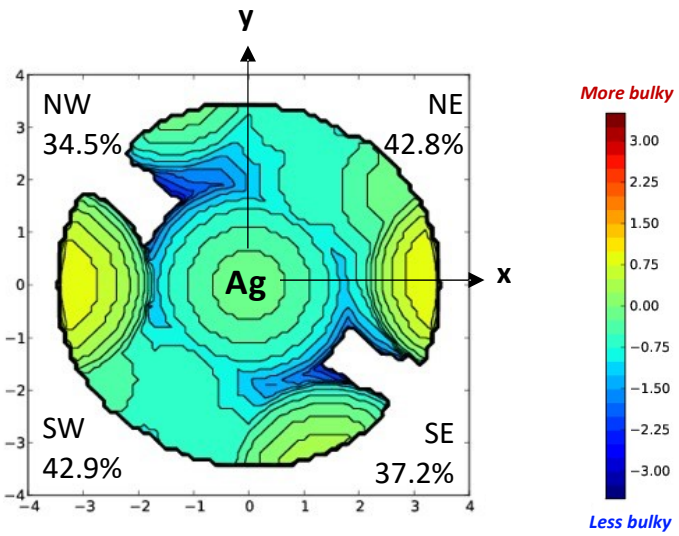


Figure S91. SambVca 2 calculated %V_{Bur} of 39.4% for [Ag(IDipp)HMDS] **3** represented by topographical streric maps including the %V_{Bur} of each quadrant NW, NE, SW and SE.

[Ag(IAd)HMDS] 4

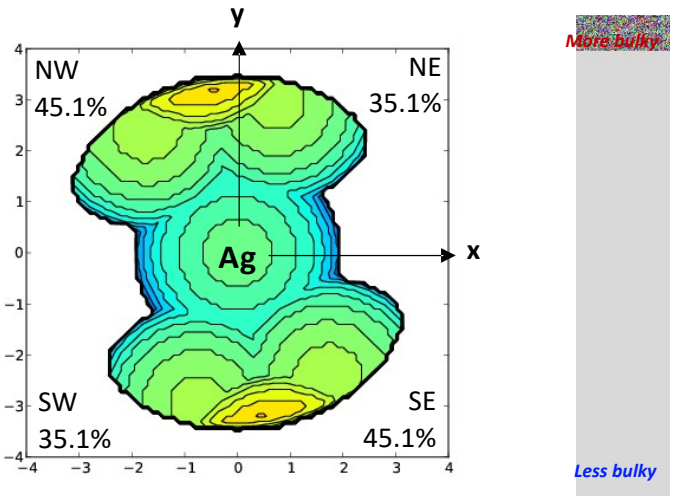


Figure S92. SambVca 2 calculated %V_{Bur} of 40.1% for [Ag(IAd)HMDS] **4** represented by topographical streric maps including the %V_{Bur} of each quadrant NW, NE, SW and SE.

[Ag(PCy$_3$)HMDS] 5

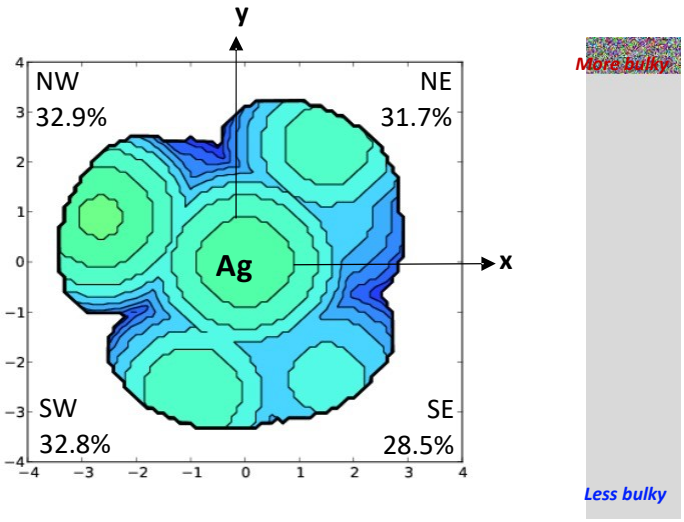


Figure S93. SambVca 2 calculated %V_{Bur} of 31.5% for [Ag(PCy$_3$)HMDS] **5** represented by topographical streric maps including the %V_{Bur} of each quadrant NW, NE, SW and SE

3D steric mapping

AtomAccess

Ray tracing of the accessible sites to the metal centre was performed on the *AtomAccess* program. [8, 9] The parameters utilised for the calculations are described in the *AtomAccess* manual,[9] where radial cut off defined as r_{max} is set to the default value of 5Å to account for the whole molecule. Finally, density was set to the default value of 10 as this provides a balance between precise values and accurate clustering. [9]

[Ag(IDipp)HMDS] 3

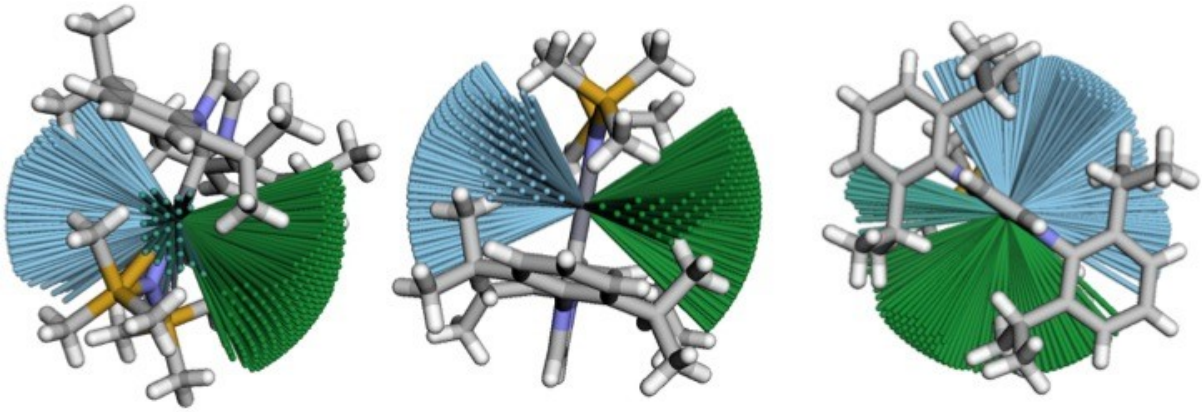
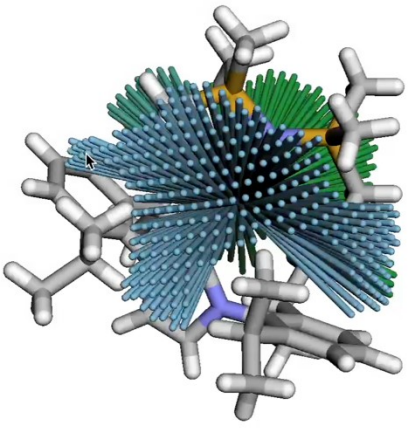


Figure S94. *AtomAccess* ray tracing of accessible sites to silver centre for [Ag(IDipp)HMDS] **3** using the atomic coordinates from the SCXRD dataset. Ray tracing obtained for **3**: Largest cluster: light blue (11.0%); minor clusters: green (9.0%) and teal (1.1%).



Video 1. Rotational video of the ray tracing of accessible sites to silver for **3**

[Ag(IAd)HMDS] 4

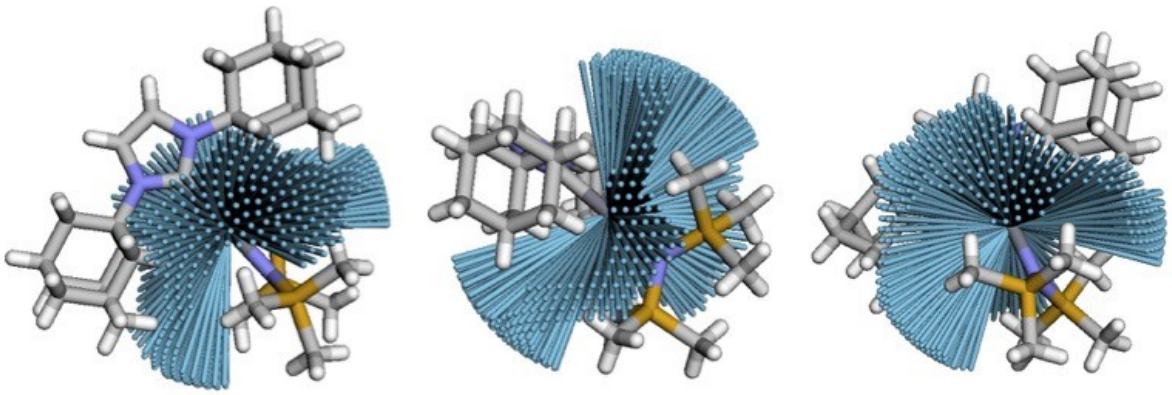
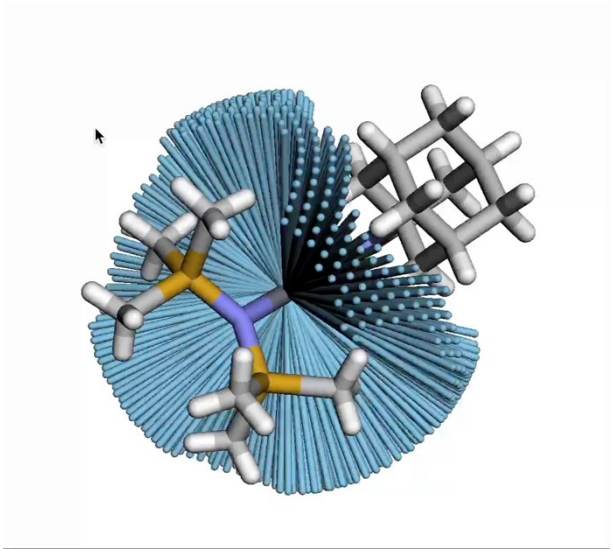


Figure S95. *AtomAccess* ray tracing of accessible sites to silver centre for [Ag(IAd)HMDS] **4** using the atomic coordinates from the SCXRD dataset. Ray tracing obtained for **4**: Largest cluster: light blue (22.6%).



Video 2. Rotational video of the ray tracing of accessible sites to silver for **4**

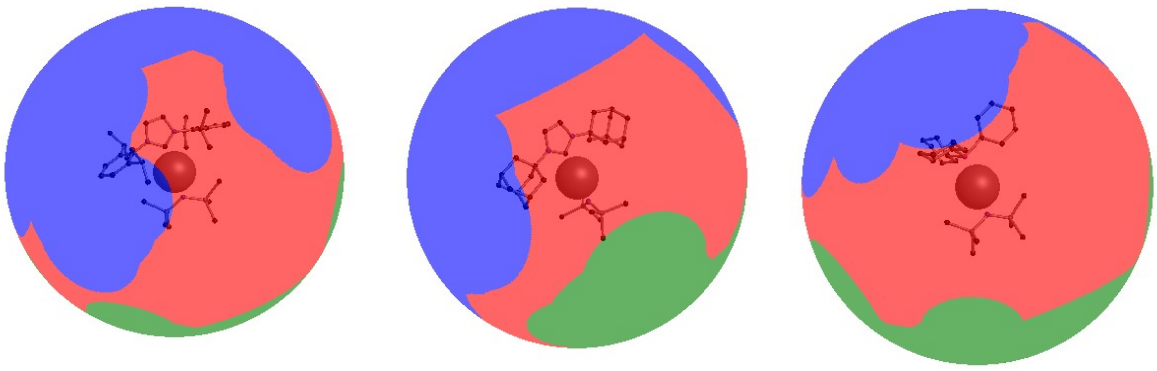
G-parameter

The solid G-angles for complexes **3**-**5** were calculated using the Solid-G web program. [10] The parameters utilised for the solid G-angle calculation includes G_M and $G_{2.28}$. The G_M depicts experimental values for the metal-carbene (M-C) distance calculated from the crystal structures of complexes **3**-**5**. The $G_{2.28}$ depicts the M-C normalised bond distance of 2.28 Å. Figure S89 depicts the solid angle (blue shading on the red sphere) for complexes **3**-**5** respectively.

Table S7. Calculated steric differences between complexes **3**-**5** calculated using $\%V_{Bur}$ and solid angle measurements (*G*-values)

Complex	$\%V_{Bur}$[a]	$\%V_{Bur}$[b]	G_M[b]	$G_{2.28}$[c]
[Ag(IDipp)HMDS] **3**	39.4	35.5	43.9	41.4
[Ag(IAd)HMDS] **4**	40.1	36.9	40.3	37.1
[Ag(PCy_3)HMDS] **5**	31.5	32.8	31.0	31.9

$\%V_{Bur}$ calculated using SambVca 2.1,[39] see ESI for details. Solid angle measurements (G-values) were calculated using Solid-G.[54] [a] $\%V_{Bur}$ was calculated using the M-C distances from the crystal structures of complexes **3**-**5**. [b] G-values were calculated using the M-C distances from the crystal structures of complexes **3**-**5**. [b] G-values were calculated using a normalised bond distance of 2.28 Å between M-C for complexes **3**-**5**.



3

$G_M = 43.9$
$\%V_{Bur} = 39.4\%$

4

$G_M = 40.3$
$\%V_{Bur} = 40.1\%$

5

$G_M = 31.0$
$\%V_{Bur} = 31.5\%$

Figure S96. Representation of the solid angle for complexes **3**-**5** using solid G-angles, for **3** $G_M = 43.9$, **4** $G_M = 40.3$ and **5** $G_M = 31.0$.

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