Supplementary Data for:

Carbonyl and Olefin Hydrosilylation Mediated by an Air-Stable Phosphorus(III) Dication Under Mild Conditions

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1. General Considerations

1.1. Chemicals and Materials

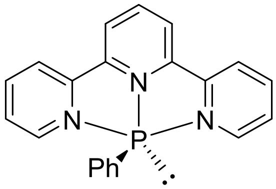
All manipulations were performed under an atmosphere of dry and deoxygenated N_2 under standard glovebox or Schlenk techniques unless otherwise stated. All glassware was dried in an oven at 220^{o}C followed by dynamic vacuum over several hours prior to use. After suitable drying procedures, all solvents were stored over 4 Å molecular sieves for a minimum of 24 hours prior to use. 4 Å molecular sieves were activated by heating in a sand bath (> 200^{o}C) under dynamic vacuum over 48 hours. Toluene, pentane, and diethyl ether (Et_2O) were purchased from Sigma Aldrich and were dried using a Grubbs-type Innovative Technologies solvent purification system. Dichloromethane (CH_2Cl_2) was purchased from Sigma Aldrich and was dried using a Grubbs-type Innovative Technologies solvent purification system followed by distillation from CaH_2. Chlorobenzene, acetonitrile-d3 (CD_3CN), 1,2-dichlorobenzene (o-$C_6H_4Cl_2$), 1,2-difluorobenzene (o-$C_6H_4F_2$), chloroform-d ($CDCl_3$) were distilled from CaH_2 and tetrahydrofuran (THF) was distilled from sodium-benzophenone prior to use. Triethylsilane (Et_3SiH) was purchased from Tokyo Chemical Industry (TCI) America and was used without further purification. Mesitylene and hexafluorobenzene (C_6F_6) were purchased from Sigma Aldrich and were used without further purification. All other silanes and substrates were used as purchased without further purification unless otherwise stated. Hamilton micro-syringes were used to transfer small amounts of liquid substrates (<25 µL). Small scale catalytic reactions were conducted in an NMR tube sealed with electrical tape and parafilm, containing standards of mesitylene and hexafluorobenzene. Plastic syringes and disposable needles were evacuated in the antechamber of the glovebox overnight prior to use.

1.2. Physical Methods

All NMR spectra were collected at 298 K on Bruker Avance III 400, Agilent DD2 400, Agilent DD2 500, or Agilent DD2 600 spectrometers in 3 or 5 mm diameter NMR tubes or in a J-Young tube. ^{1}H NMR spectra are referenced related to residual deuterated-solvent or protio-solvent signals. ^{19}F NMR spectra are referenced to an external standard of hexafluorobenzene (capillary containing hexafluorobenzene and mesitylene in $CDCl_3$). An external standard of mesitylene was used to measure the conversion of starting materials to products over time as monitored by NMR studies. Departmental facilities were used for mass spectrometry (DART: JEOL AccuTOF). GC-MS spectra were obtained on an Agilent Technologies 5975C VL MSD with TripleAxis Detector and 7890A GC System: Agilent Column 19091S-433 (30m × 250µm × 0.25µm) with helium as the carrier gas. The following 53-minute program was used to analyze samples: initial temperature of 50 °C (inlet temperature 250 °C), increase temperature 10 °C/min to 250 °C and hold for 3 minutes (23 minutes total), increase temperature 1 °C/min to 280 °C (30 minutes total). The solvent delay was 5 mins (DCM) with an injection volume of 1 µL.

2. Catalyst Synthesis

[TerpyPPh][B(C_6F_5)$_4$]$_2$ (1)



A solution of 2,2′:6′,2″-terpyridine (100 mg, 0.428 mmol) in 5 mL of dichloromethane was added over 5 minutes to a suspension of Na[B(C_6F_5)$_4$] (602 mg, 0.858 mmol) and $PhPCl_2$ (77 mg, 0.43 mmol) in 5 mL of dichloromethane. Immediately, a bright yellow solution was produced and stirring was maintained for an additional hour. The solution was filtered and the volatiles were removed *in vacuo* to afford a yellow oil. After washing with pentane (3 x 5 mL) and drying *in vacuo*, **(1)** was produced as a yellow powder (719 mg, 0.423 mmol, 98.8% yield). The characterization of **(1)** was consistent with reported literature values.[1]

3. General Procedure for Hydrosilylation Catalysis

Representative procedure for the hydrosilylation of ketones and aldehydes
A solution of the corresponding ketone or aldehyde (0.05 mmol) and triethylsilane (8.8 μL, 0.055 mmol) in dichloromethane (0.7 mL) was added to an NMR tube containing an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. An initial NMR spectrum was taken and then **1** (4.2 mg, 5 mol%) was added. The subsequent reaction was performed at either room temperature or in a monitored oil bath at 50°C. Conversion and yield were monitored by ^1H NMR spectroscopy. **1** can be removed *via* the addition of 0.5 mL of pentane to the reaction mixture followed by filtration through a plug of silica gel, eluting with additional pentane (1 mL). Removal of the volatiles *in vacuo* affords the product. GCMS data was collected by dissolving the product in 1.2mL of dichloromethane.

Representative procedure for the hydrodeoxygenation of ketones
A solution of the corresponding ketone or aldehyde (0.05 mmol) and triethylsilane (17.6 μL, 0.11 mmol) in dichloromethane (0.7 mL) was added to an NMR tube containing an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. An initial NMR spectrum was taken and then **1** (4.2 mg, 5 mol%) was added. The subsequent reaction was performed at either room temperature or in a monitored oil bath at 50°C. Conversion and yield were monitored by ^1H NMR spectroscopy. **1** can be removed *via* the addition of 0.5 mL of pentane to the reaction mixture followed by filtration through a plug of silica gel, eluting with additional pentane (1 mL). Removal of the volatiles *in vacuo* affords the product. GCMS data was collected by dissolving the product in 1.2mL of dichloromethane.

Representative procedure for the hydrosilylation of olefins or alkynes
A solution of the corresponding olefin or alkyne (0.05 mmol) and triethylsilane (8.8 μL, 0.055 mmol) in dichloromethane (0.7 mL) was added to an NMR tube containing an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. An initial NMR spectrum was taken and then **1** (4.2 mg, 5 mol%) was added. The subsequent reaction was performed at either room temperature

or in a monitored oil bath at 50°C. Conversion and yield were monitored by ^{1}H NMR spectroscopy. **1** can be removed *via* the addition of 0.5 mL of pentane to the reaction mixture followed by filtration through a plug of silica gel, eluting with additional pentane (1 mL). Removal of the volatiles *in vacuo* affords the product. GCMS data was collected by dissolving the product in 1.2mL of dichloromethane.

Representative procedure for catalyses with isolated products.

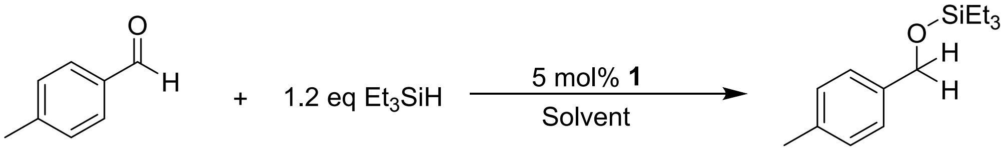
A solution of **1** (84 mg, 0.05 mmol) in dichloromethane (1 mL) was added to a solution of the corresponding substrate (1 mmol) and triethylsilane (176 mg, 1.1 mmol) in dichloromethane (10 mL). The resulting yellow solution was stirred for 24 hours, before 5 mL of pentane was added before filtering through a plug of silica gel, and eluted with additional pentane. The volatiles were removed *in vacuo* to yield the product.

Representative procedure for reactions performed under ambient air

1 (4.2 mg, 5 mol %) was let stand in ambient air for 6 hours before being added to a solution of the corresponding substrate (0.05 mmol) and triethylsilane (8.8 µL, 0.055 mmol) in dichloromethane (0.7 mL), which had been placed under a stream of air for 2 minutes. The resulting mixture was added to an NMR tube and was reacted for the required amount of time as monitored by ^{1}H NMR spectroscopy.

4. Catalysis Optimization

4.1. Hydrosilylation of 4-methylbenzaldehyde with Et_3SiH with different solvents



Solvent	**Temperature**	**Time**	**Conversion (%)**
CH_2Cl_2	25°C	13 hr	>99%
Toluene	25°C	24 hr	0%
C_6H_5Cl	25°C	24 hr	41%
THF	25°C	13 hr	26 %
$CDCl_3$	25°C	24 hr	80%
o-$C_6H_4Cl_2$	25°C	13 hr	>99%
o-$C_6H_4F_2$	25°C	13 hr	>99%
Et_2O	25°C	13 hr	0%
CD_3CN	25°C	24 hr	<10%
None	25°C	13 hr	>99%

Table S1. Summary of the solvent optimization for the catalytic hydrosilylation of 4-methylbenzaldehyde.

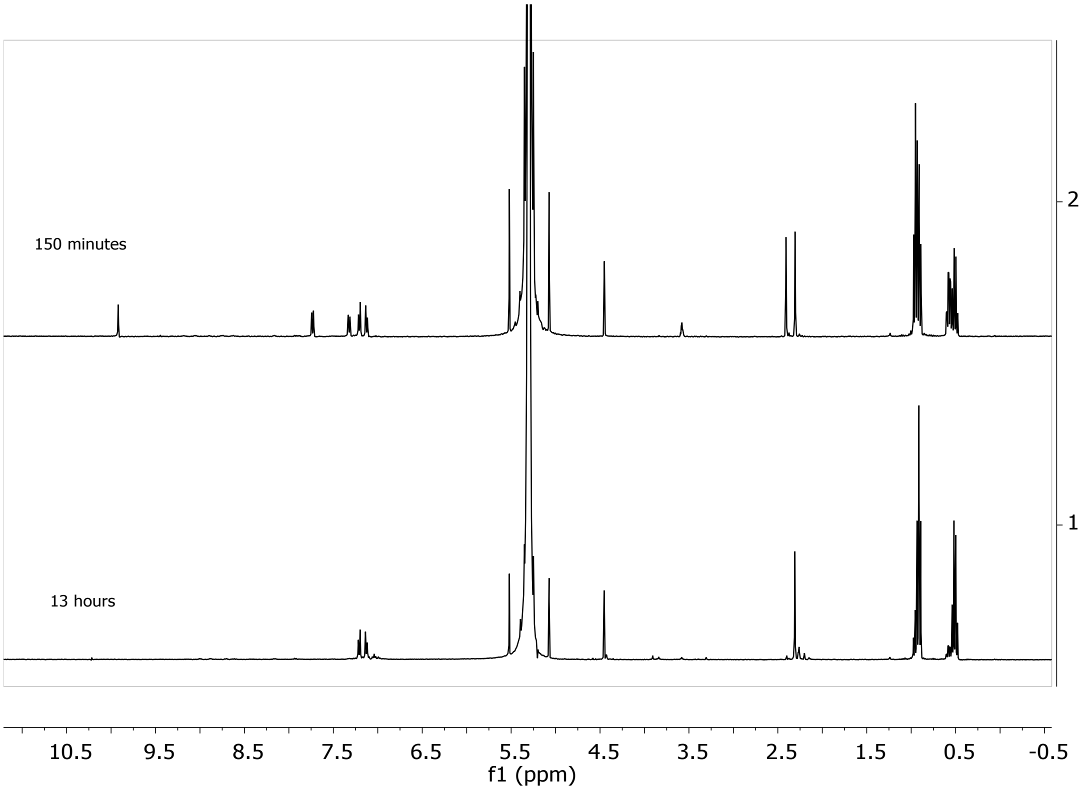


Figure S1. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

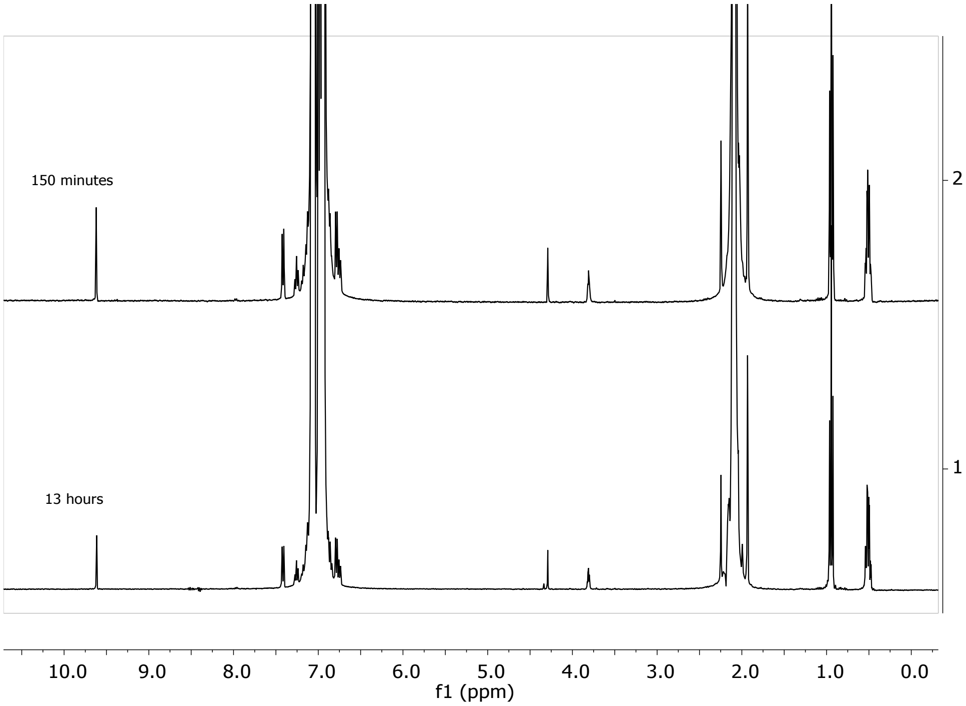


Figure S2. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in toluene. The NMR spectra are referenced to the $CH_3C_6H_5$ resonance at 2.09 ppm.

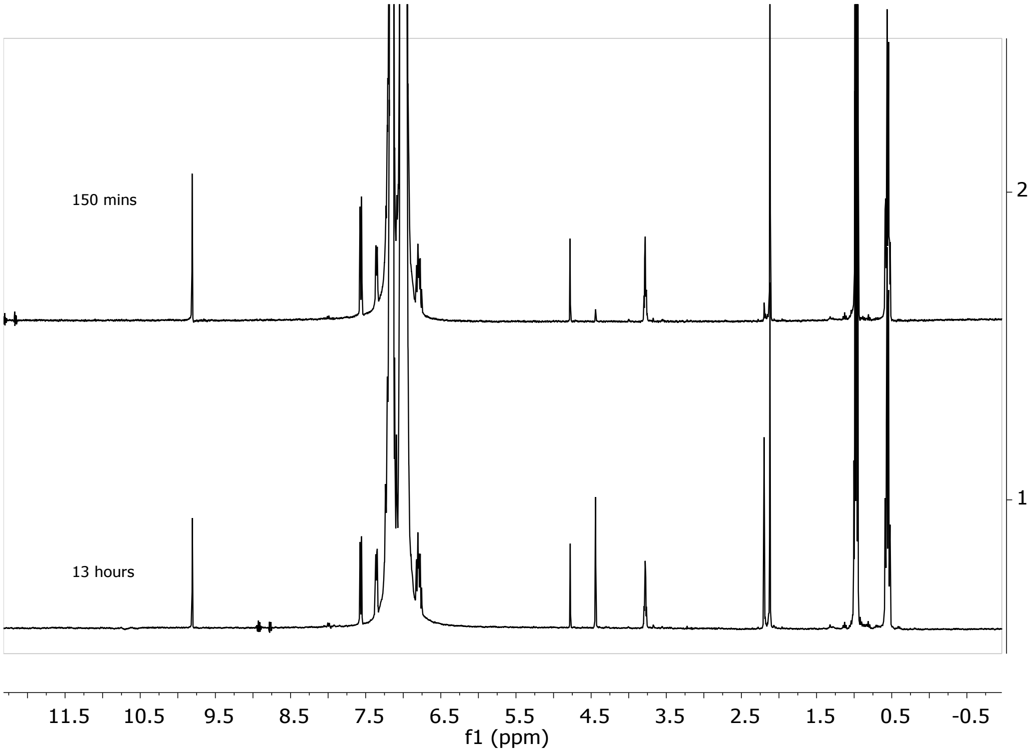


Figure S3. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in CH_5Cl. The NMR spectra are referenced to the CH_5Cl resonance at 7.14 ppm.

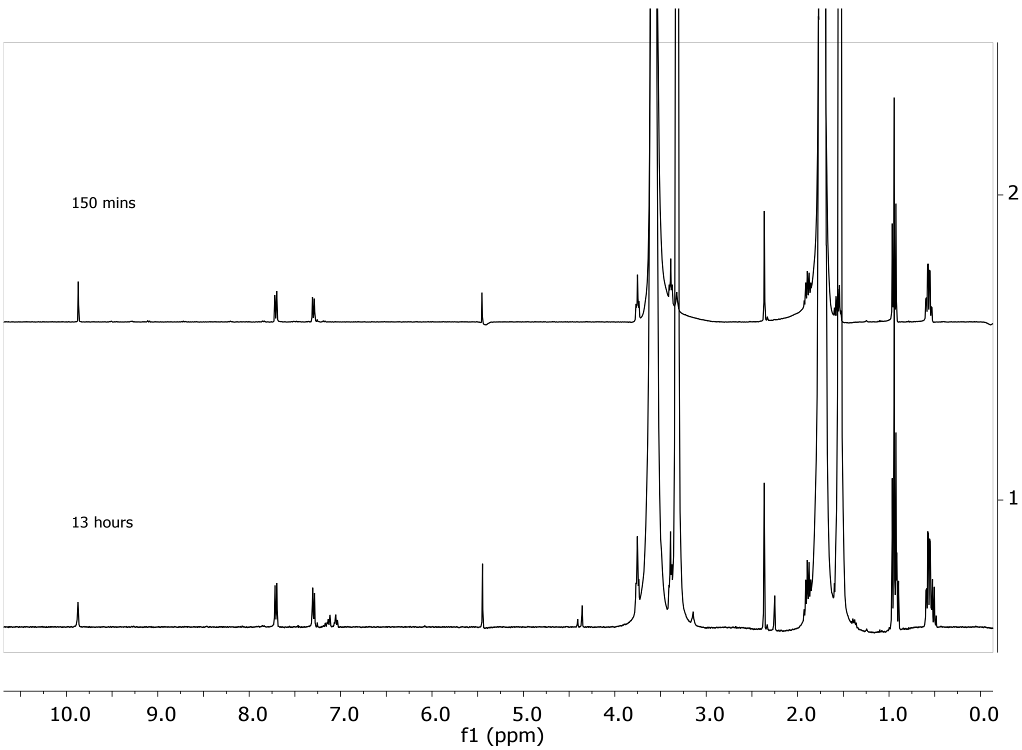


Figure S4. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in tetrahydrofuran. The NMR spectra are referenced to the THF resonance at 1.75 ppm.

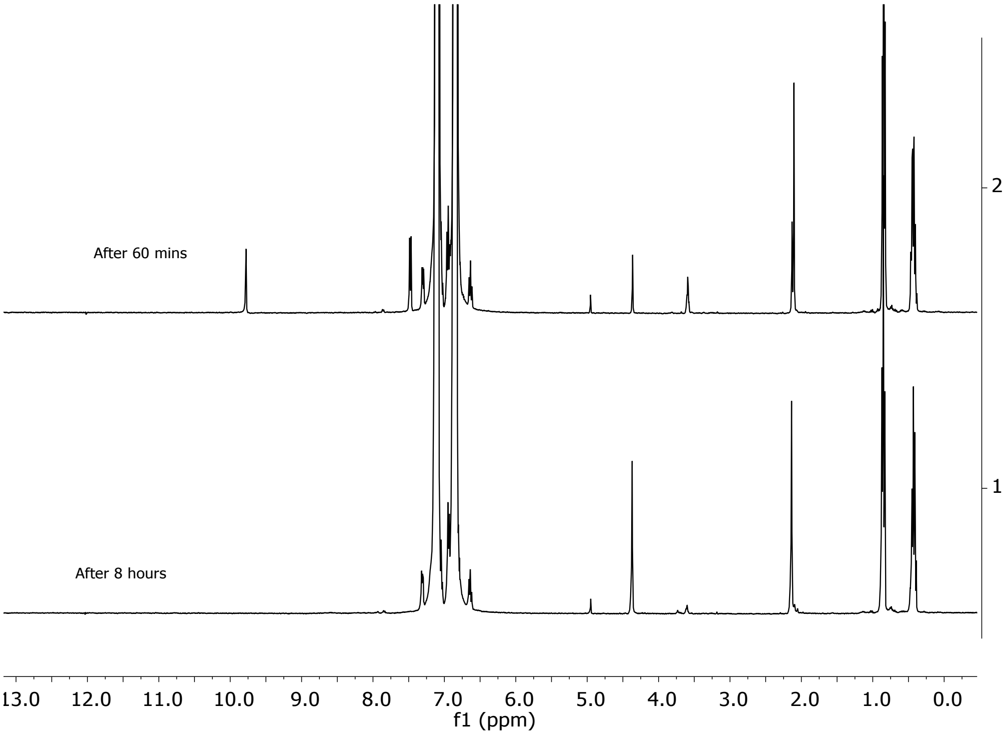


Figure S5. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in orthodichlorobenzene. The NMR spectra are referenced to the $C_6H_4Cl_2$ signal at 7.11 ppm.

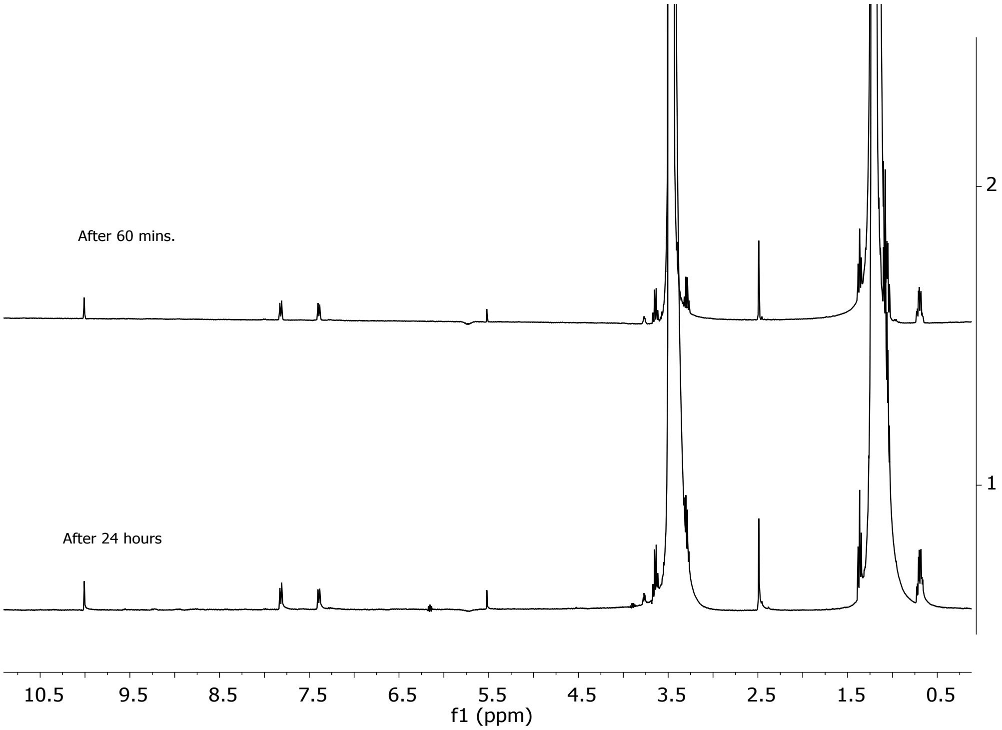


Figure S6. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in diethyl ether. The NMR spectra are referenced to the Et_2O signal at 1.21 ppm.

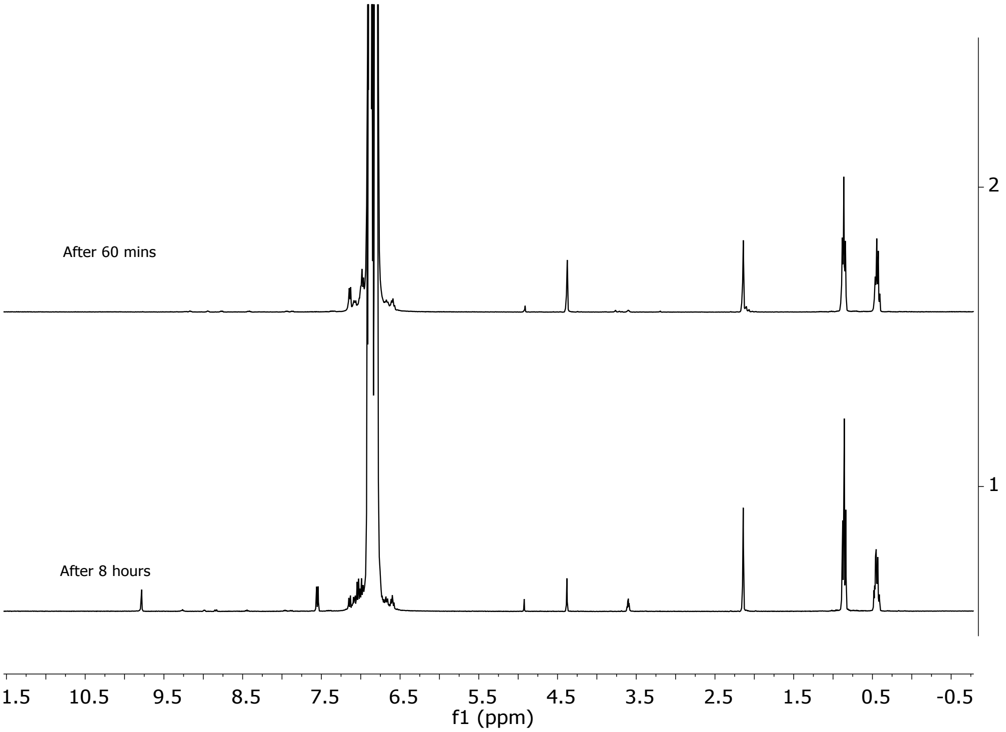


Figure S7. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in orthodifluorobenzene. The NMR spectra are referenced to the $C_6F_2H_4$ signal at 6.81 ppm.

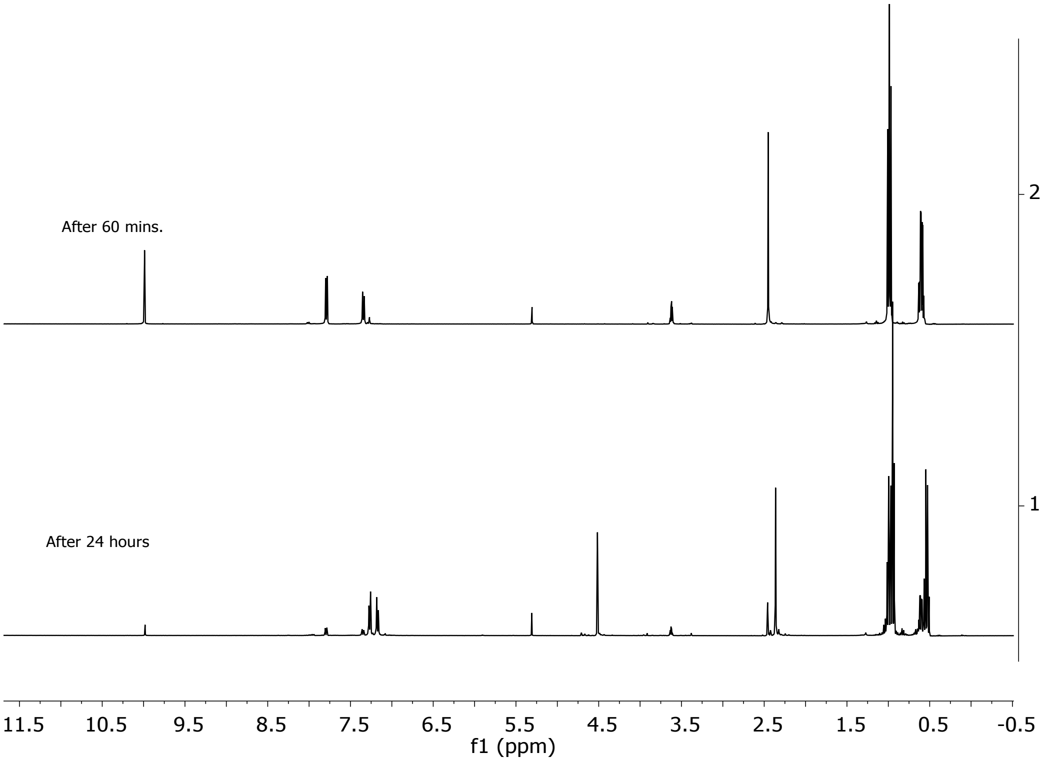


Figure S8. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in chloroform-d. The NMR spectra are referenced to the $CDCl_3$ signal at 7.27 ppm.

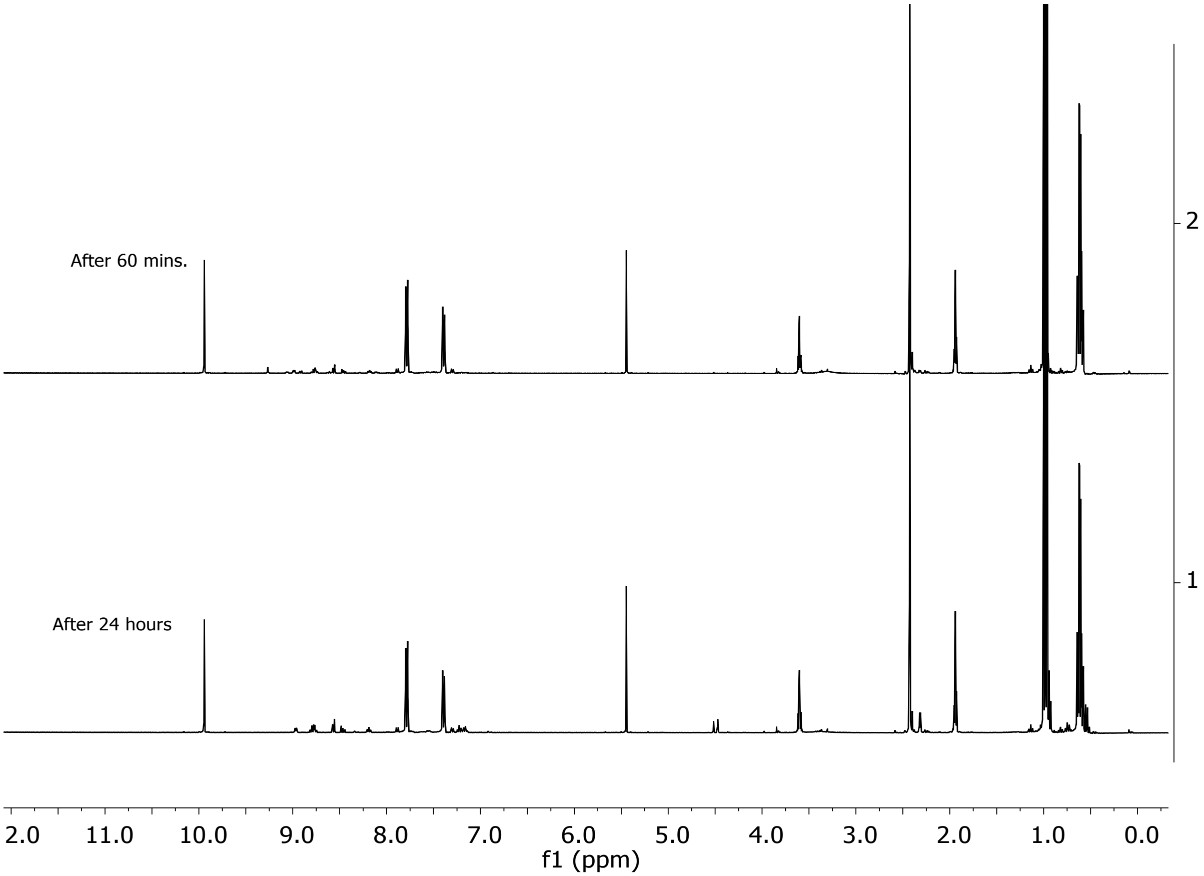
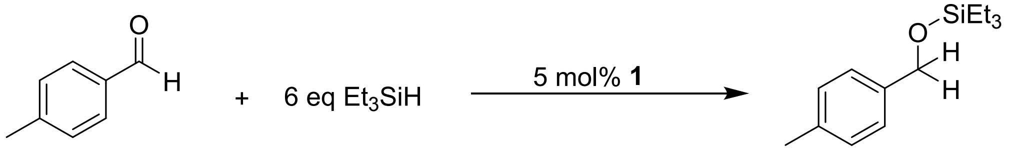


Figure S9. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in acetonitrile-d3. The NMR spectra are referenced to the CD_3CN signal at 1.94 ppm.

4.2. Hydrosilylation of 4-methylbenzaldehyde with Et_3SiH without a solvent



Procedure: 4-methylbenzaldehyde (5.9 μL, 0.050 mmol) and Et_3SiH (48 μL, 0.30mmol) was added to **1** (4.2 mg, 5 mol%) and the resulting suspension was stirred. After 13 hours, the mixture was dissolved in CH_2Cl_2 and the conversion was immediately monitored by ^{1}H NMR spectroscopy.

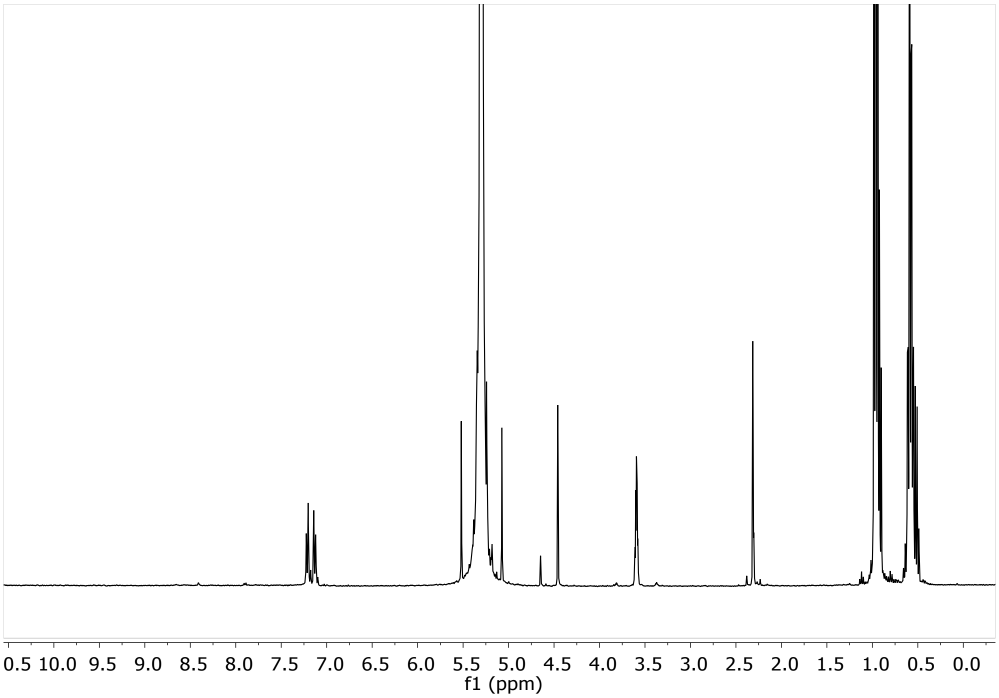
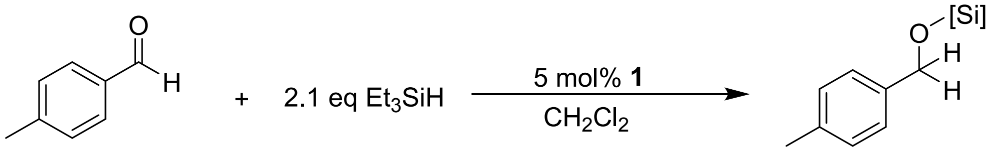


Figure S10. ^{1}H NMR (298K, 400 MHz) spectrum for the catalytic hydrosilylation of 4-methylbenzaldehyde without a solvent after 13 hours. NMR spectrum is referenced to the CH_2Cl_2 resonance at 5.30 ppm.

4.3. Hydrosilylation of 4-methylbenzaldehyde with silanes and siloxanes



* = equivalents per Si-H present in silane or siloxane

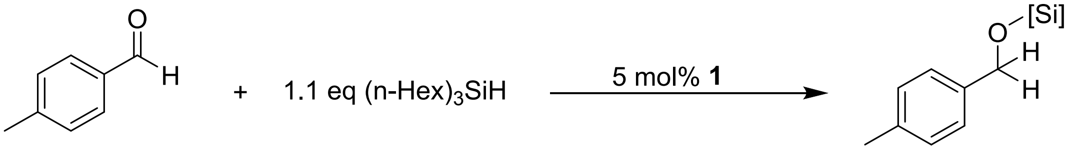
To an NMR tube containing 4-methylbenzaldehyde (5.9 µL, 0.05 mmol) and the corresponding silane or siloxane (0.055 mmol) in dichloromethane (0.7 mL) was added **1** (4.2 mg, 5 mol%). The resulting mixture was settled in an NMR tube and reacted at room temperature. Conversion was monitored by ^{1}H NMR spectroscopy.

Silane/Siloxane	**Time**	**Conversion (%)**
Et_3SiH	24 hr	>99%
$(nHex)_3SiH$	24 hr	26%
$(Me_3Si)_3SiH$	24 hr	0%
Ph_2MeSiH	24 hr	59%
Ph_3SiH	24 hr	0%
Ph_2SiH	24 hr	0%

$(C_6F_5)_3SiH$	24 hr	0%
$(EtO)_3SiH$	24 hr	0%
$(NMe_2)_3SiH$	30 min	>99%
Pentamethyldisiloxane $[Me_3SiOSi(Me_2)H]$	30 min	>99%
1,1,3,3-tetramethyldisiloxane $[(Me_2HSi)_2O]$	30 min	>99%
1,1,1,2,2,3,3-heptamethyltrisiloxane	30 mins	>99%
1,1,1,2,2,3,3-heptamethyltrisiloxane[1]	5 hr	68%
1,1,1,2,2,3,3-heptamethyltrisiloxane[1]	24 hr	75%
$(Me_3SiO)_3SiH$	24 hr	0%
Poly(methylhydrosiloxane) (PMHS)	24 hr	23%

[1] Reaction performed on benchtop, after components were mixed under ambient conditions

Table S2. Summary of the catalytic hydrosilylation reactions of 4-methylbenzaldehyde with different silanes and siloxanes.



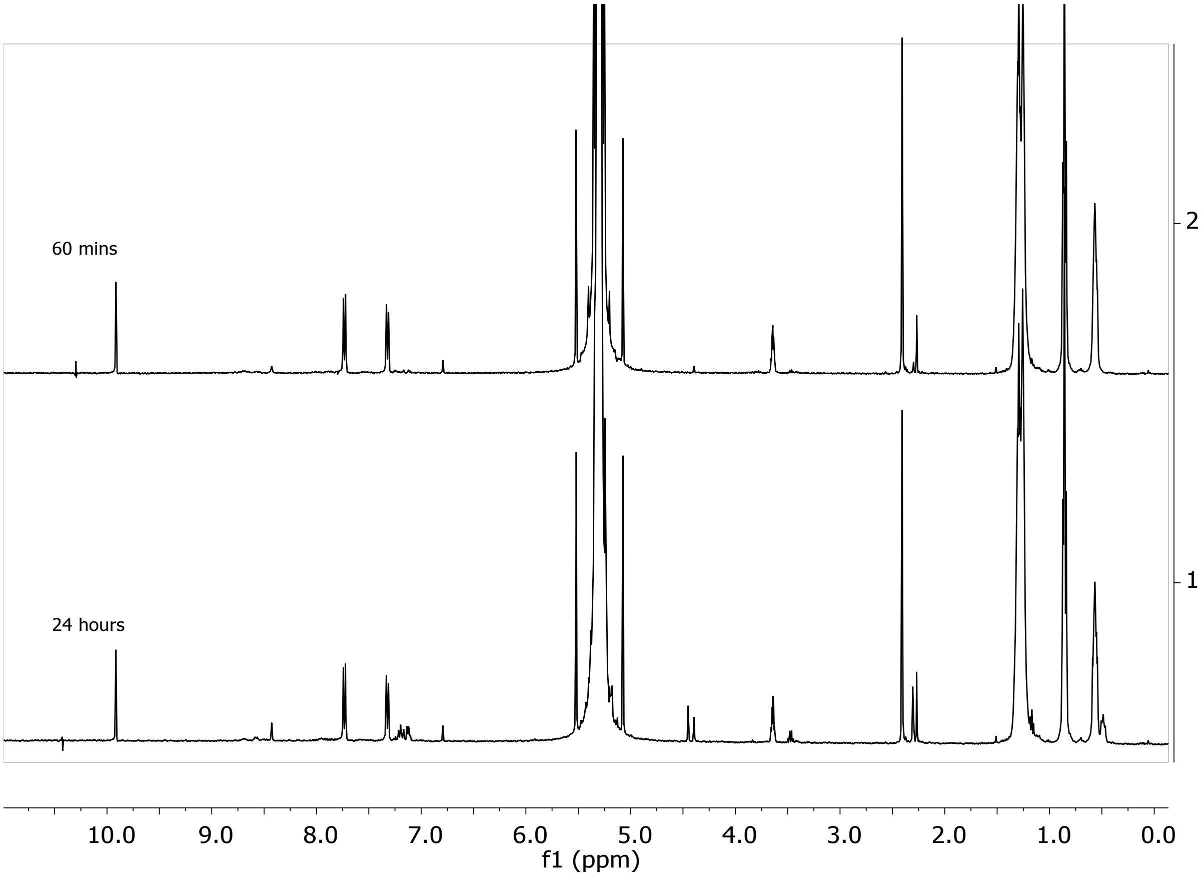


Figure S11. ^1H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tris(n-hexyl)silane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

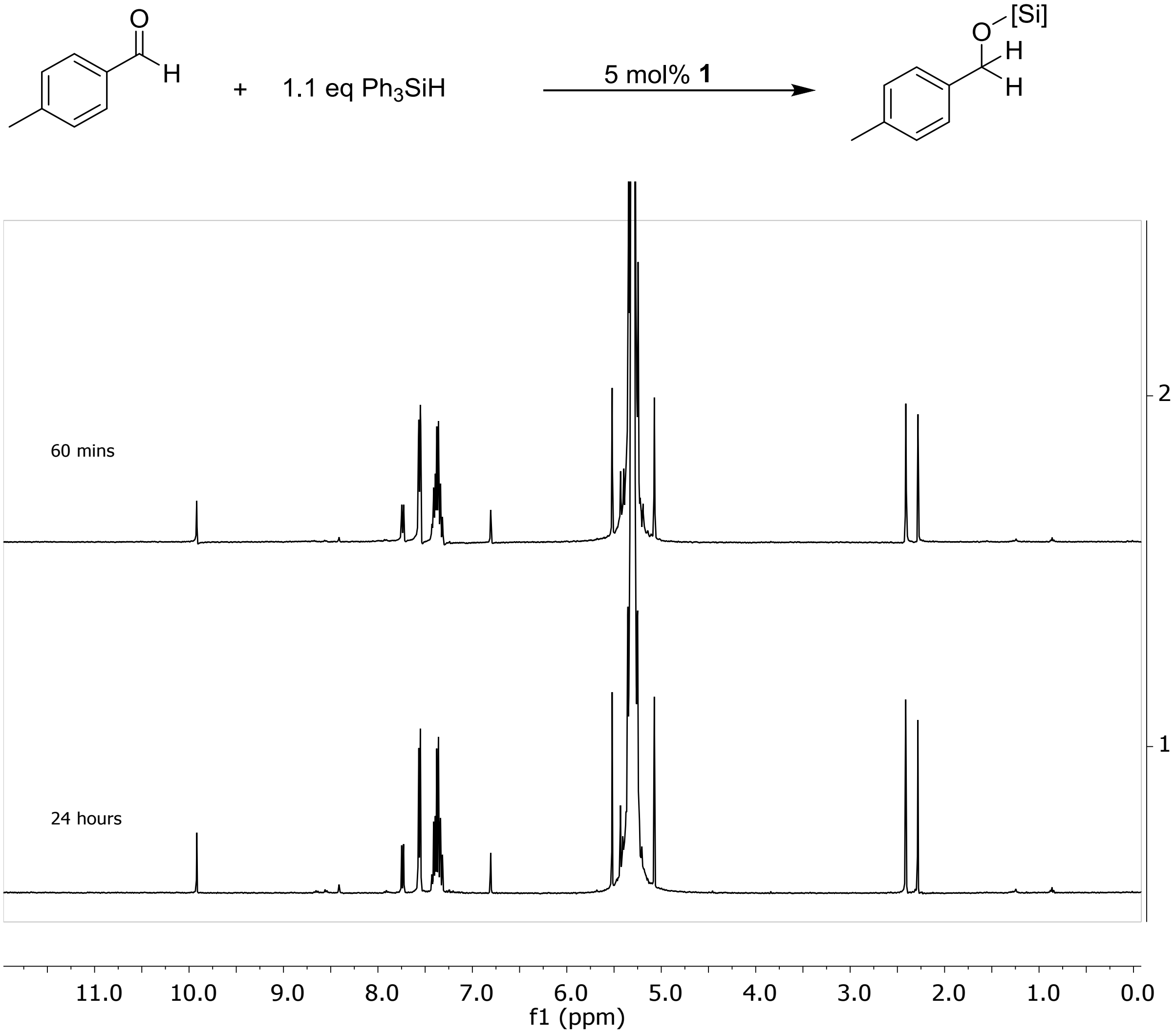


Figure S12. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with triphenylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

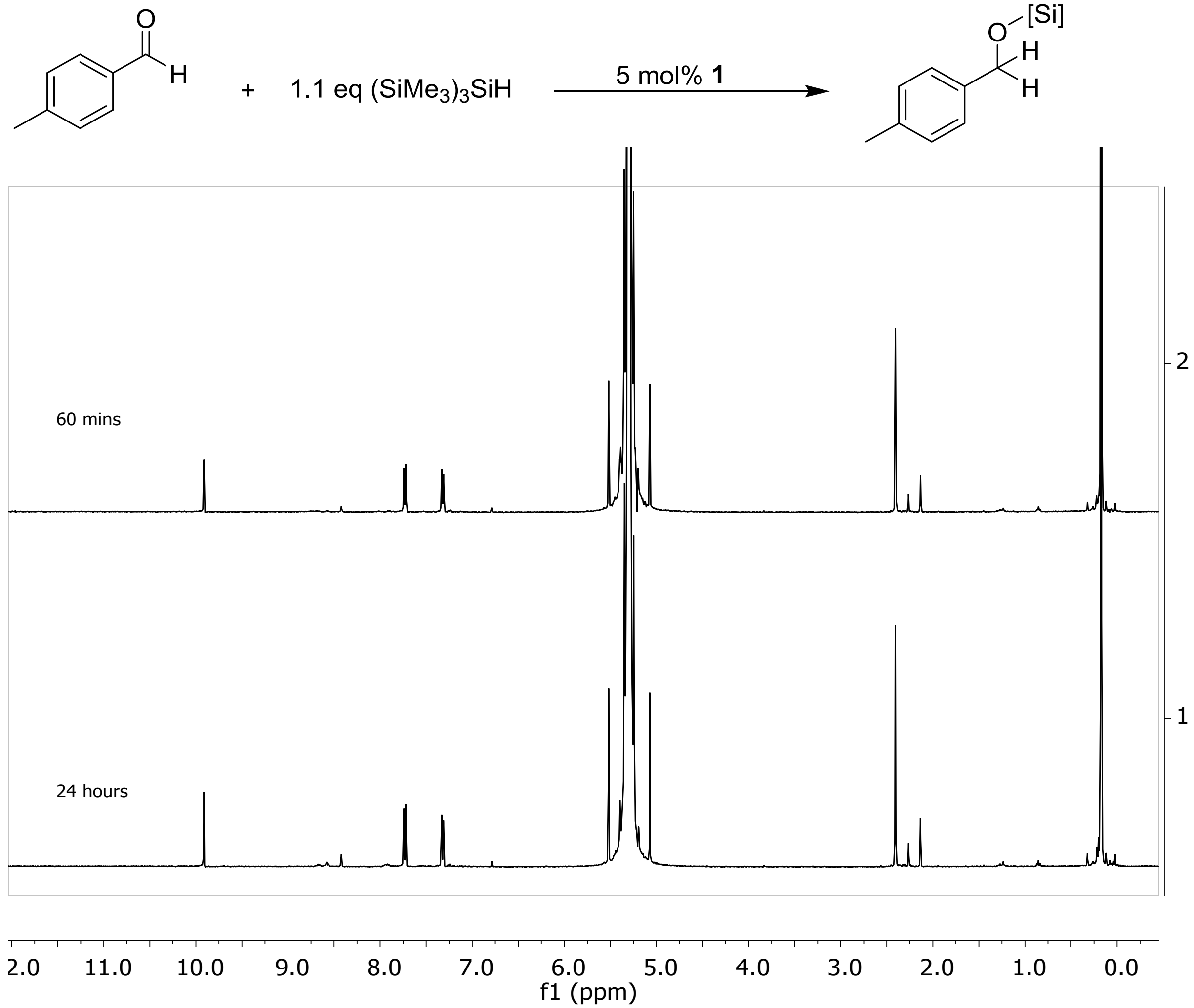


Figure S13. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tris(trimethylsilyl)silane. The NMR spectra are referenced to the CH$_2$Cl$_2$ resonance at 5.30 ppm.

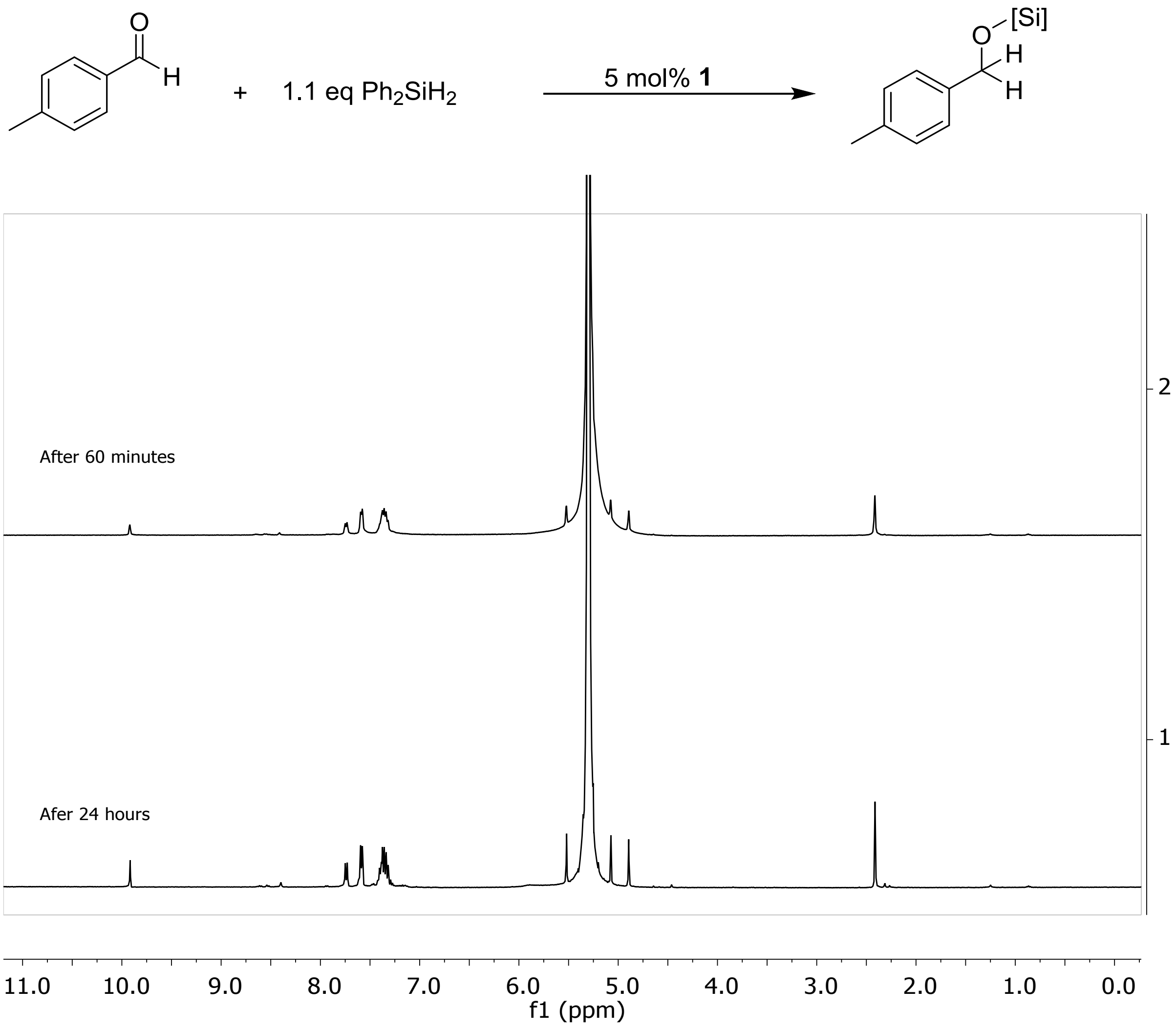


Figure S14. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with diphenylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

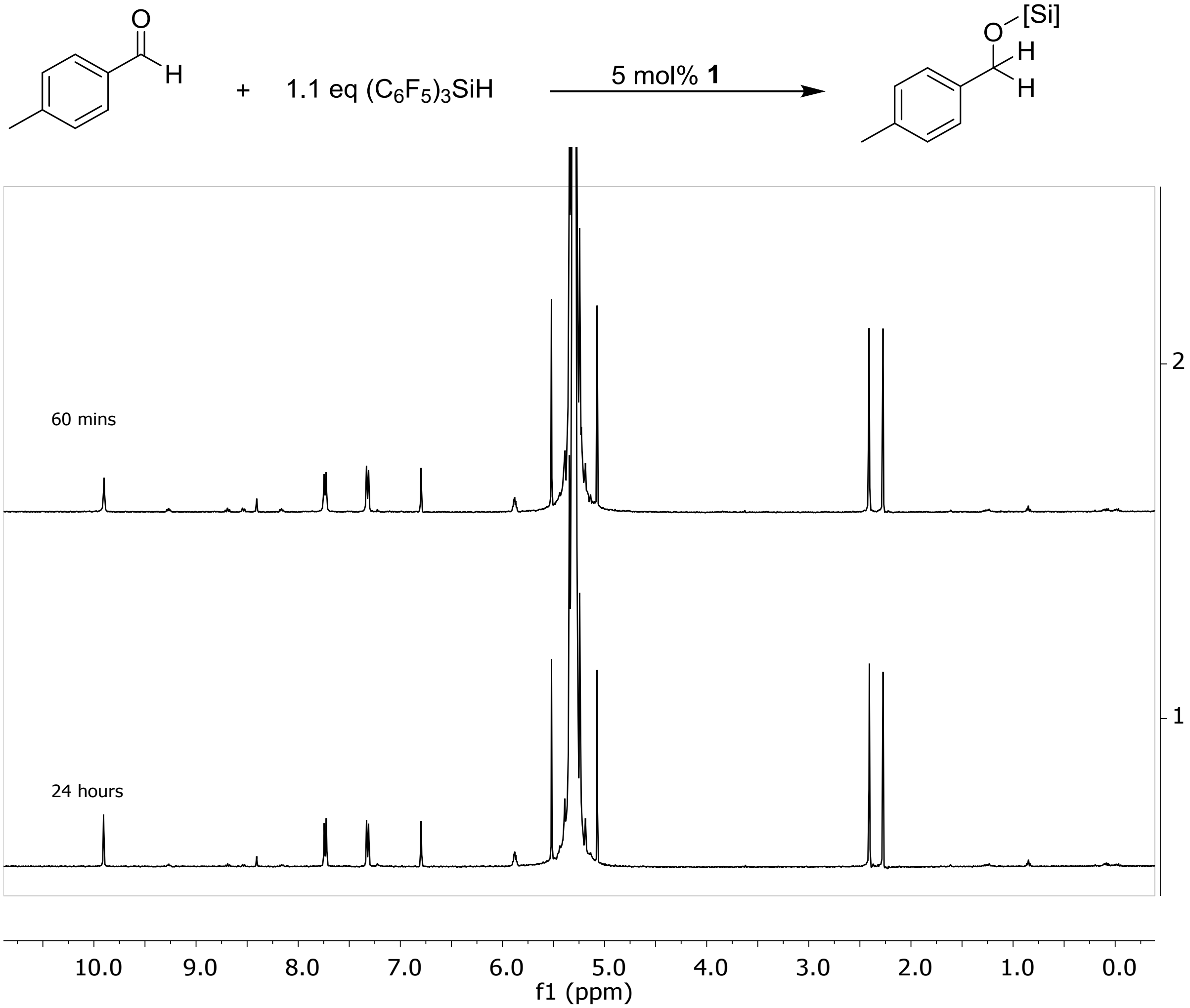


Figure S15. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tris(pentafluorophenyl)silane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

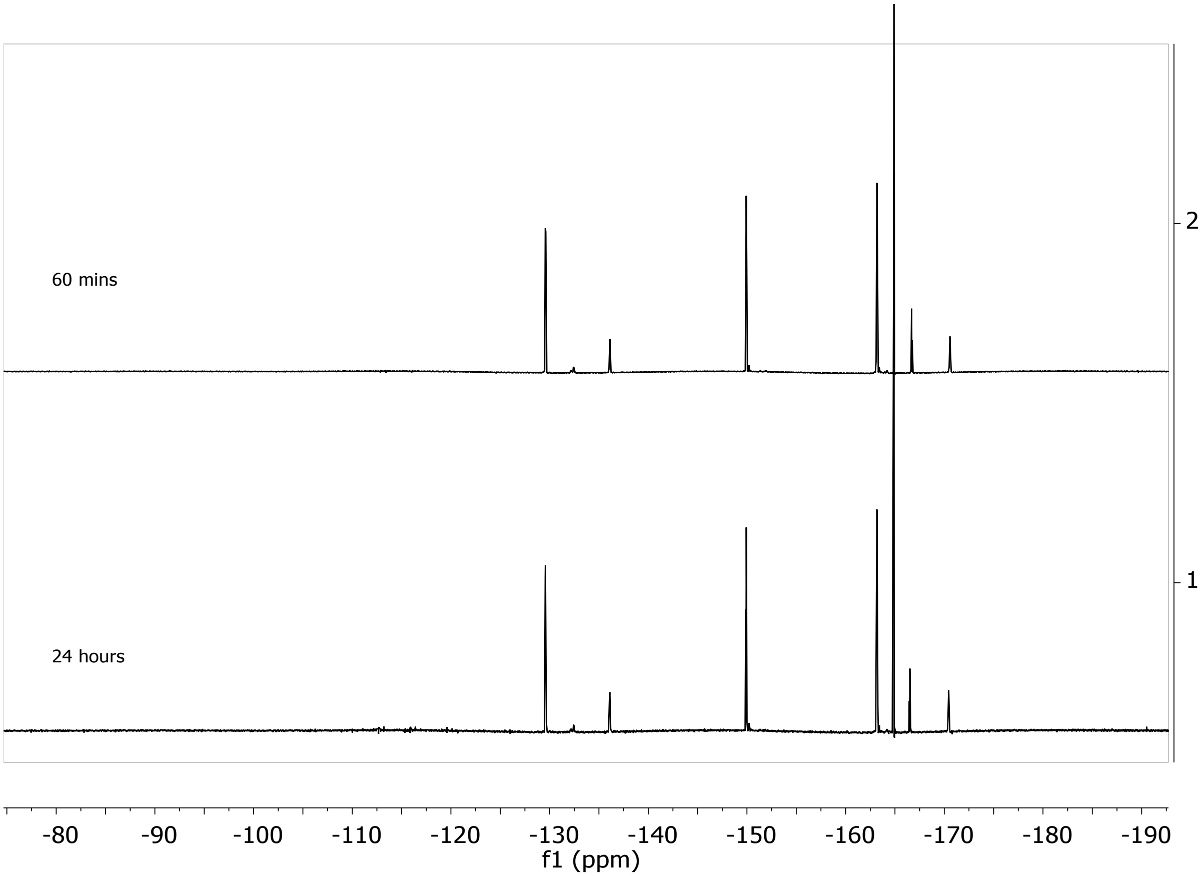
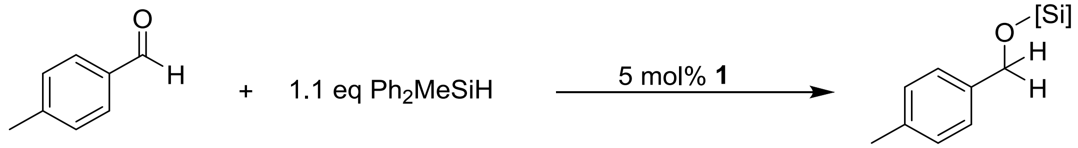


Figure S16. $^{19}F\{^{1}H\}$ NMR (298K, 377 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tris(pentafluorophenyl)silane. The NMR spectra are referenced to the hexafluorobenzene resonance at -163.0 ppm by using an external standard of hexafluorobenzene and mesitylene in $CDCl_3$.



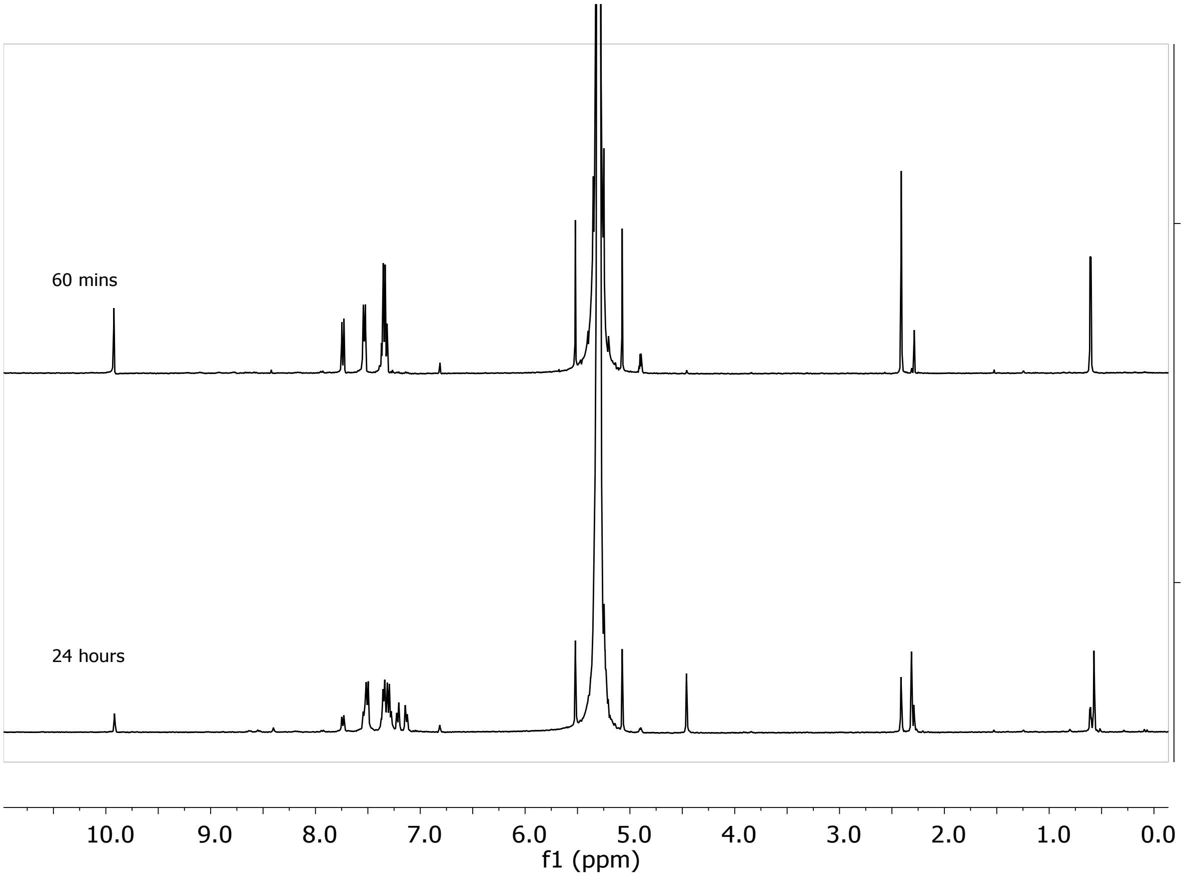


Figure S17. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with methyldiphenylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

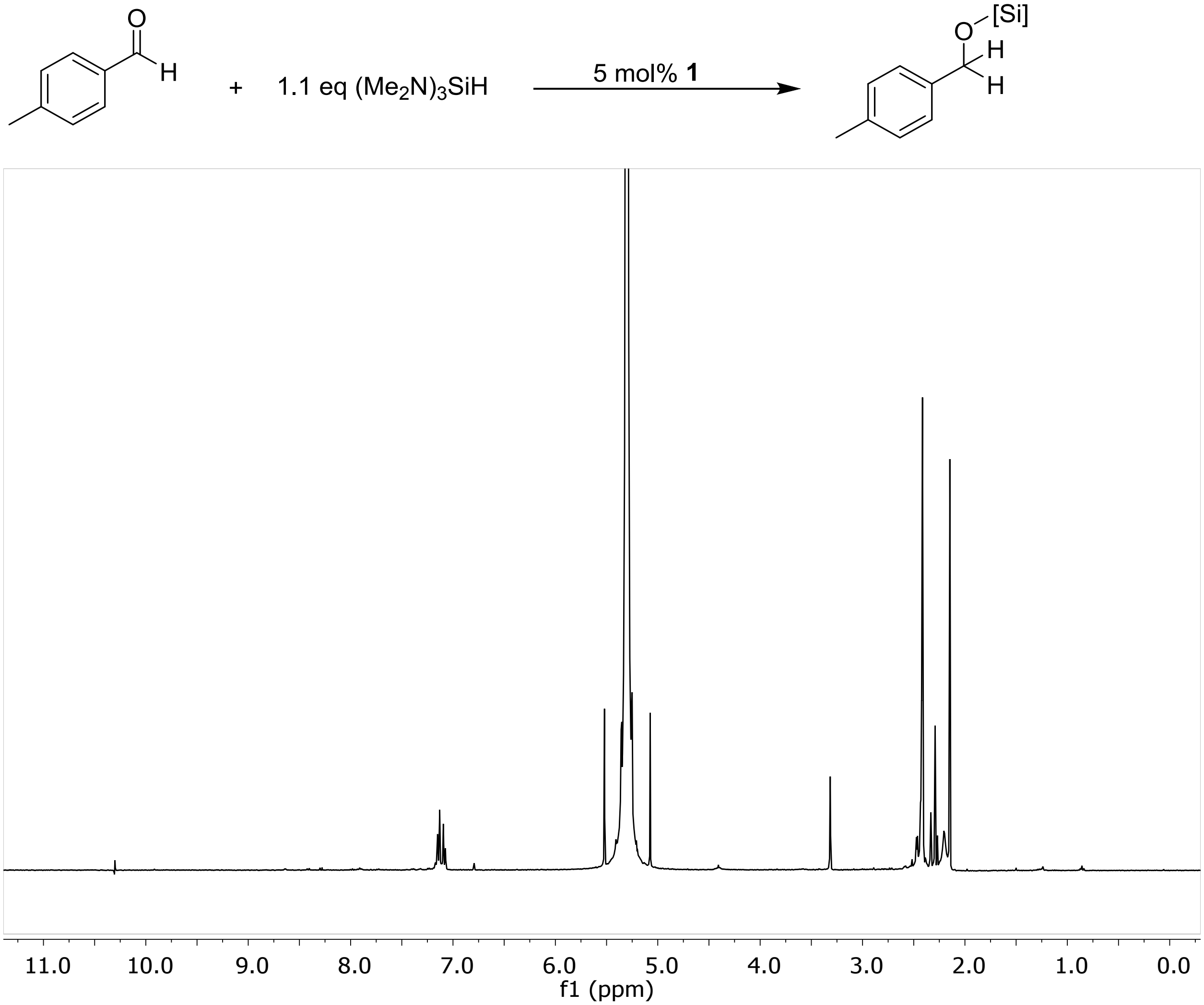


Figure S18. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tris(dimethylamino)silane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm. NMR spectrum taken after 60 minutes.

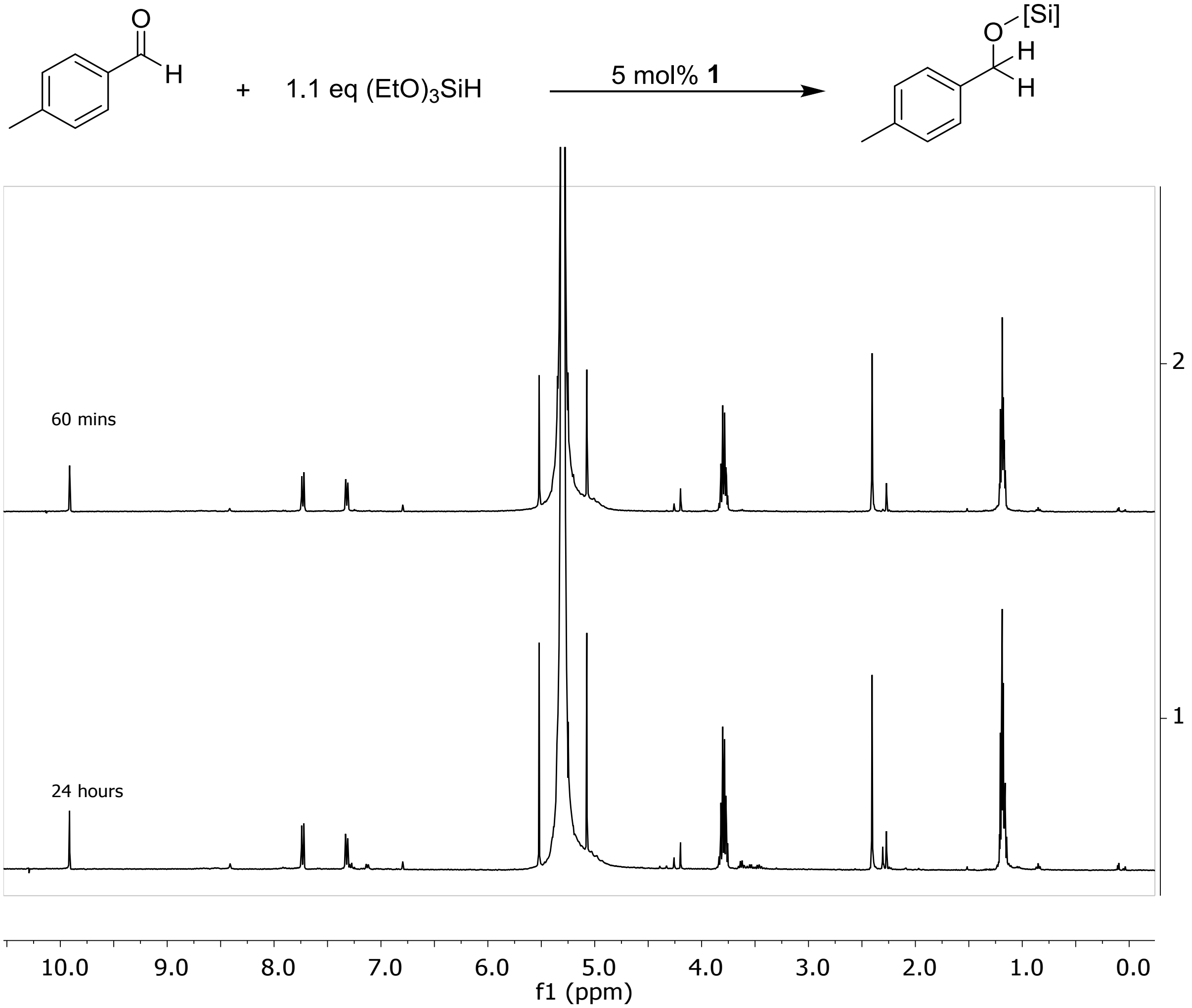


Figure S19. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with triethoxysilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

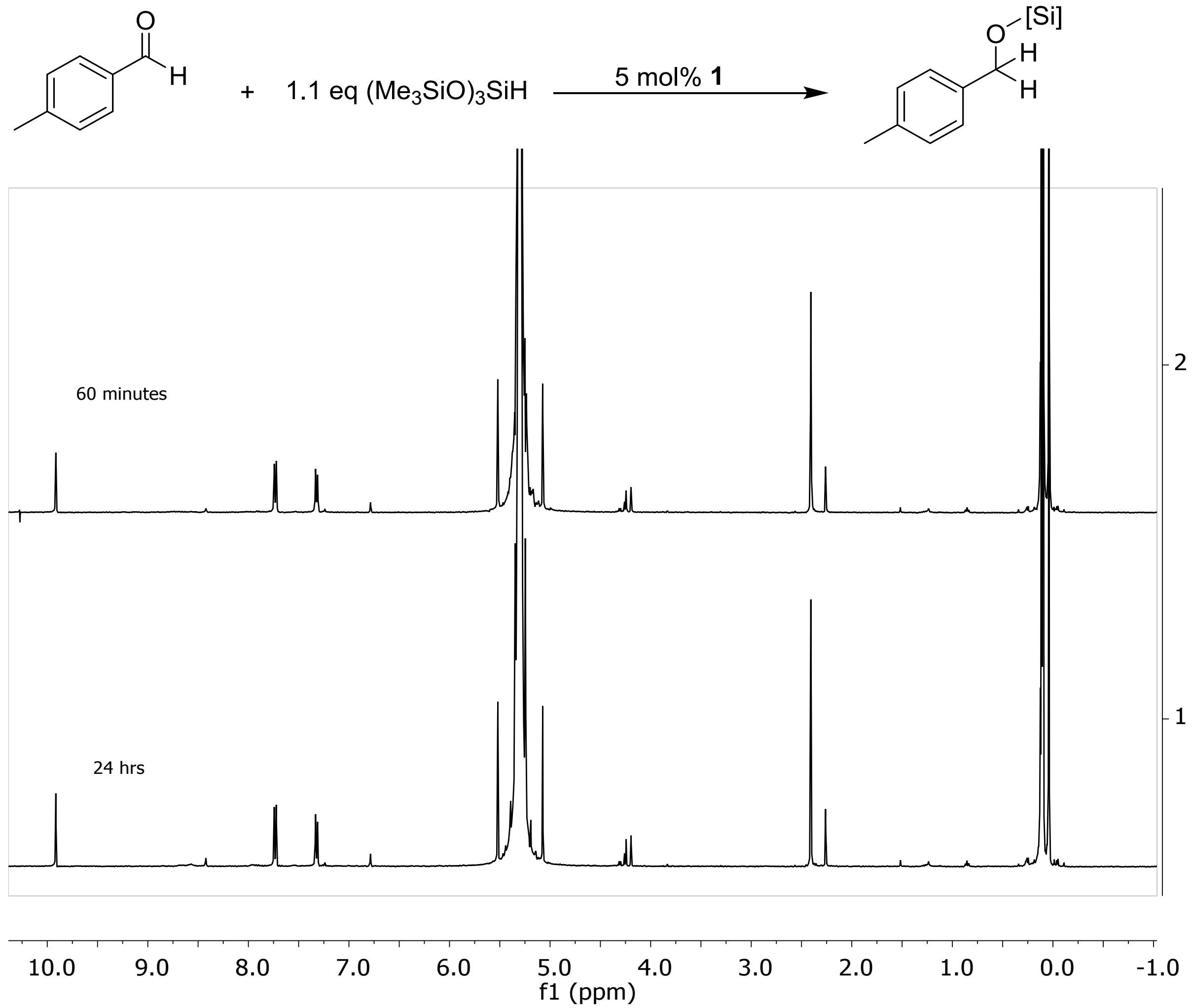
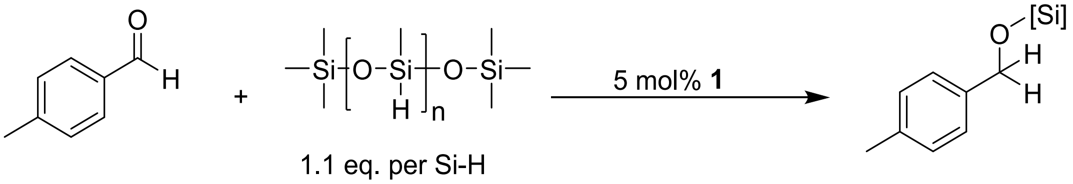


Figure S20. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tris(trimethylsiloxy)silane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



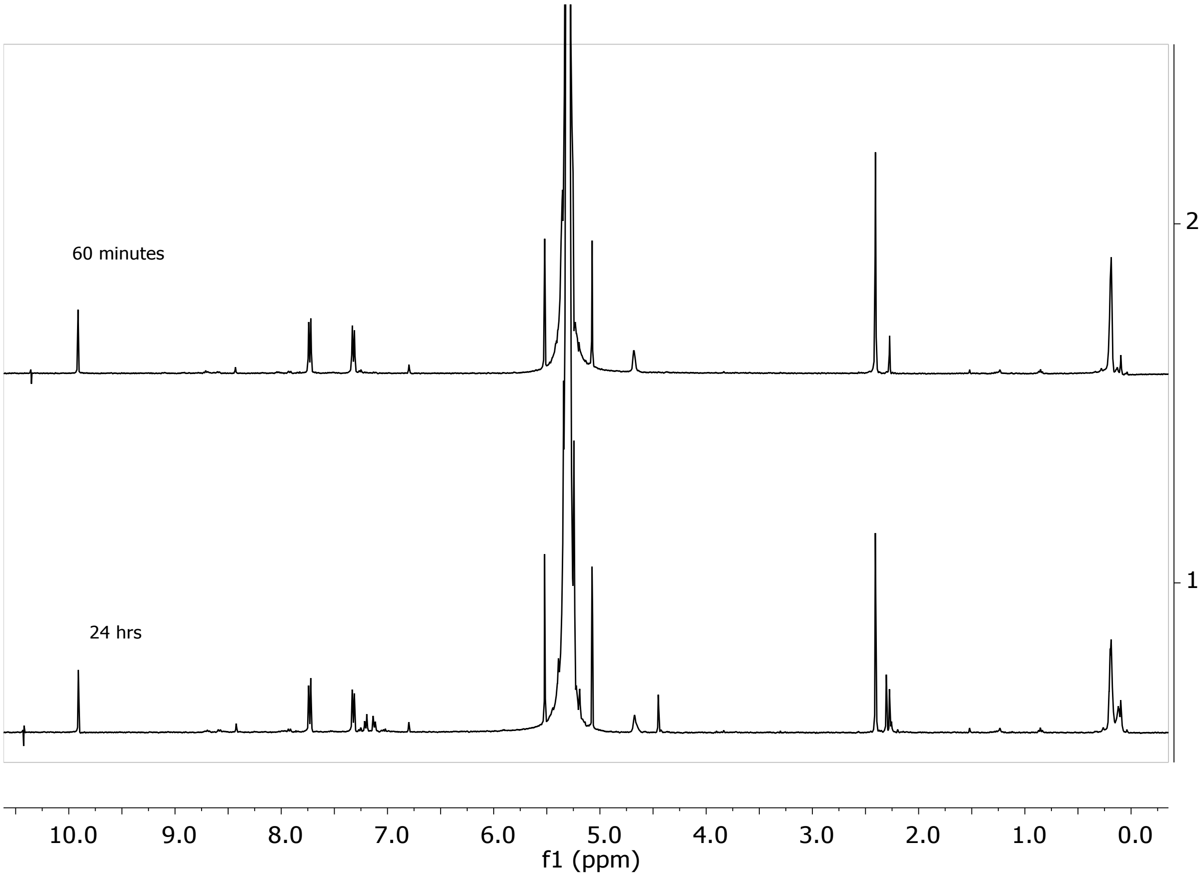


Figure S21. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with polymethylhydrosiloxane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

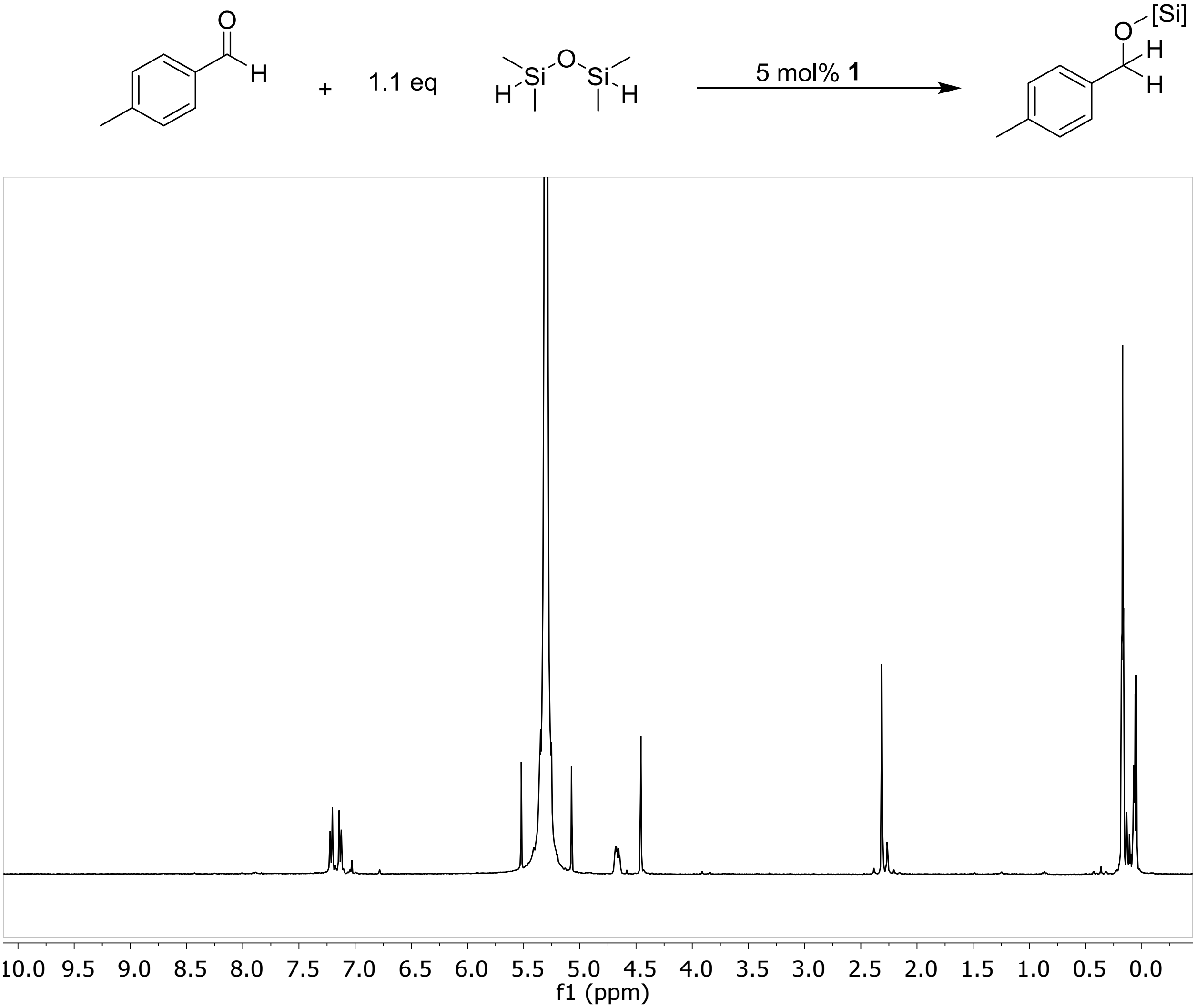
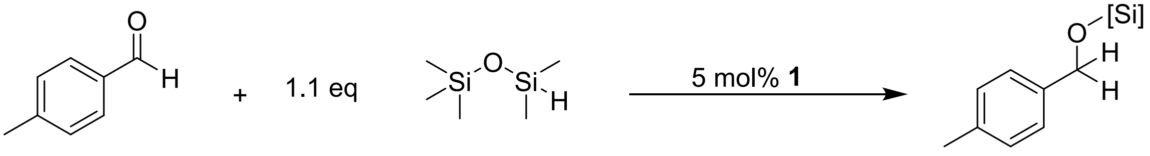


Figure S22. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with tetramethyldisiloxane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm. NMR spectrum taken after 60 minutes.



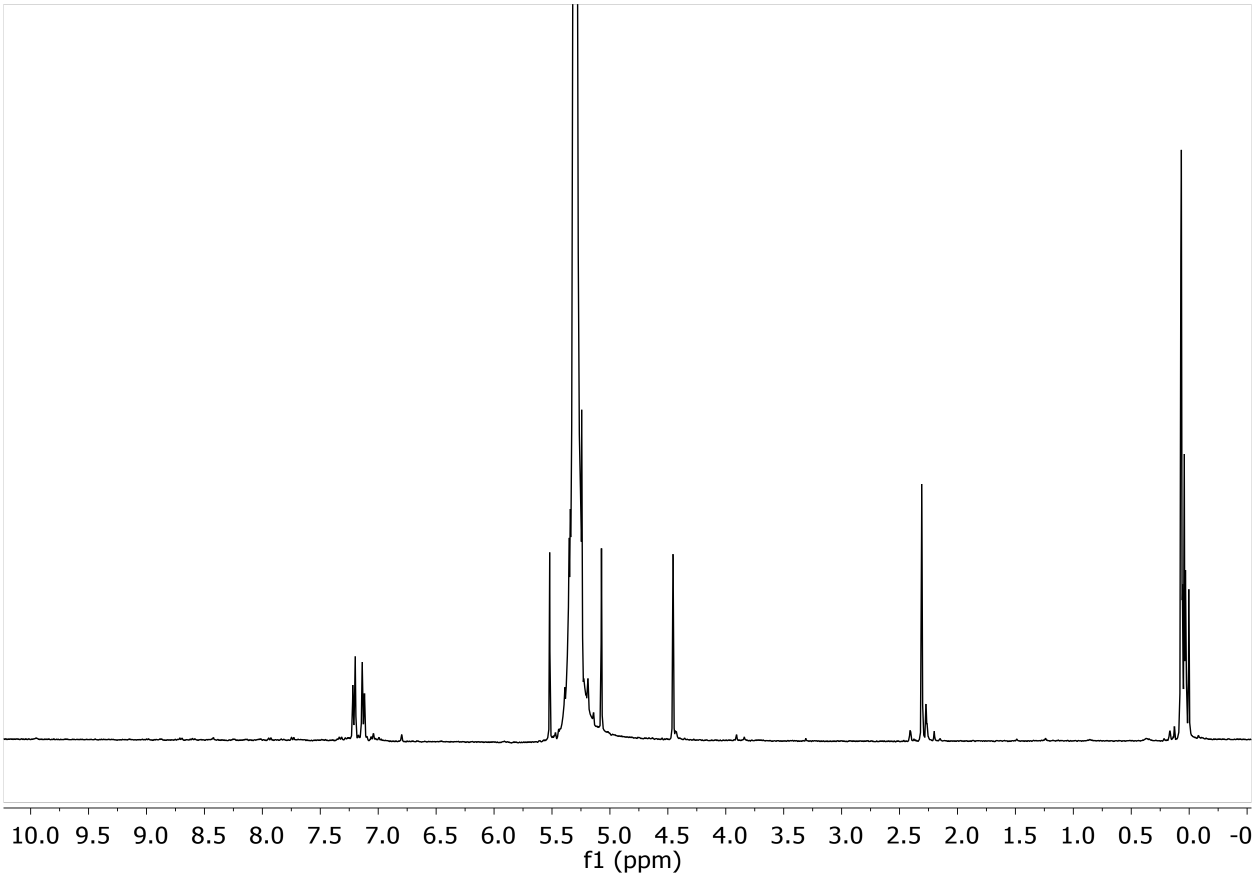


Figure S23. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with pentamethyldisiloxane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm. NMR spectrum recorded after 30 minutes.

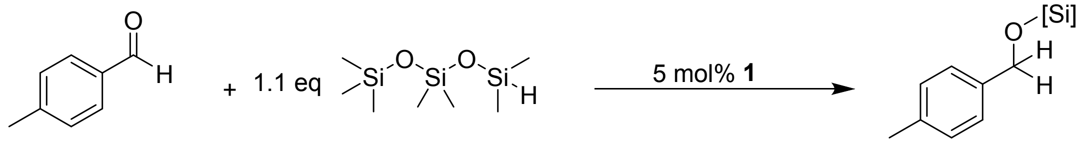


Figure S24. ^{1}H NMR (CH_2Cl_2, 298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with 1,1,1,2,2,3,3-heptamethyltrisiloxane. Reaction performed on the benchtop with dry solvent. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

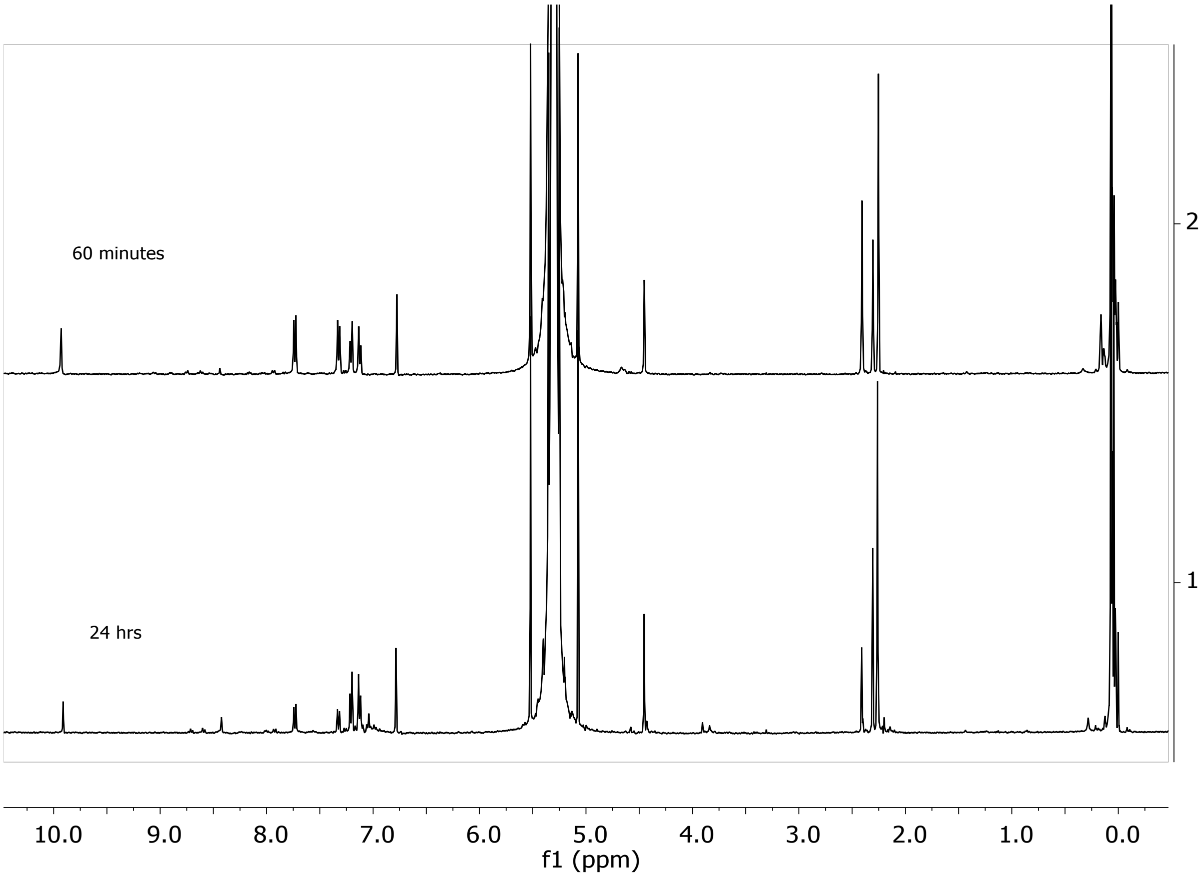
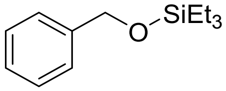


Figure S25. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with 1,1,1,2,2,3,3-heptamethyltrisiloxane. Reaction performed on the benchtop with dry solvent. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

5. Catalytic Hydrosilylation Reactions with Triethylsilane

5.1. Catalytic Hydrosilylation of Aldehydes



Triethyl(benzyloxy)silane (entry 1): %Conversion (%Yield): >99% (92.5%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[2] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.40 – 7.25 (m, 5H), 4.54 (s, 2H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.52 (q, *J* = 7.9 Hz, 6H). GCMS (m/z): 107.1 ($[M-SiEt_3]^+$, calc'd. 107.05).

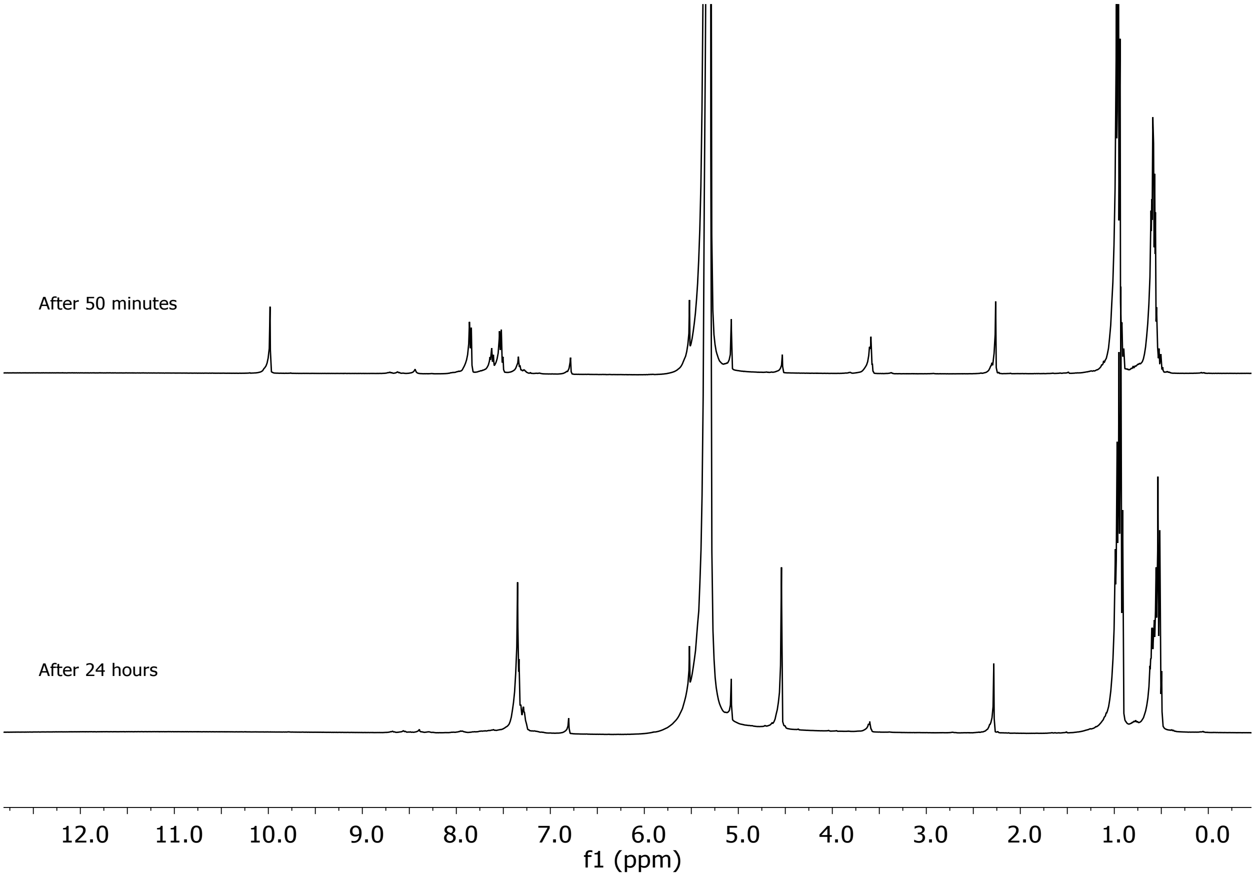
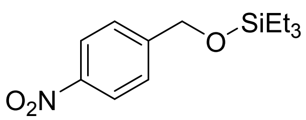


Figure S26. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of benzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((4-nitrobenzyl)oxy)silane (entry 2): %Conversion (%Yield): >99% (98.9%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[3] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 8.14 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 4.81 (s, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H).

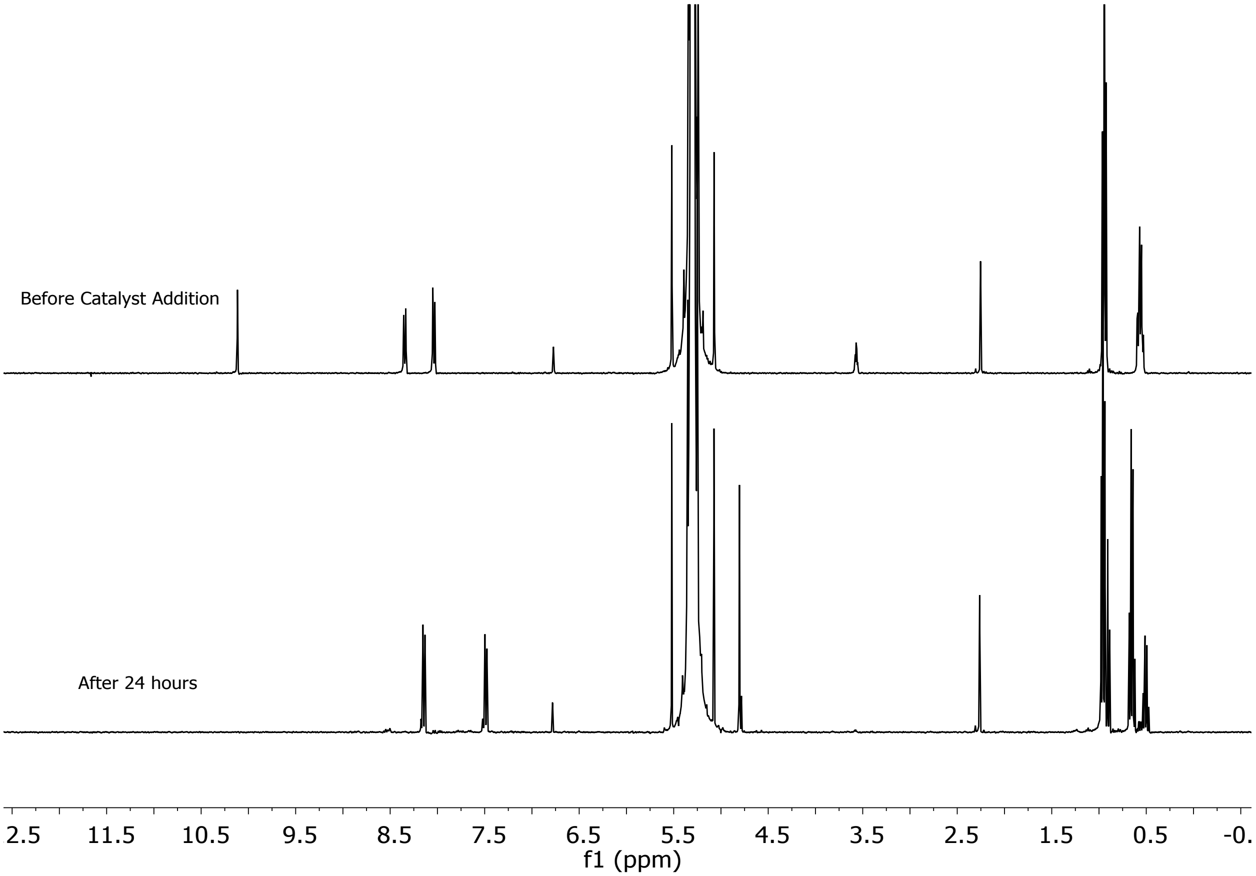
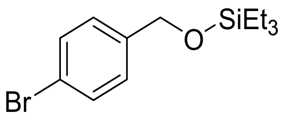


Figure S27. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-nitrobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm



Triethyl((4-bromobenzyl)oxy)silane (entry 3): %Conversion (%Yield): >99% (83.5%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[3] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.49 – 7.41 (m, 2H), 7.21 (t, *J* = 8.4 Hz, 2H), 4.64 (s, 2H), 0.90 (t, *J* = 7.9Hz, 9H), 0.49 (q, *J* = 7.9H, 6H).

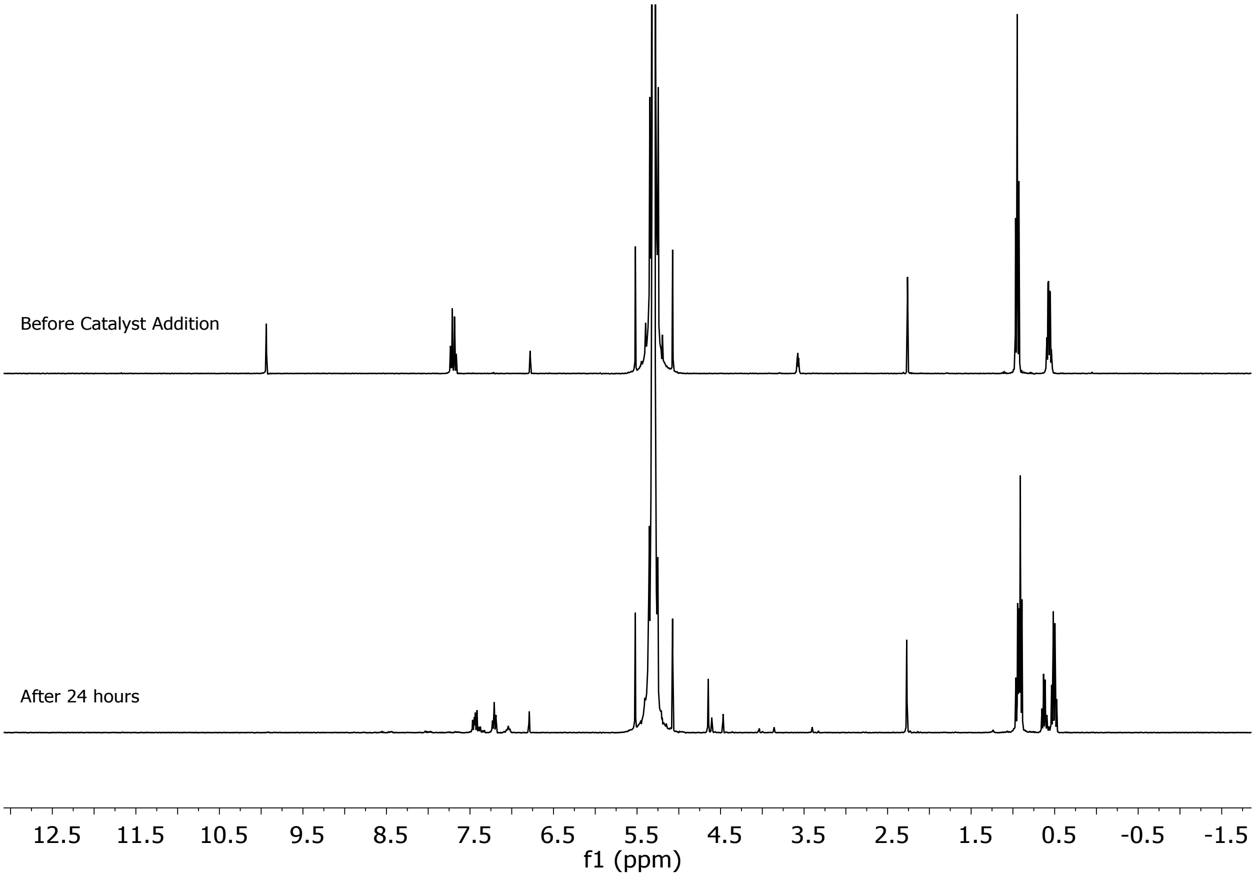
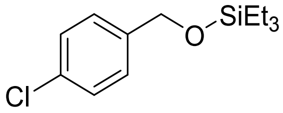


Figure S28. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-bromobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm



Triethyl((4-chlorobenzyl)oxy)silane (Entry 4): >99% (33%) over 90 minutes as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[4] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.32 – 7.25 (m, 4H), 4.65 (s, 2H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.9 Hz, 6H). GCMS: 140.9 ($[M-SiEt_3]^+$, calc'd. 141.01).

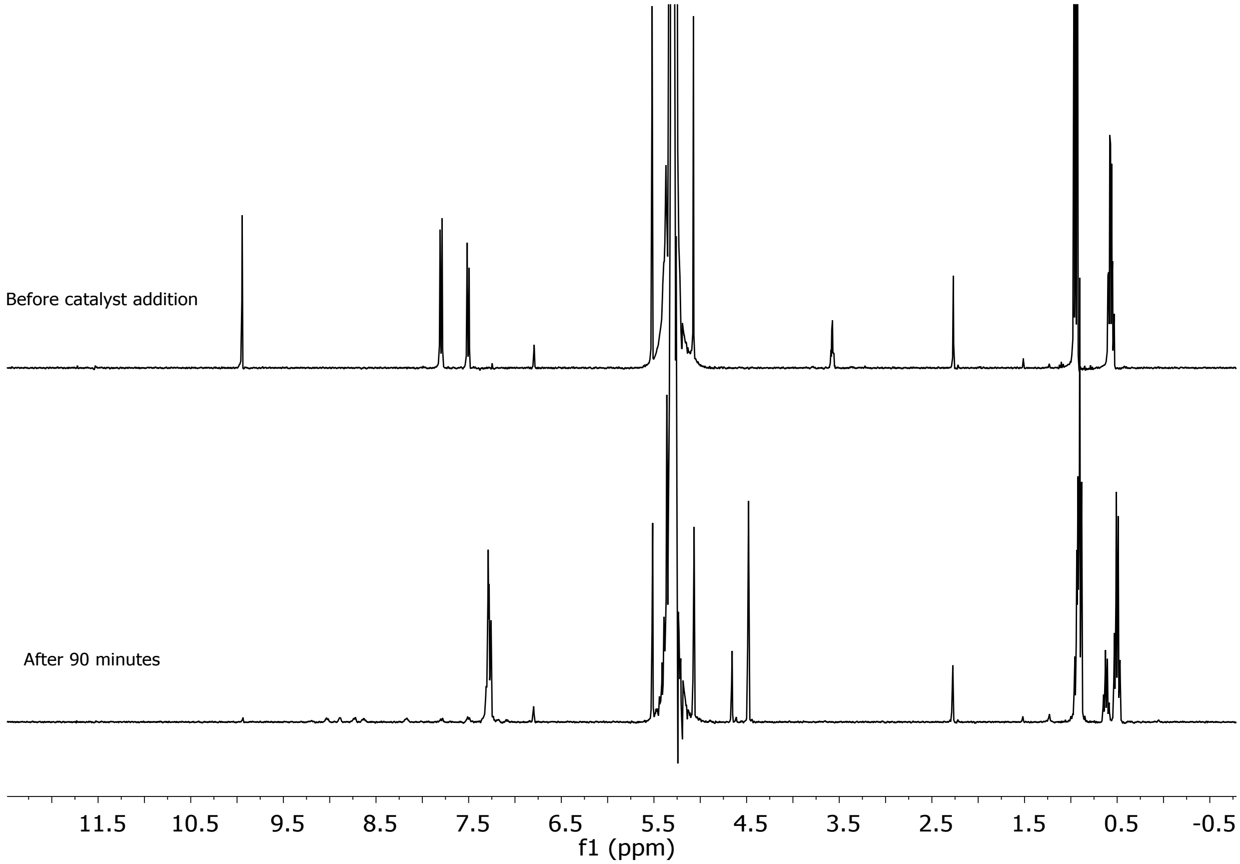
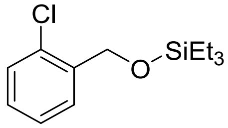


Figure S29. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-chlorobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((2-chlorobenzyl)oxy)silane (Entry 5): >99% (87.0%) over 90 minutes as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[4] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.55 (d, J = 7.7 Hz, 1H), 7.36 - 7.24 (m, 2H), 7.21 – 7.14 (m, 2H), 4.76 (s, 2H), 0.96 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). GCMS: 227.1 ($[M\text{-}CH_2CH_3]^+$, calc'd. 227.07).

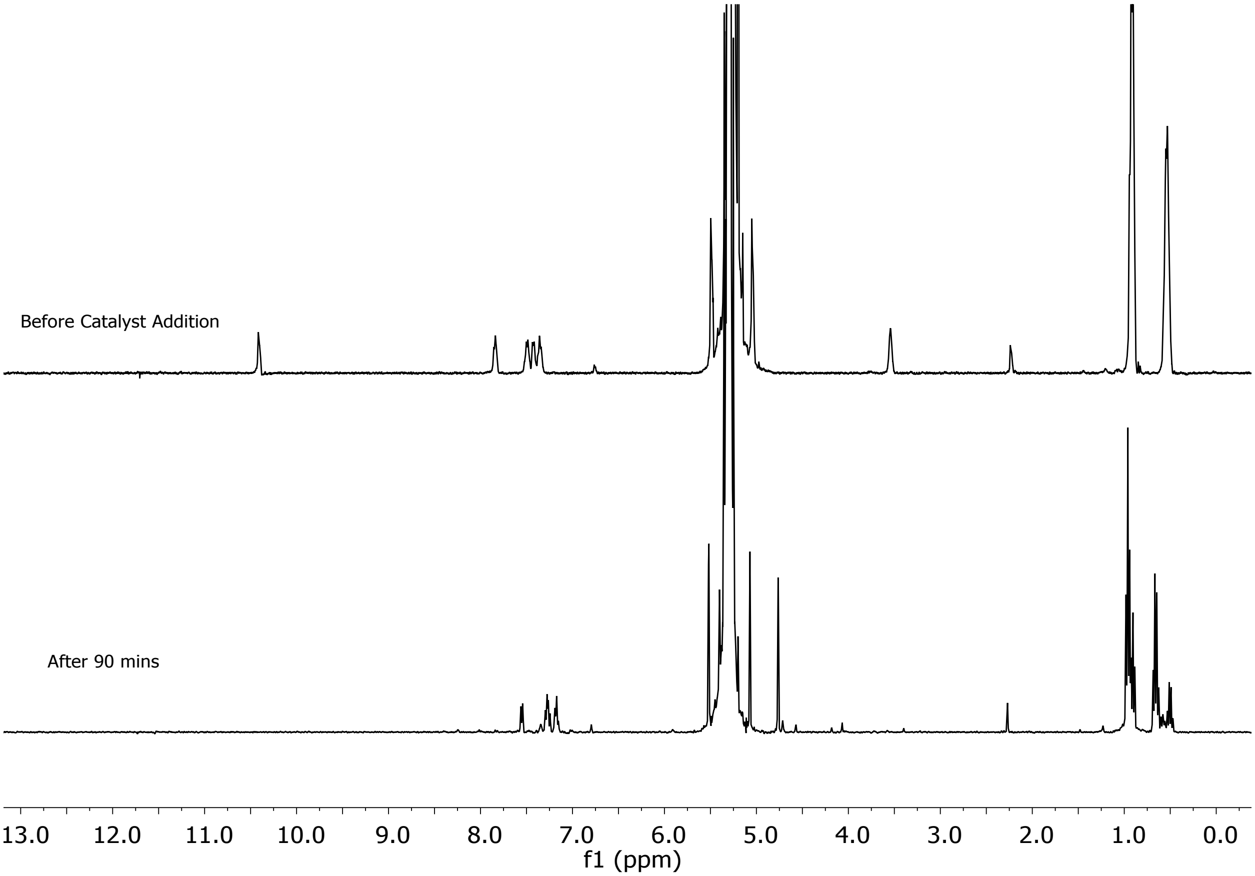
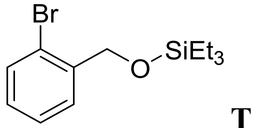


Figure S30. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 2-chlorobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((2-bromobenzyl)oxy)silane (Entry 6): %Conversion (%Yield): >99% (50%) over 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.**[5]** ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.49 (d, *J* = 8.1 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.30 (t, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 7.9 Hz, 1H), 4.66 (s, 2H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.62 (q, *J* = 7.9 Hz, 6H). GCMS: 185.0 ([M-SiEt$_3$]$^+$, calc'd. 184.96).

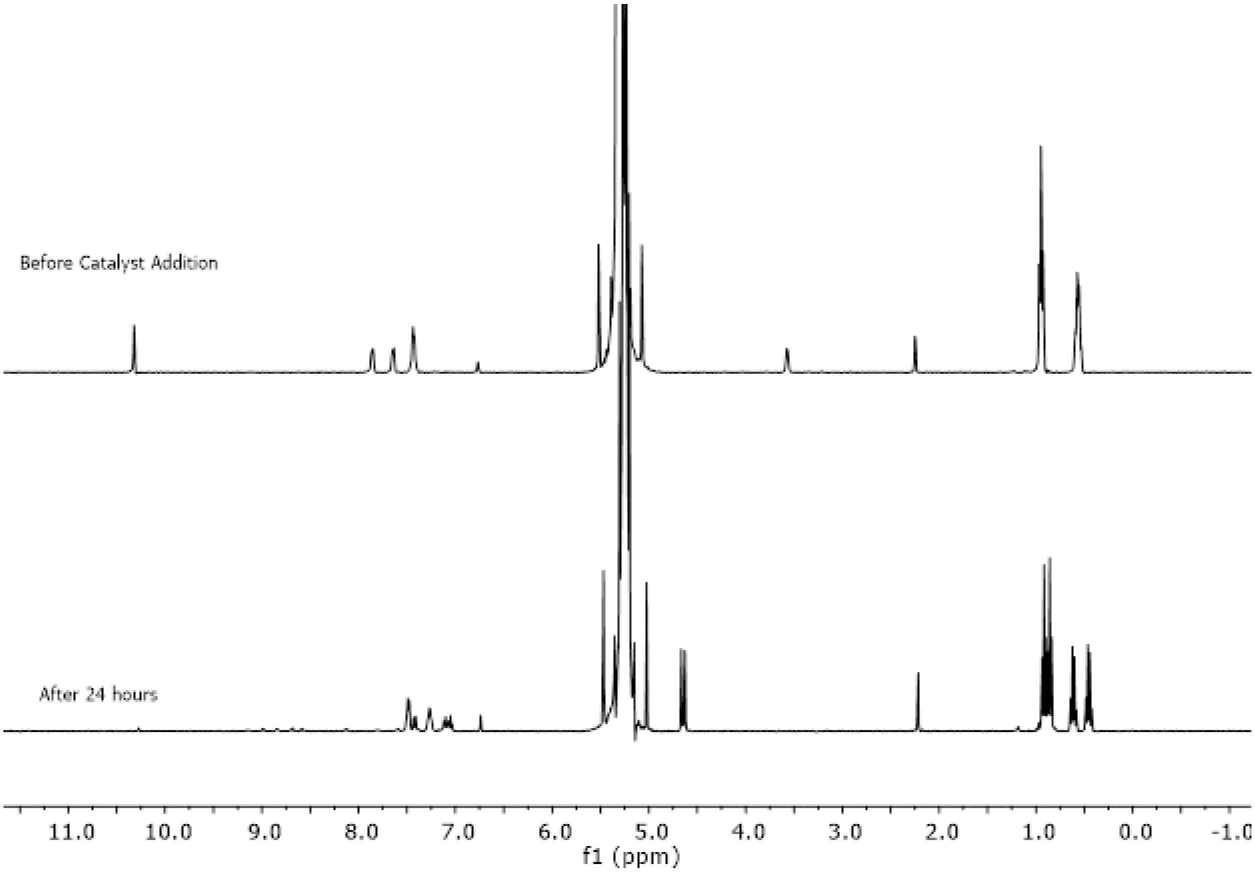
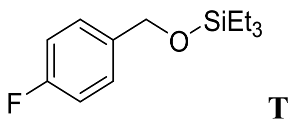


Figure S31. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 2-bromobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((4-fluorobenzyl)oxy)silane (Entry 7): %Conversion (%Yield): 56.3% (56.3%) over 24 hours as determined by ^{19}F{^{1}H} NMR spectroscopy using an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. Characterization corresponds with reported literature values.[6] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.30 (t, *J* = 8.7 Hz, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.48 (s, 2H), 1.01 – 0.86 (m, overlapping signals with residual Et_3SiH signals, 9H), 0.50 (q, *J* = 7.9 Hz, 6H). ^{19}F{^{1}H} NMR (376 MHz, 298K, CH_2Cl_2): δ (ppm) -116.9 (1F). GCMS (m/z): 125.0 ($[M-SiEt_3]^+$, calc'd. 125.04).

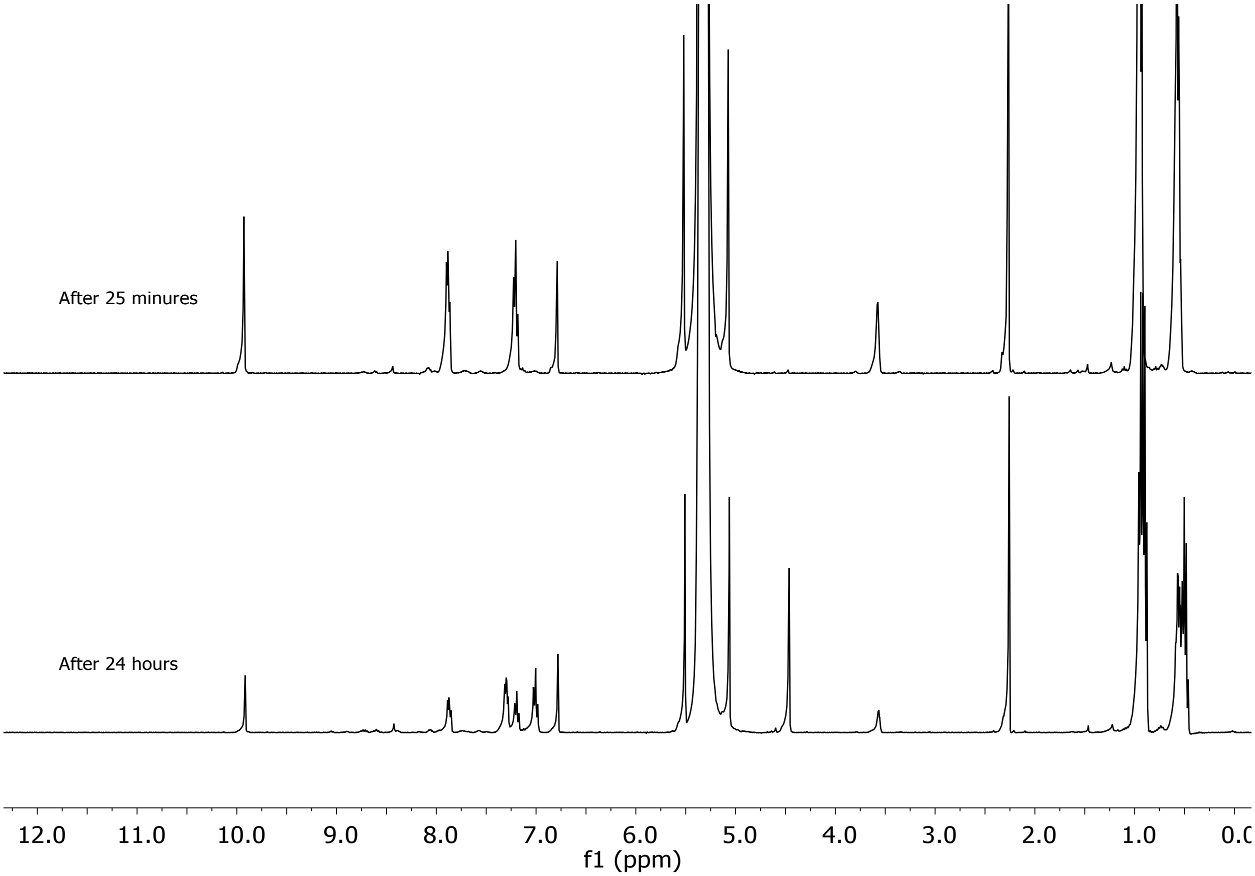


Figure S32. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-fluorobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

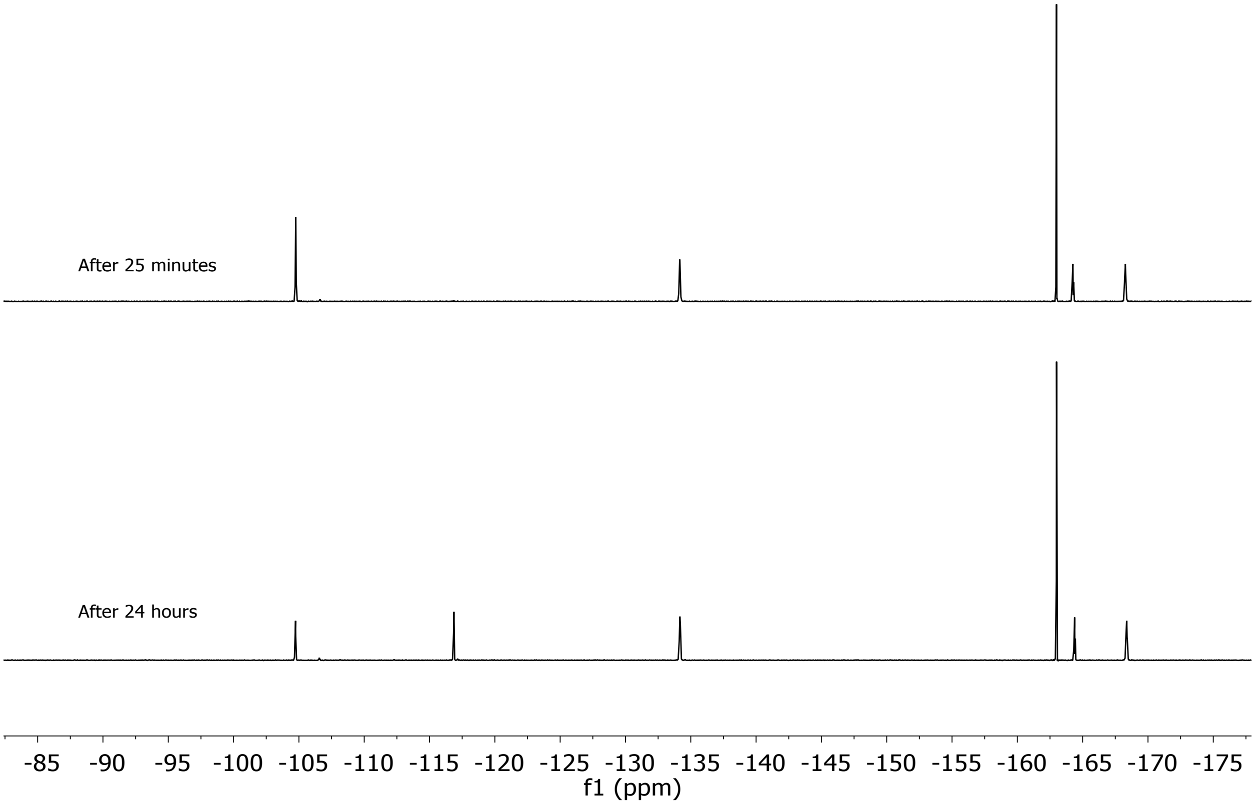
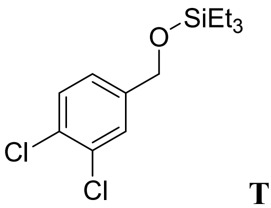


Figure S33. ^{19}F NMR (298K, 376 MHz) spectra for the catalytic hydrosilylation of 4-fluorobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the hexafluorobenzene signal at -163 ppm.



Triethyl((3,4-dichlorobenzyl)oxy)silane (Entry 8): %Conversion (%Yield): 99% (95%) over 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. ^{1}H NMR (500 MHz, 298K, $CDCl_3$): δ (ppm) 7.45 – 7.44 (m, 1H, Ar-$C(CH_2)C\textit{H}C(Cl)$), 7.40 (d, *J* = 8.0 Hz, Ar-C(Cl)C(*H*)C(H)), (d, *J* = 8.3 Hz, Ar-C(Cl)C(*H*)C(H)), 7.17 (dm, *J* = 8.0 Hz, Ar-C(Cl)C(H)C(*H*)), 4.69 (s, 2H, Ar-$C\textit{H}_2$), 0.99 z(t, *J* = 7.7 Hz, 9H, $SiCH_2C\textit{H}_3$), 0.67 (q, *J* = 7.7 Hz, 6H, $SiC\textit{H}_2CH_3$). $^{13}C\{^1H\}$ NMR (126 MHz, 298K, $CDCl_3$): δ (ppm) 141.9, 132.5, 130.8, 130.3, 128.2, 125.5, 63.5, 6.9, 4.6. GCMS (m/z): 291.1 ($[M+H]^+$, calc'd. 291.07).

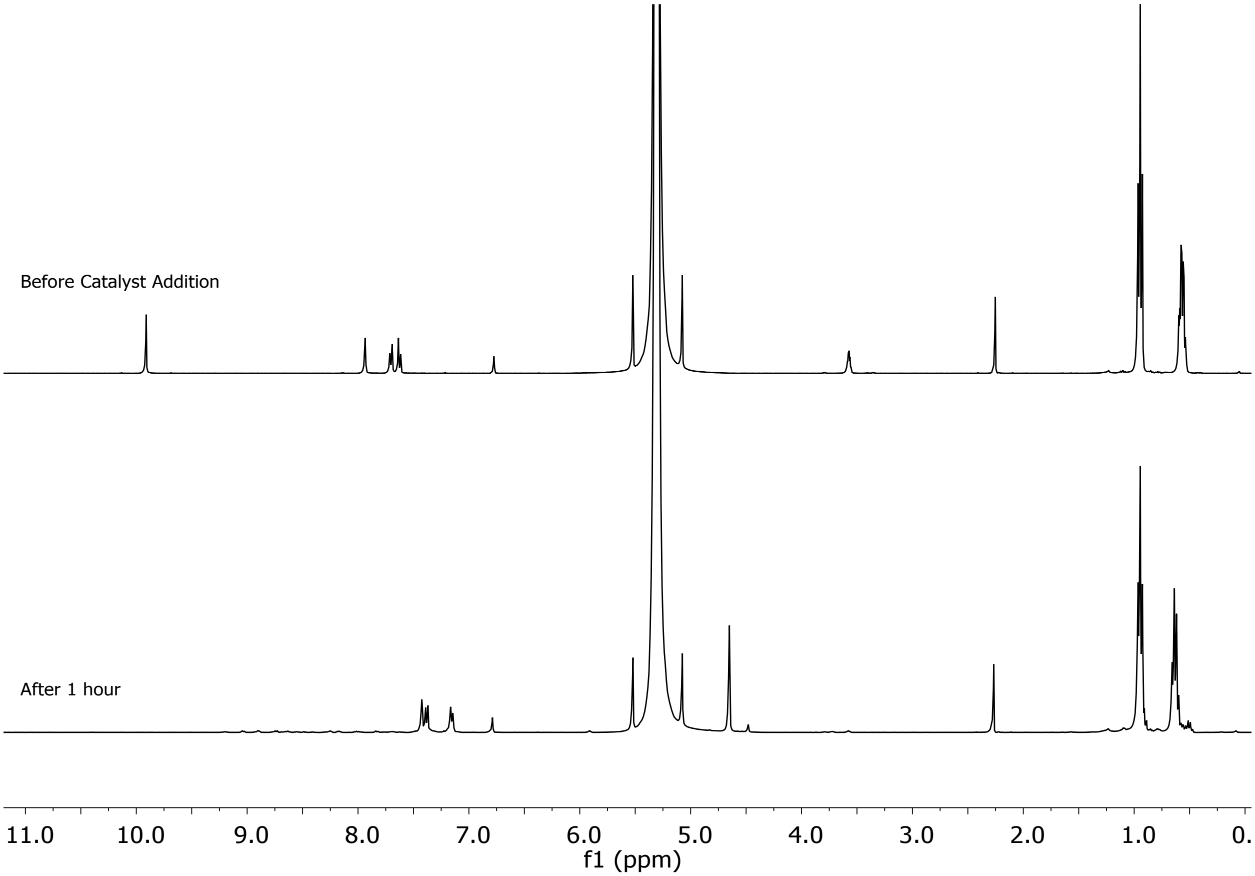


Figure S34. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 3,4-dichlorobenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

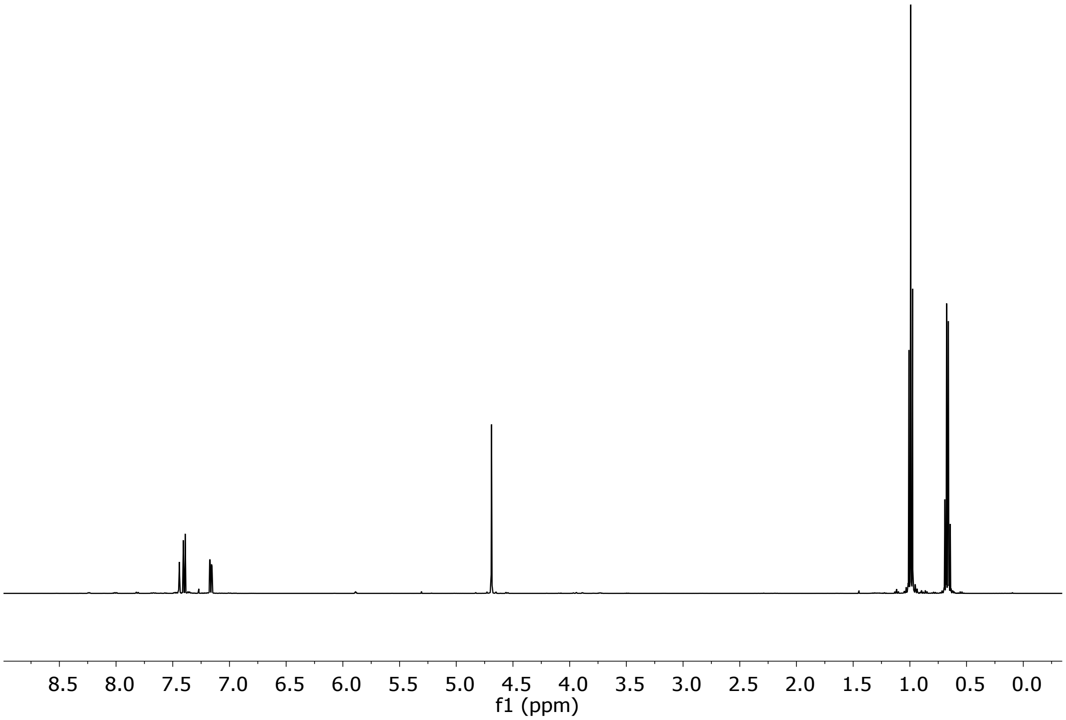


Figure S35. ^{1}H NMR (298K, 500 MHz) spectrum for triethyl((3,4-dichlorobenzyl)oxy)silane. The NMR spectrum is referenced to the $CDCl_3$ resonance at 7.27 ppm.

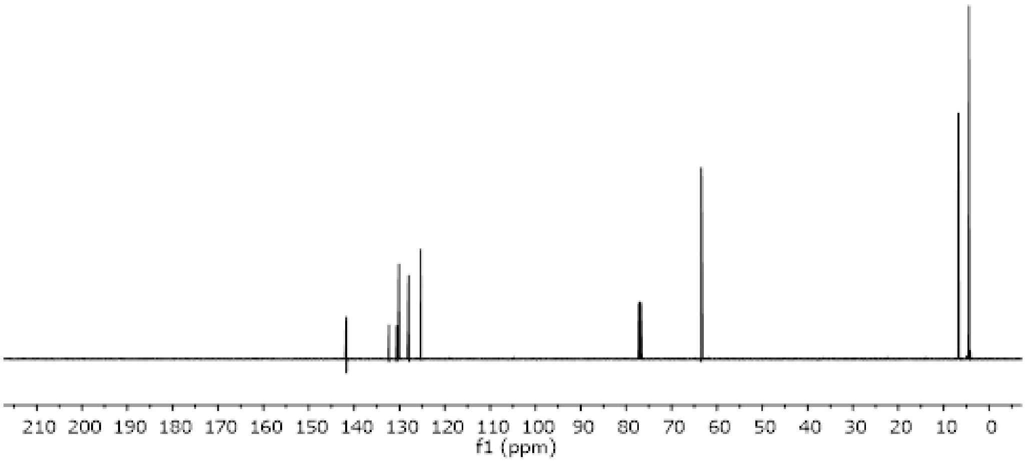
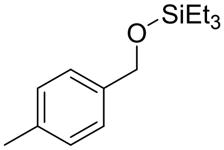


Figure S36. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 298K, 126 MHz) spectrum for triethyl((3,4-dichlorobenzyl)oxy)silane. The NMR spectrum is referenced to the $CDCl_3$ resonance at 77.2 ppm.



Triethyl(4-methylbenzyloxy)silane (Entry 9): %Conversion (%Yield): 99% (96%) over 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[4] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.21 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 4.46 (s, 2H), 2.31 (s, 3H), 0.91 (t, *J* = 8.0 Hz, 9H), 0.50 (1, *J* = 8.0 Hz, 6H). GCMS: 207.1 ($[M-CH_2CH_3]^+$, calc'd. 207.12).

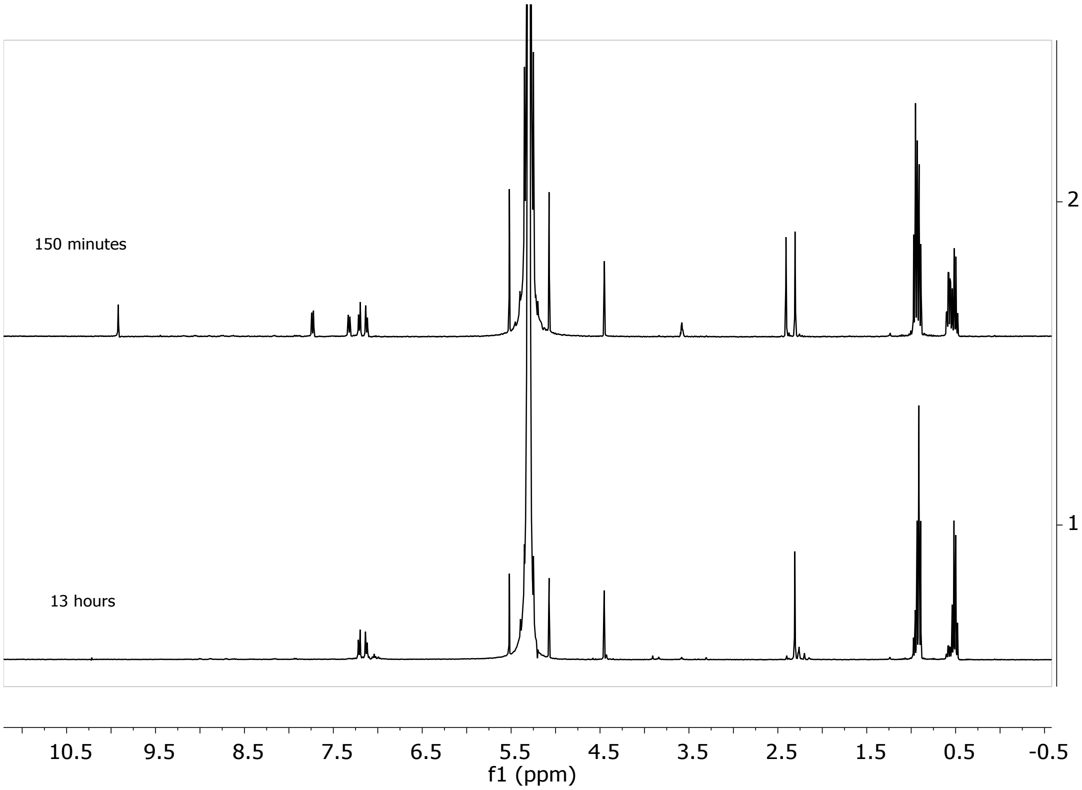
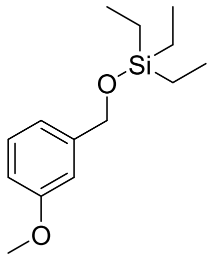


Figure S37. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylbenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((3-methoxybenzyl)oxy)silane (entry 10): %Conversion (%Yield): >99% (97.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[7] ^{1}H NMR (500 MHz, 298K, CH_2Cl_2): δ (ppm) 7.23 (t, *J* = 7.8 Hz, 1H), 6.93 – 6.88 (m, 2H), 6.82 – 6.78 (m, 2H), 4.50 (s, 2H), 3.75 (s, J 3H), 0.92 (t, *J* = 7.9 Hz, 9H), 0.52 (q, *J* = 7.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (500 MHz, 298K, CH_2Cl_2): δ (ppm) 160.0, 140.1, 129.3, 119.8, 113.0, 112.9, 72.0, 55.1, 6.5, 6.3.

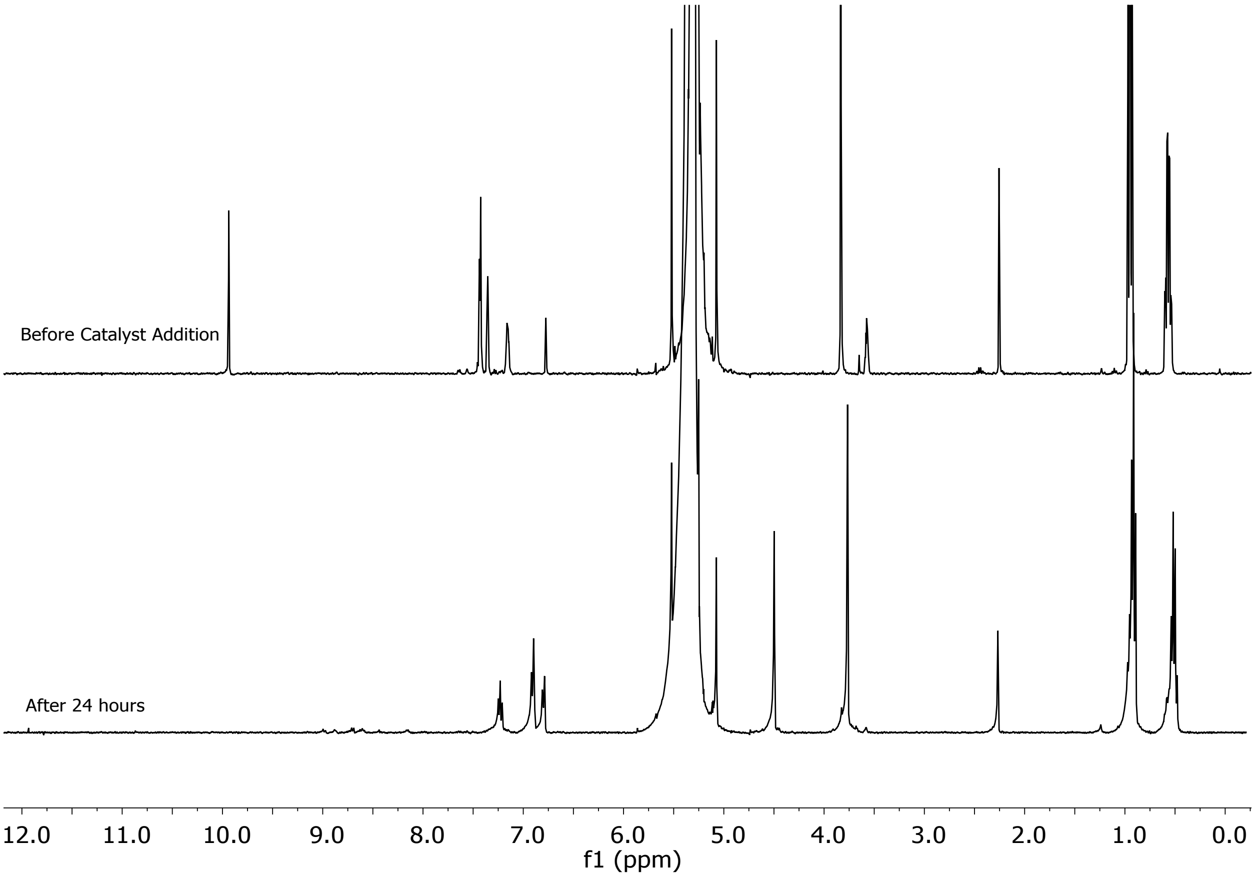


Figure S38. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 3-methoxybenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

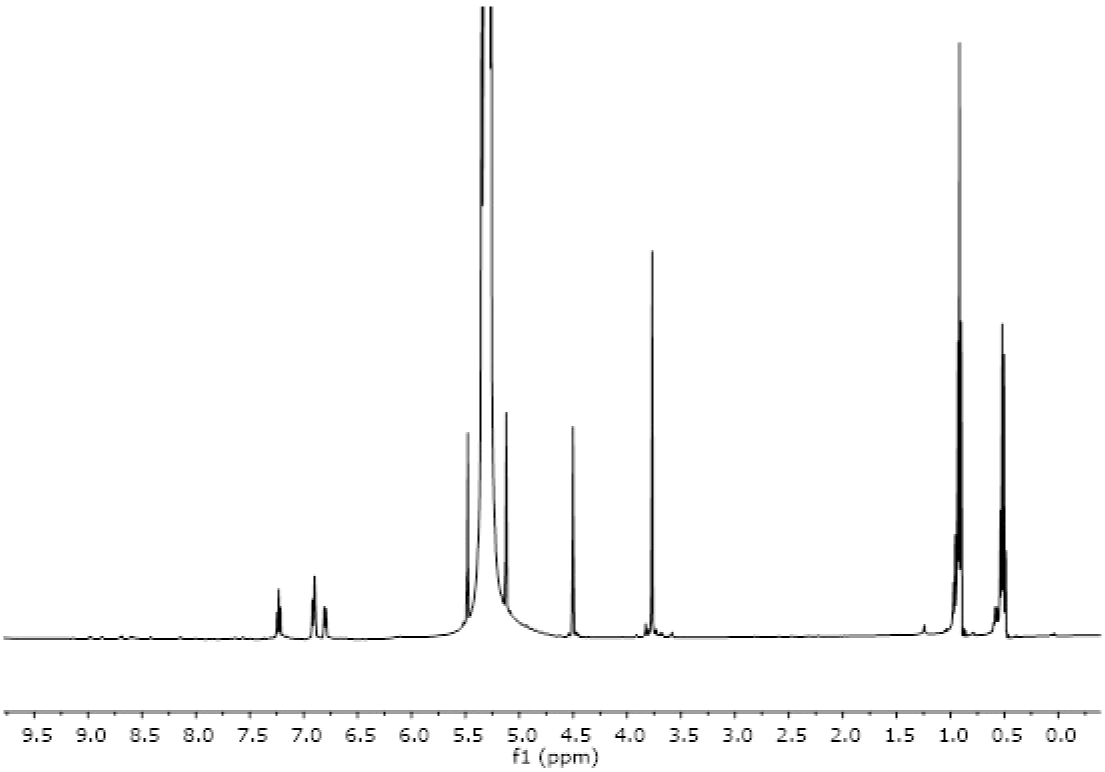


Figure S39. ^{1}H NMR (298K, 500 MHz) spectrum for triethyl((3-methoxybenzyl)oxy)silane. The NMR spectrum is referenced to the CH_2Cl_2 resonance at 5.30 ppm.

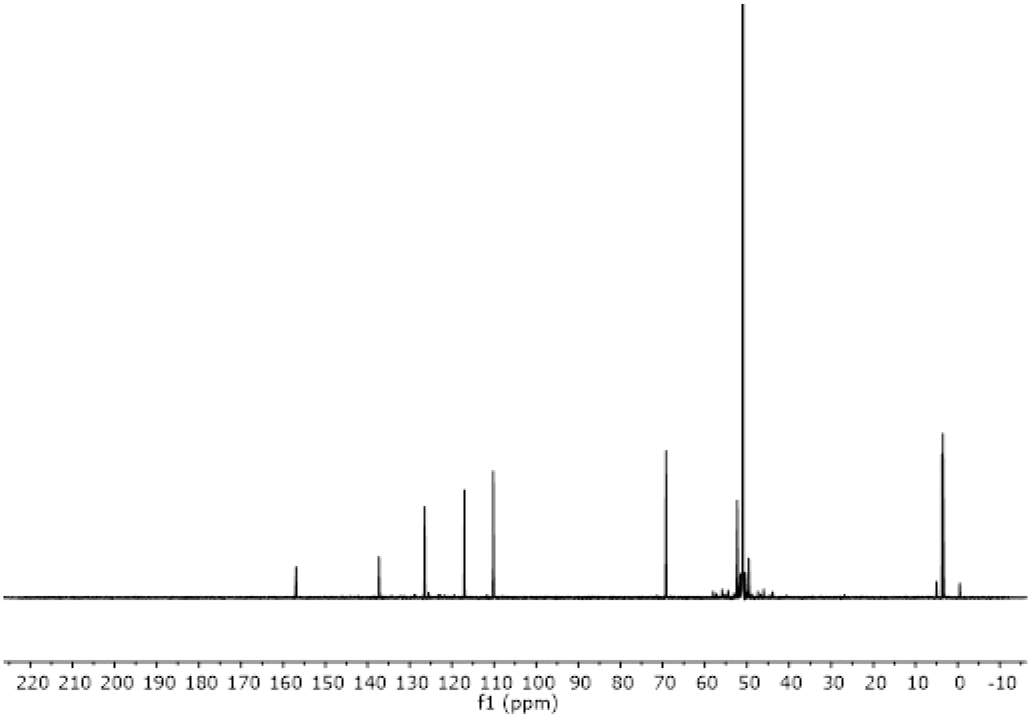
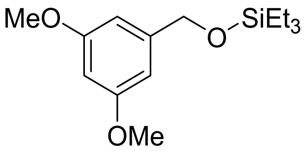


Figure S40. $^{13}C\{^{1}H\}$ NMR (298K, 126 MHz) spectrum for triethyl((3-methoxybenzyl)oxy)silane. The NMR spectrum is referenced to the CH_2Cl_2 resonance at 54.0 ppm.



Triethyl((3,5-dimethoxybenzyl)oxy)silane (Entry 11): %Conversion (%Yield): >99% (98.7%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[8] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 6.54 (s, 2H), 6.41 (s, 1H), 4.54 (s, 2H), 3.81 (s, 6H), 1.04 – 0.95 (m, 9H), 0.56 (q, J = 7.9 Hz, 6H).

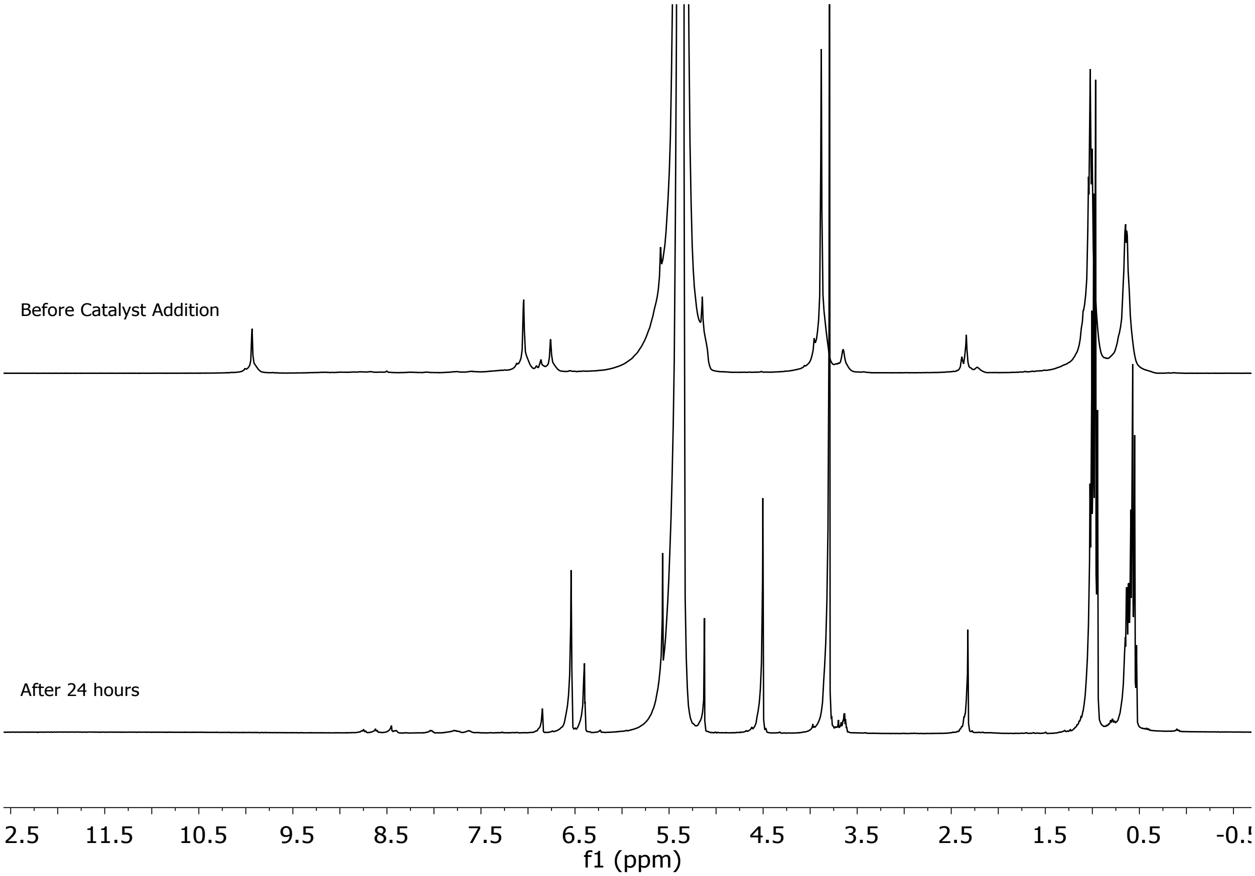
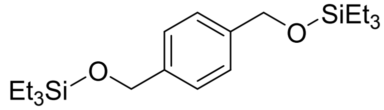


Figure S41. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 3,5-dimethoxybenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



1,4-bis((trimethylsilyl)oxy)methyl)benzene (Entry 12): %Conversion (%Yield): 94.4 % (93.8%) after 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[9] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.30 (s, 4H), 4.53 (m, 4H), 1.01 – 0.88 (m, 18H), 0.60 – 0.48 (m, 12H).

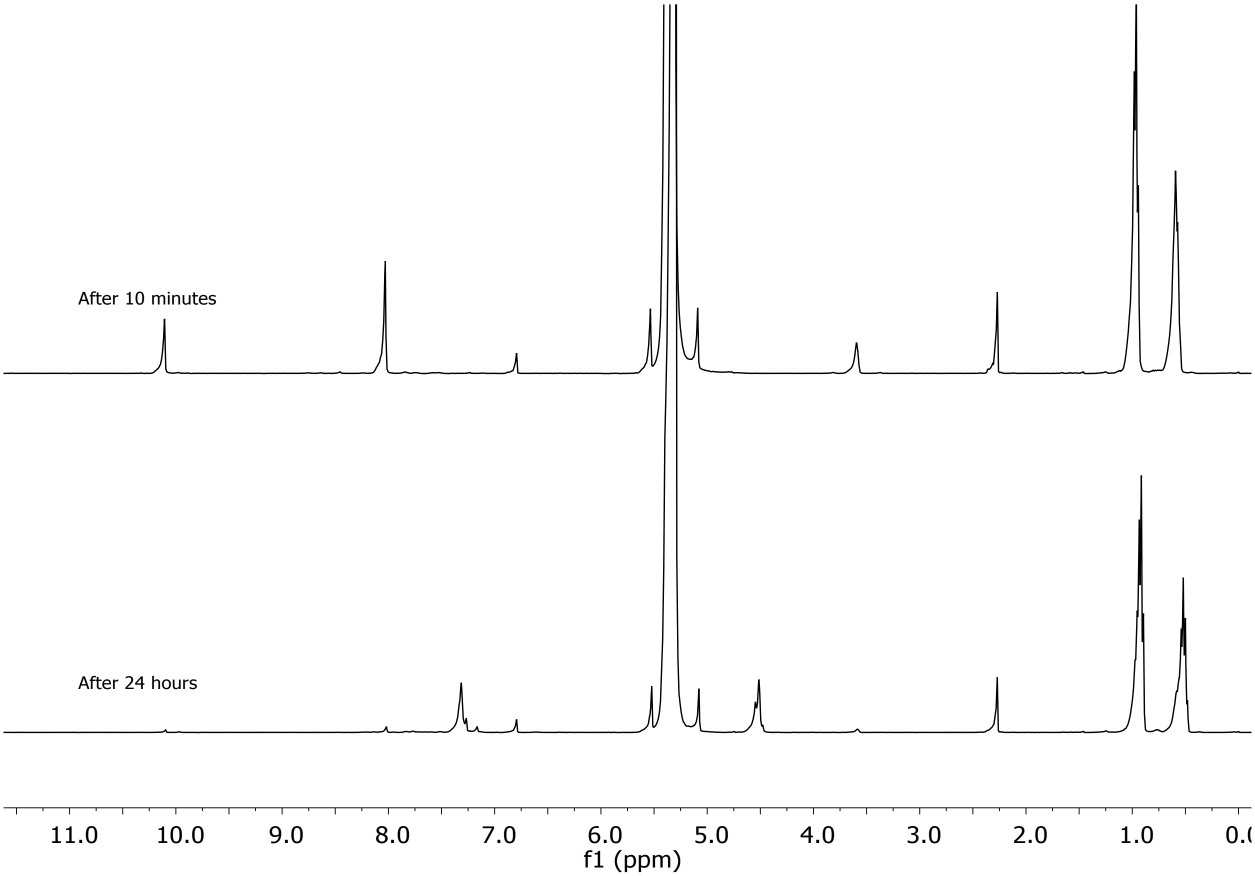
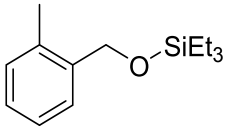


Figure S42. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of terephthaldicarboxaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((2-methylbenzyl)oxy)silane (Entry 13): %Conversion (%Yield): 24.7% (23.8%) after 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in CDCl$_3$. Characterization corresponds with reported literature values.[10] ^{1}H NMR (400 MHz, 298K, CH$_2$Cl$_2$): δ (ppm) 7.33 – 7.30 (m, 1H), 7.18 – 7.11 (m, 3H), 4.55 (s, 2H), 2.29 (s, 3H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.50 (q, *J* = 8.0 Hz, 6H). GCMS: 121.1 ([M-SiEt$_3$]$^+$, calc'd. 121.07).

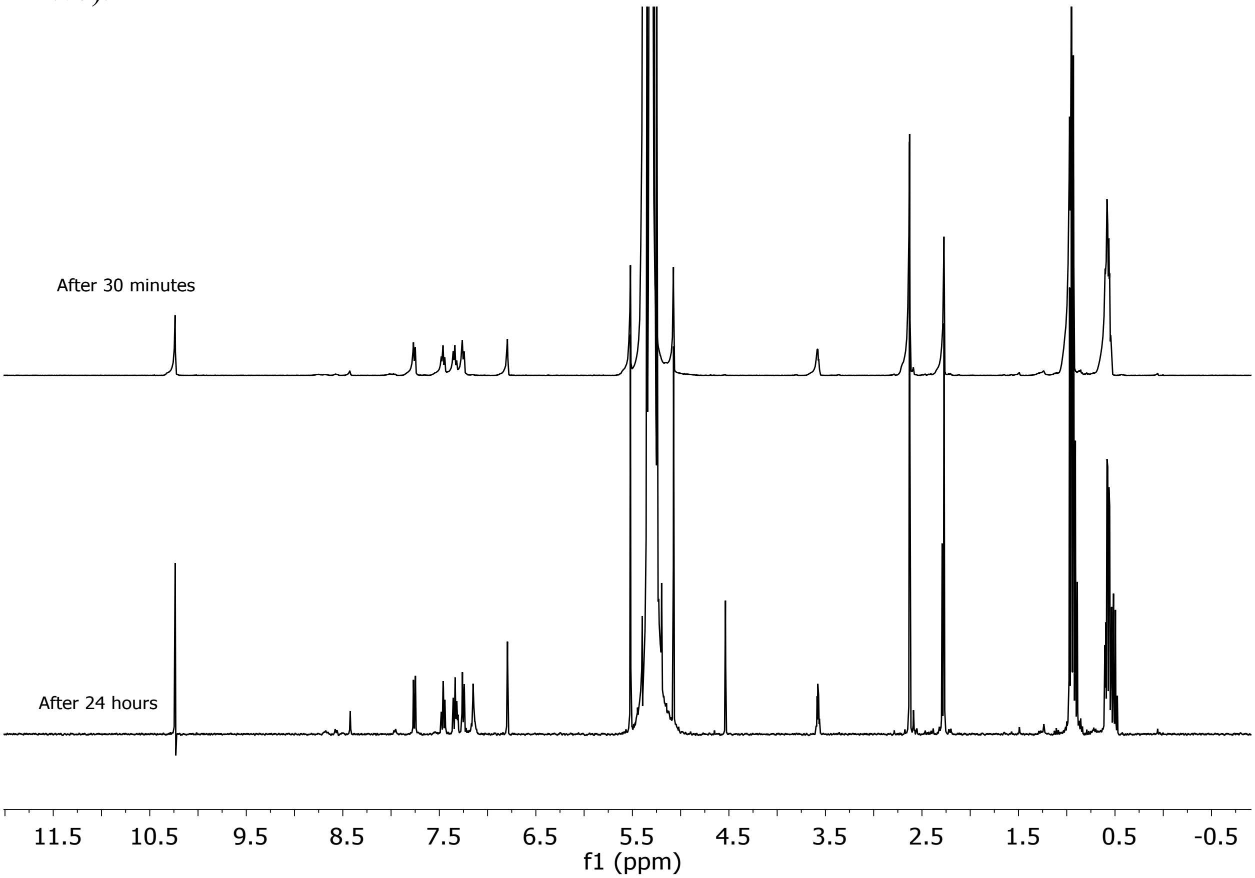
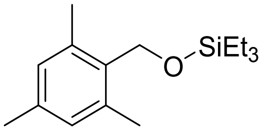


Figure S43. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 2-methylbenzaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH$_2$Cl$_2$ resonance at 5.30 ppm.



2,4,6-trimethylbenzaldehyde (Entry 14): %Conversion: <1% over 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$.

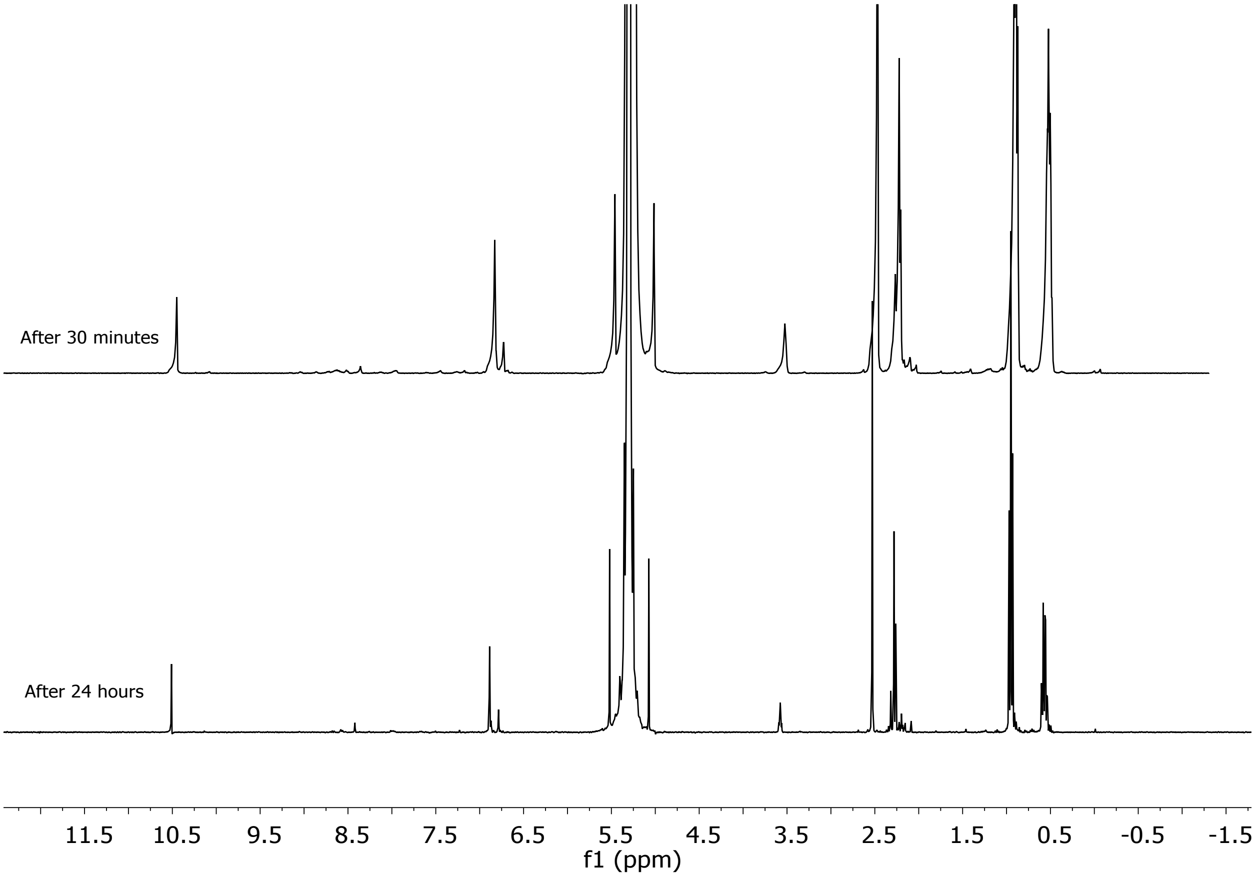
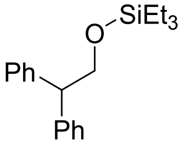


Figure S44. ^{1}H NMR (298K, 400 MHz) spectra for the attempted catalytic hydrosilylation of mesitaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(2,2-diphenylethoxysilane (Entry 15): >99% (97.7%) over 90 minutes as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[11] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.31 - 7.21 (m, 7H), 7.20 – 7.11 (m, 3H), 4.14 (m, 2H), 3.98 (m, 1H), 0.86 (t, *J* = 8.0 Hz, 6H), 0.52 (q, *J* = 8.0 Hz, 6H).

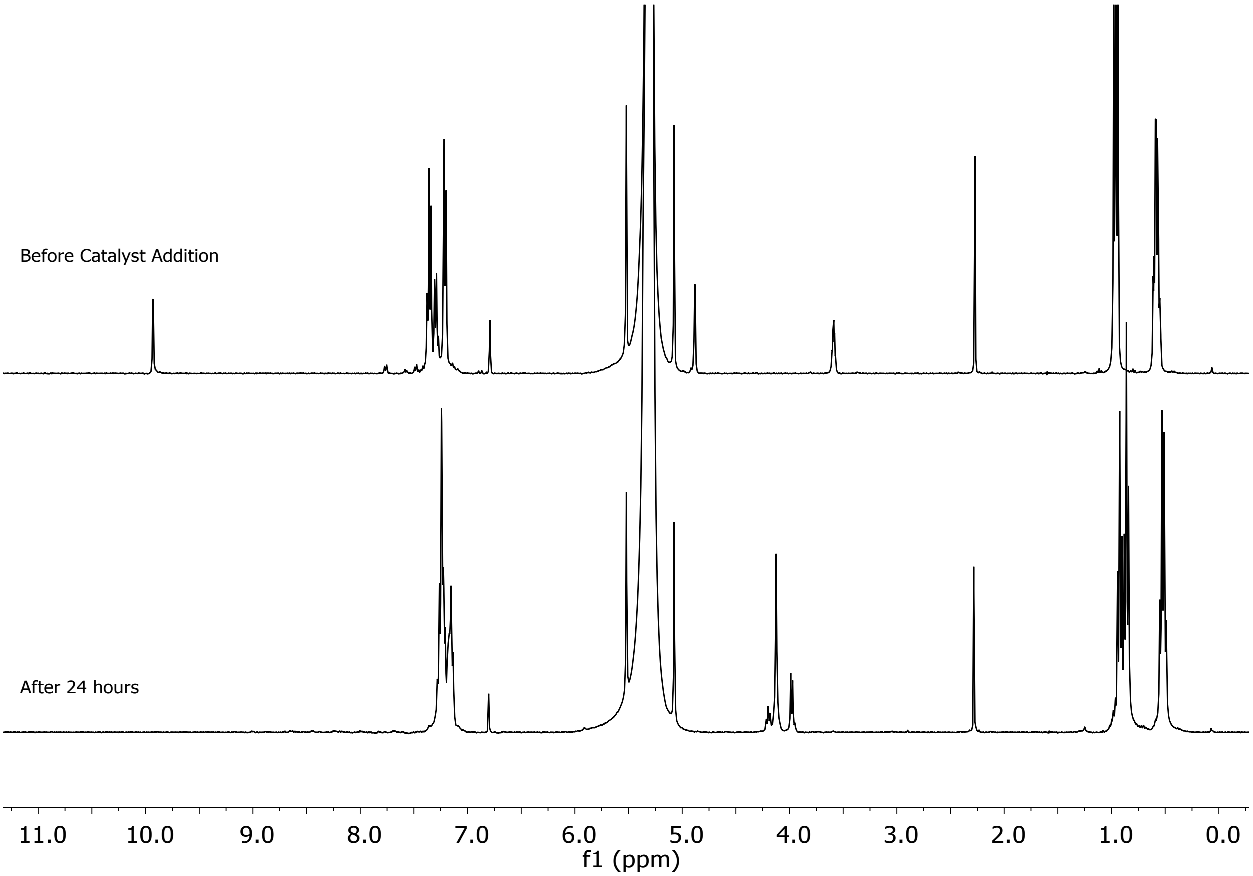
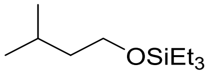


Figure S45. 1H NMR (298K, 400 MHz) spectra for the attempted catalytic hydrosilylation of diphenylacetaldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(isopentyloxy)silane (Entry 16): %Conversion (%Yield): >99% (99.0%) after 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[12] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 3.36 (t, *J* = 6.7 Hz, 2H), 1.63 (septet, *J* = 6.6 Hz,1H), 1.43 – 1.33 (m, 2H), 0.96 – 0.82 (overlapping signals, 15H), 0.50 (q, *J* = 7.7 Hz, 6H).

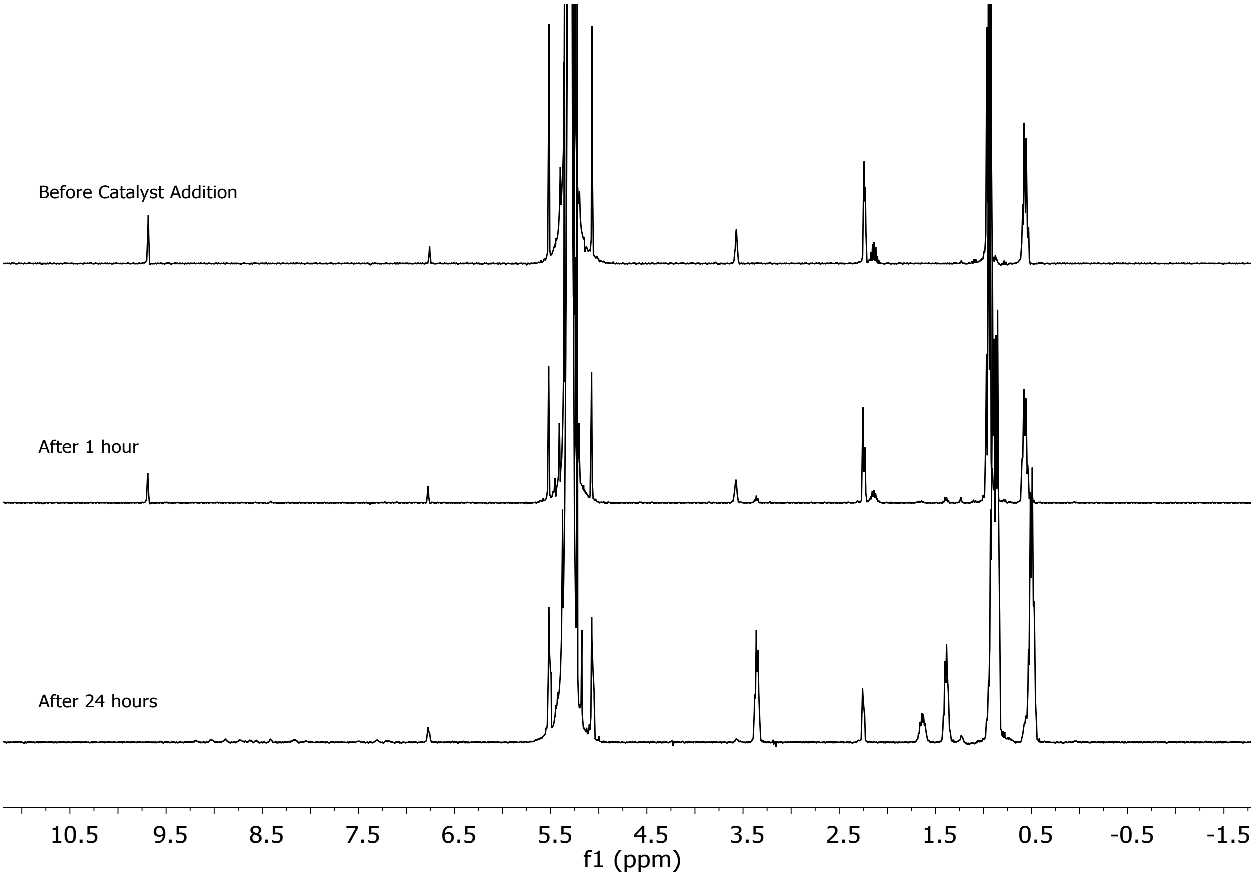
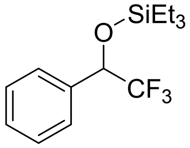


Figure S46. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of isovaleraldehyde in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

5.2. Catalytic Hydrosilylation of Ketones



Triethyl(2,2,2-trifluoro-1-phenylethoxy)silane (Entry 17): %Conversion (%Yield): 66.4% (60.9%) as determined by $^{19}F\{^1H\}$ NMR spectroscopy using an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. Characterization corresponds with reported literature values.[13] ^1H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 0.57 (m, 9H, overlapping with residual triethylsilane signal), 0.87 (t, *J* = 8.0 Hz, 9H), 4.93 (q, *J* = 6.6 Hz, 1H), 7.38 – 7.31 (m, 3H), 7.47 – 7.40 (m, 2H). $^{19}F\{^1H\}$ NMR (377 MHz, 298K, CH_2Cl_2): δ (ppm) -79.9 (3F).

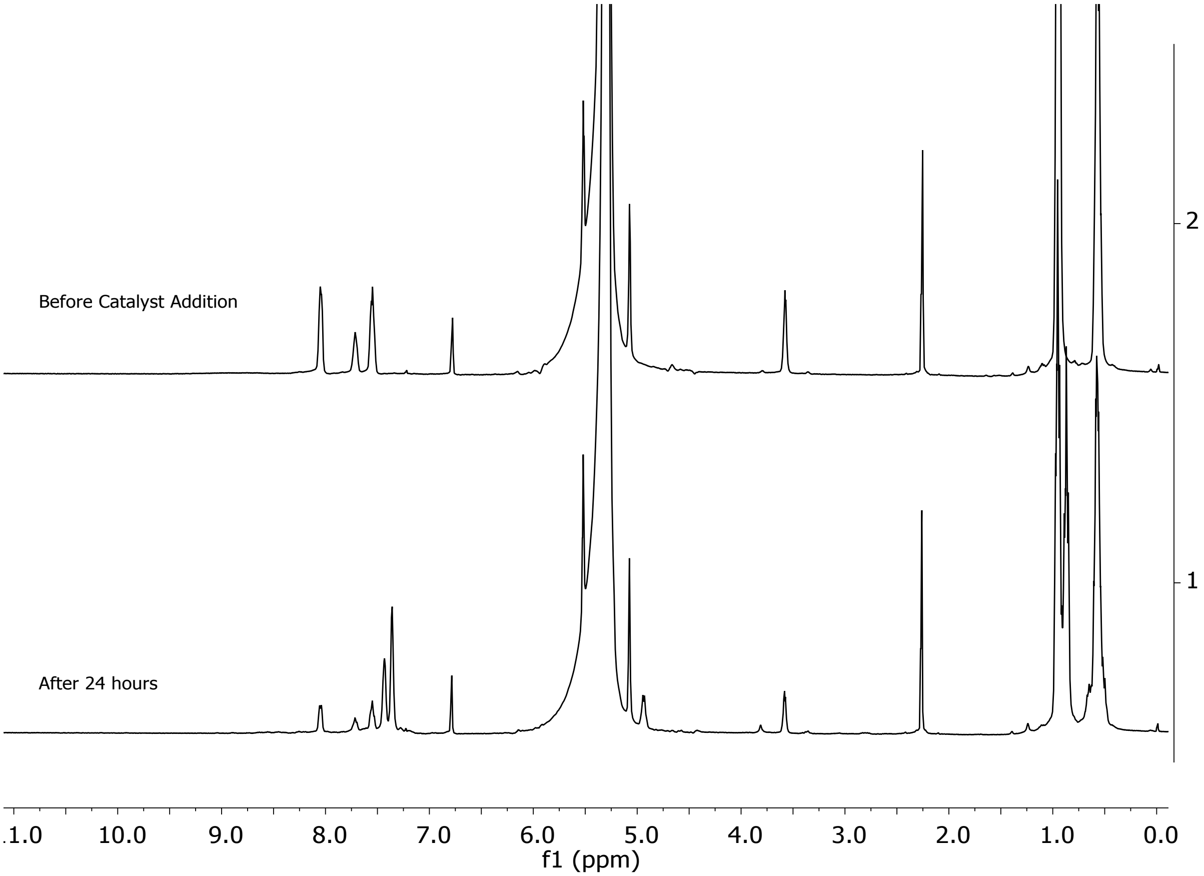


Figure S47. ^1H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 2,2,2-trifluoroacetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

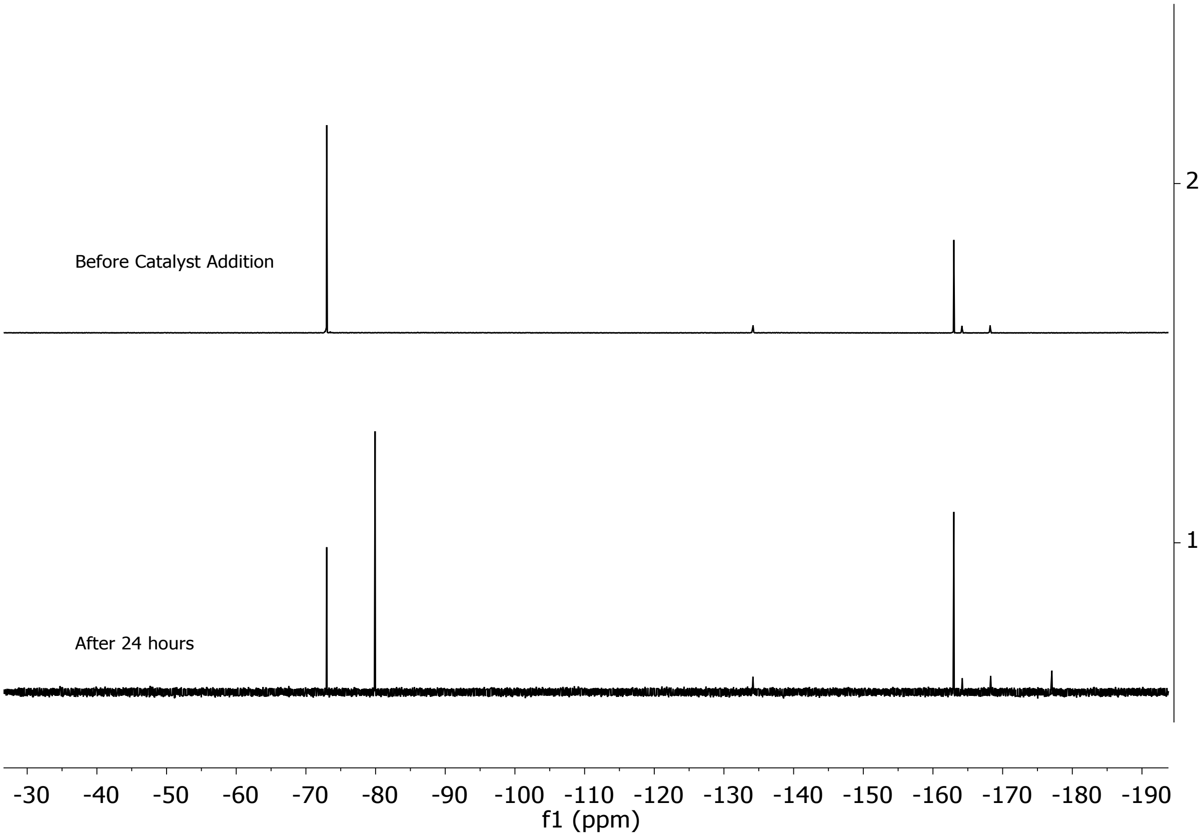
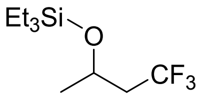


Figure S48. $^{19}F\{^{1}H\}$ NMR (298K, 376 MHz) spectra for the catalytic hydrosilylation of 2,2,2-trifluoroacetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the hexafluorobenzene signal at -163 ppm.



Triethyl((4,4,4-trifluorobutan-2-yl)oxy)silane (Entry 18): %Conversion (%Yield): 16% (16%) as determined by ^{19}F NMR spectroscopy using an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. The reaction was performed at 50°C and the product was not isolated. ^{1}H NMR (400 MHz, 298K, $CDCl_3$): δ (ppm) 4.21 – 4.15 (m, 1H, C*H*OSi), 1.26 (d, *J* = 6.7 Hz, 3H, C*H₃*), 0.93 (t, *J* = 7.9 Hz, 9H, OSiCH$_2$C*H*$_3$), 0.51 (q, *J* = 7.9 Hz, 6H, OSiC*H*$_2$CH$_3$), C*H*$_2$CF$_3$ signal was not observed. ^{19}F NMR (376 MHz, 298K, $CDCl_3$): δ (ppm) -65.2 (t, $^{3}J_{H\text{-}F}$ = 11.0 Hz). No hydrodefluorination was observed.

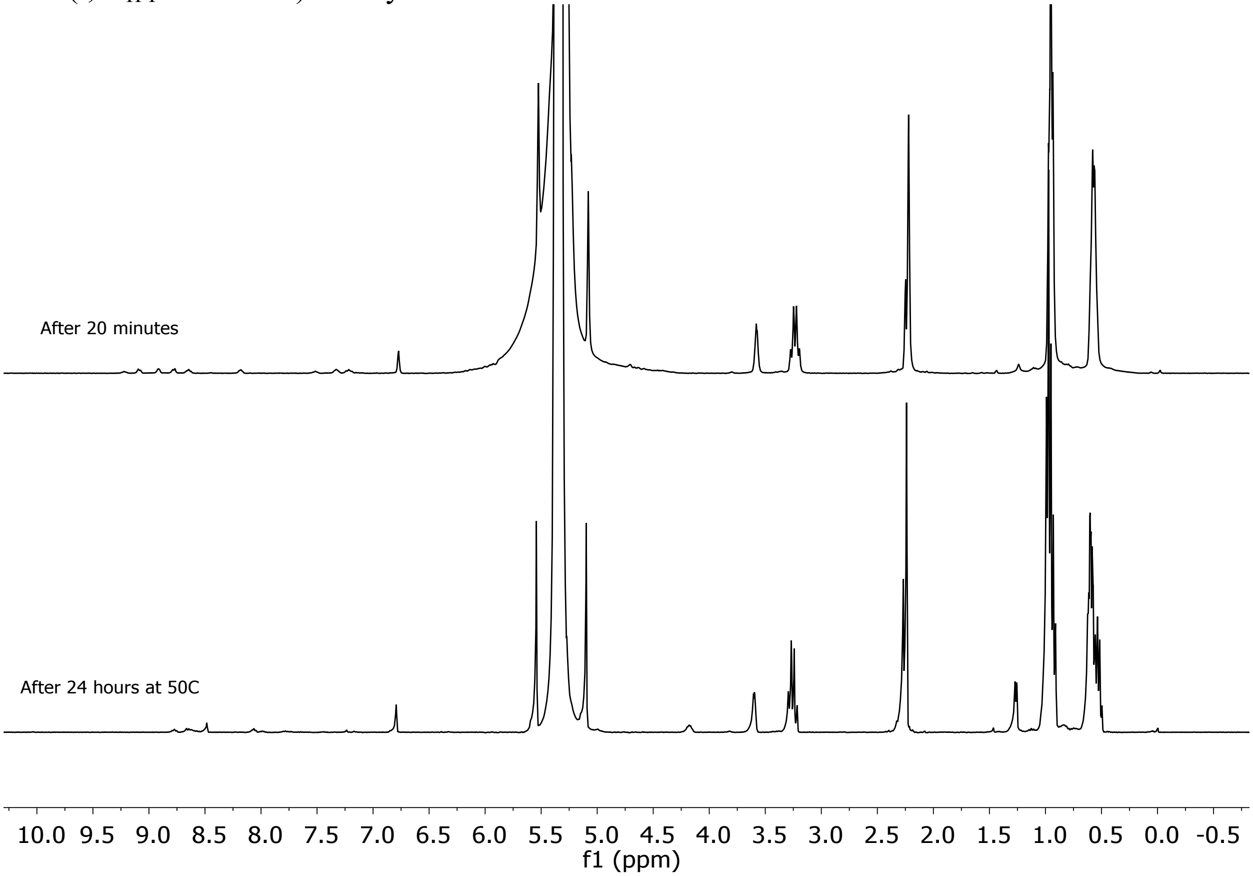


Figure S49. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4,4,4-trifluorobutan-2-one in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

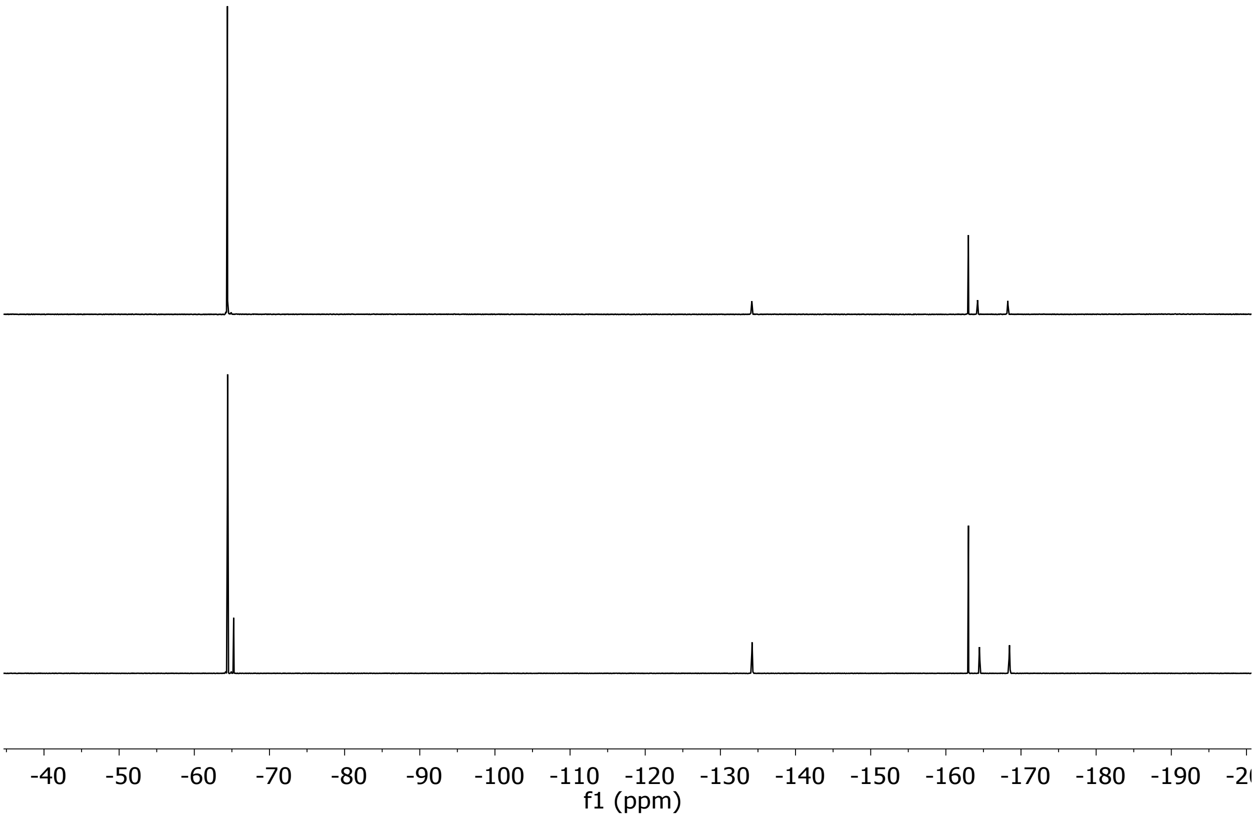
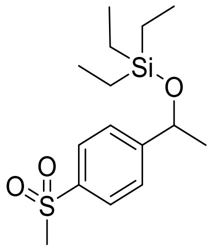


Figure S50. ^{19}F NMR (298K, 376 MHz) spectra for the catalytic hydrosilylation of 4,4,4-trifluorobutan-2-one in dichloromethane with triethylsilane. The NMR spectra are referenced to the hexafluorobenzene signal at -163 ppm.



Triethyl(1-(4-(methylsulfonyl)phenyl)ethoxy)silane (Entry 19): %Conversion (%Yield): >99% (96.8%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in CDCl$_3$. ^{1}H NMR (400 MHz, 298K, C$_6$D$_6$): δ (ppm) 7.78 (d, J = 8.3 Hz, 2H, Ar-*H*), 7.20 (d, J = 8.3 Hz, 2H, Ar-*H*), 4.65 (q, J = 6.4 Hz, 1H, C*H*(OSiEt$_3$)), 2.28 (s, 3H, Ar-S(O)$_2$C*H*$_3$), 1.24 (d, J = 6.4 Hz, 3H, C(OSi)C*H*$_3$), 0.92 (t, J = 8.2 Hz, 9H, OSiCH$_2$C*H*$_3$), 0.52 (dq, J = 8.2 Hz, J = 2.5 Hz, 6H, OSiC*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (101 MHz, 298K, C$_6$D$_6$): δ (ppm) 152.8, 140.5, 127.8, 126.1, 70.4, 43.8, 27.2, 7.0, 5.1. GCMS: 286.1 ([M-CH$_2$CH$_3$]$^+$, calc'd. 286.11).

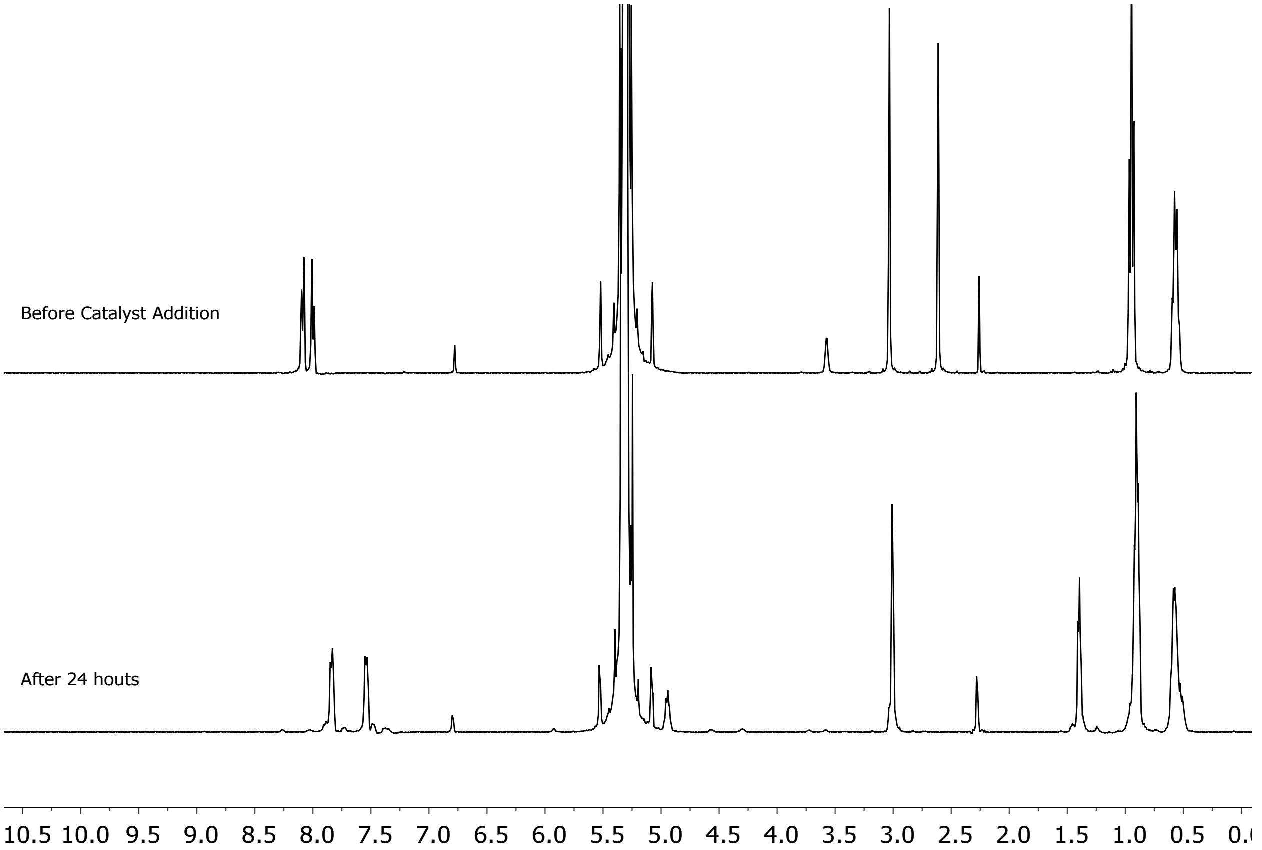


Figure S51. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-methylsulfonylacetophenone in dichloromethane with 1 equivalent of triethylsilane. The NMR spectra are referenced to the CH$_2$Cl$_2$ resonance at 5.30 ppm.

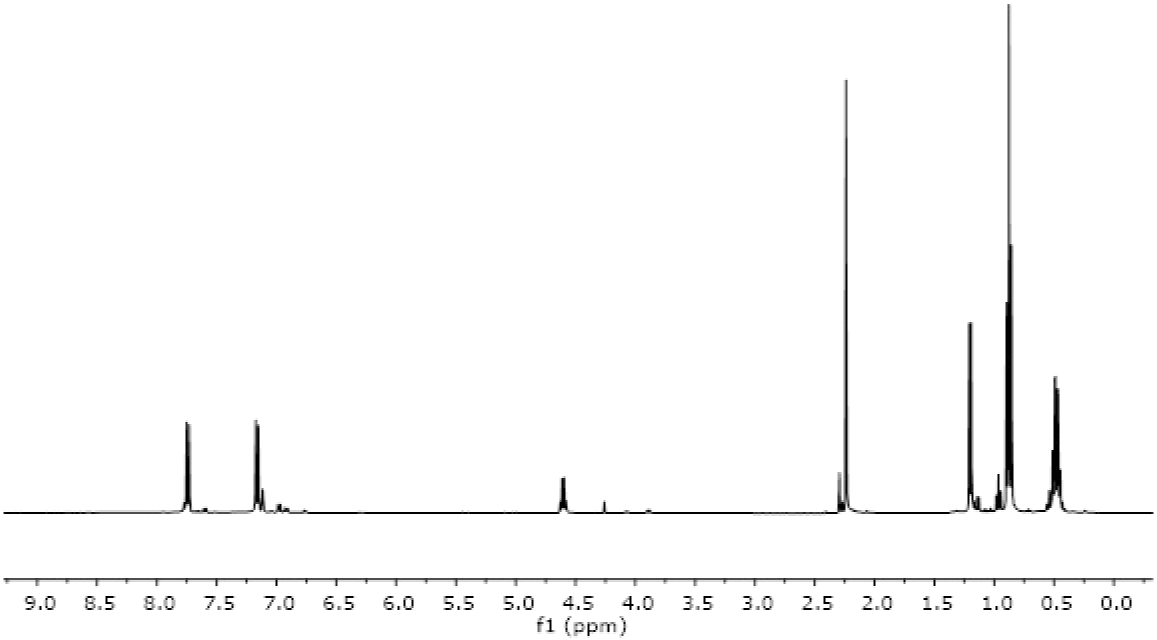


Figure S52. ^{1}H NMR (400 MHz, 298K, CDCl3) of triethyl(1-(4-(methylsulfonyl)phenyl)ethoxy)silane.

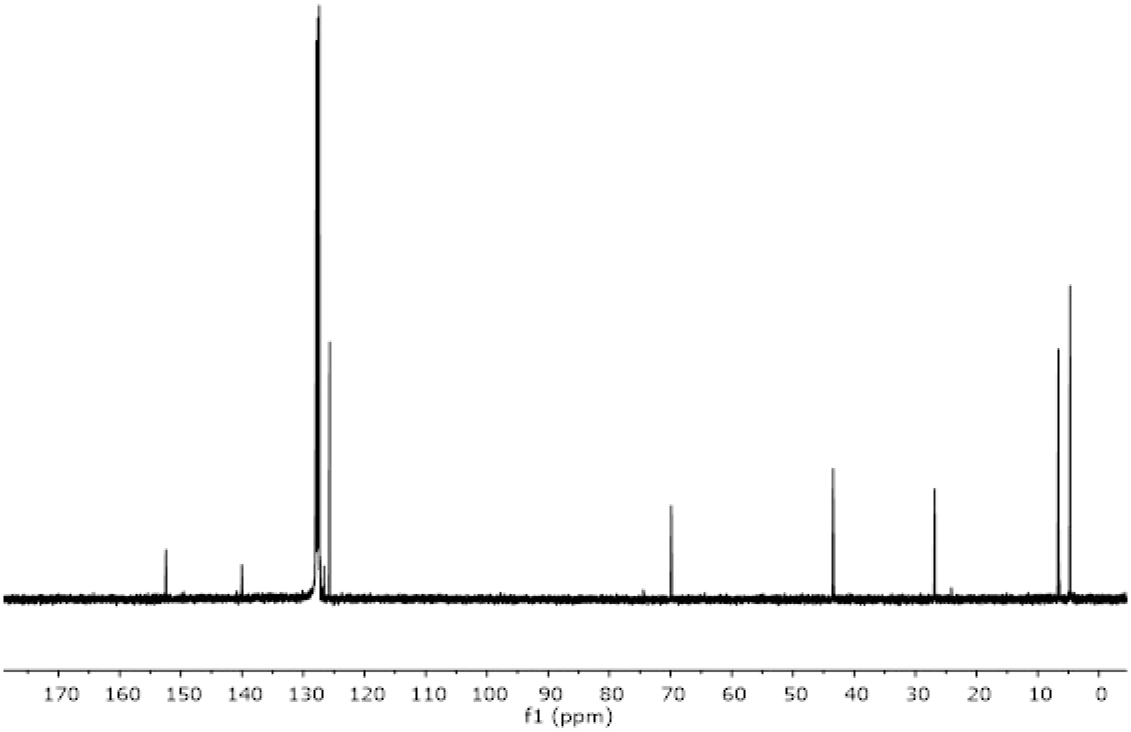
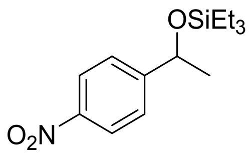


Figure S53. ^{13}C{^{1}H} NMR (101 MHz, 298K, C_6D_6) of triethyl(1-(4-(methylsulfonyl)phenyl)ethoxy)silane.



Triethyl(1-(4-nitrophenyl)ethoxy)silane (Entry 20): %Conversion (%Yield): >99% (92%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[2] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 8.08 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H). 4.90 (q, J = 6.5 Hz, 1H), 1.35 (d, J = 6.5 Hz, 3H), 0.84 (t, J = 7.6 Hz, 9H), 0.52 (q, J = 7.6 Hz, 6H).

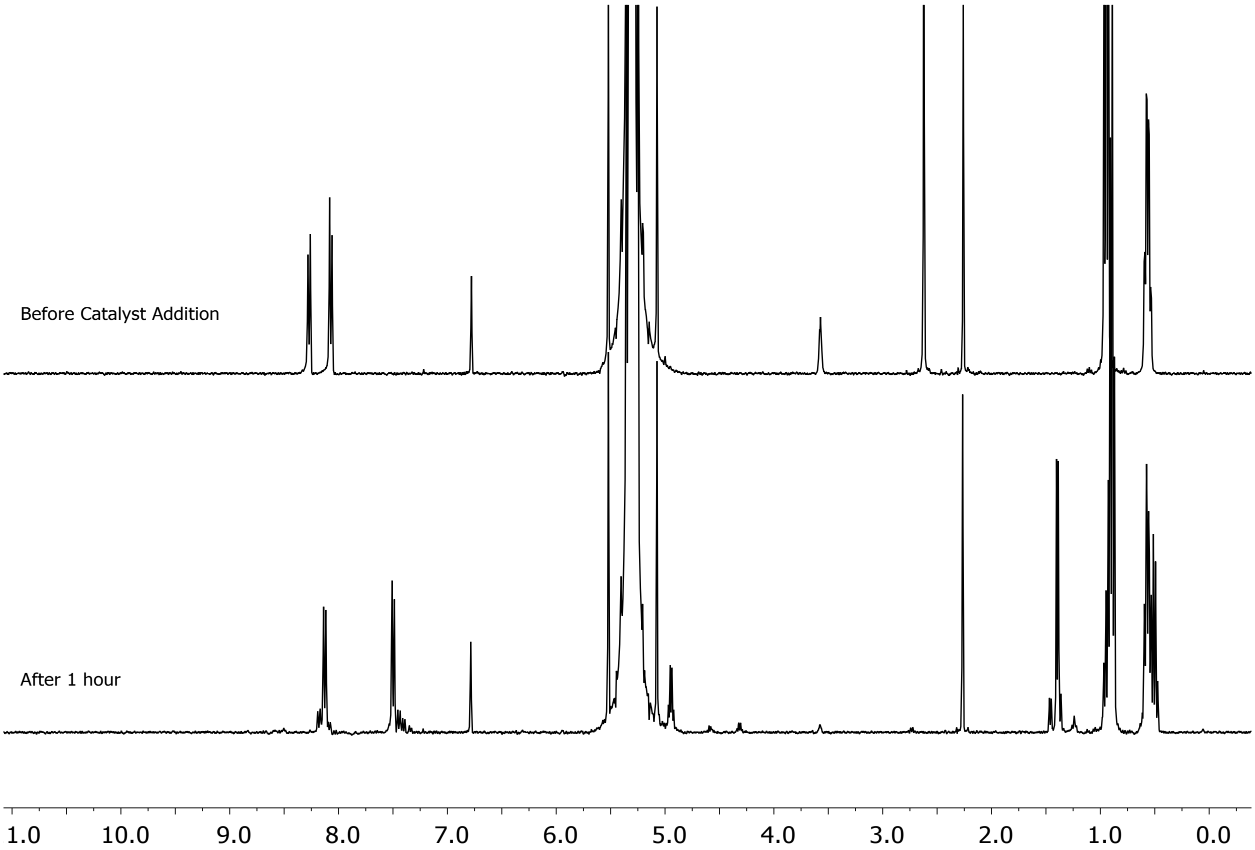
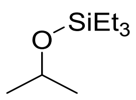


Figure S54. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-nitroacetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



(Isopropoxy)triethylsilane (Entry 21): %Conversion (%Yield): >99% (98.3%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[14] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 3.66-3.59 (m, 1H), 1.05 (d, *J* = 6.1 Hz, 6H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.50 (1, *J* = 7.9 Hz, 6H).

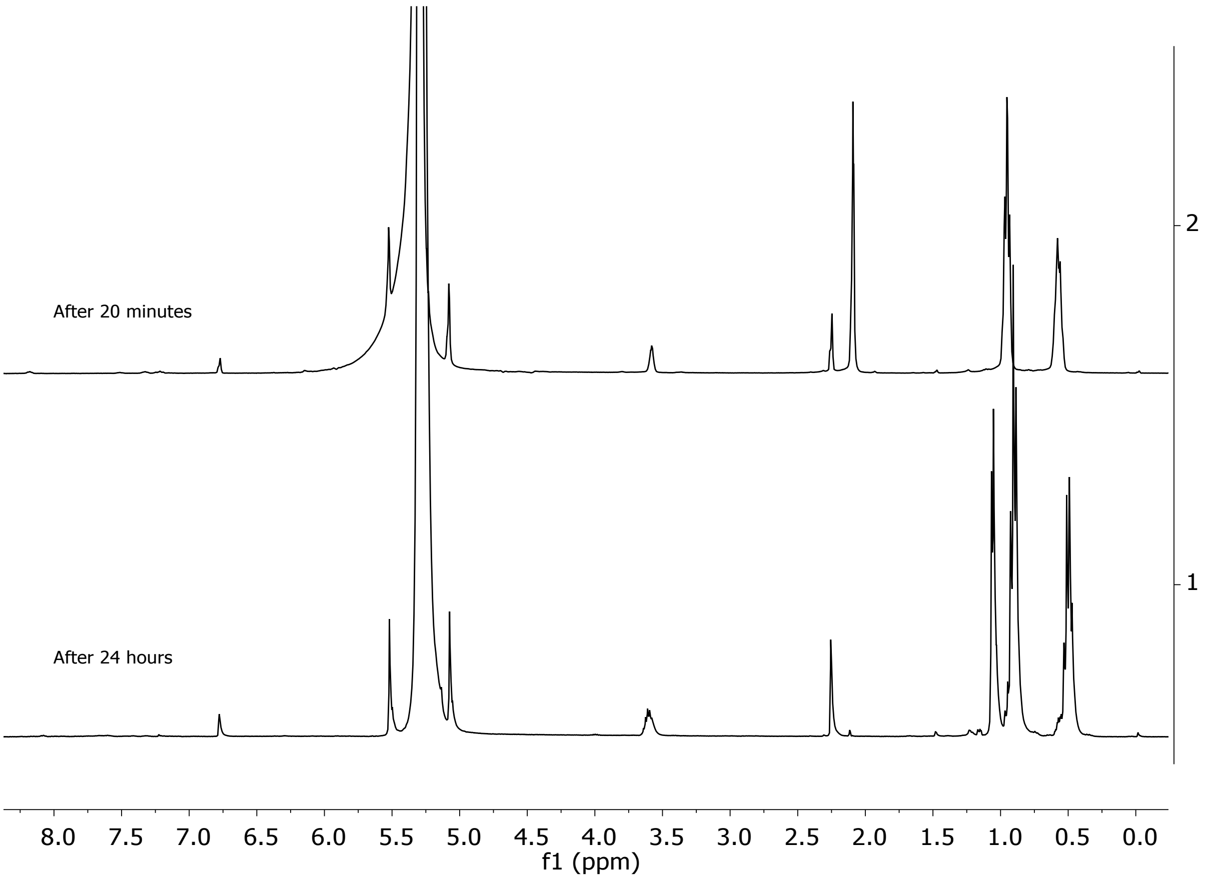
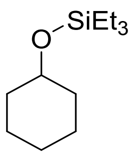


Figure S55. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of acetone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



(Cyclohexyloxy)triethylsilane (Entry 22): %Conversion (%Yield): >99% (98.9%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[15] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 3.32 – 3.24 (m, 1H), 1.86 – 1.76 (m, 2H), 1.72 – 1.64 (m, 2H), 1.54 – 1.45 (m. 1H), 0.92 t, *J* = 8.0 Hz, 9H), 0.50 (q, *J* = 8.0 Hz, 6H).

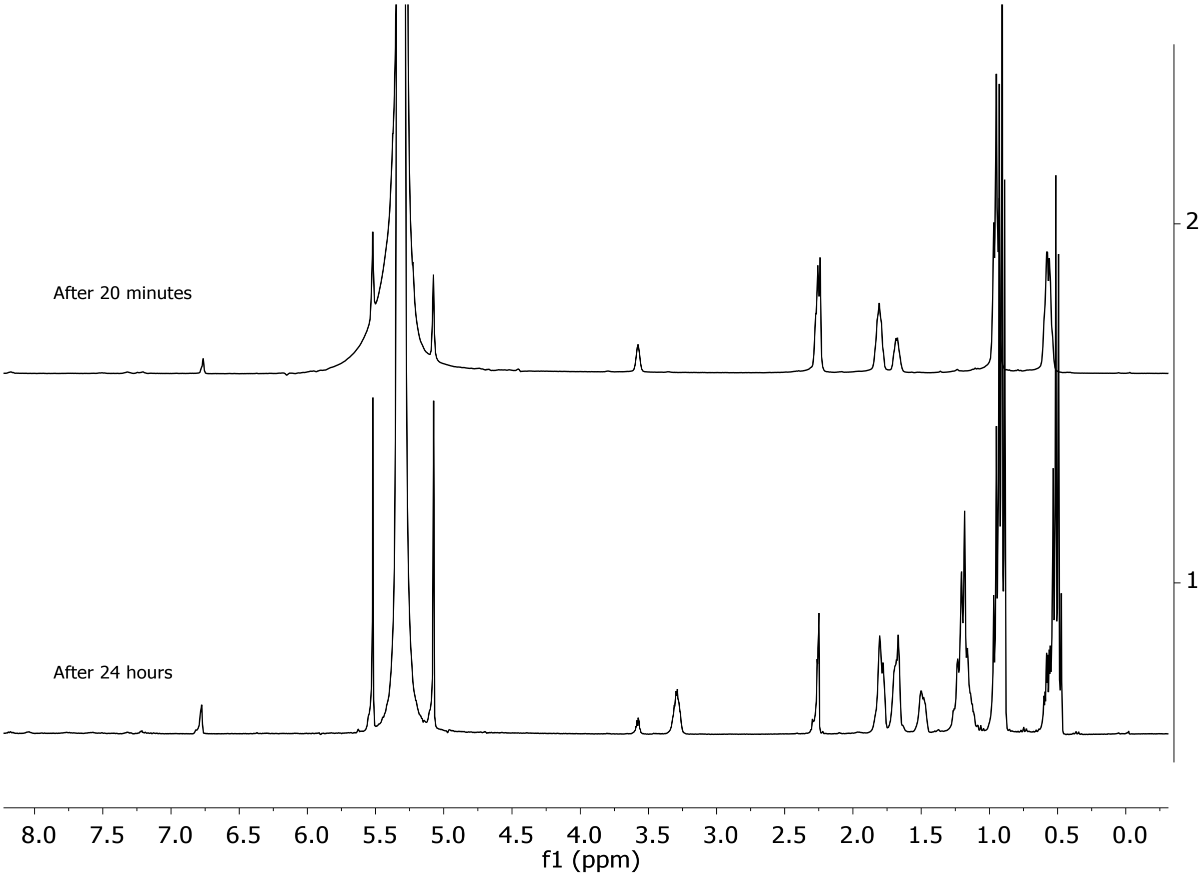
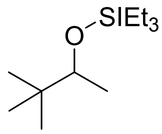


Figure S56. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of cyclohexanone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(1,2,2-trimethylpropoxy)silane (Entry 23): %Conversion (%Yield): >99% (79%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[16] ^{1}H NMR (400 MHz, 298K, $CDCl_3$): δ (ppm) 3.45 (q, *J* = 6.3 Hz, 1H), 1.02 (d, *J* = 6.3 Hz, 3H), 0.93 (m, 9H), 0.82 (s, 9H), 0.57 (q, *J* = 7.9 Hz, 6H).

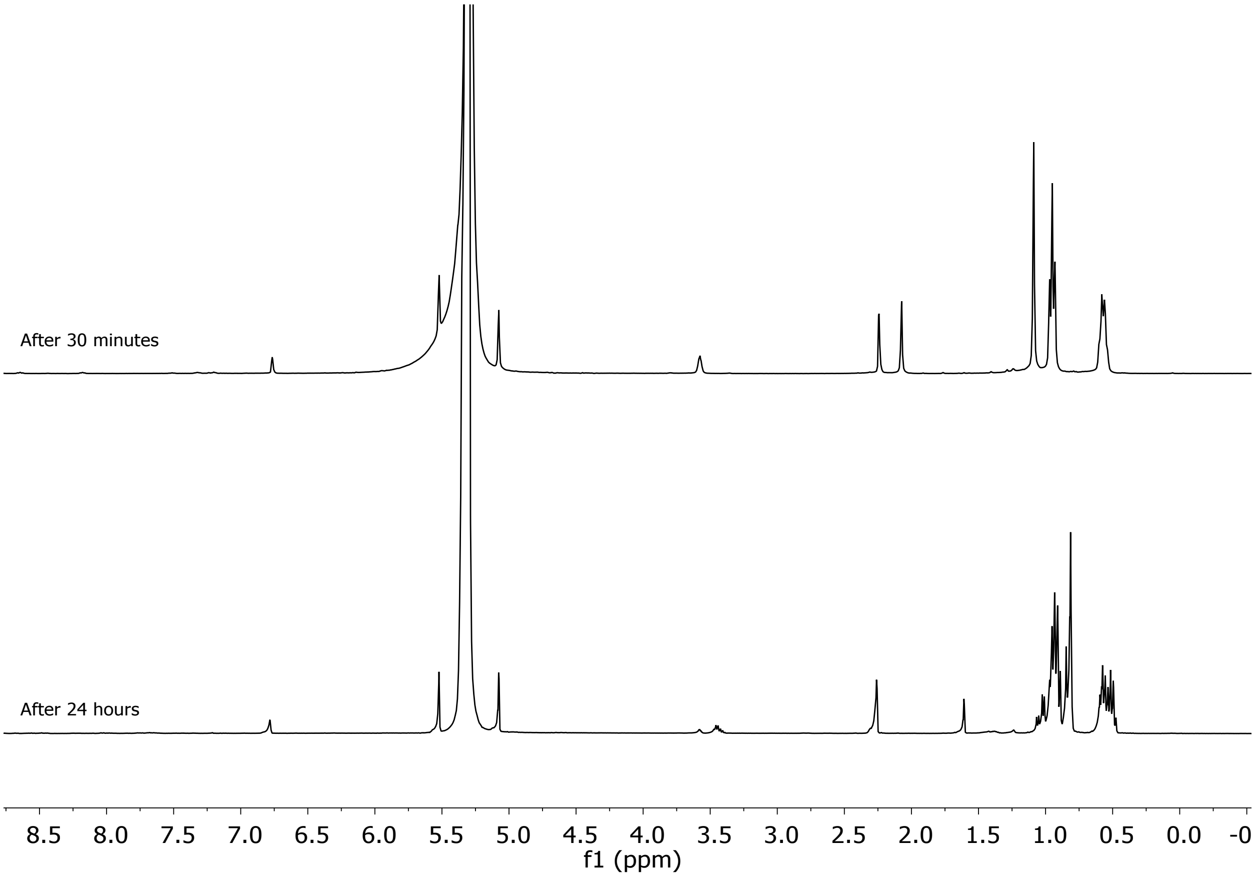
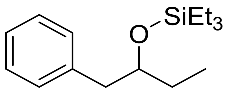


Figure S57. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 3 3-dimethyl-2-butanone in dichloromethane with triethylsilane in air. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl((1-phenylbutan-2-yl)oxy)silane (Entry 24, 25): %Conversion (%Yield): >99% (95.4%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. ^{1}H NMR (400 MHz, 298K, C_6D_6): δ (ppm) 7.15 – 7.07 (m, 3H, Ar-*H*), 7.06 – 7.01 (m, 1H, Ar-*H*), 3.75 (p, *J* = 6.2 Hz, 1H, C*H*OSi), 2.66 (qd, *J* = 13.3 Hz, *J* = 6.2 Hz, 2H, Ar-C*H*$_2$R), 1.47 – 1.39 (m, 2H, C(H)C*H*$_2$CH$_3$), 1.00 – 0.84 (m, 12H, SiCH$_2$C*H*$_3$ and C(H)CH$_2$C*H*$_3$), 0.48 (qd, *J* = 8.0 Hz, *J* = 2.1 Hz, 6H, SiC*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (101 MHz, 298K, C_6D_6): δ (ppm) 139.8, 130.0, 128.5, 126.4, 75.1, 44.0, 30.0, 9.7, 7.2, 5.4. GCMS: 235.2 ([M-CH_2CH_3]$^+$, calc'd. 235.15).

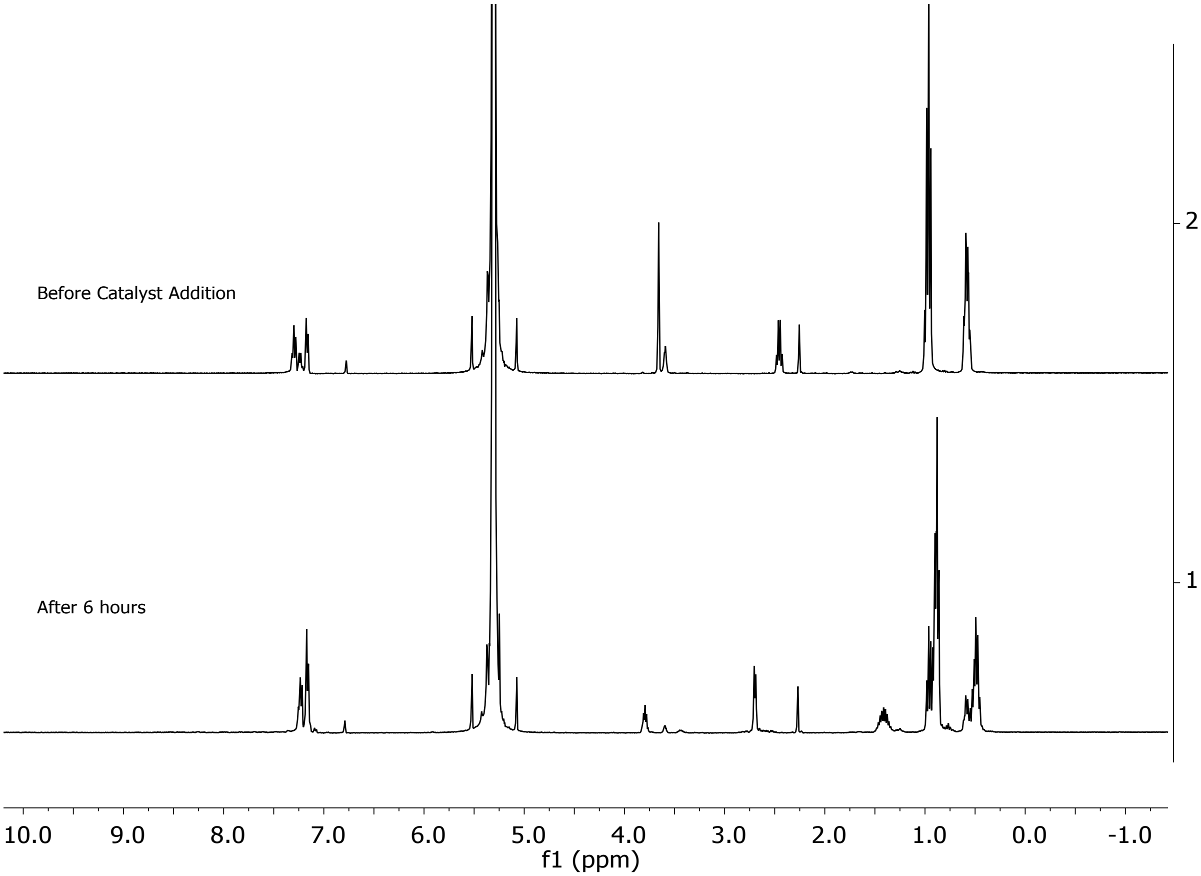


Figure S58. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 1-phenylbutan-2-one in dichloromethane with 1.1 equivalents of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm

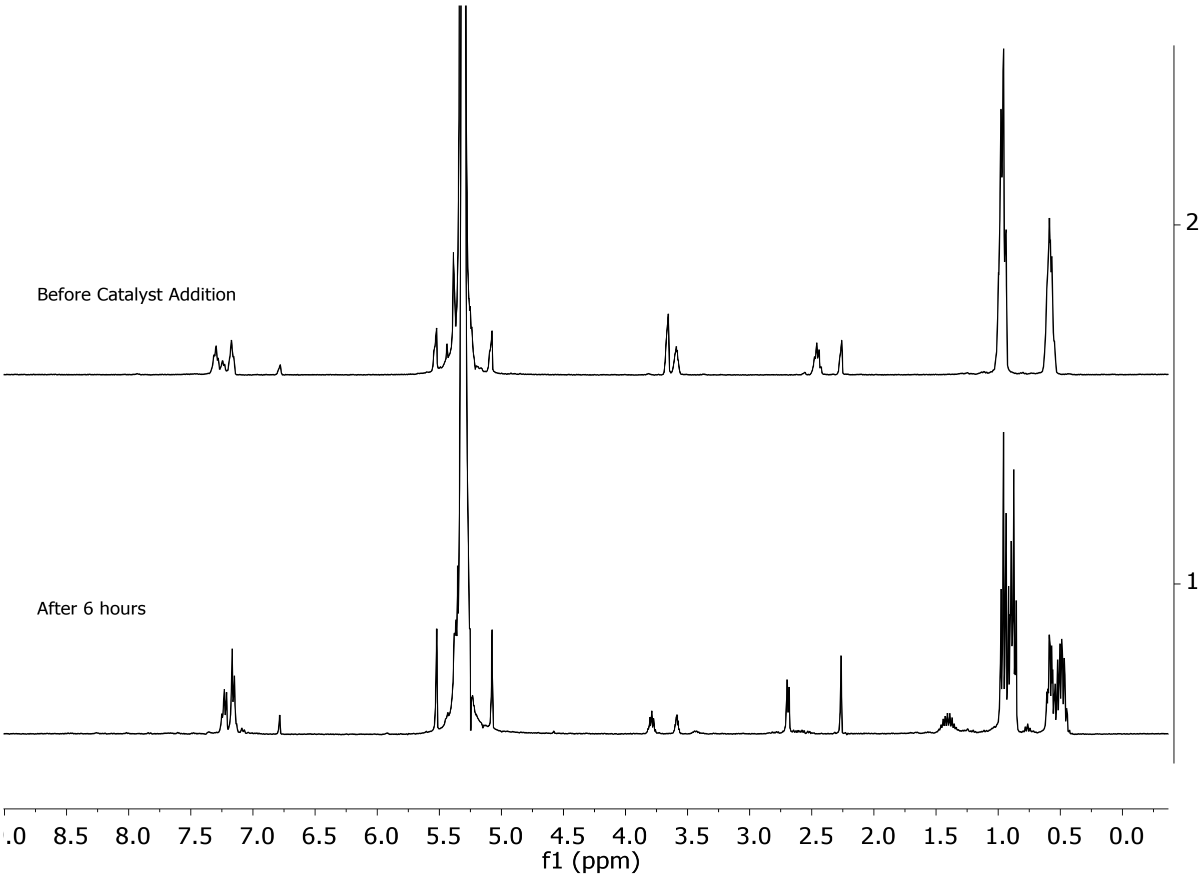


Figure S59. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 1-phenylbutan-2-one in dichloromethane with 2 equivalents of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

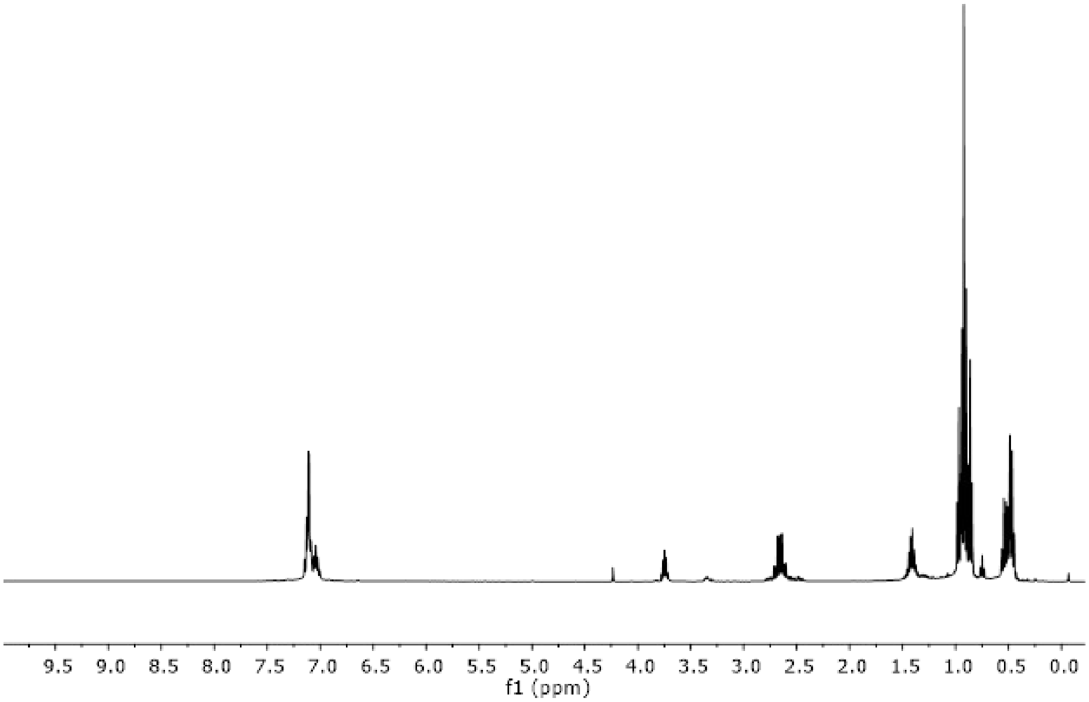


Figure S60. ^{1}H NMR (400 MHz, 298K, CDCl3) for triethyl((1-phenylbutan-2-yl)oxy)silane.

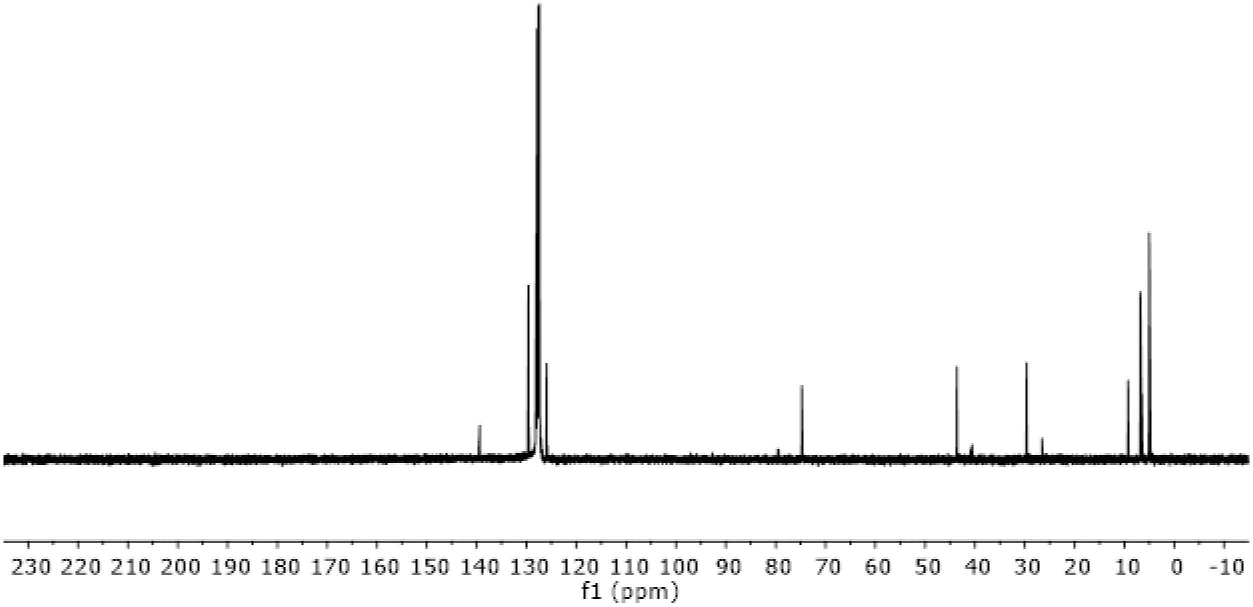
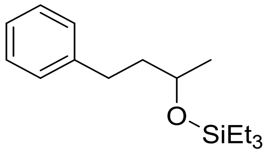


Figure S61. $^{13}C\{^{1}H\}$ NMR (101 MHz, 298K, C_6D_6) of triethyl((1-phenylbutan-2-yl)oxy)silane.



Triethyl(1-methyl-3-phenyl-propoxy)silane (Entry 26): %Conversion (%Yield): >99% (96.8%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[16] ^{1}H NMR (400 MHz, 298K, $CDCl_3$): δ (ppm) 7.26 - 7.19 (m, 2H), 7.15 – 7.09 (m, 3H), 3.87 – 3.78 (m, 1H), 2.71 – 2.52 (m, 2H), 1.74 – 1.61 (m, 2H), 1.15 (d, *J* = 6.0Hz, 3H), 0.95 – 0.89 (m, 9H), 0.58 (q, *J* = 7.9 Hz, 6H).

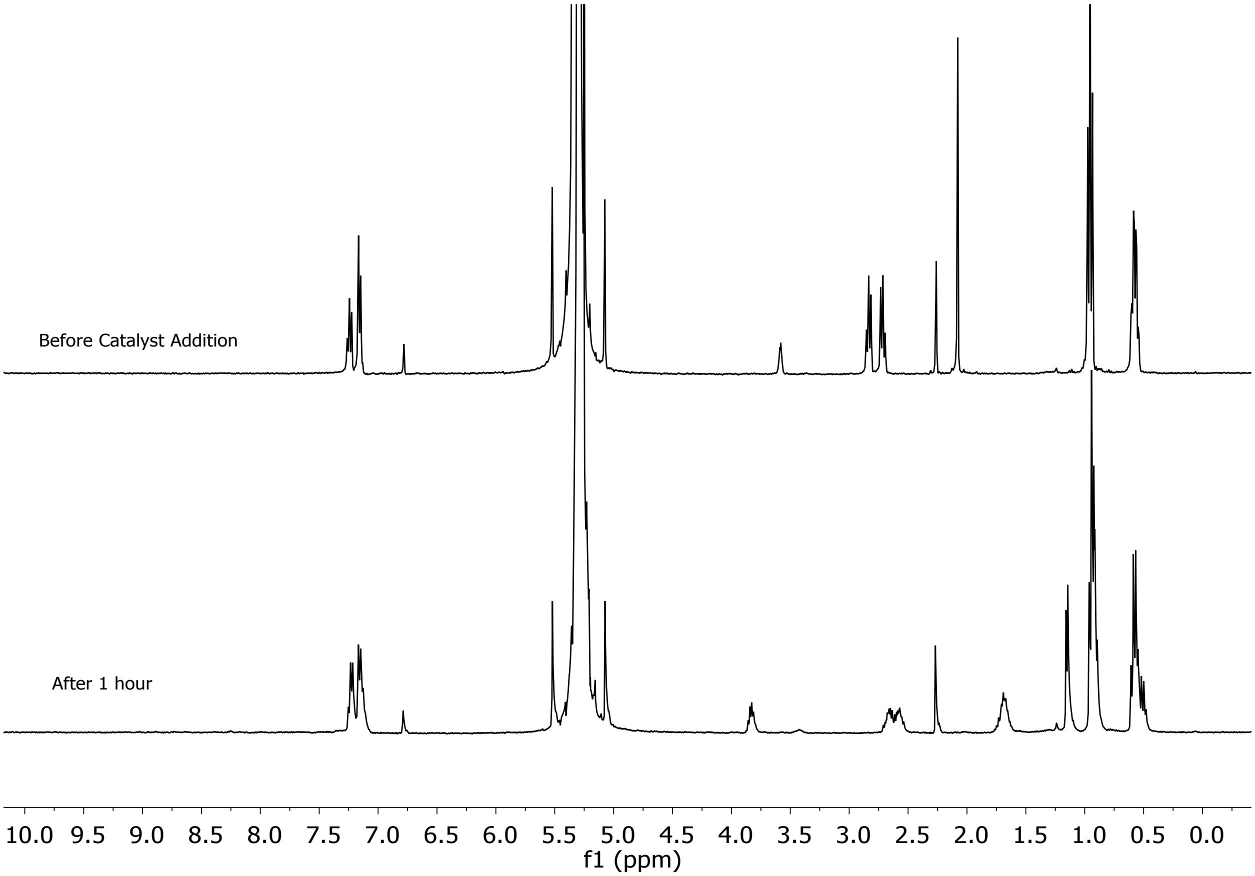
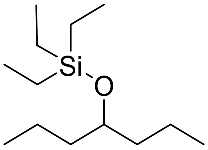


Figure S62. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-phenylbutan-2-one in dichloromethane with 1 equivalent of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(heptan-4-yloxy)silane (Entry 27): %Conversion (%Yield): >99% (99%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[17] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 3.65 – 3.62 (m, 1H), 1.44 – 1.26 (m, 8H), 0.99 – 0.86 (m, 15H), 0.60 – 0.50 (m, 6H).

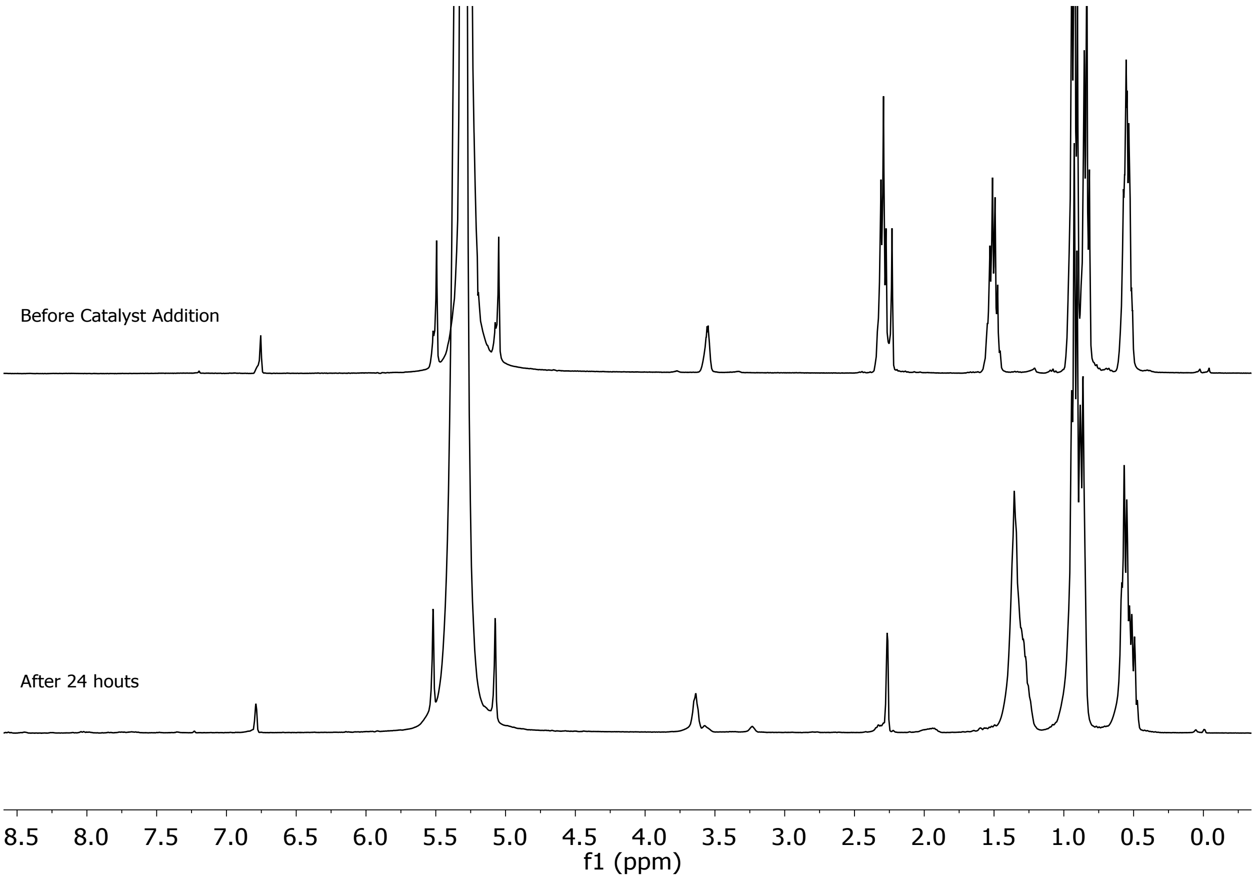
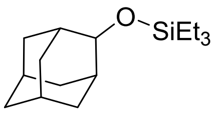


Figure S63. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-heptanone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(2-adamantyloxy)silane (Entry 28): %Conversion (%Yield): >99 % (99%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. ^{1}H NMR (400 MHz, 298K, $CDCl_3$): 3.81 (t, *J* = 3.3 Hz, 1H, C(*H*)OSi), 2.16 (d, *J* = 12.6 Hz, 2H, C*H*C(H)OSiEt$_3$), 1.86 – 1.63 (m, 10H), 1.43 (d, *J* = 12.2 Hz, 2H, C*H*$_2$(CH)$_2$), 0.94 (t, *J* = 7.9Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H).0. ^{13}C{^{1}H} NMR (101 MHz, 298K, $CDCl_3$): 74.6, 37.7, 36.5, 35.3, 35.2, 27.6, 27.1, 6.8, 4.9. HRMS (DART-ESI+ Ionization, m/z): m/z calc'd for C16H31OSi ([M+H]$^+$): 267.21442, Found 267.21282.

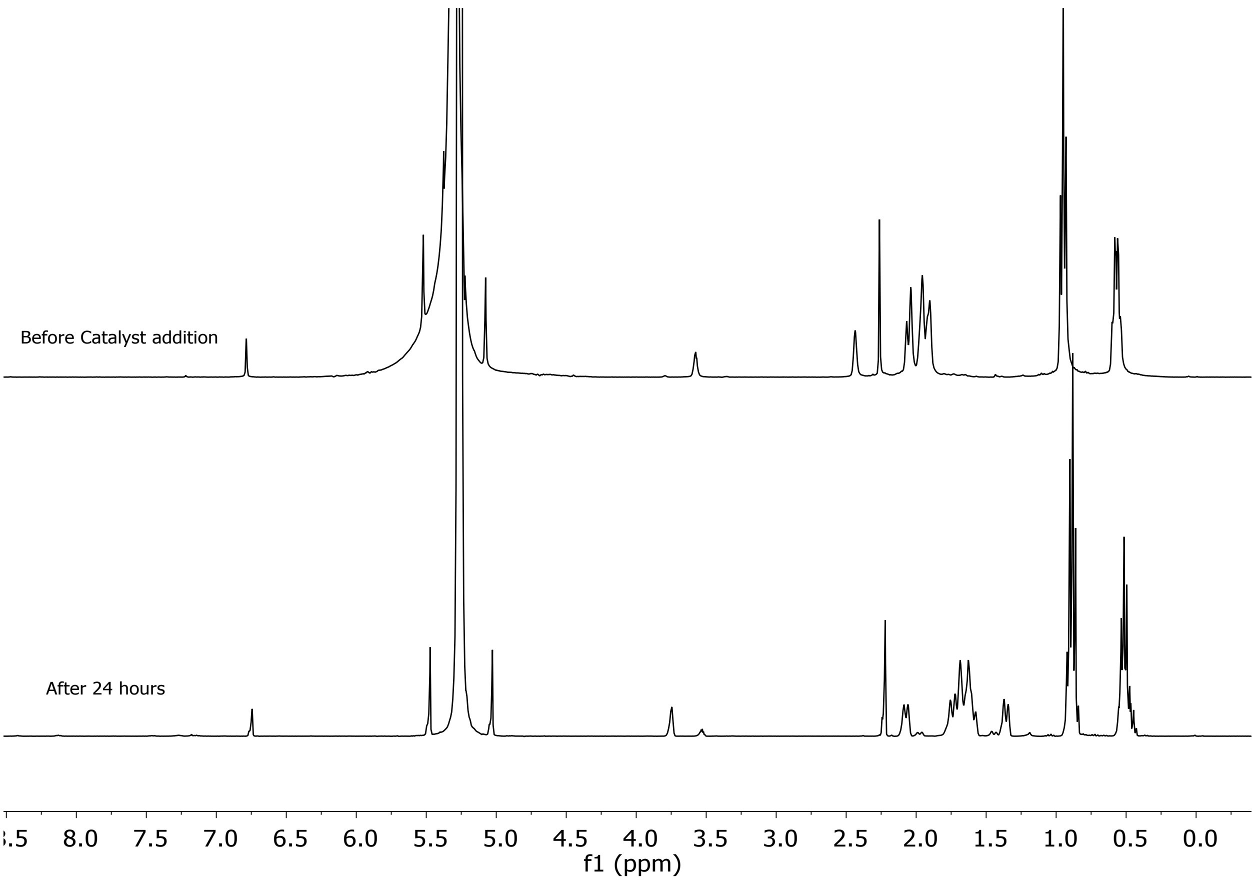


Figure S64. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 2-adamantanone in dichloromethane with 1 equivalent of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

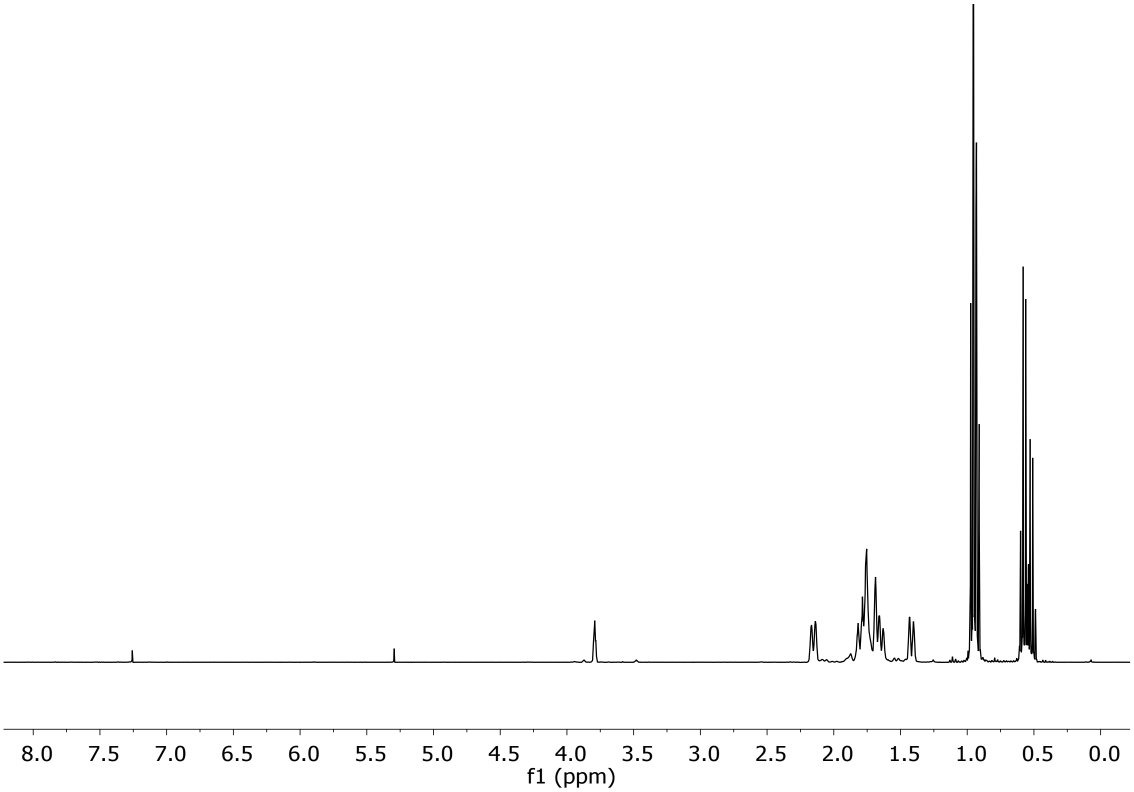


Figure S65. ^{1}H NMR (400 MHz, 298K, CDCl3) for triethyl(2-adamantyloxy)silane.

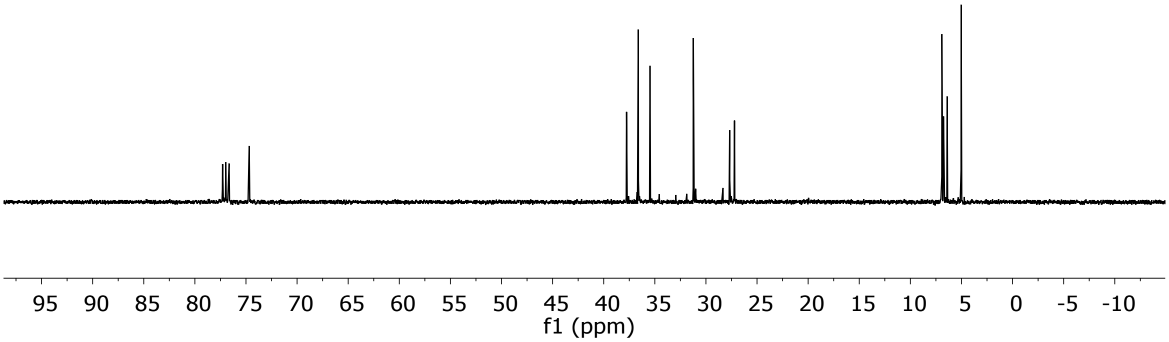
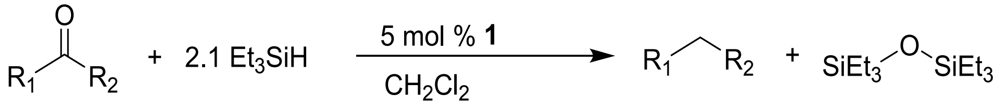
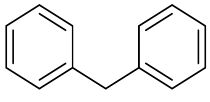


Figure S66. $^{13}C\{^1H\}$ NMR (101 MHz, 298K, $CDCl_3$) of triethyl(2-adamantyloxy)silane.

5.3. Catalytic Reductive Deoxygenation of Ketones

General Reaction Scheme:





Diphenylmethane (Entries 29-31): %Conversion (%Yield): >99 % (93.6%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[18] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.13-7.29 (m, 10H), 3.99 (s, 2H). GCMS: 167.2 ($[M]^+$, calc'd. 168.09).

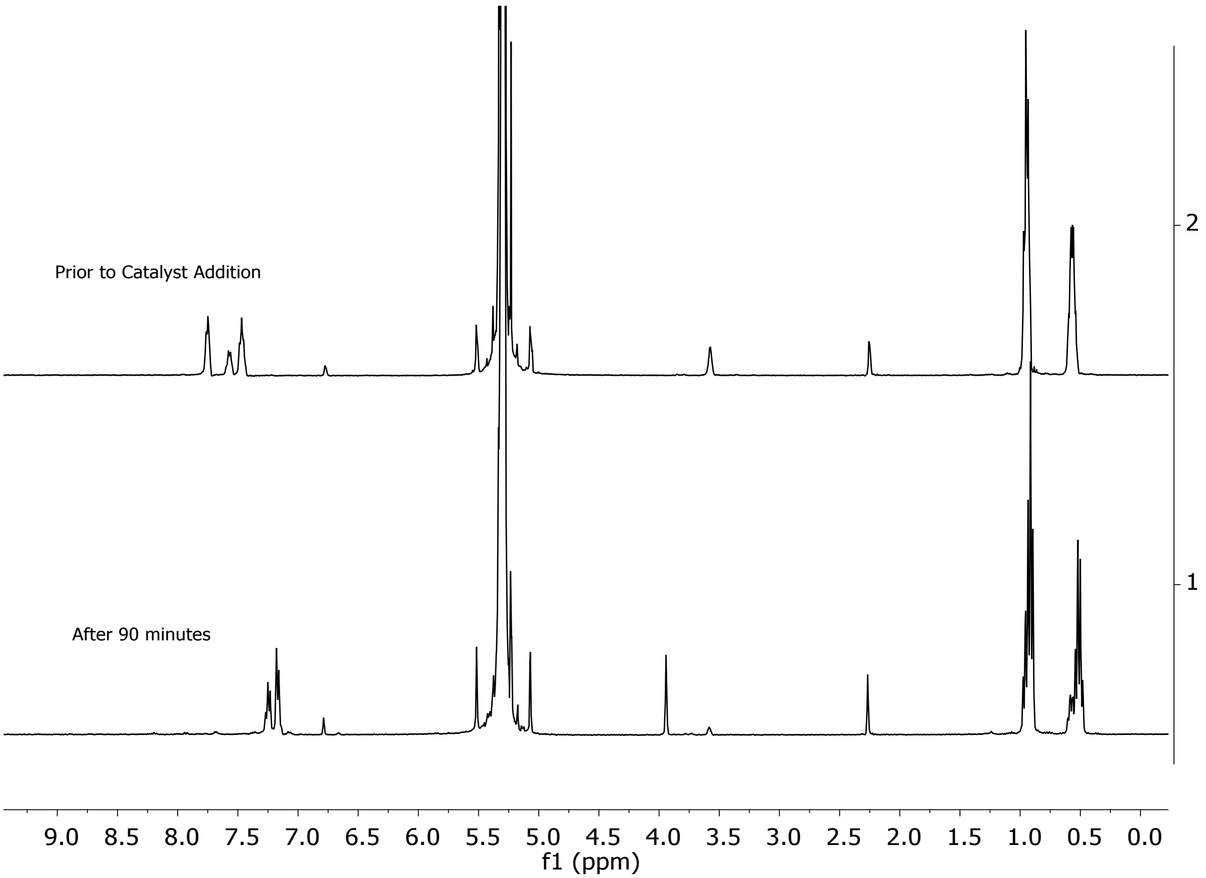


Figure S67. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of benzophenone in dichloromethane with 2.1 equivalents of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

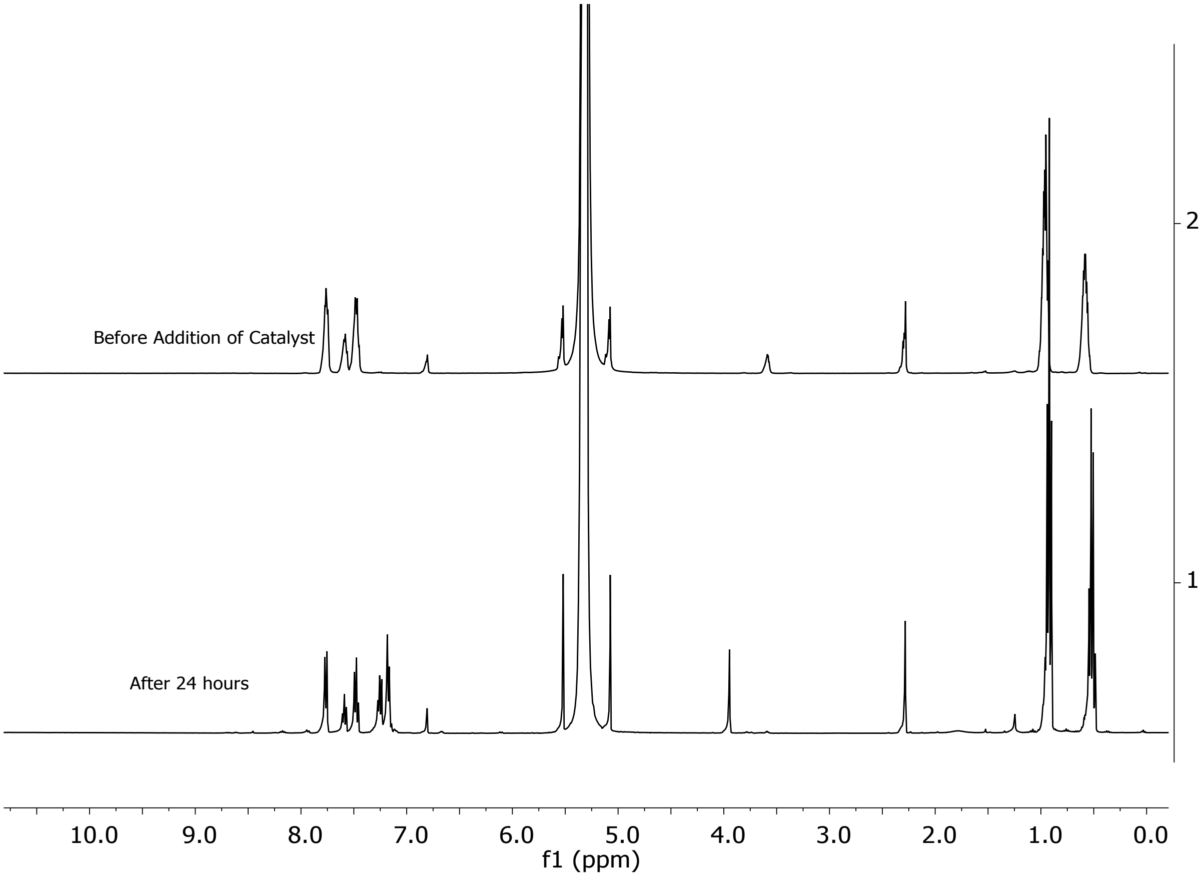


Figure S68. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of benzophenone in dichloromethane with 1 equivalent of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

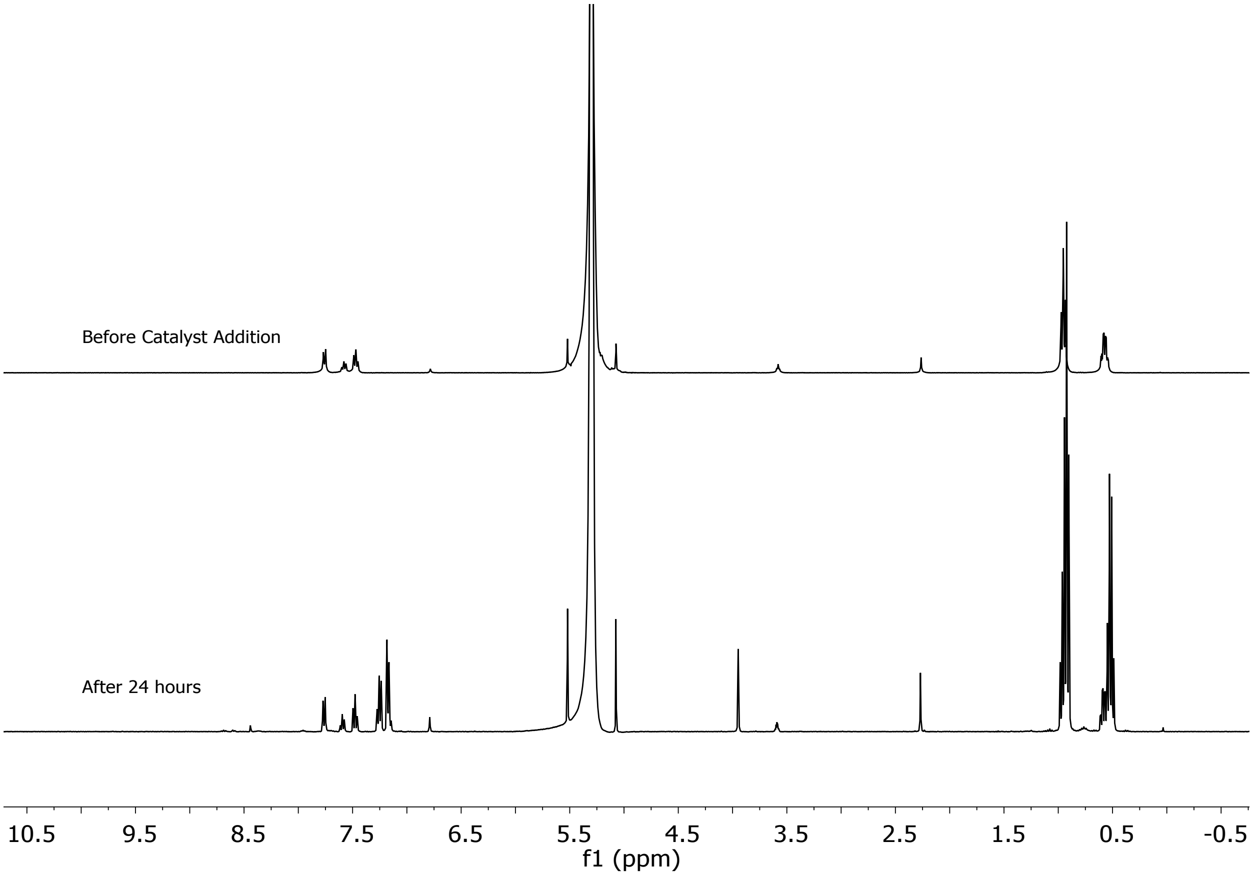
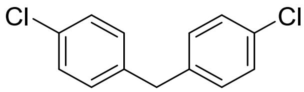


Figure S69. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of benzophenone in dichloromethane with 2 equivalents of triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm. The reaction was setup under ambient air. % Conversion (% yield) = 66% (66%).



4,4’-dichlorodiphenylmethane (Entry 32): %Conversion (%Yield): >99 % (89.7%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[19] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.03-7.26 (m, 8H), 3.91 (s, 2H). GCMS: 236.1 ([M]+, calc’d. 236.02).

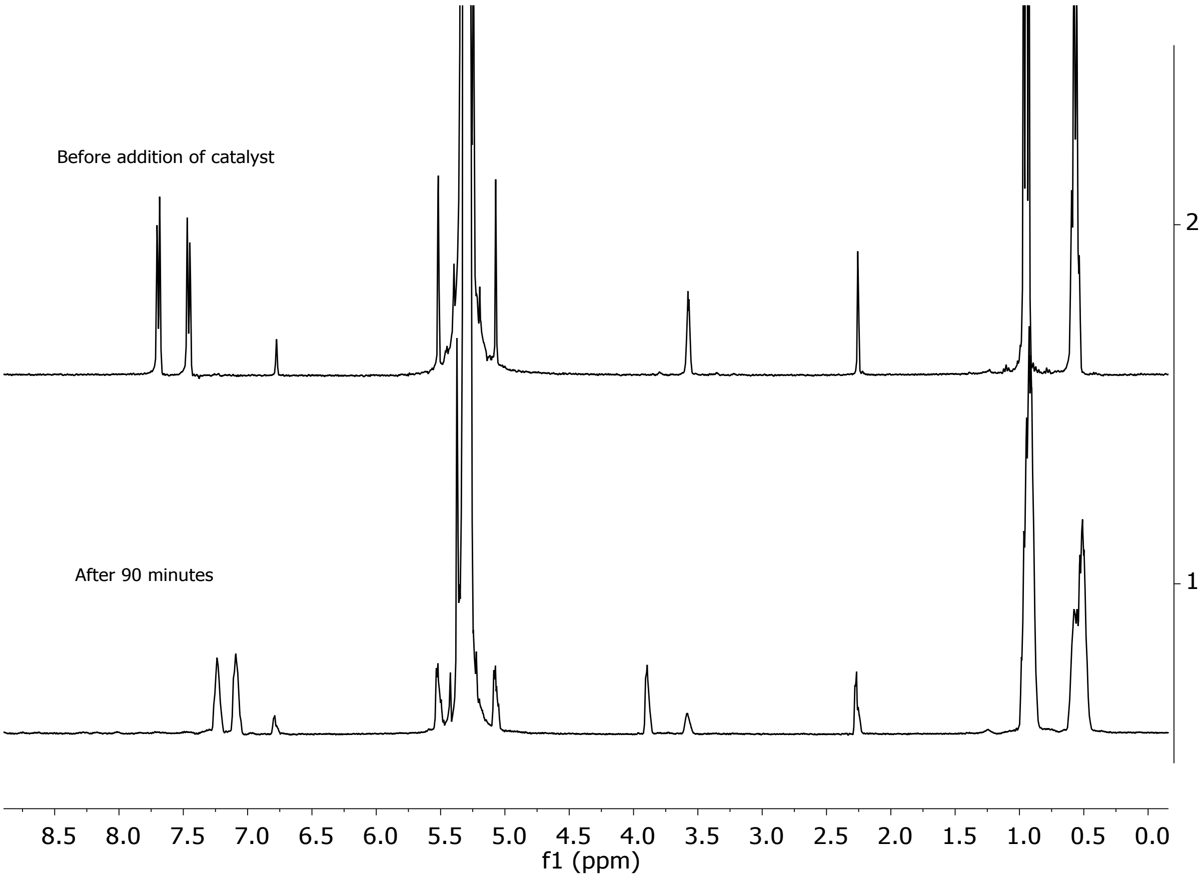
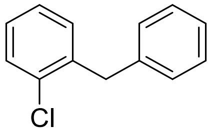


Figure S70. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4,4’-dichlorobenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



2-Chlorodiphenylmethane (Entry 33): %Conversion (%Yield): >99 % (98.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[20] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.37-7.32 (m, 1H), 7.27-7.21 (m, 2H), 7.20-7.10 (m, 6H), 4.09 (s, 2H). GCMS: 202.1 ($[M]^+$, calc'd. 202.05).

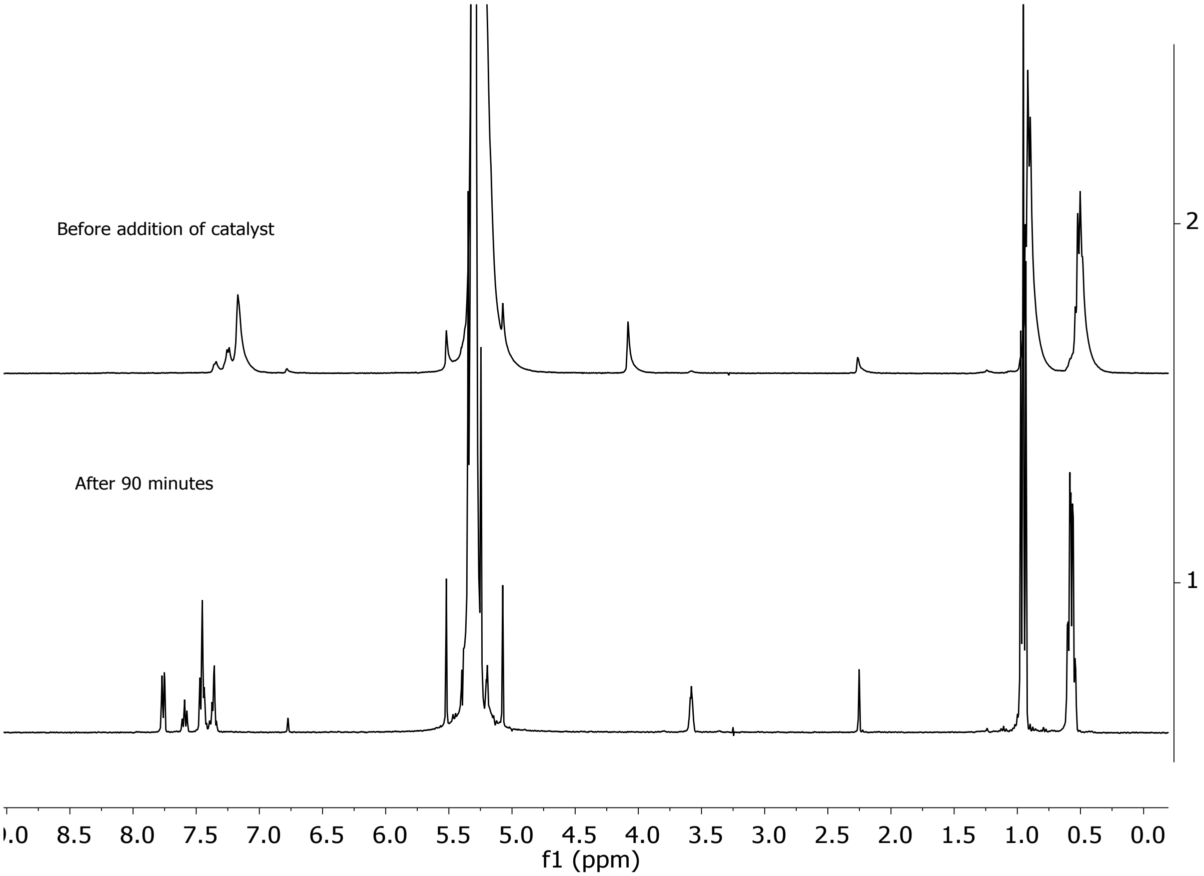
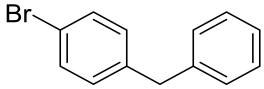


Figure S71. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 2-chlorobenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

**4-Bromodiphenylmethane (Entry 34)**: %Conversion (%Yield): 89.6% (89.2%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[18] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.30 (d, 8.0Hz, 2H), 7.25 (d, 7.4Hz, 2H), 7.20 - 7.17 (m, 1H), 7.16 (d, 7.4Hz, 2H), 7.06 (d, 8.0Hz, 2H), 3.91 (s, 2H). GCMS: 246.1 ([M]$^{+}$, calc'd. 246.00).

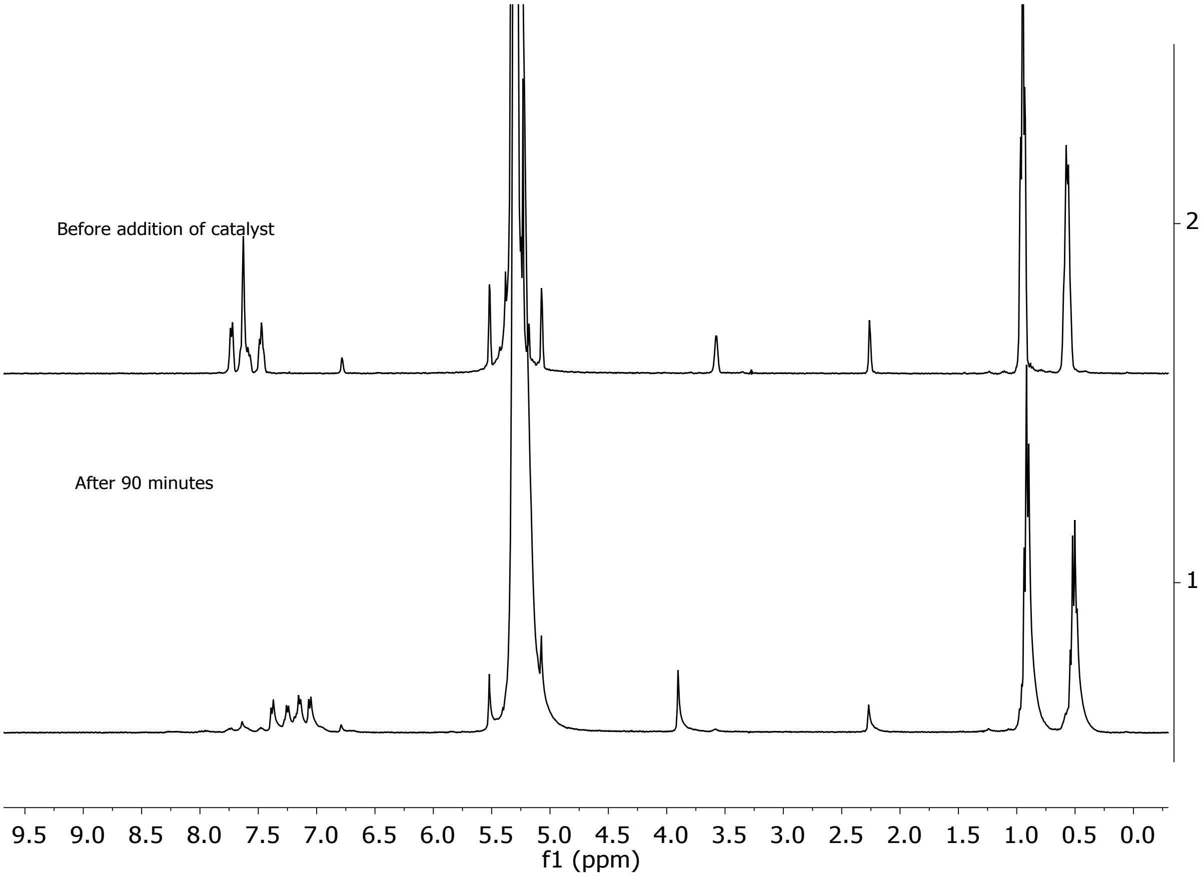
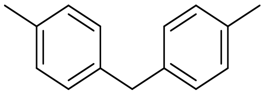


Figure S72. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4-bromoobenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

**4,4'-dimethyldiphenylmethane (Entry 35)**: %Conversion (%Yield): >99% (96.5%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[19] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.12 – 6.99 (m, 8H), 3.87 (s, 2H), 2.25 (s, 6H). GCMS: 196.2 ([M]$^{+}$, calc'd. 196.13).

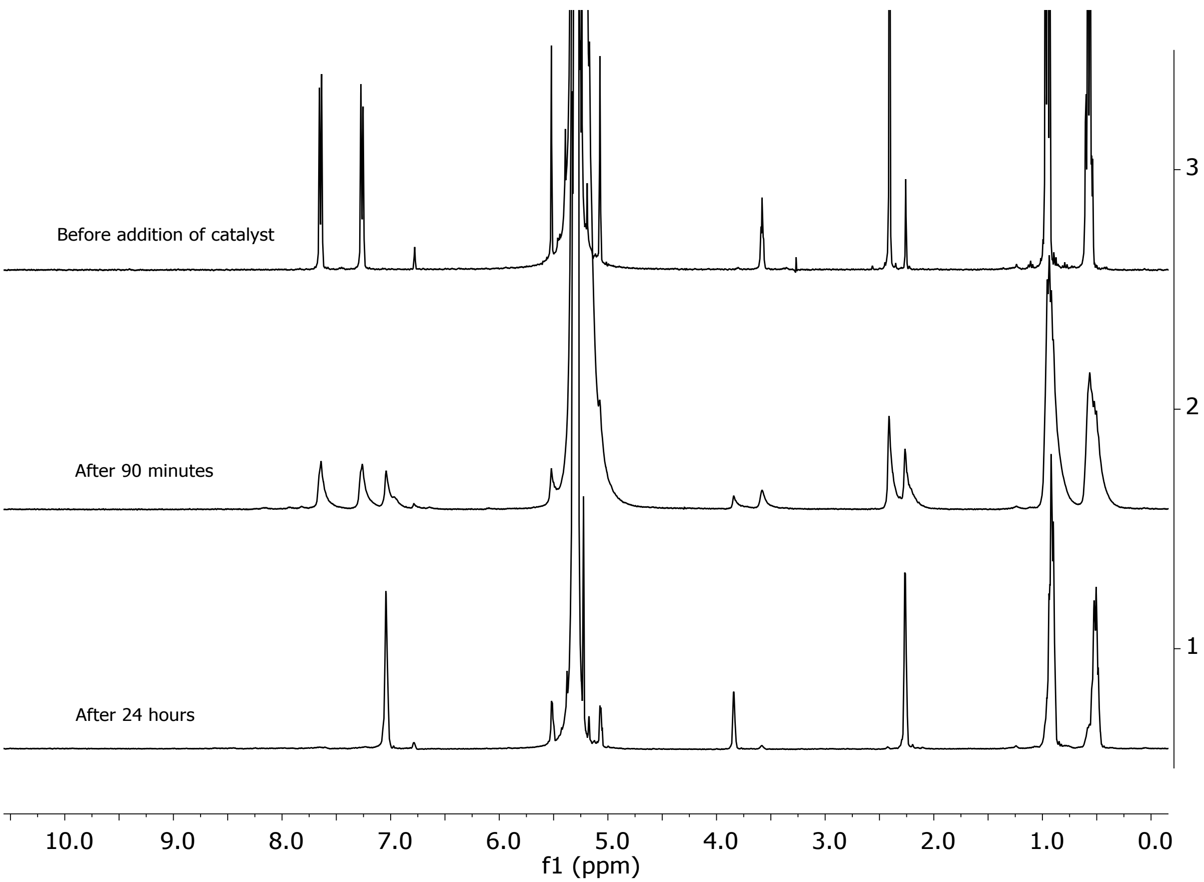
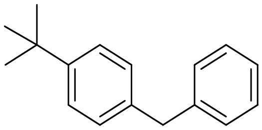


Figure S73. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4,4'-dimethylbenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm. Methyl peaks in the product overlap with the mesitylene peaks in the external standard.



4-tert-butyldiphenylmethane (Entry 36): %Conversion (%Yield): >99% (98.1%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[21] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.31 - 7.23 (m. 4H), 7.21-7.15 (m, 3H), 7.11 (d, *J* = 8.0Hz, 2H), 3.91 (s, 2H), 1.27 (s, 9H). GCMS: 224.2 ([M]$^+$, calc'd. 224.16).

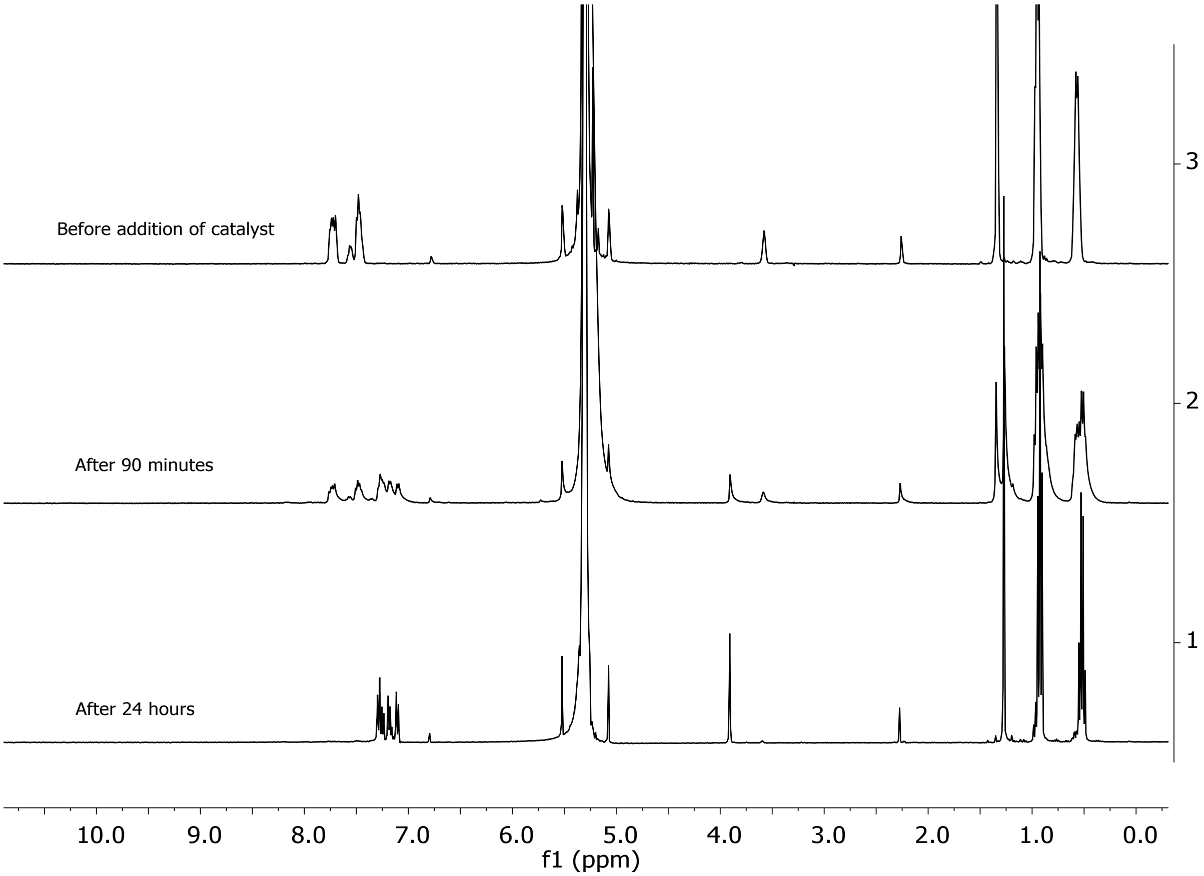
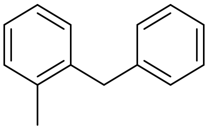


Figure S74. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4-tert-butylbenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



2-methyldiphenylmethane (Entry 37): %Conversion (%Yield): >99% (97.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[22] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.27-7.19 (m, 2H), 7.16-7.03 (m, 7H), 3.95 (s, 2H), 2.21 (s, 3H). GCMS: 182.2 ([M]$^+$, calc'd. 182.11).

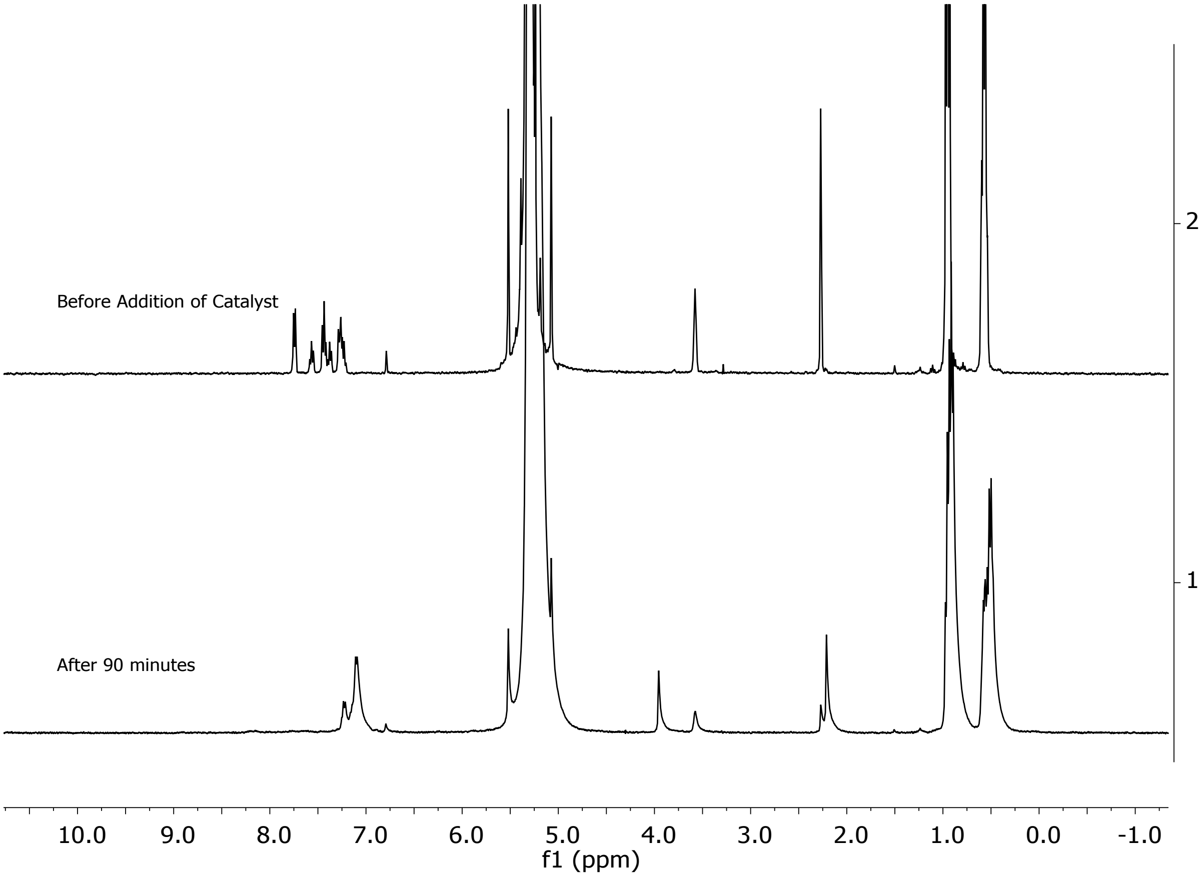
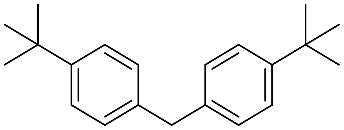


Figure S75. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 2-methyllbenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



4,4’-di-tert-butyldiphenylmethane (Entry 38): %Conversion (%Yield): 15.6% (15.5%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[23] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.28 (d, J = 8.2Hz, 4H), 7.10 (d, J = 8.2Hz, 4H), 3.86 (s, 2H), 1.26 (s, 18H). GCMS: 280.3 ($[M]^+$, calc’d. 280.22).

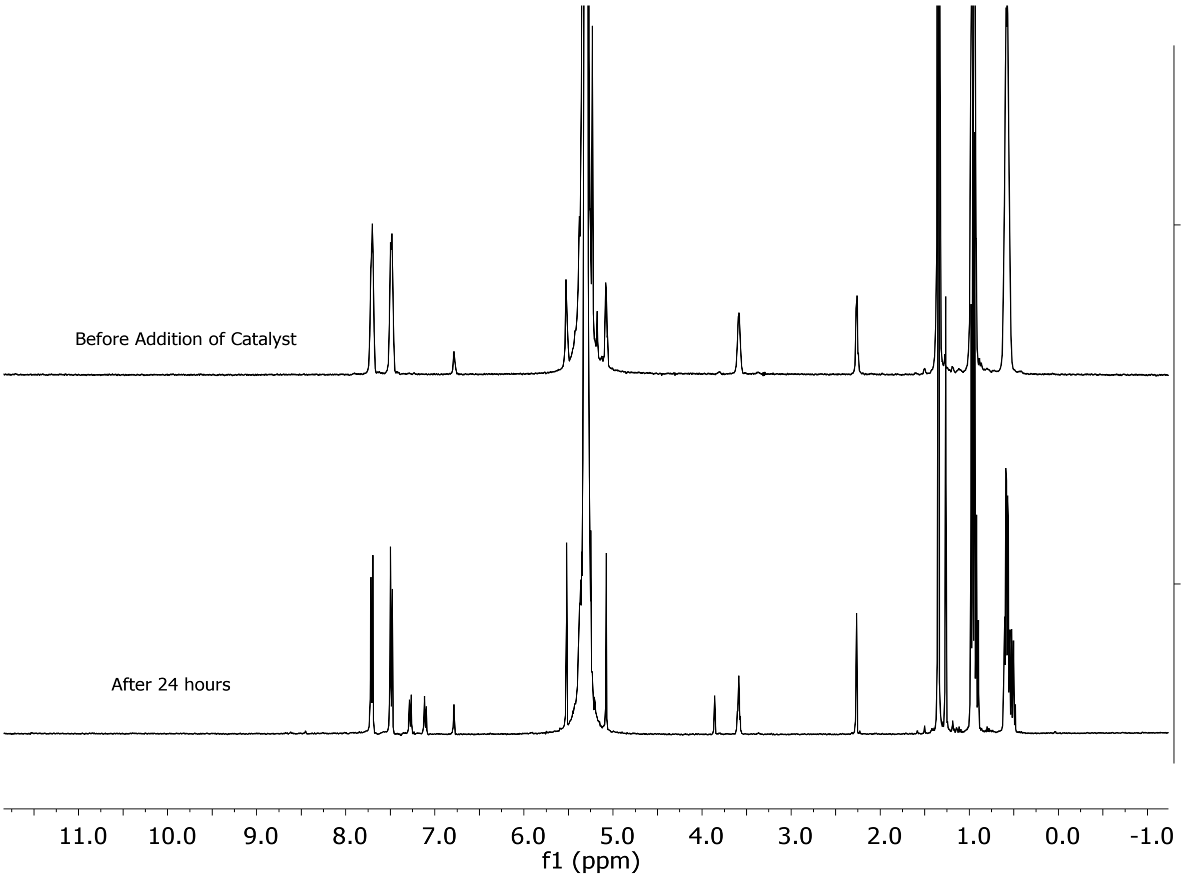
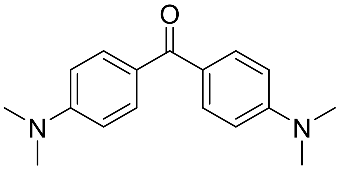


Figure S76. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4,4’-di(tert-butyl)benzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



4,4’-bis(dimethylamino)benzophenone (Entry 39): %Conversion: <1% over 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$.

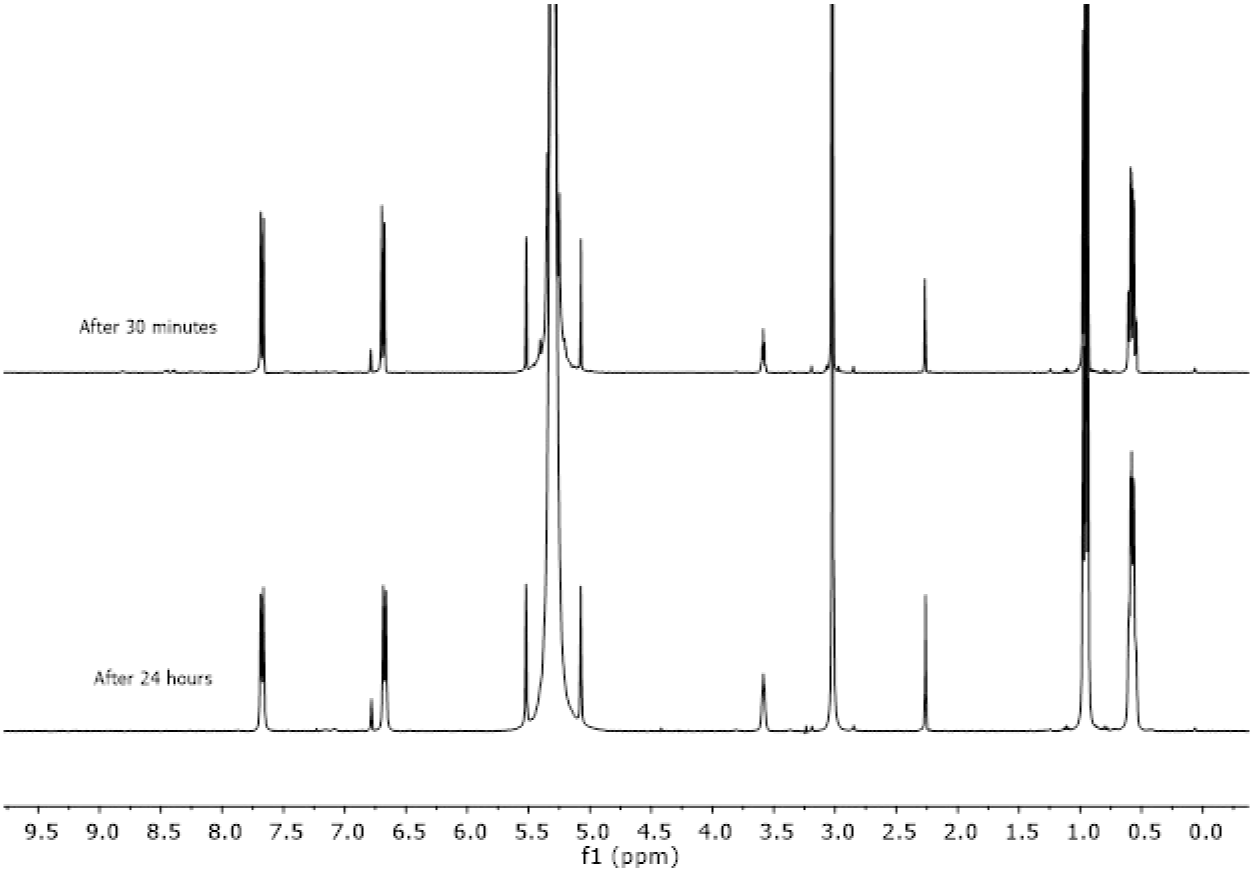
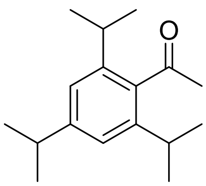


Figure S77. ^{1}H NMR (298K, 400 MHz) spectra for the attempted catalytic deoxygenation of tris(2’,4’,6’-triisopropyl)acetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Tris(2’,4’,6’-triisopropyl)acetophenone (Entry 40): %Conversion: <1% over 24 hours as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$.

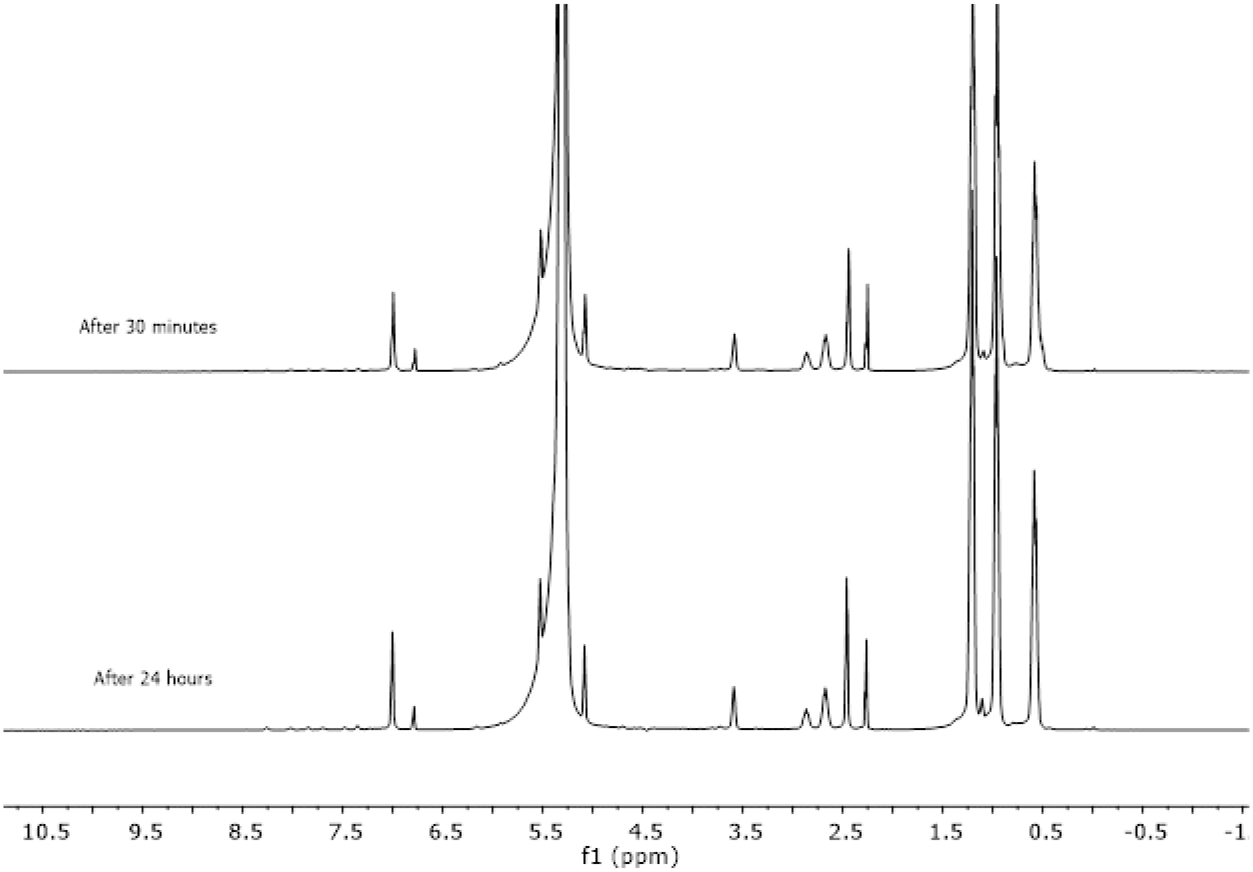
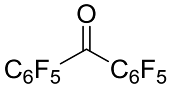


Figure S78. ^{1}H NMR (298K, 400 MHz) spectra for the attempted catalytic deoxygenation of tris(2’,4’,6’-triisopropyl)acetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Decafluorobenzophenone (Entry 41): %Conversion: <1% over 24 hours as determined by ^{1}H NMR and ^{19}F NMR spectroscopy using an external standard of mesitylene and hexafluorobenzene in $CDCl_3$.

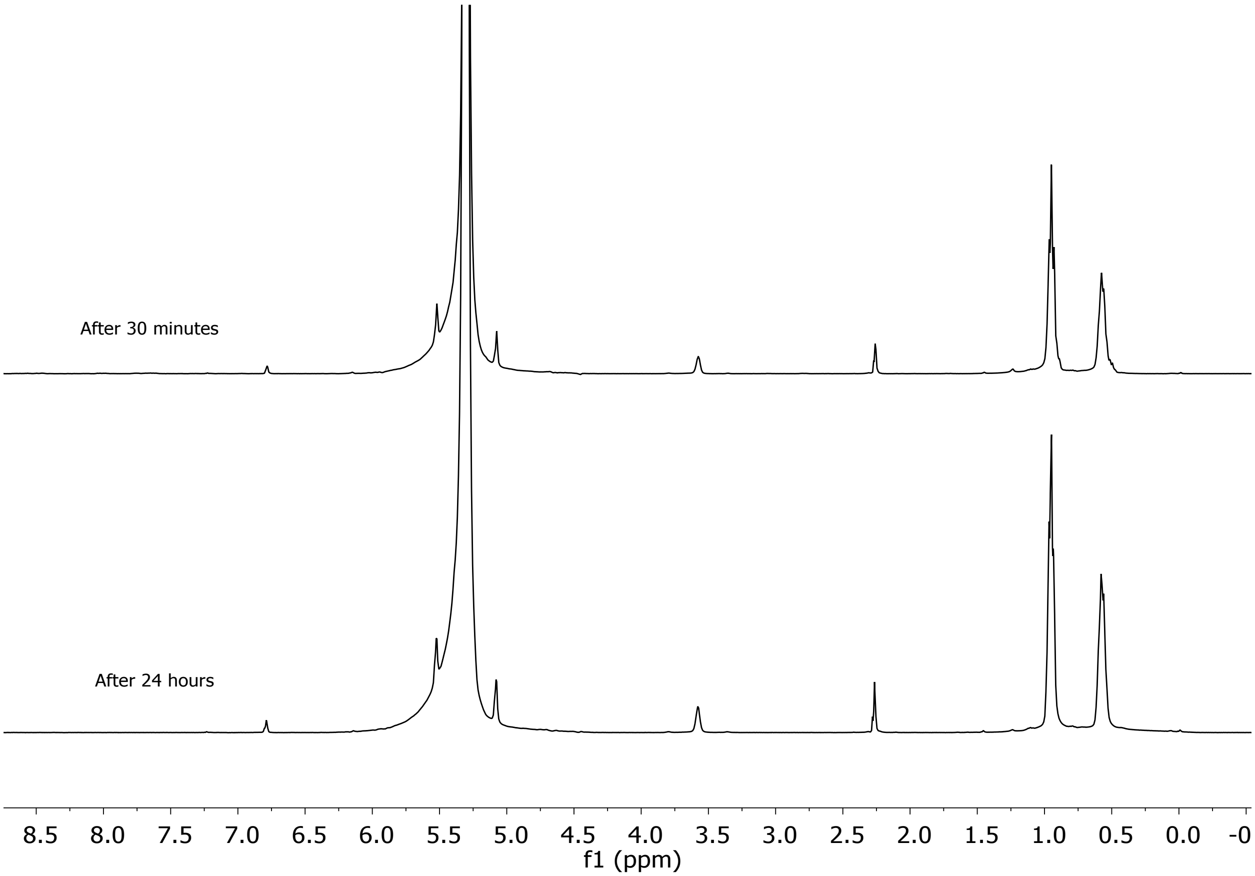


Figure S79. ^{1}H NMR (298K, 400 MHz) spectra for the attempted catalytic deoxygenation of decafluorobenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

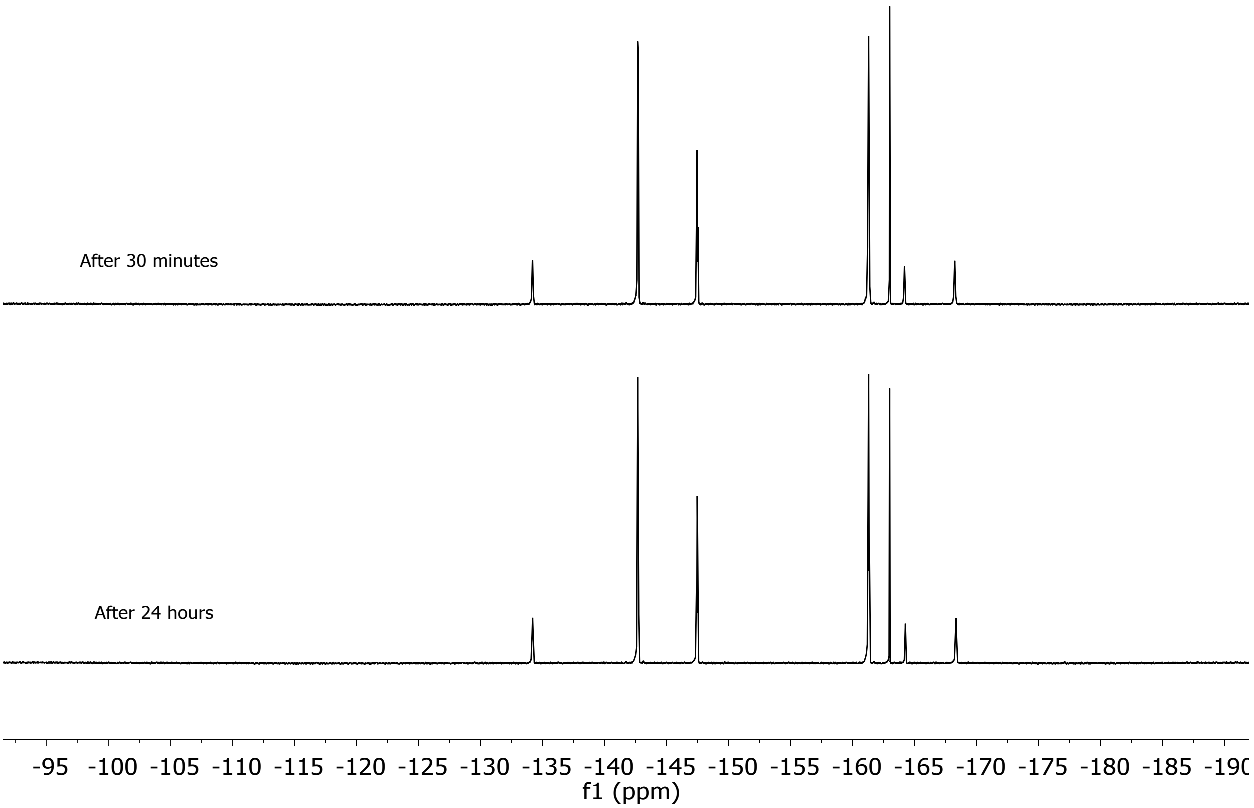
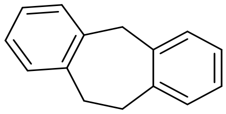


Figure S80. ^{9}F NMR (298K, 377 MHz) spectra for the attempted catalytic deoxygenation of decafluorobenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the hexafluorobenzene external standard signal at -163.0 ppm



Dibenzosuberane (Entry 42): %Conversion (%Yield): >99% (99.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[24] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.17-7.13 (m, 2H), 7.11-7.03 (m, 6H), 4.09 (s, 2H), 3.14 (s, 4H). GCMS: 194.2 ($[M]^+$, calc'd. 194.11).

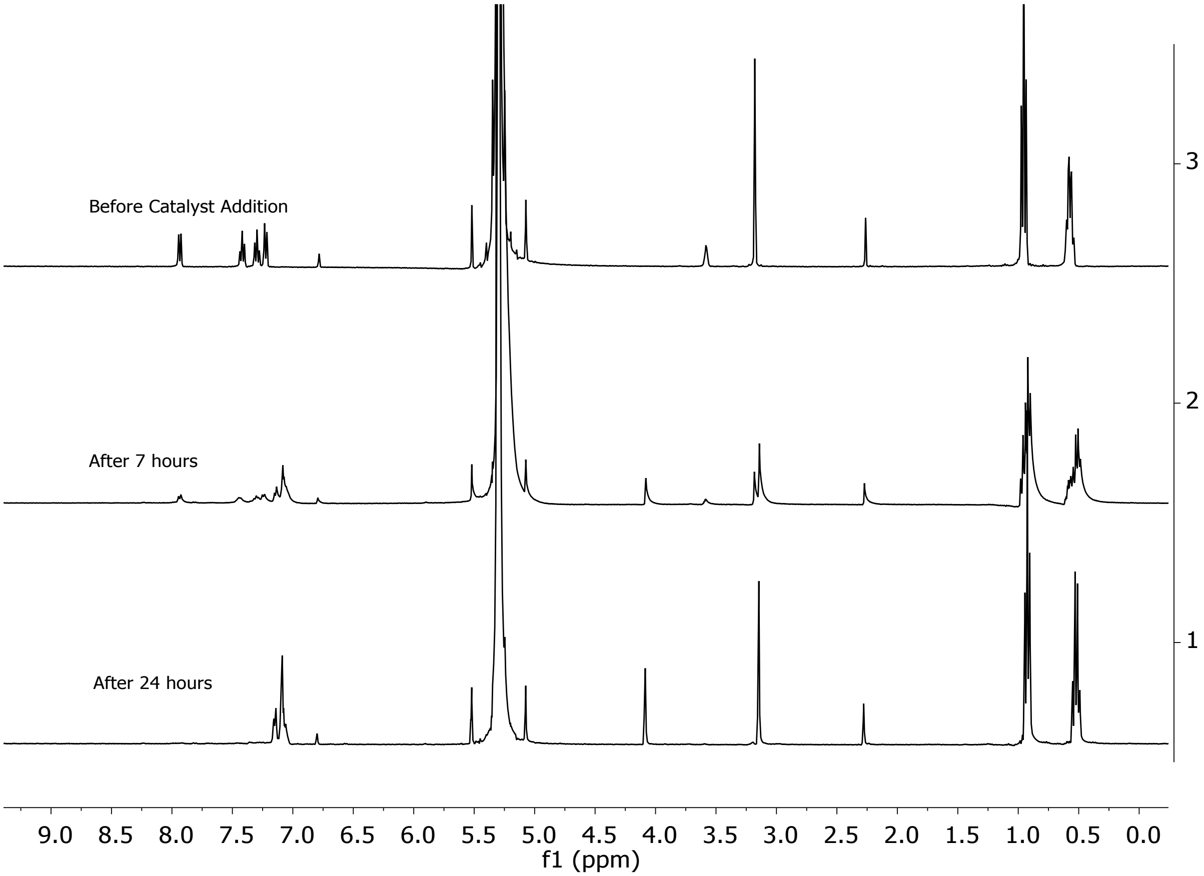
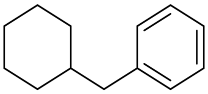


Figure S81. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of dibenzosuberone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



(Cyclohexylmethyl)benzene (Entry 43): %Conversion (%Yield): >99% (97.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[18] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.22 (t, *J* = 7.4Hz, 2H), 7.16-7.09 (m, 3H), 2.45 (d, *J* = 7.0Hz, 2H), 1.70 – 1.57 (m, 5H), 1.53-1.43 (m, 1H), 1.27 -1.11 (m, 3H), 1.01-0.86 (1H overlapping with hexaethyldisiloxane signal). GCMS: 174.2 ([M]$^+$, calc'd. 174.11).

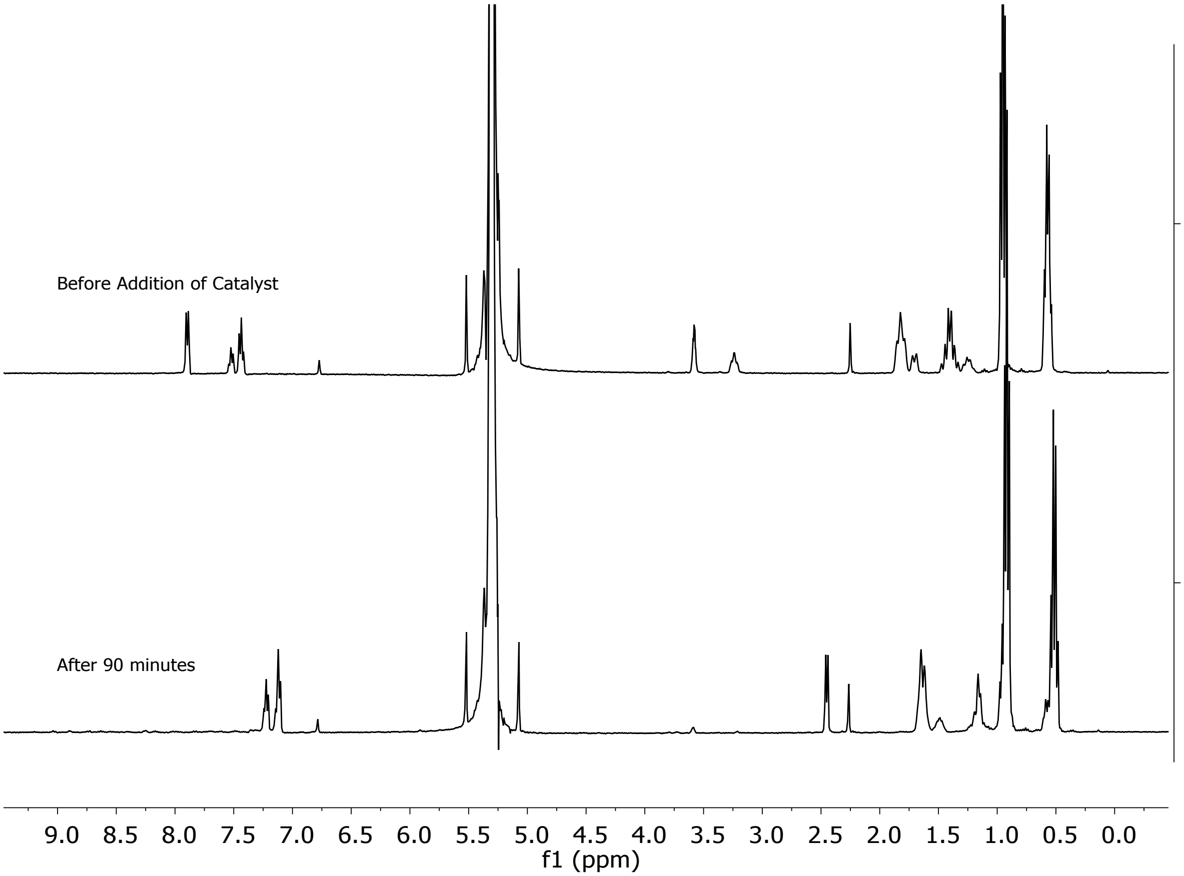
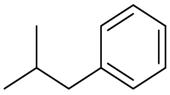


Figure S82. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of phenyl(cyclohexyl)ketone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Isobutylbenzene (Entry 44): %Conversion (%Yield): >99% (97.6%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[25] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): 7.28-7.20 (m, 2H), 7.17-7.10 (m, 3H), 2.47 (d, *J* = 6.7 Hz, 2H), δ (ppm) 1.89-1.79 (m, 1H), 0.90 (d, 6H, overlapping with hexaethyldisiloxane signal).

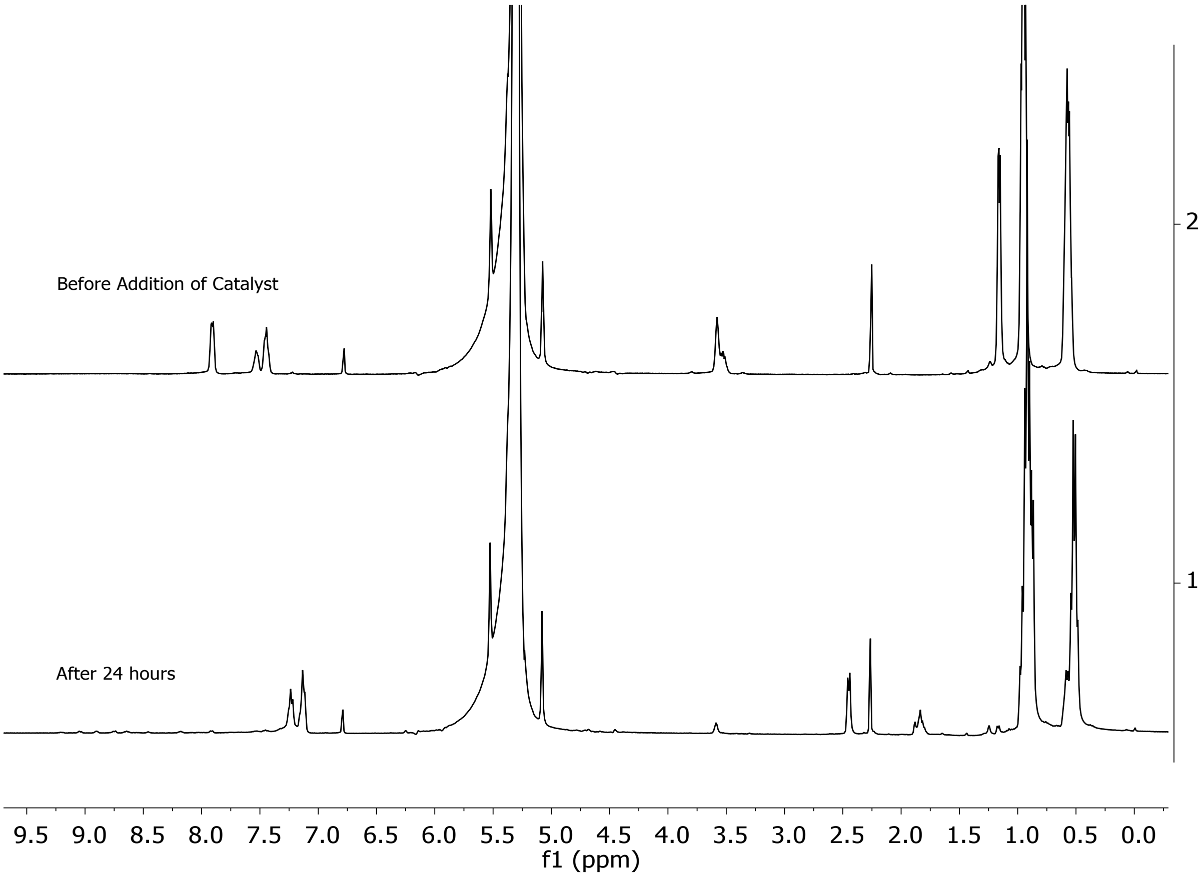
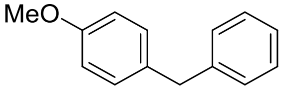


Figure S83. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of phenyl(isopropyl)ketone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



4-methoxydiphenylmethane (Entry 45): %Conversion (%Yield): 59.7% (58.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[19] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.28-7.22 (m, 2H), 7.19-7.13 (m, 3H), 7.09 (d, 8.4 Hz, 2H),6.84-6.77 (m, 2H), 3.90 (s, 2H), 3.72 (s, 3H).

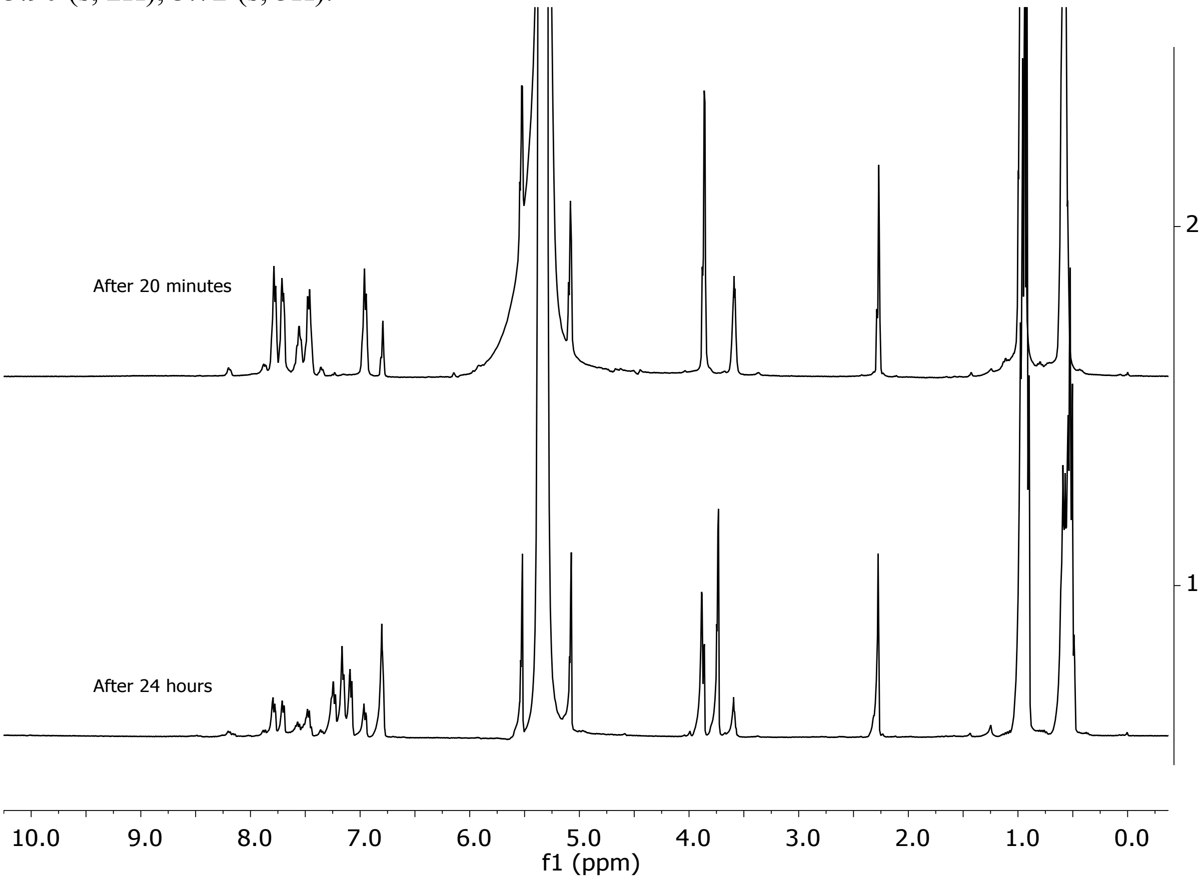
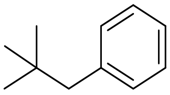


Figure S84. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4-methoxybenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Neopentylbenzene (Entry 46): %Conversion (%Yield): >99% (91.0%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[26] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.29-7.19 (m, 2H), 7.16-7.06 (m, 3H), 2.46 (s, 2H), 0.95 (s, 9H, overlaps with hexaethyldisiloxane signal).

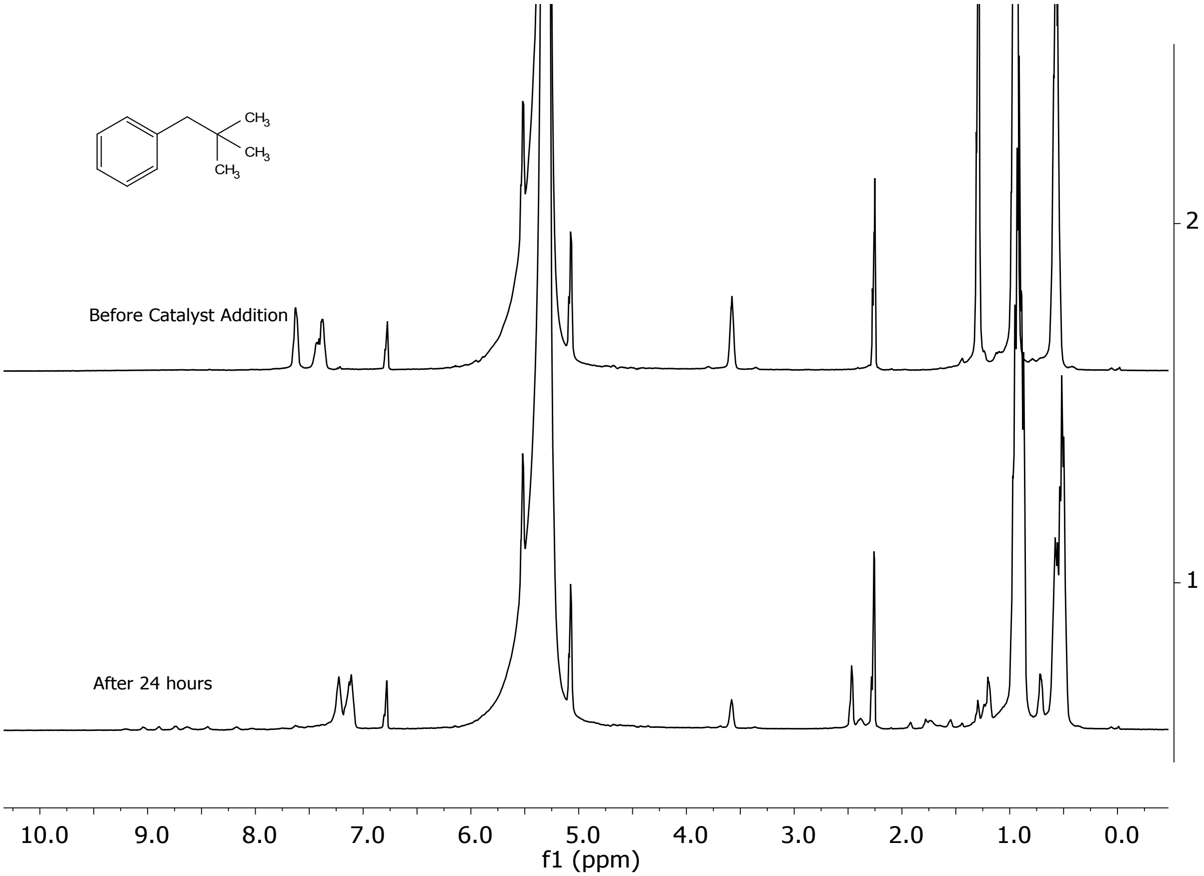
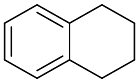


Figure S85. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 2,2,2-trimethylacetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



1,2,3,4-tetrahydronaphthalene (Entry 47): %Conversion (%Yield): >99% (98.5%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[27] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.03-7.00 (m, 4H), 2.76 – 2.71 (m, 4H), 1.79 – 1.73 (m, 4H). GCMS: 132.1 ($[M]^+$, calc'd. 132.2).

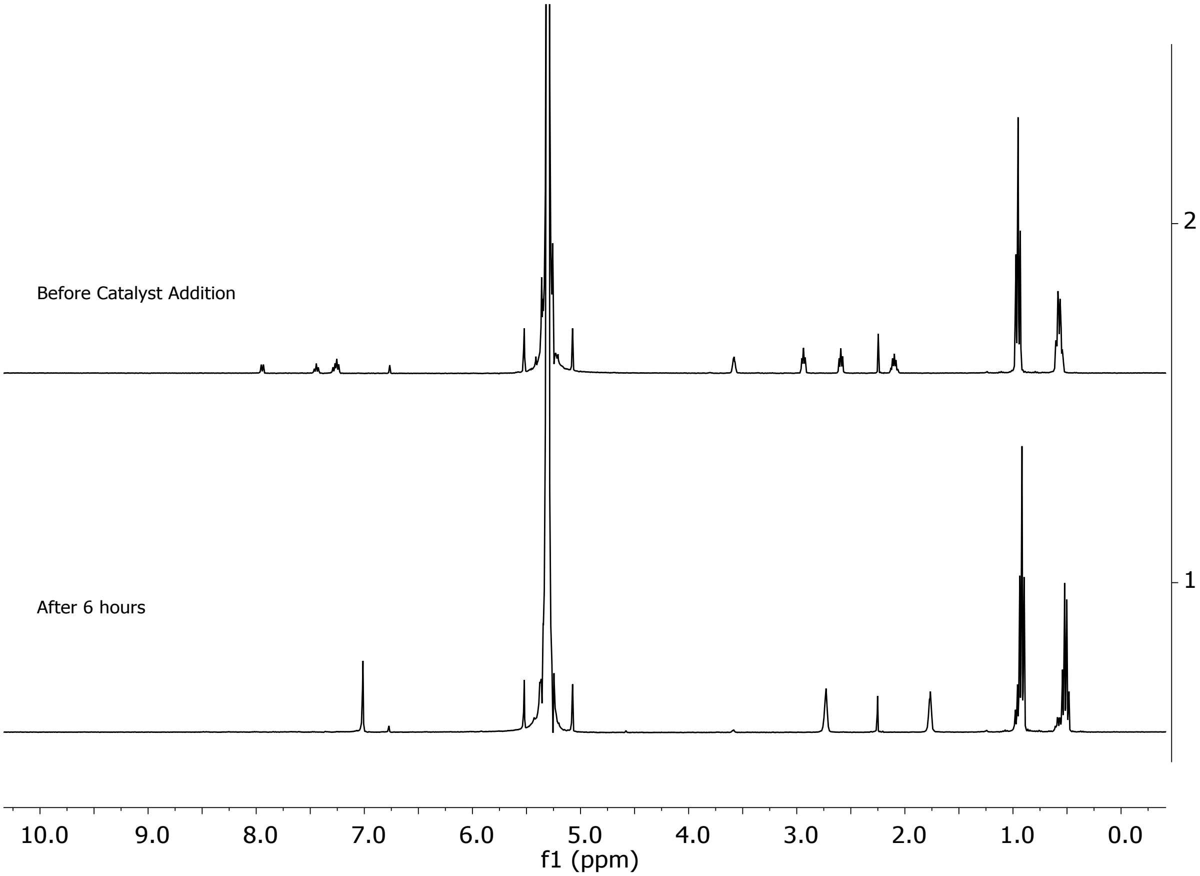
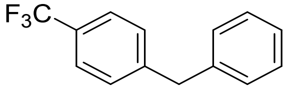


Figure S86. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 1-tetralone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



4-(trifluoromethyl)diphenylmethane (Entry 48): %Conversion (%Yield): >99% (98%) as determined by ^{19}F NMR spectroscopy using an external standard of hexafluorobenzene and mesitylene in $CDCl_3$. Some hydrodefluorination (2%) is observed by the formation of fluorotriethylsilane signals at -177 ppm in the ^{19}F NMR spectrum. Characterization corresponds with reported literature values.[28] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.52 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.6 Hz, 1H), 7.22 – 7.15 (m, 4 H), 4.02 (s, 2H). ^{19}F NMR (377 MHz, 298K, CH_2Cl_2): δ (ppm) -64.5 (s, 3F). GCMS: 236.2 ([M]$^+$, calc'd. 236.08).

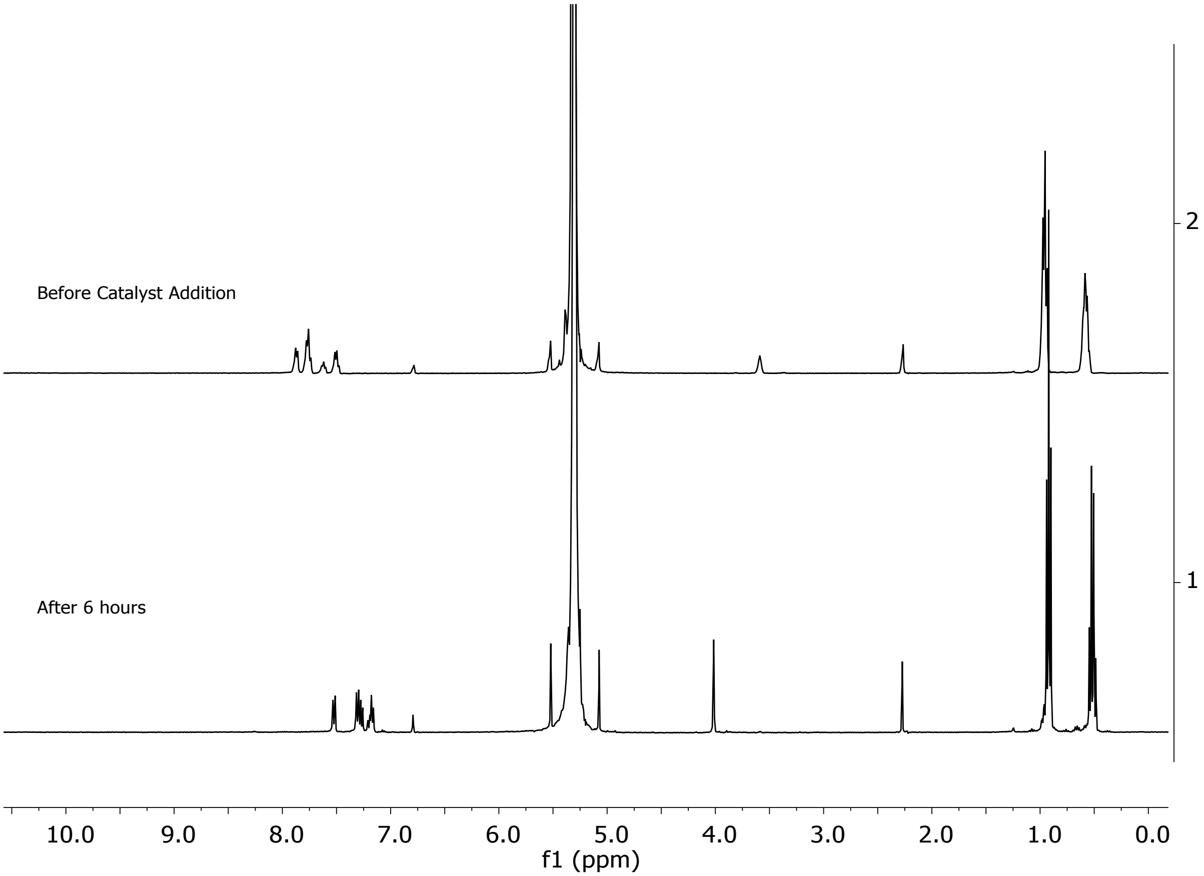


Figure S87. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 4-trifluoromethylbenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

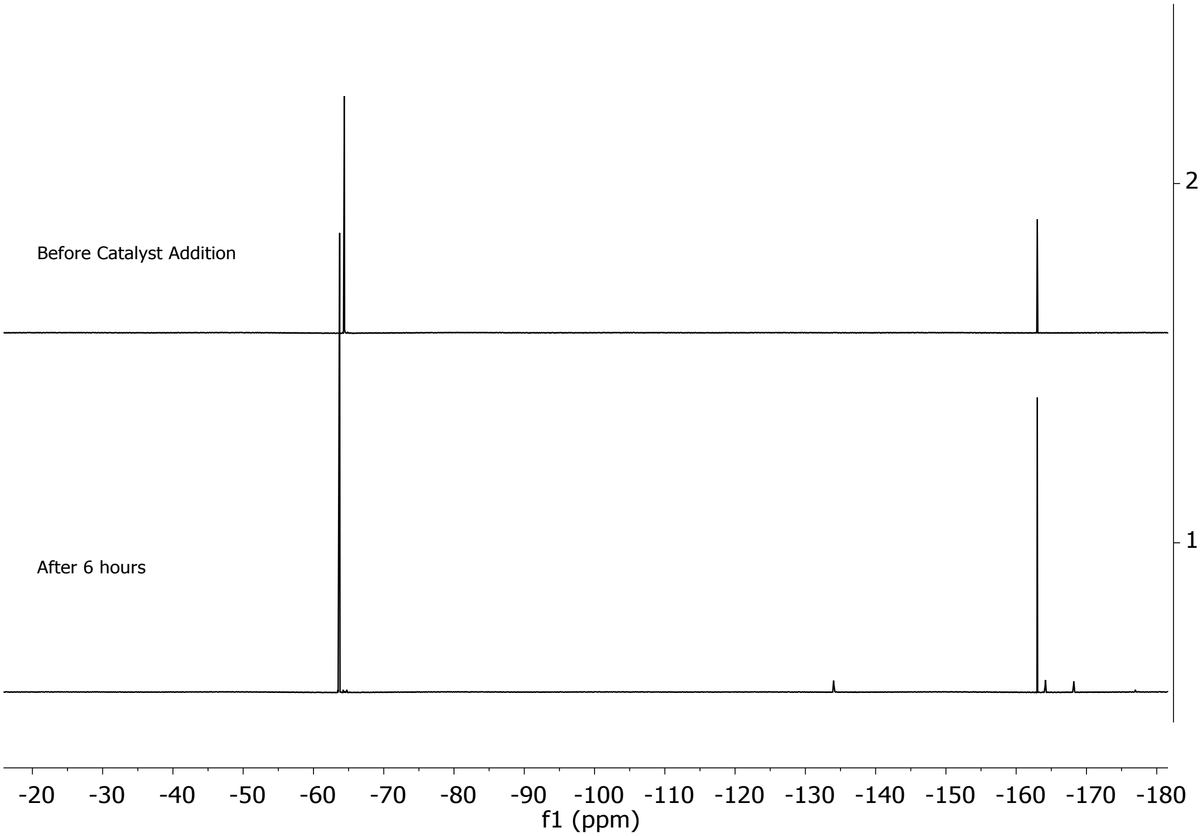
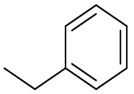


Figure S88. ^{19}F NMR (298K, 377 MHz) spectra for the catalytic deoxygenation of 4-trifluoromethylbenzophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the hexafluorobenzene external standard signal at -163.0 ppm.



Ethylbenzene (Entry 49): %Conversion (%Yield): >99% (96.4%) as determined by ^1H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[29] ^1H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.24 (t, 7.8 Hz, 2H), 7.20 – 7.11 (m, 3H), 2.62 (q, 7.6 Hz, 2H), 1.21 (t, 7.6 Hz, 3H).

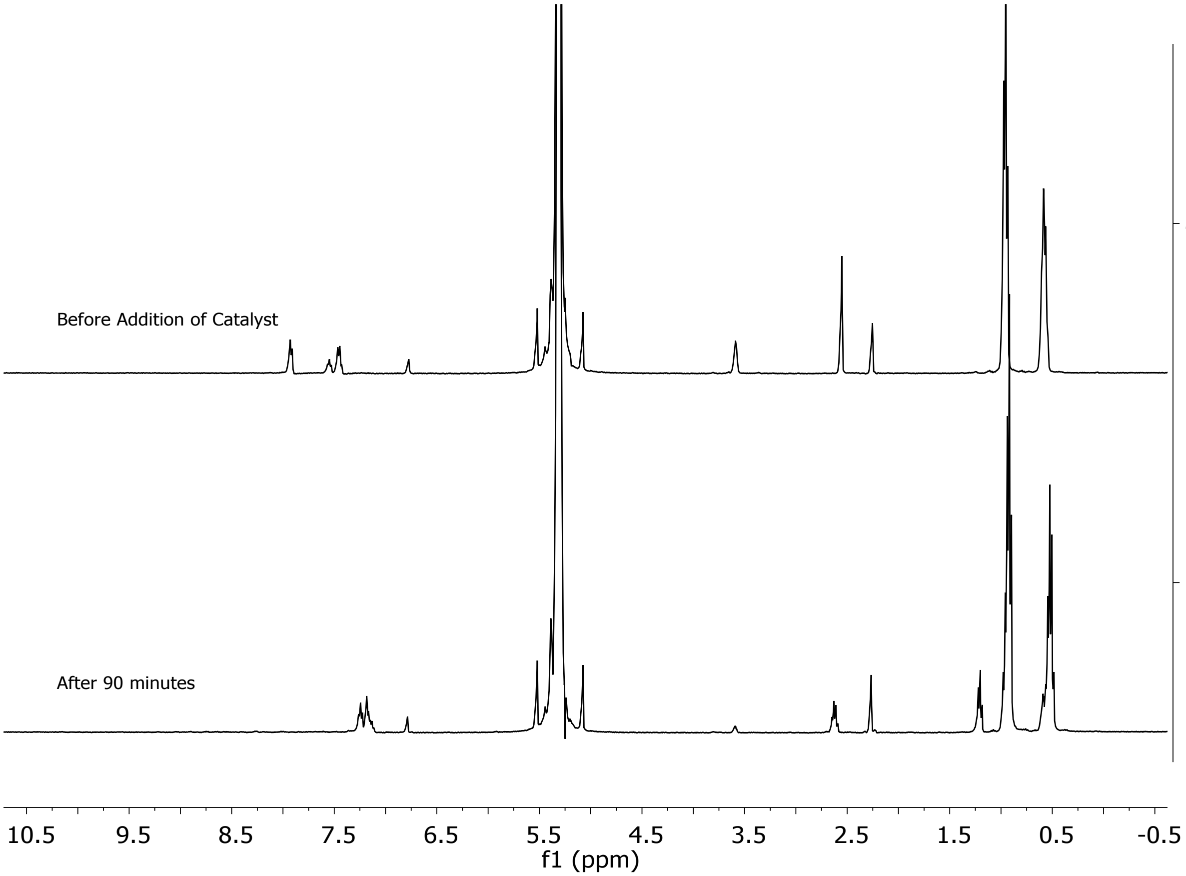
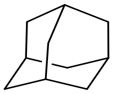


Figure S89. ^1H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of acetophenone in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Adamantane (Entry 50): %Conversion (%Yield): >99% (94%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in CDCl$_3$. Characterization corresponds with reported literature values.[30] ^{1}H NMR (400 MHz, 298K, *o*-CH$_4$Cl$_2$): δ (ppm) 1.81 - 1.74 (br s, 4H), 1.70 – 1.60 (br s , 12H).

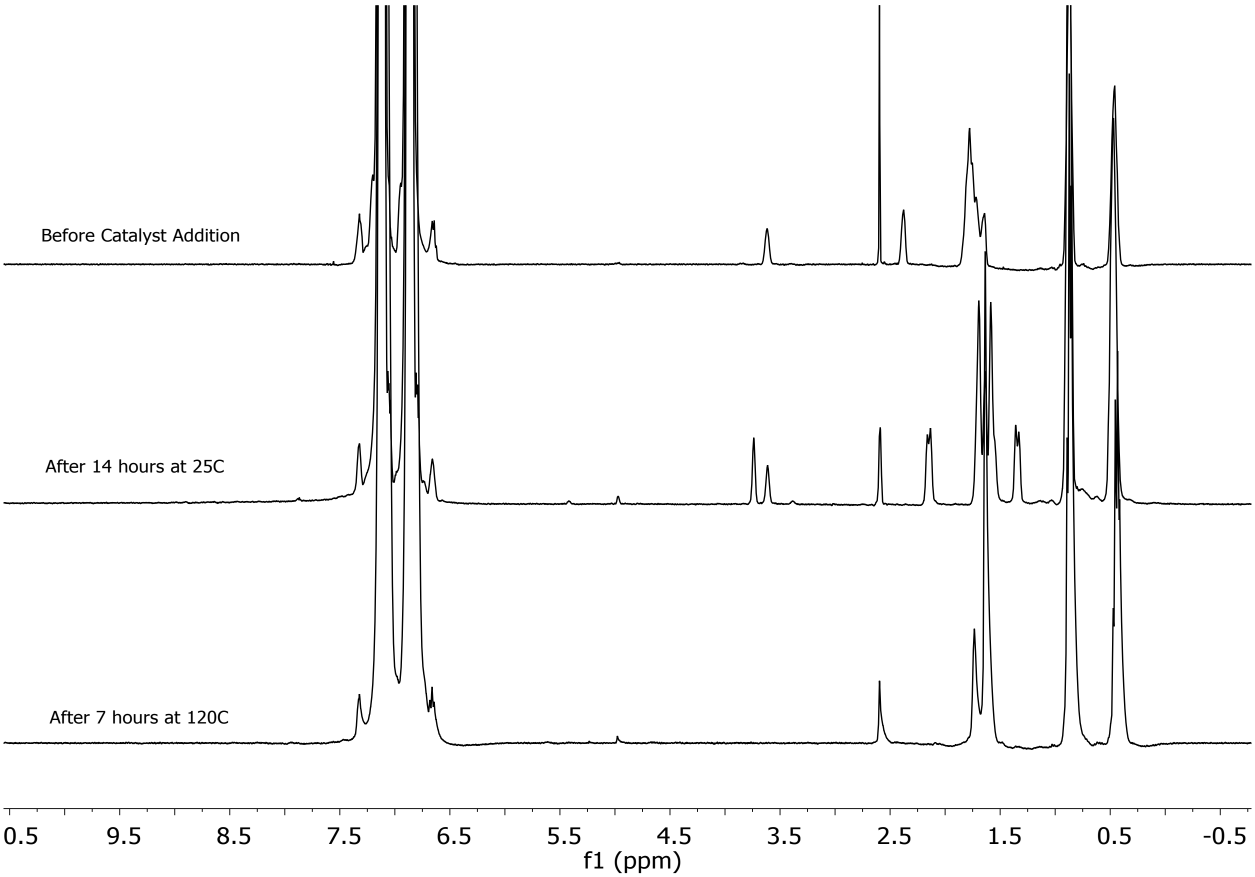
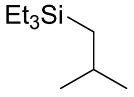


Figure S90. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic deoxygenation of 2-adamantanone in dichloromethane with triethylsilane. The middle spectrum shows the formation of the silyl ether at room temperature, whereas the bottom spectrum shows the formation of adamantane. The NMR spectra are referenced to the *o*-CH$_4$Cl$_2$ resonance at 7.12 ppm.

5.4. Catalytic Hydrosilylation of Olefins



Triethyl(isobutyl)silane (Entry 51): %Conversion: >99% after 30 minutes as determined by ^{1}H NMR spectroscopy, where conversion was monitored by the consumption of isobutene signals. Characterization corresponds with reported literature values.[31] ^{1}H NMR (500 MHz, 298K, CDCl$_3$): δ (ppm) 1.77 (nonet, *J* = 6.6 Hz, 1H, -C*H*), 0.94 (d, *J* = 6.5 Hz, 6H, -C*H$_3$*), 0.93 (t, *J* = 7.8 Hz, 9H, -Si(CH$_2$C*H$_3$*)$_3$), 0.53 (q, *J* = 7.8Hz, 6H, -Si(C*H$_2$*CH$_3$)$_3$), 0.52 (d, *J* = 6.6 Hz, 2H, -CHC*H$_2$*Si). ^{13}C{^{1}H} NMR (126 MHz, 298K, CDCl$_3$): δ (ppm) 26.9, 25.1, 22.3, 7.9, 4.5. GCMS: 143.2 ([M-C$_2$H$_5$]$^+$, calc'd. 143.13).

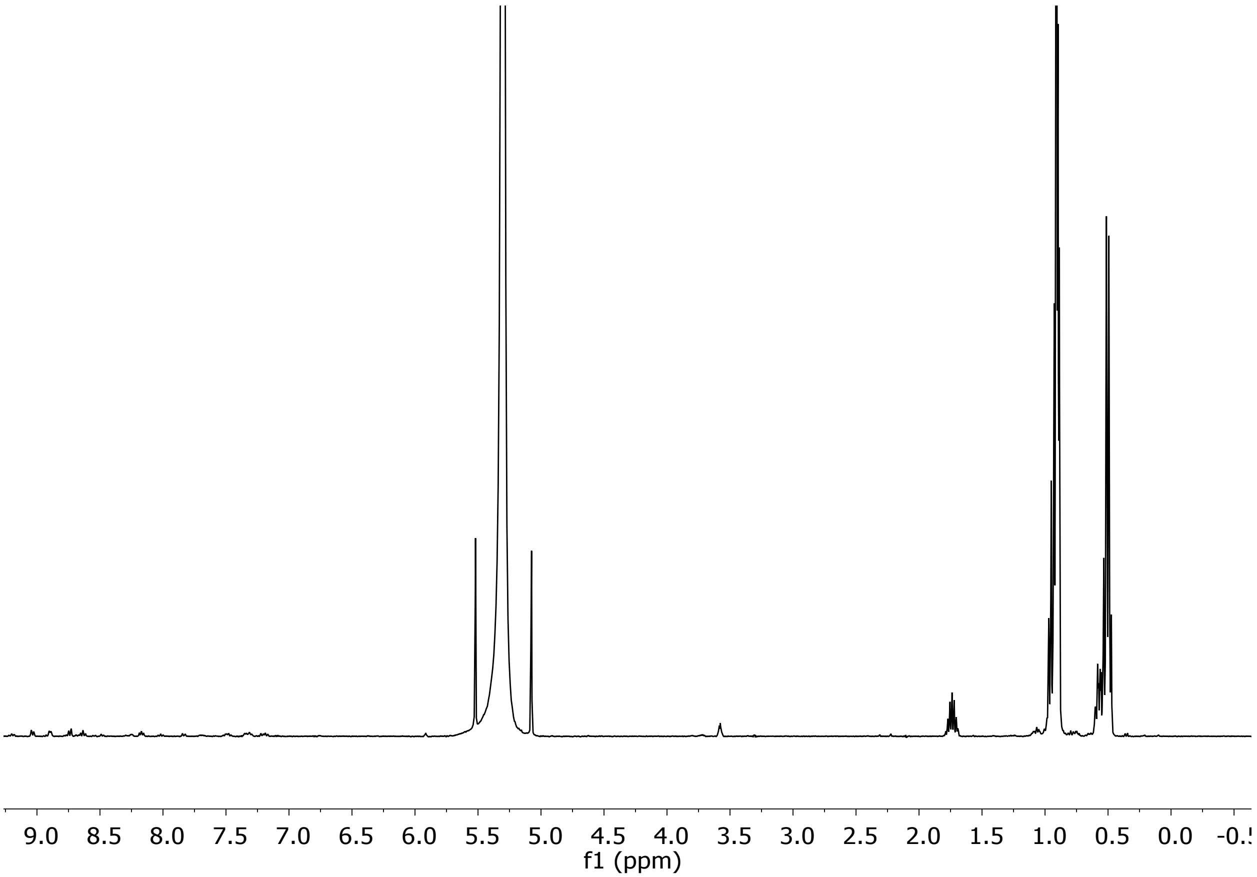


Figure S91. ^{1}H NMR (298K, 400 MHz) spectrum for the catalytic hydrosilylation of isobutene in dichloromethane with triethylsilane after 30 minutes. The NMR spectrum is referenced to the CH$_2$Cl$_2$ resonance at 5.30 ppm.

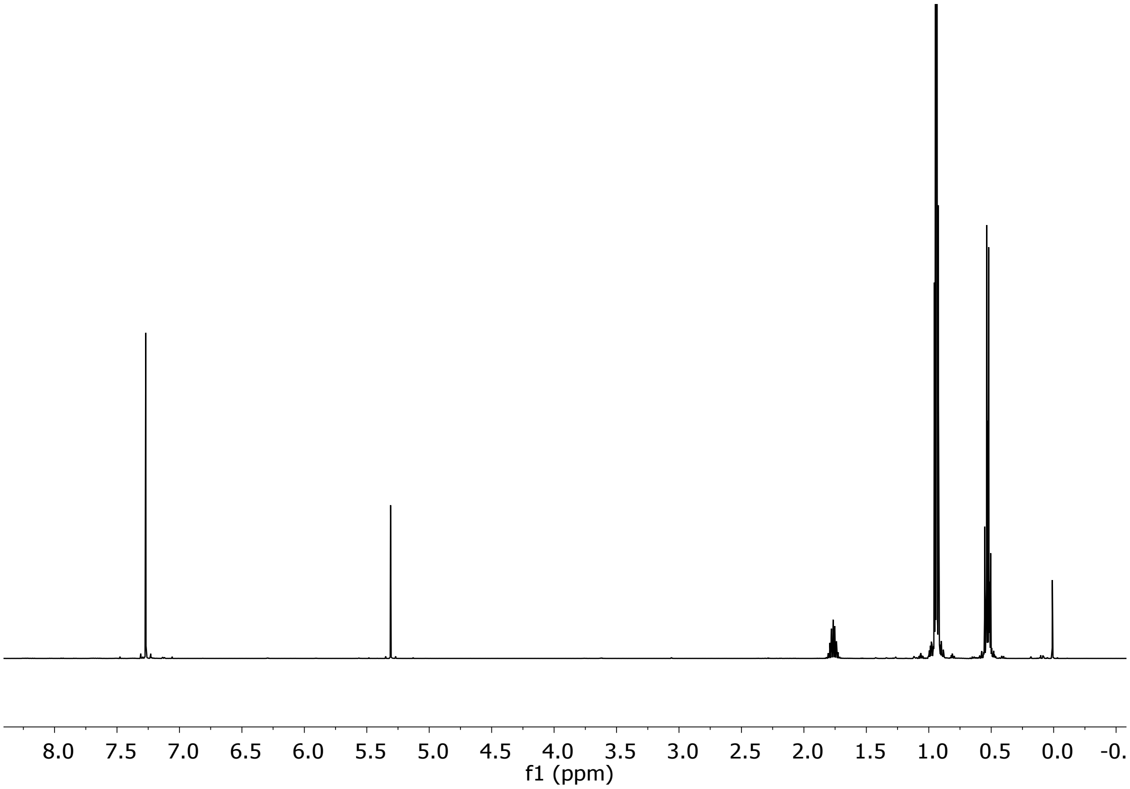


Figure S92. ^{1}H NMR (500 MHz, 298K, CDCl$_3$) spectrum for triethyl(isobutyl)silane.

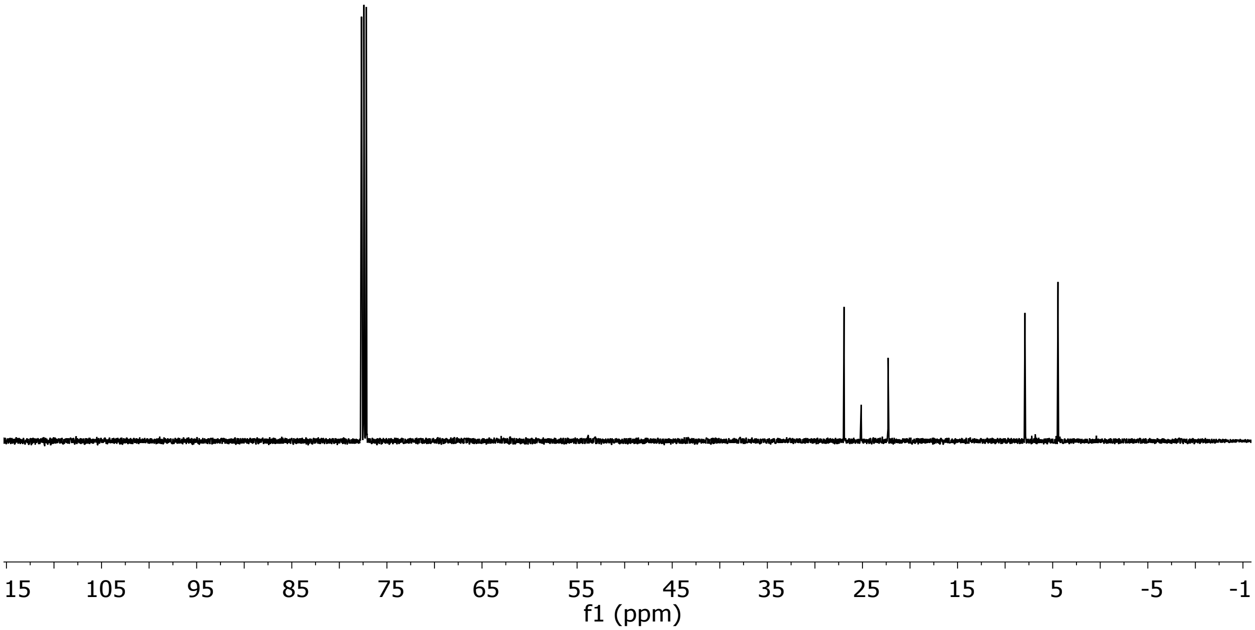
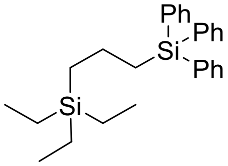


Figure S93. $^{13}C\{^{1}H\}$ NMR (126 MHz, 298K, $CDCl_3$) spectrum for triethyl(isobutyl)silane.



Triethyl(3-(triphenylsilyl)propyl)silane (Entry 52): %Conversion (%Yield): >99% (96%) as determined by ^1H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Product was not isolated but was detected by GCMS. GCMS: 415.2 ($[M-H]^+$, calc'd. 415.23).

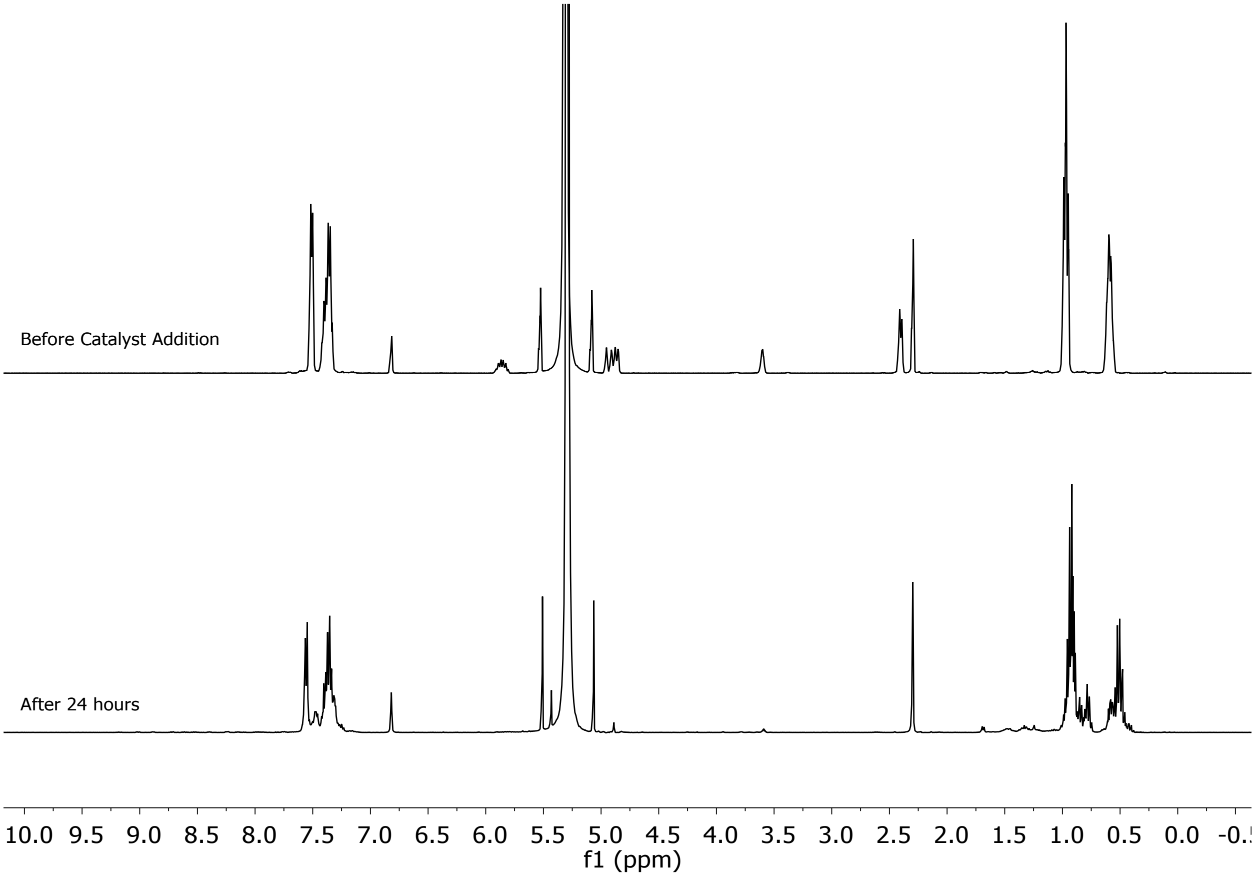


Figure S94. ^1H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of allyltriphenylsilane in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

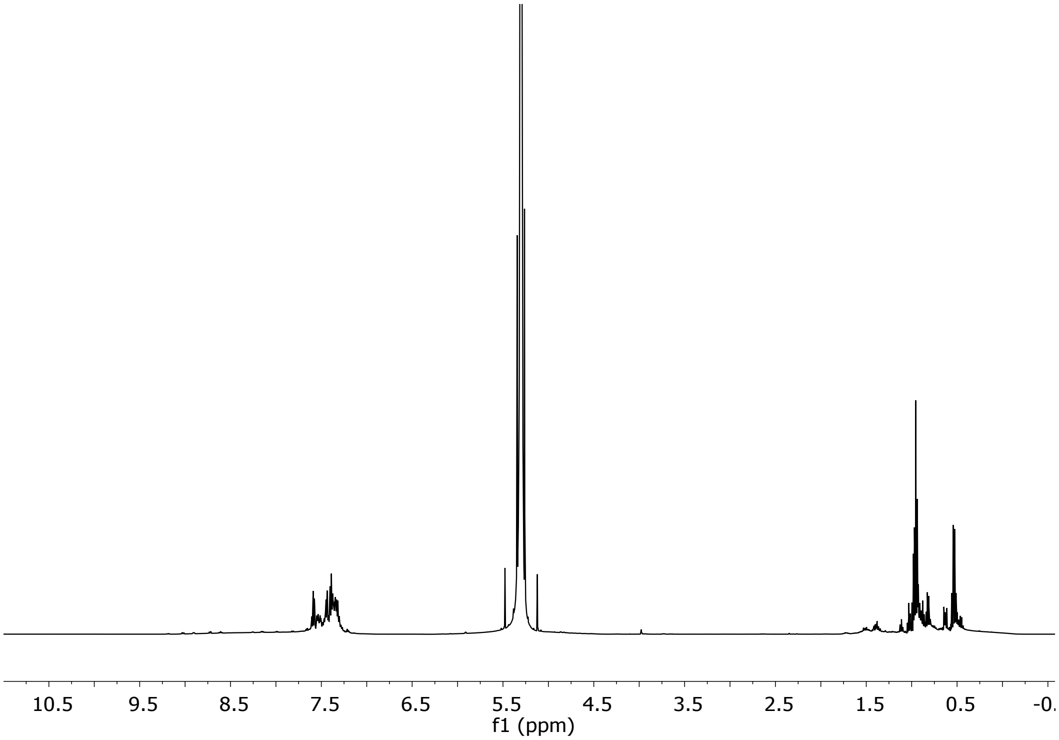


Figure S95. ^{1}H NMR (298K, 500 MHz) spectra for the reaction mixture of the catalytic hydrosilylation of allyltriphenylsilane in dichloromethane with triethylsilane after the catalysis. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

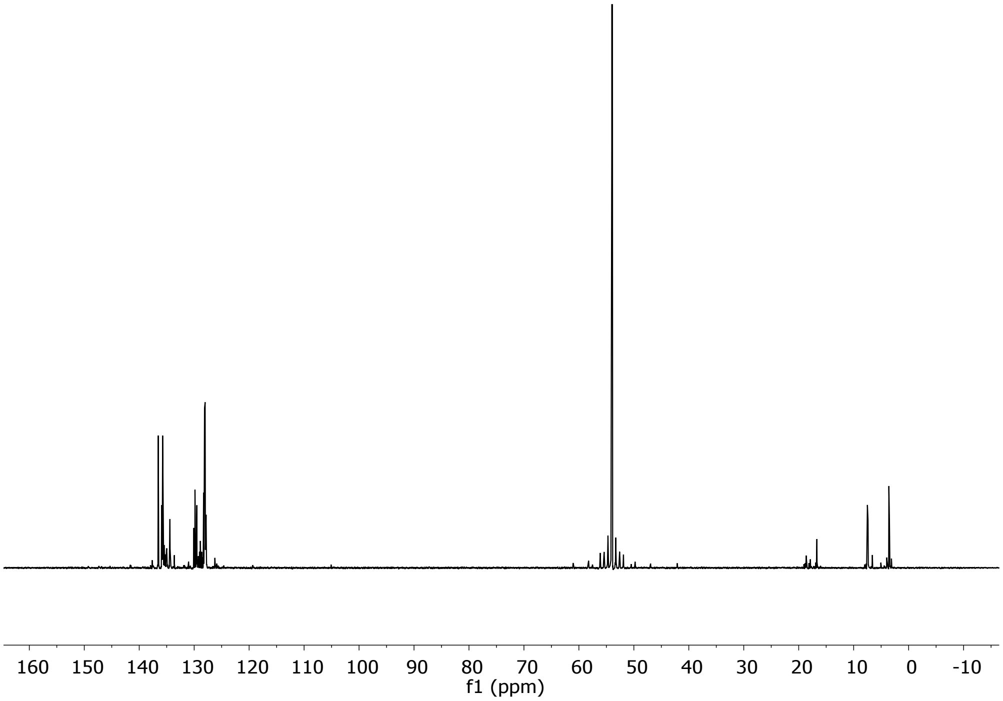
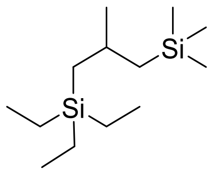


Figure S96. $^{13}C\{^1H\}$ NMR (298K, 126 MHz) spectra for the reaction mixture of the catalytic hydrosilylation of allyltriphenylsilane in dichloromethane with triethylsilane after the catalysis. The NMR spectra are referenced to the CH_2Cl_2 resonance at 54 ppm.



Triethyl(2-methyl-3-(trimethylsilyl)propyl)silane (Entry 53): %Conversion (%Yield): >99% (84%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Product was not isolated, but was detected by GCMS. GCMS: 243.2 ([M-H]$^+$, calc'd. 243.20).

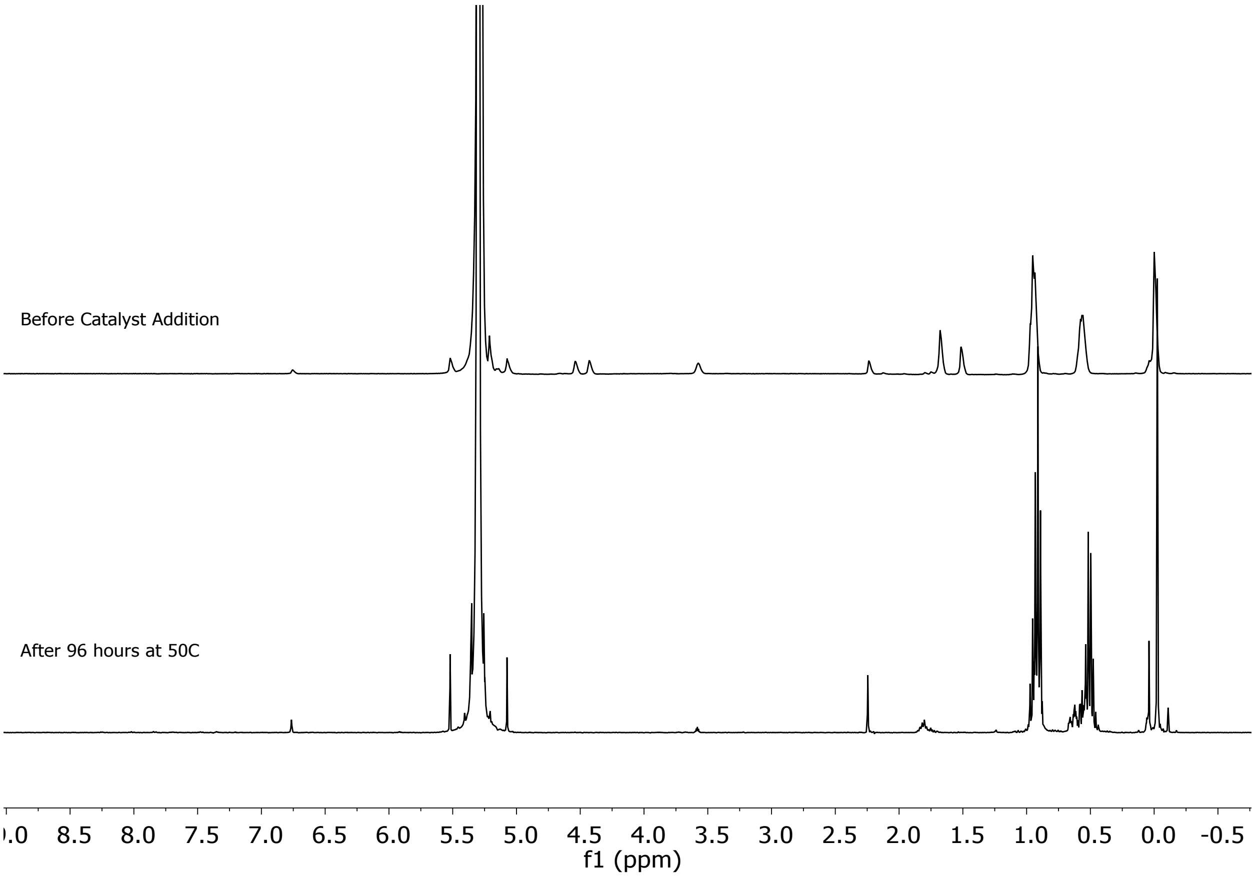


Figure S97. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of methallyltrimethylsilane in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

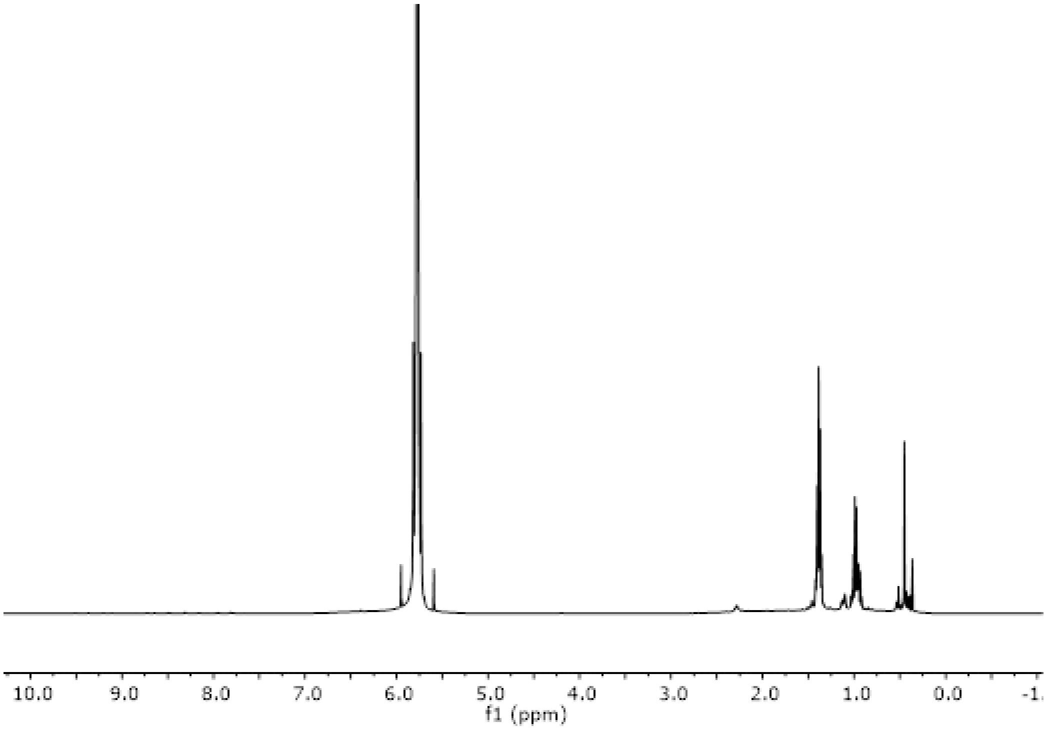


Figure S98. ^{1}H NMR (298K, 500 MHz) spectra for the reaction mixture of the catalytic hydrosilylation of allyltriphenylsilane in dichloromethane with triethylsilane after the catalysis. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

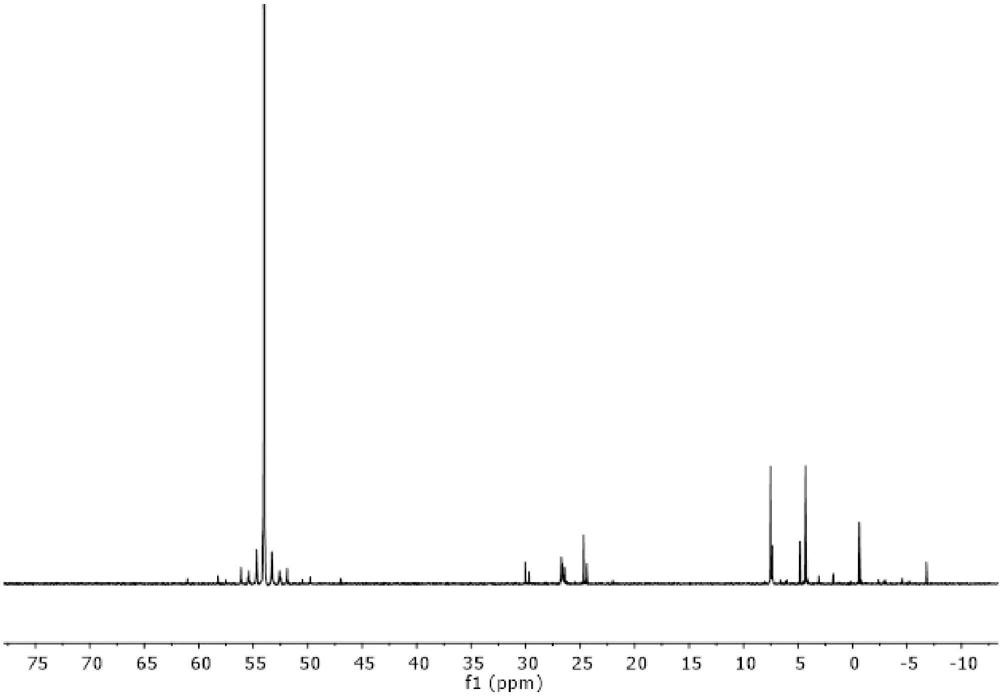
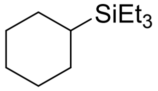


Figure S99. $^{13}C\{^1H\}$ NMR (298K, 126 MHz) spectra for the reaction mixture of the catalytic hydrosilylation of methallyltrimethylstyrene in dichloromethane with triethylsilane after the catalysis. The NMR spectra are referenced to the CH_2Cl_2 resonance at 54 ppm.



Triethyl(cyclohexyl)silane (Entry 54): %Conversion (%Yield): >99% (98.5%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[32] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 1.73 – 1.62 (m, 5H), 1.21 – 1.10 (m, 5H), 0.93 – 0.87 (m, 9H), 0.72 (t, *J* = 12.0 Hz, 1H), 0.52 – 0.46 (m, 6H).

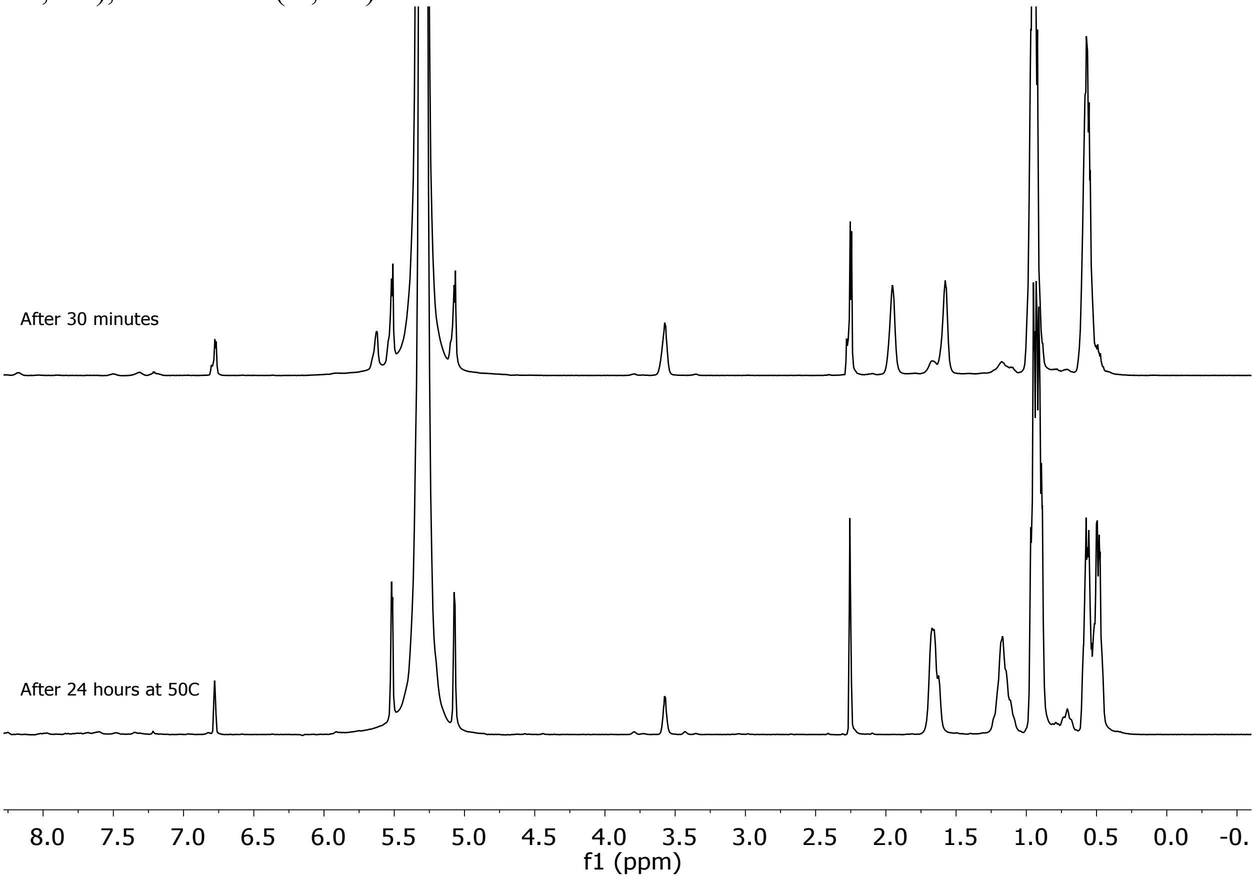
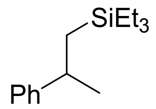


Figure S100. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of cyclohexene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(2-propylphenyl)silane (Entry 55): Product was isolated as a clear liquid with an isolated yield of 96% (225 mg, 1 mmol of olefin). Characterization corresponds with reported literature values.[31] ^{1}H NMR (400 MHz, 298K, CDCl$_3$): δ (ppm) 7.29 – 7.21 (m, 4H), 7.19 – 7.15 (m, 1H), 2.88 (sextet, *J* = 7.1 Hz, 1H), 1.28 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 7.4 Hz, 1H), 0.93 (d, *J* = 7.4 Hz, 1H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.48 – 0.36 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, 298K, CDCl$_3$): δ (ppm) 150.3, 128.4, 126.7, 125.9, 36.3,

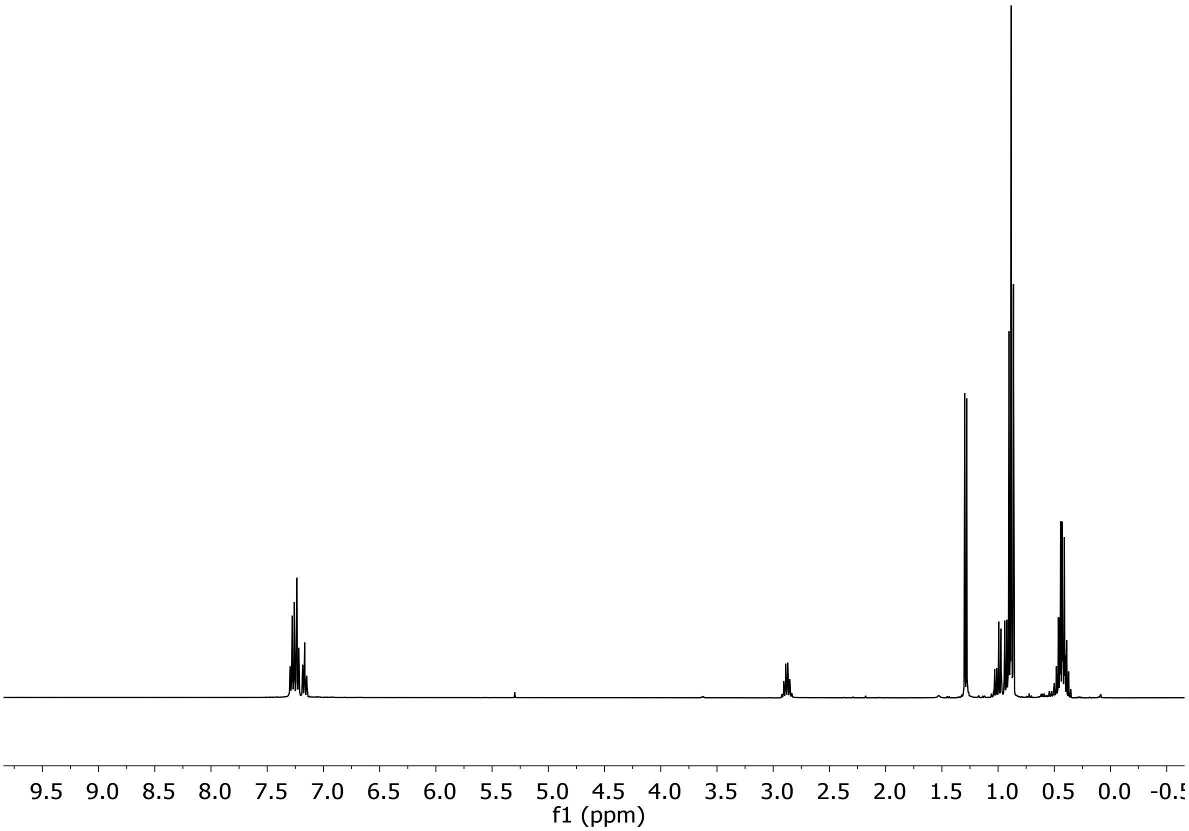


Figure S101. ^{1}H NMR spectrum (CDCl$_3$, 400 MHz, 298K) for triethyl(2-propylphenyl)silane.

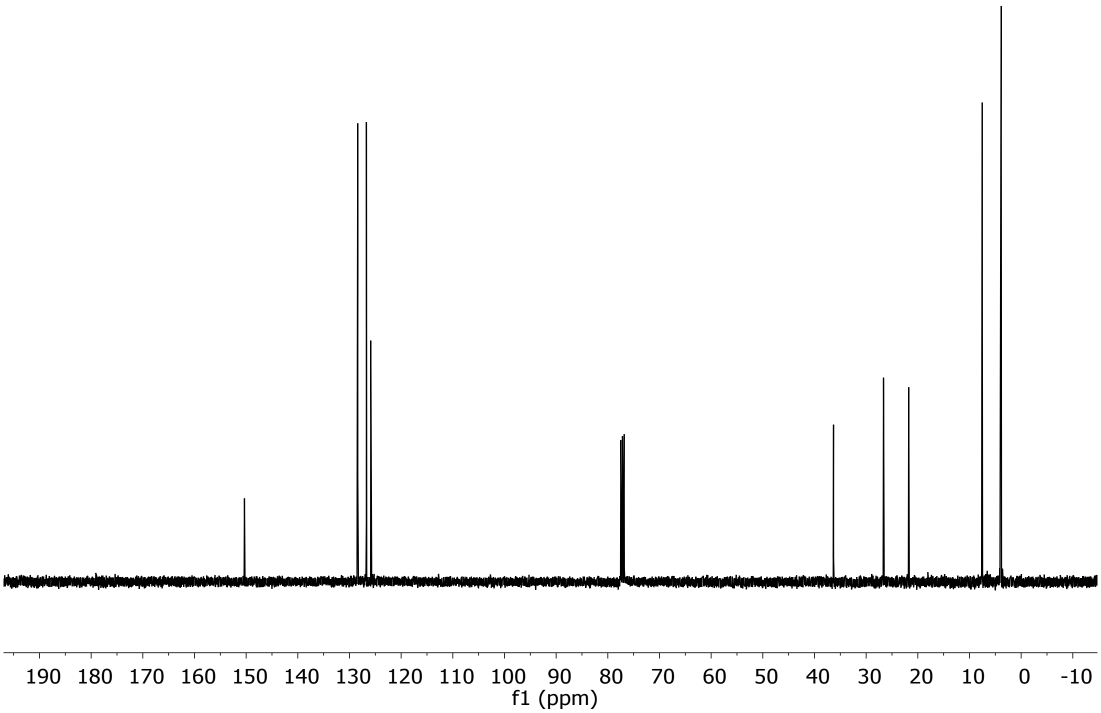
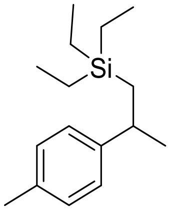


Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz, 298K) for triethyl(2-propylphenyl)silane.



Triethyl(2-(4-tolyl)propyl)silane (Entry 56): %Conversion (%Yield): >99% (98%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[31] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.11-7.04 (m, 4H), 2.83 (sextet, $J = 7.2$ Hz, 1H), 2.29 (s, 3H), 1.23 (d, $J = 7.0$ Hz, 3H), 0.98 (m, 1H), 0.90 (m, 1H), 0.87 (t, $J = 8.0$ Hz, 9H), 0.41 (m, 6H). GCMS: 219.16 ($[M-CH_2CH_3]^+$, calc'd. 219.2).

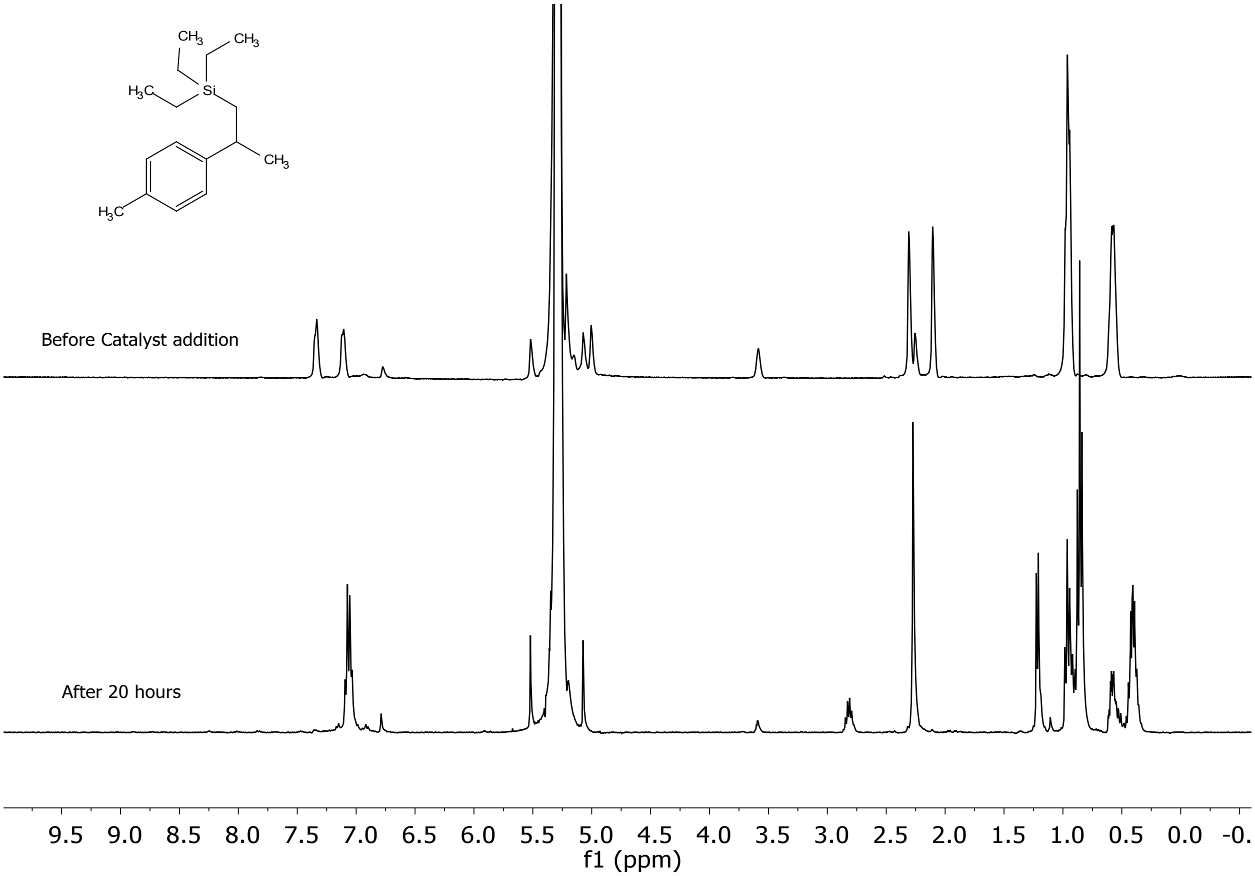
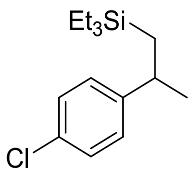


Figure S103. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4,α-dimethylstyrene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(2-(4-chlorophenyl)propyl)silane (Entry 57): %Conversion (%Yield): >99% (95%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$. Characterization corresponds with reported literature values.[31] ^{1}H NMR (400 MHz, 298K, CH_2Cl_2): δ (ppm) 7.21 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 2.85 (sextet, *J* = 7.0 Hz, 1H), 1.21 (d, *J* = 7.0 Hz, 3H), 0.99 – 0.86 (m, 2H), 0.85 (t, *J* = 7.9Hz, 9H), 0.42 – 0.38 (m, 6H).

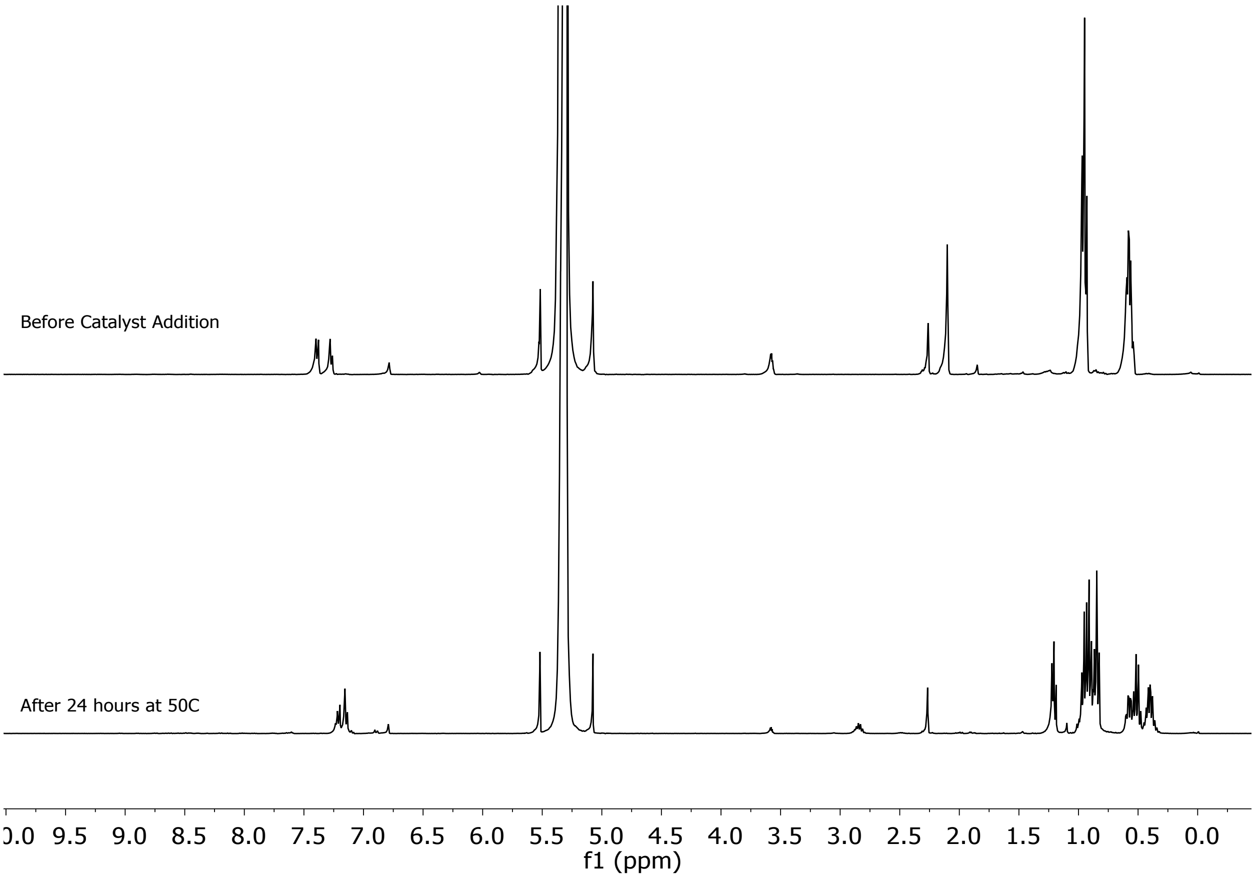
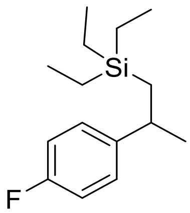


Figure S104. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-Chloro-α-methylstyrene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.



Triethyl(2-(4-fluorophenyl)propyl)silane (Entry 58): %Conversion (%Yield): 79% (73%) as determined by ^{1}H NMR spectroscopy using an external standard of mesitylene in CDCl$_3$.[31] ^{1}H NMR (500 MHz, 298K, CH$_2$Cl$_2$): δ (ppm) 7.17 (dd, $^3J_{\text{C-H}}$ = 8.8 Hz, $^3J_{\text{C-F}}$ = 5.6 Hz, 2H, Ar-C*H*), 6.93 (t, J = 8.8 Hz, 2H, Ar-C*H*), 2.86 (sextet, J = 7.0Hz, 1H, C*H*CH$_3$), 1.23 (d, J = 7.0 Hz, 3H, -C*H$_3$*), 0.96 – 0.90 (m, 2H, -CHC*H$_2$*), 0.85 (t, J = 8.0 Hz, 9H, -CH$_2$C*H$_3$*), 0.45 – 0.35 (m, 6H, -C*H$_2$*CH$_3$) . ^{13}C{^{1}H} (126 MHz, 298K, CH$_2$Cl$_2$): δ (ppm) 161.3 (d, ^{1}J$_{\text{C-F}}$ = 242.0 Hz), 146.2 (d, $^4J_{\text{C-F}}$ = 3.1 Hz), 128.2 (d, ^{3}J$_{\text{C-F}}$ = 7.7 Hz), 114.9 (d, $^2J_{\text{C-F}}$ = 21.0 Hz), 35.7, 26.8, 21.8, 7.3, 3.8. ^{19}F NMR (376 MHz, 298K, CH$_2$Cl$_2$): δ (ppm) -119.9 (m). GCMS: 223.2 ([M]$^+$, calc'd. 223.13).

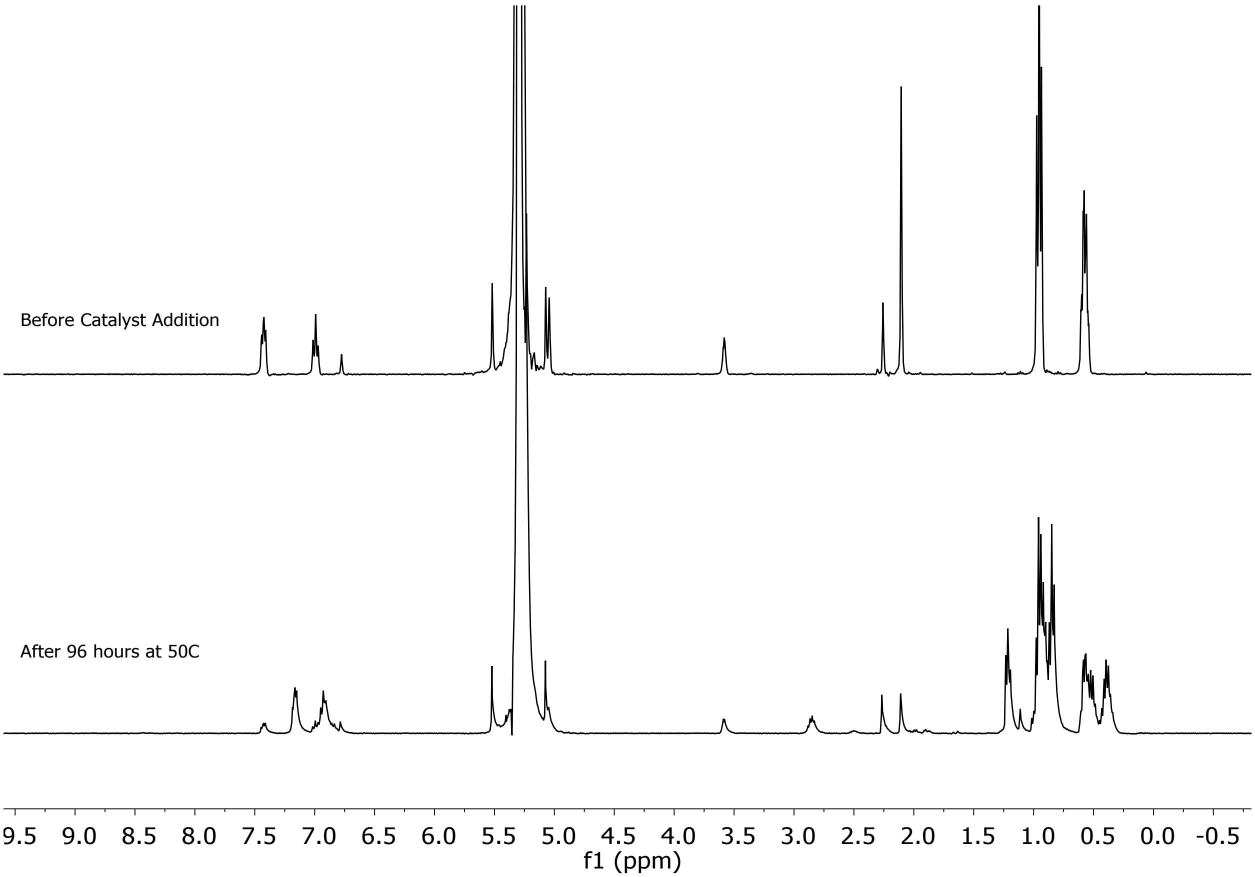


Figure S105. ^{1}H NMR (298K, 400 MHz) spectra for the catalytic hydrosilylation of 4-fluoro-α-methylstyrene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH$_2$Cl$_2$ resonance at 5.30 ppm.

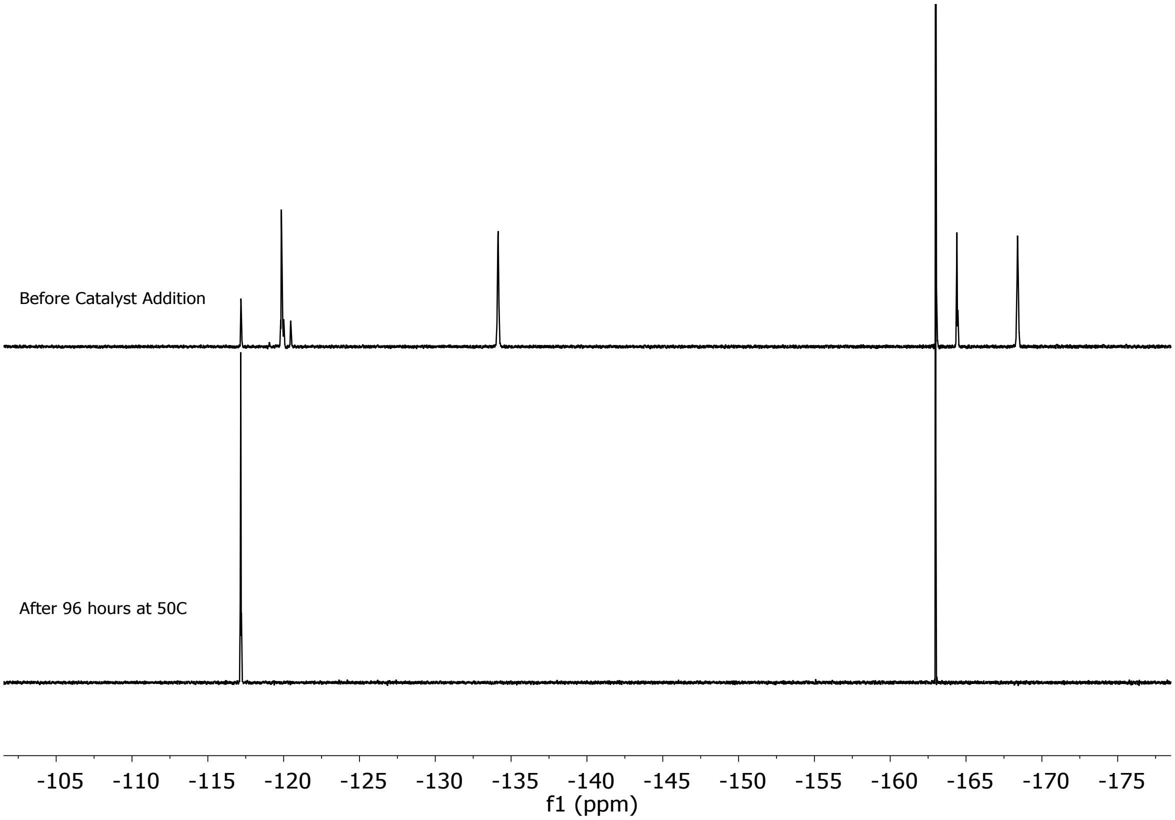


Figure S106. ^{19}F NMR (298K, 376 MHz) spectra for the catalytic hydrosilylation of 4-fluoro-α-methylstyrene in dichloromethane with triethylsilane. The NMR spectra are referenced to the hexafluorobenzene signal at -163 ppm.

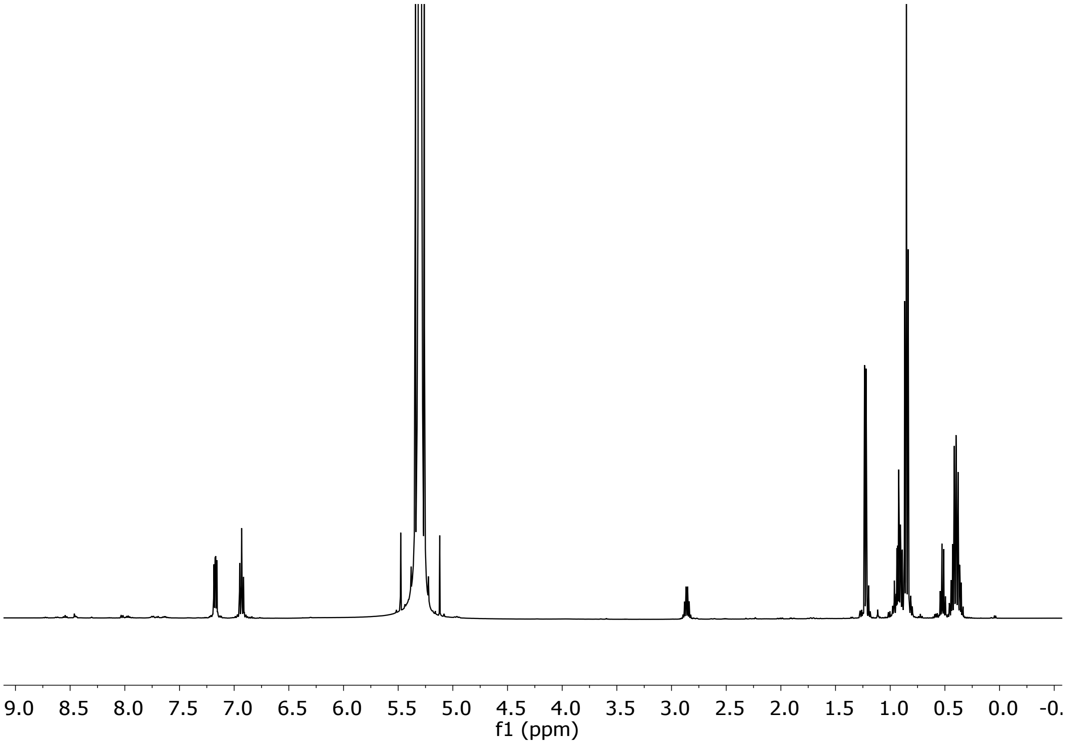


Figure S107. ^{1}H NMR (298K, 500 MHz) spectrum for triethyl(2-(4-fluorophenyl)propyl)silane after the reaction. The NMR spectrum is referenced to the CH_2Cl_2 resonance at 5.30 ppm.

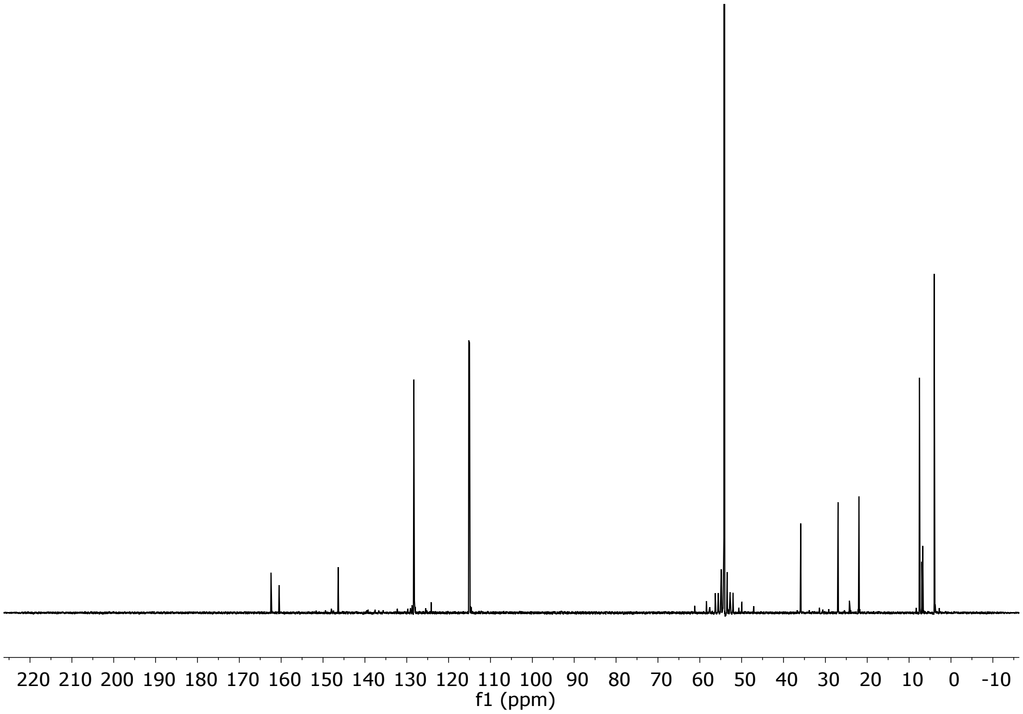


Figure S108. $^{13}C\{^{1}H\}$ NMR (298K, 126 MHz) spectrum for triethyl(2-(4-fluorophenyl)propyl)silane. The NMR spectrum is referenced to the CH_2Cl_2 resonance at 54.0 ppm.

1-methylcyclopentene: <1% conversion as monitored by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$.

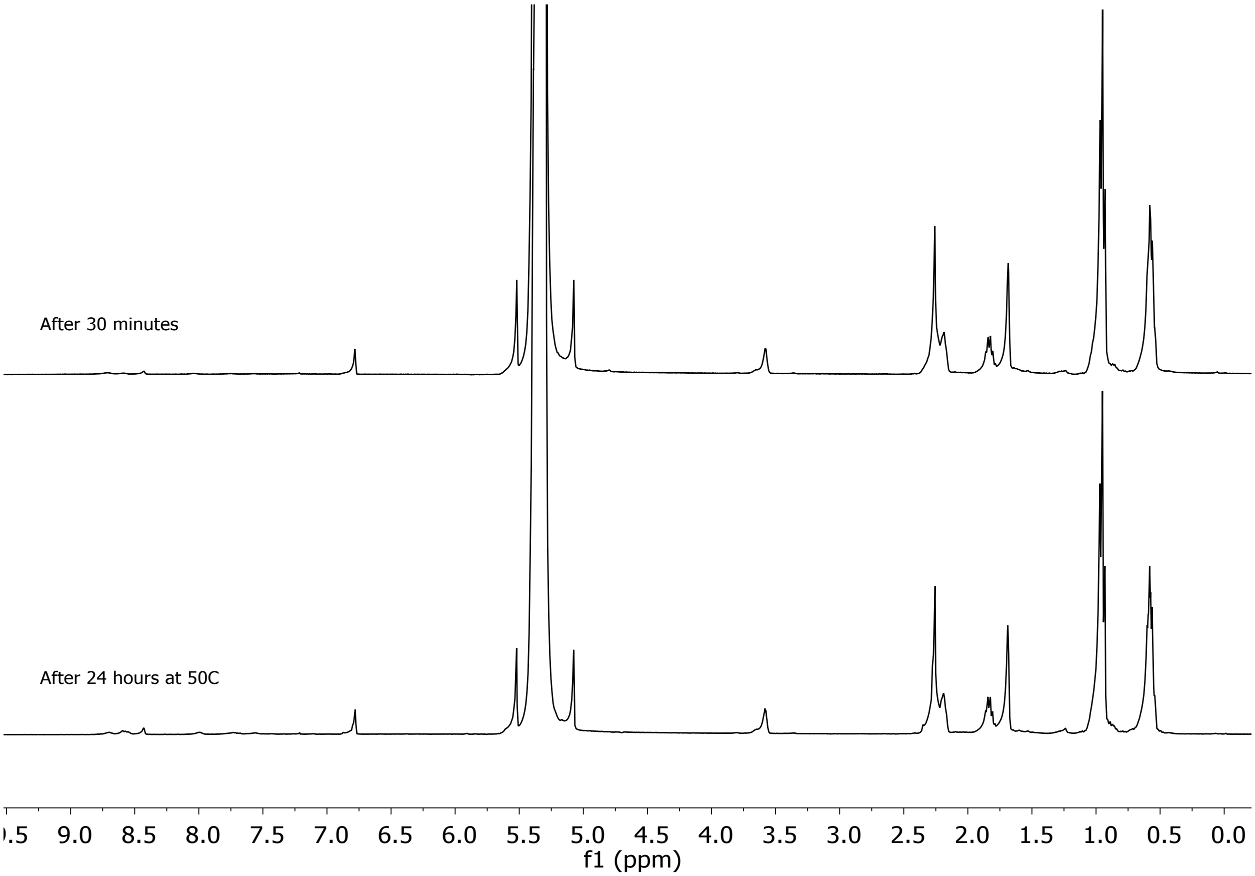


Figure S109. ^{1}H NMR (CH_2Cl_2, 298K, 400 MHz) of the attempted hydrosilylation of 1-methylcyclopentene with triethylsilane.

Triphenylethylene: <1% conversion as monitored by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$.

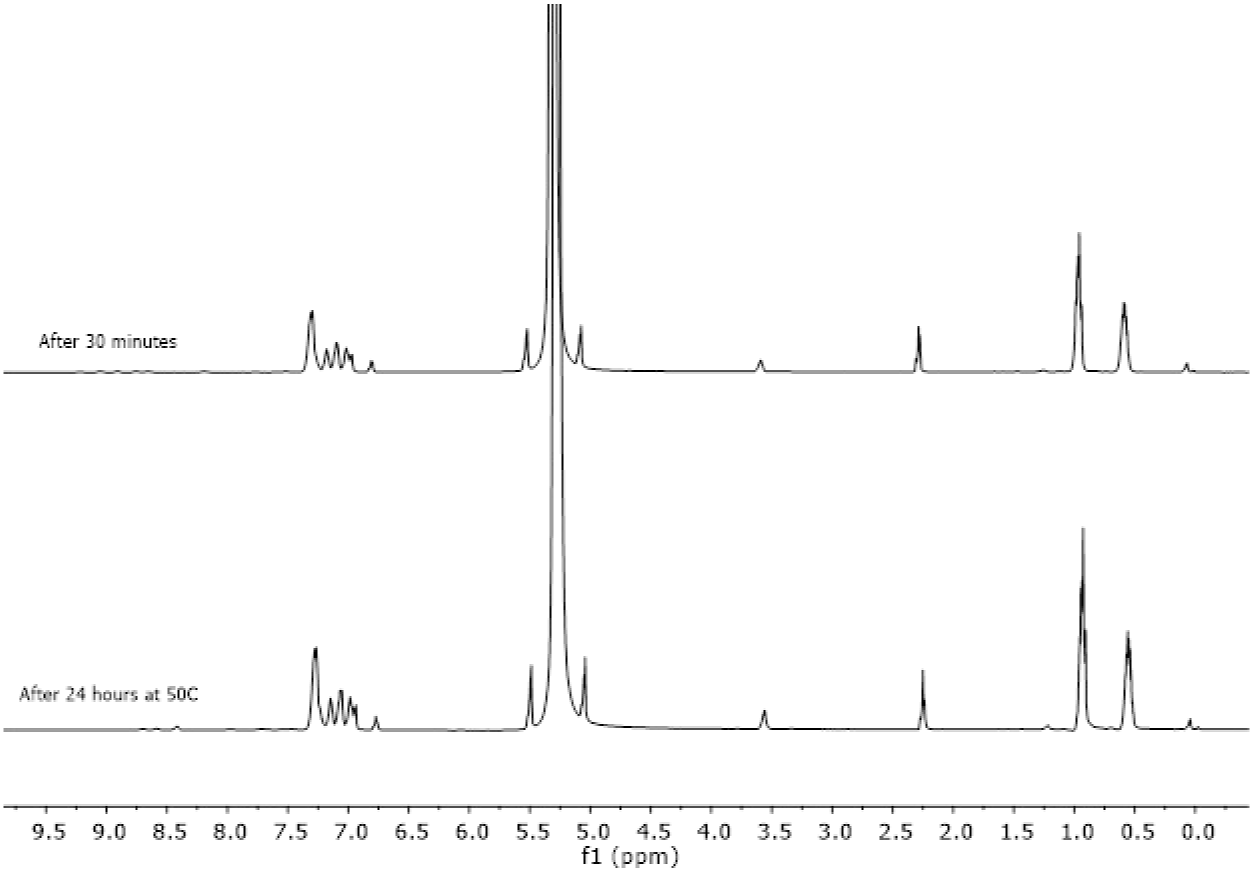


Figure S110. ^{1}H NMR (CH_2Cl_2, 298K, 400 MHz) of the attempted hydrosilylation of triphenylethylene with triethylsilane.

Trans-α-methylstilbene: <1% conversion as monitored by ^{1}H NMR spectroscopy using an external standard of mesitylene in $CDCl_3$.

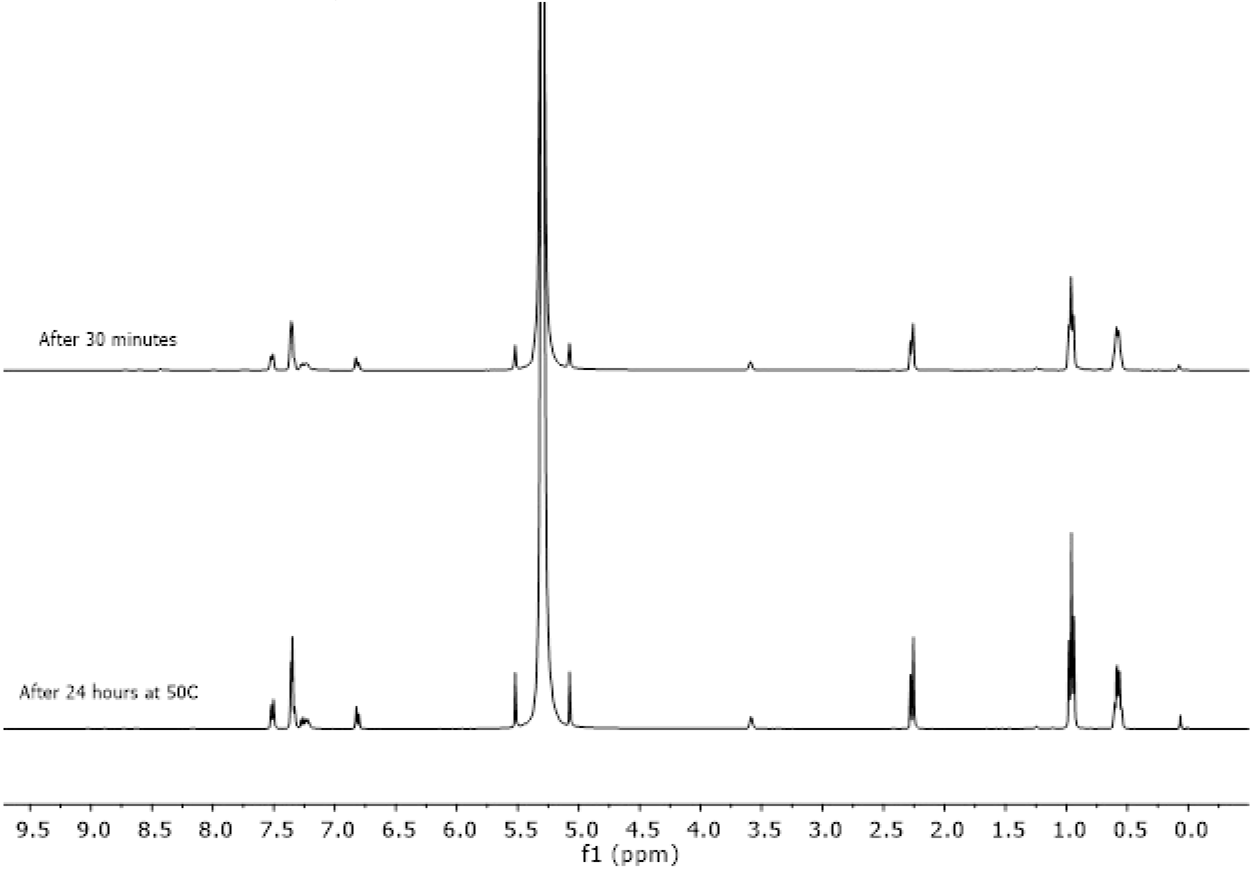


Figure S111. ^{1}H NMR (CH_2Cl_2, 298K, 400 MHz) of the attempted hydrosilylation of with trans-α-methylstilbene.

5.5. Catalytic Reaction with 1 Generated in-situ

Procedure: A mixture of 4-methylbenzaldehyde (12 µL, 0.10 mmol), Et_3SiH (17.6 µL, 0.12 mmol) in dry CH_2Cl_2 was added to a stirring solution of terpyridine (2.3 mg, 10 mol%), $PhPCl_2$ (1.4 µL, 10 mol%) and $Na[B(C_6F_5)_4]$ (14 mg, 20 mol%). The yellow solution was transferred to an NMR tube and the conversion was monitored by ^1H NMR spectroscopy.

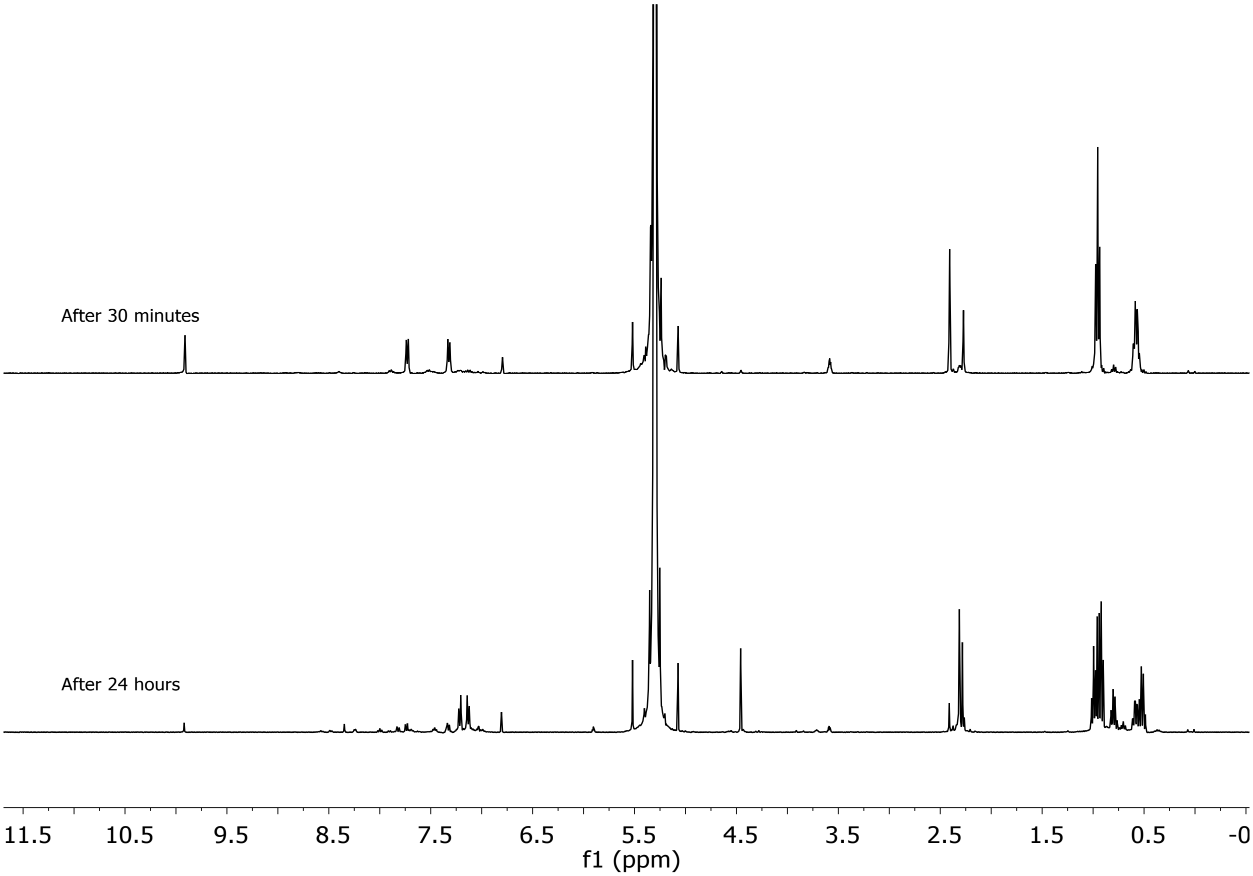


Figure S112. ^1H NMR (CH_2Cl_2, 298K, 400 MHz) for the catalytic hydrosilylation of 4-methylbenzaldehyde with **1** generated *in situ*.

5.6. Attempted Catalytic Reactions/Inhibition involving Alkynes

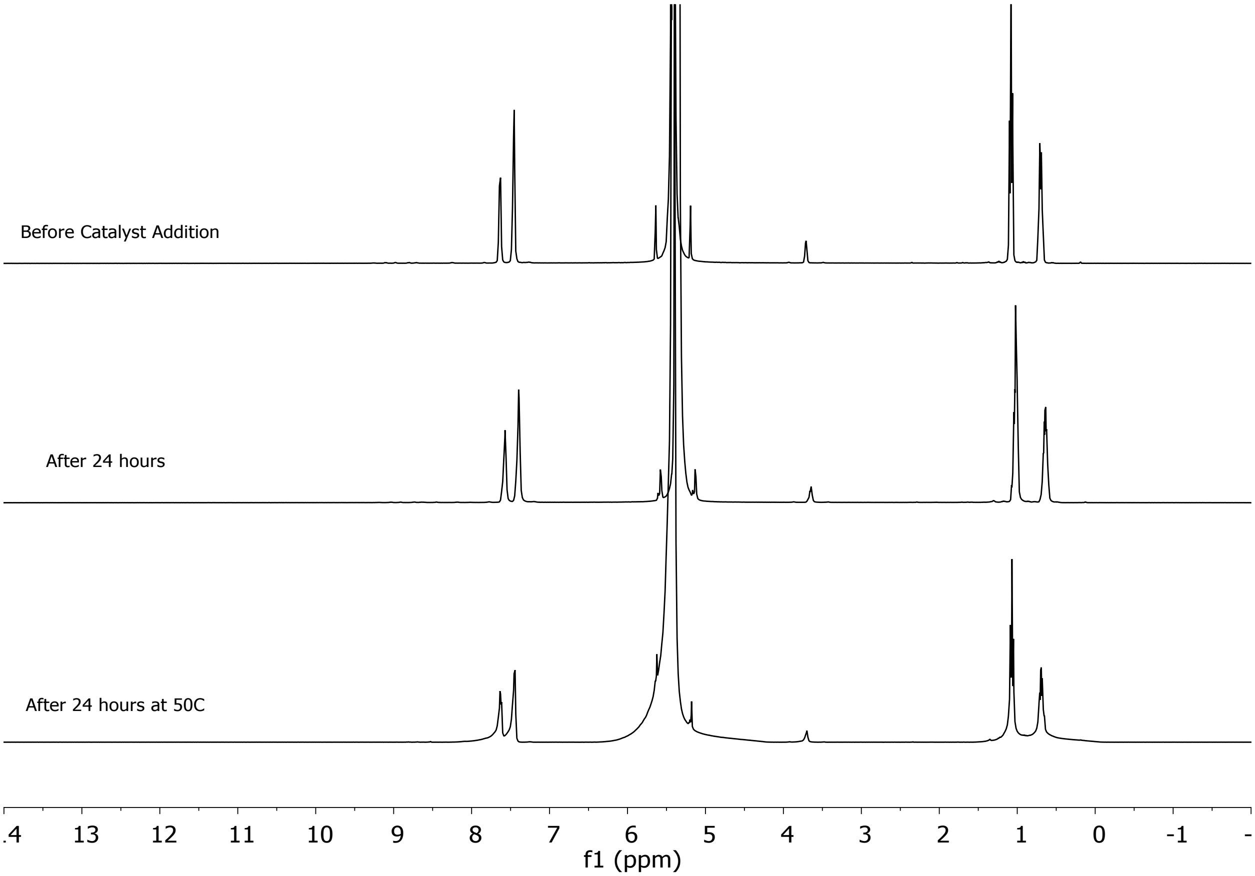


Figure S113. ^{1}H NMR (298K, 400 MHz) spectra for the attempted catalytic hydrosilylation of diphenylacetylene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

Procedure for the attempted hydrosilylation of α-methylstyrene in the presence of phenylacetylene.

α-methylstyrene (11.2 mg, 0.10 mmol) was added to a solution of **1** (8.4 mg, 10 mol%), phenylacetylene (10.2 mg, 0.10 mmol) and triethylsilane (17.6 µL, 0.11 mmol) in dichloromethane (0.7 mL). The solution was transferred to an NMR tube containing an external standard of mesitylene and hexafluorobenzene in $CDCl_3$. An NMR spectrum was initially taken of the mixture, and the reaction was monitored at room temperature and at 50°C by ^1H NMR spectroscopy.

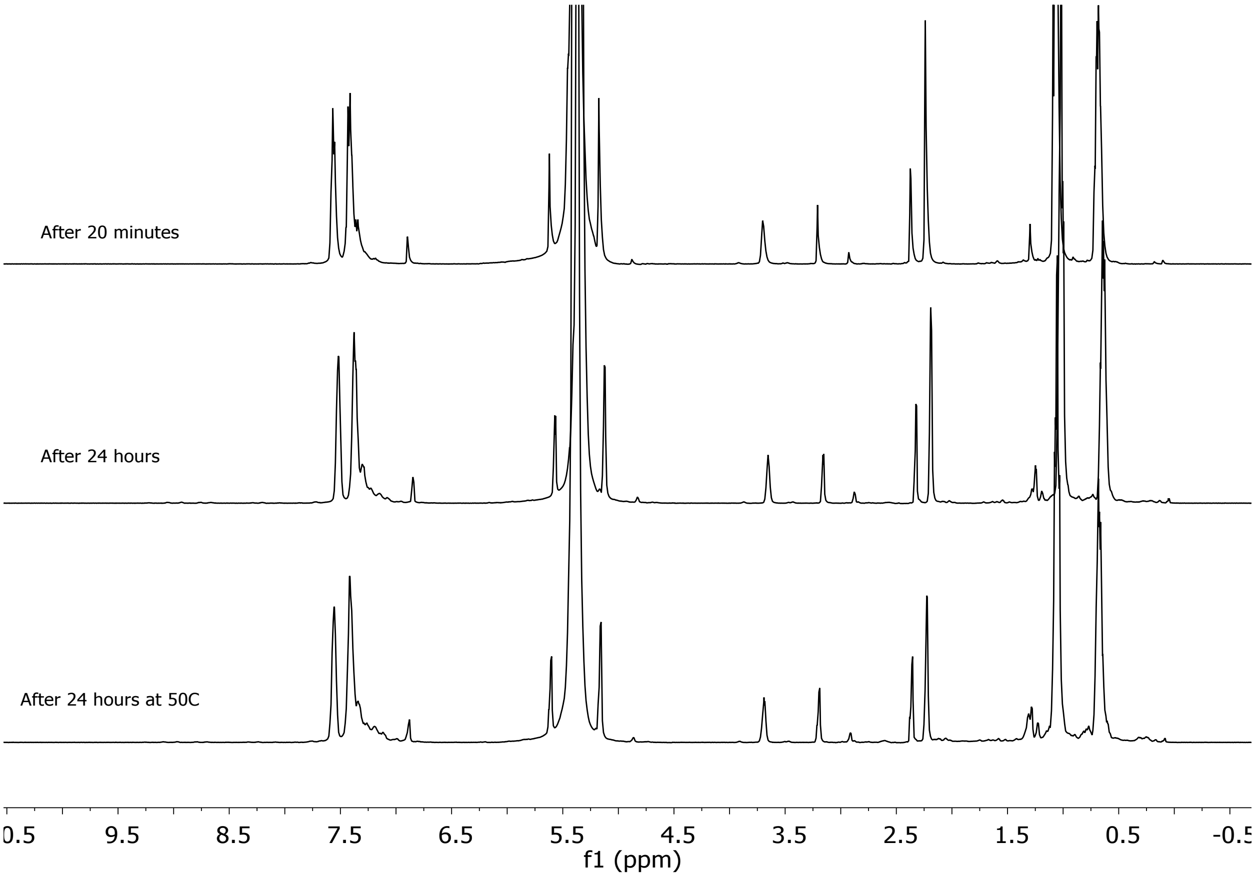


Figure S114. ^1H NMR (298K, 400 MHz) spectra for the competitive catalytic hydrosilylation of α-methylstyrene and phenylacetylene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

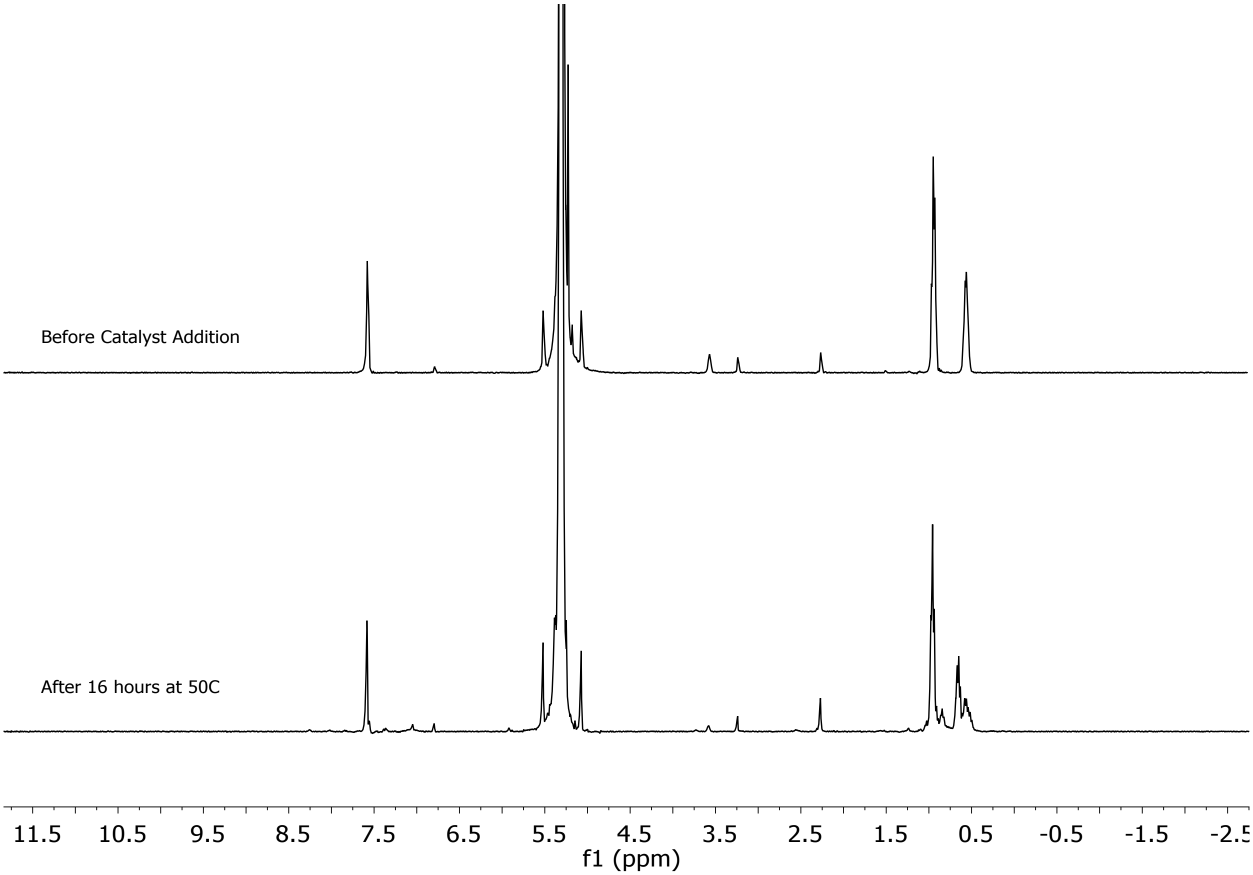


Figure S115. ^{1}H NMR (298K, CH_2Cl_2 400 MHz) spectra for the attempted catalytic hydrosilylation of 4-trifluoromethylphenylacetylene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

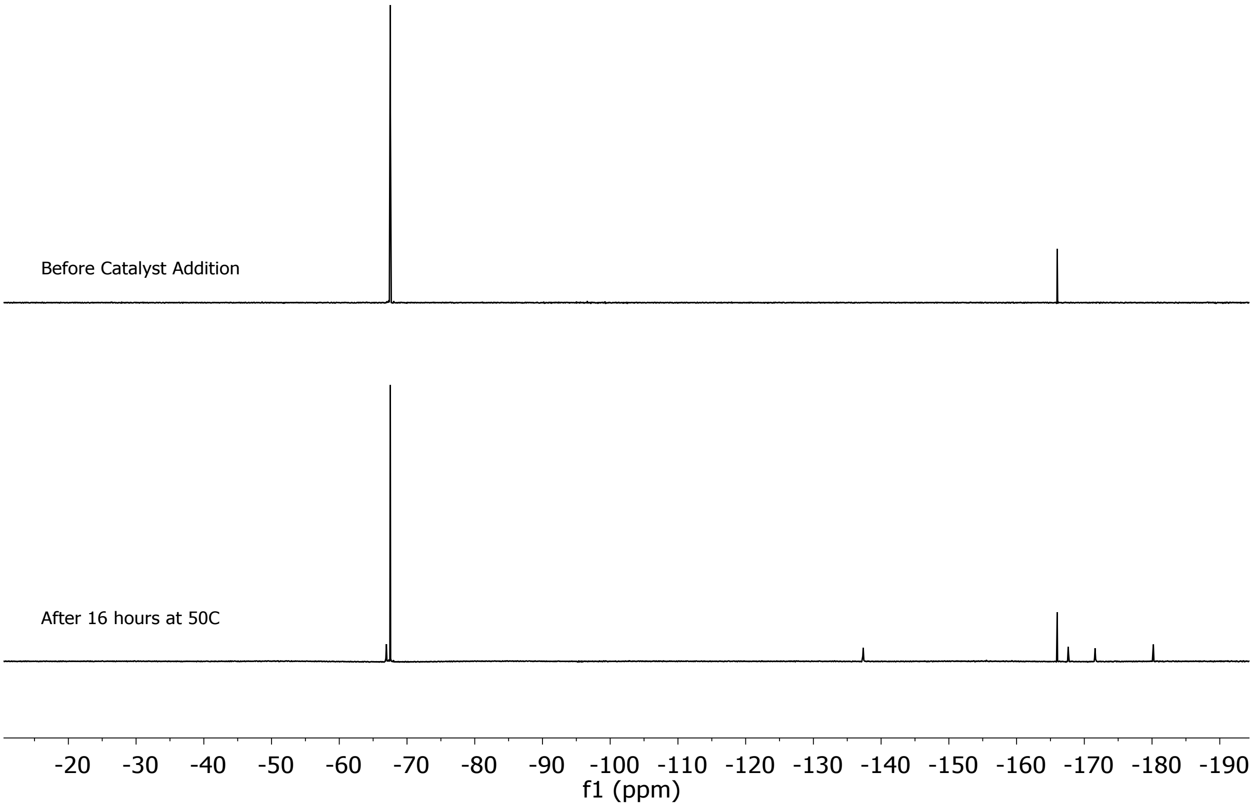


Figure S116. ^{19}F NMR (298K, CH_2Cl_2 376 MHz) spectra for the attempted catalytic hydrosilylation of 4-trifluoromethylphenylacetylene in dichloromethane with triethylsilane. The NMR spectra are referenced to the CH_2Cl_2 resonance at 5.30 ppm.

Procedure for attempted reactions of 1 with alkynes: 1 (24 mg, 0.014 mmol) in dichloromethane (0.7 mL) was added to diphenylacetylene (5.0 mg, 0.028 mmol) or phenylacetylene (2.9 mg, 0.028 mmol) and the resulting solution was monitored by ^{31}P NMR spectroscopy.

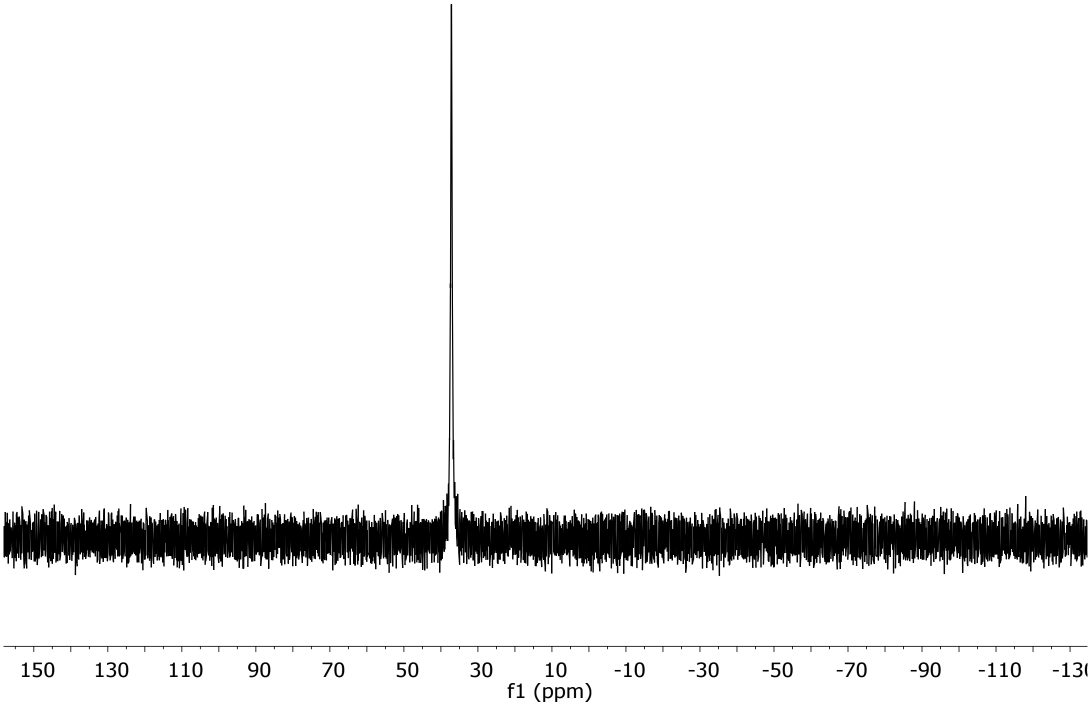


Figure S117. ^{31}P{^{1}H} NMR (CH_2Cl_2, 298K, 400 MHz) spectrum for the attempted reaction between **1** and diphenylacetylene.

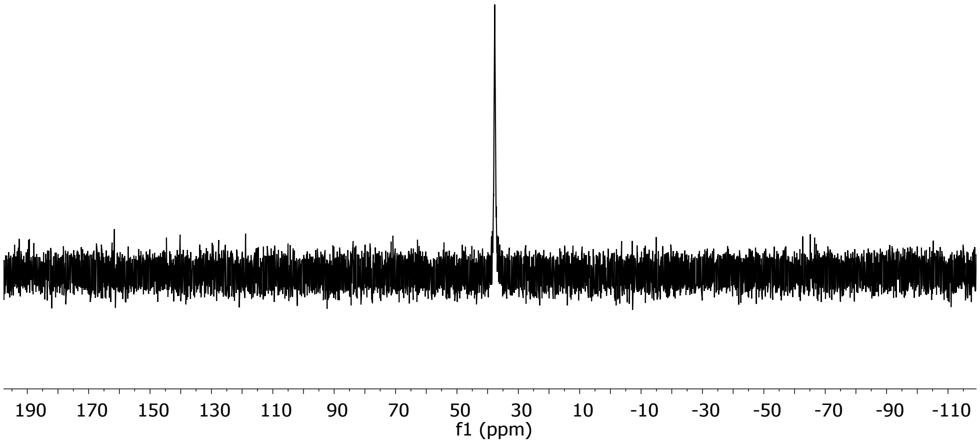


Figure S118. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 298K, 400 MHz) spectrum for the attempted reaction between **1** and phenylacetylene.

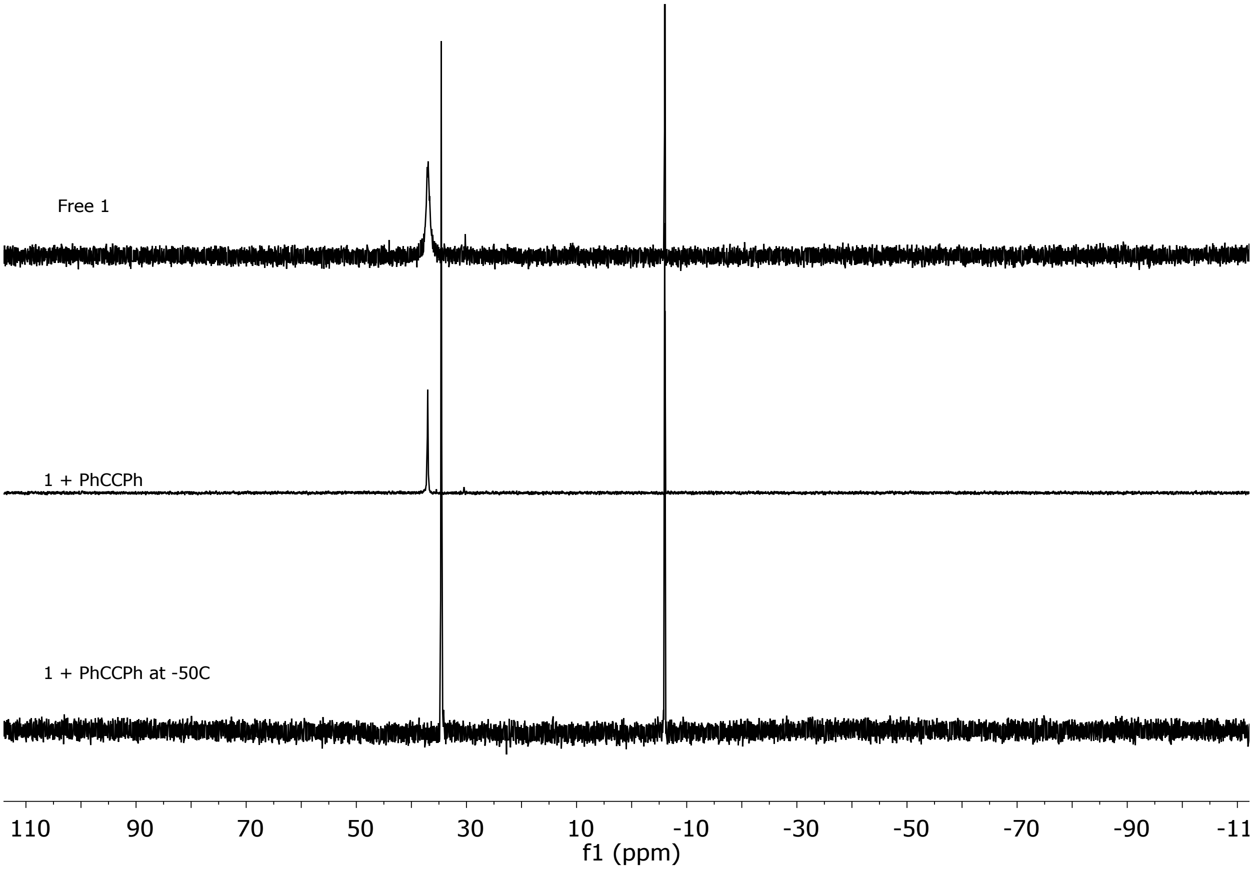


Figure S119. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 298K, 400 MHz) spectra for the interactions between diphenylacetylene and **1** with an external standard of PPh_3.

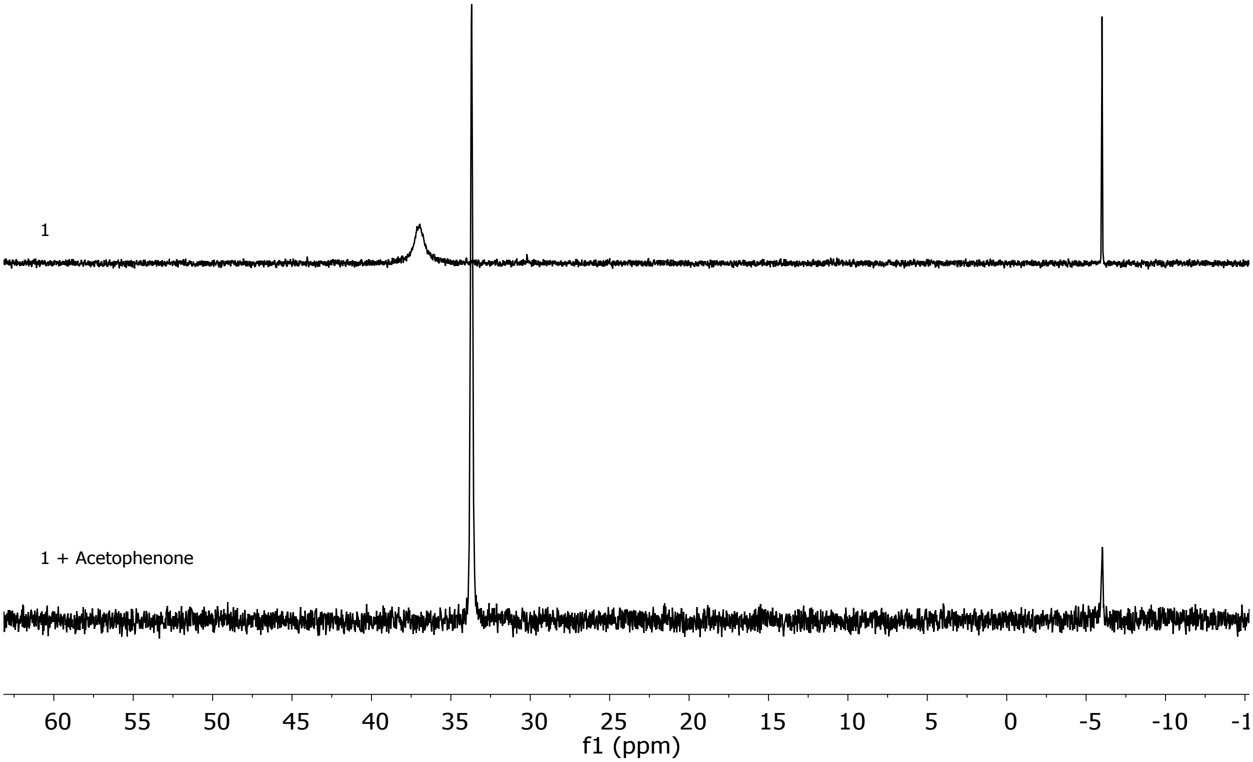
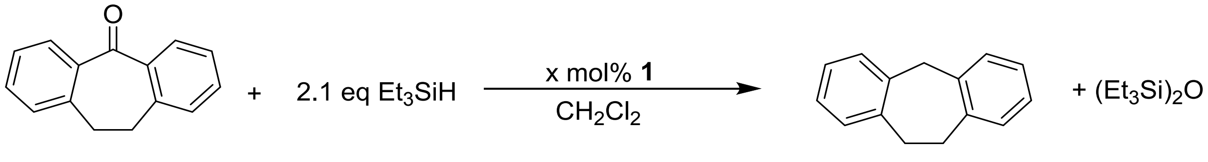


Figure S120. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 298K, 400 MHz) spectra for the interactions between acetophenone and **1** with an external standard of PPh_3.

6. Mechanistic Considerations

6.1. Monitoring 1 *in situ* by ^{31}P NMR Spectroscopy



Procedure:

A mixture of dibenzosuberone (0.1 mmol) and triethyl silane (0.21 mmol) in dichloromethane (0.7 mL) was added to an NMR tube containing **1** (x mol %) and a capillary containing hexafluorobenzene and mesitylene in CDCl$_3$. The product conversion and catalyst identity was monitored overtime by ^{1}H NMR spectroscopy and ^{31}P{^{1}H} NMR spectroscopy, respectively.

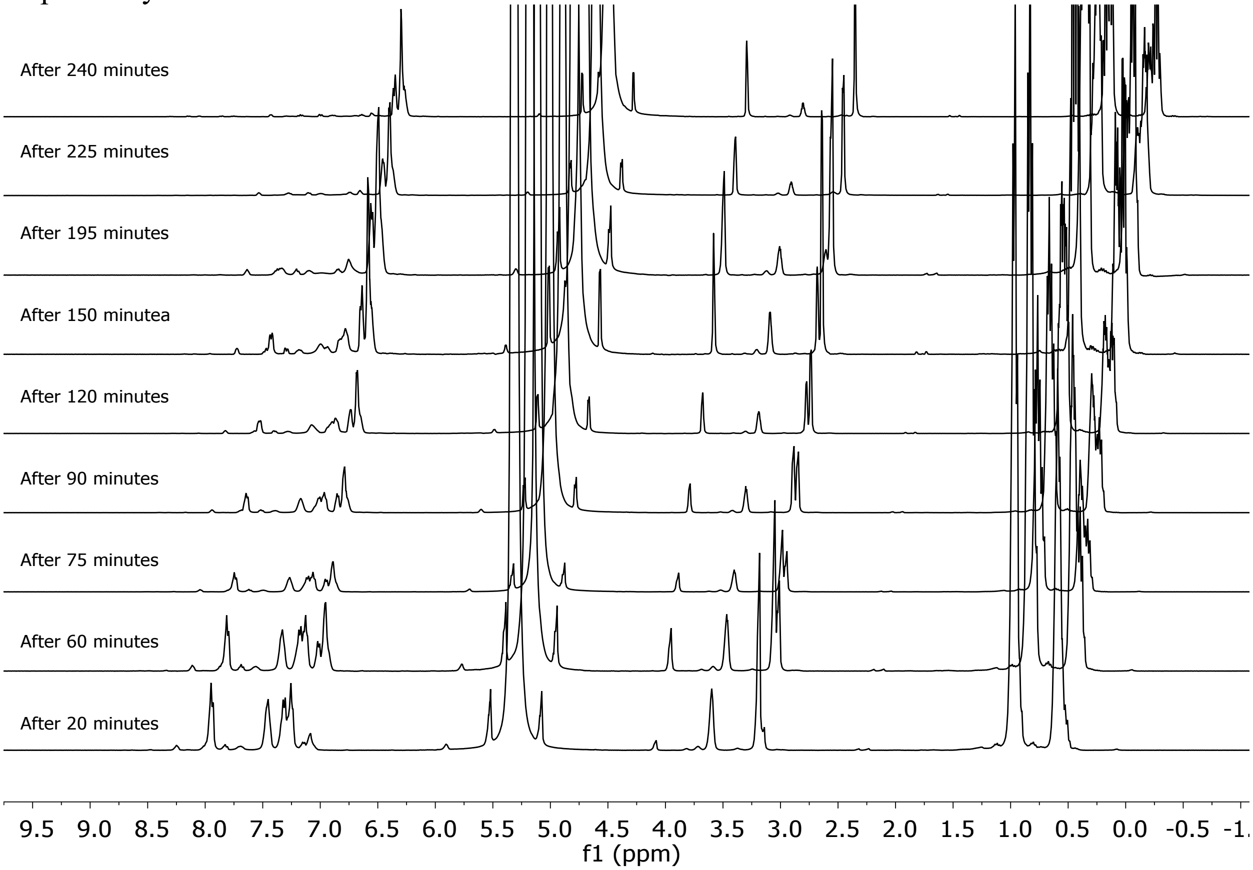


Figure S121. ^{1}H NMR spectra for the reductive deoxygenation of dibenzosuberone using 6 mol% of **1**.

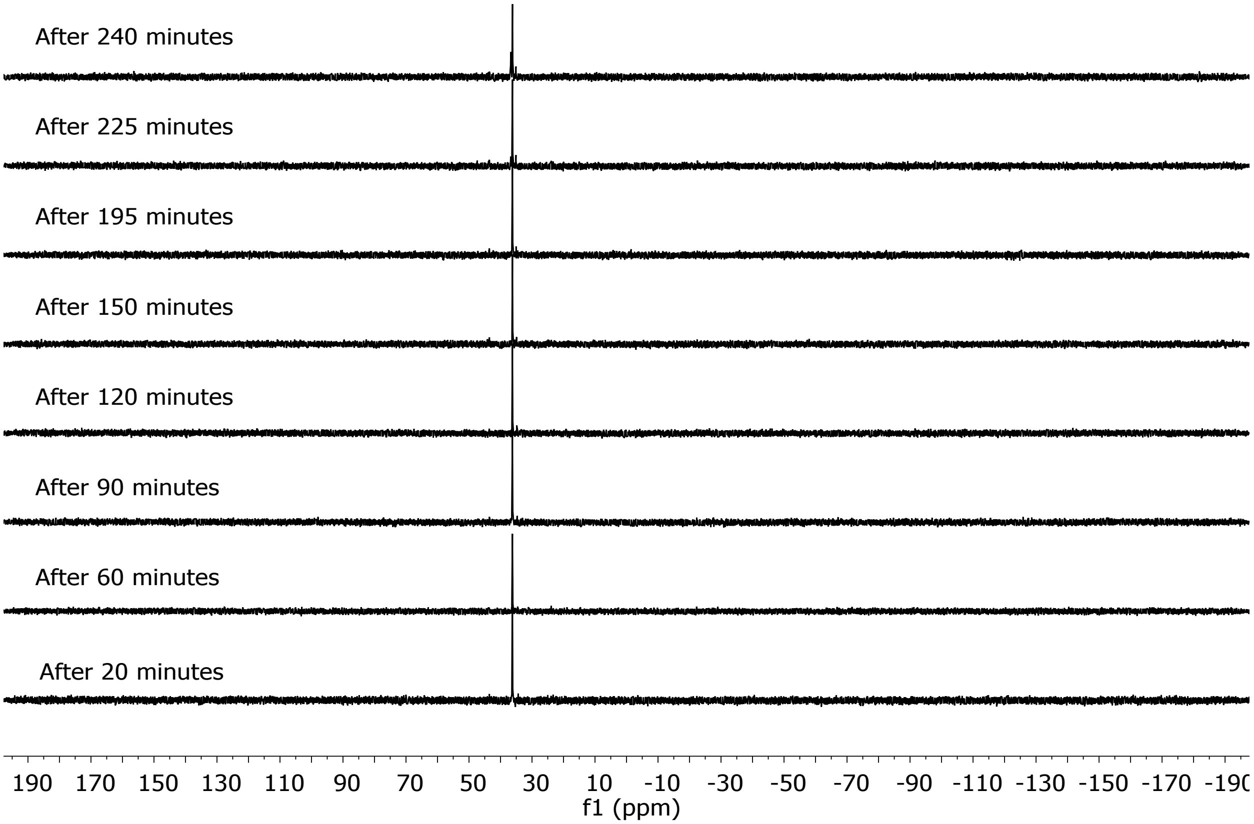


Figure S122. $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 298 K, 126 MHz) spectra for the reductive deoxygenation of dibenzosuberone using 6 mol% of **1**.

6.2. Attempted Synthesis of a hydride containing intermediate.

$$\mathbf{1} + 2\ \mathrm{Na[HBEt_3]} \xrightarrow[-40^{o}\mathrm{C\ to\ RT}]{\mathrm{CH_2Cl_2}} \mathrm{PhPH_2} + \mathrm{Terpyridine}$$

Procedure: To a stirring solution of **1** (20 mg, 0.0089 mmol) in CH_2Cl_2 (1 mL) at -40°C was added Na[$HBEt_3$] (1.0 M in toluene, 8.9 μL, 0.0089 mmol) slowly. The resulting faint yellow solution was monitored by ^{31}P NMR spectroscopy, and $PhPH_2$ was identified as the major product. $PhPH_2$ $\delta\ ^{31}P = -123$ ppm (t, $^1J_{P-H} = 196$ Hz).[33]

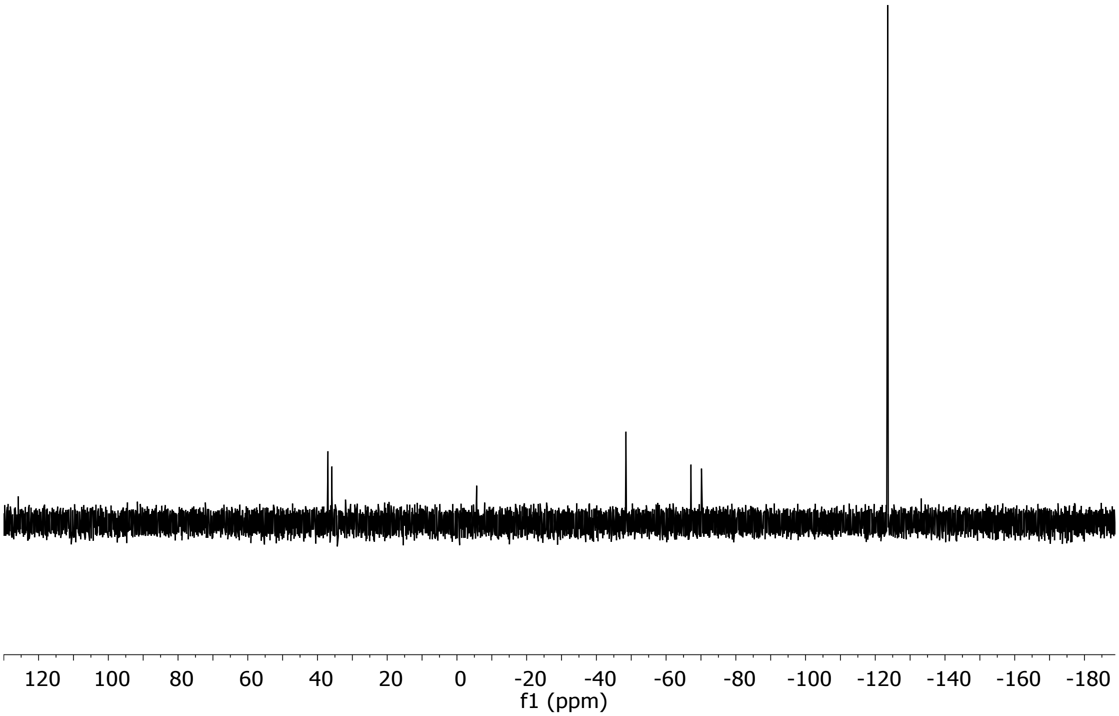


Figure S123. $^{31}P\{^{1}H\}$ NMR (CH_2Cl_2, 298 K, 126 MHz) for the reaction of **1** with Na[$HBEt_3$].

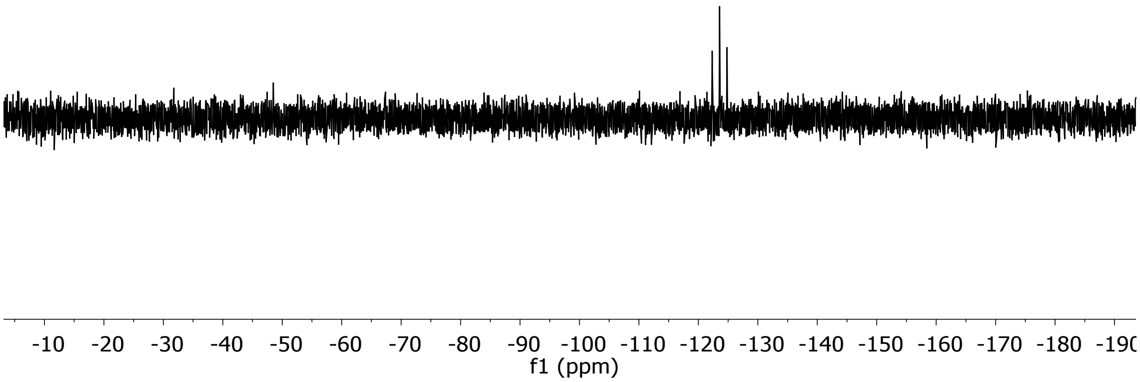


Figure S124. ^{31}P NMR (CH_2Cl_2, 298 K, 126 MHz) for the reaction of **1** with Na[$HBEt_3$].

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