Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Efficient Carbon-Supported Heterogeneous Molybdenum-Dioxo Catalyst for Chemoselective Reductive Carbonyl Coupling

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Experimental Section

General considerations. Activated carbon (06-0100, Lot#2562087) was purchased from Strem Chemicals. The reagents 4-formyl-trans-stilbene, 4-ethylbenzaldehyde, 3-chlorobenzaldehyde, and 2,6-dichlorobenzaldehyde were purchased from TCI America. All other starting materials and solvents were purchased from Sigma-Aldrich. All chemicals were used without further purification unless otherwise noted. **Mo@C** was prepared and fully characterized previously by this group from (dme)Mo(=O)$_2$Cl$_2$ (dme = 1,2-dimethoxyethane) and activated carbon (Mouat, A. R.; Lohr, T. L.; Wegener, E. C.; Miller, J. T.; Delferro, M.; Stair, P. C.; Marks, T. J. *ACS Catal.* **2016**, *6*, 6762-6769.).

Analytical Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a fully automated 400 MHz Agilent DD MR-400 system equipped with an Agilent 7600 96-sample autosampler. Chemical shifts (δ) for ^{1}H and ^{13}C are referenced to TMS. Mesitylene was used as an internal standard unless otherwise noted. GC/MS analysis were recorded on an Agilent 7890 GC-TOF equipped with a 30 meter DB-5 column. The starting temperature was 75 ^{o}C and was held for 2 min before applying a ramp rate of 20 ^{o}C/min until 300 ^{o}C and held for an additional 10 min. ICP analysis of the Mo metal loading was performed by Galbraith Labs (Knoxville, TN).

X-ray photoelectron spectroscopy. XPS spectra were collected on a Thermo Scientific ESCALAB 250Xi, equipped with an Al K alpha radiation source and electron flood-gun, in a pressure of 8x10^{-8} mbar with a pass energy of 50 eV. Binding energies were referenced against that of adventitious carbon, which was set at 284.8 eV. Typically, a 20 ms dwell time and 40-50 scans were used for each spectrum. Spectra were normalized using Origin.

Catalytic reductive carbonyl coupling reactions. In a typical experiment, n-octanal (1.00 mL, 6.4 mmol), dimethylphenylsilane (1.18 mL, 7.7 mmol, 1.2 eq.), mesitylene (0.30 mL, 2.1 mmol), anhydrous 1,1,2,2-tetrachloroethane (5.0 mL) and **Mo@C** (0.015 g, 0.1 mol% Mo) were added to a round bottom flask with Morton indentations in air. The reaction mixture was stirred at 500 rpm and heated to 100 ^{o}C for 3 h with a condenser attached. NMR samples were collected and analyzed before and after the reaction. Conversion and selectivity were calculated by ^{1}H-NMR through integration against the internal standard. For isolated yields, the catalyst was filtered off and the solvent was evaporated, the final ether product was obtained by column chromatography with a mixture of hexanes and dichloromethane (8:2). All reported products were compared to published ^{1}H/^{13}C NMR values when possible and verified by GC/MS when appropriate. No difference in product selectivity was observed under inert atmosphere.

Catalyst recycling. After the initial reaction, the reaction mixture was transferred into a centrifuge tube and centrifuged at a speed of 5000 rpm for 5 min. The supernatant was pipetted out, hexanes (20 mL) was added to the mixture and centrifuged again. This process was repeated two more times and then the catalyst was collected and dried under flowing air. The recyclability test was performed for reductive carbonyl coupling of octanal under the same conditions as mentioned above.

Hot filtration procedure. Mo@C (0.018 g) was added to 5.0 mL of 1,1,2,2-tetrachloroethane and heated to 100 °C in air for 3 hours. The solution was then filtered hot using a cannula filter into another flask. After cooling, benzaldehyde (0.20 mL, 1.7 mmol), dimethylphenylsilane (0.4 mL, 2.6 mmol, 1.5 eq.), mesitylene (0.10 mL, 0.7 mmol) was added to the flask and heated to 100 °C for 3 hours. The solution remained clear and ^{1}H NMR was only able to detect < 2% conversion of benzaldehyde to benzyl alcohol.

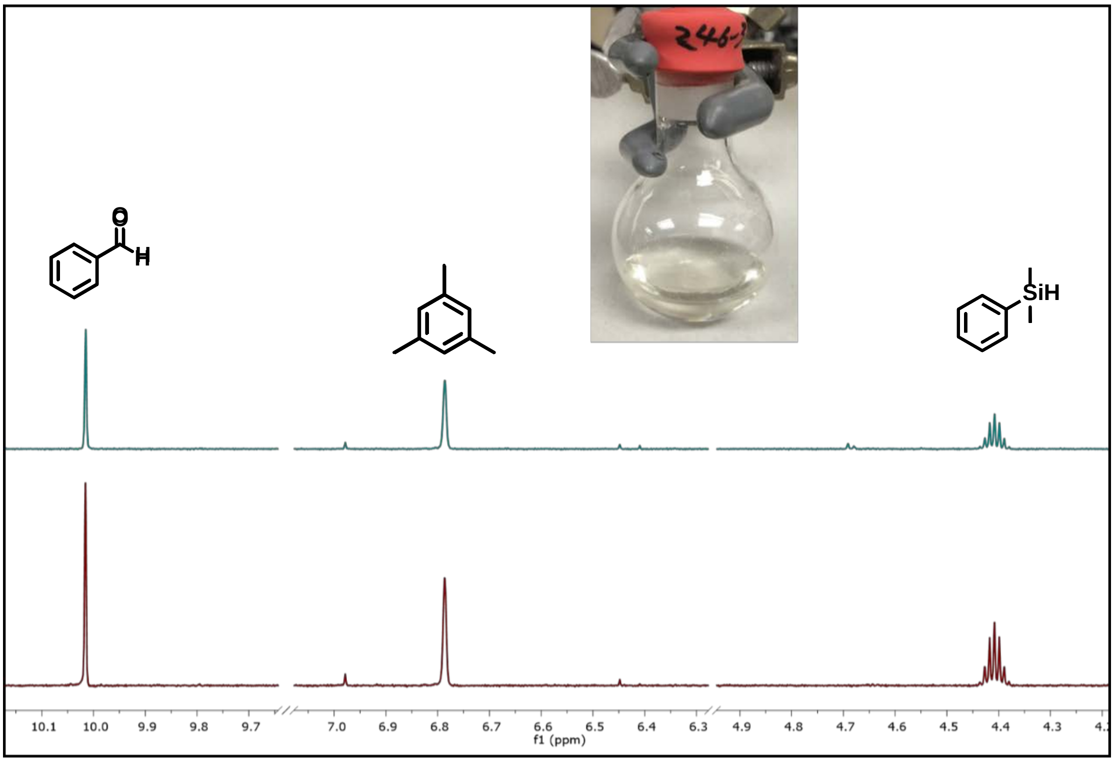
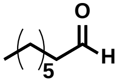
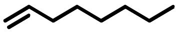
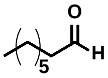
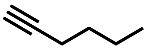
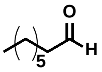
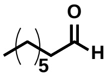
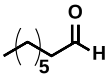
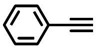
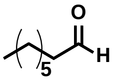
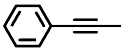


Figure S1. Hot filtration Test. ^{1}H-NMR (in $CDCl_3$) before (red) and after (turquoise) the reaction using the hot filtrate; a photo of the clear reaction mixture after heating is shown in the inset.

Table S1. Intermolecular Chemoselective carbonyl couplings using **Mo@C**

Entry	Substrate[a]	Temp.	Time	Conv.	Selectivity		
					Ether	Alcohol	Silyl Ether
1		60 °C	3 h	100%	99%	<1%	<1%
				NR			
2		60 °C	3 h	100%	100%	<1	<1%
				NR			
3		100 °C	6 h	100%	92%	<1%	8%
				NR			
4		60 °C	3 h	100%	99%	<1%	<1%
				NR			
5		60 °C	6 h	100%	100%	<1%	<1%
				NR			
6		60 °C	3 h	100%	100%	<1%	<1%
				NR			

In a typical experiment, octanal (0.5 mL, 3.2 mmol), 1-octene (0.5 mL, 3.2 mmol, 1 eq.), dimethylphenylsilane (1.18 mL, 7.7 mmol), mesitylene (0.30 mL, 2.1 mmol), 1,1,2,2-tetrachloroethane (5.0 mL) and **Mo@C** (0.015 g, 0.1 mol% Mo) were added to a round bottom flask with Morton indents in air. The reaction mixture was stirred at 500 rpm and heated to 60 °C for 3 hours with a condenser attached. NMR samples were collected and analyzed before and after the reaction. Conversion and selectivity were calculated by ^{1}H-NMR through integration against the internal standard mesitylene, products were identified and matched with reported NMR values (see Spectroscopy Data section for details).

Preliminary Kinetic Analysis. Kinetic analysis of the reductive coupling reaction described above was carried out by collecting multiple data points under moderate conversion (<50%). Product concentration was measured from ^{1}H NMR integration against mesitylene as the internal standard. PhMe$_2$SiH concentrations were varied from 50% to 300% (relative to carbonyl substrate), catalyst concentration was varied from 0.05 mol% to 0.2 mol% (relative to carbonyl) and the carbonyl concentration was varied from 50% to 400% (relative to silane). Data obtained from these measurements were used to obtain the initial rate of the reaction according to eq. S1 where *t* is time, [*Δcarbonyl*] is the concentration of the converted carbonyl and *m* is the rate of the reaction. The initial rate was then used to plot ln[rate] against ln[carbonyl] (eq. S2). The negative rate of disappearance of the carbonyl is proportional to the concentration of the carbonyl to the order. Thus, the order is the slope of the plot (eq. 3).

$$[\Delta carbonyl] = m \times t \qquad \text{(eq. S1)}$$

$$\frac{-d[carbonyl]}{dt} = \mathrm{k}_{obs}[carbonyl]^{\alpha} \qquad \text{(eq. S2)}$$

$$ln[rate] = lnk_{obs} + \alpha ln[carbonyl] \qquad \text{(eq. S3)}$$

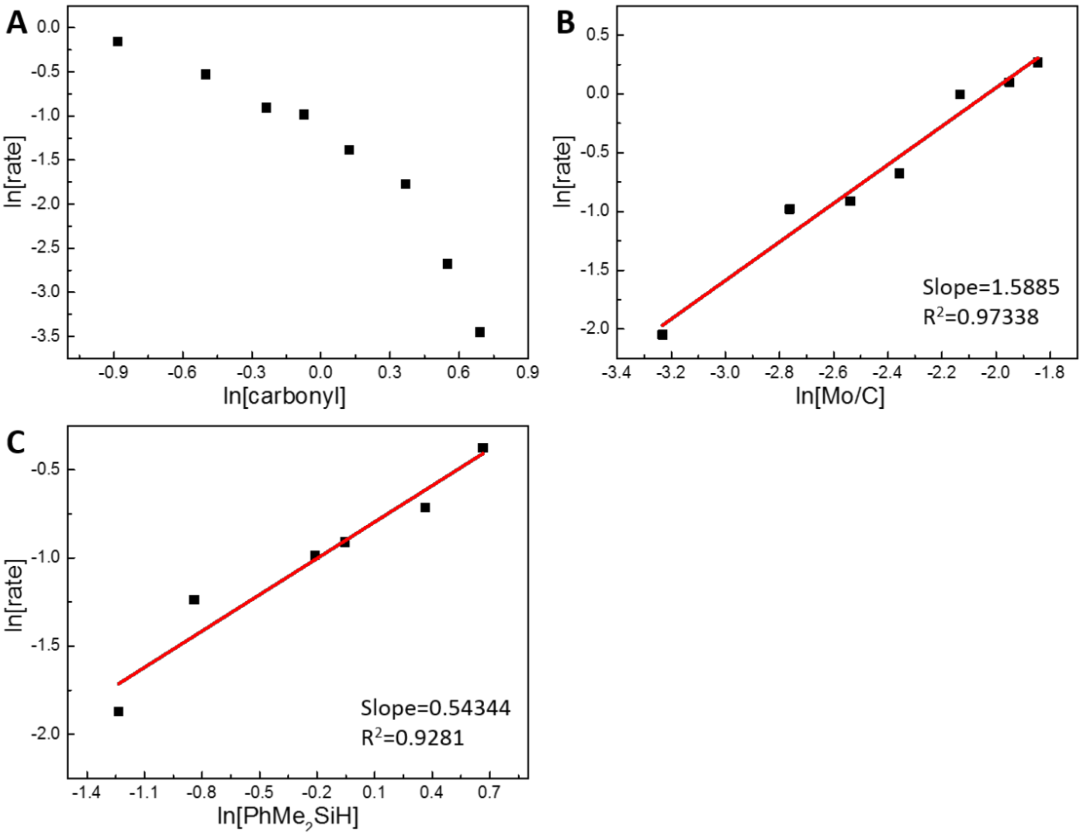
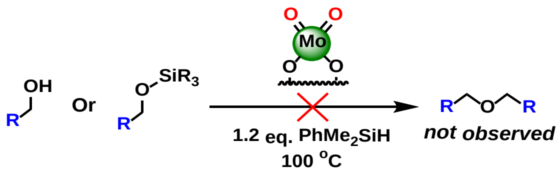


Figure S2. (A) Plot of reaction rate law order in [carbonyl]; (B) Plot of reaction rate law order in [Mo@C]; (C) Plot of reaction rate law order in [PhMe$_2$SiH].

Note the increase in negative reaction order at higher carbonyl concentrations is consistent with previous observations of carbonyl blocking/deactivating the Mo@C catalyst by competitive adsorption (T. L. Lohr, A. R. Mouat, N.M. Schweitzer, M. Delferro, P. C. Stair and T. J. Marks, *Energy Environ. Sci.*, 2017, submitted).

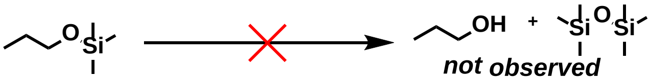
Control Experiments Probing Silylether and Alcohol in the Reaction



Scheme S1. Unsuccessful coupling of alcohols and silylethers using **Mo@C.**

Ether formation through sequential hydrosilylation, hydrolysis, and dehydration (Scheme S1) was ruled out because all attempts to produce the ether with alcohols or silylethers were unsuccessful. Instead, it was observed that water present on the surface of **Mo@C** catalyzes the hydrolysis of the silylether (trimethyl(propoxy)silane was used as a model substrate) to give the corresponding alcohol (Figures S3-S5, see each section for details), which is in accord with our results where both species are observed as side products in the reaction.

A) In a small flask, trimethyl(propoxy)silane (1.0 mL, 5.8 mmol) and mesitylene (0.3 mL, 2.1 mmol) was dissolved in 5 mL of 1,1,2,2-tetrachloroethane in air. The flask was attached to a condenser and heated to 100 ^{o}C for 24 h after which an NMR sample was collected and analyzed.



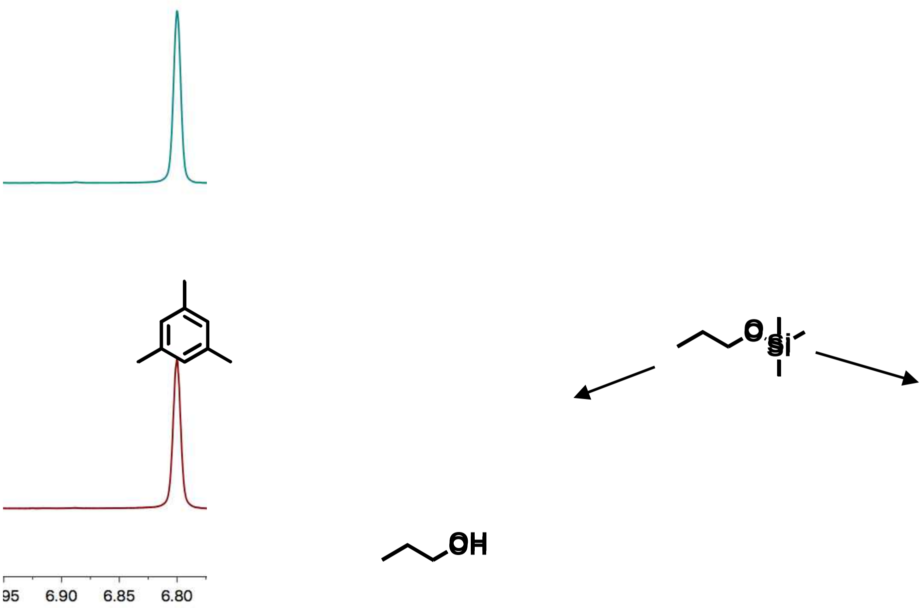
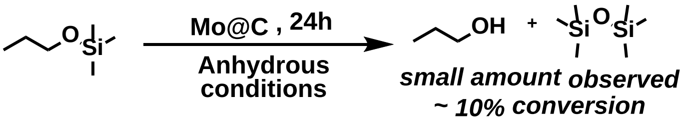


Figure S3. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the hydrolysis of trimethyl(propoxy)silane in air without **Mo@C** (trace amounts of the alcohol were present in the starting material but did not increase during the reaction).

B) 15 mg of **Mo@C** was added to a round bottom flask and kept under vacuum overnight before backfilling with N_2. Trimethyl(propoxy)silane (1.0 mL, 5.8 mmol), mesitylene (0.3 mL, 2.1 mmol), and 5 mL of anhydrous 1,1,2,2-tetrachloroethane was added and the mixture was heated to 100 °C for 24 h under N_2 before an NMR sample was collected and analyzed.



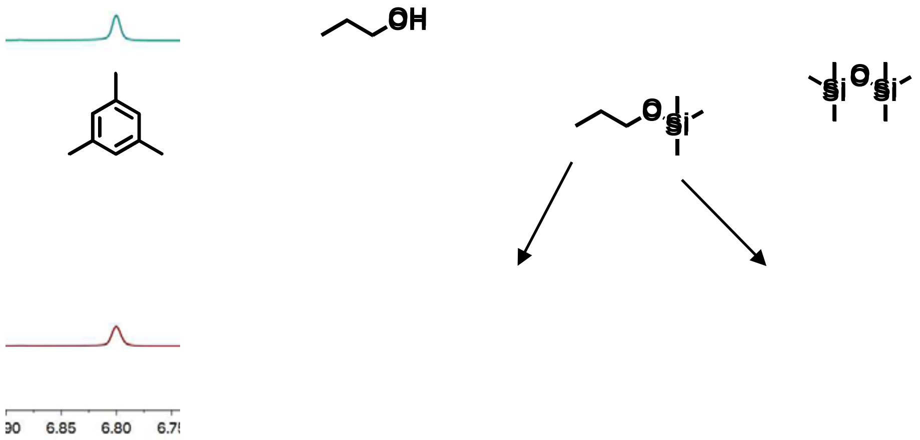
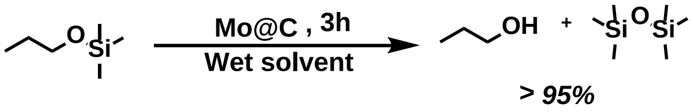


Figure S4. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) hydrolysis of trimethyl(propoxy)silane with **Mo@C** under anhydrous conditions.

Some of the larger quantities of alcohol observed may also be due to hydrolysis of molybdenum siloxy species from the adsorbed water present on the catalyst surface (See species **d** in Scheme 2 of the text) which would result in the elimination of the alcohol side product instead of the silyl ether.

C) In a small flask, trimethyl(propoxy)silane (1.0 mL, 5.8 mmol), mesitylene (0.3 mL, 2.1 mmol), and DI water (0.1 mL, 5.6 mmol) was dissolved in 5 mL of 1,1,2,2-tetrachloroethane in air. 15 mg of **Mo@C** was added to the flask which was then attached to a condenser and heated to 100 °C for 3 h after which an NMR sample was collected and analyzed.



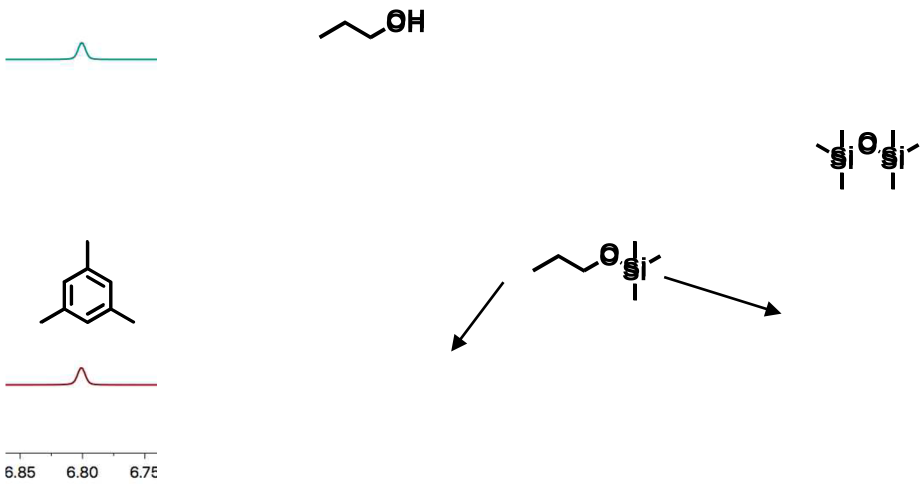


Figure S5. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the hydrolysis of trimethyl(propoxy)silane with **Mo@C** in wet solvent.

Catalytic Reductive Coupling Between *n*-Octanal and Benzyl Alcohol.

To further confirm the role of the alcohol in the reaction, attempts were made to synthesize unsymmetrical ethers through reductive coupling of n-octanal and benzyl alcohol (Figure S6). While the reaction was sluggish and mixtures of products were obtained, the hetero coupling product was obtained in about 40% yield (Figure S6, yield based on aldehyde), further corroborating the proposed reaction mechanism (Scheme 2, f, step *V* in the manuscript).

Experimental details: *n*-Octanal (0.50 mL, 3.2 mmol), benzyl alcohol (0.33 mL, 3.2 mmol) dimethylphenylsilane (1.18 mL, 7.7 mmol), mesitylene (0.30 mL, 2.1 mmol), 1,1,2,2-tetrachloroethane (5.0 mL) and **Mo@C** (0.015 g, 0.1 mol% Mo) were added to a round bottom flask with Morton indentations in air. The reaction mixture was stirred at 500 rpm and heated to 100 °C for 10 h with a condenser attached. A small amount of the reaction liquid was collected, filtered, and analyzed with ^{1}H NMR (based on R_1–O-CH_2-R_2 proton chemical shift) by comparison to literature values (see spectroscopy data section for full details). Mass balance for both n-octanal and benzyl alcohol were over 90% and accounted for in the products identified.

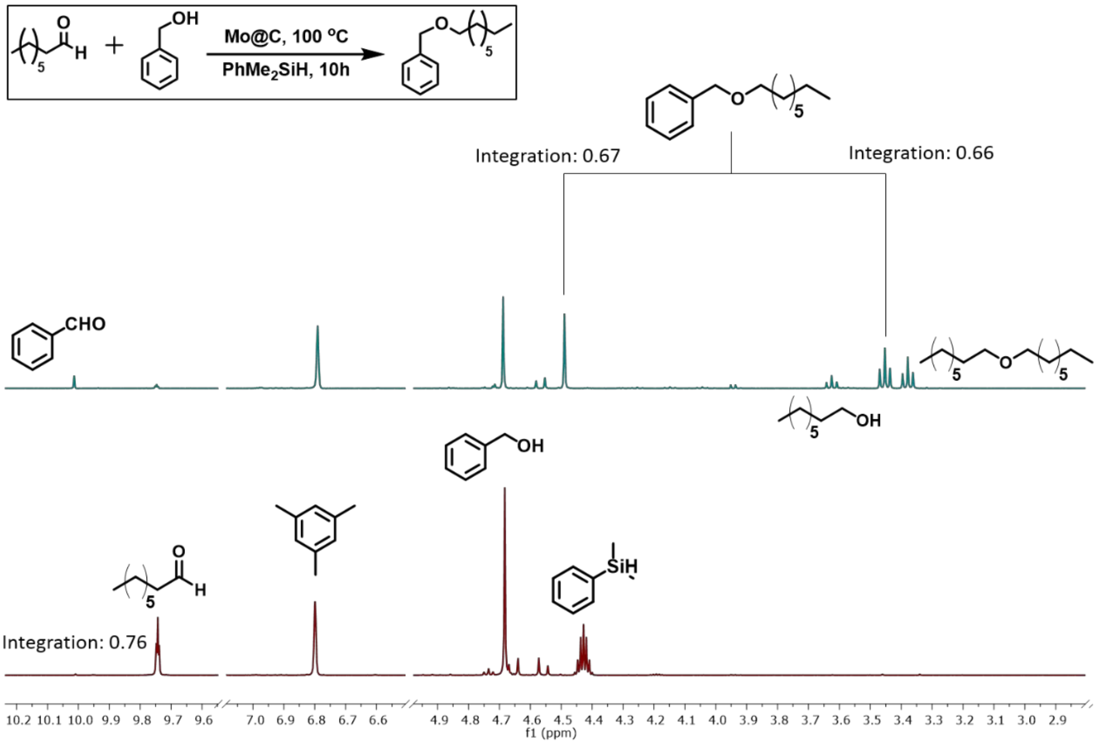


Figure S6. ^{1}H-NMR (CDCl$_3$) before (red) and after (turquoise) the reductive hetero coupling reaction of n-octanal and benzyl alcohol with **Mo@C** and PhMe$_2$SiH. Starting material n-octanal (9.76 ppm), benzyl alcohol (4.68 ppm), and PhMe$_2$SiH (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm), n-octanol (3.63 ppm), 1-(phenoxy)octane (3.45, 4.49 ppm) as the observed products.

^{1}H NMR of Reaction Products in Table 1

The following figures list the ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reaction given in Table 1. In a typical analysis, conversion and selectivity are calculated by the following equations where [*Carbonyl*] is the peak area of the ^{1}H NMR against the internal standard at each respective time point, other products were identified in a similar fashion.

$$\text{Conversion} = \frac{[Carbonyl]_{t0} - \ [Carbonyl]_{t}}{[Carbonyl]_{t0}} \times 100\% \qquad \text{(eq. S4)}$$

$$\text{Selectivity} = \frac{[Ether]_{t}}{[Carbonyl]_{t0} - \ [Carbonyl]_{t}} \times 100\% \qquad \text{(eq. S5)}$$

Product selectivity was calculated using the R_1–O-C*H*$_2$-R_2 proton and identified by comparison with previous reported literature values when available (see spectroscopy data for full values and references), ethers that have not been previously reported were prepared by alternative methods and compared accordingly (see spectroscopy sections for individual details). Typically the products' R_1–O-C*H*$_2$-R_2 proton chemical shift values increases in the order of Ether < Silylether < Alcohol. For alcohols and silylethers where literature ^{1}H-NMR values are not available, these side products were empirically assigned in that order.

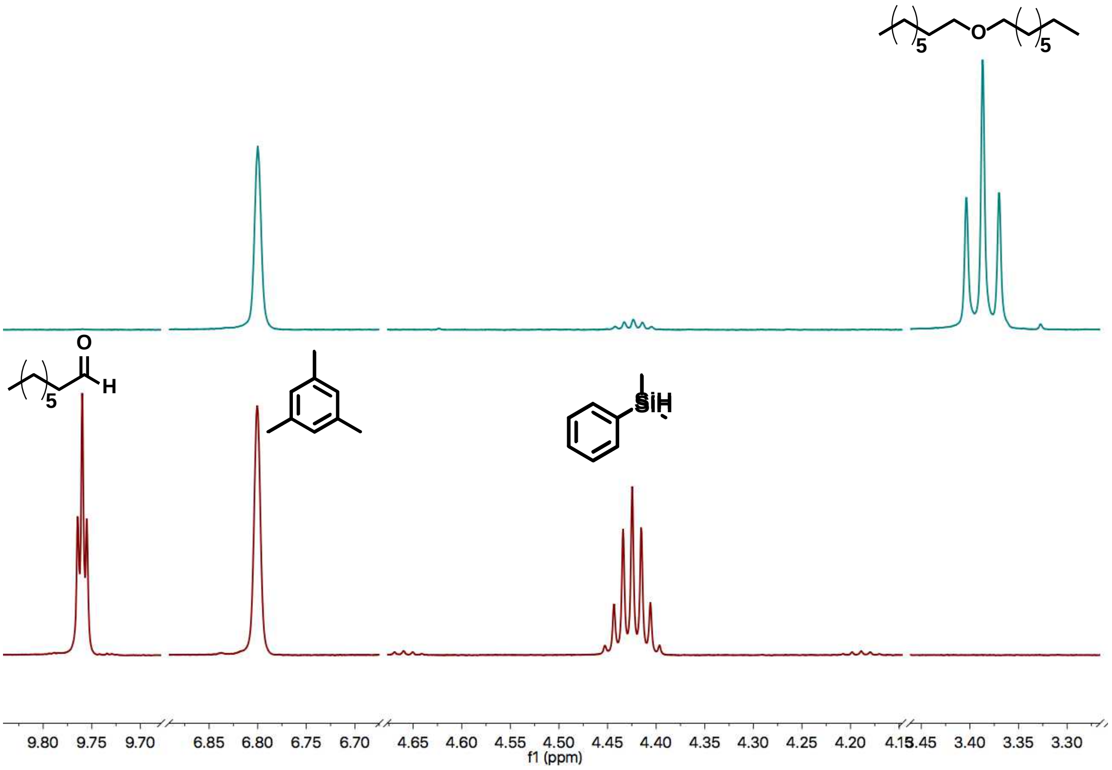


Figure S7. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of n-octanal. Starting material n-octanal (9.76 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm) as the observed product (Table 1 Entry 1).

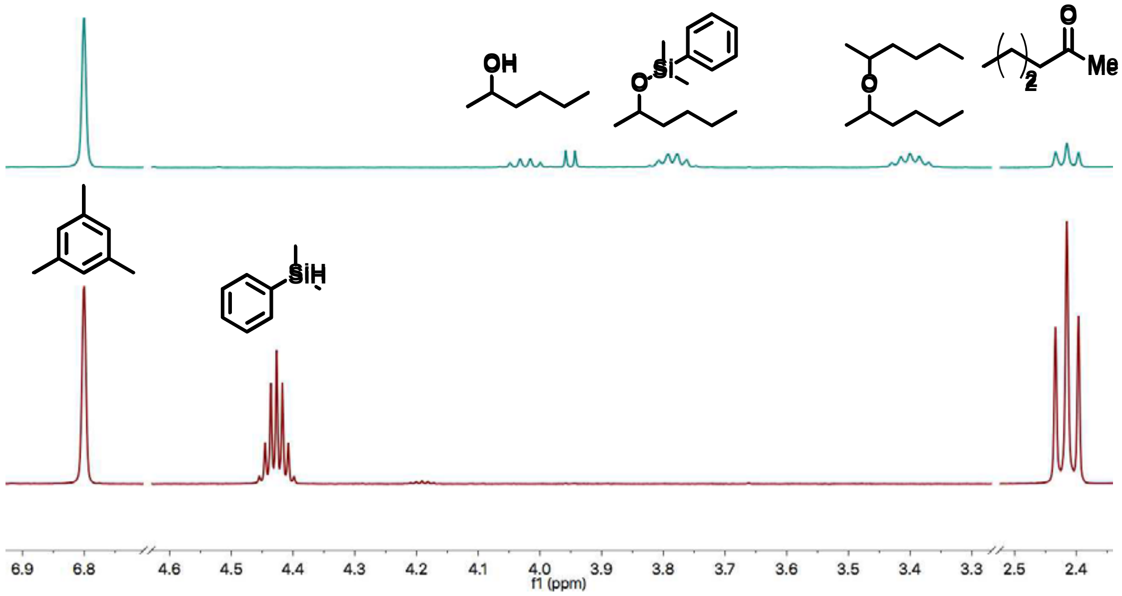


Figure S8. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 2-hexanone. Starting material 2-hexanone (2.41 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(2-hexyl) ether (3.42 ppm), dimethyl[(1-methylpentyl)oxy]phenyl silane (3.78 ppm) and 2-hexanol (4.02 ppm) as the observed products (Table 1 Entry 2).

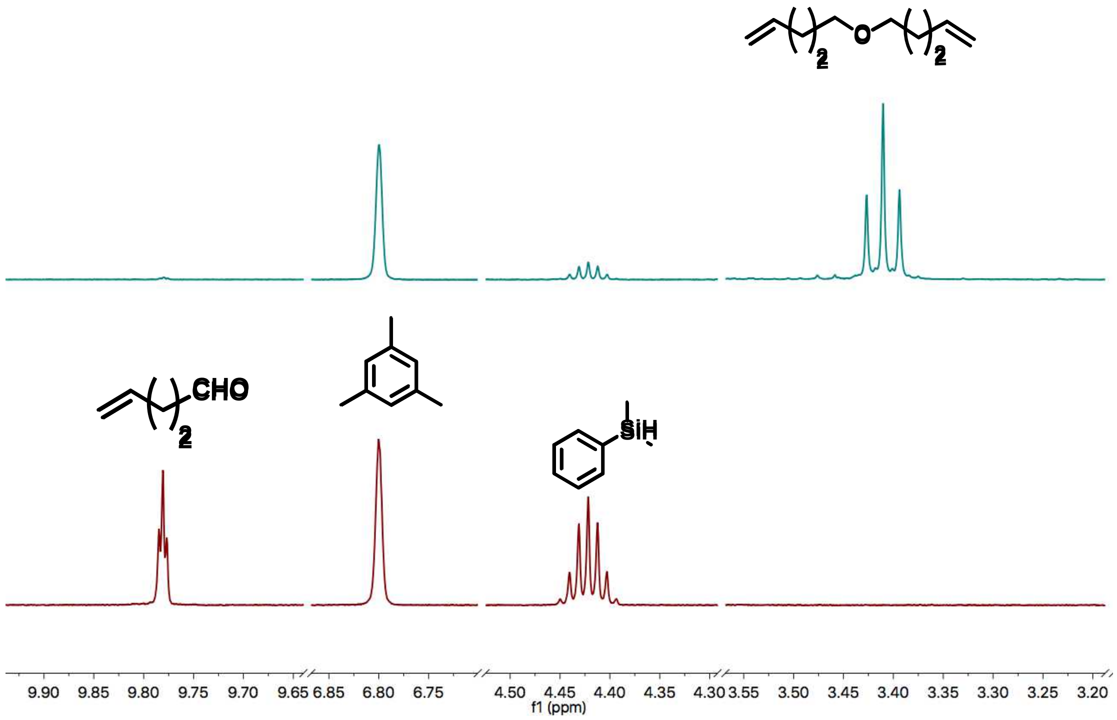


Figure S9. ^1H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 4-pentenal. Starting material 4-pentenal (9.77 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(4-pentenyl) ether (3.41 ppm) as the observed product (Table 1 Entry 3).

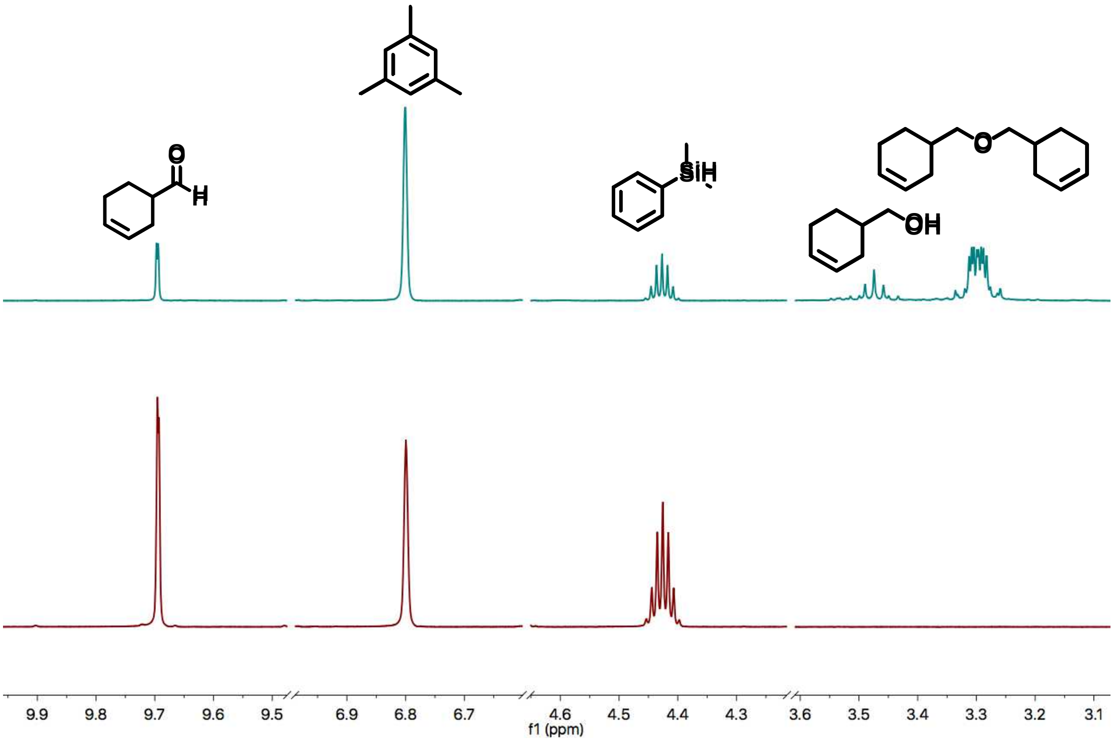


Figure S10. ^1H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 3-cyclohexene-1-carboxaldehyde. Starting material 3-cyclohexene-1-carboxaldehyde (9.70 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give 3-cyclohexene-1-methanol (3.49 ppm) and 4,4'-[oxybis(methylene)]bis-cyclohexene (3.31 ppm) as the observed products (Table 1 Entry 4).

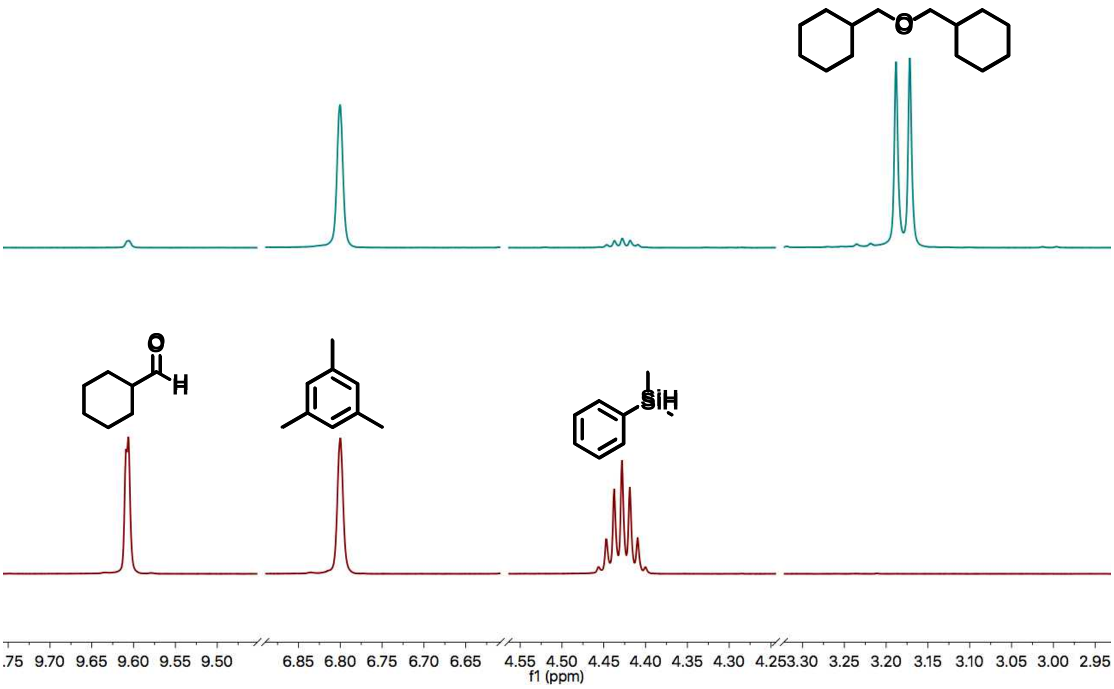


Figure S11. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of hexahydrobenzaldehyde. Starting material hexahydrobenzaldehyde (9.62 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(cyclohexylmethyl)-ether (3.17 ppm) as the observed product (Table 1 Entry 5).

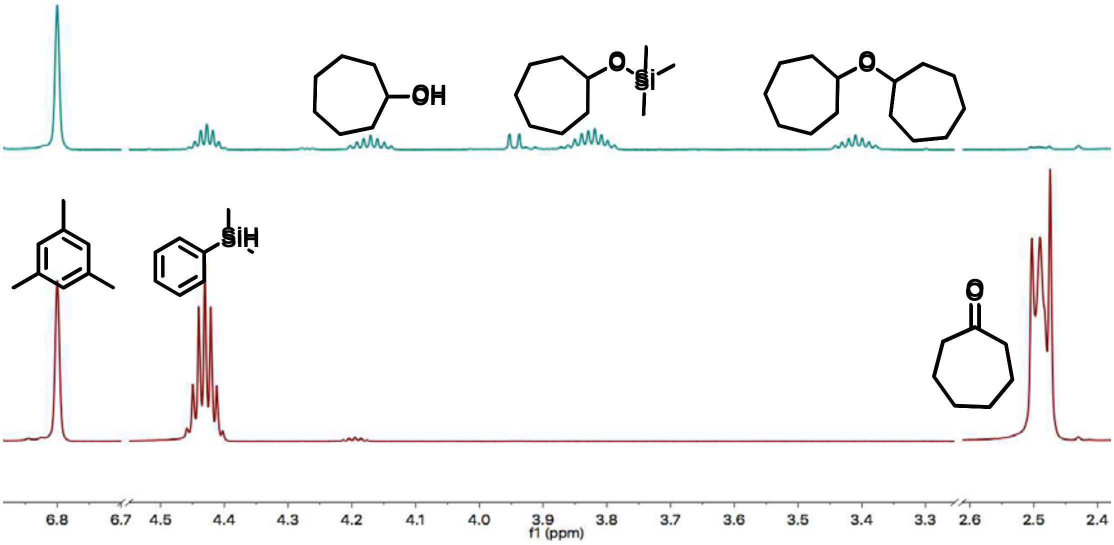


Figure S12. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of cycloheptanone. Starting materil cycloheptanone (2.49 ppm) and $PhMe_2SiH$ (4.42

ppm) reacted to give dicycloheptyl ether (3.40 ppm), [(cycloheptyloxy)dimethylsilyl]benzene (3.82 ppm) and cycloheptanol (4.18 ppm) as the observed products (Table 1 Entry 6).

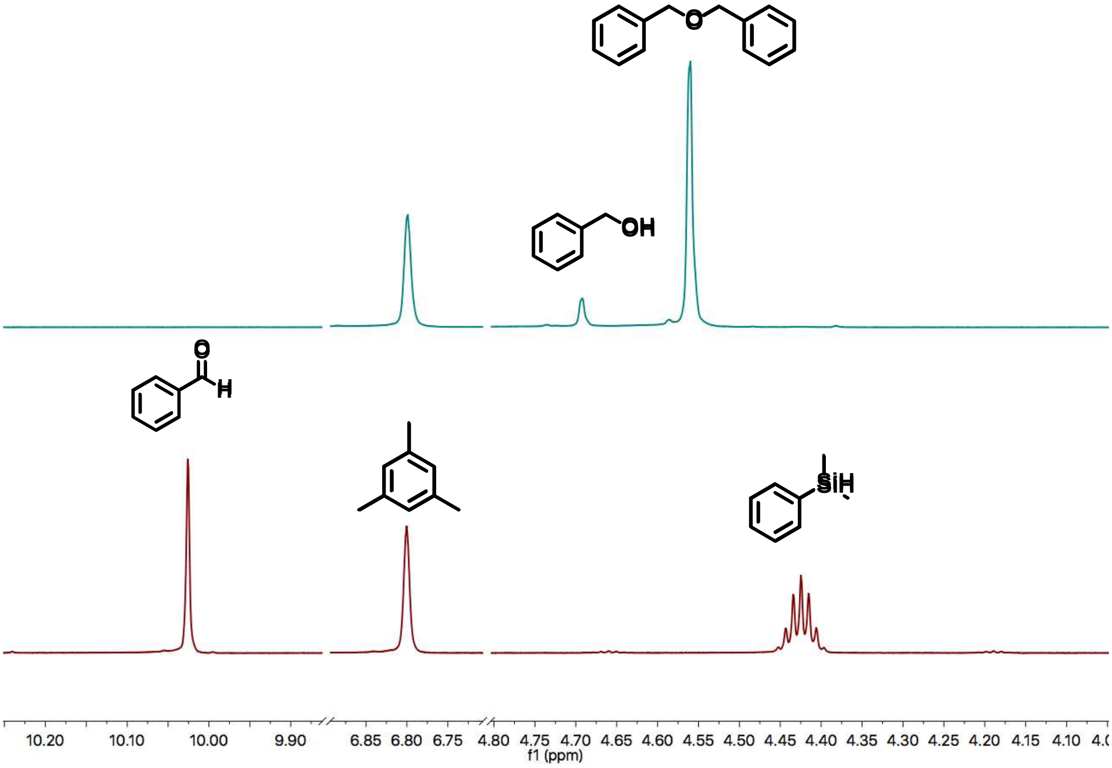


Figure S13. ^{1}H-NMR (CDCl$_3$) before (red) and after (turquoise) the reductive carbonyl coupling of benzaldehyde. Starting material benzaldehyde(10.02 ppm) and PhMe$_2$SiH (4.42 ppm) reacted to give benzyl ether (4.57 ppm) and benzyl alcohol (4.70 ppm) as the observed products (Table 1 Entry 7).

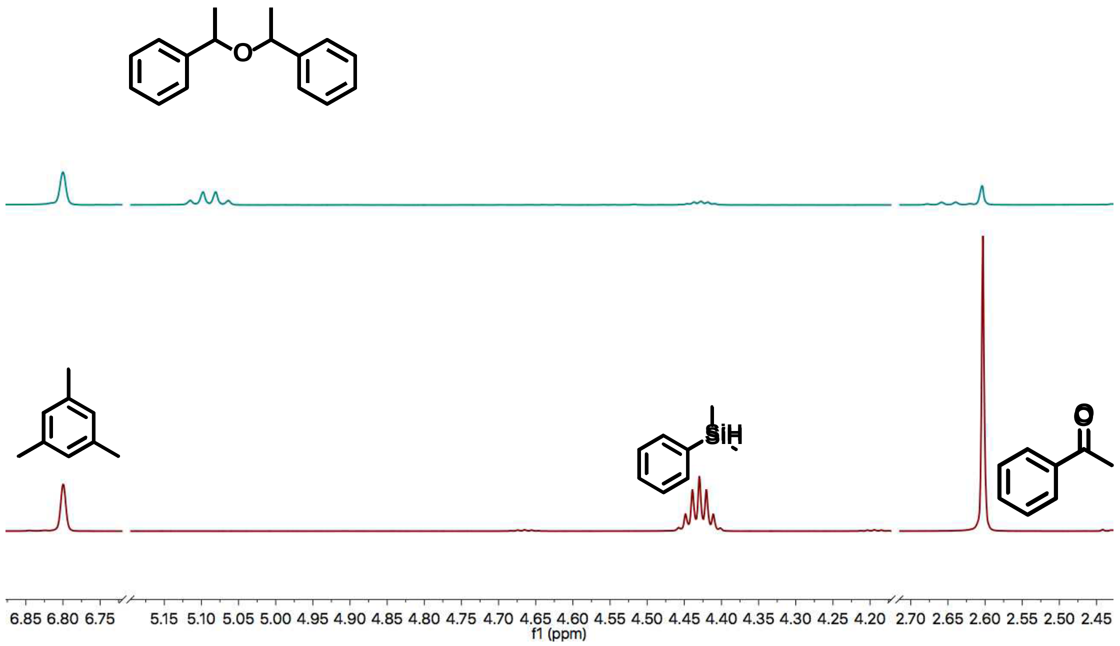


Figure S14. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of acetophenone. Starting material acetophenone (2.61 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis(1-phenylethyl) ether (5.10 ppm) as the observed product (Table 1 Entry 8).

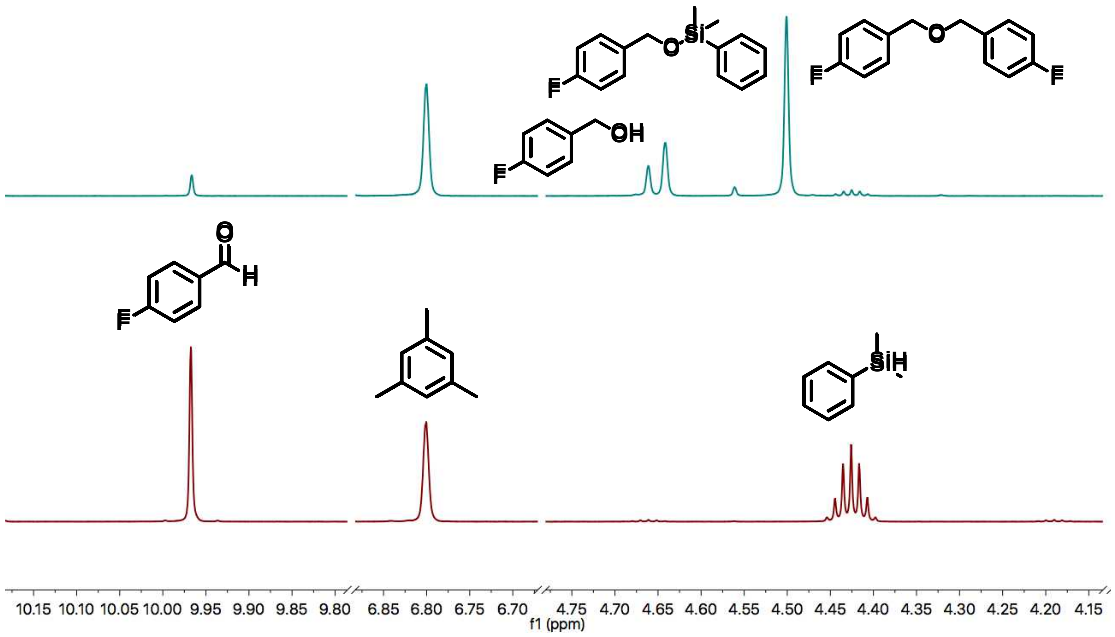


Figure S15. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 4-fluorobenzaldehyde. Starting material 4-fluorobenzaldehyde (9.96 ppm) and

PhMe$_2$SiH (4.42 ppm) reacted to give bis-(4-fluoro-benzyl)-ether (4.52 ppm), 1-[[(dimethylphenylsilyl)oxy]methyl]-4-fluoro-benzene (4.64 ppm) and 4-fluorophenyl-methanol (4.66 ppm) as the observed products (Table 1 Entry 9).

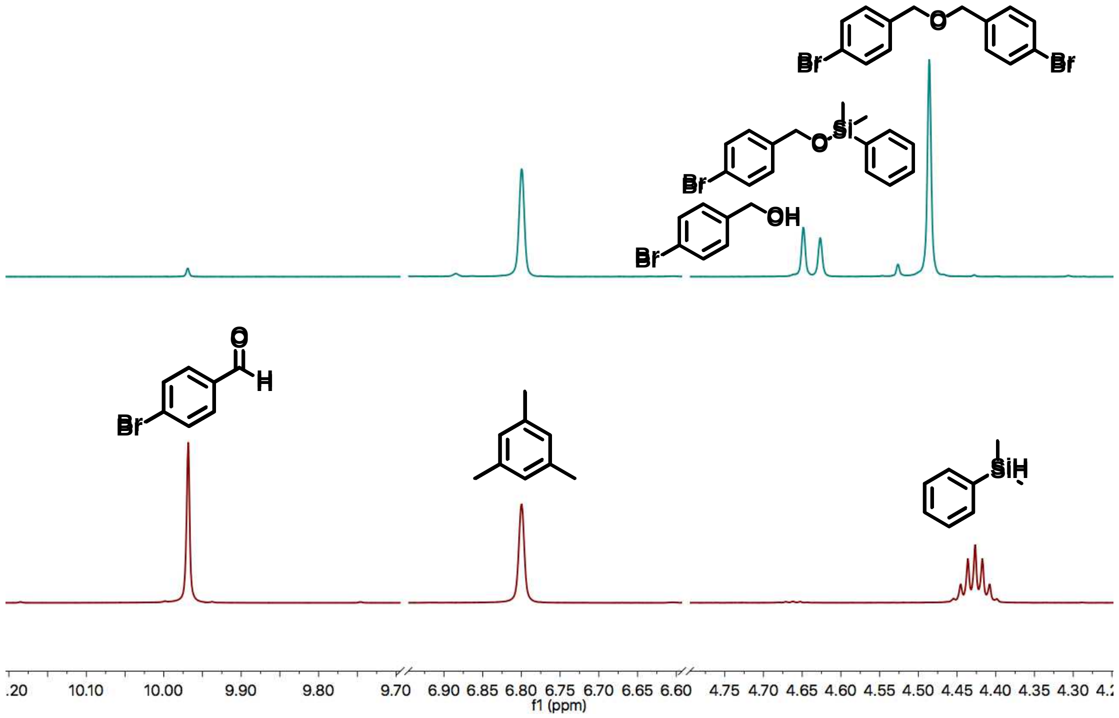


Figure S16. ^{1}H-NMR (CDCl$_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 4-bromobenzaldehyde.Starting material 4-bromobenzaldehyde (9.97 ppm) and PhMe$_2$SiH (4.42 ppm) reacted to give bis-(4-bromo-benzyl)-ether (4.49 ppm), 1-[[(dimethylphenylsilyl)oxy]methyl]-4-bromo-benzene (4.64 ppm) and 4-bromophenyl-methanol (4.66 ppm) as the observed products (Table 1 Entry 10).

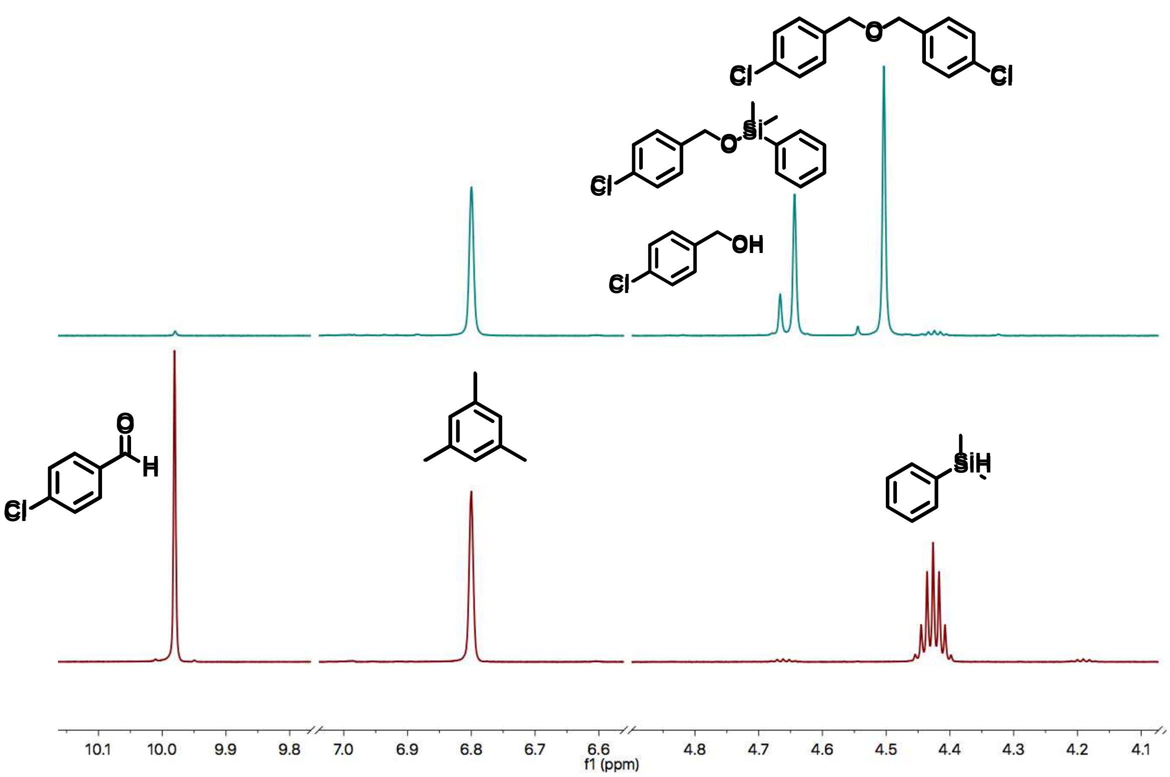


Figure S17. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 4-chlorobenzaldehyde. Starting material 4-chlorobenzaldehyde (9.99 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(4-chloro-benzyl)-ether (4.50 ppm), 1-[[(dimethylphenylsilyl)oxy]methyl]-4-chloro-benzene (4.64 ppm) and 4-chlorophenyl-methanol (4.66 ppm) as the observed products (Table 1 Entry 11).

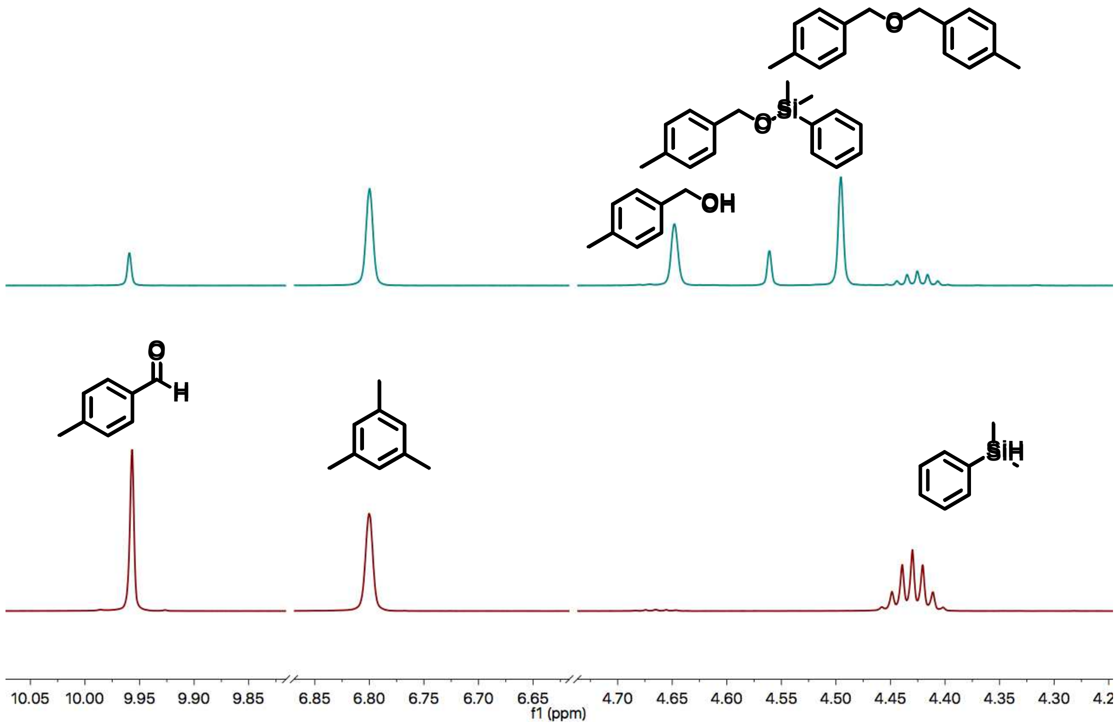


Figure S18. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 4-methylbenzaldehyde. Starting material 4-methylbenzaldehyde (9.95 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(4-methylbenzyl)-ether (4.49 ppm), 1-[[(dimethylphenylsilyl)oxy]methyl]-4-methyl-benzene (4.57 ppm) and 4-methylphenyl-methanol (4.66 ppm) as the observed products (Table 1 Entry 12).

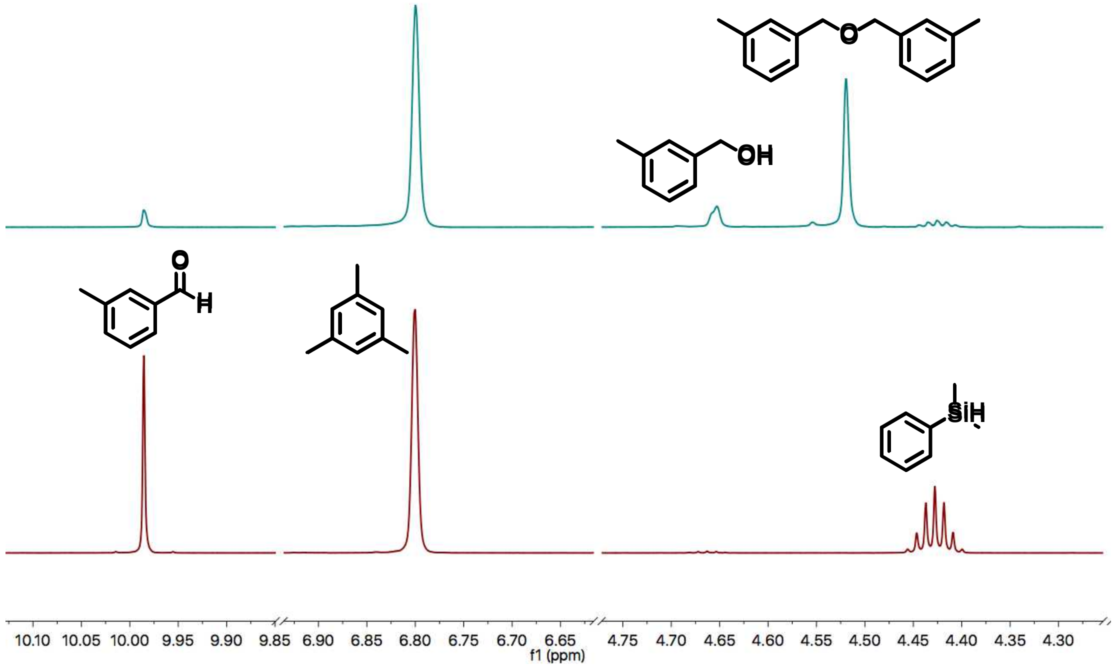


Figure S19. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 3-methylbenzaldehyde. Starting material 3-methylbenzaldehyde (9.98 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(3-methylbenzyl)-ether (4.51 ppm), and 3-methylphenyl-methanol (4.66 ppm) as the observed products (Table 1 Entry 13).

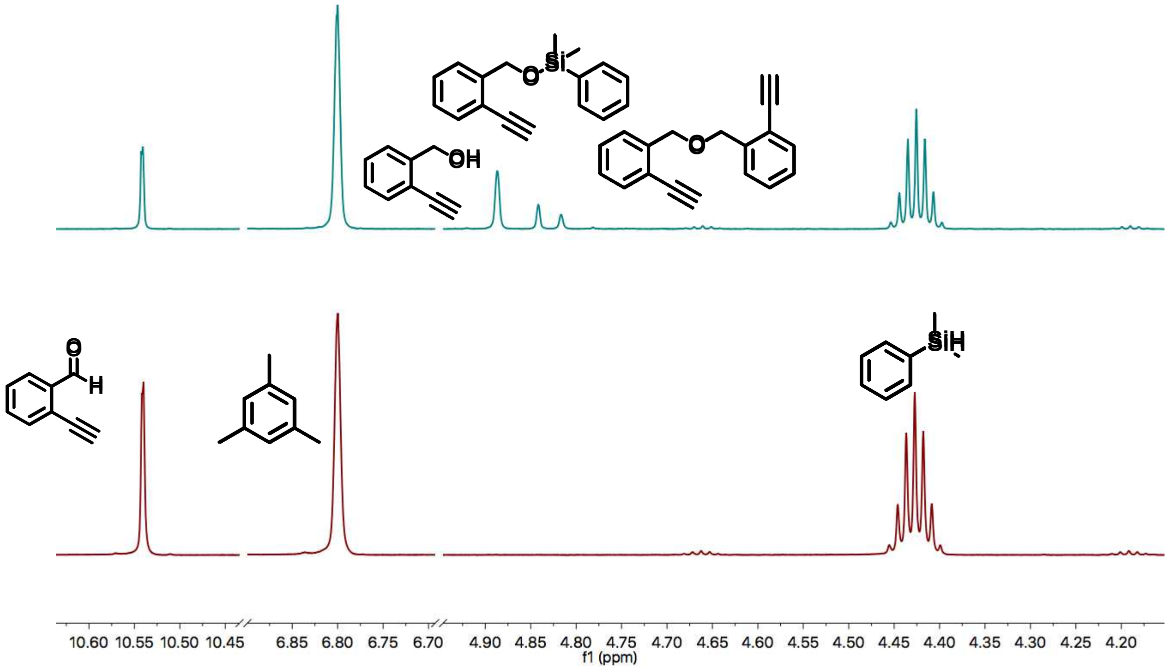


Figure S20. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 2-ethynylbenzaldehyde. Starting material 2-ethynylbenzaldehyde (10.54 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(2-ethynylbenzyl)-ether (4.82 ppm), (2-ethynylbenzyloxy)-dimethylphenyl silane (4.84 ppm) and 2-ethynylbenzyl alcohol (4.89 ppm) as the observed products (Table 1 Entry 14).

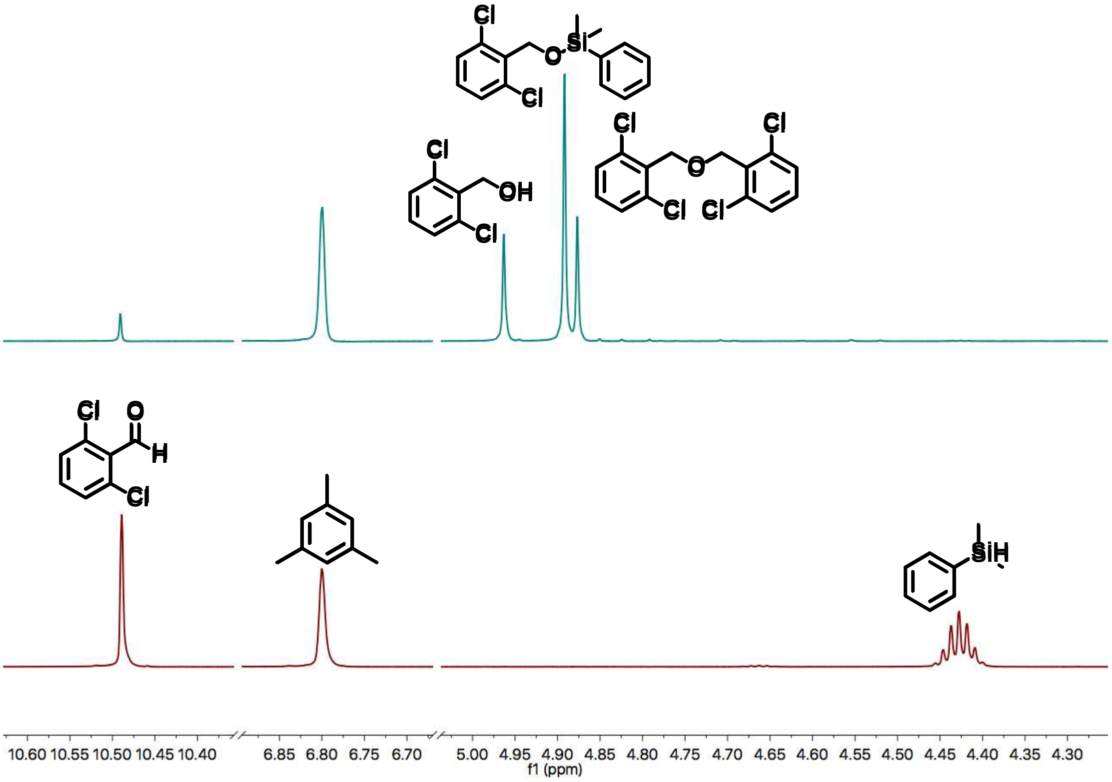


Figure S21. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the reductive carbonyl coupling of 2,6-dichlorobenzaldehyde. Starting material 2,6-dichlorobenzaldehyde (10.49 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give bis-(2,6-dichlorobenzyl)-ether (4.87 ppm), 1-[[(dimethylphenylsilyl)oxy]methyl]-2,6-dichloro-benzene (4.89 ppm) and 2,6-dichlorophenyl-methanol (4.96 ppm) as the observed products (Table 1 Entry 15).

^{1}H NMR of Reaction Products in Table S1.

^{1}H NMR ($CDCl_3$) before (red) and after (turquoise) reaction. In a typical analysis, conversion and selectivity are calculated from eq. S4 and eq. S5 as discussed above. Product selectivities are typically calculated using the R_1–O-CH_2-R_2 proton signal and identified by comparison with previous reported literature values (see spectroscopy data for full values and references). In all cases the alkene and alkyne remained unreactive.

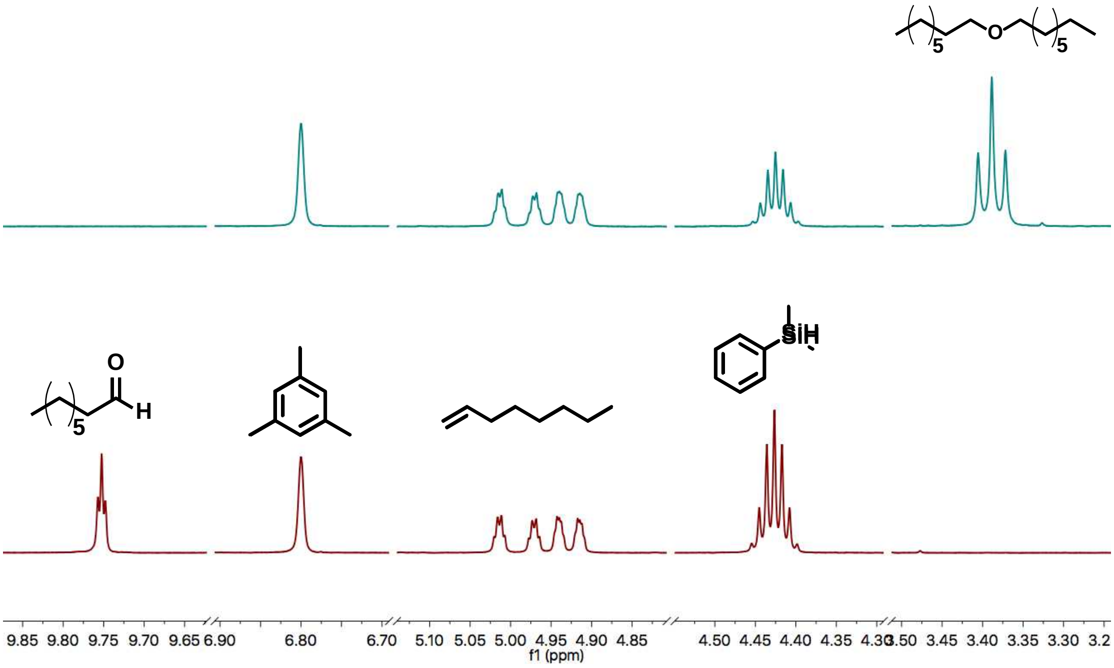


Figure S22. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the intermolecular chemoselective reductive carbonyl coupling of n-octanal in the presence of 1-octene. Starting material n-octanal (9.76 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give di-n-octyl ether(3.38 ppm) as the observed product while 1-octene remained unchanged (Table S1 Entry 1).

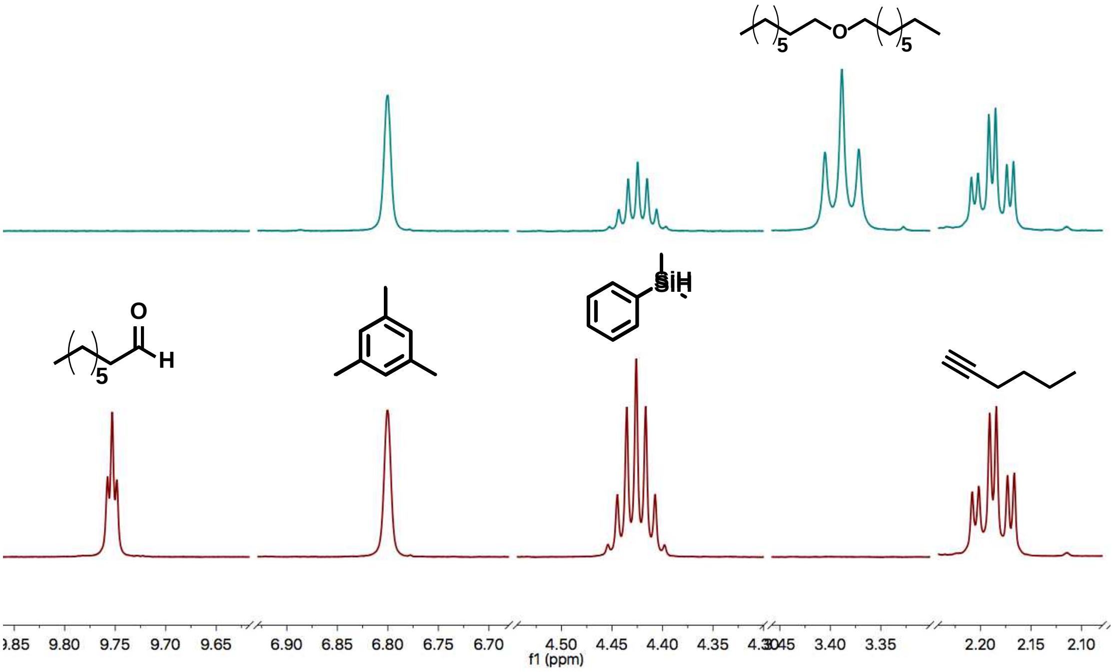


Figure S23. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the intermolecular chemoselective reductive carbonyl coupling of n-octanal in the presence of 1-hexyne. Starting material n-octanal (9.76 ppm) and PhMe$_2$SiH (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm) as the observed product while 1-hexyne remained unchanged (Table S1 Entry 2).

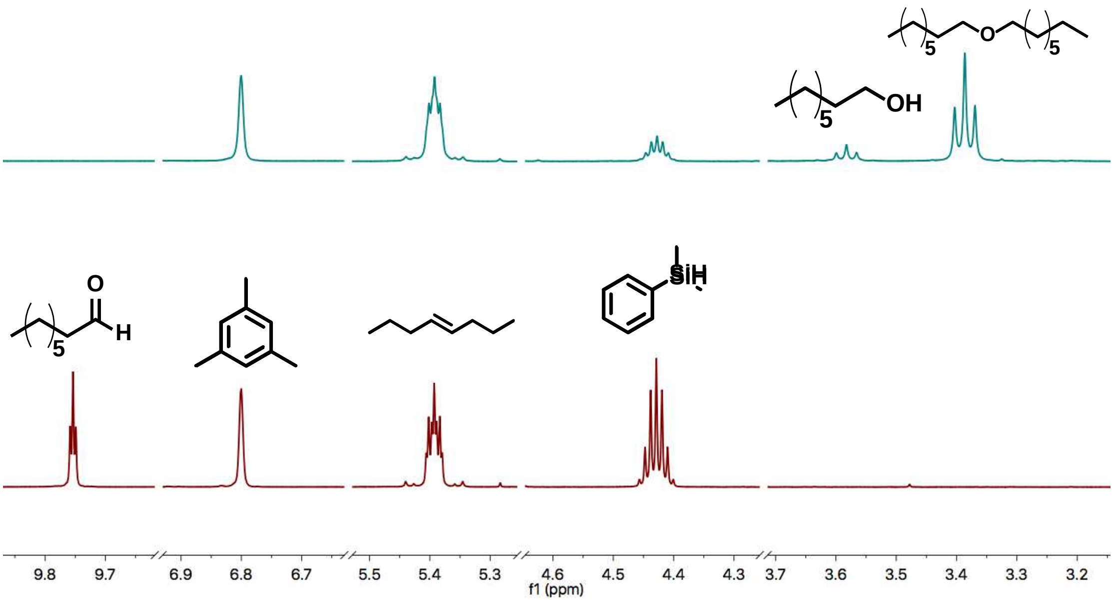


Figure S24. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the intermolecular chemoselective reductive carbonyl coupling of n-octanal in the presence of 4-octene. Starting material n-octanal (9.76 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm) as the observed product while 4-octene remained unchanged (Table S1 Entry 3).

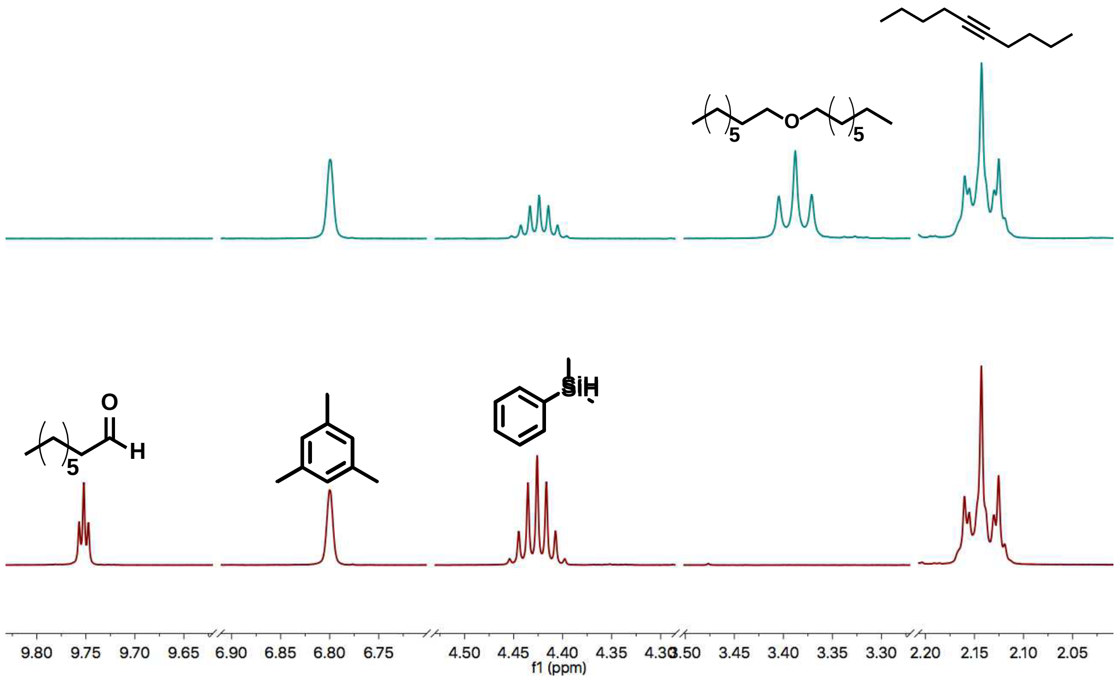


Figure S25. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the intermolecular chemoselective reductive carbonyl coupling of n-octanal in the presence of 5-decyne.Starting material n-octanal (9.76 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm) as the observed product while 5-decyne remained unchanged (Table S1 Entry 4).

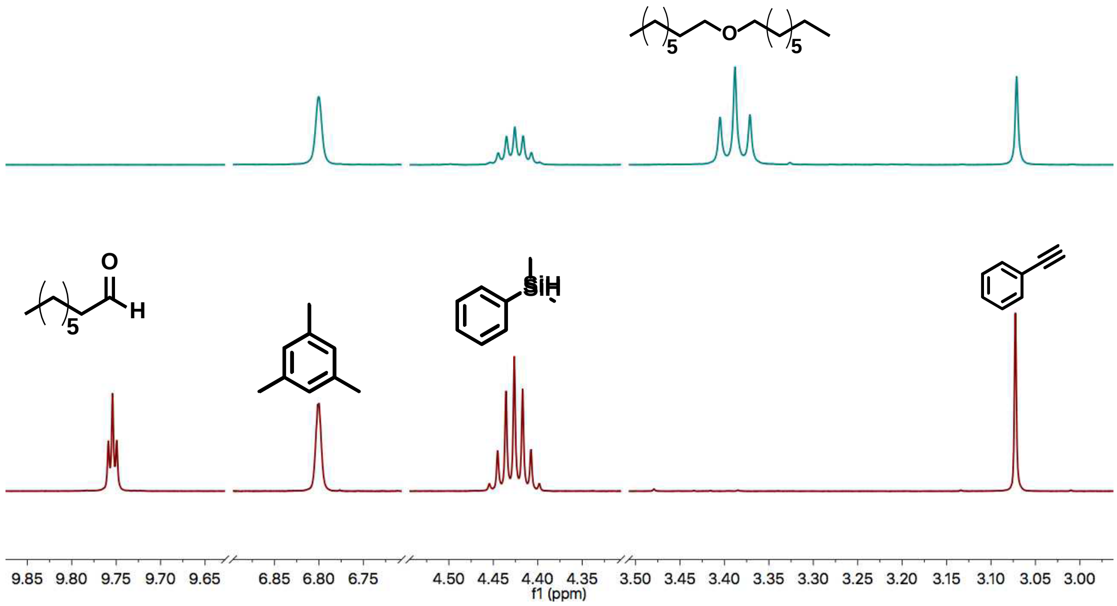


Figure S26. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the intermolecular chemoselective reductive carbonyl coupling of n-octanal in the presence of ethynylbenzene. Starting material n-octanal (9.76 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm) as the observed product while ethynybenzene remained unchanged (Table S1 Entry 5).

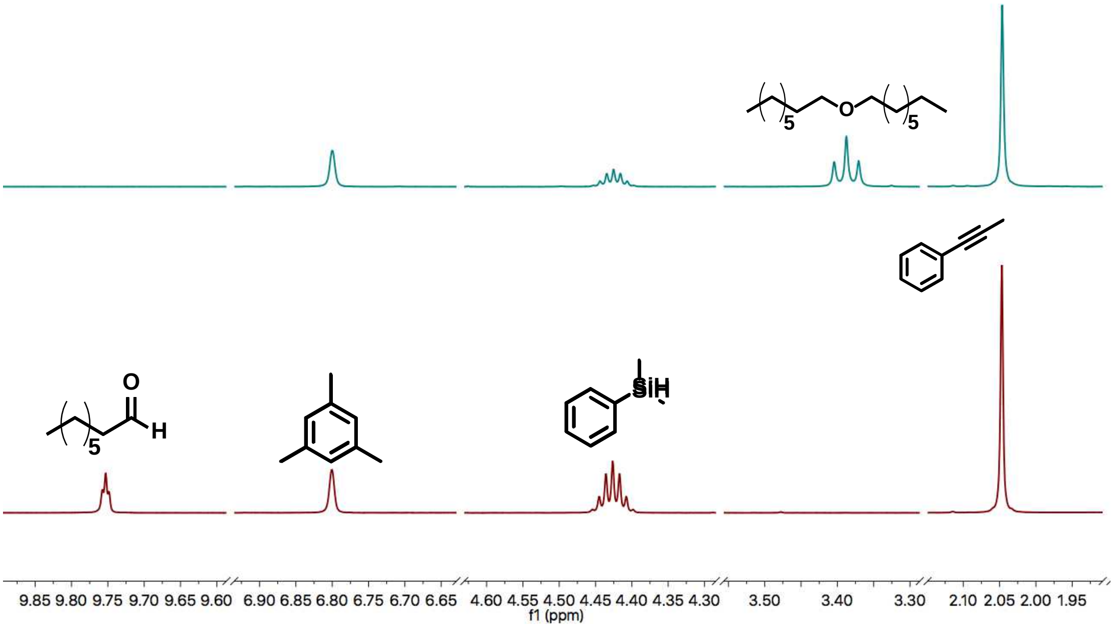
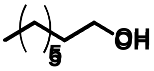


Figure S27. ^{1}H-NMR ($CDCl_3$) before (red) and after (turquoise) the intermolecular chemoselective reductive carbonyl coupling of n-octanal in the presence of 1-phenyl-1-propyne. Starting material n-octanal (9.76 ppm) and $PhMe_2SiH$ (4.42 ppm) reacted to give di-n-octyl ether (3.38 ppm) as the observed product while 1-phenyl-1-propyne remained unchanged (Table S1 Entry 6).

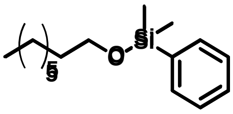
Spectroscopy Data ofor Ether, Silylether and Alcohol Products



1-Octanol (Table 1, entry 1)

^{1}H-NMR spectrum has been previously reported.**[1]**

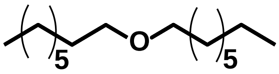
^{1}H NMR ($CDCl_3$) δ ppm 3.63 (t, 2H), 1.6-1.5 (m, 3H), 1.4-1.2 (m, 10H), 0.88 (t, 3H).



(Octyloxy)dimethylphenylsilane (Table 1, entry 1)

^{1}H-NMR spectrum has been previously reported.**[2]**

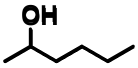
^{1}H NMR ($CDCl_3$) δ ppm 7.59-7.56 (m, 2H), 7.39-7.35 (m, 3H), 3.58 (t, 2H), 1.52 (m, 2H), 1.25(m, 10H), 0.87 (t, 3H), 0.37 (s, 6H).



Dioctyl Ether (Table 1, entry 1)

^{1}H-NMR spectrum has been previously reported.**[3]**

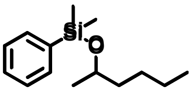
^{1}H NMR ($CDCl_3$) δ ppm 3.40 (t, 4H), 1.58 (m, 4H), 1.38–1.18 (m, 20H), 0.89 (t, 6H).



2-Hexanol (Table 1, entry 2)

^{1}H-NMR spectrum has been previously reported.[4]

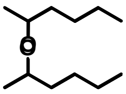
^{1}H NMR ($CDCl_3$) δ ppm 3.79 (m, 1H), 1.71 (br s, 1H), 1.51-1.17 (m, 6H), 1.18 (d, 3 H), 0.91 (t, 3 H).



Dimethyl[(1-methylpentyl)oxy]phenyl silane (Table 1, entry 2)

^{1}H-NMR spectrum has been previously reported.[5]

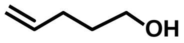
^{1}H NMR ($CDCl_3$) δ ppm 7.72-7.19 (m, 5H), 3.74(m, 1H), 1.02 (q, 3H), 1.5-0.6 (br m, 9H), 0.31 (s, 6H).



Bis(2-hexyl) ether (Table 1, entry 2)

^{1}H-NMR spectrum has been previously reported.[6]

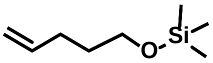
^{1}H NMR ($CDCl_3$) δ ppm 3.42-3.39 (m, 2H), 1.49-1.45 (m, 2H), 1.38-1.21 (m, 10H), 1.11 (d, 3H), 1.10 (t, 3H), 1.09 (d, 3H), 0.89 (t, 3H).



4-penten-1-ol (Table 1, entry 3)

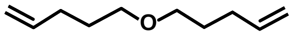
^{1}H-NMR spectrum has been previously reported.[7]

^{1}H NMR (CDCl$_3$) δ ppm 5.84 (m, 1H), 5.06 (m, 1H), 4.98 (m, 1H), 3.67 (dd, 2H), 2.19-2.11 (m, 2H), 1.72-1.64 (m, 2H), 1.61 (s, 1H).



[(7E)-7-Decene-1-yloxy]-dimethylphenyl silane (Table 1, entry 3)

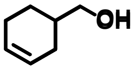
This product was not observed by ^{1}H-NMR.



Bis(4-pentenyl) Ether (Table 1, entry 3)

^{1}H-NMR spectrum has been previously reported.[8]

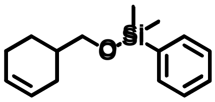
^{1}H NMR (CDCl$_3$) δ ppm 5.80 (m, 1H), 4.95 (m, 2H), 3.40 (m, 2H), 2.11 (m, 2H), 1.67 (m, 2H).



3-Cyclohexene-1-methanol (Table 1, entry 4)

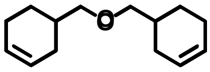
^{1}H-NMR spectrum has been previously reported.[1]

^{1}H NMR (CDCl$_3$) δ ppm 5.68-5.66 (m, 2H), 3.57-3.52 (m, 2H), 2.15-1.74 (m, 6H), 1.35-1.22 (m, 2H).



[(3-Cyclohexen-1-ylmethoxy)dimethylsilyl]-benzene (Table 1, entry 4)

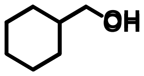
This product was not observed by ^{1}H-NMR.



4,4'-[oxybis(methylene)]bis-cyclohexene (Table 1, entry 4)

^{1}H-NMR spectrum has been previously reported.[9]

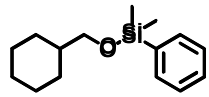
^{1}H NMR (CDCl$_3$) δ ppm 7.70-5.63 (m, 4H), 3.34-3.26 (m, 4H), 2.15-2.02 (m, 6H), 1.94-1.68 (m, 6H), 1.33-1.23 (m, 2H).



Cyclohexyl-methanol (Table 1, entry 5)

^{1}H-NMR spectrum has been previously reported.[1]

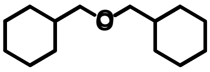
^{1}H NMR (CDCl$_3$) δ ppm 3.44 (d, 2H), 1.78-1.66 (m, 5H), 1.55-1.12 (m, 5H), 1.00-0.85 (m, 2H).



[(Cyclohexylmethoxy)dimethylsilyl]benzene (Table 1, entry 5)

^{1}H-NMR spectrum has been previously reported.[10]

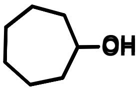
^{1}H NMR ($CDCl_3$) δ ppm 7.65-7.15 (m, 5H), 3.85-3.4 (m, 2H), 1.2 (m, 11H), 0.8 (s, 6H).



Bis-(cyclohexylmethyl)-ether (Table 1, entry 5)

^{1}H-NMR spectrum has been previously reported.[11]

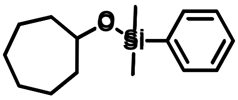
^{1}H NMR ($CDCl_3$) δ ppm 3.17 (d, 4H), 1.76-1.63 (m, 10H), 1.60-1.53 (m, 2H), 1.23 (tq, 4H), 1.15 (tq, 2H), 0.09 (dq, 4H)



Cycloheptanol (Table 1, entry 6)

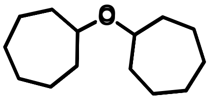
^{1}H-NMR spectrum has been previously reported.[12]

^{1}H NMR ($CDCl_3$) δ ppm 3.81 (m, 1H), 1.92-1.75 (m, 3H), 1.66-1.32 (m, 10H).



[(Cycloheptyloxy)dimethylsilyl]benzene (Table 1, entry 6)

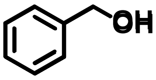
This product was empirically assigned based on the proton shift.



Dicycloheptyl ether (Table 1, entry 6)

^{1}H-NMR spectrum has been previously reported.[13]

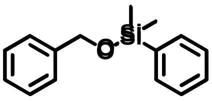
^{1}H NMR ($CDCl_3$) δ ppm 3.32 (m, 2H), 1.9-0.9 (m, 24H)



Benzyl alcohol (Table 1, entry 7)

^{1}H-NMR spectrum has been previously reported.[14]

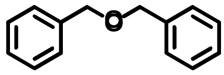
^{1}H NMR ($CDCl_3$) δ ppm 7.42-7.29 (m, 5H), 4.72 (s, 2H), 2.08 (br s, 1H).



[Dimethyl(phenylmethoxy)silyl]benzene (Table 1, entry 7)

^{1}H-NMR spectrum has been previously reported.**14**

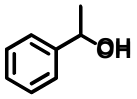
^{1}H NMR ($CDCl_3$) δ ppm 7.50-7.20 (m, 10H), 4.72 (s, 2), 0.43 (s, 6H).



Benzyl ether (Table 1, entry 7)

^{1}H-NMR spectrum has been previously reported.**15**

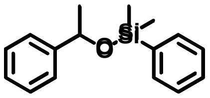
^{1}H NMR ($CDCl_3$) δ ppm 7.42-7.38 (m, 8H), 7.35-7.32 (m, 2H), 4.61 (s, 4H).



1-Phenyl-ethanol (Table 1, entry 8)

^{1}H-NMR spectrum has been previously reported.**14**

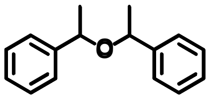
^{1}H NMR ($CDCl_3$) δ ppm 7.4-7.28 (m, 5H), 4.89 (q, 1H), 2.05 (br s, 1H), 1.5 (d, 3H).



[Dimethyl(1-phenylethoxy)silyl]benzene (Table 1, entry 8)

^{1}H-NMR spectrum has been previously reported.**14**

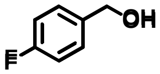
^{1}H NMR ($CDCl_3$) δ ppm 7.69-7.30 (m, 10H), 4.90 (q, 1H), 1,46 (d, 2H), 0.38-0.33 (d, 6H).



Bis(1-phenylethyl) ether (Table 1, entry 8)

^{1}H-NMR spectrum has been previously reported.**16**

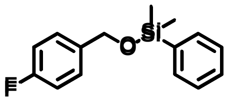
^{1}H NMR ($CDCl_3$) δ ppm 7.42-7.35 (m, 2H), 7.31-7.27 (m, 8H), 4.51 (q, 1H), 4.32 (q, 1H), 1.54 (d, 3H), 1.46 (d, 3H).



4-Fluorophenyl-methanol (Table 1, entry 9)

^{1}H-NMR spectrum has been previously reported.**14**

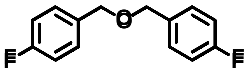
^{1}H NMR ($CDCl_3$) δ ppm 7.32 (m, 2H), 7.05 (m, 2H), 4.66 (s, 2H), 1.76 (br s, 1H).



1-[[(dimethylphenylsilyl)oxy]methyl]-4-fluoro-benzene (Table 1, entry 9)

^{1}H-NMR spectrum has been previously reported.[17]

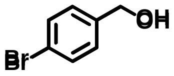
^{1}H NMR ($CDCl_3$) δ ppm 7.65-7.59 (m, 2H), 7.46-7.37 (m, 3H), 7.31-7.25 (m, 2H), 7.06-6.97 (m, 2H), 4.67 (q, 2H), 0.45 (s, 6H)



Bis-(4-fluoro-benzyl)-ether (Table 1, entry 9)

^{1}H-NMR spectrum has been previously reported.**18**

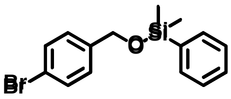
^{1}H NMR (CDCl$_3$) δ ppm 7.37 (m, 4H), 7.04 (m, 4H), 4.52 (s, 4H).



4-Bromophenyl-methanol (Table 1, entry 10)

^{1}H-NMR spectrum has been previously reported.[14]

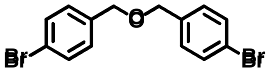
^{1}H NMR (CDCl$_3$) δ ppm 7.50 (d, 2H), 7.24 (d, 2H), 4.65 (d, 2H), 1.78 (t, 1H).



(4-Bromo-benzyloxy)-dimethyl-phenyl-silane (Table 1, entry 10)

^{1}H-NMR spectrum has been previously reported.[19]

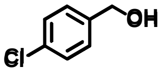
^{1}H NMR (CDCl$_3$) δ ppm 7.61-7.57 (m, 2H), 7.48-7.38 (m, 5H), 7.17 (m, 2H), 4.64 (s, 2H), 0.42 (s, 6H).



Bis-(4-bromo-benzyl)-ether (Table 1, entry 10)

^{1}H-NMR spectrum has been previously reported.[20]

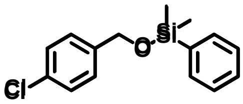
^{1}H NMR (CDCl$_3$) δ ppm 7.48-7.46 (m, 4H), 7.23-7.21 (m, 4H), 4.48 (s, 4H).



4-Chlorobenzyl alcohol (Table 1, entry 11)

^{1}H-NMR spectrum has been previously reported.[21]

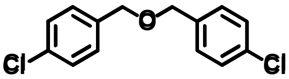
^{1}H NMR (CDCl$_3$) δ ppm 7.32 (d, 2H), 7.27 (d, 2H), 4.63 (s, 2H), 2.1 (s, br, 1H)



(4-Chlorobenzyloxy)-dimethylphenyl silane (Table 1, entry 11)

^{1}H-NMR spectrum has been previously reported.[22]

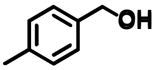
^{1}H NMR (CDCl$_3$) δ ppm 7.78 (m, 2H), 7.57 (m, 3H), 7.43 (d, 2H), 7.39 (d, 2H), 4.82 (s, 2H), 0.61 (s, 6H).



Bis-(4-chlorobenzyl)-ether (Table 1, entry 11)

^{1}H-NMR spectrum has been previously reported.[23]

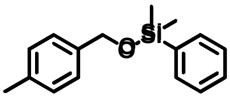
^{1}H NMR (CDCl$_3$) δ ppm 7.34-7.25 (m, 8H), 4.41 (s, 4H).



4-Methylbenzyl alcohol (Table 1, entry 12)

^{1}H-NMR spectrum has been previously reported.[24]

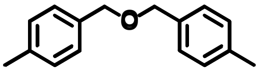
^{1}H NMR ($CDCl_3$) δ ppm 7.26 (d, 2H), 7.17 (d, 2H), 4.63 (s, 2H), 2.35 (s, 3H), 1.73 (s, 1H).



(4-Methylbenzyloxy)-dimethylphenyl-silane (Table 1, entry 12)

^{1}H-NMR spectrum has been previously reported.[25]

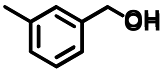
^{1}H NMR ($CDCl_3$) δ ppm 7.62–7.12 (m, 9H), 4.70 (s, 2H), 2.34 (s, 3H), 0.36 (s, 3H), 0.35 (s, 3H)



Bis-(4-methylbenzyl)-ether (Table 1, entry 12)

^{1}H-NMR spectrum has been previously reported.[26]

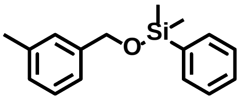
^{1}H NMR ($CDCl_3$) δ ppm 7.24 (2H, d), 7.14 (2H, d), 4.49 (4H, s), 2.34 (6H, s).



3-Methyl-benzenemethanol (Table 1, entry 13)

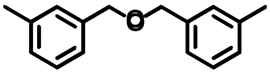
^{1}H-NMR spectrum has been previously reported.[27]

^{1}H NMR ($CDCl_3$) δ ppm 7.31-7.27 (t, 1H), 6.95-6.93 (d, 2H), 6.86 (d, 1H), 4.62 (s, 2H), 3.81(s, 3H), 3.63 (s, 1H).



1-[[(Dimethylphenylsilyl)oxy]methyl]-3-methyl-benzene (Table 1, entry 13)

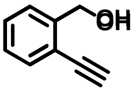
This product was empirically assigned based on the proton shift.



Bis(3-methyl)benzylether (Table 1, entry 13)

^{1}H-NMR spectrum has been previously reported.[28]

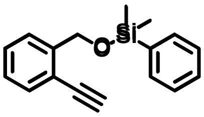
^{1}H NMR ($CDCl_3$) δ ppm d 7.23 (t, 2H), 7.18-7.14 (m, 4H), 7.01 (d, 2H), 4.51 (s, 4H), 2.34 (s, 6H);



2-Ethynyl-benzyl alcohol (Table 1, entry 14)

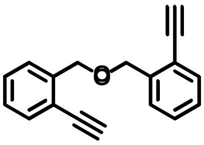
^{1}H-NMR spectrum has been previously reported.[29]

^{1}H NMR ($CDCl_3$) δ ppm 7.51 (dd, 1H), 7.45 (dd, 1H), 7.37 (td, 1H), 7.26 (td, 1H), 4.84 (s, 2H), 3.33 (s, 1H), 2.07 (d, 1H);



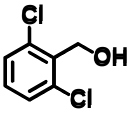
(2-Ethynyl-benzyloxy)-dimethylphenyl silane (Table 1, entry 14)

This product was empirically assigned based on the proton shift.



Bis-(2-Ethynyl-benzyl)-ether (Table 1, entry 14)

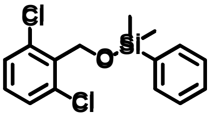
This compound was verified by an alternative synthetic method previously reported and matched accordingly.[11]



2,6-Dichlorobenzyl alcohol (Table 1, entry 15)

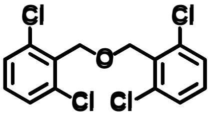
^{1}H-NMR spectrum has been previously reported.[30]

^{1}H NMR (CDCl$_3$) δ ppm 7.50-7.10 (m, 3H), 4.96 (s, 2H), 2.13 (br s, 1H).



(2,6-Dichlorobenzyloxy)-dimethylphenyl silane (Table 1, entry 15)

This product was empirically assigned based on the proton shift.



Bis-(2,6-dichlorobenzyloxy)-ether (Table 1, entry 15)

^{1}H-NMR spectrum has been previously reported.[31]

^{1}H NMR (CDCl$_3$) δ ppm 7.21 (s, 6H), 4.87 (s, 4H).

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