Supporting Information

C–H Activation on Co,O Sites: Isolated Surface Sites versus Molecular Analogs

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Experimental

      All experiments were performed under inert atmosphere using glovebox (Ar), Schlenk (Ar), or high vacuum (10^{-5} mbar) techniques. Pentane was dried by passage through two columns of activated alumina and degassed prior to use. Tetrahydrofuran (THF) was distilled from purple Na/benzophenone under Ar and stored over activated molecular sieves. C_6D_6 was vacuum distilled from purple

Na/benzophenone. HOSi(OtBu)$_3$ was obtained from Sigma-Aldrich and used as received. SiO$_{2\text{-}700}$ was prepared by calcining Aerosil-200 at 500 °C (5 °C/min) under air for 4h, evacuated to high vacuum at the same temperature for 12h, and subsequently heated to 700 °C (5 °C/min) for 4 h under high vacuum. Propyne was dried by storing over activated 4Å molecular sieves. Oxygen was removed by cooling to 77K to condense propyne gas, followed by removal of residual gas to high vacuum. ^{1}H NMR spectra (including kinetic experiments) were obtained at either 200, 300, or 400 MHz while ^{2}H NMR spectra were measured at either 61.4 or 76.8 MHz. Probe temperature was measured using a chemical shift thermometer before each kinetic run. Kinetic data by IR spectroscopy were collected using a Mettler-Toledo React IR system equipped with a Si ATR probe inside a custom made air-tight reactor to which solution could be added by syringe all of which was submerged in a constant temperature bath. This data was analyzed by global analysis to find the spectra of reactant and product molecules. X-band EPR spectra (9.5 GHz) were measured using a liquid helium cryostat at down to 4K. UV-Vis spectra were collected using a Cary 5000 UV-Vis-NIR spectrometer equipped with a diffuse reflectance sample stage. Gas chromatography was performed on an Agilent 7980A GC with flame ionization detection or equivalent machine equipped with a quadrupole MS detector. Transmission infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer. Elemental analyses were performed by the Mikroanalytisches Labor Pascher; Remagen, Germany.

Synthesis and Characterization

Synthesis of Co$_2$(OSi(OtBu)$_3$)$_4$ (**1**)

$$Co(N(SiMe_3)_2)_2THF \xrightarrow[\substack{pentane \\ -THF}]{2\ eq\ HOSi(OtBu)_3}$$

(S1)

1
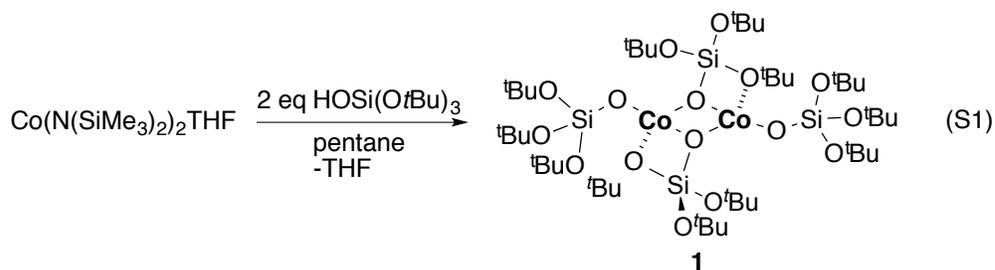
A pentane solution of HOSi(OtBu)$_3$ (1.28g (4.82 mmol) in 5 mL) was added dropwise to a solution of 0.91g (2.0 mmol) Co(N(SiMe$_3$)$_2$)$_2$THF[1] in 10 mL of pentane. The solution changed color immediately from emerald green to dark blue. After stirring this solution for 3h, the solvent was removed in vacuo to reveal a dark blue powder. This powder was heated to 55°C under high vacuum to sublime away excess silanol and THF of solvation, which caused the color to change from deep blue to light green. Isolated 0.89 g (63% yield) ^{1}H NMR (δ, C$_6$D$_6$) –3.11 ppm. UV-Vis spectrum (pentane, 0.16M) λ(nm) [ε]: 677 [23], 602 [5], 448 [3]. Magnetic moment μ_{eff} = 9.8 μ_B (Evans Method). Elemental Analysis: (Theor) 49.2 %C, 9.3 %H. (Exp) 49.0 %C, 9.0 %H. Crystals of X–ray quality were obtained by recrystallization from pentane at –40°C. Ortep diagram and crystal parameters shown below.
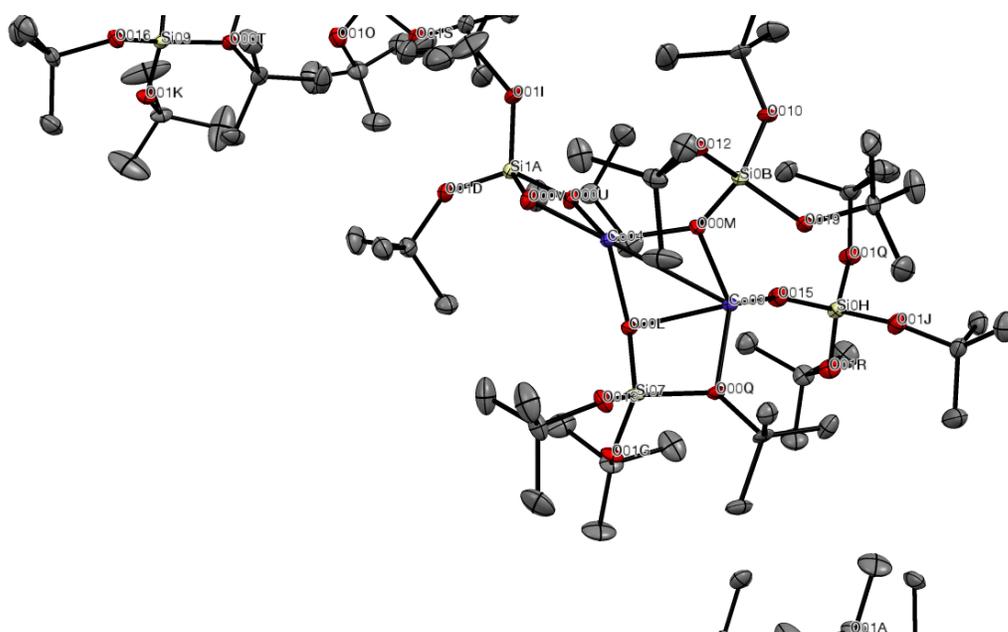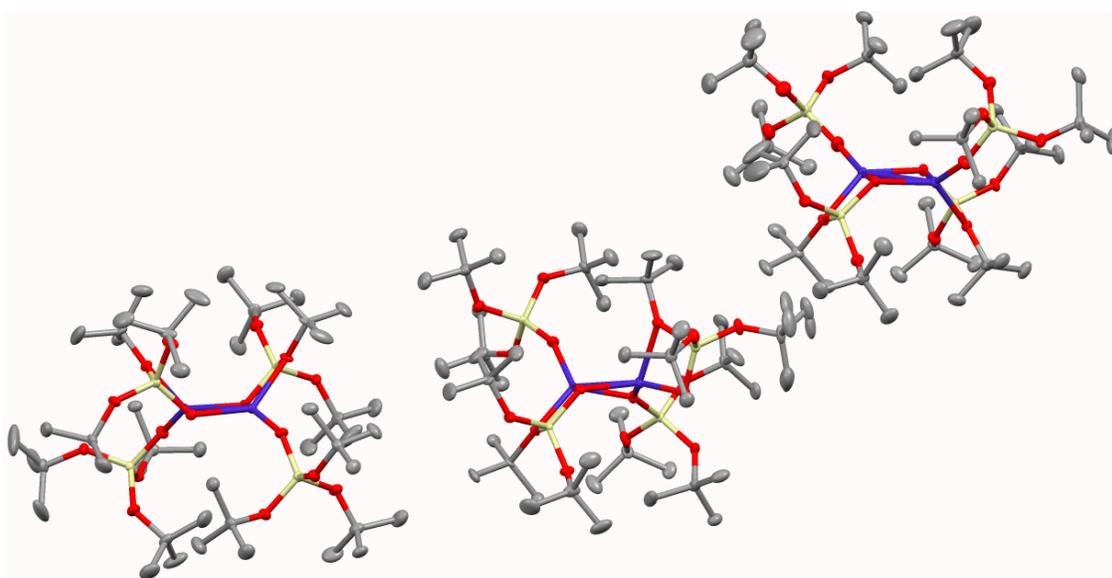
Figure S 1. Thermal ellipsoid diagram of the asymmetric unit of **1** (top) and of one of the three independent molecules in the asymmetric unit (bottom) of complex **1**. (hydrogens omitted for clarity)

Table S 1. X-ray diffraction parameters for **1**

Parameter	$Co_2(OSi(OtBu)_3)_4$ (**1**)
Chemical Formula	$C_{48}H_{108}O_{16}Si_4Co_2$

Crystal size (mm)	0.47 × 0.33 × 0.23
Space group	P -1
Volume (Å^3)	9983.9(19)
a (Å)	12.0833(14)
b (Å)	19.848(2)
c (Å)	41.813(5)
α (°)	90.457(2)
β (°)	92.824(3)
γ (°)	94.530(3)
Z	6
Formula weight (Da)	1171.56
μ	0.625
F(000)	3804
Temp (K)	103.6
Total no Reflections	35282
Unique reflections (R$_{int}$ %)	1920
Final R indices (I > 2σ(I))	4.83
Largest diff peak and hole	0.730 / -0.561
GOF	1.209
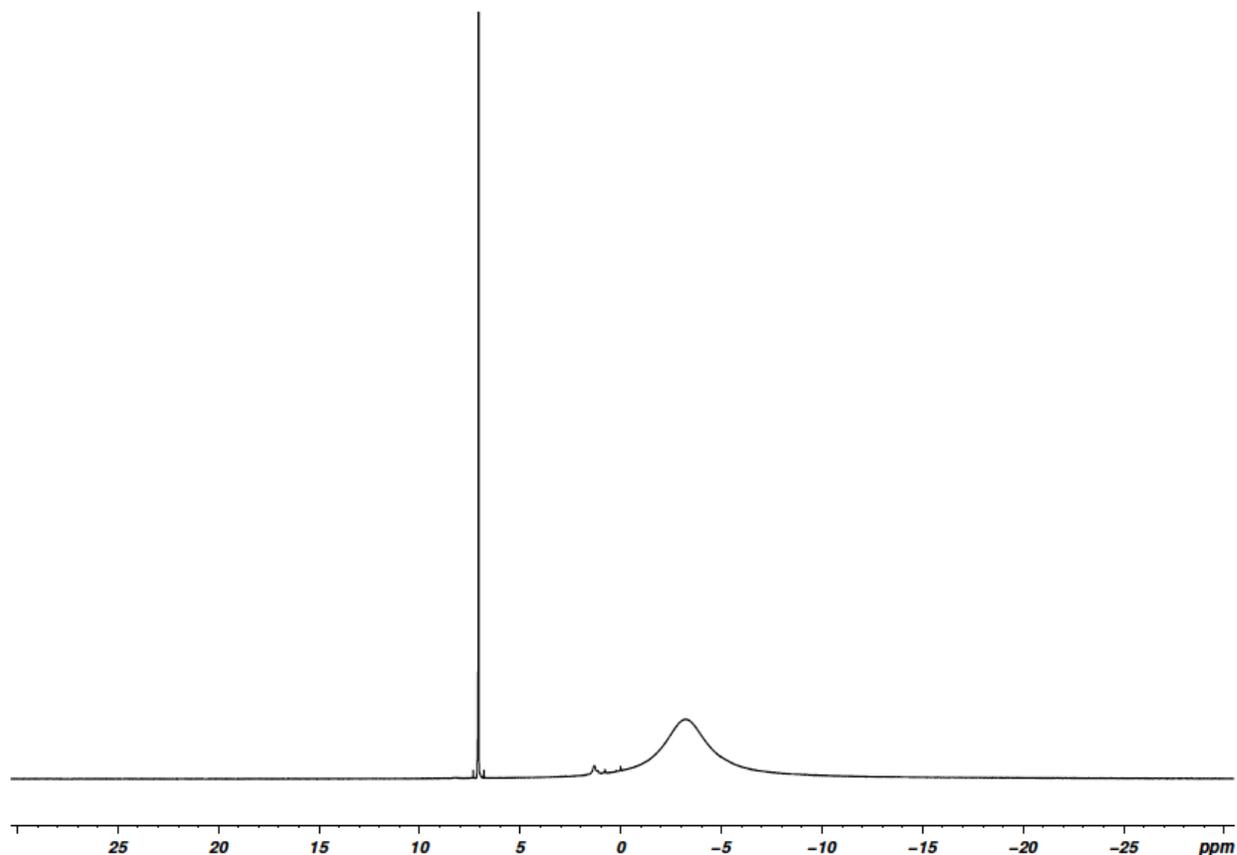
Figure S 2. ^1H NMR spectrum of **1**

*Grafting of **1** on SiO$_{2\text{-}700}$* **(2)**

Complex **1** (304 mg, 0.26 mmol) was dissolved in benzene (~ 10 mL) and added to 1 g of SiO$_{2\text{-}700}$. This slurry was stirred gently for 3h, during which time the solid gradually gained a blue color, then filtered and washed with pure benzene (3 × 10 mL) until the washings were clear. This material was then dried under high vacuum and stored under inert atmosphere. In order to asses the stoichiometry, the grafting was performed in an NMR tube by mixing 4.7 mg of **1** (0.00401 mmol), with 13 mg of SiO$_{2\text{-}700}$ (0.00338 mmol OH) in C$_6$D$_6$. ^1H NMR spectroscopy using ferrocene as internal standard showed that grafting produced 0.00378 mmol of **5** while consuming 0.00179 mmol of **1**,

corresponding to a ratio of 2 equiv of **5** produced per **1** consumed. UV-Vis λ(nm): 673, 575, 512. Elemental Analysis: 1.67 % Co, 4.96 % C, 0.92 % H.

Thermal treatment of 2 (3)

This material was subsequently heated 5°C /min under high vacuum to 300°C for 1h, then to 400°C for 3h, then to 500°C for 12h until all C–H bands in the IR spectrum had disappeared. The volatile components were collected and analyzed by ^{1}H NMR. The reaction gave off 1.9 eq isobutene and 0.8 eq *t*BuOH. DR-UV-Vis λ(nm): 678, 583, 503. Elemental Analysis: 1.77 % Co, < 0.1 % C, < 0.1 % H.
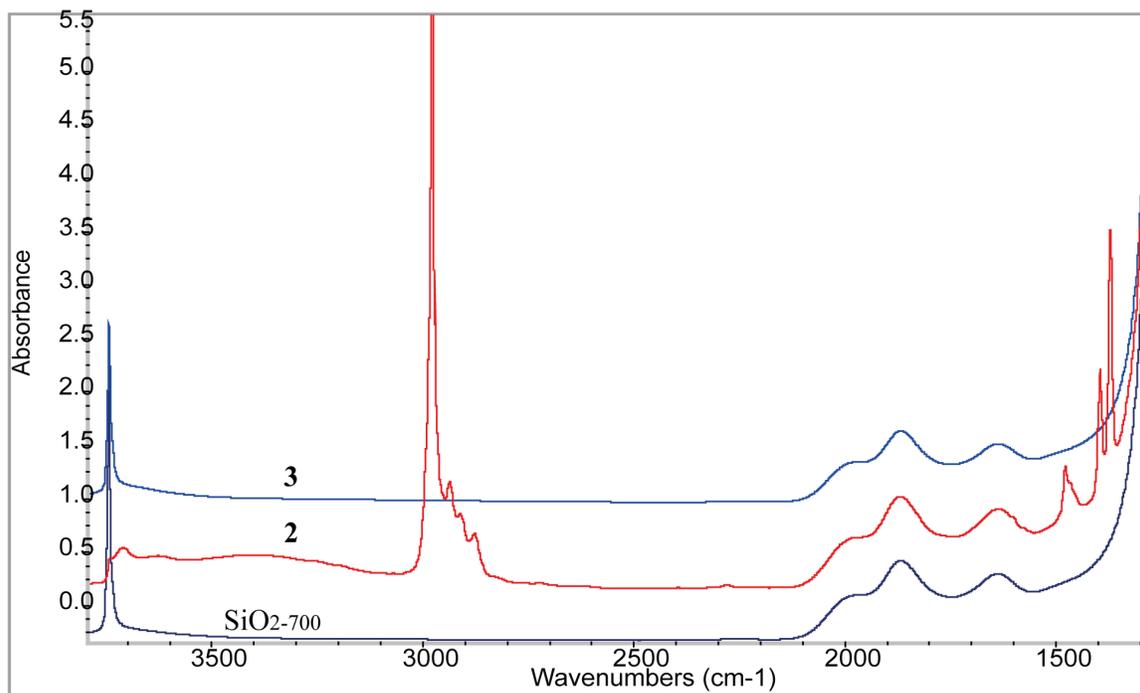
Figure S 3. IR spectra of SiO2-700 (black), **2** (red), and **3** (blue)

TMS passivation of 3 (4)

Excess dry, distilled Hexamethyldisilazane (HMDS) was vacuum transferred onto solid **6**, and stirred for 3d. After this time the excess HMDS was removed under vacuum and the remaining solid was heated at a rate of 1°C/min to 300°C and held there for 6h to

yield a blue solid of similar color to the other complexes. IR showed that almost all of the silanols had been consumed. CO absorption (2195 cm^{-1}) and XAS showed no signs of Co particle formation. Elemental Analysis: 1.79 % C, 0.31 % H, < 0.14 % N.
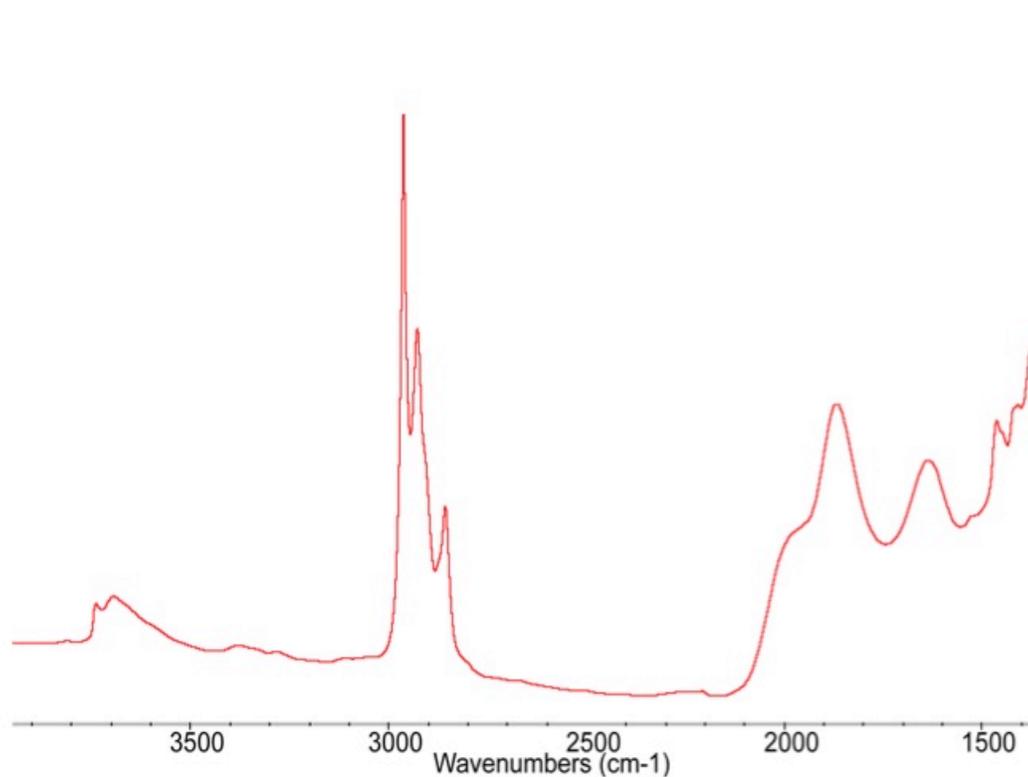

Figure S 4. IR spectrum of Co@SiO$_2$-TMS (**4**)

X-ray Absorption Spectroscopy of Co containing Species

Co K-edge transmission X-ray absorption spectroscopy was performed at the SuperXAS beamline at at SLS (PSI, Villigen, Switzerland) [P. M. Abdala *et al.*, Scientific Opportunities for Heterogeneous Catalysis Research at the SuperXAS and SNBL Beam Lines. *Chim. Int. J. Chem.*. **66**, 699–705 (2012)]. The incident photon beam provided by a 2.9 T Super Bend magnet source was selected by a Si (111) quickEXAFS monochromator and the rejection of higher harmonics and focusing were achieved by a

Si-coated collimating mirror at 2.8 mrad and a rhodium-coated torroidal mirror at 2.8 mrad. The beamline was calibrated using a Co foil (Co K edge at 7.709 keV). To avoid contact with air all samples were sealed in a glovebox. Each sample pellet (with optimized thickness for transmission detection) was placed in two aluminized plastic bags (Polyaniline (15 µm), polyethylene (15µm), Al (12µm), polyethylene (75µm) from Gruber-Folien GmbH & Co. KG) using an impulse sealer inside a glovebox; one sealing layer was removed just before the measurements. The spectra of each sample were collected for 5 min and since no X-ray damage was observed all of them were averaged. We analyzed XANES and EXAFS data using the Ifeffit program package.[2] Figure S5 shows the XANES spectra of the samples. We fitted the EXAFS spectra in R space between 1 and 4 Å with a k-weight of 3. The fitting range in k-space for sample **1** was k = 2-12.6 Å^{-1}; for **2**, **3**, and **4** it was k=2-12 Å^{-1}. So^2 was fixed at 1. Figures S6-S9 show the EXAFS fits in k- and R-space for samples **1-4**, respectively. The results are given in the Table S2.

To distinguish between contributions of Co and Si scatters in the second coordination shell we used Wavelet transform (WT) analysis of EXAFS spectra.[3] WT consist in replacement of infinitely expanded periodic function in Fourier transformation by a local function, a wavelet. WT allows plotting the experimental EAXFS spectra in two-dimensional form (in *k*- and *R*- space), helping to separate contributions from atoms of different atomic weights.

Wavelet transform of a given EXAFS signal $\chi(k)$ is defined as:

$$W_f^\psi(a, k') = \frac{1}{\sqrt{a}} \int_{-\infty}^{+\infty} \chi(k)\, \psi^*\left(\frac{k-k'}{a}\right) dk \,,$$

where the scalar product of the EXAFS signal and the complex conjugate of the wavelet (ψ^*) is calculated as a function of a and k'. a is the parameter connected with R as $a = \frac{\eta}{2R}$ and k' conform to localization of wavelet function in k space. In this work was used WT based on Morlet wavelet functions:

$$\psi(k) = \frac{1}{\sqrt{2\pi}\sigma} e^{i\eta k} e^{-k^2/2\sigma^2},$$

where parameters σ and η correspond to width and frequency of the wavelet function, respectively. These parameters should be adjusted to get an appropriate resolution in k - an R-space. For better quality of WT images we used modified WT functions described elsewhere.[3b] Figures S10-S13 show the WT of individual Co-O, Co-Co, and Co-Si scarring paths simulated from the crystallographic structure of **1** used for comparison with the WT of experimental EXAFS of **1**, **2**, **3** and **4**.
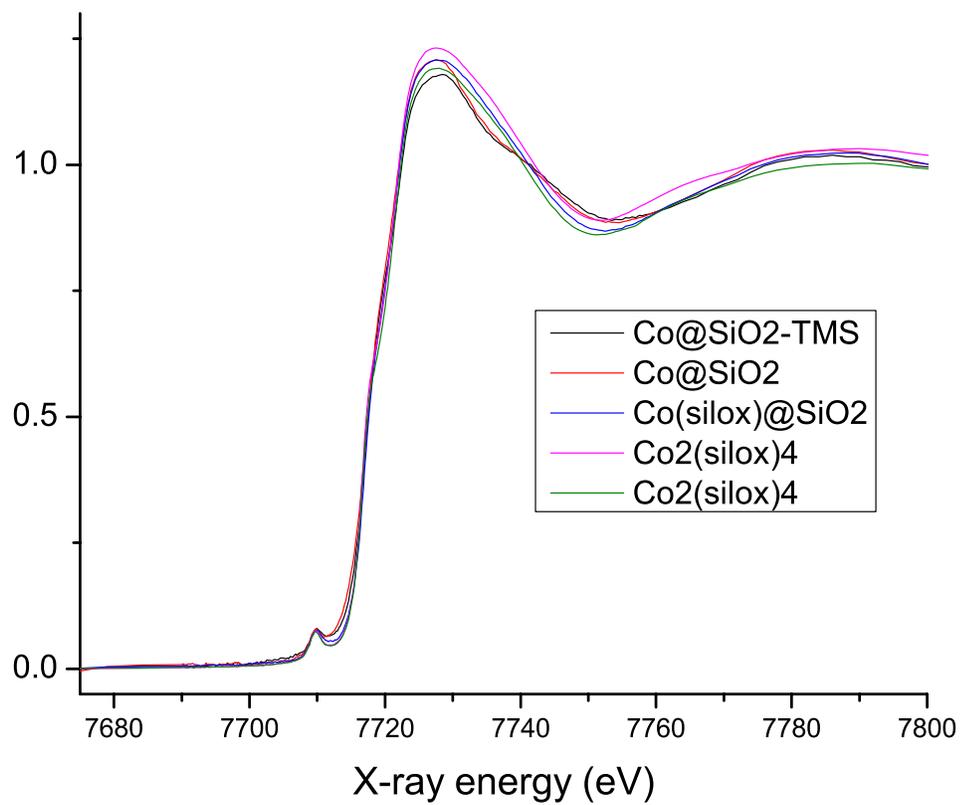
Figure S 5. XANES spectra of Co species **1**, **2**, **3**, and **4**. **1** was measured twice to check for beam damage to the sample during measurement

Table S2. Structural parameters for **1**, **2**, **3** and **4** obtained from XRD analysis and EXAFS simulations: number of neighboring atoms, r – distance to the neighboring atom, σ^2 – Debye-Waller factor, ΔE_o – threshold shift energy. Error bars are in brackets. Numbers without brackets were fixed during the fit.

	Neighbor	Number	r (Å)	σ^2 (Å^2)	ΔE_o (eV)
1[a]	O	1	1.84(4)		
		1	1.96(1)	-	-
		1	2.05(4)		
		1	2.13(4)		
	Si	1	2.77(4)		
	Co	1	2.95(4)		
	Si	1	3.24(4)		
	Si	1	3.30(4)		
1[b]	O	1	1.83(7)	0.006(6)	1(1)
		1	1.90(7)	0.006(6)	
		1	1.99(4)	0.006(6)	
		1	2.09(4)	0.006(6)	
	Si	1	2.77(2)	0.0094(8)	
	Co	1	2.92(2)	0.0094(8)	
	Si	1	3.16(4)	0.0094(8)	
	Si	1	3.42(2)	0.0094(8)	
2[b]	O	2	1.89(3)	0.008(4)	1(1)
		2	2.00(3)	0.008(4)	
	Si	1	2.74(2)	0.009(2)	
	Si	1.9(7)	3.13(2)	0.009(2)	
3[b]	O	4	1.94(1)	0.014(1)	0(1)
	Si	1.6(7)	3.12(2)	0.009(4)	
4[b]	O	4	1.97(7)	0.0099(6)	2(1)
	Si	2.0(8)	3.15(2)	0.011(4)	

a) data from XRD; b) data from EXAFS fit.
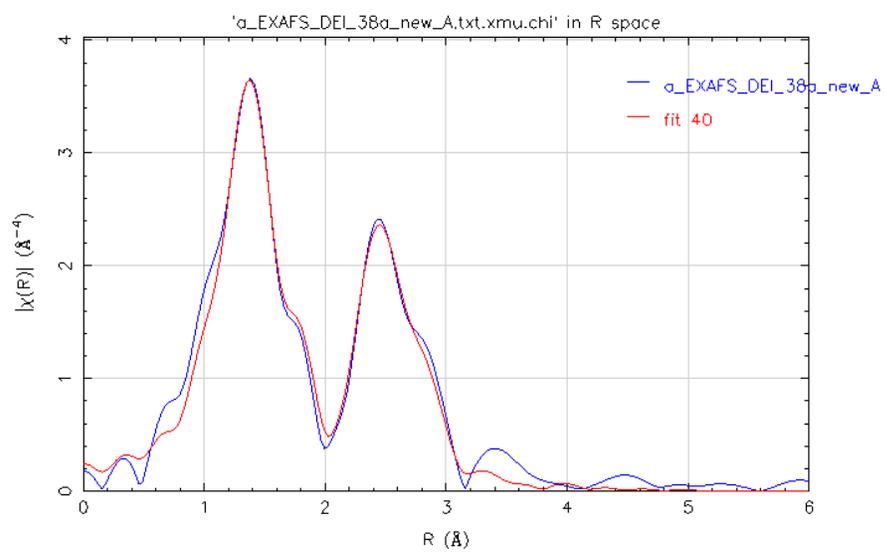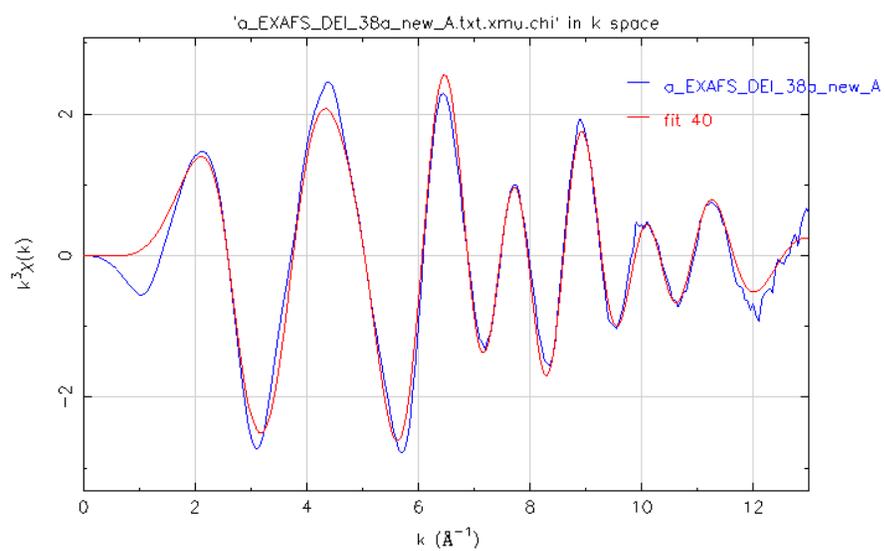
Figure S 6. EXAFS simulation of complex **1** in k (top) and R (bottom) spaces.
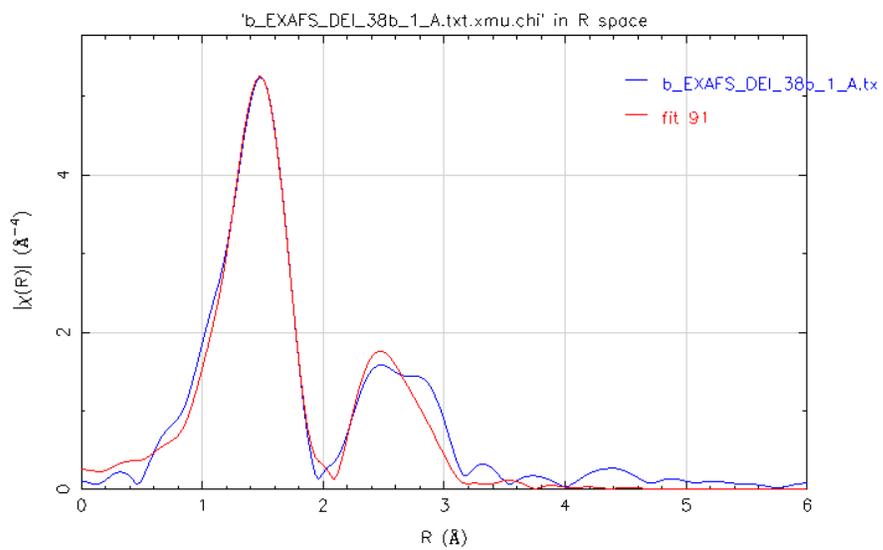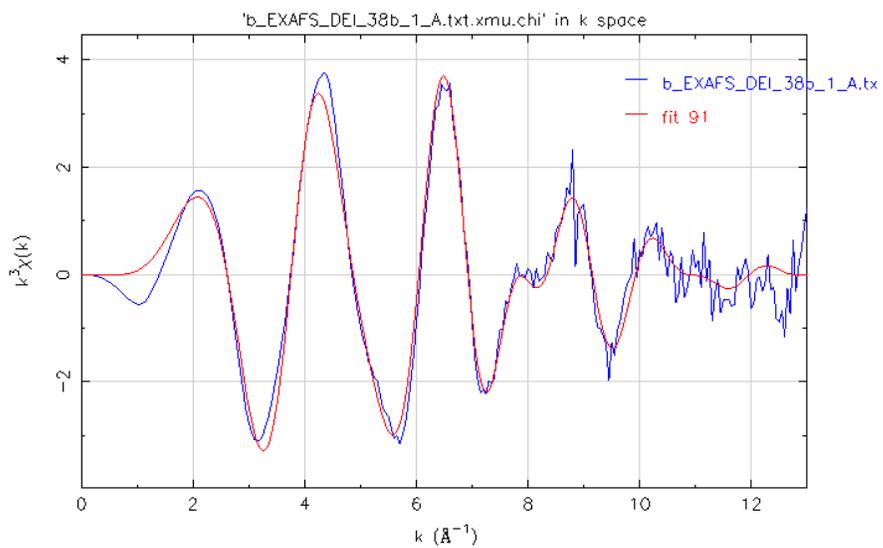
Figure S 7. EXAFS simulation of complex **2** in k (top) and R (bottom) spaces.
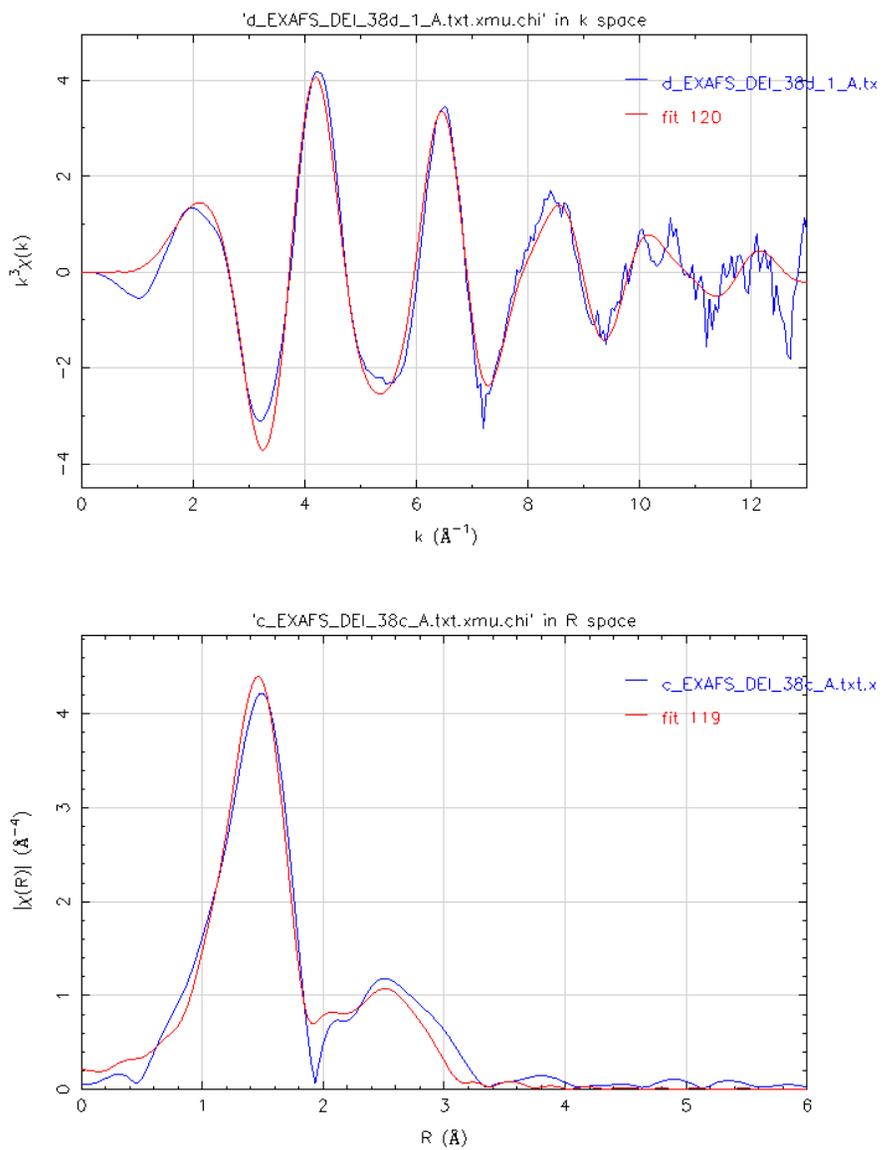
Figure S 8. EXAFS simulation of complex **3** in k (top) and R (bottom) spaces.
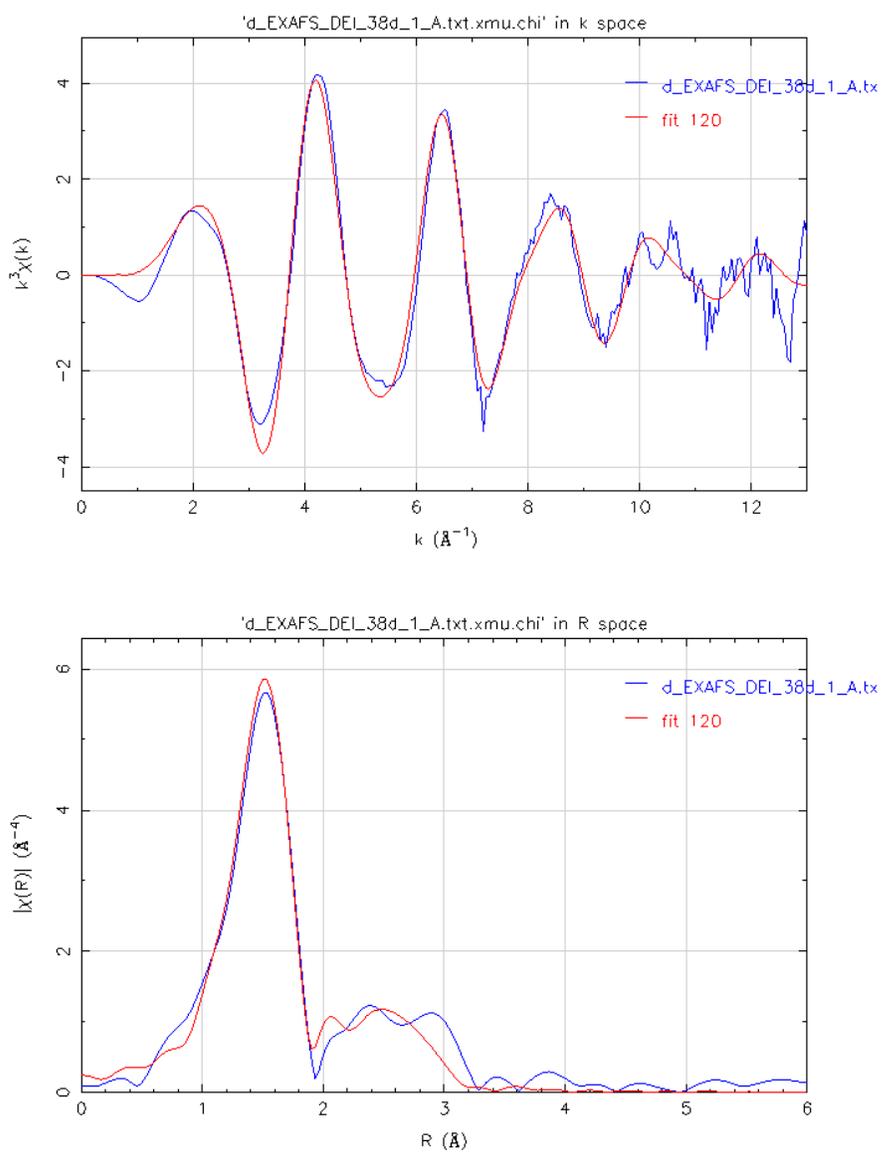
Figure S 9. EXAFS simulation of complex **4** in k (top) and R (bottom) spaces.
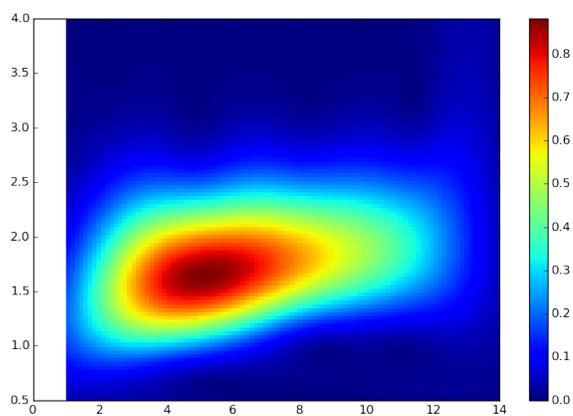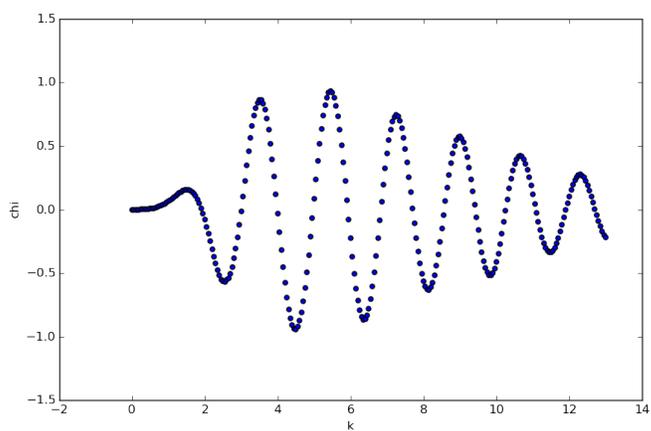
Figure S 10. WT of individual Co-O scattering path simulated from the crystallographic structure of **1**
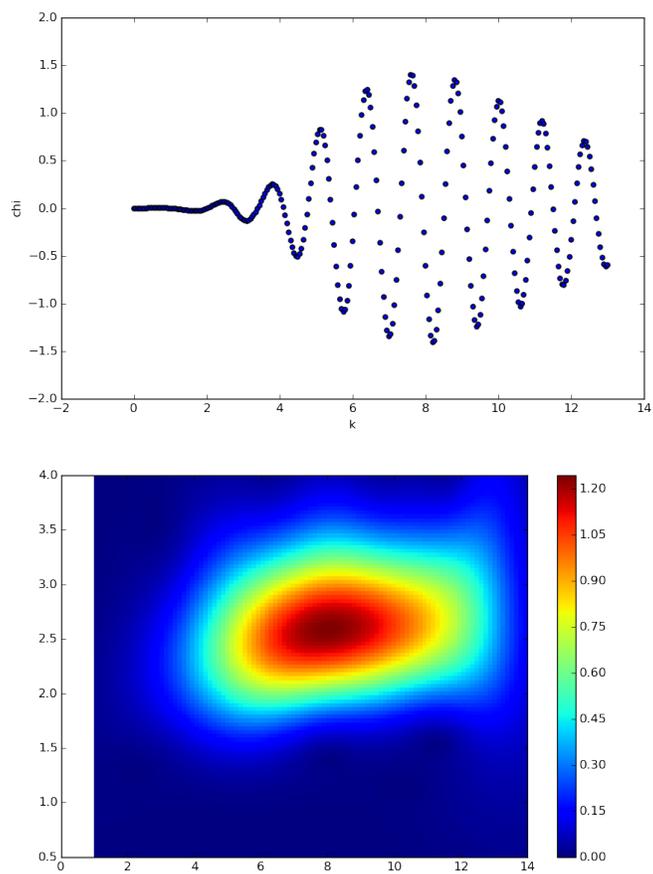
Figure S 11. WT of individual Co-Co scattering path simulated from the crystallographic structure of **1**
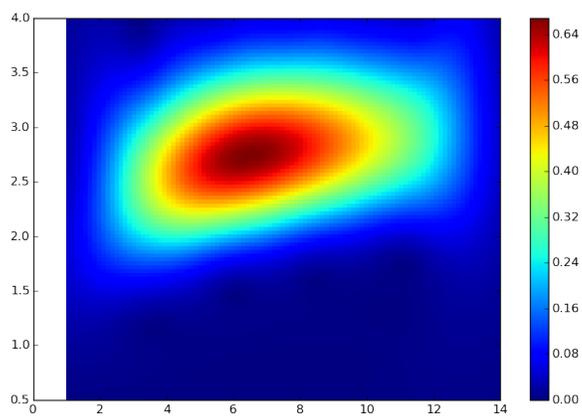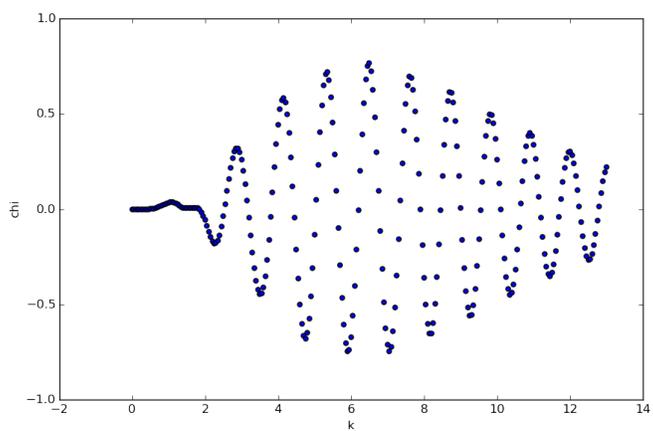
Figure S 12. WT of individual shorter (3.24 Å) Co-Si scattering path simulated from the crystallographic structure of **1**
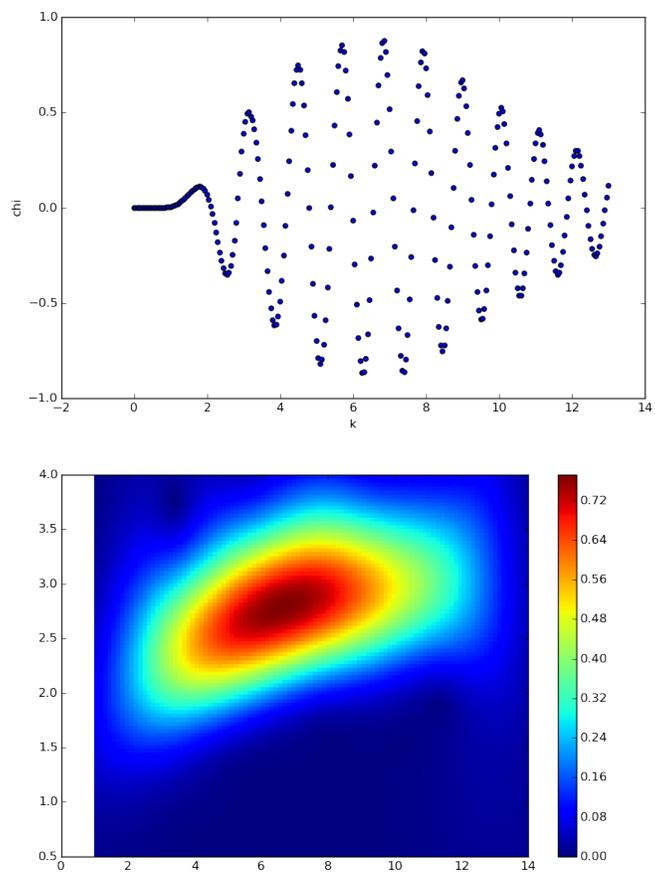
Figure S 13. WT of individual longer (3.30 Å) Co-Si scattering path simulated from the crystallographic structure of **1**

Synthesis of 1-octyne-d₁

1-octyne (1.25 mL, 0.933 g, 8.47 mmol) was mixed with excess MeLi (6 mL, 1.6 M in Et_2O, 9.6 mmol), leading to evolution of methane gas. After this, excess D_2O (5 mL) was added until no more gas evolved from the solution. This mixture was extracted with Et_2O (3 × 20 mL), dried with Na_2SO_4, and the solvent removed under reduced pressure. Residual Et_2O was removed by distillation at 120°C and atmospheric pressure. 93% D incorporation based on ¹H NMR.

Synthesis of 5-d₁

Pure D_2O (1 mL) was added to a stirring solution of $HOSi(OtBu)_3$ (5 g, 18.9 mmol) in THF (25 mL) and allowed to stir for 20 minutes. After this, the solvent was removed in vacuo and the process was repeated two more times. After the third time, the solvent was removed and the product sublimed at 50°C under vacuum. Recovered 3.76 g of material with 99% D purity.

Flow reactions

Flow reactions were performed in a stainless steel plug flow reactor (0.8 cm ID) with a capacity to run reactions at up to 10 atmg, 700°C, and as much as 100 mL/min gas flow. The plug flow reactor was loaded with between 50 and 500 mg of the desired catalyst and diluted with SiC up to a total weight of 2.5g. This ensured that the total length of the plug was more than twice the diameter of the reactor. This reactor could be sealed inside an Ar glove box in order to prevent the exposure of the catalyst to ambient atmosphere. All gases were purified with molecular sieves and Cu/Al_2O_3 catalyst prior to their entering the flow reactor. The gas flow rate was controlled by mass flow controllers that were calibrated to the desired gas for accurate flow rates that could maintain a

desired flow rate to within 0.1 mL/min. The temperature was controlled by placing the reactor in a high temperature oven inside a temperature-controlled box. The internal temperature of the catalyst was controlled during the reaction through a thermocouple immersed directly in the catalyst bed. The gas mixture was analyzed automatically by a GC injector programmed to sample the gas stream at various times throughout the reaction and analyzed by both TCD and FID. In order to ensure accurate kinetics all conversions were kept between 1 and 10% and below $0.1 \, s^{-1}$ TOF.

Reaction of propane with **3**

The above reactor was loaded with 57.5 mg of **3**, heated to 550°C under a stream of Ar, then allowed to react with a mixture of propane and Ar (flow rate 3.4 mL propane $min^{-1,}$ 1 atmg (2 atma) total pressure) for 21h. The catalyst was examined after the reaction and had turned from light blue to black. Elemental Analysis showed that the sample contained 11.86 % C, 0.21 % H. This same sample was also subjected to Co-K edge X-ray absorption spectroscopy (Figure S15, below).
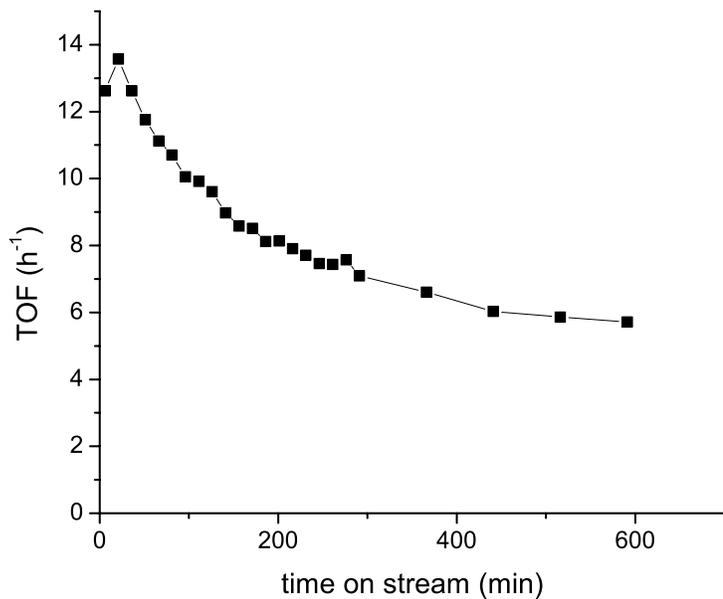
Figure S14. Activity of **3** for propane dehydrogenation as a function of time on stream.
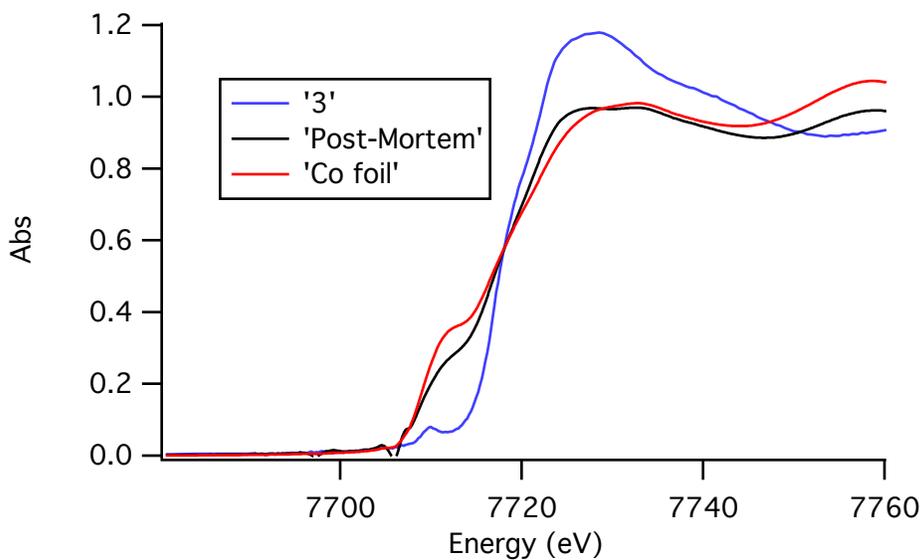
Figure S15. Co K-edge XANES spectra of spent catalyst (black), **3** (blue), and Co foil (red) (top)
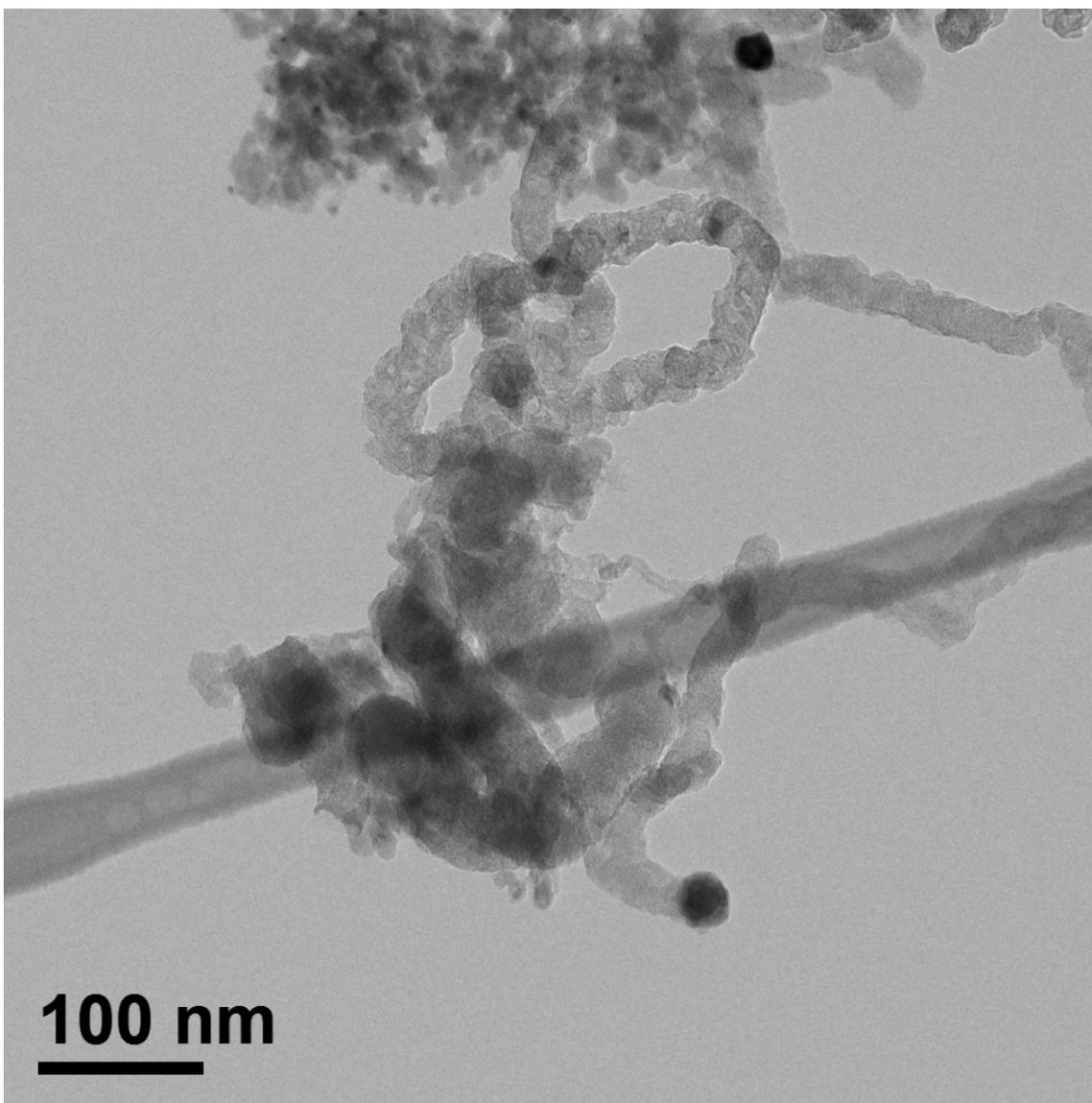
Figure S16. TEM image of the spent catalyst from reaction of propane with **3** at 550°C.

Reaction of isobutane with 3

The reaction of isobutane with **3** was done analogous to that of propane with **3**. The TOF, % conversion, and selectivity of the reaction are shown in Figure S16 as a function of time on stream. Figure S17 shows a comparison of the TOF's of isobutane and propane after they have been normalized to the number of primary C–H bond in each molecule.
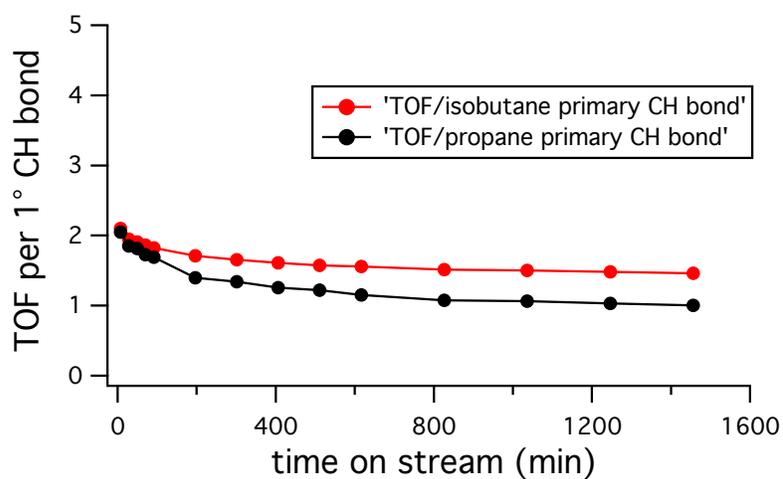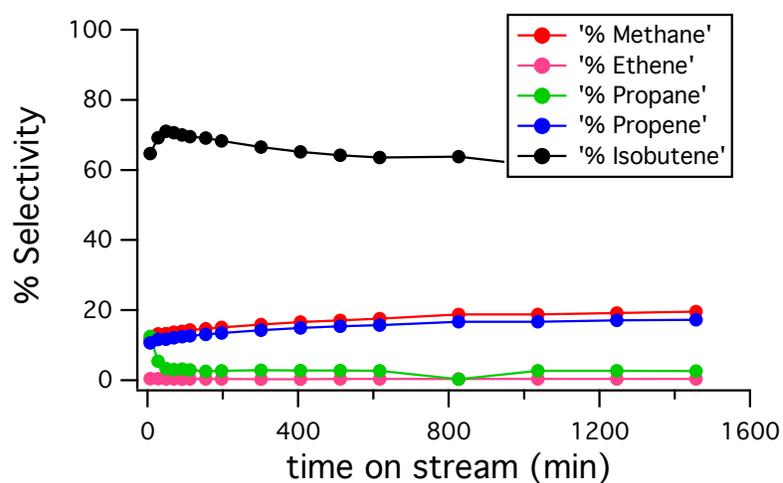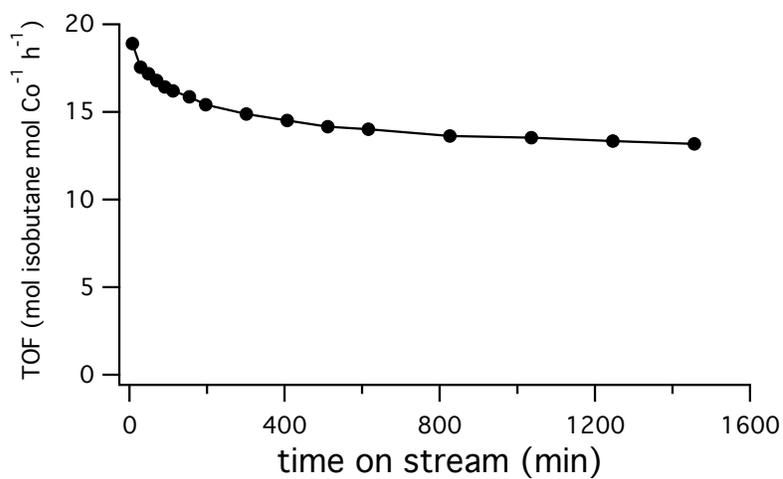
Figure S17. TOF, selectivity, and TOF normalized per primary CH bond for isobutane

dehydrogenation as a function of time on stream.

Reaction of propene and H_2 with 3

  The above reactor was loaded with 471 mg of **3**, heated to 50°C under a stream of Ar, and then allowed to react with mixtures of propene, H_2/D_2, and Ar with appropriate proportions to maintain constant flow rate of 29.4 mL/min total gas flow. No reaction was seen until the temperature reached 150°C. The partial pressures of propene and H_2 were varied in order to measure the rate dependence on these parameters. D_2 was substituted for H_2 in order to measure the kinetic isotope effect. The spent catalyst looked identical to the starting **3** and we saw no signs of catalyst deactivation over the course of 36h.
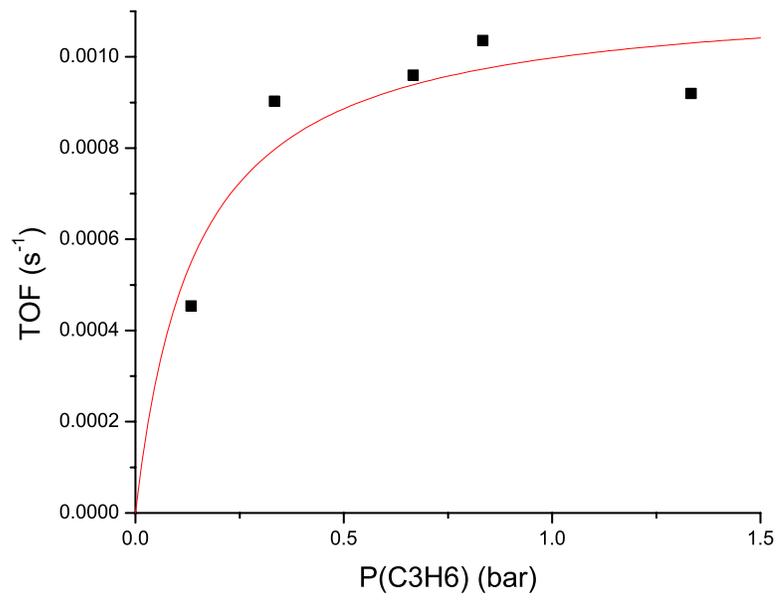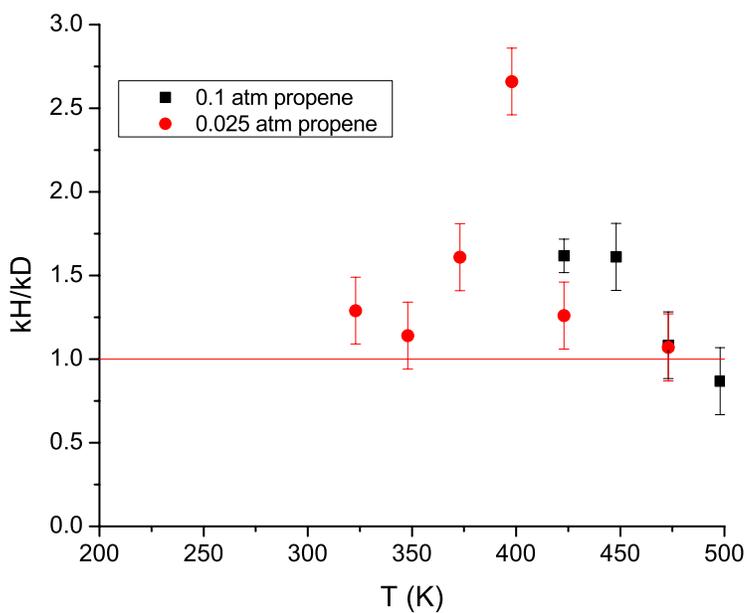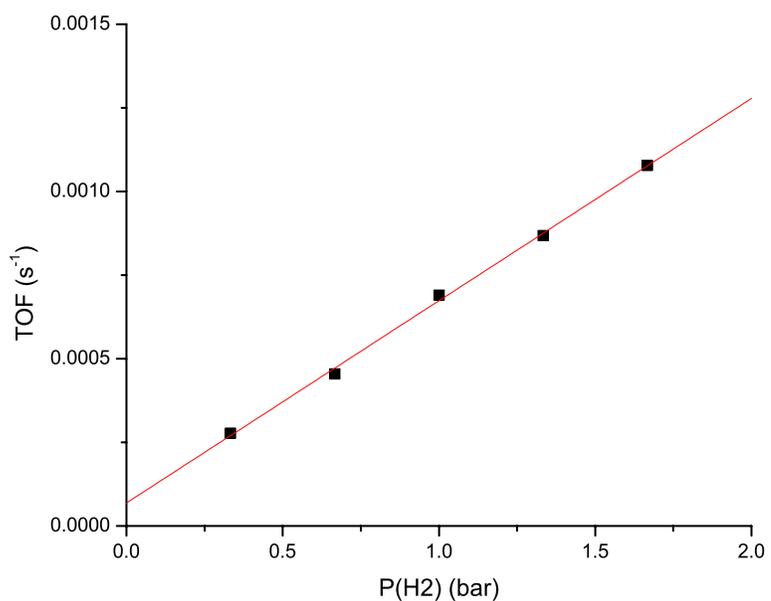
Figure S18. Propene hydrogenation rate dependence on partial pressures of propene (top) and H_2 (middle) and temperature dependence of isotope effect (bottom)

Parahydrogen Induced Polarization (PHIP) Experiments

The sealed tube with the catalyst was opened in argon atmosphere. For hydrogenation in a high magnetic field (PASADENA experiment), 30 mg of

Co(II)/SiO$_2$ catalyst was placed at the bottom of a 10 mm screw-cap NMR tube under Ar. Then the tube was positioned inside the NMR magnet. The gas mixture was supplied to the catalyst through a Teflon capillary extended to the bottom of the NMR tube at the flow rate of 1.4 to 5.7 ml/s. The mixture of propene/H$_2$ with a 1:4 ratio was used (no balance gas; total pressure 1 atm). Hydrogen gas was enriched with p-H$_2$ up to 87-88% using Bruker parahydrogen generator BPHG-90. The NMR tube with the catalyst was heated to 130 °C. ^{1}H NMR spectra were acquired on a 300 MHz Bruker AV 300 NMR spectrometer using a π/4 radiofrequency pulse that provides the maximum signal intensity for the antiphase PASADENA signals.

Reaction of propyne with 1

Propyne (700 mbar) was added to a solution of **1** in a J–Young tube and allowed to react at 50°C for 2d. New peaks in the ^{1}H NMR indicated the formation of aromatic products. GC/MS showed two new products with M+ at 120 m/z that matched the retention times of authentic mesitylene and 1,2,4–trimethylbenzene. The ratio of mesitylene to 1,2,4–trimethylbenzene is 0.5.
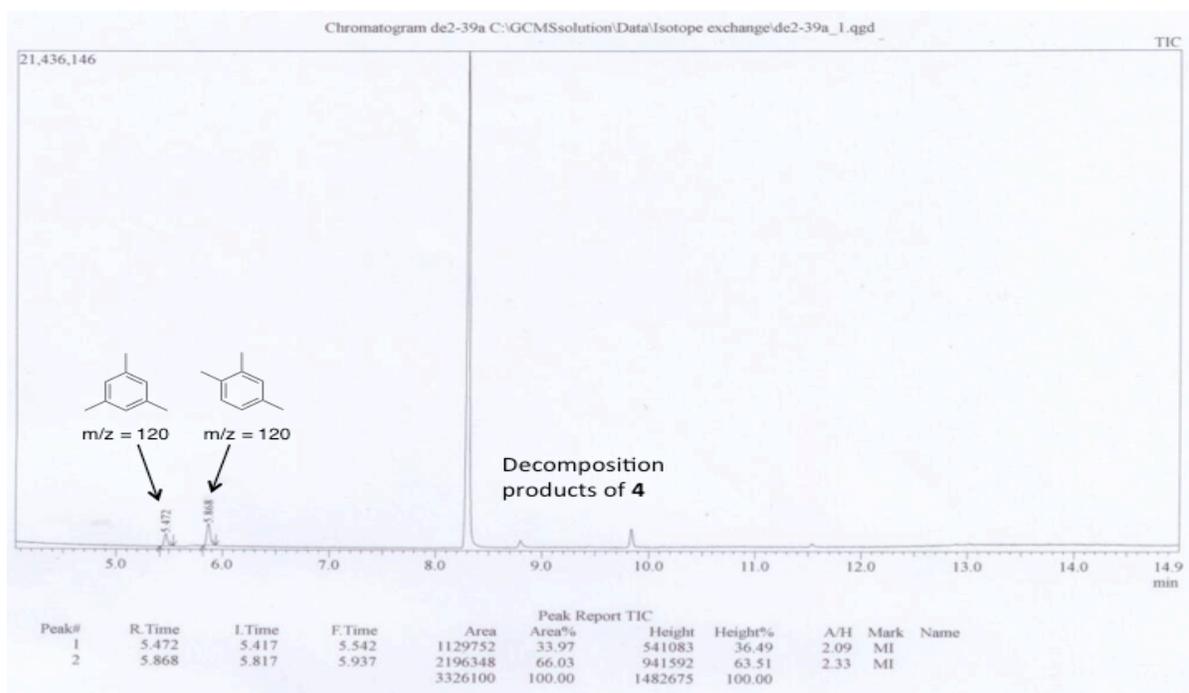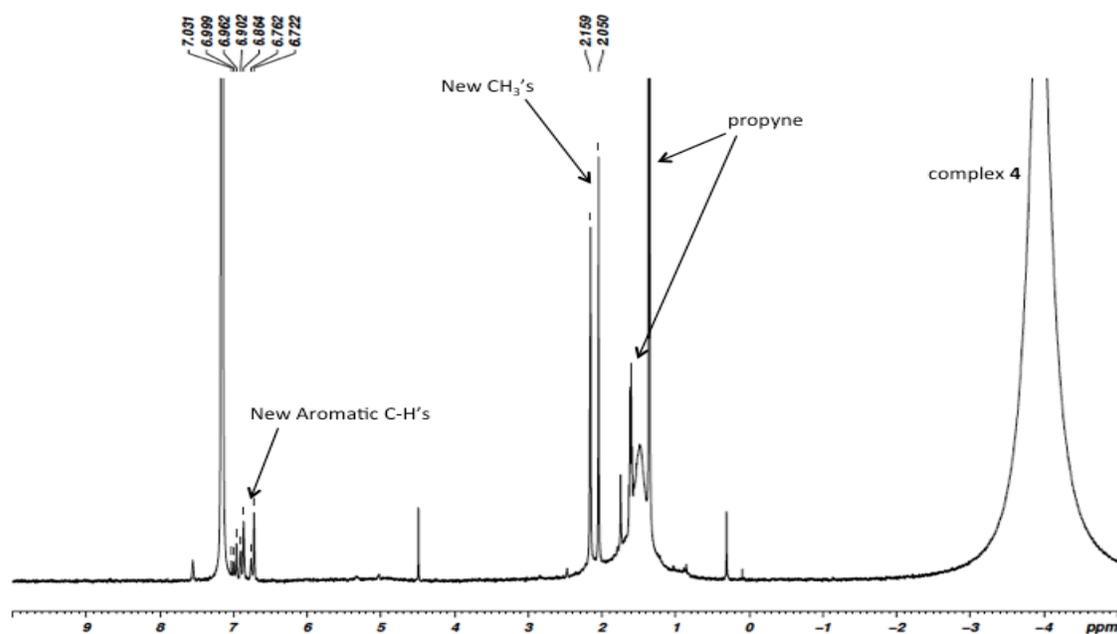
Figure S19. ¹H NMR spectrum (top) and GC/MS trace (bottom) of reaction of **1** with propyne. The peak at 4.49 ppm is allene (CH₂=C=CH₂)[4]

Reaction of propyne with 4

Propyne (700 mbar) was added to a slurry of **4** in a J–Young tube and allowed to react at 50°C for 1d. New peaks in the ^{1}H NMR indicated the formation of aromatic products. GC/MS showed two new products with M+ at 120 m/z that matched the retention times of authentic mesitylene and 1,2,4–trimethylbenzene, just like for the molecular complex. The ratio of mesitylene to 1,2,4–trimethylbenzene is also 0.5.
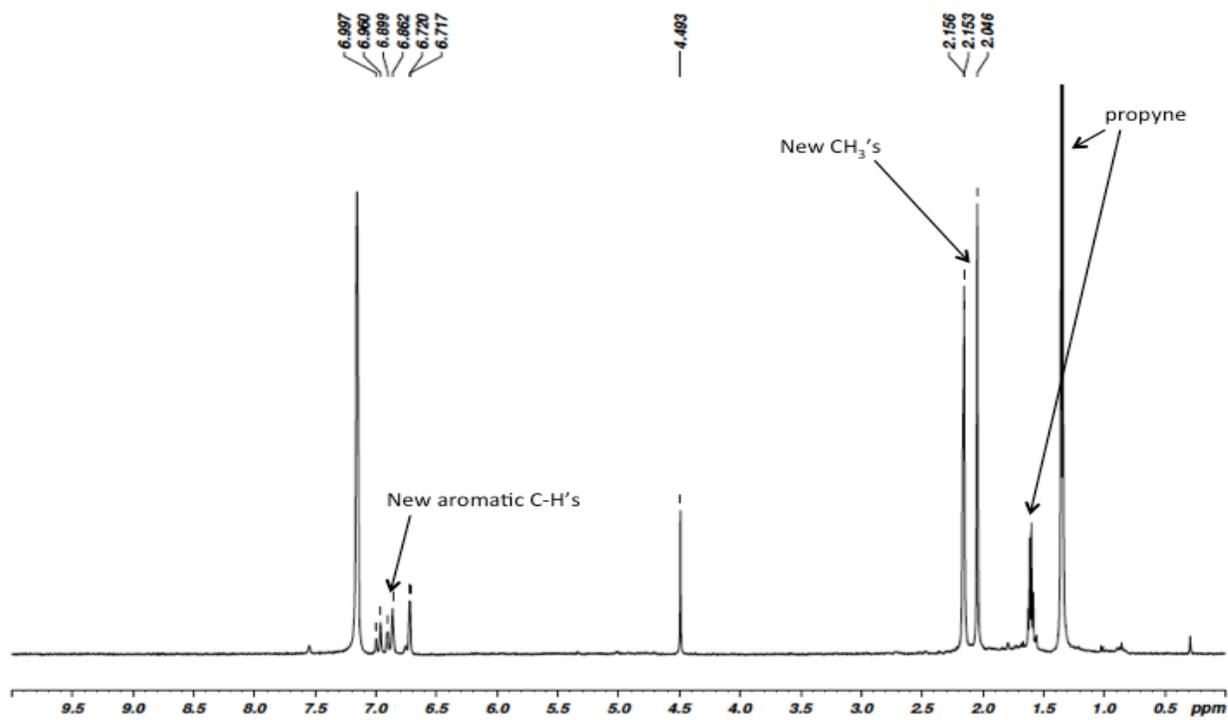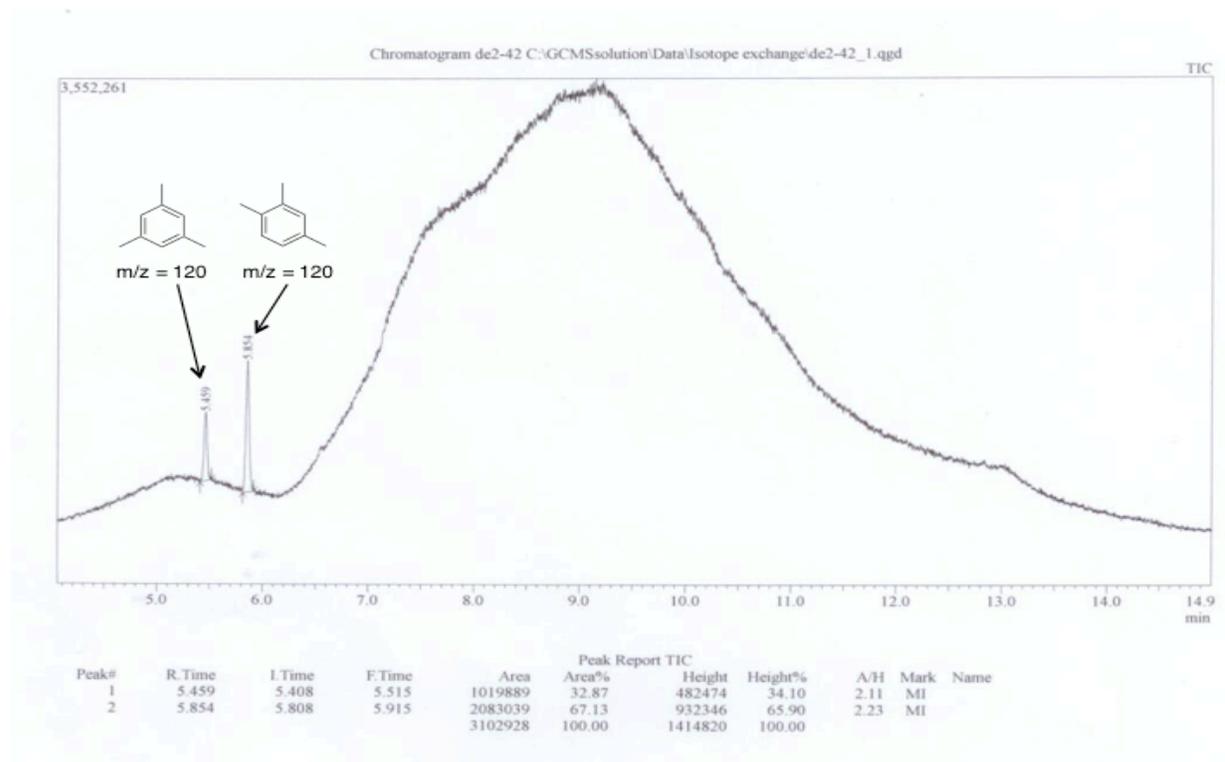
Figure S20. ^{1}H NMR (top) and GC/MS trace (bottom) of the reaction of propyne with **4.** The peak at 4.49 ppm is allene $(CH_2=C=CH_2)$[4]

Reaction of 1-octyne with excess **5-d_1** *and* **1**

A 0.9 mL pentane solution of 0.0103 M in 1-octyne, 0.145 M in **5-d_1**, 0.0128 M in

1, and 0.0328 M in C_6D_6 (as internal standard) was placed in a J-Young NMR tube and

then monitored by ^{2}H NMR over the course of 2d. At the end of this time, integration of

the peaks showed that over 90% of the 1-octyne had exchanged H for D in the terminal

alkyne position. No other products were observed in the ^{1}H NMR. The same reaction was

repeated in C_6D_6 and monitored by ^{1}H NMR. It showed that at the end of the reaction <

5% of the sp C–H bonds remained (small peak barely visible below with chemical shift

1.75 ppm).
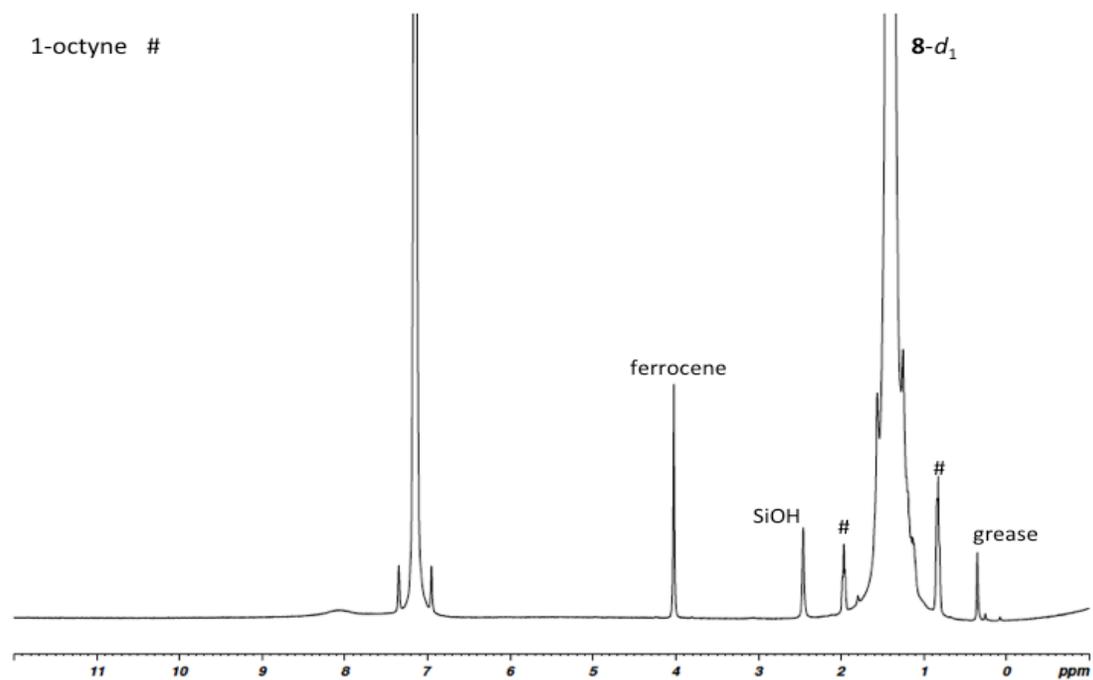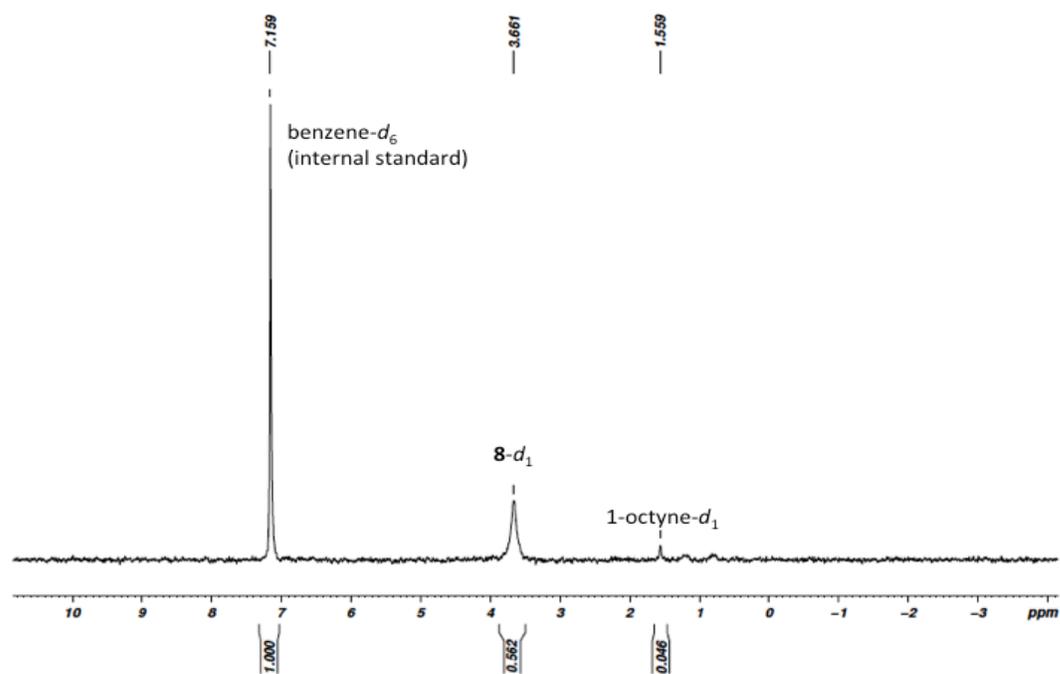
Figure S21. ^{2}H NMR (pentane, top) and ^{1}H NMR (C_6D_6, bottom) of the reaction of 1-octyne with **5**-d_1 and **1**.

Reaction of tBuCCH with 3

A pellet **3** suitable for IR spectroscopy was exposed to vapor pressure of *t*BuCCH (~500 mbar) which caused a color change from light blue to bright purple. This was accompanied by new IR bands at 3563 (br, SiOH), 3305 (s), 3265 (s, br) [sp C–H], 2976 (vs), 2939, 2908, 2877 [sp^3 C–H], 2134 (w, br), 2100 (m) [C≡C stretch], 1687, 1597 [C=C stretch], 1480, 1460, 1395, and 1367 [δ C–H bands]. Upon heating with a heat gun, the bands at 3563, 3305, 3265, 2134, and 2100 disappeared and new bands at 3070, and 3040 cm^{-1} appeared while the peaks at 1687 and 1597 intensified. TGA analysis of this heating transition showed that no mass was lost during this process under vacuum, showing that a reaction was taking place on the surface.
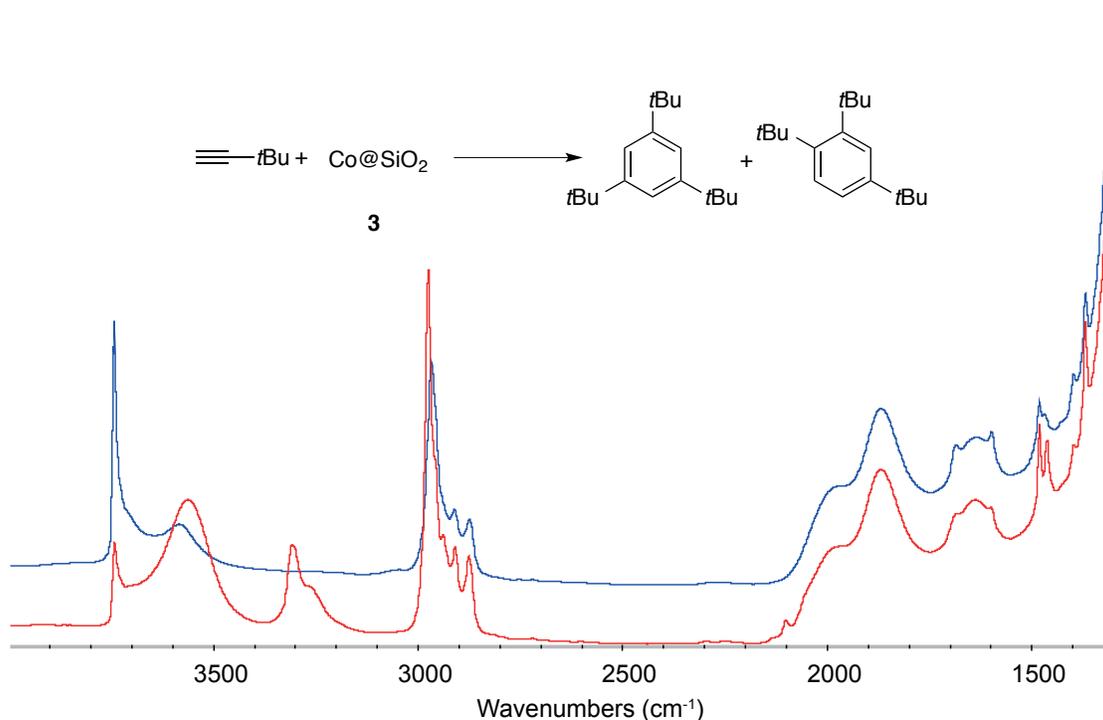

Figure S22. IR spectra of **3** after exposure to *t*BuCCH (red) and after evacuation of excess *t*BuCCH (blue)

Reaction of tBuCCD with SiO$_2$

A pellet of SiO$_{2\text{-}700}$ was exposed to 6 mbar of dry *t*BuCCD and the reaction monitored by IR spectroscopy. New bands appeared on the silica surface at 2976 – 2877

and $2755 - 2500$ cm^{-1}. Upon evacuation of this with mild heating all of the peaks

between 2976 and 2877 disappeared and only a peak at 2759 cm^{-1} remained, which can

be assigned as the terminal SiOD stretch.
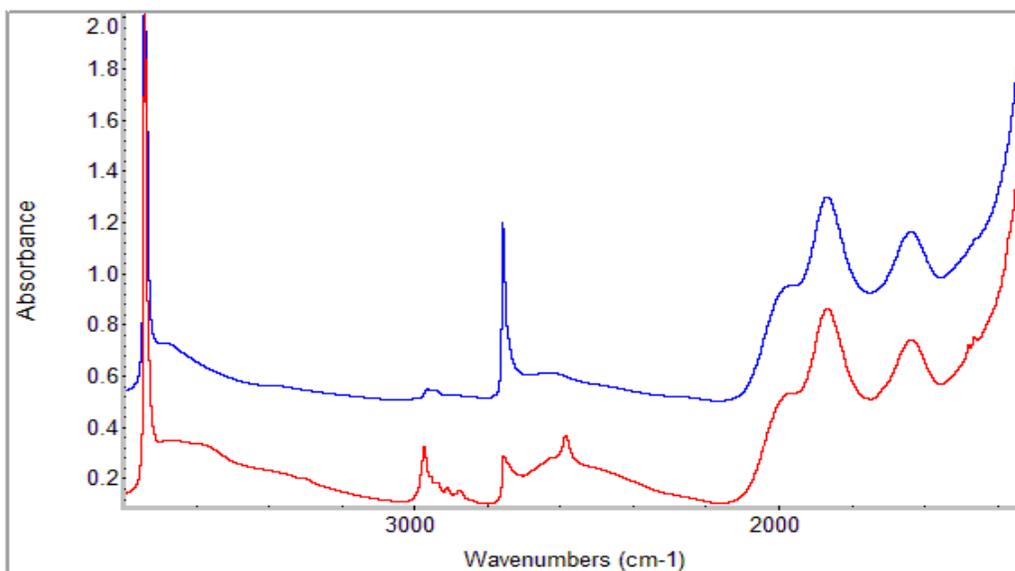
Figure S23. IR spectra of SiO$_{2-700}$ upon exposure to *t*BuCCD (red, bottom) and then after evacuation (blue, top)

Reaction of propene with D$_2$ catalyzed by 3

A reactor was filled with 50 mg of **3**, 50 mbar of propene, and 300 mbar of D$_2$ and

heated at 250°C for overnight. After this time the condensable gases in the reactor were

condensed with liquid nitrogen, the D$_2$ pumped off, and the remaining gases transferred

into a J-young NMR tube. 13C NMR showed the presence of a small amount of C3H8

(present as an impurity in propene) and 1,2-dideuteropropane: ^{13}C NMR (δ, 100 MHz,

C$_6$D$_6$) 16.3 (1:1:1 triplet, $^2J_{CD} = 19.5$ Hz), 16.2 (1:1:1 triplet, $^2J_{CD} = 19.2$ Hz) ppm.
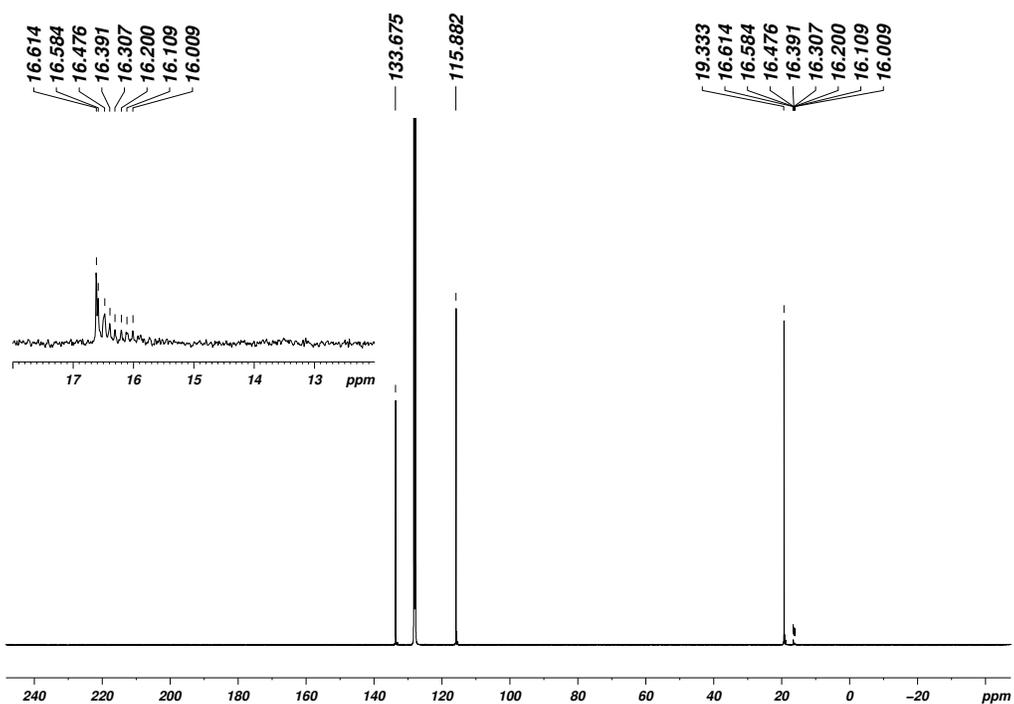
Figure S24. ^{13}C NMR spectrum of condensable gases from the reaction of propene and D_2 catalyzed by **3**.

*Reaction of D_2 with **5** catalyzed by **3***

Catalyst **3** (125 mg) along with 0.54 g of **5** in 20 mL toluene were added to a high pressure reactor and sealed under Ar. This reactor was then pressurized with 40 atm of D_2 gas and stirred at 50 °C overnight. The pressure was vented, catalyst filtered off, then solvent removed in vacuo to give a white crystalline solid. This solid was analyzed by both ^{1}H NMR and ^{2}H NMR and found to consist of 86% **5** and 14% **5**-d_1.
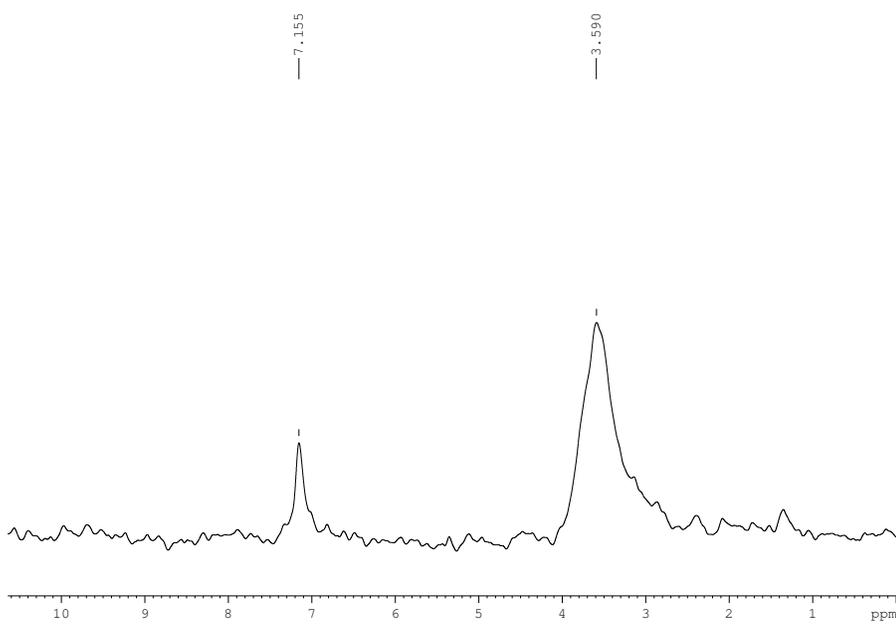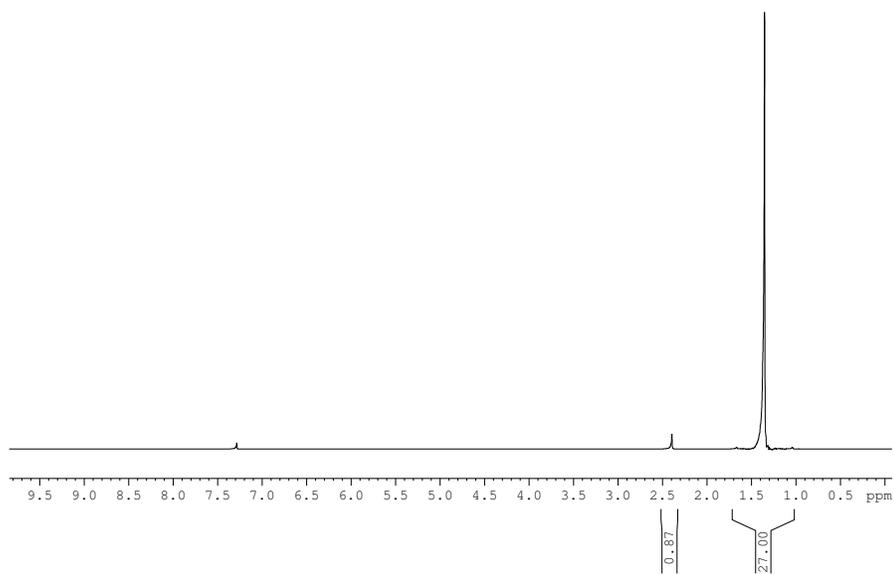
Figure S25. ^{1}H (top) and ^{2}H (bottom) NMR spectra of **5** after treatment with 40 atm D$_2$ in the presence of

3.

Details of Kinetic Measurements

Appropriate amounts of stock solutions (C_6D_6) of 1-octyne, **1**, and **5**-$d_1$were added separately to a J–Young tube and frozen in separate layers with appropriate concentrations to achieve a 10–fold excess of **5**-d_1 over 1-octyne. This was kept frozen until immediately prior to the experiment, when it was melted, mixed, and inserted in to the probe of a 400 MHz NMR spectrometer that had been equilibrated to $40.0 \pm 0.5°C$ using an ethylene glycol/DMSO-d_6 chemical shift thermometer. Spectra were taken either every 3 or 6 minutes depending on the total experiment time and the integral of the SiOH resonance (located somewhere between 2.5 – 3.5 ppm, depending on concentration) was compared with that of an internal standard of known concentration (ferrocene). Reactions were monitored through (at least) 4 half lives of starting material and fit to a first order exponential.

For heterogeneous reactions, between 10 – 20 mg of **4** was weighed into a J–Young NMR tube and then stock solutions of **5**-d_1 and 1-octyne were frozen in separate layers on top of this solid until immediately before beginning the reaction. This was then thawed and ^{1}H NMR taken as a starting reference point. This tube was submerged in a constant temperature bath at 40°C and agitated using a rotavap motor to assist diffusion into the catalyst. NMR spectra were taken every 30 min – 1 h over the course of the reaction and the integral of the SiOH peak was monitored versus that of the Ferrocene internal standard. These reactions were also fit to a first order exponential expression and the fitted endpoint was always within error of the theoretical yield.
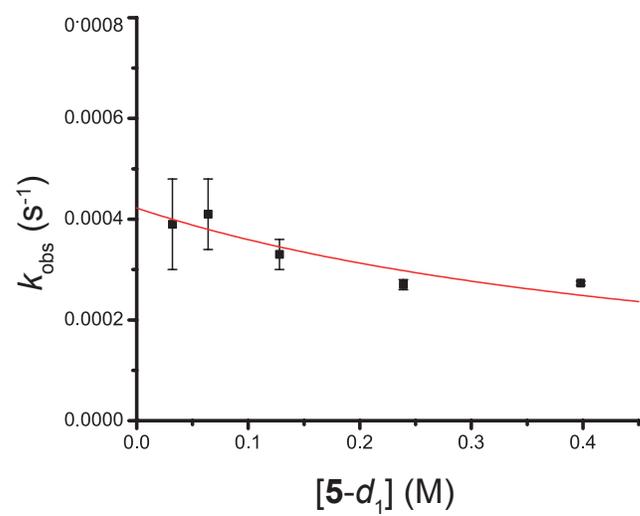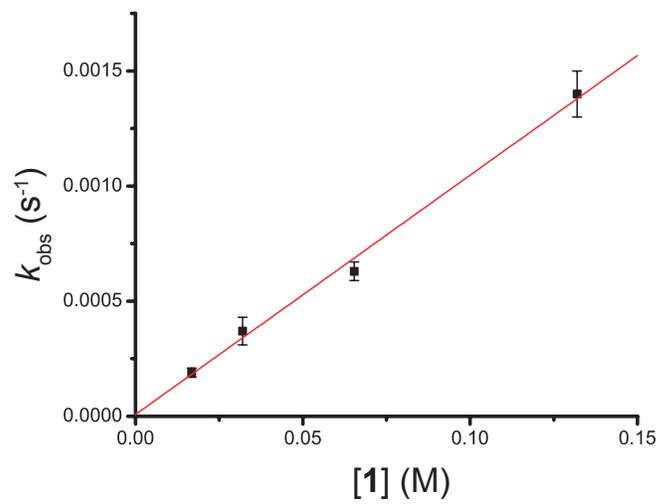
Figure S26. Kinetic dependence of **1** catalyzed H/D exchange reaction on **1** and **5**-d_1
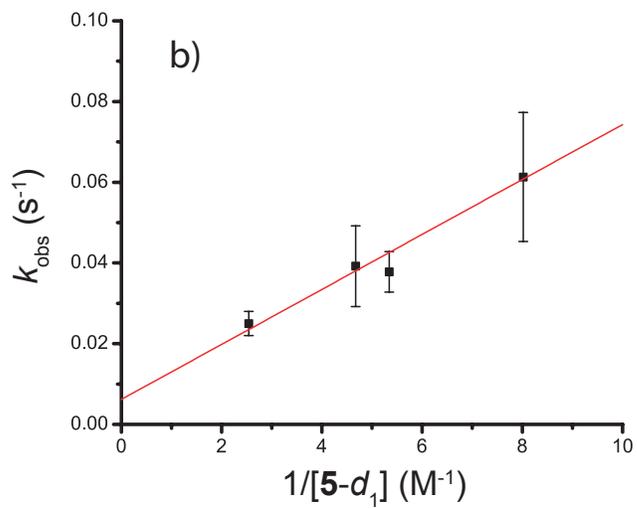
**Figure S27.** Inverse dependence of rate of **4** catalyzed H/D exchange on **5**-d_1
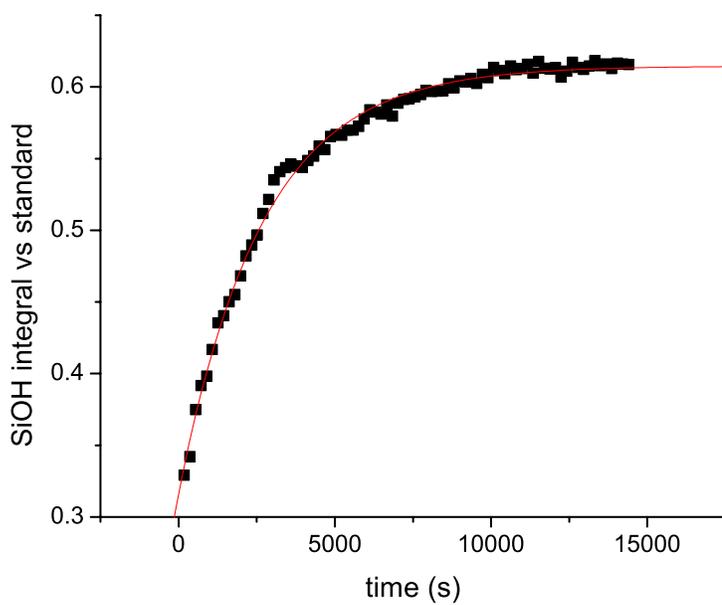

**Figure S28.** Kinetics at 0.064M **5**-d_1
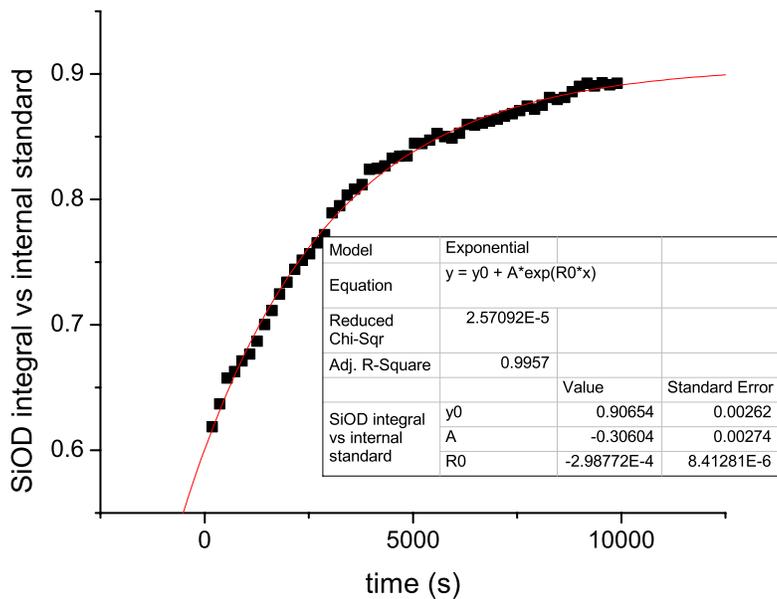
Figure S29. Kinetics at 0.127M **5**-d_1
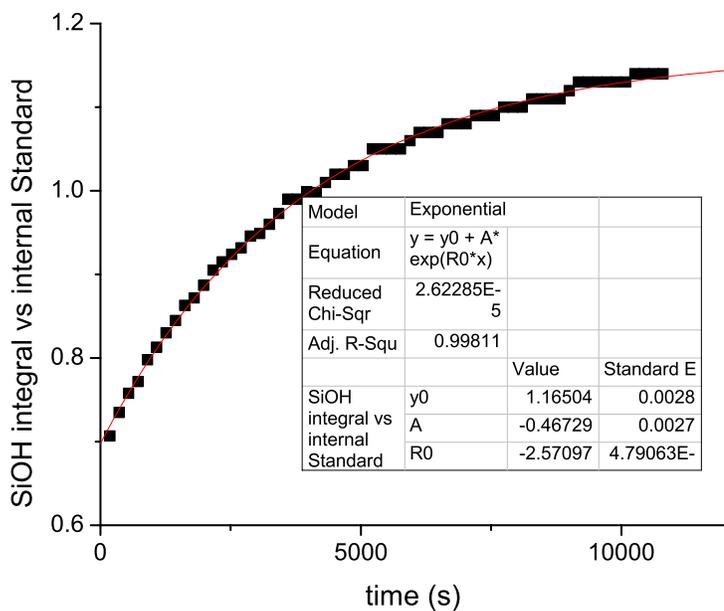
Figure S30. Kinetics at 0.239M **5**-d_1
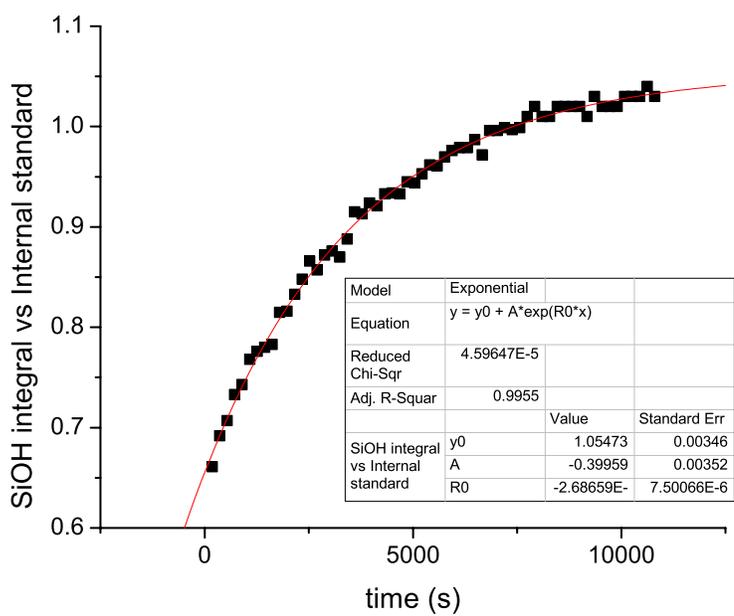
Figure S31. Kinetics at 0.398M **5**-d_1
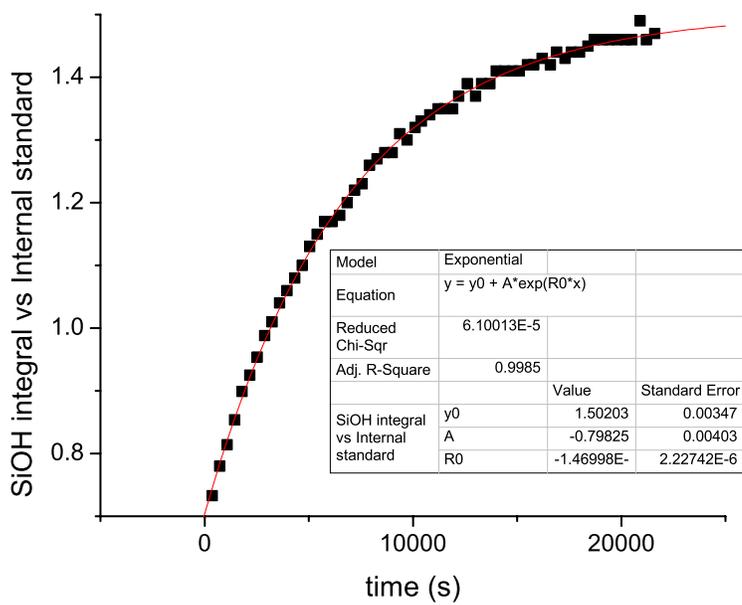
Figure S32. Kinetics at 0.0168M **1**
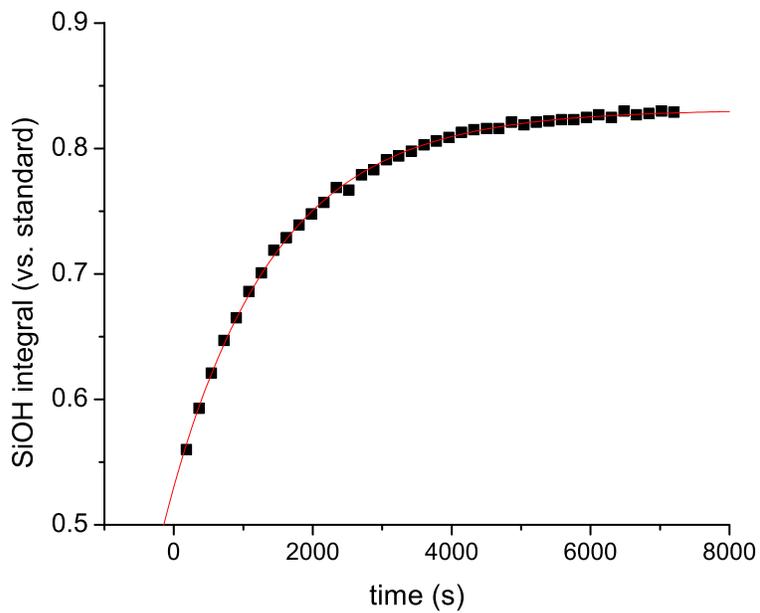
Figure S33. Kinetics at 0.0654M **1**

Model	Exponential		
Equation	y = y0 + A*exp(R0*x)		
Reduced Chi-Sqr	8.24464E-6		
Adj. R-Square	0.99499		
		Value	Standard Error
SiOH integral vs internal standard	y0	0.5247	7.46452E-4
	A	-0.20993	0.00395
	R0	-0.00146	4.13024E-5
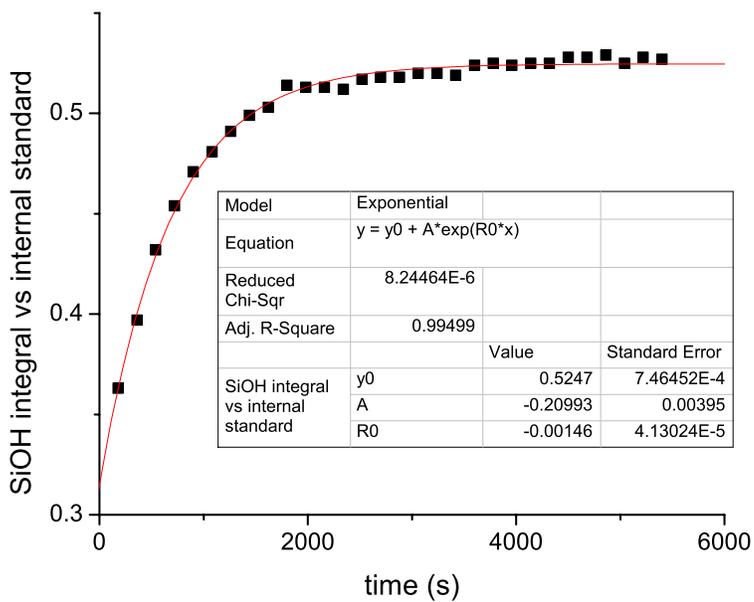
Figure S34. Kinetics at 0.132M **1**

Model	Exponential		
Equation	y = y0 + A*exp(R0*x)		
Reduced Chi-Sqr	2.14183E-6		
Adj. R-Square	0.9885		
		Value	Standard Error
SiOD singnal intensity	y0	0.06379	2.95567E-4
	A	-0.05706	0.001
	R0	-2.16896E-4	7.12561E-6
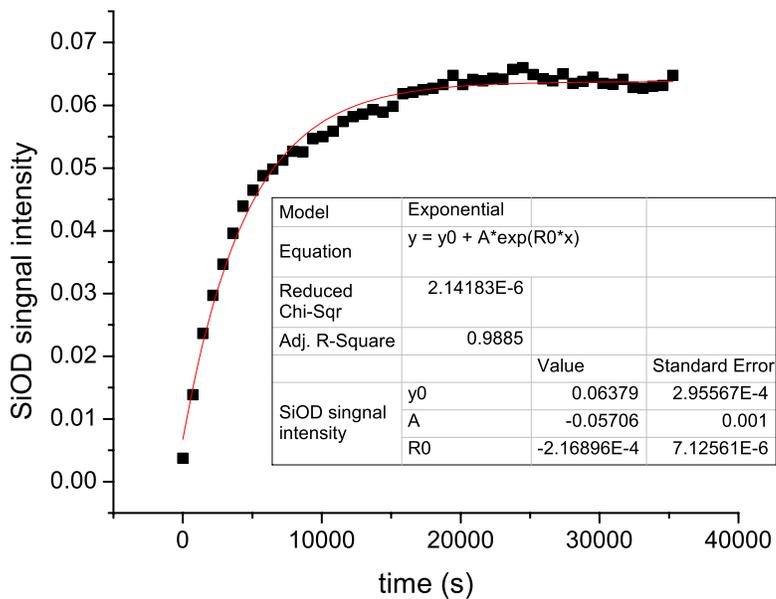
Figure S35. Kinetics of reaction of 1-octyne-d_1 with **5** by ReactIR

Model	Exponential		
Equation	y = y0 + A*exp(R0*x)		
Reduced Chi-Sqr	2.66891E-8		
Adj. R-Square	0.99786		
		Value	Standard Error
C-D intensity	y0	-0.00277	5.20909E-5
	A	-0.01315	1.55396E-4
	R0	-6.92716E-4	1.69497E-5
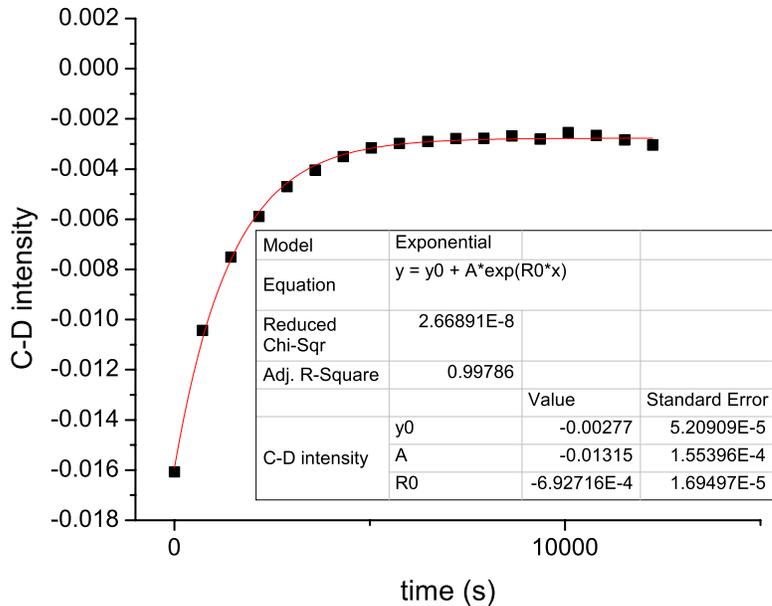
Figure S36. Kinetics of reaction of 1-octyne with **5**-d_1 by React IR

| Model	Exponential		
Equation	y = y0 + A*exp(R0*x)		
Reduced Chi-Sqr	2.66076E-7		
Adj. R-Square	0.9683		
		Value	Standard Error
[8]	y0	0.03583	0.00103
[8]	A	-0.01149	9.23735E-4
[8]	R0	-1.14782E-4	3.17555E-5
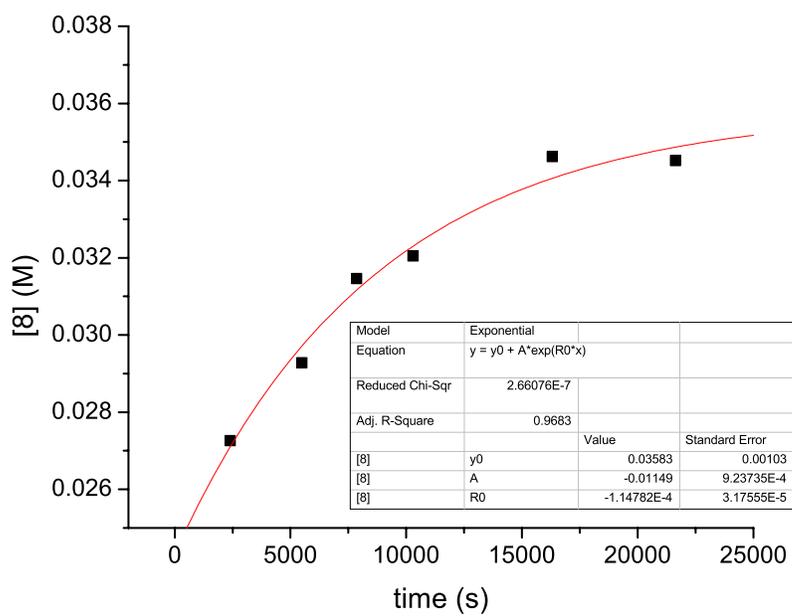
**Figure S37.** Kinetics with **4** as catalyst (0.125M **5**-d_1)
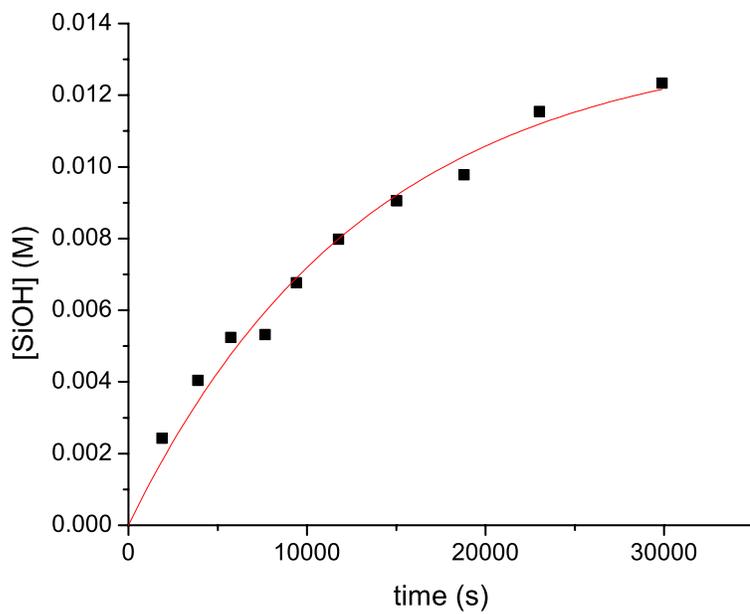
Figure S38. Kinetics with **4** as catalyst (0.187M **5**-d_1)
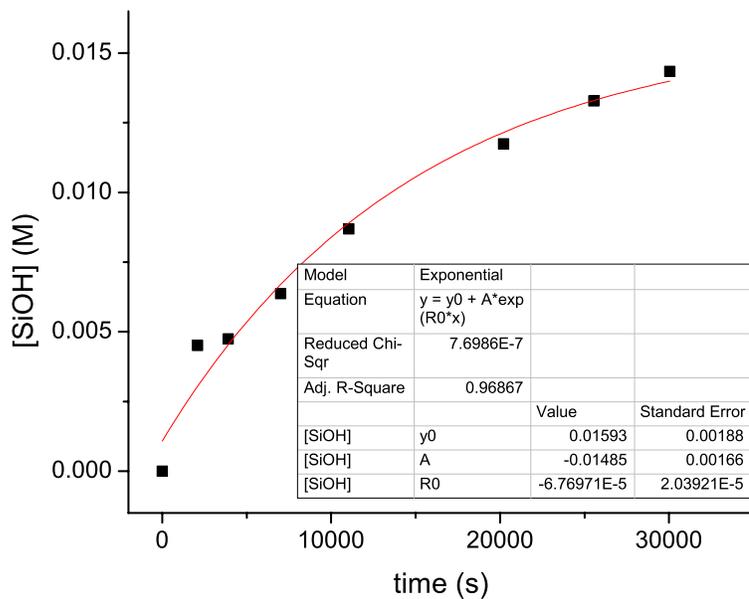
**Figure S39.** Kinetics with **4** as catalyst (0.214M **5-**d_1)
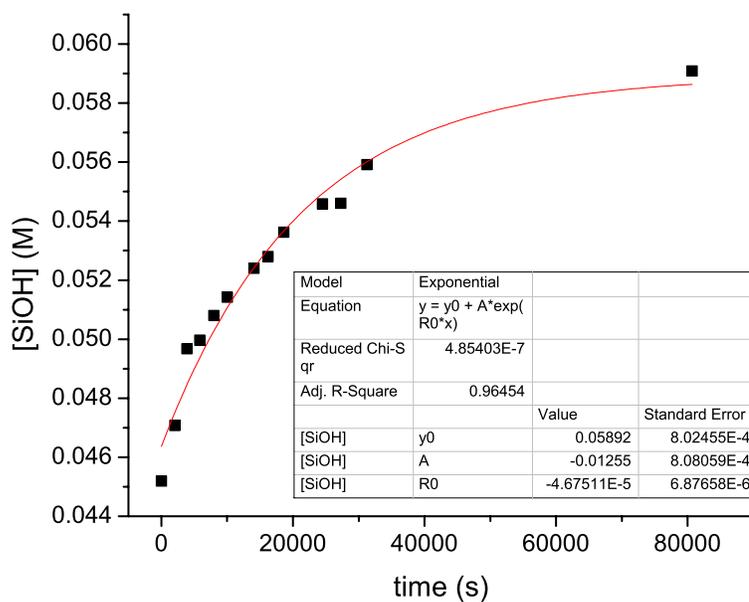
Figure S40. Kinetics with **4** as catalyst (0.398M **5-**d_1)

References

1. Bryan, A. M.; Long, G. J.; Grandjean, F.; Power, P. P. *Inorg. Chem.* **2013**, *52*, 12152

2. Ravel, B.; Newville, M. *J. Synchrotron Radiat.* **2005**, *12*, 5

3. a) Funke, H.; Chukalina, M.; Scheinost, A. C. *J. Synchrotron Radiat.* **2007**, *14*, 426 ; b) Timoshenko, J.; Kuzmin, A. *Comput. Phys. Commun.* **2009**, *180*, 920 ; c) Penfold, T. J.; Tavernelli, I.; Milne, C. J.; Reinhard, M.; Nahhas, A. E.; Abela, R.; Rothlisberger, U.; Chergui, M. *J. Chem. Phys.* **2013**, *138*, 014104

4. Kohn, B. L.; Jarvo, E. R. *Org. Lett.* **2011**, *13*, 4858