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A Mild Route to Convert SiH Compounds to Their Alkoxy Analogues

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Abstract

Alkoxysilanes, particularly ethoxysilanes, are widely used crosslinkers for the moisture induced, room temperature vulcanization of silicones. Karstedt's platinum catalyst is shown to be effective at converting commercially available small hydrosiloxanes containing 1-8 SiH groups, and higher molecular weight telechelic and pendant hydrosiloxane polymers, into the corresponding alkoxy-compounds. Kinetic studies demonstrated that relatively high concentrations of platinum – 500 ppm – were required for practical reaction rates to be realized. As with other silyl ether forming processes, steric hindrance at both carbon (alcohol) and silicon center retard reaction progress. This alternative use of the platinum catalyst, employed widely in the silicone industry, permits

1
2
3 ready formation of small molecule and polymeric RTV alkoxy siloxane crosslinkers that can be
4 used to tailor network structures.
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8 9 **Introduction**

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12 Moisture cure room temperature vulcanization – RTV (note: some platinum-catalyzed
13 hydrosilylation processes are also labelled RTV) constitutes an important cure technology that is
14 used in a variety of applications from silicone caulking, that will be familiar to consumers, to
15 commercial assembly of structural glazing.¹ The mechanism of tin-catalyzed moisture cure is not
16 completely understood, but the seminal paper by van der Weij clarifies the roles of water, tin,
17 silanol and functional silane crosslinker.² The rates of cure are controlled by the concentrations of
18 the various constituents and by the leaving group abilities of the functional groups. The relative
19 reactivities of industrial crosslinkers follow the order SiOCOR (acetate or other carboxylates) >
20 Si-oxime (typically derived from acetone) > SiOR (normally R = Me, Et).³
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33 One problem with RTV cure is associated with controlling the rate of cure so that elastomer
34 formation is sufficiently rapid during application (e.g., skinover in 5 minutes, complete cure in 24
35 hours), but precured materials have an acceptable pot life. Alkoxy silanes are preferred as
36 crosslinkers for the latter reason.⁴ To speed up cure, for example in glazing applications, an RTV-2
37 process (two components that are mixed during application) is used, with water provided in one
38 of the components. RTV-1 processes – a single component - utilize moisture from the atmosphere
39 to control cure rate and, in general, acetoxy- or oxime-modified silanes as crosslinkers. In both
40 cases, reaction rates slow dramatically with substitution: $\text{Si(OR)}_4 > (\text{SiliconeO})\text{Si(OR)}_3 >$
41 $(\text{SiliconeO})_2\text{Si(OR)}_2 \gg (\text{SiliconeO})_3\text{Si(OR)}$.³
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3 A relatively small library of alkoxy-compounds are normally used in commercial RTV
4 processes, primarily, $\text{Si}(\text{OR})_4$ and $\text{MeSi}(\text{OR})_3$, $\text{R} = \text{Me}, \text{Et}$. Note that some commercial adhesives
5
6 have polymers terminated with $\text{MeSi}(\text{OR})_2$ -silicone groups, which constitutes a related class of
7
8 compounds.⁴ It is clear that better elastomeric products arise from better control of structures,
9
10 including overall network structures.^{5, 6} There is therefore an incentive to develop new alkoxy-
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12 functional crosslinkers that could be used to control both rates of cure and final network properties.
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17 There are many synthetic routes leading to alkoxysilanes. A very common process, because of
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19 the availability of starting materials, uses simple alcoholysis of the chlorosilanes produced in the
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21 Direct Process. While this is a facile process for simple silane monomers, it is not very convenient
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23 when more complicated structures containing Si-O-Si linkages are also present, as these undergo
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25 a variety of concomitant reactions in the presence of the HCl byproduct; base-catalyzed alcoholysis
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27 is equally compromised. That is, any residual catalyst can facilitate the depolymerization of
28
29 silicone polymers present.³
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33 Another route for the preparation of alkoxysilanes utilizes hydrosilanes, which also undergo
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35 alcoholysis under mild conditions: *Note the reaction occurs with concomitant formation of*
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37 *hydrogen gas, which is a safety issue due both to the flammability of hydrogen and the potential*
38
39 *for increases in pressure.* Normally, these processes are catalyzed by base⁷ or a variety of metals,
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41 including Ir, Ru, Rh, Sn, etc., as described in excellent reviews.^{8, 9} Karstedt's platinum catalyst is
42
43 the workhorse in the silicone industry for hydrosilylation cure of elastomers,¹⁰ and has been shown
44
45 to catalyze alcoholysis of small silanes.^{11, 12} The group of Marciniec, preminent experts on
46
47 transition metal hydrosilylation,¹³ has recently examined the utilization of selected Pd and Pt
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49 catalysts in the oxidation of silsesquioxanes compounds with attached Si-H moieties.¹⁴ Note that
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3 the related hydrolysis of SiH groups ($\text{SiH} \rightarrow \text{SiOH}$) can also be catalyzed by a variety of transition
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5 metals.^{15, 16}
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8 We report the use of Karstedt's catalyst to prepare alkoxy siloxanes, including polymeric
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10 structures, as RTV crosslinkers and chain extenders. The process is mild, facile and occurs at
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12 moderate rates, which facilitates the handling of the hydrogen gas by-product. We examine the
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14 viability and optimize reaction conditions of the process for different alcohols and, more
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16 importantly, different alkoxy siloxane structural motifs.
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21 Experimental Section

22 Materials

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27 Hydride-terminated polydimethylsiloxanes— $\text{HMe}_2\text{Si}(\text{OSiMe}_2)_n\text{OSiMe}_2\text{H}$; **H-D₈-H** $n = 8$, $M_n =$
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29 728 g mol^{-1} , DMS-H03; **H-D₁₅-H** $n = 15$, $M_n = 1250 \text{ g mol}^{-1}$ DMS-H11; and **H-D₁₄₅-H** $n = 145$,
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31 $M_n = 10890 \text{ g mol}^{-1}$ DMS-H25) measured in all cases by end group analysis using ^1H NMR,
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33 methylhydrosiloxane-dimethylsiloxane trimethylsiloxane-terminated copolymers—
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35 $(\text{Me}_3\text{SiO}(\text{HMeSiO})_m(\text{Me}_2\text{SiO})_n\text{-SiMe}_3$, **D^H₈D₇** $m \sim 8$, $n \sim 7$, $\text{MW} = 900 - 1200 \text{ g/mol}$, HMS-501;
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37 **D^H₈D₇₂** $m \sim 8$, $n \sim 72$, $\text{MW} = 5500 - 6500 \text{ g/mol}$, HMS-082; and **D^H₅D₂₀** $m \sim 5$, $n \sim 20$, $\text{MW} =$
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39 $1900 - 2000 \text{ g/mol}$, HMS-151, octakis(dimethylsiloxy)-T8-silsesquioxane ((**Q^M**)₈),
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41 tetrakis(dimethylsiloxy)silane ((**HMe₂SiO**)₄Si) (**Q^M**)₄, methyltris-(dimethylsiloxy)silane
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43 ((**HMe₂SiO**)₃SiMe), phenyltris(dimethylsiloxy)silane ((**HMe₂SiO**)₃SiPh), and
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45 pentamethyldisiloxane (**HMe₂SiOSiMe₃**) were purchased from Gelest. Platinum(0)-1,3-divinyl-
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47 1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst, Pt ~ 2 %, in xylene) and
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49 anhydrous alcohols (methanol (MeOH), ethanol (EtOH), *n*-butyl alcohol (*n*-BuOH), 2-propanol
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51 (IPA), *t*-butyl alcohol (*t*-BuOH), and benzyl alcohol (PhCH₂OH)) were obtained from Sigma
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3 Aldrich. Chromium(III) acetylacetonate was purchased from Sigma-Aldrich. All alcohols were
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5 dried over molecular sieves before use. Toluene and dichloromethane (Caledon) were dried over
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7 a column of activated alumina. Activated carbon, granular, 4-14 mesh was supplied by Aldrich
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9
10 Chemical Company, Inc. Celite[®]545 was purchased from Millipore Sigma.

11 12 13 14 15 **Methods**

16
17 Nuclear magnetic resonance (¹H NMR, 500 MHz; ²⁹Si NMR, @ 99.4 MHz) characterization
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19 was performed on a Bruker AV 500 MHz spectrometer at room temperature using deuterated
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21 solvents chloroform-*d* or toluene-*d*₈. A small amount of chromium(III) acetylacetonate was added
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23 to sample as a relaxation agent for the ²⁹Si NMR spectra. When NMR used to follow the kinetics
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25 of reactions of Si-H with alcohols, all the reagents were placed in the NMR tube and mixed but,
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27 before placing the tube into the Bruker AV 500 MHz spectrometer auto sampler, the normal NMR
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29 cap was exchanged for one with a small hole to reduce any pressure created by adventitious H₂
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31 development.
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35 Mass spectroscopy (MS) was performed using electrospray ionization mass spectrometry (ESI-
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37 MS) on an Agilent 6340 Ion Trap mass spectrometer; ammonia or NH₄OAc was added for analysis.
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39 40 **Kinetic study of the Alcoholysis of Si-H Compounds**

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42 Reactions were performed directly in NMR tube at room temperature. ¹H NMR spectra were
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44 collected during the reaction at different time points. The reaction rates were calculated by
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46 following the loss of the Si-*H* signal and growth of a Si-O-CH₂- signal that, in most cases, was
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48 quite distinct from the free alcohol (Figure 1).
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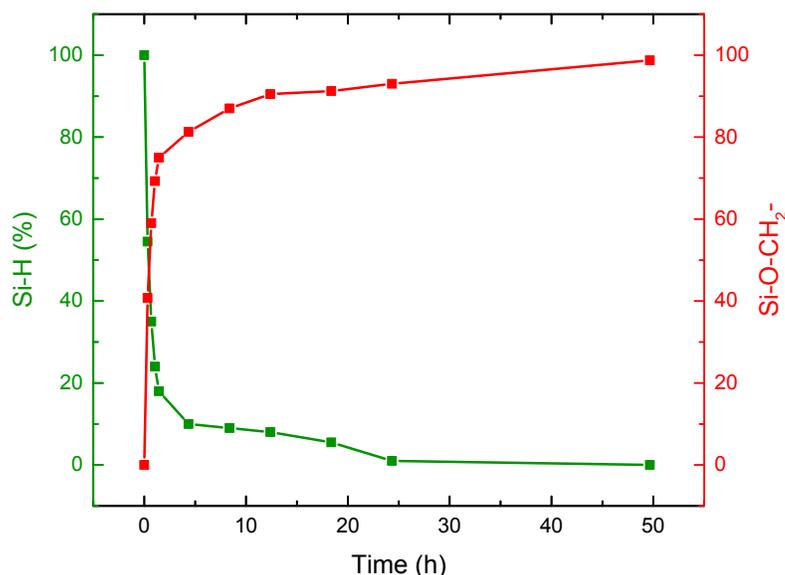


Figure 1 Rates of ethanolsis of **H-D₈-H** in presence of 500 ppm of Karstedt's catalyst (model reaction). The loss of the Si-H (%) and the growth of the Si-O-CH₂- (%) were calculated by following the corresponding ¹H NMR spectra signals over the reaction time (Supporting Information).

Optimizing the quantity of Karstedt's catalyst

Five identical solutions consisting of **H-D₈-H** (20mg, 0.054 mmol), 5 eq. of ethanol (15.7 μ L, 0.269 mmol), and toluene-*d*₈ (0.7 mL) were prepared in Eppendorf tubes and subsequently transferred into NMR tubes to collect initial ¹H NMR spectra. After the initial spectra were recorded, 50, 250, 500, 750, and 1000 ppm of Pt, respectively (Table 1), was pipetted separately into the 5 NMR tubes and quickly mixed with the rest of the solution by shaking the closed NMR tube. At 750 and 1000 ppm of Pt, it was possible to observe evolution of H₂ bubbles. Note: ppm refers to the mass of Pt / mass of hydrosiloxane $\times 10^6$. ¹H NMR spectra were run at given time intervals. See Figure 2.

Table 1. Amounts of Karstedt's catalyst added into the solutions.

| Karstedt's catalyst | | | | | |
|-----------------------|-----------------------------|------|----------------------------|------|-------|
| Pt (ppm) ^a | 50 | 250 | 500 | 750 | 1000 |
| μL | 0.05wt% solution in toluene | | 0.1wt% solution in toluene | | |
| | 1.17 | 5.85 | 5.85 | 8.77 | 11.70 |

^a ppm is calculated in mass of Pt / mass of hydrosiloxane x 10⁶.

Efficiency of reaction of simple alcohols: General procedure shown for ethanol (model reaction)

A solution consisting of **H-D₈-H** (20 mg, 0.054 mmol), 5 eq. of ethanol (15.7 μL, 0.269 mmol), and 0.7 mL of toluene-*d*₈ was prepared in an Eppendorf tube and subsequently transferred into an NMR tube to collect the initial spectra. After the initial ¹H NMR spectrum was run, Karstedt's catalyst (500 ppm of Pt, 5.85 μL of a 0.1wt% solution in toluene) was pipetted into the NMR tubes and quickly mixed with the rest of the solution by shaking the closed NMR tube. ¹H NMR spectra were run at given time intervals.

The same procedure was repeated with methanol (10.89 μL, 0.269 mmol), butanol (24.61 μL, 0.269 mmol), IPA (20.48 μL, 0.269 mmol), *t*-BuOH (25.71 μL, 0.269 mmol), benzyl alcohol (23.64 μL, 0.269 mmol). The toluene-*d*₈ was added to reach total solvent volume 715.70 μL, which was the solvent volume of the reaction above, considered as the model reaction. See Figure 3.

Ethanolysis of HMe₂SiOSiMe₃, (HMe₂SiO)₃SiMe, (HMe₂SiO)₃SiPh, Q(M^H)₄ and (QM^H)₈

The general method was used: **HMe₂SiOSiMe₃** (20 mg, 0.135 mmol), 5 eq of ethanol (39.36 μL, 0.674 mmol), toluene-*d*₈ (added to reach total solvent volume 715.7 μL), and Karstedt's catalyst (500 ppm of Pt, 5.85 μL of a 0.1wt% solution in toluene). ¹H NMR spectra were run at given time intervals.

(**HMe₂SiO**)₃**SiMe** (20 mg, 0.223 mmol), EtOH (65.21 μL, 1.117 mmol); (**HMe₂SiO**)₃**SiPh** (20 mg, 0.181 mmol), EtOH (52.97 μL, 0.907); **Q(M^H)₄** (20 mg, 0.243 mmol), EtOH (71.05 μL, 1.217 mmol); (**QM^H**)₈ (20 mg, 0.157 mmol). See Figure 4.

Ethanolysis of H-D₈-H, H-D₁₅-H, H-D₁₄₅-H, D^H₈D₇, D^H₈D₇₂, and D^H₅D₂₀

The general method was used: **H-D₈-H** (20 mg, 0.054 mmol), 5 eq. of ethanol (15.7 μL, 0.269 mmol), toluene-*d*₈ (added to reach total solvent volume 715.70 μL), and Karstedt's catalyst (500 ppm of Pt, 5.85 μL of a 0.1wt% solution in toluene). ¹H NMR spectra were run at given time intervals.

H-D₁₅-H (20 mg, 0.032 mmol), EtOH (9.26 μL, 0.159 mmol). **H-D₁₄₅-H** (20 mg, 0.003 mmol), EtOH (8.75 μL of 9.1 wt% solution in toluene, 0.014 mmol). **D^H₈D₇** (20 mg, 0.148 mmol), EtOH (43.10 μL, 0.738 mmol). **D^H₈D₇₂** (20 mg, 0.026 mmol), EtOH (7.56 μL, 0.129 mmol); **D^H₅D₂₀** (20 mg, 0.052 mmol), EtOH (15.134 μL, 0.259 mmol). See Figure 4.

Larger Scale Synthesis: General procedure shown for (QM^{OEt})₈

(QM^H)₈ (3 g, 23.576 mmol) was placed in a 50 mL round-bottomed flask and dissolved in 30 mL of dry toluene. After the (QM^H)₈ had dissolved, 5 eq. of ethanol (6.88 mL, 117.881 mmol) was added followed by addition of Karstedt's catalyst (1000 ppm of Pt, 175.44 μL). The reaction was allowed to run overnight at room temperature under a nitrogen blanket. Complete conversion of Si-H group to the Si-OEt was determined by ¹H NMR. Karstedt's catalyst was removed by stirring the reaction solution over activated carbon. The product was collected by filtration through Celite and evaporation of the solvents on rotary evaporator.

(QM^{OEt})₈: ¹H NMR (600 MHz, chloroform-*d*): δ 3.77 (q, 15.04H, *J* = 7 Hz, OCH₂CH₃), 1.21 (t, 24.2H, *J* = 7 Hz, OCH₂CH₃), 0.15 (s, 48H, SiMe₂), ²⁹Si NMR (99.4 MHz, chloroform-*d*): δ -9.89 (q, 8.24 Si, Si(Me)₂OCH₂CH₃), δ -110.04 (s, 8 Si, 110.04 (s, 8 Si, SiO_{4/2}). High Res MS calc. for [C₃₂H₈₈O₂₈Si₁₆ + NH₄]⁺ 1388.2109, found 1388.2085. Reaction yield 96%.

EtO-D₈-OEt: H-D₈-H (3 g, 8.065 mmol), dry toluene (5 mL), EtOH (5 eq., 2.35 mL, 40.323 mmol), and Karstedt's catalyst (300 ppm of Pt, 52.63 μ L).

¹H NMR (600 MHz, chloroform-*d*): δ 3.67 (q, 4H, OCH₂CH₃, *J* = 7 Hz), δ 1.14 (t, 6.17H, *J* = 7 Hz, OCH₂CH₃), δ 0.13 – 0.10 (m, 62.23H, SiMe₂). Reaction yield 85%.

(EtOMe₂SiO)₃SiMe: (HMe₂SiO)₃SiMe (0.5 g, 580.59 μ L, 5.584 mmol), dichloromethane (1 mL), EtOH (5eq., 1.63 mL, 27.922 mmol), and Karstedt's catalyst (500 ppm of Pt, 14.62 μ L).

Dichloromethane was used as lower boiling point solvent to reduce product losses during the solvent evaporation. Reaction yield 44% (due to starting material volatility).

¹H NMR (600 MHz, chloroform-*d*): δ 3.84 - 3.69 (m, 4.21H, OCH₂CH₃), δ 1.25 – 1.2 (m, 6.28H, OCH₂CH₃), δ 0.23 - 0.08 (m, 21H, SiMe + SiMe₂). calc. for [C₁₃H₃₆O₆Si₄ + NH₄]⁺ 418.1927, found 418.1930.

Results

Alcoholysis of a telechelic linear silicone polymer

Initial experiments focused on optimizing reaction conditions for alcoholysis of a model telechelic silicone polymer **H-D₈-H**. The optimization reactions were conducted in NMR tubes with spectra taken at different time points. The reaction rates were calculated by following the loss of Si-H and the growth of Si-O-CH₂- signals from the **EtO-D₈-OEt** formed (Figure S1).

Quantities of Karstedt's catalyst ranging from 50 ppm to 1000 ppm were investigated. From the graph in Figure 2 it can be seen that the loss of the Si-H groups matches the growth of the Si-O-CH₂CH₃ groups. This correlation signifies that no significant side reactions such as hydrolysis or condensation were occurring in the tested range of catalyst concentrations. A concentration of 500 ppm was subsequently chosen to facilitate alcoholysis of the model hydrosiloxane (**H-D₈-H**) at

room temperature, as it balances the need for a relatively rapid reaction rate with the quantity of expensive platinum catalyst required. These are much higher platinum catalyst concentrations compared to the quantity used for hydrosilylation of alkenes. As a result of Pt colloid formation during the reaction,¹⁷ the reaction solutions turn yellow to brown at the end of reaction. In addition, at the 750 and 1000 ppm level of catalyst, it was possible to directly observe the evolution of H₂ gas.

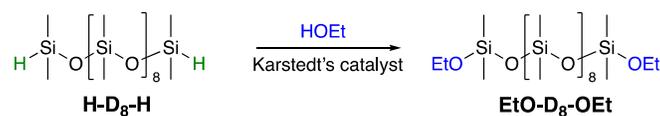
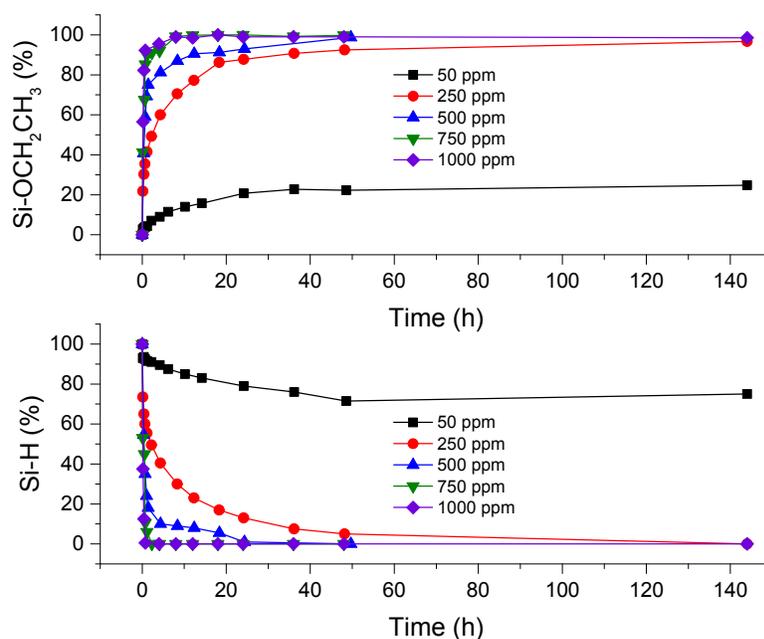


Figure 2. Loss of Si-H group (%) and growth of Si-OCH₂CH₃ group (%) concentration during the ethanolsis of **H-D₈-H** using different quantities of Karstedt's catalyst.

The efficiency of alcoholysis of **H-D₈-H** with different alcohols was tested using a Karstedt's catalyst concentration of 500 ppm. In all cases, except *t*-BuOH and benzyl alcohol, the Si-O-CH₂-

signal was quite distinct from that of the free alcohol HO-CH₂-. As before, the direct relation between loss of Si-H and growth of Si-O-CH₂- signals showed that no side reactions are occurring (Figure 3). As expected,^{18, 19} the efficiency of the alcoholysis reaction dropped with increased steric bulk at the alcohol, with the exception of methanol, following the order shown in Figure 3. The small differences in rates of EtOH and *n*-BuOH are inferred to be within experimental error.

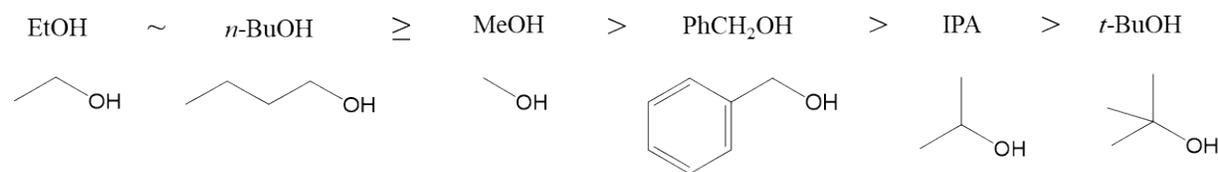
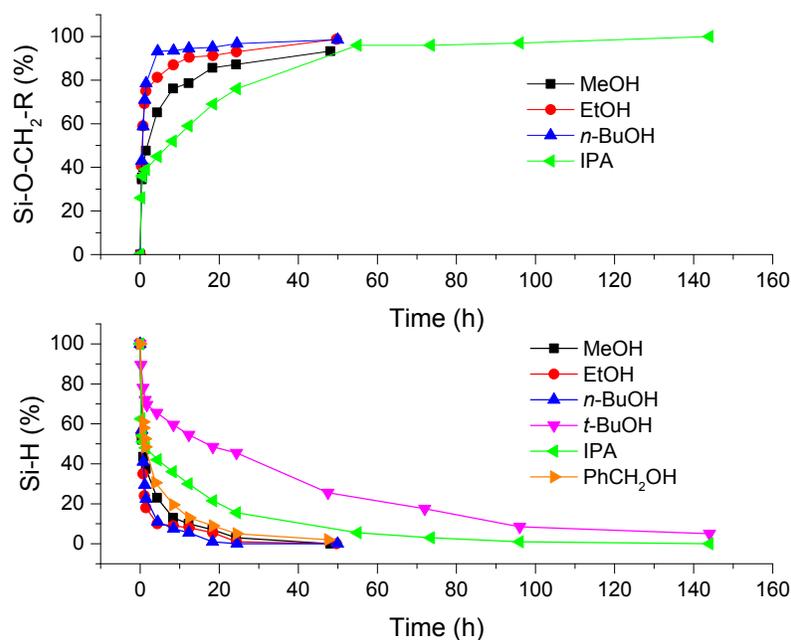


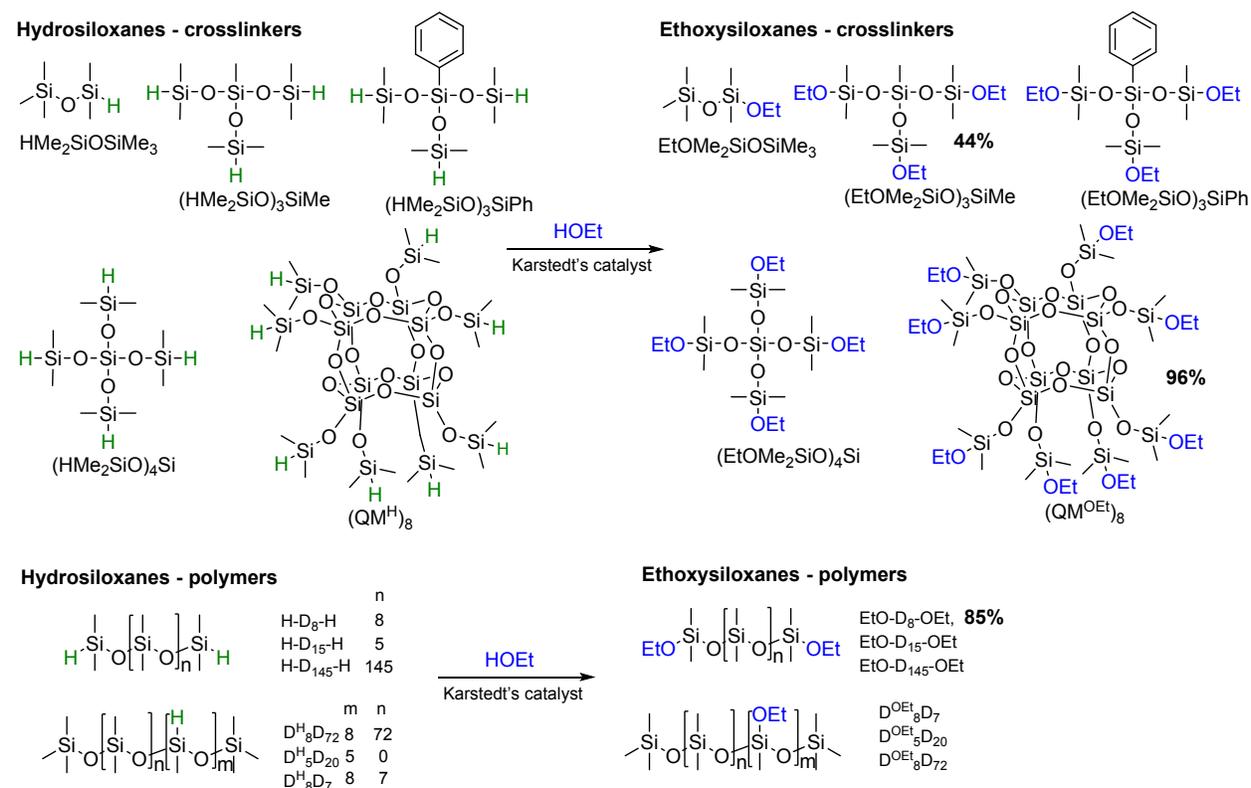
Figure 3. Loss of Si-H group (%) and growth of Si-O-CH₂-R group (%) during the alcoholysis of **H-D₈-H** using 500 ppm of Karstedt's catalyst (top). The order of alcohol efficiency (bottom).

Ethanolysis of hydrosiloxanes

The relative reactivities of a variety of siloxanes structural motifs to alcoholysis was studied (Figure 4). In all cases, ethanol was chosen as the alcohol, as ethoxysilanes are the most widely

used reagents for RTV moisture cure silicone elastomers.³ The studied compounds included telechelic and pendant SiH-containing polymers, monofunctional capping agents and tri-, tetra- and octa-functional crosslinkers. The reactions were performed in NMR tubes with ethanol and 500 ppm of Pt. In most cases, the Si-O-CH₂- signal was quite distinct from the free alcohol, which allowed simultaneous tracking of both moieties (Figure 4).

A



B

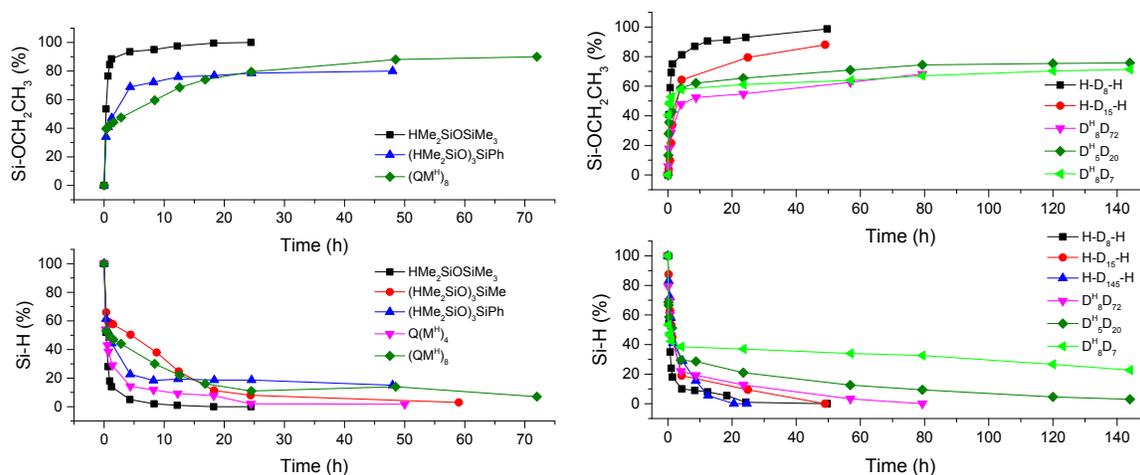


Figure 4. A: Ethanolsis of selected hydroxysiloxanes using Karstedt's catalyst (top). B: Loss of Si-H group (%) and growth of Si-OCH₂CH₃ group (%) concentration during the ethanolsis using 500 ppm of Karstedt's catalyst.

Hydride-terminated polydimethylsiloxanes **H-D_n-H** were slowly converted to ethoxy-terminated analogues (within 2 days). Pendant methylhydrosiloxane-dimethylsiloxane trimethylsiloxane terminated copolymers **D^H_mD_n** were found to require higher concentrations of the catalyst to reach full conversion of the Si-H groups over the same time period. This observation was expected due to higher steric hindrance near the HMeSiO moieties on the polymer backbone. All tested SiH crosslinkers were fully converted to the ethoxy equivalents except (HMe₂SiO)₃SiPh and (QM^H)₈ that required yet higher concentrations of platinum to be used.

Synthesis of alkoxyloxanes– larger scale reactions

Selected hydrosiloxanes were converted with ethanol to the corresponding ethoxy analogues in larger scale (Figure 4). The reactions were done at room temperature and led to products without side reactions either from hydrolysis or condensation of the functional groups. Both crosslinkers and linear polymer chains were prepared. The trifunctional crosslinker (EtOMe₂SiO)₃SiMe was

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3 prepared only with a relatively low reaction yield (~ 44%), which was a consequence of the high
4 volatility of the starting material. By contrast, the higher molecular weight, octa-functional
5 crosslinker (QM^{OEt})₈ was synthesized in a high reaction yield of ~96% and a linear polymer
6 derived from non-volatile starting materials was also prepared in high yield (EtO-D₈-OEt, 85%,
7 Figure 4).
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14 **Discussion**

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18 The hydrosilylation of alkenes catalyzed by Karstedt's catalyst, commonly used as a silicone
19 elastomer curing technology, is extremely efficient. For most formulations, only a few ppm of
20 platinum are required for efficient processes. However, the alcoholysis of hydrosiloxanes is much
21 less efficient. For practical reactions to occur (within less than a day), approximately 500 ppm Pt
22 were required (Figure 2). This quantity is similar to that reported for the preparation of
23 tris(alkoxydimethylsilyl)methane derivatives.¹² In part, this requirement for high Pt loadings may
24 be attributed to the competing reaction of platinum colloid formation from Karstedt's catalyst,
25 which is known to occur in HSi-rich media, particularly when good recipients for hydrosilylation,
26 such as alkenes, are not available.^{17, 20} That is, a fraction of the active platinum catalyst is lost
27 through conversion to much less reactive platinum colloids, which was shown by the production
28 of a yellow to brown color during the reaction.²¹
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43 Alkoxysilanes (silyl ethers) are widely used in the organic community as protecting groups,
44 particularly for alcohols.^{19, 22} The relationship between the formation/hydrolytic cleavage reactions
45 of the alkoxysilanes and steric bulk is well known. The rates of both reactions are retarded as the
46 bulk on silicon increases and, to a much lesser extent, to the bulk on carbon. This trend was
47 similarly observed here (Figure 3), where *t*-BuOH reacted much more sluggishly than primary
48 alcohols.
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3 Methanol was an outlier, as it was expected to react most rapidly on steric grounds. The effect
4 may be ascribed to issues of solubility. The work of Lee et al. showed that the solubility of PDMS
5 in alcohols followed the trend: methanol ($S = 1.02$) < ethyl alcohol ($S = 1.04$) < 1-propanol (1.09),
6 where S represents the ratio between the length of PDMS in the solvent over the length of the dry
7 PDMS.²³ The reaction rates shown in Figure 3 are then influenced by combination of two factors:
8 the solubility of the H-D₈-H and Karstedt's catalyst in the alcohols; and, the steric effect of the
9 alcohols. The slower reaction rate of the methanolysis compared to the ethanolysis or butanolysis
10 can be then explained by lower solubility of the H-D₈-H and Karstedt's catalyst in methanol.
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22 The group of Marciniak has demonstrated the extremely efficient conversion of a variety of
23 silsesquioxane hydrides into the corresponding alkoxy equivalents (contaminated, in some cases,
24 with very small amounts of disiloxanes), mostly using a palladium catalyst.¹⁴ However, they
25 showed Karstedt's catalyst, at the higher end of the concentrations examined here, was able to
26 convert a mono SiH → SiOMe silsesquioxane, and other hydridosilsesquioxanes into phenoxy-
27 substituted silsesquioxanes. Their experience suggests that Pd/C (Pd on activated carbon) is a good
28 alternative for oxidation of hydrosiloxanes.
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38 What is the justification for silicone manufacturers, in particular, to consider using Karstedt's
39 catalyst to create alkoxy siloxanes? There are several advantages. When silicone polymers are
40 exposed to (even low concentrations of) acids or bases, an equilibrium is established between
41 shorter molecular weight silicones and cyclic siloxane monomers.³ The main benefit of this
42 method is related to the mild reaction conditions that do not lead to silicone equilibration. In
43 addition, one simple alcoholysis reaction can be used to create both small molecule and polymeric
44 alkoxy siloxanes crosslinkers or chain extenders (Figure 4). Finally, while more catalyst is required
45 for this alcoholysis than hydrosilylation, Pt is widely used in house, and spent catalyst can be
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3 recovered since the products are readily removed from the catalyst by filtration. Efficient methods
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5 for Pt recovery and reuse are already in use;²⁴ and the starting H-Si compounds are already used
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7 in commerce.
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10 Moisture cure RTV is a mild convenient route to well defined silicone elastomers. However, the
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12 traditional use of small molecule silane crosslinkers has its disadvantages. The rate of reaction of
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14 polyfunctional molecules drops off dramatically in sol-gel curing processes. With
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16 tetraethoxysilane (TEOS), for example, the first and second EtO group are rapidly replaced by
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18 silanol-terminated polymer nucleophiles. The third and fourth groups react significantly more
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20 slowly, frequently as a consequence of steric constraints.²⁵ In practice, ‘final cure’ may take a very
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22 long time or, due to low degrees of mobility, be impossible for elastomers based on single point
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24 silicon crosslinkers (i.e., (RO)₃SiR’, or (RO)₄Si). Tri- and tetrafunctional crosslinkers prepared
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26 using alcoholysis that have much higher degrees of freedom – (Q(M^{OEt}))₄, (QM^{OEt})₈,
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28 (EtOMe₂SiO)₃SiMe – will be far less susceptible to steric constraints; all the functional groups are
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30 located at chain termini (Figure 4), which will allow creation of specific network structures at more
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32 convenient rates.
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38 Silicone elastomer properties depend on network structure. One would like to design networks
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40 that will readily form without the steric issues noted above and, in addition, go beyond traditional
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42 tri- and tetrafunctional crosslinkers. The ability to use the alcoholysis process to create telechelic
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44 EtO-D_n-OEt and pendent D^{OEt}_mD_n ethoxysilane-based compounds allows further tailoring of
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46 networks formed during RTV processes. That is, it should be possible to prepare designer
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48 elastomers that cure in convenient time scales from commercial telechelic silanol polymers and
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50 one or more small molecule and polymeric alkoxysiloxanes (Figure 4) to permit control over
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3 network structures, including M_C and, therefore, desirable properties including extension at break,
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5 modulus, etc.^{5, 26}
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8 Small molecule and polymeric hydrosiloxanes are commercially available and commonly used
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10 for the synthesis of addition curing silicone elastomers. The range of commercially available RO-
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12 compounds is rather limited compared to the H-compound analogues. However, H-Si compounds
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14 can be easily converted into RTV-active RO-Si compounds using the same platinum catalyst as is
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16 used for addition cure. That is, the chain-extending and crosslinking entities used for
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18 hydrosilylation may now be accessed as alkoxy siloxane analogues for RTV cure. Although
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20 expensive Karstedt's platinum catalyst is required for the alcoholysis reaction, it can readily be
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22 recovered from the process. The alcoholysis reaction avoids redistribution processes that can
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24 initiate loss of silicone structural features, including molecular weight. This permits complex,
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26 active RTV crosslinkers and chain extenders to be prepared in good yield that, in turn, can be used
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28 to design complex RTV networks.
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32 33 **Conclusions** 34 35

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37 Commercially available small molecule and polymeric hydrosiloxanes, commonly used for
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39 preparation of addition curing silicone elastomers, were converted to their alkoxy analogous using
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41 mild conditions in the presence of Karstedt's catalyst. Although relatively high amounts of the
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43 Karstedt's catalyst are required, the catalyst can be collected and regenerated after the reaction is
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45 completed. The alkoxy analogues of the SiH compounds prepared in this study enrich the
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47 possibilities to tailor network structures derived from moisture induced, room temperature
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49 vulcanization.
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53 **Supporting Information.** Stacked NMR plots for kinetics experiments.
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56 57 **Acknowledgments** 58 59 60

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