Supplementary Material (ESI) for Chemical Communications

Liquid/Liquid Separation of Polysiloxane-Supported Catalysts

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Experimental Section

Materials. Pt-divinyltetramethyldisiloxane complex (Karstedt's catalyst) in xylene (2% Pt), α,ω-bis(hydrosilyl)polydimethylsiloxane (Gelest DMS-H21) (**1**), α,ω-bis(trimethylsilyloxy)copoly[methylhydrosiloxane/dimethylsiloxane] (Gelest HMS-013) (**2**), 1:144 by ^{1}H NMR integration, and α,ω-bis(trimethylsilyloxy)copoly[methylhydrosiloxane/methyloctylsiloxane] (Gelest HAM-301) (**3**), 1:3 by ^{1}H NMR integration, were acquired from Gelest. All other reagents and solvents were obtained from other commercial sources and used without purification.

Instrumentation. ^{1}H NMR spectra were acquired on an Inova-400 300 MHz spectrometer operating in the FT mode. Five percent w/v $CDCl_3$ solutions were used and residual $CDCl_3$ served as the internal standard. IR spectra of neat films on NaCl plates were recorded using a Mattson Instruments Galaxy Series 4021 FT-IR spectrometer. Gel permeation chromatography (GPC) analysis of the molecular weight distribution of **1-3** were performed on a Viscotek triple detector GPC system equipped with an isocratic solvent delivery pump and a two channel in-line solvent degasser. An oven heater housed the manual sample injection valve and column. The detector system consisted of three detectors in series: refractive index (RI), right angle laser light scattering (RALLS), and viscometer (VP). A ViscoGEL™ HR-Series (7.8 mm x 30 cm) packed with divinylbenzene crosslinked polystyrene (SDVB) was used for the analysis. The eluting solvent was HPLC grade toluene at a flow rate of 1.0 mL/min. The column and injector were maintained at a temperature of 25 °C. The detectors were calibrated with a polystyrene (PS) narrow standard with the following parameters: Mw (66K), polydispersity (1.03); intrinsic viscosity (0.845 dL/g); dn/dc (0.112 mL/g). All solutions

were filtered with 0.45 micron filter prior to injection. In the case of **3**, its very low molecular weight required high injection concentrations (60 to 140 mg/mL) for detection by RALLS. In this case, the dn/dc value was calculated (0.052) by generating a plot of the RI detector peak area versus sample concentration. Data analysis was performed with Viscotek OmniSec software, version 4.0. Thus, the following values were obtained: **1** (M_w/M_n = 6,080/3,730); **2** (M_w/M_n = 136,380/82,480); **3** (M_w/M_n = 985/625). All phase selectivity measurements were obtained with a Varian Cary 100 scanning UV/vis spectrophotometer. Samples were diluted as needed with appropriate solvent before measurement. Extinction coefficients were considered to be solvent-independent. Phase selectivity of the polymer was calculated by ratio of the absorbance measured for the dye-labeled polymer in each phase of the system. Enantiomeric excess (% ee) was determined with a Dynamax HPLC equipped with a Daicel Chiralpak AD column. The eluting solvent was hexane/isopropyl alcohol (9:1 vol:vol) set to a flow rate of 1.0 mL/min.

General Procedure for Phase Selectivity Studies. Polymer concentrations for the phase-selective solubility studies were that which would be required if the polymers were used as soluble catalyst supports in catalytic reactions. Reagent concentrations of 0.1-0.5 M would typically require 0.1-0.2 mol % of catalyst. Thus, the amount of polymer necessary to support this quantity of catalyst was tested for phase selectivity. Standard curves were prepared to observe the linearity of the absorbance readings. For thermomorphic solvent systems, the polymer was dissolved in the heptane phase and an equal volume of a DMF (heptane-saturated) phase was then added. The system was heated to promote phase miscibility (to about 70 ˚C) followed by cooling to induce phase separation. For latent biphasic solvent systems, the polymer was dissolved in the heptane (nonpolar) phase and the ethanol (polar) phase was added. Phase separation occurred upon addition of water so that the final concentrations of solvents was 10: 8: 2 (vol:vol:vol) of heptane, ethanol, and water. Centrifugation with a Jouan CT422 centrifuge was applied to efficiently and completely separate the phases. The solvent

layers were isolated and diluted with the predominant solvent until the absorbance readings were within the predetermined linear range using the UV spectrophotometer.

General Hydrosilylation Procedure. Hydrosilylation reactions were run under a N_2 atmosphere. The progress of the reaction was monitored with IR spectroscopy by the disappearance of the Si-H (~2100 cm^{-1}) absorbance. After the initial reaction time of ~12 h at elevated temperatures, an aliquot of the reaction solution was evaporated on a NaCl plate and the IR spectrum measured. In the case of an incomplete reaction, additional Karstedt's catalyst (50% of the original volume) was added to the reaction solution and allowed to proceed for another ~12 h before recording the IR spectrum. This cycle was repeated as necessary until no Si-H absorbance was observed in the IR spectrum. Typically, no additional Kartstedt's catalyst was required to complete the reaction. After a complete reaction, the reaction mixture was allowed to cool to room temperature (RT) and the toluene removed under reduced pressure. A small amount of DCM: ethyl acetate (2:1 vol:vol) was added to the residue and the solution passed through a short silica gel column with similar solvent to remove the residual Pt. Volatiles were removed under reduced pressure.

Methyl Red. Methyl red was prepared according to standard procedures. In a 400 mL beaker equipped with a Teflon-covered magnetic stir bar, 4.42 g of $NaCO_3$ was dissolved in 150 mL of water. Next, *p*-aminobenzoic acid (4.42 g, 0.042 mol) was added to the solution and dissolved with minimal heating. After cooling to RT, $NaNO_2$ (5.74 g, 0.83 mol) was added. This above solution was then added drop wise to a solution of 13.3 mL HCl and 65 mL of water at 0 °C. N,N-dimethylaniline (10 mL, 0.079 mol) and 16 mL of acetic acid were then added with vigorous stirring. After warming to RT over one h, a red suspension formed. The crude precipitate was gravity filtered and dissolved in 30 mL of acetic acid and 8 mL of HCl. Recrystallization in DMF (2 L) followed by sequential washing with water and methanol and finally vacuum drying at 60 °C afforded methyl red (10.8 g, 95% yield).

Methyl red dye-substituted styrene derivative.[1] Into 35 mL of DMF (dry) were sequentially dissolved methyl red (1.35 g, 5 mmol), Et_3N (1.05 mL, 7.53 mmol), and 4-vinylbenzylchloride (1.4 mL, 9.85 mmol). The solution was stirred vigorously for 24 h and then combined with 200 mL of water. The product was extracted from the aqueous phase with DCM (3X), the organic layer dried with $MgSO_4$, filtered, and volatiles removed under reduced pressure. The isolated crude product was purified by column chromatography with hexanes/ethyl acetate (4:1 vol:vol) as the eluent. The product was isolated in 53 % yield. ^{1}H NMR spectra was in agreement to that previously reported.

Synthesis of 4. **1** (4 g), dye-substituted styrene derivative (0.594, 1.54 mmol), and Karstedt's catalyst (15 μL) were reacted in 40 mL of toluene as described above and subsequently purified. In this way, **4** (4.43 g, 96% yield) was isolated.

Synthesis of 5. **2** (10 g), dye-substituted styrene derivative (0.536 g, 1.39 mmol), and Karstedt's catalyst (30 μL) were reacted in 85 mL of toluene as above and subsequently purified. In this way, **5** (8.66 g, 82% yield) was isolated.

Synthesis of 6. **3** (10 g), dye-substituted styrene derivative (0.056 g, 1.45 mmol), and Karstedt's catalyst (30 μL) were reacted in 65 mL of toluene as above. After ~12 h, complete reaction of the dye-substituted styrene derivative was confirmed by the absence of vinyl peaks in the ^{1}H NMR spectrum. Following purification as above, **6** (9.0 g, 89% yield) was isolated. The ratio of repeat units was calculated directly from integration of appropriate peaks in the ^{1}H NMR spectrum of purified **6**.

Synthesis of 7. In a 35 mL Ace pressure tube equipped with Teflon-covered stir bar, **6** (2.0 g), 1-octene (0.76 g, 6.76 mmol), and Karstedt's catalyst (20 μL) were combined with 7 mL of toluene. The tube was sealed and the reaction mixture heated to 125 °C for 48 h. The product was isolated as above. In this way, **7** (2.66 g, 96 % yield) was isolated.

Quinine Acetate.[2-5] Quinine (2.0 g, 6.2 mmol, 1 equiv) and Et_3N (0.94 g, 9.3 mmol, 1.5 equiv) were combined with 45 mL of DCM in a flame-dried 100 mL 3-neck round bottom (rb) flask equipped with a Teflon-covered stir bar and pressure-equalizing addition funnel. After cooling to 0 °C, a solution of acetyl chloride (0.65 g, 8.3 mmol)

was added over one h. The reaction mixture was allowed to stir 17 h at RT, sat. aq. $NaHCO_3$ solution added, and the aq. layer extracted with DCM. The combined organic layer was dried with $MgSO_4$, filtered, volatiles evaporated, and purified via column chromatography with ethyl acetate:methanol (10:1 vol:vol) as the eluent. This provided quinine acetate (1.83 g, 81% yield). ^{1}H NMR δ: 1.49-1.60 (m, 2H), 1.68-1.78 (m, 1H), 1.85-1.93 (m, 2H), 2.13 (s, 3H, -OCOC$\underline{H}_3$), 2.23-2.34 (m, 1H), 2.58-2.72 (m, 2H), 3.02-3.16 (m, 2H), 3.39 (q, 1H, *J* = 8.4 Hz), 3.96 (s, 3H, -O$\underline{CH}_3$), 4.98-5.01 (m, 1H, -C$\underline{H}_2$=CH), 5.02-5.06 (m, 1H, -C$\underline{H}_2$=CH), 5.79-5.91 (m, 1H, CH_2=C$\underline{H}$), 6.50 (d, 1H, $\underline{H}$-C-OCOCH$_3$, *J* = 7.2 Hz), 7.36-7.40 (m, 2H), 7.45 (d, 1H, *J* = 2.7 Hz), 8.02 (d, 1H, *J* = 9.0 Hz), 8.75 (d, 1H, *J* = 4.8 Hz).

α,ω-Bis(quinine acetate)polydimethylsiloxane. In a 250 mL rb flask equipped with stir bar, 9.0 g of α,ω-bis(hydrosilyl)polydimethylsiloxane (**1**), quinine acetate (1.13 g, 3.1 mmol), and Karstedt's catalyst (30 μL) were combined with 120 mL of toluene and heated at 65 °C for 12 h under N_2. Toluene was evaporated and the residue passed through a short silica gel plug with ethyl acetate:DCM (1:2 vol:vol) as the eluent and solvents evaporated. The residue was dissolved in heptane and washed sequentially with 90% aq. methanol (3X) and acetonitrile (6X), dried with $MgSO_4$, filtered, and volatiles were evaporated. This provided α,ω-bis(quinine acetate)polydimethylsiloxane (6.8 g, 67% yield). ^{1}H NMR δ: 0.023-0.156 (m, 681H, $\underline{CH}_3$-SiO), 0.46-0.52 (m, 4H, Si-$\underline{CH}_2$-CH_2-), 1.27-1.38 (m, 4H, Si-CH_2-$\underline{CH}_2$-), 1.40-1.55 (m, 4H), 1.68-1.90 (m, 6H), 2.13 (s, 6H, -OCOC$\underline{H}_3$), 2.26-2.34 (m, 2H), 2.59-2.69 (m, 2H), 3.01-3.15 (m, 4H), 3.35 (m, 2H), 3.97 (s, 6H, -O$\underline{CH}_3$), 6.52 (d, 2H, $\underline{H}$-C-OH, *J* = 7.2 Hz), 7.36-7.40 (m, 4H), 7.47 (d, 2H, *J* = 2.7 Hz), 8.03 (d, 2H, *J* = 9.0 Hz), 8.75 (d, 2H, *J* = 4.8 Hz).

α,ω-Bis(quinine)polydimethylsiloxane (8). In a 250 mL rb flask equipped with a stir bar, α,ω-bis(quinine acetate)polydimethylsiloxane (5.1 g) was dissolved in 150 mL of a 0.15 wt% K_2CO_3 in 90% aq EtOH. The mixture was allowed to stir at 55 ºC for 12 h. The solvent was evaporated and the residue dissolved in 300 mL of heptane, washed 3X with DI water, the organic layer dried ($MgSO_4$), filter, and solvents removed under reduced pressure. In this way, **8** (4.1 g, 81% yield). ^{1}H NMR δ: 0.01-0.19 (m, 671H,

$\underline{CH_3}$-SiO), 0.40-0.48 (m, 4H, Si-$\underline{CH_2}$-CH_2-), 1.20-1.77 (m, 4H, Si-CH_2-$\underline{CH_2}$-), 1.40-1.55 (m, 4H), 1.75-1.90 (m, 6H), 2.30-2.43 (m, 2H), 2.59-2.70 (m, 2H), 3.01-3.15 (m, 4H), 3.54-3.65 (m, 2H), 3.94 (s, 6H, -O$\underline{CH_3}$), 5.74 (s, 2H, $\underline{H}$-C-OH), 7.27-7.36 (m, 4H), 7.57 (d, 2H, J = 4.2 Hz), 8.01 (d, 2H, J = 9.3 Hz), 8.63-8.69 (m, 2H).

Michael addition reaction in a latent biphasic system. α,ω-Bis(quinine)polydimethylsiloxane (**8**) was first dissolved in heptane (10 mL). Next, ethanol (9 mL), Michael donor (3.3 mmol), and Michael acceptor (3.6 mmol) were added. After running the reaction in the homogenous (monophasic) mixture for 24 h at RT, 1 mL of DI H_2O was added to induce phase separation. Thus, the product in the aq. ethanol phase was isolated via thorough solvent removal. The product from the reaction of 4-mercaptobenzoic acid and MVK was isolated as a white precipitate and dried. The heptane phase containing **8** was combined with fresh substrates and 9 mL of ethanol for subsequent cycles. For each substrate pairs, reactions were performed in the absence of catalyst, with 1 mol% "free" quinine (**Table 1**), and with 10 mol% of **8** (over 5 cycles). Michael addition products isolated as above were characterized by solution state ^{1}H NMR spectroscopy (see **Figures 5-9**). In the case of the asymmetric addition of thiophenol and 2-cyclohexen-1-one, % ee was determined by HPLC.

References

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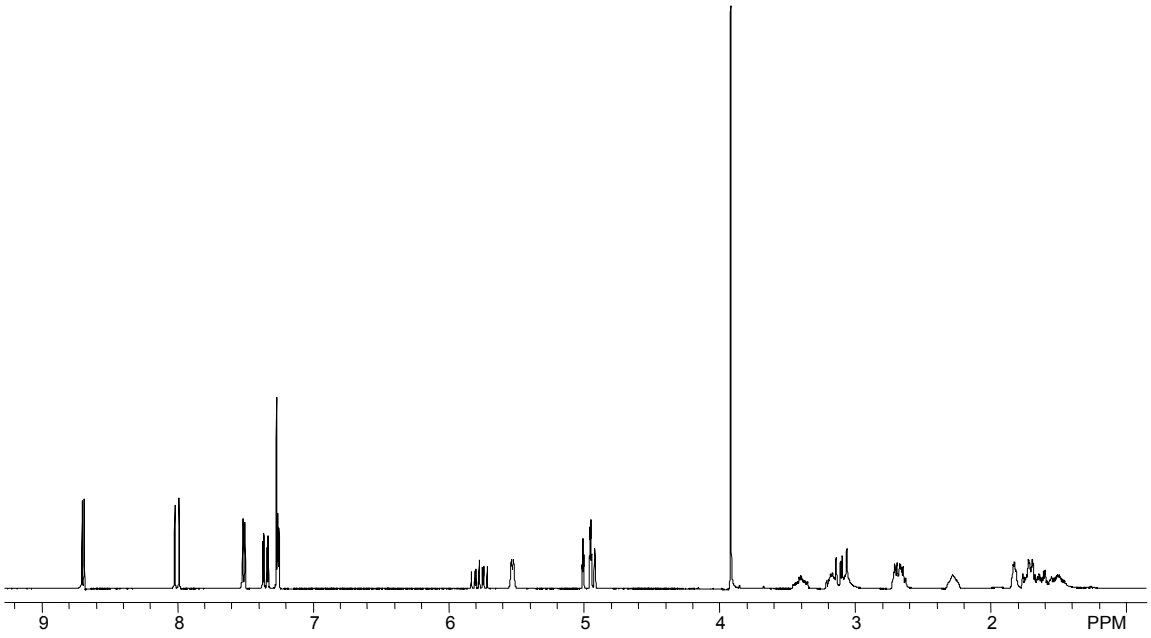

Figure 1. ^{1}H NMR of quinine.

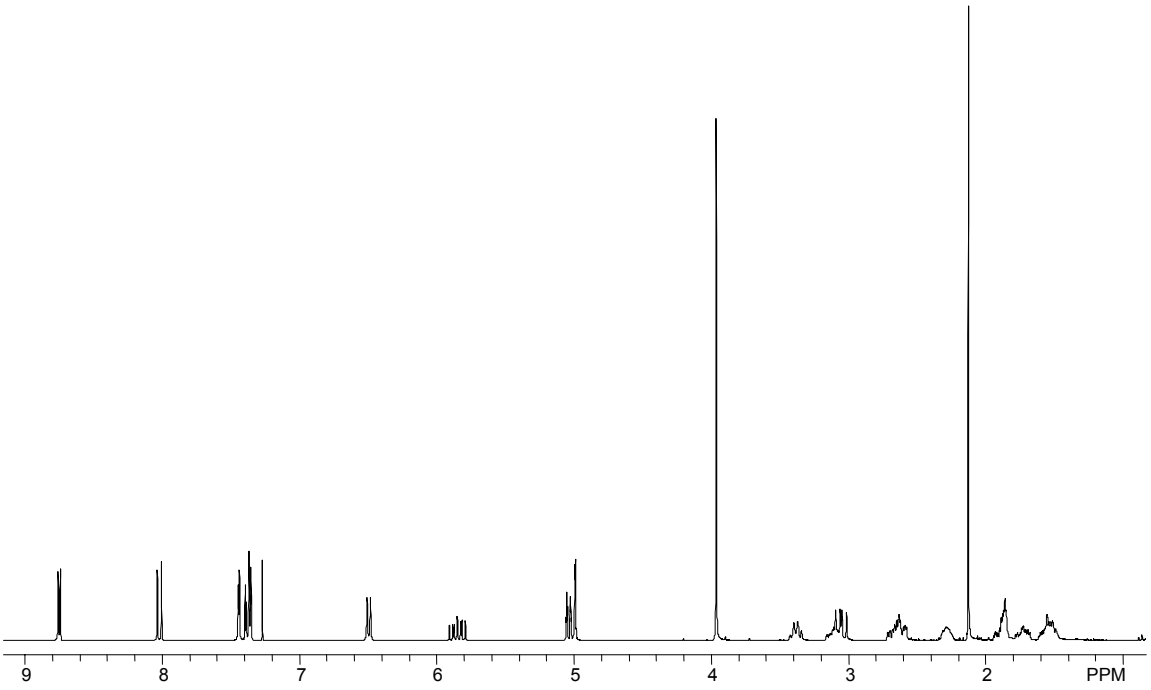

Figure 2. ^{1}H NMR of quinine acetate.

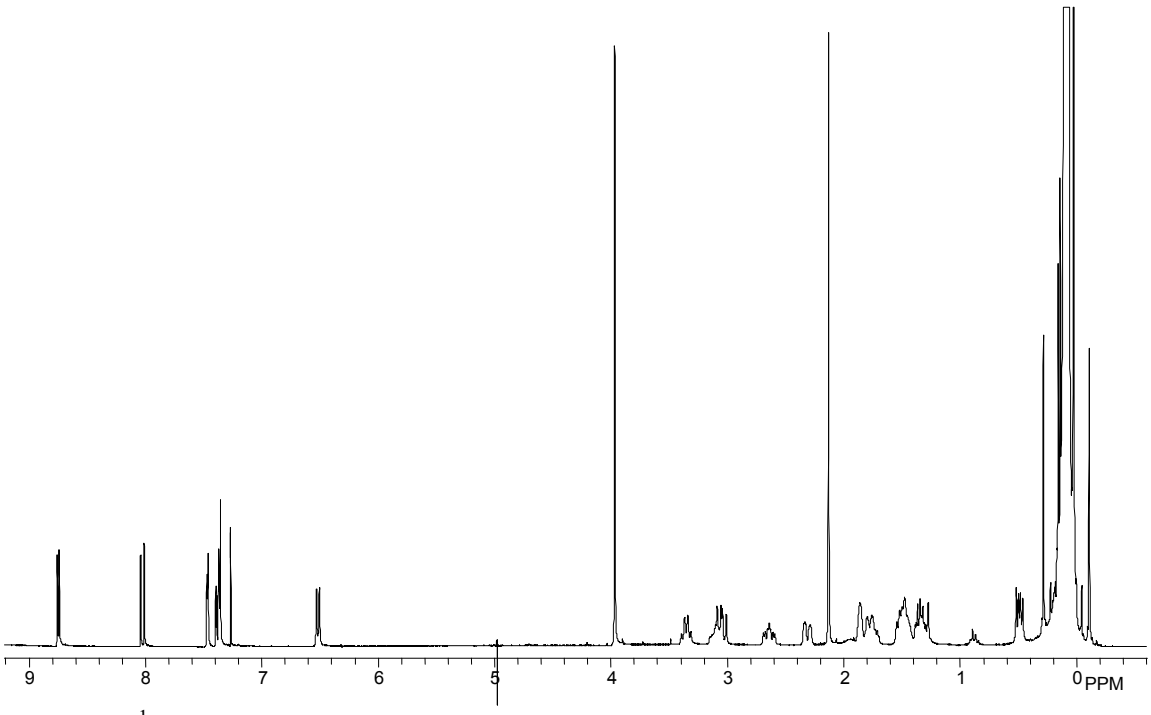

Figure 3. ^{1}H NMR of α,ω-bis(quinine acetate)polydimethylsiloxane.

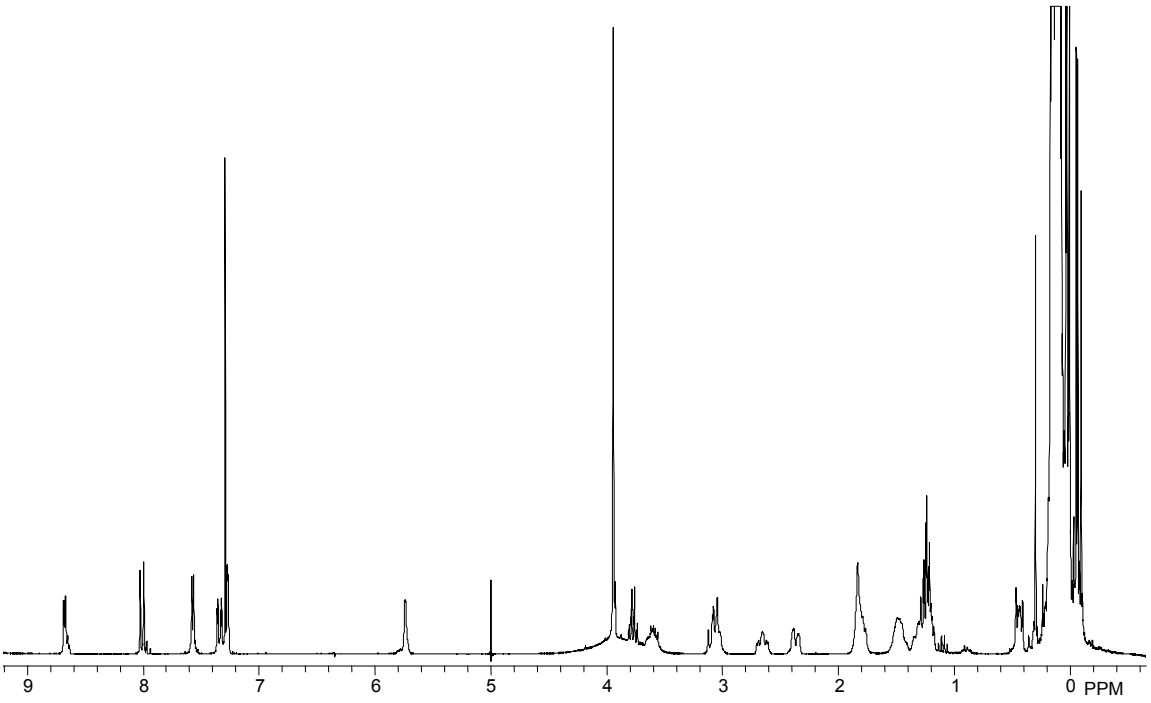

Figure 4. ^{1}H NMR of α,ω-bis(quinine)polydimethylsiloxane **(8).**

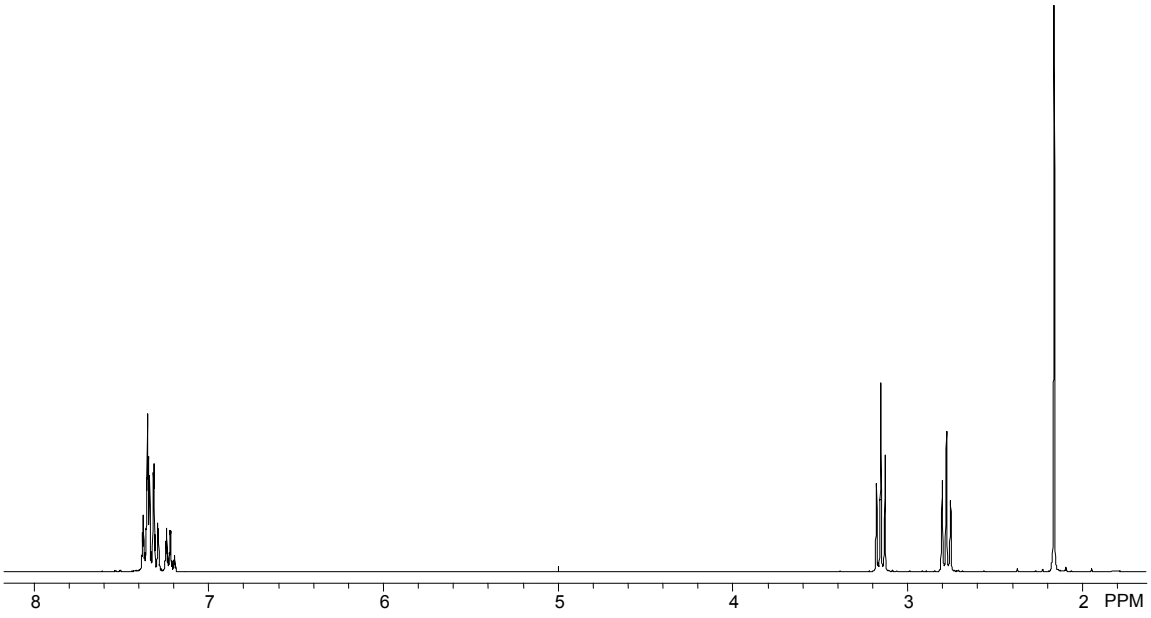

Figure 5. ^{1}H NMR of Michael addition product of C_6H_5SH and $H_2C{=}CHCOCH_3$ catalyzed by **8** (10 mol%).

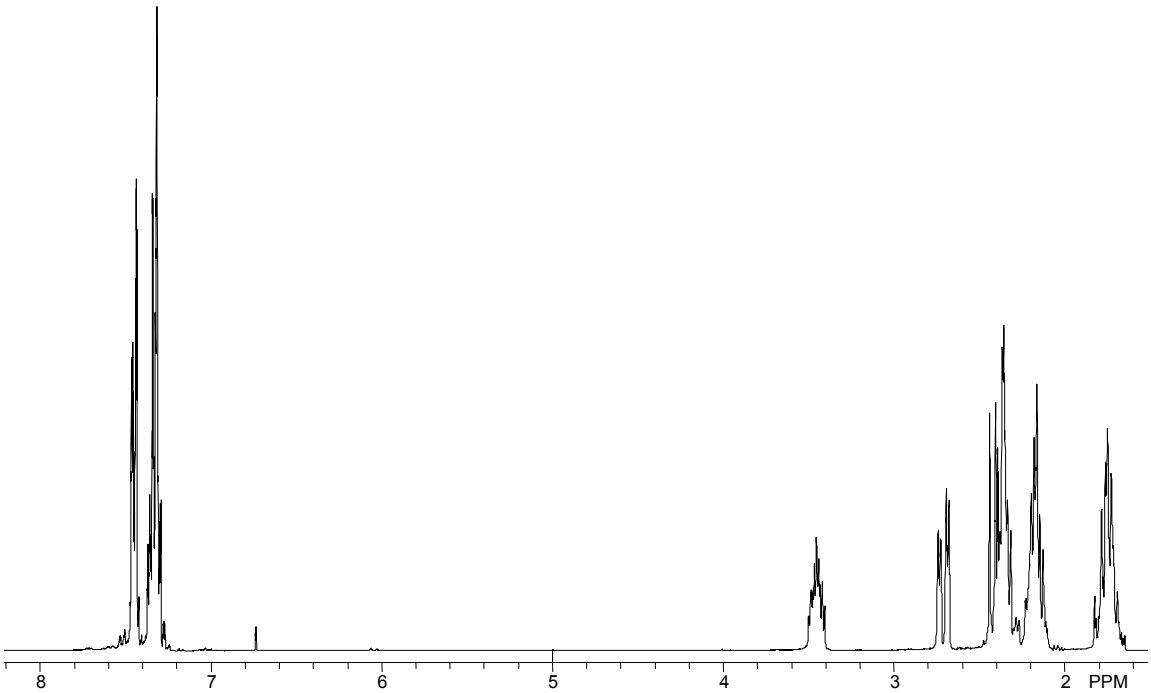

Figure 6. ^{1}H NMR of Michael addition product of C_6H_5SH and 2-cyclohexen-1-one catalyzed by **8** (10 mol%).

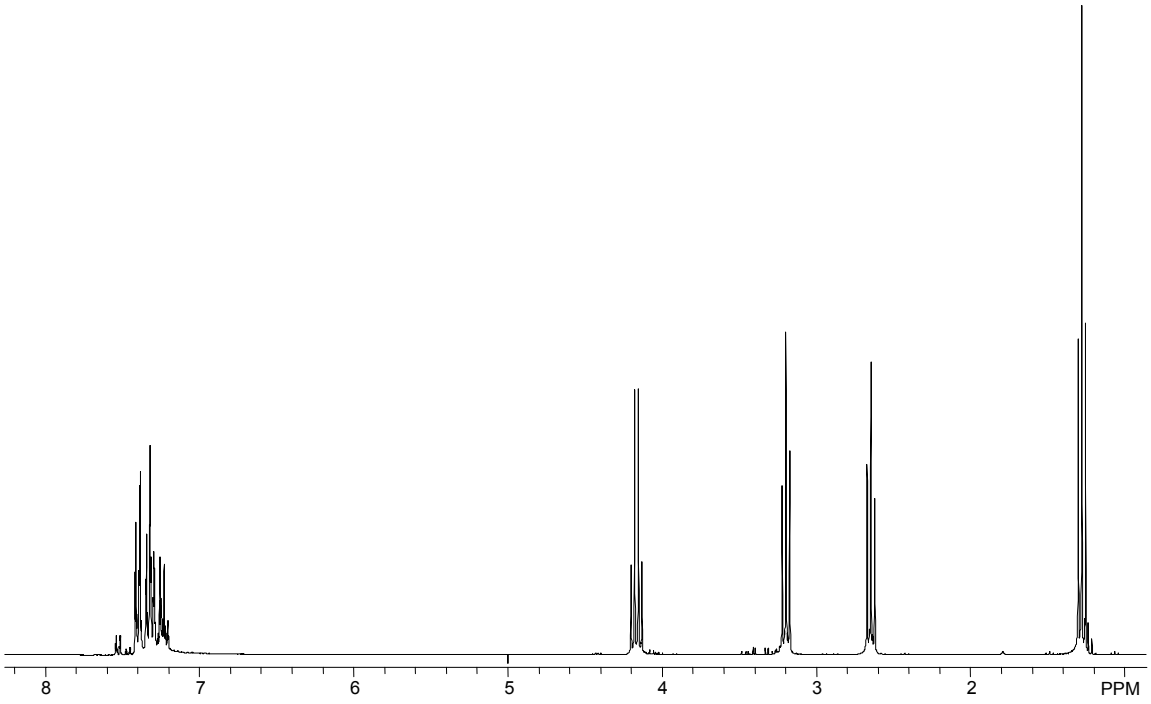

Figure 7. ^{1}H NMR of Michael addition product of C_6H_5SH and $H_2C{=}CHCO_2Et$ catalyzed by **8** (10 mol%).

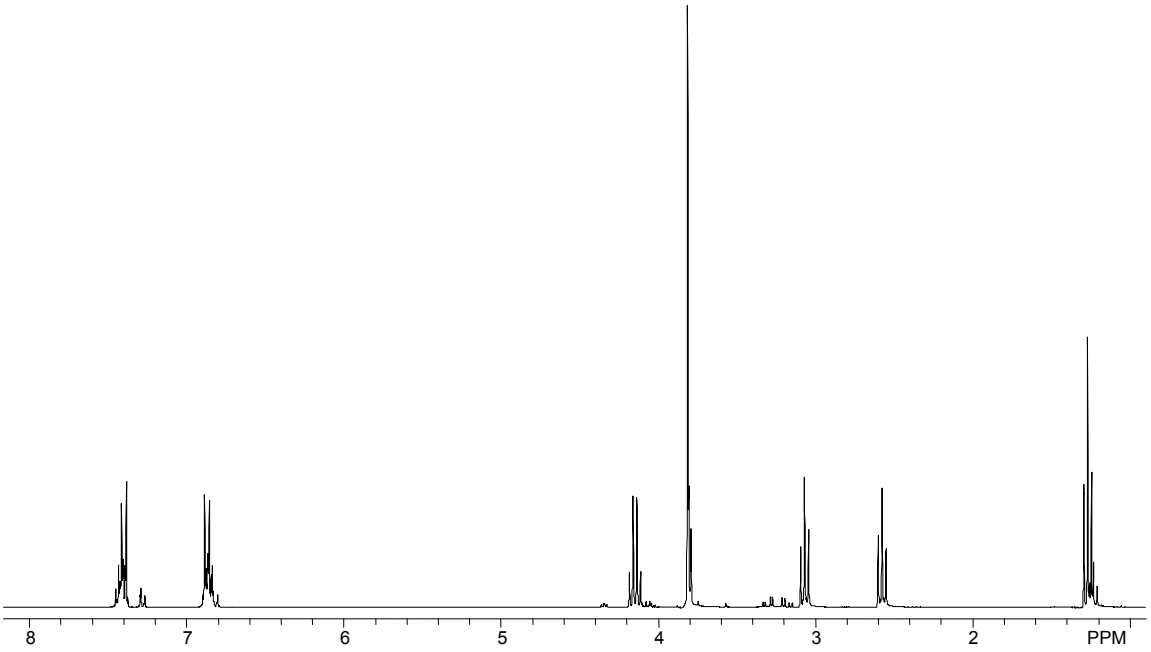

Figure 8. ^{1}H NMR of Michael addition product of *p*-$CH_3OC_6H_4SH$ and $H_2C{=}CHCO_2Et$ catalyzed by **8** (10 mol%).

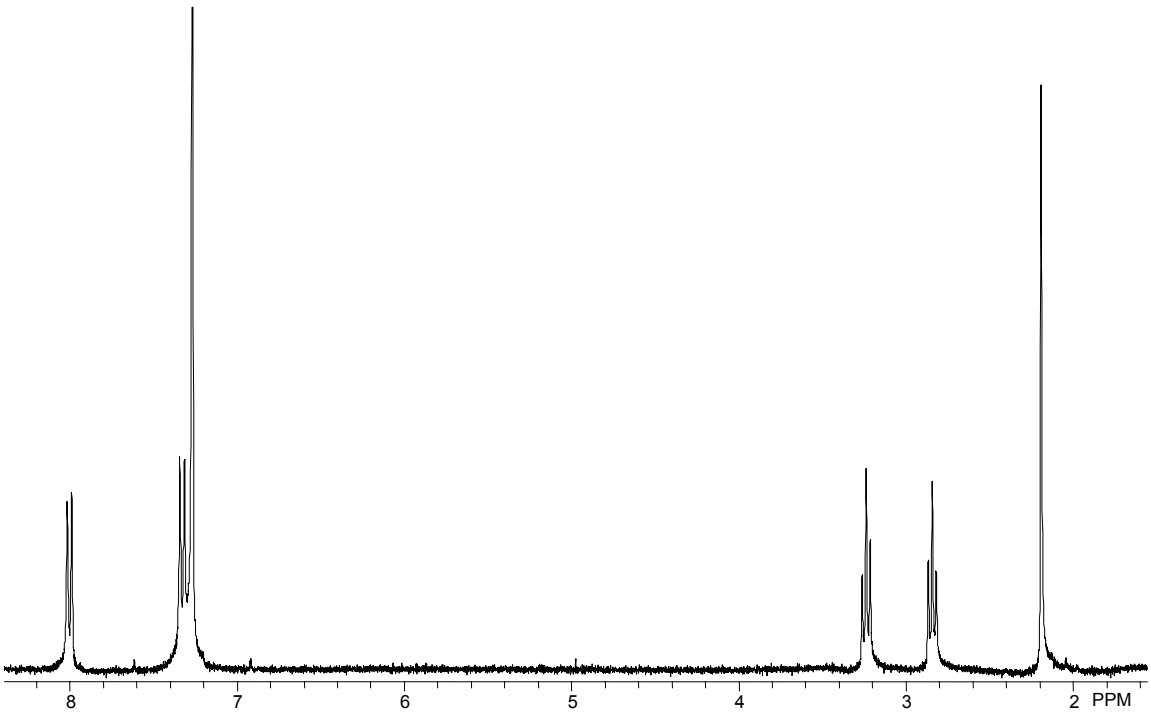

Figure 9. ^{1}H NMR of Michael addition product of *p*-$HO_2CC_6H_4SH$ and $H_2C{=}CHCOCH_3$ catalyzed by **8** (10 mol%).

Table 1. Product yields for Michael addition reactions ran with no catalyst and with | 1 mol% of quinine (not immobilized on **1**).

Michael Donor	Michael Acceptor	No catalyst Product Yield	1 mol% quinine Product Yield
C_6H_5SH	$H_2C{=}CHCOCH_3$	47%	78%
C_6H_5SH	2-cyclohexen-1-one	36%	81%
C_6H_5SH	$H_2C{=}CHCO_2Et$	30%	57%
p-$CH_3OC_6H_4SH$	$H_2C{=}CHCO_2Et$	23%	58%
p-$HO_2CC_6H_4SH$	$H_2C{=}CHCOCH_3$	42%	88%