Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Mechanistic Investigations of Alcohol Silylation with Isothiourea Catalysts

Brandon K. Redden, Robert W. Clark, Ziyuan Gong, Md. Mamdudur Rahman, Dmitry V. Peryshkov, and Sheryl L. Wiskur*

Table of Contents.

General Information

All kinetic studies were performed with flame-dried glassware under either a nitrogen or argon atmosphere. Molecular sieves were activated in an oven at 170 ^{o}C at least 24 h prior to use. Tetrahydrofuran (THF) was degassed and passed through a column of activated alumina prior to use and stored over 4Å molecular sieves. Triphenylsilyl chloride was recrystallized before use. Tetramisole was freebased with NaOH and dried under vacuum prior to use. Sodium tetrakis3,5-bis(trifluoromethyl)phenylborate was recrystallized and dried in a drying pistol before use in both the NMR and kinetic studies, and triphenylsilyl chloride and benzotetramisole were also dried the same way for the NMR binding studies. Unless otherwise stated, all reagents or starting materials were obtained from commercially available sources and used without further purification. The solutions for NMR binding studies and NaBArF kinetic studies were prepared in a glove box. Kinetic experiments were monitored on a Mettler-Toledo ReactIR™ iC10 instrument equipped with a silicon probe. IR data was analyzed using Mettler-Toledo's iC IR software. NMR spectra taken of the kinetic runs were obtained with a 300 MHz Bruker spectrometer and the NMR binding study was done with a 400 MHz Bruker spectrometer. All spectra were obtained in CDCl3 using TMS as an internal standard (TMS 0.00 ppm for ^{1}H) unless otherwise stated.

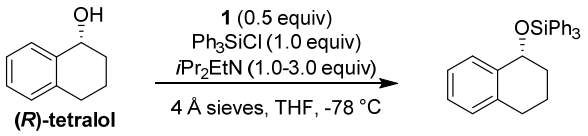
General Procedure for Kinetic Analysis Experiments

A three-necked reaction vessel was flame-dried, equipped with a flea stir bar and 4Å sieves, and sealed with a septa. The vessel was purged with nitrogen and the ReactIR probe was inserted into the flask and clamped. A background was taken on air, then the specified amount of THF was added to the reaction vessel and a solvent background was taken. Data recording was initiated, and the solvent was brought to -78 ^{o}C using a dry ice/acetone bath. A 1 mL stock solution of dry THF consisting of the alcohol, catalyst, and base was made of which 810 µL was added to the reaction vessel. The reaction was left to equilibrate for 30 minutes. At 30 minutes (t_0), 590 µL of a solution of silyl chloride in THF was added to the reaction flask beginning the reaction. Data was recorded at a rate of one scan every 15 seconds. Aliquots for NMR analysis (~100 µL) were removed and quenched with methanol at various times over the course of the reaction. Aliquots of the reaction were analyzed by ^{1}H NMR, by integrating the proton peak geminal to the alcohol oxygen for the starting material (tetralol) and the product (silylated derivative). The product proton is observed at 4.96 ppm and the starting material at 4.79 ppm with no overlap from other reaction components. The integrations were used to determine the fraction conversion, which was used to determine the concentration of the remaining alcohol starting material [ROH]. This alcohol concentration was used to determine the Beer's law relationship between absorbance and concentration. After obtaining the Beer's law constants, that information was used to calculate the alcohol concentration from the IR absorbance data by employing the Beer's Law equation.

The percent conversion or product conversation can also be obtained by subtracting the alcohol concentration at each time from the starting alcohol concentration. This data is plotted with time on the x-axis and the percent conversion on the y-axis. The NMR data obtained above was used to confirm both methods give the same conversion data. This ensures the data obtained from the in situ IR is accurate throughout the experiment. With concentration of product [P] obtained at every point of reaction time from in situ IR measurements, the rate of the reaction can now be determined by taking the derivative of an equation that fits the concentration over time data. The conversion versus time data was fit to a 9th-11th order polynomial equation employing a mathematical program (Origin version 6.6 or PolySolve version 3.7). The derivative of this polynomial equation through the use of the power rule yields d[P]/dt, or rate. Prior to the polynomial fit all data was smoothed through simple adjacent three points averaging.

This smoothing step facilitates the non-linear curve fitting process. A plot is produced containing rate vs time data. The rate data obtained from this method can then be plotted in various ways to form graphical rate equations.

Different Excess Study of Hünig's Base with Tetramisole – Determining the Order of Hünig's Base



Eq. S1

1.0 equiv. of Hünig's Base

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 2 mL volumetric flask using THF as the solvent. The following amounts were utilized: 108.6 mg of (*R*)-tetralol (**4**), 76.0 mg of tetramisole (**1**), 128 µL of *i*Pr$_2$NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.1 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 840 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 210.4 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79.1 mM, [Ph$_3$SiCl]: 79.9 mM, [Cat]: 40.2 mM, [Base]: 79.4 mM.

3.0 equiv of Hünig's Base

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.3 mg of (*R*)-tetralol (**4**), 37.5 mg of tetramisole (**1**), 192 µL of *i*Pr$_2$NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.1 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 840 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 210.4 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79.1 mM, [Ph$_3$SiCl]: 79.3 mM, [Cat]: 40 mM, [Base]: 238 mM.

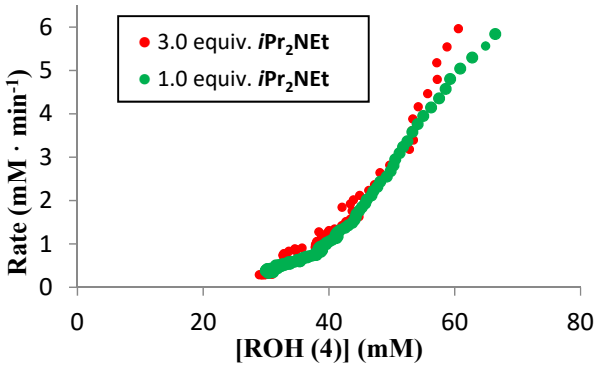
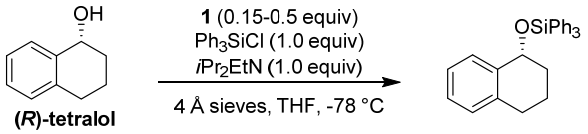


Figure S1. Graphical rate equation with varied base concentration**.** Reaction was run with 50 mol% of **1** and 1 equivalent of silyl chloride with respect to alcohol **4**. See Eq. S1. The equivalents of *i*Pr$_2$NEt are 1.0 and 3.0. The amine base is zero order because the runs overlap without dividing the rate by the concentration of base.

Different Excess Study of Tetramisole – Determining the Order of Tetramisole 1



Eq. S2

50 mol % of catalyst 1

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.2 mg of (*R*)-tetralol (**4**), 37.5 mg of tetramisole (**1**), 64 µL of iPr$_2$NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.1 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 840 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 210.4 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph$_3$SiCl]: 79.9 mM, [Cat]: 39.7 mM, [Base]: 79.4 mM.

35 mol % of catalyst 1

The *General Procedure for Kinetic Analysis* was employed. Everything was done exactly the same as the *50 mol% of catalyst **1*** run, with only 26.0 mg of tetramisole (**1**) in the starting material stock solution. Overall, the concentrations of catalyst was: [Cat]: 27.5 mM.

25 mol % of catalyst 1

The *General Procedure for Kinetic Analysis* was employed. Everything was done exactly the same as the *50 mol% of catalyst **1*** run, with only 18.7 mg of tetramisole (**1**) in the starting material stock solution. Overall, the concentrations of catalyst was: [Cat]: 19.8 mM.

15 mol % of catalyst 1

The *General Procedure for Kinetic Analysis* was employed. Everything was done exactly the same as the *50 mol% of catalyst **1*** run, with only 11.2 mg of tetramisole (**1**) in the starting material stock solution. Overall, the concentrations of catalyst was: [Cat]: 11.8 mM.

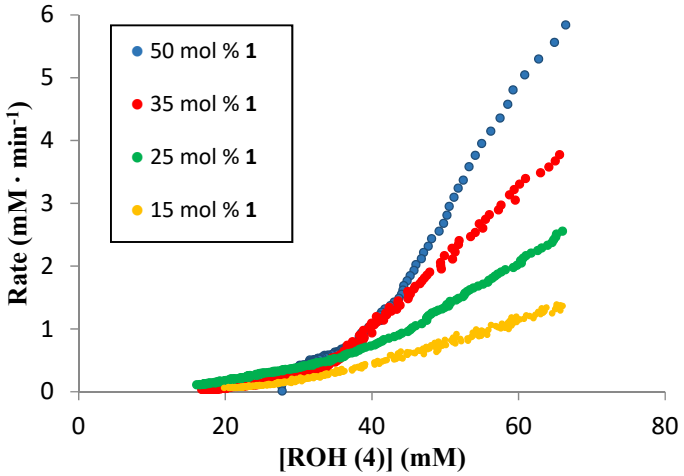


Figure S2. Graphical rate equation with varying amounts of catalyst **1**. The graph shows that the catalyst is positive order, since the concentration of the catalyst increases the rate of the reactions. The reaction

was run with the shown mol% of **1**, 1.0 equiv. of silyl chloride and 1.0 equiv. of *i*Pr_2NEt with respect to alcohol **4** (Eq S2).

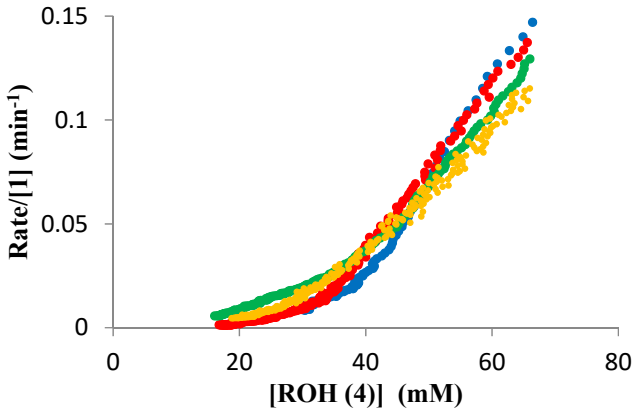
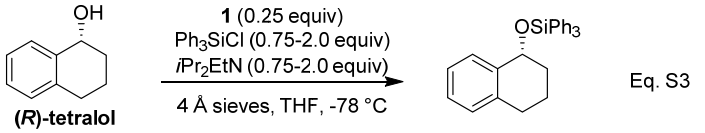


Figure S3. Normalized graphical rate equation with varying amounts of catalyst **1**. Overlay of turnover frequency versus alcohol concentration. The rate is divided by initial catalyst concentration. The reaction was run with the shown mol% of **1**, 1.0 equiv. of silyl chloride and 1.0 equiv. of *i*Pr_2NEt with respect to alcohol **4** (Eq S2).

Different Excess Experiments of Silyl Chloride to Alcohol with (-)-Tetramisole - Determining Order of Alcohol and Silyl Chloride



Eq. S3

0.75 equiv of Ph_3SiCl

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.2 mg of (*R*)-tetralol (**4**), 18.7 mg of tetramisole (**1**), 48 µL of *i*Pr_2NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.2 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 770 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 168.8 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 58.3 mM, [Cat]: 19.8 mM, [Base]: 59.5 mM.

1 equiv of Ph_3SiCl

The *General Procedure for Kinetic Analysis* was employed. Everything was done exactly the same as the *0.75 equiv of Ph_3SiCl* run, except using 2.1 mL of THF for the solvent background, 64 µL of *i*Pr_2NEt in the starting material stock solution, and using 1.25 mL of the stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 210.3 mg of silyl chloride. Overall, the concentration of silyl chloride and base was: [Ph_3SiCl]: 79.9 mM, [Base]: 79.3 mM.

1.5 equiv of Ph_3SiCl

Everything was done exactly the same as the 0.75 equiv of Ph_3SiCl run, except using 1.7 mL of THF for the solvent background, 96 µL of *i*Pr_2NEt in the starting material stock solution, and using 840 µL of the

stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 210.3 mg of silyl chloride. Overall, the concentration of silyl chloride and base was: [Ph_3SiCl]: 119 mM, [Base]: 119 mM.

2 equiv of Ph_3SiCl

Everything was done exactly the same as the 0.75 equiv of Ph_3SiCl run, except using 2.35 mL of THF for the solvent background, 128 µL of *i*Pr_2NEt in the starting material stock solution, and using 590 µL of the stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 588.6 mg of silyl chloride. Overall, the concentration of silyl chloride and base was: [Ph_3SiCl]: 157 mM, [Base]: 159 mM.

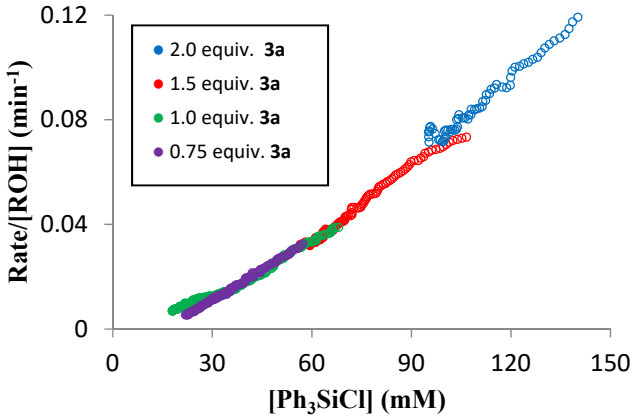
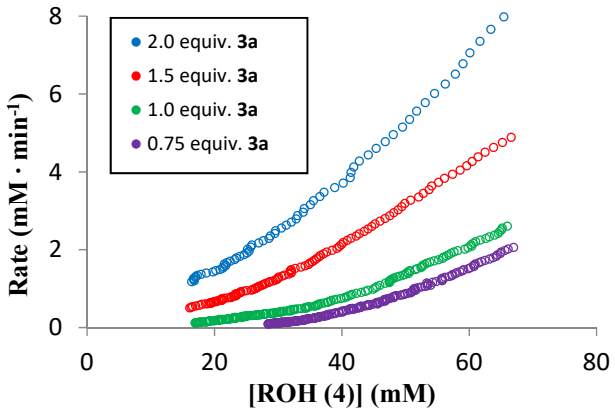
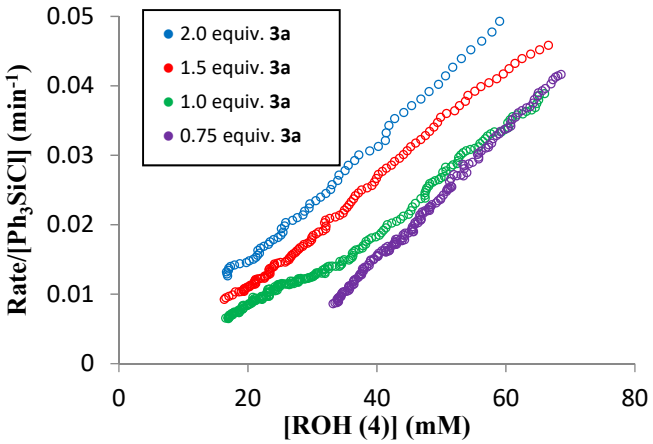


Figure S4. Normalized graphical rate equation with respect to alcohol with varying amounts of silyl chloride. Determining the Order with Respect to Alcohol with "Different Excess" Protocol. Reaction was run with the shown 25 mol% of catalyst, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt to match the silyl chloride concentration. See Eq S3.

A.



B



C

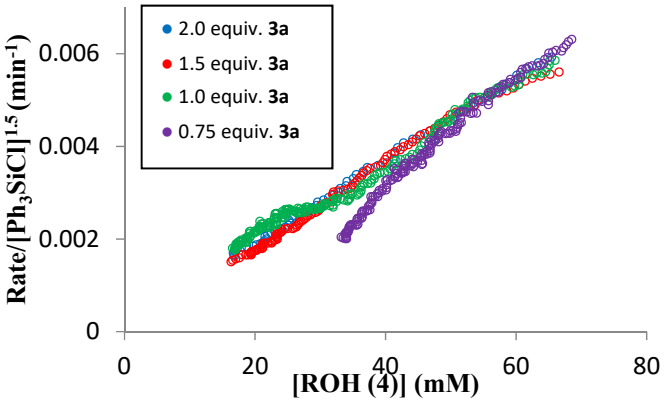
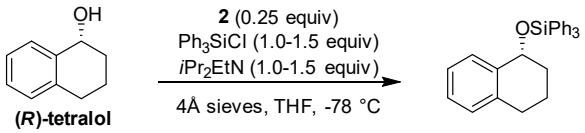


Figure S5. A. Graphical Rate Equation of rate versus alcohol concentration with silyl chloride ranging from 0.75 to 2 equivalents. B. The normalized graphical rate equation of the rate divided by the [**3a**] versus alcohol concentration. C. The normalized graphical rate equation of the rate divided by the [**3a**]$^{1.5}$ versus alcohol concentration, showing the silyl chloride order is more than one. (Reactions were run with the shown 25 mol% of catalyst, the shown equivalents of silyl chloride with an equivalent of *i*Pr$_2$NEt to match the silyl chloride concentration. See Eq. S3.)

Different Excess Experiments of Silyl Chloride to Alcohol with (-)-Benzotetramisole (2) – Determining the Order of Silyl Chloride



Eq. S4

1.0 equiv of Ph_3SiCl

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.1 mg of (*R*)-tetralol (**4**), 22.8 mg of benzotetramisole (**2**), 65 µL of *i*Pr_2NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.2 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 296.0 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 79 mM, [Cat]: 19.8 mM, [Base]: 80.6 mM.

1.5 Equiv.of Ph_3SiCl

Everything was done exactly the same as the 1.0 equiv of Ph_3SiCl run, except using 1.7 mL of THF for the solvent background, 95 µL of *i*Pr_2NEt in the starting material stock solution, and using 590 µL of the stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 443.8 mg of silyl chloride. Overall, the concentration of silyl chloride and base was: [Ph_3SiCl]: 118 mM, [Base]: 118 mM.

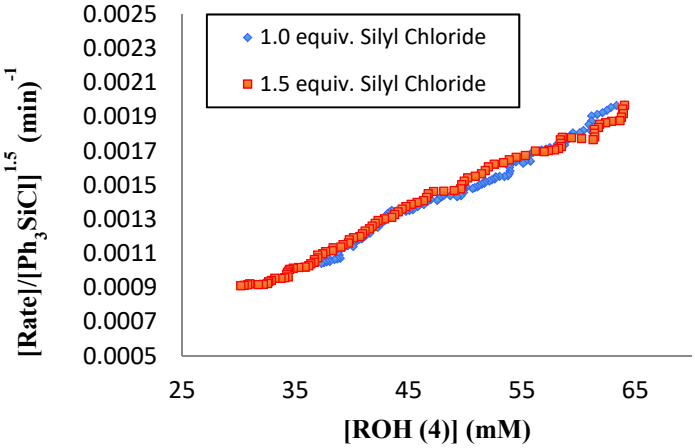
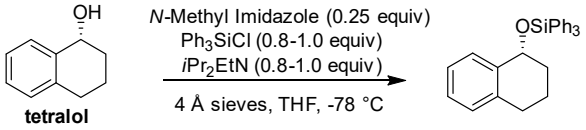


Figure S6. The normalized graphical rate equation of rate divided by the [**3a**]$^{1.5}$ versus alcohol concentration with silyl chloride ranging from 1 to 1.5 equivalents employing catalyst **2**. This shows the silyl chloride order is more than one. (Reactions were run with the shown 25 mol% of **2**, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt to match the silyl chloride concentration. See Eq. S4.)

Different Excess Experiments with N-Methyl Imidazole – Determining the Order of Silyl Chloride



Eq. S5

0.8 Equiv. of Ph_3SiCl

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.1 mg of racemic tetralol (**4**), 7.5 µL *N*-methyl imidazole, 51 µL of *i*Pr_2NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.35 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 237.0 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 63 mM, [Cat]: 20 mM, [Base]: 63 mM.

1.0 Equiv. of Ph_3SiCl

Everything was done exactly the same as the 0.8 equiv of Ph_3SiCl run, except using 65 µL of *i*Pr_2NEt in the starting material stock solution, and using 296 mg of silyl chloride. Overall, the concentration of silyl chloride and base was: [Ph_3SiCl]: 79 mM, [Base]: 80.6 mM.

$$\int_0^{t_n} [SiCl]^{\beta} dt \approx \sum_{i=1}^{n} \left(\frac{[SiCl]_i + [SiCl]_{i-1}}{2}\right)^{\beta} (t_i - t_{i-1}) \quad \textbf{Eq. S6}$$

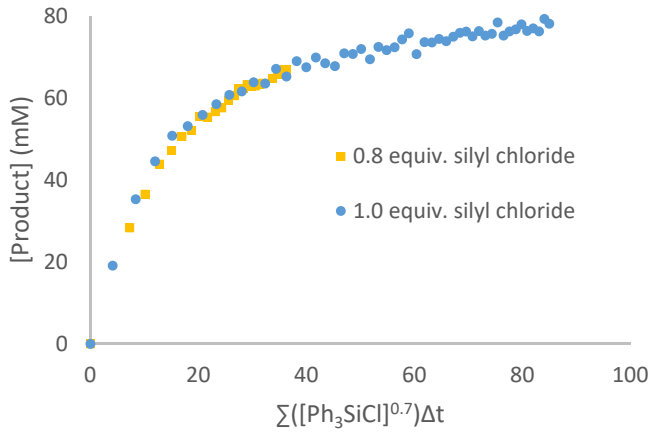
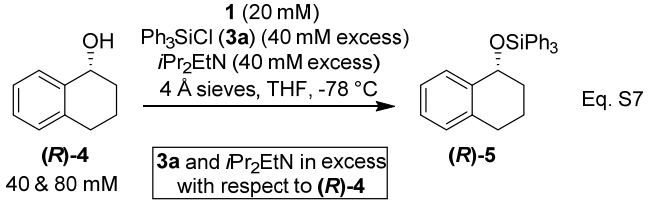


Figure S7. Variable time normalized analysis (Eq. S6) to determine the order of silyl chloride employing NMI as the catalyst. (Reactions were run with the shown 25 mol% of NMI, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt to match the silyl chloride concentration. See Eq. S5.)

Same Excess Experiment with Tetramisole Catalyst (1) – Excess of 40 mM on both runs



Eq. S7

Run 1 – Alcohol at 40 mM and Ph_3SiCl at 80 mM - ["Excess"]: 40 mM

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were

utilized: 27.1 mg of (*R*)-tetralol (**4**), 18.7 mg of tetramisole (**1**), 64 µL of *i*Pr$_2$NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.1 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 835 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 210.3 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 39.6 mM, [Ph$_3$SiCl]: 79.5 mM, [Cat]: 20 mM, [Base]: 79.5 mM.

Run 2 – Alcohol at 79 mM and Ph$_3$SiCl at 119 mM - ["Excess"]: 40 mM

Everything was done exactly the same as the Run 1 of the "Same Excess" run above, except using 1.7 mL of THF for the solvent background, 54.1 mg of (*R*)-tetralol and 96 µL of *i*Pr$_2$NEt in the starting material stock solution, and using 1.25 mL of the stock solution of silyl chloride. Overall, the concentration of silyl chloride and base was: [ROH]: 79 mM, [Ph$_3$SiCl]: 119 mM, [Cat]: 20 mM, [Base]: 119 mM.

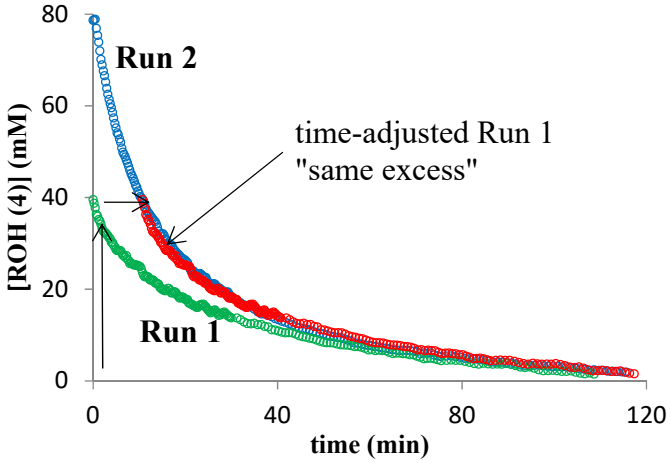
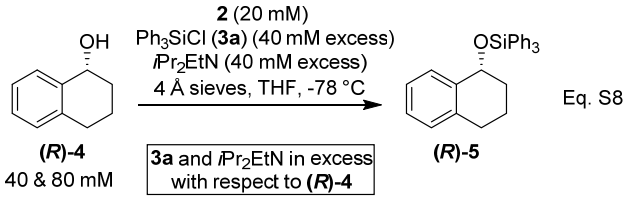


Figure S8. Time-adjusted "Same Excess" experiment. Run 1 and 2 were run with 25 mol% of catalyst **1** and 40 mM excess of silyl chloride with a matching equivalent of *i*Pr$_2$NEt with respect to [ROH/**4**]. Run 2 used 80 mM of alcohol; Run 1 used 40 mM of alcohol. See Eq. S7.

Same Excess Experiment with (-)-Benzotetramisole Catalyst (2) – Excess of 40 mM on both runs



Run 1 – Alcohol at 79 mM and Ph$_3$SiCl at 118 mM - ["Excess"]: 40 mM

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.1 mg of (*R*)-tetralol (**4**), 22.8 mg of benzotetramisole (**2**), 95 µL of *i*Pr$_2$NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.35 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric

flask using 443.8 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 118 mM, [Cat]: 20 mM, [Base]: 118 mM.

Run 2– Alcohol at 39 mM and Ph_3SiCl at 79 mM - ["Excess"]: 40 mM

Everything was done exactly the same as the Run 1 of the "Same Excess" run above, except using 27.0 mg of (*R*)-tetralol and 65 µL of *i*Pr_2NEt in the starting material stock solution, and using 295.6 mg triphenylsilyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 39 mM, [Ph_3SiCl]: 79 mM, [Cat]: 20 mM, [Base]: 81 mM.

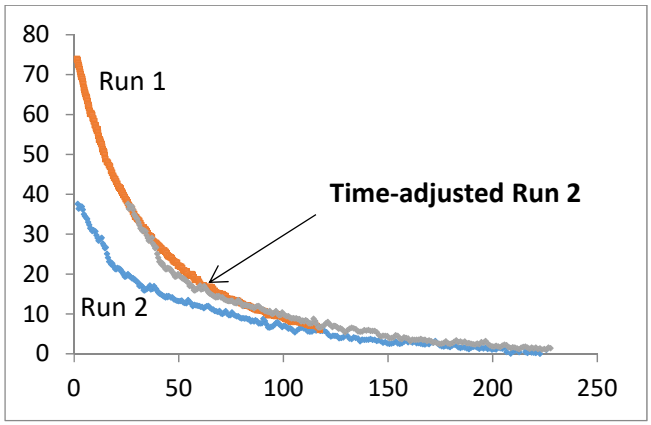
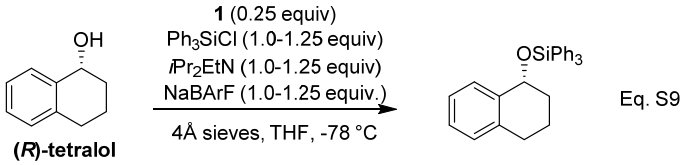


Figure S9. Time-adjusted "Same Excess" experiment. Run 1 and 2 were run with 25 mol% of catalyst **2** and 40 mM excess of silyl chloride with a matching equivalent of *i*Pr_2NEt with respect to [ROH]. Run 1 used 80 mM of alcohol; Run 2 used 40 mM of alcohol. See Eq. S8.

Different Excess with Sodium Tetrakis[3,5-bis(trifluoromethyl)phenyl] Borate (NaBArF) – Determining the Order of Silyl Chloride



Eq. S9

1.0 Equiv of Ph_3SiCl and 1.0 Equiv of NaBArF

The *General Procedure for Kinetic Analysis* was employed, except that NaBArF (263 mg) was placed in the reaction vessel while under a glove box nitrogen atmosphere and then attached to the IR probe. The insitu IR was set to begin taking measurements of the dry reaction vessel and after one minute, an initial 2.35 mL THF was added and allowed to cool to -78 °C. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.2 mg of (*R*)-tetralol (**4**), 18.7 mg of tetramisole (**1**), 65 µL of *i*Pr_2NEt. The solution was thoroughly mixed under argon. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric flask using 295.6 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride

and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 79 mM, [Cat]: 20 mM, [NaBArF]: 79 mM, [Base]: 80 mM.

1.25 Equiv of Ph_3SiCl and 1.25 Equiv of NaBArF

Everything was done exactly the same as the "**1.0 Equiv of SiCl and 1.0 Equiv of NaBArF**" run above, except using 329 mg of NaBArF, and 80 µL of *i*Pr_2NEt in the starting material stock solution, and using 369.2 mg triphenylsilyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 99 mM, [Cat]: 20 mM, [NaBArF]: 99 mM, [Base]: 99 mM

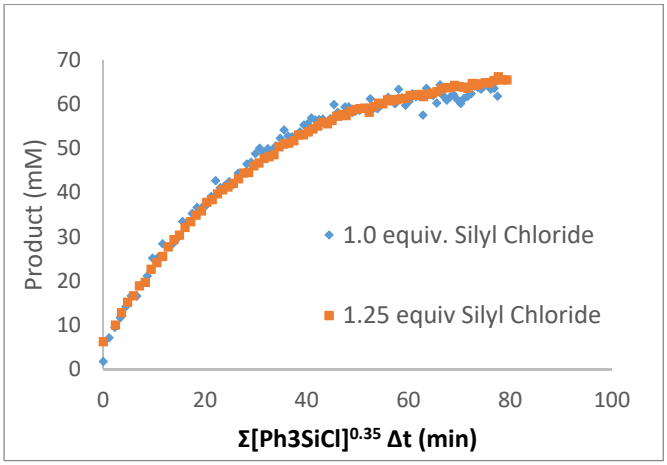
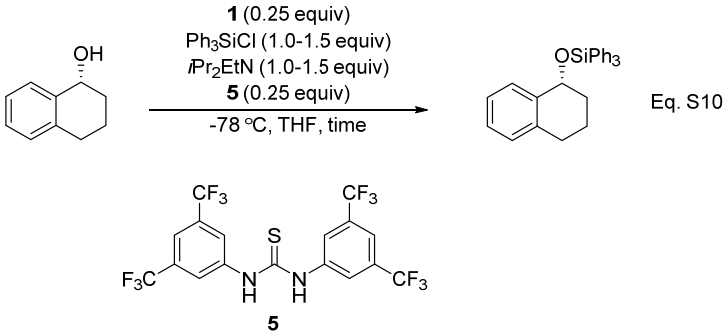


Figure S10. Variable time normalized analysis (Eq. S6) to determine the order of silyl chloride employing **1** as the catalyst in the presence of **NaBArF**. (Reactions were run with the shown 25 mol% of **1**, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt and an equivalent of **NaBArF** to match the silyl chloride concentration. See Eq. S9.)

Different Excess Experiments of Silyl Chloride to Alcohol with Schreiner's Thiourea Catalyst as an Additive – Determining the Order of Silyl Chloride.



1.0 Equiv of SiCl and 0.25 Equiv of 5

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.1 mg of (*R*)-tetralol (**4**), 18.7 mg of tetramisole (**1**), 65 µL of *i*Pr_2NEt, 45 mg of **5**. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.35 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric

flask using 296 mg of silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [Ph_3SiCl]: 79 mM, [Cat]: 20 mM, [Base]: 80 mM, [thiourea **5**]: 19.4

1.5 Equiv of SiCl and 0.25 Equiv of 5

Everything was done exactly the same as the "**1.0 Equiv of SiCl and 0.25 Equiv of 5**" run above, except using 95 µL of *i*Pr_2NEt in the starting material stock solution, and using 443.1 mg triphenylsilyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst, thioureas, and base were: [ROH]: 79 mM, [Ph_3SiCl]: 118 mM, [Cat]: 20 mM, [Base]: 118 mM, [thiourea **5**]: 19.4

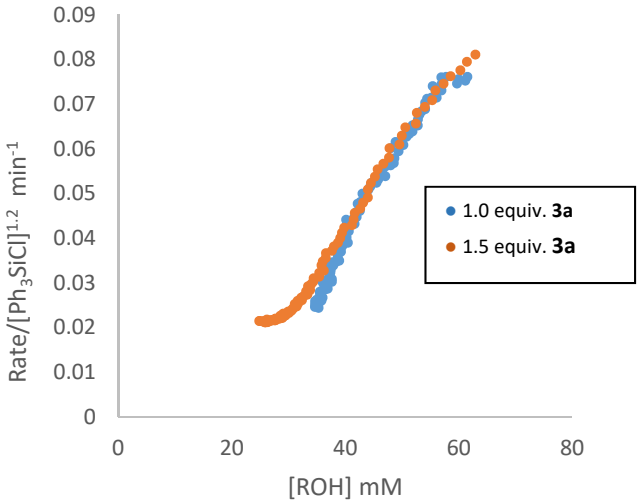
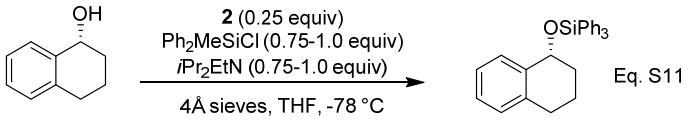


Figure S11. The normalized graphical rate equation of rate divided by the [**3a**]$^{1.2}$ versus alcohol concentration with silyl chloride ranging from 1 to 1.5 equivalents employing catalyst **1** in the presence of thioureas **5**. This shows the silyl chloride order is more than one. (Reactions were run with the shown 25 mol% of **1** and 25 mol % of **5**, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt to match the silyl chloride concentration. See Eq. S10.)

Different Excess Experiments Using $Ph_2MeSiCl$ as the Silyl Source – Determining the Order of the Silyl Chloride



Eq. S11

0.75 Equiv of $Ph_2MeSiCl$

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.1 mg of (*R*)-tetralol (**4**), 22.7 mg of benzotetramisole (**2**), 50 µL of *i*Pr_2NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.35 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 2 mL volumetric

flask using 160 µL of diphenylmethylsilyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [$Ph_2MeSiCl$]: 60 mM, [Cat]: 19 mM, [Base]: 62 mM.

1.0 Equiv of $Ph_2MeSiCl$

Everything was done exactly the same as the "**0.75 Equiv of $Ph_2MeSiCl$**" run above, except using 65 µL of *i*Pr_2NEt in the starting material stock solution, and using 210 µL of diphenyl methyl silyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [$Ph_2MeSiCl$]: 79 mM, [Cat]: 19 mM, [Base]: 80.6 mM.

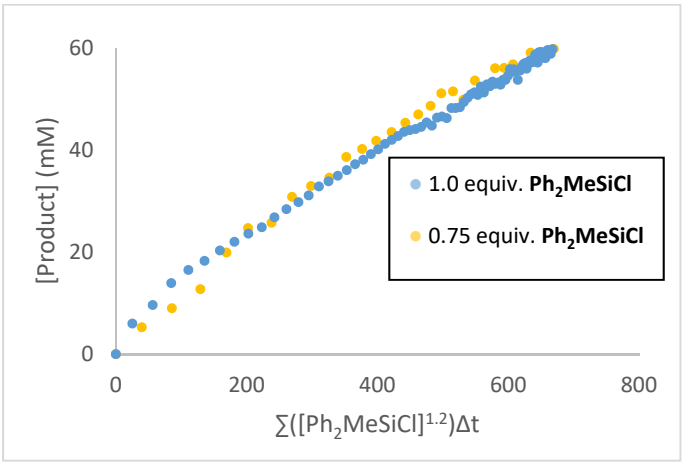
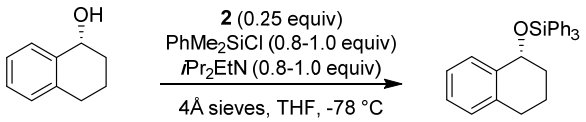


Figure S12. Variable time normalized analysis (Eq. S6) to determine the order of $Ph_2MeSiCl$ employing **2** as the catalyst. (Reactions were run with the shown 25 mol% of **2**, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt to match the silyl chloride concentration. See Eq. S11.)

Different Excess Experiments Using $PhMe_2SiCl$ as the Silyl Source – Determining the Order of the Silyl Chloride



Eq. S12

0.8 Equiv of $PhMe_2SiCl$

The *General Procedure for Kinetic Analysis* was employed. A stock solution of starting materials was prepared under argon in a 1 mL volumetric flask using THF as the solvent. The following amounts were utilized: 54.2 mg of (*R*)-tetralol (**4**), 22.7 mg of benzotetramisole (**2**), 50 µL of *i*Pr_2NEt. The solution was thoroughly mixed under argon. The solvent background run was performed on 2.35 mL of THF. Once the THF had cooled to -78 °C, 810 µL of the starting material stock solution was added. Finally, the reaction was initiated with 590 µL of a stock solution of silyl chloride, which was prepared in a 1 mL volumetric flask using 70 µL of phenyldimethylsilyl chloride. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [$PhMe_2SiCl$]: 65.6 mM, [Cat]: 19 mM, [Base]: 62 mM.

1.0 Equiv of $PhMe_2SiCl$

Everything was done exactly the same as the "**0.8 Equiv of $PhMe_2SiCl$**" run above, except using 64 µL of *i*Pr_2NEt in the starting material stock solution, and using 170 µL of phenyldimethylsilyl chloride in a 2 mL stock solution. Overall, the concentrations of alcohol, silyl chloride and catalyst and base were: [ROH]: 79 mM, [$PhMe_2SiCl$]: 80 mM, [Cat]: 19 mM, [Base]: 79.4 mM.

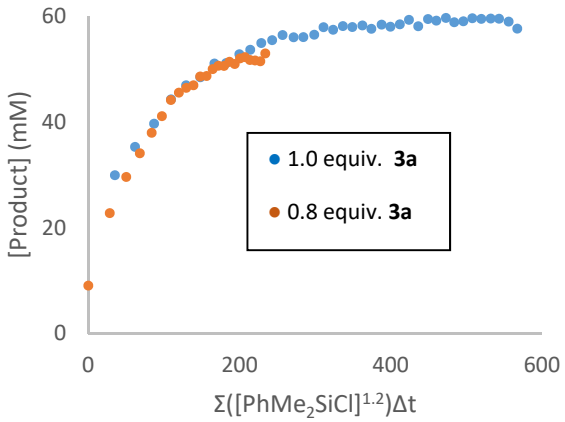


Figure S13. Variable time normalized analysis (Eq. S6) to determine the order of $PhMe_2SiCl$ employing **2** as the catalyst. (Reactions were run with the shown 25 mol% of **2**, the shown equivalents of silyl chloride with an equivalent of *i*Pr_2NEt to match the silyl chloride concentration. See Eq. S12.)

Binding Study on Triphenyl Silyl Chloride with (-)-Benzotetramisole

Triphenyl silyl chloride was recrystallized from pentane. Catalyst **2** was dried under vacuum in a sand bath. NMR samples (1 mL volume) were prepared in a glovebox with 0.16 M of **2** in THF and 0.5 to 8 equivalents of silyl chloride **3a**. Four drops of deuterated benzene was added to the sample for locking and the sample was loaded into an NMR tube and immediately taken for ^1H NMR analysis. A solvent suppression protocol was used to minimize THF interference. A reference spectra of just **2** and was taken and all Δ ppm were referenced to the THF.

Binding Study on Triphenyl Silyl Chloride with (-)-Benzotetramisole and NaBArF

Triphenyl silyl chloride was recrystallized from pentane. **NaBArF** was dried for 3 days in a drying pistol using toluene as the solvent and P_2O_5 as the drying agent. Catalyst **2** was dried under vacuum in a sand bath. NMR samples (1 mL volume) were prepared with 0.09 M of **2** in THF and 0.5 to 5 equivalents of silyl chloride **3a** and **NaBArF** (in equivalent amounts to each other). All solids were dried with a drying pistol, and solvent was distilled before use. Four drops of deuterated benzene was added to the sample for locking and the sample was loaded into an NMR tube and immediately taken for ^1H NMR analysis. A solvent suppression protocol was used to minimize THF interference. A reference spectra of **2** and **NaBArF** was taken and all Δppm were references to the THF.

Data for RKPA or VTNA Plots

Figure S1

3 equiv of Hunig's base			1 equiv of Hunig's base	
[ROH (4)]	**d[P]/dt**		**[ROH (4)]**	**d[P]/dt**
70.43719	9.378165		71.10071	7.085556
68.58757	8.657073		69.31357	6.752412
68.60105	8.031967		67.91712	6.434082
65.15377	7.452993		67.35955	6.110232
64.17901	6.917236		66.42466	5.839657
62.31025	6.421927		64.90252	5.562504
60.58689	5.964445		62.75117	5.298044
58.76575	5.542302		60.85036	5.045787
57.14786	5.178107		59.26148	4.80526
57.21851	4.794744		58.53176	4.576002
55.67833	4.464992		57.49302	4.357568
54.1856	4.161899		56.21326	4.149529
53.332	3.883584		54.96678	3.951468
53.20992	3.612026		54.09599	3.76298
53.41762	3.394288		53.2541	3.583677
52.79795	3.180057		52.46022	3.369156
50.67249	2.984097		51.77153	3.240614
49.67246	2.816451		51.20772	3.097161
48.11541	2.641485		50.53883	2.950945
48.50519	2.492293		50.23719	2.812147
47.24125	2.364958		49.77767	2.680451
46.32981	2.23236		49.17715	2.555548
44.86928	2.119527		48.14308	2.437143
43.88831	2.016833		47.68008	2.317682
43.40355	1.923395		47.05161	2.218688
42.08051	1.843811		46.74424	2.118096
43.67551	1.761053		46.00939	2.022914
44.08282	1.69067		45.75206	1.932896
44.76828	1.62658		45.22451	1.847802
43.36538	1.568169		44.81458	1.767402
42.7024	1.51487		44.34208	1.691475
42.55637	1.469273		44.23852	1.619807
42.03011	1.42155		44.03791	1.552192
42.10019	1.3806		43.68803	1.488433
40.88111	1.3429		43.04151	1.428339

39.99975	1.308075		42.53365	1.371728
38.40061	1.275783		41.76102	1.318423
39.68801	1.247654		41.31764	1.268257
39.90103	1.217578		41.06306	1.221066
39.52449	1.191125		41.37325	1.176695
38.81886	1.166119		41.17916	1.134994
39.62841	1.142353		40.49914	1.095819
41.10754	1.119639		40.02927	1.059034
39.28988	1.097812		39.55553	1.024506
38.62971	1.076722		39.54463	0.992109
38.06486	1.056241		39.00617	0.961722
38.77767	1.036254		38.57224	0.933229
37.96779	1.016663		38.42195	0.906519
38.12519	0.998659		38.28628	0.881486
37.85357	0.978339		38.90143	0.85803
38.73829	0.959475		38.73292	0.836053
38.50027	0.94074		38.6478	0.815463
37.80706	0.922094		37.94697	0.796172
35.72614	0.903506		37.80653	0.778096
34.58521	0.886191		38.04694	0.761154
34.83016	0.866424		37.99415	0.745272
34.62547	0.847905		37.30647	0.730375
33.61219	0.829395		36.82571	0.716396
32.81076	0.773968		36.35151	0.703268
32.67547	0.73722		36.5339	0.69093
32.7911	0.700802		35.86203	0.679322
33.32363	0.664897		35.87401	0.668388
33.68614	0.629707		35.72889	0.658076
33.38666	0.595444		35.6707	0.648334
32.77264	0.562321		35.28675	0.639117
32.33646	0.530543		34.93192	0.630378
31.91423	0.500302		34.98916	0.622077
31.21281	0.471771		35.2524	0.614172
31.52001	0.4451		35.41562	0.606626
31.24951	0.420416		35.31891	0.599405
31.14204	0.397817		34.52649	0.592474
30.14657	0.377374		34.02183	0.585804
30.34347	0.359128		33.5509	0.579365
30.44092	0.343093		33.90741	0.573129
29.9786	0.329255		33.62984	0.567073
30.62212	0.317573		33.58919	0.561171

30.59048	0.307983		33.29064	0.555402
30.95714	0.300394		33.74335	0.549745
30.07641	0.294699		33.75988	0.544183
29.17766	0.290769		33.23251	0.538697
29.42147	0.288461		32.67848	0.533271
28.92231	0.287616		32.60601	0.527891
29.79119	0.288066		33.01408	0.522542
29.35033	0.289634		32.81791	0.517214
29.81489	0.292138		32.05642	0.511894
29.20222	0.295391		31.54265	0.506573
			32.14492	0.501241
			32.38893	0.49589
			32.37802	0.490513
			31.77007	0.485103
			31.63036	0.479655
			31.42896	0.474164
			31.44673	0.468625
			31.66926	0.463035
			31.64177	0.457391
			31.76158	0.45169
			31.53033	0.445931
			31.8015	0.440112
			31.12108	0.434231
			30.66685	0.428289
			30.16882	0.422285
			30.22825	0.416219
			30.38618	0.410091
			30.29218	0.403902
			30.11985	0.397653
			29.97294	0.391344
			29.94848	0.384977
			29.98452	0.378552
			30.17658	0.372072
			30.79791	0.365537
			31.0643	0.358949
			31.11557	0.35231
			30.50465	0.34562
			30.45826	0.33888
			30.31967	0.332093
			30.19817	0.325259

Figure S3

15 mol% **1**			25 mol% **1**			35 mol% **1**			50 mol% **1**	
[ROH (**4**)]	Rate/[**1**] min^{-1}		[ROH (**4**)]	Rate/[**1**] min^{-1}		[ROH (**4**)]	Rate/[**1**] min^{-1}		[ROH (**4**)]	Rate/[**1**] min^{-1}
65.22	0.117		65.99	0.129		65.61	0.137		66.43	0.127
65.71	0.116		65.18	0.127		65.01	0.134		64.90	0.121
66.01	0.115		65.08	0.125		64.15	0.130		62.75	0.116
65.20	0.114		64.79	0.122		63.01	0.127		60.85	0.111
63.82	0.113		64.57	0.120		60.95	0.123		59.26	0.107
63.18	0.112		63.98	0.118		60.15	0.120		58.53	0.102
65.01	0.111		63.16	0.116		59.41	0.117		57.49	0.098
63.20	0.110		62.62	0.114		58.77	0.114		56.21	0.094
65.71	0.109		61.72	0.112		59.56	0.111		54.97	0.090
63.56	0.108		61.03	0.110		57.62	0.108		54.10	0.086
62.70	0.107		60.63	0.108		57.26	0.105		53.25	0.083
63.35	0.106		60.29	0.106		56.03	0.103		52.46	0.078
64.61	0.105		60.39	0.104		55.49	0.100		51.77	0.076
63.02	0.104		59.80	0.102		54.64	0.097		51.21	0.073
62.30	0.103		59.30	0.100		55.14	0.095		50.54	0.070
61.07	0.102		58.21	0.098		54.10	0.092		50.24	0.067
61.52	0.102		57.64	0.096		53.46	0.090		49.78	0.064
59.71	0.101		57.15	0.095		51.90	0.088		49.18	0.061
59.06	0.100		56.79	0.093		51.81	0.085		48.14	0.059
62.05	0.099		56.42	0.091		50.94	0.083		47.68	0.056
60.76	0.098		55.96	0.090		51.35	0.081		47.05	0.054
60.19	0.097		55.80	0.088		49.88	0.079		46.74	0.052
59.87	0.096		55.18	0.087		51.01	0.077		46.01	0.050
58.83	0.095		54.49	0.085		49.36	0.075		45.75	0.048
59.60	0.095		53.83	0.084		49.38	0.073		45.23	0.046
59.75	0.094		53.36	0.082		49.48	0.071		44.82	0.044
58.60	0.093		53.00	0.081		47.89	0.069		44.34	0.042
59.31	0.092		52.68	0.079		47.51	0.068		44.24	0.041
57.75	0.091		52.59	0.078		47.17	0.066		44.04	0.039
58.38	0.091		52.42	0.077		46.83	0.064		43.69	0.038
56.25	0.090		51.81	0.075		46.56	0.063		43.04	0.036
59.06	0.089		51.48	0.074		45.90	0.061		42.53	0.035
56.93	0.088		50.64	0.073		45.74	0.060		41.76	0.034
58.62	0.087		50.72	0.071		44.90	0.058		41.32	0.032
57.23	0.087		50.21	0.070		45.25	0.057		41.06	0.031

58.17	0.086		50.47	0.069		45.03	0.055		41.37	0.030
57.60	0.085		49.94	0.068		44.93	0.054		41.18	0.029
58.66	0.084		49.59	0.067		43.58	0.053		40.50	0.028
54.24	0.084		49.04	0.066		43.56	0.051		40.03	0.027
55.89	0.083		48.64	0.065		43.85	0.050		39.56	0.026
54.96	0.082		48.18	0.063		42.36	0.049		39.55	0.025
55.08	0.081		48.04	0.062		43.38	0.048		39.01	0.025
54.44	0.081		47.75	0.061		42.64	0.047		38.57	0.024
55.33	0.080		47.60	0.060		41.88	0.046		38.42	0.023
53.77	0.079		47.46	0.059		42.01	0.044		38.29	0.022
55.35	0.079		47.45	0.058		40.62	0.043		38.90	0.022
54.57	0.078		47.48	0.058		41.50	0.042		38.73	0.021
51.54	0.077		46.82	0.055		41.59	0.042		38.65	0.021
55.73	0.077		45.96	0.053		40.75	0.041		37.95	0.020
53.87	0.076		45.50	0.052		39.97	0.040		37.81	0.020
54.91	0.075		45.25	0.050		40.31	0.039		38.05	0.019
54.59	0.075		44.91	0.048		39.73	0.038		37.99	0.019
53.66	0.074		44.09	0.047		38.84	0.036		37.31	0.018
53.53	0.073		43.67	0.046		40.01	0.034		36.83	0.018
51.08	0.073		43.05	0.044		38.32	0.033		36.35	0.017
51.42	0.072		42.31	0.043		38.93	0.031		36.53	0.017
53.05	0.071		41.61	0.042		38.79	0.030		35.86	0.017
52.06	0.071		41.39	0.041		37.36	0.029		35.87	0.016
51.27	0.070		41.00	0.040		37.91	0.028		35.73	0.016
49.98	0.070		40.68	0.039		36.65	0.027		35.67	0.016
50.83	0.069		40.37	0.038		37.51	0.026		35.29	0.015
53.13	0.068		39.84	0.037		37.50	0.025		34.93	0.015
52.20	0.068		39.14	0.036		36.86	0.024		34.99	0.015
49.08	0.067		38.73	0.035		36.18	0.023		35.25	0.015
51.08	0.067		38.32	0.034		36.21	0.023		35.42	0.015
49.85	0.066		38.25	0.033		36.00	0.022		35.32	0.014
48.58	0.066		37.86	0.033		35.64	0.021		34.53	0.014
51.40	0.065		37.75	0.032		35.50	0.021		34.02	0.014
49.26	0.064		37.25	0.031		34.95	0.020		33.55	0.014
49.40	0.064		36.71	0.031		34.54	0.020		33.91	0.014
49.70	0.063		36.45	0.030		35.62	0.019		33.63	0.013
50.11	0.063		36.20	0.029		34.54	0.019		33.59	0.013
48.08	0.062		36.27	0.029		35.27	0.018		33.29	0.013
49.63	0.062		36.16	0.028		35.04	0.018		33.74	0.013
48.75	0.061		35.88	0.028		34.99	0.017		33.76	0.013
48.86	0.061		35.66	0.027		33.20	0.017		33.23	0.013

47.41	0.060		34.92	0.027		33.94	0.016		32.68	0.013
49.18	0.060		34.69	0.026		34.21	0.016		32.61	0.012
47.87	0.059		34.26	0.026		34.16	0.016		33.01	0.012
48.77	0.059		34.53	0.025		33.69	0.015		32.82	0.012
47.89	0.058		34.37	0.025		33.22	0.015		32.06	0.012
46.98	0.058		34.20	0.025		32.82	0.015		31.54	0.012
47.61	0.057		33.63	0.024		32.73	0.015		32.15	0.012
47.10	0.057		33.05	0.024		32.70	0.014		32.39	0.012
47.10	0.056		32.61	0.024		33.84	0.014		32.38	0.012
49.07	0.056		32.32	0.023		32.92	0.014		31.77	0.012
46.29	0.055		32.51	0.023		33.37	0.013		31.63	0.011
46.55	0.055		31.97	0.023		32.57	0.013		31.43	0.011
47.10	0.054		31.89	0.022		33.64	0.013		31.45	0.011
43.96	0.054		31.59	0.022		33.04	0.013		31.67	0.011
48.82	0.054		31.92	0.022		32.63	0.013		31.64	0.011
44.83	0.053		31.97	0.021		31.69	0.012		31.76	0.011
45.20	0.053		31.45	0.021		31.46	0.012		31.53	0.011
45.77	0.052		30.89	0.021		32.56	0.012		31.80	0.011
45.90	0.052		30.59	0.021		31.74	0.012		31.12	0.011
43.61	0.051		30.53	0.020		30.88	0.012		30.67	0.011
43.55	0.051		30.50	0.020		31.38	0.011		30.17	0.010
47.09	0.050		30.27	0.020		31.11	0.011		30.23	0.010
44.73	0.050		30.15	0.020		30.96	0.011		30.39	0.010
44.88	0.050		30.09	0.020		31.41	0.011		30.29	0.010
42.63	0.049		29.84	0.019		31.03	0.011		30.12	0.010
42.50	0.049		29.71	0.019		29.99	0.010		29.97	0.010
43.77	0.048		29.42	0.019		30.58	0.010		29.95	0.010
42.98	0.047		29.36	0.019		29.47	0.010		29.99	0.010
43.67	0.046		29.11	0.019		29.68	0.010		30.18	0.010
44.00	0.045		28.91	0.018		30.08	0.010		30.80	0.010
44.20	0.045		28.72	0.018		29.87	0.010		31.06	0.009
43.30	0.044		28.19	0.018		29.21	0.009		31.12	0.009
43.04	0.043		27.98	0.018		30.50	0.009		30.51	0.009
42.04	0.043		27.78	0.018		30.19	0.009		30.46	0.009
41.78	0.042		28.00	0.017		29.07	0.009		30.32	0.009
40.80	0.041		27.76	0.017		29.77	0.009		30.20	0.009
41.42	0.041		27.82	0.017		28.76	0.009		29.99	0.009
40.87	0.040		27.78	0.017		28.74	0.008		29.61	0.009
40.34	0.039		27.27	0.017		29.16	0.008		29.25	0.008
40.93	0.039		26.89	0.017		28.48	0.008		28.41	0.007
40.55	0.038		26.59	0.016		28.74	0.008		27.94	0.006

41.03	0.038		27.13	0.016		28.34	0.008		27.67	0.005
39.08	0.037		26.84	0.016		28.06	0.008		27.75	0.004
40.39	0.036		26.66	0.016		28.19	0.008		27.57	0.003
38.81	0.036		26.29	0.016		27.58	0.007		27.10	0.003
38.72	0.035		26.40	0.016		27.57	0.007		26.41	0.002
38.55	0.035		25.96	0.015		27.94	0.007		25.97	0.002
39.02	0.034		25.59	0.015		27.36	0.007		25.78	0.001
38.52	0.034		25.25	0.015		27.27	0.007		25.78	0.001
38.10	0.033		25.16	0.015		26.52	0.007		26.00	0.001
38.23	0.033		24.97	0.015		26.94	0.007		26.00	0.001
37.69	0.032		24.78	0.015		26.99	0.006		25.67	0.001
38.35	0.032		24.61	0.015		26.68	0.006		25.07	0.001
38.64	0.031		24.93	0.014		26.06	0.006		24.79	0.001
37.51	0.031		24.72	0.014		26.05	0.006		24.94	0.001
35.87	0.030		24.66	0.014		25.69	0.006		25.31	0.001
37.27	0.030		24.18	0.014		25.62	0.006		25.53	0.002
35.78	0.030		24.35	0.014		26.03	0.006		25.51	0.002
35.18	0.029		24.27	0.014		25.35	0.006		25.23	0.002
35.70	0.029		24.54	0.014		25.57	0.006		24.83	0.002
37.32	0.028		24.29	0.013		25.92	0.005		24.58	0.002
35.67	0.028		24.22	0.013		24.55	0.005		24.43	0.002
36.28	0.028		23.38	0.013		25.49	0.005		24.49	0.001
35.84	0.027		23.19	0.013		25.50	0.005		24.61	0.001
36.08	0.027		23.08	0.013		25.48	0.005		24.61	0.001
35.75	0.026					25.81	0.005		24.27	0.001
34.59	0.026					25.24	0.005		24.23	0.001
35.07	0.026					24.68	0.005		23.90	0.000
35.63	0.025					23.72	0.005			
35.20	0.025									
35.10	0.025									
33.80	0.024									
34.94	0.024									
34.03	0.024									
33.57	0.023									
33.81	0.023									
33.61	0.023									
34.08	0.023									
33.96	0.022									
33.41	0.022									
33.08	0.022									
33.55	0.021									

33.10	0.021									
33.19	0.021									
32.08	0.021									
32.44	0.020									
32.55	0.020									
31.92	0.020									
32.80	0.020									
31.88	0.020									
31.27	0.019									
32.95	0.019									
30.23	0.019									
31.52	0.019									
30.32	0.018									
32.05	0.018									
31.32	0.018									
31.50	0.018									
30.71	0.018									
31.15	0.017									
29.10	0.017									
29.70	0.017									
30.87	0.017									
29.88	0.017									
30.00	0.016									
30.68	0.016									
30.31	0.016									
29.84	0.016									
30.31	0.016									
29.32	0.016									
30.39	0.015									
29.81	0.015									
29.72	0.015									
29.79	0.015									
29.87	0.015									
29.54	0.015									
28.96	0.015									
29.22	0.014									
29.27	0.014									
30.43	0.014									
29.00	0.014									
29.06	0.014									
28.84	0.014									

29.54	0.014									
28.64	0.014									
28.03	0.013									
29.60	0.013									
28.23	0.013									
28.98	0.013									
29.53	0.013									
28.11	0.013									
27.21	0.013									
29.00	0.013									
28.69	0.012									
27.59	0.012									
27.86	0.012									
28.13	0.012									
28.14	0.012									
27.54	0.012									
27.71	0.012									
29.02	0.012									
27.39	0.012									
27.85	0.012									
26.91	0.011									
27.01	0.011									
26.90	0.011									
27.12	0.011									
27.13	0.011									
27.45	0.011									
27.21	0.011									
27.20	0.011									
26.89	0.011									
26.78	0.010									
26.03	0.010									
25.87	0.010									
25.91	0.010									
27.11	0.010									
26.59	0.010									
26.69	0.010									
26.05	0.010									
26.01	0.010									
25.95	0.009									
26.24	0.009									
25.52	0.009									

26.60	0.009									
26.10	0.009									
25.90	0.009									
26.15	0.009									
24.65	0.009									
24.79	0.009									
24.34	0.009									
25.02	0.009									
25.17	0.009									
24.36	0.008									
24.82	0.008									
24.81	0.008									
25.69	0.008									
23.23	0.008									

Figure S4

0.75 equiv Ph_3SiCl			1 equiv Ph_3SiCl			1.5 equiv Ph_3SiCl			2 equiv Ph_3SiCl	
[Ph_3SiCl]	**rate/[ROH]**		**[Ph_3SiCl]**	**rate/[ROH]**		**[Ph_3SiCl]**	**rate/[ROH]**		**[Ph_3SiCl]**	**rate/[ROH]**
63.38959	0.037575		74.59	0.04111		100.49	0.0705669		141.88	0.120813502
63.19083	0.03689		73.64	0.040877		99.61	0.06970521		140.17	0.119168086
63.02866	0.036203		72.12	0.040982		98.58	0.06905634		138.59	0.11739364
62.58158	0.035668		71.70	0.040466		97.38	0.06864131		137.51	0.11479667
61.94092	0.035237		71.27	0.039961		96.14	0.06831257		136.31	0.112554164
60.97756	0.034971		70.77	0.039504		95.19	0.06765944		134.73	0.111193336
60.00873	0.034719		69.78	0.039337		94.13	0.06718377		133.04	0.110173659
59.3137	0.034343		68.92	0.039101		93.73	0.06591671		131.57	0.108853081
58.96691	0.033809		68.05	0.038879		92.81	0.06531937		130.23	0.107415494
58.74645	0.033226		67.03	0.038756		92.08	0.06440084		129.11	0.105625246
58.02612	0.032892		66.22	0.038519		90.81	0.06440849		128.03	0.103898759
57.26755	0.032585		66.12	0.037868		89.89	0.06390377		126.56	0.103092002
56.77565	0.032161		65.83	0.037344		89.42	0.06285501		125.30	0.101973877
56.41521	0.031685		65.61	0.036784		88.83	0.0619844		123.86	0.101391049
56.01344	0.031239		65.02	0.036446		88.16	0.06124766		122.64	0.100452631
55.70593	0.030759		64.20	0.036241		87.53	0.06048355		121.24	0.100058993
54.85354	0.030539		63.66	0.035891		86.80	0.05987957		120.35	0.098598794
54.34037	0.030172		62.76	0.035749		86.01	0.05937553		119.92	0.096171495
53.7464	0.029851		62.07	0.035497		85.24	0.05887667		119.80	0.093154395
53.61183	0.029329		61.67	0.03508		84.71	0.05808639		118.69	0.092282655
53.13332	0.028973		61.33	0.034641		84.12	0.05740304		117.36	0.092474871
52.96822	0.028486		61.43	0.033958		83.51	0.05677038		115.68	0.093463583
52.4735	0.028155		60.84	0.033671		82.75	0.05637003		115.04	0.092041918
51.91515	0.02786		60.34	0.033344		82.27	0.05562175		114.03	0.091639639
51.18976	0.027647		59.25	0.033358		81.47	0.05532566		113.55	0.089963532
50.65267	0.027359		58.68	0.033087		80.86	0.054789		112.59	0.089636992
50.21454	0.027035		58.19	0.032769		80.22	0.05433276		112.41	0.087356996
49.67491	0.026763		57.83	0.032386		79.95	0.05340709		111.54	0.086971851
49.44525	0.026364		57.46	0.032019		79.63	0.05256915		111.31	0.084986554
49.49365	0.025855		57.00	0.031708		79.25	0.05182859		110.55	0.084463384
48.96819	0.0256		56.84	0.031237		78.49	0.05163128		109.75	0.084158295
48.5785	0.025295		56.22	0.03103		77.63	0.05159041		109.00	0.083798462
47.8711	0.025131		55.53	0.030867		77.14	0.05107418		108.07	0.084015858
47.68946	0.024753		54.87	0.030696		76.66	0.05056352		107.97	0.082003725
47.25193	0.024489		54.40	0.030422		76.38	0.04979849		107.27	0.081737726
46.74459	0.024262		54.04	0.030098		76.02	0.04917574		107.02	0.080266358

46.50943	0.023929		53.72	0.029753		75.70	0.04851407		106.13	0.080694676
46.07314	0.023686		53.63	0.029282		75.38	0.04787912		105.42	0.080701646
46.0191	0.023293		53.46	0.028872		74.97	0.04739237		104.34	0.081943803
45.5998	0.023056		52.85	0.028707		74.77	0.04663719		104.16	0.080431659
44.90864	0.022936		52.52	0.028393		74.24	0.04634438		103.67	0.079999931
44.49136	0.022712		51.68	0.028371		73.56	0.04628342		103.92	0.077261613
44.33741	0.022386		51.76	0.027845		72.70	0.04650958		103.60	0.076396688
44.51065	0.021939		51.25	0.02765		72.05	0.04646806		103.14	0.075967849
44.49513	0.021577		51.51	0.027045		71.91	0.04571503		102.46	0.07630391
43.55576	0.02158		50.98	0.026872		72.12	0.04449305		101.91	0.076285256
42.99191	0.021444		50.63	0.026606		72.07	0.04366428		101.65	0.075357642
42.05589	0.021462		50.08	0.026457		71.66	0.04335018		100.96	0.075899184
42.25294	0.021034		49.68	0.026233		70.98	0.04342617		100.42	0.0760385
42.2624	0.02069		49.22	0.026043		70.59	0.04312998		100.02	0.075723707
42.67406	0.020202		49.08	0.02569		70.10	0.04298729		100.26	0.073245026
42.15466	0.020073		48.79	0.025423		69.92	0.04242253		99.96	0.072618598
41.77971	0.019896		48.64	0.025086		69.90	0.04166704		99.73	0.071808267
41.13809	0.019823		48.50	0.024755		69.61	0.04129366		99.33	0.071605013
40.66408	0.019693		48.49	0.024363		69.24	0.04104808		98.69	0.072288683
40.21269	0.019559		48.52	0.023956		68.68	0.04108511		98.24	0.072370897
39.98389	0.019345		47.86	0.023157		68.50	0.0406029		97.21	0.074700948
40.21553	0.018965		47.00	0.022863		68.08	0.04048969		96.39	0.076490762
40.34608	0.018632		46.54	0.022387		67.87	0.04008163		95.78	0.077480524
40.05557	0.018458		46.29	0.021834		67.58	0.03980893		95.51	0.077041463
39.7745	0.018284		45.95	0.021343		67.38	0.03941784		95.47	0.075617518
39.74635	0.018025		45.13	0.021105		67.07	0.03919929		95.16	0.07535997
39.57854	0.017821		44.71	0.020691		66.80	0.03894586		95.23	0.073459945
39.50582	0.017588		44.09	0.020393		66.70	0.03845358		95.33	0.071477778
39.02875	0.0175		43.35	0.020168		66.43	0.03822006			
38.64632	0.017383		42.65	0.019942		66.38	0.03767265			
38.59119	0.017157		42.43	0.019507		66.03	0.03757699			
38.2351	0.017039		42.04	0.01917		65.80	0.03733298			
37.90935	0.016913		41.72	0.01882		65.04	0.03787559			
37.25714	0.016905		41.41	0.018479		64.57	0.03801175			
37.07534	0.016737		40.88	0.018255		64.12	0.03815641			
36.93837	0.016557		40.18	0.018122		64.14	0.03756091			
36.78958	0.016385		39.77	0.017878		64.01	0.03721232			
36.78318	0.016169		39.36	0.017641		63.74	0.03709972			
36.8769	0.015924		39.29	0.017264		63.40	0.03711024			
36.3828	0.015879		38.90	0.017051		63.27	0.03679163			
36.17132	0.015742		38.79	0.016725		63.39	0.03610627			

35.72427	0.015687		38.29	0.016581		63.35	0.03566553			
35.85955	0.015442		37.75	0.016471		63.45	0.03504168			
35.37146	0.015405		37.49	0.016247		63.20	0.03494545			
35.39173	0.015205		37.24	0.016033		62.95	0.0348707			
35.56151	0.01496		37.31	0.015689		62.63	0.03490834			
35.55447	0.014777		37.20	0.015436		62.63	0.03445791			
35.52661	0.014604		36.92	0.015264		62.56	0.03412467			
35.04145	0.014577		36.70	0.015079		61.99	0.03457967			
35.09631	0.014383		35.96	0.015127		61.51	0.03491026			
34.63072	0.014354		35.73	0.014962		61.19	0.03500867			
34.60946	0.014189		35.30	0.014897		61.15	0.03464743			
34.23629	0.014136		35.57	0.014534		61.04	0.03440788			
34.2451	0.013967		35.41	0.014371		61.12	0.03387584			
34.06721	0.013858		35.24	0.014216		61.22	0.03332681			
34.26705	0.013637		34.67	0.014234		61.10	0.03312801			
34.40836	0.013438		34.09	0.014268		60.71	0.03336266			
34.2776	0.013322		33.65	0.01425		60.40	0.03348466			
33.6187	0.013364		33.36	0.014174		60.29	0.03329551			
33.09109	0.01337		33.55	0.013896		60.24	0.03300655			
32.79234	0.013309		33.01	0.013939		59.92	0.03316055			
33.01492	0.013094		32.93	0.01379		59.81	0.03298476			
32.85036	0.012997		32.63	0.01374		59.52	0.03310488			
33.01713	0.012806		32.96	0.013423		59.39	0.03296985			
32.62998	0.012777		33.01	0.013235		59.34	0.03271303			
32.35298	0.012718		32.49	0.013291		59.40	0.03225746			
31.81319	0.012738		31.93	0.013367		59.43	0.03186815			
31.63413	0.012653		31.63	0.013342		58.98	0.03228184			
31.64545	0.012514		31.57	0.013211		58.61	0.03258636			
31.49345	0.012425		31.54	0.013074		58.05	0.03325505			
31.59894	0.012263		31.31	0.013028		57.62	0.03236751			
31.76305	0.012087		31.19	0.012935		57.06	0.03244572			
31.53566	0.012023		31.13	0.012821		56.59	0.03239032			
31.38028	0.011941		30.88	0.012789		56.35	0.03190776			
31.28206	0.011844		30.75	0.012708		56.12	0.03143114			
31.02594	0.011792		30.46	0.012699			0.03142364			
30.40521	0.011845		30.40	0.012592			0.03172023			
30.04153	0.011826		30.15	0.012573			0.03179821			
30.43648	0.011594		29.95	0.012531			0.03098634			
30.67647	0.01141		29.76	0.012485			0.03063859			
30.56942	0.011324		29.23	0.012593			0.03037937			
30.18543	0.011313		29.02	0.01256			0.03041197			

30.08412	0.011226		28.82	0.012524			0.0301153			
29.79395	0.01097		29.04	0.012301			0.02998774			
29.49901	0.010831		28.80	0.012285			0.02958276			
28.99433	0.010744		28.86	0.012141			0.02936073			
28.76103	0.010603		28.82	0.012039			0.02917756			
28.88851	0.010364		28.31	0.012143			0.02934678			
28.89045	0.010163		27.93	0.012195			0.02906856			
28.82215	0.009985		27.63	0.012213			0.02864467			
28.26527	0.009932		28.17	0.011853			0.02796966			
28.2044	0.009751		27.88	0.01186			0.02766251			
27.76612	0.009679		27.70	0.011827			0.02767674			
27.74297	0.009502		27.33	0.011872			0.02747362			
27.47766	0.009387		27.44	0.011706			0.02709253			
27.53945	0.009196		27.00	0.011788			0.02654417			
27.15789	0.009113		26.63	0.011838			0.02653321			
26.81917	0.009017		26.29	0.01188			0.0265638			
26.48809	0.008932		26.20	0.011805			0.025876			
26.6343	0.008733		26.01	0.011775			0.02563257			
26.65134	0.008568		25.82	0.011747			0.02499617			
26.43974	0.008458		25.65	0.011708			0.02490168			
26.31348	0.008331		25.97	0.011438			0.02494109			
26.12456	0.00822		25.76	0.011416			0.0251075			
26.33439	0.008025		25.70	0.011328			0.02539858			
26.02025	0.007946		25.22	0.011434			0.02487668			
25.84584	0.007835		25.39	0.011239			0.02488939			
25.5096	0.00777		25.31	0.011159			0.02476632			
25.21676	0.007693		25.58	0.010921			0.02448728			
25.09633	0.007581		25.33	0.010917			0.02391815			
25.08245	0.007451		25.26	0.010832			0.0240575			
25.1661	0.007303		24.42	0.011103			0.02359542			
25.06232	0.007193		24.23	0.011075			0.02383057			
24.74684	0.007135		24.12	0.011008			0.02340385			
24.46568	0.007068		24.49	0.010717			0.02327849			
24.35647	0.006969		24.38	0.010654			0.02343345			
24.37794	0.006847		24.09	0.010667			0.0229482			
24.51498	0.006708		24.00	0.010596			0.02295665			
24.3717	0.00662		23.98	0.010487			0.02218455			
24.08215	0.006569		24.31	0.010224			0.02191982			
23.75286	0.006523		24.38	0.010084			0.02145109			
23.49928	0.006466		24.27	0.010018			0.02157344			
23.33099	0.006395		23.96	0.010044			0.0216014			

23.24537	0.006311		23.76	0.010018			0.02262205			
23.12486	0.006233		23.47	0.010036			0.02177566			
23.16523	0.006135		23.21	0.010039			0.02159776			
23.09712	0.006056		23.11	0.009973			0.02087491			
22.97592	0.005988		23.25	0.0098			0.02216255			
22.97598	0.005902		23.31	0.009661			0.02271304			
22.73108	0.00586		23.23	0.009587			0.02290662			
22.78305	0.005767		22.79	0.009672			0.0220575			
22.54985	0.005731		22.33	0.009772			0.02145899			
22.75335	0.00562		21.81	0.009905			0.02177584			
22.7224	0.005552		22.01	0.009699			0.02213917			
22.77171	0.005473		22.27	0.009471			0.02281302			
22.54708	0.00544		22.19	0.009401			0.02305767			
22.23643	0.00542		21.90	0.009424			0.02275914			
21.93743	0.005406		21.70	0.009408			0.02305828			
21.73661	0.005375		21.74	0.009285			0.02329126			
21.70964	0.005318		21.69	0.009203			0.02440448			
21.72381	0.005256		21.67	0.00901			0.02500343			
21.50518	0.005233		21.49	0.008938			0.0248554			
21.57267	0.005165		21.19	0.008923			0.02478628			
21.64609	0.005102		21.17	0.008785			0.02485963			
21.7609	0.005033		20.99	0.008718			0.02544392			
21.71669	0.00499		20.85	0.00864			0.02645657			
21.51812	0.004972		20.35	0.008718			0.02751876			
21.33241	0.004953		20.19	0.008653			0.02848552			
21.08911	0.004944		20.22	0.0085			0.02761318			
21.21558	0.004882		20.35	0.008315			0.02640017			
21.04944	0.004864		20.26	0.008225			0.02554997			
20.91712	0.004843		20.20	0.008125			0.02615994			
20.49726	0.004866		19.88	0.008136			0.02594542			
20.51217	0.004825		19.87	0.008022			0.0260805			
20.59179	0.004775		19.61	0.008015			0.02459837			
20.57964	0.004739		19.74	0.007843			0.02462763			
20.25233	0.004752		19.74	0.00773			0.0238633			
20.40484	0.004694		19.66	0.007653			0.02444838			
20.41263	0.004659		19.23	0.007725			0.02424837			
20.71319	0.00458		18.92	0.007751			0.02553608			
20.29814	0.004609		18.92	0.007648			0.0256518			
20.0774	0.004608		18.75	0.007619			0.02768182			
19.99528	0.004588		18.69	0.007547			0.02695353			
20.12113	0.004539		18.50	0.007527			0.02949906			

19.97839	0.004528		18.69	0.007354			0.03125639			
19.91147	0.004507		18.50	0.007343			0.03643232			
19.68057	0.004509		18.30	0.007334			0.04110933			
19.98585	0.004435		18.14	0.007314			0.04900057			
19.87908	0.00442		18.21	0.007197			0.05912904			
19.87556	0.00439		18.24	0.007102			0.07387769			
19.38338	0.00443		18.16	0.007053						
19.27	0.004414		18.08	0.007001						
19.18669	0.004397		17.98	0.006965						
19.60417	0.004306		17.95	0.006902						
19.626	0.004272		18.01	0.006799						
19.41923	0.00427		17.60	0.00689						
19.1066	0.004282		17.56	0.006833						
19.08265	0.004253		17.14	0.006935						
19.2267	0.0042		17.31	0.006784						
19.23919	0.004166		17.01	0.00684						
19.19383	0.004139		17.29	0.006649						
19.05297	0.004124		17.29	0.006579						
18.98039	0.004098		17.54	0.006408						
18.73556	0.004097		17.15	0.006489						
18.77934	0.004056		17.03	0.006468						
18.62447	0.00404		16.68	0.00654						
18.59825	0.004007		16.52	0.006531						
18.43151	0.003991		16.33	0.006541						
18.35204	0.003962		16.30	0.006475						
18.15888	0.00395		16.42	0.006353						
18.21121	0.003903		16.55	0.006223						
18.19094	0.003865		16.42	0.006202						
18.19113	0.003823		16.33	0.006161						
18.08692	0.003795		16.34	0.006079						
18.03161	0.003758		16.45	0.005958						
18.25759	0.003688		16.39	0.005903						
17.99689	0.003677		16.30	0.00586						
17.90666	0.003644		15.83	0.005965						
17.6033	0.003637		15.72	0.005925						
17.74631	0.003574		15.30	0.00601						
17.48748	0.003558		15.50	0.005838						
17.53805	0.003506		15.75	0.005655						
17.31464	0.003486		15.82	0.00554						
17.22409	0.003359		15.70	0.005493						
17.17238	0.003266		15.40	0.005516						

17.13347	0.003173		15.75	0.005293						
17.31431	0.003055		15.75	0.005201						
17.20135	0.00297		15.70	0.005124						
17.1817	0.002876		15.28	0.005174						
17.06745	0.002793		15.23	0.005092						
16.98891	0.002709		15.12	0.005033						
16.96223	0.002619		14.80	0.005042						
16.88241	0.00254		14.80	0.004936						
16.81537	0.00246		14.85	0.004814						
16.76407	0.002383		15.13	0.004612						
16.56023	0.002324		15.10	0.004513						
16.57529	0.002251		15.21	0.004368						
16.34964	0.002203		15.32	0.004231						
16.45426	0.002132		15.12	0.004183						
16.23338	0.002094		14.74	0.004187						
16.20839	0.002046		14.48	0.004153						
16.23254	0.002001		14.57	0.004011						
16.31544	0.001958		14.54	0.003904						
16.45372	0.001919		14.62	0.003764						
16.11874	0.001918		14.64	0.003647						
15.91969	0.001915		14.42	0.00359						
15.73844	0.001917		14.36	0.00349						
15.95962	0.001896		14.49	0.003342						
16.06751	0.001888		14.85	0.003142						
15.98789	0.001899		14.99	0.003						
15.80361	0.001922		14.83	0.002923						
15.54439	0.001955		14.54	0.002875						
15.42513	0.001981		14.33	0.002808						
15.36308	0.002005		14.35	0.002692						
15.44628	0.002021		14.39	0.002573						
15.47943	0.002041		14.50	0.002445						
15.40859	0.00207		14.57	0.002327						
15.26593	0.002104		14.67	0.002207						
15.17148	0.002132		14.53	0.002128						
15.09503	0.002156		14.62	0.002013						
15.02604	0.002177		14.43	0.001943						
15.0587	0.002185		14.19	0.001879						
15.11963	0.002185		13.75	0.001846						
15.15248	0.002183		13.88	0.001731						
15.11327	0.002181		14.05	0.001617						
14.98206	0.00218		13.94	0.001542						

14.96688	0.002164		13.98	0.00145						
14.83068	0.002153		13.76	0.001391						
14.77361	0.00213		13.85	0.001298						
14.66592	0.002107		13.65	0.001242						
14.67654	0.002072		13.84	0.00115						
14.5843	0.002046		14.01	0.001065						
14.45891	0.002025		14.18	0.000986						
14.37426	0.002007		14.23	0.000922						
14.30282	0.001998		13.98	0.000881						
14.32325	0.001997		13.79	0.000837						
14.33371	0.002017		13.77	0.000789						
14.32346	0.002069		13.73	0.000744						
14.43378	0.002147		13.98	0.000687						
14.3074	0.00229		14.00	0.000648						
14.23422	0.002487		14.10	0.000609						
13.91441	0.002776		13.56	0.000605						
13.73252	0.003151		13.52	0.00058						
13.70847	0.003596		13.47	0.00056						
13.66281	0.004181		13.83	0.000527						
13.63033	0.004896		13.83	0.000514						
13.54213	0.005788		13.72	0.00051						
13.5224	0.006835		13.74	0.000505						
			13.82	0.000502						
			13.82	0.000506						
			13.57	0.000525						
			13.33	0.000548						
			13.40	0.000562						
			13.63	0.000572						
			13.76	0.00059						
			13.92	0.000611						
			13.81	0.000648						
			13.84	0.000681						
			13.92	0.000715						
			13.98	0.000754						
			13.92	0.000802						
			13.94	0.000849						
			14.25	0.000878						
			14.14	0.000939						
			14.09	0.000997						
			14.05	0.001058						
			14.07	0.001116						

			13.94	0.00119						
			13.93	0.001256						
			14.01	0.001312						
			13.99	0.001381						
			13.68	0.001485						
			13.49	0.001579						
			13.56	0.001644						
			13.80	0.001683						
			13.91	0.001741						
			13.71	0.001839						
			13.18	0.001995						
			13.17	0.002071						
			13.20	0.002141						
			13.57	0.002148						
			13.44	0.002242						
			13.64	0.002274						
			13.26	0.002413						
			13.44	0.002445						
			13.48	0.002501						
			13.65	0.002528						
			13.71	0.002573						
			13.45	0.002685						
			13.19	0.002796						
			12.97	0.0029						
			13.25	0.002882						
			13.32	0.002909						
			13.09	0.003004						
			12.67	0.003152						
			12.87	0.003132						
			13.01	0.003124						
			13.20	0.0031						
			13.18	0.003124						
			13.28	0.003113						
			12.95	0.003209						
			12.96	0.00321						
			12.71	0.003281						
			12.81	0.003248						
			12.57	0.003303						
			12.66	0.003262						
			12.48	0.003291						
			12.55	0.003245						

			12.47	0.003235						
			12.49	0.003193						
			12.39	0.003177						
			12.61	0.003067						
			12.93	0.002933						
			13.19	0.002816						
			12.88	0.002827						
			12.76	0.002792						
			12.67	0.002741						
			12.73	0.002652						
			12.81	0.002552						
			12.83	0.002466						
			12.80	0.002385						
			12.70	0.002314						
			12.81	0.0022						
			12.99	0.002073						
			12.75	0.002016						
			12.53	0.001951						
			12.62	0.001833						
			12.78	0.001703						
			12.66	0.001614						
			12.30	0.001554						
			12.14	0.001464						
			12.23	0.001341						
			12.26	0.001222						
			12.41	0.0011						
			11.98	0.00103						
			12.08	0.000912						
			11.62	0.000839						
			12.26	0.000687						
			12.14	0.000593						
			12.60	0.000474						
			12.27	0.000393						
			12.27	0.000303						
			12.25	0.000217						
			12.29	0.000134						
			11.94	5.78E-05						

Figure S5

1 equiv Ph_3SiCl			1.5 equiv Ph_3SiCl	
[ROH (4)]	**Rate/$[Ph_3SiCl]^{1.5}$**		**[ROH]**	**[Rate/$[Ph_3SiCl]^{1.5}$**
65.81	0.00207		66.65	0.002005845
64.91	0.00207		66.11	0.001992575
64.77	0.00204		65.37	0.001985311
64.59	0.00201		64.45	0.001983787
64.71	0.00197		64.03	0.001968714
64.02	0.00197		63.87	0.001946938
63.33	0.00197		63.94	0.001919416
62.84	0.00196		63.76	0.001899292
62.48	0.00194		63.64	0.001878442
62.08	0.00192		62.89	0.001875103
61.63	0.00191		62.38	0.001865937
61.14	0.00191		61.85	0.001857654
61.11	0.00188		61.73	0.001838505
60.89	0.00186		61.36	0.00182665
61.04	0.00182		61.39	0.001804659
60.41	0.00182		61.41	0.001783424
60.08	0.00181		61.27	0.001766878
59.48	0.00181		60.25	0.001773863
59.30	0.00179		59.37	0.001777822
59.09	0.00177		58.54	0.001780816
58.82	0.00176		58.38	0.001766051
58.74	0.00174		58.43	0.001745819
58.09	0.00174		58.47	0.001726529
57.99	0.00172		58.22	0.001715113
57.44	0.00172		57.86	0.001706927
57.10	0.00171		57.34	0.001703494
56.70	0.00171		56.95	0.001696576
56.38	0.00170		56.17	0.001700128
55.99	0.00169		55.29	0.001674075
55.73	0.00168		54.47	0.00166389
55.43	0.00168		53.87	0.001648677
55.74	0.00164		53.36	0.001631694
55.28	0.00164		52.54	0.001623418
55.09	0.00163		52.02	0.00160783

54.45	0.00164		51.75	0.001586288
54.11	0.00163		51.41	0.001567071
53.94	0.00162		50.87	0.001553601
53.88	0.00160		50.20	0.001543573
53.92	0.00158		49.89	0.001524665
53.86	0.00157		49.67	0.001503733
53.74	0.00156		49.59	0.001479815
53.43	0.00155		49.00	0.001468942
53.01	0.00155		48.10	0.001465857
52.67	0.00155		47.20	0.001463163
52.59	0.00154		46.71	0.001450126
52.32	0.00153		46.57	0.00142873
52.11	0.00152		46.31	0.001410392
51.72	0.00152		45.74	0.001399931
51.67	0.00151		45.21	0.001388443
51.44	0.00151		44.75	0.001375666
51.20	0.00150		44.41	0.001360049
51.06	0.00149		44.05	0.001344854
50.82	0.00149		43.74	0.001328895
50.62	0.00148		43.49	0.001311769
50.10	0.00149		42.86	0.001303635
49.86	0.00148		42.29	0.0012943
49.70	0.00148		42.04	0.00127756
49.83	0.00146		41.77	0.001261627
49.61	0.00144		41.52	0.001245311
49.27	0.00143		41.14	0.001232397
48.66	0.00144		40.90	0.001216461
48.12	0.00144		40.68	0.001200664
47.90	0.00143		40.12	0.001192482
47.67	0.00142		39.74	0.001180488
47.50	0.00141		39.68	0.001162033
46.94	0.00142		39.20	0.001152922
46.70	0.00141		39.00	0.001138039
46.33	0.00141		38.32	0.001133924
46.33	0.00139		38.25	0.001117109
45.94	0.00139		37.66	0.001111706
45.78	0.00137		37.41	0.001099458
45.41	0.00137		36.96	0.001091753
45.36	0.00136		36.96	0.001074911

45.05	0.00135		36.67	0.001064763
44.75	0.00135		36.66	0.001049208
44.25	0.00135		36.37	0.001039892
43.93	0.00135		36.17	0.001029075
43.49	0.00135		35.85	0.001021208
43.31	0.00134		35.29	0.001018611
43.12	0.00133		34.81	0.001014934
43.05	0.00132		34.49	0.001008249
42.93	0.00131		34.37	0.000998021
42.88	0.00129		34.29	0.000987534
42.69	0.00128		34.22	0.000977158
42.55	0.00127		34.36	0.000963436
42.38	0.00126		34.05	0.000958727
42.26	0.00125		33.72	0.000954948
41.87	0.00125		33.18	0.000955624
41.77	0.00124		32.87	0.000942957
41.46	0.00124		32.63	0.000934844
41.56	0.00122		32.54	0.000924565
41.20	0.00122		32.17	0.000920323
41.17	0.00120		31.73	0.000918344
40.86	0.00120		30.98	0.000922861
40.86	0.00119		30.78	0.000917443
40.60	0.00118		30.47	0.000914504
40.33	0.00118		30.18	0.000911731
40.14	0.00117			
40.13	0.00116			
40.09	0.00114			
39.63	0.00115			
39.37	0.00114			
39.04	0.00114			
38.91	0.00113			
38.83	0.00112			
38.76	0.00111			
38.85	0.00109			
38.94	0.00107			
38.69	0.00107			
38.44	0.00106			
37.93	0.00107			
38.03	0.00105			

37.74	0.00105			
37.51	0.00105			
37.28	0.00104			
37.22	0.00103			
36.95	0.00103			
36.54	0.00103			
36.42	0.00102			
36.55	0.00100			
36.61	0.00099			
36.51	0.00098			
36.25	0.00098			
36.25	0.00096			
36.00	0.00096			
35.69	0.00096			
35.43	0.00096			
35.21	0.00096			
35.34	0.00094			
35.36	0.00093			
35.57	0.00091			
35.58	0.00089			
35.47	0.00089			
35.24	0.00088			
35.13	0.00088			
34.84	0.00088			
34.70	0.00087			
34.55	0.00087			
34.56	0.00085			
34.54	0.00083			
34.60	0.00082			
34.27	0.00082			
34.09	0.00081			
33.78	0.00081			
33.95	0.00079			
33.66	0.00079			
33.38	0.00078			
32.98	0.00078			
33.03	0.00077			
32.97	0.00076			
33.02	0.00075			

32.86	0.00074			
32.86	0.00073			
32.82	0.00072			
32.97	0.00070			
32.66	0.00070			
32.42	0.00070			
32.10	0.00070			
32.04	0.00069			
31.91	0.00068			
31.86	0.00067			
31.76	0.00066			
31.56	0.00066			
31.32	0.00066			
31.44	0.00064			
31.35	0.00064			
31.46	0.00062			
31.22	0.00062			
31.37	0.00061			
31.29	0.00060			
31.14	0.00060			
30.88	0.00059			
30.75	0.00059			
30.74	0.00058			
30.88	0.00057			
30.63	0.00057			
30.39	0.00056			
30.21	0.00056			
30.32	0.00055			
30.34	0.00054			
30.27	0.00053			
30.19	0.00053			
30.28	0.00052			
30.05	0.000516754			

Figure S6

1 equiv Ph_3SiCl			1.5 equiv Ph_3SiCl	
[ROH]	**[Rate/[SiCl]$^{1.5}$**		**[ROH]**	**[Rate/[SiCl]$^{1.5}$**
64.02	0.001968692		64.03	0.001968714
63.33	0.00196629		63.87	0.001946938
62.84	0.001955382		63.94	0.001919416
62.48	0.001938557		63.76	0.001899292
62.08	0.001924637		63.64	0.001878442
61.63	0.001914017		62.89	0.001875103
61.14	0.00190547		62.38	0.001865937
61.11	0.001875826		61.85	0.001857654
60.89	0.00185608		61.73	0.001838505
61.04	0.001820063		61.36	0.00182665
60.41	0.001820199		61.39	0.001804659
60.08	0.001806936		61.41	0.001783424
59.48	0.001806578		61.27	0.001766878
59.30	0.001787566		60.25	0.001773863
59.09	0.001770569		59.37	0.001777822
58.82	0.001757054		58.54	0.001780816
58.74	0.001735275		58.38	0.001766051
58.09	0.001739588		58.43	0.001745819
57.99	0.001719629		58.47	0.001726529
57.44	0.001720278		58.22	0.001715113
57.10	0.001711593		57.86	0.001706927
56.70	0.001706457		57.34	0.001703494
56.38	0.001698361		56.95	0.001696576
55.99	0.001693265		56.17	0.001700128
55.73	0.001683082		55.29	0.001674075
55.43	0.001675128		54.47	0.00166389
55.74	0.00164022		53.87	0.001648677
55.28	0.001639987		53.36	0.001631694
55.09	0.001627975		52.54	0.001623418
54.45	0.001636443		52.02	0.00160783
54.11	0.001631882		51.75	0.001586288
53.94	0.001620139		51.41	0.001567071
53.88	0.001603802		50.87	0.001553601
53.92	0.001583077		50.20	0.001543573

53.86	0.001567564		49.89	0.001524665
53.74	0.001555017		49.67	0.001503733
53.43	0.001550645		49.59	0.001479815
53.01	0.001551854		49.00	0.001468942
52.67	0.001549547		48.10	0.001465857
52.59	0.001536261		47.20	0.001463163
52.32	0.001531371		46.71	0.001450126
52.11	0.001524151		46.57	0.00142873
51.72	0.001524832		46.31	0.001410392
51.67	0.001511093		45.74	0.001399931
51.44	0.001505427		45.21	0.001388443
51.20	0.001500364		44.75	0.001375666
51.06	0.00149103		44.41	0.001360049
50.82	0.001486439		44.05	0.001344854
50.62	0.001480265		43.74	0.001328895
50.10	0.001488495		43.49	0.001311769
49.86	0.001484063		42.86	0.001303635
49.70	0.0014766		42.29	0.0012943
49.83	0.001456527		42.04	0.00127756
49.61	0.001438282		41.77	0.001261627
49.27	0.001432194		41.52	0.001245311
48.66	0.001438575		41.14	0.001232397
48.12	0.001442257		40.90	0.001216461
47.90	0.001431881		40.68	0.001200664
47.67	0.00142235		40.12	0.001192482
47.50	0.001410665		39.74	0.001180488
46.94	0.001416124		39.68	0.001162033
46.70	0.001407749		39.20	0.001152922
46.33	0.001405233		39.00	0.001138039
46.33	0.00138662		38.32	0.001133924
45.94	0.001385491		38.25	0.001117109
45.78	0.001374157		37.66	0.001111706
45.41	0.001372247		37.41	0.001099458
45.36	0.001356372		36.96	0.001091753
45.05	0.00135232		36.96	0.001074911
44.75	0.001347688		36.67	0.001064763
44.25	0.001352683		36.66	0.001049208
43.93	0.0013495		36.37	0.001039892
43.49	0.001351851		36.17	0.001029075

43.31	0.001342791		35.85	0.001021208
43.12	0.001333811		35.29	0.001018611
43.05	0.001319353		34.81	0.001014934
42.93	0.001307809		34.49	0.001008249
42.88	0.00129296		34.37	0.000998021
42.69	0.001284516		34.29	0.000987534
42.55	0.001274011		34.22	0.000977158
42.38	0.00126498		34.36	0.000963436
42.26	0.001253348		34.05	0.000958727
41.87	0.001254199		33.72	0.000954948
41.77	0.00124219		33.18	0.000955624
41.46	0.00123996		32.87	0.000942957
41.56	0.001218969		32.63	0.000934844
41.20	0.001218911		32.54	0.000924565
41.17	0.001204154		32.17	0.000920323
40.86	0.001201798		31.73	0.000918344
40.86	0.001186177		30.98	0.000922861
40.60	0.001181835		30.78	0.000917443
40.33	0.001177748		30.47	0.000914504
40.14	0.001170301		30.18	0.000911731
40.13	0.001155339			
40.09	0.001141724			
39.63	0.001146436			
39.37	0.001142426			
39.04	0.001141711			
38.91	0.001131912			
38.83	0.001120749			
38.76	0.001108602			
38.85	0.001090286			
38.94	0.001071885			
38.69	0.00106796			
38.44	0.00106411			
37.93	0.001071304			
38.03	0.001053162			
37.74	0.001050951			
37.51	0.001046751			
37.28	0.001042377			

Figure S7

0.8 equiv Ph_3SiCl			1 equiv Ph_3SiCl	
$\Sigma[Ph3SiCl]^{0.7}$ Δt (min)				
Normalized Time	**[Product] mM**		**Normalized Time**	**[Product] mM**
0.00	0.00		**0.00**	0.00
7.30	28.32		4.12	19.10
10.12	36.55		8.40	35.31
12.83	43.89		12.00	44.54
15.01	47.21		15.15	50.80
16.96	50.64		18.04	53.15
18.72	52.13		20.77	55.89
20.29	55.54		23.34	58.50
21.73	55.37		25.74	60.76
23.12	56.67		28.04	61.62
24.33	57.60		30.23	63.85
25.59	59.50		32.36	63.55
26.62	60.59		34.37	67.15
27.52	62.34		36.32	65.27
28.32	62.39		38.20	69.02
29.02	63.26		40.00	67.54
29.80	62.86		41.76	69.93
30.54	62.97		43.48	68.49
31.26	63.29		45.29	67.80
31.94	63.65		47.00	70.95
33.71	64.85		48.60	70.76
34.61	65.79		50.16	71.98
35.38	65.82		51.76	69.50
35.97	66.97		53.35	72.49
36.35	67.02		54.84	71.73
			56.34	72.42
			57.74	74.34
			58.98	75.80
			60.38	70.74
			61.87	73.68
			63.24	73.58
			64.58	74.44
			65.91	73.88
			67.21	75.00
			68.42	75.92
			69.58	76.26

			70.77	75.06
			71.96	76.35
			73.15	75.27
			74.36	75.70
			75.42	78.47
			76.50	75.26
			77.61	76.30
			78.80	76.80
			79.83	78.01
			80.88	76.38
			81.98	77.02
			83.09	76.28
			84.08	79.34
			84.98	78.14

Figure S8 – Same Excess for catalyst 1

Run 1 - 40 mM **4**			Run 1 - time shifted 10 minutes			Run 2 - 80 mM **4**	
Time (min)	**[ROH]**		**Time (min)**	**[ROH]**		**Time (min)**	**[ROH]**
0	39.54606		10.7	39.54606		0	78.64362
0.2	38.7376		10.9	38.7376		0.2	78.78151
0.45	37.72252		11.15	37.72252		0.45	78.89544
0.7	36.31083		11.4	36.31083		0.7	76.88748
0.95	35.92148		11.65	35.92148		0.95	75.38153
1.2	35.17993		11.9	35.17993		1.2	73.8977
1.45	34.8627		12.15	34.8627		1.45	71.96525
1.7	34.1704		12.4	34.1704		1.7	70.12931
1.95	33.31249		12.65	33.31249		1.95	68.93574
2.2	32.59368		12.9	32.59368		2.2	67.62636
2.45	32.41039		13.15	32.41039		2.45	66.58714
2.7	32.29948		13.4	32.29948		2.7	65.2166
2.95	31.89745		13.65	31.89745		2.95	63.82831
3.2	31.69612		13.9	31.69612		3.2	62.5073
3.45	31.22717		14.15	31.22717		3.45	61.40368
3.7	30.97458		14.4	30.97458		3.7	60.47626
3.95	30.25195		14.65	30.25195		3.95	59.60079
4.2	30.19517		14.9	30.19517		4.2	58.56921
4.45	29.64354		15.15	29.64354		4.45	57.36793
4.7	29.23831		15.4	29.23831		4.7	56.12594
4.95	28.65208		15.65	28.65208		4.95	55.17913
5.2	28.42736		15.9	28.42736		5.2	54.11395
5.45	28.51488		16.15	28.51488		5.45	53.71325
5.7	28.41526		16.4	28.41526		5.7	52.79261
5.966667	28.3682		16.66667	28.3682		5.966667	52.06406
6.2	27.91706		16.9	27.91706		6.2	50.79957
6.45	27.40894		17.15	27.40894		6.45	49.88044
6.7	27.37516		17.4	27.37516		6.7	49.40974
6.95	26.96472		17.65	26.96472		6.95	48.82136
7.2	27.32639		17.9	27.32639		7.2	48.14915
7.45	26.50961		18.15	26.50961		7.45	47.51979
7.7	26.24885		18.4	26.24885		7.7	46.78606
7.95	25.60333		18.65	25.60333		7.95	45.99629
8.2	25.74446		18.9	25.74446		8.2	45.22472
8.45	25.51647		19.15	25.51647		8.45	44.69808
8.7	25.39549		19.4	25.39549		8.7	44.1093
8.95	25.2418		19.65	25.2418		8.95	43.50151

9.2	25.26224		19.9	25.26224		9.2	42.73662
9.45	25.28189		20.15	25.28189		9.45	42.25609
9.7	25.13507		20.4	25.13507		9.7	41.45318
9.95	25.03326		20.65	25.03326		9.95	40.85155
10.2	24.9396		20.9	24.9396		10.2	40.20928
10.45	24.44697		21.15	24.44697		10.45	39.93428
10.7	23.58788		21.4	23.58788		10.7	39.61346
10.95	22.99052		21.65	22.99052		10.95	39.23805
11.2	22.67797		21.9	22.67797		11.2	38.47183
11.45	22.90645		22.15	22.90645		11.45	37.61345
11.7	22.74645		22.4	22.74645		11.7	37.12327
11.95	22.66415		22.65	22.66415		11.95	36.646
12.2	22.17207		22.9	22.17207		12.2	36.37025
12.45	21.94958		23.15	21.94958		12.45	36.00757
12.7	21.95172		23.4	21.95172		12.7	35.68983
12.95	22.04561		23.65	22.04561		12.95	35.36879
13.2	21.77205		23.9	21.77205		13.2	34.95425
13.45	21.34544		24.15	21.34544		13.45	34.75419
13.7	21.32059		24.4	21.32059		13.7	34.22663
13.95	21.22888		24.65	21.22888		13.95	33.54662
14.2	21.09103		24.9	21.09103		14.2	32.68418
14.45	20.42963		25.15	20.42963		14.45	32.03499
14.7	20.18697		25.4	20.18697		14.7	31.89435
14.95	19.9677		25.65	19.9677		14.95	32.10476
15.2	20.01931		25.9	20.01931		15.2	32.05679
15.45	19.70747		26.15	19.70747		15.45	31.64731
15.7	19.64341		26.4	19.64341		15.7	30.97097
15.95	19.77614		26.65	19.77614		15.95	30.5776
16.2	20.18073		26.9	20.18073		16.2	30.08963
16.45	20.13517		27.15	20.13517		16.45	29.91114
16.7	19.75446		27.4	19.75446		16.7	29.88189
16.95	19.17117		27.65	19.17117		16.95	29.59288
17.2	19.21627		27.9	19.21627		17.2	29.22445
17.45	19.37976		28.15	19.37976		17.45	28.66962
17.7	19.45933		28.4	19.45933		17.7	28.49148
17.95	19.25387		28.65	19.25387		17.95	28.06671
18.2	18.70966		28.9	18.70966		18.2	27.85816
18.45	18.51774		29.15	18.51774		18.45	27.56618
18.7	18.10691		29.4	18.10691		18.7	27.36659
18.95	18.03961		29.65	18.03961		18.95	27.05752
19.2	18.31288		29.9	18.31288		19.2	26.78263

19.45	18.26022		30.15	18.26022		19.45	26.68217
19.7	18.08856		30.4	18.08856		19.7	26.41216
19.95	17.77111		30.65	17.77111		19.95	26.36937
20.2	17.77786		30.9	17.77786		20.2	26.02117
20.45	17.7323		31.15	17.7323		20.45	25.78518
20.7	17.05781		31.4	17.05781		20.7	25.02692
20.95	16.90599		31.65	16.90599		20.95	24.56076
21.2	16.77733		31.9	16.77733		21.2	24.10308
21.45	16.67479		32.15	16.67479		21.45	24.12517
21.7	16.43298		32.4	16.43298		21.7	23.99779
21.95	16.33985		32.65	16.33985		21.95	23.72587
22.2	16.28312		32.9	16.28312		22.2	23.38383
22.45	16.02642		33.15	16.02642		22.45	23.2572
22.7	16.02551		33.4	16.02551		22.7	23.3722
22.95	16.33067		33.65	16.33067		22.95	23.33924
23.2	16.54962		33.9	16.54962		23.2	23.43575
23.45	16.69246		34.15	16.69246		23.45	23.18866
23.7	16.50064		34.4	16.50064		23.7	22.934
23.95	16.72342		34.65	16.72342		23.95	22.6129
24.2	16.28344		34.9	16.28344		24.2	22.61569
24.45	16.17019		35.15	16.17019		24.45	22.54813
24.7	15.75194		35.4	15.75194		24.7	21.97371
24.95	15.44161		35.65	15.44161		24.95	21.49708
25.2	15.17975		35.9	15.17975		25.2	21.17516
25.45	14.83909		36.15	14.83909		25.45	21.13783
25.7	14.96523		36.4	14.96523		25.7	21.03103
25.95	15.20848		36.65	15.20848		25.95	21.10917
26.2	15.41072		36.9	15.41072		26.2	21.20626
26.45	15.47847		37.15	15.47847		26.45	21.08684
26.7	15.04693		37.4	15.04693		26.7	20.69882
26.95	14.74383		37.65	14.74383		26.95	20.38957
27.2	14.30056		37.9	14.30056		27.2	20.27509
27.45	14.52664		38.15	14.52664		27.45	20.22498
27.7	14.42617		38.4	14.42617		27.7	19.90899
27.95	14.7982		38.65	14.7982		27.95	19.7962
28.2	14.72671		38.9	14.72671		28.2	19.51044
28.45	15.02756		39.15	15.02756		28.45	19.37957
28.7	14.71744		39.4	14.71744		28.7	19.32317
28.95	14.52693		39.65	14.52693		28.95	19.3884
29.2	14.17011		39.9	14.17011		29.2	19.41875
29.45	14.05639		40.15	14.05639		29.45	18.96956

29.7	13.88903		40.4	13.88903		29.7	18.59718
29.95	13.7483		40.65	13.7483		29.95	18.0352
31.2	13.72793		41.9	13.72793		31.2	17.60845
31.95	13.35093		42.65	13.35093		31.95	17.04641
32.7	12.84664		43.4	12.84664		32.7	16.576
33.45	12.48955		44.15	12.48955		33.45	16.33868
34.2	12.44646		44.9	12.44646		34.2	16.10856
34.95	12.55686		45.65	12.55686		34.95	15.65036
35.7	12.27152		46.4	12.27152		35.7	15.06076
36.45	12.30889		47.15	12.30889		36.45	14.59494
37.2	11.88034		47.9	11.88034		37.2	14.54989
37.95	11.77359		48.65	11.77359		37.95	14.29471
38.7	11.15848		49.4	11.15848		38.7	14.00419
39.45	11.11834		50.15	11.11834		39.45	13.58796
40.2	10.87162		50.9	10.87162		40.2	13.32715
40.95	10.60144		51.65	10.60144		40.95	12.99767
41.7	10.46888		52.4	10.46888		41.7	12.79418
42.45	10.51225		53.15	10.51225		42.45	12.5165
43.2	10.46944		53.9	10.46944		43.2	12.22807
43.95	10.19224		54.65	10.19224		43.95	11.80225
44.7	9.858166		55.4	9.858166		44.7	11.56609
45.45	9.646002		56.15	9.646002		45.45	11.3926
46.2	9.514006		56.9	9.514006		46.2	11.3244
46.95	9.282701		57.65	9.282701		46.95	11.11306
47.7	9.196072		58.4	9.196072		47.7	10.78027
48.45	8.896338		59.15	8.896338		48.45	10.54033
49.2	8.627607		59.9	8.627607		49.2	10.3744
49.95	8.403519		60.65	8.403519		49.95	10.27812
50.7	8.313001		61.4	8.313001		50.7	9.981662
51.45	8.309096		62.15	8.309096		51.45	9.679741
52.2	8.234979		62.9	8.234979		52.2	9.648985
52.95	8.034741		63.65	8.034741		52.95	9.459914
53.7	7.853855		64.4	7.853855		53.7	9.423112
54.45	7.826523		65.15	7.826523		54.45	9.190262
55.2	7.797797		65.9	7.797797		55.2	8.917469
55.95	7.701188		66.65	7.701188		55.95	8.611479
56.7	7.482331		67.4	7.482331		56.7	8.278105
57.45	7.468368		68.15	7.468368		57.45	8.221535
58.2	7.328469		68.9	7.328469		58.2	7.996359
58.95	7.105079		69.65	7.105079		58.95	7.822986
59.7	6.746012		70.4	6.746012		59.7	7.705428

60.45	6.801527		71.15	6.801527		60.45	7.685951
61.2	6.602012		71.9	6.602012		61.2	7.448275
61.95	6.70148		72.65	6.70148		61.95	7.4056
62.7	6.60959		73.4	6.60959		62.7	7.153913
63.45	6.555693		74.15	6.555693		63.45	7.110424
64.2	6.211191		74.9	6.211191		64.2	6.981586
64.95	5.980069		75.65	5.980069		64.95	6.776818
65.7	6.03449		76.4	6.03449		65.7	6.76548
66.45	6.08141		77.15	6.08141		66.45	6.615479
67.2	5.957369		77.9	5.957369		67.2	6.700131
67.95	5.90527		78.65	5.90527		67.95	6.640596
68.7	5.699505		79.4	5.699505		68.7	6.648968
69.45	5.692203		80.15	5.692203		69.45	6.481816
70.2	5.376362		80.9	5.376362		70.2	6.35042
70.95	5.137913		81.65	5.137913		70.95	5.95222
71.7	4.818879		82.4	4.818879		71.7	6.073325
72.45	4.879274		83.15	4.879274		72.45	6.017801
73.2	4.950051		83.9	4.950051		73.2	6.12257
73.95	4.812249		84.65	4.812249		73.95	5.674311
74.7	4.599815		85.4	4.599815		74.7	5.451228
75.45	4.406516		86.15	4.406516		75.45	5.324832
76.63333	4.464623		87.33333	4.464623		76.63333	5.407217
77.65	4.548533		88.35	4.548533		77.65	5.458263
78.65	4.467701		89.35	4.467701		78.65	5.289134
79.63333	4.479467		90.33333	4.479467		79.63333	5.121692
80.65	4.259966		91.35	4.259966		80.65	4.895121
81.63333	4.035546		92.33333	4.035546		81.63333	4.775934
82.65	3.788728		93.35	3.788728		82.65	4.772504
83.63333	3.638455		94.33333	3.638455		83.63333	4.650991
84.63333	3.845073		95.33333	3.845073		84.63333	4.547212
85.65	3.719328		96.35	3.719328		85.65	4.286163
86.63333	3.649716		97.33333	3.649716		86.63333	4.133895
87.65	3.676543		98.35	3.676543		87.65	4.107151
88.63333	3.620895		99.33333	3.620895		88.63333	4.068139
89.63333	3.78686		100.3333	3.78686		89.63333	4.003429
90.65	3.559432		101.35	3.559432		90.65	3.856684
91.63333	3.309936		102.3333	3.309936		91.63333	3.654997
92.65	3.023749		103.35	3.023749		92.65	3.456333
93.63333	2.916854		104.3333	2.916854		93.63333	3.280983
94.65	3.047823		105.35	3.047823		94.65	3.317611
95.65	2.760028		106.35	2.760028		95.65	3.395344

96.63333	2.422419		107.3333	2.422419		96.63333	3.426449
97.65	2.223528		108.35	2.223528		97.65	3.257844
98.63333	2.236378		109.3333	2.236378		98.63333	3.192785
99.65	2.321452		110.35	2.321452		99.65	3.076854
100.65	2.193771		111.35	2.193771		100.65	3.155052
101.6333	2.060176		112.3333	2.060176		101.6333	3.044703
102.65	2.057469		113.35	2.057469		102.65	3.030168
103.6333	2.177889		114.3333	2.177889		103.6333	2.857318
104.65	1.876661		115.35	1.876661		104.65	2.787201
105.65	1.667493		116.35	1.667493		105.65	2.575572
106.6333	1.548491		117.3333	1.548491		106.6333	2.51749
						107.65	2.319292
						108.6333	2.409408
						109.65	2.277722
						110.65	2.28028
						111.6333	2.128593
						112.65	2.114988
						113.6333	2.029697
						114.65	1.97304
						115.65	1.876847

Figure S9 – Same Excess for catalyst 2

Run 1 - 80 mM **4**			Run 2 - 40 mM **4**			Run 2 - time shifted 24 minutes	
Time (min)	**[ROH]**		**Time (min)**	**[ROH]**		**Time (min)**	**[ROH]**
1.43	73.90743		1.70	37.604		25.70	37.604
1.68	73.59197		2.20	36.4084		26.20	36.4084
1.93	72.86368		2.72	36.8494		26.72	36.8494
2.18	72.36266		3.20	36.9369		27.20	36.9369
2.43	71.9367		3.70	36.9014		27.70	36.9014
2.68	71.32281		4.20	36.1395		28.20	36.1395
2.93	70.65413		4.70	34.9763		28.70	34.9763
3.18	70.10398		5.20	34.4903		29.20	34.4903
3.43	69.50136		5.72	34.1515		29.72	34.1515
3.68	69.34416		6.20	33.8097		30.20	33.8097
3.93	68.85312		6.70	33.0269		30.70	33.0269
4.18	68.24069		7.20	32.337		31.20	32.337
4.43	67.60622		7.70	31.5022		31.70	31.5022
4.68	66.69529		8.20	31.2825		32.20	31.2825
4.93	66.12612		8.70	30.7889		32.70	30.7889
5.18	65.61241		9.20	31.0176		33.20	31.0176
5.43	65.2134		9.70	30.8148		33.70	30.8148
5.68	64.68049		10.22	30.6923		34.22	30.6923
5.93	64.35947		10.70	29.7288		34.70	29.7288
6.18	64.02479		11.20	29.0572		35.20	29.0572
6.43	63.35887		11.70	28.3515		35.70	28.3515
6.68	62.53053		12.20	28.6647		36.20	28.6647
6.93	62.20912		12.70	28.8603		36.70	28.8603
7.18	61.72413		13.20	29.0702		37.20	29.0702
7.43	60.89563		13.70	27.6461		37.70	27.6461
7.68	60.19045		14.20	27.1147		38.20	27.1147
7.93	60.12569		14.72	26.5018		38.72	26.5018
8.18	60.32682		15.20	26.6654		39.20	26.6654
8.43	60.09482		15.70	25.0794		39.70	25.0794
8.68	59.80215		16.20	24.1305		40.20	24.1305
8.93	59.04819		16.70	23.1133		40.70	23.1133
9.18	58.95619		17.20	23.134		41.20	23.134
9.43	58.27528		17.70	22.4424		41.70	22.4424
9.68	58.27681		18.22	22.6768		42.22	22.6768

9.93	57.31581		18.70	22.1066		42.70	22.1066
10.18	57.23959		19.20	21.6592		43.20	21.6592
10.43	56.64562		19.70	21.2311		43.70	21.2311
10.68	56.36686		20.20	21.2177		44.20	21.2177
10.93	55.96447		20.70	21.5454		44.70	21.5454
11.18	56.20454		21.20	21.4041		45.20	21.4041
11.43	55.39089		21.70	21.3383		45.70	21.3383
11.68	54.6422		22.20	21.1072		46.20	21.1072
11.93	53.62377		22.70	20.5986		46.70	20.5986
12.18	53.76139		23.20	20.4201		47.20	20.4201
12.43	53.56502		23.70	19.8489		47.70	19.8489
12.68	53.16487		24.22	19.3549		48.22	19.3549
12.93	52.67594		24.70	19.366		48.70	19.366
13.18	52.50237		25.20	19.6162		49.20	19.6162
13.43	51.90265		25.70	20.0026		49.70	20.0026
13.68	51.22458		26.20	19.6132		50.20	19.6132
13.93	50.7025		26.70	19.4216		50.70	19.4216
14.18	50.78125		27.20	19.2197		51.20	19.2197
14.43	50.48948		27.70	18.8821		51.70	18.8821
14.68	49.79269		28.20	18.9721		52.20	18.9721
14.93	48.79643		28.70	18.6331		52.70	18.6331
15.68	48.16112		29.20	18.5721		53.20	18.5721
16.18	47.86595		29.70	18.1929		53.70	18.1929
16.68	47.25557		30.22	18.0049		54.22	18.0049
17.18	46.90292		30.70	17.7874		54.70	17.7874
17.68	45.89386		31.20	17.0204		55.20	17.0204
18.18	45.3836		31.70	17.1822		55.70	17.1822
18.68	44.60862		32.20	17.0391		56.20	17.0391
19.18	44.08508		32.70	16.8101		56.70	16.8101
19.68	43.75134		33.20	15.9806		57.20	15.9806
20.18	43.18852		33.70	15.8805		57.70	15.8805
20.68	42.62692		34.20	16.1635		58.20	16.1635
21.18	41.96217		34.70	16.23		58.70	16.23
21.68	41.64606		35.20	16.4421		59.20	16.4421
22.18	41.41984		35.70	16.695		59.70	16.695
22.68	40.75346		36.22	17.1422		60.22	17.1422
23.18	40.3442		36.70	16.1356		60.70	16.1356
23.68	39.75632		37.20	16.3043		61.20	16.3043
24.18	39.29669		37.70	16.3482		61.70	16.3482

24.68	38.77351		38.20	16.96		62.20	16.96
25.18	38.40058		38.70	16.4885		62.70	16.4885
25.68	37.90177		39.20	16.2343		63.20	16.2343
26.18	37.31978		39.70	15.8227		63.70	15.8227
26.68	36.82401		40.20	15.4197		64.20	15.4197
27.18	36.58686		40.70	15.1093		64.70	15.1093
27.68	36.24672		41.20	14.9897		65.20	14.9897
28.18	35.54634		41.70	14.8594		65.70	14.8594
28.68	35.00751		42.20	14.6993		66.20	14.6993
29.18	34.36883		42.70	14.457		66.70	14.457
29.68	34.20301		43.20	14.3739		67.20	14.3739
30.18	33.77964		43.70	14.1315		67.70	14.1315
30.68	33.53079		44.20	14.5057		68.20	14.5057
31.18	33.31562		44.70	14.2225		68.70	14.2225
31.68	32.73511		45.20	14.4987		69.20	14.4987
32.18	32.2312		46.20	14.1178		70.20	14.1178
32.68	31.57843		46.95	14.1575		70.95	14.1575
33.18	31.61193		47.70	13.6256		71.70	13.6256
33.68	31.25822		48.45	13.4965		72.45	13.4965
34.18	31.07825		49.22	13.2819		73.22	13.2819
34.68	30.67768		49.95	13.1838		73.95	13.1838
35.18	30.2183		50.72	13.2238		74.72	13.2238
35.68	29.63901		51.45	13.3669		75.45	13.3669
36.18	29.5299		52.20	12.8624		76.20	12.8624
36.68	29.39563		52.95	12.7261		76.95	12.7261
37.18	29.14983		53.70	12.6765		77.70	12.6765
37.68	28.30257		54.45	13.4807		78.45	13.4807
38.18	28.10659		55.22	12.9805		79.22	12.9805
38.68	27.82572		55.95	12.657		79.95	12.657
39.18	27.76661		56.70	11.9499		80.70	11.9499
39.68	27.47381		57.45	12.2919		81.45	12.2919
40.18	27.20089		58.20	12.1572		82.20	12.1572
40.68	26.95463		58.95	12.0855		82.95	12.0855
41.18	26.63336		59.72	11.9882		83.72	11.9882
41.68	26.39619		60.45	11.7897		84.45	11.7897
42.18	26.07315		61.20	11.7618		85.20	11.7618
42.68	25.83315		61.95	11.4321		85.95	11.4321
43.18	25.83464		62.70	11.711		86.70	11.711
43.68	25.57429		63.45	11.9585		87.45	11.9585

44.18	25.1771		64.20	12.0081		88.20	12.0081
44.68	24.66187		64.97	11.5568		88.97	11.5568
45.18	24.40085		65.70	11.2141		89.70	11.2141
45.68	24.27127		66.45	11.1097		90.45	11.1097
46.18	24.14556		67.20	10.7502		91.20	10.7502
46.68	23.94873		67.95	10.6924		91.95	10.6924
47.18	23.4803		68.70	10.5041		92.70	10.5041
47.68	23.15393		69.45	10.7421		93.45	10.7421
48.18	23.05137		70.22	10.1262		94.22	10.1262
48.68	22.8344		70.95	9.99754		94.95	9.99754
49.18	22.77515		71.70	10.3099		95.70	10.3099
49.68	22.07786		72.45	10.6961		96.45	10.6961
50.18	22.03812		73.20	10.0481		97.20	10.0481
50.68	21.82247		73.95	9.68444		97.95	9.68444
51.18	21.77008		74.72	9.72216		98.72	9.72216
51.68	21.46977		75.45	10.4055		99.45	10.4055
52.18	20.795		76.22	9.8489		100.22	9.8489
52.68	20.83269		76.95	9.57836		100.95	9.57836
53.18	20.65876		77.70	9.38454		101.70	9.38454
53.68	20.6215		78.45	9.43042		102.45	9.43042
54.18	19.99579		79.20	9.05676		103.20	9.05676
54.68	19.69266		79.97	8.85042		103.97	8.85042
55.18	19.56264		80.70	8.9678		104.70	8.9678
55.68	19.8658		81.45	8.8479		105.45	8.8479
56.18	19.92582		82.20	8.90599		106.20	8.90599
56.68	19.7755		82.95	8.7008		106.95	8.7008
57.18	19.15469		83.70	8.69386		107.70	8.69386
57.68	18.62103		84.45	8.11991		108.45	8.11991
58.18	18.51096		85.22	8.32995		109.22	8.32995
58.68	18.66344		85.95	8.11316		109.95	8.11316
59.18	18.60833		86.70	8.41752		110.70	8.41752
59.68	18.00832		87.45	8.19803		111.45	8.19803
60.18	17.53639		88.20	7.6312		112.20	7.6312
61.20	17.12902		88.95	7.63712		112.95	7.63712
61.93	17.12133		89.72	7.65237		113.72	7.65237
62.70	16.71936		90.45	8.78038		114.45	8.78038
63.43	16.74682		91.22	8.21877		115.22	8.21877
64.18	16.63111		91.95	7.38852		115.95	7.38852
64.93	16.79286		92.70	6.64085		116.70	6.64085

65.68	16.61717		93.45	6.59212		117.45	6.59212
66.43	16.23813		94.20	6.7702		118.20	6.7702
67.18	15.76503		94.97	6.84627		118.97	6.84627
67.93	15.34096		95.70	7.26928		119.70	7.26928
68.68	15.17841		96.47	7.69523		120.47	7.69523
69.45	15.11344		97.20	7.99882		121.20	7.99882
70.18	14.93704		97.95	7.44149		121.95	7.44149
70.93	14.90866		98.70	7.17436		122.70	7.17436
71.68	14.64435		99.45	6.7233		123.45	6.7233
72.43	14.44396		100.22	7.03939		124.22	7.03939
73.18	13.84055		100.95	6.92633		124.95	6.92633
73.93	13.67461		101.72	6.64667		125.72	6.64667
74.68	13.70589		102.45	6.29552		126.45	6.29552
75.45	13.64764		103.20	6.41957		127.20	6.41957
76.18	13.44604		103.95	6.17212		127.95	6.17212
76.95	13.24432		104.70	5.79999		128.70	5.79999
77.68	13.33423		105.47	5.36792		129.47	5.36792
78.43	13.22341		106.65	5.91313		130.65	5.91313
79.18	12.9241		107.65	6.29659		131.65	6.29659
79.93	12.62174		108.65	6.54549		132.65	6.54549
80.68	12.43884		109.65	6.37322		133.65	6.37322
81.43	12.17427		110.65	6.16892		134.65	6.16892
82.18	12.04962		111.65	5.63806		135.65	5.63806
82.95	12.06127		112.65	5.54664		136.65	5.54664
83.68	11.94469		113.65	5.58752		137.65	5.58752
84.43	11.73083		114.65	5.95151		138.65	5.95151
85.18	11.49945		115.65	5.81916		139.65	5.81916
85.93	11.30998		116.65	5.99351		140.65	5.99351
86.68	11.11708		117.65	5.72076		141.65	5.72076
87.43	10.93533		118.65	5.75346		142.65	5.75346
88.20	10.8976		119.65	5.72794		143.65	5.72794
88.93	10.92704		120.65	5.40791		144.65	5.40791
89.68	10.81742		121.65	4.7471		145.65	4.7471
90.43	10.72819		122.65	4.35101		146.65	4.35101
91.18	10.53566		123.65	4.5485		147.65	4.5485
91.93	10.16114		124.65	4.50109		148.65	4.50109
92.68	9.815984		125.65	4.46808		149.65	4.46808
93.43	9.651654		126.65	3.89832		150.65	3.89832
94.18	9.963531		127.65	3.96661		151.65	3.96661

94.95	9.811061		128.65	4.10772		152.65	4.10772
95.68	9.565623		129.65	4.66576		153.65	4.66576
96.43	9.445119		130.65	4.51432		154.65	4.51432
97.18	9.726034		131.65	3.8215		155.65	3.8215
97.93	9.825558		132.65	3.68559		156.65	3.68559
98.68	9.462366		133.65	4.14486		157.65	4.14486
99.43	9.247626		134.65	3.96552		158.65	3.96552
100.20	9.0021		135.65	3.83735		159.65	3.83735
100.93	8.809837		136.65	3.14381		160.65	3.14381
101.68	8.640573		137.65	3.5711		161.65	3.5711
102.43	8.41275		138.65	3.50954		162.65	3.50954
103.18	8.278959		139.65	3.54228		163.65	3.54228
103.93	7.967895		140.65	3.55066		164.65	3.55066
104.68	7.983167		141.65	3.71873		165.65	3.71873
105.43	8.099345		142.65	3.51343		166.65	3.51343
106.20	8.232094		143.65	3.52732		167.65	3.52732
106.93	8.149775		144.65	3.20222		168.65	3.20222
107.68	7.850811		145.65	3.35762		169.65	3.35762
108.43	7.766978		146.65	3.16816		170.65	3.16816
109.18	7.665738		147.65	2.77572		171.65	2.77572
109.93	7.694889		148.65	2.94322		172.65	2.94322
110.68	7.537917		149.65	2.59475		173.65	2.59475
111.45	7.270017		150.65	2.48115		174.65	2.48115
112.18	7.167221		151.65	2.58094		175.65	2.58094
112.93	7.040692		152.65	2.73074		176.65	2.73074
113.68	7.123744		153.65	3.11592		177.65	3.11592
114.43	7.166118		154.65	2.63104		178.65	2.63104
115.18	7.2559		155.65	2.48313		179.65	2.48313
115.93	6.9072		156.65	2.66241		180.65	2.66241
116.68	6.634695		157.65	3.00782		181.65	3.00782
117.45	5.968424		158.65	3.35399		182.65	3.35399
			159.65	2.90575		183.65	2.90575
			160.65	3.10279		184.65	3.10279
			161.65	2.79919		185.65	2.79919
			162.65	3.09533		186.65	3.09533
			163.65	2.67076		187.65	2.67076
			164.65	2.68974		188.65	2.68974
			165.65	2.53682		189.65	2.53682
			166.65	2.41612		190.65	2.41612

			167.65	2.34367		191.65	2.34367
			168.65	2.56102		192.65	2.56102
			169.65	2.41236		193.65	2.41236
			170.65	2.94002		194.65	2.94002
			171.65	2.75938		195.65	2.75938
			172.65	3.19571		196.65	3.19571
			173.65	2.62148		197.65	2.62148
			174.65	2.12251		198.65	2.12251
			175.65	1.87806		199.65	1.87806
			176.65	1.79963		200.65	1.79963
			177.65	1.9982		201.65	1.9982
			178.65	1.85555		202.65	1.85555
			179.65	1.6983		203.65	1.6983
			180.65	2.03067		204.65	2.03067
			181.65	2.28273		205.65	2.28273
			182.65	2.15155		206.65	2.15155
			183.65	1.66813		207.65	1.66813
			184.65	1.45757		208.65	1.45757
			185.65	1.63361		209.65	1.63361
			186.65	1.58651		210.65	1.58651
			187.65	1.37549		211.65	1.37549
			188.65	1.15456		212.65	1.15456
			189.65	1.50867		213.65	1.50867
			190.65	1.72774		214.65	1.72774
			191.65	1.8028		215.65	1.8028
			192.65	1.55332		216.65	1.55332
			193.65	1.26214		217.65	1.26214
			194.65	1.56086		218.65	1.56086
			195.65	1.34349		219.65	1.34349
			196.65	1.56342		220.65	1.56342
			197.65	1.1998		221.65	1.1998
			198.65	1.3832		222.65	1.3832
			199.65	1.03193		223.65	1.03193
			200.65	1.19707		224.65	1.19707
			201.65	1.08354		225.65	1.08354
			202.65	1.55375		226.65	1.55375
			203.65	1.40528		227.65	1.40528
			204.65	1.29792		228.65	1.29792
			205.65	1.58544		229.65	1.58544

			206.65	0.43667		230.65	0.43667
			207.65	1.60545		231.65	1.60545
			208.65	0.06244		232.65	0.06244
			209.65	0.51512		233.65	0.51512
			210.65	0.74899		234.65	0.74899
			211.65	1.10981		235.65	1.10981
			212.65	0.41354		236.65	0.41354
			213.65	-0.0899		237.65	-0.0899
			214.65	1.58102		238.65	1.58102
			215.65	0.46075		239.65	0.46075
			216.65	0.20386		240.65	0.20386
			217.65	1.08245		241.65	1.08245
			218.65	0.31302		242.65	0.31302
			219.65	0.30386		243.65	0.30386
			220.65	0.21968		244.65	0.21968
			221.65	0.47751		245.65	0.47751
			222.65	0.00342		246.65	0.00342

Figure S10

1 equiv Ph_3SiCl & NaBArF			1.25 equiv Ph_3SiCl & NaBArF	
$\Sigma[Ph3SiCl]^{0.35}$ Δt (min)				
Normalized Time (min)	**[Product] mM**		**Normalized Time (min)**	**[Product] mM**
0.00	1.73		0.00	6.24
1.13	7.12		2.38	9.99
2.24	9.46		3.57	12.81
3.34	11.64		4.76	15.20
4.42	14.20		5.93	16.64
5.49	16.62		7.09	18.88
6.55	16.57		8.25	19.69
7.60	19.30		9.39	22.65
8.64	21.11		10.53	24.15
9.67	25.15		11.65	25.55
10.67	25.23		12.77	27.69
11.67	28.44		13.88	29.38
12.66	27.74		14.98	30.40
13.65	28.44		16.07	32.14
14.63	29.72		17.15	33.43
15.60	33.48		18.23	34.93
16.55	33.33		19.29	35.86
17.49	35.29		20.35	37.83
18.42	36.64		21.40	38.44
19.35	36.64		22.45	39.73
20.28	37.21		23.49	40.66
21.19	39.13		24.52	41.30
22.08	42.72		25.55	42.14
22.97	41.11		26.57	43.14
23.86	41.56		27.59	44.44
24.74	42.51		28.60	44.58
25.63	41.90		29.60	46.09
26.50	44.38		30.60	46.72
27.36	44.39		31.60	47.80
28.22	46.49		32.58	48.15
29.06	46.88		33.57	48.61
29.89	48.85		34.55	50.41
30.71	50.06		35.51	51.03
31.53	48.86		36.48	51.23
32.35	49.95		37.44	51.77
33.16	49.54		38.40	53.08

33.97	50.62		39.35	53.12
34.77	52.31		40.30	53.75
35.55	54.20		41.24	54.45
36.32	52.82		42.18	55.11
37.11	52.63		43.12	55.94
37.89	52.94		44.05	55.61
38.67	53.77		44.98	56.39
39.43	55.34		45.90	57.34
40.19	55.62		46.82	57.75
40.93	56.93		47.74	57.47
41.67	56.46		48.65	58.43
42.41	56.58		49.56	58.89
43.16	56.67		50.47	59.07
43.90	55.67		51.37	59.19
44.65	56.76		52.28	58.24
45.37	59.97		53.19	59.50
46.08	58.19		54.09	60.31
46.81	57.30		54.99	60.16
47.53	59.43		55.88	61.05
48.24	59.44		56.77	60.79
48.95	58.17		57.66	61.13
49.67	58.53		58.55	61.27
50.39	58.67		59.44	61.38
51.10	59.10		60.32	62.03
51.81	59.15		61.20	62.07
52.51	61.27		62.08	62.27
53.21	59.17		62.97	61.78
53.92	59.03		63.85	62.30
54.62	59.91		64.73	62.58
55.32	60.50		65.60	62.92
56.01	61.61		66.47	63.51
56.69	61.17		67.34	63.82
57.38	60.15		68.21	63.80
58.06	63.41		69.07	64.30
58.72	61.49		69.93	64.07
59.41	59.79		70.80	63.91
60.11	60.69		71.67	63.67
60.79	62.39		72.53	64.77
61.46	61.74		73.39	64.34
62.14	61.84		74.25	64.69
62.84	57.56		75.11	64.92

63.53	63.64		75.96	64.87
64.19	62.56		76.82	65.42
64.86	62.05		77.67	66.28
65.54	60.30		78.51	65.54
66.21	64.43		79.37	65.54
66.87	61.90			
67.55	60.95			
68.23	61.70			
68.91	62.14			
69.58	61.09			
70.28	60.19			
70.96	61.43			
71.64	61.80			
72.31	62.44			
72.97	64.14			
73.61	63.89			
74.26	63.46			
74.91	64.22			
75.55	64.36			
76.19	63.44			
76.84	63.65			

Figure S11

1 equiv Ph_3SiCl and 5			1.5 equiv Ph3SiCl and 5	
[ROH]	**[Rate/[SiCl]$^{1.2}$**		**[ROH]**	**[Rate/[SiCl]$^{1.2}$**
61.51	0.076130655		62.91242	0.083024853
61.15	0.075250416		61.40798	0.081402963
59.95	0.075614992		60.26132	0.079483654
59.68	0.074606939		58.54696	0.078168768
57.75	0.076132855		57.30236	0.076449367
56.91	0.076001826		55.87179	0.074961078
56.94	0.074481738		55.30549	0.072706798
56.92	0.073064279		53.9978	0.071207857
55.39	0.074027204		52.58066	0.06986067
56.09	0.071473548		52.4209	0.067420259
55.17	0.071461073		50.56263	0.066570185
54.40	0.071221775		49.95401	0.064651282
54.07	0.070299875		49.51364	0.062652706
54.05	0.068897918		47.78307	0.061822447
53.43	0.068432052		47.67525	0.059656401
53.04	0.067618579		46.71039	0.058274835
52.79	0.066594096		45.68142	0.056996221
52.78	0.065231197		45.21533	0.05531407
51.83	0.065258828		44.51372	0.053878892
51.83	0.063895428		43.9644	0.052380681
51.26	0.06337009		43.95743	0.05053557
50.79	0.062708018		43.13066	0.049360889
50.15	0.062315126		42.61503	0.048010646
50.22	0.060859481		41.6522	0.047029626
48.86	0.061549262		41.47065	0.045549471
49.37	0.059463087		41.13606	0.044234987
48.01	0.060149921		39.80025	0.043640896
48.65	0.05788935		39.38826	0.042471641
48.52	0.05679889		39.09878	0.0412747
47.98	0.056302716		38.70604	0.040195881
47.18	0.056170854		38.00089	0.03935917
46.67	0.055643171		37.61271	0.038369999
47.05	0.053868816		36.57373	0.037819543
45.89	0.054262721		36.54092	0.036703406
45.79	0.053172951		36.0049	0.035932328
45.48	0.052394556		35.77762	0.035024597

44.62	0.052402588		36.20722	0.033799363
44.38	0.051549733		35.38577	0.033308599
44.04	0.05084582		35.39274	0.032407648
43.69	0.050161495		34.42002	0.0320659
43.00	0.049970224		34.34907	0.031282834
43.25	0.048490481		33.9984	0.030683584
42.69	0.048129857		33.42323	0.030232624
42.17	0.047721014		33.79557	0.029341539
42.57	0.046114195		33.07407	0.029026516
41.94	0.045867787		33.30148	0.028282212
42.00	0.044745113		32.70135	0.027966571
41.47	0.044403913		32.24362	0.027611145
41.62	0.043196326		32.35131	0.02702007
40.12	0.044117064		31.59459	0.026857334
40.22	0.042984556		31.70025	0.02632399
40.61	0.04153768		31.09164	0.026142002
40.09	0.041224327		31.42192	0.025562552
40.22	0.040143113		30.97597	0.025353849
40.44	0.038989148		30.73818	0.025075566
39.77	0.038894744		30.60173	0.024775007
39.51	0.038332407		30.41296	0.024518373
39.21	0.037826172		29.93497	0.02440591
39.22	0.036987445		30.02758	0.02406768
38.71	0.036745096		29.56529	0.023984394
38.67	0.03599267		29.05904	0.023937136
38.92	0.034952154		29.46419	0.023519636
38.42	0.034742867		29.19928	0.023401445
37.82	0.034654936		28.54911	0.02345985
37.87	0.033880072		28.93361	0.023098417
37.32	0.033757574		28.88117	0.022934182
37.43	0.032957173		28.57116	0.022888605
37.37	0.032346331		28.41495	0.022791336
37.25	0.031826236		28.08986	0.022774743
37.61	0.030832161		27.65545	0.022814251
37.61	0.030232692		27.66292	0.022679893
36.61	0.030629414		27.66495	0.02255726
36.68	0.029979418		27.6875	0.02243496
36.03	0.030069778		27.52078	0.022398213
36.90	0.028682778		27.08497	0.022479686
36.47	0.028567304		27.07166	0.022393423
36.12	0.028396729		26.93256	0.022365273

35.81	0.028201214		26.17521	0.022601215
35.50	0.028013307		26.32318	0.022463123
35.54	0.027520476		26.53754	0.022302877
35.98	0.026678886		26.24894	0.02235621
35.65	0.026552048		26.52373	0.022179097
35.80	0.026017952		25.98809	0.022341794
35.03	0.026313917		26.34396	0.022136517
35.12	0.025855945		26.29417	0.02210235
34.67	0.025888975		25.73307	0.022282763
35.22	0.02506478		26.27314	0.022007131
34.67	0.025204021		26.10008	0.022028425
35.27	0.02438223		25.99063	0.022024469
34.62	0.024626778		25.63602	0.02212295
			25.46512	0.02214576
			25.87014	0.021929068
			24.93758	0.022270205
			24.81343	0.022273102

Figure S12

0.75 equiv $Ph_2MeSiCl$			1 equiv Ph2MeSiCl	
$\Sigma[Ph3SiCl]^{1.25}\Delta t$ (min)				
Normalized Time (min)	**[Product] mM**		**Normalized Time (min)**	**[Product] mM**
0.00	0.00		**0.00**	0.00
25.16	2.57		39.56	0.69
56.21	6.21		85.76	4.43
84.63	10.51		129.31	8.17
110.79	13.09		169.00	15.37
135.53	14.86		202.17	20.16
159.05	16.91		237.96	21.21
181.38	18.60		269.44	26.30
202.66	20.23		298.51	28.43
223.04	21.46		326.34	30.06
242.44	23.42		352.31	34.12
260.73	25.02		376.47	35.68
279.27	26.40		398.06	37.30
294.73	27.73		421.61	39.01
310.37	29.47		442.56	40.85
325.19	30.48		462.43	42.48
339.39	31.59		481.28	44.16
352.94	32.67		497.68	46.62
365.84	33.85		515.51	47.00
378.15	34.74		531.47	45.35
389.88	35.83		549.02	49.15
401.04	36.77		564.79	47.65
411.63	37.84		579.83	51.55
421.71	38.62		593.71	51.61
431.36	39.39		607.36	52.30
440.58	40.20		621.07	51.45
449.48	40.54		634.10	54.60
458.23	40.75		645.55	54.13
466.81	41.18		658.57	54.76
475.04	42.06		669.65	55.36
483.20	41.43		681.91	56.06
491.11	42.98			
498.55	43.21			
506.01	42.90			
513.03	44.87			
519.54	44.88			

526.01	45.02			
532.18	46.06			
537.87	46.88			
543.19	47.58			
548.23	47.97			
553.31	47.44			
558.11	49.07			
562.80	47.91			
567.38	49.53			
571.66	49.14			
575.82	50.05			
579.86	49.62			
583.95	49.88			
588.07	49.45			
592.06	50.42			
595.83	50.41			
599.42	51.17			
602.52	52.51			
605.45	51.94			
608.38	52.48			
611.27	52.14			
614.64	50.39			
617.99	52.22			
620.76	52.97			
623.24	53.47			
625.57	53.69			
628.09	52.61			
630.60	53.71			
632.77	54.16			
634.93	53.78			
637.10	54.14			
639.23	53.95			
641.10	55.33			
642.80	54.78			
644.83	53.80			
646.64	55.79			
648.25	54.74			
649.85	55.89			
651.39	55.00			
653.16	54.78			
654.91	55.09			

656.68	54.67			
658.37	55.50			
659.75	56.23			
661.02	55.98			
662.30	56.23			
663.62	55.78			
665.08	55.51			
666.32	56.88			
667.38	56.43			
668.26	57.87			
669.04	56.96			
669.87	57.64			

Figure S13

0.8 equiv $PhMe_2SiCl$			1 equiv $PhMe_2SiCl$	
$\Sigma[Ph3SiCl]^{1.2}\Delta t$ (min)				
Normalized Time (min)	**[Product] mM**		**Normalized Time (min)**	**[Product] mM**
0.00	9.06		35.15	29.94
28.33	22.78		61.68	35.31
50.02	29.61		86.92	39.69
68.19	34.10		109.27	44.31
83.82	37.97		129.34	46.95
97.38	41.14		148.12	48.49
109.14	44.19		166.80	51.10
109.14	45.57		182.38	51.16
128.88	46.50		199.63	52.84
138.37	46.97		214.02	53.69
147.27	48.63		228.81	54.95
155.69	48.73		243.06	55.50
163.74	50.02		256.86	56.46
171.28	50.65		271.42	56.05
178.66	50.62		284.26	56.08
185.84	51.41		298.79	56.52
192.93	51.00		311.00	57.95
199.84	52.06		323.80	57.48
206.41	52.31		336.54	58.18
213.06	51.75		349.12	57.98526
219.89	51.65		362.52	58.28939
226.77	51.51		374.33	57.65226
233.31	52.98		387.78	58.43873
			399.44	58.04634
			411.92	58.50402
			424.03	59.33447
			436.24	58.13581
			449.21	59.50311
			460.28	59.20883
			472.86	59.72435
			483.95	58.89754
			496.03	59.06263
			507.88	59.65058
			519.60	59.54369
			532.13	59.58395
			543.08	59.55723

			555.77	59.02589
			567.36	57.69774