

Supporting Information for:

Cooperative Hydrogen-bonding Effects in Silanediol Catalysis

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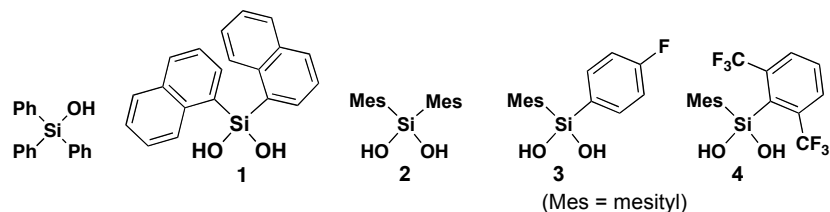
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I. General Information

Instruments and Analyses. All nuclear magnetic resonance (NMR) spectra were obtained on Varian Mercury Plus 300 (300 MHz for ^1H ; 75 MHz for ^{13}C ; and 282 MHz for ^{19}F), Varian Inova 400 (400 MHz for ^1H ; 100 MHz for ^{13}C), and/or Varian VNMRS 600 (600 MHz for ^1H ; 119 MHz for ^{29}Si) at room temperature. Chemical shifts were reported in parts per million (δ scale), and referenced according to the following standards: tetramethylsilane internal standard for ^1H signals in chloroform, benzene residual solvent (δ 7.16) for ^1H signals in benzene, deuterated chloroform, or benzene carbon resonances (middle peak is δ 77.1 or δ 128.1, respectively) for $^{13}\text{C}\{^1\text{H}\}$ signals, trifluoromethylbenzene external standard (peak is δ -62.7 in C_6D_6) for $^{19}\text{F}\{^1\text{H}\}$ signals, and tetramethylsilane external standard in CDCl_3 for $^{29}\text{Si}\{^1\text{H}\}$ signals. Coupling constants were reported in Hertz (Hz) and multiplicities were reported as follows: singlet (s), broad singlet (br s), doublet (d), triplet (t), quartet (q), octet (o), and multiplet (m).

Materials and Purification. Dichloromethane (DCM), hexane, ethyl acetate (EtOAc), toluene (PhMe), and diethyl ether (Et_2O) were obtained from EMD Chemicals. Magnesium turnings, 1,2-dibromoethane, palladium on carbon (5 wt%), anhydrous magnesium sulfate, boron trichloride (1.0 M in DCM), and 2-mesitylmagnesium bromide solution (1.0 M in Et_2O) were acquired from Sigma Aldrich. Indole, *n*-butyllithium (1.6 M in hexanes), 1,3-bis(trifluoromethyl)benzene, lithium aluminum hydride (4.0 M in Et_2O), and trichlorosilane were purchased from Acros Organics. *Trans*- β -nitrostyrene was purchased from Alfa-Aesar. 1-Bromonaphthalene was obtained from Eastman Kodak Company. All chemicals were used as purchased, without further purification. *n*-Butyllithium was titrated before use with diphenylacetic acid to obtain accurate concentration for reactions. Reactions were analyzed by thin layer chromatography (TLC) on EMD glass plates that were pre-coated with silica gel 60 F_{254} , and the reactions were purified by column chromatography using Acros silica gel 60 Å (0.035-0.070 mm) or Sigma Aldrich silica gel 150 Å grade 62 (60-200 mesh).

II. Preparation of Silanols and Silanediol Catalysts



General Procedures and Physical State of Silanediol Catalysts

Triphenylsilylanol and silanediol catalysts **1-4** were synthesized according to procedures previously reported in the literature, which ensure access to pure and dry silanediols that do not contain trace HCl.^{1,2,3,4,5} Silanediol **1** was synthesized by two different methods (A and B, see

¹ Tran, N. T.; Min, T.; Franz, A. K. *Chem. Eur. J.* **2011**, *17*, 9897-9900.

² Rozga-Wijas; K.; Chojnowski, J. *Macromolecules*. **1996**, *29*, 2711-2721.

³ Simons, R. S.; Haubrich, S. T.; Mork, B. V.; Niemeyer, M.; Power, P. P. *Main Group Chem.* **1998**, *2*, 275-283.

procedures below). Method A is used to prepare silanediol **1** from the di-(1-naphthyl)silane precursor, and method B is an alternate, shorter procedure to synthesize di-(1-naphthyl)silane. Silanediol **1** was evaluated as a catalyst in reactions in powdered, microcrystalline and macrocrystalline form. Triphenylsilanol and silanediol **2** were evaluated as catalysts in reactions in *microcrystalline* as well as *macrocrystalline* forms. Herein, *microcrystalline* is defined as needle-shaped crystal with width and length sizes of < 0.1 mm and *macrocrystalline* is defined as block-shaped crystal with dimensions > 0.2 mm. The microcrystalline form was obtained by slow evaporation from dichloromethane and the macrocrystalline form was obtained by growing crystals from slow evaporation from benzene. Silanediol catalyst **4** is a viscous film, and this form was used for all Michael reactions and binding studies. Spectral data for all silanediols is consistent with literature data.¹ Copies of all ¹H spectra are included to confirm purity.

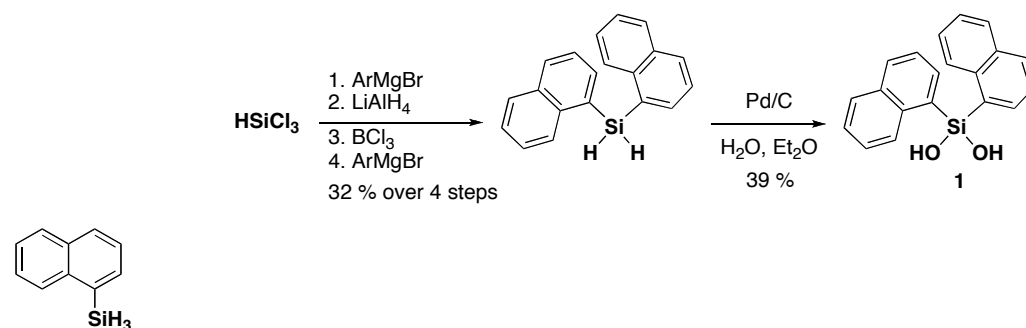
Spectral data for Ph₃SiOH: ¹H NMR (400 MHz, C₆D₆): δ 7.63 (dt, *J* = 6.4, 1.6 Hz, 6H), 7.17 (tt, *J* = 7.2, 1.6 Hz, 3H), 7.11 (m, 6H), 3.45 (s, 3H).

Spectral data for dimesitylsilanediol (**2**): ¹H NMR (400 MHz, CDCl₃): ¹H NMR (600 MHz, CDCl₃) δ 6.72 (s, 4H), 3.41 (s, 2H), 2.30 (s, 12H), 2.20 (s, 6H).

Spectral data for 4-fluorophenylmesitylsilanediol (**3**): ¹H NMR (600 MHz, CDCl₃) δ 7.51 (dd, *J* = 9.0, 6.6 Hz, 2H), 6.96 (dd, *J* = 9.0, 8.4 Hz, 2H), 6.81 (s, 2H), 3.88 (br s, 2H), 2.35 (s, 6H), 2.29 (s, 3H).

Spectral data for (2,6-bis-(trifluoromethyl)phenyl)(mesityl)silanediol (**4**): ¹H NMR (400 MHz, C₆D₆): δ 7.91 (br d, *J* = 8.0 Hz, 1H), (br s, 1H), 7.24 (br d, *J* = 8.0 Hz, 1H), 6.70 (s, 2H), 3.49 (s, 2H), 2.32 (s, 6H), 2.09 (s, 3H).

Procedure for the Synthesis of Silanediol **1** (Method A)



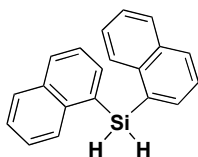
1-Naphthylsilane.⁶ An oven-dried, round-bottom flask was charged with Mg (0.969 g, 39.88 mmol, 2.01 equiv), anhydrous diethyl ether (20 mL), and a stirbar. After purging with argon for 15 min, 1,2-dibromoethane (0.02 mL, 0.23 mmol, 0.01 equiv) was added and the reaction was allowed to stir at room temperature until it became a faint cloudy mixture. At which point, 1-bromonaphthalene (2.78 mL, 19.87 mmol, 1.00 equiv) was added and the reaction was allowed to stir for 2 h at reflux. Upon cooling to room temperature, the aryl Grignard reagent was transferred by syringe to a round-bottom flask containing HSiCl₃ (2.05 mL, 20.31 mmol, 1.02

⁴ Minge, O.; Nogai, S.; Schmidbaur, H. *Z. Naturforsch., B: Chem. Sci.* **2004**, *59*, 153-160.

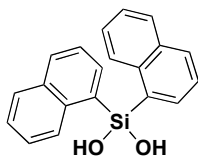
⁵ Söldner, M.; Sandor, M.; Schier, A.; Schmidbaur, H. *Chem. Ber./Recueil.* **1997**, *130*, 1671-1676.

⁶ Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Angew. Chem.* **1986**, *98*, 472-473.

equiv) in anhydrous diethyl ether (20 mL). After stirring at room temperature for 1 h, the reaction was cooled to -78 °C and LiAlH₄ (4.0 M in Et₂O, 15.0 mL, 60.0 mmol, 3.02 equiv) was added dropwise. The reaction was allowed to stir while warming up to room temperature over 2 h. Then the reaction was cooled to -78 °C before the addition of 10 mL of Rochelle's salt (NaKtartrate, sat. aq.) and the resulting mixture was filtered over celite and washed with diethyl ether (5 x 15 mL). The filtrate was concentrated *in vacuo*, and purification by distillation to afford 1-naphthylsilane (1.939 g, 62 %) as a colorless oil. Spectra matched the previously reported values. ¹H NMR (600 MHz, CDCl₃): δ 7.92 (br d, *J* = 8.4 Hz, 2H), 7.77 (m, 4H), 7.44 (m, 1H), 7.41 (m, 1H), 7.36 (dd, *J* = 8.4, 7.2 Hz, 1H), 5.56 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 137.5, 136.9, 133.1, 131.1, 129.0, 128.0, 127.4, 126.6, 126.1, 125.4; ²⁹Si NMR (119 MHz, CDCl₃): δ -61.6.



Di-(1-naphthyl)silane.⁷ 1-Naphthylsilane (1.939 g, 12.25 mmol, 1.00 equiv) was dissolved in hexanes (15 mL) and the resulting solution was purged with argon. Under positive argon pressure, BCl₃ (1.0 M in DCM, 12.25 mL, 12.25 mmol, 1.00 equiv) was added dropwise. After 18 h, the solvent was removed *in vacuo* and the chloro(1-naphthyl)silane was transferred into another round bottom flask using anhydrous diethyl ether (20 mL). After purging with argon for 15 min and cooling to 0 °C, 1-naphthylmagnesium bromide was added dropwise. [Prepared according to the procedure described above using Mg (0.628 g, 25.82 mmol, 2.11 equiv) and 1-bromonaphthalene (1.80 mL, 12.87 mmol, 1.05 equiv).] After stirring for 3 h at room temperature, the reaction was quenched with 10 mL of sat. aq. NaHCO₃. The aqueous layer was extracted with ethyl acetate (3 x 5 mL), and the combined organic layer was washed with brine (2 x 5 mL), dried over MgSO₄, filtered, and concentrated *in vacuo* to give a pale yellow film. The crude product was purified using column chromatography with hexanes to yield 1.792 g of silane (51 %) as a white crystalline solid. ¹H NMR (600 MHz, CDCl₃): δ 8.08 (m, 2H), 7.83 (br d, *J* = 8.4 Hz, 2H), 7.78 (m, 2H), 7.71 (dd, *J* = 6.6, 1.2 Hz, 2H), 7.39 (m, 4H), 7.32 (dd, *J* = 6.6, 7.8 Hz, 2H), 5.56 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): 137.6, 137.0, 133.3, 131.1, 129.8, 129.0, 128.1, 126.5, 126.0, 125.5; ²⁹Si NMR (119 MHz, CDCl₃): δ -38.7.



Di-(1-naphthyl)silane-1,1-diol (1).^{8,9} To a mixture containing Pd/C (5 wt%, 0.662 g, 0.31 mmol, 0.05 equiv), deionized water (0.57 mL, 32 mmol, 5.0 equiv) and anhydrous diethyl ether (10 mL), was added di-(1-naphthyl)silane (1.792 g, 6.30 mmol, 1.0 equiv). The hydrogen gas that formed

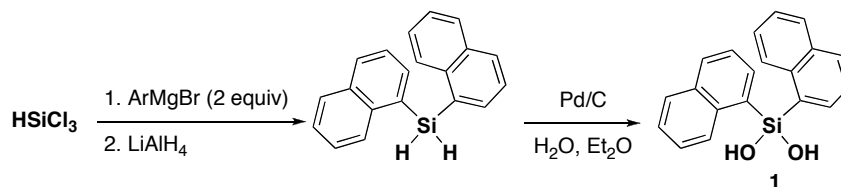
⁷ Tour, J. M.; John, J. A.; Stephens, E. B. *J. Organomet. Chem.* **1992**, 429, 301-310.

⁸ Kondo, S.-I.; Harada, T.; Tanaka, R.; Unno, M. *Org. Lett.* **2006**, 8, 4621-4624.

⁹ Schafer, A. G.; Wieting, J. M.; Mattson, A. E. *Org. Lett.* **2011**, 13, 5228-5231.

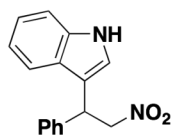
was allowed to escape through a vent needle. After stirring for 18 h at room temperature, the Pd/C was removed by filtration and the filtrate was dried over MgSO₄. The crude product was purified by column chromatography (10:1 hexanes/diethyl ether) to afford di-(1-naphthyl)silanediol (**1**) as a white powder (0.782 g, 39 %). Spectra matched the previously reported values⁹ and showed that the silanediol did not contain any water or trace HCl in the sample, which is possible when preparing the catalyst directly from the silyl chloride. ¹H NMR (400 MHz, CDCl₃): δ 8.31 (d, *J* = 8.0 Hz, 2H), 7.96 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.47-7.37 (m, 6H), 3.34 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): 136.8, 135.8, 133.5, 132.8, 131.5, 129.0, 128.5, 126.6, 125.9, 125.3; ²⁹Si NMR (119 MHz, CDCl₃): δ -25.2. Microcrystalline and macrocrystalline forms of silanediol **1** were grown by dissolving the silanediol in either dichloromethane or a 1:1 mixture of dichloromethane/diethyl ether, and allowing the solvent to slowly evaporate. A suitable crystal of the latter was used for X-ray structure analysis. Co-crystals of silanediol **1** with diethyl ether were grown from slow evaporation of the silanediol in a 1:10 mixture of dichloromethane/diethyl ether solvents.

Procedure for the Synthesis of Silanediol **1** (Method B)



Di-(1-naphthyl)silanediol (1**).**^{8,9} An alternate procedure was used for the di-(1-naphthyl)silane and then hydrolysis was performed using the same procedure as described above in Method A. 1-Bromonaphthalene (1.49 mL, 10 mmol, 2 equiv) and magnesium (485 mg, 10 mmol, 2 equiv) were added to an Ar purged, oven dried round-bottom flask. The mixture was diluted with 20 mL anhydrous Et₂O and heated at reflux for 3 h. Then the reaction was allowed to cool to room temperature and transferred to a cooled (-78 °C), Ar purged solution of trichlorosilane (0.5 mL, 5 mmol, 1 equiv) in Et₂O (50 mL). The mixture was allowed to warm to room temperature over 12 h. The solution was then cooled to -78 °C and a solution of lithium aluminum hydride solution (4.0 M in Et₂O, 1.25 mL, 5 mmol, 1 equiv) was added dropwise. The solution was allowed to warm to room temperature. The reaction was once again cooled to -78 °C and quenched with Rochelle's salt (NaKtartrate, sat. aq.), filtered over celite, and washed with Et₂O (5 x 15 mL). The product was concentrated *in vacuo*. Hydrolysis to the silanediol was carried out using Pd/C and water according to the procedure described above.

III. Michael Additions with *trans*- β -Nitrostyrene



3-(2-nitro-1-phenylethyl)-1H-indole (9). *trans*- β -Nitrostyrene (56 mg, 0.375 mmol, 1 equiv), catalyst (0.075 mmol, 20 mol %) and 1.0 mL of DCM were added to a vial containing a stirbar and stirred at room temperature. After 10 min, indole **7** (67 mg, 0.563 mmol, 1.5 equiv) was added, immediately followed by an additional 0.1 mL of anhydrous DCM. The reaction was stirred at room temperature for 24 h and then the product was purified by loading directly onto silica gel for flash chromatography (5% to 20% EtOAc/hexanes) to give product (see Table S1 for yields and replicates of reactions performed). As silica gel can also promote formation of the product, it is important to load on to silica gel and purify immediately to avoid any effect on product yield and get accurate comparisons of catalytic activity. Spectral data are consistent with literature data.¹⁰ Solution phase reactions were performed with two or more replicates and an average of the yields was reported (Table S1).¹¹ Spectral data for **9**: ¹H NMR (400 MHz, CDCl₃) δ 7.98 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.14-7.28 (m, 7H), 7.05 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 5.15 (t, *J* = 8.0 Hz, 1H), 5.00 (dd, *J* = 12.5, 8.0 Hz, 1H), 4.88 (dd, *J* = 12.5, 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.5, 136.7, 129.2, 128.0, 127.8, 126.3, 122.9, 121.9, 120.2, 119.2, 114.5, 111.7, 79.8, 41.8.

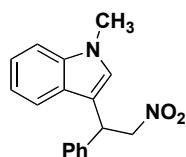
Table S1. Yields with standard deviation for indole addition to *trans*- β -nitrostyrene (**Table 1**)

entry	catalyst	replicates	yield in DCM (%)	average yield with std dev (%)
1	none	2	12, 8	10.0 \pm 2.0
2	Ph ₃ SiOH	3	11, 12, 8	10.3 \pm 2.1
3	Ph ₂ Si(OH) ₂	3	13, 25	19.0 \pm 8.5
4	1	4	40, 40, 25, 25	32.5 \pm 8.7
5	2	2	45, 35	40.0 \pm 7.1
6	3	2	75, 61	68.0 \pm 9.9
7	4	2	92, 91	91.5 \pm 0.7
8	silica gel	2	83, 99	91 \pm 11.3

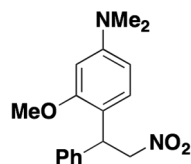
Reactions were performed according to the procedure described above and purified directly on silica gel for flash chromatography (5% to 20% EtOAc/hexanes).

¹⁰ Lin, C.; Hsu, J.; Sastry, M. N. V.; Fang, H.; Tu, Z.; Liu, J.-T.; Ching-Fa, Y. *Tetrahedron* **2005**, *61*, 11751-11757.

¹¹ Ganesh, M.; Seidel, D. *J. Am. Chem. Soc.* **2008**, *130*, 16464-16465.



1-Methyl-3-(2-nitro-1-phenylethyl)-indole. *trans*- β -Nitrostyrene (56 mg, 0.375 mmol, 1 equiv), silanediol **4** (0.075 mmol, 20 mol %), and 0.1 mL of anhydrous DCM was added to a vial containing a stirbar and stirred at room temperature. After 10 min, 1-methylindole (67 mg, 0.563 mmol, 1.5 equiv) was added immediately followed by 0.1 mL of anhydrous DCM. The reaction was stirred at room temperature for 24 h and then the product was purified by loading directly onto silica gel for flash chromatography (5% to 20% EtOAc/Hexanes) to give product in 99% yield. As silica gel can also promote this reaction, it is important to load on to silica gel and purify immediately to avoid any effect on product yield. Spectral data are consistent with literature data.¹² Spectral data: ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.18-7.33 (m, 7H), 7.05 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.82 (s, 1H), 5.15 (t, *J* = 8.0 Hz, 1H), 5.00 (dd, *J* = 12.5, 8.0 Hz, 1H), 4.88 (dd, *J* = 12.5, 8.0 Hz, 1H), 3.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 139.7, 137.5, 129.2, 128.0, 127.8, 126.8, 126.6, 122.5, 119.7, 119.2, 113.0, 109.8, 79.8, 41.8, 33.0.



3-Methoxy-*N,N*-dimethyl-4-(2-nitro-1-phenylethyl)aniline (11).¹³ *trans*- β -Nitrostyrene (56 mg, 0.375 mmol, 1 equiv), catalyst (0.075 mmol, 20 mol %), and 0.2 mL of anhydrous DCM were added to a vial containing a stirbar and stirred at room temperature. After 10 min, *N,N*-dimethyl-*m*-anisidine (82 μ L, 0.563 mmol, 1.5 equiv) was added immediately followed by 0.1 mL of anhydrous DCM. The reaction was stirred at room temperature for either 24 or 48 h and then the product was purified by loading directly onto silica gel for flash chromatography (15% EtOAc/hexanes) to give product (see Table S2 for yields and replicates of reactions performed). Solution phase reactions were performed with two or more replicates and an average of the yields was reported (Table S2). All solution phase yields were an average of two or more replicates. Spectral data are consistent with literature data.¹⁴ ¹H NMR (400 MHz, CDCl₃): δ 7.30-7.23 (m, 4H), 7.23-7.16 (m, 1H), 6.85 (d, *J* = 9.2 Hz, 1H), 6.24-6.19 (m, 2H), 5.13 (dd, *J* = 9.2, 7.2 Hz, 1H), 5.00-4.87 (m, 2H), 3.80 (s, 3H), 2.90 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 157.7, 151.3, 139.8, 129.1, 128.7, 127.9, 127.0, 115.4, 104.6, 96.2, 78.3, 55.3, 43.0, 40.6.

¹² Lin, C.; Hsu, J.; Sastry, M. N. V.; Fang, H.; Tu, Z.; Liu, J.-T.; Ching-Fa, Y. *Tetrahedron* **2005**, 61 (49), 11751-11757.

¹³ Dessole, G.; Herrera, R. P.; Ricci, A. *Synlett*. **2004**, 2374-2378.

¹⁴ Takenaka, N.; Sarangthem, R. S.; Seerla, S. K. *Org. Lett.* **2007**, 9, 2819-2822.

Table S2. Yields with standard deviation for addition of *N,N*-dimethyl-*m*-anisidine to *trans*- β -nitrostyrene (**Table 3**)

entry	catalyst	replicates	yield in DCM (%)	average yield with std. dev. (%)
1	none	2	5, 4	4.5 \pm 0.7
2	Ph ₃ SiOH	2	2, 16	9.0 \pm 9.9
3	Ph ₂ Si(OH) ₂	2	4, 3	3.5 \pm 0.7
4	1	3	11, 31, 19	20.3 \pm 10.1
5	2	2	29, 18	23.5 \pm 7.8
6	4	2	38, 41	39.5 \pm 2.1
7	silica gel	2	82, 94	88.0 \pm 8.5

Reactions were performed according to the procedure described above and purified directly on silica gel using flash chromatography (15% EtOAc/hexanes).

General Procedure for Solvent-Free Reactions. *trans*- β -Nitrostyrene (56 mg, 0.375 mmol, 1 equiv) and catalyst (0.075 mmol, 20 mol %) were added to a vial containing a stir-bar at room temperature. After stirring for ten minutes, the nucleophile was added to the reaction. The mixture of solids turns into an oil over time as the reaction proceeds. The reaction was stirred for 24 h, at which point it was diluted and purified by loading directly on silica gel for flash chromatography (15% EtOAc/hexanes).

Table S3. Yields with standard deviation for the solvent-free indole addition to *trans*- β -nitrostyrene (**Table 1**)

entry	catalyst	replicates	solvent free yields (%)	average with std. dev. (%)
1	none	1	32	-
2	Ph ₃ SiOH	1	45	-
3	Ph ₂ Si(OH) ₂	1	52	-
4	1	2	75, 54	64.5 \pm 14.8
5	2	1	73	-
6	3	1	83	-
7	4	1	92 (run for 4 h)	-
8	silica gel	1	78	-

Reactions were performed according to the procedure described above and purified directly on silica gel using flash chromatography (5% to 20% EtOAc/hexanes).

Temperature and Concentration Effects on Reaction (Table 2). *trans*- β -Nitrostyrene (56 mg, 0.375 mmol, 1 equiv), silanediol **4** (0.075 mmol, 20 mol %) was added to a vial containing a stirbar. To the mixture was added one-half of the total amount of anhydrous DCM that is needed to obtain the desired concentration and the mixture was stirred at the indicated temperature. After 10 min, indole (67 mg, 0.563 mmol, 1.5 equiv) was added immediately followed by the second half of anhydrous DCM. The reaction was stirred at the indicated temperature for 24 h and then the product was purified by loading directly onto silica gel for flash chromatography (5% to 20% EtOAc/hexanes) to give product in the indicated yield.

Effects of Water on Reaction and Comparison of Spectra Containing Water or HCl

The route used for the synthesis of silanediols is important to obtain pure, stable silanediols that are effective hydrogen-bonding catalysts. A trace amount of HCl can be produced upon hydrolysis of a silyl chloride, which can be readily removed upon simple workup with NaHCO_3 or upon column chromatography. The presence of HCl does not provide an accurate assessment of silanediol catalytic activity. Our synthetic route described here utilizes a silane precursor to avoid production of HCl. The presence of HCl can be detected by NMR spectroscopy due to a *sharp* peak at 1.6 ppm (in *d*-chloroform), compared to a *broad* peak with water. The SiOH peak also remains sharp with HCl, but is broad in the presence of water. See Figure S1 for a comparison of spectra. The effect of water and HCl on silanediol catalysis is presented below in Table S4.

General procedure for additive studies (Table S4). The procedure for the preparation of 3-(2-nitro-1-phenylethyl)-1*H*-indole (**9**) above was used except water one or more equiv. of water (relative to the nitrostyrene) was added and the reaction mixture was allowed to stir for 15 min *before* the addition of indole for entries 2, 6, and 7. For entries 3 and 4, the procedure for 3-(2-nitro-1-phenylethyl)-1*H*-indole (**9**) above was also used with catalyst **1** pre-treated with HCl as follows: Catalyst **1** (0.075 mmol, 20 mol %) was dissolved in chloroform (1 mL) and allowed to stir in a biphasic mixture with 1.0 M HCl (aq, 0.1 mL) for 0.5 h. At which point, the aqueous layer was removed and the organic phase was concentrated under vacuum and dried *in vacuo* for 4 d (entry 3) or 6 h (entry 4). The NMR spectra of silanediol comparing water and HCl (aq) in CDCl_3 is shown in Figure S1.

Table S4. Yields with standard deviation for indole addition to *trans*- β -nitrostyrene with either water or HCl additive.

entry	catalyst	additive ^a	yield in DCM (%)
1	1	none	33
2	1	H ₂ O (1 equiv)	35
3	1	HCl	65
4	1	HCl	99
5	4	none	92
6	4	H ₂ O (1 equiv)	68
7	4	H ₂ O (xs)	57

^a equivalents relative to nitrostyrene

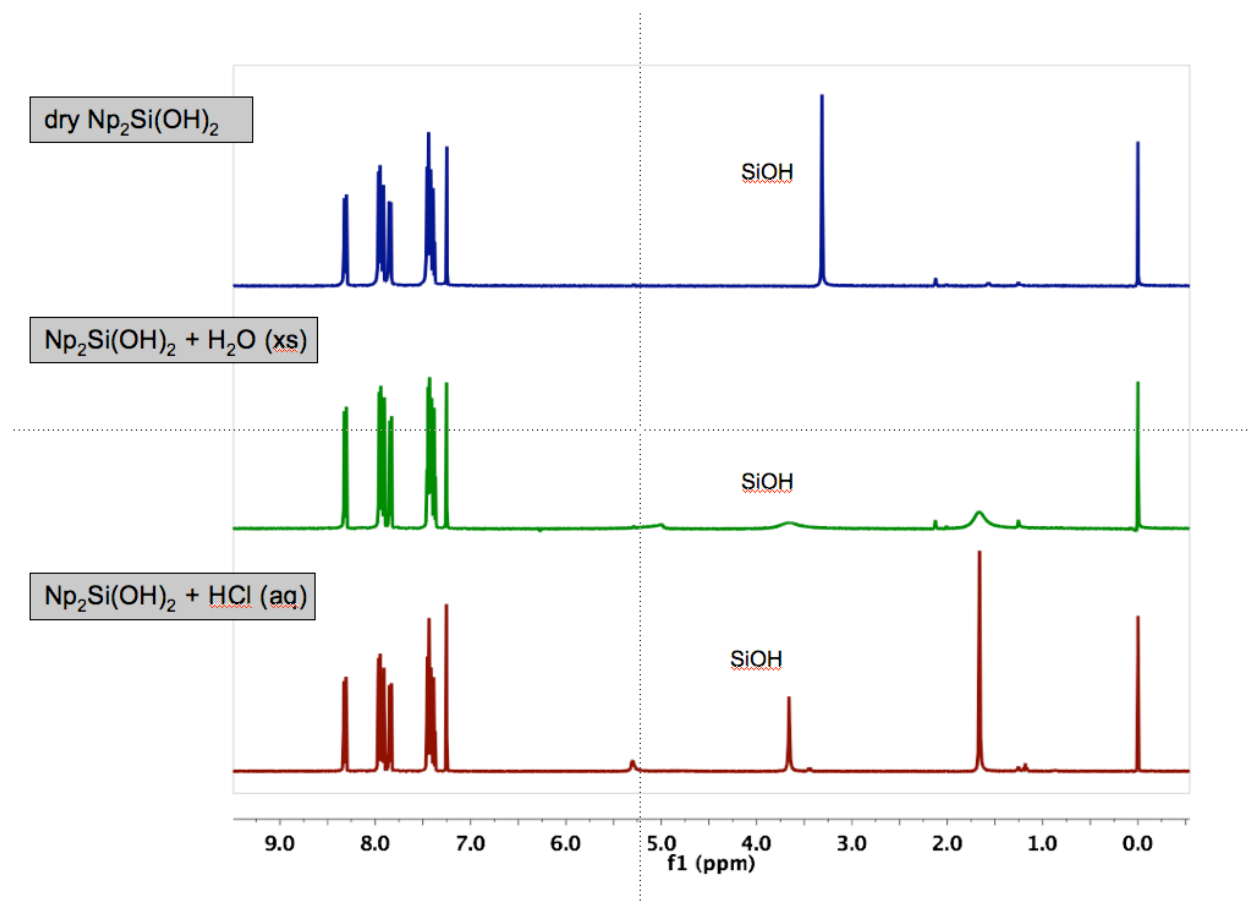


Figure S1. Comparison of NMR spectra (in *d*-chloroform, 400 MHz NMR) for di-(1-naphthyl)silanediol (**1**): a) pure and dry silanediol; b) silanediol with H₂O added; c) silanediol with HCl (aq) added. The SiOH peak is sharp in a pure sample, but becomes broad in the presence of water; the SiOH peak is also sharp when HCl (aq) is added.

IV. NMR Studies on Silanols and Silanediols^{8,1,15}

NMR binding studies were performed at several silanediol concentrations with several Lewis bases. For each NMR binding study at 0.01 M concentration of silanediol, two stock solutions were each made by dissolving 0.06 mmol of silanediol in 6.0 mL of deuterated solvent (C₆D₆ or CDCl₃). A Lewis base (0.30 mmol, 5 equiv) was added to only one of the stock solutions. Then different volumes of each stock solution were mixed to make 0.6 mL of solution with the desired equivalents of Lewis base. The NMR spectrum of each solution was recorded after eight scans at room temperature. The binding constant was determined by fitting a nonlinear curve with Microsoft Excel Solver with the model equation below.^{16,17} No constraints

¹⁵ Billo, E. J. *Excel for Chemists: A Comprehensive Guide*, 3rd ed.; John Wiley & Sons: New Jersey, 2011, 480-484.

¹⁶ Walsh, S.; Diamond, D. *Talanta*, **1995**, 42, 561-572.

¹⁷ Wilcox, C. S. in *Frontiers in Supramolecular Organic Chemistry and Photochemistry*; Schneider, H.-J.; Durr, H. (Eds.), VCH: Weinheim, Federal Republic of Germany; New York, **1991**, 123-143.

were used, and the only variable being changed/optimized by the Solver is K_a . There was negligible self-association at 10 mM in C_6D_6 and $CDCl_3$.

$$\Delta\delta_i = \delta_{obs,i} - \delta_{free} = \frac{C}{R_0} \Delta\delta$$

where

$$C = \frac{(K_a R_0 + 1 + K_a S_0) \pm \sqrt{(K_a R_0 + 1 + K_a S_0)^2 - 4K_a^2 R_0 S_0}}{2K_a},$$

$\Delta\delta = \delta_{complex} - \delta_{free}$; $\delta_{complex}$ = chemical shift (ppm) of hydroxyl proton in the bound Lewis base (substrate), or the chemical shift where the binding curve levels off and it is estimated by extrapolation of the binding curve; δ_{free} = chemical shift of hydroxyl proton of unbound state (e.g. no Lewis base added); $\Delta\delta_i$ = the observed changed in chemical shift at i equivalence of Lewis base; $\delta_{obs,i}$ = chemical shift of hydroxyl proton at i equivalence of Lewis base; R_0 = initial concentration of silanediol (or receptor) in M; S_0 = initial concentration of Lewis base (or substrate) in M, and K_a = binding constant in M^{-1} .

The above steps were repeated for the binding studies at 0.40 M concentration of silanediol, except 40 times as much solutes were used to prepare the stock solutions. Based on the NMR shift data, which indicates that the cyclic dimeric form of silanediol interacts with *trans*- β -nitrostyrene at these concentrations, we crudely estimate the binding constant at 0.40 M using the above procedures.

Self-association constants for silanediols were determined based on the procedures outlined for the monomer-dimer equilibrium model in reference 15. The association constant was determined by fitting a nonlinear curve with Microsoft Excel Solver with the model equation below.^{18,5} No constraints were used, and the only variables being optimized by the Solver are K and δ_2 .

$$\delta_{calc} = \frac{[U]\delta_1 + 2K[U]^2\delta_2}{[U]_T}$$

where $[U]_T$ is the total concentration of silanediol in M^{-1} , $[U]$ is the concentration in M^{-1} of the monomer at a given concentration $[U]_T$ and is estimated by

$$[U] = \frac{\sqrt{8K[U]_T + 1} - 1}{4K},$$

and K is the association constant in M^{-1} . δ_1 is the chemical shift in ppm of the hydroxyl proton of the monomeric form and it is determined at concentration below the level of silanediol self-association (e.g. $\leq 0.01M$). δ_2 is the chemical shift in ppm of the hydroxyl proton of the dimeric form.

¹⁸ Walsh, S.; Diamond, D. *Talanta*, **1995**, 42, 561-572.

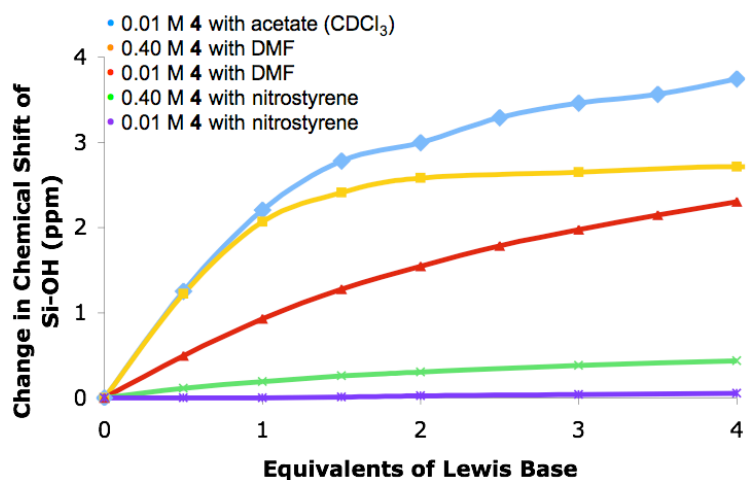


Figure S2. Comparison of binding affinity of silanediol **4** to Lewis bases. All binding studies were performed in C_6D_6 , except for $n\text{-Bu}_4\text{NOAc}$, which was performed in $CDCl_3$ due to solubility reasons.

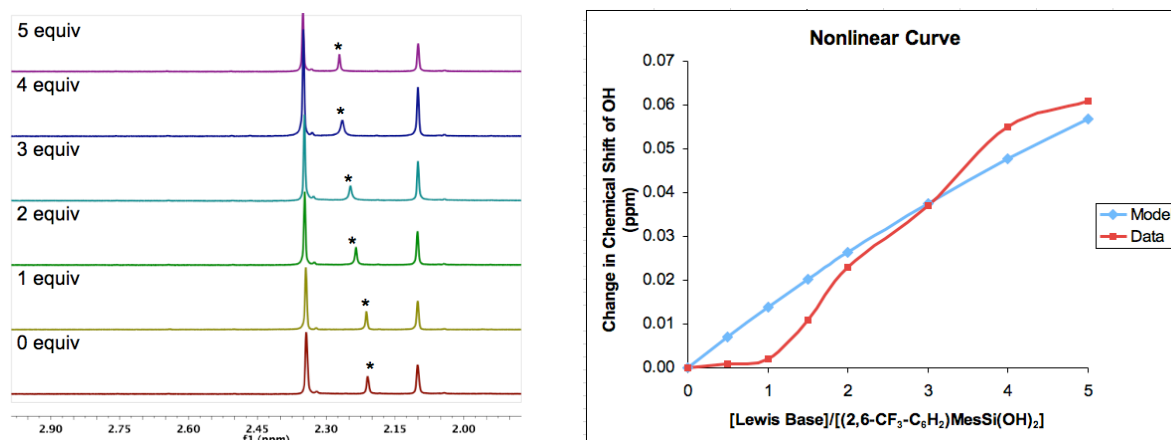


Figure S3. Spectra and binding curve for $(2,6\text{-CF}_3\text{-C}_6\text{H}_2)\text{MesSi(OH)}_2$ **4** as a 10 mM solution in C_6D_6 with *trans*- β -nitrostyrene ($K_a \leq 6.5 \pm 5.2 \text{ M}^{-1}$). A shift of 0.06 ppm is observed for hydroxy protons (indicated with *) when 5.0 equivalents of *trans*- β -nitrostyrene are added.

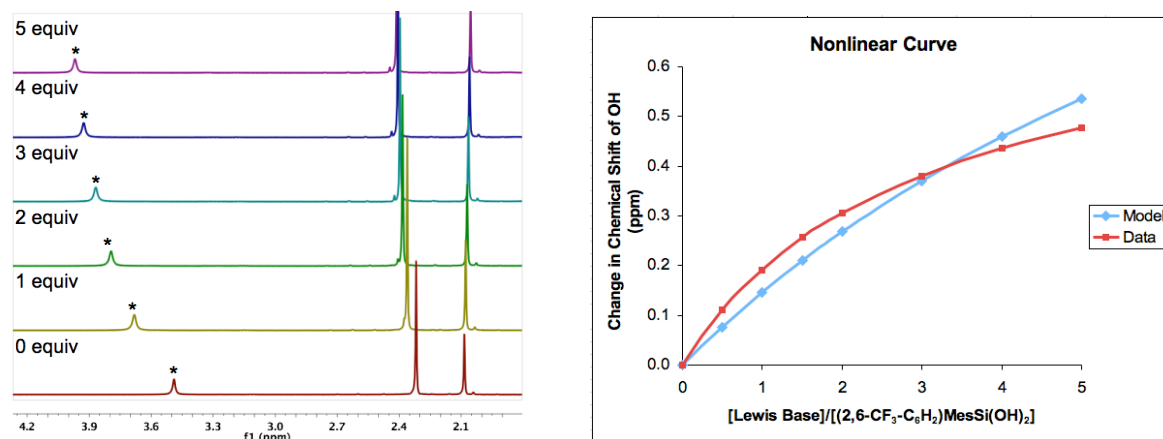


Figure S4. Spectra and binding curve for $(2,6\text{-CF}_3\text{-C}_6\text{H}_2)\text{MesSi(OH)}_2$ (**4**) as a 400 mM solution in C_6D_6 with *trans*- β -nitrostyrene ($K_a = 11.9 \pm 0.1 \text{ M}^{-1}$). A shift of 0.48 ppm is observed for hydroxy protons (indicated with *) when 5.0 equivalents of *trans*- β -nitrostyrene are added.

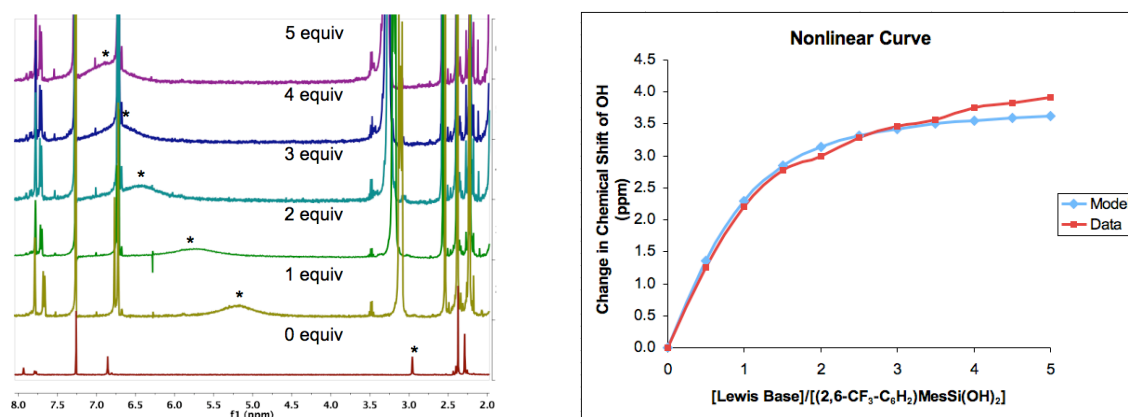


Figure S5. Spectra and binding curve for (2,6-CF₃-C₆H₂)MesSi(OH)₂ (4) as a 10 mM solution in CDCl₃ with *n*Bu₄NOAc ($K_a = 357.2 \pm 46 \text{ M}^{-1}$). A shift of 3.91 ppm is observed for hydroxy protons (indicated with *) when 5.0 equivalents of *n*Bu₄NOAc are added.

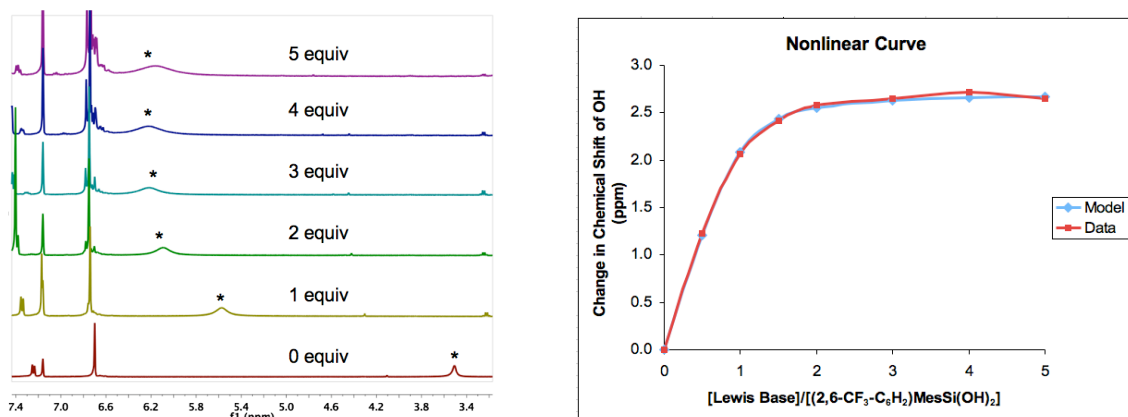


Figure S6. Spectra and binding curve for (2,6-CF₃-C₆H₂)MesSi(OH)₂ (4) as a 400 mM solution in C₆D₆ with DMF ($K_a = 1434.1 \pm 50 \text{ M}^{-1}$). A shift of 2.64 ppm is observed for hydroxy protons (indicated with *) when 5.0 equivalents of DMF are added.

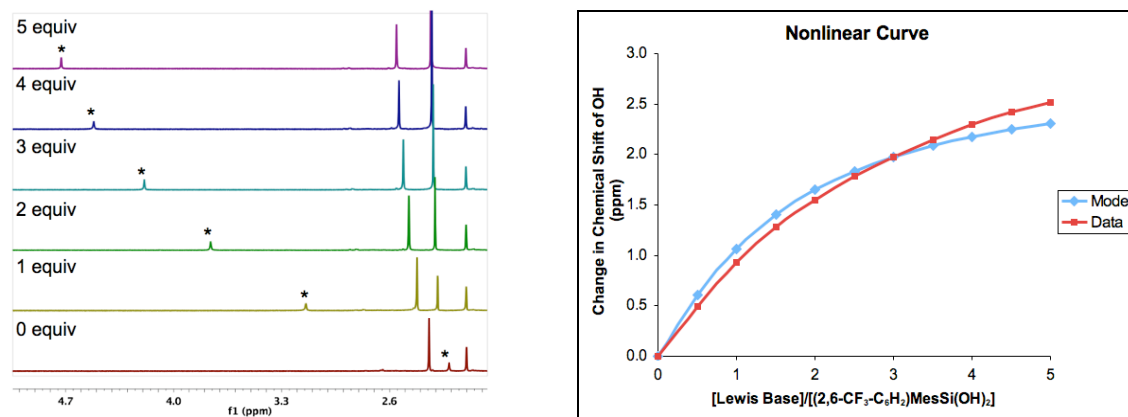


Figure S7. Spectra and binding curve for (2,6-CF₃-C₆H₂)MesSi(OH)₂ (4) as a 10 mM solution in C₆D₆ with DMF ($K_a = 90.8 \pm 0.4 \text{ M}^{-1}$). A shift of 2.51 ppm is observed for hydroxy protons (indicated with *) when 5.0 equivalents of DMF are added. Figures reproduced from literature (Tran, N. T.; Min, T.; Franz, A. K. *Chem. Eur. J.* **2011**, *17*, 9897-9900) and provided here for comparison and to construct Figure S2.

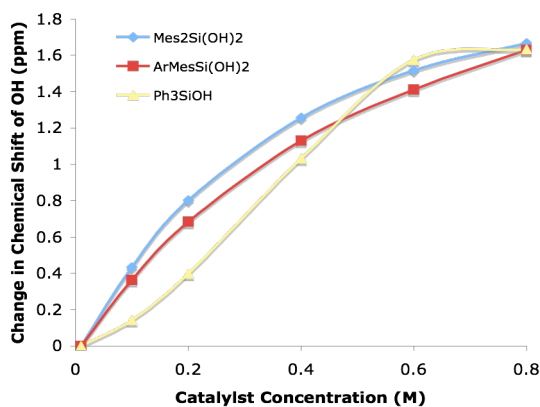


Figure S8. Self-association of silanediols and triphenolsilanol. Ar = 2,6-CF₃-C₆H₃. Similar curves were obtained for CDCl₃ and CD₂Cl₂ except the hydroxy shifts were not as prominent.

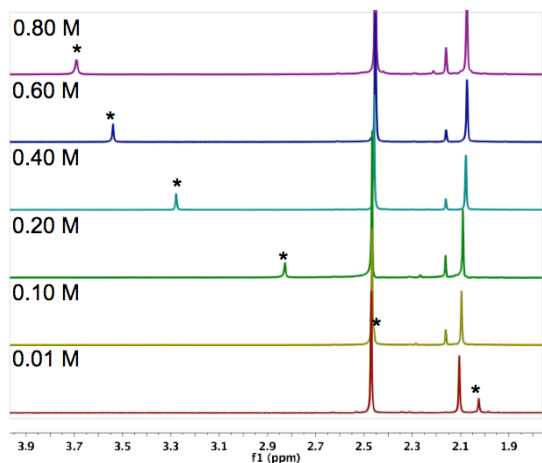


Figure S9. Spectra of self-recognition for Mes₂Si(OH)₂ (**2**) in C₆D₆ ($K_a = 7.7 \pm 1.5 \text{ M}^{-1}$). A shift of 1.67 ppm is observed for hydroxy protons (indicated with *) at 0.80 M.

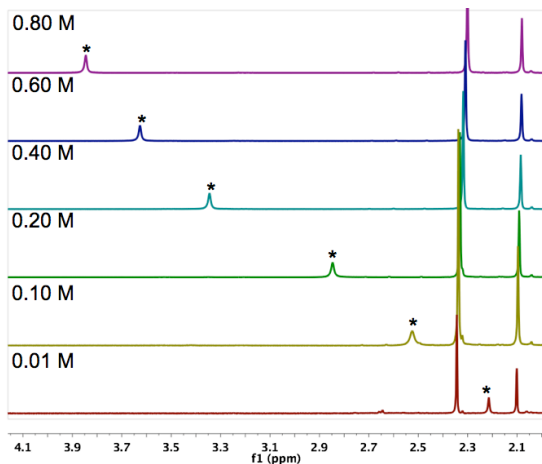
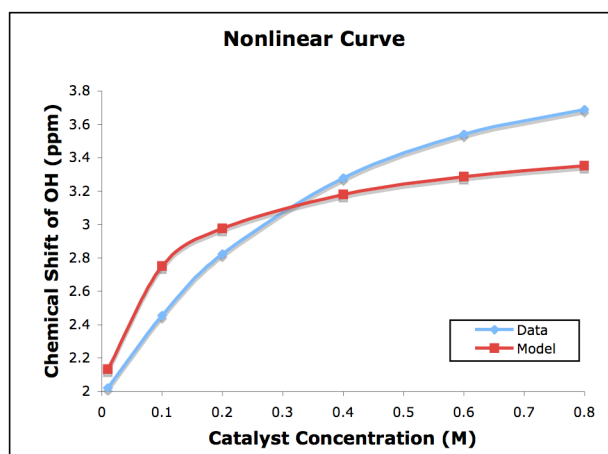
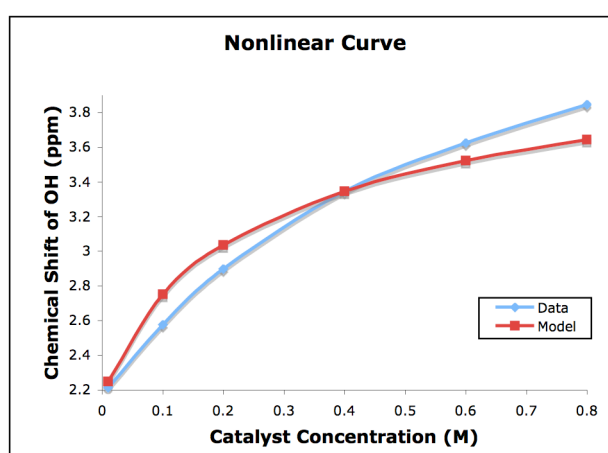


Figure S10. Spectra of self-association for (2,6-CF₃-C₆H₂)MesSi(OH)₂ (**4**) in C₆D₆ ($K_a = 4.6 \pm 2.4 \text{ M}^{-1}$). A shift of 1.63 ppm is observed for hydroxy protons (indicated with *) at 0.80 M.



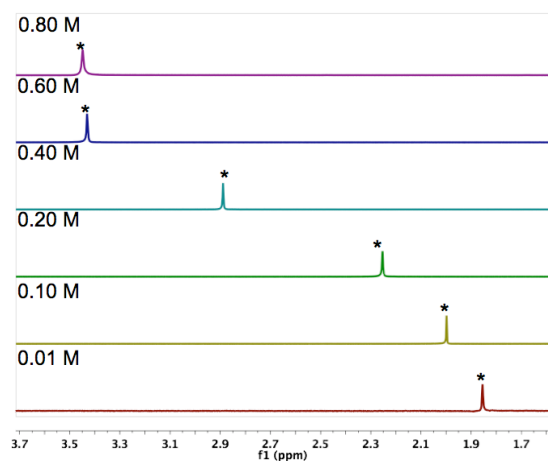


Figure S11. Spectra of self-association for Ph_3SiOH in C_6D_6 . A shift of 1.59 ppm is observed for hydroxy protons (indicated with *) at 0.80 M.

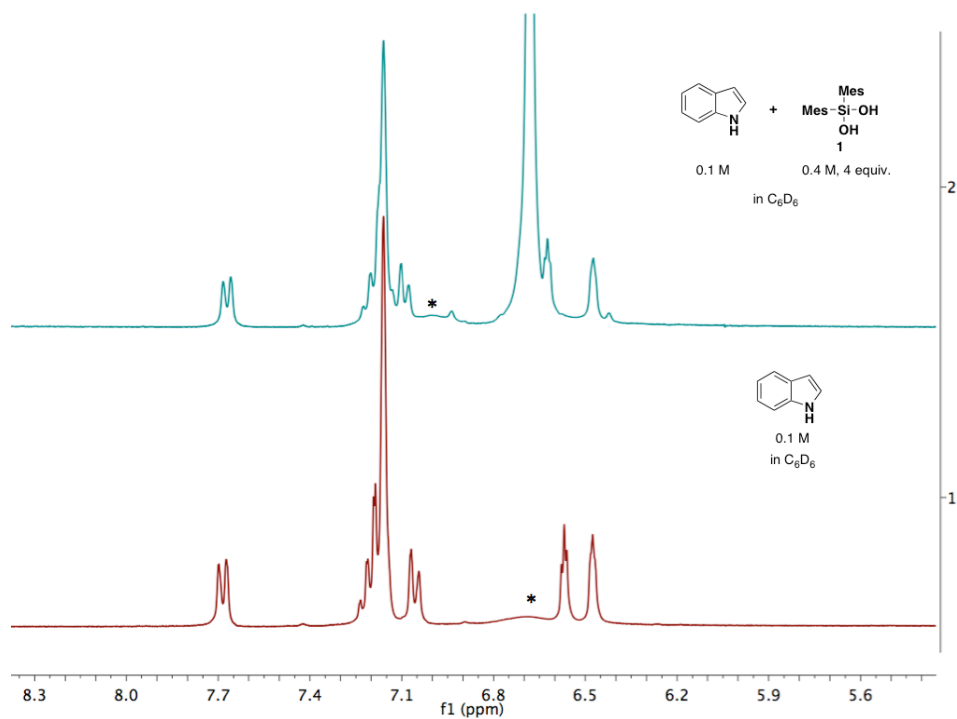


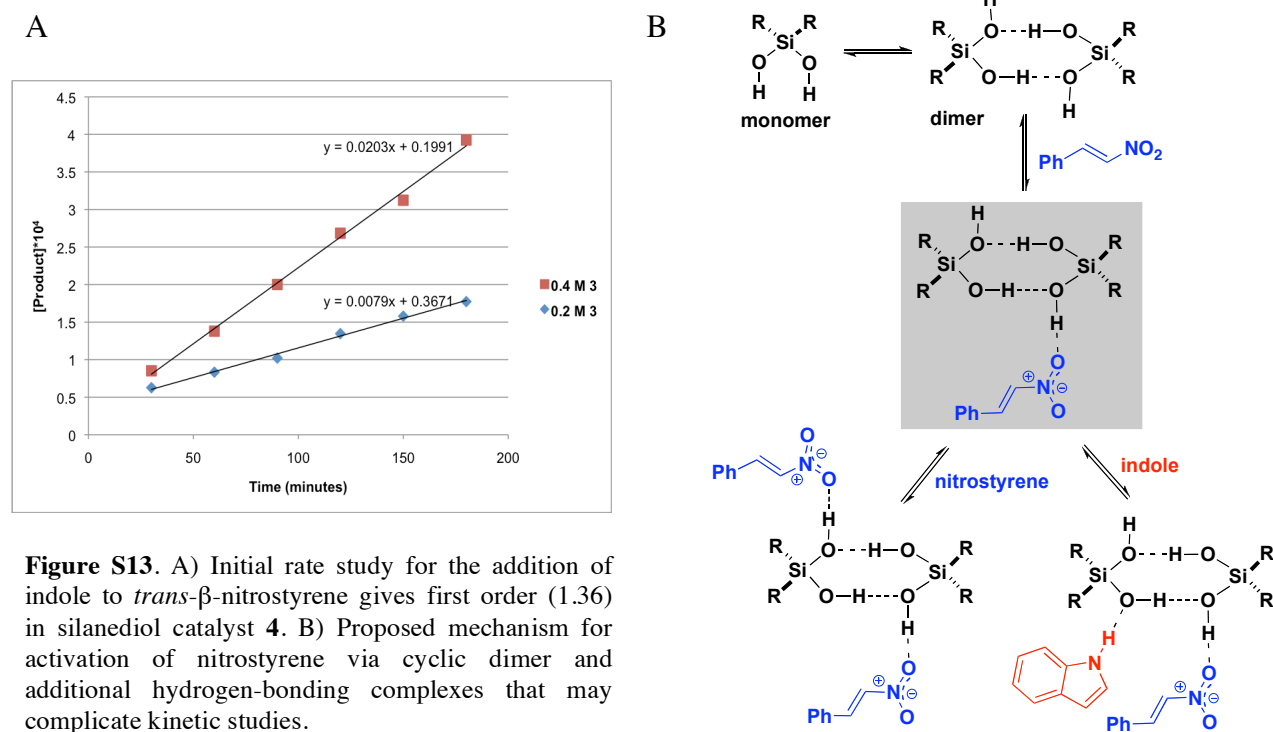
Figure S12. Spectra of $\text{Mes}_2\text{Si}(\text{OH})_2$ (**2**) binding with indole (**8**) in C_6D_6 . A shift of 0.30 ppm and broadening is observed for NH protons (indicated with *).

V. Preliminary Kinetic Studies

Kinetic studies of hydrogen-bonding catalyst systems in the literature have been used to elucidate reaction mechanisms and improve catalyst design.¹⁹ We hypothesized that the reaction would be second order in catalyst if the cyclic dimer (observed by X-ray and indicated by NMR binding) was the primary active species and only activates nitrostyrene in a 2:1 complex.²⁰

Preliminary kinetic studies were performed and setup using the indole addition procedure as described according to the general procedure indicated above. Aliquots (5 μ L) were removed from the reaction and diluted to 1.5 mL with a 10% *i*PrOH/Hexanes mixture. The progress of the reaction was monitored by concentration of products, determined by HPLC peak height in relation to a calibration curve. ¹H NMR was not used due to high concentrations of reactants and non-ideal separation of diagnostic peaks. The calibration curve was created by diluting 44 mg of silanediol **4** in 25 mL of 10% *i*PrOH/hexanes, and then five other samples were created by consecutive two-fold dilutions. HPLC analysis was performed using a Chiralpak AD-H column, n-hexane/*i*-PrOH = 90:10, 1.0 mL/min, t_R = 14.8, 16.3 min.

The preliminary data here indicates that the indole addition reaction is first-order (1.36) in catalyst under these conditions. Because the cyclic dimer provides a cluster with two hydrogen-bonding sites, the first-order rates may suggest that the cyclic dimer can activate two molecules of reactant at the current concentration. More detailed kinetic studies are underway.



¹⁹ Vachal, P.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124* (34), 10012-10014.

²⁰ (a) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33* (6), 421-431; (b) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118* (44), 10924-10925.

VI. Crystallography Data

The structural data provided here demonstrates that the crystal structure of di-(1-naphthyl)silanediol (**1**) is a linear hydrogen-bonding network (Figure S14) that blocks the free H-bond donor sites from intermolecular interactions with Lewis basic molecules. Due to lower solubility, the silanediol cannot as easily access what is presumed to be a more active cyclic dimer that displays H-bond donors to interact with Lewis bases. This hypothesis partially explains why di-(1-naphthyl)silanediol (**1**) exhibits similar reactivity to the less acidic dimesitylsilanediol, which has similar hydrogen-bonding patterns.¹

Crystal Structure Collection and Determination. Crystals were grown from slow evaporation of silanediol (and one equivalent of Lewis base) from benzene or dichloromethane. Suitable crystals were mounted on glass fibers with silicone grease and placed in the cold N₂ stream of a Bruker SMART Apex II diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 90(2) K.²¹ Reflections were integrated and corrected for Lorentz and polarization effects, and absorption was corrected by using Blessing's method²² with the program SADABS.²³ Structures were solved by direct methods and refined using all data (based on F^2) and the software SHELXTL 6.1.^{24,25,26} All non-hydrogen atoms were refined anisotropically. In general, as many hydrogen atoms were located on a difference map as possible and then the missing hydrogen atoms were added geometrically. The position and thermal parameters of hydrogen atoms were allowed to refine freely.

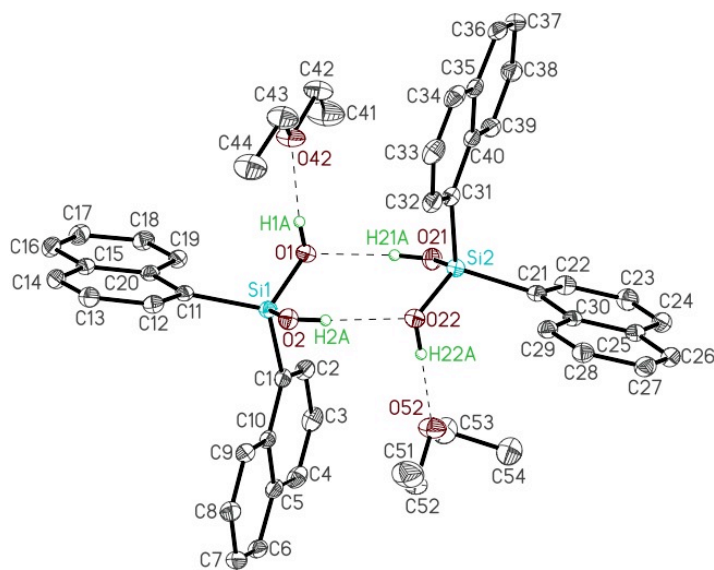


Figure S14. Asymmetric unit contains a cyclic dimer cluster supramolecular motif and intermolecular hydrogen bonding with diethyl ether. Selected hydrogens in thermal displacement plot, which shows 35% probability displacement ellipsoids for non-hydrogens, are omitted for clarity.

²¹ Bruker (2002). SMART (Version 5.054) and SAINT (Version 7.23a). Bruker AXS Inc., Madison, Wisconsin, USA.

²² Blessing, R. H. *Acta Cryst.* **1995**, A51, 33.

²³ Sheldrick, G.M., *SADABS*, Version 2.10; Universitat Gottingen: Gottingen, Germany, 2003.

²⁴ Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.

²⁵ Sheldrick, G. M., **1997**. *SHELXS97* and *SHELXL97*. Universitat Gottingen: Gottingen, Germany.

²⁶ Sheldrick, G.M., **2002**. *SHELXTL 6.1*. Bruker AXS Inc., Madison, Wisconsin, USA.

Table S5. Crystal data and structure refinement for di(1-naphthyl)silanediol (**1**) with diethyl ether solvate.

Identification code	NT105	
Empirical formula	C ₂₄ H ₂₆ O ₃ Si	
Formula weight	390.54	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.1046(8) Å	$\alpha = 80.0010(10)^\circ$.
	b = 16.1014(15) Å	$\beta = 82.9910(10)^\circ$.
	c = 16.2436(16) Å	$\gamma = 83.3600(10)^\circ$.
Volume	2062.2(3) Å ³	
Z	4	
Density (calculated)	1.258 Mg/m ³	
Absorption coefficient	0.136 mm ⁻¹	
F(000)	832	
Crystal size	0.33 x 0.30 x 0.25 mm ³	
Crystal color and habit	colorless block	
Diffractometer	Bruker SMART 1000	
Theta range for data collection	2.96 to 27.51°.	
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -20 ≤ l ≤ 21	
Reflections collected	19660	
Independent reflections	9180 [R(int) = 0.0313]	
Observed reflections (I > 2σ(I))	7432	
Completeness to theta = 27.51°	96.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9667 and 0.9570	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	9180 / 0 / 713	
Goodness-of-fit on F ²	1.023	
Final R indices [I > 2σ(I)]	R1 = 0.0378, wR2 = 0.0985	
R indices (all data)	R1 = 0.0497, wR2 = 0.1078	
Largest diff. peak and hole	0.437 and -0.311 e.Å ⁻³	

Table S6. Hydrogen bonds for NT105 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(21)-H(21A)...O(1)	0.83(2)	1.95(2)	2.7690(15)	166.7(19)
O(2)-H(2A)...O(22)	0.83(2)	1.96(2)	2.7754(15)	167(2)
O(22)-H(22A)...O(52)	0.84(2)	1.80(2)	2.6310(15)	174.1(19)
O(1)-H(1A)...O(42)	0.76(2)	1.96(2)	2.7120(14)	174(2)

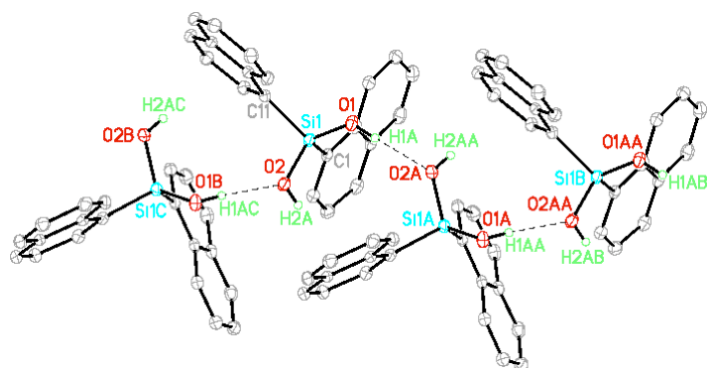


Figure S15. Asymmetric unit repeated three times to show polymeric supramolecular assembly and intermolecular hydrogen bonding. Selected hydrogens in ORTEP figure, which shows 35% probability displacement ellipsoids for non-hydrogens, are omitted for clarity.

Table S7. Crystal data and structure refinement for di(1-naphthyl)silanediol (**1**).

Identification code	NT107	
Empirical formula	C ₂₀ H ₁₆ O ₂ Si	
Formula weight	316.42	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 9.389(3) Å	α = 90°.
	b = 19.374(6) Å	β = 93.933(4)°.
	c = 8.611(3) Å	γ = 90°.
Volume	1562.8(9) Å ³	
Z	4	
Density (calculated)	1.345 Mg/m ³	
Absorption coefficient	0.157 mm ⁻¹	
F(000)	664	
Crystal size	0.47 x 0.16 x 0.09 mm ³	
Crystal color and habit	colorless plate	
Diffractometer	Bruker SMART 1000	
Theta range for data collection	3.03 to 27.51°.	
Index ranges	-11 ≤ h ≤ 12, -25 ≤ k ≤ 24, -11 ≤ l ≤ 11	
Reflections collected	14440	
Independent reflections	3538 [R(int) = 0.0412]	
Observed reflections (I > 2σ(I))	2672	
Completeness to theta = 27.51°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9854 and 0.9290	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	3538 / 0 / 272	
Goodness-of-fit on F ²	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0360, wR2 = 0.0829	
R indices (all data)	R1 = 0.0585, wR2 = 0.0961	
Largest diff. peak and hole	0.332 and -0.310 e.Å ⁻³	

Table S8. Hydrogen bonds for NT107 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(2)#1	0.81(3)	2.00(3)	2.8070(19)	171(2)

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+3/2, z+1/2

VII. Computational Studies of Silanol Acidity^{1,27}

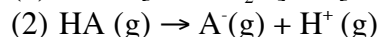
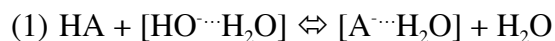
A. Description of Gas-phase Acidity (ΔH_{acid})

All calculations were conducted using *Gaussian03* programs. The geometry of each species in equation (1) was optimized with the B3LYP/6-31+G(d) method. The deprotonated forms of the acid (HA) and H₂O were used as the initial guesses for the geometry optimizations of their conjugate bases (e.g. A⁻ and OH⁻). The initial guesses for [A⁻⋯H₂O] and [HO⁻⋯H₂O] complexes involve adding one H₂O molecule to each optimized geometry of a conjugate base such that the hydrogen of H₂O faces and is at approximately 1.63 Å away from the negatively charged atom (the deprotonated atom of the acid). To confirm that an optimized geometry is a real minimum on the potential energy surface, frequency calculation using B3LYP/6-31+G(d) was conducted to ensure that there is no imaginary frequency. Zero-point vibrational corrections were obtained as unscaled frequencies. Gas-phase acidity was determined from the free energies obtained at the B3LYP/6-31+G(d) level and equation (2). All gas-phase calculations correspond to the reference state, 1 atm and 298 K.

B. Description of pK_a ^{1,26}

Since gas-phase geometries usually do not change significantly upon solvation, the optimized gas-phase geometries from above were used for all solution-phase calculations. Single-point solution-phase free energies of HA, H₂O, [A⁻⋯H₂O] and [HO⁻⋯H₂O] were determined by using the HF/6-31+G(d,p) method and PCM solvation model that has the following modified parameters: TSARE = 0.4, radii = bondi, and alpha = 1.00. These free energies correspond to the reference state, 1 mol/L and 298 K.

The pK_a values for a series of reference acids, including three silanols, were determined using a semi-empirical method. First, $\Delta G_{\text{exchange}}$ was calculated from the solution-phase Gibbs free energies from above and equation (1). Then, $\Delta G_{\text{exchange}}$ was used in equation (3) to determine computational pK_a (B3LYP). The least squares linear regression equation (4a) was obtained by using Microsoft Excel to make a graph of pK_a (B3LYP) versus experimental pK_a (see Figure S25). Since there were several large deviations from the linear regression equation (see Figure S25 and Table S1), pK_a values were also calculated using only electronic energies. By computing $\Delta H_{\text{exchange}}$ and using $\Delta H_{\text{exchange}}$ in place of $\Delta G_{\text{exchange}}$ in the above steps, we identified that there was a better correlation with electronic energies (see least squares linear regression equation in Figure S26 and Table S1). Using the latter method, we calculated pK_a values for unknown silanols in Table 1, (Figures S25 and S26 and Table S1).



$$(3) pK_a(\text{B3LYP}) = 15.1 - \Delta G_{\text{exchange}} / (2.303 \cdot 298.15 \cdot 1.9858775 \cdot 1000)$$

(4) linear regression equations

$$\text{a. } pK_a(\text{EXP}) = pK_a(\text{B3LYP}) \cdot 2.315 - 16.891 \text{ for } \Delta G_{\text{exchange}}$$

$$\text{b. } pK_a(\text{EXP}) = pK_a(\text{B3LYP}) \cdot 0.4911 + 7.2871 \text{ for } \Delta H_{\text{exchange}}$$

²⁷ Fu, Y.; Liu, L.; Li, R.-Q.; Liu, R.; Guo, Q.-X. *J. Am. Chem. Soc.* **2004**, *126*, 814-822.

Di-(1-naphthyl)silanediol

B3LYP/6-31+G(d)

HF = -1211.870486 hartrees (-760460.84866986 kcal/mol)

Imaginary Frequencies: none found

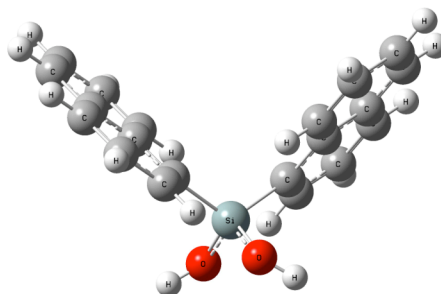
Zero-point correction = 0.304829 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1211.565657 hartrees (-760269.56542407 kcal/mol)

Sum of electronic and thermal Free Energies =

-1211.614193 hartrees (-760300.02224943 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -1205.5562811 hartrees (-756498.621953061 kcal/mol)

Zero-point correction = 0.323388 (Hartree/Particle)

Sum of electronic and zero-point Energies = -1205.232893 hartrees (-756295.69268643 kcal/mol)

Sum of electronic and thermal Free Energies = -1205.276672 hartrees (-756323.16444672 kcal/mol)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	0.000215	-0.015405	1.736585
2	8	-0.374910	-1.357447	2.663895
3	8	0.374785	1.308907	2.689298
4	6	-1.506319	0.568249	0.772857
5	6	-1.978082	1.855670	1.000301
6	6	-3.118043	2.365314	0.331689
7	6	-3.792741	1.581375	-0.575788
8	6	-3.360084	0.255932	-0.852791
9	6	-4.050830	-0.563072	-1.788205
10	6	-3.630104	-1.847790	-2.053144
11	6	-2.493335	-2.366700	-1.387373
12	6	-1.803139	-1.596356	-0.474835
13	6	-2.205016	-0.263126	-0.173022
14	6	1.507258	-0.581165	0.762954
15	6	1.981560	-1.871017	0.970646
16	6	3.122643	-2.368052	0.294512
17	6	3.796005	-1.568881	-0.600569
18	6	3.360673	-0.240255	-0.857382
19	6	4.049980	0.594355	-1.779972
20	6	3.626588	1.882051	-2.025504
21	6	2.488421	2.388289	-1.352417
22	6	1.799614	1.602693	-0.451914
23	6	2.204345	0.265956	-0.170083
24	1	-1.219147	-1.332364	3.136245
25	1	1.221855	1.277965	3.156203
26	1	-1.461325	2.493837	1.711514
27	1	-3.454246	3.377949	0.540400
28	1	-4.668551	1.964919	-1.095458
29	1	-4.922818	-0.153540	-2.294078
30	1	-4.166275	-2.463647	-2.770608
31	1	-2.161227	-3.380071	-1.598319
32	1	-0.935954	-2.017494	0.023797
33	1	1.466043	-2.521078	1.671915
34	1	3.460838	-3.383087	0.487763
35	1	4.672809	-1.942581	-1.125706
36	1	4.922997	0.194384	-2.291693
37	1	4.161629	2.509862	-2.733386
38	1	2.154015	3.403926	-1.548293
39	1	0.930991	2.014190	0.052212

Deprotonated Di-(1-naphthyl)silanediol

B3LYP/6-31+G(d)

HF = -1211.3169808 hartrees (-760113.518621808 kcal/mol)

Imaginary Frequencies: none found

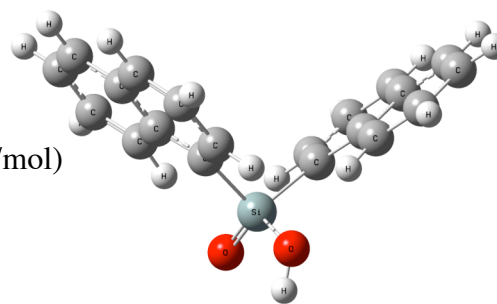
Zero-point correction = 0.292099 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1211.024882 hartrees (-759930.22370382 kcal/mol)

Sum of electronic and thermal Free Energies =

-1211.073049 hartrees (-759960.44897799 kcal/mol)



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	-0.062423	-0.327166	1.769217
2	8	-0.672270	-1.557371	2.539316
3	8	0.638076	0.889549	2.756678
4	6	-1.313430	0.678453	0.691565
5	6	-1.184040	2.056845	0.579022
6	6	-2.025591	2.838073	-0.252879
7	6	-3.020041	2.239717	-0.994401
8	6	-3.228137	0.835973	-0.908088
9	6	-4.264529	0.193968	-1.643211
10	6	-4.478673	-1.163375	-1.530221
11	6	-3.667537	-1.935086	-0.660667
12	6	-2.651184	-1.344419	0.062618
13	6	-2.381376	0.053099	-0.047094
14	6	1.338424	-0.856996	0.544198
15	6	1.317289	-2.202060	0.194679
16	6	2.224320	-2.763485	-0.738575
17	6	3.178550	-1.974415	-1.341500
18	6	3.272957	-0.594095	-1.015530
19	6	4.263156	0.237327	-1.611140
20	6	4.367047	1.571214	-1.279431
21	6	3.482118	2.126577	-0.321995
22	6	2.509686	1.346412	0.270121
23	6	2.354217	-0.033202	-0.057933
24	1	0.493092	0.638265	3.681105
25	1	-0.411197	2.561573	1.153413
26	1	-1.875979	3.915660	-0.308713
27	1	-3.663377	2.829666	-1.646676
28	1	-4.892521	0.799537	-2.296331
29	1	-5.275996	-1.640728	-2.097651
30	1	-3.856135	-3.001753	-0.554329
31	1	-2.054486	-1.917682	0.769813
32	1	0.577469	-2.842454	0.669829
33	1	2.159944	-3.823653	-0.980071
34	1	3.874754	-2.393180	-2.067672
35	1	4.944552	-0.204725	-2.337644
36	1	5.129481	2.194622	-1.743178
37	1	3.575616	3.175299	-0.046313
38	1	1.862904	1.769290	1.030208

Deprotonated Di-(1-naphthyl)silanediol and Water

B3LYP/6-31+G(d)

HF = -1287.7693317 hartrees (-808088.133335067 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.317481 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1287.451851 hartrees (-807888.91102101 kcal/mol)

Sum of electronic and thermal Free Energies =

-1287.503660 hartrees (-807921.4216866 kcal/mol)

HF/6-31+G(d,p)//B3LYP/6-31+G(d)

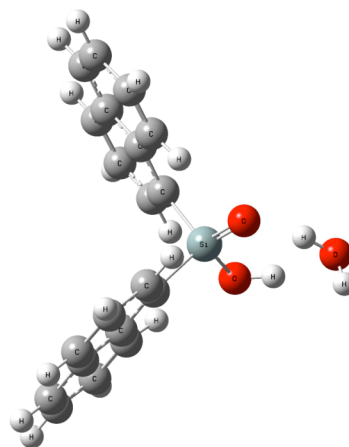
HF = -1281.1103265 hartrees (-803909.540982015 kcal/mol)

Zero-point correction = 0.337168 (Hartree/Particle)

Sum of electronic and zero-point Energies = -1280.773158 hartrees (-803697.96437658 kcal/mol)

Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

Sum of electronic and thermal Free Energies = -1280.819605 hartrees (-803727.11033355 kcal/mol)



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	-0.047704	1.491606	-0.243632
2	8	-0.652821	2.629025	0.689829
3	8	0.634742	2.073600	-1.683880
4	6	-1.318473	0.169048	-0.829400
5	6	-1.224796	-0.341199	-2.117493
6	6	-2.077907	-1.368693	-2.593677
7	6	-3.045336	-1.904803	-1.773269
8	6	-3.214295	-1.412204	-0.450353
9	6	-4.221612	-1.931637	0.410910
10	6	-4.397349	-1.428271	1.682290
11	6	-3.574803	-0.368829	2.140722
12	6	-2.586147	0.153789	1.332104
13	6	-2.356259	-0.357022	0.019596
14	6	1.333591	0.505374	0.671578
15	6	1.309622	0.602715	2.057417
16	6	2.212349	-0.107945	2.887630
17	6	3.163934	-0.933466	2.331579
18	6	3.259860	-1.064040	0.919242
19	6	4.247970	-1.895877	0.321145
20	6	4.351976	-2.005150	-1.048988
21	6	3.469666	-1.271861	-1.880737
22	6	2.499131	-0.459472	-1.330480
23	6	2.345312	-0.331863	0.081864
24	1	0.492592	3.041465	-1.731577
25	1	-0.473640	0.065005	-2.790382
26	1	-1.959355	-1.736866	-3.611776
27	1	-3.697329	-2.703243	-2.126052
28	1	-4.858545	-2.735327	0.042510
29	1	-5.173003	-1.834133	2.329439
30	1	-3.733055	0.043751	3.135240
31	1	-1.985939	0.999025	1.660048
32	1	0.572838	1.258935	2.515056
33	1	2.146861	-0.000257	3.969374
34	1	3.857573	-1.490938	2.960265
35	1	4.927746	-2.445934	0.971229
36	1	5.112962	-2.644793	-1.492321
37	1	3.563824	-1.344116	-2.962462
38	1	1.854107	0.128506	-1.973873
39	1	-0.442417	4.043424	-0.122302

40	8	-0.134877	4.773931	-0.760747
41	1	0.627685	5.168992	-0.313266

Bis(trifluoromethyl)silanediol

B3LYP/6-31+G(d)

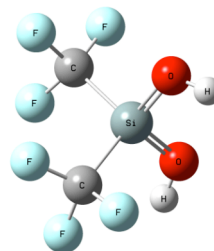
HF = -1116.5451776 hartrees (-700643.264395776 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.056159 (Hartree/Particle)

Sum of electronic and zero-point Energies = -1116.489018 hartrees (-700608.02368518 kcal/mol)

Sum of electronic and thermal Free Energies = -1116.529600 hartrees (-700633.489296 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -1112.3343404 hartrees (-698000.921944404 kcal/mol)

Zero-point correction = 0.061092 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1112.273248 hartrees (-697962.58585248 kcal/mol)

Sum of electronic and thermal Free Energies = -1112.309105 hartrees (-697985.08647855 kcal/mol)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	0.007953	0.743844	-0.003125
2	6	-1.562615	-0.397156	-0.036585
3	6	1.588221	-0.367801	-0.004131
4	8	0.121816	1.649044	-1.355774
5	1	-0.483600	2.387479	-1.513913
6	8	-0.080248	1.673439	1.346532
7	1	-0.380922	1.300488	2.188373
8	9	-1.460710	-1.461232	-0.865339
9	9	-1.844379	-0.883406	1.209290
10	9	-2.656887	0.316269	-0.431261
11	9	1.544758	-1.244921	1.043244
12	9	1.727549	-1.103254	-1.132661
13	9	2.719335	0.366332	0.142007

Deprotonated Bis(trifluoromethyl)silanediol

B3LYP/6-31+G(d)

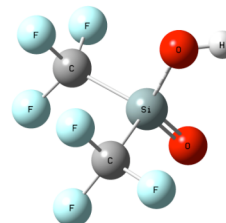
HF = -1116.0267858 hartrees (-700317.968357358 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.044759 (Hartree/Particle)

Sum of electronic and zero-point Energies = -1115.982027 hartrees (-700289.88176277 kcal/mol)

Sum of electronic and thermal Free Energies = -1116.023167 hartrees (-700315.69752417 kcal/mol)



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	0.000000	0.872062	-0.140169
2	6	1.532358	-0.361713	-0.016865
3	6	-1.532360	-0.361711	-0.016866
4	8	-0.000008	1.550132	1.407908
5	1	0.000033	2.515963	1.333499
6	8	0.000008	1.813505	-1.379033
7	9	1.545973	-1.173908	1.093130
8	9	1.641188	-1.217462	-1.085241
9	9	2.725851	0.319512	0.025463
10	9	-1.641141	-1.217513	-1.085205
11	9	-1.546017	-1.173850	1.093168
12	9	-2.725857	0.319511	0.025380

Deprotonated Bis(trifluoromethyl)silanediol and Water

B3LYP/6-31+G(d)

HF = -1192.4742608 hartrees (-748289.523394608 kcal/mol)

Imaginary Frequencies: none found

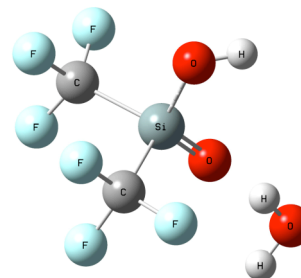
Zero-point correction = 0.068829 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1192.405432 hartrees (-748246.33263432 kcal/mol)

Sum of electronic and thermal Free Energies =

-1192.453037 hartrees (-748276.20524787 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -1187.9220494 hartrees (-745432.965218994 kcal/mol)

Zero-point correction = 0.075114 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1187.846936 hartrees (-745385.83080936 kcal/mol)

Sum of electronic and thermal Free Energies =

-1187.887245 hartrees (-745411.12510995 kcal/mol)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	-0.267093	-0.034823	0.532952
2	6	0.571706	1.581744	-0.206928
3	6	0.830082	-1.480856	-0.220687
4	8	0.251001	0.002730	2.132913
5	1	-0.505723	-0.068298	2.733518
6	8	-1.793166	-0.161335	0.247777
7	9	1.917686	1.703327	0.036884
8	9	0.440739	1.691436	-1.568342
9	9	0.006856	2.721250	0.308738
10	9	0.700875	-1.615535	-1.579373
11	9	2.180106	-1.361638	0.003151
12	9	0.482982	-2.700527	0.304017
13	8	-4.440798	-0.300345	-0.359616
14	1	-3.494965	-0.279609	-0.053301
15	1	-4.370241	-0.043100	-1.290131

Dimethylsilanediol Dimer

B3LYP/6-31+G(d)

HF = -1042.2112673 hartrees (-653997.992343423 kcal/mol)

Imaginary Frequencies: none found

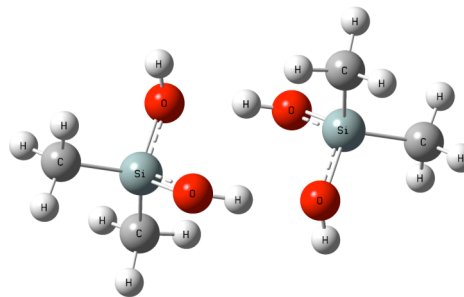
Zero-point correction = 0.208165 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1042.003102 hartrees (-653867.36653602 kcal/mol)

Sum of electronic and thermal Free Energies =

-1042.048209 hartrees (-653895.67162959 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -1038.399553 hartrees (-651606.10350303 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.220344 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1038.179209 hartrees (-651467.83543959 kcal/mol)

Sum of electronic and thermal Free Energies =

-1038.219214 hartrees (-651492.93897714 kcal/mol)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	2.164309	0.030510	-0.032354
2	8	1.310555	-0.276554	1.412226
3	1	1.344684	-1.187279	1.740671
4	8	1.371824	-0.649655	-1.321042
5	1	0.446233	-0.365682	-1.482482
6	14	-2.164318	-0.030556	0.032349
7	8	-1.310287	0.276295	-1.412129
8	1	-1.343227	1.187323	-1.739854
9	8	-1.371791	0.649509	1.321099
10	1	-0.446229	0.365437	1.482587
11	6	-3.847957	0.786730	-0.032861
12	1	-4.418622	0.563515	0.876799
13	1	-3.756558	1.878245	-0.097135
14	1	-4.431425	0.439347	-0.893738
15	6	-2.212709	-1.902537	0.106101
16	1	-2.662897	-2.247228	1.044759
17	1	-2.797045	-2.315914	-0.724906
18	1	-1.202445	-2.324470	0.038392
19	6	3.848186	-0.786307	0.032616
20	1	3.757129	-1.877860	0.096705
21	1	4.418712	-0.562747	-0.877046
22	1	4.431616	-0.438877	0.893504
23	6	2.212096	1.902527	-0.106071
24	1	2.796765	2.316095	0.724604
25	1	2.661608	2.247405	-1.044985
26	1	1.201725	2.324116	-0.037734

Deprotonated Dimethylsilanediol Dimer

B3LYP/6-31+G(d)

HF = -1041.6664898 hartrees (-653656.139014398 kcal/mol)

Imaginary Frequencies: none found

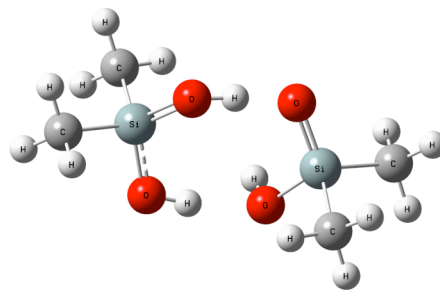
Zero-point correction = 0.195074 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1041.471416 hartrees (-653533.72825416 kcal/mol)

Sum of electronic and thermal Free Energies =

-1041.516198 hartrees (-653561.82940698 kcal/mol)



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	-2.093998	0.011017	-0.121763
2	8	-1.399935	0.285399	1.456604
3	1	-1.194447	1.224893	1.579857
4	8	-1.148892	0.534022	-1.288915
5	1	0.320971	-0.040448	-1.449769
6	14	2.100731	-0.007376	-0.028306
7	8	1.287967	-0.388133	-1.405500
8	8	1.348424	-0.509718	1.383314
9	1	0.383397	-0.330591	1.453996
10	6	3.754179	-0.918711	-0.051178
11	1	4.337399	-0.712913	0.856192
12	1	3.584580	-2.001429	-0.106487
13	1	4.355276	-0.625585	-0.921846
14	6	2.401029	1.865241	0.078177
15	1	2.907445	2.145413	1.012173
16	1	3.012283	2.215358	-0.765010
17	1	1.443504	2.400368	0.030904
18	6	-3.790257	0.888496	-0.066891
19	1	-3.660278	1.977547	0.007950
20	1	-4.352996	0.694772	-0.990759
21	1	-4.403165	0.558151	0.783760
22	6	-2.394870	-1.863712	-0.037840
23	1	-2.999793	-2.148598	0.834304
24	1	-2.911611	-2.210560	-0.943197
25	1	-1.437832	-2.397797	0.021286

Deprotonated Dimethylsilanediol Dimer and Water

B3LYP/6-31+G(d)

HF = -1118.1155646 hartrees (-701628.697942146 kcal/mol)

Imaginary Frequencies: none found

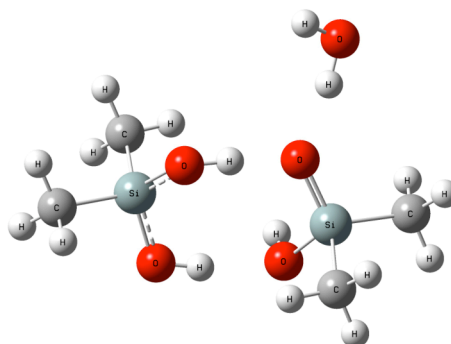
Zero-point correction = 0.219632 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1117.895933 hartrees (-701490.87691683 kcal/mol)

Sum of electronic and thermal Free Energies =

-1117.947421 hartrees (-701523.18615171 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -1113.9596464 hartrees (-699020.817712464 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.233365 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-1113.726282 hartrees (-698874.37921782 kcal/mol)

Sum of electronic and thermal Free Energies =

-1113.769456 hartrees (-698901.47133456 kcal/mol)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	-1.921194	-0.548522	-0.012711
2	8	-1.032835	-1.518898	1.123955
3	1	-0.914734	-1.051825	1.965339
4	8	-1.189857	0.849291	-0.276952
5	1	0.341103	0.840188	-0.849649
6	14	2.270812	-0.022855	-0.003454
7	8	1.319648	0.748452	-1.108070
8	8	1.732370	-1.554343	0.408446
9	1	0.775638	-1.641072	0.620074
10	6	3.965430	-0.285531	-0.787011
11	1	4.645466	-0.808191	-0.101718
12	1	3.868560	-0.892148	-1.696086
13	1	4.425015	0.671393	-1.066112
14	6	2.429952	1.016126	1.575687
15	1	3.024891	0.501771	2.342689
16	1	2.900572	1.986560	1.367137
17	1	1.435265	1.220663	1.992758
18	6	-3.661570	-0.355541	0.732669
19	1	-3.625115	0.229316	1.662136
20	1	-4.319840	0.186029	0.040107
21	1	-4.122868	-1.327339	0.957090
22	6	-2.003080	-1.725814	-1.495092
23	1	-2.452809	-2.692673	-1.230987
24	1	-2.594315	-1.280860	-2.306560
25	1	-0.994345	-1.913213	-1.884141
26	1	-1.144762	3.808669	-0.693271
27	8	-1.928199	3.450331	-0.251264
28	1	-1.735789	2.467905	-0.218921

Bis(trifluoromethyl)silanediol Dimer

B3LYP/6-31+G(d)

HF = -2233.1060032 hartrees (-1401296.34806803 kcal/mol)

Imaginary Frequencies: none found

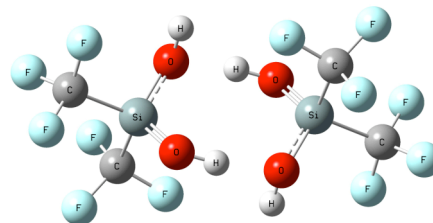
Zero-point correction = 0.115926 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-2232.990077 hartrees (-1401223.60321827 kcal/mol)

Sum of electronic and thermal Free Energies =

-2233.052360 hartrees (-1401262.6864236 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -2224.6623061 hartrees (-1395997.84370081 kcal/mol)

Imaginary Frequencies: none found

Zero-point correction = 0.125870 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-2224.6622874 hartrees (-1395997.83196637 kcal/mol)

Sum of electronic and thermal Free Energies =

-2224.587858 hartrees (-1395951.12677358 kcal/mol)

Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	-2.104954	-0.103755	0.097868
2	8	-1.207081	-0.467582	-1.254526
3	1	-1.091558	-1.406618	-1.477396
4	8	-1.454633	-0.554803	1.519761
5	1	-0.511415	-0.344183	1.677699
6	14	2.105011	0.103852	-0.097972
7	8	1.207078	0.468106	1.254268
8	1	1.091673	1.407208	1.476923
9	8	1.454854	0.554706	-1.520003
10	1	0.511518	0.344502	-1.677794
11	6	3.825540	0.973871	0.016642
12	6	2.292402	-1.820834	0.011195
13	6	-3.825334	-0.974068	-0.016767
14	6	-2.292667	1.820918	-0.010949
15	9	-4.534098	-0.930826	1.131090
16	9	-3.649797	-2.290416	-0.338476
17	9	-4.596729	-0.429273	-0.993686
18	9	-3.234038	2.279233	0.849734
19	9	-2.611207	2.274420	-1.243137
20	9	-1.110021	2.426683	0.338902
21	9	3.650220	2.290321	0.338056
22	9	4.534407	0.930254	-1.131137
23	9	4.596732	0.429136	0.993753
24	9	3.234099	-2.279398	-0.849002
25	9	2.610331	-2.274215	1.243590
26	9	1.109834	-2.426475	-0.339100

Deprotonated Bis(trifluoromethyl)silanediol Dimer

B3LYP/6-31+G(d)

HF = -2232.6274072 hartrees (-1400996.02429207 kcal/mol)

Imaginary Frequencies: none found

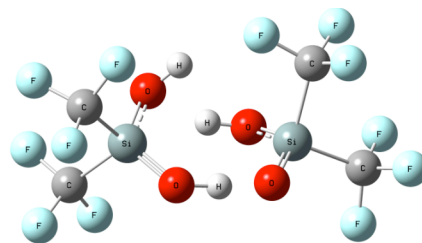
Zero-point correction = 0.101930 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-2232.525478 hartrees (-1400932.06269978 kcal/mol)

Sum of electronic and thermal Free Energies =

-2232.587069 hartrees (-1400970.71166819 kcal/mol)



Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	2.115600	-0.274635	0.106968
2	8	1.213024	-0.359849	1.390810
3	8	1.655451	-1.027436	-1.303349
4	1	0.700484	-0.998391	-1.484999
5	14	-2.029593	-0.049787	0.175677
6	8	-1.156975	0.301696	-1.191704
7	1	-0.563420	1.072920	-1.159706
8	8	-1.241360	-0.157161	1.558811
9	1	-0.161628	-0.263236	1.541794
10	6	-3.443726	1.277537	0.360280
11	6	-2.914084	-1.702875	-0.343942
12	6	3.929271	-0.944662	0.362442
13	6	2.357553	1.600722	-0.435196
14	9	4.694471	-0.937492	-0.771971
15	9	3.945698	-2.232889	0.816358
16	9	4.627948	-0.209968	1.284046
17	9	3.232014	1.811353	-1.460865
18	9	2.736303	2.445545	0.559850
19	9	1.138315	2.111272	-0.897099
20	9	-2.921054	2.542955	0.363035
21	9	-4.162561	1.157122	1.510086
22	9	-4.353029	1.248499	-0.661188
23	9	-3.857511	-2.091446	0.565733
24	9	-3.554906	-1.633972	-1.547287
25	9	-2.027329	-2.734504	-0.444274

Deprotonated Bis(trifluoromethyl)silanediol Dimer and Water

B3LYP/6-31+G(d)

HF = -2309.0668892 hartrees (-1448962.56364189 kcal/mol)

Imaginary Frequencies: none found

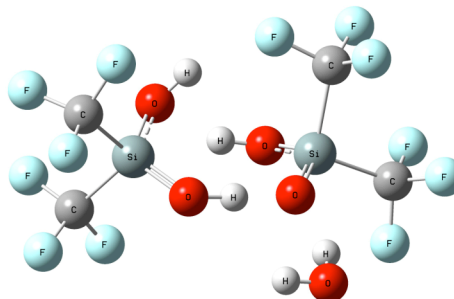
Zero-point correction = 0.127067 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-2308.939822 hartrees (-1448882.82770322 kcal/mol)

Sum of electronic and thermal Free Energies =

-2309.006370 hartrees (-1448924.5872387 kcal/mol)



HF/6-31+G(d,p)//B3LYP/6-31+G(d)

HF = -2300.2593285 hartrees (-1443435.73122703 kcal/mol)

Zero-point correction = 0.582093 (Hartree/Particle)

Sum of electronic and zero-point Energies =

-2300.2592519 hartrees (-1443435.68315977 kcal/mol)

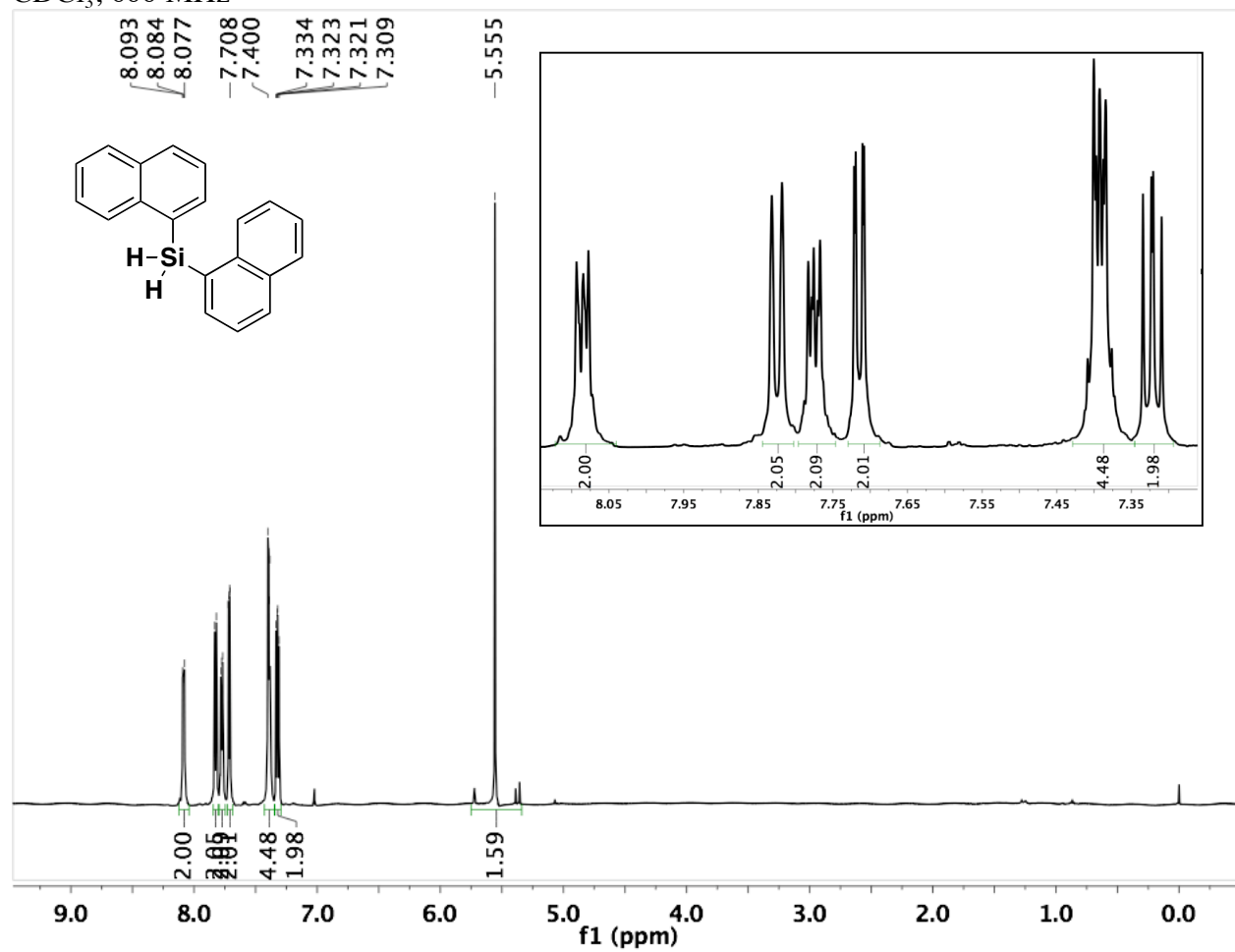
Sum of electronic and thermal Free Energies =

-2299.729484 hartrees (-1443103.24850484 kcal/mol)

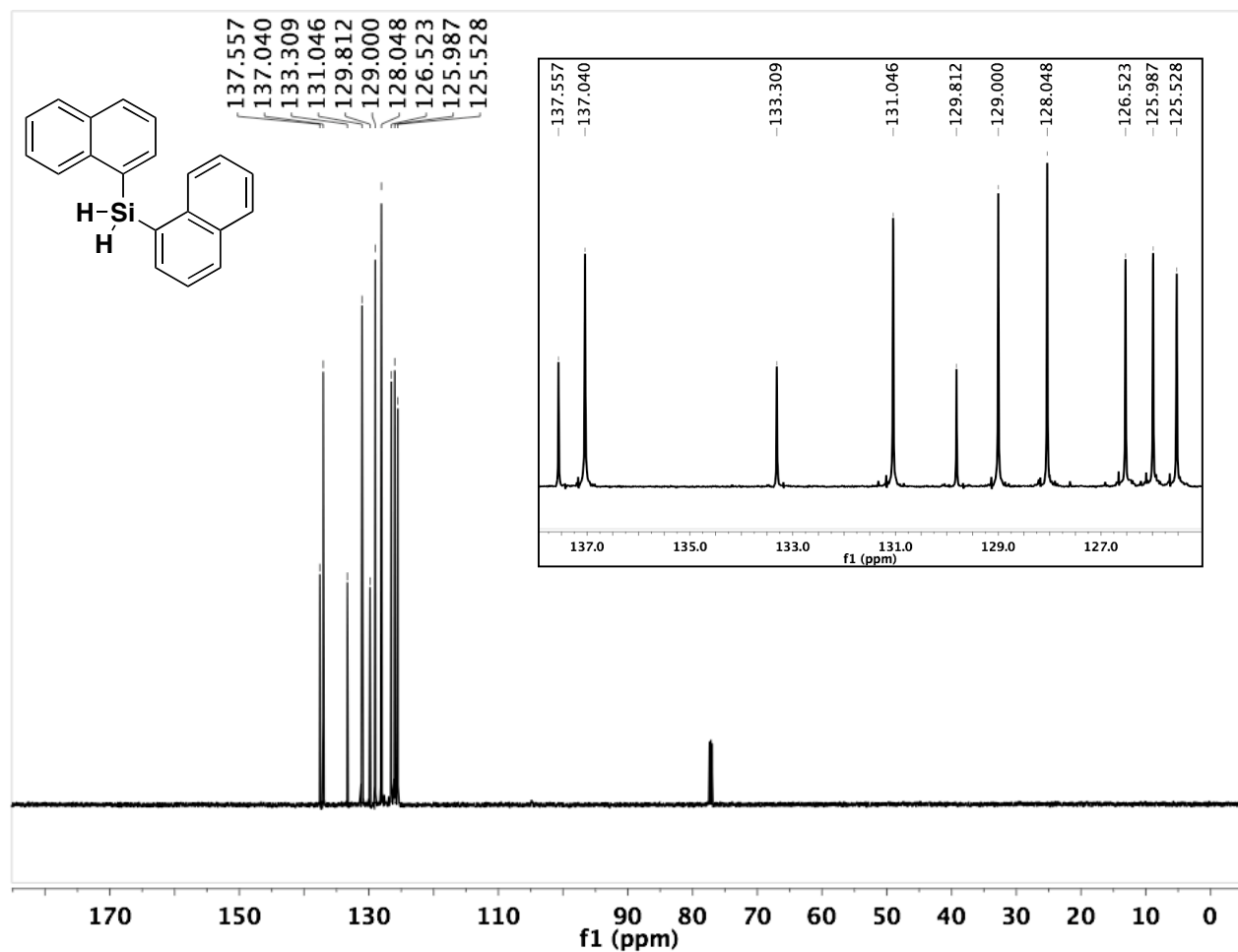
Center Number	Atomic Number	Coordinates (Angstroms)		
		X	Y	Z
1	14	2.075778	-0.200524	-0.166576
2	8	1.229142	-0.511937	1.128310
3	8	1.533640	-0.705221	-1.652540
4	1	0.575582	-0.620711	-1.798718
5	14	-2.085580	-0.028504	0.015287
6	8	-1.228786	0.564488	-1.273299
7	1	-0.647617	1.330839	-1.118230
8	8	-1.263380	-0.355939	1.351344
9	1	-0.211007	-0.441538	1.278376
10	6	-3.511995	1.219067	0.455322
11	6	-2.942655	-1.591324	-0.758324
12	6	3.895618	-0.892432	-0.124606
13	6	2.276220	1.742584	-0.380434
14	9	4.600873	-0.663909	-1.273976
15	9	3.927223	-2.241563	0.075270
16	9	4.636324	-0.339219	0.884158
17	9	3.089825	2.138812	-1.399331
18	9	2.703492	2.404391	0.724452
19	9	1.028431	2.306589	-0.680228
20	9	-3.010012	2.473675	0.666606
21	9	-4.201728	0.884372	1.579182
22	9	-4.439403	1.344082	-0.540611
23	9	-3.864590	-2.142435	0.085558
24	9	-3.599465	-1.335364	-1.925968
25	9	-2.035388	-2.569674	-1.035511
26	8	1.115554	-1.252412	3.865862
27	1	1.356794	-1.019283	2.942107
28	1	0.150747	-1.159930	3.868936

VIII. ^1H NMR Spectra

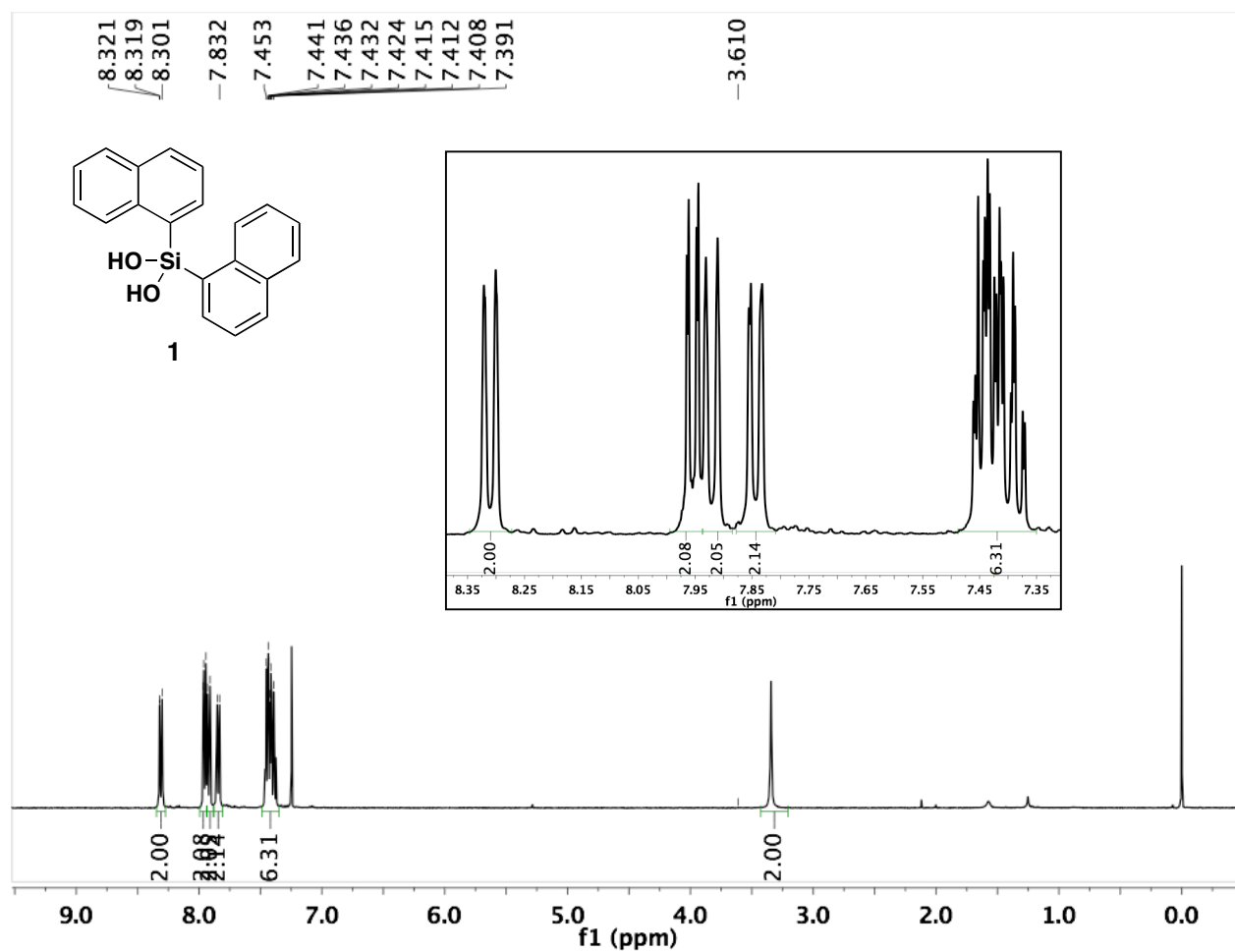
CDCl_3 , 600 MHz



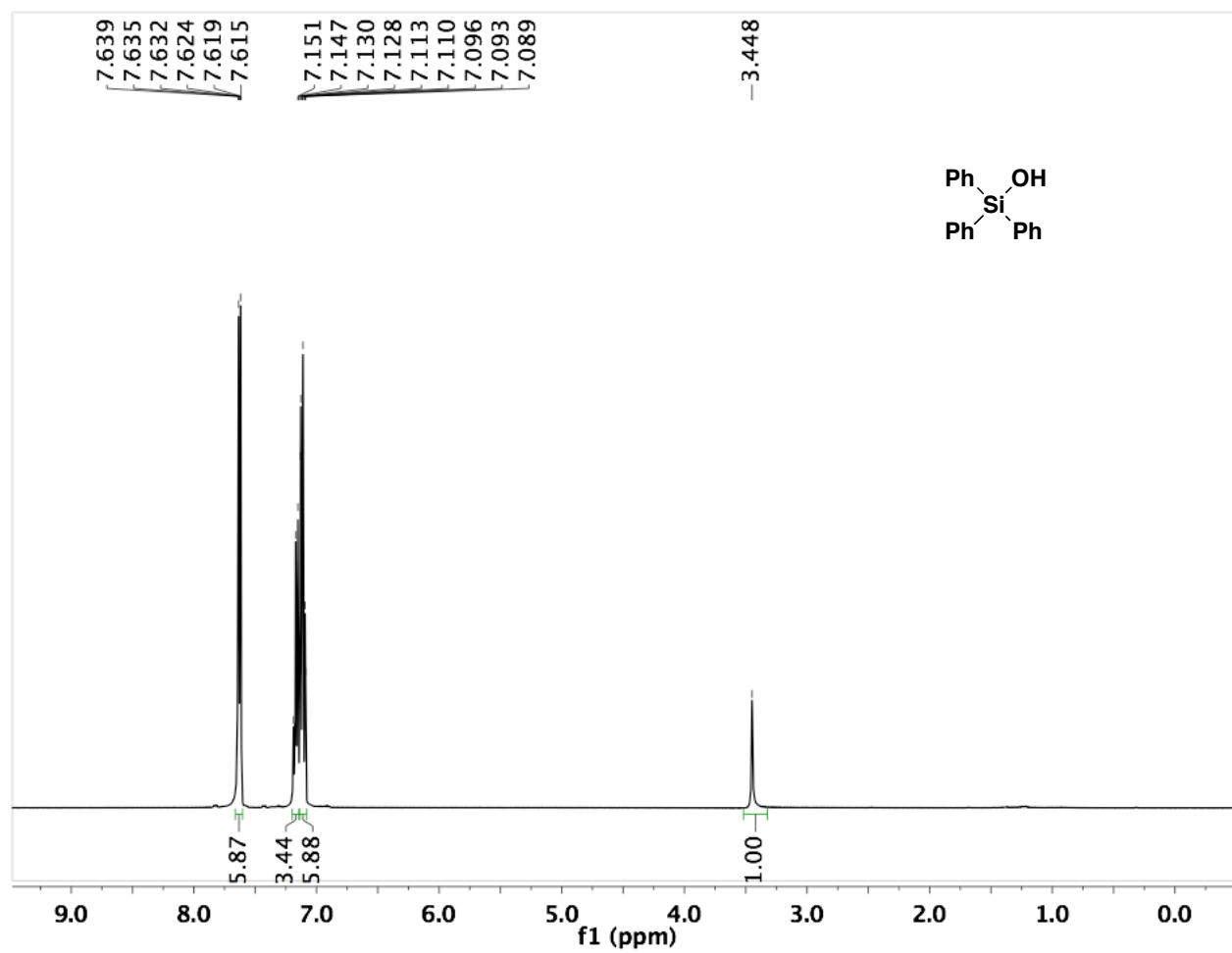
CDCl₃, 150 MHz



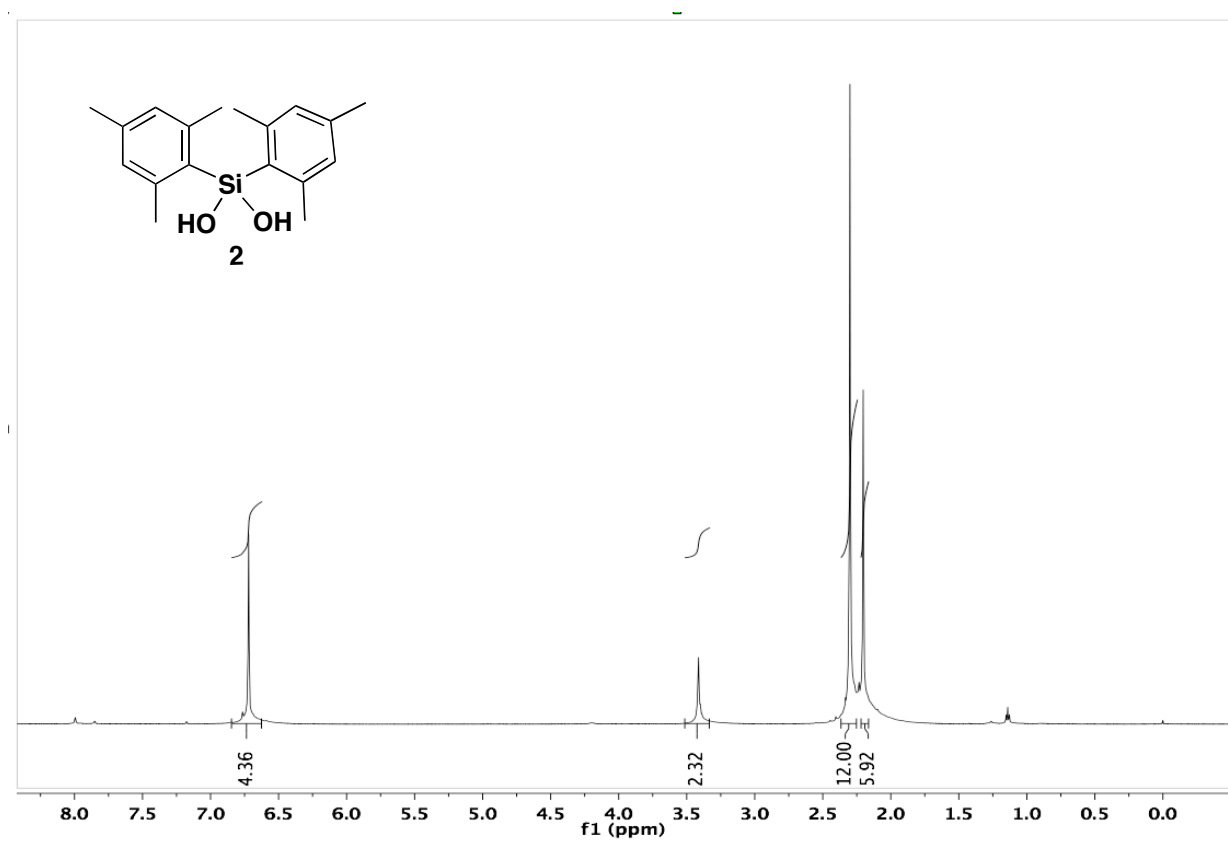
CDCl₃, 400 MHz



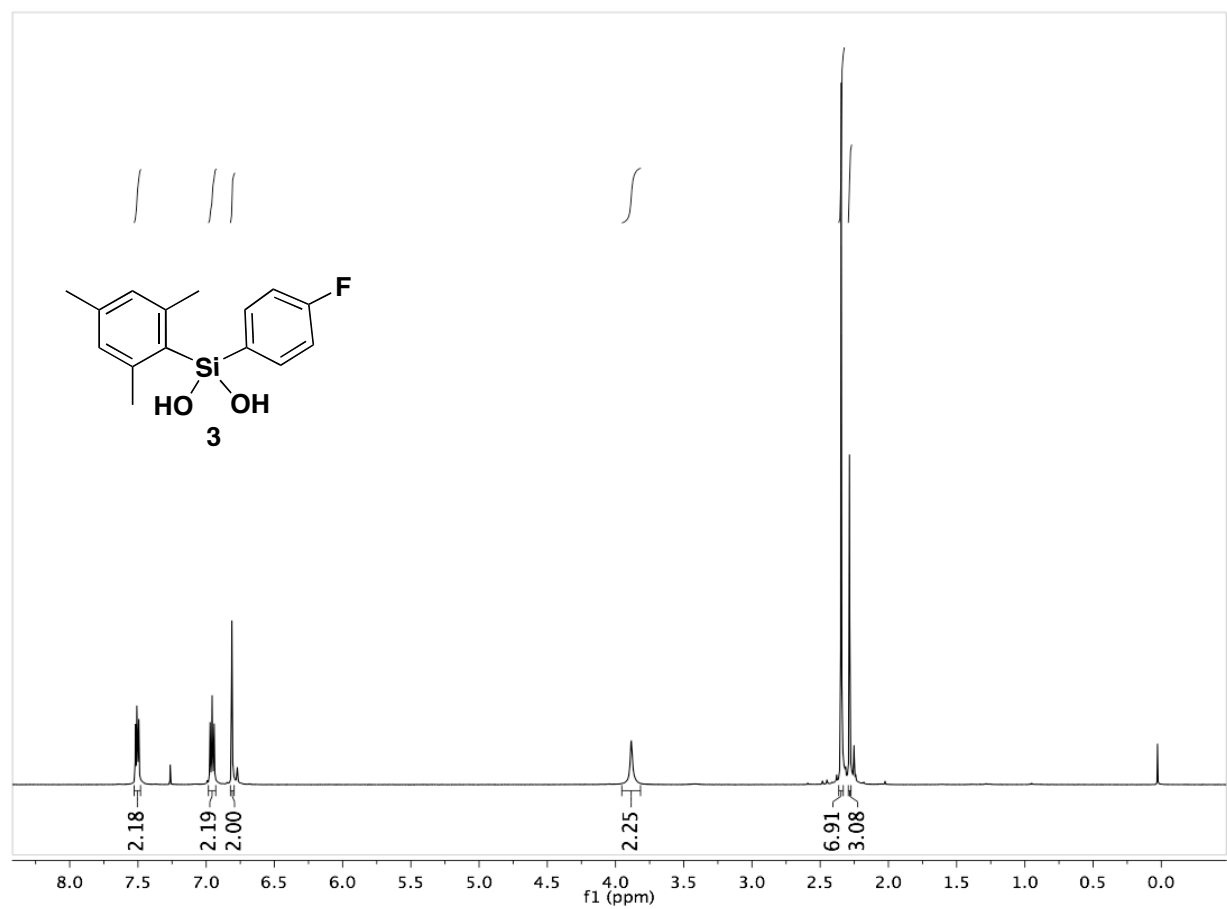
C₆D₆, 400 MHz



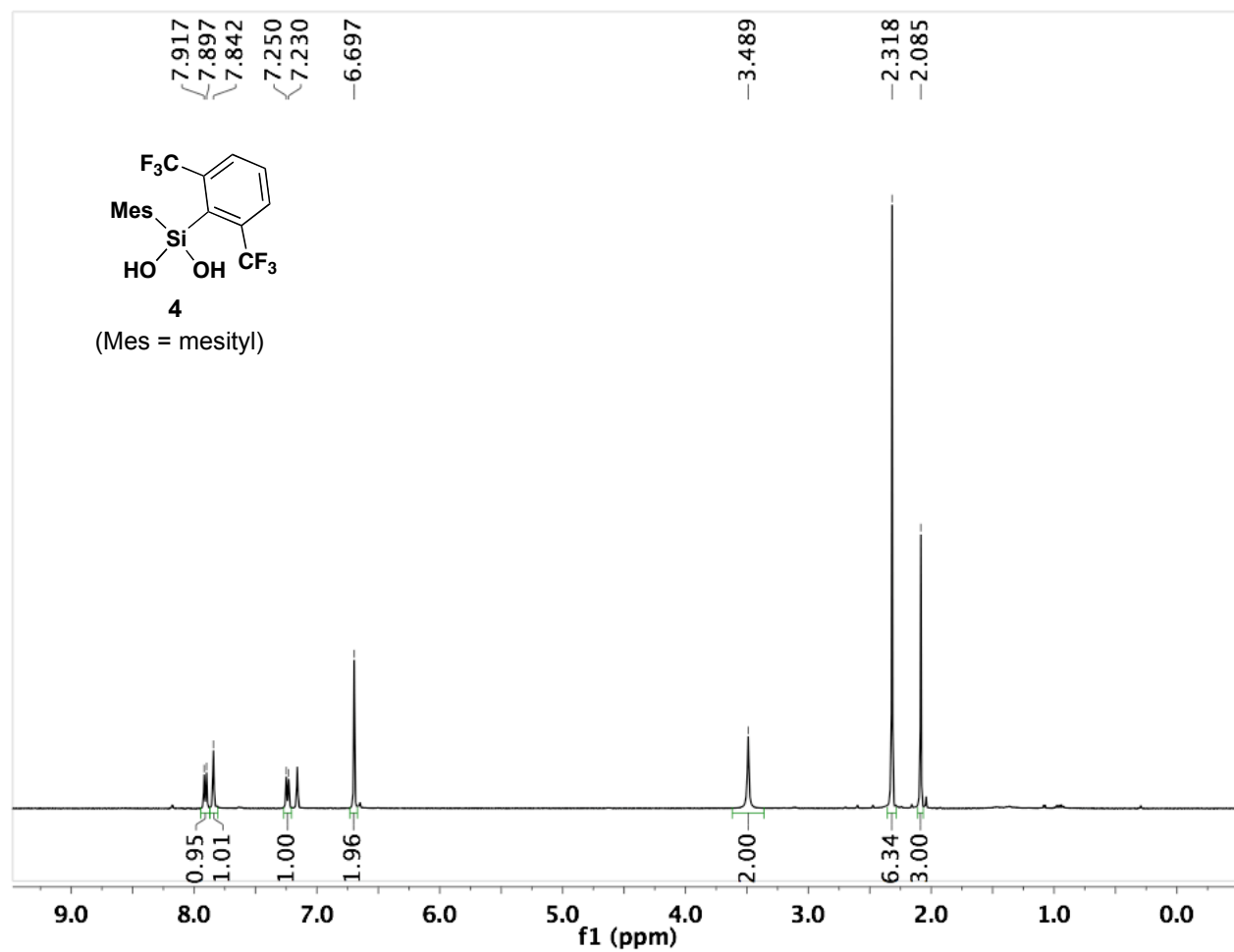
CDCl₃, 600 MHz



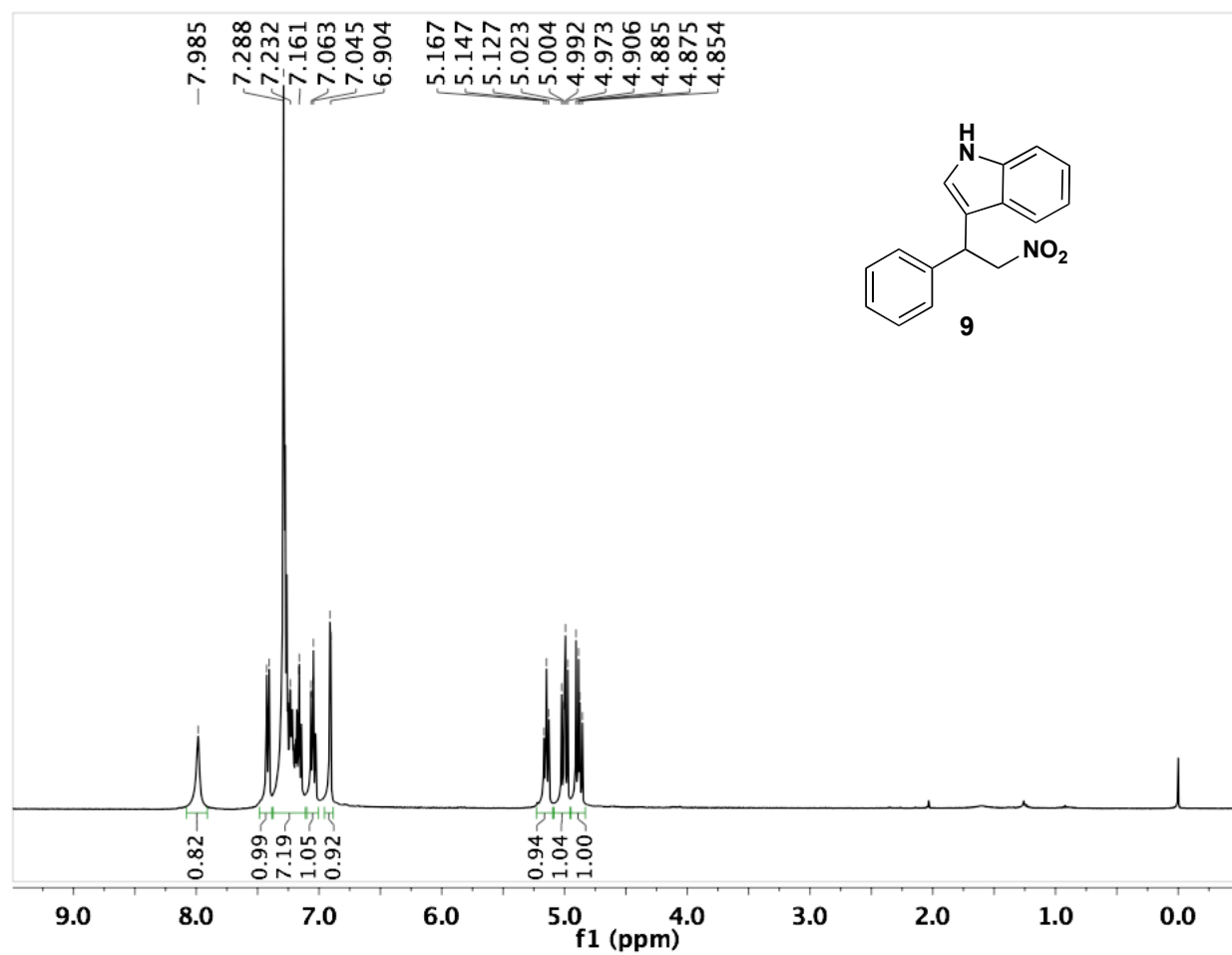
CDCl₃, 600 MHz



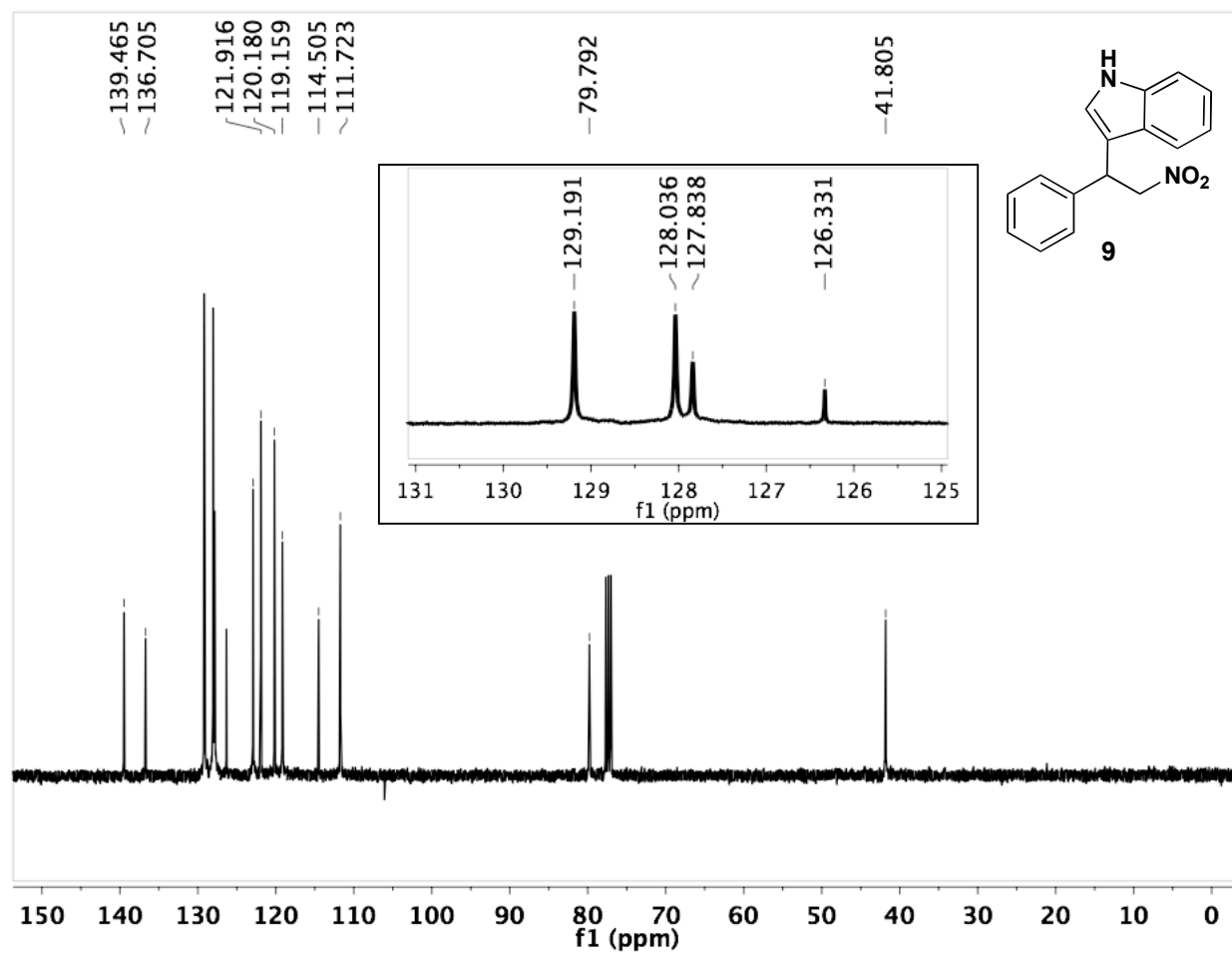
C₆D₆, 400 MHz



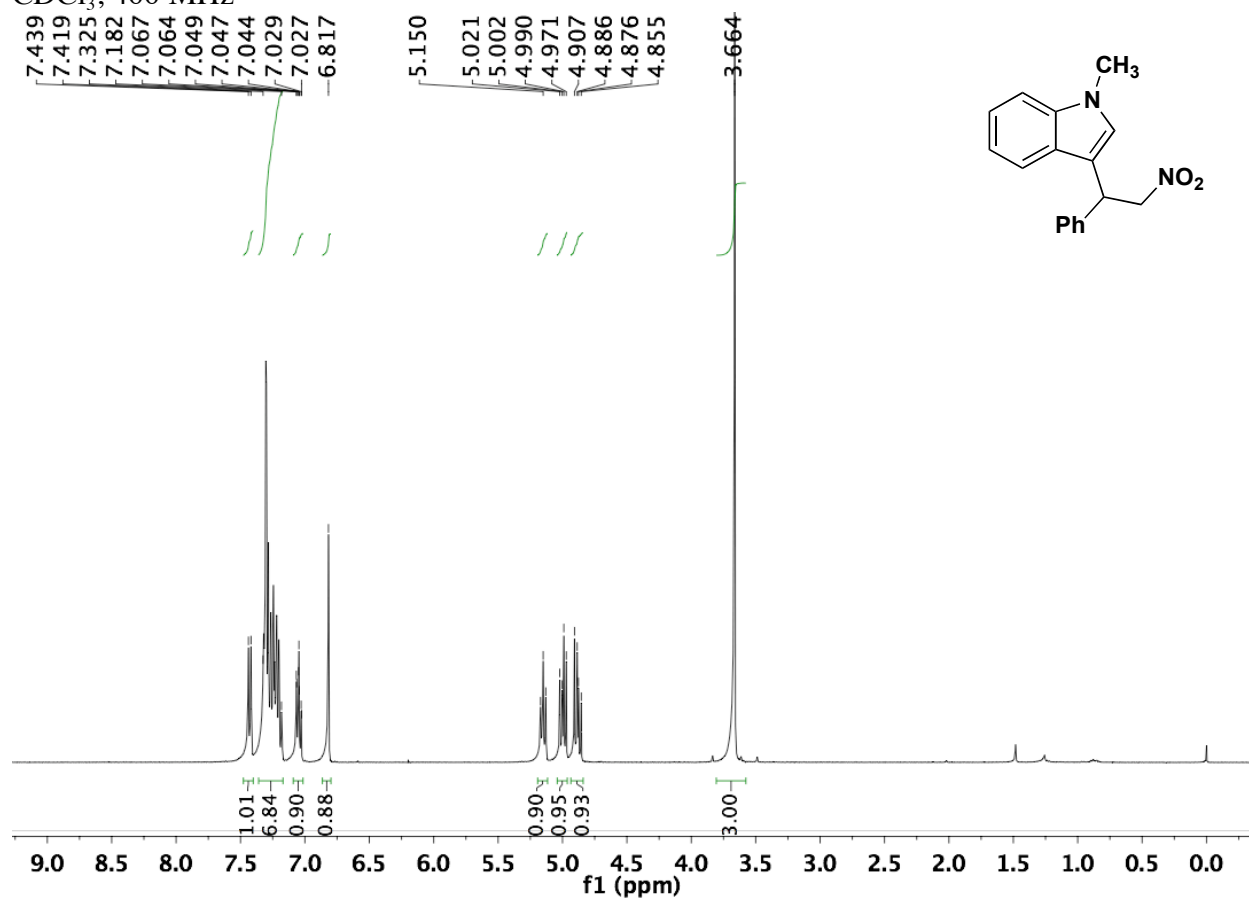
CDCl₃, 400 MHz



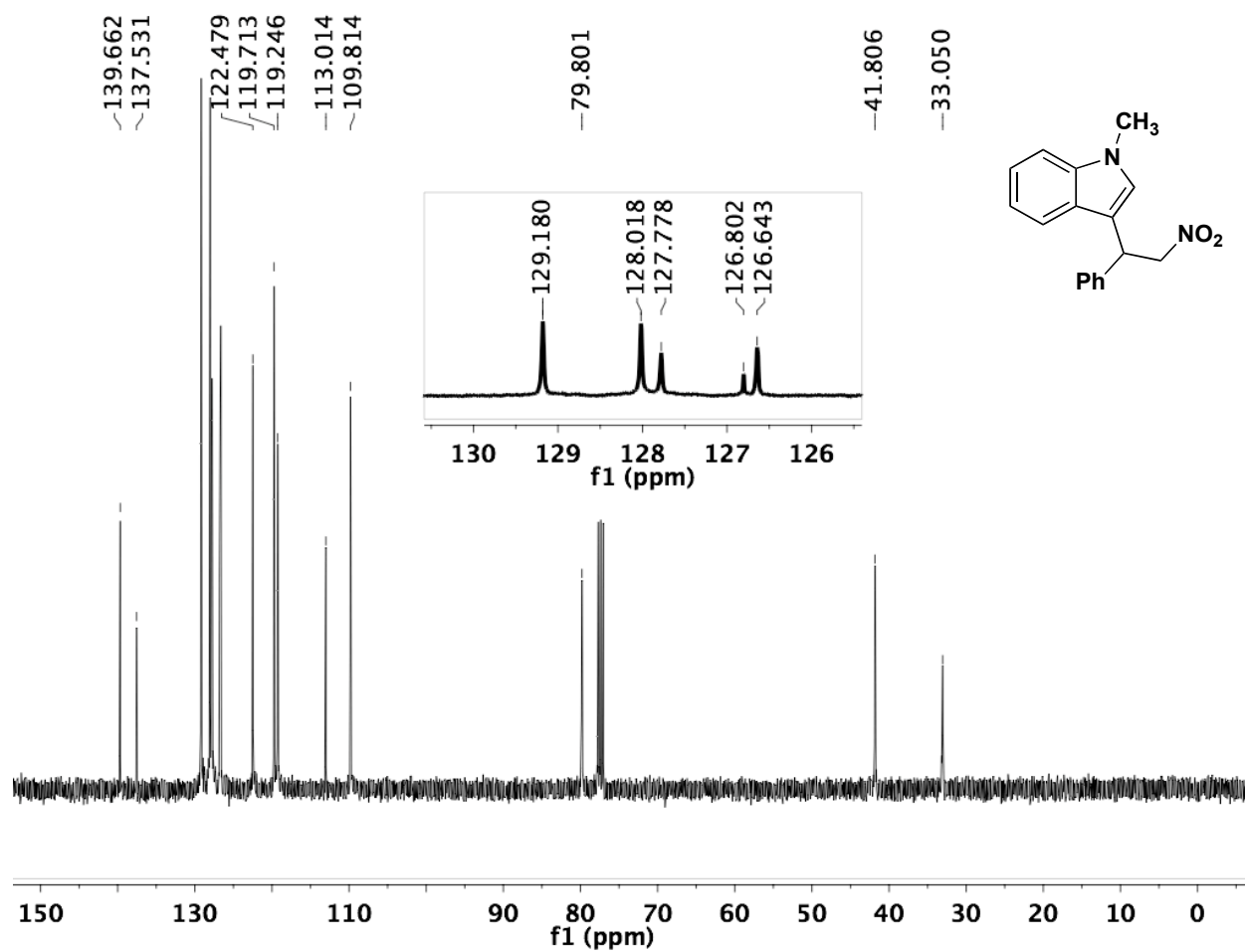
CDCl₃, 100 MHz



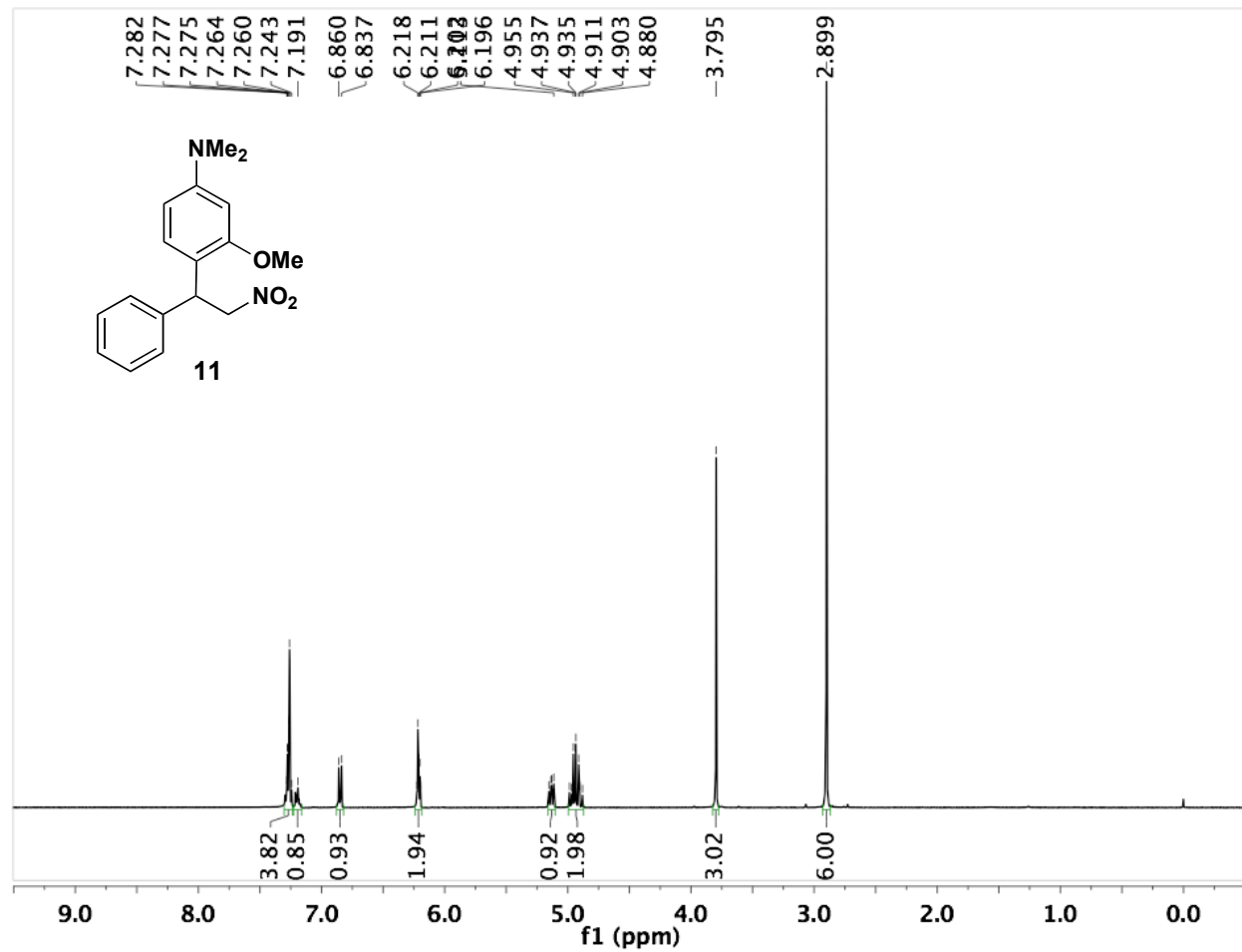
CDCl₃, 400 MHz



CDCl₃, 100 MHz



CDCl₃, 400 MHz



CDCl₃, 100 MHz

