

Supporting Information for:

**NMR and X-ray Studies of Hydrogen Bonding for
Amide-containing Silanediols**

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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), Varian Inova 400 (400 MHz for ^1H ; 100 MHz for ^{13}C), and/or Varian VNMRs 600 (600 MHz for ^1H ; 150 MHz for ^{13}C ; 119 MHz for ^{29}Si) at room temperature unless noted otherwise. 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, acetonitrile residual solvent (δ 1.94), 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, for ^{13}C signals in acetonitrile residual solvent (δ 118.67) 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), doublet (d), triplet (t), quartet (q), octet (o), and multiplet (m), broadened (b).

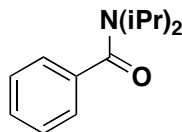
All HPLC analyses were performed on a Shimadzu LC-20AB system using a Daicel CHIRALPAK® AD-H column (4.6 x 250 mm, 5 μm), with a guard column, a flow rate of 0.8 mL/min (isopropanol/hexanes isocratic system) unless otherwise indicated, a Shimadzu SPD-M20A photodiode array detector, and 40 °C column oven temperature.

Compounds were analyzed for HRMS on a Thermo Fisher Orbitrap (San Jose, CA) using electrospray in the positive ion mode at >60,000 resolution and using typical ESI source values. These settings result in mass accuracies <5 ppm. Some compounds were analyzed in the positive ion mode by an Applied Biosystems Qtrap (Foster City, CA). Source parameters were 5kV spray voltage, with a curtain plate temperature of 275 °C and sheath gas setting of 15. Samples were analyzed via flow injection analysis by injecting 20 μL samples into a stream of 80% MeOH/20% 0.1% Formic Acid flowing at 200 μL per minute.

Materials and Purification. Dichloromethane (DCM), hexanes, ethyl acetate (EtOAc), tetrahydrofuran (THF), ammonium hydroxide, and diethyl ether (Et_2O) were obtained from EMD Chemicals. Palladium on carbon (5 wt%), anhydrous magnesium sulfate, boron trichloride (1.0 M in DCM), *sec*-butyllithium (1.4 M in cyclohexane), iodoethane, 1-naphthoyl chloride, benzoyl chloride, 3-fluorobenzoyl chloride, acetic acid (AcOH) and 2-mesitylmagnesium bromide solution (1.0 M in Et_2O) were acquired from Sigma Aldrich. 2-propanol (IPA), lithium aluminum hydride (4.0 M in Et_2O), and trichlorosilane were purchased from Acros Organics. Diisopropylamine and tetramethylethylenediamine (TMEDA) were purchased from Alfa-Aesar. Trifluoroacetic acid (TFA) was purchased from B&J BioSyn. Pyridine was purchased from Fisher Scientific. All chemicals were used as purchased, without further purification. Mesitylchlorosilane was synthesized according to procedures previously reported in literature.¹ *sec*-Butyllithium was titrated with diphenylacetic acid before use 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).

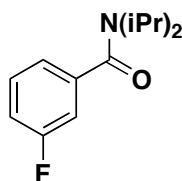
¹ Tran, N. T.; Min, T.; Franz, A. K. *Chem. Eur. J.* **2011**, *17*, 9897-9900.

II. Experimental Procedures and Characterization

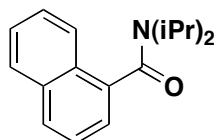


General procedure for diisopropylamides.

***N,N*-diisopropylbenzamide (5a).** An oven-dried, round-bottom flask was charged with diisopropylamine (0.77 mL, 5.5 mmol, 1.1 equiv), anhydrous DCM (12.5 mL), triethylamine (0.84 mL, 6 mmol, 1.2 equiv) and a stirbar under argon. The solution was cooled to 0 °C and the corresponding acyl chloride (5 mmol, 1 equiv) was added dropwise. Upon addition, the solution bubbled and solid precipitated out. After stirring for 2 h at 0 °C the solution was quenched upon addition of 1 N HCl (10 mL) and the organic and aqueous layers were separated. The aqueous layer was extracted with DCM (3 x 10 mL). The combined organic layers were washed with H₂O (3 x 10 mL), brine (1 x 10 mL), dried over MgSO₄, filtered, and concentrated. The resulting solid was recrystallized in hexanes/EtOAc to give 657 mg of amide **5a** (64% yield). Spectroscopic data matched that of literature reports.²



3-fluoro-*N,N*-diisopropylbenzamide (5b). The general procedure for diisopropylamides was followed starting with 3-fluorobenzoyl chloride (2.43 mL, 20 mmol) and subjected to column chromatography (15% EtOAc/Hexanes) to give 4.039 g (90% yield) of amide **5b** as a light yellow liquid which solidified upon standing. Spectral data was consistent with previously reported data.³

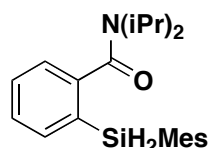


***N,N*-diisopropyl-1-naphthalenecarboxamide (5c).** The general procedure for the synthesis of diisopropylamides was followed using 1-naphthoyl chloride (0.75 mL, 5.0 mmol). The crude mixture was purified by recrystallization (hexanes/EtOAc) to give 0.753 g of amide **5c** (59% yield) as a white powder. Spectroscopic data matched that of previously reported literature.⁴

² Beak, P.; Kerrick, S. T.; Gallagher, D. J. *J. Am. Chem. Soc.* **1993**, *115*, 10628-10636.

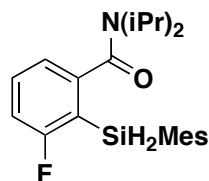
³ Arnold, K.; Batsanov, A. S.; Davies, B.; Whiting, A. *Green Chemistry*. **2008**, *10*, 124-134.

⁴ Clayden, J.; Pink, J. H.; Westlund, N.; Frampton, C. S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 901-917.

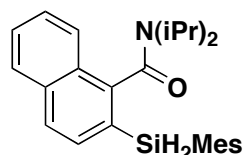


General Procedure for Lithiation/Silylation.

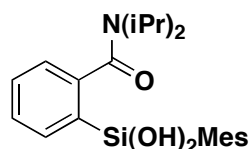
***N,N*-Diisopropyl-2-(mesitylsilyl)benzamide (6a).** An oven-dried, round-bottom flask was charged with *N,N*-diisopropylbenzamide (300 mg, 1.46 mmol, 1 equiv), TMEDA (0.22 mL, 1.61 mmol, 1.1 equiv), anhydrous THF (1.5 mL), and a stirbar under argon and subsequently cooled to $-78\text{ }^{\circ}\text{C}$. Freshly titrated *sec*-BuLi (1.30 M, 1.35 mL, 1.75 mmol, 1.2 equiv) was added dropwise and allowed to react for 2 h at $-78\text{ }^{\circ}\text{C}$. A separate solution of **5a** (351 mg, 1.90 mmol, 1.3 equiv) in anhydrous THF (1.5 mL) under argon was prepared and added dropwise to the lithiated solution at $-78\text{ }^{\circ}\text{C}$. Upon complete addition of the chlorosilane, the reaction mixture was removed from the cold bath and allowed to warm to $23\text{ }^{\circ}\text{C}$. Within 5 min the solution color changes from red to clear, indicating complete reaction. The solution was diluted in Et₂O and washed with 1 N HCl. The aqueous layer was extracted with Et₂O (3 x 10 mL). The combined organic layers were washed with H₂O (3 x 10 mL), brine (1 x 10 mL), dried over MgSO₄, filtered, and excess solvent was removed *in vacuo* to give a light-yellow oil. The product was purified by column chromatography (5% EtOAc/hexanes) to give 181 mg of silane **6a** (35% yield) as a clear oil. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.29 (m, 2H), 7.29 – 7.15 (m, 2H), 6.87 (s, 2H), 5.02 (s, 2H), 3.95 – 3.70 (bs, 1H), 3.66 – 3.35 (bs, 1H), 2.39 (s, 6H), 2.28 (s, 3H), 1.69 – 1.34 (bs, 6H), 1.30 – 0.96 (bs, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 171.5, 145.6, 145.3, 140.1, 136.8, 130.9, 129.4, 128.5, 128.3, 126.4, 124.9, 51.3, 46.2, 24.0, 21.5, 20.9. ²⁹Si NMR (119 MHz, CDCl₃) δ -47.2. HRMS *m/z* [M - H]⁺ calcd for C₂₂H₃₀NOSi, 352.2097. Found 352.2083.



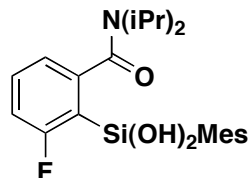
3-fluoro-*N,N*-diisopropyl-2-[(mesityl)silyl]benzamide (6b). Substrate **5b** (222 mg, 0.994 mmol) was subjected to the general procedure for lithiation/silylation. The product was purified by column chromatography (hexanes to 7% EtOAc/hexanes) to give 100 mg (27% yield) of silane **6b** as a white powder. ¹H NMR (600 MHz, CDCl₃) δ 7.38 (ddd, *J* = 6.1, 6.1, 4.6 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.94 (dd, *J* = 8.4, 8.4 Hz, 1H), 6.86 (s, 2H), 5.05 (d, *J* = 4.0 Hz, 2H), 3.76 (dt, *J* = 12.9, 6.4 Hz, 1H), 3.50 (dt, *J* = 13.2, 6.5 Hz, 1H), 2.48 (s, 6H), 2.28 (s, 3H), 1.56 (d, *J* = 6.7 Hz, 6H), 1.14 (d, *J* = 6.5 Hz, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 169.6 (d, *J*_{CF}⁴ = 2.2 Hz), 167.7 (d, *J*_{CF}¹ = 243.9 Hz), 147.0 (d, *J*_{CF}³ = 8.4 Hz), 145.2, 139.9, 131.9 (d, *J*_{CF}³ = 8.9 Hz), 128.3, 125.2 (*J*_{CF}⁴ = 1.9 Hz), 121.1 (d, *J*_{CF}⁴ = 2.9 Hz), 117.5 (d, *J*_{CF}² = 29.3 Hz), 114.8 (d, *J*_{CF}² = 25.8 Hz), 51.0, 46.1, 23.6, 21.2, 20.7, 20.4. ²⁹Si NMR (119 MHz, CDCl₃) δ -59.3 (d, *J*_{SiF}³ = 11.2 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -96.2. HRMS *m/z* [M - H]⁺ calcd for C₂₂H₂₉FNOSi, 370.2002. Found 370.1995.



***N,N*-diisopropyl-2-[(mesityl)silyl]naphthalene-1-carboxamide (6c).** Substrate **5c** (300 mg, 1.17 mmol, 1 equiv) was subjected to the general procedure for lithiation/silylation. The product was purified by column chromatography (100% hexanes to 7% EtOAc/hexanes) to give 218 mg of silane **6c** (46% yield) as a white powder. ^1H NMR (600 MHz, CDCl_3) δ 7.89 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.2 Hz, 1H), 7.53 – 7.40 (m, 2H), 7.25 (d, J = 8.2 Hz, 1H), 6.91 (s, 2H), 5.16 (d, J = 5.0 Hz, 1H), 5.13 (d, J = 5.0 Hz, 1H), 3.70 – 3.61 (m, 1H), 3.60 – 3.51 (m, 1H), 2.43 (s, 6H), 2.30 (s, 3H), 1.79 (d, J = 6.7 Hz, 3H), 1.73 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.3 Hz, 3H), 1.00 (d, J = 6.2 Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 169.8, 145.5, 144.3, 140.2, 134.0, 131.0, 129.4, 128.4, 128.1, 127.2, 126.9, 126.5, 125.8, 125.5, 125.2, 51.3, 46.5, 23.9, 21.3, 21.0, 21.0, 20.7, 20.6. ^{29}Si NMR (119 MHz, CDCl_3) δ -53.3. HRMS m/z $[\text{M} - \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{32}\text{NOSi}$, 402.2253. Found 402.2243.

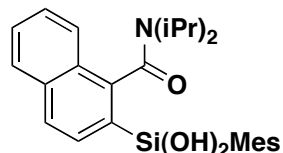


2-[dihydroxy(mesityl)silyl]-*N,N*-diisopropylbenzamide (1). A round-bottom flask was charged with **6c** (181 mg, 0.511 mmol, 1.0 equiv), 1.0 mL THF, Pd/C (10 wt. %, 55 mg, 0.0511 mmol, 0.1 equiv), and a magnetic stir bar. To this mixture was added deionized H_2O (92 μL , 5.11 mmol, 10.0 equiv) and the round-bottom flask was capped with a rubber septa while using a needle to vent H_2 gas produced during reaction. The reaction was stirred overnight, at which point the solution was diluted with Et_2O and excess H_2O was dried with Na_2SO_4 (this also helps with removal of Pd/C). It should be noted that MgSO_4 should not be used as it promotes condensation with less stable silanediols. The solution was filtered over Celite and excess solvent was removed *in vacuo*. The crude product was purified by column chromatography (15% EtOAc/hexanes) to give 179 mg (91% yield) of silanediol **1** as a colorless liquid (the product solidified upon washing with hexanes and drying *in vacuo*). mp = 65–68 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ 7.67 – 7.64 (m, 1H), 7.32 (ddd, J = 9.0, 9.0, 1.5 Hz, 1H), 7.28 (ddd, J = 9.0, 9.0, 1.5 Hz, 1H), 7.16 – 7.13 (m, 1H), 6.75 (s, 2H), 4.59 (s, 2H), 3.82 – 3.63 (m, 1H), 3.41 – 3.24 (m, 1H), 2.39 (s, 6H), 2.23 (s, 3H), 1.38 (d, J = 6.8 Hz, 6H), 0.94 (d, J = 6.6 Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 173.6, 145.5, 142.4, 139.7, 137.3, 135.6, 128.9, 128.8, 128.4, 128.2, 124.9, 51.6, 45.9, 24.2, 21.1, 20.3, 20.2. ^{29}Si NMR (119 MHz, CDCl_3) δ -24.8. IR (neat) 3345, 1602, 1342, 907, 748 cm^{-1} . HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{31}\text{NNaO}_3\text{Si}$, 408.1965. Found 408.1966.

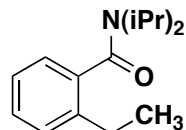


2-[dihydroxy(2,4,6-trimethylphenyl)silyl]-3-fluoro-*N,N*-diisopropylbenzamide (2). Substrate **5b** (169 mg, 0.455 mmol) was subjected to the general procedure for hydrolysis of silanes. The product was purified by column chromatography (100% hexanes to 7% EtOAc/hexanes) to give

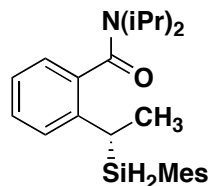
152 mg of silanediol **2** as a colorless liquid (83% yield), which solidified upon washing with hexanes and concentrating. mp = 59-62 °C. ¹H NMR (600 MHz, CD₃CN) δ 7.50 – 7.38 (m, 1H), 7.14 – 7.01 (m, 2H), 6.81 (s, 2H), 4.91 (s, 2H), 3.80 – 3.62 (m, 1H), 3.59 – 3.45 (m, 1H), 2.41 (s, 6H), 2.24 (s, 3H), 1.44 (d, *J* = 6.8 Hz, 6H), 1.03 (d, *J* = 5.6 Hz, 6H). ¹³C NMR (150 MHz, CD₃CN) δ 173.3, 168.4 (d, *J*_{CF} = 241.8 Hz), 146.2 (d, *J*³ = 9.1 Hz), 146.0, 141.0, 133.0 (d, *J*³ = 9.3 Hz), 131.4, 130.2, 125.4 (d, *J*² = 27.1 Hz), 123.3, 116.9 (d, *J*² = 26.9 Hz), 53.0, 47.1 24.6, 21.6, 21.1 20.8. ²⁹Si NMR (119 MHz, CDCl₃) δ -29.0 (d, *J*_{SiF}³ = 9.3 Hz). ¹⁹F NMR (282 MHz, CDCl₃) δ -98.7. IR (neat) 3348, 2972, 1606, 1343, 796 cm⁻¹. HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₂H₃₀FNNaO₃Si, 426.1877. Found 426.1865.



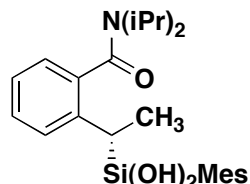
2-[dihydroxy(mesityl)silyl]-N,N-diisopropynaphthalene-1-carboxamide (3). Substrate **6c** was subjected to the general procedure for hydrolysis of silanes. The product was purified by column chromatography (hexanes to 7% EtOAc/hexanes) to give 98 mg of silanediol **3** (56% yield). mp = 86-90 °C. ¹H NMR (600 MHz, CD₃CN) δ 7.96 – 7.89 (m, 1H), 7.89 – 7.86 (m, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 1H), 6.85 (s, 2H), 5.10 (s, 1H), 4.86 (s, 1H), 3.73 – 3.53 (m, 1H), 3.49 – 3.23 (m, 1H), 2.43 (s, 6H), 2.26 (s, 3H), 1.70 (d, *J* = 6.8 Hz, 3H), 1.55 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (150 MHz, CD₃CN) δ 173.3, 146.8, 143.0, 141.3, 135.1, 134.8, 132.2, 130.3 130.3, 130.2, 129.6, 128.6, 128.5, 128.0, 126.4, 53.2, 47.5, 25.1, 21.6, 21.4, 20.9, 20.7, 20.6. ²⁹Si NMR (119 MHz, CH₃CN) δ -23.8. IR (neat) 3334, 2965, 2929, 1591, 1503 cm⁻¹. HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₆H₃₃NNaO₃Si, 458.2122. Found 458.2119.



2-ethyl-N,N-diisopropylbenzamide (7). An oven-dried, round-bottom flask was charged with **5a** (3.000 g, 14.61 mmol, 1 equiv), TMEDA (2.40 mL, 16.07 mmol, 1.1 equiv.), anhydrous THF (40 mL) under argon and cooled to -78 °C. To the pre-cooled solution was added freshly titrated *sec*-butyllithium dropwise (1.30 M in cyclohexane, 12.4 mL, 16.07 mmol, 1.1 equiv) and the mixture was allowed to stir at -78 °C. After 1.5 h, iodoethane (2.3 mL, 29.23 mmol, 2.0 equiv) was added dropwise. The reaction was allowed to slowly warm to room temperature overnight at which point the reaction was quenched with 1 N HCl. The aqueous layer was extracted with Et₂O (3 x 15 mL). The combined organic layers were washed with H₂O (3 x 10 mL), brine (1 x 10 mL), dried over MgSO₄, filtered, and excess solvent was removed *in vacuo* to give a white powder. The crude mixture was purified by recrystallization (EtOAc/hexanes) to give 2.693 g of amide **7** as a white solid (79% yield). All spectroscopic data matched that of previously reported literature.²



***N,N*-diisopropyl-2-[(1*S*)-1-[(mesityl)silyl]ethyl]benzamide (8).** An oven-dried, round-bottom flask was charged with **7** (216 mg, 0.926 mmol, 1 equiv), (-)-sparteine (0.23 mL, 1.019 mmol, 1.1 equiv), anhydrous Et₂O (2 mL), and a stirbar under argon and subsequently cooled to -78 °C. Freshly titrated *sec*-BuLi (1.40 M, 0.79 mL, 1.111 mmol, 1.2 equiv) was added dropwise and allowed to react for 6 h at -78 °C. A separate solution of MesSiH₂Cl (205 mg, 1.11 mmol, 1.2 equiv) in anhydrous THF (1 mL) under argon was prepared and added dropwise to the lithiated solution at -78 °C. Upon complete addition of the chlorosilane the mixture was allowed to stir at -78 °C for 2 h. The solution was diluted in Et₂O washed with 5% H₃PO₄. The aqueous layer was extracted with Et₂O (3 x 10 mL). The combined organic layers were washed with H₂O (3 x 10 mL), brine (1 x 10 mL), dried over MgSO₄, filtered, and excess solvent was removed *in vacuo* to give a light yellow oil. The product was purified by column chromatography (hexanes to 7% EtOAc/hexanes) to give 235 mg of silane **8** (67% yield) as a colorless oil. Enantiomeric excess was determined by HPLC with a Daicel CHIRALPAK® AD-H column (5% IPA/hexanes), 0.8 mL/min, 40 °C. *t_R* (major) = 5.5 min, *t_R* (minor) = 21.6 min. 76:24 *er*. [α]_D²³ = +3.4 (*c* 0.210, MeOH). The absolute configuration was assigned by analogy to previous literature reports.⁵ The product is an inseparable 2:1 mixture of rotamers. The characterization for the major conformer is as follows: ¹H NMR (600 MHz, CDCl₃) δ 7.21 (d, *J* = 3.9 Hz, 1H), 7.11 – 7.00 (m, 3H), 6.80 (s, 2H), 4.45 – 4.38 (m, 2H), 3.72 – 3.58 (m, 1H), 3.50 – 3.37 (m, 1H), 2.65 – 2.54 (m, 1H), 2.39 (s, 6H), 2.21 (s, 3H), 1.53 (d, *J* = 6.1, 3H), 1.52 (d, *J* = 5.8, 3H), 1.36 (d, *J* = 7.4, 3H), 1.01 (d, *J* = 7.1 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 170.4, 145.2, 141.5, 139.7, 137.5, 128.4, 128.3, 128.2, 127.1, 125.1, 124.9, 50.5, 45.6, 24.0, 22.1, 21.2, 20.9, 20.8, 20.5, 20.5, 18.1. ²⁹Si NMR (119 MHz, CDCl₃) δ -35.2 (minor rotamer δ -37.0). HRMS *m/z* [M - H]⁺ calcd for C₂₄H₃₄NOSi, 380.2410. Found 380.2396.



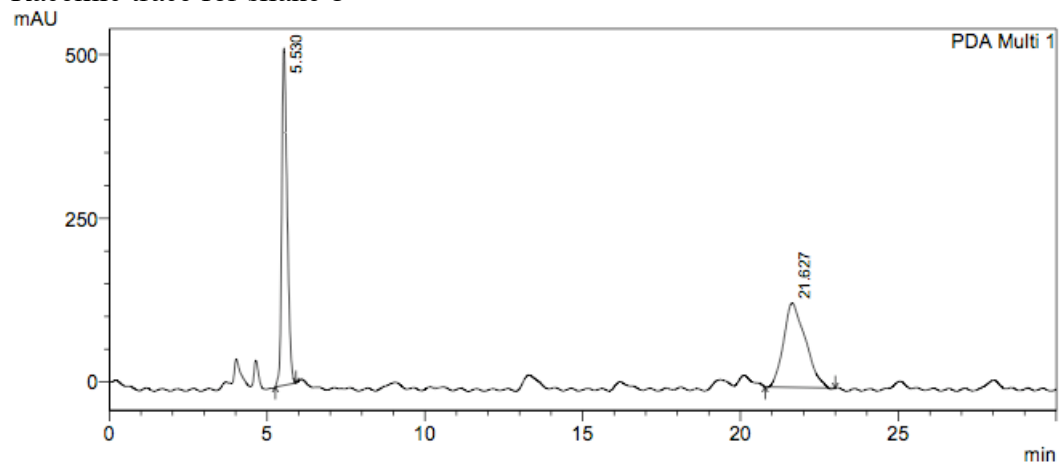
2-[(1*S*)-1-[dihydroxy(2,4,6-trimethylphenyl)silyl]ethyl]-*N,N*-diisopropylbenzamide (4). Substrate **8** (235 mg, 0.616 mmol) was subjected to the general procedure for hydrolysis of silanes. The product was purified by column chromatography (100% hexanes to 7% EtOAc/Hexanes) to give 81 mg of silanediol **4** as a colorless liquid (32% yield), which solidified upon washing with hexanes and concentrating. It is important to note that the product “trails” on column and may be very difficult to see by TLC at low concentrations present in test tubes. Enantiomeric excess was determined by HPLC with a Daicel CHIRALPAK® AS-H column (10% IPA/hexanes), 0.8 mL/min, 40 °C. *t_R* (major) = 5.9 min, *t_R* (minor) = 5.2 min. 76:24 *er*. [α]_D²⁴ = -2.5 (*c* 0.120, MeOH). mp = 69-72 °C. ¹H NMR (600 MHz, CD₃CN) δ 7.25 (ddd, *J* = 5.6, 4.8, 1.4 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.07 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.76 (s, 2H), 5.97 (s,

⁵ Thayumanavan, S.; Lee, S.; Liu, C.; Beak, P. *J. Am. Chem. Soc.* **1994**, *116*, 9755-9756.

¹H), 4.79 (s, 1H), 3.66 – 3.56 (m, 2H), 2.35 – 2.32 (m, 1H), 2.36 (s, 6H), 2.19 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H), 1.49 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 7.6 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.7, 3H). ¹³C NMR (150 MHz, CD₃CN) δ 174.0, 146.6, 141.6, 140.3, 137.5, 129.9, 129.6, 129.5, 129.0, 125.7, 125.4, 52.6, 46.9, 29.2, 25.0, 21.5, 21.2, 21.1, 20.6 20.1, 15.3. ²⁹Si NMR (119 MHz, CD₃CN) δ -20.7. IR (neat): 3264, 2969, 1606, 1031, 835 cm⁻¹. HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₄H₃₅NNaO₃Si, 436.2278. Found 436.2275.

III. HPLC Chromatograms

Racemic trace for silane **8**

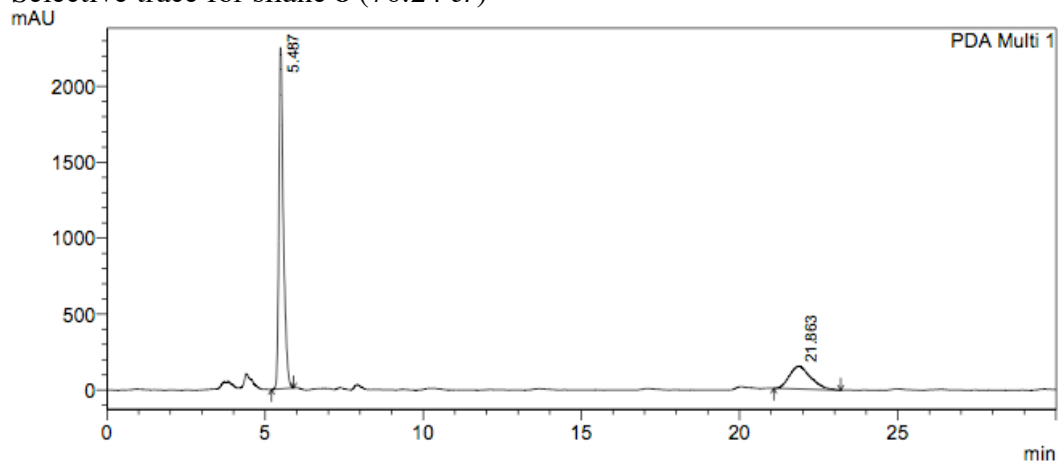


1 PDA Multi 1/206nm 4nm

PDA Ch1 206nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.530	6129113	515176	49.597	79.957
2	21.627	6228822	129140	50.403	20.043
Total		12357935	644316	100.000	100.000

Selective trace for silane **8** (76:24 *er*)



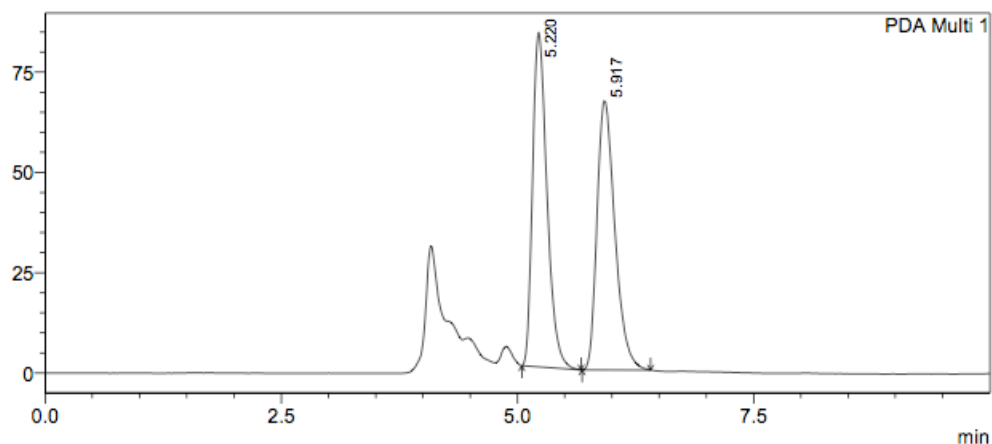
1 PDA Multi 1/195nm 4nm

PDA Ch1 195nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.487	22075958	2250164	75.969	93.765
2	21.863	6983046	149619	24.031	6.235
Total		29059004	2399782	100.000	100.000

Racemic trace for silanediol **4**

mAU



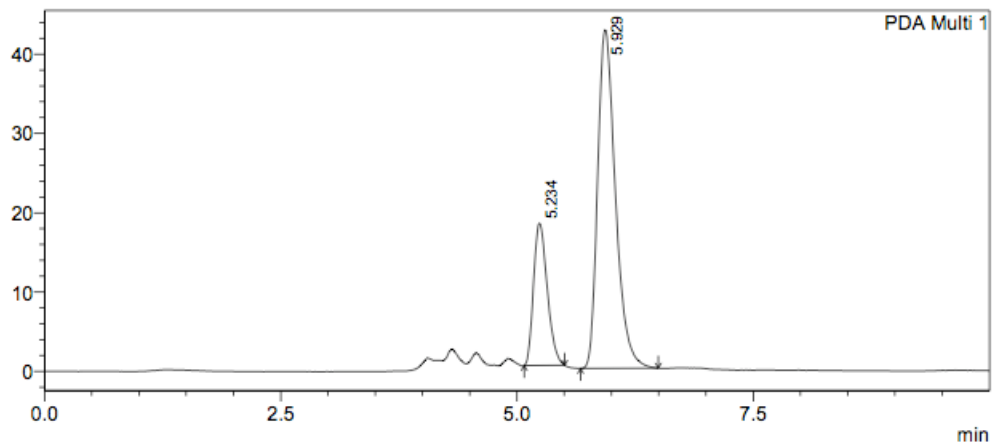
1 PDA Multi 1/256nm 4nm

PDA Ch1 256nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.220	885485	83426	49.810	55.373
2	5.917	892254	67237	50.190	44.627
Total		1777739	150663	100.000	100.000

Selective trace for silanediol **4** (76:24 *er*)

mAU



1 PDA Multi 1/256nm 4nm

PDA Ch1 256nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.234	181181	17977	24.466	29.628
2	5.929	559345	42698	75.534	70.372
Total		740526	60675	100.000	100.000

IV. Low Temperature and Binding Studies

Low Temperature Studies:

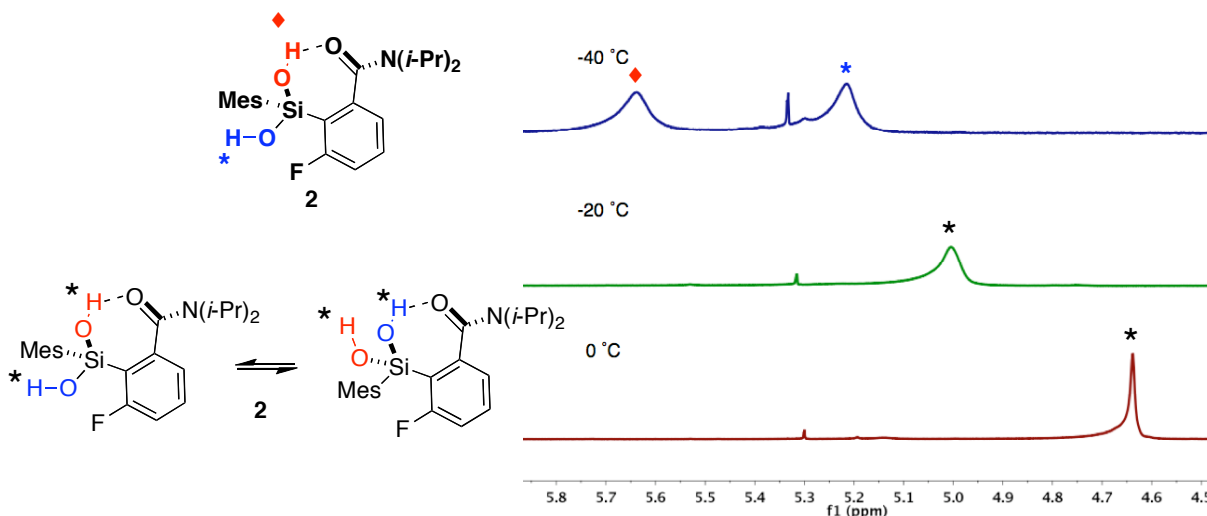


Figure S1. Decreasing the temperature promotes a single mode of intramolecular hydrogen bonding for silanediol **2**, as observed by ¹H NMR spectroscopy at low temperature in CDCl₃.

Binding Studies: 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 0.10 mmol of silanediol in 10.0 mL of C₆D₆. A Lewis base (0.50 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.

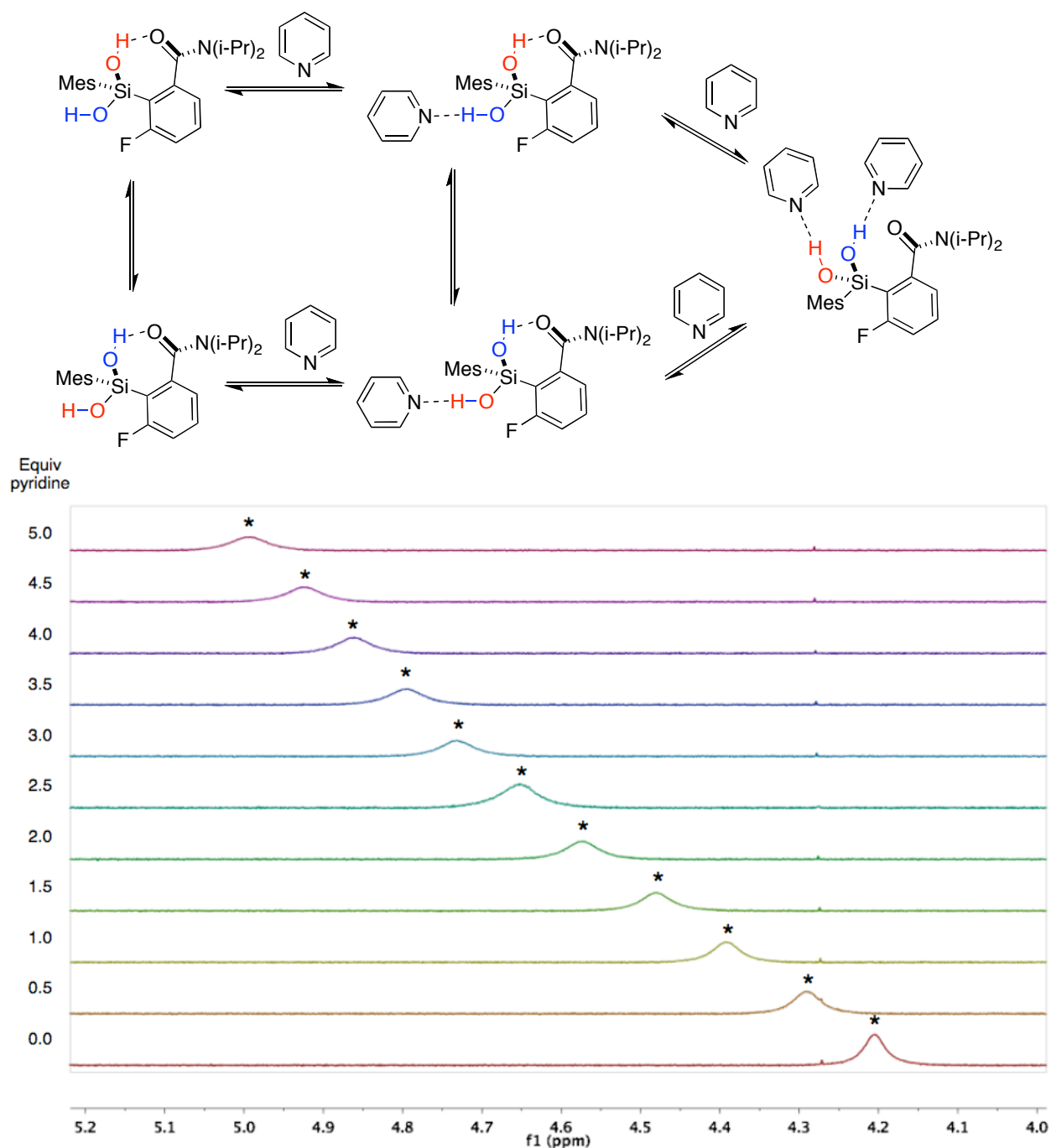


Figure S2. Spectra for silanediol **2** as a 10 mM solution in C_6D_6 with pyridine. A shift of 0.79 ppm is observed for the hydroxy protons (indicated with *) when 5.0 equivalents of pyridine are added. The increased broadening of the line shape is attributed to multiple modes of intra- and intermolecular binding for the silanediol suggested above.

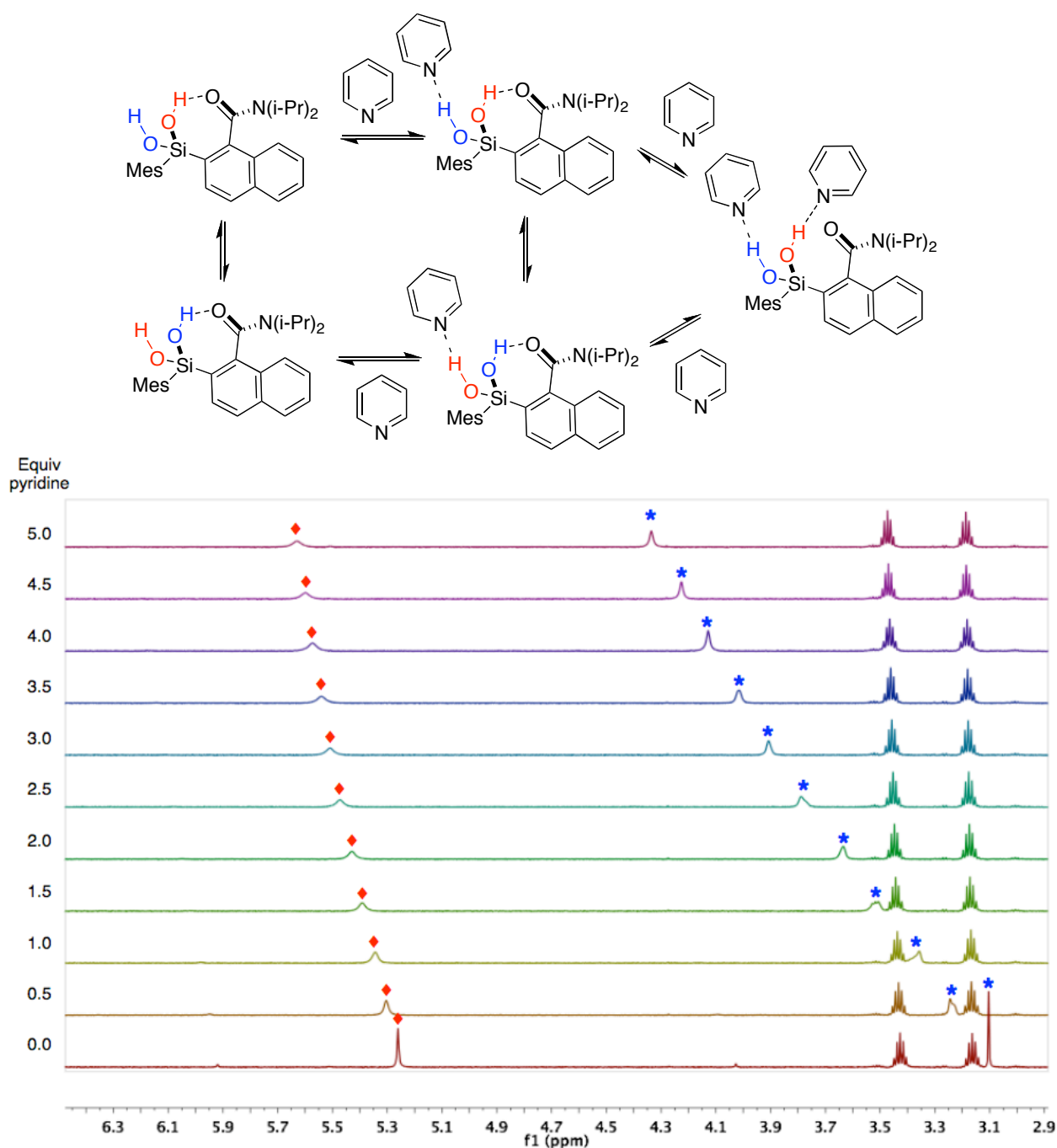


Figure S3. Spectra for silanediol **3** as a 10 mM solution in C_6D_6 with pyridine. A shift of 0.37 ppm is observed for the downfield hydroxy proton (indicated with *) and a shift of 1.23 ppm is observed for the upfield hydroxy proton (indicated with ♦) when 5.0 equivalents of pyridine are added. Although both proton signals broaden slightly, the line shape generally maintains a consistent level of broadening at various equivalents of pyridine, which is attributed to a more rigid system that generally favors a single mode of binding.

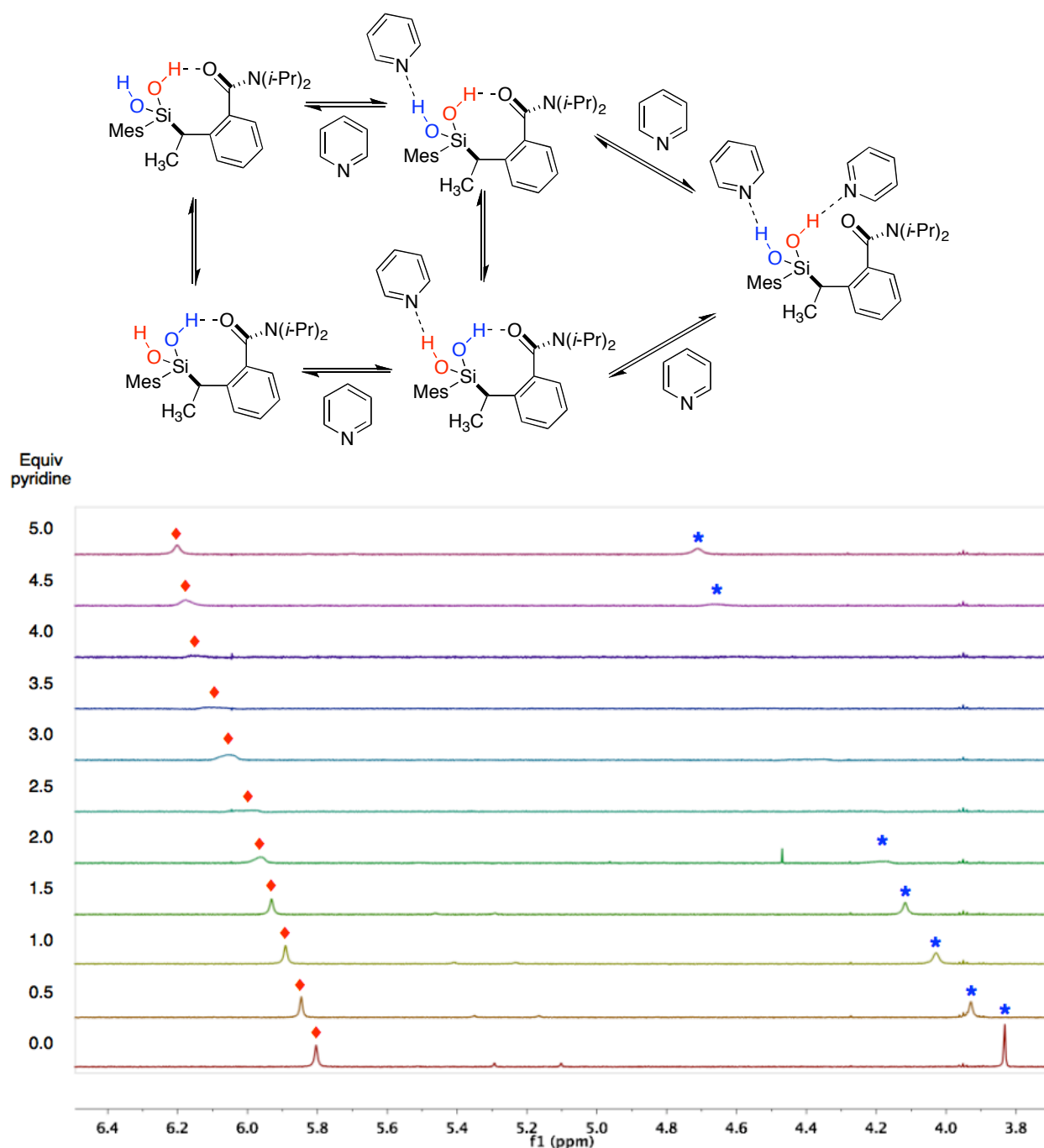


Figure S4. Spectra for silanediol **4** as a 10 mM solution in C₆D₆ with pyridine. A shift of 0.40 ppm is observed for the downfield hydroxy proton (indicated with *) and a shift of 0.88 ppm is observed for the upfield hydroxy proton (indicated with ♦) when 5.0 equivalents of pyridine are added. Initial significant broadening is observed for both proton signals (between 2 and 4 equivalents of pyridine), which indicates that multiple modes of pyridine binding are present. However, this line broadening is followed by sharpening upon addition of a large excess of pyridine (5 equivalents), which is attributed to the transition to a strong, single mode of hydrogen bonding.

V. Stability Studies by ^1H NMR Spectroscopy and ESI-MS

^1H NMR Spectroscopy Studies: ^1H NMR spectroscopy studies were performed using low concentration solutions (9 mM) of amide-silanediols **3** and **4** to assess their stability towards condensation and decomposition. NMR solvents CDCl_3 and CD_3CN were dried with activated with 4 Å molecular sieves and passed through a silica plug directly before utilization to remove traces of water. 9 mM Solutions were prepared by dissolving the appropriate silanediol in CDCl_3 or CD_3CN , followed by addition of additives, if appropriate.

To assess the stability of silanediol **3** and **4** in CDCl_3 , a solution described above was prepared with no additives and NMR spectra were recorded as previously stated. To assess the stability of silanediol **3** and **4** towards acetic acid (AcOH), 50 μL (0.9 M) of reagent grade AcOH were added to a solution in CDCl_3 as described above and NMR data was collected as previously stated. To assess the stability towards water, excess D_2O (50 μL , 2.3 M) was added to a solution in CD_3CN prepared as described above (it should be noted that silanediols **3** and **4** is not soluble in water) and NMR data is shown below. To assess the stability of silanediols **3** and **4** towards trifluoroacetic acid (TFA), TFA (10 μL , 0.1 M) was added to a solution in CDCl_3 prepared as described above and NMR data as shown in Figure S4. To assess the stability of silanediols in basic media, 50 μL (1.2 M) of NH_4OH was added to a solution in CDCl_3 prepared as described above. Approximately 0.60 mL of each solution were transferred to a separate NMR tube, sealed with Teflon tape and stored at ambient conditions. ^1H NMR spectra were obtained on a 600 MHz instrument at 25 °C after 8 scans.

ESI-MS Studies: For each experiment, 10 μL aliquots of the samples prepared above in ^1H NMR Spectroscopy Studies were diluted to 1.0 mL with methanol. Reaction mixtures and samples were prepared and analyzed using ESI-MS in the positive ion mode on a Qtrap spectrometer. Source parameters were 5kV spray voltage, with a curtain plate temperature of 275 °C and sheath gas setting of 15. Samples were analyzed via flow injection analysis by injecting 20 μL samples into a stream of 80:20 MeOH/aqueous 0.1% formic acid, flowing at 300 $\mu\text{L}/\text{min}$. All raw ESI-Mass Spectrum data files were analyzed using Applied Biosystems Analyst Software v.1.4.2, build 1228. Spectra were processed for publication figures using Microsoft Excel 2004.

Table S1. Summary of silanediol stability studies

entry	silanediol	solvent	additive	stability
1	3	CDCl_3	none	stable >7 days
2	4	CDCl_3	none	stable >7 days
3	3	CDCl_3	AcOH (50 μL , 0.9 M)	stable >7 days
4	4	CDCl_3	AcOH (50 μL , 0.9 M)	stable >7 days
5	3	CD_3CN	D_2O (50 μL , 2.6 M)	stable >7 days
6	4	CD_3CN	D_2O (50 μL , 2.6)	stable >7 days
7	3	CDCl_3	TFA (10 μL , 0.1 M)	immediate protodesilylation and oligomerization
8	4	CDCl_3	TFA (10 μL , 0.1 M)	immediate protodesilylation and oligomerization
9	3	CDCl_3	NH_4OH (50 μL , 1.2 M)	stable >7 days
10	4	CDCl_3	NH_4OH (50 μL , 1.2 M)	stable >7 days

Stability was monitored by both ^1H NMR spectroscopy and ESI-MS over a period of 7 days. Silanediols were kept in a solution of indicated deuterated solvent at low concentration (9 mM).

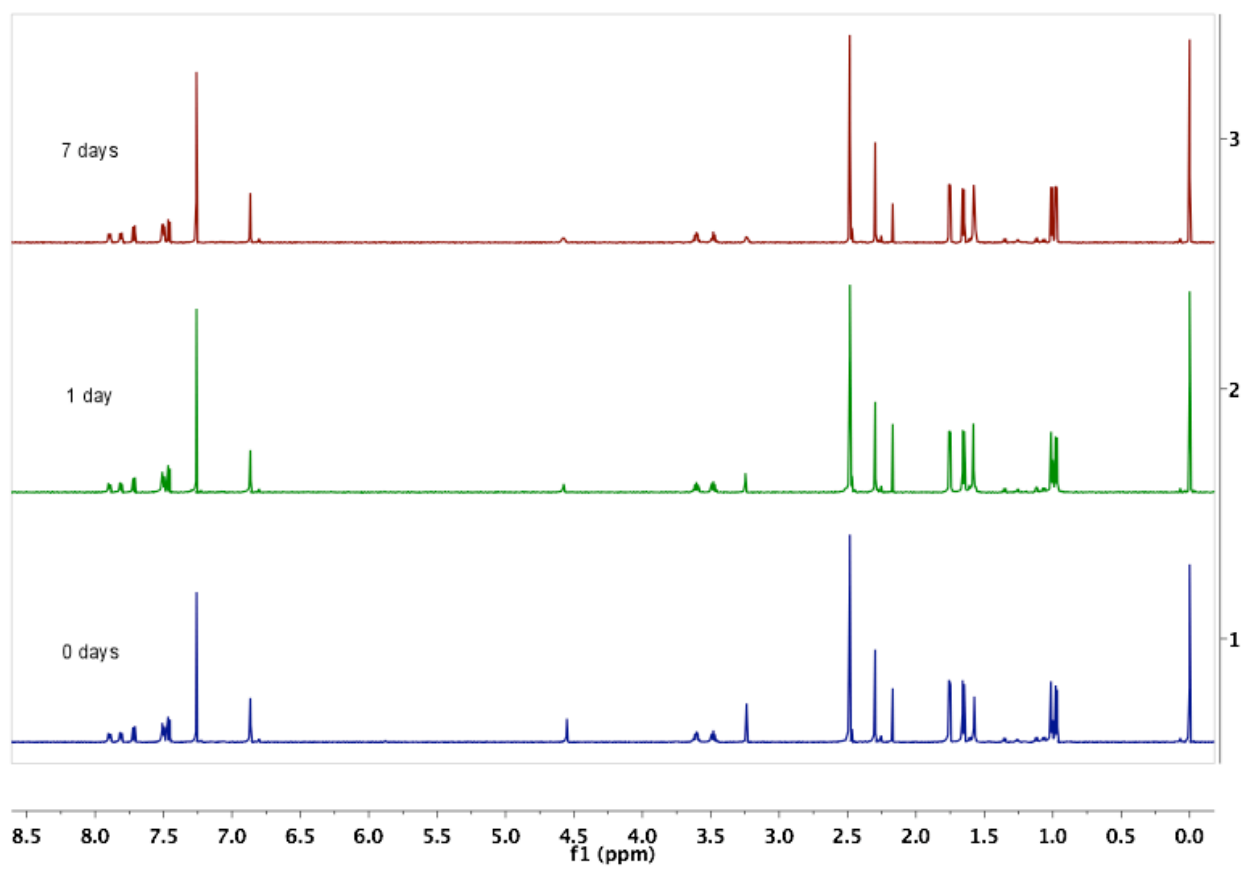


Figure S5. ¹H NMR spectra of silanediol **3** in CDCl₃ demonstrating that **3** is stable towards condensation and no degradation is observed over the period of 7 days at ambient conditions.

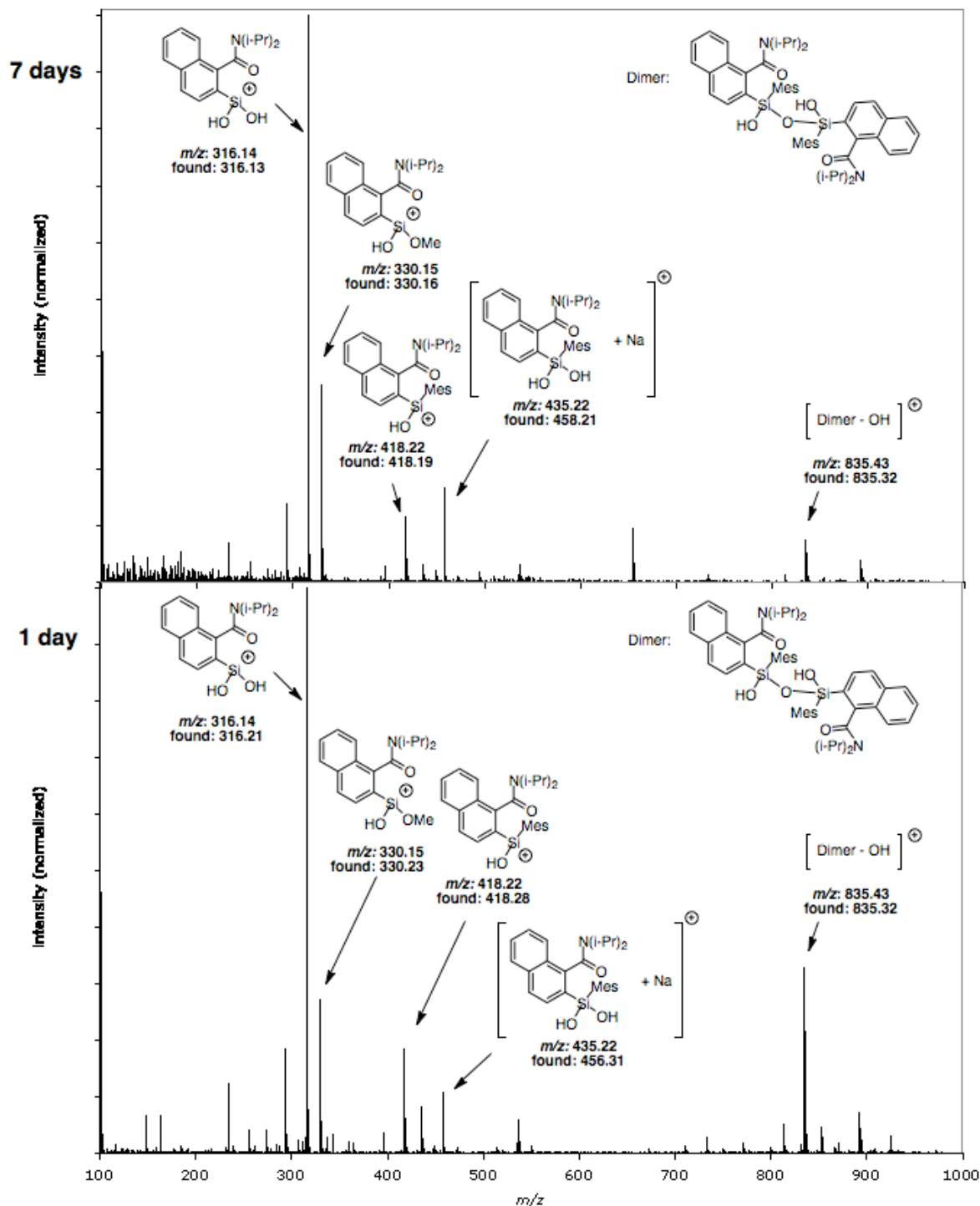


Figure S6. A comparison of ESI-MS of silanediol **3** after one and seven days in CDCl_3 demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed only under mass spectrometry conditions (diluted to 9 μM in MeOH and injected with 80:20 MeOH/aqueous 0.1% formic acid) because no degradation is observed when monitoring by ^1H NMR spectroscopy.

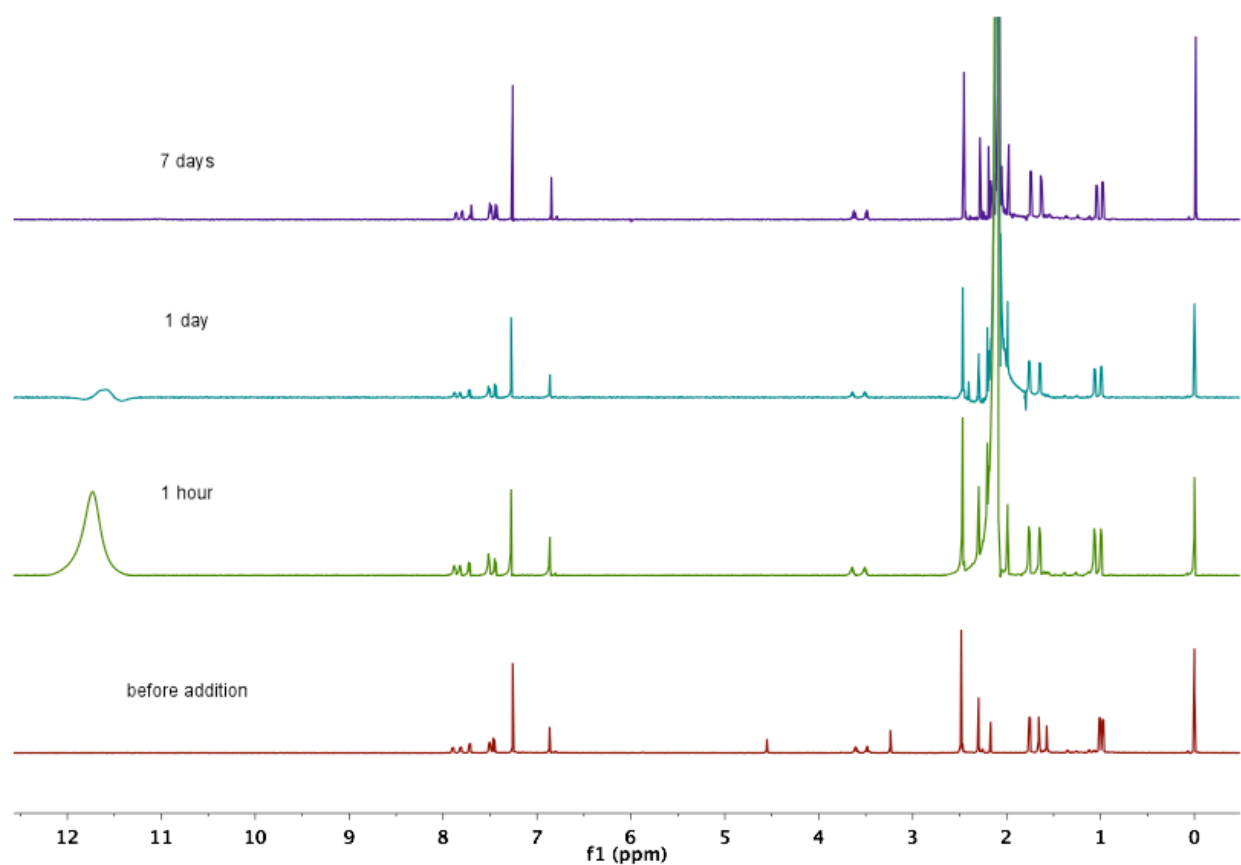


Figure S7. ^1H NMR spectra of silanediol **3** in CDCl_3 demonstrating the stability of **3** towards condensation and no degradation in the presence of AcOH (0.9 M) over a period of 7 days at ambient conditions. The disappearance of the OH peak in AcOH is attributed to the slow diffusion of atmospheric H_2O into solution over time.

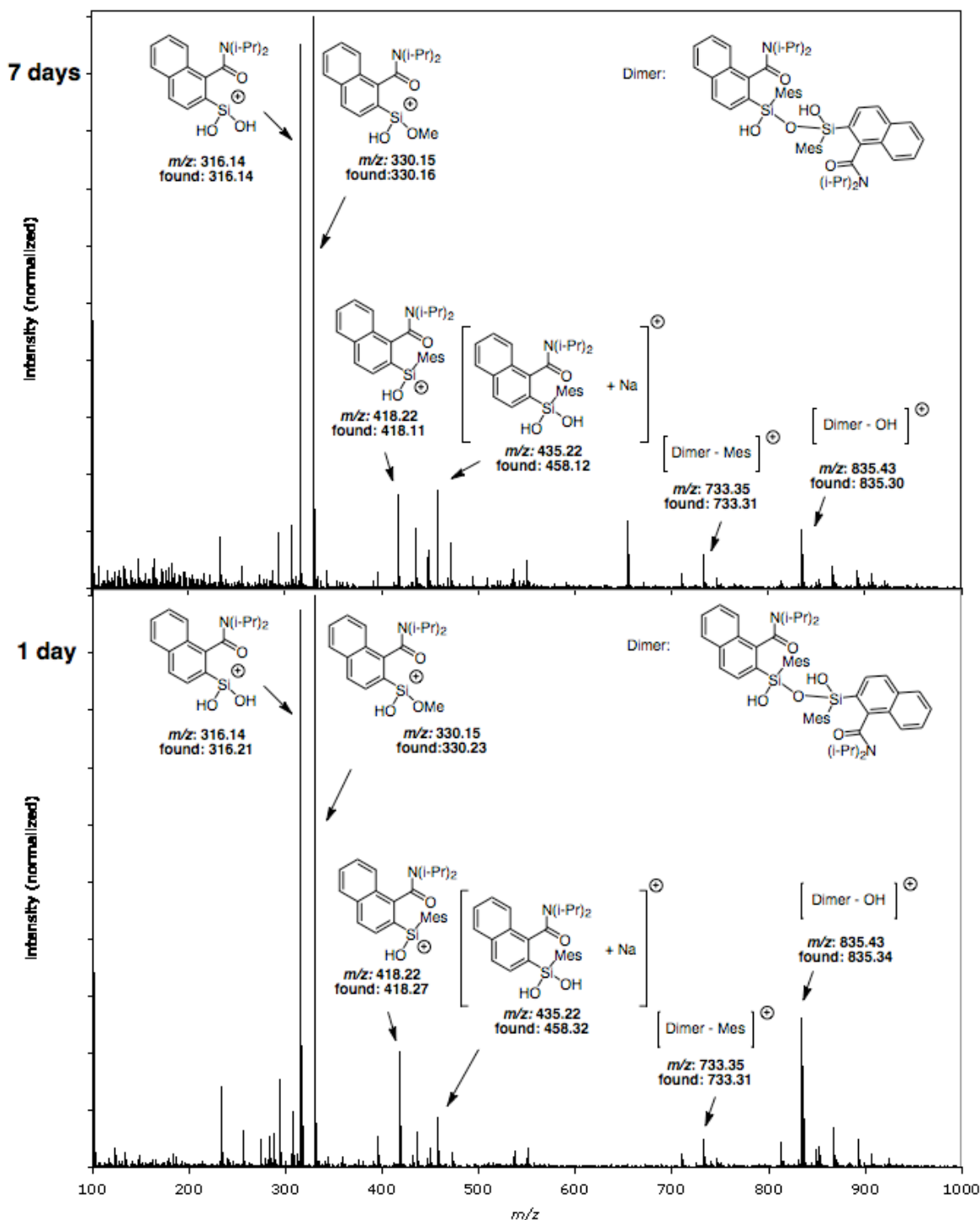


Figure S8. A comparison of ESI-MS of silanediol **3** after one and seven days in the presence of 50 μ L of AcOH (0.9 M in CDCl_3), demonstrating stability towards condensation. Dimer seen in ESI-MS is likely being formed only under mass spectrometry conditions (diluted to 9 μ M in MeOH and injected with 80:20 MeOH/aqueous 0.1% formic acid) because no degradation of the silanediol is observed by ^1H NMR spectroscopy.

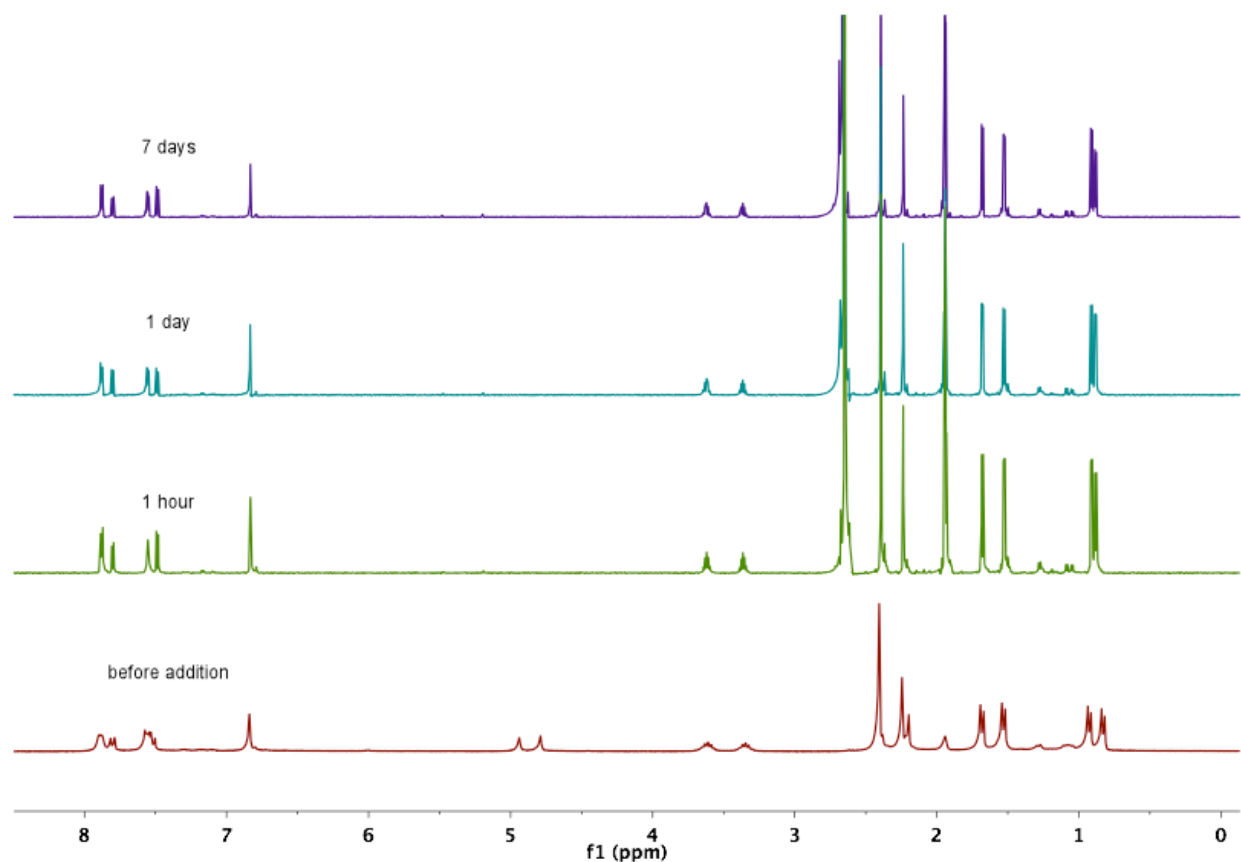


Figure S9. ^1H NMR spectra of silanediol **3** in CD_3CN shows stability towards condensation and no degradation in the presence of excess D_2O (2.6 M) over a period of 7 days when stored under ambient conditions.

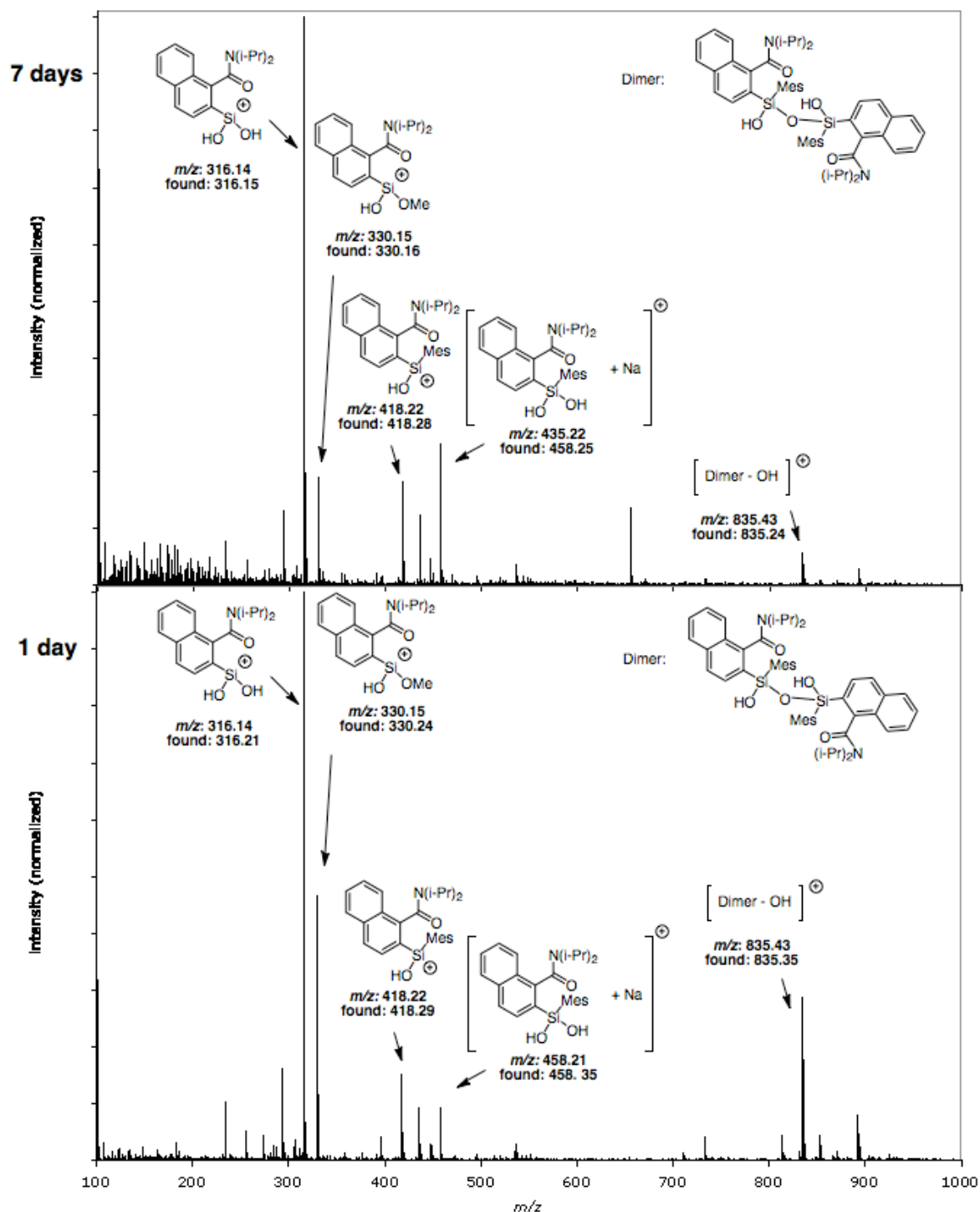


Figure S10. A comparison of ESI-MS of silanediol **3** after one and seven days in CD_3CN with 50 μL of D_2O (2.6 M), demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed under mass spectrometry conditions (9 μM at conditions described above) because no degradation is observed by monitoring of the silanediols by ^1H NMR spectroscopy. Protodesilylation followed by addition of methanol (solvent) leads to fragment m/z : 330.15.

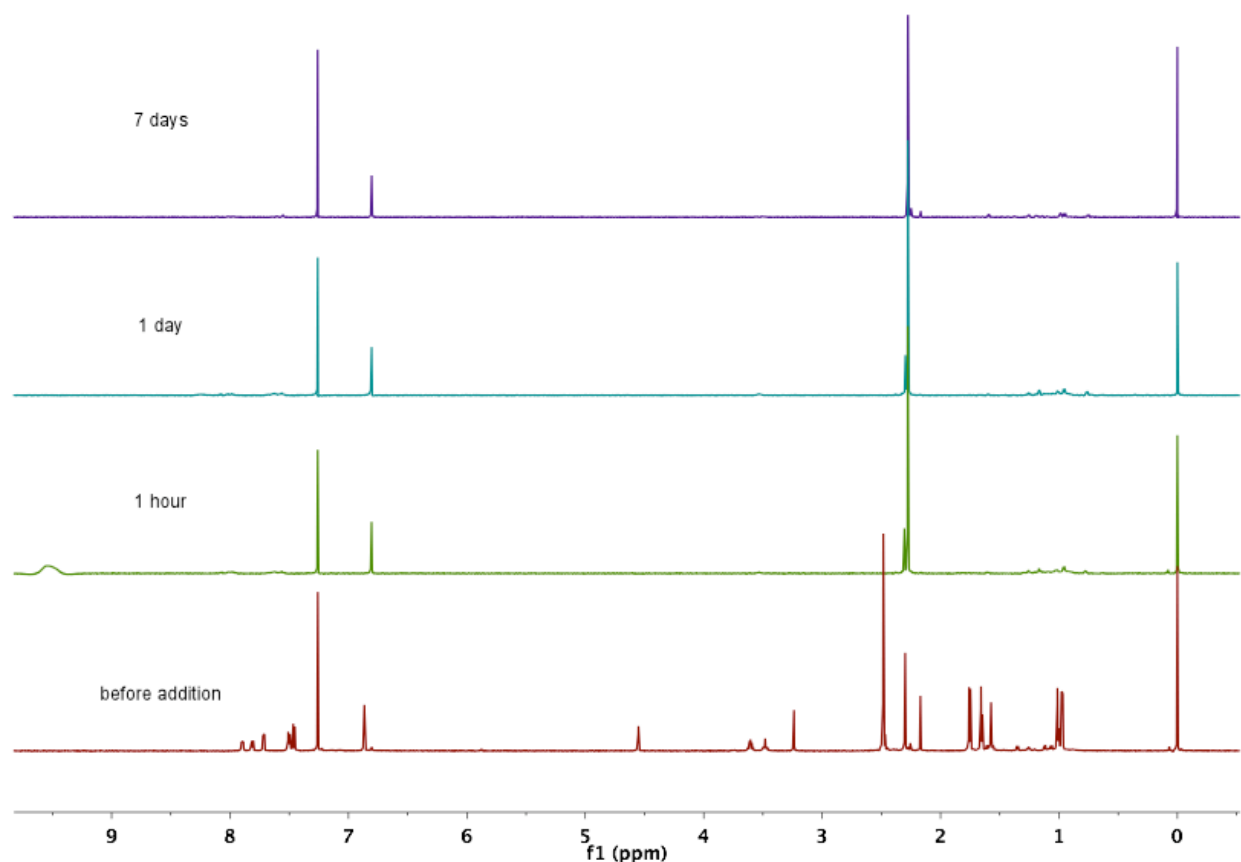


Figure S11. ^1H NMR spectra of silanediol **3** in CDCl_3 in the presence of TFA (0.1 M) shows rapid degradation and formation of several products, including mesitylene, as seen by the disappearance of well-defined peaks and appearance of several unidentifiable new peaks.

ESI-MS analysis of this sample showed no signals above the background after initial addition of TFA.

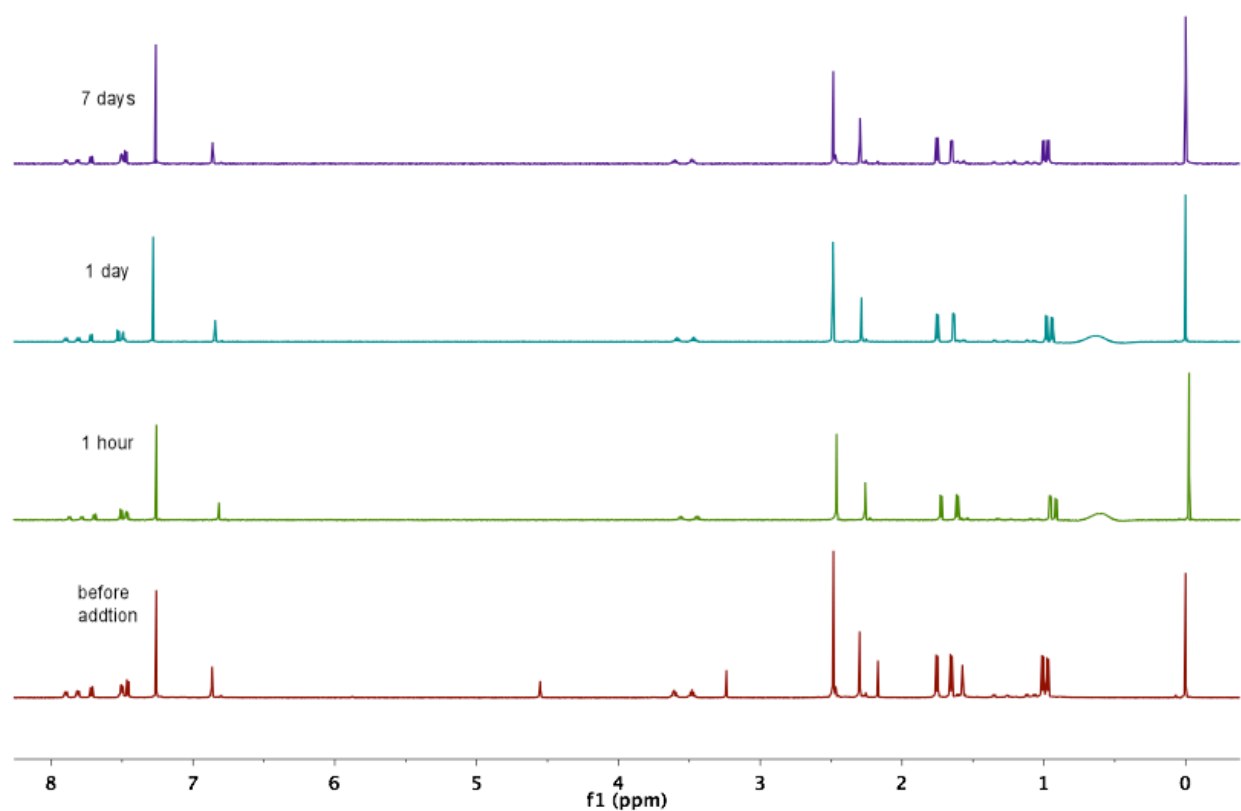


Figure S12. ^1H NMR spectra of silanediol **3** in CDCl_3 demonstrating the stability of **3** towards condensation and no degradation in the presence of excess NH_4OH (1.2 M) over a period of 7 days at ambient conditions.

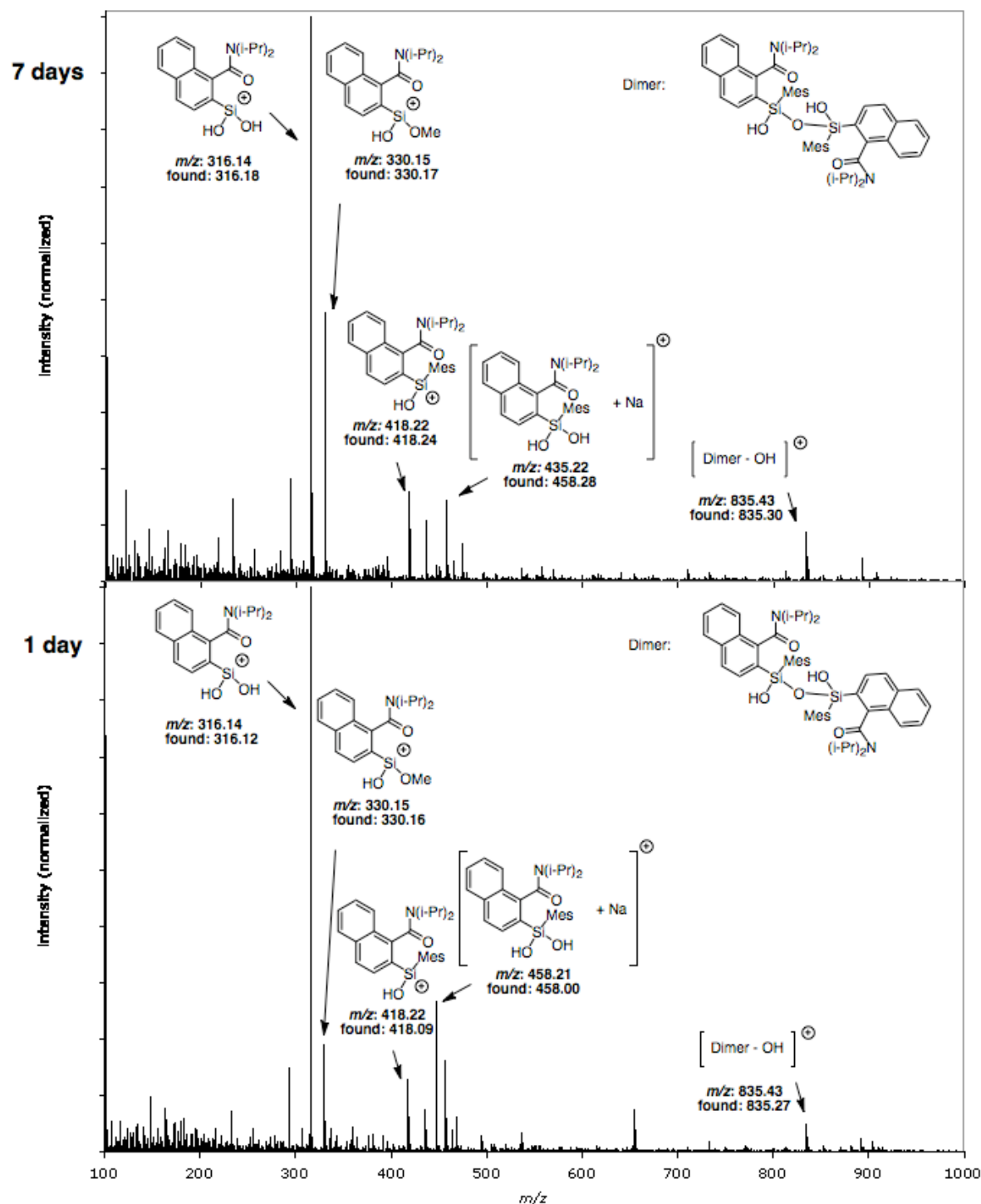


Figure S13. ESI-MS of silanediol **3** in CDCl_3 in the presence of 50 μL of NH_4OH (1.2 M) after one and seven days, demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed under mass spectrometry conditions (9 μM at conditions described above) because no degradation is observed by monitoring of the silanediols by ^1H NMR spectroscopy. Protodesilylation followed by addition of methanol (solvent) leads to fragment m/z : 330.15.

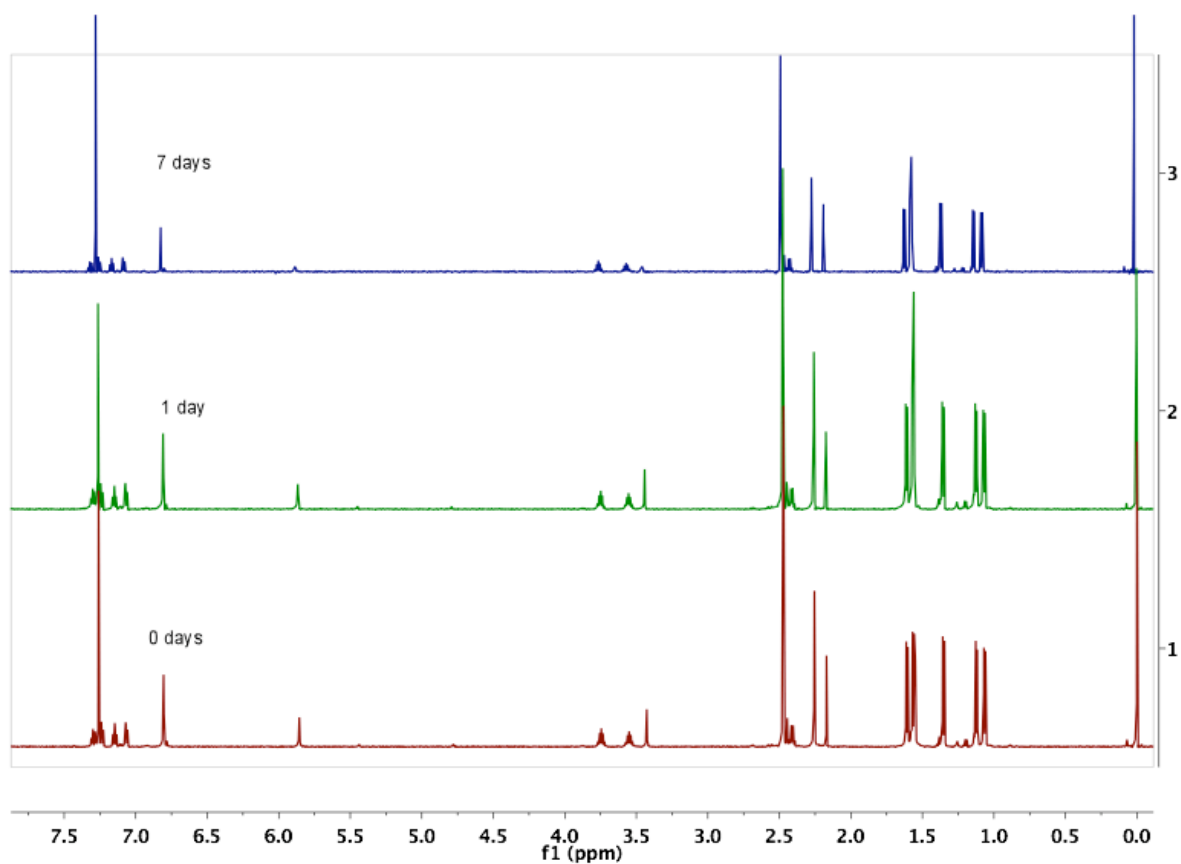


Figure S14. ^1H NMR spectra of silanediol **4** in CDCl_3 is stable towards condensation and no degradation is observed over the period of 7 days at ambient conditions.

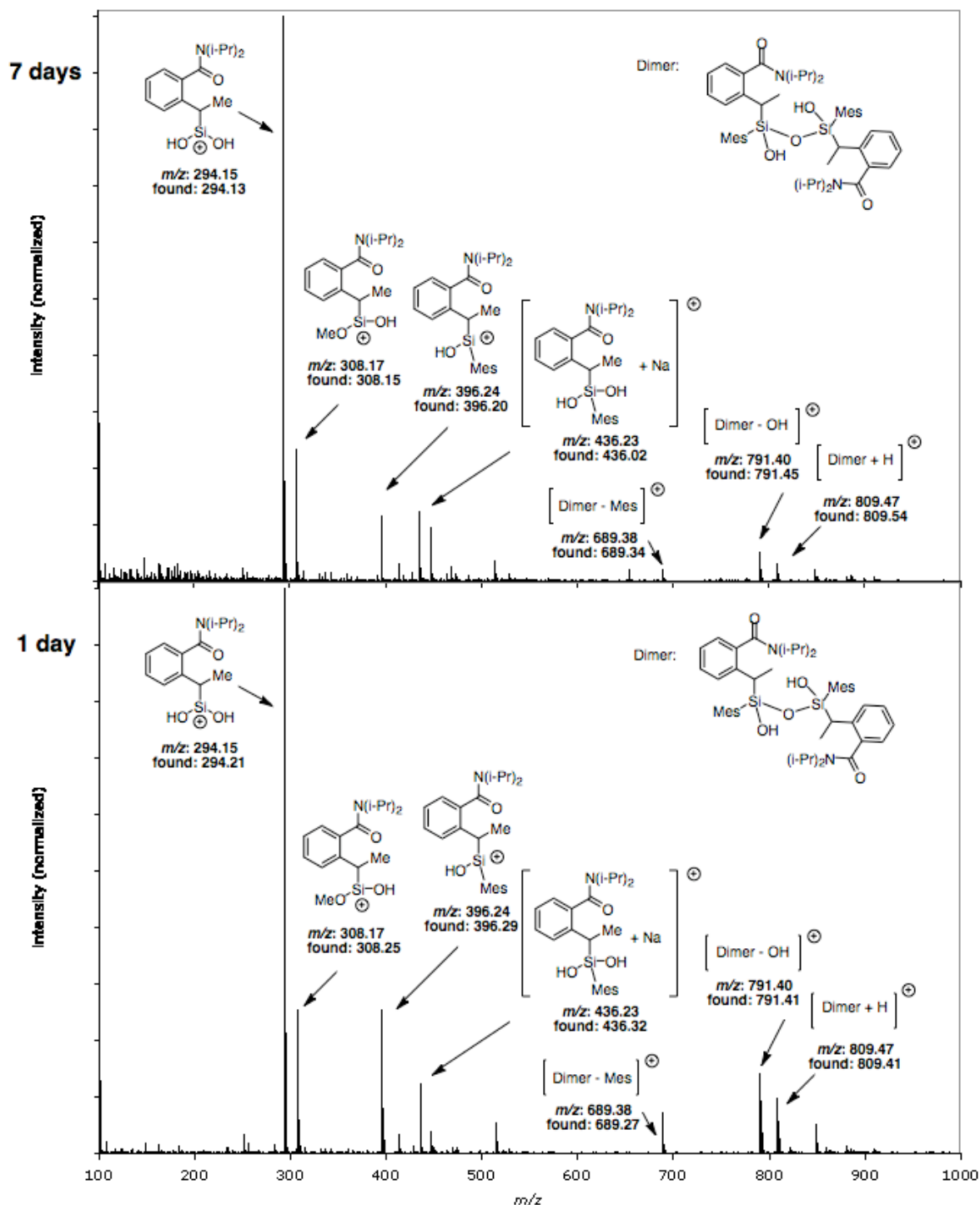


Figure S15. ESI-MS of silanediol **4** in CDCl_3 after one and seven days, demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed under mass spectrometry conditions ($9\ \mu\text{M}$ at conditions described above) because no degradation is observed by monitoring of the silanediols by ^1H NMR spectroscopy. Protodesilylation followed by addition of methanol (solvent) leads to fragment m/z : 308.17.

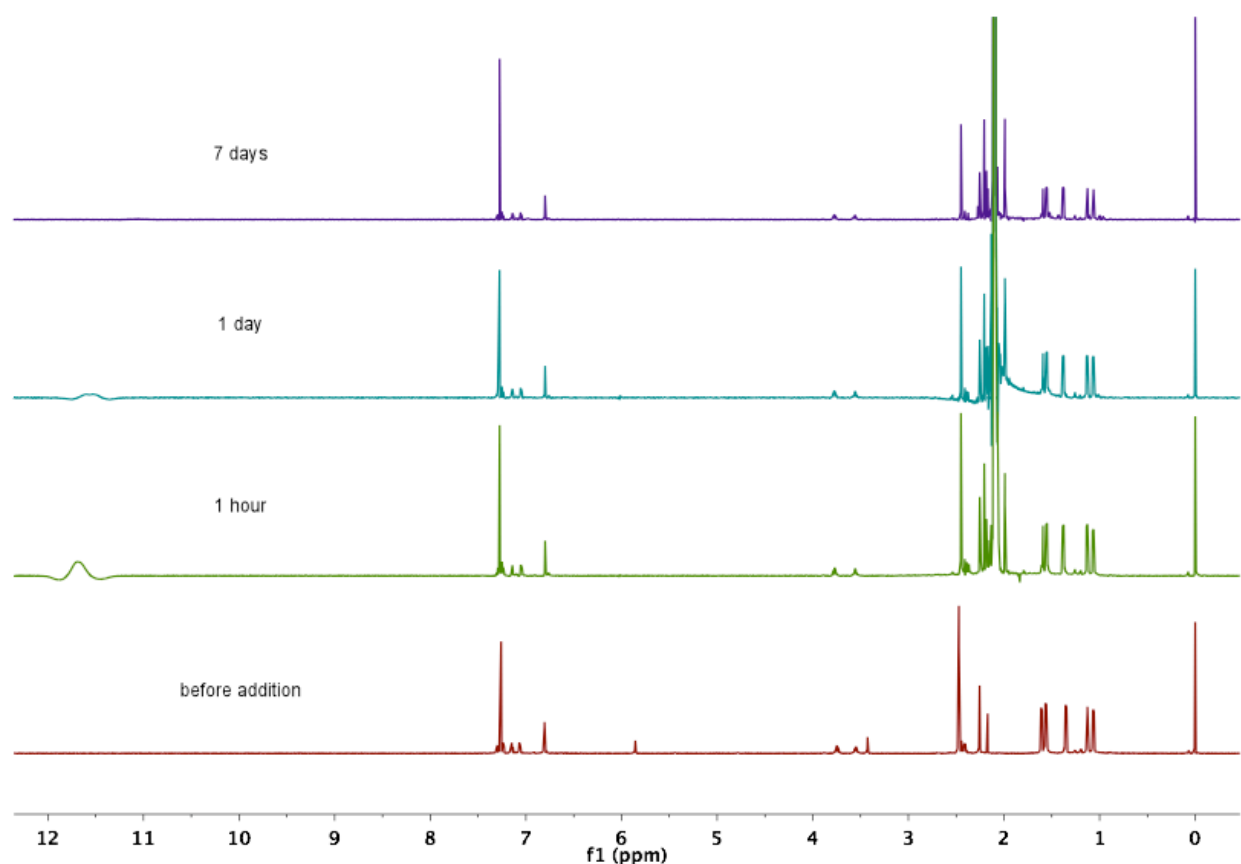


Figure S16. ^1H NMR spectra of silanediol **4** in CDCl_3 in the presence of AcOH (0.9 M) shows the stability towards condensation and no degradation over a period of 7 days at ambient conditions. Disappearance of the OH peak from AcOH is attributed to slow diffusion of atmospheric H_2O into solution.

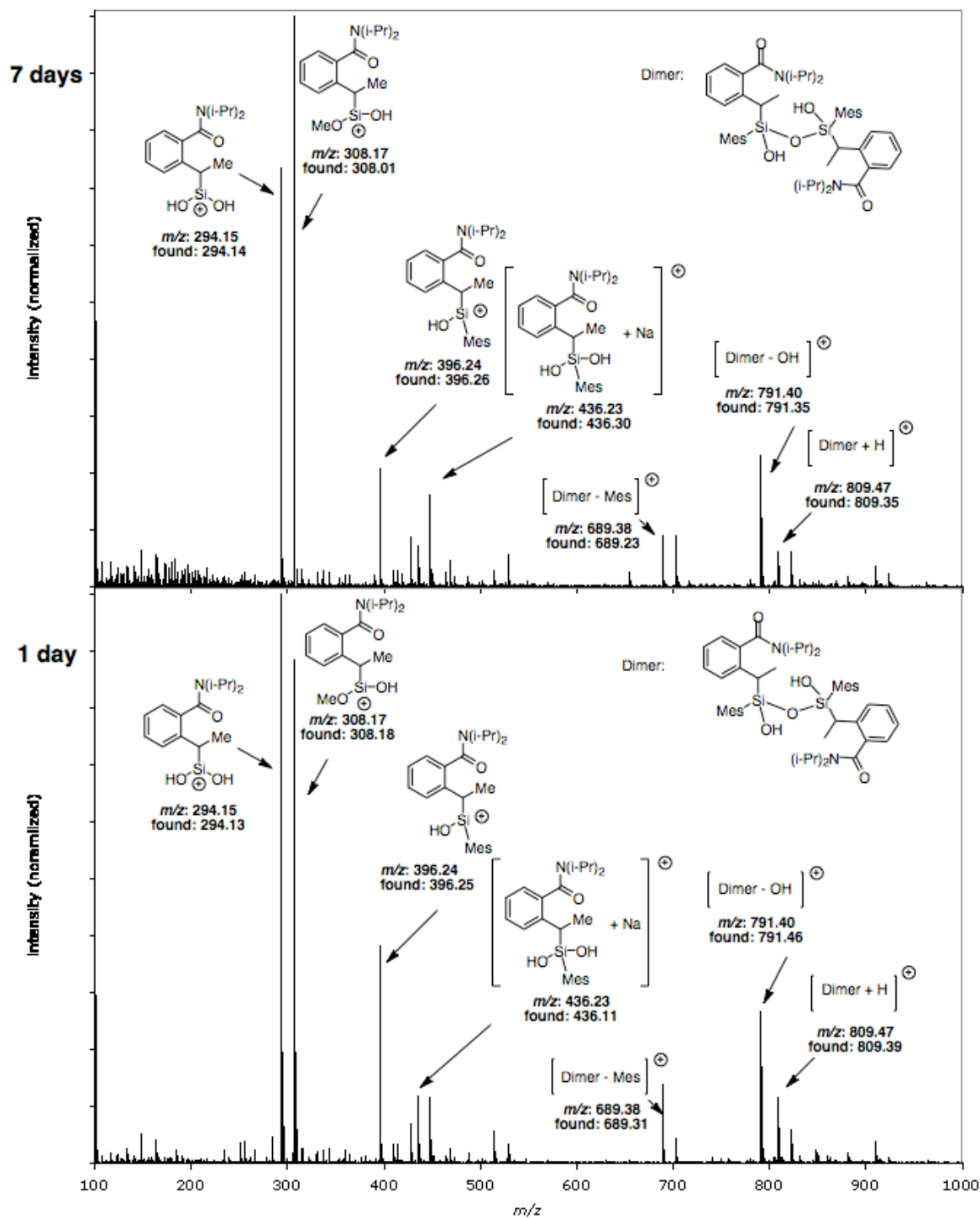


Figure S17. ESI-MS of silanediol **4** in CDCl_3 in the presence of 50 μL of AcOH (0.9 M) after one and seven days, demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed under mass spectrometry conditions (9 μM at conditions described above) because no degradation is observed by monitoring of the silanediols by ^1H NMR spectroscopy. Protodesilylation followed by addition of methanol (solvent) leads to fragment m/z : 308.17.

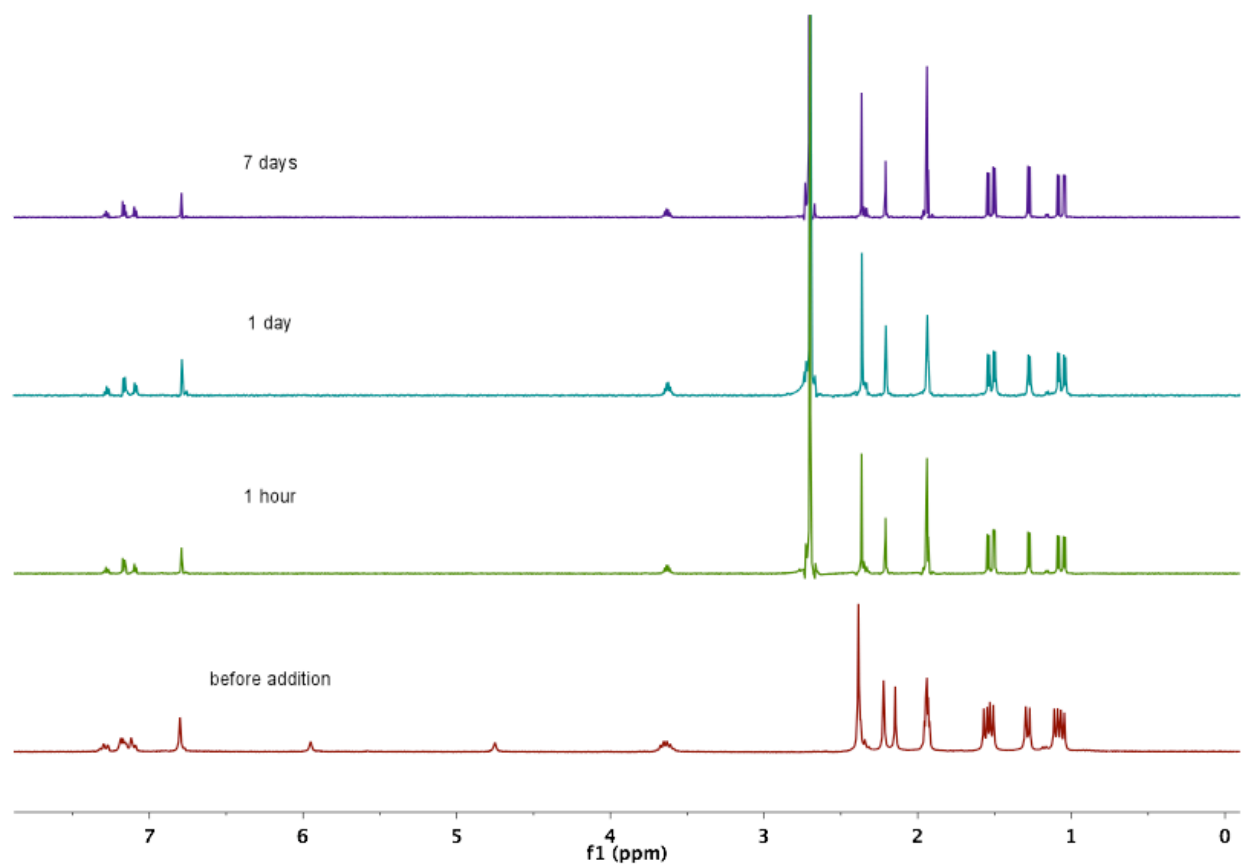


Figure S18. ^1H NMR spectra of silanediol **4** in CD_3CN shows stability towards condensation and no degradation in the presence of excess D_2O (2.6 M) over a period of 7 days when stored under ambient conditions.

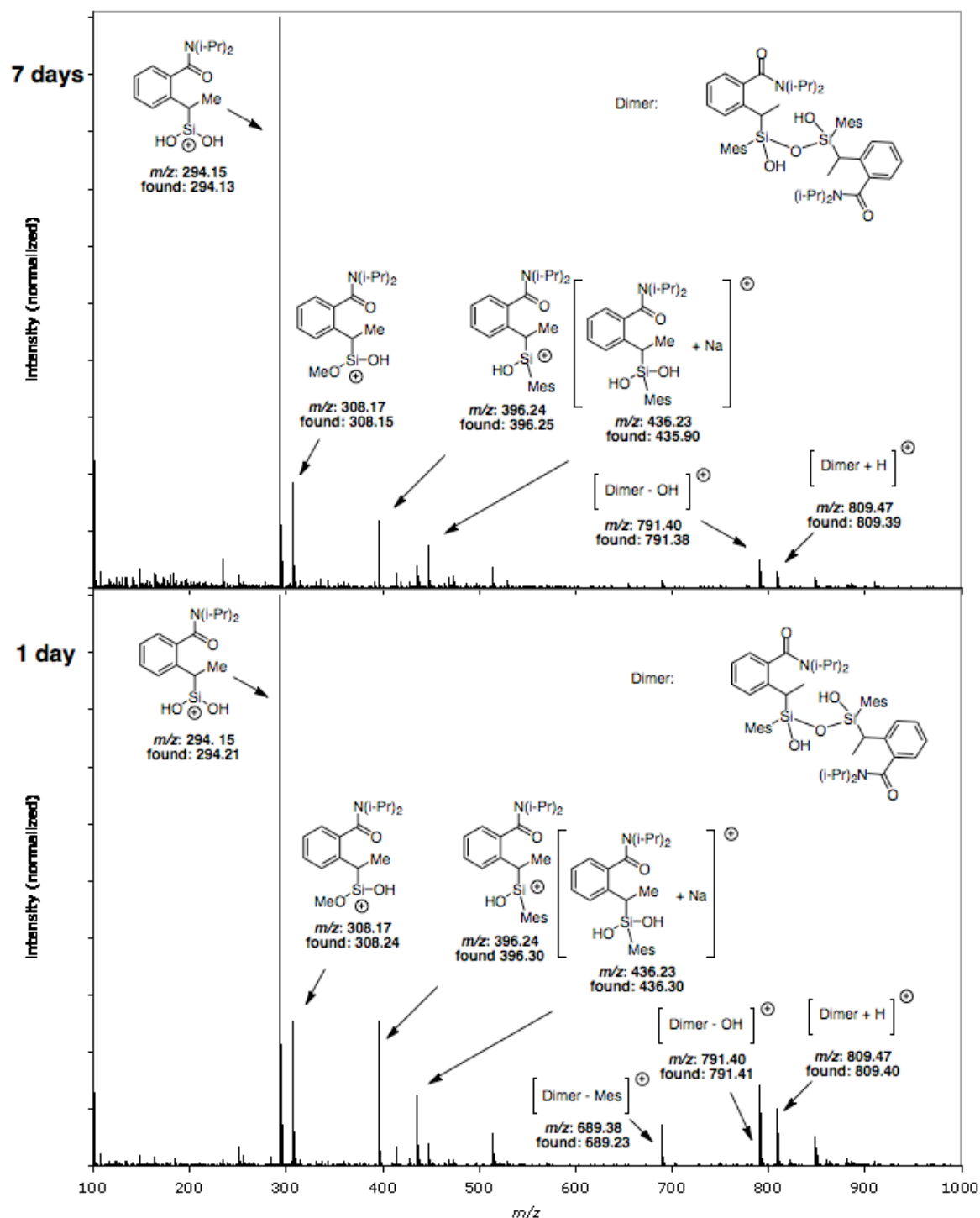


Figure S19. ESI-MS of silanediol **4** in CD₃CN in the presence of 50 μ L of D₂O (2.6 M) after one and seven days, demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed under mass spectrometry conditions (9 μ M at conditions described above) because no degradation is observed by monitoring of the silanediols by ¹H NMR spectroscopy. Protodesilylation followed by addition of methanol (solvent) leads to fragment m/z : 308.17.

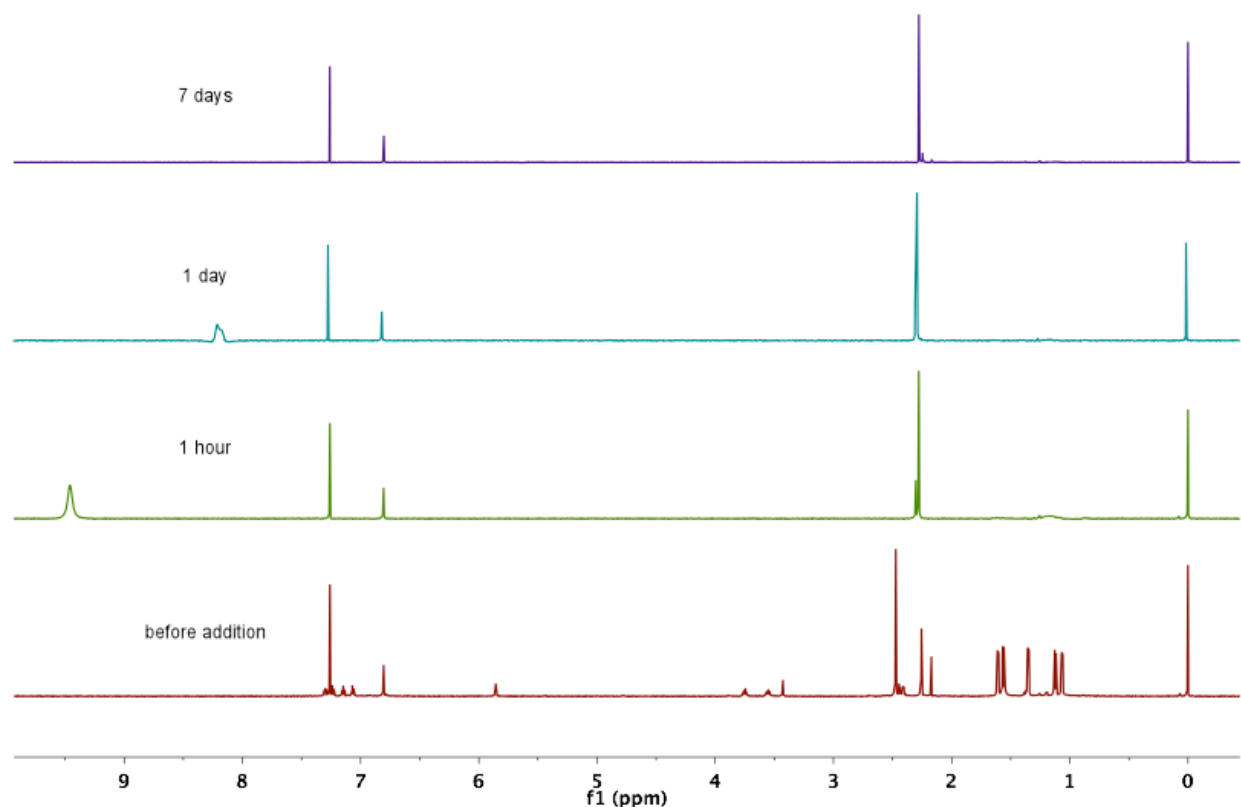


Figure S20. ^1H NMR spectra of silanediol **4** in CDCl_3 shows rapid degradation and formation of several products including mesitylene in the presence of trifluoroacetic acid (0.1 M) as seen by the disappearance of well-defined peaks and appearance of several unidentifiable new peaks. Disappearance of OH peak from TFA is attributed to slow diffusion of atmospheric H_2O over time.

ESI-MS analysis of sample showed no signals above the background after initial addition of TFA.

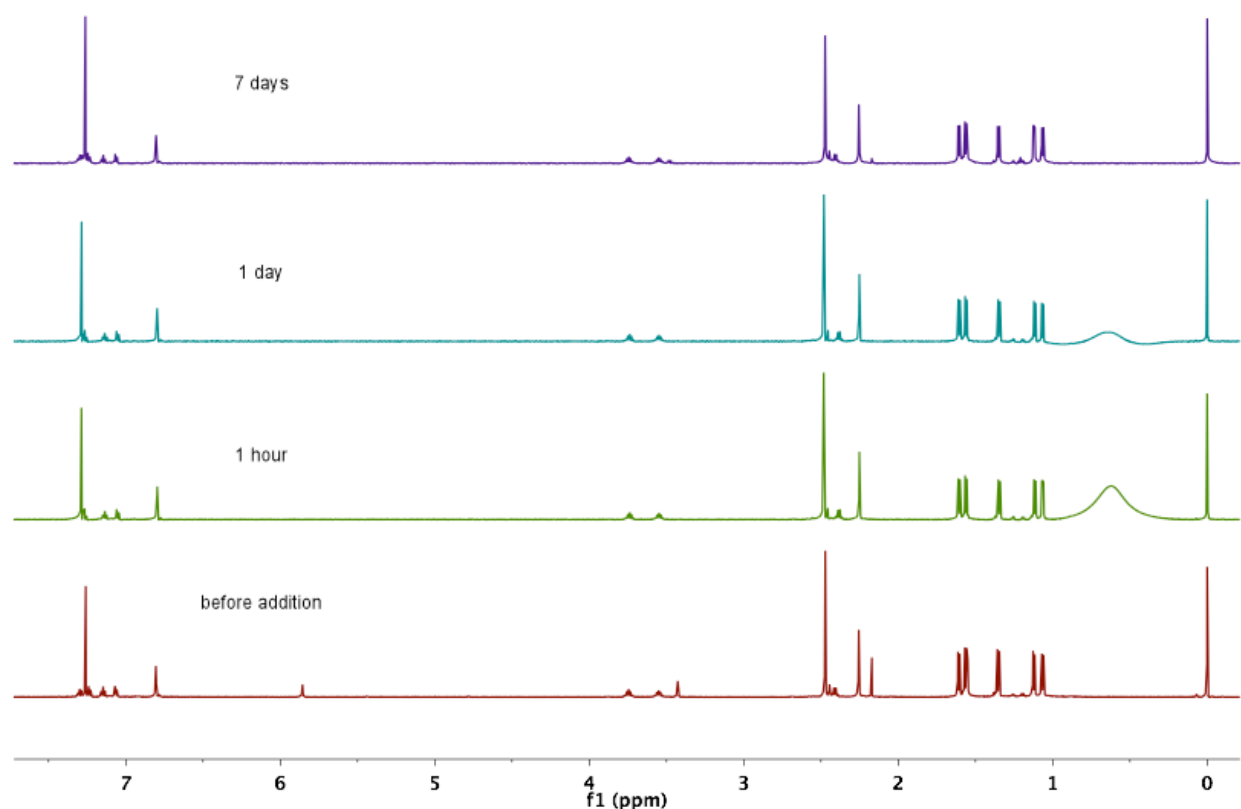


Figure S21. ^1H NMR spectra of silanediol **4** in CDCl_3 shows the stability towards condensation and no degradation in the presence of excess NH_4OH (1.2 M) over a period of 7 days at ambient conditions. Disappearance of the OH peak for NH_4OH is attributed to slow diffusion of atmospheric H_2O into solution.

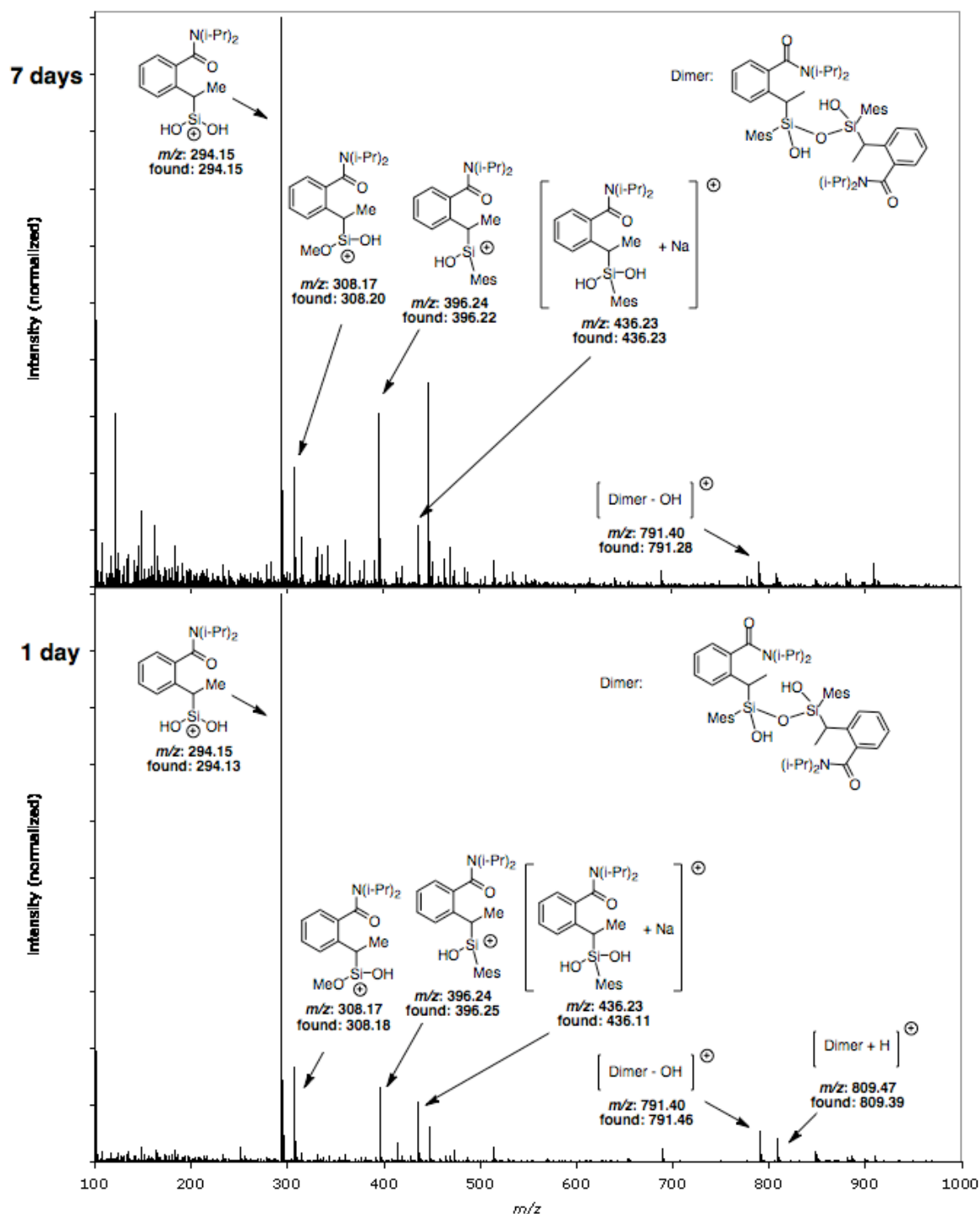


Figure S22. ESI-MS of silanediol **4** in CDCl_3 in the presence of 50 μL of NH_4OH (1.2 M) after one and seven days, demonstrating stability towards condensation. Dimer seen in spectrum is likely being formed under mass spectrometry conditions (9 μM at conditions described above) because no degradation is observed by monitoring of the silanediols by ^1H NMR spectroscopy. Protodesilylation followed by addition of methanol (solvent) leads to fragment m/z : 308.17.

VI. IR Spectroscopy Studies

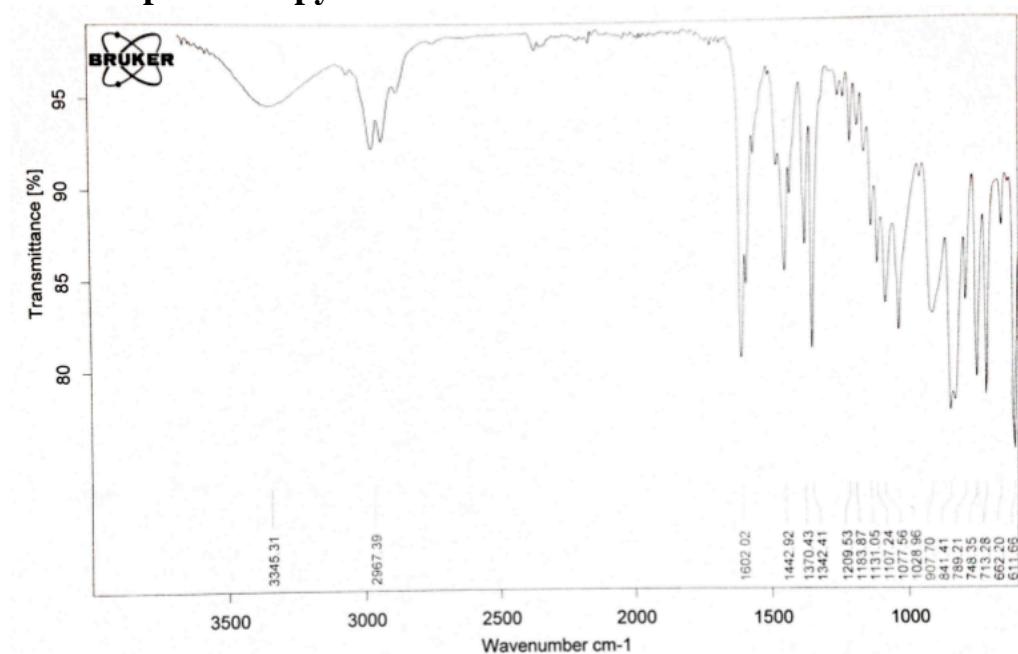


Figure S23. IR spectra of powdered form of silanediol **1** shows a single, broad O-H peak, which suggests multiple modes of hydrogen-bonding interactions in powder form.

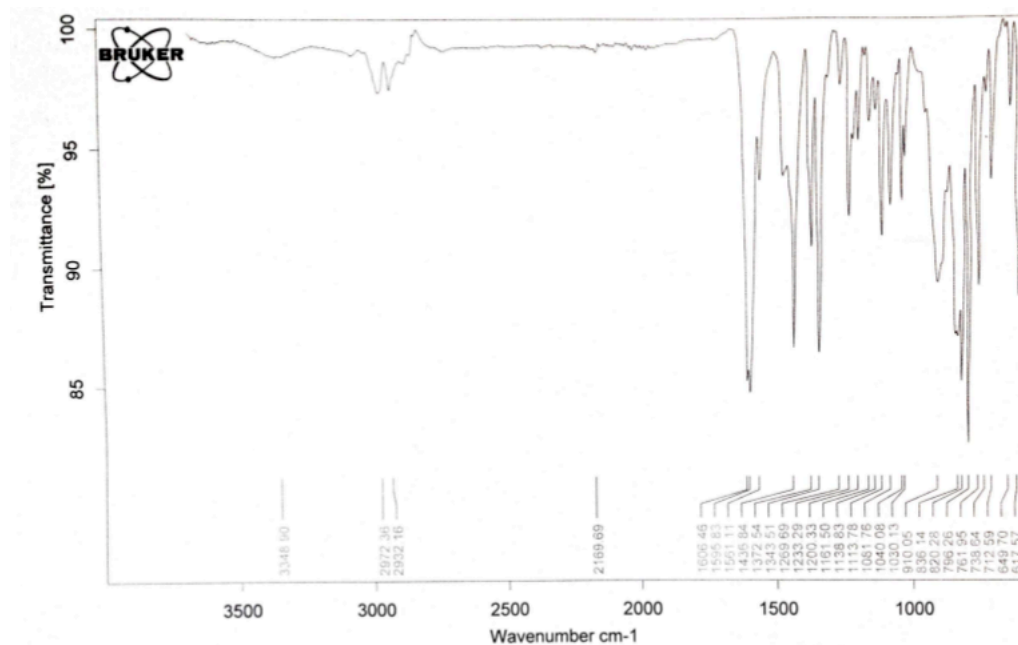


Figure S24. IR spectra of powdered form of silanediol **2** shows a single, broad O-H peak, which suggests multiple modes of hydrogen-bonding interactions in powder form.

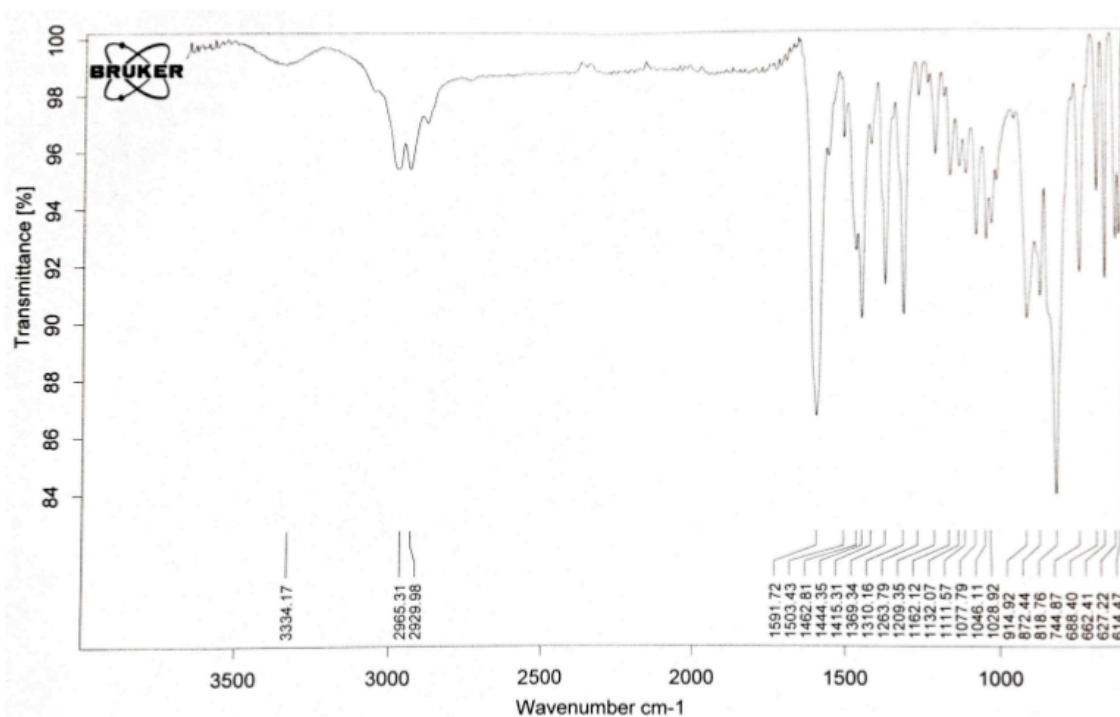


Figure S25. IR spectra of powdered form of silanediol **3** shows a single, broad O-H peak, which suggests multiple modes of hydrogen-bonding interactions in powder form.

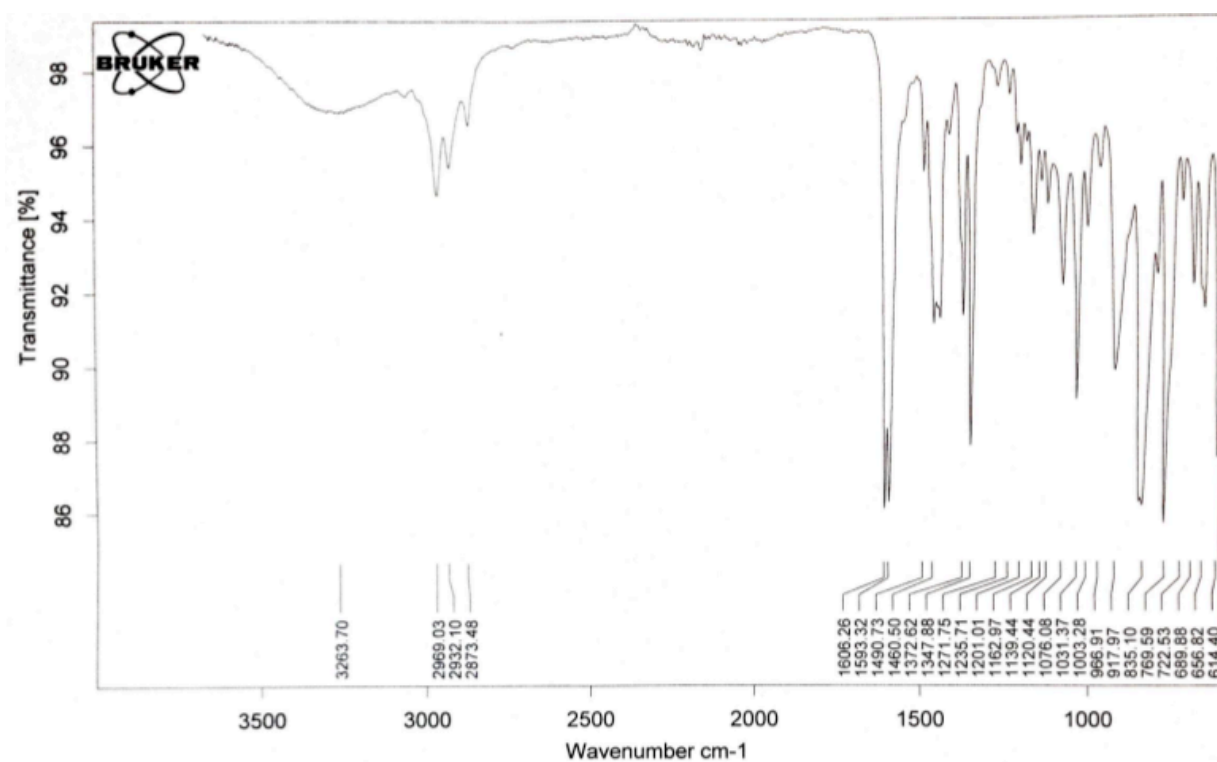


Figure S26. IR spectra of silanediol **4** shows a single, broad O-H peak, which suggests multiple modes of hydrogen-bonding interactions in powdered form.

VII. Crystallography Data^{6,7,8,9,10,11}

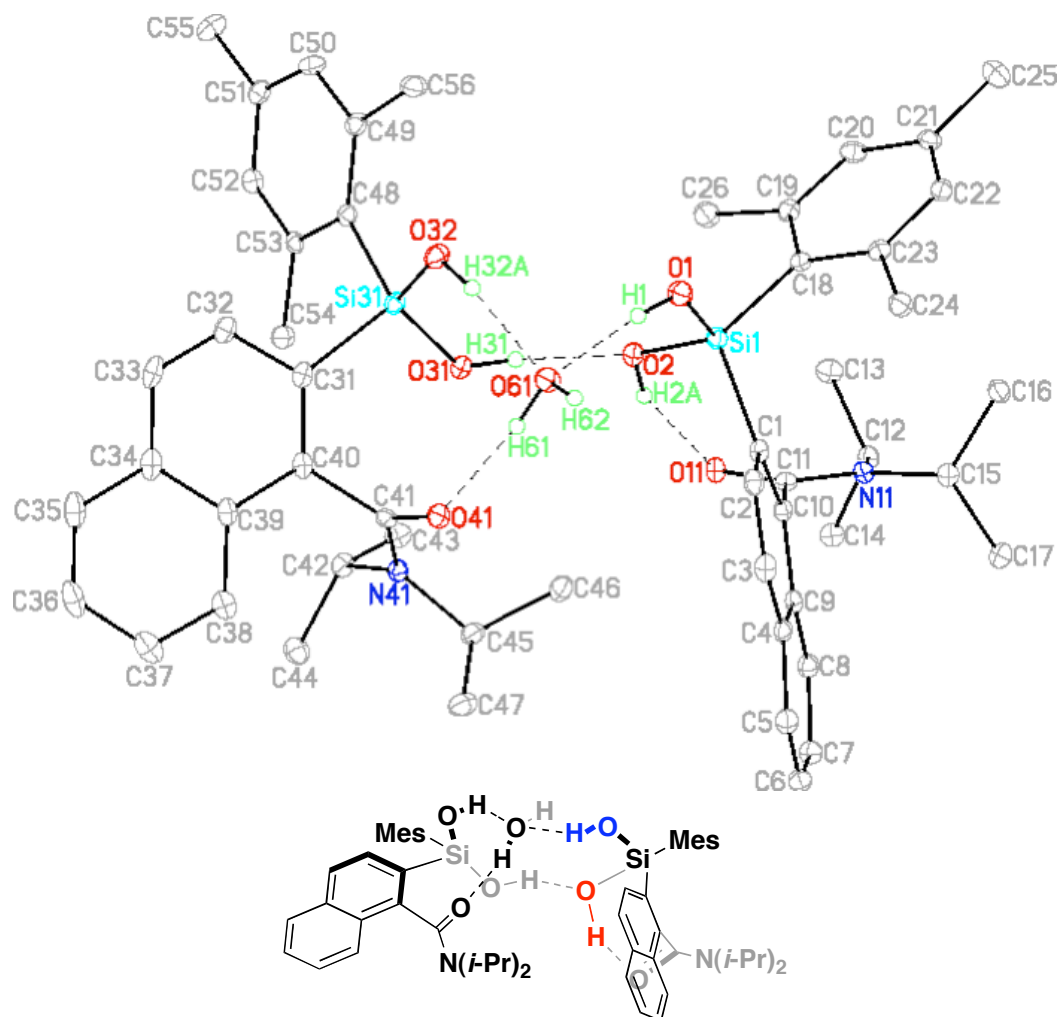


Figure S27. X-ray Crystal Structure of NT103 (**3**). Thermal displacement plot shows 30% probability displacement ellipsoids for non-hydrogens.

⁶ Bruker (2002). SMART (Version 5.054) and SAINT (Version 7.23a). Bruker AXS Inc., Madison, Wisconsin.

⁷ An Empirical Correction for Absorption Anisotropy, Blessing, R. H. (1995). *Acta Cryst.*, A51, 33-38.

⁸ Sheldrick, G.M., SADABS (2008) Version 2008/2, 'Siemens Area Detector Absorption Correction' Universität Göttingen: Göttingen, Germany.

⁹ Sheldrick, G.M., (2002). SHELXTL. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.

¹⁰ Sheldrick, G. M., (1997). SHELXS97 and SHELXL97. Universität Göttingen: Göttingen, Germany.

¹¹ On Enantiomorph-Polarity Estimation, Flack, H.D. (1983). *Acta Cryst.*, A39, 876-881.

Table S2. Crystal data and structure refinement for 2-[dihydroxy(mesityl)silyl]-N,N-diisopropyl-naphthalene-1-carboxamide.

Identification code	NT103	
Empirical formula	C ₅₂ H ₆₈ N ₂ O ₇ Si ₂	
Formula weight	889.26	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.944(3) Å	α = 96.38(2)°.
	b = 14.793(5) Å	β = 100.07(2)°.
	c = 16.344(3) Å	γ = 110.888(19)°.
Volume	2390.3(10) Å ³	
Z	2	
Density (calculated)	1.236 Mg/m ³	
Absorption coefficient	0.128 mm ⁻¹	
F(000)	956	
Crystal size	0.24 x 0.24 x 0.16 mm ³	
Crystal color and habit	colorless plate	
Diffractometer	Bruker SMART 1000	
Theta range for data collection	2.90 to 27.55°.	
Index ranges	-12 ≤ h ≤ 14, -19 ≤ k ≤ 19, -21 ≤ l ≤ 21	
Reflections collected	17867	
Independent reflections	10483 [R(int) = 0.0469]	
Observed reflections (I > 2σ(I))	6171	
Completeness to theta = 27.55°	94.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9795 and 0.9701	
Solution method	SHELXS-97 (Sheldrick, 2008)	
Refinement method	SHELXL-97 (Sheldrick, 2008)	
Data / restraints / parameters	10483 / 0 / 840	
Goodness-of-fit on F ²	0.988	
Final R indices [I > 2σ(I)]	R1 = 0.0500, wR2 = 0.1005	
R indices (all data)	R1 = 0.1105, wR2 = 0.1240	
Largest diff. peak and hole	0.424 and -0.398 e.Å ⁻³	

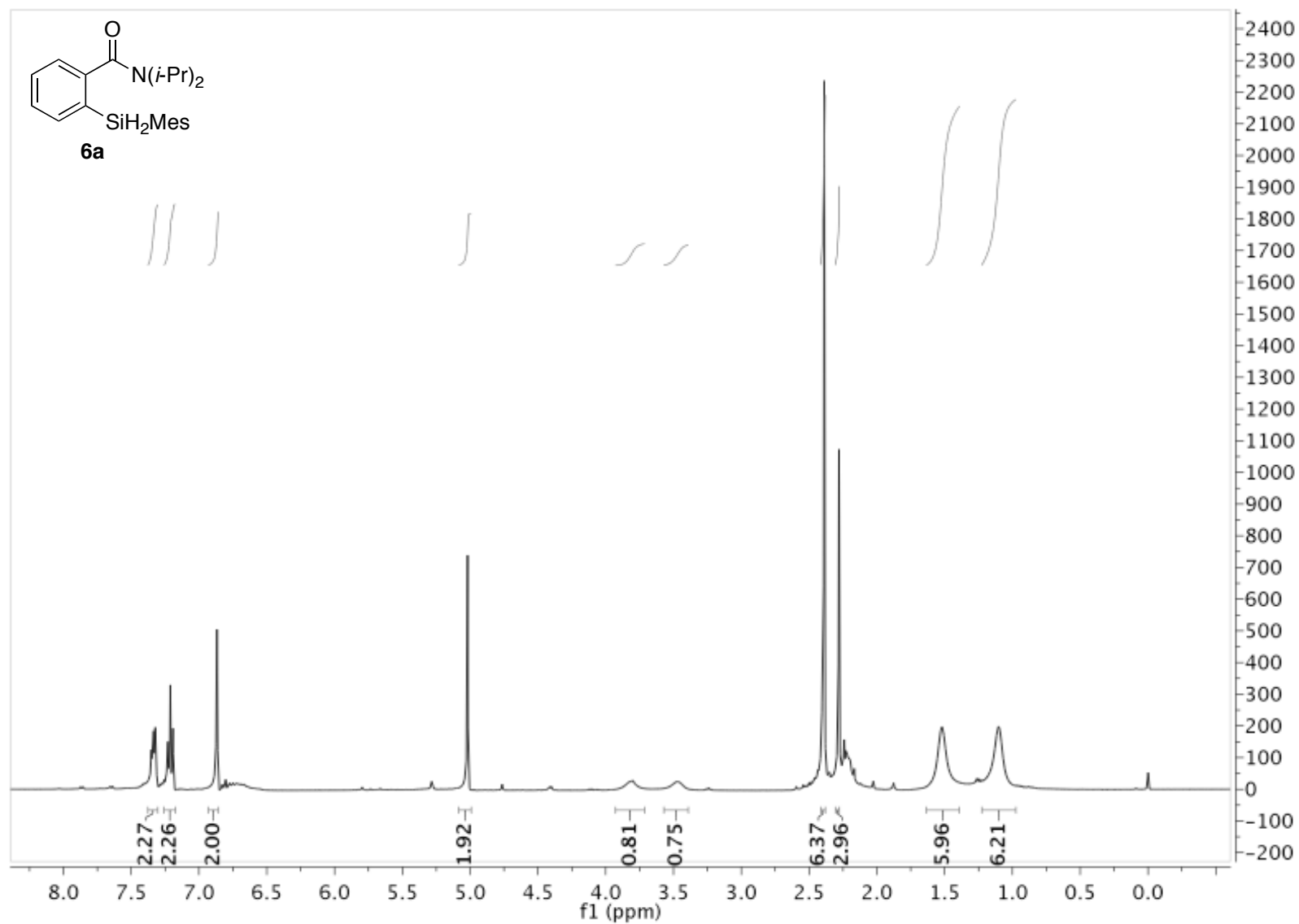
Table S3. Hydrogen bonds for NT103 (**3**) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(31)-H(31)...O(2)	0.84(3)	1.87(3)	2.707(3)	169(3)
O(2)-H(2A)...O(11)	0.85(4)	1.94(4)	2.746(3)	157(3)
O(1)-H(1)...O(61)	0.82(4)	1.98(4)	2.798(3)	172(4)
O(32)-H(32A)...O(61)	0.83(3)	1.94(3)	2.758(3)	168(3)
O(61)-H(61)...O(41)	0.91(3)	1.92(4)	2.826(3)	173(3)

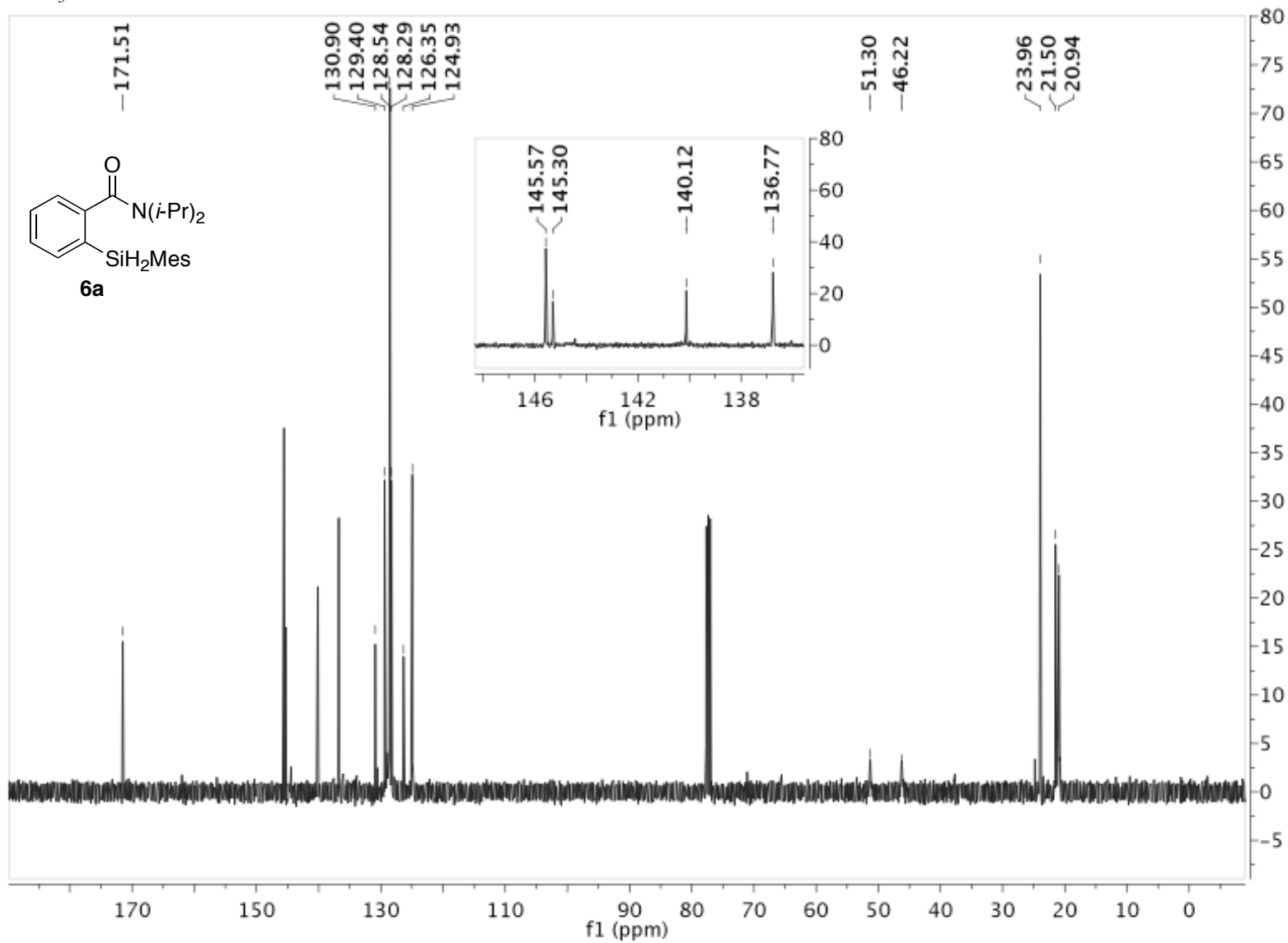
Symmetry transformations used to generate equivalent atoms:

VIII. ^1H , ^{13}C , and ^{29}Si NMR spectra

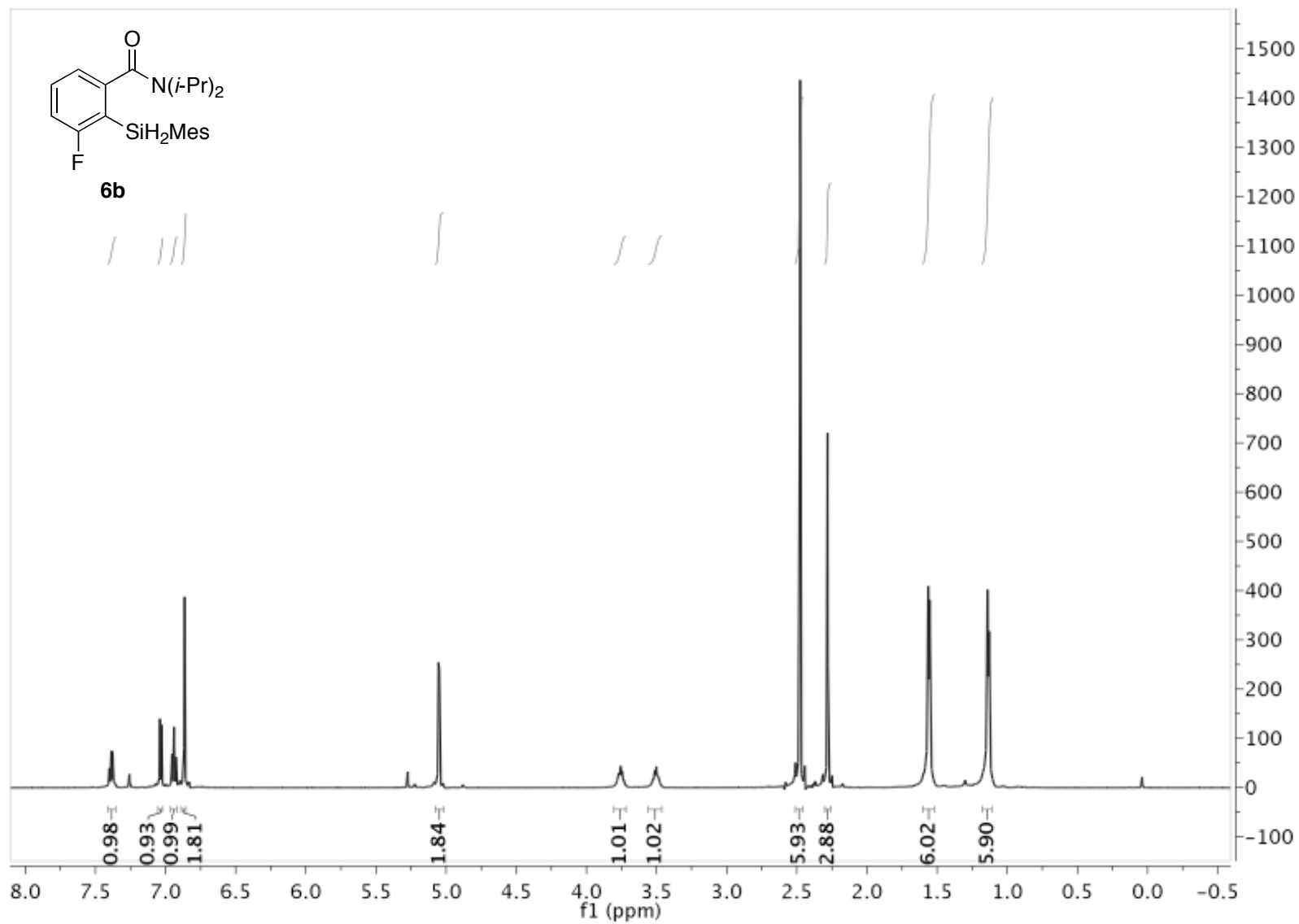
CDCl_3 , 400 MHz



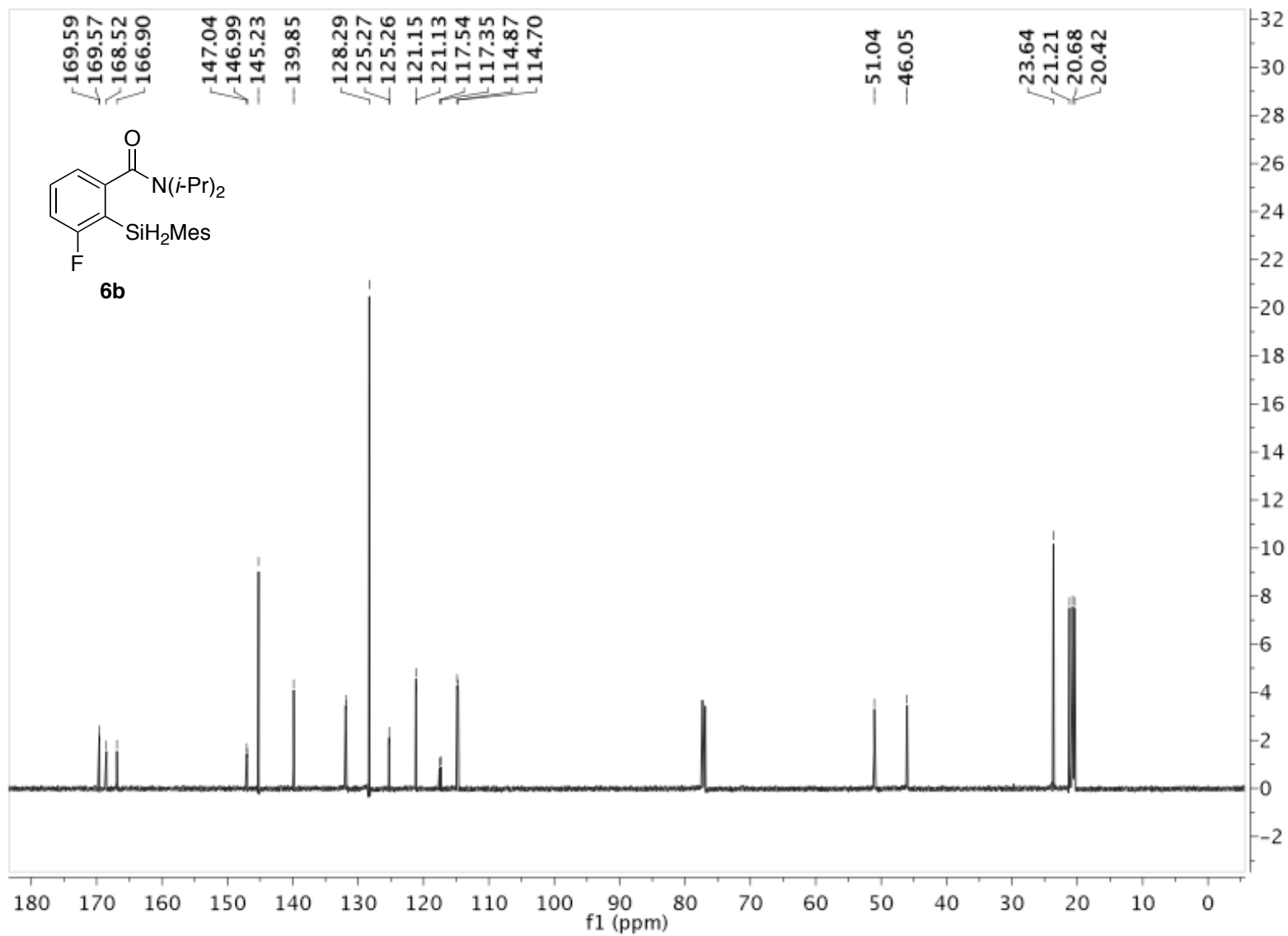
CDCl₃, 100 MHz



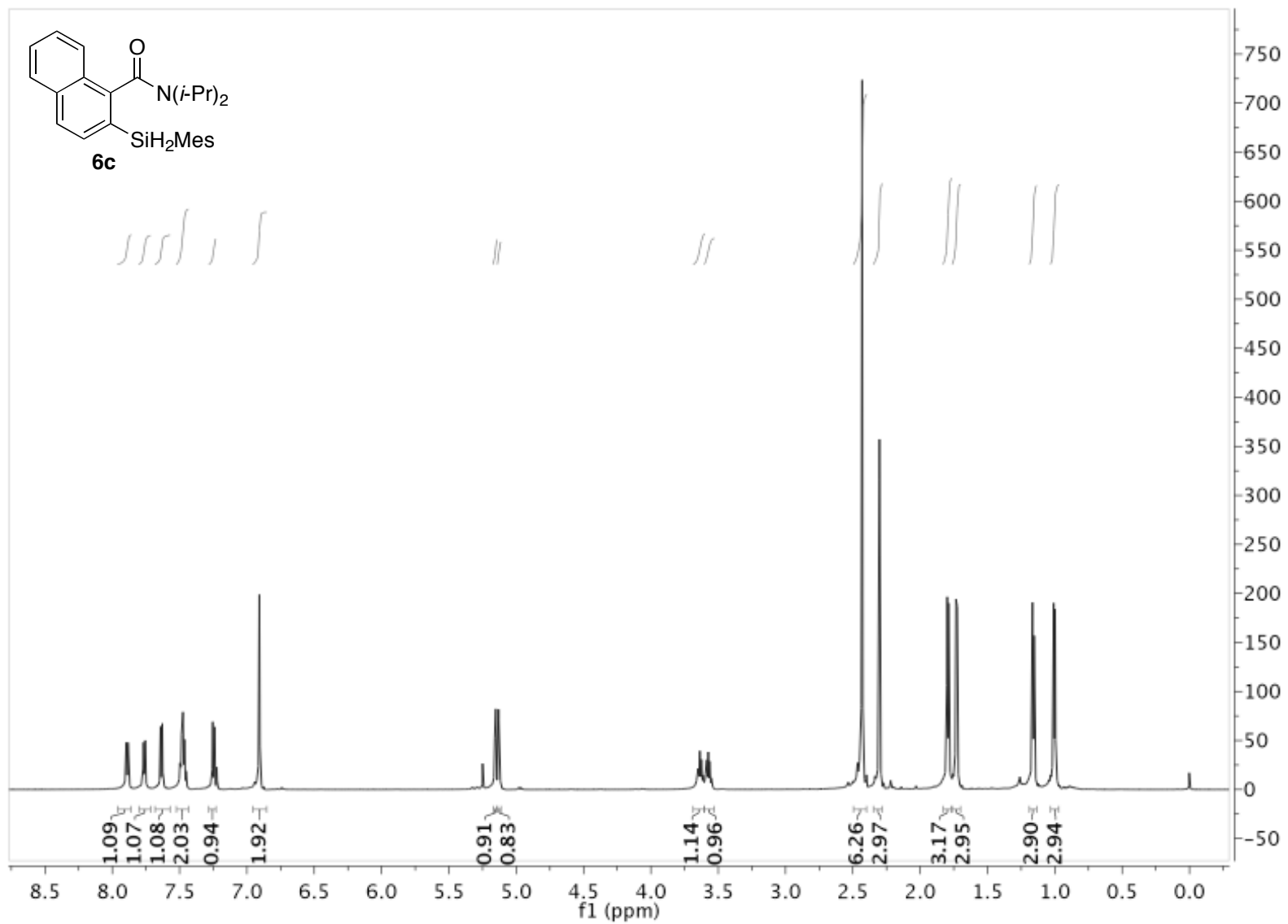
CDCl₃, 600 MHz



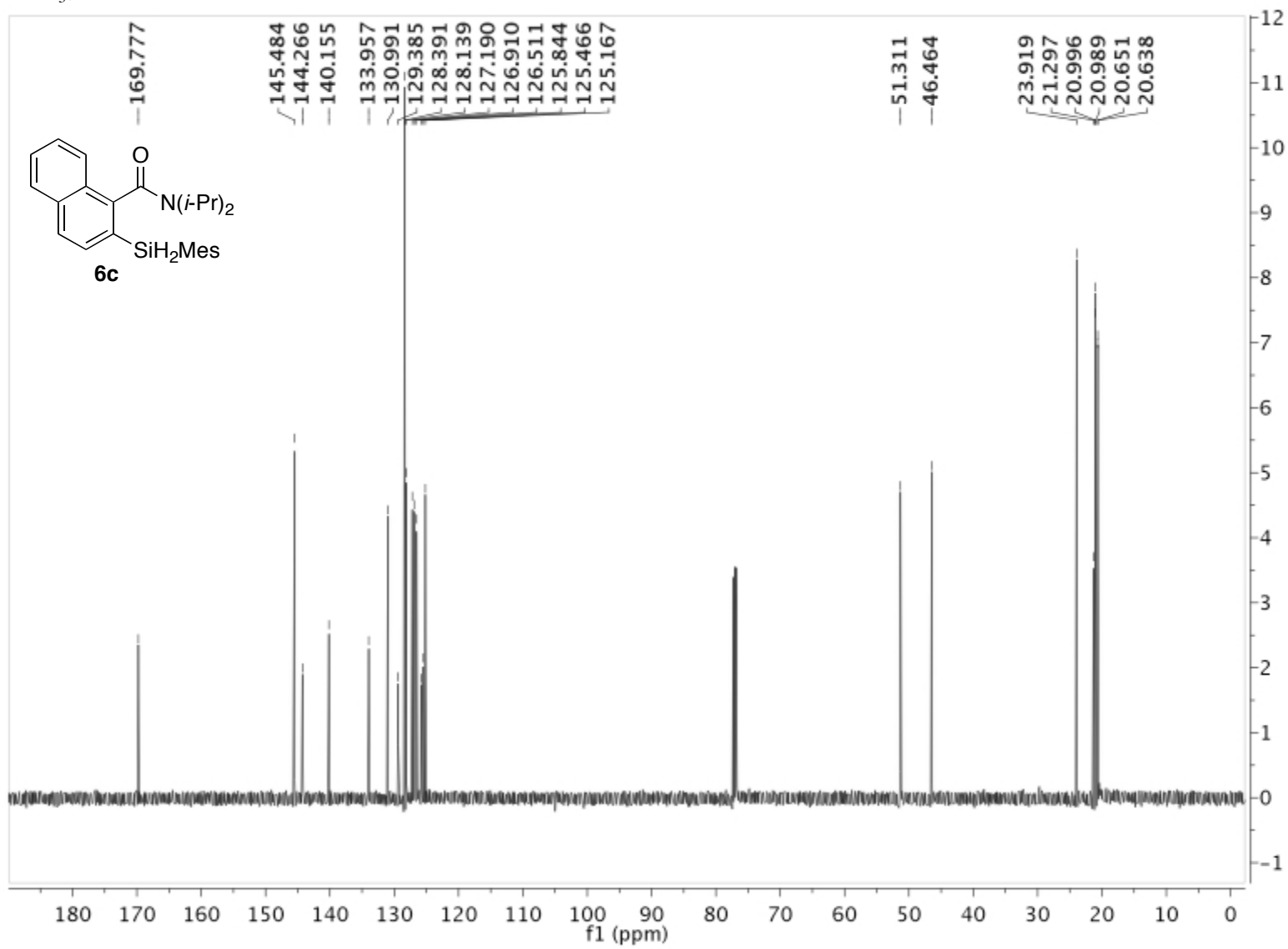
CDCl₃, 150 MHz



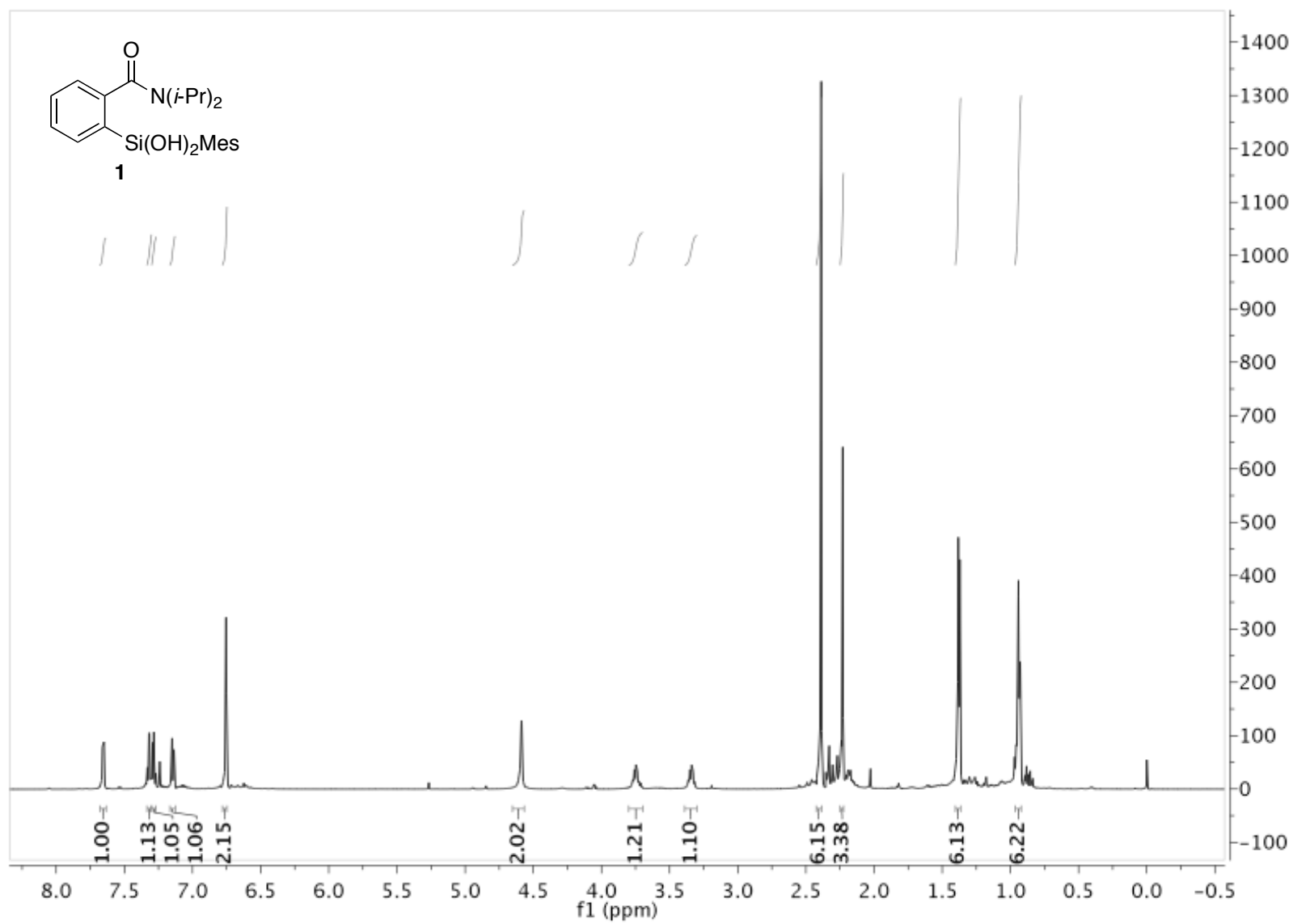
CDCl₃, 600 MHz



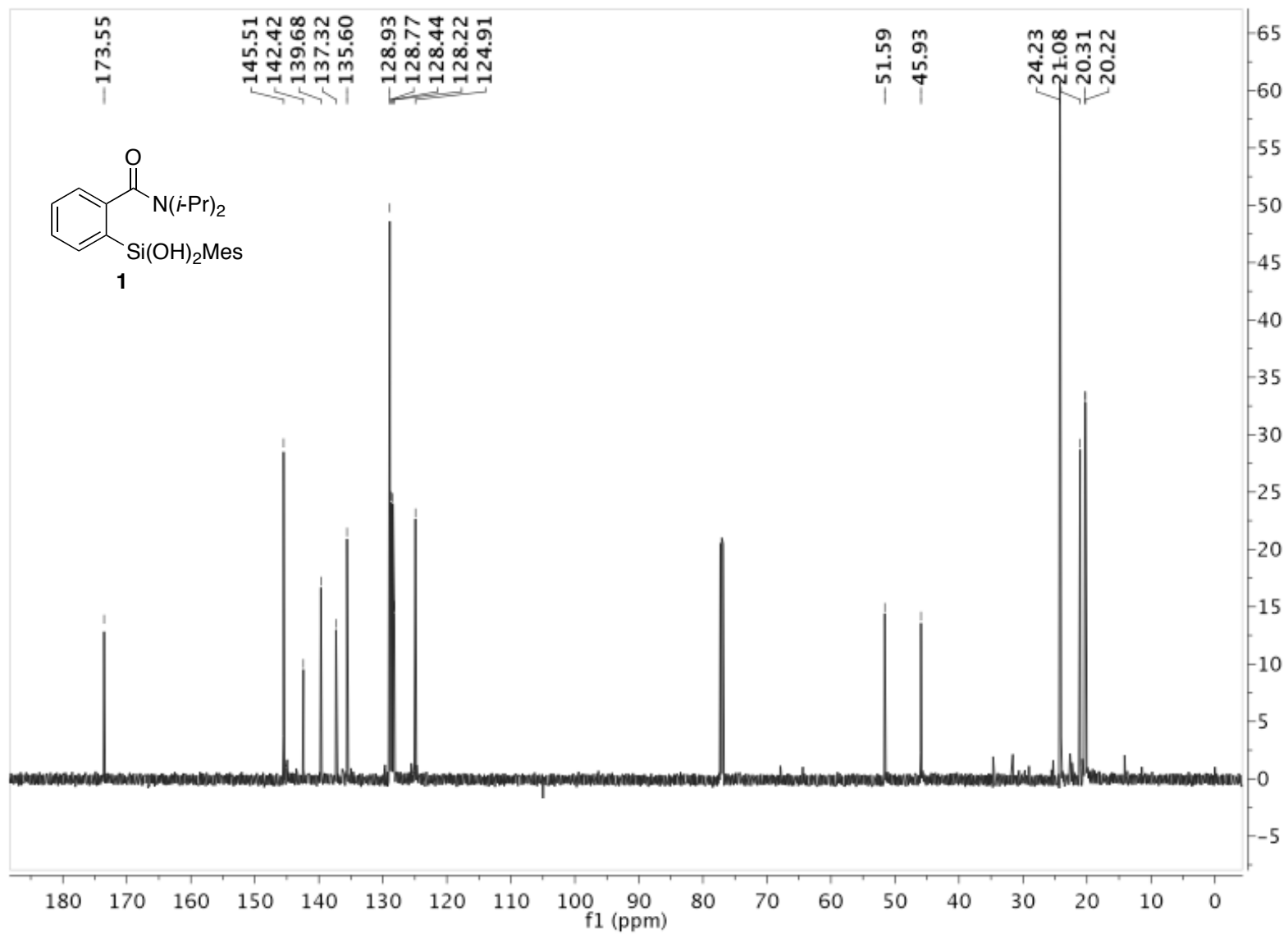
CDCl₃, 150 MHz



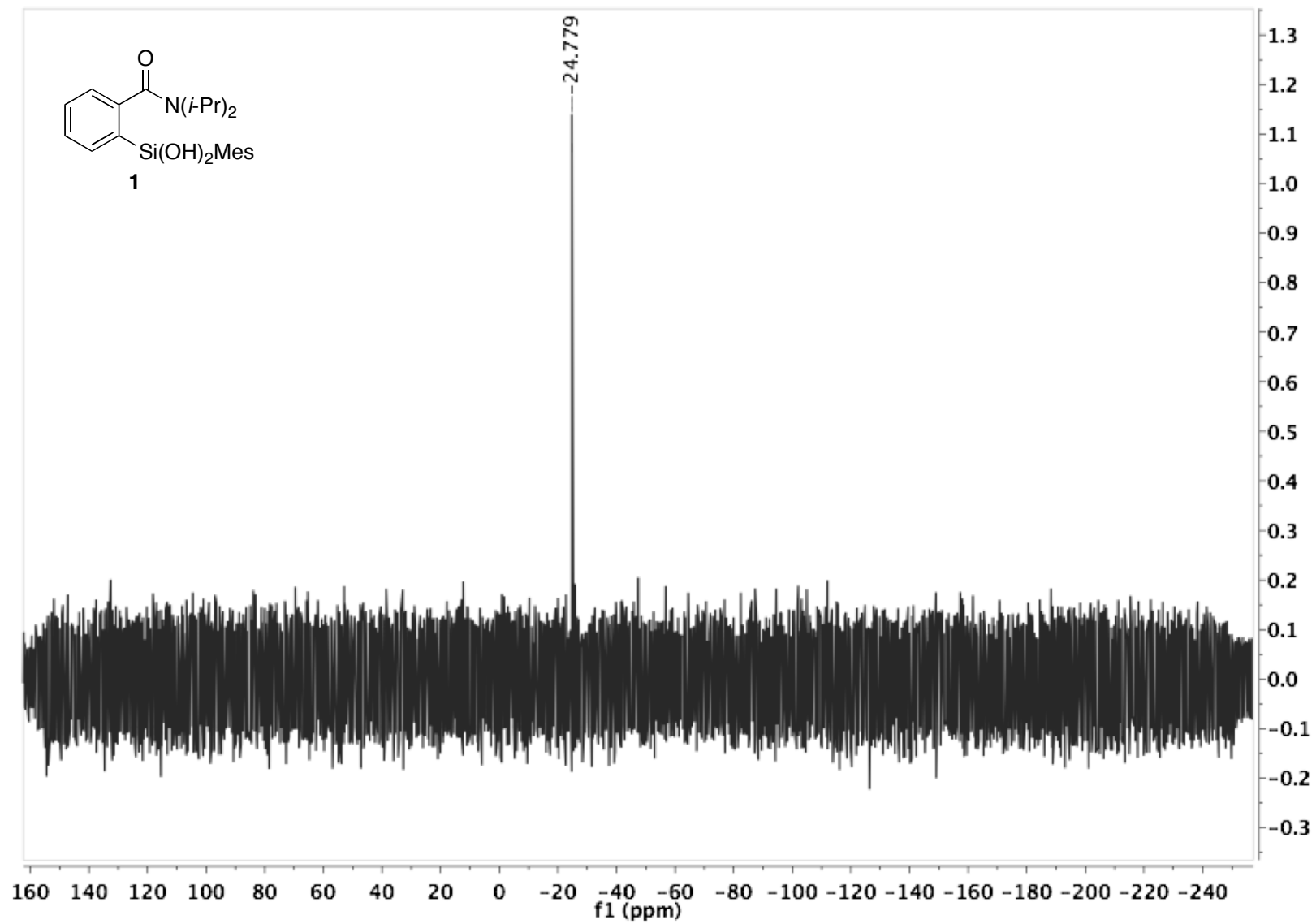
CDCl₃, 600 MHz



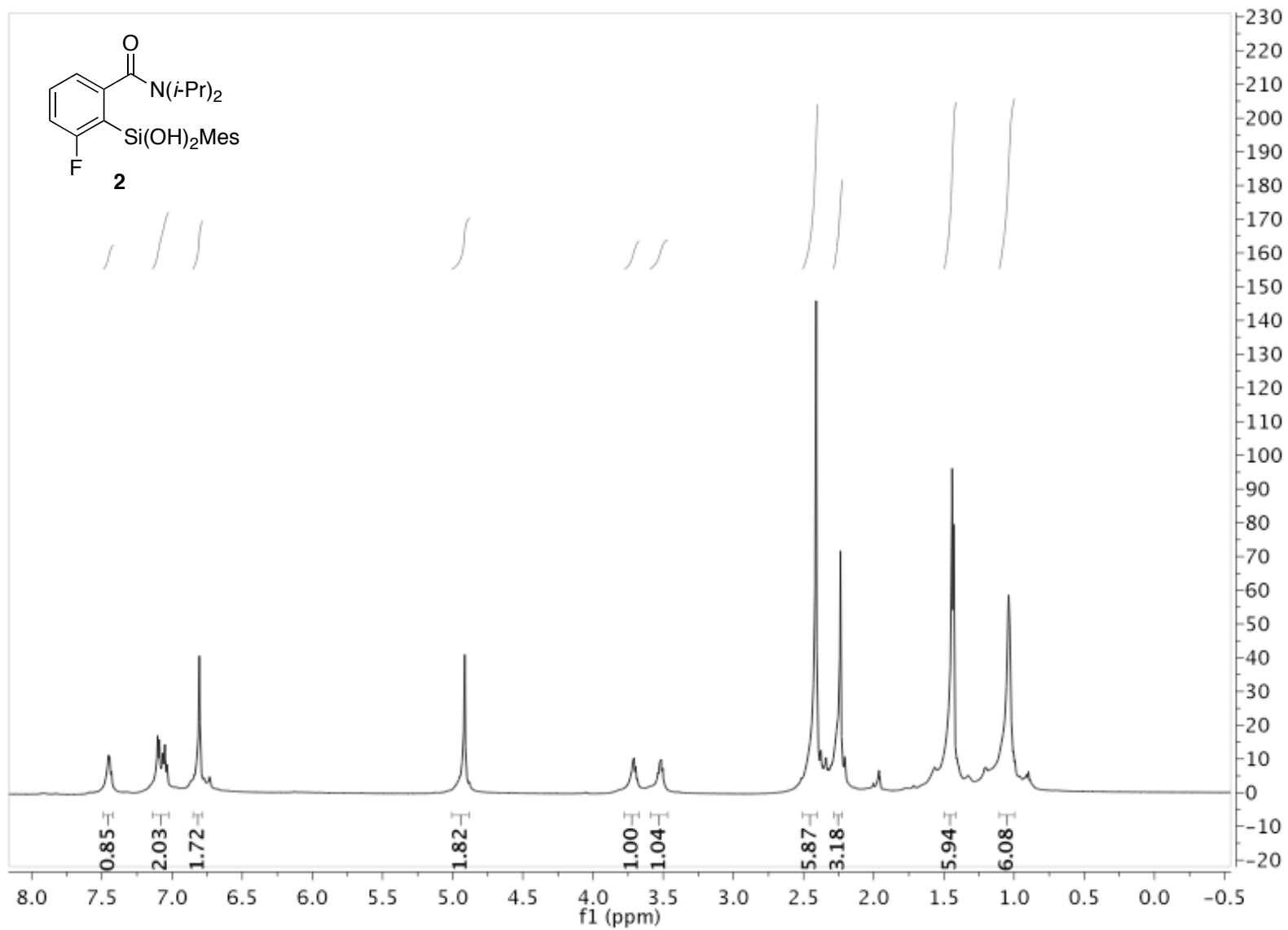
CDCl₃, 150 MHz



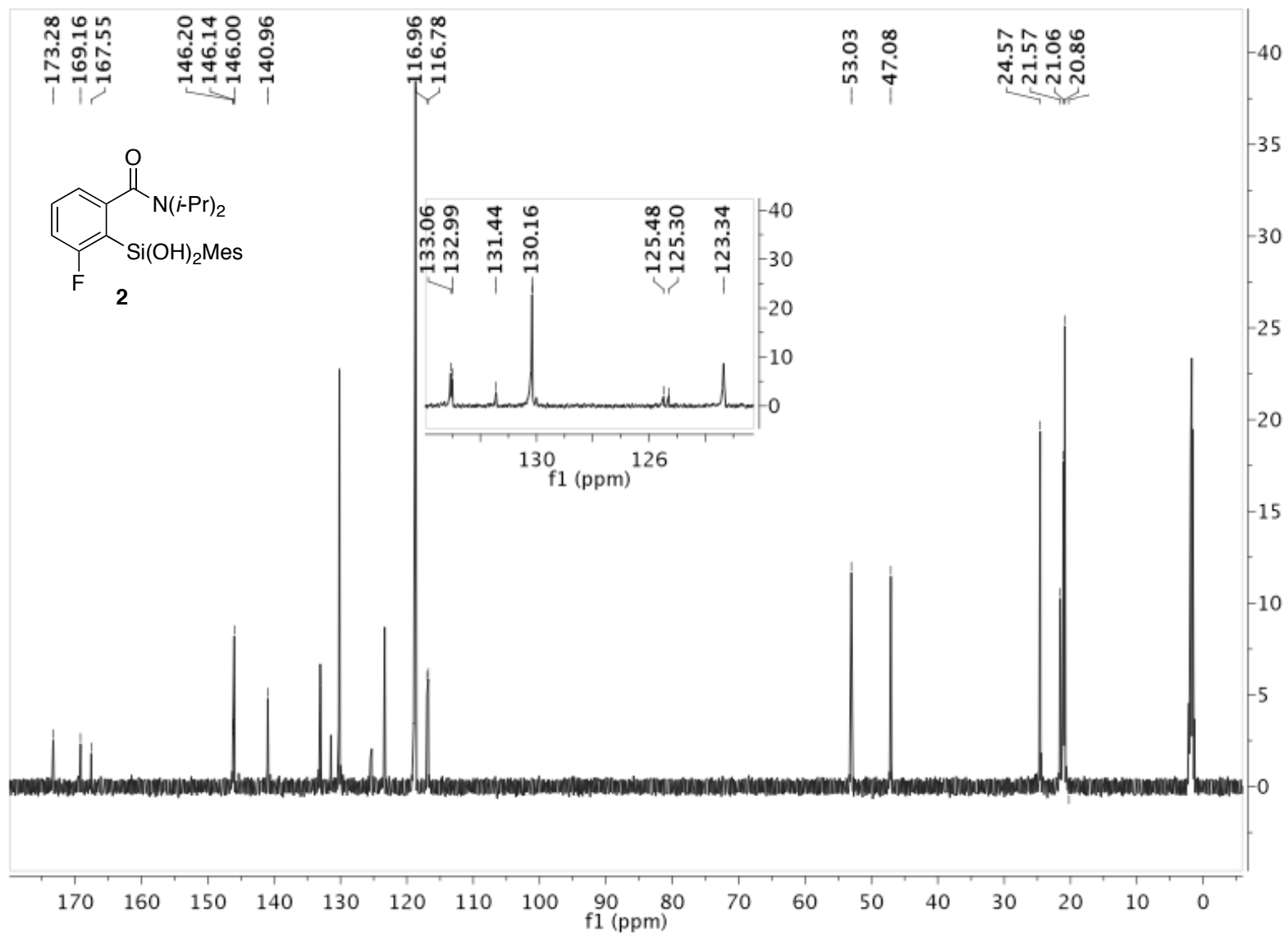
^{29}Si NMR, CDCl_3 , 119 MHz



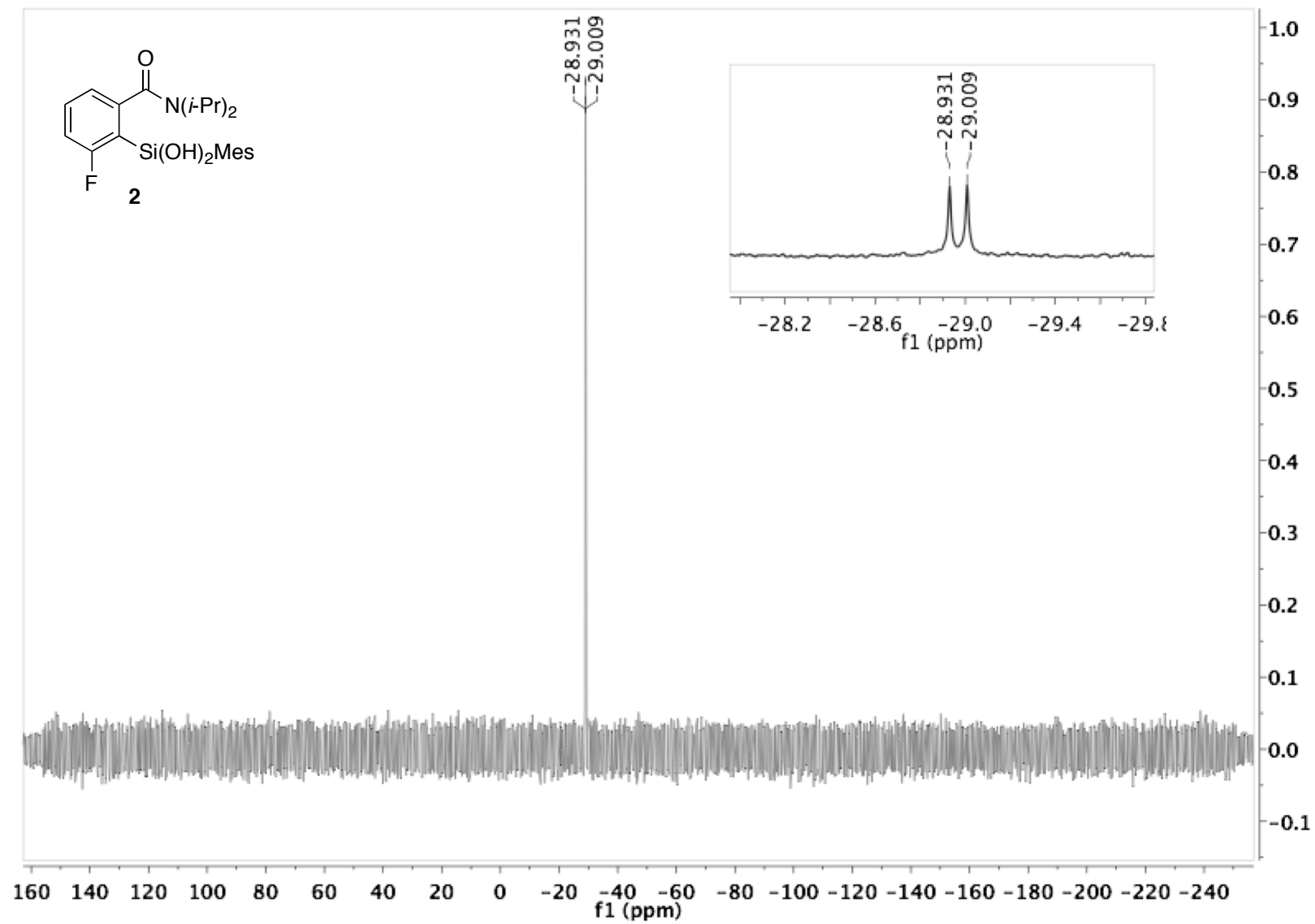
CD₃CN, 600 MHz



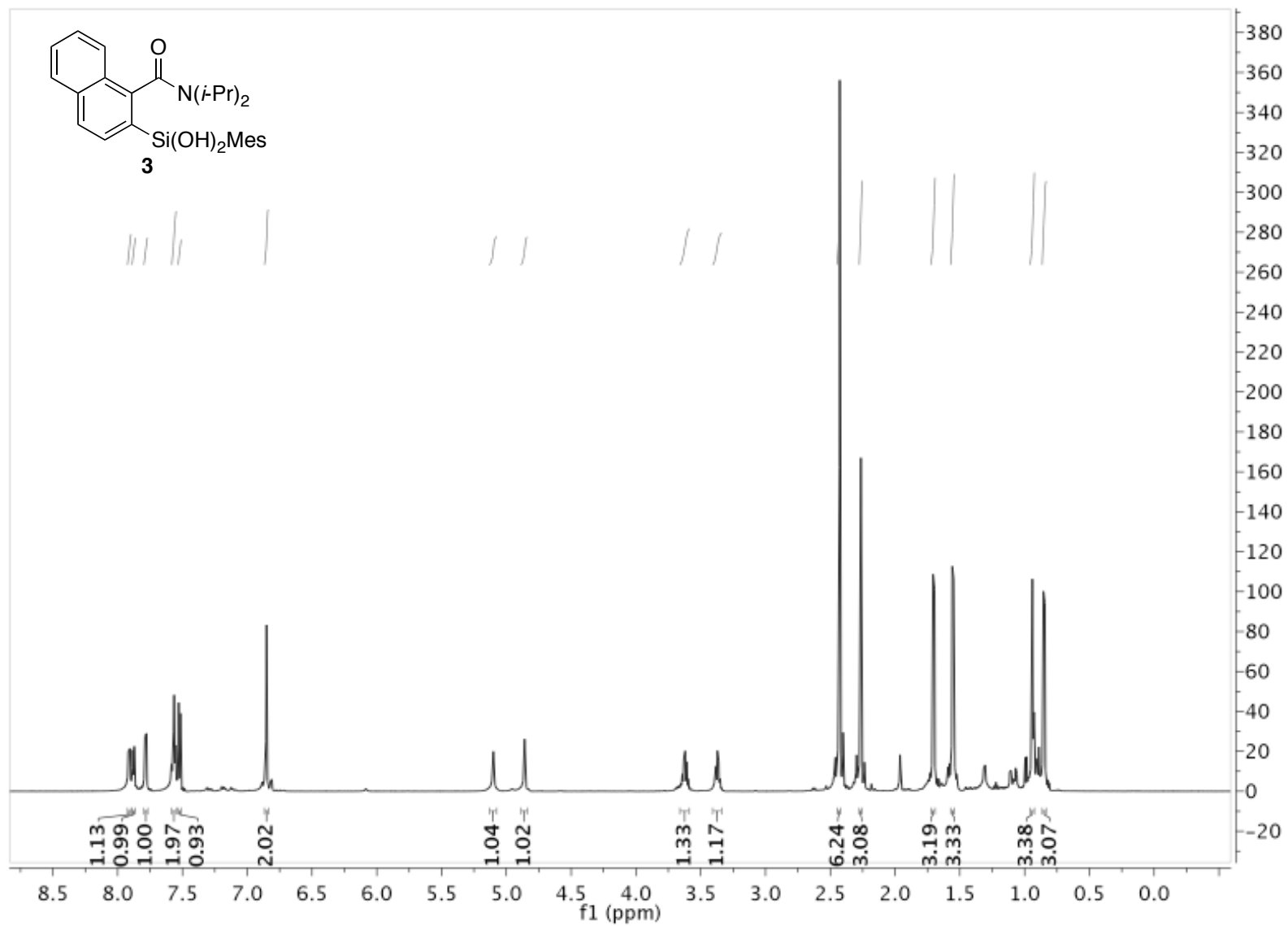
CD₃CN, 150 MHz



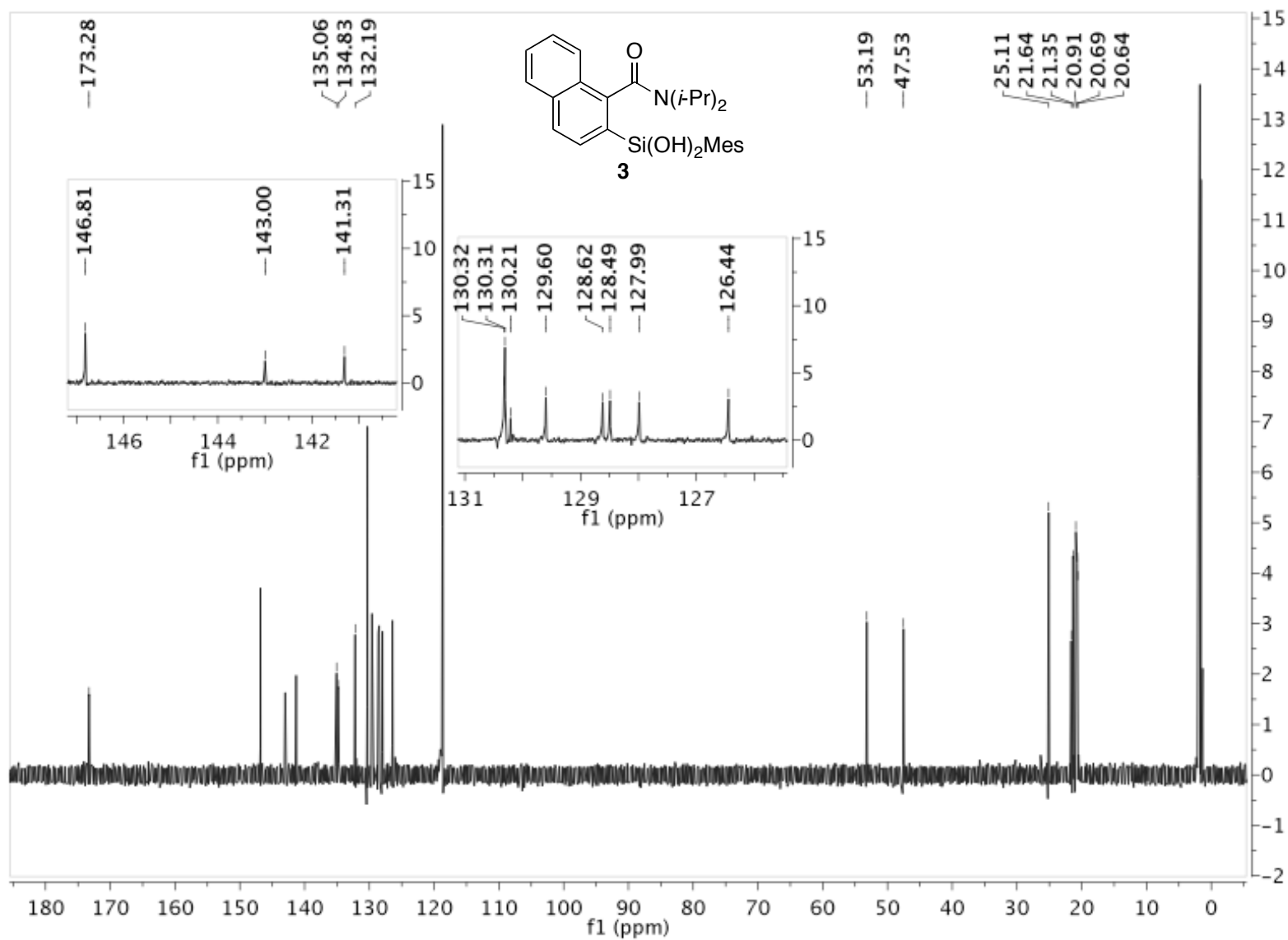
^{29}Si NMR, CDCl_3 , 119 MHz



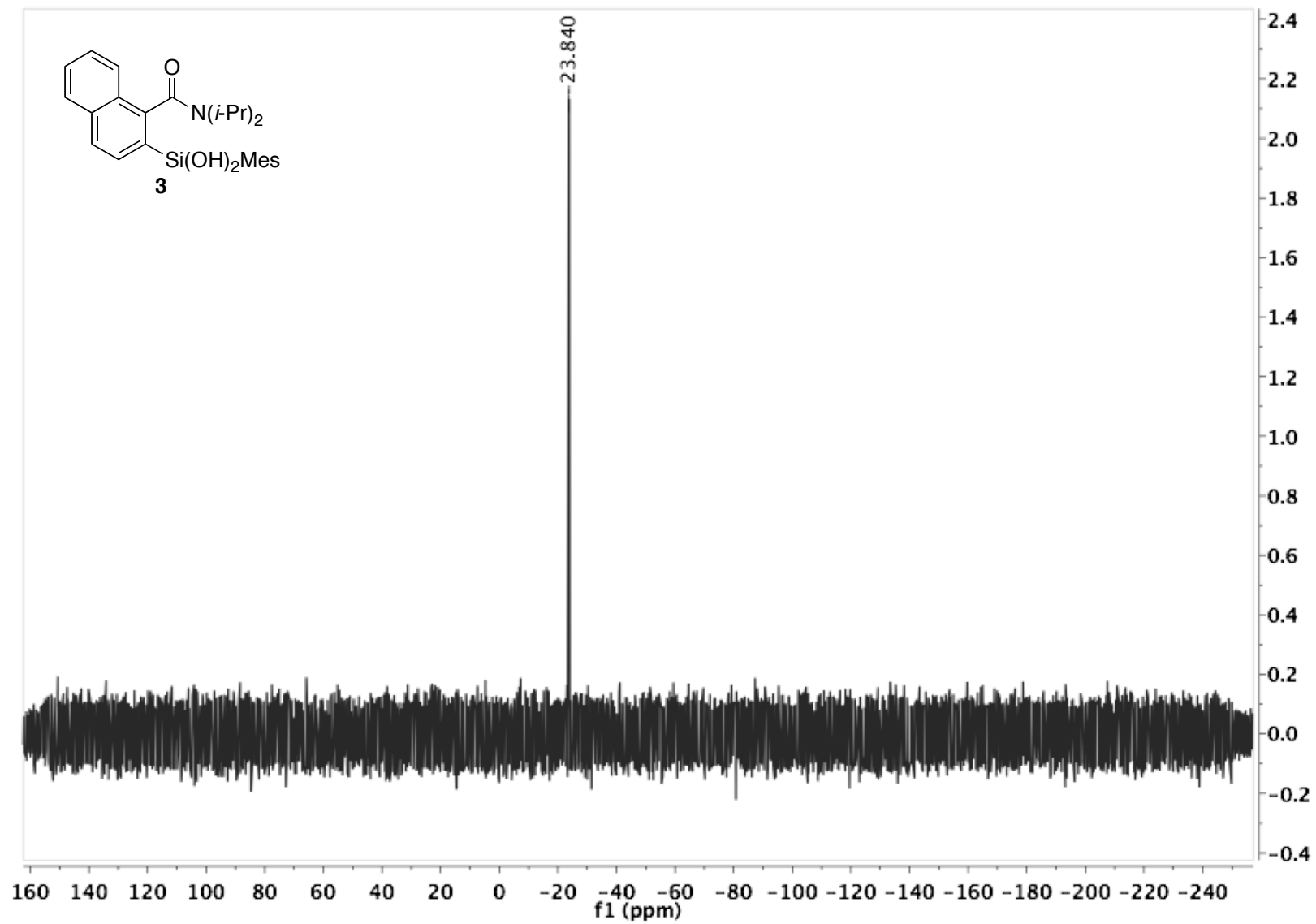
CD₃CN, 600 MHz



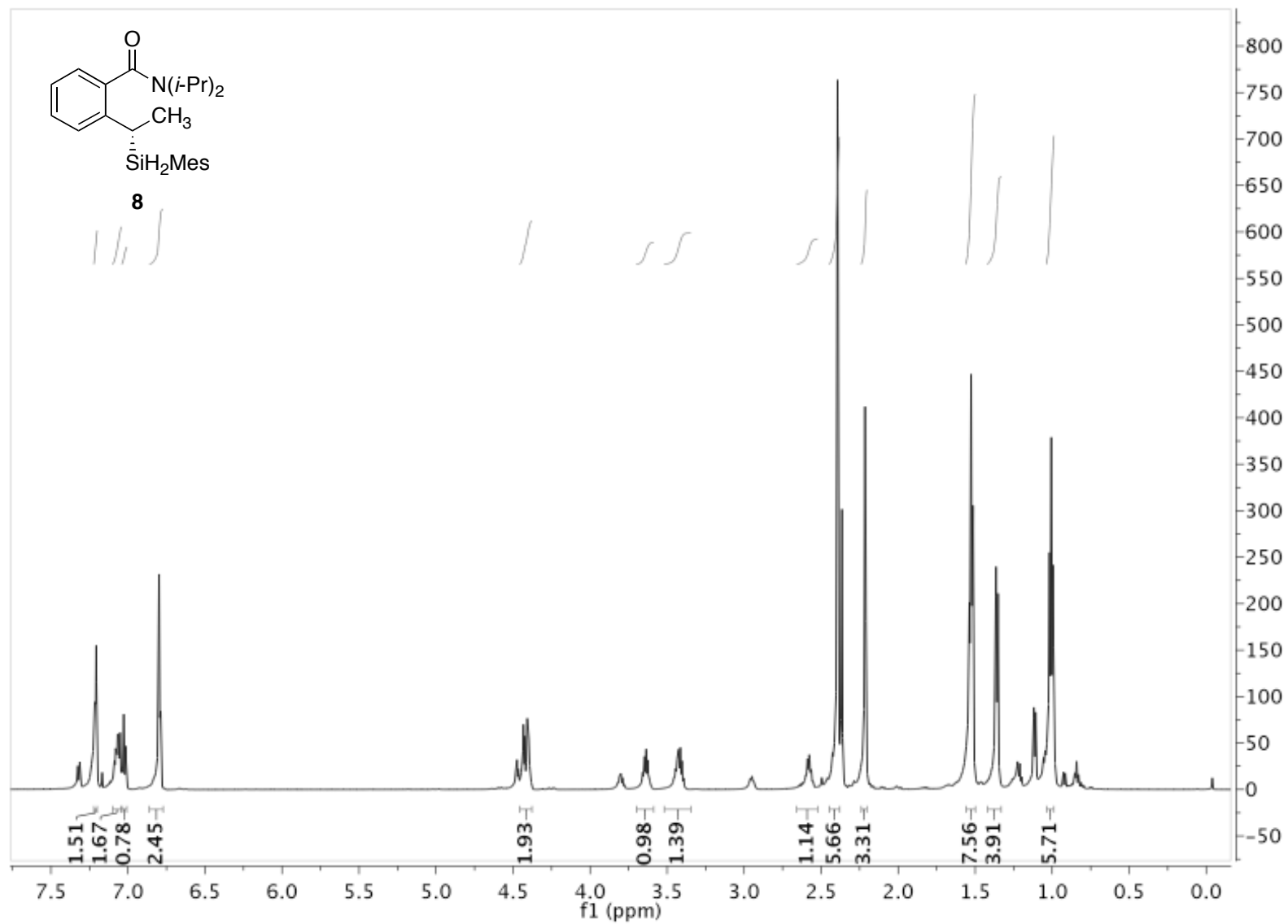
CD₃CN, 150 MHz



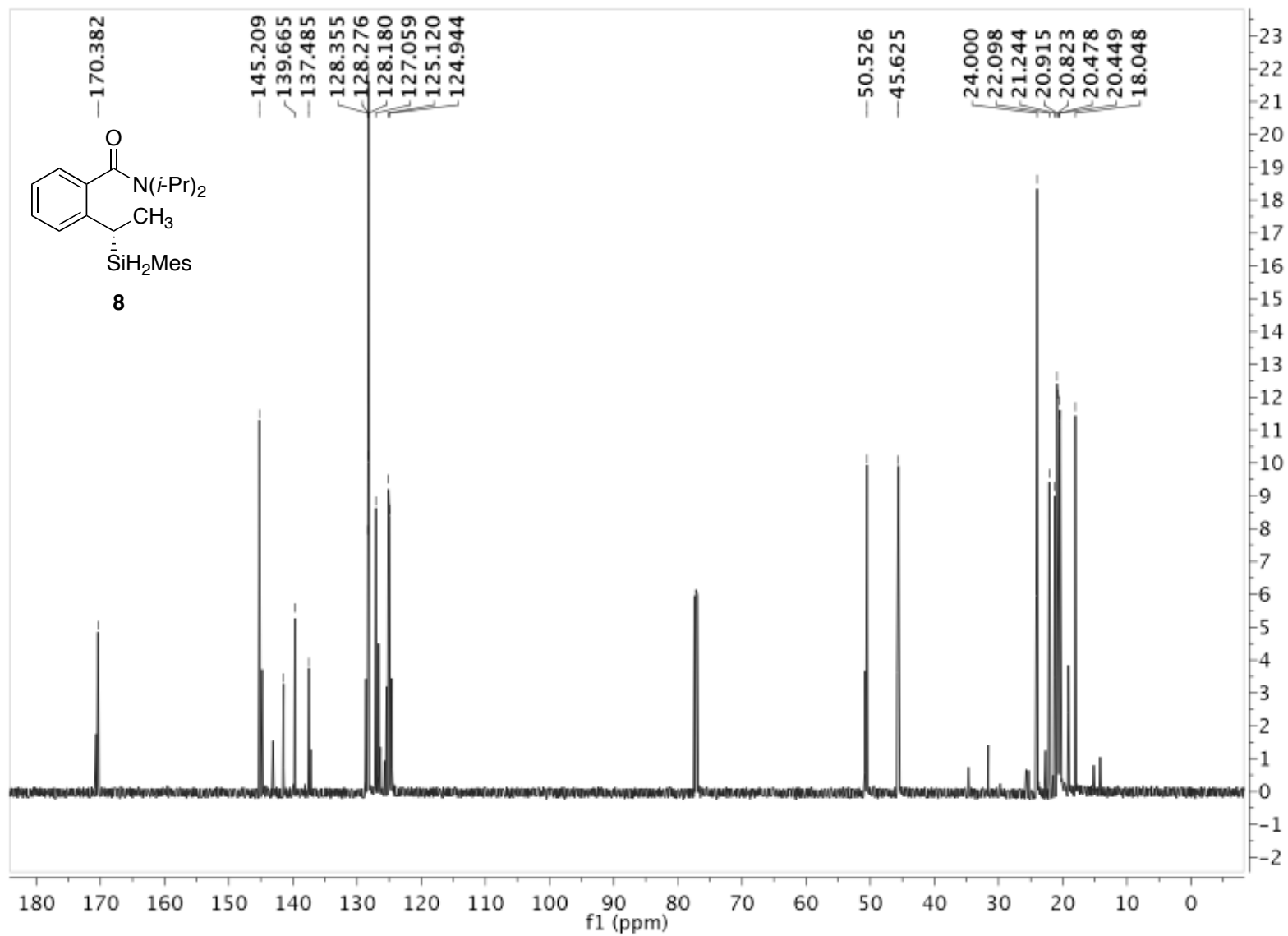
^{29}Si NMR, CD_3CN , 119 MHz



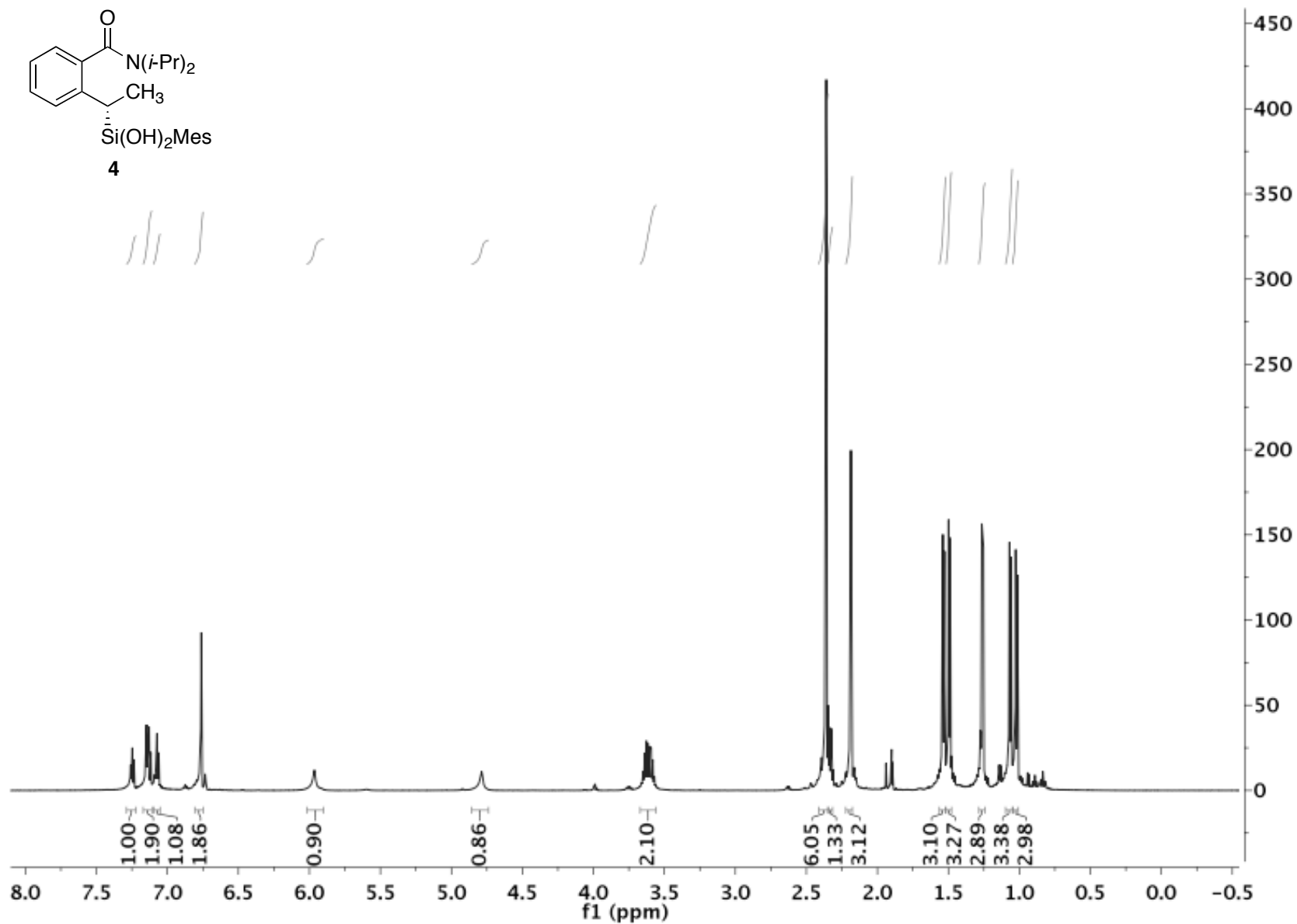
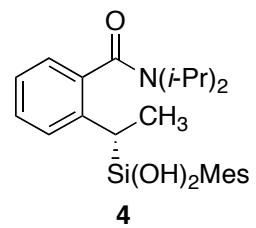
CDCl₃, 600 MHz



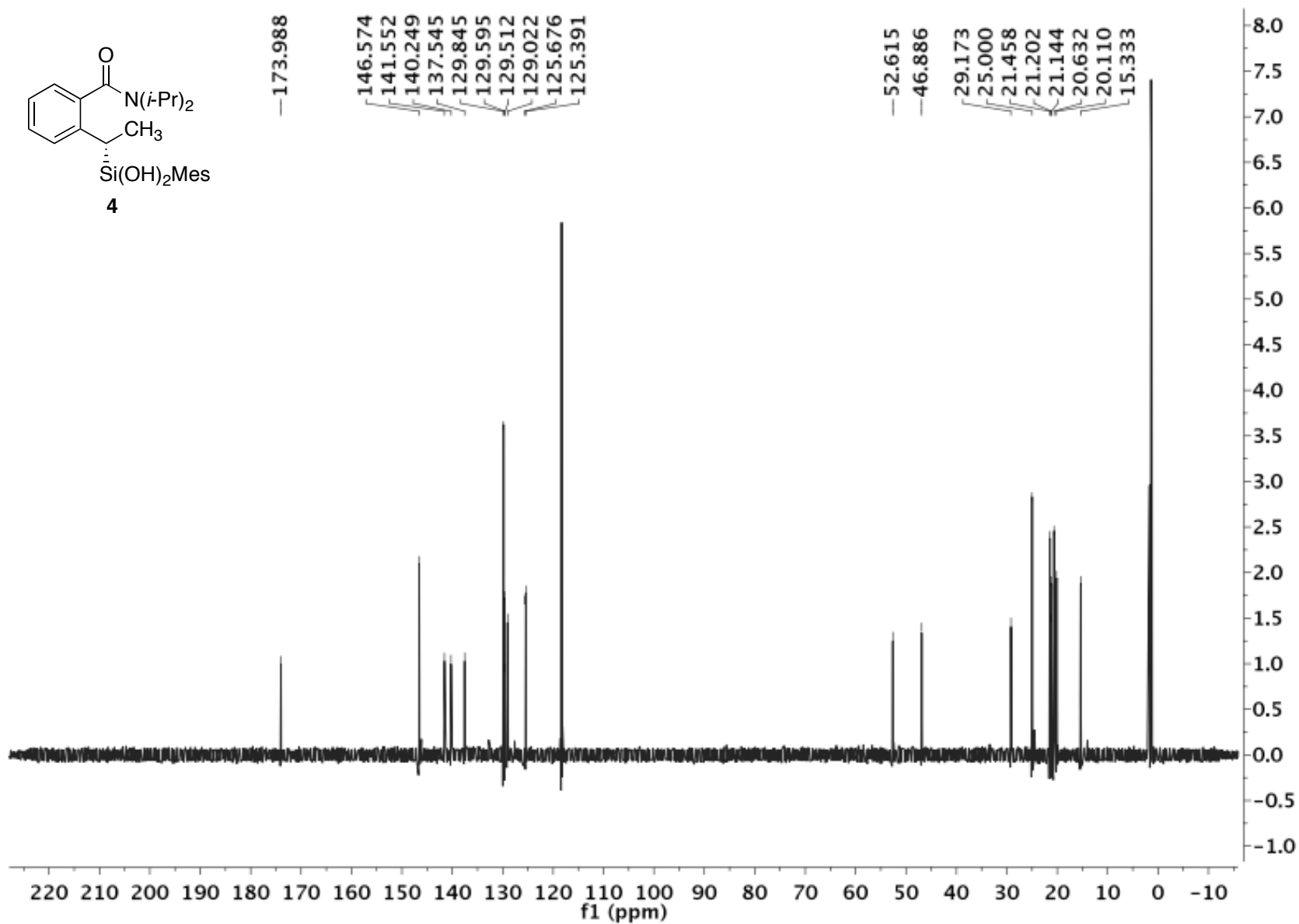
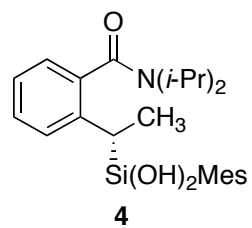
CDCl₃, 150 MHz



CD₃CN, 600 MHz



CD₃CN, 150 MHz



^{29}Si NMR, CD_3CN , 119 MHz

