

Supporting Information for:

Metal-free Synthesis of 1,3-disiloxanediols and Aryl Siloxanols

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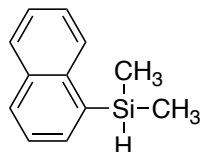
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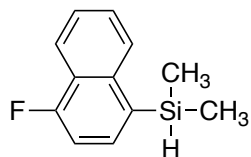
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I. Synthesis of Silanes for Structural investigation of Tamao Fleming vs. Silane Hydrolysis

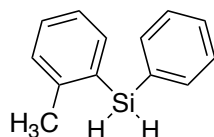


Synthesis of dimethyl(naphthalen-1-yl)silane (4f): Magnesium turnings (0.264 g, 11.0 mmol, 1.1 equiv) were added to 20 mL of THF in an Ar-charged round-bottom flask. The 1-bromonaphthalene (1.4 mL, 10 mmol, 1 equiv) was then added and was allowed to stir at room temp for 3 h. The solution was then cooled to -78°C and dimethylchlorosilane (1.11 mL, 10 mmol, 1 equiv) was then added quickly. The reaction was warmed to room temperature and stirred for 16 h. The reaction was then quenched by the addition of a solution of saturated aqueous ammonium chloride (5 mL) and filtered over celite. The organic layer was separated, and the aqueous layer was washed with Et_2O (3 x 10 mL), then the organic layers were combined and washed with brine (10 mL), dried over anhydrous MgSO_4 , filtered, and then concentrated in vacuo. The crude product was purified via flash column chromatography (hexanes) to yield **4f** as a colorless oil. Yield: 1.135 g (61 %); ^1H NMR (CDCl_3 , 600 MHz) δ : 8.13 (d, $J = 8.0$ Hz, 1H), 7.88 (t, $J = 7.9$ Hz, 2H), 7.74 (d, $J = 6.5$ Hz, 1H), 7.51 (ddd, $J = 26.0, 14.4, 7.1$ Hz, 3H), 4.96 – 4.79 (m, 1H), 0.52 – 0.49 (m, 6H); ^{13}C NMR (CDCl_3 , 150 MHz) δ : 136.9, 135.6, 133.6, 133.1, 130.0, 128.9, 127.6, 125.9, 125.5, 125.1, -3.3 ; ^{29}Si NMR (CDCl_3 , 119 MHz) δ : -19.67 . Matched literature spectra.³⁰

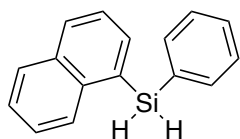


Synthesis of (4-fluoronaphthalen-1-yl)dimethylsilane (4g): Magnesium turnings (0.264 g, 11 mmol, 1.1 equiv) were added to 20 mL of THF in an Ar-charged round-bottom flask. The 1-bromonaphthalene (1.4 mL, 10 mmol, 1 equiv) was then added and was allowed to stir at room temp for 3 h. The solution was then cooled to -78°C and dimethylchlorosilane (1.11 mL, 10 mmol, 1 equiv) was then added quickly. The reaction was warmed to room temperature and stirred for 16 h. The reaction was then quenched by the addition of a solution of saturated aqueous ammonium chloride (5 mL) and filtered over celite. The organic layer was separated, and the aqueous layer was washed with Et_2O (3 x 10 mL), then the organic layers were combined and washed with brine (10 mL), dried over anhydrous MgSO_4 , filtered, and then concentrated in vacuo. The crude product was purified via flash column chromatography (hexanes) to

yield **4g** as a colorless oil. Yield: 1.304 g (64 %); ^1H NMR (CDCl_3 , 600 MHz) δ : 8.17 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 6.5 Hz, 1H), 7.57 (m J = 7.2 Hz, 2H), 7.17 – 7.08 (m, 3H), 4.96 – 4.73 (m, 1H), 0.59 – 0.33 (m, 9H); ^{13}C NMR (CDCl_3 , 150 MHz) δ : 160.3 (d, J = 254.5 Hz), 138.5 (d, J = 4.7 Hz), 133.6 (d, J = 8.4 Hz), 131.3 (d, J = 5.3 Hz), 127.4 (d, J = 3.5 Hz), 126.9, 125.8 (d, J = 2.2 Hz), 123.7 (d, J = 15.1 Hz), 121.2 (d, J = 6.4 Hz), 108.8 (d, J = 18.5 Hz), –3.3; ^{19}F NMR (CDCl_3 , 282 MHz) δ : –121.14; ^{29}Si NMR (CDCl_3 , 119 MHz) δ : –19.71.

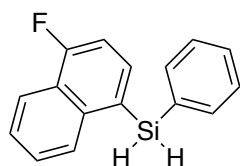


Synthesis of phenyl(o-tolyl)silane (4l): Magnesium turnings (0.132 g, 5.5 mmol, 1.1 equiv) were added to 10 mL of THF in an Ar-charged round-bottom flask. The 2-bromotoluene (0.60 mL, 5 mmol, 1 equiv) was then added and was allowed to stir at room temp for 3 h. The solution was then cooled to –78 °C and PhSiHCl_2 (0.74 mL, 5 mmol, 1 equiv) was then added quickly. The reaction was warmed to room temperature and stirred for 16 h. The reaction was then cooled to –78 °C and LAH (1.5 mL of 4.0 M in Et_2O , 6 mmol, 1.2 equiv) was added and the reaction was allowed to stir at room temperature for 3 h. The reaction was then quenched by the addition of a solution of saturated aq. sodium bicarbonate (5 mL) and filtered over celite. The organic layer was separated, and the aqueous layer was washed with Et_2O (3 x 10 mL), then the organic layers were combined and washed with brine (10 mL), dried over anhydrous MgSO_4 , filtered, and then concentrated in vacuo. The crude product was purified via flash column chromatography (hexanes) to yield **4l** as a colorless oil. Yield: 0.56 g (56 %); ^1H NMR (CDCl_3 , 600 MHz) δ : 7.58 (d, J = 21.2 Hz, 1H), 7.47 – 7.35 (m, 2H), 7.25 – 7.19 (m, 1H), 5.08 – 4.89 (m, 1H), 2.43 (s, 1H) ; ^{13}C NMR (CDCl_3 , 150 MHz) δ : 144.5, 137.1, 135.6, 131.5, 130.8, 130.5, 129.7, 129.4, 128.1, 125.3, 22.6; ^{29}Si NMR (CDCl_3 , 119 MHz) δ : –36.28.

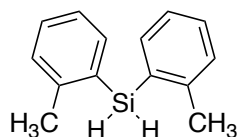


Synthesis of naphthalene-1-yl(phenyl)silane (4h): Magnesium turnings (0.528 g, 22 mmol, 1.1 equiv) were added to 10 mL of THF in an Ar-charged round-bottom flask. The 1-bromo-naphthalene (0.900 g, 20 mmol, 1 equiv) was then added and was allowed to stir at room temp for 3 h. The solution was then cooled to –78 °C and PhSiHCl_2 (2.96 mL, 20 mmol, 1 equiv) was then added quickly. The reaction was warmed to room temperature and stirred for 16 h. The reaction was then cooled to –78 °C and LAH (6 mL

of 4M in Et₂O, 24 mmol, 1.2 equiv) was added and the reaction was allowed to stir at room temperature for 3h. The reaction was then quenched by the addition of a solution of saturated aq. sodium bicarbonate (20 mL) and filtered over celite. The organic layer was separated, and the aqueous layer was washed with Et₂O (3 x 30 mL), then the organic layers were combined and washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and then concentrated in vacuo. The crude product was purified via flash column chromatography (hexanes) to yield **4i** as a colorless oil. Yield: 4.21 g (90 %); ¹H NMR (CDCl₃, 600 MHz) δ: 8.04 (d, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.91 – 7.87 (m, 1H), 7.83 (d, *J* = 6.7 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.53 – 7.46 (m, 3H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 5.26 (s, 2H). Matched Literature spectra.³¹

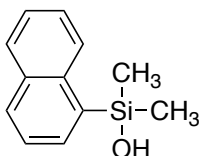


Synthesis of (4-fluoronaphthalen-1-yl)(phenyl)silane (4i): Magnesium turnings (0.528 g, 22 mmol, 1.1 equiv) were added to 10 mL of THF in an Ar-charged round-bottom flask. The 1-bromo-4-fluoronaphthalene (0.900 g, 20 mmol, 1 equiv) was then added and was allowed to stir at room temp for 3 h. The solution was then cooled to –78 °C and PhSiHCl₂ (2.96 mL, 20 mmol, 1 equiv) was then added quickly. The reaction was warmed to room temperature and stirred for 16 h. The reaction was then cooled to –78 °C and LAH (6 mL of 4.0 M in Et₂O, 24 mmol, 1.2 equiv) was added and the reaction was allowed to stir at room temperature for 3h. The reaction was then quenched by the addition of a solution of saturated aq. sodium bicarbonate (20 mL) and filtered over celite. The organic layer was separated, and the aqueous layer was washed with Et₂O (3 x 30 mL), then the organic layers were combined and washed with brine (20 mL), dried over anhydrous MgSO₄, filtered, and then concentrated in vacuo. The crude product was purified via flash column chromatography (hexanes) to yield **4i** as a colorless oil. Yield: 3.53 g (70 %); ¹H NMR (CDCl₃, 600 MHz) δ: 8.19 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.76 (t, *J* = 6.7 Hz, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.56 (p, *J* = 6.9 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.19 – 7.14 (m, 1H), 5.24 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ: 160.9 (d, *J*¹_{CF} = 255.8 Hz), 138.8 (d, *J*³_{CF} = 4.6 Hz), 136.9 (d, *J*³_{CF} = 8.4 Hz), 135.6, 131.1, 130.0, 128.2, 127.8 (d, *J*³_{CF} = 3.1 Hz), 127.3, 126.2 (d, *J*⁴_{CF} = 1.8 Hz), 125.7 (d, *J*⁴_{CF} = 4.9 Hz), 123.8 (d, *J*²_{CF} = 15.4 Hz), 121.2 (d, *J*⁴_{CF} = 6.1 Hz), 109.2 (d, *J*²_{CF} = 18.7 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ: –117.91, –120.45 (m); ²⁹Si NMR (CDCl₃, 119 MHz) δ: –35.81.

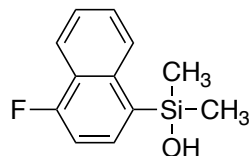


Synthesis of di-*o*-tolylsilane (4j): Prepared using known literature procedure.²⁷ Yield: 2.25 g (53 %). ¹H NMR (CDCl₃, 400 MHz) δ : 7.48 (dd, J = 7.3, 1.2 Hz, 2H), 7.34 (ddd, J = 7.5, 1.4 Hz, 2H), 7.23 – 7.14 (m, 4H), 4.97 (s, 2H), 2.41 (s, 6H). Matched Literature spectra.²⁷

General synthesis of silanol standards for ¹H NMR spectroscopy comparisons (Method B): The 100 mg of the corresponding silane was dissolved in THF (2 mL). Pd/C (50 mg) was then added followed by 5 drops of water. The reaction was allowed to stir overnight and then a fraction of product was isolated by prep TLC (15% EtOAc in hexanes) or crystallized in DCM. These reactions are un-optimized and complete isolation of product was not performed.

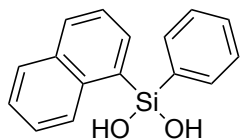


Dimethyl(naphthalen-1-yl)silanol (5f): Prepared from **4f** using Method B, and isolated by prep. TLC. ¹H NMR (CDCl₃, 600 MHz) δ : 8.27 (d, J = 8.2 Hz, 1H), 7.91 – 7.84 (m, 2H), 7.77 (d, J = 6.7 Hz, 1H), 7.55 – 7.43 (m, 3H), 2.01 (s, 1H), 0.59 (s, 6H); ¹³C NMR (CDCl₃, 150 MHz) δ : 169.6, 133.4, 130.6, 129.2, 128.2, 126.2, 125.7, 125.2, 120.3, 110.1, 1.5; HRMS-ESI (m/z): Calcd for C₁₂H₁₅SiO⁺ [M + H]⁺, 203.0887. Found, 203.1735.

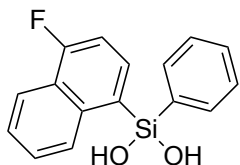


(4-Fluoronaphthalen-1-yl)dimethylsilanol (5g): Prepared from **4g** using Method B, and isolated by prep. TLC. ¹H NMR (CDCl₃, 600 MHz) δ : 8.29 (d, J = 7.8 Hz, 1H), 8.17 (d, J = 7.8 Hz, 1H), 7.70 (dd, J = 6.6 Hz, 1H), 7.57 (m, J = 7.3 Hz, 2H), 7.13 (t, J = 9.1 Hz, 1H), 2.04 (s, 1H), 0.57 (s, 6H); ¹³C NMR (CDCl₃, 150 MHz) δ : 160.4 (d, J = 255.3 Hz), 138.3 (d, J = 4.9 Hz), 133.4 (d, J = 8.8 Hz), 132.7 (d, J = 5.9 Hz), 127.9 (d, J = 3.5 Hz), 127.0, 125.8 (d, J = 2.1 Hz), 123.8 (d, J = 15.7 Hz), 121.3 (d, J = 6.3 Hz), 108.6 (d,

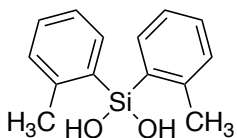
$J = 18.8$ Hz), 1.3; ^{19}F NMR (CDCl_3 , 282 MHz) δ : -120.43 ; HRMS-ESI (m/z): Calcd for $\text{C}_{12}\text{H}_{15}\text{SiO}^+$ [$\text{M} + \text{H}$] $^+$, 221.0792. Found, 221.1300.



Naphthalen-1-yl(phenyl)silanediol (5h): Prepared from **4h** using Method B, and isolated by recrystallization from DCM. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.33 – 8.24 (m, 1H), 7.97 (dd, $J = 11.3$, 7.6 Hz, 2H), 7.87 (dd, $J = 5.8$, 3.5 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.53 – 7.42 (m, 4H), 7.42 – 7.35 (m, 2H), 2.99 (s, 2H); HRMS-ESI (m/z): Calcd for $\text{C}_{16}\text{H}_{14}\text{SiO}_2^-$ [$\text{M} - \text{H}$] $^-$, 265.0690. Found, 265.0689.



(4-Fluoronaphthalen-1-yl)(phenyl)silanediol (5i): Prepared from **4i** using Method B, and isolated by filtration of crude material over celite. ^1H NMR (CD_3OD , 600 MHz) δ : 7.71 (d, $J = 7.3$ Hz, 1H), 7.28 (dd $J = 7.4$ Hz, 1H), 7.19 – 7.10 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (CD_3OD , 150 MHz) δ : 145.1, 136.7, 136.5, 131.0, 130.6, 125.7, 23.0; HRMS-ESI (m/z): Calcd for $\text{C}_{14}\text{H}_{16}\text{SiO}_2^-$ [$\text{M} - \text{H}$] $^-$, 243.0619. Found, 243.0847.



Phenyl(o-tolyl)silanediol (5k): Prepared from **4k** using Method B, and isolated by prep TLC. ^1H NMR (CDCl_3 , 600 MHz) δ : 7.71 (d, $J = 7.3$ Hz, 1H), 7.63 (d, $J = 7.1$ Hz, 2H), 7.42 (t, $J = 7.4$ Hz, 1H), 7.35 (dd $J = 7.2$ Hz, 3H), 7.21 – 7.13 (m, 2H), 2.93 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (CDCl_3 , 150 MHz) δ : 144.3, 135.8, 135.1, 134.30, 132.8, 130.9, 130.5, 130.1, 128.1, 125.1, 23.0; HRMS-ESI (m/z): Calcd for $\text{C}_{13}\text{H}_{14}\text{SiO}_2^-$ [$\text{M} - \text{H}$] $^-$, 243.0619. Found, 243.0619.

II. Structural Investigation of Tamao Fleming vs. Silane Hydrolysis

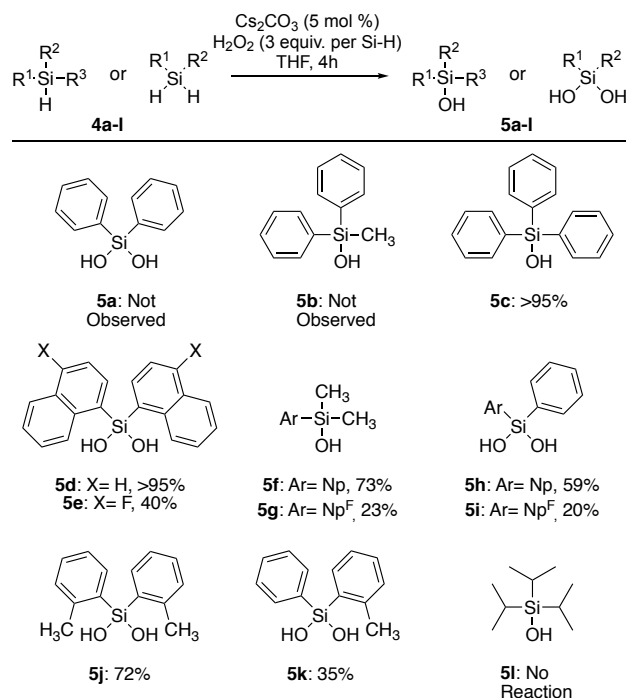


Figure S1. Investigation of structural effect on Tamao-Fleming vs. Silane Hydrolysis

Given the propensity of the silicon-phenyl bond to oxidize, we investigated if this reactivity trended with naphthyl rings. The ability of naphthyl rings to suppress carbon-silicon bond oxidation was confirmed by the synthesis of **5d-g**. The ability to synthesize **5h** and **5i** was especially exciting given that the naphthyl ring was able to suppress the oxidation of the carbon-silicon bond between the silicon atom and the phenyl ring. This led to the hypothesis that the lack of silicon-carbon bond oxidation is due to the silicon bearing a minimum of one aryl substituent with an ortho substituent. To further support this hypothesis, we attempted the synthesis of **5j-5m**. Silanediol **5j** was produced cleanly, this compound confirms that ortho substitution stabilizes the silanediol from being further oxidized. **5k** was synthesized as well albeit with a lower yield. **5l** and **5m** were also synthesized showing that the ortho substitution remarkably suppresses the oxidation of the phenyl ring. Finally, the method was tested on hindered tri-alkyl silane **5l** which resulted in no reaction. We attribute this to the alkyl silane **5l** having a much more electron-rich silicon center and steric encumbrance acting as a poor electrophile toward addition of the peroxy anion.

III. Proposed mechanism for the cesium carbonate-catalyzed hydrolysis of silanes

Based on the data presented here, we propose the following catalytic cycle for the cesium carbonate catalyzed-hydrolysis of silanes that accounts for both the hydrolysis pathway and the competing C–Si oxidation pathway (Figure 6). This mechanism features numerous branch points based on substituent migration opportunities. First, the peroxy anion **A** is formed under basic conditions. One equivalent of **A** then adds to silane **B** to produce a pentacoordinate peroxy silane **C**. The reactivity of **C** is dependent on the substituents. For instance, if R^1 , R^2 , and R^3 are all phenyl rings then the hydride will migrate, cleave the peroxide, and generate silanol **5c** which is then stable to further oxidation under reaction conditions. However, if R^1 and R^2 are ^1Np and R^3 is $\text{O-Si}(\text{Np})_2\text{H}$ then the pathway can divert again. If the hydride migrates to cleave the peroxide bond, then 1-hydro-3-disiloxanol **E** is formed which can then react further to produce disiloxanediol **2b**. The hydride can also migrate and cleave the siloxane giving silanol **F** which then further reacts to form silanediol **5d**. Peroxy silane **C** can also undergo Tamao-Fleming oxidation if $R^1 = R^2 = \text{Ph}$ and $R^3 = \text{H}$ and generate phenoxy silane **H** which is then undergoes hydrolysis to generate phenol **I**.

When R^1 is H then the hydride can migrate to the peroxide generating silanol **D**. A second equivalent of peroxy anion **A** then adds to **D** generating a new peroxy silanol **G**. After this addition, the pathway again branches based on which substituents are present on the silicon. If R^3 is ^1Np , the remaining hydride present on **G** migrates to the peroxide and generates silanediol **5h**. If $R^3 = \text{Ph}$ then here the pathway diverges once again. One of the phenyl rings present on the silicon can migrate to the peroxide and generate phenoxy silanol **H** which then undergoes hydrolysis generating phenol **N** or the hydride migrates to the peroxide generating silanediol **5a**. A third equivalent of **A** then adds to silanediol **5a** and generates peroxy silanediol **J**. Now, with no hydride present to migrate, one of the phenyl rings migrates to cleave the peroxide bond and generate phenoxy silanediol **K** which is then hydrolyzed to form phenol **I**. This also regenerates the hydroxide anion, which returns to the catalytic cycle.

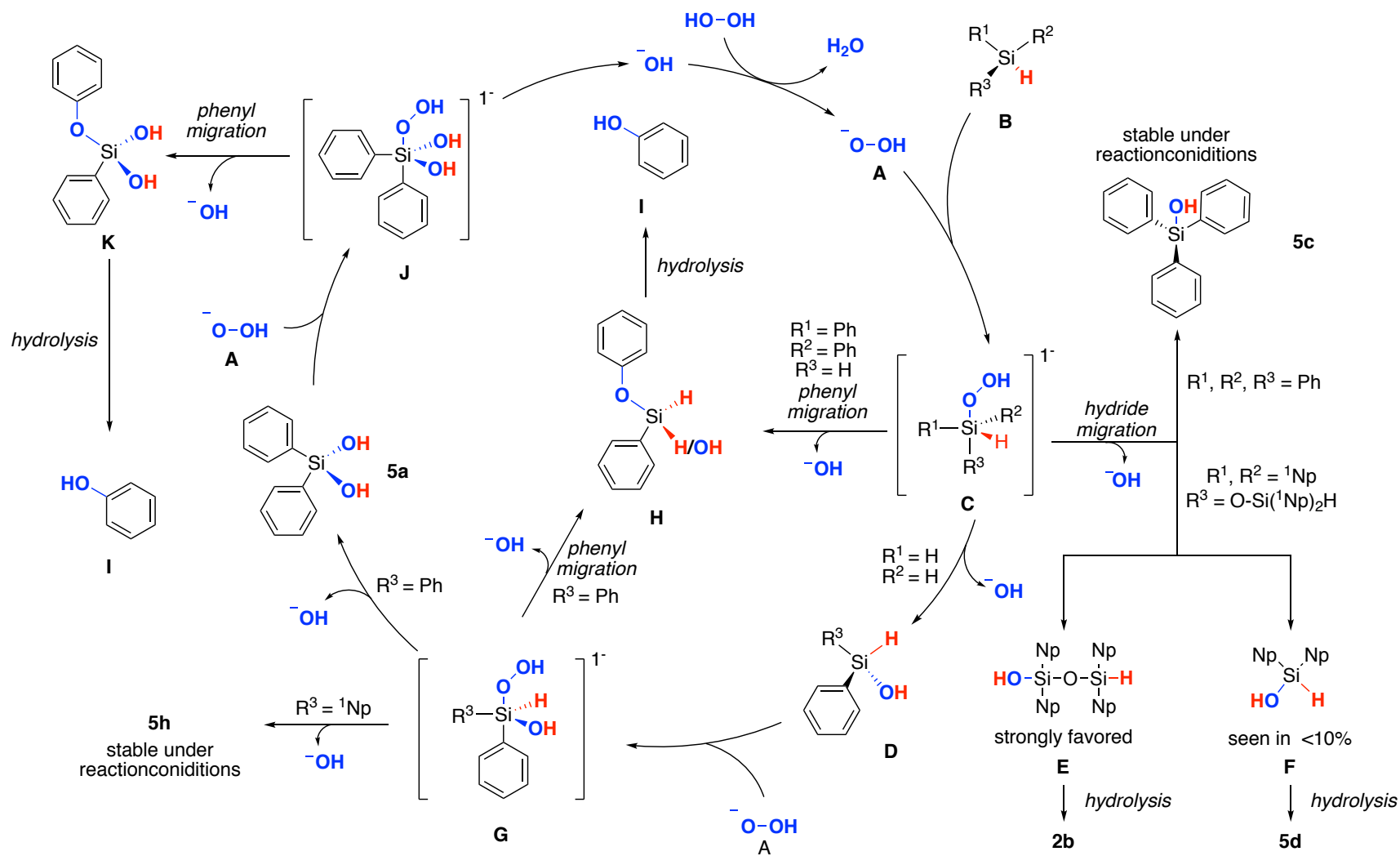
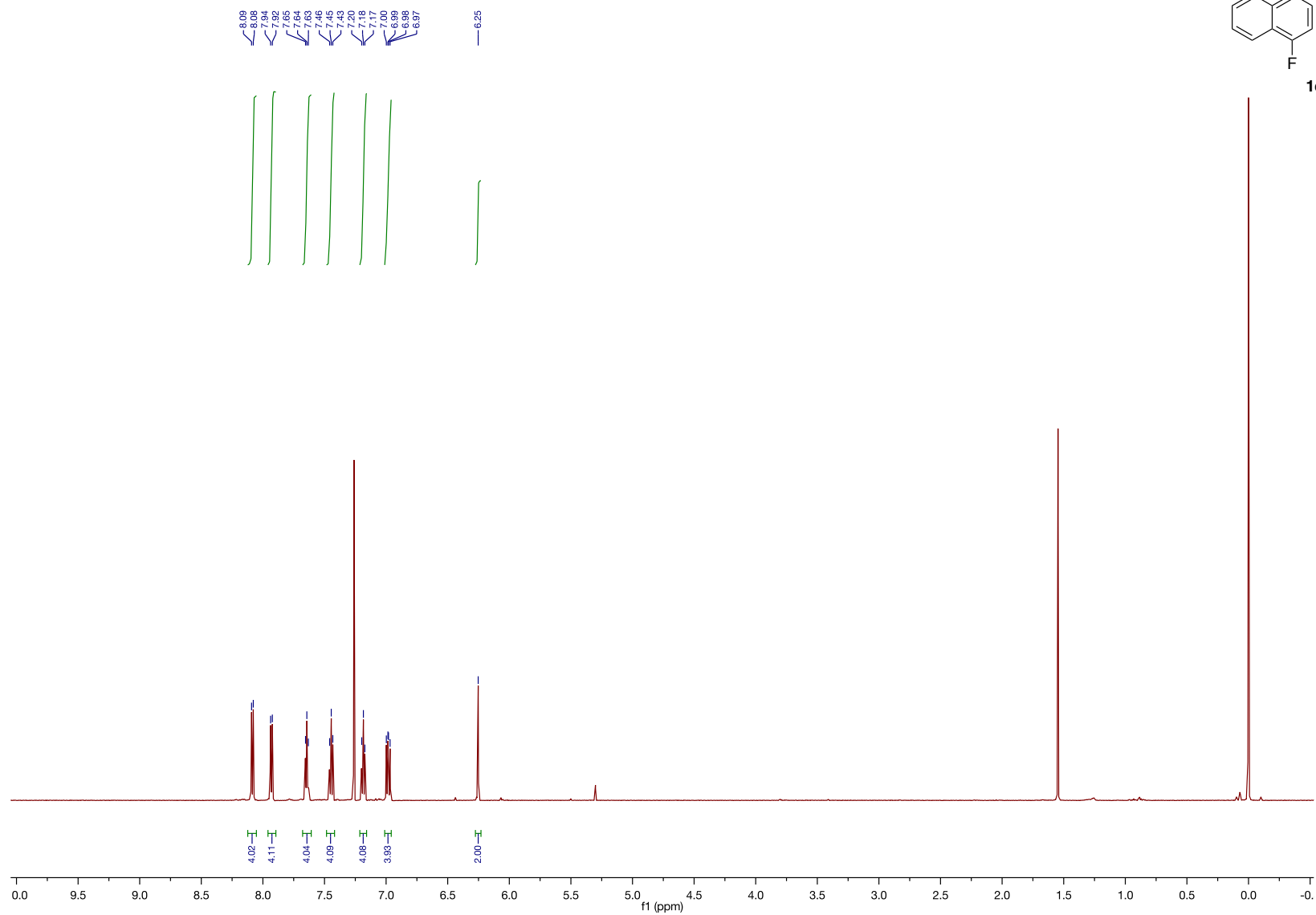


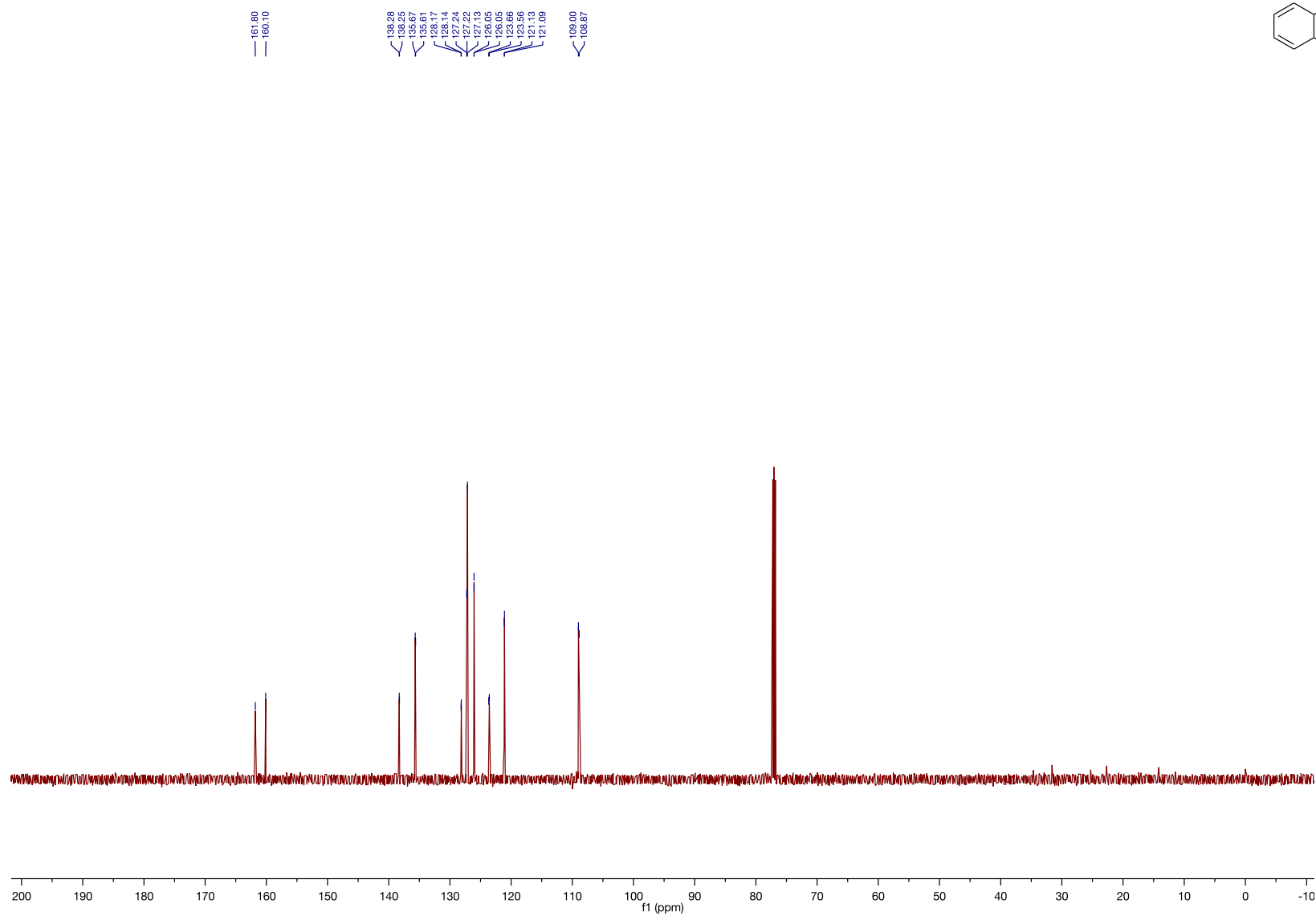
Figure S2. Mechanism of Cesium Carbonate-catalyzed Si-H hydrolysis

IV. Copies of ^1H , ^{13}C , and ^{29}Si NMR spectra

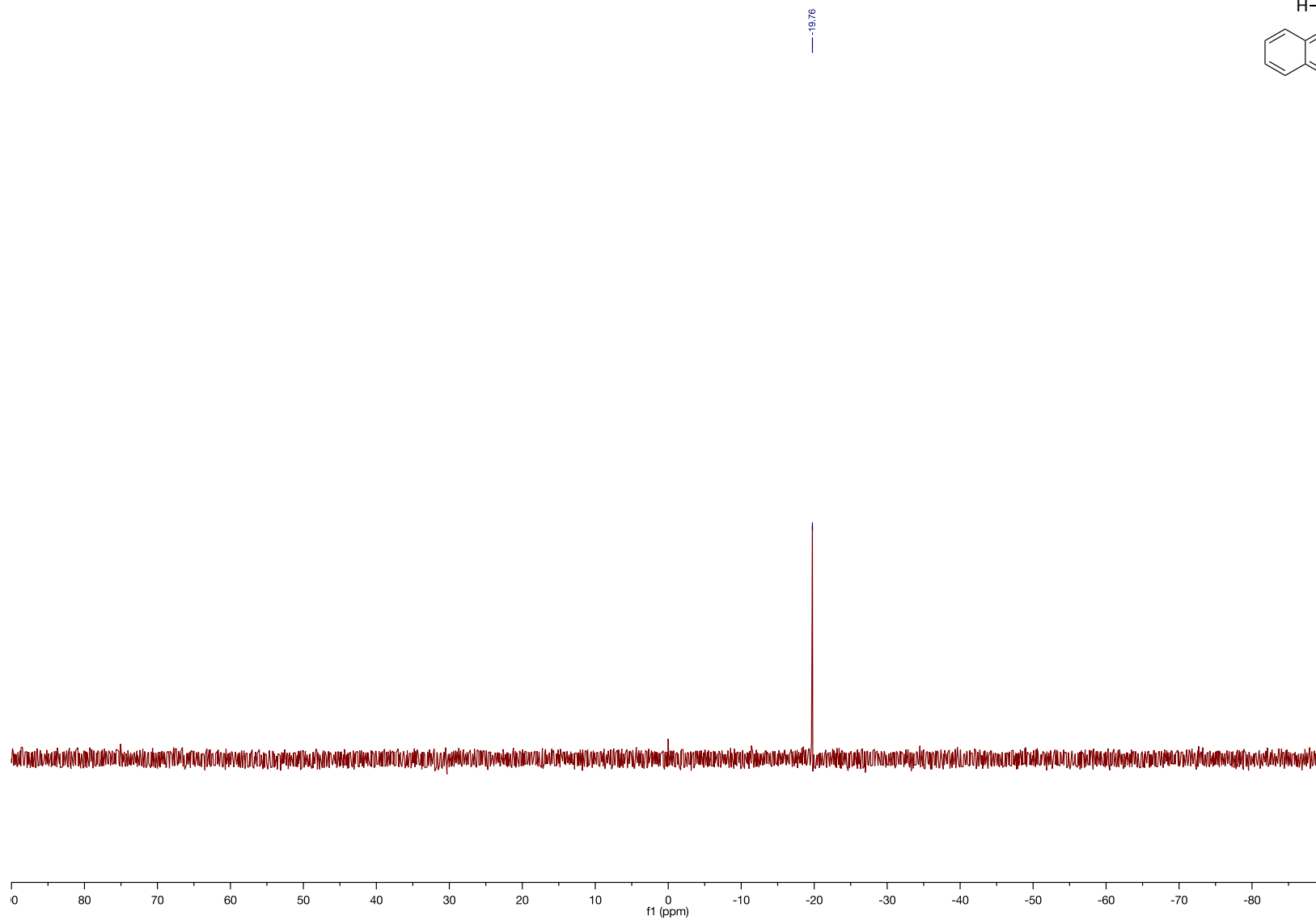
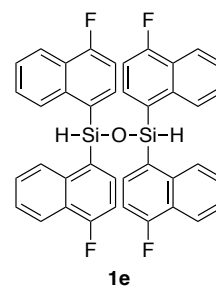
CDCl_3 , 600 MHz, ^1H NMR



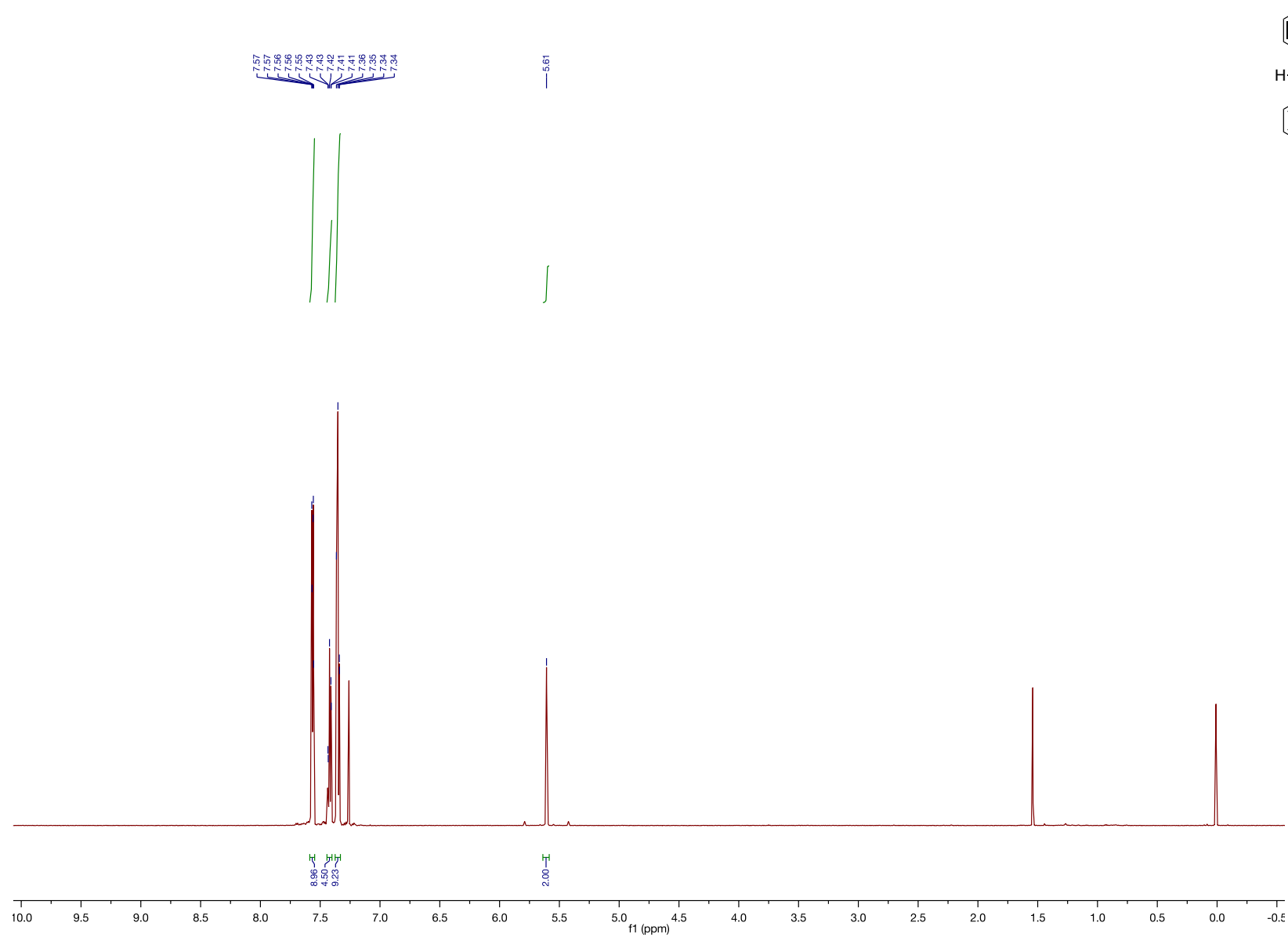
CDCl₃, 125 MHz, ¹³C NMR



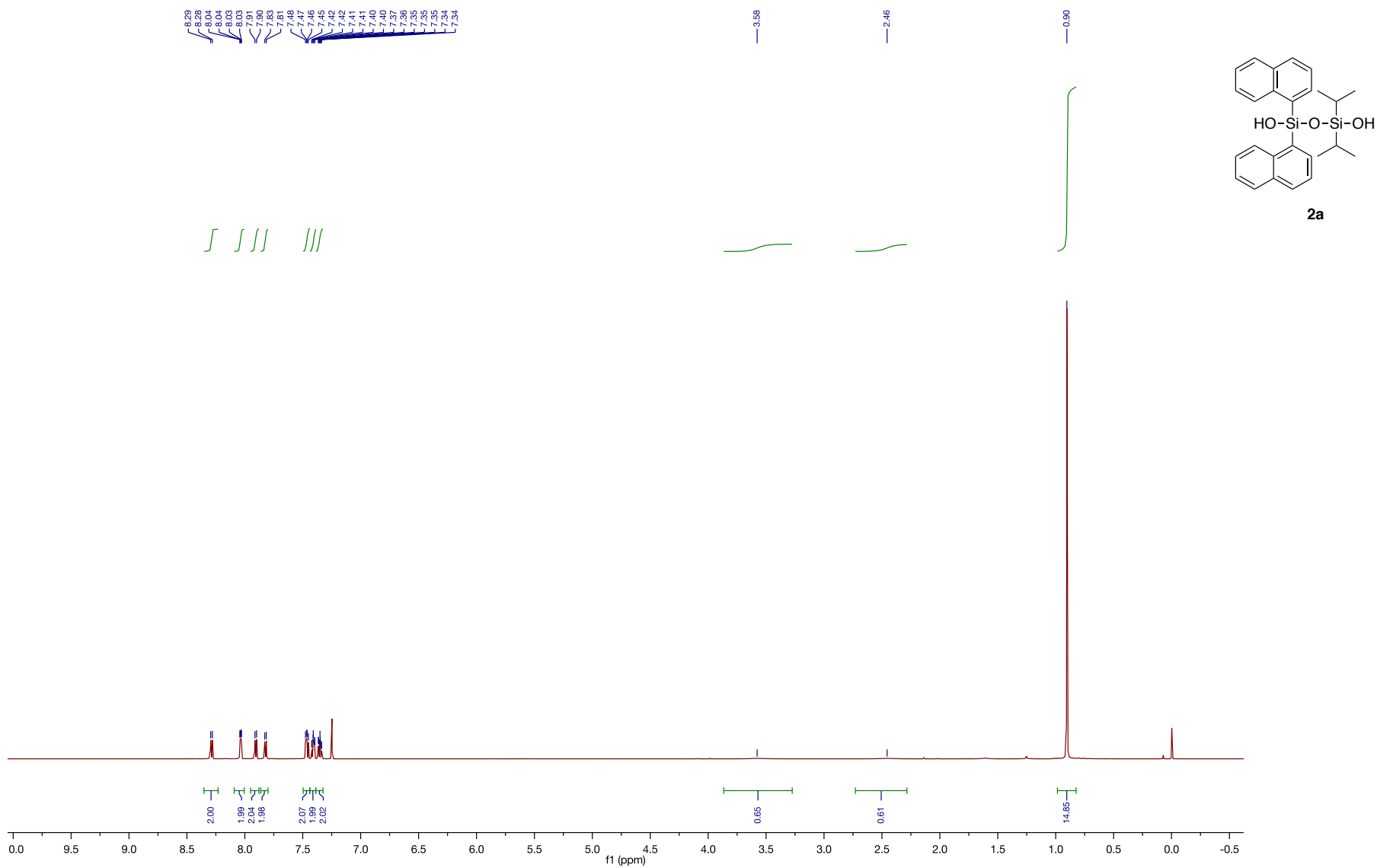
CDCl₃, 600 MHz, ²⁹Si NMR



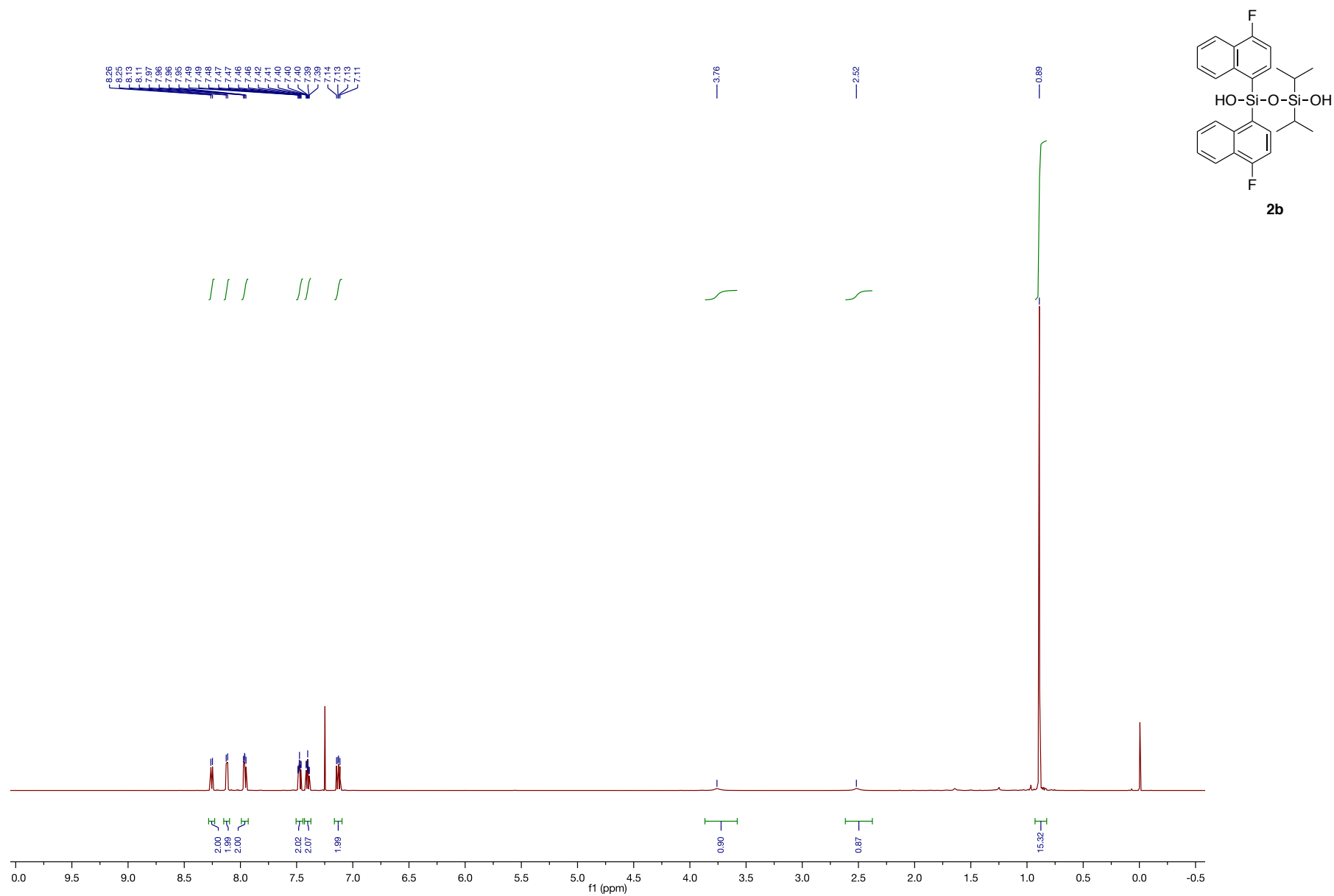
CDCl₃, 600 MHz, ¹H NMR



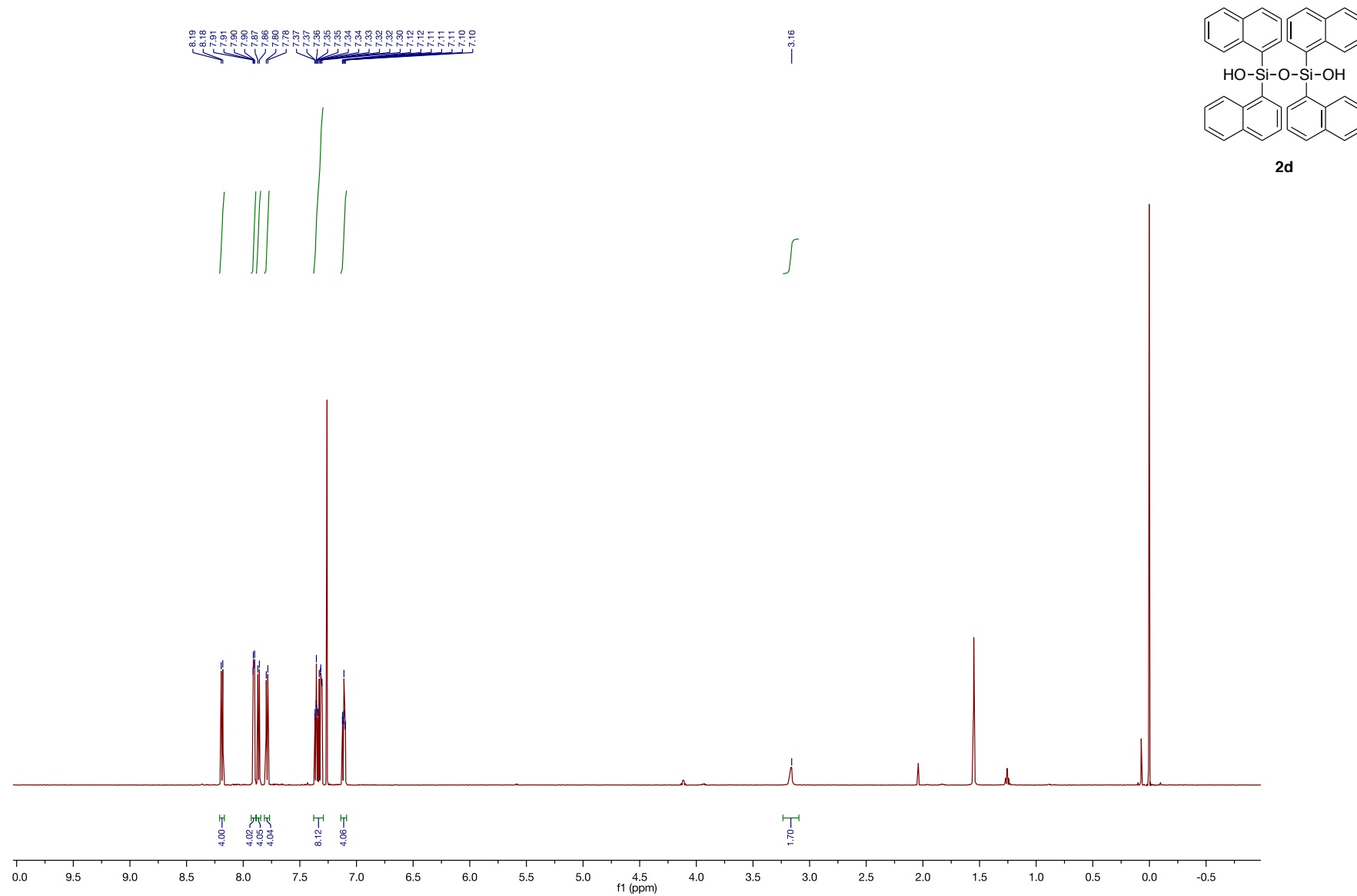
CDCl₃, 600 MHz, ¹H NMR



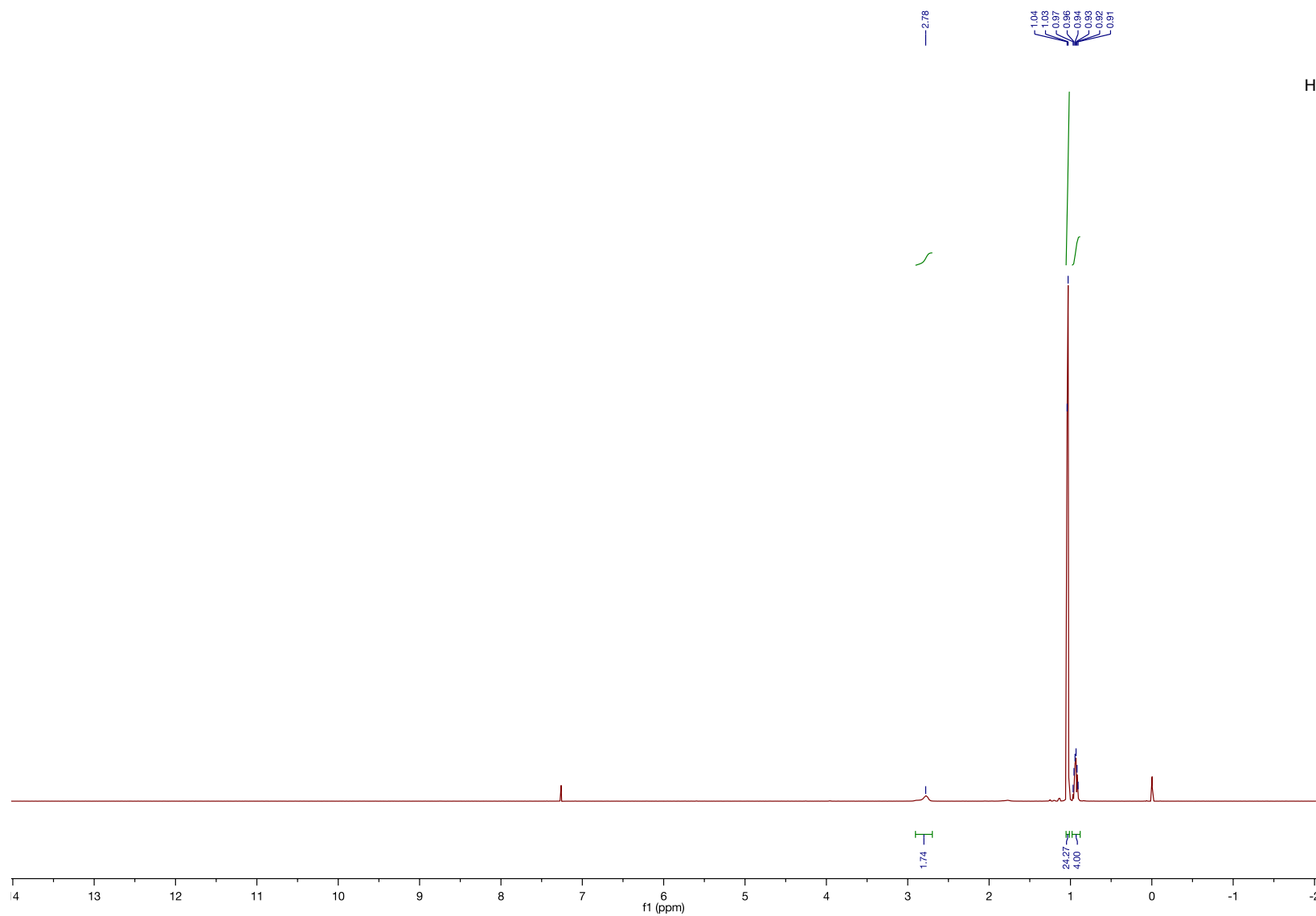
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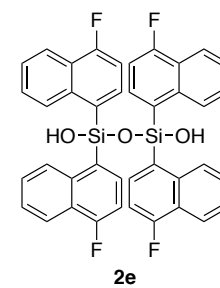
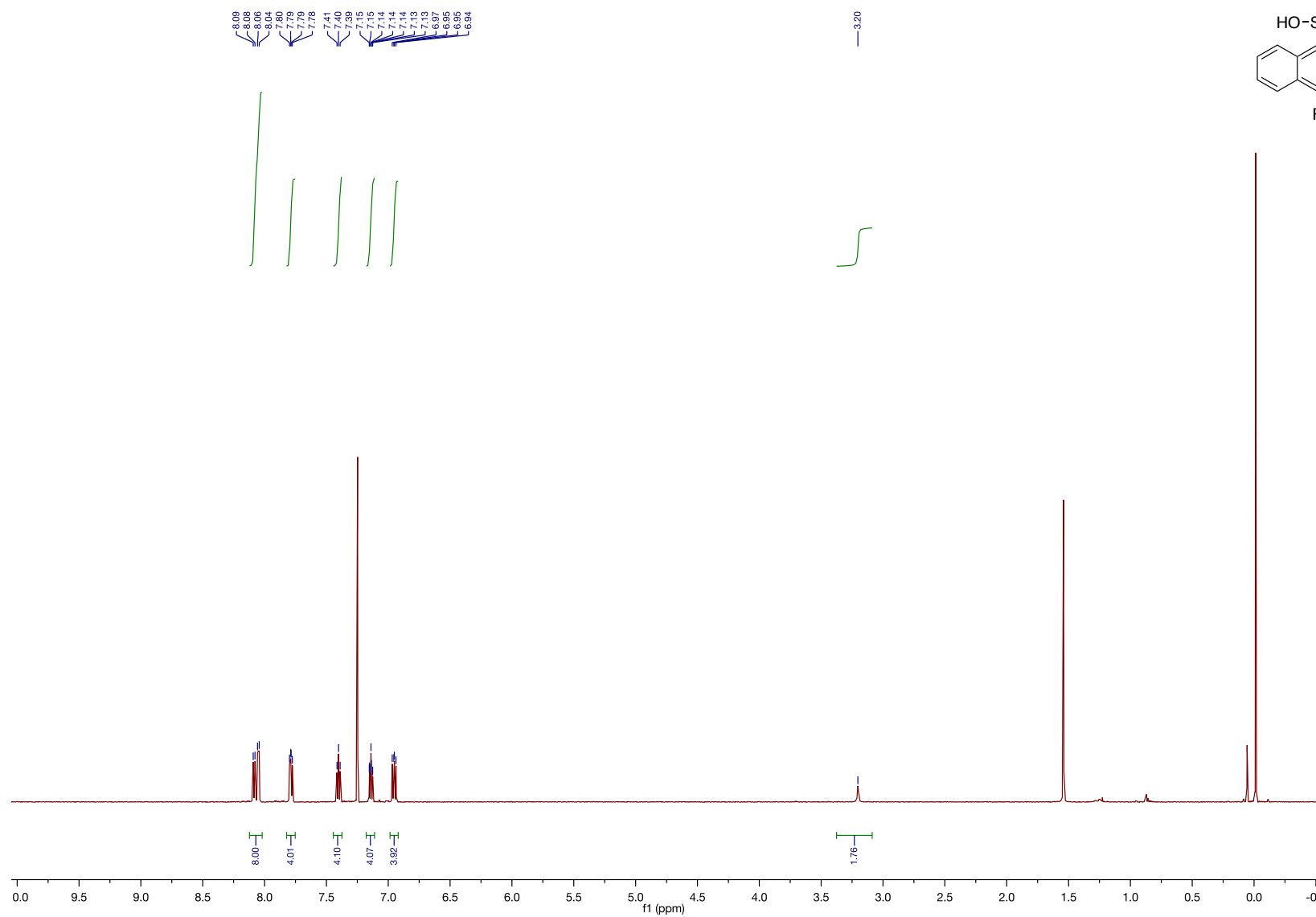
CDCl₃, 600 MHz, ¹H NMR



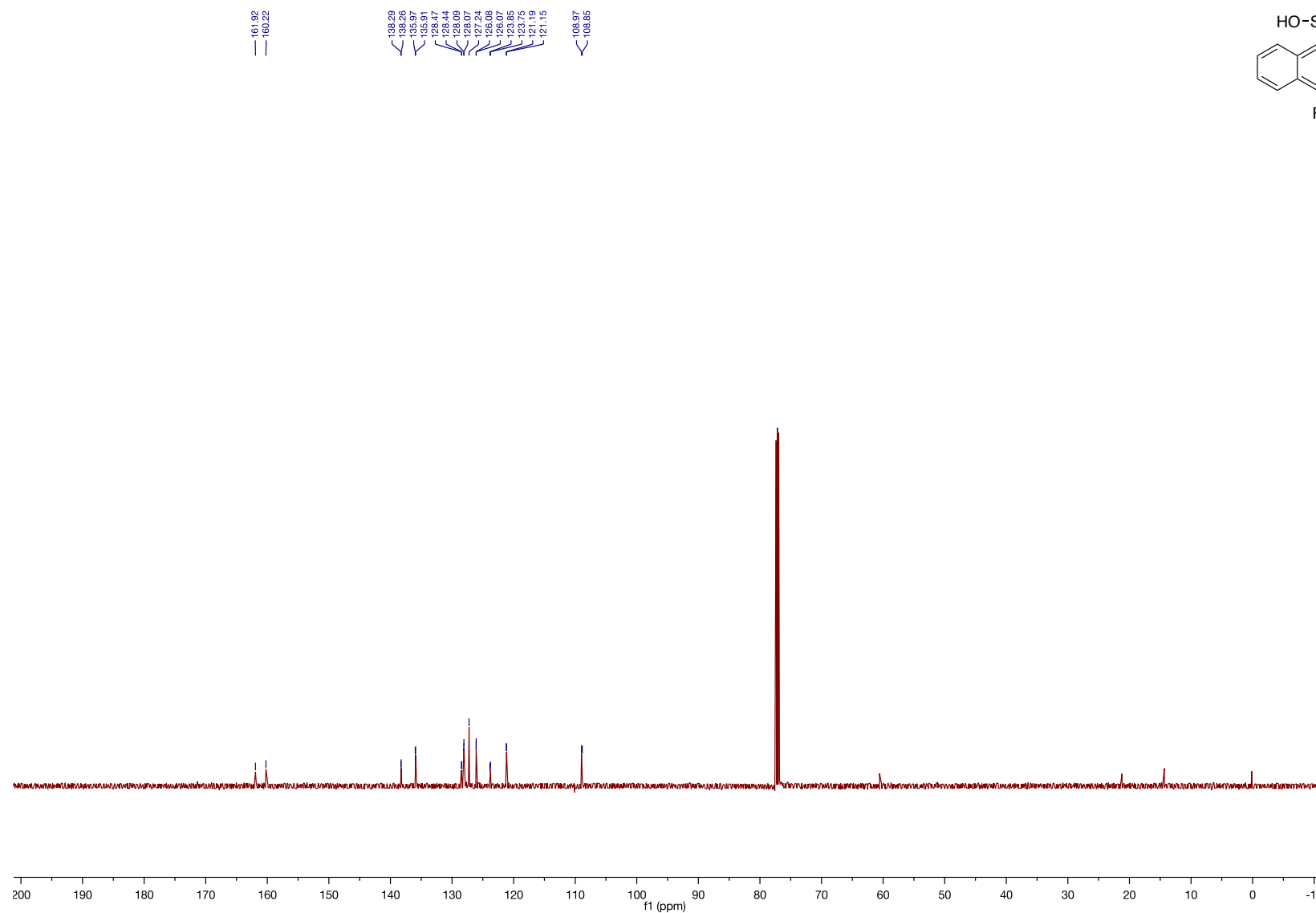
CDCl₃, 600 MHz, ¹H NMR



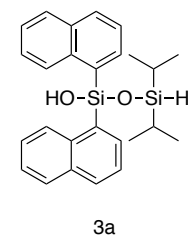
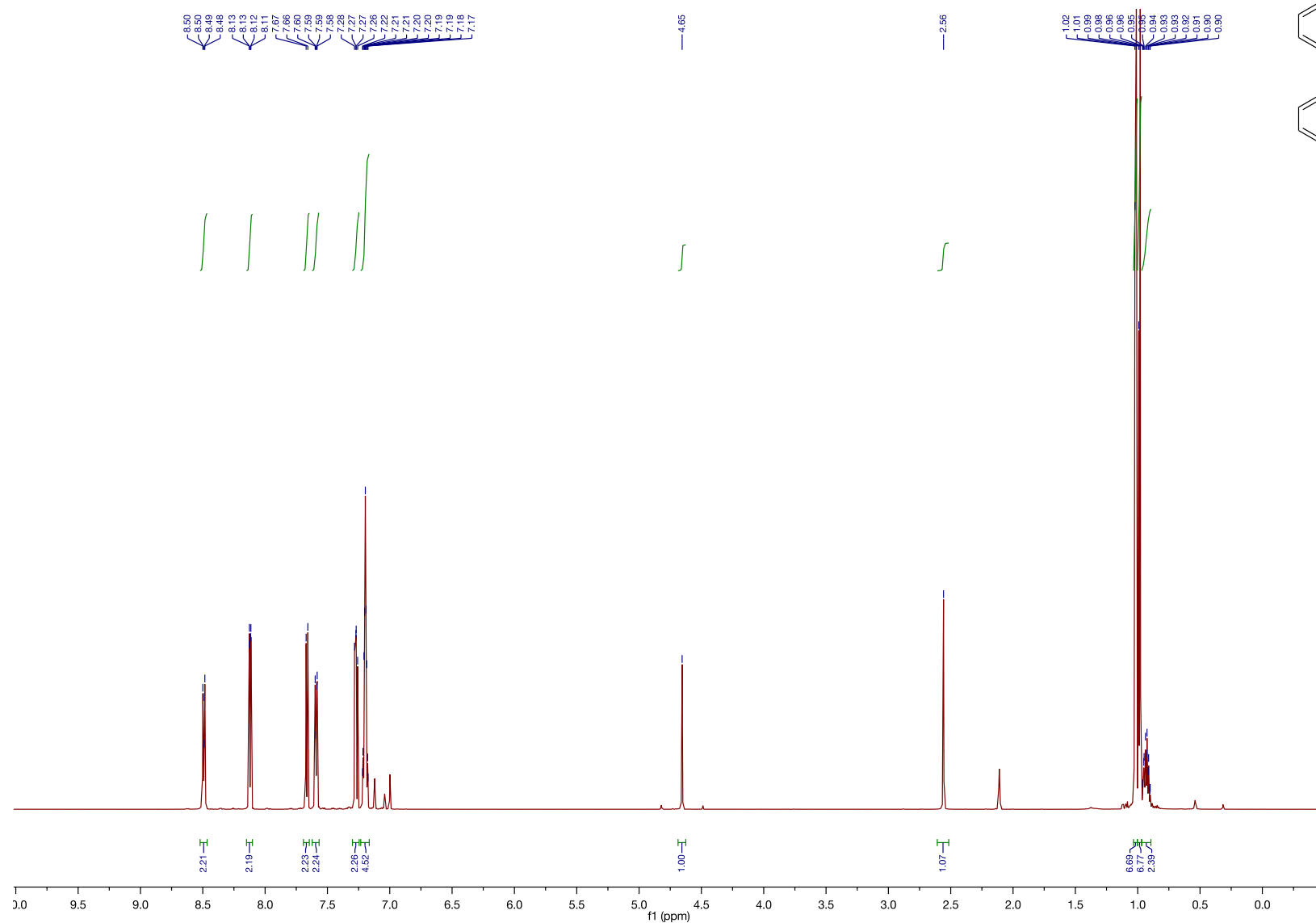
CDCl₃, 600 MHz, ¹H NMR



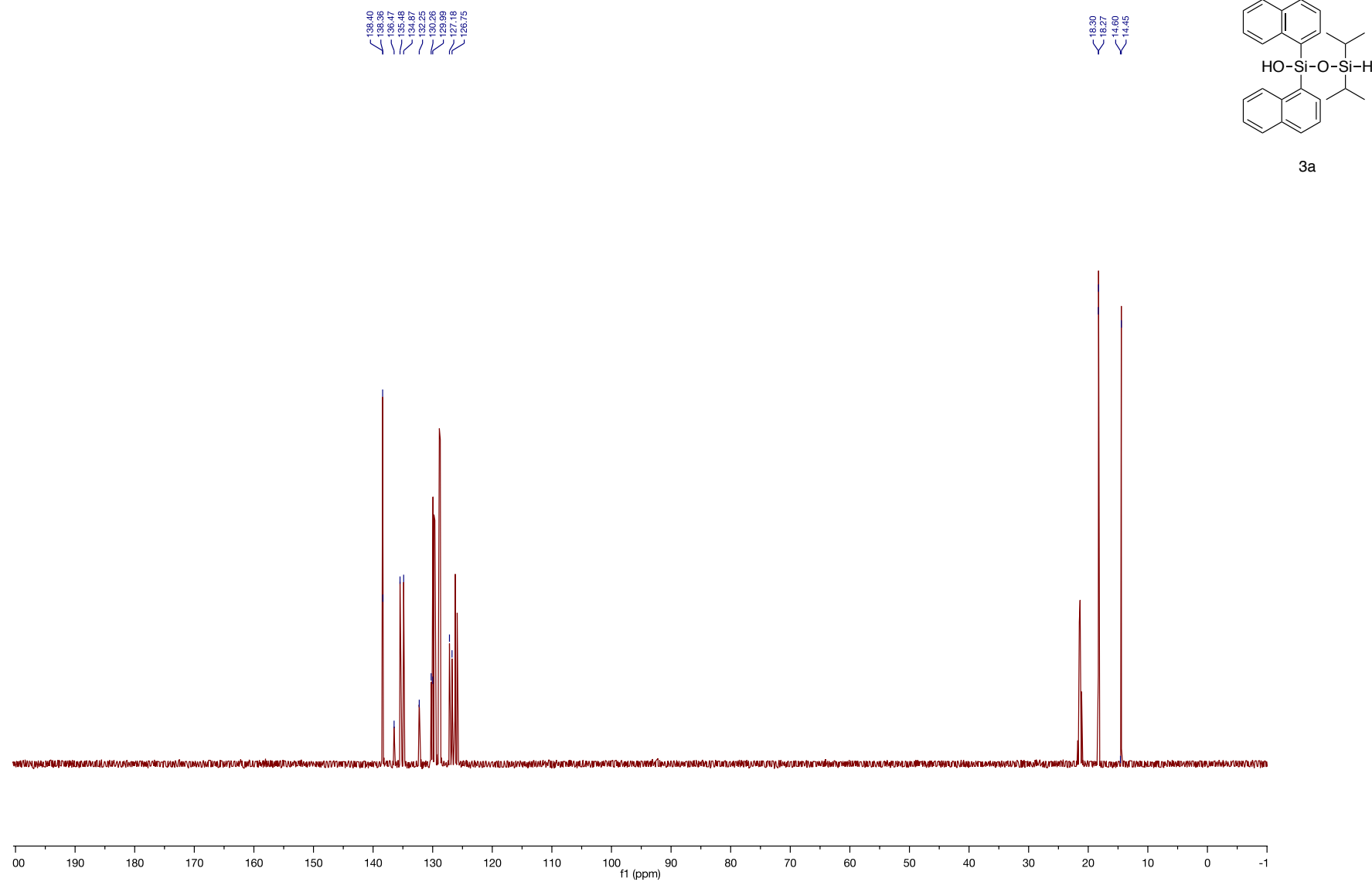
CDCl₃, 150 MHz, ¹³C NMR



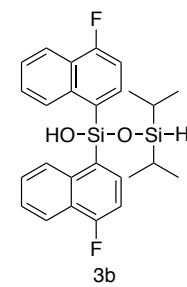
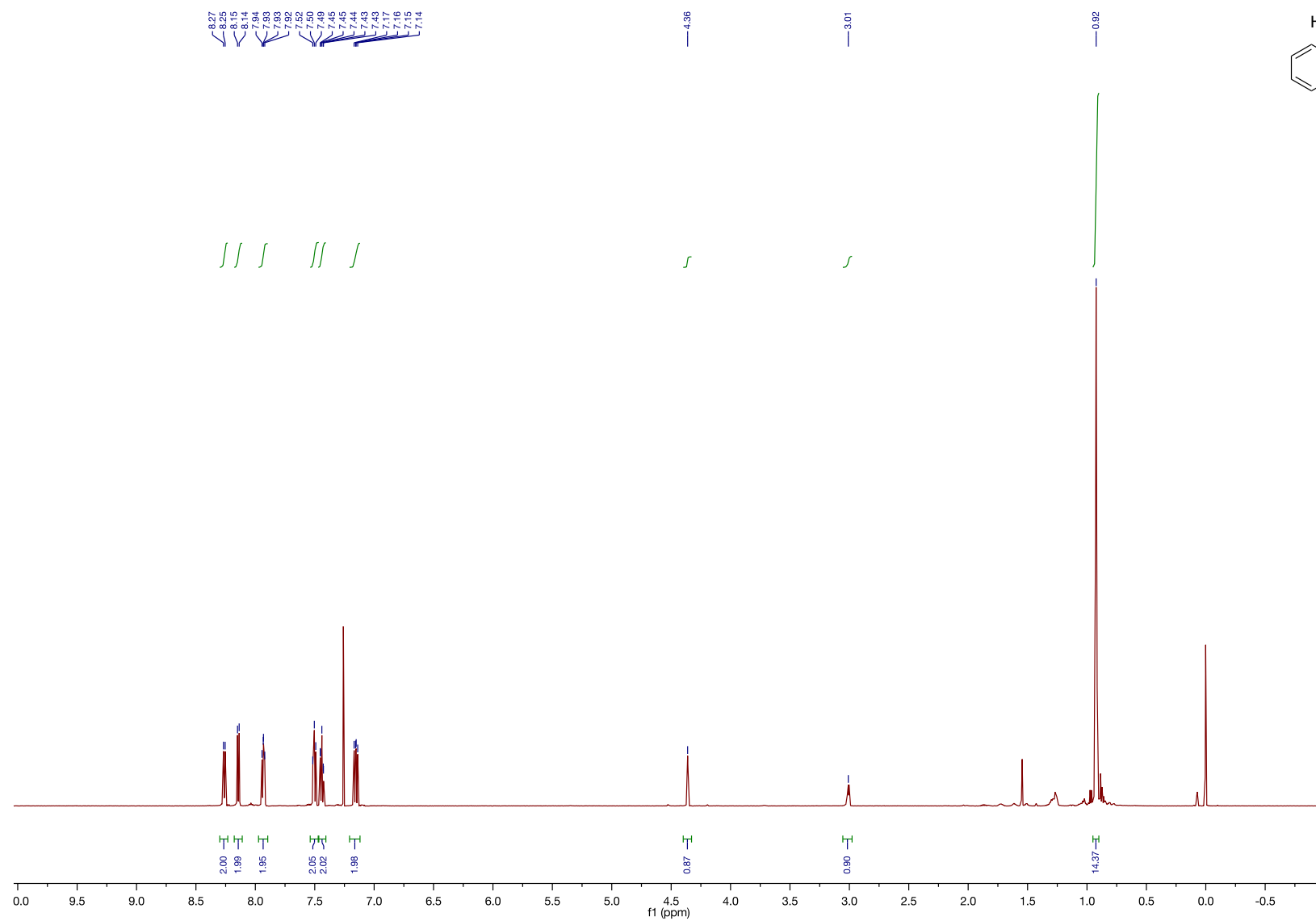
C₇D₈, 600 MHz, ¹H NMR



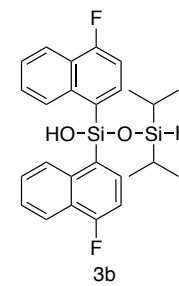
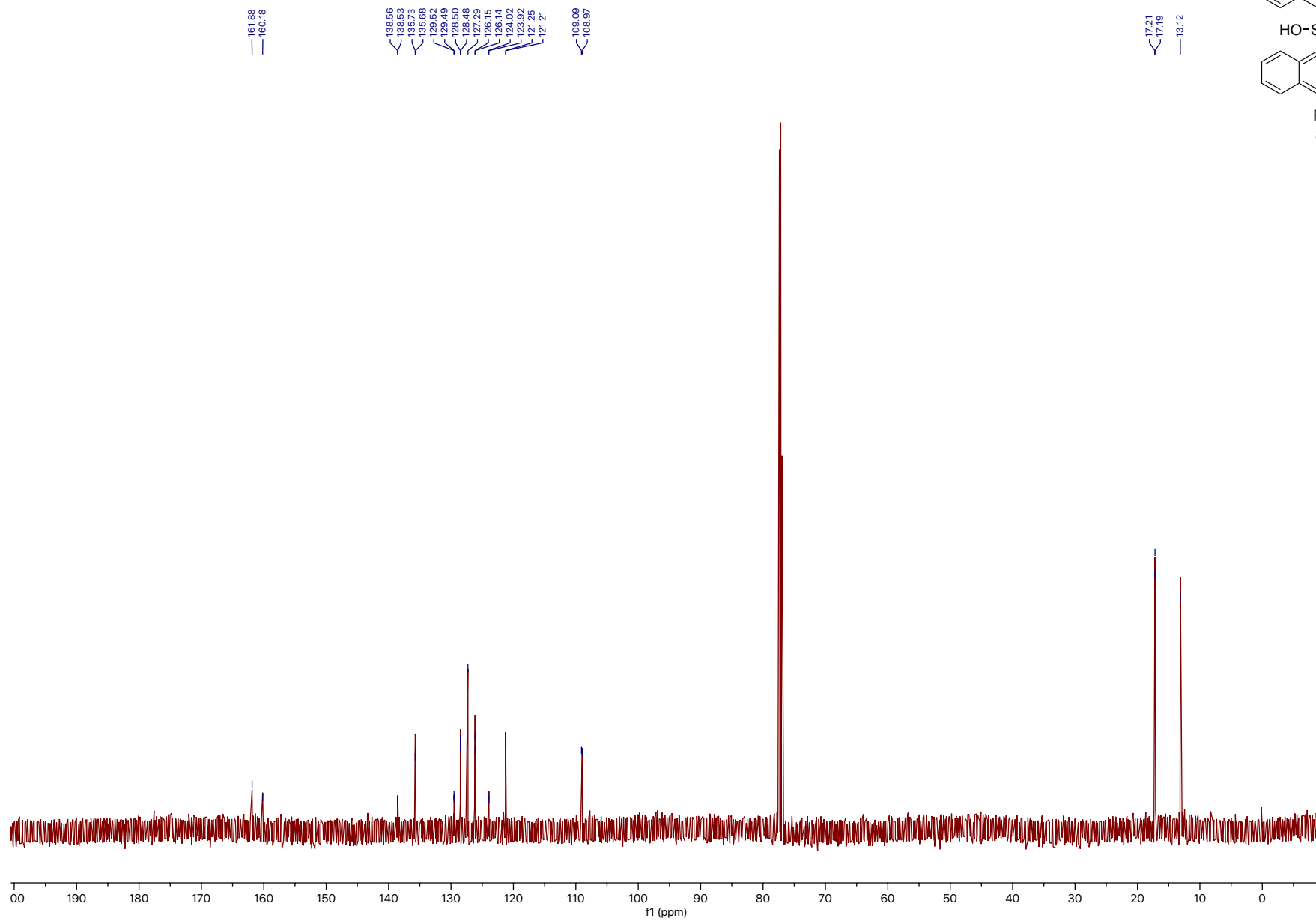
C₇D₈, 150 MHz, ¹³C NMR



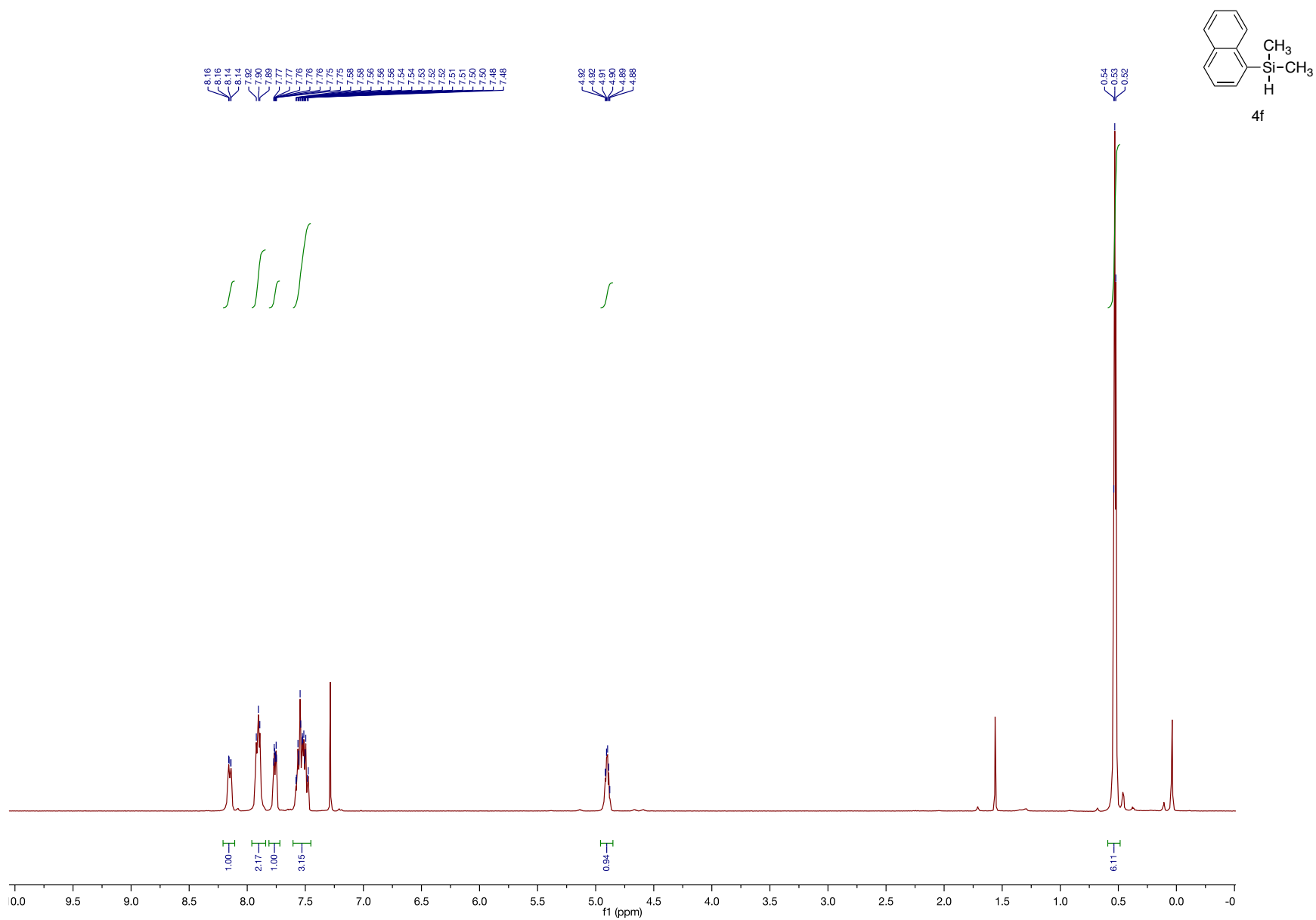
CDCl₃, 600 MHz, ¹H NMR



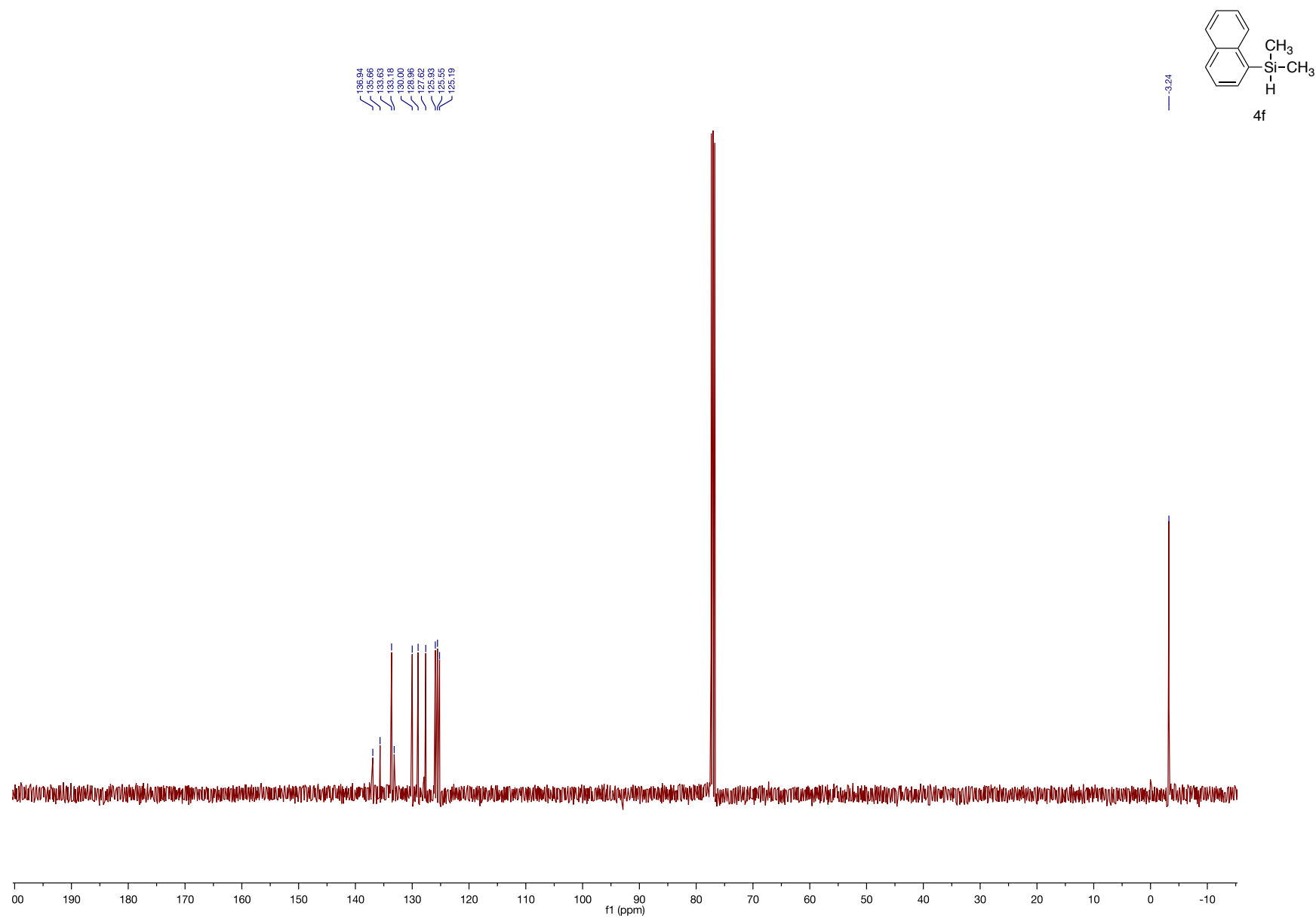
CDCl₃, 150 MHz, ¹³C NMR



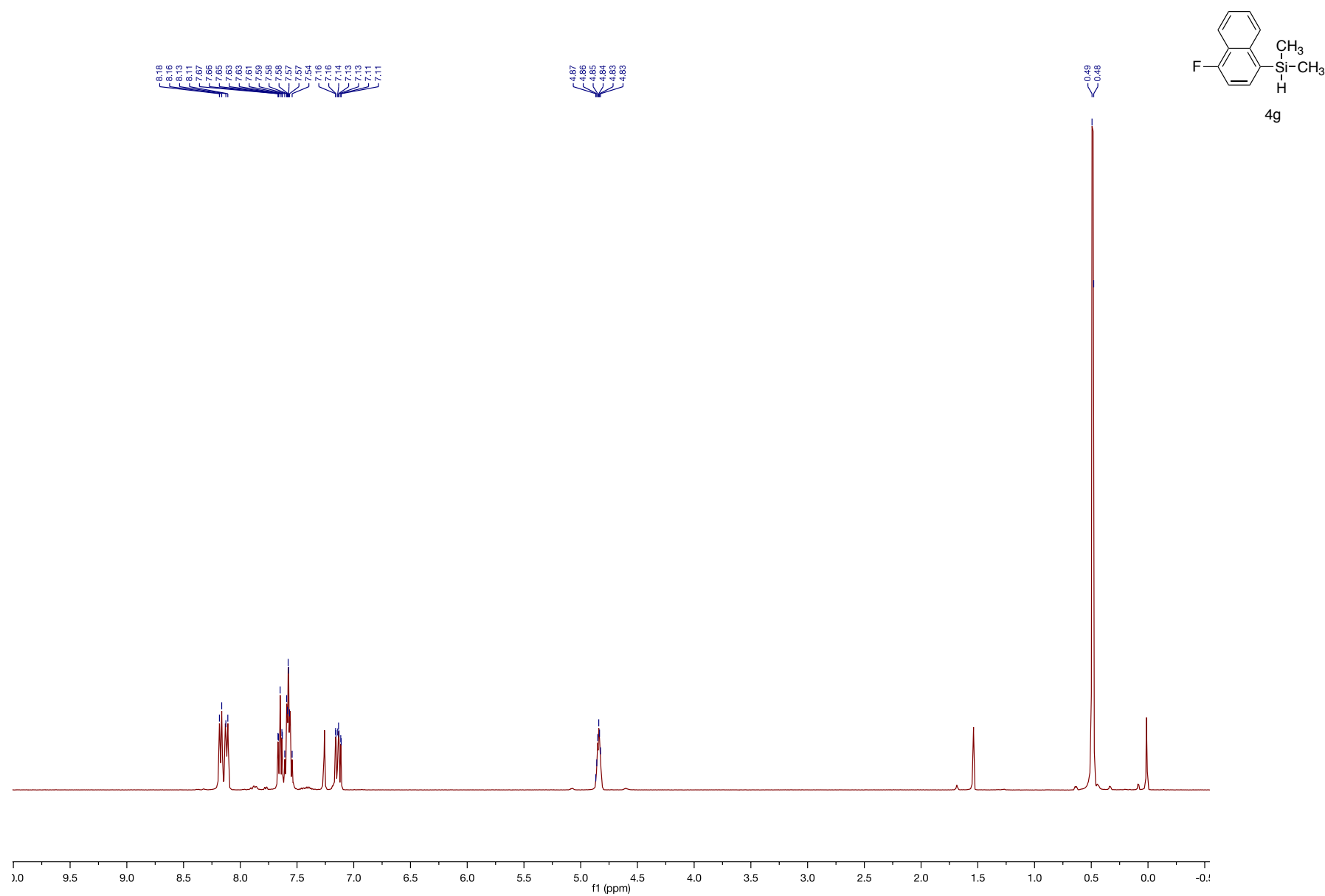
CDCl₃, 400 MHz, ¹H NMR



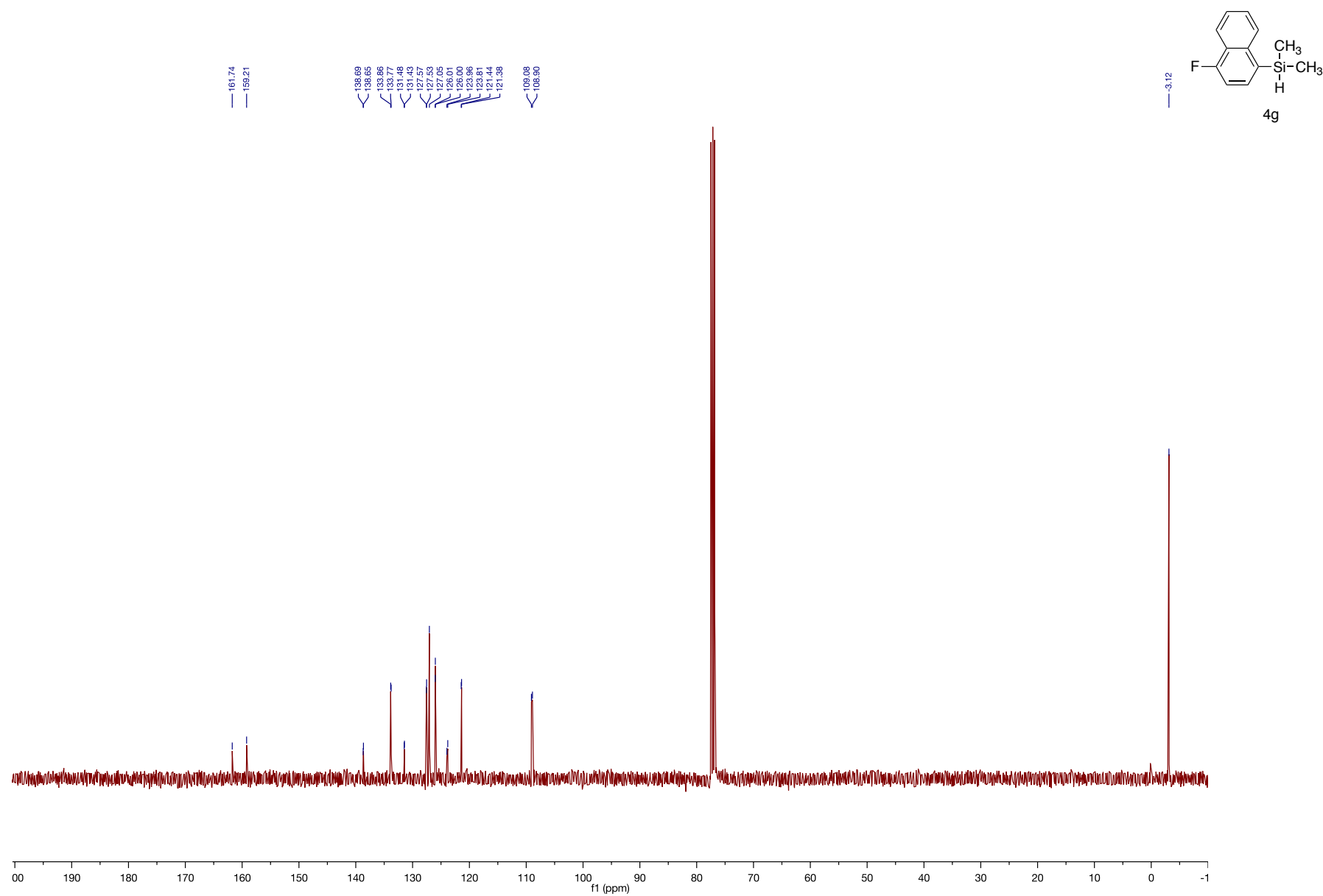
CDCl₃, 100 MHz, ¹³C NMR



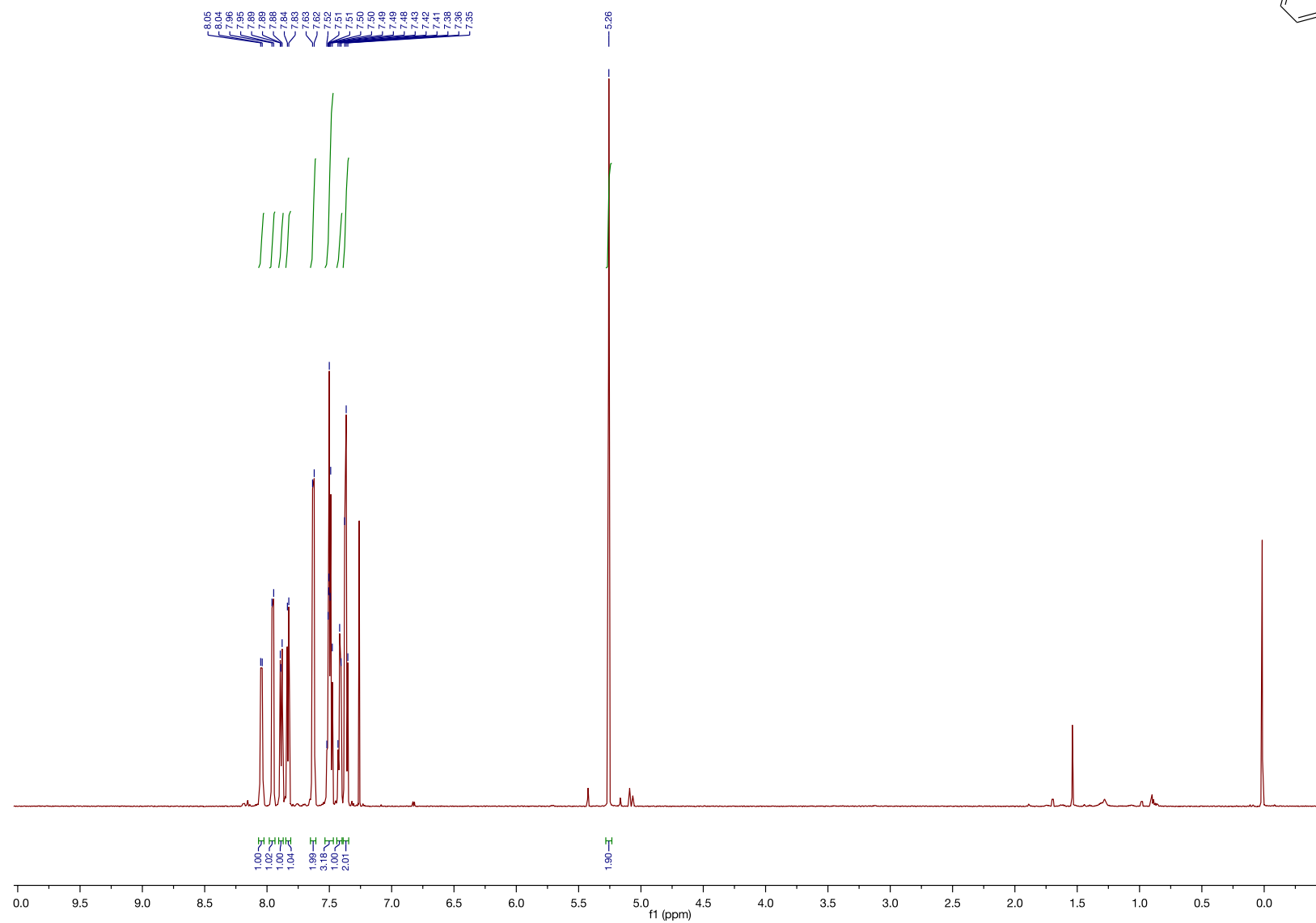
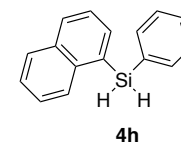
CDCl₃, 400 MHz, ¹H NMR



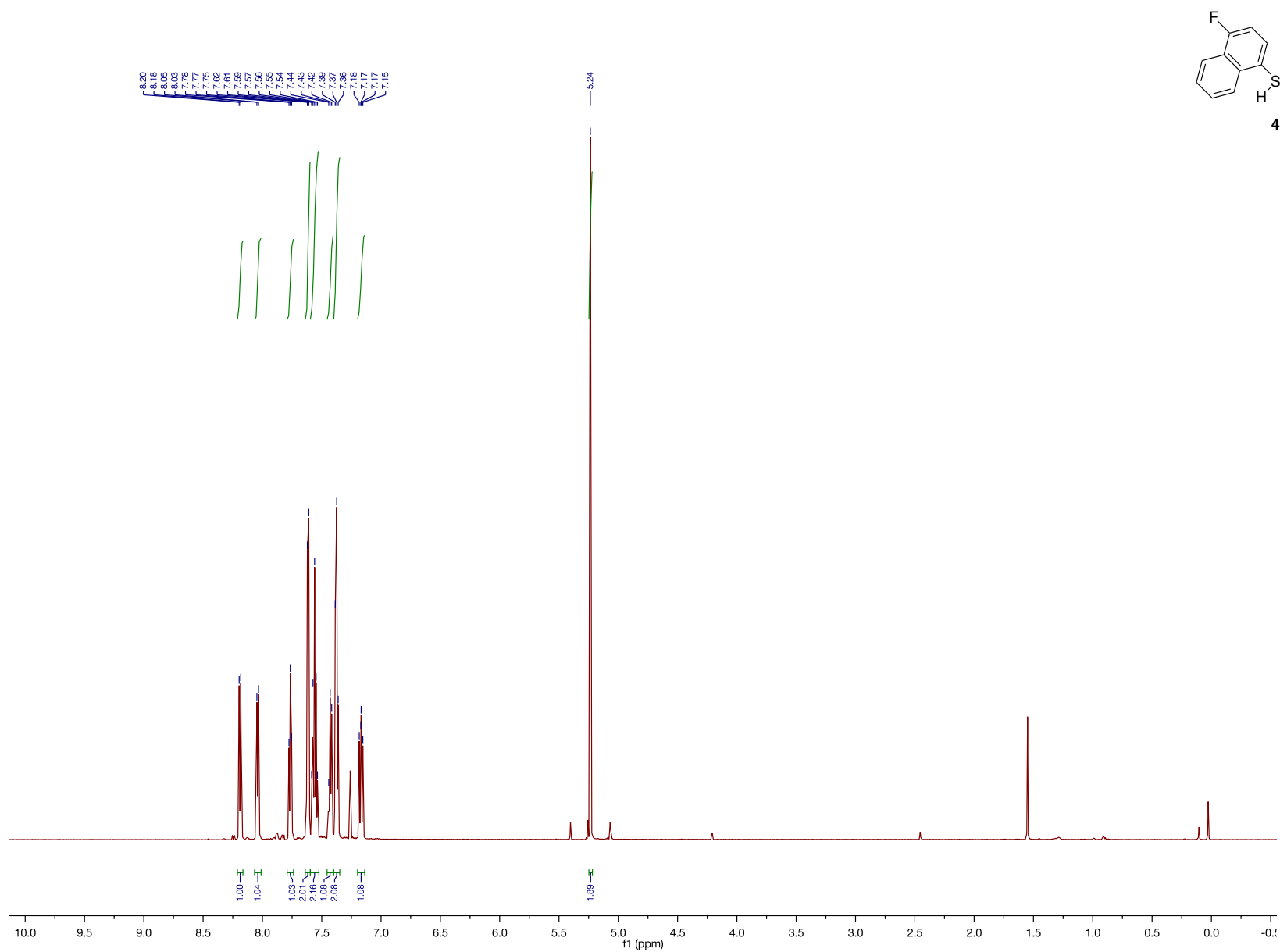
CDCl₃, 101 MHz, ¹³C NMR



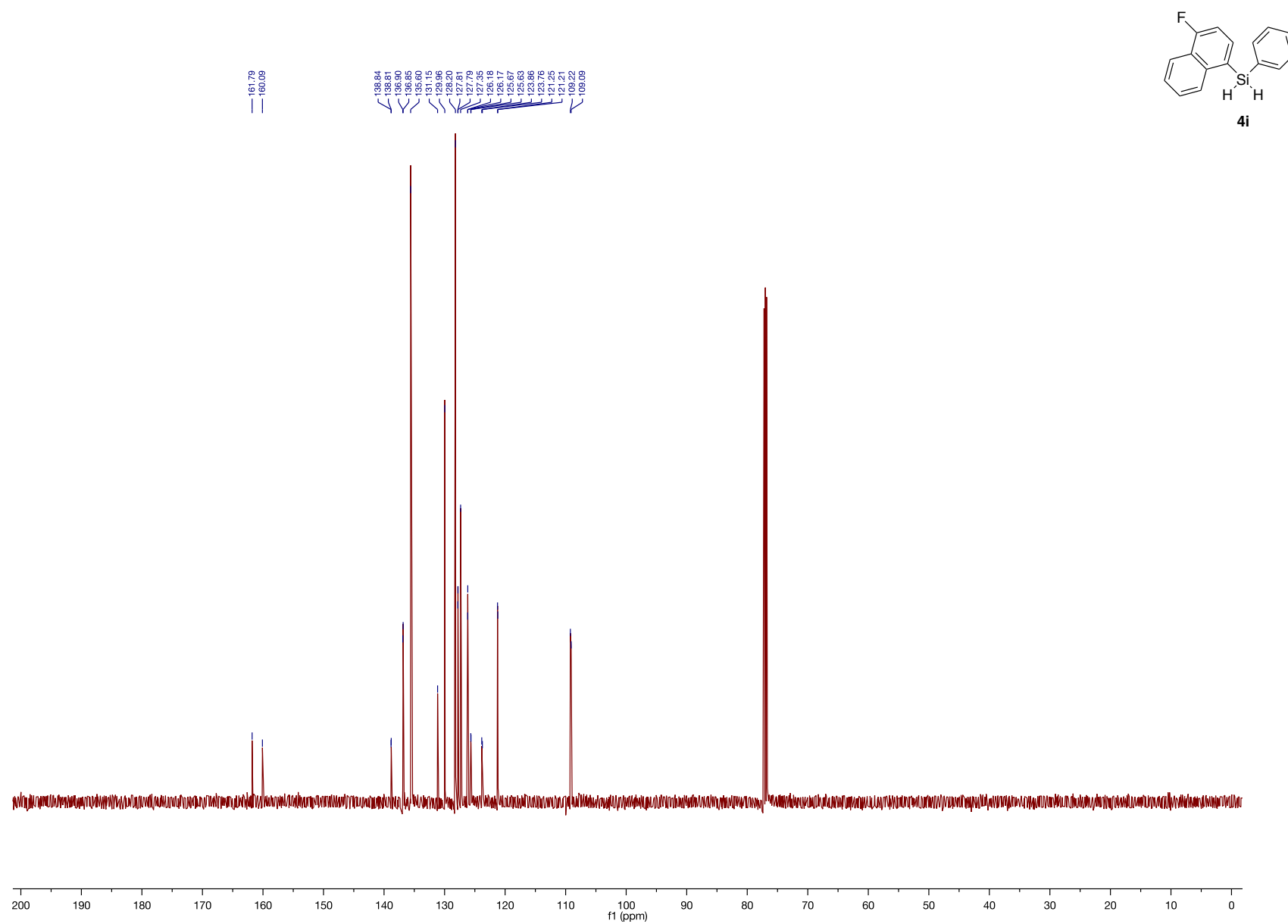
CDCl₃, 600 MHz, ¹H NMR



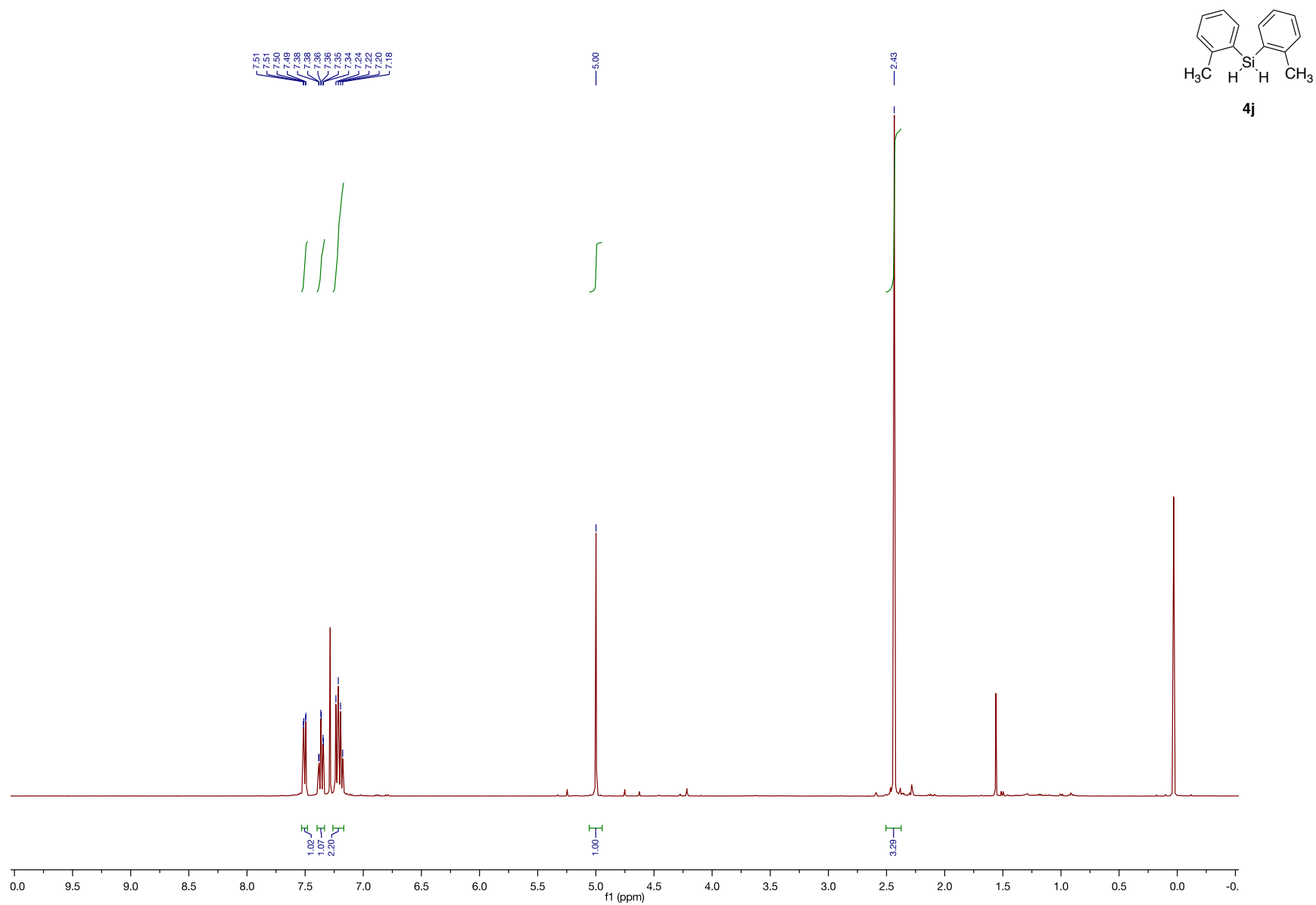
CDCl₃, 600 MHz, ¹H NMR



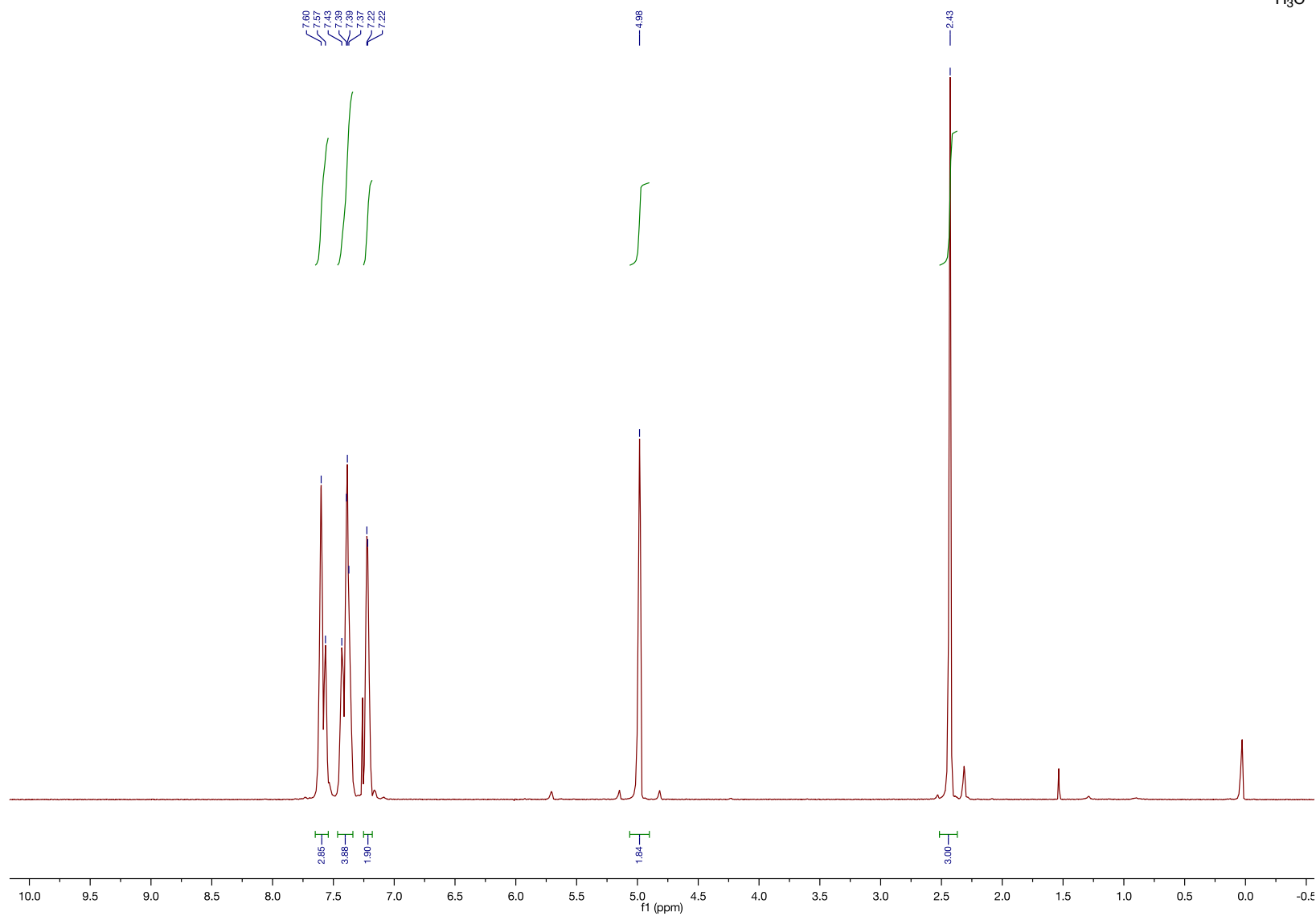
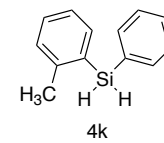
CDCl₃, 150 MHz, ¹³C NMR



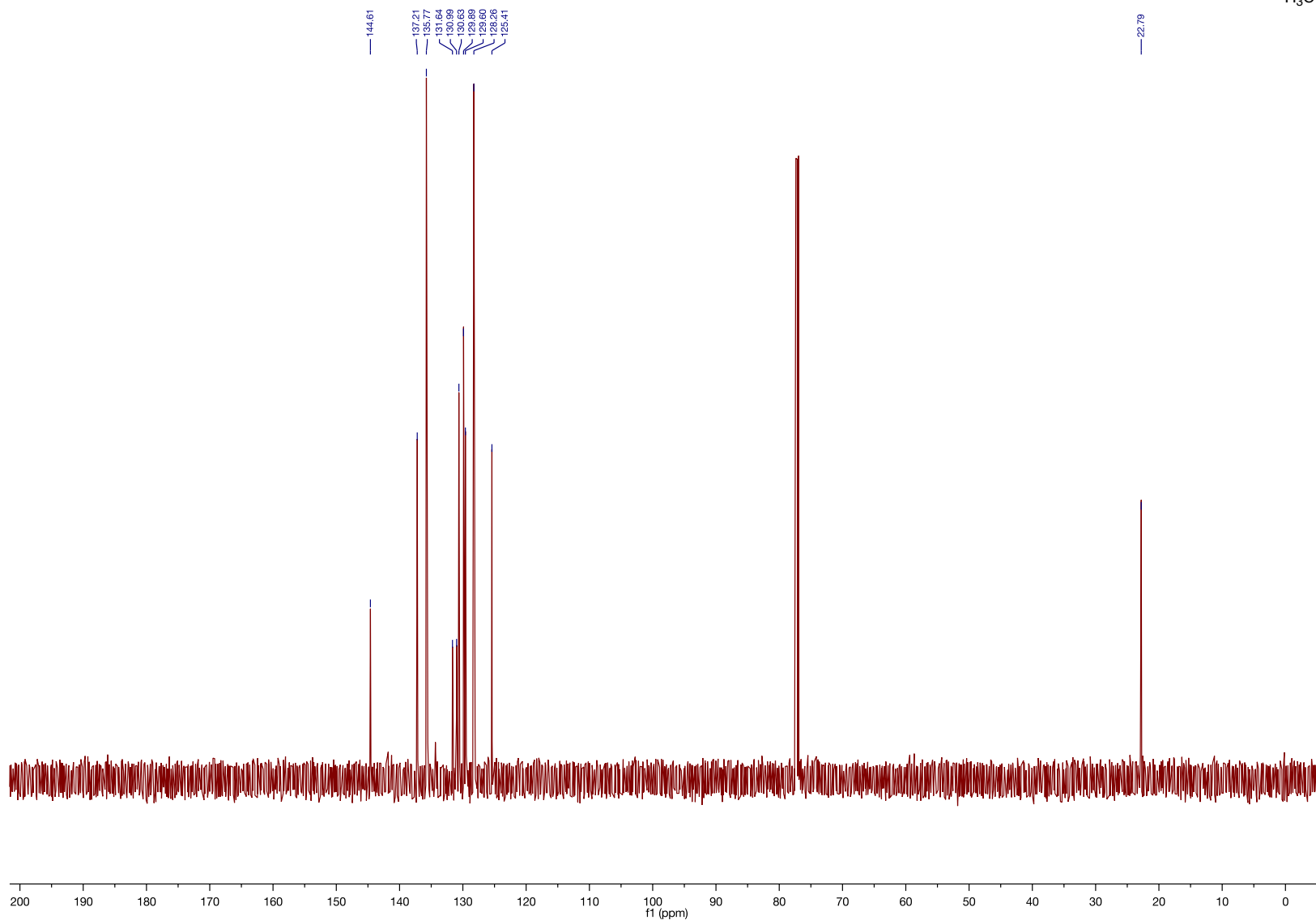
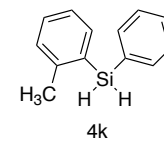
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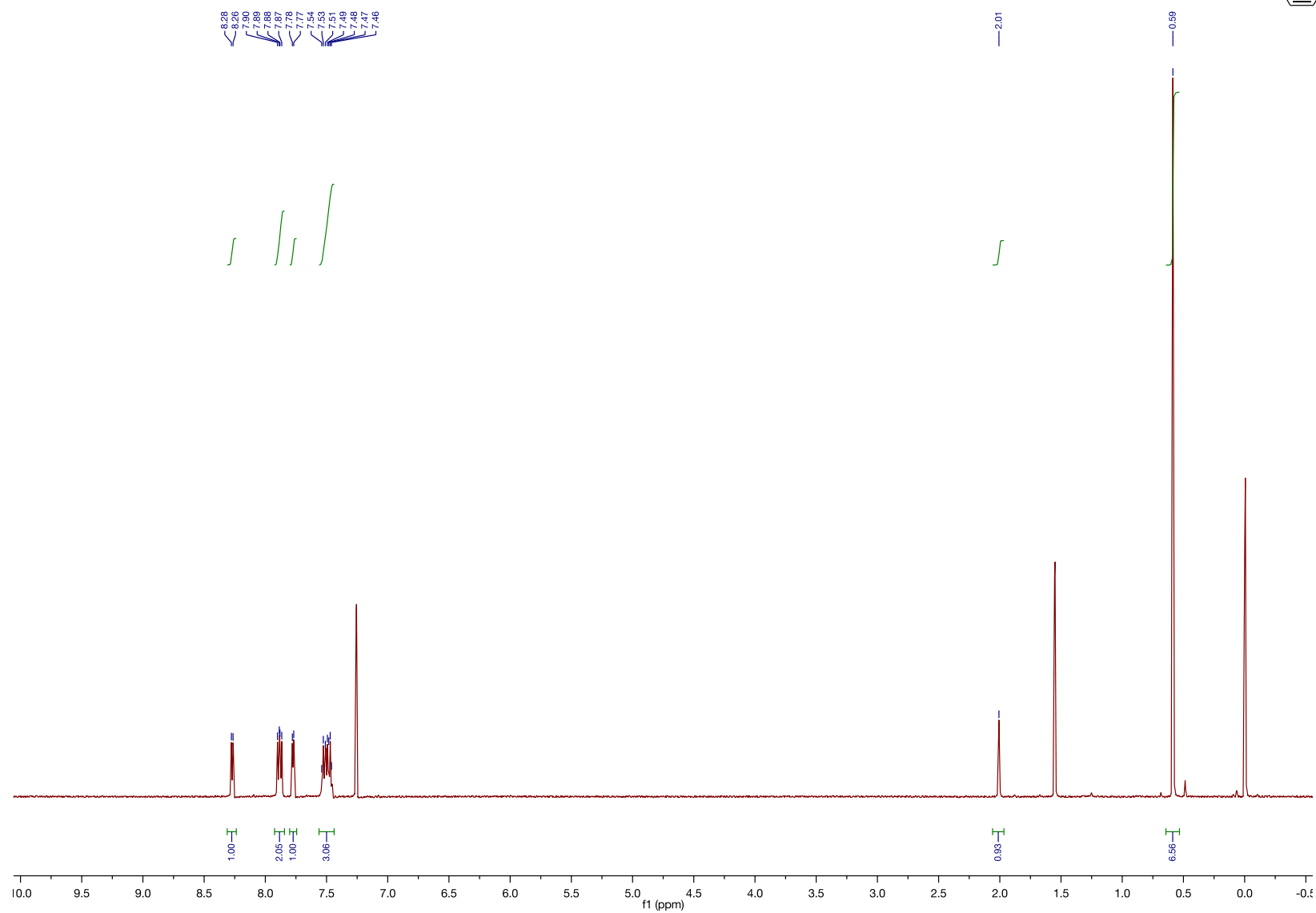
CDCl₃, 600 MHz, ¹H NMR



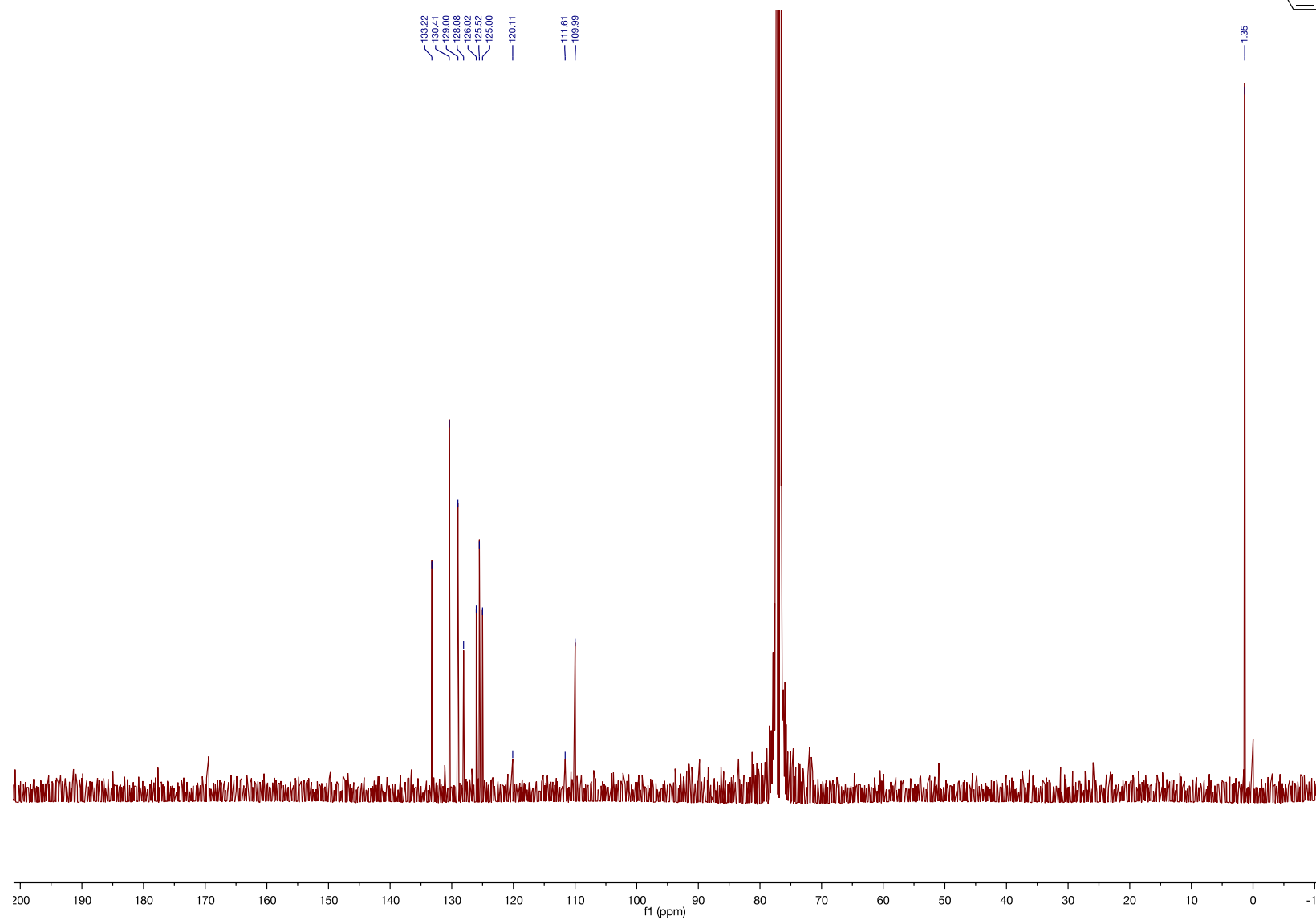
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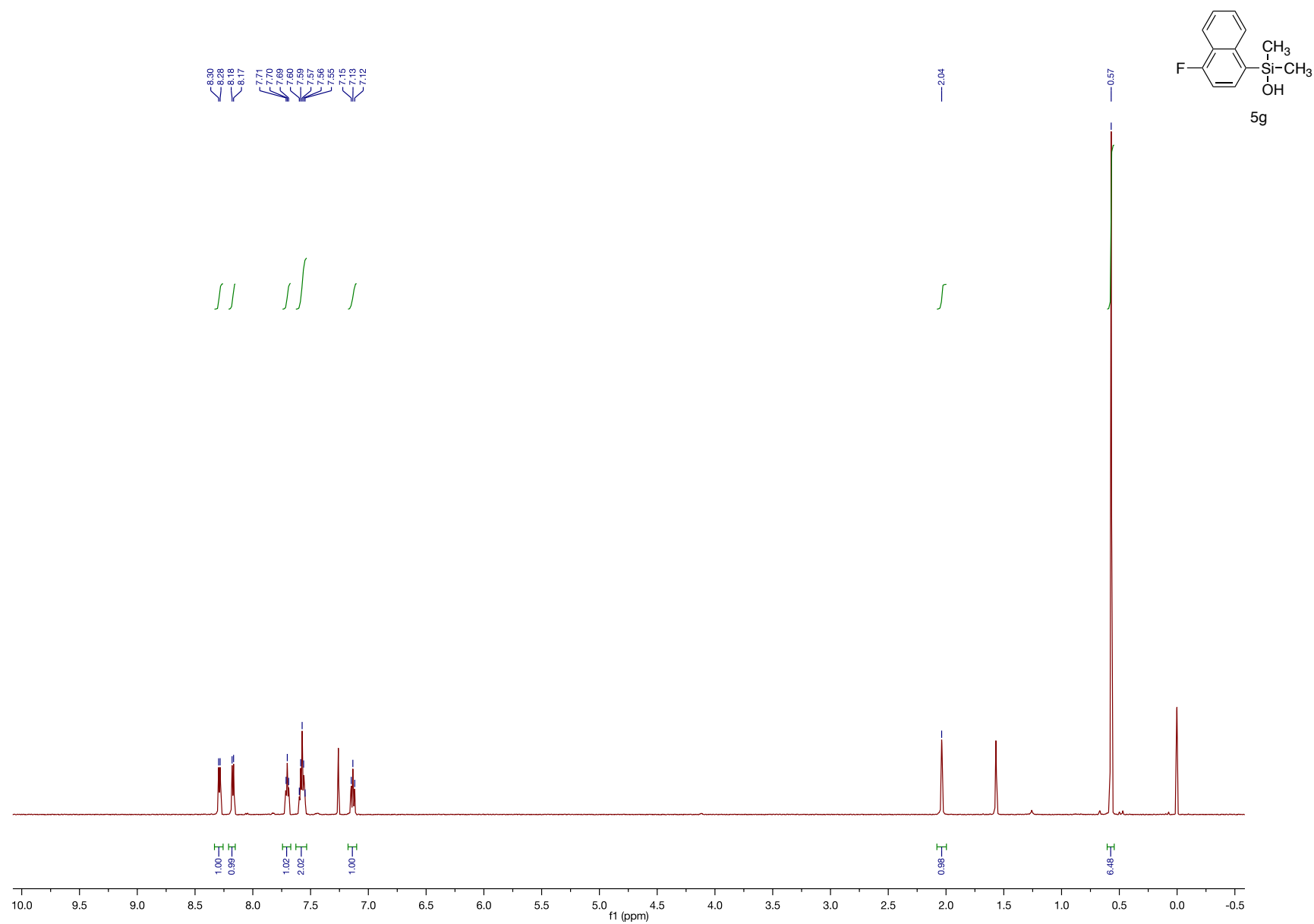
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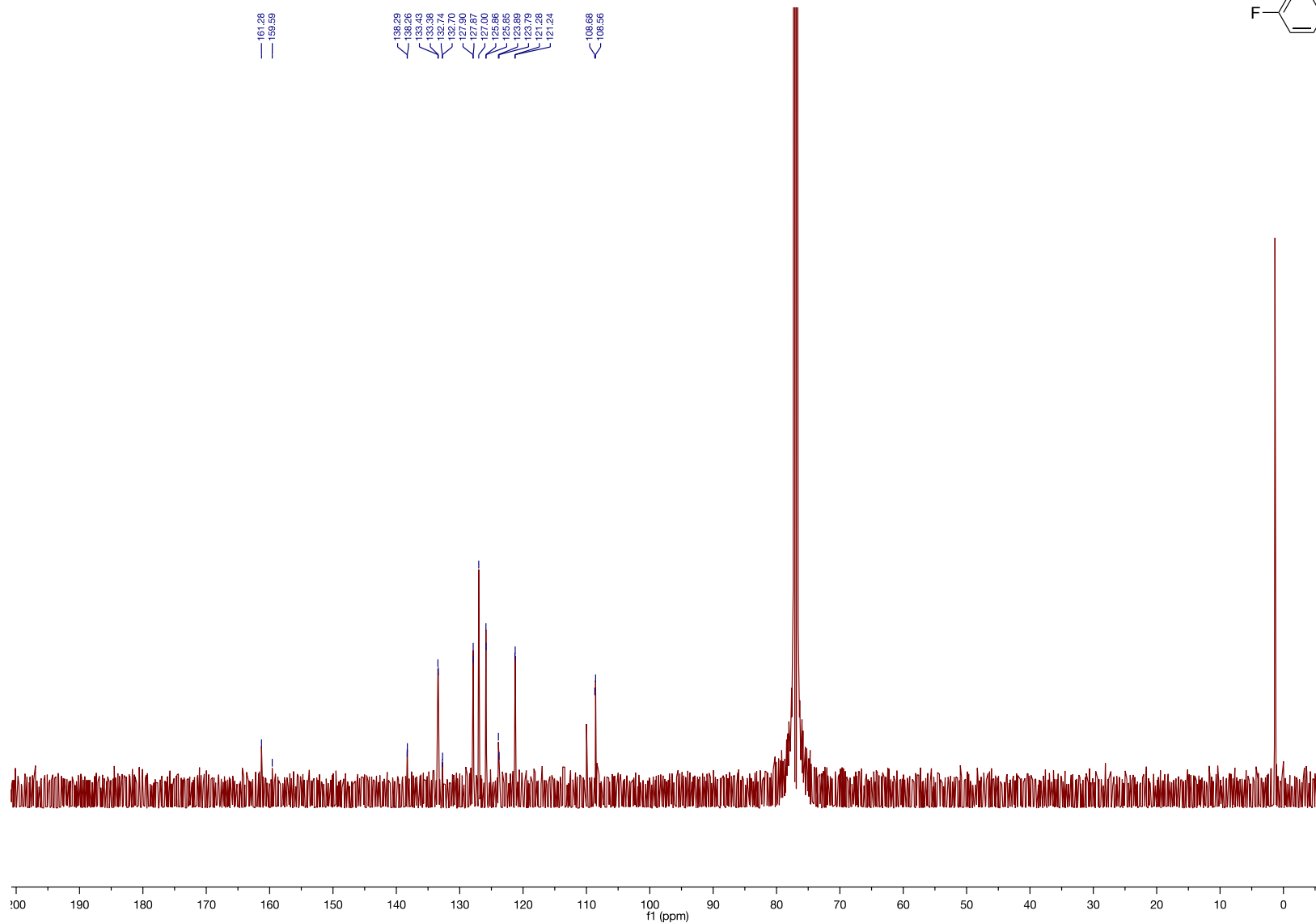
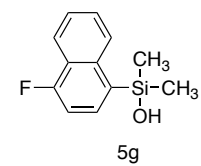
CDCl₃, 150 MHz, ¹³C NMR



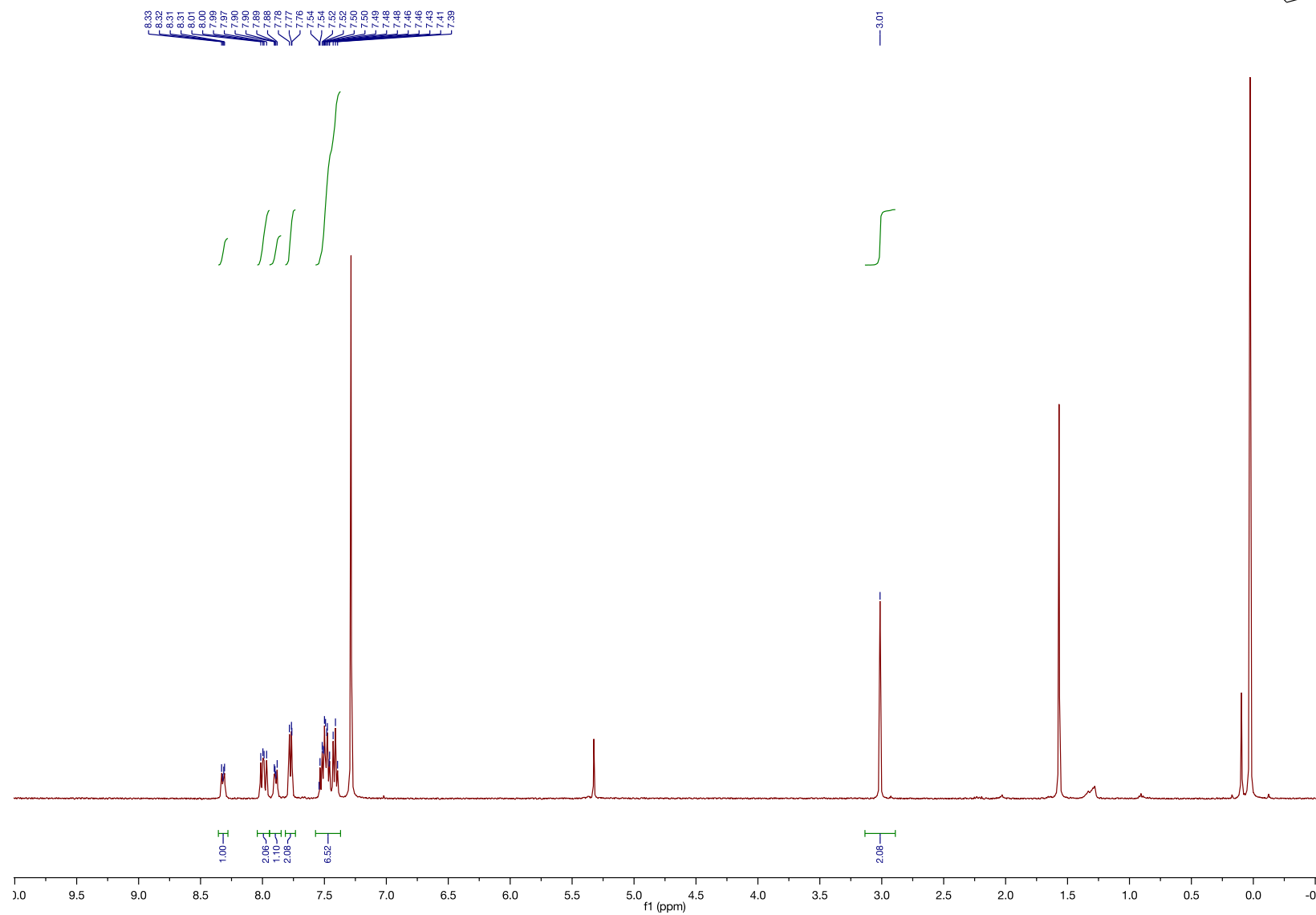
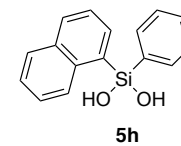
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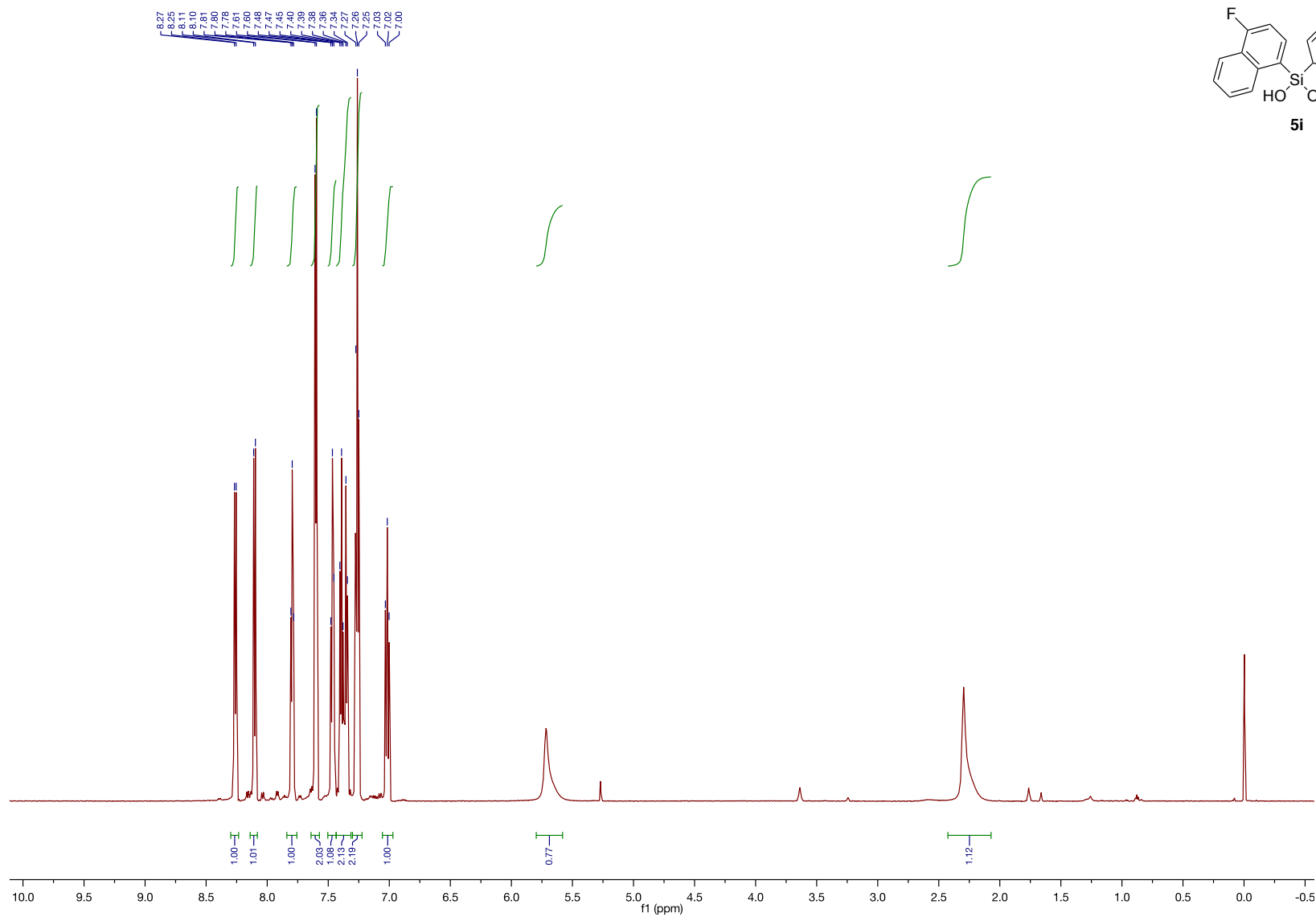
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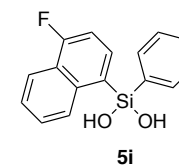
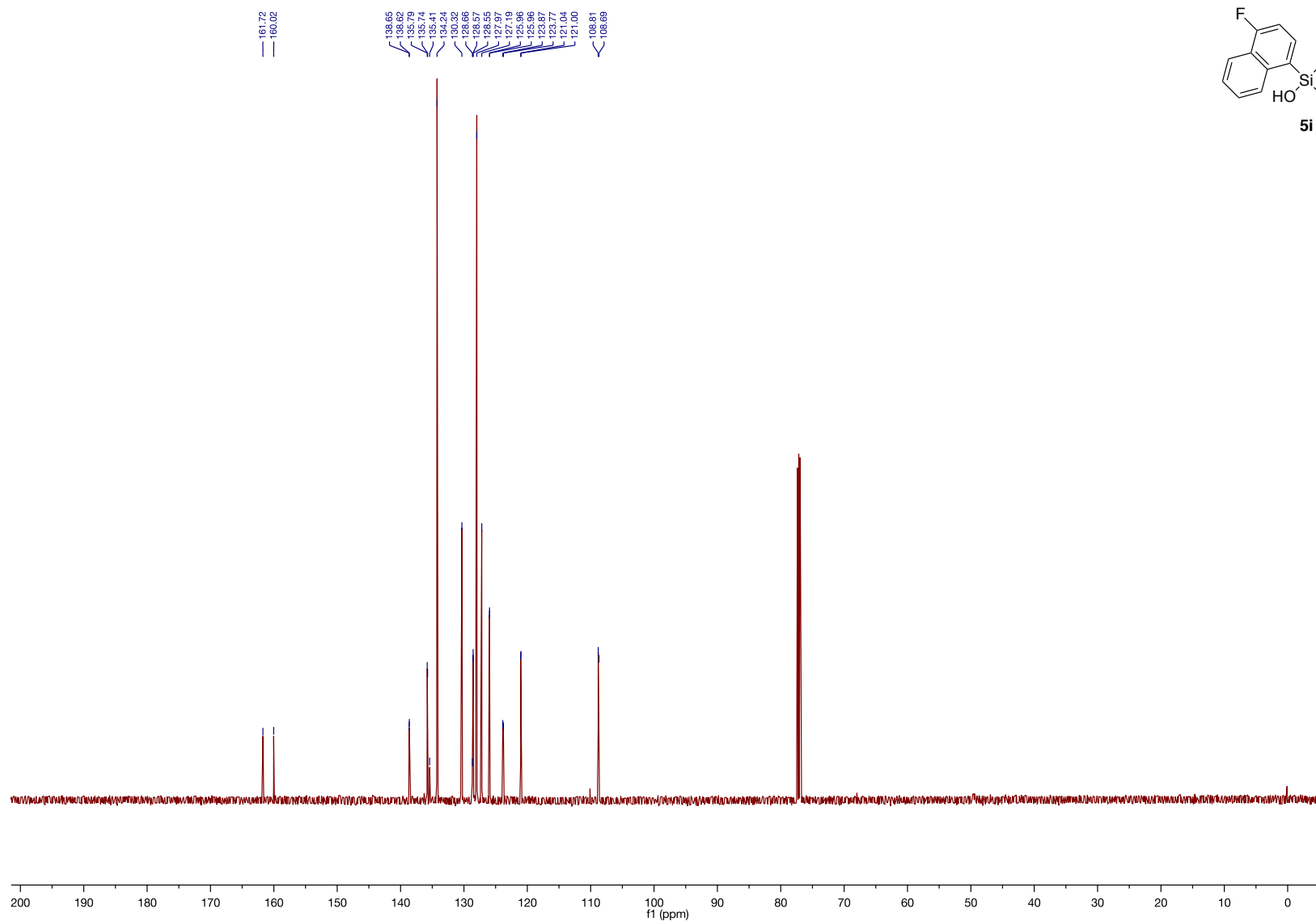
CDCl₃, 600 MHz, ¹H NMR



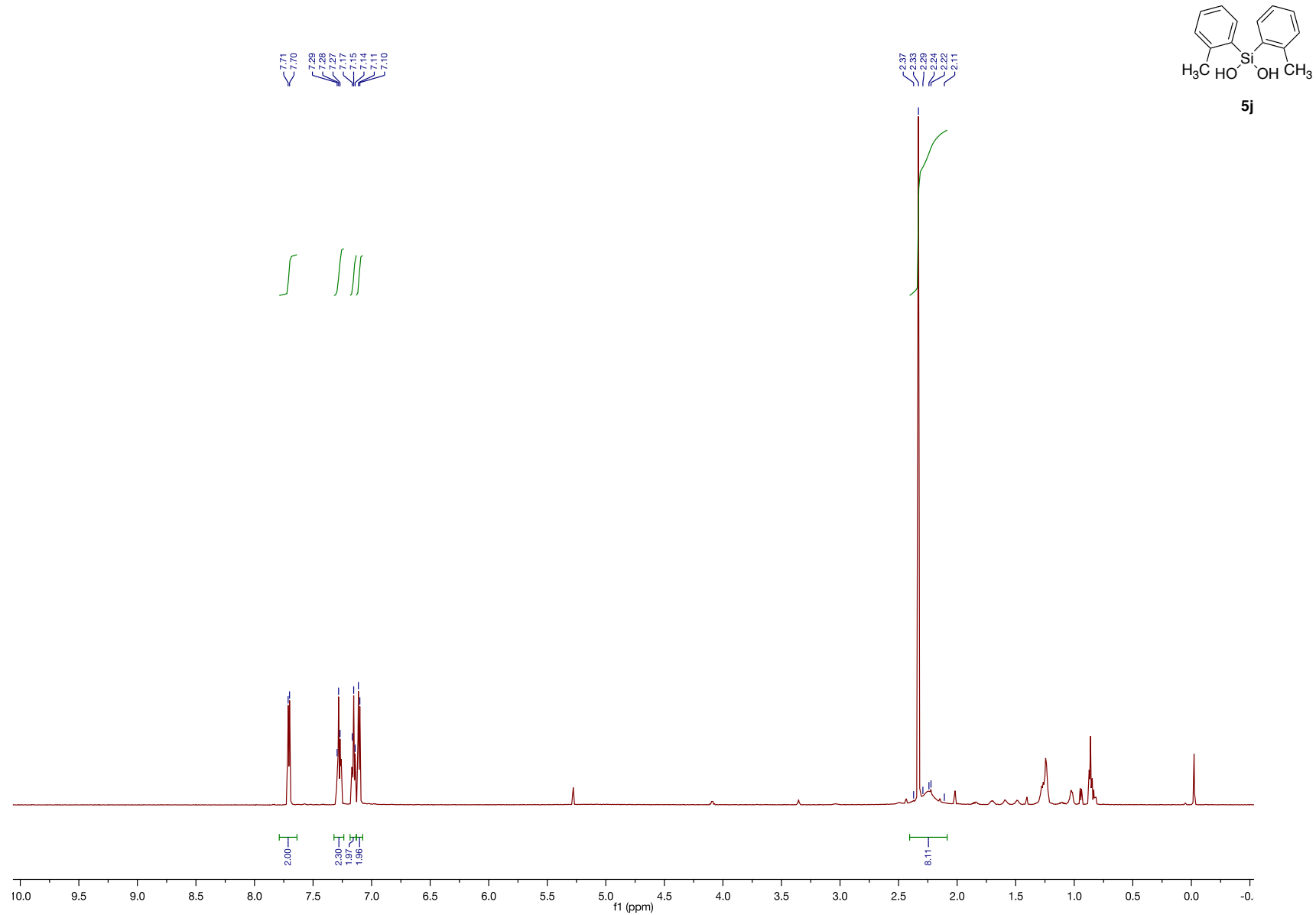
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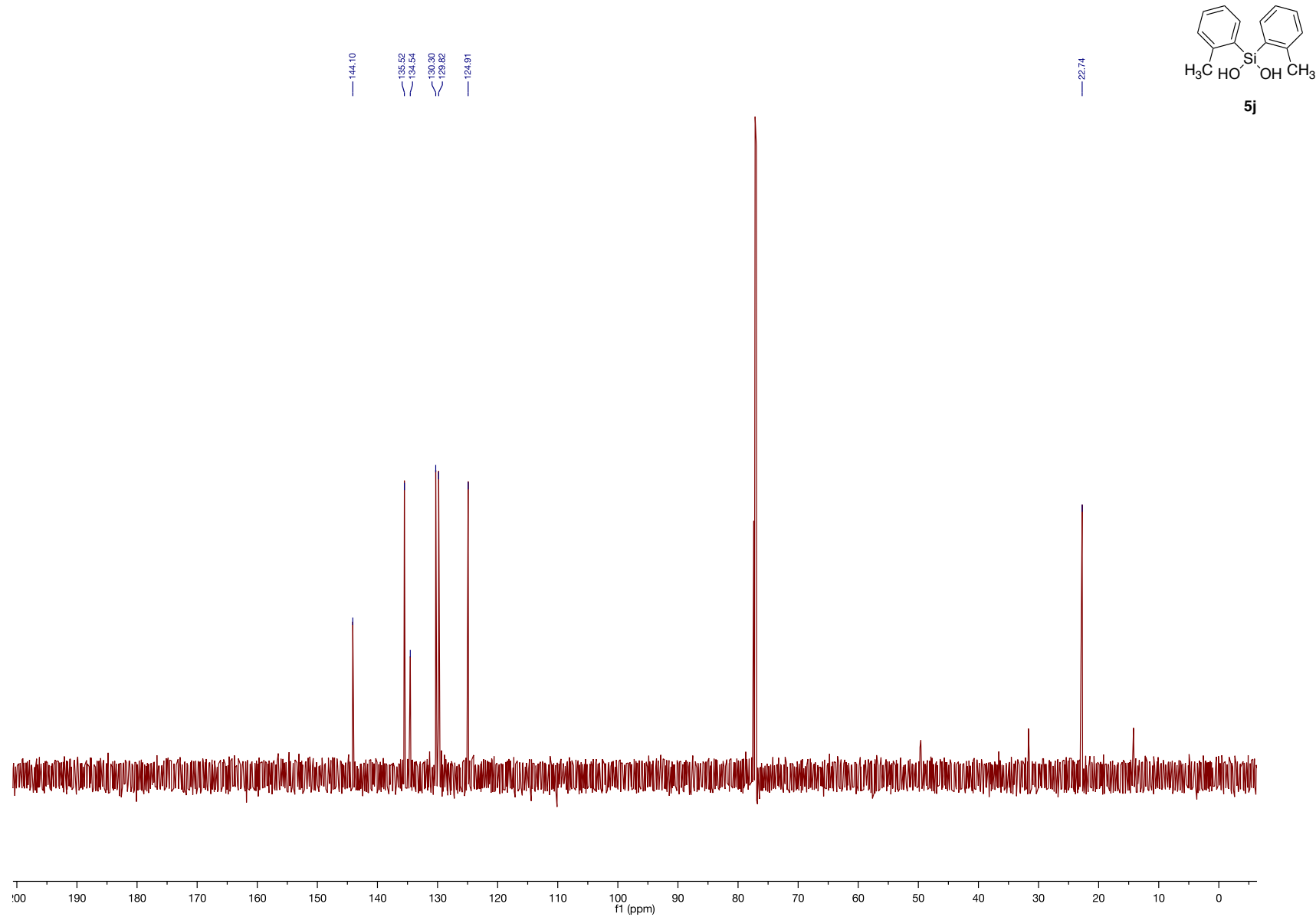
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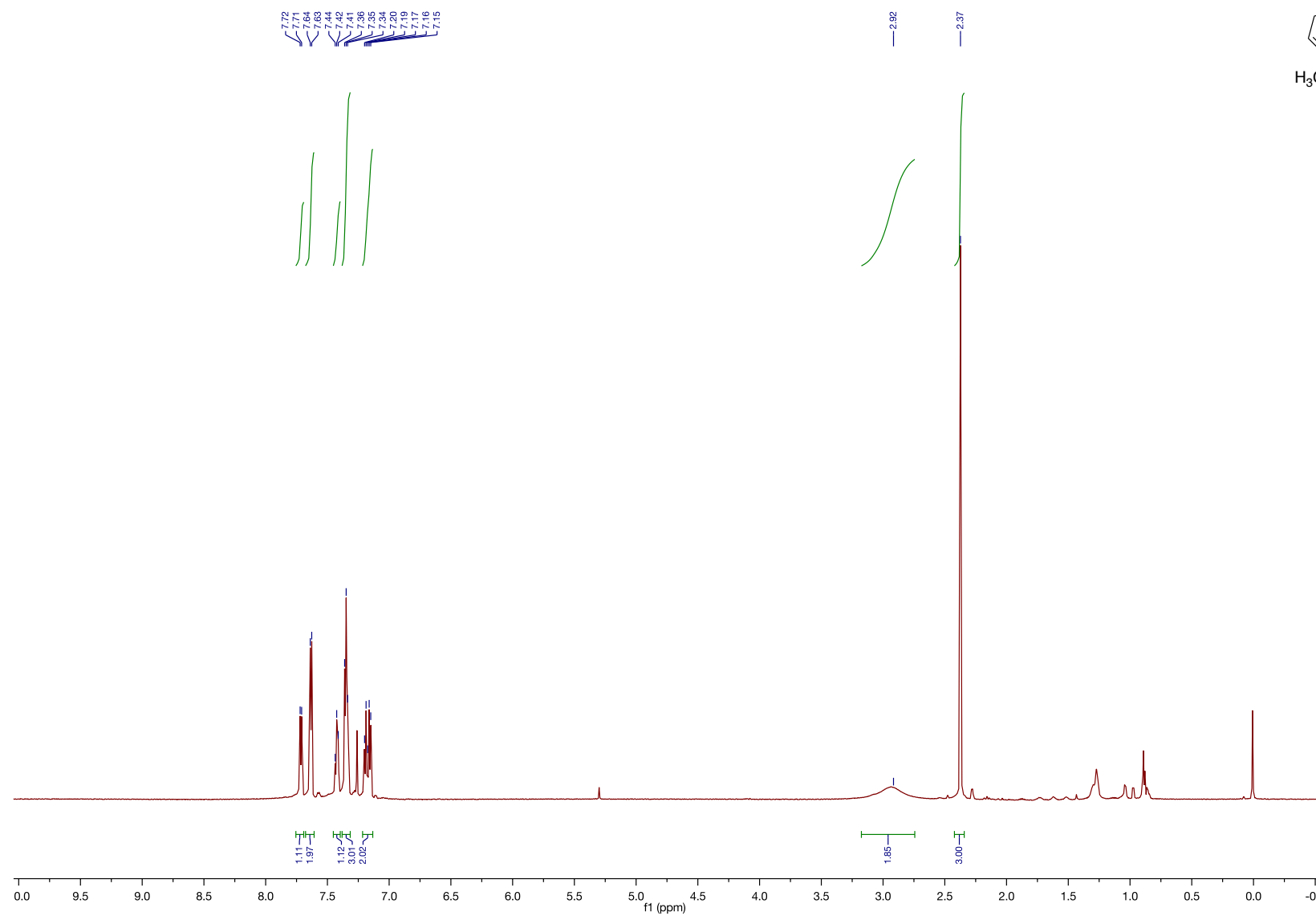
CDCl₃, 600 MHz, ¹H NMR



CDCl₃, 150 MHz, ¹³C NMR



CDCl₃, 600 MHz, ¹H NMR



CDCl₃, 150 MHz, ¹³C NMR

