Supporting Information

Dimethoxytetramethyldisilane: overcoming the limitations of palladium-catalyzed C-H silacyclization of 2-iodobiphenyls

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Table of Contenes

1 General Information

^{1}H-NMR and ^{13}C-NMR spectra were recorded at room temperature using a Bruker Avance-500 instrument (^{1}H NMR at 500 MHz, ^{13}C NMR at 125 MHz and ^{19}F NMR at 470 MHz), NMR spectra of all products were reported in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26 ppm), ^{13}C NMR: $CDCl_3$ (77.00 ppm)]. Signal patterns are indicated as s, singlet; d, doublet; dd, doublets of doublet; t, triplet, and m, multiplet. X-ray data were taken on an agilent Super Nova, X-ray diffractometer equipped with a large area CCD detector. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC system coupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). High-resolution mass spectra (HRMS) were equipped with electrospray ionization (ESI) sources. Reactions were monitored by thin-layer chromatography (TLC). Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Analytical grade solvents and commercially available reagents were purchased from commercial sources and used directly without further purification unless otherwise stated.

2 Reaction of 2-Iodobiphenyls with ODCS[1]

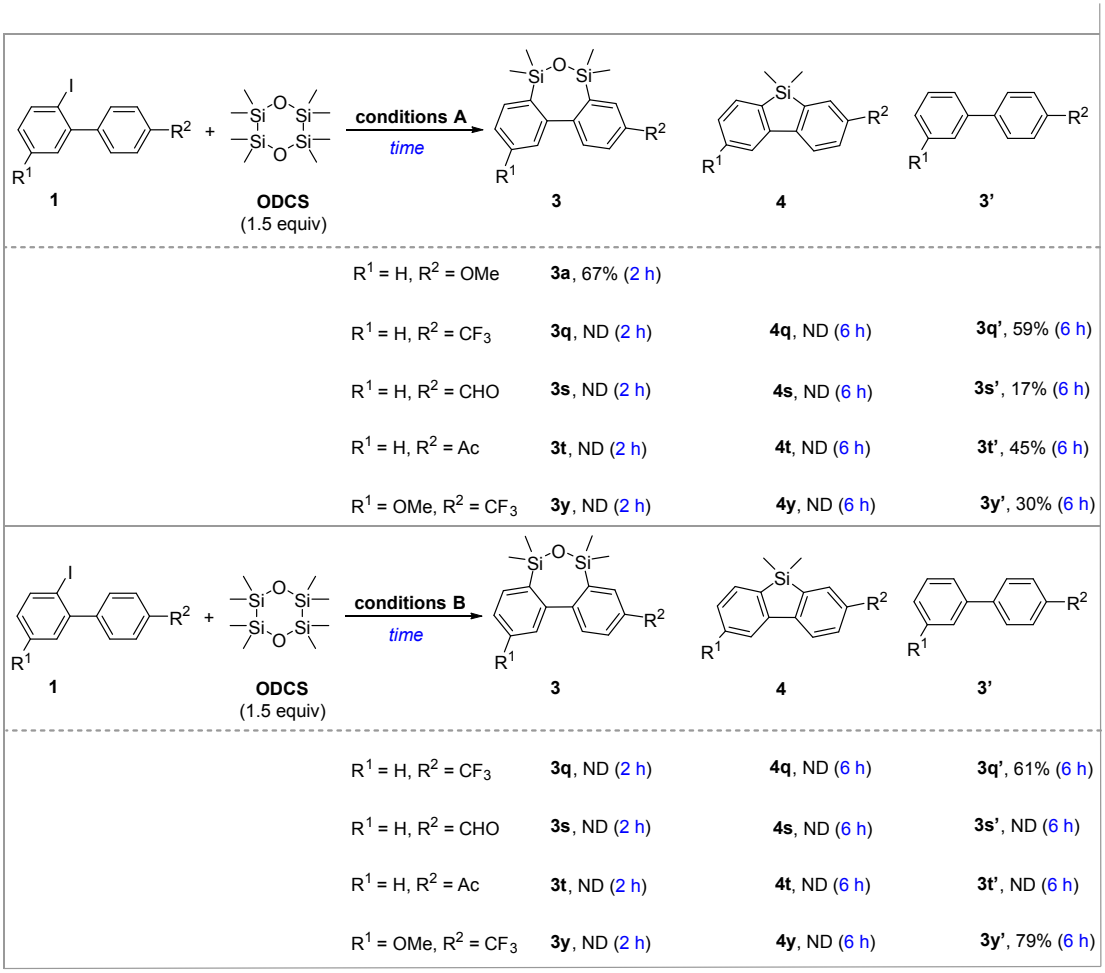
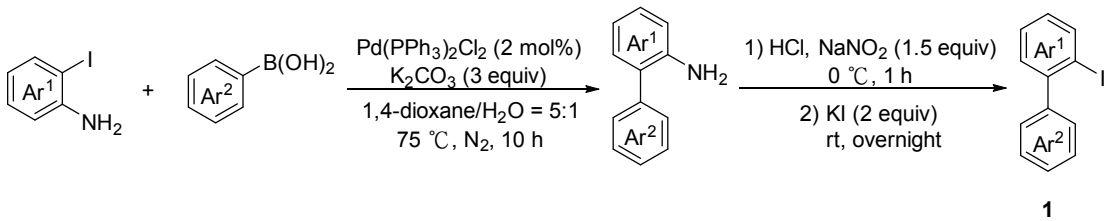


Figure S1. Reaction of 2-iodobiphenyls with ODCS

Reaction conditions A: **1** (0.2 mmol), ODCS (1.5 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), K_3PO_4 (3 equiv), and DMF (2 mL) at 100 °C under nitrogen atmosphere. Reaction conditions B: **1** (0.2 mmol), ODCS (1.5 equiv), $Pd(OAc)_2$ (10 mol%), PPh_3 (10 mol%), K_2CO_3 (3 equiv), and DMF (2 mL) at 100 °C under nitrogen atmosphere.

3 Synthetic Methods of Starting Materials

3.1 General Procedures for the Synthesis of Substrates 1[2]

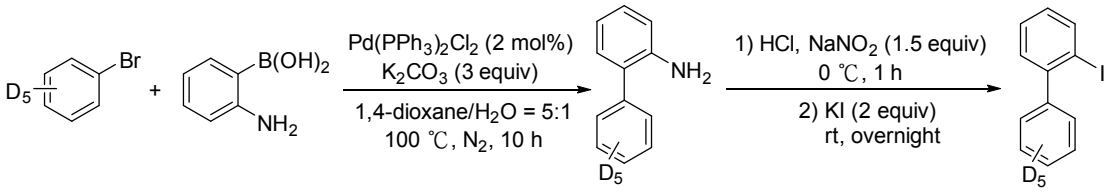


Step I: A 100 mL schlenk tube was charged with substituted 2-iodoanilines (5

mmol), substituted phenylboronic acids (1.2 equiv), $Pd(PPh_3)_2Cl_2$ (2 mol%), K_2CO_3 (3 equiv), 1,4-dioxane (20 mL) and water (4 mL). The mixture was heated in an oil bath at 75 °C for 10 h. After the completion of the reaction, it was allowed to attain to room temperature, then the reaction mixture was filtered and the filtrate diluted in ethyl acetate, and washed with water. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography (petroleum ether/EtOAc unless otherwise noted) to give the corresponding substituted 2-aminobiphenyls.

Step II: A solution of concn HCl (36-38%; 1 mL, 2.7 mmol) in water (4 mL) was added slowly to the prepared 2-aminobiphenyls (2 mmol) at 0 °C in portions. After stirring for 1 h at 0 °C, the aqueous solution of $NaNO_2$ (1.5 equiv) was added to the reaction mixture below 5 °C within 10 min and stirred for 1 h. Then an aqueous solution of KI (2 equiv) in water (4 mL) was added and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction, saturated aqueous $NaHCO_3$ was added to neutralize the acid and adjust the solution to pH > 7. Then the residue was extracted into ethyl acetate (3×5 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography to give the desired 2-iodobiphenyls **1**.

3.2 General Procedures for the Synthesis of Substrate 1b-D_5[2]



1b-D_5

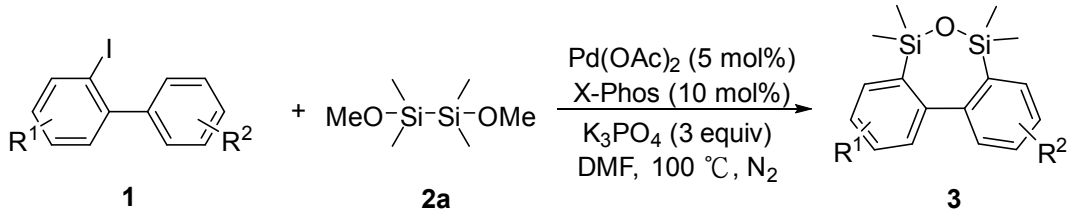
Step I: A 100 mL schlenk tube was charged with (2-aminophenyl)boronic acid (1.2 equiv), bromobenzene-D_5 (5 mmol), $Pd(PPh_3)_2Cl_2$ (2 mol%), K_2CO_3 (3 equiv), 1,4-dioxane (20 mL) and water (4 mL). The mixture was heated in an oil bath at 100 °C for 10 h. After the completion of the reaction, it was allowed to attain to room temperature, then the reaction mixture was filtered and the filtrate diluted in ethyl acetate, and washed with water. The combined organic layers were dried over

anhydrous Na_2SO_4 and evaporated under vacuum. The crude product was purified by silica gel column chromatography to give the corresponding [1,1'-biphenyl]-2-amine-D_5.

Step II: A solution of concn HCl (36-38%; 1 mL, 2.7 mmol) in water (4 mL) was added slowly to the prepared [1,1'-biphenyl]-2-amine-D_5 (2 mmol) at 0 ℃ in portions. After stirring for 1 h at 0 °C, the aqueous solution of $NaNO_2$ (1.5 equiv) was added to the reaction mixture below 5 °C within 10 min and stirred for 1 h. Then an aqueous solution of KI (2 equiv) in water (4 mL) was added and the reaction mixture was stirred at room temperature overnight. After the completion of the reaction, saturated aqueous $NaHCO_3$ was added to neutralize the acid and adjust the solution to pH > 7. Then the residue was extracted into ethyl acetate (3×5 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography to give the desired product **1b-D_5**.

4 Typical Procedures

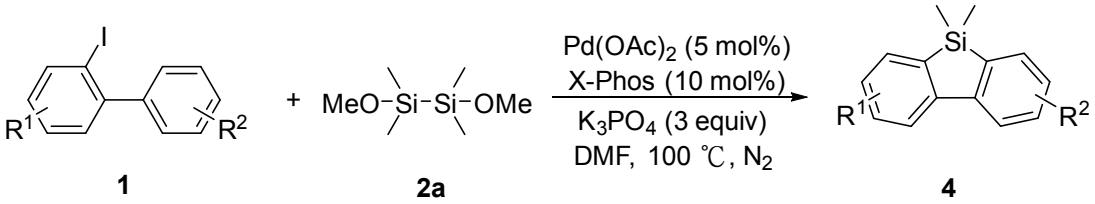
4.1 Typical procedures for the synthesis of dibenzooxadisilepines 3



1 **2a** **3**

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, 2-iodobiphenyls **1** (0.2 mmol), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (1.5 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), and K_3PO_4 (3 equiv) were added, and dissolved in DMF (2 mL). The vessel was evacuated, backfilled with N_2, and stirred at 100 °C for 2 h. The reaction mixture was filtered, and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the desired products **3**.

4.2 Typical procedures for the synthesis of dibenzosiloles 4

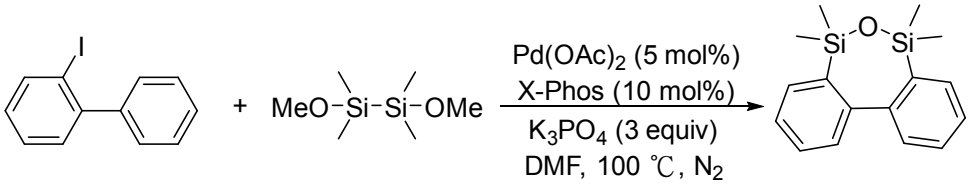


1 **2a** **4**

To an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar, 2-iodobiphenyls **1** (0.2 mmol), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (1.5 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), and K_3PO_4 (3 equiv) were added, and dissolved in DMF (2 mL). The vessel was evacuated, backfilled with N_2, and stirred at 100 °C for 6 h. The reaction mixture was filtered, and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure. The crude product was purified by flash column chromatography to afford the desired products **4**.

5 Gram-Scale Reaction

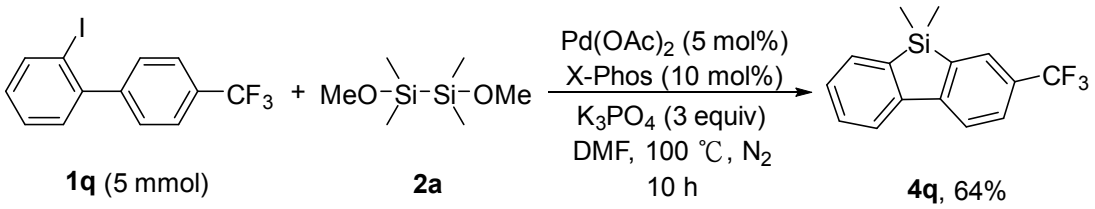
5.1 Gram-scale synthesis of 3b



1b (5 mmol) **2a** 5 h **3b**, 89%

To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, 2-iodo-1,1'-biphenyl **1b** (5 mmol), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (1.5 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), and K_3PO_4 (3 equiv) were added, and dissolved in DMF (25 mL). The vessel was evacuated, backfilled with N_2, and stirred at 100 °C for 5 h. The reaction mixture was filtered, and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure. The crude product was purified by flash column chromatography (eluent: petroleum ether/EtOAc = 400:1) to afford the desired product **3b** in 89% isolated yield (1.26 g).

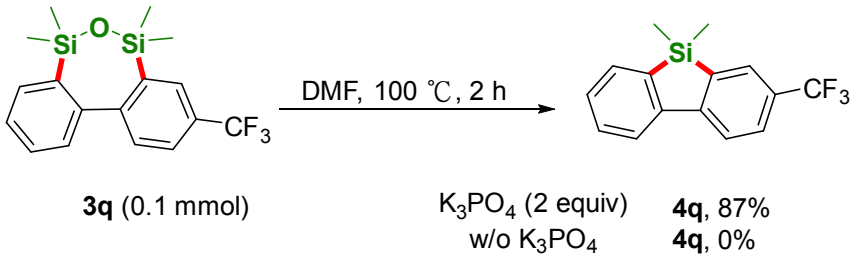
5.2 Gram-scale synthesis of 4q



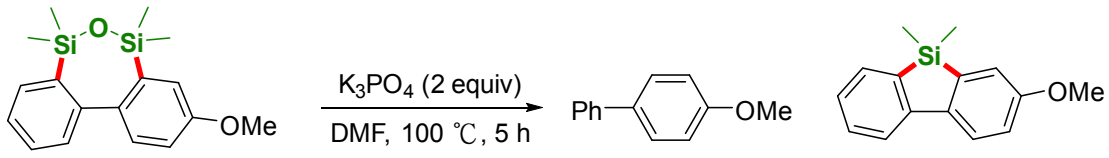
To an oven-dried 100 mL Schlenk tube equipped with a magnetic stir bar, 2-iodo-4'-(trifluoromethyl)-1,1'-biphenyl **1q** (5 mmol), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (1.5 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), and K_3PO_4 (3 equiv) were added, and dissolved in DMF (25 mL). The vessel was evacuated, backfilled with N_2, and stirred at 100 °C for 10 h. The reaction mixture was filtered, and the filtrate was washed by H_2O and saturated salt solution and then evaporated under reduced pressure. The crude product was purified by flash column chromatography (eluent: petroleum ether/EtOAc = 400:1) to afford the desired product **4q** in 64% isolated yield (0.89g).

6 Mechanistic Experiments

6.1 The transformation of 3 to 4



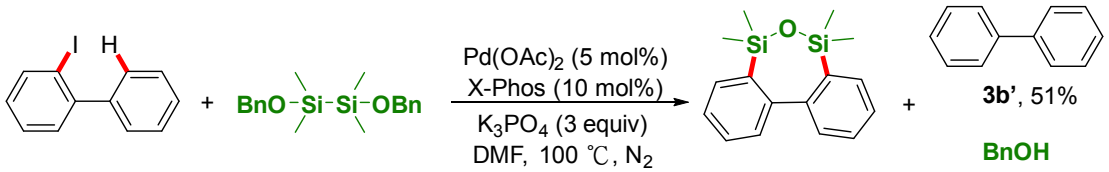
To a 25 mL Schlenk tube was added **3q** (0.1 mmol), K_3PO_4 (2 equiv), and DMF (1 mL). Then the tube was stirred at 100 °C for about 2 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate, dried over Na_2SO_4. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography to afford the product **4q** in 87% yield. Without K_3PO_4, the product **4q** was not detected.



3a (0.1 mmol) **3a'**, 91% **4a**, ND

To a 25 mL Schlenk tube was added **3a** (0.1 mmol), K_3PO_4 (2 equiv), and DMF (1 mL). Then the tube was stirred at 100 °C for about 5 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate, dried over Na_2SO_4. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography to afford the product **3a'** in 91% yield. The product **4a** was not detected.

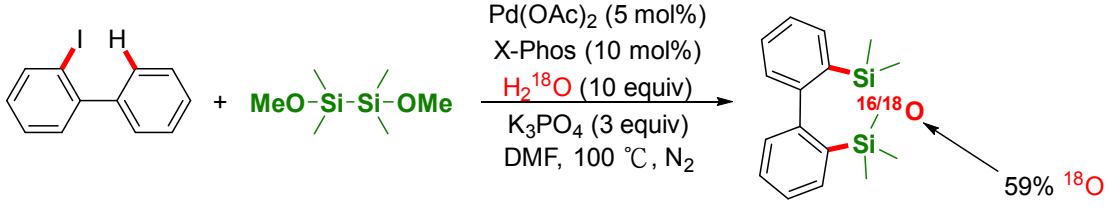
6.2 The reaction of 1b with 2b



1b (0.2 mmol) **2b** (0.3 mmol) **3b**, 25%

To a 25 mL Schlenk tube was added 2-iodo-1,1'-biphenyl **1b** (0.2 mmol), 1,2-bis(benzyloxy)-1,1,2,2-tetramethyldisilane **2b** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), K_3PO_4 (3 equiv), and DMF (2 mL). Then the tube was evacuated briefly under high vacuum and charged with nitrogen, and was stirred at 100 °C for 2 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate, dried over Na_2SO_4. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography to afford the products **3b** in 26% yield, **3b'** in 51% yield, and **5** in 53% yield.

6.3 ^{18}O-Isotope labeling experiment



1b (0.1 mmol) **2a** (0.15 mmol) **3b**, 81%

To a 25 mL Schlenk tube was added 2-iodo-1,1'-biphenyl **1b** (0.1 mmol),

1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (0.15 mmol), $H_2{}^{18}O$ (10 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), K_3PO_4 (3 equiv), and DMF (1 mL). Then the tube was evacuated briefly under high vacuum and charged with nitrogen, and was stirred at 100 °C for 2 h. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate, dried over Na_2SO_4. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography (eluent: petroleum ether/EtOAc = 400:1) to give products **3b-^{18}O** and **3b-^{16}O**. The abundance ratio shows that the ratio of **3b-^{18}O** to **3b-^{16}O** is 1.44.

Table S1. Data of GC-MS from 3b-^{18}O

m/z	abundance	m/z	abundance	m/z	abundance
73.08	422999.22	165.09	2274264	255.09	18049.52
97.58	314459.44	166.09	434025.75	269.15	5322311.5
104.96	162892.56	167.06	359198.94	270.16	1965796.8
120.54	181363.14	179.07	305529.81	272.13	2443470
127.13	430330.05	180.06	394159.34	273.12	937050.5
128.05	594129.56	181.05	547798.38	274.12	163884.75
128.73	195273.12	193.08	723027.31	**284.14**	**1107863.5**
134.65	337991.19	195.08	811607.44	285.17	366951.09
135.57	475074.09	195.1	34830545	**286.14**	**1586602.25**
152.09	335273.66	197.08	249477.78	287.14	452000.41
153.05	172170.33	209.1	331431.62		

Figure S4. GC-MS for 3b-^{16}O

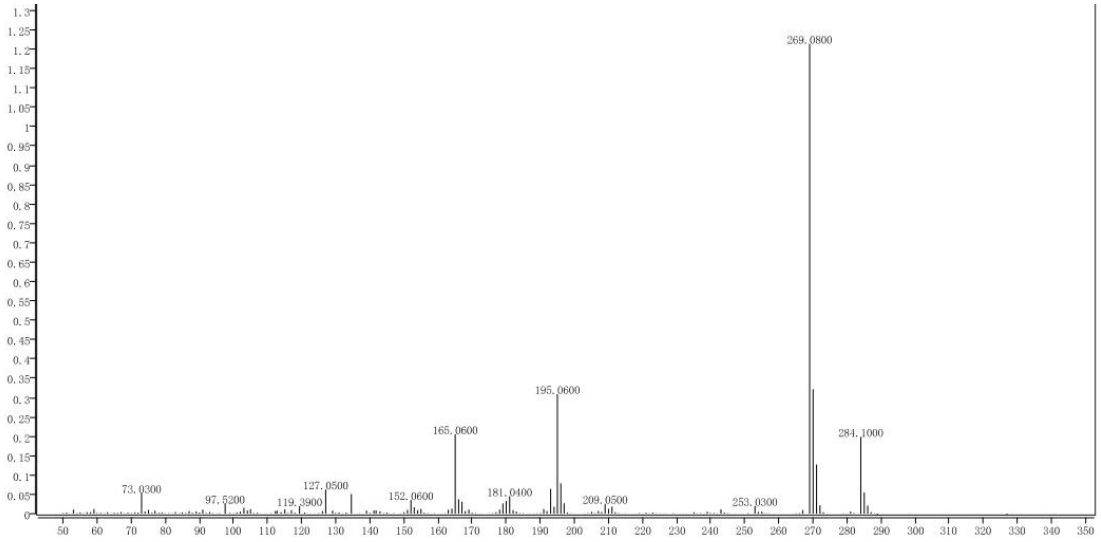
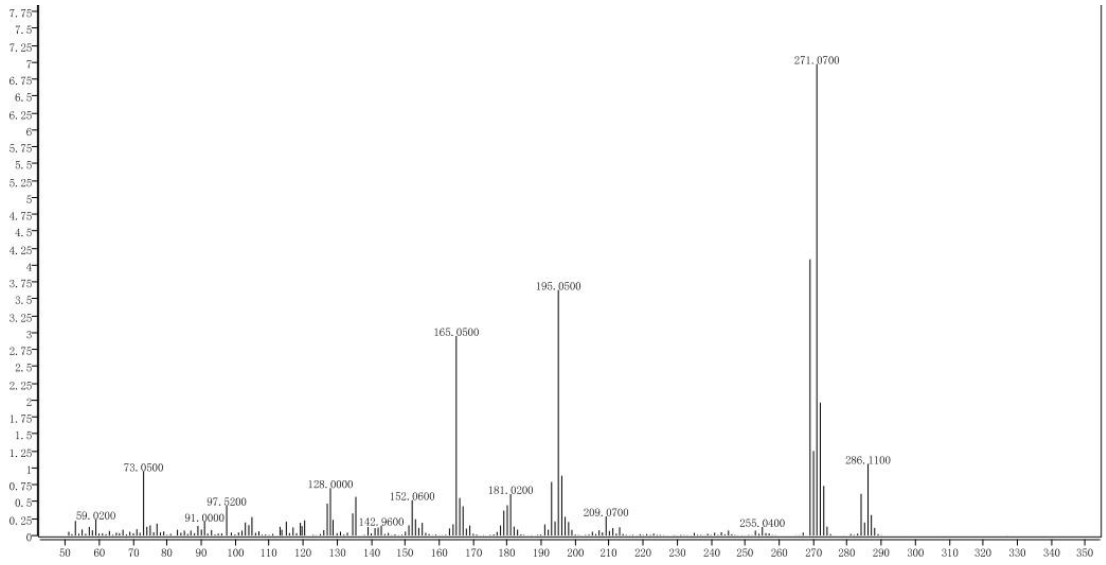
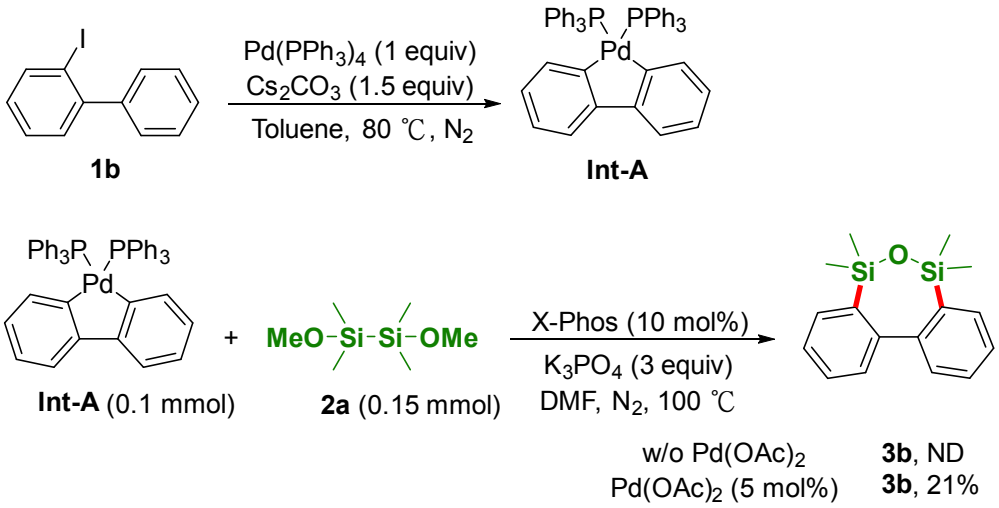


Figure S5. GC-MS for 3b-^{18}O



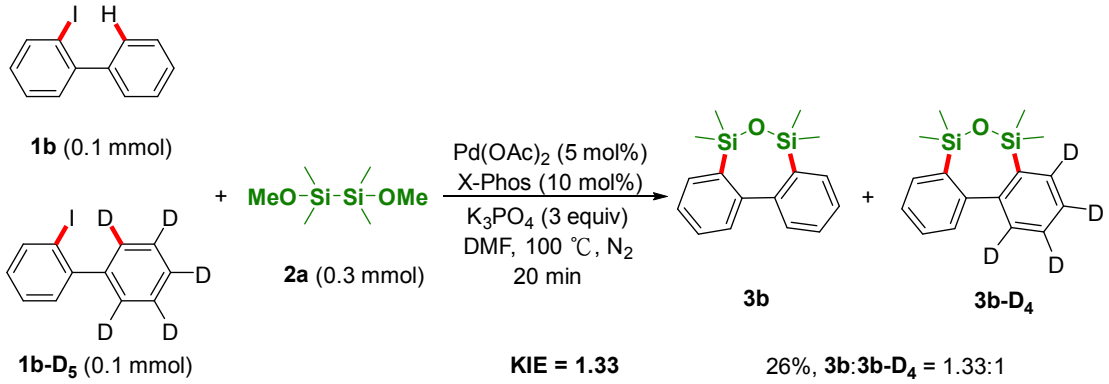
6.4 The reaction of palladacycle with 2a[3]



To a 25 mL Schlenk tube were added 2-iodo-1,1'-biphenyl **1b** (0.2 mmol, 1 equiv), $Pd(PPh_3)_4$ (1 equiv), Cs_2CO_3 (1.5 equiv), and toluene (2 mL). Then the tube was charged with nitrogen, and was stirred at 80 °C for the indicated time (about 12 h) until complete consumption of starting material as monitored by TLC analysis. The reaction mixture was cooled to room temperature. Once cooled, the reaction was passed through a plug of celite using DCM and concentrated in vacuo. Once solidified, hexane was used to triturate the compound. The mixture was passed through glass wool and the collected solid was redissolved in DCM and concentrated in vacuo. The palladacycle **Int-A** then recrystallized Et_2O and hexanes to obtain a pale yellow solid.

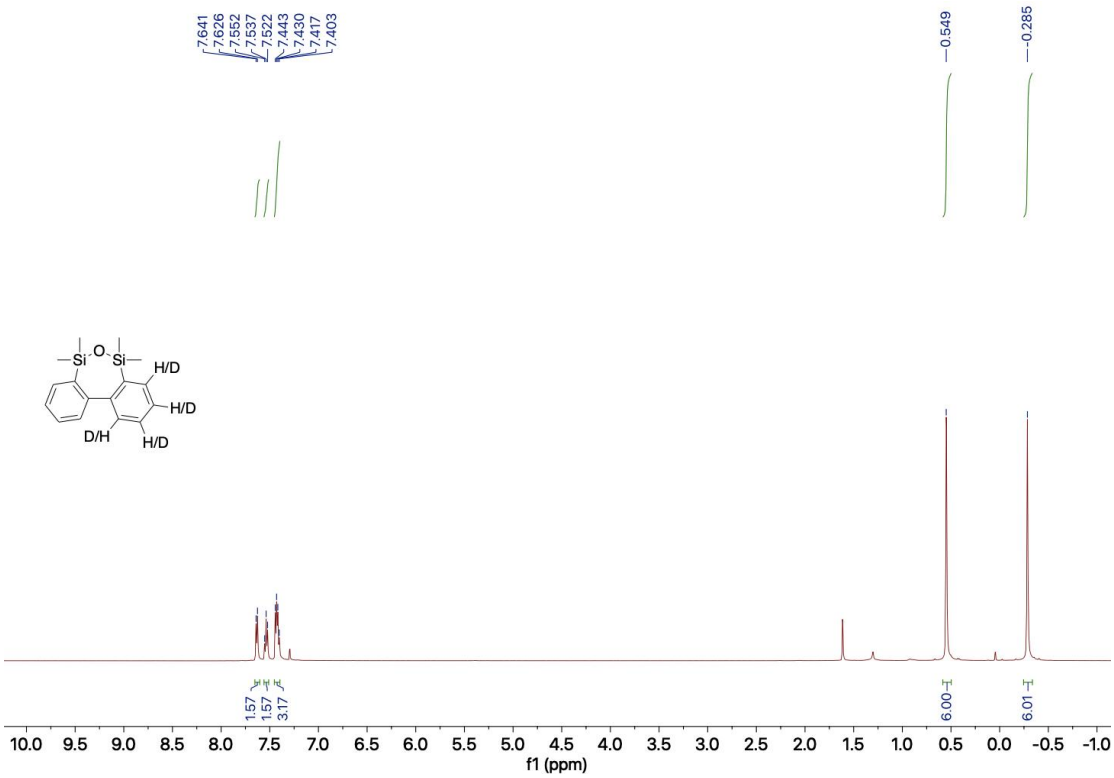
To a 25 mL Schlenk tube were added palladacycle **Int-A** (0.1 mmol), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (1.5 equiv), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), K_3PO_4 (3 equiv), and DMF (1 mL). Then the tube was charged with nitrogen, and was stirred at 100 °C for 2 h until complete consumption of starting material as monitored by TLC analysis. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography (eluent: petroleum ether/EtOAc = 400:1) to give the product **3b** in 21% yield. Without $Pd(OAc)_2$, the product **3b** was not detected.

6.5 Competition experiment



To a 25 mL Schlenk tube was added 2-iodo-1,1'-biphenyl **1b** (0.1 mmol), 2-iodo-1,1'-biphenyl-D_5 **1b-D_5** (0.1 mmol), 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), K_3PO_4 (3 equiv), and DMF (2 mL). Then the tube was evacuated briefly under high vacuum and charged with nitrogen, and was stirred at 100 °C for 20 min. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate, dried over Na_2SO_4. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography to afford the products **3b** and **3b-D_4** in 26% yield.

The KIE value for this reaction was estimated to be K_H/K_D = 1.33 by ^1H NMR spectra.



6.6 Parallel experiment

Parallel reactions of 2-iodo-1,1'-biphenyl **1b** (0.1 mmol) and 2-iodo-1,1'-biphenyl-D_5 **1b-D_5** (0.1 mmol) with 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (0.15 mmol), respectively, were carried out under the standard conditions and stopped at different periods of times. The corresponding yields of **3b** and **3b-D_4** were obtained. As a result, the slope values of two graphs were 0.06 mmol/h and 0.042 mmol/h, thus the KIE value was 1.43.

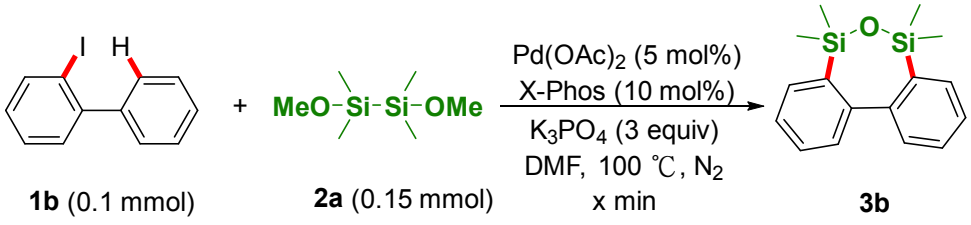
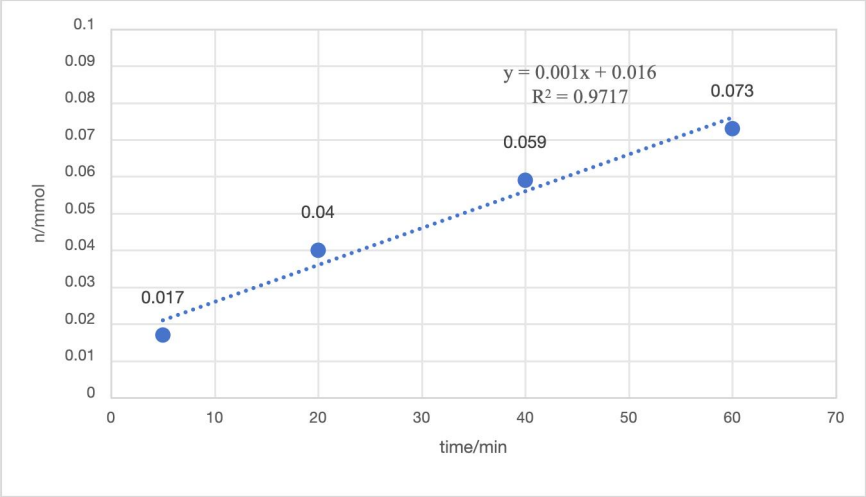


Figure S2. Determination of a reaction rate when **1b** was used as a substrate.

Entry	Time/min	NMR Yield/%	n/mmol
1	5	17	0.017
2	20	40	0.040
3	40	59	0.059
4	60	73	0.073



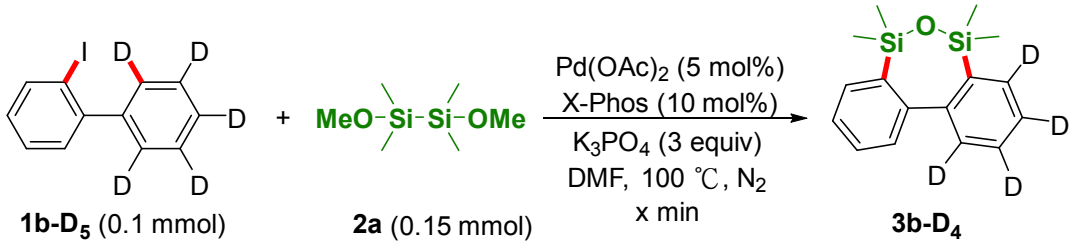
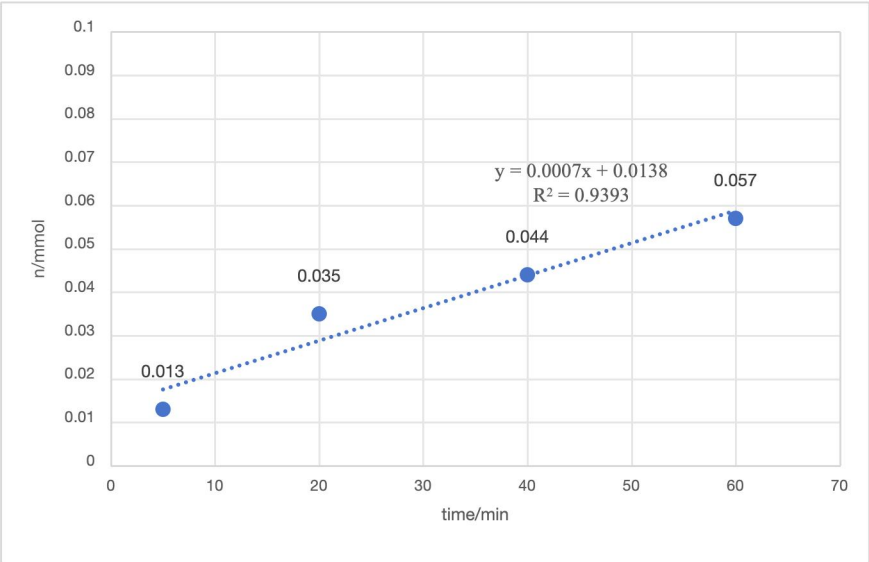
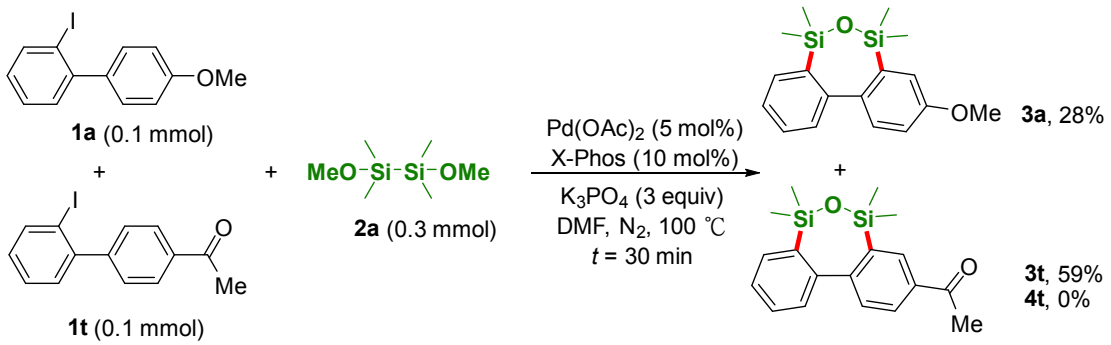


Figure S3. Determination of a reaction rate when **1b-D$_5$** was used as a substrate

Entry	Time/min	NMR Yield/%	n/mmol
1	5	13	0.013
2	20	35	0.035
3	40	44	0.044
4	60	57	0.057



6.7 Intermolecular competition experiment



To a 25 mL Schlenk tube were added 2-iodo-4'-methoxy-1,1'-biphenyl **1a** (0.1 mmol), 1-(2'-iodo-[1,1'-biphenyl]-4-yl)ethan-1-one **1t** (0.1 mmol) 1,2-dimethoxy-1,1,2,2-tetramethyldisilane **2a** (0.3 mmol), $Pd(OAc)_2$ (5 mol%), X-Phos (10 mol%), K_3PO_4 (3 equiv), and DMF (2 mL). Then the tube was charged with nitrogen, and was stirred at 100 °C for 30 min. After the reaction was finished, the resulting suspension was filtered and washed with ethyl acetate. The combined filtrates were concentrated under reduced pressure and purified on a silicagel column chromatography to give the products **3a** in 28% yield and **3t** in 59% yield.

7 Crystal Culture Procedure of Product 3j and 4G

To a round-bottom flask (25 mL) was added **3j** (10 mg) or **4G** (10 mg). Dichloromethane (1 mL) was added slowly to make it dissolve completely. Then petroleum ether (5 mL) was added. Finally, the round-bottom flask was sealed with a rubber stopper, and connected the air with a syringe needle. Putting the flask in a dry and ventilated place to make the organic solvent volatilize slowly. After a few days, the crystal of **3j** and **4G** were separated out.

8 The X-ray Single-Crystal Diffraction Analysis of 3j and 4G

8.1 The X-ray single-crystal diffraction analysis of 3j

A suitable crystal of **3j** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the olex2.solve3 structure solution program using Charge Flipping and refined with the ShelXL4 refinement package using Least Squares minimisation.

Crystallographic data for **3j** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 2386122, respectively.

Table S2. Crystallographic data details of **3j**

CCDC deposition No.	2386122
Empirical formula	$C_{19}H_{25}NO_2Si_2$
Formula weight	355.58
Temperature/K	300
Crystal system	monoclinic
Space group	P21/c
a/Å	12.7549(3)
b/Å	7.7430(10)
c/Å	21.0221(4)
α/°	90
β/°	106.561(2)
γ/°	90
Volume/Å^3	1990.04(7)
Z	4
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	1.698
F(000)	760.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	CuKα (λ = 1.54184)
The range for data collection/°	7.23 to 133.134
Index ranges	-13 ≤ h ≤ 15, -9 ≤ k ≤ 8, -24≤ l ≤ 23
Reflections collected	12375
Independent reflections	3493 [R_{int} = 0.0292, R_{sigma} = 0.0258]
Data/restraints/parameters	3493/151/302
Goodness-of-fit on F^2	1.025

Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1065
Final R indexes [all data]	R_1 = 0.0449, wR_2 = 0.1126
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27

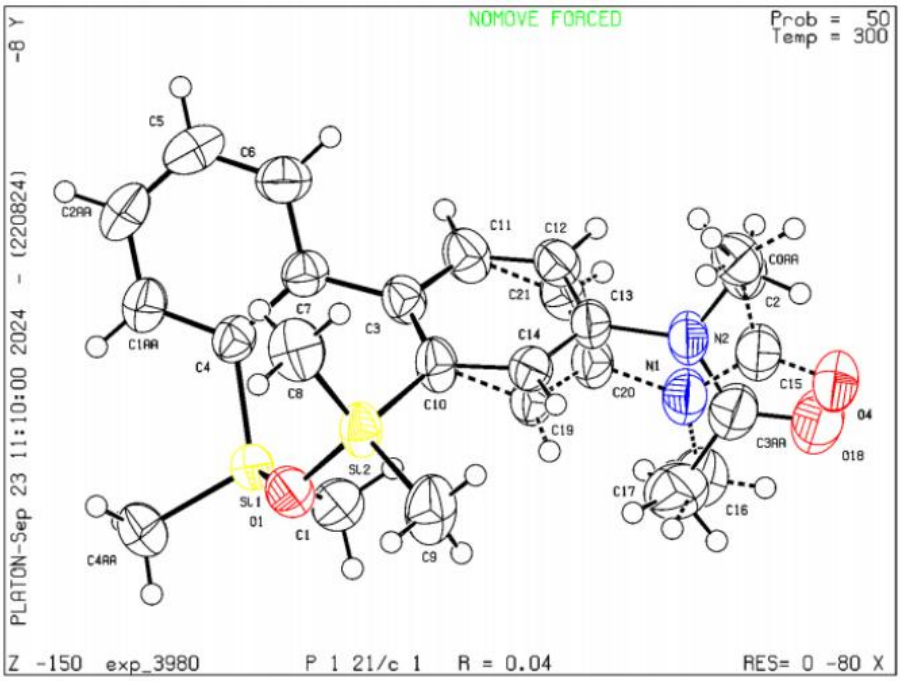


Figure S6 X-ray of 3j

8.2 The X-ray single-crystal diffraction analysis of 4G

A suitable crystal of **4G** was selected and measured on a SuperNova, Dual, Cu at zero, EosS2 diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2, the structure was solved with the olex2.solve3 structure solution program using Charge Flipping and refined with the ShelXL4 refinement package using Least Squares minimisation.

Crystallographic data for **4G** has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 2378238, respectively.

Table S3. Crystallographic data details of **4G**

CCDC deposition No.	2378238
Empirical formula	$C_{16}H_{12}F_3NSi$
Formula weight	303.36
Temperature/K	293

Crystal system	Orthorhombic
Space group	Pnma
a/Å	11.1316(2)
b/Å	7.2514(2)
c/Å	18.4272(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1487.44(6)
Z	4
ρ_{calc}g/cm^3	1.355
μ/mm^{-1}	1.636
F(000)	624.0
Crystal size/mm^3	0.3 × 0.2 × 0.1
Radiation	CuKα (λ = 1.54184)
The range for data collection/°	9.282 to 133.088
Index ranges	-8 ≤ h ≤ 13, -8 ≤ k ≤ 8, -11≤ l ≤ 21
Reflections collected	3197
Independent reflections	1422 [R_{int} = 0.0113, R_{sigma} = 0.0129]
Data/restraints/parameters	1422/36/134
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1117
Final R indexes [all data]	R_1 = 0.0416, wR_2 = 0.1132
Largest diff. peak/hole / e Å^{-3}	0.24/-0.23

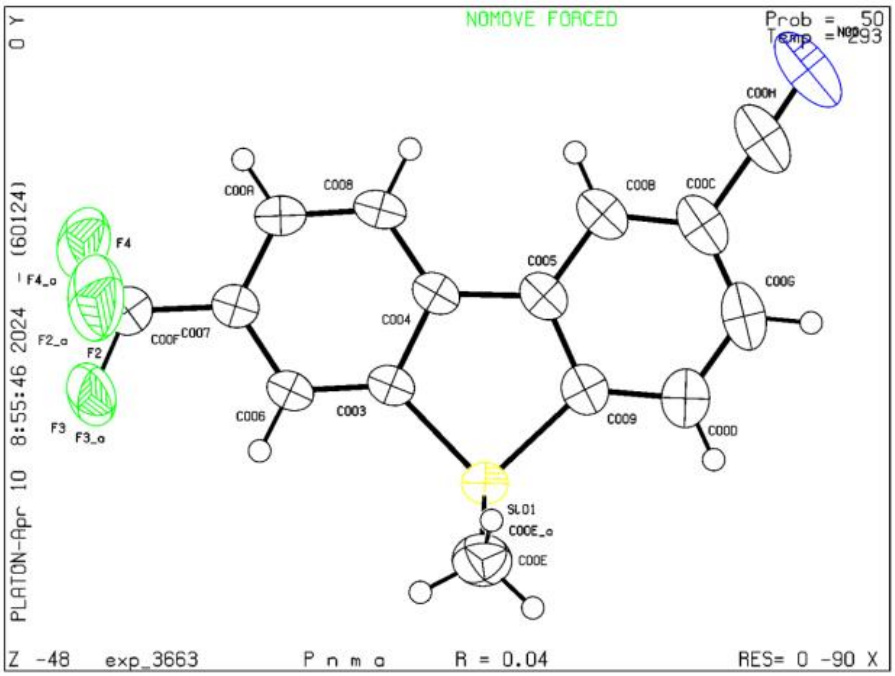
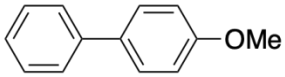
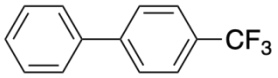


Figure S7 X-ray of 4G

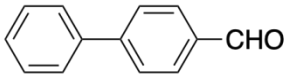
9 Characterization Data



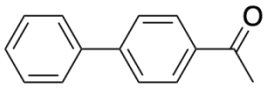
4-methoxy-1,1'-biphenyl (3b'): known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.62 – 7.55 (m, 4H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.90 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3.



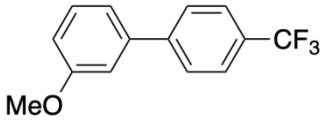
4-(trifluoromethyl)-1,1'-biphenyl (3q'): known compound.[4] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (s, 4H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 144.7, 139.8, 129.0, 128.2, 127.4, 127.3, 125.7 (q, *J* = 3.4 Hz). **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.4.



[1,1'-biphenyl]-4-carbaldehyde (3s'): known compound.[5] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.08 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 191.8, 147.0, 139.5, 135.0, 130.1, 128.9, 128.4, 127.5, 127.2.

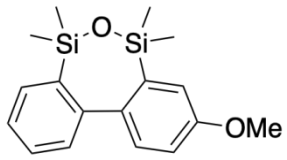


1-([1,1'-biphenyl]-4-yl)ethan-1-one (3t'): known compound.[6] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 2.68 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 197.7, 145.6, 139.7, 135.7, 128.9, 128.8, 128.2, 127.2, 127.1, 26.6.

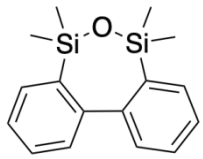


3-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3y'): known compound.[7] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.73 (s, 4H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.16 (s, 1H), 7.01 - 6.99 (m, 1H), 3.92 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 160.0, 144.6, 141.22, 129.6, 128.6 (q, *J* = 31.0 Hz), 127.5, 125.7 (q, *J* = 3.5 Hz), 124.3 (q, *J* = 270.0 Hz), 119.7, 113.4, 113.1, 55.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ =

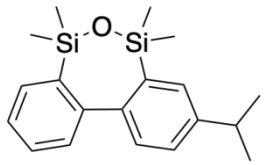
-62.4.



3-methoxy-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3a): Compound **3a** was obtained in 97% yield according to the general procedure (2-iodo-4'-methoxy-1,1'-biphenyl was used, petroleum ether/ethyl acetate, 200:1, 61.2 mg, 0.2 mmol scale), or compound **3a** was obtained in 95% yield following the general procedure (2-iodo-4-methoxy-1,1'-biphenyl was used, petroleum ether/ethyl acetate, 200:1, 59.9 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (td, *J* = 1.5, 7.5 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.20 (d, *J* = 2.5 Hz, 1H), 7.08 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.93 (s, 3H), 0.57 (s, 6H), -0.23 (d, *J* = 16.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.1, 149.1, 141.8, 139.5, 137.9, 133.0, 132.0, 130.5, 130.0, 126.1, 119.0, 114.5, 55.2, 0.2, 0.1, -0.66, -0.70. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_2Si_2^+$ 315.1231; Found 315.1224.

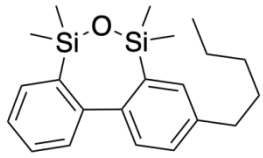


5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3b): Compound **3b** was obtained in 93% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 52.8 mg, 0.2 mmol scale), known compound.[1] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.48 – 7.42 (m, 4H), 0.58 (s, 6H), -0.25 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.4, 138.0, 133.0, 130.6, 130.0, 126.5, 0.1, -0.7.

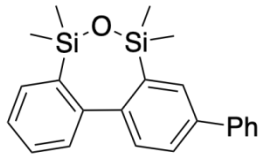


4-isopropyl-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3c): Compound **3c** was obtained in 91% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 59.3 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 7.0 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.45 (t,

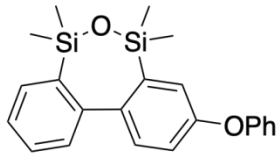
J = 7.5Hz, 2H), 7.42 – 7.36 (m, 3H), 3.03 (p, *J* = 7.0 Hz, 1H), 1.36 (d, *J* = 7.0 Hz, 6H), 0.56 (d, *J* = 7.0 Hz, 6H), -0.28 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.5, 146.9, 146.8, 138.0, 137.7, 133.0, 131.3, 130.6, 130.5, 130.0, 127.9, 126.2, 33.9, 24.1, 0.2, 0.1, -0.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}OSi_2^+$ 327.1595; Found 327.1590.



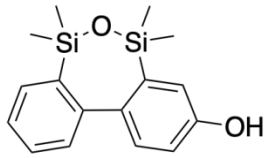
5,5,7,7-tetramethyl-3-pentyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3d): Compound **3d** was obtained in 92% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 65.2 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.69 (d, *J* = 7.0 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.51 – 7.44 (m, 3H), 7.42 – 7.40 (m, 2H), 2.80 – 2.74 (m, 2H), 1.81 – 1.75 (m, 2H), 1.50 – 1.44 (m, 4H), 1.04 – 1.01 (m, 3H), 0.61 (s, 6H), -0.22 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.5, 146.8, 140.9, 138.0, 137.7, 133.1, 133.0, 130.6, 130.5, 130.02, 129.98, 126.2, 35.7, 31.5, 31.2, 22.5, 14.1, 0.2, 0.1, -0.6, -0.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{31}OSi_2^+$ 355.1908; Found 355.1902.



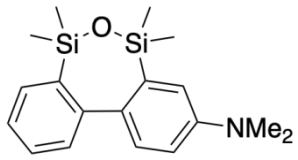
5,5,7,7-tetramethyl-3-phenyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3e): Compound **3e** was obtained in 93% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 67.0 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 2.0 Hz, 1H), 7.82 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.78 – 7.74 (m, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.62 – 7.52 (m, 5H), 7.49 – 7.44 (m, 2H), 0.66 (s, 3H), 0.62 (s, 3H), -0.18 (d, *J* = 8.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.0, 148.5, 140.9, 139.0, 138.5, 138.0, 133.1, 131.8, 131.1, 130.6, 130.1, 128.8, 128.7, 127.3, 127.1, 126.5, 0.3, 0.2, -0.57, -0.64. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}OSi_2^+$ 361.1438; Found 361.1430.



5,5,7,7-tetramethyl-3-phenoxy-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3f): Compound **3f** was obtained in 84% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 63.2 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.66 – 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 8.5 Hz, 1H), 7.46 – 7.39 (m, 5H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.09 (m, 3H), 0.57 (s, 3H), 0.49 (s, 3H), -0.19 (s, 3H), -0.26 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 157.2, 155.7, 148.8, 144.5, 140.2, 138.0, 133.1, 132.2, 130.5, 130.1, 129.8, 126.4, 123.5, 123.2, 120.1, 118.6, 0.2, 0.0, -0.7, -0.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}O_2Si_2^+$ 377.1388; Found 377.1380.

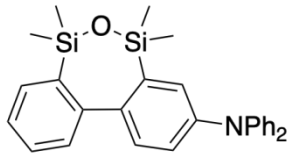


5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepin-3-ol (3g): Compound **3g** was obtained in 95% yield according to the general procedure (petroleum ether/ethyl acetate, 20:1, 57.1 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.18 (s, 1H), 7.09 (dd, *J* = 2.5, 8.0 Hz, 1H), 5.34 (s, 1H), 0.62 (d, *J* = 11.5 Hz, 6H), -0.15 (s, 3H), -0.19 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 154.2, 149.0, 142.0, 139.8, 137.8, 133.0, 132.2, 130.5, 130.0, 126.1, 119.7, 116.8, 0.1, 0.0, -0.68, -0.70. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_2Si_2^+$ 301.1075; Found 301.1068.

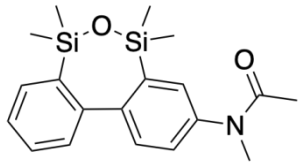


***N,N*,5,5,7,7-hexamethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepin-3-amine (3h)**: Compound **3h** was obtained in 77% yield according to the general procedure (petroleum ether/ethyl acetate, 100:1, 50.4 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.60 (d, *J* = 8.5 Hz, 1H), 7.50 (td, *J* = 1.5, 7.5 Hz, 1H),

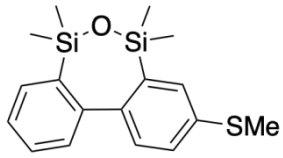
7.42 – 7.40 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.32 (m, 2H), 6.99 (d, *J* = 2.5 Hz, 1H), 6.91 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.06 (s, 6H), 0.54 (s, 6H), -0.22 (s, 3H), -0.27 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.7, 148.8, 138.4, 137.8, 137.5, 133.0, 131.6, 130.4, 130.0, 125.6, 116.9, 114.0, 40.5, 0.3, 0.2, -0.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{26}NOSi_2^+$ 328.1547; Found 328.1545.



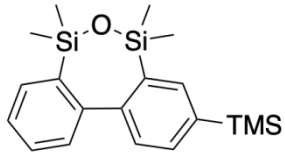
5,5,7,7-tetramethyl-*N*,*N*-diphenyl-5,7-dihydrodibenzo[*c*,*e*][1,2,7]oxadisilepin-3-amine (3i): Compound **3i** was obtained in 73% yield according to the general procedure (petroleum ether/ethyl acetate, 100:1, 65.8 mg, 0.2 mmol scale) as white solid (114.9 - 117.4 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 8.0 Hz, 1H), 7.53 (td, *J* = 1.5, 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.40 (td, *J* = 1.0, 7.5 Hz, 1H), 7.37 (d, *J* = 2.5 Hz, 1H), 7.35 – 7.31 (m, 5H), 7.24 – 7.18 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 2H), 0.57 (s, 3H), 0.31 (s, 3H), -0.13 (s, 3H), -0.27 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.2, 147.6, 146.2, 143.4, 138.9, 137.9, 133.0, 131.7, 130.3, 130.0, 129.2, 128.2, 126.2, 125.1, 124.2, 122.9, 0.2, 0.1, -0.7, -0.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{30}NOSi_2^+$ 452.1860; Found 452.1852.



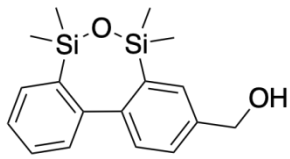
***N*-methyl-*N*-(5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c*,*e*][1,2,7]oxadisilepin-3-yl) acetamide (3j):** Compound **3j** was obtained in 84% yield according to the general procedure (petroleum ether/ethyl acetate, 10:1, 59.7 mg, 0.2 mmol scale) as white solid (139.3 - 143.0 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 3.36 (s, 3H), 1.96 (s, 3H), 0.54 (d, *J* = 10.5 Hz, 6H), -0.28 (d, *J* = 3.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 170.5, 148.9, 148.2, 143.0, 140.3, 138.0, 133.1, 132.0, 131.3, 130.4, 130.2, 128.3, 126.9, 37.2, 22.4, 0.13, 0.10, -0.7, -0.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{26}NO_2Si_2^+$ 356.1497; Found 354.1490.



5,5,7,7-tetramethyl-3-(methylthio)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3k): Compound **3k** was obtained in 81% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 53.5 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.44 – 7.37 (m, 4H), 2.59 (s, 3H), 0.56 (s, 6H), -0.22 (s, 3H), -0.27 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.8, 146.2, 138.7, 137.9, 136.7, 133.1, 131.1, 130.5, 130.1, 127.8, 126.4, 15.8, 0.3, 0.1, -0.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}OSSi_2^+$ 331.1003; Found 331.0997.

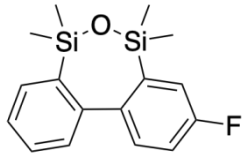


5,5,7,7-tetramethyl-3-(trimethylsilyl)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3l): Compound **3l** was obtained in 61% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 43.5 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.79 (s, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.46 – 7.41 (m, 3H), 0.57 (d, *J* = 8.0 Hz, 6H), 0.38 (s, 9H), -0.27 (d, *J* = 5.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.8, 149.4, 138.01, 137.98, 137.9, 136.9, 135.1, 133.0, 130.6, 130.0, 129.7, 126.5, 0.23, 0.17, -0.6, -0.7, -1.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{29}OSi_3^+$ 357.1521; Found 357.1513.

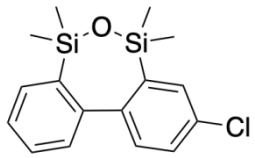


(5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepin-3-yl)methanol (3m): Compound **3m** was obtained in 76% yield according to the general procedure (petroleum ether/ethyl acetate, 20:1, 47.7 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.66 (d, *J* = 7.0 Hz, 1H), 7.63 (s, 1H), 7.60 – 7.54 (m, 2H), 7.49 –7.43 (m, 3H), 4.84 (s, 2H), 1.91 (s, 1H), 0.58 (d, *J* = 8.0 Hz, 6H), -0.25 (d,

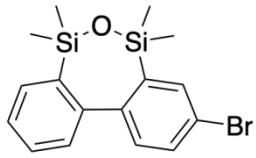
J = 6.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 149.1, 149.0, 138.7, 138.4, 138.0, 133.0, 131.7, 130.9, 130.6, 130.1, 128.8, 126.5, 65.2, 0.3, 0.1, -0.6, -0.7. **HRMS** (ESI-TOF) m/z: $[M+H-H_2O]^+$ Calcd for $C_{17}H_{21}OSi_2^+$ 297.1125; Found 297.1121.



3-fluoro-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3n): Compound **3n** was obtained in 68% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 41.1 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 7.5 Hz, 1H), 7.55 (td, *J* = 1.0, 7.5 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.33 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.22 (td, *J* = 2.5, 8.5 Hz, 1H), 0.57 (d, *J* = 5.5 Hz, 6H), -0.22 (s, 3H), -0.26 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 161.8 (d, *J* = 247.5 Hz), 148.4, 145.3 (d, *J* = 3.3 Hz), 140.8 (d, *J* = 3.9 Hz), 138.0, 133.1, 132.5 (d, *J* = 6.9 Hz), 130.6, 130.1, 126.6, 119.4 (d, *J* = 18.9 Hz), 116.7 (d, *J* = 21.0 Hz), 0.2, -0.1, -0.7, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -116.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}FOSi_2^+$ 303.1031; Found 303.1028.

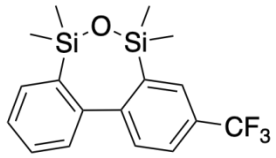


4-chloro-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3o): Compound **3o** was obtained in 73% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 46.4 mg, 0.2 mmol scale), known compound.[2] **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.65 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 2.0 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.51 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 0.57 (s, 6H), -0.21 (s, 3H), -0.27 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.2, 147.7, 140.5, 137.9, 133.2, 133.1, 132.7, 132.1, 130.6, 130.2, 129.9, 126.8, 0.3, -0.1, -0.70, -0.74.

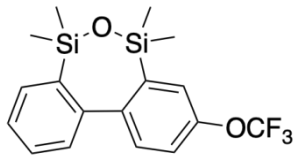


3-bromo-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3p):

Compound **3p** was obtainedin 28% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 20.3 mg, 0.2 mmol scale) as white solid (81.0 - 85.1 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 2.0 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.54 (td, *J* = 1.5, 7.5 Hz, 1H), 7.43 (td, *J* = 1.5, 7.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 0.55 (d, *J* = 2.5 Hz, 6H), -0.22 (s, 3H), -0.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.2, 148.1, 141.0, 137.9, 135.6, 133.2, 132.9, 132.4, 130.5, 130.2, 126.8, 121.7, 0.3, -0.1, -0.71, -0.73. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}BrOSi_2^+$ 363.0231; Found 363.0224.

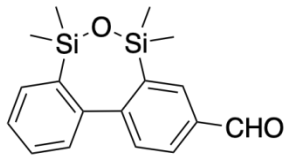


5,5,7,7-tetramethyl-3-(trifluoromethyl)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3q): Compound **3q** was obtained in 85% yield according to the general procedure (2-iodo-4'-(trifluoromethyl)-1,1'-biphenyl was used, petroleum ether/ethyl acetate, 400:1, 59.9 mg, 0.2 mmol scale), or compound **3q** was obtained in 74% yield according to the general procedure (2-iodo-4-(trifluoromethyl)-1,1'-biphenyl was used, petroleum ether/ethyl acetate, 400:1, 52.1 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.90 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 0.63 (d, *J* = 13.0 Hz, 6H), -0.21 (d, *J* = 2.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.1, 148.0, 139.3, 138.1, 133.2, 130.8, 130.7, 130.2, 129.5 (q, *J* = 3.6 Hz), 128.5 (q, *J* = 31.8 Hz), 127.2, 126.7 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 270.6 Hz), 0.3, -0.1, -0.7, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}F_3OSi_2^+$ 353.0999; Found 353.0995.

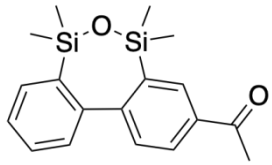


5,5,7,7-tetramethyl-3-(trifluoromethoxy)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3r): Compound **3r** was obtained in 67% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 49.3 mg, 0.2 mmol scale) as colorless

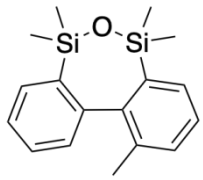
oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5, 1H), 7.44 – 7.34 (m, 5H), 0.53 (d, *J* = 2.5 Hz, 6H), -0.29 (d, *J* = 7.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.05, 147.99, 140.7, 138.0, 133.2, 132.2, 130.6, 130.2, 126.9, 125.1, 122.0, 120.5 (q, *J* = 255.5 Hz), 0.2, -0.2, -0.7, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -57.6. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}F_3O_2Si_2^+$ 369.0948; Found 369.0945.



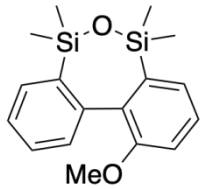
5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine-3-carbaldehyde (3s): Compound **3s** was obtained in 82% yield according to the general procedure (petroleum ether/ethyl acetate, 50:1, 51.1 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.15 (s, 1H), 8.13 (s, 1H), 8.04 (dd, *J* = 1.5, 7.5 Hz, 1H), 7.67 (d, *J* = 7.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.44 (m, 2H), 0.64 (s, 3H), 0.57 (s, 3H), -0.26 (d, *J* = 2.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 192.3, 155.8, 148.1, 139.3, 138.0, 134.7, 134.0, 133.2, 131.3, 131.0, 130.6, 130.2, 127.3, 0.3, -0.1, -0.7, -0.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{21}O_2Si_2^+$ 313.1075; Found 313.1071.



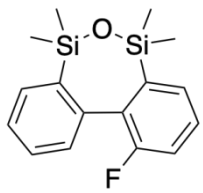
1-(5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepin-3-yl)ethan-1-one (3t): Compound **3t** was obtained in 89% yield according to the general procedure (petroleum ether/ethyl acetate, 50:1, 58.0 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.22 (d, *J* = 2.0 Hz, 1H), 8.11 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.45 (td, *J* = 1.5, 7.5 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 2.70 (s, 3H), 0.62 (s, 3H), 0.56 (s, 3H), -0.27 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 198.1, 154.3, 148.2, 138.7, 138.0, 134.7, 133.2, 132.9, 130.8, 130.6, 130.1, 129.9, 127.2, 26.6, 0.3, 0.0, -0.69, -0.74. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}O_2Si_2^+$ 327.1231; Found 327.1226



1,5,5,7,7-pentamethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3u): Compound **3u** was obtained in 55% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 32.8 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.73 (d, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 2.26 (s, 3H), 0.58 (s, 3H), 0.56 (s, 3H), -0.28 (s, 3H), -0.38 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.0, 147.3, 138.6, 138.1, 135.9, 133.2, 132.3, 131.3, 130.6, 129.0, 126.7, 126.4, 21.4, -0.1, -0.3, -0.4, -0.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}OSi_2^+$ 299.1282; Found 299.1277.

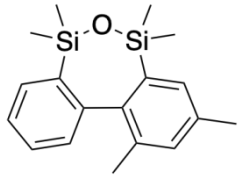


1-methoxy-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3v): Compound **3v** was obtained in 62% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 38.9 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.74 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 4.0 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 0.60 (s, 3H), 0.58 (s, 3H), -0.19 (s, 3H), -0.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 156.5, 143.9, 140.4, 138.1, 137.2, 133.3, 132.4, 128.7, 128.3, 126.5, 125.4, 113.4, 55.8, -0.1, -0.2, -0.4, -0.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}O_2Si_2^+$ 315.1231; Found 315.1225.

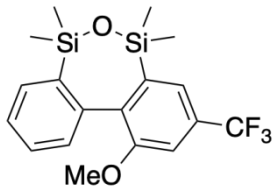


1-fluoro-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3w): Compound **3w** was obtained in 87% yield according to the general procedure

(petroleum ether/ethyl acetate, 400:1, 52.6 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.71 (d, *J* = 7.5 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.48 – 7.41 (m, 3H), 7.31 – 7.26 (m, 1H), 0.56 (d, *J* = 8.0 Hz, 6H), -0.22 (s, 3H), -0.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 159.7 (d, *J* = 247.4 Hz), 141.8, 141.3, 138.6, 135.4 (d, *J* = 11.3 Hz), 133.5, 131.8 (d, *J* = 3.9 Hz), 129.2, 128.8, 128.7 (d, *J* = 2.5 Hz), 127.1, 117.6 (d, *J* = 23.9 Hz), 0.0, -0.1, -0.4, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -114.9. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}FOSi_2^+$ 303.1031; Found 303.1028.

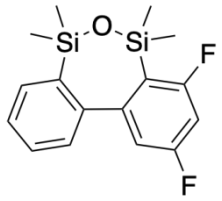


1,3,5,5,7,7-hexamethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3x): Compound **3x** was obtained in 72% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 44.9 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.25 (s, 1H), 2.45 (s, 3H), 2.19 (s, 3H), 0.53 (d, *J* = 12.0 Hz, 6H), -0.30 (s, 3H), -0.42 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 147.4, 145.2, 138.5, 138.3, 136.0, 135.8, 133.13, 133.07, 131.5, 131.3, 129.0, 126.2, 21.3, 21.2, 0.0, -0.2, -0.4, -0.8. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}OSi_2^+$ 313.1438; Found 313.1432.

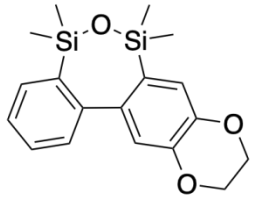


1-methoxy-5,5,7,7-tetramethyl-3-(trifluoromethyl)-5,7-dihydrodibenzo[*c,e*][1,2,7] oxadisilepine (3y): Compound **3y** was obtained in 91% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 69.5 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 7.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.45 – 7.40 (m, 2H), 7.30 (s, 1H), 3.82 (s, 3H), 0.53 (s, 6H), -0.26 (s, 3H), -0.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 156.7, 142.7, 141.7, 140.9, 138.2, 133.4, 132.2,

130.1 (q, J = 31.6 Hz), 128.9, 127.1, 124.1 (q, J = 271.0 Hz), 121.6 (q, J = 3.8 Hz), 109.6 (q, J = 3.5 Hz), 56.0, 0.1, -0.4, -0.5, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}F_3O_2Si_2^+$ 383.1105; Found 383.1096.

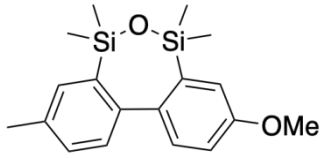


2,4-difluoro-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3z): Compound **3z** was obtained in 69% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 44.2 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.59 (d, J = 7.0 Hz, 1H), 7.53 (t, J = 7.0 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.80 (td, J = 2.0, 9.0 Hz, 1H), 0.58 – 0.53 (m, 6H), -0.17 (s, 3H), -0.36 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 166.3 (dd, J = 242.5, 12.1 Hz), 163.7 (dd, J = 249.3, 14.5 Hz), 153.3 (dd, J = 12.3, 8.9 Hz), 147.5, 138.0, 132.9, 130.5, 130.2, 127.3, 120.2 (dd, J = 29.3, 3.6 Hz), 114.5 (dd, J = 20.0, 3.0 Hz), 102.2 (dd, J = 32.3, 23.3 Hz), 2.8 (d, J = 12.4 Hz), 1.1, 0.2, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -94.7, -108.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}F_2OSi_2^+$ 321.0937; Found 321.0931.

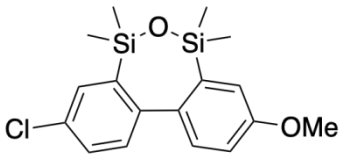


5,5,7,7-tetramethyl-5,7,10,11-tetrahydro-[1,4]dioxino[2',3':4,5]benzo[1,2-*c*]benzo[*e*][1,2,7]oxadisilepine (3A): Compound **3A** was obtained in 81% yield according to the general procedure (petroleum ether/ethyl acetate, 100:1, 55.4 mg, 0.2 mmol scale) as white solid (108.2 - 110.7 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.63 (d, J = 7.0 Hz, 1H), 7.52 (td, J = 1.5, 8.0 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.15 (s, 1H), 7.01 (s, 1H), 4.38 (s, 4H), 0.56 (s, 3H), 0.52 (s, 3H), -0.17 (s, 3H), -0.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.7, 144.6, 143.2, 142.3, 137.8, 133.0, 131.0, 130.4, 130.0, 126.2, 122.0, 119.6, 64.6, 64.4, 0.3, 0.2, -0.6, -0.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd

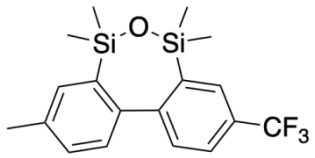
for $C_{18}H_{23}O_3Si_2^+$ 343.1180; Found 343.1176.



2-methoxy-5,5,7,7,9-pentamethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3B): Compound **3B** was obtained in 99% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 64.9 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.44 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.19 (d, *J* = 3.0 Hz, 1H), 7.07 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.94 (s, 3H), 2.48 (s, 3H), 0.57 (s, 6H), -0.22 (d, *J* = 4.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 157.9, 146.2, 141.8, 139.4, 137.7, 135.4, 133.7, 131.9, 130.7, 130.5, 118.9, 114.4, 55.1, 21.2, 0.24, 0.16, -0.6, -0.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}O_2Si_2^+$ 329.1388; Found 329.1382.

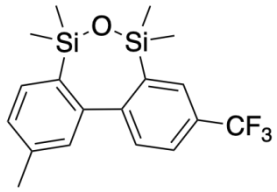


3-chloro-9-methoxy-5,5,7,7-tetramethyl-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3C): Compound **3C** was obtained in 80% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 55.7 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.53 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.33 (dd, *J* = 2.0, 8.0 Hz, 2H), 7.15 (d, *J* = 2.5 Hz, 1H), 7.05 (dd, *J* = 3.0, 8.5 Hz, 1H), 3.91 (s, 3H), 0.54 (s, 6H), -0.23 (s, 3H), -0.26 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 158.3, 147.4, 140.5, 140.4, 139.5, 132.70, 132.67, 132.1, 132.0, 129.9, 119.2, 114.5, 55.2, 0.3, 0.0, -0.7. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}ClO_2Si_2^+$ 349.0841; Found 349.0835.

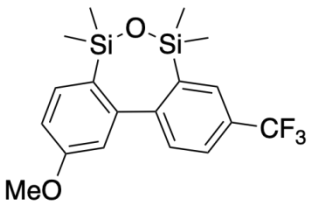


3,5,5,7,7-pentamethyl-9-(trifluoromethyl)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3D): Compound **3D** was obtained in 86% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 62.9 mg, 0.2 mmol scale) as colorless

oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.85 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 2.51 (s, 3H), 0.60 (d, *J* = 12.0 Hz, 6H), -0.23 (d, *J* = 9.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.1, 145.2, 139.2, 137.9, 136.8, 134.0, 130.9, 130.8, 130.7, 129.5 (q, *J* = 3.5 Hz), 128.2 (q, *J* = 32.0 Hz), 126.7 (q, *J* = 3.5 Hz), 124.5 (q, *J* = 270.8 Hz), 21.3, 0.4, 0.0, -0.7, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}F_3OSi_2^+$ 367.1156; Found 367.1152.

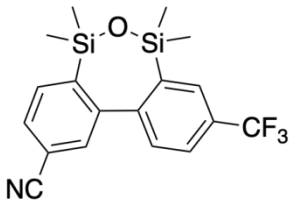


2,5,5,7,7-pentamethyl-9-(trifluoromethyl)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3E): Compound **3E** was obtained in 85% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 62.2 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.83 (s, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.0 Hz, 2H), 7.28 (d, *J* = 7.5Hz, 1H), 7.24 (s, 1H), 2.47 (s, 3H), 0.58 (s, 3H), 0.54 (s, 3H), -0.27 (d, *J* = 10.0 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 153.2, 148.1, 140.2, 139.3, 134.7, 133.4, 131.6, 130.8, 129.5 (q, *J* = 3.6 Hz), 128.4 (q, *J* = 31.9 Hz), 128.0, 126.7 (q, *J* = 3.8 Hz), 124.5 (q, *J* = 270.6 Hz), 21.5, 0.4, 0.0, -0.7, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}F_3OSi_2^+$ 367.1156; Found 367.1149.

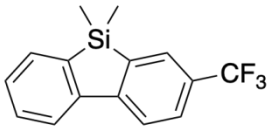


2-methoxy-5,5,7,7-tetramethyl-9-(trifluoromethyl)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine (3F): Compound **3F** was obtained in 93% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 71.1 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 4.0, 8.5 Hz, 2H), 7.01 (dd, *J* = 2.5, 8.0 Hz, 1H), 6.97 (d, *J* = 2.5 Hz, 1H), 3.93 (s, 3H), 0.59 (s, 3H), 0.54 (s, 3H), -0.22 (s, 3H), -0.29 (s, 3H). **^{13}C NMR** (125

MHz, $CDCl_3$) δ = 161.0, 152.8, 149.8, 139.3, 135.0, 130.6, 129.6, 129.5 (q, *J* = 3.8 Hz), 128.6 (q, *J* = 31.8 Hz), 126.7 (q, *J* = 3.5 Hz), 124.4 (q, *J* = 270.8 Hz), 116.7, 112.4, 55.2, 0.5, 0.0, -0.6, -0.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}F_3O_2Si_2^+$ 383.1105; Found 383.1097.

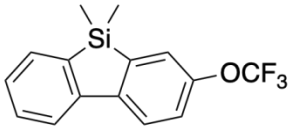


5,5,7,7-tetramethyl-9-(trifluoromethyl)-5,7-dihydrodibenzo[*c,e*][1,2,7]oxadisilepine-2-carbonitrile (3G): Compound **3G** was obtained in 79% yield according to the general procedure (petroleum ether/ethyl acetate, 100:1, 59.6 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.85 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.71 (m, 2H), 7.68 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 0.59 (d, *J* = 10.5 Hz, 6H), -0.25 (d, *J* = 4.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 150.6, 149.0, 144.3, 139.4, 133.9, 133.4, 130.9, 130.2, 129.8 (q, *J* = 3.5 Hz), 129.5 (q, *J* = 32.1 Hz), 127.1 (q, *J* = 3.4 Hz), 124.1 (q, *J* = 270.8 Hz), 118.4, 114.0, 0.2, 0.0, -0.8, -0.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.5. HRMS did not ionize using ESI.

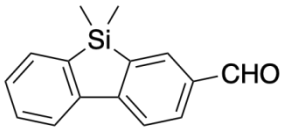


5,5-dimethyl-3-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole (4q): Compound **4q** was obtained in 78% yield according to the general procedure (2-iodo-4'-(trifluoromethyl)-1,1'-biphenyl was used, petroleum ether/ethyl acetate, 400:1, 43.4 mg, 0.2 mmol scale), or compound **4q** was obtained in 67% yield according to the general procedure (2-iodo-4-(trifluoromethyl)-1,1'-biphenyl was used, petroleum ether/ethyl acetate, 400:1, 37.3 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.96 – 7.88 (m, 3H), 7.74 – 7.70 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 0.50 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.1, 146.3, 139.8, 139.4, 132.9, 130.4, 129.3 (q, *J* = 3.8 Hz), 129.0 (q, *J* = 31.5 Hz), 128.4, 127.3 (q, *J* = 3.8 Hz), 124.6 (q, *J* = 270.5 Hz), 121.6, 120.7, -3.5. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.2. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{14}F_3Si^+$

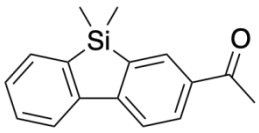
279.0811; Found 279.0806.



5,5-dimethyl-3-(trifluoromethoxy)-5*H*-dibenzo[*b,d*]silole (4r): Compound **4r** was obtained in 60% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 35.3 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.29 (m, 1H), 0.49 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 148.8, 146.5, 146.3, 141.5, 138.8, 132.8, 130.4, 127.6, 124.8, 122.7, 121.9, 121.0, 120.6 (q, *J* = 255.3 Hz), -3.4. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -57.6. HRMS did not ionize using ESI.

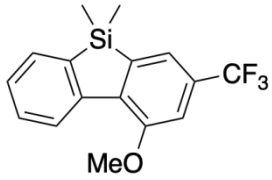


5,5-dimethyl-5*H*-dibenzo[*b,d*]silole-3-carbaldehyde (4s): Compound **4s** was obtained in 70% yield according to the general procedure (petroleum ether/ethyl acetate, 50:1, 46.0 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 10.06 (s, 1H), 8.18 (s, 1H), 8.00 – 7.96 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 0.49 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 192.3, 153.8, 146.3, 140.4, 139.8, 135.1, 134.0, 133.0, 132.6, 130.5, 128.7, 122.1, 121.1, -3.5. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{15}OSi^+$ 239.0887; Found 239.0882.

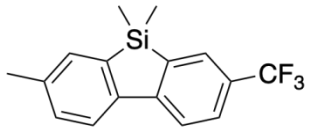


1-(5,5-dimethyl-5*H*-dibenzo[*b,d*]silol-3-yl)ethan-1-one (4t): Compound **4t** was obtained in 75% yield according to the general procedure (petroleum ether/ethyl acetate, 50:1, 37.8 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.33 (s, 1H), 8.12 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 6.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 2.73 (s, 3H), 0.55 (s,

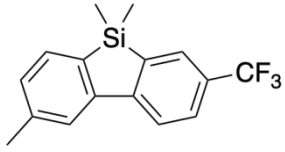
6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 198.1, 152.4, 146.5, 140.2, 139.3, 135.7, 132.9, 132.7, 130.9, 130.4, 128.4, 121.9, 120.7, 26.7, -3.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}OSi^+$ 253.1043; Found 253.1040.



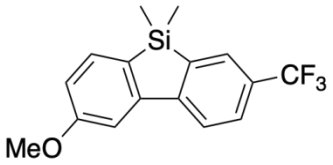
1-methoxy-5,5-dimethyl-3-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole (4y): Compound **4y** was obtained in 85% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 52.4 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.63 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.35 (t, *J* = 7.0 Hz, 1H), 7.25 (s, 1H), 4.07 (s, 3H), 0.48 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 157.0, 146.4, 142.8, 139.4, 138.6, 132.2, 130.3, 130.0 (q, *J* = 31.5 Hz), 127.4, 124.3 (q, *J* = 270.8 Hz), 120.9 (q, *J* = 3.8 Hz), 110.1 (q, *J* = 3.9 Hz), 55.4, -3.4. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}F_3OSi^+$ 309.0917; Found 309.0914.



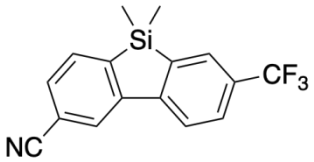
3,5,5-trimethyl-7-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole (4D): Compound **4D** was obtained in 79% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 46.2 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.91 – 7.87 (m, 2H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.53 (s, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 2.46 (s, 3H), 0.49 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.2, 143.7, 139.52, 139.48, 138.2, 133.6, 131.2, 129.3 (q, *J* = 3.6 Hz), 128.6 (q, *J* = 31.5 Hz), 127.2 (q, *J* = 3.8 Hz), 124.7 (q, *J* = 270.5 Hz), 121.4, 120.4, 21.3, -3.4. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}F_3Si^+$ 293.0968; Found 293.0964.



2,5,5-trimethyl-7-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole (4E): Compound **4E** was obtained in 76% yield according to the general procedure (petroleum ether/ethyl acetate, 400:1, 44.3 mg, 0.2 mmol scale) as colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.0 Hz, 1H), 7.91 (s, 1H), 7.76 – 7.71 (m, 2H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 2.51 (s, 3H), 0.51 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 151.1, 146.6, 140.5, 140.2, 135.9, 132.8, 129.34, 129.27 (q, *J* = 3.9 Hz), 129.0 (q, *J* = 31.5 Hz), 127.2 (q, *J* = 3.6 Hz), 124.7 (q, *J* = 270.4 Hz), 122.4, 120.6, 21.8, -3.4. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}F_3Si^+$ 293.0968; Found 293.0962.

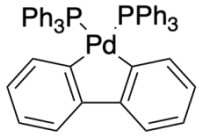


2-methoxy-5,5-dimethyl-7-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole (4F): Compound **4F** was obtained in 84% yield according to the general procedure (petroleum ether/ethyl acetate, 200:1, 51.7 mg, 0.2 mmol scale) as white solid (63.3 - 64.2 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 7.91 – 7.87 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 6.96 (dd, *J* = 2.5, 8.0 Hz, 1H), 3.95 (s, 3H), 0.48 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ = 162.0, 150.8, 148.3, 140.9, 134.0, 130.3, 129.2 (q, *J* = 3.8 Hz), 129.1 (q, *J* = 31.5 Hz), 127.1 (q, *J* =3.6 Hz), 124.6 (q, *J* = 270.5 Hz), 120.7, 114.0, 107.7, 55.3, -3.3. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.1. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{16}F_3OSi^+$ 309.0917; Found 309.0912.



5,5-dimethyl-7-(trifluoromethyl)-5*H*-dibenzo[*b,d*]silole-2-carbonitrile (4G): Compound **4G** was obtained in 69% yield according to the general procedure (petroleum ether/ethyl acetate, 50:1, 41.8 mg, 0.2 mmol scale) as white solid (169.8 - 174.5 °C). **^{1}H NMR** (500 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 7.96 – 7.93 (m, 2H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.65 (dd, *J* = 1.5, 7.5 Hz, 1H), 0.53 (s, 6H). **^{13}C NMR** (125 MHz,

$CDCl_3$) δ = 148.9, 147.1, 145.7, 139.5, 133.5, 131.3, 130.2 (q, *J* = 31.9 Hz), 129.6 (q, *J* = 3.5 Hz), 127.7 (q, *J* = 3.5 Hz), 124.6, 124.3 (q, *J* = 270.6 Hz), 121.3, 118.9, 114.1, -3.8. **^{19}F NMR** (470 MHz, $CDCl_3$) δ = -62.4. **HRMS** (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}F_3NSi^+$ 304.0764; Found 304.0758.



Int-A: pale yellow solid, isolated yield 69% (107.9 mg, 0.2 mmol scale); known compound.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 – 7.31 (m, 22H), 7.25 (t, *J* = 7.0 Hz, 12H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.70 – 6.66 (m, 1H), 6.65 – 6.60 (m, 1H), 6.37 (t, *J* = 7.5 Hz, 1H).

10 References

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[4] E. Shirakawa, K. Itoh, T. Higashino and T. Hayashi, *tert*-Butoxide-Mediated Arylation of Benzene with Aryl Halides in the Presence of a Catalytic 1,10-Phenanthroline Derivative, *J. Am. Chem. Soc.,* 2010, **132**, 15537–15539.

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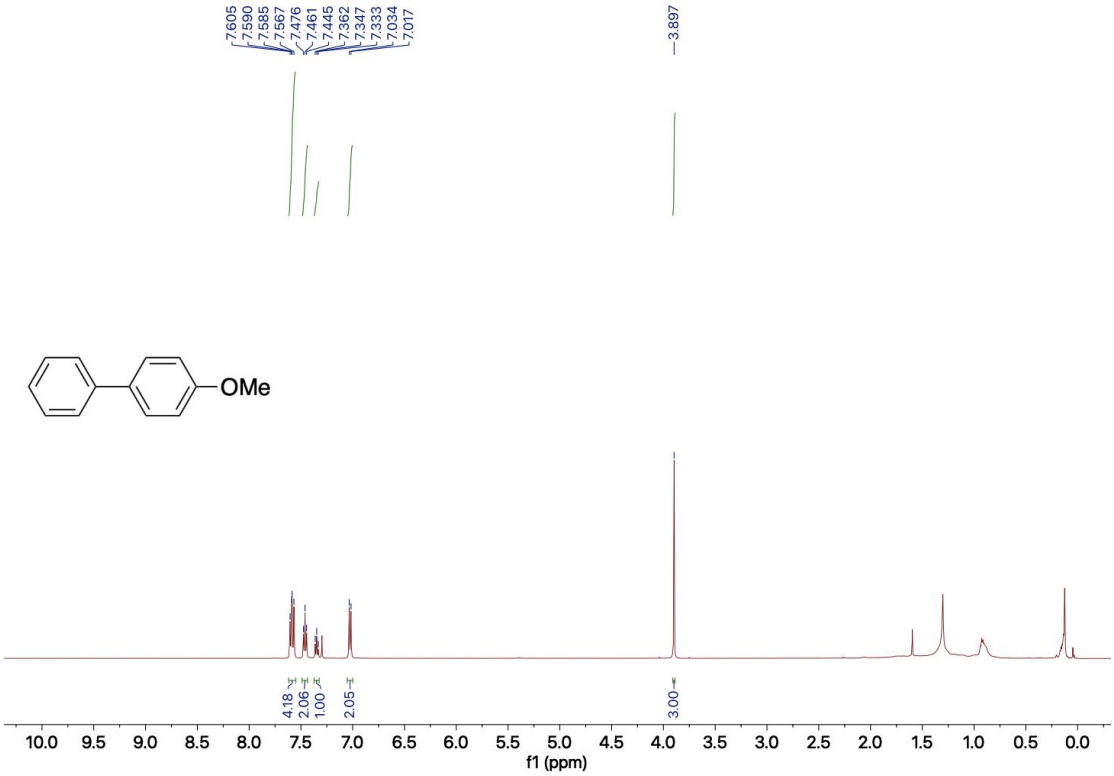
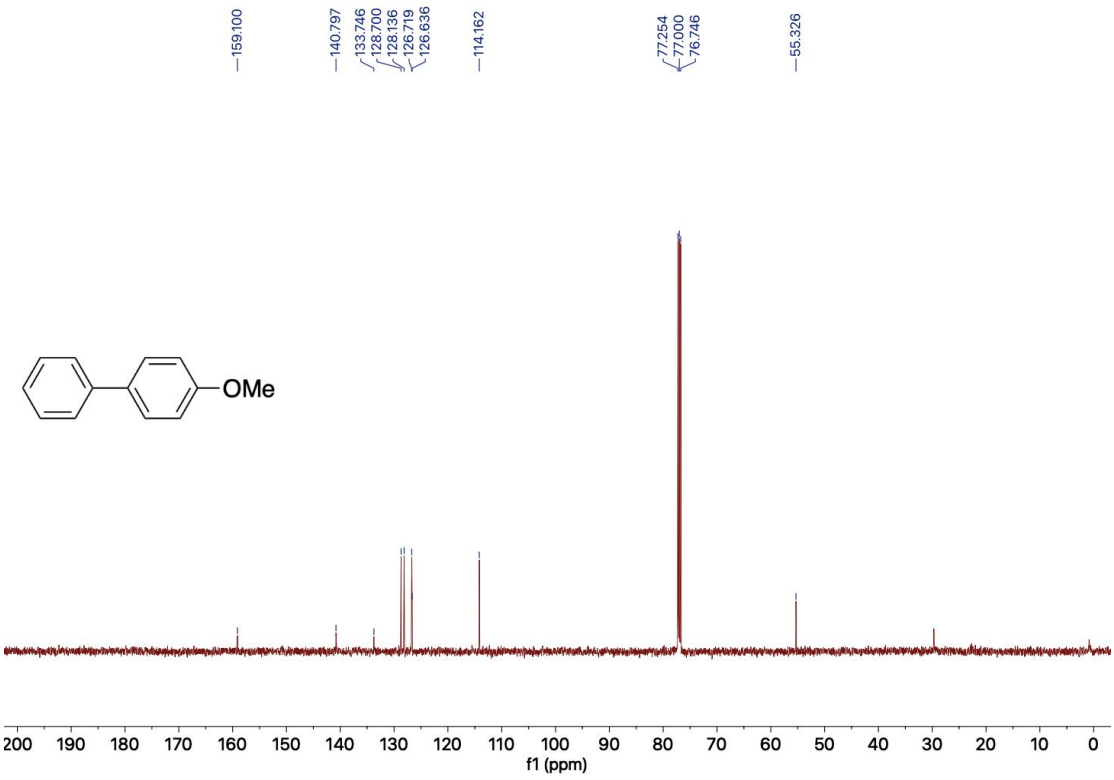
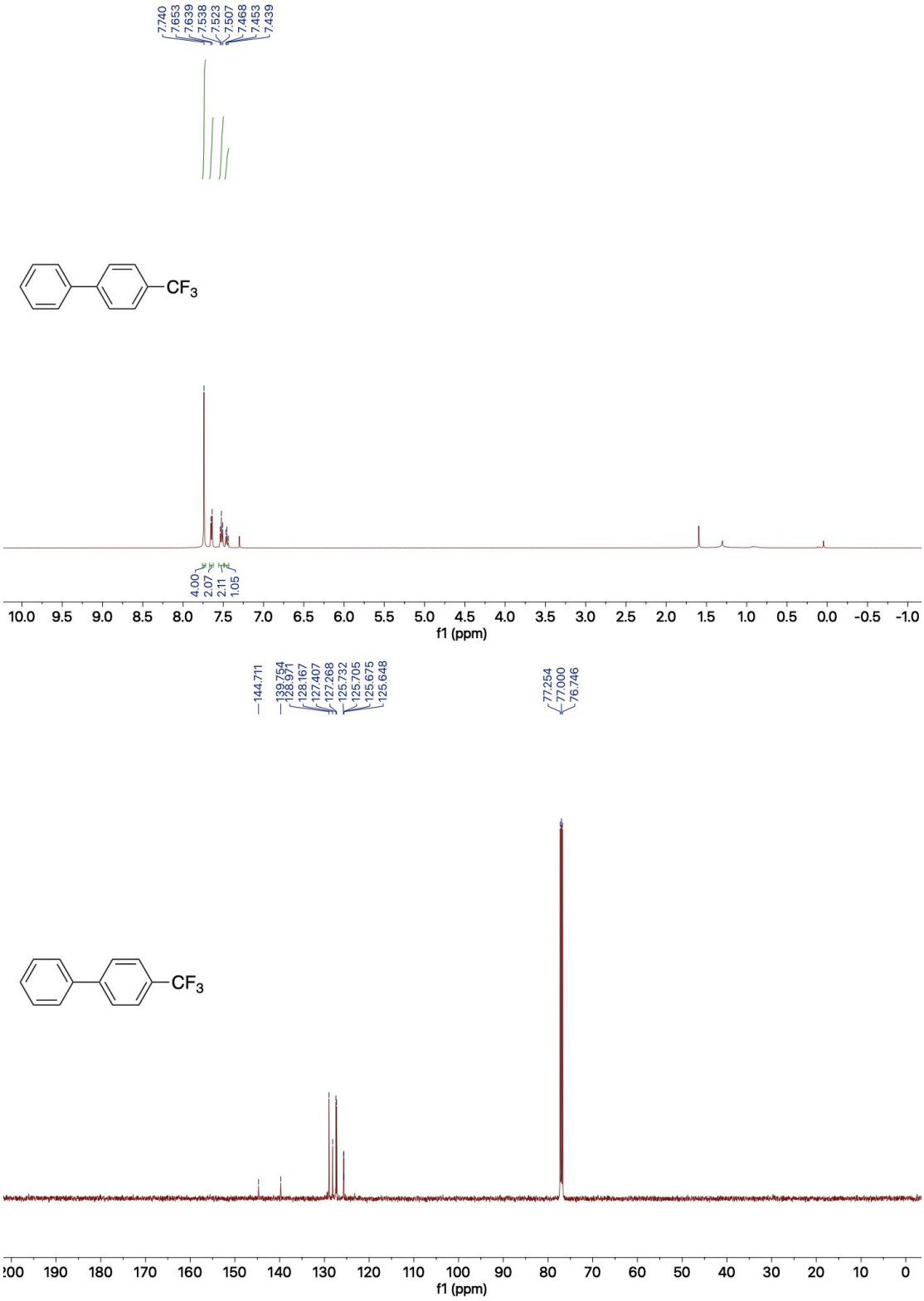
11 Copies of NMR Spectra

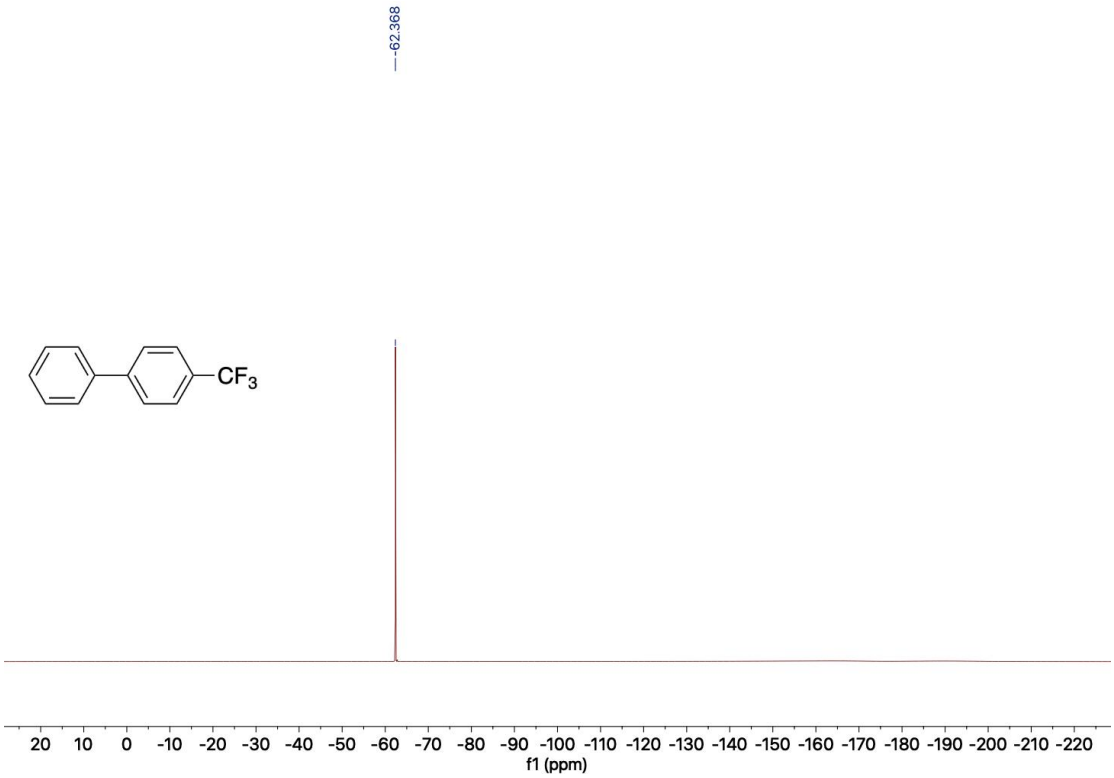
^{1}H NMR of **3b'** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3b'** (125 MHz, $CDCl_3$)



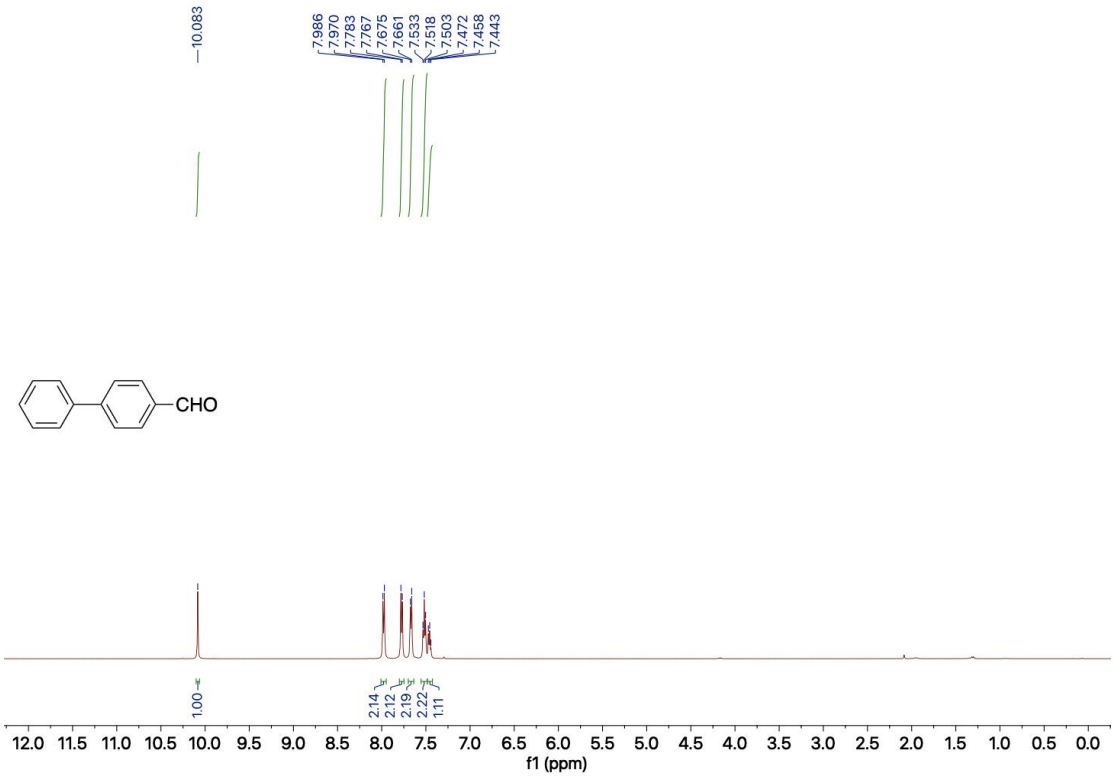


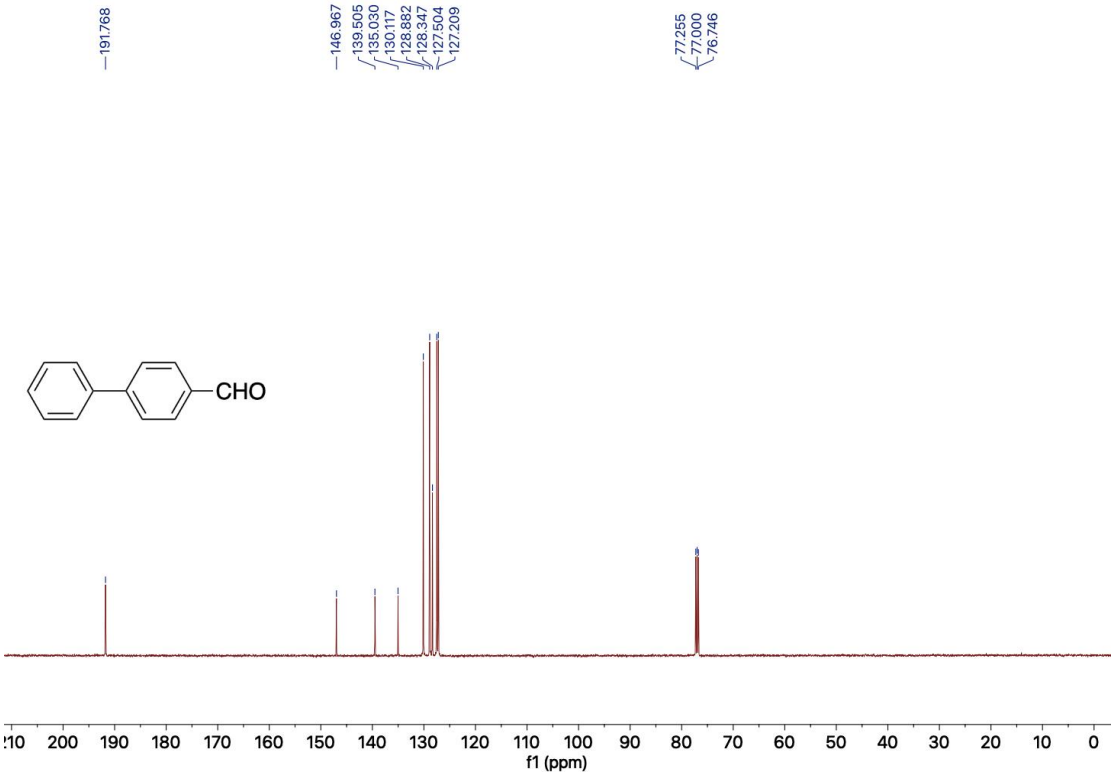
^{1}H NMR of **3q'** (500 MHz, $CDCl_3$), ^{13}C NMR of **3q'** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3q'** (470 MHz, $CDCl_3$)



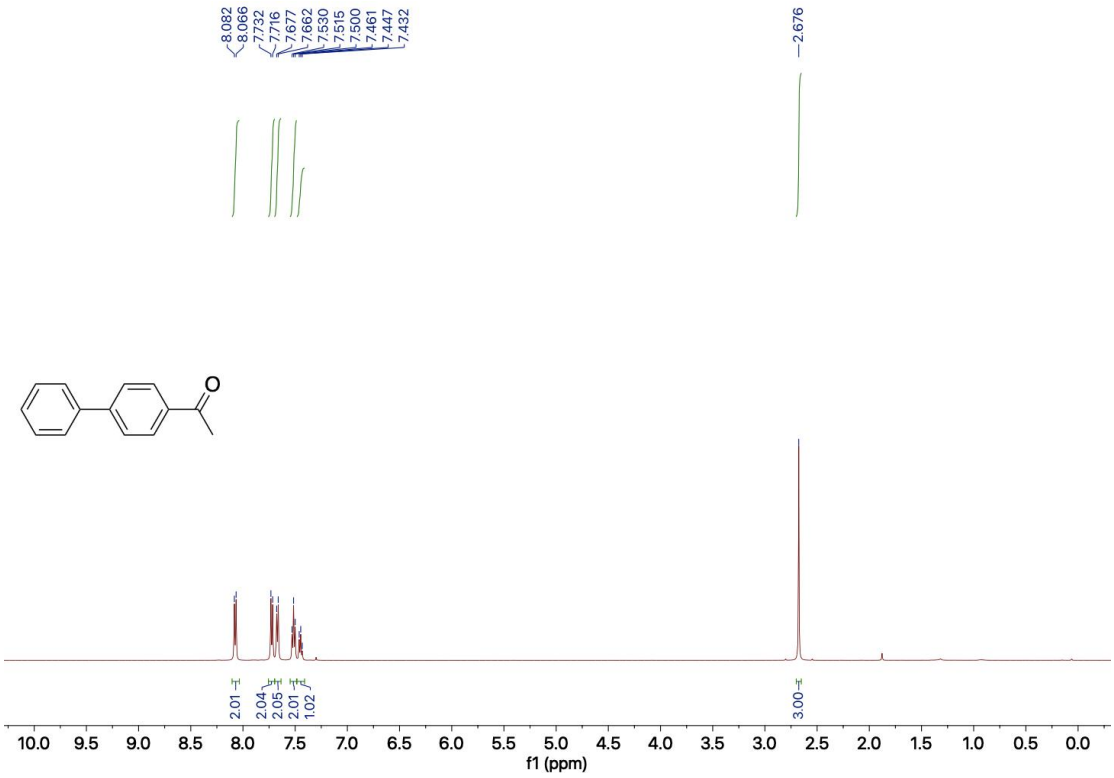

-62.368
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

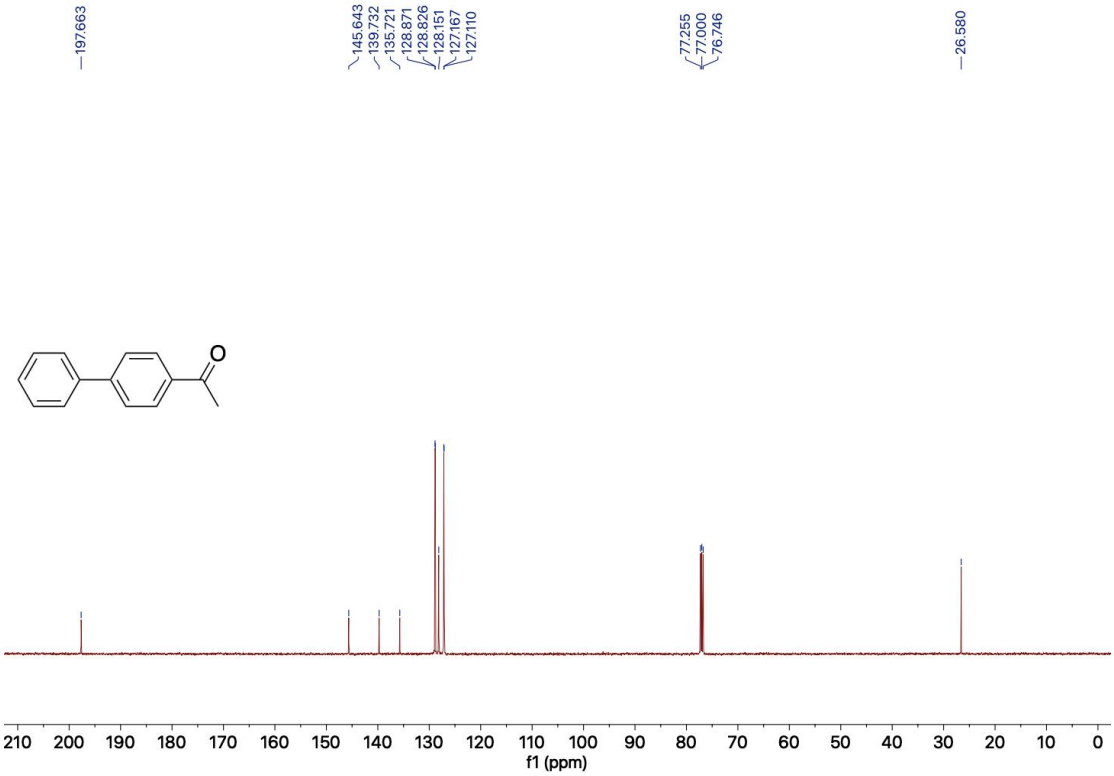
^{1}H NMR of **3s'** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3s'** (125 MHz, $CDCl_3$)



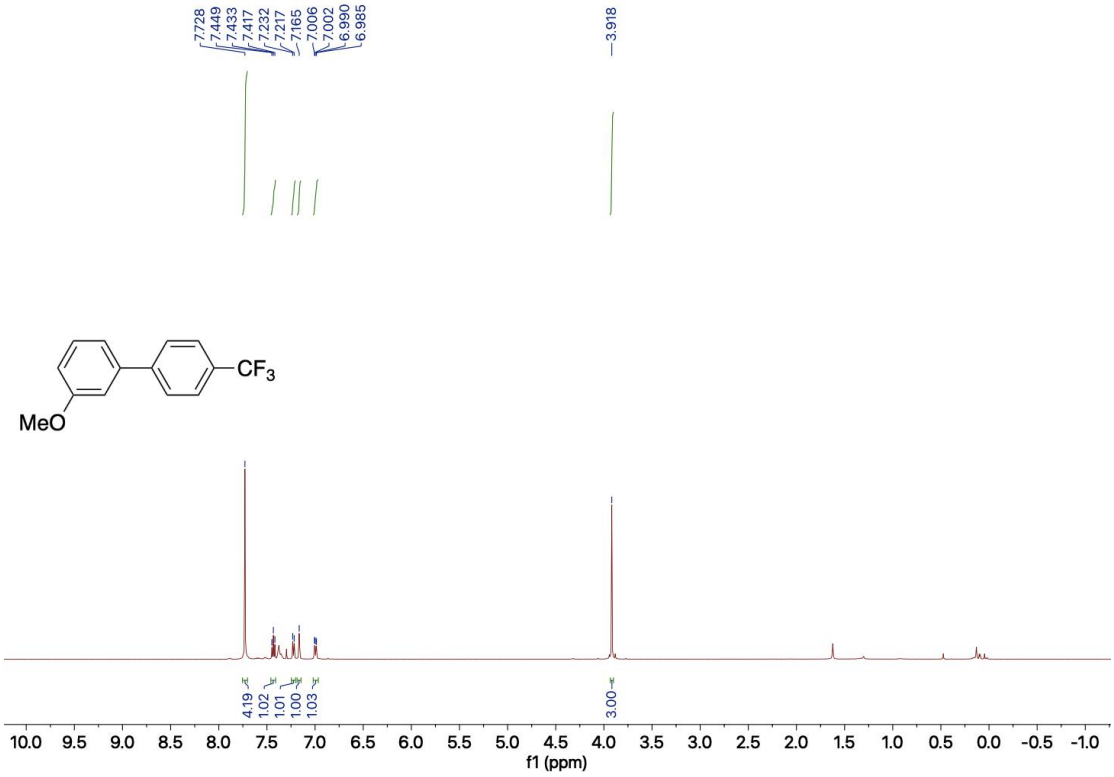


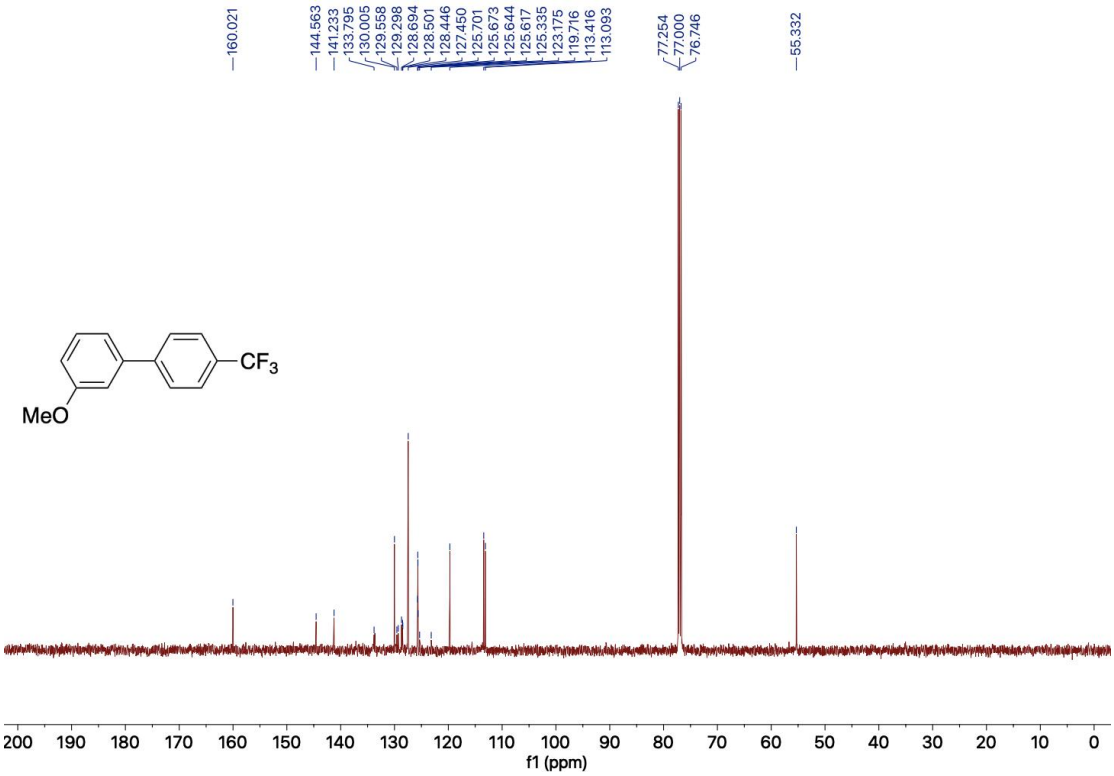
^{1}H NMR of **3t'** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3t'** (125 MHz, $CDCl_3$)

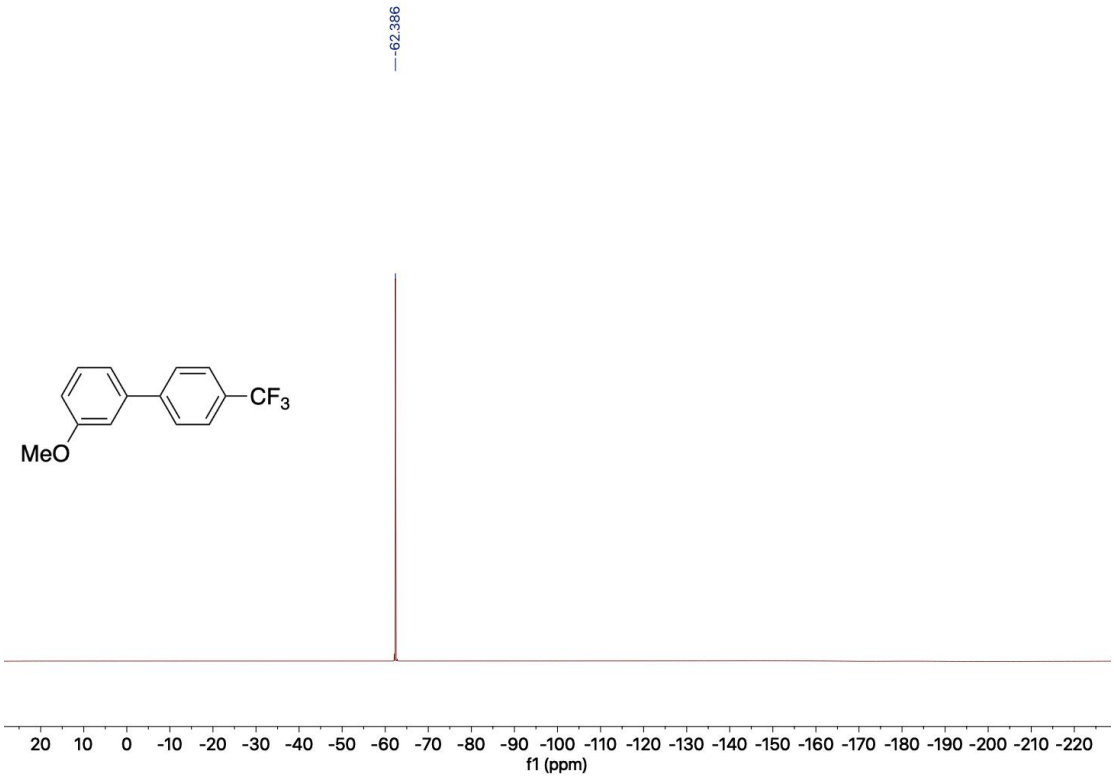




^{1}H NMR of **3y'** (500 MHz, $CDCl_3$), ^{13}C NMR of **3y'** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3y'** (470 MHz, $CDCl_3$)



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CF3
MeO
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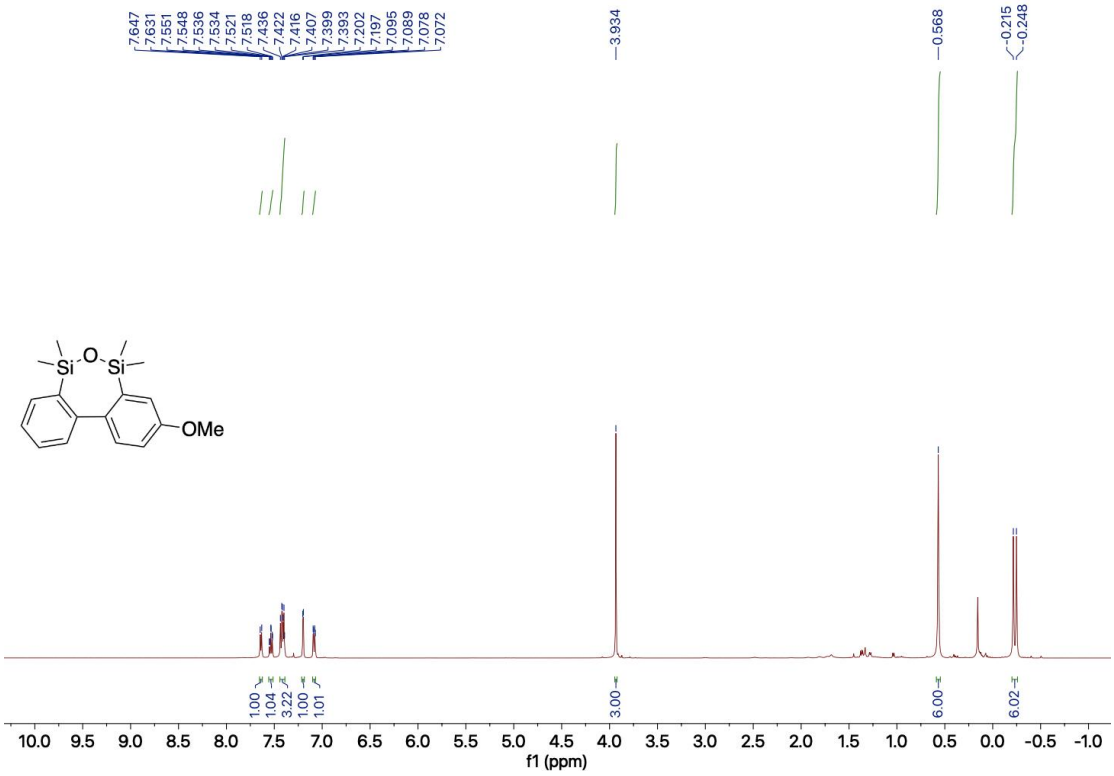
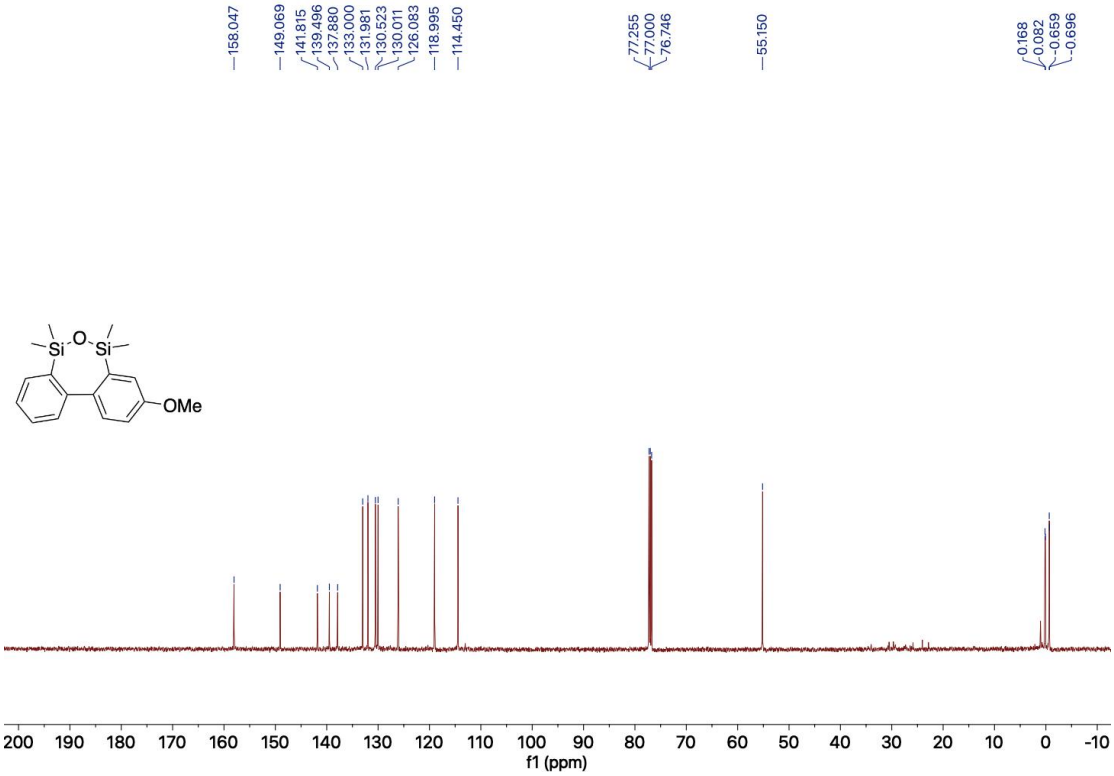
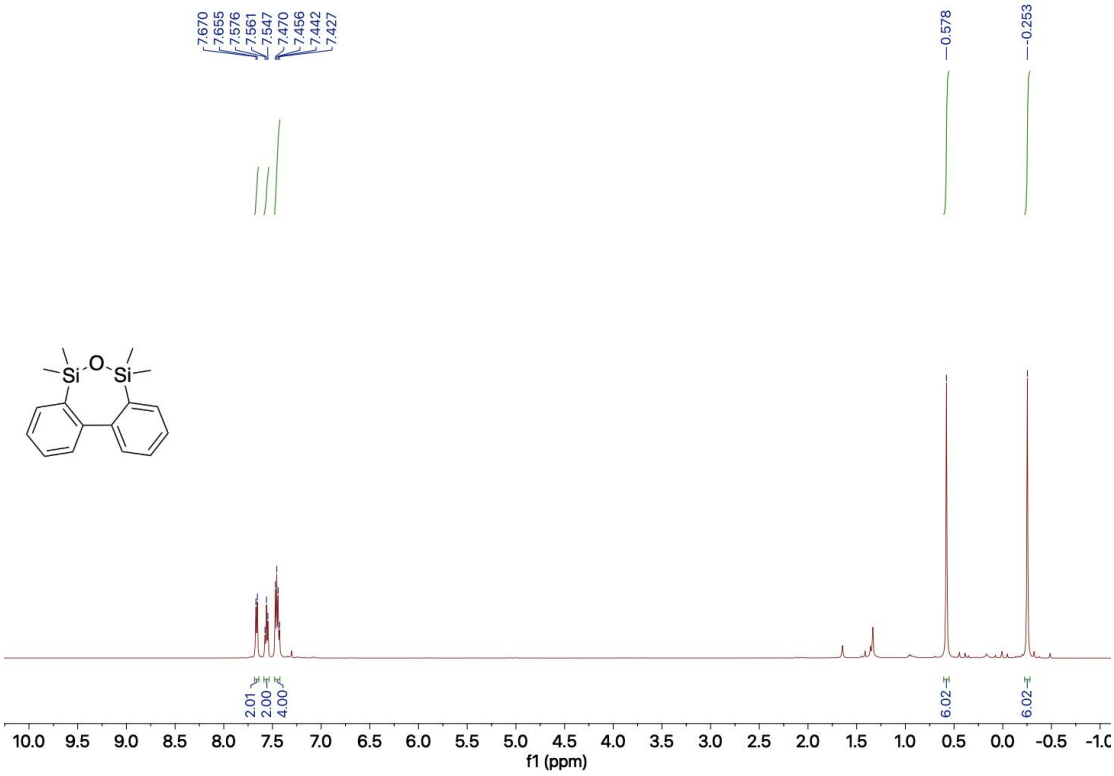
f1 (ppm)

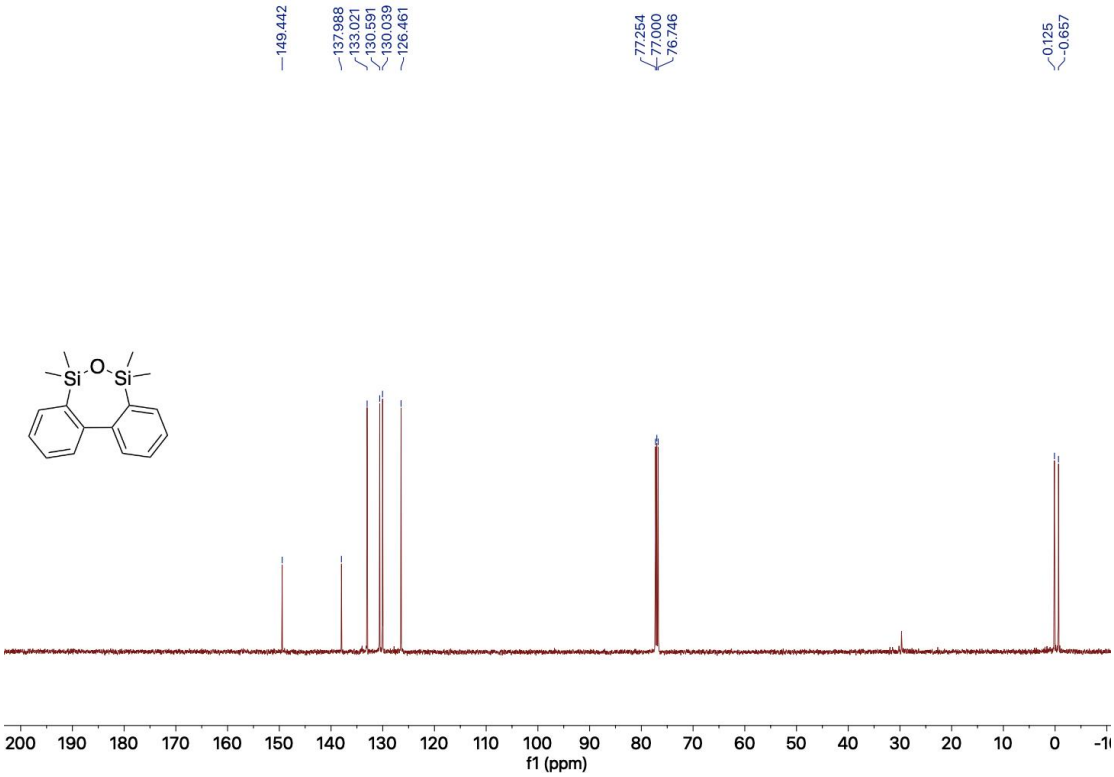
^{1}H NMR of **3a** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3a** (125 MHz, $CDCl_3$)



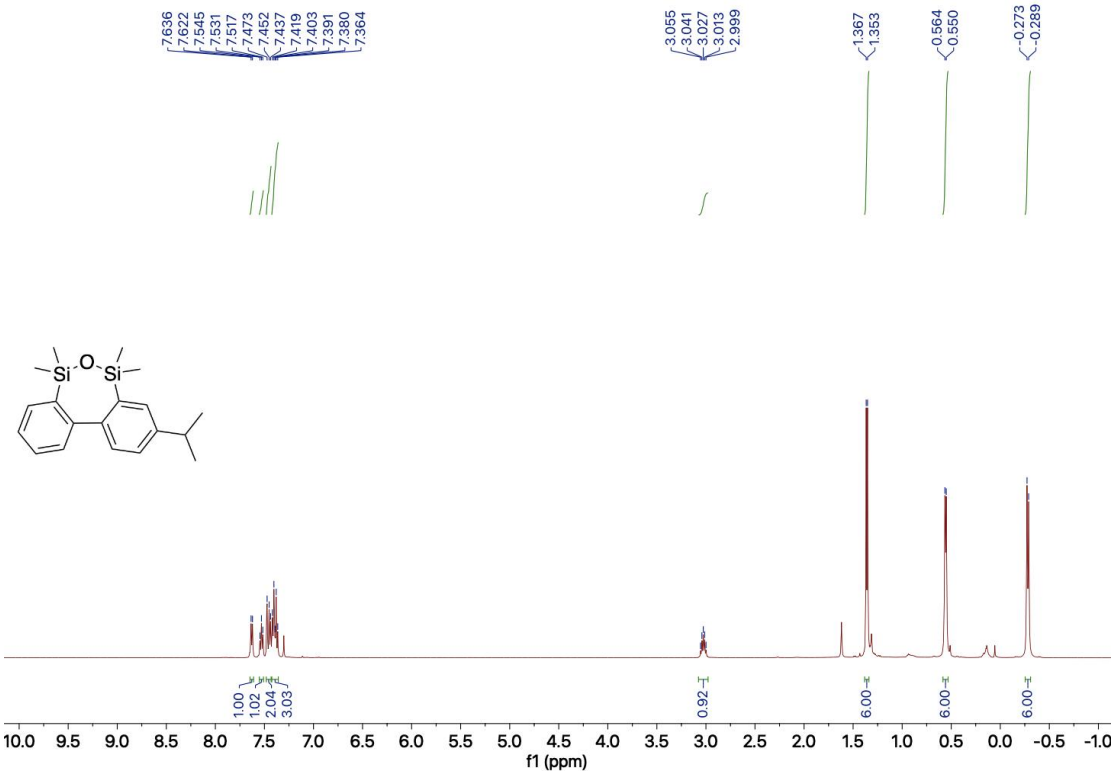


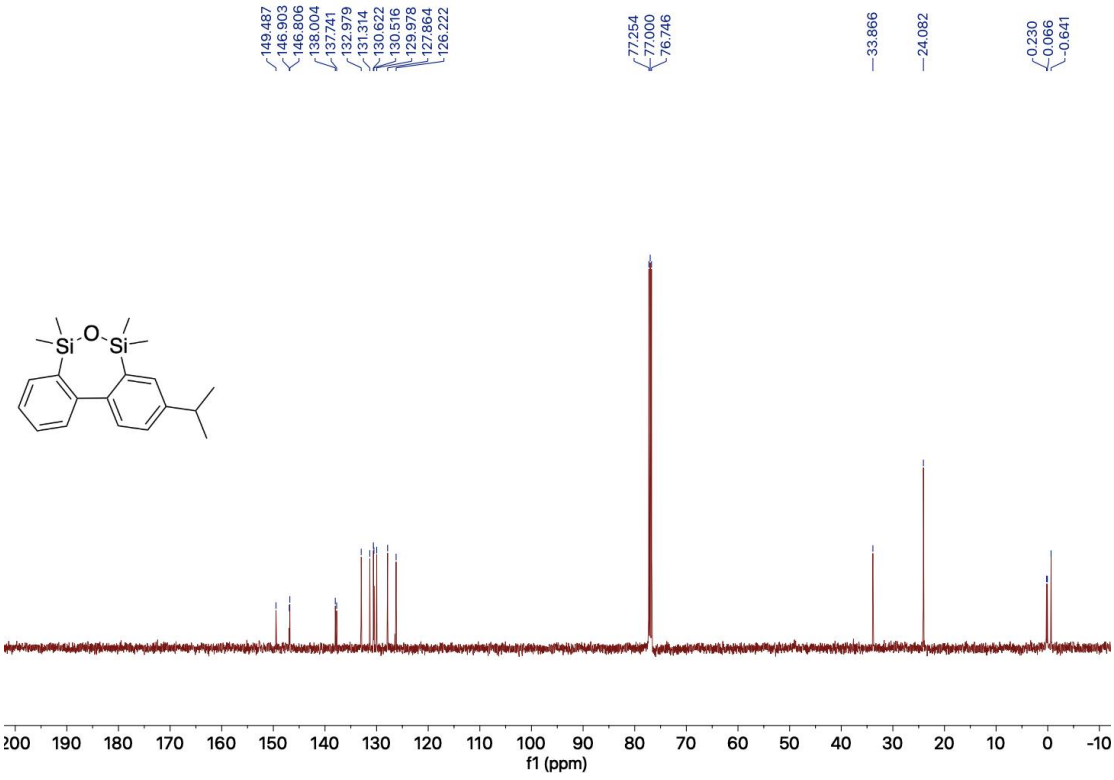
^{1}H NMR of **3b** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3b** (125 MHz, $CDCl_3$)



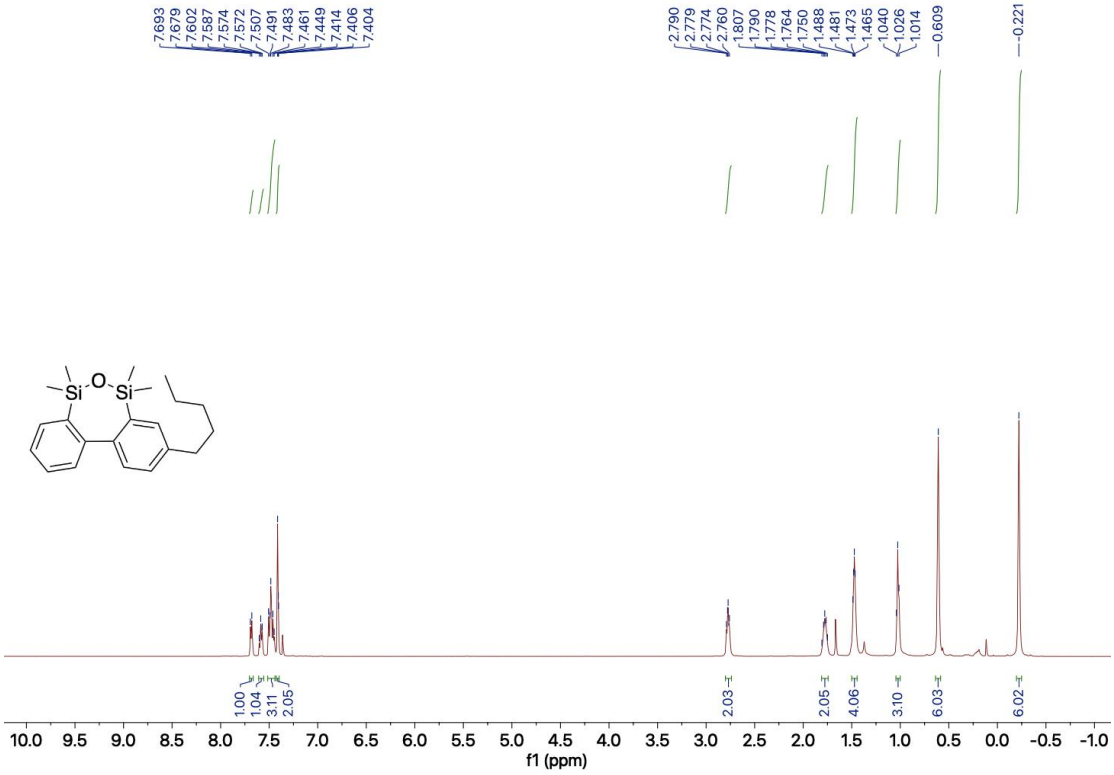


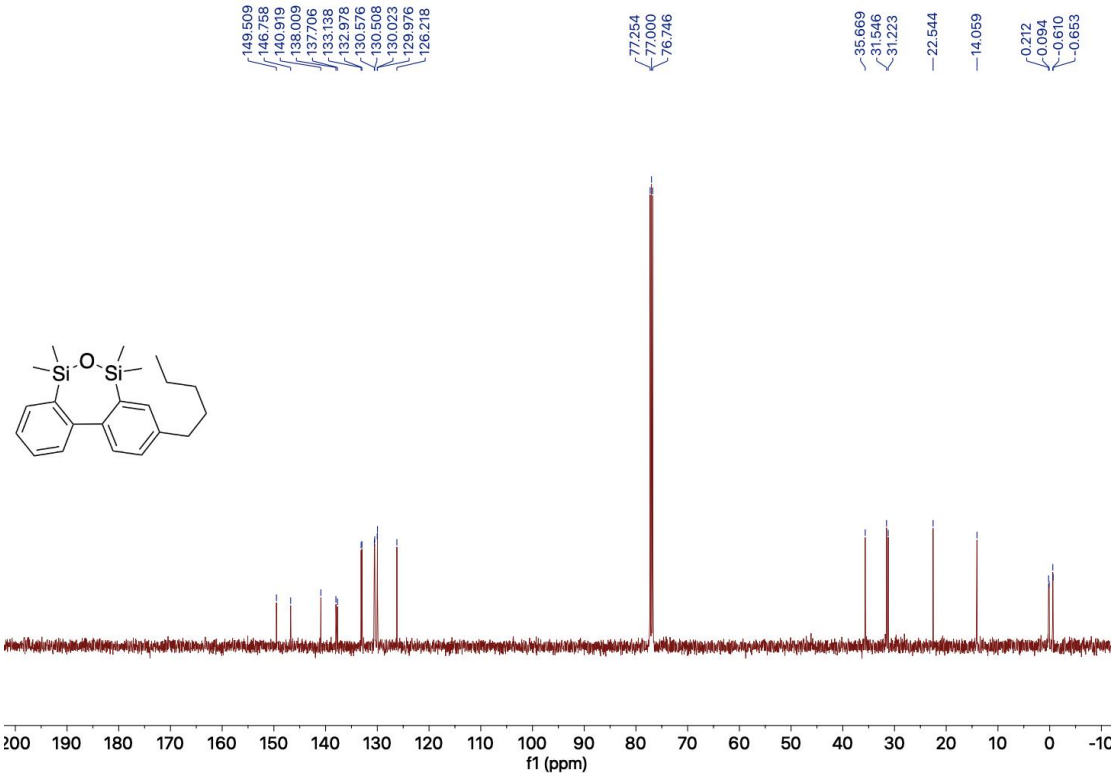
^{1}H NMR of **3c** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3c** (125 MHz, $CDCl_3$)



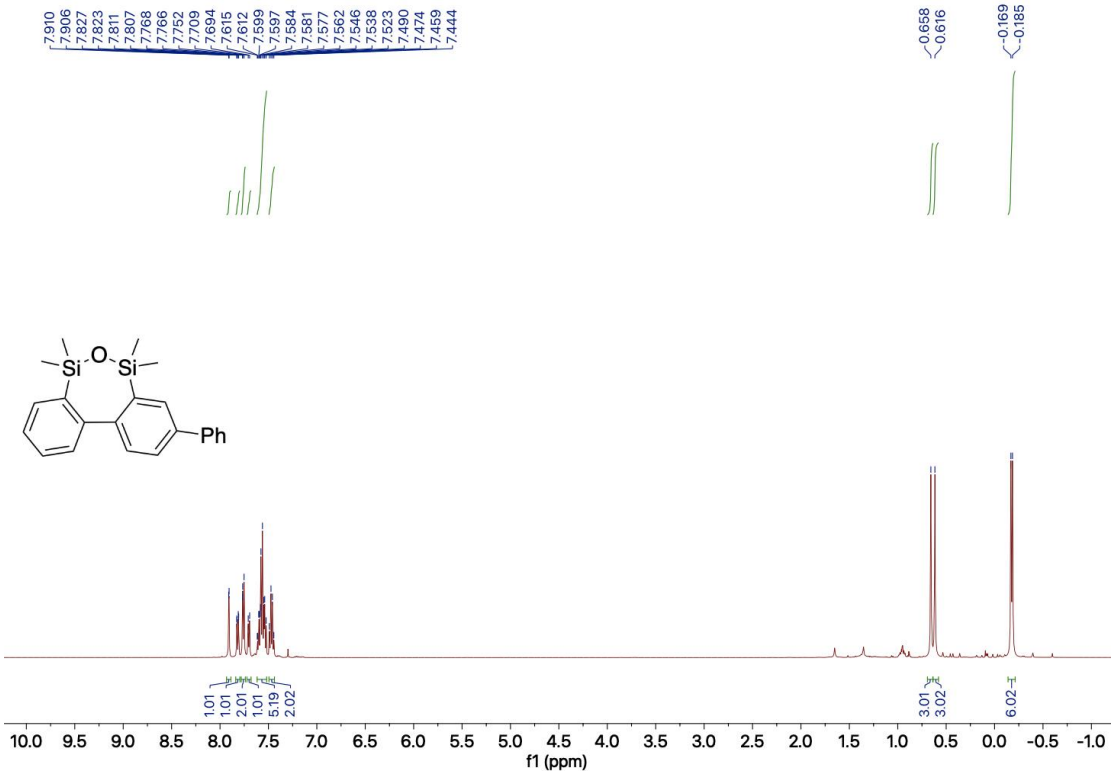


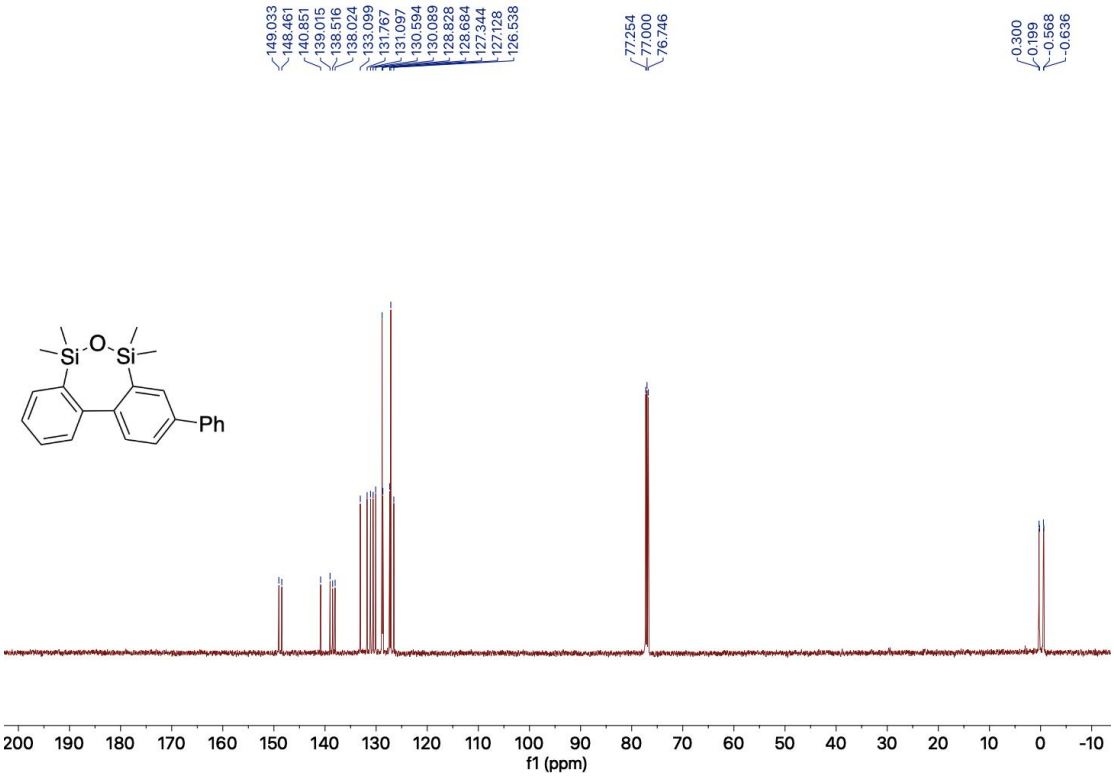
^{1}H NMR of **3d** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3d** (125 MHz, $CDCl_3$)



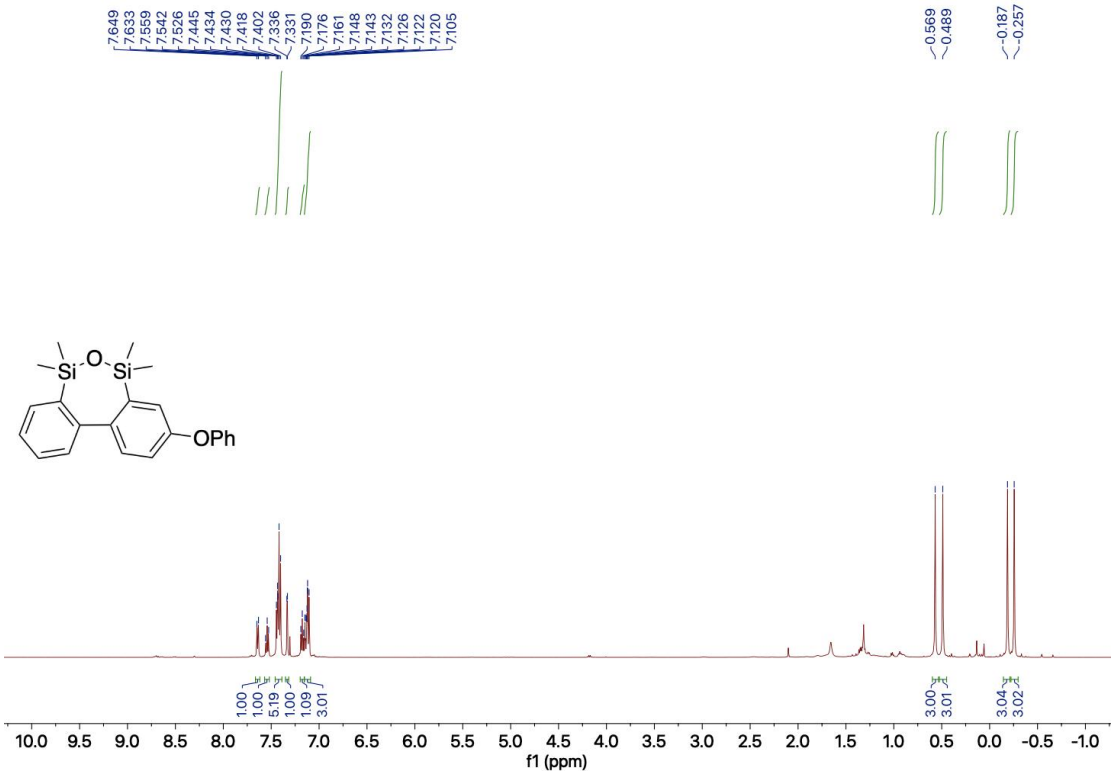


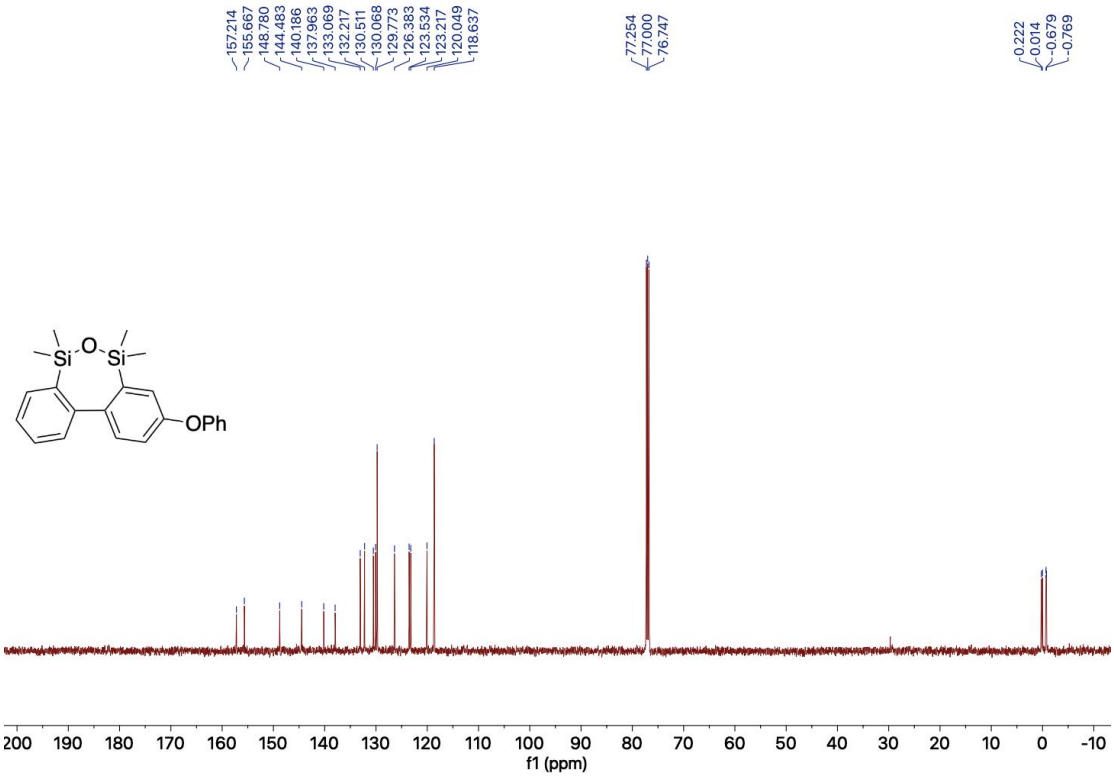
^{1}H NMR of **3e** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3e** (125 MHz, $CDCl_3$)



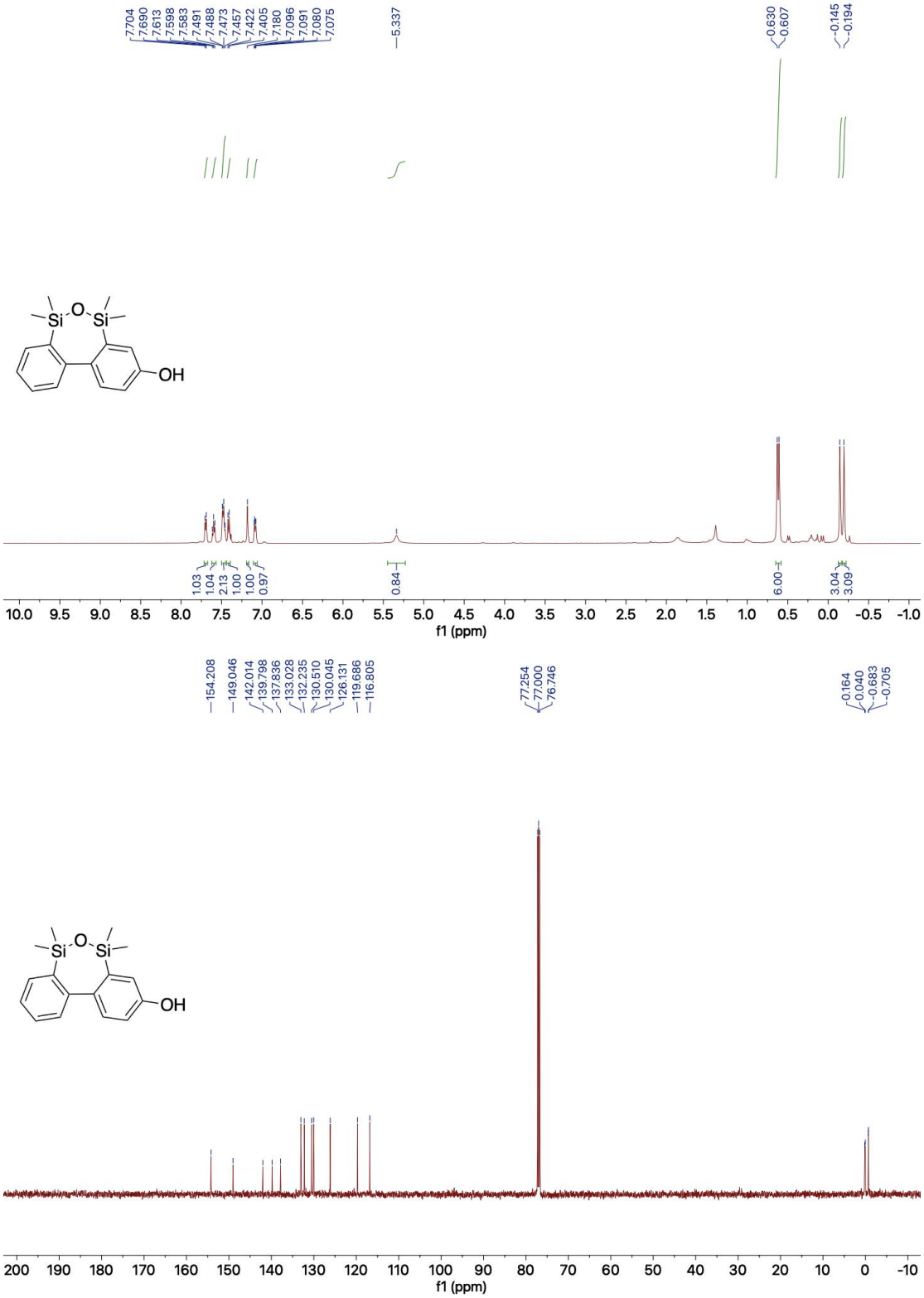


^{1}H NMR of **3f** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3f** (125 MHz, $CDCl_3$)

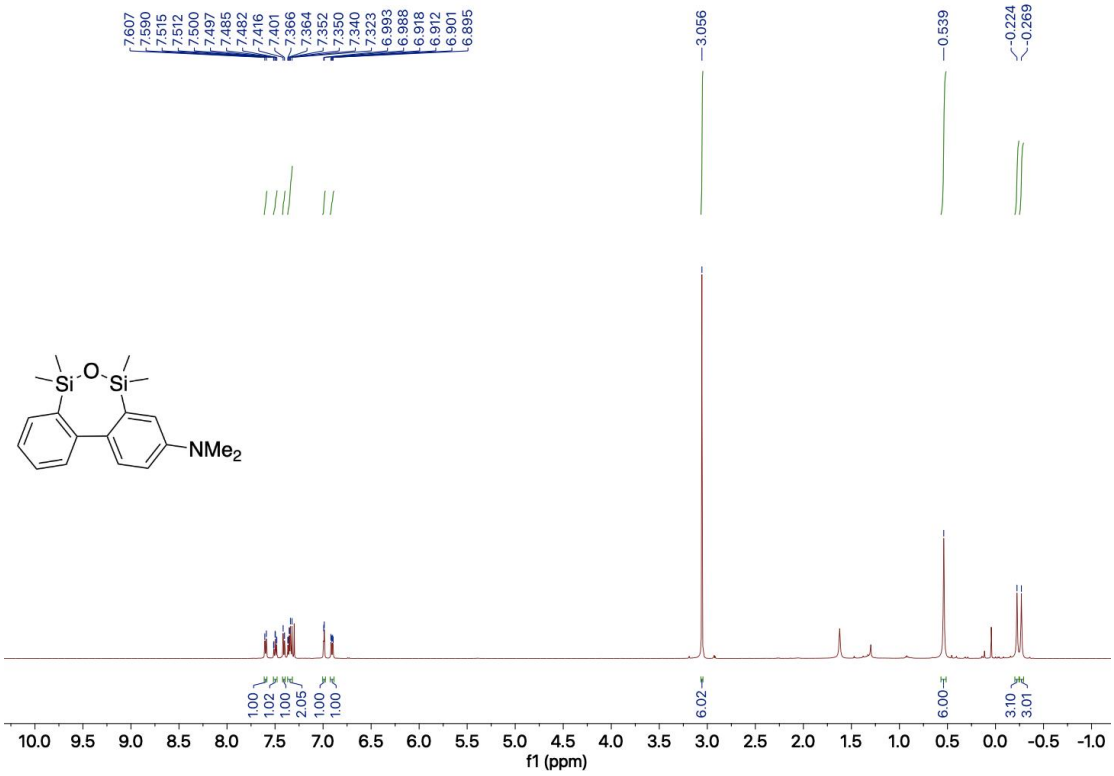


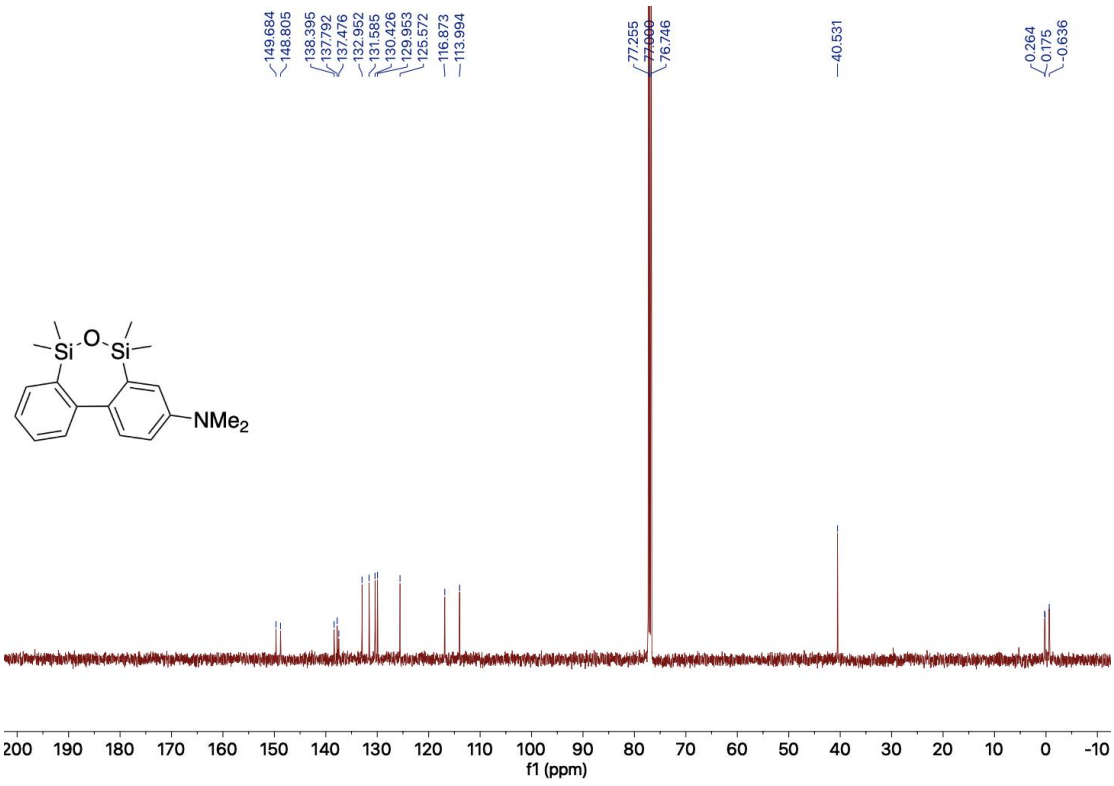


^{1}H NMR of **3g** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3g** (125 MHz, $CDCl_3$)

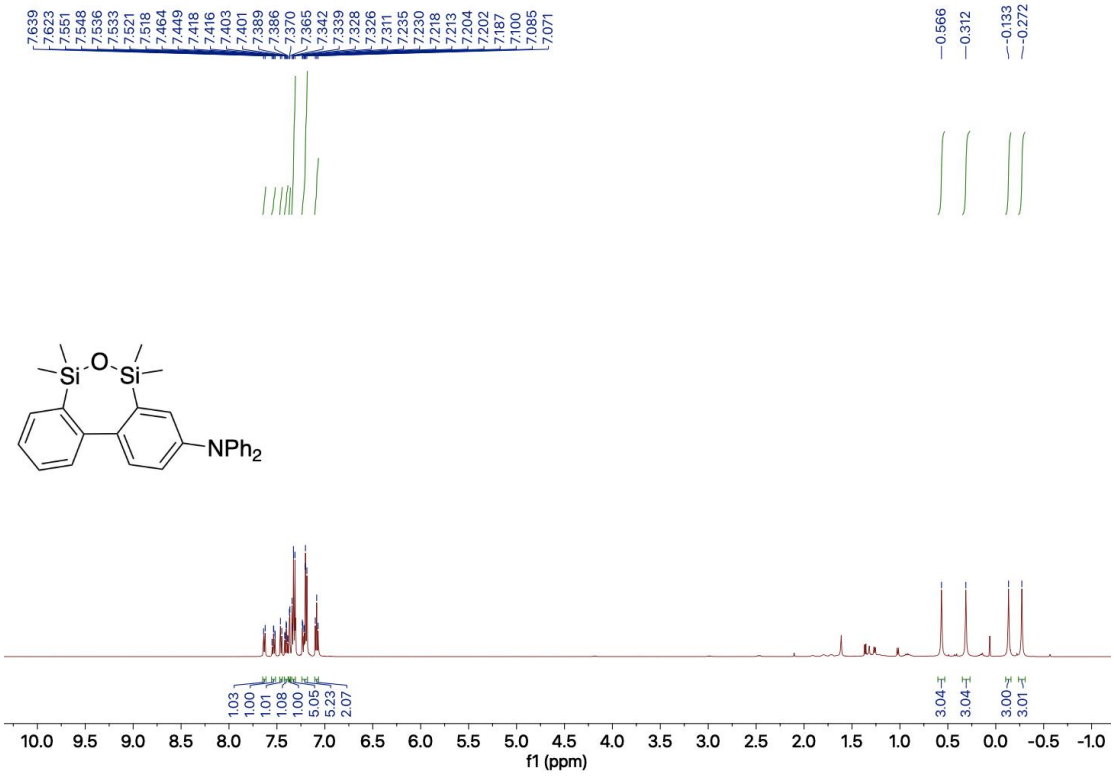


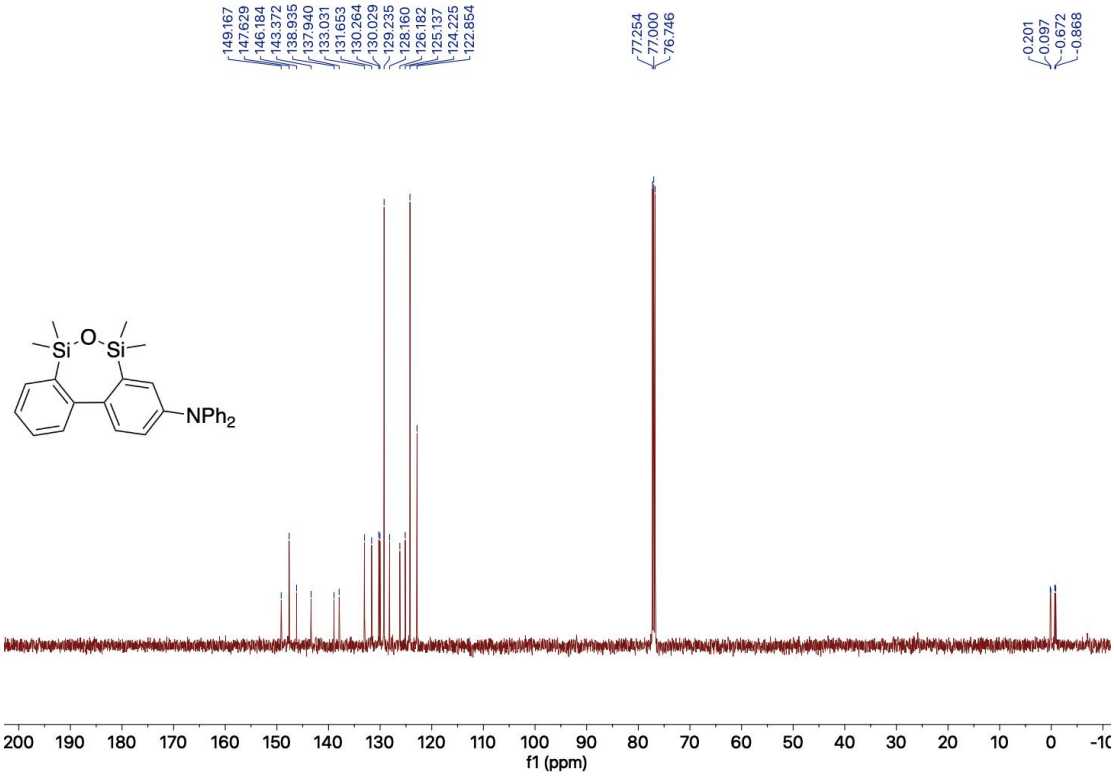
^{1}H NMR of **3h** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3h** (125 MHz, $CDCl_3$)



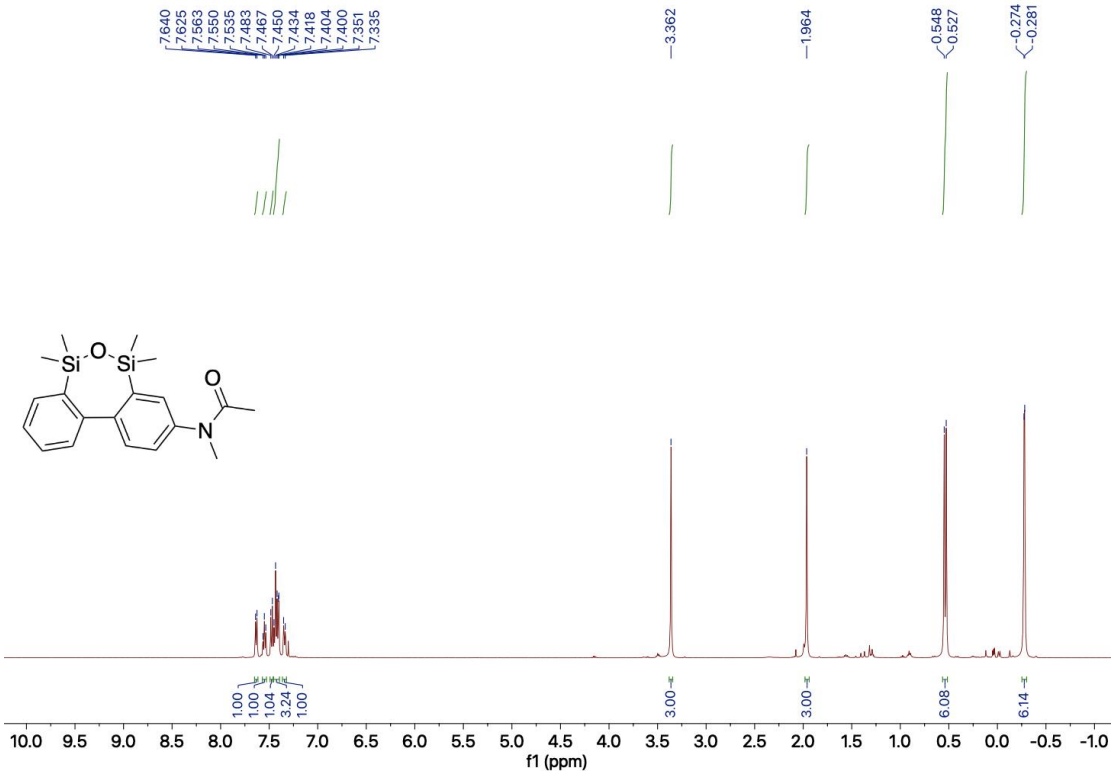


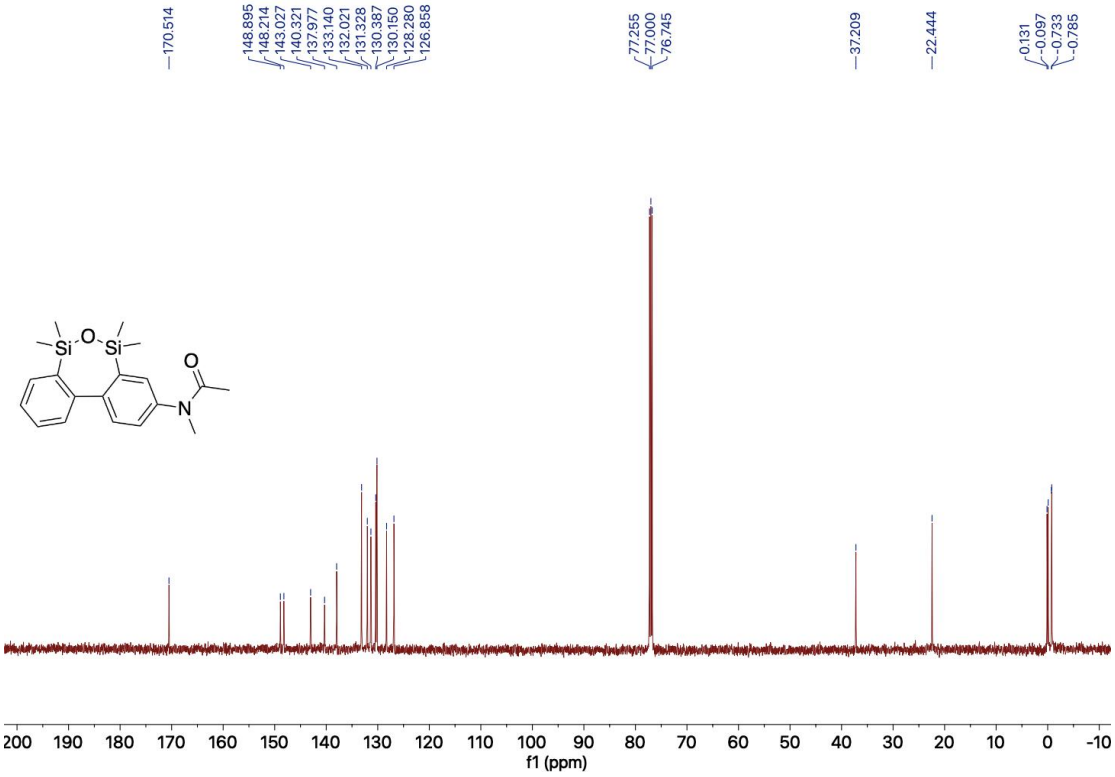
^{1}H NMR of **3i** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3i** (125 MHz, $CDCl_3$)



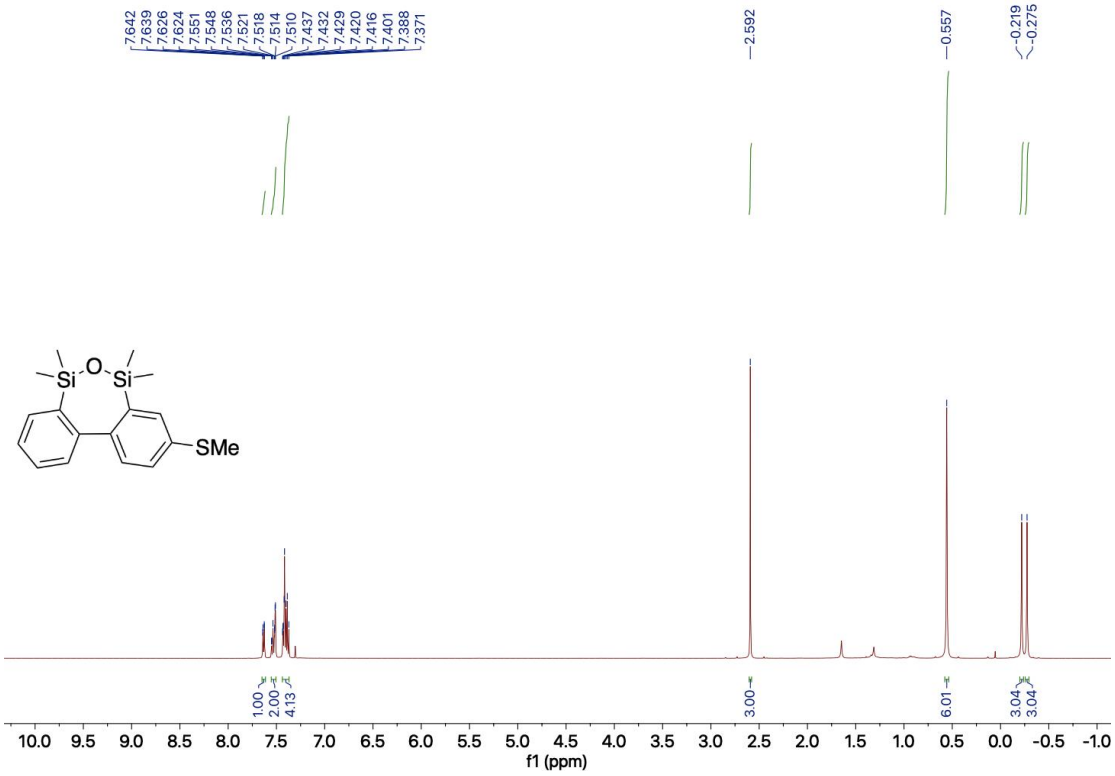


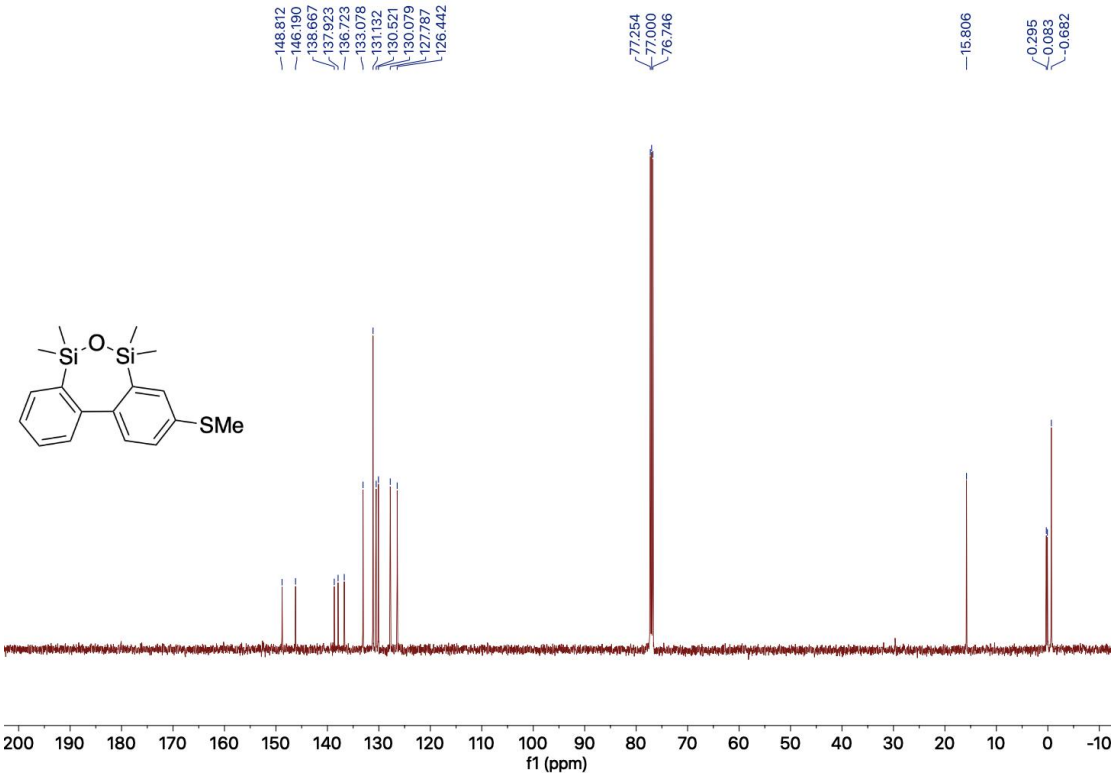
^{1}H NMR of **3j** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3j** (125 MHz, $CDCl_3$)



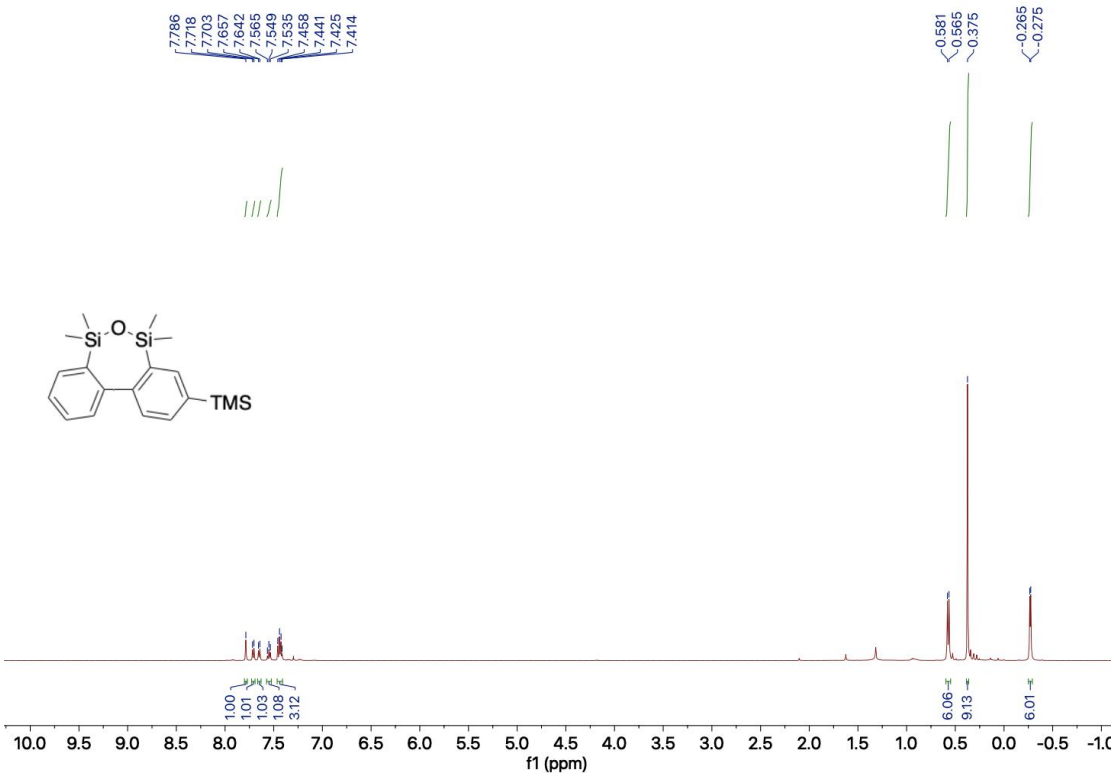


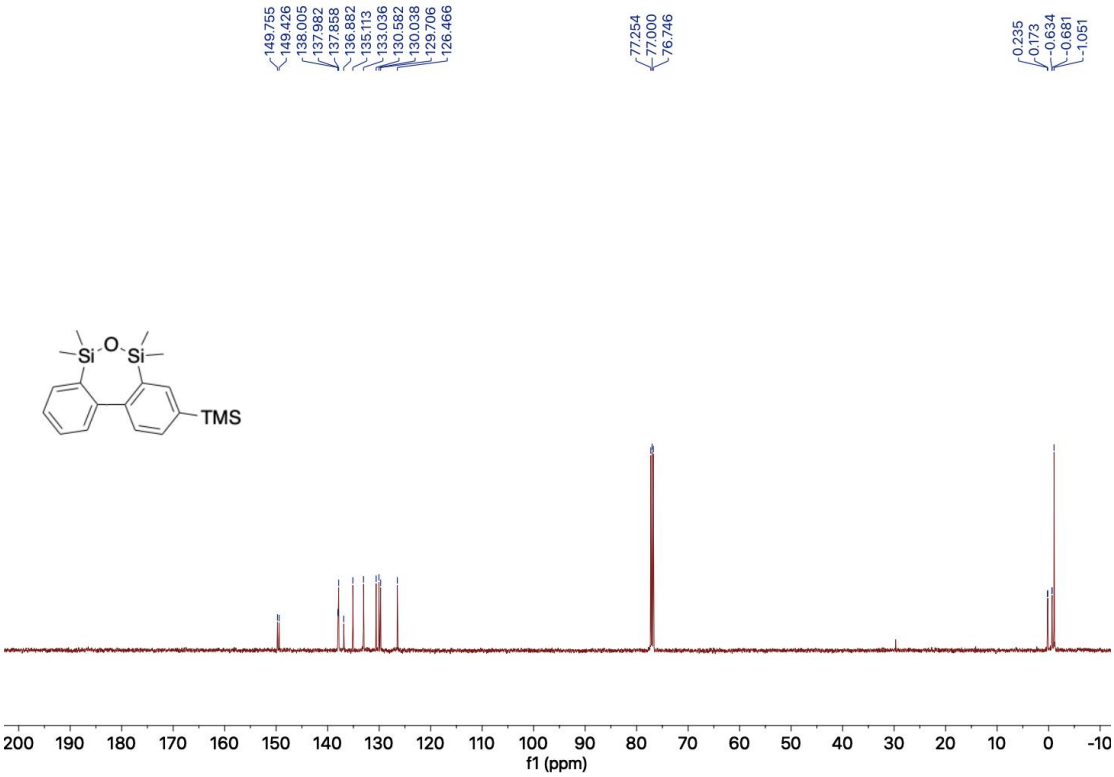
^{1}H NMR of **3k** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3k** (125 MHz, $CDCl_3$)



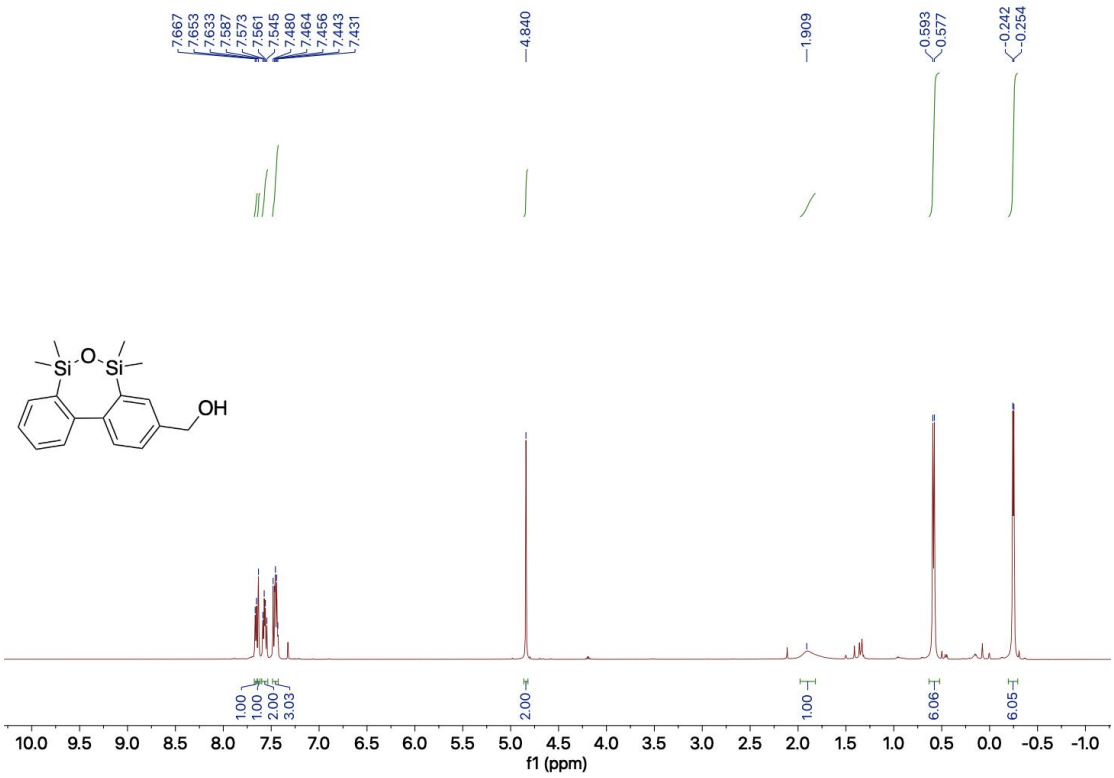


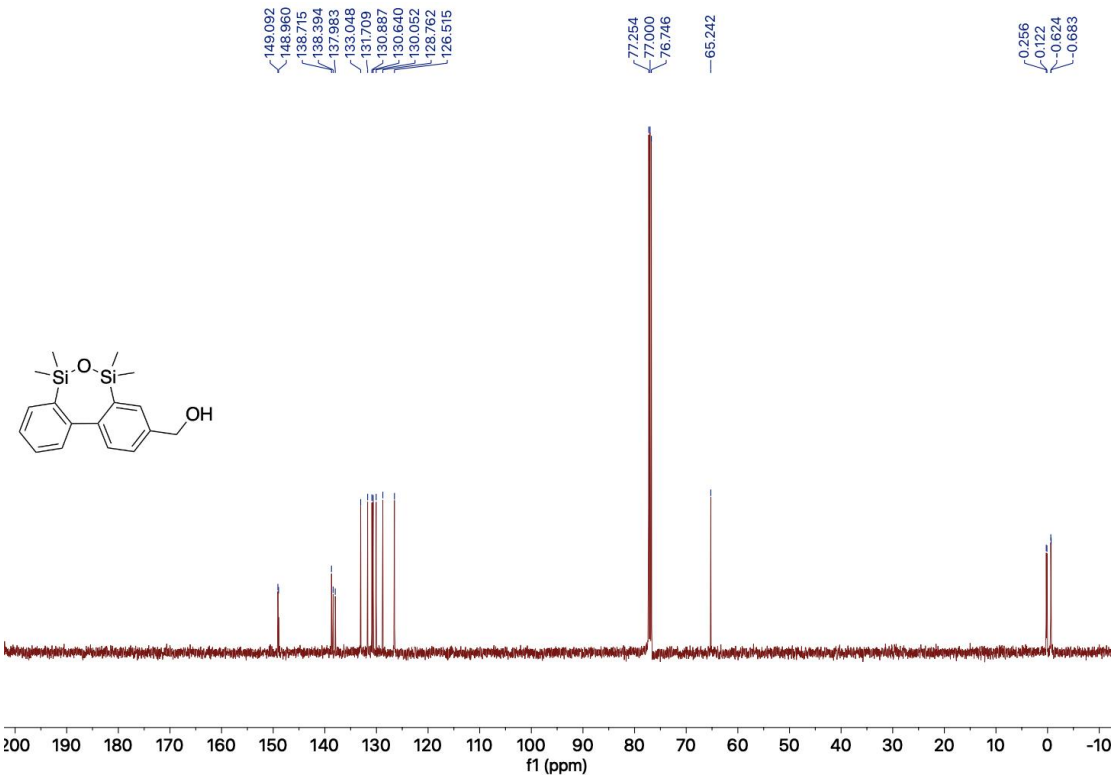
^{1}H NMR of **3l** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3l** (125 MHz, $CDCl_3$)



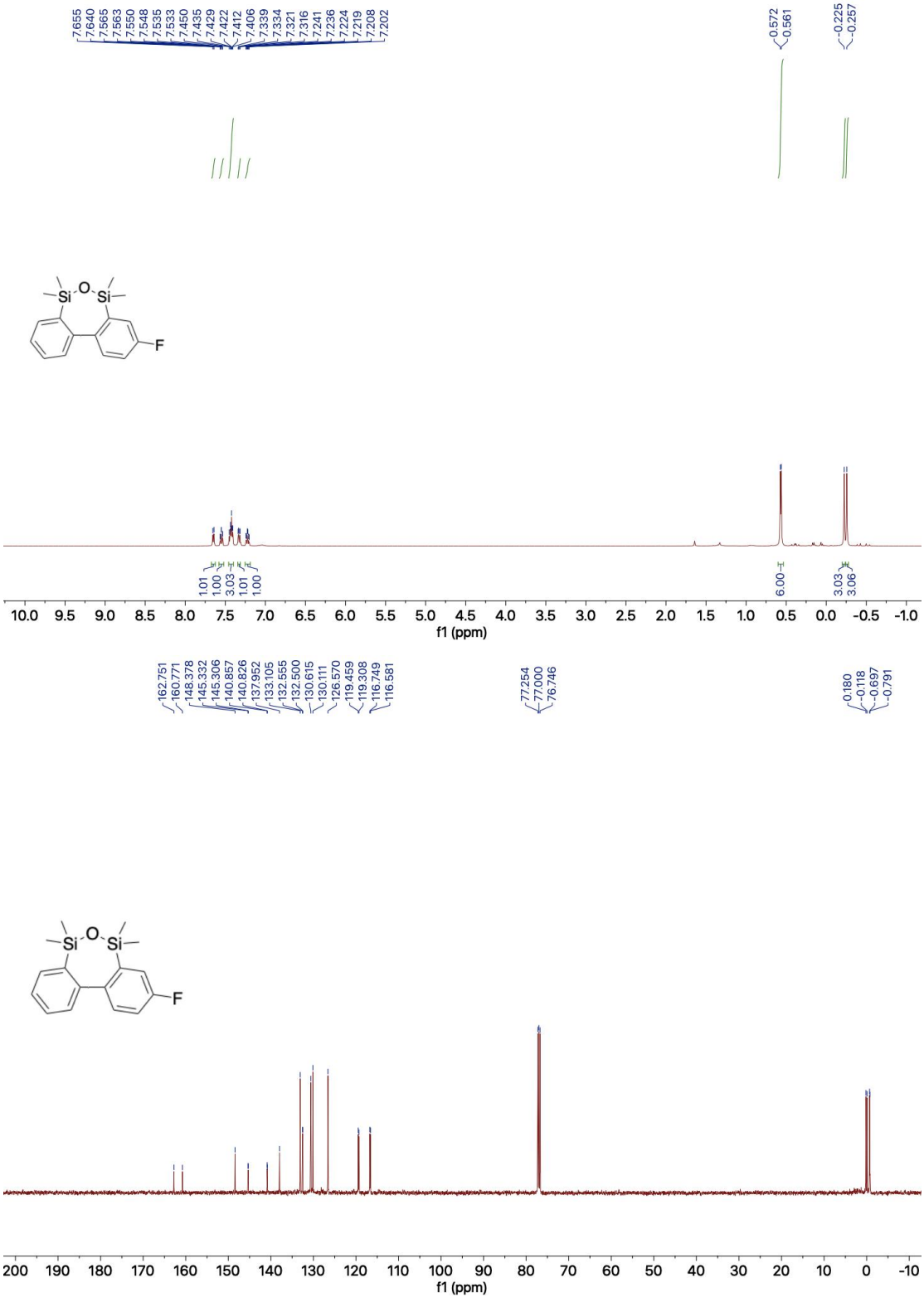


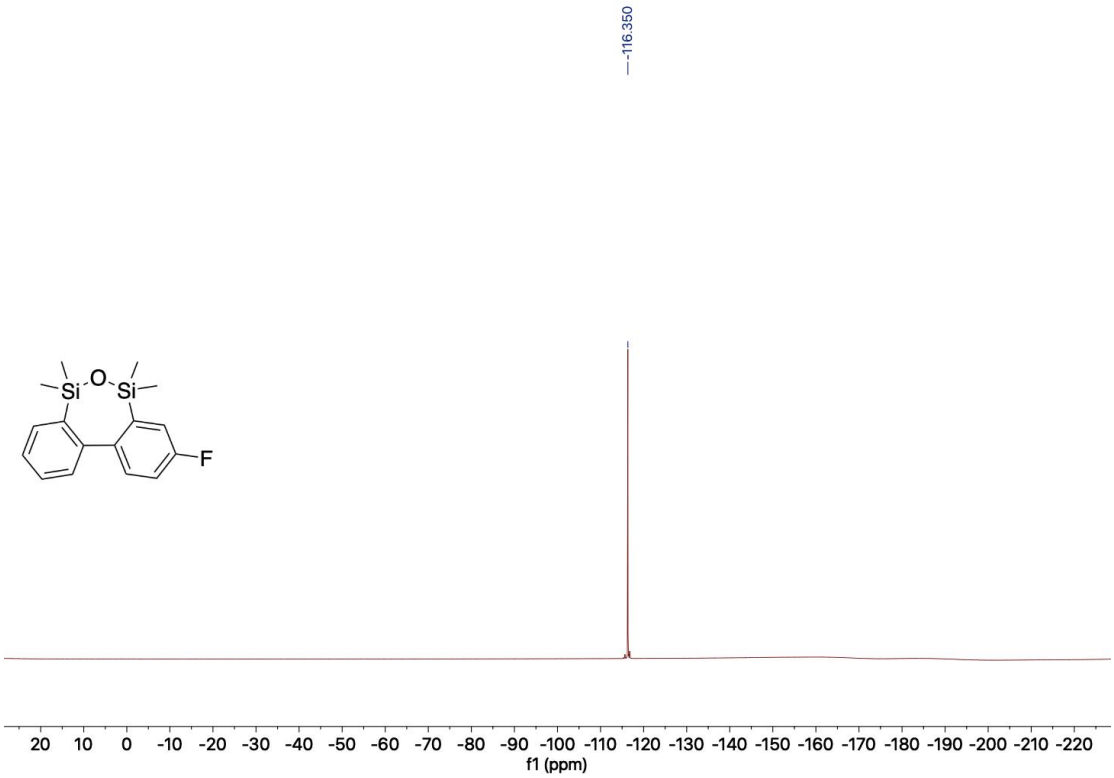
^{1}H NMR of **3m** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3m** (125 MHz, $CDCl_3$)



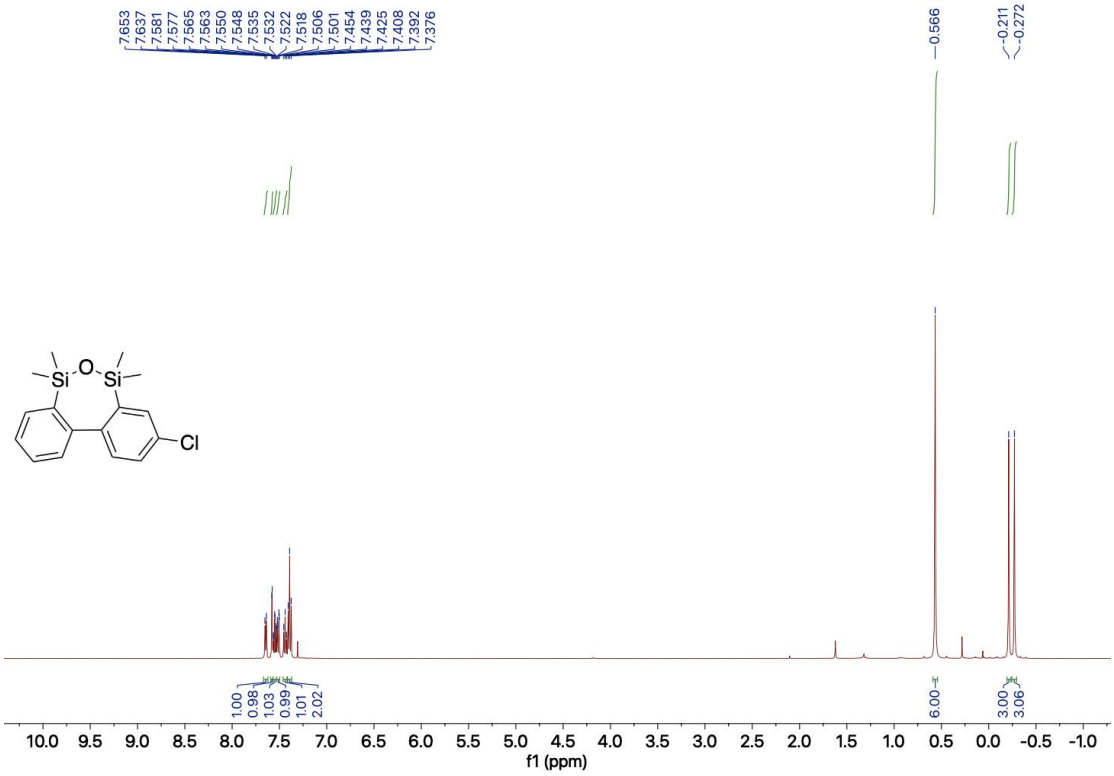


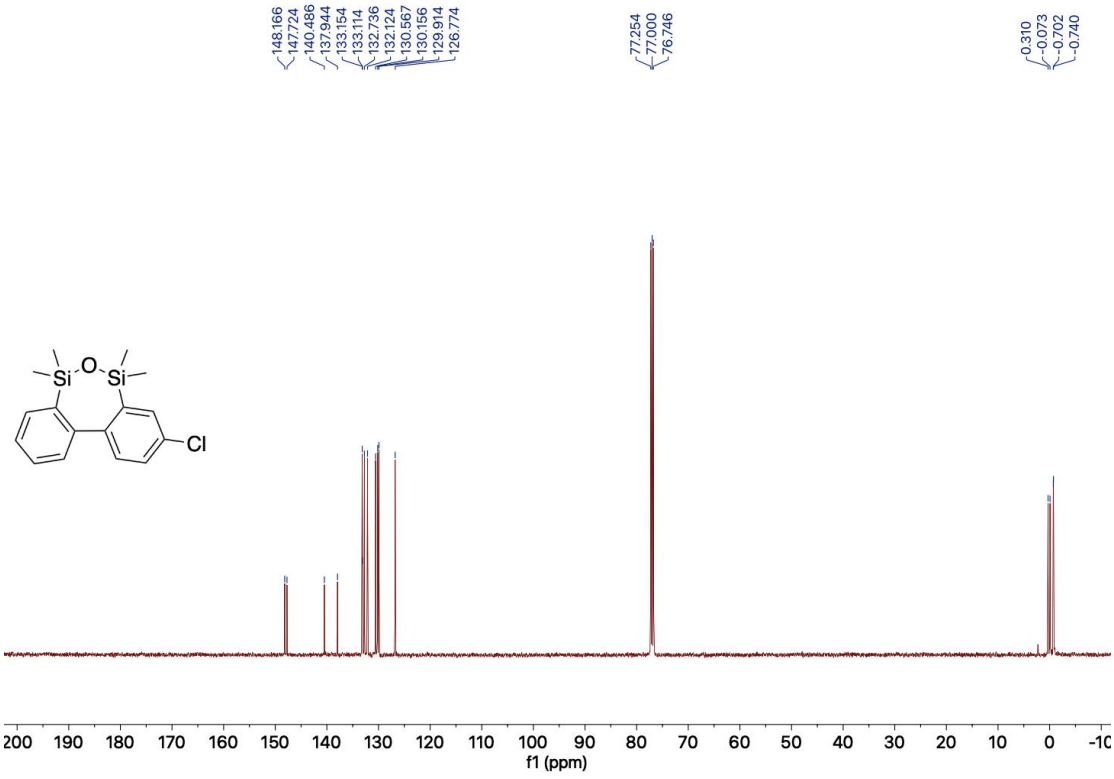
^{1}H NMR of **3n** (500 MHz, $CDCl_3$), ^{13}C NMR of **3n** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3n** (470 MHz, $CDCl_3$)



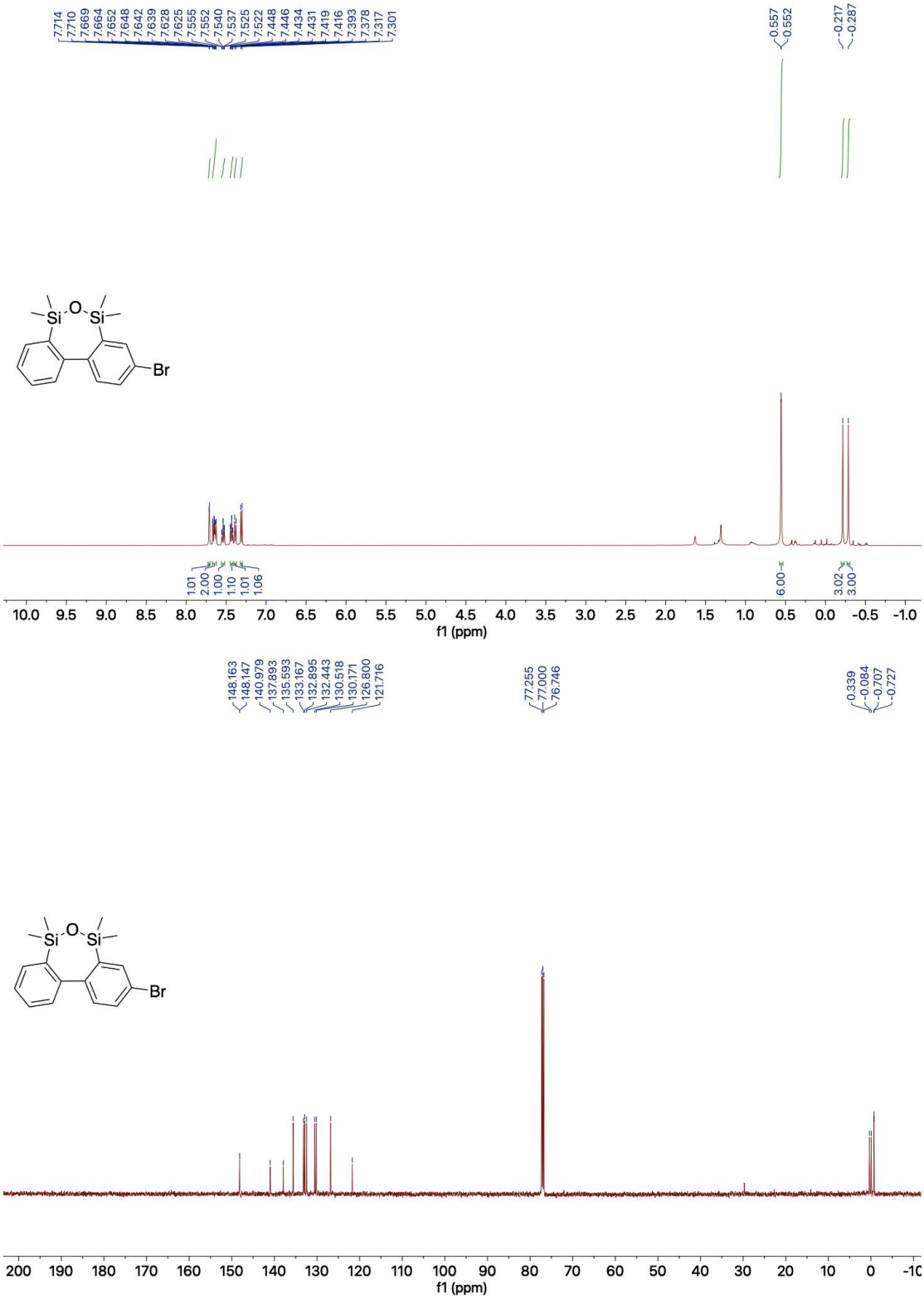

-116.350
Si
O
Si
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

^{1}H NMR of **3o** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3o** (125 MHz, $CDCl_3$)

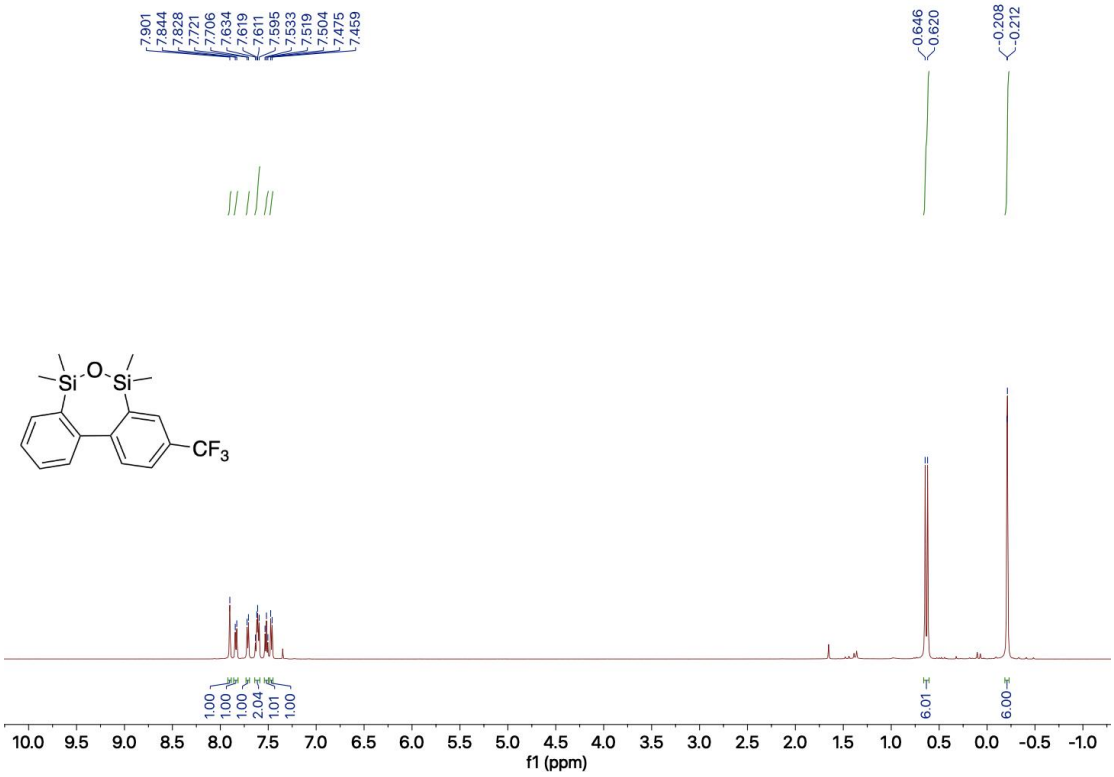


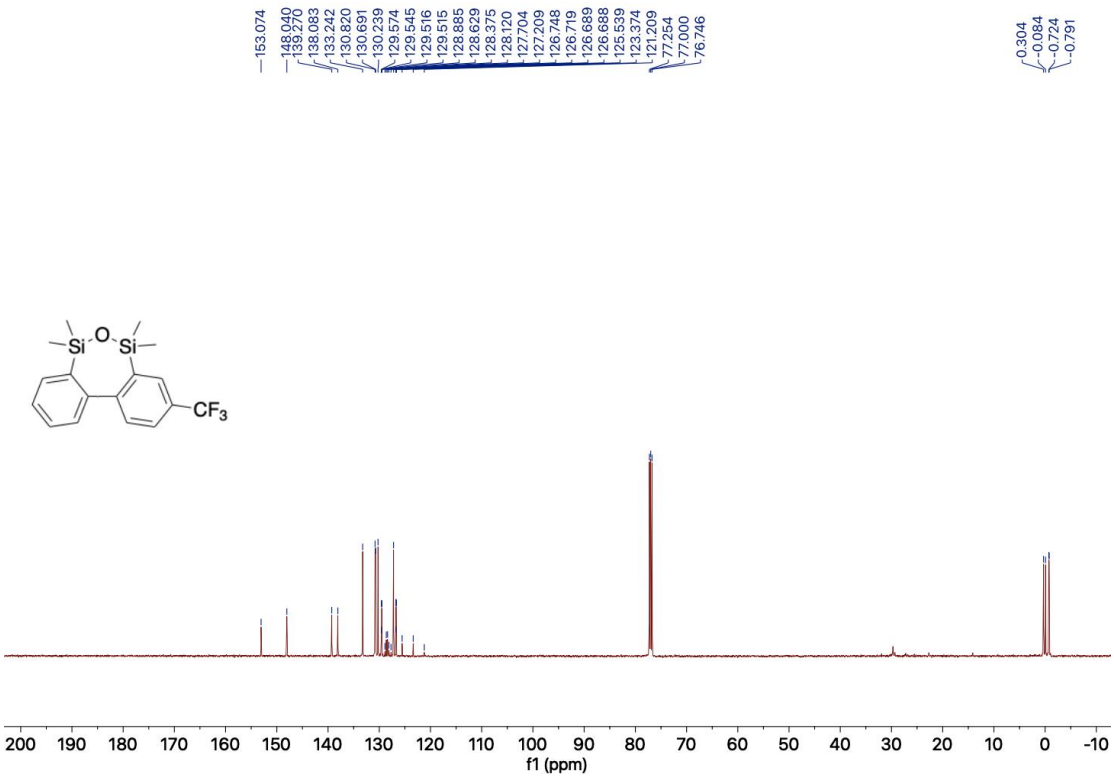


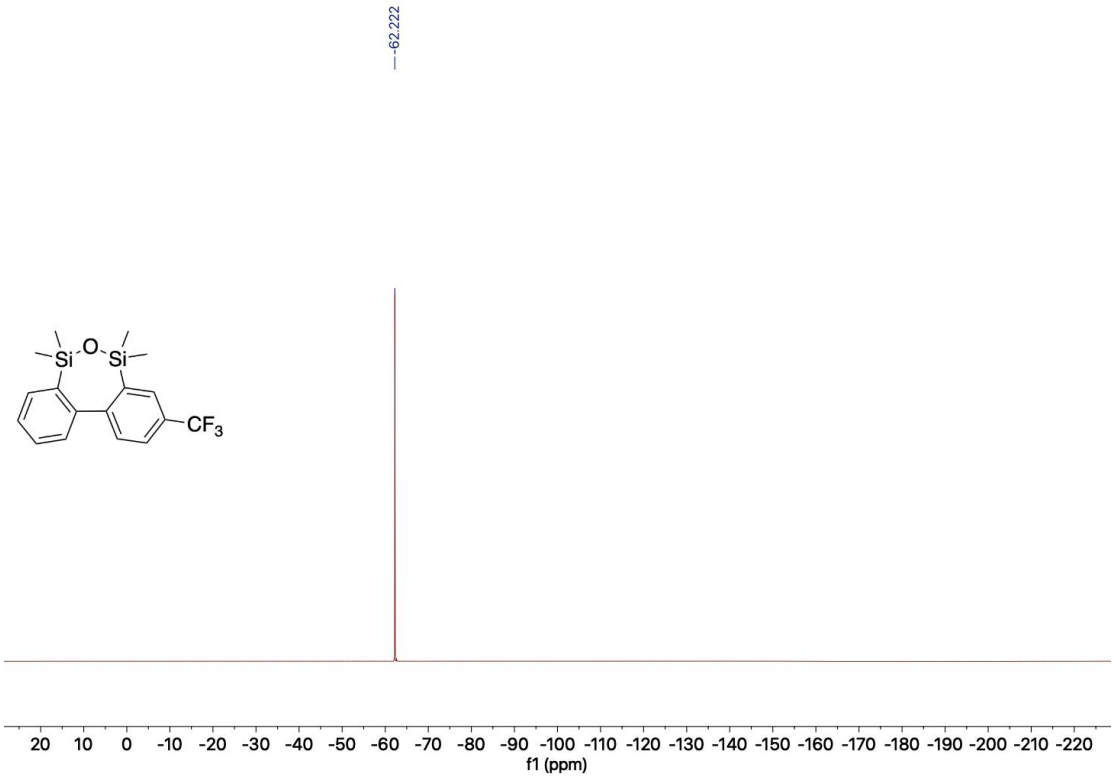
^{1}H NMR of **3p** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3p** (125 MHz, $CDCl_3$)



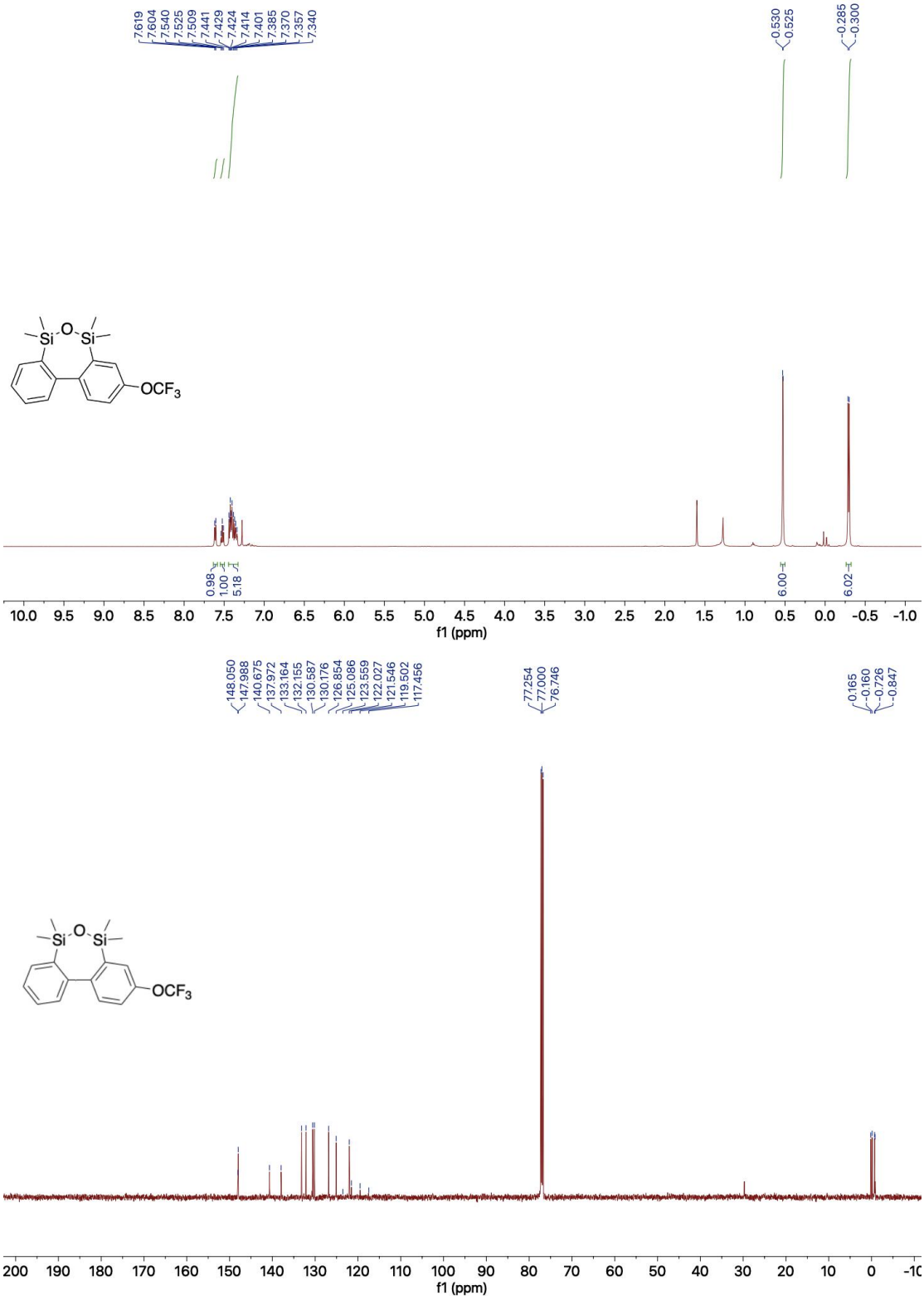
^{1}H NMR of **3q** (500 MHz, $CDCl_3$), ^{13}C NMR of **3q** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3q** (470 MHz, $CDCl_3$)

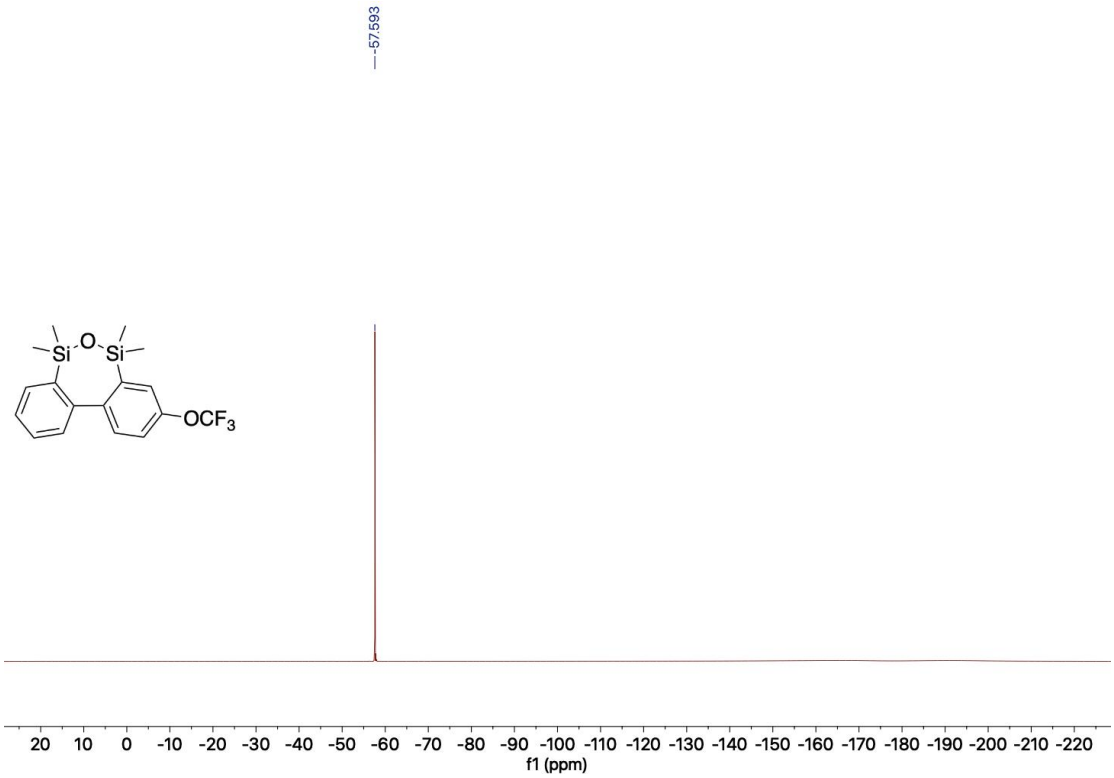




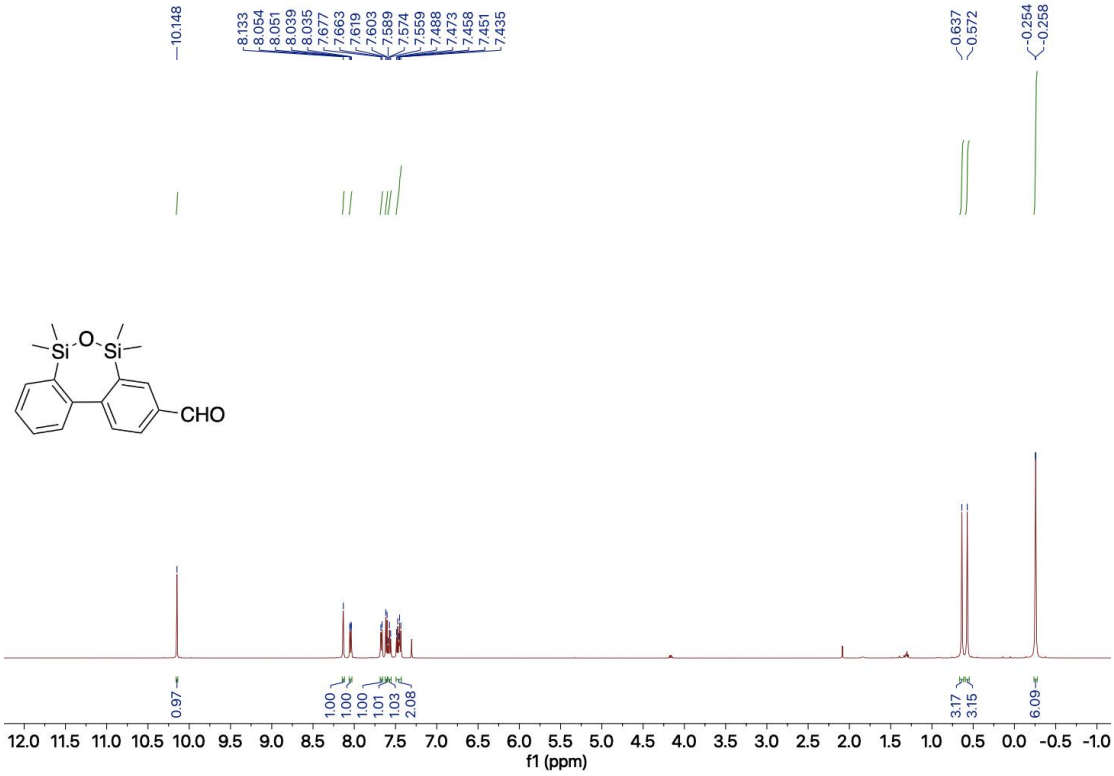

-62.222
Si
O
Si
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

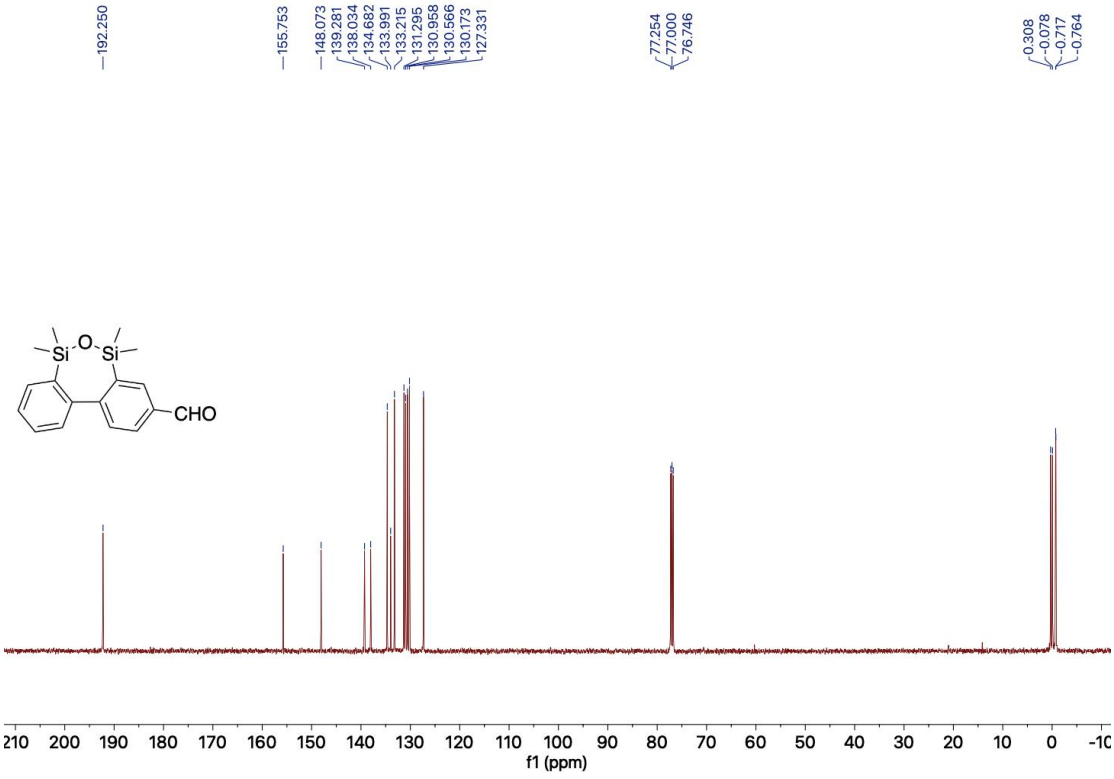
^{1}H NMR of **3r** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3r** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3r** (470 MHz, $CDCl_3$)



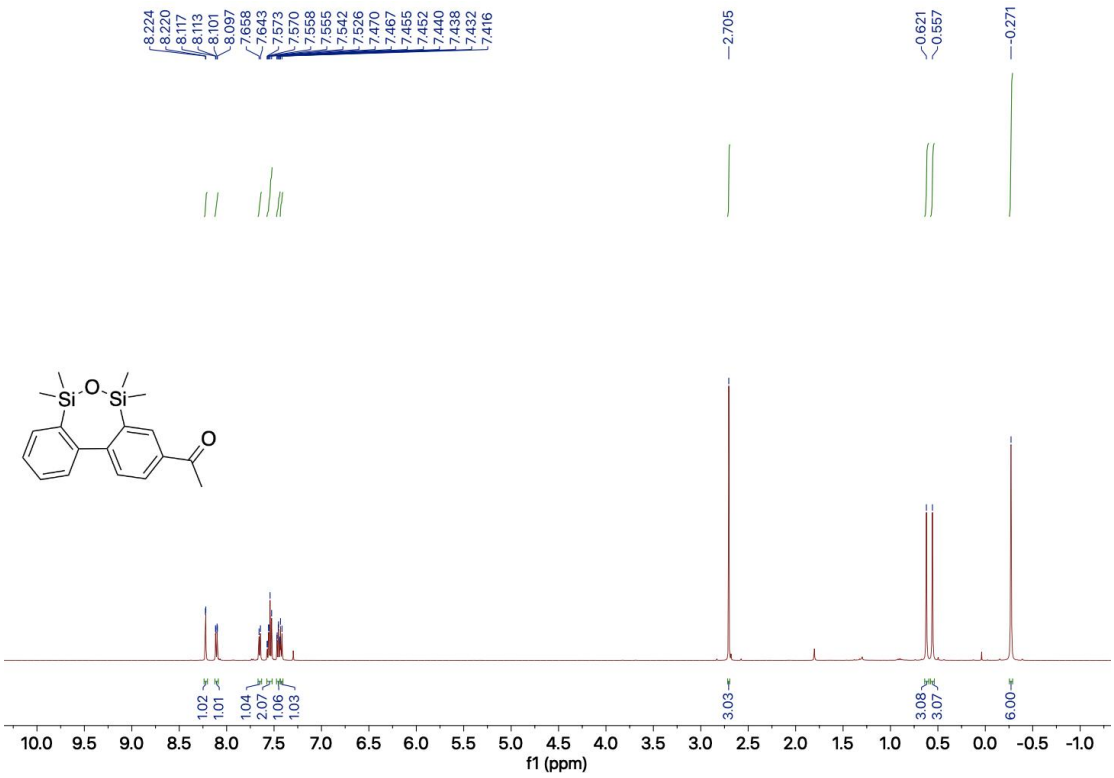

-57.593
Si
O
Si
OCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

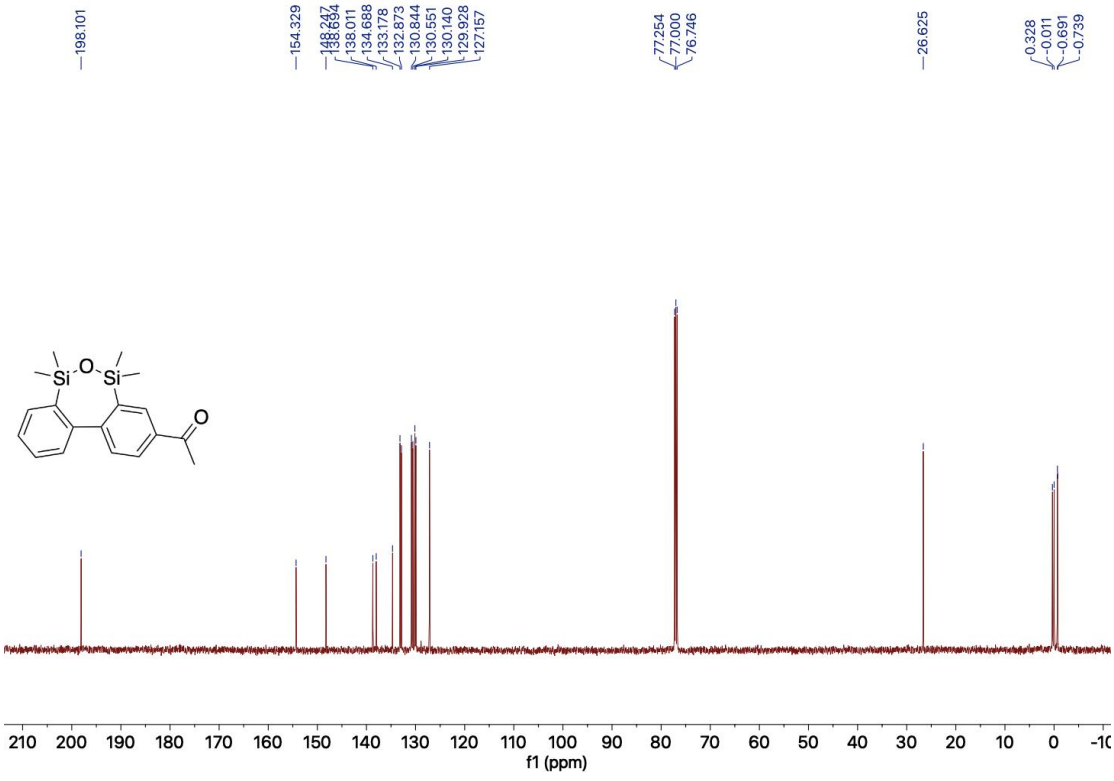
^{1}H NMR of **3s** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3s** (125 MHz, $CDCl_3$)



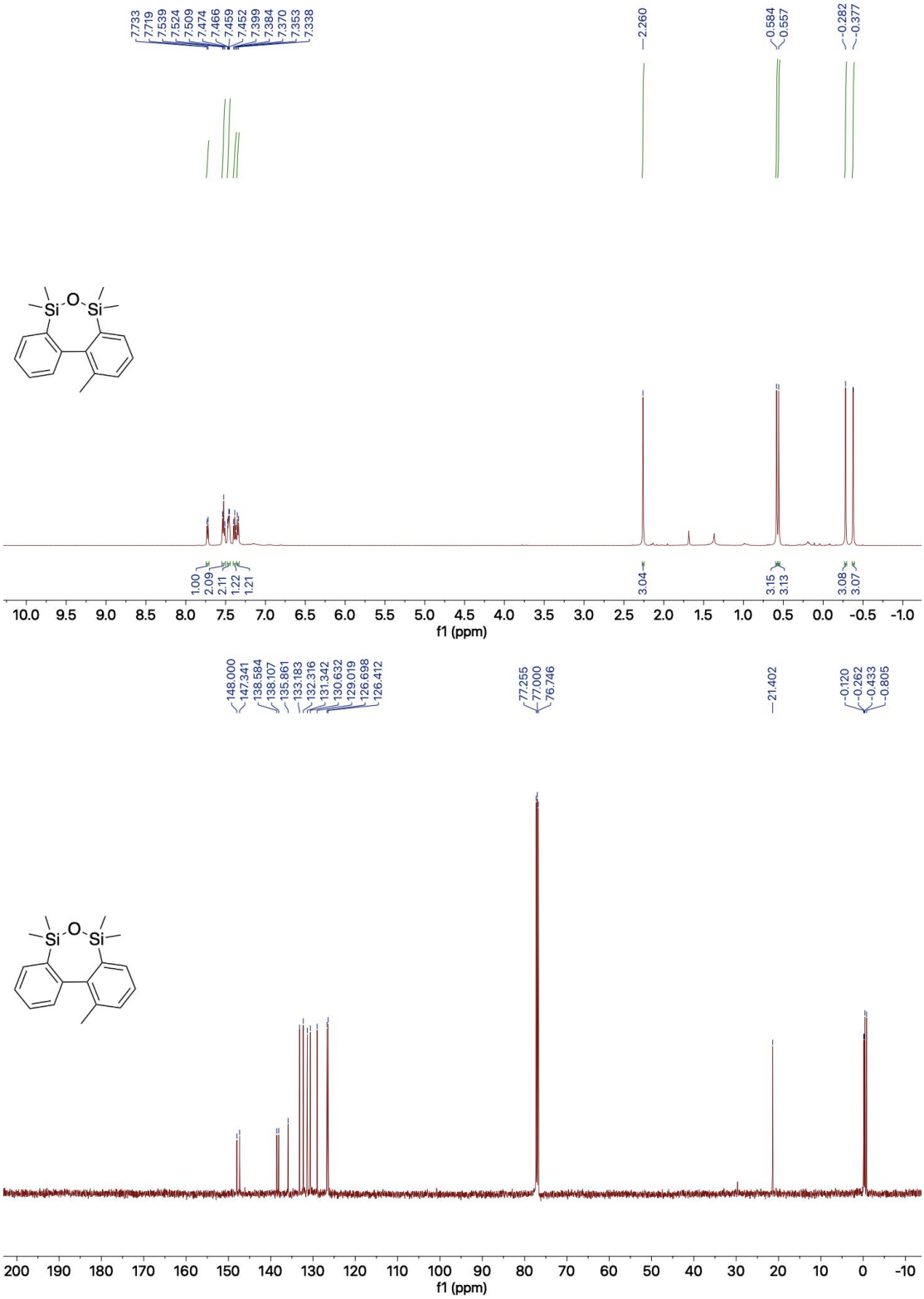


^{1}H NMR of **3t** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3t** (125 MHz, $CDCl_3$)

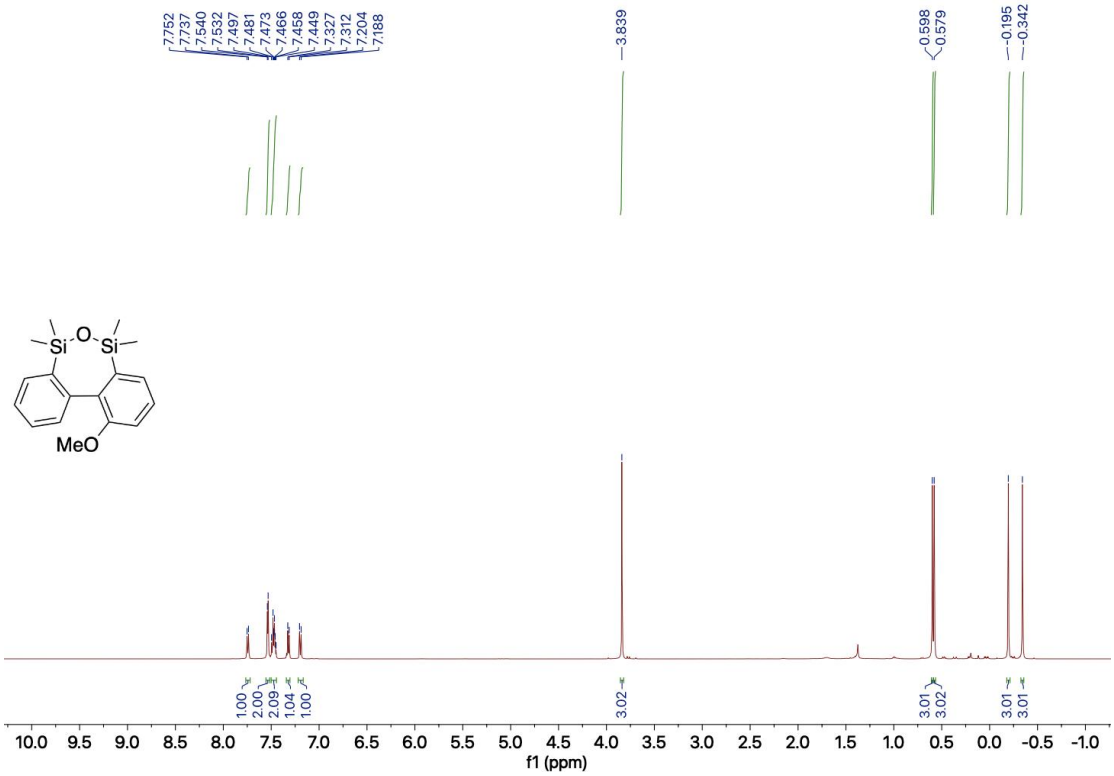


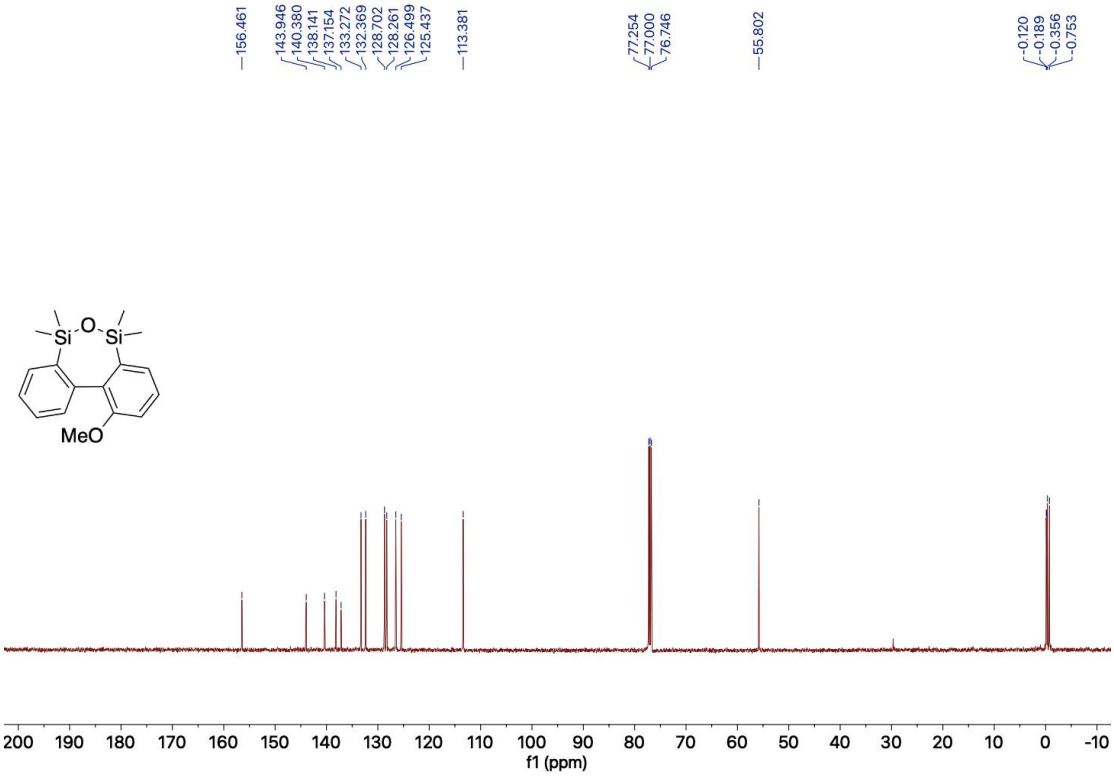


^{1}H NMR of **3u** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3u** (125 MHz, $CDCl_3$)

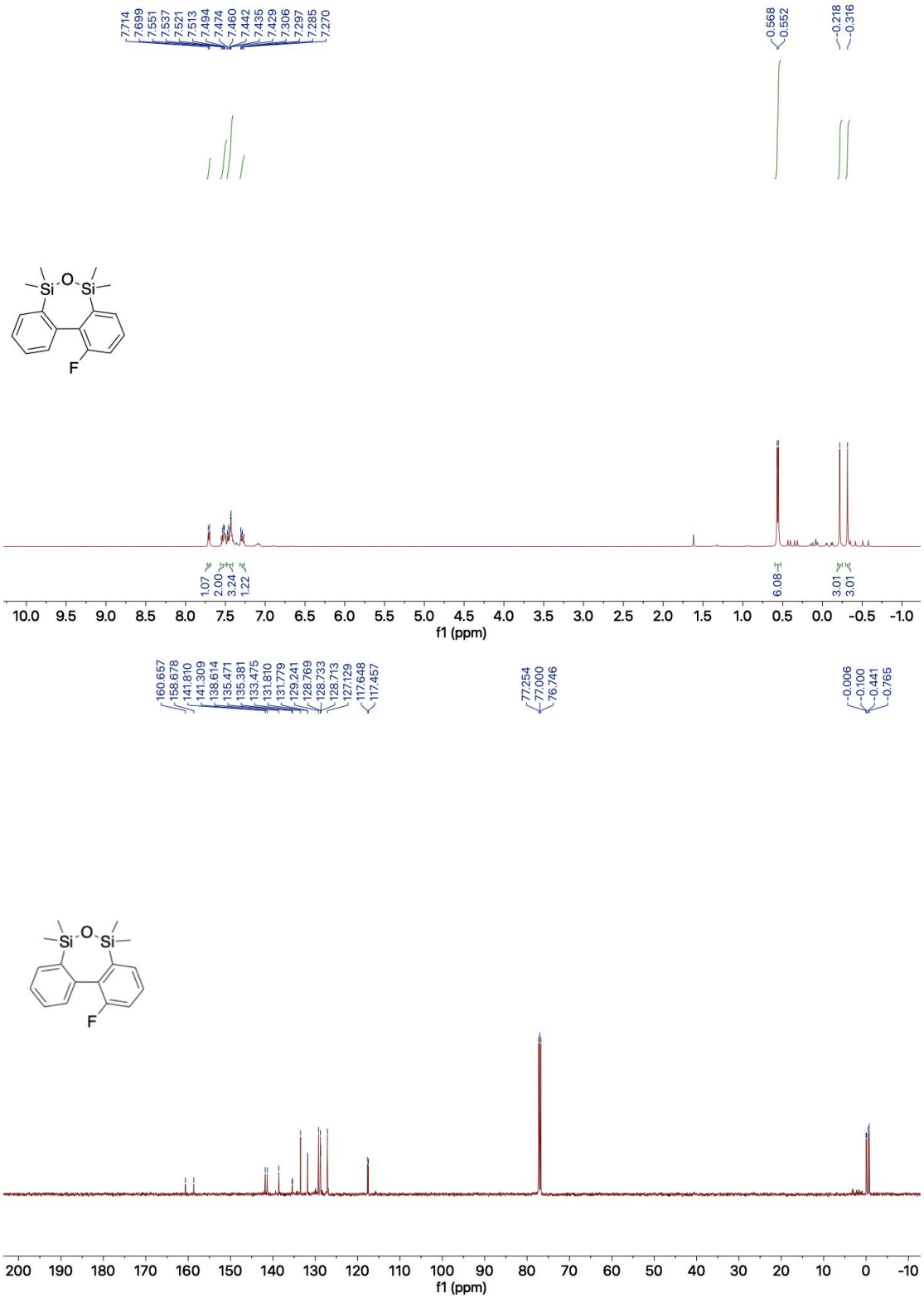


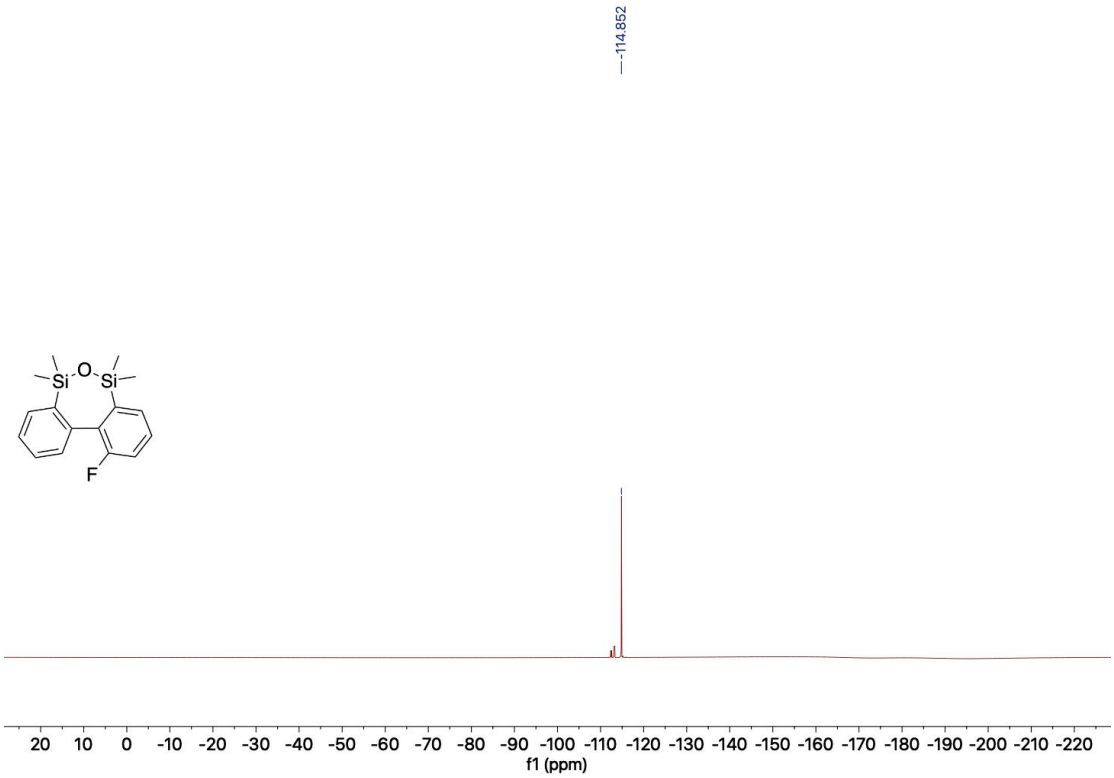
^{1}H NMR of **3v** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3v** (125 MHz, $CDCl_3$)



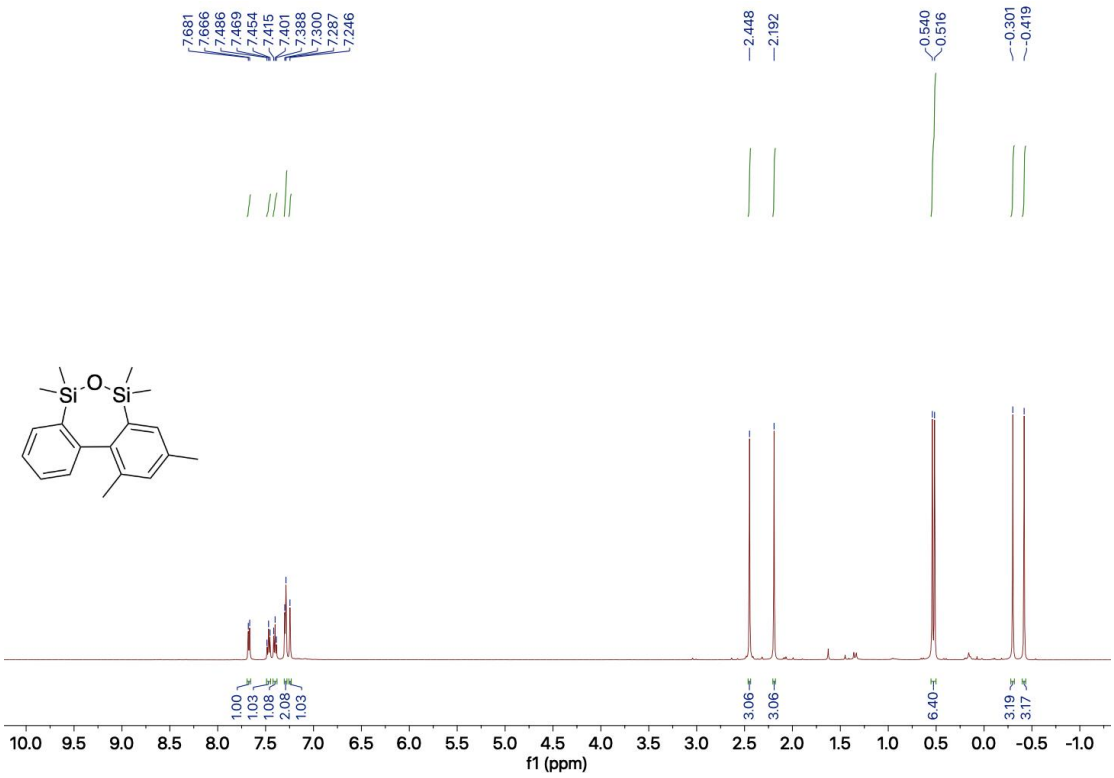


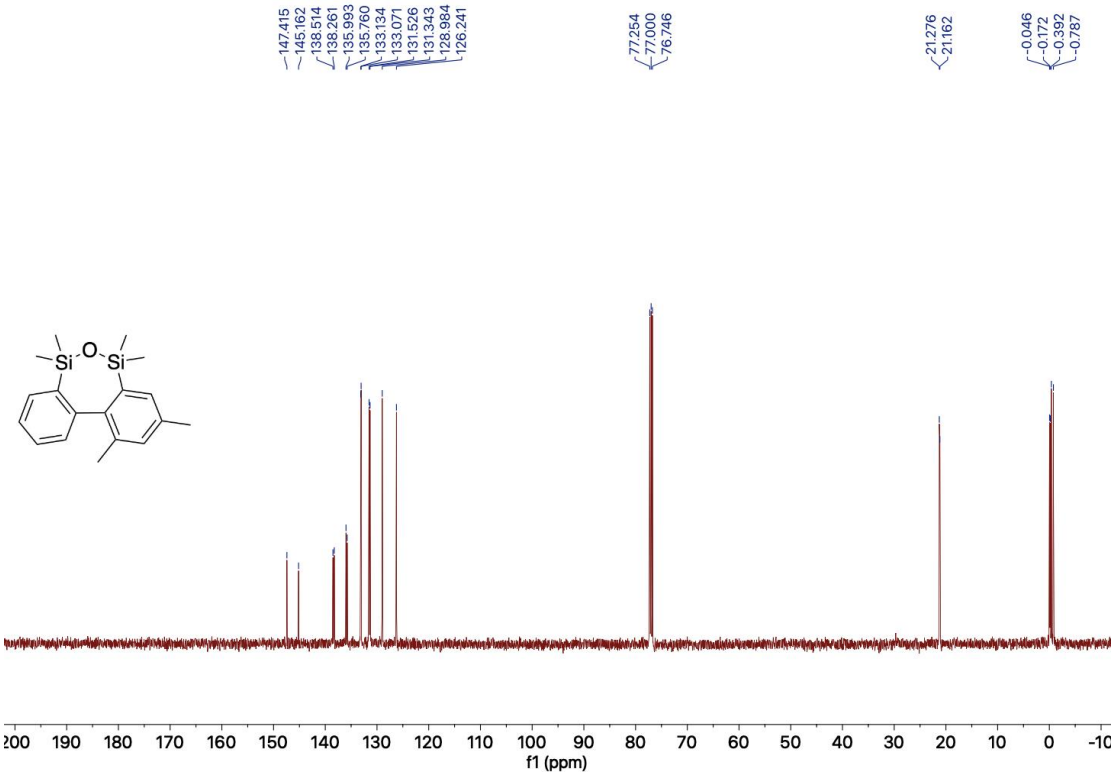
^{1}H NMR of **3w** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3w** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3w** (470 MHz, $CDCl_3$)



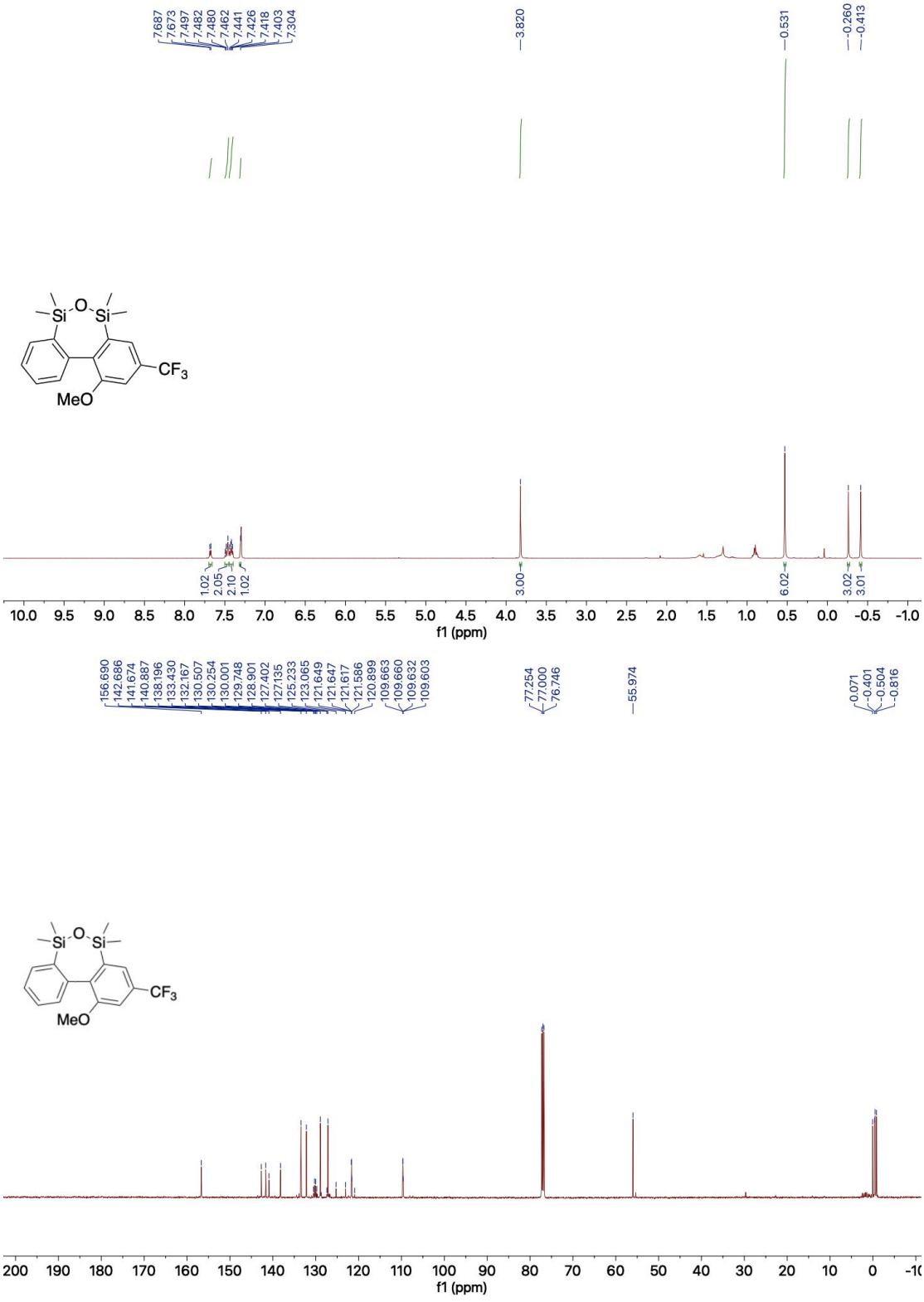

-114.852
Si
O
Si
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

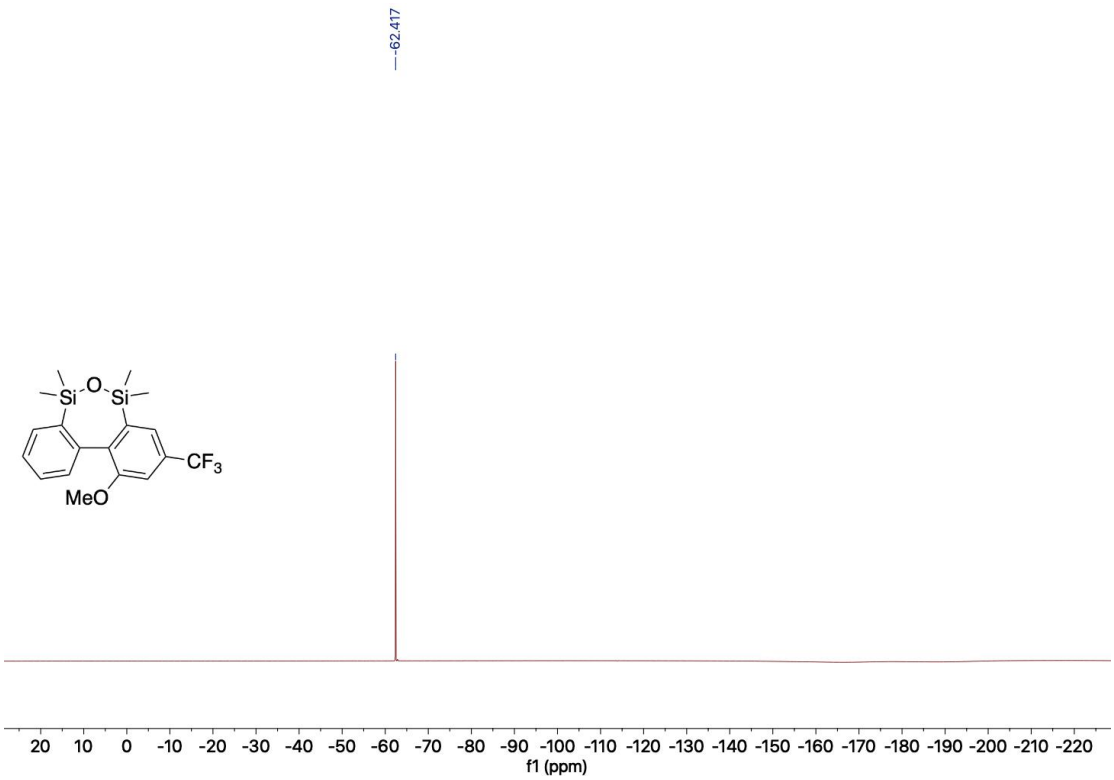
^{1}H NMR of **3x** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3x** (125 MHz, $CDCl_3$)



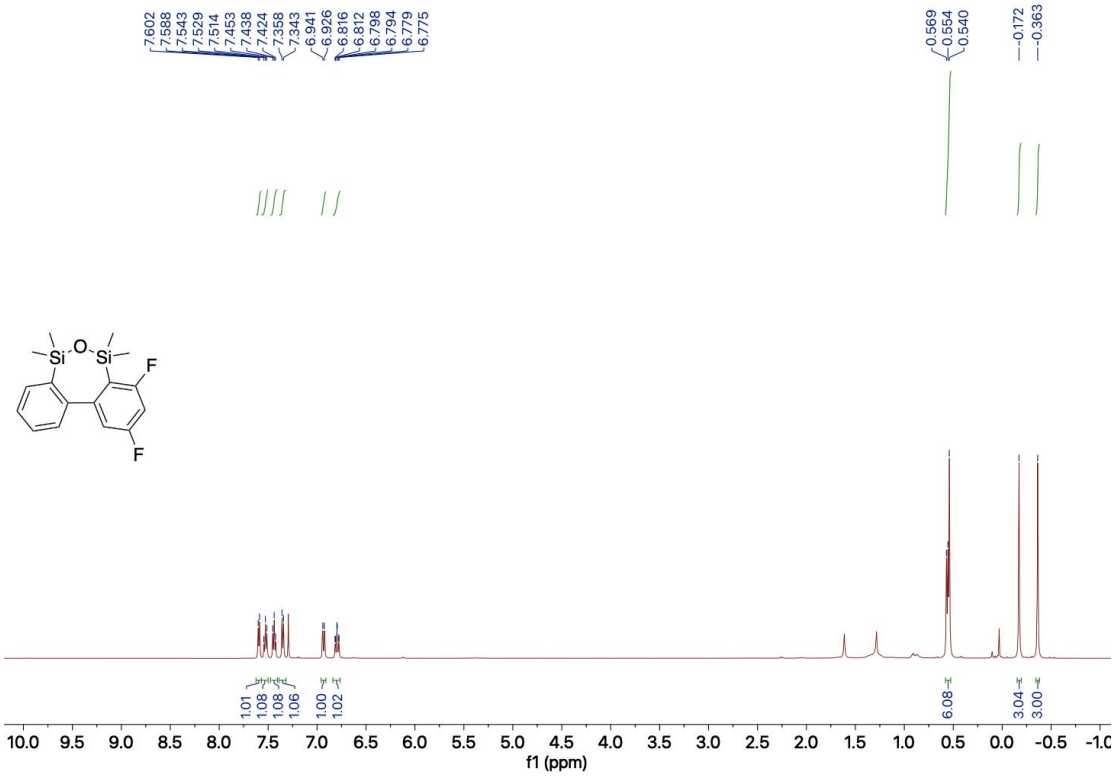


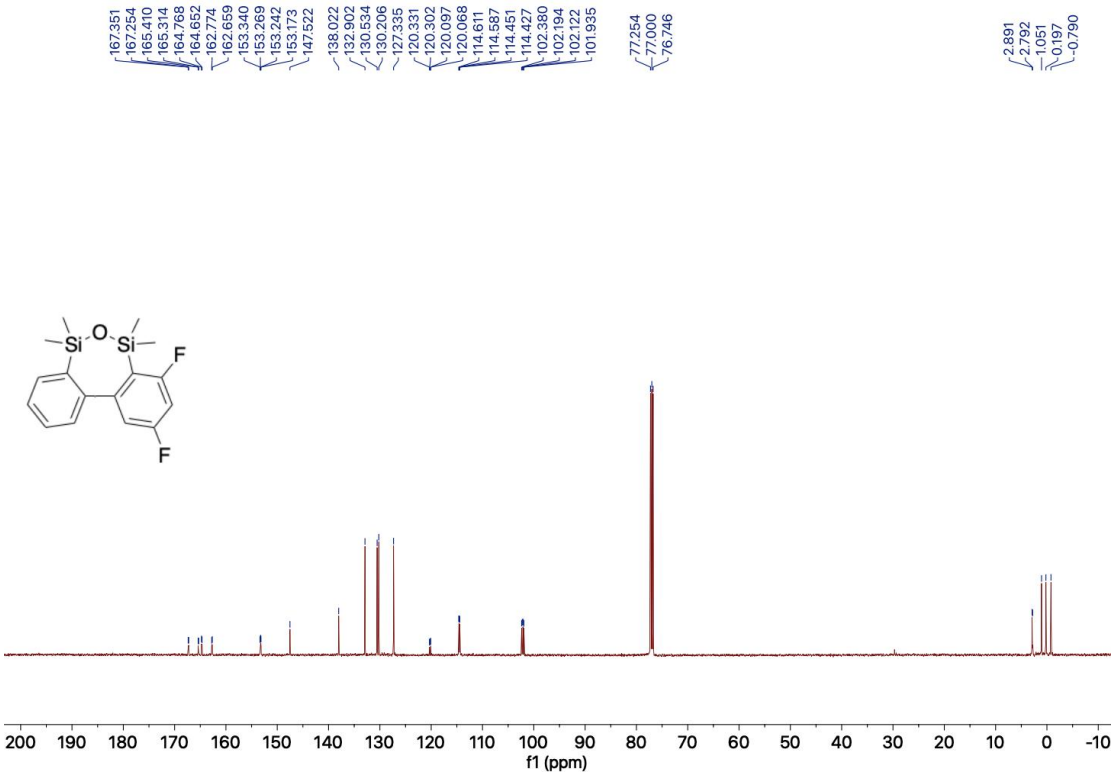
^{1}H NMR of **3y** (500 MHz, $CDCl_3$), ^{13}C NMR of **3y** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3y** (470 MHz, $CDCl_3$)

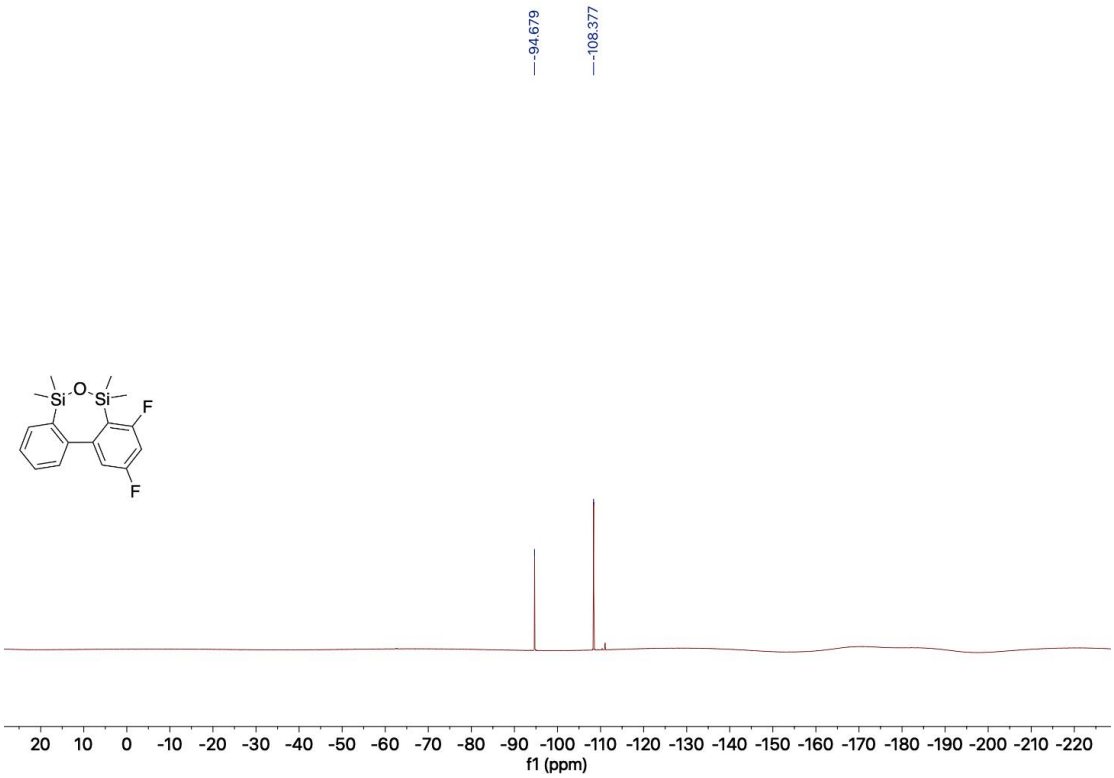



-62.417
Si
O
Si
CF3
MeO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

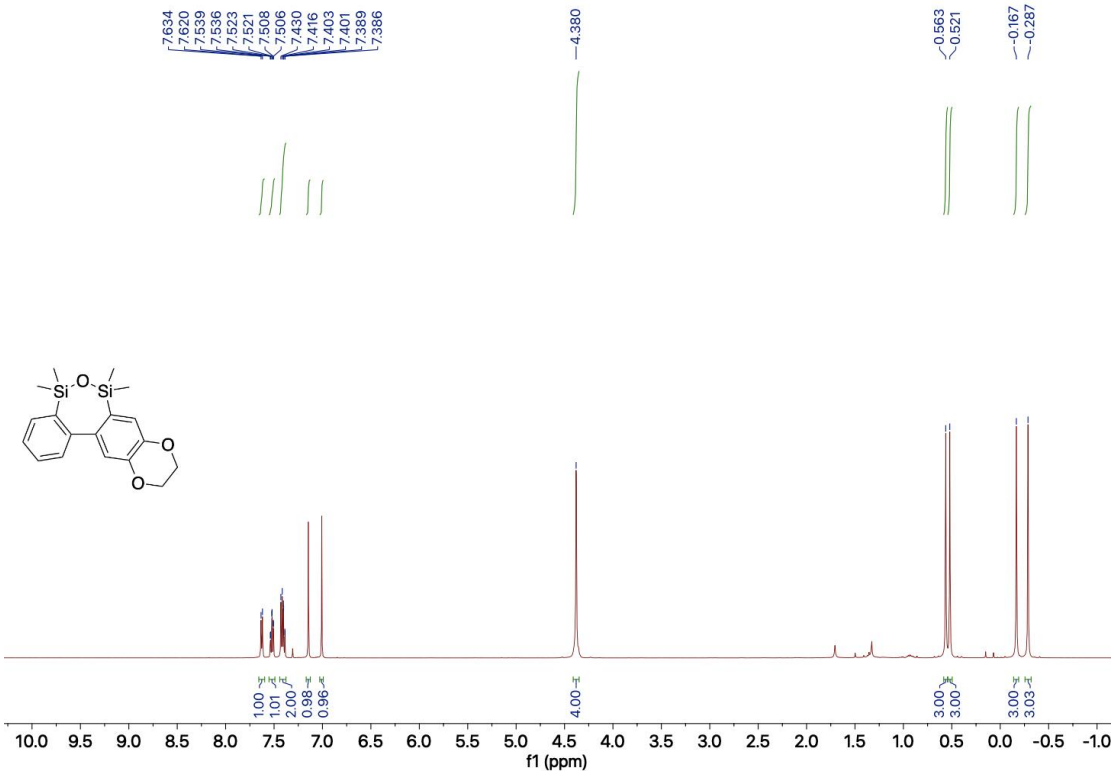
^{1}H NMR of **3z** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3z** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3z** (470 MHz, $CDCl_3$)

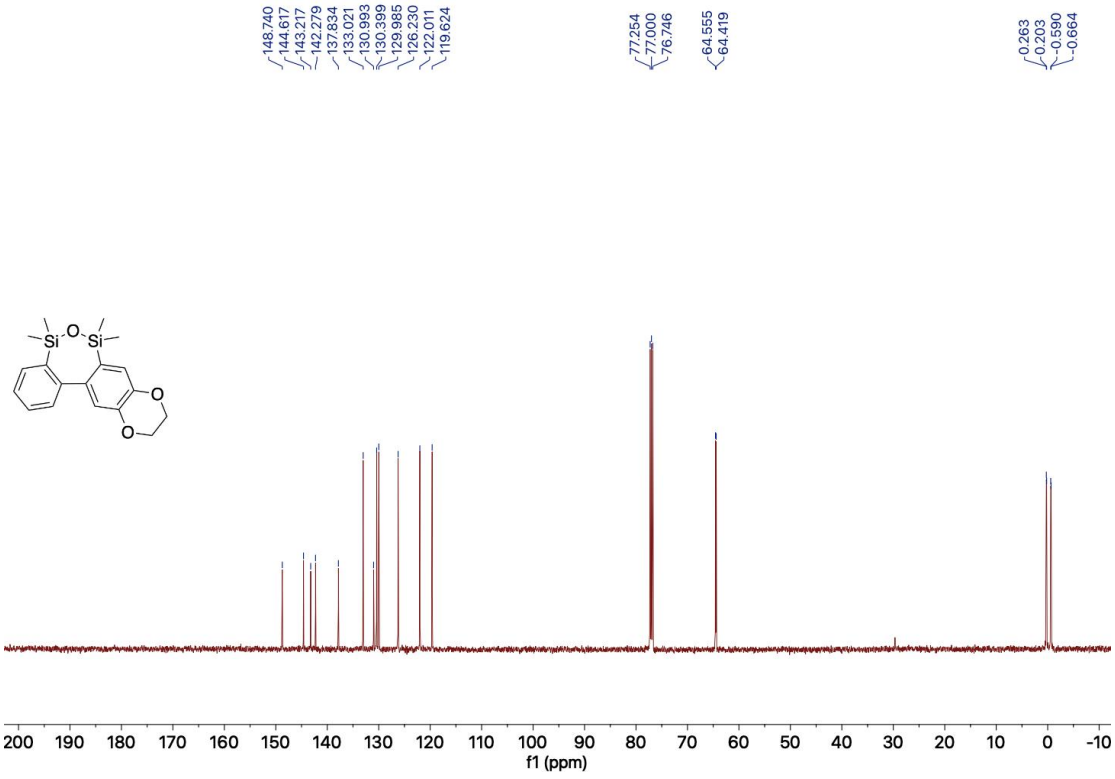




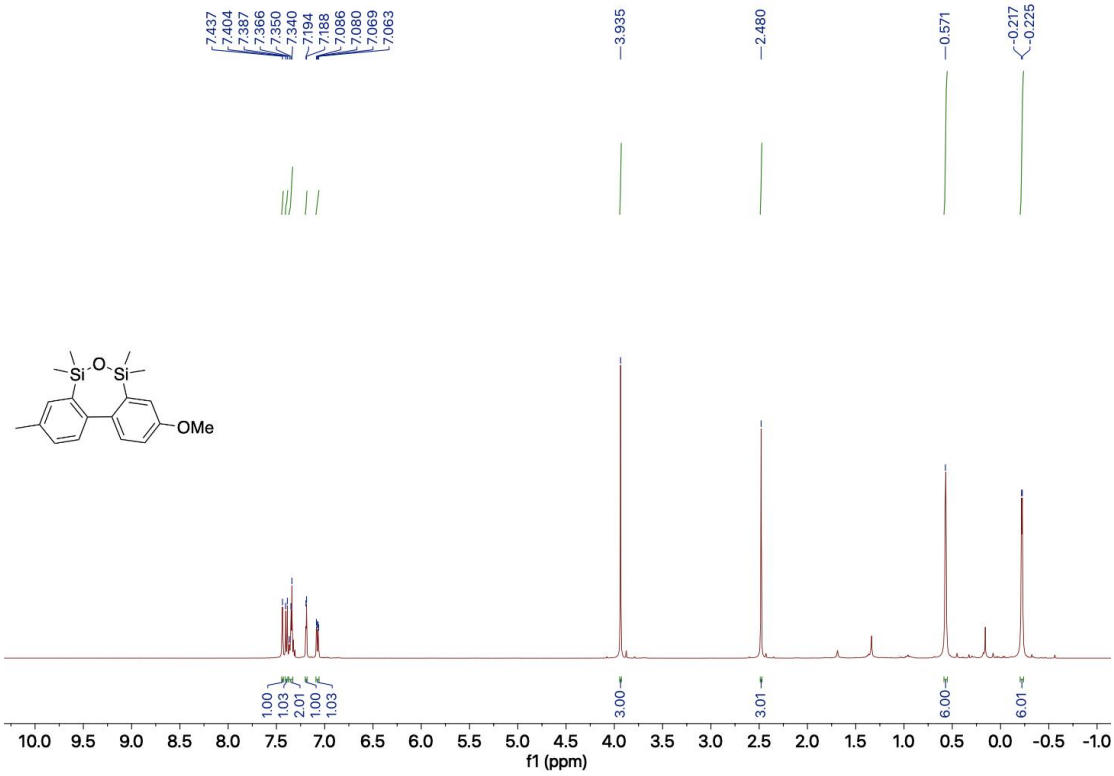

-94.679
-108.377
Si
O
Si
F
F
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

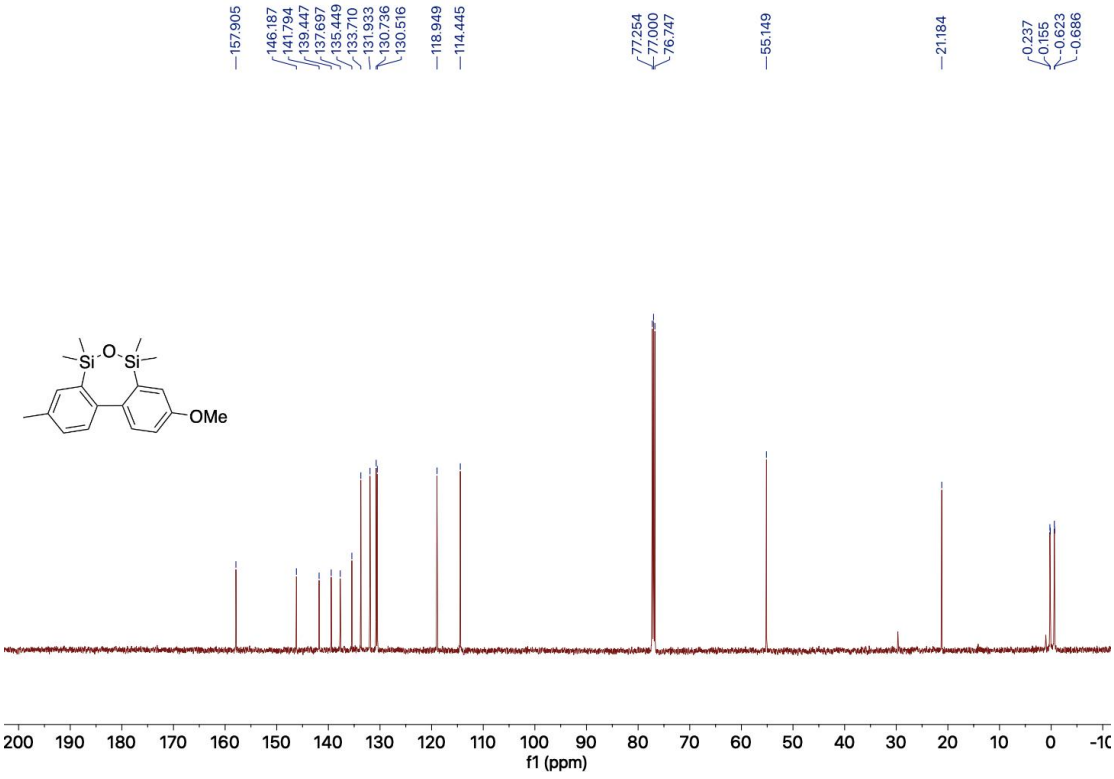
^{1}H NMR of **3A** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3A** (125 MHz, $CDCl_3$)



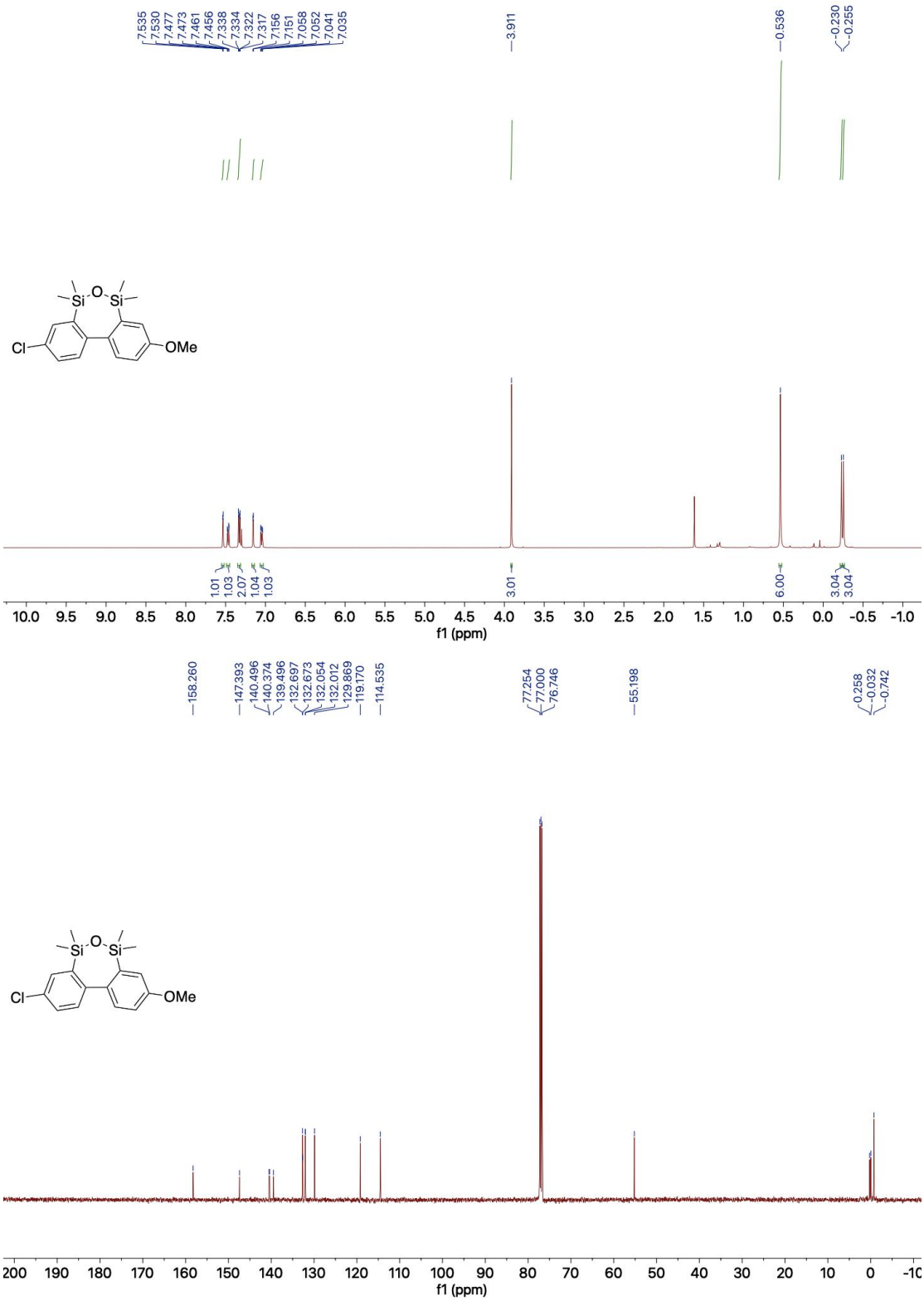


^{1}H NMR of **3B** (500 MHz, $CDCl_3$) and ^{13}C NMR of **3B** (125 MHz, $CDCl_3$)

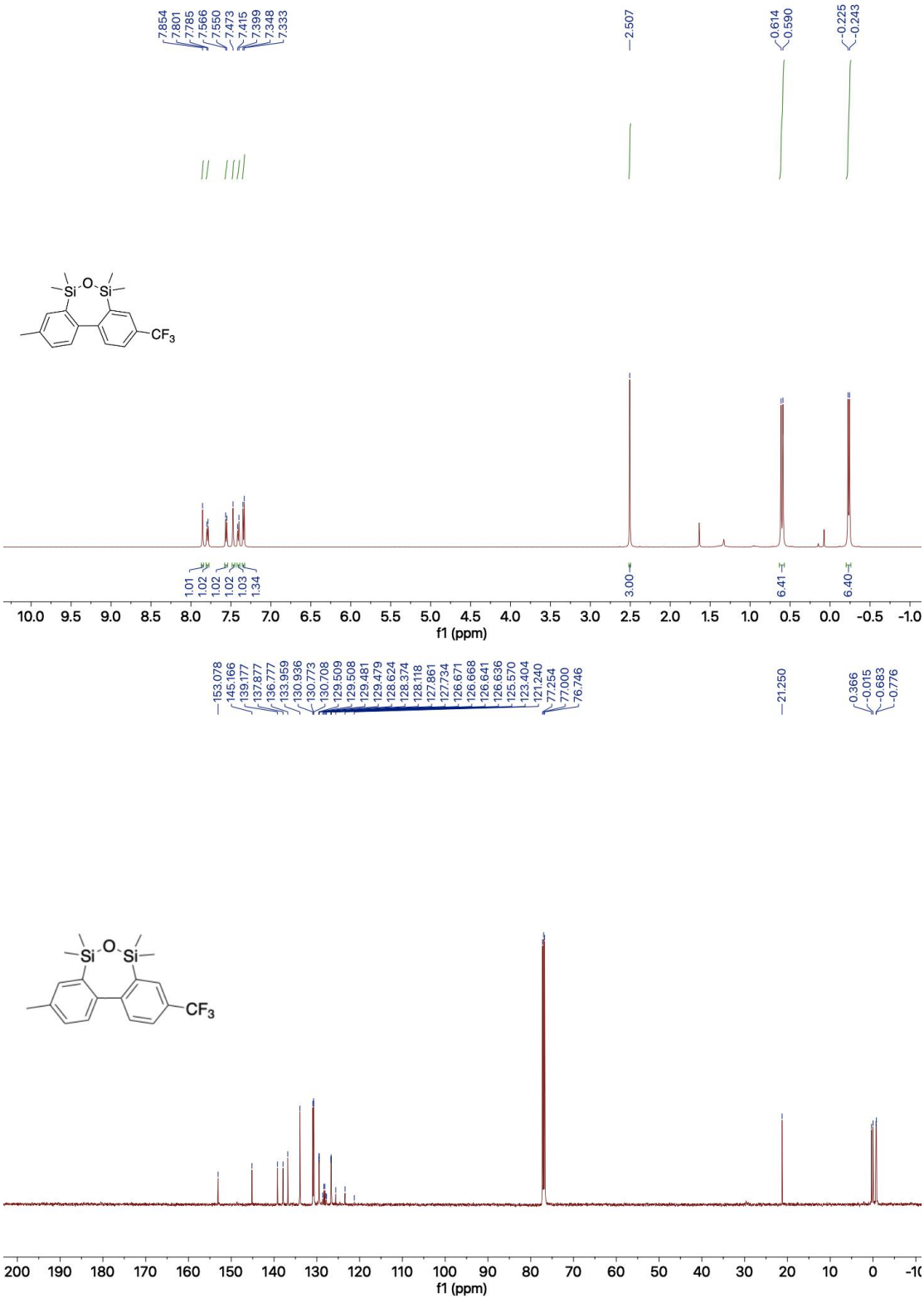


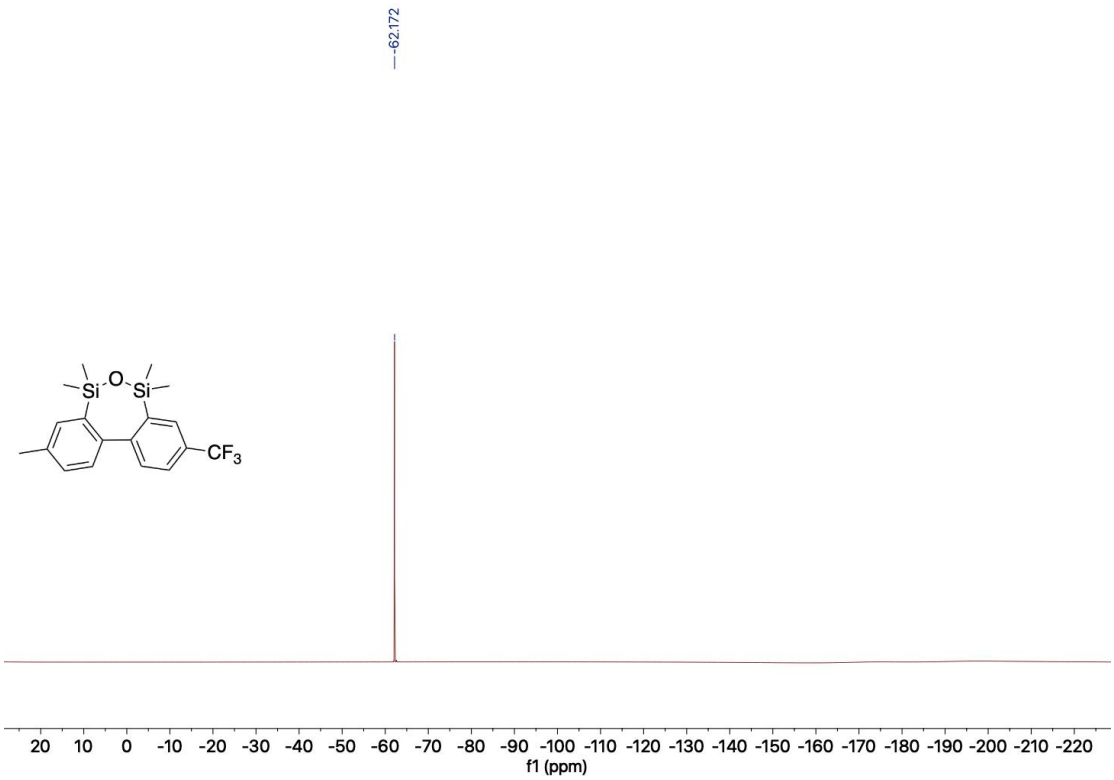


^{1}H NMR of **3C** (500 MHz, $CDCl_3$), ^{13}C NMR of **3C** (125 MHz, $CDCl_3$)

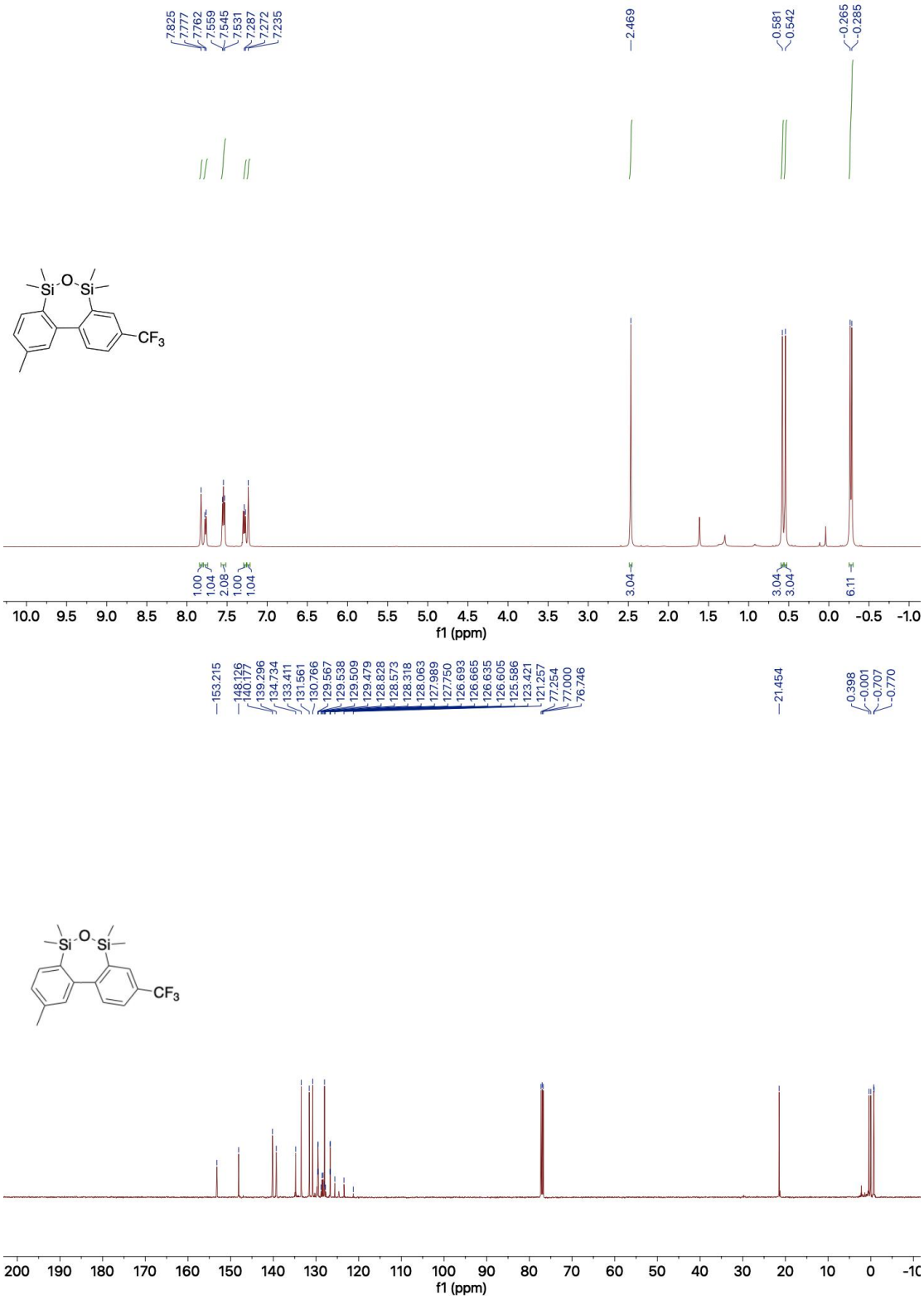


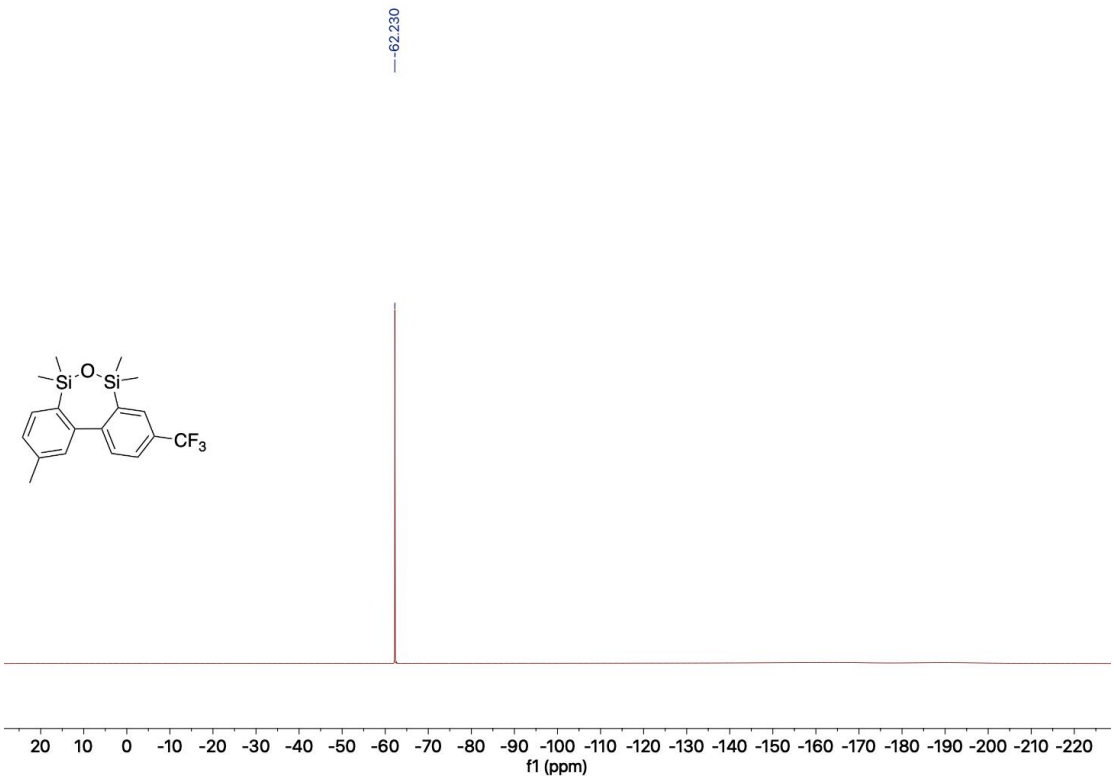
^{1}H NMR of **3D** (500 MHz, $CDCl_3$), ^{13}C NMR of **3D** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3D** (470 MHz, $CDCl_3$)



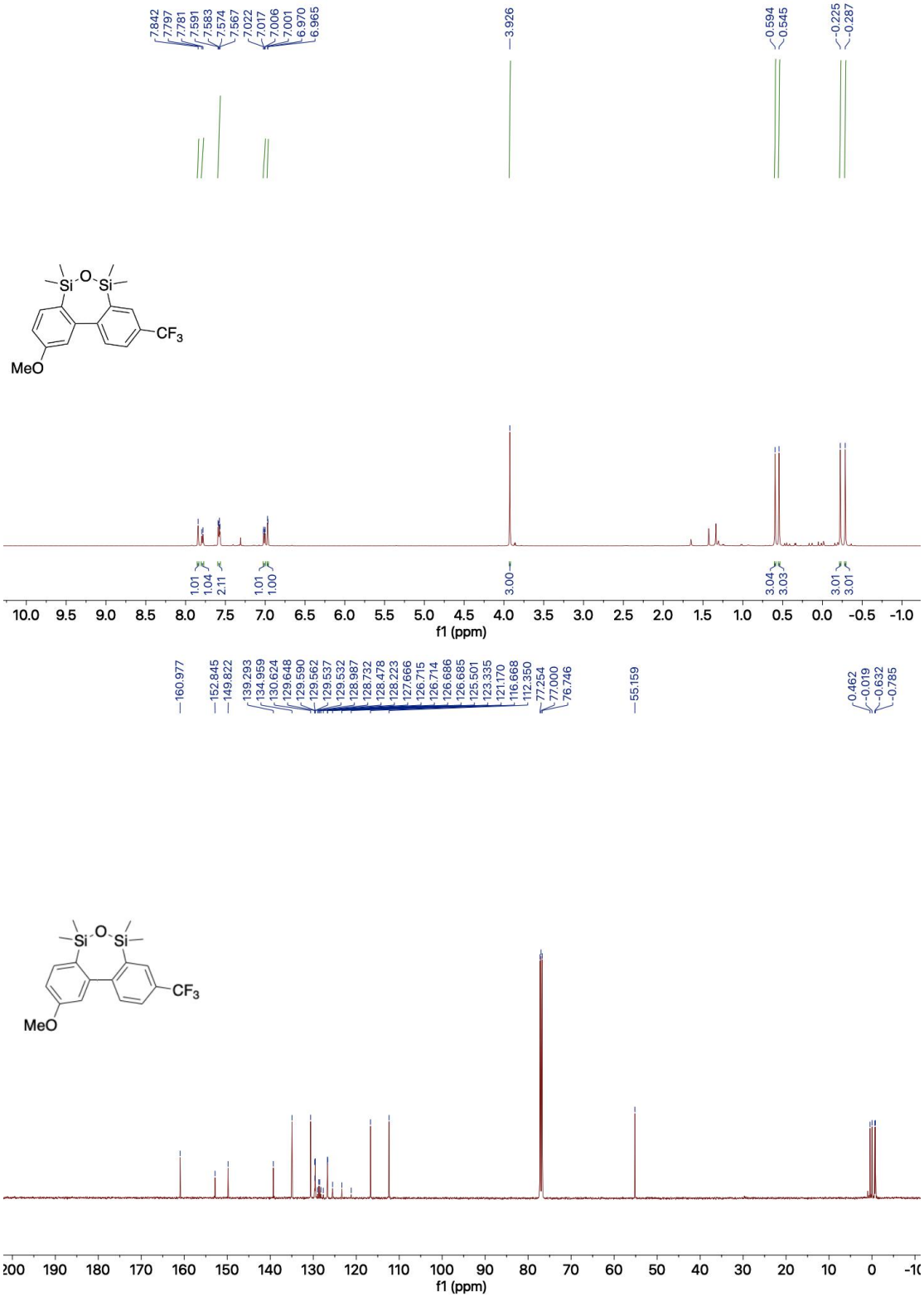

-62.172
Si
O
Si
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

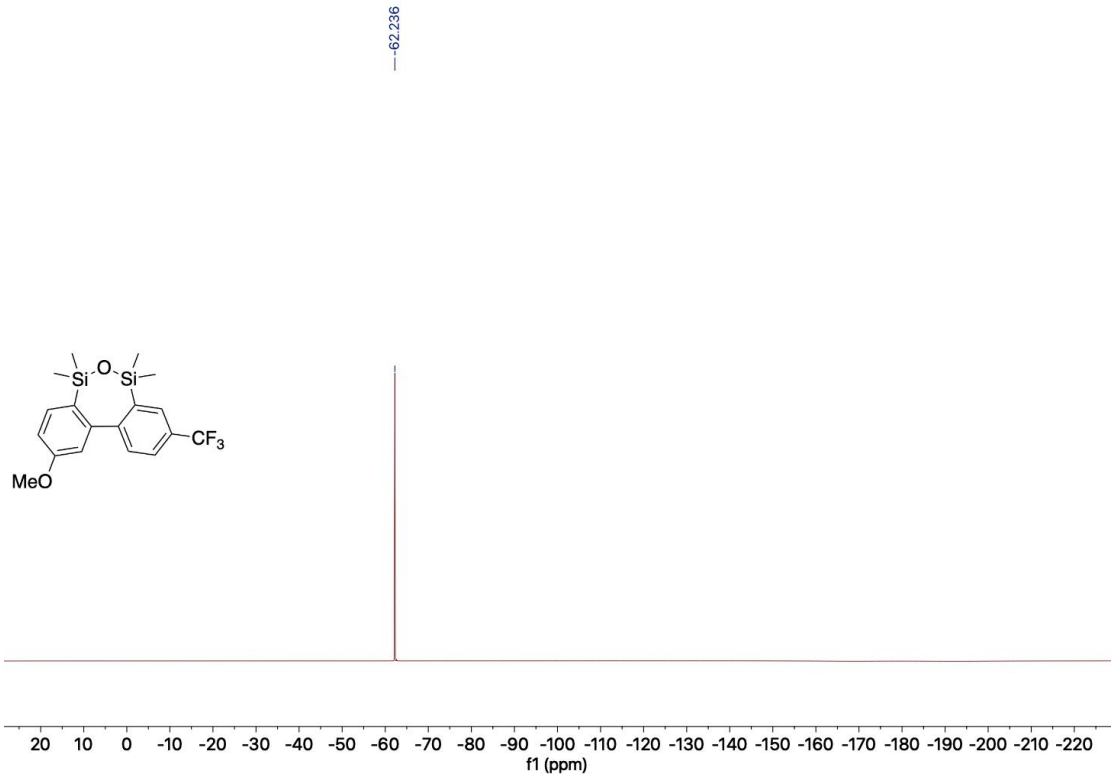
^{1}H NMR of **3E** (500 MHz, $CDCl_3$), ^{13}C NMR of **3E** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3E** (470 MHz, $CDCl_3$)



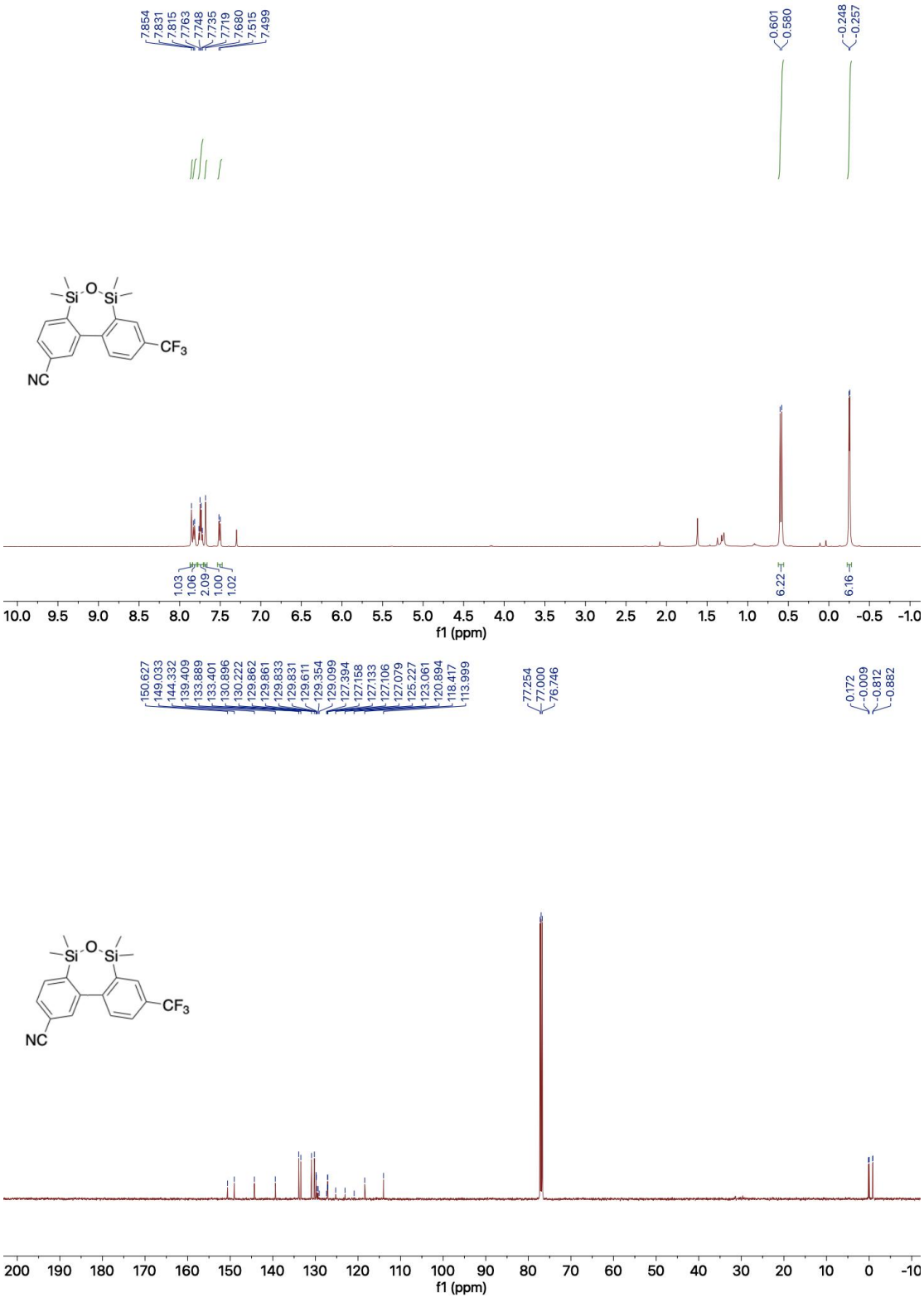

-62.230
Si
O
Si
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

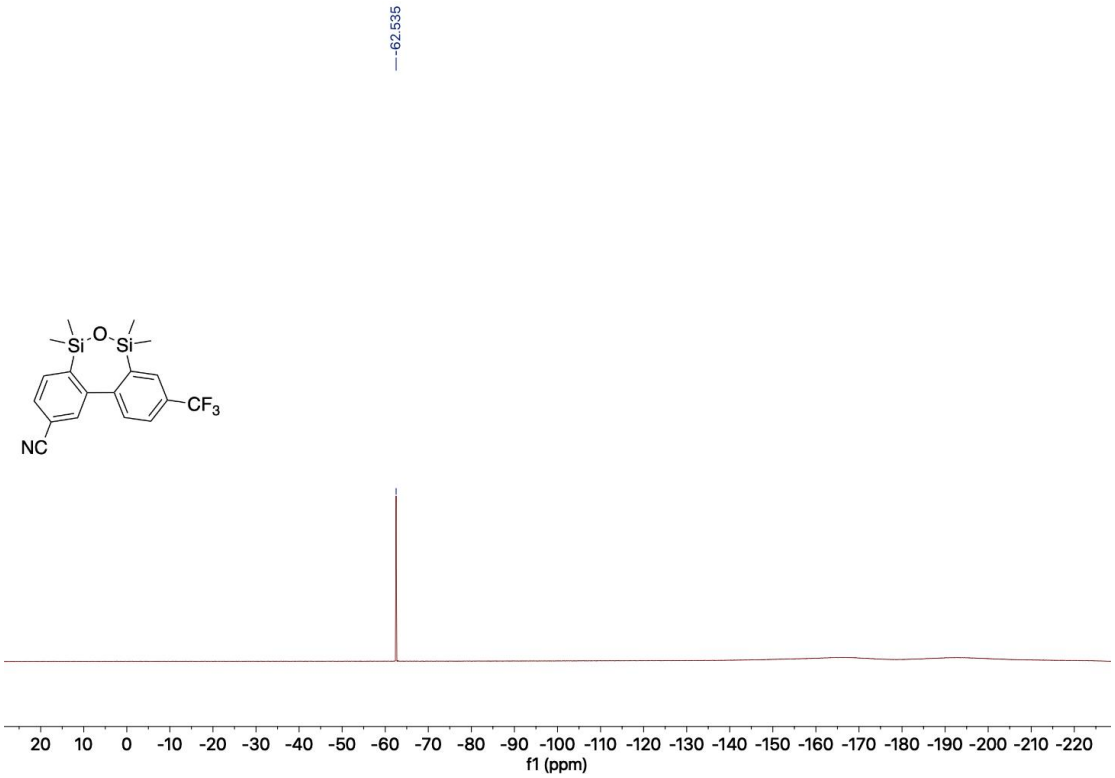
^{1}H NMR of **3F** (500 MHz, $CDCl_3$), ^{13}C NMR of **3F** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3F** (470 MHz, $CDCl_3$)



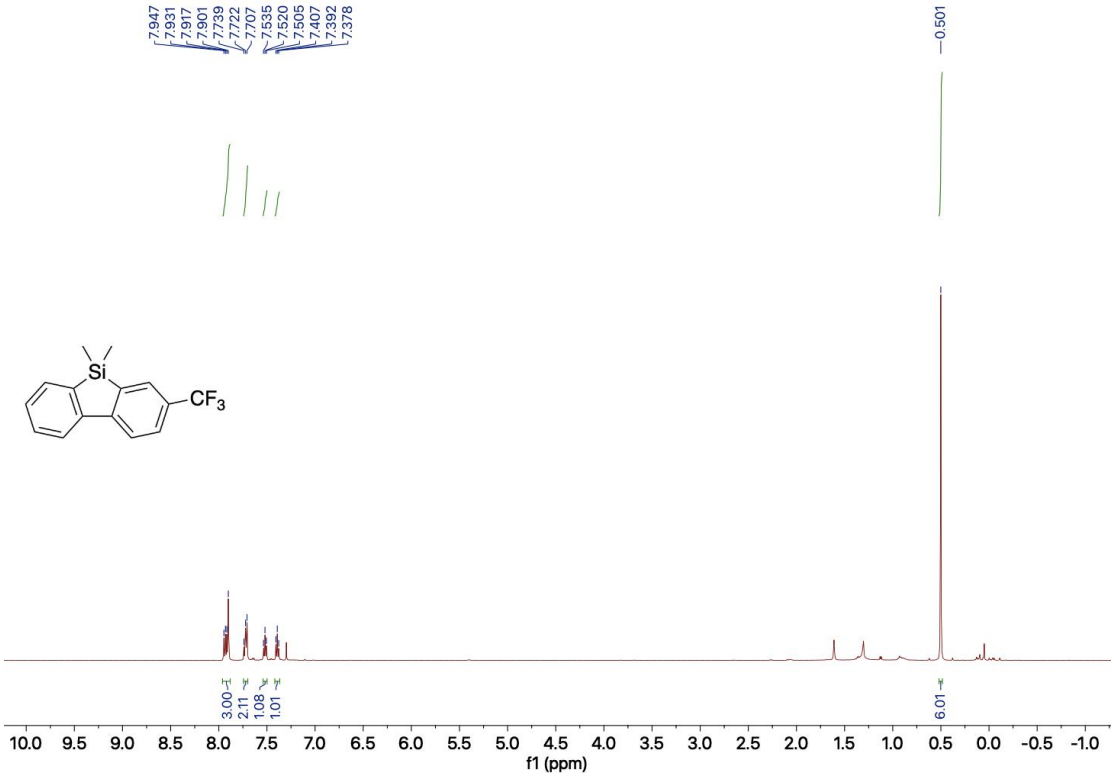

-62.236
Si
O
Si
CF3
MeO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

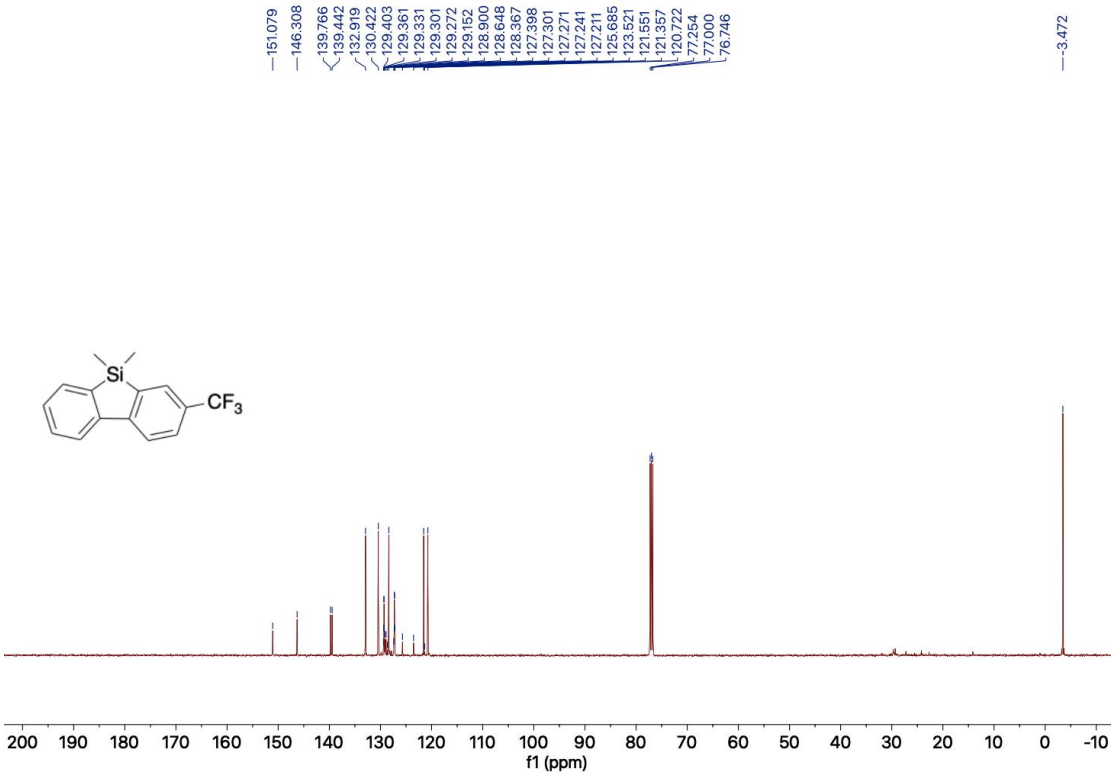
^{1}H NMR of **3G** (500 MHz, $CDCl_3$), ^{13}C NMR of **3G** (125 MHz, $CDCl_3$) and ^{19}F NMR of **3G** (470 MHz, $CDCl_3$)

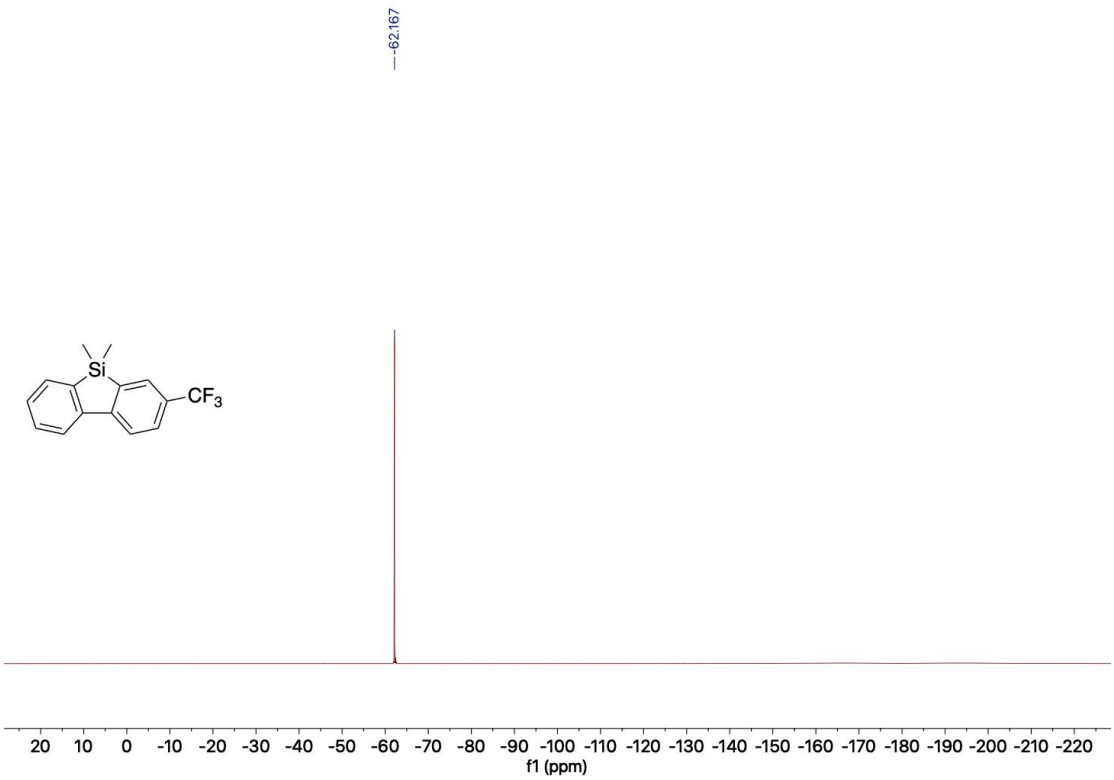



-62.535
Si
O
Si
CF3
NC
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

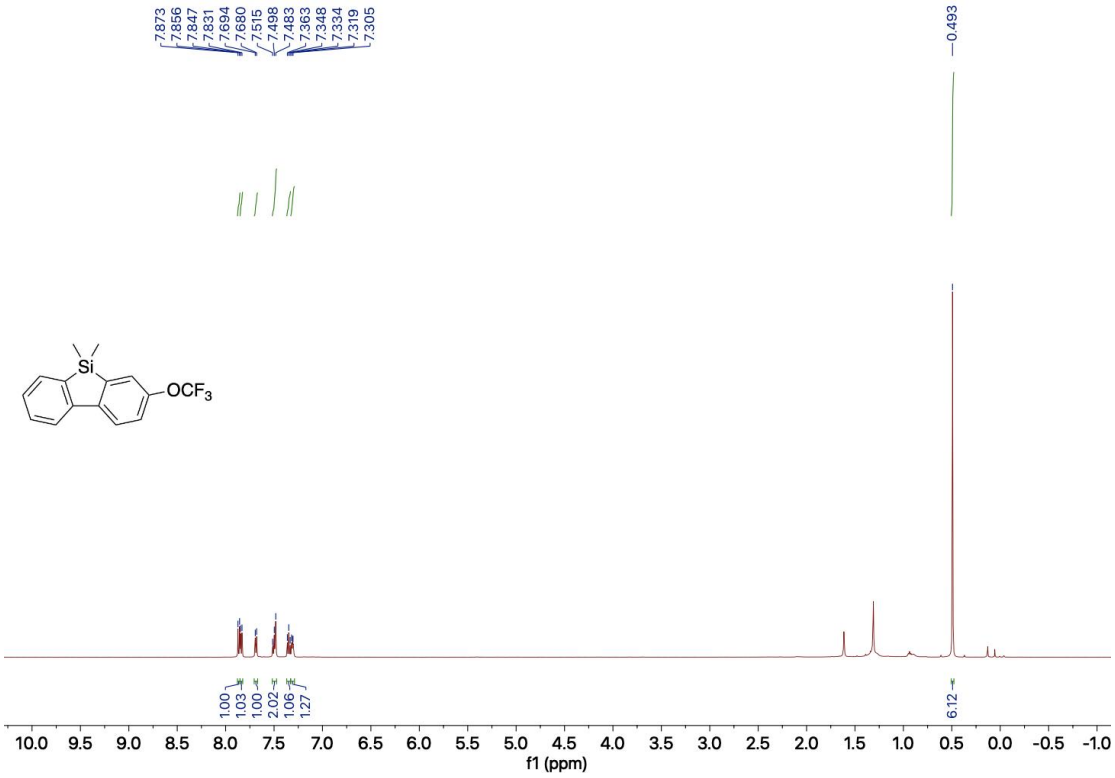
^{1}H NMR of **4q** (500 MHz, $CDCl_3$), ^{13}C NMR of **4q** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4q** (470 MHz, $CDCl_3$)

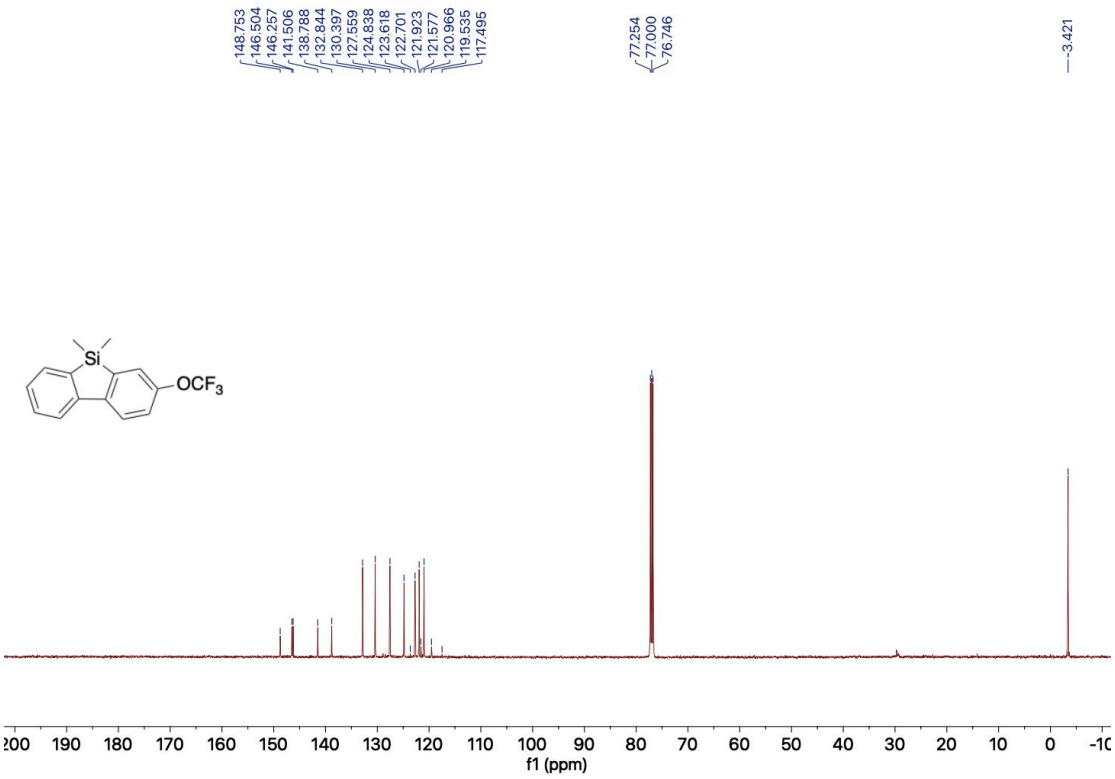


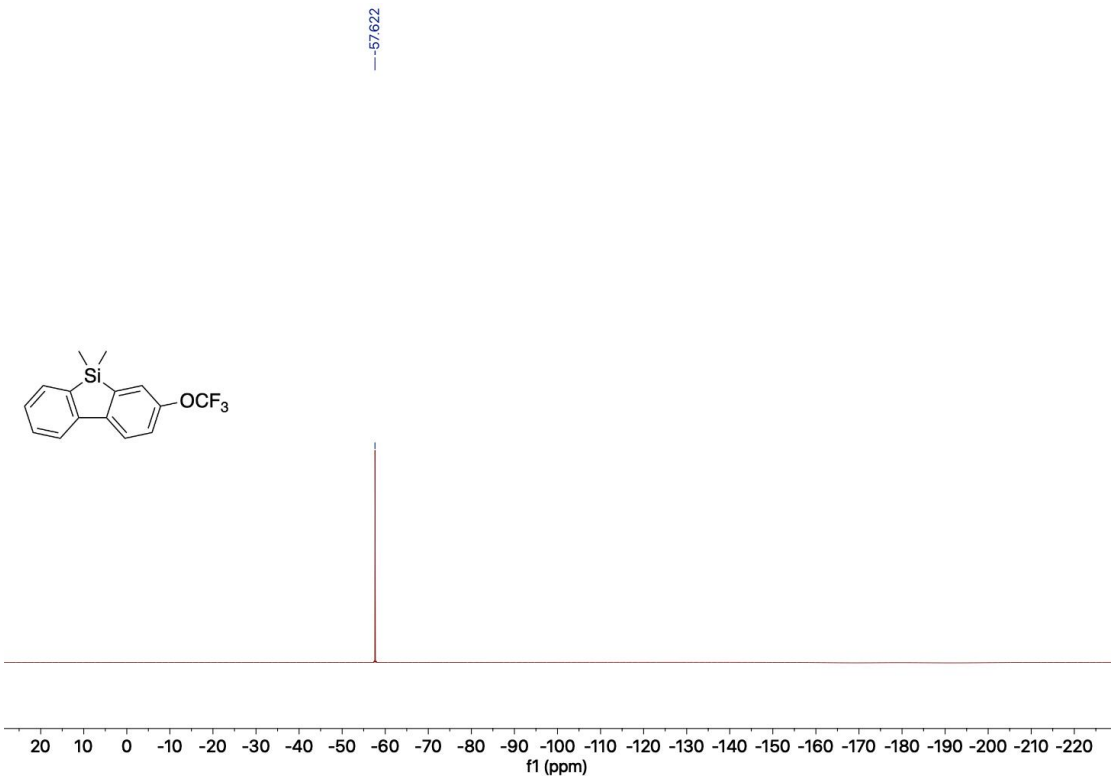



-62.167
Si
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

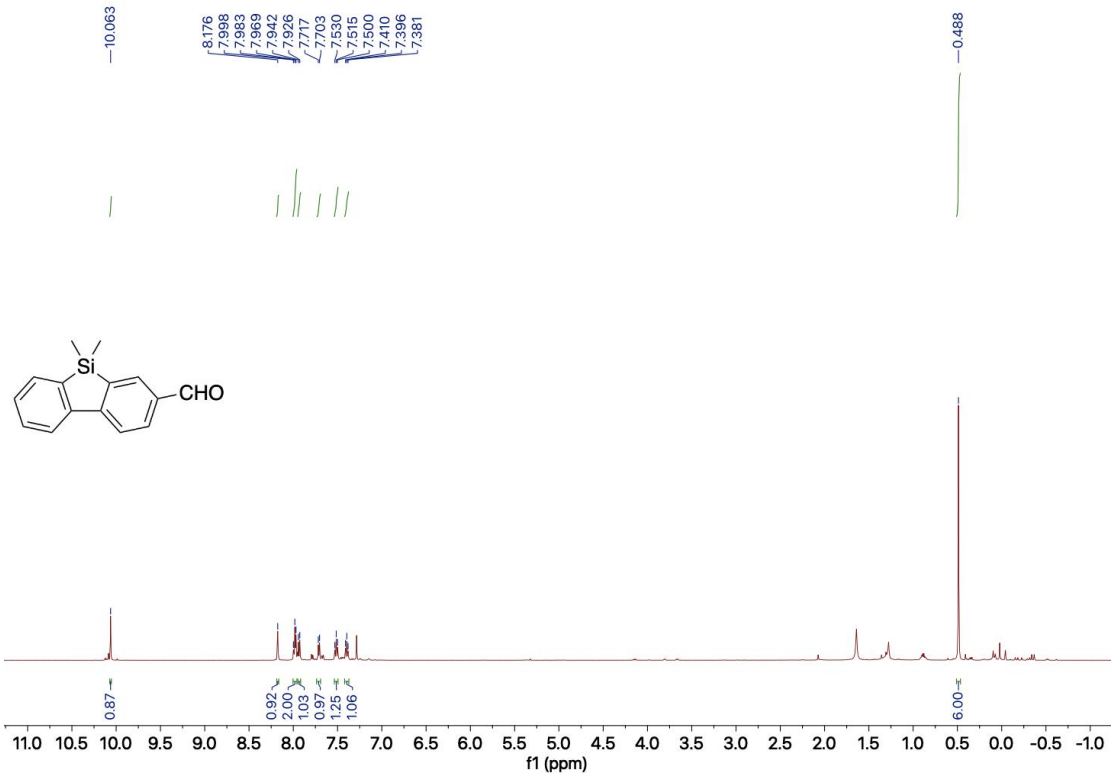
^{1}H NMR of **4r** (500 MHz, $CDCl_3$) and ^{13}C NMR of **4r** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4r** (470 MHz, $CDCl_3$)

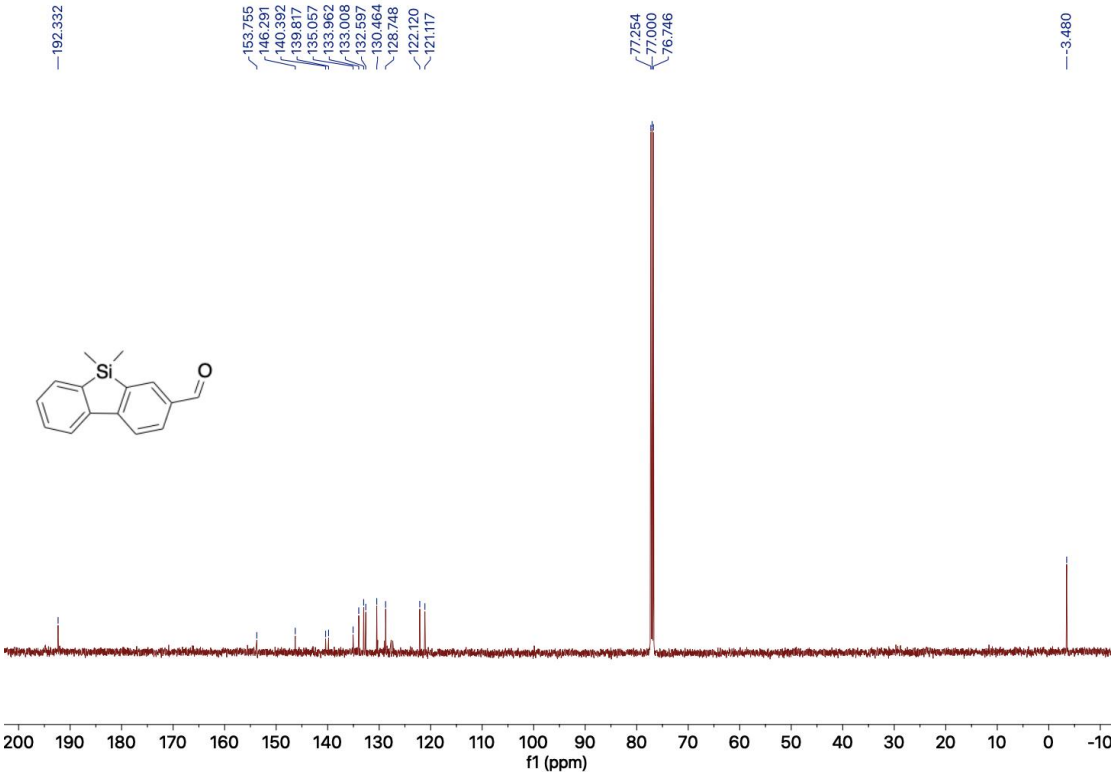




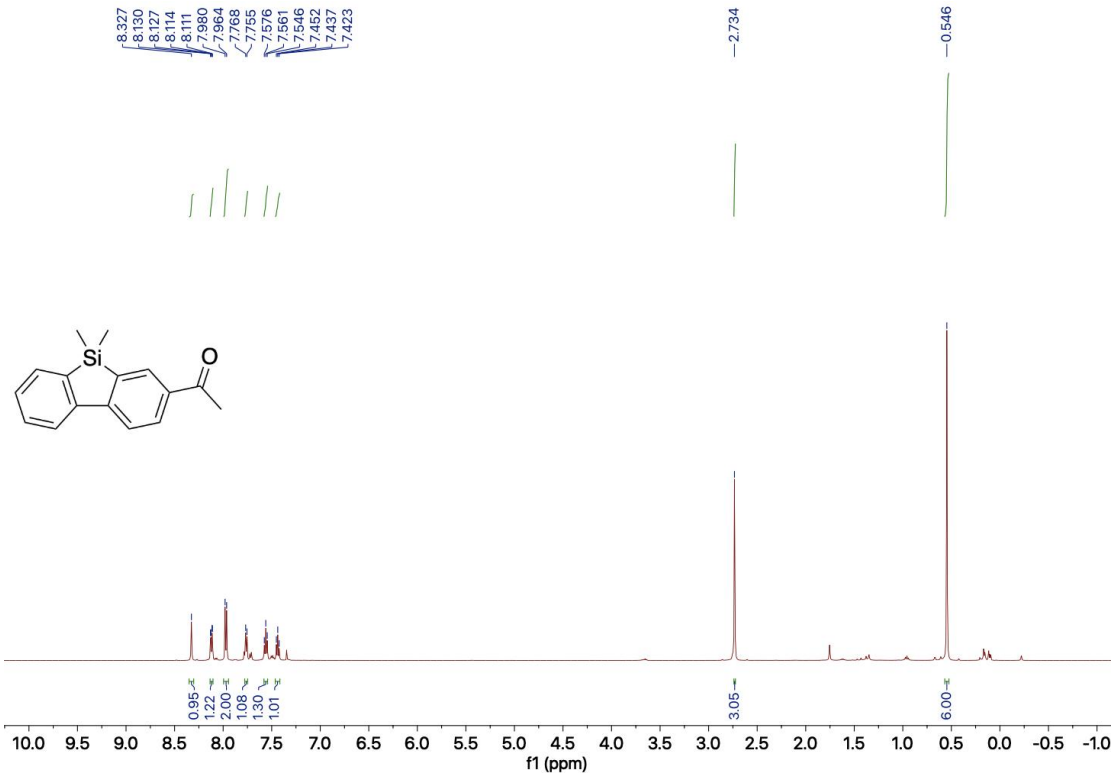

-57.622
Si
OCF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

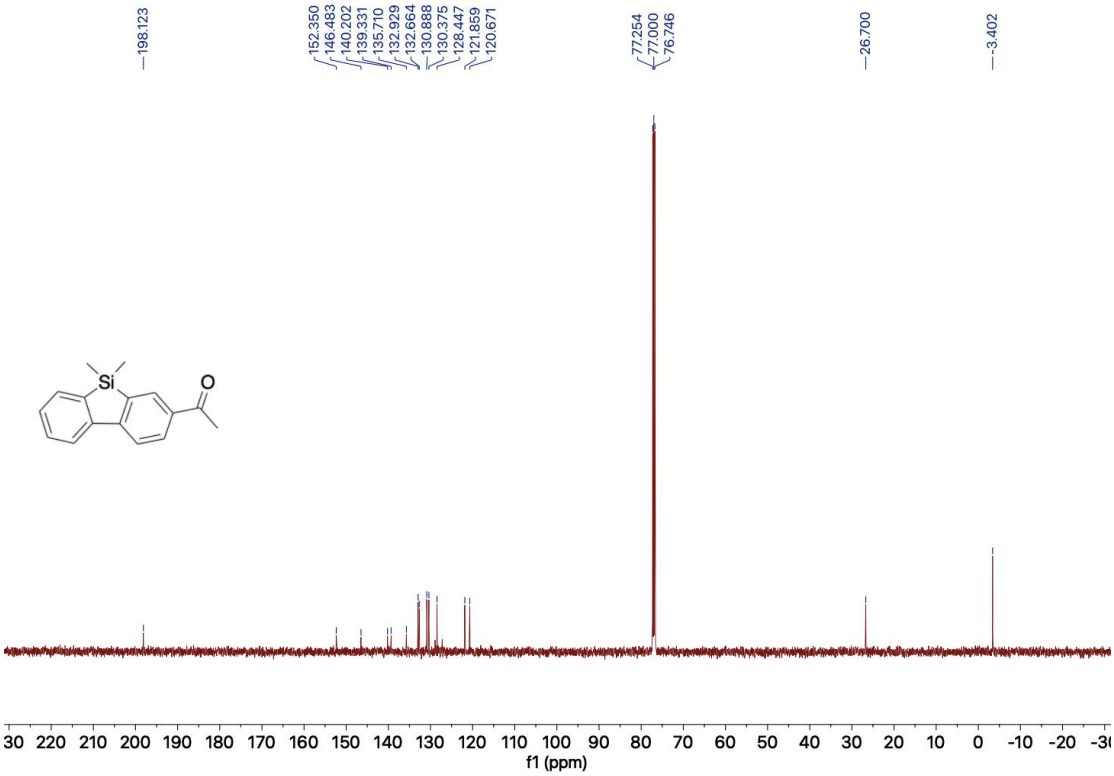
^{1}H NMR of **4s** (500 MHz, $CDCl_3$) and ^{13}C NMR of **4s** (125 MHz, $CDCl_3$)



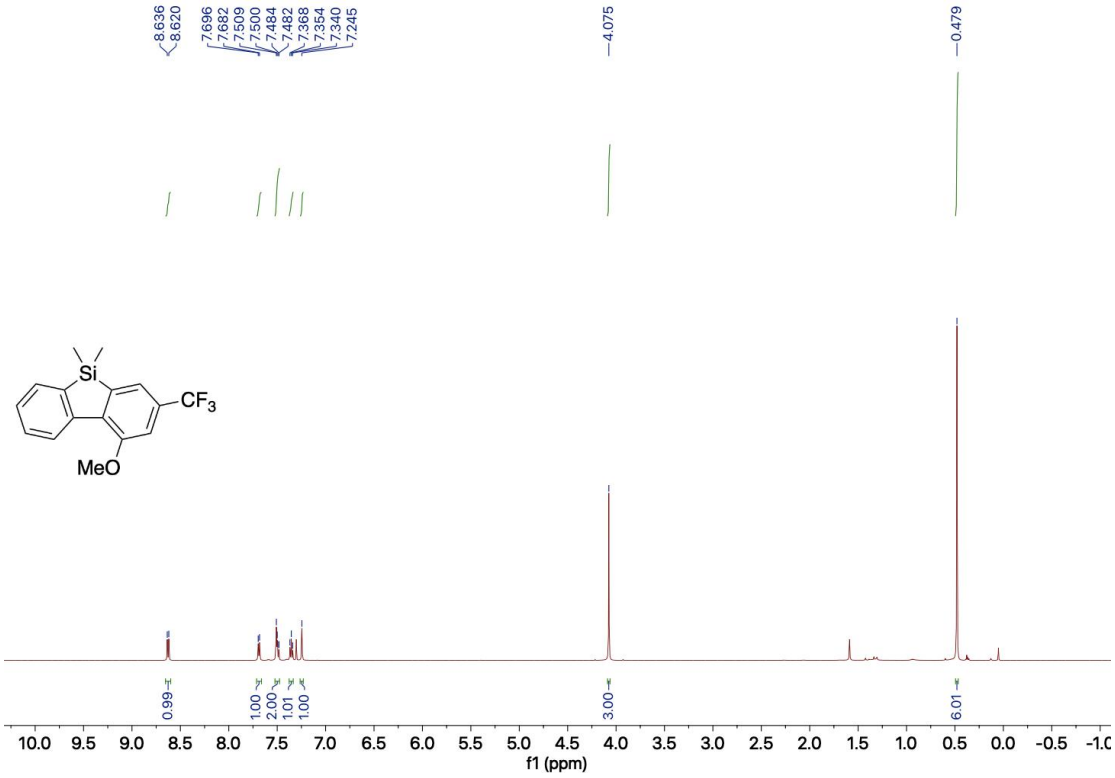


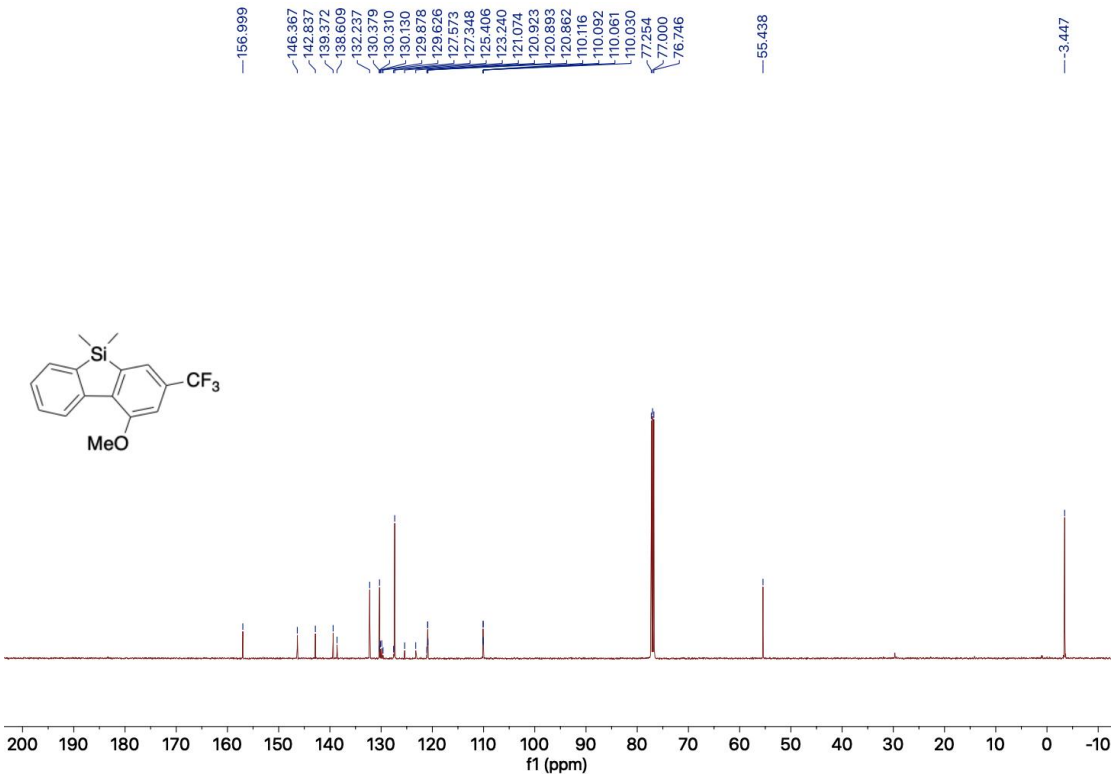
^{1}H NMR of **4t** (500 MHz, $CDCl_3$) and ^{13}C NMR of **4t** (125 MHz, $CDCl_3$)

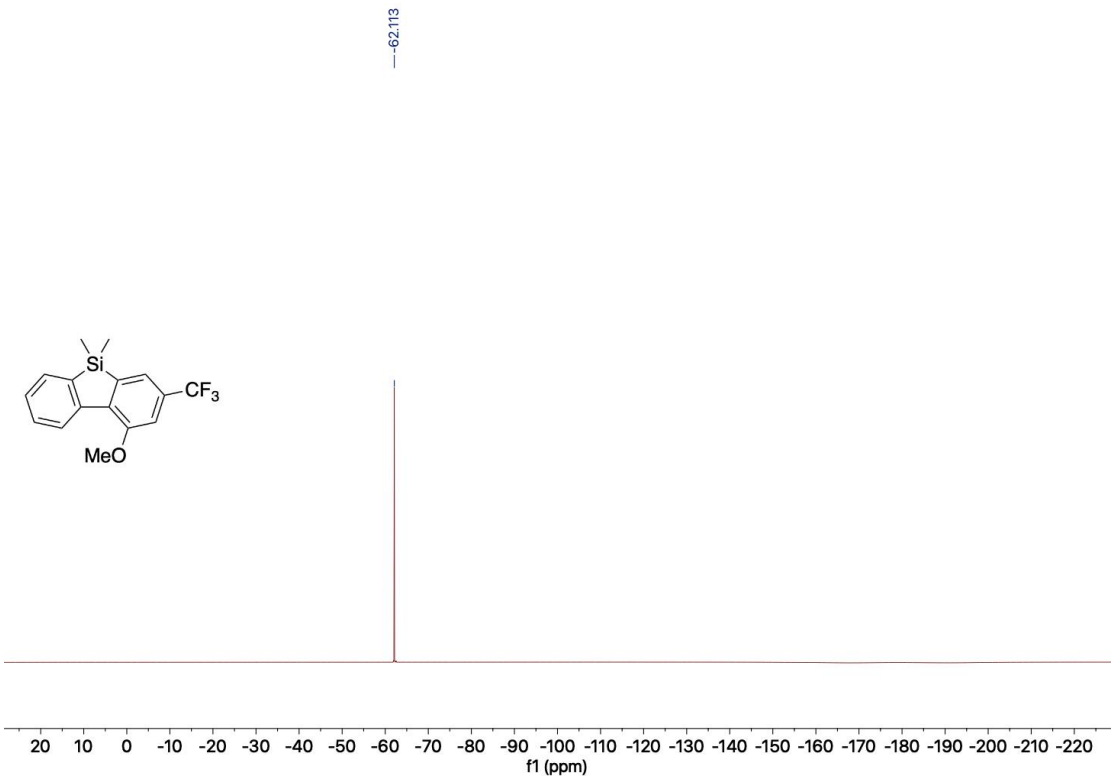




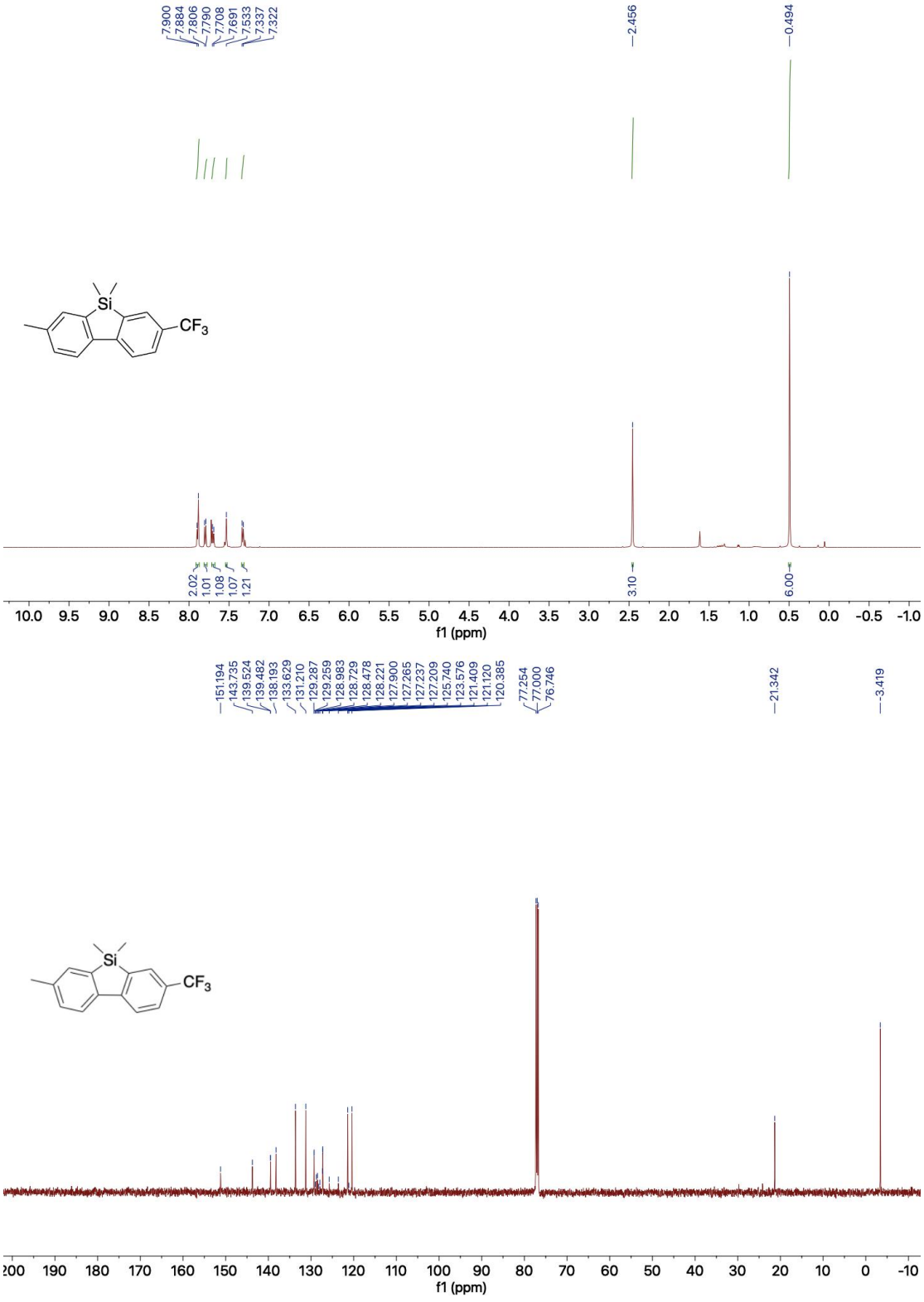
^{1}H NMR of **4y** (500 MHz, $CDCl_3$), ^{13}C NMR of **4y** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4y** (470 MHz, $CDCl_3$)

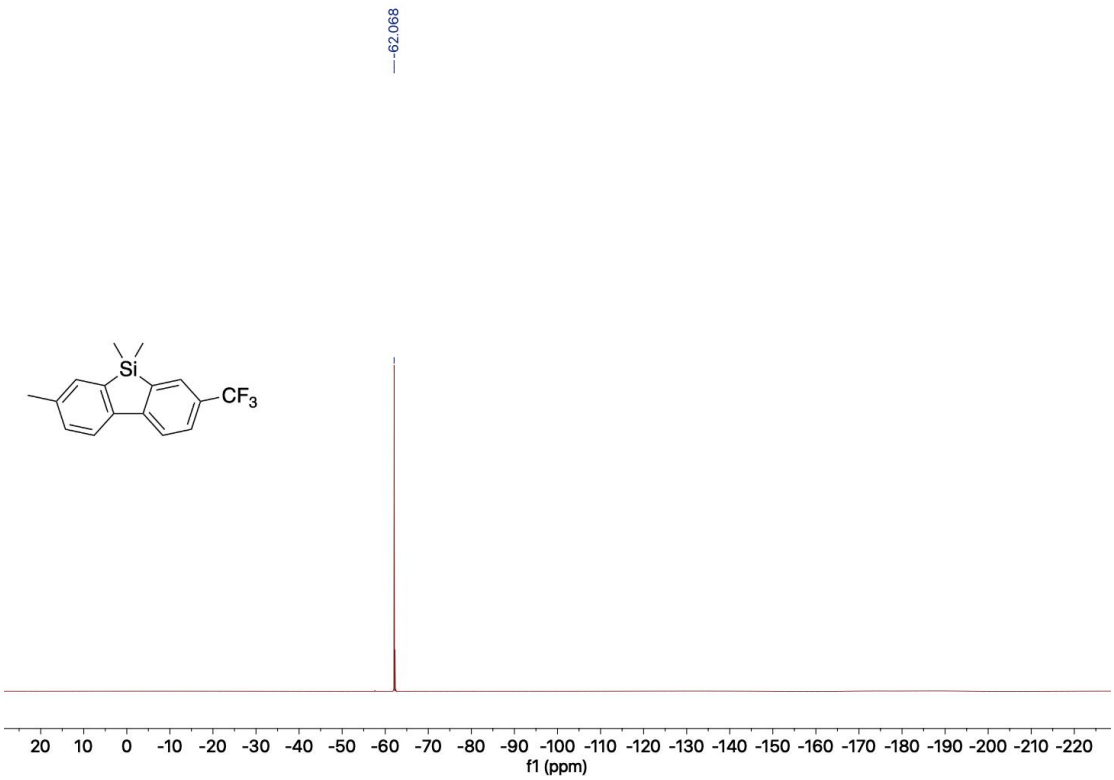




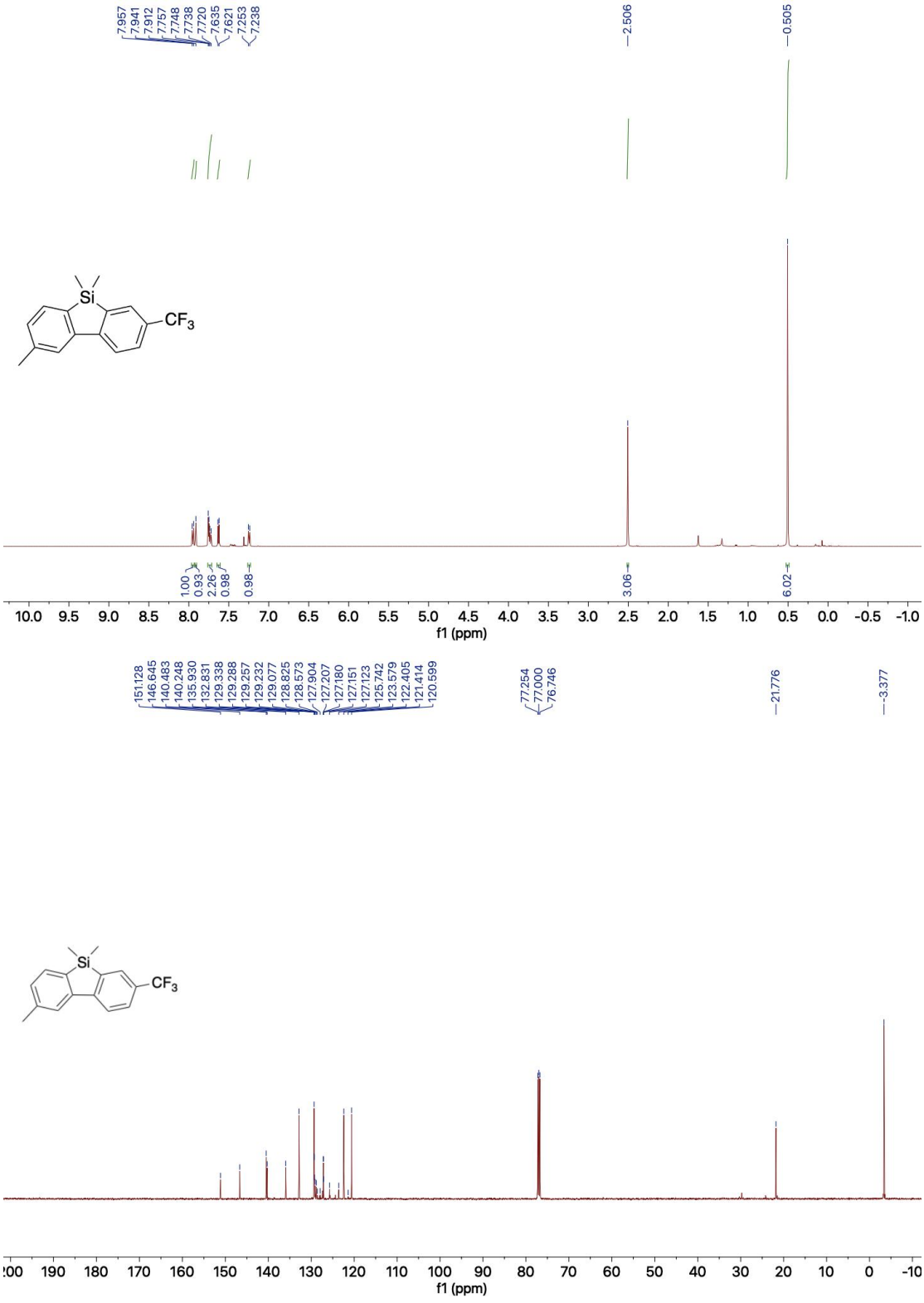

-62.113
Si
CF3
MeO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

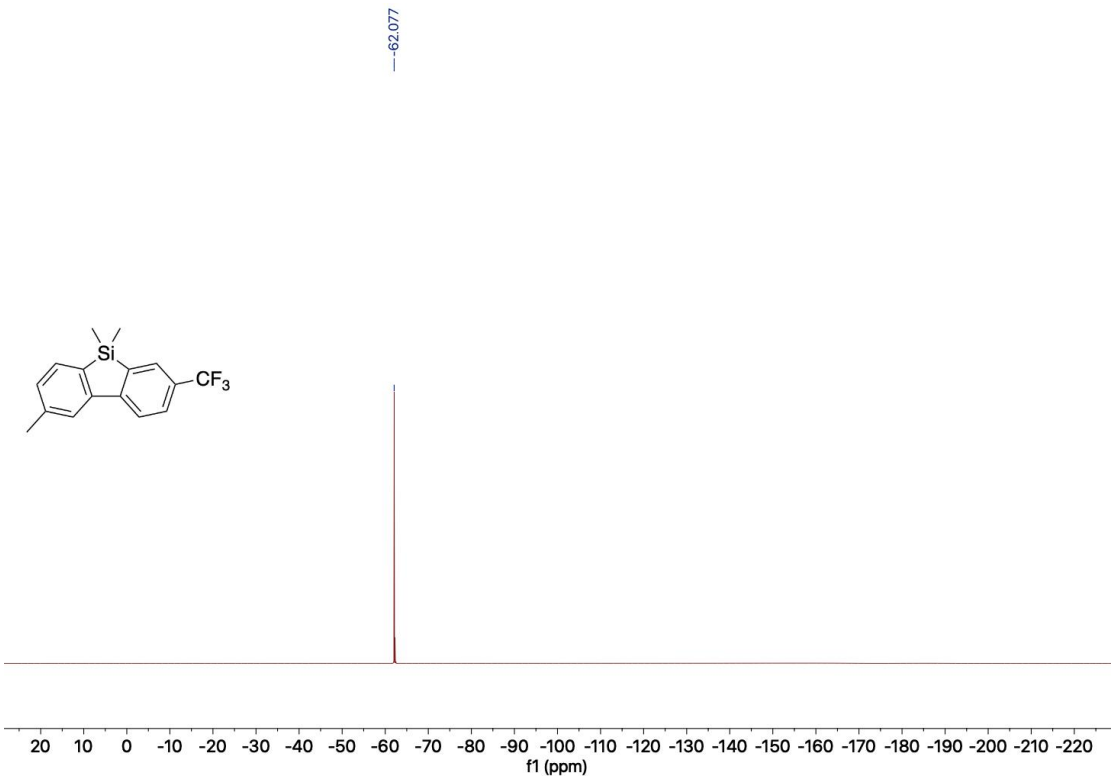
^{1}H NMR of **4D** (500 MHz, $CDCl_3$), ^{13}C NMR of **4D** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4D** (470 MHz, $CDCl_3$)



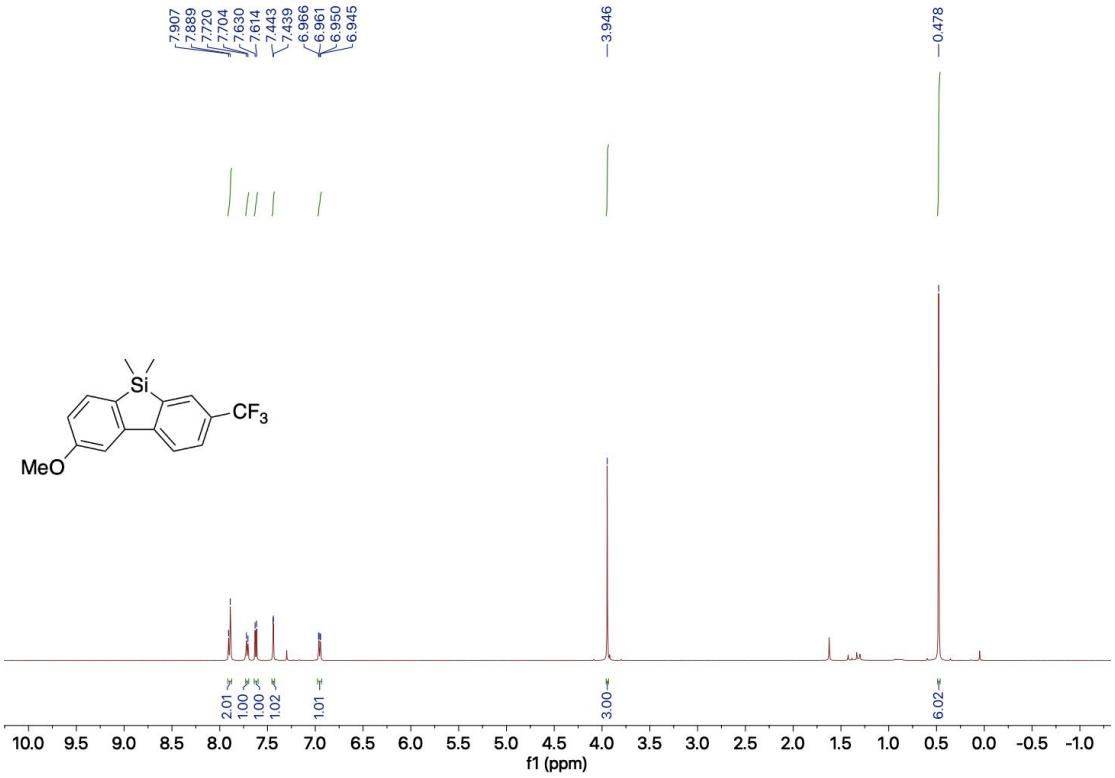

-62.068
Si
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

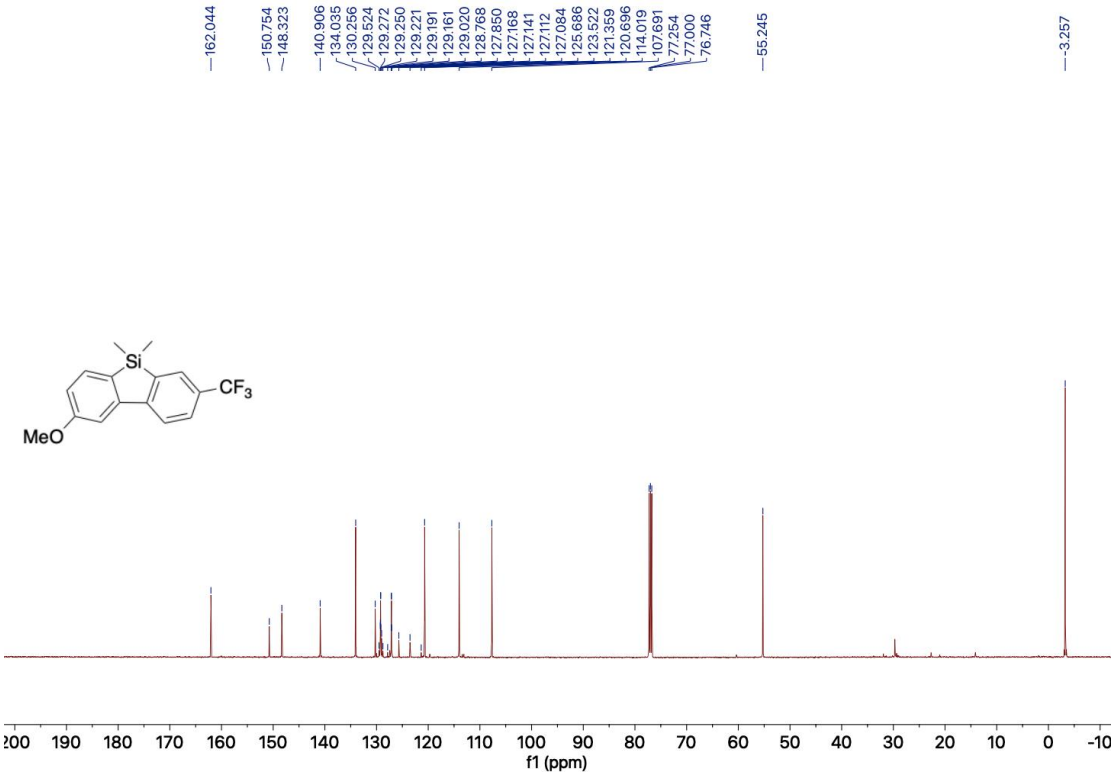
^{1}H NMR of **4E** (500 MHz, $CDCl_3$), ^{13}C NMR of **4E** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4E** (470 MHz, $CDCl_3$)

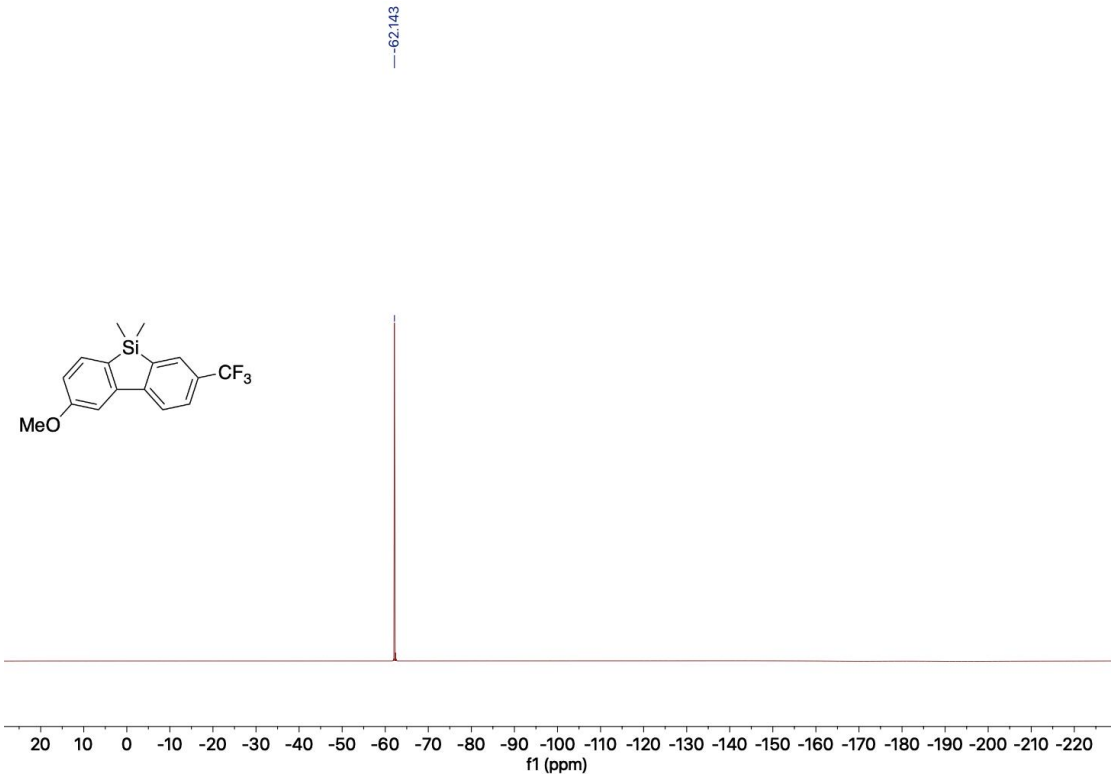



-62.077
Si
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

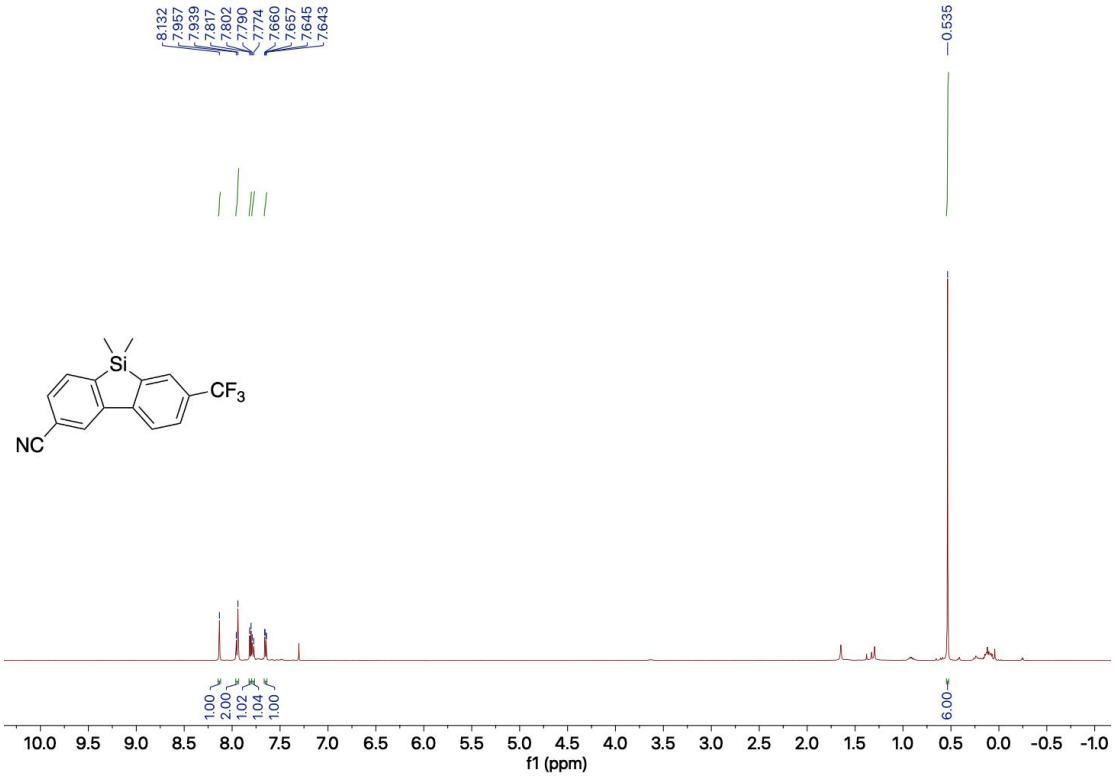
^{1}H NMR of **4F** (500 MHz, $CDCl_3$), ^{13}C NMR of **4F** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4F** (470 MHz, $CDCl_3$)

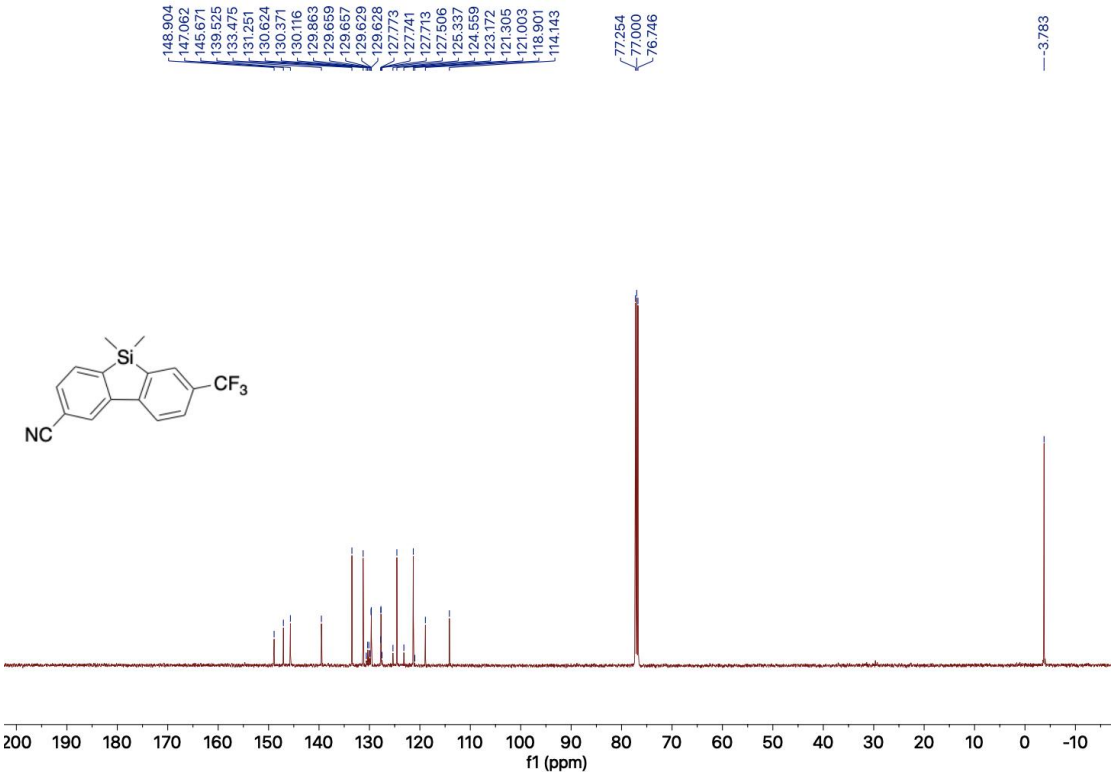


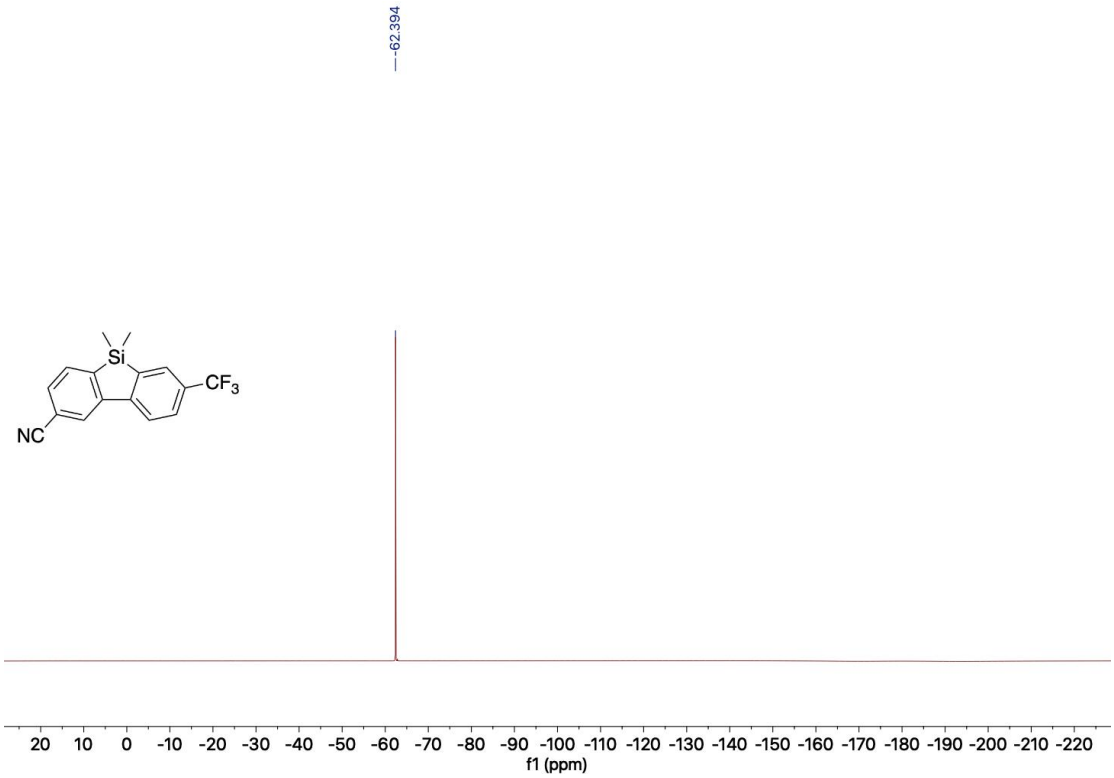



-62.143
Si
CF3
MeO
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

^{1}H NMR of **4G** (500 MHz, $CDCl_3$), ^{13}C NMR of **4G** (125 MHz, $CDCl_3$) and ^{19}F NMR of **4G** (470 MHz, $CDCl_3$)







^{1}H NMR of **Int-A** (500 MHz, $CDCl_3$)