

Supplementary information

Cobalt-catalyzed dehydrative approach for the synthesis of unsymmetric disiloxanes and polysiloxanes

Bingbin Yang,† Peng Guo,† Xinglei He, Ke-Yin Ye*

Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), College of Chemistry,
Fuzhou University, Fuzhou 350108

E-mail: kyye@fzu.edu.cn

†These authors contributed equally to this work.

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1. General Information

All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise indicated. All commercial reagents were used without further purification unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate. Yields refer to products isolated after purification by column chromatography unless otherwise stated. Proton nuclear magnetic resonance (^1H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra, and fluorine nuclear magnetic resonance (^{19}F NMR) were recorded on Bruker AV-400 (400 MHz), and JEOL-500 (500 MHz) spectrometers. NMR samples were dissolved in CDCl_3 (unless specified otherwise) and chemical shifts are reported in ppm referenced to residual nondeuterated solvent. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR. HRMS were obtained on an Exactive Plus LC-MS (ESI/APCI) mass spectrometer with the use of a quadrupole analyzer.

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index ($\text{PDI} = M_w/M_n$) of the obtained polymers were determined by a Waters 1515 series gel permeation chromatograph (GPC) equipped with a Waters 2414 refractive index detector, using a Styragel HR3THF (7.8×300 mm) Column, and a Styragel HR4THF (7.8×300 mm) Column with measurable molecular weights ranging from 102 to 106 g mol^{-1} . DSC and TGA were performed on Instruments STA449C/6/G (purge gas: Ar_2 , flow rate: 20 mL/min, ramp rate: 30 $^\circ\text{C}/\text{min}$, temperature range: 30 $^\circ\text{C}$ to 800 $^\circ\text{C}$). All commercial chemical reagents were purchased from Energy Chemical and Innochem without further purification.

2. General Procedures

General Procedure 1 (GP 1) - *Co-catalyzed the synthesis of unsymmetric disiloxanes*

To a Schlenk tube with a stirring bar was added aryl silanol (5 mmol), alkyl silanol (10 mmol, 2.0 equiv.), $\text{CoF}_4 \cdot \text{H}_2\text{O}$ (0.025 mmol, 0.5 mol%), L6 (0.05 mmol, 1.0 mol%), and MeCN (2.5 mL) under air for 8 h at 60 $^\circ\text{C}$ (heating module). Upon completion, the reaction mixture was directly concentrated by rotary evaporation. The unsymmetrical siloxane products were isolated by silica column chromatography (typically pure petroleum ether).

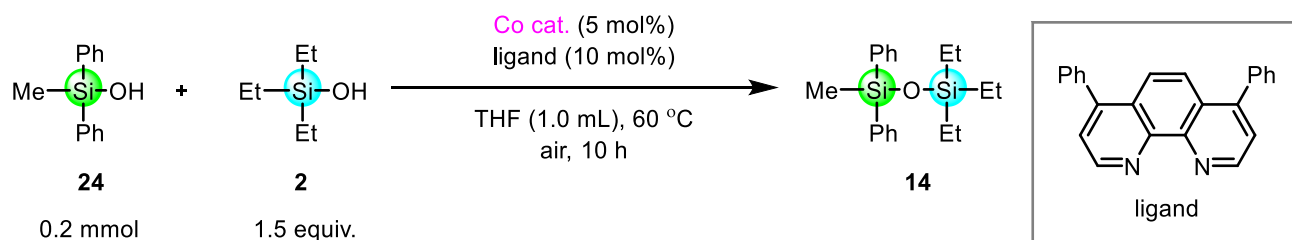
General Procedure 2 (GP 2) - *Co-catalyzed the synthesis of polysiloxanes*

To a Schlenk tube with a stirring bar was added aryl silanol (5 mmol), alkyl silanol (10 mmol, 2.0 equiv.), $\text{CoF}_4 \cdot \text{H}_2\text{O}$ (0.025 mmol, 0.5 mol%), L6 (0.05 mmol, 1.0 mol%), and MeCN (8.0 mL) under air for 8 h at 60 $^\circ\text{C}$ (heating module). After the polymerization, the reaction mixture was cooled to room temperature, and the content was purified by the precipitation method.

All of the polymers are soluble in dichloromethane and insoluble in methanol, so these two solvents were used in the precipitation process. The reaction mixture was first homogenized by the addition of as low as possible amount of DCM (5 mL), then, cold methanol was added to dichloromethane (20 mL) until it turned into a biphasic mixture. The top layer was taken out, and the bottom viscous/solid layer was washed with methanol two times until it gave a white/light yellow color viscous/solid polymer. The resulting polymer was dried to a constant weight and characterized by ^1H NMR, ^{13}C NMR, GPC and TG.

3. Optimization of the Reaction Conditions

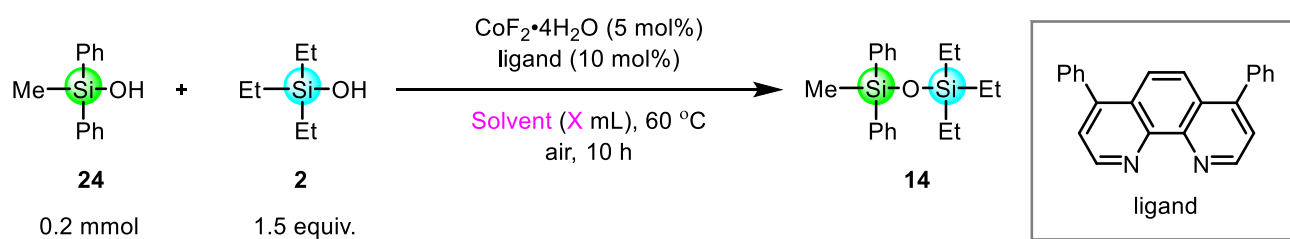
3.1 Screening of catalysts



Entry ^a	Co cat.	Yield (%) ^b
1	Co(acac) ₃	n.d.
2	Co(acac) ₂	12
3	Co(OAc) ₂	n.d.
4	Co(OAc) ₂ ·4H ₂ O	trace
5	CoF ₂	14
6	CoF ₂ ·4H ₂ O	60
7	CoCl ₂	n.d.
8	CoBr ₂	n.d.
9	Co(NO ₃) ₂ ·6H ₂ O	n.d.
10	CoCl ₂ O ₈ ·6H ₂ O	n.d.
11	Co(OH) ₂	n.d.
12	NaF	n.d.
13	MnF ₂	n.d.

^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), catalyst (0.01 mmol, 5 mol%) and ligand (0.02 mmol, 10 mol%) were added to THF (1.0 mL) under air for 10 h at 60 °C. ^b The yields were given with CH₂Br₂ as the internal standard.

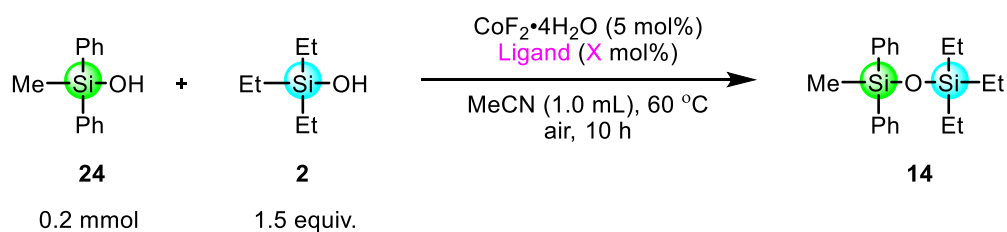
3.2 Screening of solvents



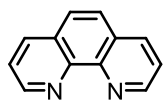
Entry ^a	Solvent	X	Yield (%) ^b
1	DCM	1.0	14
2	DCE	1.0	n.d.
3	DMF	1.0	52
4	EA	1.0	38
5	Hexane	1.0	13
6	1,4-dioxane	1.0	n.d.
7	Et ₂ O	1.0	68
8	THF	1.0	60
9	Toluene	1.0	n.d.
10	CH ₃ OH	1.0	n.d.
11	PhCN	1.0	15
12	MeCN	1.0	72
13 ^c	MeCN	0.5	64
14 ^d	MeCN	2.0	66
15 ^e	MeCN	4.0	23
16 ^f	-	-	60

^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), CoF₂·4H₂O (0.01 mmol, 5 mol%) and ligand (0.02 mmol, 10 mol%) were added to solvent (X mL) under air for 10 h at 60 °C. ^b The yields were given with CH₂Br₂ as the internal standard.

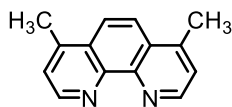
3.3 Screening of ligands



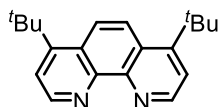
Entry ^a	Ligand	X	Yield (%) ^b
1	L1	10	n.d.
2	L2	10	71
3	L3	10	70
4	L4	10	72
5	L5	10	50
6	L6	10	79
7	L7	10	n.d.
8	L8	10	n.d.
9	L9	10	n.d.
10	L10	10	n.d.
11 ^c	L6	5	59
12 ^d	L6	7.5	70
13 ^e	L6	15	78



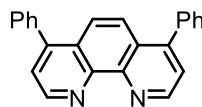
L1



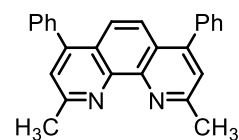
L2



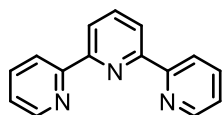
L3



L4



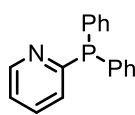
L5



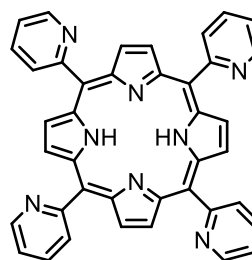
L6



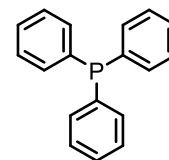
L7



L8



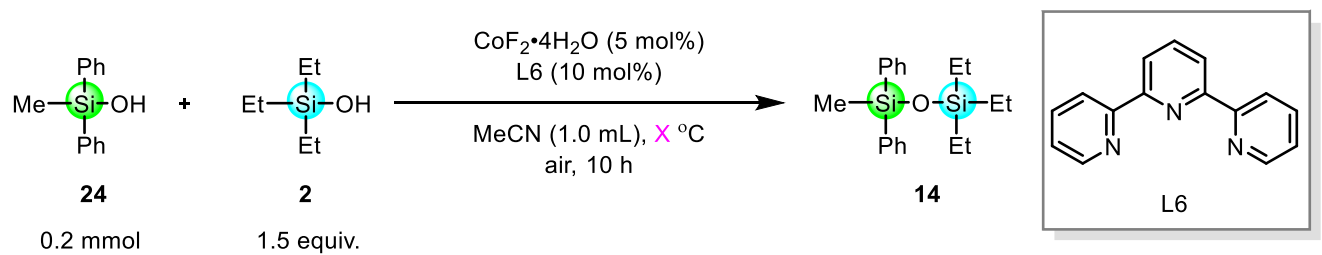
L9



L10

^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ (0.01 mmol, 5 mol%) and ligand (X mol%) were added to MeCN (1.0 mL) under air for 10 h at 60 °C. ^b The yields were given with CH_2Br_2 as the internal standard.

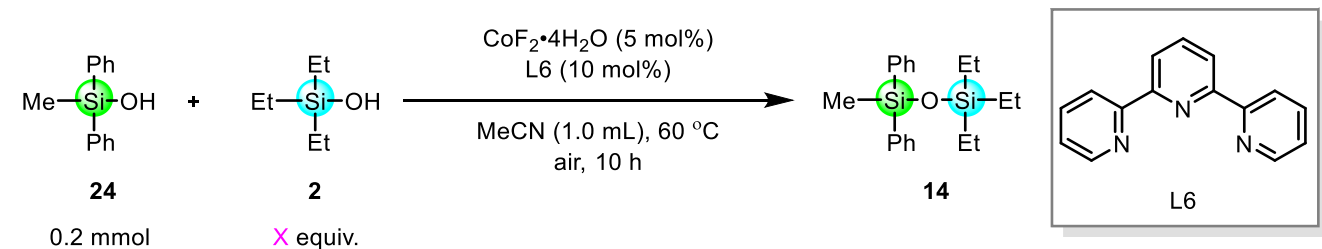
3.4 Screening of temperature



Entry ^a	X	Yield (%) ^b
1	R.T.	51
2	40	69
3	60	79
4	80	76

^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ (0.01 mmol, 5 mol%) and L6 (0.02 mmol, 10 mol%) were added to MeCN (1.0 mL) under air for 10 h at X °C. ^b The yields were given with CH_2Br_2 as the internal standard.

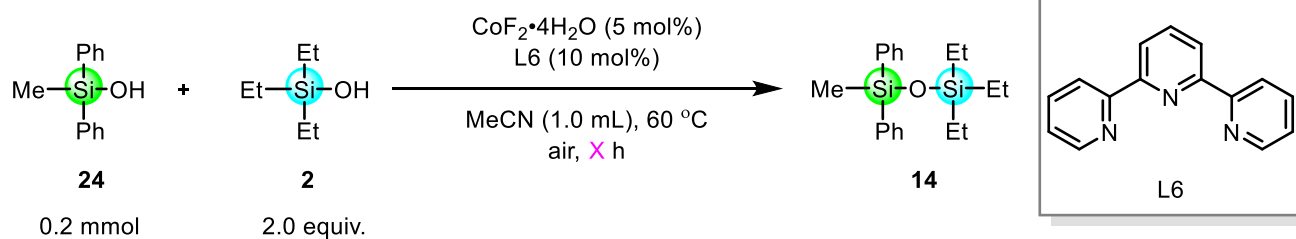
3.5 Screening of the amount of triethylsilanol



Entry ^a	X	Yield (%) ^b
1	1.0	73
2	1.5	79
3	2.0	88
4	2.5	80

^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (X equiv.), $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ (0.01 mmol, 5 mol%) and L6 (0.02 mmol, 10 mol%) were added to MeCN (1.0 mL) under air for 10 h at 60 °C. ^b The yields were given with CH_2Br_2 as the internal standard.

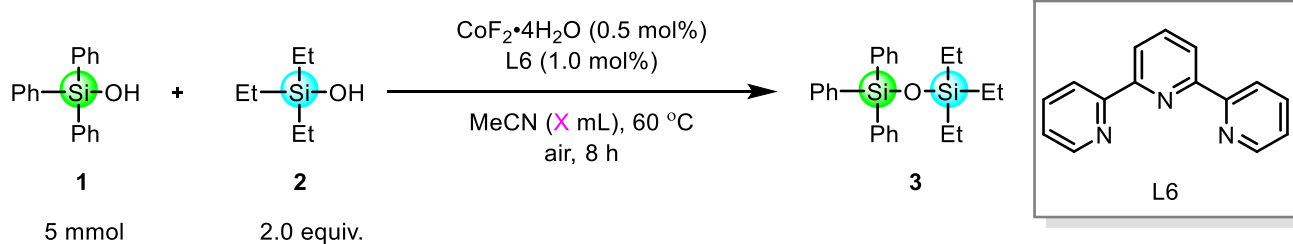
3.5 Screening of reaction time



Entry ^a	X	Yield (%) ^b
1	1	40
2	2	48
3	4	63
4	6	75
5	8	88 (83) ^c
6	10	88
7	12	88
8	24	65

^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $\text{CoF}_2\cdot 4\text{H}_2\text{O}$ (0.01 mmol, 5 mol%) and L6 (0.02 mmol, 10 mol%) were added to MeCN (1.0 mL) under air for X h at 60 °C. ^b The yields were given with CH_2Br_2 as the internal standard. ^c Isolated yields.

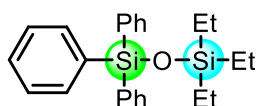
3.6 Screening of the gram-scale reaction



Entry ^a	X	Yield(%) ^b
1	0.5	15
2	1.0	38
3	1.5	70
4	2.0	73
5	2.5	76
6	3.0	76
7	4.0	75

^a Reaction conditions: **1** (5 mmol, 1.0 equiv.), **2** (10 mmol, 2.0 equiv.), $\text{CoF}_4\cdot \text{H}_2\text{O}$ (0.025 mmol, 0.5 mol%), L6 (0.05 mmol, 1.0 mol%) were added to MeCN (X mL) under air for 8 h at 60 °C. ^b Isolated yields.

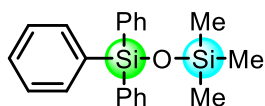
4.Characterization of unsymmetric disiloxanes



3, 1,1,1-triethyl-3,3,3-triphenyldisiloxane^[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.48 g (76% yield) of the desired product as a colorless oil.

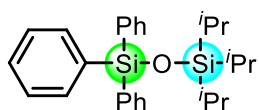
¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 6.3 Hz, 6H), 7.47 – 7.34 (m, 9H), 0.90 (t, *J* = 8.0 Hz, 9H), 0.59 (q, *J* = 8.0 Hz, 6H).



4, 1,1,1-trimethyl-3,3,3-triphenyldisiloxane^[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.56 g (90% yield) of the desired product as a white solid.

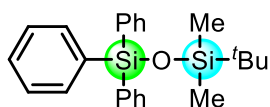
¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.2 Hz, 6H), 7.48 – 7.31 (m, 9H), 0.11 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 136.4, 135.1, 129.9, 127.9, 2.2.



5, 1,1,1-triisopropyl-3,3,3-triphenyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.04 g (2% yield) of the desired product as a white solid.

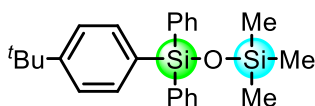
¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.1 Hz, 6H), 7.47 – 7.31 (m, 9H), 1.12 – 1.03 (m, 3H), 0.98 (d, *J* = 7.0 Hz, 18H). **¹³C NMR** (101 MHz, CDCl₃) δ 136.5, 135.4, 129.8, 127.8, 18.1, 13.1. **IR** (neat, cm⁻¹): 2941 (m), 1463 (m), 1247 (s), 1007 (m), 698 (s); **HRMS (APCI)** *m/z*: [M+H]⁺ Calcd. for C₂₇H₃₇OSi₂: 433.2377; Found: 433.2378.



6, 1-(tert-butyl)-1,1-dimethyl-3,3,3-triphenyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.12 g (6% yield) of the desired product as a white solid.

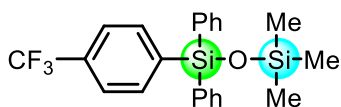
¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.58 (m, 6H), 7.49 – 7.32 (m, 9H), 0.90 (s, 9H), 0.03 (s, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 136.3, 135.2, 129.9, 127.8, 26.0, 18.5, -2.3. **IR** (neat, cm⁻¹): 2954 (m), 1428 (m), 1254 (m), 1049 (m), 696 (s); **HRMS (ESI)** m/z: [M+H]⁺ Calcd. for C₂₄H₃₁OSi₂: 391.1908; Found: 391.1913.



7, 1-(4-(tert-butyl)phenyl)-3,3,3-trimethyl-1,1-diphenyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.84 g (91% yield) of the desired product as a colorless oil.

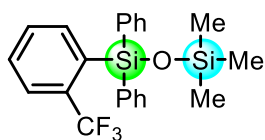
¹H NMR (400 MHz, CDCl₃) δ 7.59 (dd, *J* = 7.9, 1.7 Hz, 4H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.32 (m, 8H), 1.32 (s, 9H), 0.09 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 152.8, 136.7, 135.1, 134.9, 132.7, 129.8, 127.8, 124.8, 34.9, 31.4, 2.2. **IR** (neat, cm⁻¹): 2959 (m), 1428 (m), 1251 (m), 1059 (s), 699 (s); **HRMS (ESI)** m/z: [M+Na]⁺ Calcd. for C₂₅H₃₂OSi₂Na: 427.1884; Found: 427.1877.



8, 1,1,1-trimethyl-3,3-diphenyl-3-(4-(trifluoromethyl)phenyl)disiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.33 g (64% yield) of the desired product as a colorless oil.

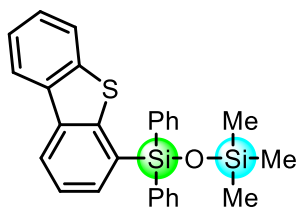
¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.54 (m, 4H), 7.47 – 7.42 (m, 2H), 7.41 – 7.35 (m, 4H), 0.11 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.5, 135.4, 135.4, 135.1, 131.8 (q, *J* = 32.1 Hz), 130.29, 128.1, 124.5 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 274.7 Hz), 2.15. **¹⁹F NMR** (471 MHz, CDCl₃) δ -62.7. **IR** (neat, cm⁻¹): 2958 (m), 1429 (m), 1252 (m), 1057 (s), 697 (s); **HRMS (ESI)** m/z: [M+H]⁺ Calcd. for C₂₂H₂₅F₃OSi₂: 417.1313; Found: 417.1304.



9, 1,1,1-trimethyl-3,3-diphenyl-3-(2-(trifluoromethyl)phenyl) disiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.24 g (60% yield) of the desired product as a colorless oil.

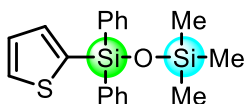
¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.58 – 7.50 (m, 5H), 7.52 – 7.34 (m, 7H), 0.12 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 138.1, 136.4, 136.1 (q, *J* = 31.5 Hz), 135.1, 134.5, 130.6, 130.0, 129.9, 127.8, 126.5 (q, *J* = 5.1 Hz), 124.8 (q, *J* = 274.4 Hz), -1.9. **¹⁹F NMR** (376 MHz, CDCl₃) δ -57.4. **IR** (neat, cm⁻¹): 2958 (m), 1429 (m), 1252 (m), 1057 (s), 697 (s); **HRMS (ESI)** m/z: [M+H]⁺ Calcd. for C₂₂H₂₅F₃OSi₂: 417.1312; Found: 417.1321.



10, 1-(dibenzo[b,d]thiophen-4-yl)-3,3,3-trimethyl-1,1-diphenyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 2.02 g (89% yield) of the desired product as a white solid.

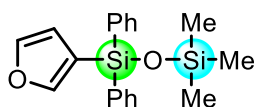
¹H NMR (400 MHz, CDCl₃) δ 8.30 (d, *J* = 7.9 Hz, 1H), 8.25 – 8.19 (m, 1H), 7.84 (dd, *J* = 6.0, 3.3 Hz, 1H), 7.79 (d, *J* = 6.5 Hz, 4H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.57 – 7.44 (m, 9H), 0.25 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 146.0, 140.2, 135.4, 135.22, 135.20, 135.1, 134.8, 130.6, 130.2, 128.0, 126.6, 124.2, 123.8, 123.3, 122.7, 121.5, 2.2. **IR** (neat, cm⁻¹): 2957 (m), 1429 (m), 1250 (m), 1023 (m), 697 (s); **HRMS (ESI)** m/z: [M+H]⁺ Calcd. for C₂₇H₂₇OSSi₂N: 472.1316; Found: 472.1327.



11, 1,1,1-trimethyl-3,3-diphenyl-3-(thiophen-2-yl) disiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.00 g (56% yield) of the desired product as a colorless oil.

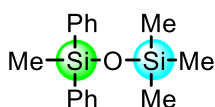
¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.71 (m, 5H), 7.54 – 7.43 (m, 7H), 7.29 (dd, *J* = 4.6, 3.4 Hz, 1H), 0.23 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 137.3, 136.2, 136.1, 134.8, 132.2, 130.1, 128.2, 127.9, 2.1. **IR** (neat, cm⁻¹): 2957 (m), 1429 (m), 1250 (m), 1049 (s), 696 (s); **HRMS (ESI)** m/z: [M+H]⁺ Calcd. for C₁₉H₂₂OSSi₂: 355.1003; Found: 355.1012.



12, 1-(furan-3-yl)-3,3,3-trimethyl-1,1-diphenyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.13 g (67% yield) of the desired product as a colorless oil.

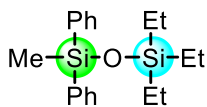
¹H NMR (500 MHz, CDCl₃) δ 7.62 – 7.59 (m, 4H), 7.55 (t, *J* = 1.6 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 5H), 6.47 (dd, *J* = 1.7, 0.9 Hz, 1H), 0.12 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 150.3, 143.3, 136.6, 134.7, 123.0, 127.9, 115.9, 113.9, 2.13. **IR** (neat, cm⁻¹): 2957 (m), 1429 (m), 1250 (m), 1023 (m), 697 (s); **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd. for C₁₉H₂₃O₂Si₂: 339.1232; Found: 339.1238.



13, 1,1,1,3-tetramethyl-3,3-diphenyldisiloxane^[3]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.12 g (78% yield) of the desired product as a colorless oil.

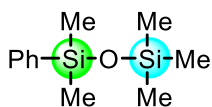
¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.64 (m, 4H), 7.52 – 7.41 (m, 6H), 0.72 (s, 3H), 0.22 (s, 9H).



14, 1,1,1-triethyl-3-methyl-3,3-diphenyldisiloxane^[4]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.89 g (54% yield) of the desired product as a colorless oil.

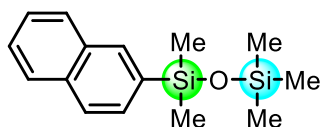
¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.59 (m, 4H), 7.48 – 7.33 (m, 6H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.68 (s, 3H), 0.62 (q, *J* = 7.9 Hz, 6H).



15, 1,1,1,3,3-pentamethyl-3-phenyldisiloxane^[5]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.82 g (73% yield) of the desired product as a colorless oil.

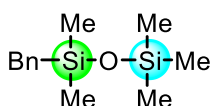
¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.72 (m, 2H), 7.57 – 7.50 (m, 3H), 0.53 (s, 6H), 0.30 (s, 9H).



16, 1,1,1,3,3-pentamethyl-3-(naphthalen-2-yl)disiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.95 g (69% yield) of the desired product as a colorless oil.

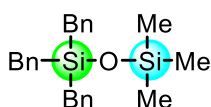
¹H NMR (500 MHz, CDCl₃) δ 8.24 (s, 1H), 8.05 – 7.95 (m, 3H), 7.83 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.64 (dt, *J* = 6.2, 3.4 Hz, 2H), 0.61 (s, 6H), 0.32 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 137.8, 134.1, 133.8, 133.1, 129.6, 128.4, 128.0, 127.1, 126.5, 126.0, 2.2, 1.1. **IR** (neat, cm⁻¹): 2956 (m), 1408 (w), 1251 (m), 1049 (m), 780 (s); **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd. for C₁₅H₂₃OSi₂: 275.1282; Found: 215.1290.



17, 1-benzyl-1,1,3,3,3-pentamethyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.83 g (70% yield) of the desired product as a colorless oil.

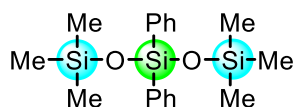
¹H NMR (400 MHz, CDCl₃) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.10 (m, 3H), 2.21 (s, 2H), 0.15 (s, 6H), 0.14 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 139.7, 128.5, 128.3, 124.2, 28.8, 2.0, 0.1. **IR** (neat, cm⁻¹): 2956 (m), 1493 (m), 1252 (s), 1050 (s), 696 (s); **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd. for C₁₂H₂₃OSi₂: 239.1282; Found: 239.1288.



18, 1,1,1-tribenzyl-3,3,3-trimethyldisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 1.47 g (75% yield) of the desired product as a white solid.

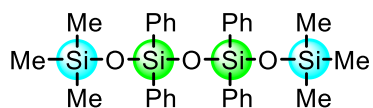
¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.22 (m, 6H), 7.12 (t, *J* = 7.4 Hz, 3H), 7.03 (d, *J* = 6.6 Hz, 6H), 2.14 (s, 6H), -0.10 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 138.6, 128.9, 128.4, 124.5, 24.9, 1.8. **IR** (neat, cm⁻¹): 2955 (m), 1492 (m), 1251 (m), 1058 (m), 695 (s); **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd. for C₂₄H₃₁OSi₂: 391.1908; Found: 391.1913.



19, 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane^[6]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.49 g (27% yield) of the desired product as a colorless oil.

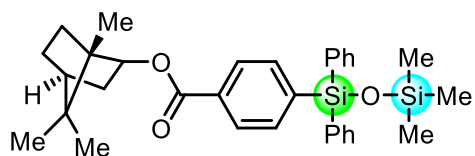
¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.61 (m, 4H), 7.46 – 7.35 (m, 6H), 0.17 (s, 18H).



20, 1,1,1,5,5,5-hexamethyl-3,3-diphenyltrisiloxane

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether) afforded 0.34 g (12% yield) of the desired product as a white solid.

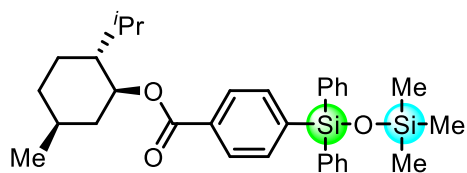
¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.54 (m, 8H), 7.41 – 7.35 (m, 4H), 7.33 – 7.27 (m, 8H), 0.00 (s, 18H). ¹³C NMR (101 MHz, CDCl₃) δ 136.1, 134.5, 129.9, 127.7, 1.9. IR (neat, cm⁻¹): 2959 (w), 1429 (m), 1251 (m), 1124 (s), 699 (s); HRMS (ESI) m/z: [M+Na]⁺ Calcd. for C₃₀H₃₈O₃Si₄Na: 581.1790; Found: 581.1802.



21, (1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(3,3,3-trimethyl-1,1-diphenyldisiloxanyl)benzoate

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether : ethyl acetate = 50 : 1) afforded 1.74 g (66% yield) of the desired product as a colorless oil.

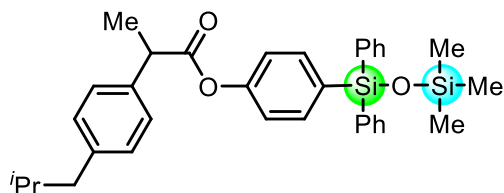
¹H NMR (500 MHz, CDCl₃) δ 8.06 – 8.02 (m, 2H), 7.69 – 7.66 (m, 2H), 7.58 – 7.54 (m, 4H), 7.45 – 7.41 (m, 2H), 7.42 – 7.33 (m, 4H), 5.11 (ddd, *J* = 9.9, 3.5, 2.1 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.12 (ddd, *J* = 13.3, 9.4, 4.4 Hz, 1H), 1.80 (tq, *J* = 12.1, 4.1 Hz, 1H), 1.73 (t, *J* = 4.5 Hz, 1H), 1.46 – 1.35 (m, 2H), 1.11 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.97 (s, 3H), 0.91 (d, *J* = 3.4 Hz, 6H), 0.11 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 166.3, 142.1, 135.3, 134.83, 134.79, 131.9, 129.9, 128.5, 127.8, 80.1, 48.9, 47.7, 44.9, 36.9, 28.0, 27.3, 19.6, 18.8, 13.5, 2.0. IR (neat, cm⁻¹): 2855 (m), 1428 (m), 1262 (m), 1058 (m), 698 (s); HRMS (ESI) m/z: [M+H]⁺ Calcd. for C₃₂H₄₁O₃Si₂: 529.2589; Found: 529.2600.



22, (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(3,3,3-trimethyl-1,1-diphenyldisiloxanyl)benzoate

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether : ethyl acetate = 50 : 1) afforded 1.96 g (74% yield) of the desired product as a colorless oil.

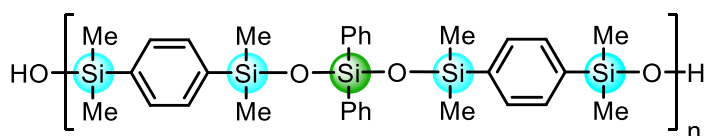
¹H NMR (500 MHz, CDCl₃) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.53 (m, 4H), 7.42 (d, *J* = 6.9 Hz, 2H), 7.39 – 7.35 (m, 4H), 4.93 (td, *J* = 10.9, 4.4 Hz, 1H), 2.15-2.09 (m, 1H), 1.96 (td, *J* = 6.9, 2.6 Hz, 1H), 1.75-1.70 (m, 2H), 1.57 – 1.49 (m, 2H), 1.17 – 1.04 (m, 2H), 0.92 (t, *J* = 7.1 Hz, 6H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.10 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 166.3, 142.3, 135.6, 135.06, 135.00, 132.0, 130.1, 128.6, 128.0, 75.0, 47.4, 41.1, 34.4, 31.6, 26.6, 23.7, 22.2, 20.9, 16.6, 2.2. **IR** (neat, cm⁻¹): 2954 (m), 1429 (m), 1251 (m), 1058 (m), 699 (s); **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd. for C₃₂H₄₃O₃Si₂: 531.2746; Found: 531.2757.



23, 4-(3,3,3-trimethyl-1,1-diphenyldisiloxanyl)phenyl 2-(4-isobutylphenyl)propanoate

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether : ethyl acetate = 50 : 1) afforded 2.26 g (82% yield) of the desired product as a colorless oil.

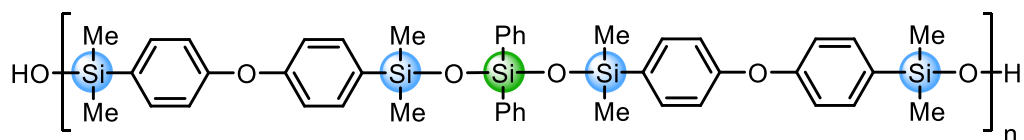
¹H NMR (500 MHz, CDCl₃) δ 7.86 – 7.79 (m, 6H), 7.61 – 7.51 (m, 8H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 1H), 2.69 (d, *J* = 7.2 Hz, 2H), 2.16 – 2.02 (m, 1H), 1.82 (d, *J* = 7.2 Hz, 3H), 1.13 (d, *J* = 6.7 Hz, 6H), 0.34 (s, 9H). **¹³C NMR** (126 MHz, CDCl₃) δ 173.1, 152.4, 140.8, 137.3, 136.3, 136.0, 135.0, 133.8, 129.9, 129.6, 127.9, 127.3, 120.9, 45.4, 45.1, 30.2, 22.5, 18.6, 2.1. **IR** (neat, cm⁻¹): 2955 (m), 1429 (m), 1251 (m), 1050 (s), 699 (s); **HRMS (ESI)** *m/z*: [M+H]⁺ Calcd. for C₃₄H₄₁O₃Si₂: 553.2589; Found: 553.2601.



26, polysilylether (**P_{AB}**)

Synthesized according to **GP 2**. Purification by precipitation method afforded 2.16 g (68% yield) of the desired product as a colorless viscous oil.

¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.30 (m, 18H), 0.60 – 0.24 (m, 24H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.1, 141.0, 140.43, 140.35, 136.1, 135.5, 134.7, 134.6, 134.4, 132.52, 132.46, 132.41, 132.35, 123.0, 127.8, 127.7, 1.1, 0.9, 0.8. **IR** (neat, cm⁻¹): 3392 (w), 2957 (w), 1120 (s), 1041 (s), 506 (s).



27, polysilylether (**P_{AC}**)

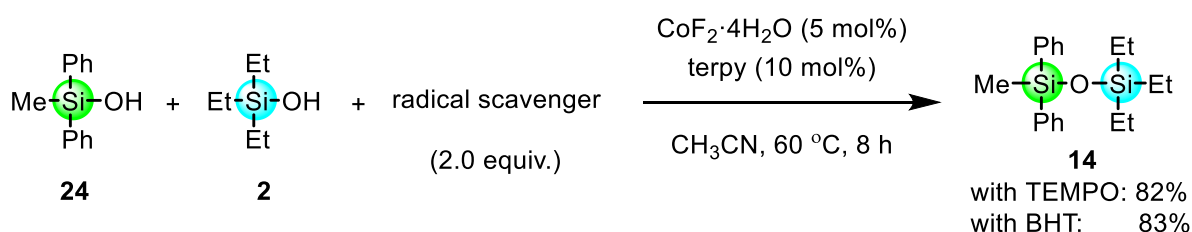
Synthesized according to **GP 2**. Purification by precipitation method afforded 3.21 g (79% yield) of the desired product as a light yellow viscous oil.

¹H NMR (400 MHz, CDCl₃) δ 8.46 – 7.32 (m, 26H), 1.27 – 0.45 (m, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 158.2, 136.0, 135.5, 135.0, 134.9, 134.5, 134.4, 133.8, 130.0, 127.8, 118.4, 1.2, 1.0. IR (neat, cm⁻¹): 3320 (w), 2757 (m), 1112 (s), 1041 (s), 510 (s).

5. Mechanism Studies

5.1 The radical inhibition experiment

Regarding the reaction mechanism, the possible radical pathway of this transformation was ruled out because the addition of radical scavengers, such as TEMPO (2,2,6,6-tetramethylpiperidinoxy) or BHT (2,6-di-tert-butyl-4-methylphenol), still afforded the target unsymmetric disiloxane (**14**) in 82% and 83%, respectively.



^a Reaction conditions: **24** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), CoF₂·4H₂O (0.01 mmol, 5 mol%) and terpy (0.02 mmol, 10 mol%), radical scavenger (10 mmol, 2.0 equiv.) were added to MeCN (1.0 mL) under air for 8 h at 60 °C. ^b The yields were given with CH₂Br₂ as the internal standard.

5.2 XPS analysis of cobalt complex K1

CoF₂·4H₂O (1.0 mmol) and terpy (2.0 equiv.) were dissolved in MeCN (10 mL) under air for 8 h at 60 °C, filtered and washed by ethanol. Then, the filtrate removed in vacuo, giving a dark brown solid **K1**. After that, this solid was washed with diethyl ether (10 mL) and dried in vacuo. (yield: 0.19 g, 51%).^[7]

To further investigate the valence change of Co before and after the reaction, we carried out a detailed study using XPS. During the reaction, CoF₂·4H₂O was coordinated with tripyridine to form a Co complex. The fine XPS spectrum of Co 2p shows that 778.9 eV is due to Co³⁺ 2p_{3/2}. 779.9 eV is attributed to Co²⁺ 2p_{3/2}.^[8] The fine XPS spectrum of F 1s shows that the valence electrons are closer to the F atom due to the oxidation of the Co complex, which causes the binding energy to shift towards the low field direction. Among them, the F signal at 683.2 eV and the bivalent Co may be caused by the inseparable CoF₂·4H₂O.

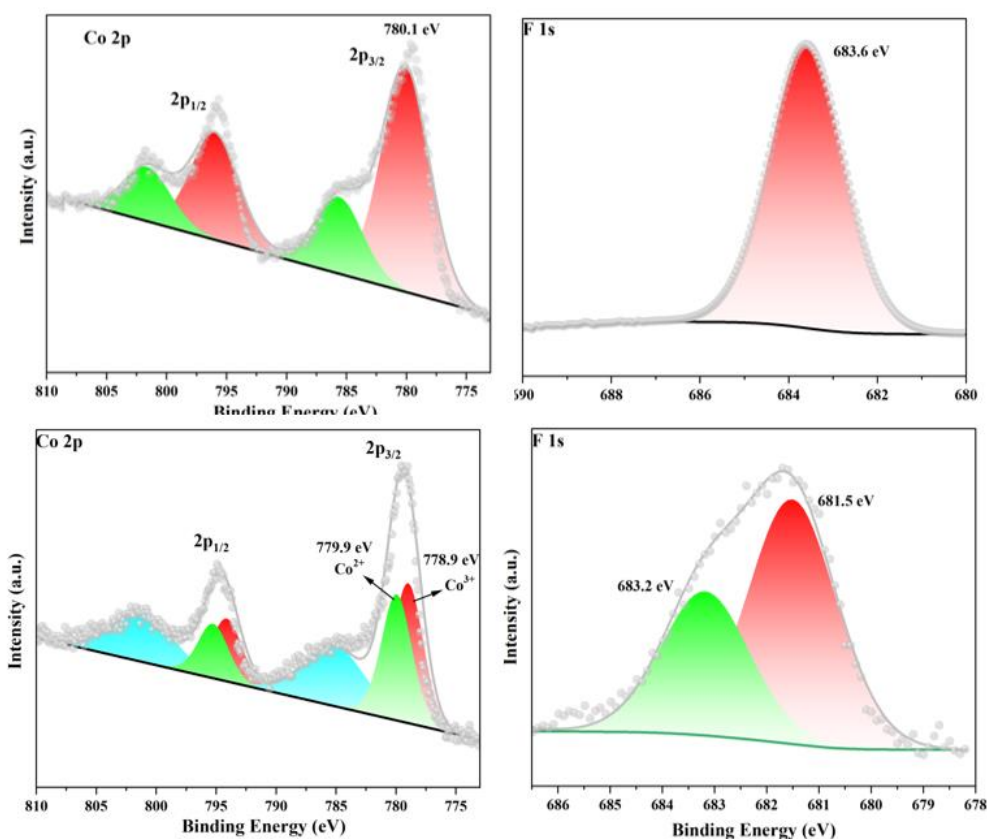
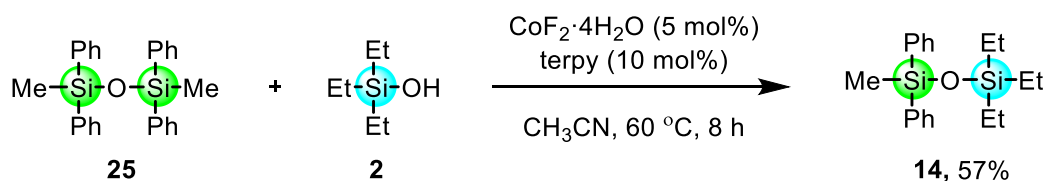


Figure S1. Comparison of XPS before and after cobalt complexation.

5.3 Control experiment

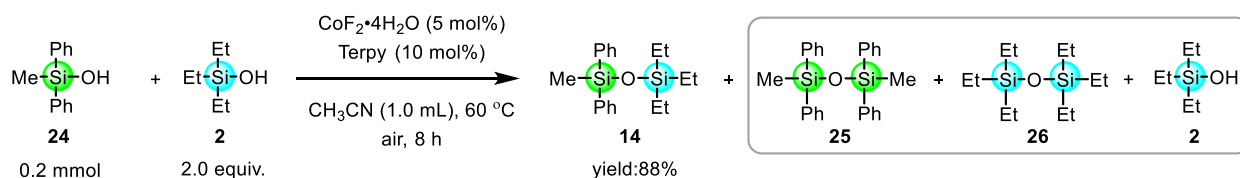
The control experiment confirmed that symmetric disiloxane (**24**) can be a competent substrate to proceed with a similar reactivity toward the formation of unsymmetric disiloxane (**14**) in 57% yield.



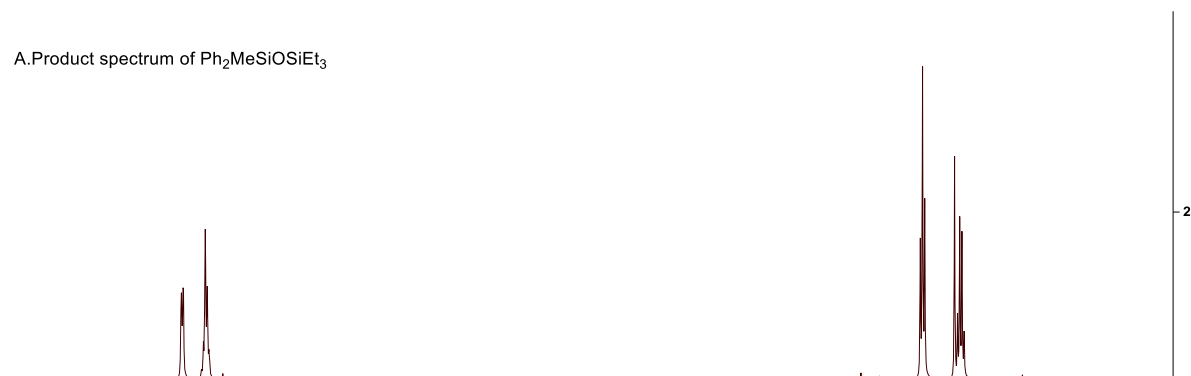
^a Reaction conditions: **25** (0.2 mmol, 1.0 equiv.), **2** (0.4 mmol, 2.0 equiv.), $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ (0.01 mmol, 5 mol%) and terpy (0.02 mmol, 10 mol%) were added to MeCN (1.0 mL) under air for 8 h at 60 °C. ^b The yields were given with CH_2Br_2 as the internal standard.

5.4 Whereabouts of excess silanols

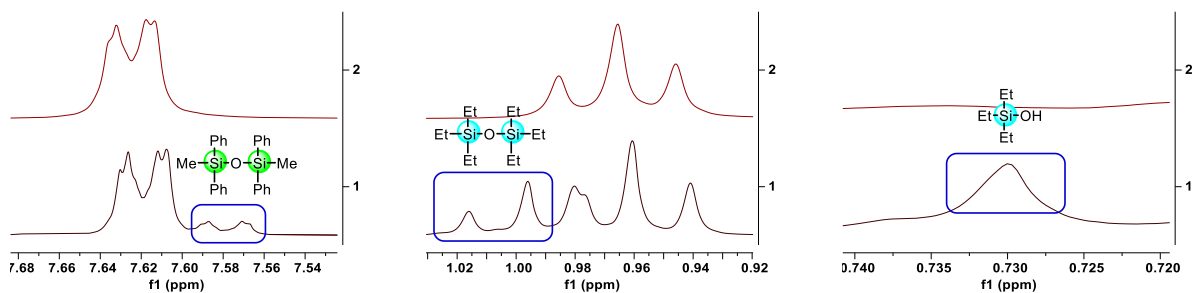
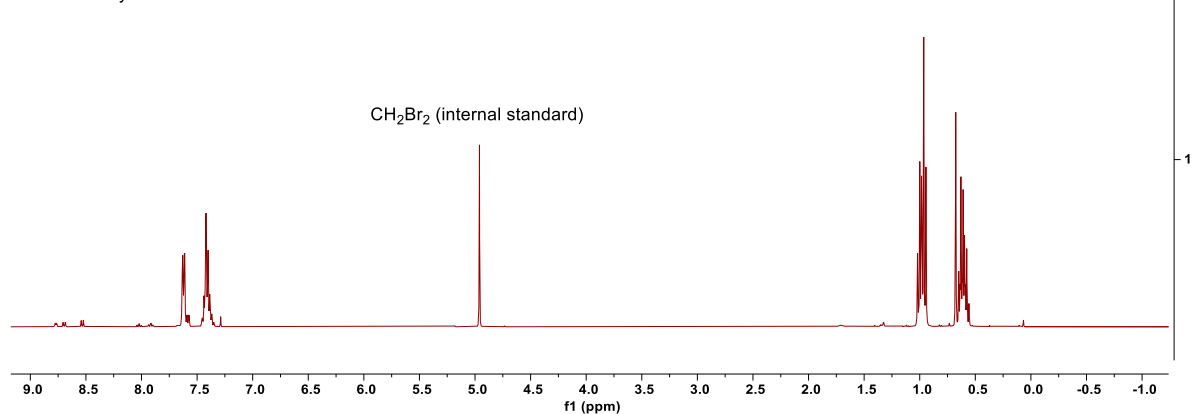
This reaction used two equiv of one silanol. To investigate the fate of excess silane alcohol, the crude nuclear magnetic spectra and product spectra were compared, and it was found that a small portion of the excess silane alcohol remained in the form of a silane alcohol, but more of it became a symmetrical disiloxane. However, the corresponding fluorine signal could not be captured by the fluorine spectrum for the formation of Si-F, so it was ruled out.



A. Product spectrum of $\text{Ph}_2\text{MeSiOSiEt}_3$

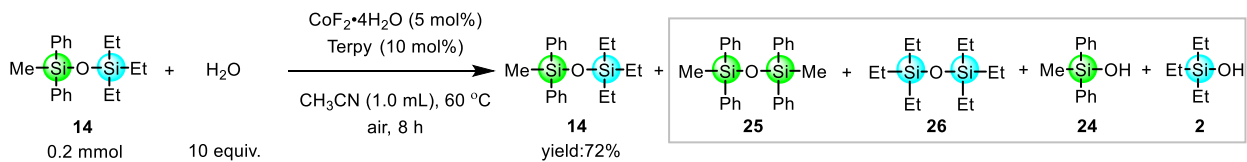


B. Reaction system



5.5 Hydrolysis of disiloxanes

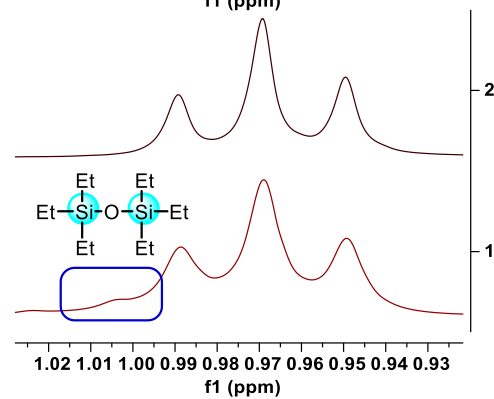
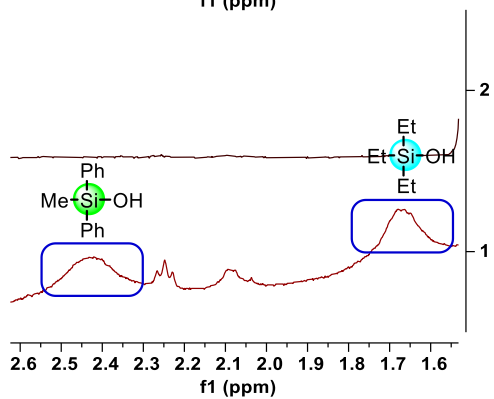
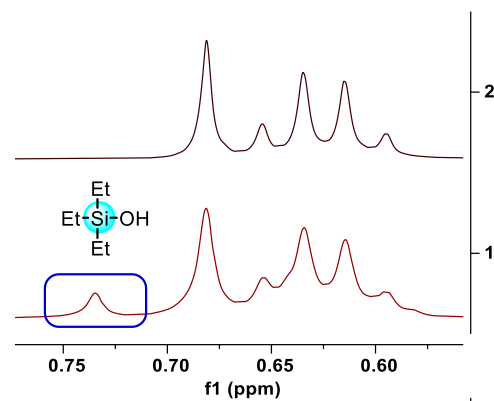
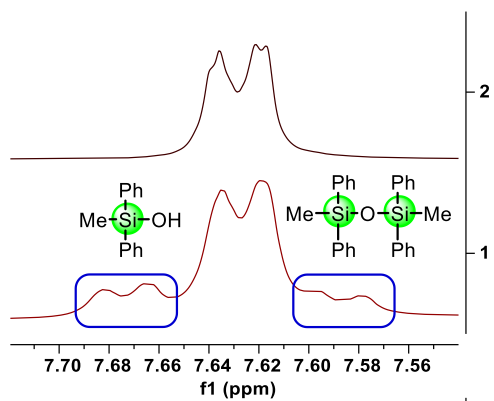
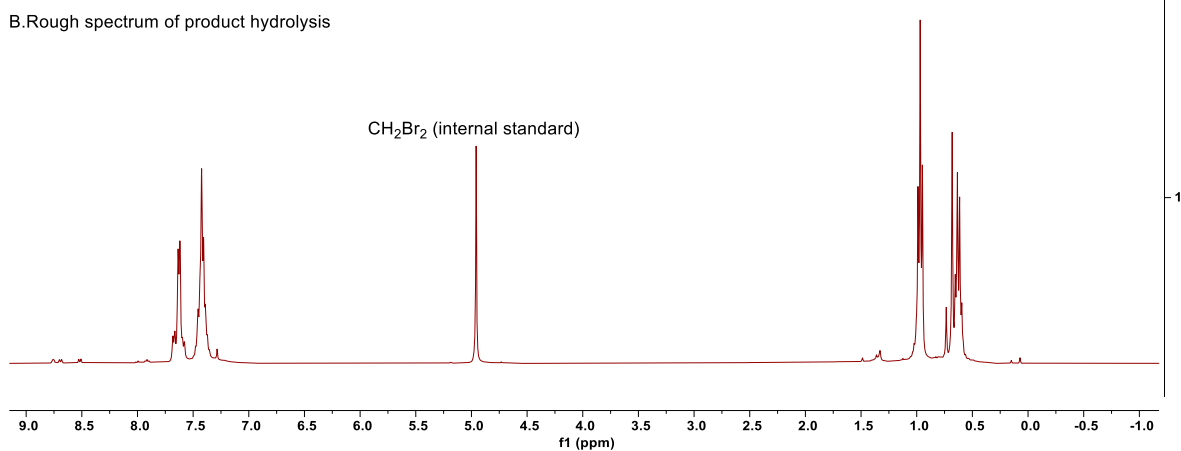
We attempted to react the product with 10 equiv. amounts of water under standard conditions. By comparing the crude nuclear magnetic resonance spectra and product spectra after hydrolysis, we found that a small amount of corresponding symmetrical siloxanes and silanols were formed after hydrolysis. This further indicates that the reaction is an equilibrium process. In addition, we compared the temperature. At room temperature, the hydrolysis reaction does not occur, indicating that this step is reversible.



A. Product spectrum of Ph₂MeSiOSiEt₃



B. Rough spectrum of product hydrolysis



5.6 The sampling experiment

The sampling experiment (Figure S1) suggested symmetric disiloxane (**24**) was preferentially formed at the early stage, which was consumed into unsymmetric disiloxane (**14**) along with the reaction time. Taken together, symmetric disiloxane (**24**) should be one reaction intermediate in this transformation.

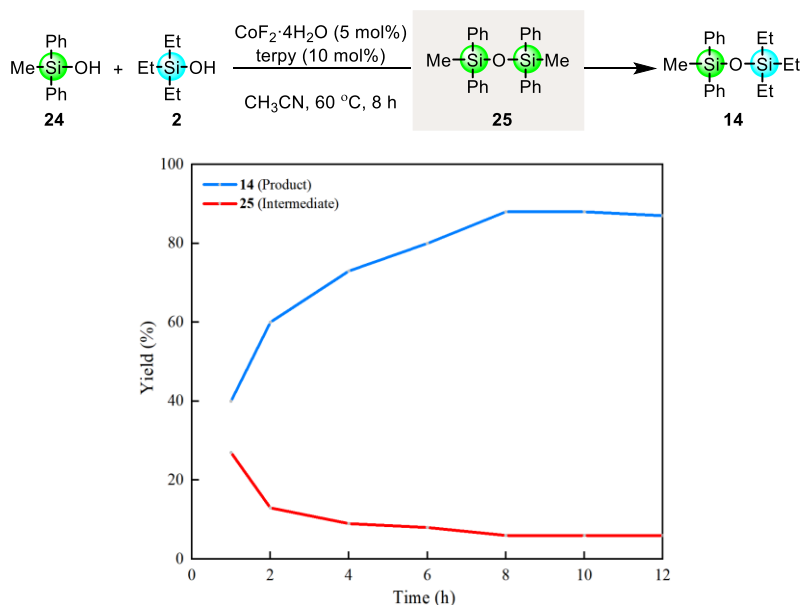
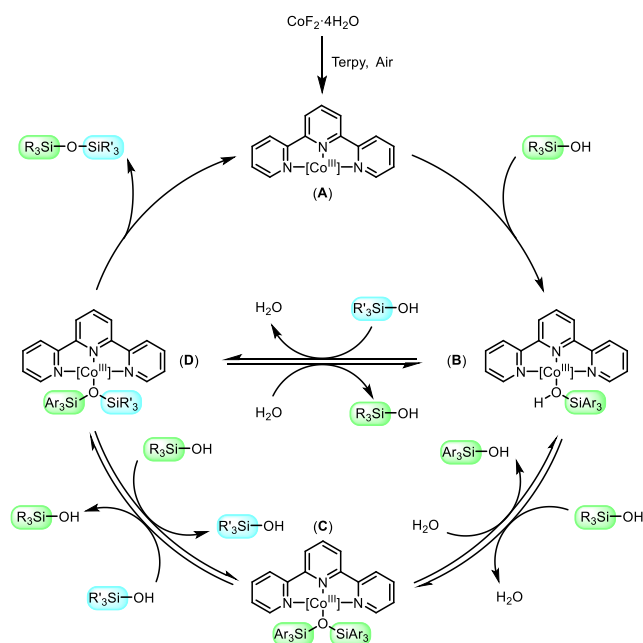


Figure S1. The sampling experiment.

Based on the literature precedence and our mechanistic studies, a proposed mechanism was illustrated in Figure S2. Firstly, $\text{CoF}_2 \cdot 4\text{H}_2\text{O}$ coordinated with terpy to provide cobalt complex (**A**) in air. The coordination of triarylsilanol to complex (**A**) provides a silanol-ligated intermediate (**B**). Another equivalent of triarylsilanol then reacts with the metal-coordinated triarylsilanol leading to the formation of symmetric disiloxane-ligated cobalt complex (**C**). After that, a siloxane-exchange reaction between the metal-bounded symmetric disiloxane (**C**) and the excess trialkylsilanol generates an unsymmetric disiloxane-ligated cobalt complex (**D**). Or (**B**) directly reacts with silanol to form (**D**), which undergoes dissociation to liberate the anticipated unsymmetric disiloxanes and regenerates cobalt complex (**A**) and completes the catalytic cycle.



Scheme S2. Proposed mechanism.

6. Properties of Polysiloxanes

6.1 Thermal properties

The thermal behavior of the resulting functional polysiloxanes was evaluated by TG analysis. The thermal decomposition temperatures of **P_{AB}**, **P_{AC}** were 490 and 504 °C in Figure S3, respectively. The results of TGA indicated these polymers exhibit good thermal stability.

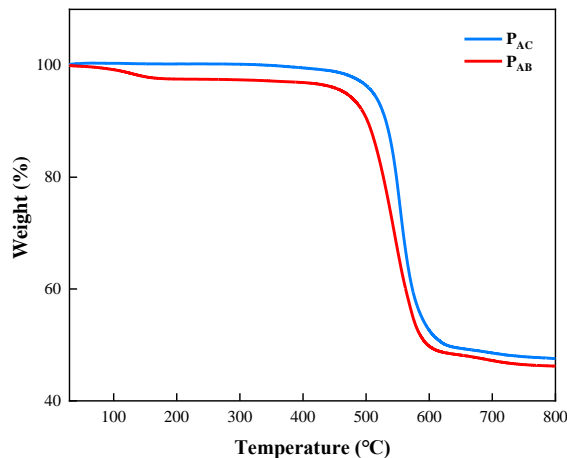


Figure S3. TGA thermograms of polysiloxane **P_{AB}** and **P_{AC}**.

6.2 UV/vis absorption spectra and fluorescence spectra

UV/vis absorption measurement: 1×10^{-5} mol/L sample in dichloromethane was placed in the UV/Vis spectrophotometer. The scan speed was set to high speed, scan range: from 200 nm to 800 nm. UV/vis absorption spectra data of samples was measured by SHIMADZU UV-2600 spectrophotometer.

Fluorescence measurement: 1×10^{-5} mol/L sample in dichloromethane was placed in the fluorescence spectrophotometer. The scan speed was set to 240 nm/min, scan range: from 280 nm to 600 nm, and both the excitation slit and emission slit were 5 nm. The fluorescence spectra were obtained by

irradiation at 260 nm. The fluorescence spectral data of samples was measured by HITACHI FLS-980 spectrofluorometer.

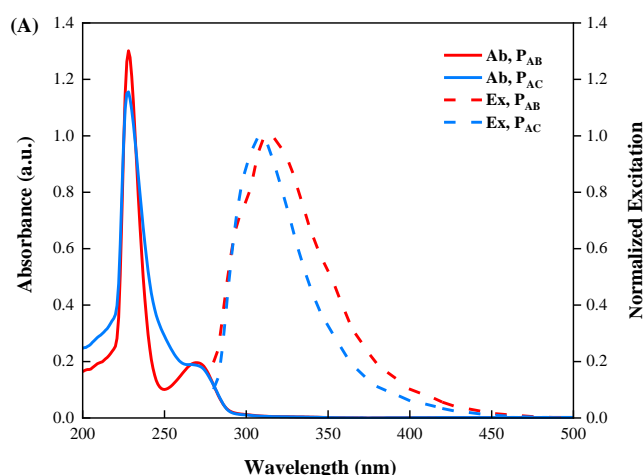


Figure S4. Absorption (solid line) and fluorescence (dotted line) of **P_{AB}** and **P_{AC}** in DCM.

Table S1. Absorption spectra and Excitation spectrum of **P_{AB}** and **P_{AC}** in DCM.

Entry	Structure	λ_{abs} (l)/nm	λ_{em} (l)/nm
P_{AB}		228	313
P_{AC}		228	309

UV/vis absorption measurement: the solid sample was placed in the UV/Vis spectrophotometer. The scan speed was set to high speed, scan range: from 200 nm to 800 nm. UV/vis absorption spectra data of samples was measured by SHIMADZU UV-2600 spectrophotometer.

Fluorescence measurement: the solid sample was placed in the fluorescence spectrophotometer. The fluorescence spectra were obtained by irradiation at 260 nm. The fluorescence spectral data of samples was measured by F-7000 spectrofluorometer.

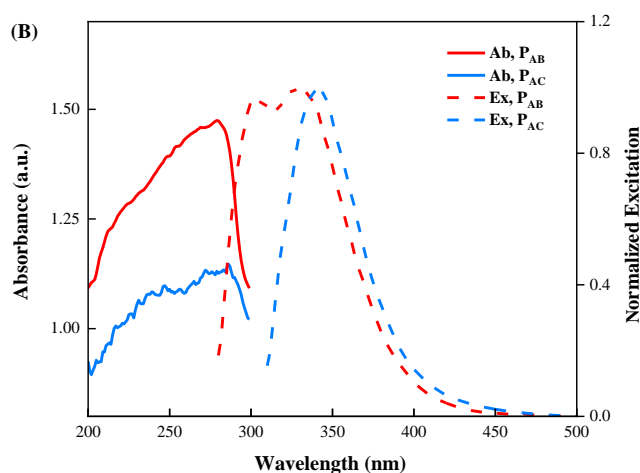


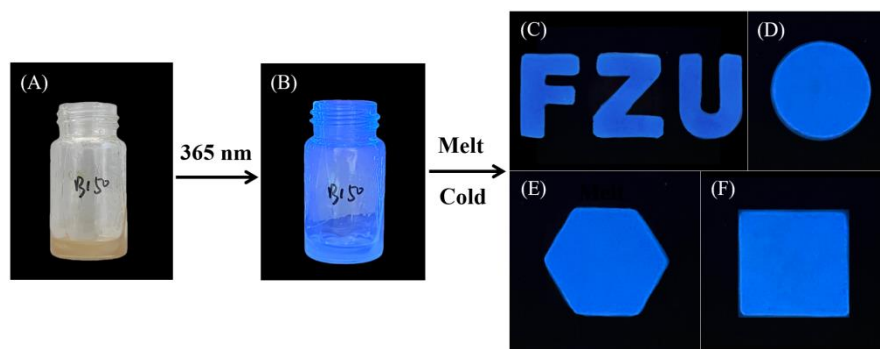
Figure S5. Absorption (solid line) and fluorescence (dotted line) of **P_{AB}** and **P_{AC}** as solid.

Table S2. UV/vis absorption spectra and Excitation spectrum of **P_{AB}** and **P_{AC}** as solid.

Entry	Structure	λ_{abs} (s)/nm	λ_{em} (s)/nm
P_{AB}		279	330
P_{AC}		286	343

6.3 Thermoplastic character

Not only did we find that radiated by a UV lamp with 365 nm wavelength, the polymer **P_{AC}** without any treatment all exhibit bright blue fluorescence in the solid state, as displayed in Figure S6A-B, we also found that it is thermoplastic. As shown in Figure S6, we heat it until the gel melts into a liquid. When it is no longer hot, we can crumb can crumble it. Then we cool it down and get a new shape (Figure S6C-F). This proved that the material was thermoplastic, because you could not melt and thermoform thermosets. It also showed that the new polysiloxane could be recycled.

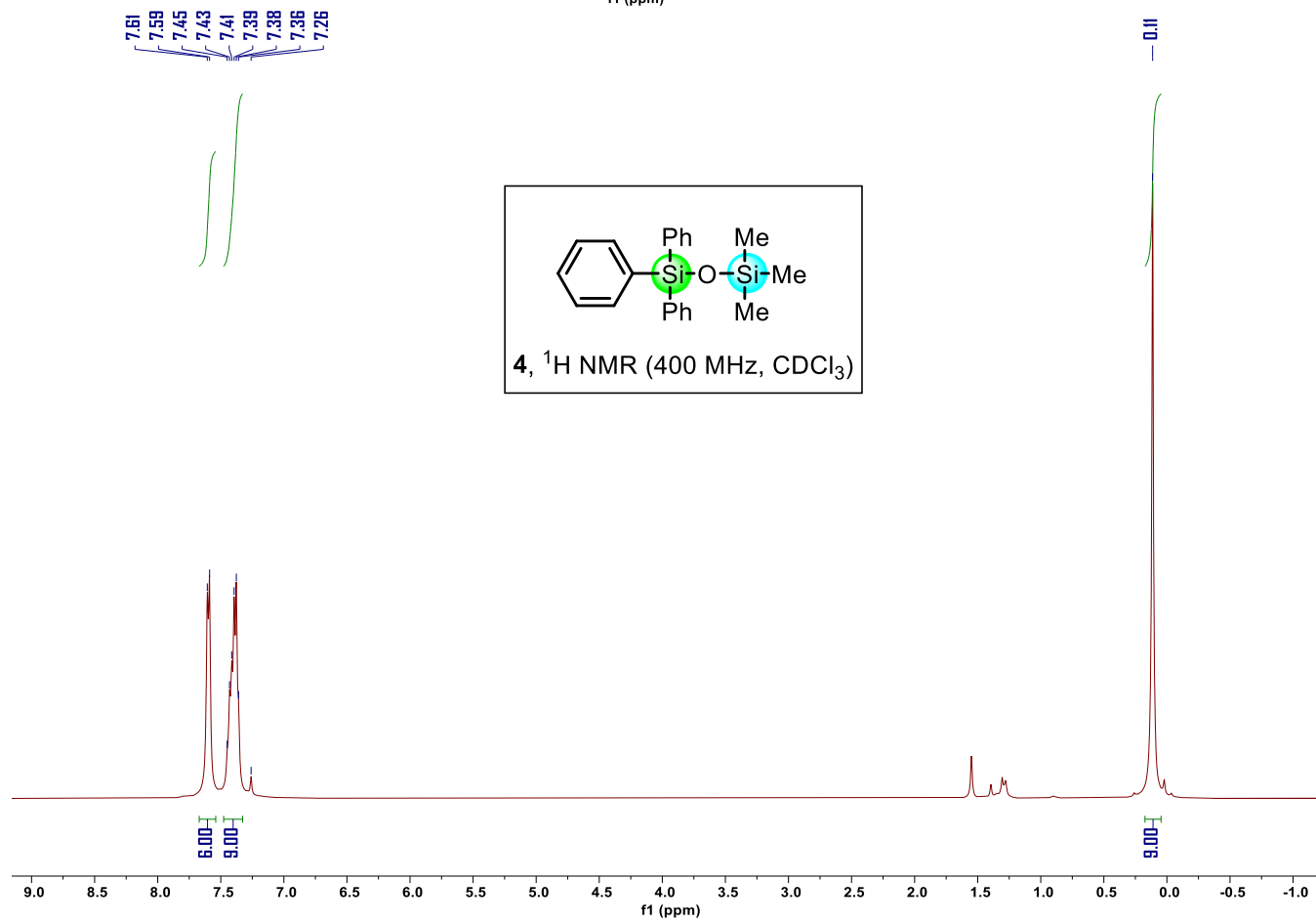
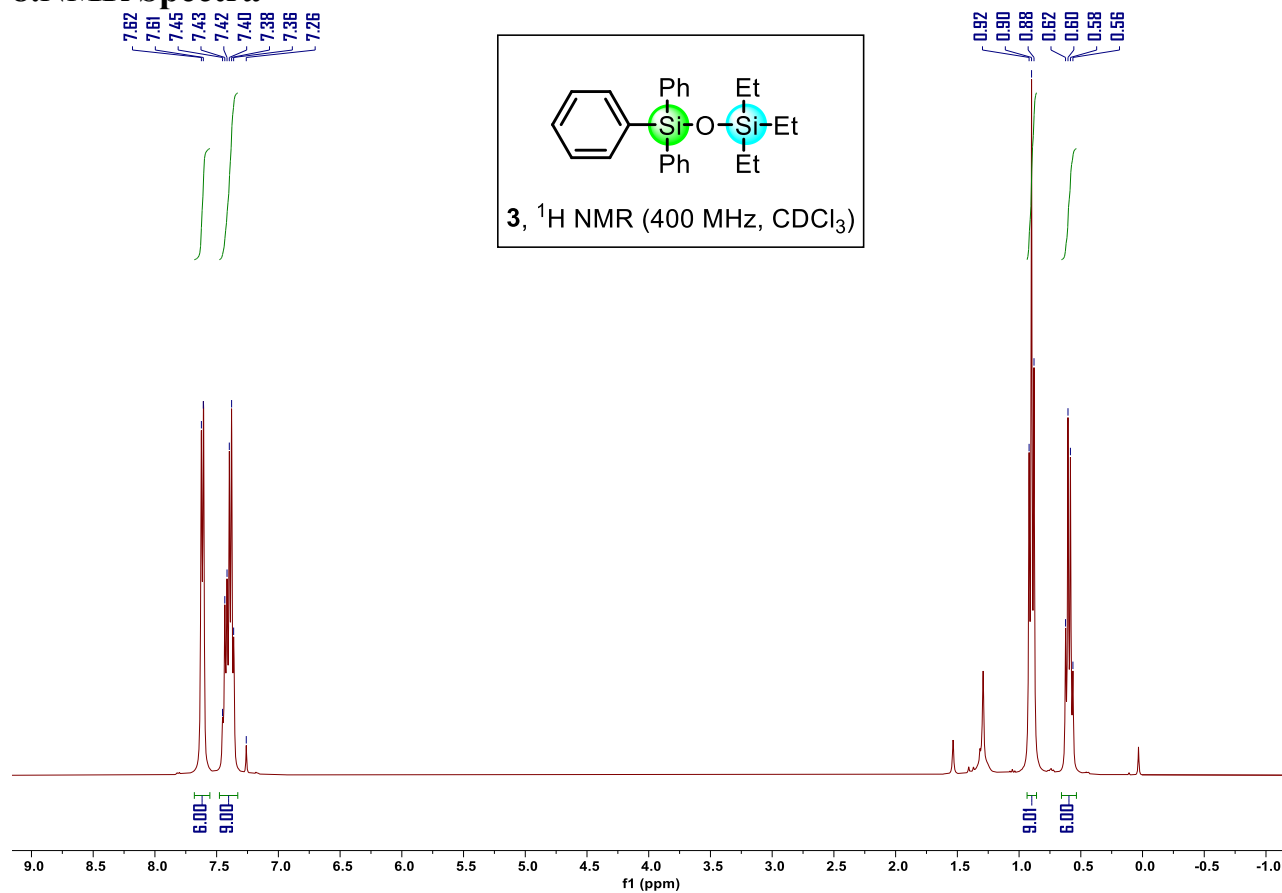
**Figure S6.** Material thermoforming process diagram.

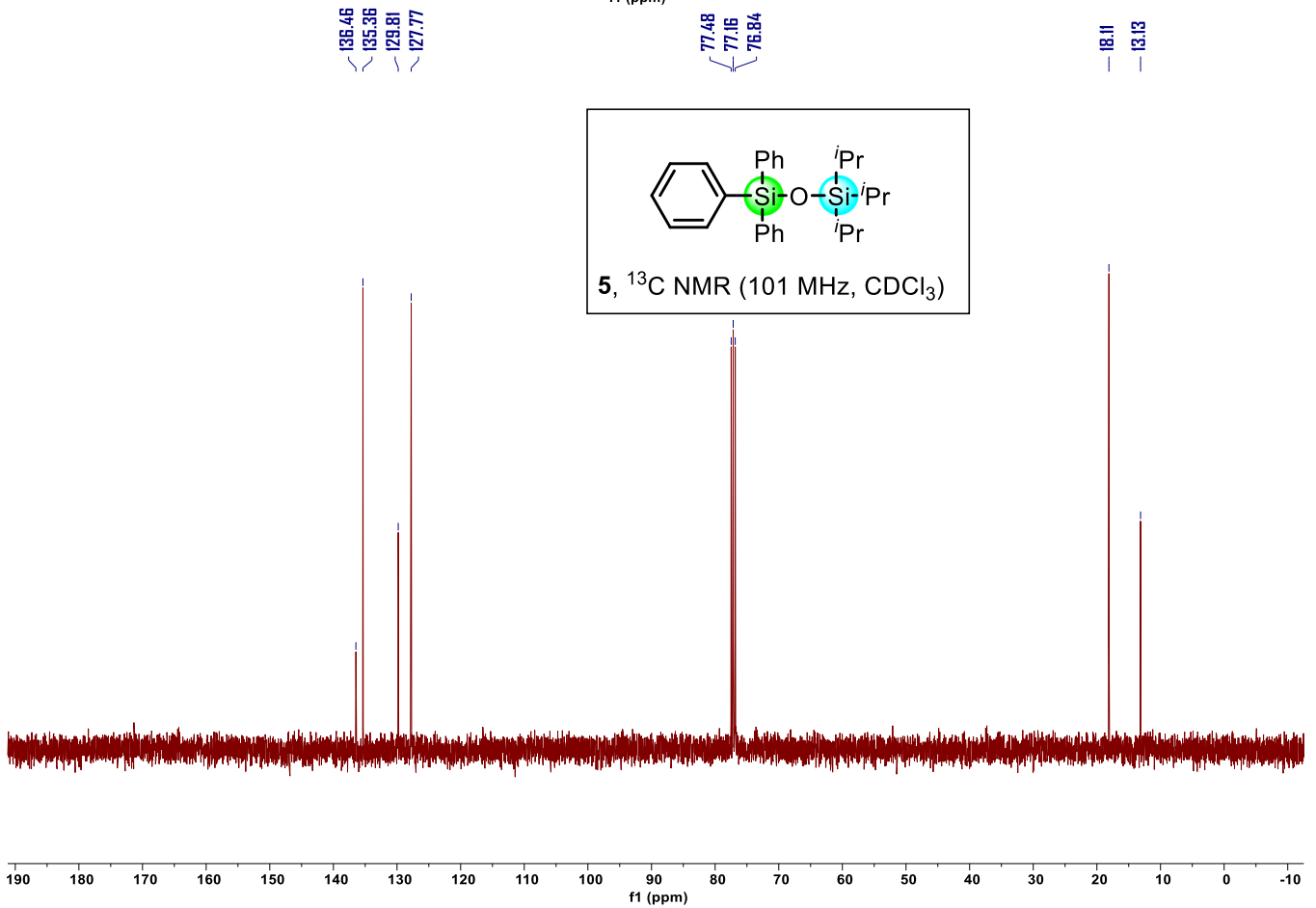
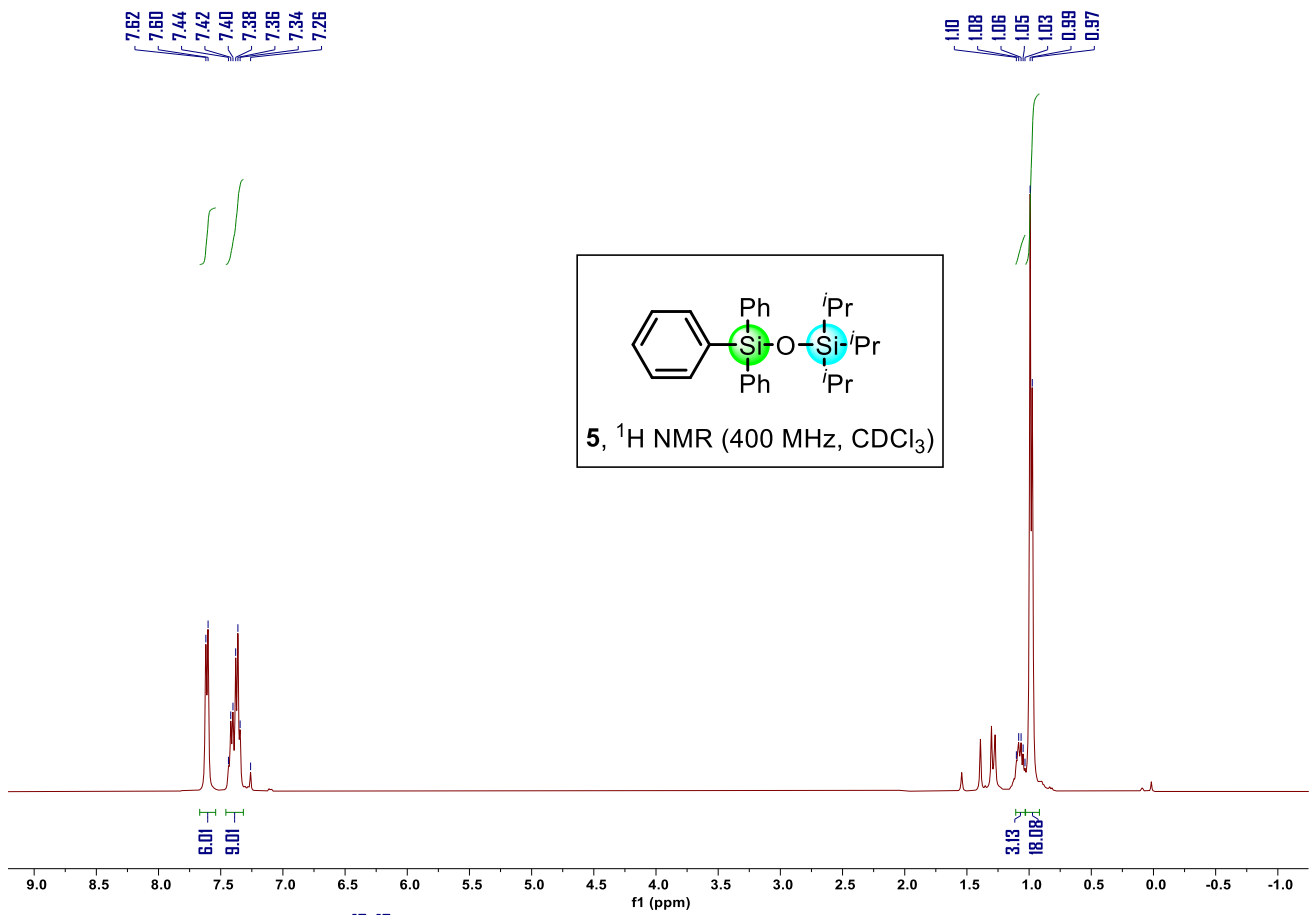
7. References

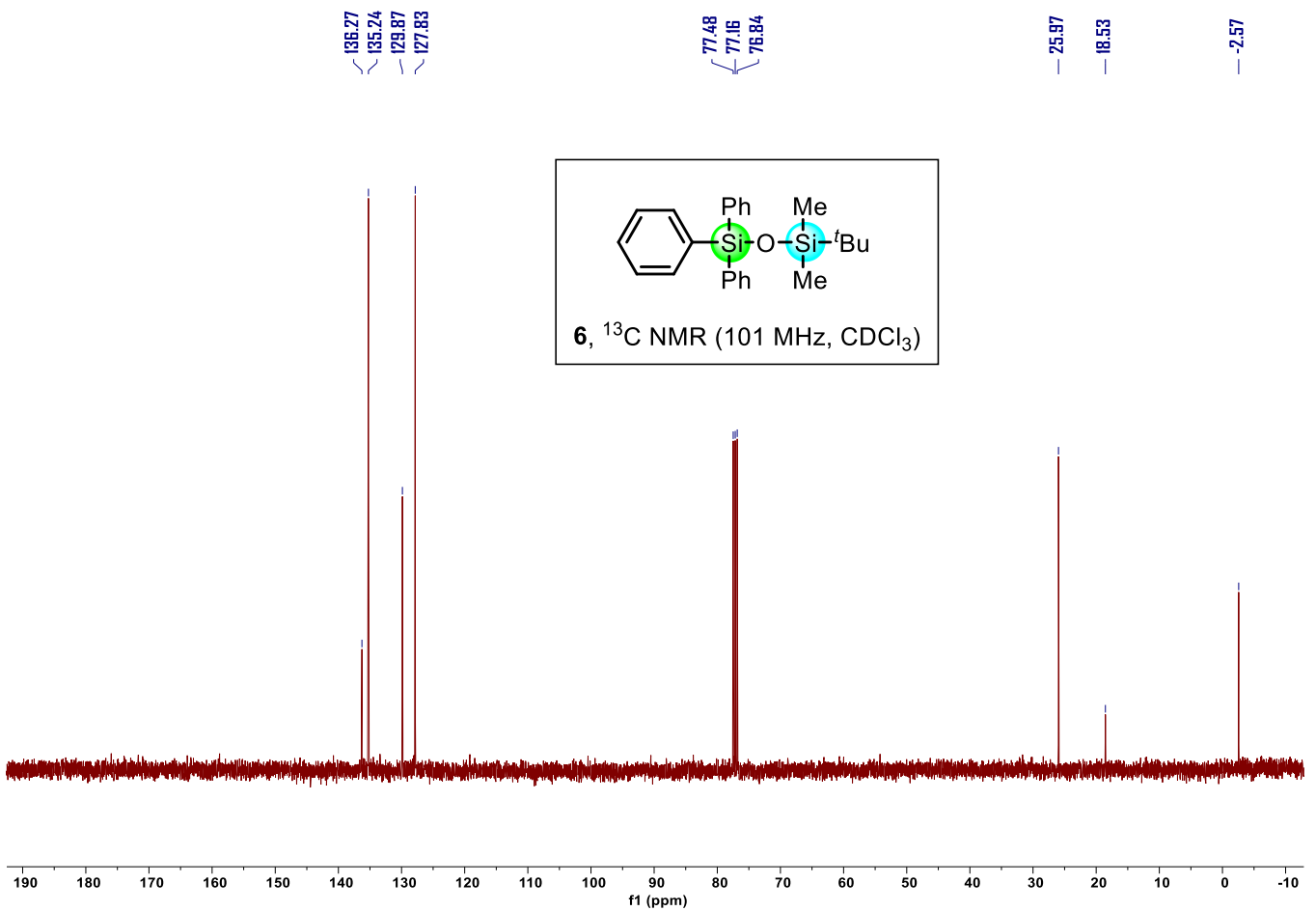
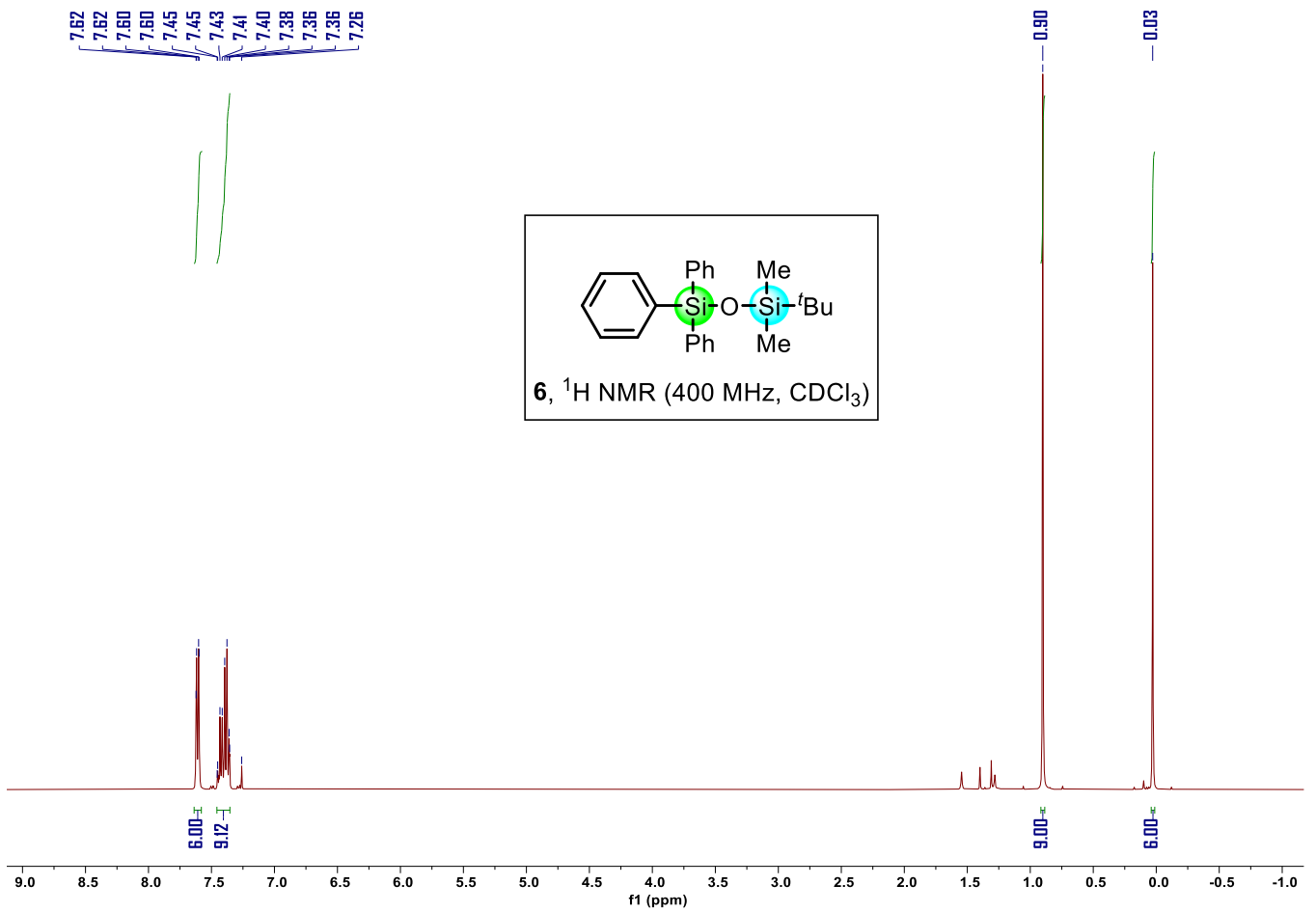
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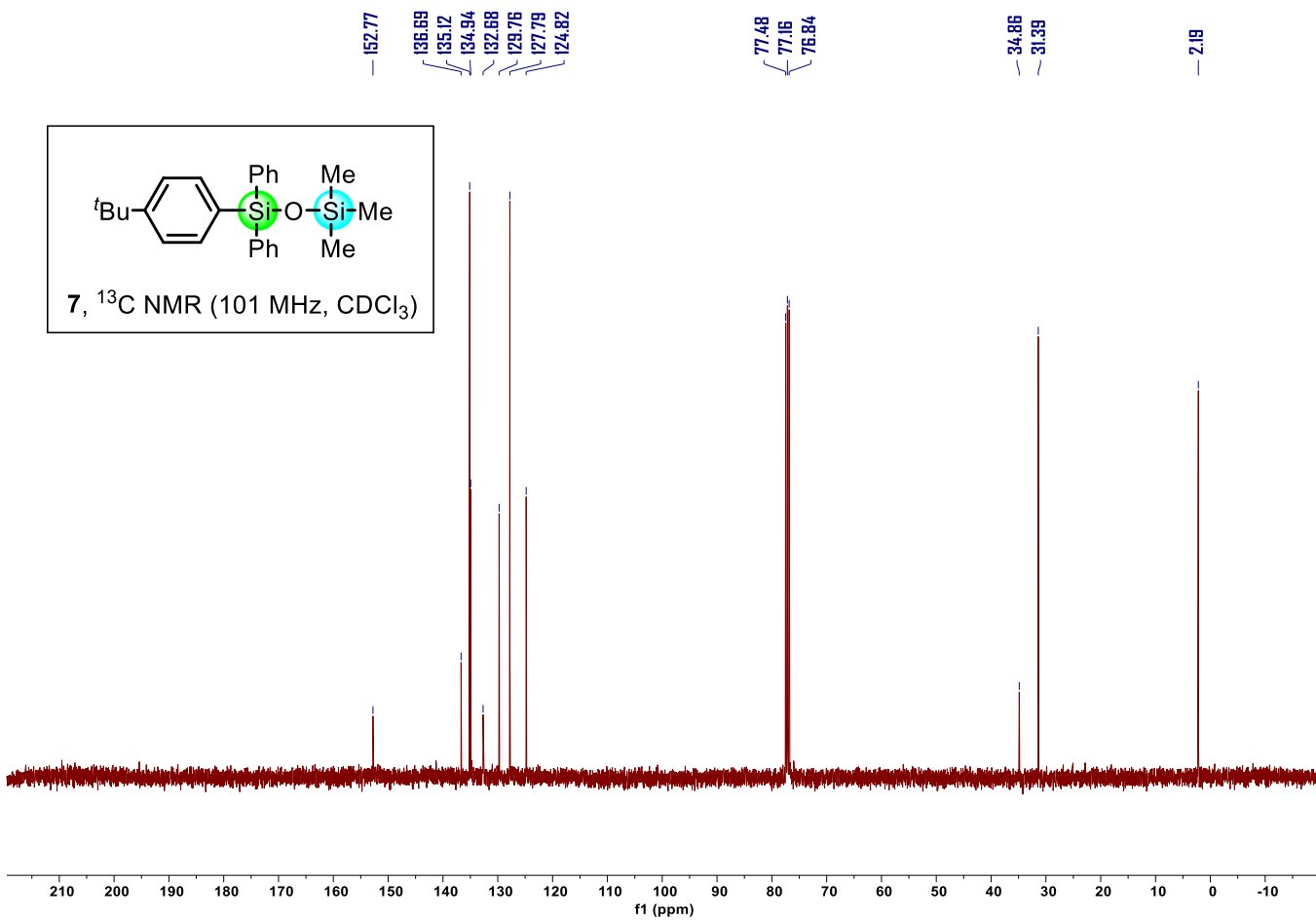
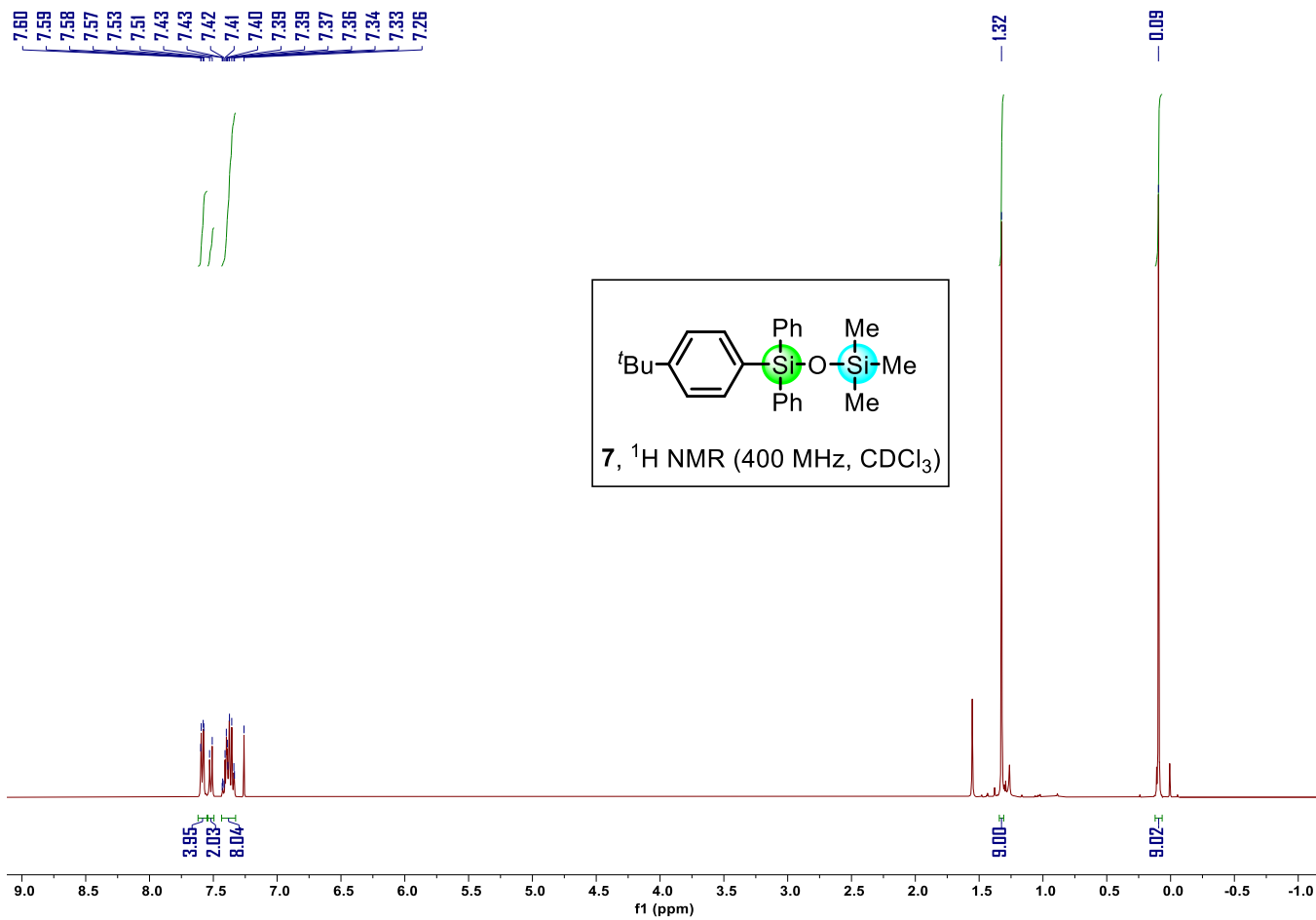
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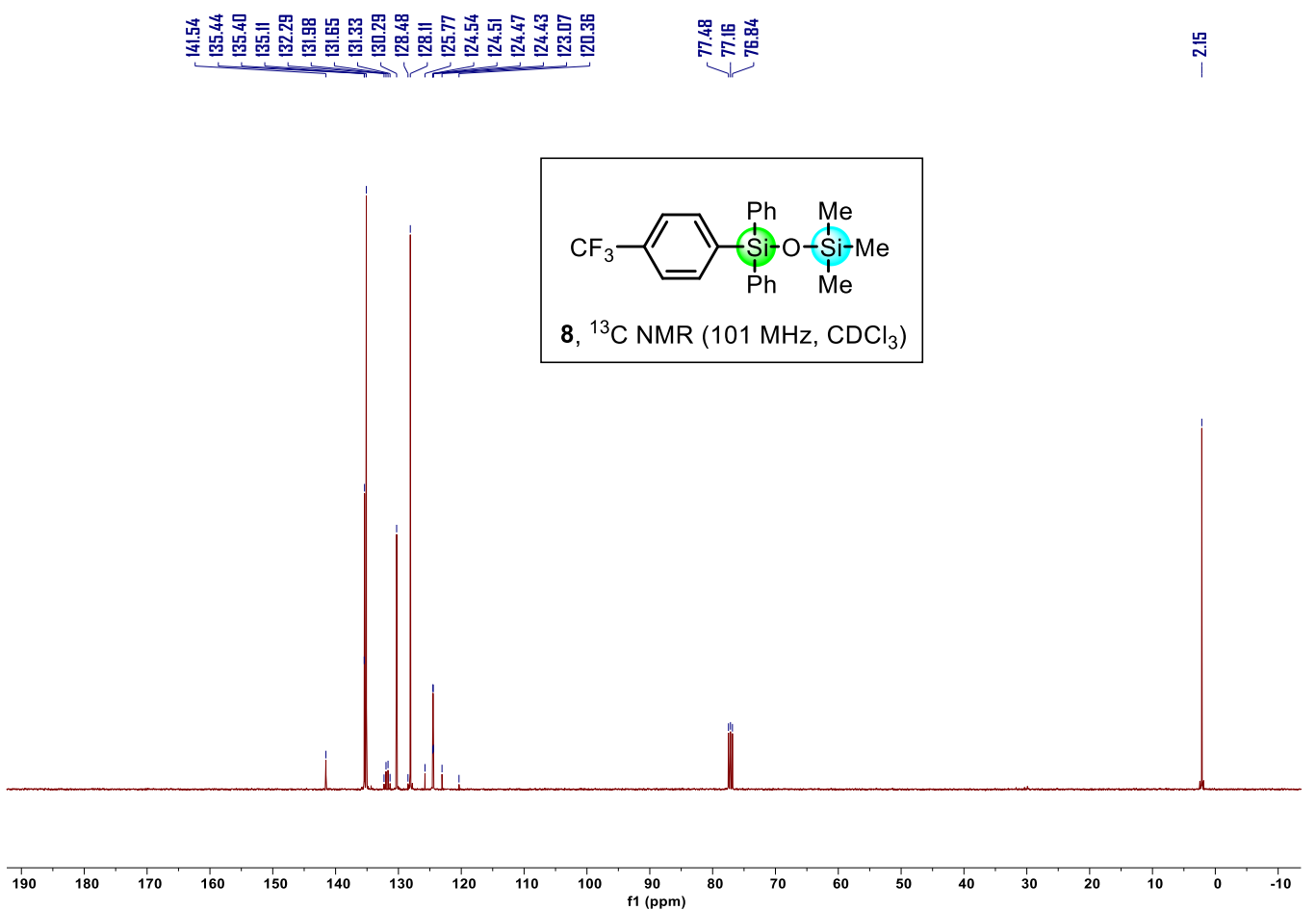
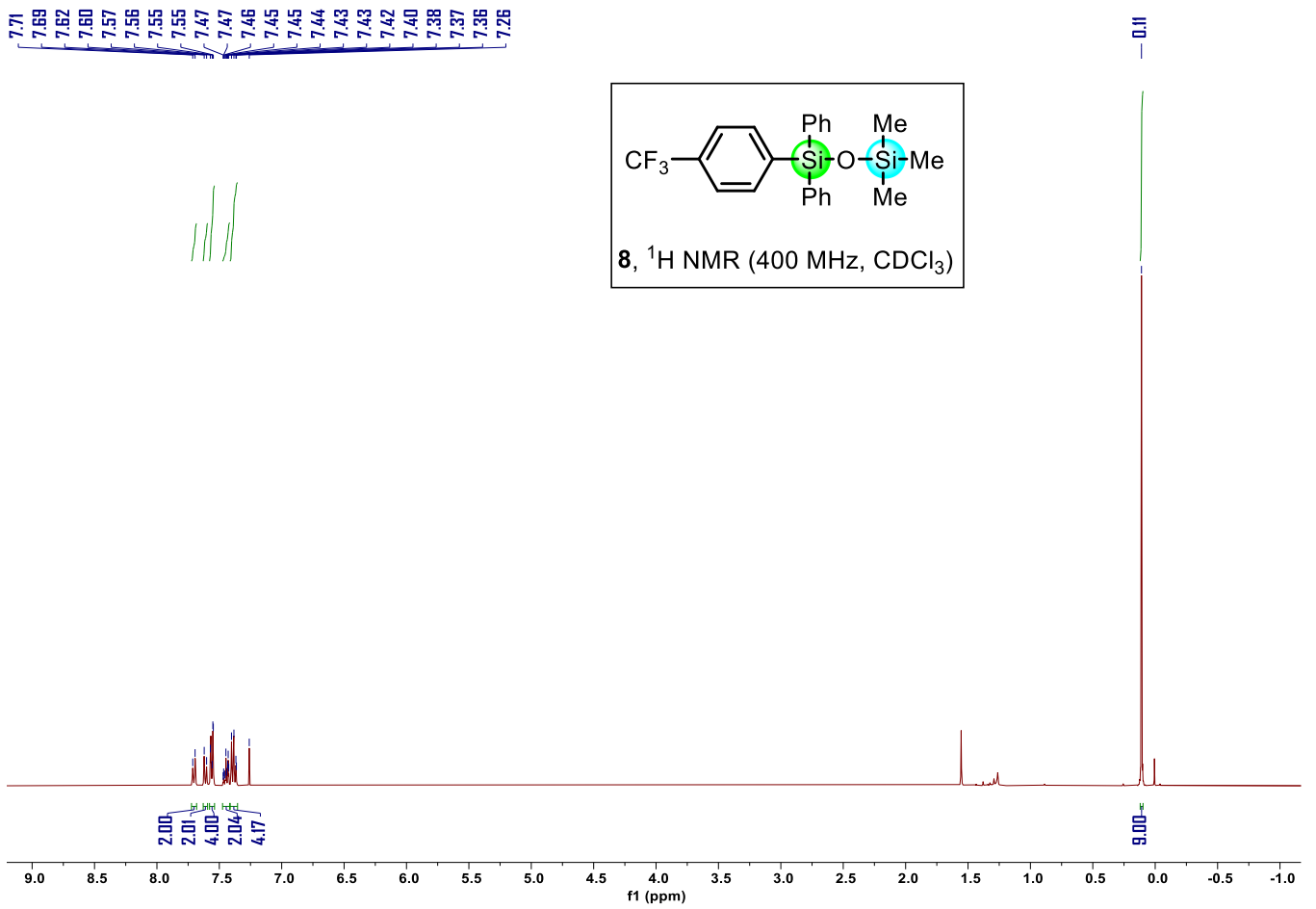
8. NMR Spectra

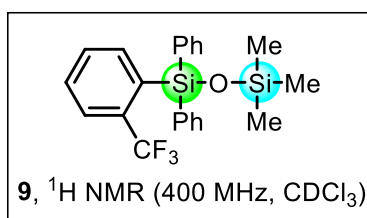
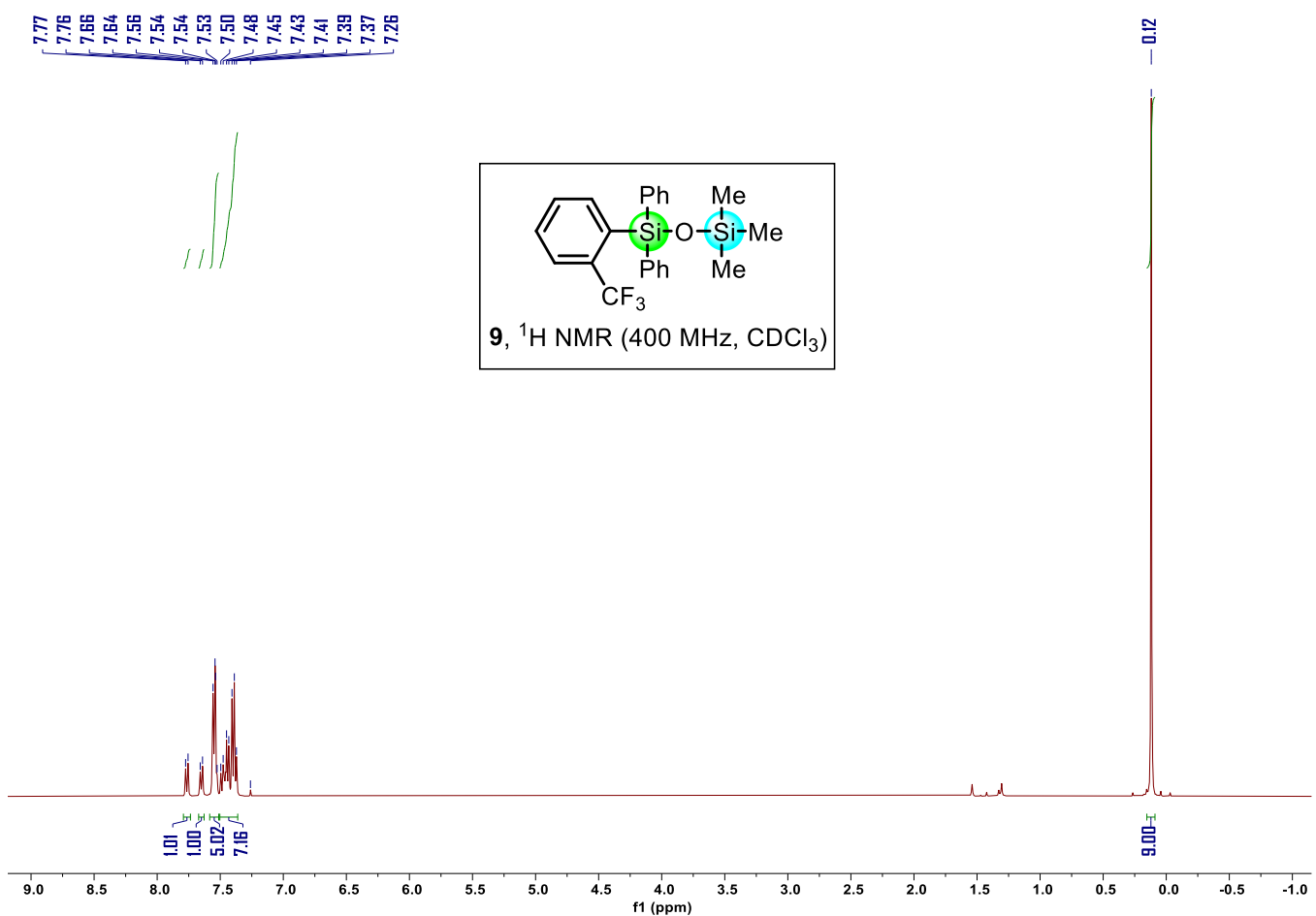
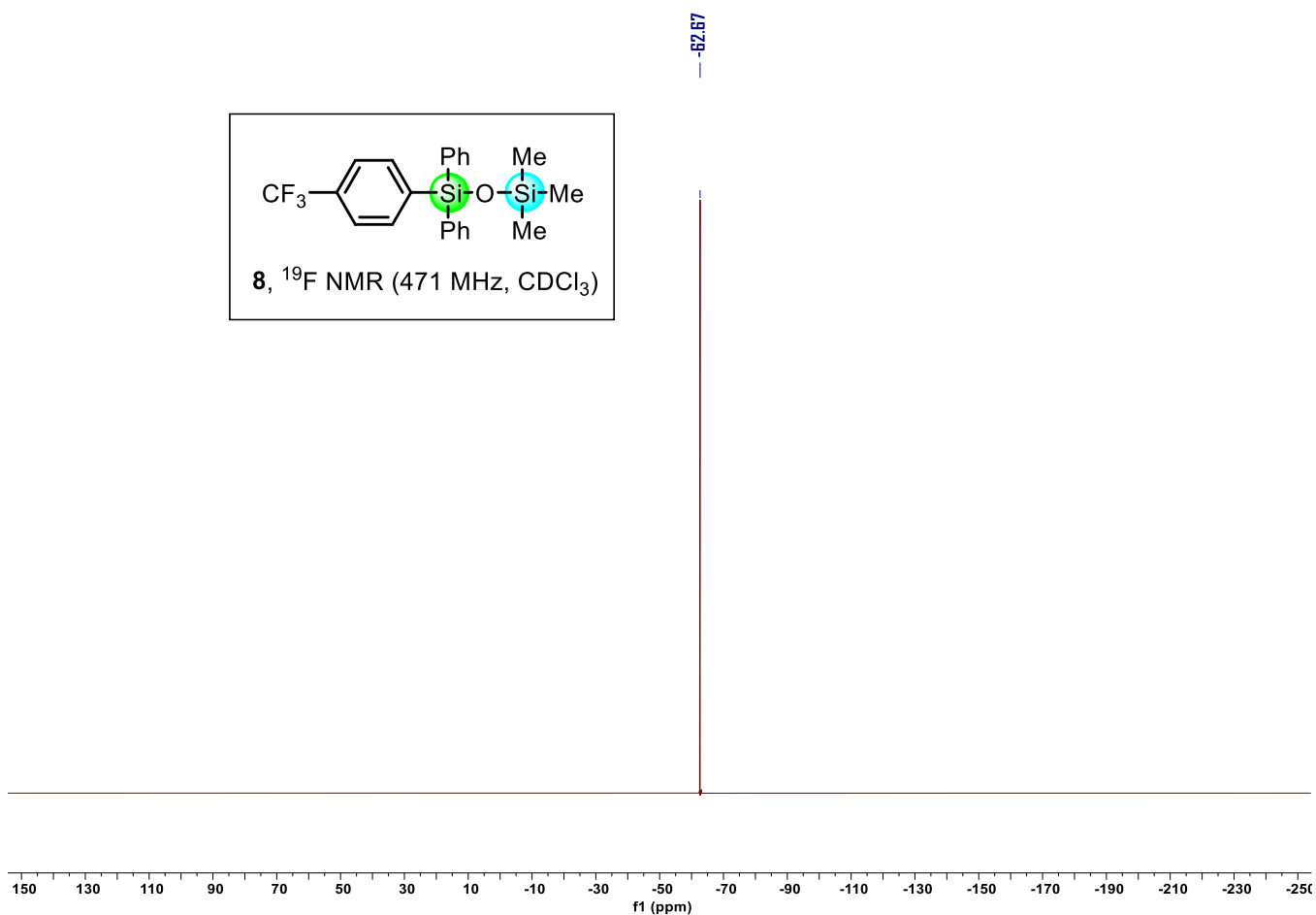
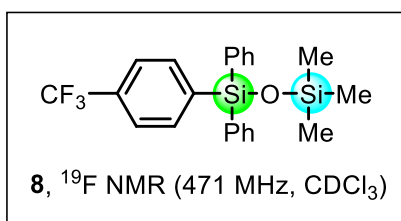


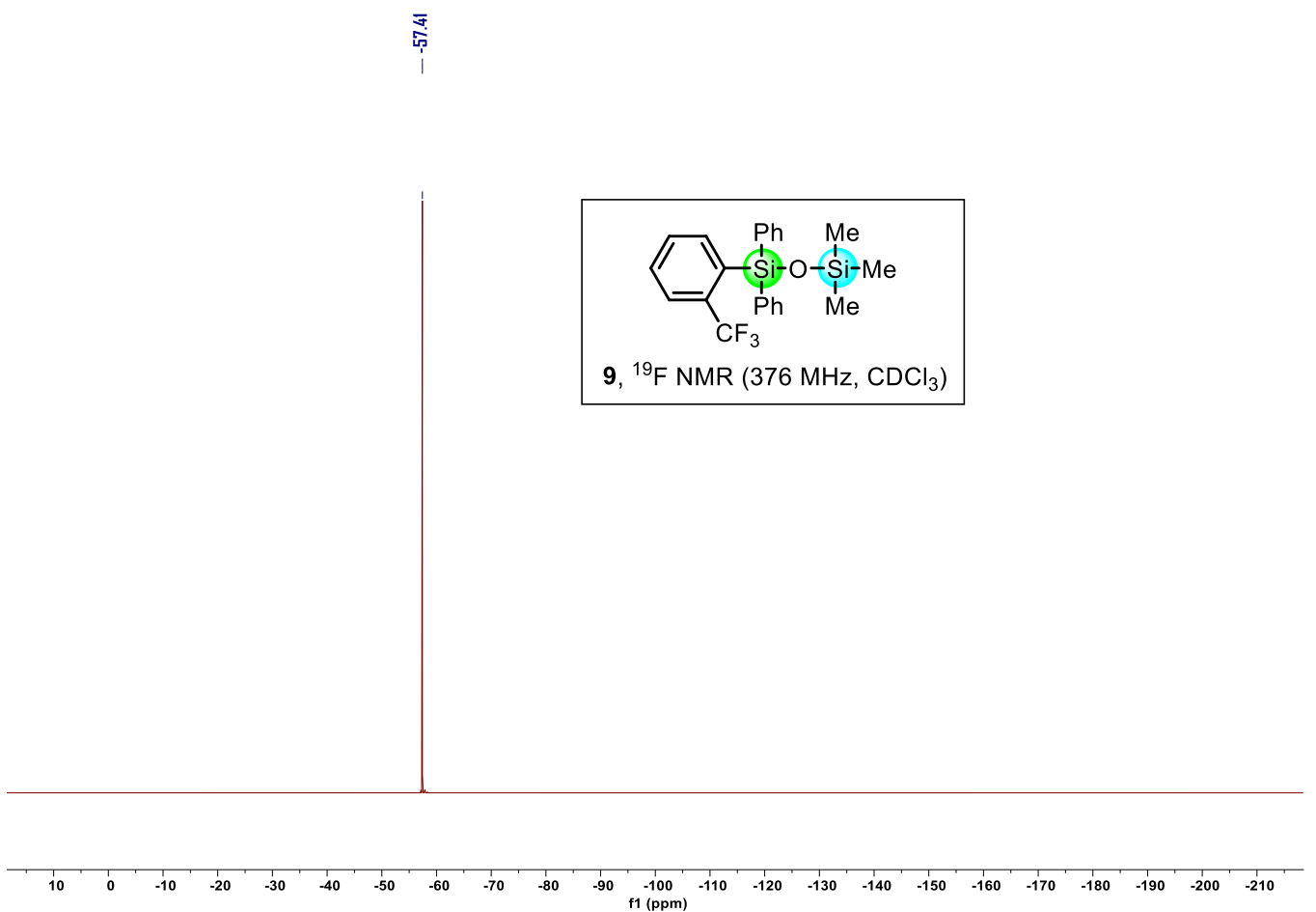
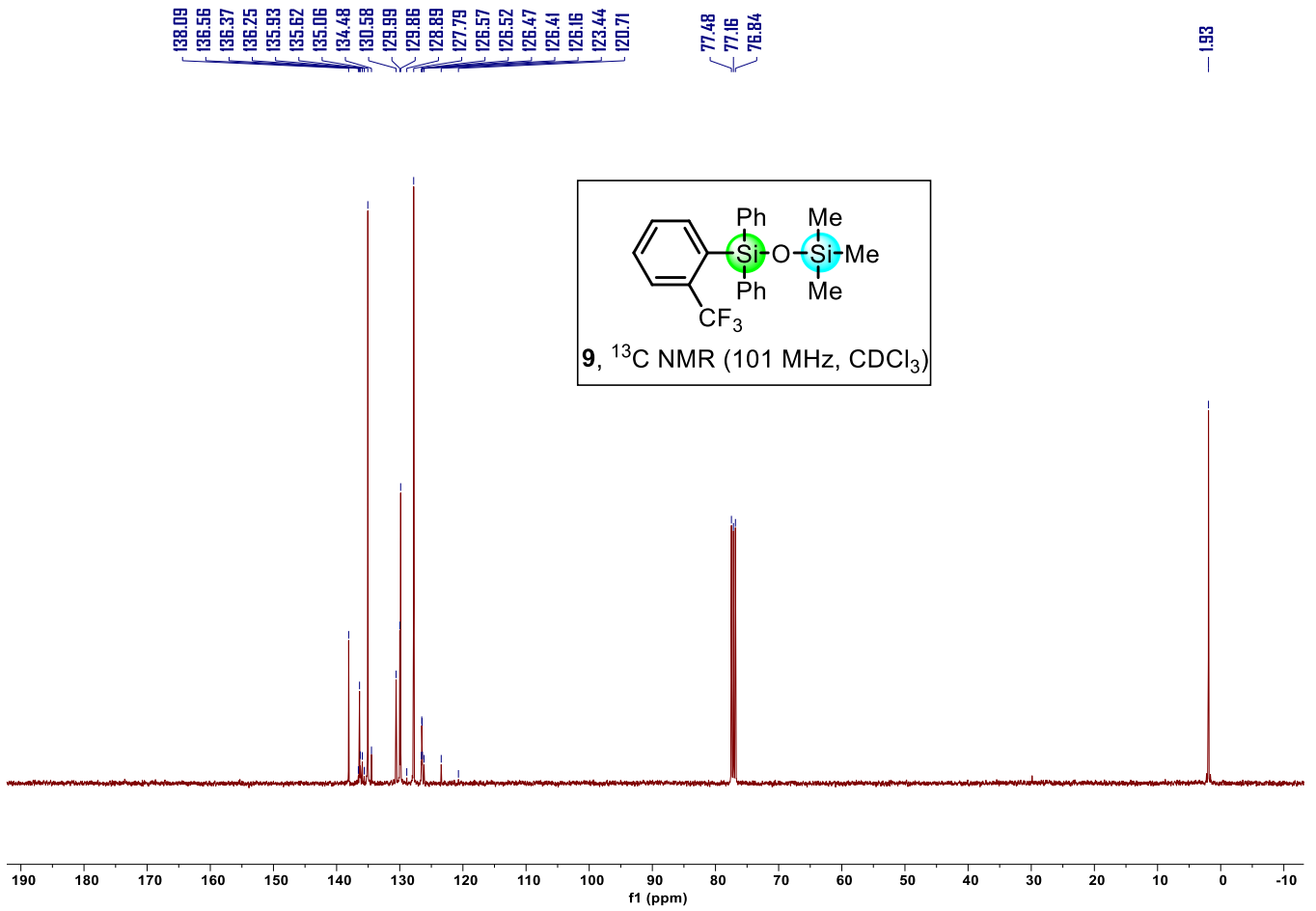


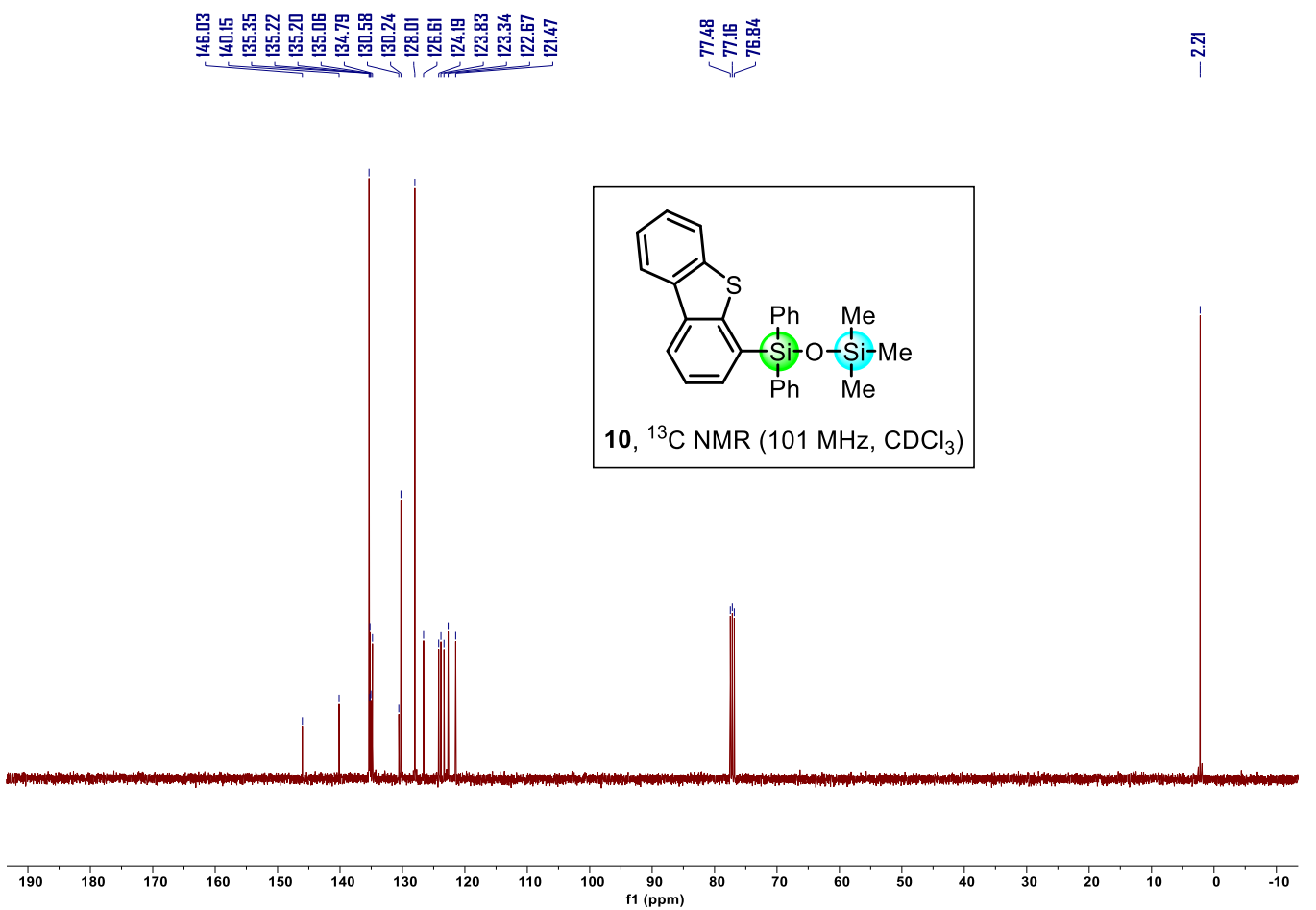
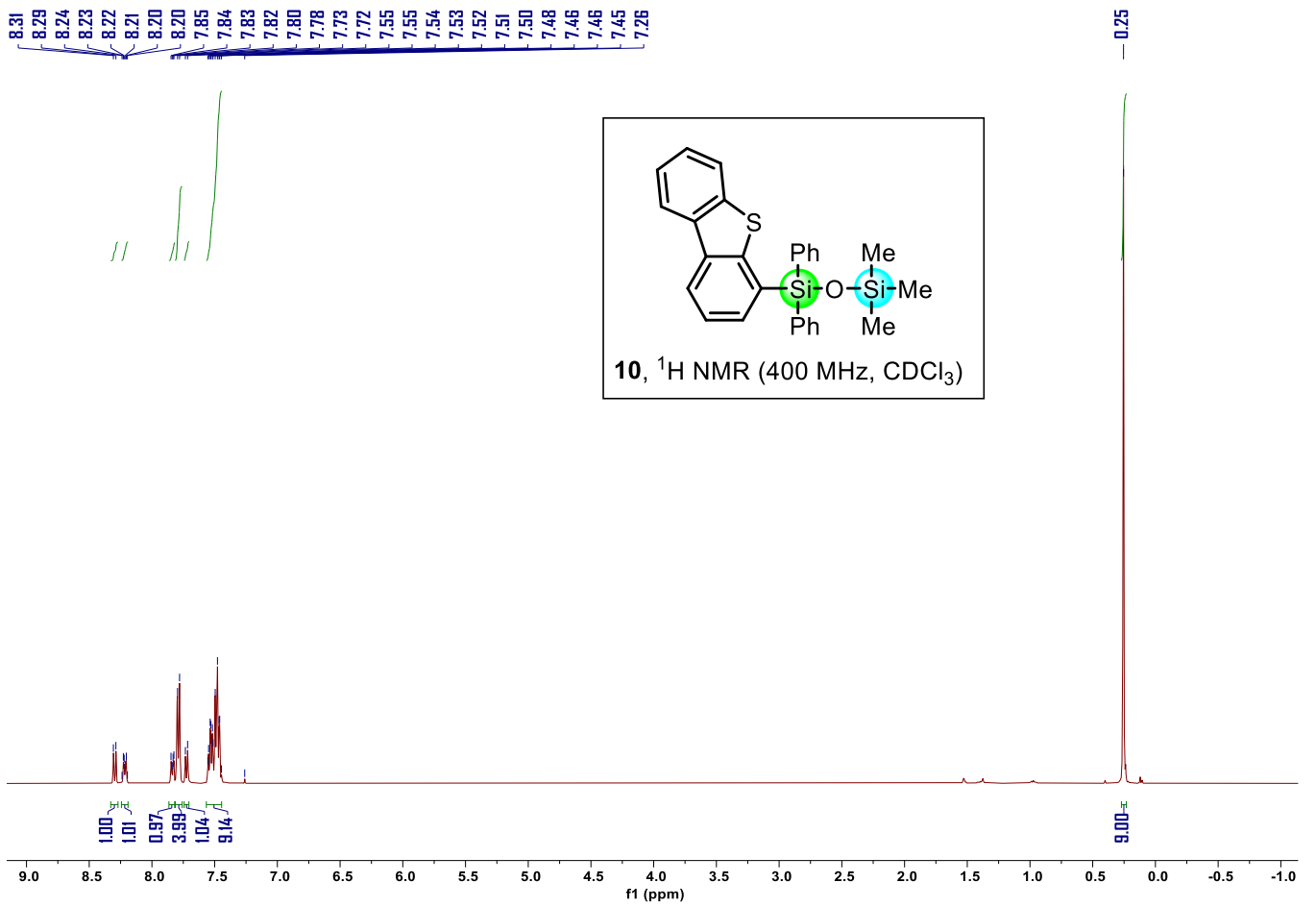


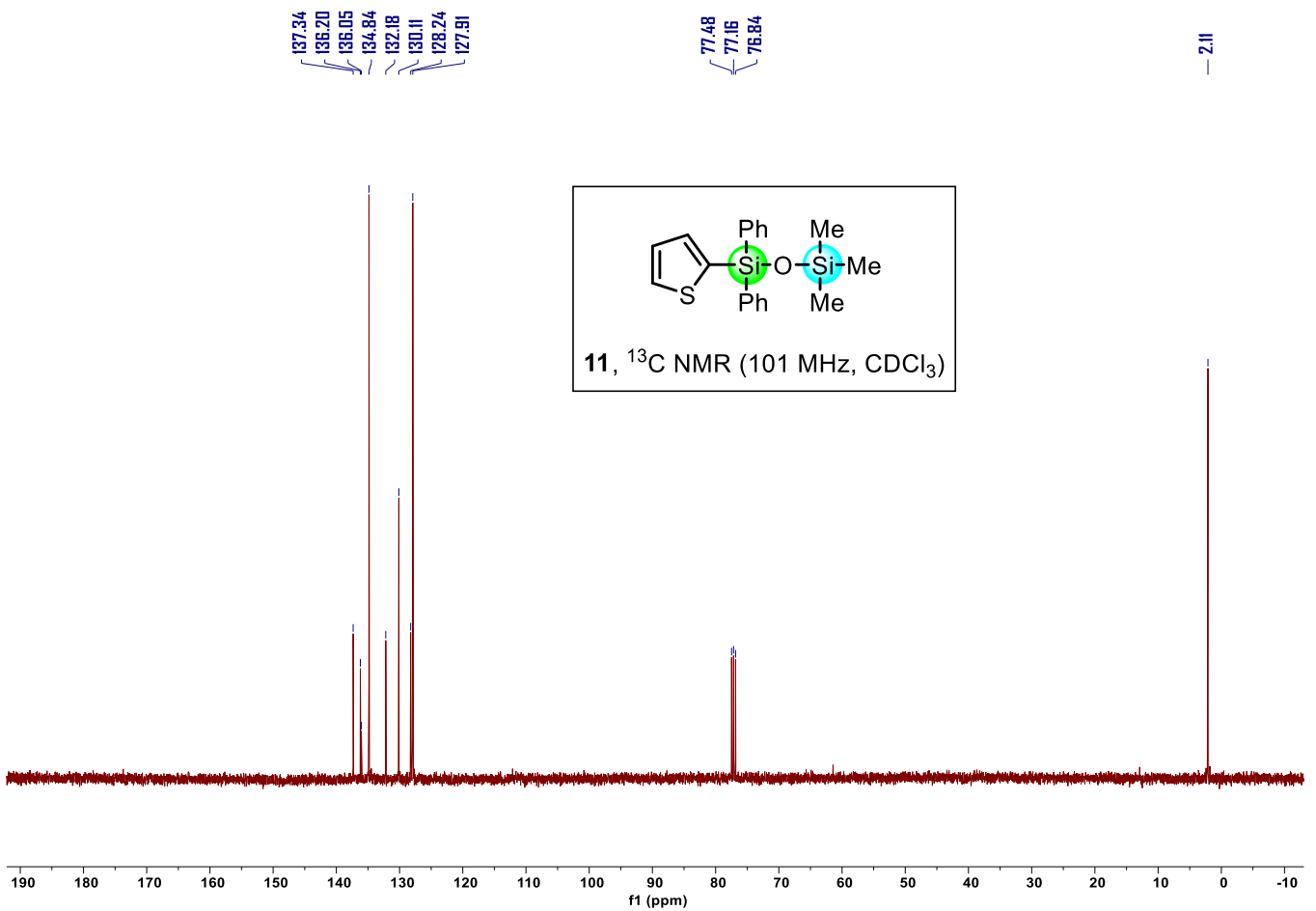
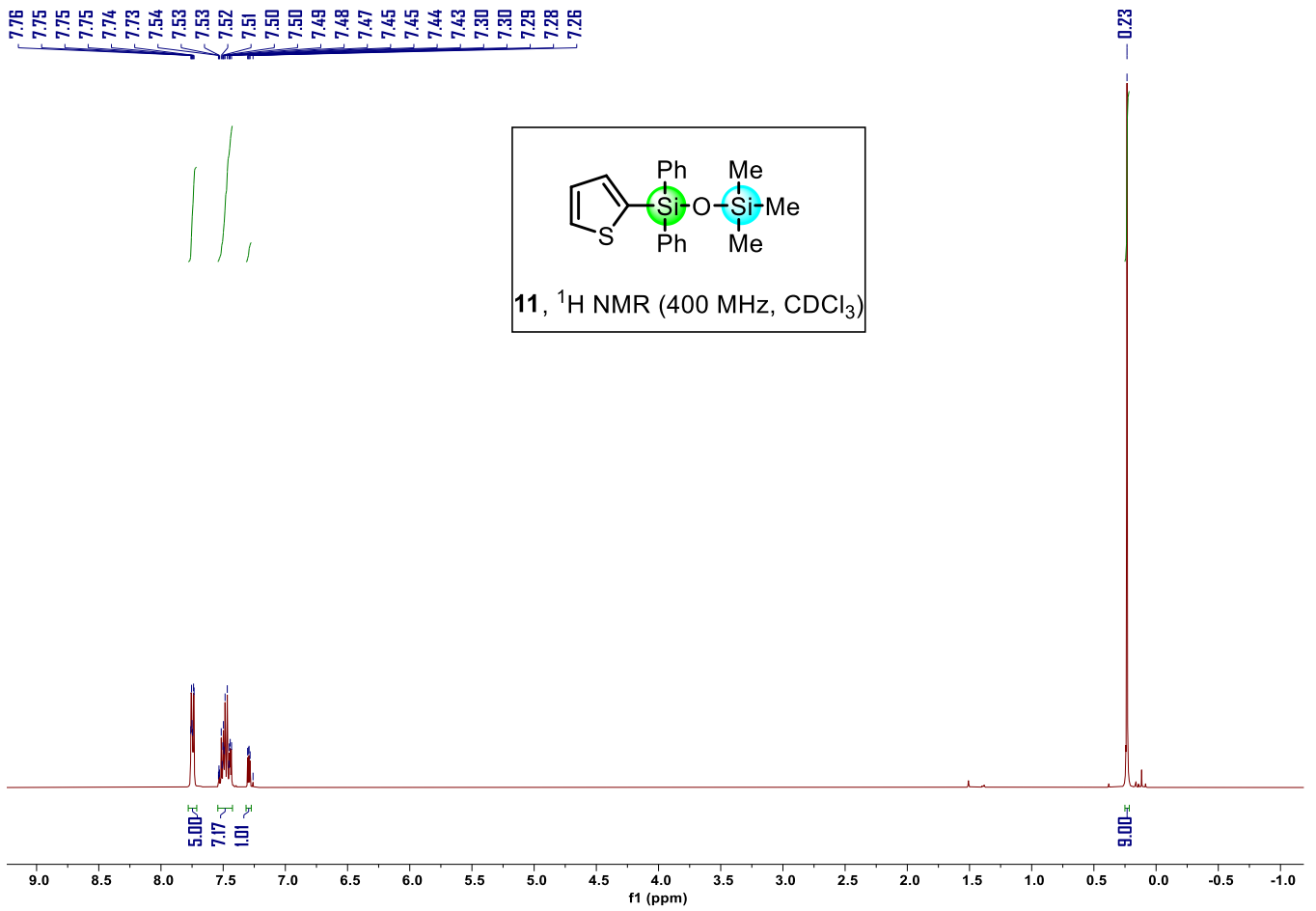


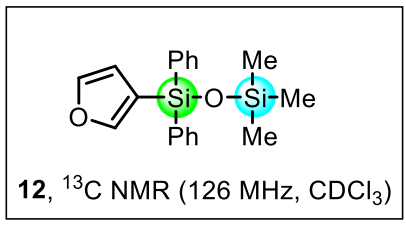
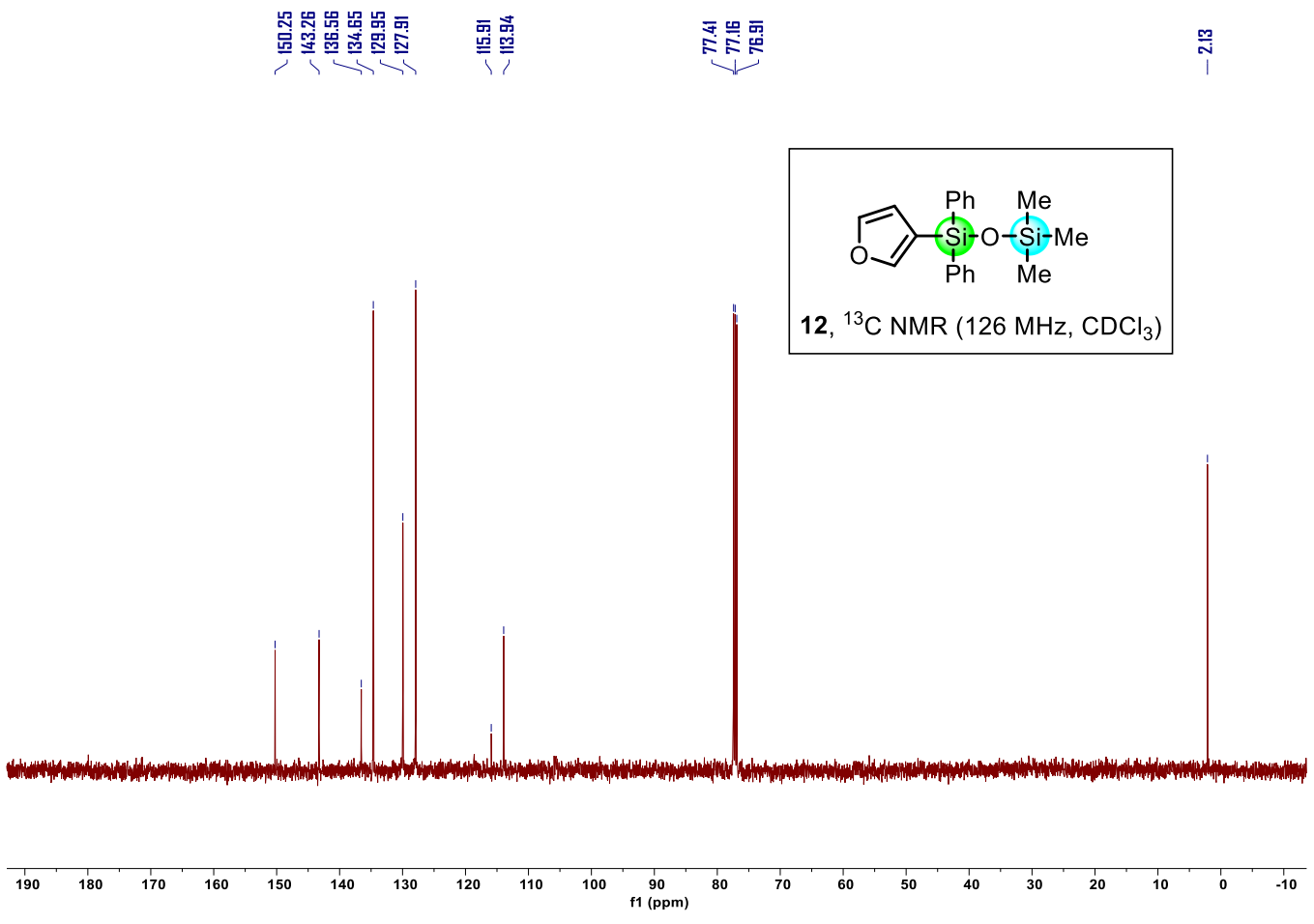
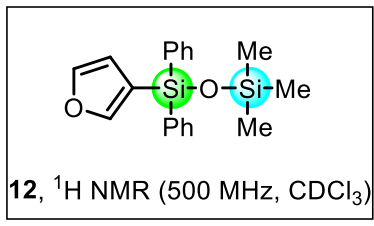
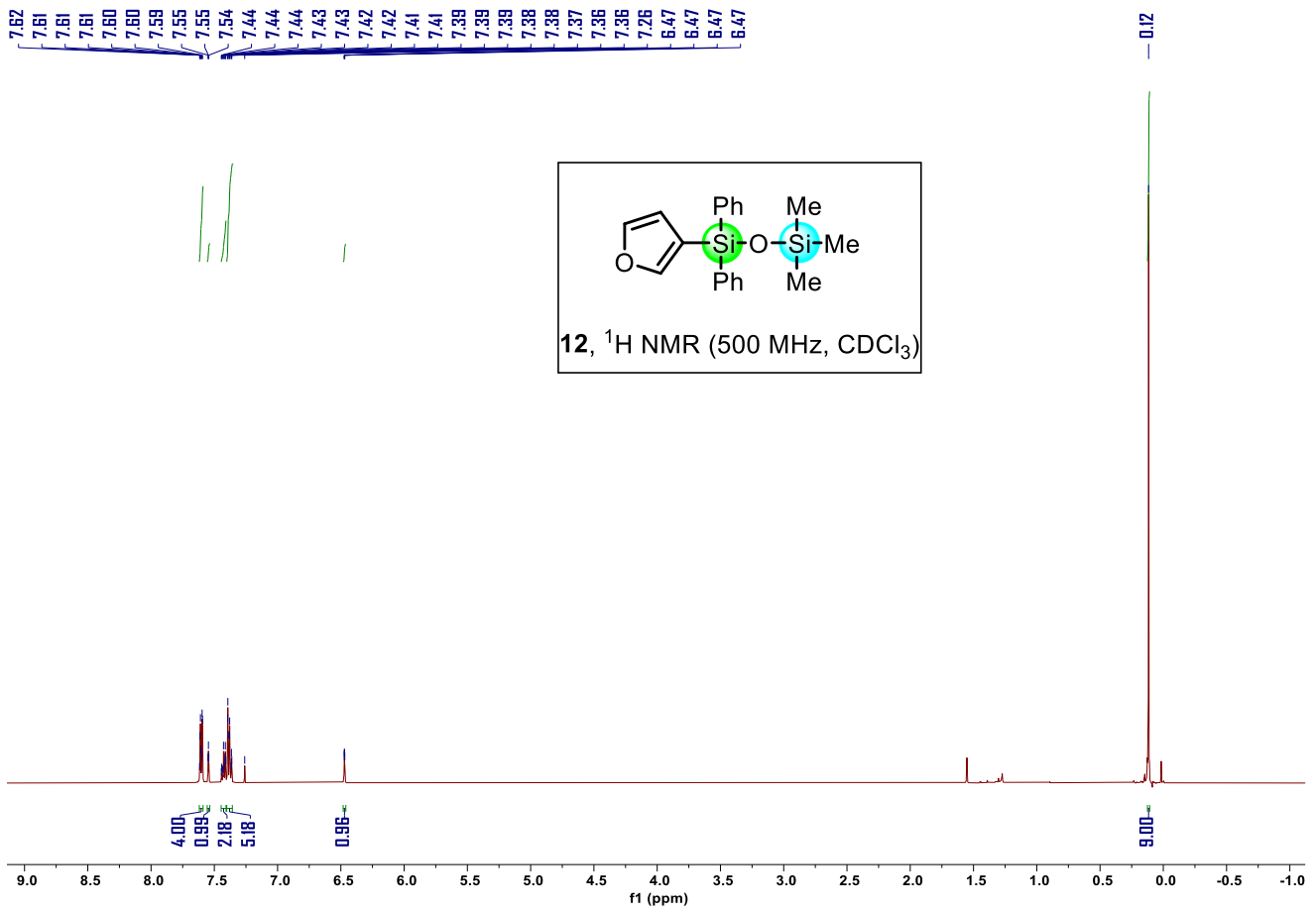


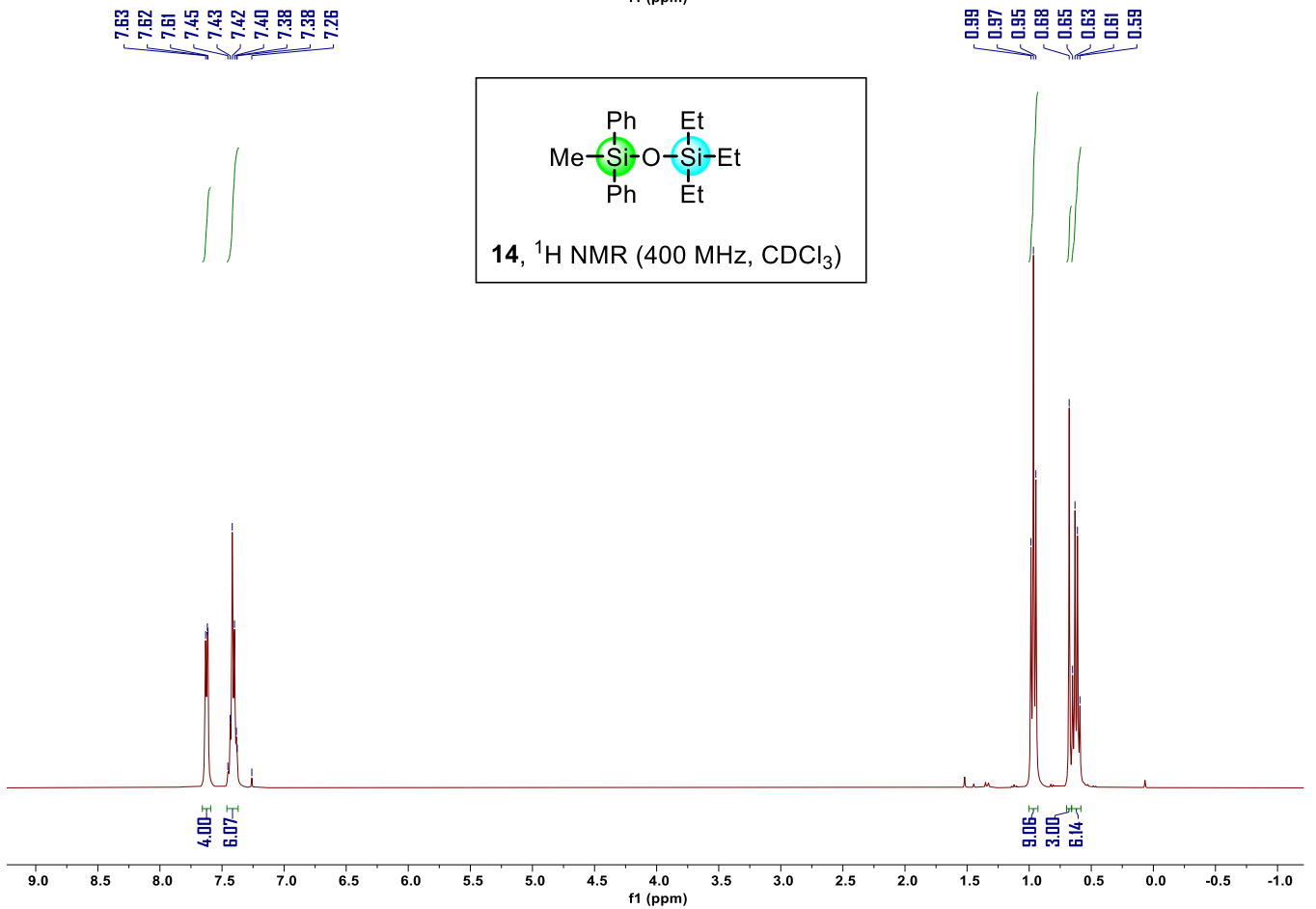
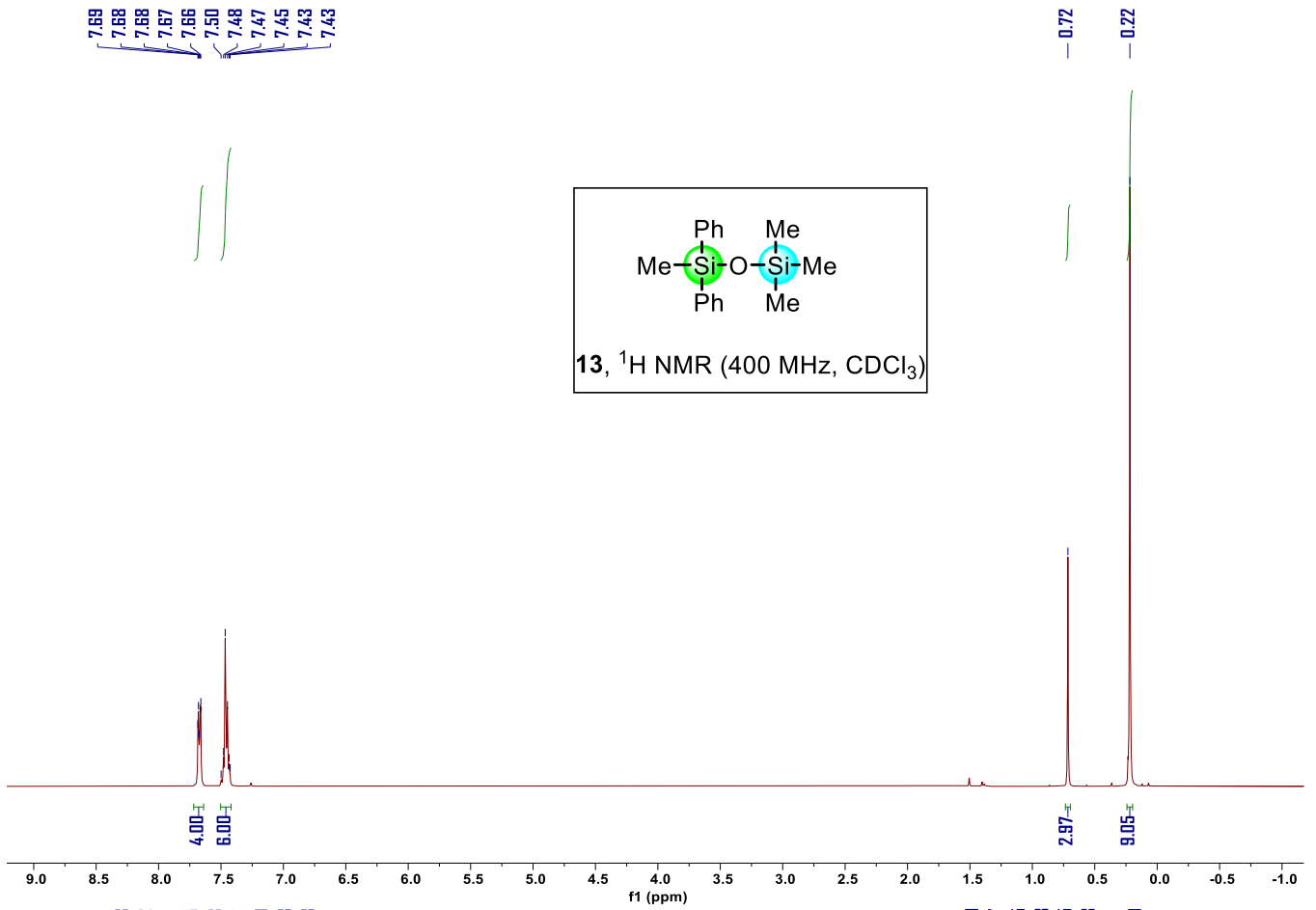


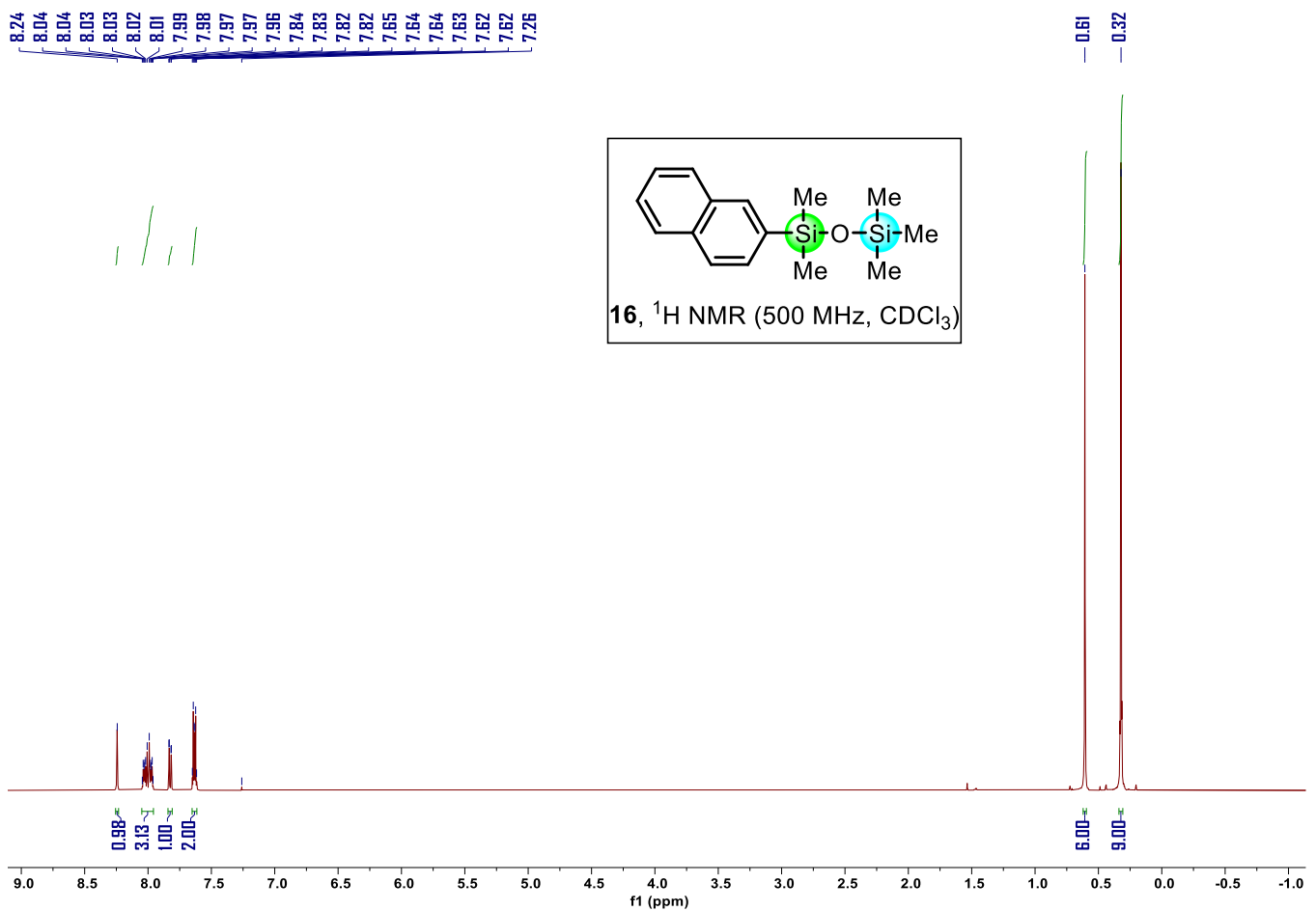
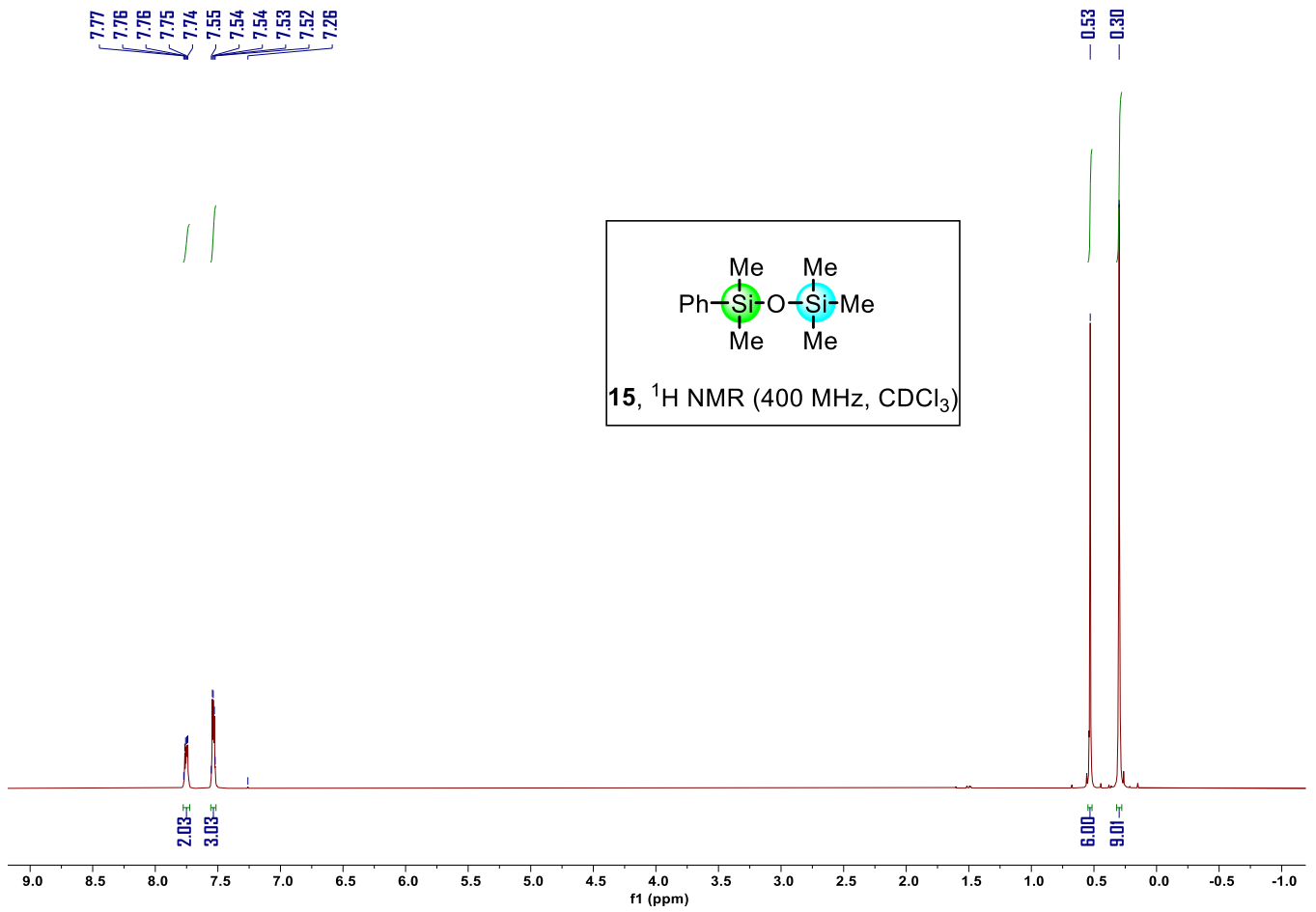


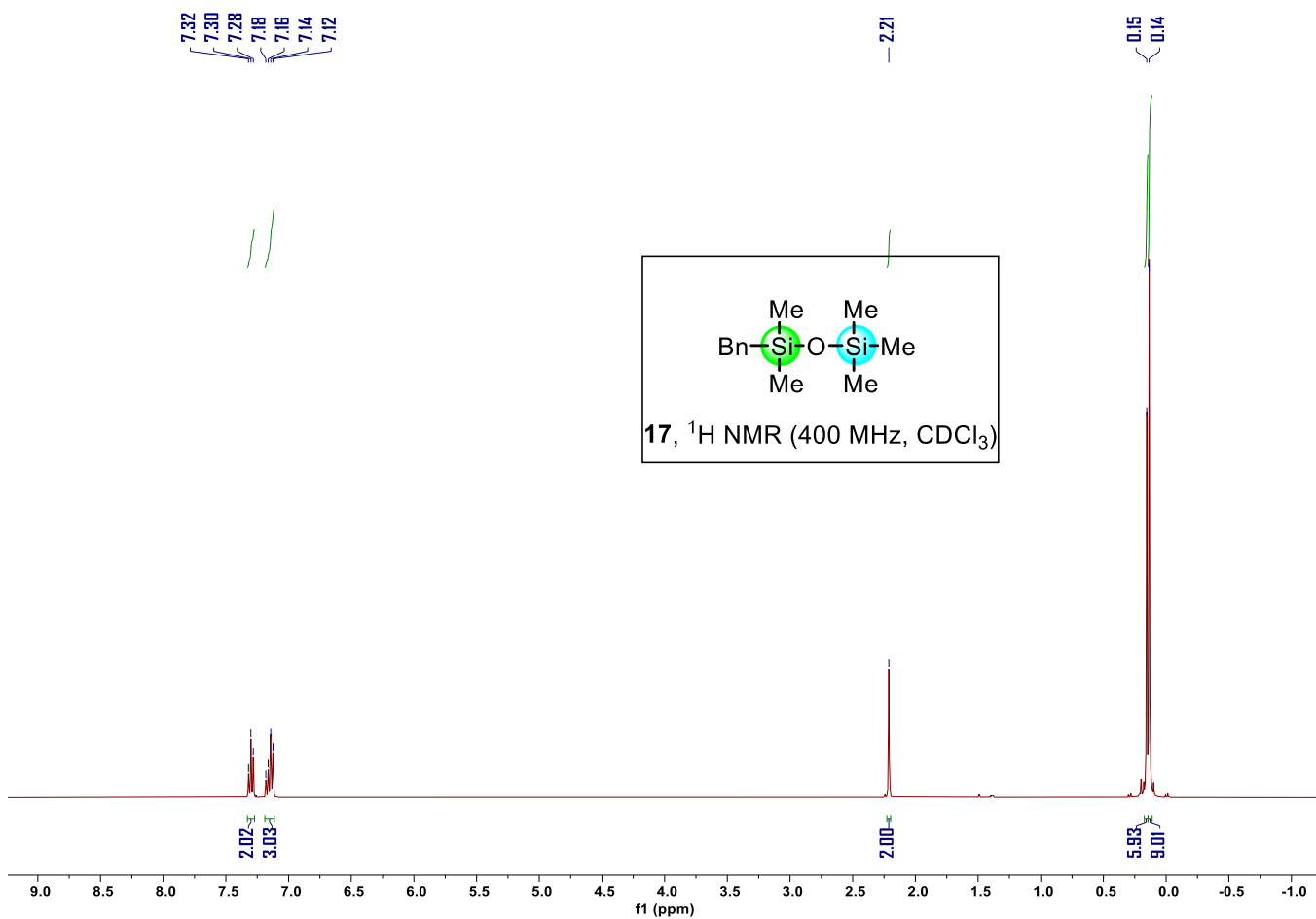
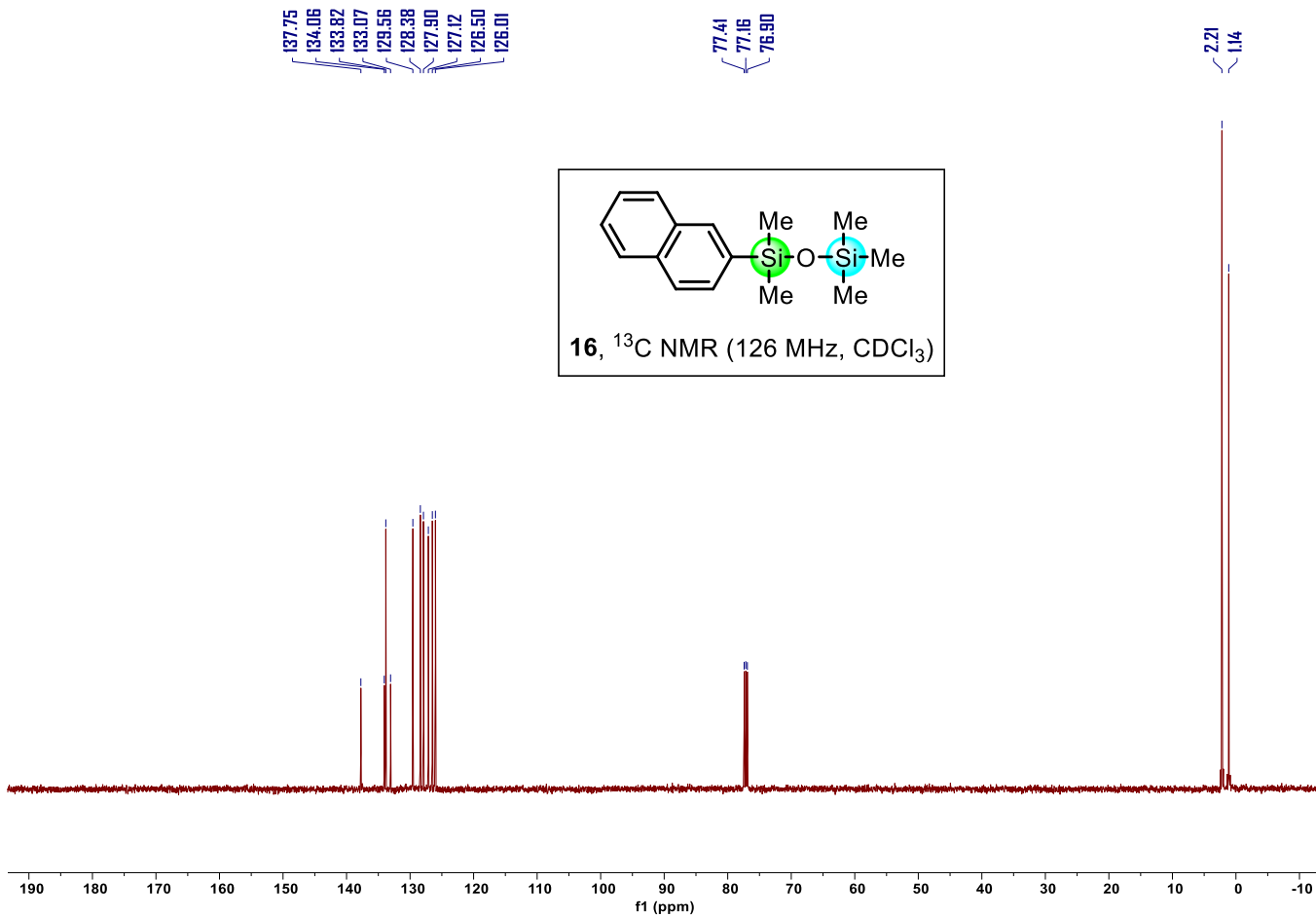


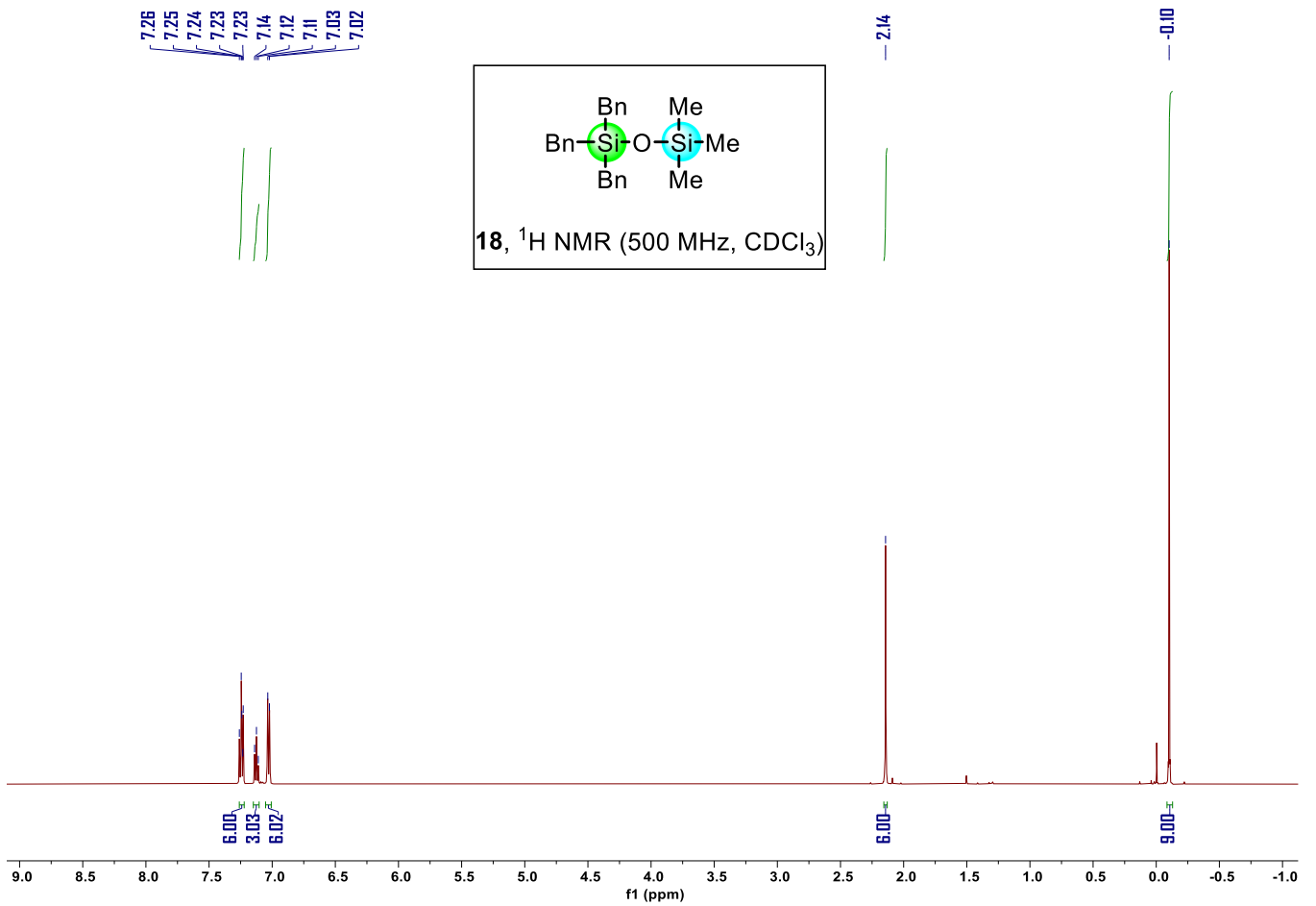
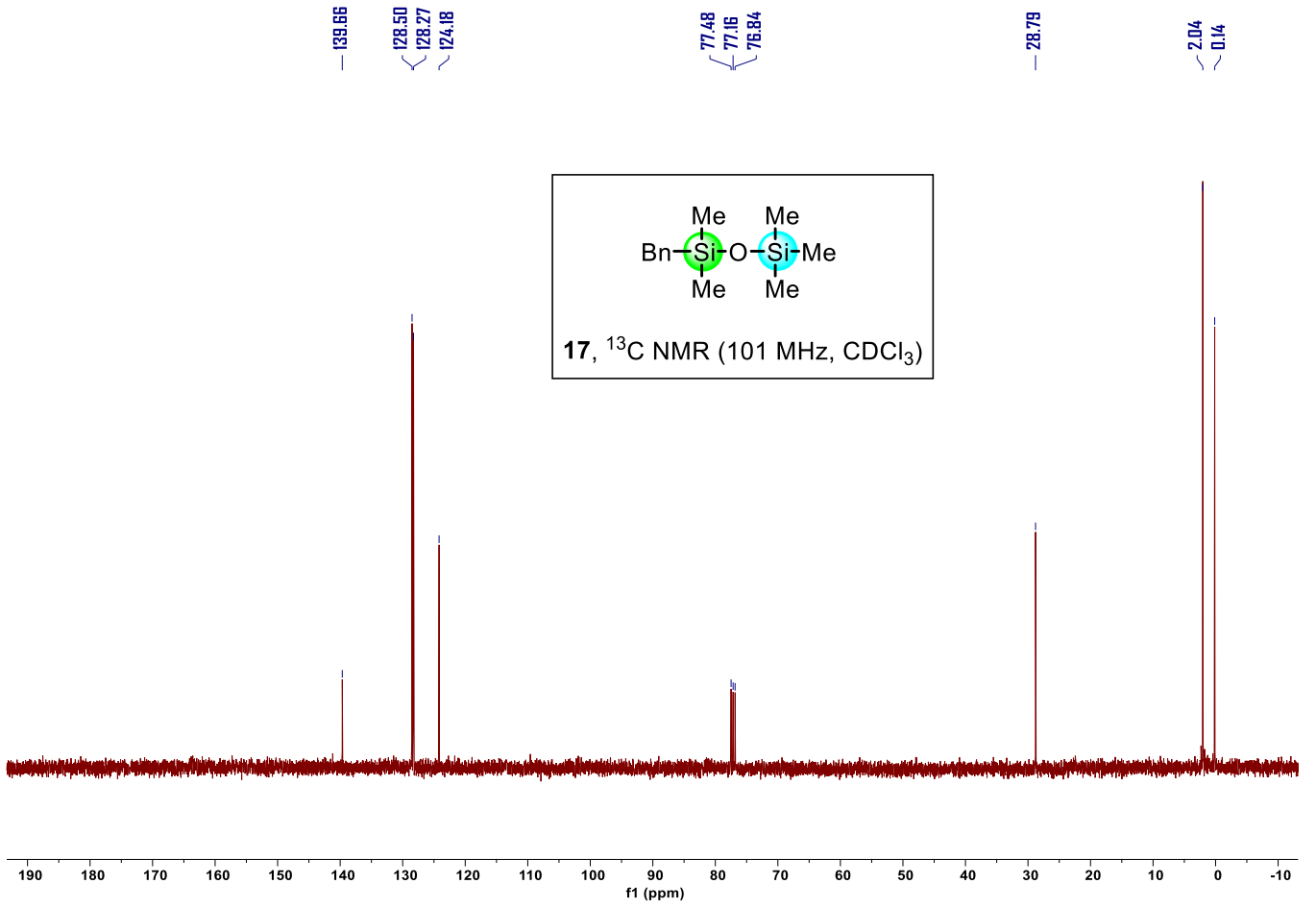


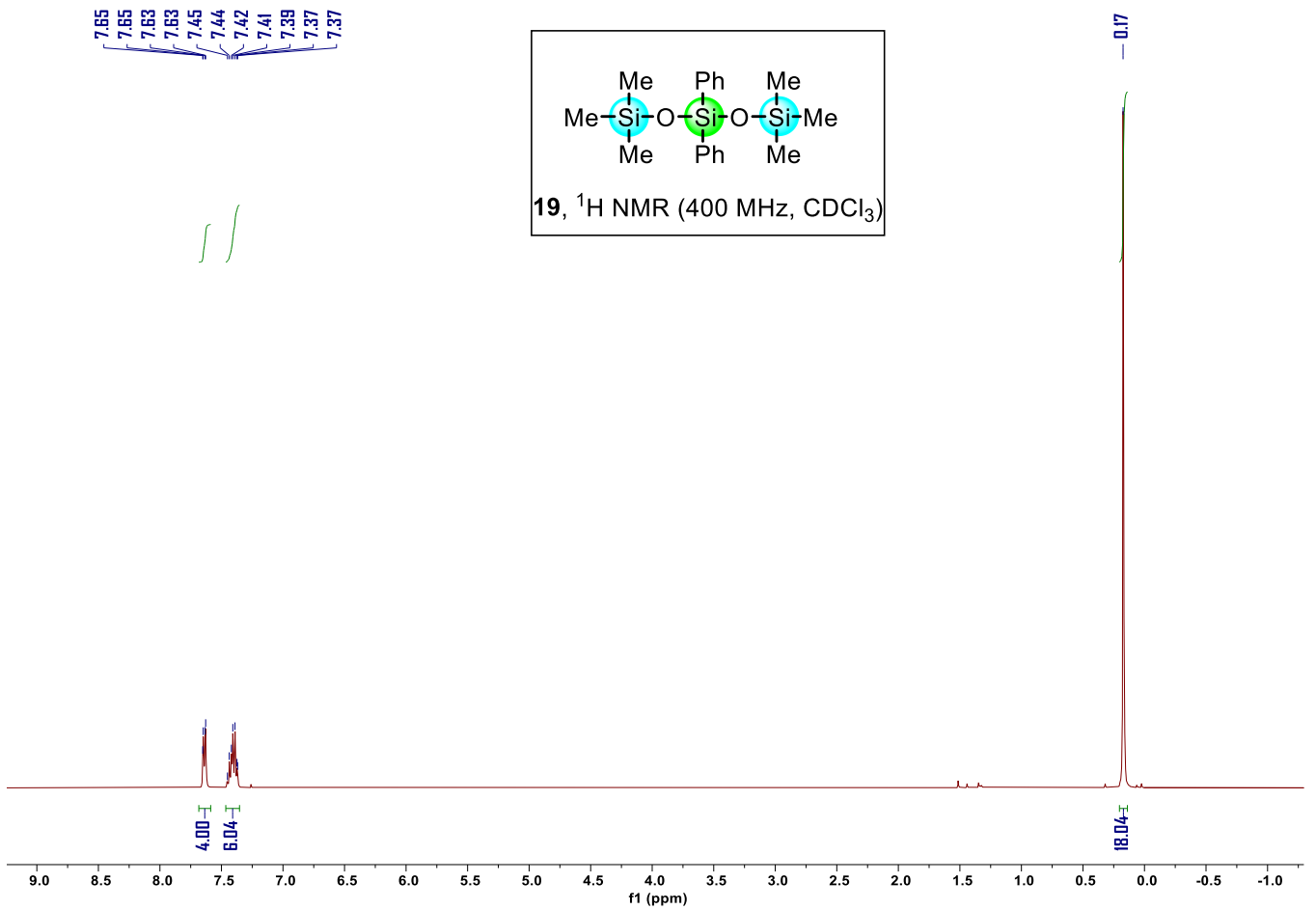
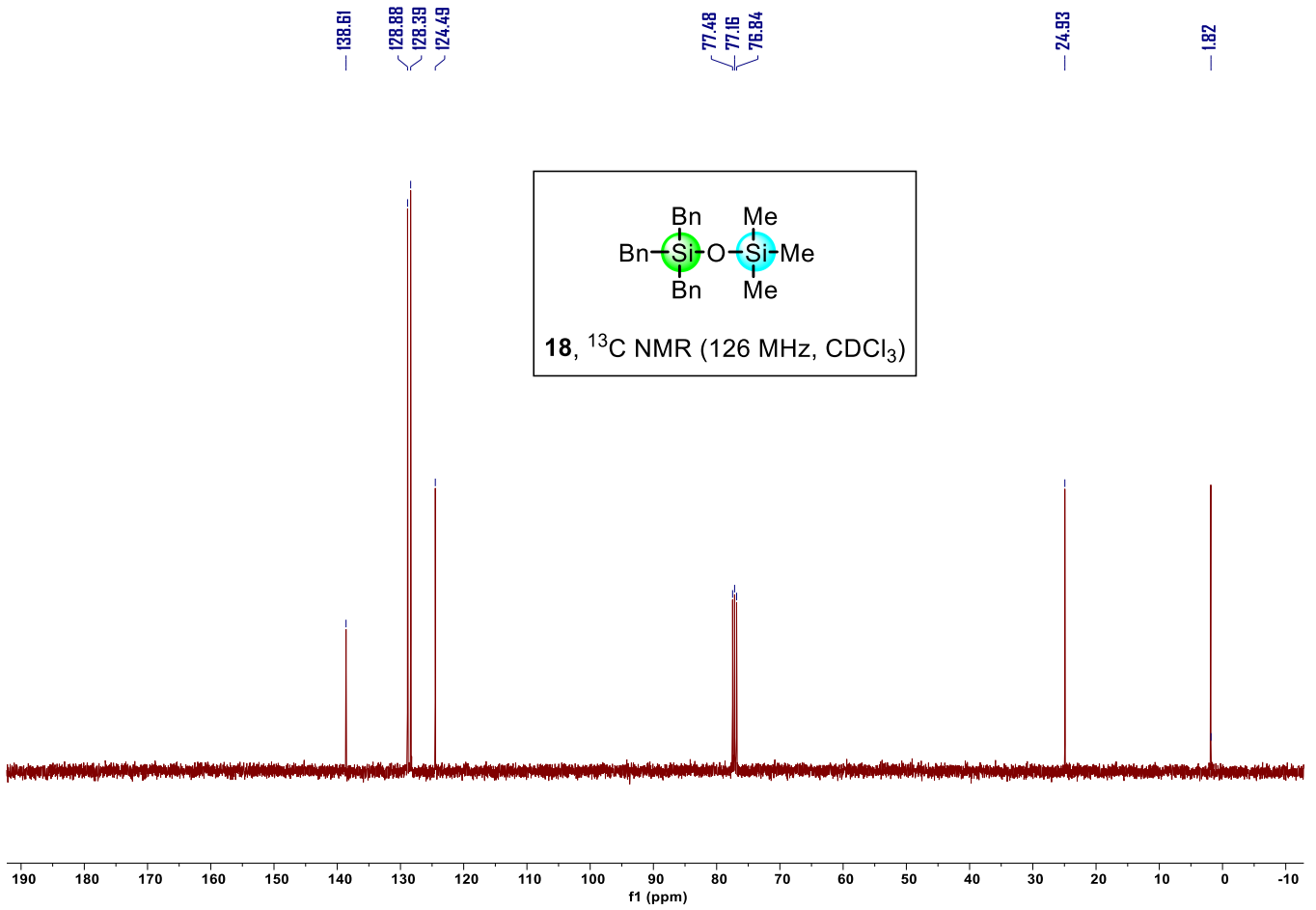


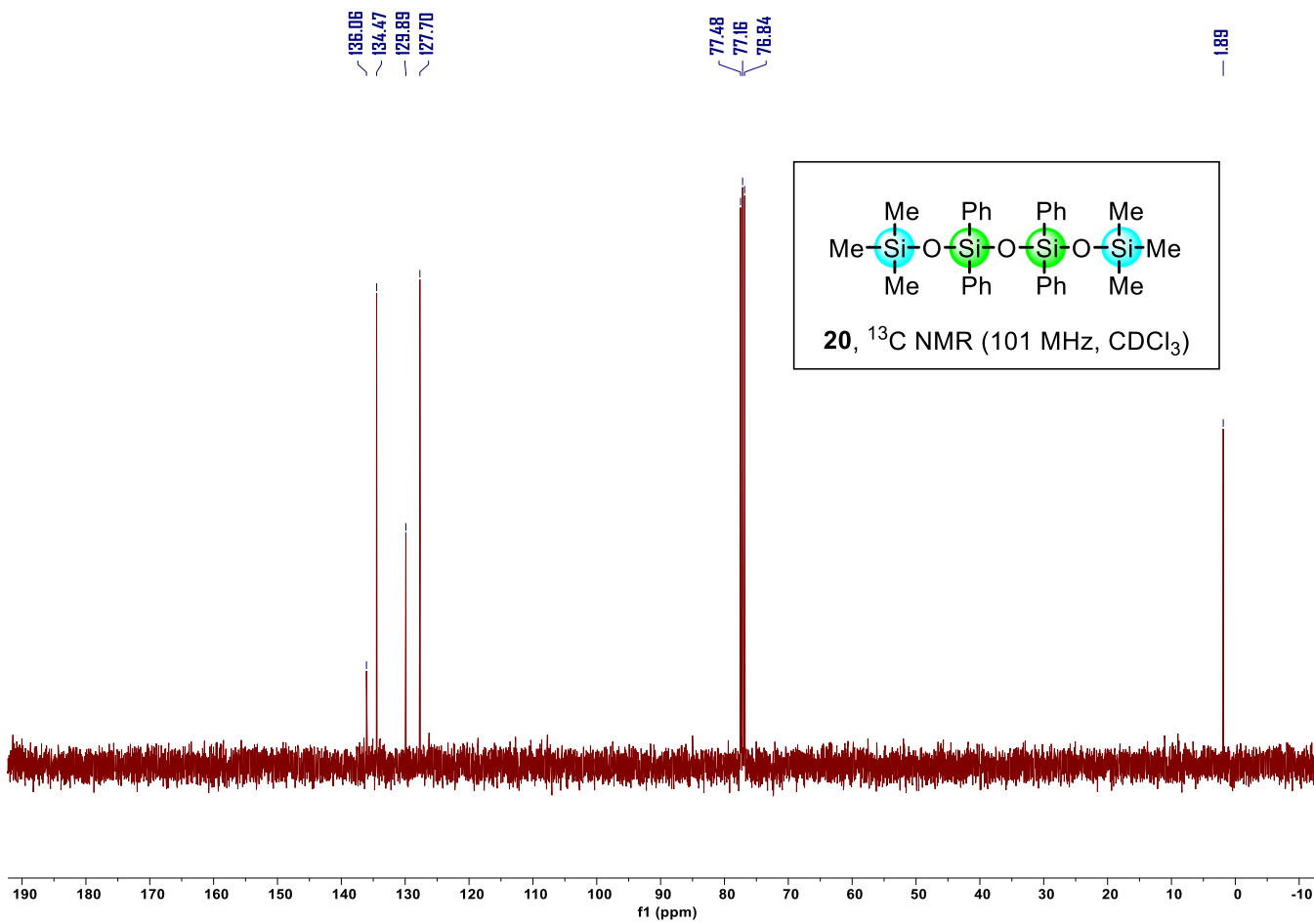
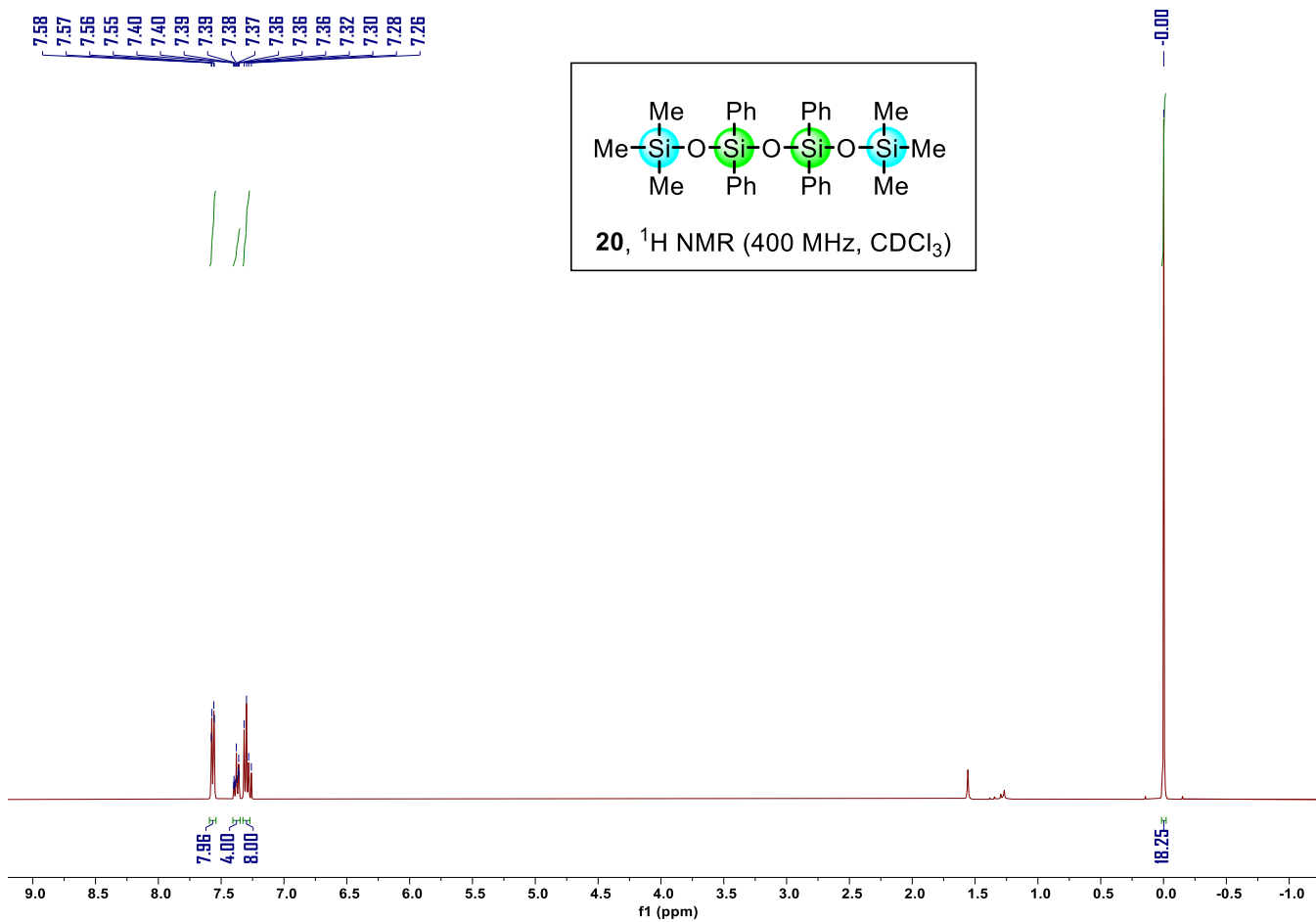


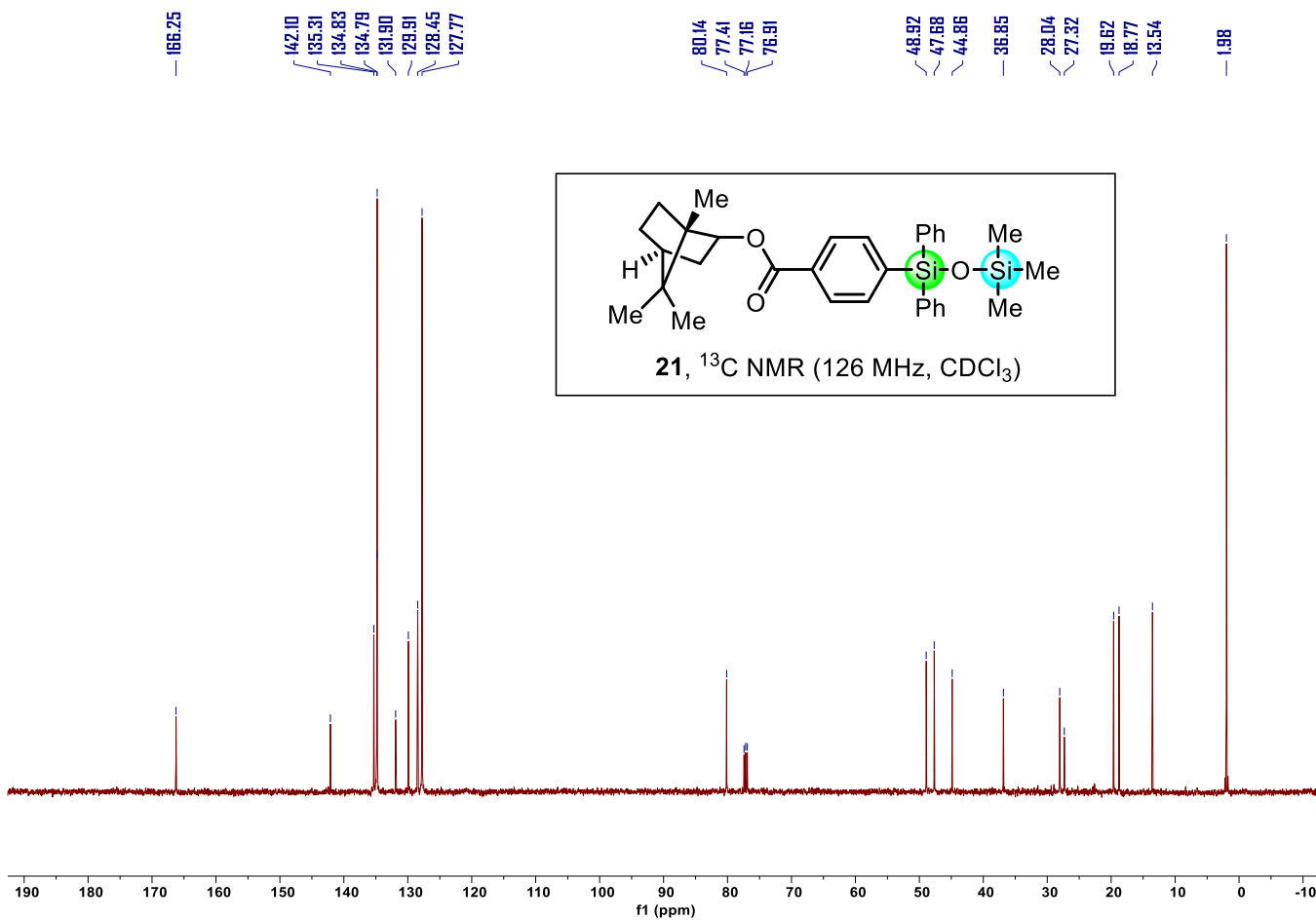
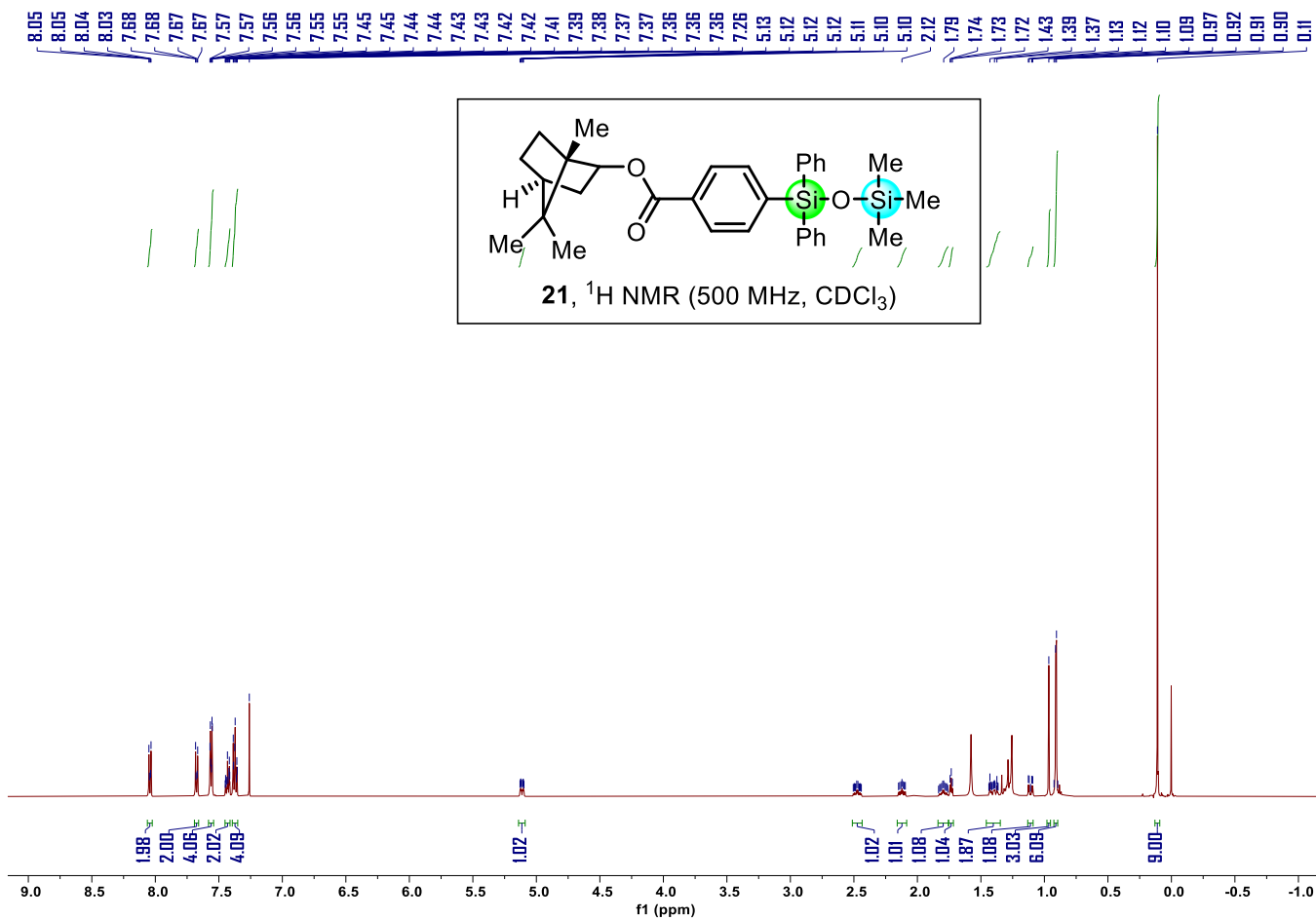


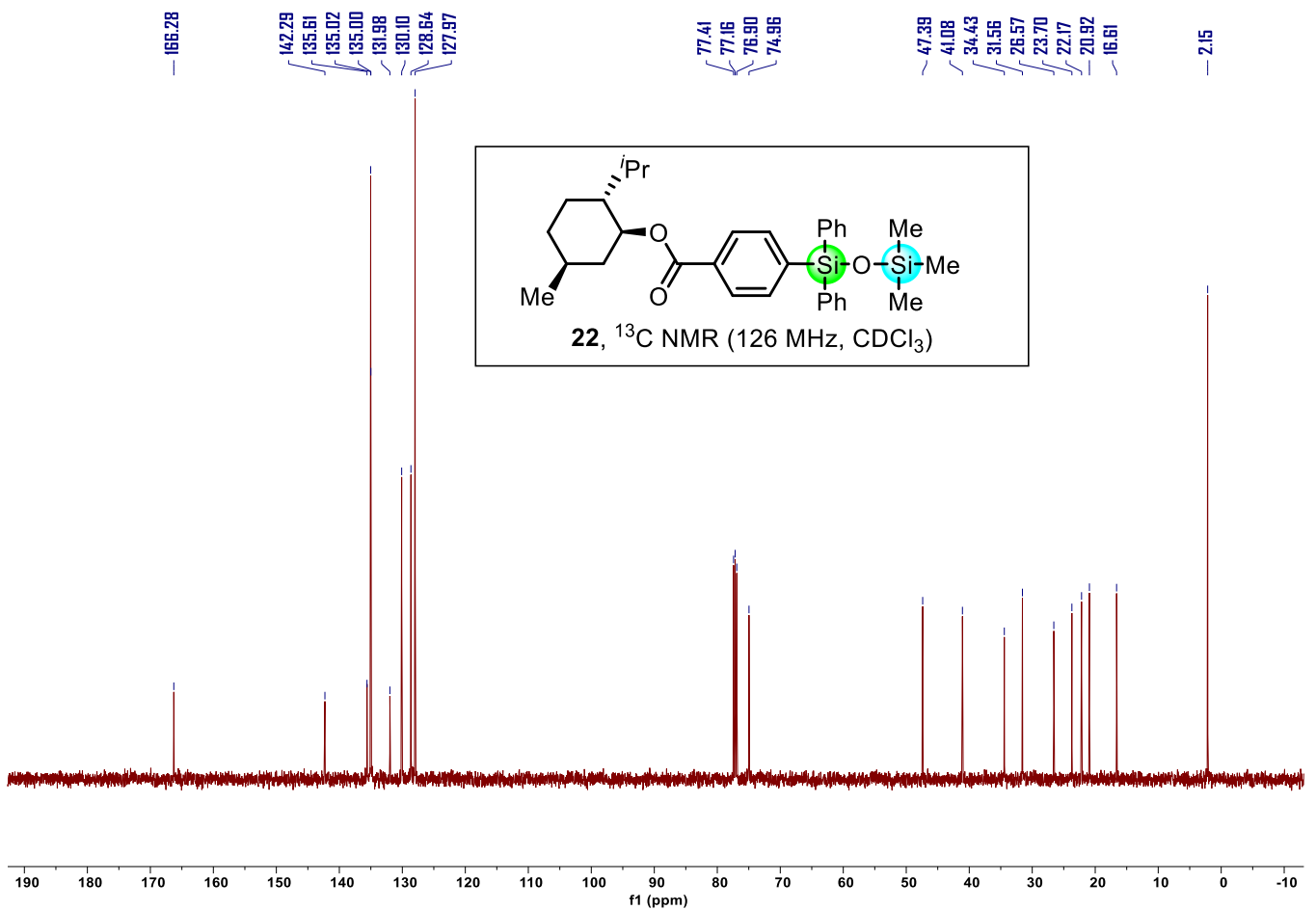
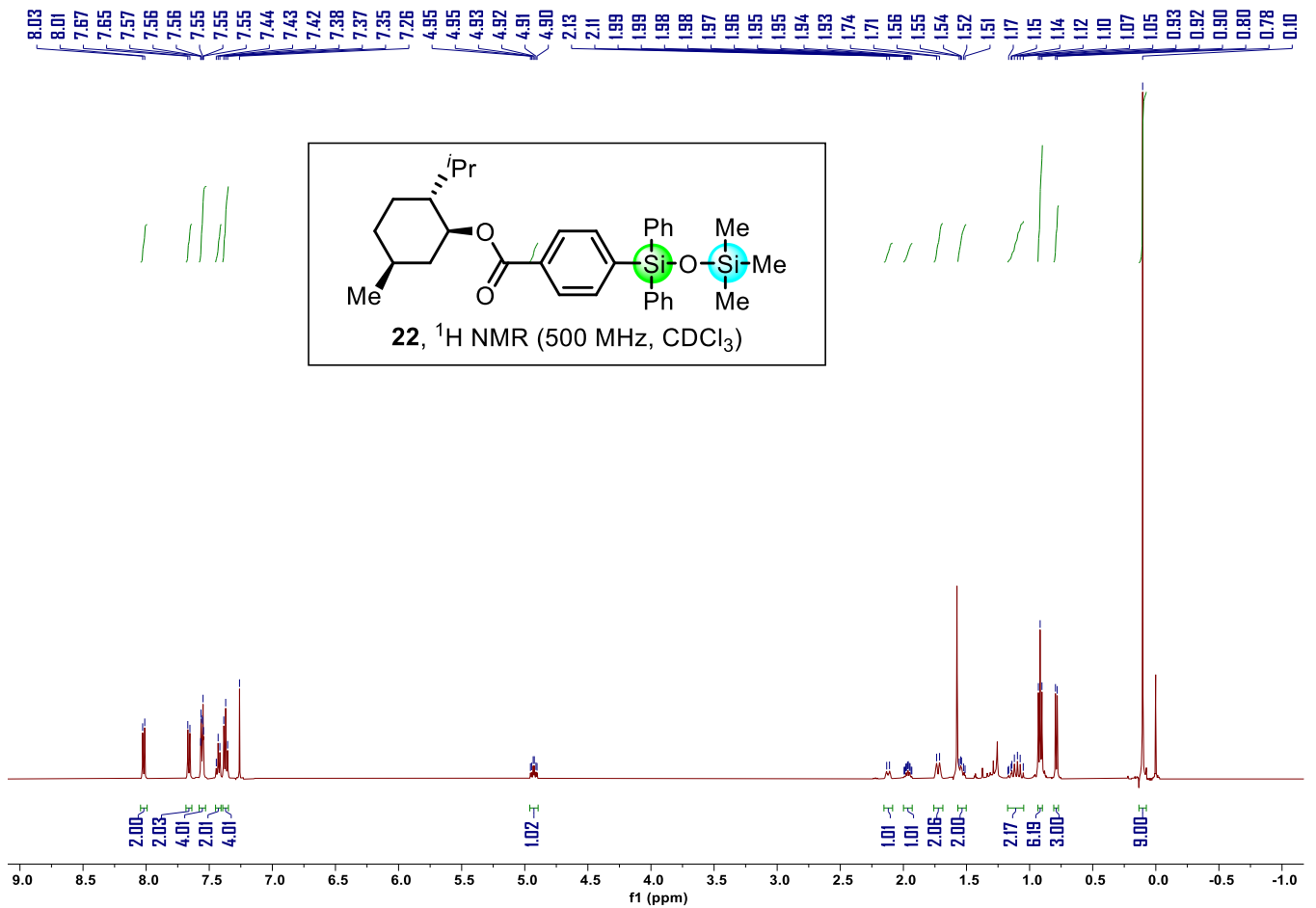


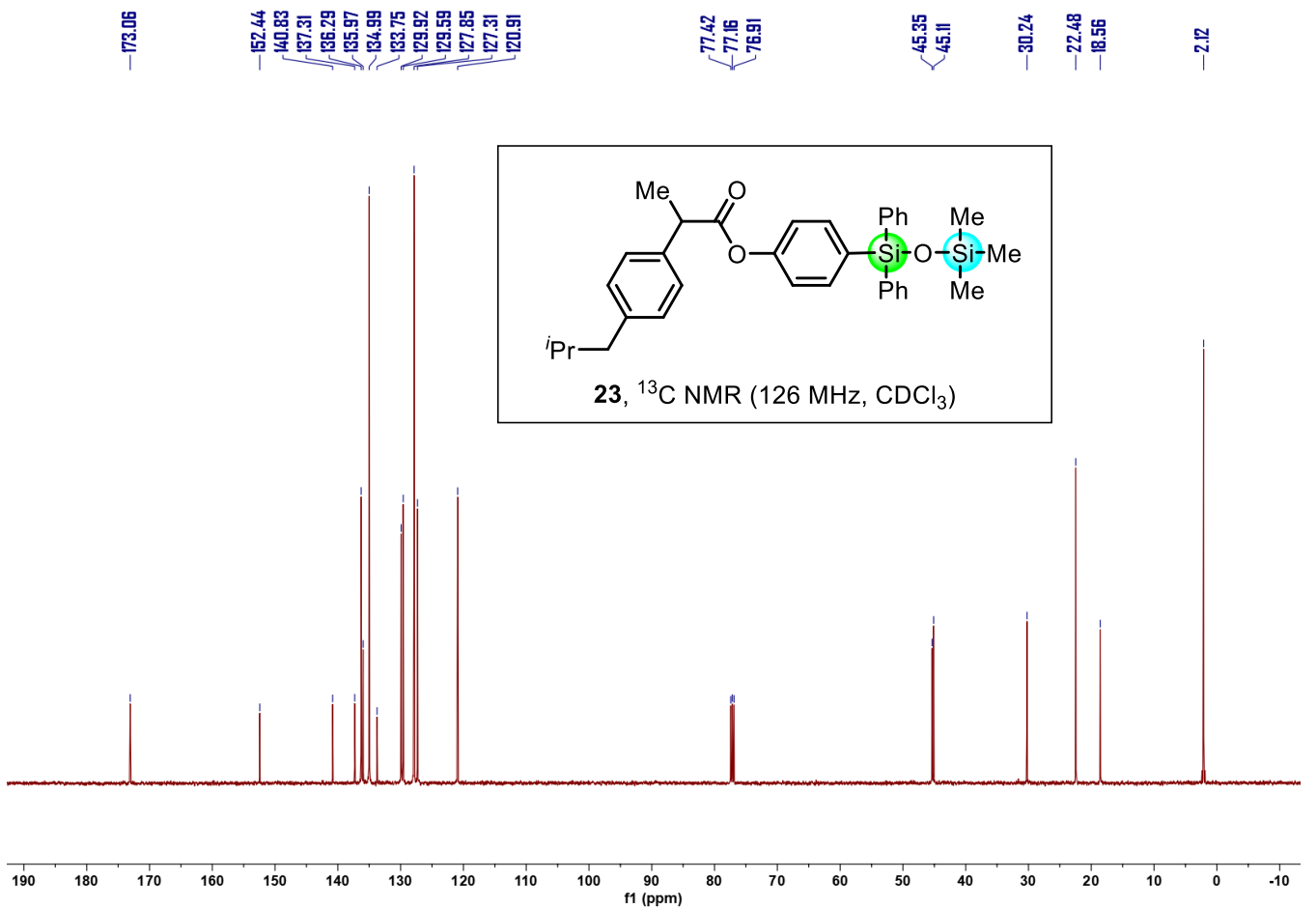
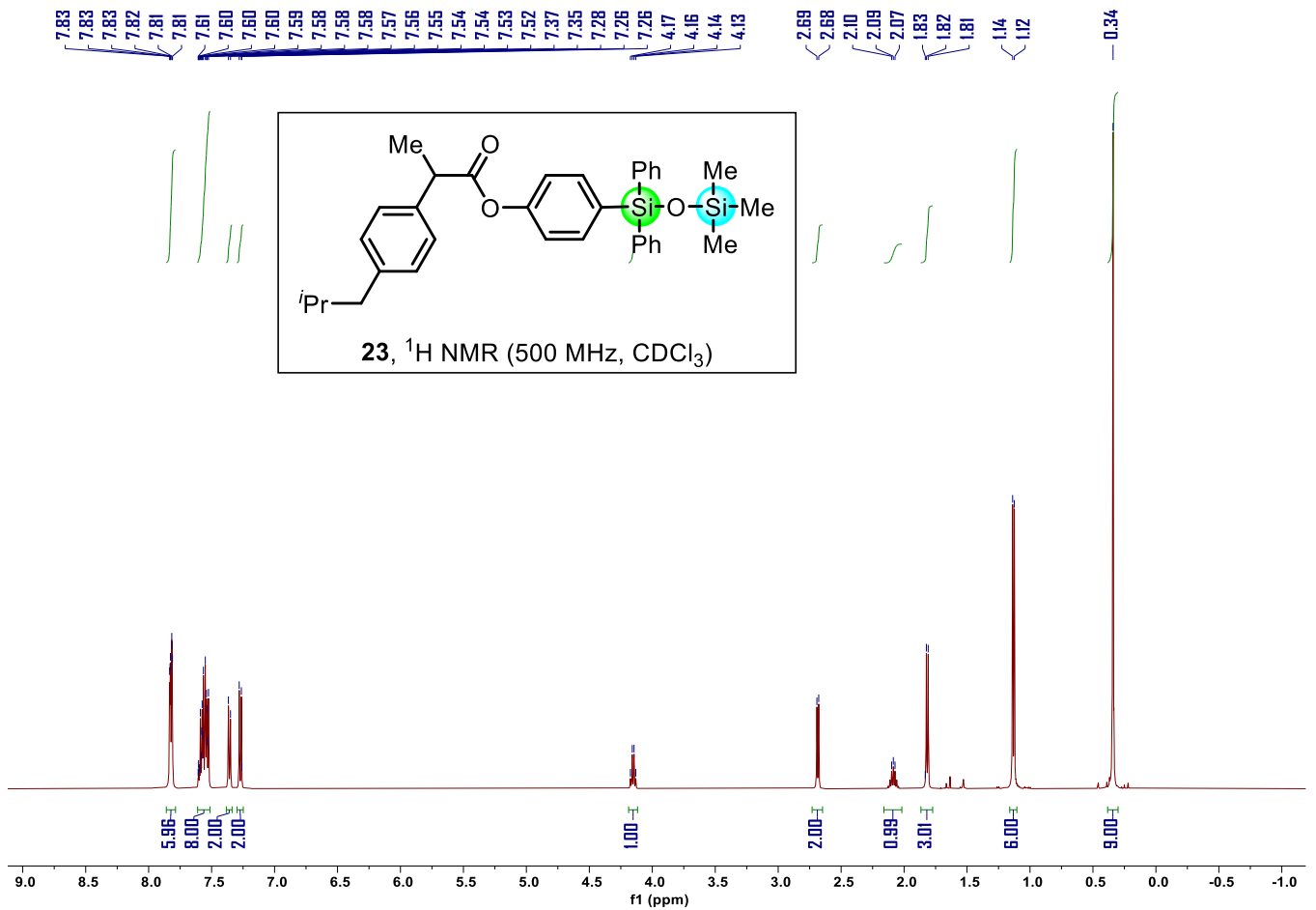


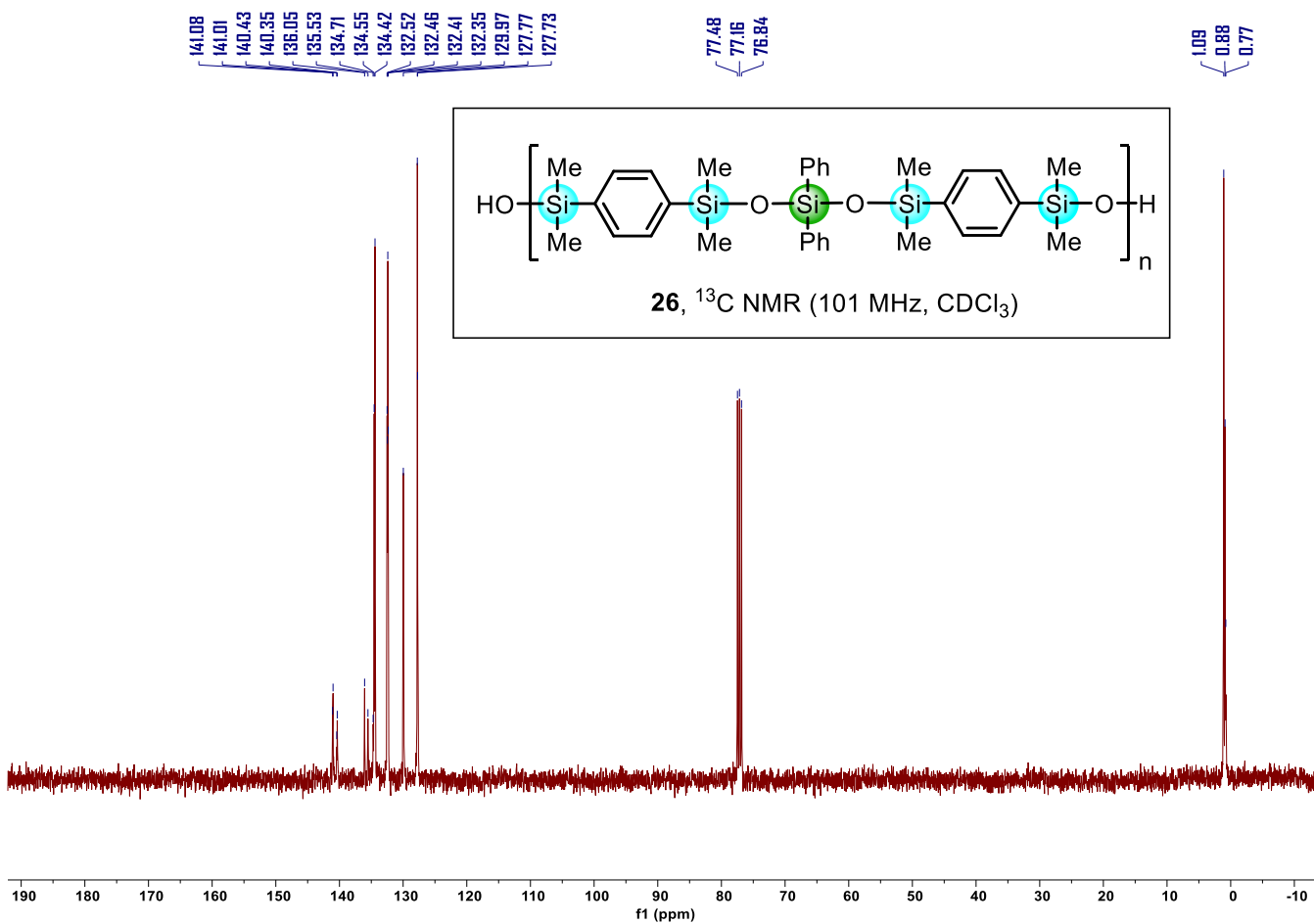
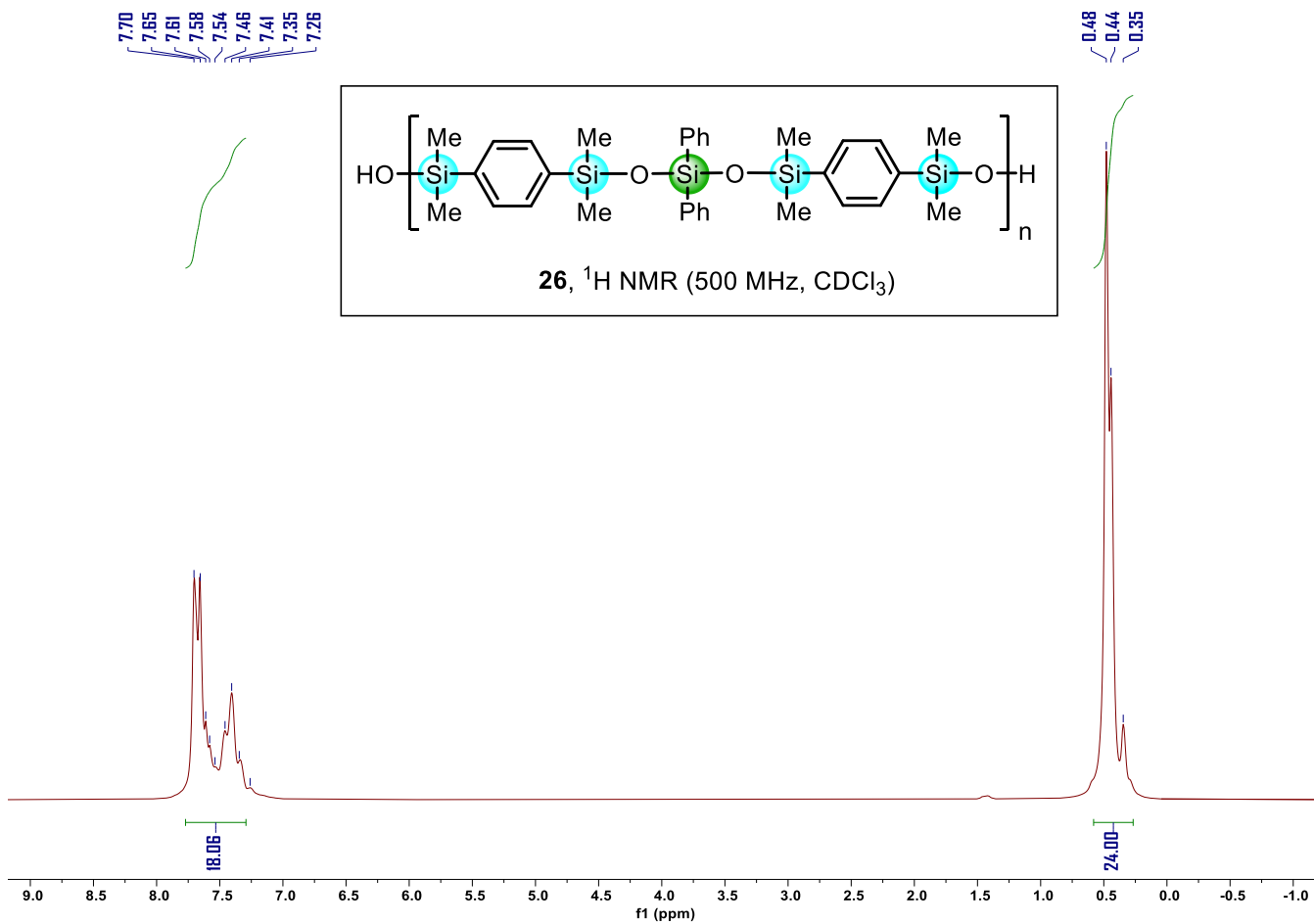






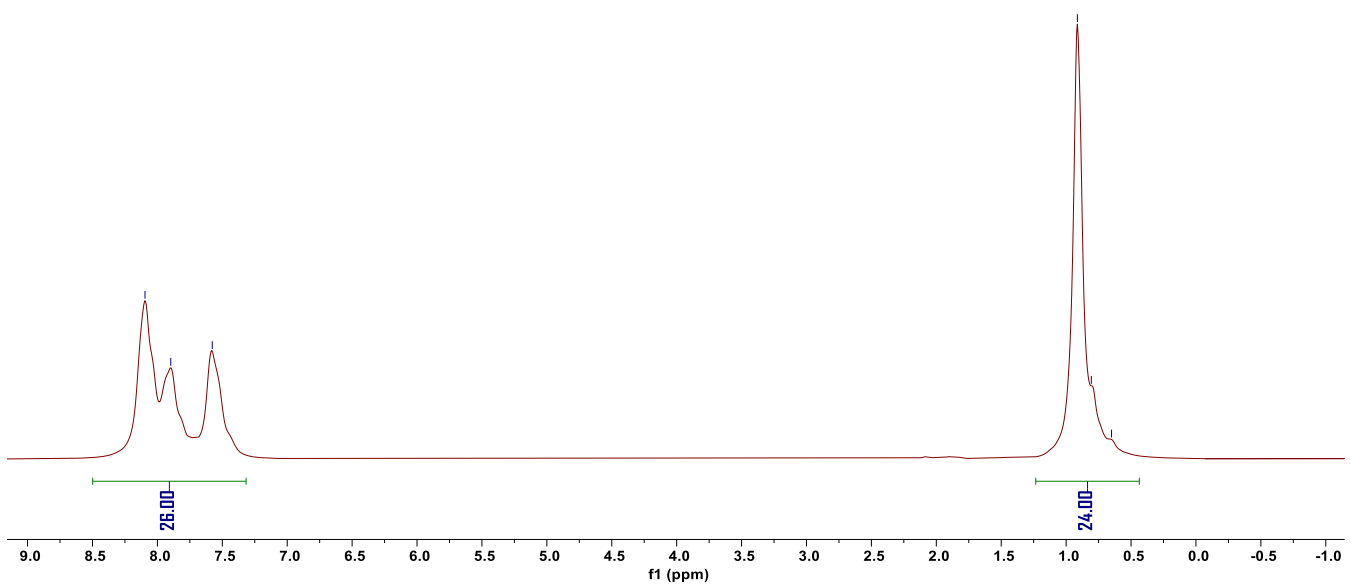
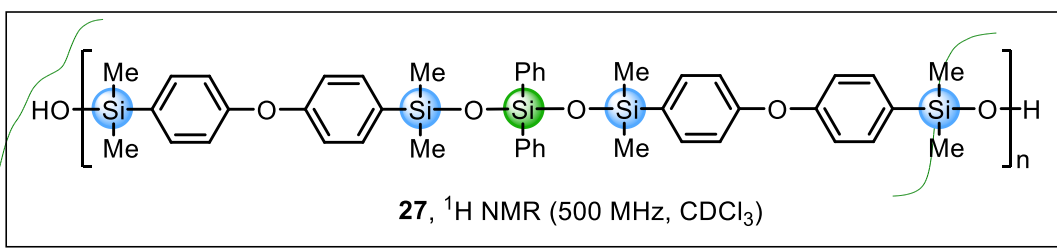






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