Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary information

Cobalt-catalyzed Highly Selective Hydroxylation of Organohydrosilanes and Hydrosiloxanes

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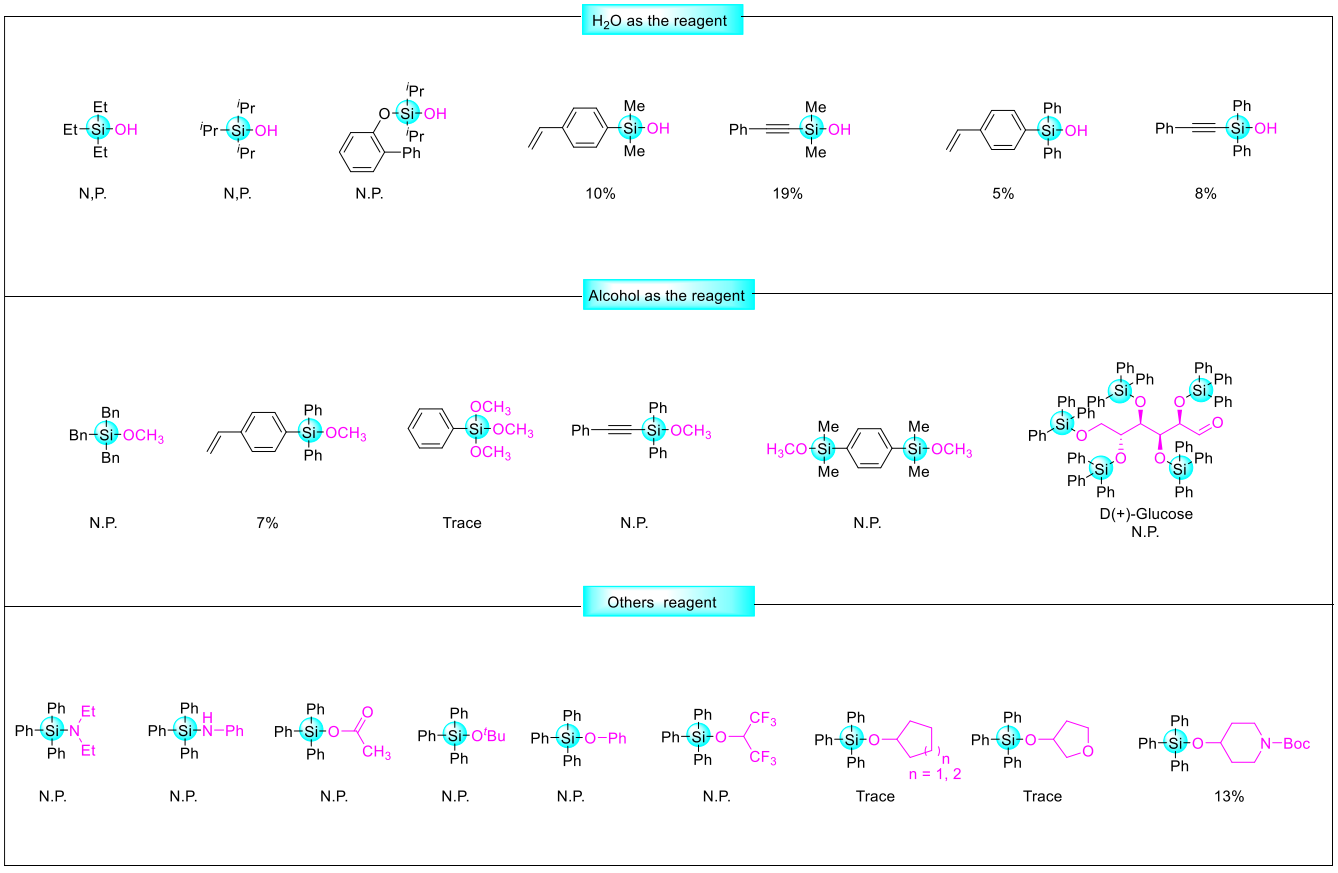
1. General Information

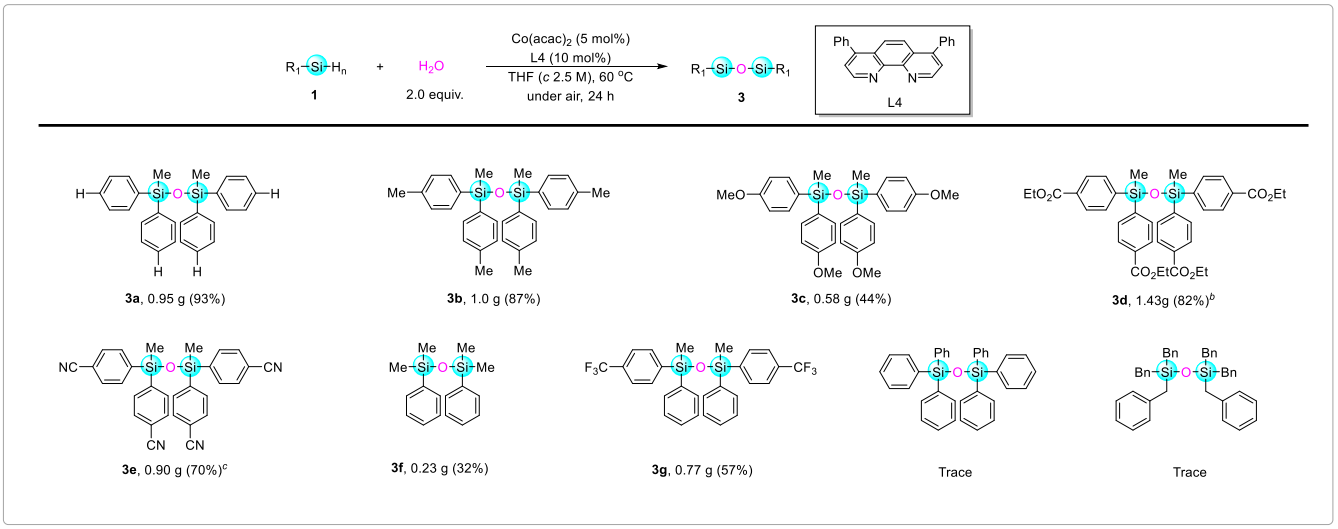
All reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques, unless otherwise indicated. All commercial reagents were used without further purification unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) analysis. TLC plates were viewed 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 (^{1}H 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 non-deuterated solvent. IR spectra were obtained from Thermo Scientific NICOLET 380 FT-IR (KCl card). HRMS were obtained on an Exactive Plus LC-MS (ESI) mass spectrometer with the use of a quadrupole analyzer or Agilent 7820A GC-MS with EI mode.

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and the Polydispersity index (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}.

Unsuccessful substrates:

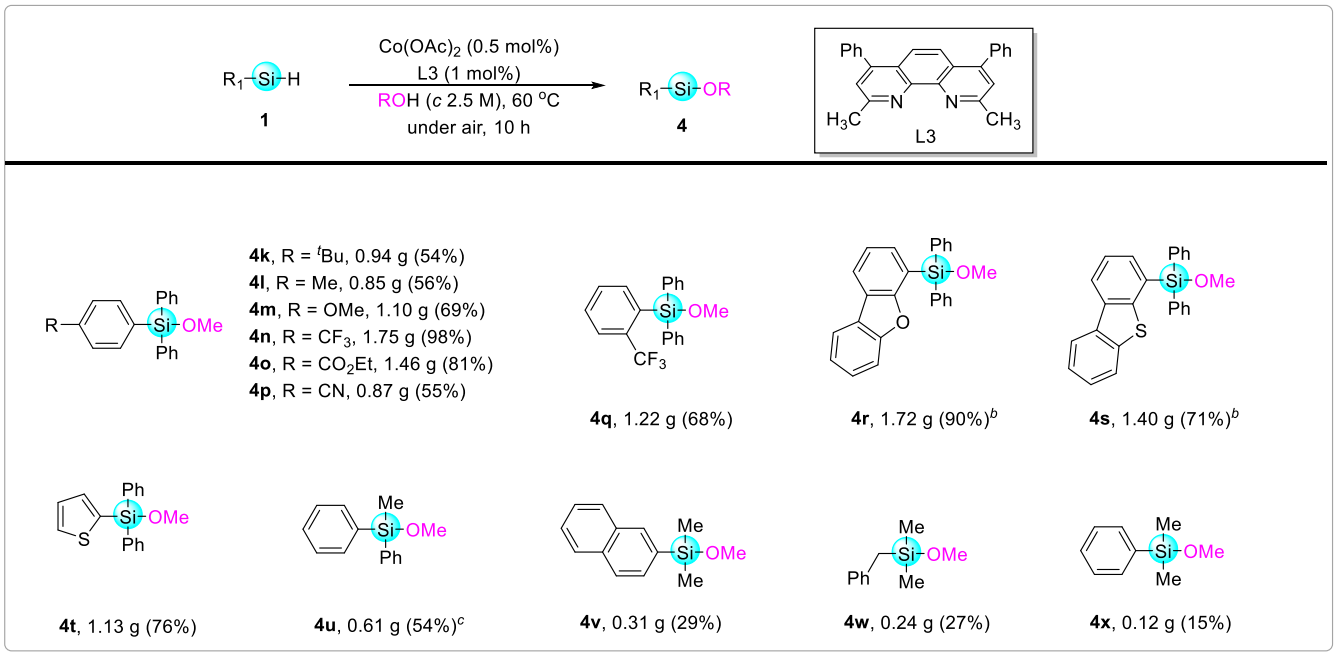


Scheme S1. Substrate scope of disiloxanes.



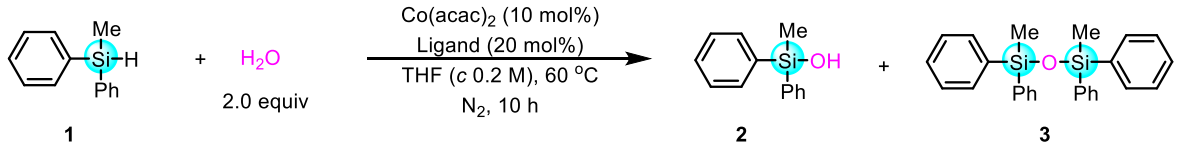
[a] Reaction conditions B: **1** (5 mmol, 1.0 equiv.), H_2O (10 mmol, 2.0 equiv.), $Co(acac)_2$ (0.25 mmol, 5 mol%), and **L4** (0.5 mmol, 10 mol%) were added THF (*c* 2.5 M) under air at 60 °C for 24 h; [b] Reaction temperature at -20 °C for 3 h; [c] Reaction temperature at -20 °C for 1 h.

Scheme S2. Addtional substrate scope of alkoxysilanes.

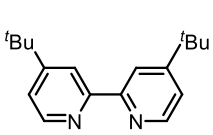


[a] Reaction conditions: **1** (5 mmol, 1.0 equiv.), $Co(OAc)_2$ (0.025 mmol, 0.5 mol%), and **L3** (0.05 mmol, 1 mol%) were added to alcohols (*c* 2.5 M) under air at 60 °C for 10 h; [b] CH_3OH (4.0 mL), dichloromethane (1.0 mL) and 1,4-dioxane (1.0 mL) as the co-solvent; [c] 5 mol% $Co(OAc)_2$.

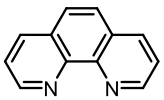
2. Optimization of Reaction Conditions



Entry[a]	Ligand	**2**[b]	**3**[b]
1	L1	68%	7%
2	L2	65%	8%
3	L3	81%	trace
4	L4	< 5%	89%
5	L5	trace	trace
6	L6	18%	trace
7	L7	43%	3%
8	L8	trace	trace
9	L9	5%	trace
10	L10	68%	trace



L1



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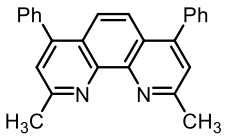

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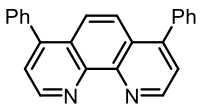
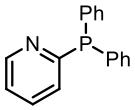
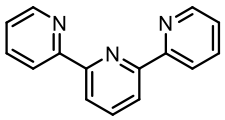


L4

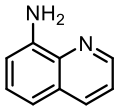
L5



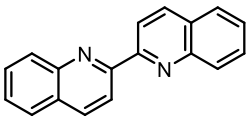
L6



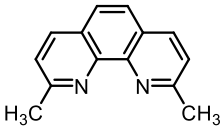
L7



L8



L9

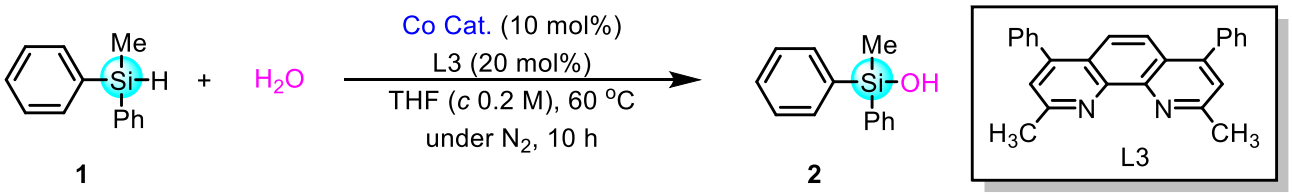


L10

[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), H_2O (0.4 mmol, 2.0 equiv.), $Co(acac)_2$ (0.02 mmol, 10 mol%) and Ligand (0.04 mmol, 20 mol%) were added to THF (*c* 0.2 M) under nitrogen atmosphere for 10 h. [b] The yield was given with CH_2Br_2 as the internal standard.

2.1 Optimization of the hydroxylation of silanes

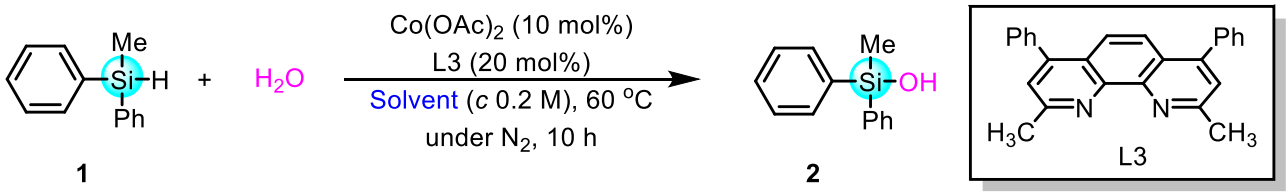
2.1.1 Screening of the cobalt catalysts



Entry[a]	Co cat.	Yield[b]
1	$Co(OAc)_2·4H_2O$	80%
2	$CoCl_2·6H_2O$	trace
3	CoF_2	27%
4	$CoCl_2$	trace
5	$CoBr_2$	trace
6	$CoF_2·4H_2O$	74%
7	$Co(BF_4)_2·6H_2O$	trace
8	$Co(OAc)_2$	87%
9	$Co(acac)_2$	81%

[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), H_2O (0.4 mmol, 2.0 equiv.), Co Cat. (0.02 mmol, 10 mol%) and **L3** (0.04 mmol, 20 mol%) were added to THF (*c* 0.2 M) under nitrogen atmosphere for 10 h. [b] The yield was given with CH_2Br_2 as the internal standard.

2.1.2 Screening of the solvents and reaction time

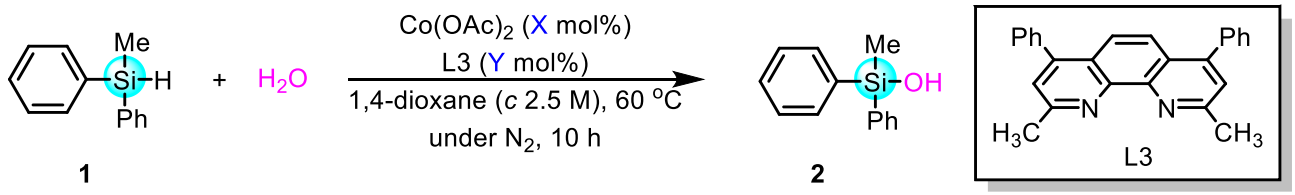


Entry[a]	Slovent	Yield[b]
1	Et_2O	11%
2	DCM	trace
3	EA	trace
4	1,4-dioxane	100%(94%)
5	DCE	trace
6	CH_3CN	67%
7	THF	87%
8[c]	1,4-dioxane	73%

[a] Reaction conditions: **1** (0.2 mmol, 1.0 equiv.), H_2O (0.4 mmol, 2.0 equiv.), $Co(OAc)_2$ (0.02 mmol, 10 mol%) and **L3** (0.04 mmol, 20 mol%) were added to solvent (*c* 0.2 M) under nitrogen atmosphere for 10 h. [b] The yield was given with

CH_2Br_2 as the internal standard and the isolated yield was given in the parentheses. [c] Reaction time = 5 h.

2.1.3 Optimization of gram-scaled hydroxylation reaction

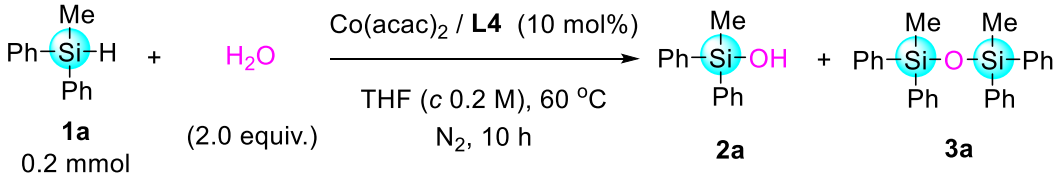


Entry[a]	X	Y	Yield[b]
1	0.5	1	62%
2	1	2	74%
3	10	20	77%
4[c]	10	20	58%
5[c,d]	0.5	1	100% (97%)
6[c,d]	-	1	N.R.
7[c,d]	0.5	-	N.R.

[a] Reaction conditions: **1** (5 mmol, 1.0 equiv.), H_2O (10.0 mmol, 2.0 equiv.), $Co(OAc)_2$ and **L3** were added to 1,4-dioxane (*c* 2.5 M) under nitrogen atmosphere for 10 h. [b] The yield was given with CH_2Br_2 as the internal standard and the isolated yield was given in the parentheses. [c] Under air. [d] 80 °C.

2.2 Optimization for the preparation of disiloxane

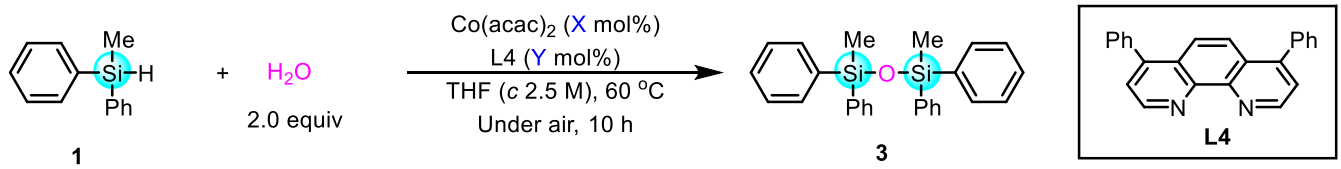
2.2.1 The ratio of $Co(acac)_2$ and ligand L4



entry	$Co(acac)_2$ / **L4**	yield (**2a**)	yield (**3a**)
1	1.0 : 1.0	30%	trace
2	1.0 : 1.5	19%	55%
3	1.0 : 2.0	trace	89%

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), H_2O (0.4 mmol, 2.0 equiv.), $Co(acac)_2$ and **L4** were added to THF (*c* 0.2 M) under N_2 for 10 h. [b] The yield was given with CH_2Br_2 as the internal standard.

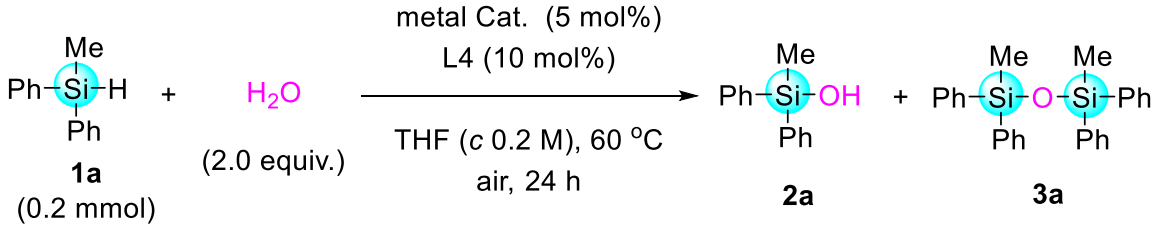
2.2.2 Optimization of gram-scale preparation



Entry[a]	X	Y	3[b]
1	0.5	1	58%
2	1	2	70%
3	5	10	86%
4	10	20	88%
5[c]	5	10	100% (93%)
6[c]	-	10	N.P.
7[c]	5	-	N.P.

[a] Reaction conditions: **1** (5 mmol, 1.0 equiv.), H_2O (10.0 mmol, 2.0 equiv.), $Co(acac)_2$ and **L4** were added to THF (*c* 2.5 M) under air for 10 h. [b] The yield was given with CH_2Br_2 as the internal standard and the isolated yield was given in the parentheses. [c] Reaction time = 24 h.

2.3 Screening of Mn or Fe as the precatalyst



Entry[a]	metal cat.	starting material[b]	yield (**2a**)[b]	yield (**3a**)[b]
1	$Fe(acac)_2$	86%	0%	0%
2	$Fe(acac)_3$	84%	0%	0%
3	$Mn(acac)_2 \cdot 2H_2O$	78%	10%	3%
4	$Mn(acac)_3$	94%	0%	0%
5	$Fe(OAc)_2$	100%	0%	0%
6	$Mn(OAc)_2 \cdot 2H_2O$	94%	0%	0%

[a] Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), H_2O (0.4 mmol, 2.0 equiv.), Metal catalyst and **L4** were added to THF (*c* 0.2 M) under air for 24 h. [b] The yield was given with CH_2Br_2 as the internal standard.

3. General Procedures

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

To a 10 mL flame-dried Schlenk tube with a stir bar was added silanes (5 mmol), $Co(OAc)_2$ (0.5 mol%), and **L3** (1 mol%). H_2O (175 μL) and 1,4-dioxane (2.5 M) were added *via* syringe at 80 ºC (oil bath) under air for 10 h. After that, the reaction mixture was directly concentrated by rotary evaporation. The hydroxylated products were isolated by silica column chromatography (typically 10% of ethyl acetate in petroleum ether).

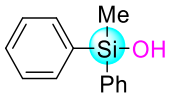
General Procedure 2 (GP 2) - *Co-catalyzed the synthesis of disiloxanes*

To a 10 mL flame-dried Schlenk tube with a stirring bar was added silane (5 mmol), $Co(acac)_2$ (5 mol%), **L4** (10 mol%), H_2O (10 mmol) and THF (2.5 M) at 60 ºC (oil bath) under air for 24 h. After that, the reaction mixture was directly concentrated by rotary evaporation. The disiloxane products were isolated by silica column chromatography (typically 10% of ethyl acetate in petroleum ether).

General Procedure 3 (GP 3) - *Co-catalyzed the synthesis of alkyloxylsilanes*

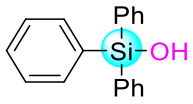
To a 10 mL flame-dried Schlenk tube with a stirring bar was added silane (5 mmol), $Co(OAc)_2$ (0.5 mol%), **L3** (1 mol%), and related alcohols (2.5 M) as solvent at 60 ºC (oil bath) under air for 10 h. After that, the reaction mixture was directly concentrated by rotary evaporation. The alkoxylate products were isolated by silica column chromatography (typically 10% of ethyl acetate in petroleum ether).

4. Characterization of Products



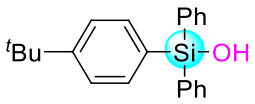
2a, Methyldiphenylsilanol[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.04 g (97% yield) of the desired product as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.65 – 7.61 (m, 4H), 7.48 – 7.44 (m, 2H), 7.43 – 7.38 (m, 4H), 2.99 (br s, 1H), 0.67 (s, 3H).



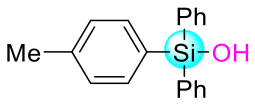
2b, Triphenylsilanol[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.30 g (94% yield) of the desired product as a white solid.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 – 7.62 (m, 6H), 7.48 – 7.42 (m, 3H), 7.41 – 7.37 (m, 6H), 2.50 (br s, 1H).



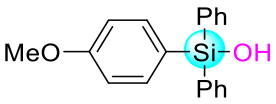
2c, (4-(tert-butyl)phenyl)diphenylsilanol[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.30 g (78% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.1 Hz, 4H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.35 (m, 8H), 2.63 (br s, 1H), 1.34 (s, 9H).



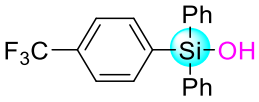
2d, diphenyl(p-tolyl)silanol[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.26 g (87% yield) of the desired product as a white solid.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.61 – 7.54 (m, 4H), 7.52 – 7.44 (m, 2H), 7.43 – 7.33 (m, 2H), 7.35 – 7.27 (m, 4H), 7.17 – 7.11 (m, 2H), 2.99 (br s, 1H), 2.33 (s, 3H).



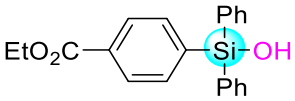
2e, (4-methoxyphenyl)diphenylsilanol[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.50 g (98% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.4 Hz, 4H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.49 – 7.34 (m, 6H), 6.94 (d, *J* = 7.8 Hz, 2H), 3.83 (s, 3H), 2.39 (br s, 1H).



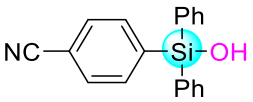
2f, diphenyl(4-(trifluoromethyl)phenyl)silanol[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.50 g (88% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.59 (dd, *J* = 8.2, 4.1 Hz, 6H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 4H), 3.54 (br s, 1H).



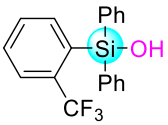
2g, ethyl 4-(hydroxydiphenylsilyl)benzoate[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.60 g (92% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.63 (dd, *J* = 8.0, 1.4 Hz, 4H), 7.49 – 7.42 (m, 2H), 7.41 – 7.33 (m, 4H), 4.38 (br s, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H).



2h, 4-(hydroxydiphenylsilyl)benzonitrile[2]

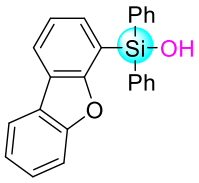
Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.37 g (91% yield) of the desired product as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 – 7.69 (m, 2H), 7.59 (dd, *J* = 8.1, 1.4 Hz, 4H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.42 – 7.35 (m, 4H), 4.13 (br s, 1H).



2i, diphenyl(2-(trifluoromethyl)phenyl)silanol

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.90 g (99% yield) of the desired product as a colorless oil.

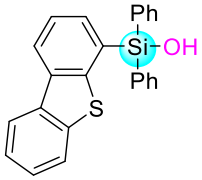
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.62 – 7.54 (m, 5H), 7.53 – 7.44 (m, 3H), 7.41 (t, *J* = 7.2 Hz, 4H), 2.93 (br s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.1, 135.3 (q, *J* = 31.1 Hz), 135.1, 134.9, 133.5, 130.8, 130.2, 130.1, 127.9, 126.3 (q, *J* = 5.2 Hz), 124.9 (q, *J* = 274.3 Hz). **^{19}F NMR** (471 MHz, Chloroform-*d*) δ -57.4. **IR** (neat, cm^{-1}): 3061 (br), 1112 (s), 699 (s), 500 (s), 822 (m); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{19}H_{15}F_3NaOSi$: 367.0736; Found: 367.0733.



2j, dibenzo[b,d]furan-4-yldiphenylsilanol[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.57 g (86% yield) of the desired product as a white solid.

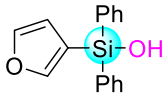
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.03 – 7.98 (m, 1H), 7.83 – 7.77 (m, 4H), 7.59 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.54 – 7.49 (m, 3H), 7.48 – 7.43 (m, 5H), 7.42 – 7.36 (m, 2H), 3.66 (br s, 1H).



2k, dibenzo[b,d]thiophen-4-yldiphenylsilanol[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.81 g (95% yield) of the desired product as a white solid.

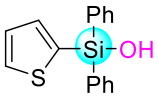
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.26 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.17 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.76 (dd, *J* = 6.9, 1.6 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.3 Hz, 4H), 7.65 – 7.61 (m, 1H), 7.52 – 7.38 (m, 9H), 2.88 (br s, 1H).



2l, furan-3-yldiphenylsilanol

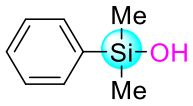
Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.31 g (98% yield) of the desired product as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.62 (m, 4H), 7.56 (t, *J* = 1.6 Hz, 1H), 7.51 – 7.36 (m, 7H), 6.51 (dd, *J* = 1.8, 0.8 Hz, 1H), 3.08 (br s, 1H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 150.3 , 143.2 , 135.2 , 134.5 , 130.1 , 127.9 , 114.7 , 113.6 . **IR** (neat, cm^{-1}): 3291 (br), 1121 (s), 827 (m), 704 (s), 499 (s). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{16}H_{14}NaO_2Si$: 289.0655; Found: 289.0652.



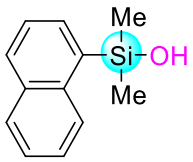
2m, diphenyl(thiophen-2-yl)silanol[3]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.40 g (99% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.67 (m, 5H), 7.54 – 7.47 (m, 2H), 7.47 – 7.39 (m, 5H), 7.27 (dd, *J* = 4.6, 3.3 Hz, 1H), 2.90 (br s, 1H).



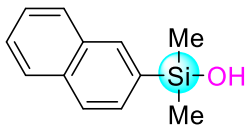
2n, dimethyl(phenyl)silanol[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.58 g (76% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.44 – 7.35 (m, 3H), 2.25 (br s, 1H), 0.41 (s, 6H).



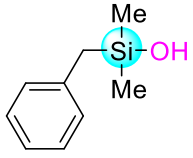
2o, dimethyl(naphthalen-1-yl)silanol[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.71 g (70% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.43 – 8.35 (m, 1H), 7.96 (dd, *J* = 8.8, 3.2 Hz, 2H), 7.85 (d, *J* = 6.8 Hz, 1H), 7.64 – 7.56 (m, 2H), 7.56 – 7.48 (m, 1H), 3.93 (br s, 1H), 0.63 (s, 6H).



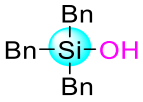
2p, dimethyl(naphthalen-2-yl)silanol[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.79 g (78% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.90 – 7.81 (m, 3H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.47 (m, 2H), 2.78 (br s, 1H), 0.49 (s, 6H).



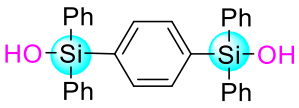
2q, Benzyldimethylsilanol[1]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.76 g (91% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 2H), 7.13 – 7.02 (m, 3H), 2.18 (s, 2H), 1.67 (br s, 1H), 0.14 (s, 6H).



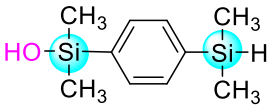
2r, Tribenzylsilanol

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.42 g (89% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.20 (m, 6H), 7.14 (d, *J* = 7.3 Hz, 3H), 7.01 (d, *J* = 7.4 Hz, 6H), 2.19 (s, 6H), 1.75 (br s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.9, 128.50, 128.47, 124.6, 24.0. **IR** (neat, cm^{-1}): 3613 (br), 776 (m), 733 (s), 698 (s), 477 (m); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{22}NaO$: 341.1332; Found: 341.1327.



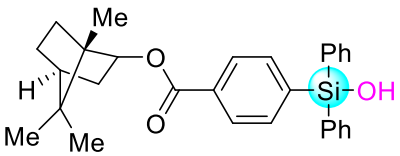
2s, 1,4-phenylenebis(diphenylsilanol) [2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.35 g (57% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.56 (m, 12H), 7.48 – 7.33 (m, 12H), 2.51 (br s, 2H).**^{13}C NMR** (101 MHz, DMSO-d_6) δ 138.1 , 136.3 , 134.5 , 133.7 , 129.7 , 127.8 .



2t, (4-(dimethylsilyl)phenyl)dimethylsilanol

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.50 g (48% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 – 7.56 (m, 4H), 4.48 (p, *J* = 3.7 Hz, 1H), 2.76 (br s, 1H), 0.42 (s, 6H), 0.40 (d, *J* = 3.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.0 , 139.0 , 133.4 , 132.4 , -0.1 , -3.9 . **IR** (neat, cm^{-1}): 3269 (br), 2121 (m), 868 (s), 826 (s), 772 (s); RMS (EI-QTOF) m/z: $[M]^+$ Calcd. for $C_{10}H_{18}OSi_2$: 210.0896; Found: 210.0899.

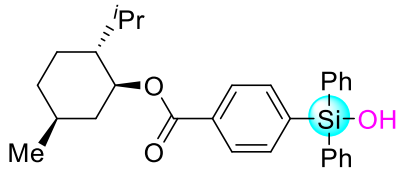


from (-)-bornel

2u, (1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(hydroxydiphenylsilyl)benzoate[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 2.00 g (88% yield, dr > 20:1) of the desired product as white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.9 Hz, 2H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 7.1 Hz, 4H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 4H), 5.16 – 5.06 (m, 1H), 3.26 (br s, 1H), 2.54 – 2.40 (m, 1H), 2.20 – 2.05 (m, 1H), 1.87 – 1.76 (m, 1H), 1.74 (t, *J* = 4.4 Hz, 1H), 1.49 – 1.35 (m, 1H), 1.35 – 1.24 (m, 1H), 1.11 (dd, *J* = 13.8, 3.3 Hz, 1H), 0.97 (s, 3H), 0.92 (d, *J* = 4.5 Hz, 6H).

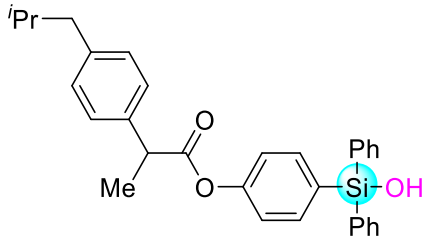


from L-menthol

2v, (1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(hydroxydiphenylsilyl)benzoate[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 2.02 g (88% yield, dr > 20:1) of the desired product as white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.58 (m, 4H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 4H), 4.95 (td, *J* = 10.8, 4.3 Hz, 1H), 3.38 (br s, 1H), 2.21 – 2.06 (m, 1H), 1.97 (pd, *J* = 6.9, 2.5 Hz, 1H), 1.80 – 1.69 (m, 2H), 1.21 – 1.05 (m, 2H), 0.90 – 0.97 (m, 2H), 0.94 (m, 7H), 0.80 (d, *J* = 6.9 Hz, 3H).

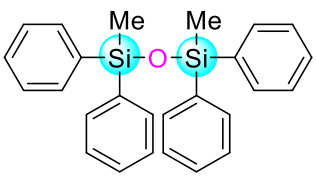


from ibuprofen

2w, 4-(hydroxydiphenylsilyl)phenyl 2-(4-isobutylphenyl)propanoate[2]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.79 g (74% yield) of the desired product as a colorless oil.

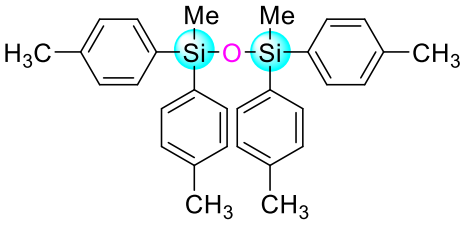
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.56 (m, 6H), 7.48 – 7.41 (m, 2H), 7.38 (t, *J* = 7.2 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 2.64 (br s, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.95 – 1.79 (m, 1H), 1.61 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H).



3a, 1,3-dimethyl-1,1,3,3-tetraphenyldisiloxane[4]

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.95 g (93% yield) of the desired product as a colorless oil.

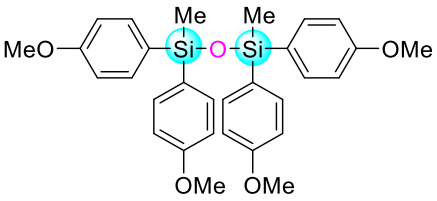
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.54 (m, 8H), 7.40 (d, *J* = 6.9 Hz, 12H), 0.67 (s, 6H).



3b, 1,3-dimethyl-1,1,3,3-tetra-p-tolyldisiloxane[5]

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.00 g (87% yield) of the desired product as a colorless oil.

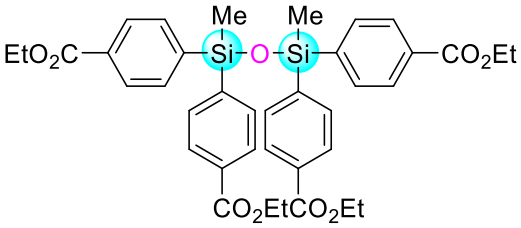
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.95 – 7.78 (m, 8H), 7.58 – 7.42 (m, 8H), 2.69 (s, 12H), 0.99 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 139.2 , 134.4 , 134.1 , 128.5 , 21.5 , -0.3.



3c, 1,1,3,3-tetrakis(4-methoxyphenyl)-1,3-dimethyldisiloxane

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.58 g (44% yield) of the desired product as a white solid.

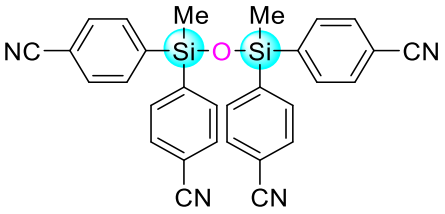
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 8.4 Hz, 8H), 6.92 (d, *J* = 8.4 Hz, 8H), 3.85 (s, 12H), 0.58 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.7 , 135.5 , 129.1 , 113.4 , 54.9 , -0.2 . **IR** (neat, cm^{-1}): 1590 (s), 1029 (s), 799 (s), 520 (m); **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{34}NaO_5Si_2$: 553.1837; Found: 553.1836.



3d, tetraethyl 4,4',4",4"'-(1,3-dimethyldisiloxane-1,1,3,3-tetrayl)tetrabenzoate

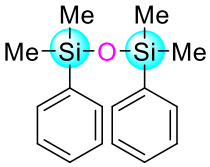
Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.43 g (82% yield) of the desired product as a colorless oil.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 8H), 7.57 (d, *J* = 8.2 Hz, 8H), 4.33 (q, *J* = 7.1 Hz, 8H), 1.33 (t, *J* = 7.2 Hz, 12H), 0.64 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 166.0 , 141.8 , 133.6 , 131.6 , 128.5 , 60.7 , 14.0 , -1.2 . **IR** (neat, cm^{-1}): 2980 (br), 1715 (s), 1267 (s), 1085 (s), 739 (s)； **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{38}H_{42}O_9Si_2$: 699.2440; Found: 699.2437.



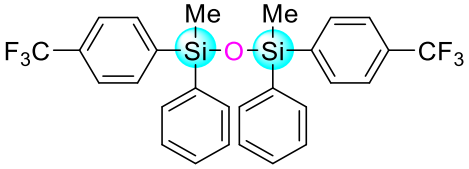
3e, 4,4',4",4"'-(1,3-dimethyldisiloxane-1,1,3,3-tetrayl)tetrabenzonitrile

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 3:1) afforded 0.90 g (70% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.8 Hz, 8H), 7.53 (d, *J* = 7.8 Hz, 8H), 0.66 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.4, 134.1, 131.5, 118.2, 114.2, -1.2. **IR** (neat, cm^{-1}): 2228 (m), 1386 (m), 1060 (s), 794 (s), 557 (s). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{30}H_{22}N_4NaOSi_2$: 533.1224; Found: 533.1228.



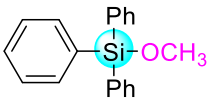
3f, 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane[4]

Synthesized according to **GP 2**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.23 g (32% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.69 (m, 4H), 7.57 – 7.47 (m, 6H), 0.52 (s, 12H).



3g, 1,3-dimethyl-1,3-diphenyl-1,3-bis(4-(trifluoromethyl)phenyl)disiloxane

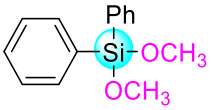
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.8 Hz, 4H), 7.56 (d, *J* = 7.9 Hz, 4H), 7.53 – 7.47 (m, 4H), 7.47 – 7.40 (m, 2H), 7.39 – 7.32 (m, 4H), 0.64 (s, 6H). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.98.**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.04, 136.15, 134.17, 133.85, 131.57 (q, *J* = 32.2 Hz), 130.12, 128.00, 124.35 (q, *J* = 3.8 Hz), 124.09 (q, *J* = 272.3 Hz), -0.80. **IR** (neat, cm^{-1}): 1322 (s), 1163 (m), 1117 (s), 1053 (s), 790 (m)； RMS (EI-QTOF) m/z: $[M]^+$ Calcd. for $C_{28}H_{24}OF_6Si_2$: 546.1270; Found: 546.1270.



4a, Methoxytriphenylsilane[2]

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.38 g (95% yield) of the desired product as a colorless oil. The gram-scale reaction was run on a 20.0 mmol scale and the desired product **4a** was obtained in 83% yield (3.80 g).

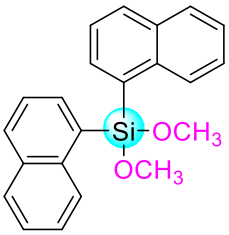
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.73 (m, 6H), 7.59 – 7.45 (m, 9H), 3.77 (s, 3H).



4b, Dimethoxydiphenylsilane[6]

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.66 g (54% yield) of the desired product as a colorless oil.

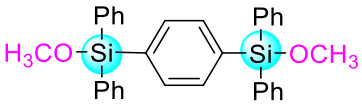
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.83 – 7.77 (m, 4H), 7.22 – 7.16 (m, 6H), 3.45 (s, 6H).



4c, dimethoxydi(naphthalen-1-yl)silane[7]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.48 g (86% yield) of the desired product as a white solid.

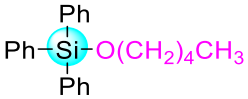
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 7.7 Hz, 2H), 8.06 (d, *J* = 6.7 Hz, 2H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.87 – 7.80 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.38 (m, 4H), 3.65 (s, 6H).



4d, 1,4-bis(methoxydiphenylsilyl)benzene

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.00 g (40% yield) of the desired product as a white solid.

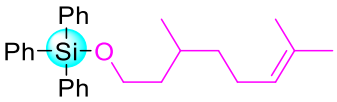
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.59 (m, 12H), 7.50 – 7.34 (m, 12H), 3.64 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.9, 135.4, 134.6, 133.7, 130.1, 127.9, 51.9.**IR** (neat, cm^{-1}): 3054 (br), 1082 (s), 696 (s), 531 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{32}H_{31}O_2Si_2$: 503.1857; Found: 503.1859.



4e, (pentyloxy)triphenylsilane

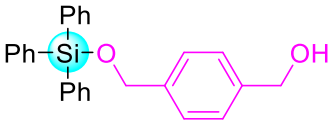
Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.85 g (49% yield) of the desired product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.57 (m, 6H), 7.56 – 7.33 (m, 9H), 3.94 – 3.67 (m, 2H), 1.76 – 1.55 (m, 2H), 1.46 – 1.15 (m, 4H), 1.02 – 0.78 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.4 , 134.5 , 129.9 , 127.8 , 64.0 , 32.2 , 27.9 , 22.4 , 14.1 . **IR** (neat, cm^{-1}): 2933 (br), 1429 (m), 1099 (s), 701 (s), 505 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{23}H_{27}OSi$: 347.1826; Found: 347.1824.



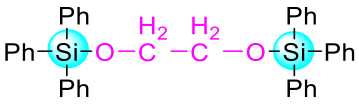
4f, ((3,7-dimethyloct-6-en-1-yl)oxy)triphenylsilane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.20 g (58% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.8 Hz, 6H), 7.49 – 7.33 (m, 9H), 5.08 (t, *J* = 6.8 Hz, 1H), 3.97 – 3.66 (m, 2H), 2.06 – 1.82 (m, 2H), 1.68 (s, 3H), 1.67 – 1.60 (m, 2H), 1.59 (s, 3H), 1.46 – 1.35 (m, 1H), 1.35 – 1.23 (m, 1H), 1.18 – 1.05 (m, 1H), 0.82 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 135.4 , 134.4 , 131.0 , 129.9 , 127.8 , 124.9 , 62.1 , 39.5 , 37.1 , 29.0 , 25.7 , 25.4 , 19.5 , 17.6 . **IR** (neat, cm^{-1}): 2919 (br), 1431 (s), 1101 (s), 704 (s), 509 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{28}H_{35}OSi$: 415.2452; Found: 415.2453.



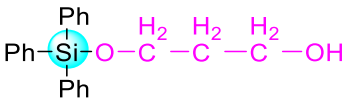
4g, (4-(((triphenylsilyl)oxy)methyl)phenyl)methanol

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.38 g (67% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (d, *J* = 6.3 Hz, 6H), 7.54 – 7.30 (m, 13H), 4.95 (s, 2H), 4.69 (s, 2H), 1.87 (br s, 1H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 134.0, 139.7, 135.4, 133.9, 130.1, 127.9, 126.9, 126.6, 65.3, 65.1. **IR** (neat, cm^{-1}): 3348 (br), 3056 (s), 1104 (s), 817 (m), 699 (s), 502 (s). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{26}H_{24}NaO_2Si$: 419.1438; Found: 419.1436.



4h, 1,1,1,6,6,6-hexaphenyl-2,5-dioxa-1,6-disilahexane

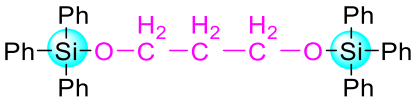
Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.94 g (67% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 6.9 Hz, 12H), 7.54 (t, *J* = 7.3 Hz, 6H), 7.46 (t, *J* = 7.3 Hz, 12H), 4.12 (s, 4H).**^{13}C NMR** (126 MHz, Chloroform-*d*) δ 135.4 , 134.1 , 129.9 , 127.8 , 65.1 . **IR** (neat, cm^{-1}): 3058 (br), 1103 (s), 705 (s), 507 (s) **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{38}H_{34}NaO_2Si_2$: 601.1990; Found: 601.1985.



4i, 3-((triphenylsilyl)oxy)propan-1-ol

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.00 g (60% yield) of the desired product as a white solid.

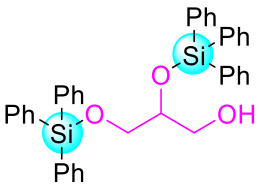
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.2 Hz, 6H), 7.53 – 7.37 (m, 9H), 4.02 (t, *J* = 5.7 Hz, 2H), 3.84 (t, *J* = 5.8 Hz, 2H), 2.30 (br s, 1H), 1.87 (p, *J* = 5.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.3 , 133.7 , 130.1 , 127.9 , 62.4 , 61.1 , 34.4 . **IR** (neat, cm^{-1}): 3058 (br), 1425 (s), 1079 (s), 706 (s), 506 (m). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{21}H_{22}NaO_2Si$: 357.1281; Found: 357.1278.



4i', 1,1,1,7,7,7-hexaphenyl-2,6-dioxa-1,7-disilaheptane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.42 g (28% yield) of the desired product as a white solid.

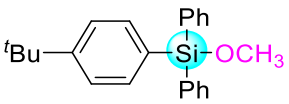
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 8.0, 1.4 Hz, 12H), 7.42 (s, 6H), 7.38 – 7.32 (m, 12H), 3.96 (t, *J* = 6.2 Hz, 4H), 1.88 (p, *J* = 6.2 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.4, 134.3, 129.9, 127.8, 60.6, 35.3. **IR** (neat, cm^{-1}): 3058 (br), 1426 (s), 1104 (s), 989 (m), 704 (s), 507 (m). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{39}H_{37}O_2Si_2$: 593.2327; Found: 593.2331.



4j, 2,3-bis((triphenylsilyl)oxy)propan-1-ol

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.31 g (20% yield) of the desired product as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 6.8 Hz, 6H), 7.51 (d, *J* = 6.7 Hz, 6H), 7.47 – 7.39 (m, 6H), 7.37 – 7.30 (m, 12H), 4.14 – 4.04 (m, 1H), 3.87 – 3.79 (m, 2H), 3.76 – 3.69 (m, 2H), 1.88 (t, *J* = 6.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.4 , 135.3 , 134.0 , 133.6 , 130.1 , 130.1 , 127.9 , 127.9 , 73.9 , 64.8 , 64.4 . **IR** (neat, cm^{-1}): 3057 (br), 1427 (m), 1111 (s), 704 (s), 510 (s). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{39}H_{36}NaO_3Si_2$: 631.2095; Found: 631.2094.

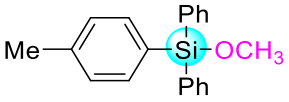


4k, (4-(tert-butyl)phenyl)(methoxy)diphenylsilane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded

0.94 g (54% yield) of the desired product as a colorless oil.

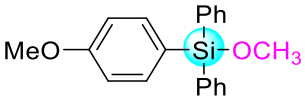
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 4H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.50 – 7.36 (m, 8H), 3.66 (s, 3H), 1.35 (s, 9H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.0 , 135.4 , 135.3 , 134.2 , 130.2 , 129.9 , 127.8 , 124.9 , 51.8 , 34.8 , 31.2 . **IR** (neat, cm^{-1}): 2958 (br), 1084 (s), 700 (s), 570 (m), 499 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{23}H_{27}OSi$: 347.1826; Found: 347.1825.



4l, methoxydiphenyl(p-tolyl)silane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.85 g (56% yield) of the desired product as a colorless oil.

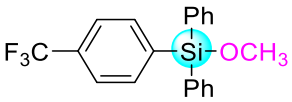
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.64 (m, 4H), 7.59 (d, *J* = 6.8 Hz, 2H), 7.54 – 7.38 (m, 6H), 7.28 (d, *J* = 7.6 Hz, 2H), 3.69 (s, 3H), 2.43 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.1 , 135.5 , 135.3 , 134.1 , 130.2 , 130.0 , 128.7 , 127.8 , 51.8 , 21.6 . **IR** (neat, cm^{-1}): 2938 (br), 1088 (s), 697 (s), 501 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}OSi$: 305.1356; Found: 305.1357.



4m, methoxy(4-methoxyphenyl)diphenylsilane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.10 g (69% yield) of the desired product as a colorless oil.

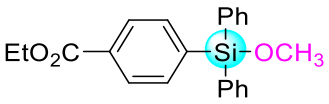
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (dt, *J* = 7.9, 1.3 Hz, 4H), 7.62 – 7.56 (m, 2H), 7.50 – 7.38 (m, 6H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H), 3.67 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 161.2 , 137.0 , 135.3 , 134.2 , 129.9 , 127.8 , 124.6 , 113.7 , 55.0 , 51.7 . **IR** (neat, cm^{-1}): 2944 (br), 1253 (m), 1104 (s), 809 (m), 701 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{20}H_{21}O_2Si$: 321.1305; Found: 321.1305.



4n, methoxydiphenyl(4-(trifluoromethyl)phenyl)silane

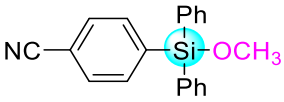
Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.75 g (98% yield) of the desired product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.68 – 7.57 (m, 6H), 7.52 – 7.37 (m, 6H), 3.66 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.12, 135.58, 135.32, 132.92, 131.87 (q, *J* = 32.2 Hz), 130.42, 128.09, 124.43 (q, *J* = 11.4 Hz), 124.14 (q, *J* = 3.8 Hz), 51.90. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.7 . **IR** (neat, cm^{-1}): 2938 (br), 1088 (s), 697 (s), 501 (s). **HRMS** (EI-QTOF) m/z: $[M]^+$ Calcd. for $C_{20}H_{17}OF_3Si$: 358.1001; Found: 358.1006.



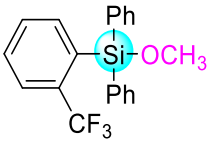
4o, ethyl 4-(methoxydiphenylsilyl)benzoate

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.46 g (81% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.4 Hz, 4H), 7.51 – 7.43 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 4H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.6 , 140.0 , 135.3 , 135.2 , 133.1 , 131.7 , 130.3 , 128.6 , 128.0 , 61.0 , 51.9 , 14.3 . **IR** (neat, cm^{-1}): 2980 (br), 1717 (s), 1086 (s), 709 (s), 511 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{22}H_{23}O_3Si$: 363.1411; Found: 363.1408.



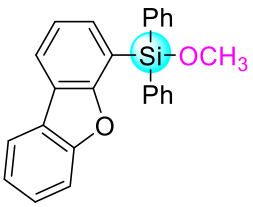
4p, 4-(methoxydiphenylsilyl)benzonitrile

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.87 g (55% yield) of the desired product as a white solid.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.72 – 7.62 (m, 6H), 7.55 – 7.41 (m, 6H), 3.71 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 140.8 , 135.5 , 135.1 , 132.3 , 131.0 , 130.4 , 128.0 , 118.6 , 113.4 , 51.8 . **IR** (neat, cm^{-1}): 3054 (br), 1087 (s), 697 (s), 567 (m), 489 (s). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{20}H_{17}NNaOSi$: 338.0972; Found: 338.0974.



4q, methoxydiphenyl(2-(trifluoromethyl)phenyl)silane

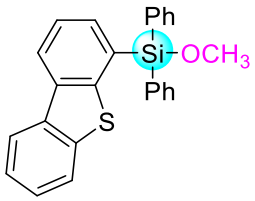
Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.22 g (68% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.93 (m, 1H), 7.81 – 7.74 (m, 1H), 7.68 – 7.61 (m, 4H), 7.61 – 7.55 (m, 2H), 7.52 – 7.46 (m, 2H), 7.46 – 7.39 (m, 4H), 3.64 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 137.9 , 136.0 (q, *J* = 31.5 Hz), 135.4 , 133.6 , 132.4 (q, *J* = 2.1 Hz), 130.7 , 130.2 , 130.0 , 127.8 , 126.4 (q, *J* = 5.0 Hz), 124.6 (q, *J* = 274.4 Hz), 51.9 . **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -57.8. **IR** (neat, cm^{-1}): 3060 (br), 1311 (s), 1104 (s), 771 (s), 702 (m). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{20}H_{18}OF_3Si$: 359.1074; Found: 359.1071.



4r, dibenzo[b,d]furan-4-yl(methoxy)diphenylsilane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.72 g (90% yield) of the desired product as a white solid.

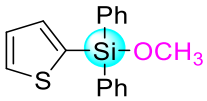
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.98 (d, *J* = 7.5 Hz, 1H), 7.76 – 7.66 (m, 4H), 7.60 (dd, *J* = 7.2, 1.3 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.43 – 7.31 (m, 7H), 3.78 (s, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.8 , 156.0 , 135.3 , 134.8 , 133.6 , 130.1 , 127.8 , 126.9 , 123.9 , 123.2 , 122.9 , 122.6 , 122.5 , 120.5 , 117.1 , 111.7 , 52.2 . **IR** (neat, cm^{-1}): 3054 (br), 1181 (m), 1087 (s), 744 (s), 701 (s). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{25}H_{20}O_2Si$: 381.1305; Found: 381.1303.



4s, dibenzo[b,d]thiophen-4-yl(methoxy)diphenylsilane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.40 g (71% yield) of the desired product as a white solid.

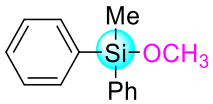
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 7.3 Hz, 1H), 7.79 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 6.9 Hz, 4H), 7.68 (d, *J* = 7.1 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.42 (t, *J* = 7.3 Hz, 6H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.2 , 140.1 , 135.6 , 135.2 , 135.0 , 134.9 , 132.8 , 130.4 , 128.4 , 128.0 , 126.6 , 124.1 , 123.8 , 123.5 , 122.5 , 121.3 , 51.9 . **IR** (neat, cm^{-1}): 3055 (br), 1085 (m), 728 (s), 503 (m), 423 (m). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{25}H_{20}NaOSSi$: 419.0896; Found: 419.0893.



4t, methoxydiphenyl(thiophen-2-yl)silane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 1.13 g (76% yield) of the desired product as a colorless oil.

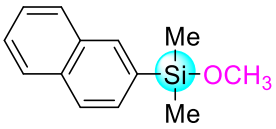
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.68 (m, 5H), 7.61 – 7.42 (m, 7H), 7.38 – 7.27 (m, 1H), 3.84 – 3.66 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.0 , 135.1 , 133.7 , 133.0 , 132.6 , 130.3 , 128.2 , 127.9 , 51.8 . **IR** (neat, cm^{-1}): 3060 (br), 1081 (s), 698 (s), 502 (s). **HRMS (ESI)** m/z: $[M+Na]^+$ Calcd. for $C_{17}H_{16}NaOSSi$: 319.0583; Found: 319.0583.



4u, methoxy(methyl)diphenylsilane[8]

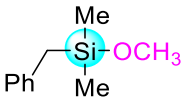
Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.61 g (54% yield) of the desired product as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.71 (m, 4H), 7.60 – 7.47 (m, 6H), 3.70 (s, 3H), 0.81 (s, 3H).



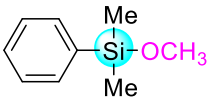
4v, methoxydimethyl(naphthalen-2-yl)silane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.31 g (29% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.98 – 7.84 (m, 3H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.47 (m, 2H), 3.55 (s, 3H), 0.53 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 134.8 , 134.4 , 134.0 , 132.9 , 129.5 , 128.2 , 127.7 , 127.14, 126.5 , 125.9 , 50.7 , -2.2 . **IR** (neat, cm^{-1}): 2954 (br), 1252 (s), 1081 (s), 794 (s), 657 (m). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{13}H_{17}OSi$: 217.1043; Found: 217.1048.



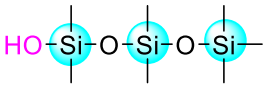
4w, benzyl(methoxy)dimethylsilane

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.24 g (27% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.20 (m, 2H), 7.15 – 7.05 (m, 3H), 3.45 (s, 3H), 2.22 (s, 2H), 0.13 (s, 6H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 138.9, 128.2, 128.24, 124.23, 50.5, 26.1, -3.0. **IR** (neat, cm^{-1}): 2953 (br), 1085 (s), 827 (s), 752 (m), 697 (m). **HRMS (ESI)** m/z: $[M+H]^+$ Calcd. for $C_{10}H_{17}OSi$: 181.1043; Found: 181.1043.



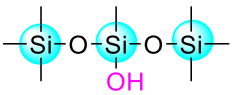
4x, methoxydimethyl(phenyl)silane[8]

Synthesized according to **GP 3**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.12 g (15% yield) of the desired product as a colorless oil.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.55 (m, 2H), 7.48 – 7.37 (m, 3H), 3.47 (s, 3H), 0.42 (s, 6H).



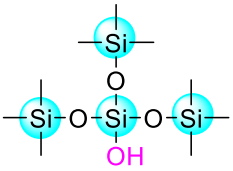
5a, 1,1,3,3,5,5,5-heptamethyltrisiloxan-1-ol[9]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.98 g (82% yield) of the desired product as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.43 (s, 1H), 0.11 (s, 18H), 0.08 (s, 3H).



5b, 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ol[10]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.73 g (61% yield) of the desired product as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.39 (s, 1H), 0.11 (s, 18H), 0.08 (s, 3H).

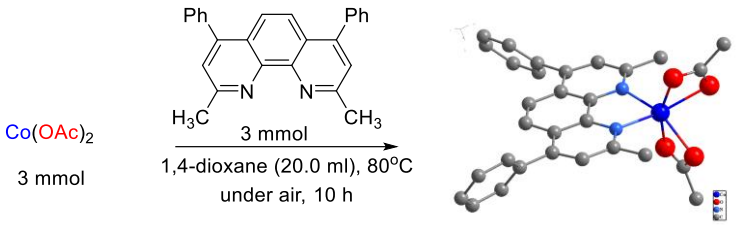


5c, tris(trimethylsilyl) hydrogen silicate[10]

Synthesized according to **GP 1**. Purification via column chromatography (petroleum ether/ethyl acetate = 10:1) afforded 0.68 g (43% yield) of the desired product as a colorless oil.
^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.14 (s, 1H), 0.12 (s, 27H).

5. X-ray Diffraction Analyses of Cobalt Complexes K1 and K2

Complex K1



CCDC: 2173145

$Co(OAc)_2$ (3.0 mmol) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (3.0 mmol) were dissolved in anhydrous 1,4-dioxane (20 mL) under air for 10 h at 80 °C. The precipitate formed was remained about 5 mL solvent by rotary evaporation and collected by filtration with cold 1,4-dioxane as eluent to give a dark orange solid (1.4 g, 80%).

The single crystals of this complex were obtained from the solution of dichloromethane and toluene. Note both the oxygen atoms of the coordinated carboxylate and toluene were partially disordered, which can be easily modified according to the standard operations. The full crystallographic data for **K1** (CCDC: 2173145) can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/solutions/csd-core/components/csd/

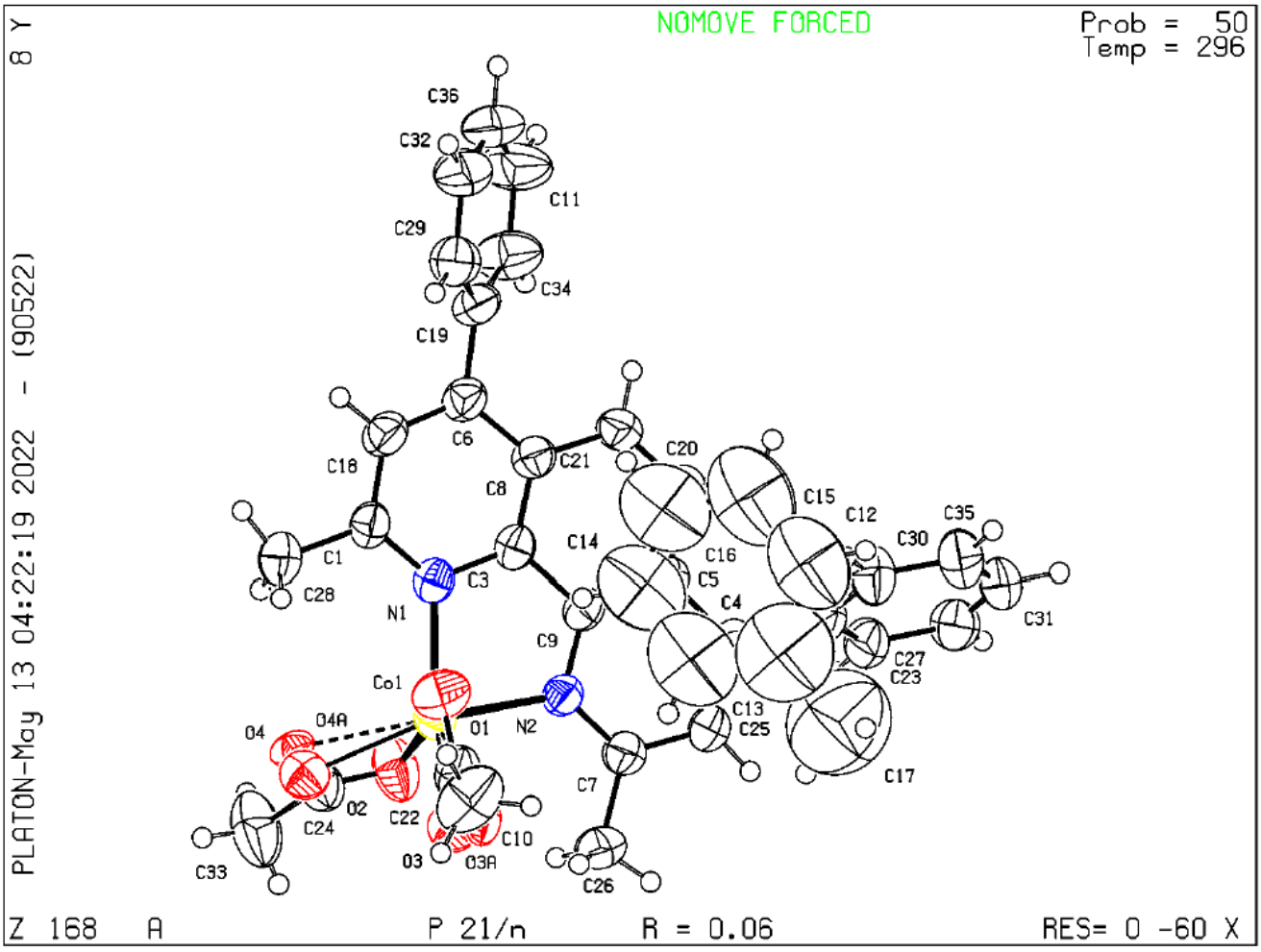
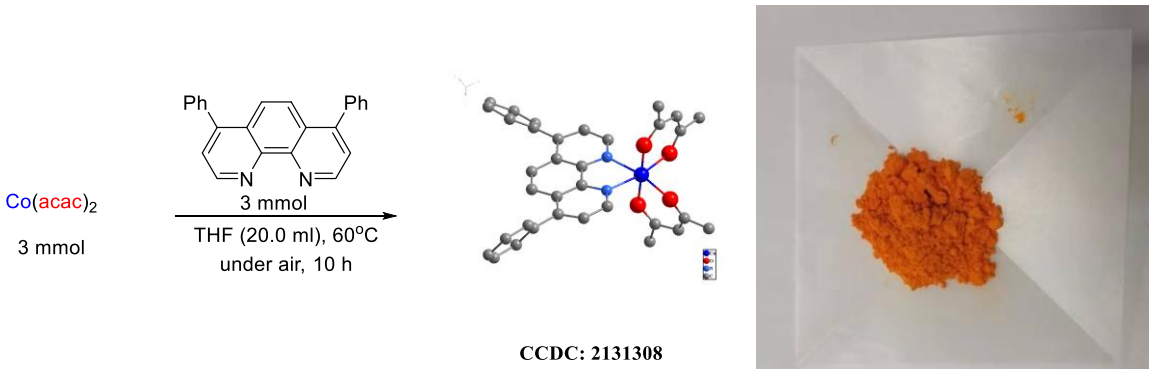


Table 1-1 Crystal data and structure refinement for K1.

Name	K1
Formula	$C_{37}H_{34}CoN_2O_4$
formula weight, fw	629.59
Temperature, *T* [K]	296(2)
crystal system	*monoclinic*
space group	*P 21/n*
a [Å]	14.962(2)
b [Å]	8.3869(9)
c [Å]	25.544(3)
α [°]	90
β [°]	94.204(4)
γ [°]	90
V [Å^3]	3196.8(7)
Z	4
ρ [g cm^{-3}]	1.308
μ [mm^{-1}]	0.579
θ range	2.557-25.037
F(000)	1316
goodness-of-fit, GOF	1.046
R_1[a] [I > 2σ (I)]	0.0618
wR_2[b] (all data)	0.1951

$^{a}R_1 = \left|\left|F_o\right| - \left|F_c\right|\right| / \left|F_o\right|$. $^{b}wR_2 = [w(\left|F_o^2\right| - \left|F_c^2\right|)^2 / w\left|F_o^2\right|^2]^{1/2}$.

Complex K2



CCDC: 2131308

Co(acac)$_2$ (3.0 mmol) and 4,7-diphenyl-1,10-phenanthroline (3.0 mmol) were dissolved in anhydrous THF (20 mL) under air for 10 h at 60 °C. The precipitate formed was remained about 5 mL solvent by rotary evaporation and collected by filtration with cold THF as eluent to give a dark orange solid (1.4 g, 80%).

The single crystals of this complex were obtained from the solution of dichloromethane and toluene. Note the coordinated dichloromethane molecules are disordered. The full crystallographic data for **K2** (CCDC:2131308) can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/solutions/csd-core/components/csd/

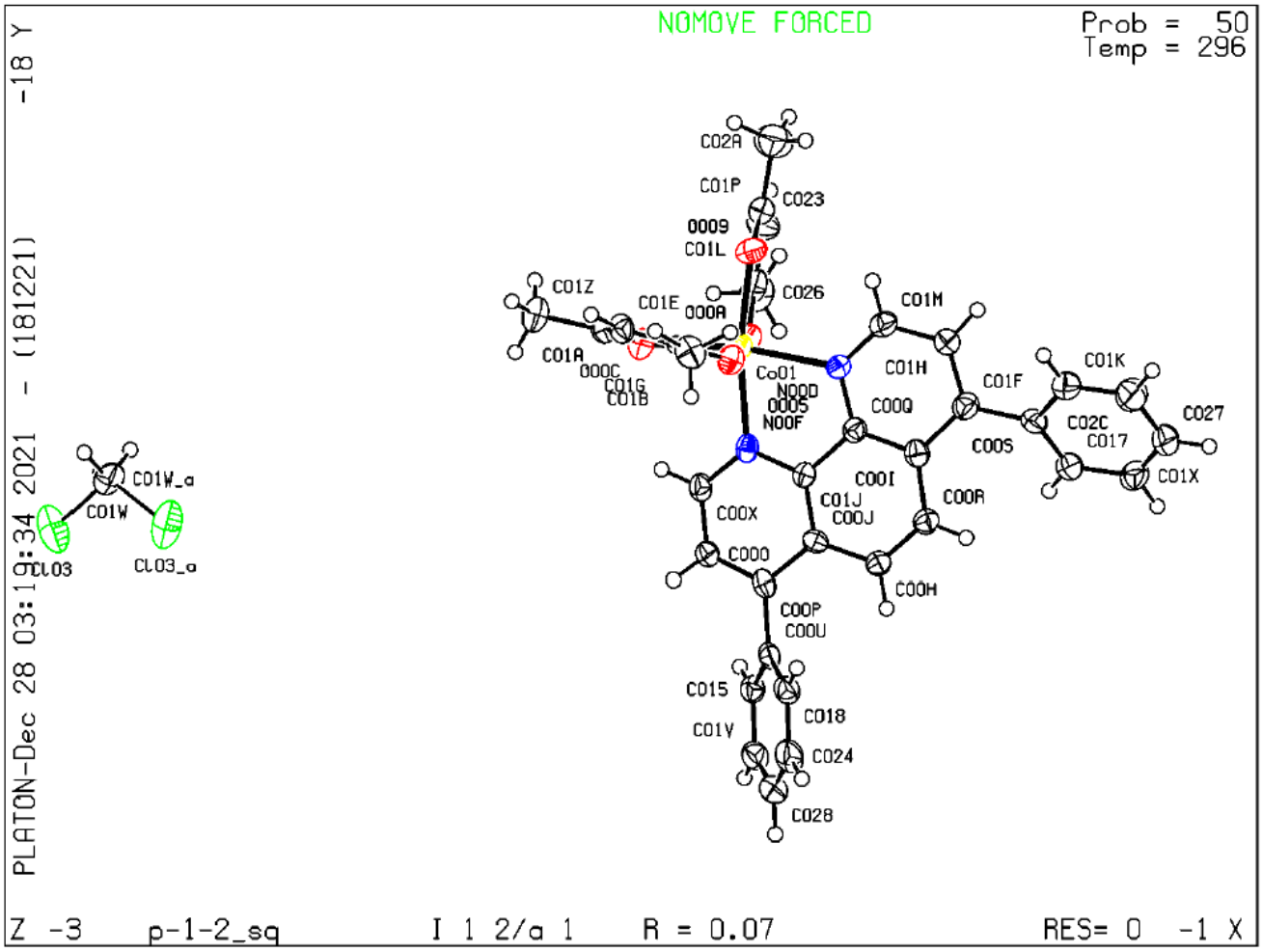


Table 2-1 Crystal data and structure refinement for K2.	
Identification code	p-1-2_sq
Empirical formula	$C_{69}H_{62}Cl_2Co_2N_4O_8$
Formula weight	1263.98
Temperature/K	296.15
Crystal system	monoclinic
Space group	I2/a
a/Å	16.2739(18)
b/Å	19.5624(17)
c/Å	22.3063(16)
α/°	90
β/°	110.570(6)
γ/°	90
Volume/Å^3	6648.6(11)
Z	4
ρ_{calc}g/cm^3	1.263
μ/mm^{-1}	0.635
F(000)	2624.0

Crystal size/mm^3	? ×? ×?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/ °	3.9 to 58.544
Index ranges	-22 ≤ h ≤ 20, -26 ≤ k ≤ 26, -30 ≤ l ≤ 28
Reflections collected	36271
Independent reflections	8229 [R_{int} = 0.1728, R_{sigma} = 0.2522]
Data/restraints/parameters	8229/0/392
Goodness-of-fit on F^2	0.949
Final R indexes [I>=2σ (I)]	R_1 = 0.0692, wR_2 = 0.1405
Final R indexes [all data]	R_1 = 0.2251, wR_2 = 0.1856
Largest diff. peak/hole / e Å^{-3}	0.37/-0.42

Table 2-2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for K2. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
Co01	-8876.5(4)	1635.9(3)	-3712.5(3)	28.8(2)
O005	-8937.9(18)	1518.4(14)	-2808.5(13)	33.3(8)
O009	-8651.2(19)	2653.5(15)	-3579.9(15)	37.4(8)
O00A	-8831.5(19)	1716.3(15)	-4620.2(14)	34.4(8)
O00C	-10217.7(18)	1720.0(15)	-4050.5(14)	34.8(8)
N00D	-7534(2)	1380.4(18)	-3244.6(17)	28.7(9)
N00F	-8848(2)	561.2(18)	-3835.4(16)	27.2(9)
C00H	-7115(3)	-721(2)	-3100(2)	29.0(11)
C00I	-6514(3)	427(2)	-2856(2)	29.2(11)
C00J	-7971(3)	-459(2)	-3477(2)	25.9(10)
C00O	-9470(3)	-541(2)	-4168(2)	30.1(11)
C00P	-8705(3)	-874(2)	-3815(2)	26.0(10)
C00Q	-7353(3)	702(2)	-3195(2)	26.9(10)
C00R	-6428(3)	-301(2)	-2808(2)	30.9(11)
C00S	-4877(3)	712(2)	-2235(2)	34.0(11)
C00U	-8682(3)	-1636(2)	-3806(2)	28.1(10)
C00X	-9519(3)	168(2)	-4162(2)	30.0(11)
C015	-8968(3)	-1987(2)	-4388(2)	31.8(11)
C017	-4452(3)	211(2)	-2457(2)	32.0(11)
C018	-8431(3)	-2000(2)	-3239(2)	35.1(12)
C01A	-10684(3)	1894(2)	-3726(2)	33.2(11)
C01B	-9418(3)	1631(2)	-1935(2)	40.5(12)
C01E	-10398(3)	1904(2)	-3055(2)	32.2(11)
C01F	-5811(3)	904(2)	-2580(2)	32.0(11)
C01G	-9576(3)	1684(2)	-2641(2)	31.2(11)
C01H	-6025(3)	1593(2)	-2644(2)	35.4(11)
C01J	-8079(3)	251(2)	-3509.7(19)	24.3(10)
C01K	-4389(3)	1075(2)	-1693(3)	47.1(14)

C01L	-8710(3)	2261(3)	-4882(2)	38.2(12)
C01M	-6884(3)	1810(2)	-2963(2)	34.1(12)
C01P	-8516(3)	3068(2)	-3973(3)	41.1(13)
C01V	-8976(3)	-2695(2)	-4390(3)	40.0(13)
C01X	-3564(3)	82(2)	-2143(2)	41.7(13)
C01Z	-11619(3)	2088(2)	-4106(2)	45.7(13)
C023	-8547(3)	2911(3)	-4592(2)	44.5(13)
C024	-8440(3)	-2704(3)	-3254(3)	44.8(13)
C026	-8741(3)	2190(3)	-5565(2)	51.0(15)
C027	-3089(3)	448(3)	-1609(3)	50.5(14)
C028	-8713(3)	-3056(3)	-3830(3)	44.4(13)
C02A	-8293(4)	3800(3)	-3735(3)	63.1(17)
C02C	-3500(3)	949(3)	-1380(3)	59.1(16)
Cl03	-18292.3(9)	59.8(8)	-5554.3(7)	68.1(5)
C01W	-17490(30)	569(4)	-4970(20)	41(3)

Table 2-3 Anisotropic Displacement Parameters (Å2×103) for k2. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
Co01	28.4(4)	29.8(4)	29.4(4)	2.2(3)	11.8(3)	3.5(3)
O005	30.6(18)	38(2)	32.5(19)	0.4(15)	12.4(16)	3.8(15)
O009	45(2)	28.1(19)	43(2)	2.8(16)	19.4(18)	5.0(15)
O00A	36.6(19)	37.6(19)	33.0(18)	10.4(16)	17.3(16)	6.4(15)
O00C	29.8(17)	43(2)	30.9(18)	2.1(16)	10.4(15)	5.2(15)
N00D	27(2)	23(2)	37(2)	1.3(18)	12.3(19)	2.5(18)
N00F	23(2)	36(2)	25(2)	3.8(18)	10.9(18)	2.2(18)
C00H	27(3)	27(3)	31(3)	5(2)	8(2)	1(2)
C00I	27(3)	34(3)	27(3)	1(2)	10(2)	-1(2)
C00J	29(3)	24(3)	27(3)	3(2)	12(2)	-3(2)
C00O	25(3)	30(3)	31(3)	-4(2)	5(2)	-2(2)
C00P	23(2)	35(3)	21(2)	-2(2)	9(2)	-5(2)
C00Q	26(3)	28(3)	29(3)	3(2)	13(2)	2(2)
C00R	29(3)	29(3)	33(3)	6(2)	10(2)	2(2)
C00S	30(3)	27(3)	39(3)	-1(2)	4(2)	-4(2)
C00U	20(2)	32(3)	33(3)	-3(2)	10(2)	-4(2)
C00X	23(2)	35(3)	28(3)	3(2)	5(2)	0(2)
C015	26(3)	34(3)	31(3)	1(2)	6(2)	0(2)
C017	32(3)	34(3)	31(3)	0(2)	12(2)	-1(2)
C018	30(3)	37(3)	37(3)	6(2)	11(2)	-4(2)
C01A	29(3)	32(3)	44(3)	3(2)	19(3)	-1(2)
C01B	42(3)	48(3)	33(3)	-6(3)	15(2)	-5(3)
C01E	27(3)	38(3)	37(3)	-8(2)	18(2)	-2(2)
C01F	31(3)	32(3)	34(3)	-2(2)	12(2)	4(2)
C01G	39(3)	23(3)	34(3)	-8(2)	15(2)	-8(2)
C01H	30(3)	31(3)	43(3)	-3(2)	10(2)	-1(2)

C01J	24(2)	28(3)	22(2)	0(2)	9(2)	2(2)
C01K	36(3)	36(3)	63(4)	-9(3)	9(3)	1(2)
C01L	26(3)	51(3)	39(3)	13(3)	13(2)	11(2)
C01M	34(3)	28(3)	39(3)	-4(2)	12(2)	4(2)
C01P	29(3)	33(3)	58(4)	-2(3)	12(3)	2(2)
C01V	32(3)	37(3)	50(3)	-12(3)	14(3)	-5(2)
C01X	38(3)	39(3)	57(4)	6(3)	27(3)	6(3)
C01Z	33(3)	55(3)	51(3)	1(3)	17(3)	9(3)
C023	47(3)	39(3)	52(4)	10(3)	22(3)	-7(3)
C024	36(3)	50(4)	48(4)	19(3)	15(3)	-4(3)
C026	52(3)	69(4)	34(3)	18(3)	19(3)	5(3)
C027	31(3)	44(3)	65(4)	-10(3)	2(3)	-2(3)
C028	35(3)	34(3)	63(4)	5(3)	16(3)	-4(2)
C02A	68(4)	48(4)	80(4)	1(3)	34(4)	-5(3)
C02C	43(3)	49(4)	67(4)	-22(3)	-4(3)	1(3)
Cl03	43.4(8)	102.9(13)	60.1(10)	-24.9(9)	20.9(8)	-20.5(8)
C01W	43(6)	45(5)	40(7)	21(15)	20(6)	10(20)

Table 2-4 Bond Lengths for K2

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co01	O005	2.067(3)	C00S	C017	1.386(6)
Co01	O009	2.027(3)	C00S	C01F	1.490(6)
Co01	O00A	2.058(3)	C00S	C01K	1.387(6)
Co01	O00C	2.050(3)	C00U	C015	1.396(6)
Co01	N00D	2.124(3)	C00U	C018	1.385(6)
Co01	N00F	2.123(4)	C015	C01V	1.386(6)
O005	C01G	1.263(5)	C017	C01X	1.390(6)
O009	C01P	1.269(5)	C018	C024	1.377(6)
O00A	C01L	1.264(5)	C01A	C01E	1.402(6)
O00C	C01A	1.265(5)	C01A	C01Z	1.508(6)
N00D	C00Q	1.355(5)	C01B	C01G	1.507(6)
N00D	C01M	1.324(5)	C01E	C01G	1.401(6)
N00F	C00X	1.324(5)	C01F	C01H	1.388(6)
N00F	C01J	1.350(5)	C01H	C01M	1.394(6)
C00H	C00J	1.444(5)	C01K	C02C	1.390(6)
C00H	C00R	1.356(5)	C01L	C023	1.408(6)
C00I	C00Q	1.414(6)	C01L	C026	1.514(6)
C00I	C00R	1.431(6)	C01P	C023	1.399(7)
C00I	C01F	1.435(6)	C01P	C02A	1.526(6)
C00J	C00P	1.423(5)	C01V	C028	1.367(6)
C00J	C01J	1.399(5)	C01X	C027	1.373(6)
C00O	C00P	1.381(5)	C024	C028	1.386(7)
C00O	C00X	1.391(5)	C027	C02C	1.382(6)

C00P	C00U	1.490(6)	Cl03	C01W	1.79(4)
C00Q	C01J	1.444(6)			

Table 2-5 Bond Angles for K2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O005	Co01	N00D	83.59(12)	C017	C00S	C01F	122.7(4)
O005	Co01	N00F	91.52(12)	C017	C00S	C01K	117.9(4)
O009	Co01	O005	92.02(12)	C01K	C00S	C01F	119.2(4)
O009	Co01	O00A	90.08(12)	C015	C00U	C00P	118.8(4)
O009	Co01	O00C	95.14(12)	C018	C00U	C00P	121.6(4)
O009	Co01	N00D	93.29(13)	C018	C00U	C015	119.5(4)
O009	Co01	N00F	168.67(12)	N00F	C00X	C00O	123.1(4)
O00A	Co01	O005	177.88(12)	C01V	C015	C00U	119.6(4)
O00A	Co01	N00D	96.63(12)	C00S	C017	C01X	120.7(4)
O00A	Co01	N00F	86.49(12)	C024	C018	C00U	119.7(5)
O00C	Co01	O005	87.56(11)	O00C	C01A	C01E	125.0(4)
O00C	Co01	O00A	91.92(11)	O00C	C01A	C01Z	115.9(4)
O00C	Co01	N00D	167.99(12)	C01E	C01A	C01Z	119.1(4)
O00C	Co01	N00F	95.77(12)	C01G	C01E	C01A	125.5(4)
N00F	Co01	N00D	76.41(13)	C00I	C01F	C00S	124.9(4)
C01G	O005	Co01	125.9(3)	C01H	C01F	C00I	117.0(4)
C01P	O009	Co01	126.4(3)	C01H	C01F	C00S	118.1(4)
C01L	O00A	Co01	125.8(3)	O005	C01G	C01B	115.8(4)
C01A	O00C	Co01	125.9(3)	O005	C01G	C01E	125.3(4)
C00Q	N00D	Co01	115.3(3)	C01E	C01G	C01B	118.9(4)
C01M	N00D	Co01	126.6(3)	C01F	C01H	C01M	121.2(4)
C01M	N00D	C00Q	117.9(4)	N00F	C01J	C00J	123.4(4)
C00X	N00F	Co01	126.5(3)	N00F	C01J	C00Q	115.6(4)
C00X	N00F	C01J	117.7(4)	C00J	C01J	C00Q	120.9(4)
C01J	N00F	Co01	115.7(3)	C00S	C01K	C02C	121.6(5)
C00R	C00H	C00J	121.9(4)	O00A	C01L	C023	125.7(4)
C00Q	C00I	C00R	118.0(4)	O00A	C01L	C026	115.6(4)
C00Q	C00I	C01F	117.1(4)	C023	C01L	C026	118.6(4)
C00R	C00I	C01F	124.9(4)	N00D	C01M	C01H	122.7(4)
C00P	C00J	C00H	124.3(4)	O009	C01P	C023	125.9(4)
C01J	C00J	C00H	117.5(4)	O009	C01P	C02A	116.0(5)
C01J	C00J	C00P	118.2(4)	C023	C01P	C02A	118.1(5)
C00P	C00O	C00X	120.6(4)	C028	C01V	C015	121.0(5)
C00J	C00P	C00U	123.5(4)	C027	C01X	C017	120.8(4)
C00O	C00P	C00J	117.0(4)	C01P	C023	C01L	126.0(4)

C00O	C00P	C00U	119.5(4)	C018	C024	C028	121.1(5)
N00D	C00Q	C00I	123.9(4)	C01X	C027	C02C	119.5(5)
N00D	C00Q	C01J	116.2(4)	C01V	C028	C024	119.1(5)
C00I	C00Q	C01J	119.9(4)	C027	C02C	C01K	119.5(5)
C00H	C00R	C00I	121.7(4)				

Table 2-6 Torsion Angles for K2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Co01	O005	C01G	C01B	-172.5(3)	C00R	C00I	C00Q	N00D	176.1(4)
Co01	O005	C01G	C01E	7.9(6)	C00R	C00I	C00Q	C01J	-3.5(6)
Co01	O009	C01P	C023	4.0(7)	C00R	C00I	C01F	C00S	3.9(7)
Co01	O009	C01P	C02A	-175.4(3)	C00R	C00I	C01F	C01H	-176.5(4)
Co01	O00A	C01L	C023	2.8(6)	C00S	C017	C01X	C027	-0.3(7)
Co01	O00A	C01L	C026	-177.7(3)	C00S	C01F	C01H	C01M	179.7(4)
Co01	O00C	C01A	C01E	-15.9(6)	C00S	C01K	C02C	C027	-0.3(8)
Co01	O00C	C01A	C01Z	165.4(3)	C00U	C015	C01V	C028	0.5(6)
Co01	N00D	C00Q	C00I	-174.8(3)	C00U	C018	C024	C028	-1.3(7)
Co01	N00D	C00Q	C01J	4.8(4)	C00X	N00F	C01J	C00J	-3.1(6)
Co01	N00D	C01M	C01H	177.4(3)	C00X	N00F	C01J	C00Q	176.2(3)
Co01	N00F	C00X	C00O	-173.3(3)	C00X	C00O	C00P	C00J	-3.1(6)
Co01	N00F	C01J	C00J	172.6(3)	C00X	C00O	C00P	C00U	177.3(4)
Co01	N00F	C01J	C00Q	-8.1(4)	C015	C00U	C018	C024	2.1(6)
O009	C01P	C023	C01L	-1.8(8)	C015	C01V	C028	C024	0.2(7)
O00A	C01L	C023	C01P	-2.0(8)	C017	C00S	C01F	C00I	43.7(7)
O00C	C01A	C01E	C01G	-4.3(7)	C017	C00S	C01F	C01H	-135.9(5)
N00D	C00Q	C01J	N00F	2.1(5)	C017	C00S	C01K	C02C	0.3(7)
N00D	C00Q	C01J	C00J	-178.6(4)	C017	C01X	C027	C02C	0.3(8)
C00H	C00J	C00P	C00O	-178.1(4)	C018	C00U	C015	C01V	-1.7(6)
C00H	C00J	C00P	C00U	1.5(6)	C018	C024	C028	C01V	0.2(7)
C00H	C00J	C01J	N00F	-178.8(3)	C01A	C01E	C01G	O005	8.6(7)
C00H	C00J	C01J	C00Q	1.9(6)	C01A	C01E	C01G	C01B	-171.0(4)
C00I	C00Q	C01J	N00F	-178.2(3)	C01F	C00I	C00Q	N00D	-3.2(6)
C00I	C00Q	C01J	C00J	1.1(6)	C01F	C00I	C00Q	C01J	177.1(4)
C00I	C01F	C01H	C01M	0.0(6)	C01F	C00I	C00R	C00H	-177.8(4)
C00J	C00H	C00R	C00I	0.1(6)	C01F	C00S	C017	C01X	175.6(4)
C00J	C00P	C00U	C015	-128.1(4)	C01F	C00S	C01K	C02C	-175.5(5)
C00J	C00P	C00U	C018	55.5(6)	C01F	C01H	C01M	N00D	-3.0(7)
C00O	C00P	C00U	C015	51.4(5)	C01J	N00F	C00X	C00O	1.9(6)
C00O	C00P	C00U	C018	-124.9(4)	C01J	C00J	C00P	C00O	1.9(6)
C00P	C00J	C01J	N00F	1.2(6)	C01J	C00J	C00P	C00U	-178.5(4)

C00P	C00J	C01J	C00Q	-178.0(4)	C01K	C00S	C017	C01X	0.0(7)
C00P	C00O	C00X	N00F	1.3(6)	C01K	C00S	C01F	C00I	-140.7(5)
C00P	C00U	C015	C01V	-178.1(4)	C01K	C00S	C01F	C01H	39.7(6)
C00P	C00U	C018	C024	178.4(4)	C01M	N00D	C00Q	C00I	0.5(6)
C00Q	N00D	C01M	C01H	2.7(6)	C01M	N00D	C00Q	C01J	-179.9(4)
C00Q	C00I	C00R	C00H	2.9(6)	C01X	C027	C02C	C01K	0.0(8)
C00Q	C00I	C01F	C00S	-176.8(4)	C01Z	C01A	C01E	C01G	174.4(4)
C00Q	C00I	C01F	C01H	2.8(6)	C026	C01L	C023	C01P	178.5(4)
C00R	C00H	C00J	C00P	177.4(4)	C02A	C01P	C023	C01L	177.6(4)
C00R	C00H	C00J	C01J	-2.6(6)					

Table 2-7 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for K2.

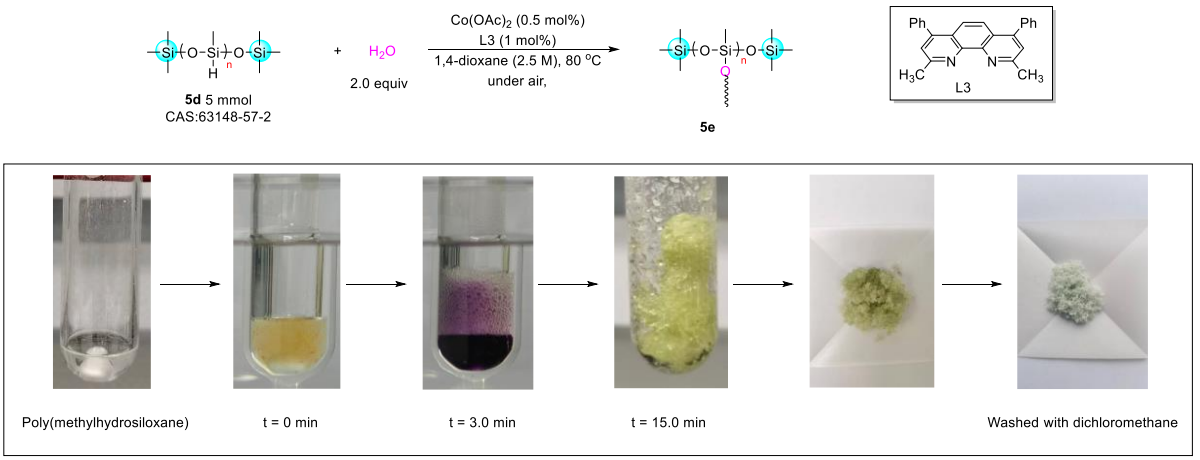
Atom	x	y	z	U(eq)
H00H	-7032.9	-1191.13	-3056.9	35
H00O	-9957.02	-793.78	-4412.36	36
H00R	-5887.07	-490.34	-2571.11	37
H00X	-10046.98	376.91	-4398.58	36
H015	-9153.23	-1746.43	-4772.65	38
H017	-4764.26	-39.9	-2819.53	38
H018	-8258.01	-1771	-2848.62	42
H01A	-9867.53	1876.13	-1839.89	61
H01B	-8854.91	1823.05	-1695.83	61
H01C	-9429.49	1158.78	-1820.42	61
H01E	-10787.71	2071.67	-2869.73	39
H01H	-5586.74	1916.79	-2471.32	43
H01K	-4662.87	1411.52	-1536.04	56
H01M	-7006.35	2275.62	-2978.51	41
H01V	-9162.08	-2928.36	-4778.18	48
H01X	-3289.33	-256.98	-2296.64	50
H01D	-11624.72	2447.05	-4400.26	69
H01F	-11903.45	2243.26	-3819.22	69
H01G	-11925.66	1697.14	-4339.02	69
H023	-8450.82	3268.02	-4834.79	53
H024	-8259.09	-2947.02	-2871	54
H02A	-9340.69	2197.02	-5851.15	76
H02B	-8474.12	1765.38	-5612.38	76
H02C	-8427.79	2562.45	-5666.03	76
H027	-2494.39	359.69	-1402.7	61
H028	-8717.63	-3531.68	-3834.51	53
H02D	-8806.14	4017.45	-3704.53	95
H02E	-8096.04	4049.04	-4030.34	95
H02F	-7837.56	3795.17	-3321.29	95
H02G	-3183.47	1200.39	-1018.3	71
H01W	-17204.67	861.58	-5188.06	49

Table 2-8. Atomic Occupancy for K2		
Atom Occupancy	Atom Occupancy	Atom Occupancy
C01W 0.5		

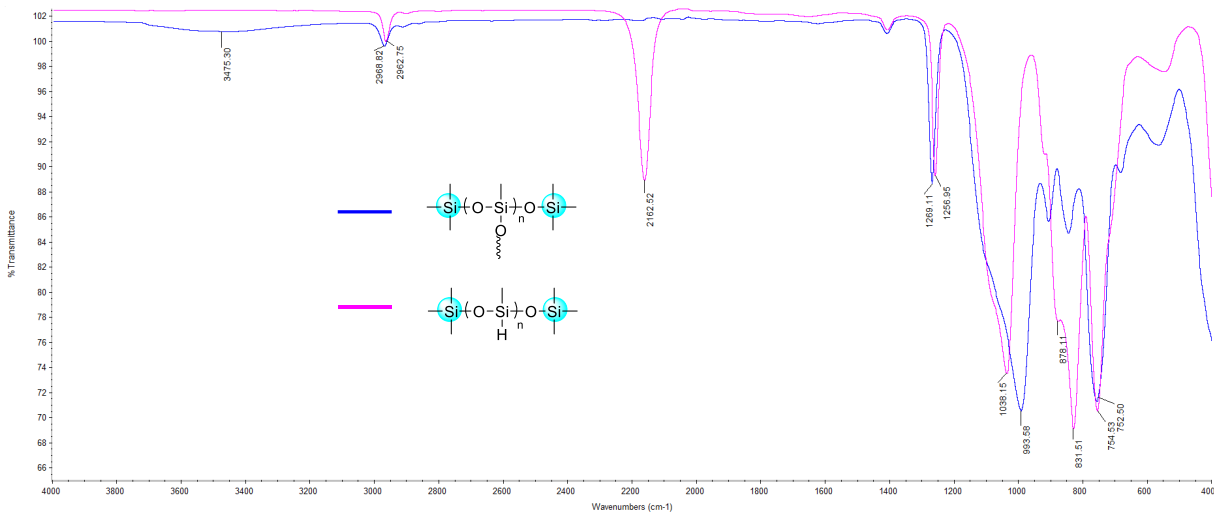
Table 2-9 Solvent masks information for K-2					
Number	X	Y	Z	Volume	Electron count Content
1	-0.017	0.000	0.000	430	109
2	-0.009	0.500	0.500	430	109

6. The Synthesis and Characterization of Silicon Polymer

Followed the GP1, this transformation was complete within 15 min, which proceeded via a purple reaction solution and vigorously released H_2 gas. To our delight, the olive color of the crude reaction materials could be removed with dichloromethane as the eluent to finally afford the pale green solid.

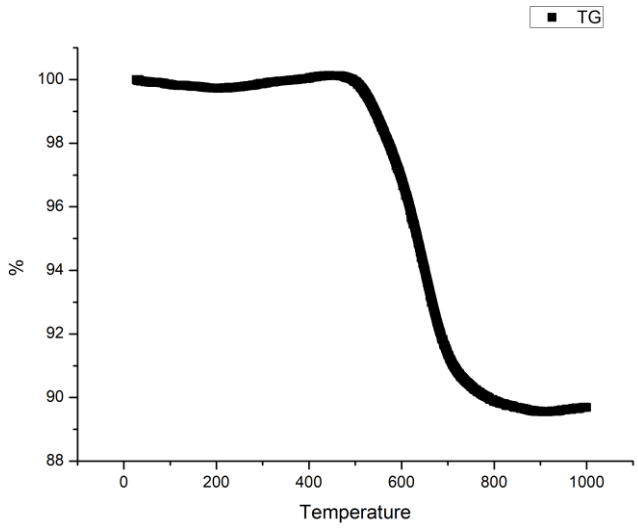


The IR spectrum of **5d** showed the characteristic absorption band of Si-H at 2163 cm^{-1} of the poly(methylhydrosiloxane) **5e** completely disappeared while a broad absorption peak at 3475 cm^{-1} appeared.

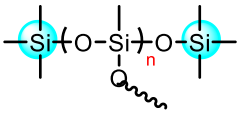
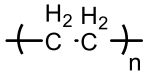
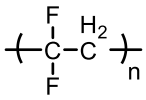
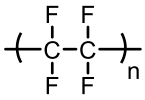
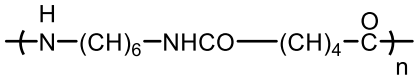


IR spectrum of silane polymer

Thermogravimetry (TG) measurement revealed it exhibits a decomposition temperature of 763 K, which is comparable to those values of polytetrafluoroethylene (782 K) and Nylon 66 (703-746 K).



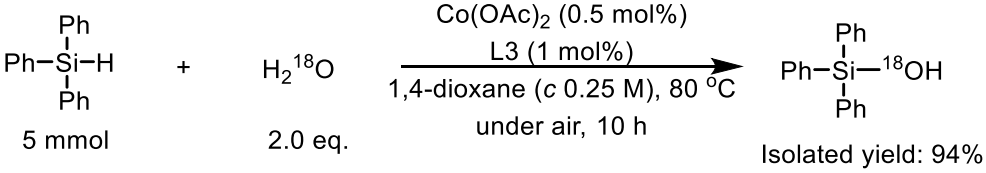
Thermogravimetry (TG) experiment

Structure	Polymer	Decomposed temperature (K)
	This work	763
	Polyethylene	687
	Polyvinylenedifluoride	738-758
	Poly(tetrafluoroethylene)	782
	Nylon 66	703-746

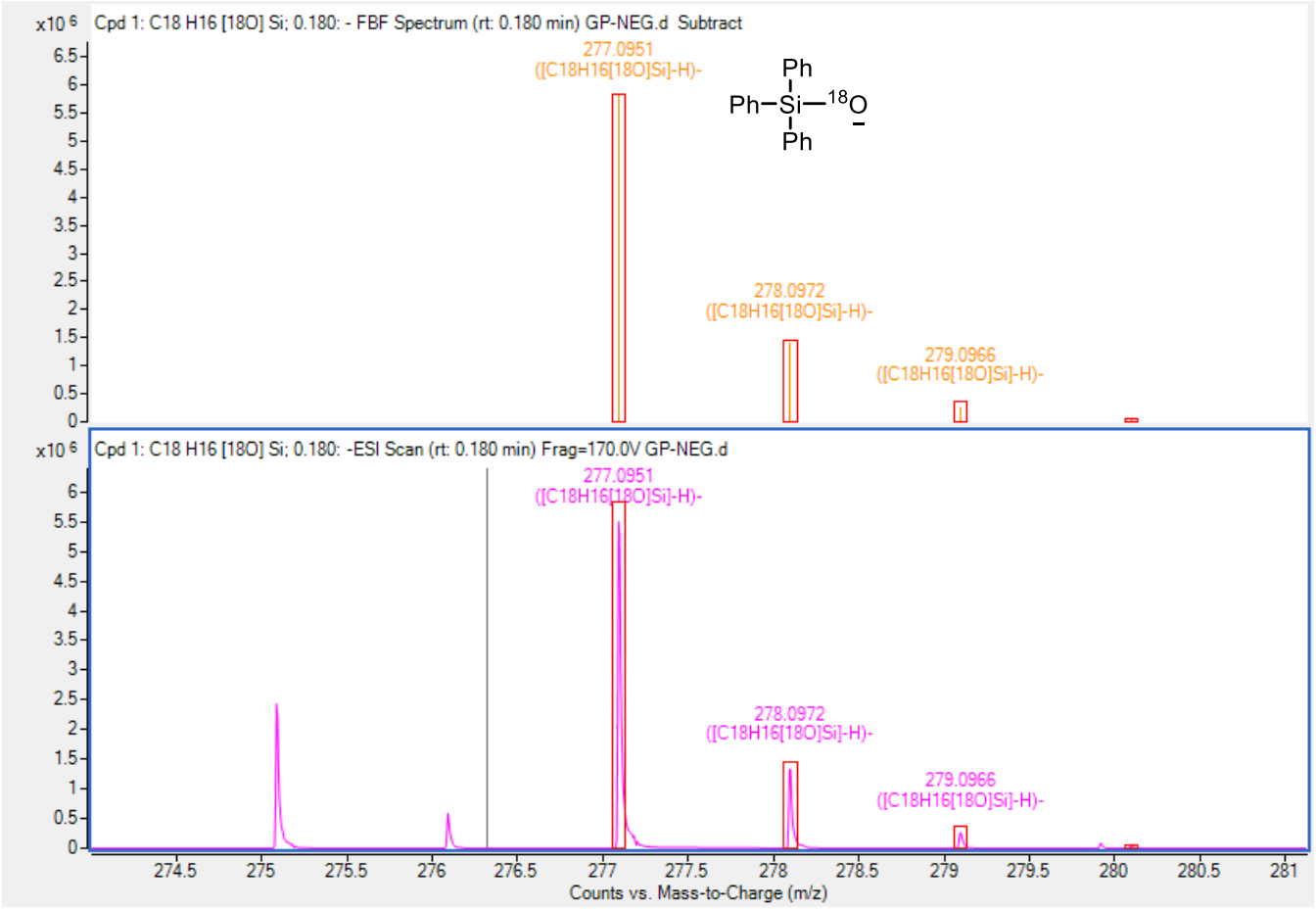
See the reference: *Morgan J. Hurley*； SFPE Handbook of Fire Protection Engineering (DOI 10.1007/978-1-4939-2565-0)

7. Mechanistic Studies

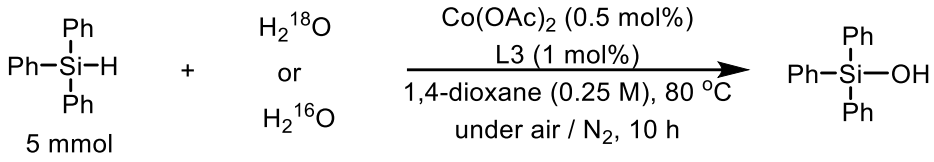
7.1 Exploration of the origin of the oxygen atom



To a mixture of silane (5 mmol), $Co(OAc)_2$ (0.5 mol%), **L3** (1 mol%) in 1,4-dioxane (*c* 2.5 M) with $H_2{}^{18}O$ under air at 80 °C for 10 h. After purification via column chromatography, the product was analyzed by ^1H NMR and HRMS. HRMS (ESI) m/z calcd. for $C_{18}H_{15}{}^{18}OSi$ $[M-H]^-$ 277.0940, found 277.0951; HRMS (ESI) m/z calcd for $C_{18}H_{15}{}^{16}OSi$ $[M-H]^-$ 275.0898, found 275.0910. It suggests the oxygen atom originated from water.



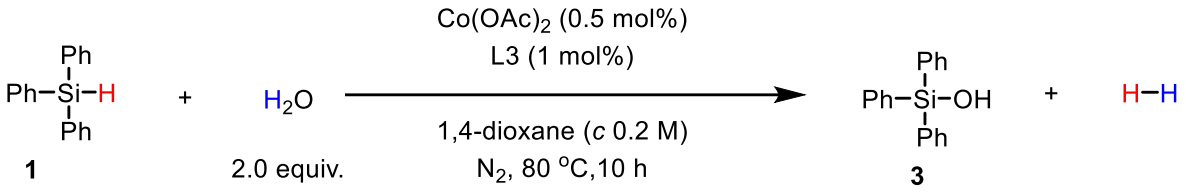
Control experiment showed there was a 9% yield of silanol without water and a 88% yield under the deoxygenated water under the nitrogen atmospher.



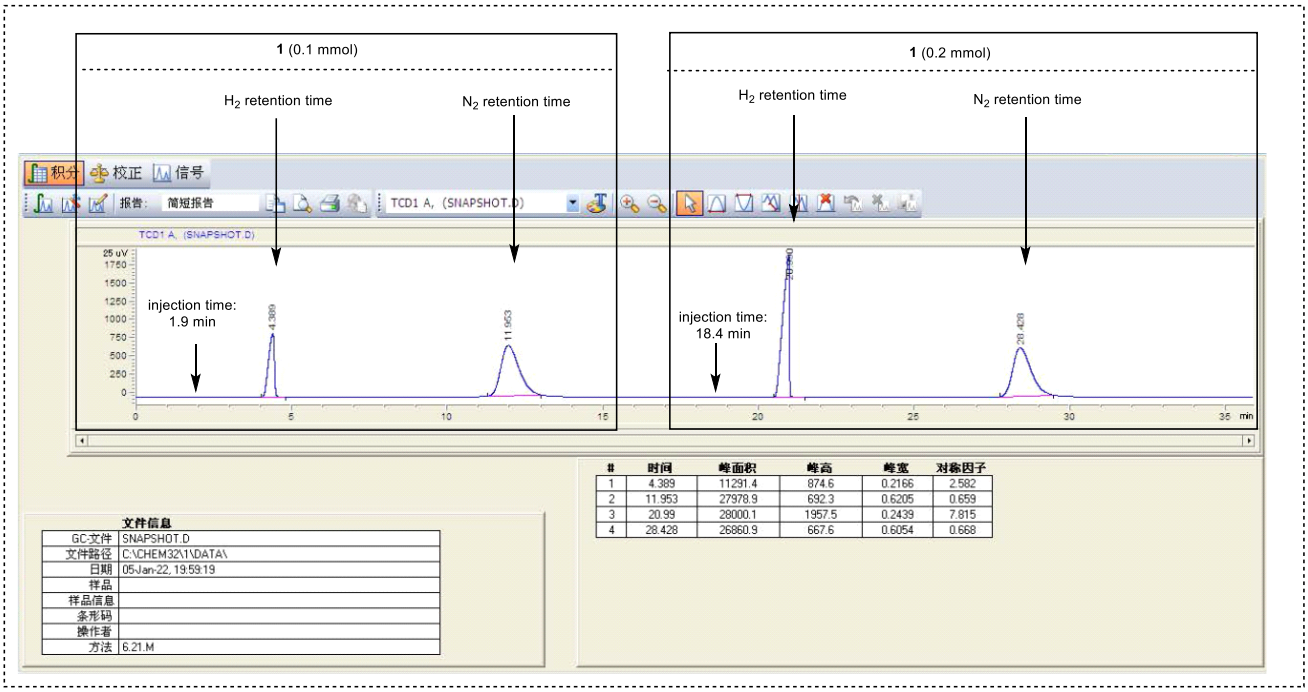
	Under air/ $H_2{}^{18}O$	Under air/$H_2{}^{16}O$	Under air	$N_2/H_2{}^{16}O$ (Deoxygenated)
Yield	94%	94%	9%	88%

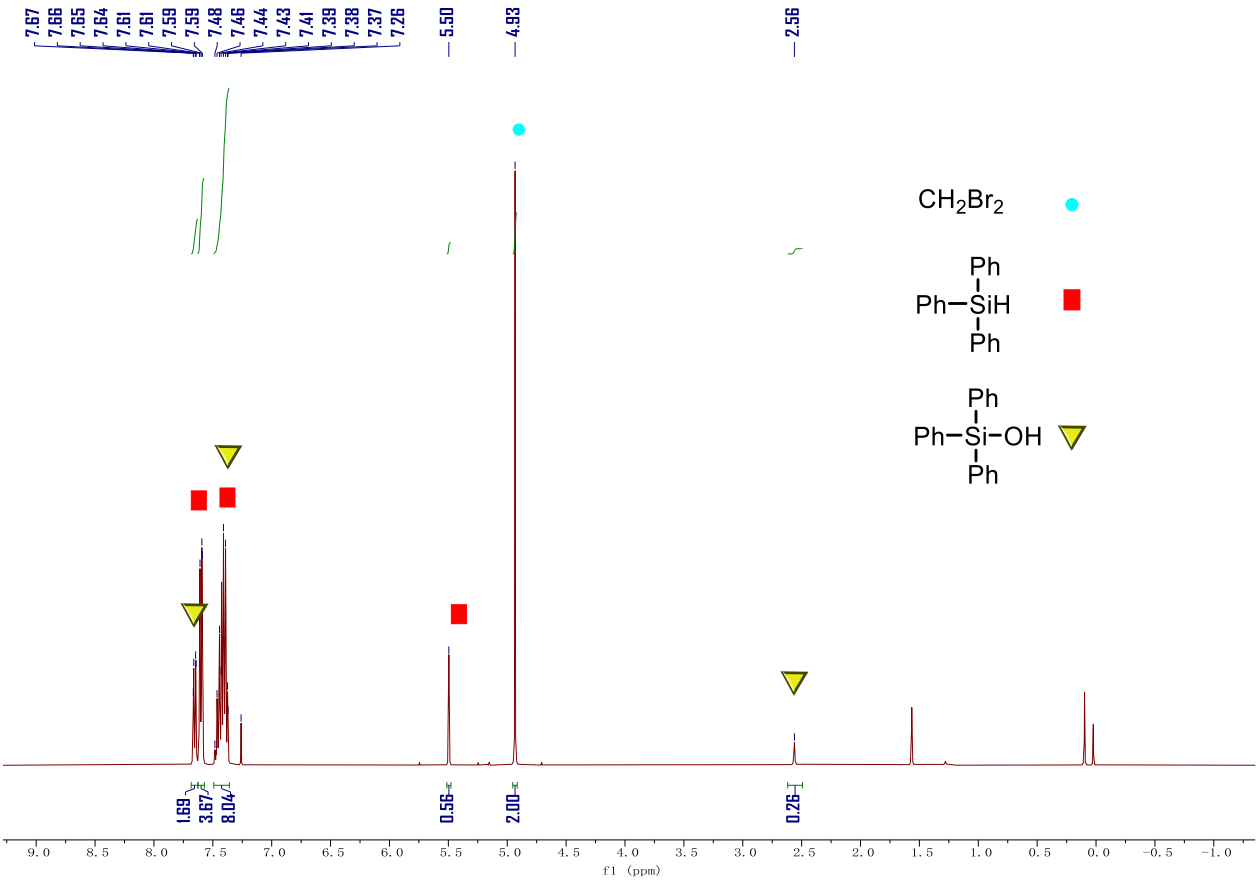
7.2 Analysis of H_2 gas by gas chromatography

To a 10 mL flame-dried Schlenk tube with a stirring bar was added silane, $Co(OAc)_2$ (0.5 mol%), and **L3** (1 mol%). H_2O and 1,4-dioxane (*c* 0.2 M) were added *via* syringe at 80 ºC (oil bath) under N_2 atmosphere for 10 h. Gas chromatography showed the interval time after injection time with 2.5 min and 10.0 min for H_2 and N_2 gases, respectively. The amount of H_2 was measured based on the area with the linear equation [H_2 (μmol)=area/90/91*29]. The yield of silanol was given with CH_2Br_2 as the internal standard.

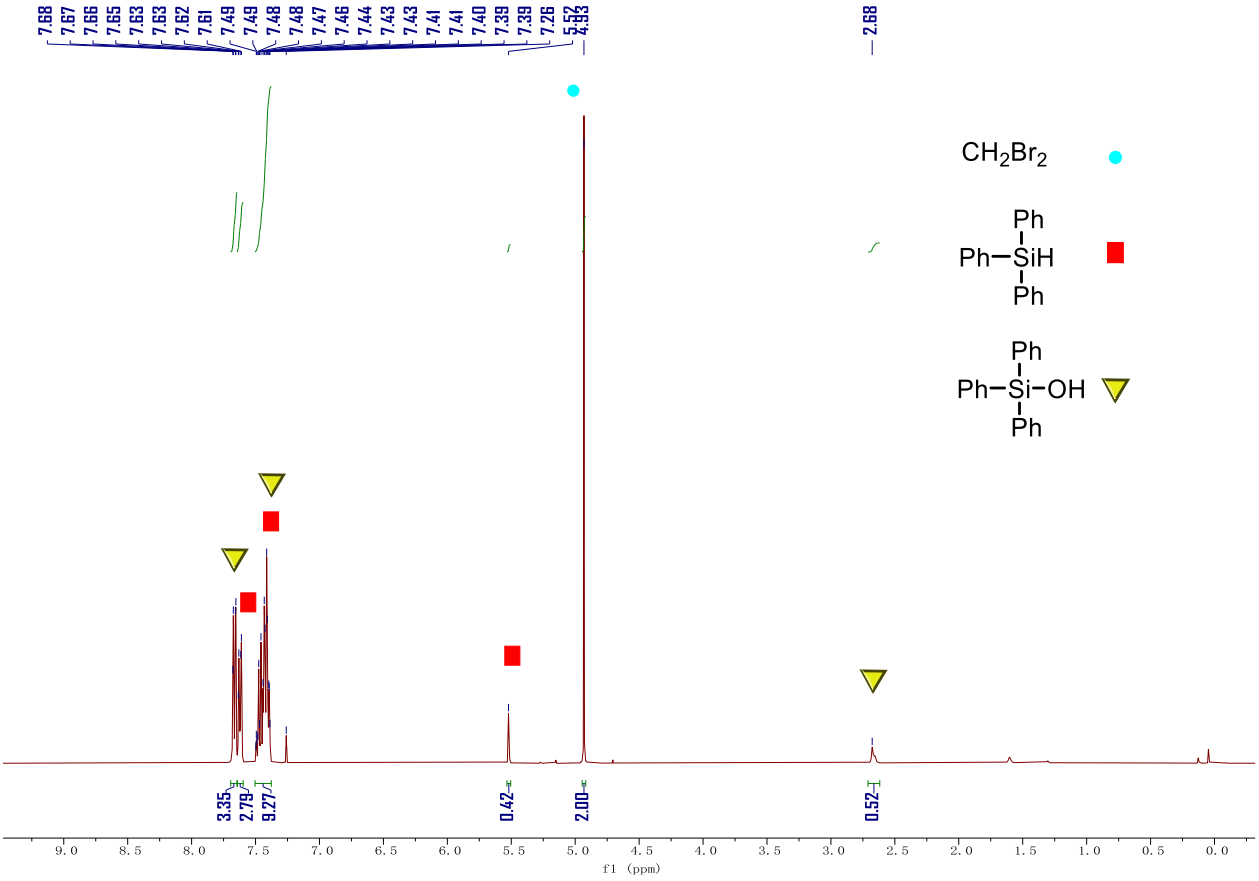


Entry	**1**	**3**	Calcd.(H_2/mmol)	Meatured (H_2/mmol)
1	0.1 mol	26%	0.026	0.040
2	0.2 mol	52%	0.104	0.0991





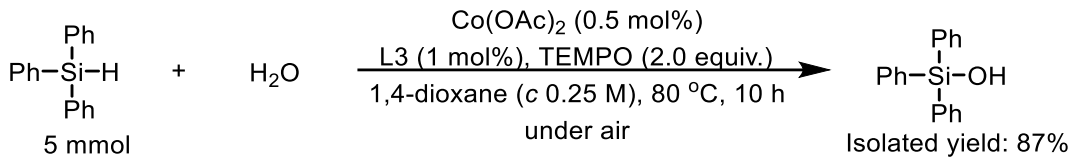
Crude ^{1}H NMR Spectrum of reaction with **1** (0.1 mmol) (CH_2Br_2 as the internal atandard)



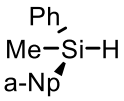
Crude ^{1}H NMR Spectrum of reaction with **1** (0.2 mmol) (CH_2Br_2 as the internal atandard)

7.3 Radical inhibition experiment

TEMPO was added to the solution of silane under standard conditions. The solvent was removed under reduced pressure and the residue was purified by column chromatography to afford the product in an 87% yield. This result ruled out the involvement of a radical intermediacy.

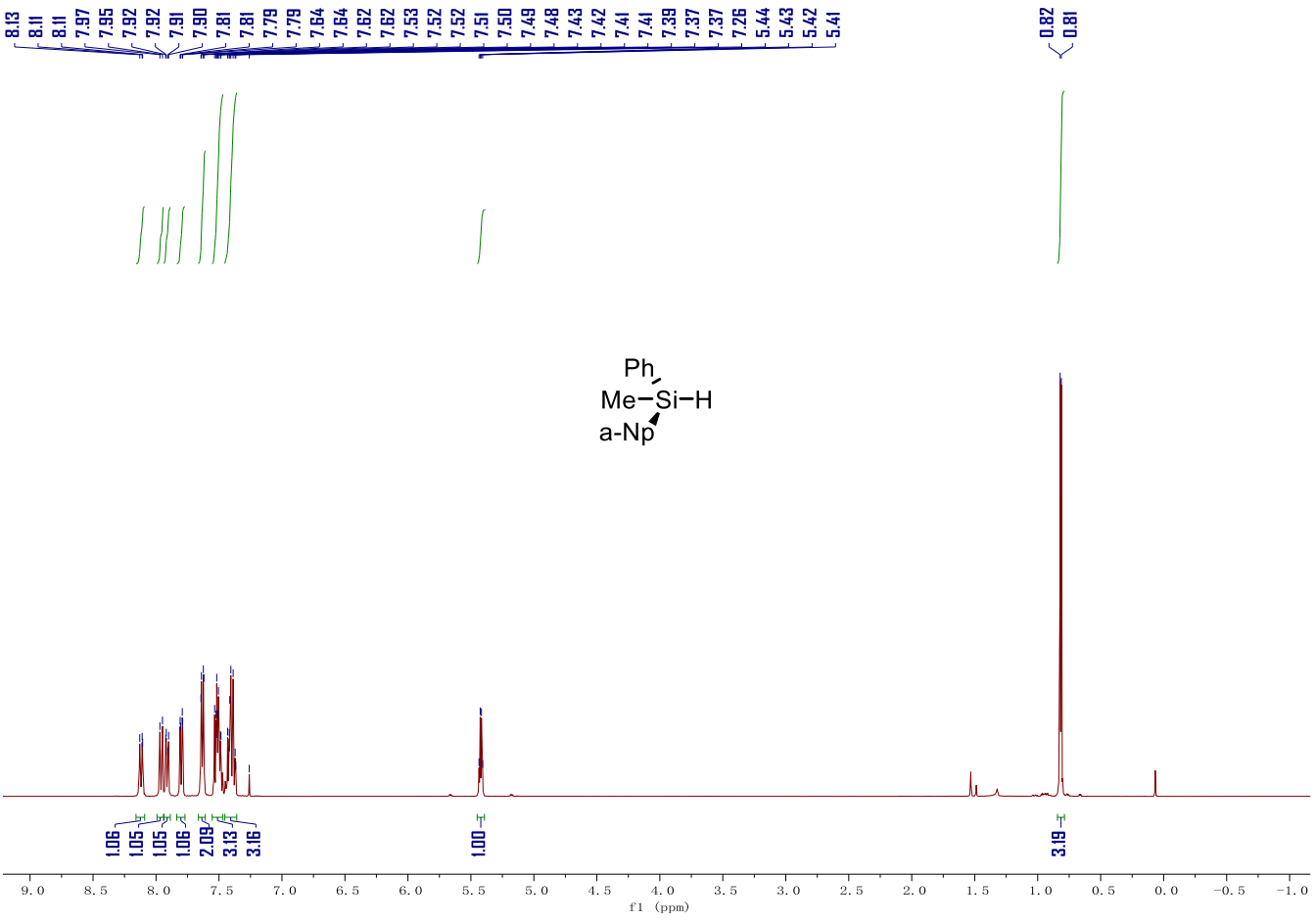


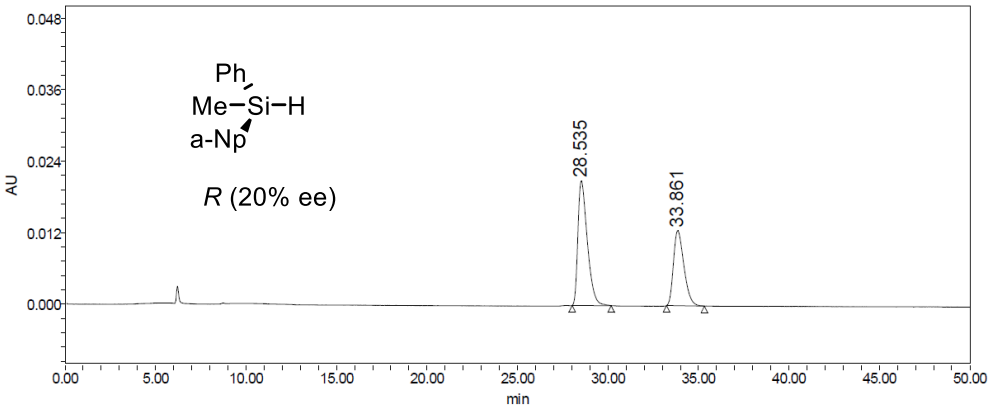
7.4 Proof of a stereo-retentive oxidation



(*R*)-methyl(naphthalen-1-yl)(phenyl)silane[1], white solid, 20% *ee*. The *ee* value was determined by HPLC [CHIRALPAK® OD-H, eluent: *n*-hexane, 0.5 mL/min, 254 nm; t_R = 28 min, t_S = 33 min].

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 8.08 (m, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.91 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.80 (dd, *J* = 6.8, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.56 – 7.46 (m, 3H), 7.46 – 7.35 (m, 3H), 5.42 (q, *J* = 3.9 Hz, 1H), 0.82 (d, *J* = 3.9 Hz, 3H).

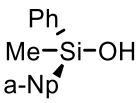




Channel: 2998 Ch1 254nm@1.2nm; Processed Channel: 2998 Ch1 254nm@1.2nm; Result Id: 21992; Processing Method: 11

Processed Channel Descr.: 2998 Ch1 254nm@1.2nm

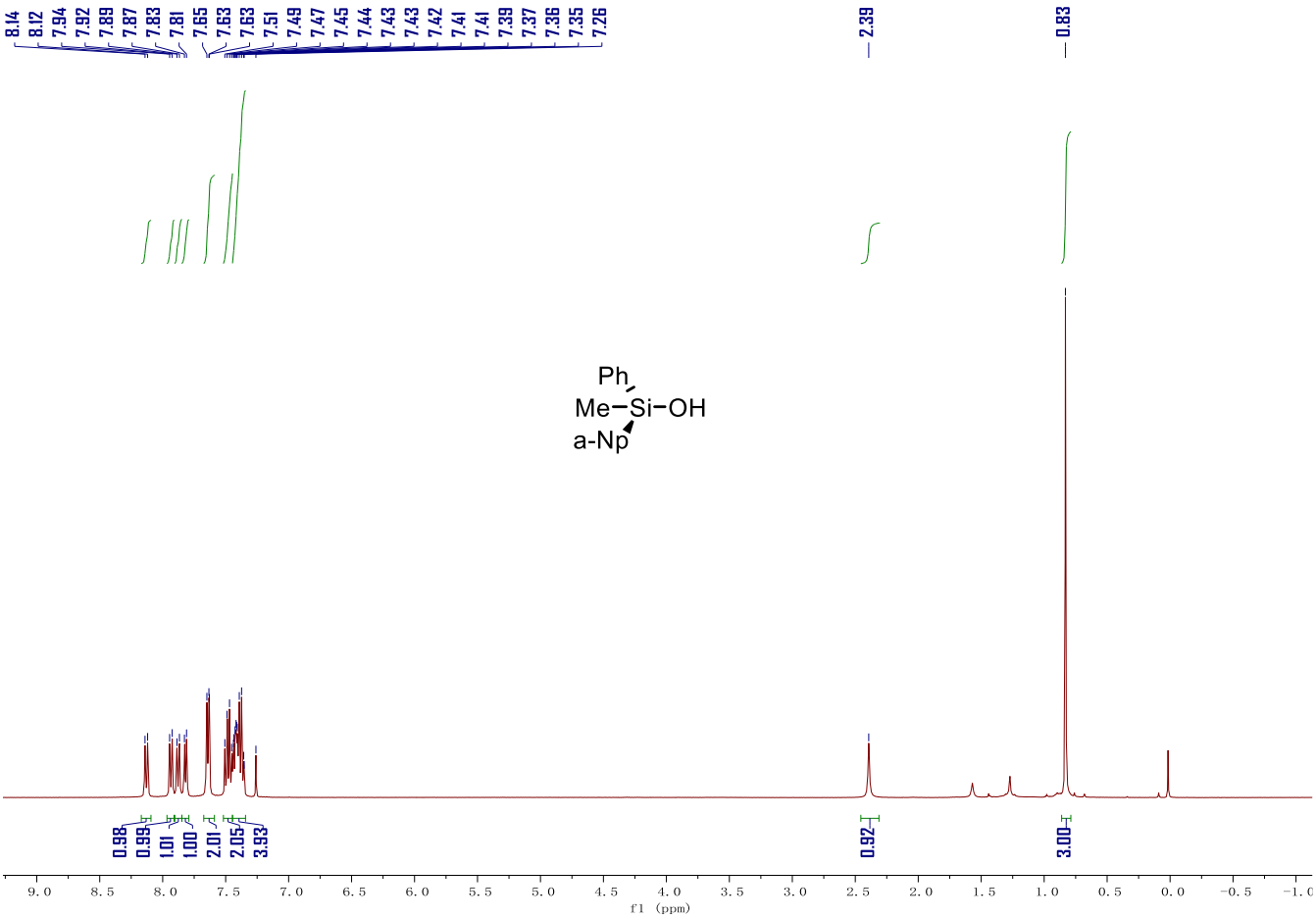
	Processed Channel Descr.	RT	Area	Height	% Area
1	2998 Ch1 254nm@1.2nm	28.535	755897	20919	59.93
2	2998 Ch1 254nm@1.2nm	33.861	505357	12605	40.07

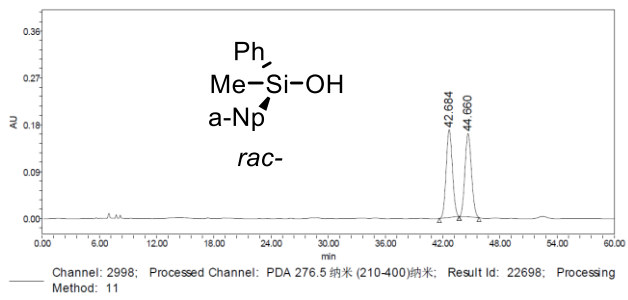


When an enantio-enriched (*R*)-methyl(naphthalen-1-yl)(phenyl)silane (20% ee) was tested, the same ee of the obtained silanol was maintained, suggesting the current transformation is a stereo-retentive oxidation process.

(*R*)-methyl(naphthalen-1-yl)(phenyl)silanol, colorless liquid, 20% *ee*. The obtained enantioenriched silanol was analyzed by HPLC [CHIRALPAK® AD-H, eluent: *n*-hexane/*i*-PrOH (97/3), 0.5 mL/min, 254 nm; t_R = 42 min, t_S = 44 min].

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 6.7 Hz, 1H), 7.71 – 7.58 (m, 2H), 7.53 – 7.45 (m, 2H), 7.44 – 7.33 (m, 4H), 2.39 (br s, 1H), 0.83 (s, 3H).

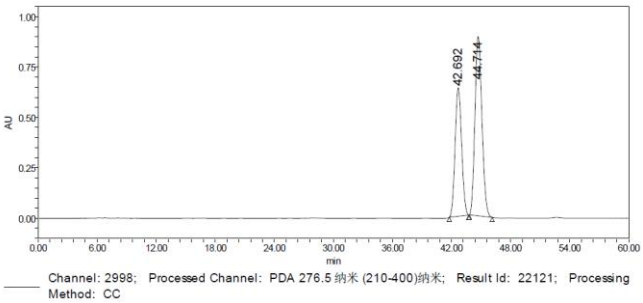




Channel: 2998; Processed Channel: PDA 276.5 纳米 (210-400)纳米; Result Id: 22698; Processing Method: 11

Processed Channel Descr.: PDA 276.5 纳米 (210-400)纳米

	Processed Channel Descr.	RT	Area	Height	% Area
1	PDA 276.5 纳米 (210-400)纳米	42.684	7689824	168298	50.21
2	PDA 276.5 纳米 (210-400)纳米	44.660	7625103	159954	49.79



Channel: 2998; Processed Channel: PDA 276.5 纳米 (210-400)纳米; Result Id: 22121; Processing Method: CC

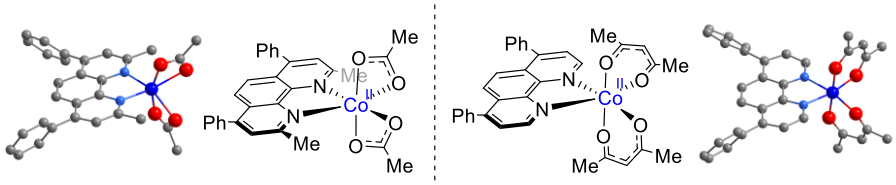
Processed Channel Descr.: PDA 276.5 纳米 (210-400)纳米

	Processed Channel Descr.	RT	Area	Height	% Area
1	PDA 276.5 纳米 (210-400)纳米	42.692	29408499	637136	40.01
2	PDA 276.5 纳米 (210-400)纳米	44.714	44098089	889810	59.99

7.5 Investigation on the selectivity of silanol and disiloxane

Notably, the cobalt complexes (**K1** and **K2**), derived from their corresponding catalytic systems, both exhibited a 1:1 ratio of cobalt and the supporting ligand, as confirmed by X-ray diffraction analyses (A). Surprisingly, both complexes exhibited only catalytic activity on the hydroxylation of hydrosilane, in contrast to the current established ligand-controlled product selectivity (B). Interestingly, the presence of extra bathophenanthroline **L4** was capable to trigger the catalytic activity of complex **K2** in the formation of disiloxane (C). Further investigations of various organic and inorganic bases revealed bathophenanthroline **L4** most likely acted as a base to facilitate the formation of disiloxane, which was different from the function of ligand **L3** for preventing decomposition of cobalt complex K1 during catalysis.

(A) Structures of cobalt phenanthroline complexes **K1** and **K2**



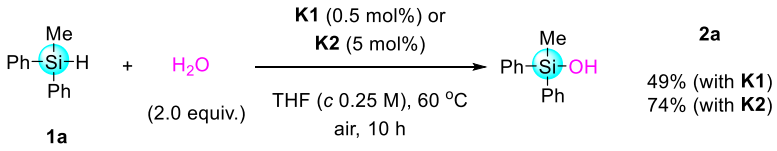
K1 (XRD)
CCDC 2173145

K1
from $Co(OAc)_2$ + **L3**

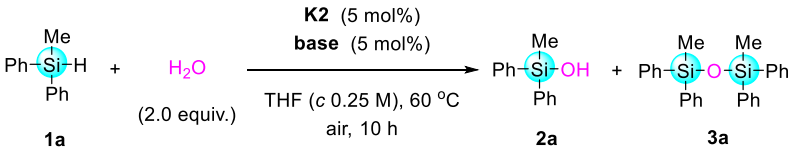
K2
from $Co(acac)_2$ + **L4**

K2 (XRD)
CCDC 2131308

(B) Cobalt complexes **K1** and **K2** catalyzed hydroxylation of hydrosilane (**1a**)

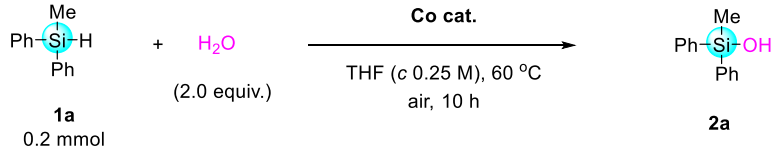


(C) Base-facilitated, cobalt complex **K2** catalyzed synthesis of disiloxane (**3a**)



entry	**base**	yield (**2a**)	yield (**3a**)
1	**L4**	< 5%	88%
2	DMAP	75%	21%
3	Et_3N	76%	<5%
4	Na_2CO_3	17%	83%
5	Cs_2CO_3	<5%	94%

(D) Ligand-coordinated, cobalt complex **K1** catalyzed synthesis of silanol (**2a**)



entry	Co cat.	yield (**2a**)
1	**K1** (0.5 mol%)	49%
2	$Co(OAc)_2$ (0.5 mol%) + **L3** (1.0 mol%)	97%
3	**K1** (0.5 mol%) + **L3** (0.5 mol%)	96%

8. References

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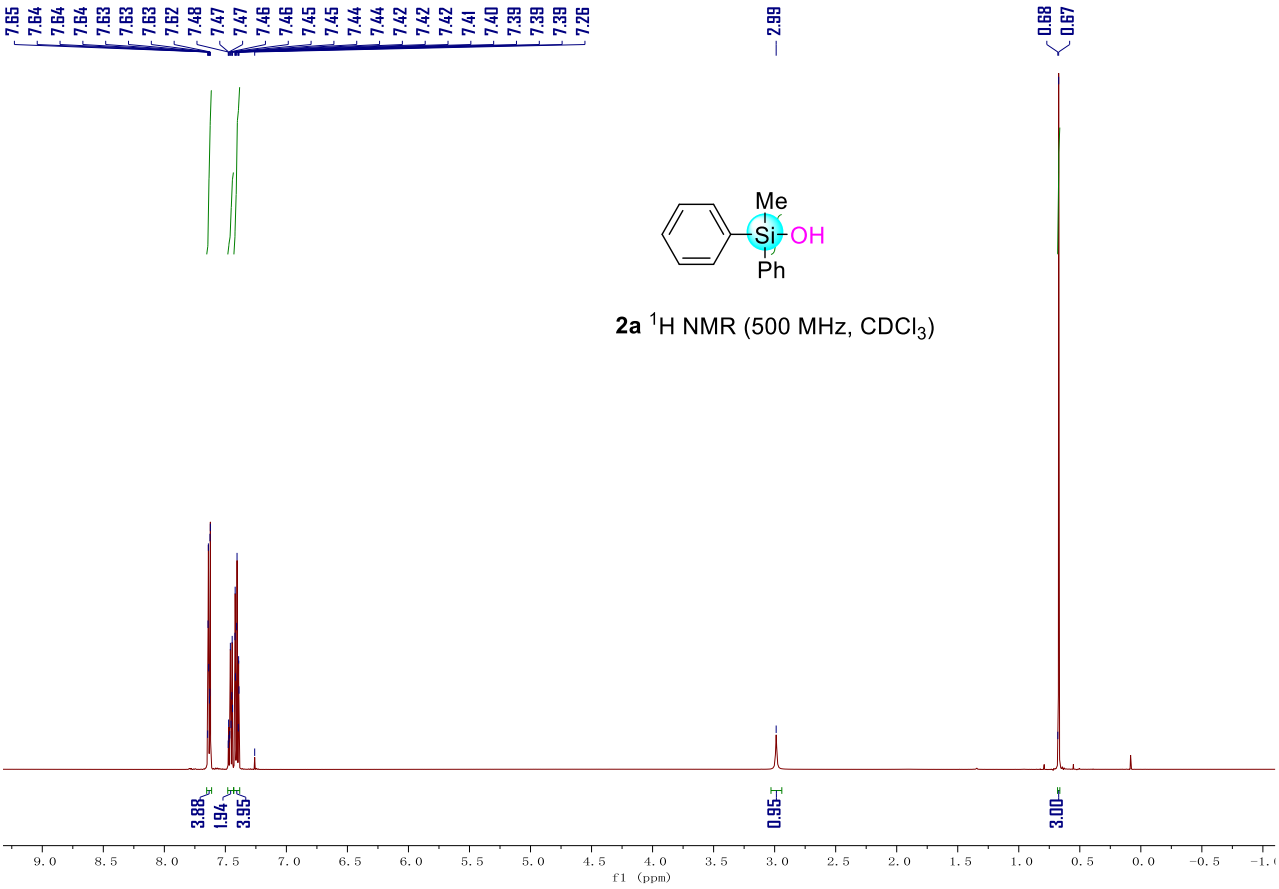
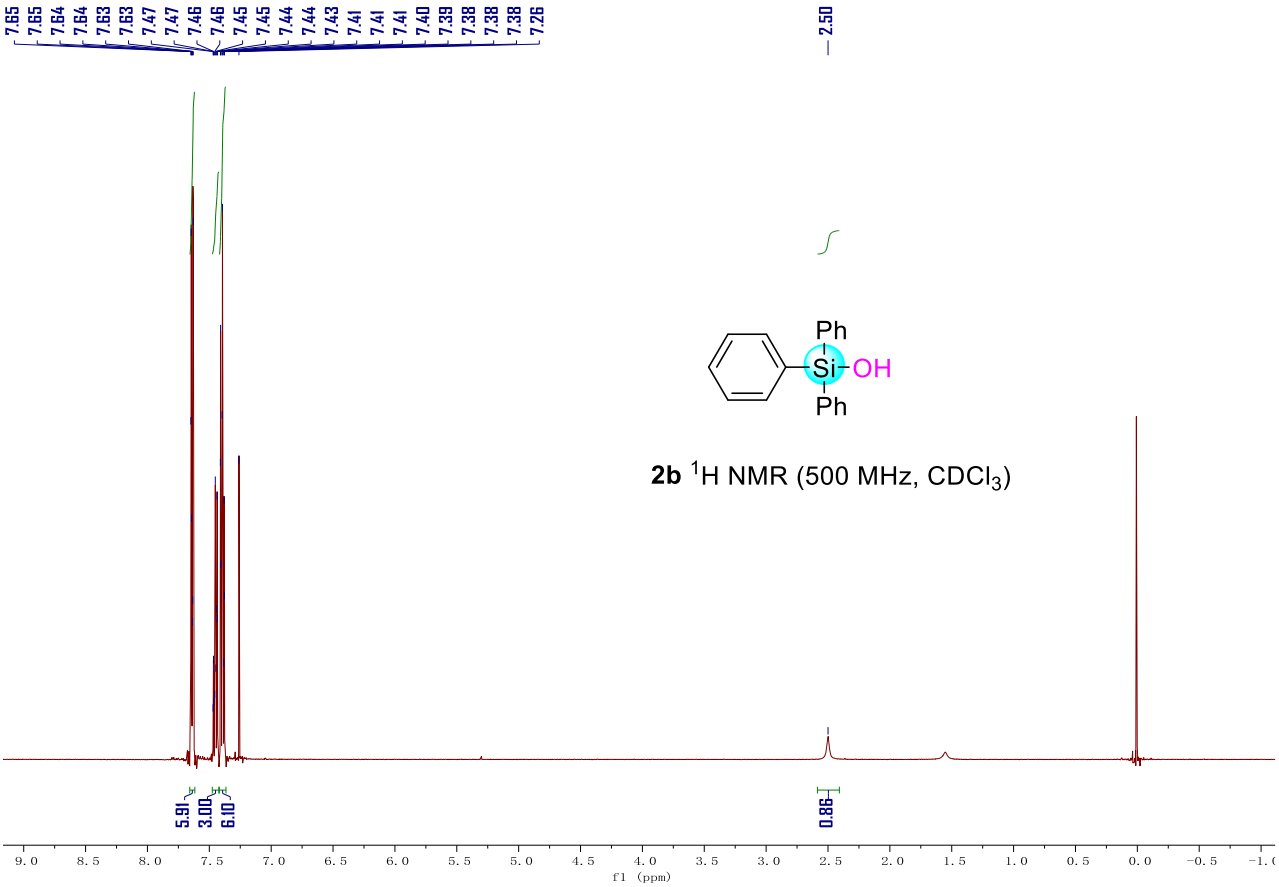
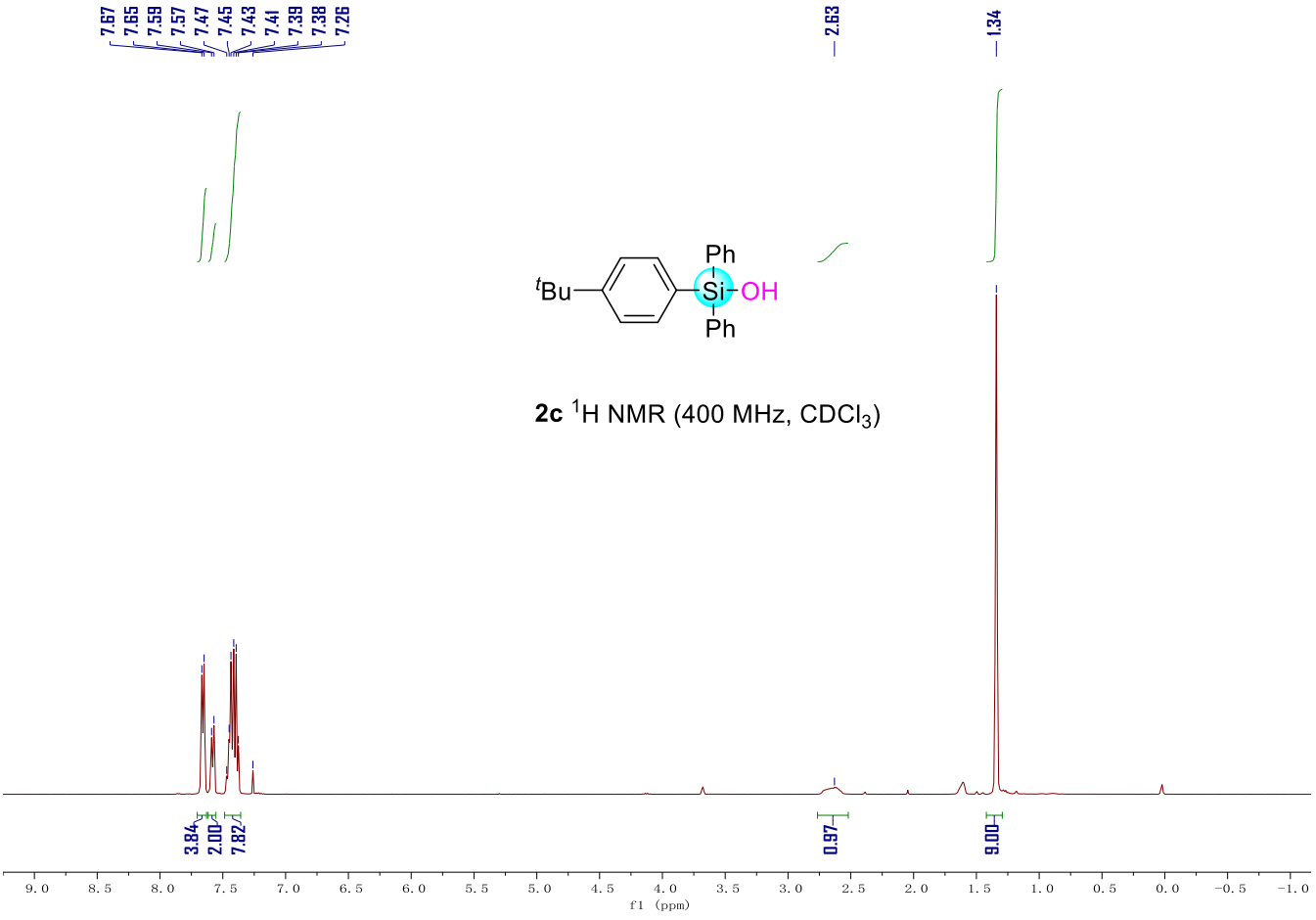
9. NMR spectra



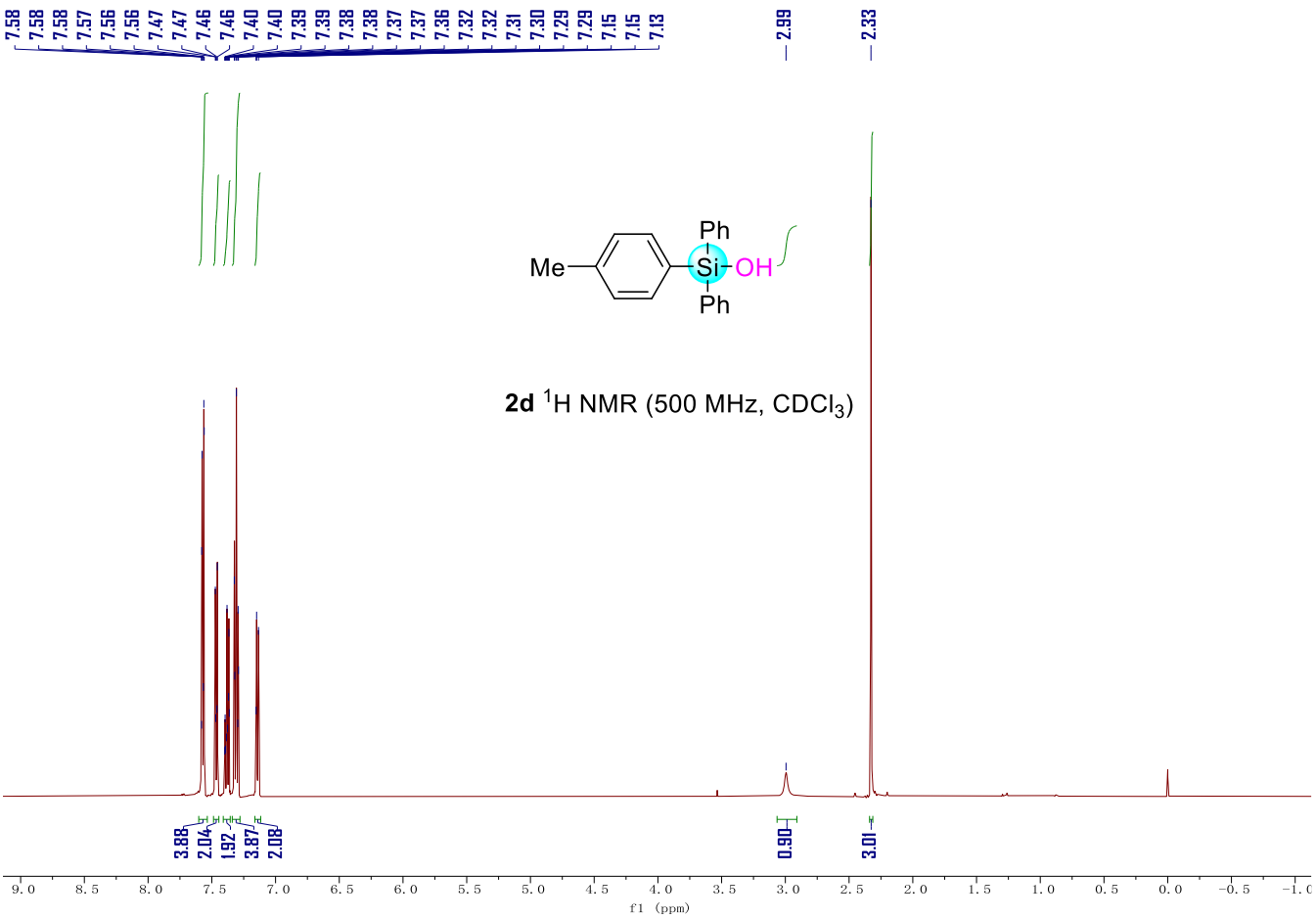
2a ^{1}H NMR (500 MHz, $CDCl_3$)



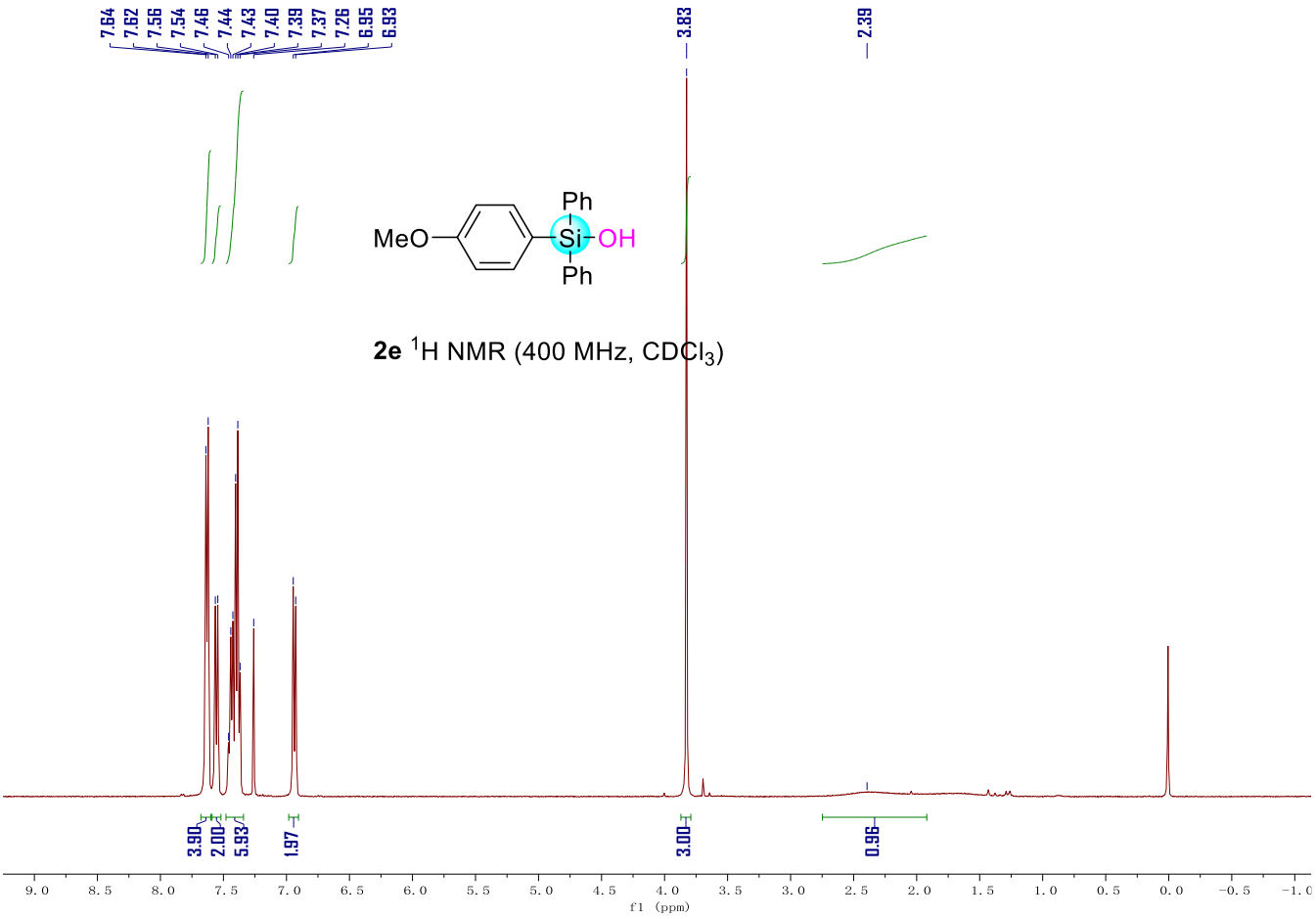
2b ^{1}H NMR (500 MHz, $CDCl_3$)



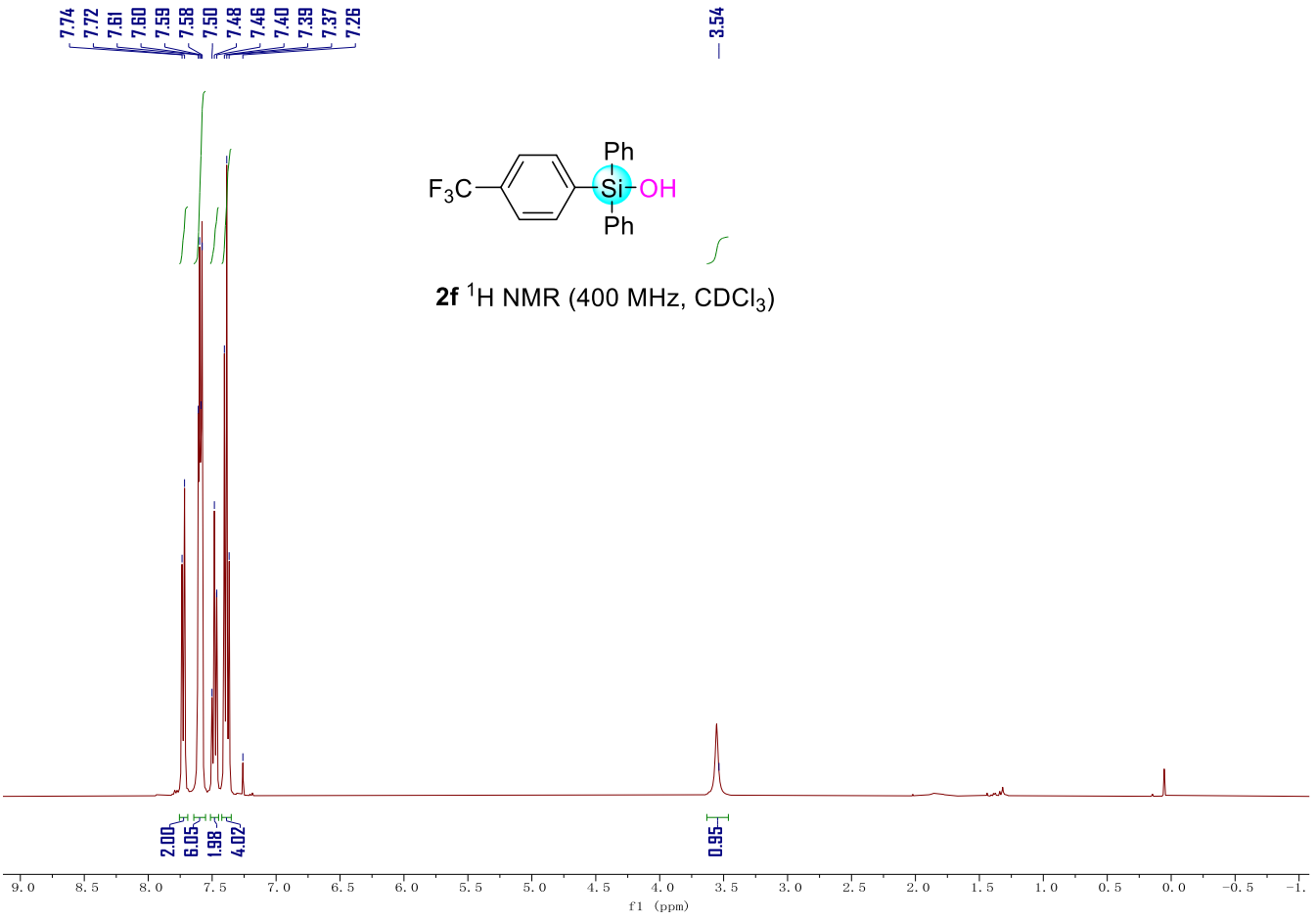
2c ^{1}H NMR (400 MHz, $CDCl_3$)



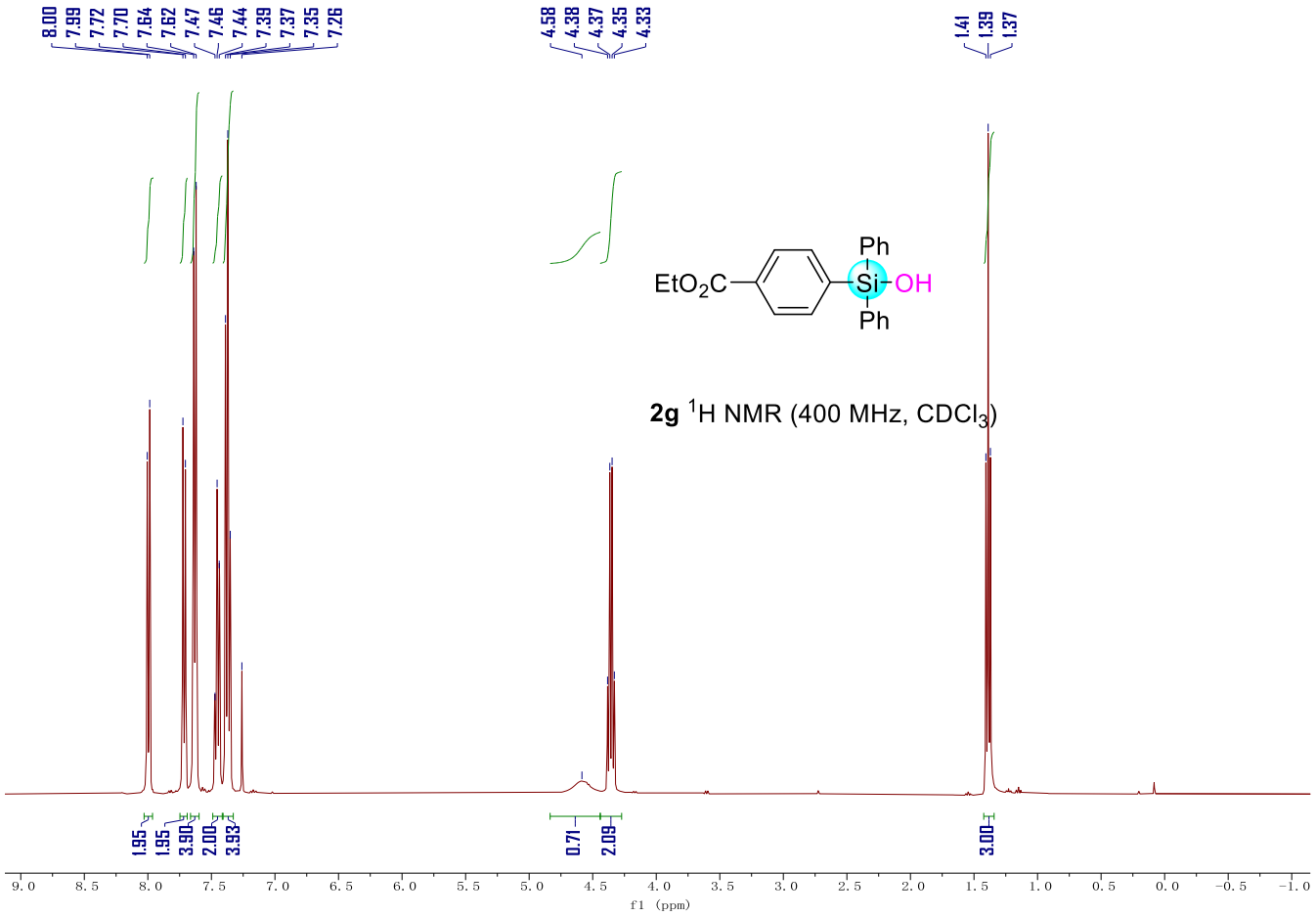
2d ^{1}H NMR (500 MHz, $CDCl_3$)



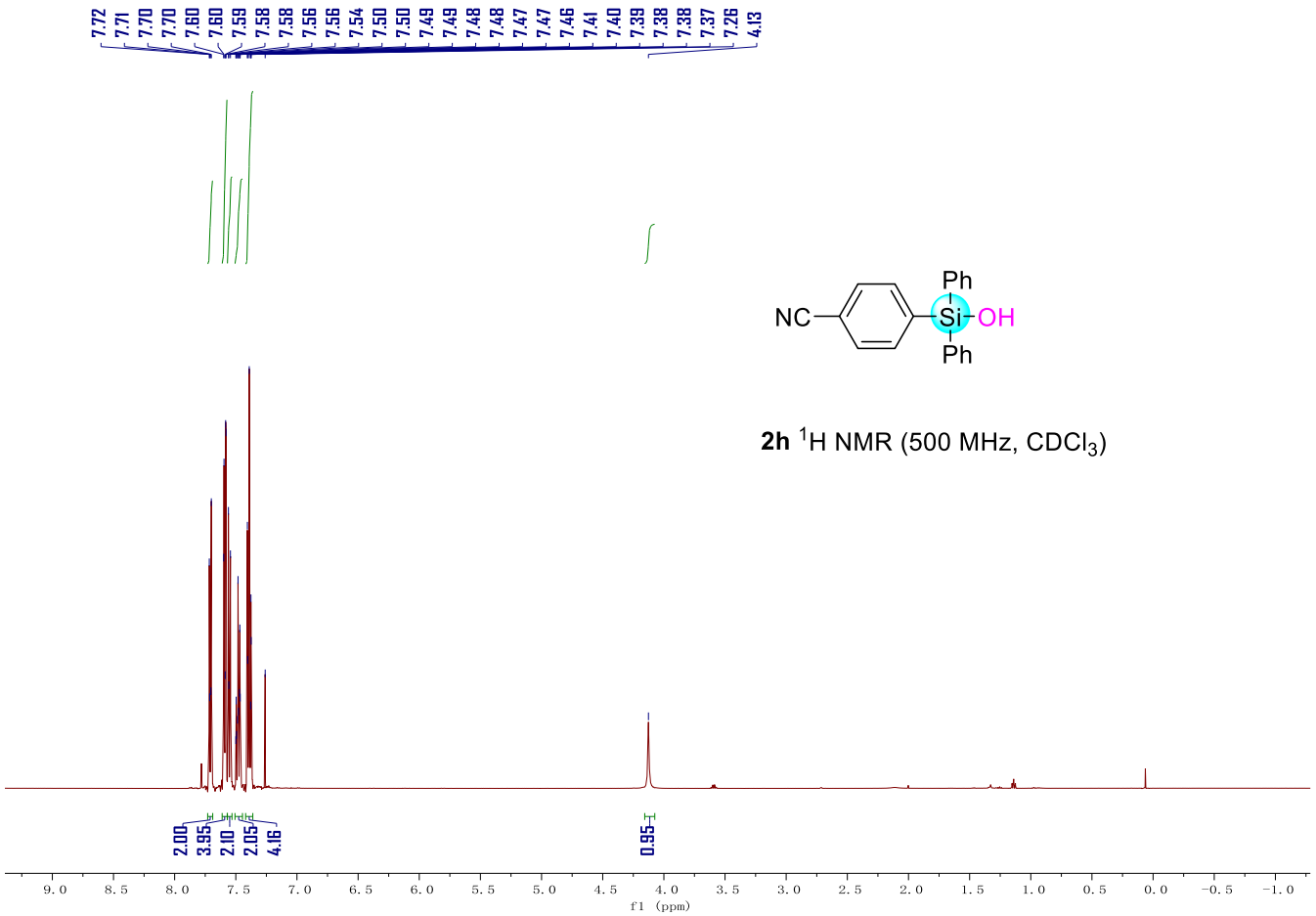
2e ^{1}H NMR (400 MHz, $CDCl_3$)



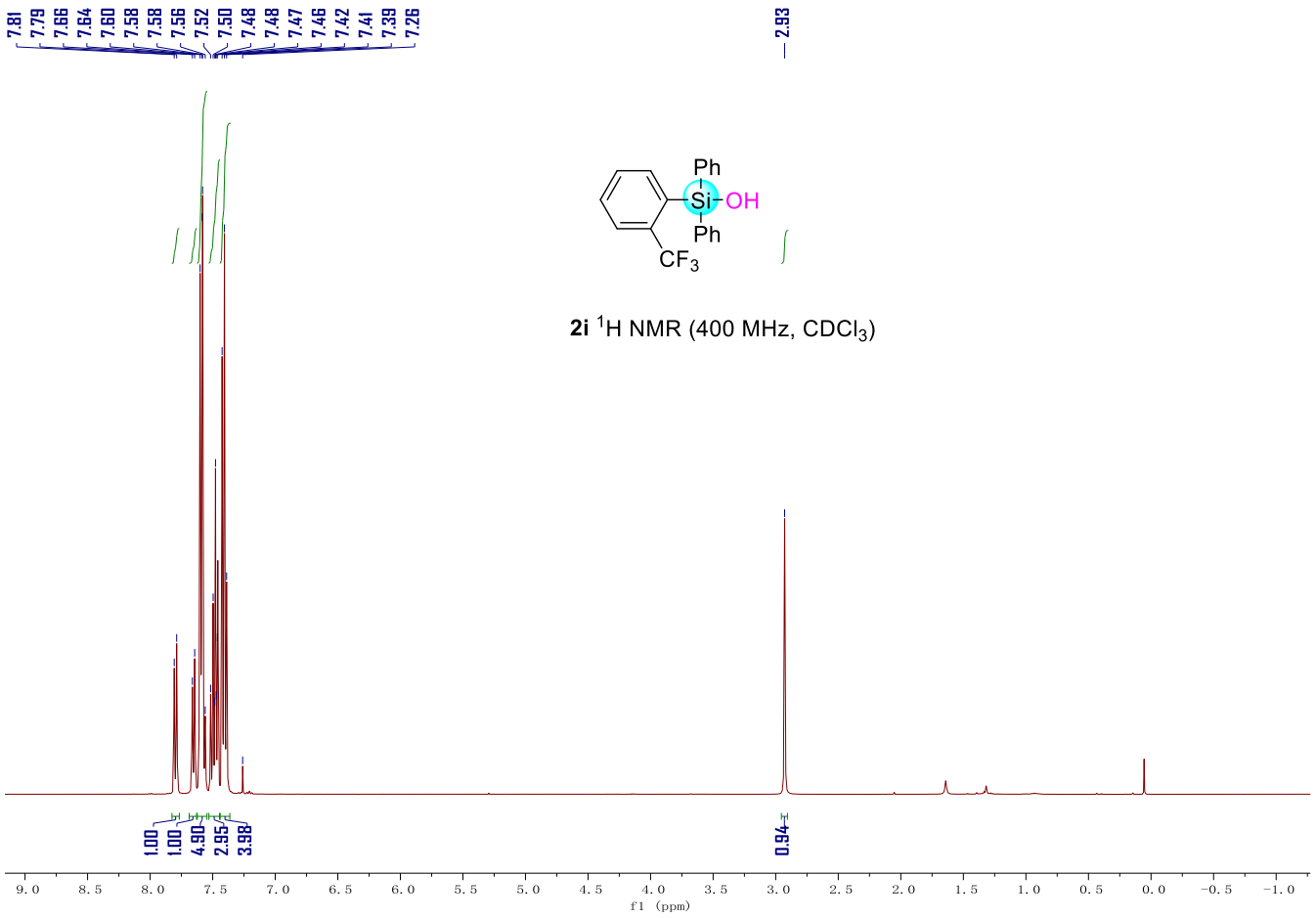
2f ^{1}H NMR (400 MHz, $CDCl_3$)



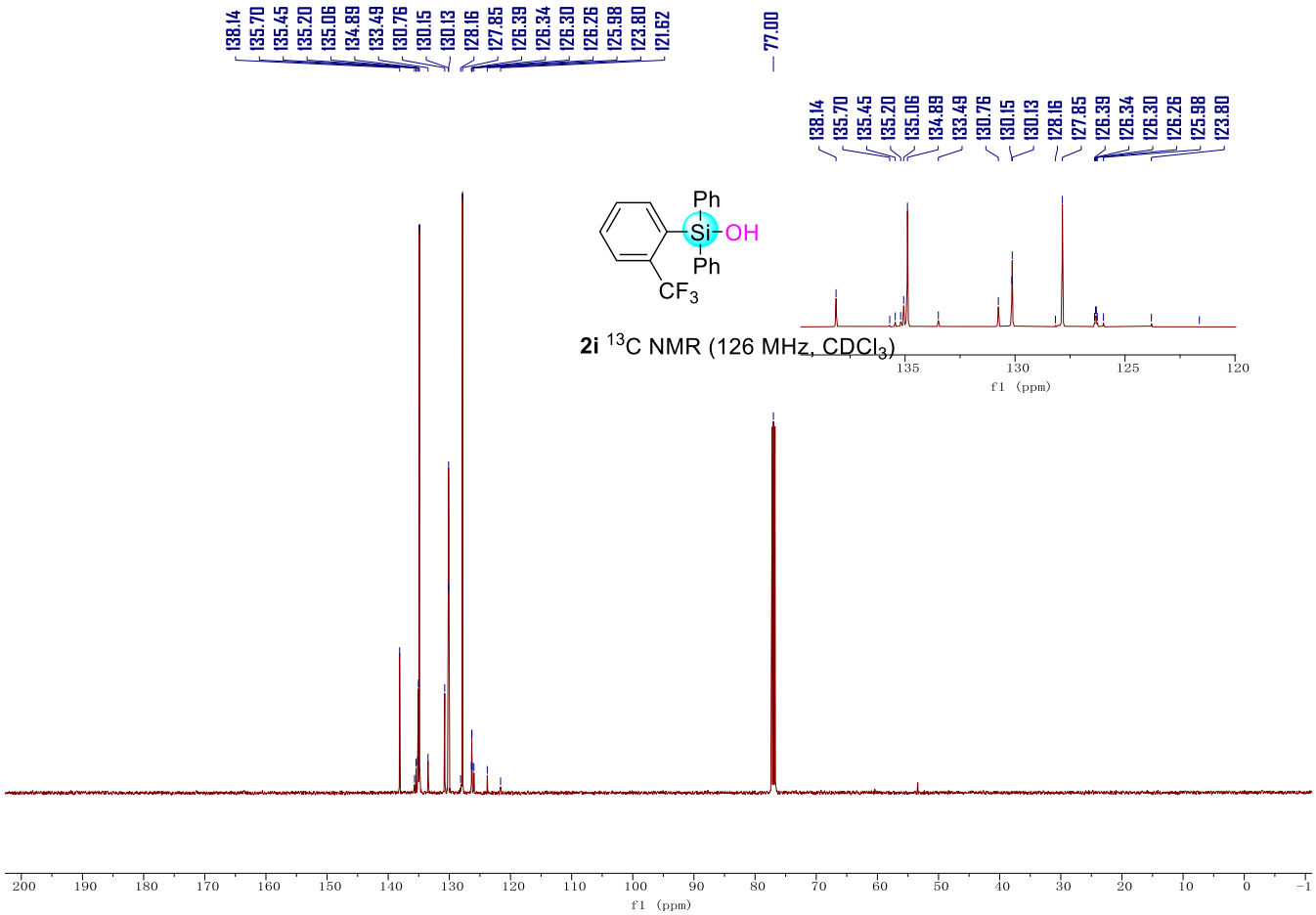
2g ^{1}H NMR (400 MHz, $CDCl_3$)



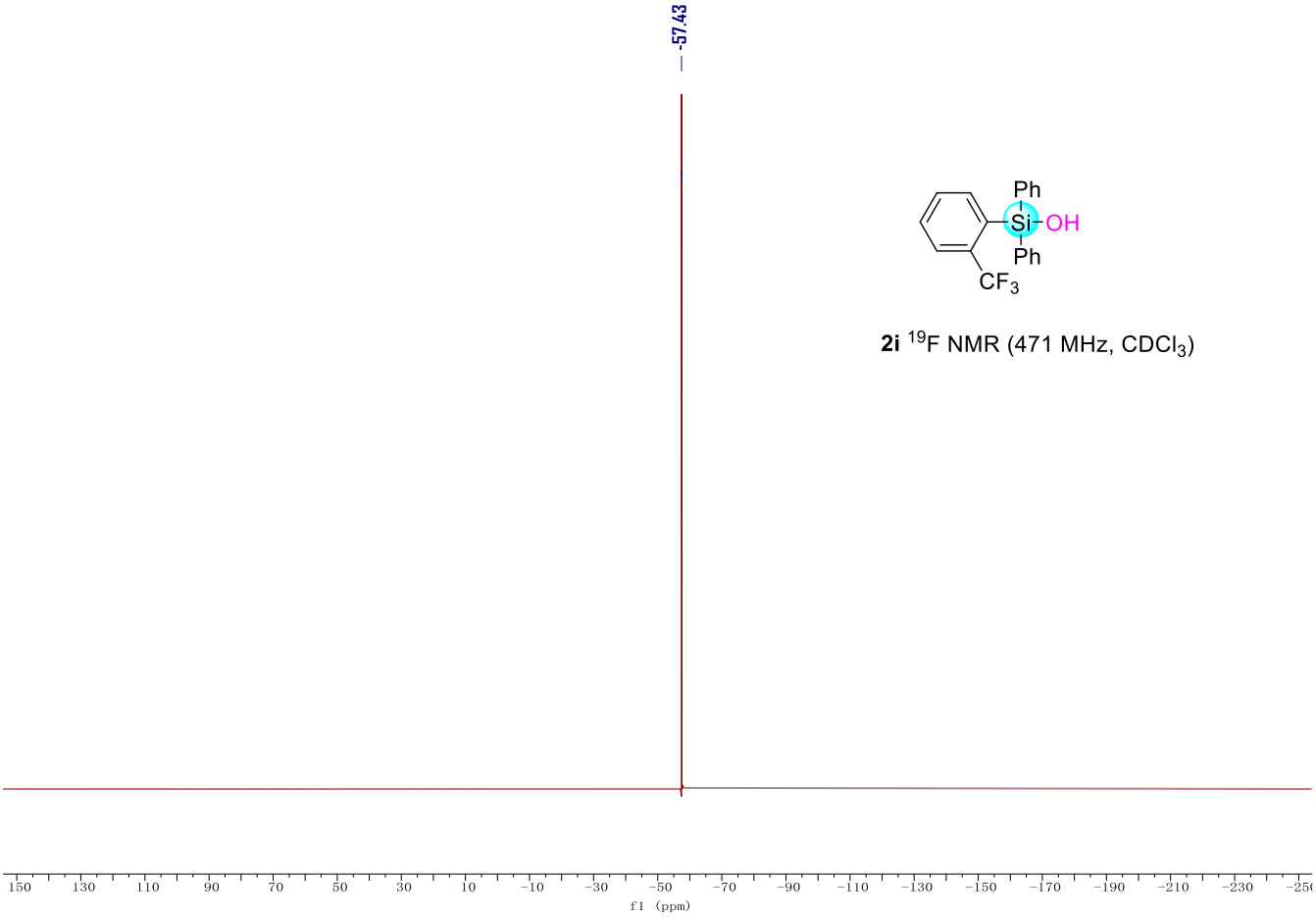
2h ^{1}H NMR (500 MHz, $CDCl_3$)



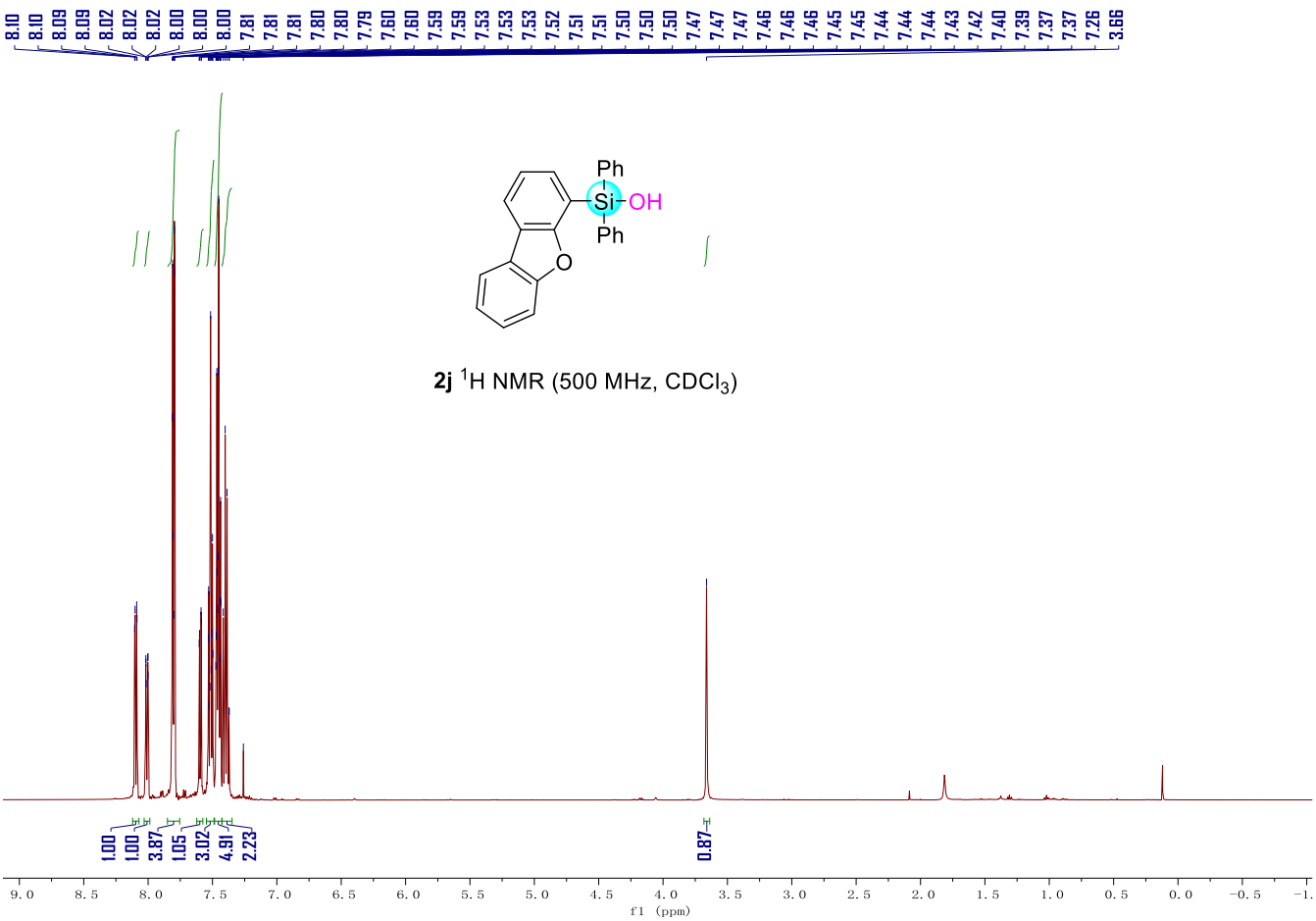
2i ^{1}H NMR (400 MHz, $CDCl_3$)



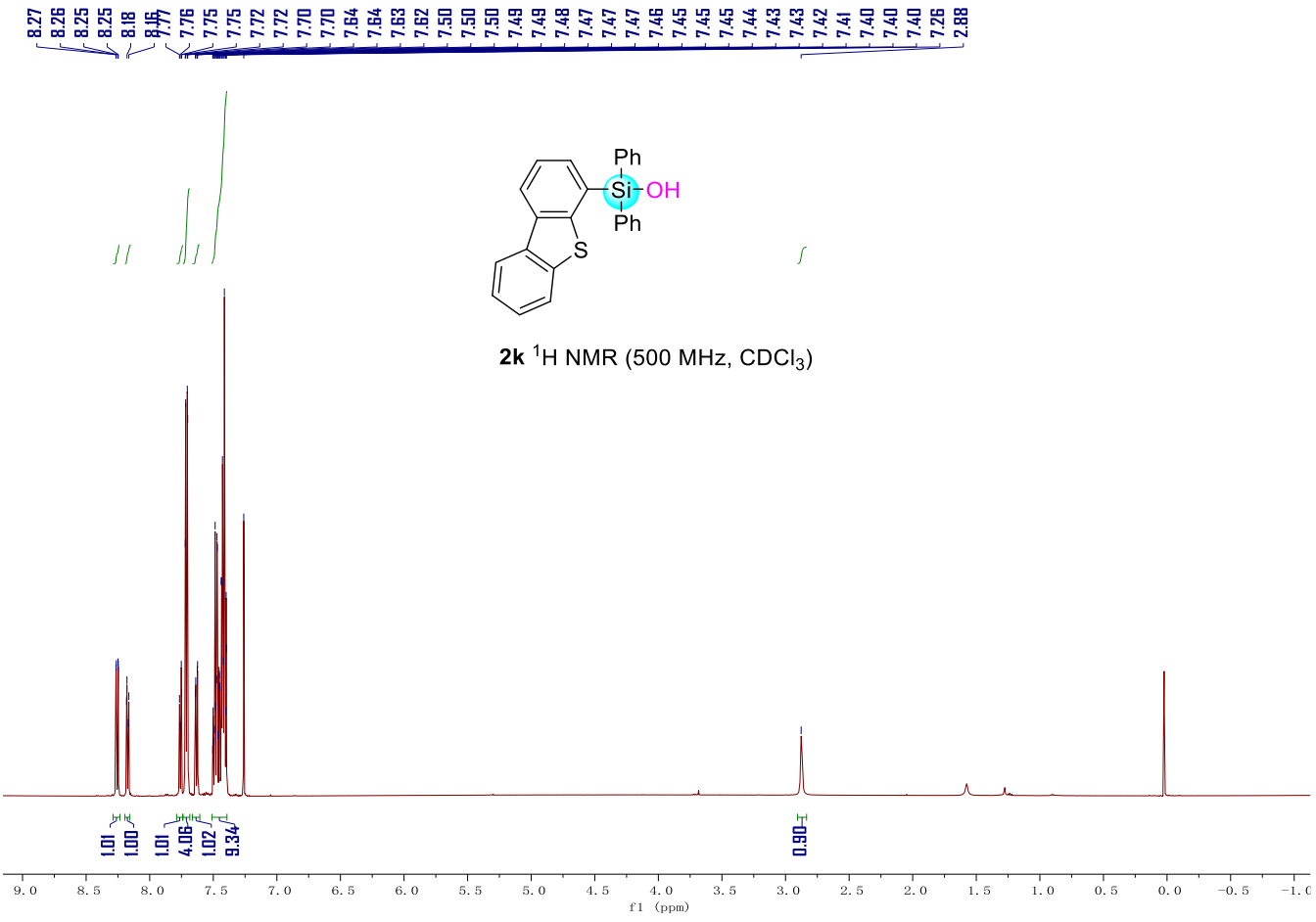
2i ^{13}C NMR (126 MHz, $CDCl_3$)



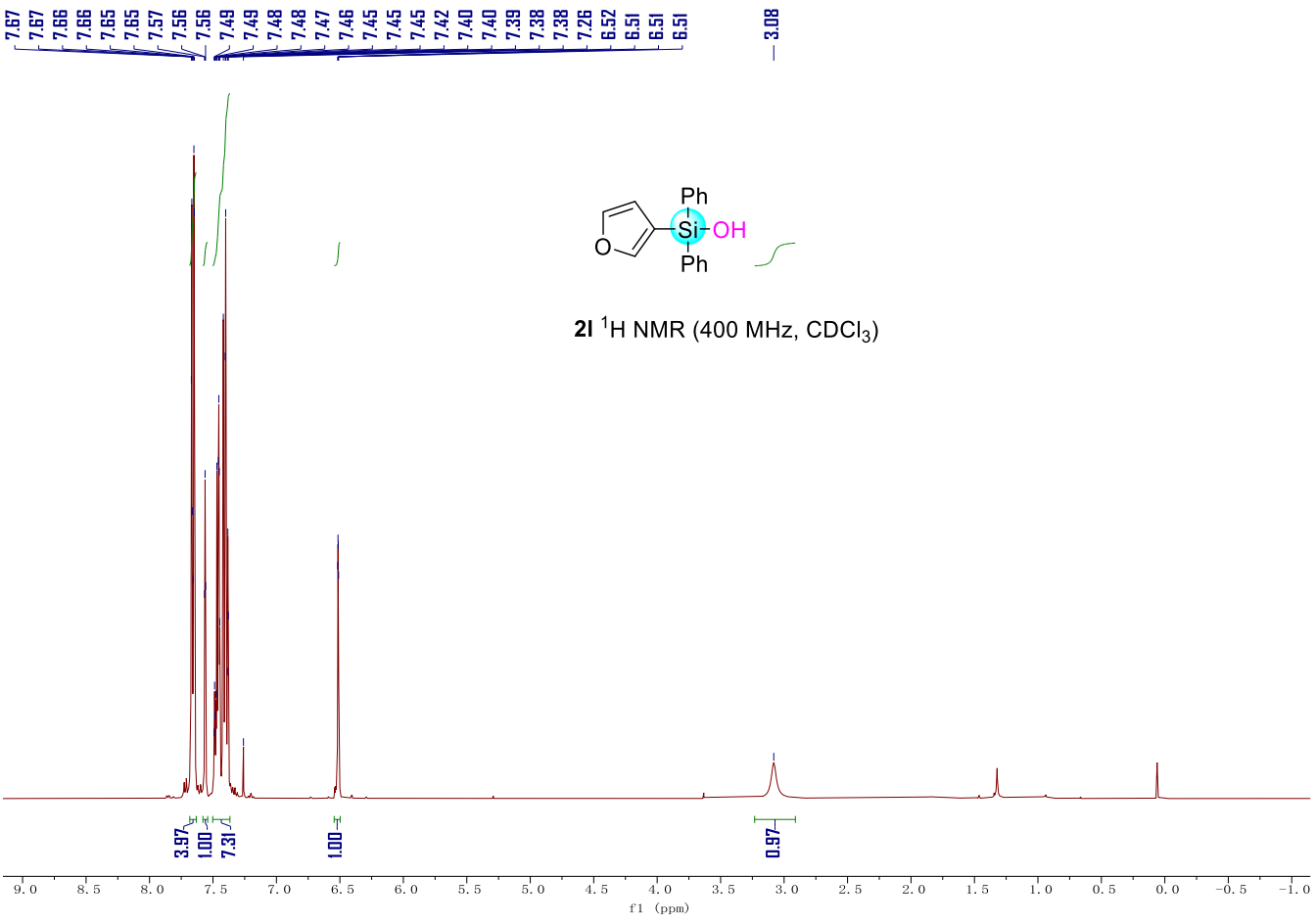
2i ^{19}F NMR (471 MHz, $CDCl_3$)



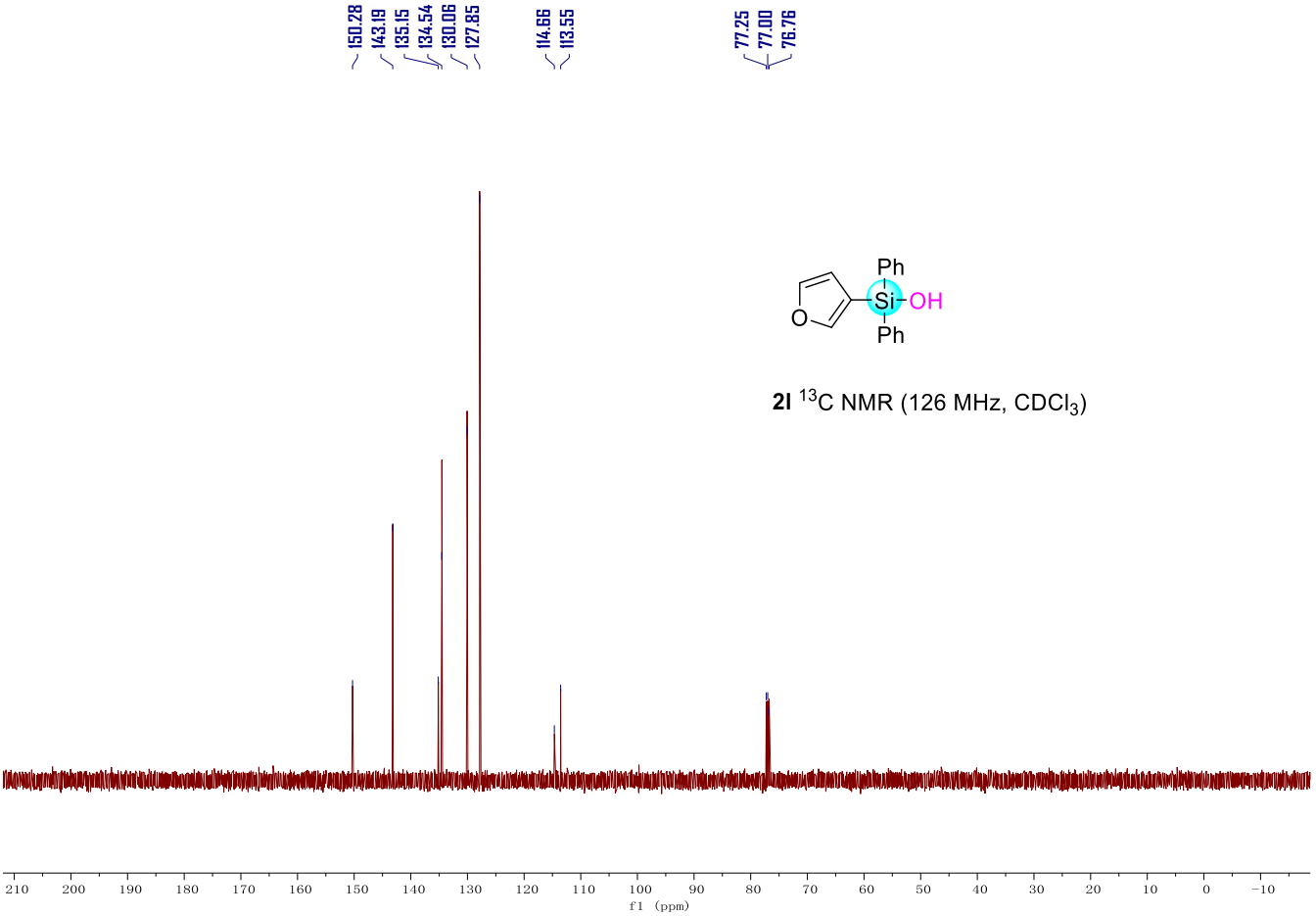
2j ^{1}H NMR (500 MHz, $CDCl_3$)



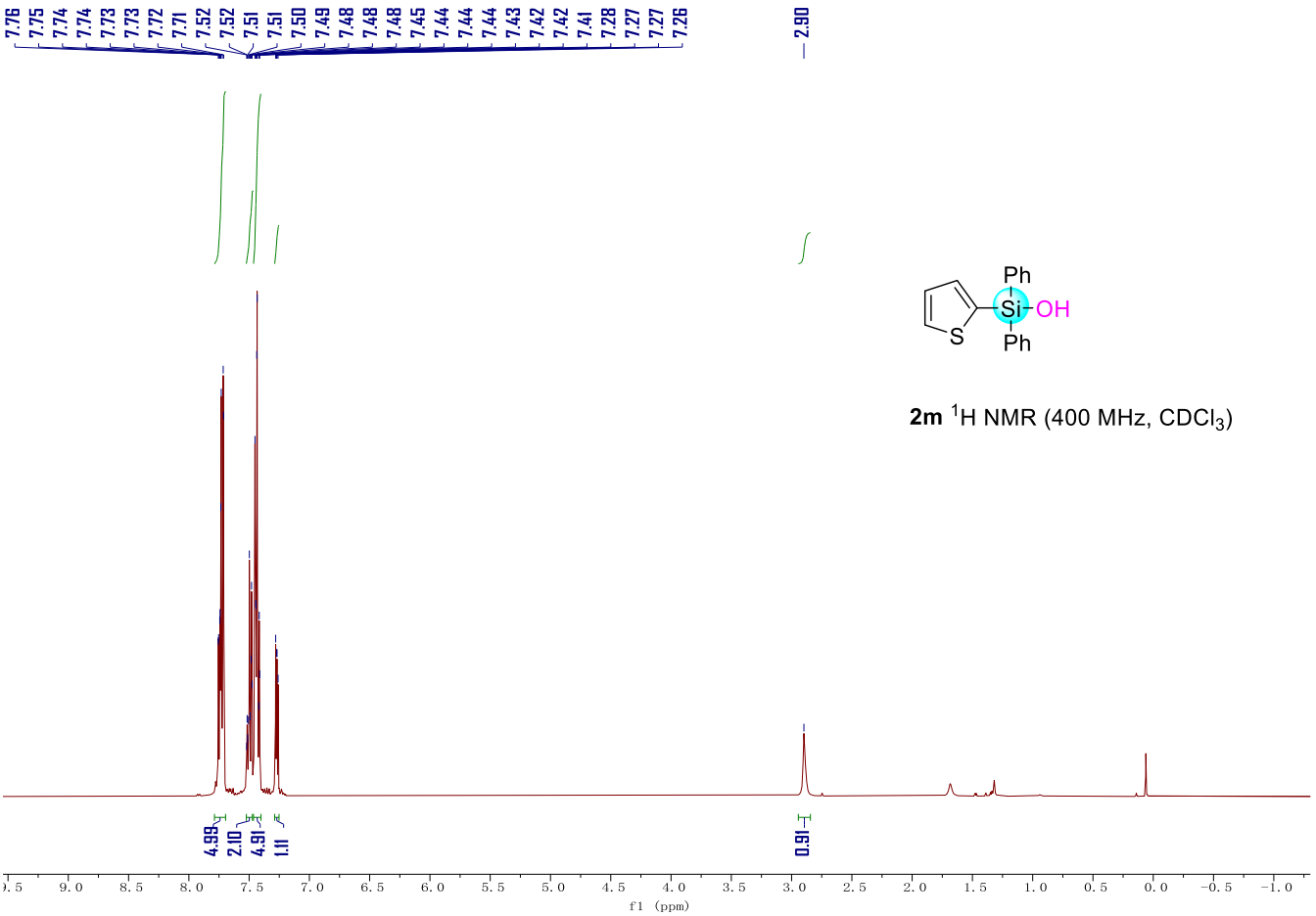
2k ^{1}H NMR (500 MHz, $CDCl_3$)



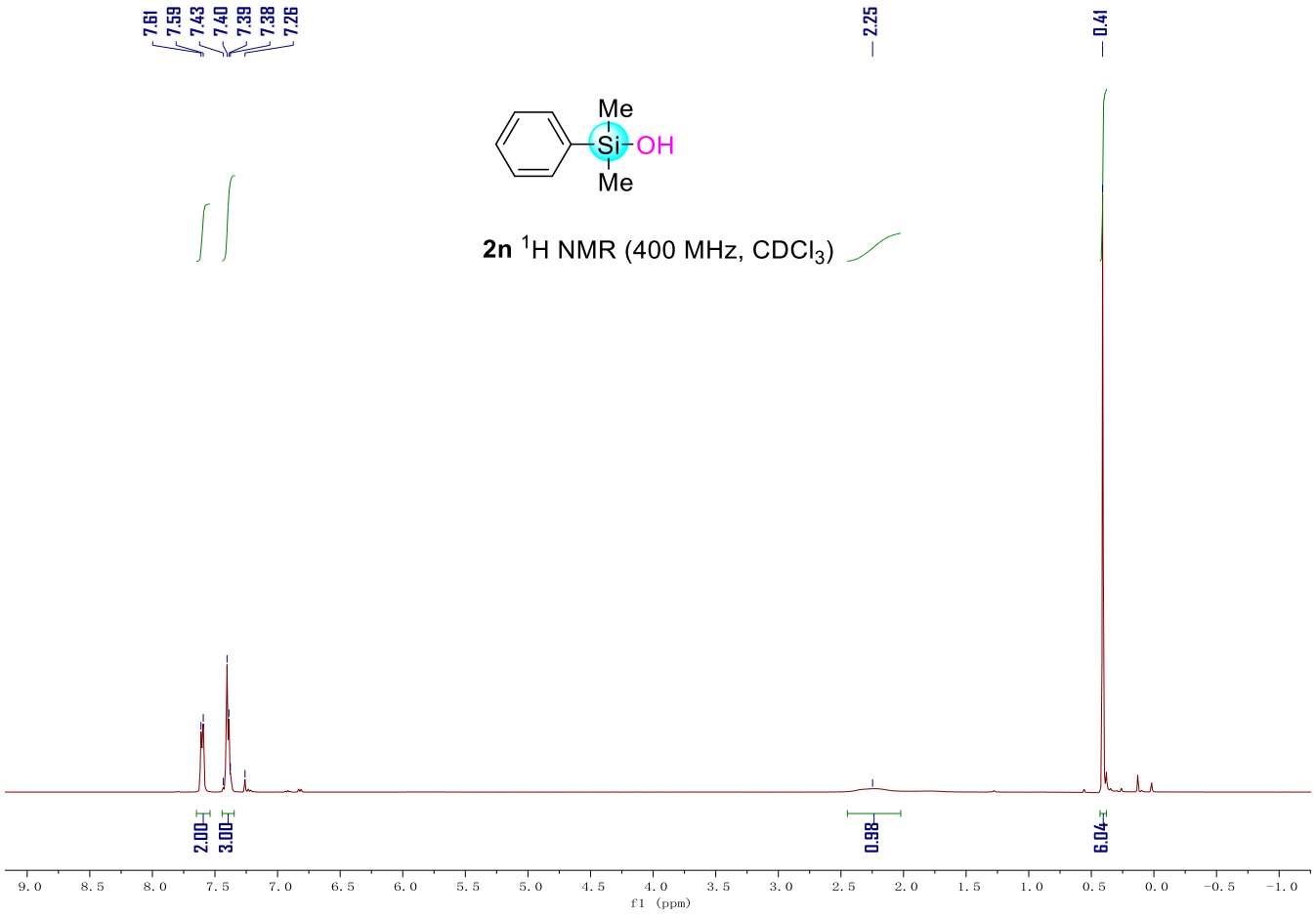
2l ^{1}H NMR (400 MHz, $CDCl_3$)



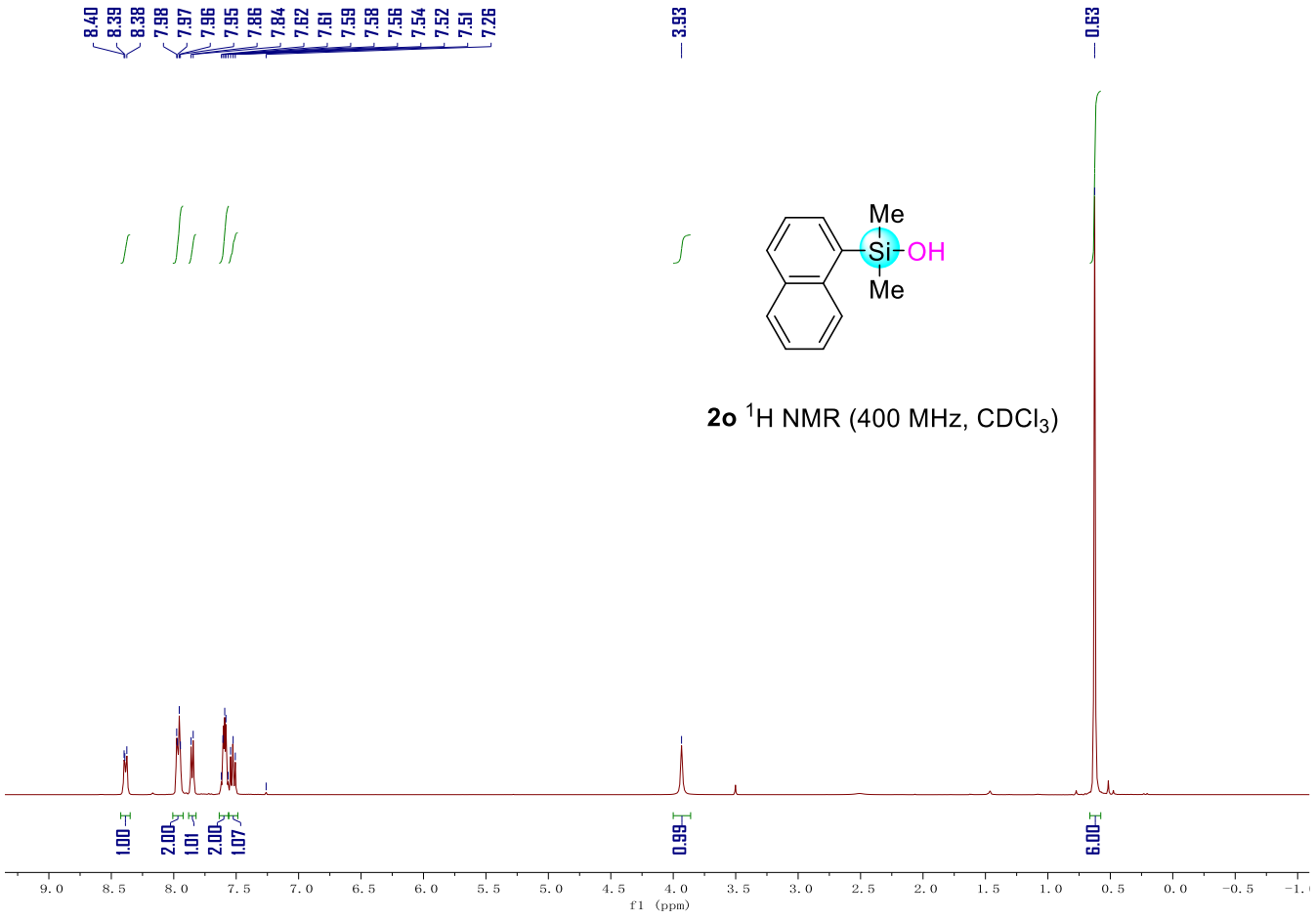
2l ^{13}C NMR (126 MHz, $CDCl_3$)



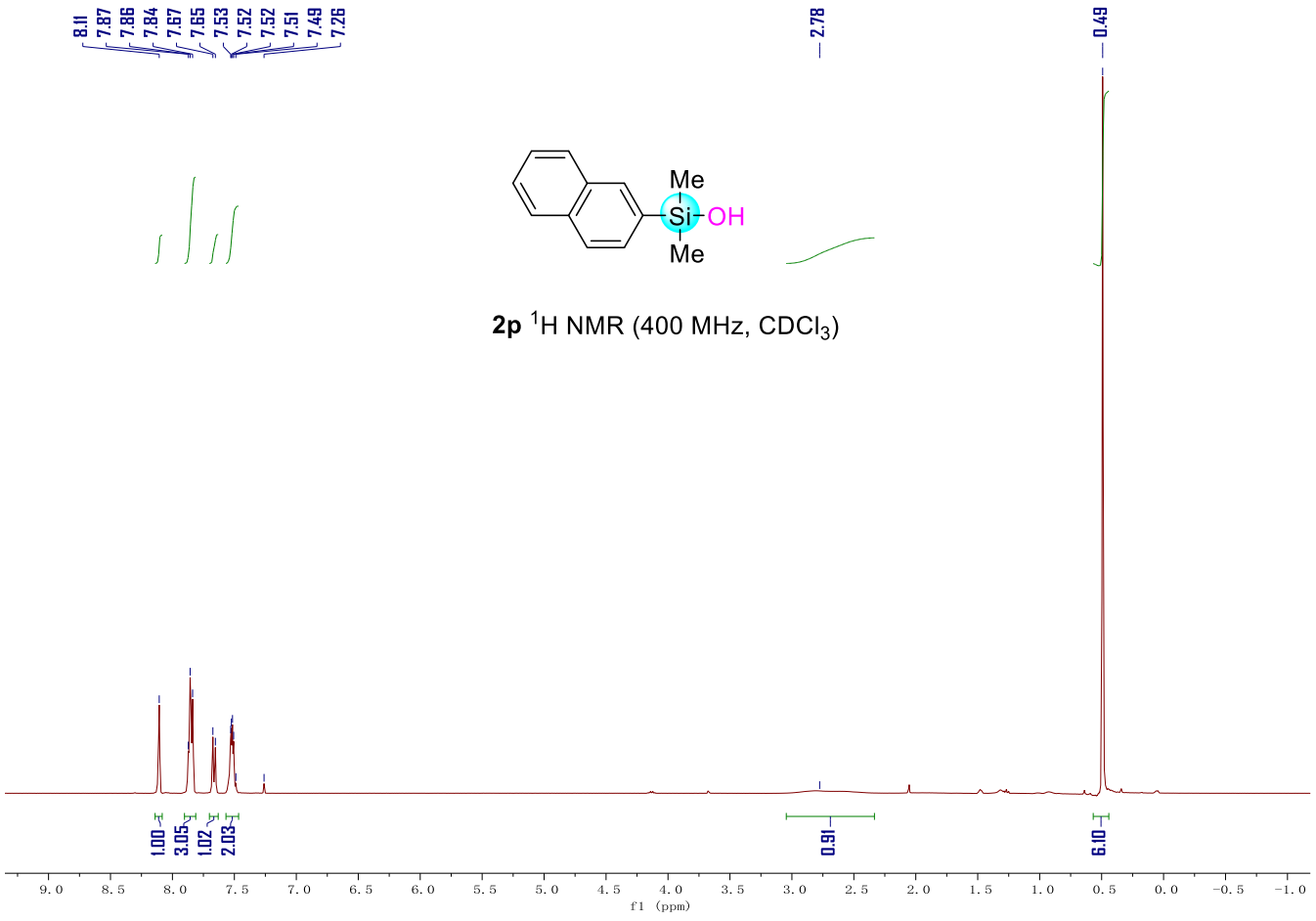
2m ^{1}H NMR (400 MHz, $CDCl_3$)



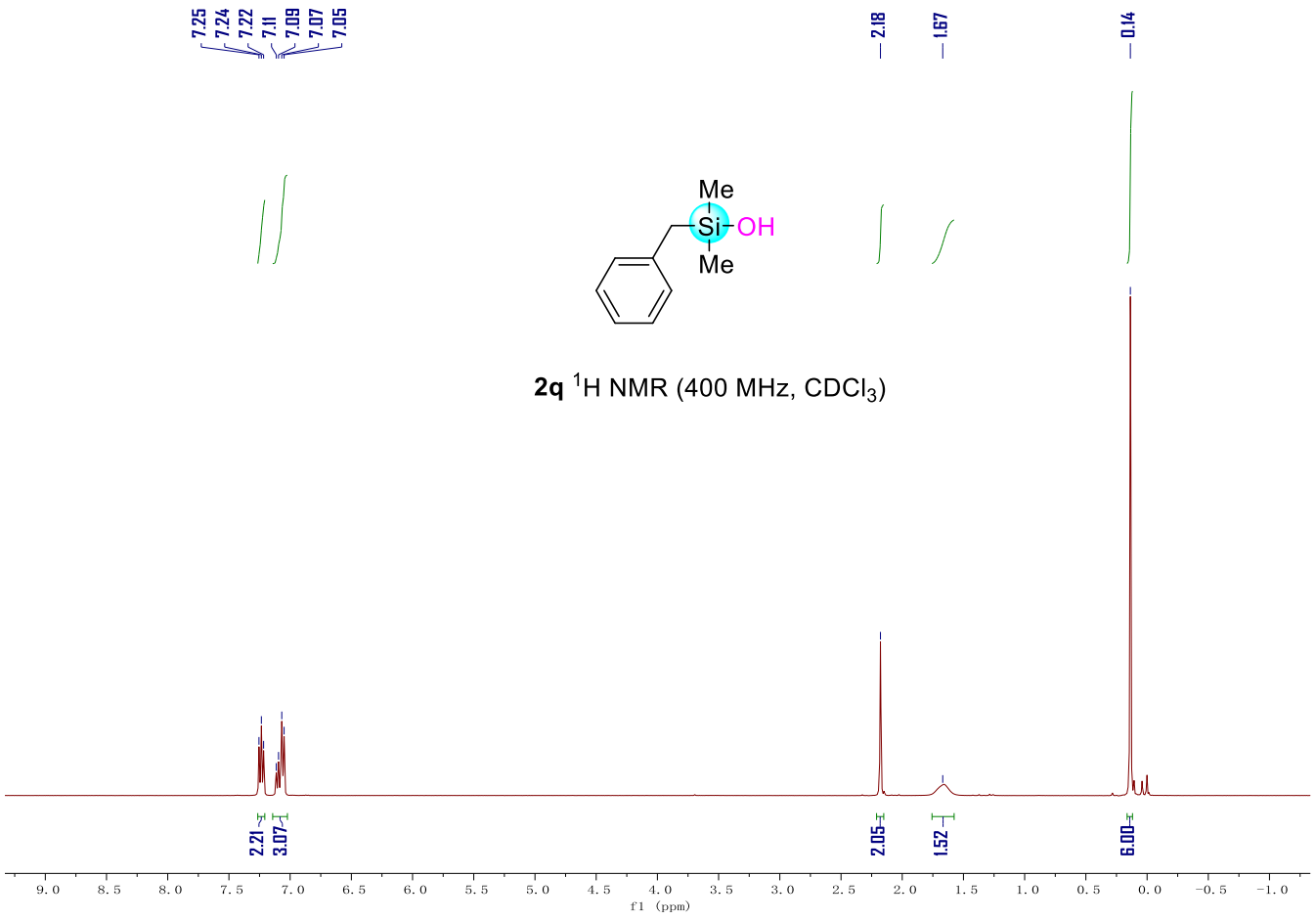
2n ^{1}H NMR (400 MHz, $CDCl_3$)



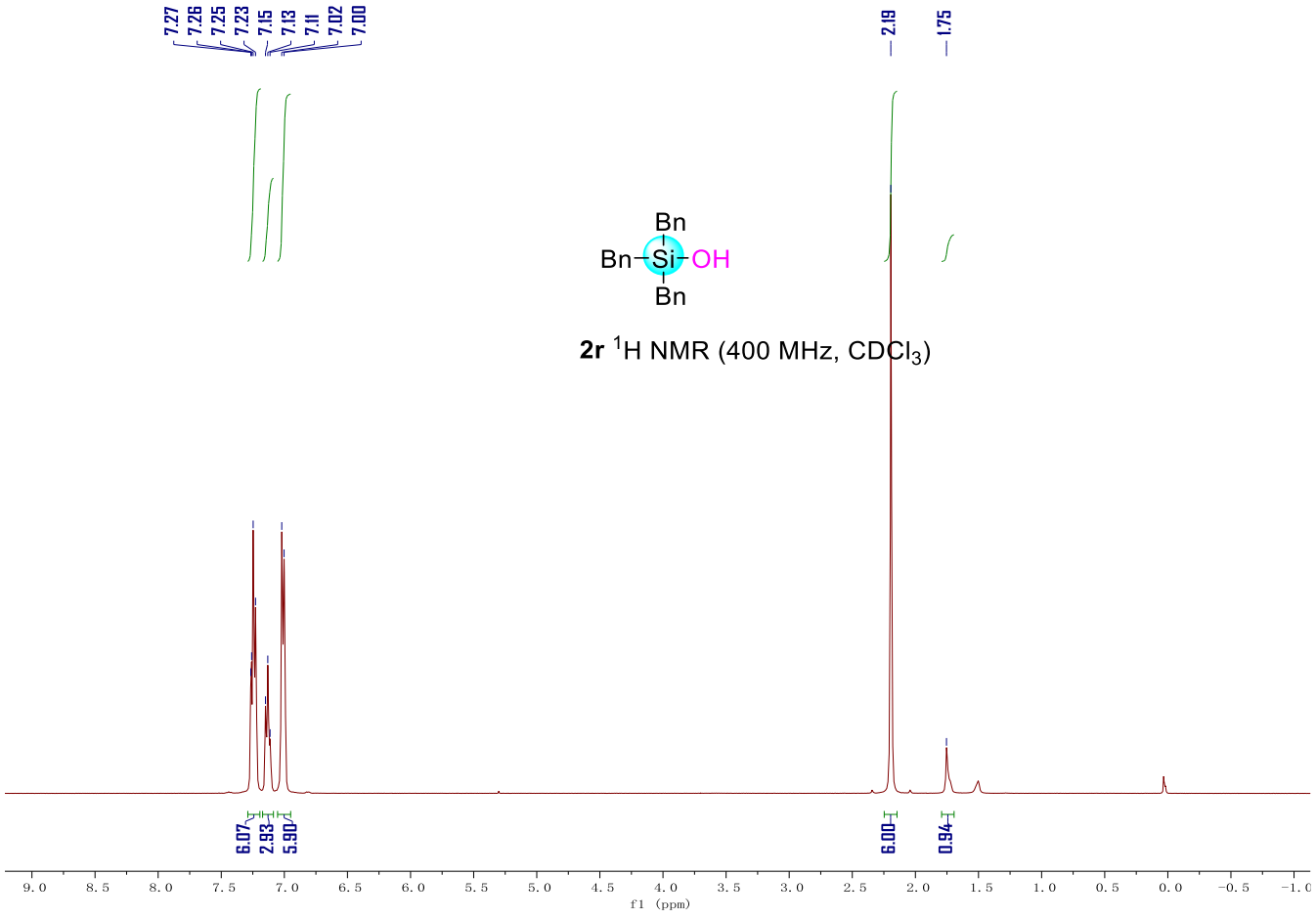
2o ^{1}H NMR (400 MHz, $CDCl_3$)



2p ^{1}H NMR (400 MHz, $CDCl_3$)

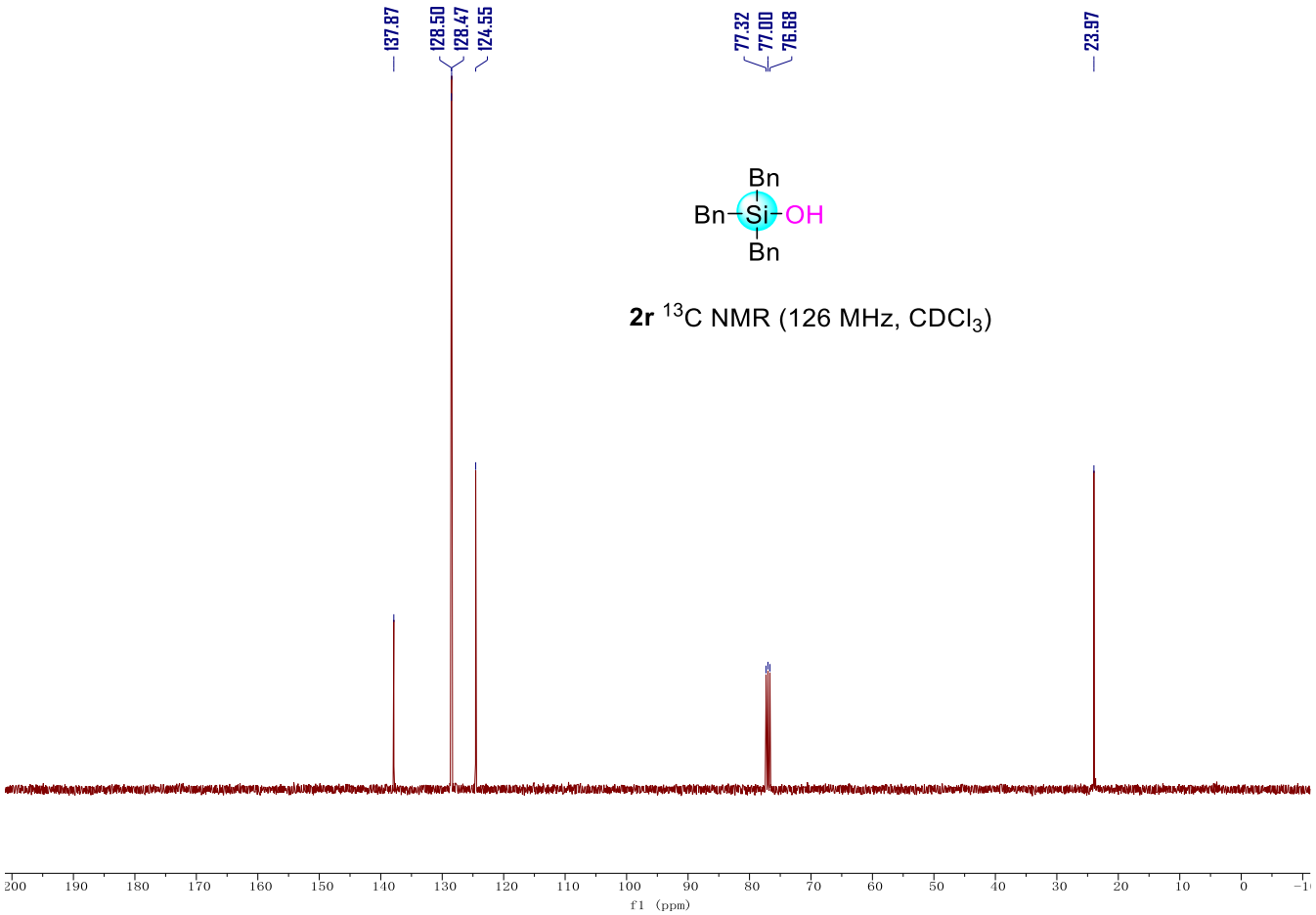


2q ^{1}H NMR (400 MHz, $CDCl_3$)



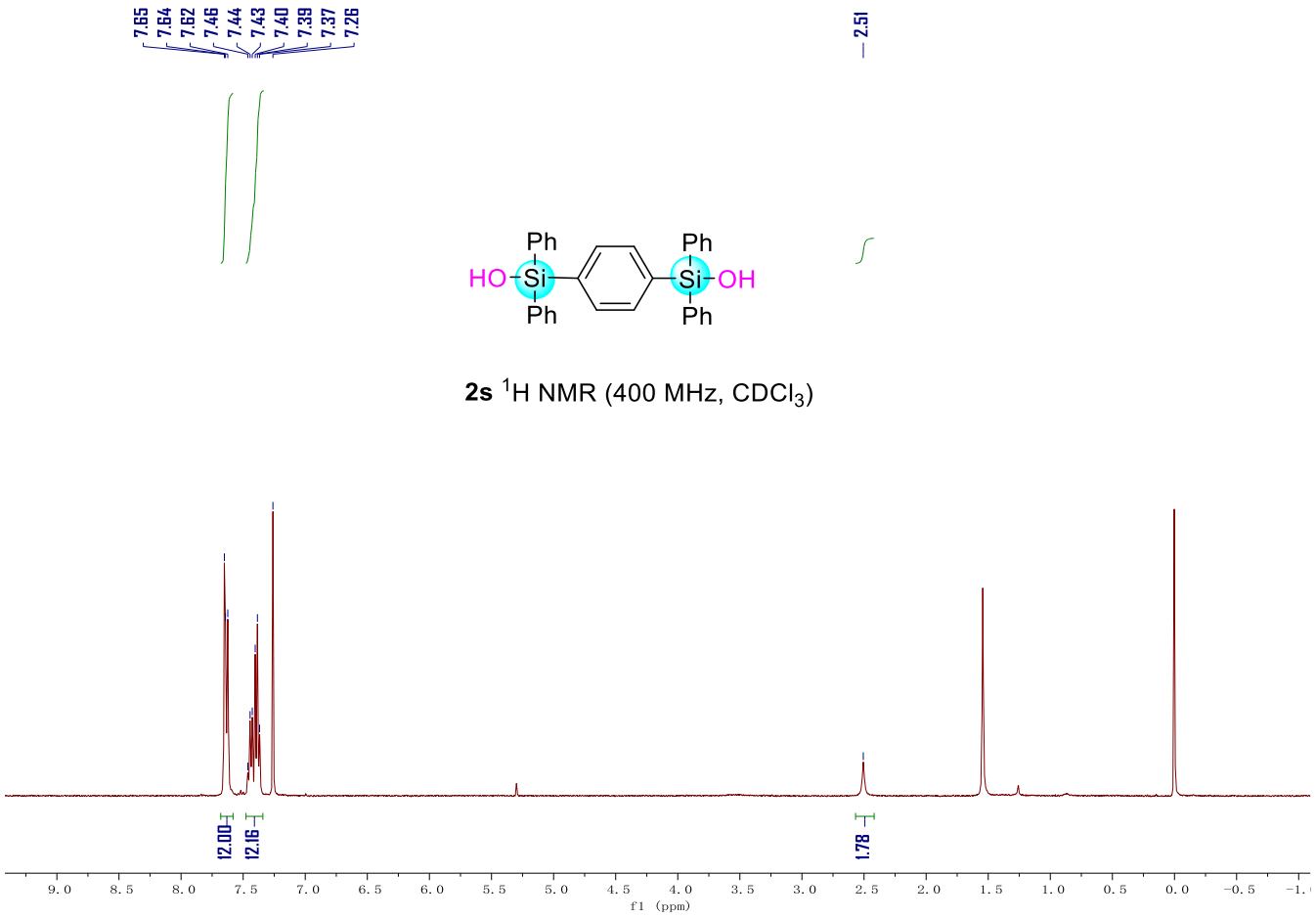
Bn
Bn–Si–OH
Bn

2r ^{1}H NMR (400 MHz, $CDCl_3$)

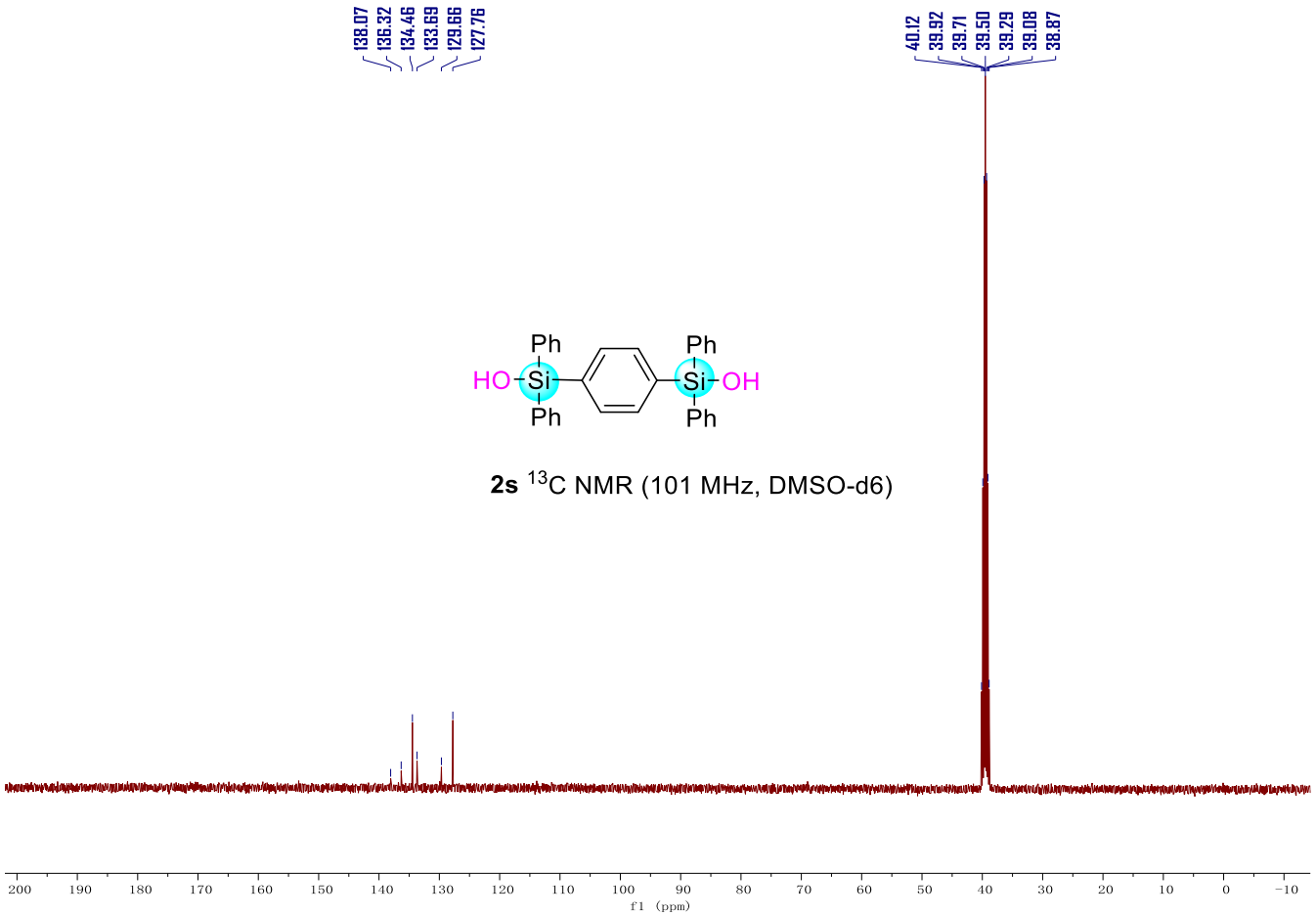


Bn
Bn–Si–OH
Bn

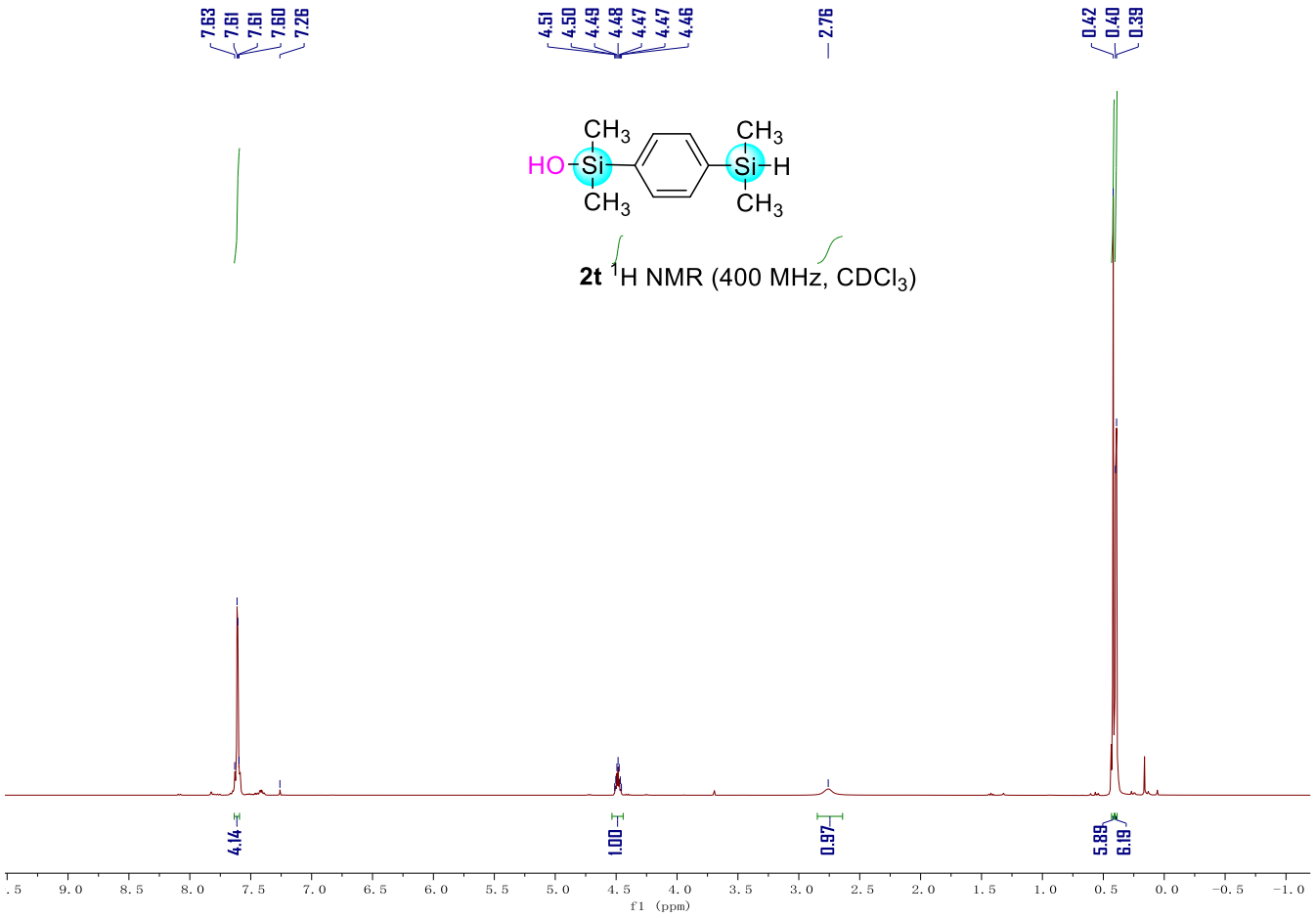
2r ^{13}C NMR (126 MHz, $CDCl_3$)



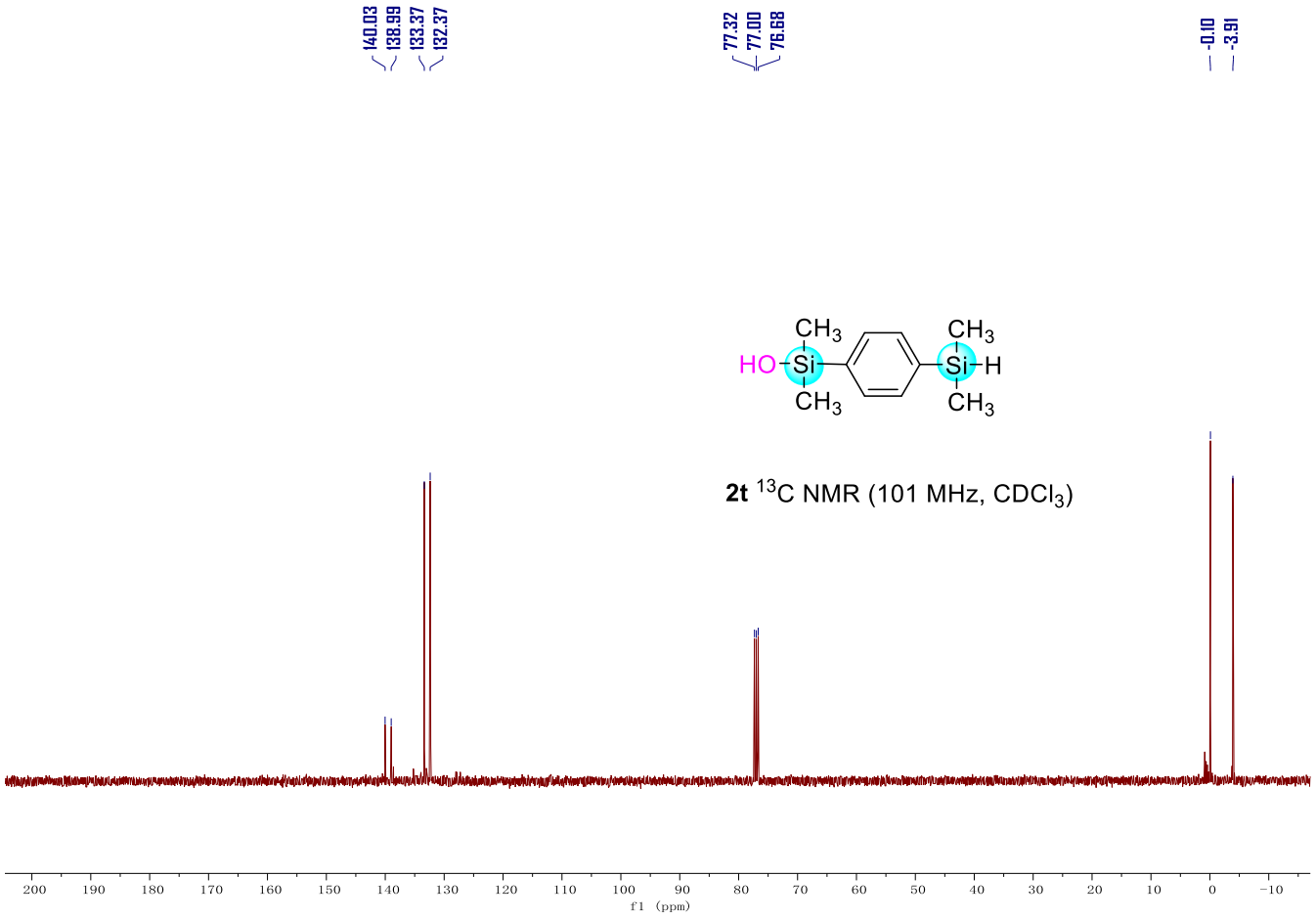
2s ^{1}H NMR (400 MHz, $CDCl_3$)



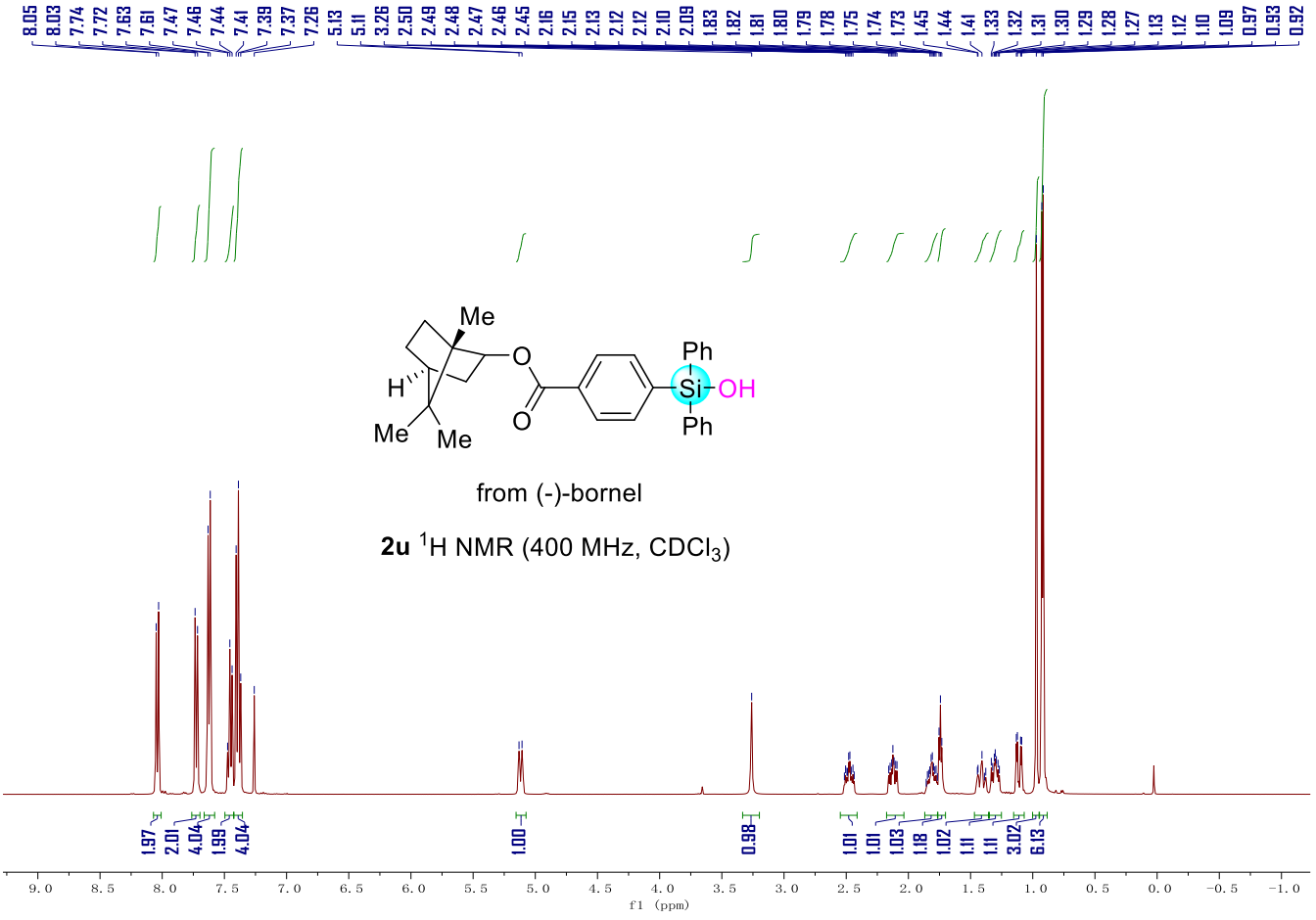
2s ^{13}C NMR (101 MHz, DMSO-d6)



2t ^{1}H NMR (400 MHz, $CDCl_3$)

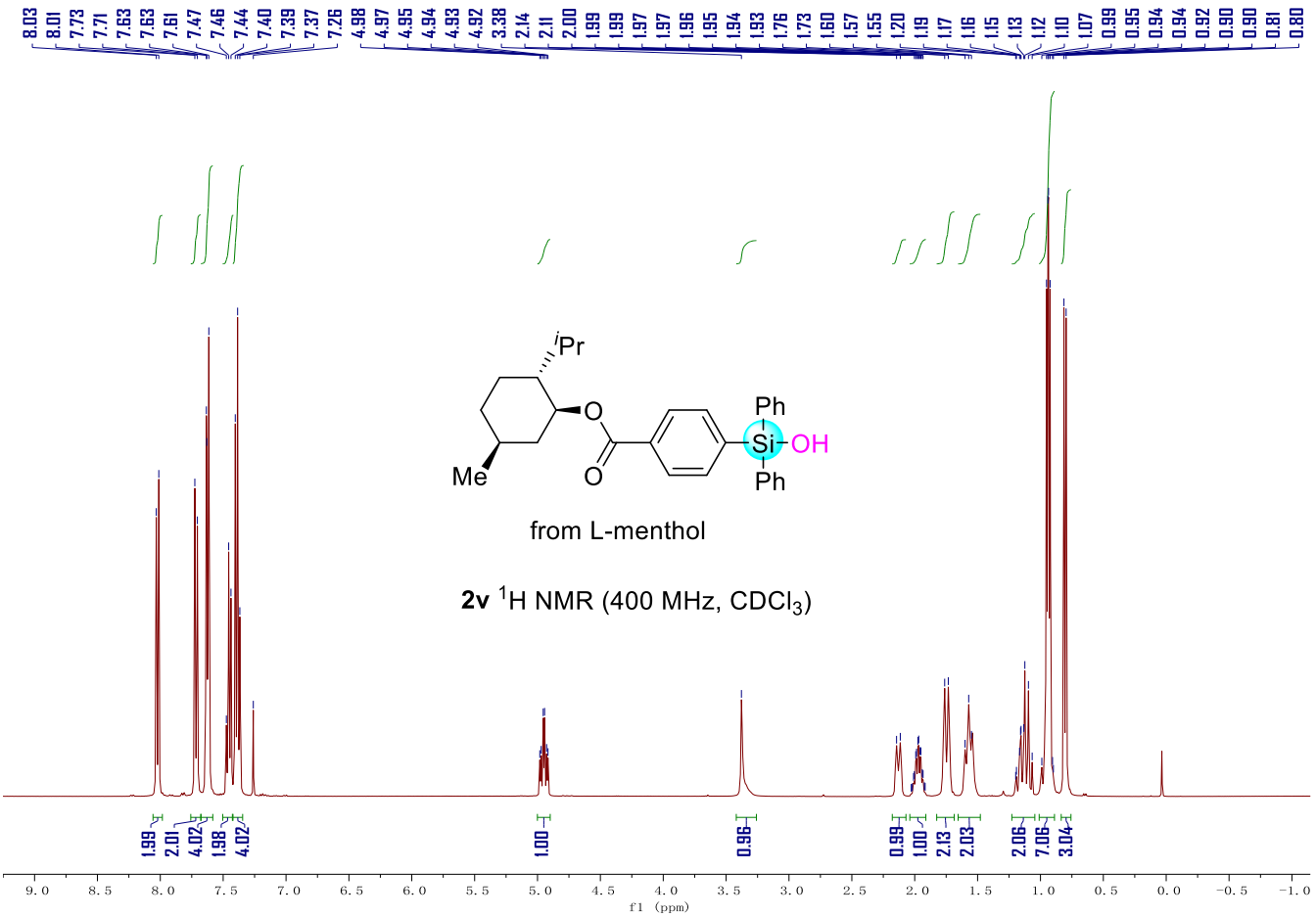


2t ^{13}C NMR (101 MHz, $CDCl_3$)



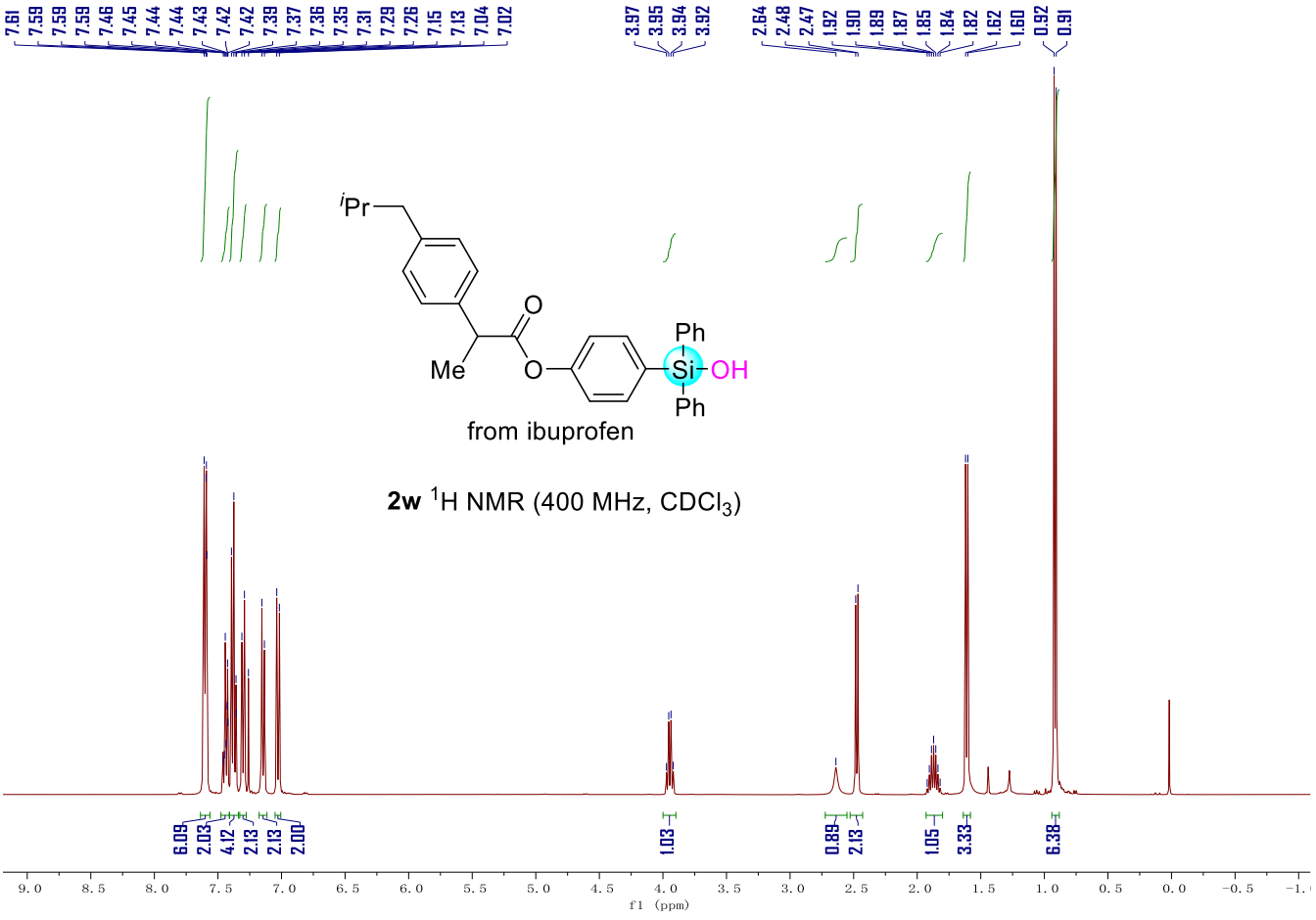
from (-)-bornel

2u ^{1}H NMR (400 MHz, $CDCl_3$)



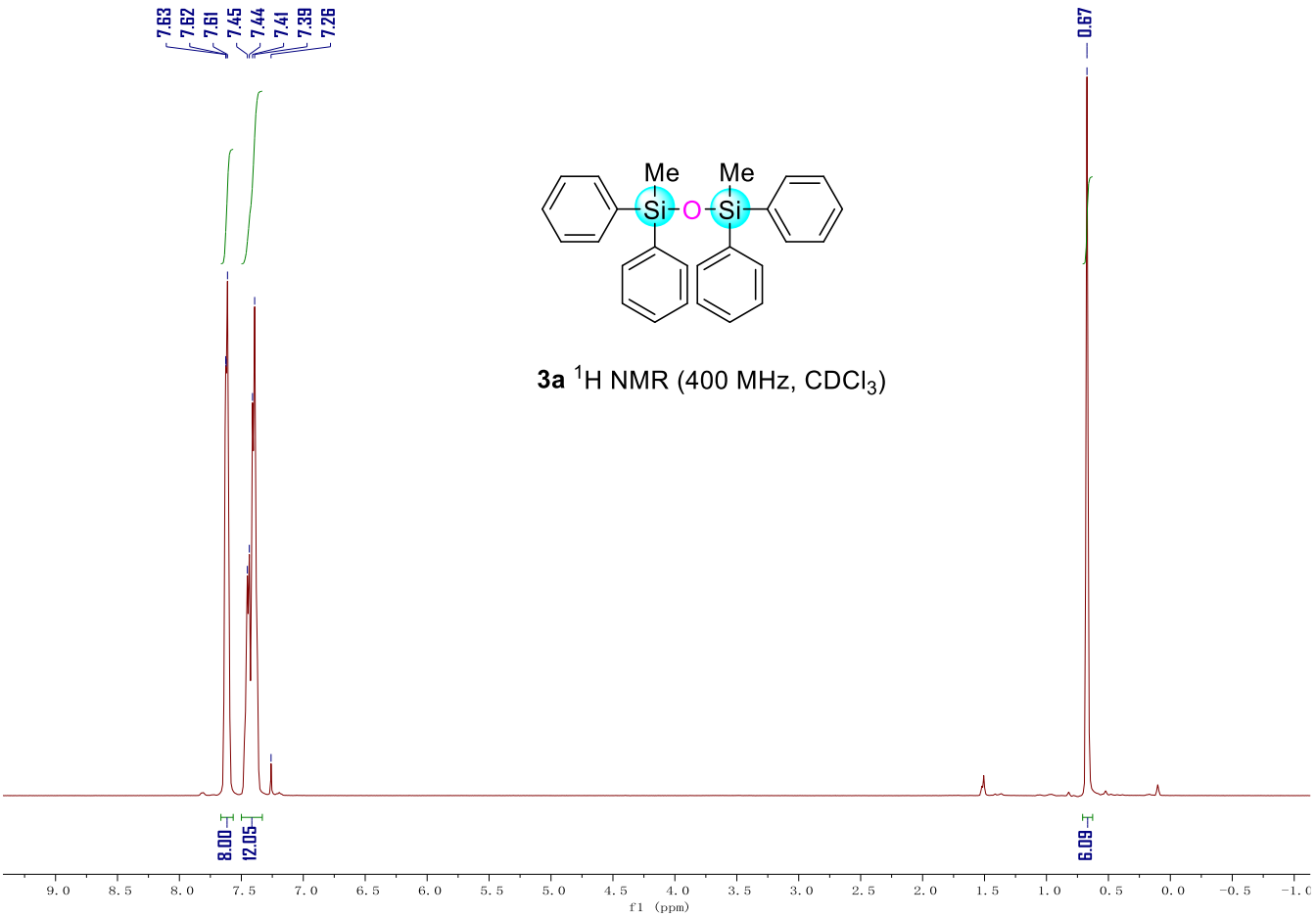
from L-menthol

2v ^{1}H NMR (400 MHz, $CDCl_3$)

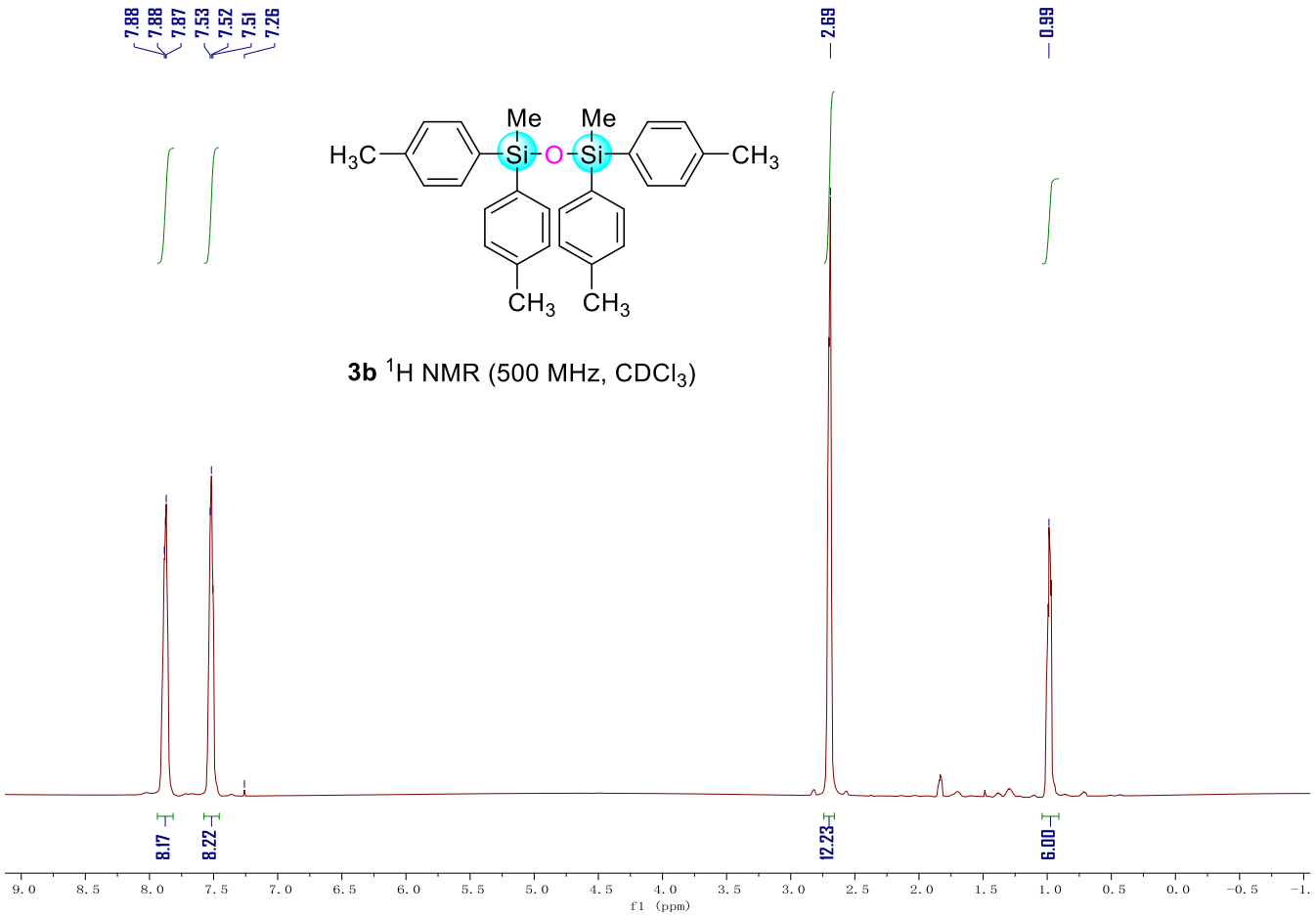


from ibuprofen

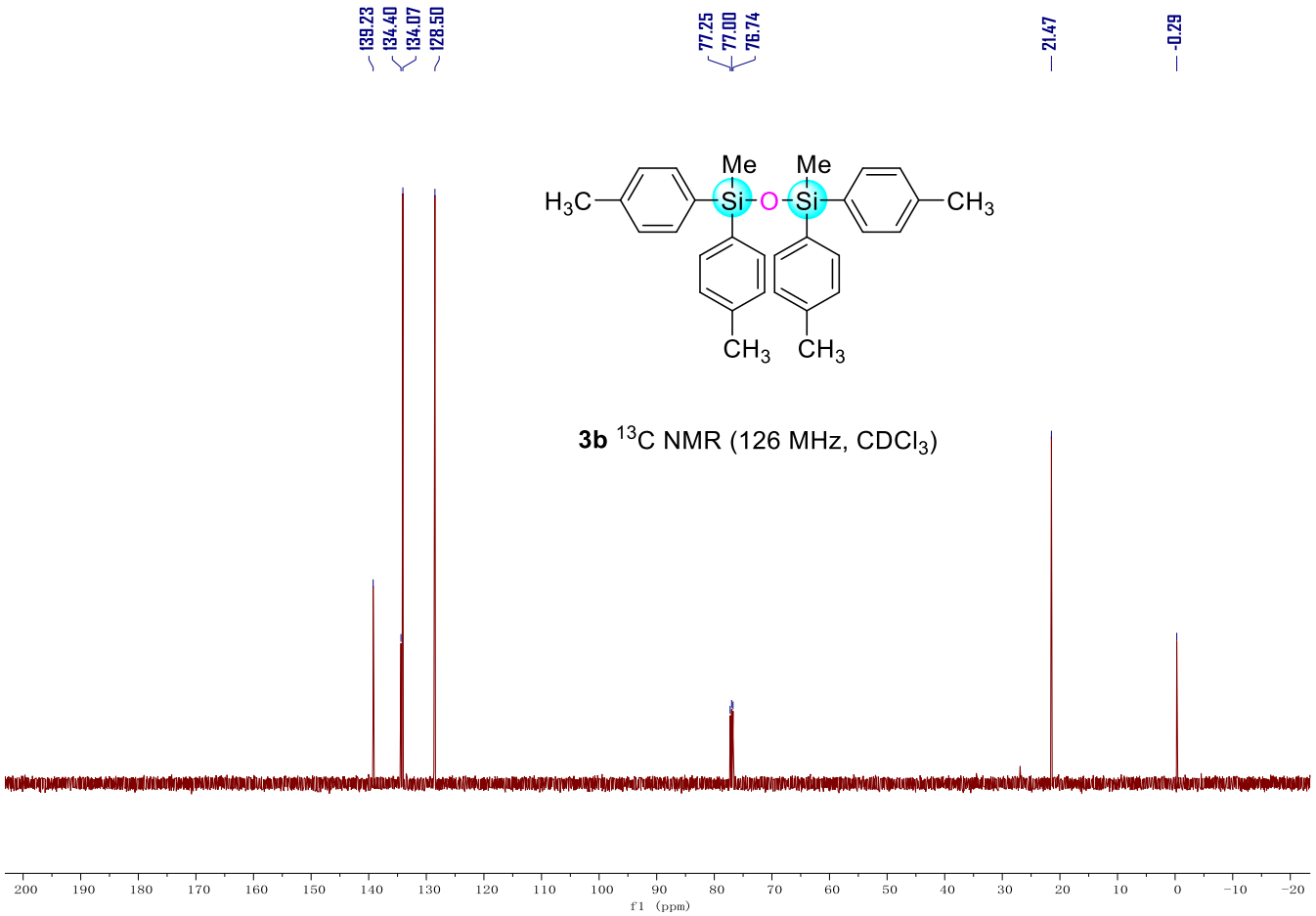
2w ^{1}H NMR (400 MHz, $CDCl_3$)



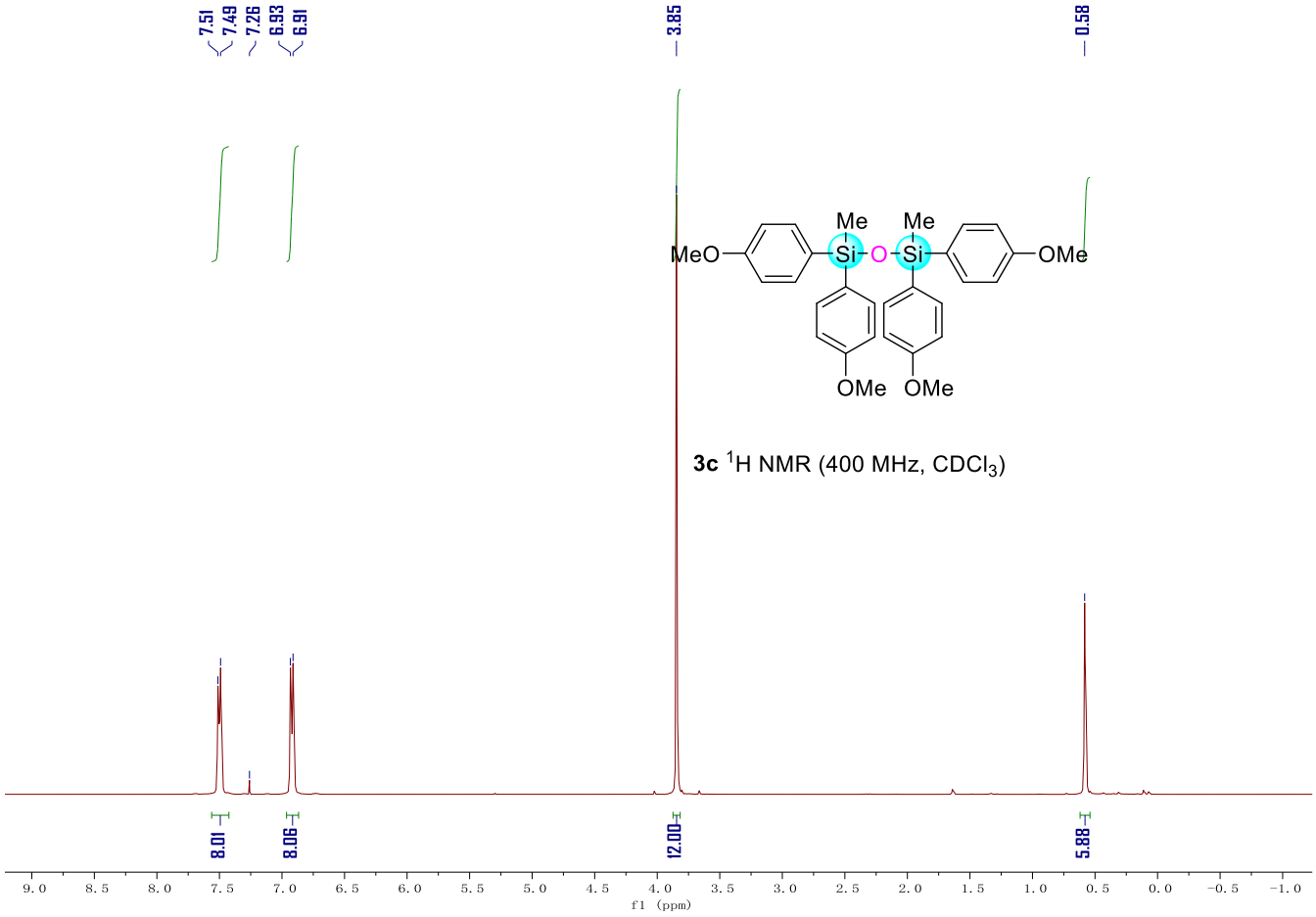
3a ^{1}H NMR (400 MHz, $CDCl_3$)



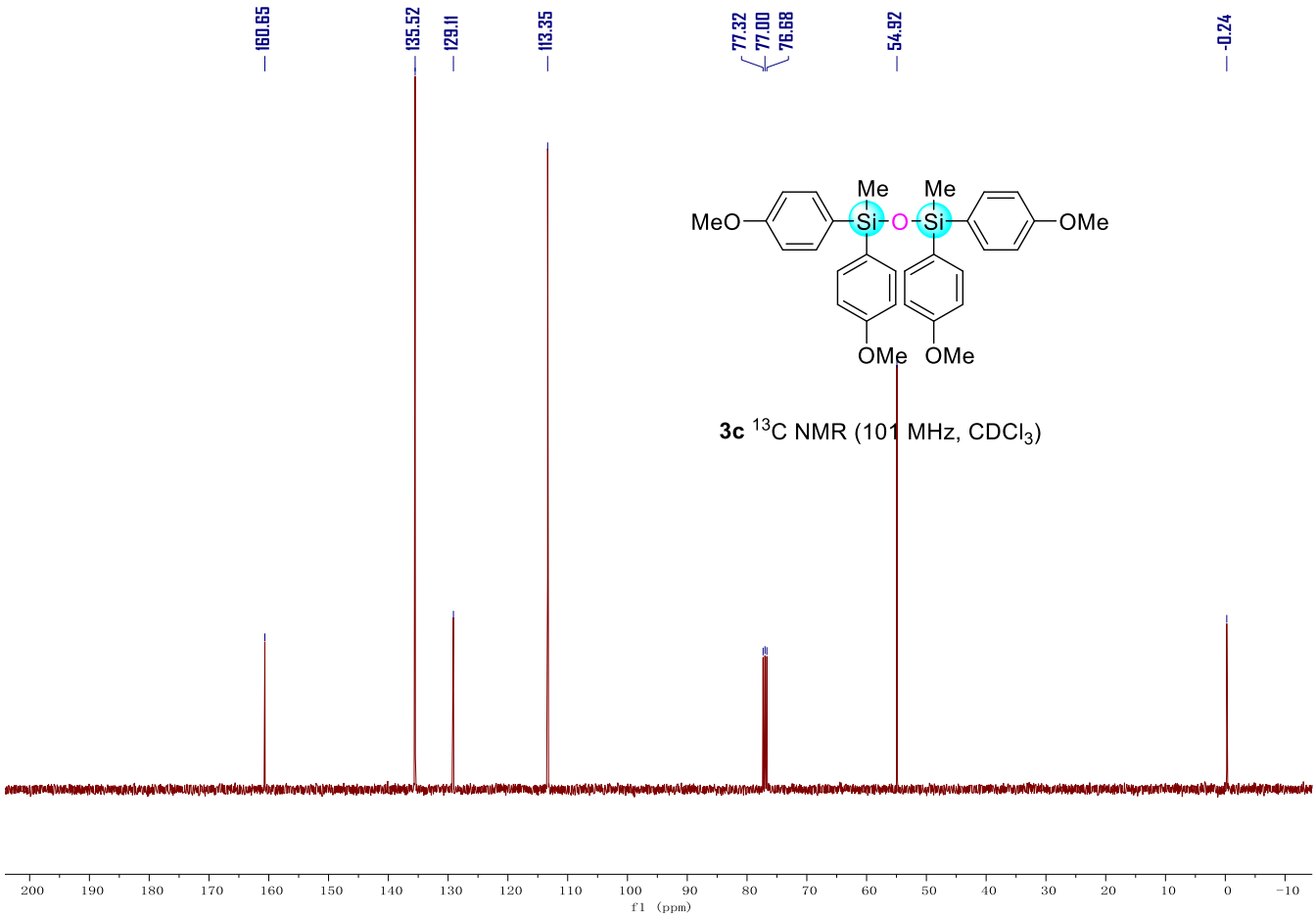
3b ^{1}H NMR (500 MHz, $CDCl_3$)



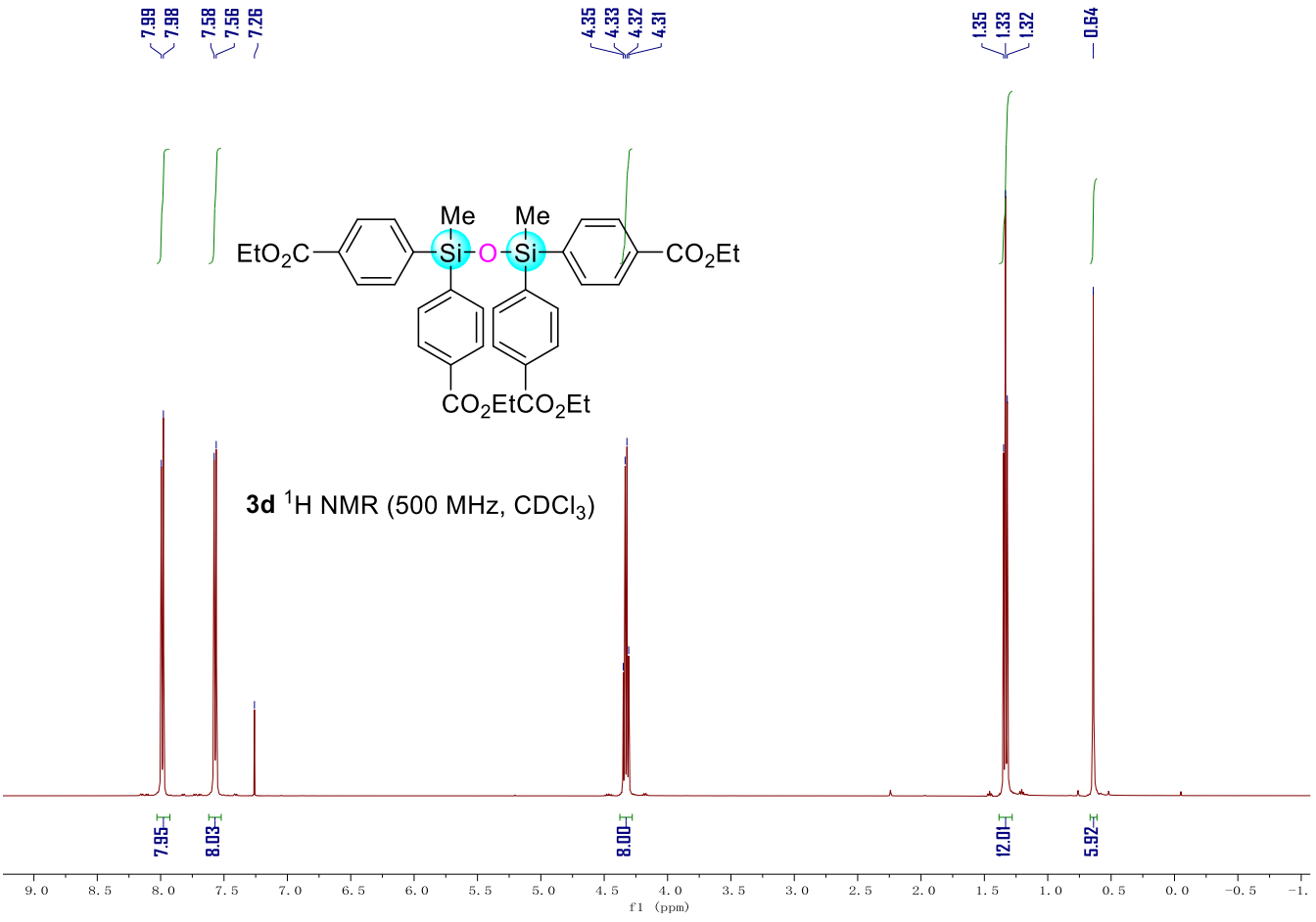
3b ^{13}C NMR (126 MHz, $CDCl_3$)



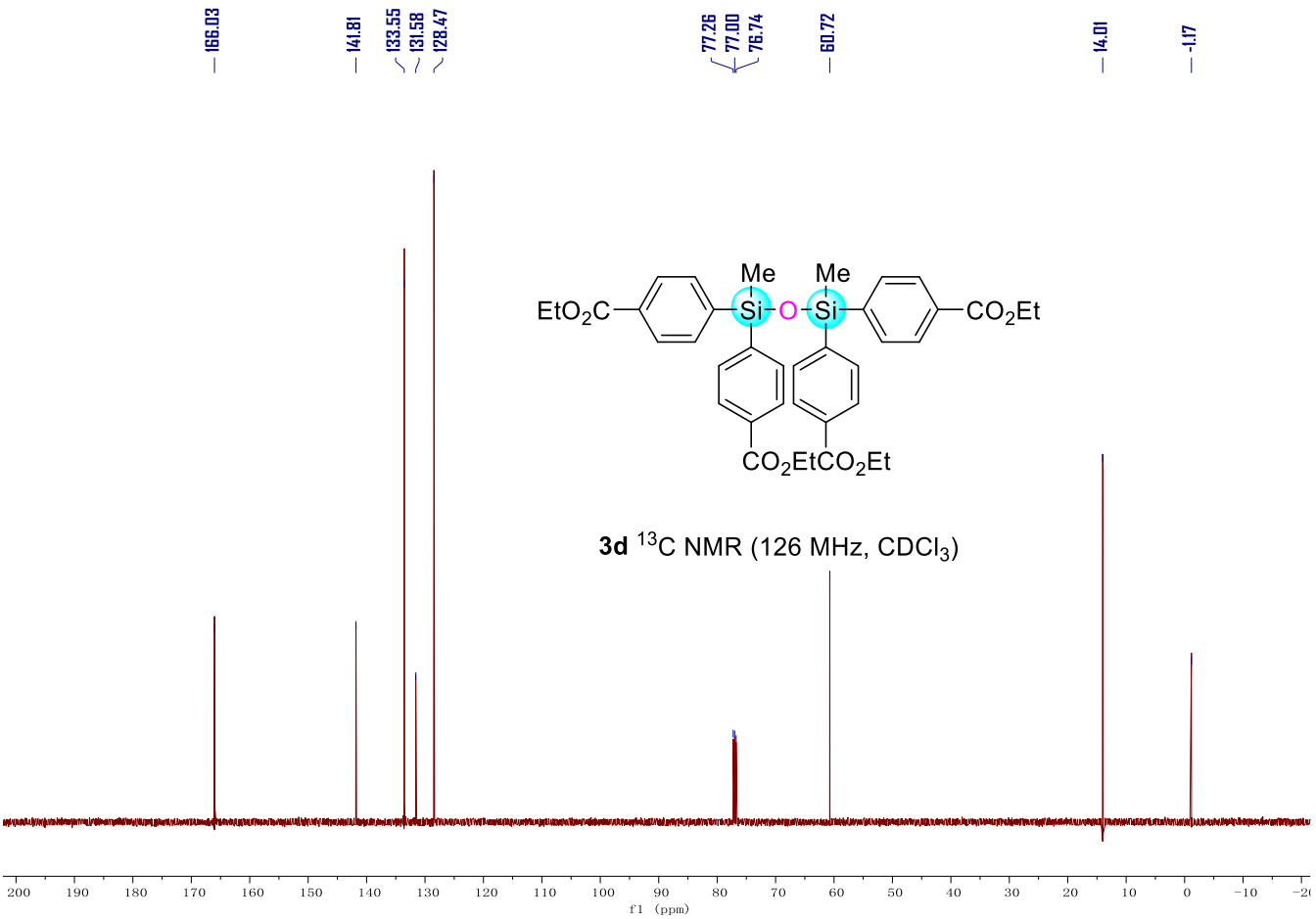
3c ^{1}H NMR (400 MHz, $CDCl_3$)



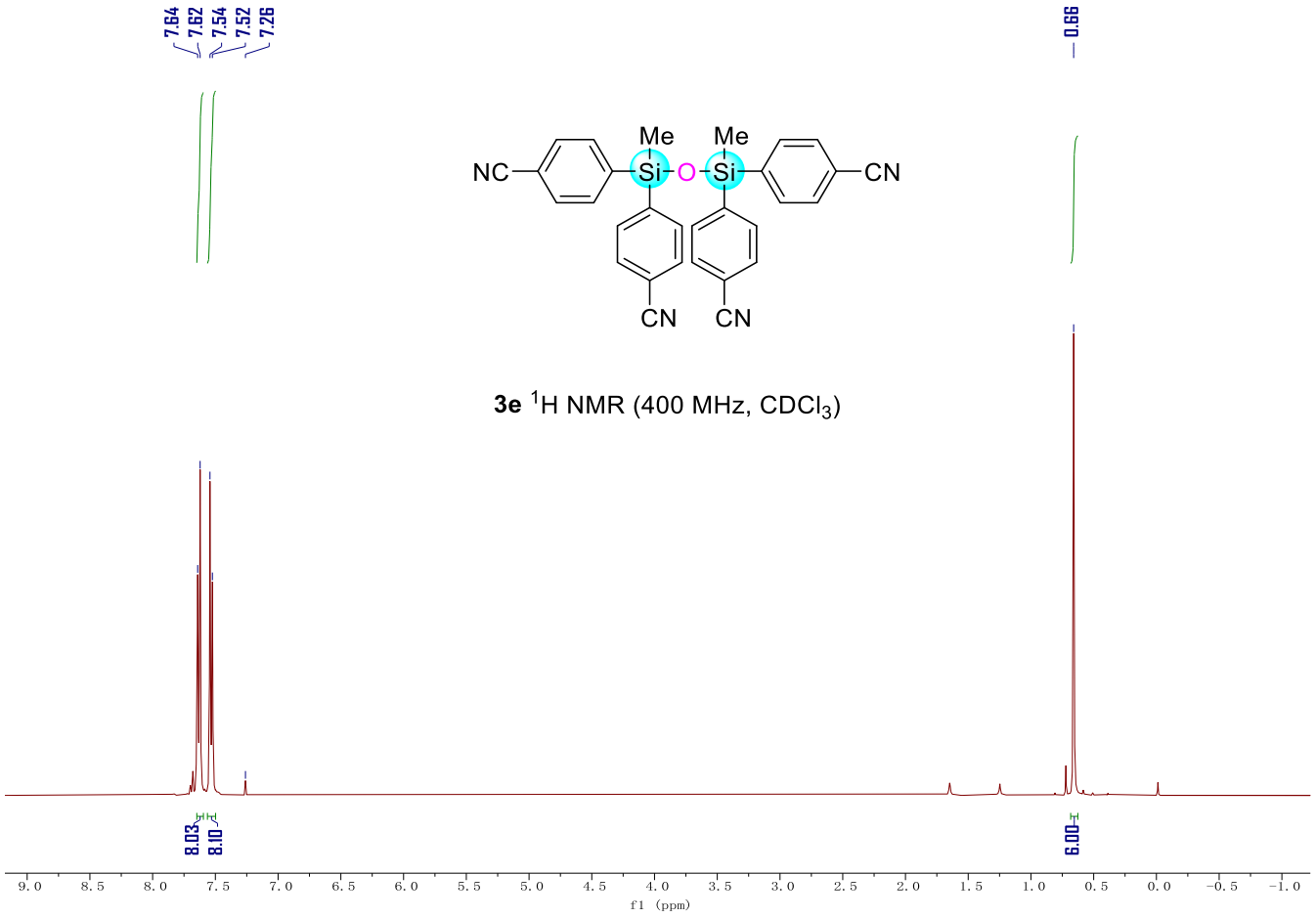
3c ^{13}C NMR (101 MHz, $CDCl_3$)



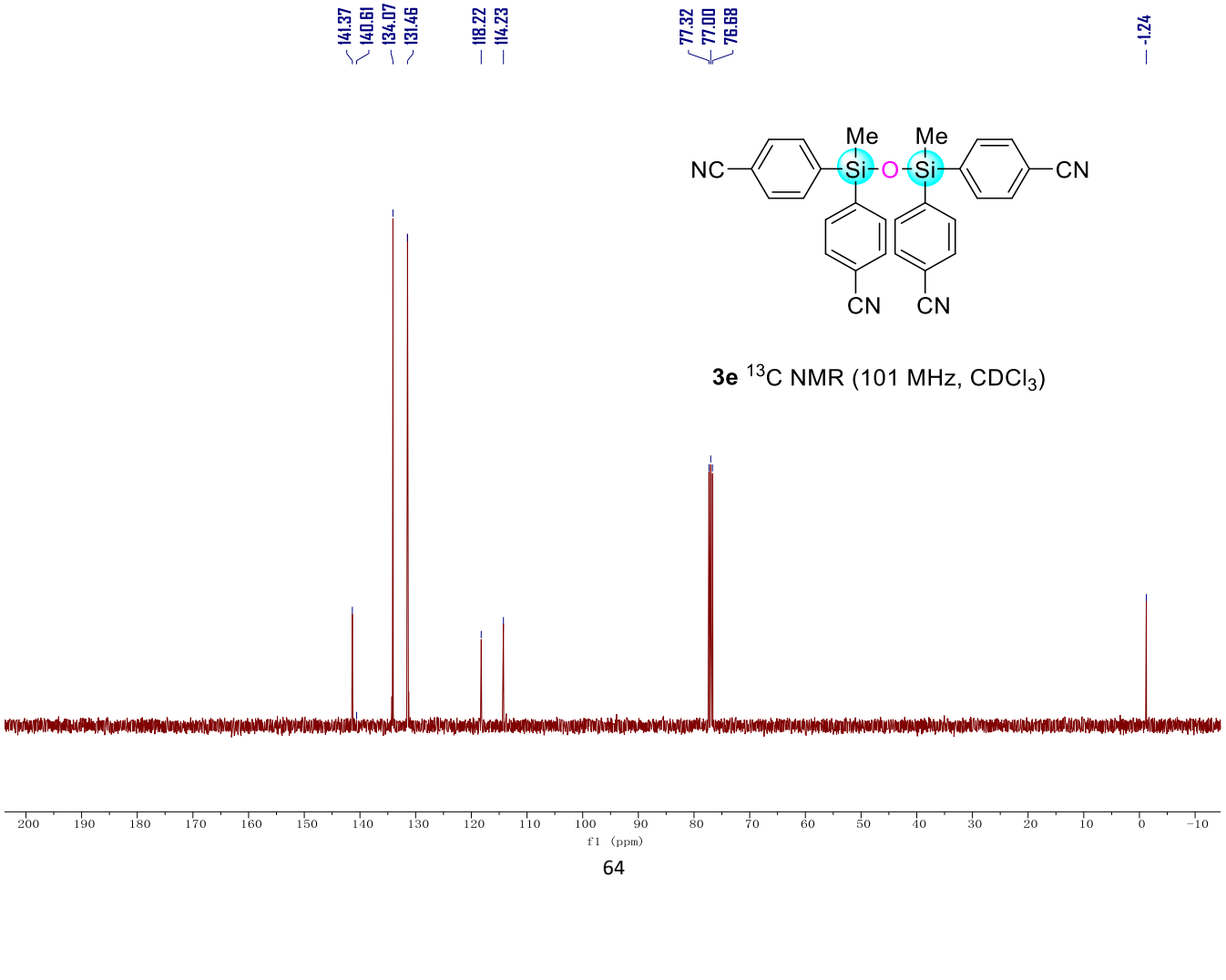
3d ^{1}H NMR (500 MHz, $CDCl_3$)



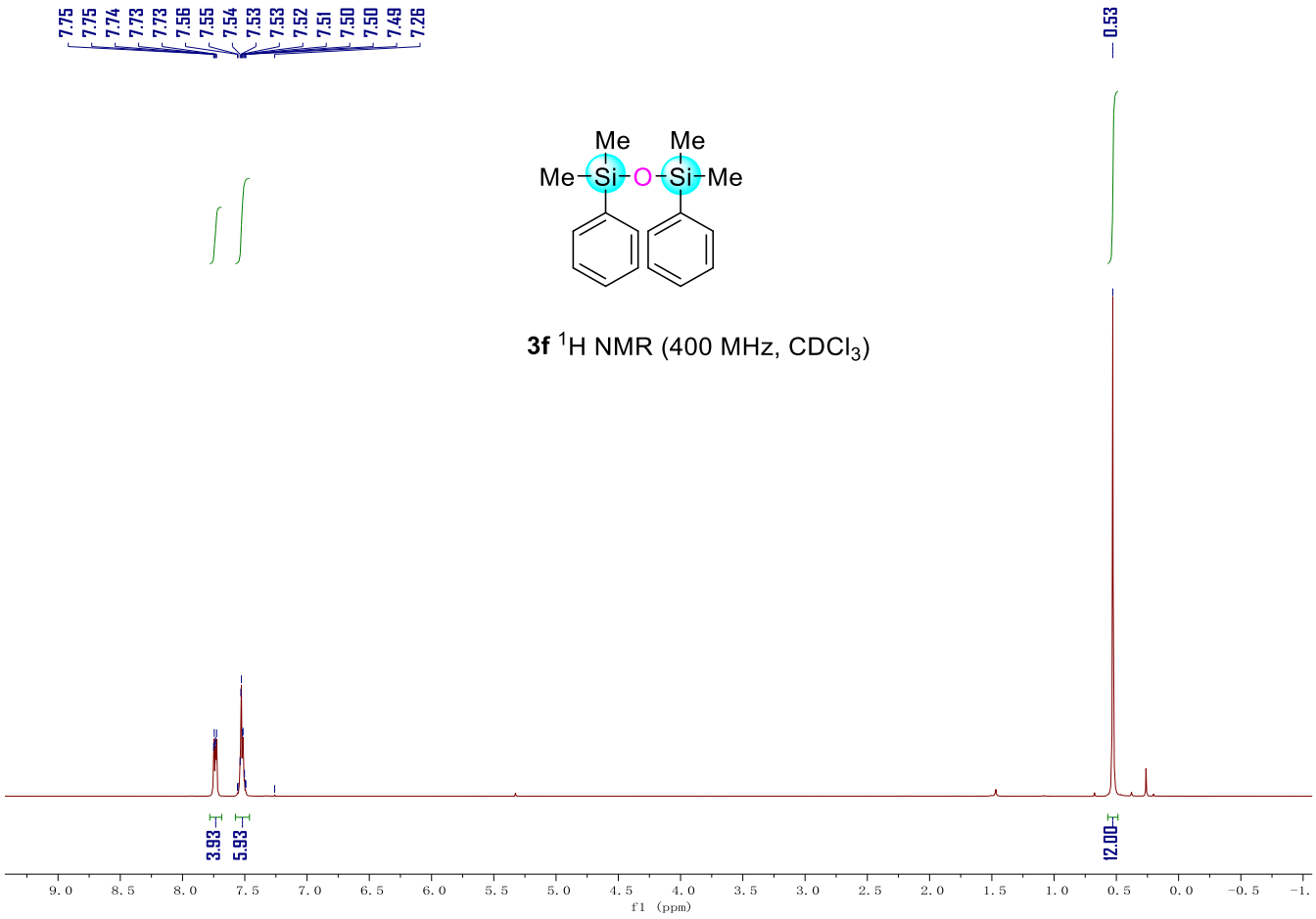
3d ^{13}C NMR (126 MHz, $CDCl_3$)



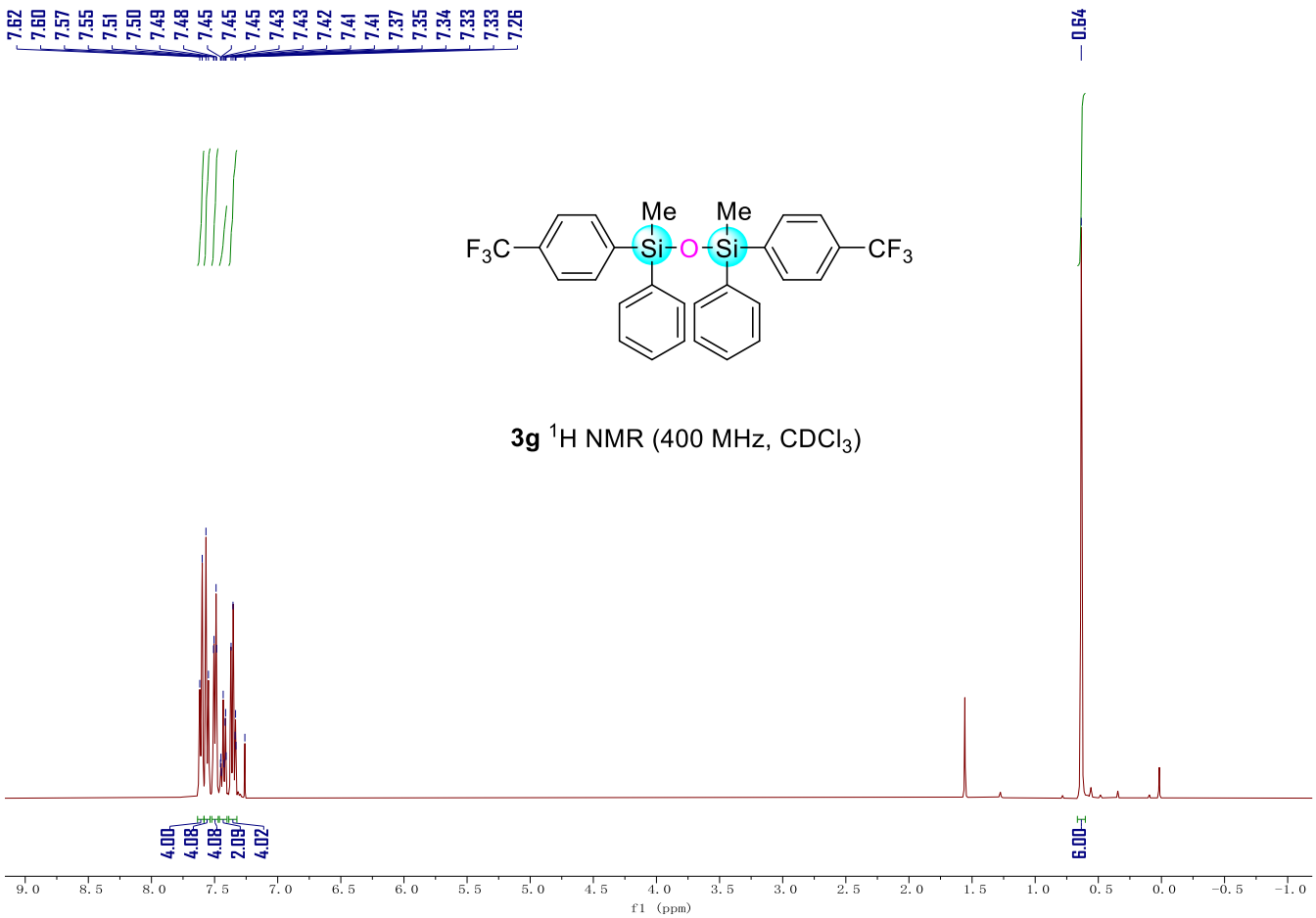
3e ^{1}H NMR (400 MHz, $CDCl_3$)



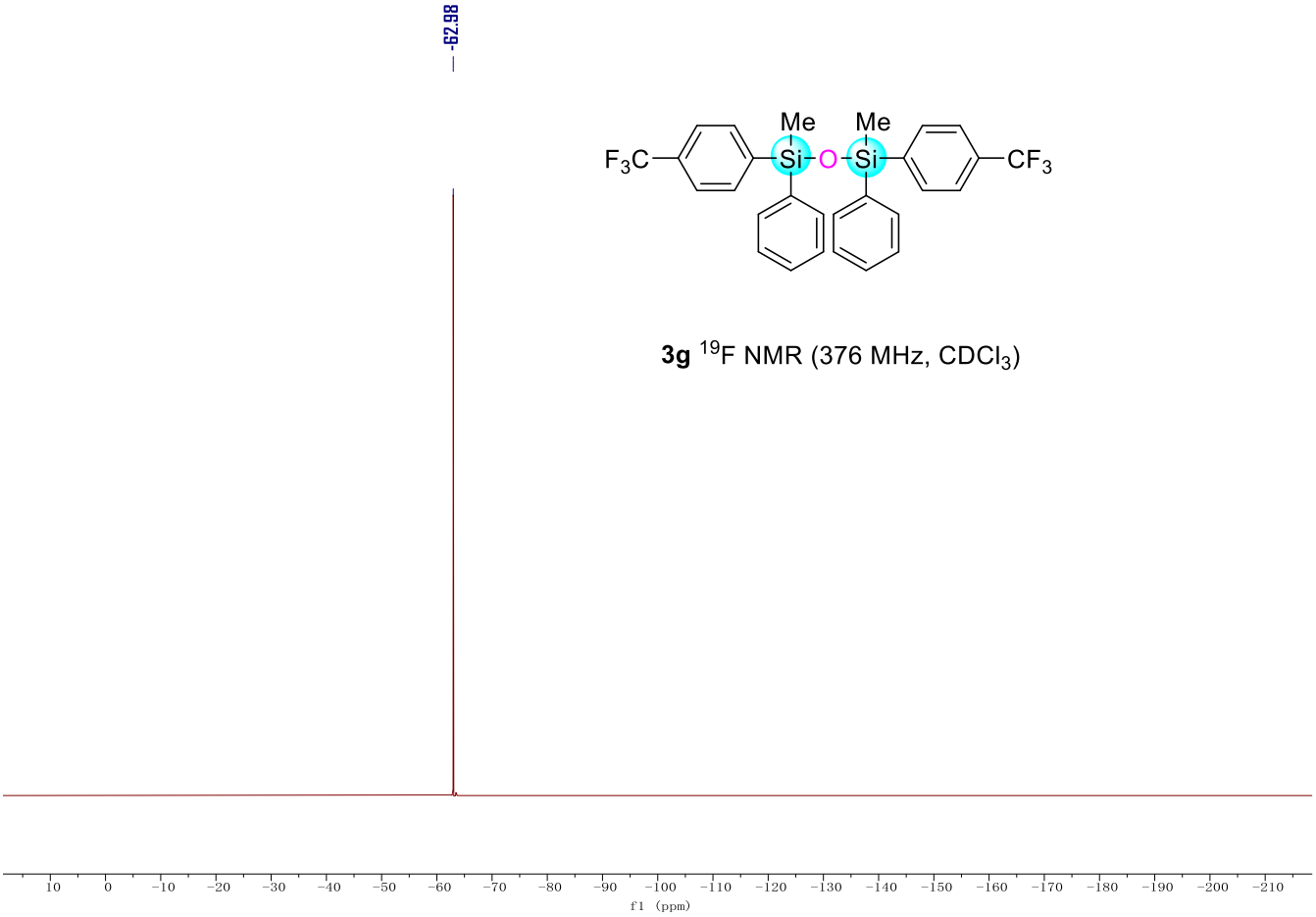
3e ^{13}C NMR (101 MHz, $CDCl_3$)



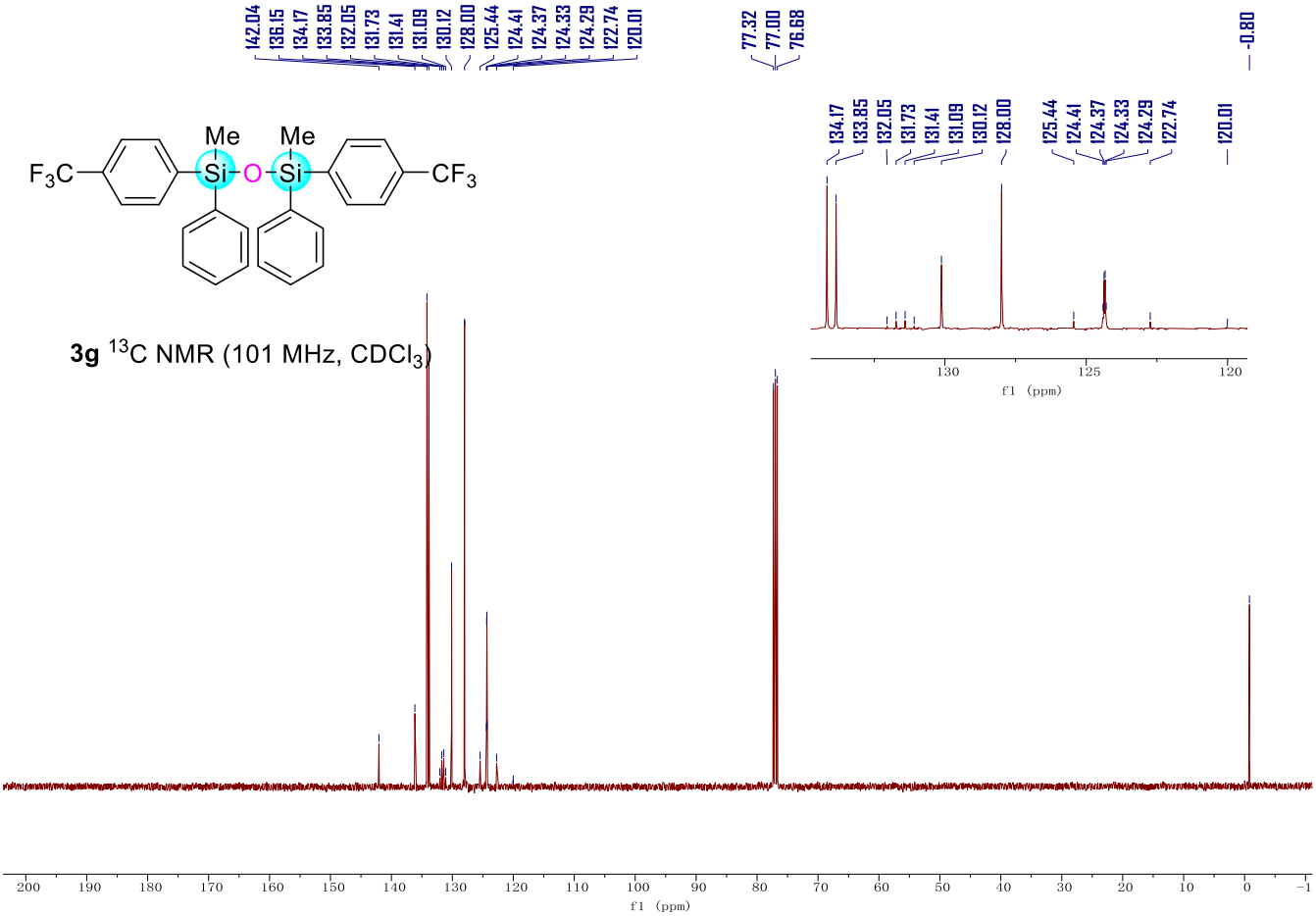
3f ^{1}H NMR (400 MHz, $CDCl_3$)



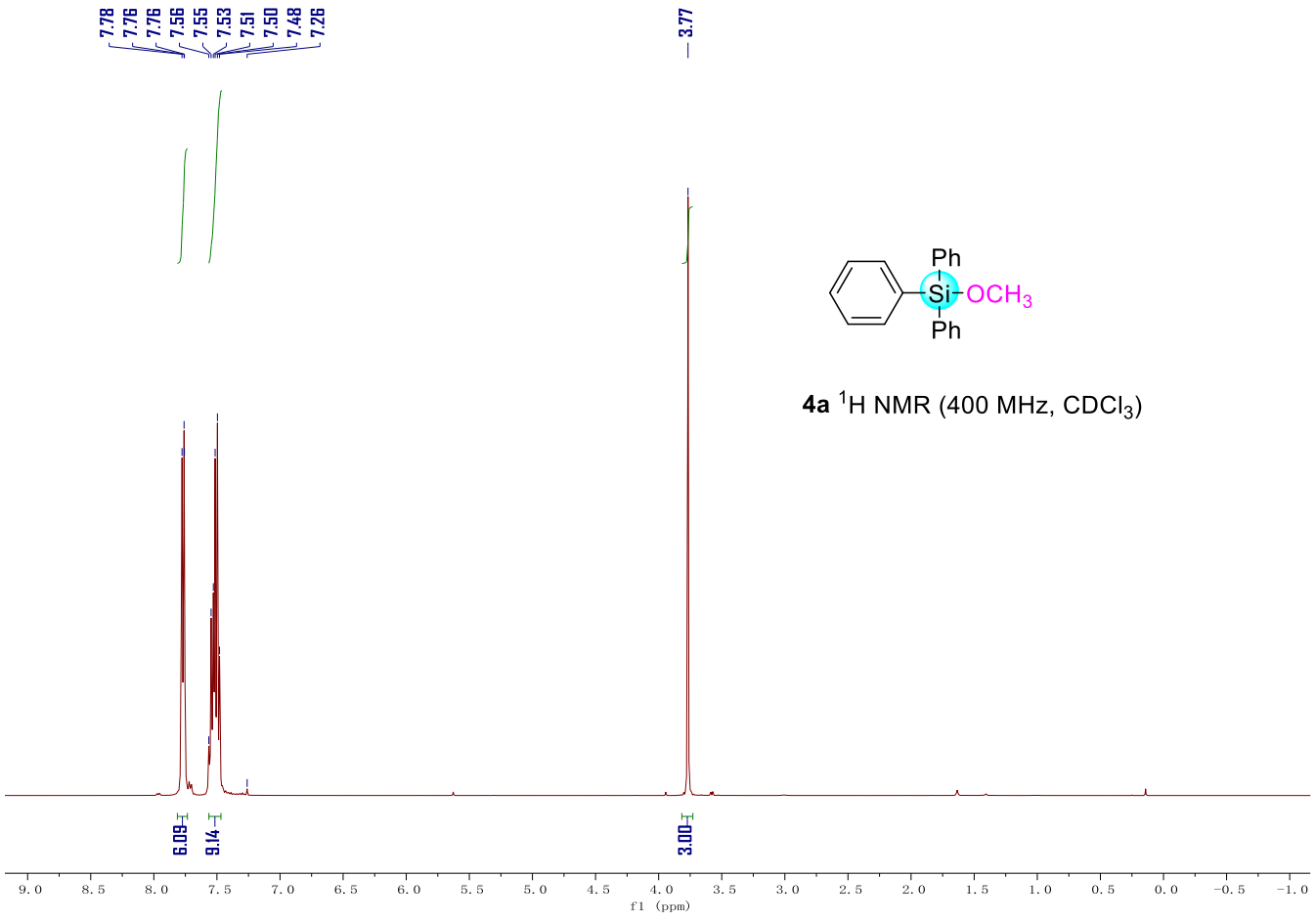
3g ^{1}H NMR (400 MHz, $CDCl_3$)



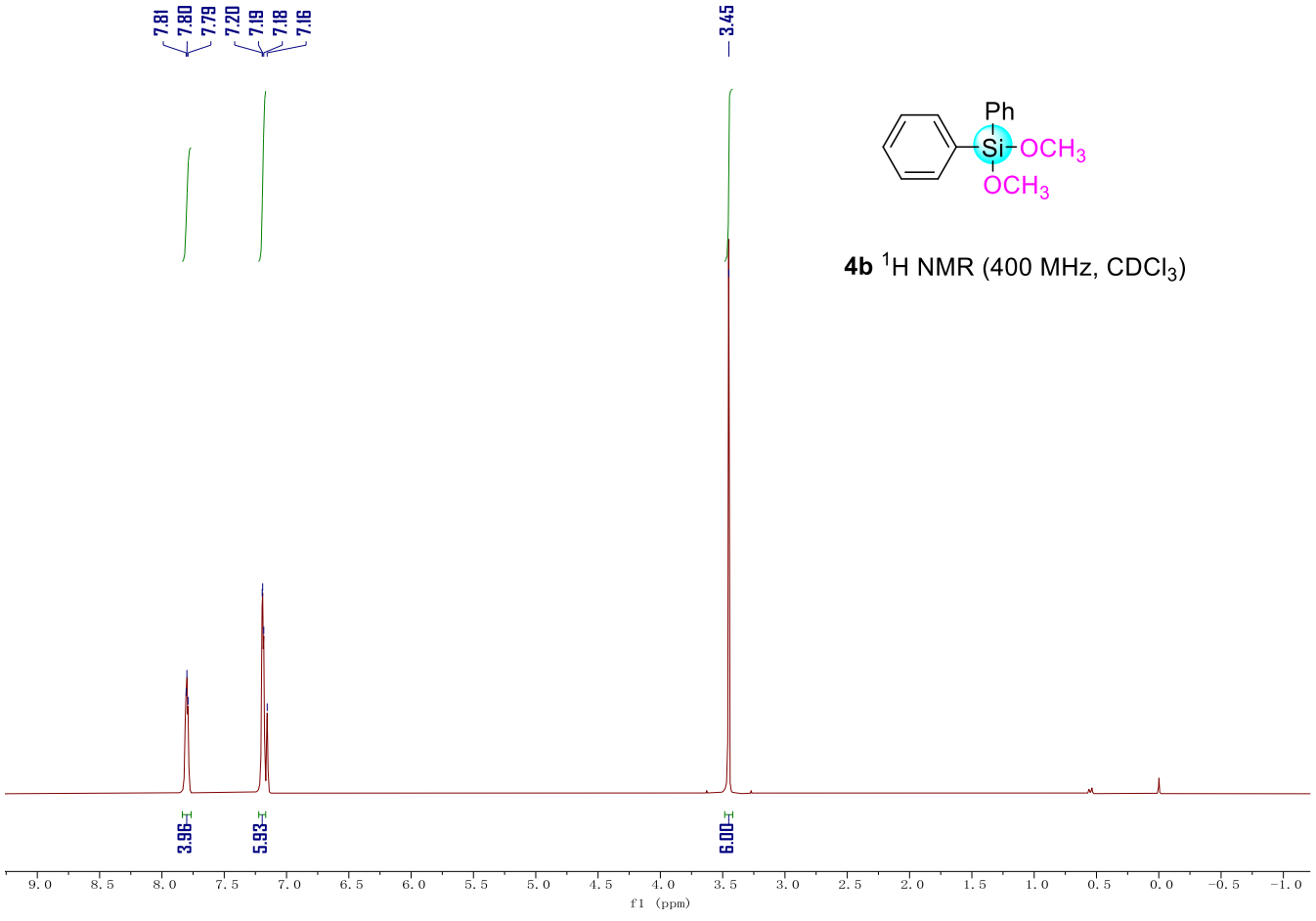
3g ^{19}F NMR (376 MHz, $CDCl_3$)



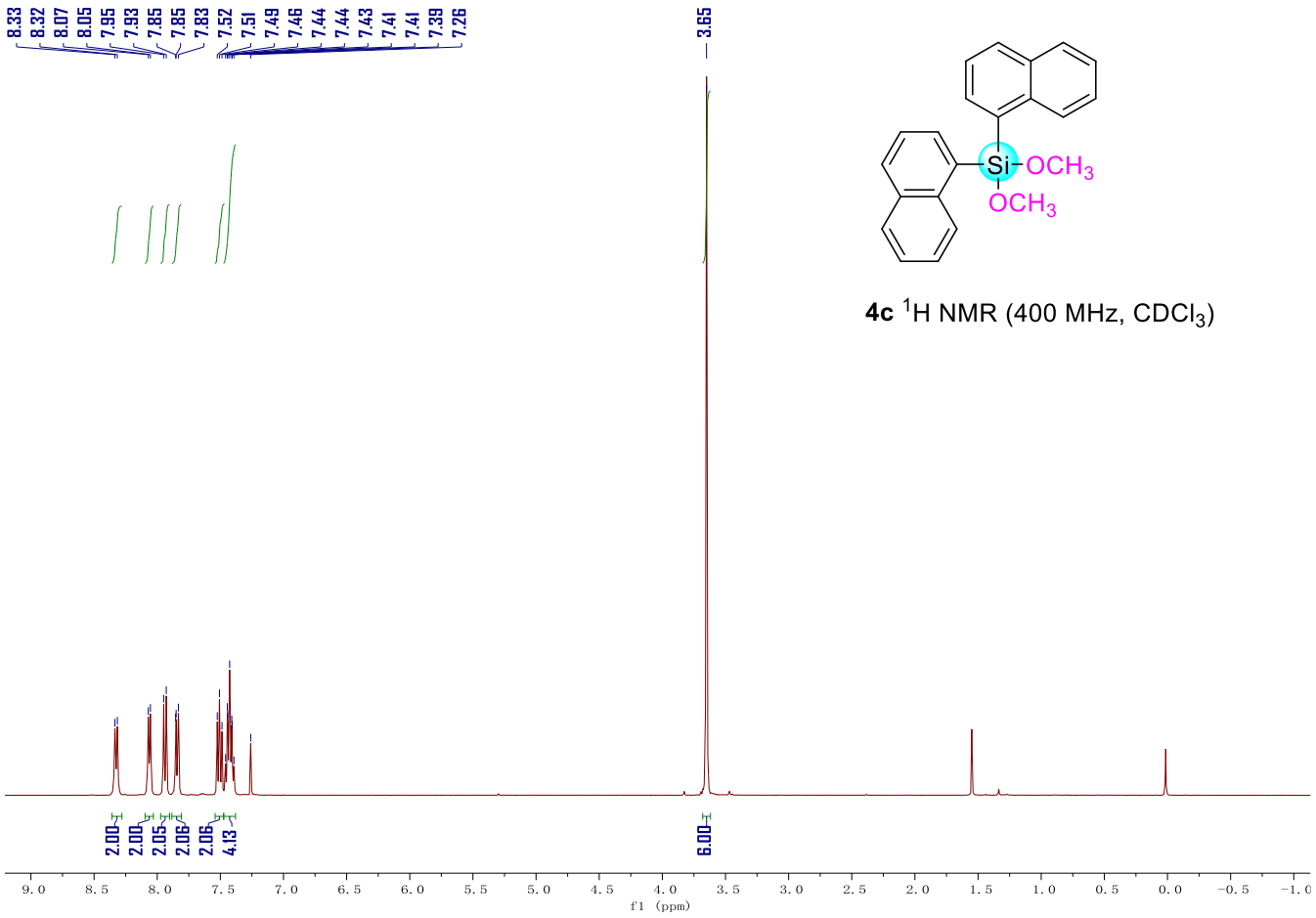
3g ^{13}C NMR (101 MHz, $CDCl_3$)



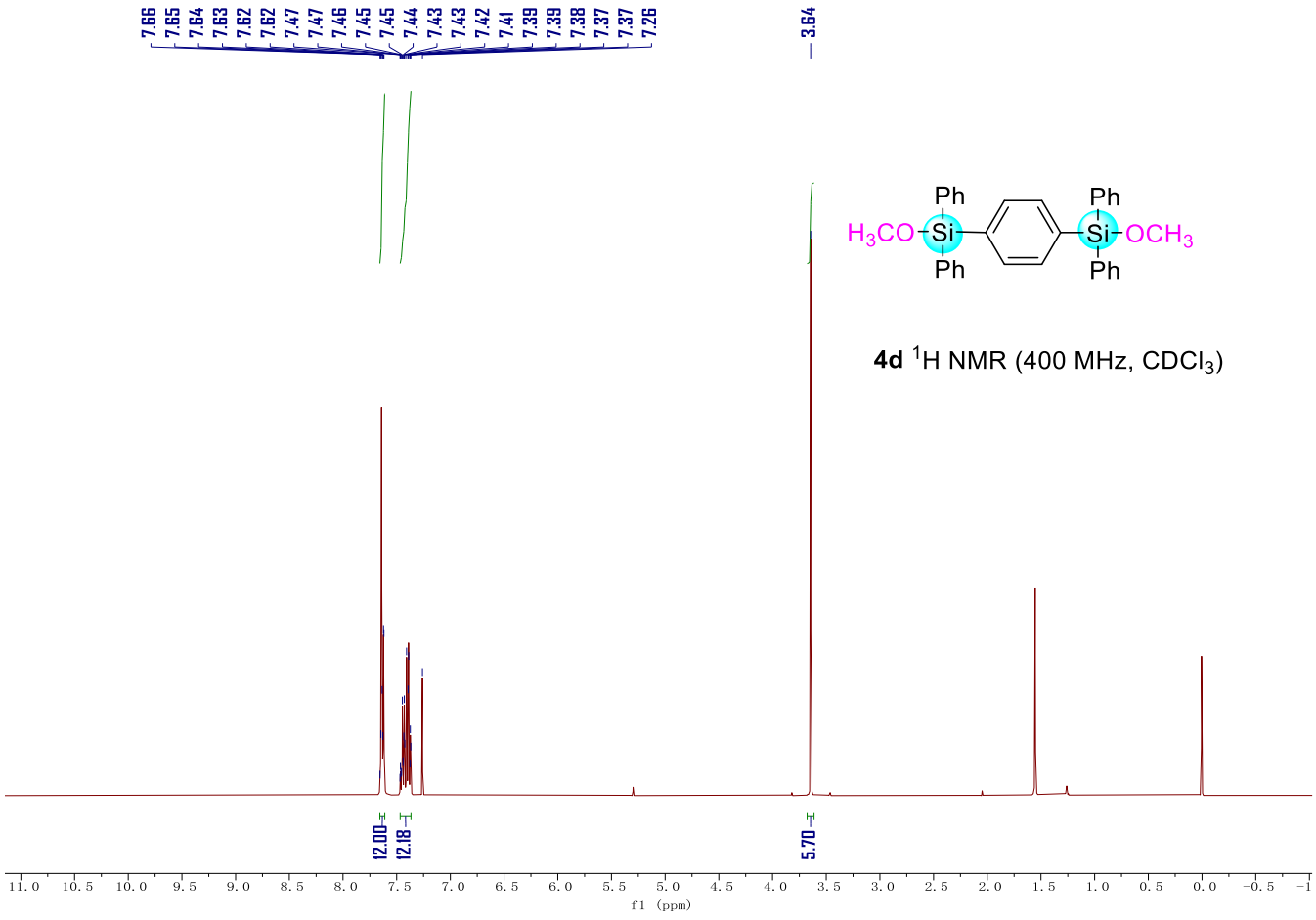
4a ^{1}H NMR (400 MHz, $CDCl_3$)



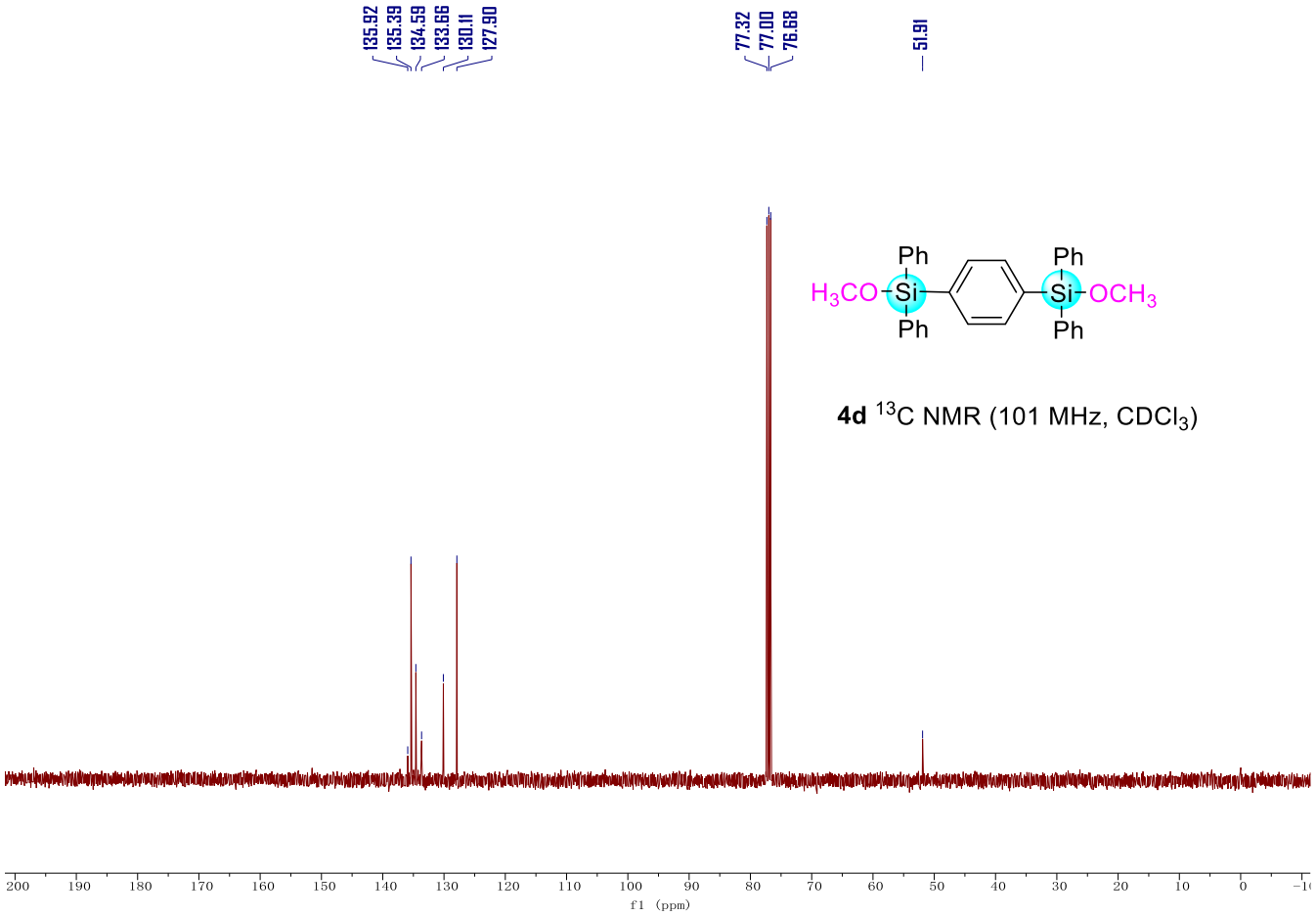
4b ^{1}H NMR (400 MHz, $CDCl_3$)



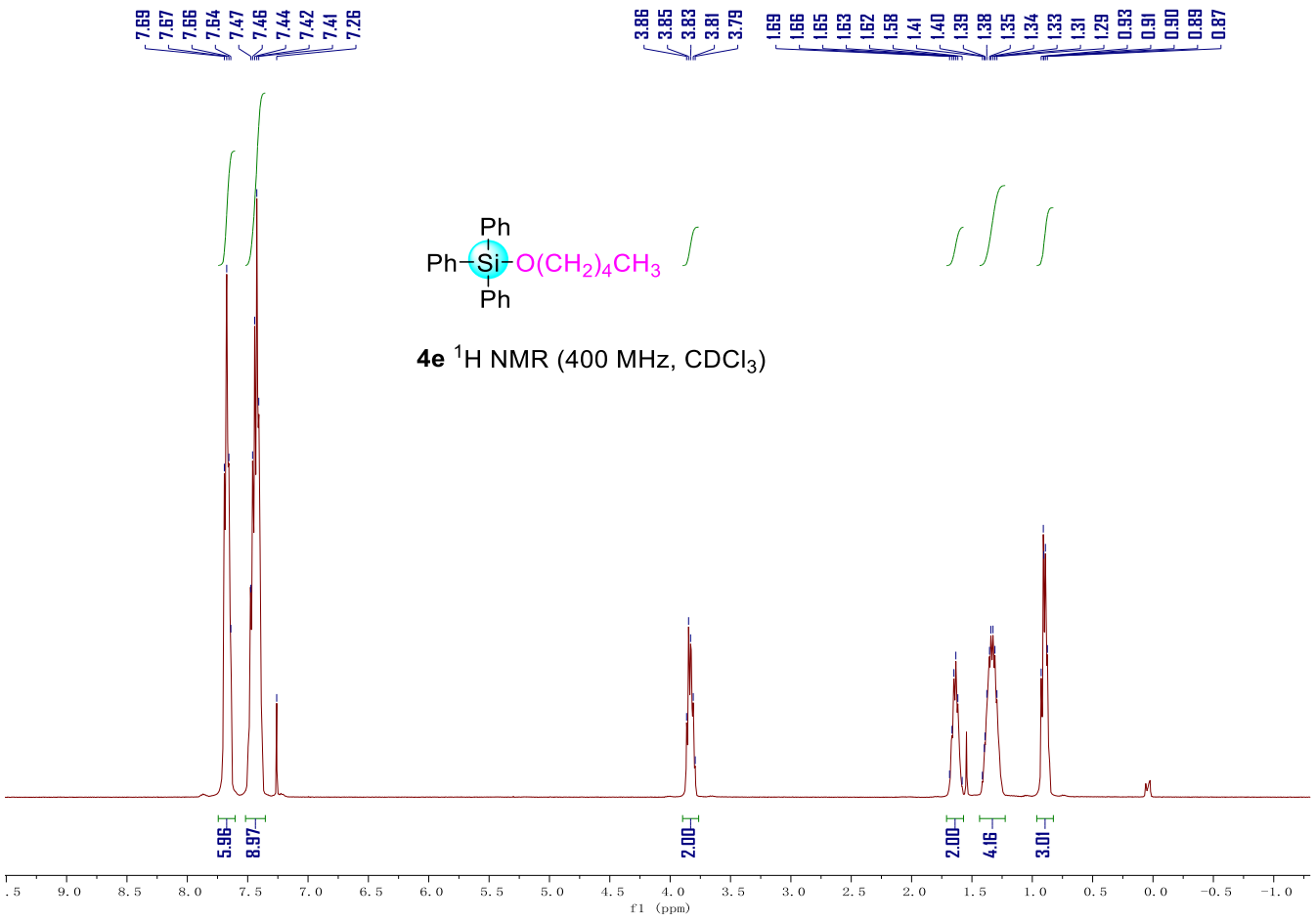
4c ^{1}H NMR (400 MHz, $CDCl_3$)



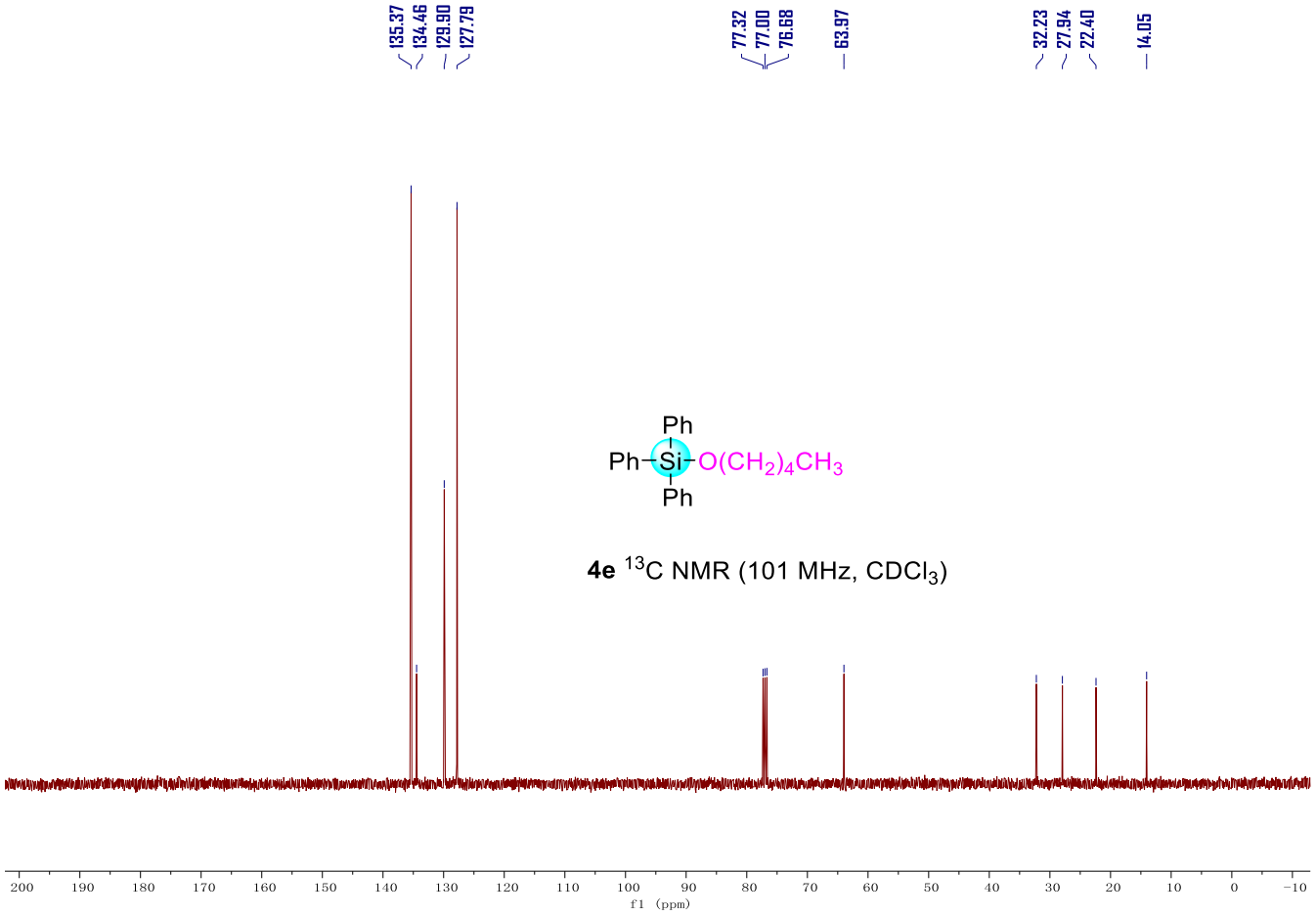
4d ^{1}H NMR (400 MHz, $CDCl_3$)



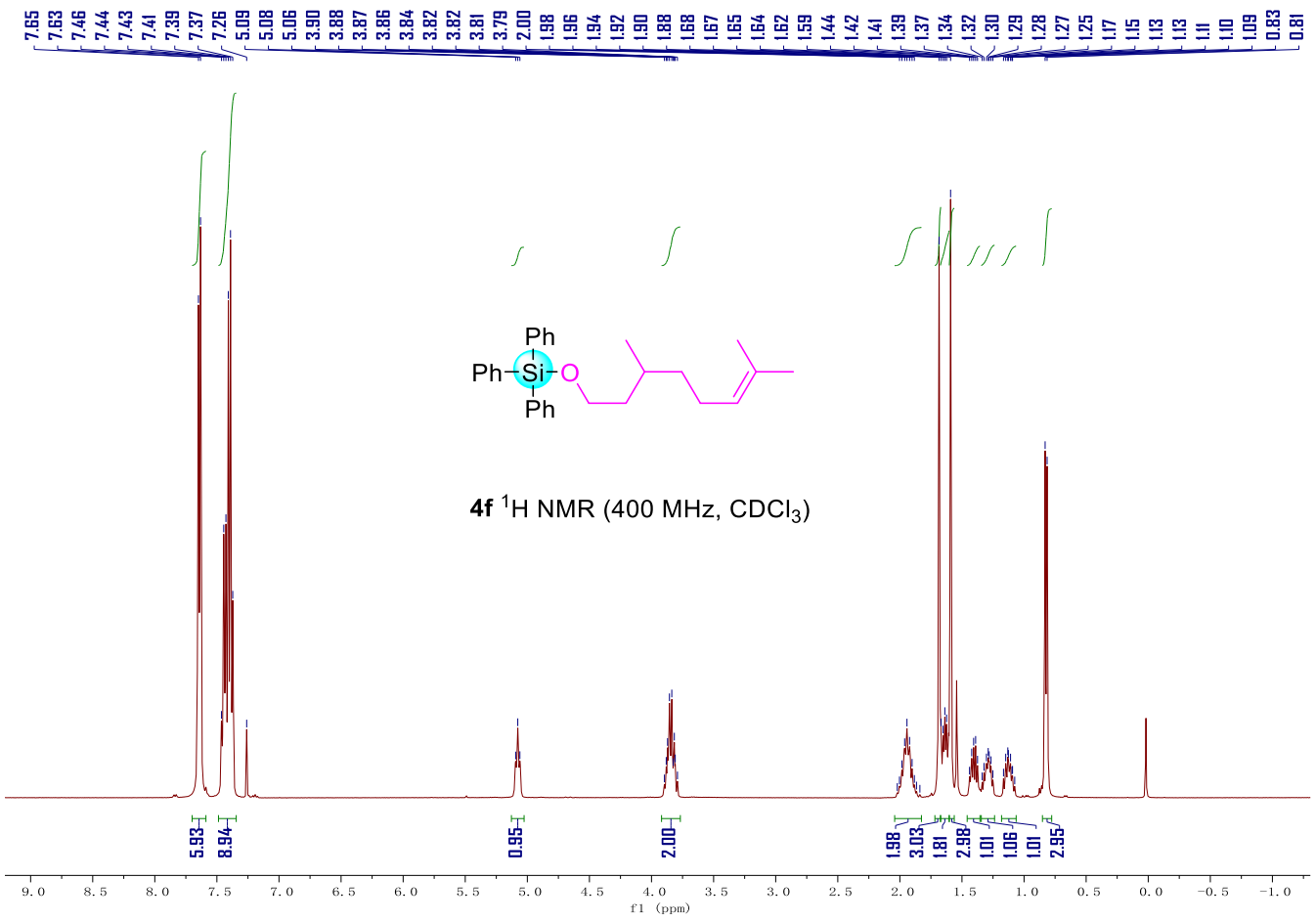
4d ^{13}C NMR (101 MHz, $CDCl_3$)



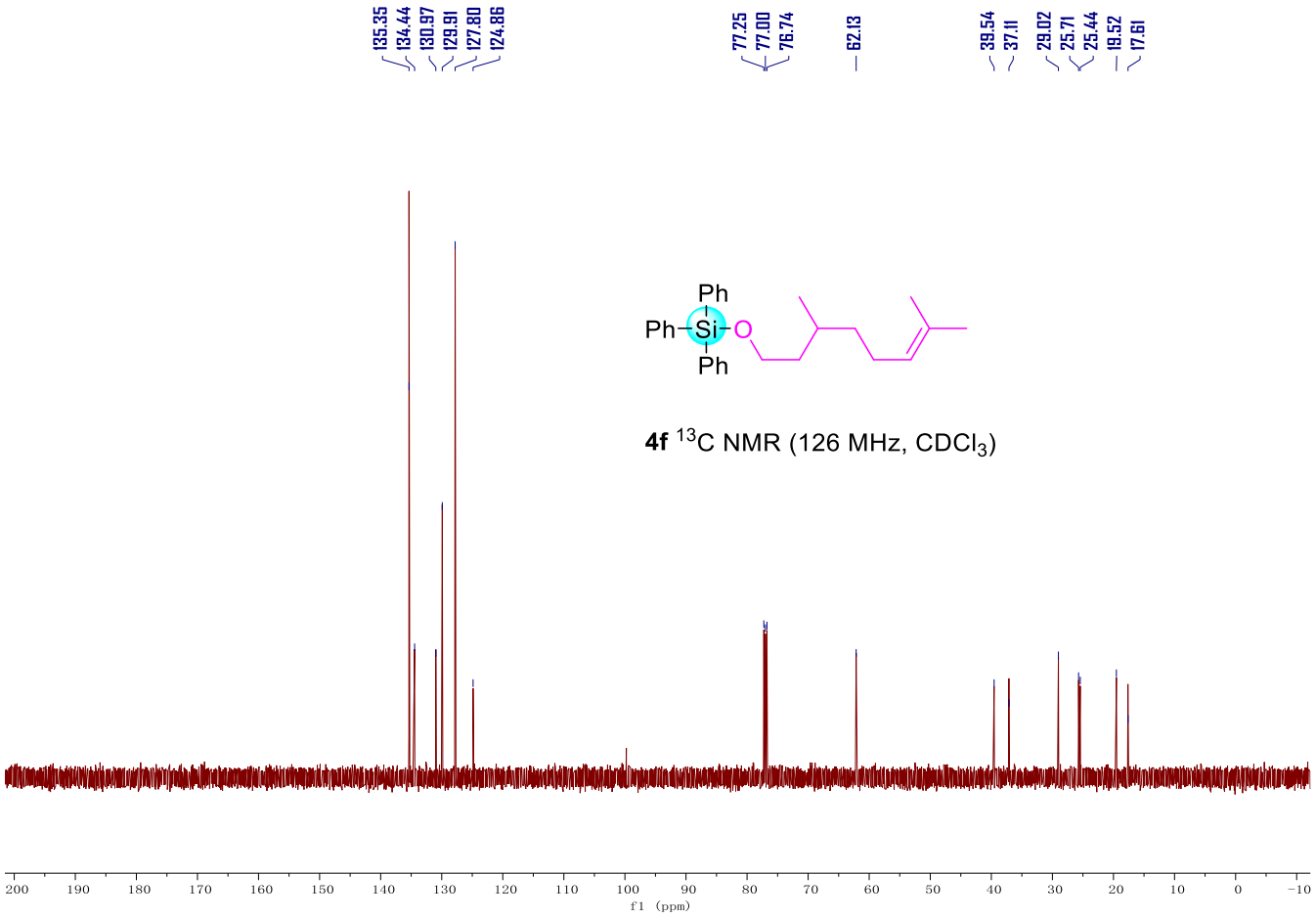
4e ^{1}H NMR (400 MHz, $CDCl_3$)



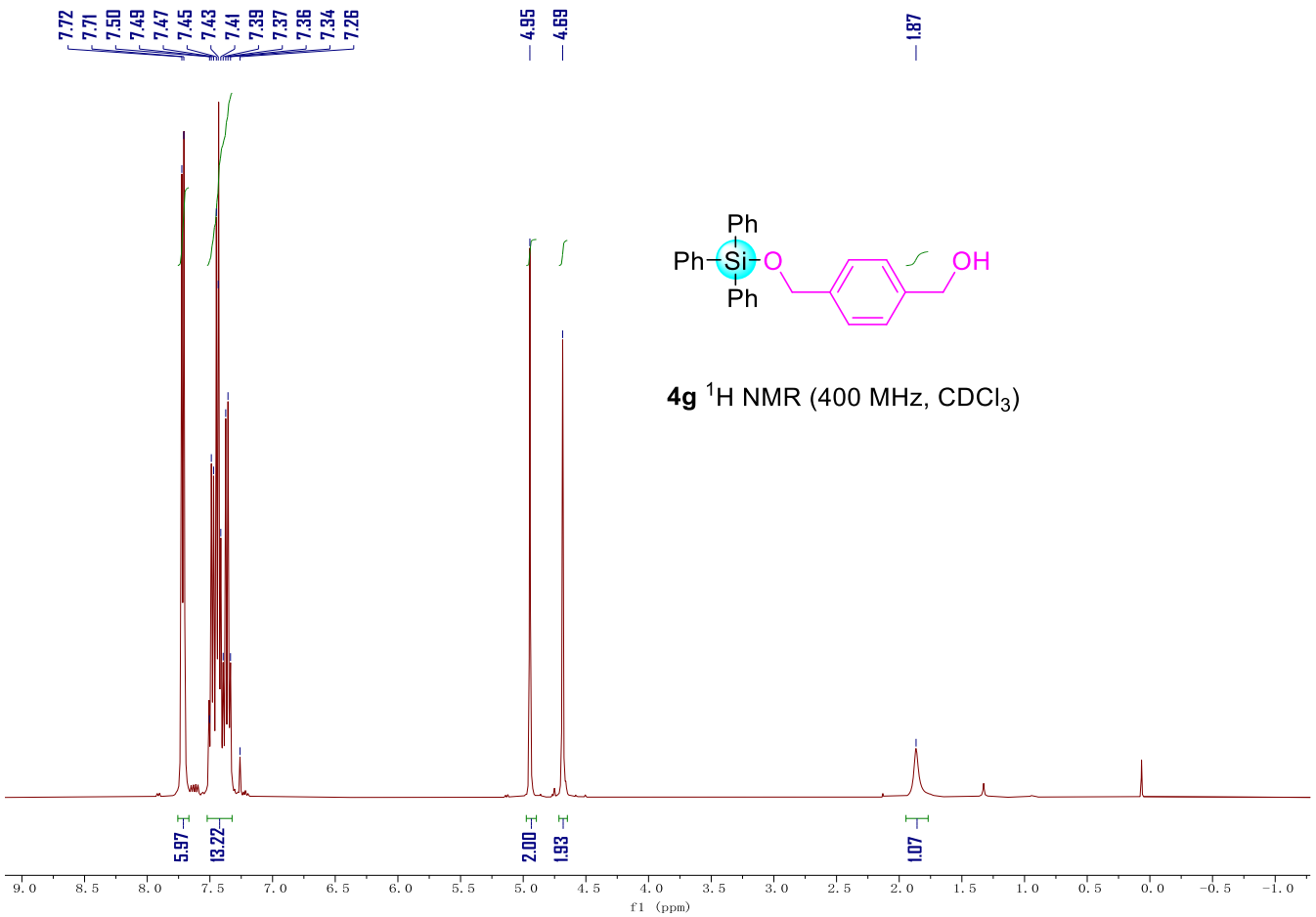
4e ^{13}C NMR (101 MHz, $CDCl_3$)



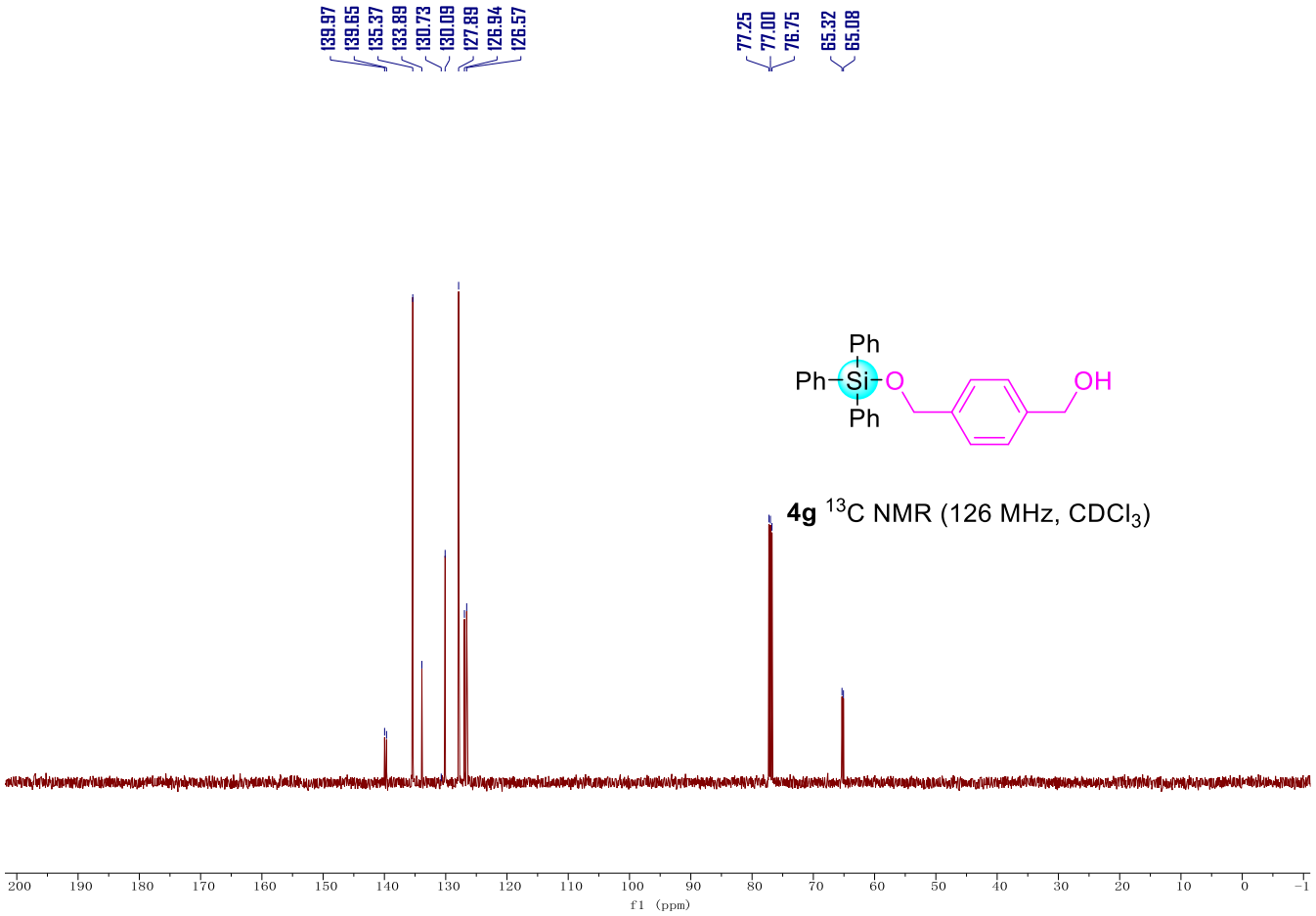
4f ^{1}H NMR (400 MHz, $CDCl_3$)



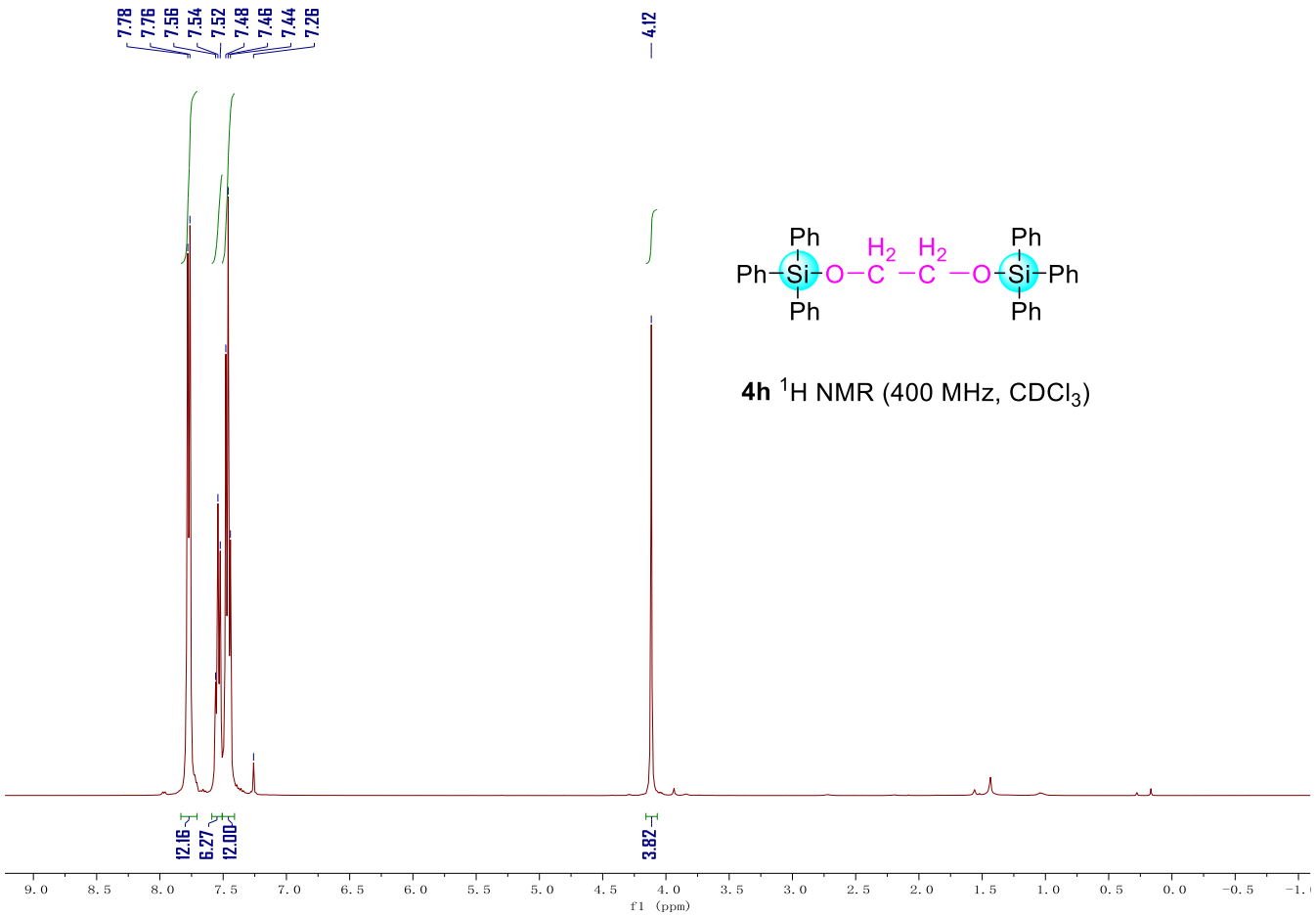
4f ^{13}C NMR (126 MHz, $CDCl_3$)



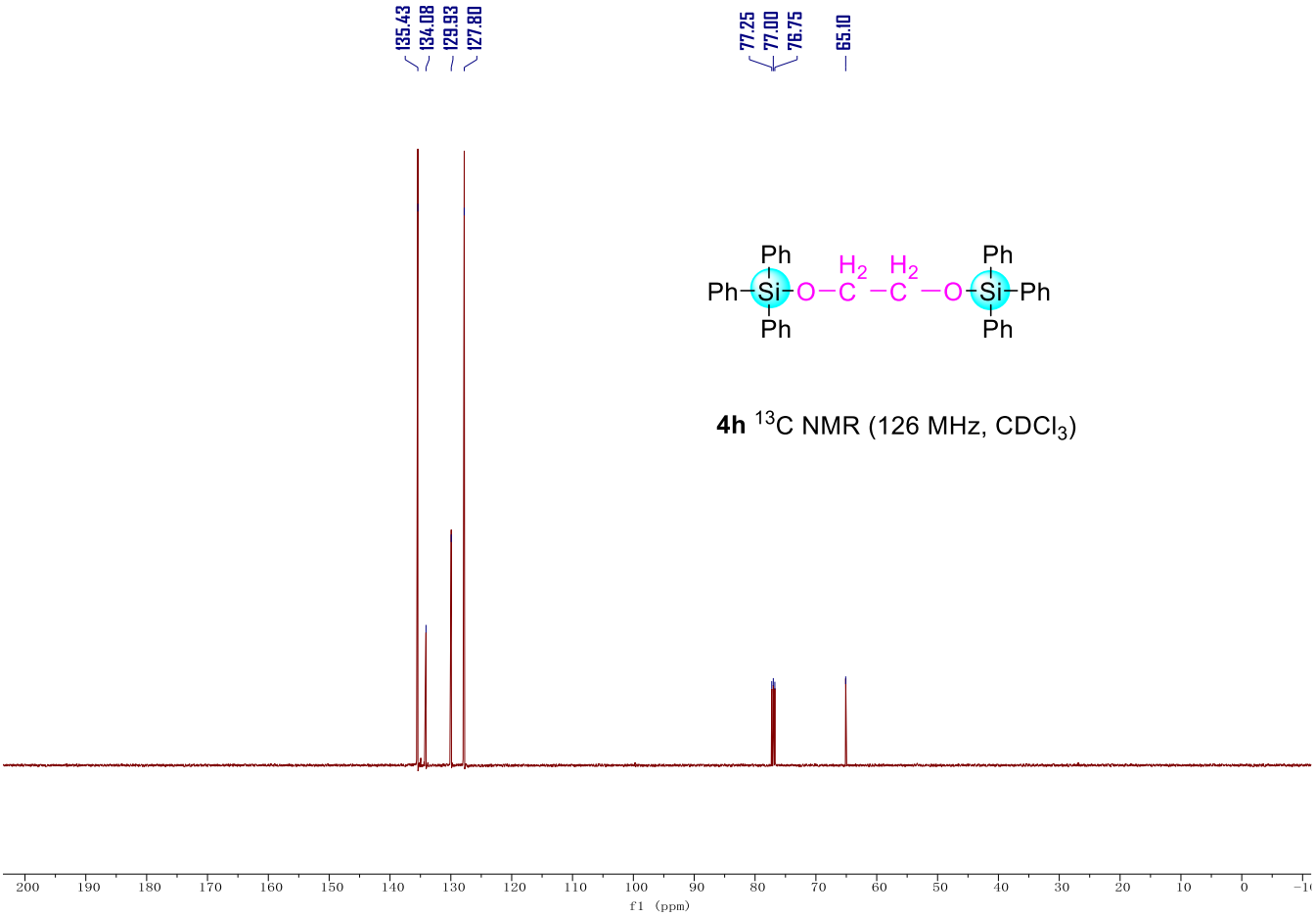
4g ^{1}H NMR (400 MHz, $CDCl_3$)



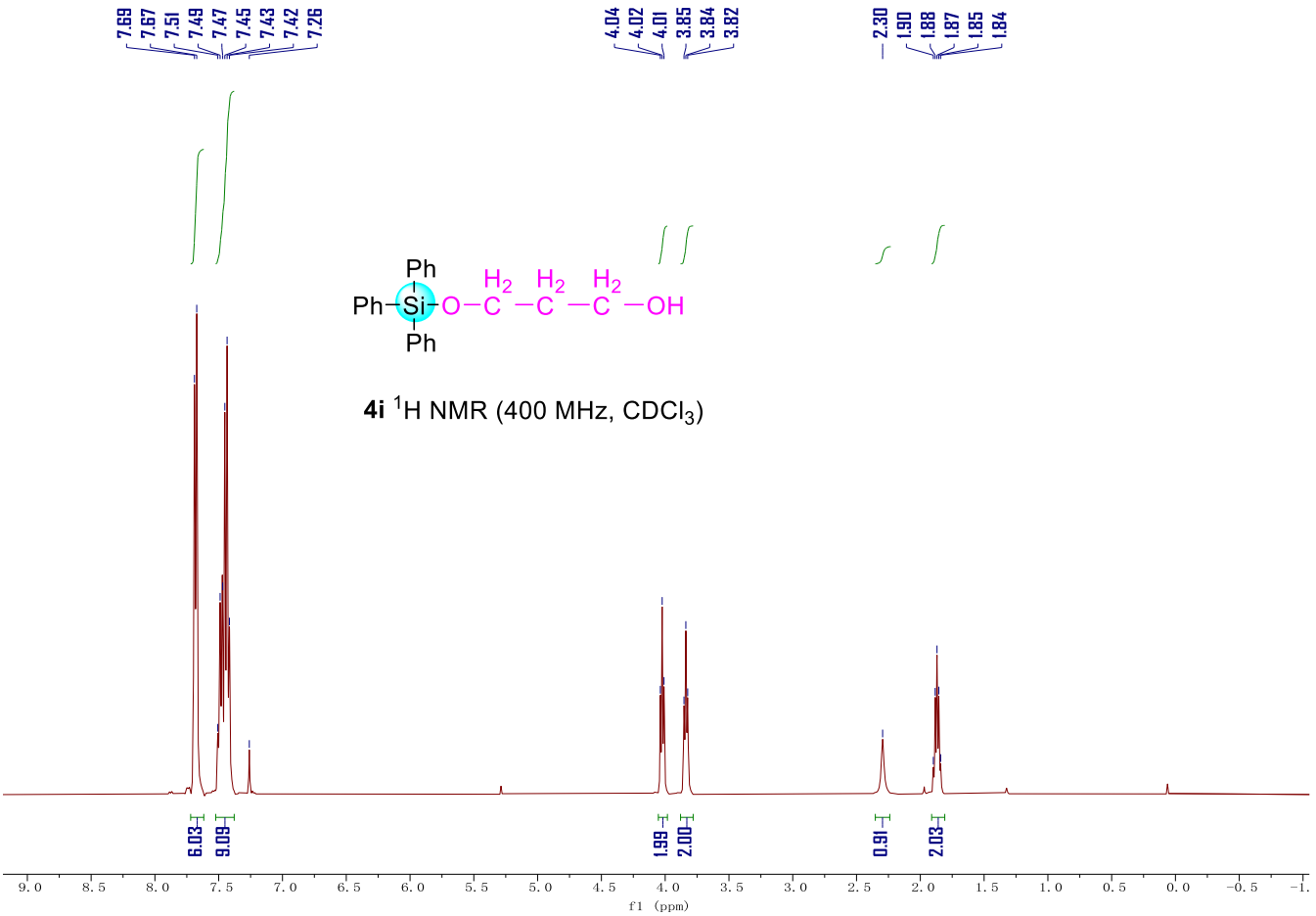
4g ^{13}C NMR (126 MHz, $CDCl_3$)



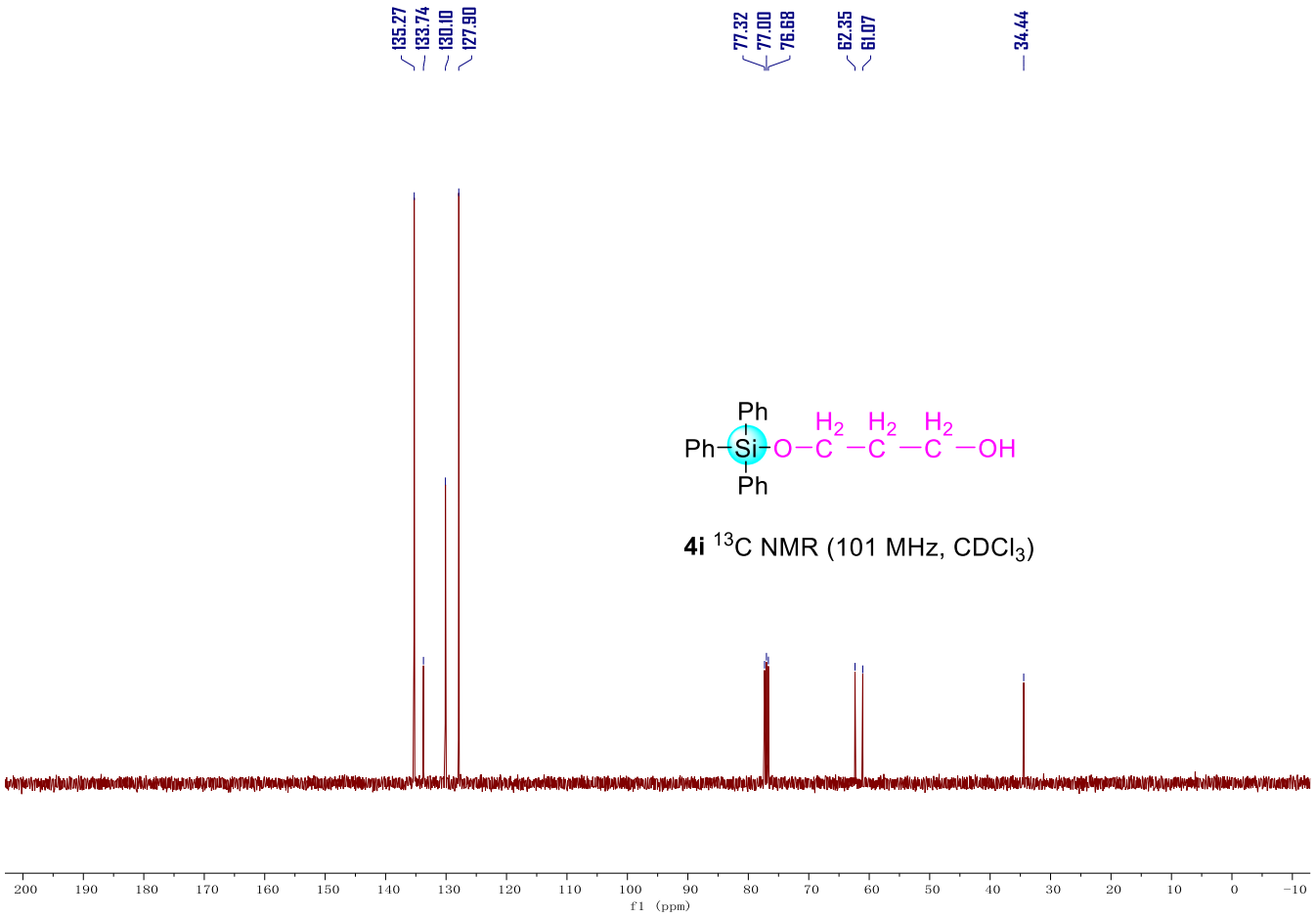
4h ^{1}H NMR (400 MHz, $CDCl_3$)



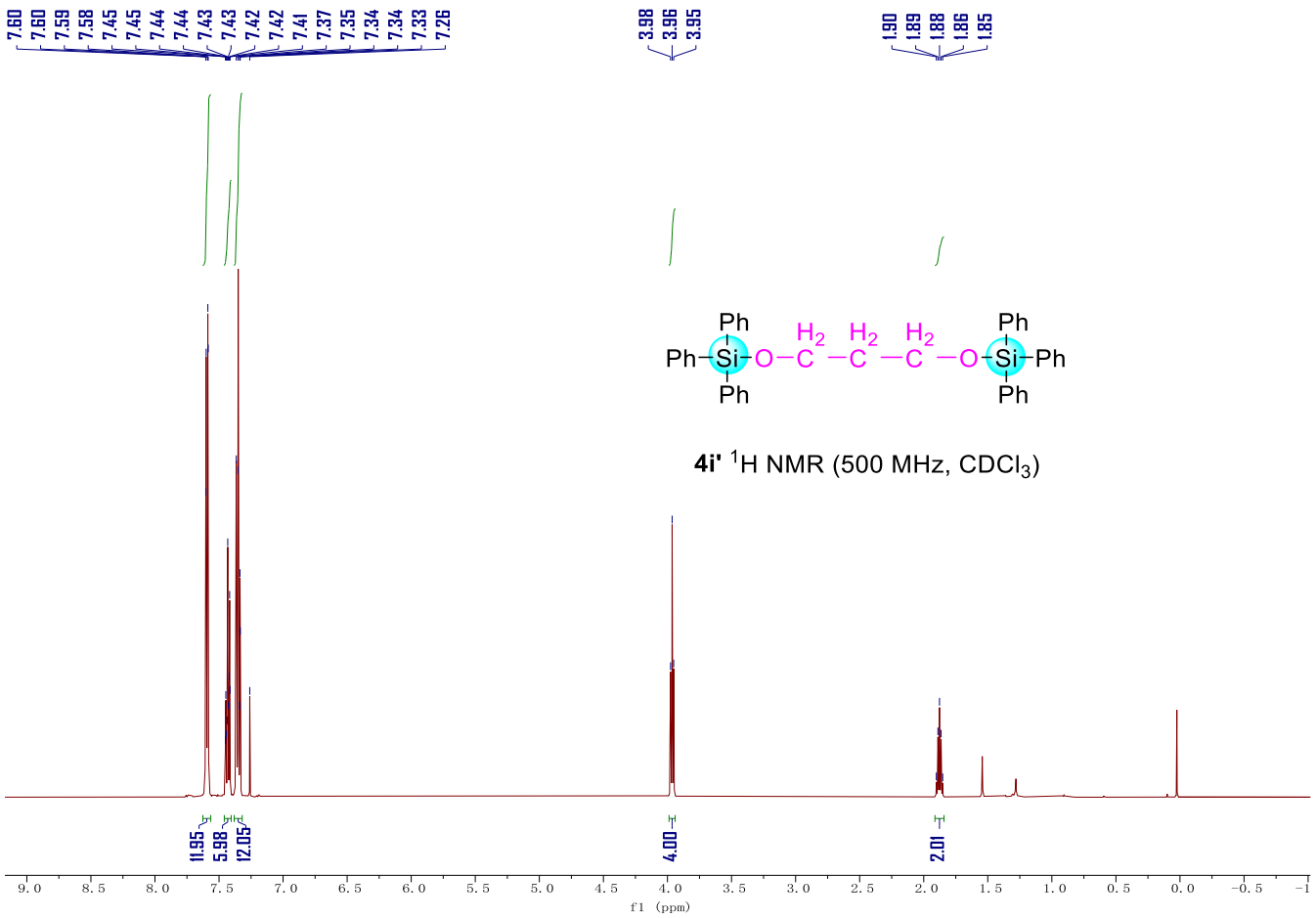
4h ^{13}C NMR (126 MHz, $CDCl_3$)



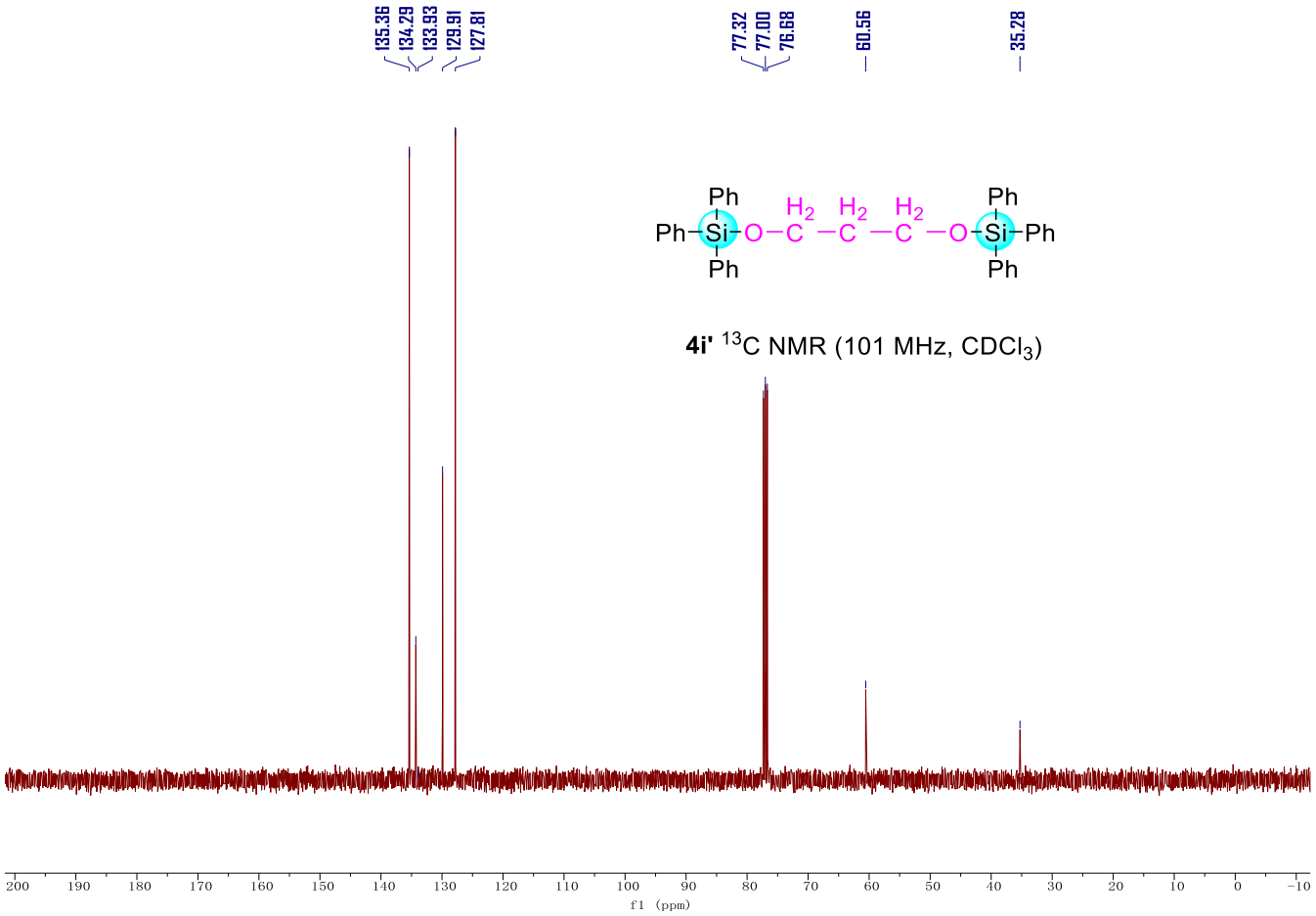
4i ^{1}H NMR (400 MHz, $CDCl_3$)

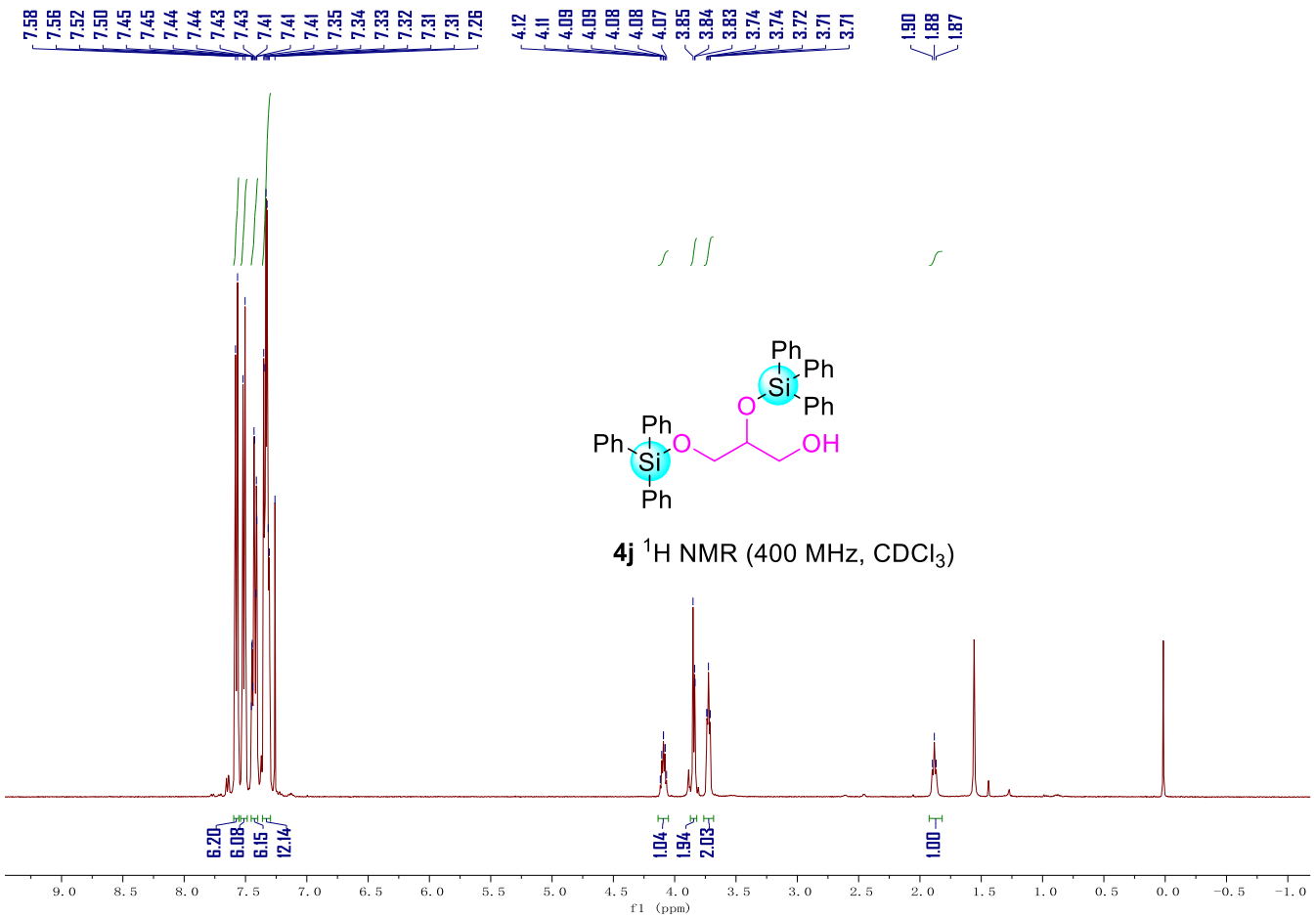


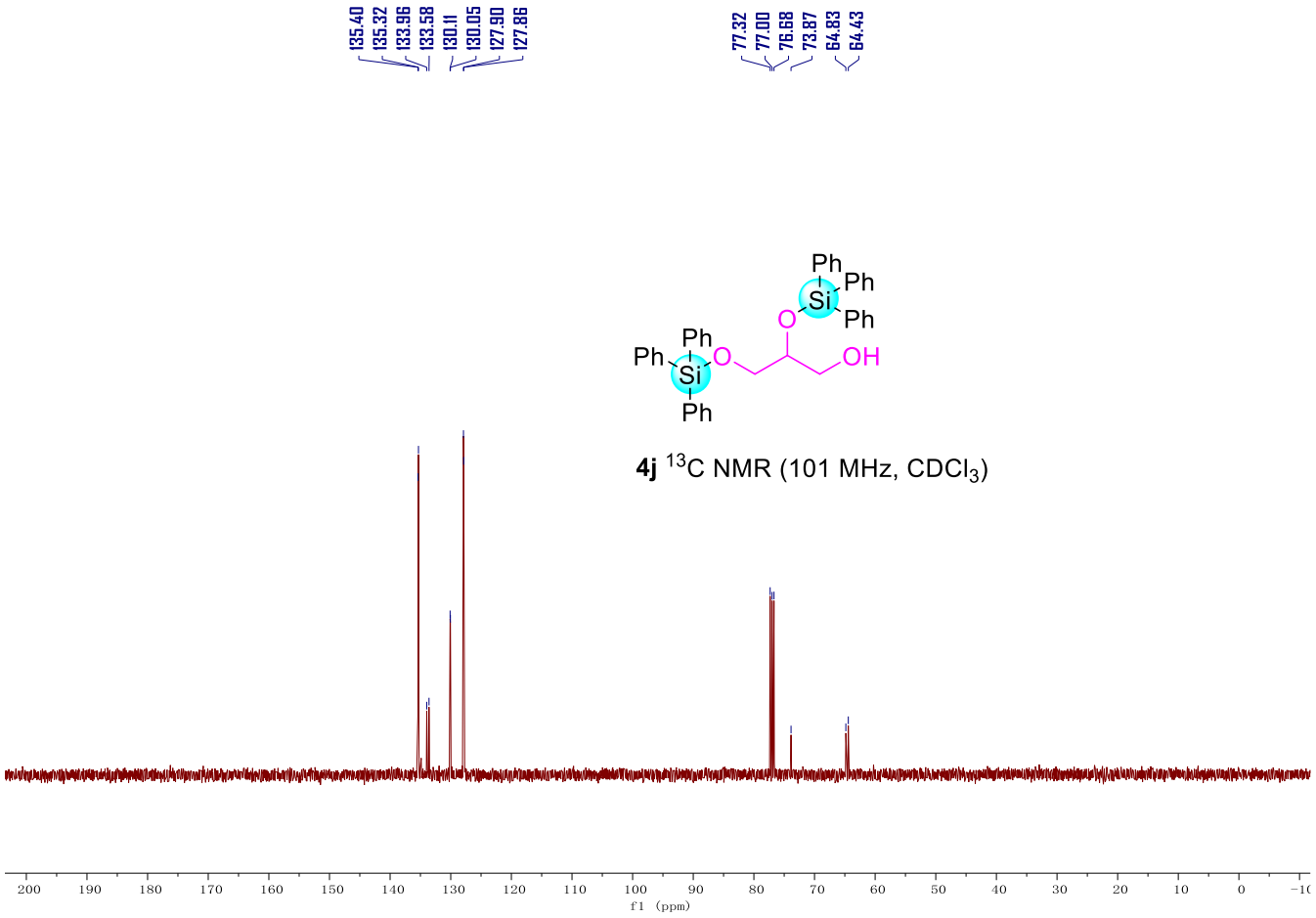
4i ^{13}C NMR (101 MHz, $CDCl_3$)



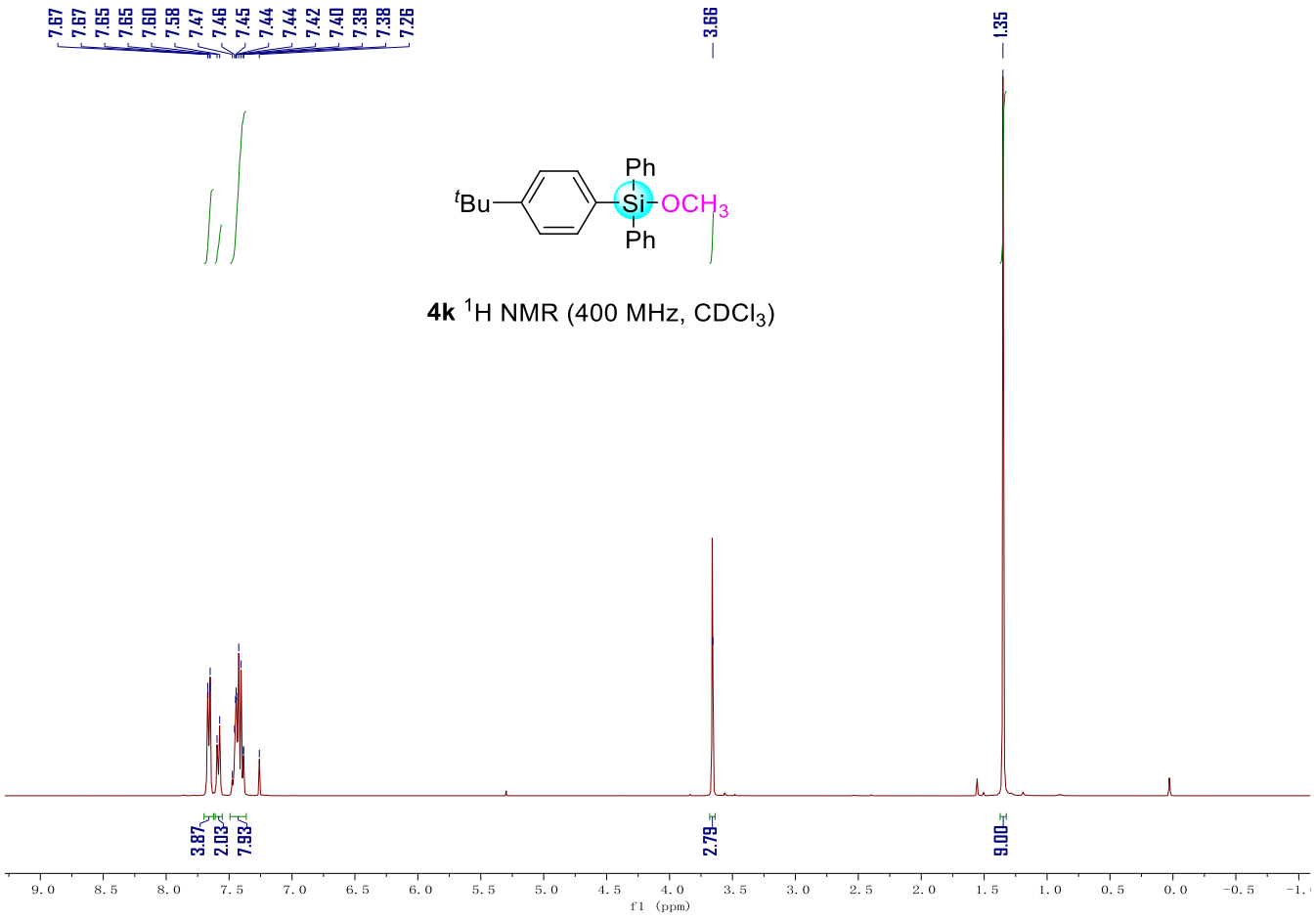
4i' ^{1}H NMR (500 MHz, $CDCl_3$)


135.36
134.29
133.93
129.91
127.81
77.32
77.00
76.68
60.56
35.28
Ph
Ph
Si
O
C
H2
Ph
Ph
Si
Ph
Ph
4i' 13C NMR (101 MHz, CDCl3)
f1 (ppm)

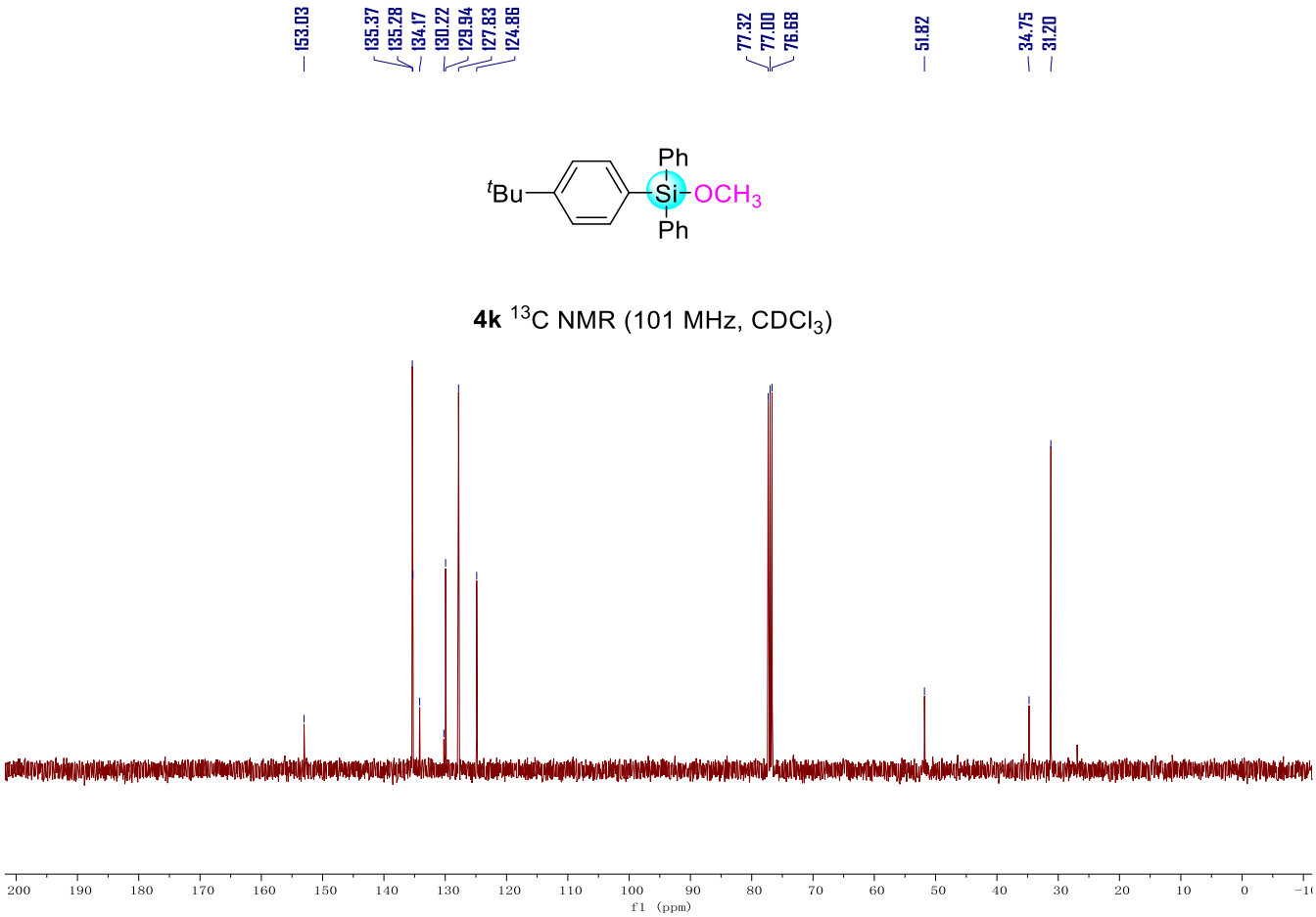

7.58
7.56
7.52
7.50
7.45
7.45
7.44
7.44
7.43
7.43
7.41
7.41
7.41
7.35
7.34
7.33
7.32
7.31
7.31
7.26
4.12
4.11
4.09
4.09
4.08
4.08
4.07
3.85
3.84
3.83
3.74
3.74
3.72
3.71
3.71
1.90
1.88
1.87
Ph
Ph
Si
O
Ph
Ph
Ph
Si
O
OH
Ph
4j 1H NMR (400 MHz, CDCl3)
6.20
6.08
6.15
12.14
1.04
1.94
2.03
1.00
f1 (ppm)

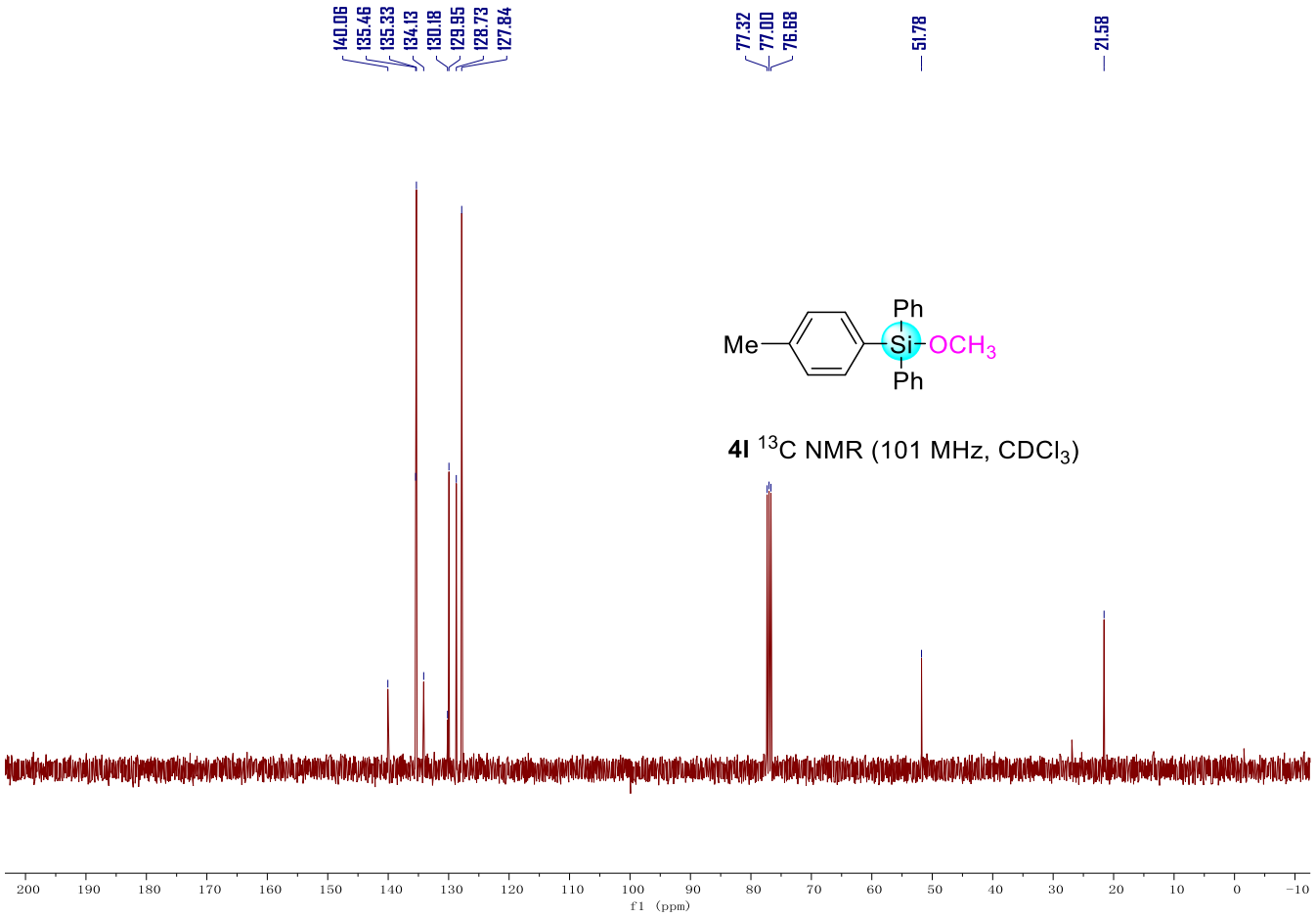


4j ^{13}C NMR (101 MHz, $CDCl_3$)

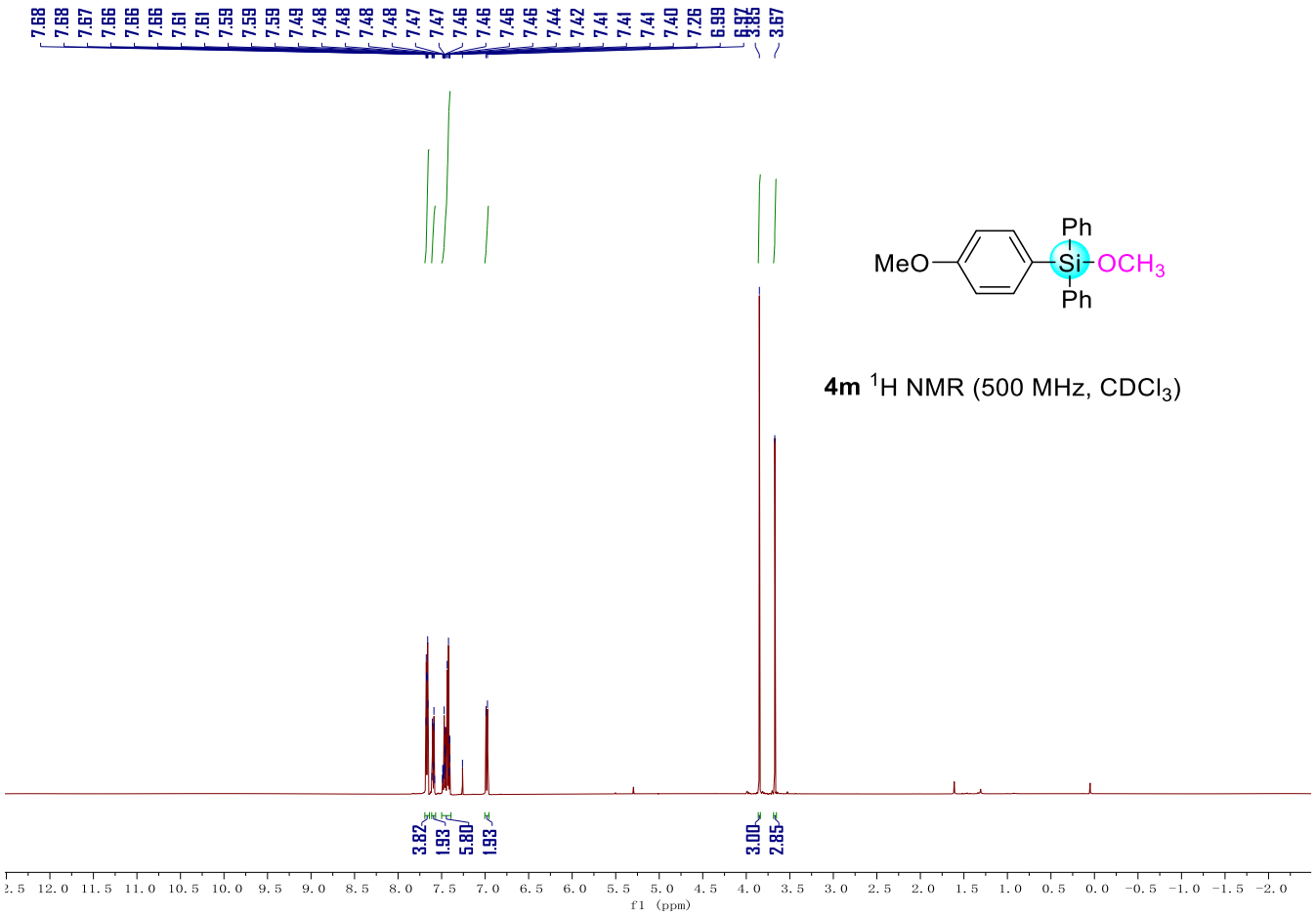


4k ^{1}H NMR (400 MHz, $CDCl_3$)

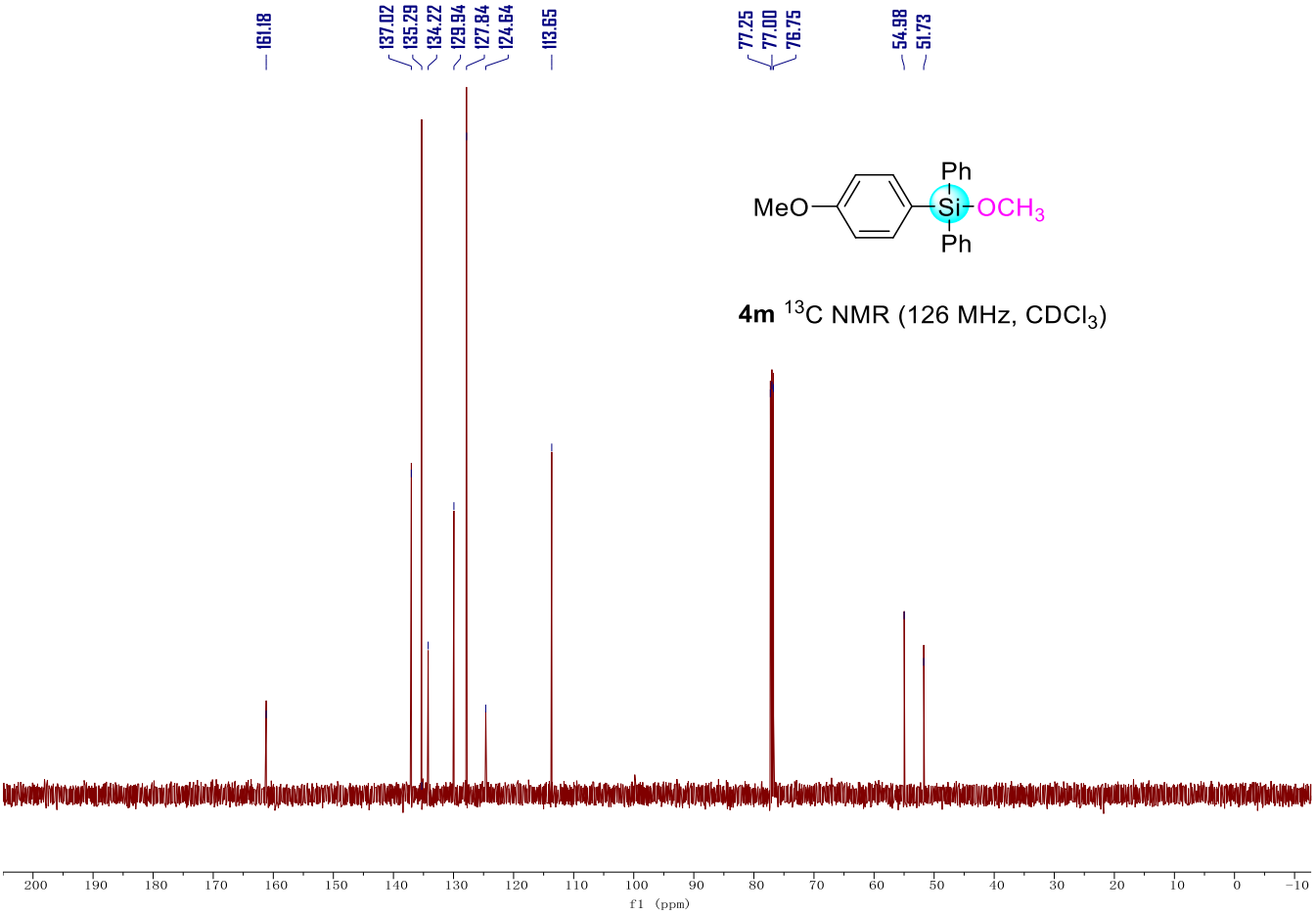

153.03
135.37
135.28
134.17
130.22
129.94
127.83
124.86
77.32
77.00
76.68
51.82
34.75
31.20
Ph
tBu
Si
OCH3
Ph
4k 13C NMR (101 MHz, CDCl3)
f1 (ppm)
7.70
7.70
7.69
7.68
7.68
7.67
7.59
7.58
7.58
7.51
7.49
7.49
7.47
7.46
7.44
7.42
7.29
7.27
3.69
2.43
Ph
Me
Si
OCH3
Ph
4l 1H NMR (400 MHz, CDCl3)
3.81
2.04
5.78
2.08
2.83
3.00
f1 (ppm)



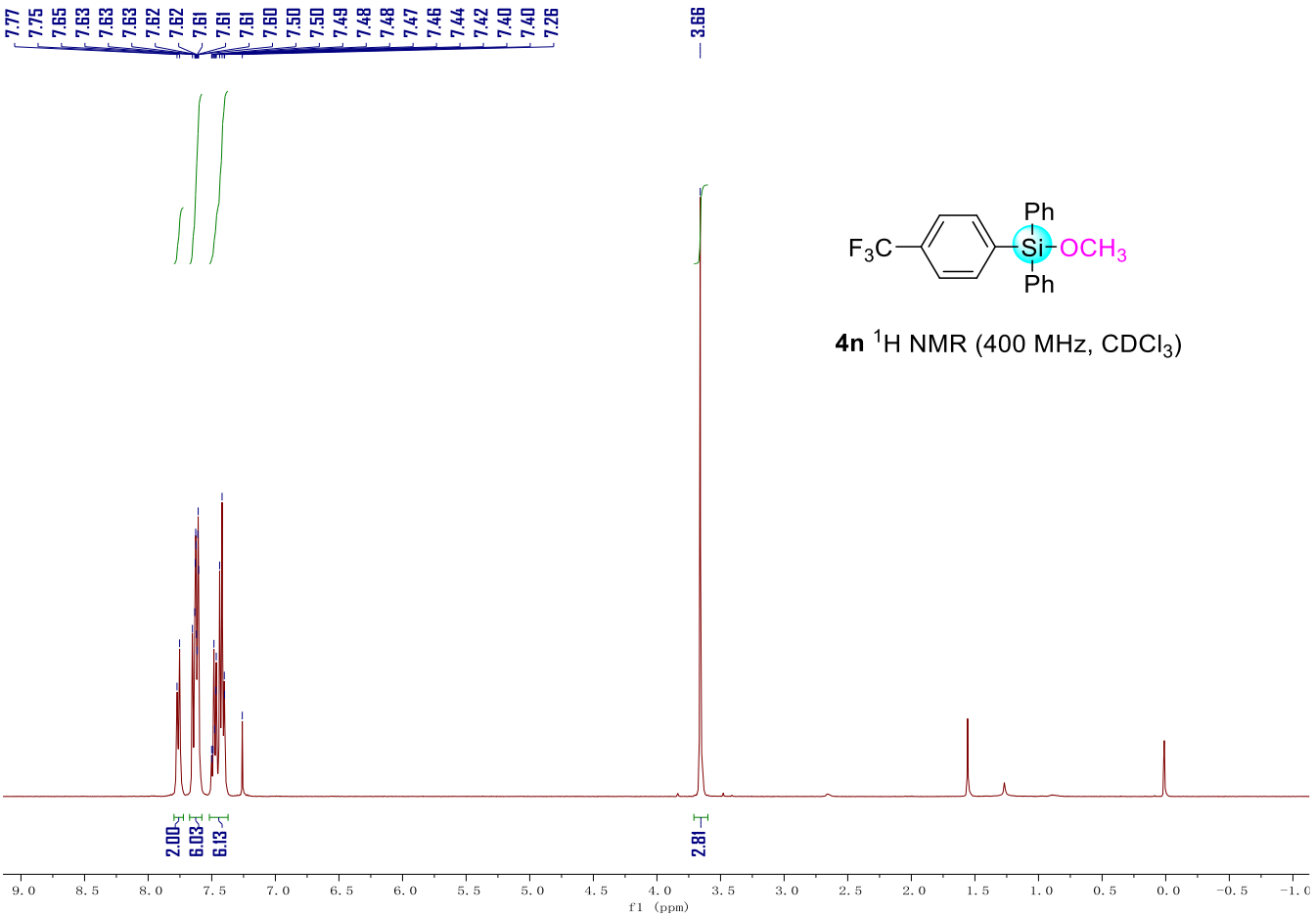
4l ^{13}C NMR (101 MHz, $CDCl_3$)



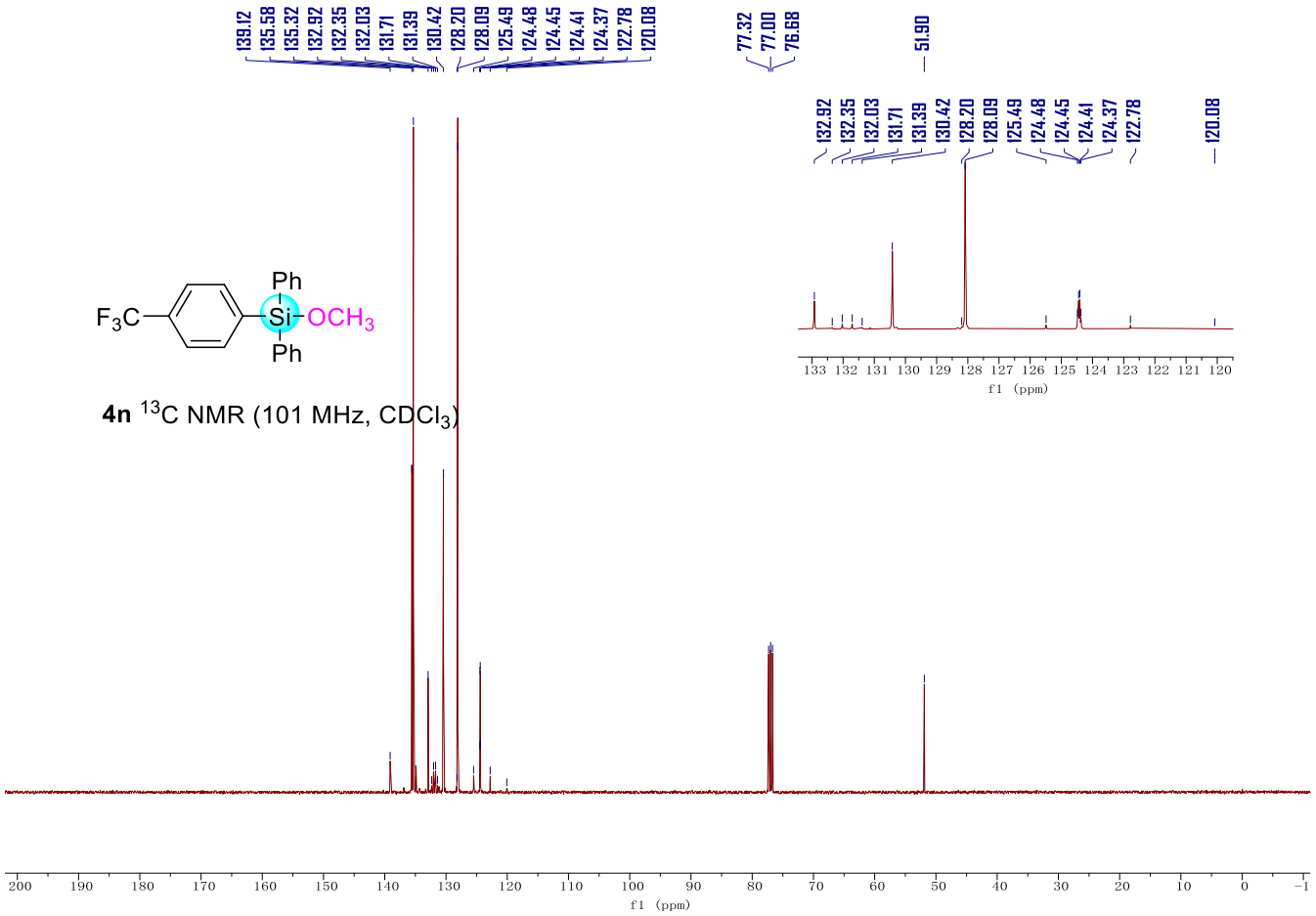
4m ^{1}H NMR (500 MHz, $CDCl_3$)



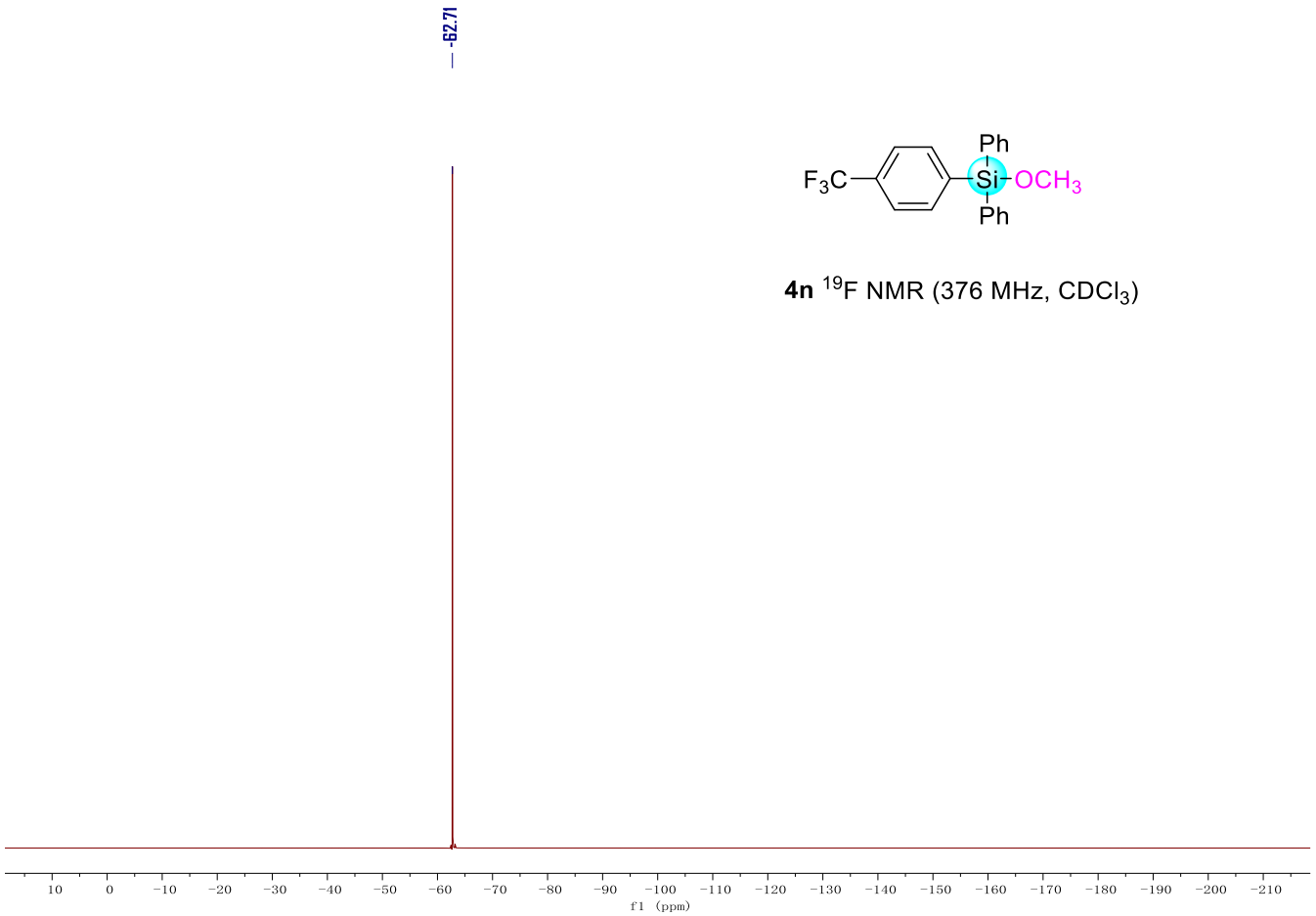
4m ^{13}C NMR (126 MHz, $CDCl_3$)



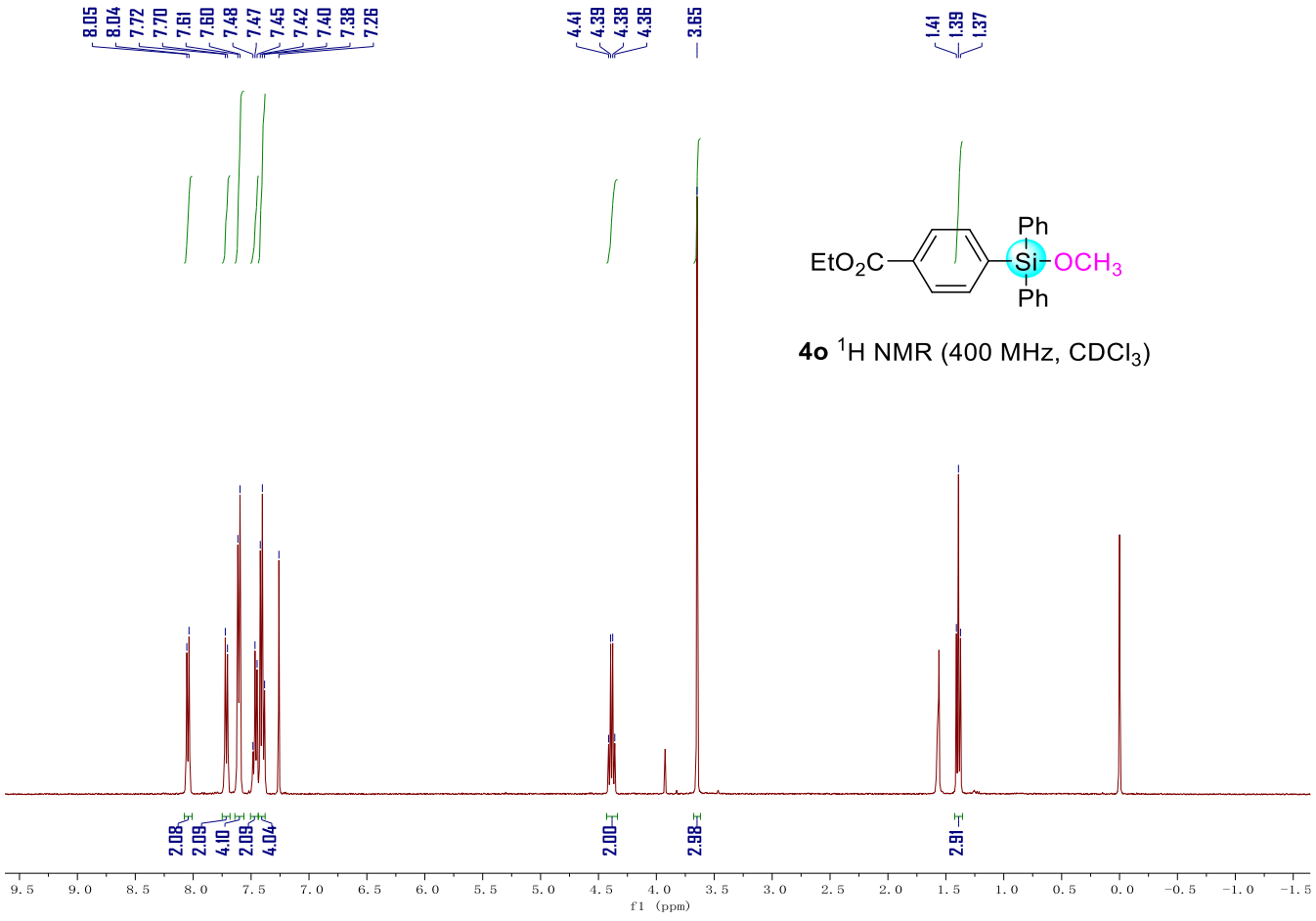
4n ^{1}H NMR (400 MHz, $CDCl_3$)



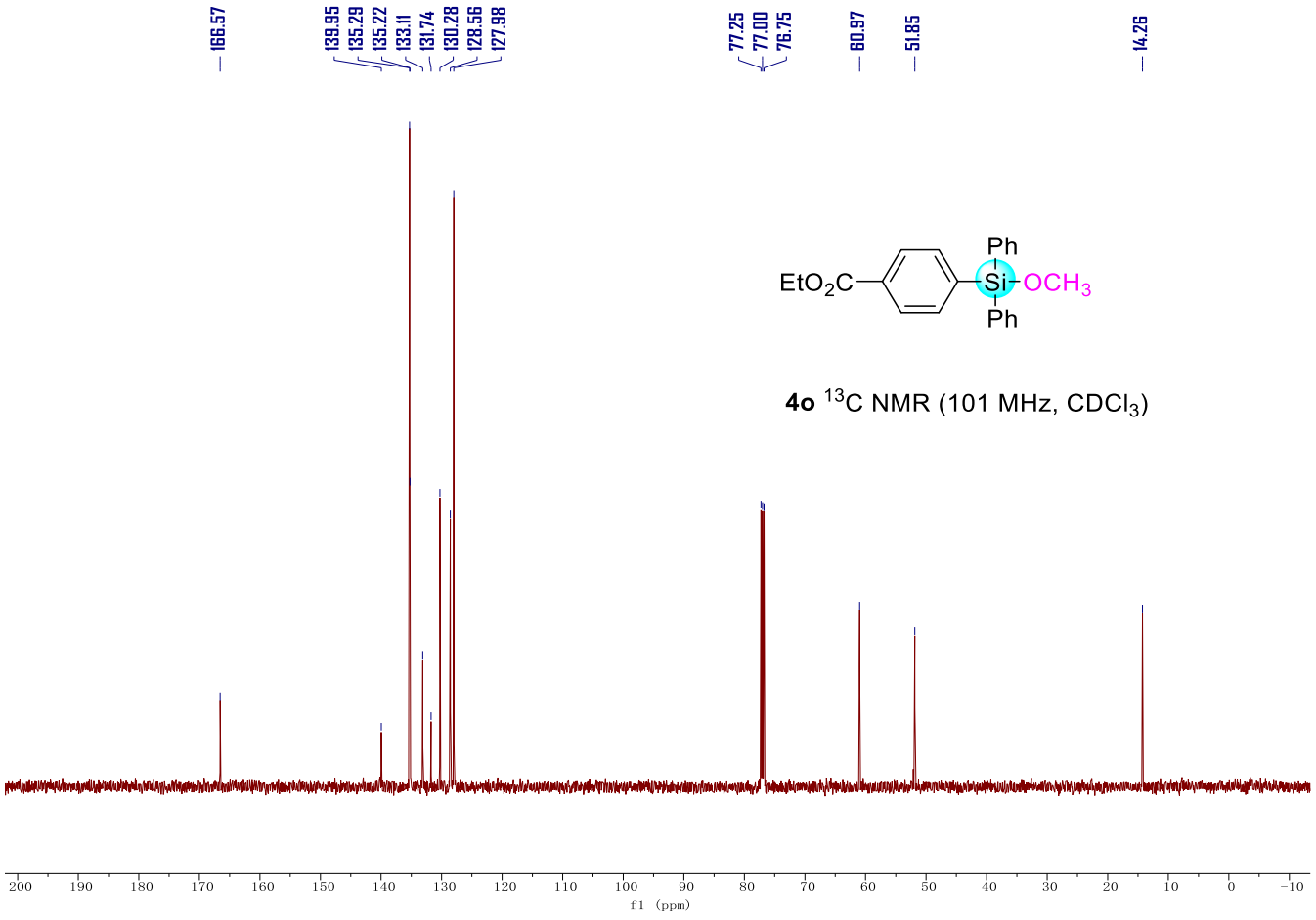
4n ^{13}C NMR (101 MHz, $CDCl_3$)



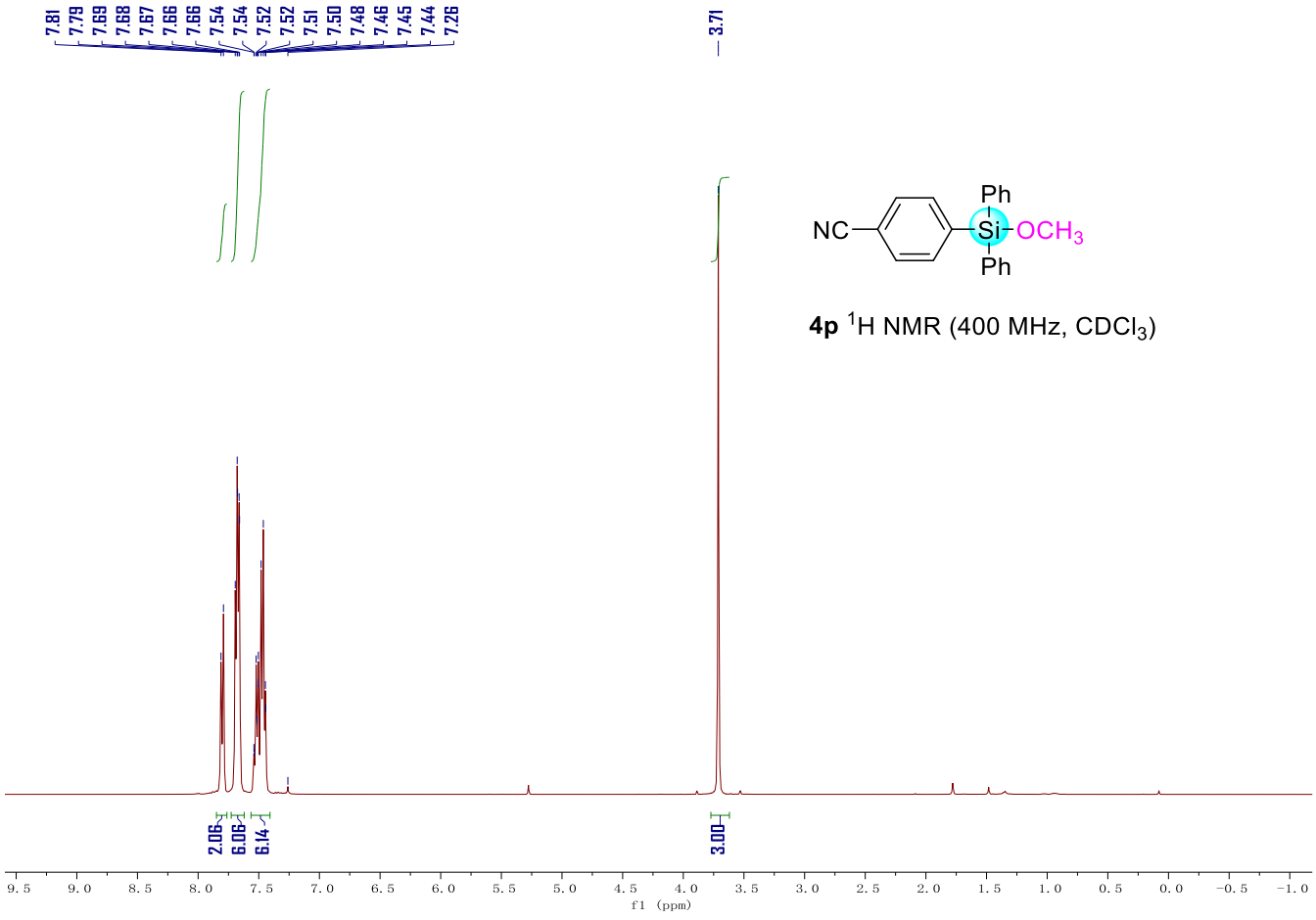
4n ^{19}F NMR (376 MHz, $CDCl_3$)



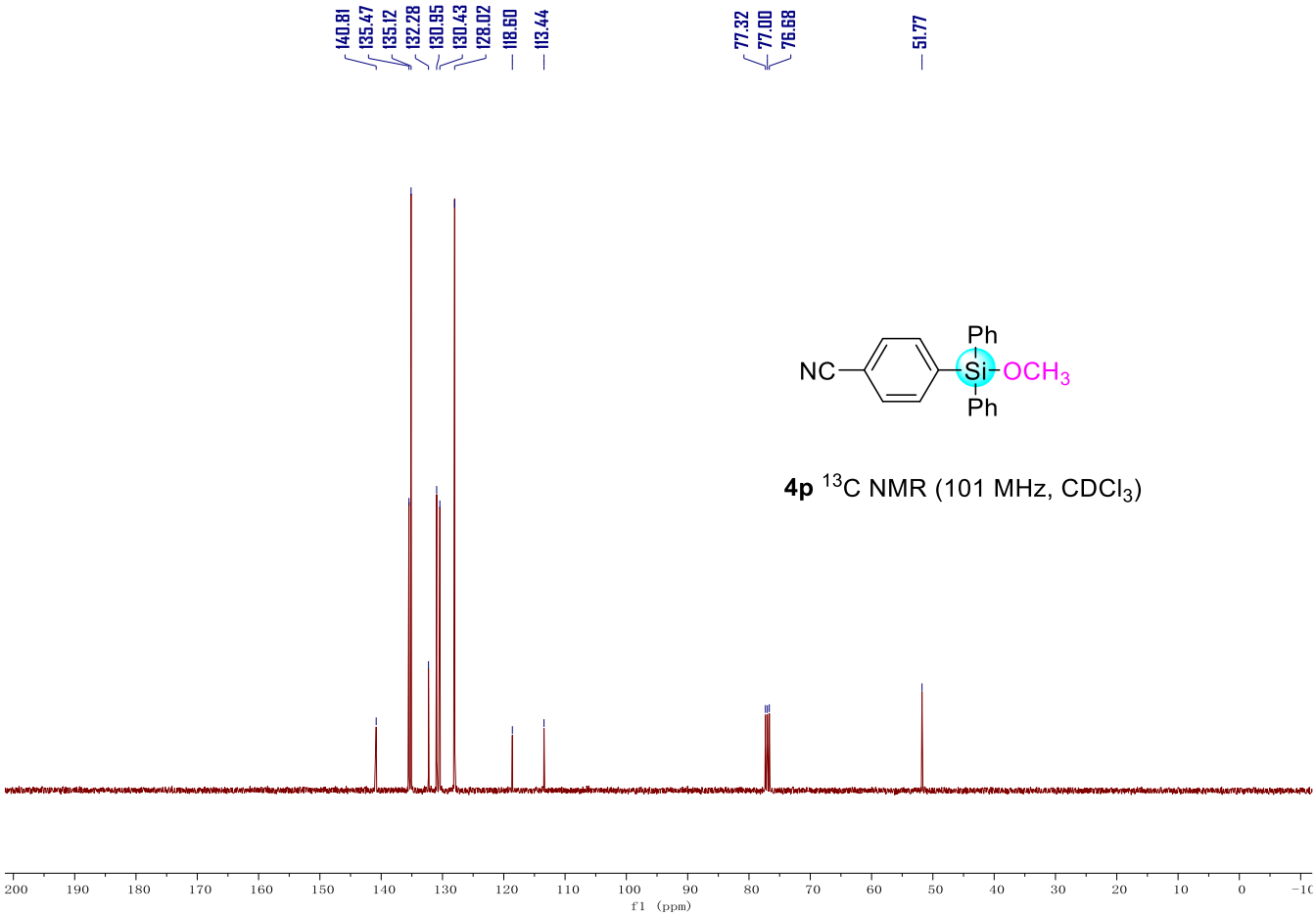
4o ^{1}H NMR (400 MHz, $CDCl_3$)



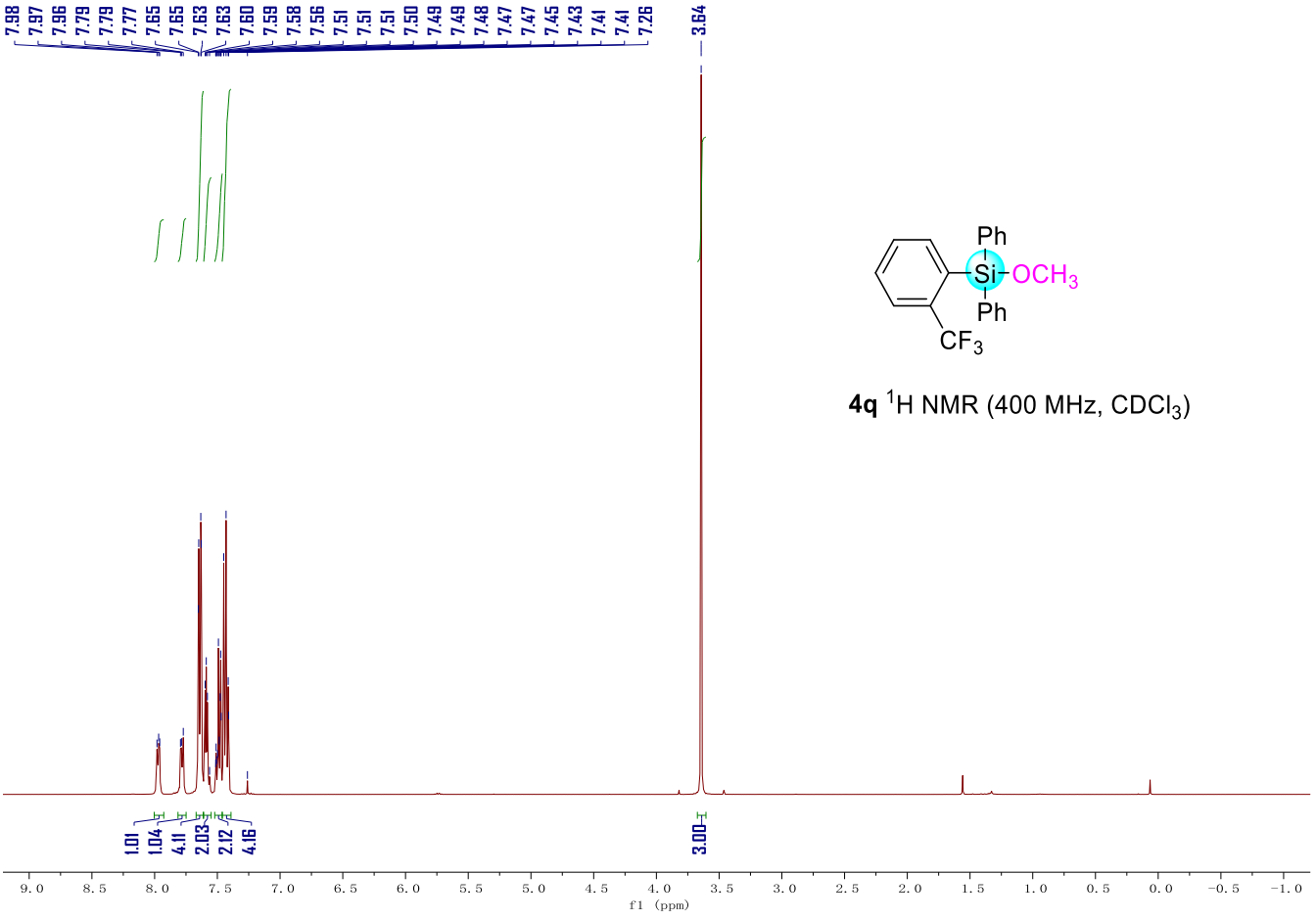
4o ^{13}C NMR (101 MHz, $CDCl_3$)



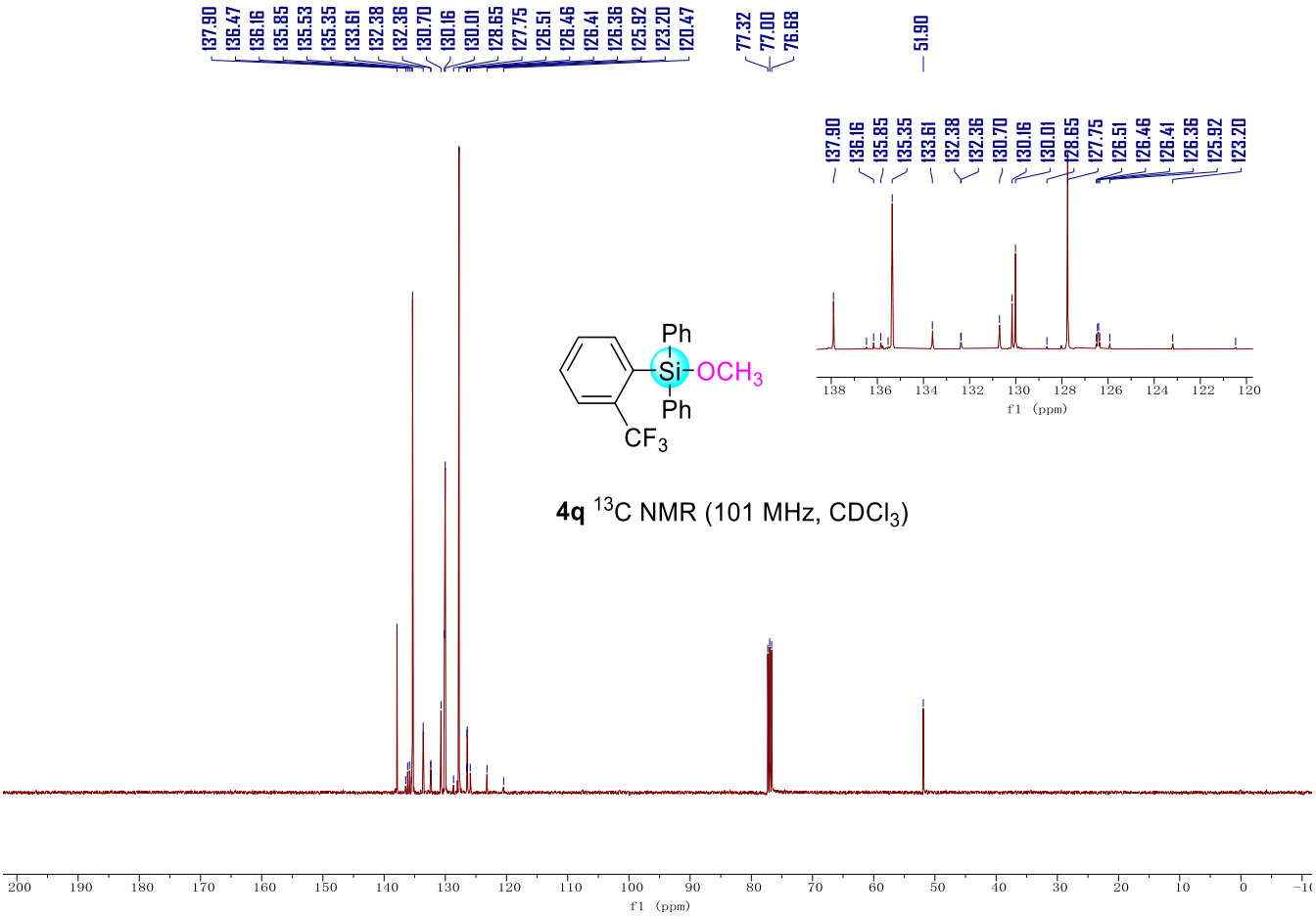
4p ^{1}H NMR (400 MHz, $CDCl_3$)



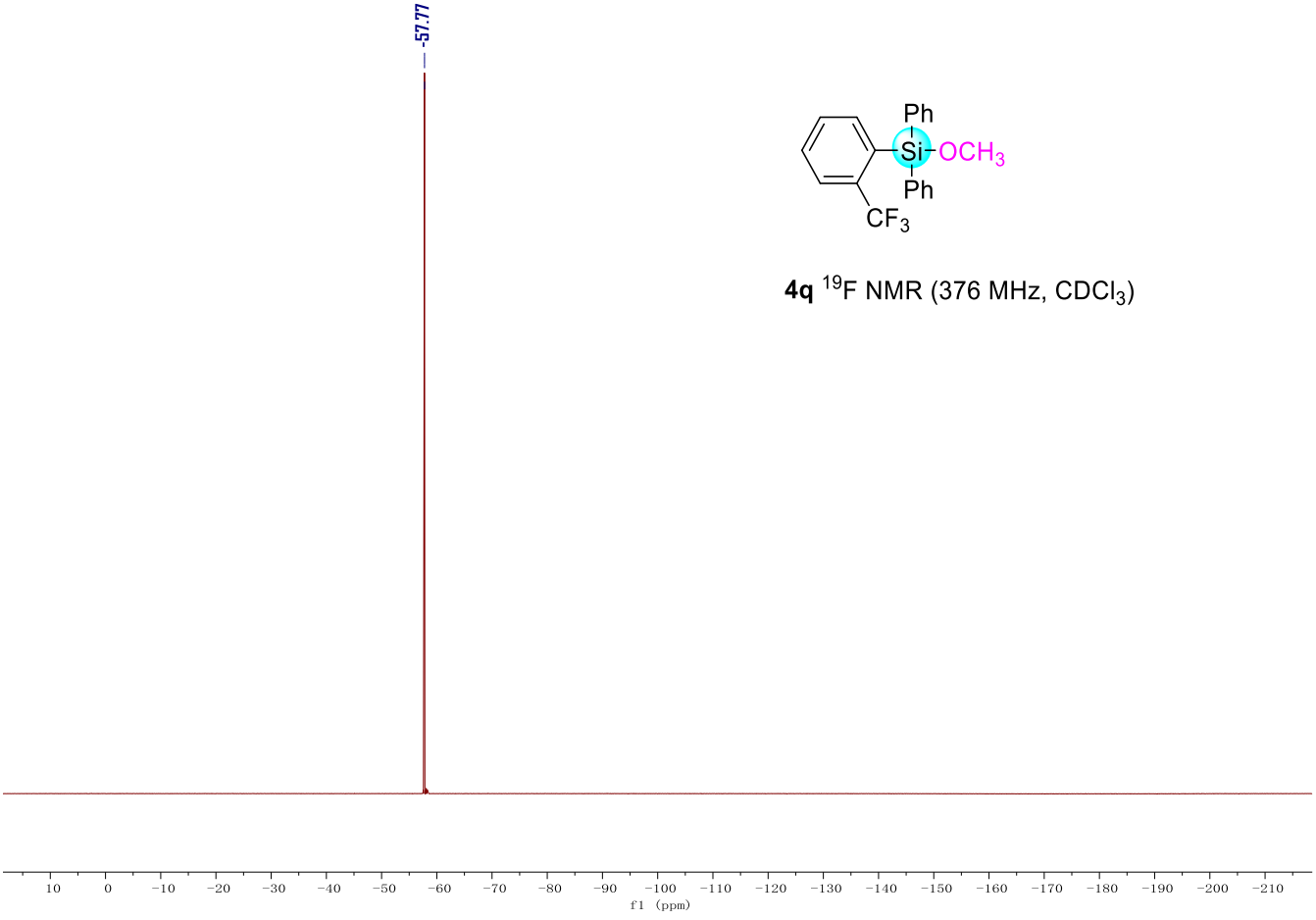
4p ^{13}C NMR (101 MHz, $CDCl_3$)



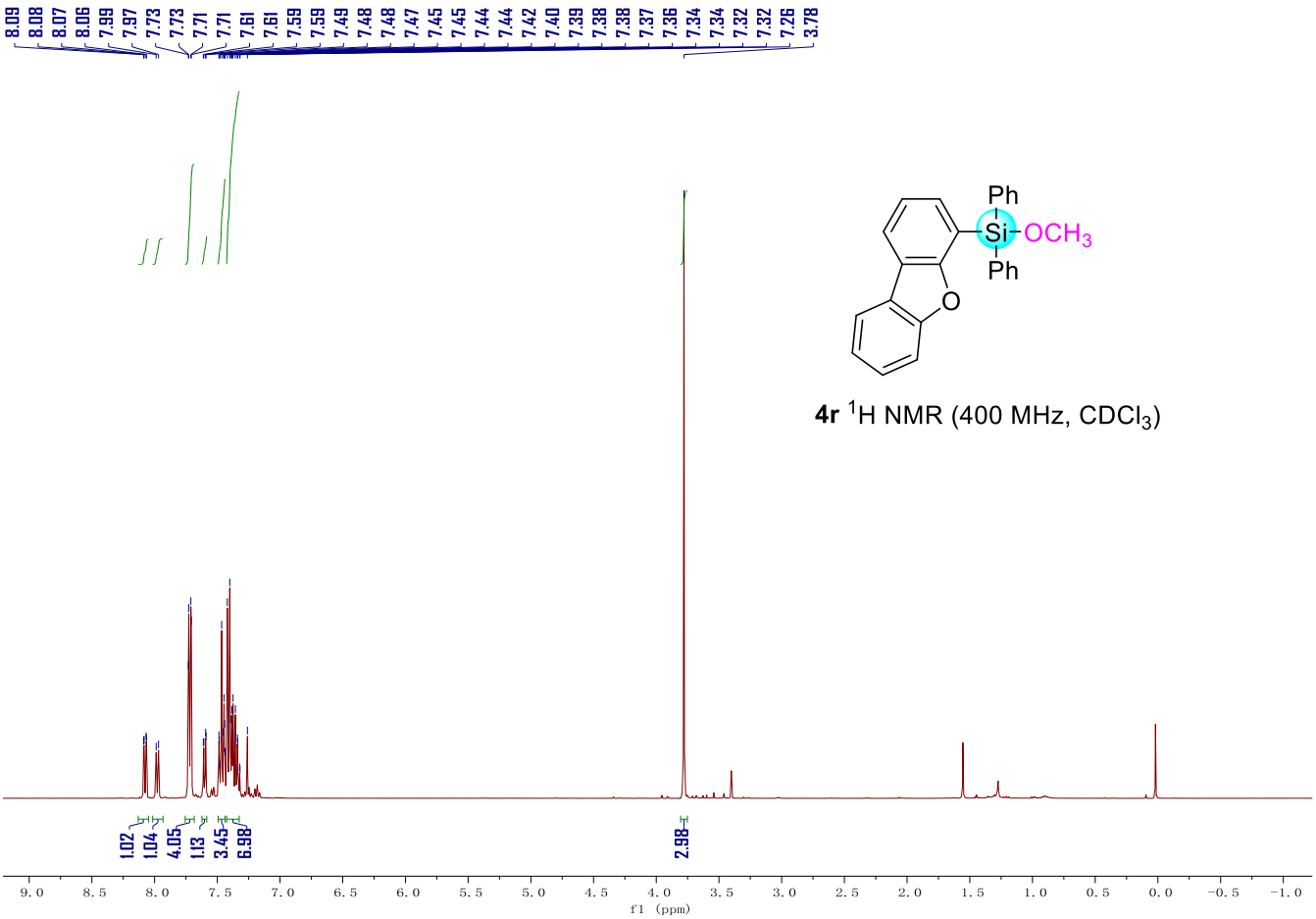
4q ^{1}H NMR (400 MHz, $CDCl_3$)



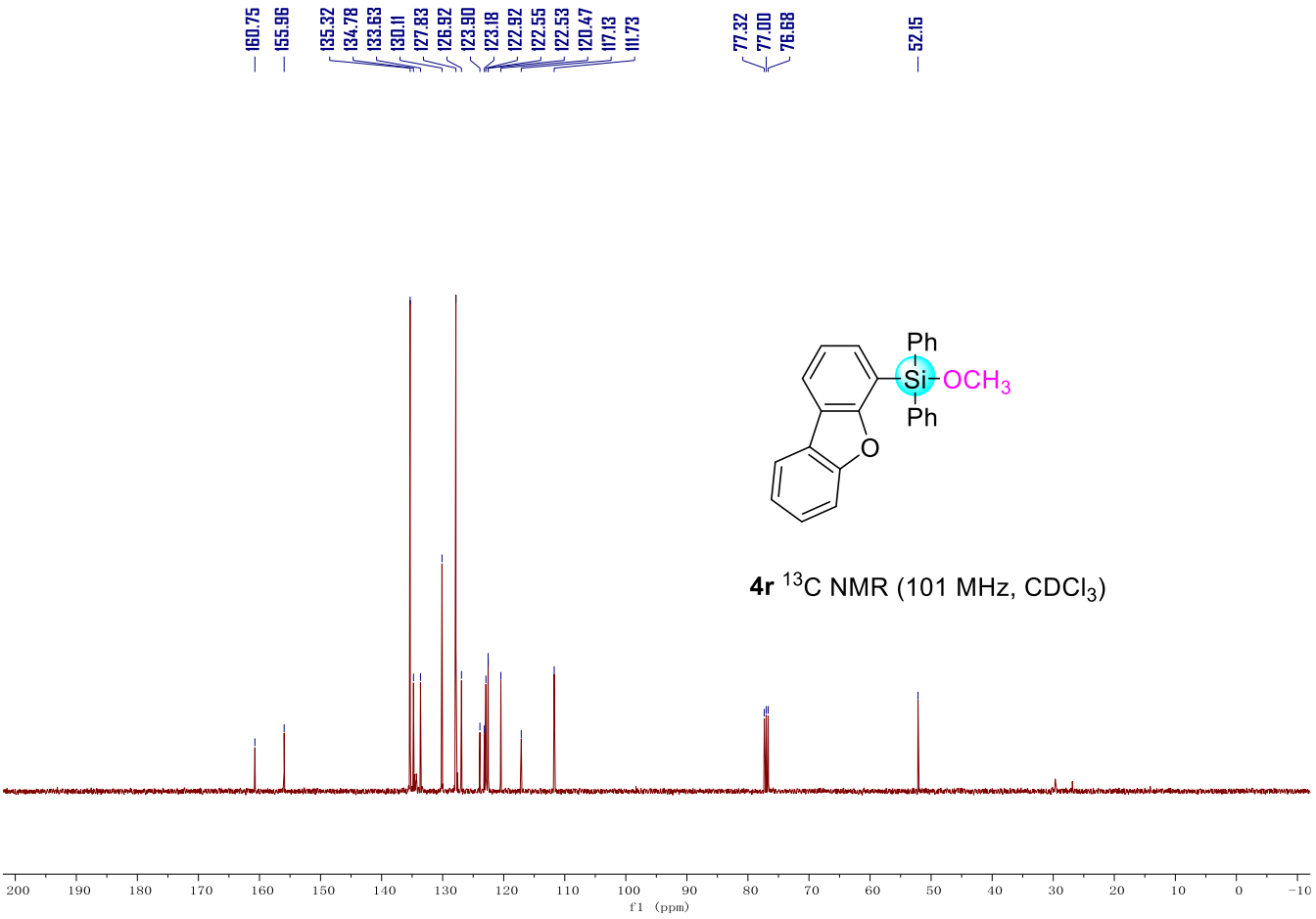
4q ^{13}C NMR (101 MHz, $CDCl_3$)



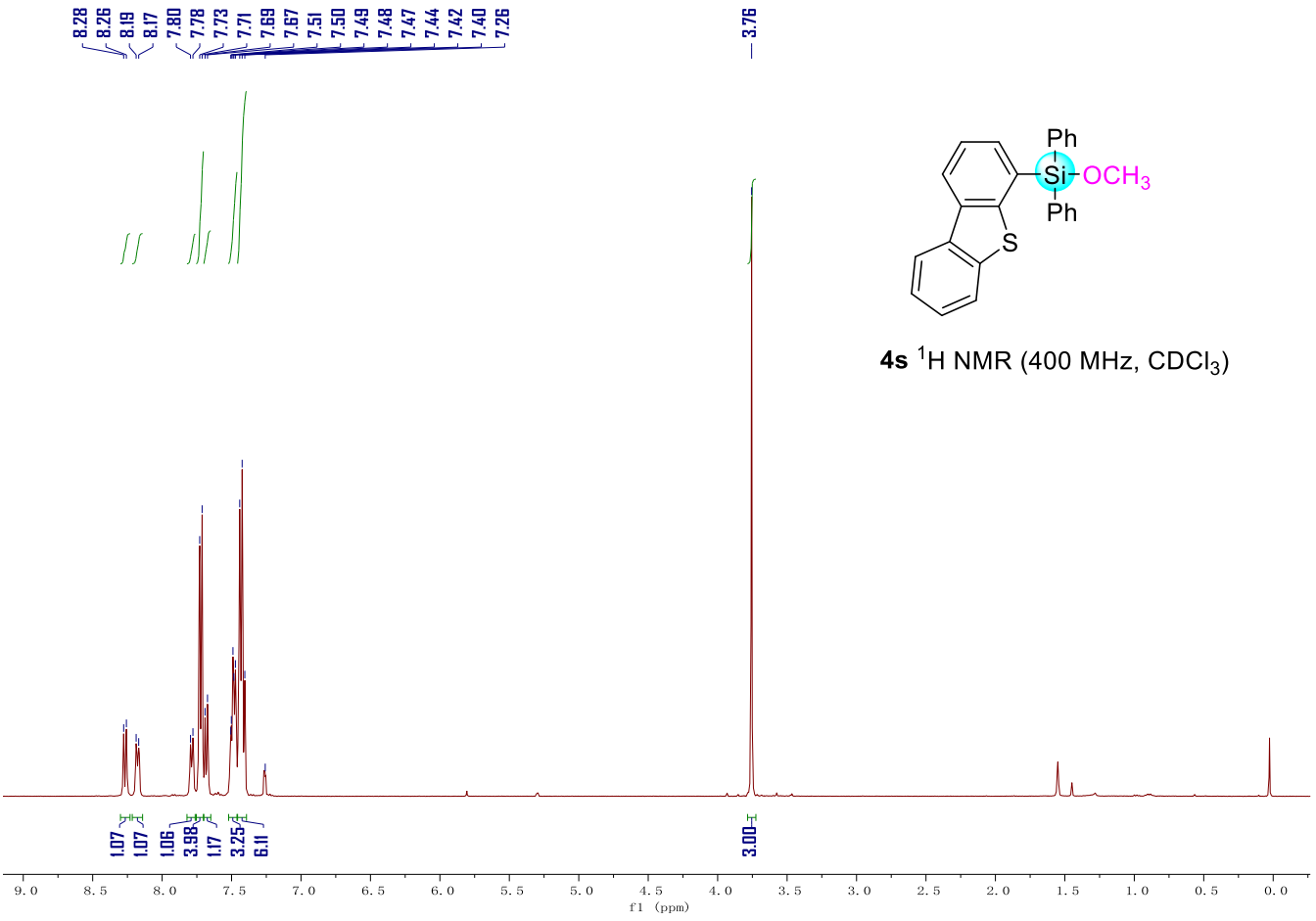
4q ^{19}F NMR (376 MHz, $CDCl_3$)



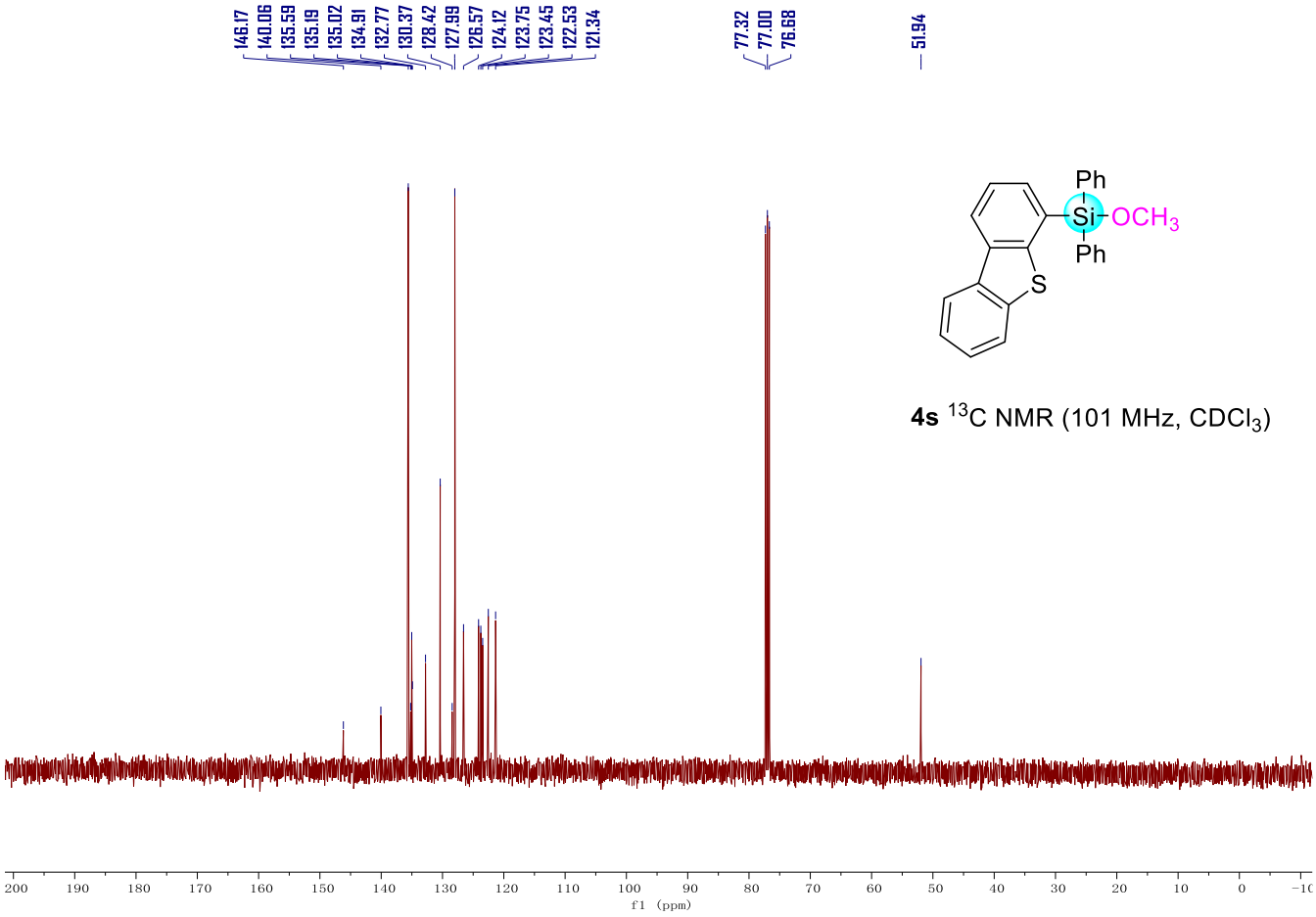
4r ^{1}H NMR (400 MHz, $CDCl_3$)



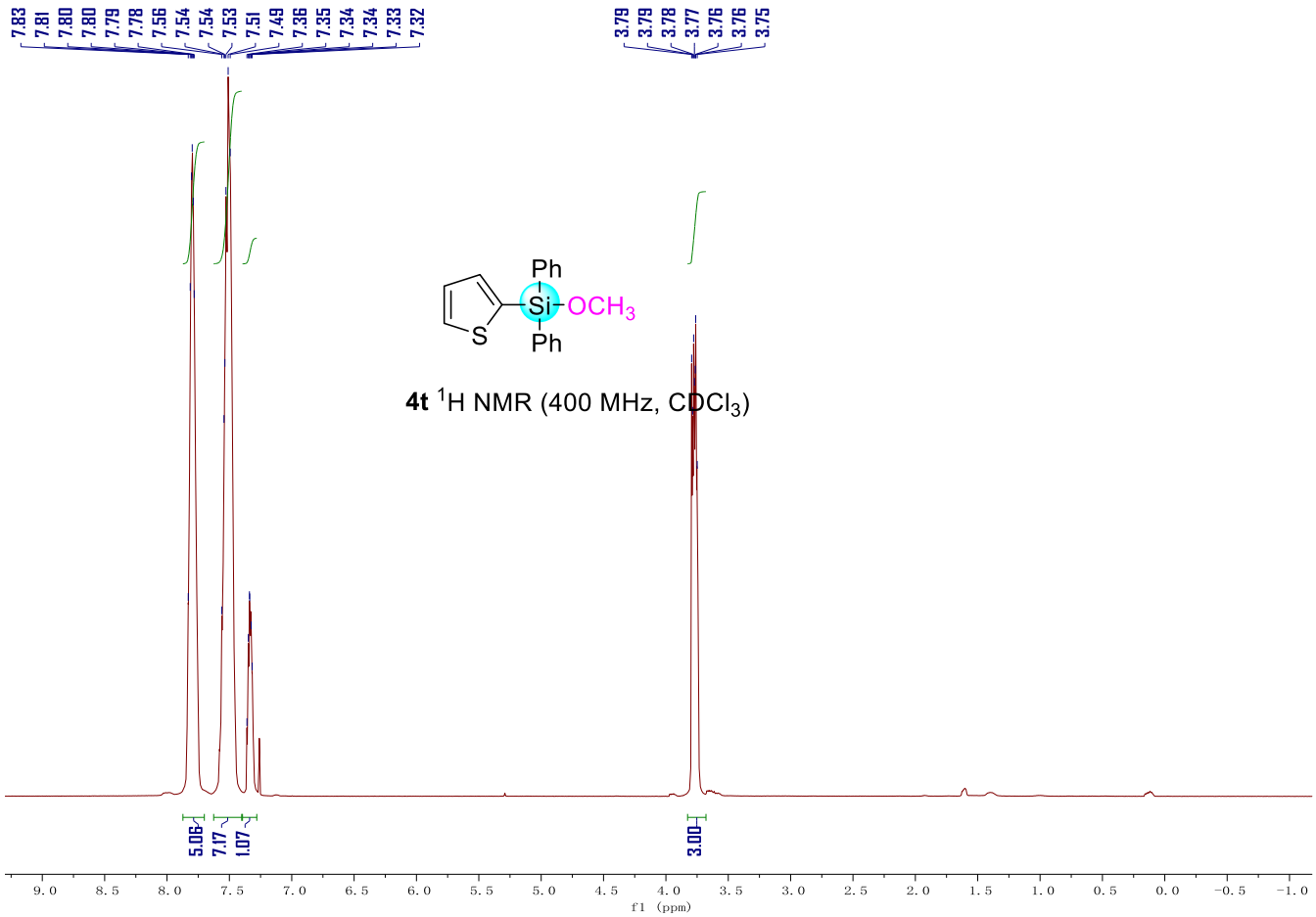
4r ^{13}C NMR (101 MHz, $CDCl_3$)



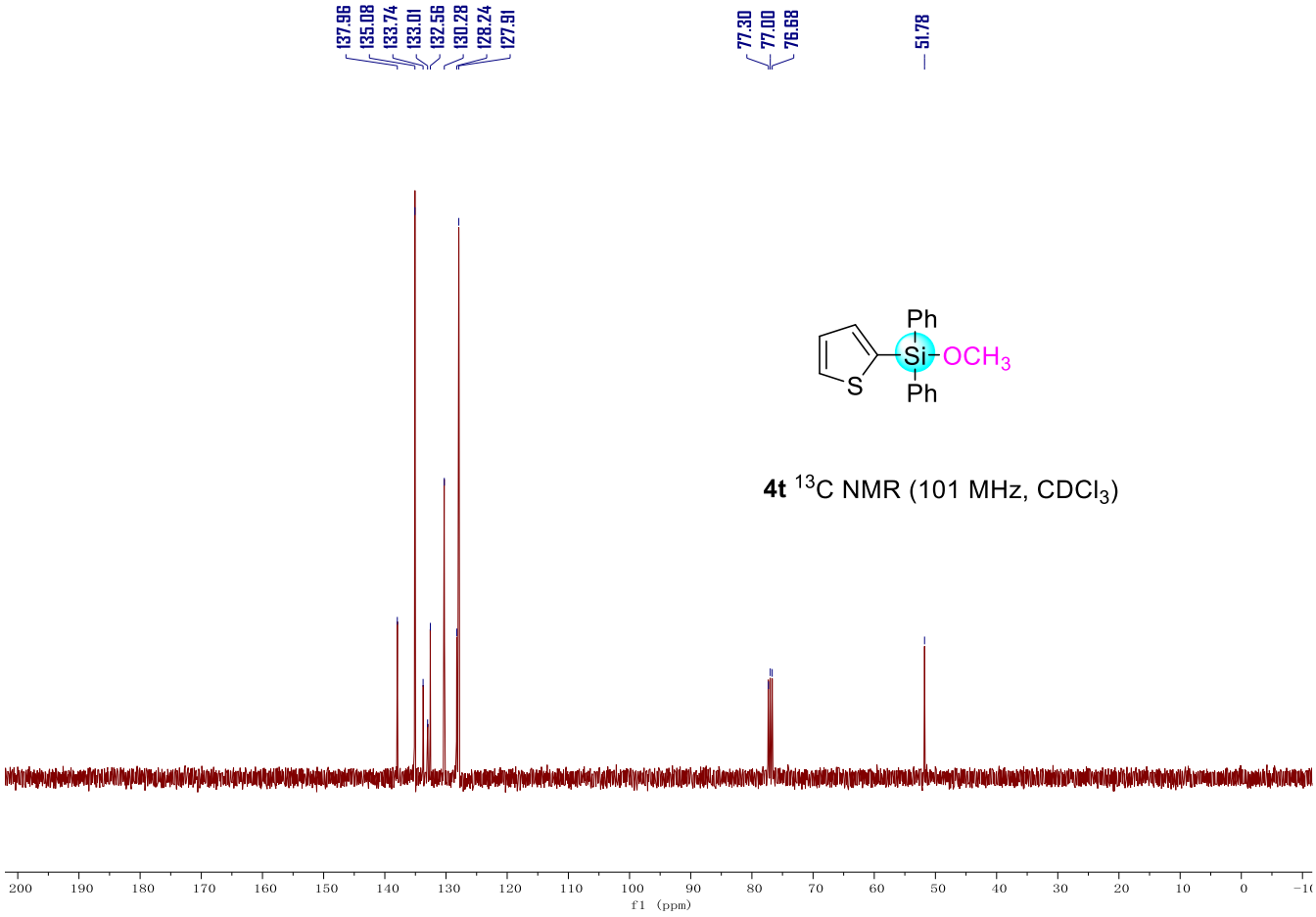
4s ^{1}H NMR (400 MHz, $CDCl_3$)



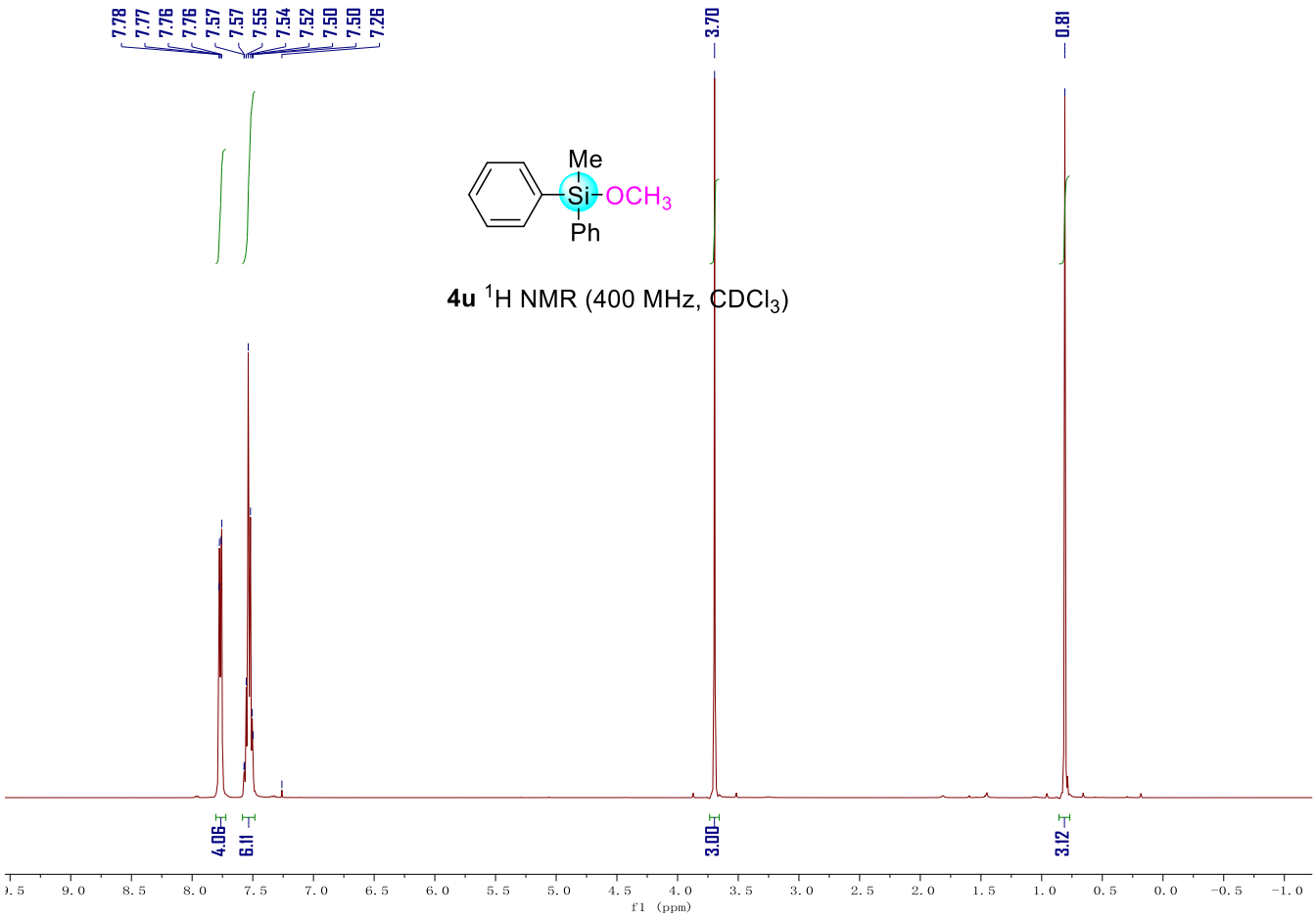
4s ^{13}C NMR (101 MHz, $CDCl_3$)



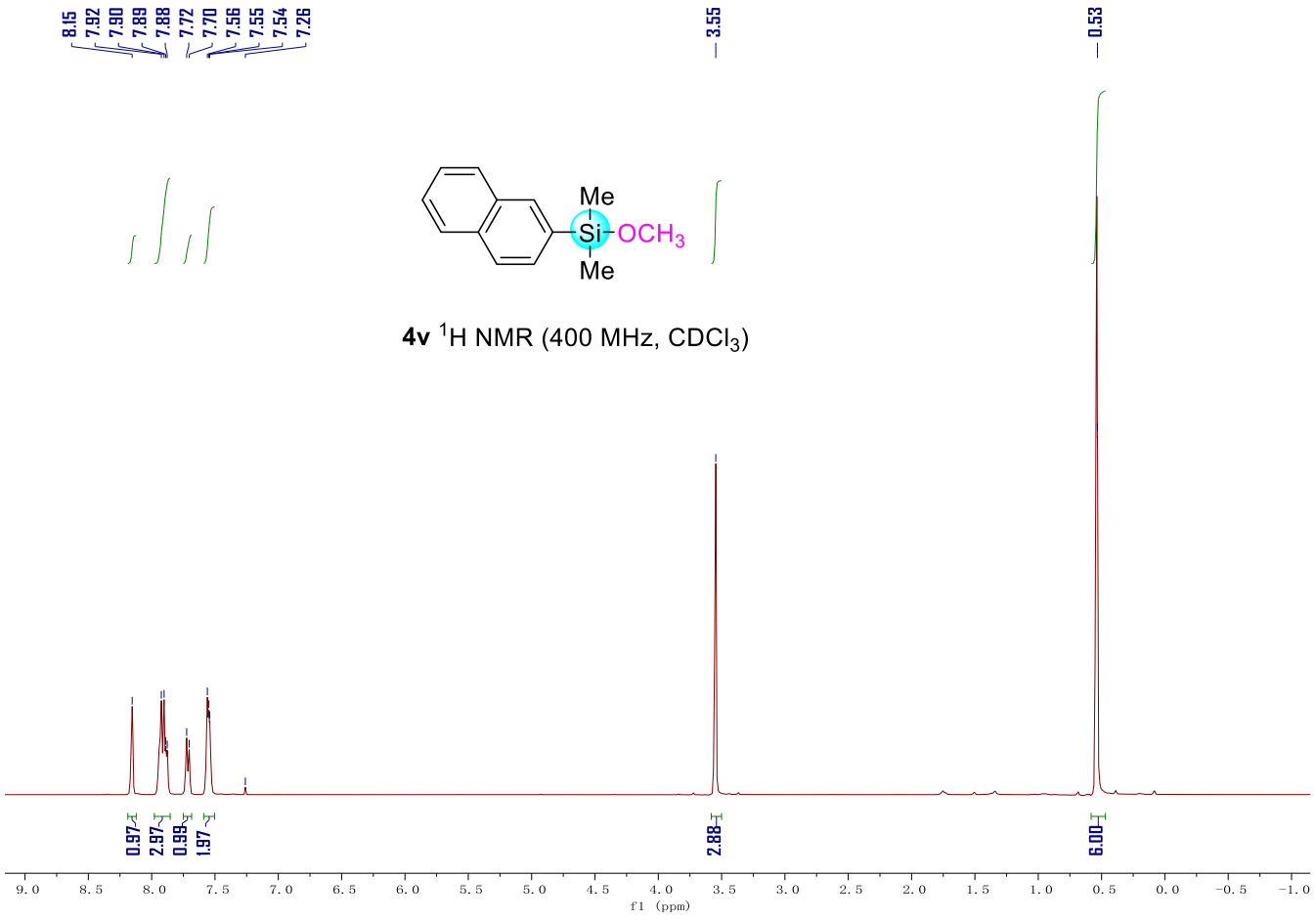
4t ^{1}H NMR (400 MHz, $CDCl_3$)



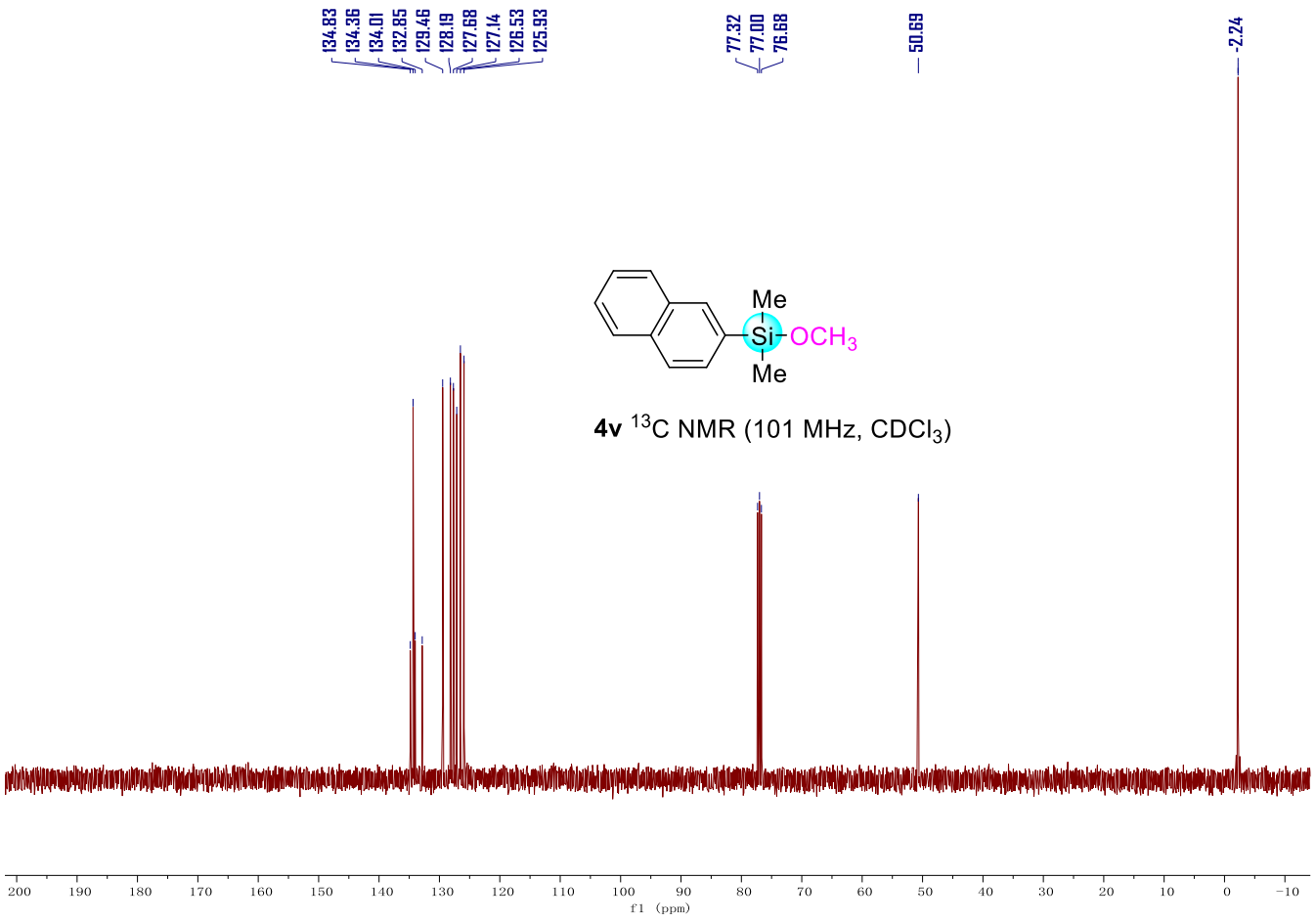
4t ^{13}C NMR (101 MHz, $CDCl_3$)



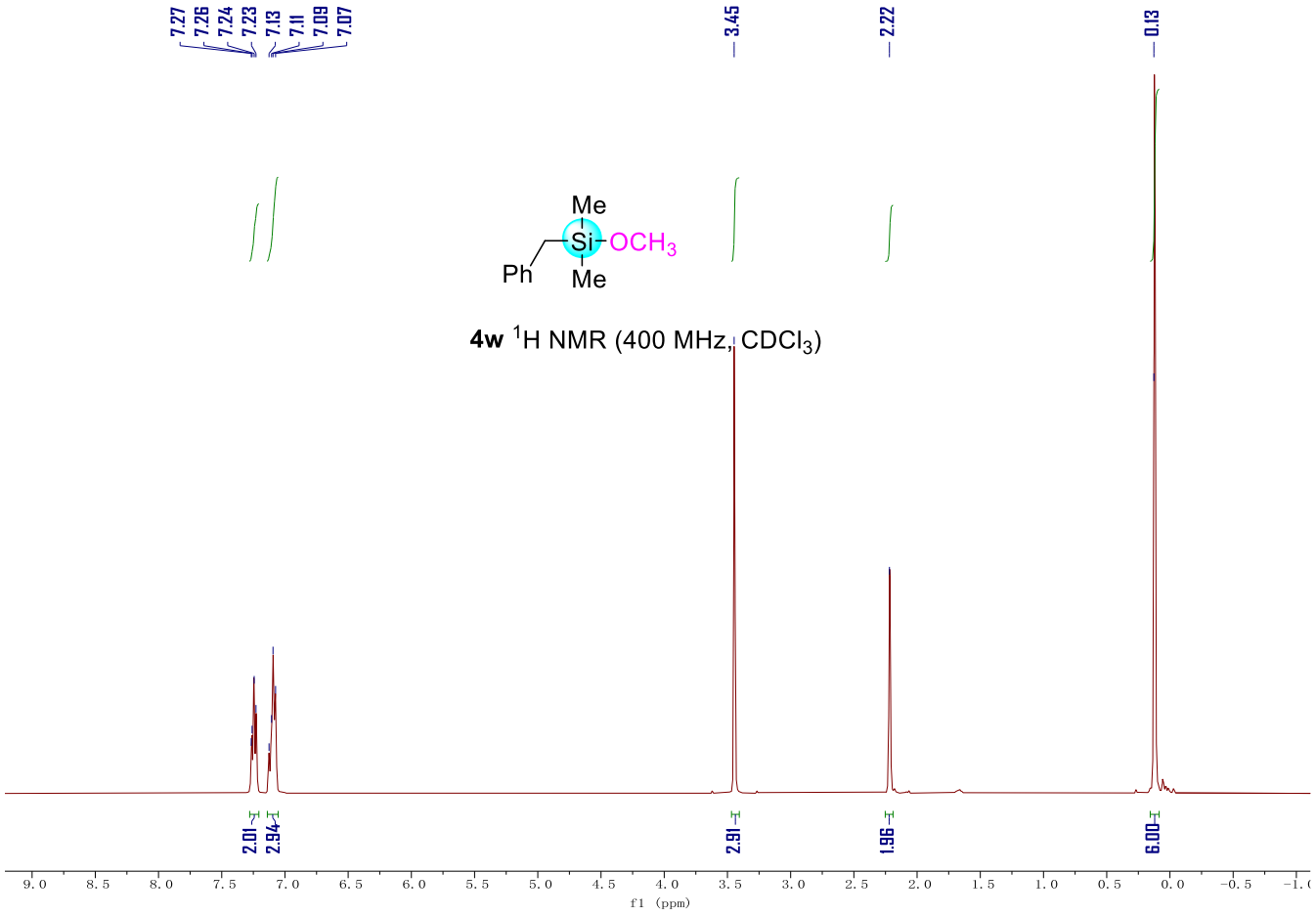
4u ^{1}H NMR (400 MHz, $CDCl_3$)



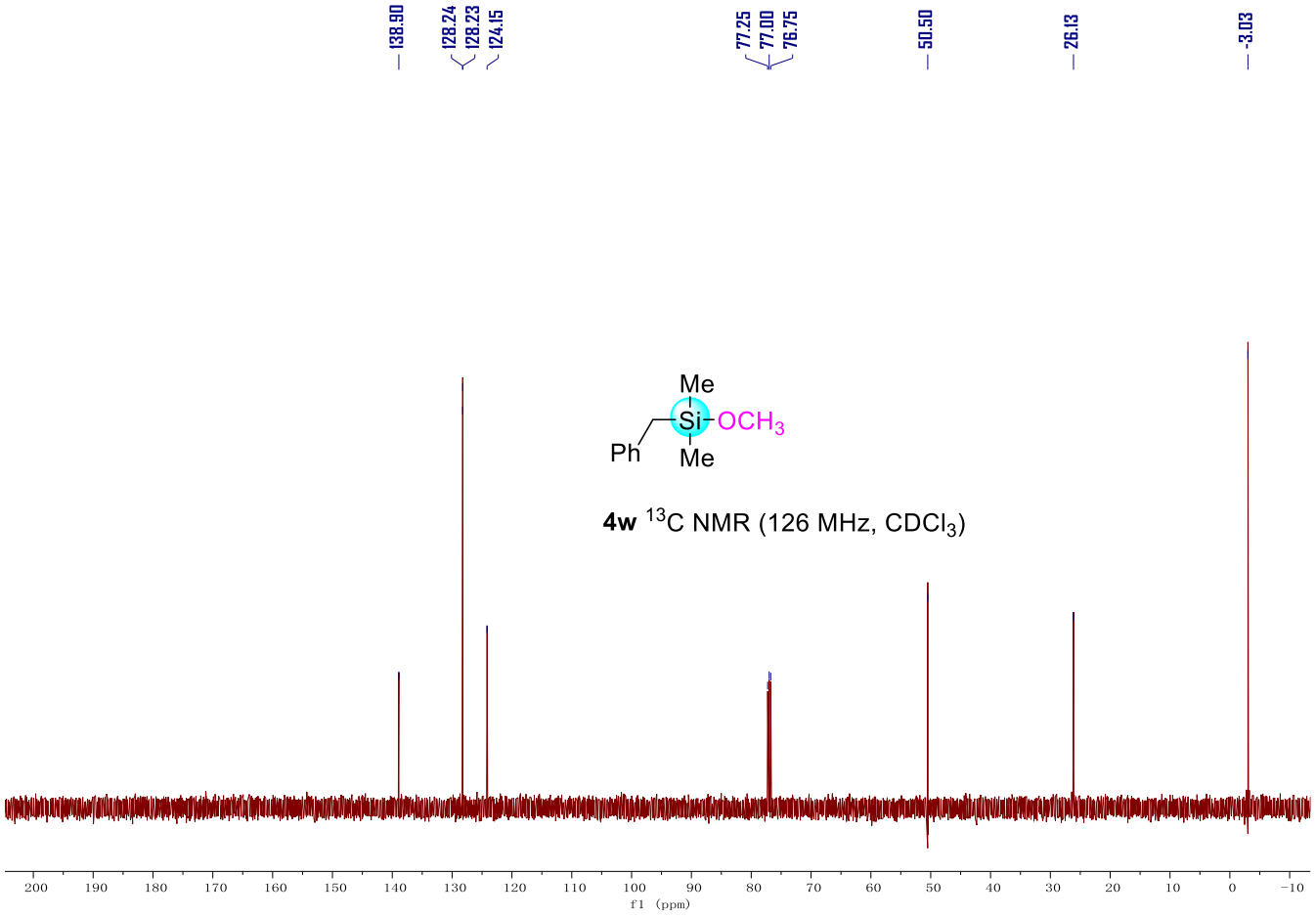
4v ^{1}H NMR (400 MHz, $CDCl_3$)



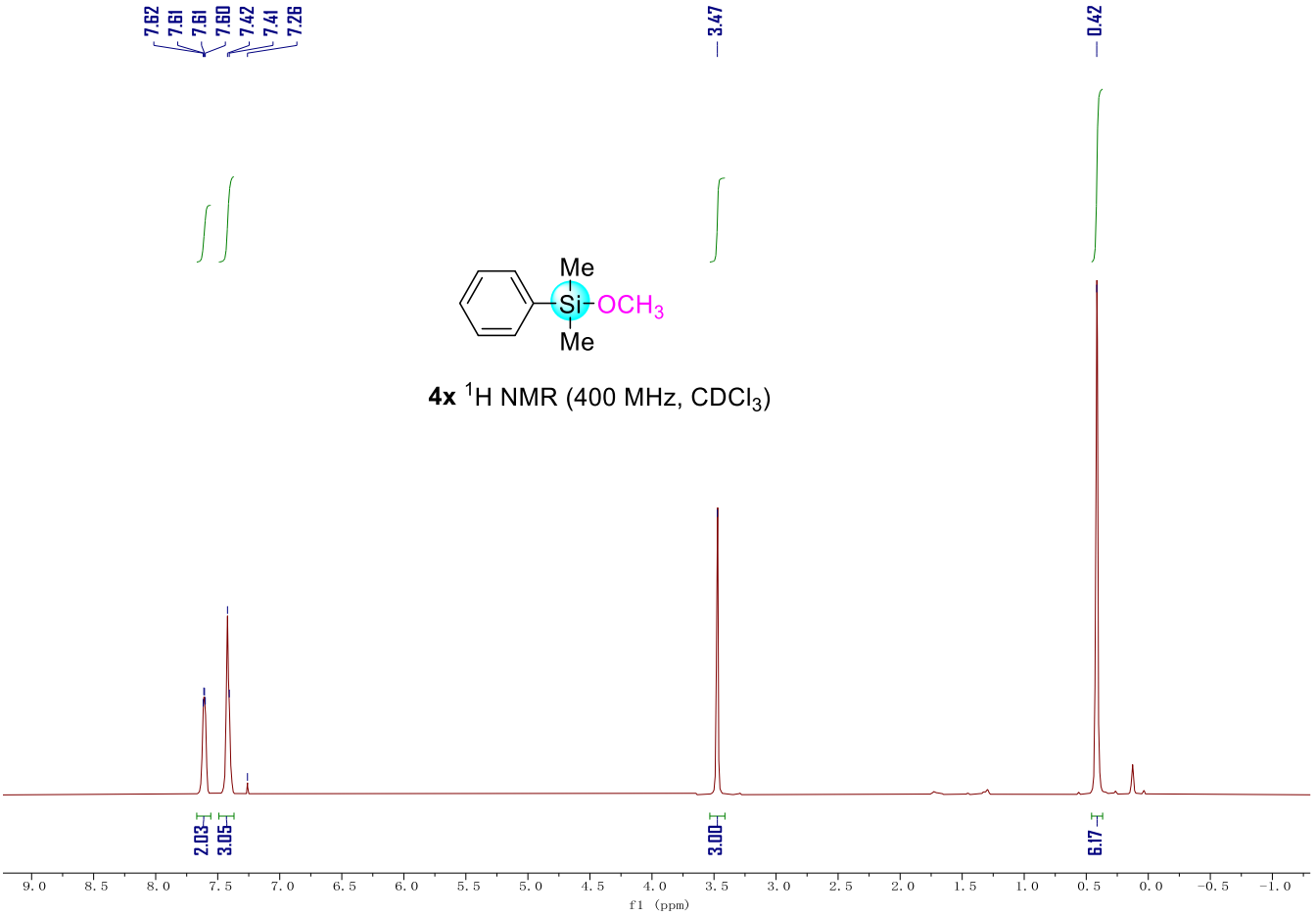
4v ^{13}C NMR (101 MHz, $CDCl_3$)



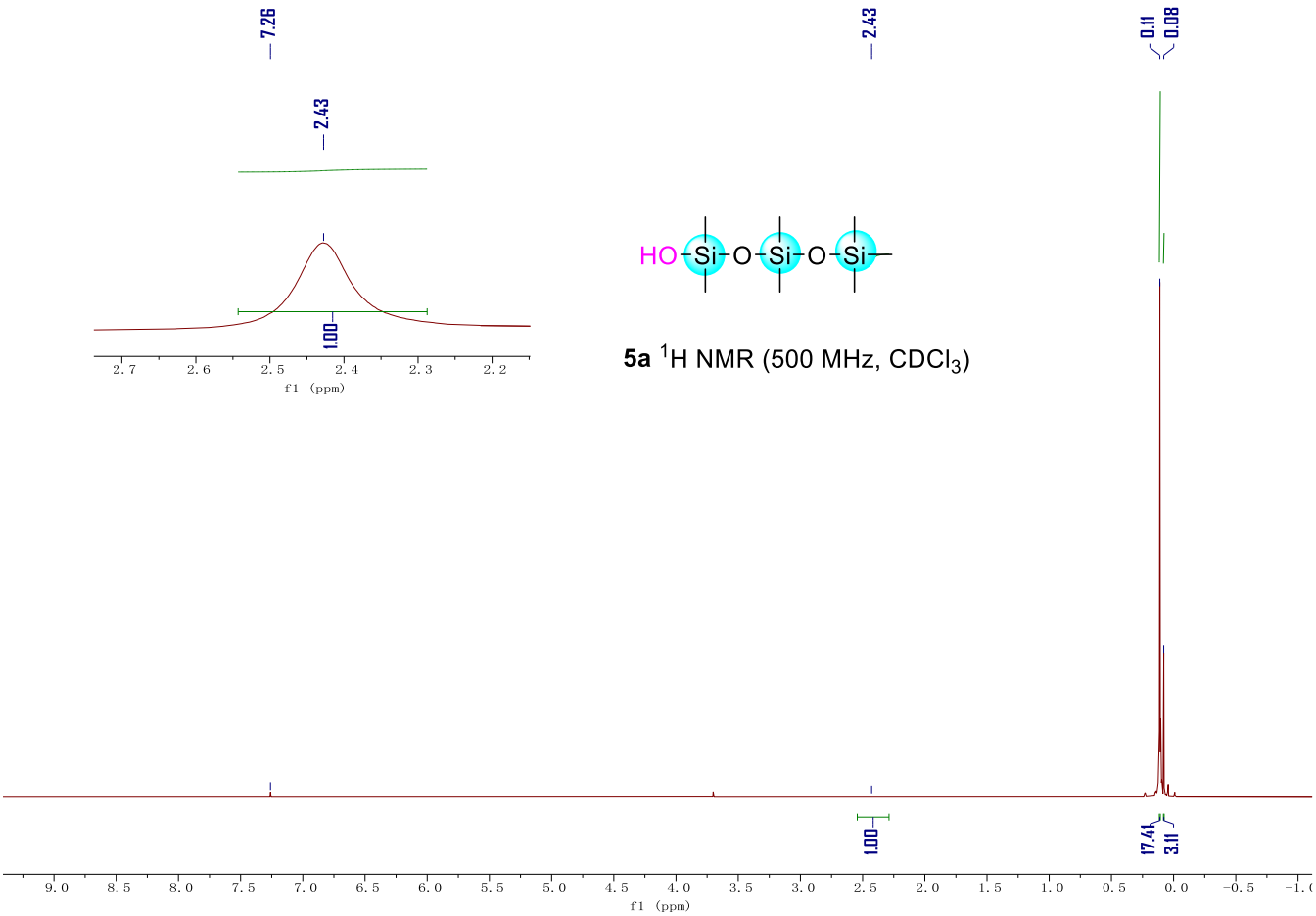
4w ^{1}H NMR (400 MHz, $CDCl_3$)



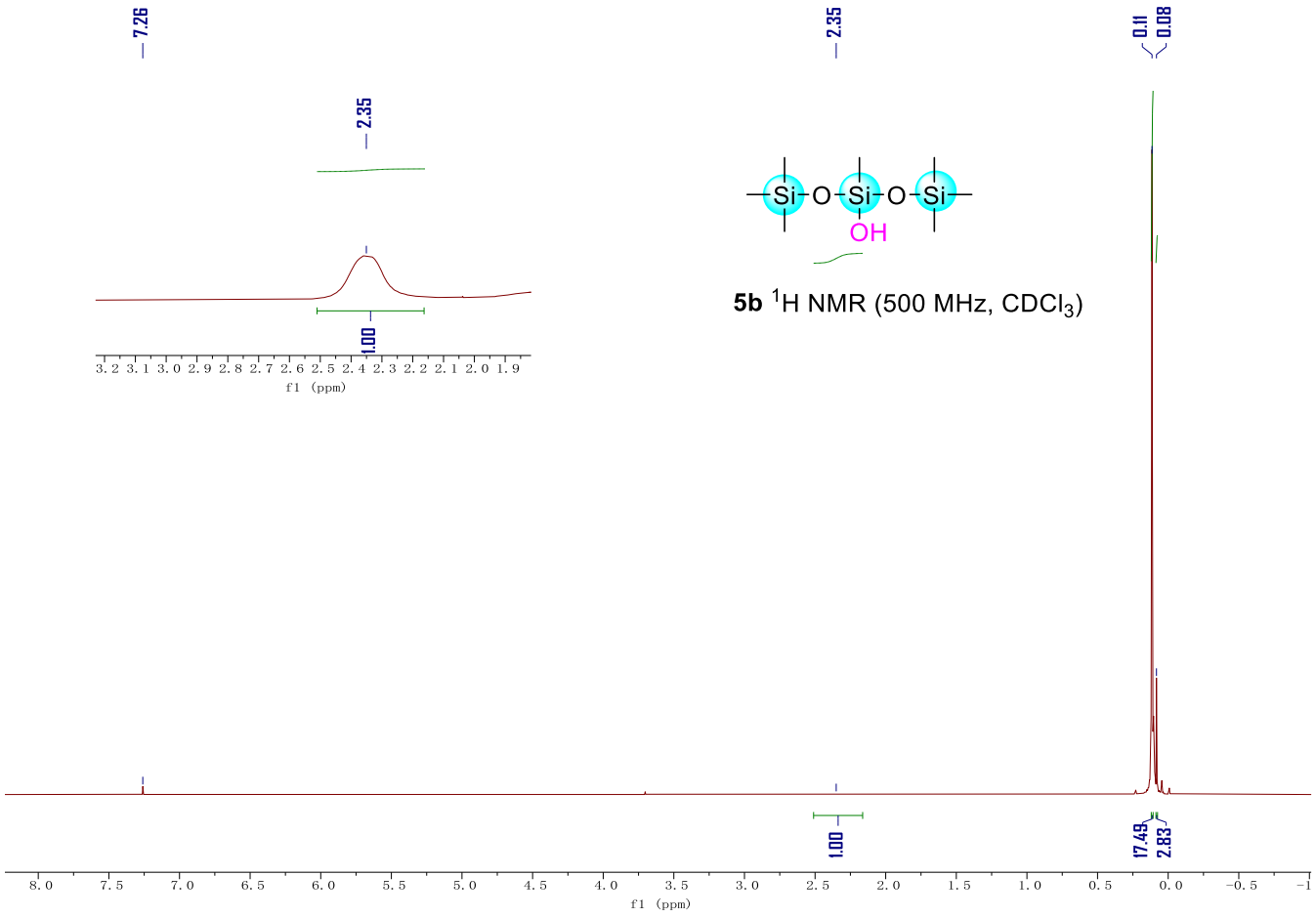
4w ^{13}C NMR (126 MHz, $CDCl_3$)



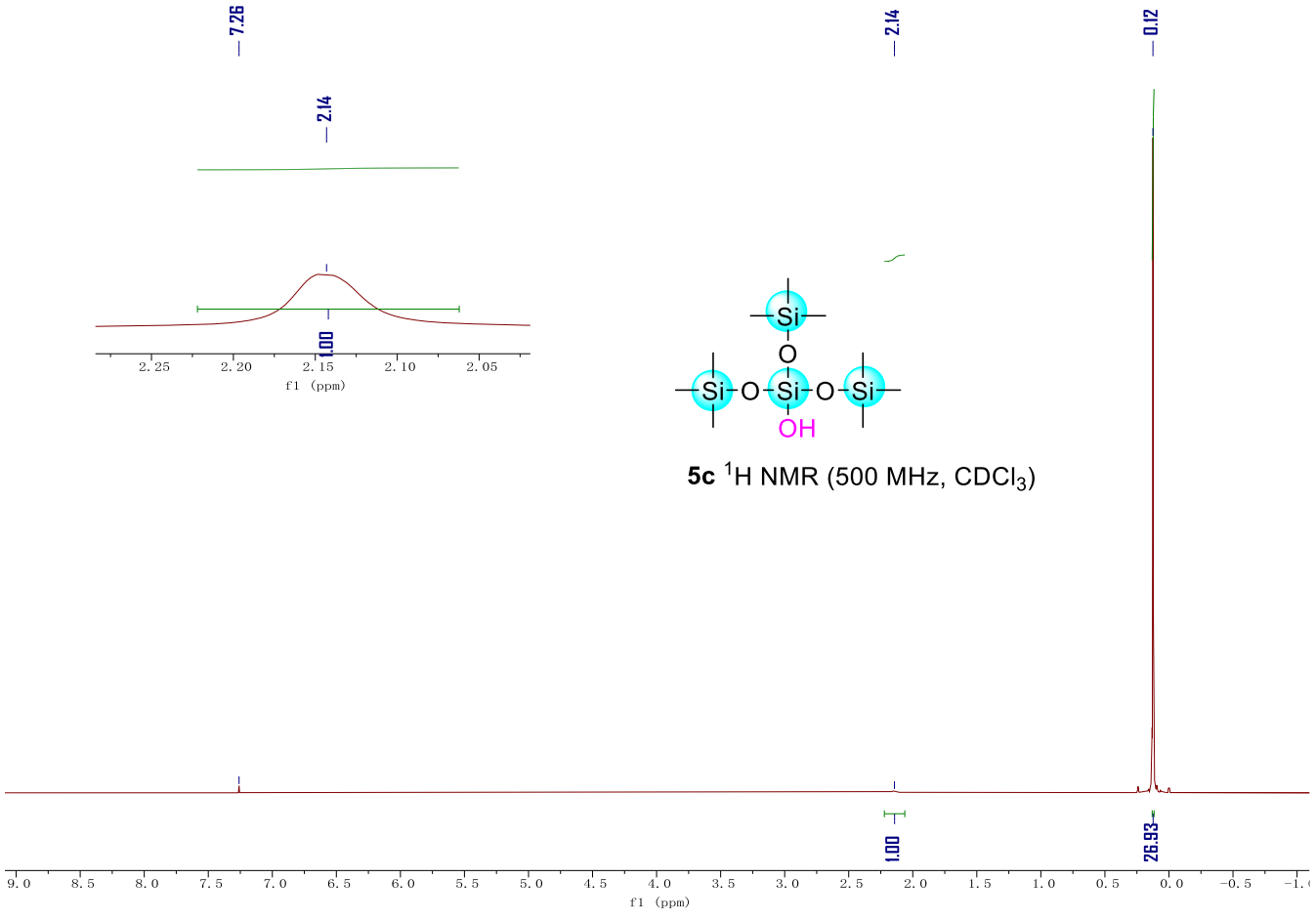
4x ^{1}H NMR (400 MHz, $CDCl_3$)



5a ^{1}H NMR (500 MHz, $CDCl_3$)



5b ^{1}H NMR (500 MHz, $CDCl_3$)



5c ^{1}H NMR (500 MHz, $CDCl_3$)