Supplementary Information

Synthesis of Unsymmetrical Dialkoxydiarylsilanes and Diarylsilanediols from Tetraalkoxysilane Having a Dioxasilepane Unit

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Instrumentation and Chemicals

^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{19}F NMR (564 MHz) spectra were recorded on a JEOL ECZ-600 spectrometer. ^{1}H NMR (594 MHz) and ^{13}C NMR (149 MHz) spectra were recorded on a JEOL ECA-600 spectrometer. Chemical shifts in ^{1}H NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to residual $CHCl_3$ (δ = 7.26 ppm) and CD_2HCOCD_3 (δ = 2.04 ppm). Chemical shifts in ^{13}C NMR spectra were recorded in delta (δ) units, parts per million (ppm) relative to $CDCl_3$ (δ = 77.00 ppm) and CD_3COCD_3 (δ = 29.80 ppm). For ^{19}F NMR spectra, fluorobenzene (^{19}F: δ = −113.50 ppm) were used as an external standard. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

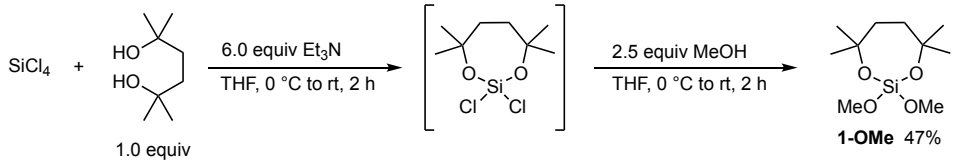
High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF II-KR spectrometer in Atmospheric Pressure Chemical Ionization (APCI) method using "LC/MS tuning mix, for APCI, low concentration" (Agilent Technologies, Inc.) as the internal standard or Electrospray Ionization (ESI) method using "ESI-L Low Concentration Tuning Mix" (Agilent Technologies, Inc.) as the internal standard. For all spectroscopic studies, spectroscopic grade solvents were used as purchased unless otherwise noted.

All non-aqueous reactions were carried out under an inert atmosphere of N_2 gas in oven-dried glassware unless otherwise noted. Dehydrated MeOH and MeCN were purchased from FUJIFILM Wako Pure Chemical Corporation and stored under nitrogen atmosphere. Dehydrated THF was purchased from Kanto Chemical Co., Inc. and stored under nitrogen atmosphere. Et_3N was used after distillation from CaH_2. All other reagents were commercially available and used without further purification unless otherwise noted.

Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25-mm thick, silica gel 60 F_{254}. Preparative flash chromatography was performed using Silica Gel (Wakosil® C-300 purchased from FUJIFILM Wako Pure Chemical Corporation, or Silica Gel 60N, spherical neutral, particle size 100-210 μm, purchased from Kanto Chemical Co., Inc.) and Alumina (activated 200 purchased from Nacalai Tesque, Inc.). Preparative recycling gel permeation chromatography (GPC) was performed on a JAI LC-9260 II NEXT system using $CHCl_3$ as the eluent.

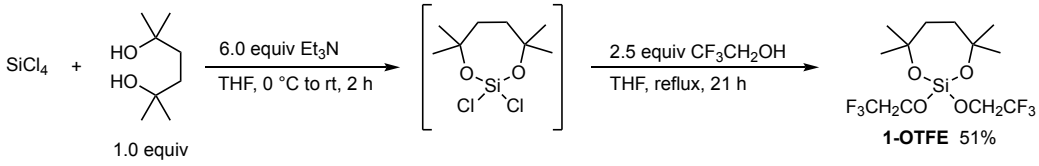
Preparation of Substrates

Preparation of 1 (1-OMe, 1-OEt)



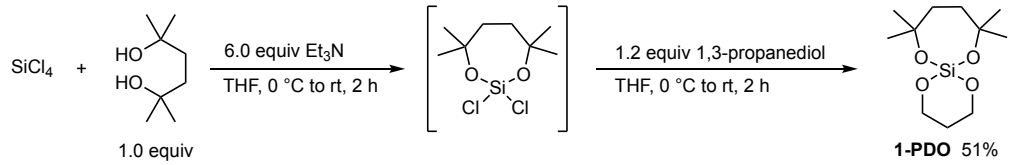
The synthesis of **1-OMe** is representative. A 500-mL, oven-dried two-necked round-bottomed flask was charged with Et_3N (42.0 mL, 301 mmol) and THF (175 mL). After the mixture was stirred at 0 °C for 5 min, tetrachlorosilane (5.73 mL, 50.0 mmol) was added. Then 2,5-dimethyl-2,5-hexanediol (7.31 g, 50.0 mmol) in THF (25 mL) was slowly added, and the resulting mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 h, then MeOH (5.06 mL, 125 mmol) was added at 0 °C, and the resulting mixture was allowed to warm to room temperature. After 2 h, hexane (175 mL) was added to the flask and the precipitate was filtered off by using a Büchner funnel. The filtrate was concentrated under reduced pressure and passed through pads of silica gel and alumina with hexane/EtOAc (10/1) as an eluent. The resulting solution was concentrated under reduced pressure and purified by distillation (87 °C / 9 torr) to give **1-OMe** as a colorless oil (5.49 g, 23.4 mmol, 47%).

Preparation of 1-OTFE



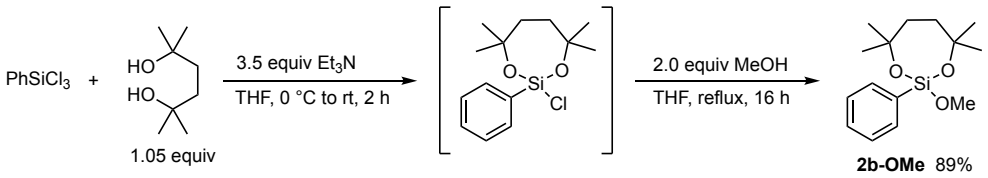
A 1-L, oven-dried two-necked round-bottomed flask was charged with Et_3N (83.7 mL, 600 mmol) and THF (350 mL). After the mixture was stirred at 0 °C for 5 min, tetrachlorosilane (11.5 mL, 100 mmol) was added to the mixture. 2,5-Dimethyl-2,5-hexanediol (14.6 g, 100 mmol) in THF (50 mL) was slowly added to the reaction mixture, and the resulting mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 h, then 2,2,2-trifluoroethanol (18.2 mL, 250 mmol) was added. After the reaction mixture was refluxed in an oil bath for 21 h, hexane (350 mL) was added to the flask and the precipitate was filtered off by using a Büchner funnel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/0 to 40/1) and then distillation of the resulting residue (46 °C / 0.12 torr) afforded **1-OTFE** as a colorless oil (19.0 g, 51.3 mmol, 51%).

Preparation of 1-PDO



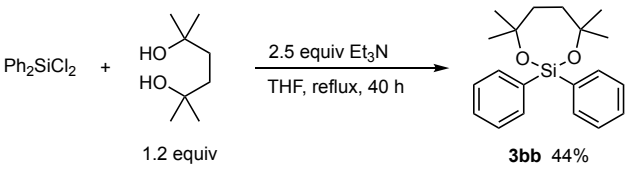
A 300-mL, oven-dried two-necked round-bottomed flask was charged with Et_3N (25.1 mL, 180 mmol) and THF (100 mL). After the mixture was stirred at 0 °C for 5 min, tetrachlorosilane (3.44 mL, 30.0 mmol) was added to the mixture. Then, 2,5-dimethyl-2,5-hexanediol (4.39 g, 30.0 mmol) in THF (20 mL) was slowly added to the reaction, and the resulting mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 h. 1,3-Propanediol (2.60 mL, 36.0 mmol) was added to the reaction mixture at 0 °C, and the resulting mixture was allowed to warm to room temperature. After 2 h, hexane (100 mL) was added to the flask and the precipitate was filtered off by using a Büchner funnel. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give **1-PDO** as a colorless oil (3.78 g, 15.3 mmol, 51%).

Preparation of 2 (2b-OMe, 2b-OEt, 2b-OTFE)



The synthesis of **2b-OMe** is representative. A 300-mL, oven-dried two-necked round-bottomed flask was charged with 2,5-dimethyl-2,5-hexanediol (3.07 g, 21.0 mmol), Et_3N (9.77 mL, 70.0 mmol), and THF (60 mL). After the mixture was stirred at 0 °C for 5 min, trichlorophenylsilane (3.20 mL, 20.0 mmol) was slowly added to the mixture and the resulting mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 h, then MeOH (1.62 mL, 40.0 mmol) was added and the reaction mixture was refluxed in an oil bath. After 16 h, hexane (60 mL) was added to the flask and the precipitate was filtered off by using a Büchner funnel. The filtrate was concentrated under reduced pressure and purified by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1) to give **2b-OMe** as a colorless oil (5.01 g, 17.9 mmol, 89%).

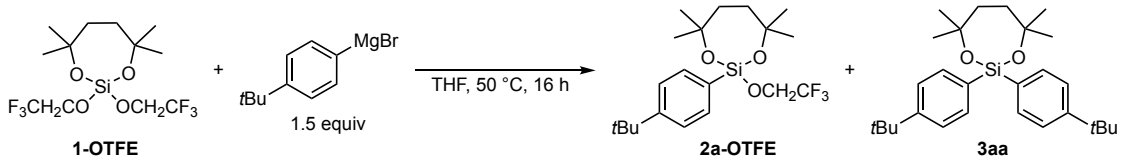
Preparation of 3bb



A 200-mL, oven-dried two-necked round-bottomed flask was charged with 2,5-dimethyl-2,5-hexanediol (2.63 g, 18.0 mmol), Et_3N (5.30 mL, 38.0 mmol), and THF (30 mL). After the mixture was stirred at 0 °C for 5 min, dichlorodiphenylsilane (3.11 mL, 15.0 mmol) was slowly added to the mixture and the resulting mixture was refluxed in an oil bath. After 40 h, hexane (30 mL) was added to the flask and the precipitate was filtered off by using a Büchner funnel. The filtrate was concentrated under reduced pressure and the residue was poured into a separatory funnel with hexane (50 mL), saturated $NaHCO_3$ aq. (30 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with hexane (50 mL × 2). The combined organic extract was washed with brine (30 mL), dried over Na_2SO_4 (ca. 30 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/0 to 50/1) to provide **3bb** as a white solid (2.15 g, 6.58 mmol, 44%).

Optimization of Reaction Conditions

Table S1.

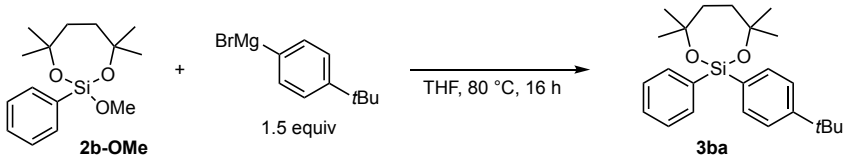


1-OTFE 2a-OTFE 3aa

entry	Deviations from standard conditions	**2a-OTFE**[a] [%]	**3aa**[a] [%]
1	none	93	3
2	1.2 equiv 4-*tert*-butylphenylmagnesium bromide	90	2
3	40 °C	91	3
4	80 °C	80	14

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

Table S2.

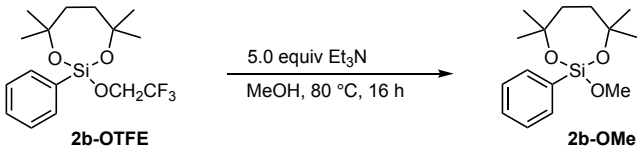


2b-OMe **3ba**

entry	Deviations from standard conditions	**3ba**[a] [%]
1	none	96
2	1.2 equiv 4-*tert*-butylphenylmagnesium bromide	94
3	50 °C	90

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

Table S3.



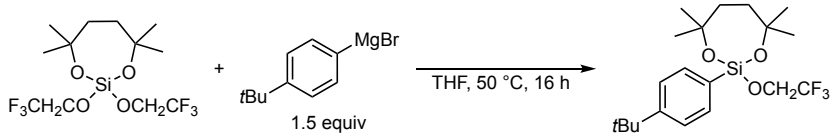
2b-OTFE **2b-OMe**

entry	Deviations from standard conditions	**2b-OTFE**[a] [%]	**2b-OMe**[a] [%]
1	none	92	0
2	DIPEA instead of Et_3N	89	3
3	DABCO instead of Et_3N	71	5
4	imidazole instead of Et_3N	51	39
5	pyridine instead of Et_3N	1	91
6	DBU instead of Et_3N	1	1
7	3.0 equiv Et_3N	89	1
8	10 equiv Et_3N	89	0

[a] Determined by ^{1}H NMR analysis using mesitylene as an internal standard.

Experimental Procedures

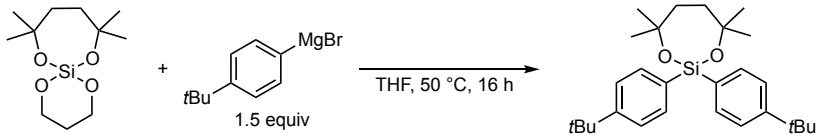
Reaction of 1-OTFE with 4-*tert*-butylphenylmagnesium bromide



1-OTFE **2a-OTFE** 96%

An oven-dried 20-mL Schlenk tube was charged with **1-OTFE** (370 mg, 0.999 mmol) and THF (0.50 mL). Then 4-*tert*-butylphenylmagnesium bromide (0.68 M in THF, 2.21 mL, 1.5 mmol) was added to the mixture at room temperature, and THF (1.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 50 °C on a preheated aluminum block. After 16 h, saturated NH_4Cl aq. (3 mL) was added, and the mixture was poured into a separatory funnel with Et_2O (20 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/0 to 40/1) to provide **2a-OTFE** as a colorless oil (388 mg, 0.960 mmol, 96%).

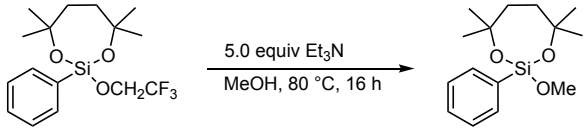
Reaction of 1-PDO with 4-*tert*-butylphenylmagnesium bromide



1-PDO **3aa** 69%

An oven-dried 20-mL Schlenk tube was charged with **1-PDO** (246 mg, 0.999 mmol) and THF (0.50 mL). Then 4-*tert*-butylphenylmagnesium bromide (0.68 M in THF, 2.21 mL, 1.5 mmol) was added to the mixture at room temperature, and THF (1.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 50 °C on a preheated aluminum block. After 16 h, saturated NH_4Cl aq. (3 mL) was added, and the mixture was poured into a separatory funnel with Et_2O (20 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/0 to 50/1) to provide **3aa** as a colorless wax (302 mg, 0.688 mmol, 69%).

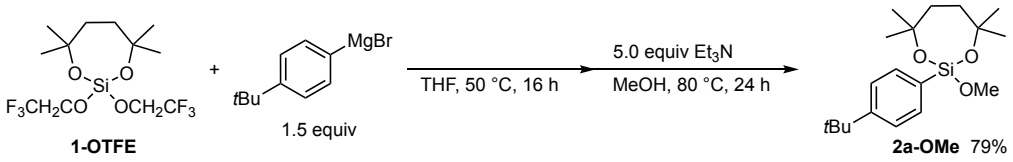
Alkoxide exchange of 2b-OTFE



2b-OTFE **2b-OMe** 93%

An oven-dried 20-mL Schlenk tube was charged with **2b-OTFE** (139 mg, 0.400 mmol) and MeOH (1.0 mL). Then Et_3N (279 μL, 2.00 mmol) was added, and MeOH (1.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 80 °C on a preheated aluminum block. After 16 h, the mixture was diluted with EtOAc (5 mL), and poured into a separatory funnel with EtOAc (20 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1) to provide **2b-OMe** as a colorless oil (105 mg, 0.373 mmol, 93%).

General procedure for first arylation and alkoxide exchange of 1-OTFE (GP1)



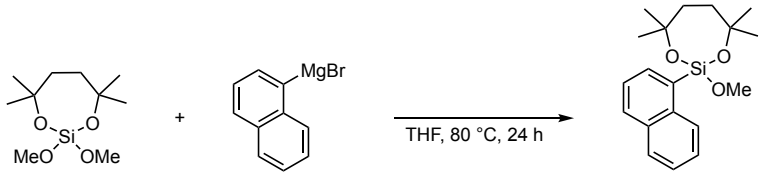
1-OTFE **2a-OMe** 79%

The synthesis of **2a-OMe** is representative. An oven-dried 20-mL Schlenk tube was charged with **1-OTFE** (370 mg, 0.999 mmol) and THF (0.50 mL). 4-*tert*-Butylphenylmagnesium bromide (0.64 M in THF, 2.34 mL, 1.5 mmol) was added to the mixture at room temperature, and THF (1.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 50 °C on a preheated aluminum block. After 16 h, saturated NH_4Cl aq. (3 mL) was added, and the mixture was poured into a separatory funnel with Et_2O (20 mL) and water (20 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was used for alkoxide exchange without purification.

An oven-dried 20-mL Schlenk tube was charged with the residue and MeOH (2.0 mL). Et_3N (0.70 mL, 5.0 mmol) was added to the mixture, and MeOH (3.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 80 °C on a preheated

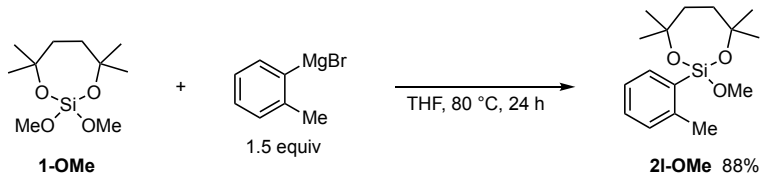
aluminum block. After 24 h, the mixture was diluted with EtOAc (5 mL) and poured into a separatory funnel with EtOAc (20 mL) and water (20 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with EtOAc (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/toluene = 1/0 to 1/1) to provide **2a-OMe** as a colorless oil (266 mg, 0.791 mmol, 79%).

Reaction of 1-OMe with naphthalen-1-ylmagnesium bromide (GP2)



An oven-dried 20-mL Schlenk tube was charged with 2,2-dimethoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepane **1-OMe** (234 mg, 0.998 mmol). Then naphthalen-1-ylmagnesium bromide (0.20 M in THF, 7.50 mL, 1.5 mmol) was added to the mixture at room temperature, and THF (0.50 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 80 °C on a preheated aluminum block. After 24 h, saturated NH_4Cl aq. (3 mL) was added, and the mixture was poured into a separatory funnel with Et_2O (20 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/toluene = 1/0 to 3/1) to provide **2k-OMe** as a colorless oil (240 mg, 0.726 mmol, 73%).

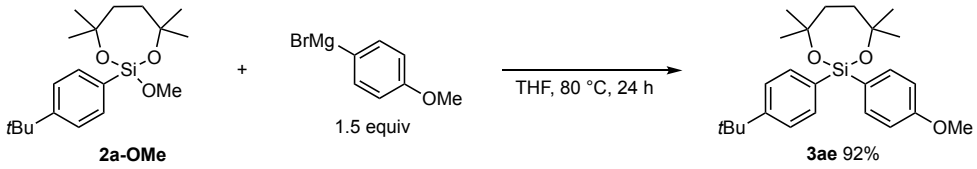
Reaction of 1-OMe with *o*-tolylmagnesium bromide (GP3)



1-OMe **2l-OMe** 88%

An oven-dried 20-mL Schlenk tube was charged with **1-OMe** (234 mg, 0.998 mmol) and THF (0.50 mL). Then *o*-tolylmagnesium bromide (0.73 M in THF, 2.05 mL, 1.5 mmol) was added to the mixture at room temperature, and THF (1.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 80 °C on a preheated aluminum block. After 24 h, saturated NH_4Cl aq. (3 mL) was added, and the mixture was poured into a separatory funnel with Et_2O (20 mL), water (20 mL) and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/toluene = 1/0 to 1/1) to provide **2l-OMe** as a colorless oil (259 mg, 0.880 mmol, 88%).

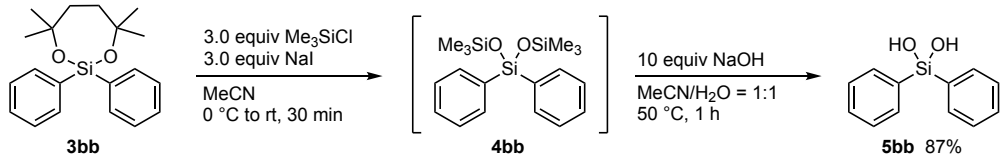
General procedure for second arylation of 2a-OMe (GP4)



2a-OMe **3ae** 92%

The synthesis of **3ae** is representative. An oven-dried 20-mL Schlenk tube was charged with **2a-OMe** (337 mg, 1.00 mmol) and THF (0.50 mL). 4-Methoxyphenylmagnesium bromide (0.82 M in THF, 1.83 mL, 1.5 mmol) was added to the mixture at room temperature, and THF (1.0 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 80 °C on a preheated aluminum block. After 24 h, saturated NH_4Cl aq. (3 mL) was added to the reaction at room temperature. The mixture was poured into a separatory funnel with Et_2O (20 mL) and water (20 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/toluene = 1/0 to 3/1) to provide **3ae** as a colorless oil (381 mg, 0.924 mmol, 92%).

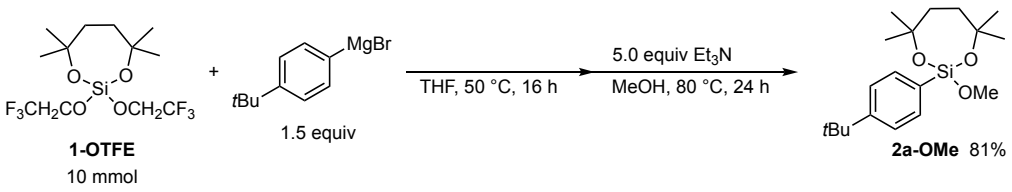
General procedure for synthesis of 5 (GP5)



The synthesis of **5bb** is representative. An oven-dried 20-mL Schlenk tube was charged with **3bb** (163 mg, 0.499 mmol), sodium iodide (225 mg, 1.50 mmol) and MeCN (1.0 mL). After the mixture was stirred at 0 °C for 5 min, chlorotrimethylsilane (0.189 mL, 1.50 mmol) was slowly added to the mixture, and MeCN (1.5 mL) was added to wash the inner side of the tube. The resulting mixture was allowed to warm to room temperature and stirring was continued for 30 min. Saturated NH_4Cl aq. (3 mL) was added to the reaction, and the mixture was poured into a separatory funnel with Et_2O (20 mL), water (20 mL), saturated Na_2SO_3 aq. (2 drops) and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, and concentrated under reduced pressure.

A 200-mL round-bottomed flask was charged with the residue, MeCN (25 mL), H_2O (25 mL), and NaOH aq. (1.0 M, 5.0 mL). The resulting mixture was stirred at 50 °C in a preheated oil bath. After 1 h, saturated NH_4Cl aq. (10 mL) was added, and the mixture was poured into a separatory funnel with Et_2O (20 mL) and water (20 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (20 mL × 2). The combined organic extract was washed with brine (10 mL), dried over Na_2SO_4 (ca. 10 g), filtered, concentrated under reduced pressure. The residue was recrystallized from DCM/hexane to provide **5bb** as a white solid (93.7 mg, 0.433 mmol, 87%).

Gram-scale synthesis of 2a-OMe



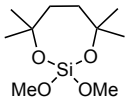
An oven-dried 200-mL Schlenk tube was charged with **1-OTFE** (3.70 g, 9.99 mmol) and THF (5.0 mL). 4-*tert*-Butylphenylmagnesium bromide (0.65 M in THF, 23.1 mL, 15 mmol) was added to the mixture at room temperature, and THF (10 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 50 °C in an oil bath. After 16 h, saturated NH_4Cl aq. (30 mL) was added. The mixture was poured into a separatory funnel with Et_2O (100

mL) and water (100 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with Et_2O (50 mL × 2). The combined organic extract was washed with brine (50 mL), dried over Na_2SO_4 (ca. 20 g), filtered, and concentrated under reduced pressure. The residue was used for alkoxide exchange without purification.

An oven-dried 100-mL Schlenk tube was charged with the residue and MeOH (30 mL). Et_3N (7.0 mL, 50 mmol) was added to the mixture, and MeOH (20 mL) was added to wash the inner side of the tube. The resulting mixture was stirred at 80 °C in an oil bath. After 24 h, the mixture was diluted with EtOAc (30 mL), and the reaction mixture was poured into a separatory funnel with EtOAc (100 mL) and water (100 mL), and partitioned. The organic phase was collected, and the aqueous phase was extracted with EtOAc (50 mL × 2). The combined organic extract was washed with brine (50 mL), dried over Na_2SO_4 (ca. 50 g), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel with an eluent (hexane/toluene = 1/0 to 1/1) to provide **2a-OMe** as a colorless oil (2.73 g, 8.10 mmol, 81%).

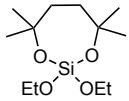
Characterization Data

2,2-Dimethoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (1-OMe):



R_f = 0.36 (hexane/EtOAc = 20/1); ^{1}H NMR ($CDCl_3$): δ 3.54 (s, 6H), 1.79 (br, 4H), 1.30 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 74.0, 50.9, 37.1, 30.1 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{10}H_{22}O_4Si$ 234.1282; Found 234.1273.

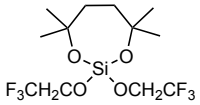
2,2-Diethoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (1-OEt):



Obtained as a colorless oil (7.36 g, 28.0 mmol, 56%) from tetrachlorosilane (5.73 mL, 50.0 mmol). Purification was done by distillation (44 °C / 0.15 torr). R_f = 0.45 (hexane/EtOAc = 20/1). ^{1}H NMR ($CDCl_3$): δ 3.81 (q, J = 6.9 Hz, 4H), 1.78 (br, 4H), 1.30 (s, 12H), 1.22 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$): δ 73.9, 58.9, 37.3, 30.2 (br, four methyl groups), 18.0; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{12}H_{26}O_4Si$ 262.1595; Found 262.1596.

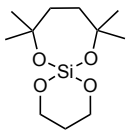
4,4,7,7-Tetramethyl-2,2-bis(2,2,2-trifluroethoxy)-1,3,2-dioxasilepane (1-OTFE):

R_f = 0.37 (hexane/EtOAc = 40/1); ^{1}H NMR ($CDCl_3$): δ 4.06 (q, J = 8.5 Hz, 4H), 1.82 (br, 4H), 1.30 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 123.8 (q, J = 279.4 Hz), 75.3, 61.6 (q, J = 36.2 Hz), 37.1, 29.8 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ −77.0



(t, J = 8.7 Hz); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{12}H_{20}F_6O_4Si$ 370.1030; Found 370.1026.

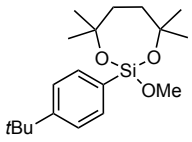
8,8,11,11-Tetramethyl-1,5,7,12-tetraoxa-6-silaspiro[5.6]dodecane (1-PDO):



R_f = 0.28 (hexane/EtOAc = 10/1); ^{1}H NMR ($CDCl_3$): δ 4.11 (dd, J = 5.5, 4.8 Hz, 4H), 1.87 (ddd, J = 10.8, 5.5, 4.8 Hz, 2H), 1.79 (br, 4H), 1.32 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 74.2, 65.0, 37.2, 30.6, 30.0 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{11}H_{22}O_4Si$ 246.1282; Found 246.1289.

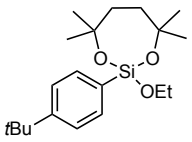
2-(4-*tert*-Butylphenyl)-2-methoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (2a-OMe):

R_f = 0.23 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.59 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.2 Hz, 2H), 3.48 (s, 3H), 1.84 (br, 4H), 1.37 (s, 6H), 1.30 (s, 9H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 152.7, 134.5, 129.1, 124.6, 74.7, 50.4, 37.5, 34.6, 31.2, 30.5 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{19}H_{32}O_3Si$ 336.2115; Found 336.2101.

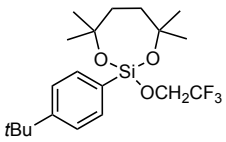


2-(4-*tert*-Butylphenyl)-2-ethoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (2a-OEt):

Obtained as a colorless oil (248 mg, 0.707 mmol, 71%) from **1-OEt** (262 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 50/1 to 30/1) and then GPC (eluent: $CHCl_3$). R_f = 0.38 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$): δ 7.60 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 3.74 (q, J = 7.2 Hz, 2H), 1.83 (br, 4H), 1.37 (s, 6H), 1.30 (s, 9H), 1.24 (s, 6H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 152.6, 134.5, 129.9, 124.5, 74.6, 58.3, 37.5, 34.6, 31.2, 30.5 (br, four methyl groups), 18.1; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{20}H_{34}O_3Si$ 350.2272; Found 350.2278.

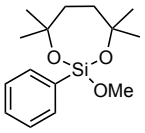


2-(4-*tert*-Butylphenyl)-4,4,7,7-tetramethyl-2-(2,2,2-trifluoroethoxy)-1,3,2-dioxasilepane (2a-OTFE):



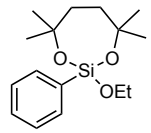
R_f = 0.47 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$): δ 7.58 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 3.98 (q, J = 8.7 Hz, 2H), 1.85 (br, 4H), 1.37 (s, 6H), 1.31 (s, 9H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 153.4, 134.6, 127.9, 124.8, 124.2 (q, J = 277.8 Hz), 75.4, 61.1 (q, J = 36.1 Hz), 37.4, 34.7, 31.2, 30.3 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ −76.5 (t, J = 8.7 Hz); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{20}H_{31}F_3O_3Si$ 404.1989; Found 404.1992.

2-Methoxy-4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepane (2b-OMe):



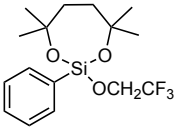
R_f = 0.24 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$): δ 7.67 (dd, J = 7.6, 1.4 Hz, 2H), 7.39 (tt, J = 7.6, 1.4 Hz, 1H), 7.35 (m, 2H), 3.48 (s, 3H), 1.84 (br, 4H), 1.38 (s, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 134.6, 132.8, 129.8, 127.6, 74.7, 50.3, 37.4, 30.4 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{15}H_{24}O_3Si$ 280.1489; Found 280.1479.

2-Ethoxy-4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepane (2b-OEt):



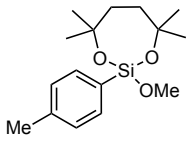
Obtained as a colorless oil (5.09 g, 17.3 mmol, 86%) from trichlorophenylsilane (3.20 mL, 20.0 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1). R_f = 0.25 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$): δ 7.67 (dd, J = 7.6, 1.4 Hz, 2H), 7.38 (tt, J = 7.6, 1.4 Hz, 1H), 7.34 (m, 2H), 3.73 (q, J = 6.9 Hz, 2H), 1.83 (br, 4H), 1.37 (s, 6H), 1.23 (s, 6H), 1.18 (t, J = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 134.6, 133.5, 129.7, 127.5, 74.7, 58.3, 37.5, 30.5 (br, four methyl groups), 18.1; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{16}H_{26}O_3Si$ 294.1646; Found 294.1636.

2-Phenyl-4,4,7,7-tetramethyl-2-(2,2,2-trifluroethoxy)-1,3,2-dioxasilepane (2b-OTFE):



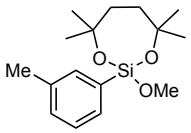
Obtained as a colorless oil (4.55 g, 13.1 mmol, 65%) from trichlorophenylsilane (3.20 mL, 20.0 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 50/1). R_f = 0.29 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$): δ 7.65 (dd, J = 7.6, 1.4 Hz, 2H), 7.42 (tt, J = 7.6, 1.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 3.97 (q, J = 8.9 Hz, 2H), 1.86 (br, 4H), 1.38 (s, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 134.6, 131.4, 130.3, 127.8, 124.2 (q, J = 277.8 Hz), 75.5, 61.0 (q, J = 36.2 Hz), 37.4, 30.3 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ −76.5 (t, J = 8.2 Hz); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{16}H_{23}F_3O_3Si$ 348.1363; Found 348.1356.

2-Methoxy-4,4,7,7-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxasilepane (2c-OMe):



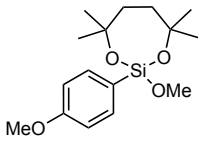
Synthesized via **GP1** by using *p*-tolylmagnesium bromide (0.68 M in THF, 2.21 mL, 1.5 mmol). Reaction time was 16 h for arylation and then 24 h for alkoxide exchange. Obtained as a pale yellow oil (237 mg, 0.804 mmol, 80%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 1/1). R_f = 0.26 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 2H), 7.17 (d, J = 7.6 Hz, 2H), 3.46 (s, 3H), 2.35 (s, 3H), 1.83 (br, 4H), 1.37 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 139.7, 134.7, 129.2, 128.4, 74.7, 50.3, 37.5, 30.4 (br, four methyl groups), 21.6; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{16}H_{26}O_3Si$ 294.1646; Found 294.1638.

2-Methoxy-4,4,7,7-tetramethyl-2-(*m*-tolyl)-1,3,2-dioxasilepane (2d-OMe):



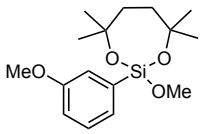
Synthesized via **GP1** by using *m*-tolylmagnesium bromide (0.71 M in THF, 2.14 mL, 1.5 mmol). Reaction time was 16 h for arylation and then 24 h for alkoxide exchange. Obtained as a colorless oil (239 mg, 0.812 mmol, 81%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 1/1). R_f = 0.28 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.47 (s, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 1H), 3.47 (s, 3H), 2.35 (s, 3H), 1.84 (br, 4H), 1.38 (s, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 136.9, 135.2, 132.5, 131.7, 130.7, 127.5, 74.7, 50.4, 37.4, 30.4 (br, four methyl groups), 21.5; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{16}H_{26}O_3Si$ 294.1646; Found 294.1634.

2-Methoxy-2-(4-methoxyphenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (2e-OMe):



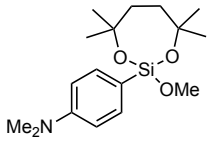
Synthesized via **GP1** by using 4-methoxyphenylmagnesium bromide (0.82 M in THF, 1.83 mL, 1.5 mmol). Reaction time was 16 h for arylation and then 24 h for alkoxide exchange. Obtained as a colorless oil (225 mg, 0.726 mmol, 73%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 0/1) and then GPC (eluent: $CHCl_3$). R_f = 0.29 (toluene); ^{1}H NMR ($CDCl_3$): δ 7.61–7.59 (d, J = 8.9 Hz, 2H), 6.89 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 3.46 (s, 3H), 1.82 (br, 4H), 1.37 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.9, 136.2, 123.9, 113.3, 74.6, 54.9, 50.3, 37.4, 30.4 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{16}H_{27}O_4Si$ 311.1673; Found 311.1681.

2-Methoxy-2-(3-methoxyphenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (2f-OMe):



Synthesized via **GP1** by using 3-methoxyphenylmagnesium bromide (0.69 M in THF, 2.17 mL, 1.5 mmol). Reaction time was 24 h for arylation then 16 h for alkoxide exchange. Obtained as a colorless oil (254 mg, 0.819 mmol, 82%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 0/1). R_f = 0.28 (toluene); ^{1}H NMR ($CDCl_3$): δ 7.29 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 2.7 Hz, 1H), 6.94–6.92 (dd, J = 8.7, 2.7 Hz, 1H), 3.82 (s, 3H), 3.47 (s, 3H), 1.84 (br, 4H), 1.38 (s, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 158.7, 134.3, 128.8, 126.9, 119.6, 115.4, 74.8, 55.0, 50.3, 37.4, 30.4 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{16}H_{26}O_4Si$ 310.1595; Found 310.1601.

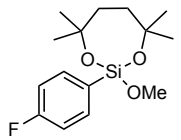
4-(2-Methoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepan-2-yl)-*N*,*N*-dimethylaniline (2g-OMe):



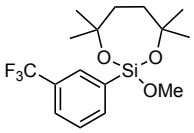
Synthesized via **GP1** by using 4-dimethylaminophenylmagnesium bromide (0.66 M in THF, 2.27 mL, 1.5 mmol). Reaction time was 16 h for arylation and then 72 h for alkoxide exchange. Obtained as a colorless oil (180 mg, 0.556 mmol, 56%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 0/1) and GPC (eluent: $CHCl_3$). R_f = 0.56 (hexane/EtOAc = 4/1); ^{1}H NMR ($CDCl_3$): δ 7.52 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 3.46 (s, 3H), 2.96 (s, 6H), 1.82 (br, 4H), 1.36 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 151.4, 135.8, 118.1, 111.5, 74.3, 50.2, 40.1, 37.5, 30.5 (br, four methyl groups); HRMS (APCI, positive): *m/z* $[M+H]^+$ Calcd for $C_{17}H_{29}NO_3Si$ 324.1989; Found 324.1990.

2-(4-Fluorophenyl)-2-methoxy-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (2h-OMe):

Synthesized via **GP1** by using 4-fluorophenylmagnesium bromide (0.67 M in THF, 2.24 mL, 1.5 mmol). Reaction time was 24 h for arylation then 16 h for alkoxide exchange. Obtained as a colorless oil (235 mg, 0.787 mmol, 79%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 1/1). R_f = 0.31 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.65 (dd, J = 8.2, 6.9 Hz, 2H), 7.03 (dd, J = 9.6, 8.2 Hz, 2H), 3.47 (s, 3H), 1.83 (br, 4H), 1.37 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 164.2 (d, J = 250.0 Hz), 136.7 (d, J = 8.7 Hz), 128.5 (d, J = 2.9 Hz), 114.8 (d, J = 18.8 Hz), 74.9, 50.4, 37.4, 30.5 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ −111.0 (tt, J = 9.9, 6.6 Hz); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{15}H_{23}FO_3Si$ 298.1395; Found 298.1389.

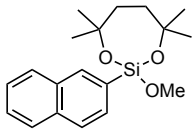


2-Methoxy-4,4,7,7-tetramethyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxasilepane (2i-OMe):



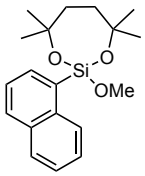
Synthesized via **GP1** by using 3-trifluoromethylphenylmagnesium bromide (0.65 M in THF, 2.31 mL, 1.5 mmol). Reaction time was 24 h for arylation and then 16 h for alkoxide exchange. Obtained as a pale yellow oil (231 mg, 0.664 mmol, 67%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 1/1). R_f = 0.63 (toluene); ^{1}H NMR ($CDCl_3$): δ 7.90 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 3.49 (s, 3H), 1.85 (br, 4H), 1.39 (s, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 137.9, 134.3, 131.1 (d, J = 4.4 Hz), 129.8 (q, J = 31.9 Hz), 127.9, 126.5 (d, J = 2.9 Hz), 124.3 (q, J = 273.5 Hz), 75.2, 50.5, 37.5, 30.4 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ −63.0; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{16}H_{23}F_3O_3Si$ 348.1363; Found 348.1365.

2-Methoxy-4,4,7,7-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxasilepane (2j-OMe):



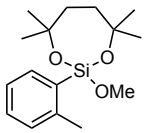
Synthesized via **GP1** by using naphthalen-2-ylmagnesium bromide (0.68 M in THF, 2.21 mL, 1.5 mmol). Reaction time was 24 h for arylation and then 16 h for alkoxide exchange. Obtained as a white solid (275 mg, 0.834 mmol, 83%) from **1-OTFE** (370 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 0/1). R_f = 0.44 (toluene); ^{1}H NMR ($CDCl_3$): δ 8.20 (s, 1H), 7.88–7.86 (m, 1H), 7.83–7.80 (m, 2H), 7.73–7.71 (m, 1H), 7.51–7.46 (m, 2H), 3.50 (s, 3H), 1.87 (br, 4H), 1.41 (s, 6H), 1.28 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 135.8, 134.1, 132.7, 130.4, 130.3, 128.3, 127.6, 126.8, 126.5, 125.6, 74.8, 50.4, 37.5, 30.4 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{19}H_{26}O_3Si$ 330.1646; Found 330.1647.

2-Methoxy-4,4,7,7-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxasilepane (2k-OMe):



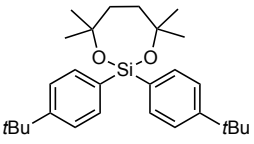
R_f = 0.31 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 8.38 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.51 (m, 1H), 7.48–7.44 (m, 2H), 3.41 (s, 3H), 1.91–1.87 (m, 4H), 1.44 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 136.9, 135.5, 133.2, 131.1, 130.6, 129.0, 128.4, 125.9, 125.3, 124.9, 75.1, 50.1, 37.6, 30.4 (br four methyl groups); HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{19}H_{26}O_3Si$ 330.1646; Found 330.1648.

2-Methoxy-4,4,7,7-tetramethyl-2-(*o*-tolyl)-1,3,2-dioxasilepane (2l-OMe):



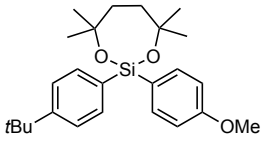
R_f = 0.22 (hexane/toluene = 1/1);^{1}H NMR ($CDCl_3$): δ 7.71 (dd, J = 7.6, 1.4 Hz, 1H), 7.28 (td, J = 7.6, 1.4 Hz, 1H), 7.15–7.13 (m, 2H), 3.43 (s, 3H), 2.50 (s, 3H), 1.83 (br, 4H), 1.39 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 144.2, 136.0, 131.7, 130.0, 129.5, 124.5, 74.8, 49.9, 37.5, 30.3 (br, four methyl groups), 22.4; HRMS (APCI, positive): *m/z* $[M+H]^+$ Calcd for $C_{16}H_{27}O_3Si$ 295.1724; Found 295.1731.

2,2-Bis(4-*tert*-butylphenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (3aa):



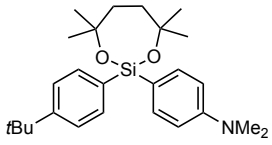
R_f = 0.37 (hexane/EtOAc = 50/1); ^{1}H NMR ($CDCl_3$): δ 7.57 (d, J = 8.2 Hz, 4H), 7.32 (d, J = 8.2 Hz, 4H), 1.85 (br, 4H), 1.29 (s, 18H), 1.28 (s, 12H); ^{13}C NMR ($CDCl_3$): δ 152.1, 134.4, 133.6, 124.3, 75.2, 37.9, 34.6, 31.3, 30.8 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{28}H_{42}O_2Si$ 438.2949; Found 438.2934.

2-(4-*tert*-Butylphenyl)-2-(4-methoxyphenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (3ae):



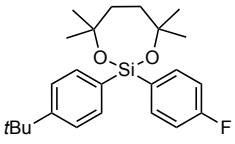
R_f = 0.42 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.58 (m, 2H), 7.55 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.2 Hz, 2H), 3.80 (s, 3H), 1.85 (br, 4H), 1.29 (s, 9H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.7, 152.2, 136.2, 134.4, 133.5, 128.2, 124.3, 113.1, 75.2, 54.9, 37.9, 34.6, 31.2, 30.7 (br, four methyl groups); HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{25}H_{36}O_3Si$ 412.2428; Found 412.2428.

2-(4-*tert*-Butylphenyl)-2-(4-dimethylaminophenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (3ag):



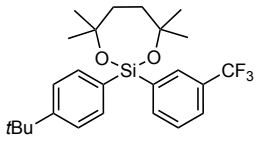
Synthesized via **GP4** by using 4-dimethylaminophenylmagnesium bromide (0.66 M in THF, 2.27 mL,1.5 mmol). Obtained as a white solid (413 mg, 0.971 mmol, 97%) from **2a-OMe** (337 mg, 1.00 mmol). Purification was done by column chromatography on silica gel (hexane/toluene=1/0 to 1/1). R_f = 0.21 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.69 (d, J = 8.2 Hz, 2H), 2.95 (s, 6H), 1.84 (br, 4H), 1.29 (s, 9H), 1.28 (br, 12H); ^{13}C NMR ($CDCl_3$): δ 151.9, 151.1, 135.8, 134.4, 134.1, 124.2, 122.3, 111.3, 74.9, 40.1, 37.8, 34.5, 31.2, 30.8 (br, four methyl groups); HRMS (APCI, positive): *m/z* $[M+H]^+$ Calcd for $C_{26}H_{40}NO_2Si$ 426.2823; Found 426.2830.

2-(4-*tert*-Butylphenyl)-2-(4-fluorophenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepane (3ah):



Synthesized via **GP4** by using 4-fluorophenylmagnesium bromide (0.67 M in THF, 2.24 mL, 1.5 mmol). Obtained as a colorless oil (364 mg, 0.910 mmol, 91%) from **2a-OMe** (337 mg, 1.00 mmol). Purification was done by column chromatography on silica gel (hexane/toluene=1/0 to 10/1). R_f = 0.32 (hexane/toluene = 10/1); ^{1}H NMR ($CDCl_3$): δ 7.63 (dd, J = 8.2, 6.9 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.00 (dd, J = 8.9, 8.2 Hz, 2H), 1.85 (br, 4H), 1.30 (s, 9H), 1.29 (s, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 164.0 (d, J = 248.8 Hz), 152.5, 136.6 (d, J = 7.2 Hz), 134.3, 132.9, 132.8 (d, J = 4.3 Hz), 124.5, 114.5 (d, J = 20.2 Hz), 75.4, 37.9, 34.6, 31.2, 30.7 (br, four methyl group); ^{19}F NMR ($CDCl_3$): δ –111.9; HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{24}H_{33}FO_2Si$ 400.2228; Found 400.2234.

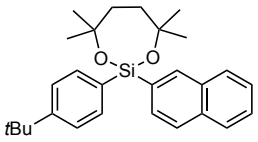
2-(4-*tert*-Butylphenyl)-4,4,7,7-tetramethyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxasilepane (3ai):



Synthesized via **GP4** by using 3-trifluoromethylphenylmagnesium bromide (0.65 M in THF, 2.31 mL, 1.5 mmol). Obtained as a white solid (366 mg, 0.811 mmol, 81%) from **2a-OMe** (337 mg, 1.00 mmol). Purification was done by column chromatography on silica gel (hexane/toluene=1/0 to 20/1). R_f = 0.39 (hexane/toluene = 10/1); ^{1}H NMR ($CDCl_3$): δ 7.93 (s, 1H), 7.81 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.55–7.53 (m, 2H), 7.42 (t, J = 7.5 Hz, 1H), 7.35–7.34 (m, 2H), 1.86 (br, 4H), 1.303 (s, 6H), 1.298 (s, 9H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 152.8, 138.8, 137.9, 134.4, 132.4, 131.0 (d, J = 4.3 Hz), 129.7 (q, J = 31.8 Hz), 127.7, 126.1 (d, J = 2.9 Hz), 124.6, 124.5 (q, J =

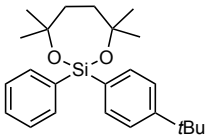
271.6 Hz), 75.8, 38.0, 34.7, 31.2, 30.7 (br, four methyl group); ^{19}F NMR ($CDCl_3$): δ –62.9; HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{25}H_{33}F_3O_2Si$ 450.2196; Found 450.2210.

2-(4-*tert*-Butylphenyl)-4,4,7,7-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxasilepane (3aj):



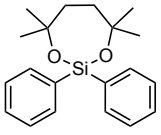
Synthesized via **GP4** by using naphthalen-2-ylmagnesium bromide (0.68 M in THF, 2.21 mL,1.5 mmol). Obtained as a white solid (351 mg, 0.811 mmol, 81%) from **2a-OMe** (337 mg, 1.00 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 50/1), then (hexane/toluene = 10/1) and GPC (eluent: $CHCl_3$). R_f = 0.47 (hexane/toluene = 3/1); ^{1}H NMR ($CDCl_3$): δ 8.18 (s, 1H), 7.84 (m, 1H), 7.81–7.79 (m, 2H), 7.74 (m, 1H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.49–7.44 (m, 2H), 7.33 (d, *J* = 8.9 Hz, 2H), 1.89 (br, 4H), 1.33 (s, 6H), 1.30 (s, 6H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 152.4, 135.6, 134.7, 134.4, 134.0, 133.2, 132.8, 130.7, 128.4, 127.7, 126.6, 126.3, 125.6, 124.5, 75.4, 38.0, 34.6, 31.2, 30.8 (br, four methyl groups); HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{28}H_{36}O_2Si$ 432.2479; Found 432.2470.

2-(4-*tert*-Butylphenyl)-4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepane (3ba):



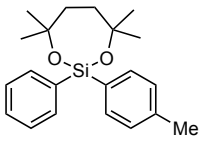
Synthesized via **GP4** by using 4-*tert*-butylphenylmagnesium bromide (0.64 M in THF, 2.34 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a colorless oil (365 mg, 0.954 mmol, 96%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 40/1). R_f = 0.58 (hexane/EtOAc = 40/1); ^{1}H NMR ($CDCl_3$): δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.36–7.30 (m, 5H), 1.86 (br, 4H), 1.29 (s, 15H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 152.3, 137.1, 134.6, 134.4, 133.2, 129.4, 127.4, 124.4, 75.3, 37.9, 34.6, 31.2, 30.8 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{24}H_{34}O_2Si$ 382.2323; Found 382.2321.

4,4,7,7-Tetramethyl-2,2-diphenyl-1,3,2-dioxasilepane (3bb):



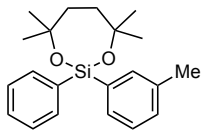
R_f = 0.26 (hexane/EtOAc = 30/1); ^{1}H NMR ($CDCl_3$): δ 7.64 (dd, *J* = 8.2, 1.4 Hz, 4H), 7.36 (tt, *J* = 7.6, 1.4 Hz, 2H), 7.32–7.30 (m, 4H), 1.86 (br, 4H), 1.28 (s, 12H) ; ^{13}C NMR ($CDCl_3$): δ 136.8, 134.5, 129.5, 127.4, 75.4, 37.9, 30.7 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{20}H_{26}O_2Si$ 326.1697; Found 326.1692.

4,4,7,7-Tetramethyl-2-phenyl-2-(*p*-tolyl)-1,3,2-dioxasilepane (3bc):



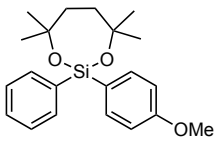
Synthesized via **GP4** by using *p*-tolylmagnesium bromide (0.68 M in THF, 2.21 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a white solid (320 mg, 0.938 mmol, 94%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 5/1). R_f = 0.27 (hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$): δ 7.63 (dd, J = 7.6, 1.4 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.35 (tt, J = 7.6, 1.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.30 (dd, J = 8.2, 1.4 Hz, 1H), 7.14 (d, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.85 (br, 4H), 1.27 (s, 6H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 139.3, 137.0, 134.6, 134.5, 133.2, 129.4, 128.3, 127.4, 75.3, 37.9, 30.7 (br, four methyl groups), 21.6; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{21}H_{28}O_2Si$ 340.1853; Found 340.1841.

4,4,7,7-Tetramethyl-2-phenyl-2-(*m*-tolyl)-1,3,2-dioxasilepane (3bd):



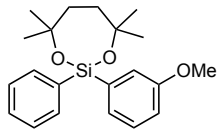
Synthesized via **GP4** by using *m*-tolylmagnesium bromide (0.71 M in THF, 2.11 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a white solid (307 mg, 0.902 mmol, 90%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 30/1). R_f = 0.28 (hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$): δ 7.64 (dd, J = 7.6, 1.4 Hz, 2H), 7.44 (m, 2H), 7.35 (tt, J = 7.6, 1.4 Hz, 1H), 7.33–7.29 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 2.32 (s, 3H), 1.86 (br, 4H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 136.9, 136.6, 136.6, 135.0, 134.5, 131.6, 130.3, 129.4, 127.4, 127.3, 75.4, 37.9, 30.7 (br, four methyl groups), 21.5; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{21}H_{28}O_2Si$ 340.1853; Found 340.1842.

2-(4-Methoxyphenyl)-4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepane (3be):



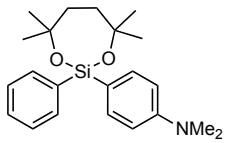
Synthesized via **GP4** by using 4-methoxyphenylmagnesium bromide (0.82 M in THF, 1.83 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a pale yellow oil (321 mg, 0.899 mmol, 90%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/EtOAc = 1/0 to 20/1) and then GPC (eluent: $CHCl_3$). R_f = 0.63 (toluene); ^{1}H NMR ($CDCl_3$): δ 7.63 (dd, J = 8.2, 1.4 Hz, 2H), 7.57 (d, J = 8.9 Hz, 2H), 7.35 (tt, J = 7.6, 1.4 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 1.85 (br, 4H), 1.272 (s, 6H), 1.266 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.7, 137.0, 136.1, 134.5, 129.4, 127.8, 127.4, 113.1, 75.2, 54.8, 37.8, 30.7 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{21}H_{28}O_3Si$ 356.1802; Found 356.1790.

2-(3-Methoxyphenyl)-4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepane (3bf):



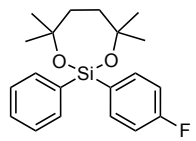
Synthesized via **GP4** by using 3-methoxyphenylmagnesium bromide (0.69 M in THF, 2.17 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a white solid (332 mg, 0.931 mmol, 93%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 1/1). R_f = 0.28 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.64 (dd, J = 8.2, 1.4 Hz, 2H), 7.35 (tt, J = 7.6, 1.4 Hz, 1H), 7.32–7.29 (m, 2H), 7.26 (tt, J = 7.6, 1.4 Hz, 1H), 7.24–7.20 (m, 2H), 6.90 (ddd, J = 8.2, 2.7, 1.4 Hz, 1H), 3.79 (s, 3H), 1.86 (br, 4H), 1.283 (s, 6H), 1.277 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 158.6, 138.3, 136.6, 134.4, 129.5, 128.7, 127.4, 126.9, 119.7, 114.9, 75.4, 54.9, 37.8, 30.6 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{21}H_{28}O_3Si$ 356.1802; Found 356.1815.

***N*,*N*-Dimethyl-4-(4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepan-2-yl)aniline (3bg):**



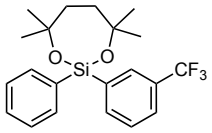
Synthesized via **GP4** by using 4-dimethylaminophenylmagnesium bromide (0.66 M in THF, 2.27 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a white solid (327 mg, 0.886 mmol, 89%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 1/1). R_f = 0.13 (hexane/toluene = 1/1); ^{1}H NMR ($CDCl_3$): δ 7.64 (dd, J = 7.6, 1.4 Hz, 2H), 7.50 (d, J = 8.9 Hz, 2H), 7.33 (tt, J = 7.6, 1.4 Hz, 1H), 7.30–7.28 (m, 2H), 6.68 (d, J = 8.9 Hz, 2H), 2.95 (s, 6H), 1.85 (br, 4H), 1.28 (s, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 151.1, 137.6, 135.7, 134.5, 129.1, 127.3, 121.8, 111.3, 75.0, 40.0, 37.8, 30.7 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M+H]^+$ Calcd for $C_{22}H_{32}NO_2Si$ 370.2197; Found 370.2201.

2-(4-Fluorophenyl)-4,4,7,7-tetramethyl-2-phenyl-1,3,2-dioxasilepane (3bh):



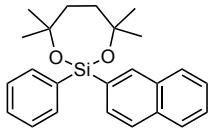
Synthesized via **GP4** by using 4-fluorophenylmagnesium bromide (0.67 M in THF, 2.24 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a white solid (318 mg, 0.924 mmol, 92%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 10/1). R_f = 0.33 (hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$): δ 7.63–7.60 (m, 4H), 7.37 (tt, J = 7.6, 1.4 Hz, 1H), 7.34–7.30 (m, 2H), 7.00 (dd, J = 8.9, 8.2 Hz, 2H), 1.85 (br, 4H), 1.271 (s, 6H), 1.266 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 164.0 (d, J = 248.5 Hz), 136.6 (d, J = 7.2 Hz), 136.5, 134.5, 132.5 (d, J = 2.9 Hz), 129.6, 127.5, 114.6 (d, J = 20.2 Hz), 75.5, 37.9, 30.6 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ −111.7 (tt, J = 9.9, 6.7 Hz); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{20}H_{25}FO_2Si$ 344.1602; Found 344.1595.

4,4,7,7-Tetramethyl-2-phenyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxasilepane (3bi):



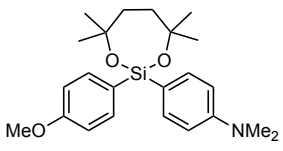
Synthesized via **GP4** by using 3-trifluoromethylphenylmagnesium bromide (0.65 M in THF, 2.31 mL, 1.5 mmol). Obtained as a white solid (331 mg, 0.840 mmol, 84%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 10/1). R_f = 0.31 (hexane/toluene = 10/1); ^{1}H NMR ($CDCl_3$): δ 7.91 (s, 1H), 7.80 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.2 Hz, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.38 (m, 1H), 7.33 (t, J = 7.2 Hz, 2H), 1.86 (br, 4H), 1.29 (s, 6H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 138.3, 137.9, 135.9, 134.5, 130.9 (d, J = 2.9 Hz), 129.8, 129.6 (q, J = 31.8 Hz), 129.5, 129.3, 127.8, 127.6, 126.2 (d, J = 4.3 Hz), 124.4 (q, J = 273.1 Hz), 75.9, 37.9, 30.6 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ –62.9; HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{21}H_{25}F_3O_2Si$ 394.1570; Found 394.1577.

4,4,7,7-Tetramethyl-2-(naphthalen-2-yl)-2-phenyl-1,3,2-dioxasilepane (3bj):



Synthesized via **GP4** by using naphthalen-2-ylmagnesium bromide (0.68 M in THF, 2.21 mL, 1.5 mmol). Reaction time was 16 h. Obtained as a white solid (352 mg, 0.935 mmol, 94%) from **2b-OMe** (280 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 5/1). R_f = 0.26 (hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$): δ 8.16 (s, 1H), 7.85–7.80 (m, 2H), 7.79 (d, J = 8.2 Hz, 1H), 7.73 (dd, J = 8.2, 1.4 Hz, 1H), 7.67 (dd, J = 8.2, 1.4 Hz, 2H), 7.49–7.44 (m, 2H), 7.37 (tt, J = 7.6, 1.4 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 1.89 (br, 4H), 1.31 (s, 6H), 1.30 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 136.7, 135.6, 134.6, 134.3, 134.0, 132.7, 130.6, 129.5, 128.4, 127.6, 127.5, 126.7, 126.4, 125.6, 75.5, 37.9, 30.7 (br, four methyl groups); HRMS (APCI-MS, positive): *m/z* $[M]^+$ Calcd for $C_{24}H_{28}O_2Si$ 376.1853; Found 376.1849.

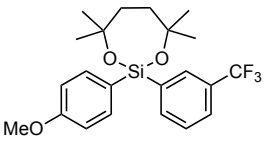
4-(2-(4-Methoxyphenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepan-2-yl)-*N*,*N*-dimethylaniline (3eg):



Synthesized via **GP4** by using 4-dimethylaminophenylmagnesium bromide (0.69 M in THF, 2.17 mL, 1.5 mmol). Obtained as a colorless oil (394 mg, 0.987 mmol, 99%) from **2e-OMe** (310 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 2/1 to 0/1). R_f = 0.27 (hexane/toluene = 1/2); ^{1}H NMR ($CDCl_3$): δ 7.56 (d, J = 8.2 Hz, 2H), 7.51 (br, 2H), 6.85 (d, J = 8.2 Hz, 2H), 6.69 (br, 2H), 3.79 (s, 3H), 2.97 (br, 6H), 1.84 (br, 4H), 1.27 (s, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 160.5, 151.1, 136.1, 135.8, 128.8, 122.3, 113.0, 111.4, 74.9, 54.8, 40.1,

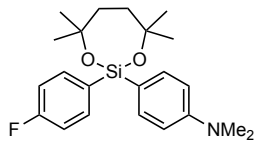
37.8, 30.7(br, four methyl groups); HRMS (APCI, positive): *m/z* $[M+H]^+$ Calcd for $C_{23}H_{34}NO_3Si$ 400.2302; Found 400.2299.

2-(4-Methoxyphenyl)-4,4,7,7-tetramethyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxasilepane (3ei):



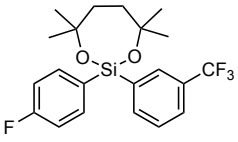
Synthesized via **GP4** by using 3-trifluoromethylphenylmagnesium bromide (0.65 M in THF, 2.31 mL, 1.5 mmol). Obtained as a colorless oil (339 mg, 0.799 mmol, 80%) from **2e-OMe** (310 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene=1/0 to 5/1). R_f= 0.24 (hexane/toluene = 5/1); ^{1}H NMR ($CDCl_3$): δ 7.90 (s, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.9 Hz, 2H), 7.42 (t, J = 7.6 Hz, 1H), 6.88 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 1.86 (br, 4H), 1.28 (s, 6H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 161.0, 138.7, 137.9, 136.1, 130.9 (d, J = 4.3 Hz) , 129.6 (q, J = 31.8 Hz), 127.7, 127.0, 126.1 (d, J = 4.3 Hz), 124.5 (q, J = 273.1 Hz), 113.4, 75.7, 54.9, 37.9, 30.6 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ –62.9; HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{22}H_{27}F_3O_3Si$ 424.1682; Found 424.1679.

4-(2-(4-Fluorophenyl)-4,4,7,7-tetramethyl-1,3,2-dioxasilepan-2-yl)-*N*,*N*-dimethylaniline (3hg):



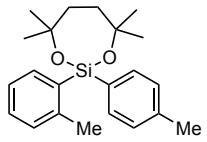
Synthesized via **GP4** by using 4-dimethylaminophenylmagnesium bromide (0.74 M in THF, 2.03 mL, 1.5 mmol). Obtained as a colorless oil (376 mg, 0.971 mmol, 97%) from **2h-OMe** (298 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene = 1/0 to 3/1). R_f = 0.21 (hexane/toluene = 3/1); ^{1}H NMR ($CDCl_3$): δ 7.61 (dd, J = 8.9, 6.2 Hz, 2H), 7.49 (brd, J = 6.9 Hz, 2H), 6.99 (dd, J = 9.6, 8.9 Hz, 2H), 6.69 (br, 2H), 2.96 (s, 6H), 1.84 (s, 4H), 1.28 (s, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 163.8 (d, J = 248.5 Hz), 151.3, 136.6 (d, J =7.2 Hz), 135.7, 133.4, 121.6, 114.4 (d, J = 20.2 Hz), 111.4, 75.1, 40.0, 37.9, 30.7 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ –112.4; HRMS (APCI, positive): *m/z* $[M+H]^+$ Calcd for $C_{22}H_{31}FNO_2Si$ 388.2103; Found 388.2119.

2-(4-Fluorophenyl)-4,4,7,7-tetramethyl-2-(3-trifluoromethylphenyl)-1,3,2-dioxasilepane (3hi):



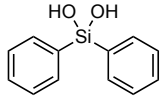
Synthesized via **GP4** by using 3-trifluoromethylphenylmagnesium bromide (0.65 M in THF, 2.31 mL, 1.5 mmol). Obtained as a colorless oil (392 mg, 0.950 mmol, 95%) from **2h-OMe** (298 mg, 0.999 mmol). Purification was done by column chromatography on silica gel (hexane/toluene=1/0 to 5/1). R_f = 0.50 (hexane/toluene = 5/1) ; ^{1}H NMR ($CDCl_3$): δ 7.89 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.62–7.58 (m, 3H), 7.43 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 8.9 Hz, 2H), 1.86 (br, 4H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 164.2 (d, J = 248.5 Hz), 138.1, 137.8, 136.6 (d, J = 7.2 Hz), 131.7 (d, J = 2.9 Hz), 130.9 (d, J = 4.3 Hz), 129.8 (q, J = 31.8 Hz), 127.8, 126.3 (d, J = 4.3 Hz), 124.4 (q, J = 271.7 Hz), 114.9 (d, J = 20.2 Hz), 76.0, 37.9, 30.6 (br, four methyl groups); ^{19}F NMR ($CDCl_3$): δ –63.0, –111.0 (tt, J = 9.5, 6.3 Hz); HRMS (APCI, positive): *m/z* $[M]^+$ Calcd for $C_{21}H_{24}F_4O_2Si$ 412.1476; Found 412.1477.

4,4,7,7-Tetramethyl-2-(*o*-tolyl)-2-(*p*-tolyl)-1,3,2-dioxasilepane (3lc):



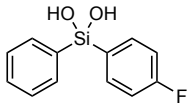
Synthesized via **GP4** by using *p*-tolylmagnesium bromide (0.74 M in THF, 2.03 mL, 1.5 mmol). Obtained as a white solid (306 mg, 0.864 mmol, 87%) from **2l-OMe** (294 mg, 0.998 mmol). Purification was done by column chromatography on silica gel (hexane/toluene=100/1 to 10/1). R_f= 0.29 (hexane/toluene = 10/1) ; ^{1}H NMR (acetone-d_6): δ 7.83 (dd, J = 7.6, 1.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 2H), 7.26 (td, J = 7.6, 1.4 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 1H), 2.29 (s, 3H), 2.27 (s, 3H), 1.88 (br, 4H), 1.26 (s, 6H), 1.25 (s, 6H); ^{13}C NMR (acetone-d_6): δ 144.3, 139.9, 136.5, 136.1, 135.2, 135.0, 130.6, 130.4, 129.0, 125.3, 76.1, 38.6, 30.9 (br, four methyl groups), 22.8, 21.5; HRMS (ESI-MS, positive): *m/z* $[M+Na]^+$ Calcd for $C_{22}H_{30}O_2SiNa$ 377.1907; Found: 377.1916.

Diphenylsilanediol (5bb):



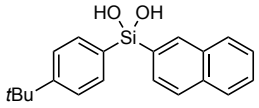
R_f= 0.38 ($CHCl_3$/MeOH = 10/1); ^{1}H NMR (acetone-d_6): δ 7.68 (d, J = 6.2 Hz, 4H), 7.37 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 4H), 5.99 (s, 2H); ^{13}C NMR (acetone-d_6): δ 138.1, 135.1, 130.3, 128.3; HRMS (APCI, negative): *m/z* $[M–H]^–$ Calcd for $C_{12}H_{11}O_2Si$ 215.0534; Found 215.0525.

(4-Fluorophenyl)(phenyl)silanediol (5bh):



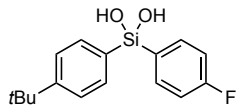
Synthesized via **GP5**. Obtained as a white solid (86.6 mg, 0.370 mmol, 74%) from **3bh** (172 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/Et_2O =1/0 to 2/1). R_f = 0.33 ($CHCl_3$/MeOH = 10/1); ^{1}H NMR (acetone-d_6): δ 7.72 (ddd, J = 8.2, 6.9, 2.1 Hz, 2H), 7.67 (dd, J = 8.2, 1.4 Hz, 2H), 7.38 (tt, J = 7.6, 1.4 Hz, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.11 (ddd, J = 9.6, 8.9, 2.1 Hz, 2H), 6.08 (s, 2H); ^{13}C NMR (acetone-d_6): δ 164.8 (d, J = 245.6 Hz), 137.8, 137.4 (d, J = 7.2 Hz), 135.0, 134.2 (d, J = 2.9 Hz), 130.4, 128.3, 115.2 (d, J = 20.2 Hz); ^{19}F NMR (acetone-d_6): δ –111.4; HRMS (APCI, negative): *m/z* [M–H]$^-$ Calcd for $C_{12}H_{10}FO_2Si$ 233.0440; Found 233.0439.

(4-*tert*-Butylphenyl)(naphthalen-2-yl)silanediol (5aj):



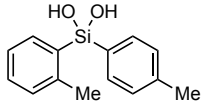
Synthesized via **GP5**. Reaction time was 6 h for the second step. Obtained as a white solid (95.9 mg, 0.297 mmol, 60%) from **3aj** (216 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/Et_2O =1/0 to 3/1). R_f = 0.48 ($CHCl_3$/MeOH = 10/1); ^{1}H NMR (acetone-d_6): δ 8.27 (s, 1H), 7.91–7.84 (m, 3H), 7.77 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.52–7.47 (m, 2H), 7.40 (d, J = 8.2 Hz, 2H), 6.04 (s, 2 H), 1.28 (s, 9H); ^{13}C NMR (acetone-d_6): δ 153.1, 135.9 (overlapped two peaks), 135.1, 134.9, 134.7, 133.7, 131.3, 129.0, 128.4, 127.4, 127.3, 126.6, 125.2, 35.1, 31.4; HRMS (APCI, negative): *m/z* [M–H]$^-$ Calcd for $C_{20}H_{21}O_2Si$ 321.1316; Found 321.1304.

(4-*tert*-Butylphenyl)(4-fluorophenyl)silanediol (5ah):



Synthesized via **GP5**. Reaction time was 2 h for the second step. Obtained as a white solid (80.0 mg, 0.275 mmol, 55%) from **3ah** (200 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/Et_2O =1/0 to 2/1). R_f = 0.50 ($CHCl_3$/MeOH = 10/1); ^{1}H NMR (acetone-d_6): δ 7.74–7.71 (m, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.12–7.09 (m, 2H), 5.94 (s, 2H), 1.29 (s, 9H); ^{13}C NMR (acetone-d_6): δ 164.8 (d, J = 247.1 Hz), 153.2, 137.4 (d, J = 7.2 Hz), 135.0, 134.5 (d, J = 2.9 Hz), 134.4, 125.2, 115.2 (d, J = 18.8 Hz), 35.1, 31.4; ^{19}F NMR (acetone-d_6): δ –111.7; HRMS (APCI, negative): *m/z* [M–H]$^-$ Calcd for $C_{16}H_{19}FO_2Si$ 289.1055; Found 289.1062.

***o*-Tolyl(*p*-tolyl)silanediol (5lc):**



Synthesized via **GP5**. Obtained as a white solid (39.0 mg, 0.160 mmol, 32%) from **3lc** (177 mg, 0.499 mmol). Purification was done by column chromatography on silica gel (hexane/Et_2O =1/0 to 1/1). R_f = 0.47 ($CHCl_3$/MeOH = 10/1); ^{1}H

NMR (acetone-d_6): δ 7.76 (dd, J = 7.6, 1.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.26 (td, J = 7.6, 1.4 Hz, 1H), 7.15 (d, J = 7.6 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 5.80 (s, 2H), 2.38 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (acetone-d_6): δ 144.7, 139.9, 136.6, 136.4, 135.2, 135.1, 130.5, 130.3, 129.0, 125.2, 23.0, 21.5; HRMS (APCI, negative): *m/z* $[M–H]^-$ Calcd for $C_{14}H_{16}O_2Si$ 243.0836; Found 243.0833.

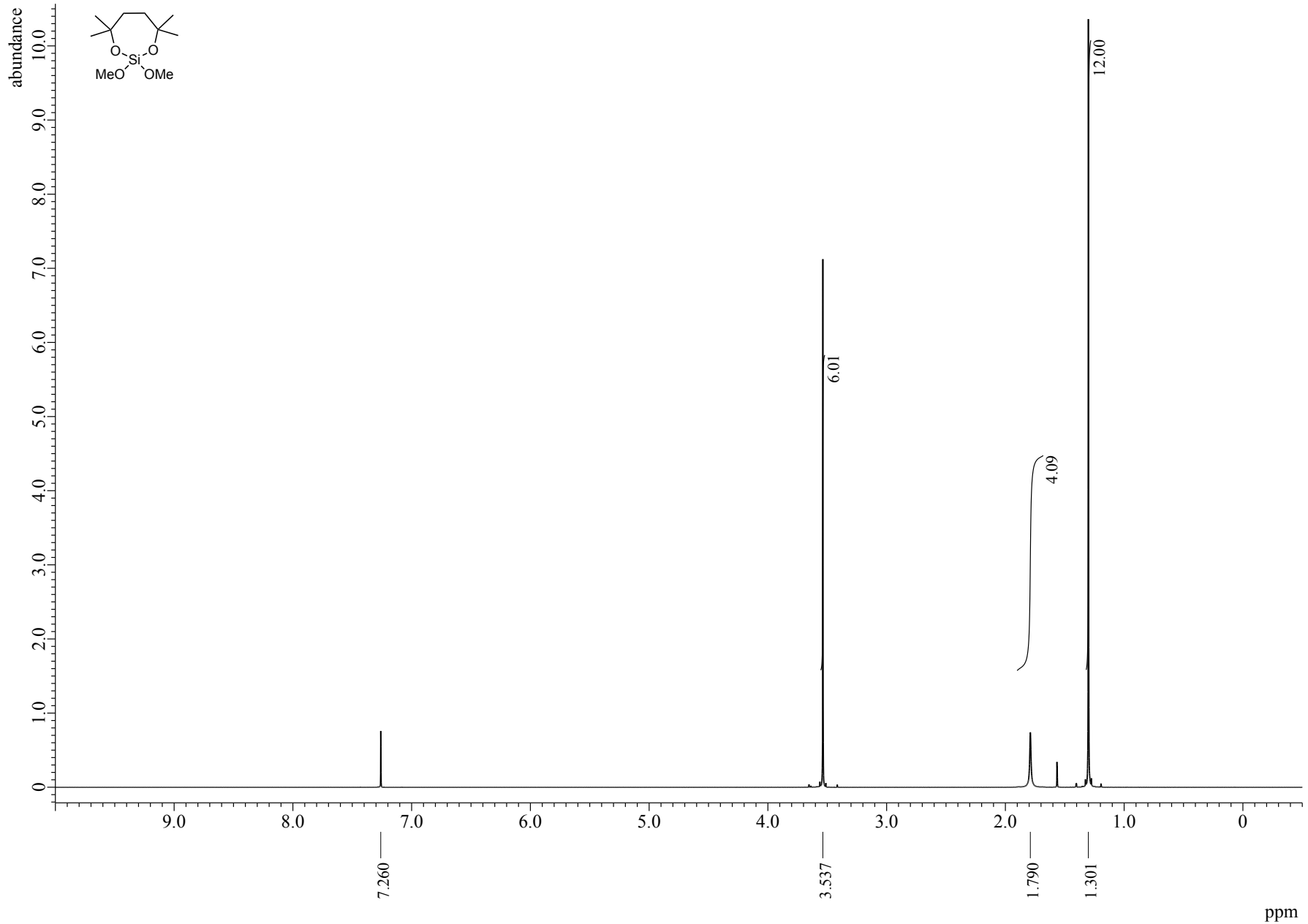


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-OMe**

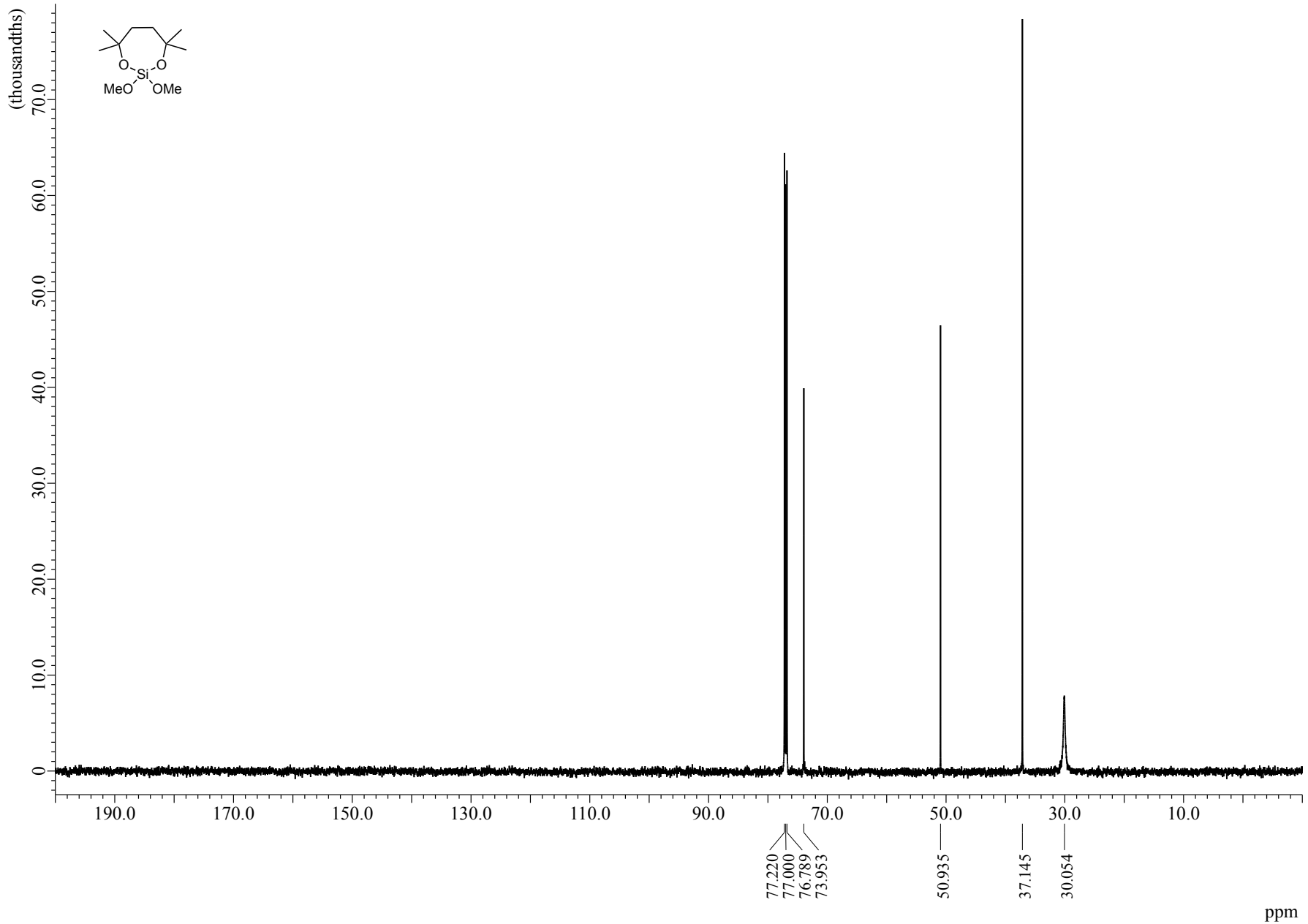


Figure S2. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-OMe**

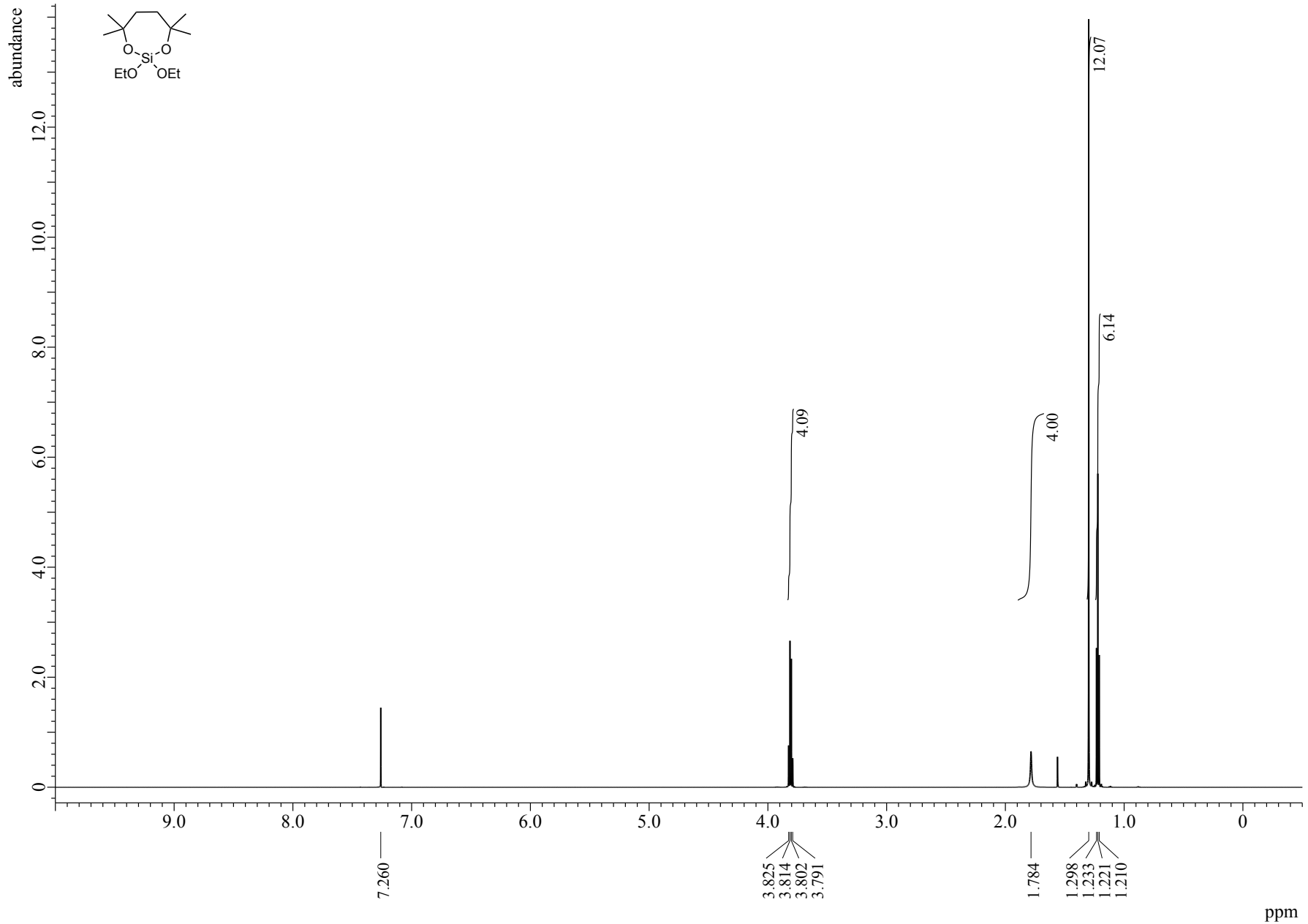


Figure S3. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-OEt**

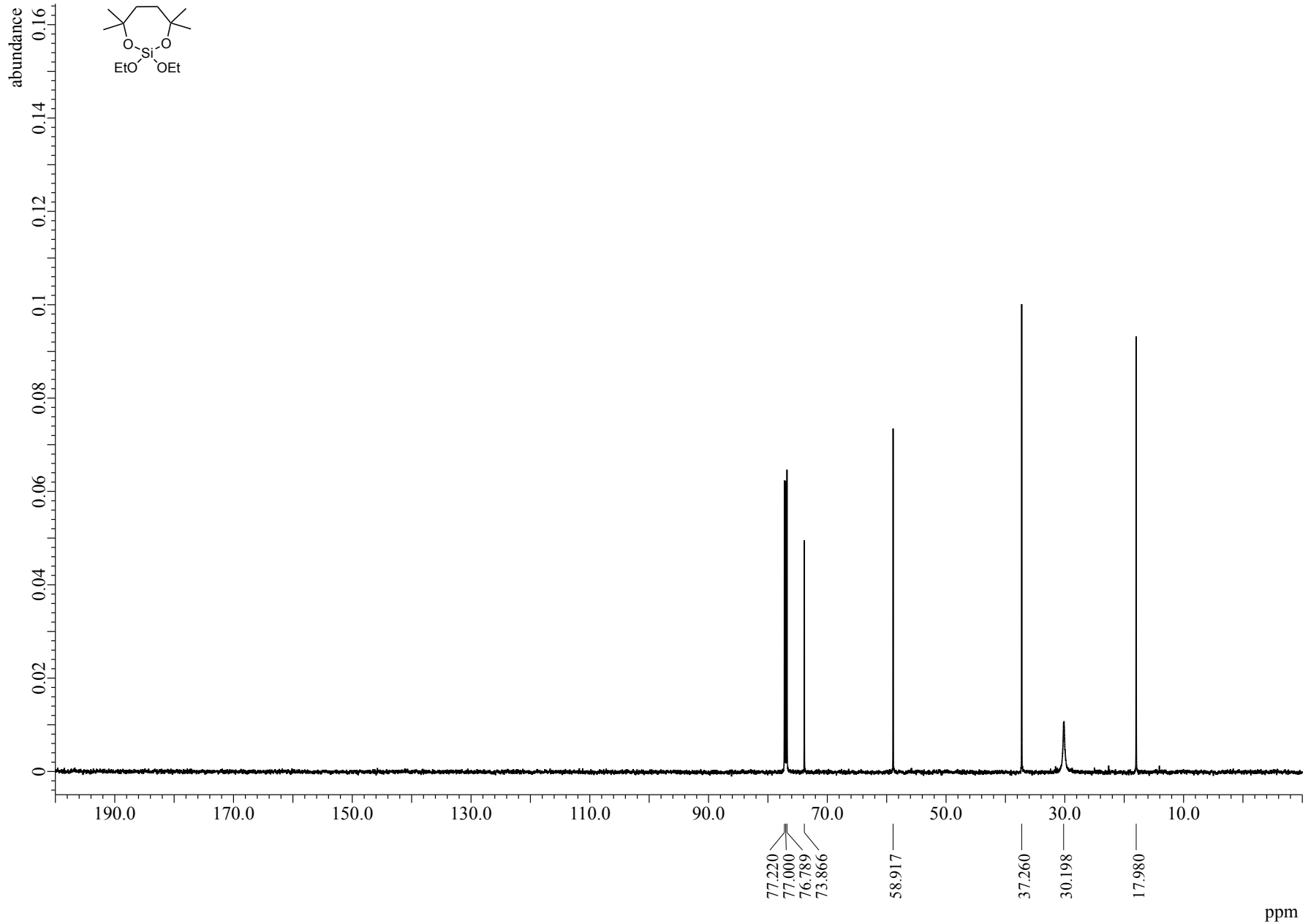


Figure S4. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-OEt**

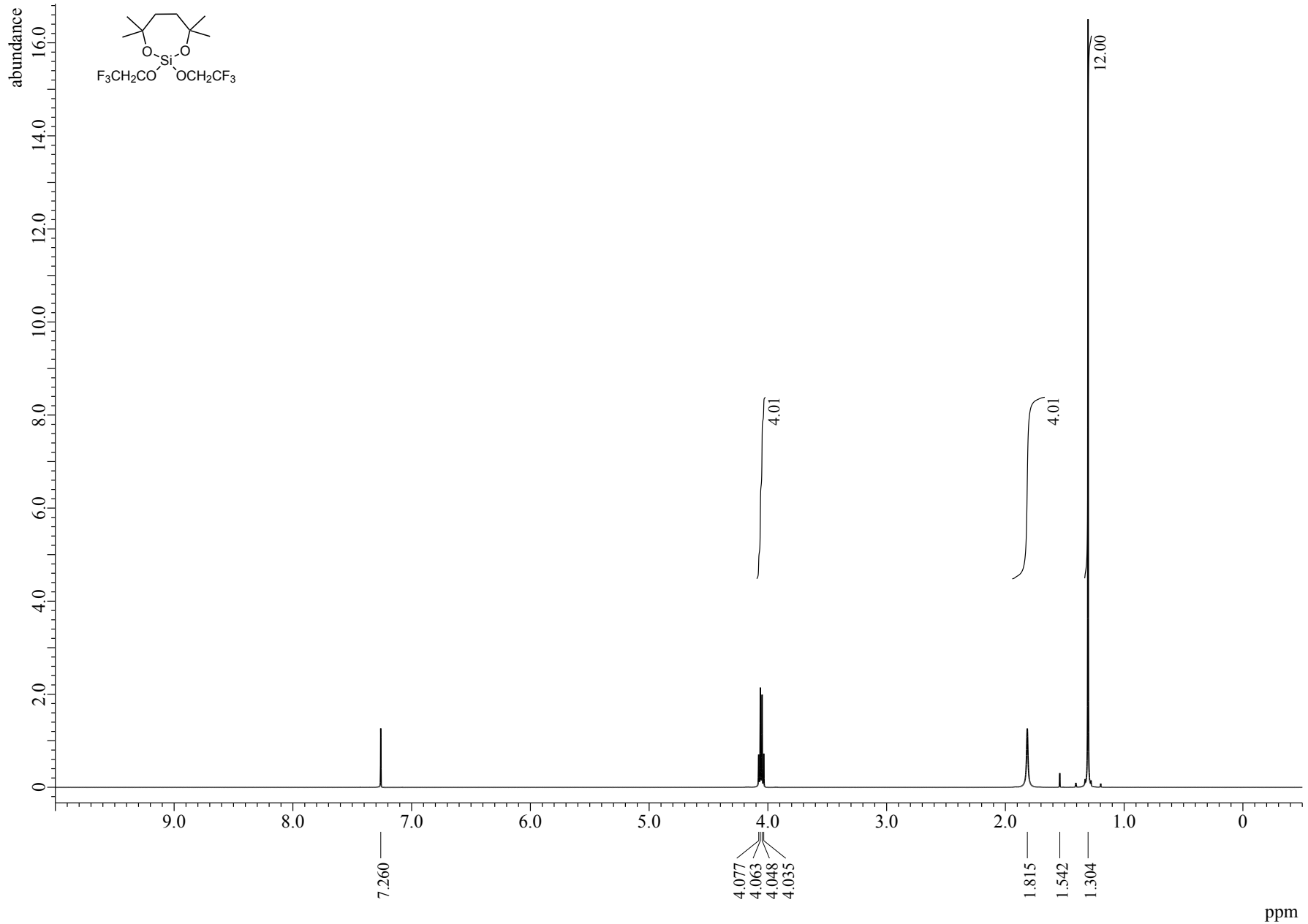


Figure S5. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-OTFE**

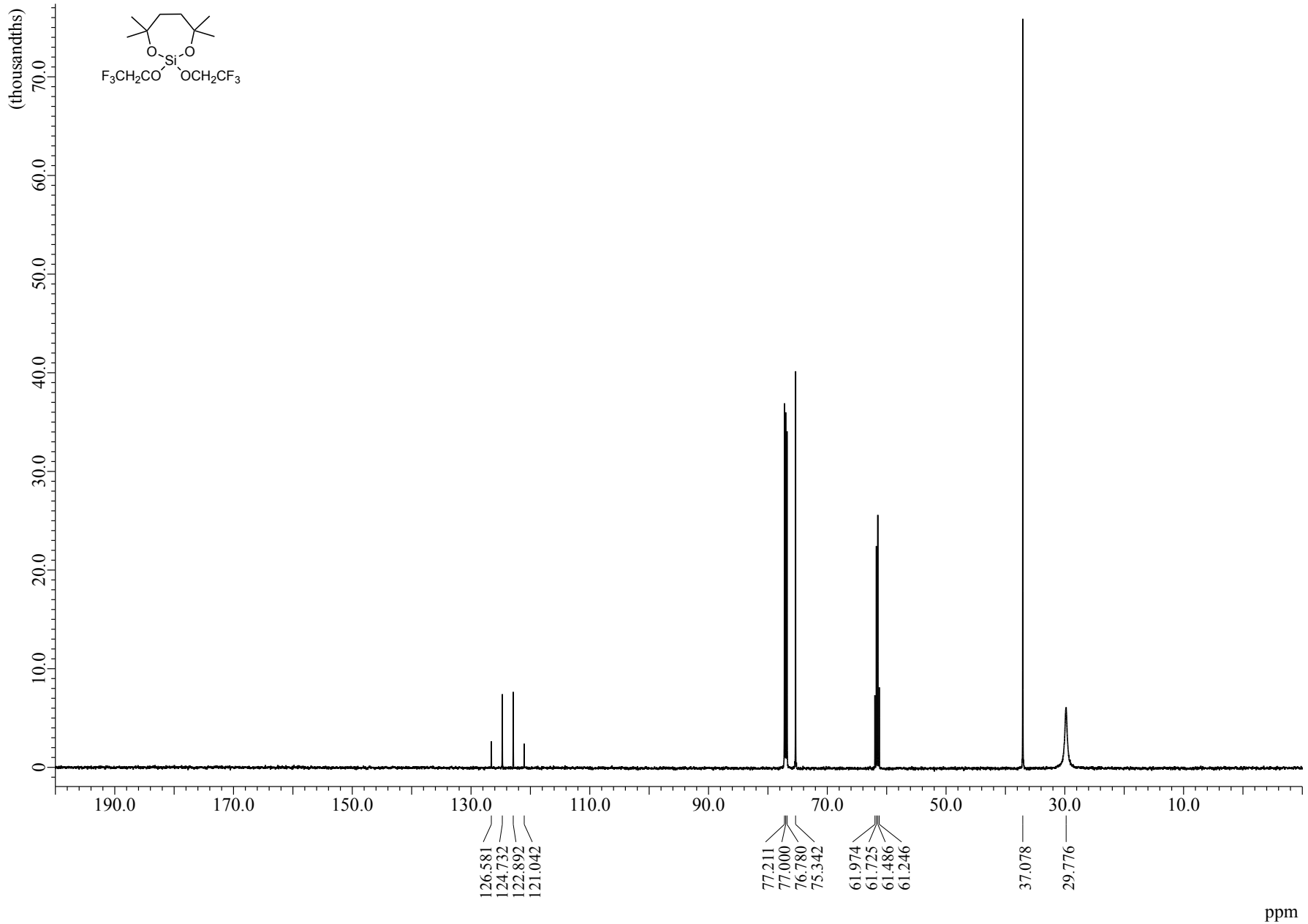


Figure S6. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-OTFE**

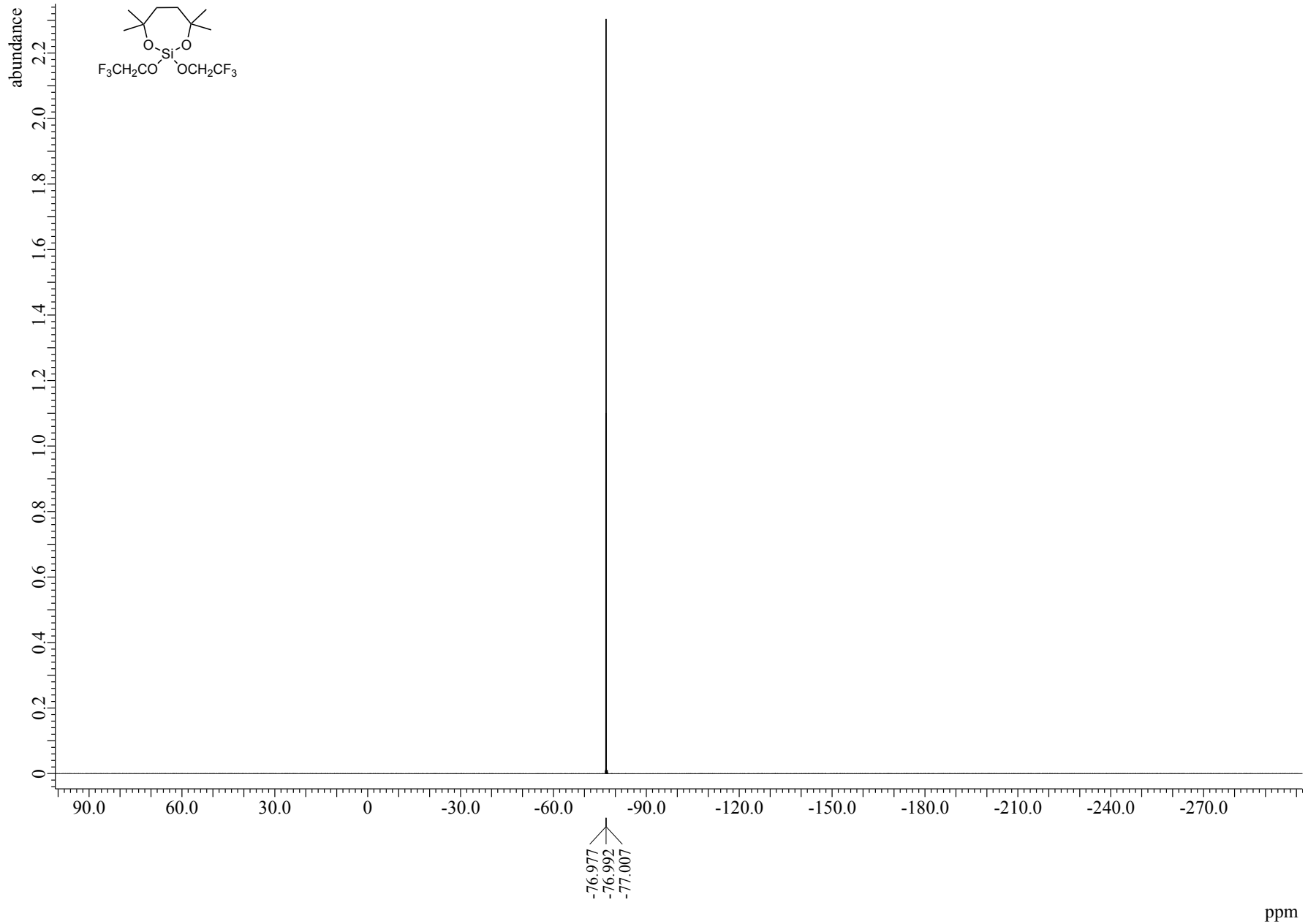


Figure S7. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **1-OTFE**

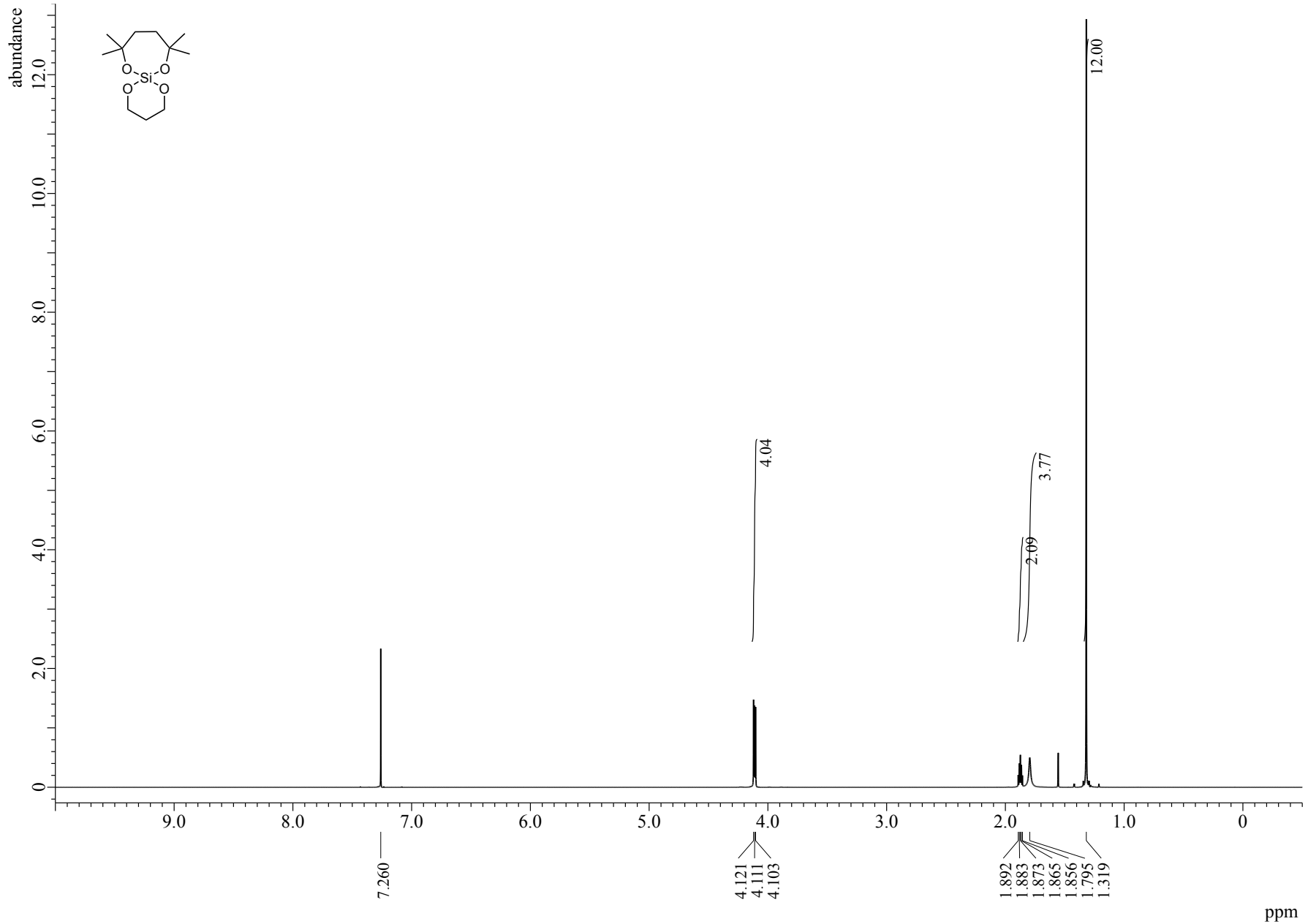


Figure S8. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1-PDO**

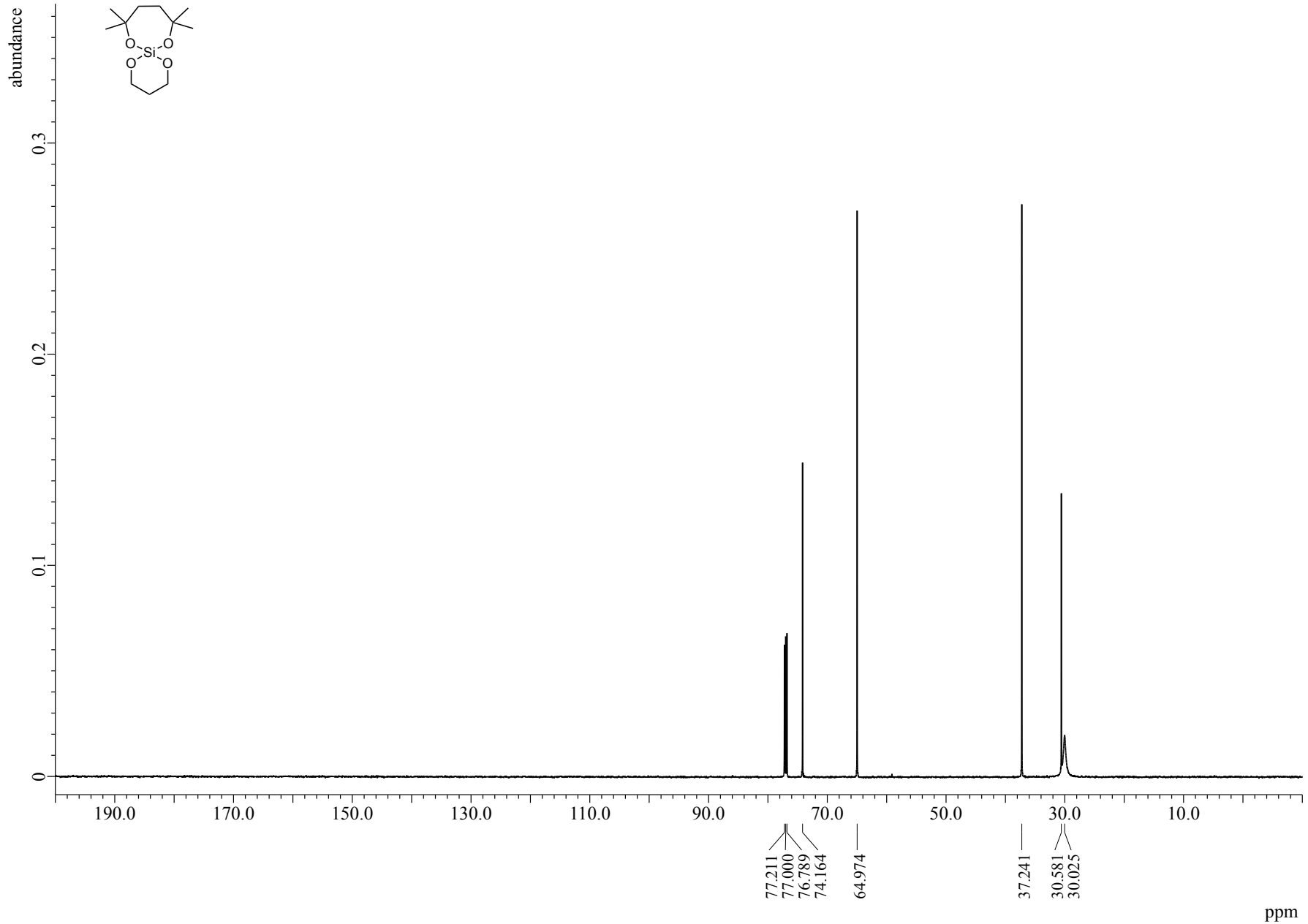


Figure S9. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1-PDO**

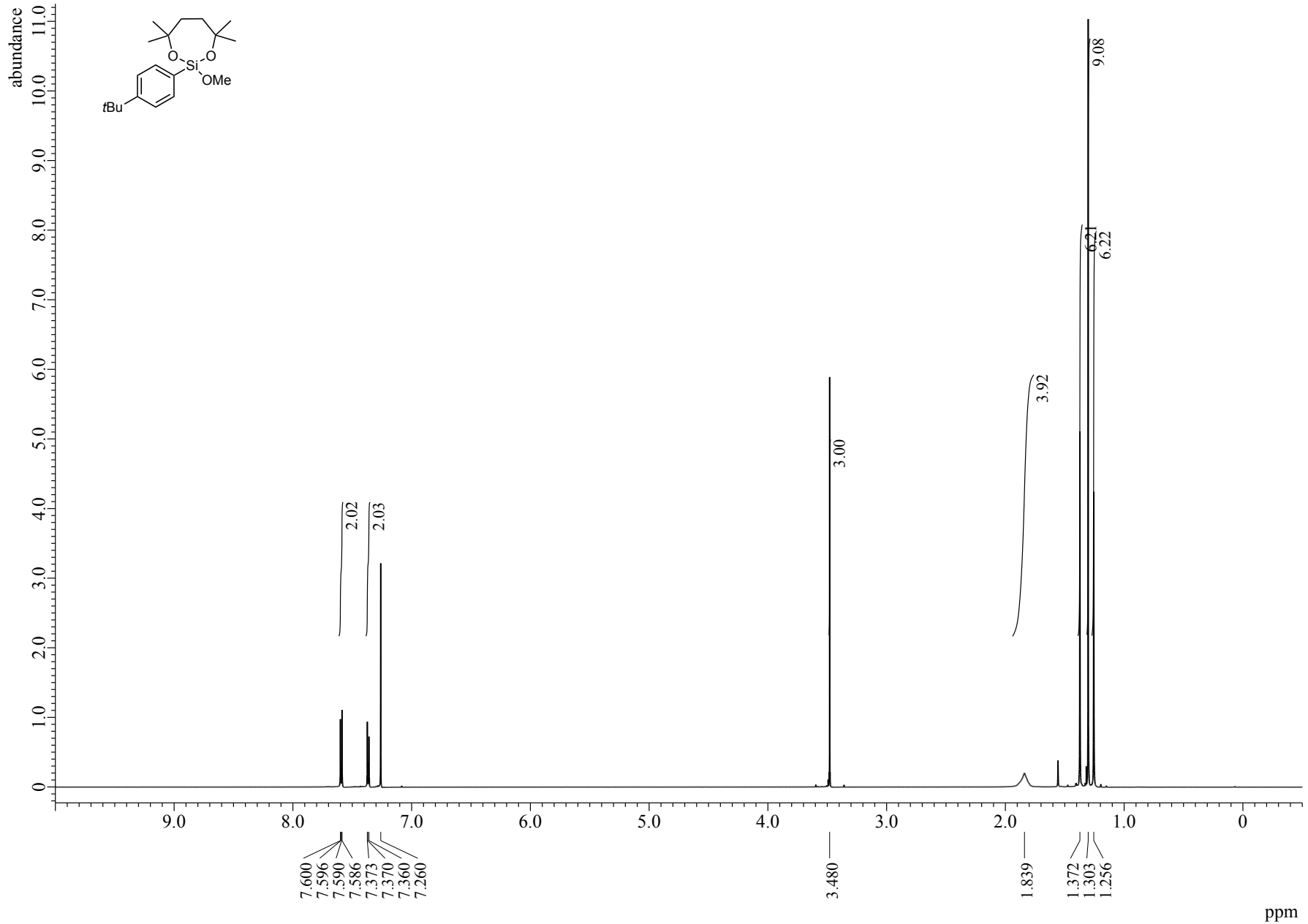


Figure S10. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a-OMe**

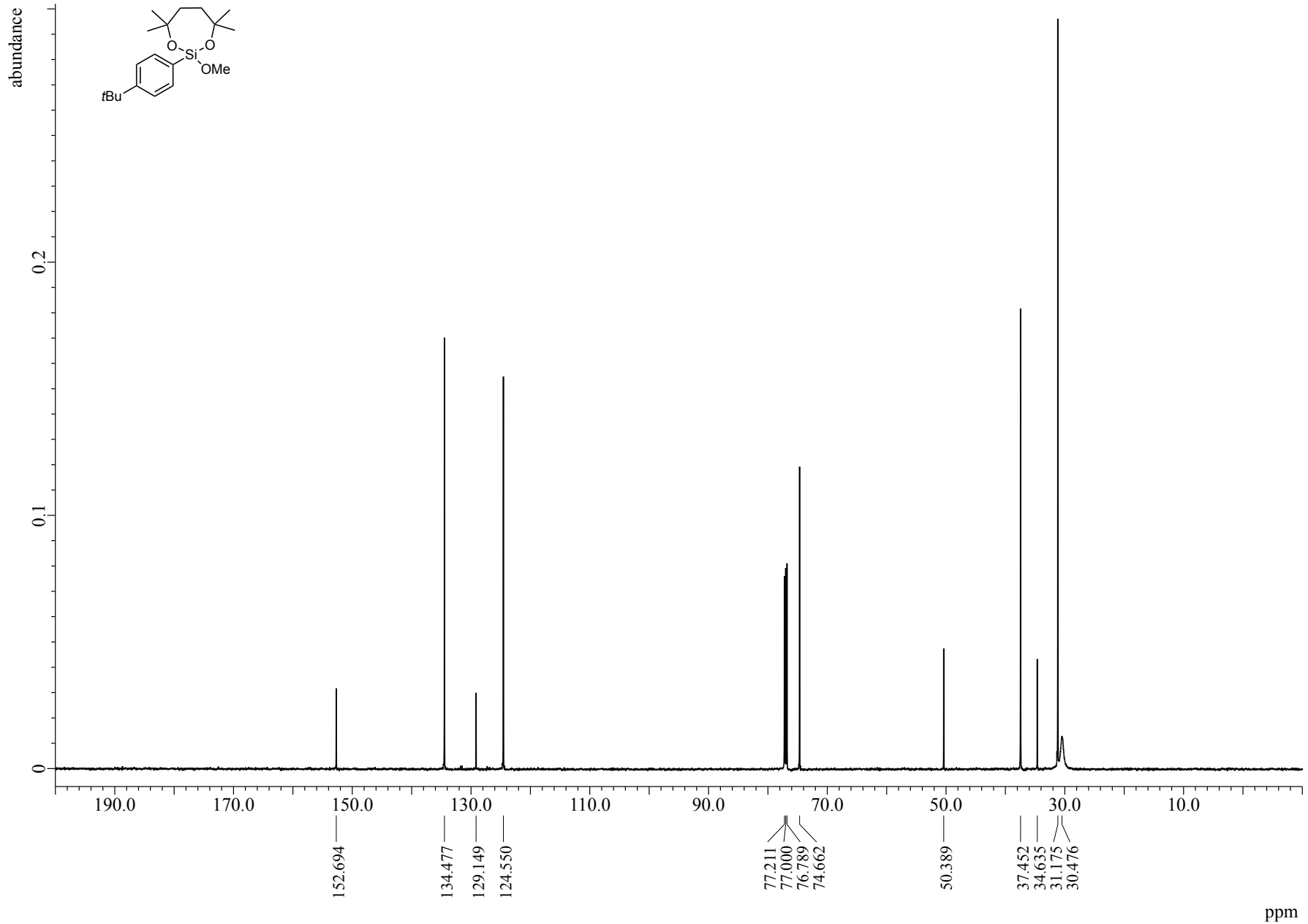


Figure S11. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2a-OMe**

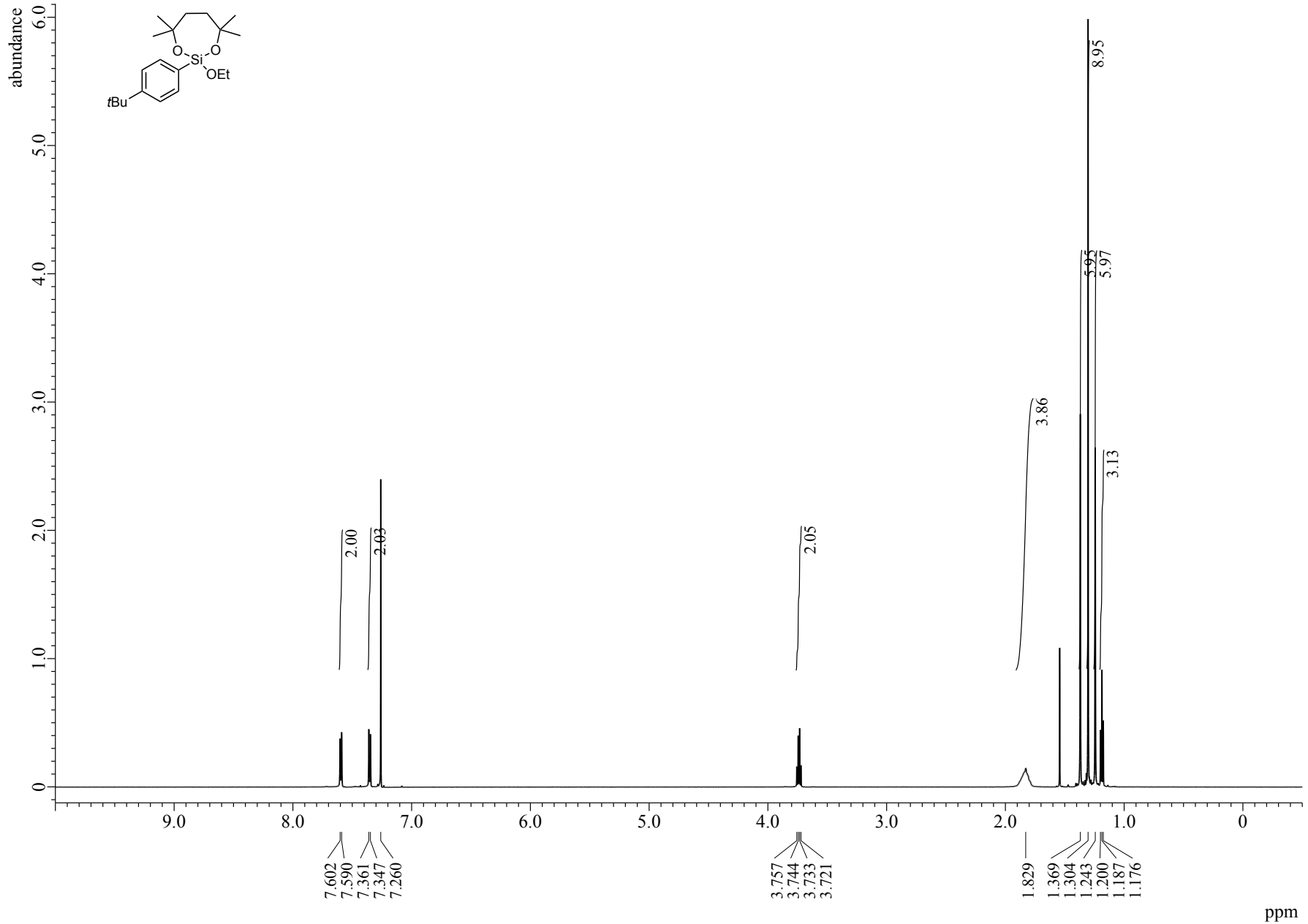


Figure S12. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a-OEt**

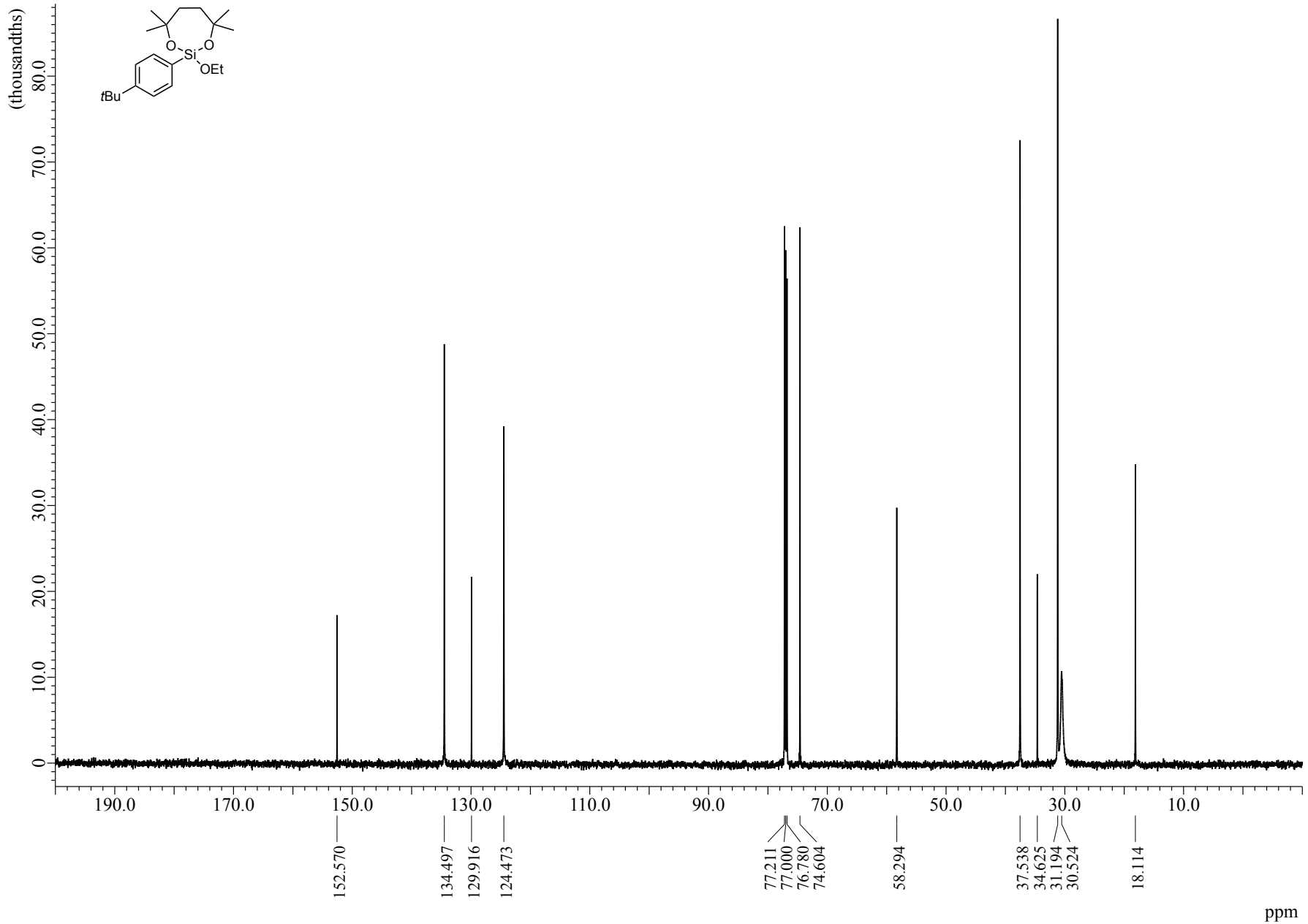


Figure S13. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2a-OEt**

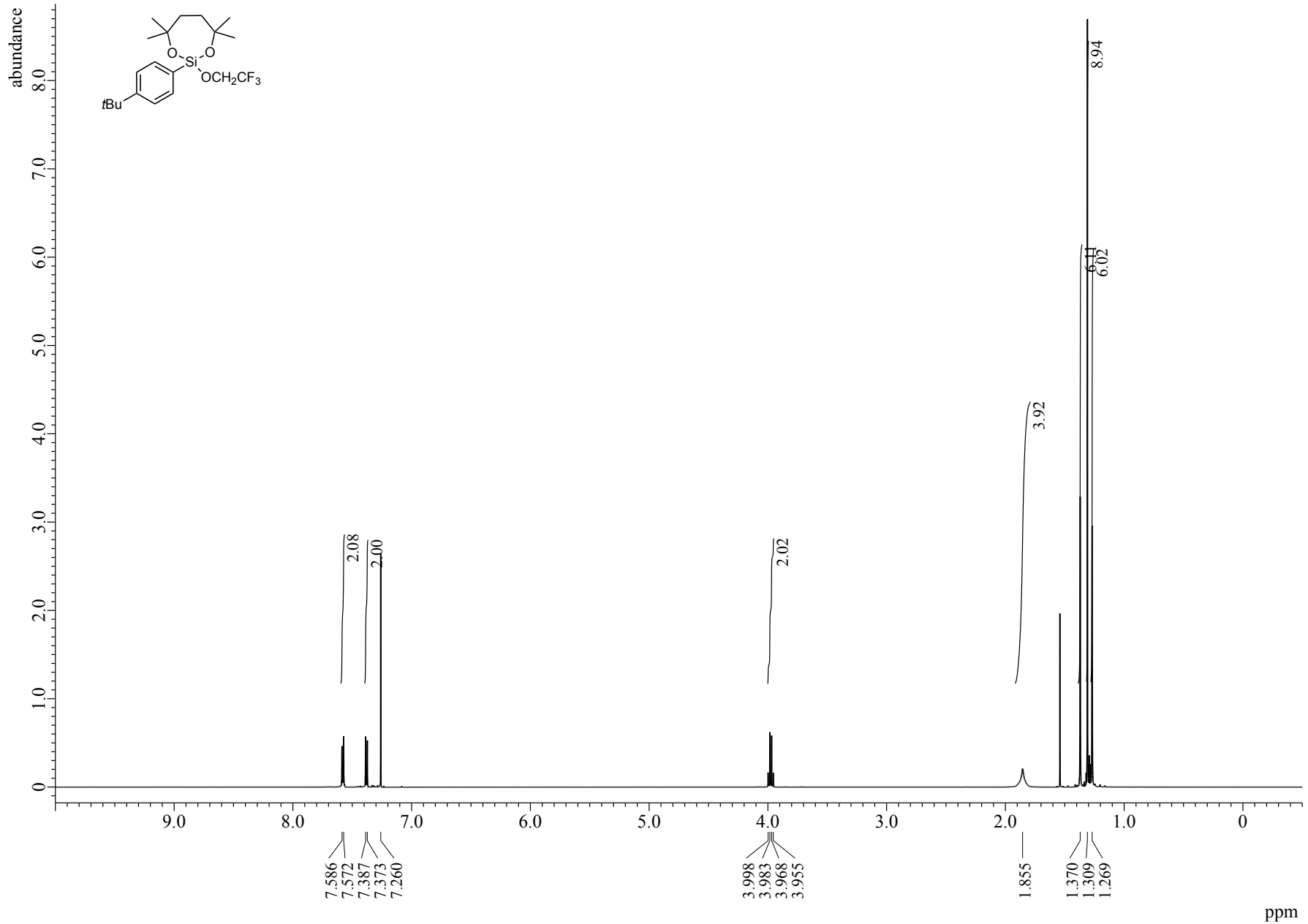


Figure S14. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a-OTFE**

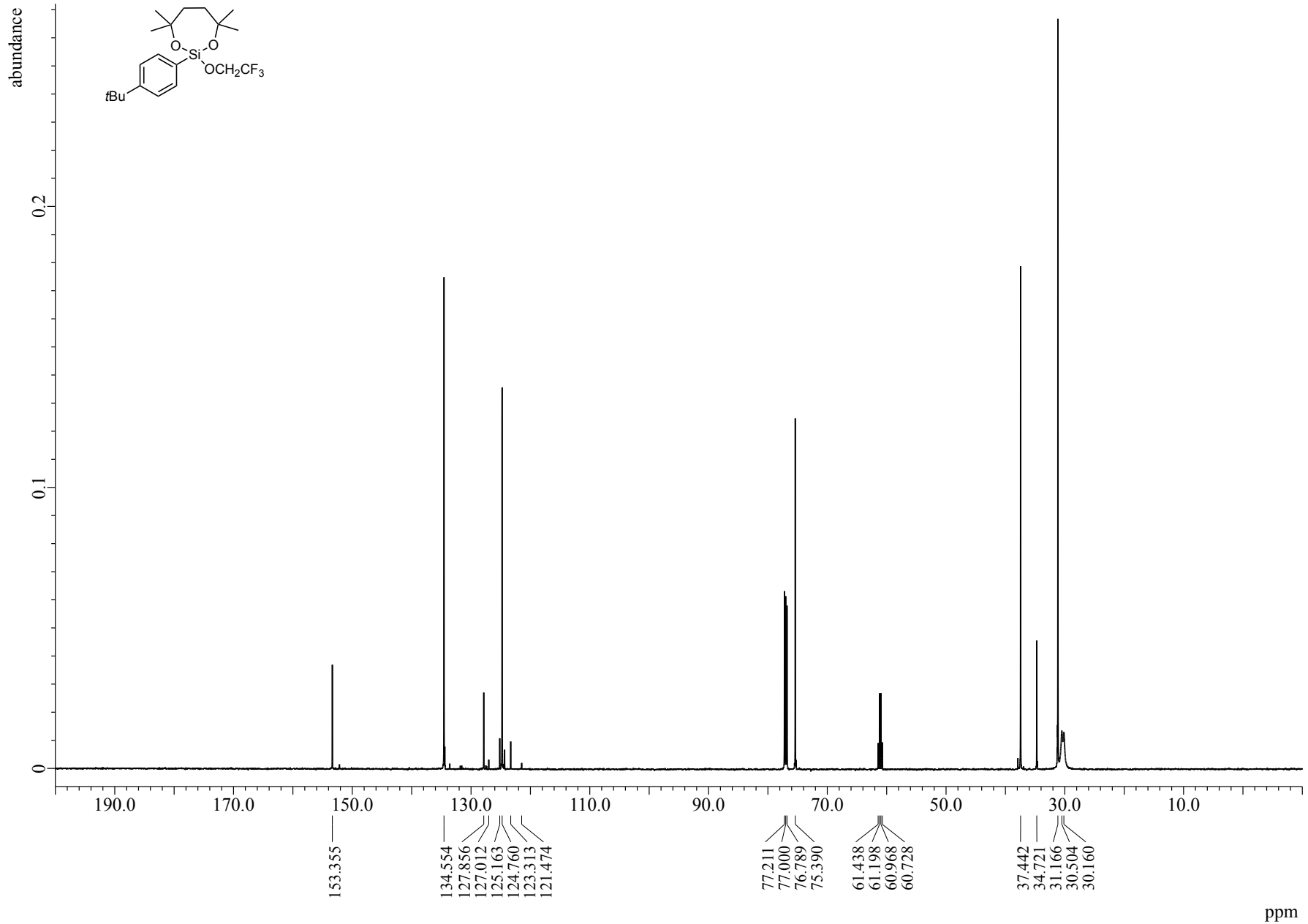


Figure S15. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2a-OTFE**

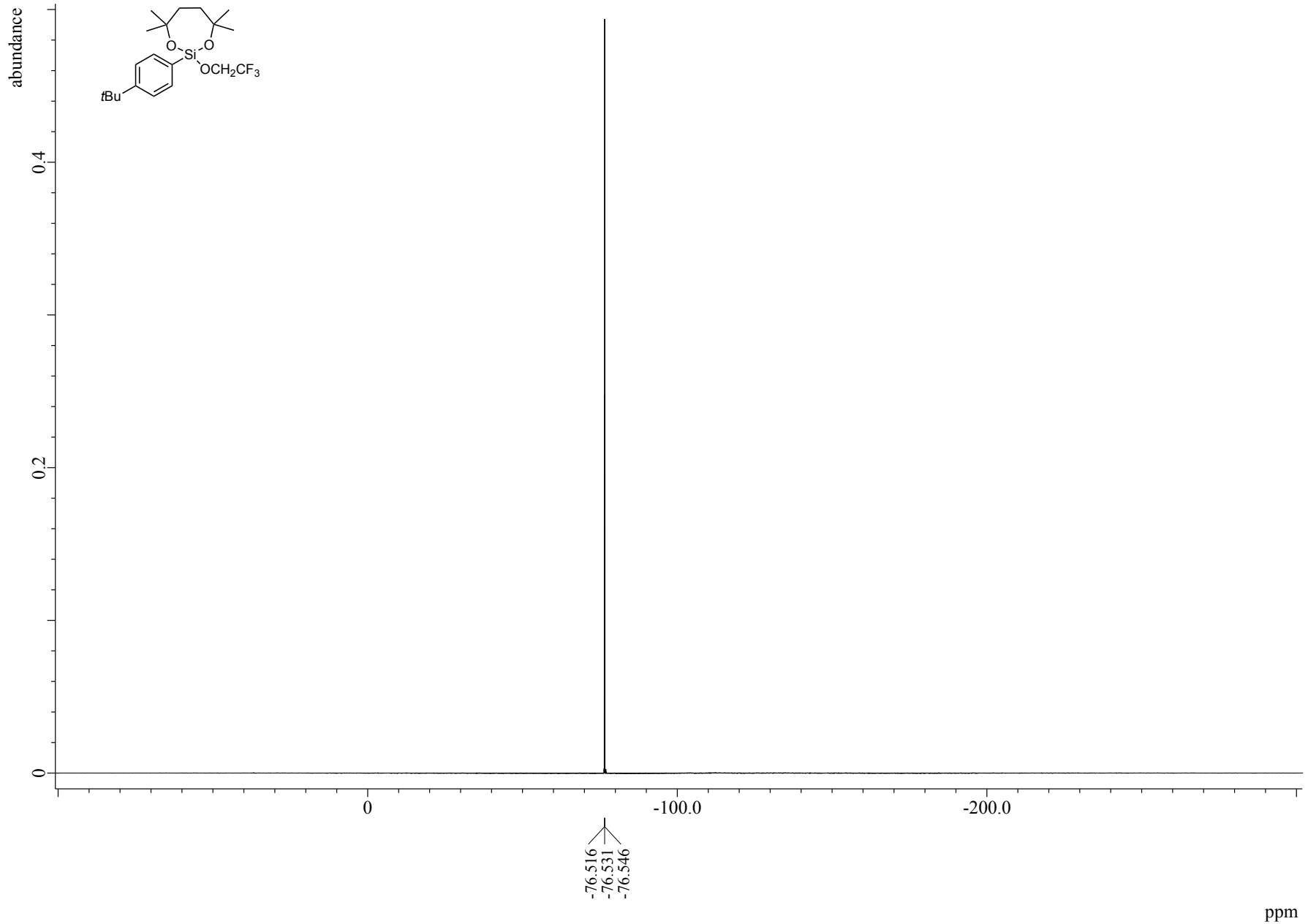


Figure S16. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2a-OTFE**

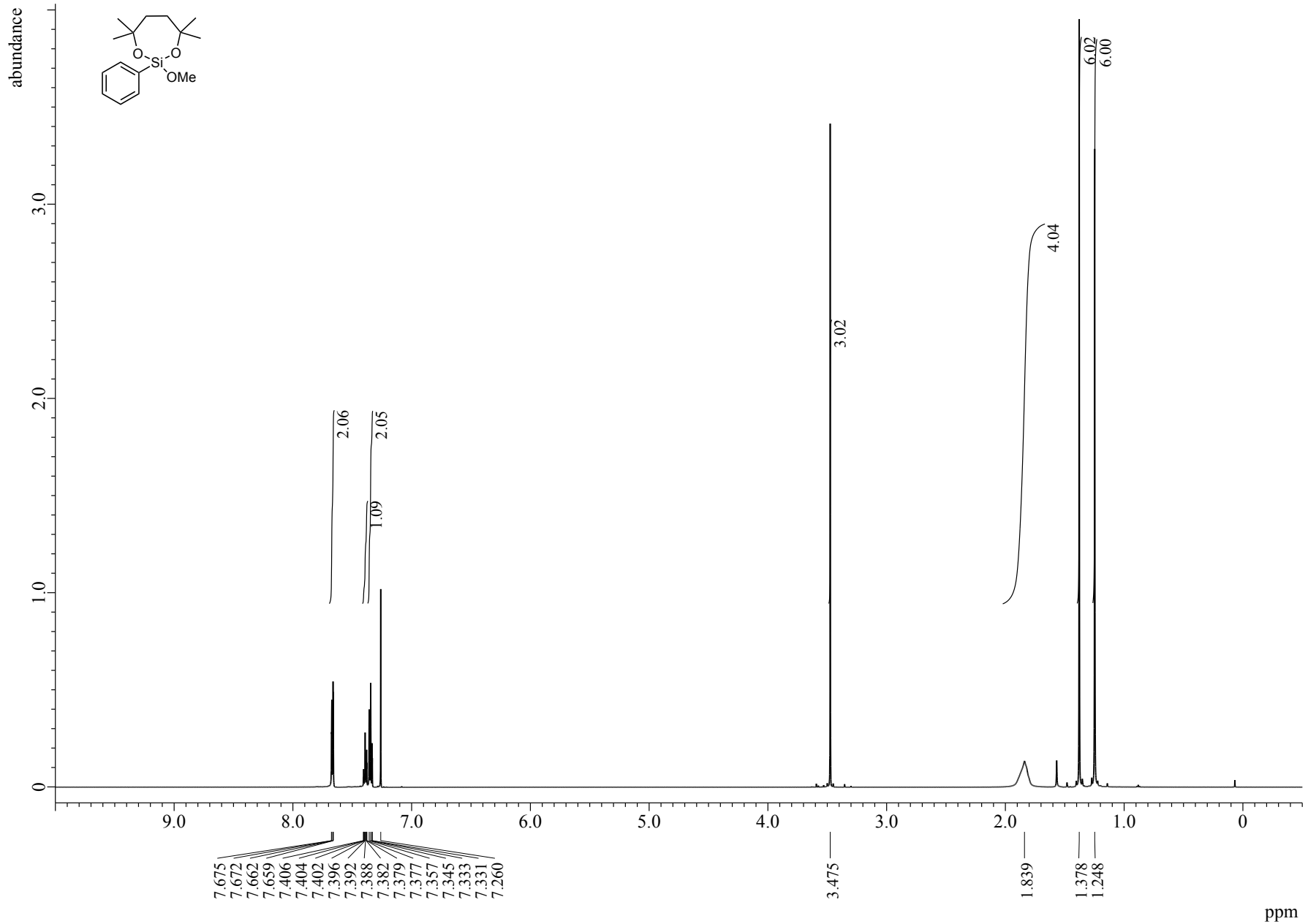


Figure S17. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b-OMe**

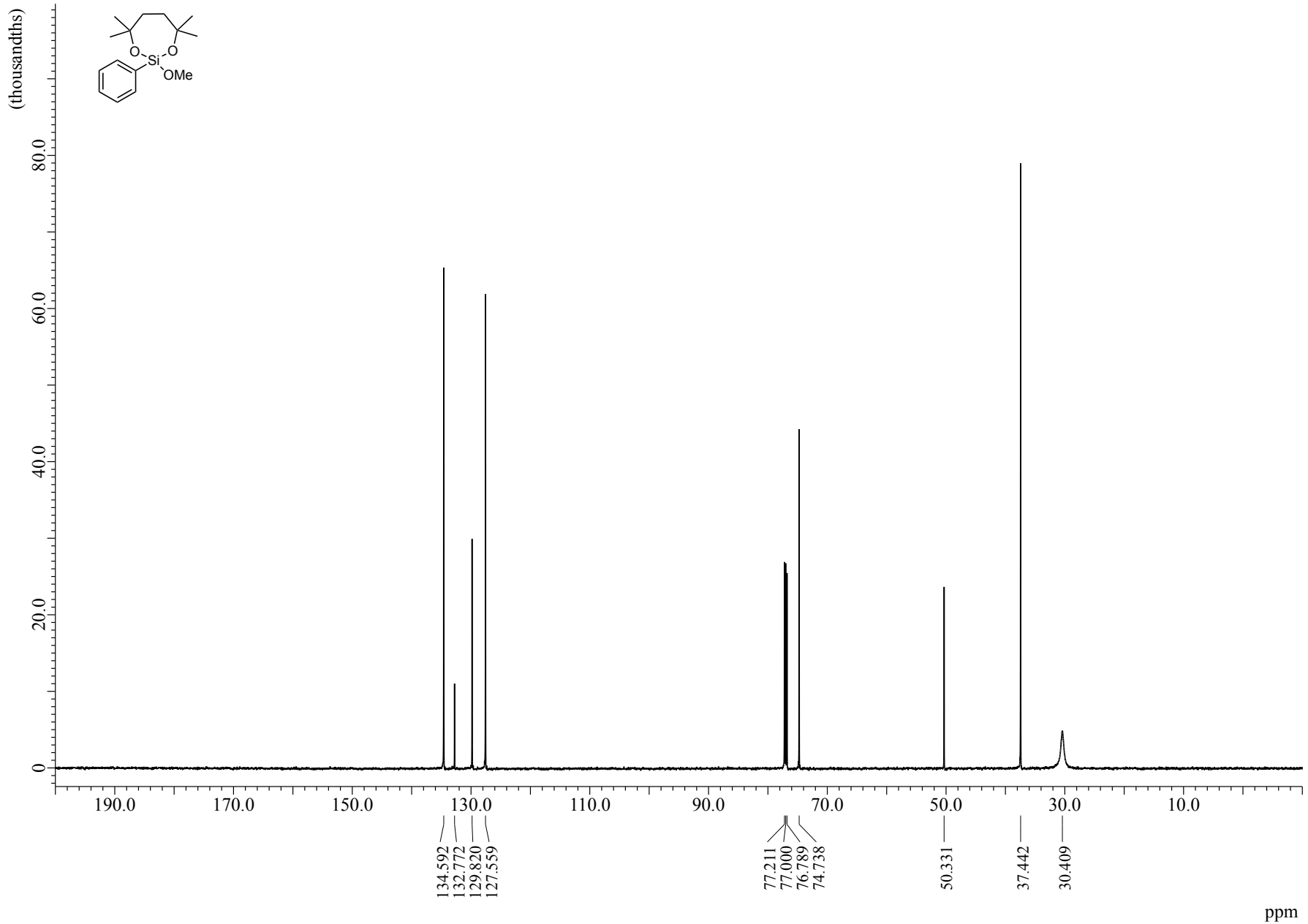


Figure S18. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2b-OMe**

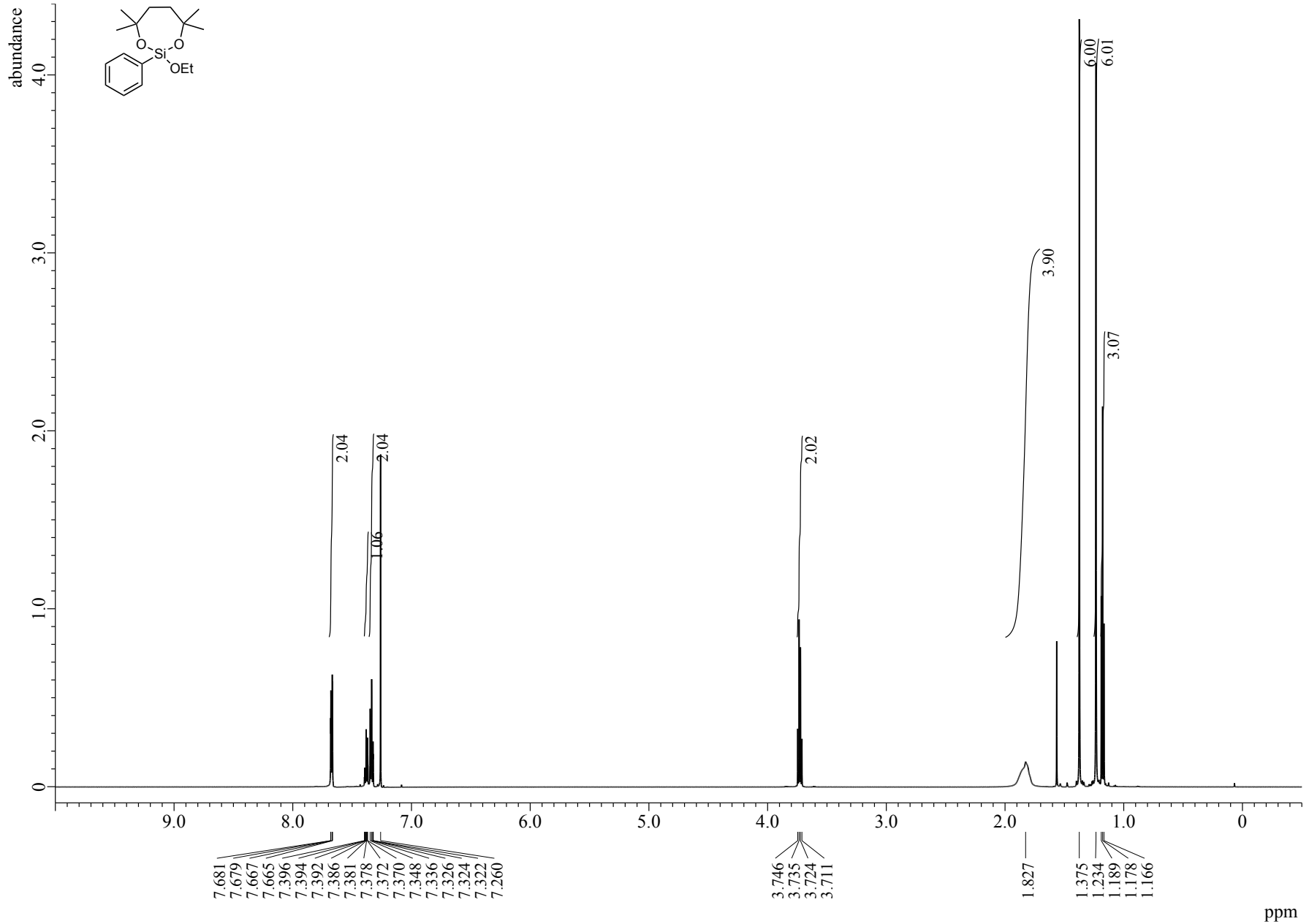


Figure S19. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b-OEt**

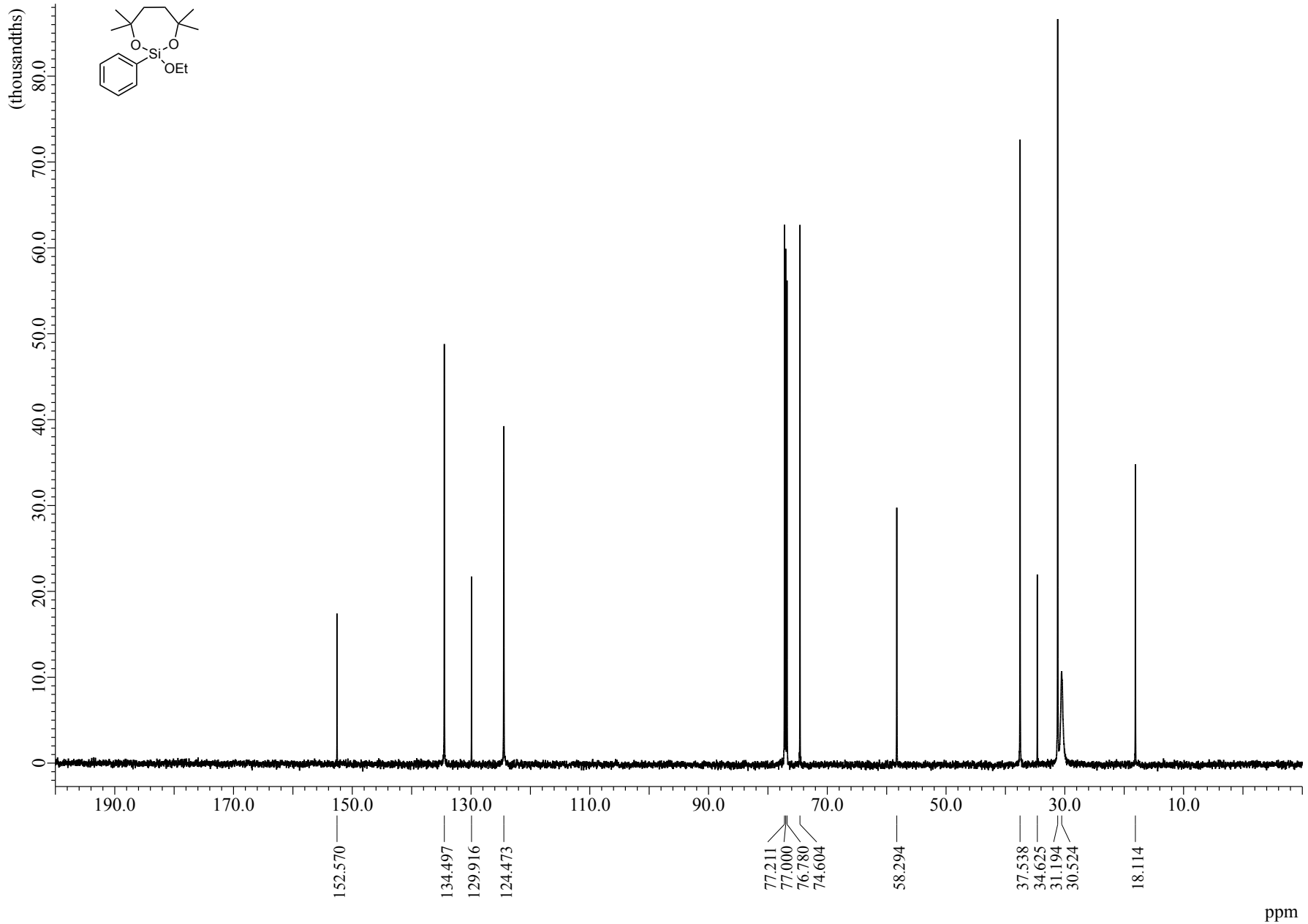


Figure S20. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2b-OEt**

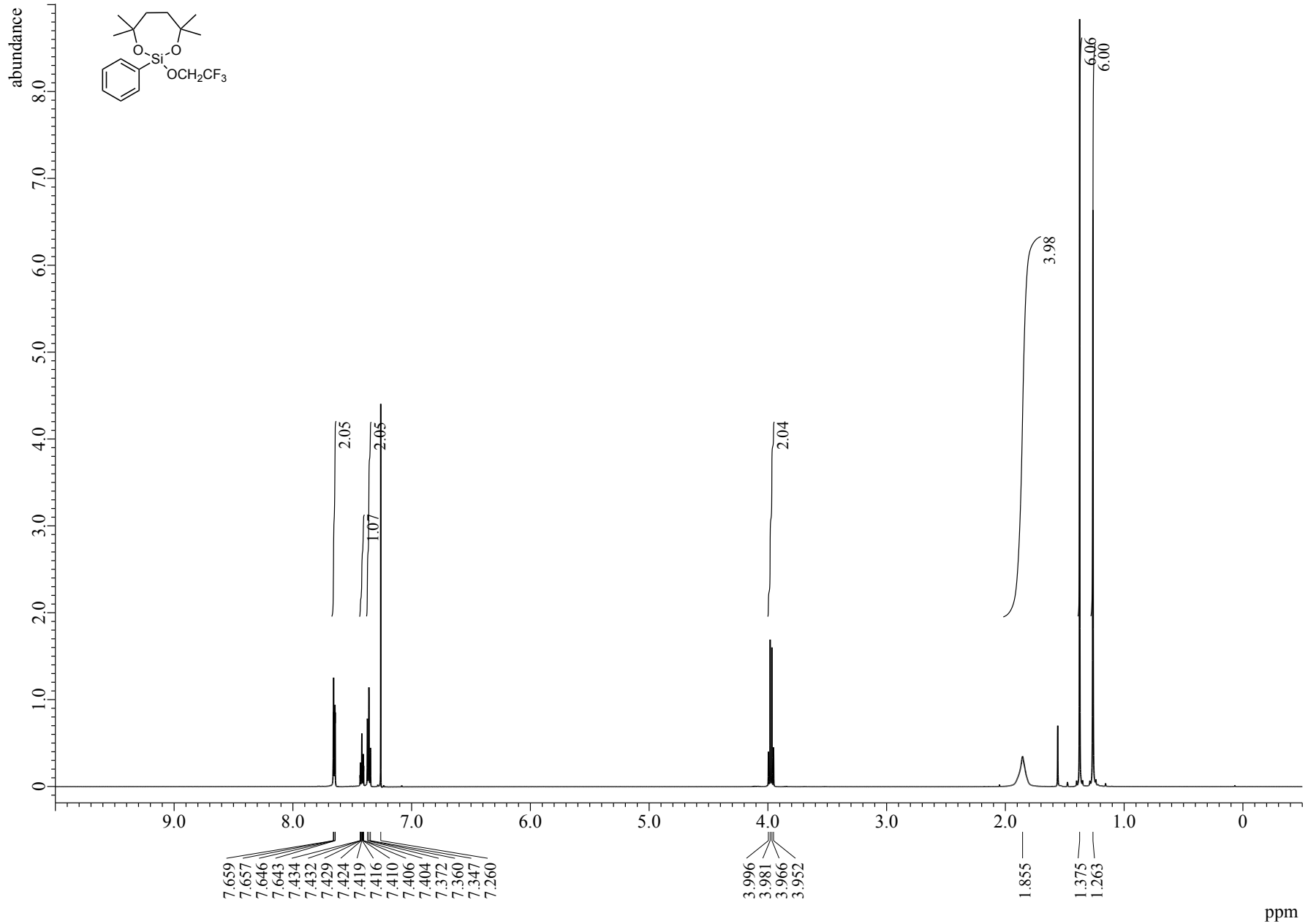


Figure S21. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b-OTFE**

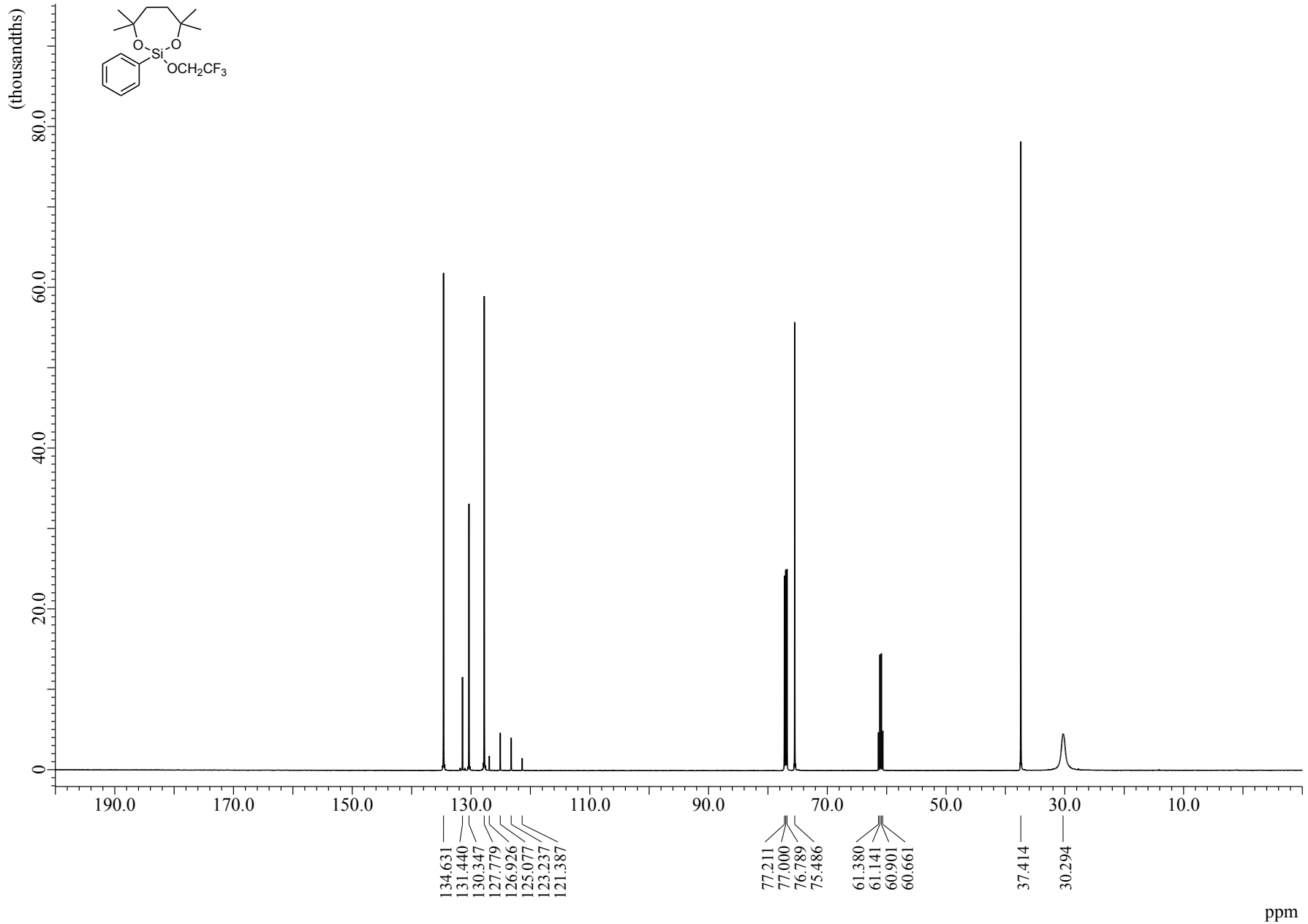


Figure S22. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2b-OTFE**

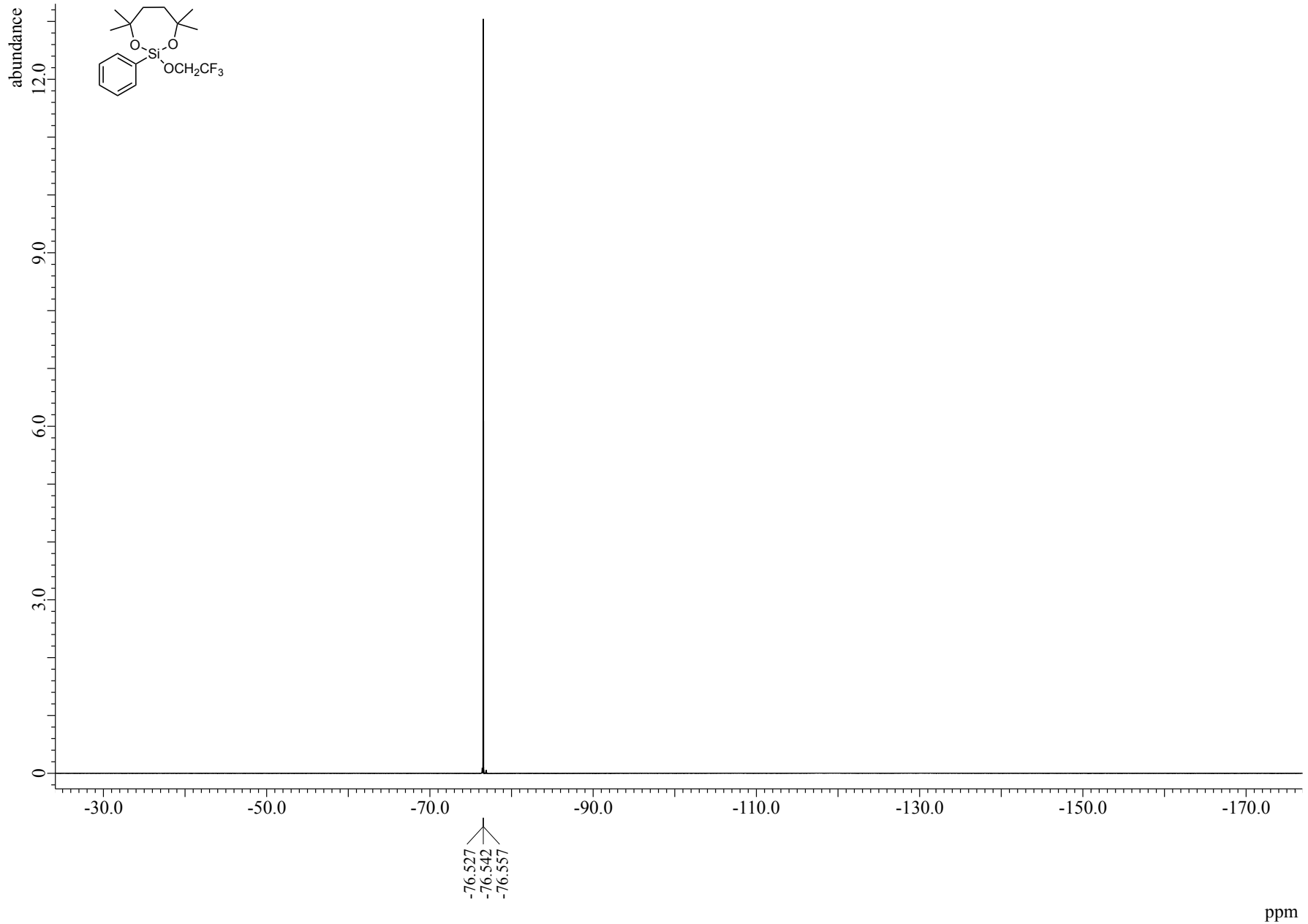


Figure S23. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2b-OTFE**

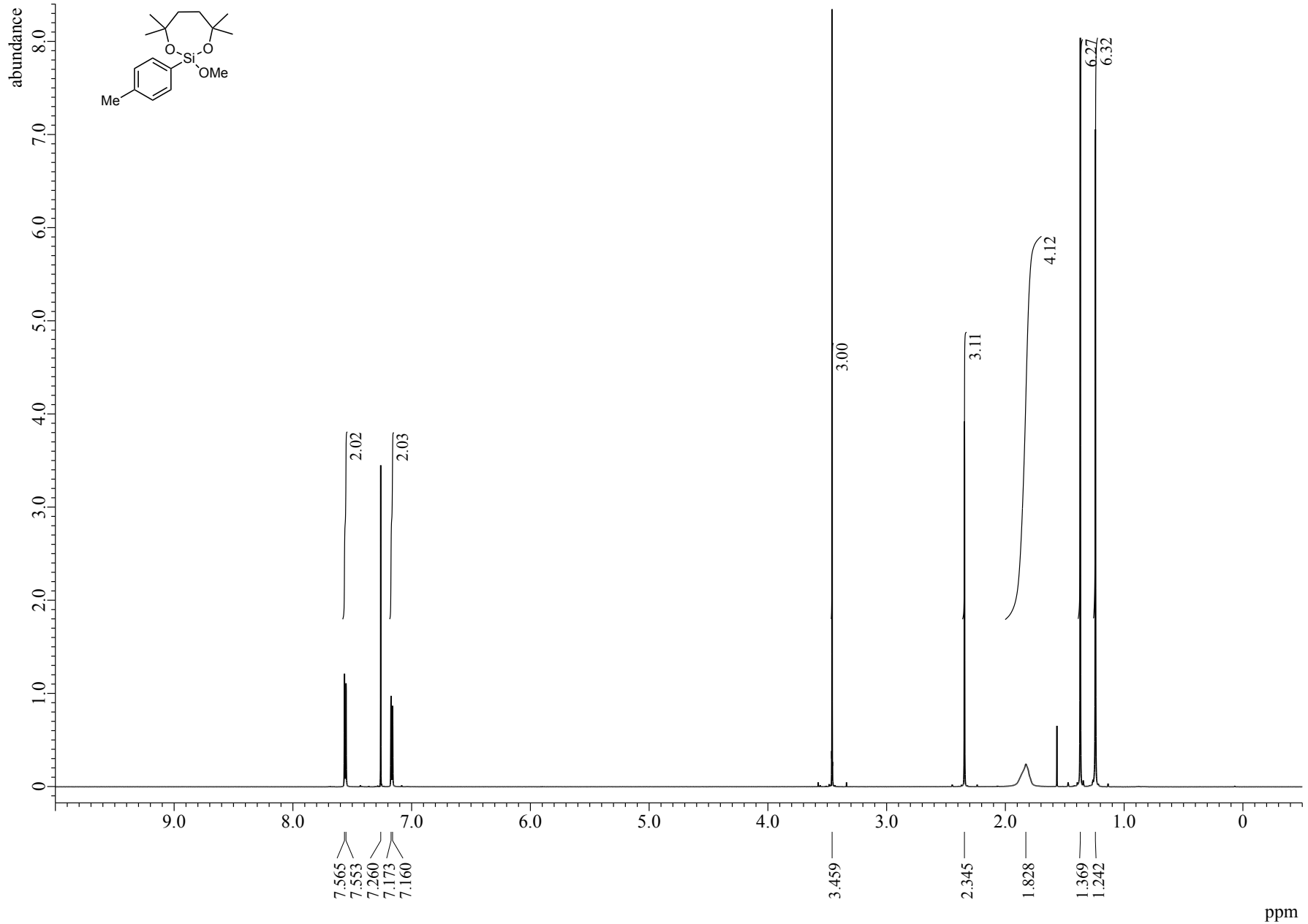


Figure S24. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2c-OMe**

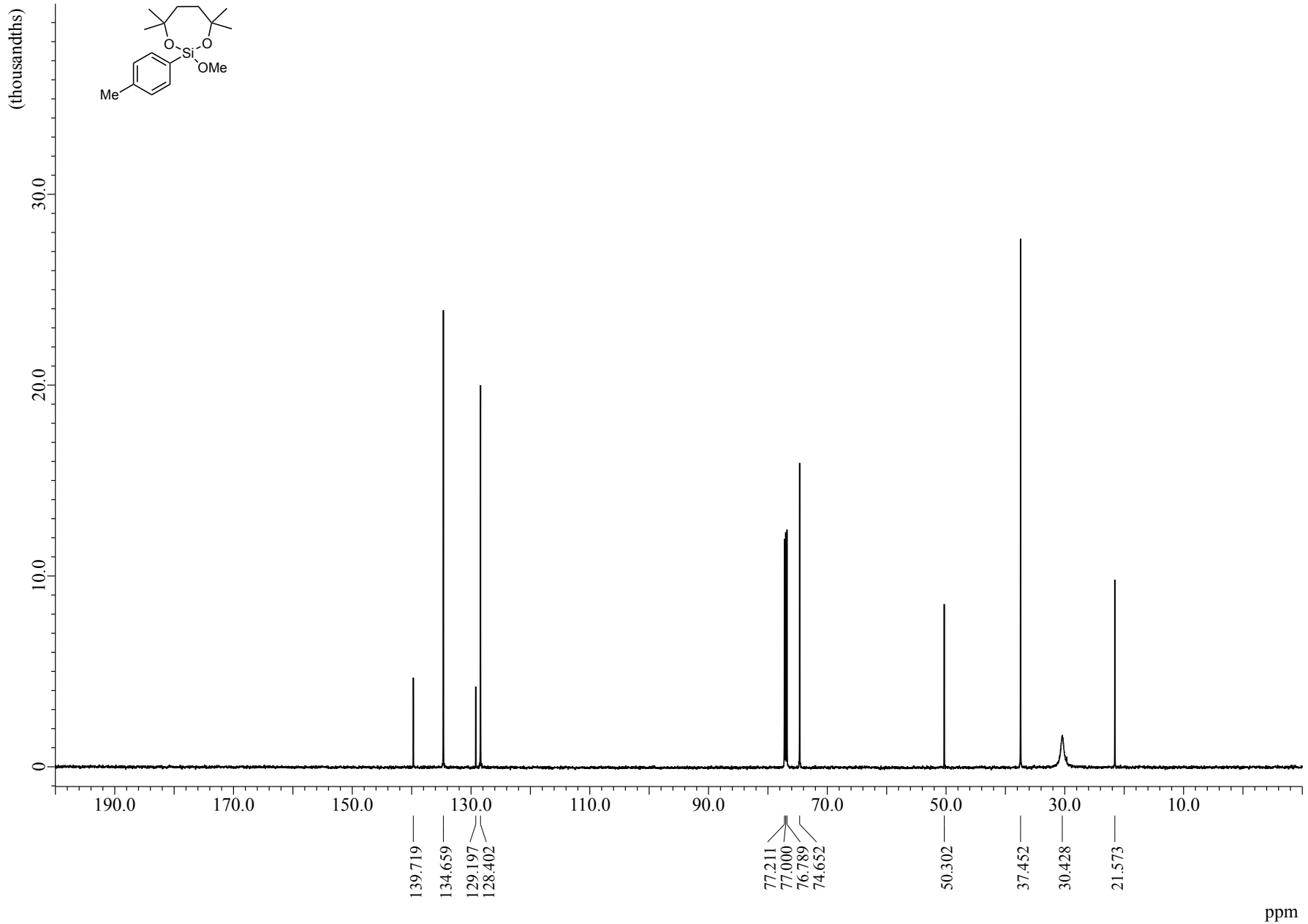


Figure S25. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2c-OMe**

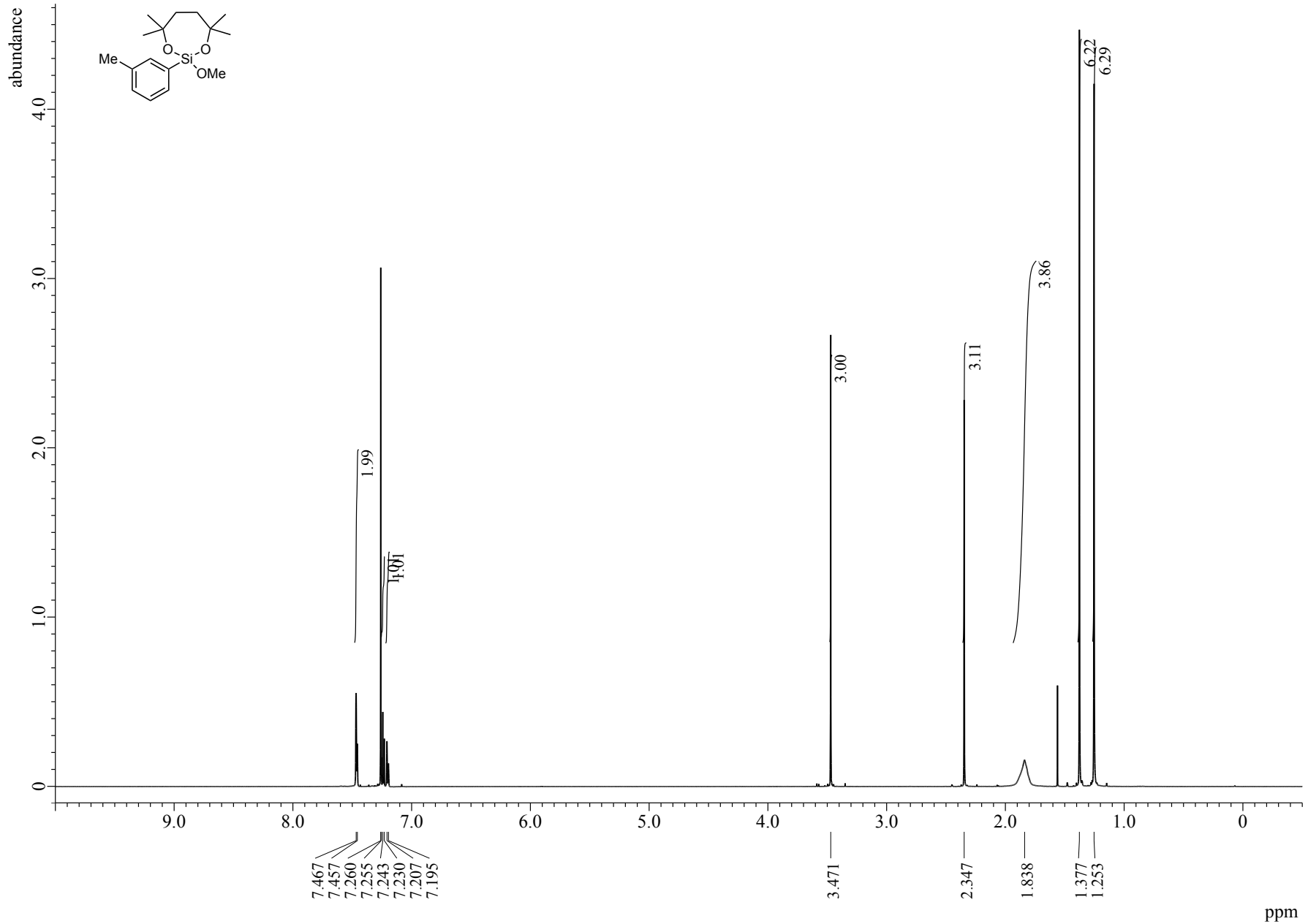


Figure S26. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2d-OMe**

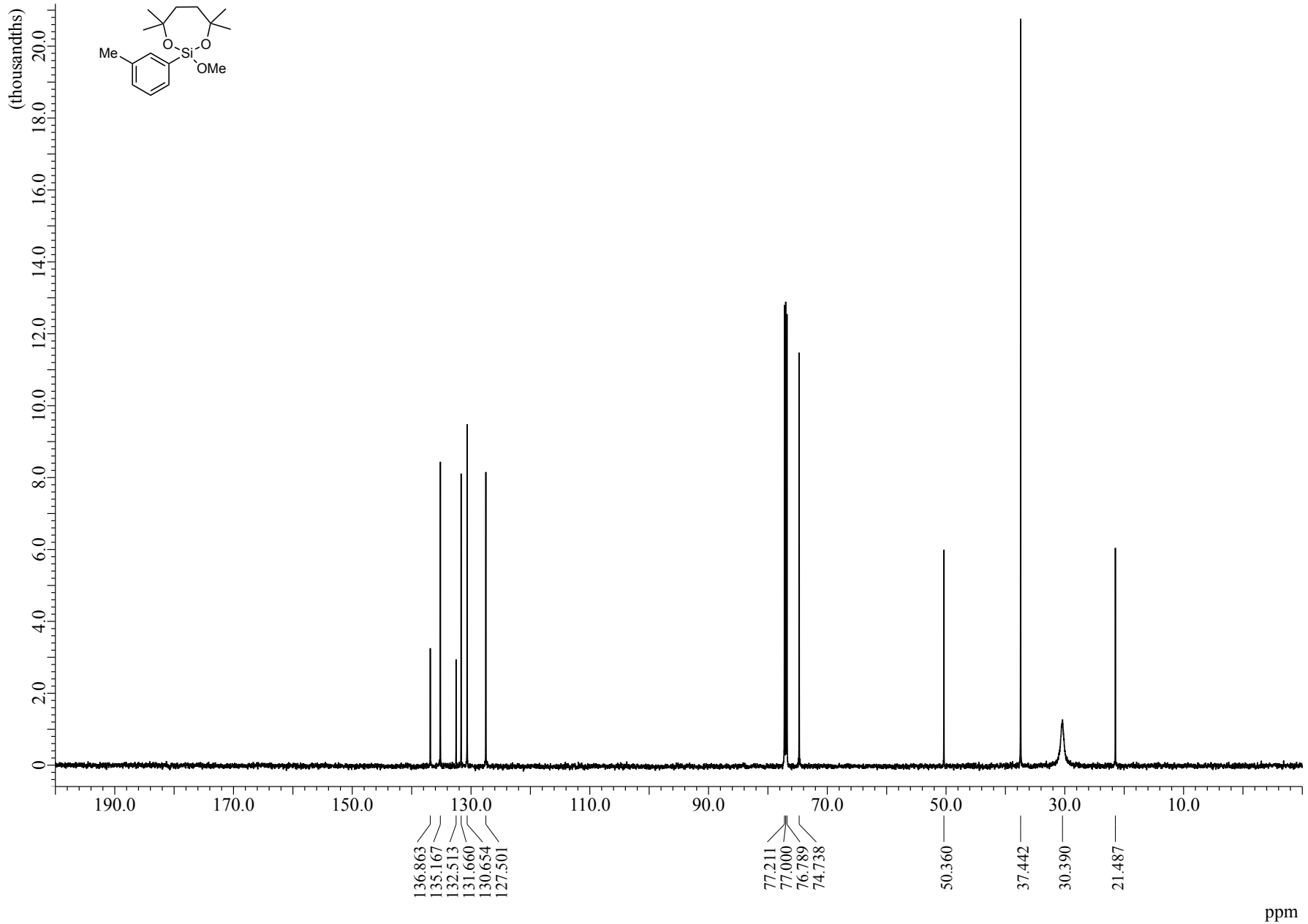


Figure S27. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2d-OMe**

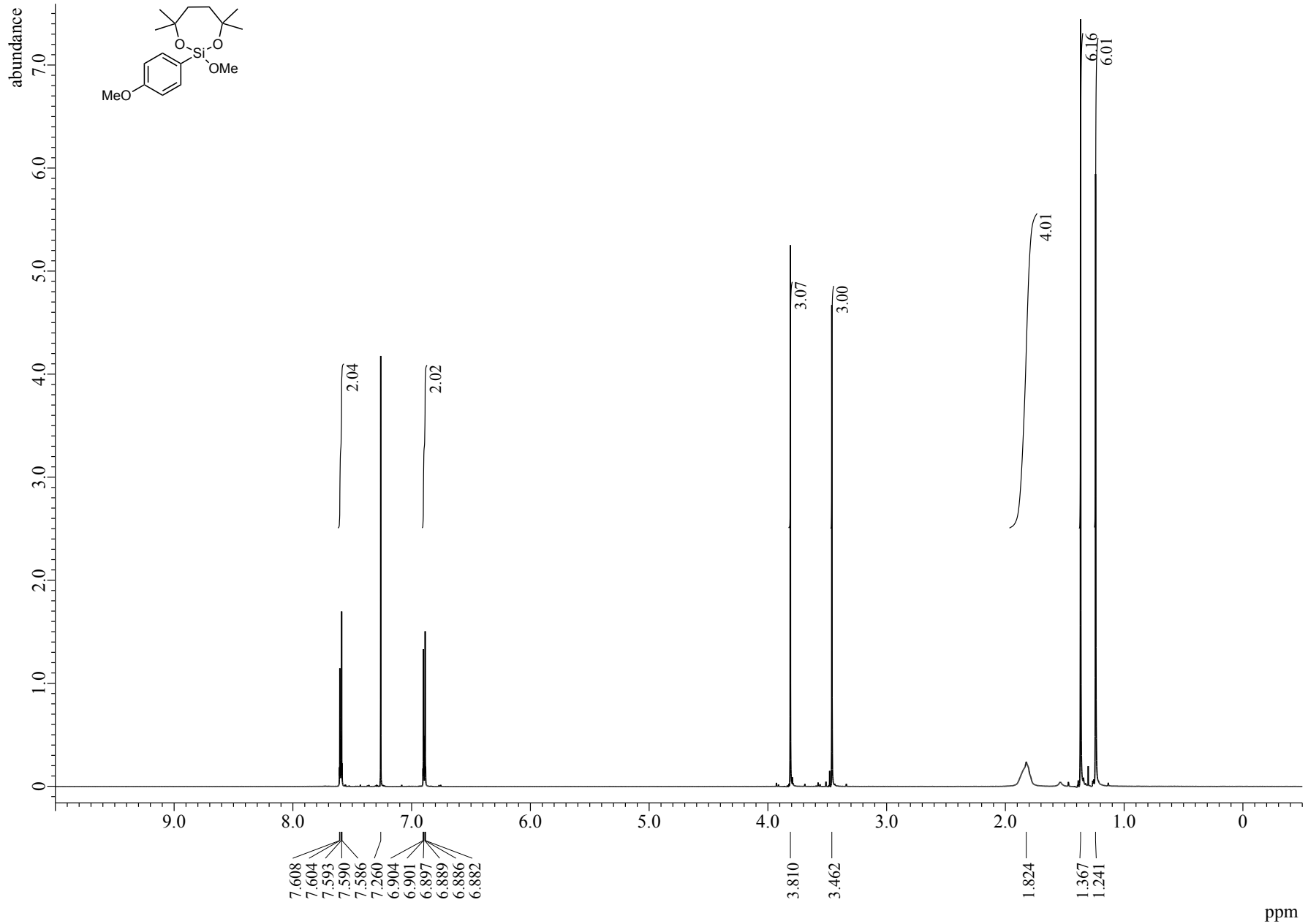


Figure S28. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2e-OMe**

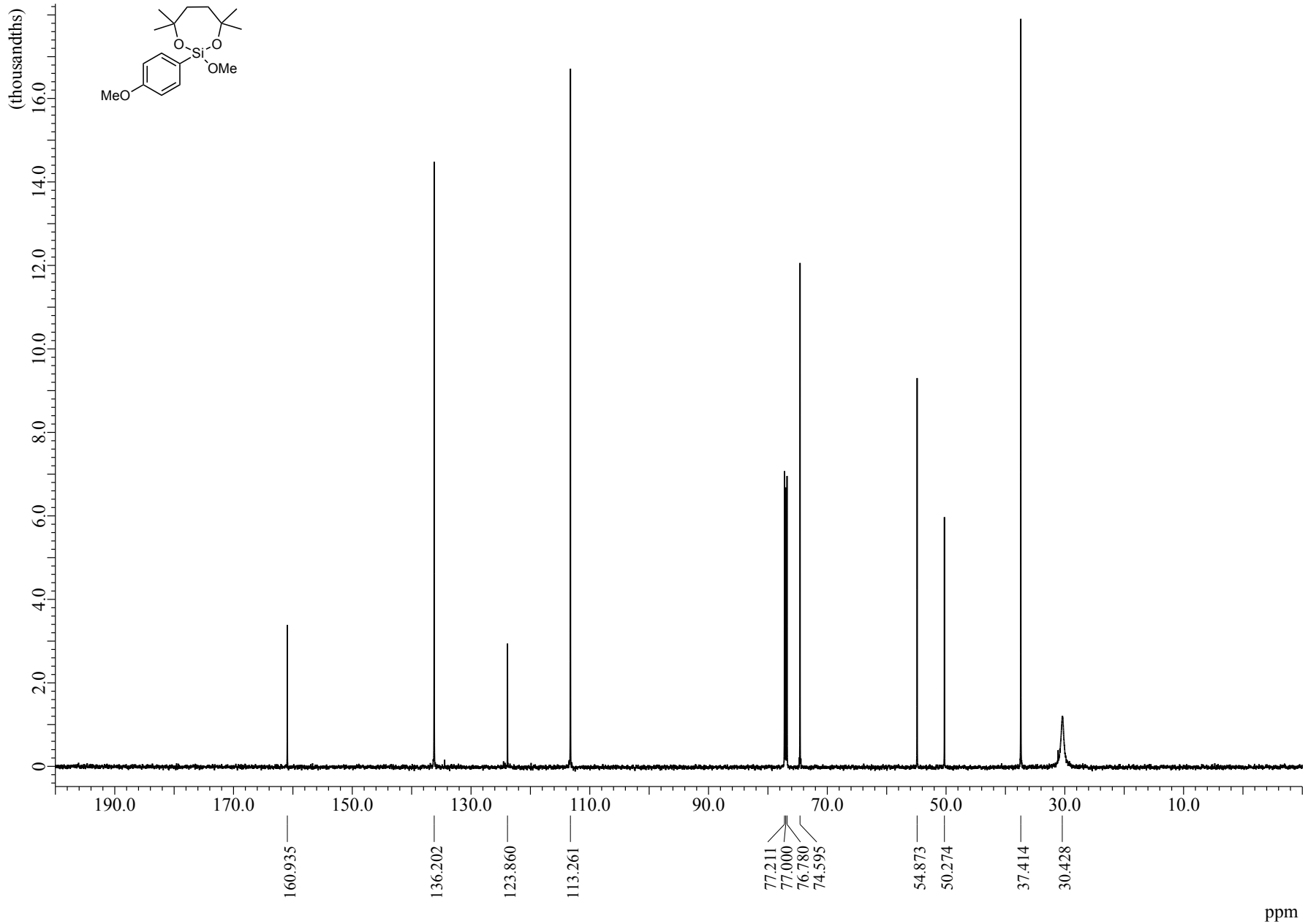


Figure S29. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2e-OMe**

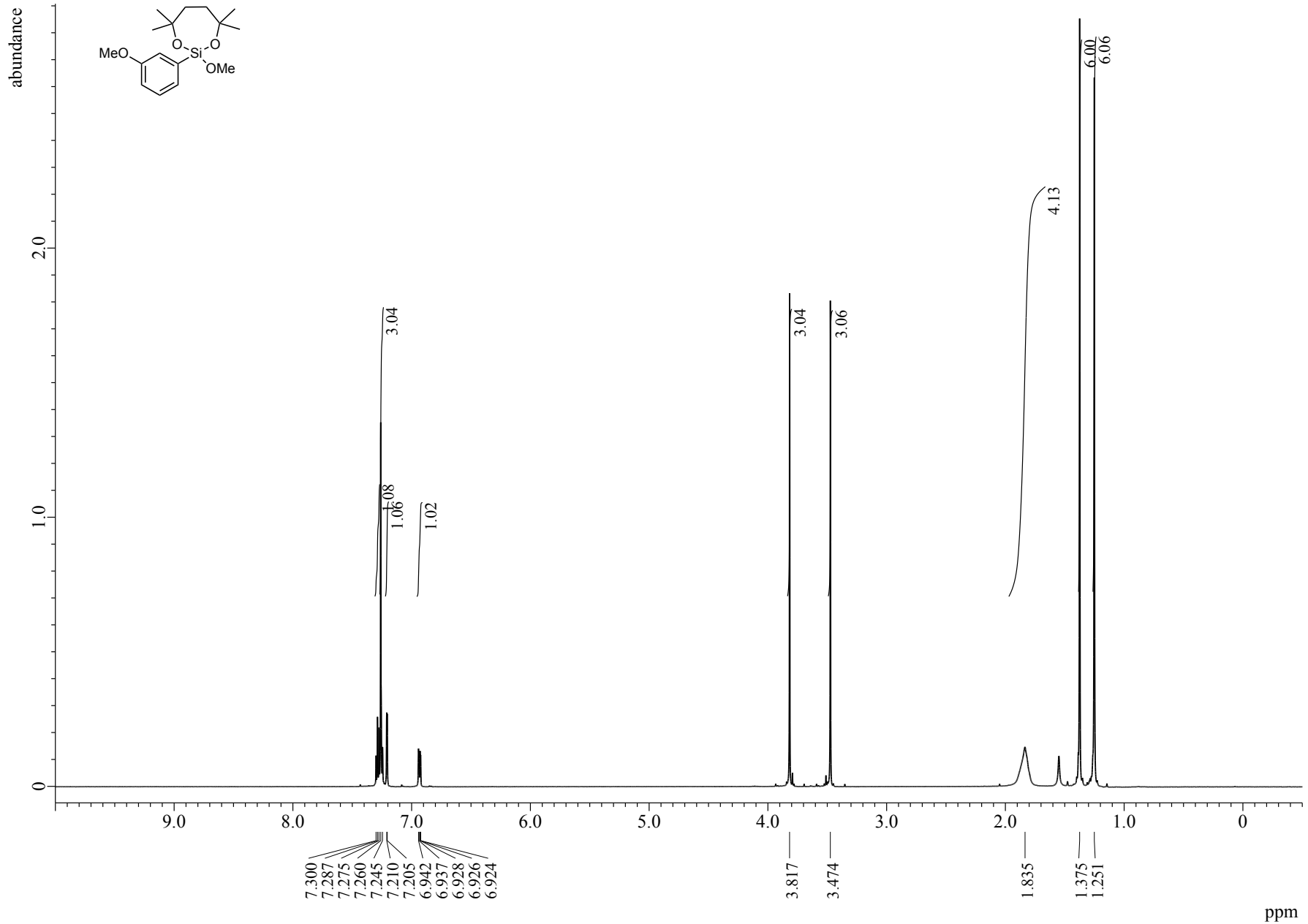


Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2f-OMe**

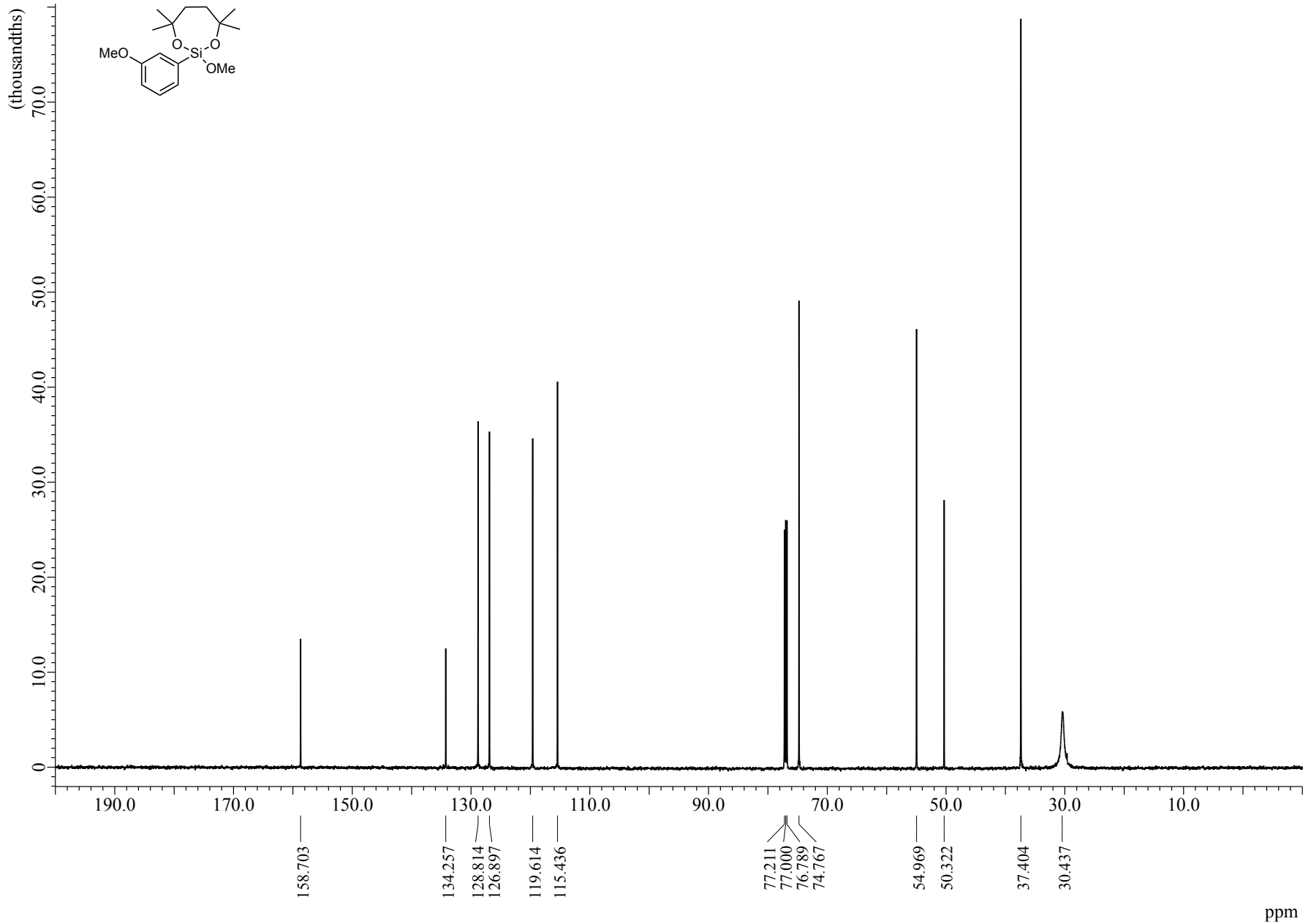


Figure S31. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2f-OMe**

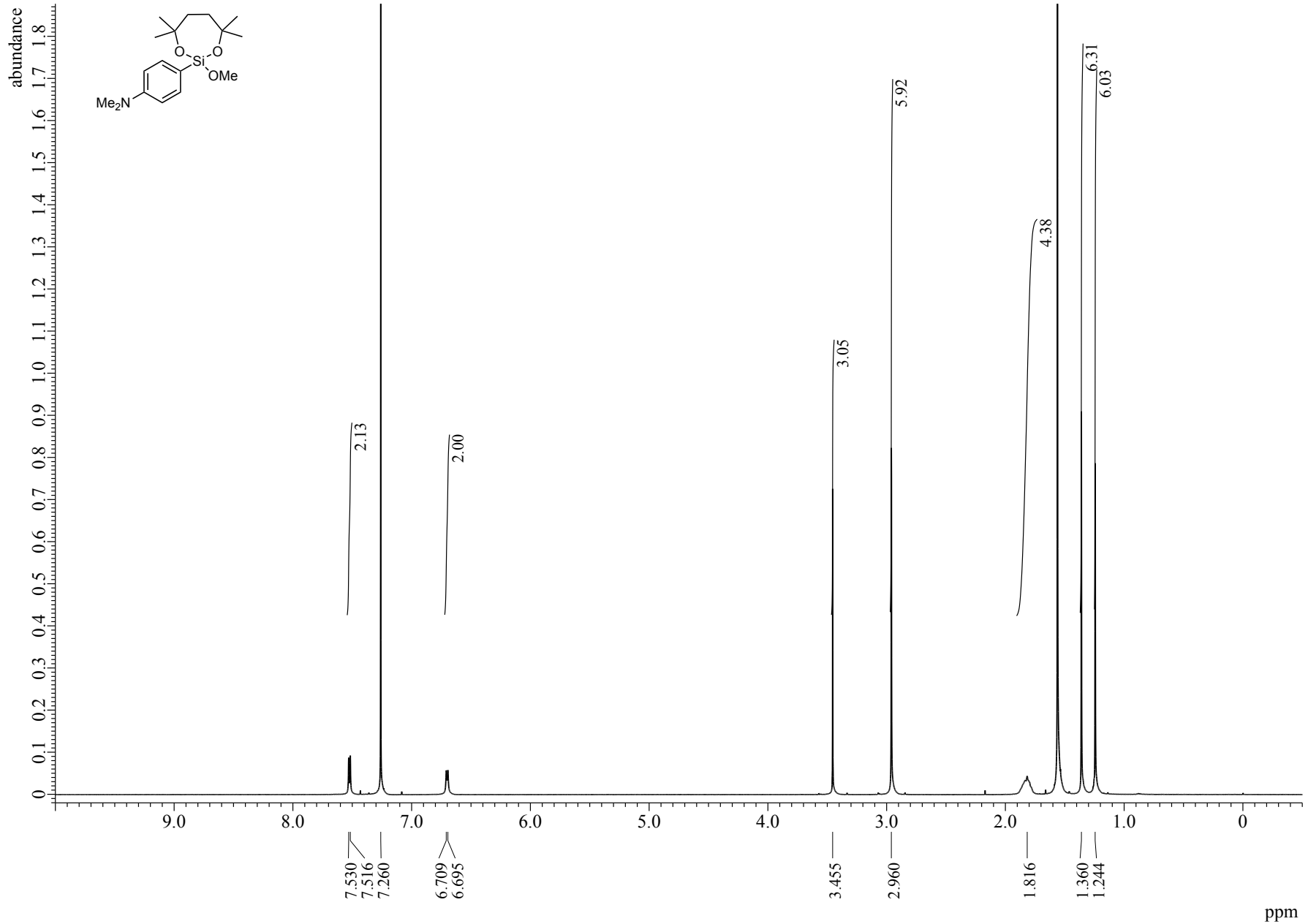


Figure S32. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2g-OMe**

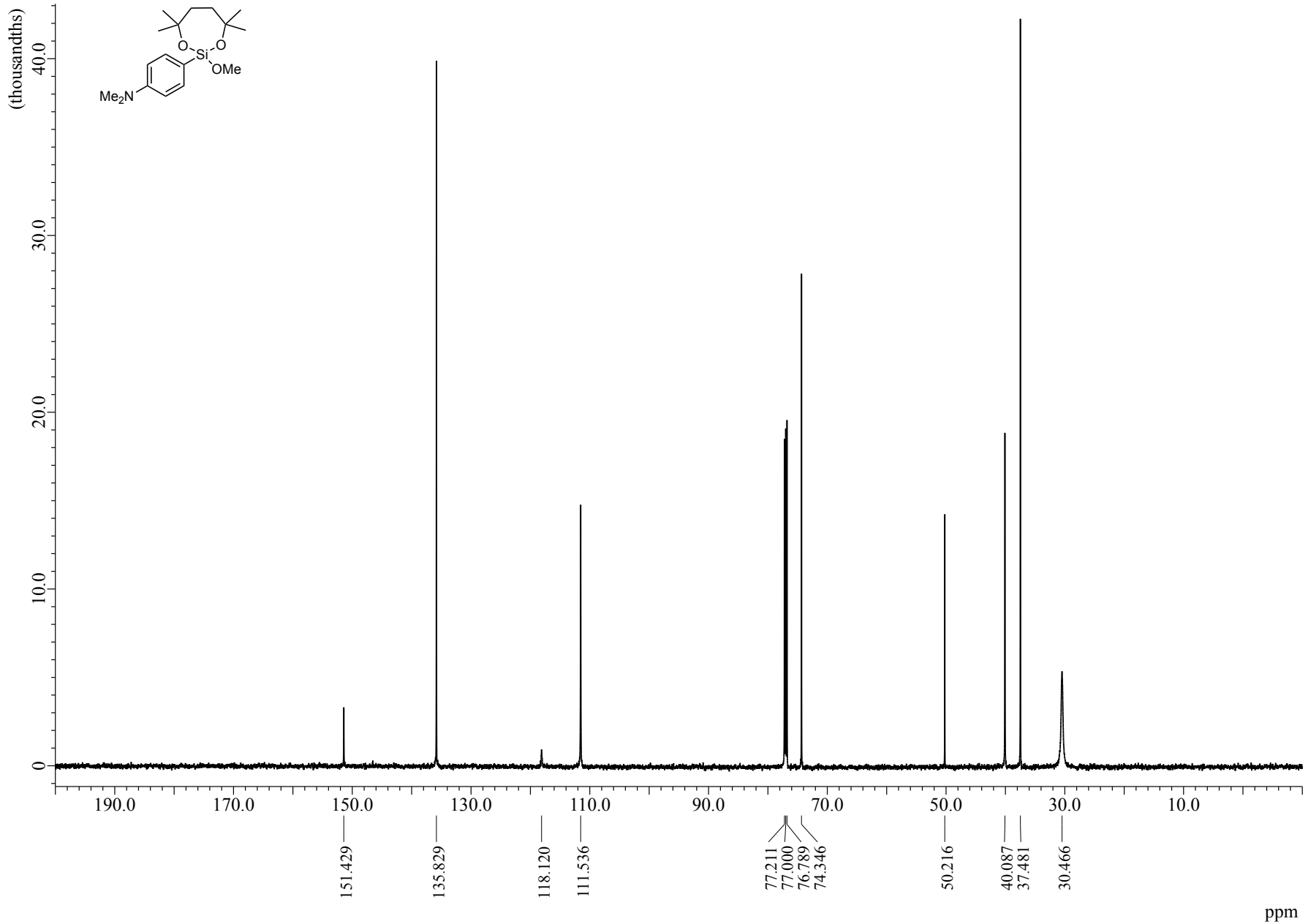


Figure S33. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2g-OMe**

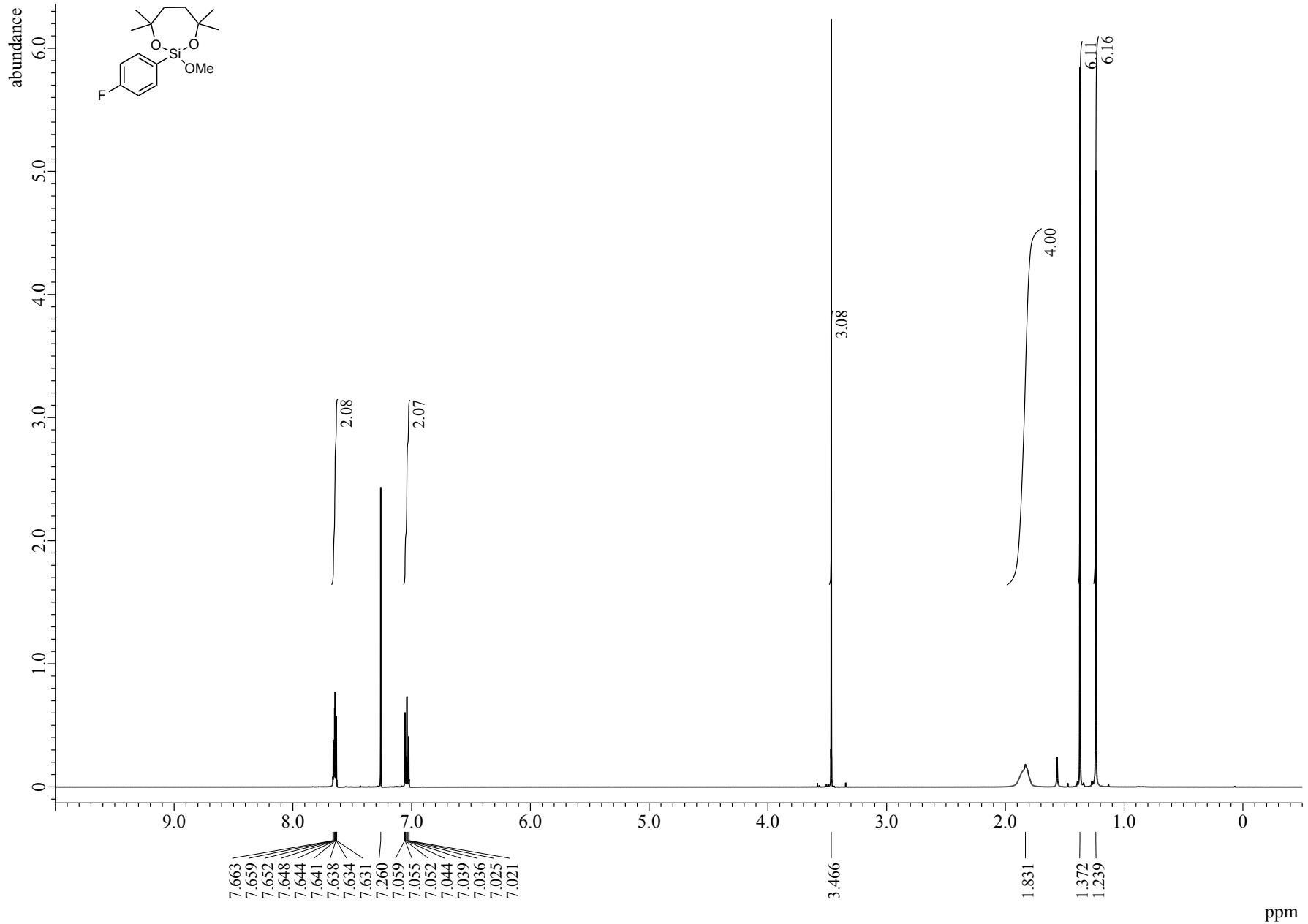


Figure S34. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2h-OMe**

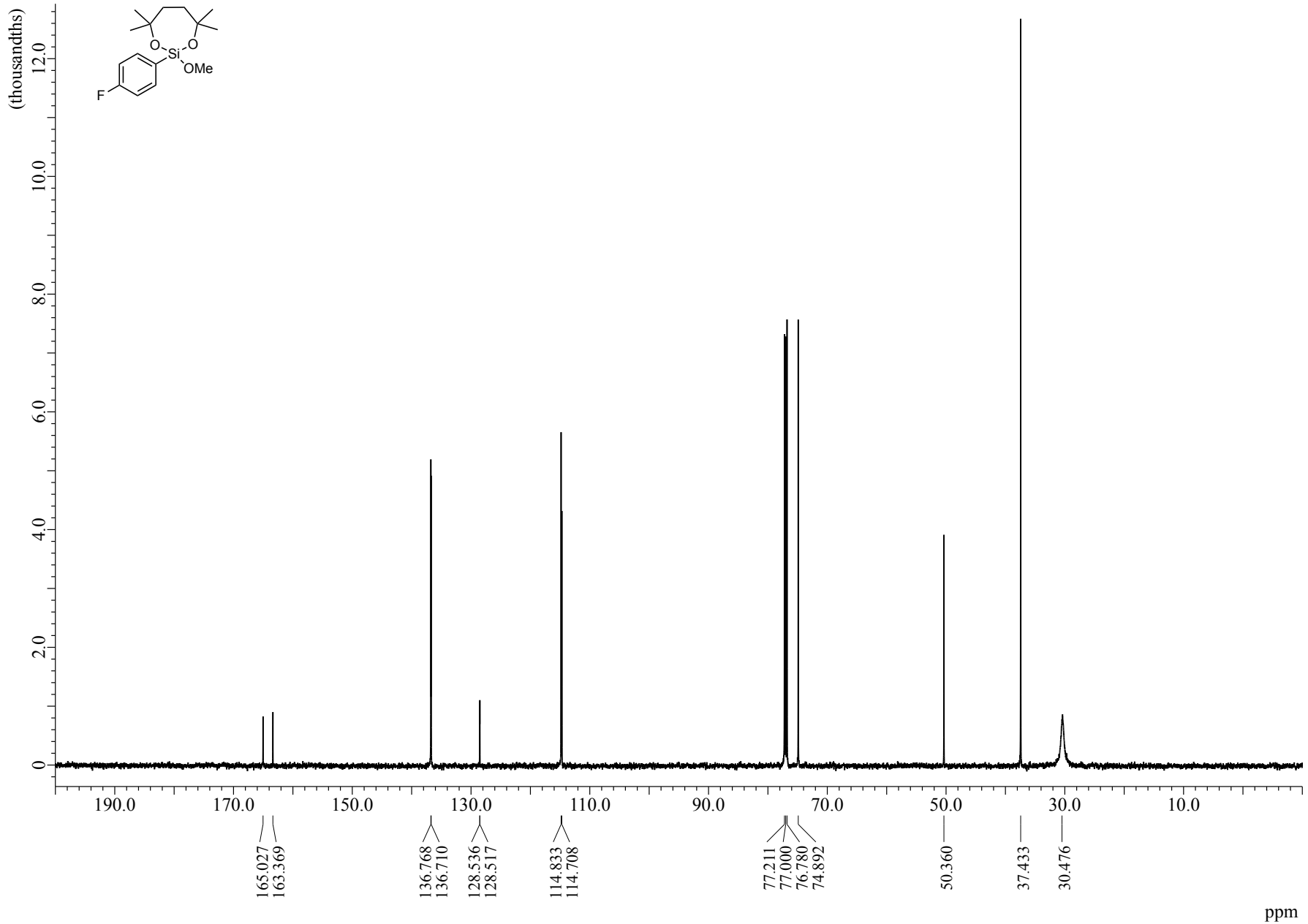


Figure S35. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2h-OMe**

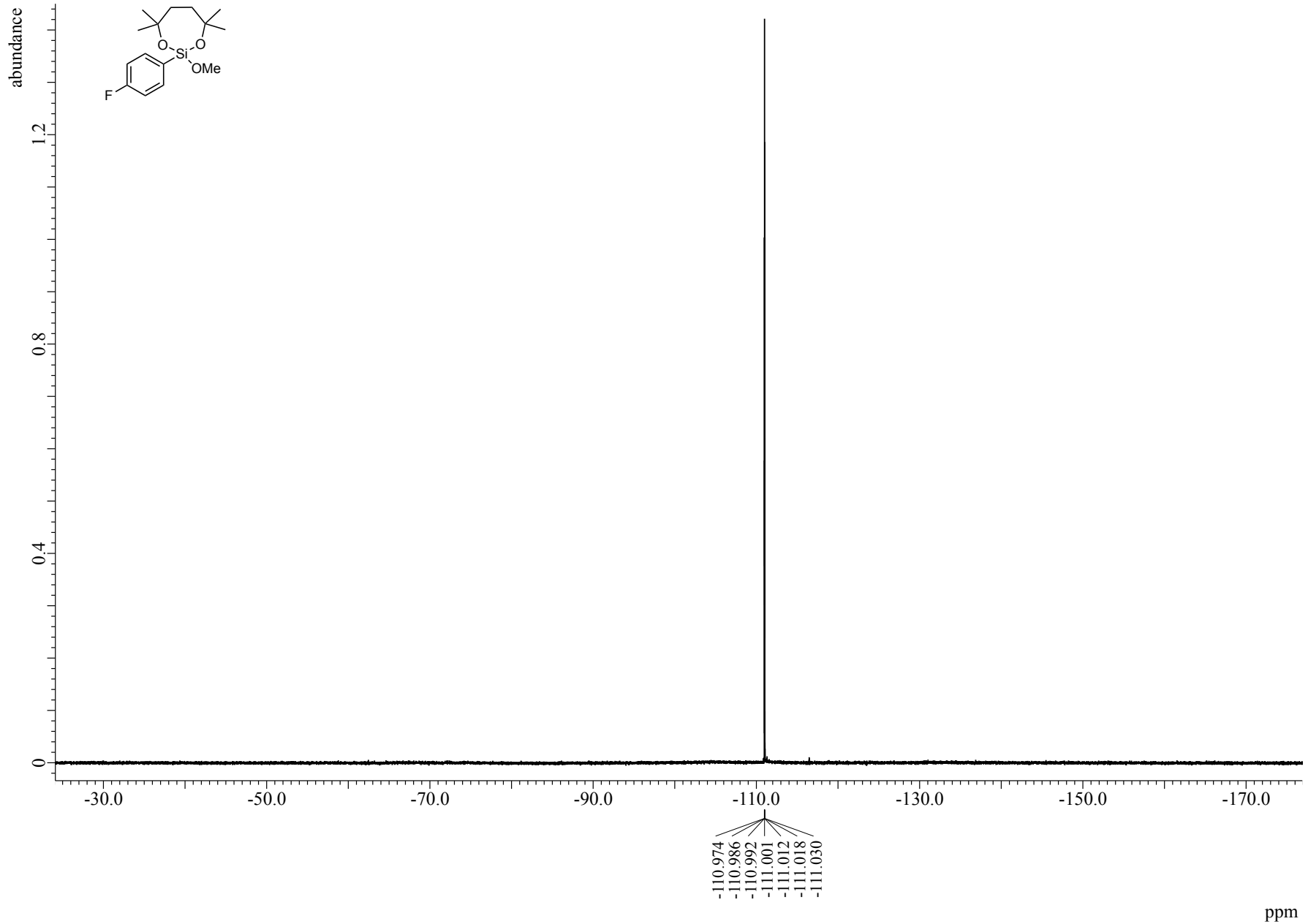


Figure S36. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2h-OMe**

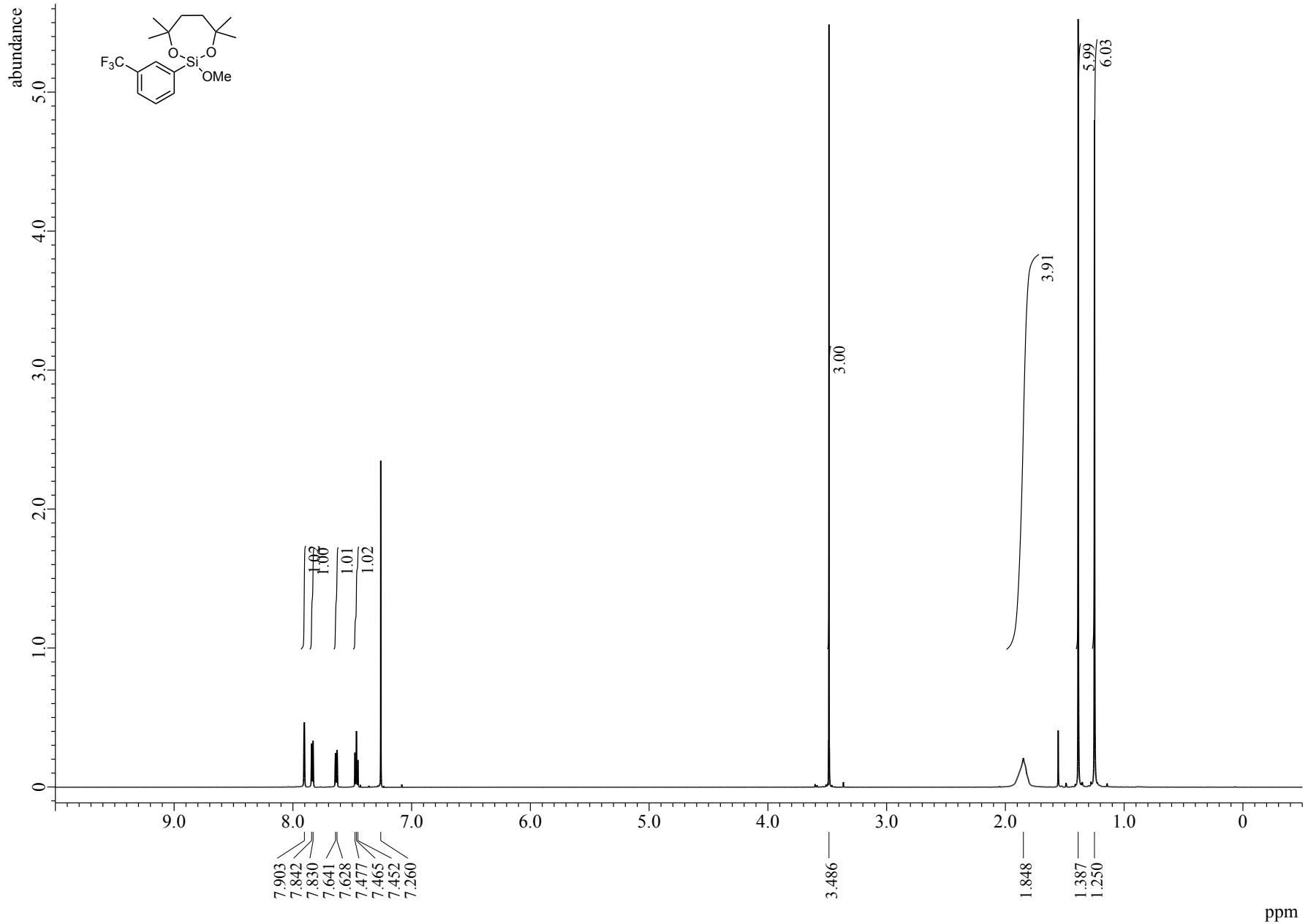


Figure S37. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2i-OMe**

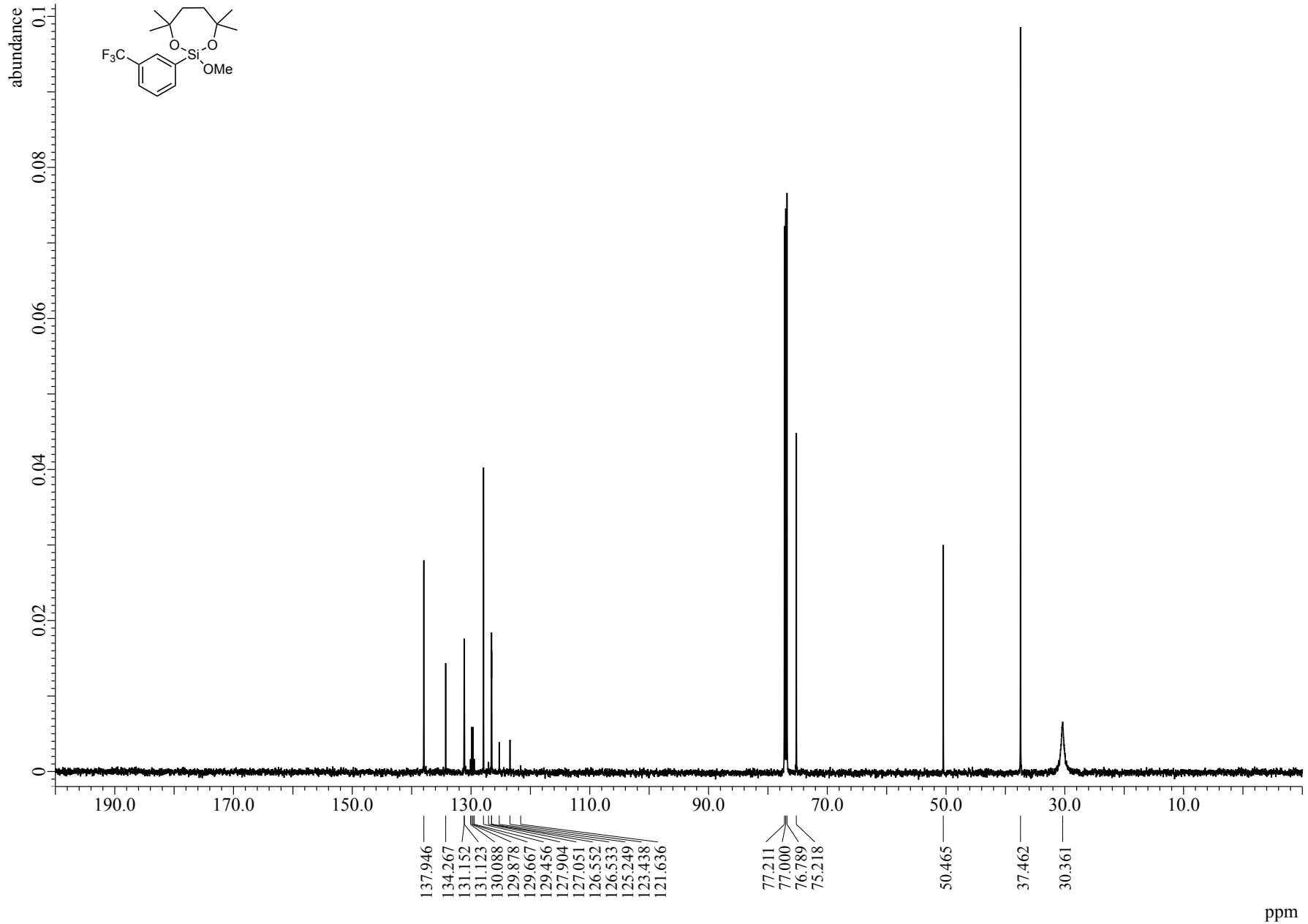


Figure S38. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2i-OMe**

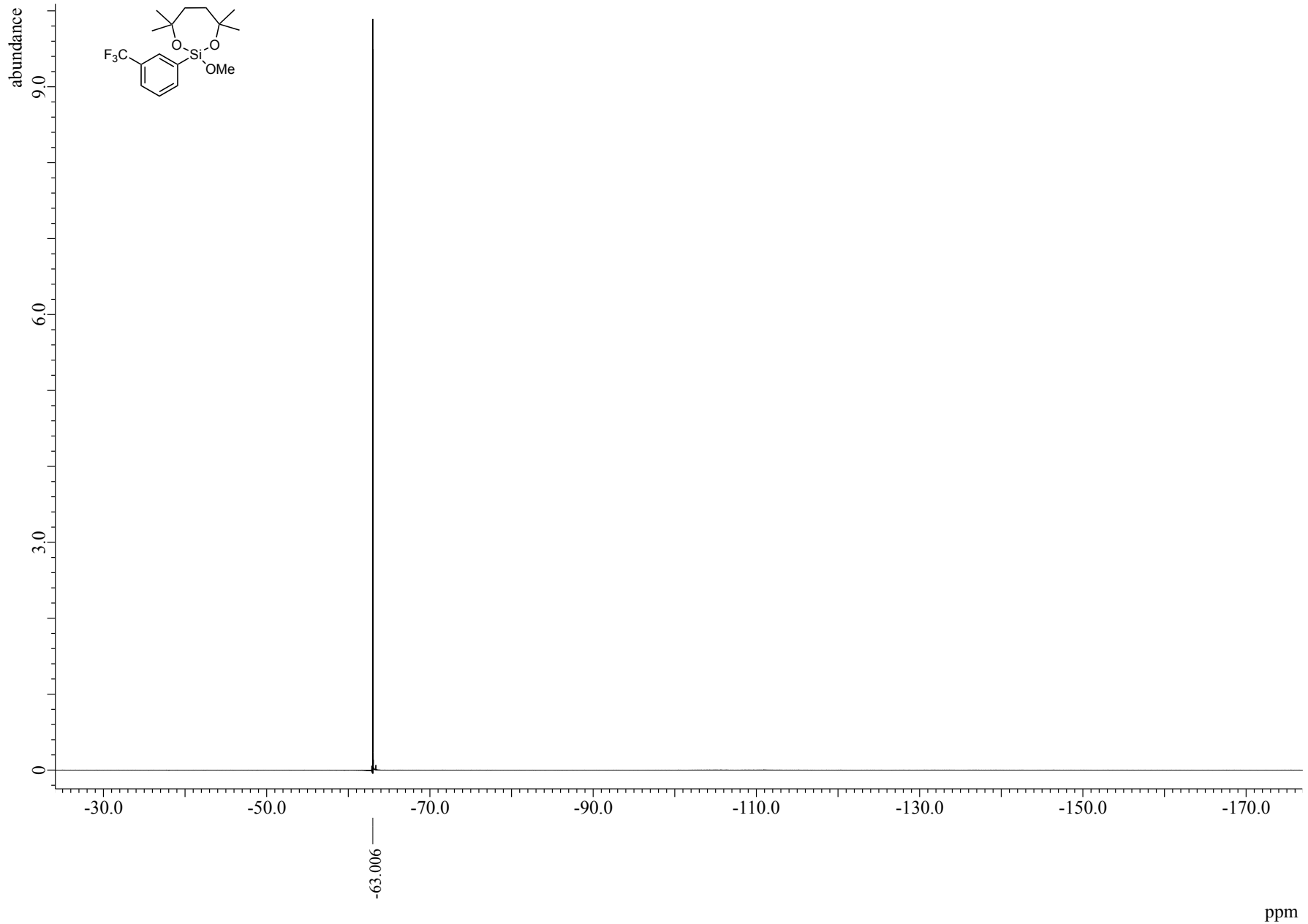


Figure S39. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **2i-OMe**

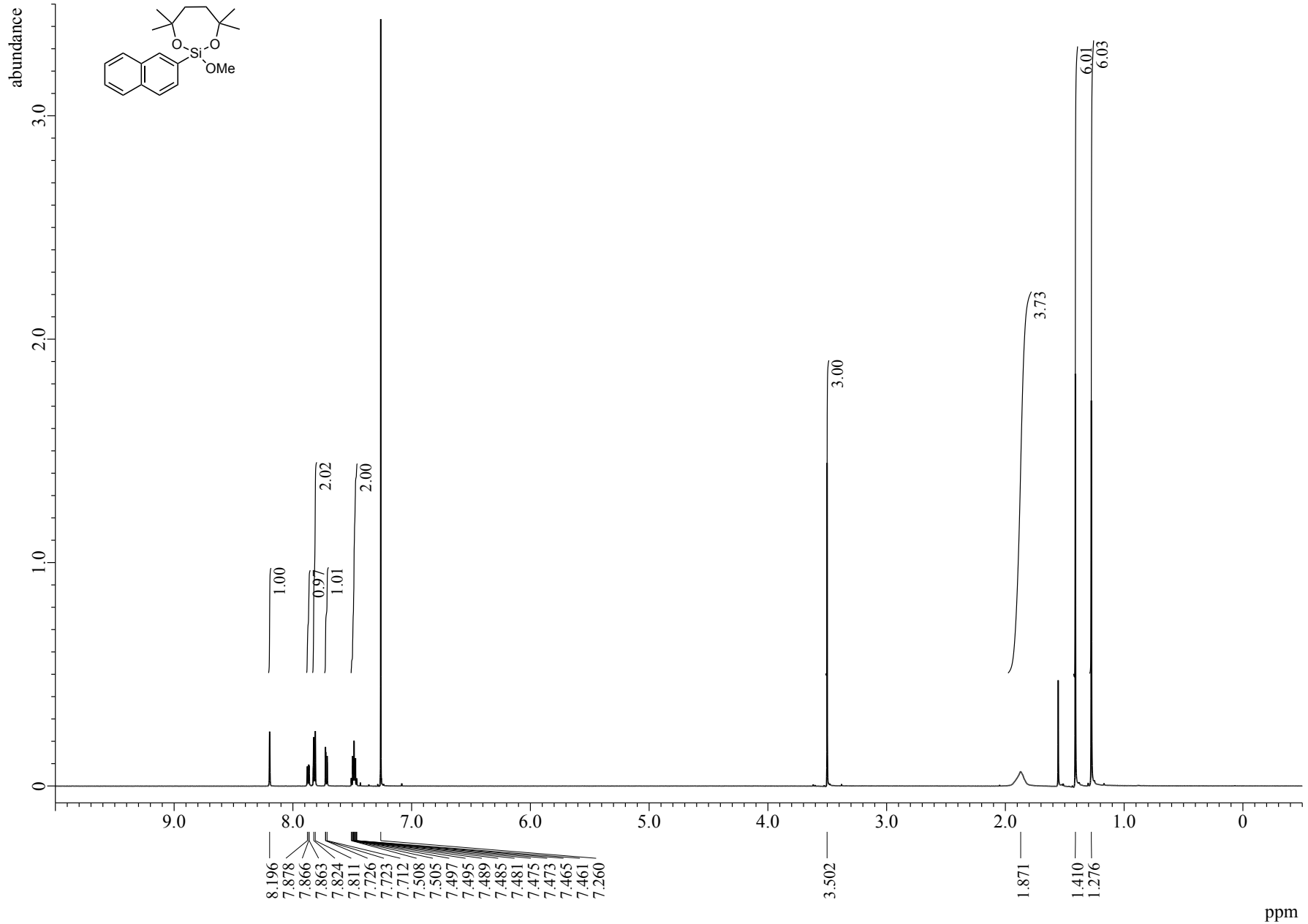


Figure S40. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2j-OMe**

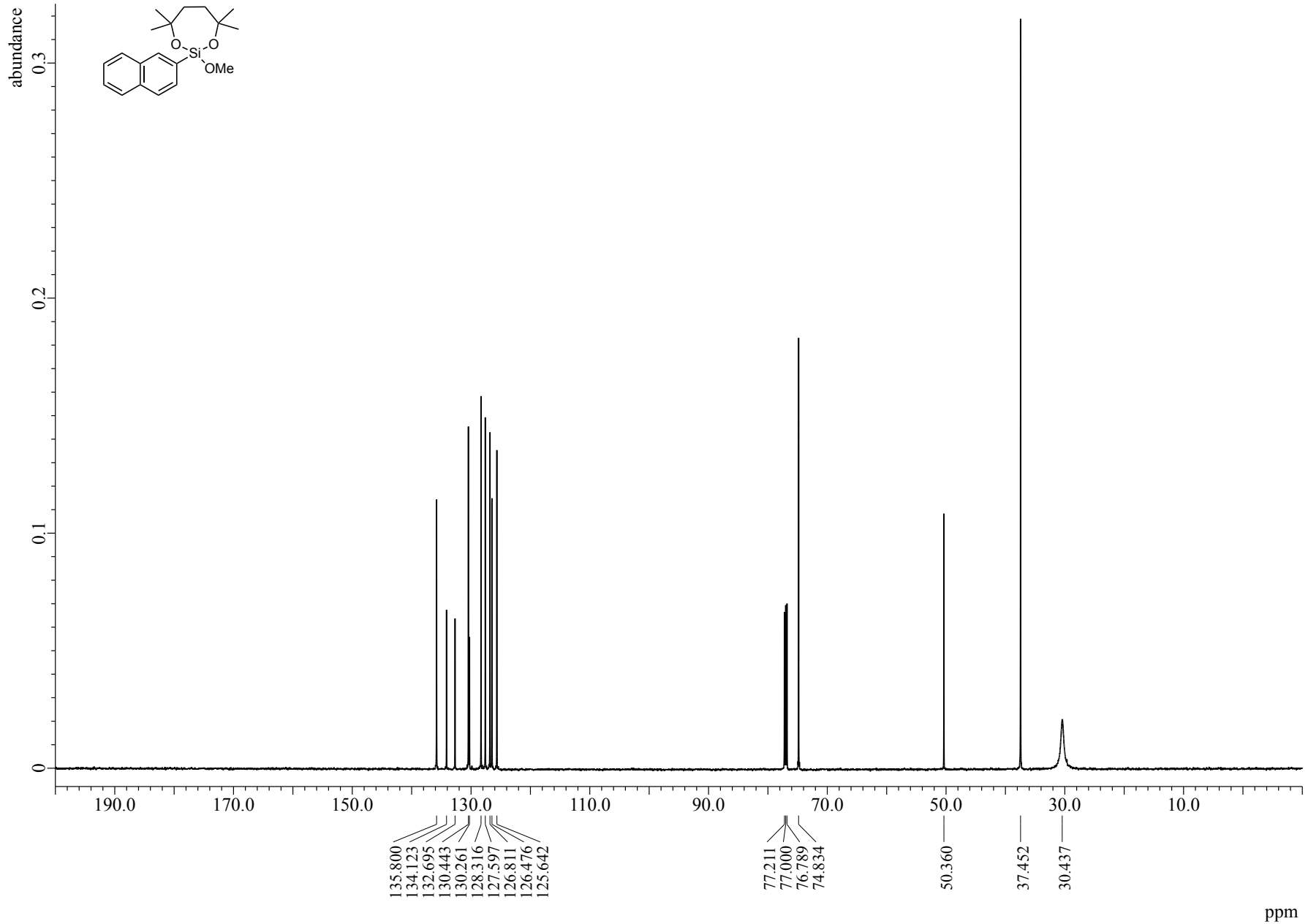


Figure S41. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2j-OMe**

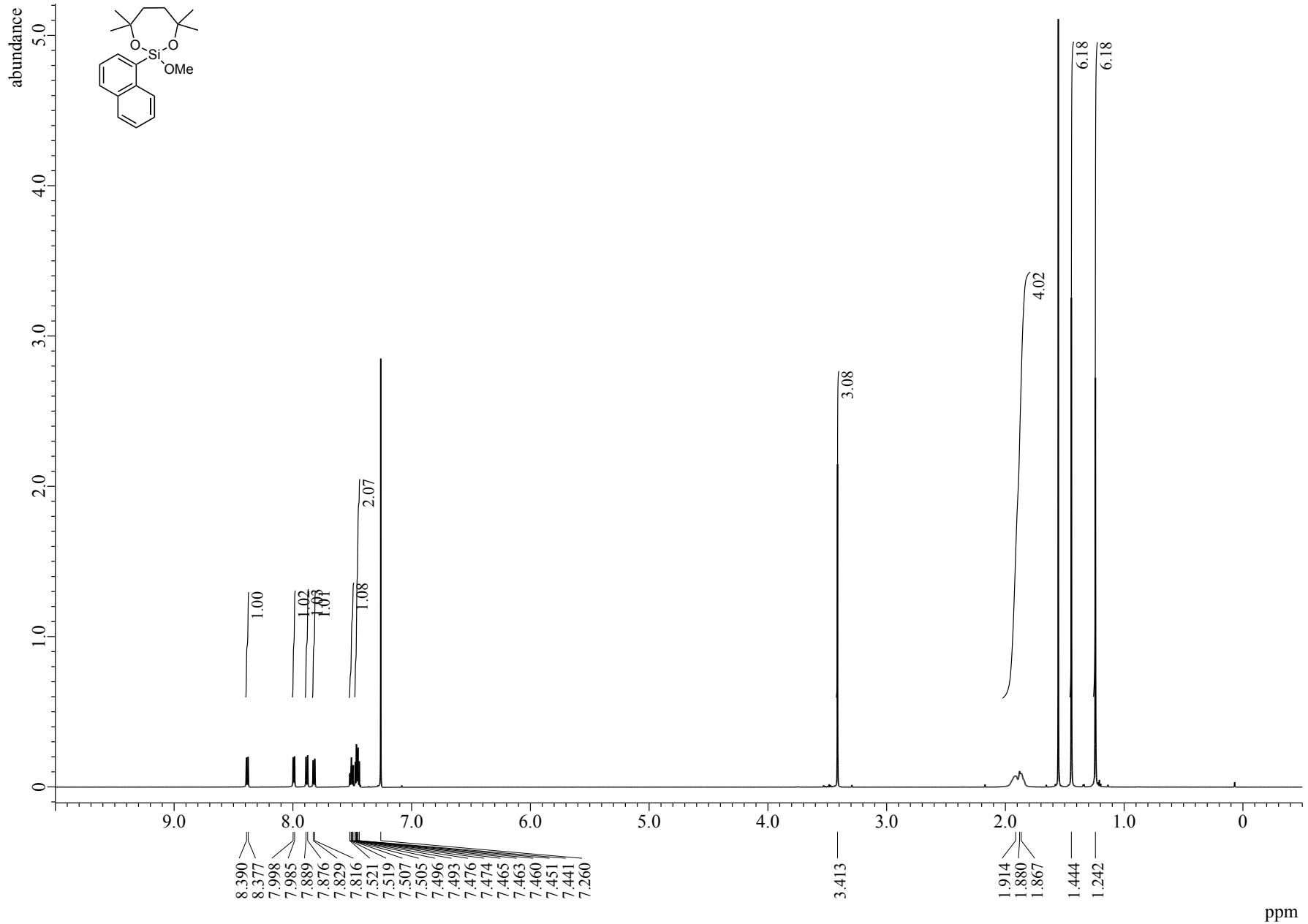


Figure S42. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2k-OMe**

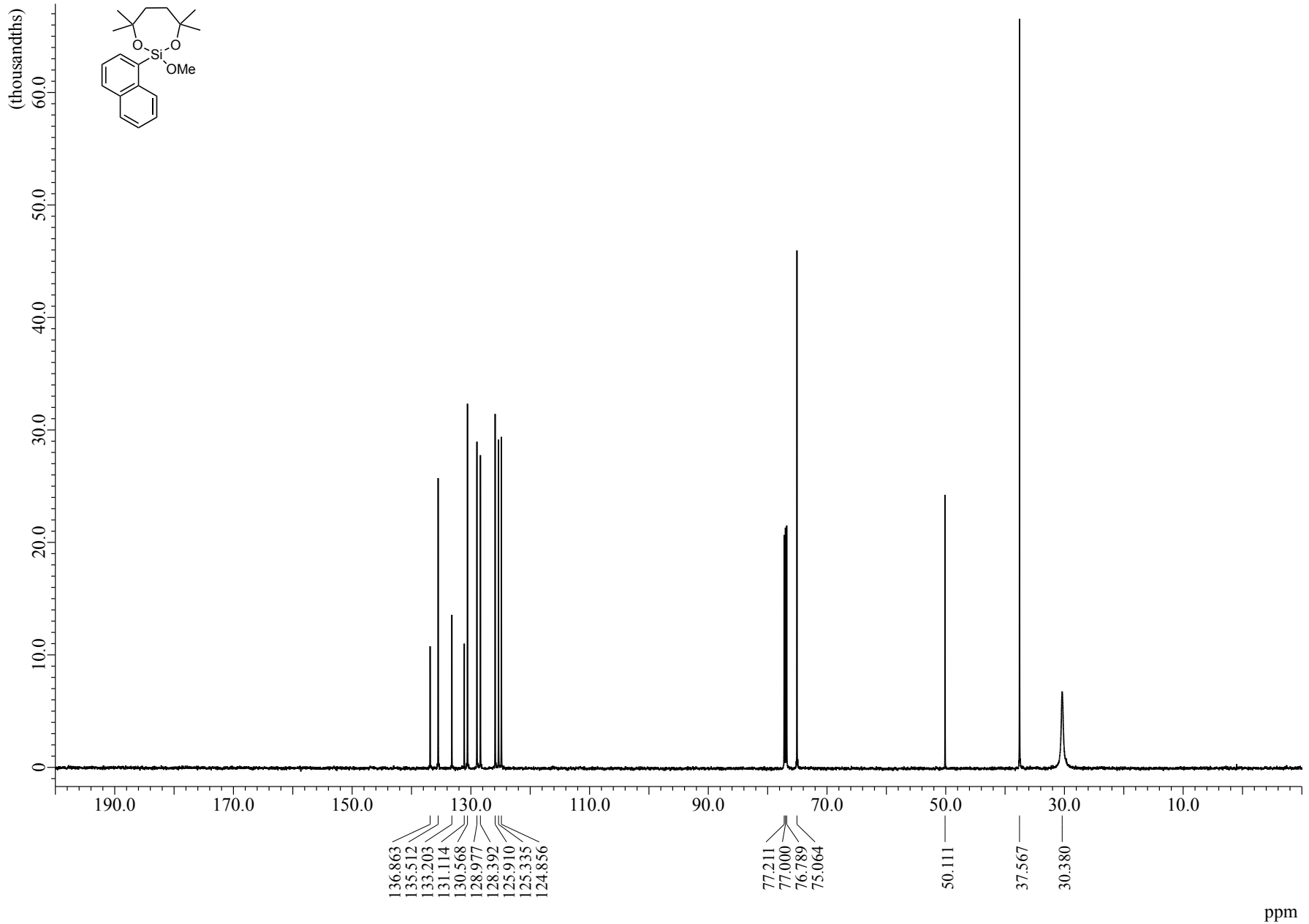


Figure S43. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2k-OMe**

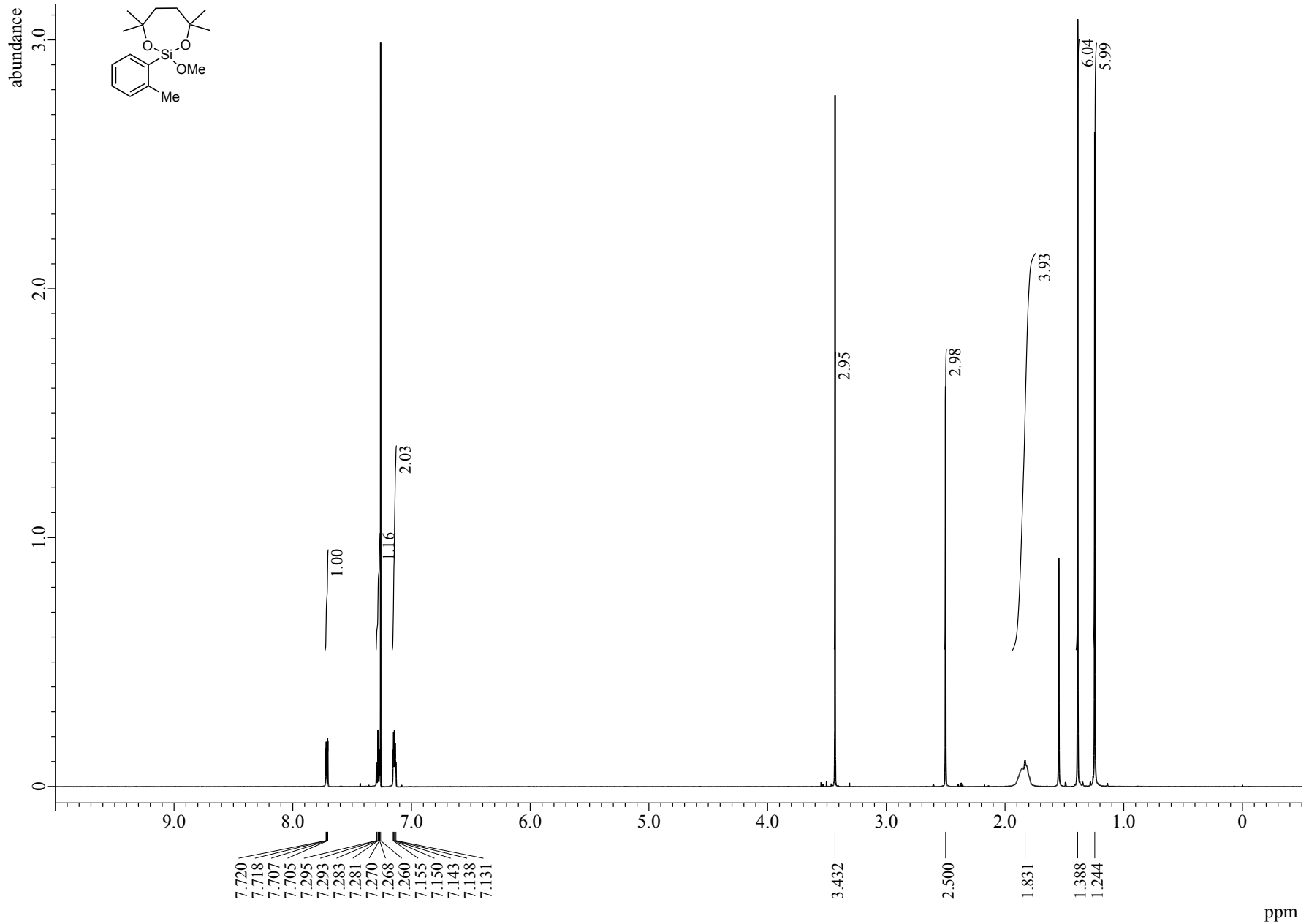


Figure S44. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2l-OMe**

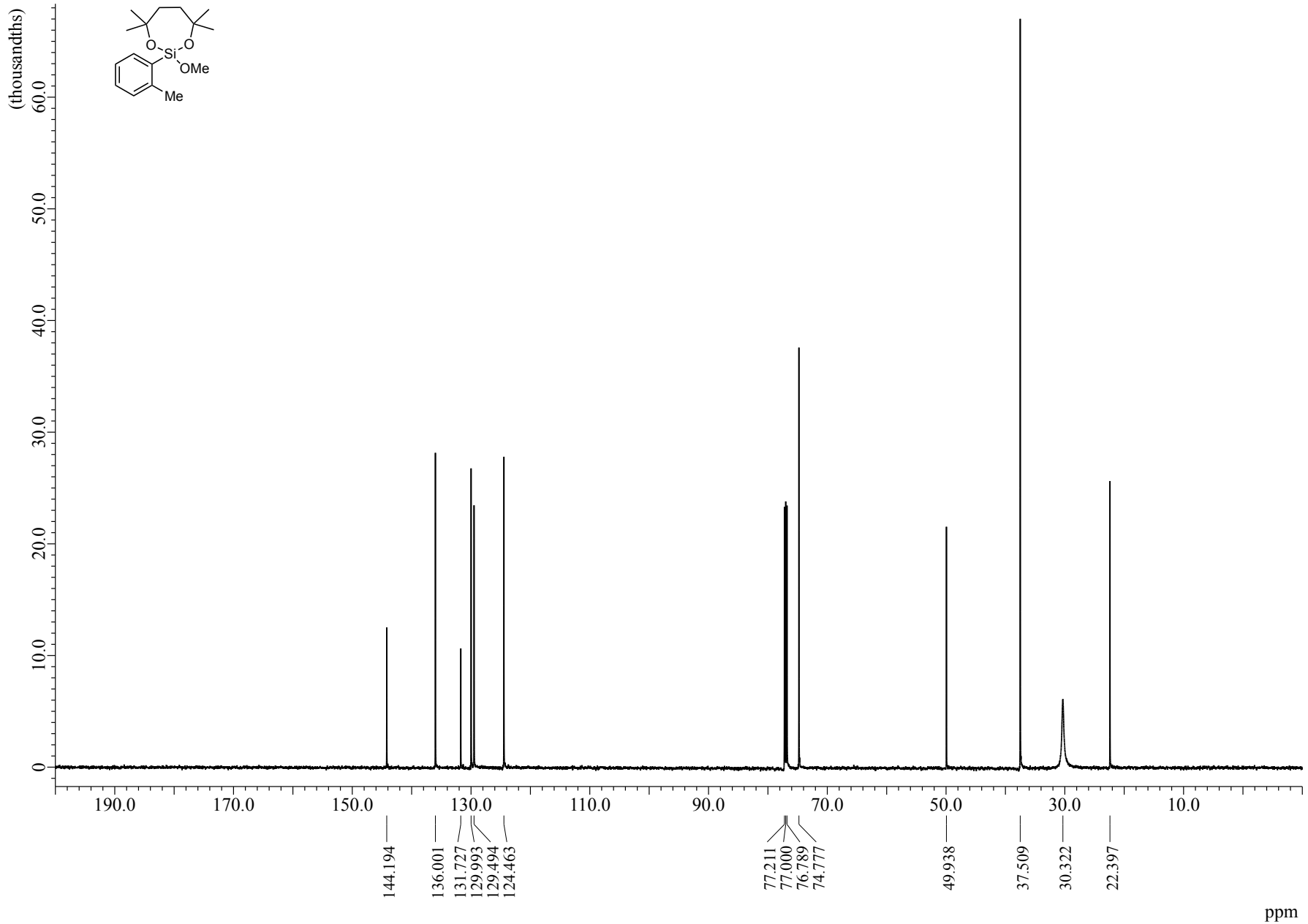


Figure S45. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2l-OMe**

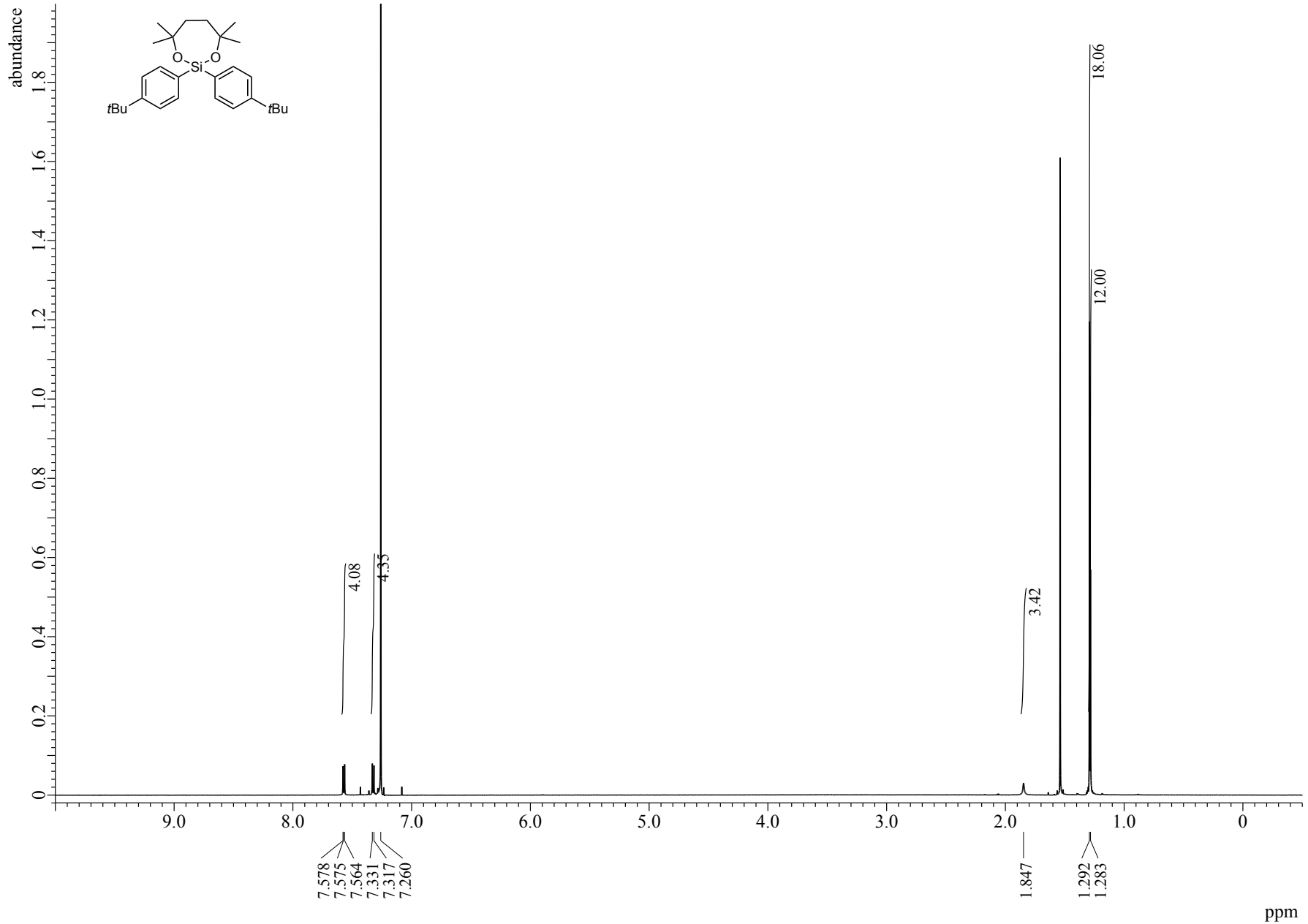


Figure S46. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aa**

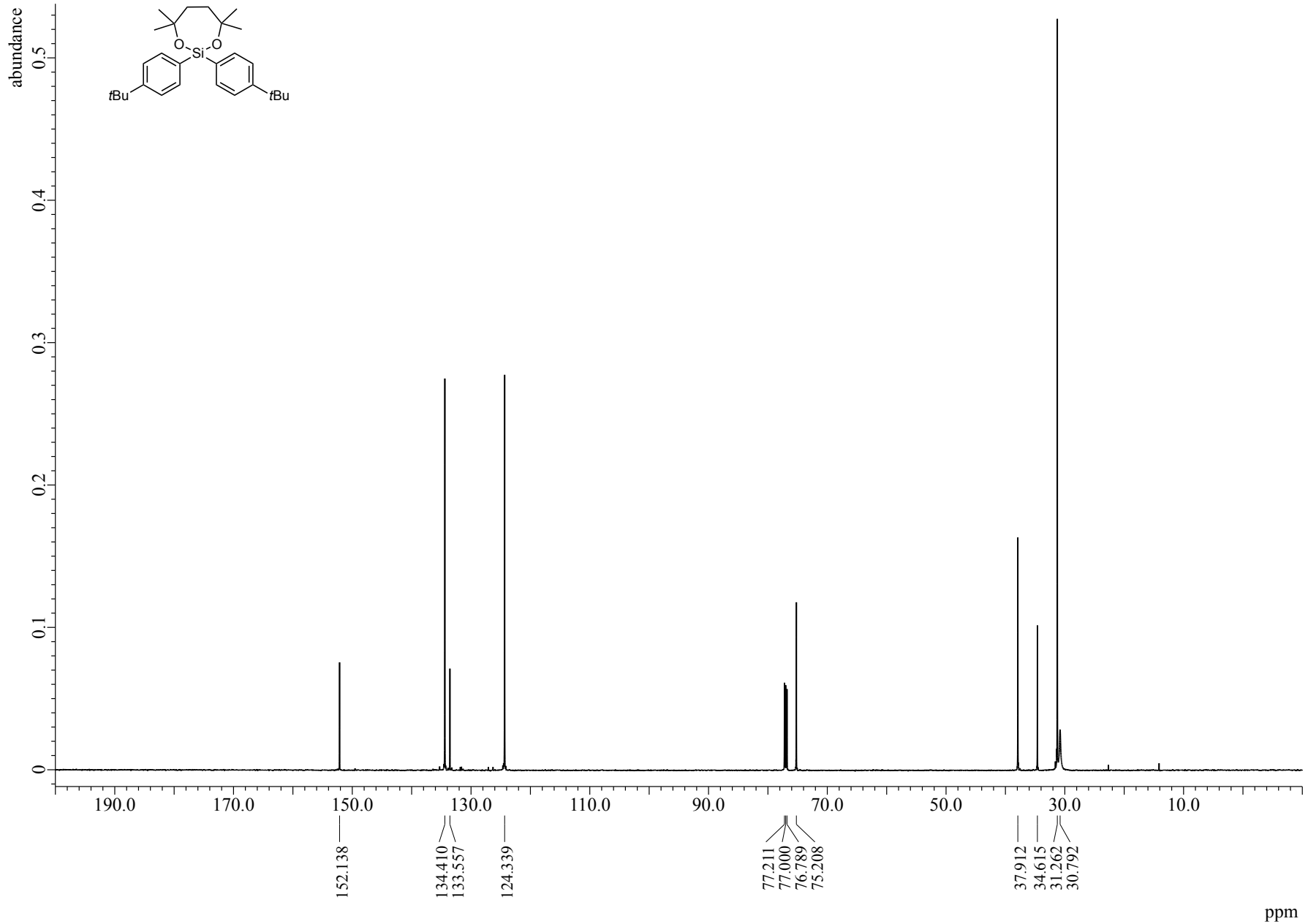


Figure S47. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3aa**

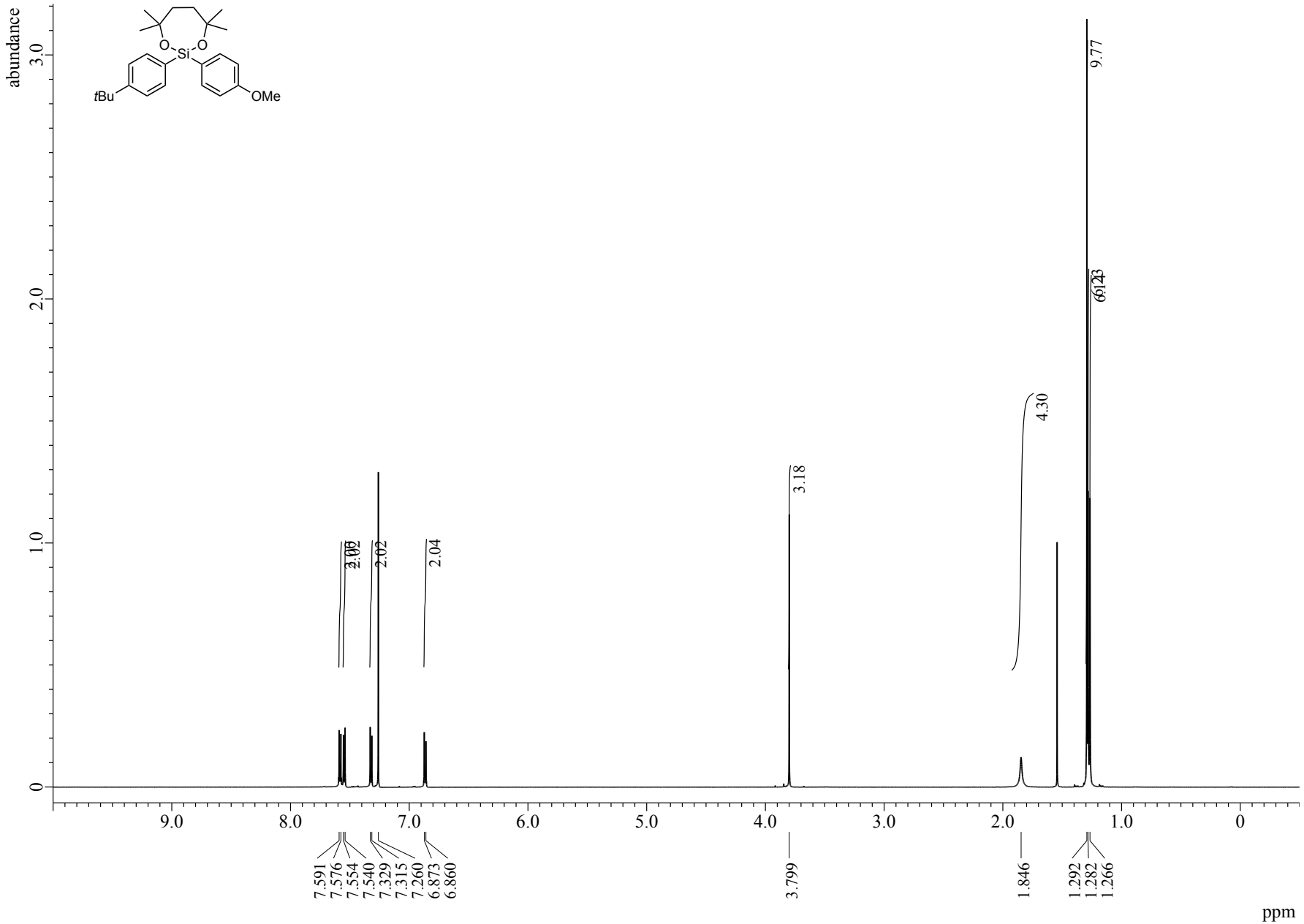


Figure S48. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ae**

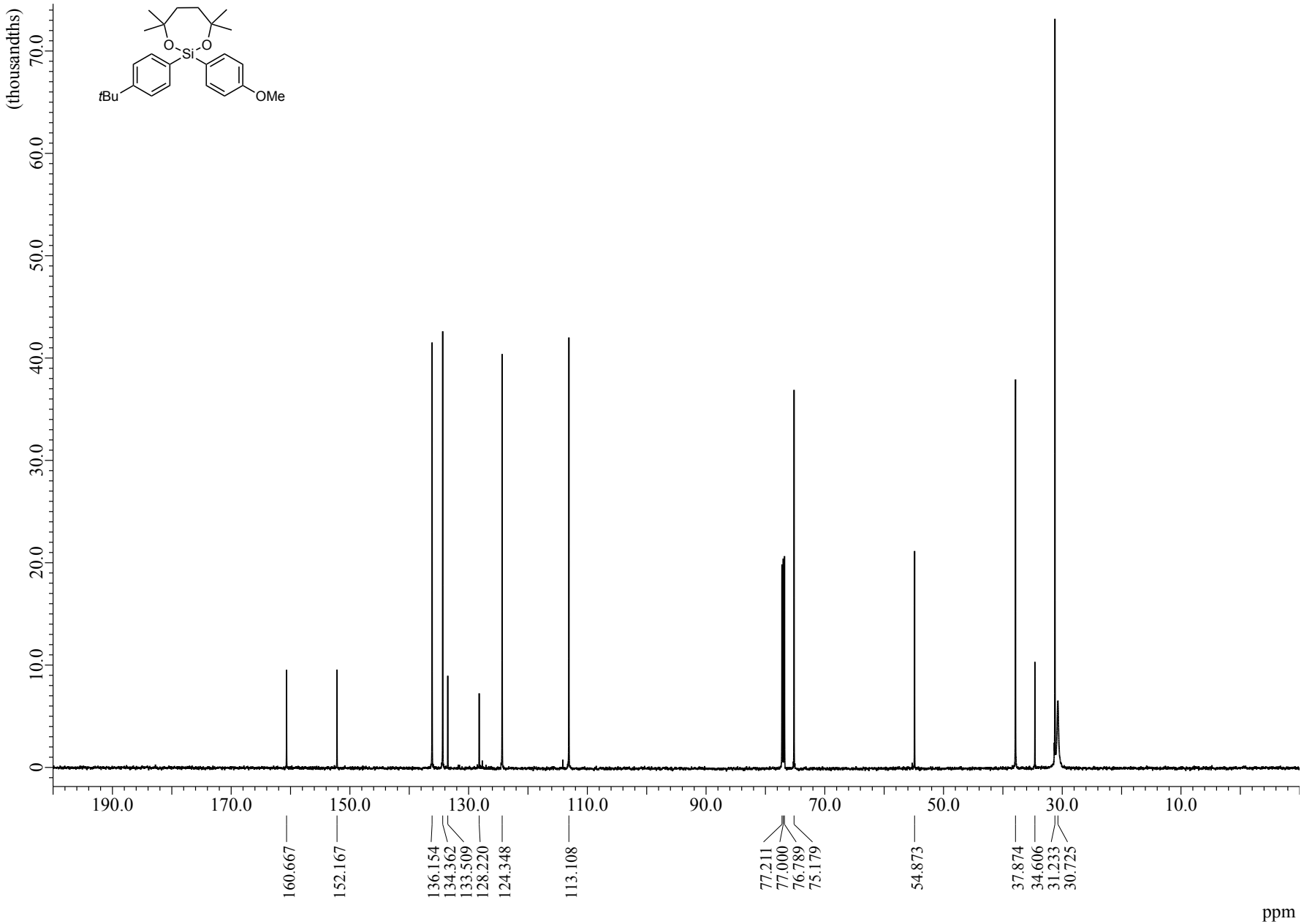


Figure S49. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ae**

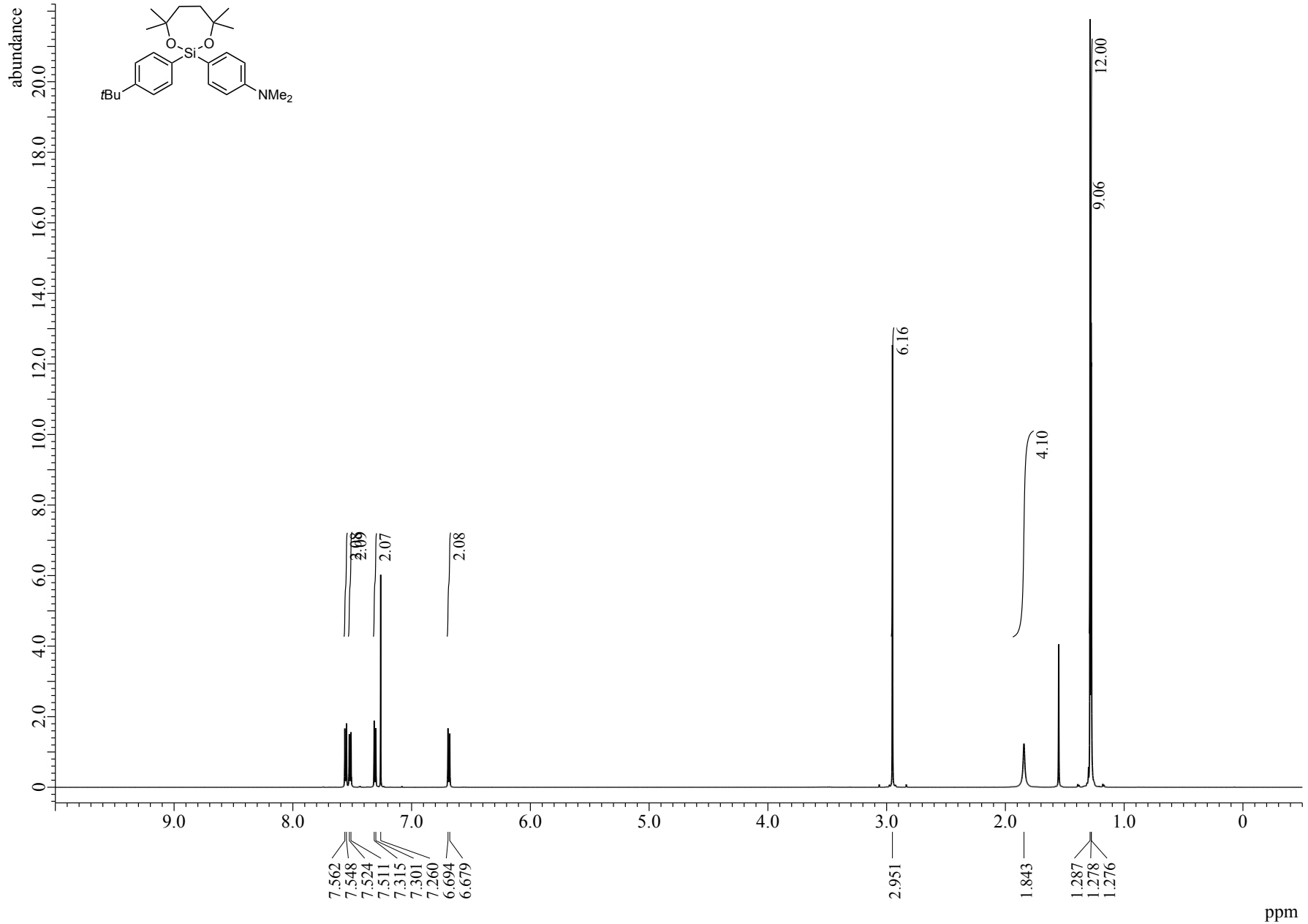


Figure S50. ^{1}H NMR (594 MHz, $CDCl_3$) spectrum of **3ag**

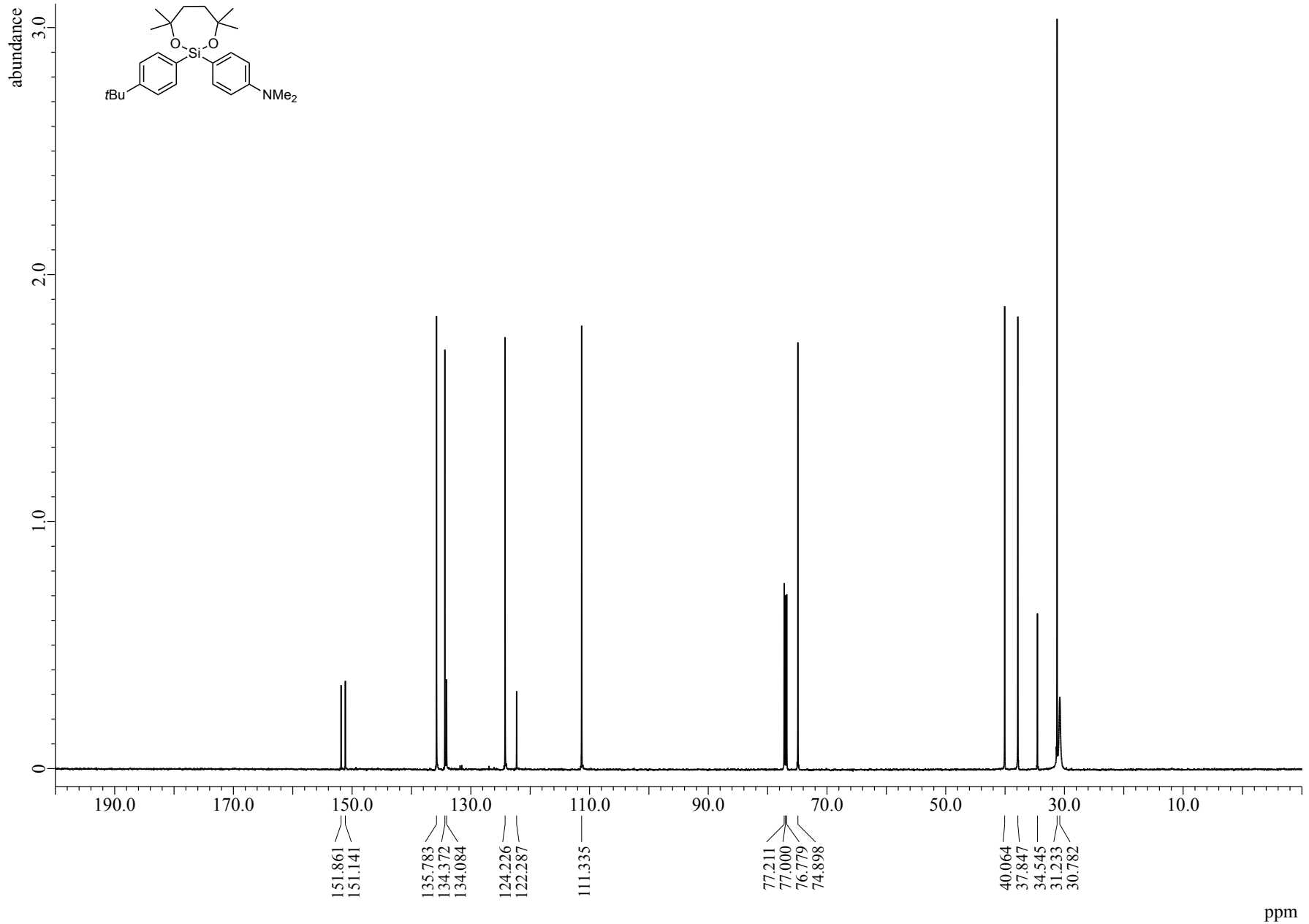


Figure S51. ^{13}C NMR (149 MHz, $CDCl_3$) spectrum of **3ag**

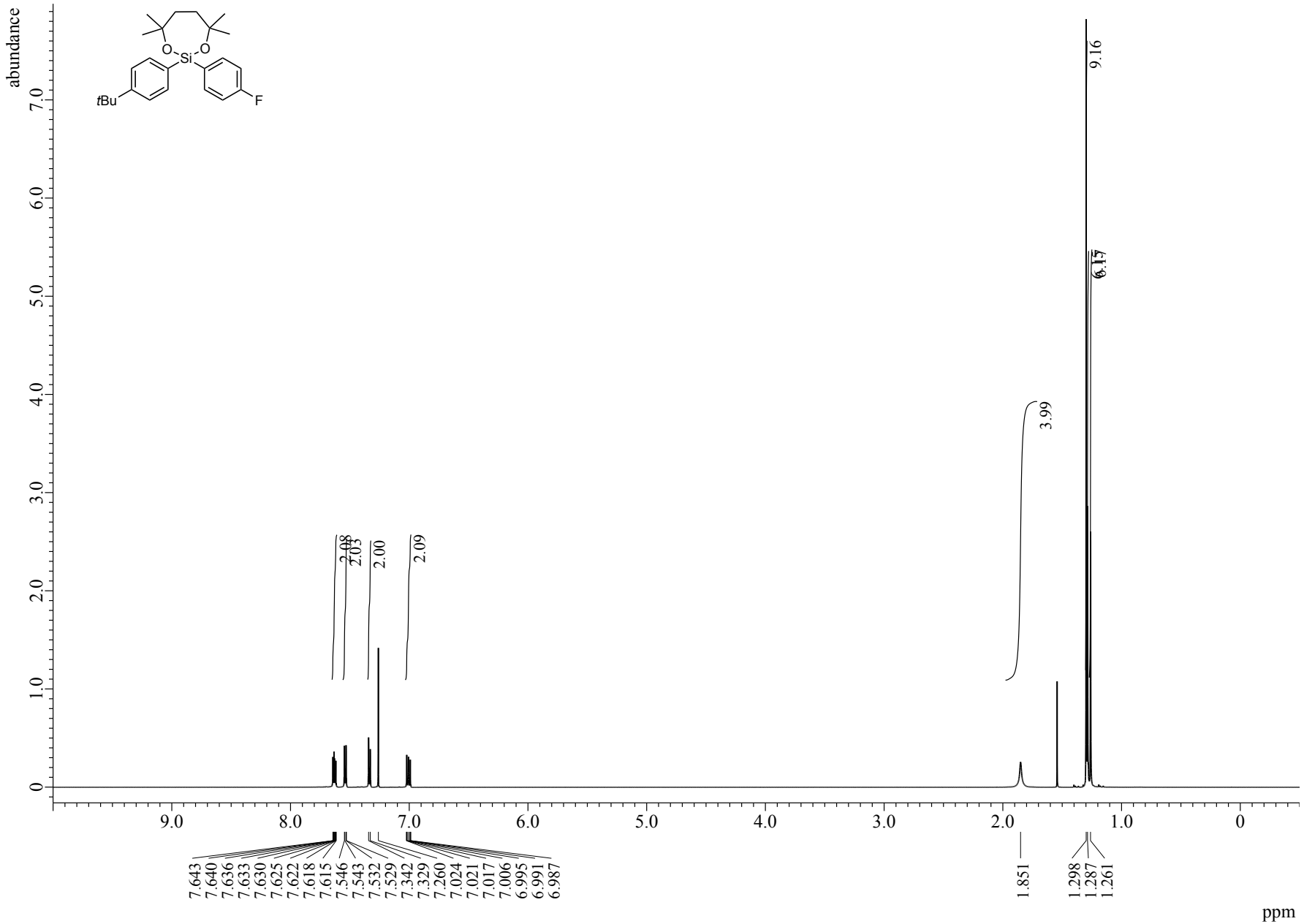


Figure S52. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ah**

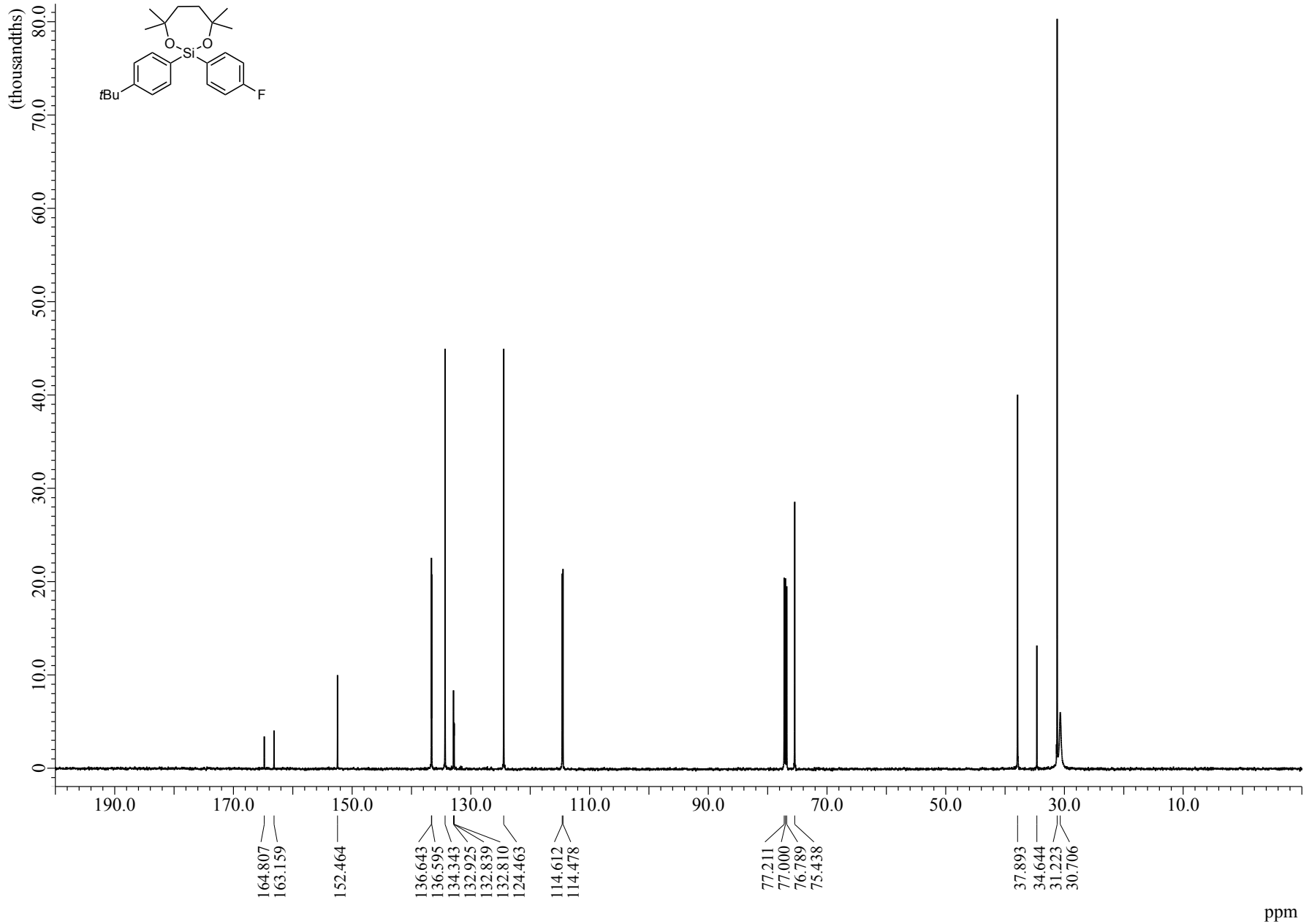


Figure S53. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ah**

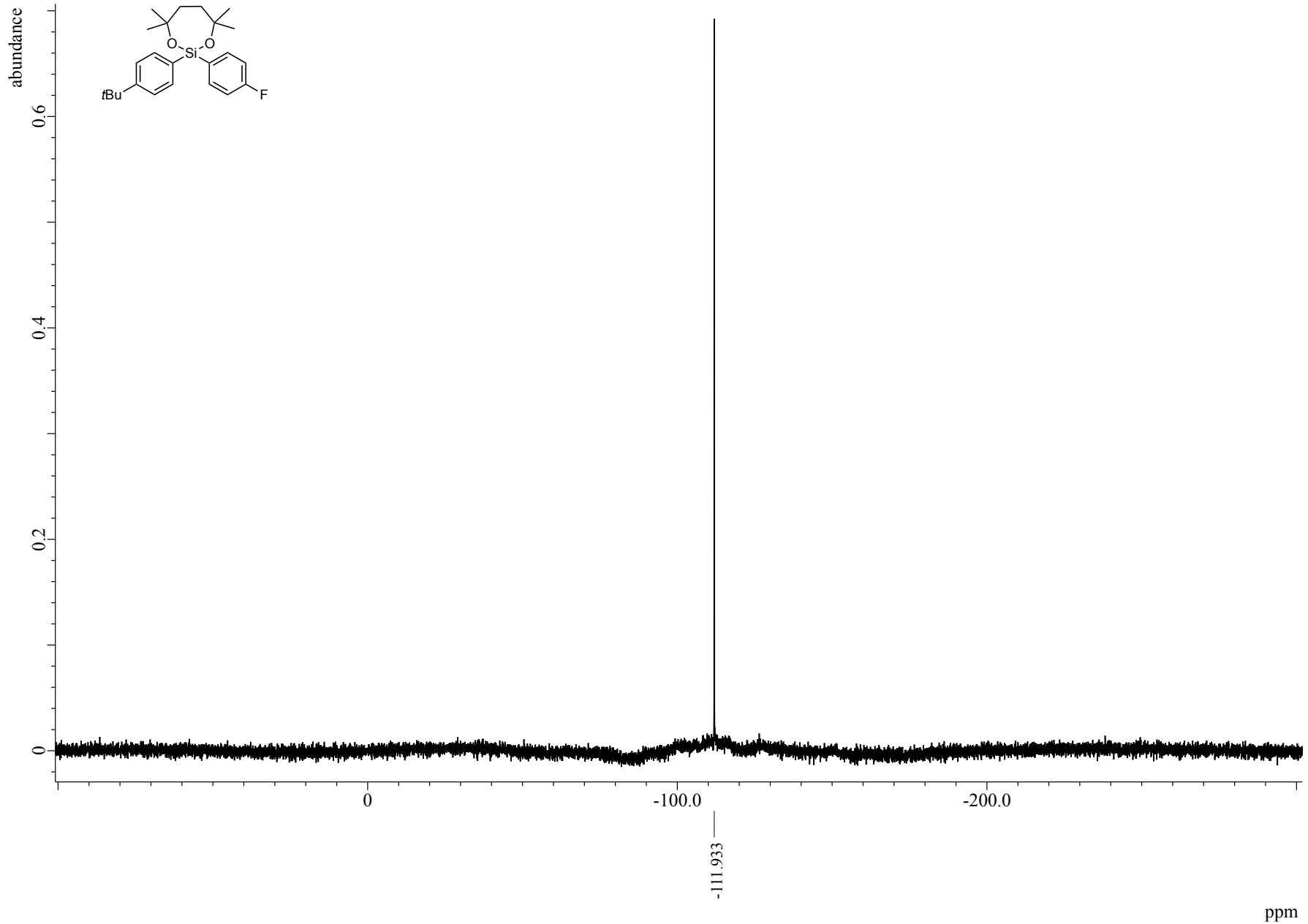


Figure S54. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3ah**

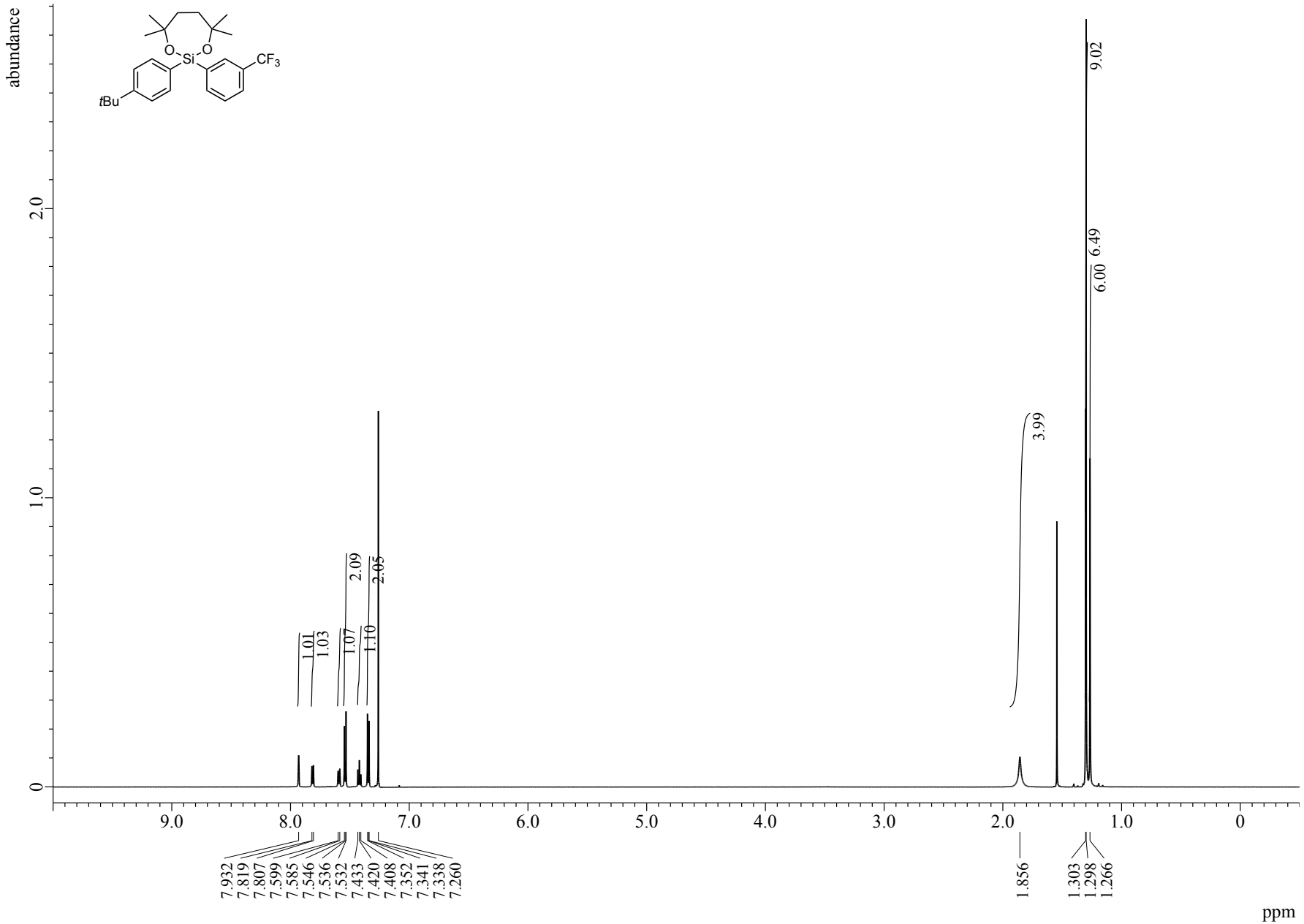


Figure S55. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ai**

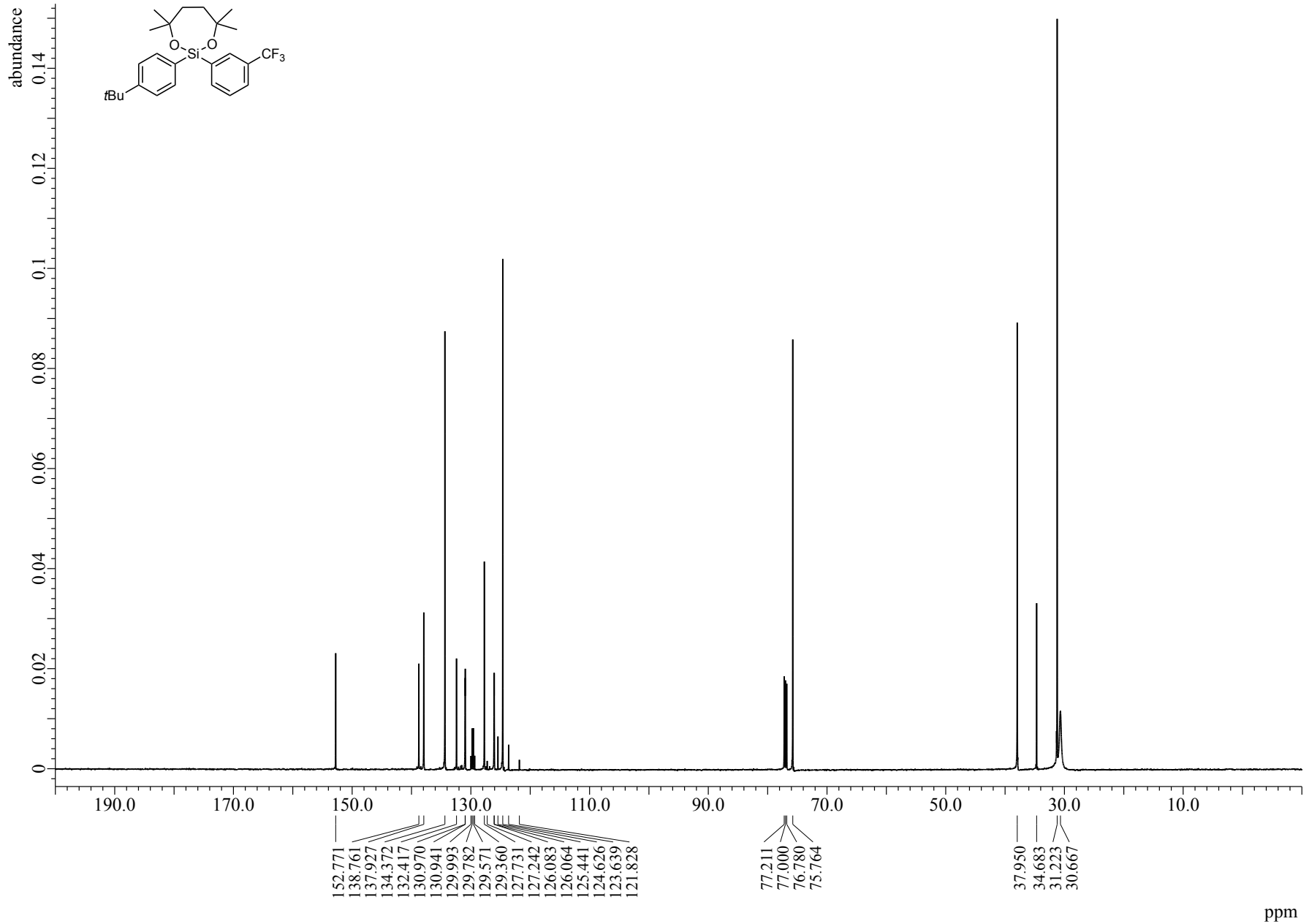


Figure S56. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ai**

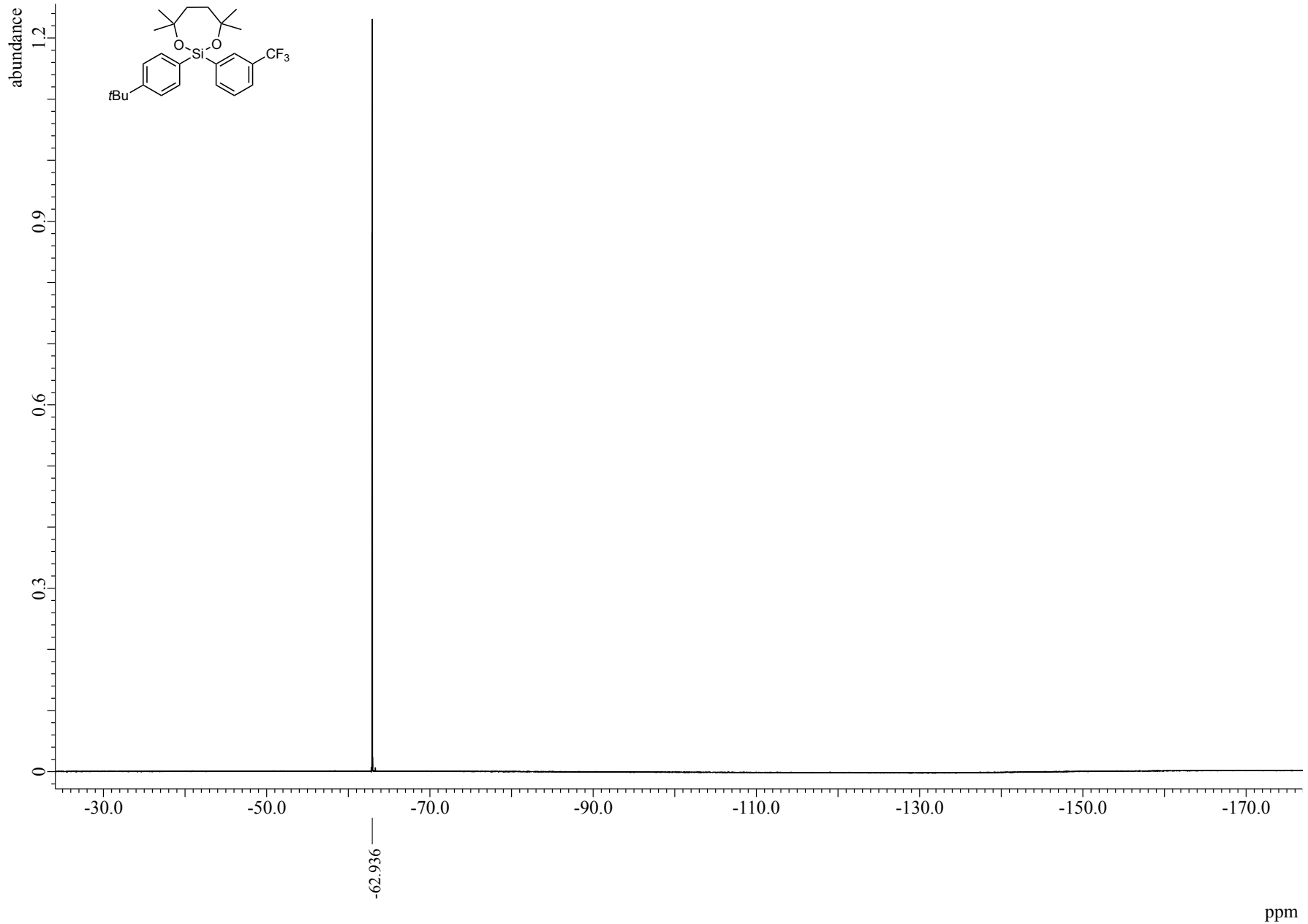


Figure S57. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3ai**

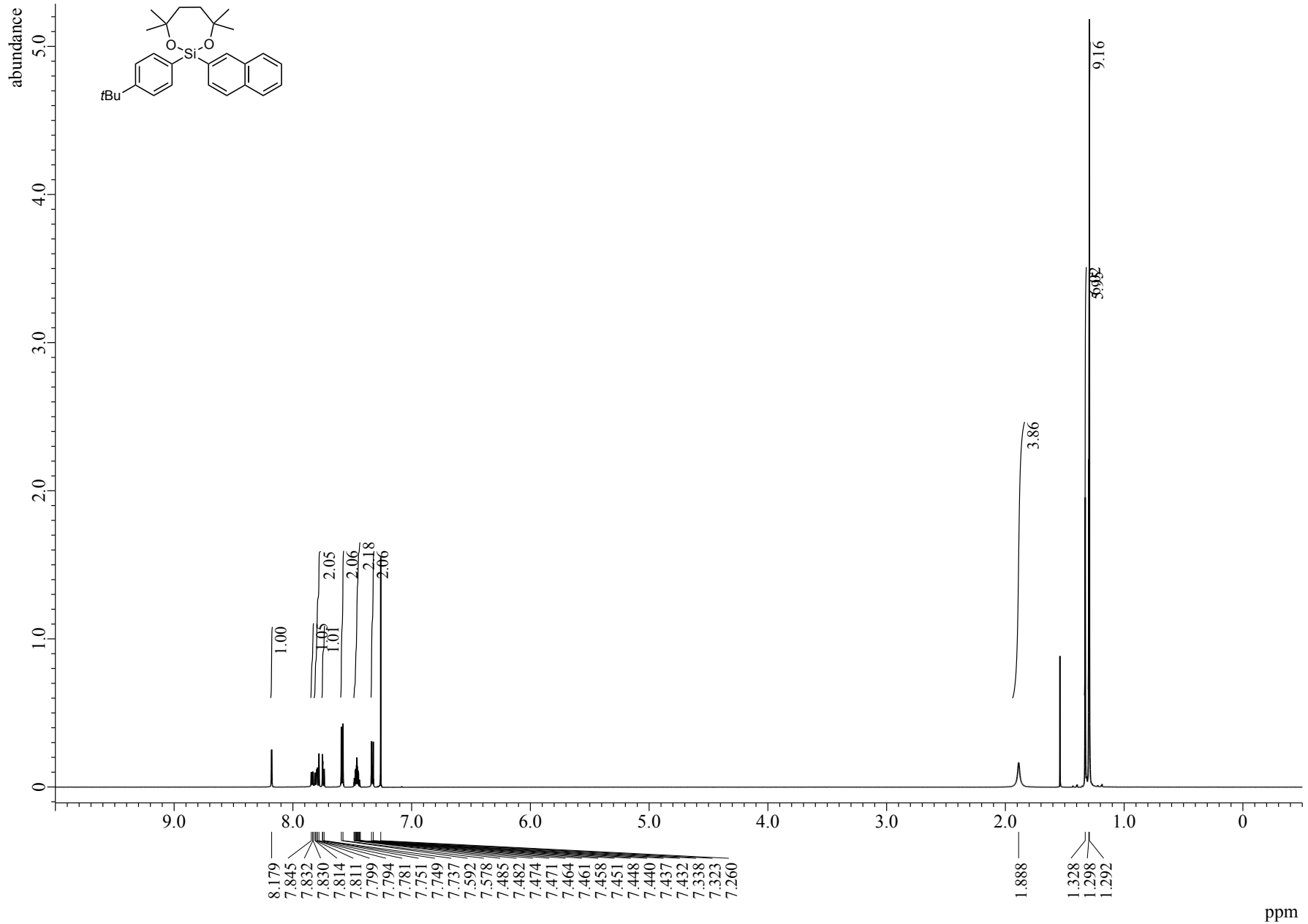


Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3aj**

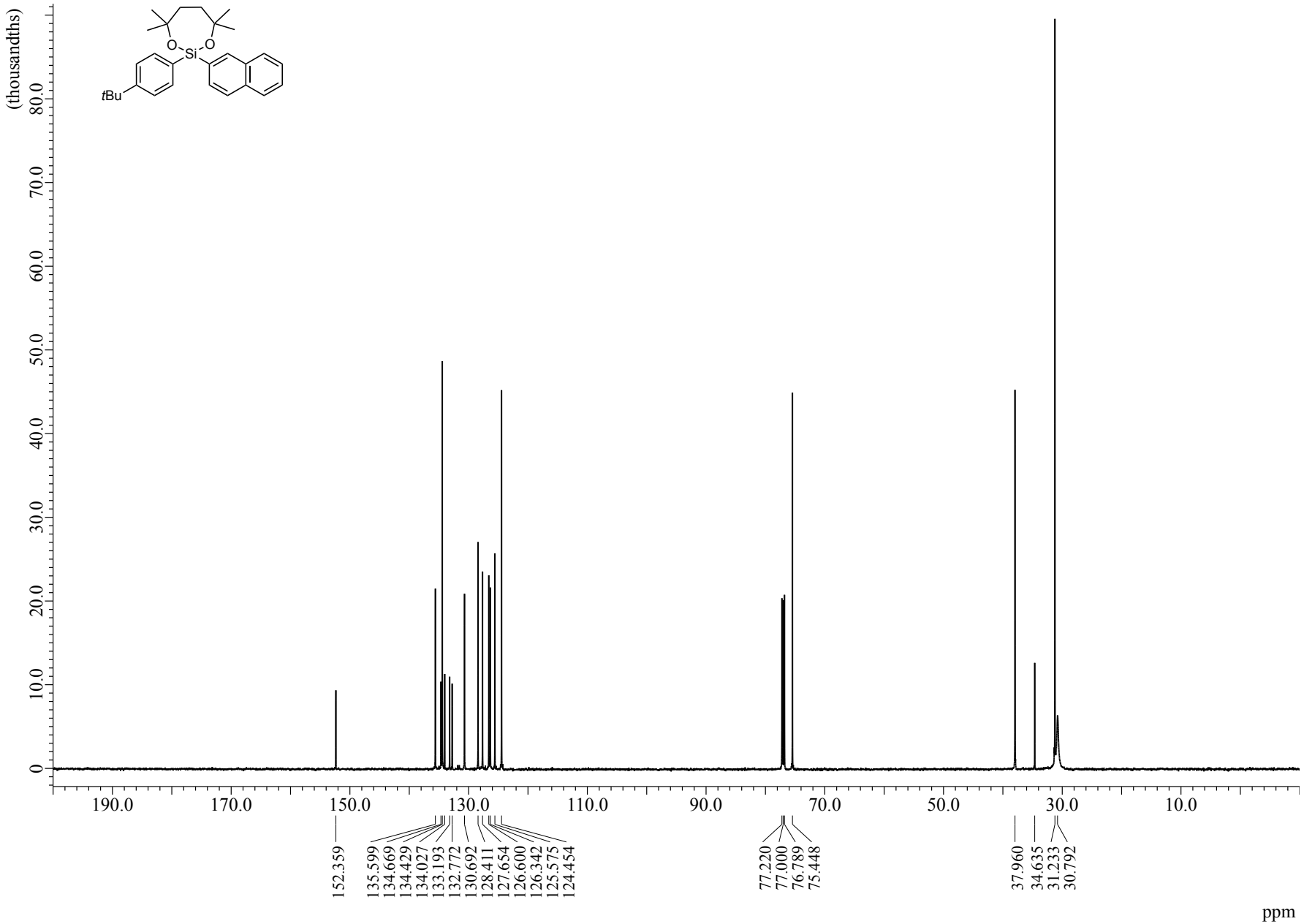


Figure S59. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3aj**

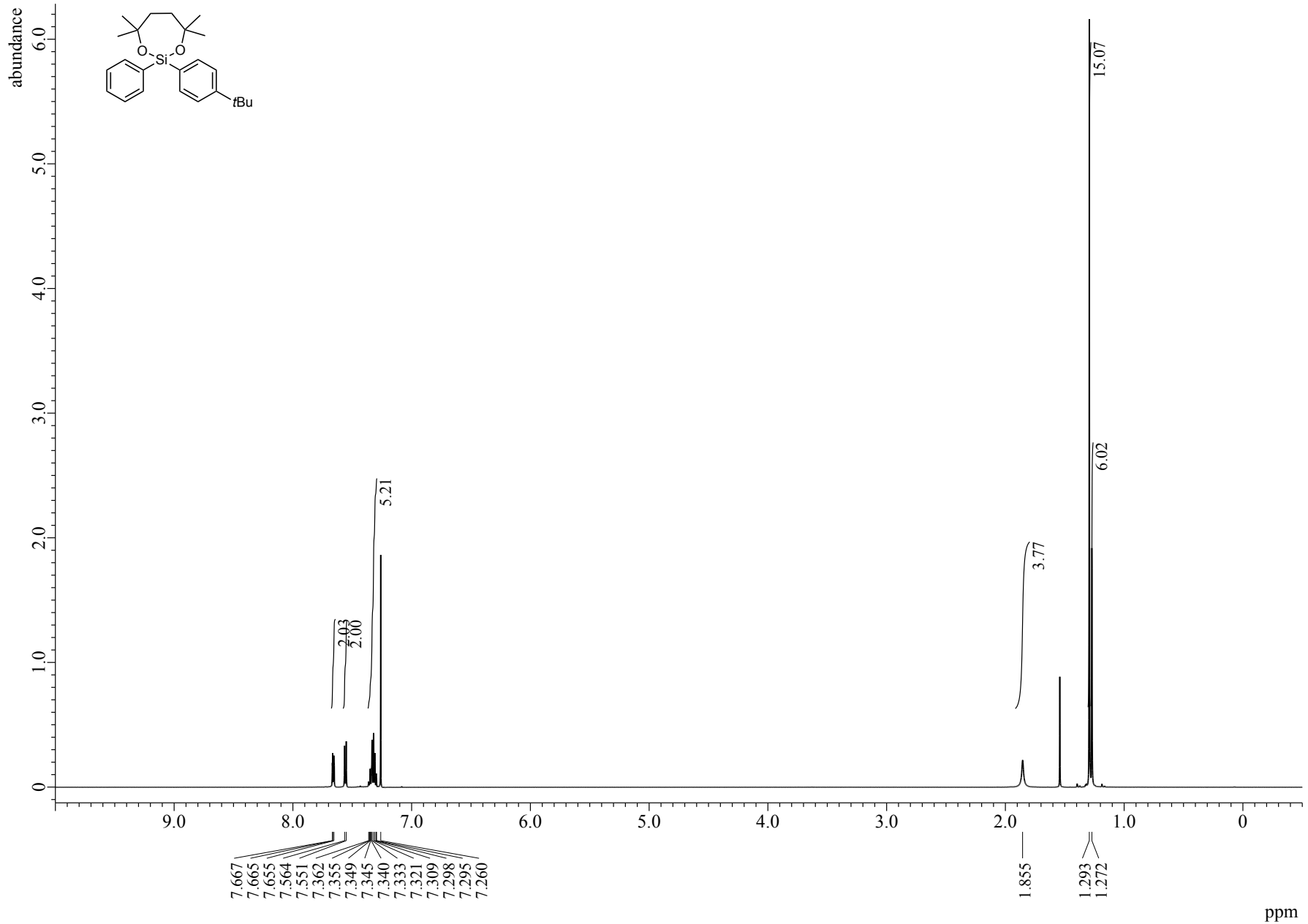


Figure S60. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ba**

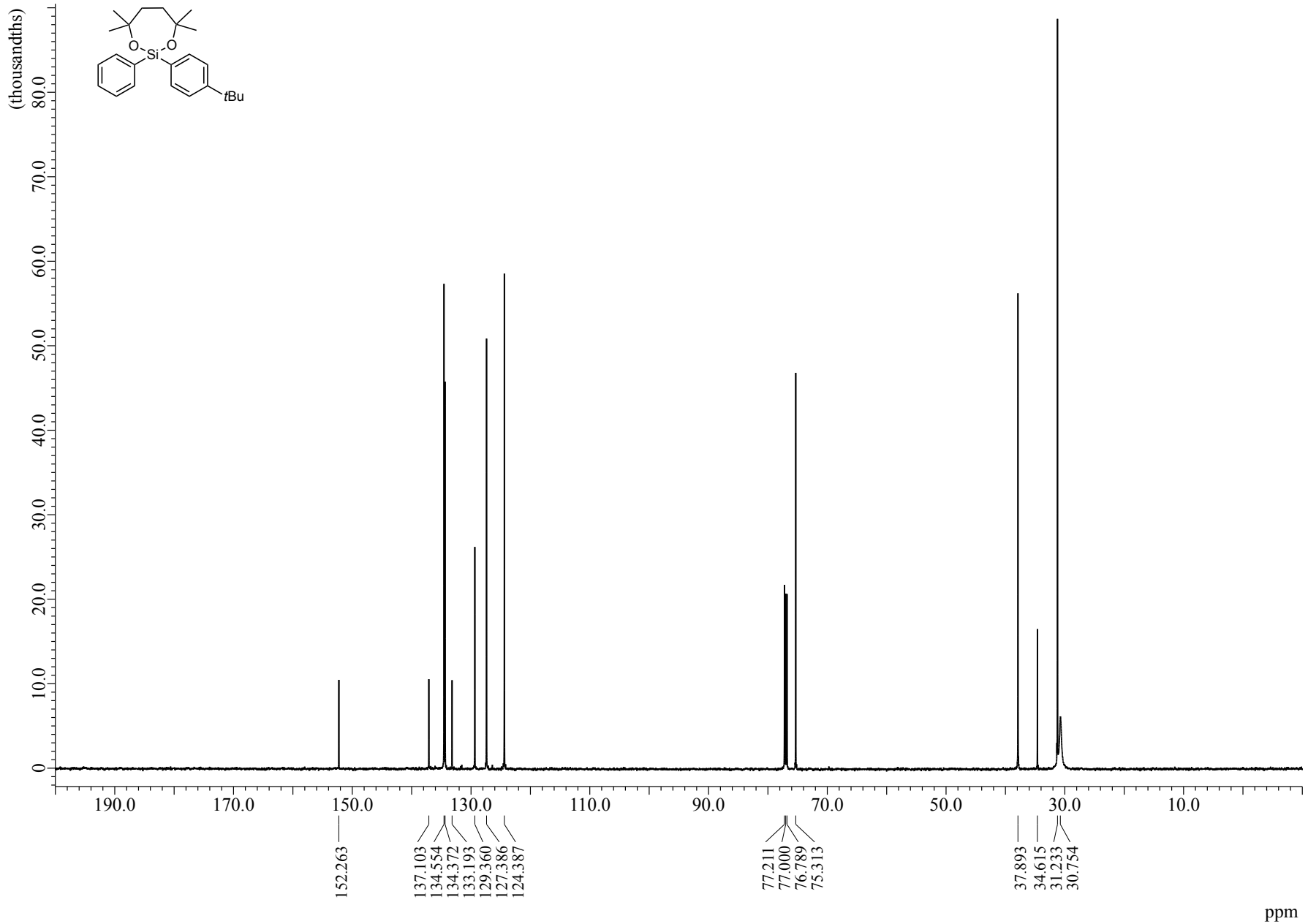


Figure S61. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ba**

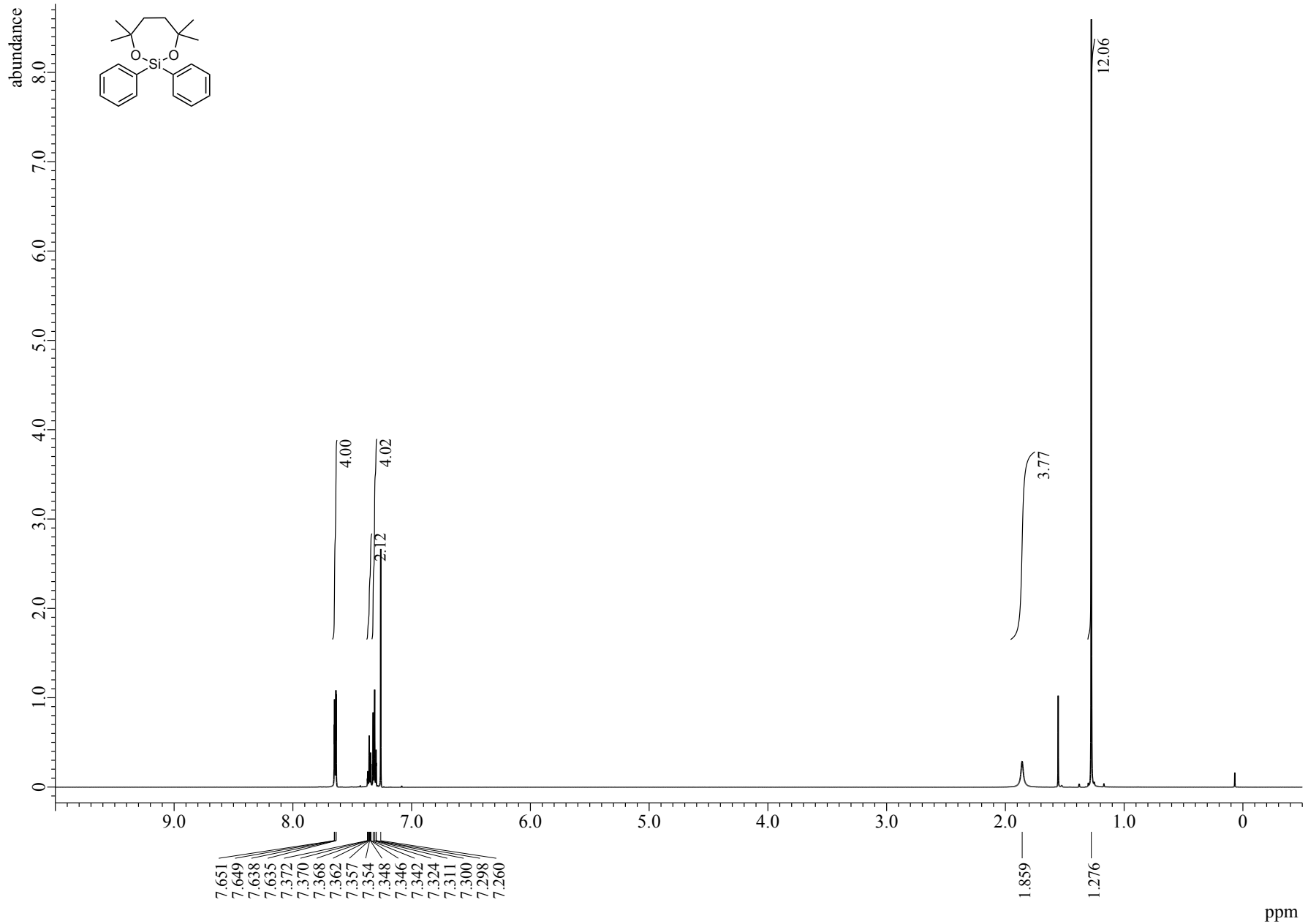


Figure S62. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bb**

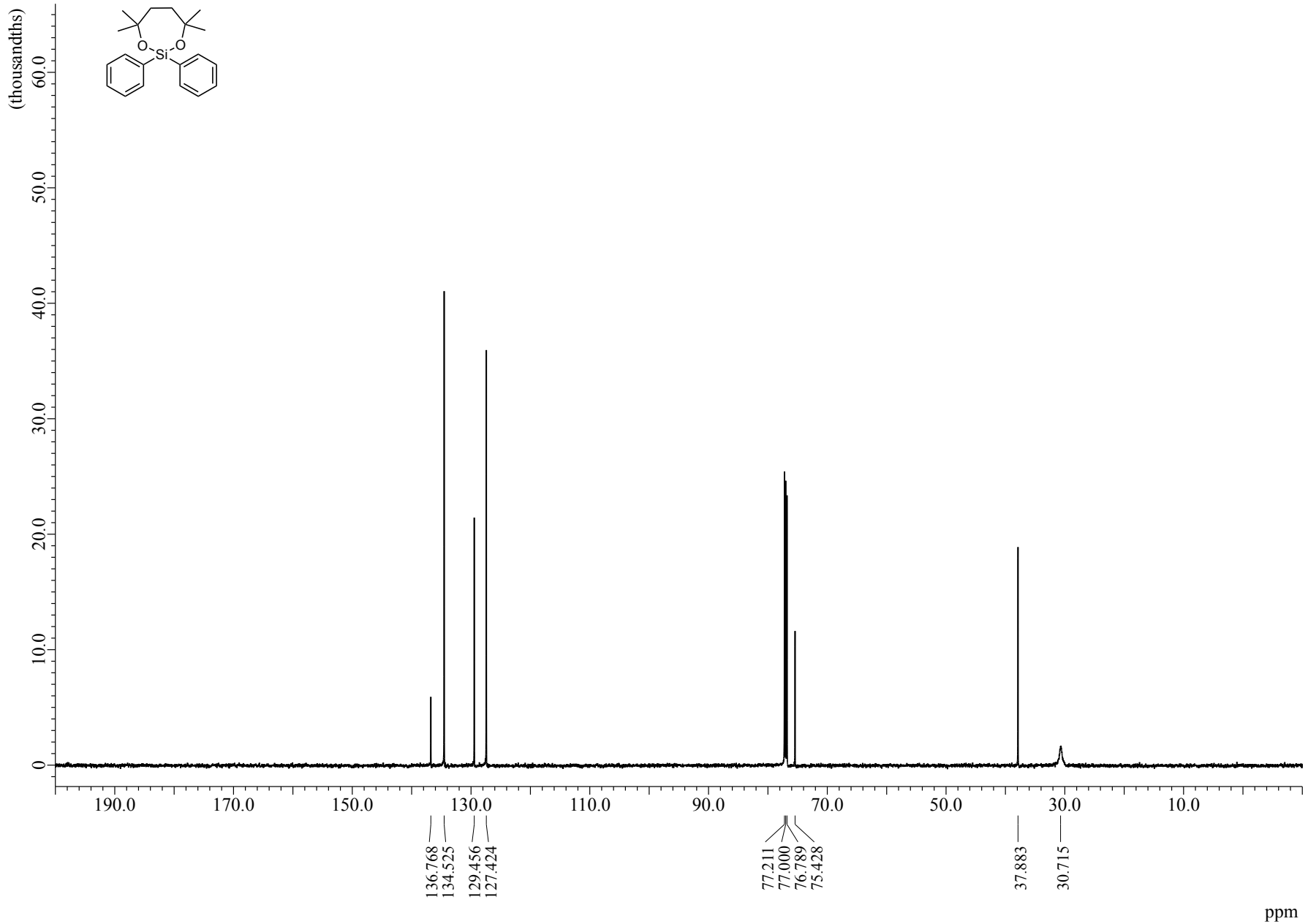


Figure S63. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bb**

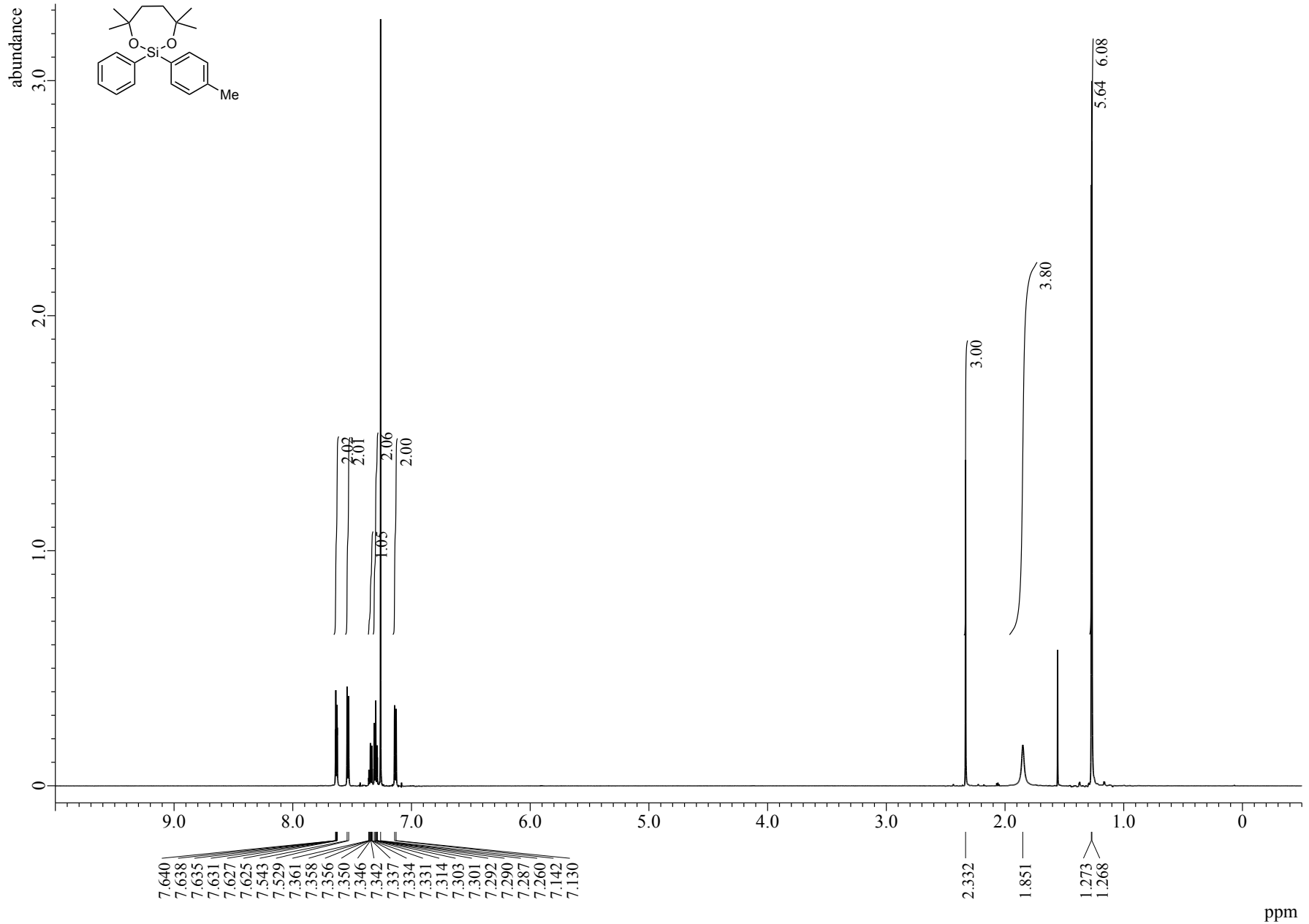


Figure S64. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bc**

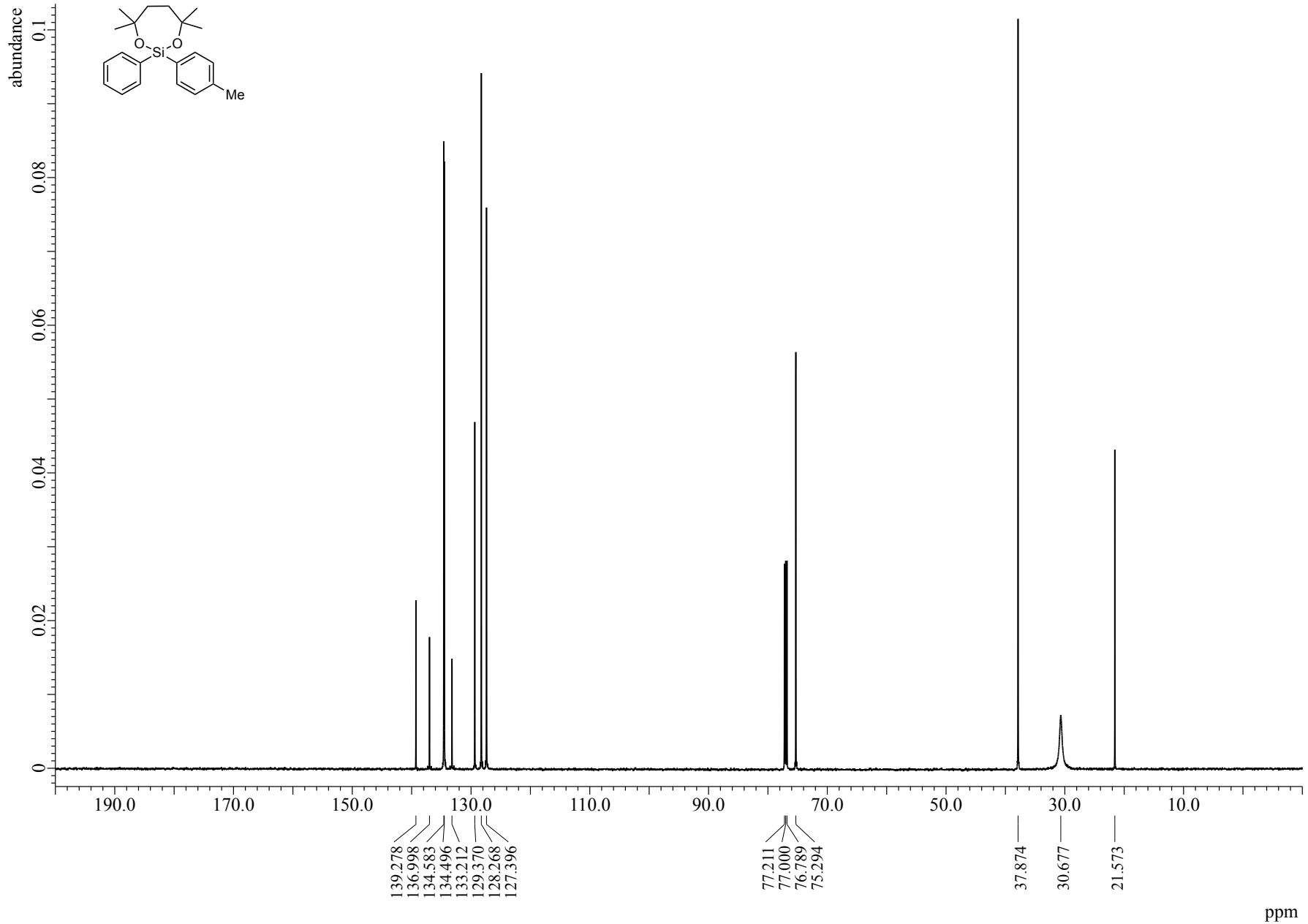


Figure S65. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bc**

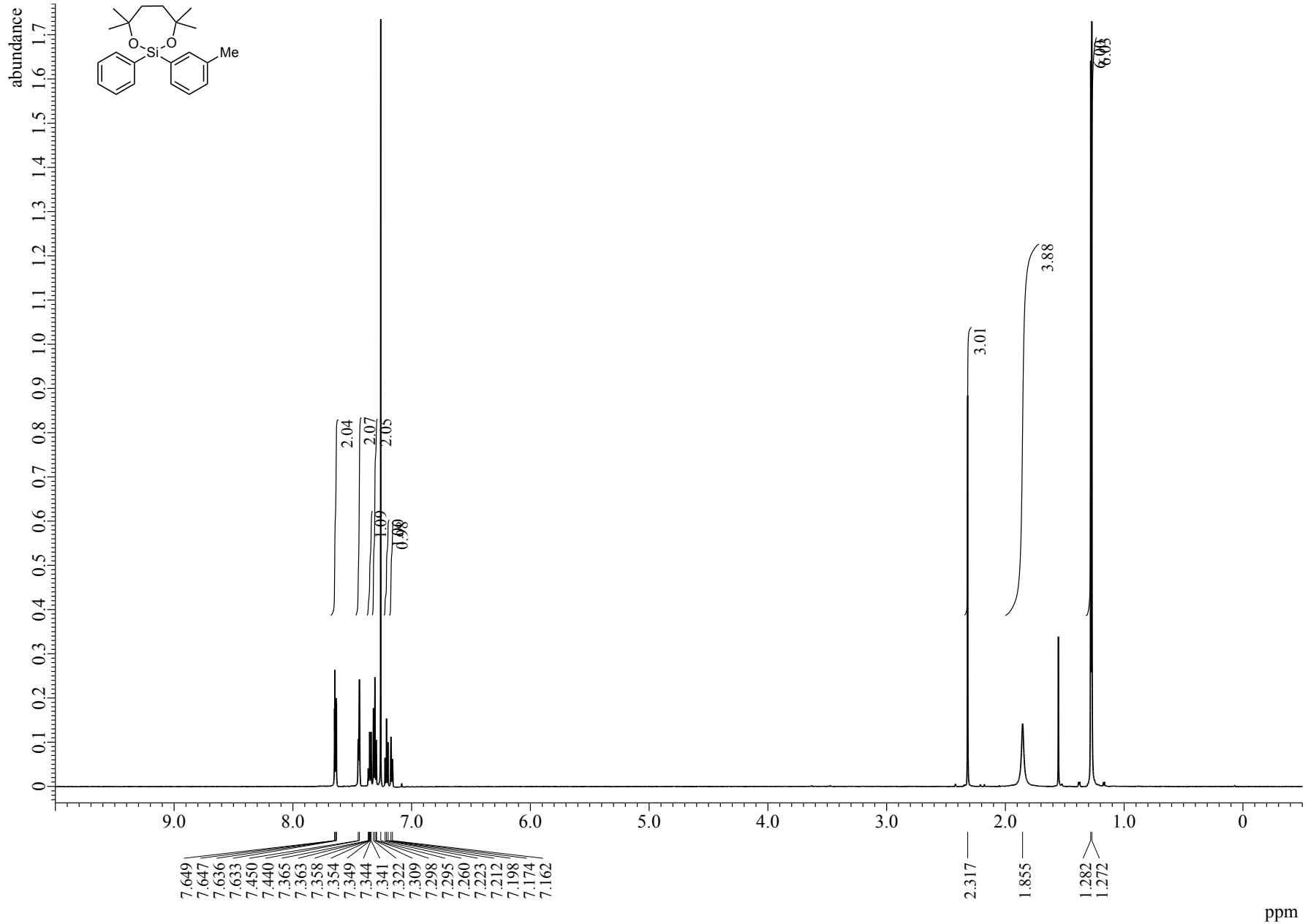


Figure S66. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bd**

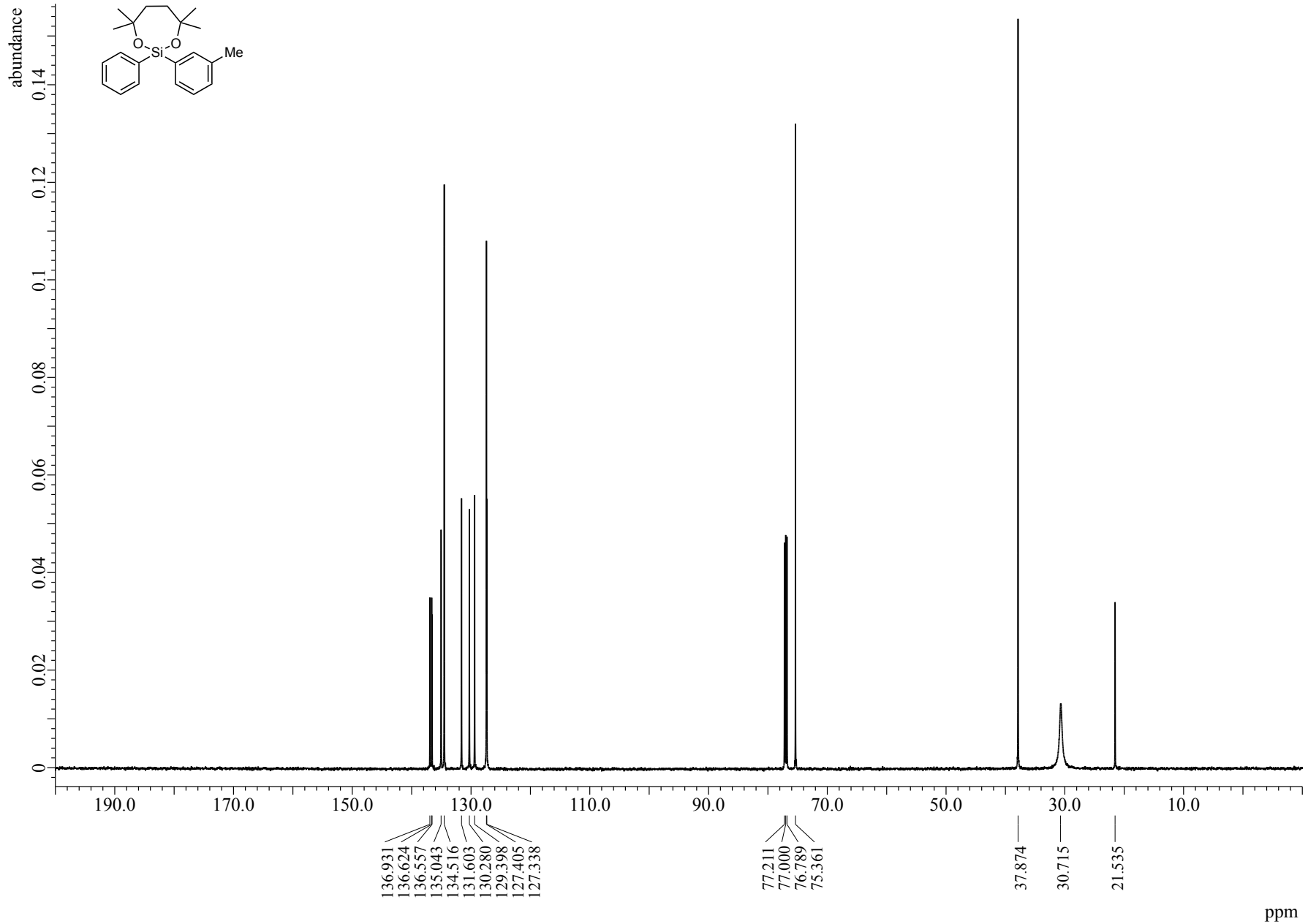


Figure S67. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bd**

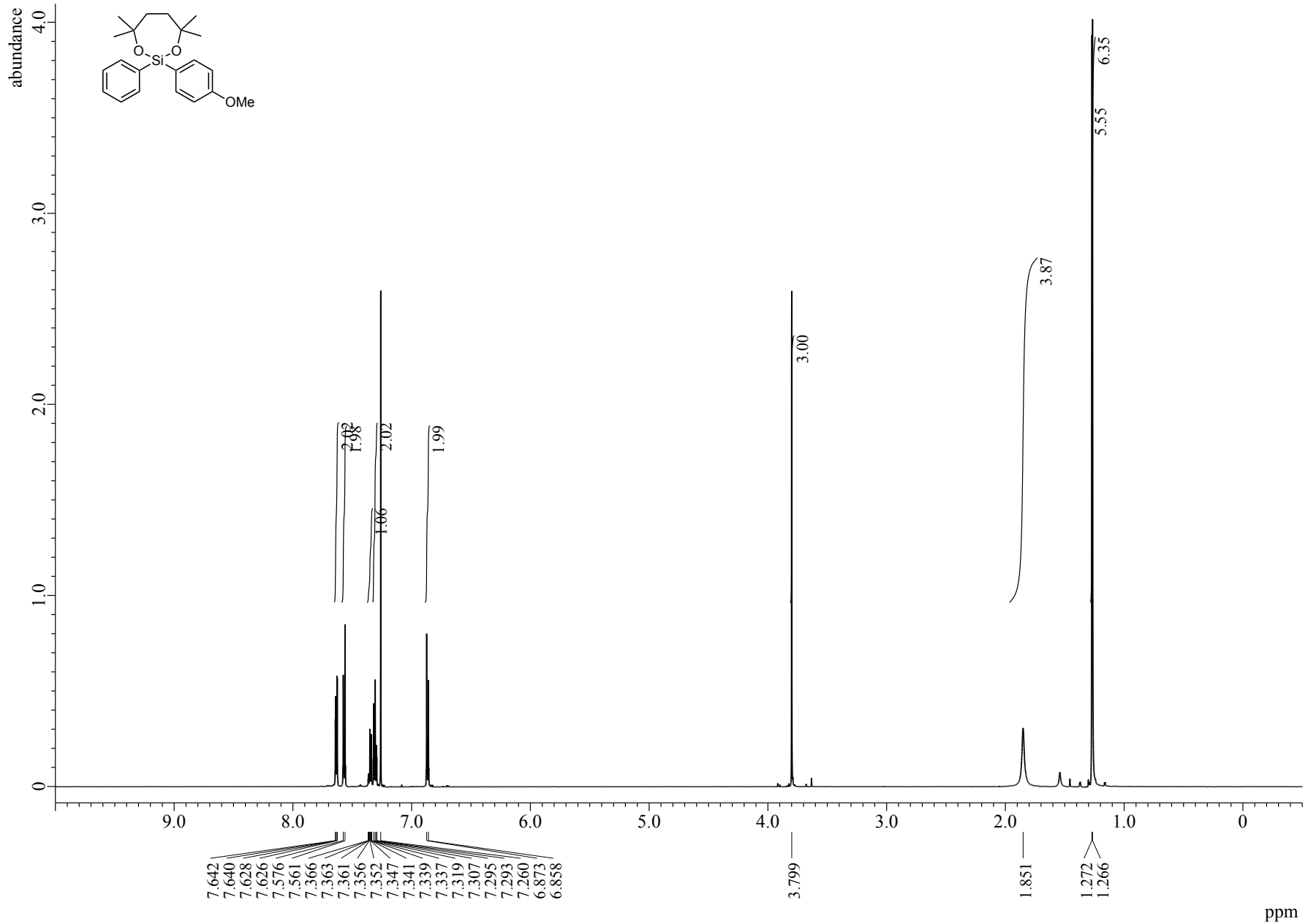


Figure S68. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3be**

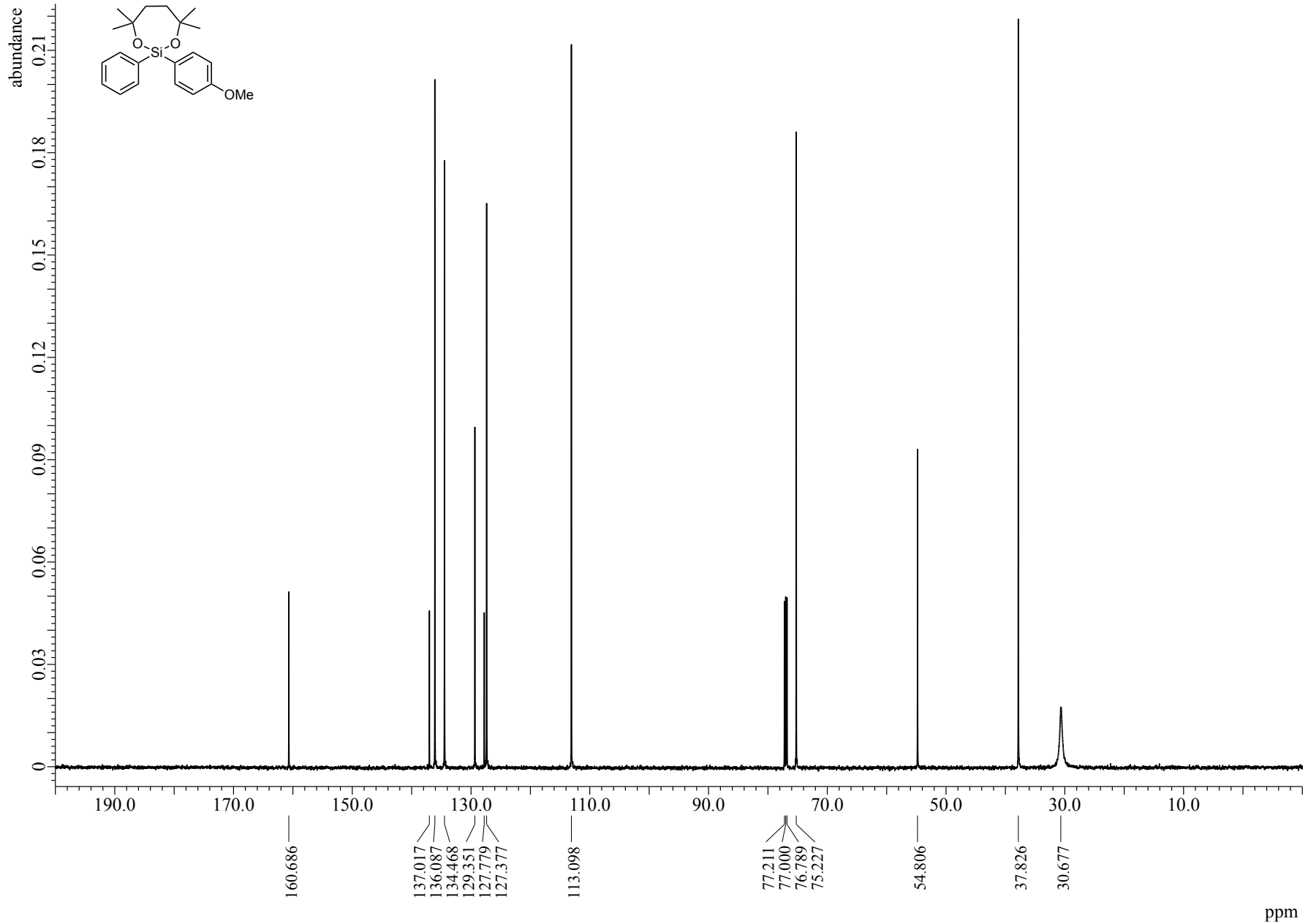


Figure S69. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3be**

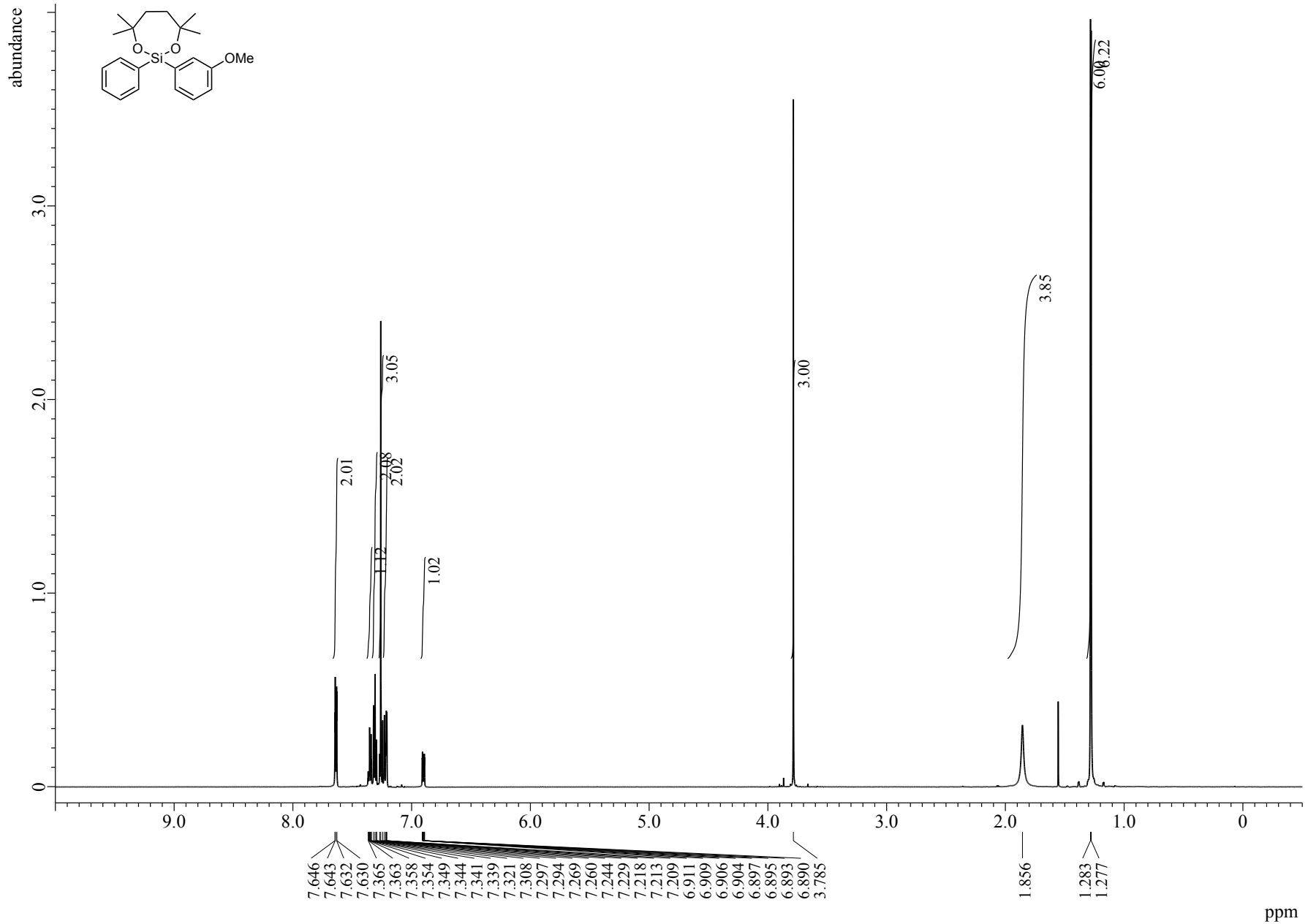


Figure S70. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bf**

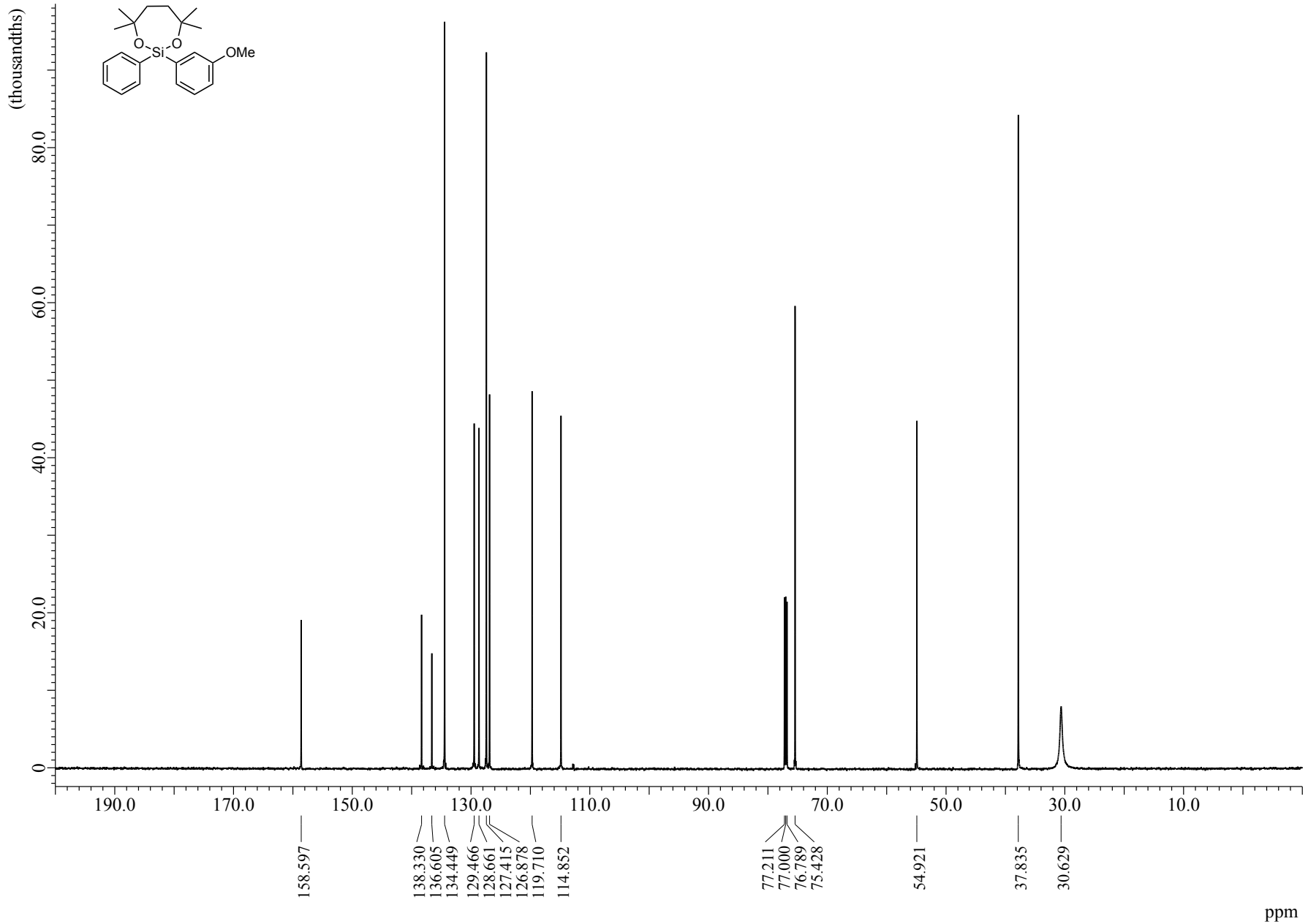


Figure S71. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bf**

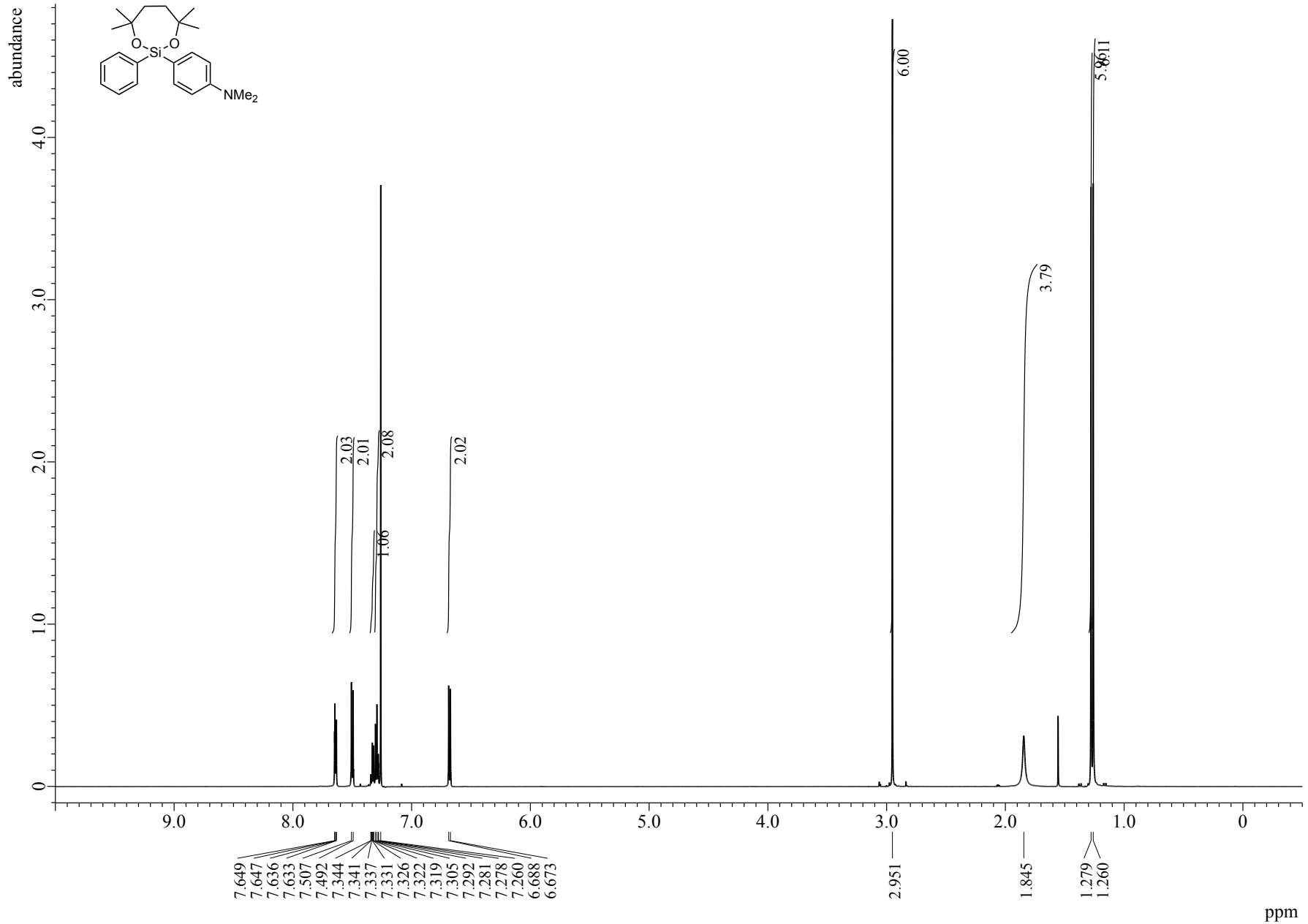


Figure S72. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bg**

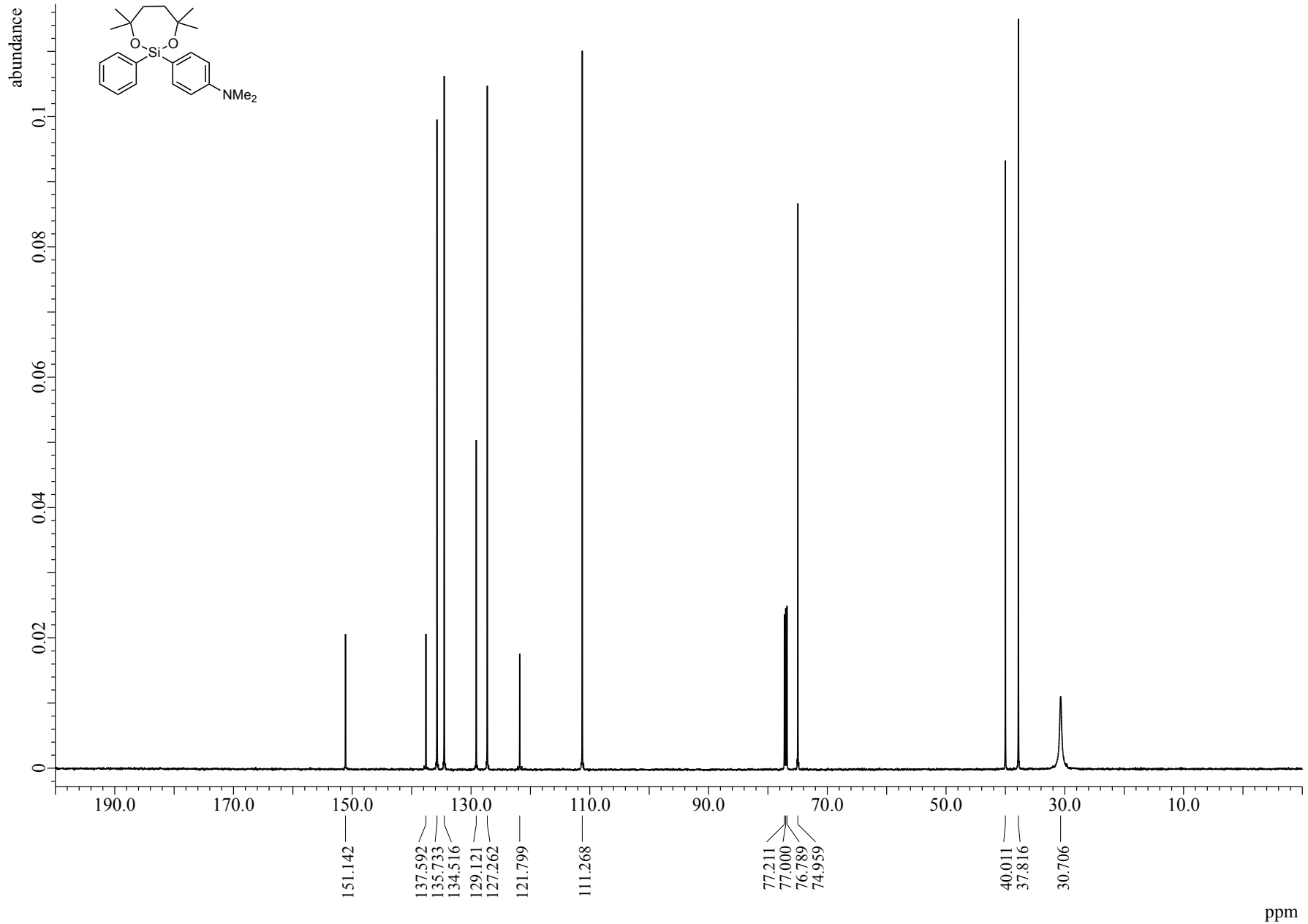


Figure S73. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bg**

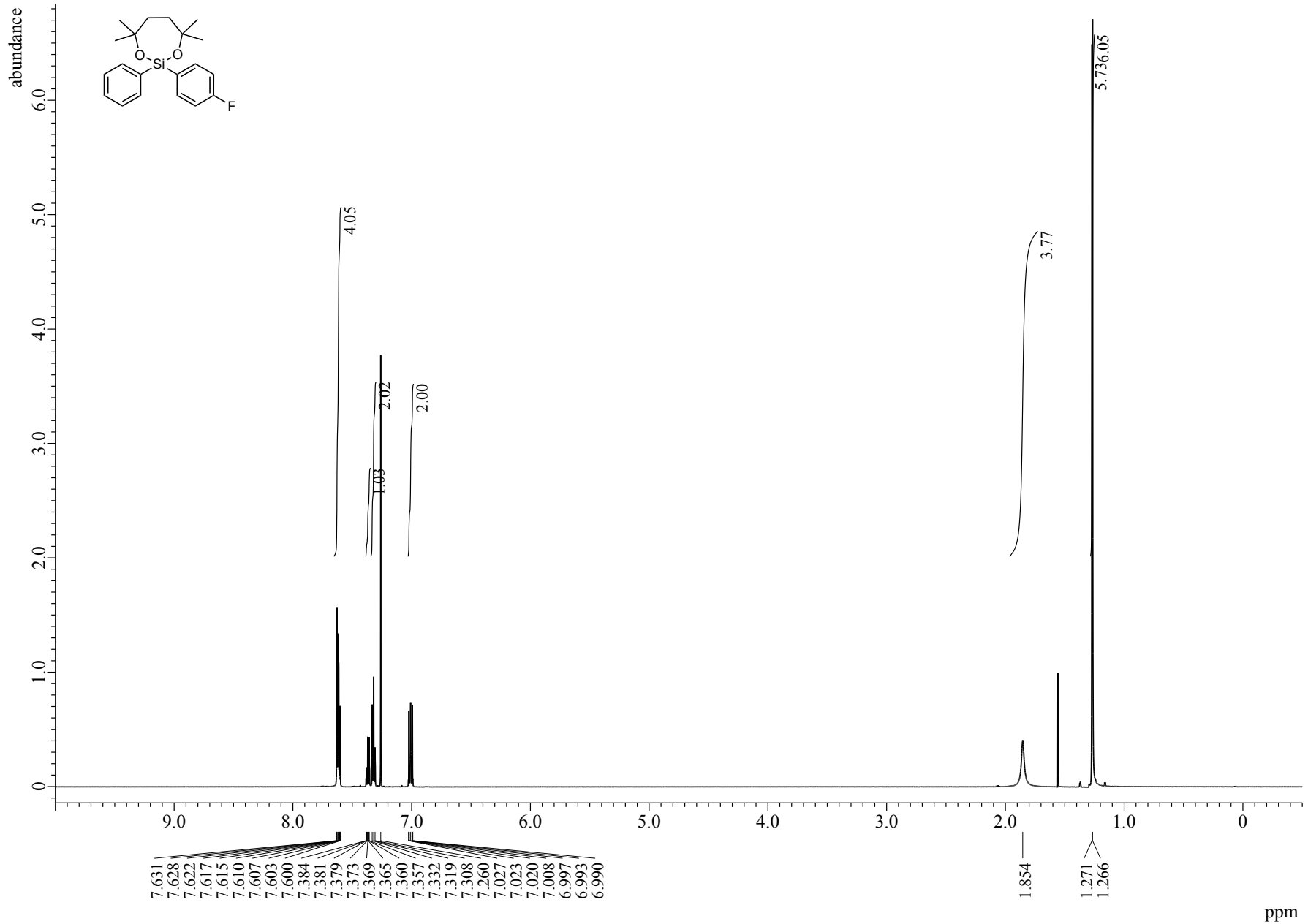


Figure S74. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bh**

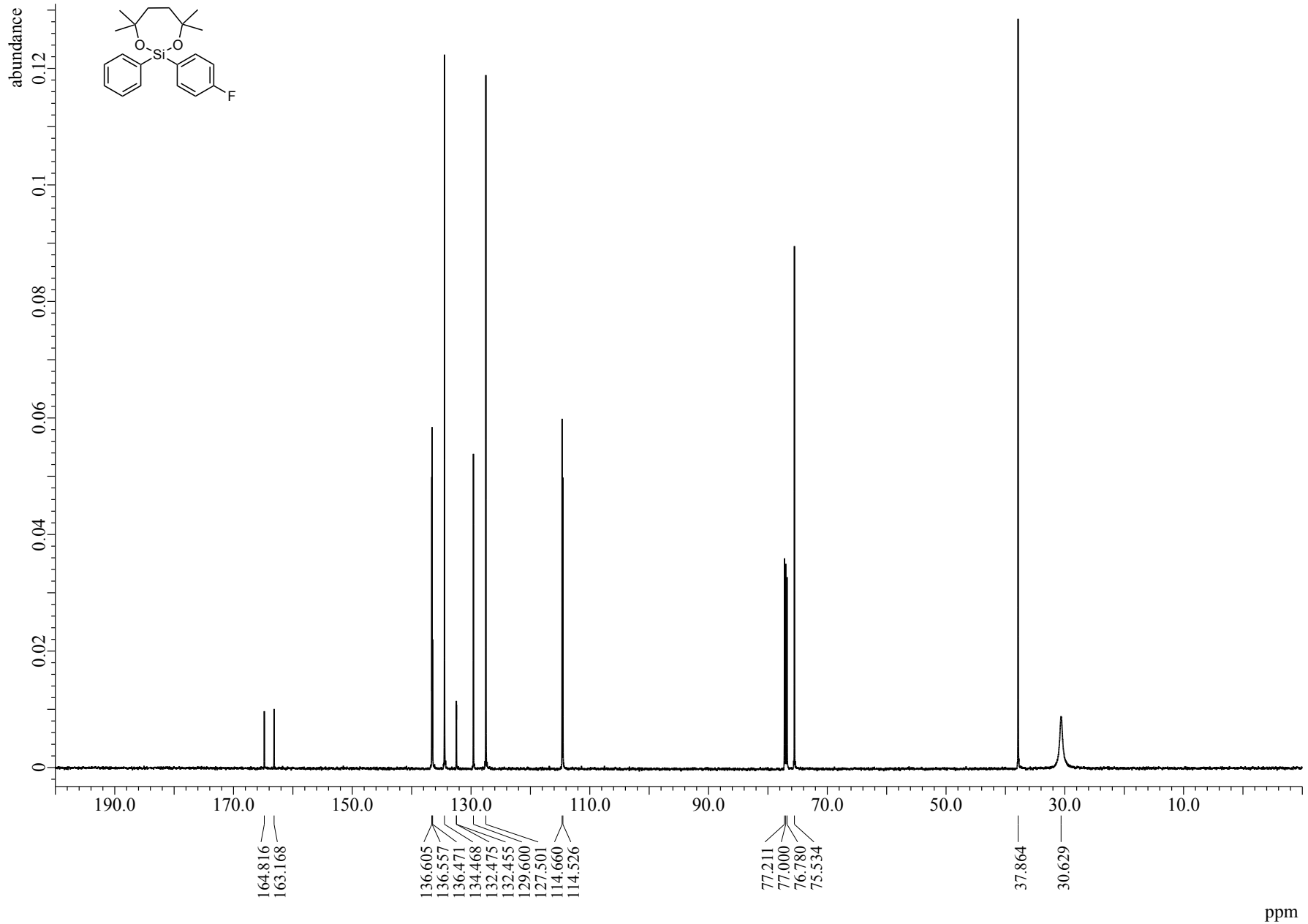


Figure S75. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bh**

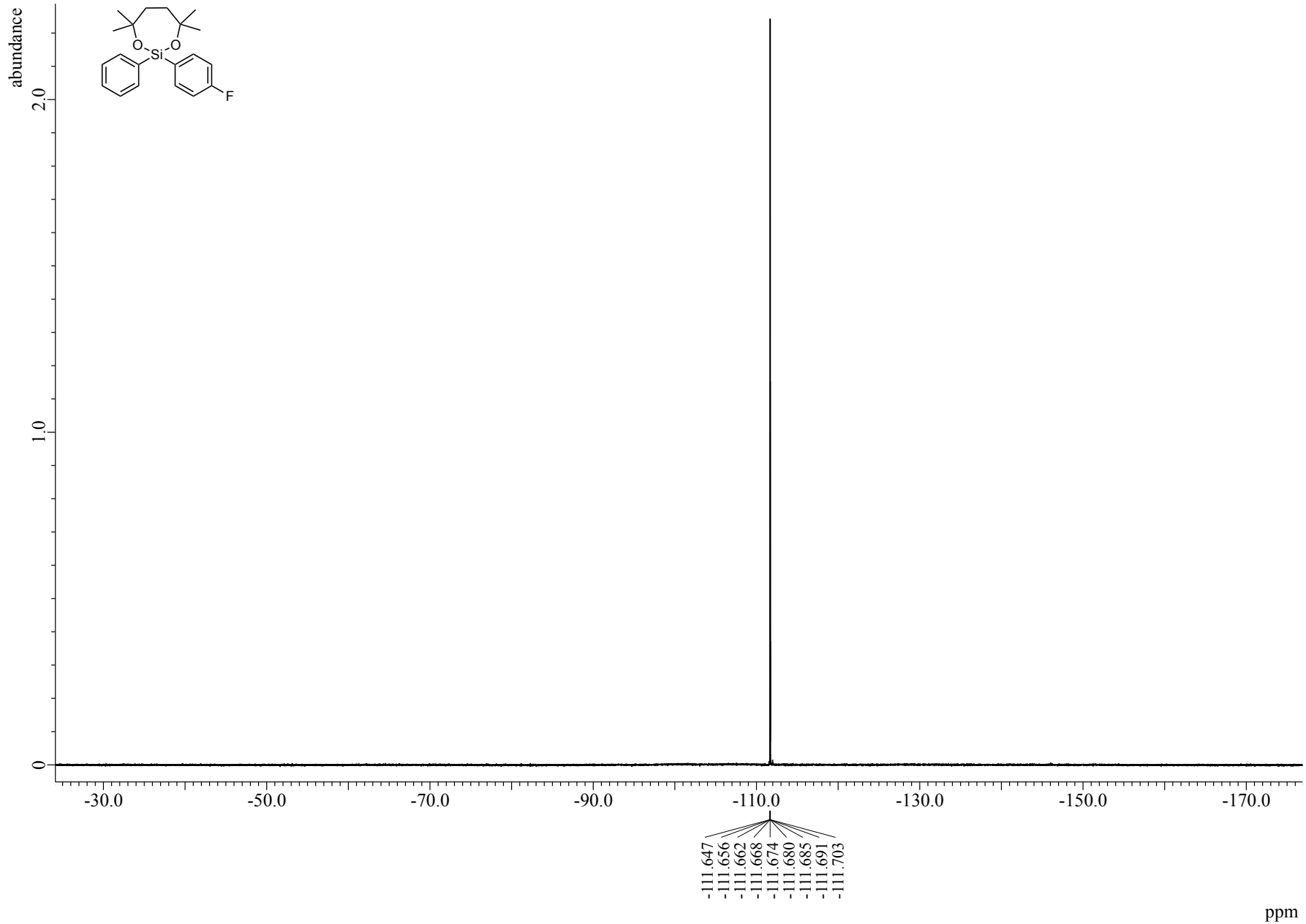


Figure S76. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3bh**

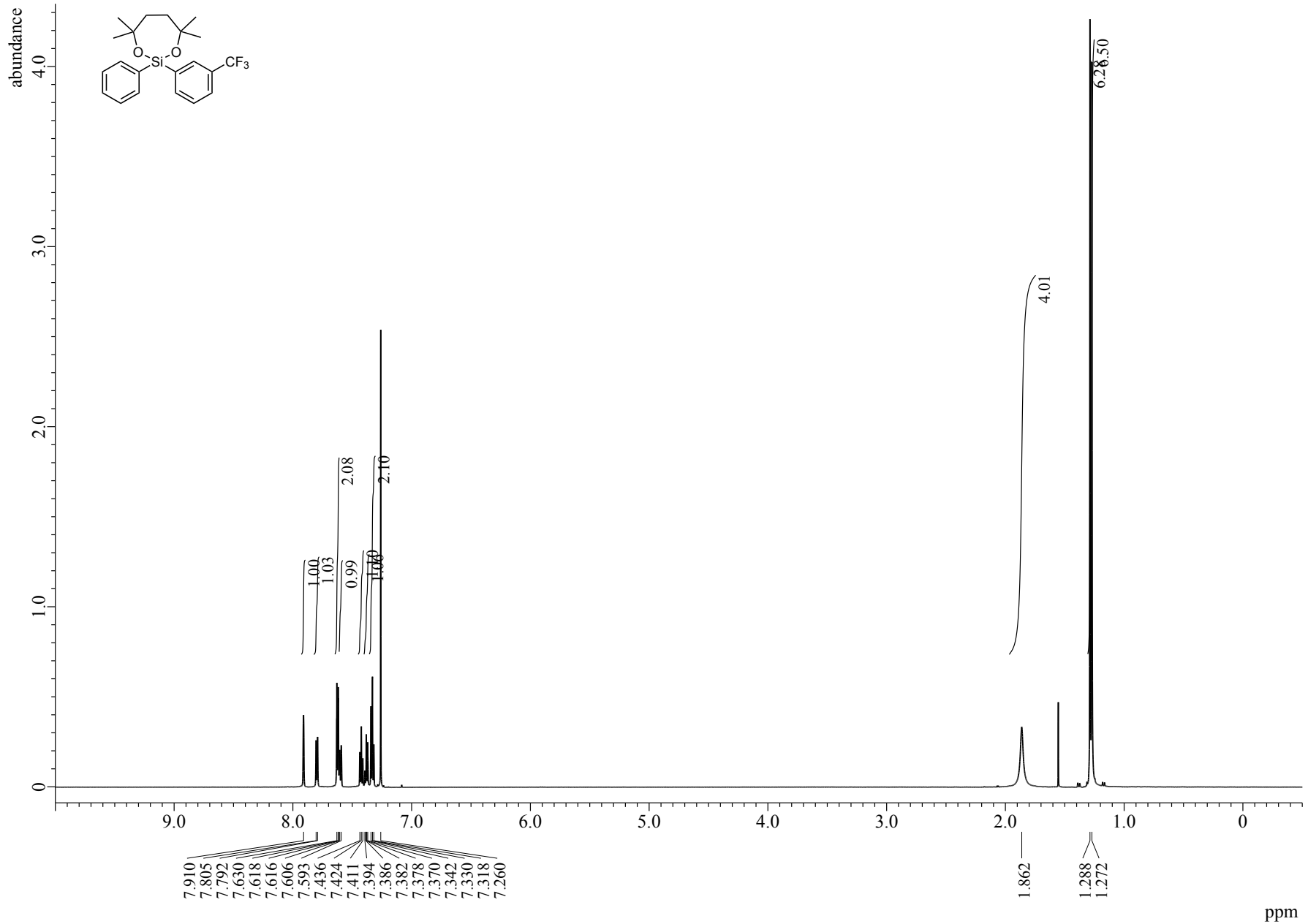


Figure S77. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bi**

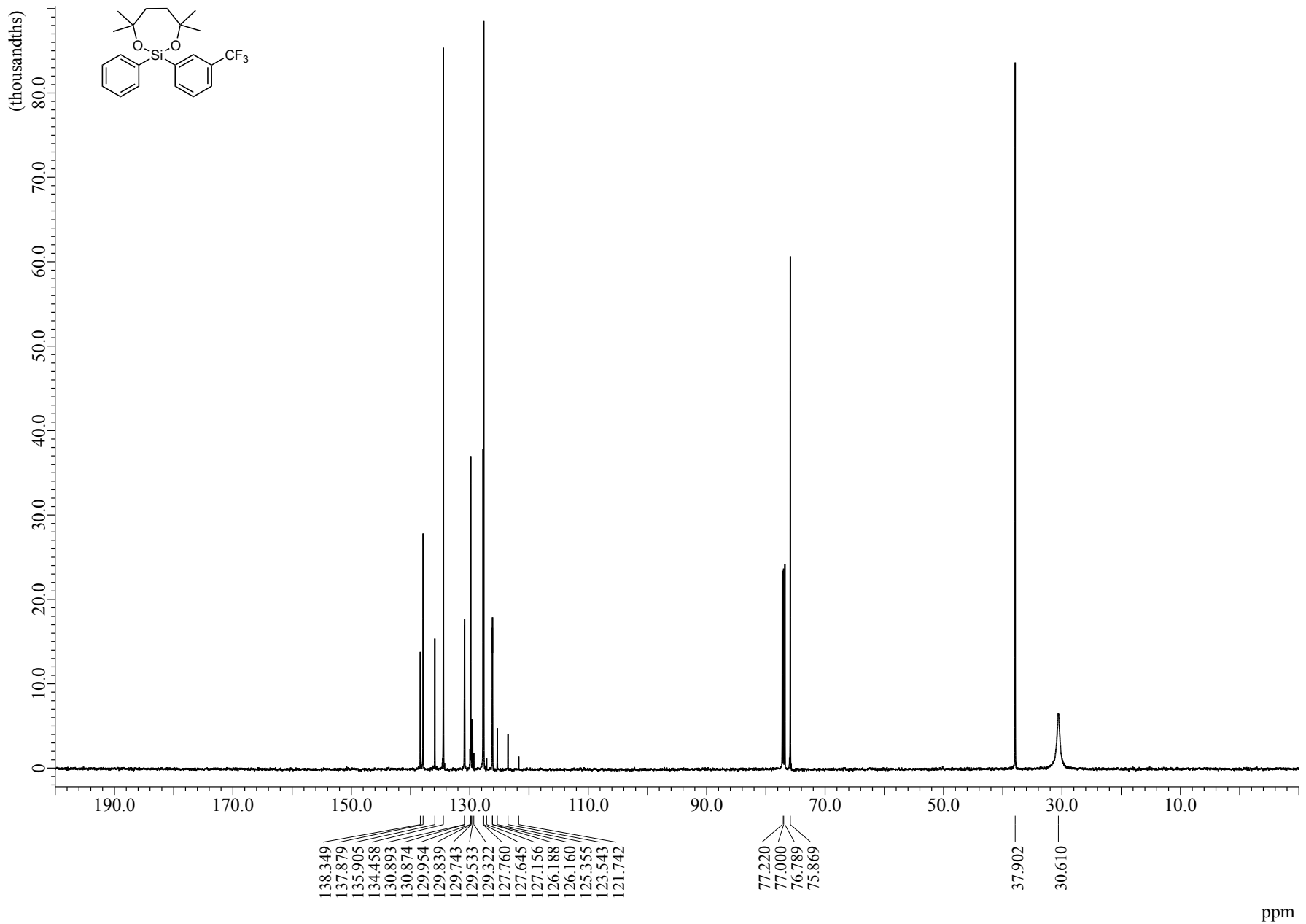


Figure S78. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bi**

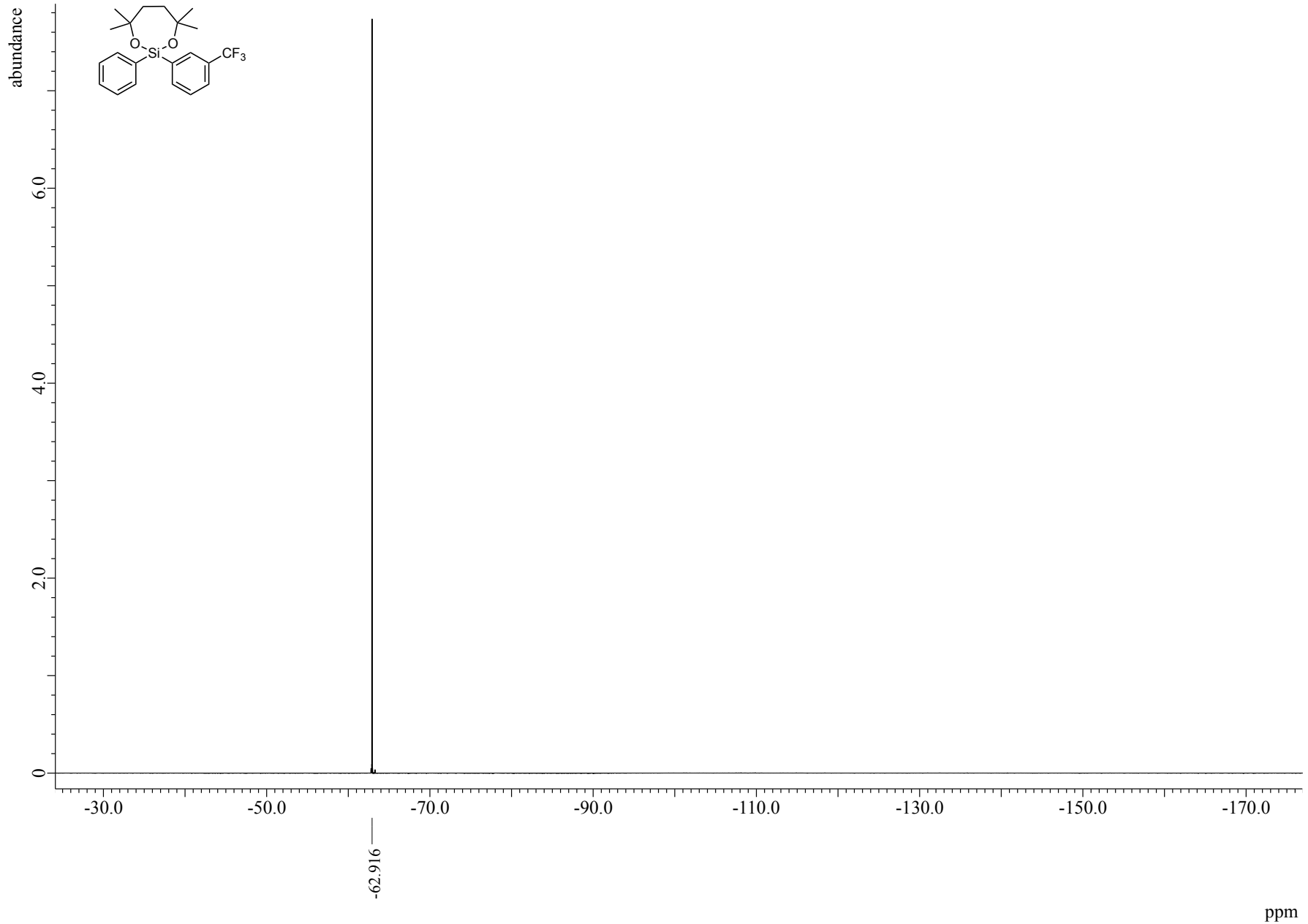


Figure S79. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3bi**

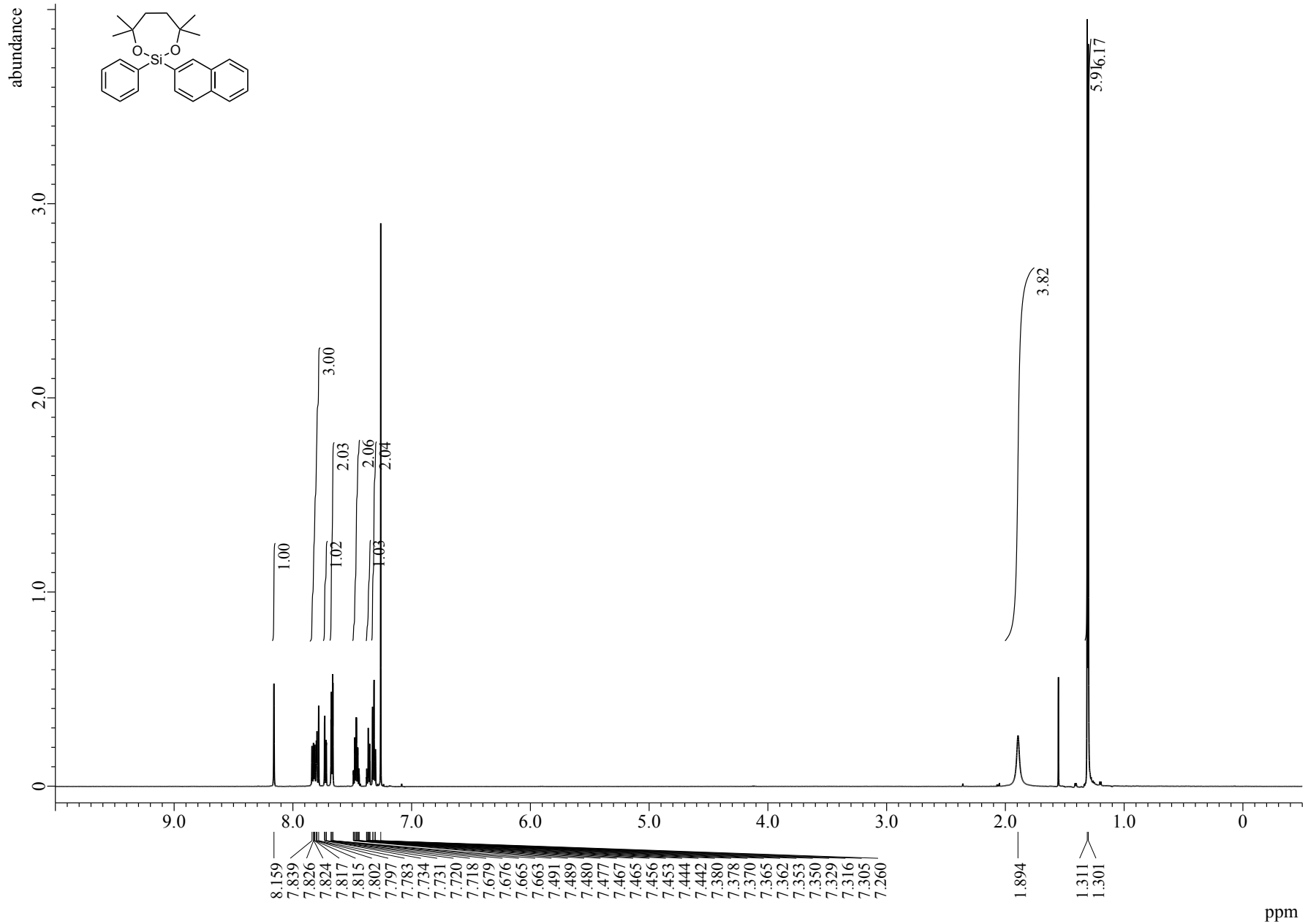


Figure S80. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3bj**

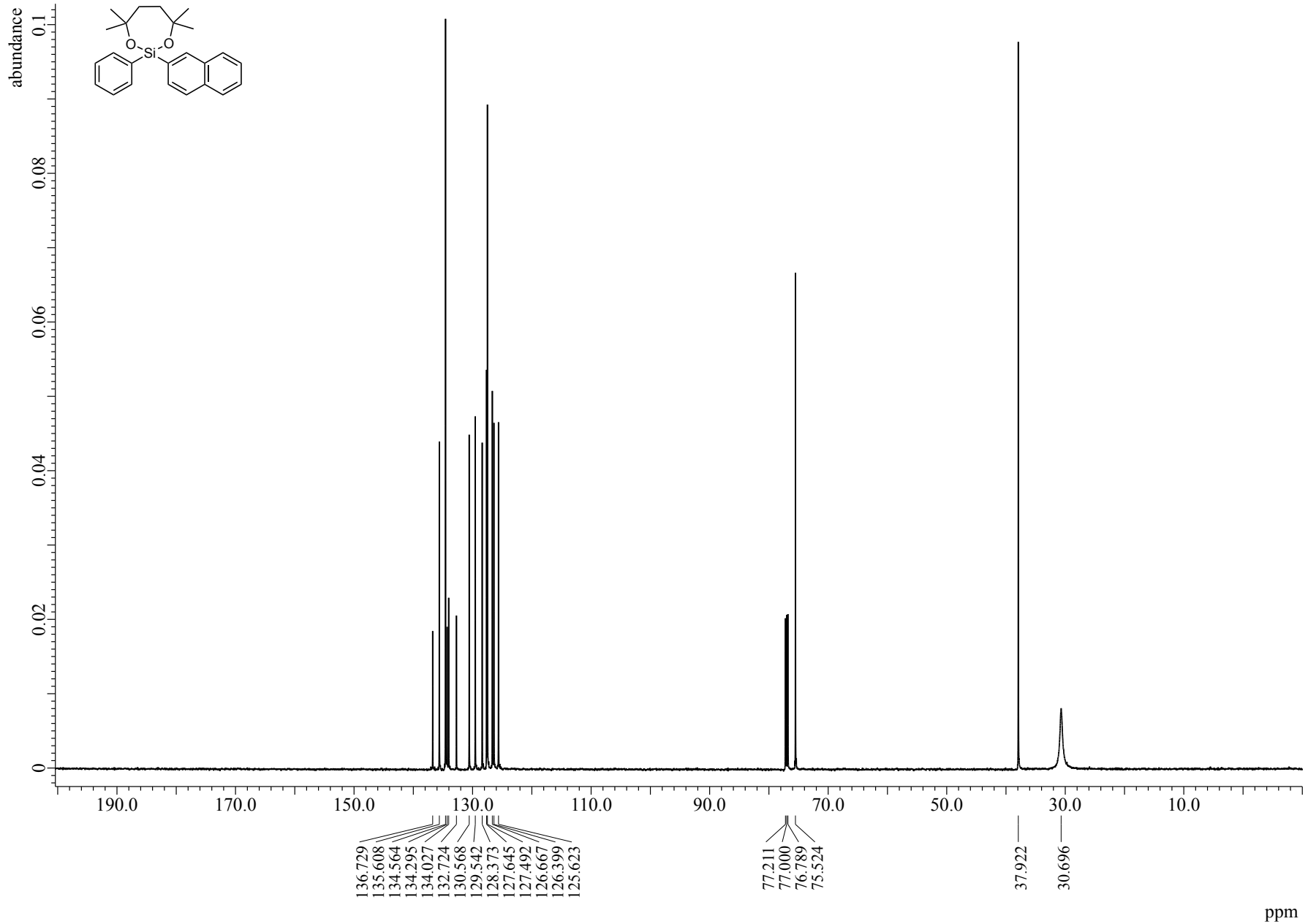


Figure S81. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3bj**

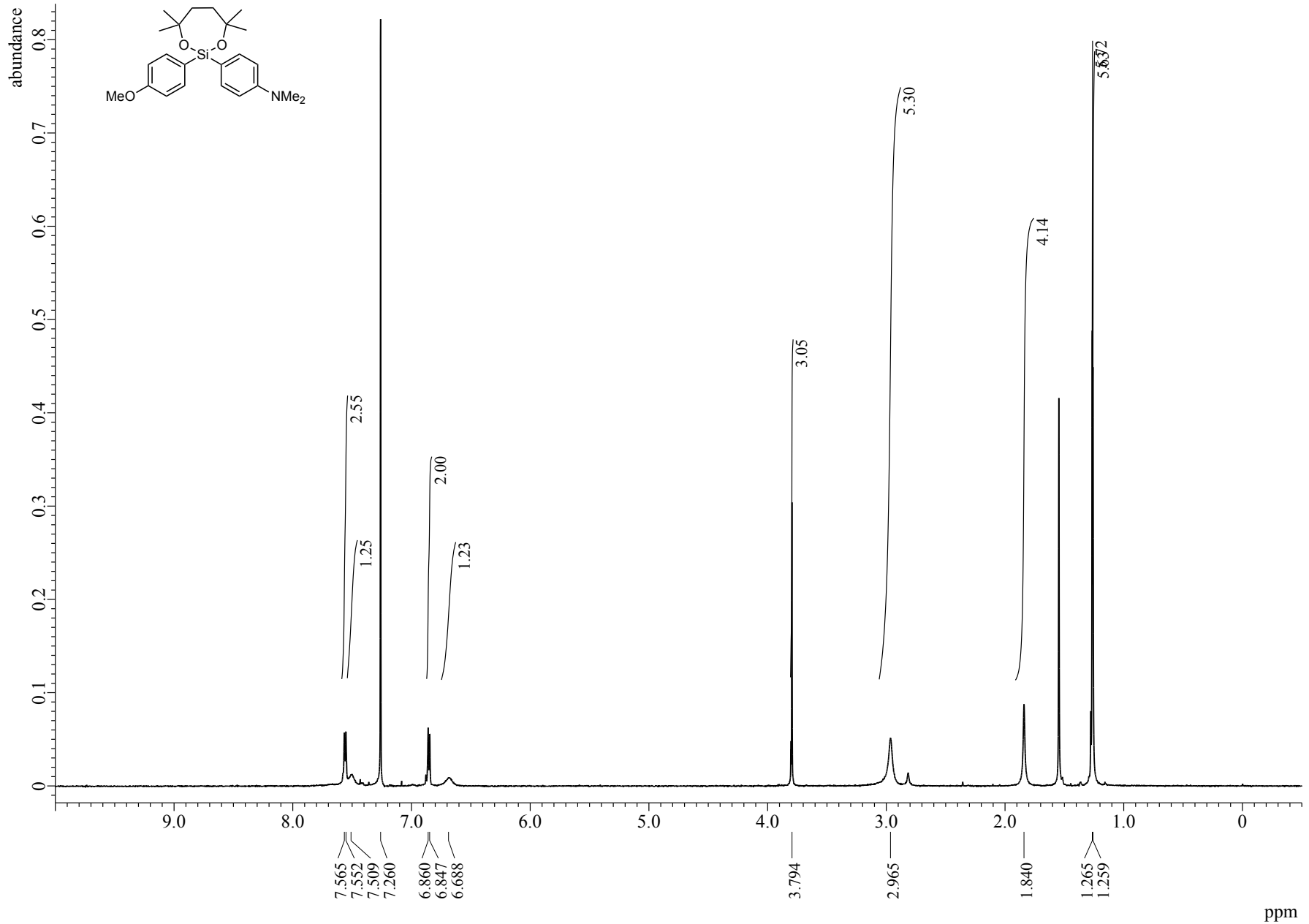


Figure S82. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3eg**

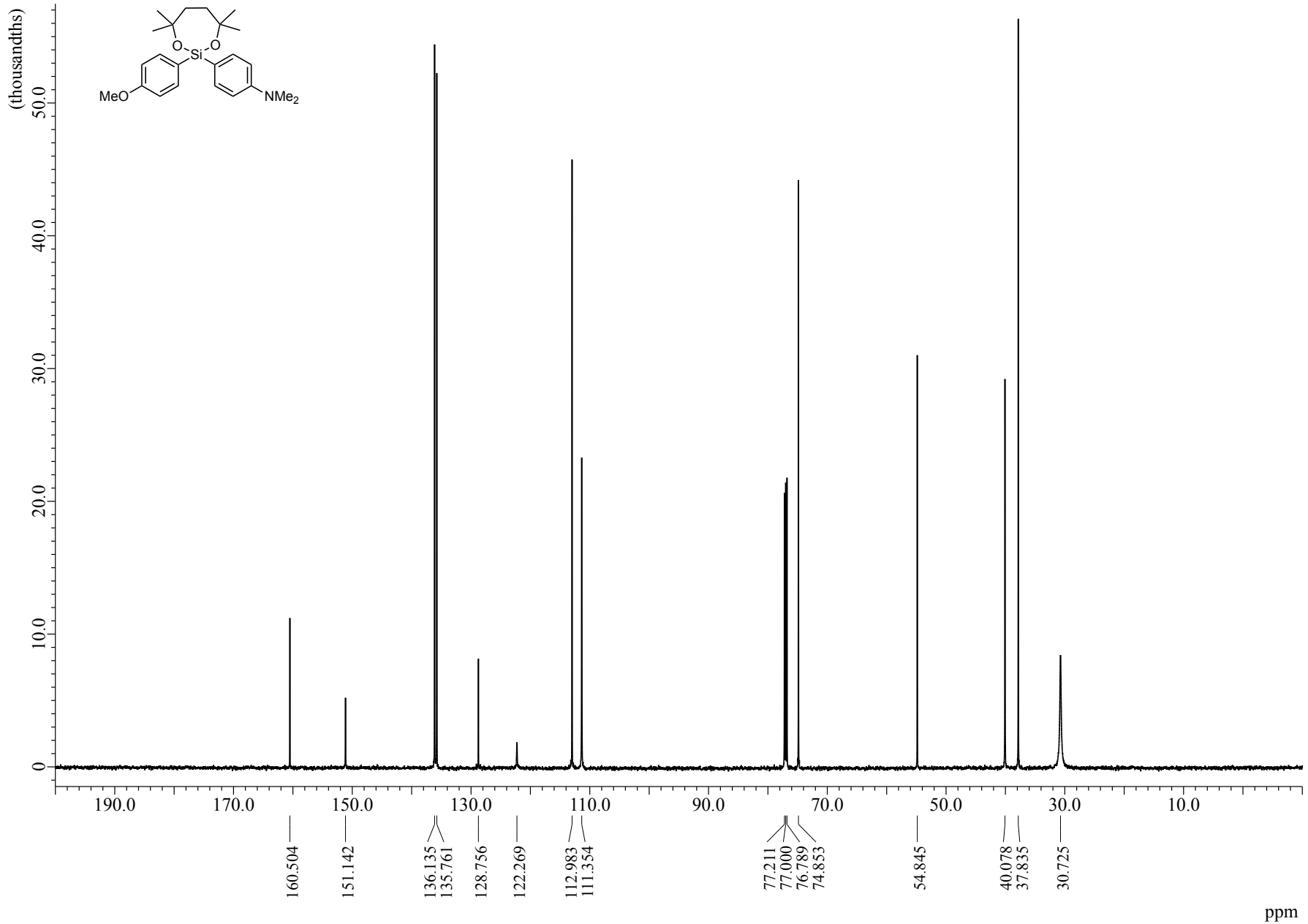


Figure S83. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3eg**

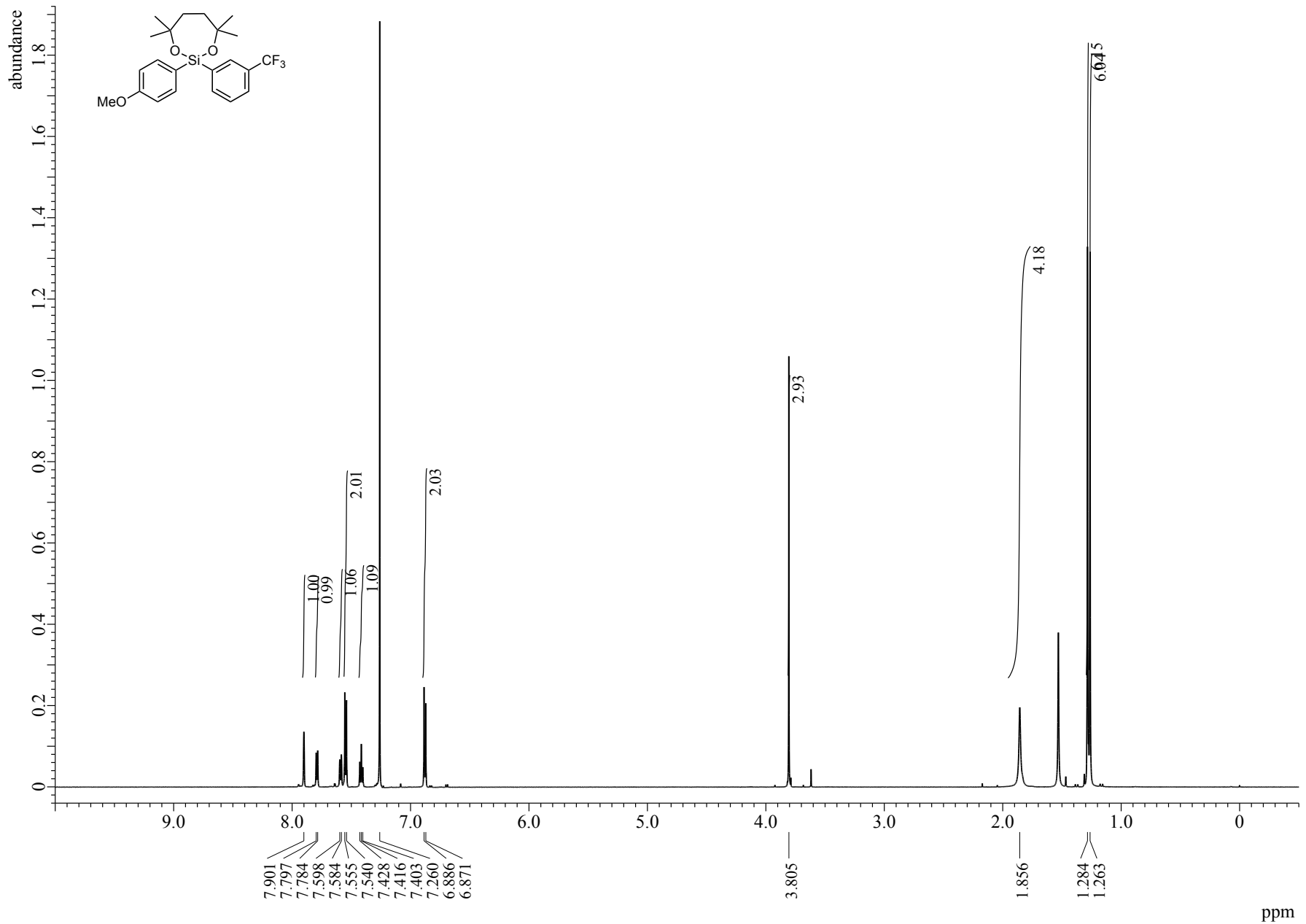


Figure S84. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3ei**

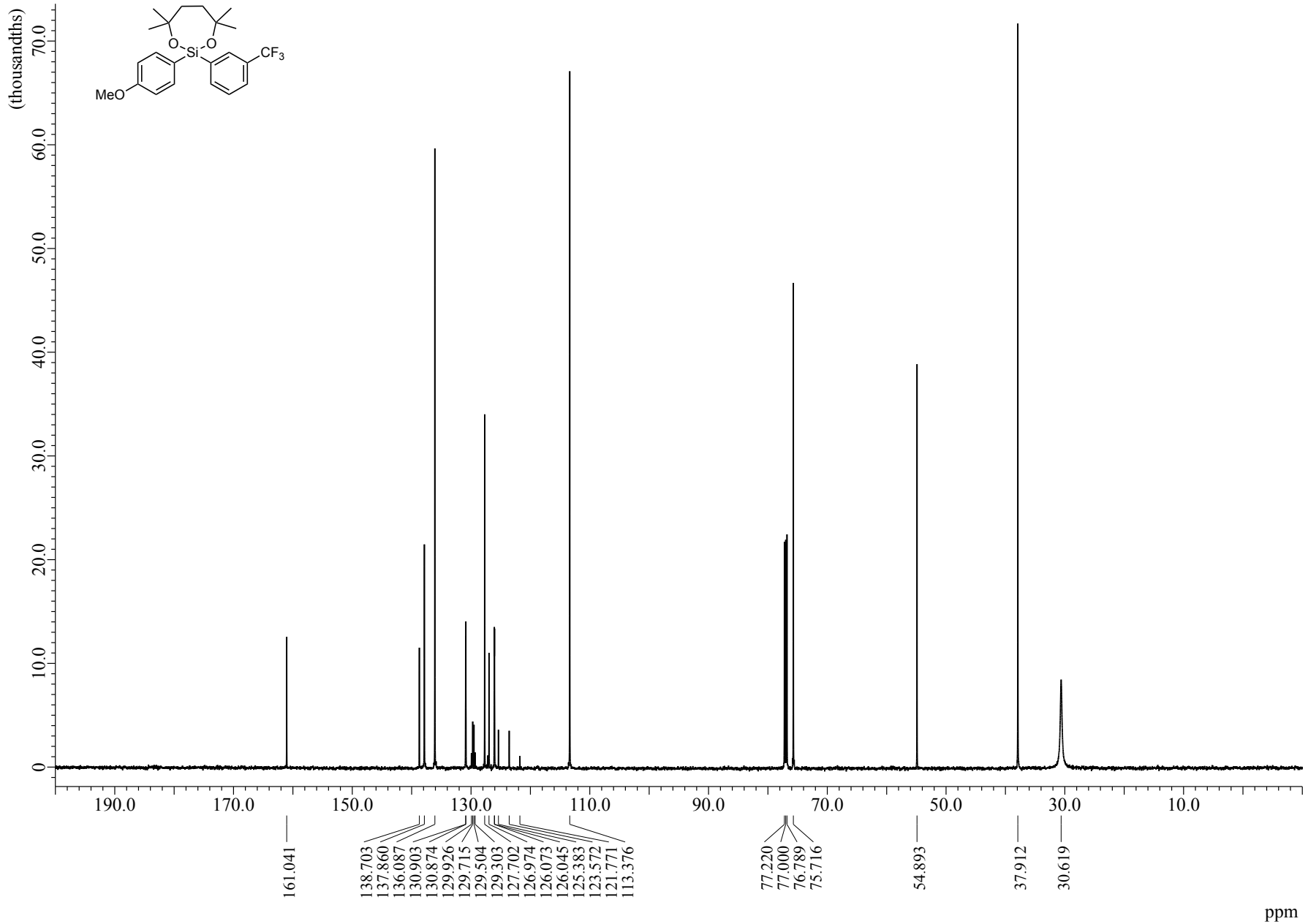


Figure S85. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3ei**

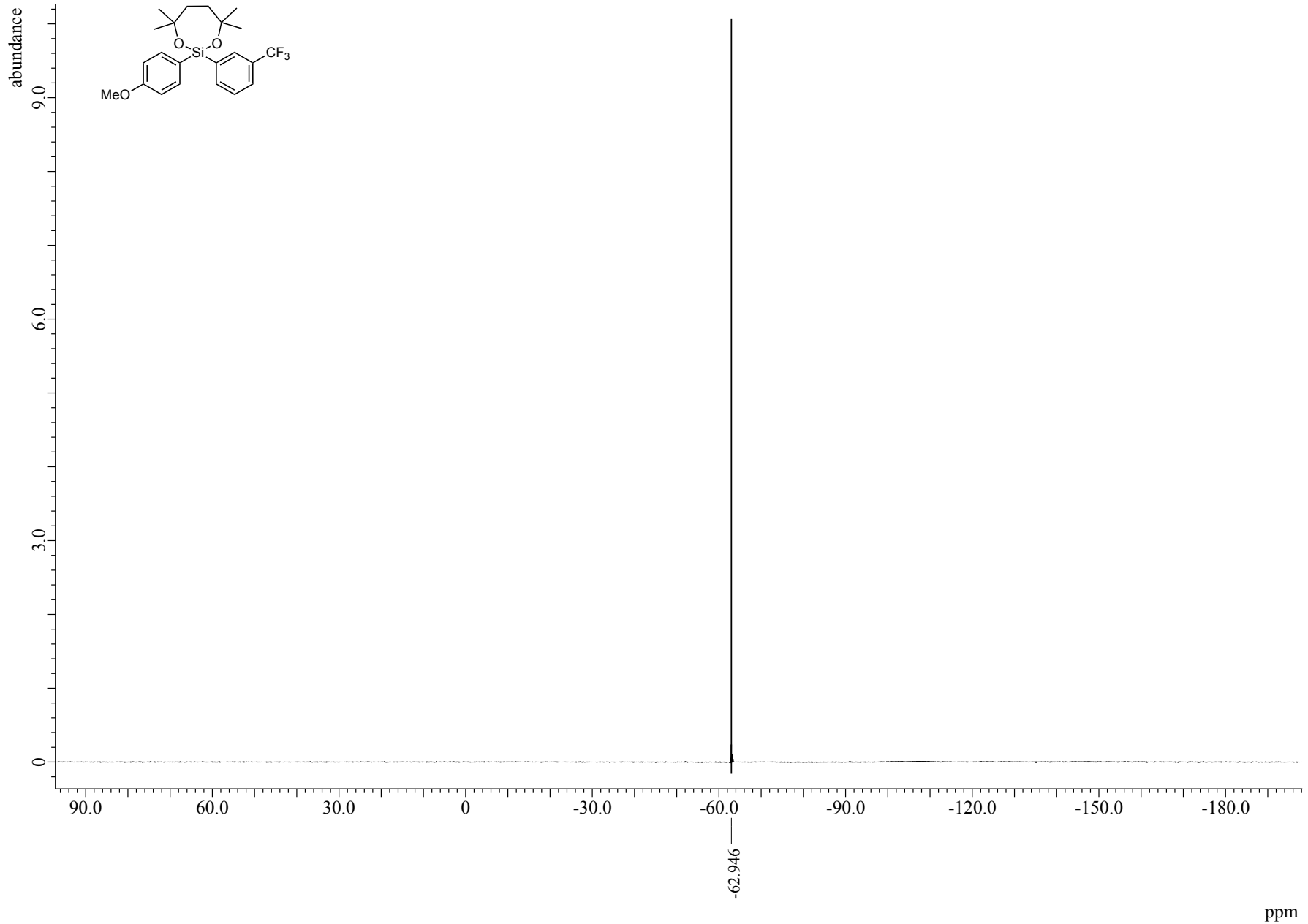


Figure S86. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3ei**

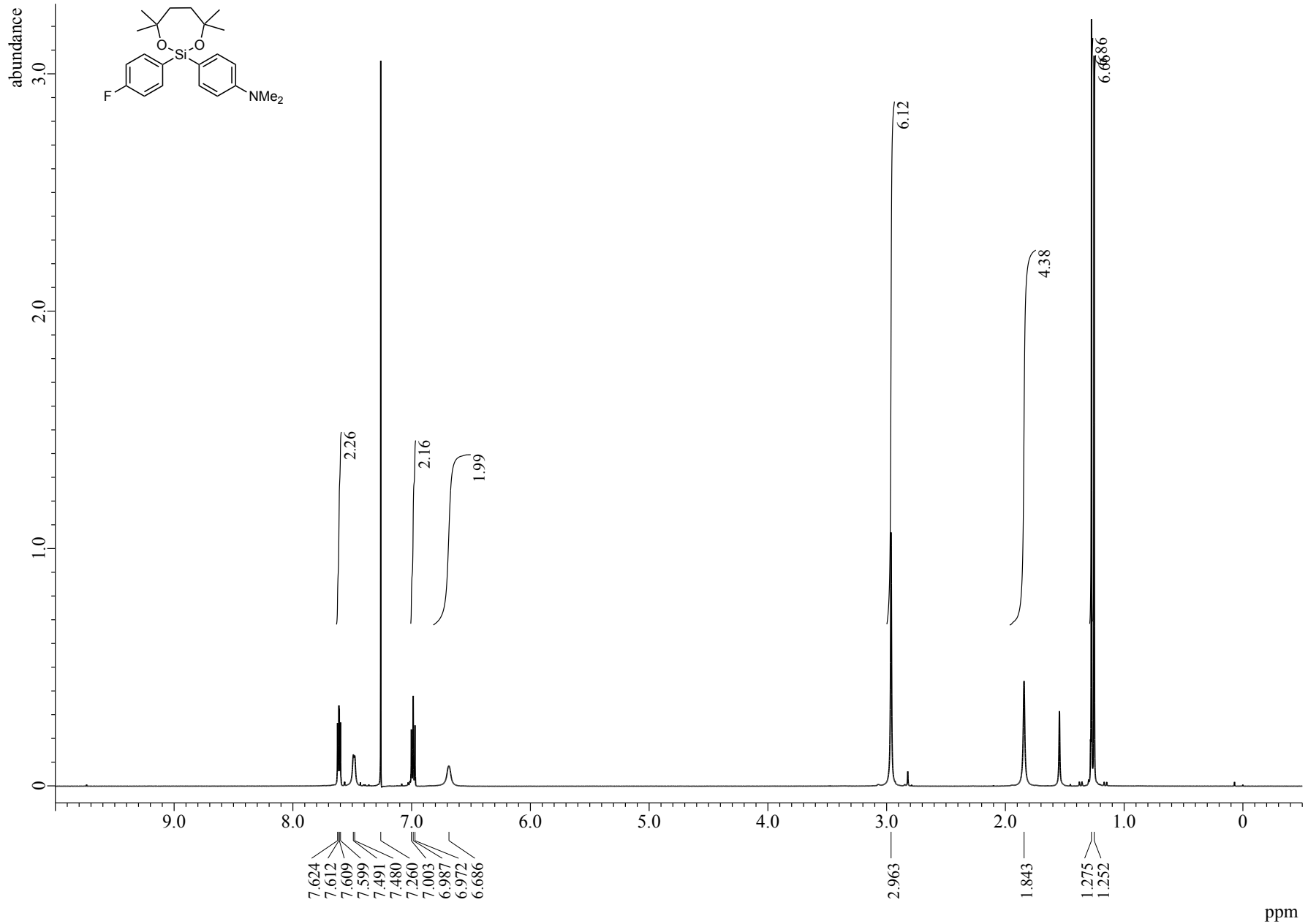


Figure S87. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3hg**

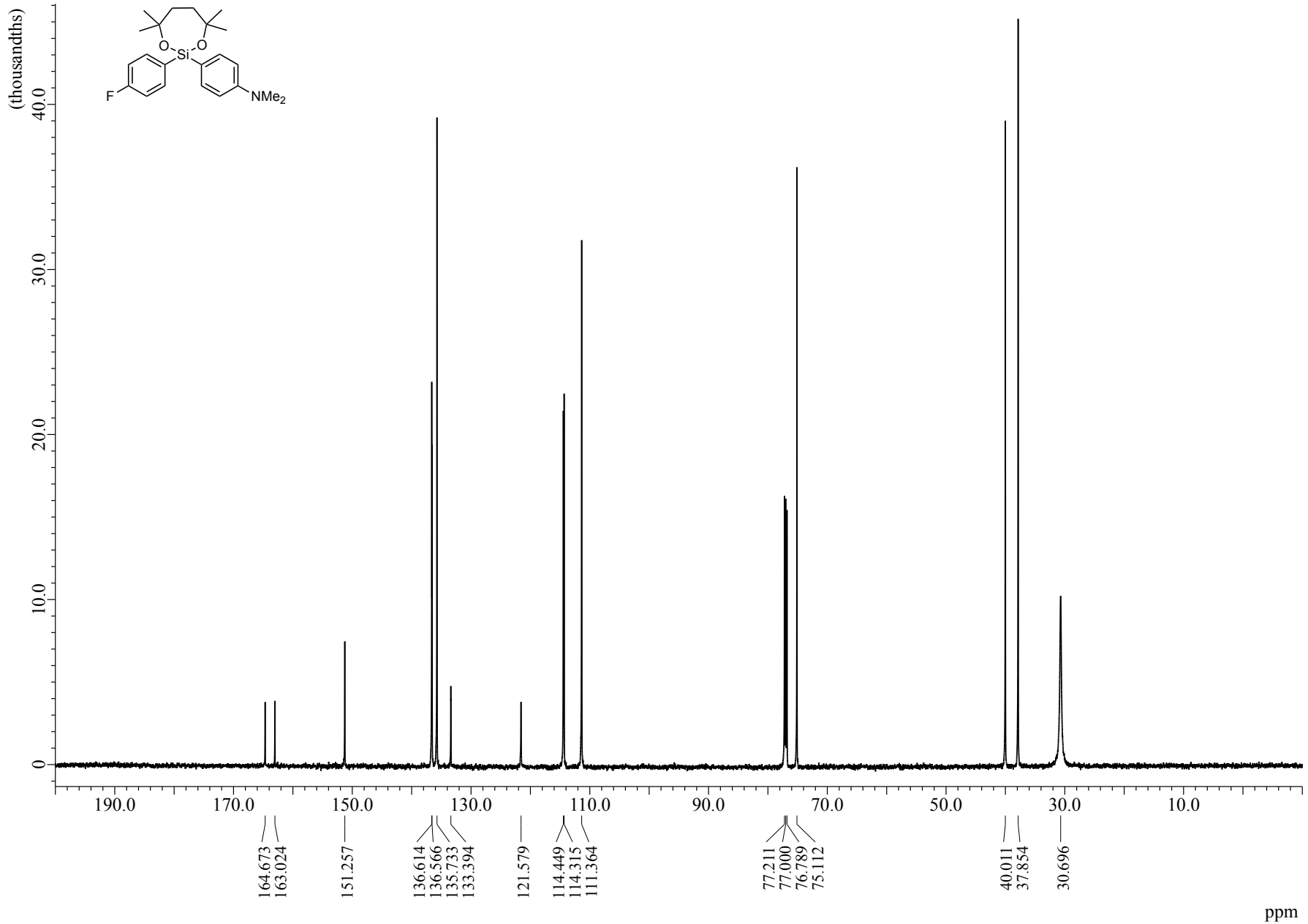


Figure S88. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3hg**

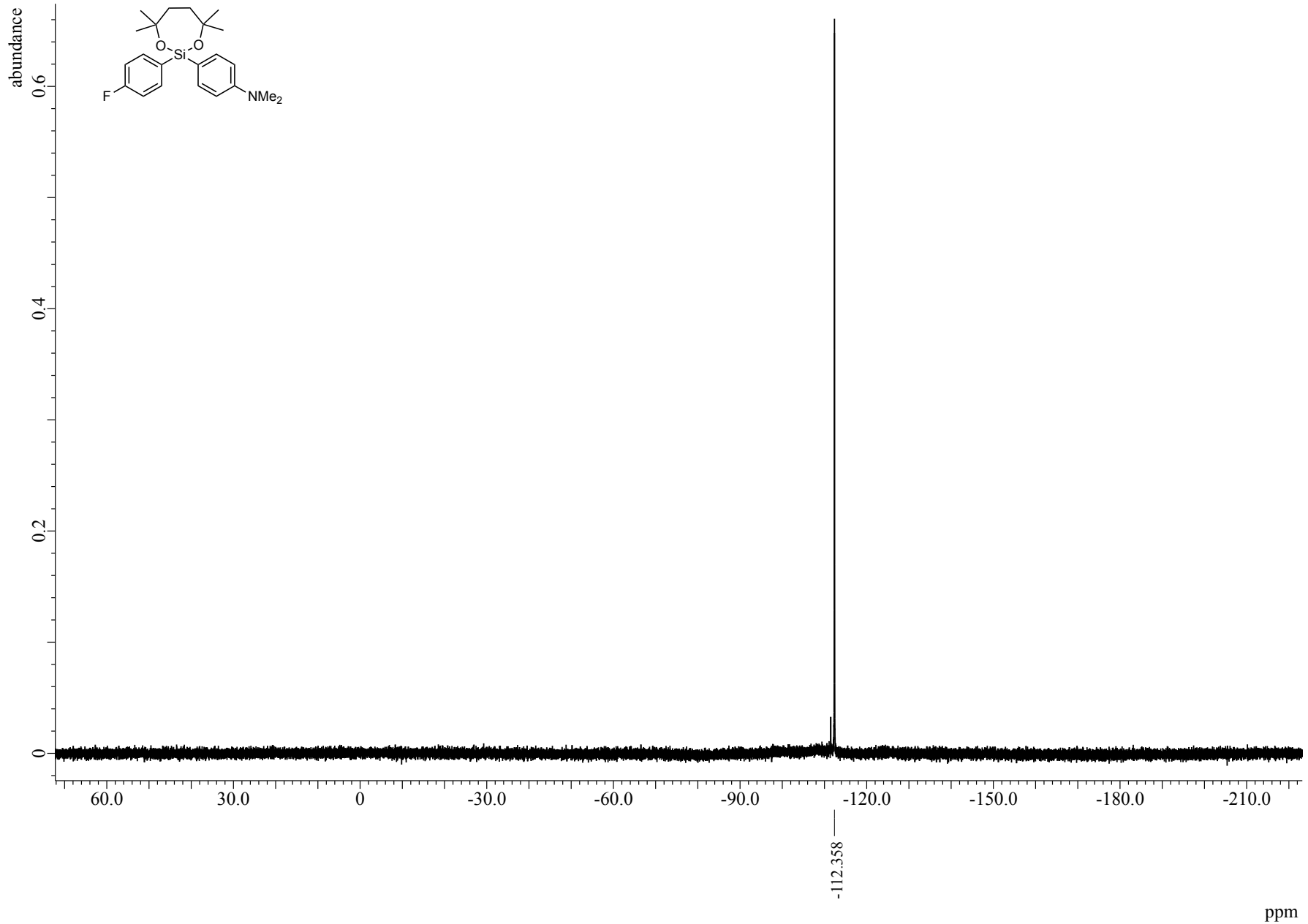


Figure S89. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3hg**

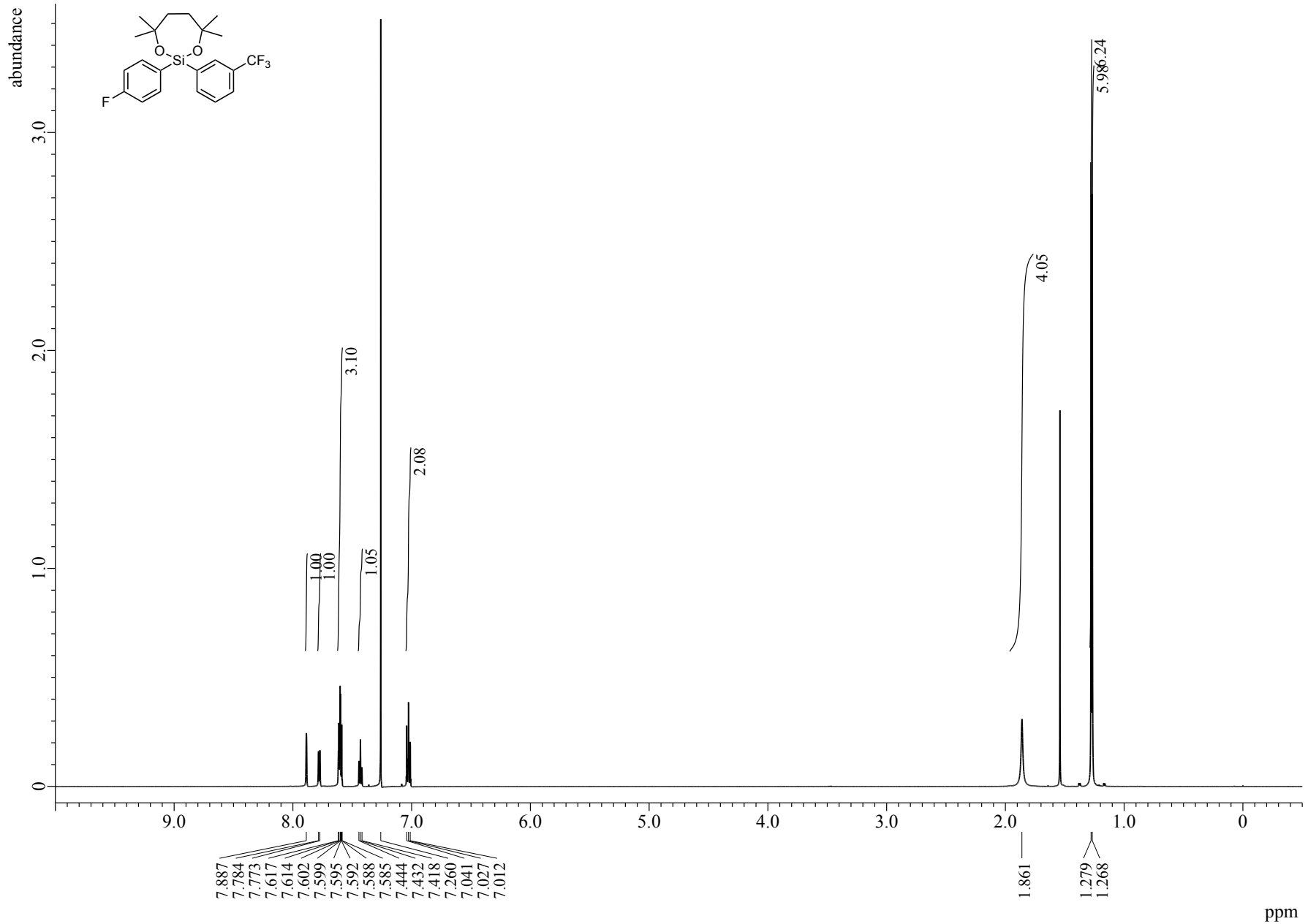


Figure S90. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3hi**

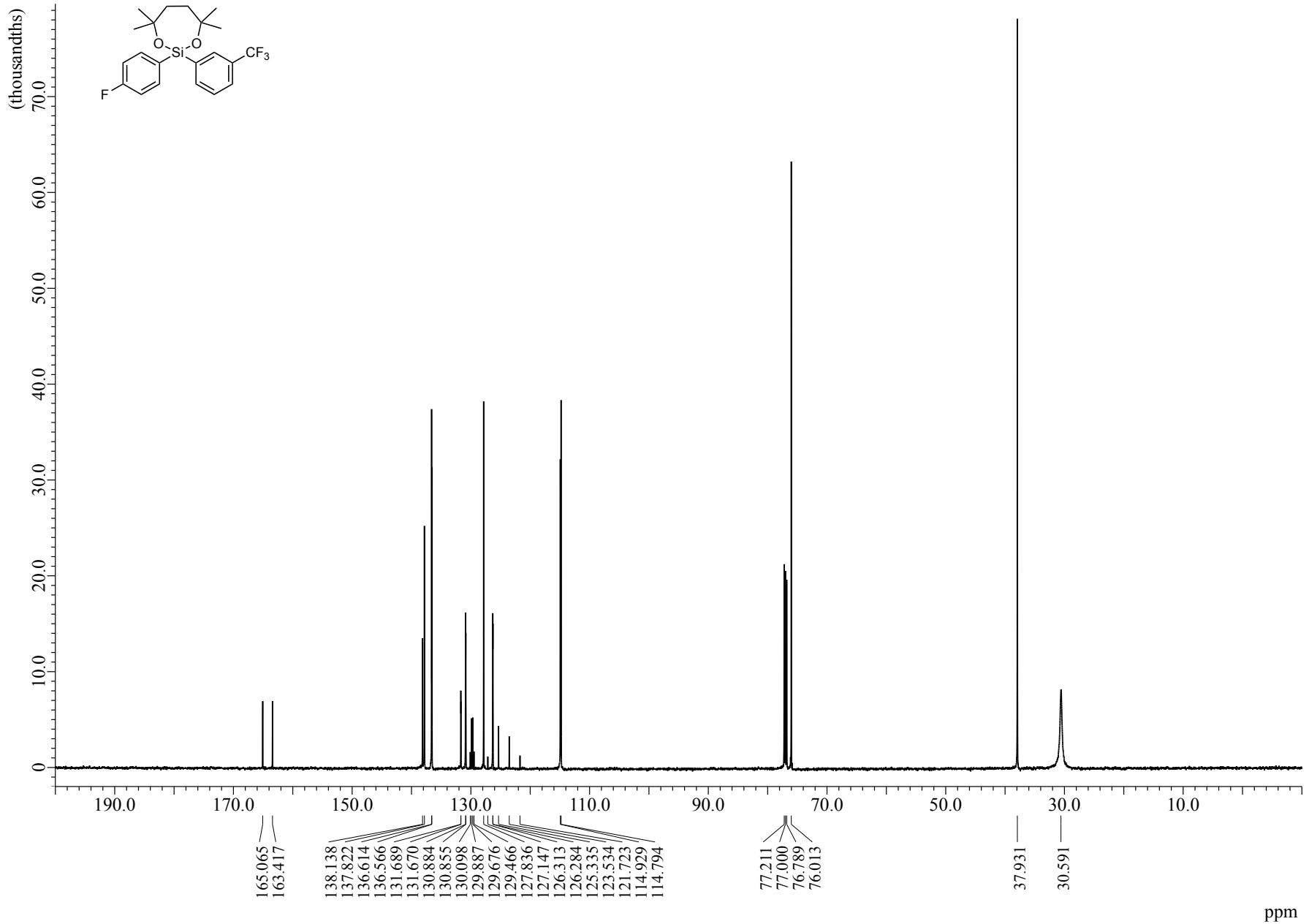


Figure S91. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3hi**

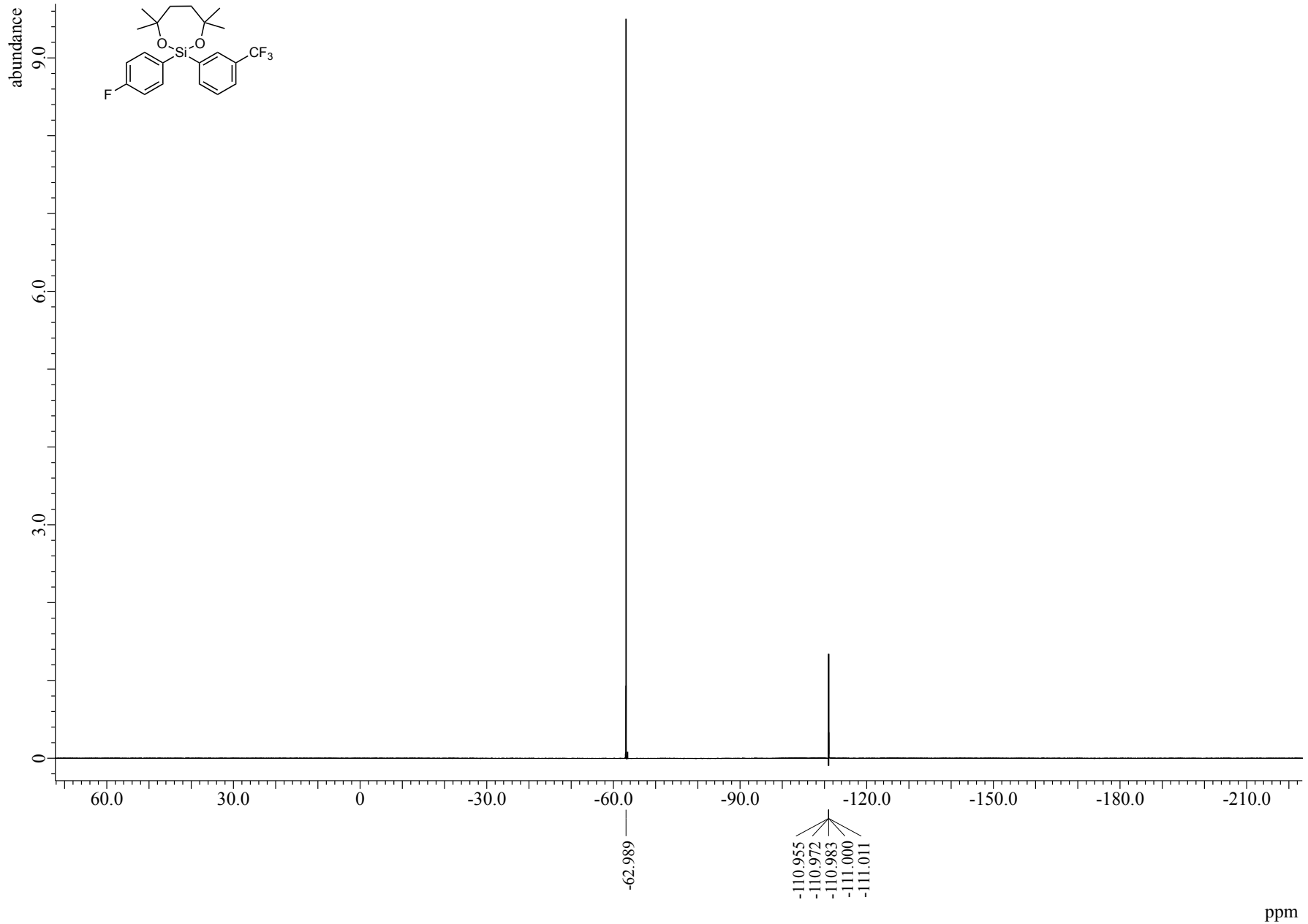


Figure S92. ^{19}F NMR (564 MHz, $CDCl_3$) spectrum of **3hi**

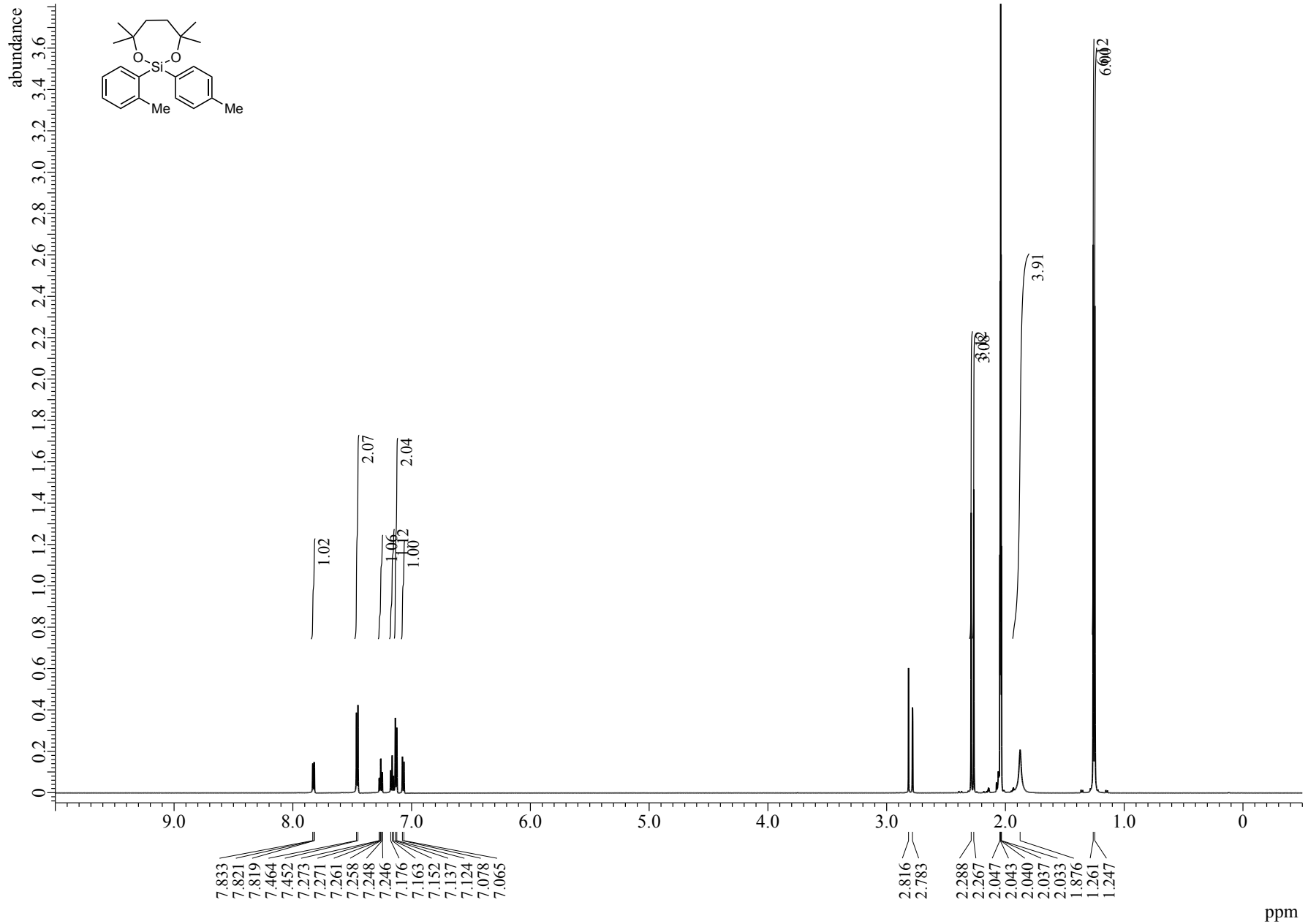


Figure S93. ^{1}H NMR (600 MHz, acetone-d_6) spectrum of **3lc**

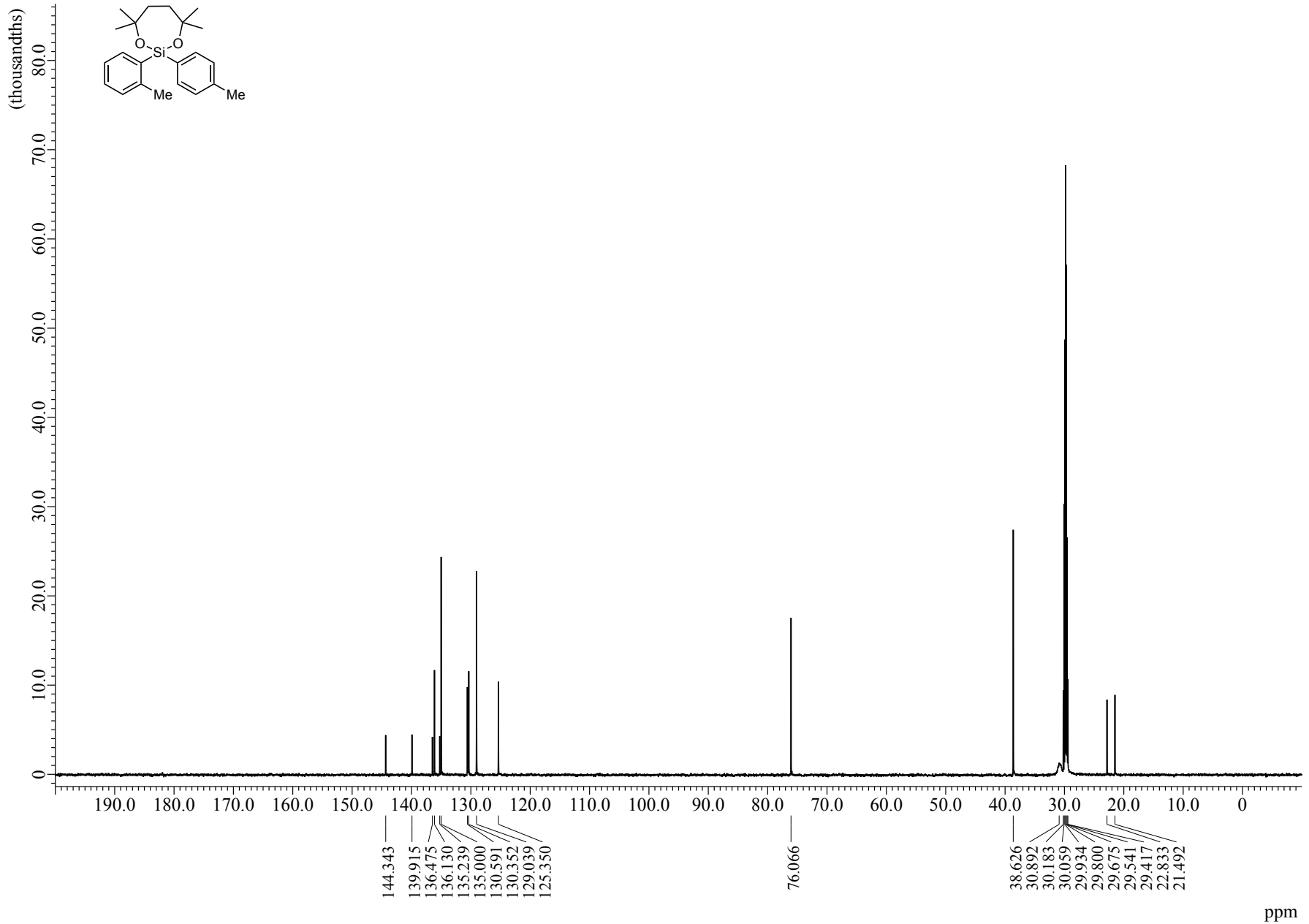


Figure S94. ^{13}C NMR (151 MHz, acetone-d_6) spectrum of **3lc**

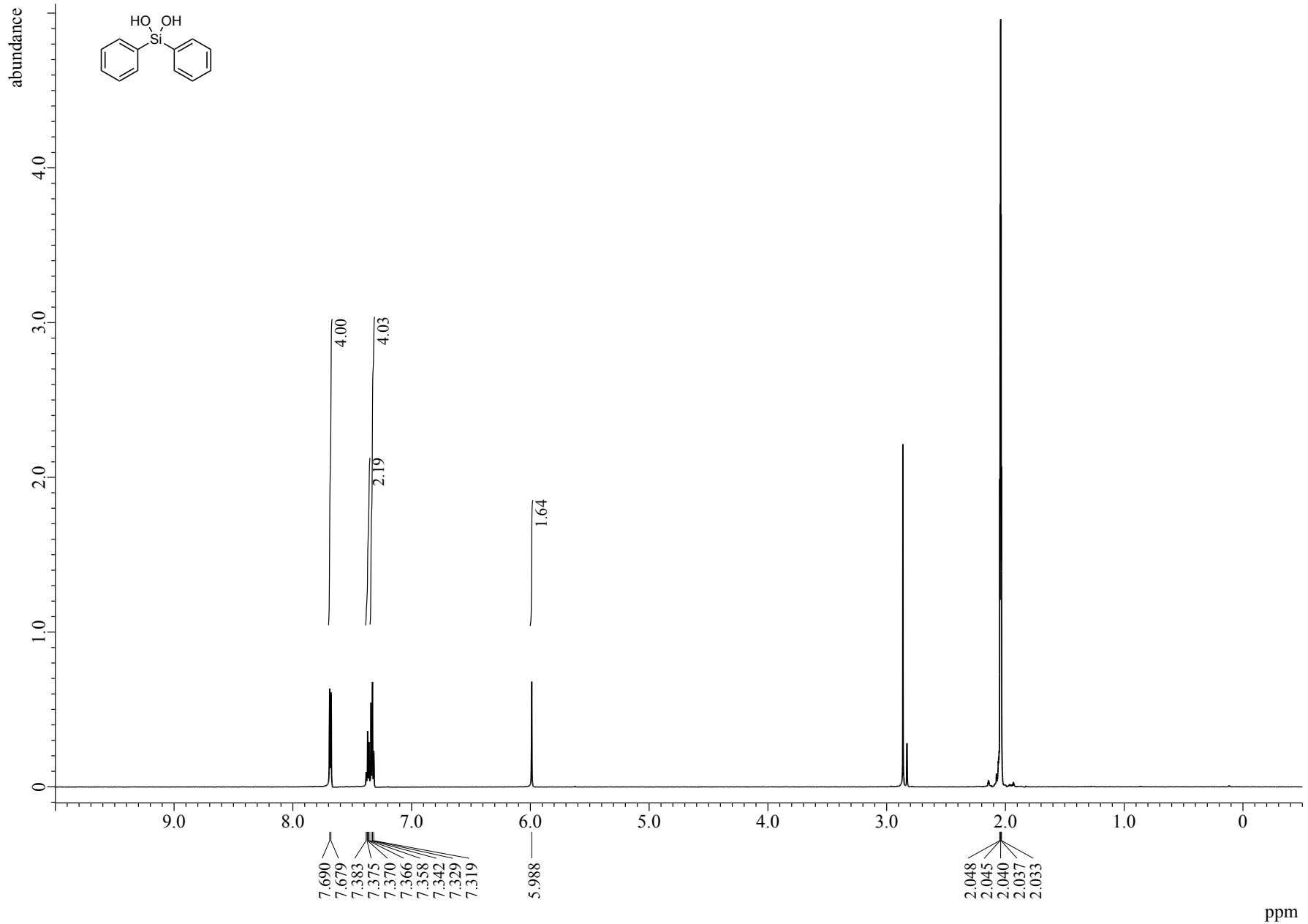


Figure S95. ^{1}H NMR (600 MHz, acetone-d_6) spectrum of **5bb**

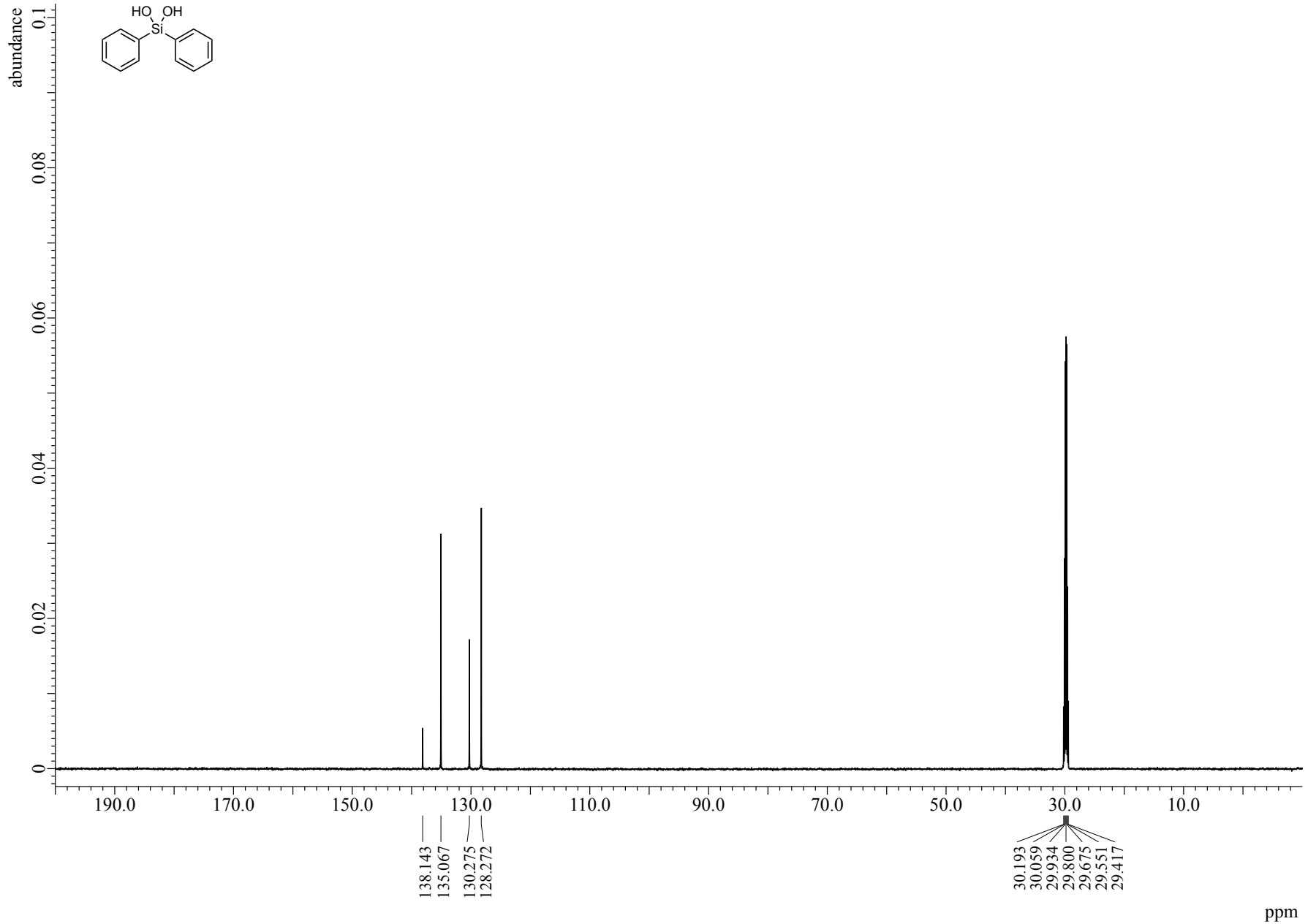


Figure S96. ^{13}C NMR (151 MHz, acetone-d_6) spectrum of **5bb**

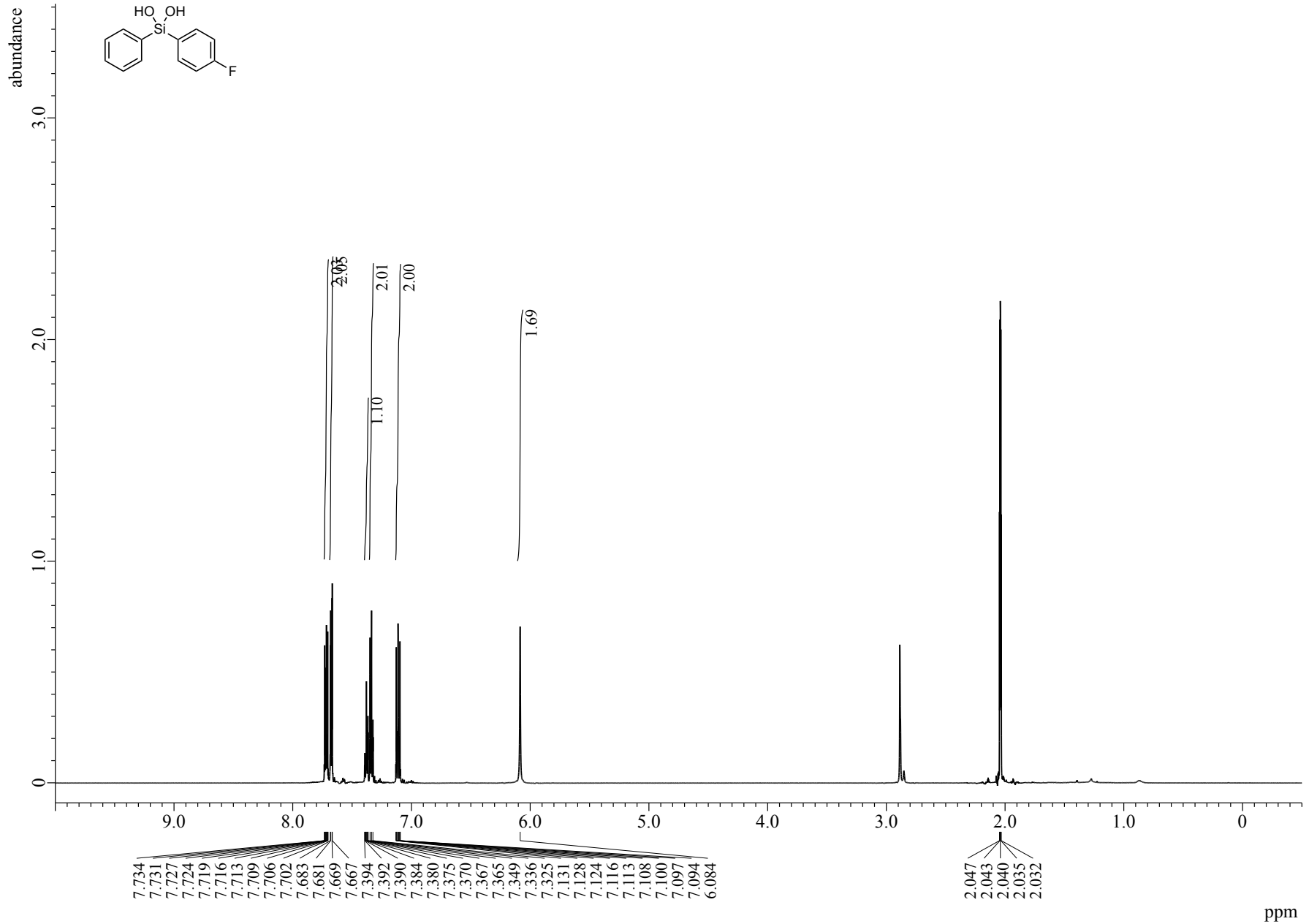


Figure S97. ^{1}H NMR (600 MHz, acetone-d_6) spectrum of **5bh**

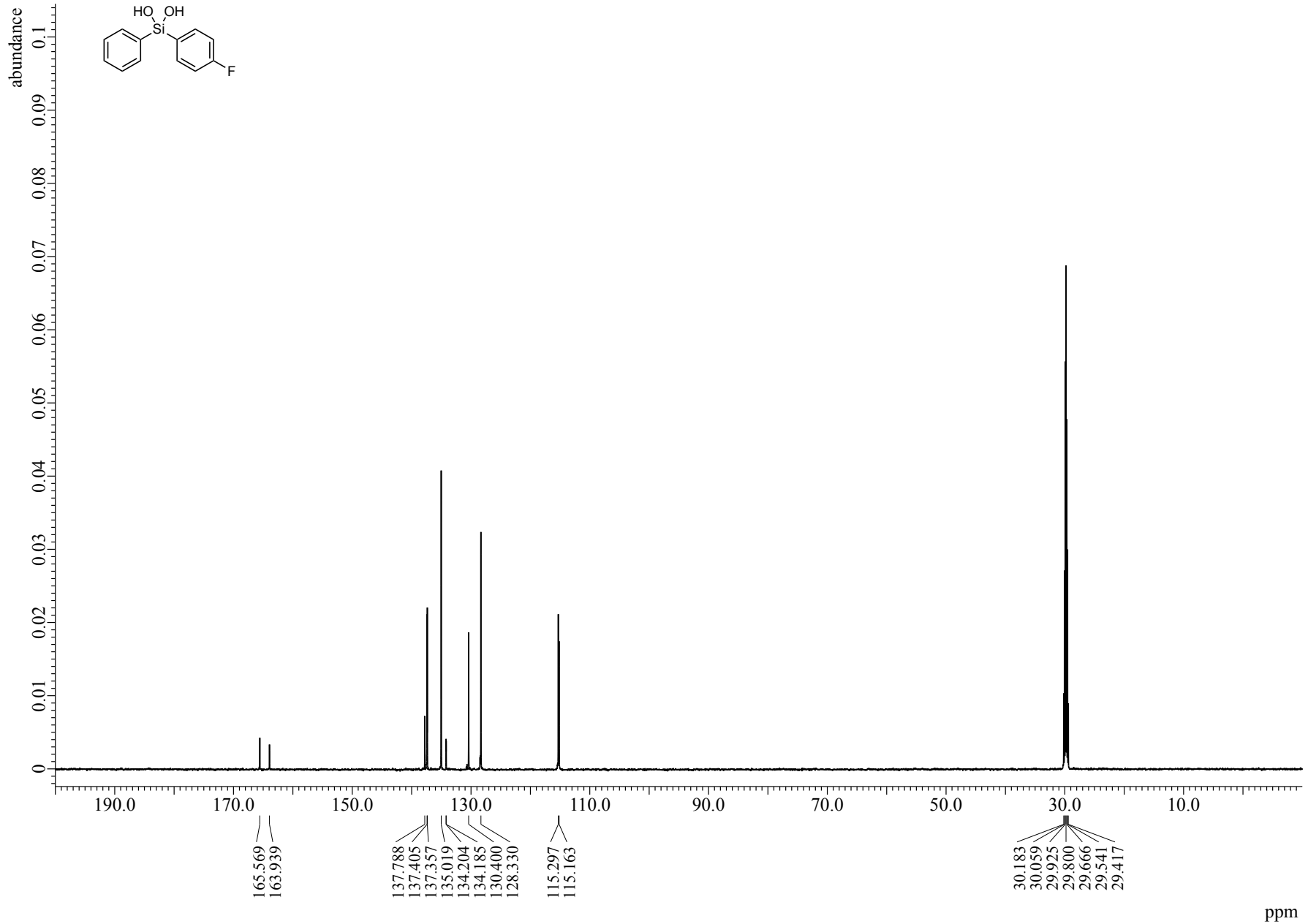


Figure S98. ^{13}C NMR (151 MHz, acetone-d_6) spectrum of **5bh**

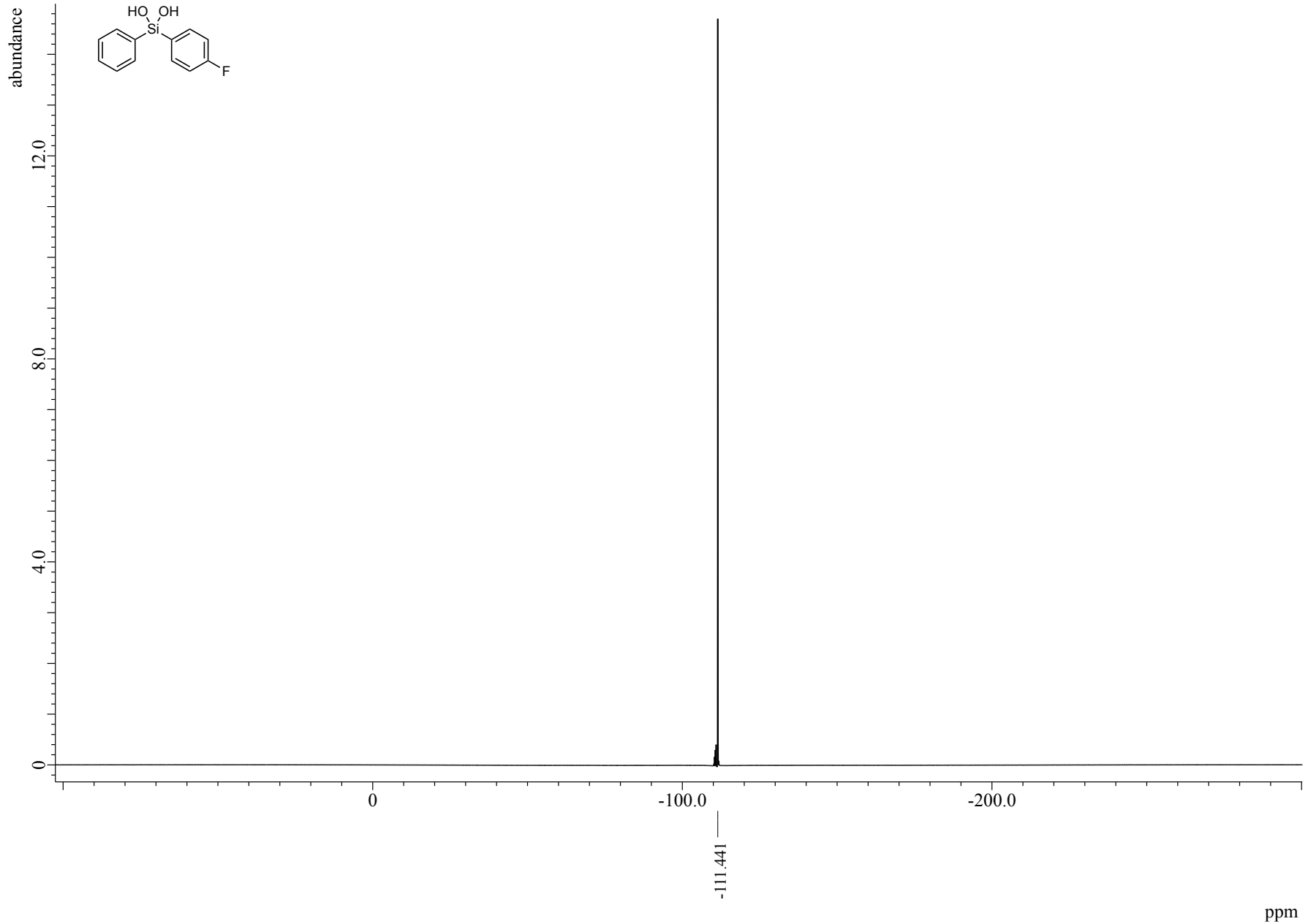


Figure S99. ^{19}F NMR (564 MHz, acetone-d_6) spectrum of **5bh**

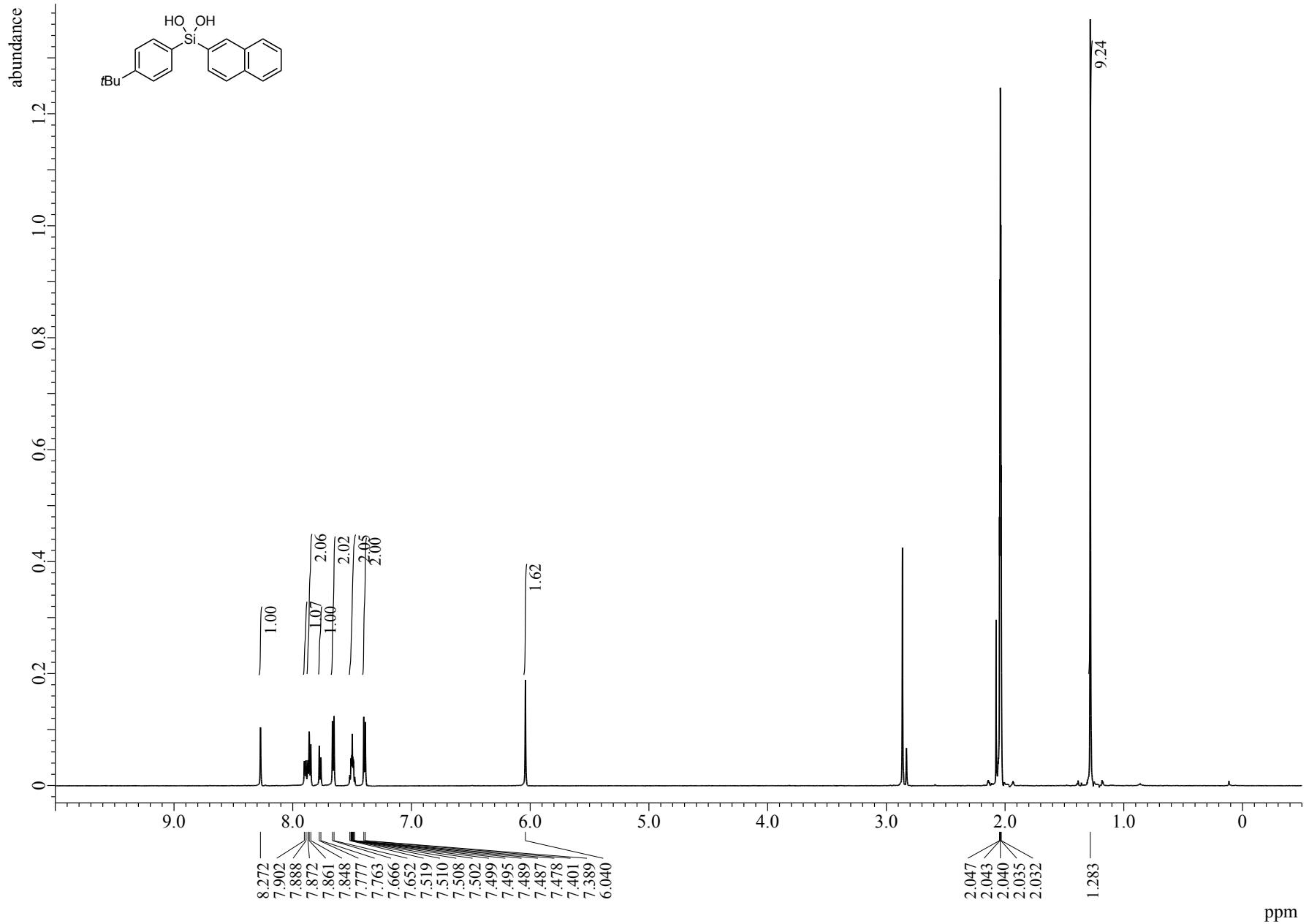


Figure S100. ^{1}H NMR (600 MHz, acetone-d_6) spectrum of **5aj**

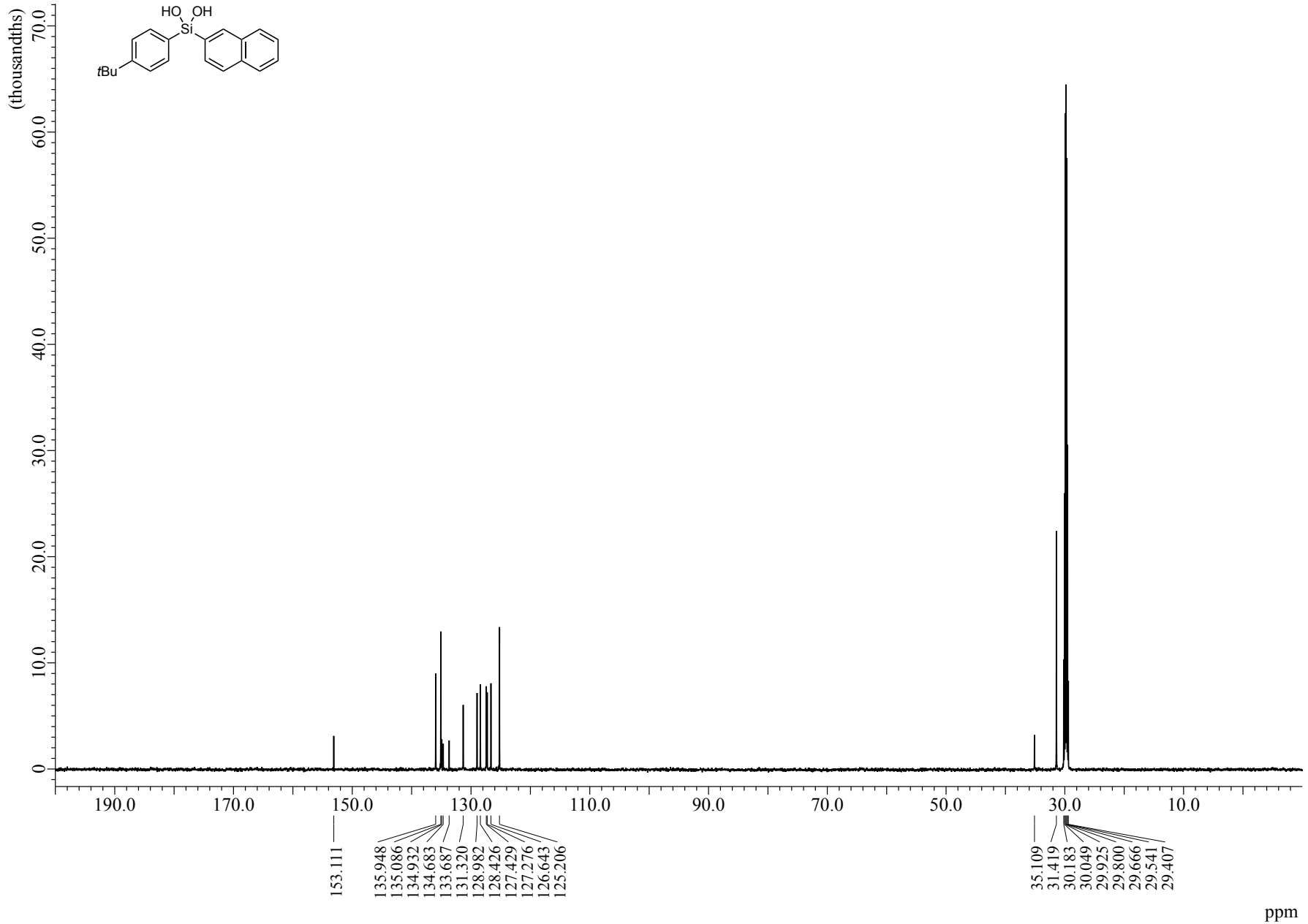


Figure S101. ^{13}C NMR (151 MHz, acetone-d_6) spectrum of **5aj**

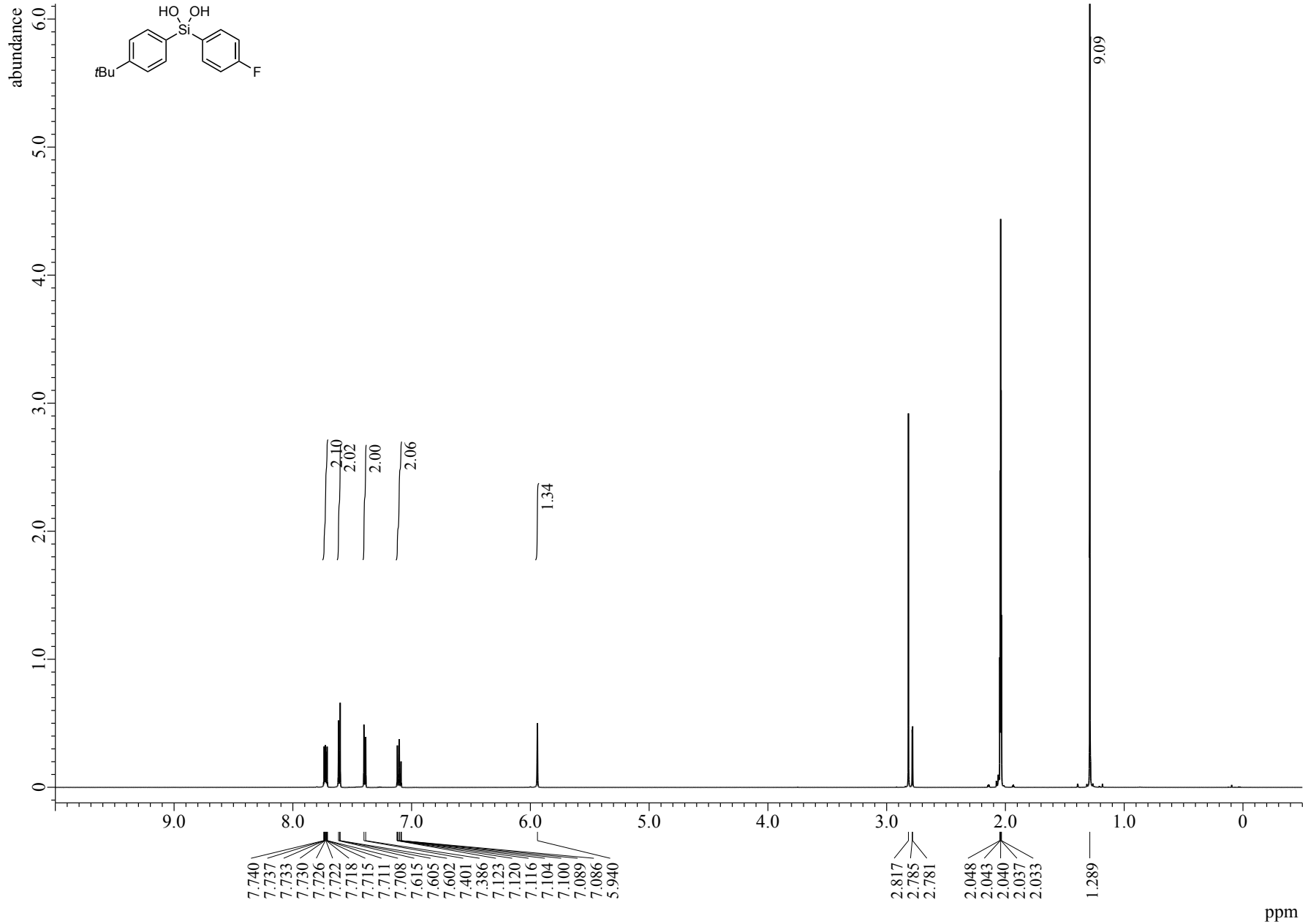


Figure S102. ^{1}H NMR (600 MHz, acetone-d_6) spectrum of **5ah**

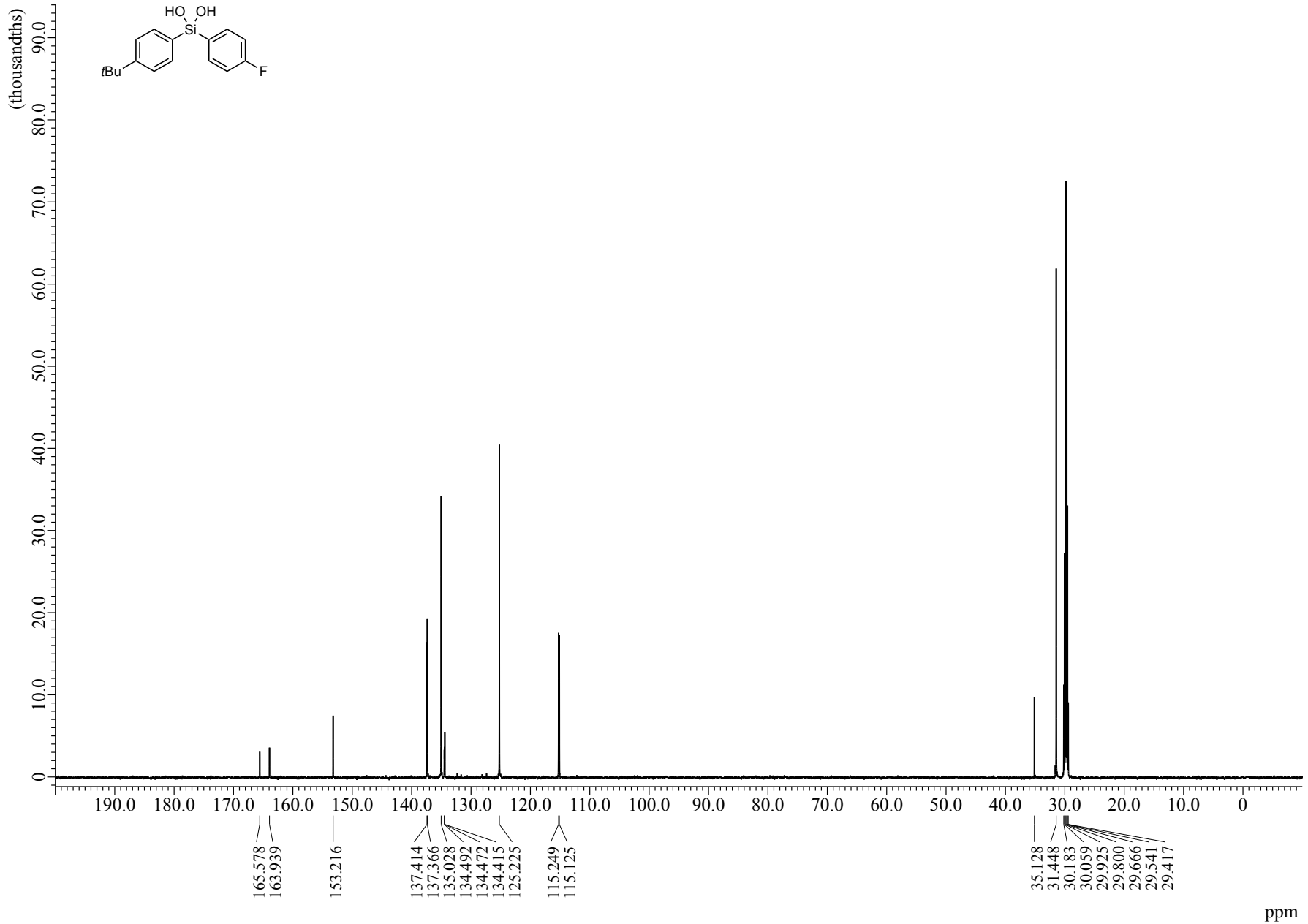


Figure S103. ^{13}C NMR (151 MHz, acetone-d_6) spectrum of **5ah**

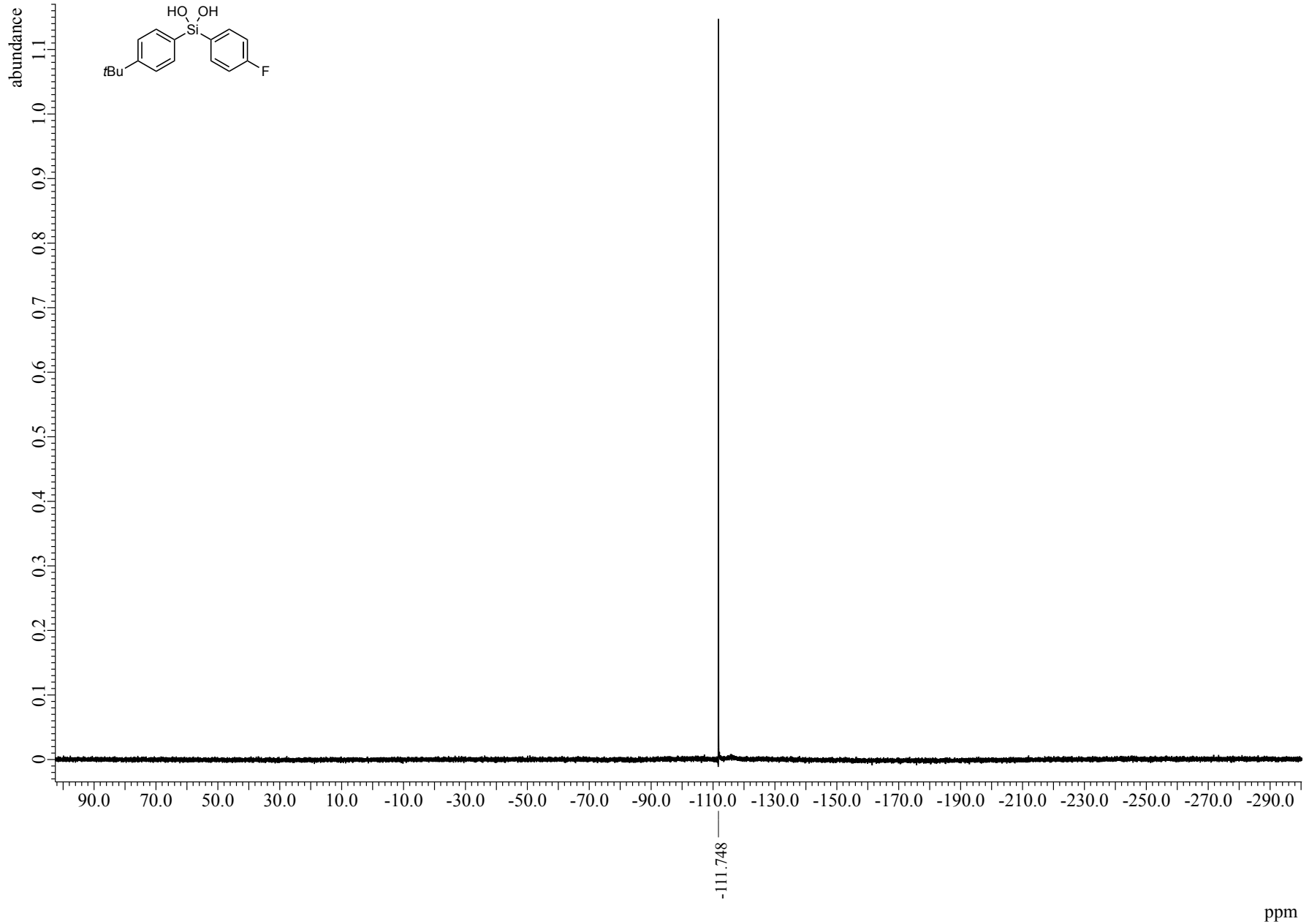


Figure S104. ^{19}F NMR (564 MHz, acetone-d_6) spectrum of **5ah**

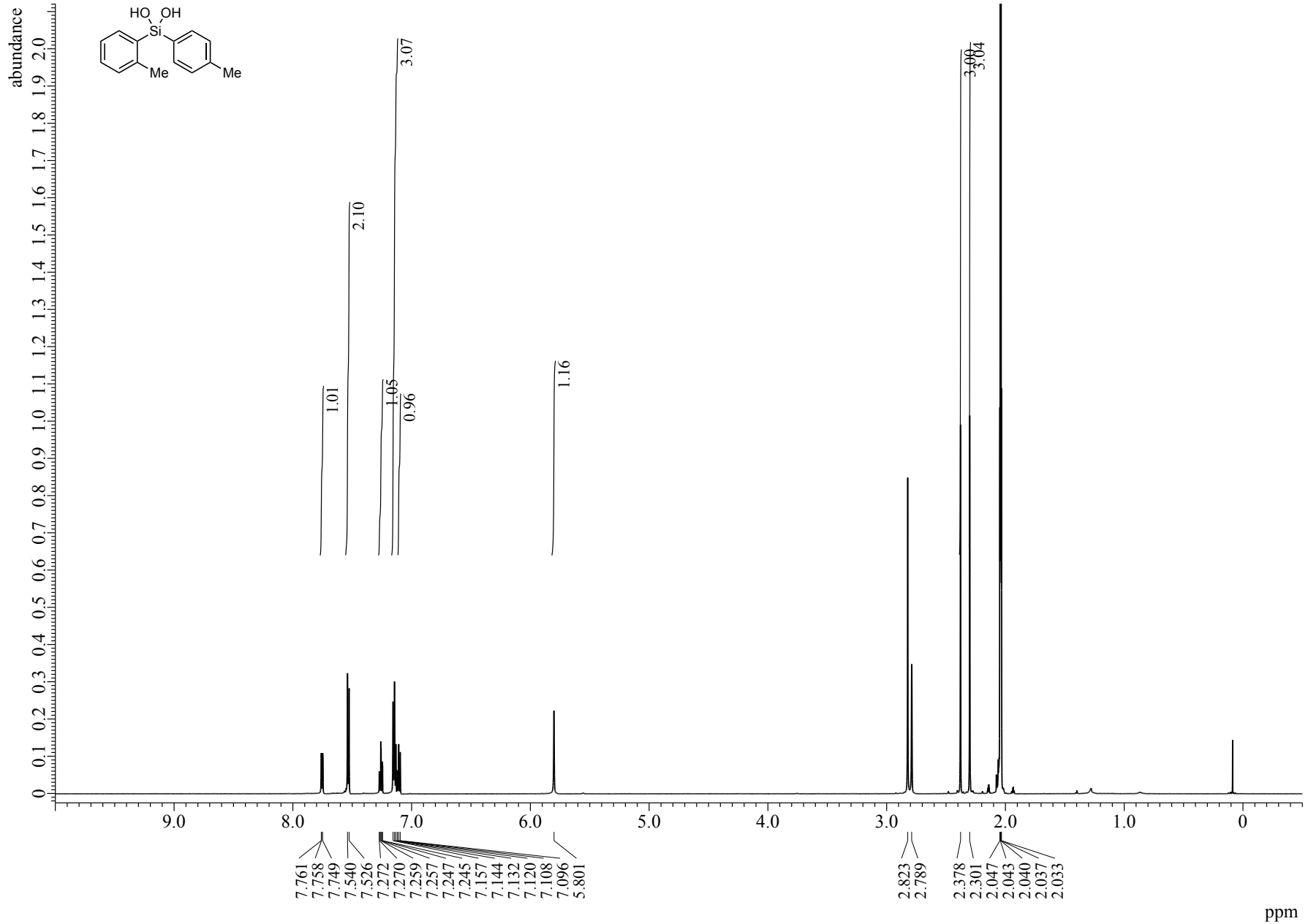


Figure S105. ^{1}H NMR (600 MHz, acetone-d_6) spectrum of **5lc**

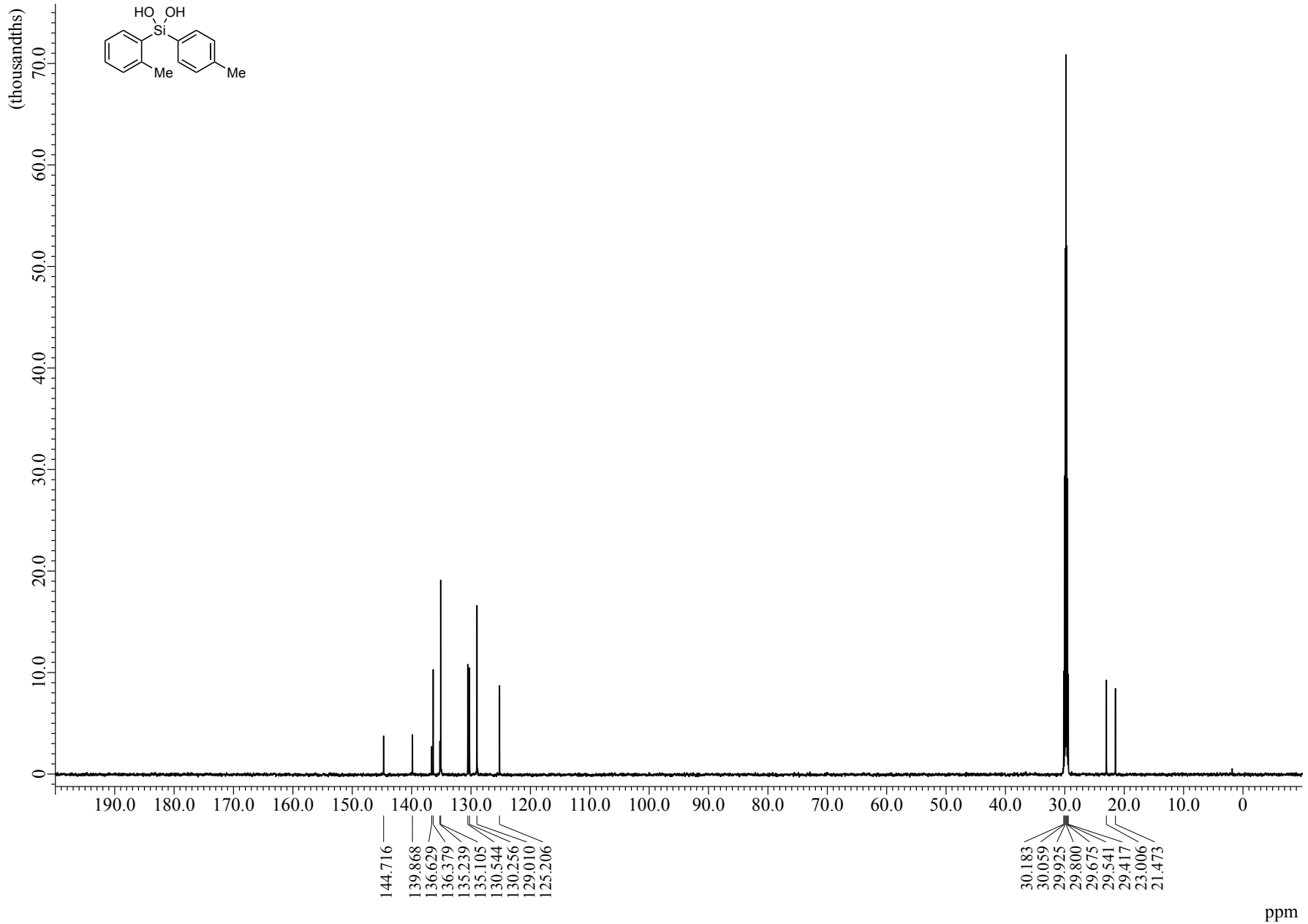


Figure S106. ^{13}C NMR (151 MHz, acetone-d_6) spectrum of **5lc**