Electronic Supplementary Information

Dioxasilepanyl Group as a Versatile Organometallic Unit: Studies in Stability, Reactivity, and Utility

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Instrumentation and Chemicals

^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), and ^{29}Si NMR (119 MHz) spectra were taken on JEOL ECA-600 and ECZ-600 spectrometers. ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ by using $CHCl_3$ (for ^{1}H, $\delta = 7.26$ ppm) and $CDCl_3$ (for ^{13}C, $\delta = 77.00$ ppm). ^{29}Si NMR spectra were obtained in $CDCl_3$ by using tetramethylsilane ($\delta = 0.00$ ppm) as an external standard.

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. Melting points were determined on a Stanford Research Systems MPA100 melting point apparatus. Single-crystal diffraction analysis data were collected with a Rigaku XtaLAB P200 by using graphite monochromated Cu-Kα radiation ($\lambda = 1.54187$ Å).

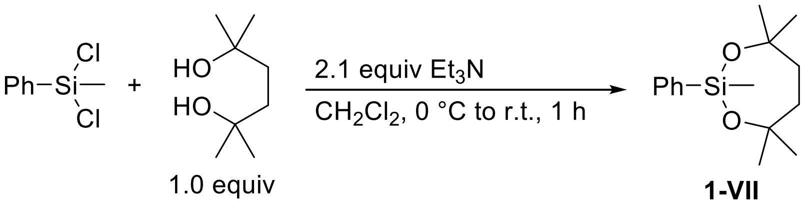
All reactions were carried out under nitrogen atmosphere. Dehydrated solvents (DMSO, DMF, 1,4-dioxane, and toluene) were purchased from FUJIFILM Wako Pure Chemical Corporation and stored under nitrogen atmosphere. Dehydrated THF and CH_2Cl_2 were purchased from Kanto Chemical Co., Inc. and stored under nitrogen atmosphere. Dehydrated 1,2-dichloroethane (DCE) was purchased from Sigma-Aldrich Co. LLC and stored under nitrogen atmosphere. *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) was purchased from a common commercial supplier and distilled prior to use. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification.

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 Silanes

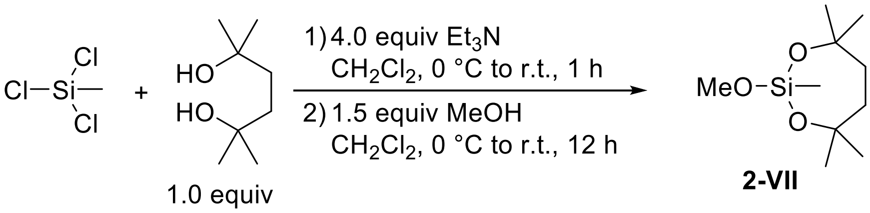
Silanes **1-I**, **1-III**, **1-VIII**, **1-IX** were synthesized by similar procedures in the literature.[1]

Preparation of Arylsilanes (TP1, Scheme 1)



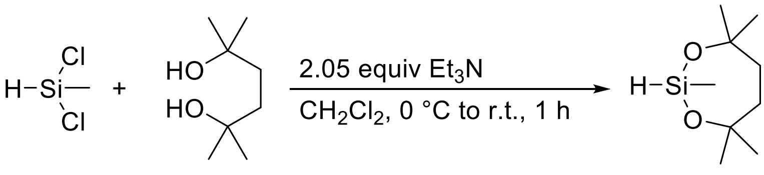
The reaction of dichloromethylphenyisilane with 2,5-dimethyl-2,5-hexanediol is representative. An oven-dried 2-L double-necked flask was charged with CH_2Cl_2 (700 mL), 2,5-dimethyl-2,5-hexanediol (29.3 g, 200 mmol), and Et_3N (58.5 mL, 420 mmol). After the resulting suspension was stirred at 0 °C in an ice bath for 5 min, dichloromethylphenylsilane (32.5 mL, 200 mmol) was added to the mixture dropwise over 10 min at 0 °C. After the reaction mixture was stirred for 1 h at room temperature, pentane (700 mL) was added to the flask and the mixture was vigorously stirred for 1 min. The precipitate thus formed was filtered off by using a Büchner funnel and the filter cake was washed with pentane (200 mL). The filtrate was concentrated under reduced pressure, and hexane (100 mL) was added to the residue. Filtration and concentration were repeated once again. Distillation of the resulting residue under reduced pressure (76 °C / 1 Torr) afforded **1-VII** as a colorless liquid (38.2 g, 144 mmol, 72%, d = 0.981 g cm^{-3}).

Preparation of 2-VII (Scheme 1)



An oven-dried 1-L double-necked flask was charged with CH_2Cl_2 (500 mL), 2,5-dimethyl-2,5-hexanediol (14.6 g, 100 mmol), and Et_3N (55.8 mL, 400 mmol). After the suspension was stirred at 0 °C in an ice bath for 5 min, trichloromethylsilane (11.7 mL, 100 mmol) was added to the mixture dropwise over 5 min at 0 °C. After the reaction mixture was stirred for 1 h at room temperature, the reaction mixture was cooled to 0 °C. Methanol (6.15 mL, 150 mmol) was slowly added to the flask and the resulting mixture was vigorously stirred for 12 h at room temperature. Pentane (500 mL) was added to the flask and the mixture was stirred for 1 min. The precipitate thus formed was filtered off by using a Büchner funnel and the filter cake was washed with pentane (200 mL). The filtrate was concentrated under reduced pressure, and hexane (100 mL) was added to the residue. Filtration and concentration were repeated once again. Distillation of the resulting residue under reduced pressure (80 °C / 18 Torr to 75 °C / 16 Torr) afforded **2-VII** as a colorless liquid (18.0 g, 82.4 mmol, 82%, d = 0.955 g cm^{-3}).

Preparation of Hydrosilanes (TP2, Scheme 1)

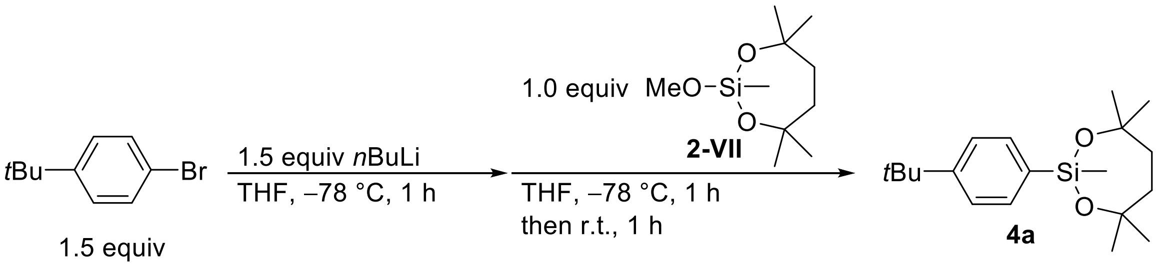


3-VII

The reaction of dichloromethylsilane with 2,5-dimethyl-2,5-hexanediol to afford **3-VII** is representative. An oven-dried 1-L double-necked flask was charged with CH_2Cl_2 (400 mL), 2,5-dimethyl-2,5-hexanediol (43.9 g, 300 mmol), and Et_3N (85.7 mL, 615 mmol). After the suspension was stirred at 0 °C in an ice bath for 5 min, dichloromethylsilane (30.8 mL, 300 mmol) was added dropwise over 5 min at 0 °C and the mixture was vigorously stirred for 1 h at room temperature. Pentane (300 mL) was added to the flask and the mixture was stirred for 1 min. The precipitate thus formed was filtered off by using a Büchner funnel and the filter cake was washed with pentane (100 mL). The filtrate was concentrated under reduced pressure, and then hexane (100 mL) was added to the residue. Filtration and concentration were repeated once again. Distillation of the resulting residue under reduced pressure (61 °C / 18 Torr) afforded **3-VII** as a colorless liquid (40.2 g, 213 mmol, 71%, d = 0.917 g cm^{-3}).

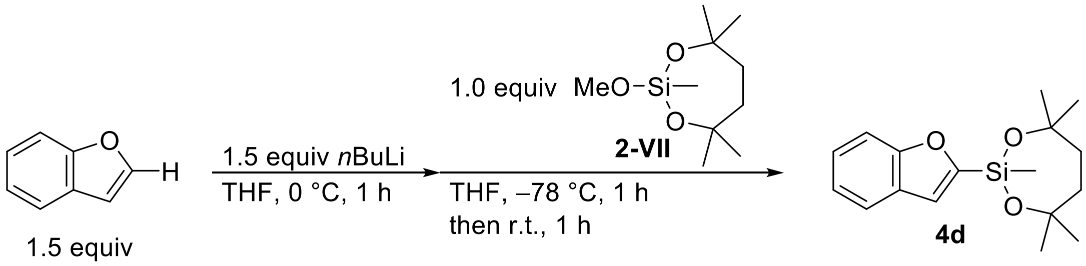
(*note*: The molar ratio of Et_3N to dichloromethylsilane is important to obtain satisfactorily pure hydrosilanes. When 2.1 equivalents of Et_3N was used, the product contained a small amount of Et_3N even after distillation.)

Preparation of Arylsilanes from Aryllithiums (TP3, Table 2)



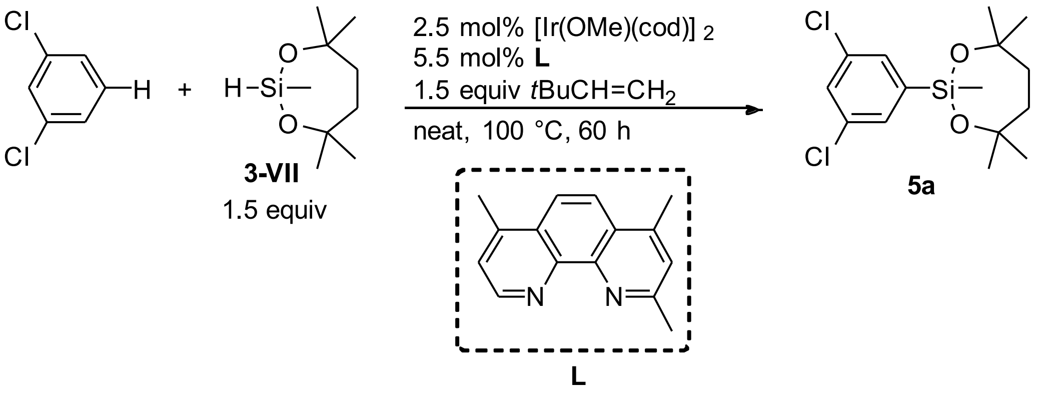
The reaction of 1-bromo-4-*tert*-butylbenzene to afford **4a** is representative. An oven-dried 200-mL double-necked flask was charged with 1-bromo-4-*tert*-butylbenzene (1.60 g, 7.50 mmol) and THF (30 mL). After the mixture was stirred at –78 ˚C in a dry ice bath for 5 min, *n*-butyllithium (1.60 M in hexane, 4.69 mL, 7.50 mmol) was added dropwise over 10 min at –78 ˚C and the resulting mixture was stirred at –78 ˚C for 1 h. **2-VII** (1.14 mL, 5.00 mmol) was added to the solution at –78 ˚C and the resulting mixture was stirred at –78 ˚C for 1 h. The flask was warmed to room temperature and stirring was continued for 1 h. The reaction mixture was poured into saturated aqueous NH_4Cl (30 mL), and the resulting biphasic solution was extracted with Et_2O three times (30 mL each). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel twice with an eluent (hexane/AcOEt = 20/1) to provide **4a** (1.53 g, 4.78 mmol, 96%) as a colorless oil.

Preparation of 4d from Benzofuran (Table 2)



An oven-dried 200-mL double-necked flask was charged with benzofuran (886 mg, 7.50 mmol) and THF (30 mL). After the mixture was stirred at 0 ˚C in an ice bath for 5 min, *n*-butyllithium (1.60 M in hexane, 4.69 mL, 7.50 mmol) was added dropwise over 10 min at 0 ˚C and the resulting mixture was stirred at 0 ˚C for 1 h. After the mixture was stirred at –78 ˚C in a dry ice bath for 5 min, **2-VII** (1.14 mL, 5.00 mmol) was added to the solution and the resulting mixture was stirred at –78 ˚C for 1 h. The flask was warmed to room temperature and stirring was continued for 1 h. The reaction mixture was poured into saturated aqueous NH_4Cl (30 mL), and the resulting biphasic solution was extracted with Et_2O three times (30 mL each). The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) to provide **4d** (1.26 g, 4.14 mmol, 83%) as a white solid.

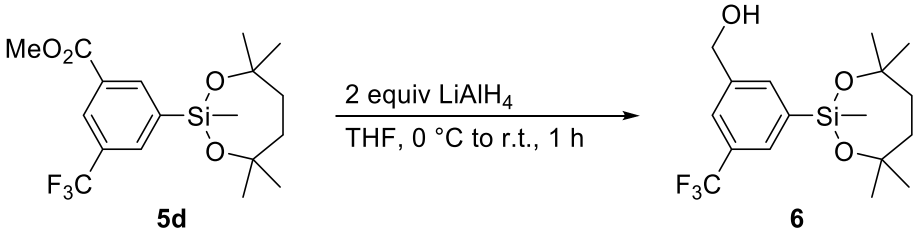
Iridium-Catalyzed C–H Silylation of Arenes with Hydrosilane 3-VII (TP4, Table 3)



The reaction of 1,3-dichlorobenzene to afford **5a** is representative. An oven-dried 20-mL Schlenk tube was charged with $[Ir(OMe)(cod)]_2$ (16.6 mg, 0.0250 mmol) and 2,4,7-trimethyl-1,10-phenanthroline (**L**, 12.2 mg, 0.0550 mmol). 3,3-Dimethyl-1-butene (126 mg, 1.50 mmol), *m*-dichlorobenzene (147 mg, 1.00 mmol), and hydrosilane **3-VII** (283 mg, 1.50 mmol) were sequentially added to the mixture. The resulting mixture was stirred at 100 °C for 60 h. After the Schlenk tube was allowed to cool to room temperature, the reaction mixture was passed through short silica gel and alumina pads (1 cm each) with Et_2O (50 mL) as an eluent (for products with polar functional groups, AcOEt was used as an eluent). The solution was concentrated under reduced pressure and the resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) to provide **5a** (299 mg, 0.898 mmol, 90%) as a white solid.

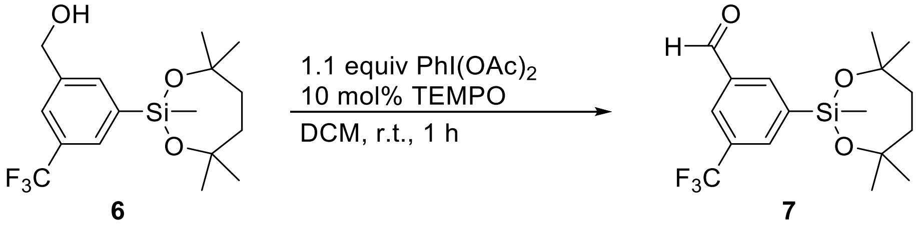
Transformations of Functionalities on Arylsilanes

Reduction of Ester 5d with $LiAlH_4$ (Scheme 2)



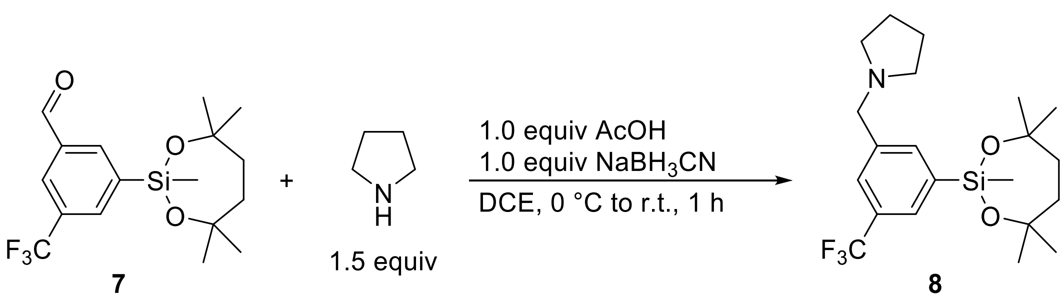
An oven-dried 20-mL Schlenk tube was charged with $LiAlH_4$ (228 mg, 6.00 mmol) and THF (4 mL). After the suspension was vigorously stirred at 0 ˚C in an ice bath for 5 min, a THF solution (2.0 mL) of **5d** (1.17 g, 3.00 mmol) was slowly added to the suspension at 0 ˚C. The resulting mixture was gradually warmed to room temperature and stirring was continued for 1 h. After cooling the mixture in an ice bath for 5 min, 0.24 mL of water was slowly added to the tube followed by additions of 0.24 mL of aqueous NaOH solution (15wt%) and 0.72 mL of water. After formation of fine alumina solid (30 min), the suspension was filtered with a celite pad (1 cm) and the filtrate was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 5/1) to provide **6** (929 mg, 2.56 mmol, 85%) as a colorless oil.

Oxidation of Alcohol 6 with PIDA/TEMPO (Scheme 2)



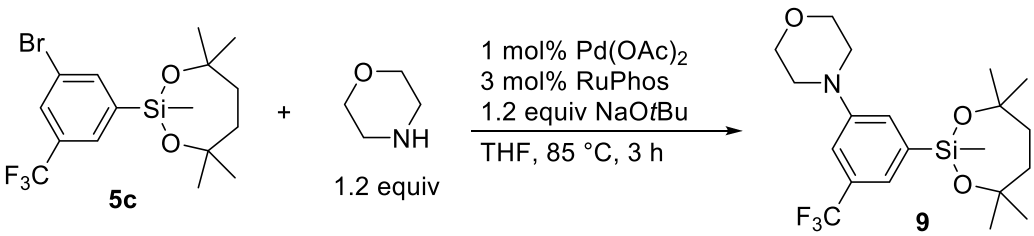
A 20-mL test tube was charged with **6** (427 mg, 1.18 mmol) and DCM (5.0 mL) under air. $PhI(OAc)_2$ (417 mg, 1.30 mmol) and TEMPO (18.4 mg, 0.118 mmol) were added slowly to the tube at room temperature and the resulting mixture was stirred for 1 h at the same temperature. The reaction mixture was quenched with saturated aqueous solutions of $Na_2S_2O_3$ (1 mL) and $NaHCO_3$ (1 mL), and the resulting mixture was extracted with DCM (20 mL) three times. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) to provide **7** (386 mg, 1.07 mmol, 91%) as a colorless oil.

Reductive Amination of Aldehyde 7 (Scheme 2)



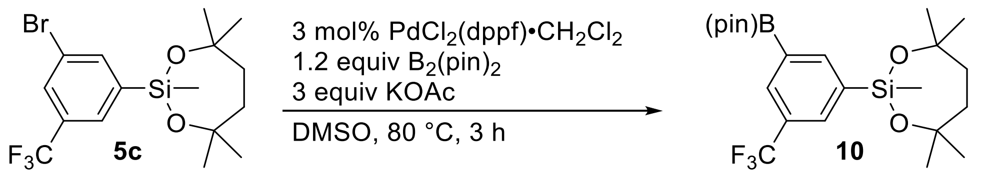
An oven-dried 20-mL Schlenk tube was charged with **7** (180 mg, 0.500 mmol) and DCE (2.5 mL). Pyrrolidine (62 µL, 0.75 mmol) and AcOH (28.6 µL, 0.500 mmol) were added to the solution. $NaBH_3CN$ (31.4 mg, 0.500 mmol) was added to the tube at room temperature portionwise over 1 min. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was partitioned between AcOEt (10 mL) and water (20 mL). The organic phase was collected and the aqueous phase was extracted with AcOEt (20 mL each) three times. The combined organic phase was dried over Na_2SO_4 and passed through a short alumina pad (1cm) with AcOEt (30 mL). The filtrate was concentrated under reduced pressure, and the resulting residue was purified by column chromatography on silica gel with an eluent ($CHCl_3$/MeOH = 20/1) to provide **8** (183 mg, 0.439 mmol, 88%) as a colorless oil.

Buchwald-Hartwig Amination (Scheme 2)



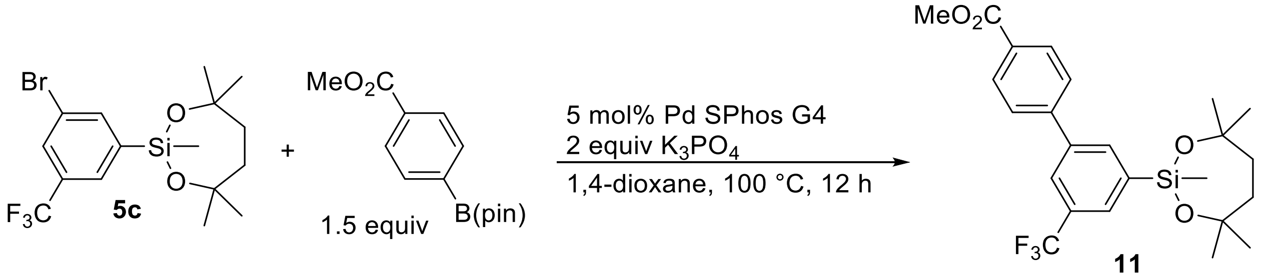
An oven-dried 20-mL Schlenk tube was charged with **5c** (206 mg, 0.500 mmol), $Pd(OAc)_2$ (1.1 mg, 0.0050 mmol), RuPhos (7.0 mg, 0.015 mmol), and NaO*t*Bu (57.7 mg, 0.600 mmol). THF (1.0 mL) and morpholine (52.3 mg, 0.600 mmol) were added to the tube and the resulting mixture was stirred at 85 ˚C for 3 h. The reaction mixture was quenched by pouring to water (10 mL) and partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) three times. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1) to provide **9** (182 mg, 0.437 mmol, 87%) as a colorless oil.

Ishiyama–Miyaura Borylation (Scheme 2)



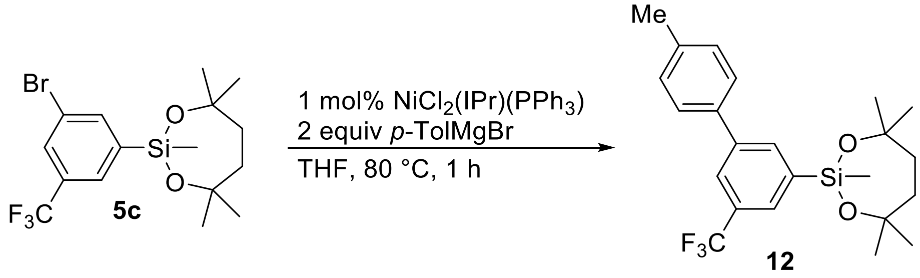
An oven-dried 100-mL Schlenk tube was charged with **5c** (1.65 g, 4.00 mmol), $PdCl_2(dppf){\bullet}CH_2Cl_2$ (98.0 mg, 0.120 mmol), $B_2(pin)_2$ (1.219 mg, 4.80 mmol), and KOAc (1.18 mg, 12.0 mmol). DMSO (25 mL) was added to the tube and the resulting mixture was stirred at 80 ˚C for 3 h. The reaction mixture was quenched by pouring to water (10 mL) and partitioned. The organic phase was collected and the resulting mixture was extracted with Et_2O (30 mL each) three times. The combined organic phase was washed with water and dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) to provide **10** (1.37 g, 2.98 mmol, 75%) as a white solid.

Suzuki-Miyaura Cross-Coupling (Scheme 2)



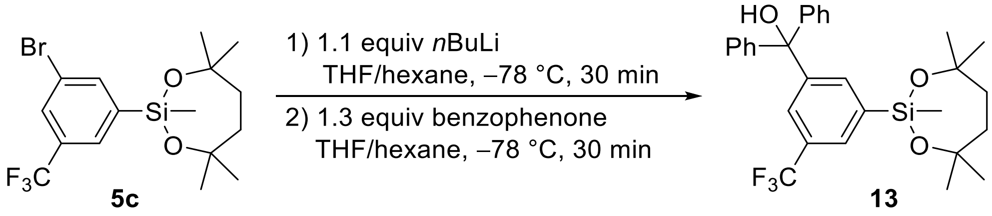
An oven-dried 20-mL Schlenk tube was charged with **5c** (206 mg, 0.500 mmol), methyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (197 mg, 0.750 mmol), K_3PO_4 (212 mg, 1.00 mmol), Pd SPhos G4 (19.9 mg, 0.0250 mmol), and 1,4-dioxane (2.0 mL). The reaction mixture was stirred at 100 ˚C for 12 h. The reaction mixture was quenched by saturated aqueous NH_4Cl (10 mL). AcOEt (20 mL) was added to the mixture and partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) to provide **11** (175 mg, 0.375 mmol, 75%) as a white solid.

Kumada-Tamao Cross-Coupling (Scheme 2)



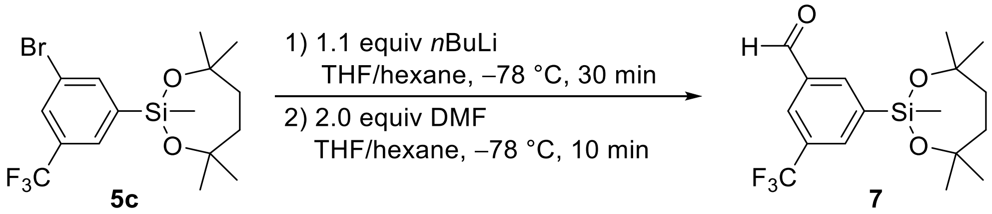
An oven-dried 20-mL Schlenk tube was charged with **5c** (206 mg, 0.500 mmol), $NiCl_2(IPr)(PPh_3)$ (3.9 mg, 0.0050 mmol), and THF (0.50 mL). After the mixture was stirred at room temperature for 1 min, *p*-TolMgBr in THF (0.89 M, 1.12 mL, 1.00 mmol) was added to the tube and the resulting mixture was stirred at 80 ˚C for 1 h. The reaction was terminated upon an addition of saturated aqueous NH_4Cl (10 mL). AcOEt (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 50/1) to provide **12** (178 mg, 0.420 mmol, 84%) as a colorless oil.

Generation of Aryllithium Followed by Trapping with Benzophenone (Scheme 2)



An oven-dried 20-mL Schlenk tube was charged with **5c** (823 mg, 2.00 mmol) and THF (5.0 mL). After the resulting solution was stirred at –78 ˚C in a dry ice bath for 10 min and *n*-butyllithium (1.58 M in hexane, 1.39 mL, 2.20 mmol) was added to the mixture at –78 ˚C dropwise over 5 min. The mixture was stirred at –78 ˚C for 30 min and a THF solution (3 mL) of benzophenone (474 mg, 2.60 mmol) was slowly added to the tube at –78 ˚C. After the resulting mixture was stirred at –78 ˚C for 30 min, the tube was slowly warmed to room temperature. The reaction mixture was quenched by saturated aqueous NH_4Cl (10 mL). AcOEt (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1) then by GPC with $CHCl_3$ to provide **13** (886 mg, 1.72 mmol, 86%) as a colorless oil.

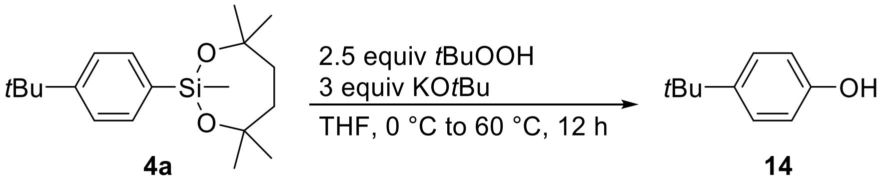
Generation of Aryllithium Followed by Trapping with DMF (Scheme 2)



An oven-dried 20-mL Schlenk tube was charged with **5c** (826 mg, 2.03 mmol) and THF (5.0 mL). After the resulting solution was stirred at –78 ˚C in a dry ice bath for 10 min and *n*-butyllithium (1.58 M in hexane, 1.39 mL, 2.20 mmol) to the mixture at –78 ˚C dropwise over 5 min. The mixture was stirred at –78 ˚C for 30 min and DMF (0.310 mL, 4.00 mmol) was slowly added to the tube at –78 ˚C. After the resulting mixture was stirred at –78 ˚C for 10 min, the tube was slowly warmed to room temperature. The reaction mixture was quenched by saturated aqueous NH_4Cl (20 mL). AcOEt (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) to provide **7** (653 mg, 1.81 mmol, 89%) as a colorless oil.

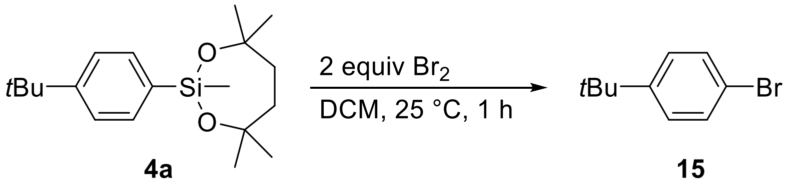
Transformations of Silicon Functionalities on Arylsilanes

Tamao-Fleming Oxidation of 4a (Scheme 3)



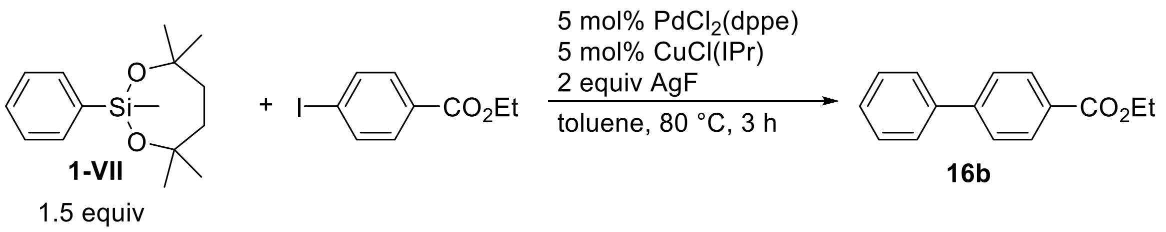
An oven-dried 20-mL Schlenk tube was charged with KO*t*Bu (168 mg, 1.50 mmol) and THF (3.0 mL). *tert*-Butyl hydroperoxide (5.5 M in octane, 0.23 mL, 1.3 mmol) and **4a** (160 mg, 0.500 mmol) were added to the mixture at 0 °C and the resulting mixture was stirred at 60 °C. After 12 h, saturated aqueous $NaHSO_3$ (5 mL), 4 M HCl (2 mL), and water (20 mL) were added to the reaction mixture. AcOEt (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The combined organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1) to provide 4-*tert*-butylphenol (**14**, 70.7 mg, 0.471 mmol, 94%) as a white solid.

Bromodesilylation of 4a (Scheme 3)



A vial tube was charged with **4a** (321 mg, 1.00 mmol) and DCM (3.0 mL) under air. After addition of Br_2 (103 µL, 2.00 mmol) to the solution at 25 °C, the resulting mixture was stirred for 1 h. Saturated aqueous $NaHCO_3$ (10 mL), saturated aqueous $Na_2S_2O_3$ (10 mL), and water (10 mL) were added to the reaction mixture. DCM (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with DCM (20 mL each) twice. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane only) to provide 1-bromo-4-*tert*-butylbenzene (**15**, 176 mg, 0.828 mmol, 83%) as a colorless oil.

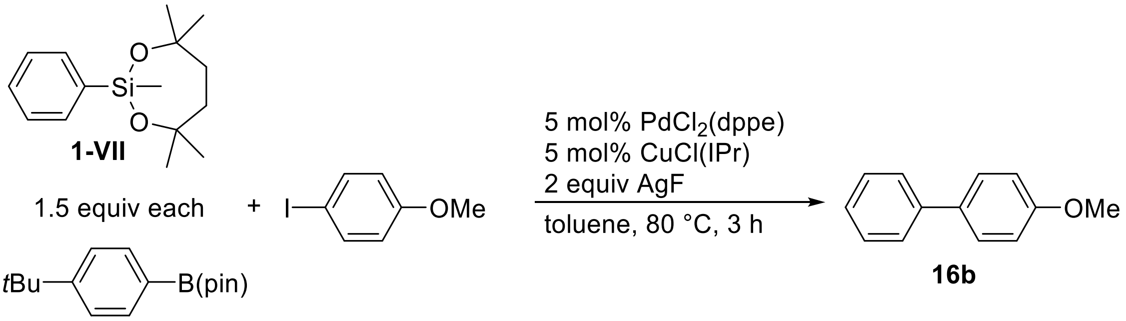
Typical Procedure for Hiyama Cross-Coupling Reactions (TP5, Table 6)



The reaction of **1-VII** with ethyl 4-iodobenzoate is representative. An oven-dried 20-mL Schlenk tube was charged with $PdCl_2(dppe)$ (14.4 mg, 0.0250 mmol), CuCl(IPr) (12.2 mg, 0.0250 mmol), AgF (127 mg, 1.00 mmol), and toluene (2 mL). **1-VII** (198 mg, 0.750 mmol) and ethyl 4-iodobenzoate (138 mg, 0.500 mmol) were added to the tube, and toluene (1 mL) was then added to wash the inner side of tube. The resulting mixture was stirred at 60 °C for 3 h. After the tube was cooled to room temperature, the reaction mixture was passed through short silica gel and alumina pads (1 cm each) with Et_2O (50 mL) as an eluent. The resulting solution was concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1) to provide **16b** (105 mg, 0.462 mmol, 92%) as a white solid.

Orthogonality between VII and B(pin) (Scheme 4)

Selective Hiyama Cross-Coupling Reactions



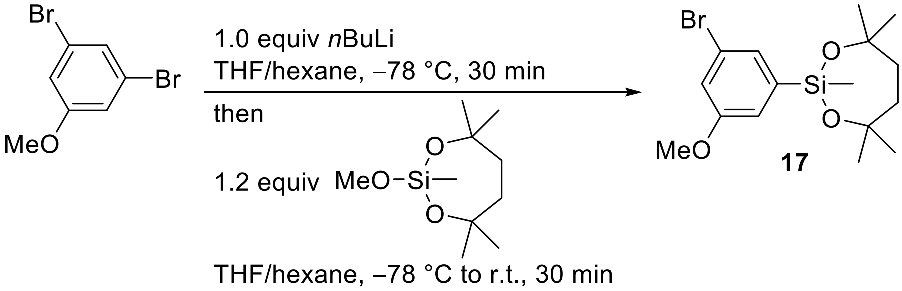
The reaction of 4-iodoanisole in the presence of **1-VII** and (4-*tert*-butylphenyl)boronic acid pinacol ester is representative. An oven-dried 20-mL Schlenk tube was charged with $PdCl_2$(dppe) (28.8 mg, 0.0500 mmol), CuCl(IPr) (24.4 mg, 0.0500 mmol), AgF (254 mg, 2.00 mmol), 4-iodoanisole (234 mg, 1.00 mmol), (4-*tert*-butylphenyl)boronic acid pinacol ester (390 mg, 1.50 mmol) and toluene (3 mL). **1-VII** (397 mg, 1.50 mmol) was added to the tube, and toluene (1 mL) was then added to wash the inner side of tube. The resulting mixture was stirred at 80 ˚C for 3 h. After the tube was cooled to room temperature, the reaction mixture was passed through short silica gel and alumina pads (1 cm each) with Et_2O (50 mL) as an eluent. The resulting solution was concentrated under reduced pressure. The resulting residue was analyzed by ^{1}H NMR with mesitylene (40.0 μL) as an internal standard.

Selective Suzuki–Miyaura Cross-Coupling Reactions

The reaction of 4-iodoanisole in the presence of **1-VII** and (4-*tert*-butylphenyl)boronic acid pinacol ester is representative. An oven-dried 20-mL Schlenk tube was charged with $PdCl_2(dppf)\cdot CH_2Cl_2$ (40.8 mg, 0.0500 mmol), CsF (304 mg, 2.00 mmol), 4-iodoanisole (234 mg, 1.00 mmol), (4-*tert*-butylphenyl)boronic acid pinacol ester (390 mg, 1.50 mmol) and DMF (4 mL). **1-VII** (397 mg, 1.50 mmol) was added to the tube, and DMF (2 mL) was then added to wash the inner side of tube. The resulting mixture was stirred at 60 ˚C for 5 h. After the tube was cooled to room temperature, saturated aqueous NH_4Cl (10 mL) and water (20 mL) were added to the reaction mixture. Et_2O (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with Et_2O (20 mL each) twice. The combined organic phase was washed with water and dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was analyzed by ^{1}H NMR with mesitylene (40.0 µL) as an internal standard.

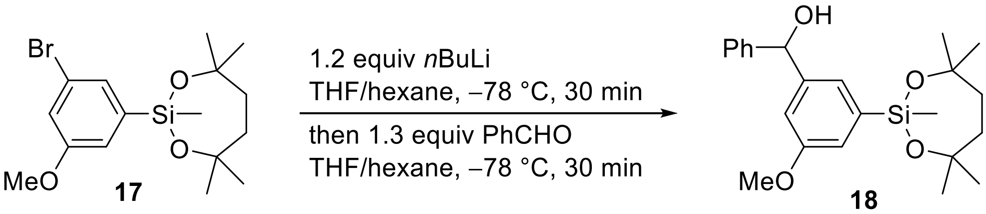
Three-Step Synthesis of 19 (Scheme 5)

Generation of Aryllithium from 3,5-Dibromoanisole to Afford 17



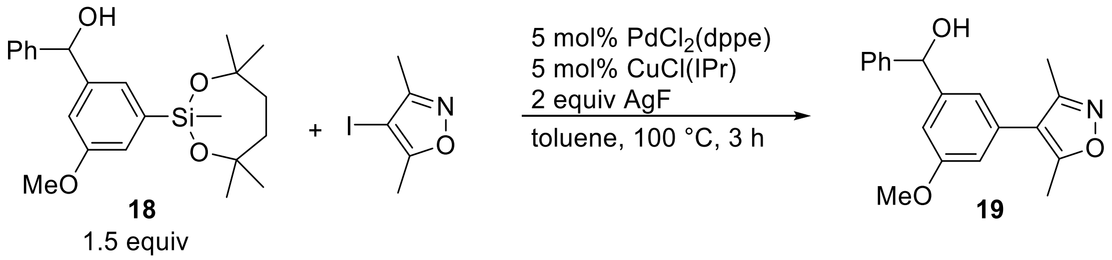
An oven-dried 100-mL Schlenk tube was charged with 3,5-dibromoanisole (1.56 g, 6.00 mmol) and THF (15 mL). The resulting solution was stirred at –78 ˚C in a dry ice bath for 10 min. After addition of *n*-butyllithium (1.60 M in hexane, 3.75 mL, 6.00 mmol) to the mixture at –78 ˚C dropwise over 5 min, the mixture was stirred for 30 min at –78 ˚C. **2-VII** (1.65 mL, 7.20 mmol) was added to the tube at –78 ˚C and the resulting mixture was slowly warmed to room temperature and stirred for 30 min. The reaction mixture was quenched by saturated aqueous NH_4Cl (20 mL). AcOEt (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The resulting residue was purified by column chromatography twice with eluents (hexane/AcOEt = 20/1, then hexane/$CHCl_3$ = 2/1) to provide **17** (1.08 g, 2.90 mmol, 48%) as a white solid.

Generation of Aryllithium from 17 to Afford 18



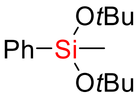
An oven-dried 20-mL Schlenk tube was charged with **17** (747 mg, 2.00 mmol) and THF (6.0 mL). The resulting solution was stirred at –78 ˚C in a dry ice bath for 10 min. After addition of *n*-butyllithium (1.60 M in hexane, 1.50 mL, 2.40 mmol) to the mixture at –78 ˚C dropwise over 5 min, the mixture was stirred for 30 min at –78 ˚C. Benzaldehyde (0.265 mL, 2.60 mmol) was added to the tube at –78 ˚C and the resulting mixture was stirred for 30 min. The reaction mixture was quenched by saturated aqueous NH_4Cl (20 mL). AcOEt (20 mL) was added to the mixture and the mixture was partitioned. The organic phase was collected and the resulting mixture was extracted with AcOEt (20 mL each) twice. The resulting residue was purified by column chromatography with an eluent (hexane/AcOEt = 4/1) and GPC ($CHCl_3$) to provide **18** (776 mg, 1.94 mmol, 97%) as a colorless oil.

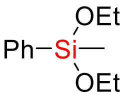
Hiyama Cross-Coupling of 18 to Afford 19

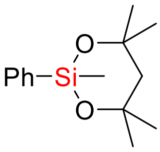


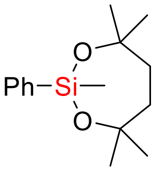
Following **TP5** for Hiyama cross-coupling, **19** was synthesized from **18** (300 mg, 0.750 mmol) and 4-iodo-3,5-dimethylisoxazole (112 mg, 0.500 mmol) and purified by column chromatography with an eluent (hexane/AcOEt = 2/1) to provide **19** (106 mg, 0.344 mmol, 69%) as a colorless oil.

^{29}Si NMR Chemical Shifts of Dialkoxyphenylsilanes









	1-III	**1-IV**	**1-VI**	**1-VII**
δ (ppm, in $CDCl_3$)	–17.8	–33.0	–17.9	–23.2

Details of NMR Experiments for Time-Course of Hydrolysis under Basic Conditions

An NMR tube were charged with acetonitrile-d_3 (0.60 mL), a phenylsilane (0.050 mmol), and 1,3,5-trimethoxybenzene (ca. 3.4 mg, ca. 20 μmol) as an internal standard. After an addition of aqueous solution of NaOD (0.10 M, 50 μL), ^{1}H NMR spectra of the resulting solution were recorded at regular intervals (*t* = 5, 35, 65… min) and the remaining phenylsilane was quantified from the ratio of the silane to the internal standard.

Figure S1. Time-Course of Hydrolysis of Trialkoxyphenylsilanes (PhSi(OMe)$_3$, **1-I**, and **1-II**).

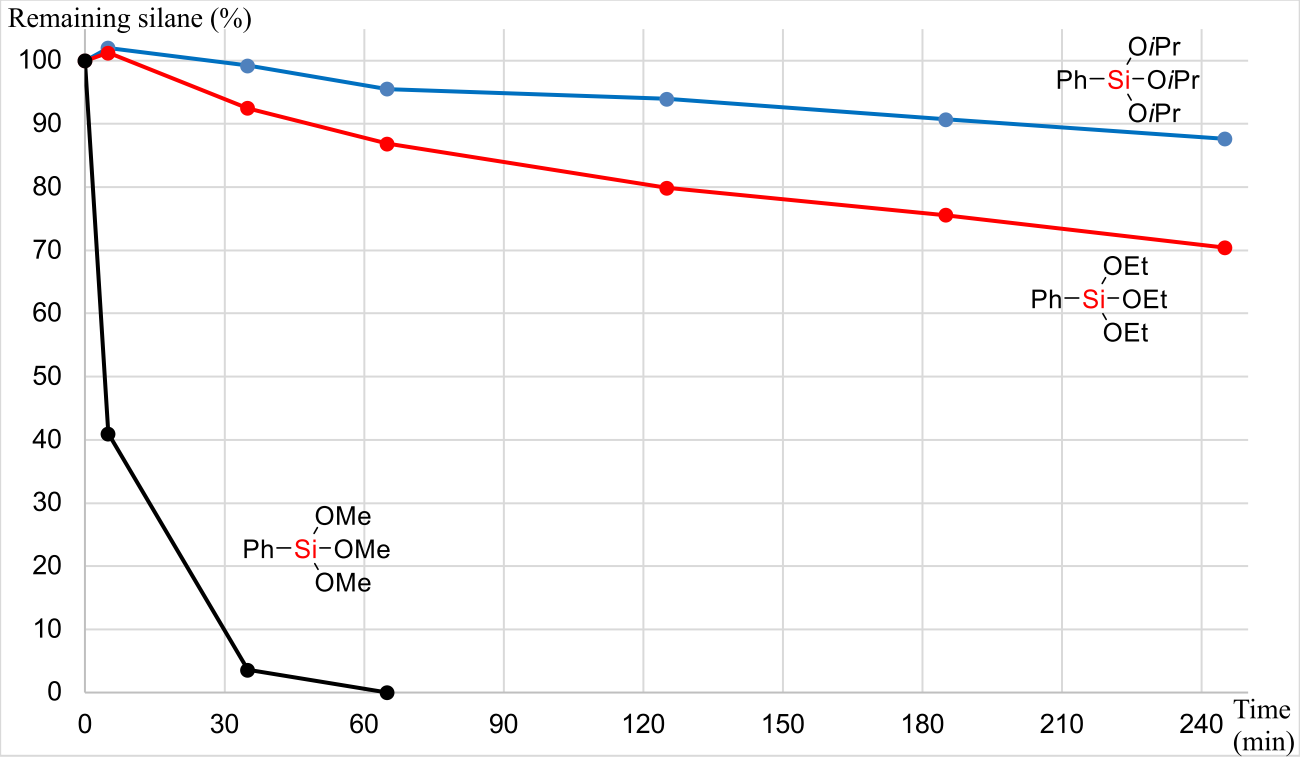
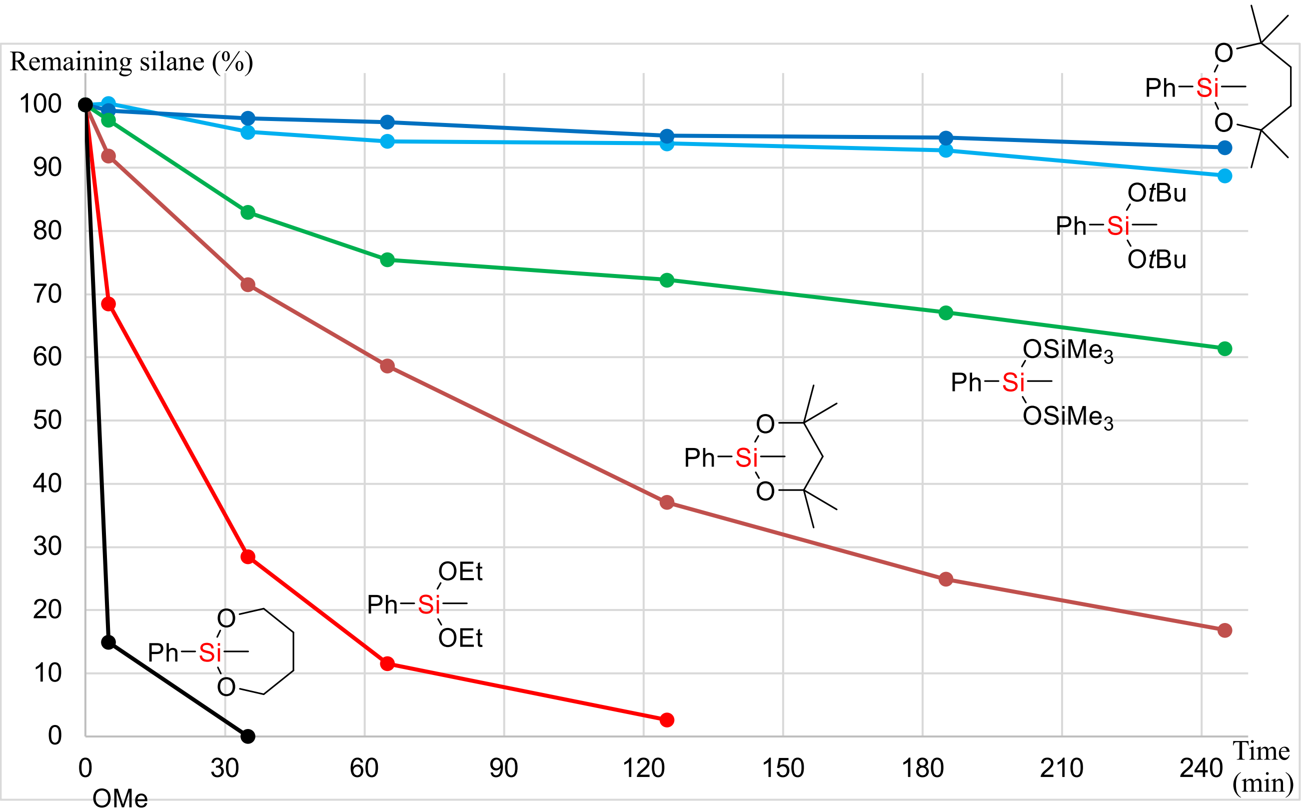
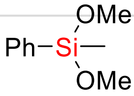


Figure S2. Time-Course of Hydrolysis of Dialkoxyphenylsilanes and a Disiloxyphenylsilane (**1-III**–**1-VIII**).

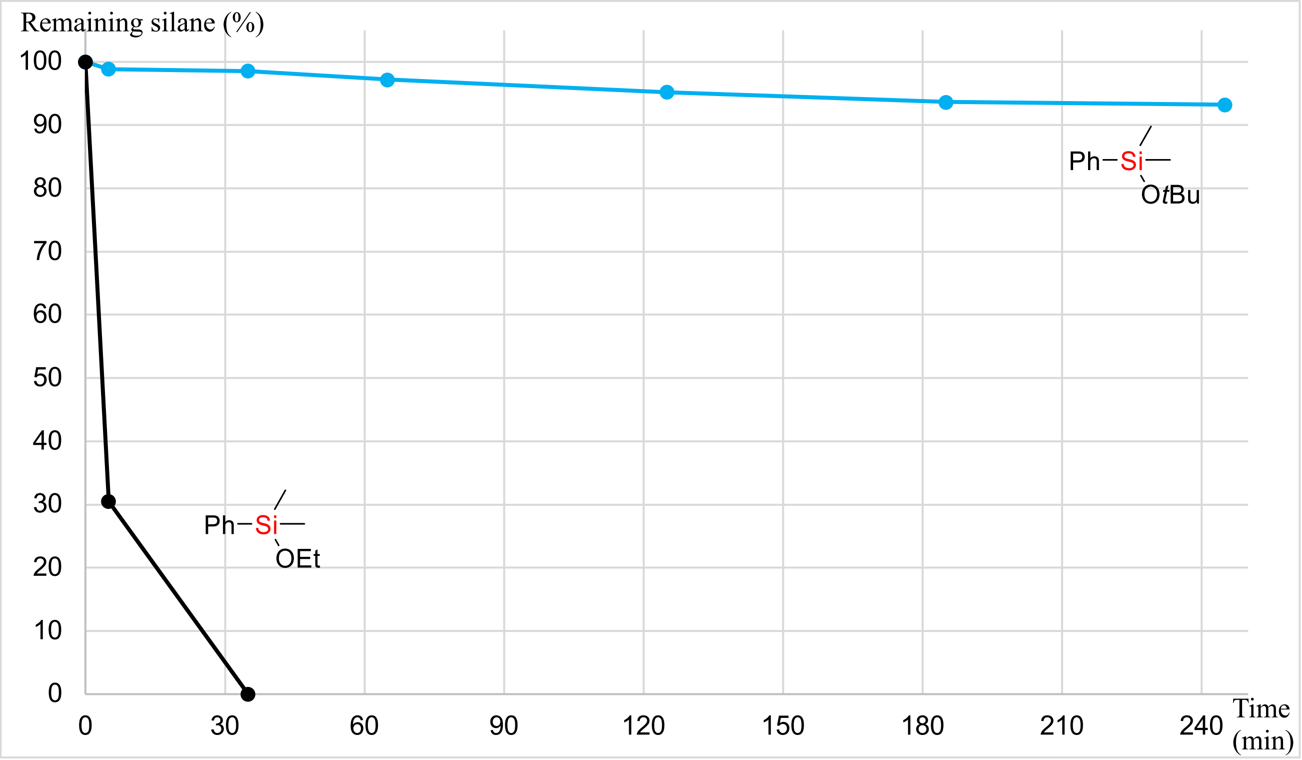




$\mathrm{Ph{-}Si(Me)(OMe)_2}$

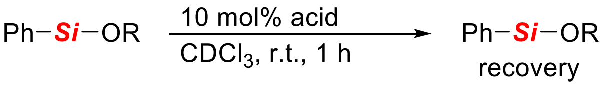
decomposed within 5 min.

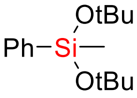
Figure S3. Time-Course of Hydrolysis of Monoalkoxyphenylsilanes (**1-IX** and **1-X**).

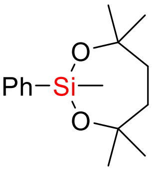


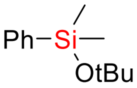
Details of NMR Experiments for Decomposition under Acidic Conditions

An NMR tube were charged with $CDCl_3$ (0.30 mL), a phenylsilane (0.050 mmol), and mesitylene (ca. 2.8 μL, ca. 20 µmol) as an internal standard. A solution of acid (0.0050 mmol) in $CDCl_3$ (0.3 mL) was added to the tube and the resulting solution was left at room temperature for 1 h. ^{1}H NMR spectra of the resulting solution were recorded and the remaining phenylsilane was quantified from the ratio of the silane to the internal standard.









recovery	**1-III**	**1-VII**	**1-IX**
TFA	89%	100%	48%
MsOH	61%	89%	33%

X-ray Crystallography

X-ray data were taken at –180 °C with a Rigaku XtaLAB P-200 system by using graphite monochromatic Cu-Kα radiation (λ = 1.54187 Å). The structures were solved by using direct method SHLEXS-2013/1 and refined by SHELXL-2014/7 program.[2] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically.

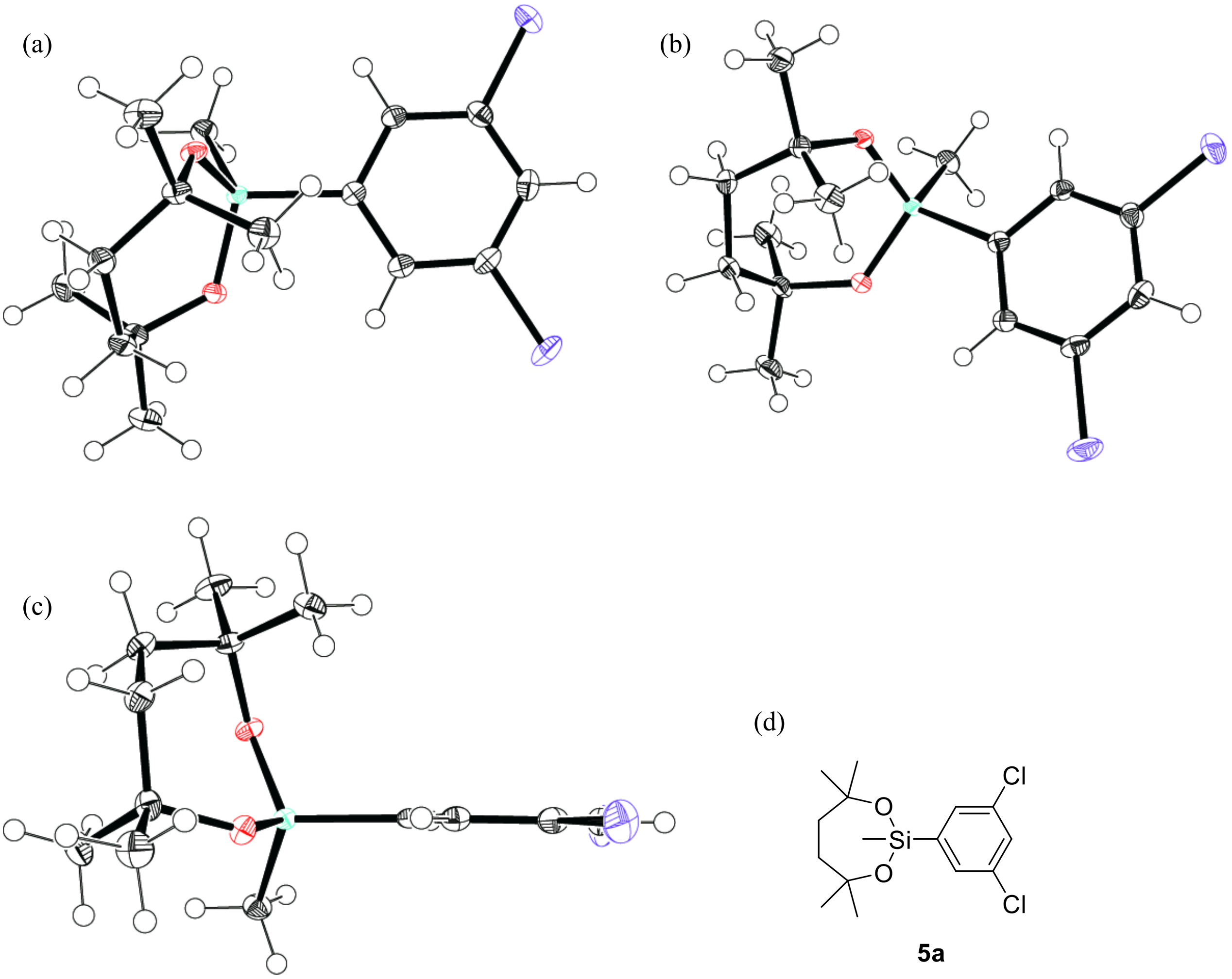


Figure S4. ORTEP representation of the crystal structure of **5a** (thermal ellipsoid at 50% probability). (a) Top view. (b) Over view. (c) Side view. (color code: white = hydrogen; black = carbon; purple = chlorine; green = silicon; red = oxygen). (d) Structure of **5a**

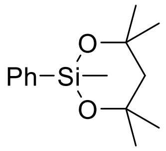
Table S1. Crystal parameters and structural refinement data for **5a**.

Compound	**5a**
Formula	$C_{15}H_{22}Cl_2O_2Si$
Solvent	hexane (solvent removal)
Formula weight	333.32
Temperature / K	93
λ (Å)	1.54187
Crystal size / mm^3	0.240×0.220×0.010
Crystal system	Monoclinic
Space group	$P2_1/c$
a / Å	8.3456(10)
b / Å	24.203(4)
c / Å	8.4795(11)
α / °	90
β / °	95.737(4)
γ / °	90
V / Å^3	170402(4)
Z	4
μ mm^{-1}	4.089
$D_{calcd.}$ / g·cm^{-3}	1.299
θ_{max}	68.422
Refl./restr./param.	11522/0/186
Completeness	0.995
GOF	1.095
R_1 ($I > 2\sigma(I)$)	0.0252
wR_2 ($I > 2\sigma(I)$)	0.0693
R_1 (all data)	0.0268
wR_2 (all data)	0.0700
Largest diff. peak and hole /e·Å^{-3}	0.295, –0.307
CCDC number	1966652

Characterization of Compounds

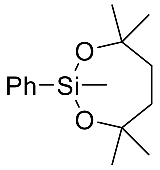
Phenylsilanes

2,4,4,6,6-Pentamethyl-2-phenyl-1,3,2-dioxasilinane (1-VI)



Colorless liquid (19.7 g, 78.7 mmol, 79%) from dichloromethylphenylsilane (19.1 g, 100 mmol) by following **TP1**. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66–7.65 (m, 2H), 7.39–7.35 (m, 3H), 1.90 (d, J = 14.1 Hz, 1H), 1.88 (d, J = 14.1 Hz, 1H), 1.45 (s, 6H), 1.33 (s, 6H), 0.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 137.6, 133.4, 129.6, 127.6, 73.2, 51.6, 32.6, 32.3, 0.3; ^{29}Si NMR (119 MHz, $CDCl_3$): δ –23.2; HRMS calcd for $C_{13}H_{19}O_2Si$ [(M–CH_3)$^+$]: 235.1149, found: 235.1140; b.p. 78 °C / 1 torr; d = 1.00 g cm^{-3}

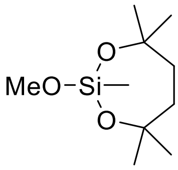
2-Phenyl-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (1-VII)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 7.5 Hz, 2H), 7.36–7.32 (m, 3H), 1.82 (br, 4H), 1.34 (s, 6H), 1.21 (s, 6H), 0.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 138.5, 133.6, 129.2, 127.4, 74.8, 37.9, 30.6 (br, four methyl groups), 0.6; ^{29}Si NMR (119 MHz, $CDCl_3$): δ –17.9. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[3]

Methoxysilane

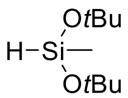
2-Methoxy-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (2-VII):



^{1}H NMR (600 MHz, $CDCl_3$): δ 3.48 (s, 3H), 1.78 (br, 4H), 1.31 (s, 6H), 1.27 (s, 6H), 0.09 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 73.9, 49.8, 37.4, 30.2 (br, four methyl groups), –4.9; HRMS calcd for $C_{10}H_{22}O_3Si$ [M$^+$]: 218.1333, found: 218.1335.

Hydrosilanes

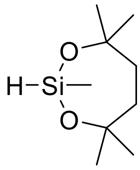
Di-*tert*-butoxydimethylsilane (3-III):



$H\text{–}Si(OtBu)_2\text{–}$

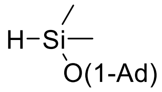
Colorless liquid (13.1 g, 68.8 mmol, 69%) from *tert*-butyl alcohol (14.8 g, 200 mmol) by following **TP2**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.80 (br, 1H), 1.31 (s, 18H), 0.18 (d, J = 1.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 72.8, 31.6, 1.5. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[4]

2,4,4,7,7-Pentamethyl-1,3,2-dioxasilepane (3-VII):



^{1}H NMR (600 MHz, $CDCl_3$): δ 4.71 (q, J = 1.8 Hz, 1H), 1.79 (br, 4H), 1.31 (s, 6H), 1.28 (s, 6H), 0.15 (d, J = 1.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 74.6, 37.7, 30.6 (br, two methyl groups), 29.4 (br, two methyl groups), –0.7; HRMS calcd for $C_9H_{19}O_2Si$ [(M–H)$^+$]: 187.1149, found: 187.1141.

(1-Adamantyloxy)dimethylsilane (3-XI):

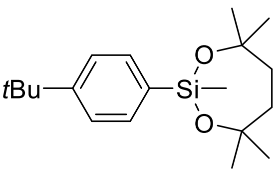


1-Ad: 1-adamantyl

White wet solid (16.5 g, 78.5 mmol, 79%) from 1-adamantanol (15.2 g, 100 mmol) and chlorodimethylsilane (9.45 g, 100 mmol) by following **TP2**. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.79 (septet, J = 2.7 Hz, 1H), 2.12 (br, 3H), 1.79 (d, J = 2.7 Hz, 6H), 1.63–1.58 (m, 6H), 0.19 (d, J = 2.7 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 71.6, 45.4, 36.2, 30.9, 1.0; HRMS calcd for $C_{12}H_{21}OSi$ [$(M–H)^+$]: 209.1356, found: 209.1352; b.p. 68 °C / 2 torr.

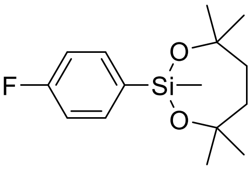
Silylation Products

2-(4-*tert*-Butylphenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (4a):



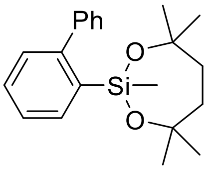
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 1.81 (br, 4H), 1.33 (s, 6H), 1.31 (s, 9H), 1.21 (s, 6H), 0.30 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 152.0, 134.9, 133.5, 124.4, 74.6, 37.9, 34.6, 31.3, 30.7 (br, four methyl groups), 0.8; HRMS calcd for $C_{19}H_{32}O_2Si$ [M^+]: 320.2166, found: 320.2178.

2-(4-Fluorophenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (4b):



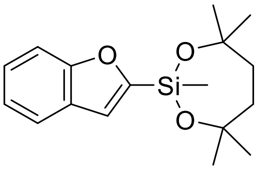
Colorless oil (1.08 g, 3.82 mmol, 76%) from 1-bromo-4-fluorobenzene (1.31 g, 7.50 mmol) by following **TP3**. Purification was done by column chromatography on silica gel twice with eluents (hexane/AcOEt = 20/1, then hexane/$CHCl_3$ = 4/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.64–7.62 (m, 2H), 7.03 (dd, J = 8.9, 8.9 Hz, 2H), 1.81 (br, 4H), 1.35 (s, 6H), 1.21 (s, 6H), 0.31 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 163.9 (d, J = 247.5 Hz), 135.7 (d, J = 7.2 Hz), 134.2 (d, J = 2.9 Hz), 114.6 (d, J = 18.9 Hz), 75.0, 37.9, 30.6 (br, four methyl groups), 0.7; HRMS calcd for $C_{15}H_{23}FO_2Si$ [M^+]: 282.1453, found: 282.1446.

2-([1,1'-Biphenyl]-2-yl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (4c):



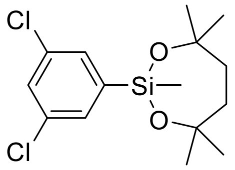
Colorless oil (988 mg, 2.90 mmol, 58%) from 2-bromobiphenyl (1.75 g, 7.50 mmol) by following **TP3** with some modification that TMEDA (1.12 mL, 7.50 mmol) was added before lithiation. Purification was done by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 (dd, J = 7.5, 1.4 Hz, 1H), 7.53–7.51 (m, 2H), 7.44–7.35 (m, 5H), 7.29 (dd, J = 7.8, 1.8 Hz, 1H), 1.81 (br, 4H), 1.31 (s, 6H), 1.27 (s, 6H), –0.20 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.6, 144.1, 136.6, 135.3, 129.8, 129.5, 122.2, 127.5, 126.9, 126.0, 74.8, 38.1, 30.5 (br, four methyl groups), 1.5; HRMS calcd for $C_{21}H_{28}O_2Si$ [M^+]: 340.1861, found: 340.1853.

2-(2-Benzofuryl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (4d):



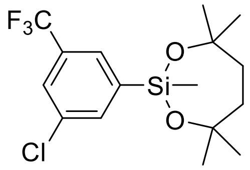
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, J = 7.5 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.30–7.27 (m, 1H), 7.20 (dd, J = 7.5, 7.5 Hz, 1H), 7.09 (s, 1H), 1.86 (br, 4H), 1.35 (s, 6H), 1.29 (s, 6H), 0.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.4, 157.8, 127.7, 124.5, 122.3, 121.3, 117.3, 111.5, 75.6, 37.7, 30.7 (br, two methyl groups), 29.9 (br, two methyl groups), –0.2; HRMS calcd for $C_{17}H_{24}O_3Si$ [M^+]: 304.1489, found: 304.1489.

2-(3,5-dichlorophenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (5a):



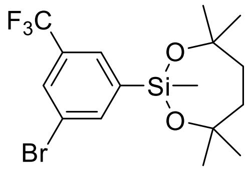
White solid (299 mg, 0.898 mmol, 90%) from *m*-dichlorobenzene (147.0 mg, 1.00 mmol) by following **TP4**. Purification was done by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.45 (d, J = 1.8 Hz, 2H), 7.33 (t, J = 1.8 Hz, 1H), 1.80 (brs, 4H), 1.34 (s, 6H), 1.21 (s, 6H), 0.28 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 143.0, 134.5, 131.6, 129.2, 75.4, 37.9, 30.5 (br, four methyl groups), 0.5; HRMS calcd for $C_{15}H_{22}{}^{35}Cl_2O_2Si$ [M$^+$]: 332.0761, found: 332.0767; m.p. 66.0–68.5 °C (after recrystallization from hexane).

2-(3-Chloro-5-(trifluoromethyl)phenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (5b):



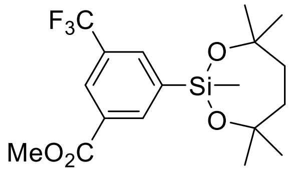
White solid (342 mg, 0.931 mmol, 93%) from 3-chlorobenzotrifluoride (181 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.75 (d, J = 1.2 Hz, 1H), 7.74 (d, J = 1.2 Hz, 1H), 7.58 (brs, 1H), 1.81 (br, 4H), 1.35 (s, 6H), 1.20 (s, 6H), 0.31 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 142.7, 136.8, 134.4, 131.5 (q, J = 31.9 Hz), 128.2 (d, J = 4.2 Hz), 126.2, 123.6 (q, J = 273.6 Hz), 75.6, 37.9, 30.5 (br, four methyl groups), 0.5; HRMS calcd for $C_{16}H_{22}{}^{35}ClF_3O_2Si$ [M$^+$]: 332.0761, found: 332.0767.

2-(3-Bromo-5-(trifluoromethyl)phenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (5c):



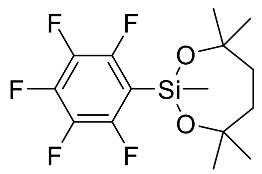
White solid (367 mg, 89.2 mmol, 89%) from 3-bromobenzotrifluoride (225 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (hexane/dichloromethane = 50/1). In a gram-scale synthesis, **5c** (3.40 g, 8.28 mmol, 83%) was obtained from 3-bromobenzotrifluoride (2.25 g, 10.0 mmol), [Ir(OMe)(cod)]$_2$ (66.3 mg, 0.100 mmol), the ligand (48.9 mg, 0.220 mmol), and 3,3-dimethyl-1-butene (1.26 g, 15.0 mmol) following **TP4**. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.90 (brs, 1H), 7.78 (brs, 1H), 7.73 (brs, 1H), 1.81 (s, 4H), 1.35 (s, 6H), 1.20 (s, 6H), 0.30 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 143.0, 139.7, 131.6 (q, J = 33.4 Hz), 129.1 (d, J = 4.4 Hz), 128.7 (d, J = 3.0 Hz), 123.4 (q, J = 273.5 Hz), 122.6, 75.6, 37.9, 30.5 (br, four methyl groups), 0.5; HRMS calcd for $C_{16}H_{22}{}^{79}BrF_3O_2Si$ [M$^+$]: 410.0519, found: 410.0520.

Methyl 3-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)-5-(trifluoromethyl)benzoate (5d):



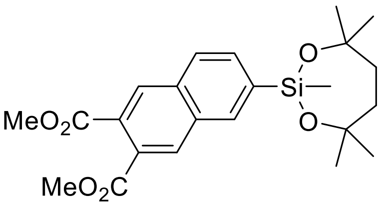
Pale yellow oil (272 g, 0.697 mmol, 70%) from ethyl 3-trifluoromethylbenzoate (204 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (hexane/dichloromethane = 4/1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.47 (s, 1H), 8.27 (s, 1H), 8.06 (s, 1H), 3.96 (s, 3H), 1.82 (br, 4H), 1.35 (s, 6H), 1.20 (s, 6H), 0.33 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 166.2, 140.9, 137.9, 134.4 (d, J = 2.9 Hz), 130.1 (q, J = 31.9 Hz), 129.9, 127.2 (d, J = 2.9 Hz), 124.0 (q, J = 273.5 Hz), 75.5, 52.4, 37.9, 30.5 (br, four methyl groups), 0.6; HRMS calcd for $C_{17}H_{22}F_3O_4Si$ [(M–CH$_3$)$^+$]: 375.1234, found: 375.1235.

2-Pentafluorophenyl-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (5e):



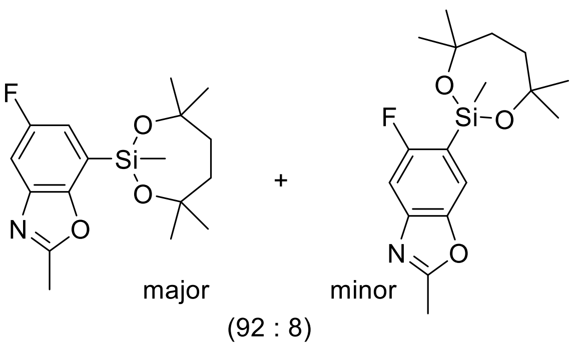
Colorless oil (350 mg, 0.988 mmol, 99%) from pentafluorobenzene (168 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel twice with eluents (hexane/AcOEt = 20/1, then hexane/chloroform = 5/1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 1.84 (br, 4H), 1.34 (s, 6H), 1.24 (s, 6H), 0.42 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 148.8 (dm, J = 250.2 Hz), 142.2 (dm, J = 254.7 Hz), 137.1 (dm, J = 251.7 Hz), 109.8 (t, J = 30.4 Hz), 76.2, 37.8, 30.5, 29.8, 2.6; HRMS calcd for $C_{15}H_{19}F_5O_2Si$ [M$^+$]: 354.1069, found: 354.1069.

Dimethyl 6-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)naphthalene-2,3-dicarboxylate (5f):



White solid (295 mg, 0.685 mmol, 69%) from dimethyl 2,3-naphthalenedicarboxylate (244.2 g, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 5/1). ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.29 (s, 1H), 8.22 (d, J = 4.5 Hz, 2H), 7.88–7.85 (m, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 1.83 (br, 4H), 1.37 (s, 6H), 1.21 (s, 6H), 0.37 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 168.1, 168.0, 139.7, 134.9, 133.7, 132.7, 132.5, 130.5, 129.8, 128.7, 128.1, 127.3, 75.1, 52.5 (Two methyl groups were overlapped.), 37.8, 30.5 (br, four methyl groups), 0.5; HRMS calcd for $C_{22}H_{27}O_5Si$ [(M–CH$_3$O)$^+$]: 399.1622, found: 399.1618.

5-Fluoro-2-methyl-7-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)benzoxazole (5g):

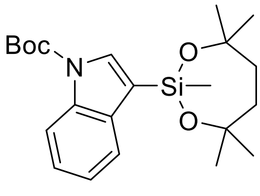


Colorless oil (237 mg, 0.702 mmol, 70%, major:minor = 92:8 based on integrations of Si–*CH$_3$* in ^{1}H NMR) from 5-fluoro-2-methylbenzoxazole (151 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1) and GPC.

For the major isomer: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.30 (dd, J = 8.3, 2.7 Hz, 1H), 7.27–7.25 (m, 1H), 2.64 (s, 3H), 1.84 (s, 4H), 1.36 (s, 6H), 1.35, 1.21 (s, 6H), 0.42 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 165.7, 159.8 (d, J = 241.6 Hz), 151.3, 141.4 (d, J = 13.0 Hz), 121.7 (d, J = 5.7 Hz), 117.1 (d, J = 24.6 Hz), 107.0 (d, J = 26.1 Hz), 75.6, 37.9 (overlapped), 30.7 (br, two methyl group), 30.3 (br, two methyl groups), 14.8, 1.0; HRMS calcd for $C_{17}H_{25}FNO_3Si$ [(M+H)]$^+$]: 338.1582, found: 338.1577.

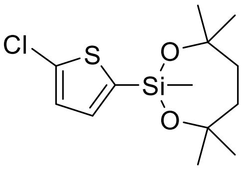
For the minor isomer: ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.70 (d, J = 3.6 Hz, 1H), 7.24 (d, J = 8.1 Hz, 1H), 2.63 (s, 3H), 1.84 (s, 4H, overlapped), 1.35 (s, 6H), 1.21 (s, 6H), 0.38 (d, J = 1.2 Hz coupled with F, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 165.9, 163.9 (d, J = 235.9 Hz), 147.6, 144.1 (d, J = 13.0 Hz), 121.5, 116.0 (d, J = 13.1 Hz), 105.4 (d, J = 30.4 Hz), 75.3, 37.9 (overlapped), 14.7, 1.3. (*note*: Peaks of the four methyl groups in the minor isomer overlapped with the corresponding peaks of the major isomer.)

***tert*-Butyl 3-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)-indole-1-carboxylate (5h):**



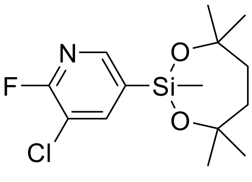
Colorless oil (348 mg, 0.863 mmol, 86%) from *N*-(*tert*-butoxycarbonyl)indole (217 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel twice with eluents (hexane/AcOEt = 20/1, then hexane/$CHCl_3$ = 2/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (brd, *J* = 7.5 Hz, 1H), 7.80 (ddd, *J* = 7.7, 1.2, 0.7 Hz, 1H), 7.71 (s, 1H), 7.28 (ddd, *J* = 7.5, 7.2, 1.2 Hz, 1H), 7.23 (ddd, *J* = 7.7, 7.2, 1.2 Hz, 1H), 1.85 (br, 4H), 1.67 (s, 9H), 1.36 (s, 6H), 1.25 (s, 6H), 0.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 149.6, 136.1, 133.9, 132.9, 123.8, 122.4 (overlapped), 115.4, 114.9, 83.4, 75.0, 37.8, 30.6 (br, two methyl groups), 30.4 (br, two methyl groups), 28.1, 1.7; HRMS calcd for $C_{22}H_{33}NO_4Si$ [M$^+$]: 403.2173, found: 403.2179.

2-(5-Chlorothiophen-2-yl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (5i):



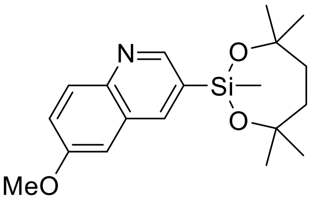
Colorless oil (234 mg, 0.767 mmol, 77%) from 2-chlorothiophene (119 mg, 1.00 mmol) by following **TP4** with 1.00 mmol of hydrosilane, purified by column chromatography on silica gel twice with eluents (hexane/AcOEt = 20/1, then hexane/chloroform = 5/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10 (d, *J* = 3.6 Hz, 1H), 6.92 (d, *J* = 3.6 Hz, 1H), 1.81 (br, 4H), 1.31 (s, 6H), 1.25 (s, 6H), 0.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 138.0, 135.0, 134.4, 127.2, 75.4, 37.7, 30.4 (br, four methyl groups), 1.1; HRMS calcd for $C_{13}H_{21}{}^{35}ClO_2SSi$ [M$^+$]: 304.0715, found: 304.0711.

3-Chloro-2-fluoro-5-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)pyridine (5j):



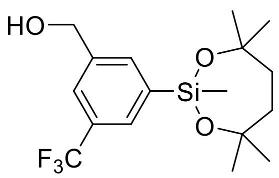
Colorless oil (286 mg, 0.899 mmol, 90%) from 3-chloro-2-fluoropyridine (131 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (m, 1H), 7.96 (dd, *J* = 9.9, 1.6 Hz, 1H), 1.81 (br, 4H), 1.34 (s, 6H), 1.21 (s, 6H), 0.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.6 (d, *J* = 238.7 Hz), 150.3 (d, *J* = 11.5 Hz), 145.8, 133.3 (d, *J* = 5.7 Hz), 116.8 (d, *J* = 33.2 Hz), 75.7, 37.9, 30.5 (br, four methyl groups), 0.8; HRMS calcd for $C_{14}H_{22}{}^{35}ClFNO_2Si$ [(M+H)]$^+$]: 318.1087, found: 318.1086.

6-Methoxy-3-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)quinoline (5k):



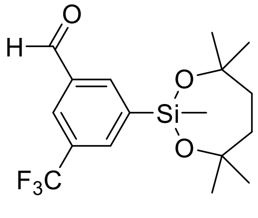
Pale yellow oil (218 mg, 0.631 mmol, 63%) from 6-methoxyquinoline (159 mg, 1.00 mmol) by following **TP4**, purified by column chromatography on silica gel with an eluent (DCM/MeOH = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.95 (d, *J* = 1.4 Hz, 1H), 8.32 (s, 1H), 8.01 (br, 1H), 7.38 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 3.94 (s, 3H), 1.84 (br, 4H), 1.37 (s, 6H), 1.23 (s, 6H), 0.39 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 157.5, 151.7, 144.4, 141.4, 131.2, 130.5, 128.5, 122.6, 105.3, 75.3, 55.4, 37.9, 30.5 (br, four methyl groups), 0.8; HRMS calcd for $C_{19}H_{28}NO_3Si$ [(M+H)]$^+$]: 346.1833, found: 346.1838.

2-(3-(Hydroxymethyl)-5-(trifluoromethyl)phenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (6):



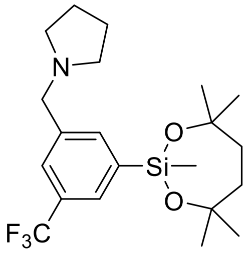
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.81 (s, 1H), 7.78 (s, 1H), 7.63 (s, 1H), 4.77 (d, J = 6.0 Hz, 2H), 1.82 (br, 4H), 1.74 (t, J = 6.0 Hz, 1H), 1.35 (s, 6H), 1.20 (s, 6H), 0.31 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 140.5, 140.2, 135.3, 130.0 (q, J = 31.8 Hz), 129.4 (d, J = 2.9 Hz), 124.5 (d, J = 3.0 Hz), 124.4 (q, J = 273.5 Hz), 75.3, 64.7, 37.9, 30.5 (br, four methyl groups), 0.7; HRMS calcd for $C_{17}H_{25}F_3O_3Si$ [M$^+$]: 362.1520, found: 362.1524.

2-(3-Formyl-5-(trifluoromethyl)phenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (7):



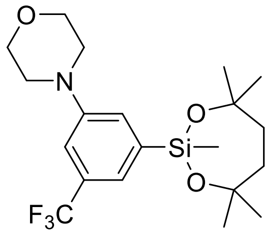
^{1}H NMR (600 MHz, CDCl$_3$): δ 10.09 (s, 1H), 8.30 (s, 1H), 8.12 (s, 1H), 8.12 (s, 1H), 1.83 (br, 4H), 1.36 (s, 6H), 1.21 (s, 6H), 0.35 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 191.3, 141.8, 138.3, 135.7, 130.8 (q, J = 33.4 Hz), 126.7, 126.7, 123.8 (q, J = 259.9 Hz), 75.6, 37.9, 30.5 (br, four methyl groups), 0.6; HRMS calcd for $C_{17}H_{23}F_3O_3Si$ [M$^+$]: 360.1363, found: 360.1367.

1-(3-(2,4,4,7,7-Pentamethyl-1,3,2-dioxasilepan-2-yl)-5-(trifluoromethyl)benzyl)pyrrolidine (8):



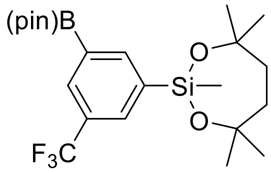
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.76 (s, 1H), 7.73 (s, 1H), 7.60 (s, 1H), 3.66 (s, 2H), 2.50 (br, 4H), 1.80–1.78 (m, 8H, overlapped), 1.34 (s, 6H), 1.19 (s, 6H), 0.31 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 139.6, 139.1, 137.4, 129.7 (q, J = 30.4 Hz), 128.8 (d, J = 2.9 Hz), 126.4 (d, J = 4.4 Hz), 124.5 (q, J = 273.5 Hz), 75.2, 60.2, 54.1, 37.9, 30.6, 23.5, 0.6; HRMS calcd for $C_{21}H_{33}F_3NO_2Si$ [(M+H)$^+$]: 416.2227, found: 416.2226.

4-(3-(2,4,4,7,7-Pentamethyl-1,3,2-dioxasilepan-2-yl)-5-(trifluoromethyl)phenyl)morpholine (9):



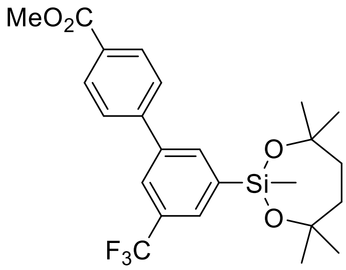
^{1}H NMR (600 MHz, CDCl$_3$): δ 7.38 (s, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.08 (br, 1H), 3.89–3.87 (m, 4H), 3.21–3.20 (m, 4H), 1.80 (br, 4H), 1.34 (s, 6H), 1.21 (s, 6H), 0.29 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$): δ 150.5, 140.7, 130.6 (q, J = 31.9 Hz), 124.5 (q, J = 273.5 Hz), 123.8, 121.4 (d, J = 4.2 Hz), 112.8 (d, J = 4.2 Hz), 75.2, 66.7, 49.0, 37.8, 30.6 (br, four methyl groups), 0.6; HRMS calcd for $C_{20}H_{30}F_3NO_3Si$ [M$^+$]: 417.1942, found: 417.1939.

2,4,4,7,7-Pentamethyl-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(trifluoromethyl)phenyl)-1,3,2-dioxasilepane (10):



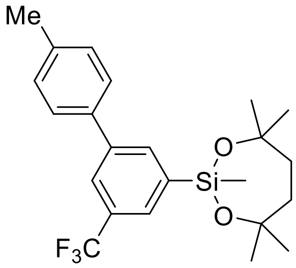
^{1}H NMR (600 MHz, CDCl$_3$): δ 8.20 (s, 1H), 8.04 (br, 1H), 7.99 (d, J = 0.9 Hz, 1H), 1.81 (br, 4H), 1.36 (s, 12H), 1.35 (s, 6H), 1.20 (s, 6H), 0.32 (s, 3H); ^{13}C NMR (151 MHz, CDCl$_3$, The carbon atom bearing the boron atom was not detected.): δ 143.2, 138.9, 132.9 (d, J = 2.9 Hz), 132.2, 129.2 (q, J = 31.9 Hz), 124.6 (q, J = 273.5 Hz), 84.1, 75.2, 38.0 30.5 (br, four methyl groups), 24.9, 0.7; HRMS calcd for $C_{22}H_{35}{}^{11}BF_3O_4Si$ [(M+H)$^+$]: 459.2349, found: 459.2341.

Methyl 3'-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate (11):



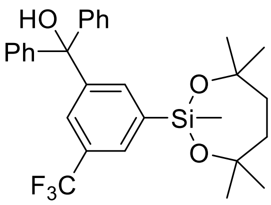
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (dt, J = 8.5, 1.8 Hz, 2H), 8.04 (s, 1H), 7.91 (s, 1H), 7.83 (s, 1H), 7.67 (dt, J = 8.5, 1.8 Hz, 2H), 3.96 (s, 3H), 1.83 (s, 4H), 1.37 (s, 6H), 1.23 (s, 6H), 0.36 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.8, 144.5, 141.0, 139.7, 135.7, 130.4 (q, J = 31.7 Hz), 130.2, 129.8 (d, J = 2.9 Hz), 129.5, 127.2, 124.3 (q, J = 273.5 Hz), 124.8 (d, J = 2.9 Hz), 75.4, 52.2, 37.9, 30.6 (br, four methyl groups), 0.7; HRMS calcd for $C_{24}H_{30}F_3O_4Si$ [$(M+H)^+$]: 467.1860, found: 467.1864.

2,4,4,7,7-Pentamethyl-2-(4'-methyl-5-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-1,3,2-dioxasilepane (12):



^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.83 (s, 1H), 7.78 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 2.41 (s, 3H), 1.83 (br, 4H), 1.36 (s, 6H), 1.23 (s, 6H), 0.34 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.8, 140.5, 137.7, 137.3, 135.5, 130.2 (q, J = 31.9 Hz), 129.7, 128.7, 127.1, 124.5 (q, J = 272.1 Hz), 124.5 (d, J = 3.0 Hz), 75.3, 37.9, 30.6 (br, four methyl groups), 21.1, 0.7; HRMS calcd for $C_{23}H_{29}F_3O_2Si$ [M^+]: 422.1883, found: 422.1877.

(3-(2,4,4,7,7-Pentamethyl-1,3,2-dioxasilepan-2-yl)-5-(trifluoromethyl)phenyl)diphenylmethanol (13):



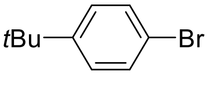
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.70 (s, 1H), 7.65 (s, 1H), 7.34–7.28 (m, 6H), 7.25–7.24 (m, 4H), 2.80 (s, 1H), 1.75–1.66 (m, 4H), 1.27 (s, 6H), 1.04 (s, 6H), 0.25 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 146.6, 146.4, 139.4, 137.0, 129.5 (q, J = 30.4 Hz), 129.0, 128.0, 127.9, 127.4, 125.1, 124.5 (q, J = 273.5 Hz), 81.8, 75.2, 37.7, 30.3 (br, four methyl groups), 0.2; HRMS calcd for $C_{29}H_{32}F_3O_2Si$ [$(M–OH)^+$]: 497.2118, found: 497.2111.

Products of Transformations of Silicon Functionalities

4-*tert*-Butylphenol (14):

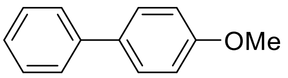
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.26 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 4.55 (br, 1H), 1.29 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 153.0, 143.6, 126.4, 114.8, 34.0, 31.5. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[5]

1-Bromo-4-*tert*-butylbenzene (15):



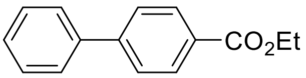
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.0, 131.0, 127.2, 119.2, 34.5, 31.2. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[6]

4-Methoxybiphenyl (16a):



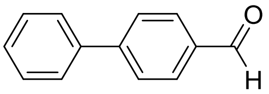
White solid (84.0 mg, 0.456 mmol, 91%) from 4-iodoanisole (117 mg, 0.500 mmol) by following **TP5**, purified by column chromatography on silica gel twice with eluents (hexane/AcOEt = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56–7.55 (m, 2H), 7.54–7.53 (m, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.8 Hz, 2H), 6.98 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.1, 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.2. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[7]

Ethyl 4-phenylbenzoate (16b):



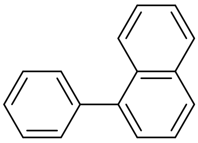
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 7.7 Hz, 2H), 7.47 (dd, J = 7.7 Hz, 7.4 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.4, 145.4, 140.0, 130.0, 129.2, 128.8, 128.0, 127.2, 126.9, 60.9, 14.3. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[7]

4-Phenylbenzaldehyde (16c):



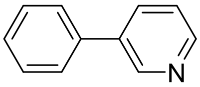
White solid (77.1 mg, 0.423 mmol, 85%) from 4-iodobenzaldehyde (116 mg, 0.500 mmol) by following **TP5**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.96 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.49 (dd, J = 7.5, 7.2 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 191.9, 147.1, 139.6, 135.1, 130.2, 128.9, 128.4, 127.6, 127.3. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[7]

1-Phenylnaphthalene (16d):



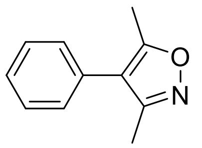
Colorless liquid (80.7 mg, 0.395 mmol, 79%) from 1-iodonaphthalene (127 mg, 0.50 mmol) by following **TP5**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 20/1) and then GPC. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02–7.96 (m, 2H), 7.94–7.92 (m, 1H), 7.61–7.54 (m, 6H), 7.52–7.50 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 140.7, 140.3, 133.8, 131.6, 130.0, 128.2 (2C, overlapped), 127.6, 127.2, 126.9, 126.0 (2C, overlapped), 125.7, 125.3. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[8]

3-Phenylpyridine (16e):



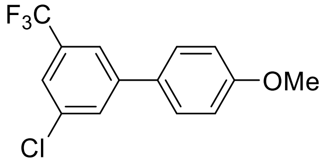
Colorless oil (68.7 mg, 0.443 mmol, 89%) from 3-iodopyridine (103 mg, 0.500 mmol) by following **TP5**, purified by column chromatography on silica gel twice with eluents (DCM/MeOH = 20/1, then hexane/AcOEt/MeOH = 20/10/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.86 (d, J = 1.4 Hz, 1H), 8.60 (d, J = 4.8 Hz, 1H), 7.90–7.88 (m, 1H), 7.59 (d, J = 6.9 Hz, 2H), 7.49 (dd, J = 7.9, 6.9 Hz, 2H), 7.43–7.40 (m, 1H), 7.38 (dd, J = 7.9, 4.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 148.4, 148.3, 137.8, 136.6, 134.3, 129.0, 128.0, 127.1, 123.5. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[9]

3,5-Dimethyl-4-phenylisoxazole (16f):



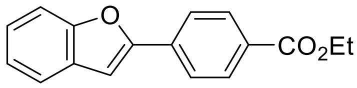
Colorless liquid (70.2 mg, 0.405 mmol, 81%) from 4-iodo-3,5-dimethylisoxazole (112 mg, 0.50 mmol) by following **TP5**, purified by column chromatography on silica gel with an eluent (hexane/AcOEt = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46–7.43 (m, 2H), 7.37–7.34 (m, 1H), 7.26–7.25 (m, 2H), 2.41 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.2, 158.7, 130.4, 129.0, 128.8, 127.5, 116.6, 11.5, 10.8. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[10]

3-Chloro-4'-methoxy-5-(trifluoromethyl)biphenyl (16g):



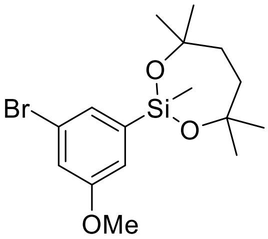
Colorless liquid (133 mg, 0.462 mmol, 92%) from 4-iodoanisole (117 mg, 0.500 mmol) and **5b** (275 mg, 0.750 mmol) by following **TP5**, purified by column chromatography with an eluent (hexane/AcOEt = 20/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (brs, 1H), 7.67 (brs, 1H), 7.53–7.50 (m, 3H), 7.01–6.99 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 160.1, 143.4, 135.2, 132.5 (q, J = 33.4 Hz), 130.7, 129.9, 128.2, 123.4 (q, J = 273.5 Hz), 123.4 (d, J = 2.9 Hz), 121.6 (d, J = 2.9 Hz), 114.5, 55.3; HRMS calcd for $C_{14}H_{10}{}^{35}ClF_3O$ [M$^+$]: 286.0367, found: 286.0364.

Ethyl 4-(benzofuran-2-yl)benzoate (16h):



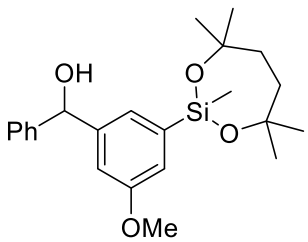
White solid (116 mg, 0.434 mmol, 87%) from ethyl 4-iodobenzoate (138 mg, 0.500 mmol) and **4d** (228 mg, 0.750 mmol) by following **TP5**, purified by column chromatography with an eluent (hexane/AcOEt = 10/1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, J = 8.2 Hz, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.55 (d, J = 8.2 Hz, 1H), 7.35–7.32 (m, 1H), 7.27–7.25 (m, 2H), 7.16 (s, 1H), 4.41 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 166.0, 154.9, 154.5, 134.2, 129.9, 129.8, 128.8, 124.9, 124.6, 123.0, 121.1, 111.2, 103.3, 60.9, 14.2. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[11]

2-(3-Bromo-5-methoxyphenyl)-2,4,4,7,7-pentamethyl-1,3,2-dioxasilepane (17):



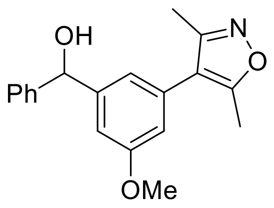
^{1}H NMR (600 MHz in $CDCl_3$): δ 7.32 (dd, J = 1.9, 0.6 Hz, 1H), 7.10 (dd, J = 2.5, 0.6 Hz, 1H), 7.03 (dd, J = 2.5, 1.9 Hz, 1H), 3.80 (s, 3H), 1.80 (br, 4H), 1.33 (s, 6H), 1.21 (s, 6H), 0.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.6, 142.4, 128.5, 122.7, 118.0, 117.7, 75.2, 55.3, 37.9, 30.6 (br, four methyl groups), 0.5; HRMS calcd for $C_{16}H_{25}{}^{79}BrO_3Si$ [M$^+$]: 372.0751, found: 372.0752.

(3-Methoxy-5-(2,4,4,7,7-pentamethyl-1,3,2-dioxasilepan-2-yl)phenyl)(phenyl)methanol (18):



^{1}H NMR ($CDCl_3$): δ 7.37 (d, J = 7.5 Hz, 2H), 7.33–7.31 (dd, J = 7.5, 7.5 Hz, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.22 (brs, 1H), 7.10 (d, J = 2.4 Hz, 1H), 6.93 (t, J = 2.0 Hz, 1H), 5.83 (s, 1H), 3.79 (s, 3H), 1.77 (br, 4H, overlapped with H_2O), 1.31 (s, 3H), 1.31 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 0.27 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 159.0, 144.6, 143.8, 140.2, 128.3, 127.3, 126.5, 124.4, 118.2, 112.9, 76.1, 74.9, 55.1, 37.8, 30.5 (br, four methyl groups), 0.5; HRMS calcd for $C_{23}H_{32}O_4Si$ [M^+]: 400.2064, found: 400.2053.

(3-(3,5-Dimethylisoxazol-4-yl)-5-methoxyphenyl)(phenyl)methanol (19):



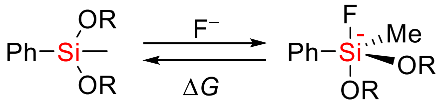
^{1}H NMR ($CDCl_3$): δ 7.41–7.39 (m, 2H), 7.37–7.35 (m, 2H), 7.31–7.28 (m, 1H), 6.97 (t, J = 1.7 Hz, 1H), 6.82 (m, 1H), 6.68 (dd, J = 2.4, 1.7 Hz, 1H), 5.85 (s, 1H), 3.82 (s, 3H), 2.37 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 165.2, 159.8, 158.6, 146.1, 143.6, 131.5, 128.4, 127.6, 126.4, 119.6, 116.5, 113.8, 110.7, 75.7, 55.2, 11.4, 10.6. All the resonances in ^{1}H and ^{13}C NMR spectra were consistent with reported values.[12]

Details of Computational Study

Conformation Search and Comparison of Free Energies to Form Fluorosilicate

Conformation search of silicates was performed with GRRM17 program[13] associated with Gaussian 16 program,[14] and the subsequent re-optimizations were performed with Gaussian 16 program. Initial search was conducted with SC-AFIR method[15] using PM7 as a Hamiltonian for a semi-empirical MO method. During the search, all atoms were chosen as target atoms of the SC-AFIR method and the collision energy parameter γ of the AFIR method was set as γ = 50.0 kJ/mol. Equilibrium structures found by SC-AFIR calculations were reoptimized at the level of ωB97X-D/jun-cc-pVTZ including solvation effect of THF with SMD method[16] and all structures were characterized by frequency calculations to confirm their identity as local minima. Free energies of all structures were obtained at the same calculation level at 298.15 K.

Table S2. Relative free energies of the most stable conformers of each substitution patterns of silicates **1-F** relative to neutral phenylsilanes **1**.



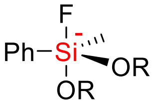
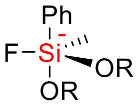
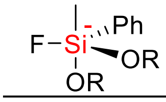
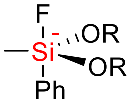
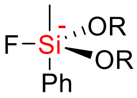
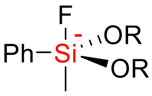
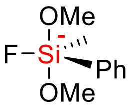
	substitution pattern	ΔG (kcal/mol)		
		1-VI-F	**1-VII-F**	**1-III-F**
A		+3.2	+8.9	+10.1
B		+9.3	+16.0	not located
C		+9.9	+16.6	+18.1
D		+15.6	+15.7	+11.7
E		not located	not located	not located
F		not located	not located	+13.6
G		not located	not located	+15.9

Table S3. Free energies for each structure in Table S2 (in Hartree).

species	**1-VI / 1-VI-F**	**1-VII / 1-VII-F**	**1-III / 1-III-F**
neutral silane	-986.568716	-1025.861029	-1027.054179
A	-1086.560673	-1125.844190	-1127.035344
B	-1086.551107	-1125.832875	not located
C	-1086.550108	-1125.831822	-1127.022668
D	-1086.541010	-1125.833341	-1127.032898
E	not located	not located	not located
F	not located	not located	-1127.029851
G	not located	not located	-1127.026084
fluoride	-99.997322		

Evaluation of Bulkiness of Silyl Groups by Employing $\%V_{\mathrm{bur}}$

All values of $\%V_{\mathrm{bur}}$[17] for phenylsilanes were calculated SambVca 2.1 web interface.[18] Structures used in this evaluation were optimized at the ωB97X-D/jun-cc-pVTZ including solvation effect of THF with SMD method. The center of the sphere was set to the carbon atom at the *ipso* position of the phenyl ring without modification of bond length between Si and C_{ipso}. 3.5 Å of the sphere radius and 1.17 of the scaling factor for bond radii were used. The phenyl ring and the silicon atom were removed and hydrogens on silyl groups were included in all calculations.

Cartesian Coordinates for Stationary Points

1-VI

C	-0.024376	-0.048086	-0.074960
H	-0.069888	-0.142104	1.011395
C	1.457727	-0.041861	-0.500098
C	-0.949538	1.109706	-0.500811
O	1.562138	0.181305	-1.914224
O	-0.834444	1.338481	-1.913214
Si	0.607945	1.266371	-2.712588
H	-0.460143	-0.960248	-0.489821
C	-0.694029	2.417101	0.246921
C	2.312839	0.985394	0.239346
C	-2.391000	0.677823	-0.257897
C	2.029111	-1.432105	-0.247427
C	0.320269	0.667490	-4.441559
C	1.422570	2.958048	-2.727789
C	2.812349	3.086342	-2.773733
C	0.656904	4.125698	-2.729054
C	1.255352	5.377053	-2.768433
C	3.417643	4.334265	-2.813233
C	2.638397	5.482645	-2.810136
H	-0.423846	4.059907	-2.686555
H	0.643674	6.269896	-2.763363
H	3.435059	2.199517	-2.766525
H	4.496739	4.411651	-2.843073
H	3.107826	6.457308	-2.838326
H	1.266334	0.599177	-4.982725
H	-0.152983	-0.315584	-4.445168
H	-0.322653	1.364289	-4.983445
H	1.988191	-1.677518	0.814905
H	1.465231	-2.184063	-0.799991
H	3.069725	-1.472722	-0.571155
H	2.045596	2.008048	-0.013693
H	2.209841	0.861666	1.318215
H	3.361663	0.844147	-0.024515
H	0.271096	2.853925	0.004273
H	-1.461541	3.144999	-0.018904
H	-0.733976	2.253594	1.324699
H	-2.618543	-0.229240	-0.818414
H	-2.560943	0.483479	0.802203
H	-3.075788	1.463683	-0.578608

1-VI-F: A

C	-0.575205	0.042191	0.198154
H	0.386854	0.158251	0.703987
C	-1.147154	1.426159	-0.173081
C	-0.431656	-0.936880	-0.974083
Si	-2.887103	-0.041036	-1.921828
O	-1.695701	-1.189161	-1.552049
O	-1.942948	1.345337	-1.323522
C	-1.951902	1.968826	1.016010
C	-3.070560	0.816261	-3.605246
C	-0.021961	2.427769	-0.461598
C	-4.274659	0.165194	-0.625651
H	-1.250411	-0.439528	0.911335
C	0.536472	-0.460851	-2.059968
C	0.064227	-2.274655	-0.425922
H	0.606621	2.580160	0.419031
H	0.612660	2.092449	-1.279942
H	-0.456048	3.388994	-0.743862
H	-2.776358	1.303330	1.268647
H	-1.315029	2.074963	1.898269
H	-2.367506	2.948794	0.771892
H	0.148756	0.422593	-2.563115
H	1.519551	-0.227649	-1.645329
H	0.657585	-1.249861	-2.804830
H	1.058840	-2.175782	0.014197
H	-0.618314	-2.648065	0.339323
H	0.112598	-3.012507	-1.228421
F	-3.794233	-1.420175	-2.608398
H	-4.112846	0.808018	-3.933698
H	-2.704855	1.842390	-3.607377
H	-2.506473	0.250031	-4.353331
C	-5.048509	1.325887	-0.569141
C	-4.527684	-0.813340	0.337681
C	-5.484816	-0.634273	1.328577
C	-6.022438	1.509818	0.403524
C	-6.237642	0.531559	1.365315
H	-3.956025	-1.734678	0.320446
H	-5.646166	-1.405843	2.071717
H	-4.876200	2.116398	-1.291435
H	-6.608262	2.420951	0.418727
H	-6.987117	0.674943	2.133356

1-VI-F: B

C	0.096224	0.134494	0.113922
H	1.127052	0.464281	0.267450
C	-0.846955	1.341217	0.116396
C	0.001951	-0.745838	-1.153943
Si	-2.808476	-0.203908	-1.131167
O	-1.213813	-0.546949	-1.819312
O	-2.182559	0.885042	0.016222
C	-0.735350	2.051353	1.464386
C	-3.421373	0.312211	-2.865043
C	-0.557217	2.350715	-0.997031
C	-4.612084	0.155823	-0.350936
H	-0.177578	-0.463345	0.987551
C	1.119575	-0.388863	-2.140429
C	0.169024	-2.217005	-0.756161
H	0.471616	2.713394	-0.943921
H	-0.722018	1.907233	-1.976722
H	-1.226482	3.207192	-0.891179
H	-0.961587	1.360682	2.278123
H	0.269621	2.450640	1.617168
H	-1.446510	2.877989	1.512425
H	1.073974	0.662235	-2.424304
H	2.104591	-0.584685	-1.710075
H	1.013629	-0.989153	-3.046175
H	1.125938	-2.381422	-0.253451
H	-0.631775	-2.521730	-0.083115
H	0.130971	-2.853100	-1.642980
F	-2.975819	-1.831271	-0.710621
H	-4.333033	-0.233572	-3.124974
H	-3.697911	1.371401	-2.841638

H	-2.685395	0.166855	-3.655633
C	-5.019953	1.466913	-0.067854
C	-5.587790	-0.830010	-0.165613
C	-6.874329	-0.539659	0.279903
C	-6.299450	1.777996	0.373630
C	-7.239039	0.770106	0.552841
H	-5.338729	-1.864600	-0.369917
H	-7.593015	-1.339932	0.414483
H	-4.304191	2.272872	-0.187003
H	-6.565600	2.807868	0.582506
H	-8.237751	1.003515	0.900553

1-VI-F: C

C	0.231862	0.677795	-0.707953
H	0.628187	0.667114	-1.727236
C	-0.753202	1.850249	-0.649771
C	-0.394762	-0.699842	-0.393295
Si	-2.701826	0.210931	-1.807729
O	-1.780820	-0.676394	-0.590488
O	-1.788758	1.636481	-1.591669
C	-1.352434	2.078131	0.739970
C	-3.689582	1.119261	-3.224297
C	-0.027382	3.121636	-1.086829
C	-4.271013	-0.116444	-0.748961
H	1.078292	0.866778	-0.042555
C	0.262639	-1.764474	-1.279217
C	-0.153535	-1.082593	1.070832
H	0.782780	3.369234	-0.397490
H	0.393903	2.995782	-2.085556
H	-0.725021	3.960568	-1.114683
H	-1.965281	1.231810	1.042188
H	-0.570353	2.231421	1.486908
H	-1.983701	2.968925	0.720663
H	0.074943	-1.552986	-2.331510
H	1.343726	-1.794576	-1.118573
H	-0.147903	-2.750194	-1.050704
H	0.913741	-1.183276	1.281881
H	-0.567060	-0.335740	1.747529
H	-0.638721	-2.037017	1.283313
F	-2.305634	-0.999546	-2.941749
H	-4.471240	0.470686	-3.635451
H	-4.177010	2.028955	-2.859810
H	-3.033698	1.410342	-4.051719
C	-4.982781	0.944775	-0.184080
C	-4.778249	-1.400661	-0.534410
C	-5.936097	-1.617960	0.201542
C	-6.131283	0.740127	0.571271
C	-6.616486	-0.545761	0.763758
H	-4.253982	-2.255276	-0.946761
H	-6.305778	-2.626523	0.342819
H	-4.631942	1.960803	-0.332327
H	-6.651005	1.585491	1.005980
H	-7.515150	-0.711045	1.344528

1-VI-F: D

C	-0.868908	0.521508	0.281915
H	-0.042491	0.623994	0.989110
C	-1.077542	1.892823	-0.405221
C	-0.621855	-0.755726	-0.556484
Si	-2.514380	0.373081	-2.134809
O	-1.615205	-0.939355	-1.549803
O	-2.066834	1.841237	-1.417697
C	-1.582209	2.862842	0.665333
C	-3.787650	0.245499	-3.548676
C	0.211767	2.463198	-1.003837
C	-3.993451	0.066482	-0.810412
H	-1.765580	0.331333	0.876374
C	0.758923	-0.781825	-1.219174
C	-0.720459	-1.947878	0.397580
H	1.025440	2.455697	-0.275067
H	0.520048	1.903732	-1.882054
H	0.039564	3.495515	-1.314679
H	-2.503174	2.489718	1.114589
H	-0.840723	3.001397	1.455418
H	-1.789875	3.834273	0.213423
H	0.820997	-0.062030	-2.029599
H	1.550035	-0.571423	-0.495919
H	0.936778	-1.771886	-1.643582
H	0.059028	-1.908751	1.161758
H	-1.692090	-1.961466	0.892766
H	-0.607434	-2.877583	-0.162618
F	-1.260983	0.635390	-3.397257
H	-3.387555	0.373054	-4.554413
H	-4.282782	-0.728643	-3.490139
H	-4.573204	0.989621	-3.386623
C	-4.777702	1.117688	-0.320477
C	-4.353738	-1.212076	-0.369433
C	-5.412932	-1.434622	0.504140
C	-5.840649	0.917843	0.553228
C	-6.164627	-0.365653	0.973170
H	-3.775109	-2.063775	-0.710787
H	-5.651263	-2.443195	0.822439
H	-4.538936	2.132467	-0.621241
H	-6.415938	1.764192	0.911040
H	-6.988915	-0.529712	1.656079

1-VII

Si	-0.410096	9.993244	6.996720
O	-0.364694	8.725235	5.948951
O	-1.972256	10.409059	7.318240
C	-2.616144	7.942020	5.450096
H	-2.413113	7.104003	6.120576
H	-3.180053	7.527260	4.611237
C	0.681032	10.252294	9.605359
H	0.299634	11.266322	9.560878
C	0.391449	11.539329	6.345531
H	1.420846	11.334759	6.044591
H	0.417043	12.312488	7.116354
H	-0.146848	11.938267	5.485091
C	-3.098900	9.542848	7.495538
C	1.831556	8.541478	10.838054
H	2.343629	8.212792	11.733009
C	0.502628	9.390955	8.520043
C	-1.267999	8.415276	4.882941
C	1.010399	8.095349	8.623144
H	0.884322	7.406995	7.796941

C	1.669290	7.672019	9.769001
C	1.335479	9.835027	10.755210
C	-3.529094	8.957763	6.141003
H	-3.730733	9.795347	5.469579
H	-4.489807	8.463232	6.303282
C	-4.217307	10.433821	8.024131
H	-3.913478	10.898734	8.962670
H	-5.124433	9.855432	8.202751
H	-4.444810	11.223658	7.306894
C	-0.621417	7.260131	4.126876
H	0.363242	7.555286	3.762843
H	-1.231562	6.963842	3.272994
H	-0.500818	6.397288	4.783454
C	-1.424153	9.614014	3.951251
H	-1.846766	10.477407	4.464560
H	-2.084979	9.362264	3.120608
H	-0.453475	9.899560	3.543935
C	-2.790038	8.452092	8.517493
H	-1.971404	7.808271	8.197463
H	-3.669289	7.824876	8.671313
H	-2.513891	8.898747	9.473210
H	1.458945	10.517739	11.585836
H	2.055487	6.662671	9.828756

1-VII-F: A

Si	0.055867	0.118431	0.065547
C	1.946601	0.248783	0.198116
F	0.110806	1.612049	-0.945535
O	0.080410	-1.367376	1.036337
C	-0.682851	-0.750051	-1.474562
O	-1.012910	0.966498	1.068262
C	-1.825166	-0.286271	-2.130064
C	-0.082942	-1.900386	-1.990136
C	-0.593511	-2.560251	-3.101268
C	-2.363940	-0.951723	-3.223067
C	-1.746529	-2.093647	-3.716815
H	0.797477	-2.302028	-1.501580
H	-0.097909	-3.445792	-3.480664
H	-2.314278	0.612526	-1.772667
H	-3.263415	-0.575995	-3.695817
H	-2.158002	-2.611336	-4.574143
H	2.387505	0.167974	-0.800048
H	2.230298	1.232834	0.579304
H	2.389249	-0.516577	0.834336
C	-1.099525	1.048797	2.475141
C	-0.930869	-2.104781	1.666329
C	0.287158	1.175124	3.110650
C	-1.887202	2.330224	2.760038
C	-1.885006	-0.129972	3.074505
C	-0.375770	-3.518497	1.867021
C	-1.231560	-1.506975	3.052046
C	-2.227484	-2.212788	0.850928
H	-2.102267	0.119579	4.117327
H	-2.851086	-0.168518	2.564592
H	-1.887813	-2.197267	3.591397
H	-0.290584	-1.479165	3.607918
H	-0.122145	-3.955687	0.899630
H	0.532529	-3.483288	2.472051
H	-1.097516	-4.172223	2.362586
H	-2.985232	-2.751110	1.425786
H	-2.627049	-1.232616	0.597574
H	-2.057135	-2.754926	-0.078921
H	0.788948	2.067601	2.732755
H	0.205157	1.262841	4.196269
H	0.907880	0.310742	2.882085
H	-1.379972	3.185790	2.312212
H	-2.886571	2.262987	2.325962
H	-1.987052	2.507131	3.832876

1-VII-F: B

Si	-0.806523	0.146474	0.263772
C	0.917946	0.867714	-0.130722
F	-2.177416	1.140762	0.159116
O	-1.019843	-1.494300	0.624445
C	-1.118257	-0.260212	-1.673552
O	-0.607495	0.662968	1.942695
C	-1.011396	-1.538111	-2.231472
C	-1.349655	0.777690	-2.588068
C	-1.470109	0.563516	-3.955434
C	-1.130652	-1.774948	-3.597777
C	-1.361608	-0.721957	-4.470867
H	-1.443711	1.794552	-2.220892
H	-1.651573	1.399374	-4.621314
H	-0.838446	-2.377030	-1.568437
H	-1.045855	-2.785508	-3.981191
H	-1.457473	-0.898380	-5.535054
H	0.794431	1.822336	-0.653469
H	1.526474	1.047421	0.755564
H	1.462320	0.212413	-0.815303
C	-1.367334	0.444131	3.097257
C	-0.394677	-2.393081	1.512692
C	-0.556179	1.038848	4.254887
C	-2.729777	1.144216	3.055888
C	-1.586183	-1.065554	3.349071
C	1.032396	-2.663487	1.037861
C	-0.362937	-1.890876	2.972054
C	-1.213049	-3.682479	1.433808
H	-1.843021	-1.211156	4.401104
H	-2.446711	-1.403989	2.767928
H	-0.267955	-2.763733	3.622137
H	0.535286	-1.290294	3.122112
H	1.030086	-3.072484	0.025870
H	1.610639	-1.738203	1.032086
H	1.535121	-3.374889	1.697064
H	-0.751153	-4.479490	2.019670
H	-2.224072	-3.518139	1.810890
H	-1.290019	-4.012773	0.396770
H	0.407586	0.535617	4.350552
H	-0.362612	2.095451	4.061725
H	-1.087363	0.951733	5.205508
H	-2.604446	2.213997	2.879112
H	-3.354091	0.741453	2.260232
H	-3.254101	1.011071	4.005977

1-VII-F: C

Si	0.389852	-0.386536	0.331474

C	2.107072	-1.051524	-0.322830
F	1.222187	1.047884	0.753286
O	0.314454	-1.740848	1.367393
C	-0.458788	-0.489312	-1.395590
O	-1.096115	0.358157	0.926992
C	-1.024134	0.628770	-2.014654
C	-0.498069	-1.688610	-2.111127
C	-1.082992	-1.778152	-3.368609
C	-1.587418	0.561006	-3.282511
C	-1.624897	-0.648073	-3.964414
H	-0.067946	-2.583575	-1.675342
H	-1.110793	-2.729473	-3.886197
H	-1.032712	1.574476	-1.486145
H	-2.007157	1.450801	-3.736322
H	-2.073056	-0.708780	-4.948168
H	2.507510	-0.404592	-1.111550
H	2.849752	-1.085162	0.481376
H	2.030646	-2.062260	-0.734217
C	-1.414487	0.858664	2.197240
C	-0.738454	-2.299662	2.124007
C	-0.981845	2.325715	2.329549
C	-2.940169	0.807282	2.336410
C	-0.739154	0.043666	3.309386
C	-0.223034	-3.657819	2.606472
C	-1.076351	-1.442349	3.375254
C	-1.969783	-2.549074	1.246838
H	0.342145	0.157234	3.199129
H	-0.995803	0.492011	4.273912
H	-2.132905	-1.578709	3.618137
H	-0.522550	-1.849763	4.225339
H	-0.015983	-4.311154	1.756968
H	0.700738	-3.528493	3.173018
H	-0.956937	-4.148847	3.249934
H	-2.758257	-3.038164	1.823499
H	-2.353491	-1.620047	0.834544
H	-1.700436	-3.204925	0.416398
H	-1.384635	2.902961	1.494792
H	-1.353628	2.762442	3.259932
H	0.102500	2.415182	2.311160
H	-3.397227	1.418542	1.555975
H	-3.317290	-0.208419	2.226305
H	-3.263768	1.190195	3.307251

1-VII-F: D

Si	0.457880	-0.069954	0.388593
C	1.880254	0.558634	-0.722726
F	1.555913	0.386391	1.751043
O	0.527611	-1.670968	0.932160
C	-0.723036	-0.519483	-1.161591
O	-0.745169	0.927141	1.038287
C	-0.247254	-1.394723	-2.147996
C	-2.038281	-0.081313	-1.330095
C	-2.835645	-0.491083	-2.396167
C	-1.025002	-1.820582	-3.215122
C	-2.333564	-1.368452	-3.345053
H	-2.453664	0.597215	-0.595105
H	-3.852282	-0.124872	-2.483998
H	0.767542	-1.774633	-2.072257
H	-0.615377	-2.507588	-3.946671
H	-2.948313	-1.694857	-4.174691
H	1.698204	0.475084	-1.793918
H	2.046983	1.614947	-0.492334
H	2.812717	0.040267	-0.484979
C	-1.261547	0.981407	2.351634
C	-0.442367	-2.440046	1.610479
C	-0.540706	2.051713	3.171115
C	-2.735293	1.371831	2.216252
C	-1.139951	-0.385143	3.057859
C	0.292218	-3.189143	2.724213
C	-1.581018	-1.581569	2.201942
C	-1.051895	-3.459440	0.644539
H	-0.102699	-0.512063	3.366313
H	-1.734650	-0.338927	3.972550
H	-2.199964	-1.232978	1.373101
H	-2.211451	-2.250585	2.791275
H	1.090703	-3.796056	2.294118
H	0.746195	-2.492798	3.429480
H	-0.385757	-3.847264	3.272116
H	-1.736770	-4.131597	1.166486
H	-1.600169	-2.956773	-0.151821
H	-0.262251	-4.058897	0.188005
H	0.517889	1.813985	3.248030
H	-0.643899	3.025431	2.687637
H	-0.964612	2.122811	4.175635
H	-2.820905	2.306835	1.660006
H	-3.299304	0.608519	1.678861
H	-3.194721	1.510239	3.197087

1-III

Si	0.223990	0.286323	0.143766
C	2.000583	0.835604	0.220404
O	-0.846480	1.532933	0.167726
O	0.138691	-0.613436	-1.233039
C	-0.234305	-0.722070	1.657891
C	0.579880	-1.788610	2.047700
C	-1.374081	-0.459370	2.418675
C	-1.695627	-1.237177	3.522679
C	0.266530	-2.568817	3.150726
C	-0.875637	-2.294197	3.890134
H	-2.019864	0.364316	2.141967
H	-2.586085	-1.017381	4.097393
H	1.472090	-2.024194	1.478543
H	0.910851	-3.391244	3.433109
H	-1.124492	-2.901385	4.750720
C	-0.937566	2.754237	-0.568262
C	-0.877424	-1.460553	-1.778238
C	-0.522820	2.555654	-2.023347
C	-2.399096	3.177585	-0.493730
C	-0.047603	3.796581	0.101698
C	-0.655679	-2.878830	-1.262017
C	-2.274944	-0.975114	-1.403037
C	-0.696338	-1.412262	-3.290390
H	2.282447	1.401208	-0.669056
H	2.176090	1.460645	1.097552
H	2.661962	-0.030733	0.285898
H	0.519899	2.244800	-2.101232

H	-1.142156	1.798825	-2.504166
H	-0.635724	3.491796	-2.571659
H	-3.036195	2.419442	-0.951182
H	-2.704169	3.301683	0.546108
H	-2.555086	4.122609	-1.015643
H	-0.317675	3.903522	1.152980
H	1.002489	3.508453	0.042082
H	-0.161805	4.766340	-0.384902
H	-0.832771	-0.393726	-3.656415
H	0.306518	-1.743996	-3.562327
H	-1.421441	-2.058652	-3.786806
H	-1.353707	-3.571007	-1.735452
H	0.360508	-3.206894	-1.484837
H	-0.806683	-2.926573	-0.183327
H	-2.425984	-0.997072	-0.322946
H	-2.442480	0.042924	-1.753603
H	-3.024427	-1.623528	-1.858825

1-III-F: A

Si	0.285261	-0.042508	0.132964
C	2.167963	-0.241054	0.290630
O	0.452619	1.716382	0.151926
F	0.194810	-1.846461	0.179245
O	-0.490917	-0.002263	-1.368185
C	-0.786194	-0.058661	1.726650
C	-0.382182	0.654824	2.857619
C	-1.995525	-0.750226	1.818738
C	-2.778825	-0.711675	2.965223
C	-1.139744	0.678276	4.021969
C	-2.350552	0.001565	4.076817
H	-2.342439	-1.328092	0.970661
H	-3.721874	-1.244163	2.994710
H	0.540990	1.221109	2.820668
H	-0.790797	1.234006	4.884063
H	-2.952612	0.027579	4.976351
C	-0.399856	2.783799	-0.160467
C	-0.863411	-0.926989	-2.365948
C	-0.163369	3.202660	-1.616415
C	-1.891244	2.474779	0.034161
C	-0.018446	3.942301	0.766493
C	0.343606	-1.730439	-2.852274
C	-1.973743	-1.860146	-1.880617
C	-1.399455	-0.083472	-3.525525
H	2.545014	-0.832992	-0.548521
H	2.699462	0.709391	0.312601
H	2.413300	-0.800746	1.197378
H	0.891579	3.443341	-1.764756
H	-0.422707	2.378466	-2.279182
H	-0.758952	4.078836	-1.886524
H	-2.188375	1.624681	-0.578716
H	-2.111545	2.243121	1.076435
H	-2.493329	3.339414	-0.255339
H	-0.182427	3.656751	1.807487
H	1.038422	4.187412	0.643428
H	-0.608284	4.838267	0.557089
H	-2.241113	0.525617	-3.191291
H	-0.622175	0.584544	-3.899914
H	-1.736284	-0.716076	-4.349379
H	1.133041	-1.051949	-3.182187
H	0.735249	-2.357147	-2.053770
H	0.067695	-2.368114	-3.695125
H	-1.615098	-2.492469	-1.071794
H	-2.820658	-1.273478	-1.518588
H	-2.324820	-2.496111	-2.696441

1-III-F: C

Si	0.415791	0.153832	0.310330
C	1.890487	0.056302	1.590232
O	0.758005	1.823270	0.187925
F	1.117949	-1.225722	-0.437716
O	-0.689740	0.277730	-1.046322
C	-0.955030	-0.329144	1.573028
C	-2.098446	0.453370	1.752127
C	-0.862913	-1.488814	2.346644
C	-1.863458	-1.863639	3.235079
C	-3.095790	0.105259	2.653797
C	-2.985489	-1.062962	3.396274
H	0.004607	-2.131079	2.244927
H	-1.766155	-2.779964	3.804710
H	-2.221178	1.351652	1.159963
H	-3.965763	0.740369	2.770688
H	-3.765227	-1.345852	4.092153
C	0.408479	2.930990	-0.612857
C	-1.361678	-0.639272	-1.866369
C	0.814284	2.709403	-2.070896
C	-1.082841	3.255167	-0.518348
C	1.208742	4.108210	-0.048646
C	-0.465669	-1.060790	-3.037628
C	-1.847749	-1.890842	-1.124876
C	-2.583768	0.100811	-2.421011
H	2.838886	0.317683	1.108407
H	1.740080	0.760758	2.414238
H	2.011461	-0.942173	2.022566
H	1.874015	2.450892	-2.126941
H	0.237167	1.894540	-2.500366
H	0.651952	3.615310	-2.659808
H	-1.669959	2.418849	-0.890076
H	-1.358522	3.448088	0.520452
H	-1.320072	4.147579	-1.102532
H	0.948258	4.272533	0.998417
H	2.278165	3.897024	-0.103394
H	1.007756	5.027103	-0.603929
H	-3.235586	0.413077	-1.602725
H	-2.267821	0.993373	-2.964500
H	-3.161298	-0.530409	-3.100481
H	-0.119688	-0.178888	-3.580332
H	0.405864	-1.601753	-2.672679
H	-1.007630	-1.701522	-3.737786
H	-1.011077	-2.442925	-0.698395
H	-2.529254	-1.623453	-0.316876
H	-2.378085	-2.552081	-1.814124

1-III-F: D

Si	-0.200244	0.430243	0.015631
C	1.333148	-0.131160	1.017123
O	-0.647273	2.063187	0.016020
F	0.842849	0.685842	-1.394332
O	-1.114363	-0.714694	-0.836636
C	-1.392534	0.139228	1.585177
C	-1.701470	1.147954	2.504922
C	-1.862136	-1.138726	1.914774
C	-2.588013	-1.399264	3.071069
C	-2.428114	0.909123	3.667052
C	-2.877519	-0.370971	3.958512
H	-1.659497	-1.957835	1.234178
H	-2.932325	-2.405889	3.279569
H	-1.368640	2.157535	2.295958
H	-2.646594	1.725781	4.345835
H	-3.445629	-0.564374	4.860058
C	-0.137503	3.257428	-0.535790
C	-0.925534	-1.520866	-1.979142
C	-0.411359	3.324783	-2.038872
C	-0.895769	4.388395	0.162928
C	1.357380	3.411277	-0.248663
C	0.403060	-2.276621	-1.912340
C	-2.074265	-2.532198	-1.959057
C	-1.014360	-0.693635	-3.262756
H	2.277563	-0.079638	0.472925
H	1.425147	0.475790	1.922759
H	1.190996	-1.162310	1.355255
H	0.124606	2.534204	-2.558919
H	-1.479684	3.199472	-2.226733
H	-0.102817	4.290272	-2.446482
H	-1.969373	4.277476	0.001595
H	-0.708643	4.362038	1.238034
H	-0.586829	5.364806	-0.216094
H	1.541084	3.328782	0.824679
H	1.929108	2.638695	-0.758153
H	1.714356	4.388486	-0.581148
H	-1.950362	-0.131421	-3.276682
H	-0.189034	0.011759	-3.323139
H	-0.991265	-1.341667	-4.141986
H	1.244225	-1.586559	-1.935120
H	0.456546	-2.857640	-0.989217
H	0.495874	-2.966681	-2.753930
H	-2.034819	-3.131642	-1.047824
H	-3.033140	-2.011656	-1.981064
H	-2.024777	-3.205221	-2.817626

1-III-F: F

Si	-0.381074	0.424396	0.357298
C	0.635146	-0.171332	1.907837
O	0.519374	1.868975	0.383577
F	-1.288357	0.997373	-1.046970
O	0.121930	-0.965504	-0.484789
C	-2.073584	0.328537	1.281841
C	-2.864780	1.453475	1.530412
C	-2.550227	-0.890393	1.772799
C	-3.753837	-0.990057	2.459660
C	-4.059884	1.373295	2.234714
C	-4.513757	0.146551	2.699406
H	-1.967402	-1.791069	1.613327
H	-4.096953	-1.954894	2.813414
H	-2.544847	2.421263	1.162247
H	-4.642070	2.269046	2.415425
H	-5.448435	0.077036	3.241363
C	0.654441	3.037577	-0.395350
C	-0.231525	-1.628577	-1.680257
C	-0.624302	3.876308	-0.376696
C	1.781244	3.836483	0.264832
C	1.056149	2.708594	-1.833824
C	0.190734	-0.827085	-2.912745
C	0.544142	-2.947795	-1.656801
C	-1.729833	-1.932305	-1.728018
H	1.704771	-0.223415	1.680934
H	0.509626	0.519256	2.748863
H	0.321666	-1.164185	2.246126
H	-1.445566	3.335439	-0.842227
H	-0.899496	4.113698	0.652901
H	-0.475906	4.816113	-0.913587
H	1.524824	4.059967	1.301837
H	2.705647	3.256250	0.261192
H	1.960600	4.777876	-0.258887
H	1.933721	2.059254	-1.835378
H	0.248297	2.199092	-2.352989
H	1.304303	3.620452	-2.381830
H	-2.021941	-2.524258	-0.858796
H	-2.309696	-1.011677	-1.728836
H	-1.977251	-2.502366	-2.626462
H	0.049124	-1.417600	-3.820971
H	-0.392109	0.086805	-2.996955
H	1.246759	-0.560179	-2.840209
H	1.617397	-2.752590	-1.619610
H	0.273194	-3.526736	-0.772166
H	0.331807	-3.549210	-2.543307

1-III-F: G

Si	-0.053058	0.509882	-0.038987
C	1.623201	0.149224	0.781471
O	-0.102490	2.216857	0.467062
F	-0.132108	1.015701	-1.650671
O	-0.062829	-1.183733	-0.610033
C	-1.641863	0.236800	1.004967
C	-2.733182	1.105905	0.954949
C	-1.768599	-0.886495	1.825709
C	-2.919236	-1.130814	2.565065
C	-3.904263	0.855111	1.658301
C	-3.999977	-0.264359	2.474312
H	-0.952937	-1.597627	1.874012
H	-2.978015	-2.004609	3.202894
H	-2.661473	1.999980	0.348028
H	-4.741005	1.538779	1.578318
H	-4.906028	-0.457934	3.034775
C	0.479954	3.393856	-0.012224
C	-0.805095	-1.879890	-1.571039
C	-0.431907	4.044340	-1.061712
C	0.607204	4.342081	1.185055
C	1.875504	3.178406	-0.614818

C	-0.058275	-1.861975	-2.911467
C	-0.915367	-3.328691	-1.082864
C	-2.225124	-1.332876	-1.782093
H	2.410357	0.162013	0.021128
H	1.881625	0.880223	1.547564
H	1.629878	-0.849009	1.221757
H	-0.535528	3.396490	-1.930899
H	-1.424440	4.208361	-0.636926
H	-0.037337	5.009209	-1.390965
H	-0.374287	4.509499	1.632602
H	1.254355	3.900309	1.945340
H	1.025101	5.308977	0.893833
H	2.554836	2.758537	0.128015
H	1.832603	2.498481	-1.465441
H	2.294809	4.126879	-0.958647
H	-2.806692	-1.390799	-0.861918
H	-2.202934	-0.292925	-2.108039
H	-2.741943	-1.916476	-2.547682
H	0.020770	-0.841984	-3.286361
H	0.951680	-2.254945	-2.776758
H	-0.567262	-2.471214	-3.663062
H	0.081233	-3.744543	-0.922004
H	-1.456047	-3.363060	-0.135061
H	-1.441747	-3.960053	-1.803139

Fluoride ion

F	0.000000	0.000000	0.000000

1-IV

C	0.295042	0.097155	0.156465
Si	2.135865	-0.046143	0.450101
C	-0.296677	1.362831	0.117362
C	-0.527094	-1.017730	-0.014437
C	-1.892828	-0.874945	-0.217330
C	-1.660620	1.511458	-0.085164
C	-2.461242	0.390004	-0.252308
H	-0.094768	-2.009875	0.007987
H	-2.513769	-1.751496	-0.348880
H	0.313824	2.250148	0.242107
H	-2.099037	2.500384	-0.113769
H	-3.525809	0.502565	-0.410876
O	2.961760	0.927051	-0.602959
C	2.666329	0.507667	2.140679
O	2.483978	-1.639190	0.180923
H	2.352876	1.537251	2.322963
H	2.217572	-0.122796	2.910515
H	3.751650	0.463436	2.248439
C	2.817161	0.817594	-2.005524
C	3.774359	-2.179494	0.385581
H	1.773614	0.933215	-2.313608
H	3.403662	1.608292	-2.473360
H	3.181824	-0.146536	-2.370573
H	4.538596	-1.624795	-0.166435
H	4.041838	-2.180610	1.446066
H	3.775213	-3.209823	0.030201

1-VIII

C	-0.554800	0.154000	0.022300
H	0.321944	0.158259	-0.629480
C	-0.939608	1.610150	0.232213
C	-1.387417	-1.257188	2.032605
O	-2.167390	1.784907	0.919067
O	-2.355347	-0.368511	2.565113
Si	-2.427939	1.272278	2.468369
H	-1.352503	-0.355802	-0.525241
H	-1.000884	-1.857653	2.859966
H	-0.135630	2.125122	0.771168
H	-1.907566	-1.937227	1.351380
H	-1.050184	2.100058	-0.736292
C	-4.144373	1.785181	2.936202
C	-1.128472	2.030399	3.591748
C	-0.793220	3.382077	3.478457
C	-0.486439	1.277607	4.576187
C	0.457730	1.850037	5.417292
C	0.150342	3.960804	4.314607
C	0.777485	3.193704	5.286777
H	-0.722614	0.225870	4.686670
H	0.944691	1.248183	6.173554
H	-1.270268	3.994755	2.721851
H	0.397945	5.008936	4.208077
H	1.514271	3.642360	5.940196
H	-4.232610	2.873244	2.931721
H	-4.879193	1.377559	2.240015
H	-4.388567	1.432227	3.939718
C	-0.213964	-0.624538	1.298179
H	0.356752	0.011083	1.981670
H	0.444997	-1.455356	1.035891

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See https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html (accessed date 1 June, 2020).

NMR Spectra of Compounds

Figure S5. ^{1}H NMR spectrum of **1-VI**.

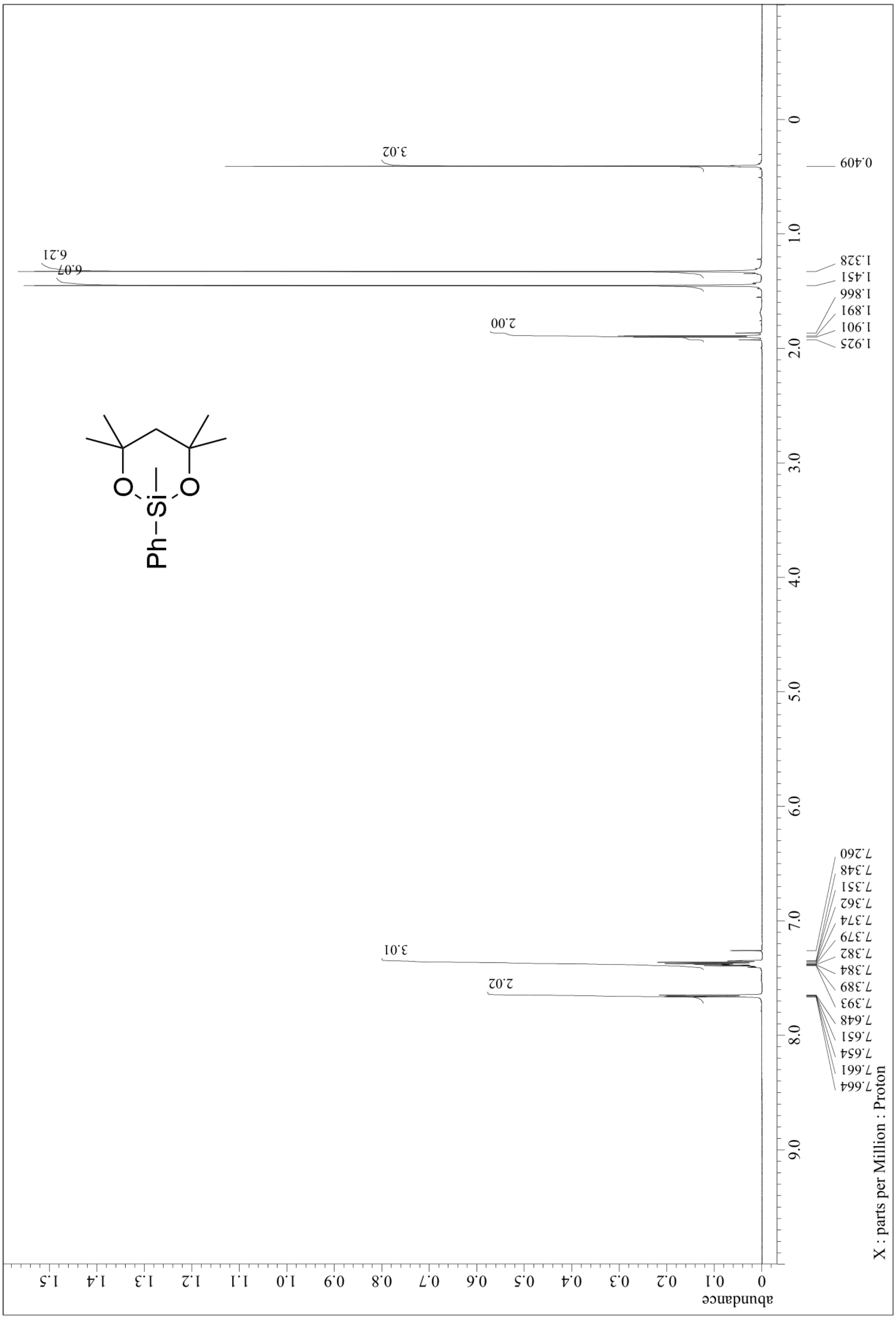

Figure S6. ^{13}C NMR spectrum of **1-VI**.

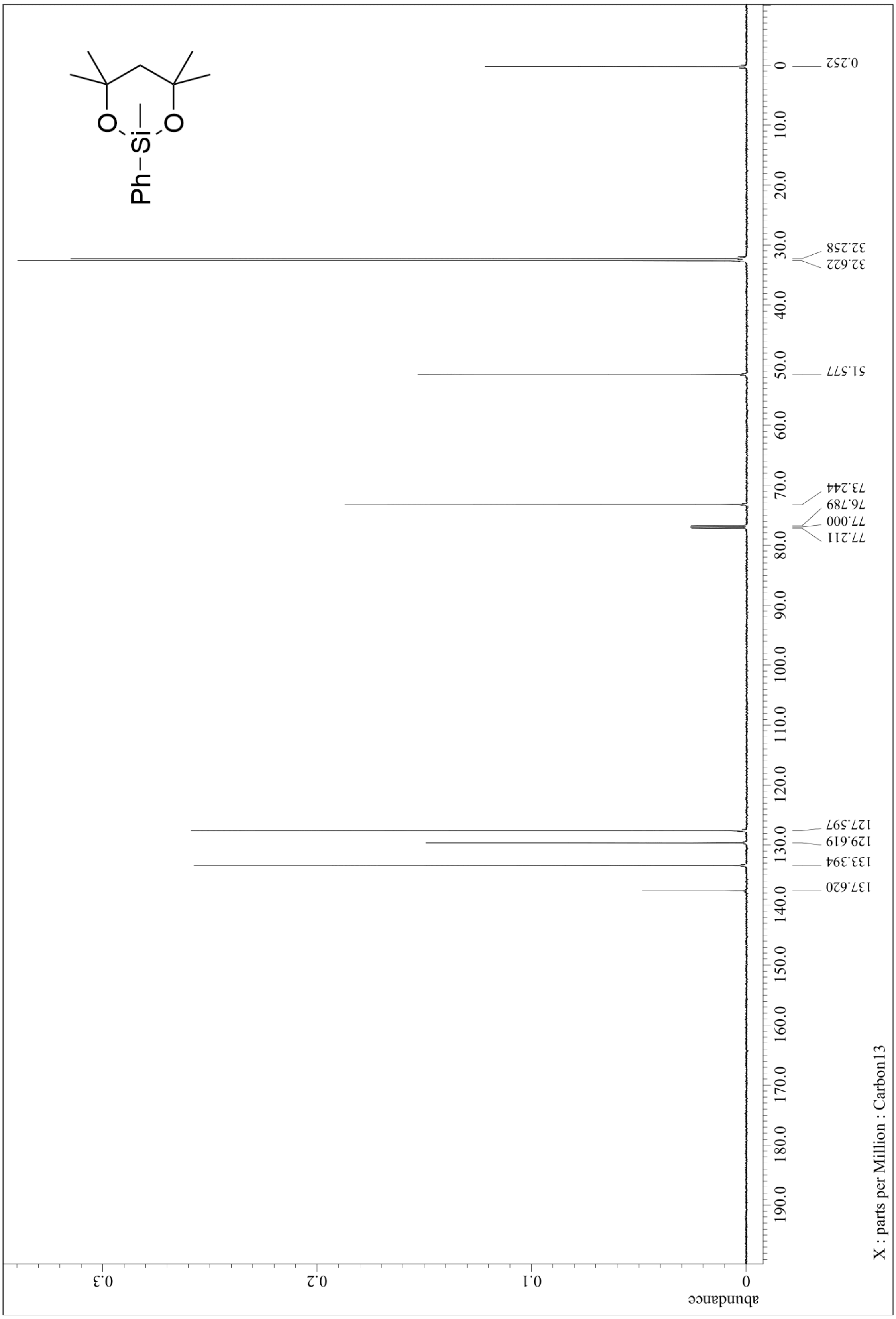

Figure S7. ^{29}Si NMR spectrum of **1-VI**.

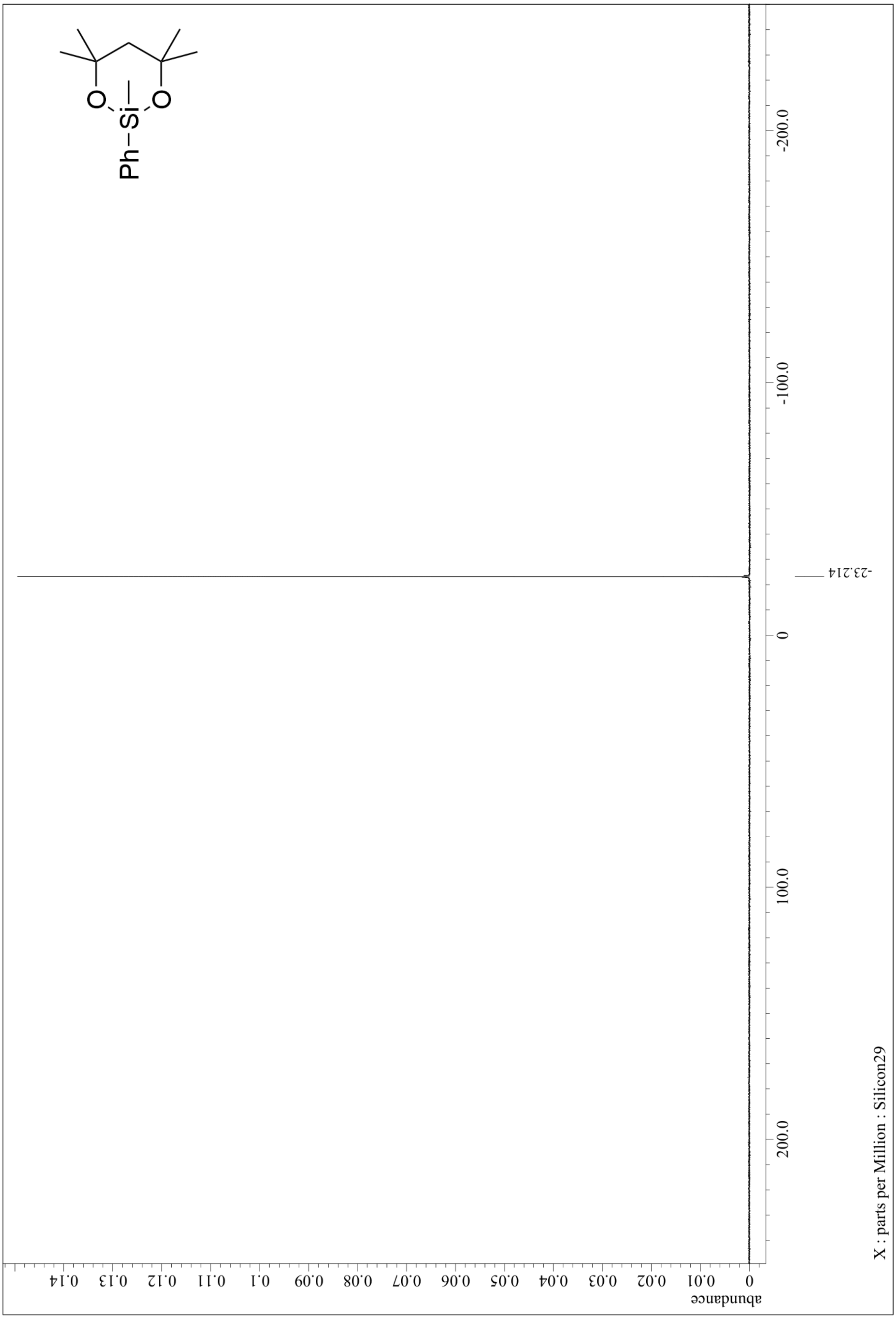

Figure S8. ^{1}H NMR spectrum of **1-VII**.

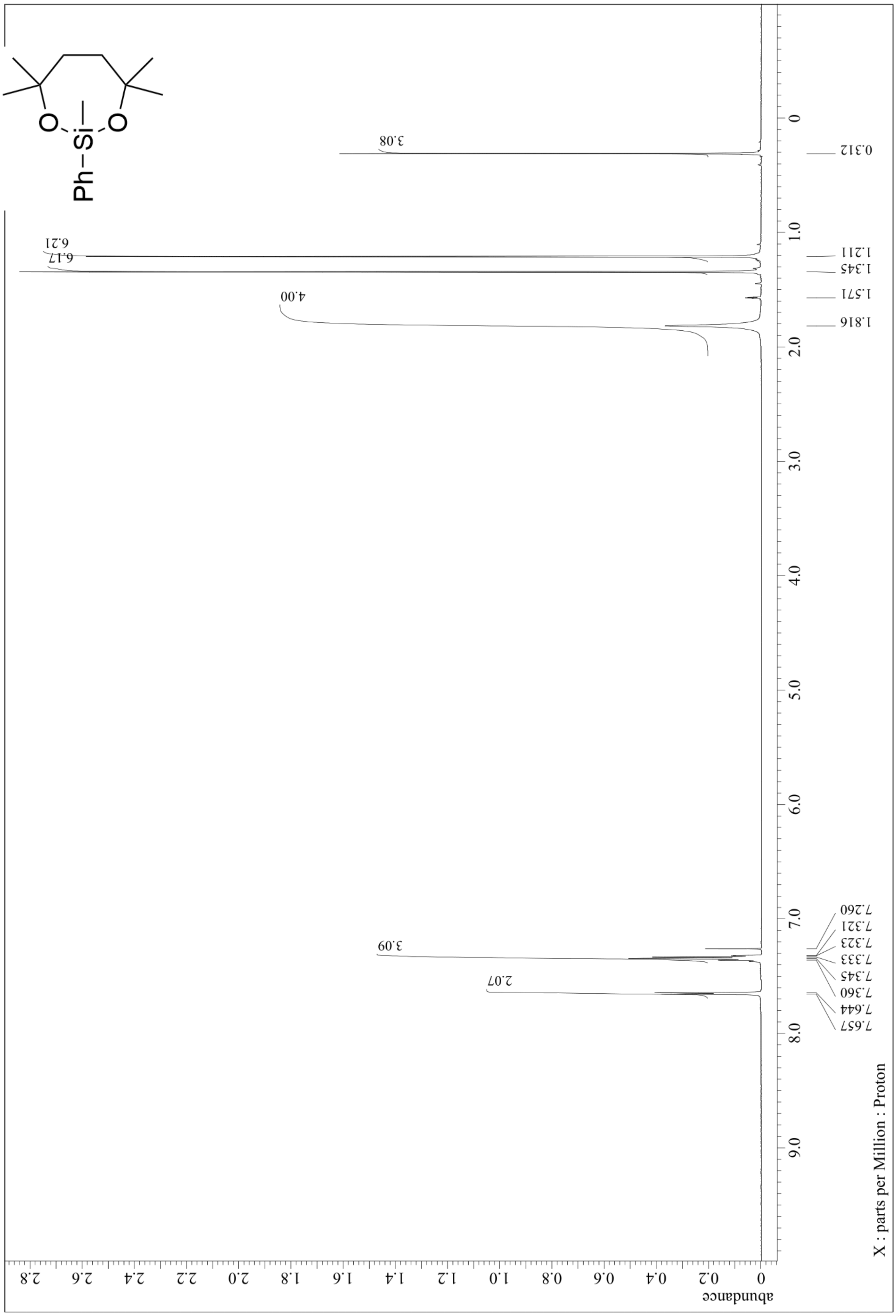

Figure S9. ^{13}C NMR spectrum of **1-VII**.

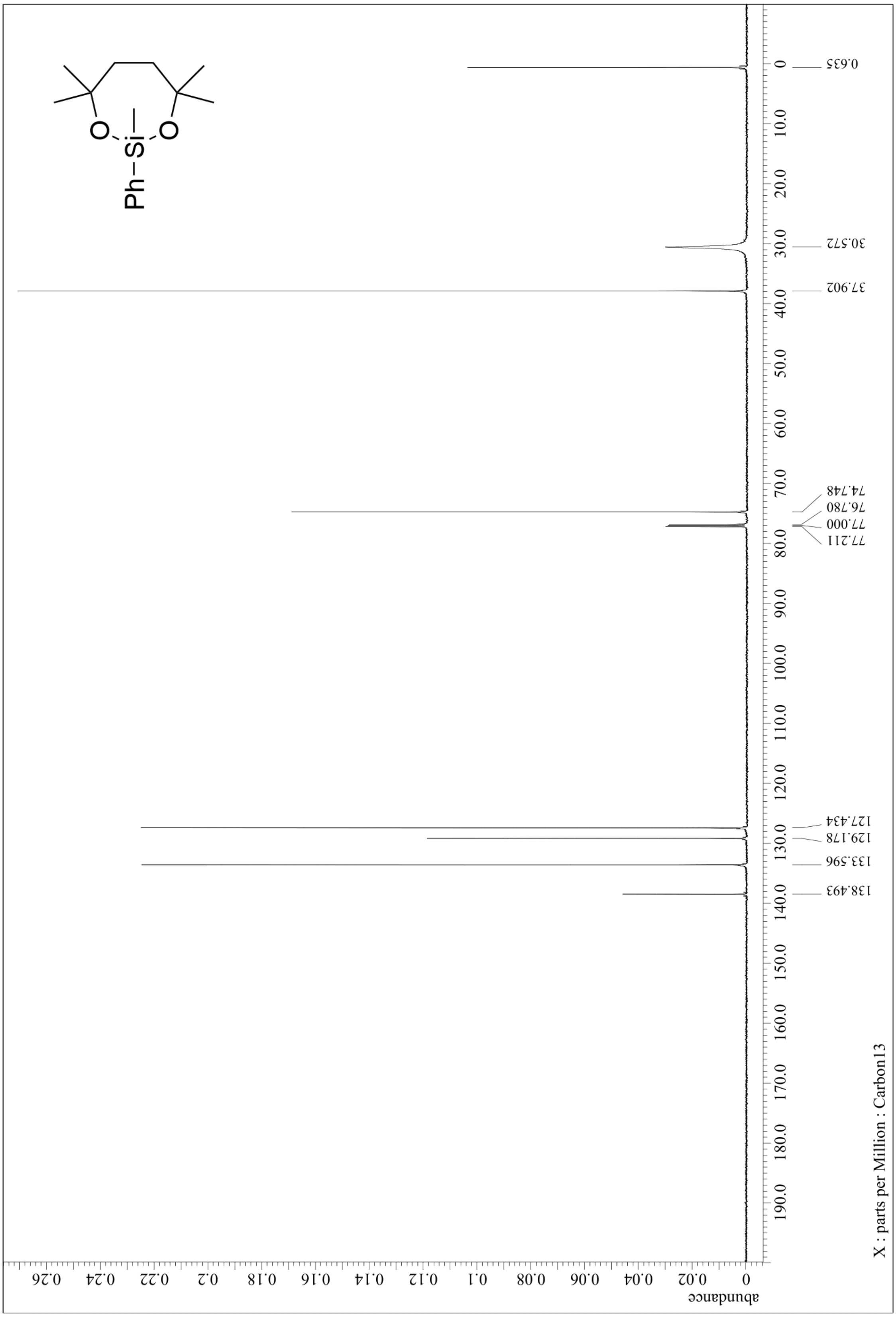

Figure S10. ^{29}Si NMR spectrum of **1-VII**.

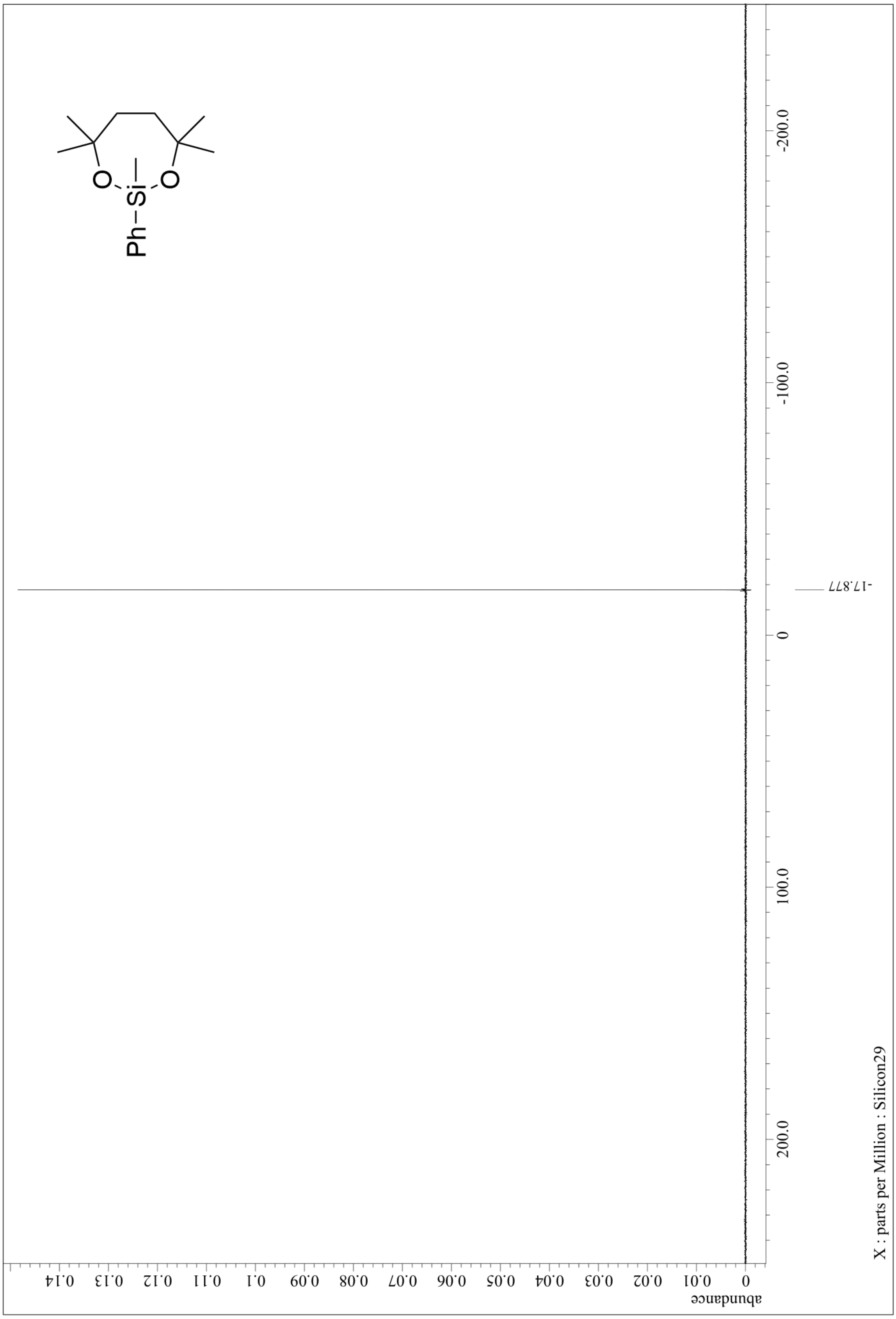

Figure S11. ^{1}H NMR spectrum of **2-VII**.

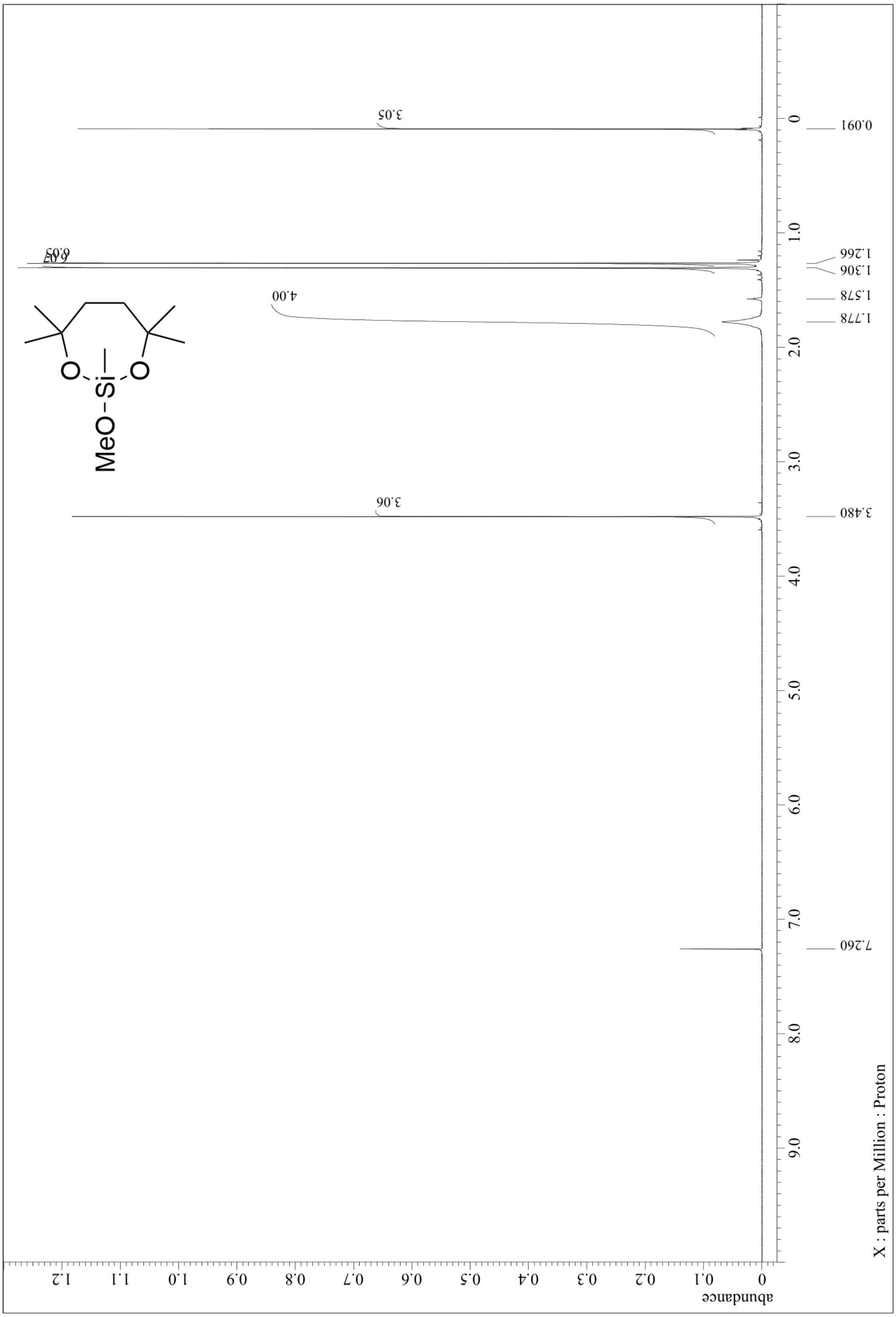

Figure S12. ^{13}C NMR spectrum of **2-VII**.

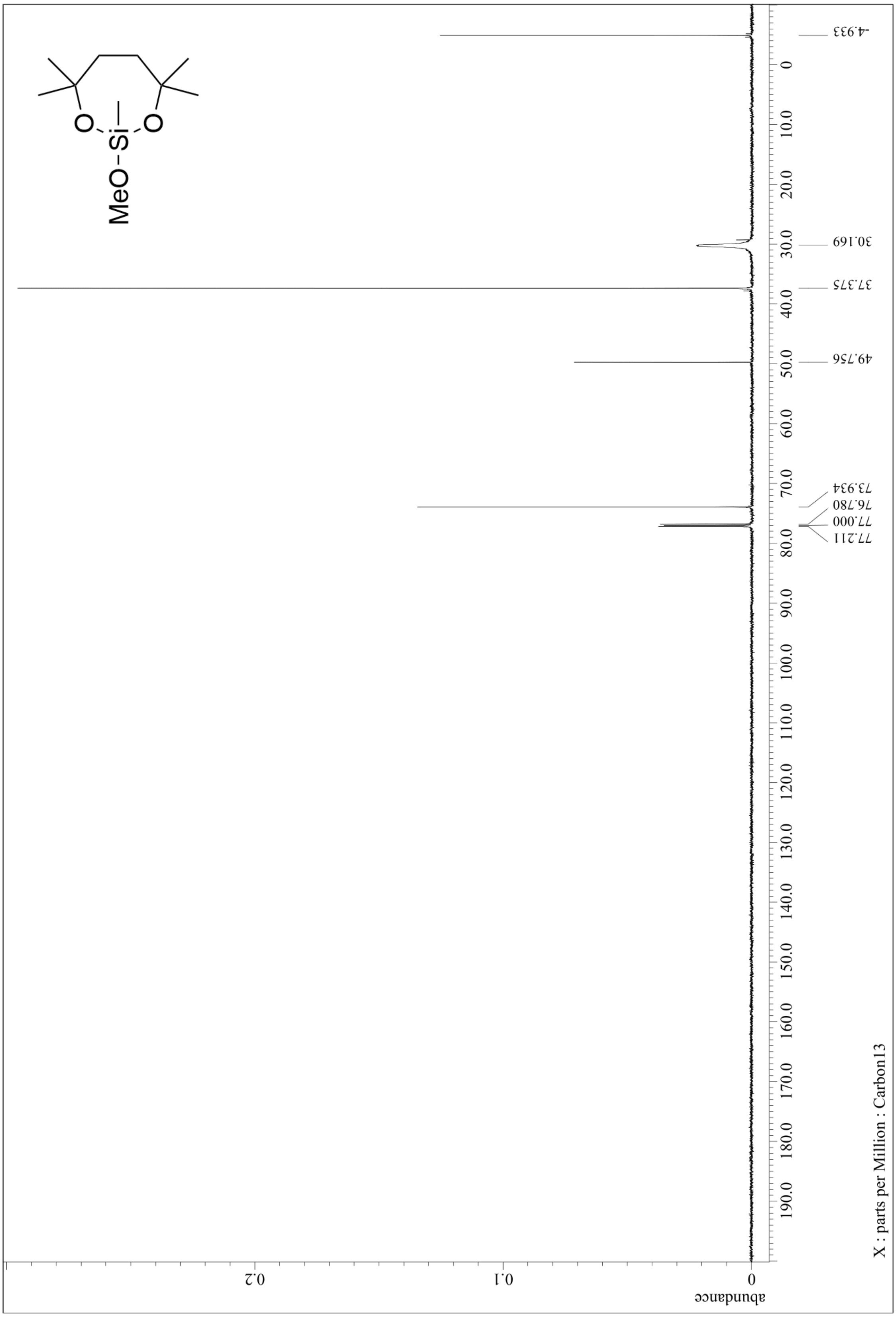

Figure S13. ^{1}H NMR spectrum of **3-III**.

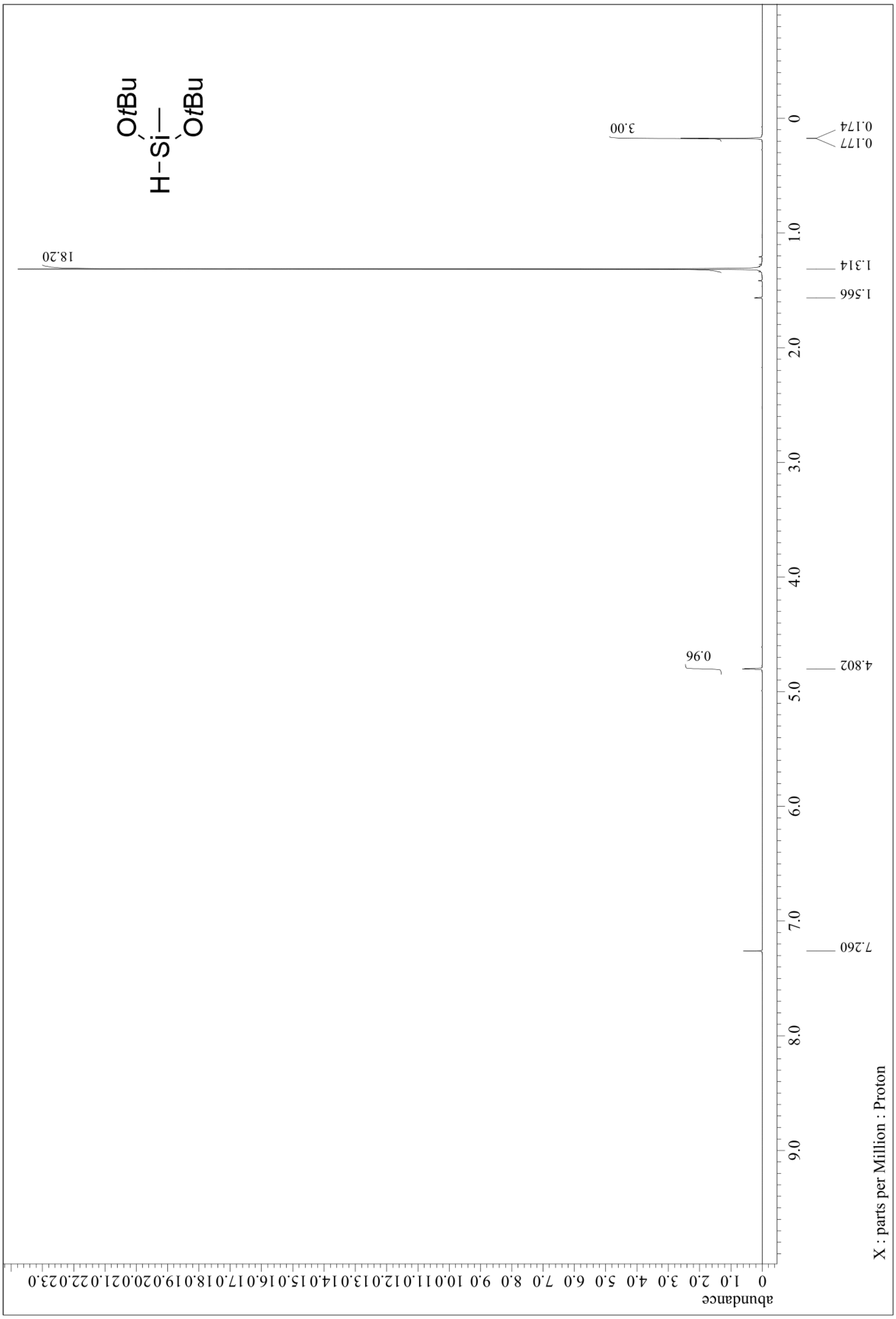

Figure S14. ^{13}C NMR spectrum of **3-III**.

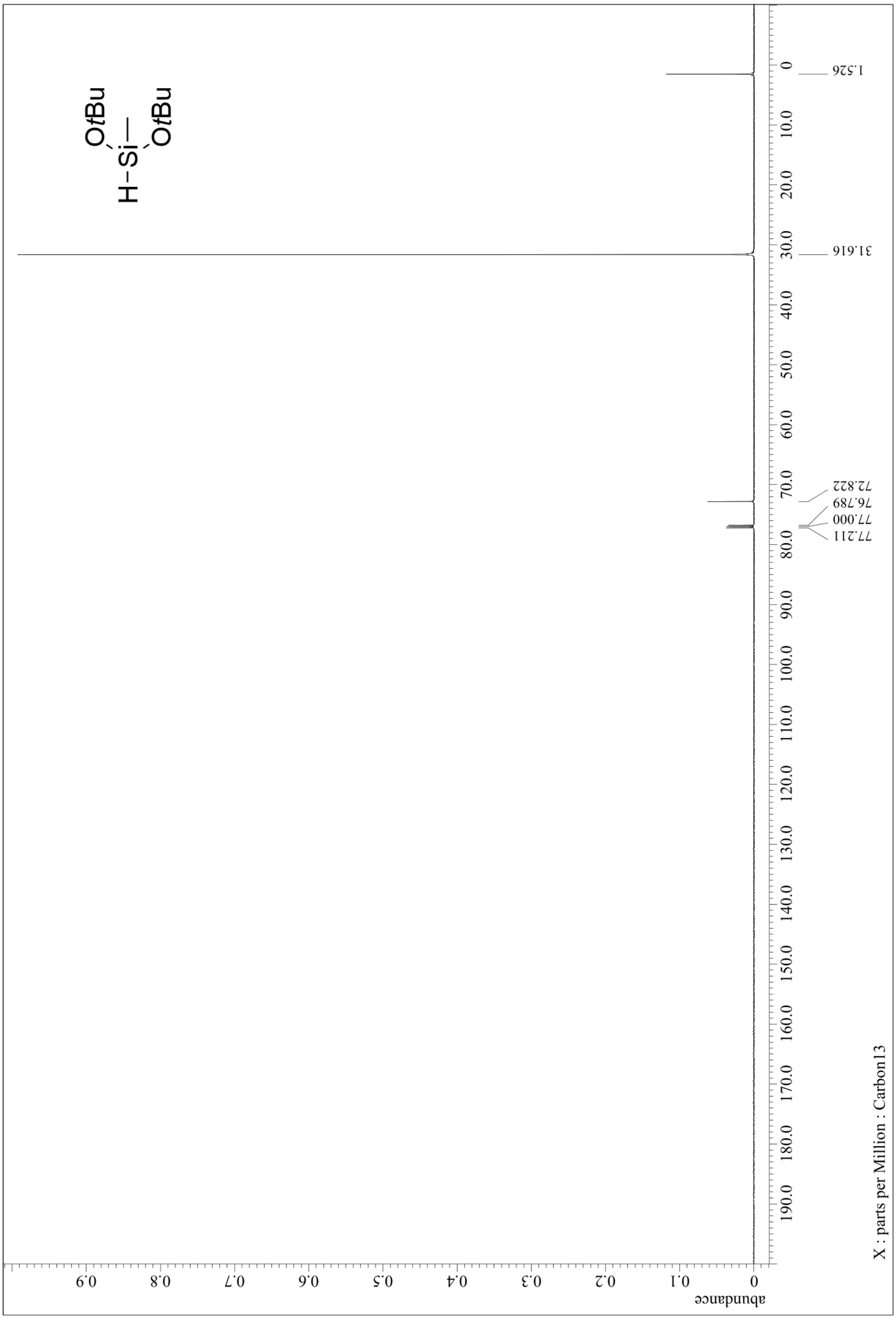

Figure S15. ^{1}H NMR spectrum of **3-VII**.

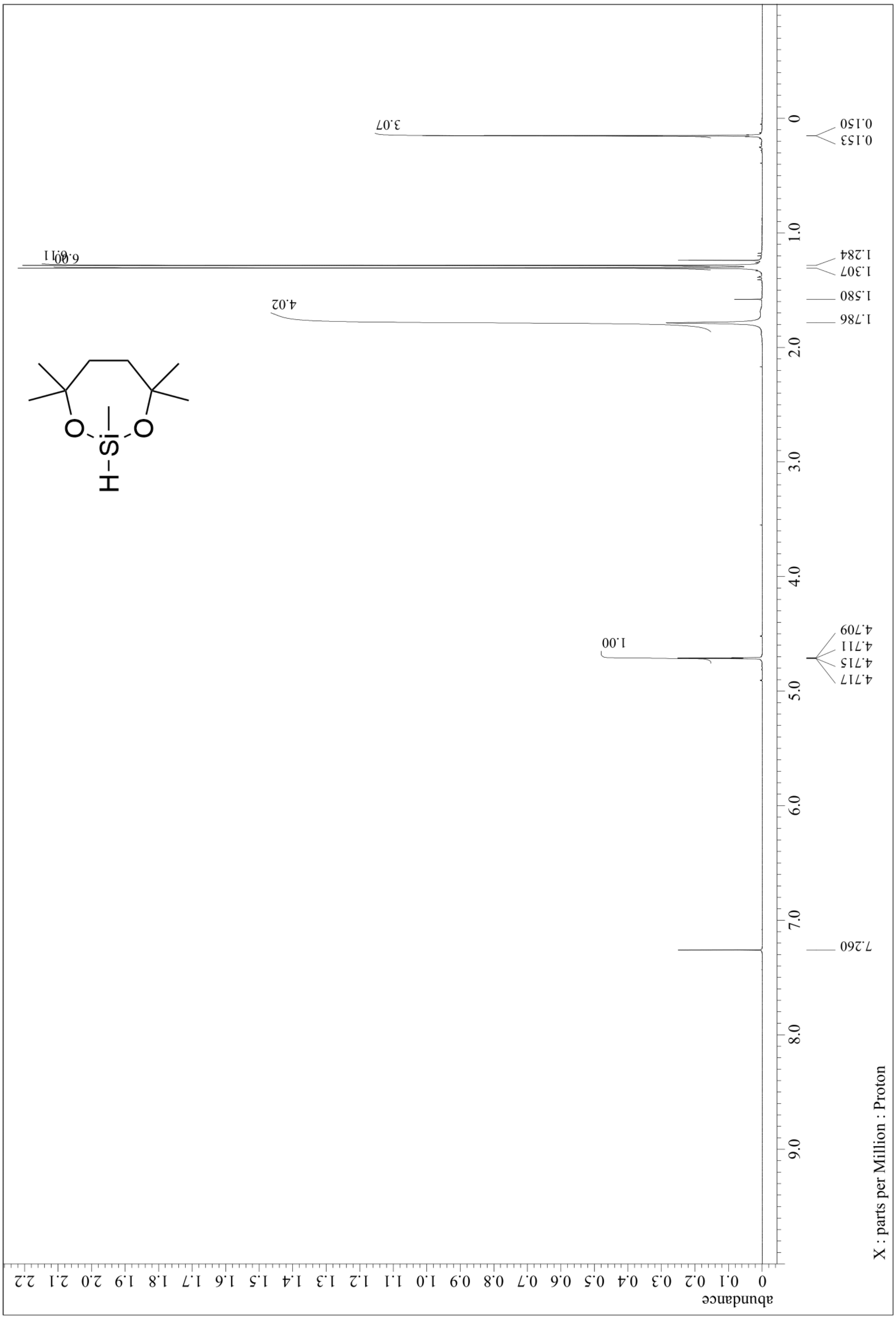

Figure S16. ^{13}C NMR spectrum of **3-VII**.

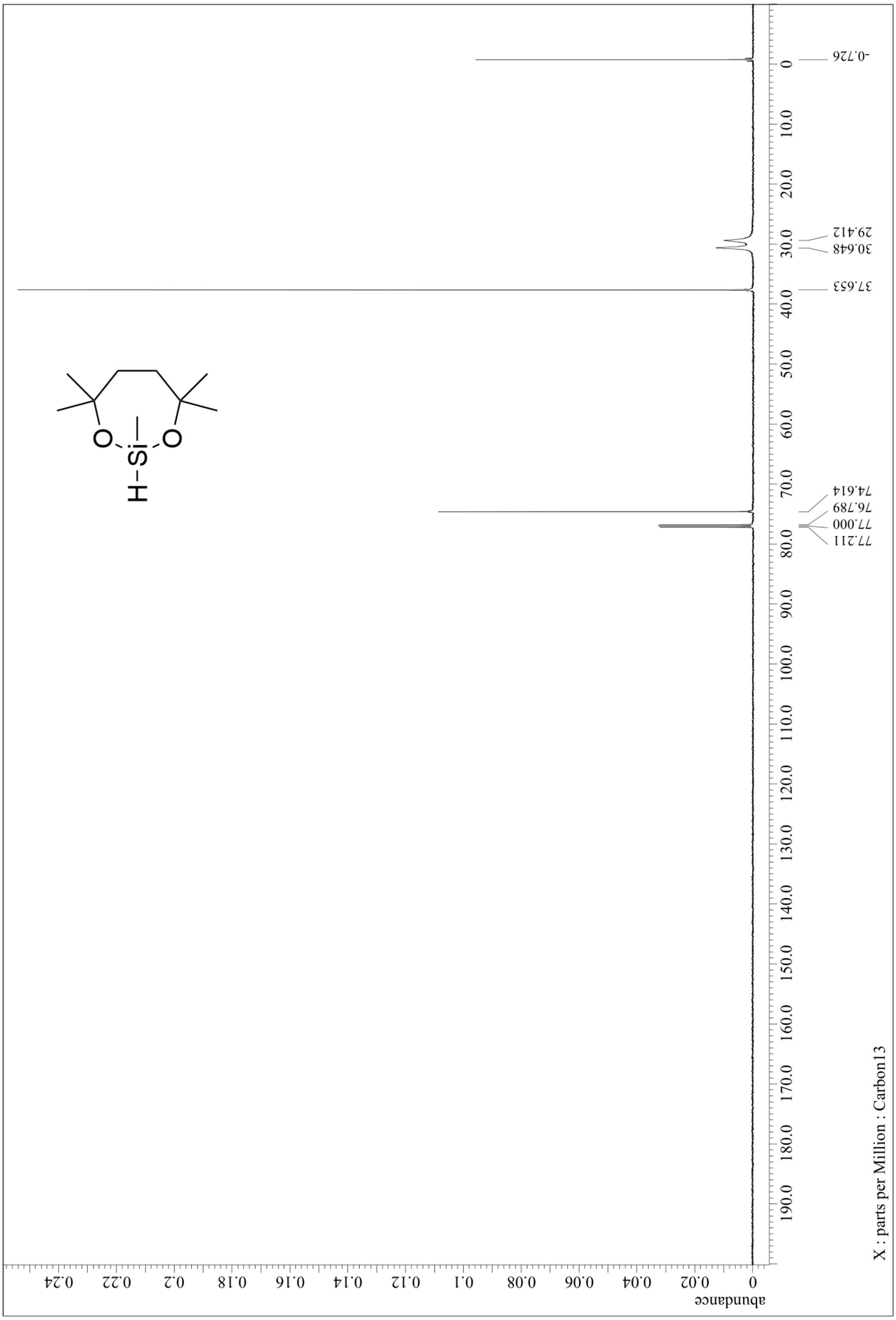

Figure S17. ^{1}H NMR spectrum of **3-XI**.

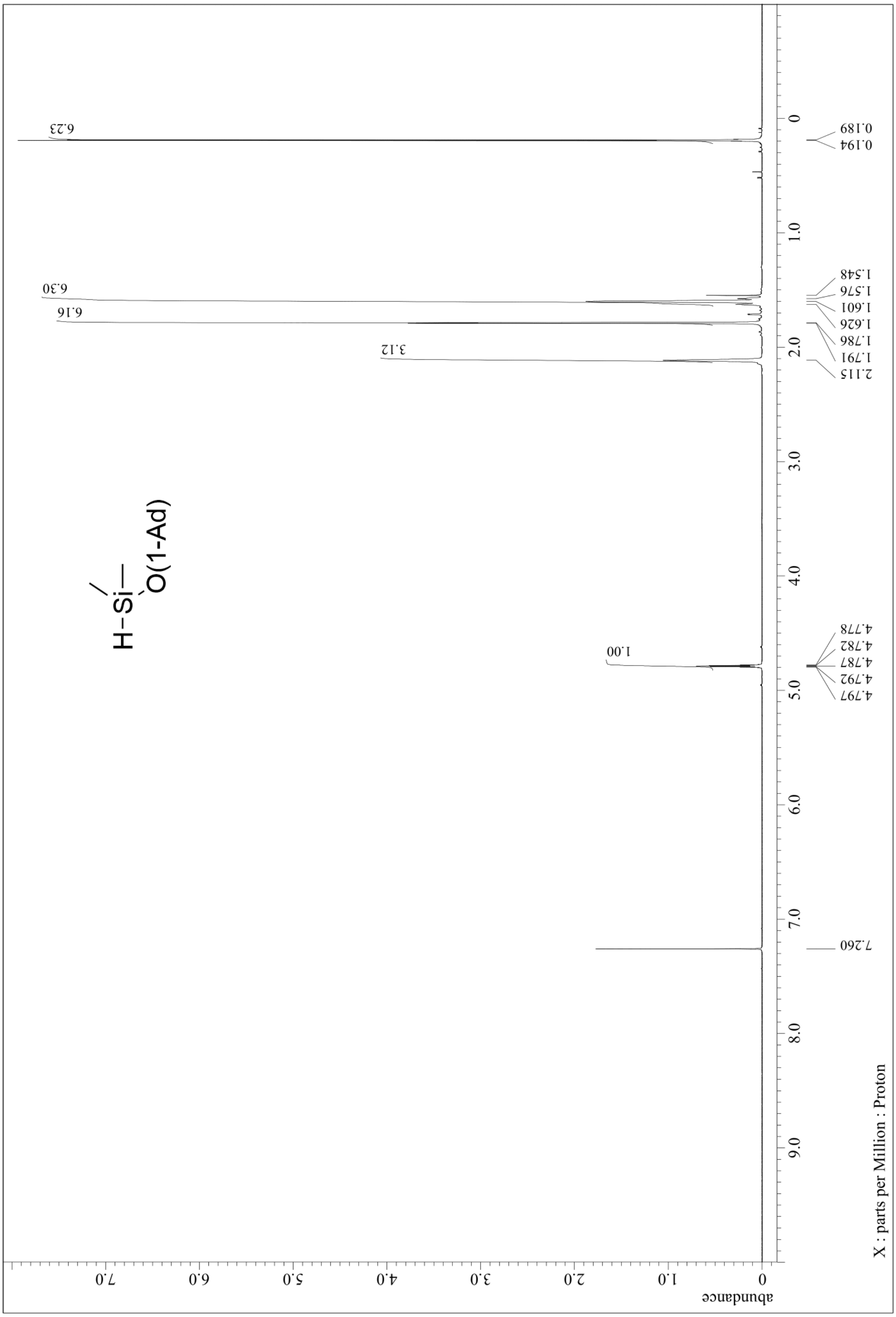

Figure S18. ^{13}C NMR spectrum of **3-XI**.

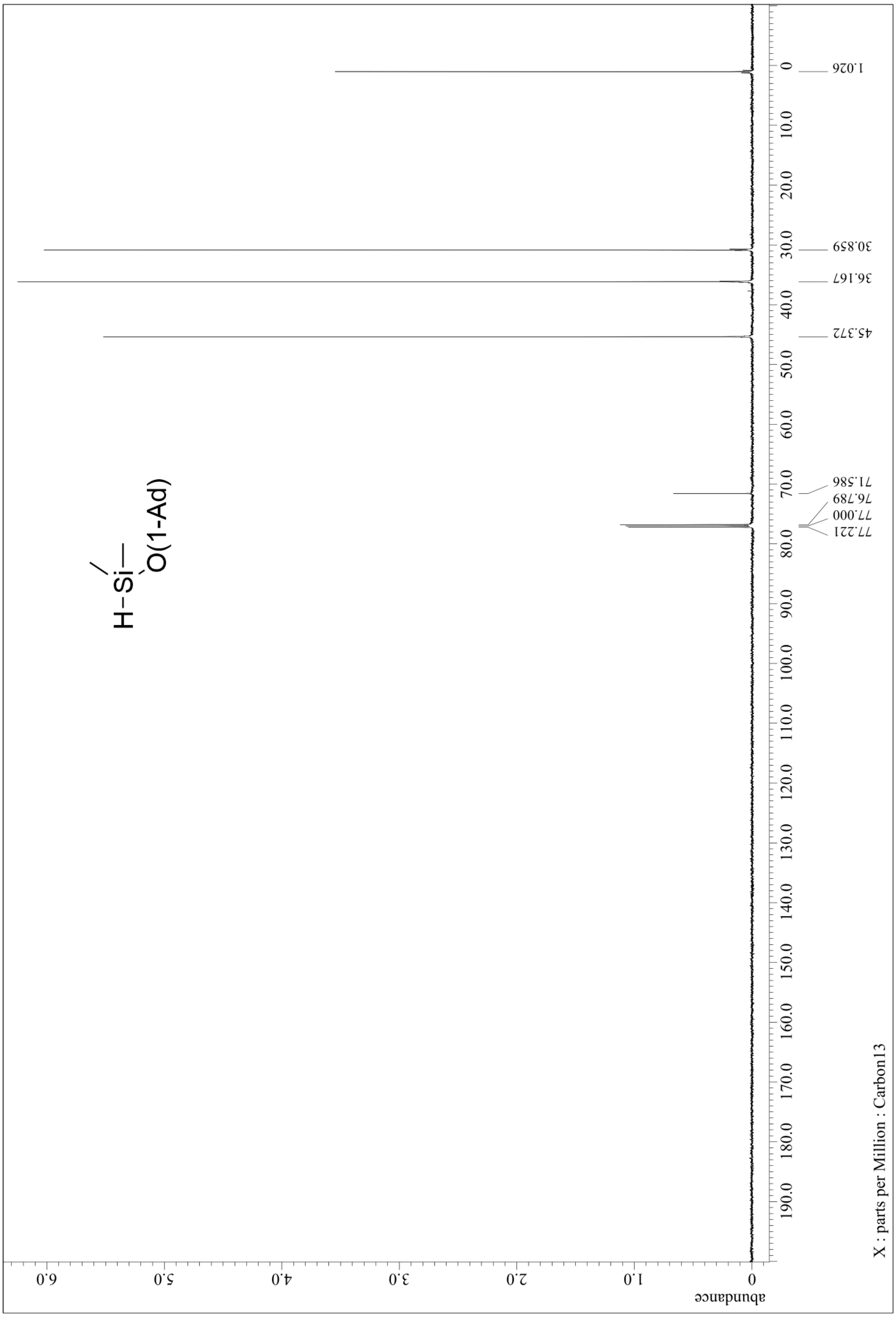

Figure S19. ^{1}H NMR spectrum of **4a**.

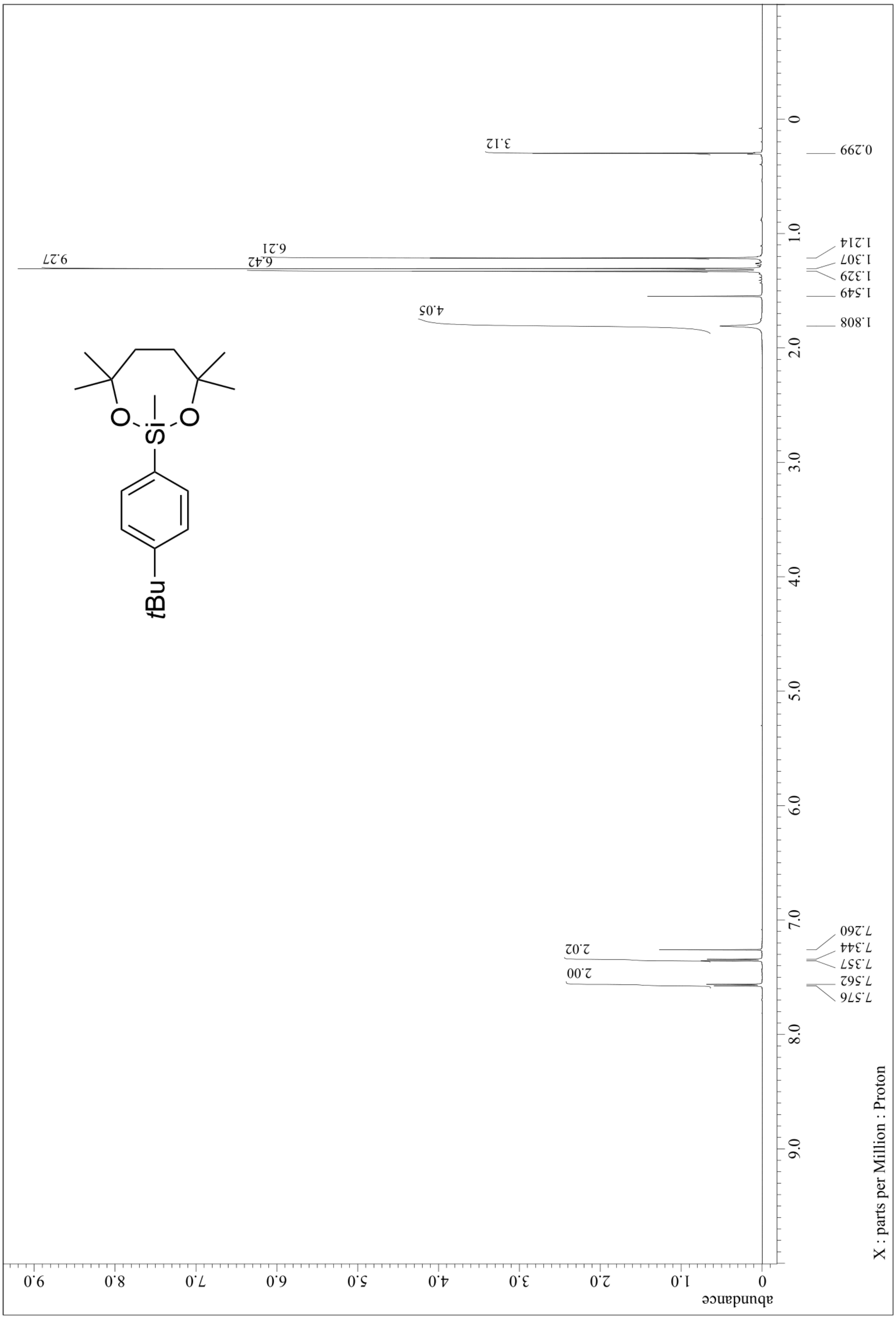

Figure S20. ^{13}C NMR spectrum of **4a**.

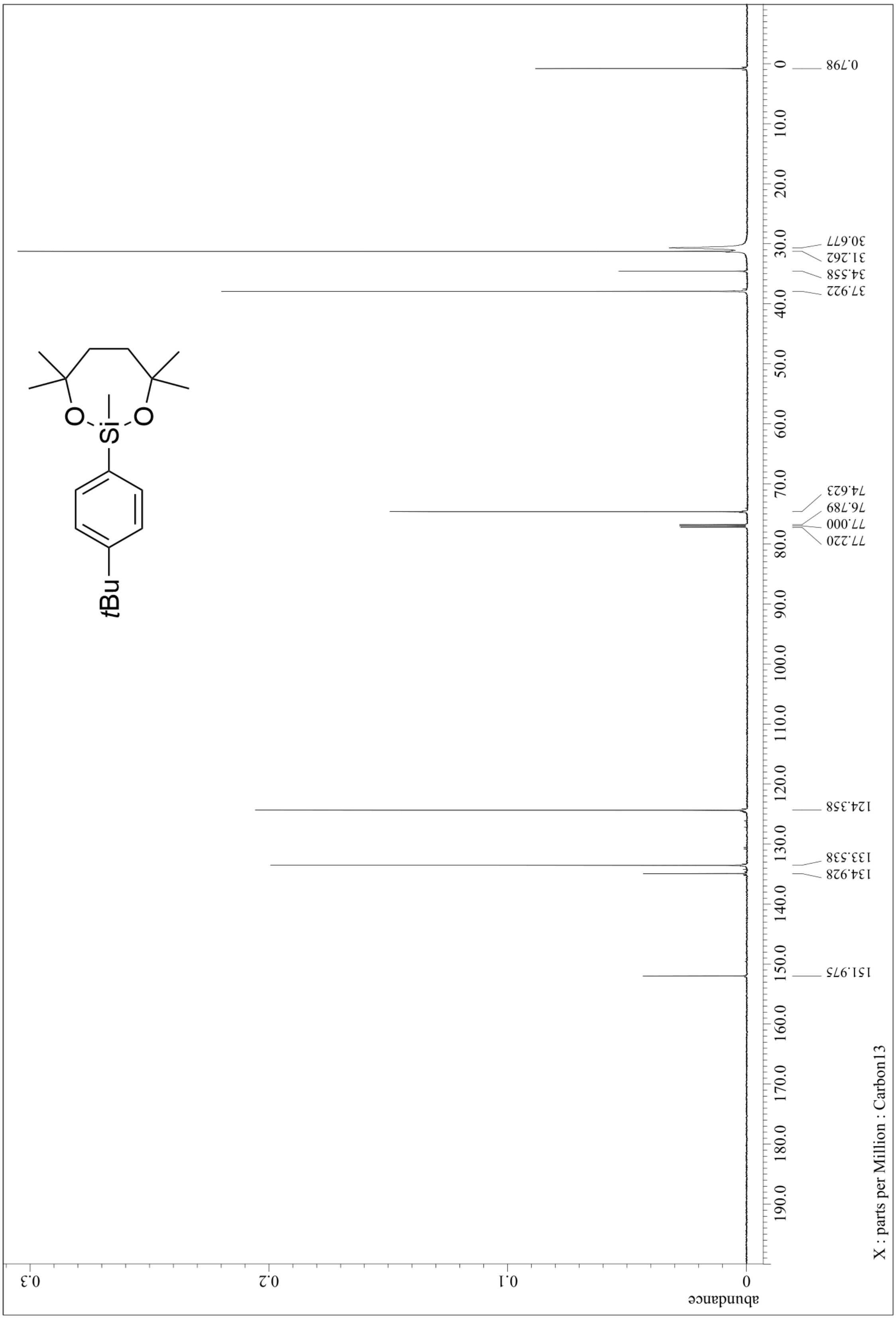

Figure S21. ^{1}H NMR spectrum of **4b**.

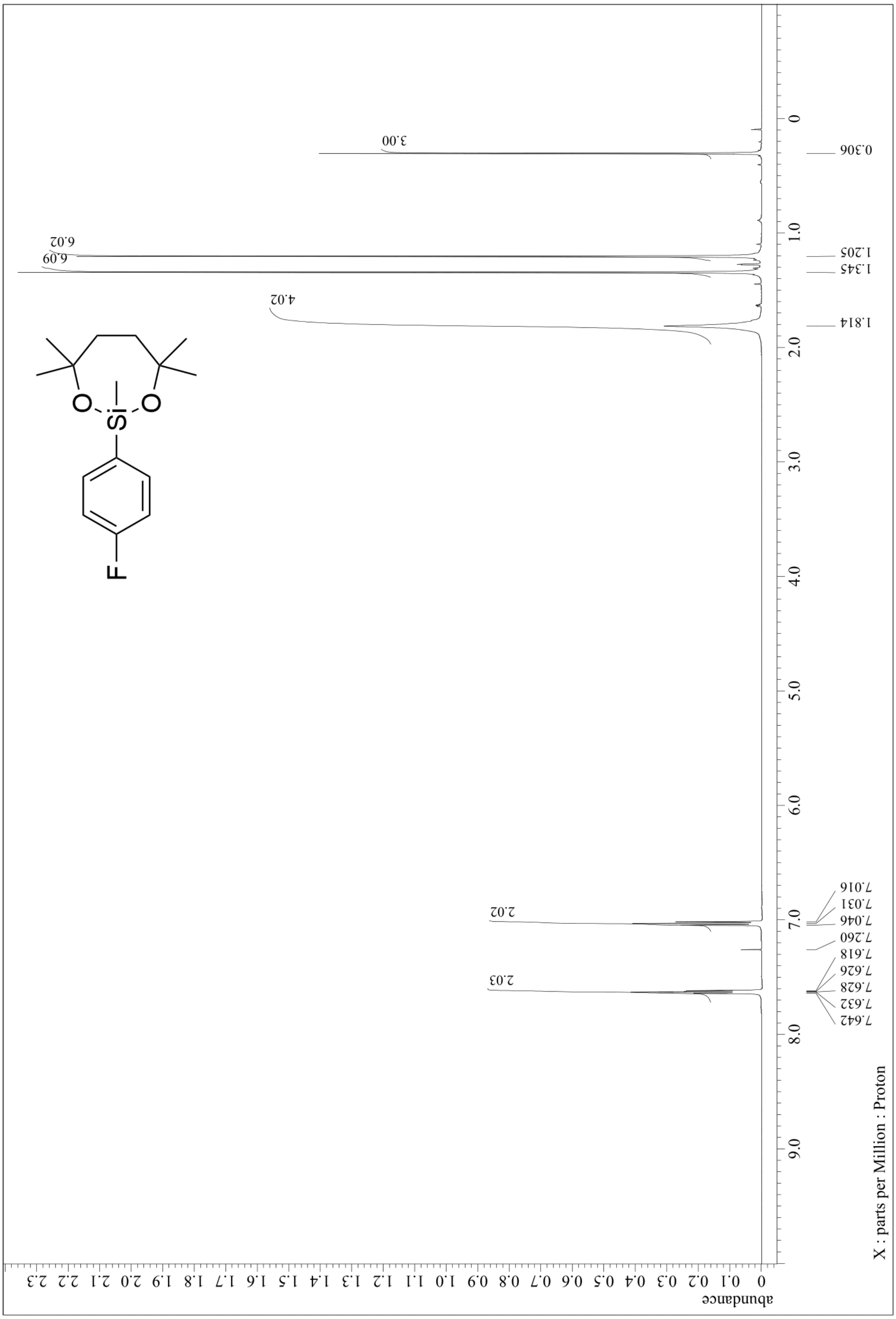

Figure S22. ^{13}C NMR spectrum of **4b**.

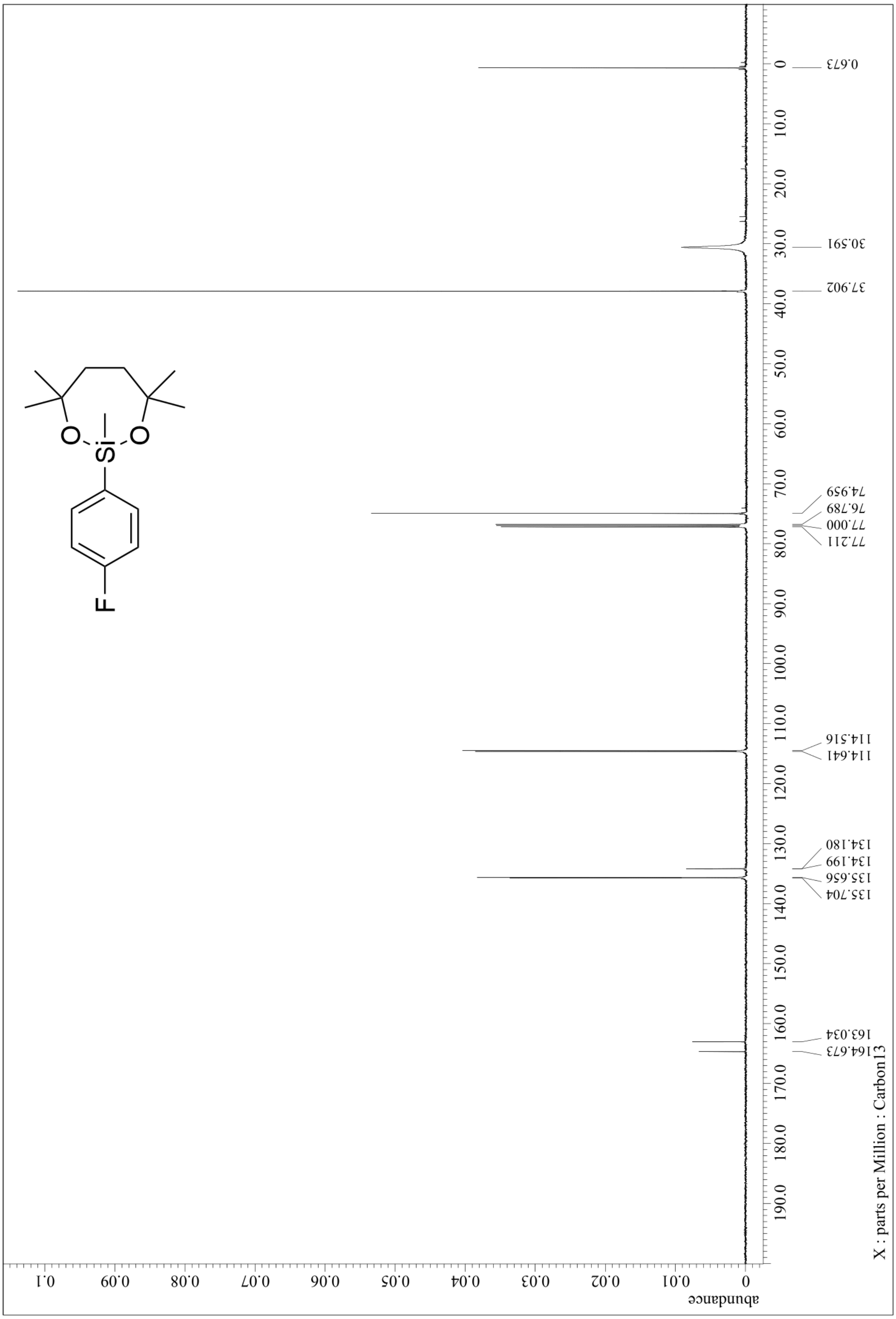

Figure S23. ^{1}H NMR spectrum of **4c**.

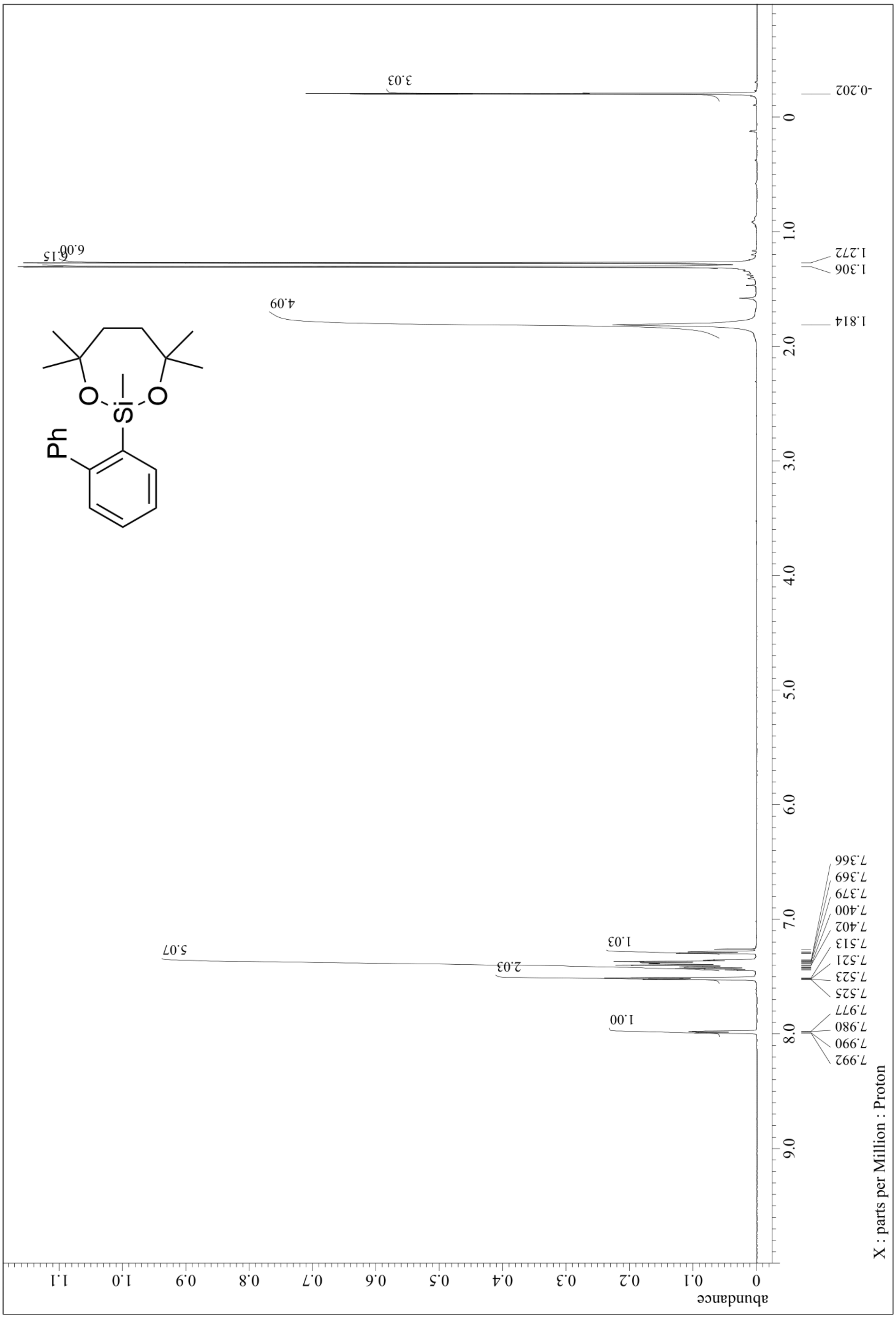

Figure S24. ^{13}C NMR spectrum of **4c**.

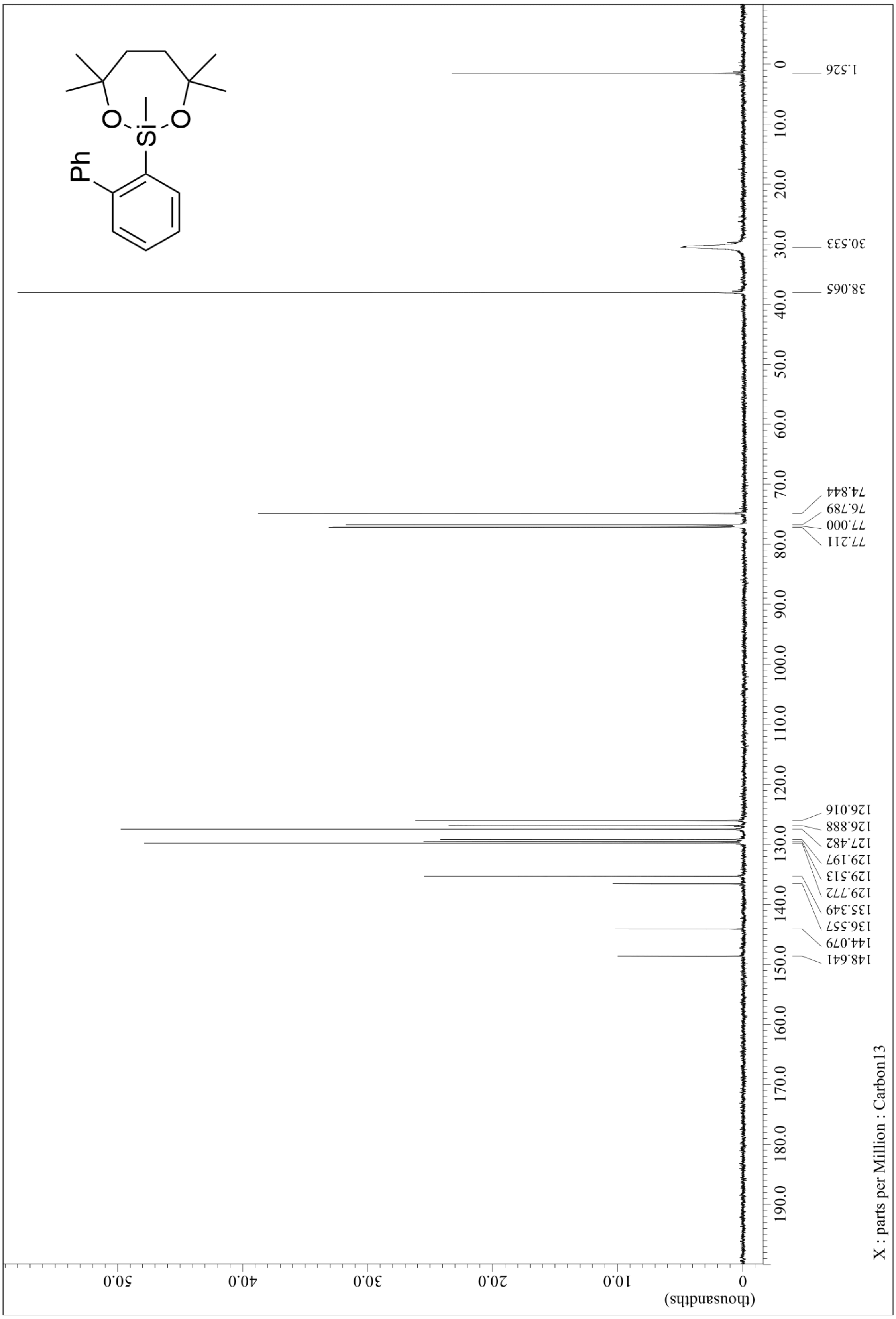

Figure S25. ^{1}H NMR spectrum of **4d**.

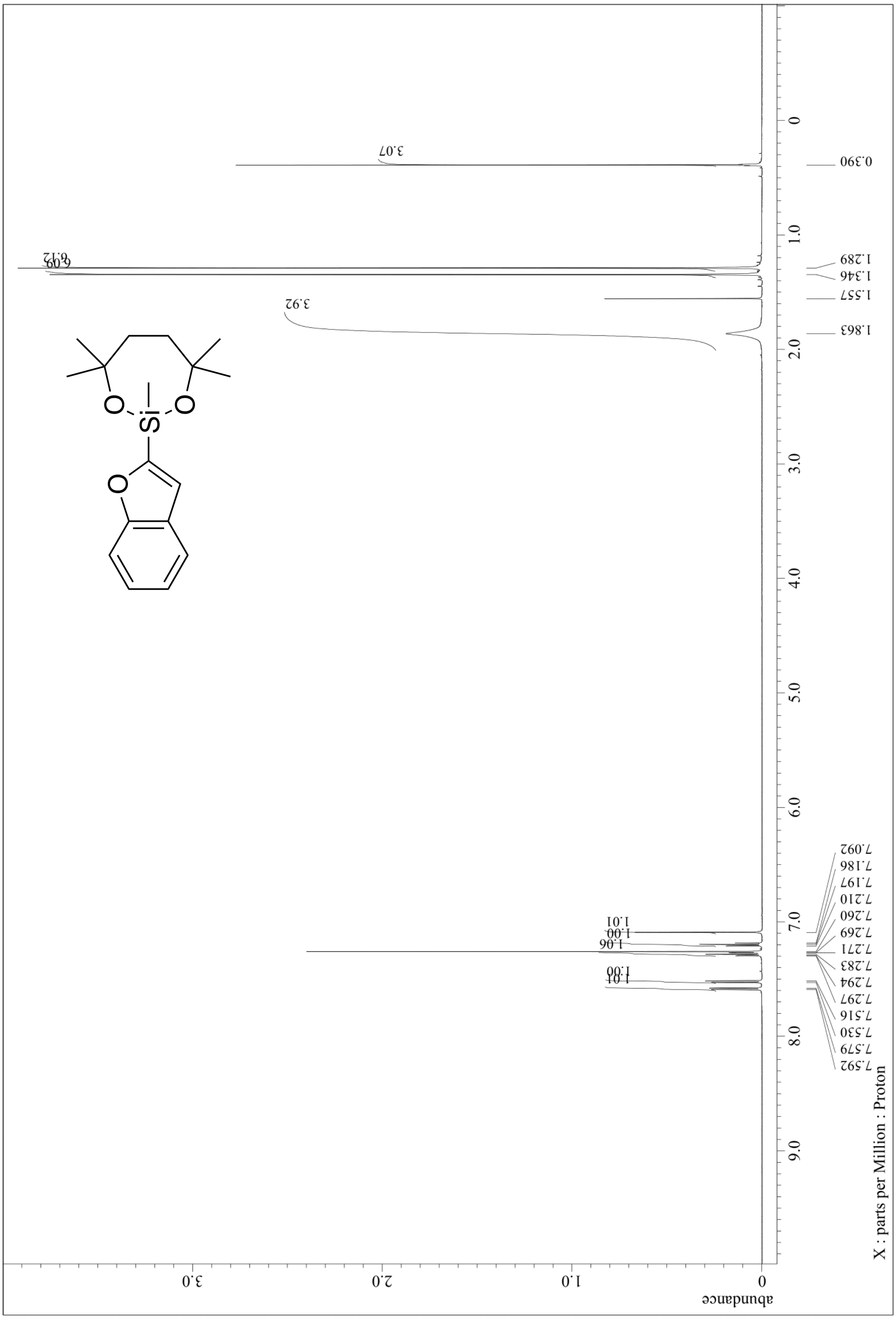

Figure S26. ^{13}C NMR spectrum of **4d**.

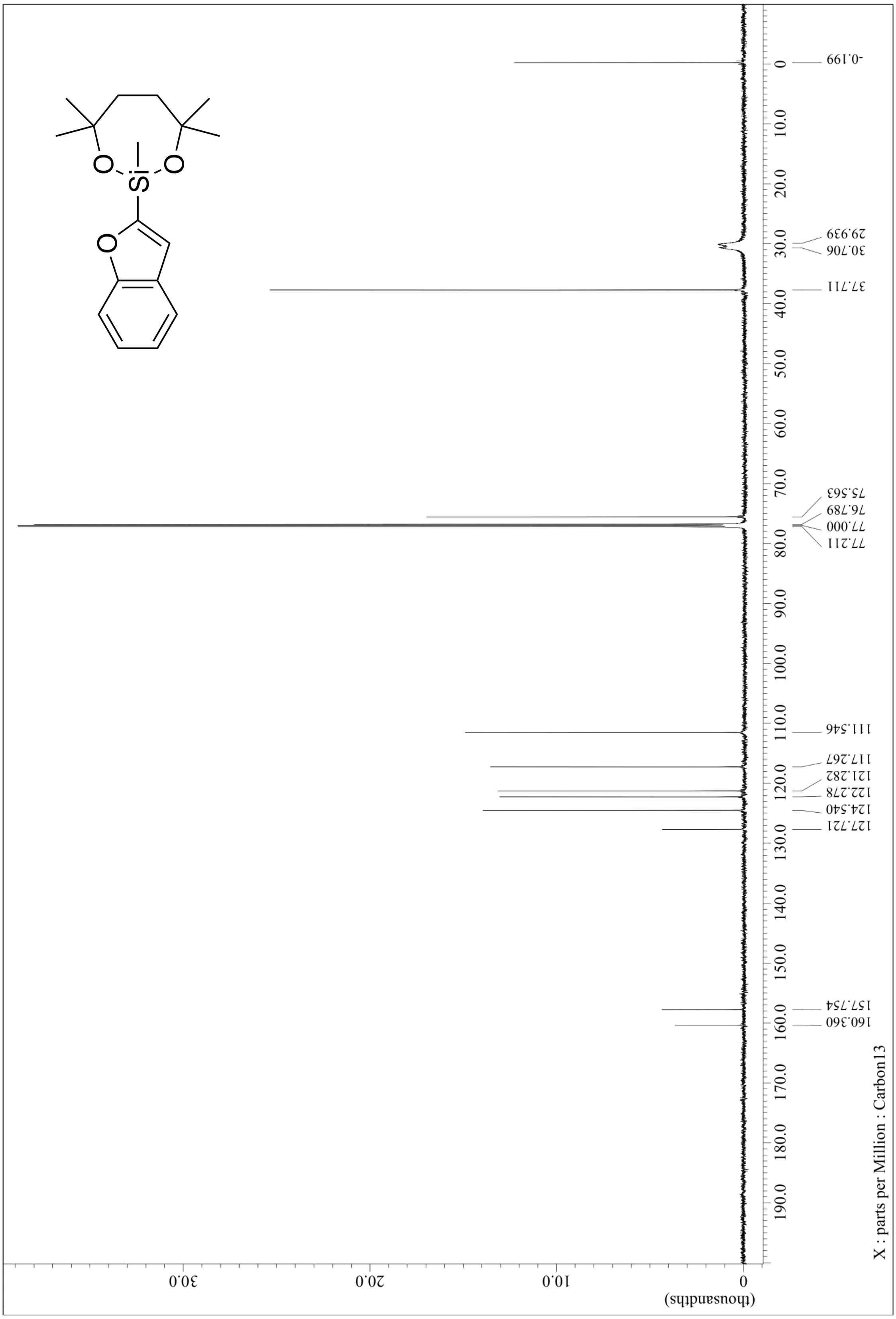

Figure S27. ^{1}H NMR spectrum of **5a**.

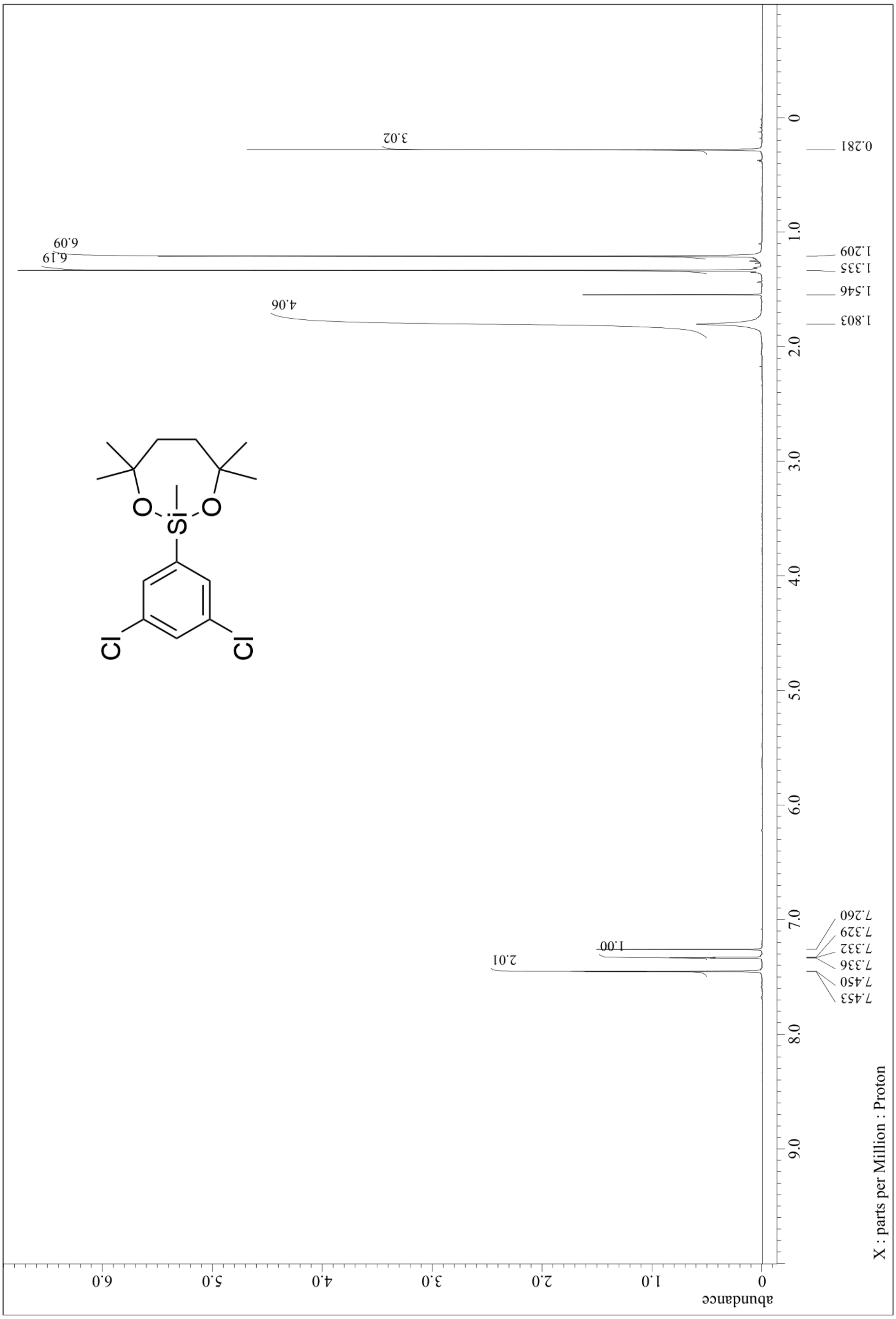

Figure S28. ^{13}C NMR spectrum of **5a**.

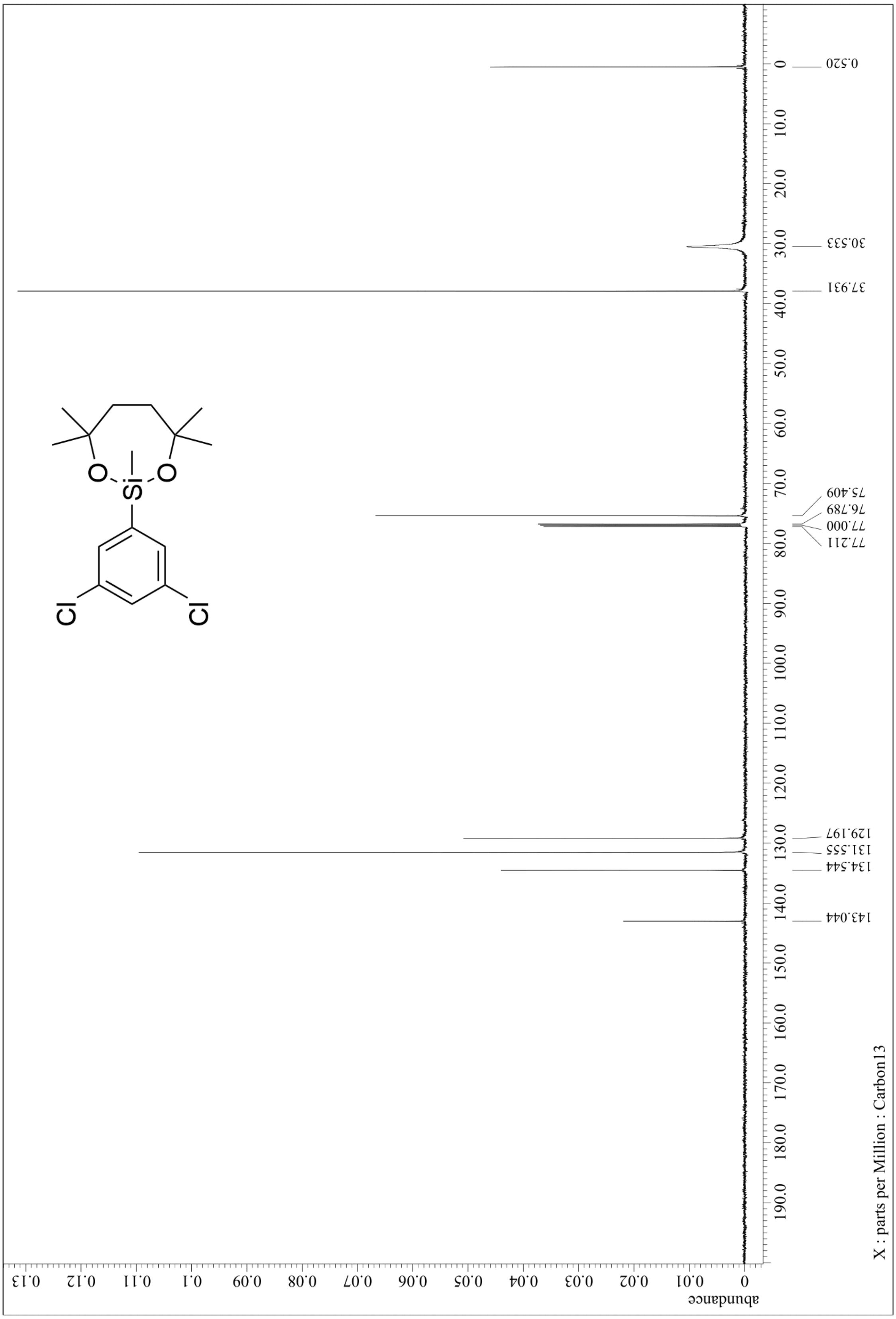

Figure S29. ^{1}H NMR spectrum of **5b**.

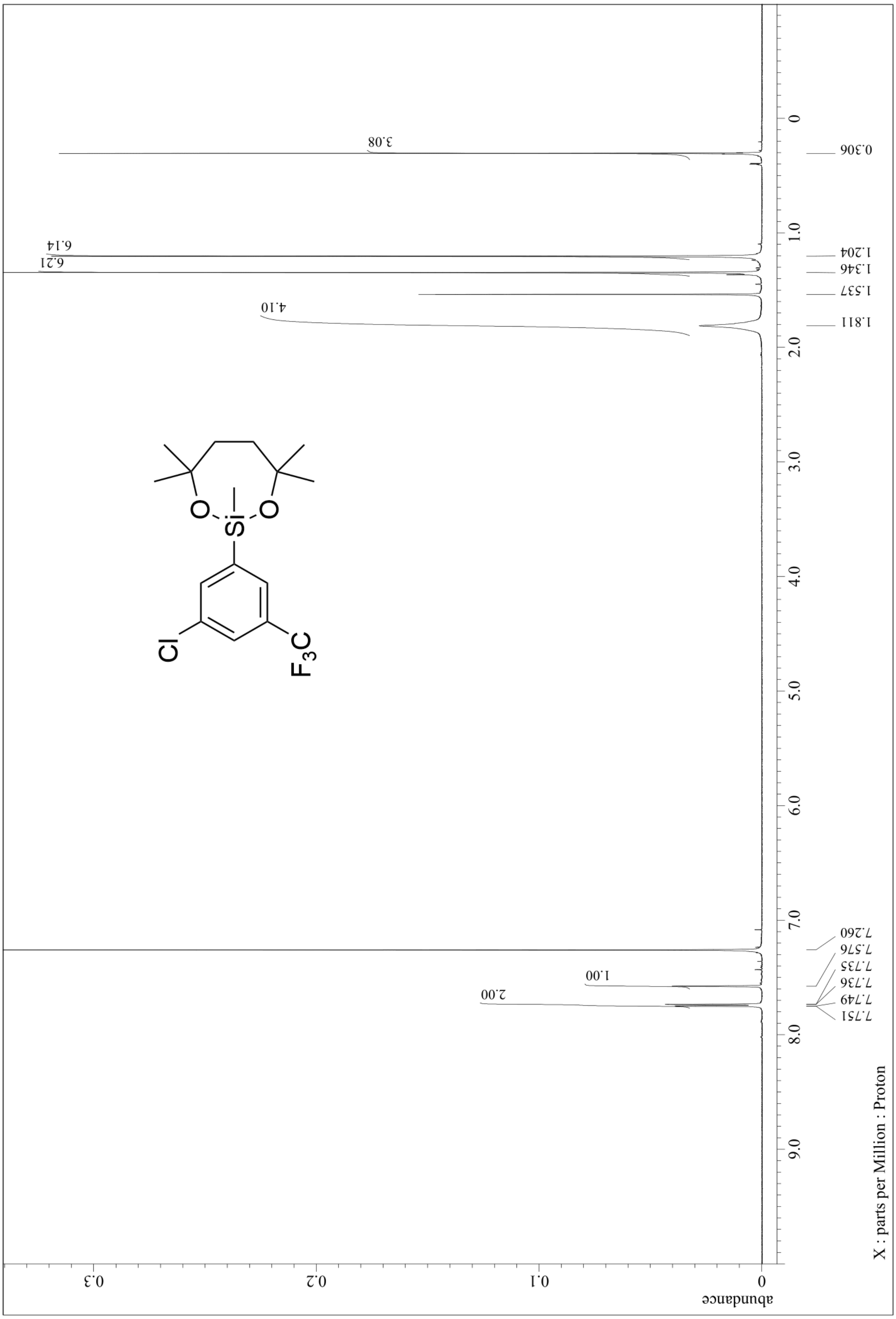

Figure S30. ^{13}C NMR spectrum of **5b**.

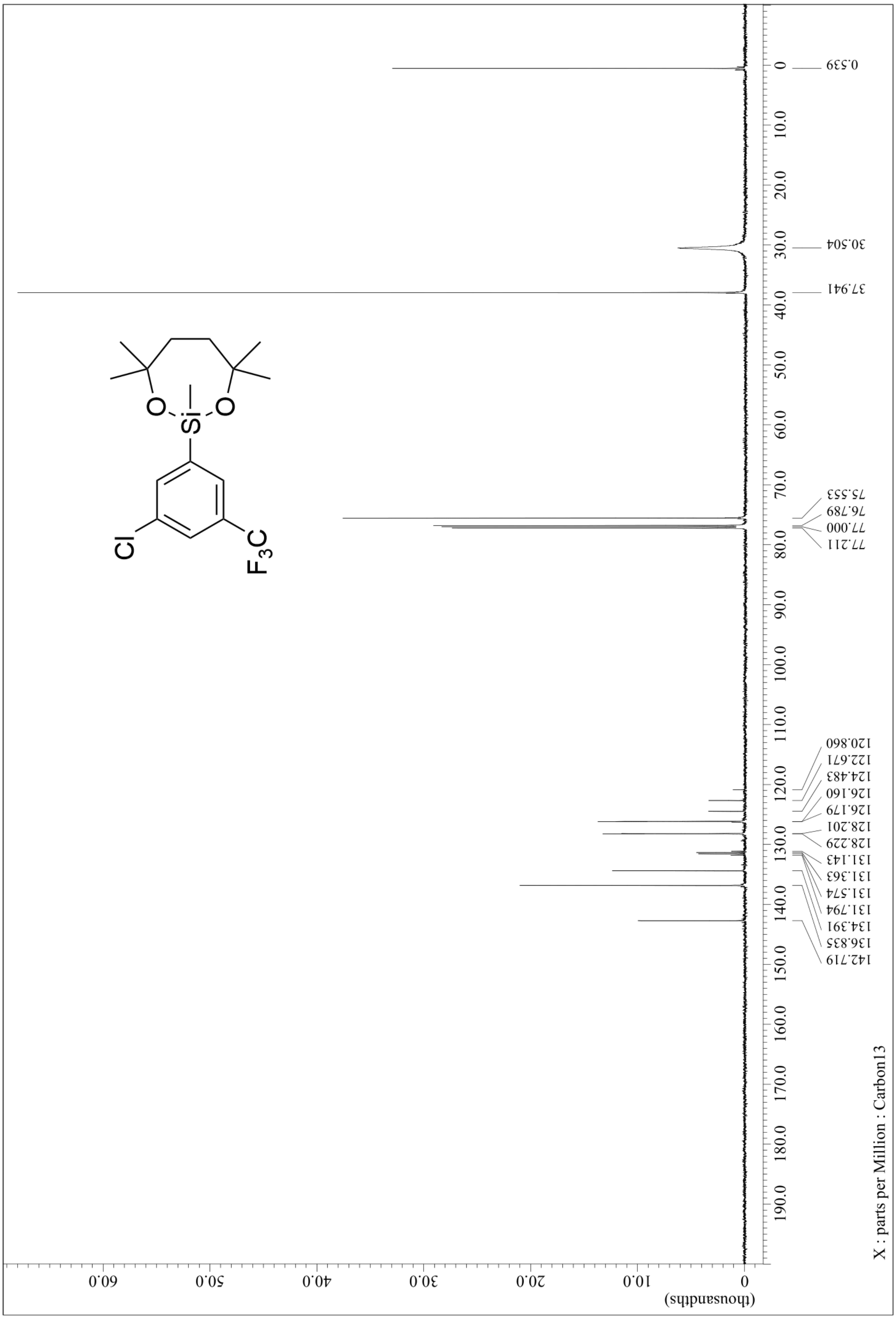

Figure S31 ^{1}H NMR spectrum of **5c**.

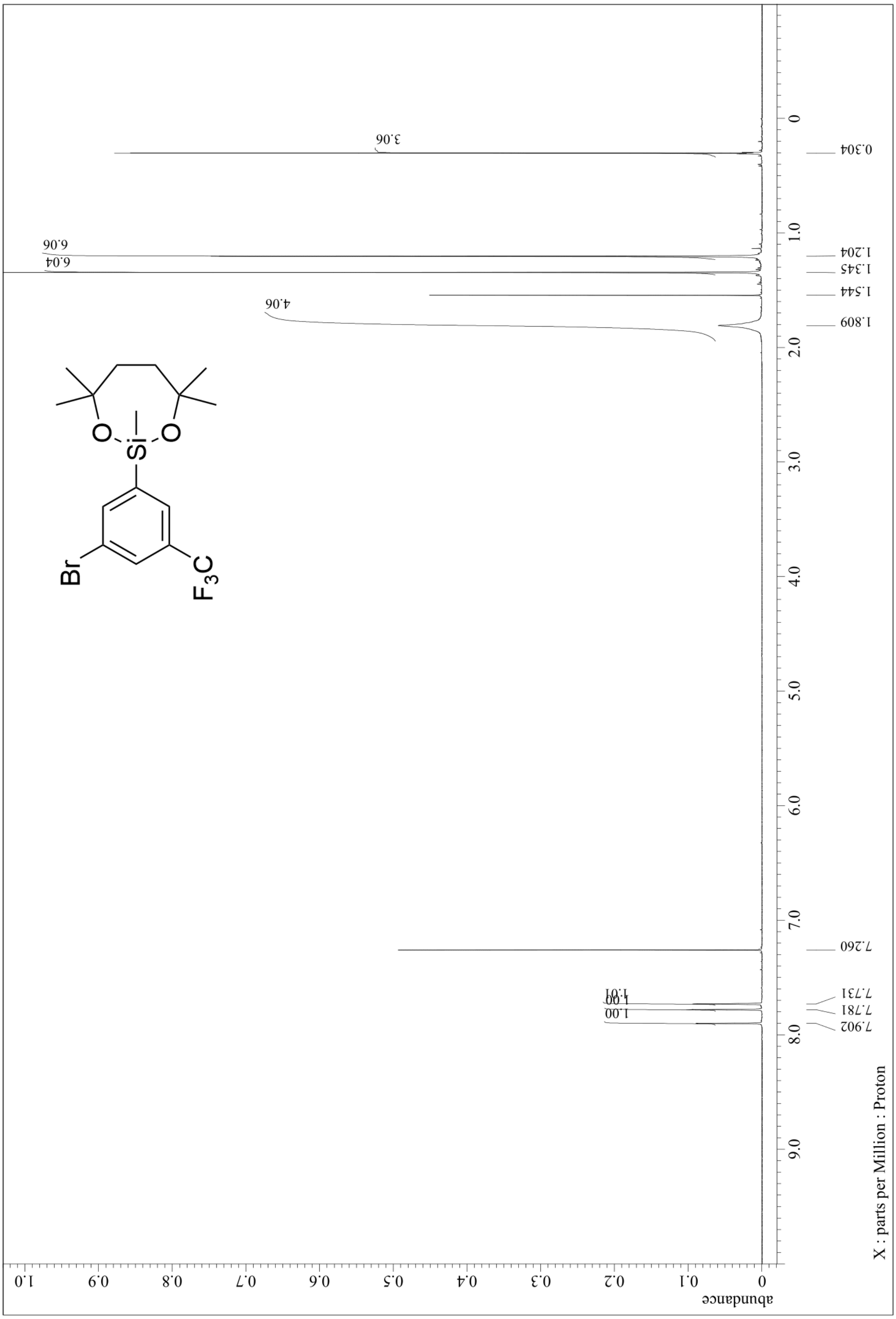

Figure S32. ^{13}C NMR spectrum of **5c**.

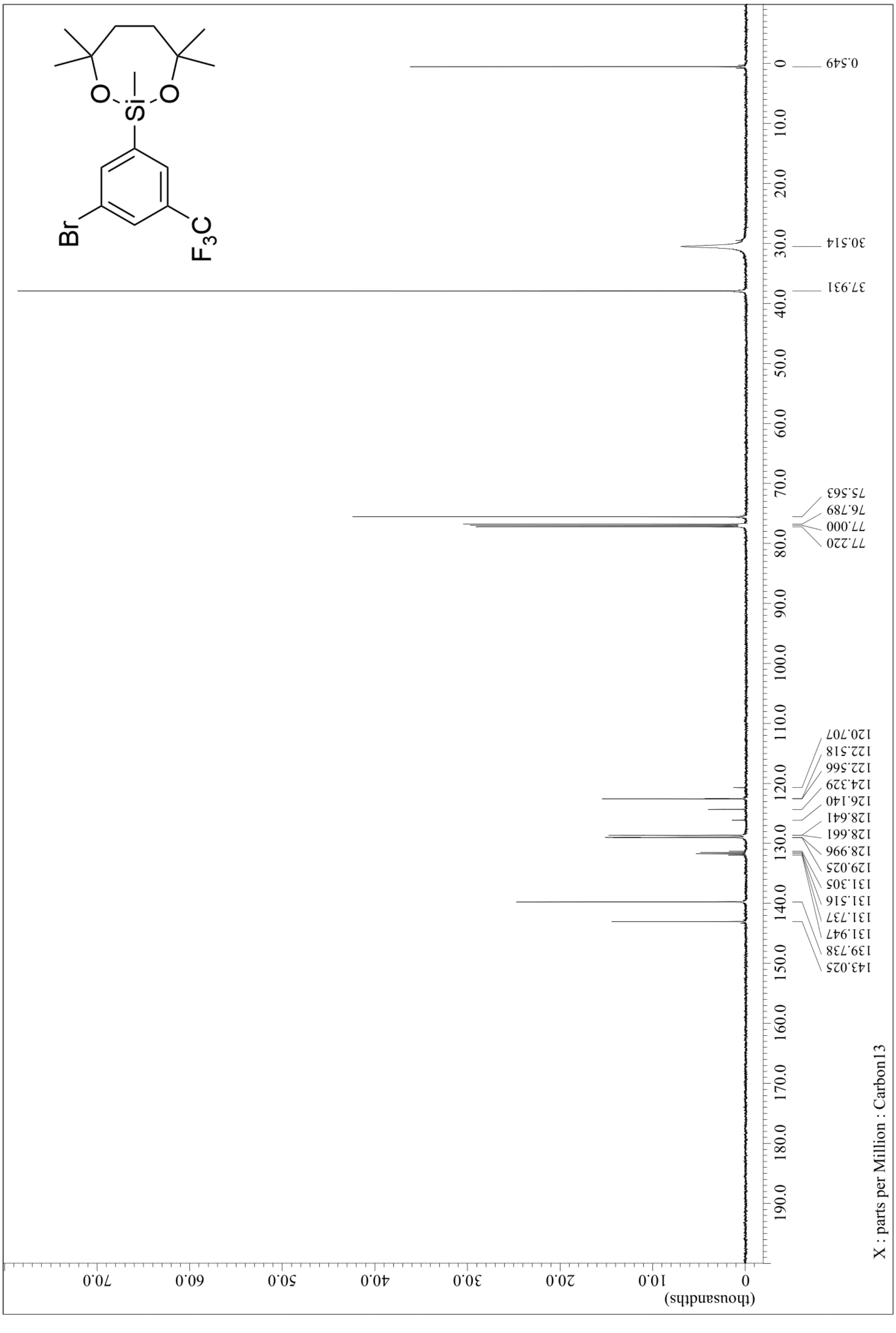

Figure S33. ^{1}H NMR spectrum of **5d**.

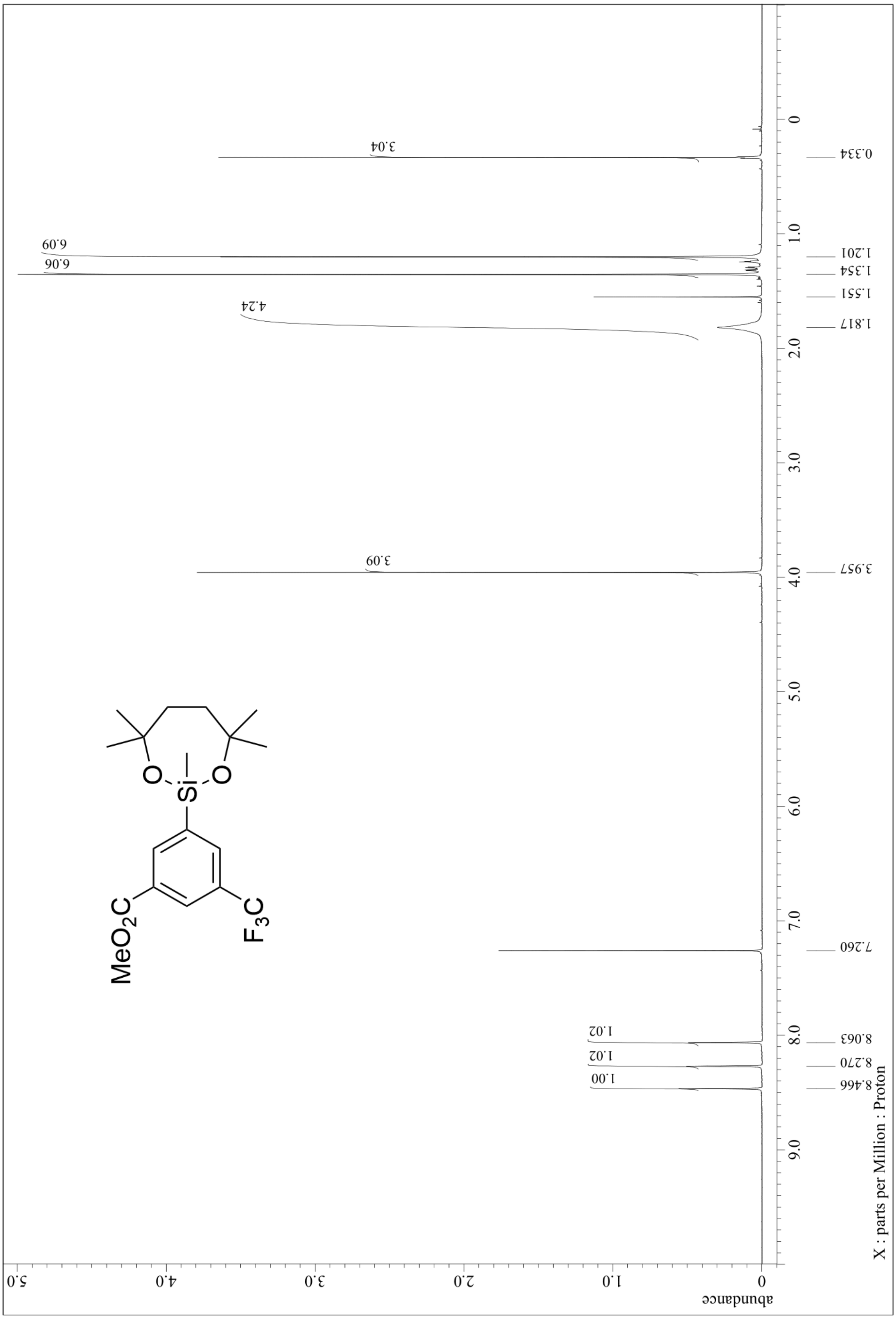

Figure S34. ^{13}C NMR spectrum of **5d**.

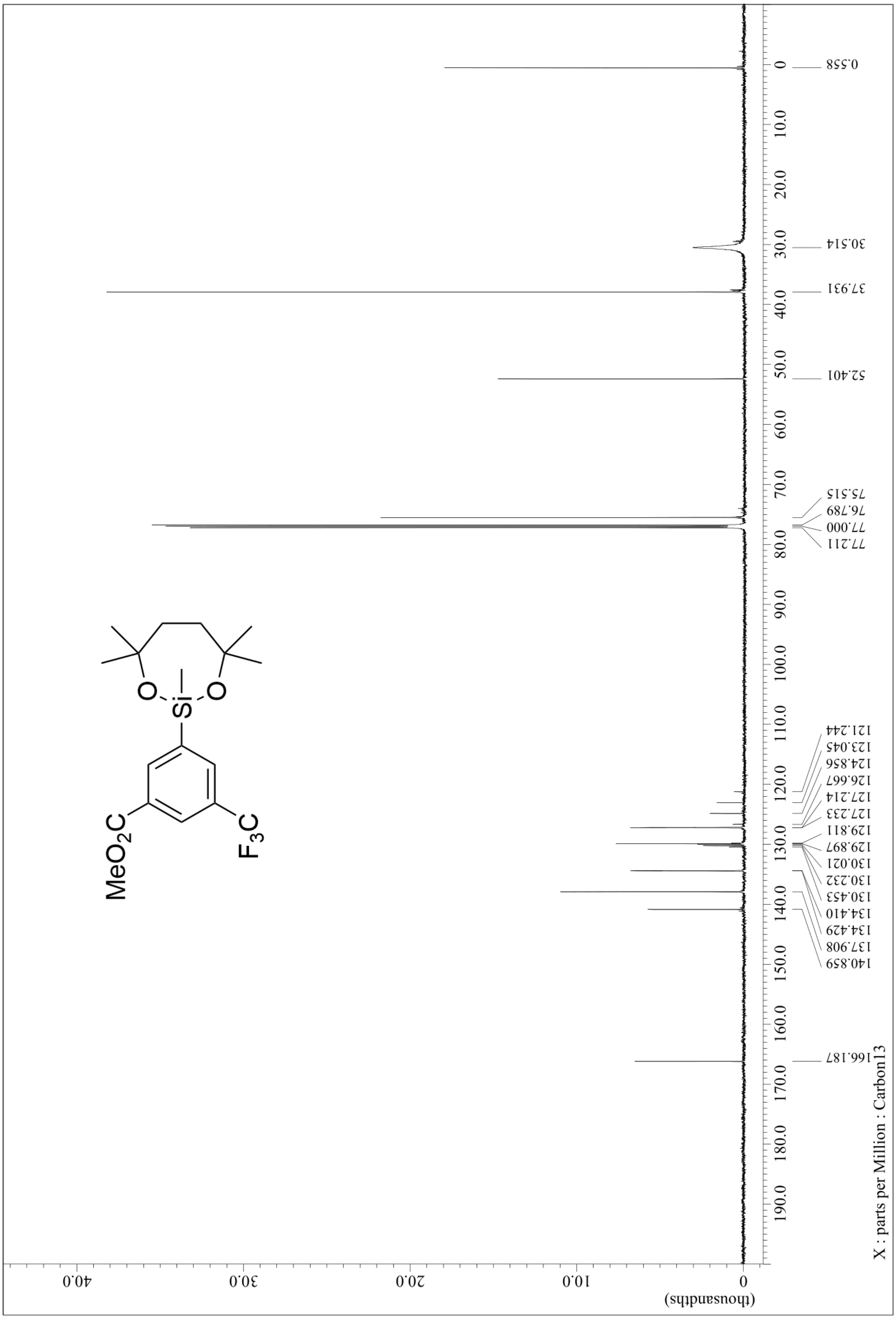

Figure S35. ^{1}H NMR spectrum of **5e**.

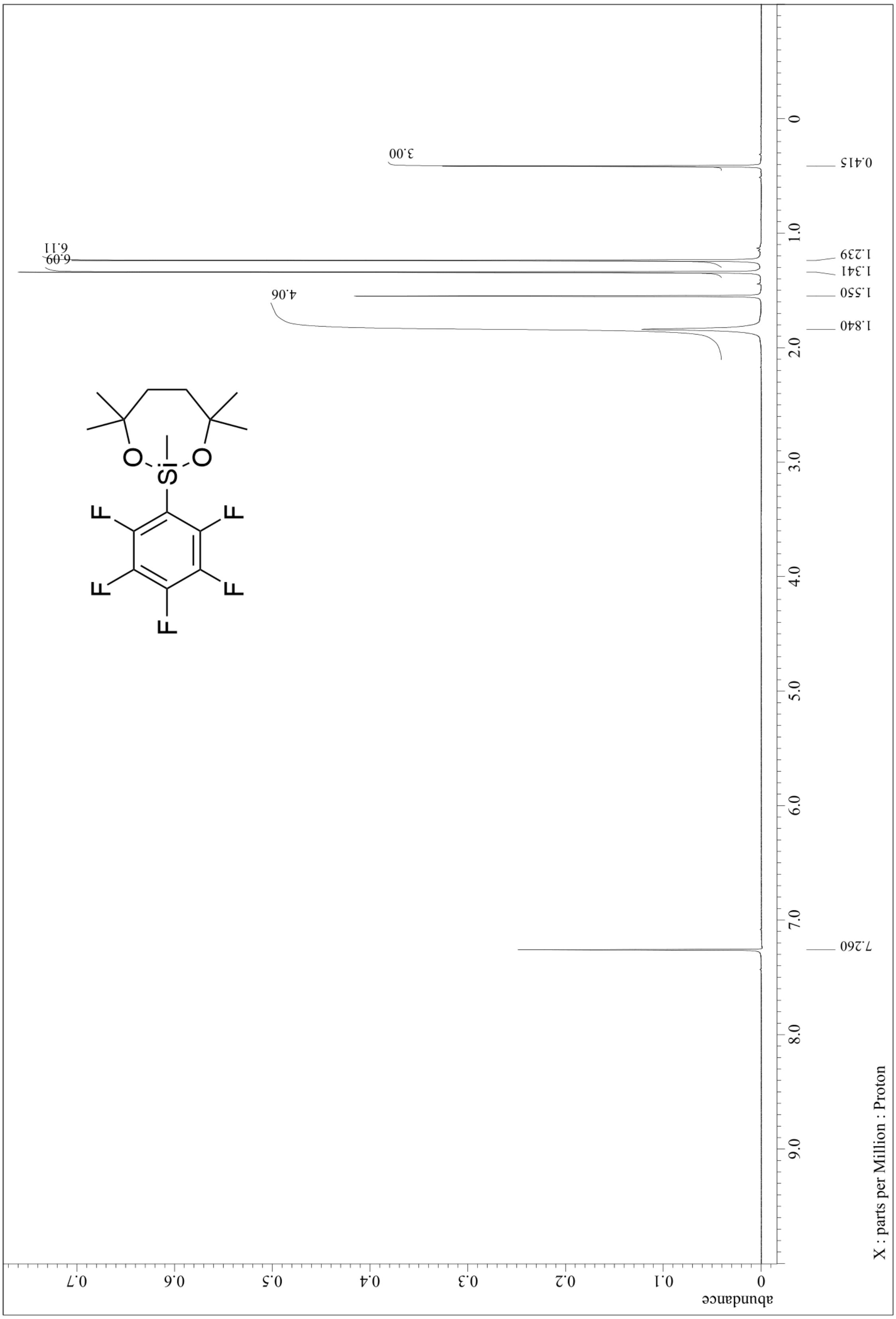

Figure S36. ^{13}C NMR spectrum of **5e**.

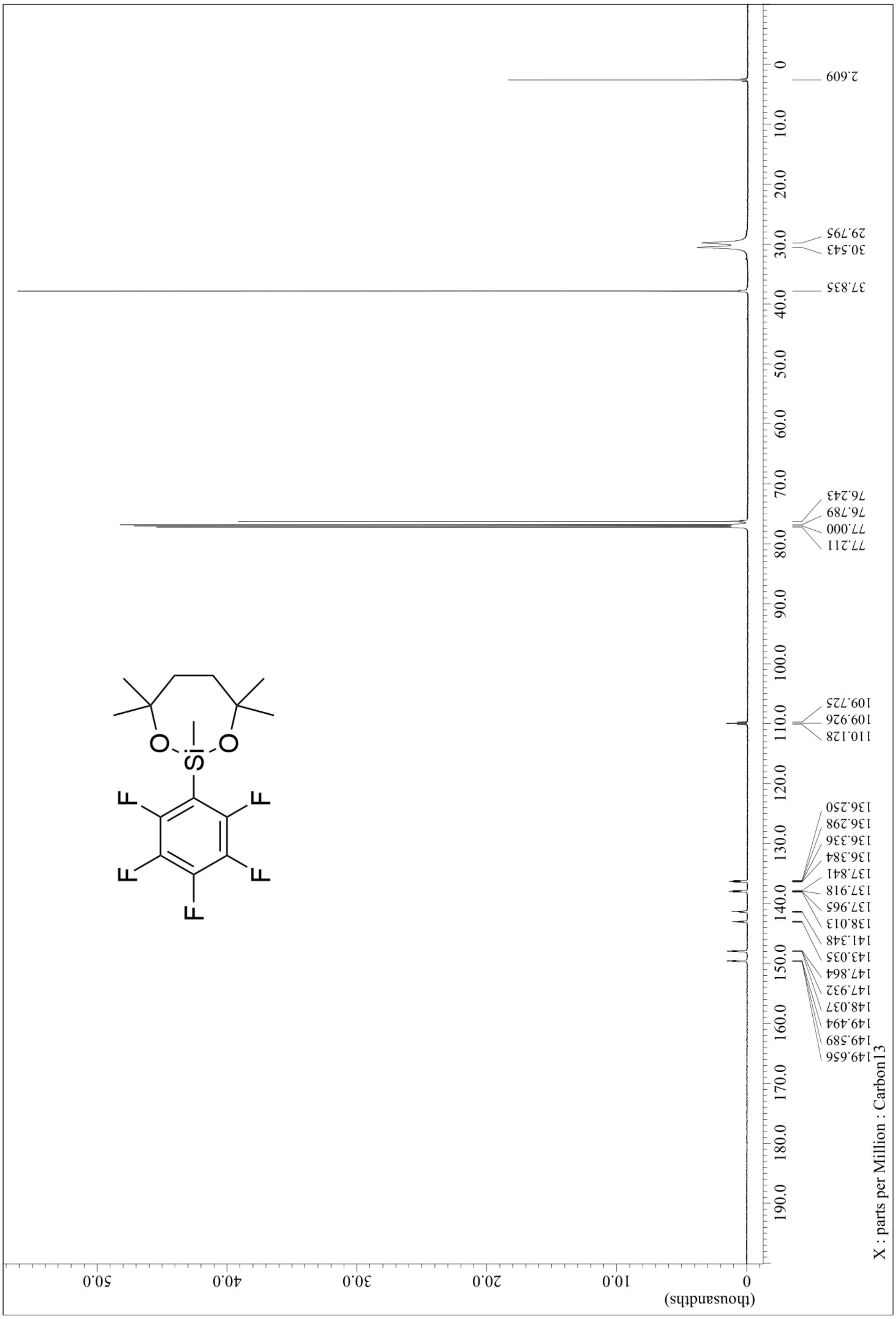

Figure S37. ^{1}H NMR spectrum of **5f**.

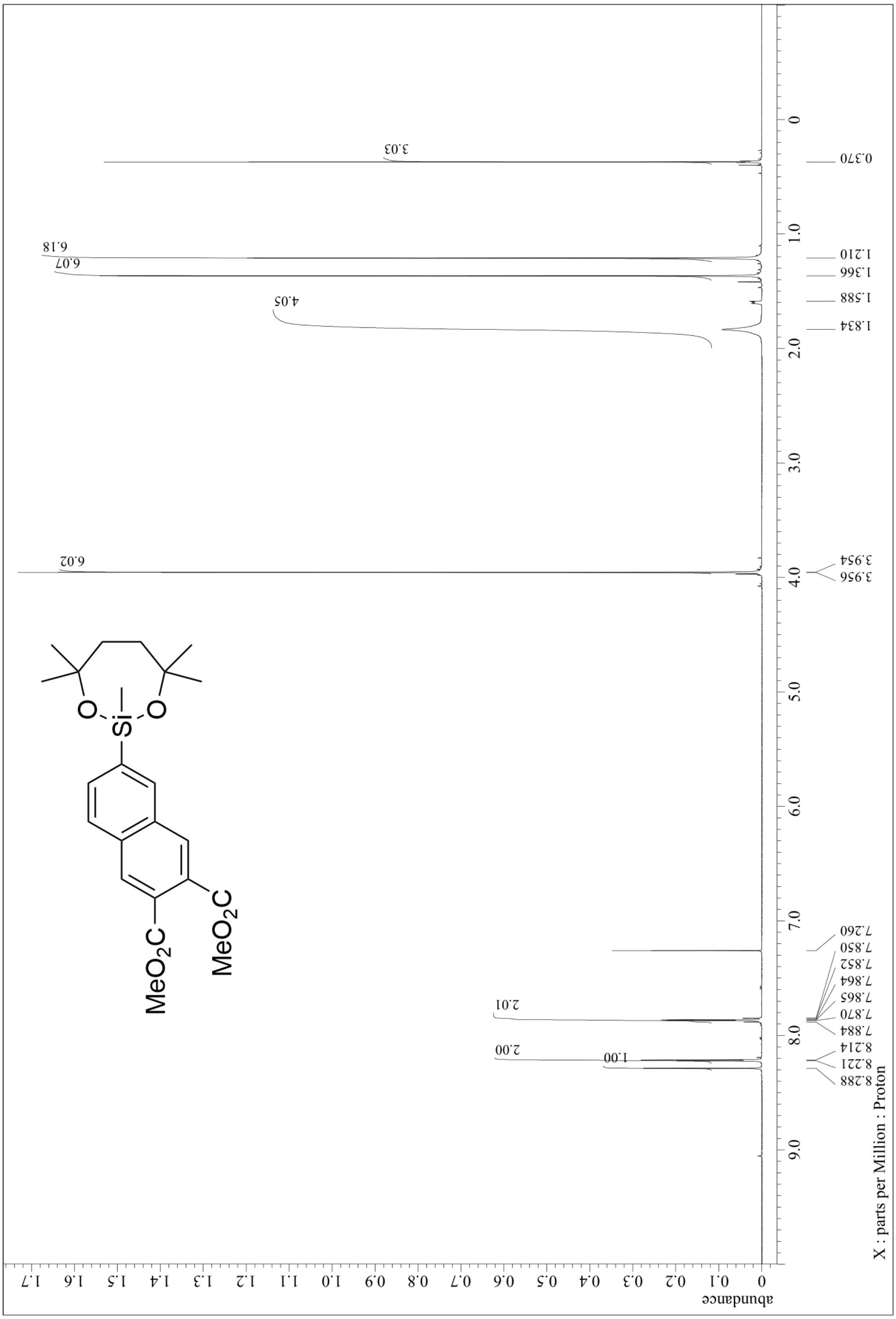

Figure S38. ^{13}C NMR spectrum of **5f**.

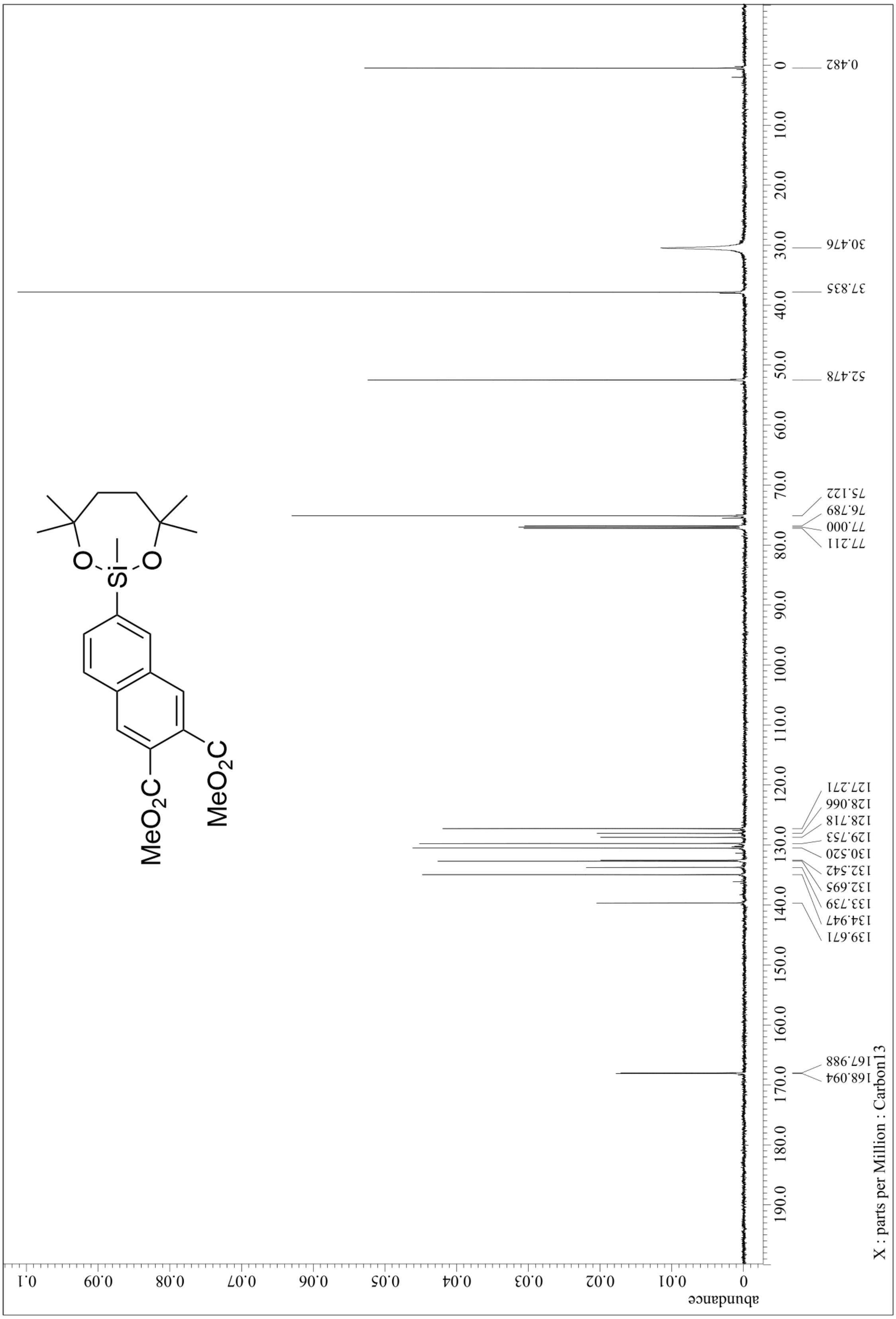

Figure S39. ^{1}H NMR spectrum of **5g**.

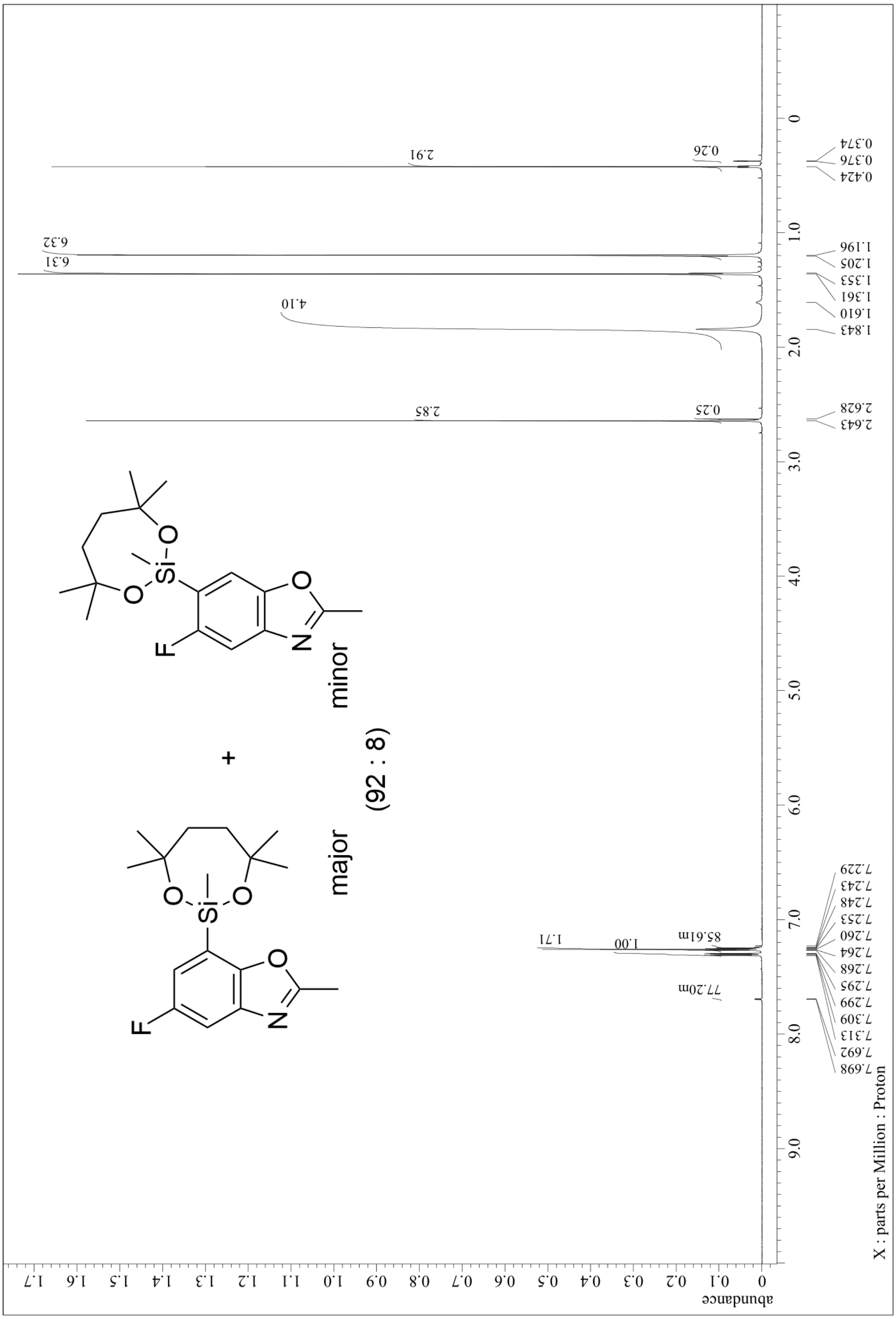

Figure S40. ^{13}C NMR spectrum of **5g**.

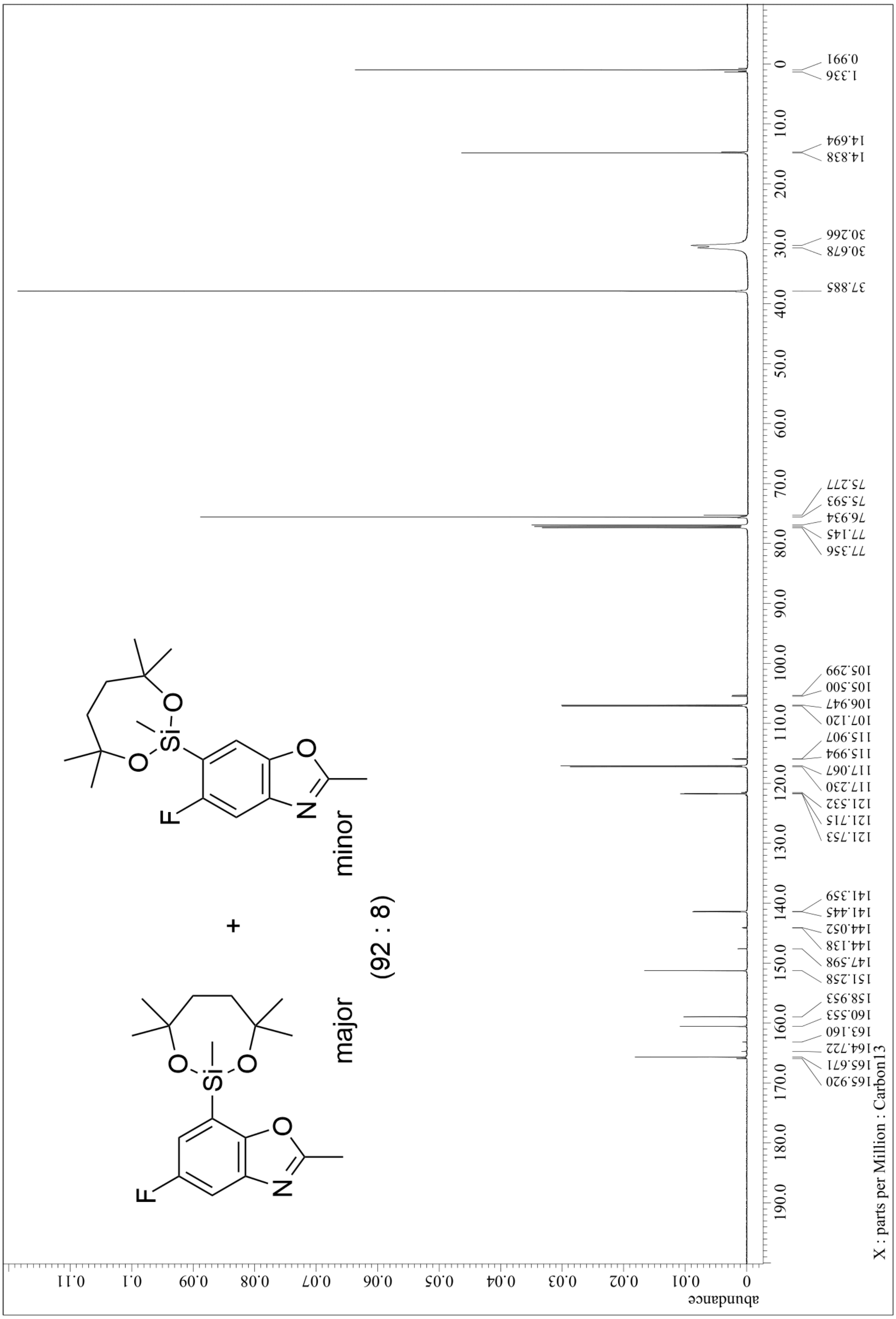

Figure S41. ^{1}H NMR spectrum of **5h**.

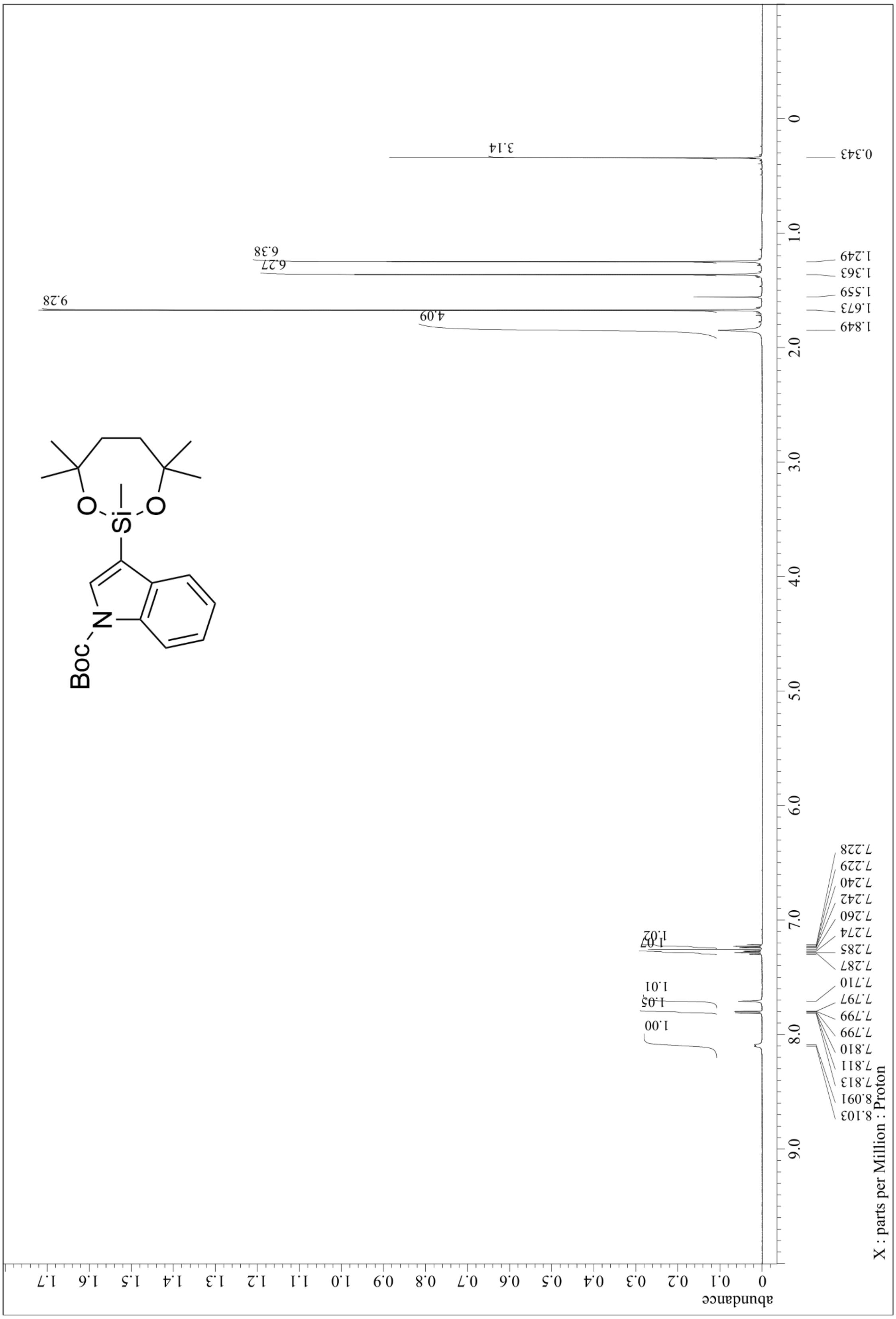

Figure S42. ^{13}C NMR spectrum of **5h**.

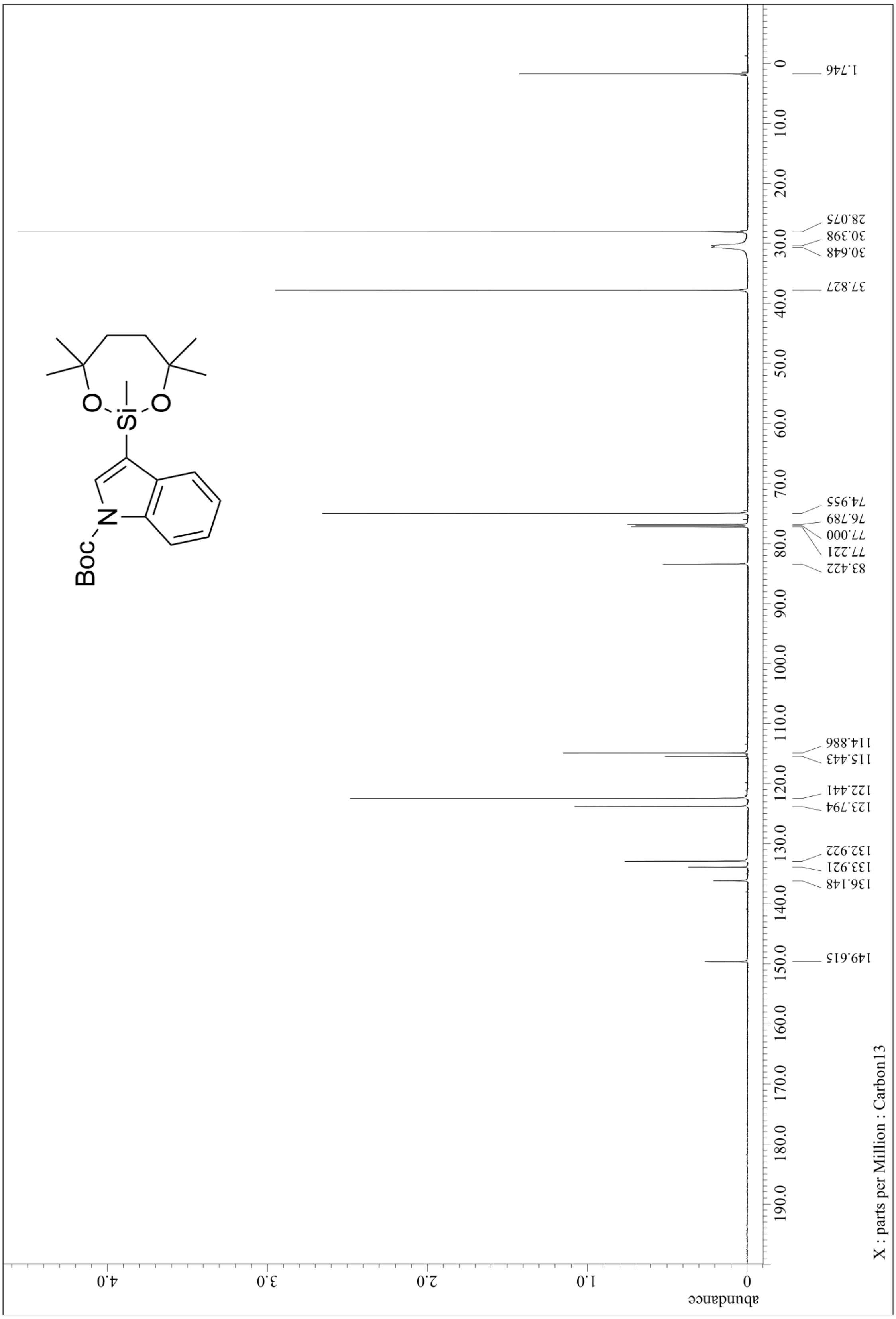

Figure S43. ^{1}H NMR spectrum of **5i**.

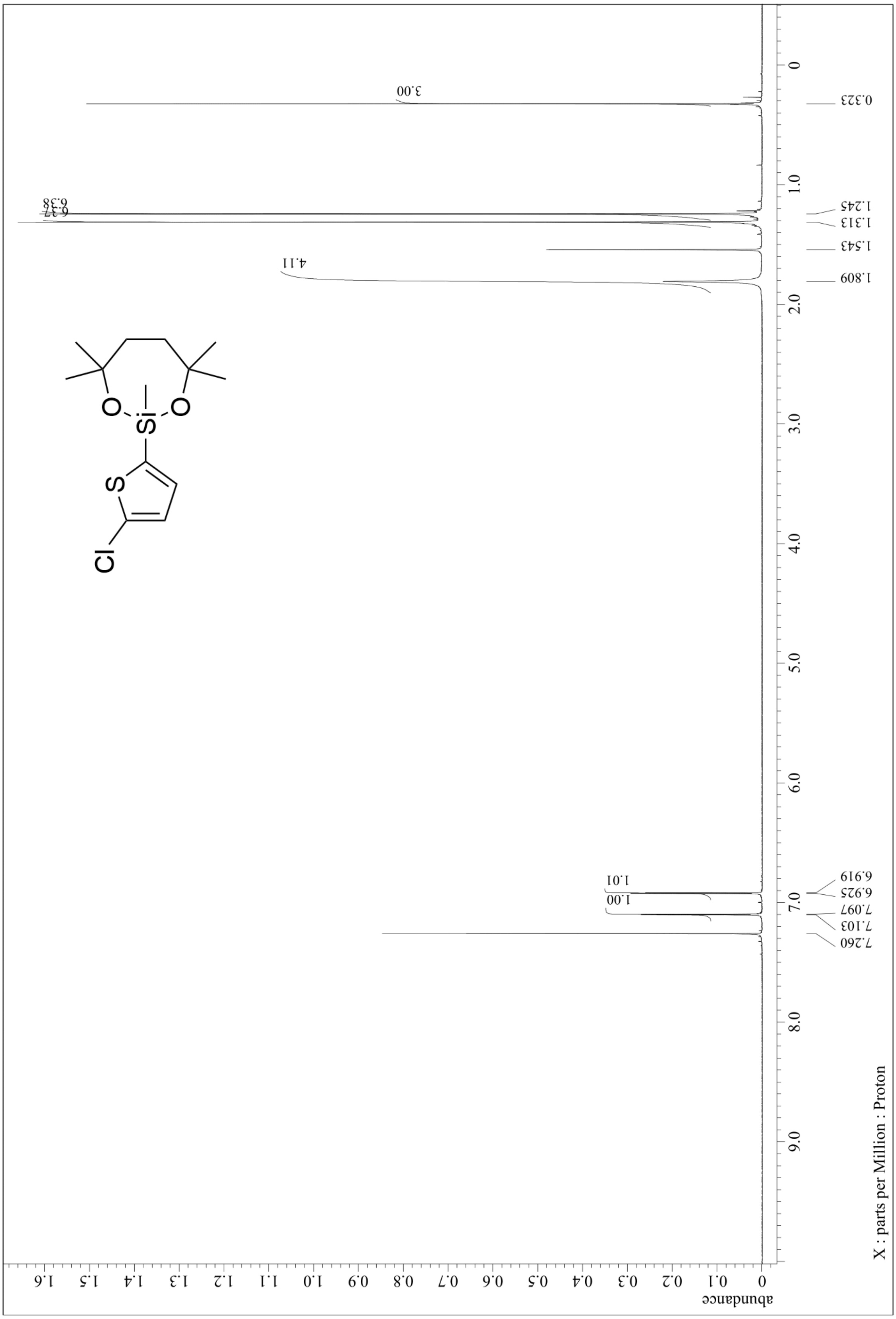

Figure S44. ^{13}C NMR spectrum of **5i**.

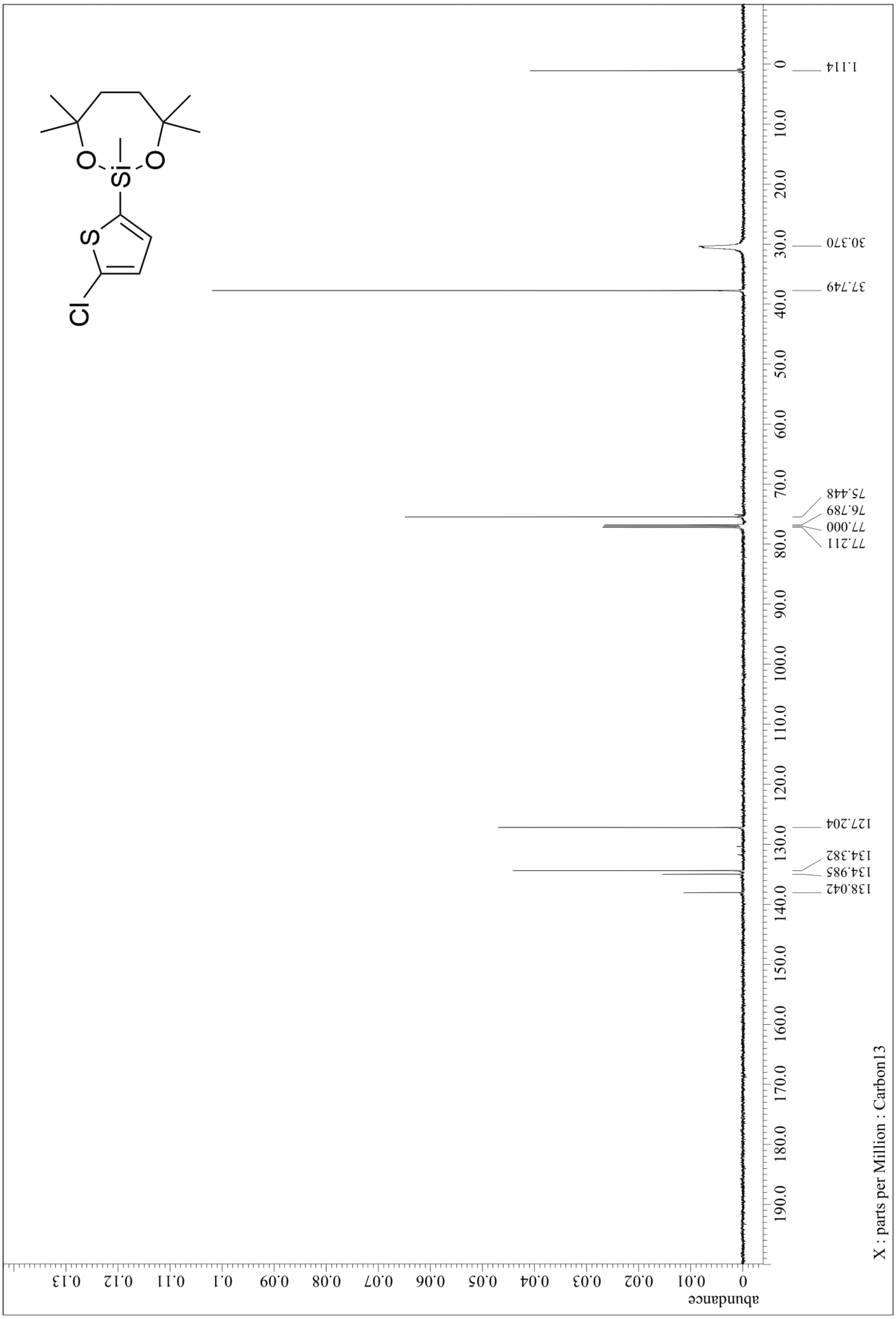

Figure S45. ^{1}H NMR spectrum of **5j**.

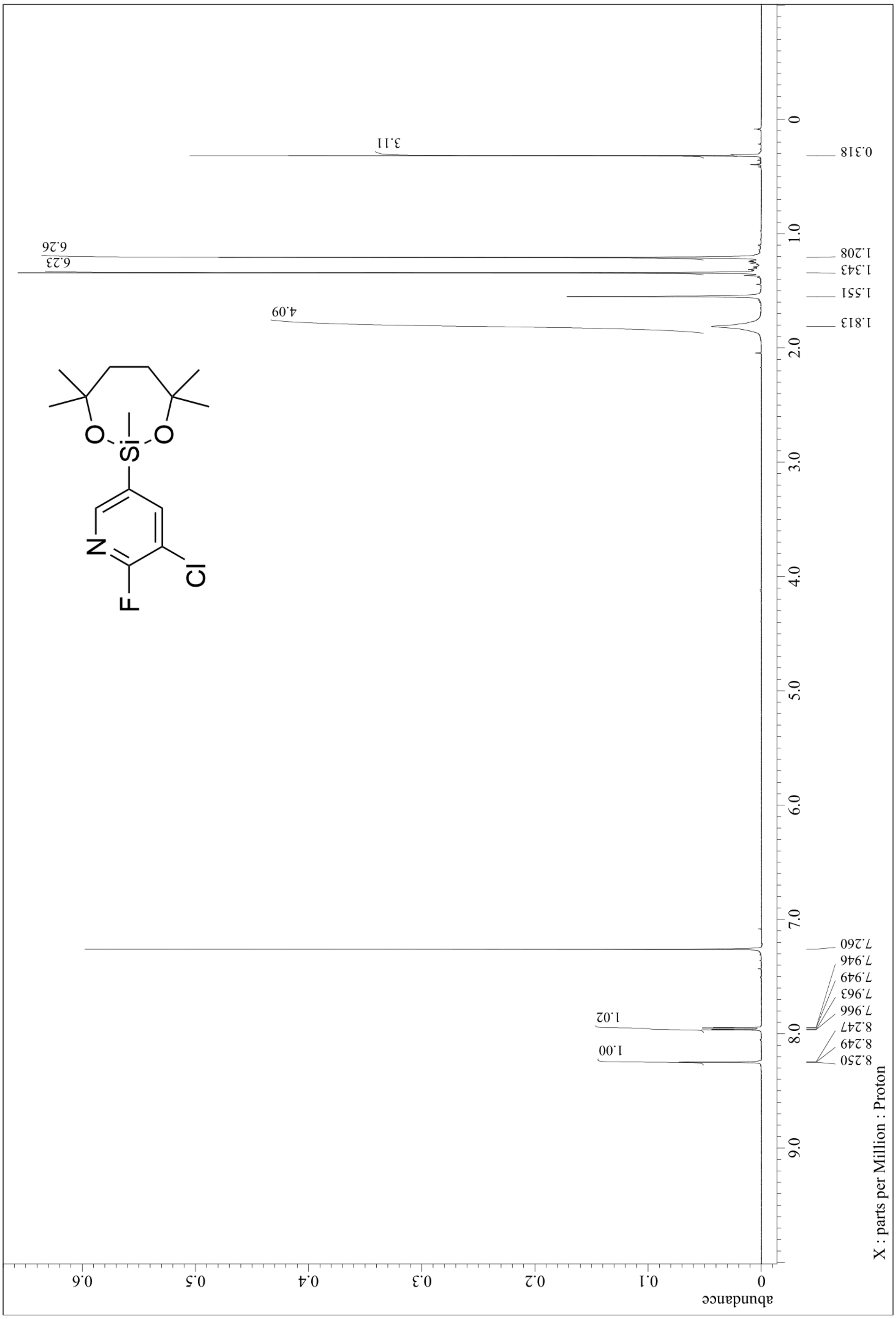

Figure S46. ^{13}C NMR spectrum of **5j**.

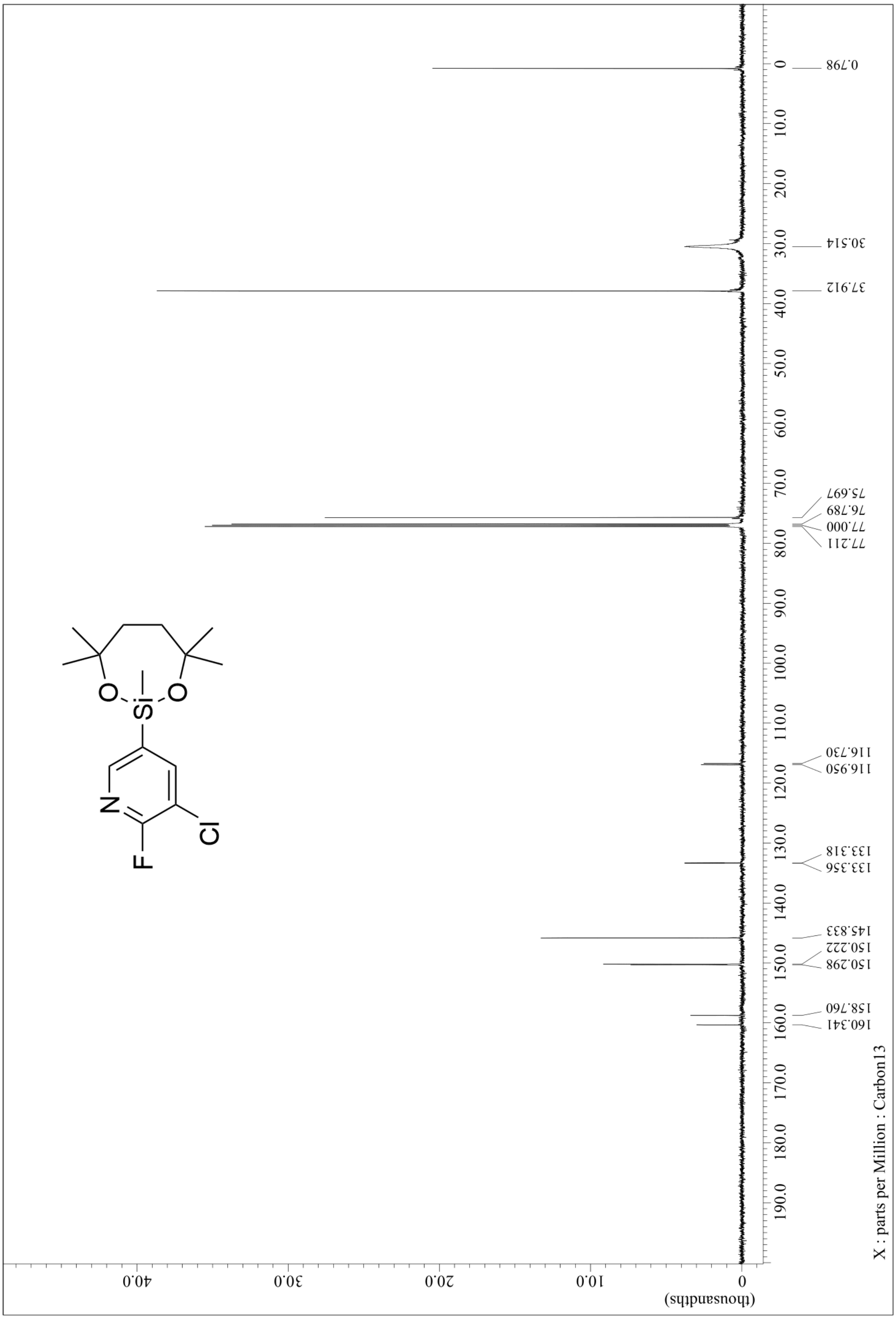

Figure S47. ^{1}H NMR spectrum of **5k**.

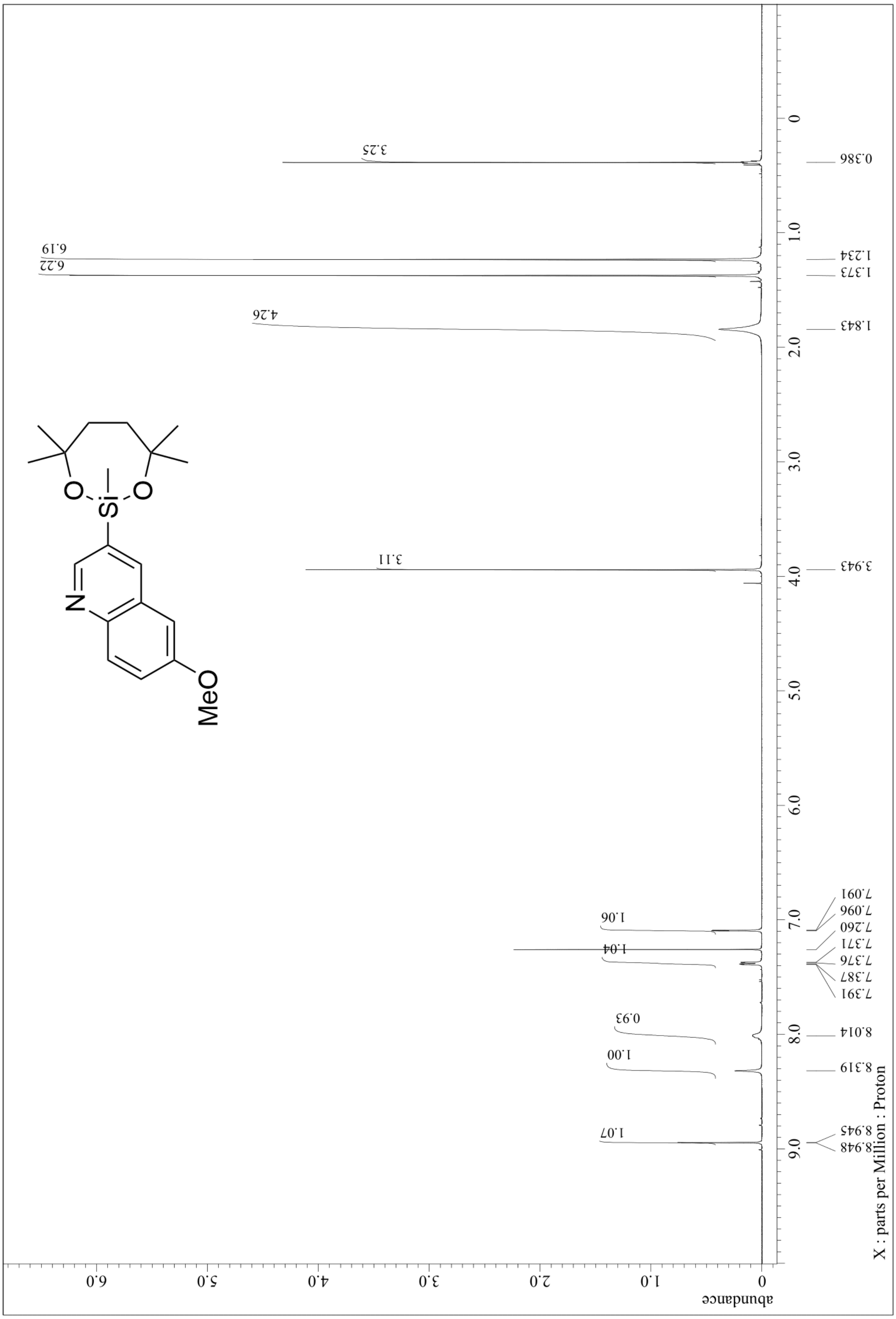

Figure S48. ^{13}C NMR spectrum of **5k**.

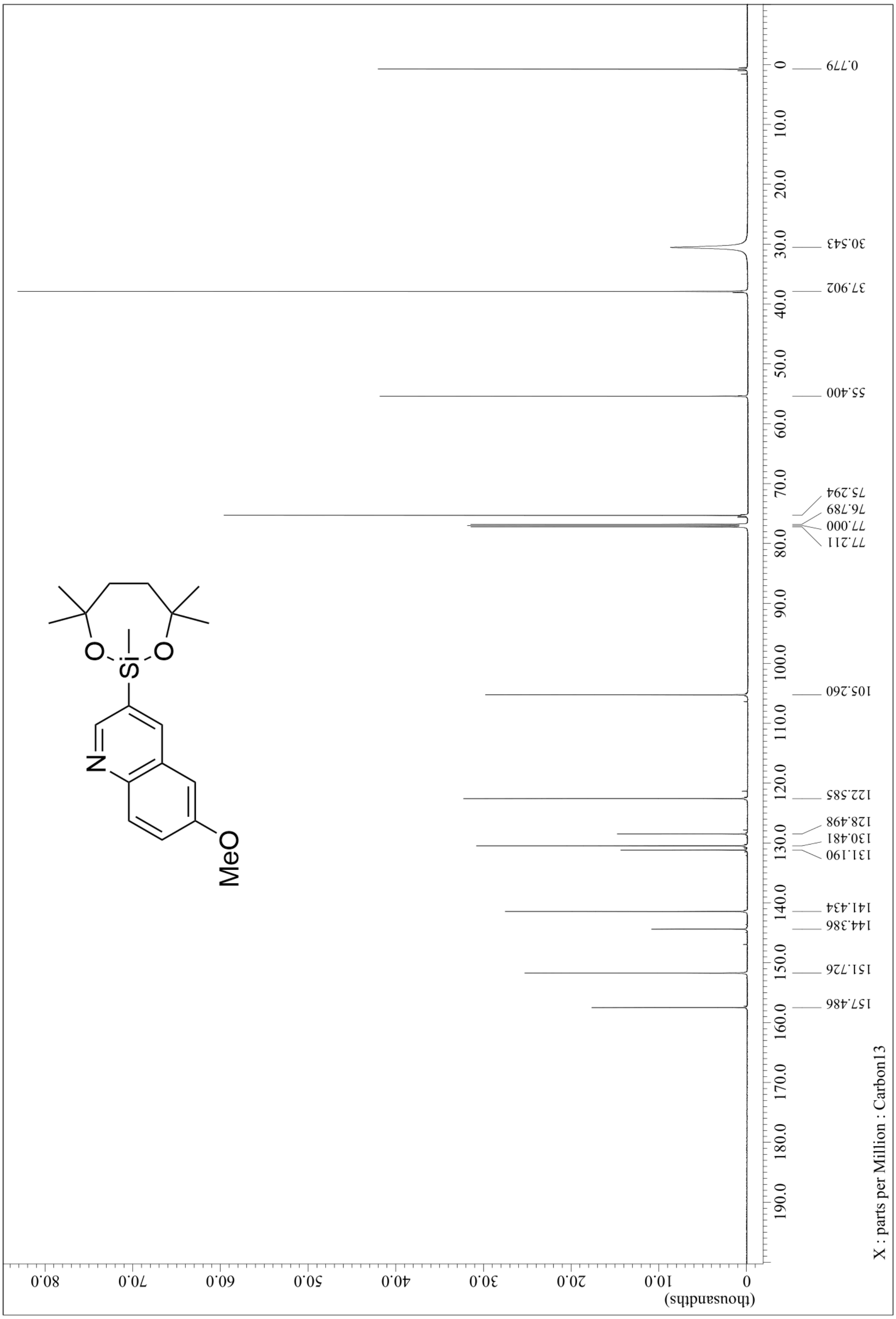

Figure S49. ^{1}H NMR spectrum of **6**.

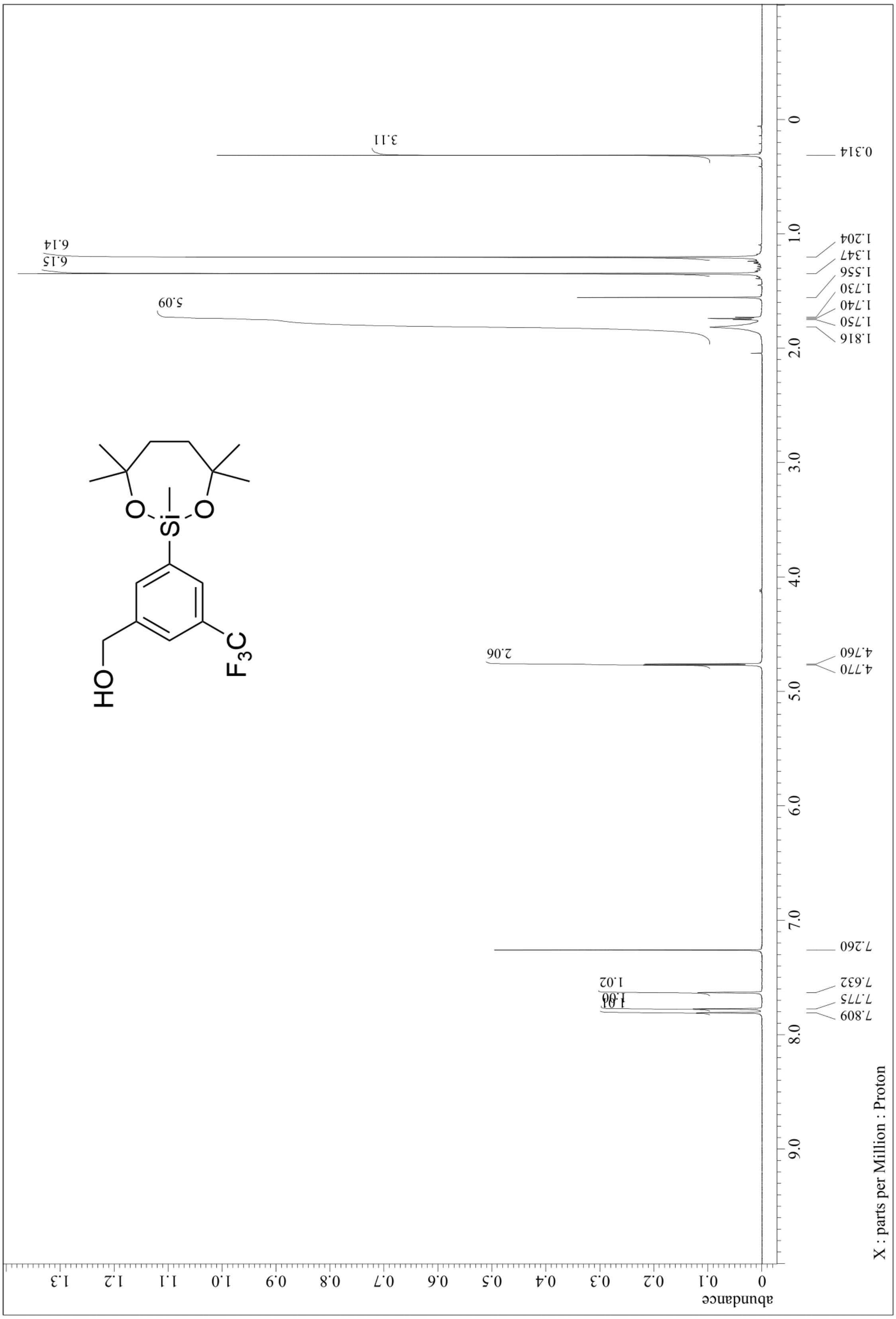

Figure S50. ^{13}C NMR spectrum of **6**.

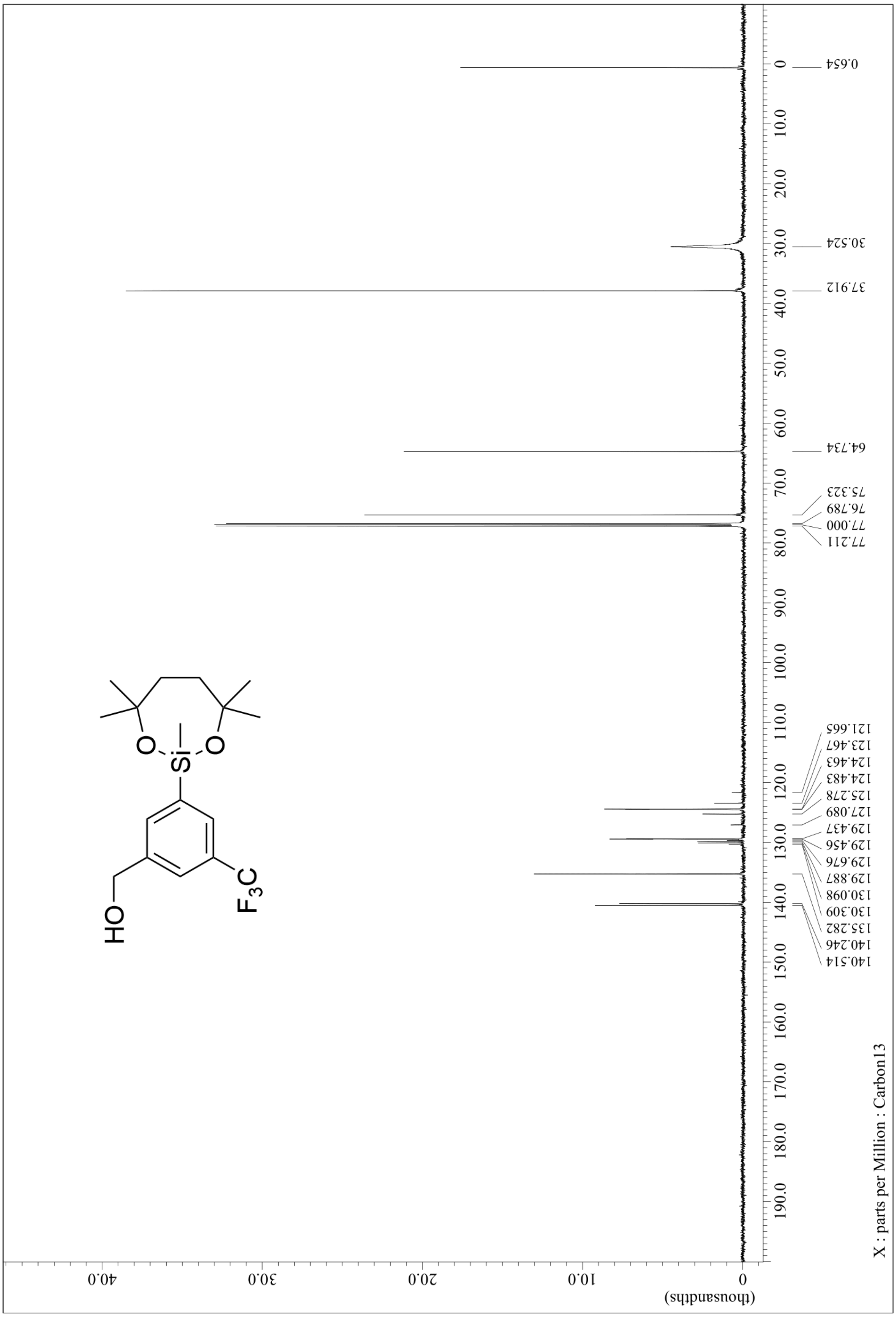

Figure S51. ^{1}H NMR spectrum of **7**.

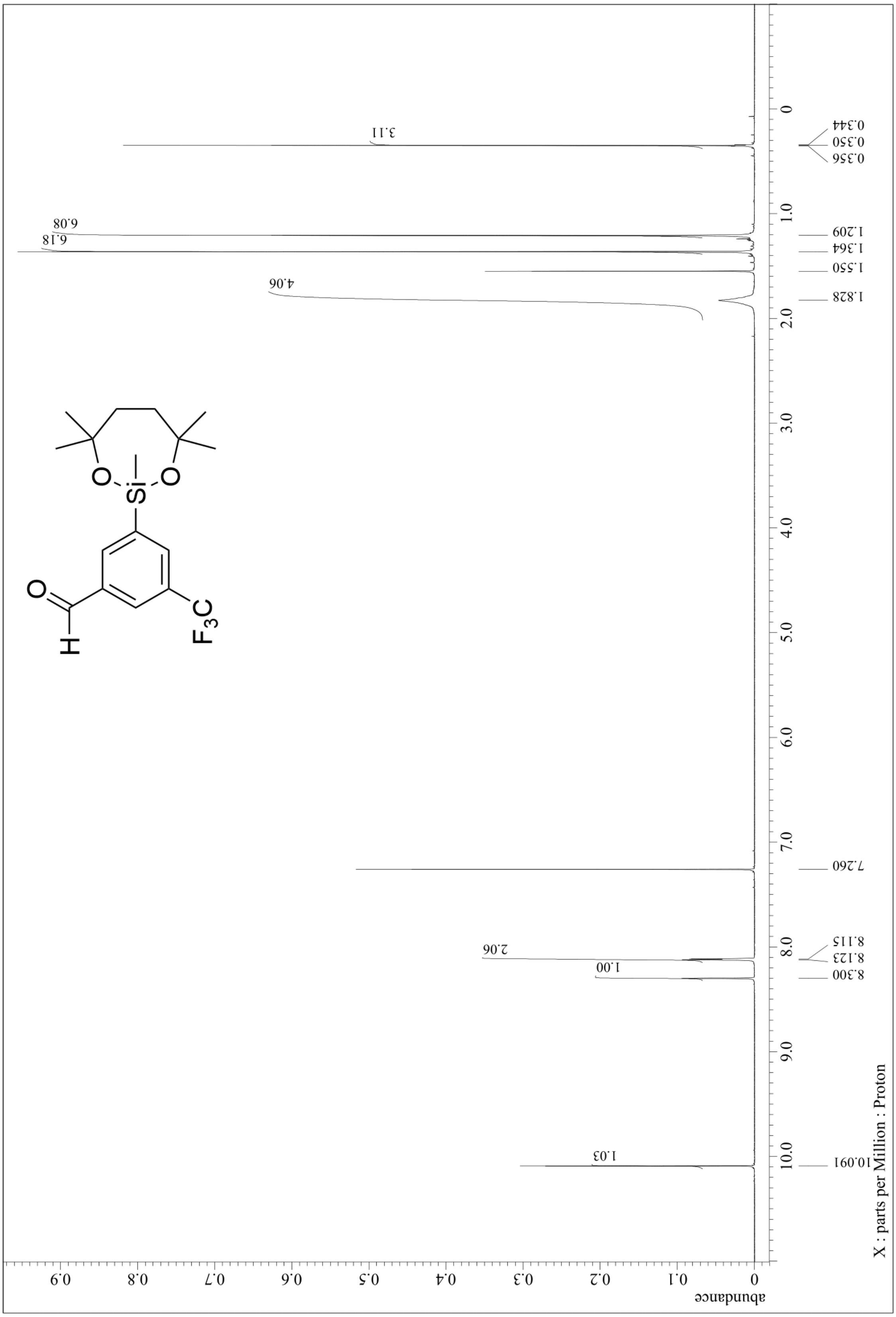

Figure S52. ^{13}C NMR spectrum of **7**.

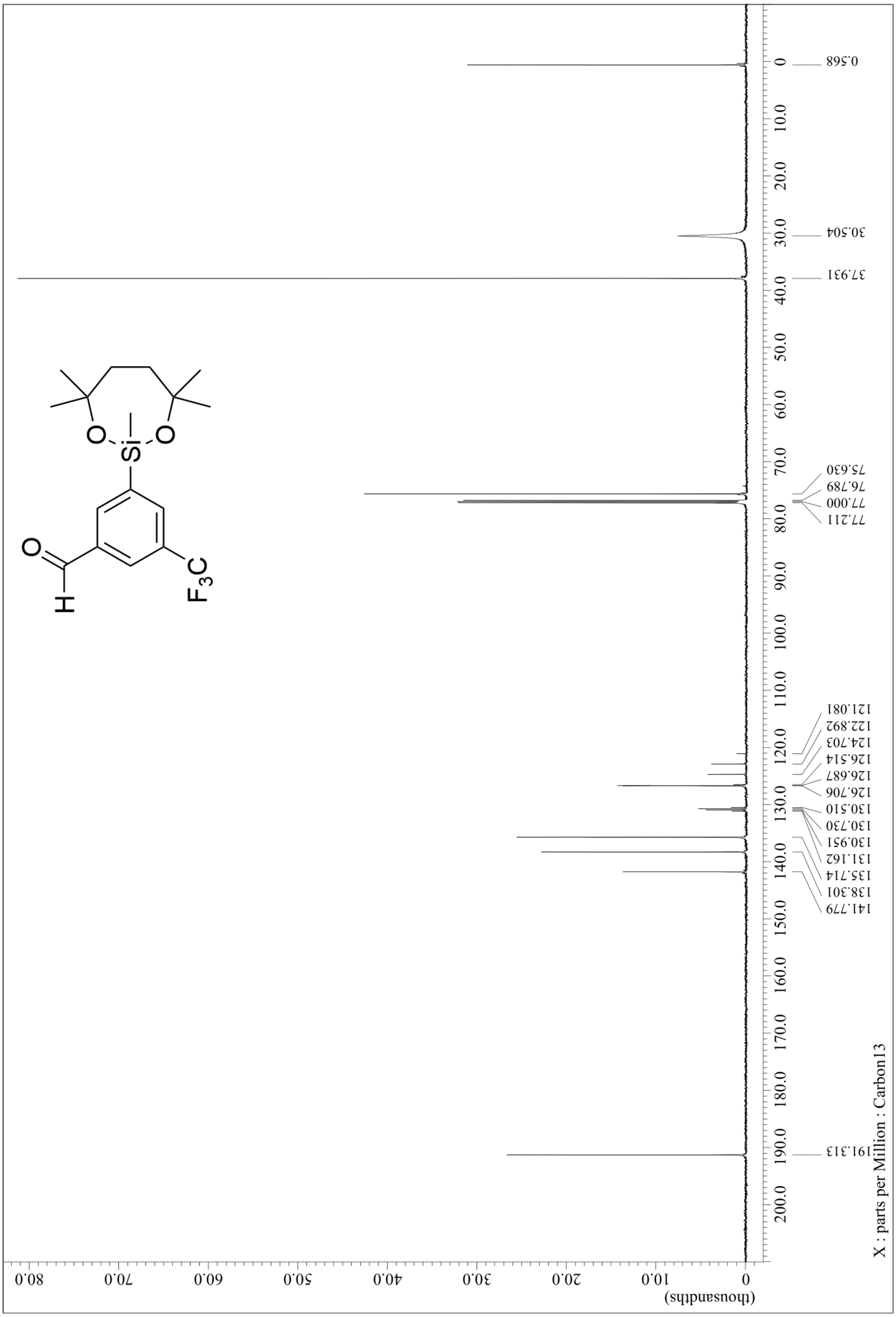

Figure S53. ^{1}H NMR spectrum of **8**.

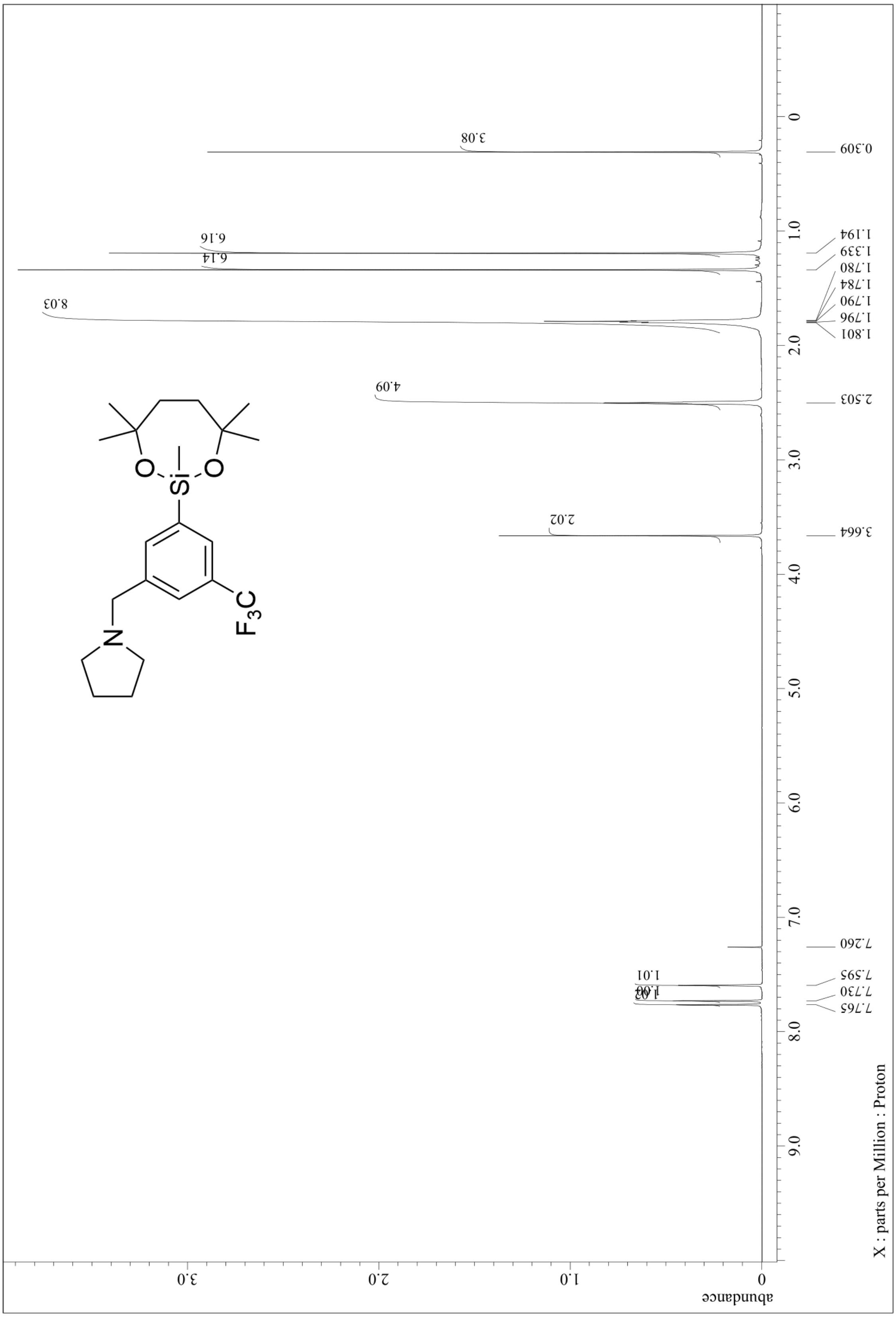

Figure S54. ^{13}C NMR spectrum of **8**.

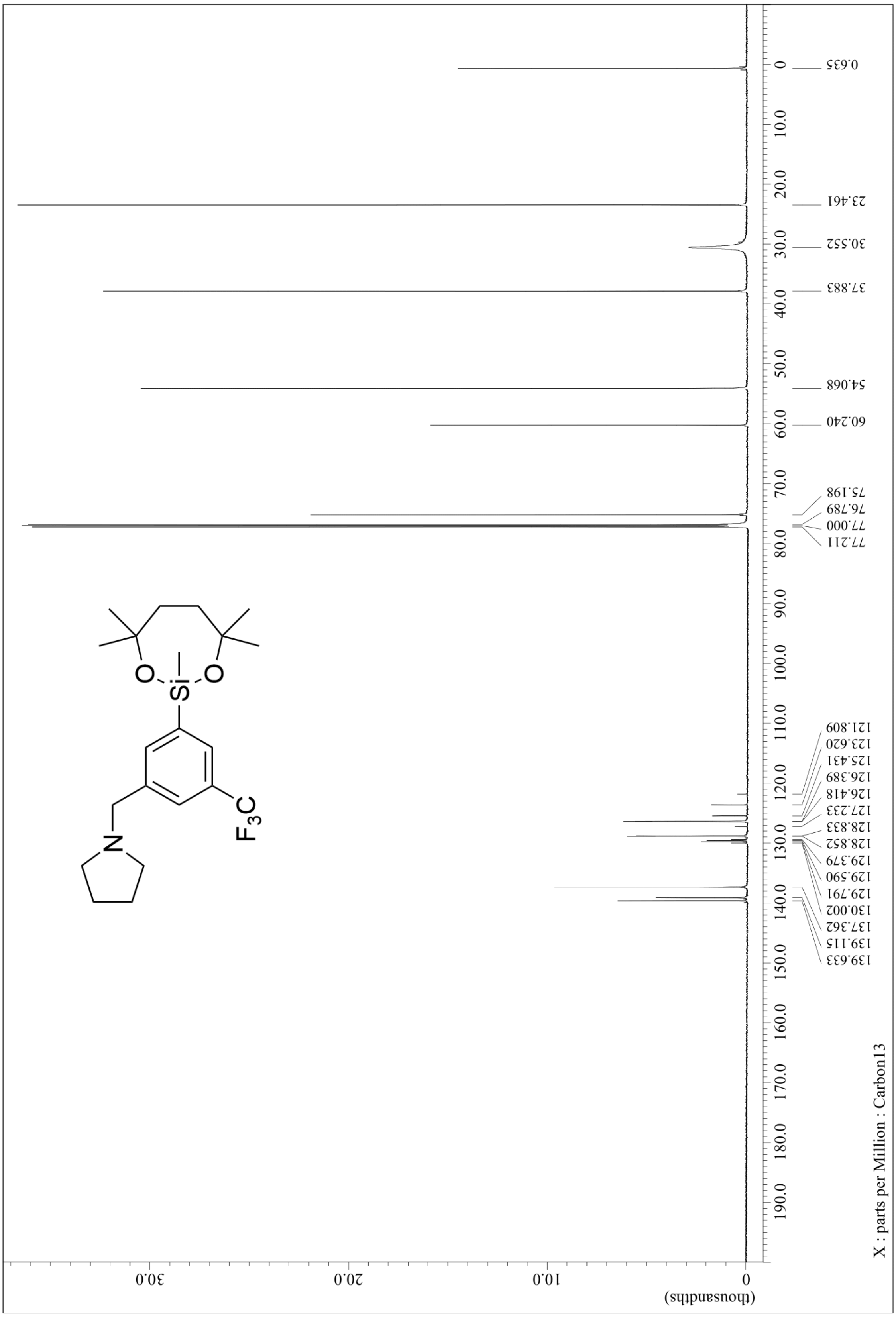

Figure S55. ^{1}H NMR spectrum of **9**.

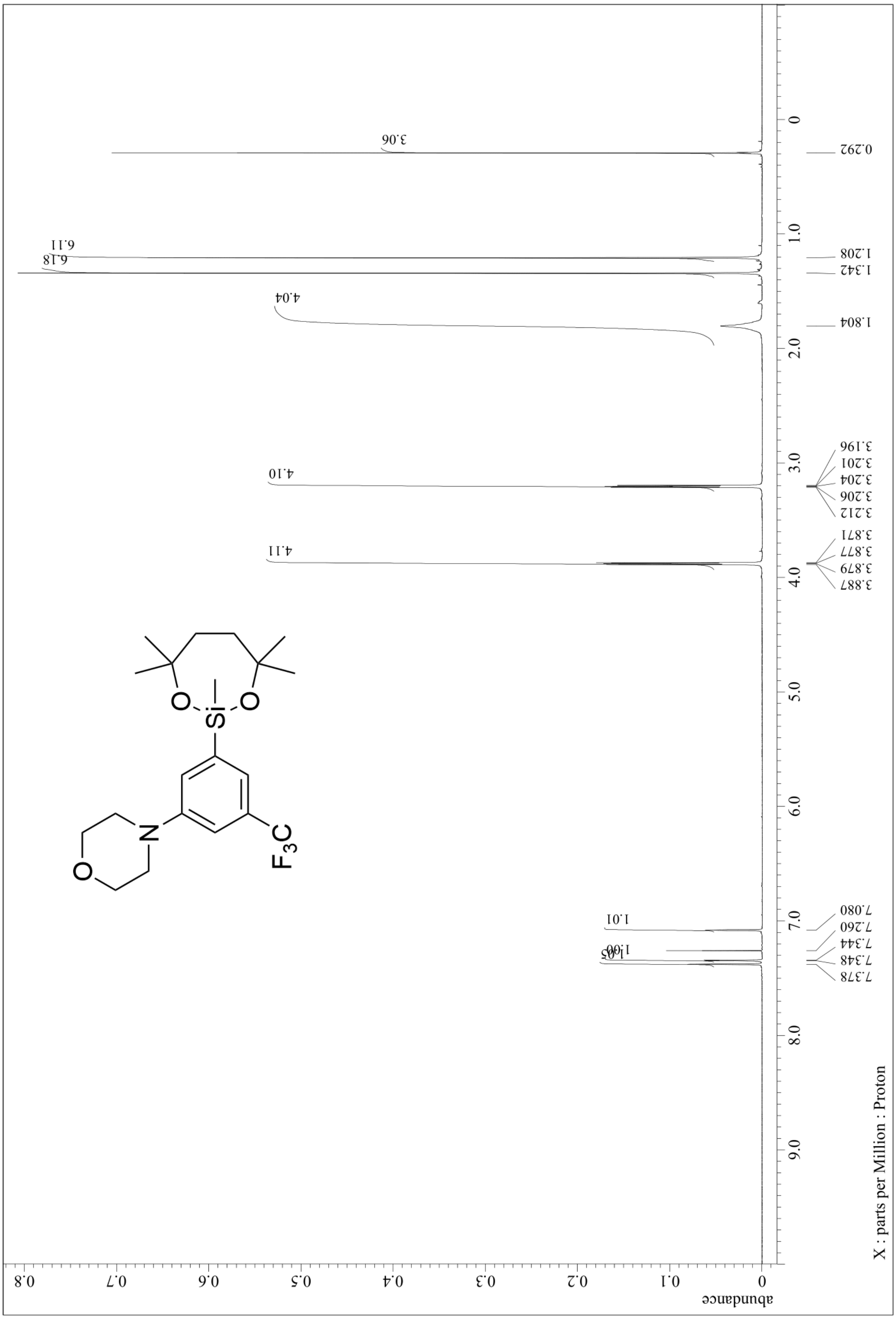

Figure S56. ^{13}C NMR spectrum of **9**.

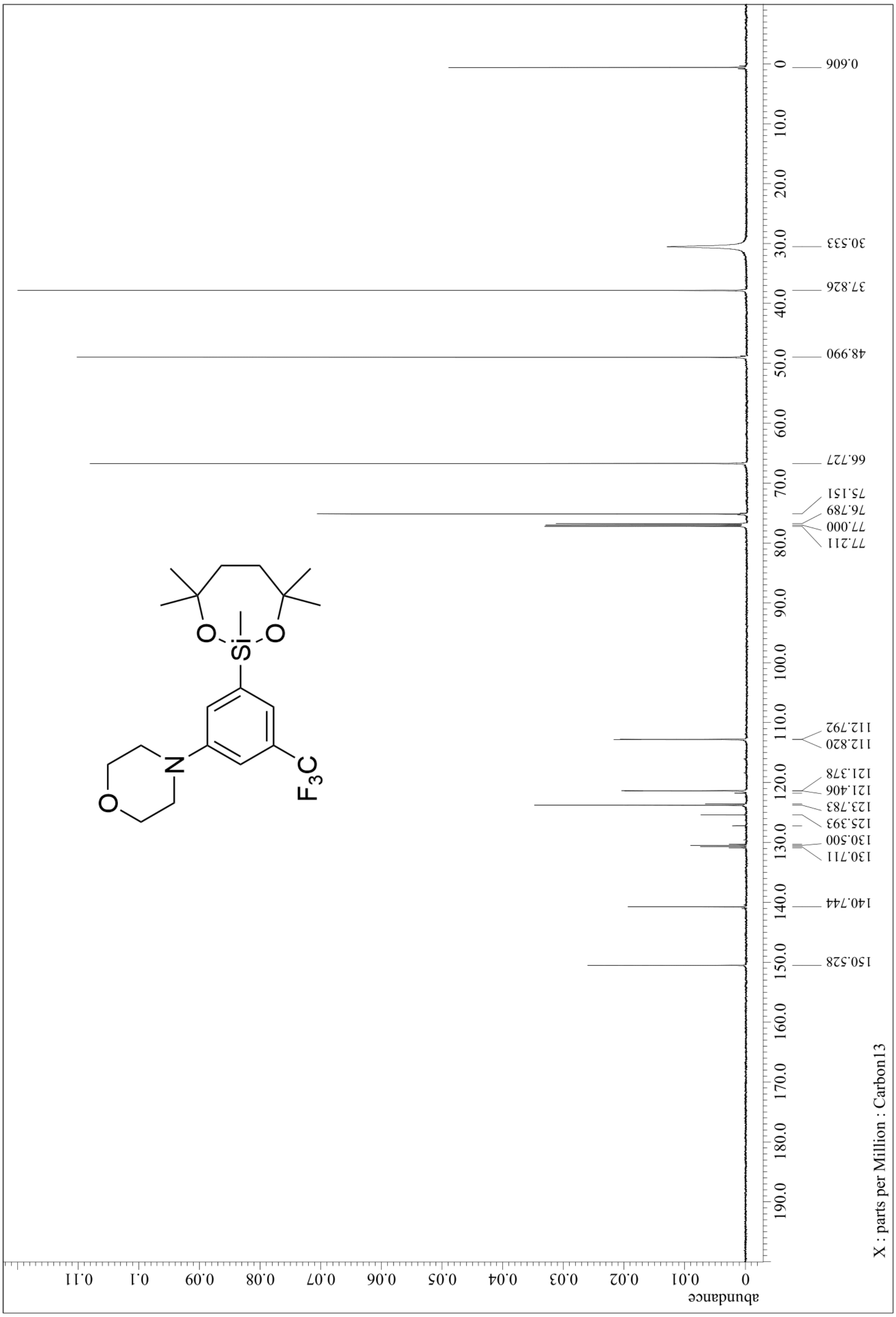

Figure S57. ^{1}H NMR spectrum of **10**.

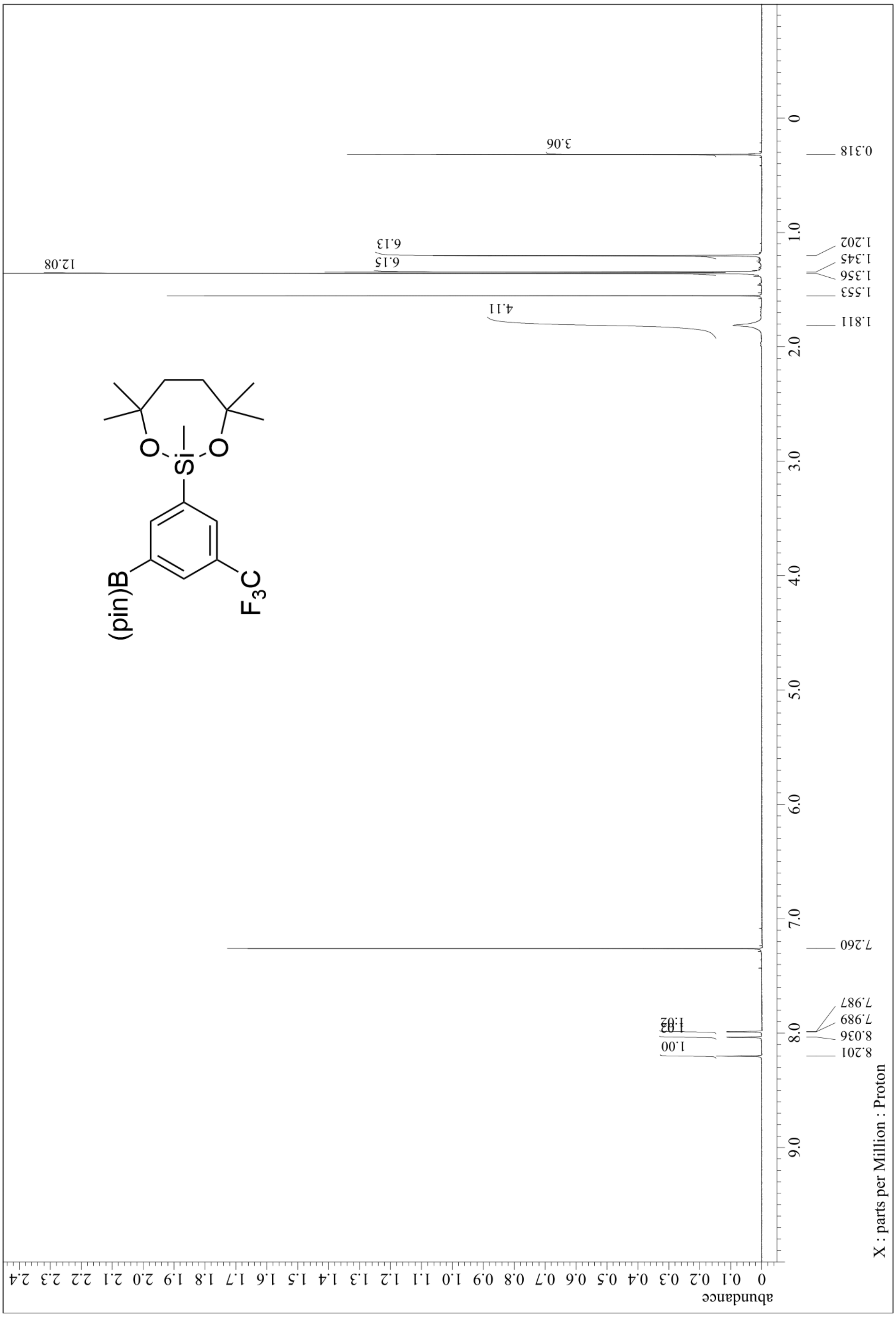

Figure S58. ^{13}C NMR spectrum of **10**.

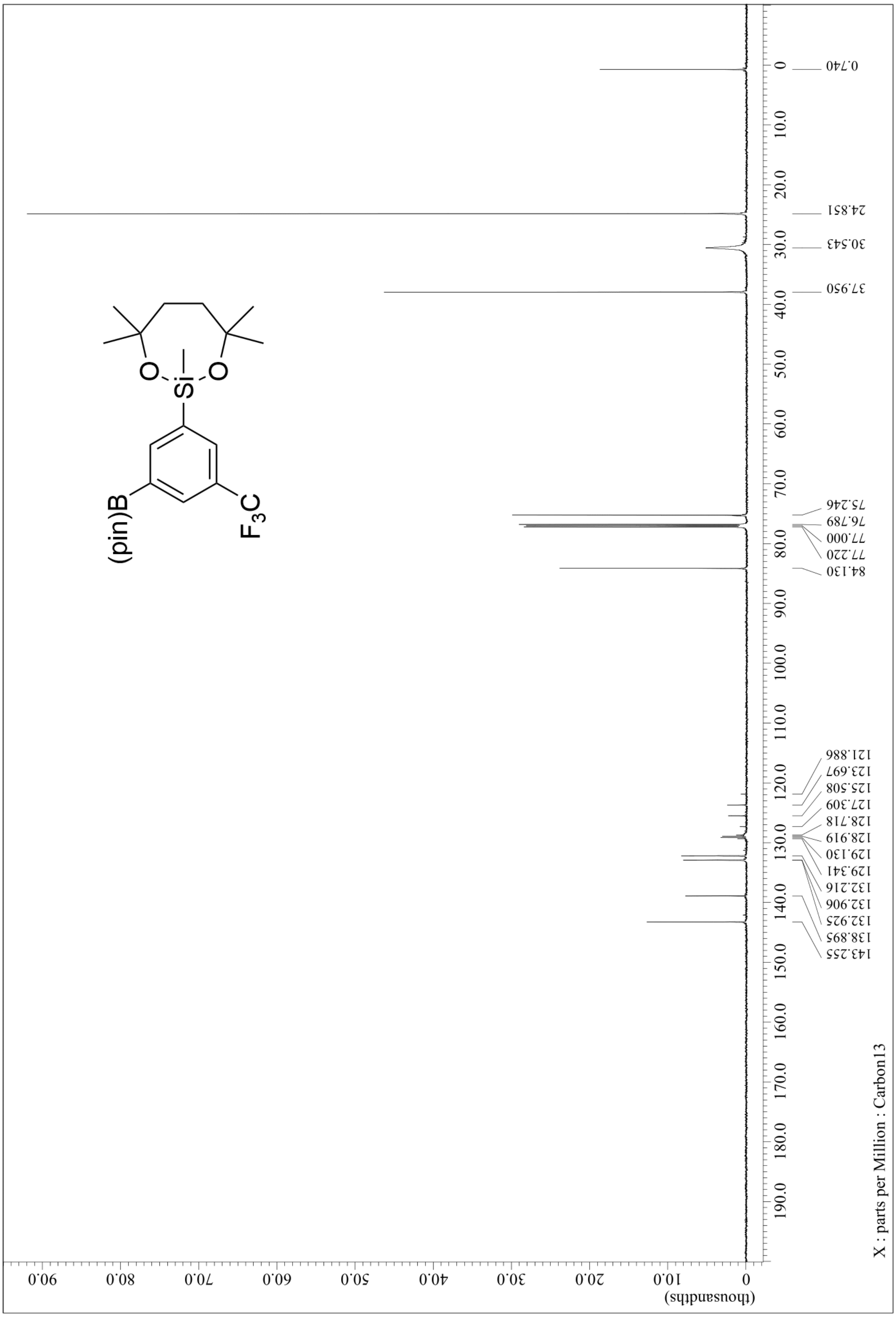

Figure S59. ^{1}H NMR spectrum of **11**.

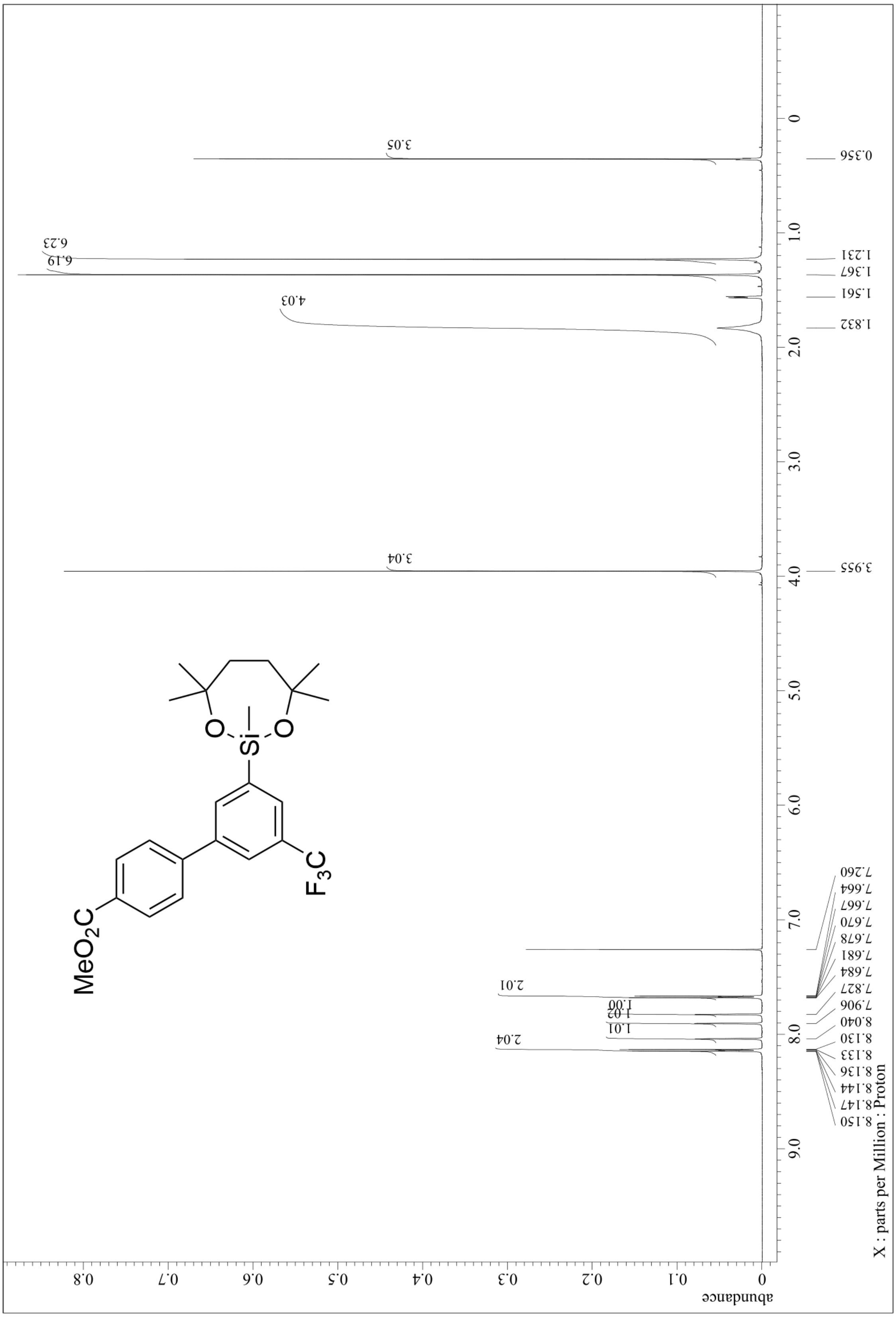

Figure S60. ^{13}C NMR spectrum of **11**.

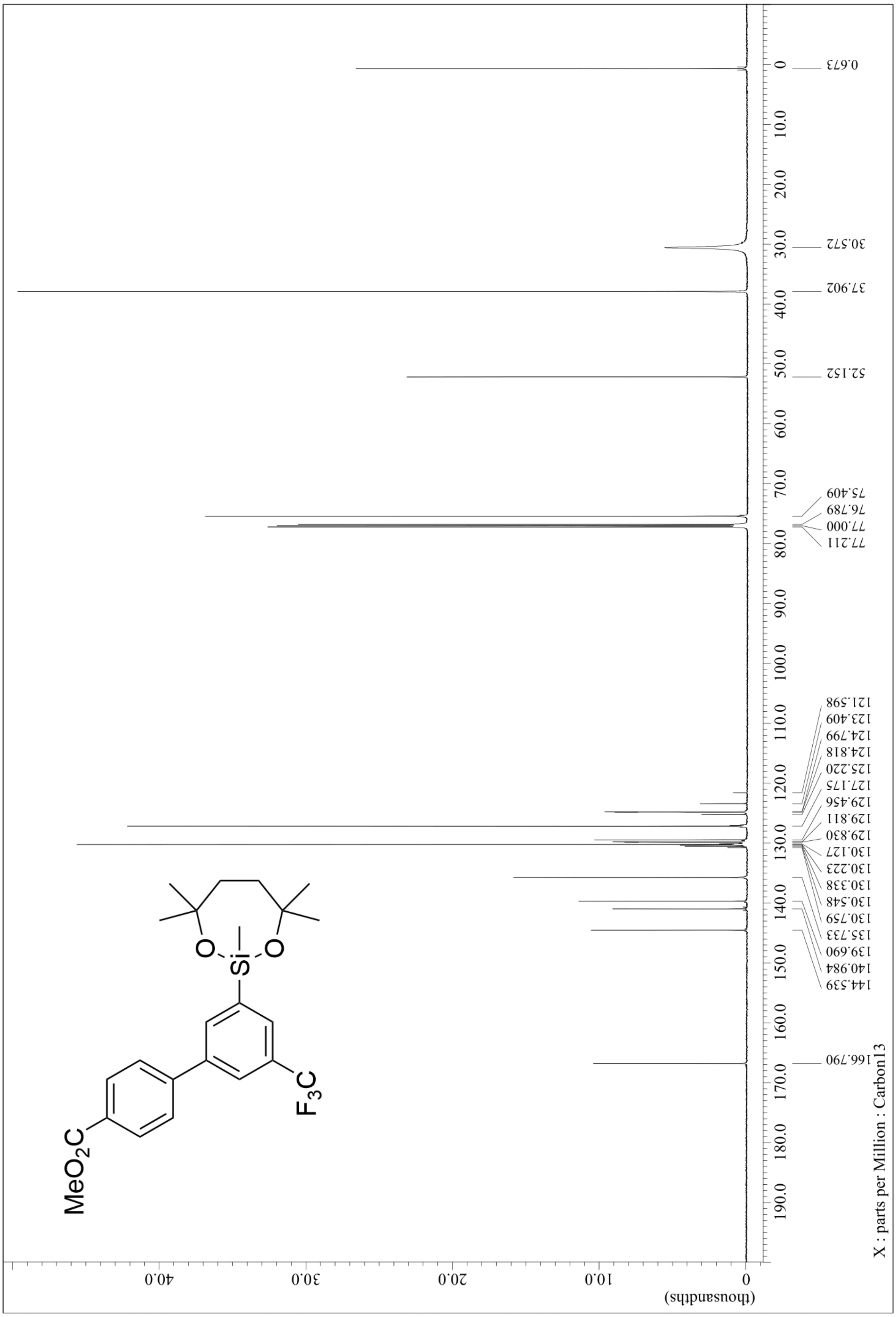

Figure S61. ^{1}H NMR spectrum of **12**.

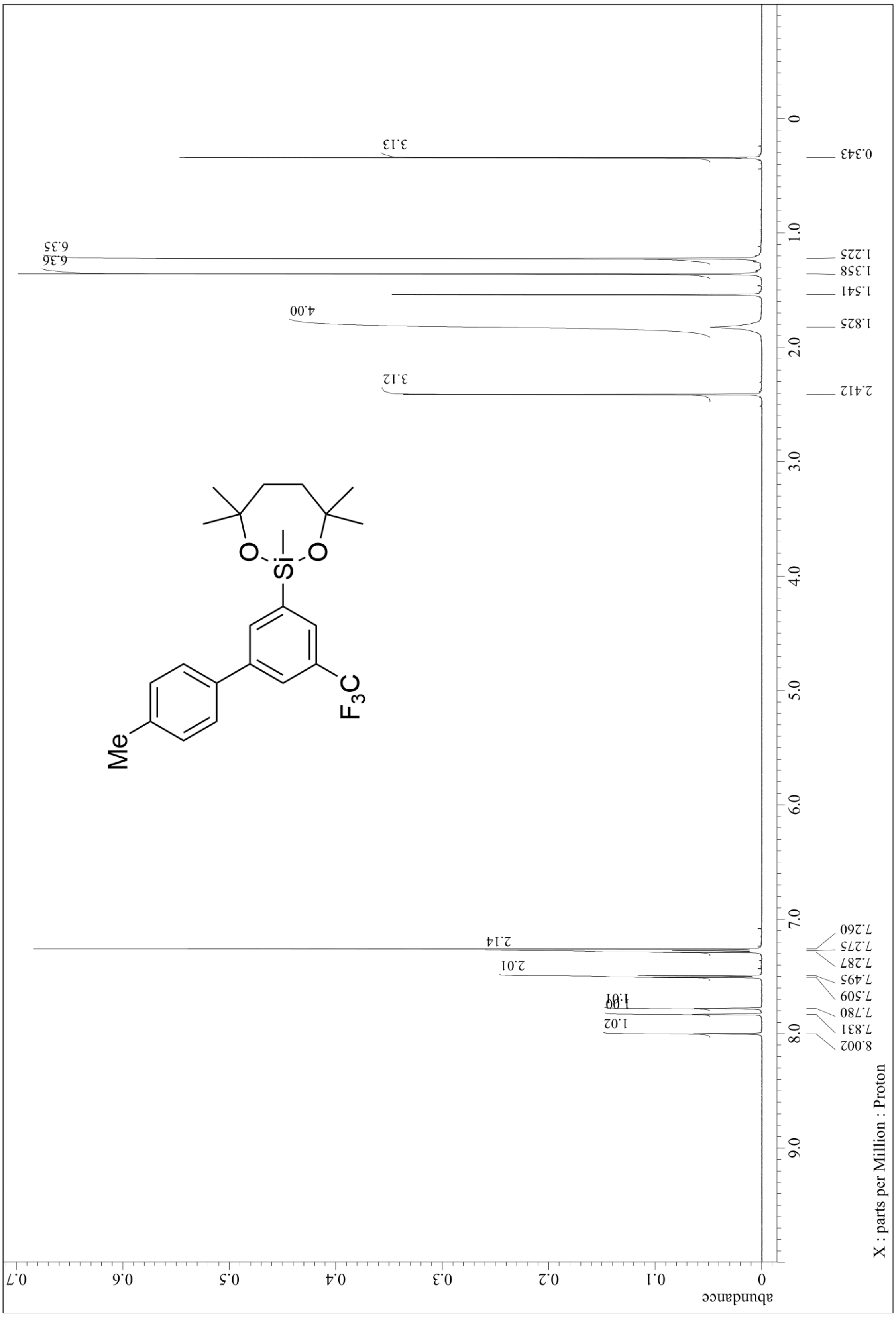

Figure S62. ^{13}C NMR spectrum of **12**.

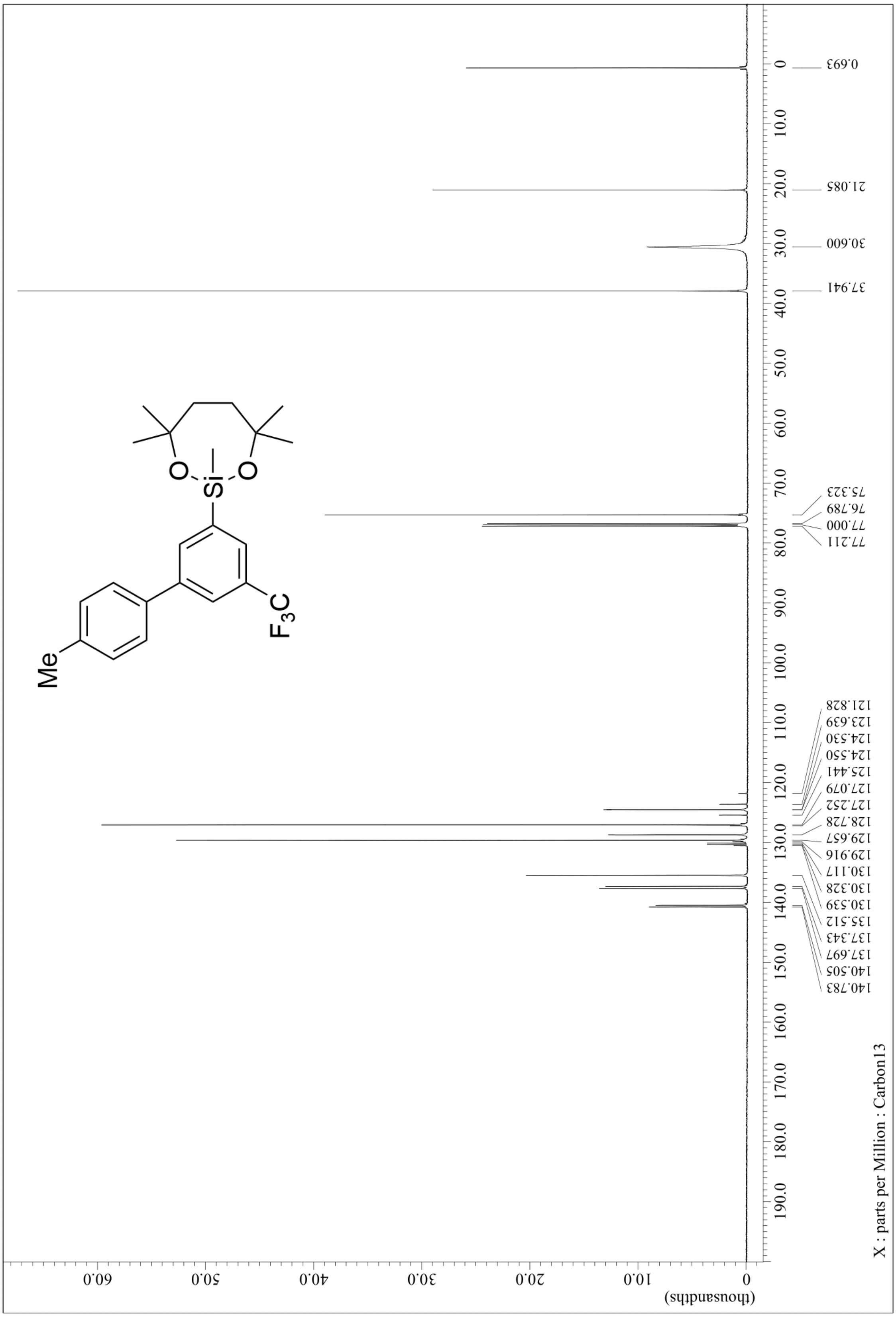

Figure S63. ^{1}H NMR spectrum of **13**.

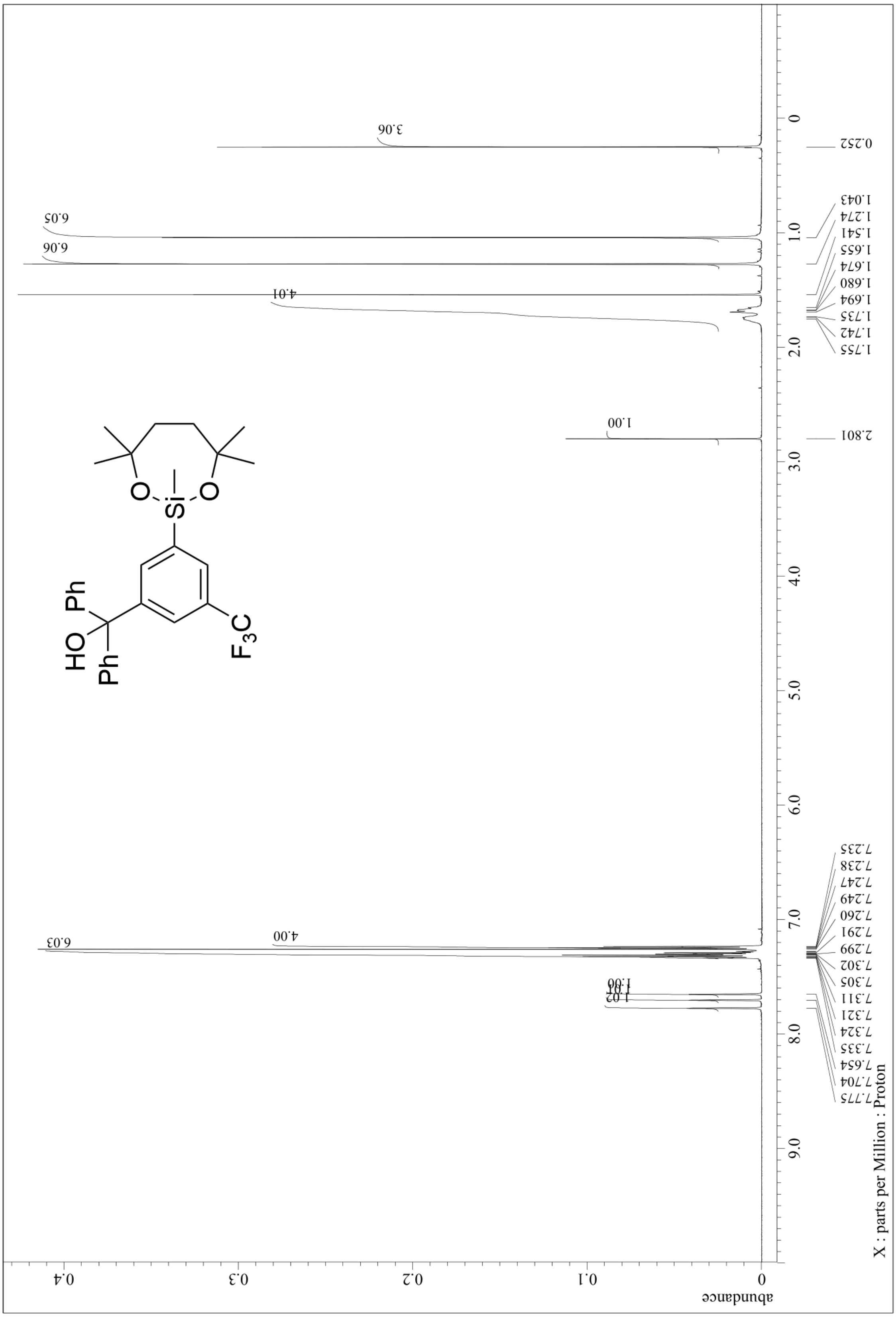

Figure S64. ^{13}C NMR spectrum of **13**.

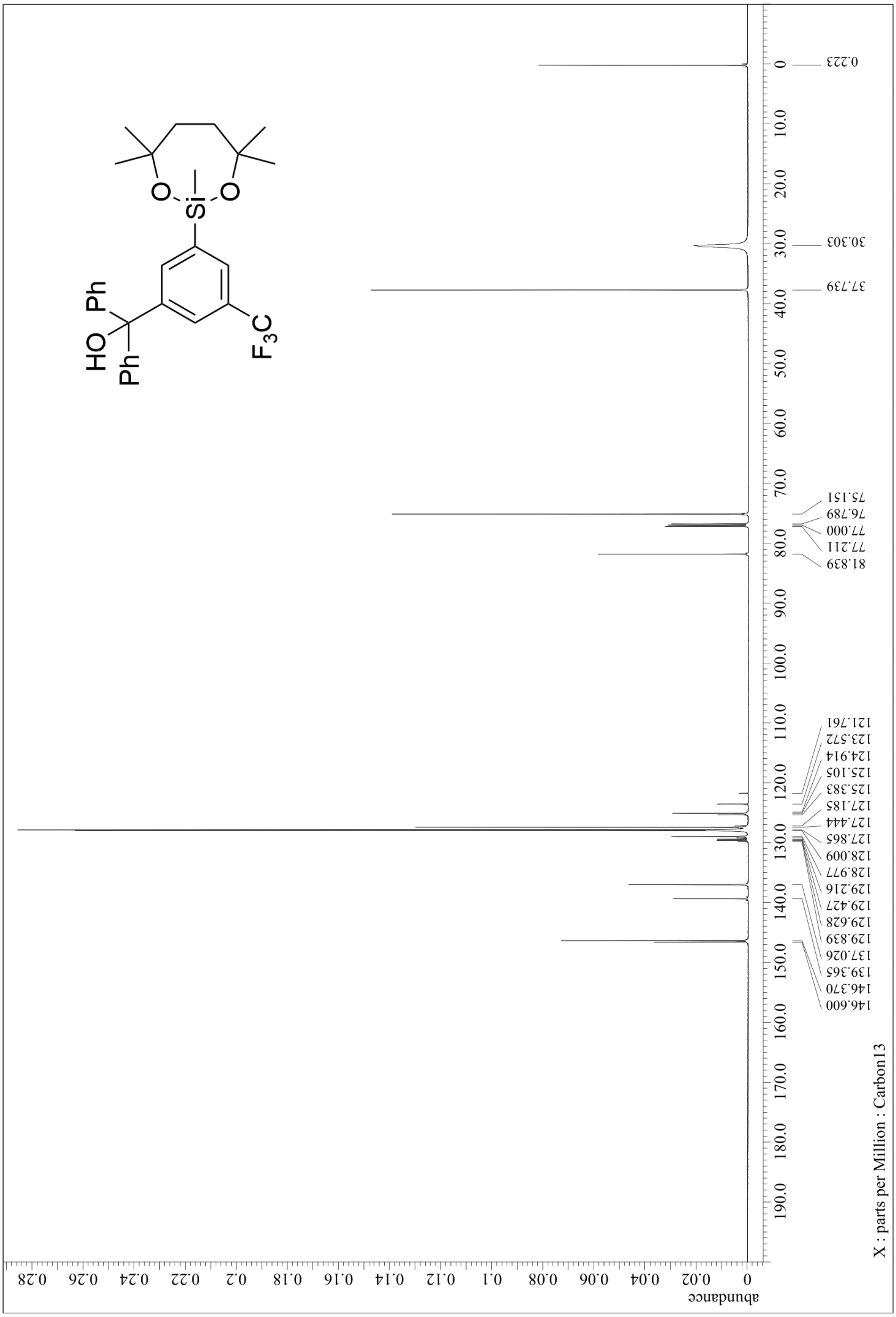

Figure S65. ^{1}H NMR spectrum of **14**.

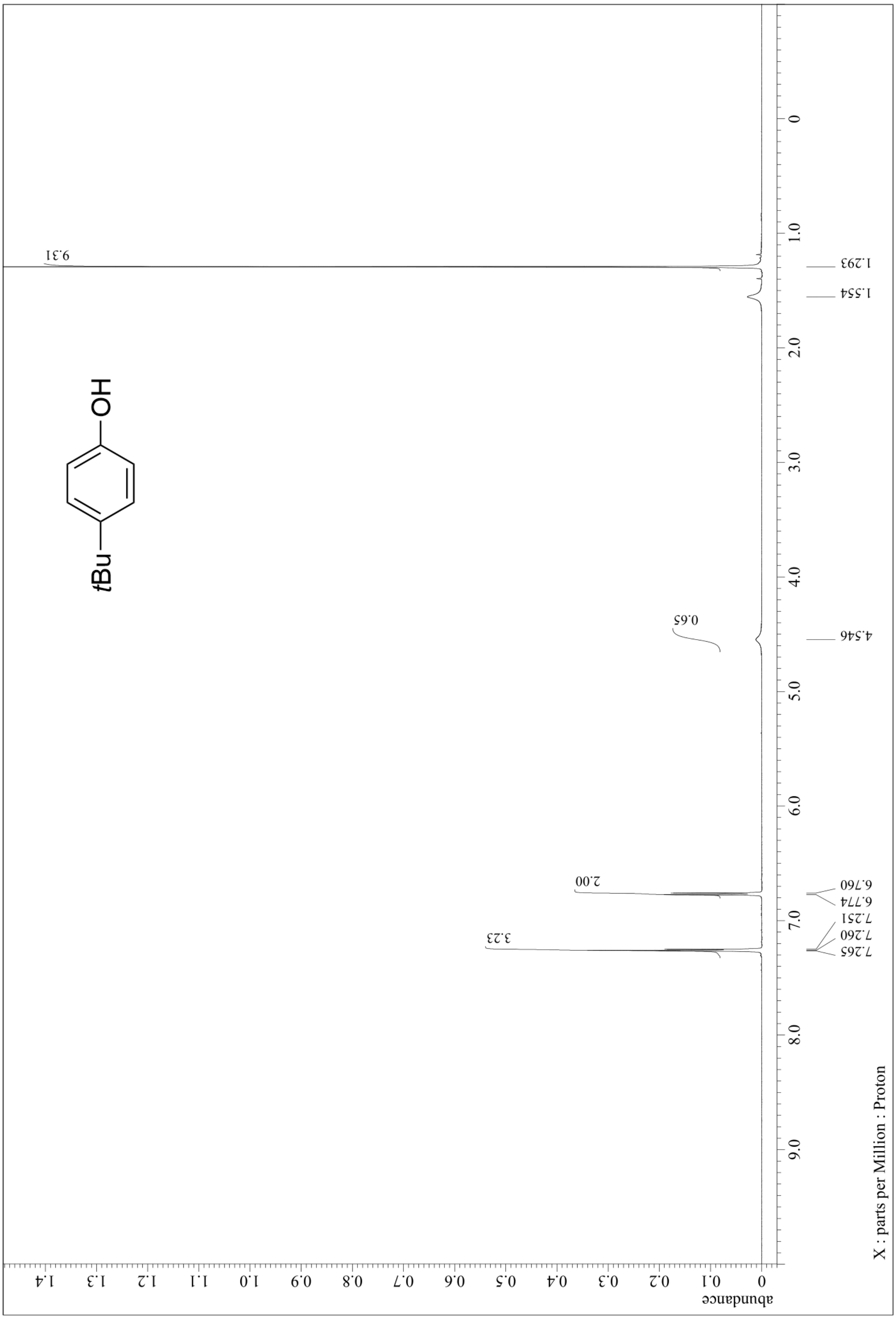

Figure S66. ^{13}C NMR spectrum of **14**.

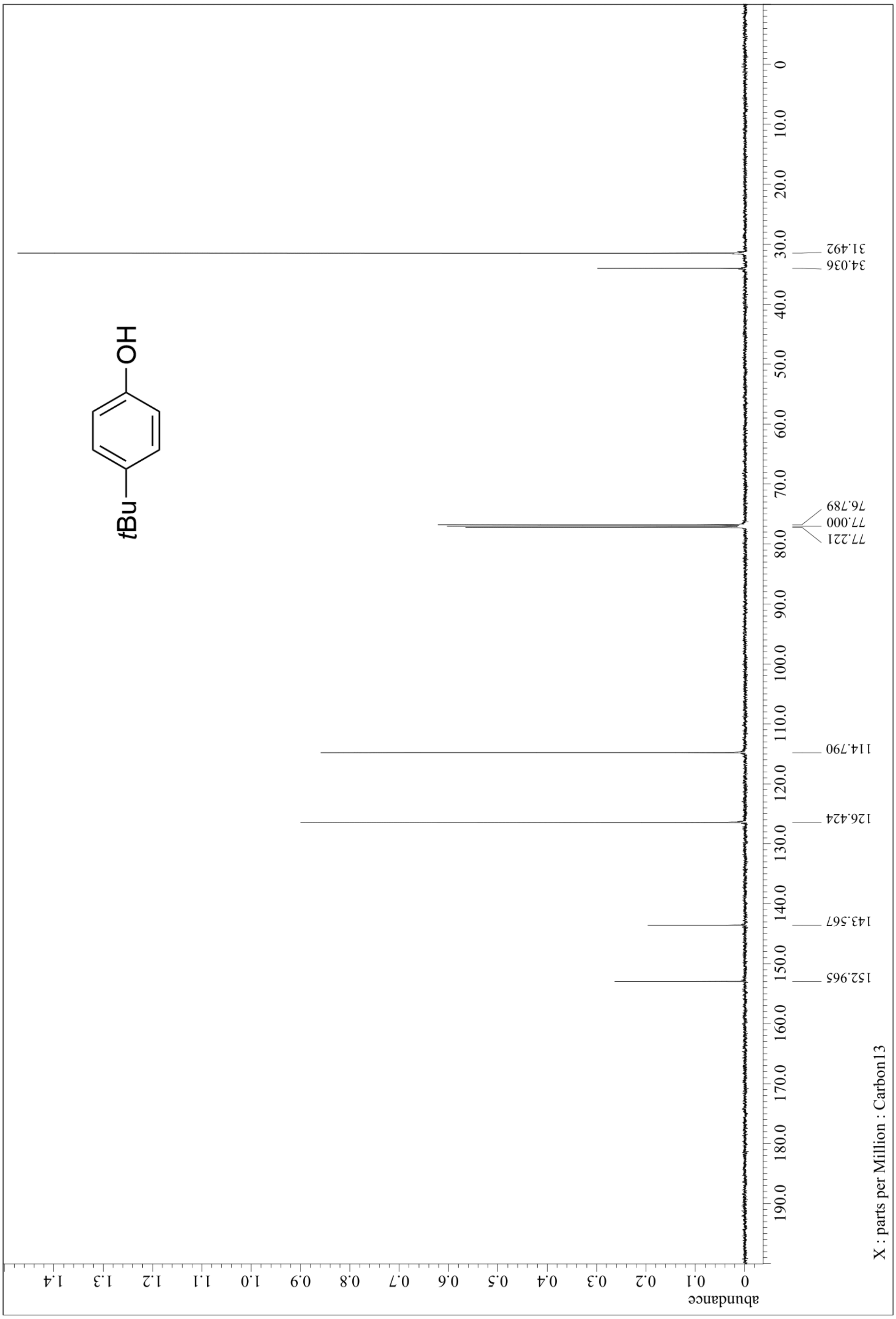

Figure S67. ^{1}H NMR spectrum of **15**.

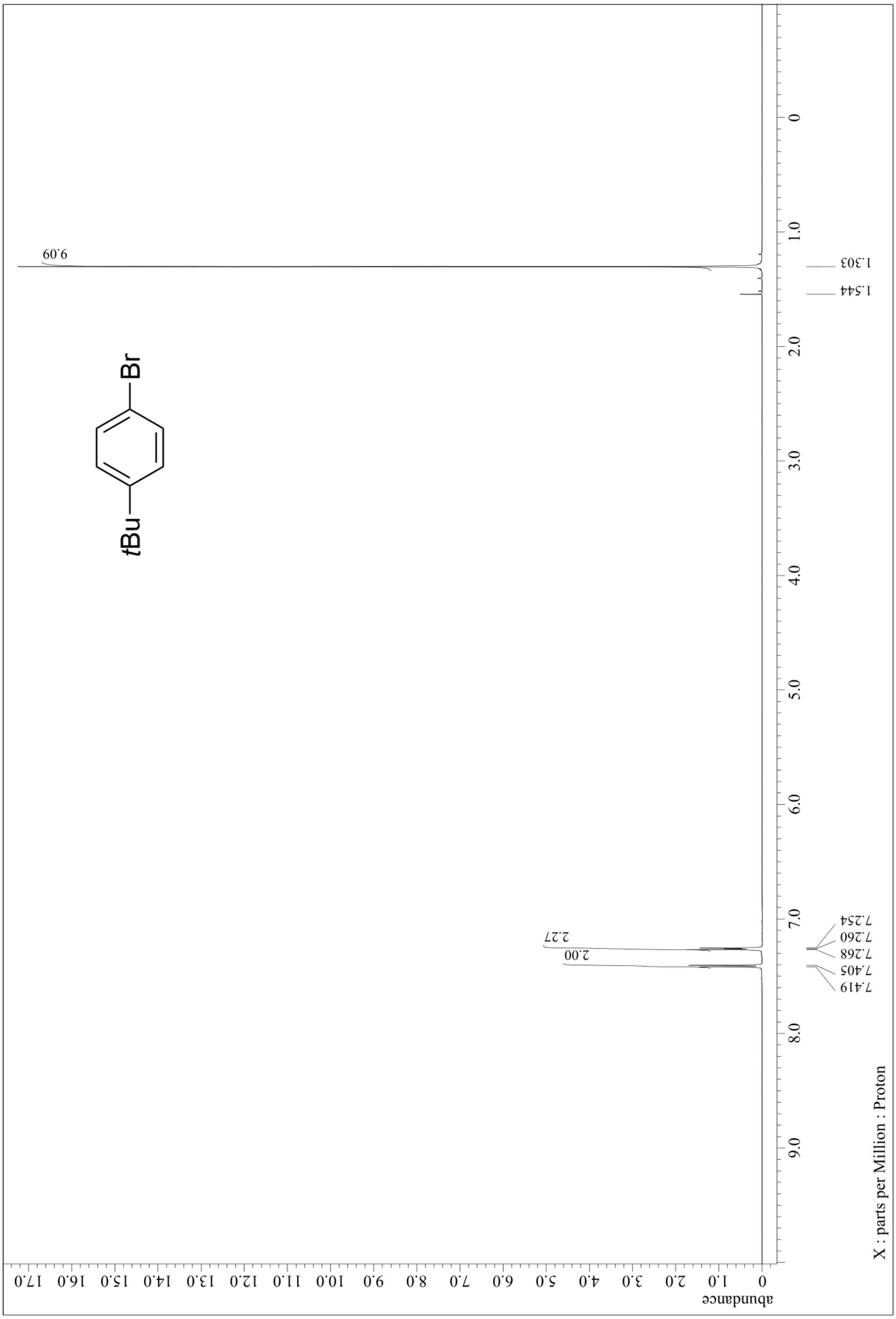

Figure S68. ^{13}C NMR spectrum of **15**.

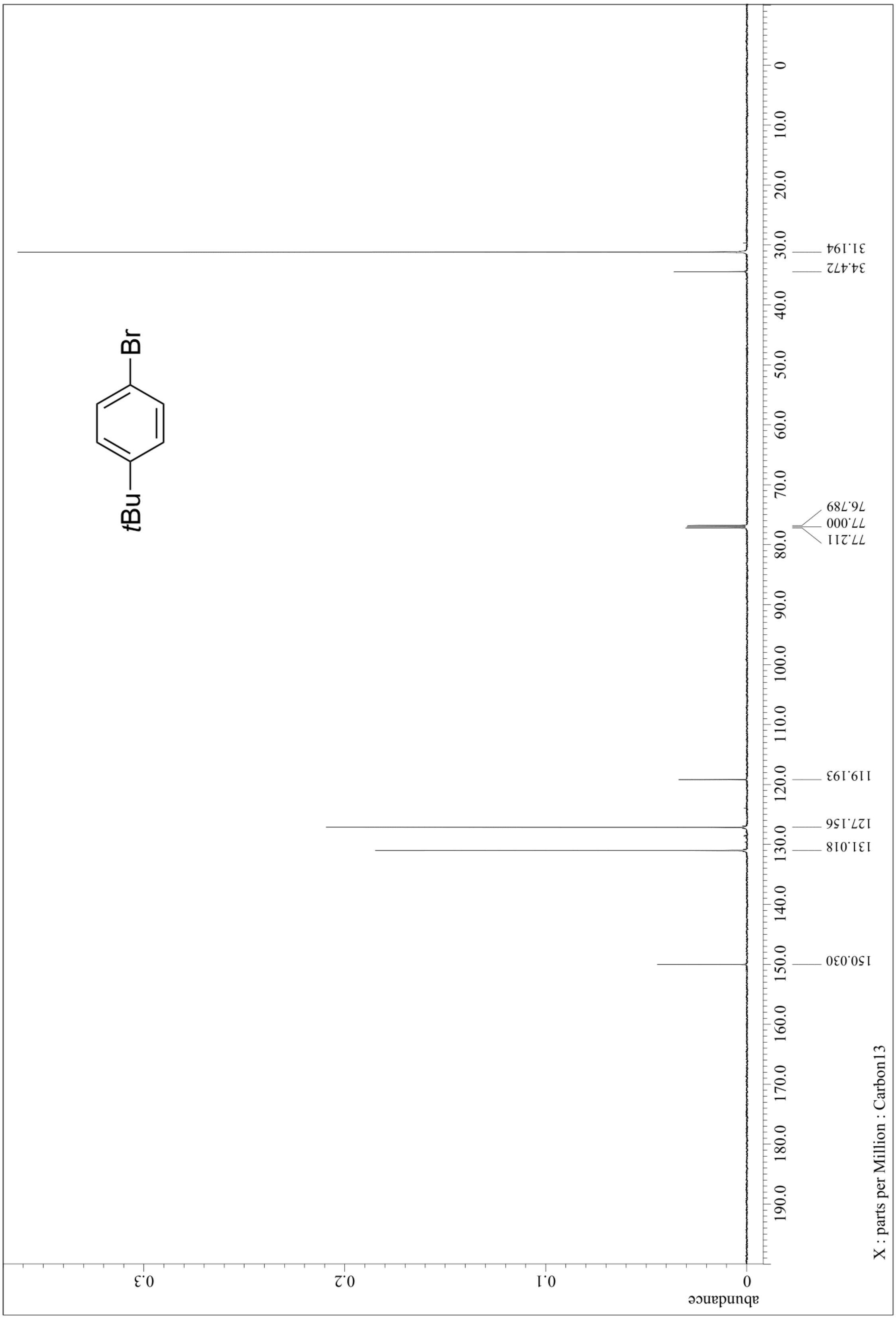

Figure S69. ^{1}H NMR spectrum of **16a**.

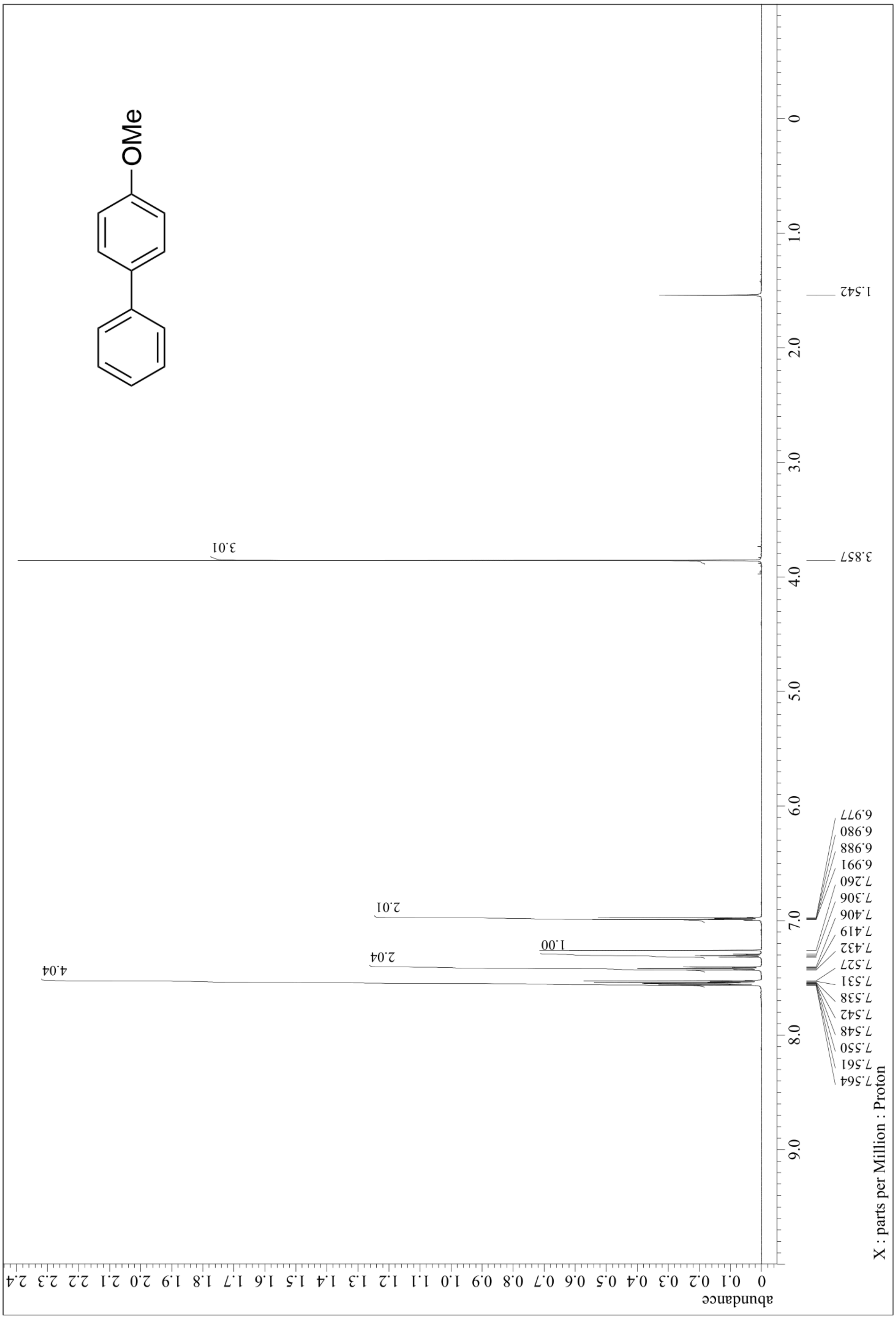

Figure S70. ^{13}C NMR spectrum of **16a**.

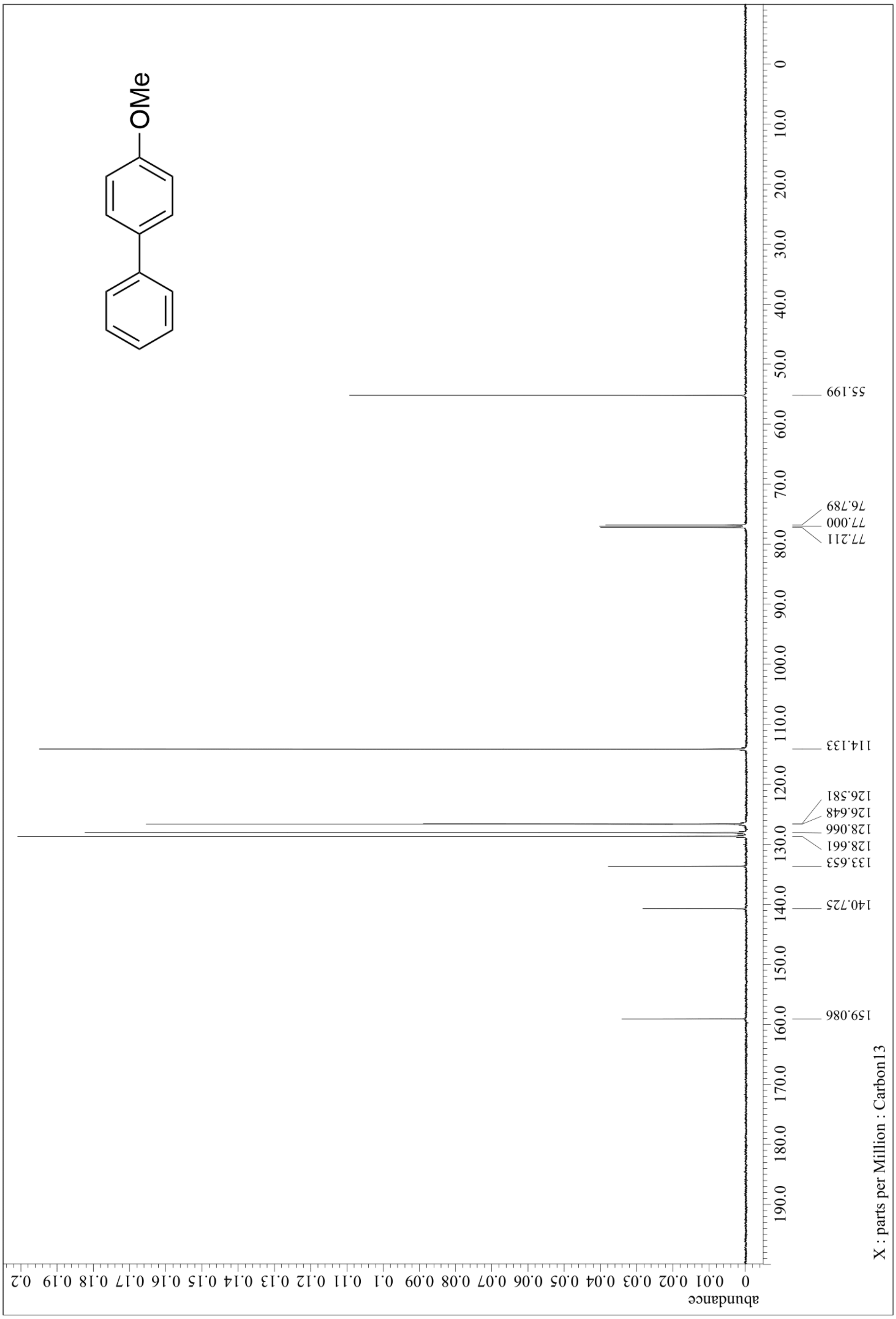

Figure S71. ^{1}H NMR spectrum of **16b**.

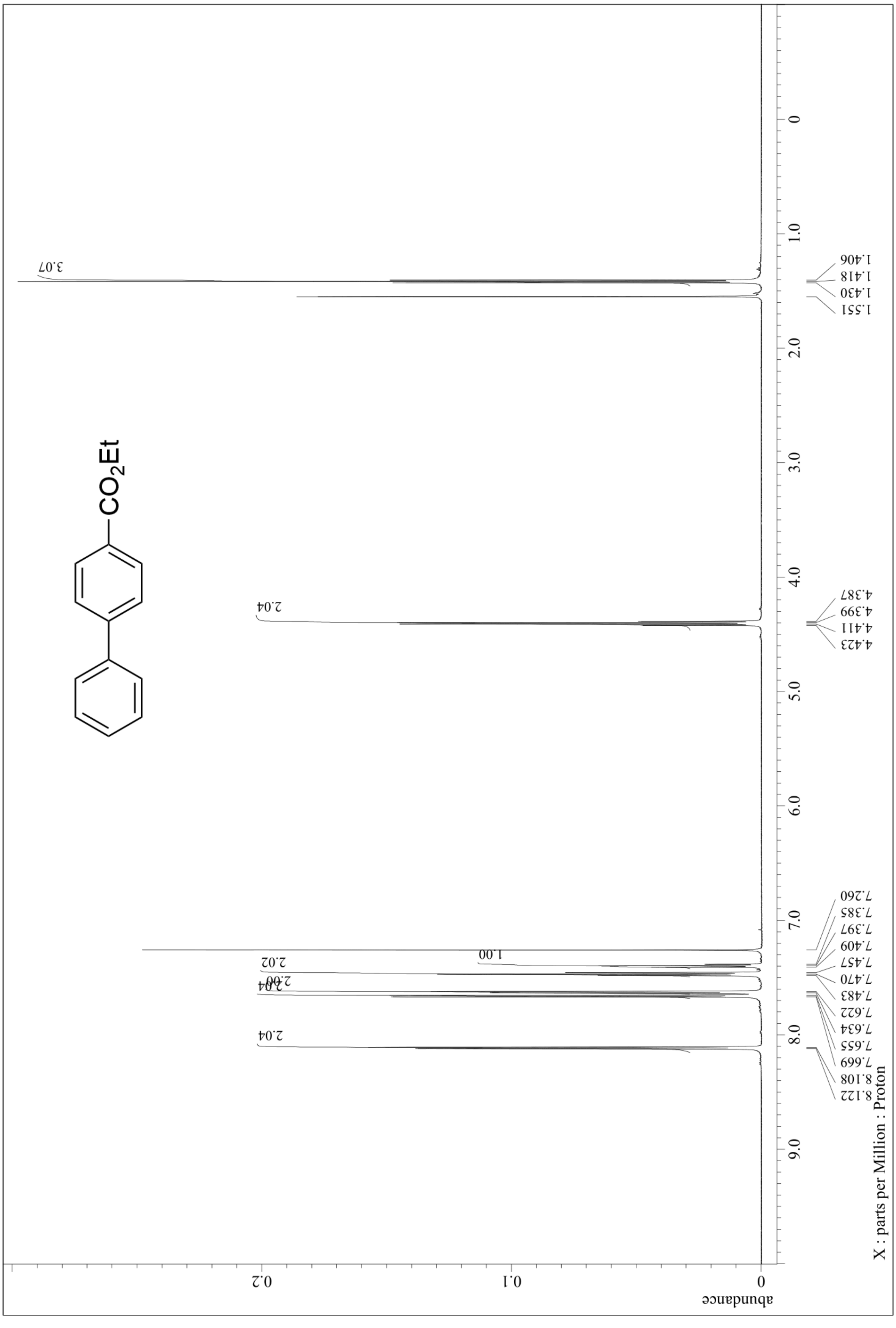

Figure S72. ^{13}C NMR spectrum of **16b**.

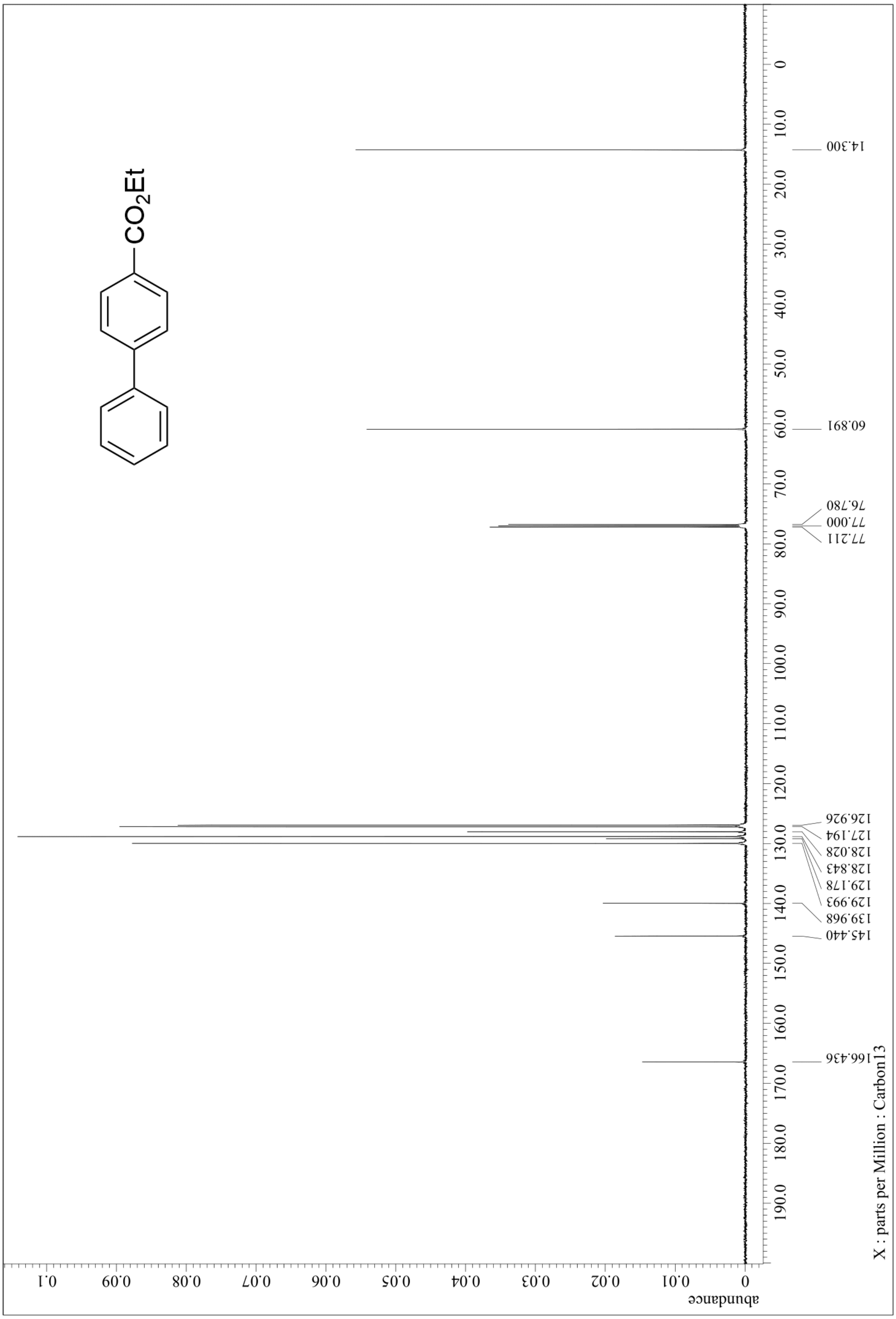

Figure S73. ^{1}H NMR spectrum of **16c**.

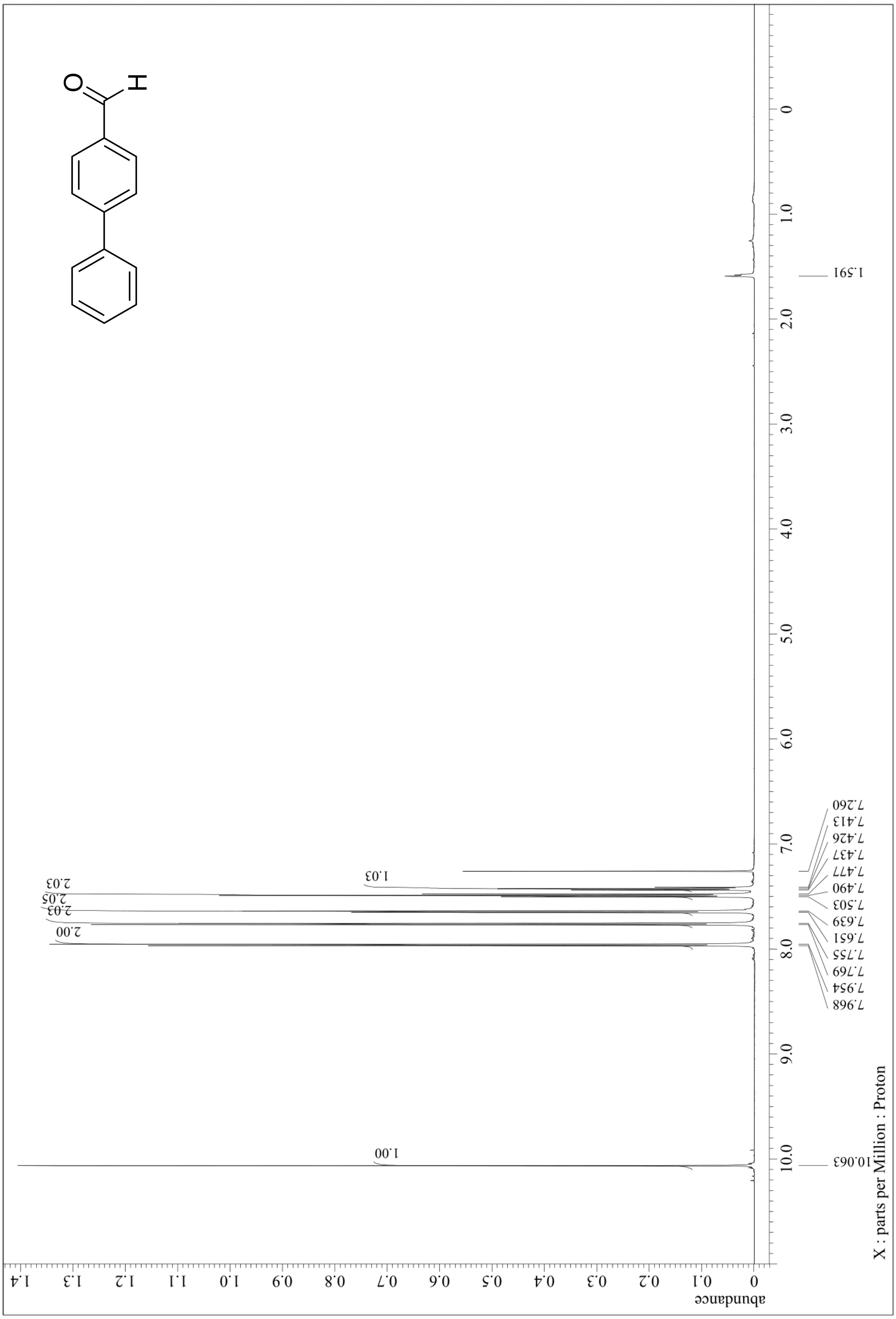

Figure S74. ^{13}C NMR spectrum of **16c**.

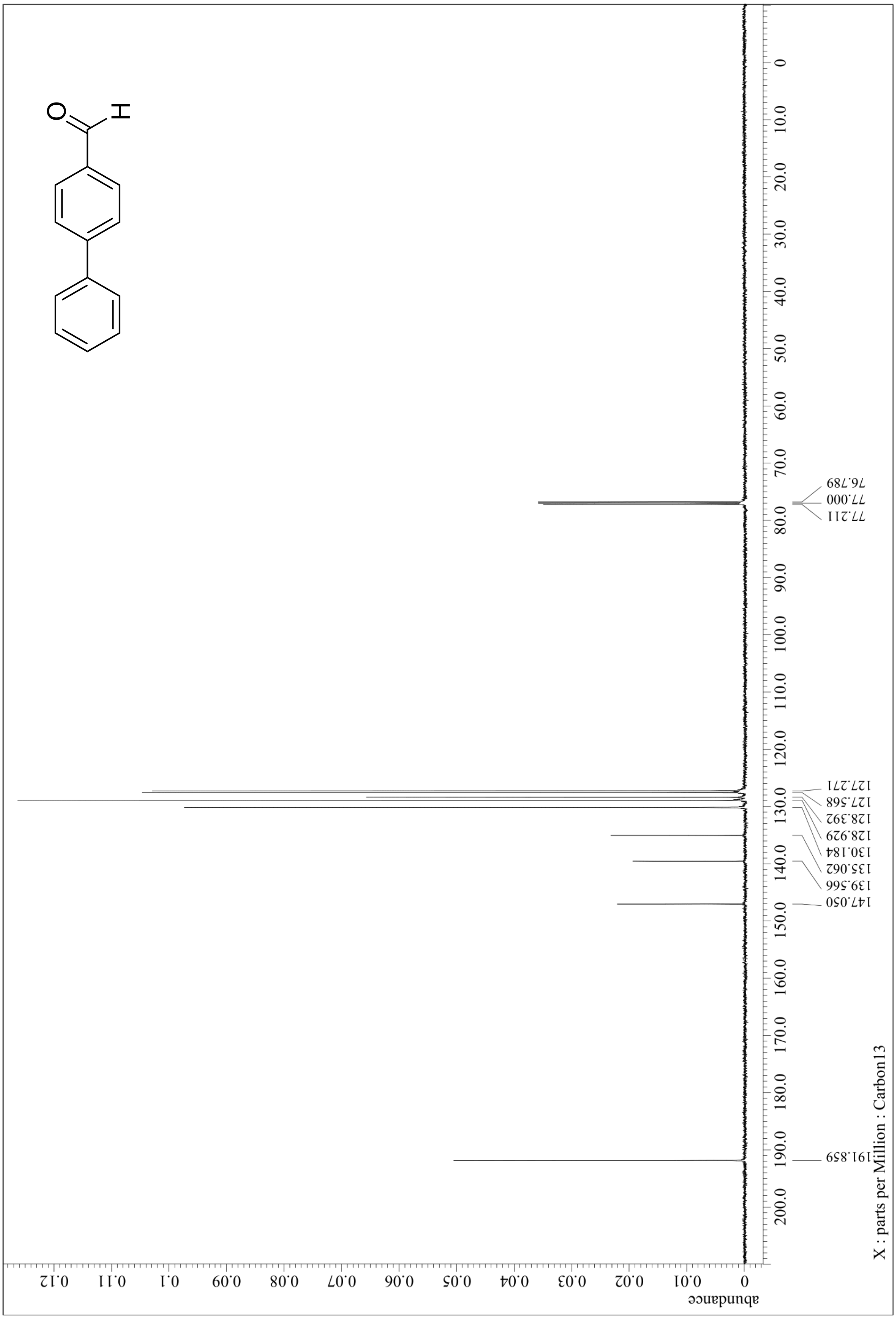

Figure S75. ^{1}H NMR spectrum of **16d**.

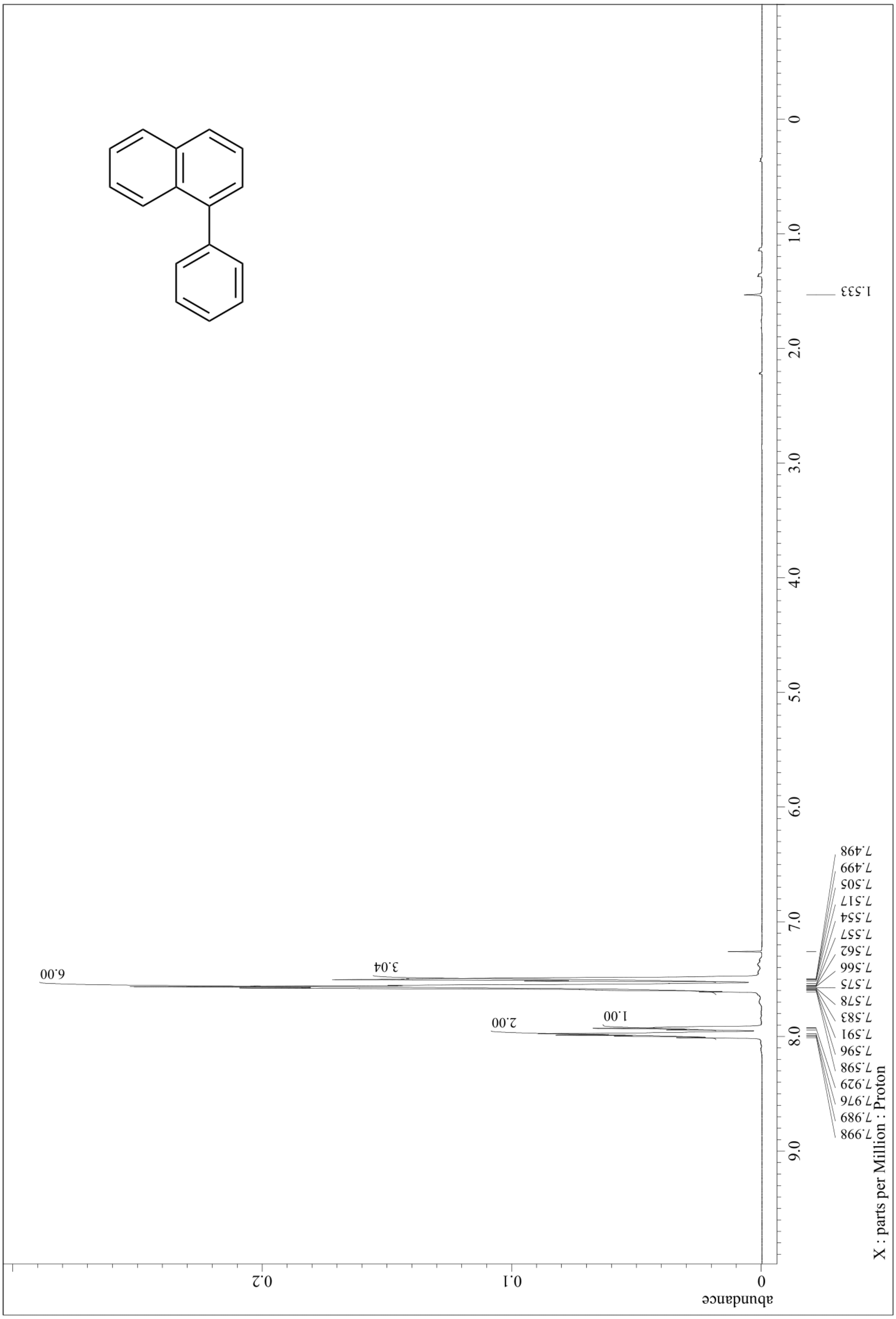

Figure S76. ^{13}C NMR spectrum of **16d**.

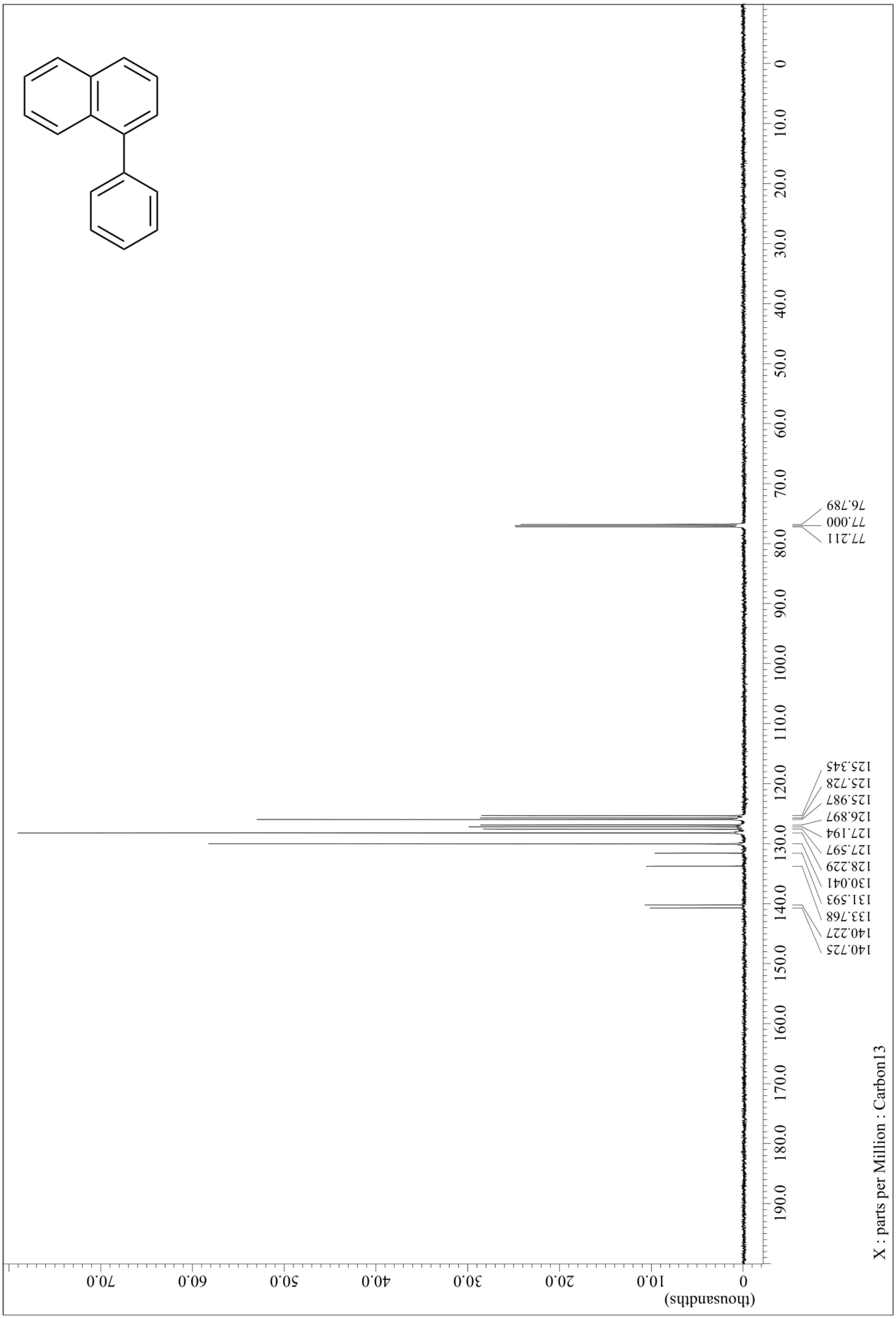

Figure S77. ^{1}H NMR spectrum of **16e**.

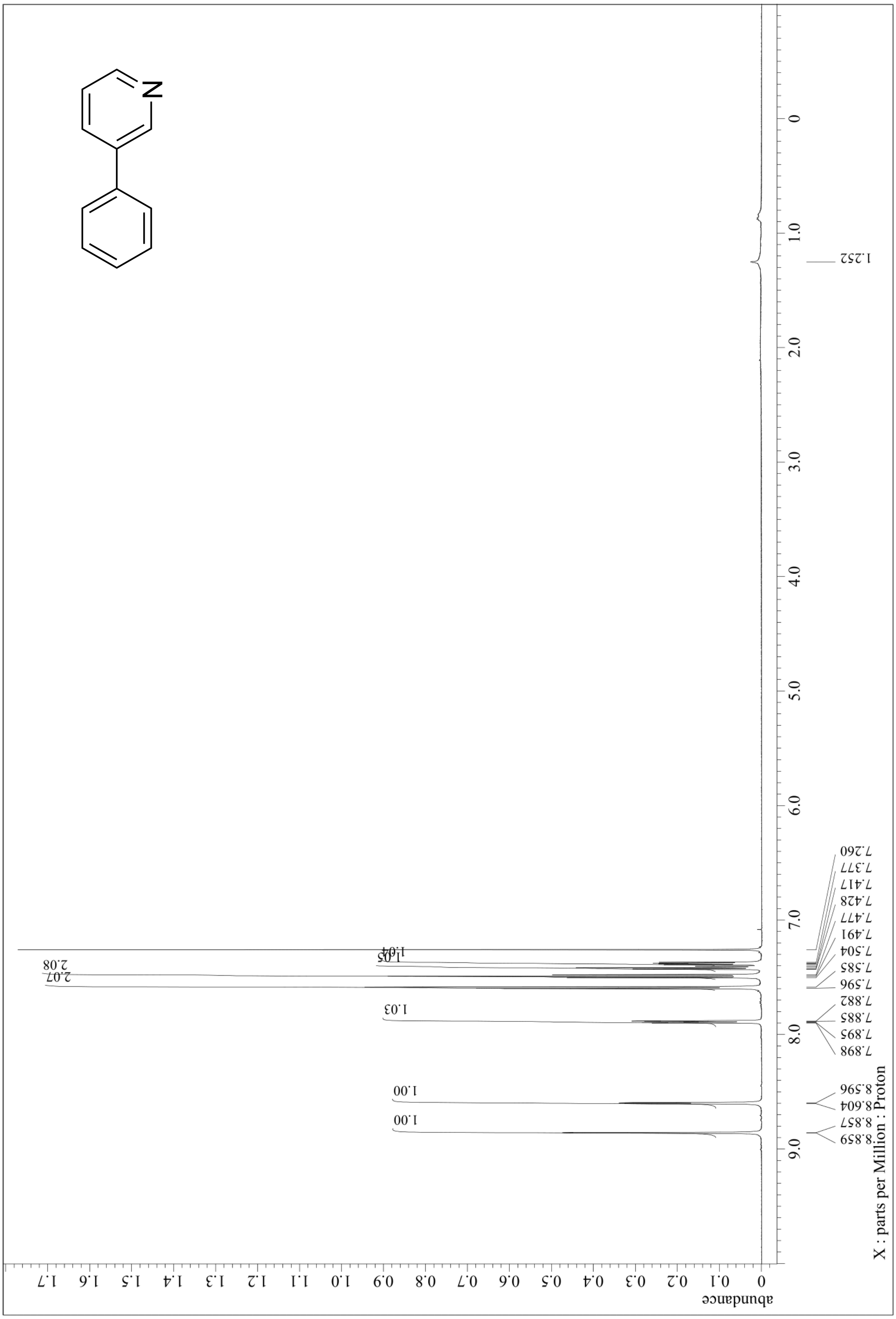

Figure S78. ^{1}H NMR spectrum of **16e**.

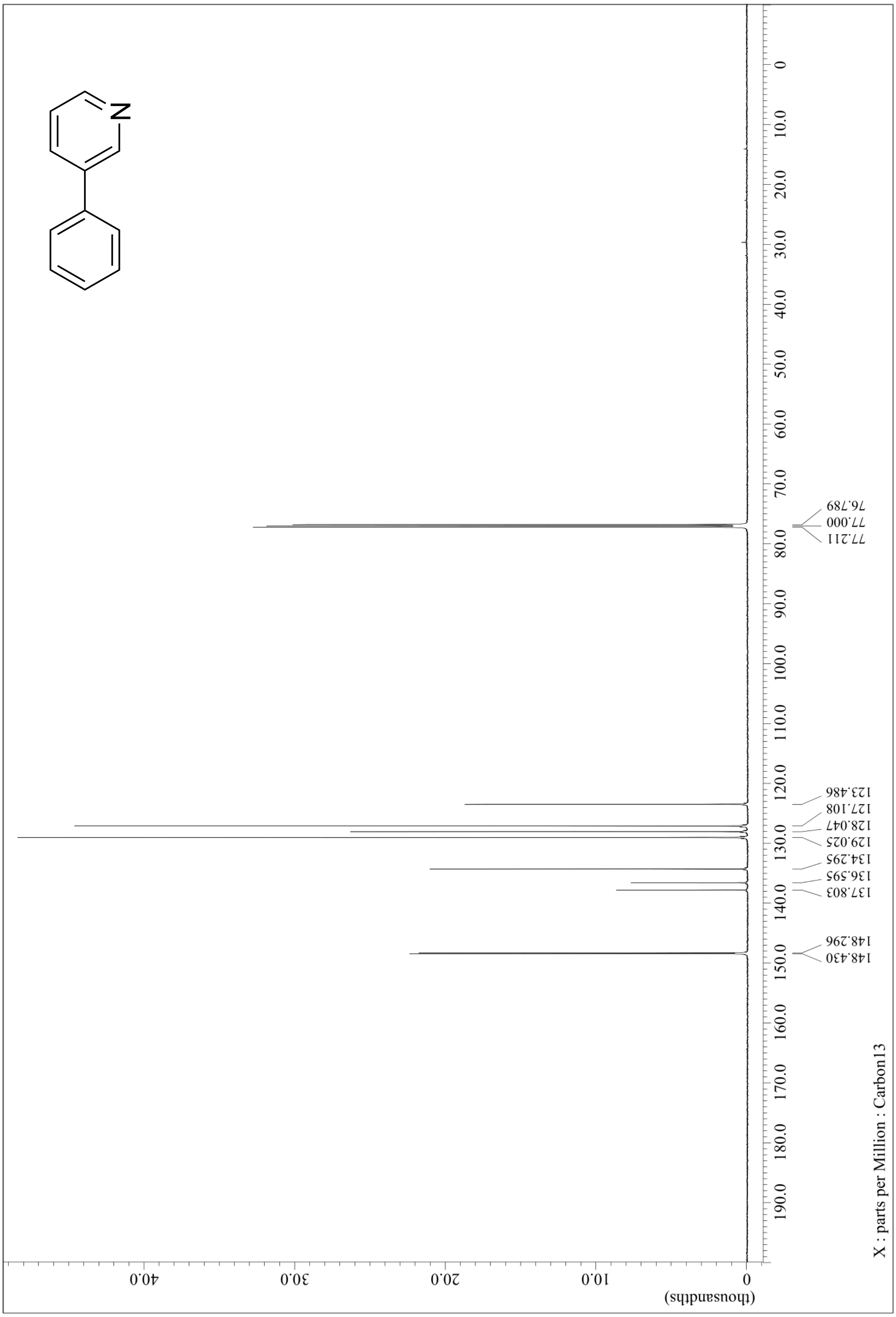

Figure S79. ^{1}H NMR spectrum of **16f**.

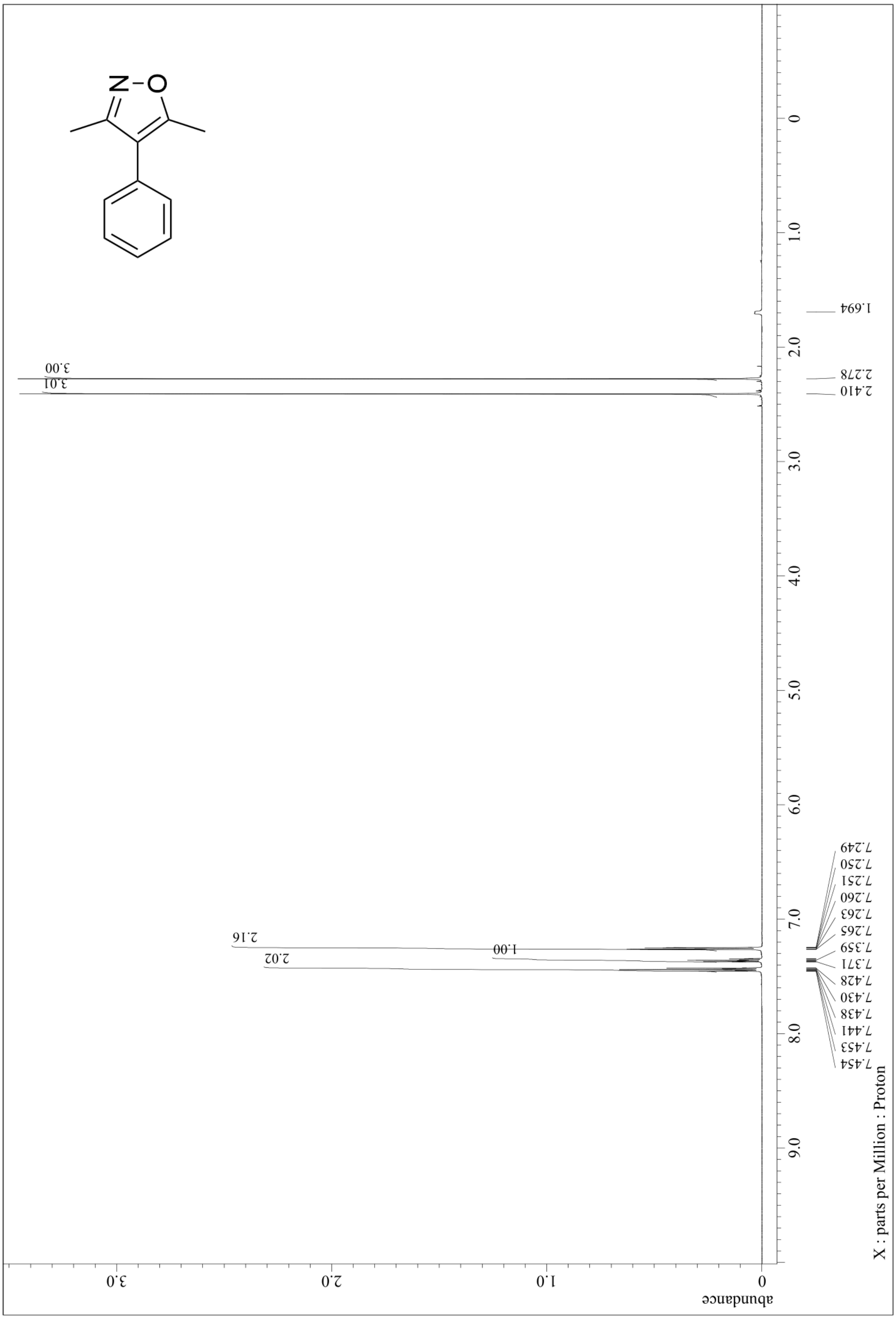

Figure S80. ^{13}C NMR spectrum of **16f**.

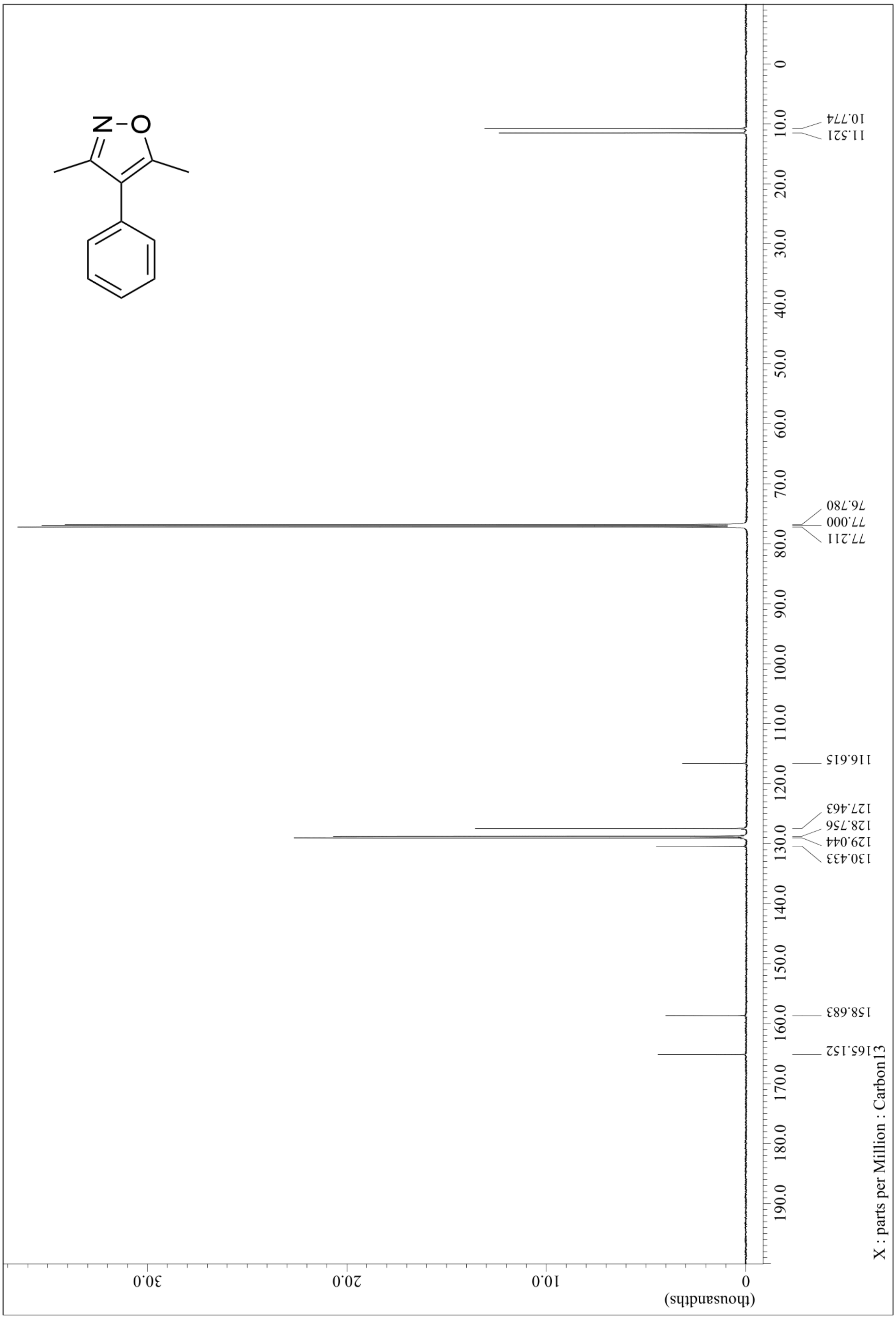

Figure S81. ^{1}H NMR spectrum of **16g**.

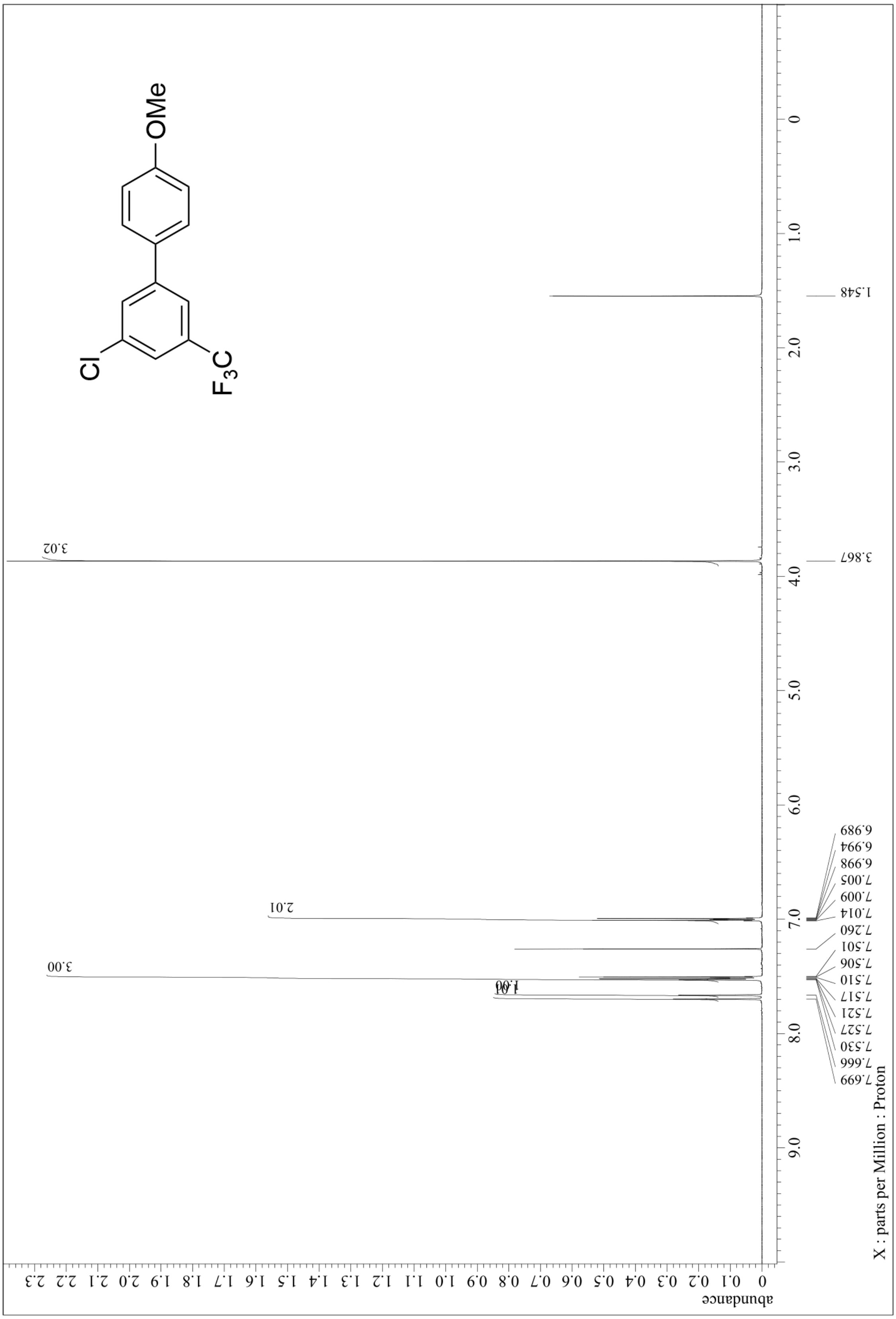

Figure S82. ^{13}C NMR spectrum of **16g**.

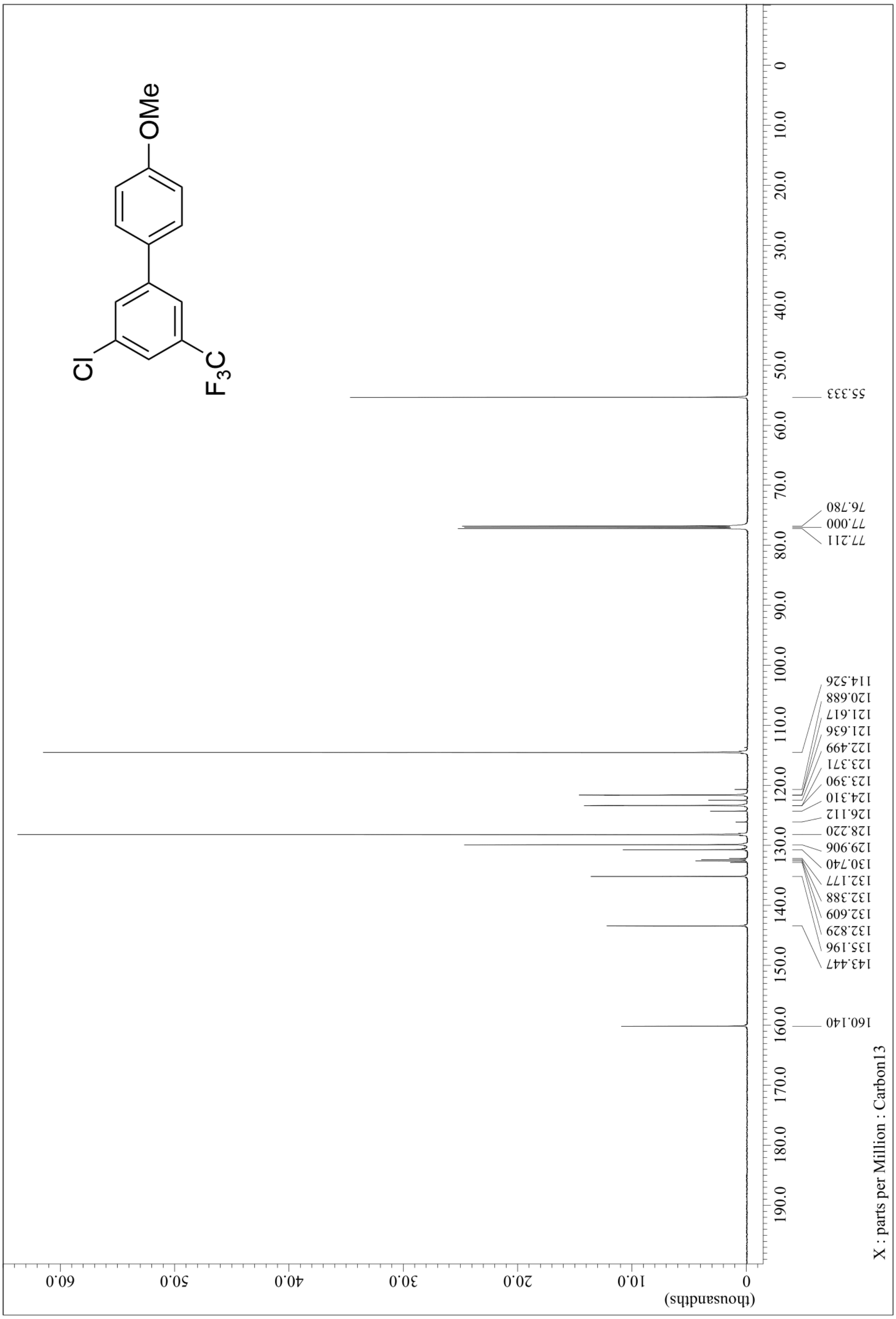

Figure S83. ^{1}H NMR spectrum of **16h**.

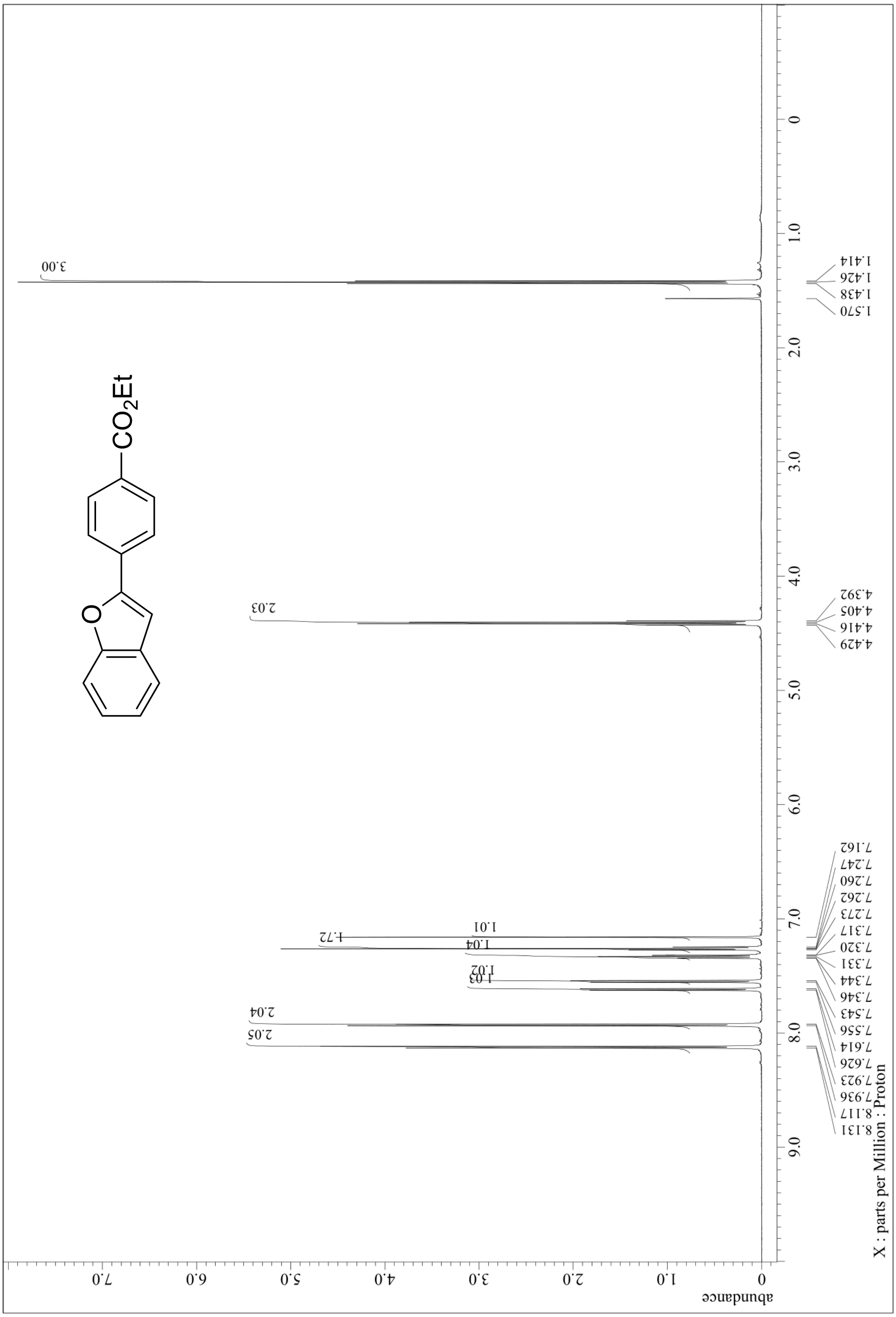

Figure S84. ^{13}C NMR spectrum of **16h**.

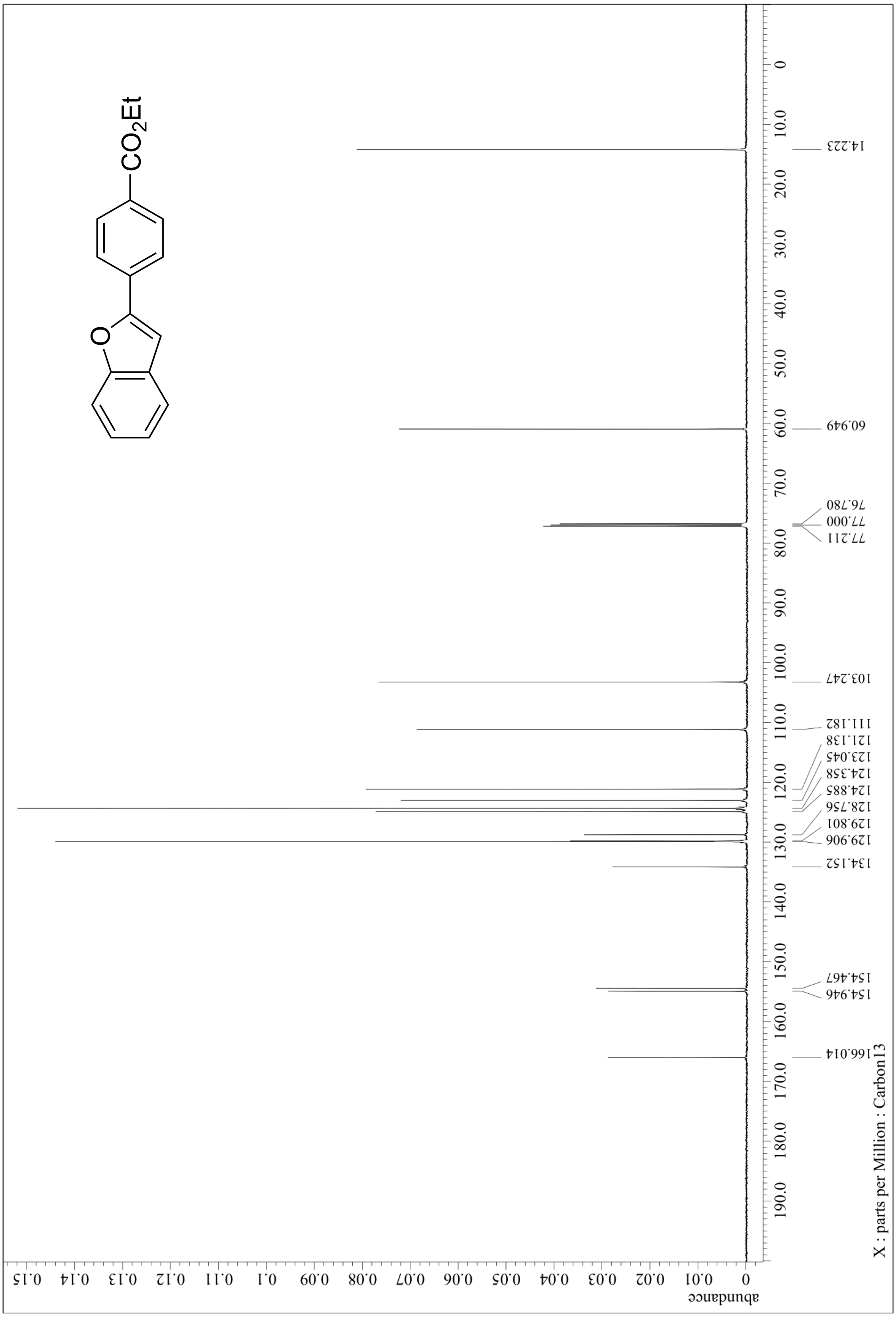

Figure S85. ^{1}H NMR spectrum of **17**.

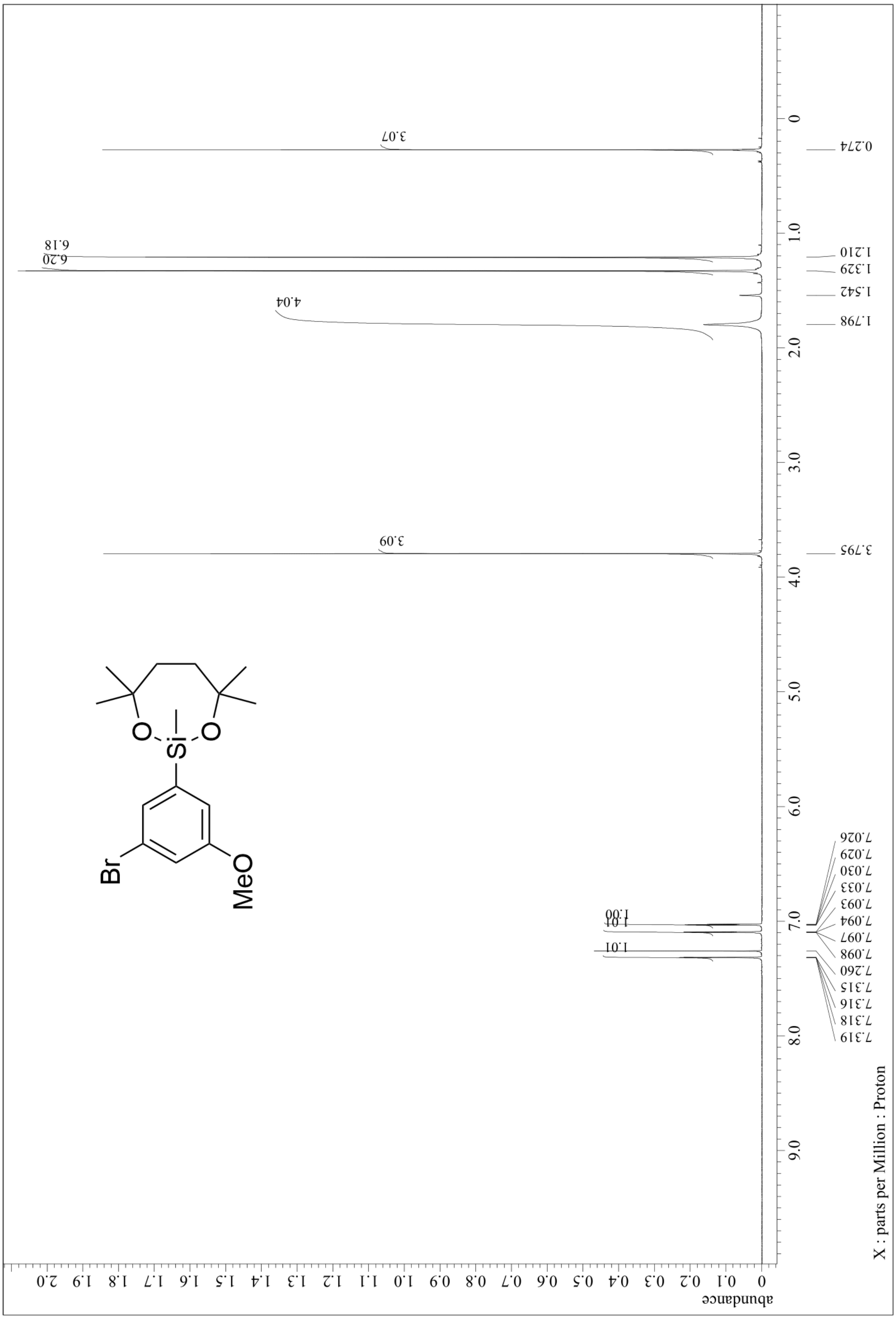

Figure S86. ^{13}C NMR spectrum of **17**.

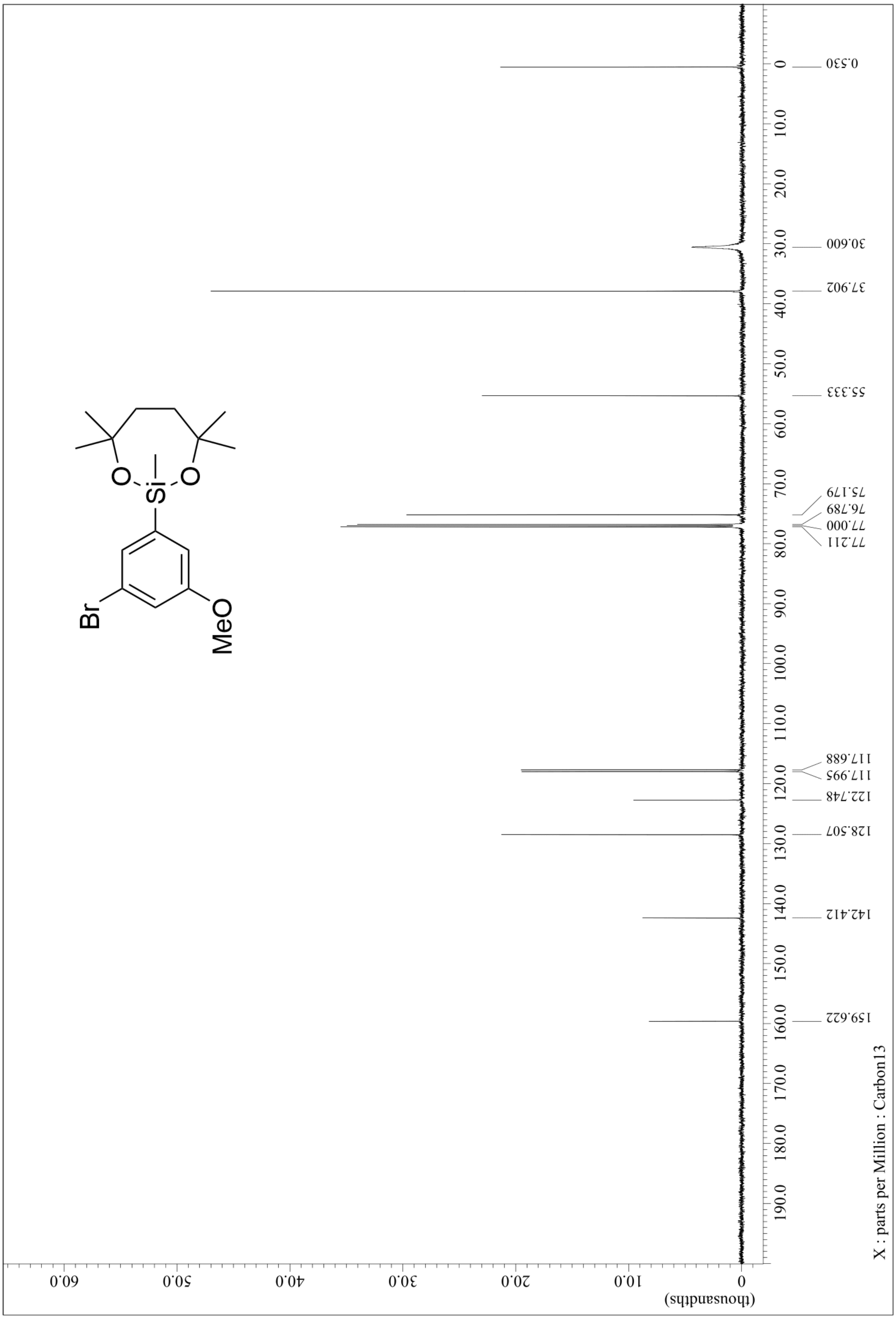

Figure S87. ^{1}H NMR spectrum of **18**.

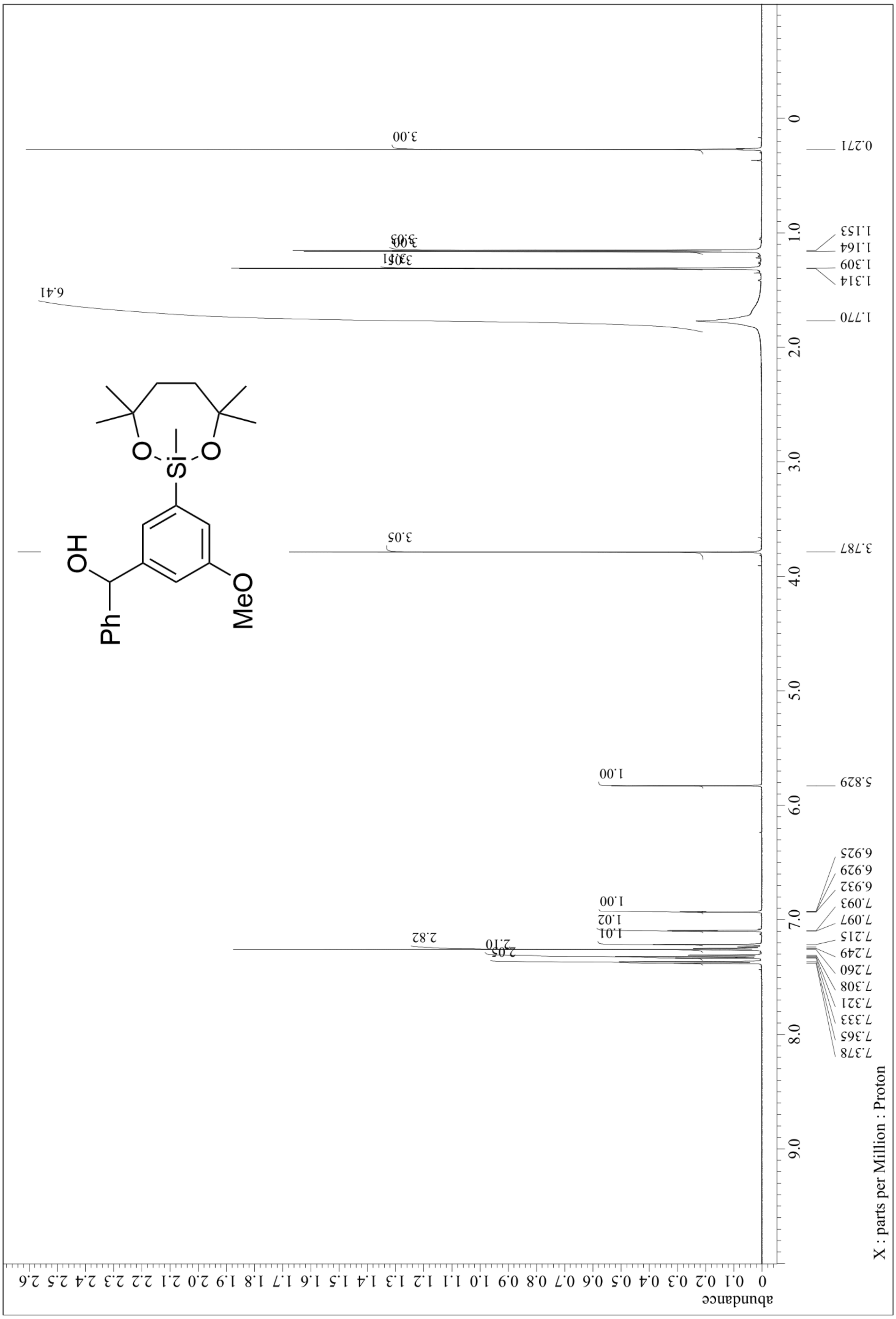

Figure S88. ^{13}C NMR spectrum of **18**.

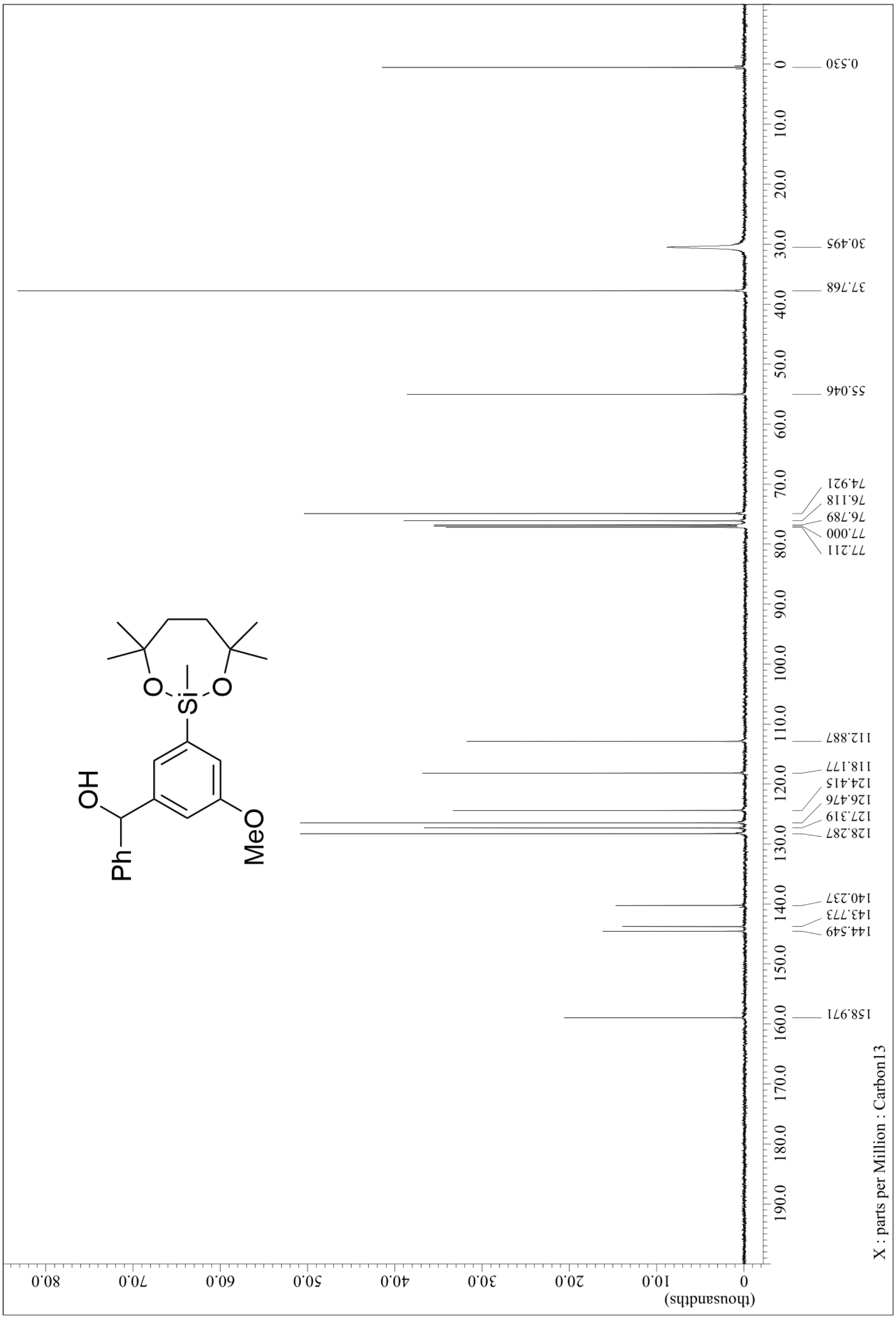

Figure S89. ^{1}H NMR spectrum of **19**.

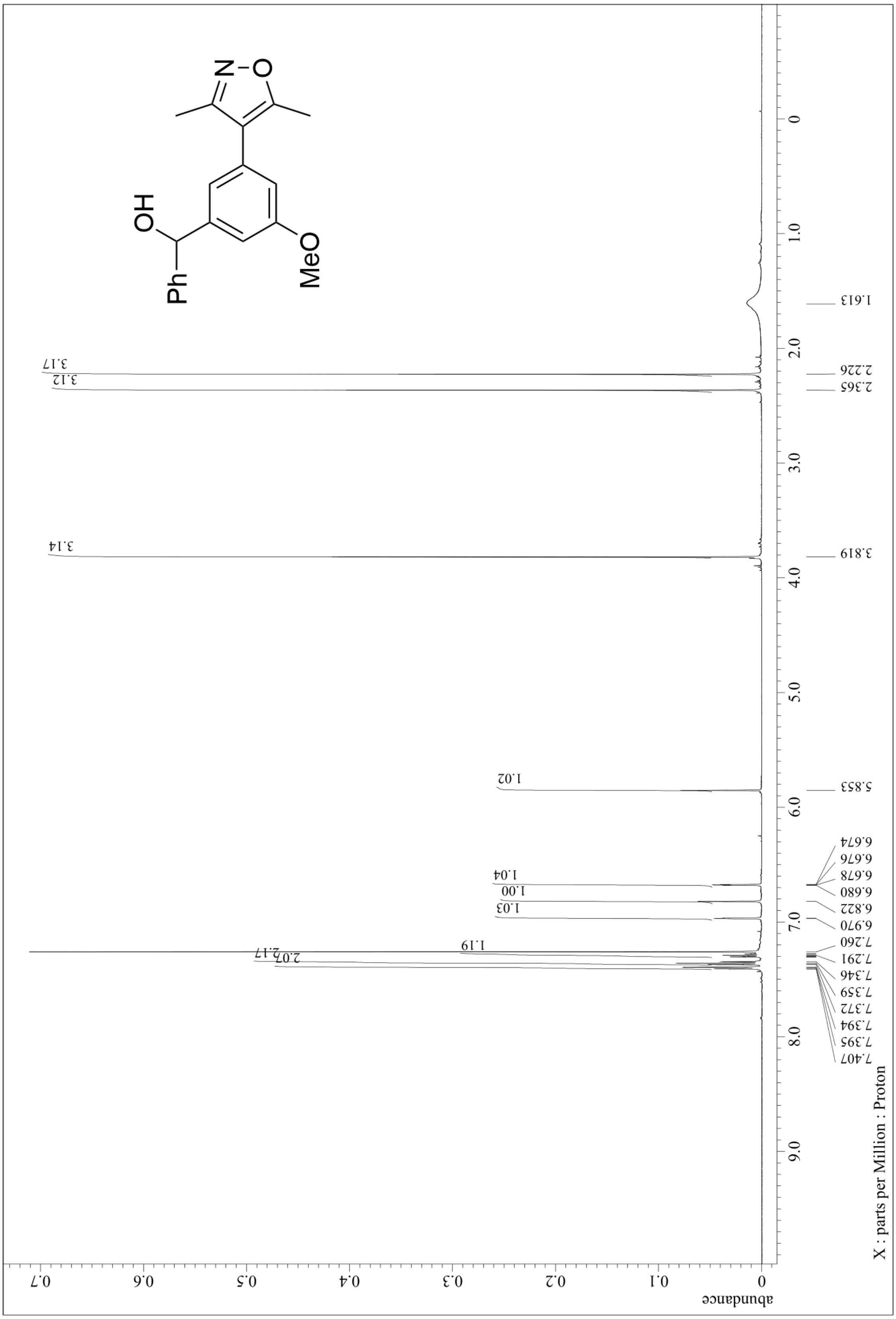

Figure S90. ^{13}C NMR spectrum of **19**.