Oxidative [1,2]-Brook Rearrangements Exploiting Single-Electron Transfer: Photoredox-Catalyzed Alkylations and Arylations

Yifan Deng, Qi Liu and Amos B. Smith, III*
Department of Chemistry, Laboratory for Research on the Structure of Matter and Monell Chemical Senses Center, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Contents

1. General
    a) Materials and Methods
    b) Photoredox-Catalyzed Reaction Experimental Setup
2. Mechanistic Studies
    a) The Radical Trapping Experiment
    b) Control Experiments
    c) Investigation of the Effects of Bases
    d) Kinetics Study
    e) Cyclic Voltammetry
3. Optimization Studies and Gram-scale Synthesis
4. Substrate Preparations and Characterizations
5. Experimental Procedures and Product Characterizations
    a) Photoredox-Catalyzed Alkylation via Brook Rearrangement
    b) Photoredox-Catalyzed Arylation via Brook Rearrangement
6. References
7. ^{1}H-NMR and ^{13}C-NMR Spectral Data

1. General

a) Materials and Methods

Reactions were performed in oven-dried glassware using syringe-septum cap techniques under an inert atmosphere of N_2. Reactions were magnetically stirred unless otherwise stated. All commercially obtained reagents were used as received. Tetrahydrofuran (THF), dichloromethane (DCM), diethyl ether (Et_2O) and toluene were dried by passage through alumina in a Pure Solve^{TM} PS-400 solvent purification system. Other solvents including dichloroethane (DCE) and *N,N*-dimethylacetamide (DMA) were obtained from commercial suppliers and used as received. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$, $Ir[dF(CF_3)ppy]_2(bpy)PF_6$ and $Ir(ppy)_3$ were prepared according to literature procedures.[1,2] All substrates whose syntheses were not described were either obtained from commercial suppliers or prepared using the referenced literature procedures. Analytical thin layer chromatography was performed on pre-coated silica gel 60 F-254 plates (particle size 40-55 micron, 230-400 mesh) and visualized by a *uv* lamp or by staining with CAM (4.8 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 0.2 g of $Ce(SO_4)_2$ in 100 mL of a 3.5 N H_2SO_4 solution). Column chromatography was performed using silica gel (Silacycle Silaflash®) P60, 40-63 micron particle size, 230-300 mesh) and compressed by air pressure with commercial grade solvents. NMR spectra were recorded at 500 MHz (^{1}H-NMR/^{13}C-NMR) on a Bruker Avance III 500 MHz spectrometer at 300 K. Chemical shifts are reported relative to chloroform (δ 7.26) for ^{1}H-NMR and chloroform (δ 77.16) for ^{13}C-NMR. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. Infrared spectra were measured on a Jasco FT/IR 480 plus spectrometer. High-resolution mass spectra (HRMS) were obtained at the University of Pennsylvania on a Waters GCT Premier spectrometer.

b) Photoredox-Catalyzed Reaction Experimental Setup:

LEDs were bought from superbrightLEDs.com company (39-inch strip, blue, white finish). The LED strips were wrapped on the inside of a clean Pyrex dish. The dish was then wrapped with a layer of aluminum foil and placed on a stirring plate. A fan was placed about 6-12 inches above the reactor to maintain the temperature at room temperature (**Figure 1-3**).

Figure 1. Side view

Figure 2. Top view.

a.

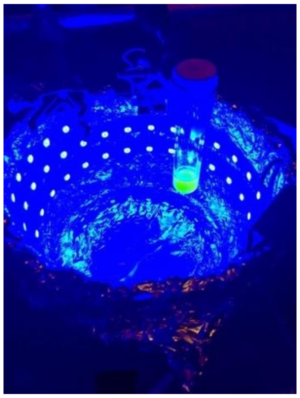
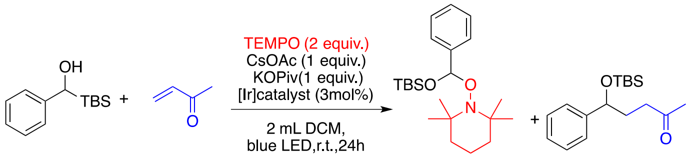


Figure 3. Reaction run under LED lamps

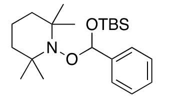
2. Mechanistic Studies

a) The Radical Trapping Experiment



1b **2a** **9** **3b**

To a 10 mL clear glass vial, (*tert*-butyldimethylsilyl)(phenyl)methanol **1b** (44.4 mg, 0.2 mmol, 1.0 equiv.), CsOAc (38.4 mg, 0.2 mmol, 1.0 equiv.), KOPiv (28 mg, 0.2 mmol, 1.0 equiv.), {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (6.6 mg, 0.006 mmol, 0.03 equiv.), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) (63 mg, 0.4 mmol, 2.0 equiv.) were added. The vial was then purged with a stream of nitrogen and 2.0 mL 1,2-dichloroethane was added, followed by methyl vinyl ketone **2a** (28 mg, 0.4 mmol, 2.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 24 hours. Then reaction mixture was then diluted with dichloromethane. The resulting solution was then concentrated and purified by column chromatography on silica gel, eluting with 5% EtOAc/Hexanes containing triethylamine (2%, v/v), to afford the product **9** as colorless oil(32 mg, 42% yield). The NMR yield of **3b** was 16%.



9

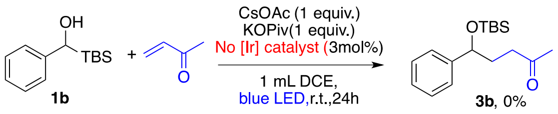
1-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methoxy)-2,2,6,6-tetramethylpiperidine (9): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.42 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.33-7.28 (m, 3H), 5.89 (s, 1H), 1.61-1.41 (m, 6H), 1.34 (s, 3H), 1.10 (s, 3H), 1.09 (s, 3H), 1.02 (s, 3H), 0.80 (s, 9H), 0.06 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.4, 128.0, 128.0, 126.6, 102.4, 60.6, 59.4, 40.6, 40.3, 34.9, 34.2, 26.1, 20.8, 20.5, 18.5, 17.5, -3.9, -4.3; IR (film) 2930, 1470, 1362, 1253, 1064, 1028, 987, 873, 836, 777, 697; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{22}H_{40}NO_2Si$) requires *m/z* 378.2828, found *m/z* 378.2816.

b) Control Experiments

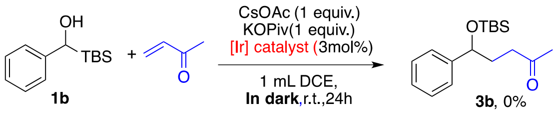
General Procedure: To a 10 mL clear glass vial, (*tert*-butyldimethylsilyl)(phenyl)methanol **1b** (22.2 mg, 0.1 mmol, 1.0 equiv.), CsOAc (19.2 mg, 1.0 equiv.), KOPiv (14 mg, 1.0 equiv.), {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (3.3 mg, 0.003 mmol, 0.03 equiv.) were added. The vial was then purged with a stream of nitrogen and 1.0 mL 1,2-dichloroethane was added, followed by methyl vinyl ketone **2a** (14 mg, 0.2 mmol, 2.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 24 hours. The reaction mixture was then concentrated and the crude NMR yield was determined using 1,3,5-trimethoxybenzene as an external standard.

(1) Without [Ir] catalyst: Following the general procedure above, except without the photoredox catalyst {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$. The reaction was exposed to blue LEDs at room temperature with stirring for

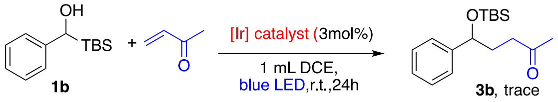
24 hours. The conversion of **1b** was lower than 3%. No desired product **3b** was detected.



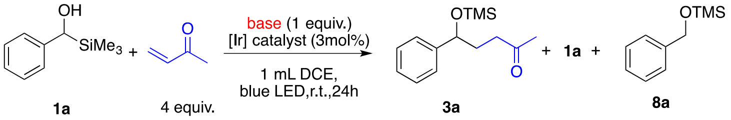
(2) Without light: Following the general procedure above, except that the reaction was run in dark at room temperature with stirring for 24 hours. The conversion of **1b** was lower than 3%. No desired product **3b** was detected.



(3) Without bases: Following the general procedure above, except without KOPiv and CsOAc. The reaction was exposed to blue LEDs at room temperature with stirring for 24 hours. Only trace amount of desired product **3b** was detected. The conversion of **1b** is 55%.



c) Investigation of the Effects of Bases



To a 10 mL clear glass vial, phenyl(trimethyl)methanol **1a** (18 mg, 0.1 mmol, 1.0 equiv.), {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (3.3 mg, 0.003 mmol, 0.03 equiv.), base (1.0 equiv.) were added. The vial was then purged with a stream of nitrogen and 1.0 mL DCE was added, followed by methyl vinyl ketone (14 mg, 0.2 mmol, 2.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 24 hours. The reaction mixture was then concentrated and the crude NMR yield was determined using 1,3,5-trimethoxybenzene as an external standard. Different Bases were tested, including NaOAc, KOAc, CsOAc, KOPiv, Cs_2CO_3, NaOMe, NaO*t*Bu. The NMR yield of **3a** and **8a** were calculated. The result showed that with weak base like NaOAc, which is not strong enough to trigger the formation of **8a**, the yield of **3a** was low. With the increasing basicity, the yield of **3a** would first increase and then decrease. With strong base (Cs_2CO_3, NaOMe and NaO*t*Bu), the byproduct **8a** (formed by the anionic Brook rearrangement) would increase and became the major product. This result indicated that the base is important to set up an equilibrium between phenyl(trimethyl)methanol and hypervalent silicate intermediate. With weak base like NaOAc, the equilibrium favors phenyl(trimethyl)methanol leading to low conversion to **3a**. With stronger bases like KOPiv and CsOAc, the equilibrium favors hypervalent silicate intermediate leading to high yield of **3a**. With even stronger bases like NaO*t*Bu, however, the anionic Brook rearrangement predominates so the starting material **1a** is quickly converted to hypervalent silicate intermediate, which is further converted to the byproduct **8a**.

Base	8a	3a
NaOAc	0%	18%
KOAc	0%	31%
CsOAc	0%	43%
KOPiv	0%	52%
Cs_2CO_3	3%	36%
NaOMe	13%	25%
NaO*t*Bu	77%	0

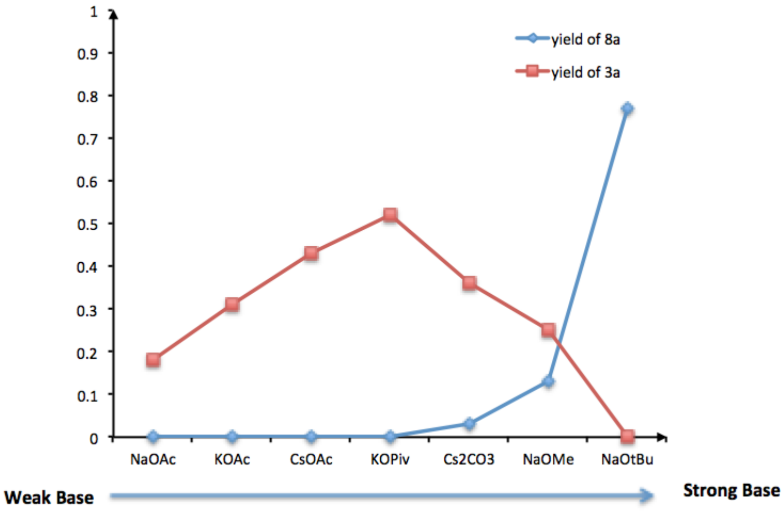


Figure 4. Investigation of the effects of the bases

d) Kinetic Study

If the reaction goes through PCET mechanism, then the PCET model would suggest that (1) rate decreases as the basicity of the anion decreases; (2) one can compensate for weaker base by using more oxidizing photocatalyst.

(1) Reaction rate with different bases:

To a 10 mL clear glass vial, (*tert*-Butyldimethylsilyl)(phenyl)methanol **1b** (44 mg, 0.2 mmol, 1.0 equiv.), {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (6.6 mg, 0.006 mmol, 0.03 equiv.), base (2.0 equiv.) and 1,4-dicyanobezene (internal standard) were added. The vial was then purged with a stream of nitrogen and 2.0 mL DCE was added, followed by methyl vinyl ketone (28 mg, 0.4 mmol, 2.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 18 hours. Different Bases were tested, including CsTFA, CsOBz, CsOAc. The NMR yield of **3a** were detected and calculated at 30 min, 1 h, 2 h, 3 h, 5 h, 7 h and 18 h. As expected, the result showed that rate decreased as the basicity of the anion decreases (p*K*a, TFA < HOBz < HOAc). This result could be explained by both mechanisms.

T (hour)	Yield with CsOAc (%)	Yield with CsOBz (%)	Yield with CsTFA (%)
0.5	14	5	0
1	24	10	1
2	37	21	3
3	47	27	6
5	54	35	11
7	58	42	14
18	63	50	14

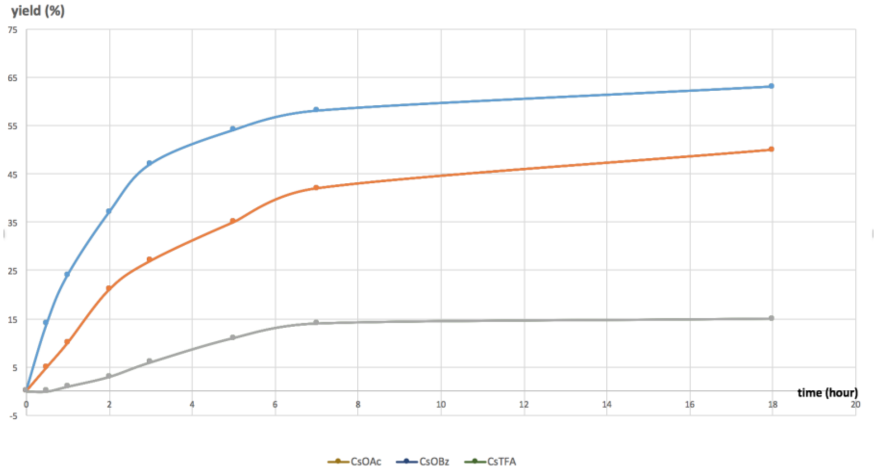


Figure 5. Reaction Rate with different bases

(1) Try to compensate the reaction rate for weaker base by using more oxidizing photocatalyst:

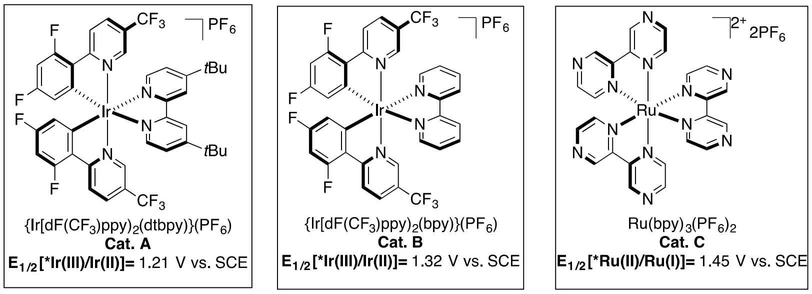


Figure 6. Catalysts Used in Kinetic Study

To a 10 mL clear glass vial, (*tert*-Butyldimethylsilyl)(phenyl)methanol **1b** (44 mg, 0.2 mmol, 1.0 equiv.), photocatalyst (0.006 mmol, 0.03 equiv.), base (2.0 equiv.) and 1,4-dicyanobezene (internal standard) were added. The vial was then purged with a stream of nitrogen and 2.0 mL DCE was added, followed by methyl vinyl ketone (28 mg, 0.4 mmol, 2.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 18 hours. Different Bases were tested, including CsTFA and CsOBz. Different photocatalysts were tested including **Cat. A**, **Cat. B** and **Cat. C** as shown above. The NMR yield of **3a** were detected and calculated at 30 min, 1 h, 2 h, 3 h, 5 h, 7 h and 18 h. For **Cat. C**, no desired product **3a** could be detected for either CsOAc, CsTFA or CsOBz, presumably because that **Cat. C** is less reducing ($E_{1/2}$ [Ru(II)/Ru(I)] = -0.80 V vs. SCE). The reaction rate did not increase by using more oxidizing photocatalyst **Cat. B**.

T (hour)	Yield with CsOBz and Cat. A (%)	Yield with CsOBz and Cat. B (%)
0.5	5	4
1	10	11
2	21	15
3	27	19
5	35	24
7	42	28

18	63	45

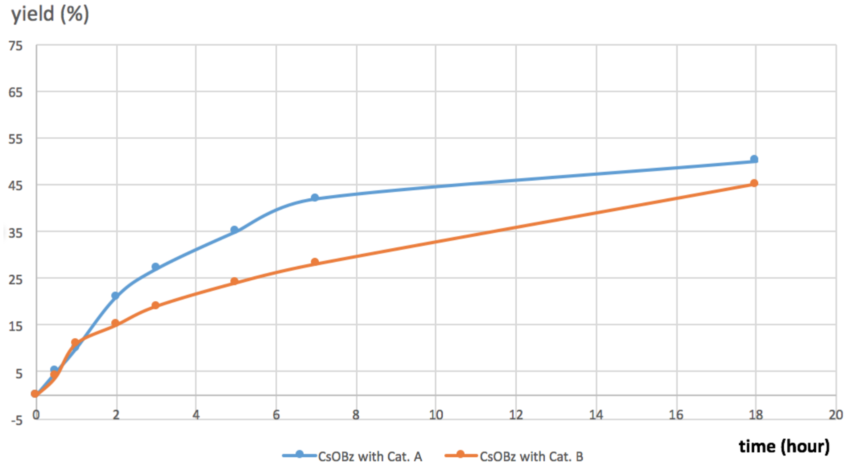


Figure 7. Reaction Rate of CsOBz with Cat. A and Cat. B

T (hour)	Yield with CsTFA and Cat. A (%)	Yield with CsTFA and Cat. B (%)
0.5	0	0
1	1	1
2	3	2
3	6	4
5	11	9
7	14	12
18	15	16

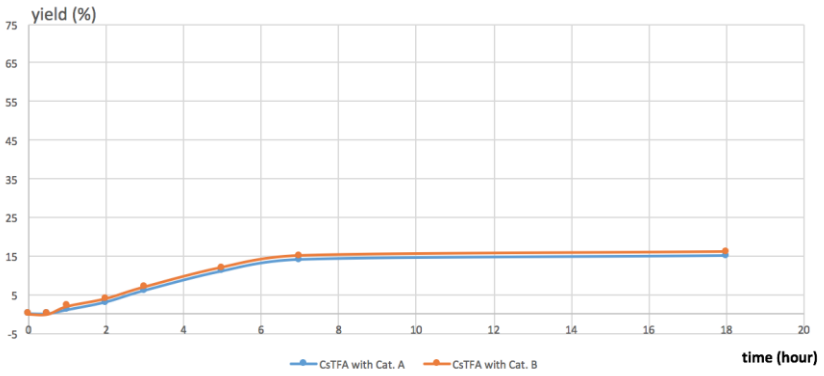


Figure 8. Reaction Rate of CsTFA with Cat. A and Cat. B

e) Cyclic Voltammetry

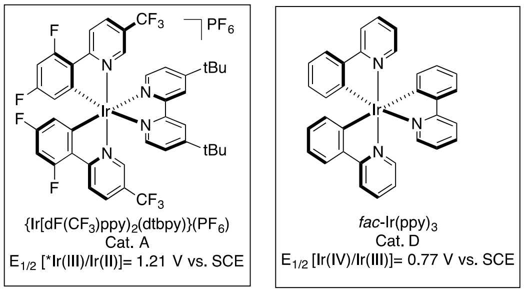
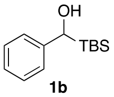


Figure 9. Catalysts Used in Oxidative Brook Rearrangement

General Procedure: The cyclic voltammetry (CV) was recorded with a three electrodes apparatus in degassed CH_3CN with Bu_4NPF_6 (100 mM) as support electrolyte. Glassy carbon, platinum plate, and Ferocene were used as working, counter, and reference electrodes, respectively.

Experiment 1 of CV: 0.1 M (*tert*-Butyldimethylsilyl)(phenyl)methanol (**1b)** in CH_3CN: 11 mg **1b** (0.05 mmol) was weighed and dissolved in 0.5 mL electrolyte. No oxidation potential could be found for **1b**.



1b

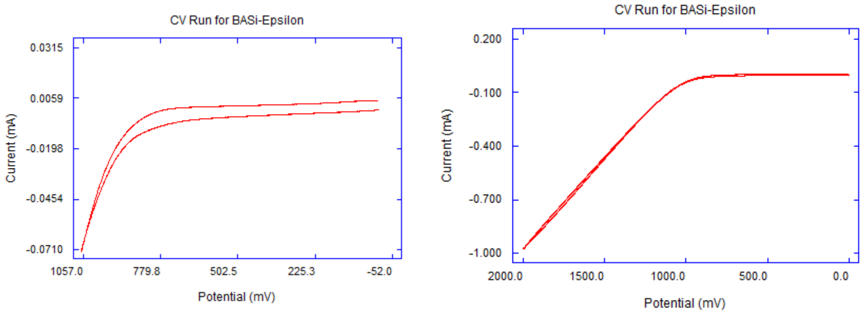
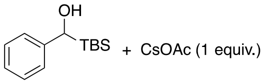


Figure 10. CV data for 1b

Experiment 2 of CV: 0.1 M (*tert*-Butyldimethylsilyl)(phenyl)methanol (**1b**) + CsOAc in CH_3CN: 11 mg **1b** (0.05 mmol) and 9.6 mg CsOAc (0.05 mmol) were weighed and dispensed in 0.5 mL electrolyte. An oxidation potential (E_{ox} = + 0.78 V versus SCE in CH_3CN) was found. The oxidation potential is reasonable based on the catalysts we used in our reaction (**Cat. A** for alkylation and **Cat. D** for arylation). This result also indicated the importance of the base in the oxidative [1,2]-Brook rearrangement. The effective BDFE is calculated and is not high enough for the homolysis of the strong O-H bond. Therefore, the PCET model is less likely.



1b

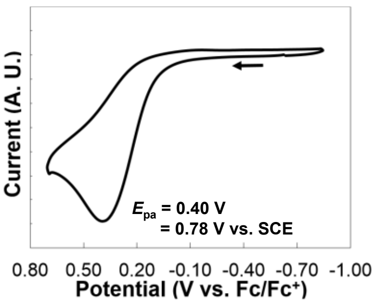
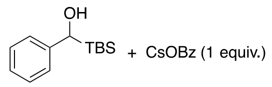


Figure 11. CV data for 1b with CsOAc

$$\begin{aligned}\text{Effective BDFE} &= 23.06\,E\text{pa} + 1.37\ \text{pKa (CsOAc)} + 54.9\ \text{(rt in MeCN)}\\ &= 23.06\times0.40 + 1.37\times23.51 + 54.9\\ &= 96\ \text{kcal/ mol} \ (< \text{O-H BDFE} \approx 105\ \text{kcal/mol})\end{aligned}$$

Experiment 3 of CV: 0.1 M (*tert*-Butyldimethylsilyl)(phenyl)methanol (**1b) +** CsOBz in CH_3CN: 11 mg **1b** (0.05 mmol) and 12 mg CsOBz (0.05 mmol) were weighed and dispensed in 0.5 mL electrolyte. An oxidation potential (E_{ox} = + 0.77 V versus SCE in CH_3CN) was found. CsOBz is a weaker base (pK_a = 20.70 in CH_3CN) compared to CsOAc (pK_a = 23.51 in CH_3CN).[3] If it is PCET mechanism, a higher oxidation potential is required to compensate for the weaker base. However, the oxidation potential remained the same. The effective BDFE is 92 kcal/mol. Therefore, the PCET model is less likely.



1b

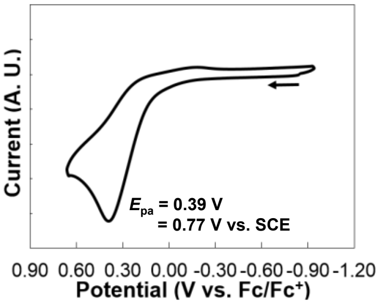
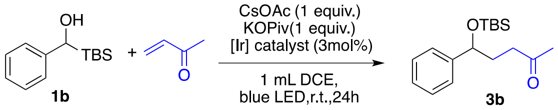


Figure 12. CV data for 1b with CsOBz

$$\begin{aligned}\text{Effective BDFE} &= 23.06\,E\text{pa} + 1.37\ \text{pKa (CsOAc)} + 54.9\ \text{(rt in MeCN)}\\ &= 23.06\times0.39 + 1.37\times20.7 + 54.9\\ &= 92\ \text{kcal/ mol} \ (< \text{O-H BDFE} \approx 105\ \text{kcal/mol})\end{aligned}$$

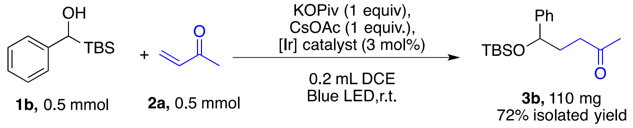
Experiment 4 of CV: 0.1 M (*tert*-Butyldimethylsilyl)(phenyl)methanol (**1b) +** base in CH_3CN: 44.4 mg **1b** (0.2 mmol) and one equivalent of other bases, including weaker bases like NaOAc and CsTFA, stronger bases like Cs_2CO_3, NaOMe were weighed and dissolved in 0.5 mL electrolyte. However, no oxidative potential could be found for these bases. We reason that the weaker bases were not able to deprotonate the alcohol well and the stronger bases led to the anionic Brook rearrangement.

3. Optimization Studies and Gram-scale Synthesis

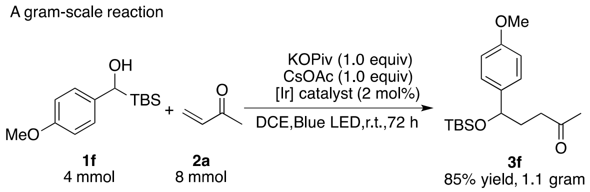


Procedure: To a 10 mL clear glass vial, (*tert*-butyldimethylsilyl)(phenyl)methanol **1b** (44.4 mg, 0.2 mmol, 1.0 equiv.), CsOAc (38.4 mg, 1.0 equiv.), KOPiv (28 mg, 1.0 equiv.), {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (6.6 mg, 0.006 mmol, 0.03 equiv.) were added. The vial was then purged with a stream of nitrogen and 1.0 mL 1,2-dichloroethane was added, followed by methyl vinyl ketone (**x** equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 24 hours. The reaction mixture was then concentrated and the crude NMR yield was determined using 1,3,5-trimethoxybenzene as an external standard.

Methyl vinyl ketone 2a (x equiv.)	NMR yield of 3b
1 equiv.	46%
1.2 equiv.	51%
1.5 equiv.	61%
1.8 equiv.	75%
2 equiv.	81%

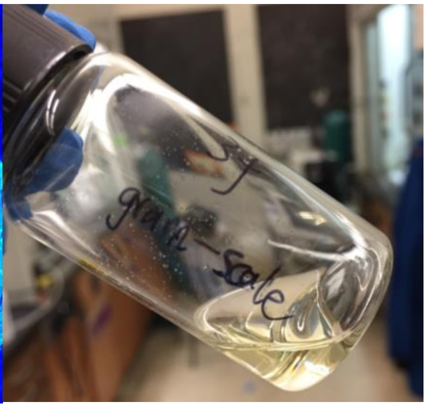


Procedure: To a 10 mL clear glass vial, (*tert*-butyldimethylsilyl)(phenyl)methanol **1b** (111 mg, 0.5 mmol, 1.0 equiv.), CsOAc (96 mg, 1.0 equiv.), KOPiv (70 mg, 1.0 equiv.), {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (17 mg, 0.015 mmol, 0.03 equiv.) were added. The vial was then purged with a stream of nitrogen and 0.2 mL 1,2-dichloroethane was added, followed by methyl vinyl ketone **2a** (35 mg, 0.5 mmol, 1.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 4 days. The reaction mixture was then concentrated and purified by column chromatography (EtOAc/hexanes =1/50) to afford the corresponding product **3b** (110 mg, 72% yield).



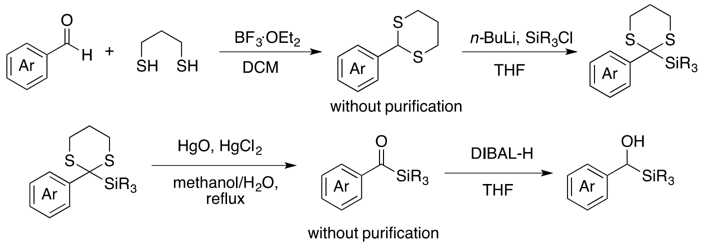
Procedure: To a 10 mL clear-colored round-bottom flask, (*tert*-butyldimethylsilyl)(phenyl)methanol **1f** (1.0 g, 4 mmol, 1.0 equiv.), {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (88 mg, 0.08 mmol, 0.02 equiv.), CsOAc (768 mg, 1.0

equiv.), KOPiv (560 mg, 1.0 equiv.), were added. The flask was then purged with a stream of nitrogen and 4 mL 1,2-dichloroethane was added, followed by methyl vinyl ketone **2a** (560 mg, 8 mmol, 2.0 equiv.). The flask was sealed and exposed to blue LEDs at room temperature with stirring for 72 hours. The reaction mixture was then concentrated and purified by column chromatography (EtOAc/hexanes =1/50) to afford the corresponding product **3f** (1.1 g, 85% yield).



4. Substrate Preparations and Characterizations

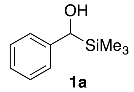
Synthesis of (trialkylsilyl)arylmethanols



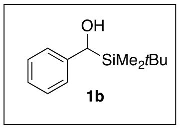
To a solution of aldehyde (10 mmol) and propane-1,3-dithiol (1.19 g, 1.1 equiv.) in CH_2Cl_2 (40 mL) was added boron trifluoride diethyl etherate (0.38 mL, 0.3 equiv.) dropwise at 0 °C. The reaction mixture was then allowed to warm to ambient temperature and stirred for 3 hours. It was then quenched with sat. $NaHCO_3$ solution. The aqueous layer was extracted by CH_2Cl_2. The organic layer was combined and dried over Na_2SO_4. The solvent was removed by rotary evaporation to provide a white solid. The crude product was directly dissolved in 150 mL THF and cooled down to -78 °C. *n*-BuLi (4.4 mL, 2.5 M in THF) was added into the solution dropwise. The reaction mixture was stirred for 2 hours at -78 °C and then corresponding trialkylsilyl chloride was added dropwise. The mixture was stirred at -78 °C for 30 minutes and allowed to warm to room temperature for 30 minutes. The mixture was then taken up in Et_2O, washed with sat. NH_4Cl solution and brine. It was then dried over Na_2SO_4, concentrated in vacuum, purified by column chromatography (EtOAc/hexanes =1/100) to afford the corresponding product.

To a suspension of HgO (2 equiv.) and $HgCl_2$ (2 equiv.) in Methanol/H_2O (9:1, 0.2 M) was added the product from last step. The reaction mixture was heated to reflux for 3 hours. It was then filtered through Celite. The aqueous layer was extracted by hexanes. The organic layer was combined and dried over Na_2SO_4. The solvent was removed by rotary evaporation to provide a yellow oil or solid. The crude product was directly dissolved in CH_2Cl_2 (0.25 M) and cooled down to -78 °C. Diisobutylaluminum hydride solution (1.5 equiv., 1 M in hexanes) was added into the solution dropwise. The reaction mixture was stirred for 1 hours at -78 °C and allowed to warm to 0 °C for 10 minutes. The reaction was quenched by sat. Rochelle salt solution and stirred at room temperature for 2 hours. The mixture was then taken up in CH_2Cl_2, washed with brine. It was then dried over Na_2SO_4, concentrated in vacuum, purified by column chromatography (EtOAc/hexanes = 1/30) to afford the (trialkylsilyl)arylmethanol.

Subtrate Characterization

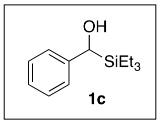

1a

Phenyl(trimethylsilyl)methanol (1a): Prepared according to the general method. The reaction of benzaldehyde (1.06 g, 10 mmol) afforded **1a** as a colorless oil (1.17 g, 65% over four steps): ^1H NMR (500 MHz, $CDCl_3$) δ 7.32-7.29 (m, 2H), 7.20-7.16 (m, 3H), 4.53 (d, *J* = 2.4 Hz, 1H), 1.69 (d, *J* = 2.4 Hz, 1H), 0.02 (s, 9H). The data for this compound matched that reported in the literature.[4]



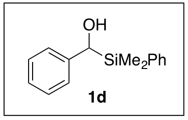
1b

(*tert*-butyldimethylsilyl)(phenyl)methanol (1b): Prepared according to the general method. The reaction of benzaldehyde (1.06 g, 10 mmol) afforded **1b** as a white solid (1.59 g, 72% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.23-7.21 (m, 2H), 7.19-7.15 (m, 1H), 4.69 (d, *J* = 2.9 Hz, 1H), 1.63 (d, *J* = 3.0 Hz, 1H), 0.97 (s, 9H), 0.01 (s, 3H), -0.19 (s, 3H). The data for this compound matched that reported in the literature.[5]



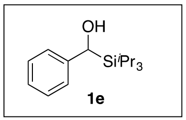
1c

Phenyl(triethylsilyl)methanol (1c): Prepared according to the general method. The reaction of benzaldehyde (1.06 g, 10 mmol) afforded **1c** as a colorless oil (1.63 g, 74% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32-7.29 (m, 2H), 7.24-7.22 (m, 2H), 7.18-7.15 (m, 1H), 4.68 (d, *J* = 3.0 Hz, 1H), 1.61 (d, *J* = 3.0 Hz, 1H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.58 (qd, *J* = 7.9, 4.0 Hz, 6H). The data for this compound matched that reported in the literature.[5]



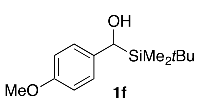
1d

(dimethyl(phenyl)silyl)(phenyl)methanol (1d): Prepared according to the general method. The reaction of benzaldehyde (1.06 g, 10 mmol) afforded **1d** as a colorless oil (1.45 g, 60% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.49-7.47 (m, 2H), 7.41-7.33 (m, 3H), 7.27-7.24 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10-7.08 (m, 2H), 4.71 (d, *J* = 2.3 Hz, 1H), 1.67 (br, 1H), 0.30 (s, 3H), 0.26 (s, 3H). The data for this compound matched that reported in the literature.[5]



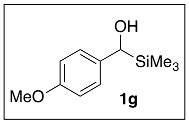
1e

phenyl(triisopropylsilyl)methanol (1e): Prepared according to the general method. The reaction of benzaldehyde (530 mg, 5 mmol) afforded **1e** as a colorless oil (530 mg, 40% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34-7.29 (m, 4H), 7.19-7.16 (m, 1H), 4.88 (s, 1H), 1.62 (s, 1H), 1.23-1.16 (m, 3H), 1.07 (d, *J* = 7.2 Hz, 18H). The data for this compound matched that reported in the literature.[6]



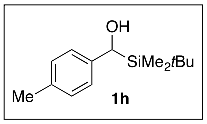
1f

(*tert*-butyldimethylsilyl)(4-methoxyphenyl)methanol (1f): Prepared according to the general method. The reaction of 4-methoxybenzaldehyde (1.36 g, 10 mmol) afforded **1f** as a white solid (1.5 g, 60% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.14 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 4.62 (d, J = 2.7 Hz, 1H), 3.80 (s, 3H), 1.55 (d, J = 2.7 Hz, 1H), 0.95 (s, 9H), 0.02 (s, 3H), -0.20 (s, 3H). The data for this compound matched that reported in the literature.[7]



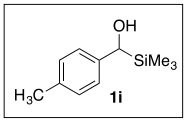
1g

(4-methoxyphenyl)(trimethylsilyl)methanol (1g): Prepared according to the general method. The reaction of 4-methoxybenzaldehyde (1.36 g, 10 mmol) afforded **1g** as a white solid (1.3 g, 62% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.12 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.46 (d, J = 2.7 Hz, 1H), 3.80 (s, 3H), 1.60 (d, J = 2.7 Hz, 1H), 0.01 (s, 9H). The data for this compound matched that reported in the literature.[4]



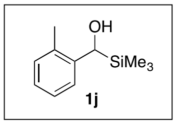
1h

(*tert*-butyldimethylsilyl)(*p*-tolyl)methanol (1h): Prepared according to the general method. The reaction of 4-methylbenzaldehyde (1.2 g, 10 mmol) afforded **1h** as a white solid (1.37 g, 58% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.12 (s, 4H), 4.64 (d, J = 2.6 Hz, 1H), 2.34 (s, 3H), 1.60 (s, 1H), 0.98 (s, 9H), 0.02 (s, 3H), -0.18 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.0, 135.6, 129.0, 125.7, 69.0, 27.1, 21.2, 17.2, -7.1, -9.2; IR (film) cm^{-1} 3440, 2952, 2927, 2884, 2856, 1510, 1471, 1362, 1247, 1141, 1008, 837, 805, 775, 687; HRMS (EI) exact mass calculated for [M]$^+$ (C$_{14}$H$_{24}$OSi) requires *m/z* 236.1596, found *m/z* 236.1602.



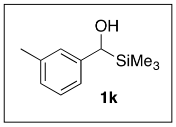
1i

***p*-tolyl(trimethylsilyl)methanol (1i):** Prepared according to the general method. The reaction of 4-methylbenzaldehyde (600 mg, 5 mmol) afforded **1i** as a colorless oil (504 mg, 52% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.12 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 2H), 4.49 (s, 1H), 2.33 (s, 3H), 1.64 (br, 1H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.3, 135.4, 129.0, 125.1, 70.6, 21.2, -4.0; IR (film) 3421, 2956, 1701, 1510, 1411, 1247, 1005, 865, 841, 761, 716, 695 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ (C$_{11}$H$_{18}$OSi) requires *m/z* 194.1127, found *m/z* 194.1128.



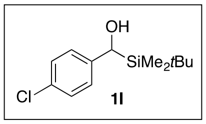
1j

***o*-tolyl(trimethylsilyl)methanol (1j):** Prepared according to the general method. The reaction of 2-methylbenzaldehyde (462 mg, 3 mmol) afforded **1j** as a colorless oil (238 mg, 41% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.38 (d, J = 8.1 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 7.11-7.07 (m, 2H), 4.80 (d, J = 2.7 Hz, 1H), 2.24 (s, 3H), 1.55 (br, 1H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.7, 133.2, 130.2, 126.2, 125.8, 125.8, 66.3, 19.9, -3.5; IR (film) 3409, 3020, 2955, 1484, 1460, 1247, 1144, 1047, 988, 860, 840, 746, 723, 694 cm^{-1}; HRMS (EI) exact mass calculated for $[M]^+$ ($C_{11}H_{18}OSi$) requires *m/z* 194.1127, found *m/z* 194.1123.



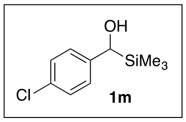
1k

***m*-tolyl(trimethylsilyl)methanol (1k):** Prepared according to the general method. The reaction of 3-methylbenzaldehyde (462 mg, 5 mmol) afforded **1k** as a colorless oil (220 mg, 38% over four steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.5 Hz, 1H), 7.01-6.98 (m, 3H), 4.49 (d, *J* = 2.6 Hz, 1H), 2.34 (s, 3H), 1.63 (d, *J* = 3.0 Hz, 1H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 137.9, 128.2, 126.7, 125.7, 122.2, 70.7, 21.7, -3.9; IR (film) 3410, 2956, 1604, 1485, 1248, 1146, 1007, 904, 842, 791, 760, 704, 612 cm^{-1}; HRMS (EI) exact mass calculated for $[M]^+$ ($C_{11}H_{18}OSi$) requires *m/z* 194.1127, found *m/z* 194.1131.



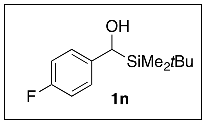
1l

(*tert*-butyldimethylsilyl)(4-chlorophenyl)methanol (1l): Prepared according to the general method. The reaction of 4-chlorobenzaldehyde (1.40 g, 10 mmol) afforded **1l** as a white solid (1.64 g, 64% over four steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 4.66 (d, *J* = 2.5 Hz, 1H), 1.62 (d, *J* = 3.1 Hz, 1H), 0.96 (s, 9H), 0.01 (s, 3H), -0.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 131.6, 128.4, 126.9, 68.6, 27.1, 17.3, -7.1, -9.3; IR (film) 3431, 2953, 2929, 2856, 1489, 1468, 1405, 1362, 1250, 1139, 1092, 1008, 840, 796, 776, 675 cm^{-1}; HRMS (EI) exact mass calculated for $[M]^+$ ($C_{13}H_{21}ClOSi$) requires *m/z* 256.1050, found *m/z* 256.1055.



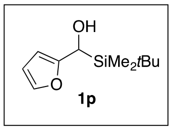
1m

(4-chlorophenyl)(trimethylsilyl)methanol (1m): Prepared according to the general method. The reaction of 4-chlorobenzaldehyde (700 mg, 5 mmol) afforded **1m** as a white solid (630 mg, 59% over four steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.50 (s, 1H), 1.68 (d, *J* = 4.0 Hz, 1H), 0.01 (s, 9H). The data for this compound matched that reported in the literature.[4]



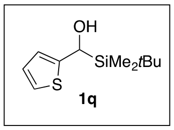
1n

(*tert*-butyldimethylsilyl)(4-fluorophenyl)methanol (1n): Prepared according to the general method. The reaction of 4-fluorobenzaldehyde (1.24 g, 10 mmol) afforded **1n** as a white solid (1.46 g, 61% over four steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.7, 5.5 Hz, 2H), 6.99 (t, *J* = 8.7 Hz, 2H), 4.66 (s, 1H), 1.62 (s, 1H), 0.96 (s, 9H), 0.00 (s, 3H), -0.20 (s, 3H). The data for this compound matched that reported in the literature.[7]



1p

(*tert*-butyldimethylsilyl)(furan-2-yl)methanol (1p): Prepared according to the general method. The reaction of furan-2-carbaldehyde (960 mg, 10 mmol) afforded **1p** as a yellow oil (670 mg, 32% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.35 (d, *J* = 1.8 Hz, 1H), 6.32 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.14 (d, *J* = 3.2 Hz, 1H), 4.58 (d, *J* = 4.5 Hz, 1H), 1.57 (d, *J* = 4.5 Hz, 1H), 0.89 (s, 9H), 0.15 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.6, 141.7, 110.5, 105.9, 61.6, 26.7, 17.0, -7.7, -7.9; IR (film) 3460, 2954, 2929, 2857, 1730, 1470, 1362, 1252, 1010, 923, 833, 780 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ ($C_{11}H_{20}O_2Si$) requires *m/z* 212.1233, found *m/z* 212.1246.



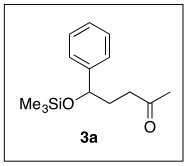
1q

(*tert*-butyldimethylsilyl)(thiophen-2-yl)methanol (1q): Prepared according to the general method. The reaction of thiophene-2-carbaldehyde (1.12 g, 10 mmol) afforded **1q** as a yellow oil (800 mg, 35% over four steps): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 (d, *J* = 5.1 Hz, 1H), 6.97 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H), 4.92 (d, *J* = 3.2 Hz, 1H), 1.81 (d, *J* = 3.2 Hz, 1H), 0.96 (s, 9H), 0.13 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.0, 126.9, 123.5, 122.6, 64.9, 27.0, 17.2, -7.4, -8.7; IR (film) 3458, 2953, 2928, 2883, 2856, 1684, 1574, 1469, 1436, 1410, 1362, 1251, 1006, 833, 777, 691 cm^{-1}; HRMS (ESI) exact mass calculated for [M-H]$^-$ ($C_{11}H_{19}OSSi$) requires *m/z* 227.0926, found *m/z* 227.0903.

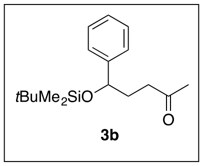
5. Experimental Procedures and Product Characerizations

a) Photoredox-Catalyzed Alkylation via Brook Rearrangement

General Procedure: To a 10 mL clear-colored glass vial, aryl(trialkylsilyl)methanol (0.2 mmol, 1.0 equiv.), CsOAc (38.4 mg, 1.0 equiv.), KOPiv (28 mg, 1.0 equiv.), {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (6.6 mg, 0.006 mmol, 0.03 equiv.) was added. The vial was then purged with a stream of nitrogen and 1.0 mL 1,2-dichloroethane was added, followed by enone (0.4 mmol, 2.0 equiv.). The vial was sealed and exposed to blue LEDs at room temperature with stirring for 24-48 hours. The color of the initially yellow solution turned black after being exposed to blue LEDs and turned back to orange or yellow when the reaction was completed. Then reaction mixture was then diluted with dichloromethane. The resulting solution was concentrated and purified by column chromatography on silica gel, eluting with EtOAc and hexanes containing triethylamine (5%, v/v), to afford the product in pure form.

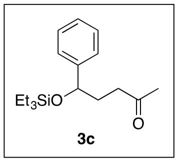


5-phenyl-5-((trimethylsilyl)oxy)pentan-2-one (3a): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 36 mg of phenyl(trimethylsilyl)methanol (**1a**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3a** as a clear oil (36 mg, 73%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32-7.28 (m, 4H), 7.25-7.22 (m, 1H), 4.70 (dd, *J* = 7.4, 4.8 Hz, 1H), 2.52-2.38 (m, 2H), 2.11 (s, 3H), 1.99-1.90 (m, 2H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.8, 144.8, 128.3, 127.2, 125.9, 73.8, 39.7, 34.5, 30.0, 0.1; IR (film) 2956, 1715, 1360, 1251, 1161, 1097, 929, 842, 752, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ ($C_{14}H_{22}NaO_2Si$) requires *m/z* 273.1287, found *m/z* 273.1290.



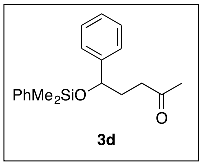
5-((*tert*-butyldimethylsilyl)oxy)-5-phenylpentan-2-one (3b): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 44 mg of (*tert*-butyldimethylsilyl)phenylmethanol (**1b**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3b** as a clear oil (45 mg, 78%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32-7.28 (m, 4H), 7.24-7.21 (m, 1H), 4.74 (dd, *J* = 6.8, 5.0 Hz, 1H), 2.53-2.47 (m, 1H), 2.42-2.36 (m, 1H), 2.10 (s, 3H), 2.00-1.89 (m, 2H), 0.89 (s, 9H), 0.02 (s, 3H), -0.14 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ

208.8, 144.9, 128.2, 127.2, 125.9, 73.8, 39.3, 34.5, 30.1, 26.0, 18.3, -4.6, -4.9; IR (film) 2954, 2929, 2857, 1717, 1362, 1255, 1161, 1096, 928, 836, 776, 701 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+H]^+$ ($C_{17}H_{29}O_2Si$) requires *m/z* 293.1937, found *m/z* 293.1942.



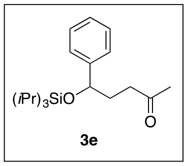
3c

5-phenyl-5-((triethylsilyl)oxy)pentan-2-one (3c): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3c** as a clear oil (47 mg, 81%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32-7.28 (m, 4H), 7.25-7.21 (m, 1H), 4.73 (t, *J* = 6.0 Hz, 1H), 2.52-2.46 (m, 1H), 2.41-2.35 (m, 1H), 2.10 (s, 3H), 1.98-1.93 (m, 2H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.52 (qd, *J* = 7.9, 3.2 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.8, 145.0, 128.2, 127.2, 126.0, 73.7, 39.4, 34.5, 30.0, 6.9, 4.9; IR (film) 2954, 2876, 1717, 1454, 1414, 1361, 1239, 1161, 1097, 1006, 806, 743, 701 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{28}NaO_2Si$) requires *m/z* 315.1756, found *m/z* 315.1765.



3d

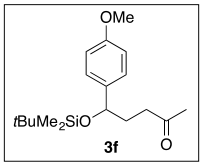
5-((dimethyl(phenyl)silyl)oxy)-5-phenylpentan-2-one (3d): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 48 mg of (dimethyl(phenyl)silyl)(phenyl)methanol (**1d**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3d** as a clear oil (35 mg, 56%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.55-7.53 (m, 2H), 7.42-7.35 (m, 3H), 7.32-7.23 (m, 5H), 4.73 (dd, *J* = 6.9, 5.3 Hz, 1H), 2.47-2.34 (m, 2H), 2.04 (s, 3H), 1.99-1.91 (m, 2H), 0.30 (s, 3H), 0.26 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.7, 144.5, 137.9, 133.6, 129.7, 128.3, 127.9, 127.3, 126.1, 74.2, 39.5, 34.2, 30.0, -0.9, -1.5; IR (film) 2956, 1715, 1427, 1361, 1253, 1095, 828, 785, 742, 700 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{19}H_{24}NaO_2Si$) requires *m/z* 335.1443, found *m/z* 335.1435.



3e

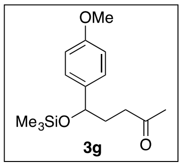
5-phenyl-5-((triisopropylsilyl)oxy)pentan-2-one (3e): Prepared according to the general procedure using

6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 53 mg of phenyl(triisopropylsilyl)methanol (**1e**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3e** as a clear oil (47 mg, 70%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32-7.28 (m, 4H), 7.25-7.21 (m, 1H), 4.90 (t, *J* = 5.5 Hz, 1H), 2.49-2.42 (m, 1H), 2.29-2.23 (m, 1H), 2. 06 (s, 3H), 2.04-1.99 (m, 2H), 1.08-1.04 (m, 3H), 1.01(d, *J* = 5.9 Hz, 9H), 0.96 (d, *J* = 6.6 Hz, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.9, 144.7, 128.2, 127.2, 126.2, 73.7, 38.6, 34.3, 30.1, 18.2, 18.1, 12.4; IR (film) 2944, 2867, 1718, 1463, 1364, 1160, 1099, 921, 883, 800, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{20}$H$_{34}$NaO$_2$Si) requires *m/z* 357.2226, found *m/z* 357.2241.



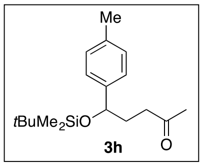
3f

5-((*tert*-butyldimethylsilyl)oxy)-5-(4-methoxyphenyl)pentan-2-one (3f): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 50 mg of (*tert*-butyldimethylsilyl)(4-methoxyphenyl)methanol (**1f**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3f** as a clear oil (62 mg, 96%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 2H), 4.68 (t, *J* = 6.0 Hz, 1H), 3.79 (s, 3H), 2.50-2.35 (m, 2H), 2.09 (s, 3H), 1.94-1.89 (m, 2H), 0.88 (s, 9H), 0.01 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.8, 158.8, 137.1, 127.1, 113.6, 73.5, 55.3, 39.5, 34.6, 30.0, 26.0, 18.3, -4.5, -4.9; IR (film) 2954, 2856, 1716, 1612, 1512, 1464, 1360, 1302, 1249, 1172, 1092, 1037, 936, 836, 777 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ (C$_{18}$H$_{30}$NaO$_3$Si) requires *m/z* 345.1862, found *m/z* 345.1850.



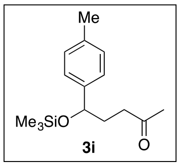
3g

5-(4-methoxyphenyl)-5-((trimethylsilyl)oxy)pentan-2-one (3g): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 42 mg of (4-methoxyphenyl)(trimethylsilyl)methanol (**1g**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3g** as a clear oil (35 mg, 63%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20 (d, *J* = 8.5 Hz, 2H) 6.85 (d, *J* = 8.5 Hz, 2H), 4.65 (t, *J* = 6.2 Hz, 1H), 3.80 (s, 3H), 2.49-2.37 (m, 2H), 2.11 (s, 3H), 1.95-1.91 (m, 2H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.9, 158.9, 137.0, 127.1, 113.7, 73.5, 55.4, 39.9, 34.5, 30.0, 0.2; IR (film) 2955, 1715, 1612, 1512, 1360, 1302, 1249, 1172, 1092, 1036, 841, 750 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{24}NaO_3Si$) requires *m/z* 303.1392, found *m/z* 303.1401.



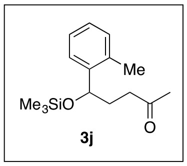
3h

5-((*tert*-butyldimethylsilyl)oxy)-5-(*p*-tolyl)pentan-2-one (3h): Prepared according to the general procedure using 6.6 mg of $\{Ir[dF(CF_3)ppy]_2(dtbbpy)\}PF_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 48 mg of (*tert*-butyldimethylsilyl)(*p*-tolyl)methanol (**1h**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3h** as a clear oil (45 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.71 (t, *J* = 5.4 Hz, 1H), 2.52-2.45 (m, 1H), 2.41-2.35 (m, 1H), 2.33 (s, 3H), 2.09 (s, 3H), 1.96-1.90 (m, 2H), 0.89 (s, 9H), 0.02 (s, 3H), -0.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 141.9, 136.7, 128.9, 125.9, 73.7, 39.4, 34.6, 30.0, 26.0, 21.2, 18.3, -4.5, -4.9; IR (film) 2929, 2857, 1718, 1513, 1471, 1360, 1254, 1161, 1092, 927, 837, 777, 667 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{18}H_{30}NaO_2Si$) requires *m/z* 329.1913, found *m/z* 329.1930.



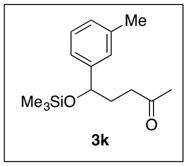
3i

5-(*p*-tolyl)-5-((trimethylsilyl)oxy)pentan-2-one (3i): Prepared according to the general procedure using 6.6 mg of $\{Ir[dF(CF_3)ppy]_2(dtbbpy)\}PF_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 39 mg of *p*-tolyl(trimethylsilyl)methanol (**1i**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3i** as a clear oil (40 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.67 (dd, *J* = 7.1, 5.2 Hz, 1H), 2.51-2.37 (m, 2H), 2.33 (s, 3H), 2.11 (s, 3H), 1.99-1.89 (m, 2H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 141.8, 136.8, 129.0, 125.9, 73.7, 39.8, 34.5, 30.0, 21.2, 0.2; IR (film) 2956, 1716, 1513, 1416, 1359, 1251, 1162, 1092, 928, 842, 752 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{24}NaO_2Si$) requires *m/z* 287.1443, found *m/z* 287.1444.



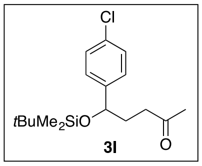
3j

5-(*o*-tolyl)-5-((trimethylsilyl)oxy)pentan-2-one (3j): Prepared according to the general procedure using 6.6 mg of $\{Ir[dF(CF_3)ppy]_2(dtbbpy)\}PF_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 39 mg of *o*-tolyl(trimethylsilyl)methanol (**1j**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3j** as a clear oil (35 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.14 (td, *J* = 7.4, 1.5 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 4.91 (dd, *J* = 8.3, 3.8 Hz, 1H), 2.58 (dt, *J* = 17.4, 7.5 Hz, 1H), 2.49 (ddd, *J* = 17.4, 7.7, 5.6 Hz, 1H), 2.35 (s, 3H), 2.15 (s, 3H), 1.95 (dtd, *J* = 14.5, 7.5, 3.8 Hz, 1H), 1.79 (dtd, *J* = 14.5, 8.3, 5.6 Hz, 1H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.9, 143.1, 133.6, 130.3, 126.9, 126.1, 126.0, 70.4, 39.8, 33.0, 30.0, 19.1, 0.1; IR (film) 2956, 1716, 1362, 1251, 1163, 1091, 1027, 927, 842, 752 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{24}NaO_2Si$) requires *m/z* 287.1443, found *m/z* 287.1454.



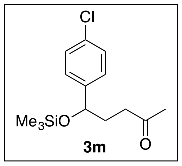
3k

5-(*m*-tolyl)-5-((trimethylsilyl)oxy)pentan-2-one (3k): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 39 mg of *m*-tolyl(trimethylsilyl)methanol (**1k**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3k** as a clear oil (37 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.4 Hz, 1H), 7.09-7.04 (m, 3H), 4.66 (dd, *J* = 7.4, 4.8 Hz, 1H), 2.52-2.39 (m, 2H), 2.34 (s, 3H), 2.11 (s, 3H), 1.99-1.89 (m, 2H), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.8, 144.8, 137.8, 128.1, 128.0, 126.6, 123.0, 73.8, 39.8, 34.5, 30.0, 21.6, -0.2; IR (film) 2956, 1716, 1358, 1251, 1161, 1088, 928, 842, 751, 703 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{15}H_{24}NaO_2Si$) requires *m/z* 287.1443, found *m/z* 287.1457.



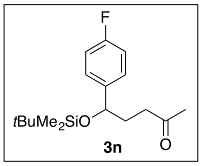
3l

5-((*tert*-butyldimethylsilyl)oxy)-5-(4-chlorophenyl)pentan-2-one (3l): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 52 mg of (*tert*-butyldimethylsilyl)(4-chlorophenyl)methanol (**1l**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3l** as a clear oil (48 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.71 (dd, *J* = 6.9, 4.9 Hz, 1H), 2.52-2.46 (m, 1H), 2.39-2.33 (m, 1H), 2.10 (s, 3H), 1.97-1.83 (m, 2H), 0.88 (s, 9H), 0.01 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 143.6, 132.8, 128.4, 127.3, 73.1, 39.1, 34.4, 30.1, 25.9, 18.3, -4.6, -4.9; IR (film) 2929, 2857, 1717, 1491, 1409, 1361, 1255, 1161, 1091, 926, 836, 777 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{27}ClNaO_2Si$) requires *m/z* 349.1367, found *m/z* 349.1369.



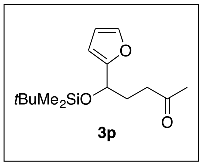
3m

5-(4-chlorophenyl)-5-((trimethylsilyl)oxy)pentan-2-one (3m): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 43 mg of (4-chlorophenyl)(trimethylsilyl)methanol (**1m**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3m** as a clear oil (35 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.68 (dd, *J* = 7.6, 4.6 Hz, 1H), 2.52-2.46 (m, 1H), 2.42-2.36 (m, 1H), 2.11 (s, 3H), 1.99-1.82 (m, 2H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.5, 143.6, 132.8, 128.5, 127.3, 73.1, 39.5, 34.4, 30.1, 0.1; IR (film) 2956, 1716, 1491, 1359, 1252, 1091, 927, 842 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{14}H_{21}ClNaO_2Si$) requires *m/z* 307.0897, found *m/z* 307.0879.



3n

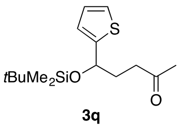
5-((*tert*-butyldimethylsilyl)oxy)-5-(4-fluorophenyl)pentan-2-one (3n): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 48 mg of (*tert*-butyldimethylsilyl)(4-fluorophenyl)methanol (**1n**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3n** as a clear oil (44 mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 8.3, 5.2 Hz, 2H), 6.99 (t, *J* = 8.3 Hz, 2H), 4.71 (dd, *J* = 6.9, 4.9 Hz, 1H), 2.52-2.45 (m, 1H), 2.41-2.35 (m, 1H), 2.10 (s, 3H), 1.94-1.87 (m, 2H), 0.88 (s, 9H), 0.01 (s, 3H), -0.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.6, 162.0 (d, *J* = 242.7 Hz), 140.7 (d, *J* = 3.0 Hz), 127.4 (d, *J* = 7.9 Hz), 115.0 (d, *J* = 21.2 Hz), 73.2, 39.2, 34.5, 30.0, 25.9, 18.3, -4.6, -4.9; IR (film) 2930, 2857, 1717, 1605, 1509, 1361, 1254, 1223, 1090, 926, 837, 777 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{17}H_{27}FNaO_2Si$) requires *m/z* 333.1662, found *m/z* 333.1664.



3p

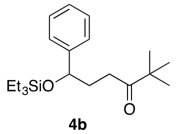
5-((*tert*-butyldimethylsilyl)oxy)-5-(furan-2-yl)pentan-2-one (3p): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF_3)ppy]$_2$(dtbbpy)}PF_6 (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 42 mg of (*tert*-butyldimethylsilyl)(furan-2-yl)methanol (**1p**, 0.2 mmol, 1.0

equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3p** as a clear oil (35 mg, 62%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.33 (d, *J* = 1.8 Hz, 1H), 6.30 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.16 (d, *J* = 3.2 Hz, 1H), 4.76 (t, *J* = 6.1 Hz, 1H), 2.55-2.41 (m, 2H), 2.12 (s, 3H), 2.09-2.03 (m, 2H), 0.87 (s, 9H), 0.04 (s, 3H), -0.07 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.5, 156.8, 141.5, 110.1, 106.2, 67.6, 39.2, 30.9, 30.1, 25.9, 18.3, -4.9, -5.0; IR (film) 2930, 2857, 1718, 1471, 1360, 1255, 1101, 1007, 926, 837, 778 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ ($C_{15}H_{26}NaO_3Si$) requires *m/z* 305.1549, found *m/z* 305.1547.



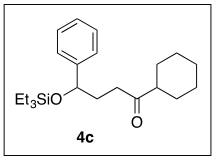
3q

5-((*tert*-butyldimethylsilyl)oxy)-5-(thiophen-2-yl)pentan-2-one (3q): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 28 mg of methyl vinyl ketone (**2a**, 0.4 mmol, 2.0 equiv.), 46 mg of (*tert*-butyldimethylsilyl)(thiophen-2-yl)methanol (**1q**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **3q** as a clear oil (24 mg, 41%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.19 (d, *J* = 5.1 Hz, 1H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.85 (d, *J* = 3.4 Hz, 1H), 5.03 (t, *J* = 5.8 Hz, 1H), 2.57-2.50 (m, 1H) 2.46-2.39 (m, 1H), 2.11 (s, 3H), 2.06-2.02 (m, 2H), 0.89 (s, 9H), 0.05 (s, 3H), -0.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.6, 149.4, 126.5, 124.0, 123.0, 70.1, 39.1, 34.8, 30.1, 25.9, 18.3, -4.8, -4.9; IR (film) 2928, 2856, 1717, 1362, 1254, 1093, 836, 777, 669 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ ($C_{15}H_{26}O_2SSi$) requires *m/z* 298.1423, found *m/z* 298.1427.



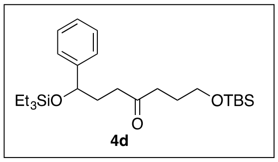
4b

2,2-dimethyl-6-phenyl-6-((triethylsilyl)oxy)hexan-3-one (4b): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 44 mg of 4,4-dimethylpent-1-en-3-one (**2b**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4b** as a clear oil (58 mg, 88%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30-7.29 (m, 4H), 7.24-7.20 (m, 1H), 4.74 (t, *J* = 6.1 Hz, 1H), 2.58-2.45 (m, 2H), 1.94-1.89 (m, 2H), 1.10 (s, 9H), 0.88 (t, *J* = 7.8 Hz, 9H), 0.52 (qd, *J* = 7.8, 2.6 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 216.1, 145.2, 128.2, 127.2, 126.0, 73.9, 44.3, 34.7, 32.4, 26.7, 6.9, 5.0; IR (film) 2956, 2876, 1706, 1457, 1365, 1237, 1087, 1007, 831, 742, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{20}H_{35}O_2Si$) requires *m/z* 335.2406, found *m/z* 335.2400.



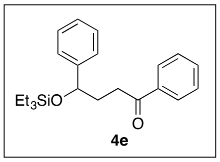
4c

1-cyclohexyl-4-phenyl-4-((triethylsilyl)oxy)butan-1-one (4c): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 55 mg of 1-cyclohexylprop-2-en-1-one (**2c**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4c** as a clear oil (47 mg, 65%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.30-7.29 (m, 4H), 7.24-7.20 (m, 1H), 4.73 (t, *J* = 6.0 Hz, 1H), 2.51-2.45 (m, 1H), 2.42-2.36 (m, 1H), 2.30-2.25 (m, 1H), 1.95-1.91 (m, 2H), 1.80-1.75 (m, 4H), 1.32-1.16 (m, 6H), 0.87 (t, *J* = 7.8 Hz, 9H), 0.52 (qd, *J* = 7.8, 3.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 214.1, 145.1, 128.2, 127.1, 126.0, 73.8, 50.9, 36.3, 34.4, 28.7, 26.0, 25.8, 6.9, 4.9; IR (film) 2931, 1708, 1451, 1240, 1090, 1006, 825, 742, 701 cm^{-1}; HRMS (EI) exact mass calculated for $[M-C_2H_5]^+$ ($C_{20}H_{31}O_2Si$) requires *m/z* 331.2093, found *m/z* 331.2084.



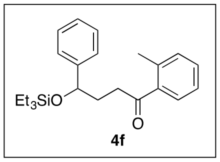
4d

13,13-diethyl-2,2,3,3-tetramethyl-11-phenyl-4,12-dioxa-3,13-disilapentadecan-8-one (4d): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 91 mg of 6-((*tert*-butyldimethylsilyl)oxy)hex-1-en-3-one (**2d**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4d** as a clear oil (62 mg, 69%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.31-7.29 (m, 4H), 7.25-7.23 (m, 1H), 4.73 (t, *J* = 6.0 Hz, 1H), 3.59 (t, *J* = 6.1 Hz, 2H), 2.53-2.36 (m, 4H), 1.98-1.94 (m, 2H), 1.81-1.73 (m, 2H), 0.89 (s, 9H), 0.88 (t, *J* = 7.8 Hz, 9H), 0.52 (qd, *J* = 7.8, 3.0 Hz, 6H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 210.9, 145.0, 128.2, 127.2, 126.0, 73.7, 62.3, 39.2, 38.5, 34.5, 27.0, 26.1, 18.4, 6.9, 4.9, -5.2; IR (film) 2954, 1715, 1463, 1363, 1254, 1099, 1007, 836, 776, 743, 701 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{25}H_{46}NaO_3Si_2$) requires *m/z* 473.2883, found *m/z* 473.2880.



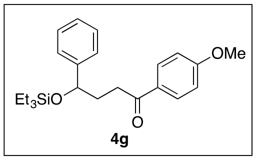
4e

1,4-diphenyl-4-((triethylsilyl)oxy)butan-1-one (4e): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 52 mg of 1-phenylprop-2-en-1-one (**2e**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4e** as a clear oil (59 mg, 84%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.91 (dd, *J* = 8.4, 1.4 Hz, 2H) 7.55-7.52 (m, 1H), 7.45-7.42 (m, 2H), 7.36-7.30 (m, 4H), 7.25-7.22 (m, 1H), 4.85 (t, *J* = 5.9 Hz, 1H), 3.05 (ddd, *J* = 17.0, 8.5, 6.2 Hz, 1H), 2.94 (ddd, *J* = 17.0, 8.5, 6.2 Hz, 1H), 2.13 (dq, *J* = 8.5, 6.2 Hz, 2H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.53 (qd, *J* = 7.9, 2.6 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.3, 145.1, 137.2, 133.0, 128.7, 128.3, 128.1, 127.2, 126.0, 73.8, 35.0, 34.4, 6.9, 5.0; IR (film) 2954, 2875, 1686, 1598, 1451, 1239, 1095, 1005, 832, 741, 700 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ ($C_{22}H_{30}O_2Si$) requires *m/z* 354.2015, found *m/z* 354.2024.



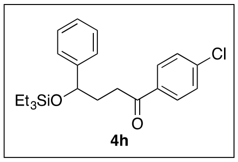
4f

4-phenyl-1-(*o*-tolyl)-4-((triethylsilyl)oxy)butan-1-one (4f): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 58 mg of 1-(*o*-tolyl)prop-2-en-1-one (**2f**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4f** as a clear oil (63 mg, 85%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.55 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.36-7.29 (m, 5H), 7.26-7.21 (m, 3H), 4.82 (t, *J* = 5.9 Hz, 1H), 2.98-2.92 (m, 1H), 2.90-2.83 (m, 1H), 2.46 (s, 3H), 2.11-2.07 (m, 2H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.52 (qd, *J* = 7.8, 2.5 Hz, 6H) ; ^{13}C NMR (125 MHz, CDCl$_3$) δ 204.5, 145.0, 138.3, 138.0, 132.0, 131.2, 128.5, 128.2, 127.2, 126.0, 125.8, 73.8, 37.4, 34.1, 21.4, 6.9, 5.0; IR (film) 2954, 1685, 1454, 1237, 1094, 1006, 832, 744, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{23}H_{33}O_2Si$) requires *m/z* 369.2250, found *m/z* 369.2238.



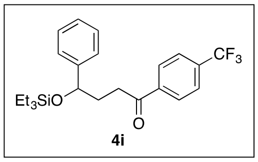
4g

1-(4-methoxyphenyl)-4-phenyl-4-((triethylsilyl)oxy)butan-1-one (4g): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 64 mg of 1-(4-methoxyphenyl)prop-2-en-1-one (**2g**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4g** as a clear oil (57 mg, 74%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.35-7.29 (m, 4H), 7.25-7.22 (m, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.83 (t, *J* = 5.9 Hz, 1H), 3.86 (s, 3H), 3.01-2.96 (m, 1H), 2.92-2.88 (m, 1H), 2.13-2.07 (m, 2H), 0.87 (t, *J* = 7.8 Hz, 9H), 0.52 (qd, *J* = 7.8, 2.8 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 198.9, 163.4, 145.1, 130.4, 130.2, 128.2, 127.2, 126.0, 113.8, 73.8, 55,6, 35.4, 34.0, 6.9, 4.9; IR (film) 2954, 1678, 1601, 1510, 1256, 1171, 1095, 842, 742 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ ($C_{23}H_{32}NaO_3Si$) requires *m/z* 407.2018, found *m/z* 407.2045.



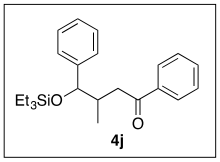
4h

1-(4-chlorophenyl)-4-phenyl-4-((triethylsilyl)oxy)butan-1-one (4h): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 66 mg of 1-(4-chlorophenyl)prop-2-en-1-one (**2h**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4h** as a clear oil (64 mg, 82%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.35-7.30 (m, 4H), 7.25-7.22 (m, 1H), 4.84 (dd, *J* = 6.7, 5.1 Hz, 1H), 3.02 (ddd, *J* = 17.2, 8.7, 6.3 Hz, 1H), 2.90 (ddd, *J* = 17.2, 8.6, 5.8 Hz, 1H), 2.17-2.05 (m, 2H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.52 (qd, *J* = 7.9, 2.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 199.1, 144.9, 139.4, 135.4, 129.6, 129.0, 128.3, 127.3, 125.9, 73.6, 34.9, 34.2, 6.9, 4.9; IR (film) 2954, 2876, 1687, 1589, 1454, 1400, 1239, 1092, 1011, 841, 744, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ ($C_{22}H_{29}ClNaO_2Si$) requires *m/z* 411.1523, found *m/z* 411.1524.



4i

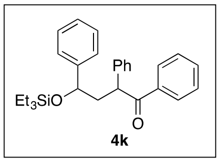
4-phenyl-4-((triethylsilyl)oxy)-1-(4-(trifluoromethyl)phenyl)butan-1-one (4i): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 80 mg of 1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**2i**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4i** as a clear oil (61 mg, 73%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.33-7.32 (m, 4H), 7.26-7.25 (m, 1H), 4.85 (t, *J* = 5.8 Hz, 1H), 3.10-3.04 (m, 1H), 2.98-2.92 (m, 1H), 2.16-2.10 (m, 2H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.52 (qd, *J* = 7.9, 2.8 Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 199.3, 144.8, 139.8, 134.4 (q, *J* = 32.2 Hz), 128.5, 128.3, 127.3, 125.9, 125.8 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 270.9 Hz), 73.6, 34.8, 34.5, 6.9, 4.9; IR (film) 2956, 2877, 1693, 1411, 1325, 1170, 1133, 1066, 1014, 849, 744, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{23}H_{30}F_3O_2Si$) requires *m/z* 423.1967, found *m/z* 423.1983.



4j

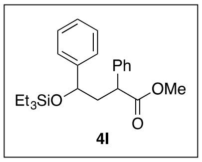
3-methyl-1,4-diphenyl-4-((triethylsilyl)oxy)butan-1-one (4j): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 58 mg of (*E*)-1-phenylbut-2-en-1-one (**2j**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc

(0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4j** in the form of a clear oil as an inseparable mixture of diastereomers (37 mg, 50%, 1: 1.6 ratio). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90-7.87 (m, 2H), 7.55-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.34-7.28 (m, 4H), 7.26-7.23 (m, 1H), 4.71 (d, *J* =4.8 Hz, 0.38H), 4.56 (d, *J* =6.2 Hz, 0.62H), 3.32 (dd, *J* =15.8, 3.6 Hz, 0.38H), 3.17 (dd, *J* =15.9, 4.5 Hz, 0.62H), 2.69 (dd, *J* =15.9, 9.6 Hz, 0.62H), 2.60 (dd, *J* =15.8, 8.7 Hz, 0.38H), 2.51-2.41 (m, 1H), 0.91-0.85 (m, 12H), 0.54-0.48 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) major isomer: δ 200.6, 143.8, 137.4, 132.9, 128.6, 128.3, 128.1, 127.3, 126.9, 79.1, 41.4, 38.8, 16.9, 7.0, 5.0; minor isomer: δ 200.3, 143.5, 137.4, 133.0, 128.6, 128.2, 127.9, 127.2, 126.9, 77.9, 41.9, 38.1, 15.2, 7.0, 5.0; IR (film) 2955, 2875, 1685, 1598, 1450, 1364, 1240, 1065, 1004, 836, 744, 701 cm^{-1}; HRMS (ESI) exact mass calculated for [M+H]$^+$ ($C_{23}H_{33}O_2Si$) requires *m/z* 369.2250, found *m/z* 369.2230.



4k

1,2,4-triphenyl-4-((triethylsilyl)oxy)butan-1-one (4k): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 83 mg of 1,2-diphenylprop-2-en-1-one (**2k**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4k** in the form of a clear oil as an inseparable mixture of diastereomers (77 mg, 90%, 1: 2 ratio). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.95-7.91 (m, 2H), 7.50-7.46 (m, 1H), 7.40-7.33 (m, 3H), 7.32-7.27 (m, 5H), 7.26-7.15 (m, 4H), 4.82 (dd, *J* = 9.5, 4.4 Hz, 0.33H), 4.72 (t, *J* = 7.0 Hz, 0.66H), 4.68 (dd, *J* = 8.1, 4.5 Hz, 0.33H), 4.51 (dd, *J* = 8.0, 5.1 Hz, 0.66H), 2.72-2.67 (m, 1H), 2.15-2.05 (m, 1H), 0.87 (t, *J* = 7.9 Hz, 6H), 0.76 (t, *J* = 7.9 Hz, 3H), 0.47 (qd, *J* = 7.9, 4.2 Hz, 4H), 0.36 (q, *J* = 7.9 Hz, 2H);^{13}C NMR (125 MHz, CDCl$_3$) major isomer: δ 199.7, 145.0, 139.3, 136.9, 132.9, 129.0, 128.8, 128.7, 128.6, 128.3, 127.5, 127.2, 126.3, 73.1, 50.0, 44.9, 7.0, 5.1; minor isomer δ 199.5, 145.4, 140.1, 136.9, 132.9, 129.0, 128.9, 128.5, 128.4, 128.3, 127.3, 127.0, 126.2, 73.1, 49.8, 44.9, 6.9, 4.9; IR (film) 2954, 2875, 1682, 1598, 1492, 1452, 1238, 1088, 1005, 826, 742, 699 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ ($C_{28}H_{34}NaO_2Si$) requires *m/z* 453.2226, found *m/z* 453.2247.

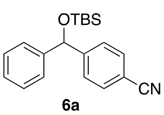


4l

methyl 2,4-diphenyl-4-((triethylsilyl)oxy)butanoate (4l): Prepared according to the general procedure using 6.6 mg of {Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)}PF$_6$ (0.06 mmol, 3%), 64 mg of methyl 2-phenylacrylate (**2l**, 0.4 mmol, 2.0 equiv.), 44 mg of phenyl(triethylsilyl)methanol (**1c**, 0.2 mmol, 1.0 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 28 mg of KOPiv (0.2 mmol, 1.00 equiv.) and 1 mL of DCE. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **4l** in the form of a clear oil as an inseparable mixture of diastereomers (66 mg, 86%, 1: 1.6 ratio). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.34-7.23 (m, 10H), 4.66 (dd, *J* = 8.2, 4.6 Hz, 0.38H), 4.52 (dd, *J* = 8.2, 4.7 Hz, 0.62H), 3.79 (dd, *J* = 10.0, 4.7 Hz, 0.38H), 3.74 (t, *J* = 7.3 Hz, 0.62H), 3.65 (s, 1.14H), 3.60 (s, 1.86), 2.57 (dt, *J* = 15.1, 7.8 Hz, 0.62H), 2.50 (ddd, *J* = 14.2, 10.0, 4.7 Hz, 0.38H), 2.12-2.02 (m, 1H), 0.88-0.82 (m, 9H), 0.52-0.41 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) major isomer: δ174.4, 144.9, 139.0, 128.8, 128.3, 128.0, 127.5, 127.4, 126.2, 73.0, 52.1, 48.2, 44.0, 6.9, 5.0; minor isomer: δ 174.3, 145.1 , 139.5, 128.8, 128.3, 128.0, 127.5, , 127.3, 126.1, 73.1, 52.0, 47.8, 44.7, 6.9, 4.9; IR (film) 2953, 2876, 1737, 1494, 1454, 1236, 1160, 1092, 1006, 730, 699 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{23}H_{32}NaO_3Si$) requires *m/z* 407.2018, found *m/z* 407.2047.

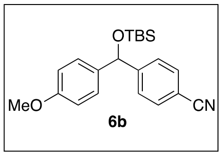
b) Photoredox-catalyzed arylation reaction via Brook rearrangement

General Procedure: To a 10 mL clear-colored glass vial, aryl(trialkylsilyl)methanol (0.6 mmol, 3.0 equiv.), CsOAc (38.4 mg, 1.0 equiv.), Ir(ppy)$_3$ (4 mg, 0.006 mmol, 0.03 equiv.), aromatic nitrile (0.2 mmol, 1.0 equiv.) were added. 1.0 mL DMA was then added, followed by octanal (30 mg, 0.24 mmol, 1.2 equiv.). The vial was sealed and then cooled to -78 ºC and degassed via vacuum evacuation, backfilled with nitrogen and warmed to room temperature. The vial was then exposed to blue LEDs at room temperature with stirring for 24-48 hours. The color of the initially yellow solution turned black after being exposed to blue LEDs and turned back to orange or yellow when the reaction was completed. Then reaction mixture was then diluted with water, extracted with EtOAc for three times. The organic layer was then concentrated and purified by column chromatography on silica gel, eluting with EtOAc and hexanes to afford the product in pure form.

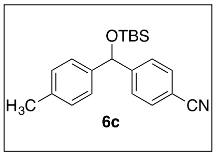


6a

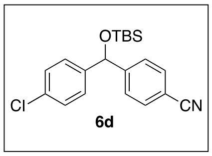
4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)benzonitrile (6a): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 132 mg of (*tert*-butyldimethylsilyl)(phenyl)methanol (**1b**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6a** as a clear oil (54 mg, 83%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.33-7.29 (m, 4H), 7.26-7.20 (m, 1H), 5.77 (s, 1H), 0.92 (s, 9H), 0.02 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.7, 144.0, 132.3, 128.6, 127.8, 126.9, 126.5, 119.1, 110.9, 76.4, 25.9, 18.4, -4.7, -4.8. The data for this compound matched that reported in the literature.[8]



4-(((*tert*-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)benzonitrile (6b): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 151 mg of (*tert*-butyldimethylsilyl)(4-methoxyphenyl)-methanol (**1f**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6b** as a clear oil (59 mg, 84%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.58 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 5.73 (s, 1H), 3.78 (s, 3H), 0.91 (s, 9H), 0.02 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 159.2, 151.0, 136.2, 132.2, 127.7, 126.8, 119.1, 114.0, 110.7, 75.9, 55.3, 25.9, 18.4, -4.6, -4.8; IR (film) 2954, 2856, 2227, 1610, 1510, 1464, 1303, 1250, 1172, 1081, 1035, 868, 837, 778 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ ($C_{21}H_{27}NO_2Si$) requires *m/z* 353.1811, found *m/z* 353.1827.

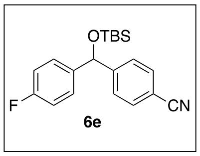


4-(((*tert*-butyldimethylsilyl)oxy)(*p*-tolyl)methyl)benzonitrile (6c): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 142 mg of (*tert*-butyldimethylsilyl)(*p*-tolyl)methanol (**1h**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6c** as a clear oil (57 mg, 85%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.73 (s, 1H), 2.31 (s, 3H), 0.91 (s, 9H), 0.01 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.0, 141.1, 137.5, 132.3, 129.3, 126.8, 126.4, 119.1, 110.8, 76.2, 25.9, 21.2, 18.4, -4.6, -4.8; IR (film) 2928, 2857, 2228, 1608, 1512, 1470, 1254, 1192, 1083, 1019, 868, 837, 778 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ ($C_{21}H_{27}NOSi$) requires *m/z* 337.1862, found *m/z* 337.1880.



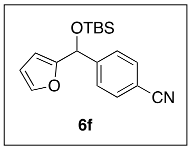
4-(((*tert*-butyldimethylsilyl)oxy)(4-chlorophenyl)methyl)benzonitrile (6d): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 154 mg of (*tert*-butyldimethylsilyl)(4-chlorophenyl)methanol (**1l**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20

equiv.), 1mL of DMA. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6d** as a clear oil (54 mg, 76%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.74 (s, 1H), 0.91 (s, 9H), 0.01 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.1, 142.5, 133.6, 132.4, 128.9, 127.8, 126.8, 118.9, 111.2, 75.8, 25.9, 18.4, -4.6, -4.8; IR (film) 2929, 2857, 2228, 1490, 1410, 1254, 1190, 1088, 1014, 866, 838, 779 cm^{-1}; HRMS (EI) exact mass calculated for [M]$^+$ ($C_{20}H_{24}ClNOSi$) requires *m/z* 357.1316, found *m/z* 357.1330.



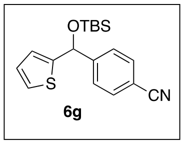
6e

4-(((*tert*-butyldimethylsilyl)oxy)(4-fluorophenyl)methyl)benzonitrile (6e): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 144 mg of (*tert*-butyldimethylsilyl)(4-fluorophenyl)methanol (**1n**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6e** as a clear oil (45 mg, 66%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 8.2, 5.6 Hz, 2H), 6.99 (t, *J* = 8.2 Hz, 2H), 5.75 (s, 1H), 0.91 (s, 9H), 0.01 (s, 3H), -0.04 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 162.3 (d, *J* = 243.8 Hz), 150.4, 139.9 (d, *J* = 3.0 Hz), 132.4, 128.1 (d, *J* = 8.1 Hz), 126.8, 119.0, 115.6 (d, *J* = 21.4 Hz), 111.1, 75.7, 25.9, 18.4, -4.6, -4.8; IR (film) 2930, 2857, 2228, 1606, 1508, 1470, 1254, 1224, 1156, 1082, 866, 837, 778 cm^{-1}; HRMS (ESI) exact mass calculated for [M+Na]$^+$ ($C_{20}H_{24}FNNaOSi$) requires *m/z* 364.1509, found *m/z* 364.1519.



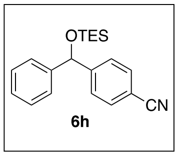
6f

4-(((*tert*-butyldimethylsilyl)oxy)(furan-2-yl)methyl)benzonitrile (6f): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 127 mg of (*tert*-butyldimethylsilyl)(furan-2-yl)methanol (**1p**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6f** as a clear oil (46 mg, 74%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 1H), 6.30-6.29 (m, 1H), 6.11 (d, *J* = 3.1 Hz, 1H), 5.82 (s, 1H), 0.92 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 155.6, 147.5, 142.6, 132.2, 127.1, 119.0, 111.4, 110.4, 107.4, 70.1, 25.9, 18.4, -4.9, -5.0. The data for this compound matched that reported in the literature.[8]



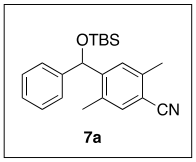
6g

4-(((*tert*-butyldimethylsilyl)oxy)(thiophen-2-yl)methyl)benzonitrile (6g): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 137 mg of (*tert*-butyldimethylsilyl)(thiophen-2-yl)methanol (**1q**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6g** as a clear oil (33 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 5.1 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.80 (d, *J* = 3.5 Hz, 1H), 6.01 (s, 1H), 0.93 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 148.7, 132.4, 126.8, 126.7, 125.5, 124.2, 119.0, 111.4, 72.6, 25.9, 18.4, -4.8, -4.8. The data for this compound matched that reported in the literature.[8]



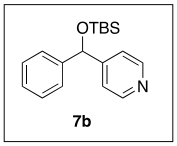
6h

4-(phenyl((triethylsilyl)oxy)methyl)benzonitrile (6h): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 26 mg of terephthalonitrile (**5a**, 0.2 mmol, 1.00 equiv.), 88 mg of phenyl(triethylsilyl)methanol (**1c**, 0.4 mmol, 2.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **6h** as a clear oil (40 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.32-7.28 (m, 4H), 7.26-7.22 (m, 1H), 5.76 (s, 1H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.7, 144.0, 132.2, 128.6, 127.8, 126.9, 126.5, 119.1, 110.9, 76.0, 6.8, 4.9; IR (film) 2955, 2876, 2228, 1454, 1411, 1240, 1190, 1189, 1067, 1007, 847, 729, 699 cm^{-1}; HRMS (ESI) exact mass calculated for $[M+Na]^+$ ($C_{20}H_{25}NaNOSi$) requires *m/z* 346.1603, found *m/z* 346.1616.



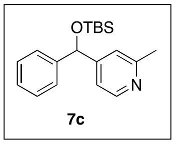
7a

4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2,5-dimethylbenzonitrile (7a): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 32 mg of 2,5-dimethylterephthalonitrile (**5b**, 0.2 mmol, 1.00 equiv.), 133 mg of (*tert*-butyldimethylsilyl)(phenyl)-methanol (**1b**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **7a** as a clear oil (49 mg, 71%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.62 (s, 1H), 7.35-7.24 (m, 6H), 5.87 (s, 1H), 2.57 (s, 3H), 2.21 (s, 3H), 0.93 (s, 9H), 0.02 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.8, 142.6, 139.3, 134.2, 132.9, 128.6, 128.3, 127.3, 126.8, 118.3, 111.2, 73.9, 25.8, 20.2, 18.8, 18.2, -4.8, -4.9. The data for this compound matched that reported in the literature.[8]



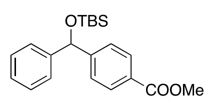
7b

4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)pyridine (7b): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 21 mg of isonicotinonitrile (**5c**, 0.2 mmol, 1.00 equiv.), 133 mg of (*tert*-butyldimethylsilyl)(phenyl)methanol (**1b**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **7b** as a clear oil (40 mg, 67%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.51 (d, *J* = 6.1 Hz, 2H), 7.34-7.29 (m, 6H), 7.26-7.23(m, 1H), 5.70 (s, 1H), 0.92 (s, 9H), 0.03 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.2, 149.8, 143.7, 128.7, 127.9, 126.6, 121.2, 75.8, 26.0, 18.5, -4.6, -4.8. The data for this compound matched that reported in the literature.[8]



7c

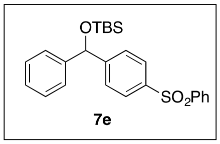
4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)-2-methylpyridine (7c): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 24 mg of 2-methylisonicotinonitrile (**5d**, 0.2 mmol, 1.00 equiv.), 133 mg of (*tert*-butyldimethylsilyl)(phenyl)methanol (**1b**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **7c** as a clear oil (39 mg, 63%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.43 (d, *J* = 5.1 Hz, 2H), 7.38-7.31 (m, 4H), 7.28-7.25 (m, 1H), 7.16-7.14 (m, 1H), 5.68 (s, 1H), 2.54 (s, 3H), 0.94 (s, 9H), 0.04 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 158.3, 154.5, 149.0, 143.8, 128.6, 127.7, 126.5, 120.7, 118.4, 75.9, 25.9, 18.4, -4.7, -4.8. The data for this compound matched that reported in the literature.[8]



7d

Methyl 4-(((*tert*-butyldimethylsilyl)oxy)(phenyl)methyl)benzoate (7d): Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 32 mg of methyl 4-

cyanobenzoate (**5e**, 0.2 mmol, 1.00 equiv.), 133 mg of (*tert*-butyldimethylsilyl)(phenyl)methanol (**1b**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 48 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 5% ethyl acetate in hexanes) to afford the product **7d** as a clear oil (30 mg, 42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 7.29 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.1 Hz, 1H), 5.78 (s, 1H), 3.89 (s, 3H), 0.92 (s, 9H), -0.01 (s, 3H), -0.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 150.5, 144.5, 129.8, 128.9, 128.5, 127.4, 126.4, 126.3, 76.5, 52.2, 26.0, 18.4, -4.7, -4.7. The data for this compound matched that reported in the literature.[8]



7e

***tert*-butyldimethyl(phenyl(4-(phenylsulfonyl)phenyl)methoxy)silane (7e):** Prepared according to the general procedure using 4 mg of tris[2-phenylpyridinato-C2,*N*]iridium(III) (0.006 mmol, 3%), 36 mg of 4-(methylsulfonyl)benzonitrile (**5f**, 0.2 mmol, 1.00 equiv.), 133 mg of (*tert*-butyldimethylsilyl)(phenyl)-methanol (**1b**, 0.6 mmol, 3.00 equiv.), 38.4 mg of CsOAc (0.2 mmol, 1.00 equiv.), 30 mg of octanal (0.24 mmol, 1.20 equiv.), 1mL of DMA. After 24 hours, the reaction mixture was subjected to the workup protocol and purified by flash chromatography (silica gel: 2% ethyl acetate in hexanes) to afford the product **7e** as a clear oil (50 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 8.1 Hz, 2H), 7.56-7.47 (m, 5H), 7.31-7.26 (m, 4H), 7.24-7.21 (m, 1H), 5.75 (s, 1H), 0.90 (s, 9H), -0.01 (s, 3H), -0.07 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 144.0, 141.8,140.1, 133.2, 129.4, 128.6, 127.8, 127.8, 127.7, 126.9, 126.5, 76.3, 25.9, 18.4, -4.7, -4.8. The data for this compound matched that reported in the literature.[8]

6. References

1. Tellis, J. C.; Primer, D. N.; Molander, G. A. *Science* **2014**, *345*, 433-436.

2. Zhang, J.; Li, Y.; Zhang, F.; Hu, C.; Chen, Y. *Angew. Chem. Int. Ed.* **2016**, *55*, 1872-1875.

3. Raamat, E.; Kaupmees, K.; Ovsjannikov, G.; Trummal, A.; Kütt, A.; Saame, J.; Koppel, I.; Kaljurand, I.; Lipping, L.; Rodima, T.; Pihl, V.; Koppel, I. A.; Leito, I. *J. Phys. Org. Chem.* **2013**, *26*, 162-170.

4. Patrocínion, A. F.; Corrêa, I. R., Jr.; Moran, P. J. S. *J. Chem. Soc., Perkin Trans. 1,* **1999**, *21*, 3133-3137.

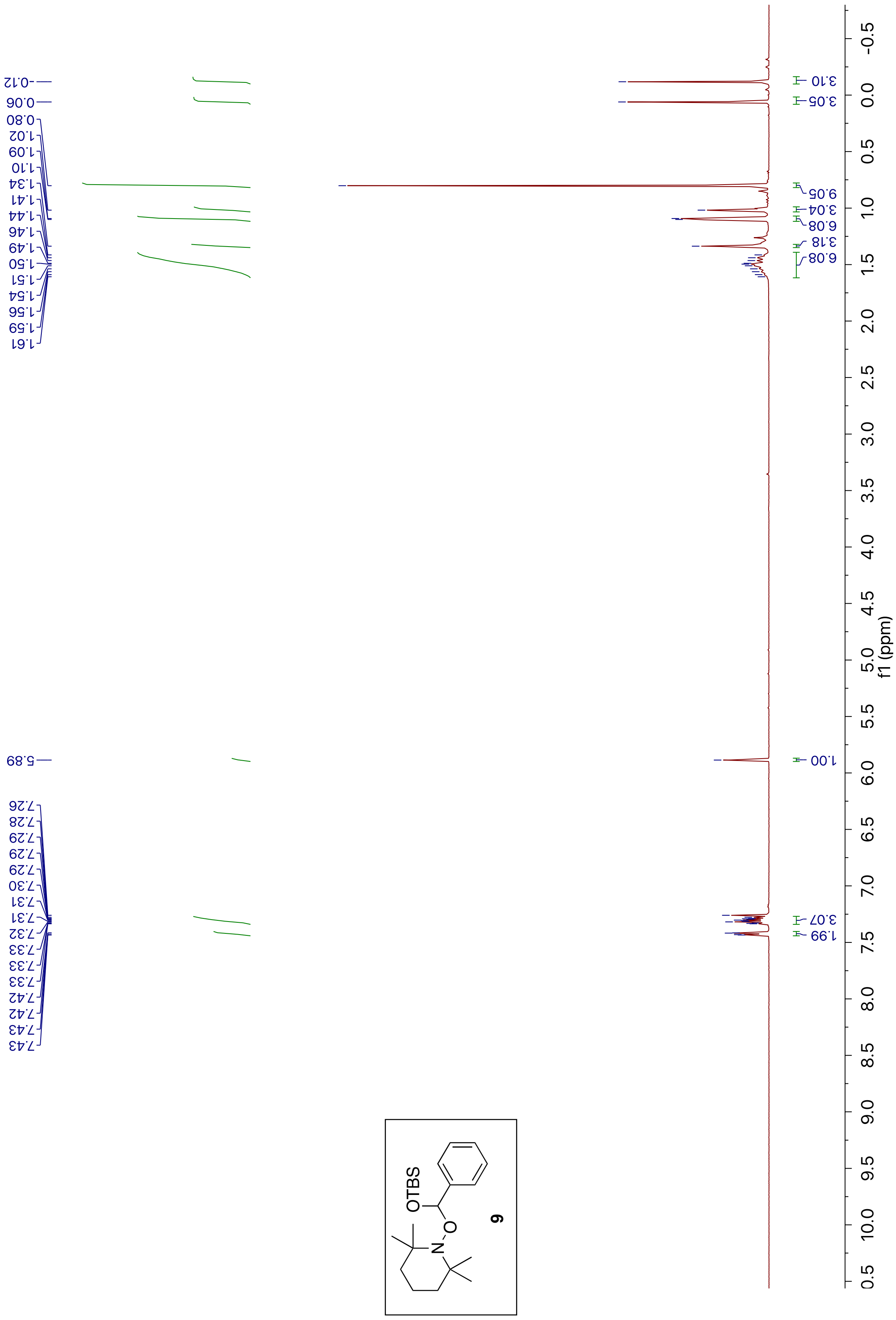
5. Huckins, J. R.; Rychnovsky, S. D. *J. Org. Chem.* **2003**, *68*, 10135-10145.

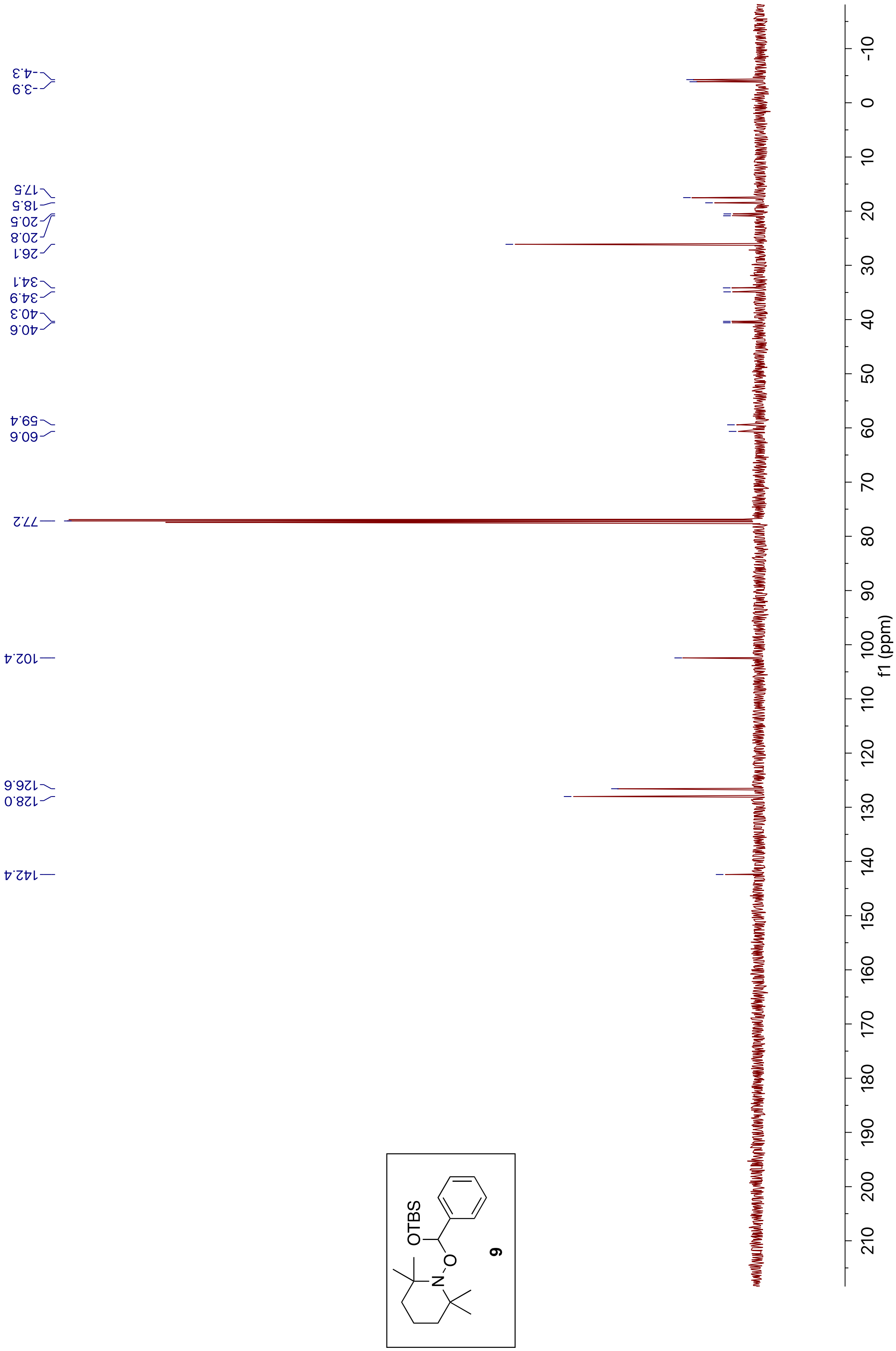
6. Soderquist, J. A.; Miranda, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 10078-10079.

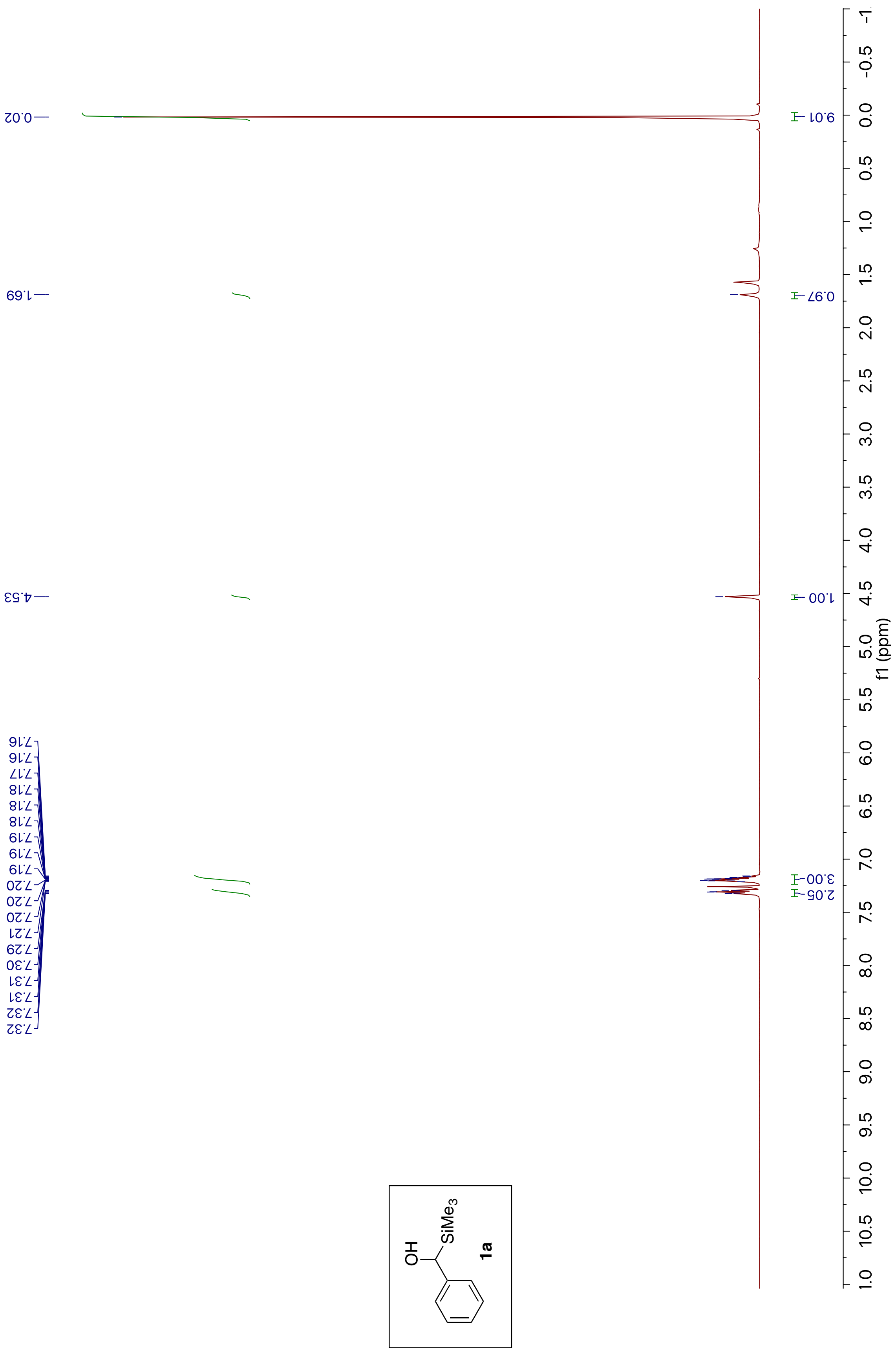
7. Arai, N.; Suzuki, K.; Sugizaki, S.; Sorimachi, H.; Ohkuma, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 1770-1773.

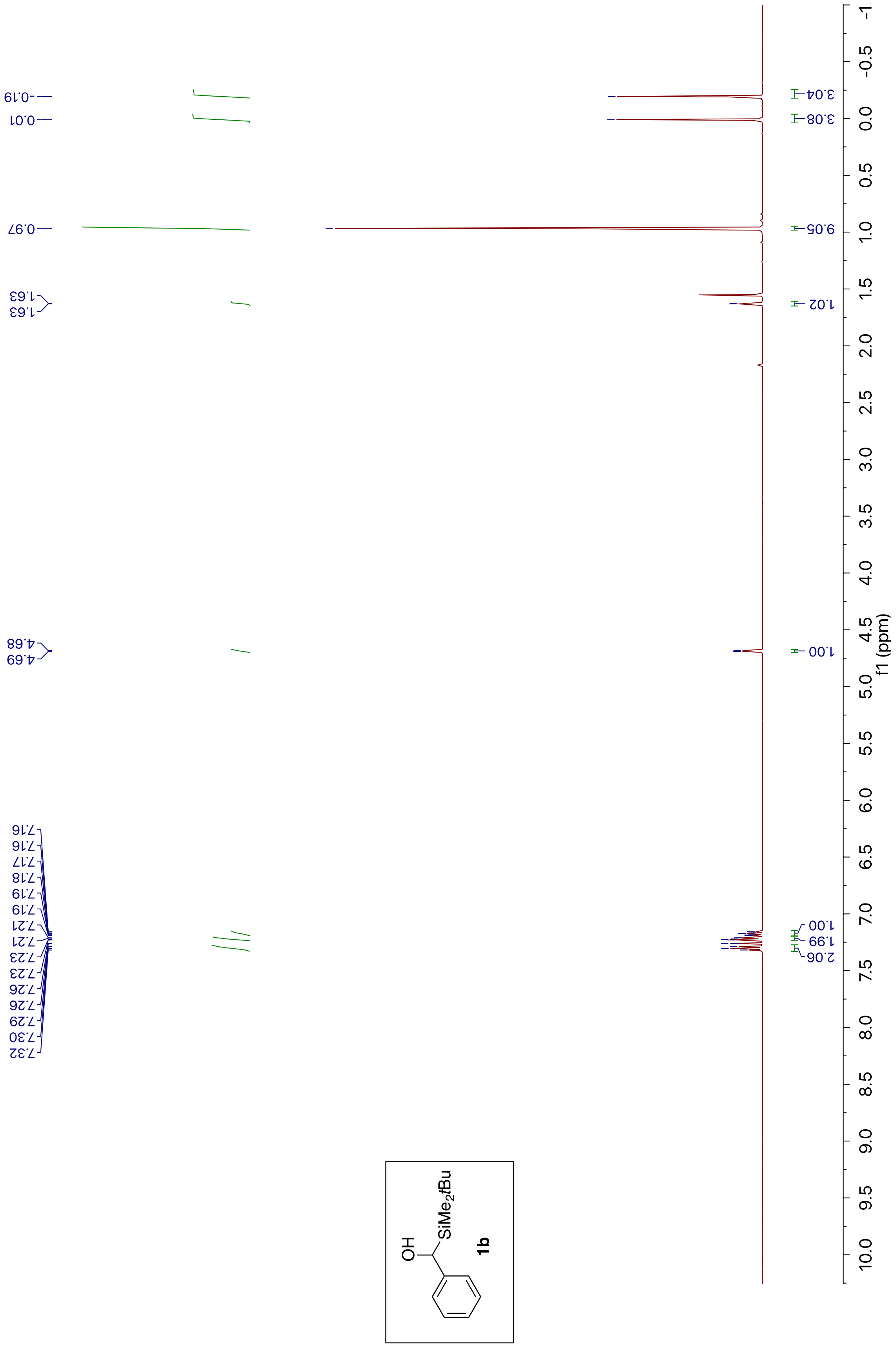
8. Qvortup, K.; Rankic, D. A.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2014**, *136*, 626-629.

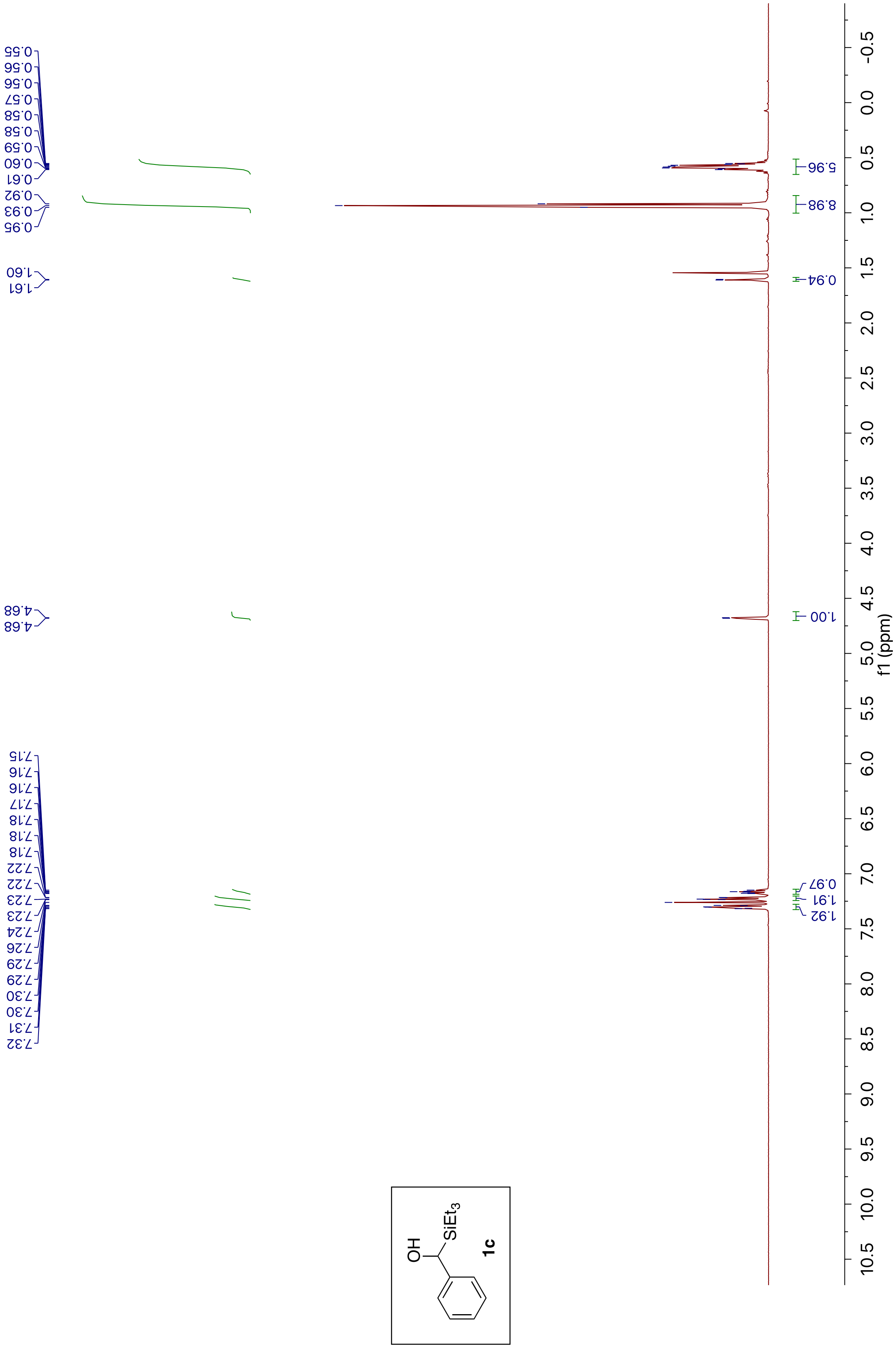
7. ^{1}H-NMR and ^{13}C-NMR Spectral Data

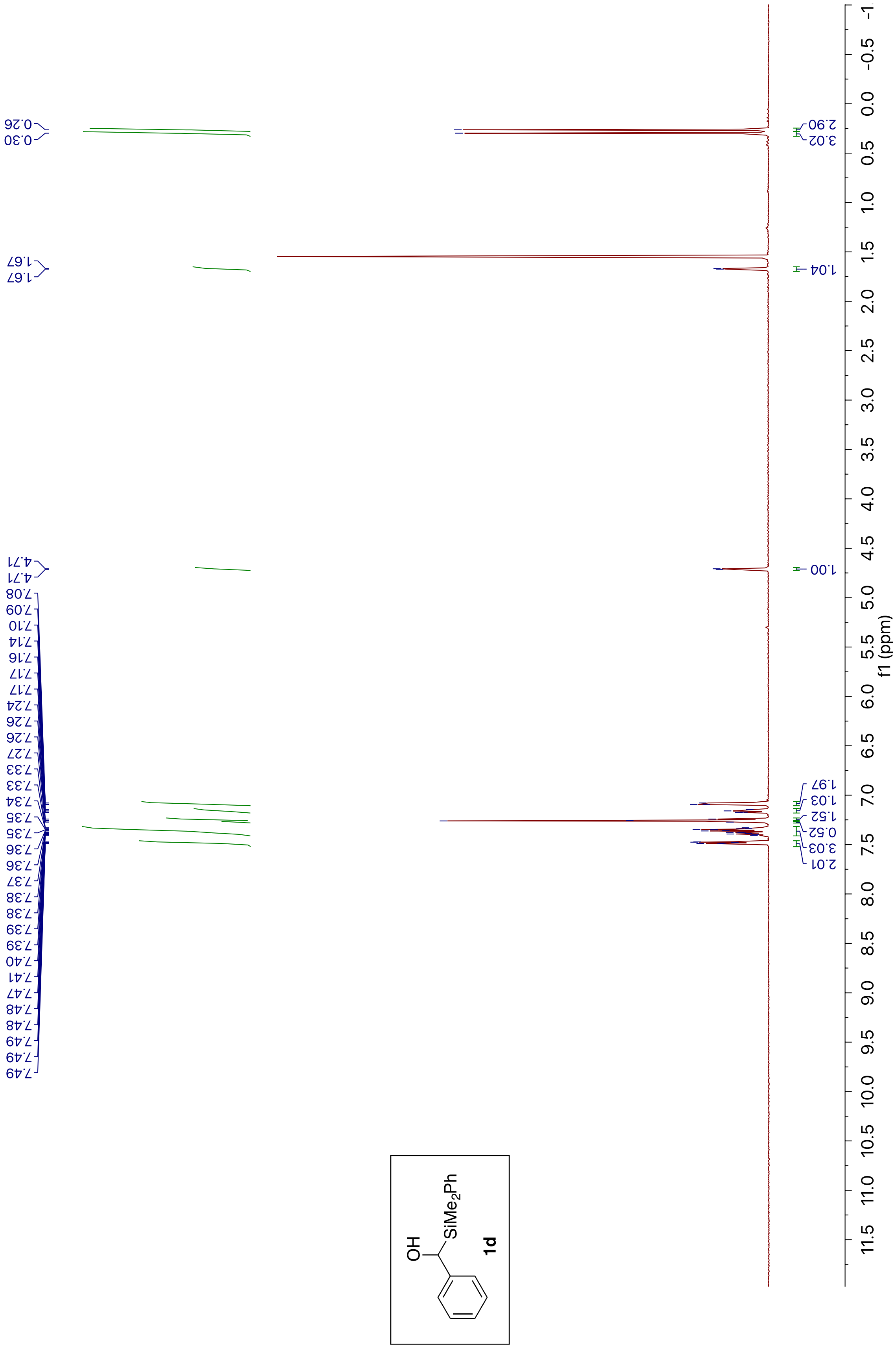


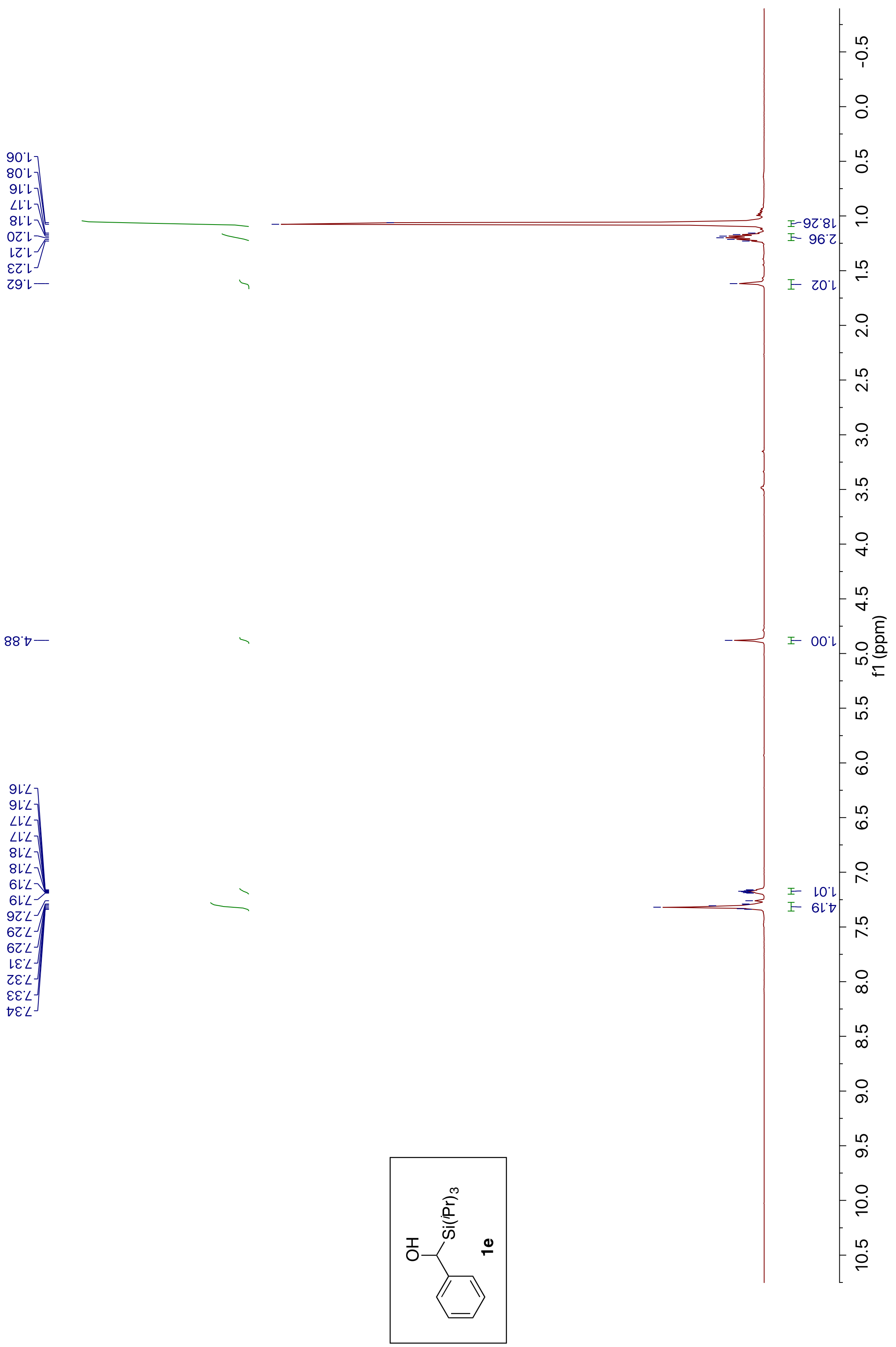

-4.3
-3.9
17.5
18.5
20.5
20.8
26.1
34.1
34.9
40.3
40.6
59.4
60.6
77.2
102.4
126.6
128.0
142.4
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
OTBS
N
O
9

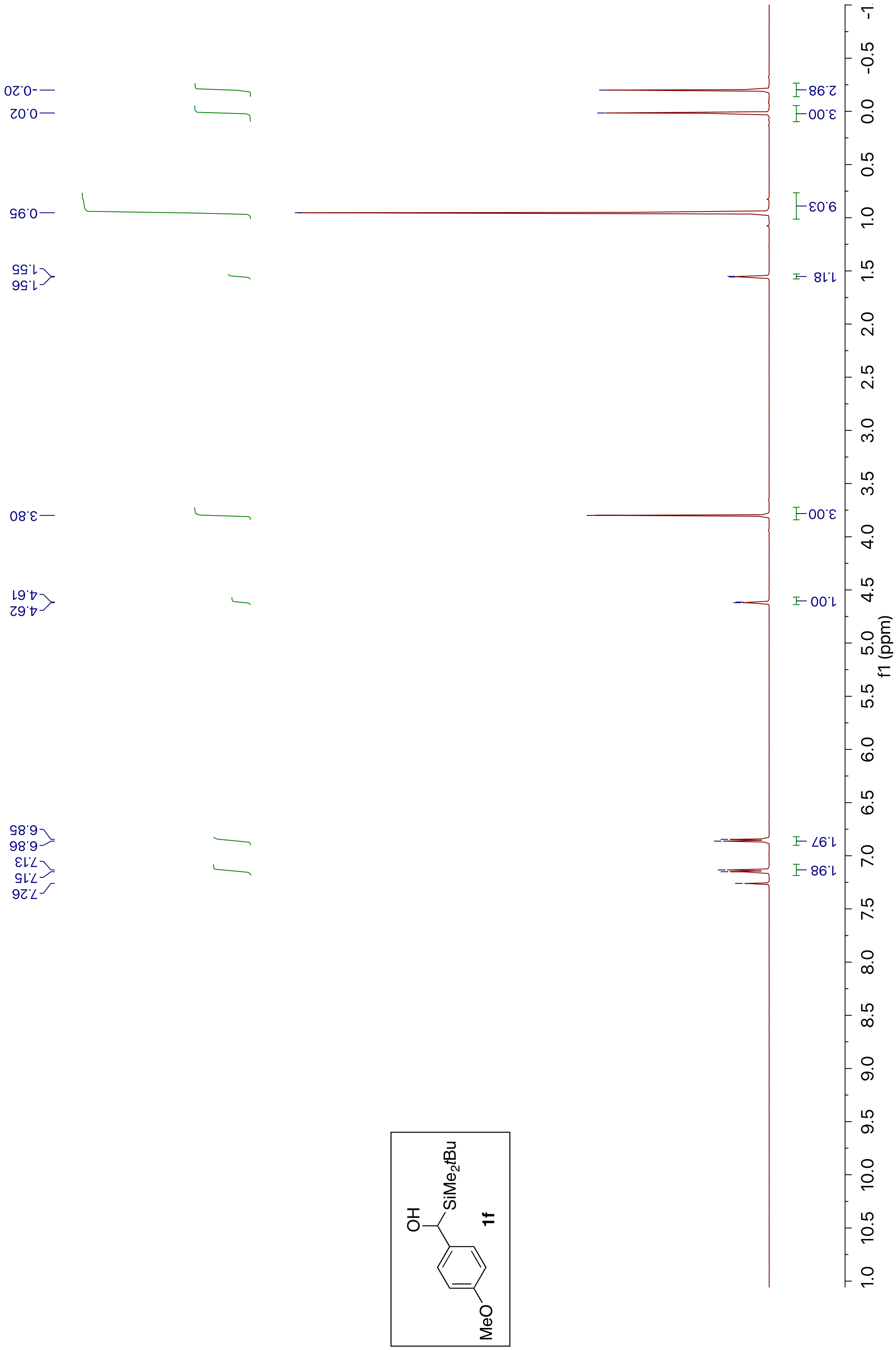

0.02
1.69
4.53
7.32
7.32
7.31
7.31
7.30
7.29
7.21
7.20
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
7.16
7.16
9.01
0.97
1.00
3.00
2.05
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
OH
SiMe$_3$
1a

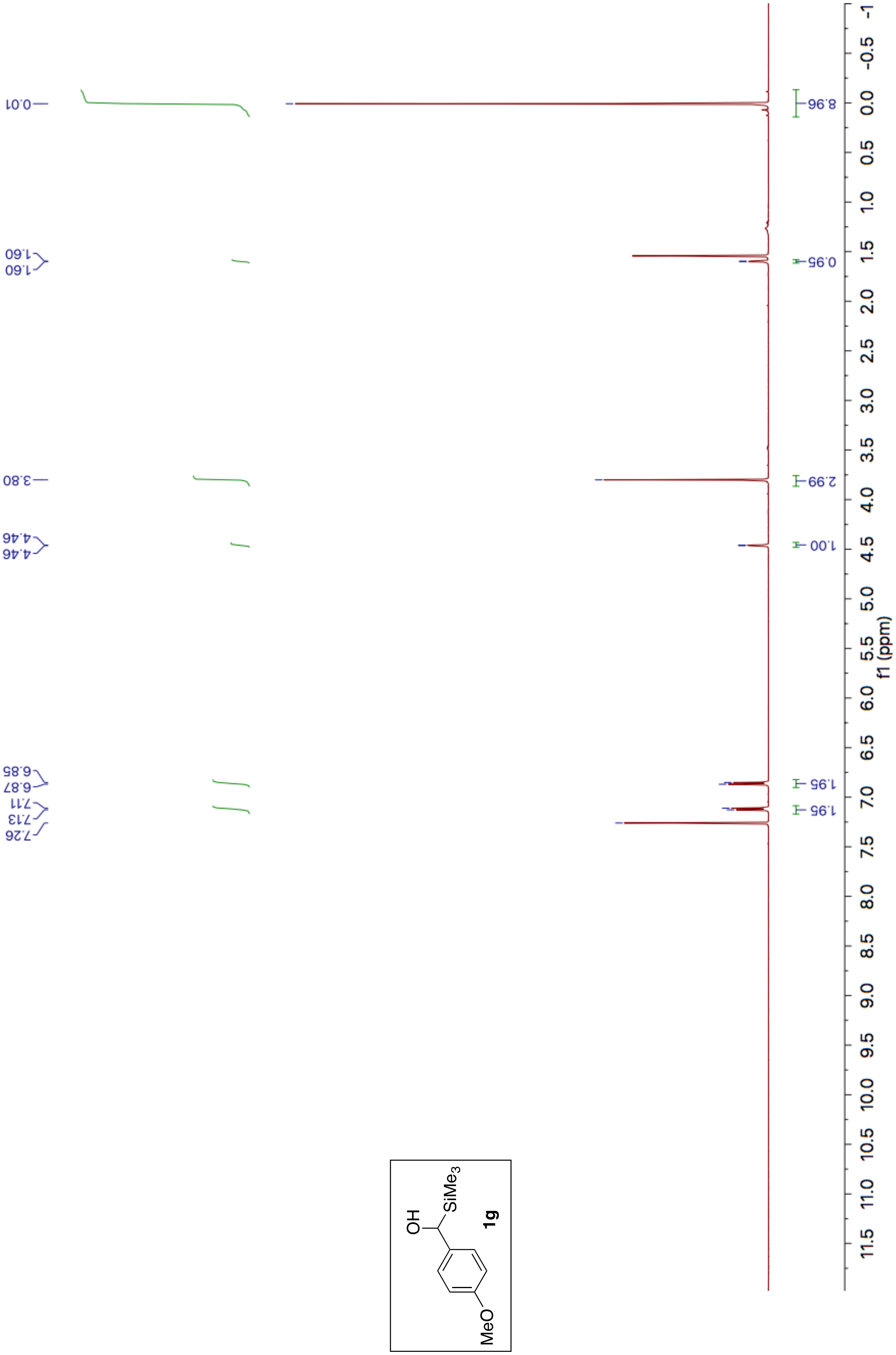

-0.19
0.01
0.97
1.63
1.63
4.68
4.69
7.16
7.16
7.17
7.18
7.19
7.19
7.21
7.21
7.23
7.23
7.26
7.26
7.29
7.30
7.32
3.04
3.08
9.05
1.02
1.00
1.00
1.99
2.06
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
OH
SiMe2tBu
1b

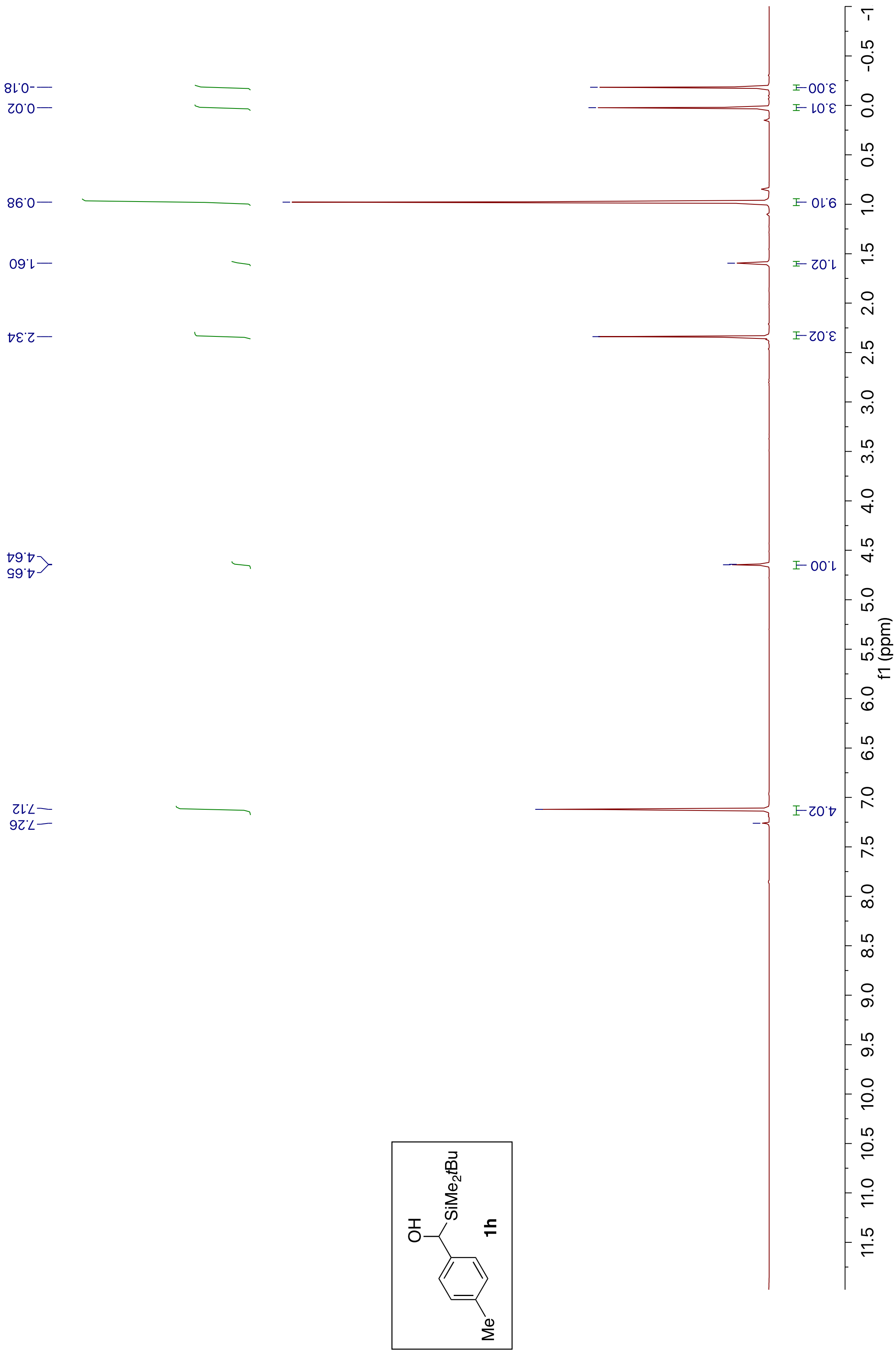

0.55
0.56
0.56
0.57
0.58
0.58
0.59
0.60
0.61
0.92
0.93
0.95
1.60
1.61
4.68
4.68
7.15
7.16
7.16
7.17
7.18
7.18
7.18
7.22
7.22
7.23
7.23
7.24
7.26
7.26
7.29
7.30
7.30
7.31
7.32
5.96
8.98
0.94
1.00
0.97
1.91
1.92
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OH
SiEt3
1c

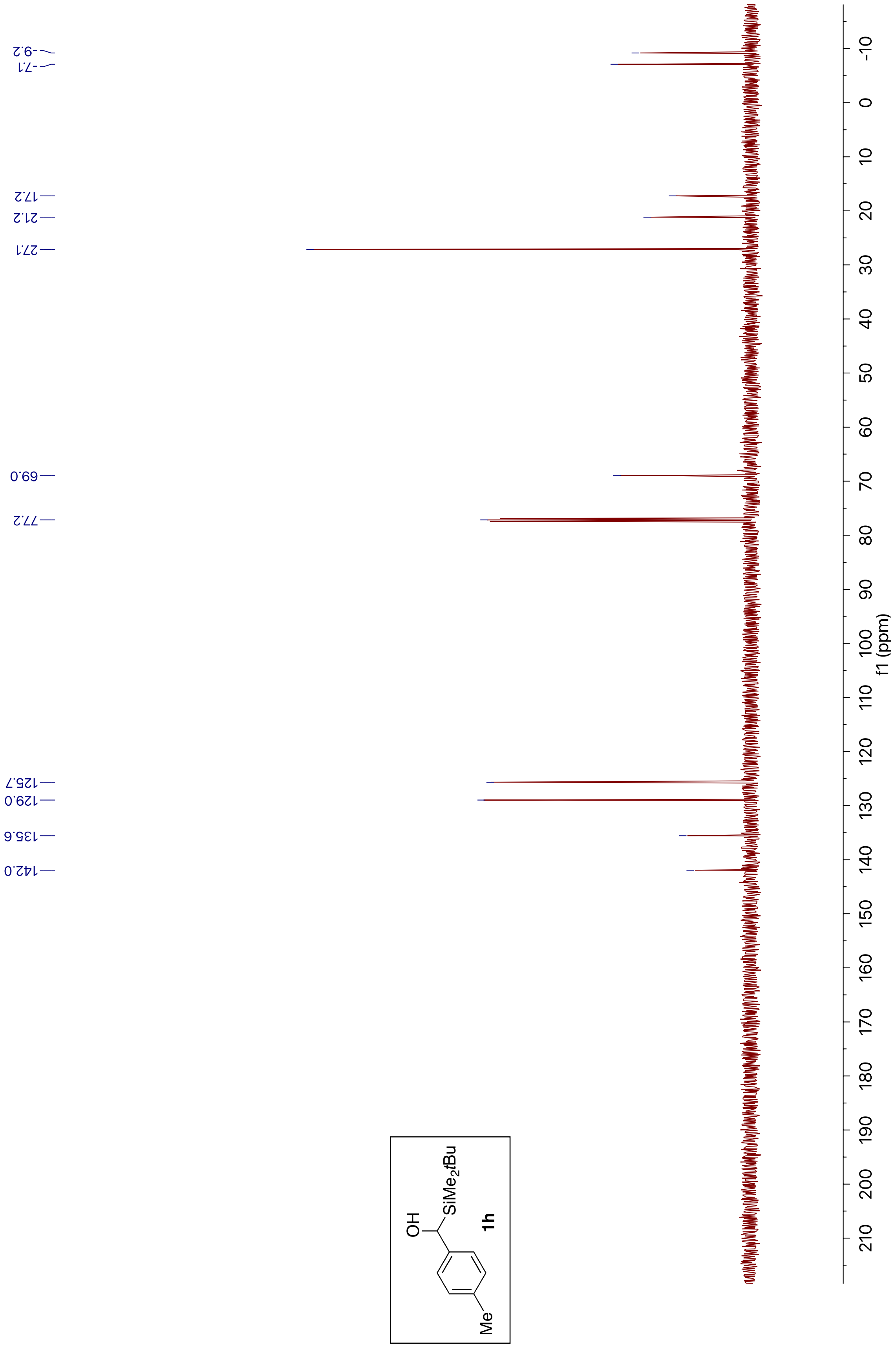

0.26
0.30
1.67
1.67
4.71
4.71
7.08
7.09
7.10
7.14
7.16
7.17
7.17
7.24
7.26
7.26
7.27
7.33
7.33
7.34
7.35
7.35
7.36
7.36
7.37
7.38
7.38
7.39
7.39
7.40
7.41
7.47
7.48
7.48
7.49
7.49
7.49
2.90
3.02
1.04
1.00
1.97
1.03
1.52
0.52
3.03
2.01
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OH
SiMe2Ph
1d


1.06
1.08
1.16
1.17
1.18
1.20
1.21
1.23
1.62
4.88
7.16
7.16
7.17
7.17
7.18
7.18
7.19
7.19
7.26
7.29
7.29
7.31
7.32
7.33
7.34
18.26
2.96
1.02
1.00
1.01
4.19
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OH
Si(iPr)3
1e

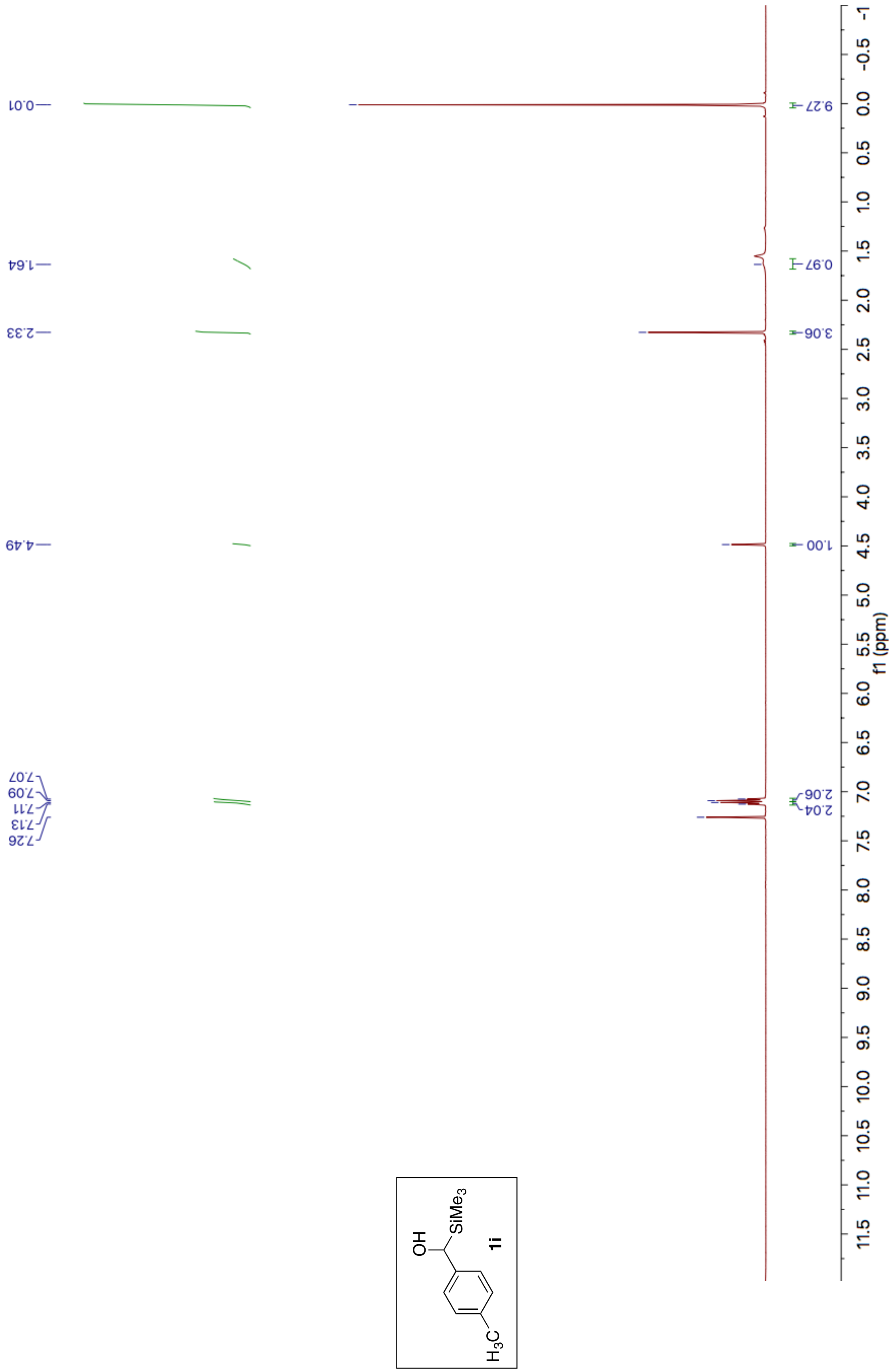

-0.20
0.02
0.95
1.55
1.56
3.80
4.61
4.62
6.85
6.86
7.13
7.15
7.26
2.98
3.00
9.03
1.18
3.00
1.00
1.97
1.98
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
f1 (ppm)
MeO
OH
SiMe2tBu
1f

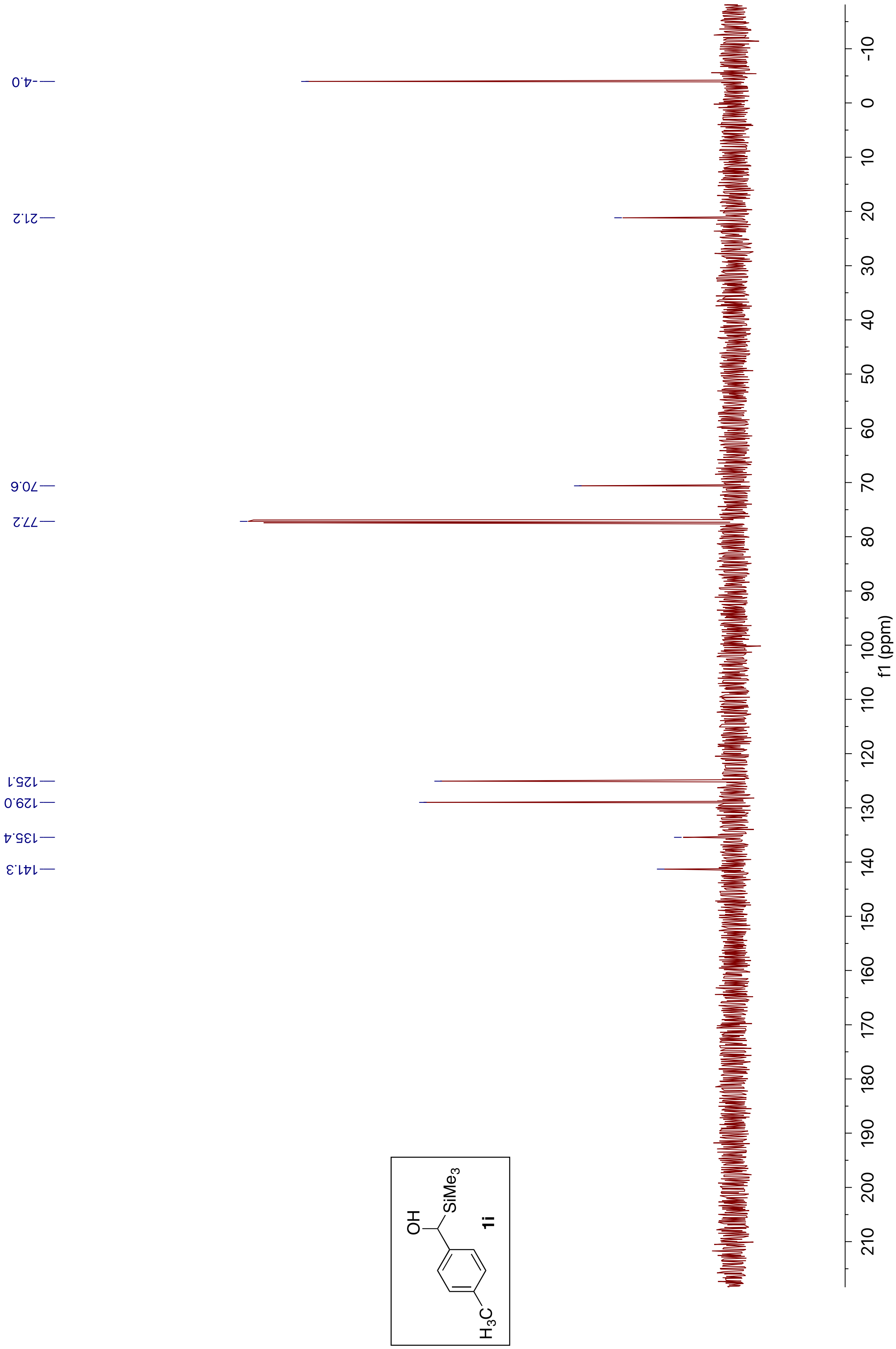

0.01
1.60
1.60
3.80
4.46
4.46
6.85
6.87
7.11
7.13
7.26
8.96
0.95
2.99
1.00
1.95
1.95
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OH
$SiMe_3$
MeO
1g

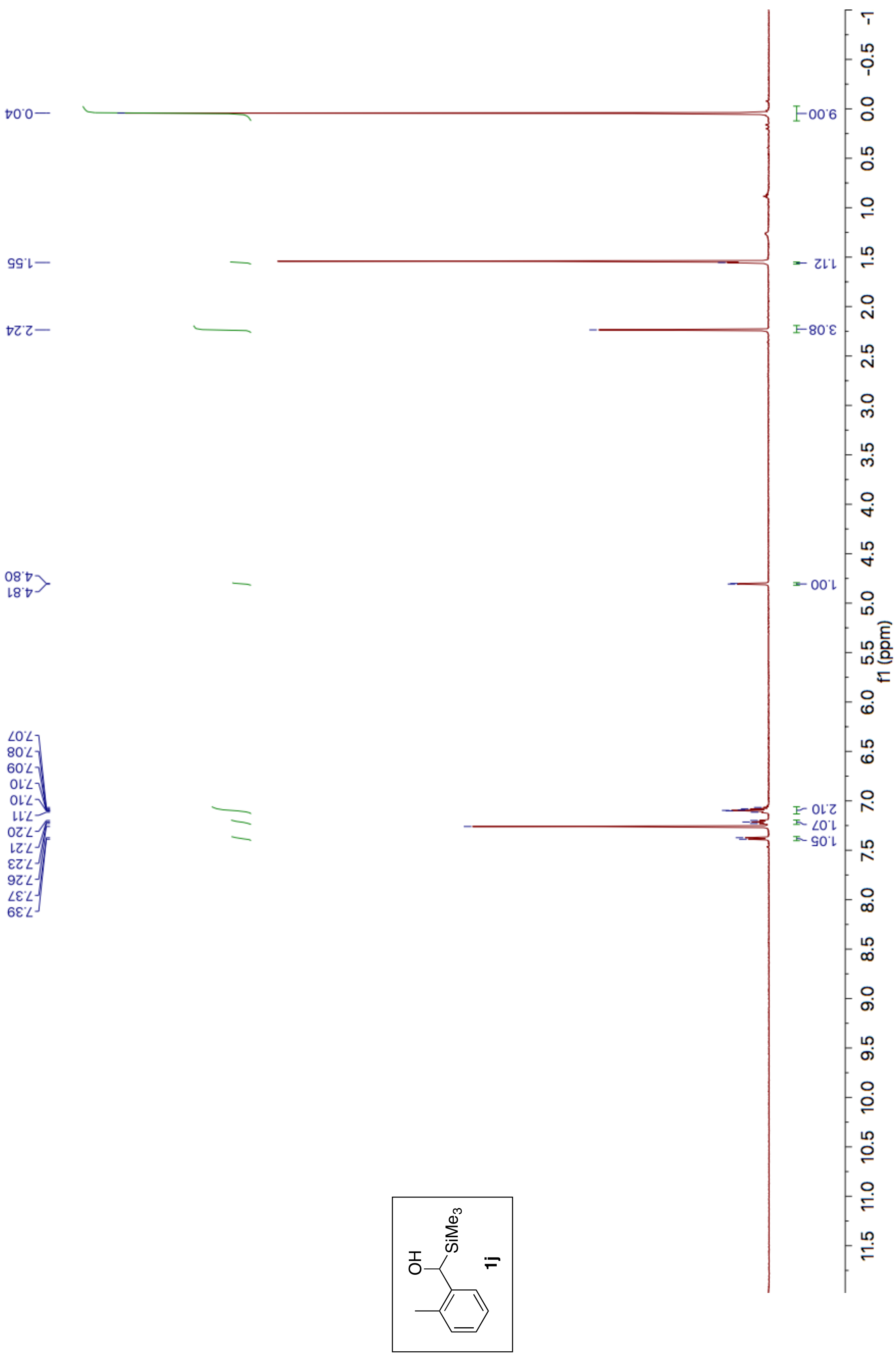

-0.18
0.02
0.98
1.60
2.34
4.64
4.65
7.12
7.26
3.00
3.01
9.10
1.02
3.02
1.00
4.02
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
OH
SiMe$_2$*t*Bu
Me
1h

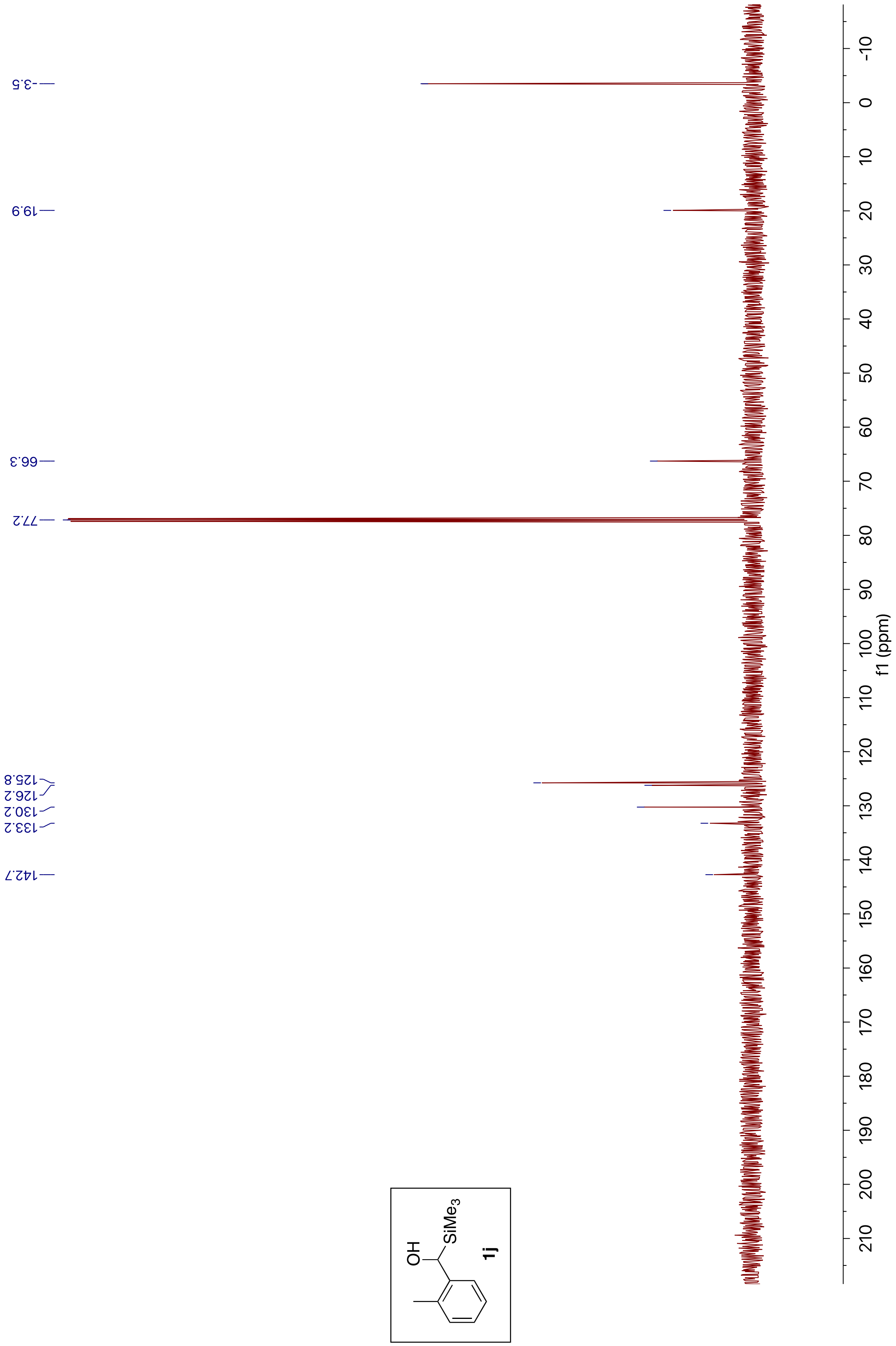

-9.2
-7.1
17.2
21.2
27.1
69.0
77.2
125.7
129.0
135.6
142.0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OH
$SiMe_2tBu$
Me

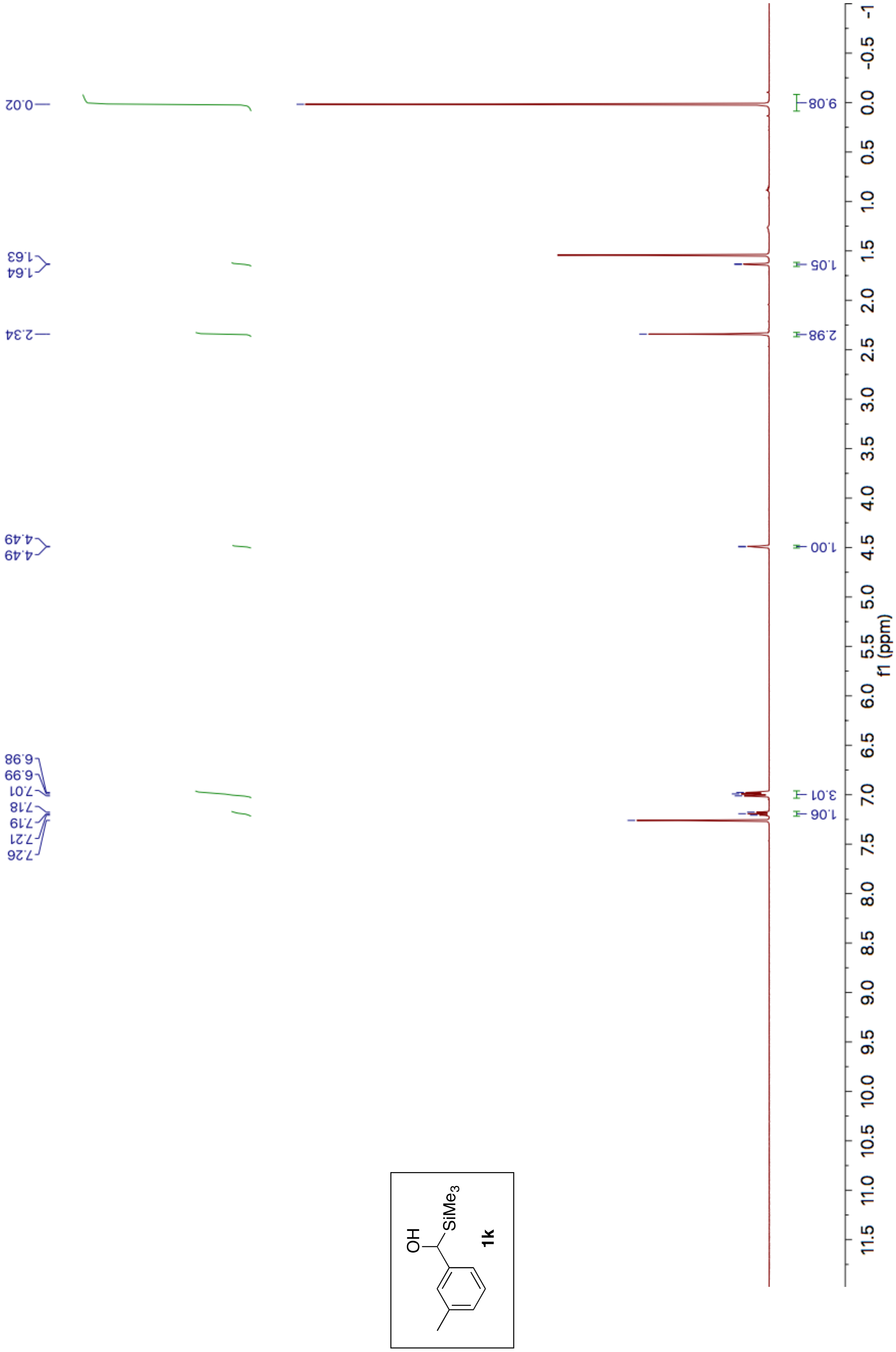
1h


0.01
1.64
2.33
4.49
7.07
7.09
7.11
7.13
7.26
9.27
0.97
3.06
1.00
2.06
2.04
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
OH
SiMe3
H3C
1i

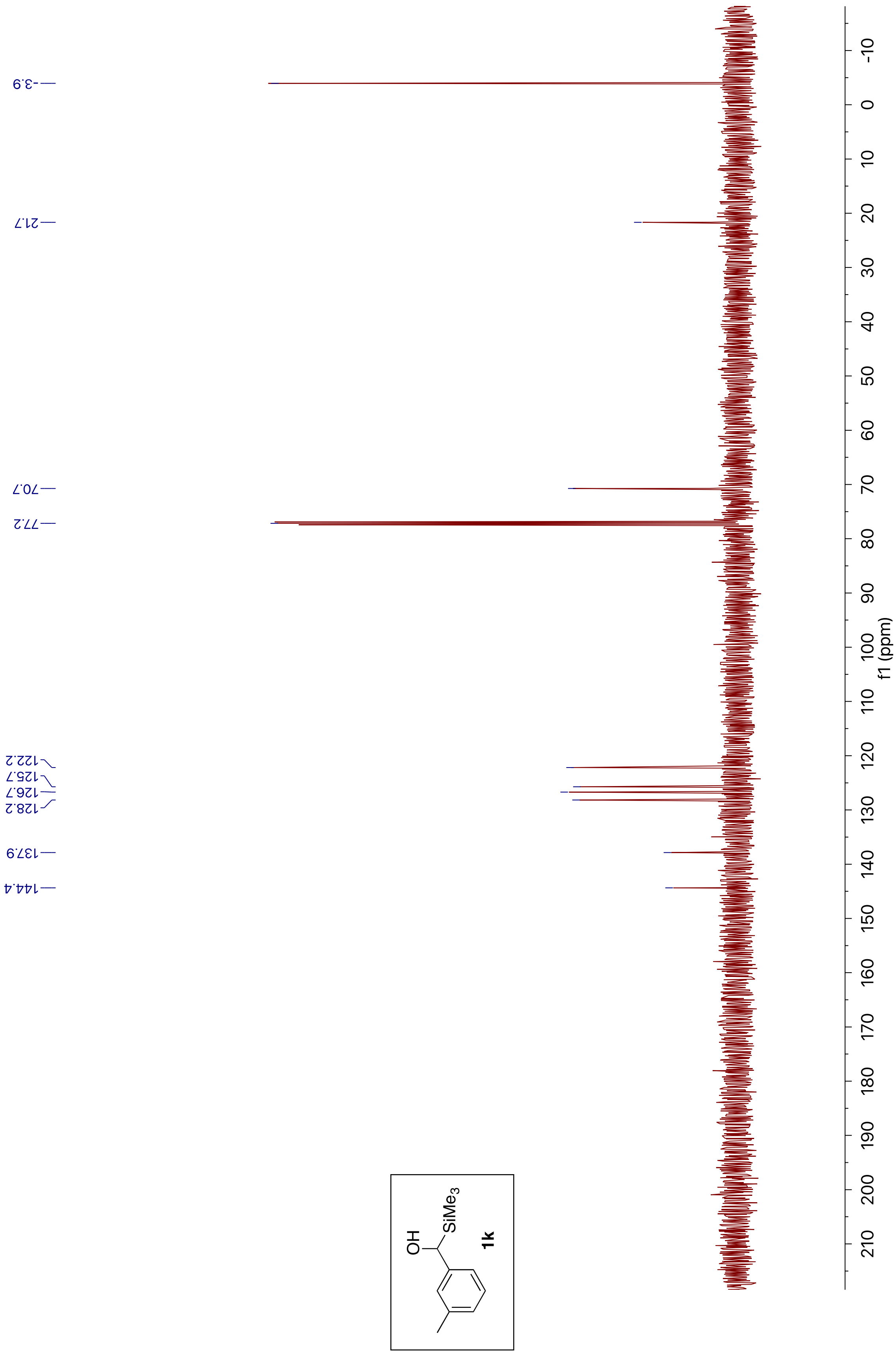

-4.0
21.2
70.6
77.2
125.1
129.0
135.4
141.3
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
OH
SiMe$_3$
H$_3$C
1i

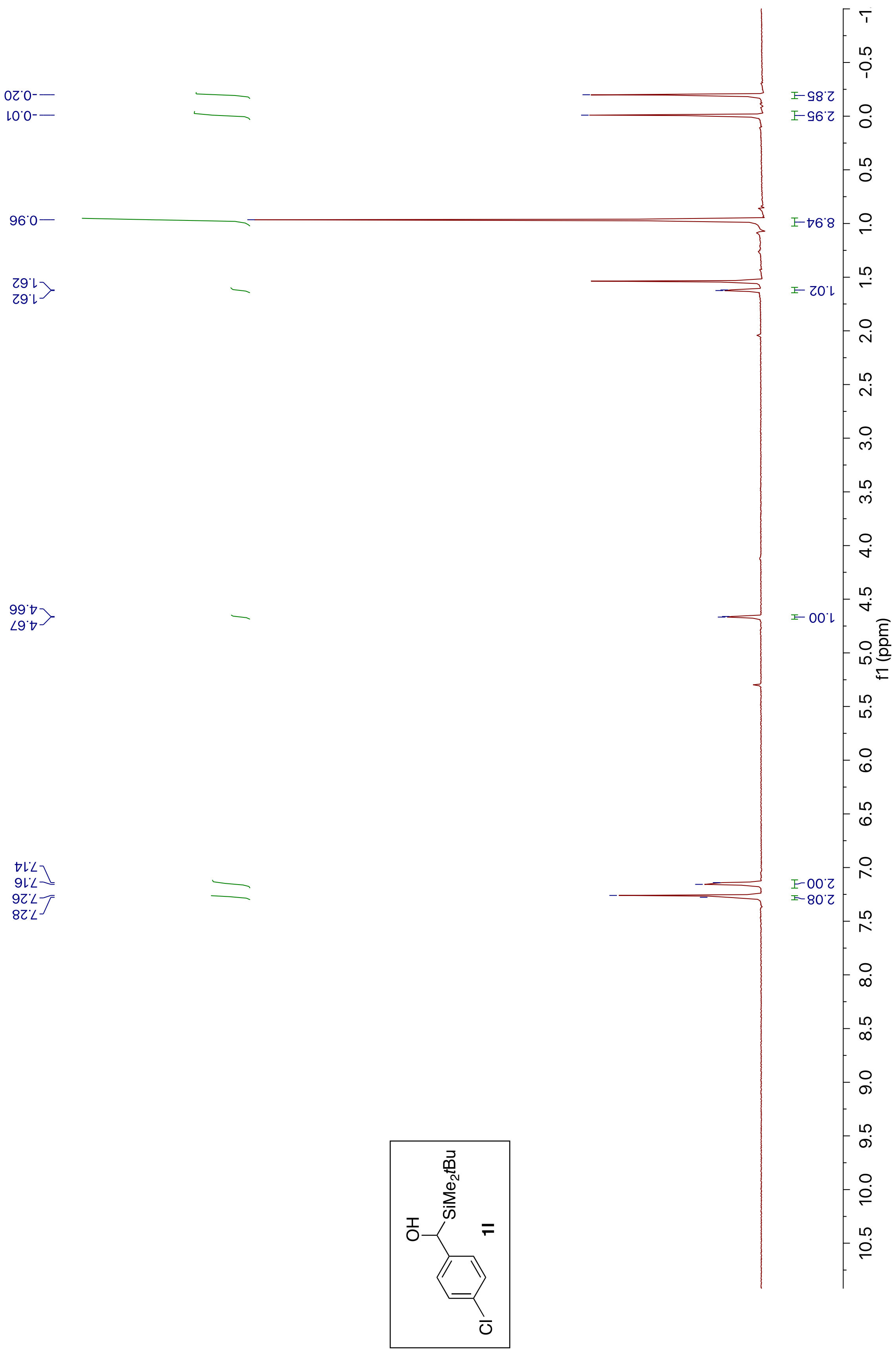

0.04
1.55
2.24
4.80
4.81
7.07
7.08
7.09
7.10
7.10
7.11
7.20
7.21
7.23
7.26
7.37
7.39
9.00
1.12
3.08
1.00
2.10
1.07
1.05
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OH
SiMe$_3$
1j

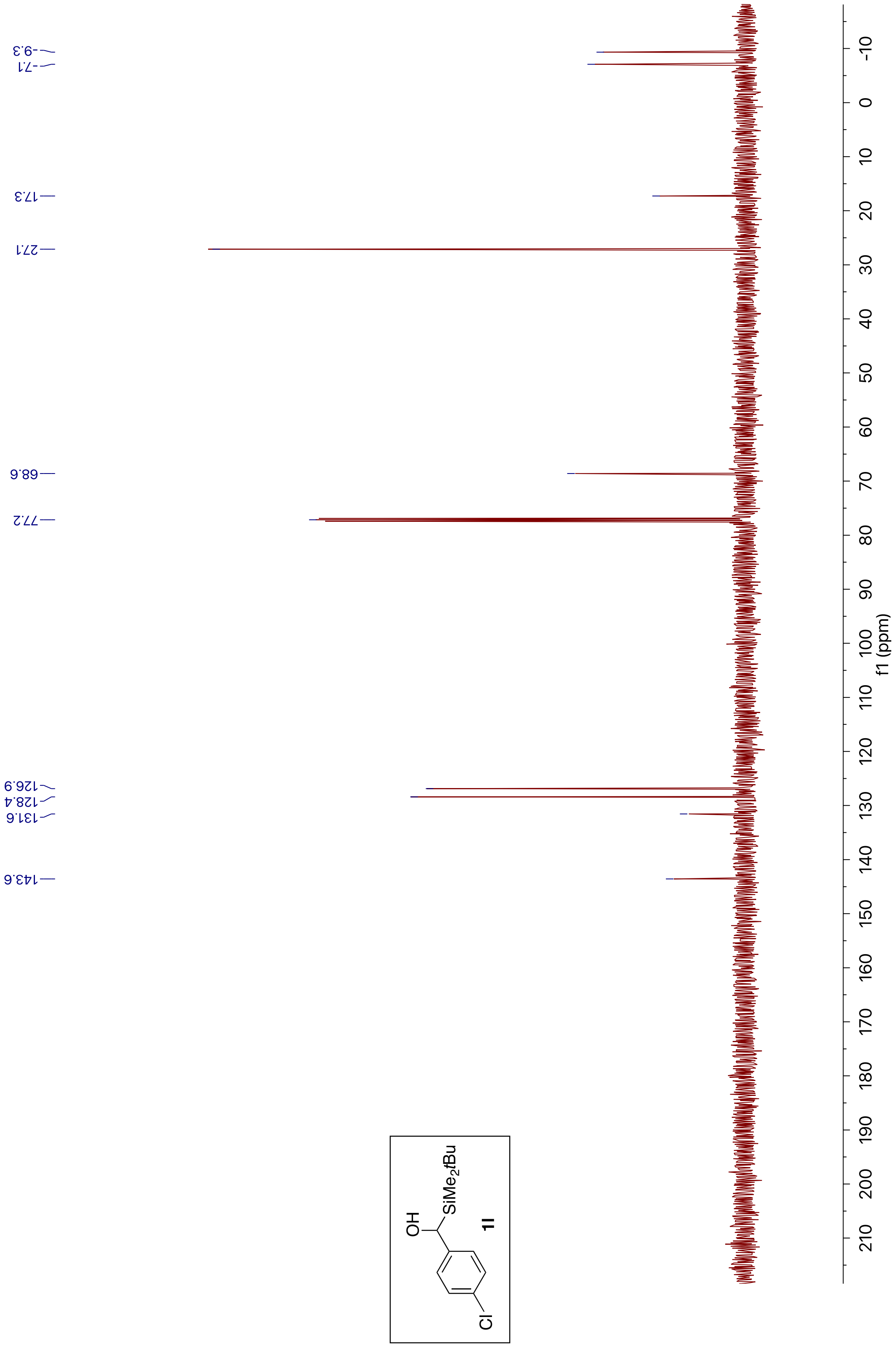

-3.5
19.9
66.3
77.2
125.8
126.2
130.2
133.2
142.7
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OH
SiMe$_3$
1j

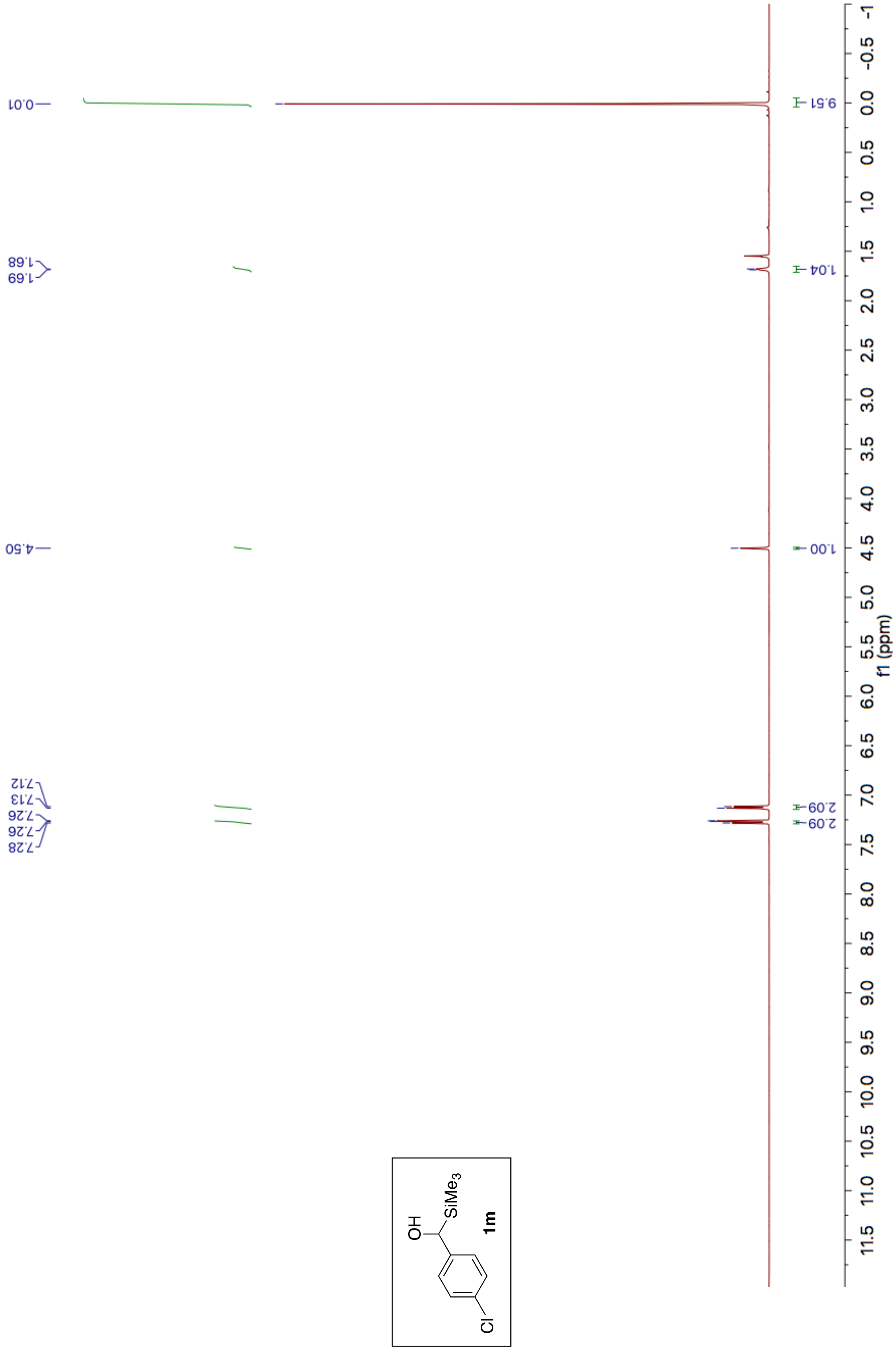

0.02
1.63
1.64
2.34
4.49
4.49
6.98
6.99
7.01
7.18
7.19
7.21
7.26
9.08
1.05
2.98
1.00
3.01
1.06
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OH
$SiMe_3$

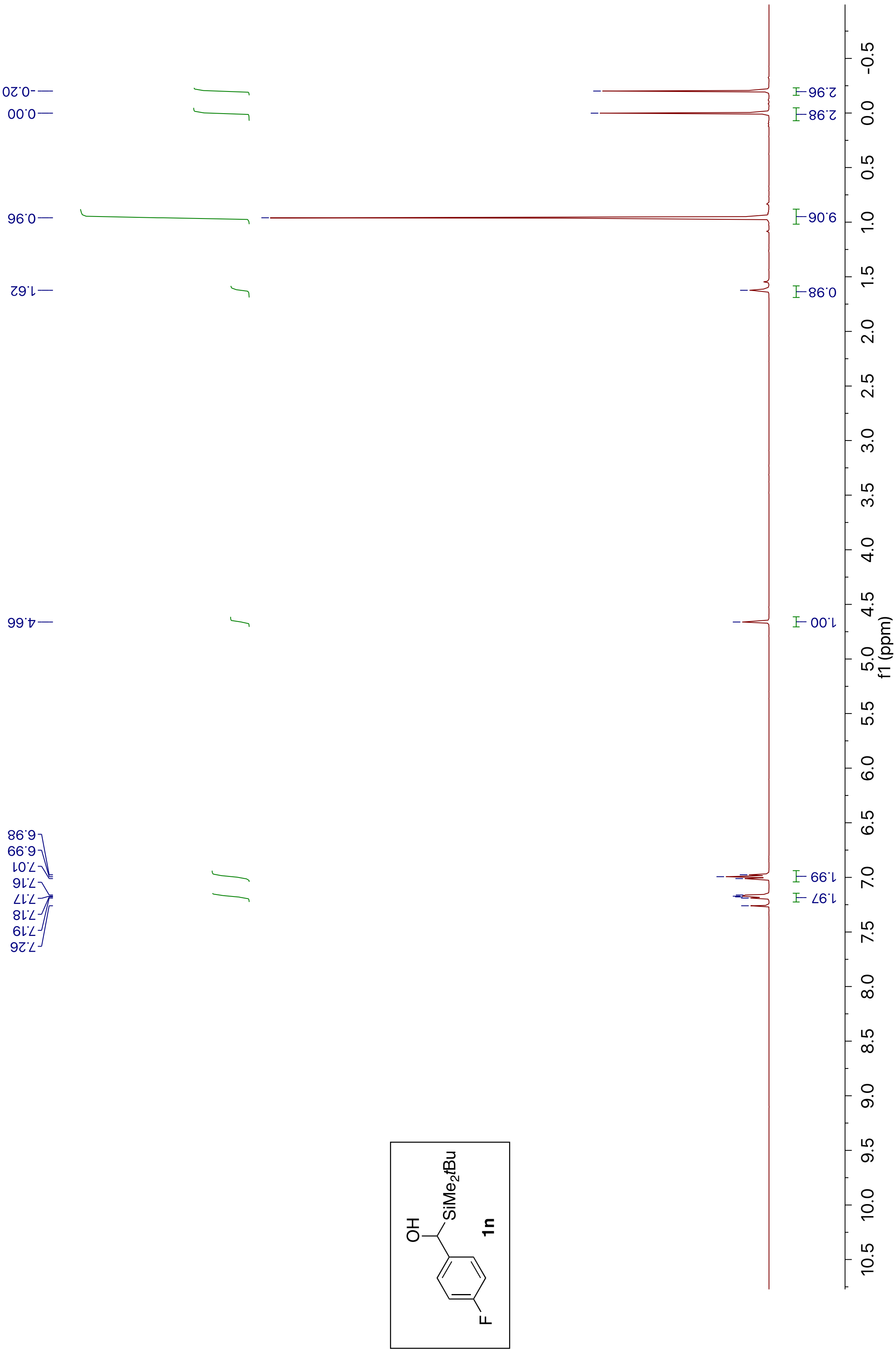
1k

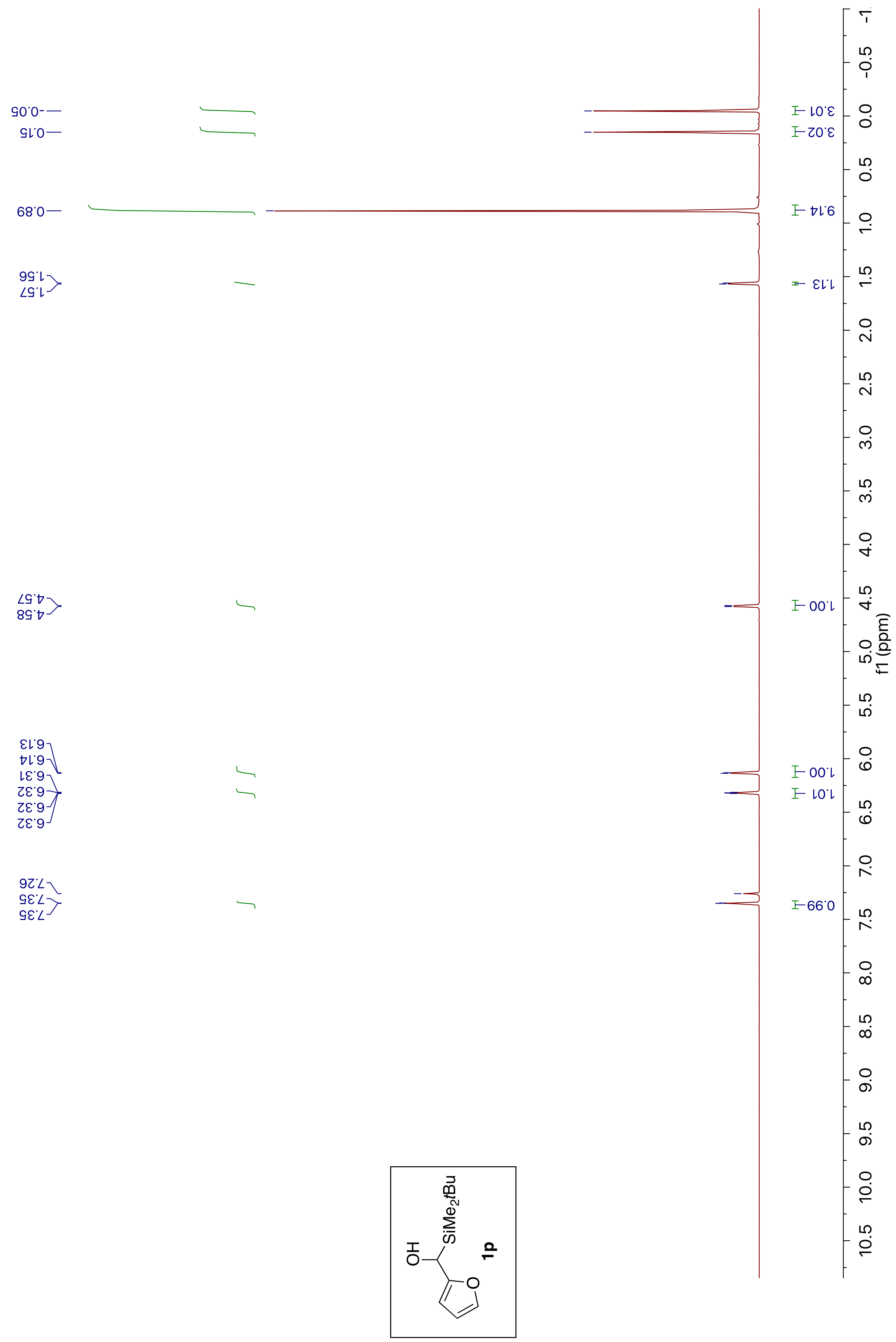

-3.9
21.7
70.7
77.2
122.2
125.7
126.7
128.2
137.9
144.4
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OH
SiMe3
1k

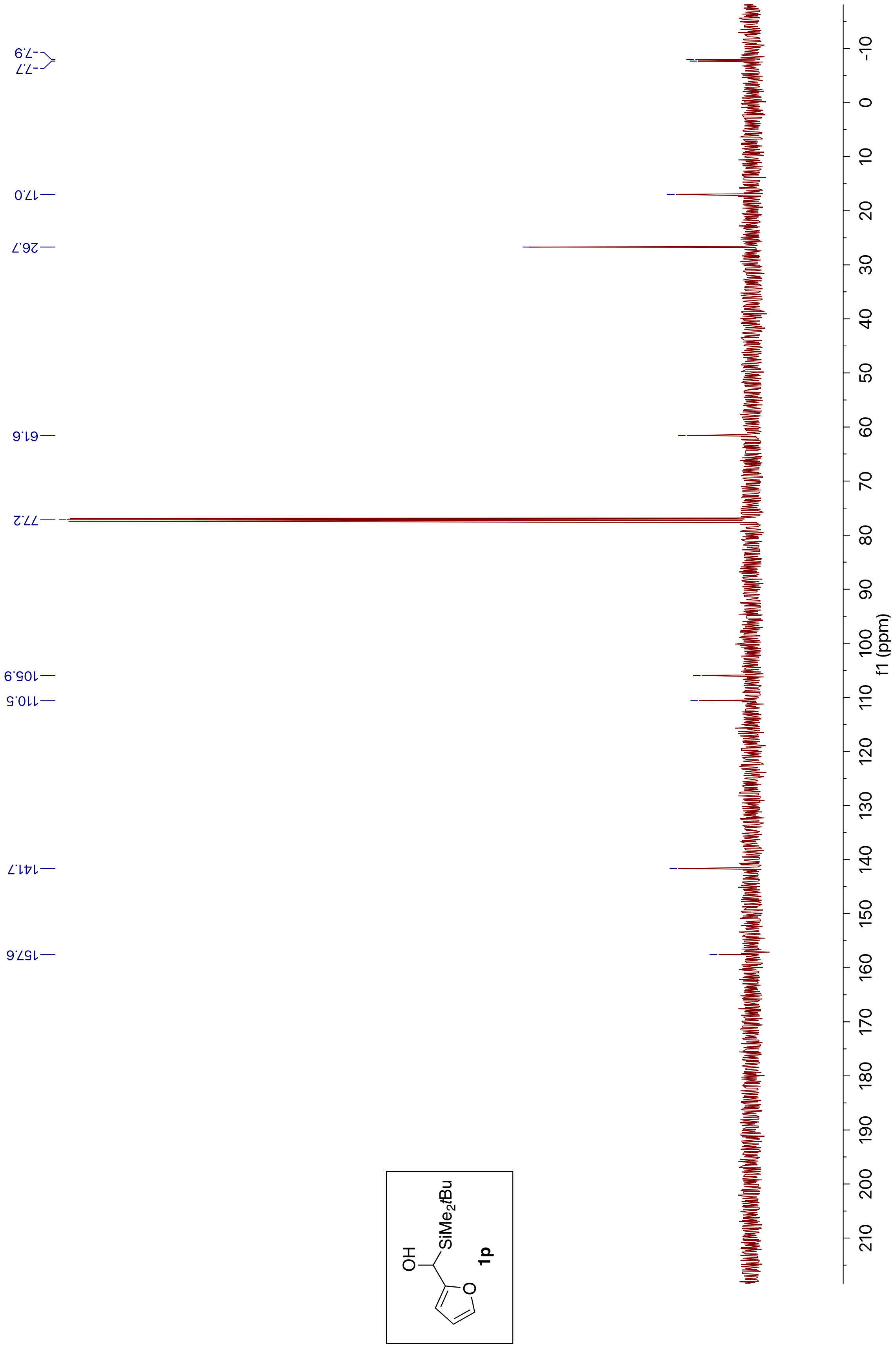

-0.20
-0.01
0.96
1.62
1.62
4.66
4.67
7.14
7.16
7.26
7.28
2.85
2.95
8.94
1.02
1.00
2.00
2.08
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
OH
SiMe2tBu
Cl
1l


-9.3
-7.1
17.3
27.1
68.6
77.2
126.9
128.4
131.6
143.6
OH
SiMe2tBu
Cl
1l
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

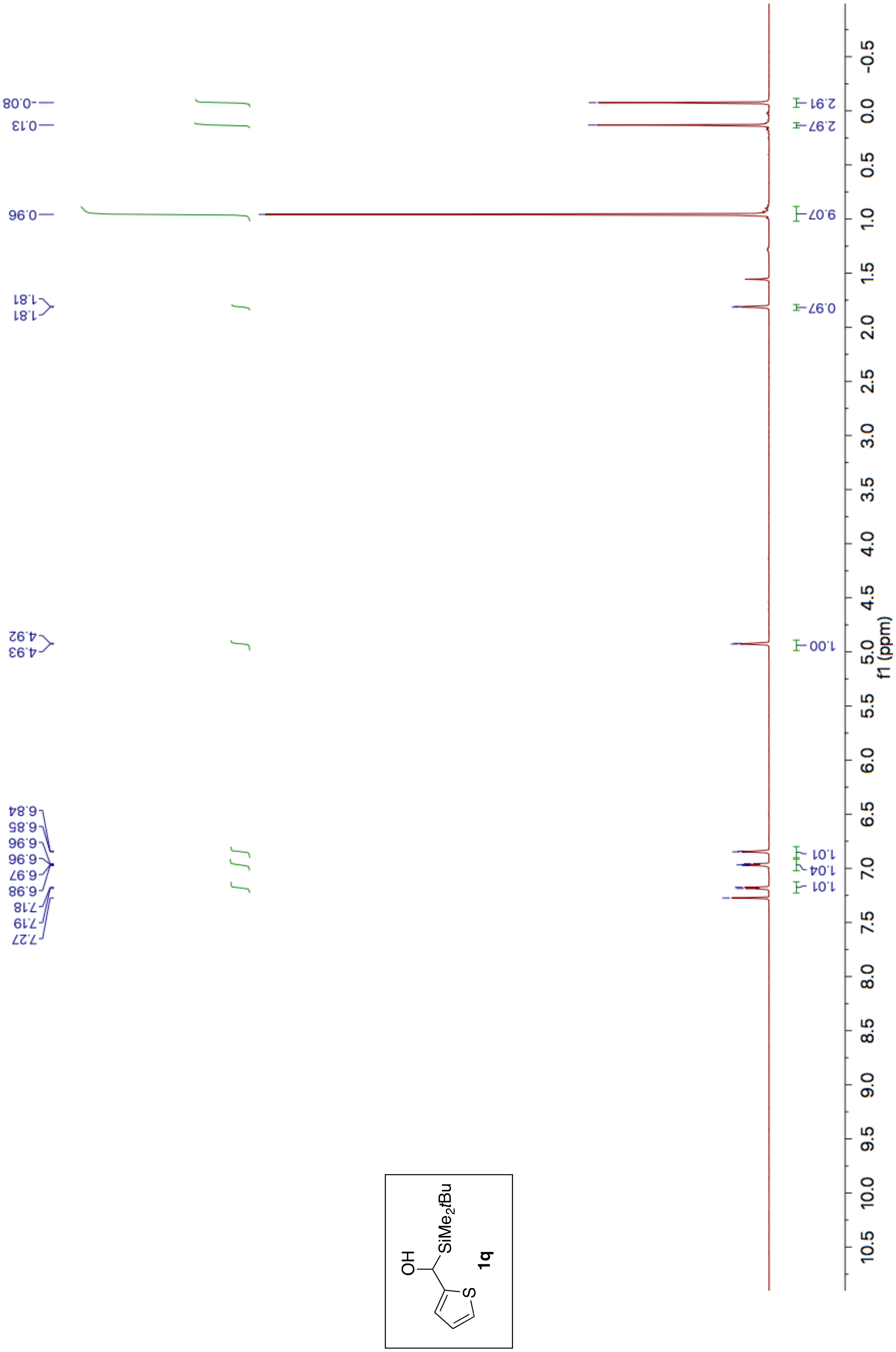

0.01
1.68
1.69
4.50
7.12
7.13
7.26
7.26
7.28
9.51
1.04
1.00
2.09
2.09
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OH
SiMe$_3$
Cl
1m

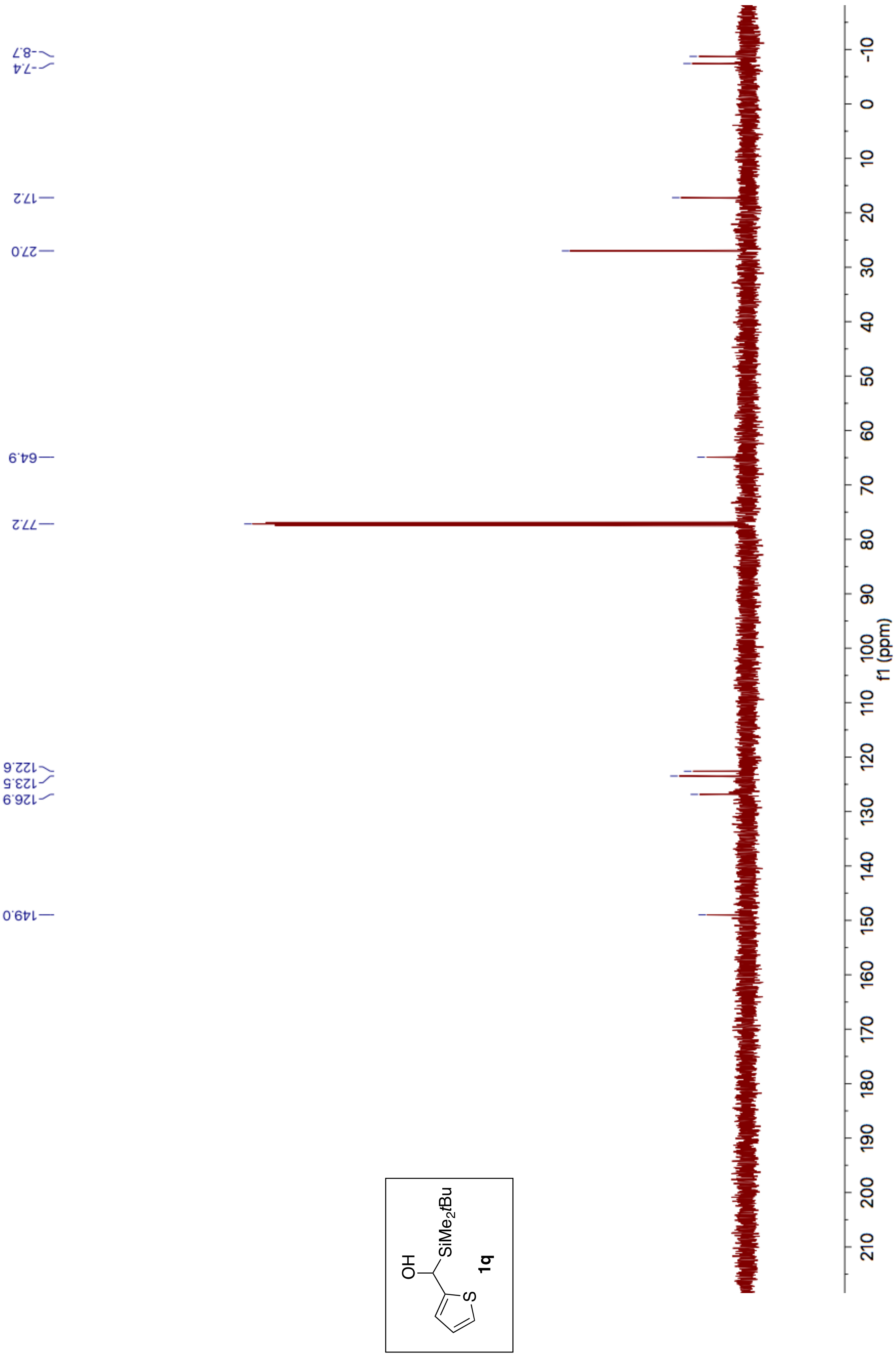

7.26
7.19
7.18
7.17
7.16
7.01
6.99
6.98
4.66
1.62
0.96
0.00
-0.20
1.97
1.99
1.00
0.98
9.06
2.98
2.96
f1 (ppm)
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
OH
$SiMe_2tBu$
F
1n


-0.05
0.15
0.89
1.56
1.57
4.57
4.58
6.13
6.14
6.31
6.32
6.32
6.32
7.26
7.35
7.35
3.01
3.02
9.14
1.13
1.00
1.00
1.01
0.99
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
OH
SiMe2tBu
O
1p

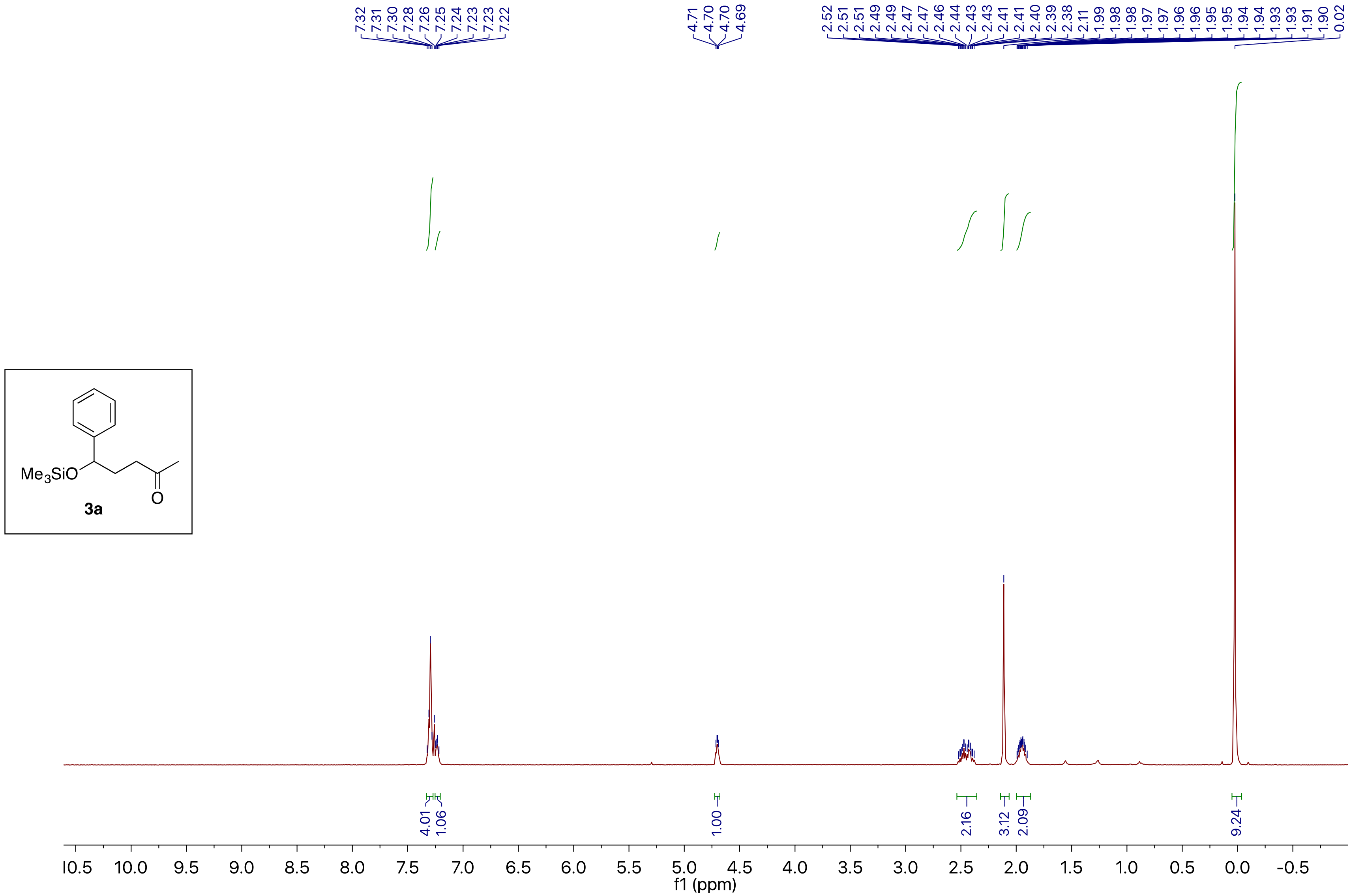

-7.7
-7.9
17.0
26.7
61.6
77.2
105.9
110.5
141.7
157.6
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OH
SiMe2tBu
O

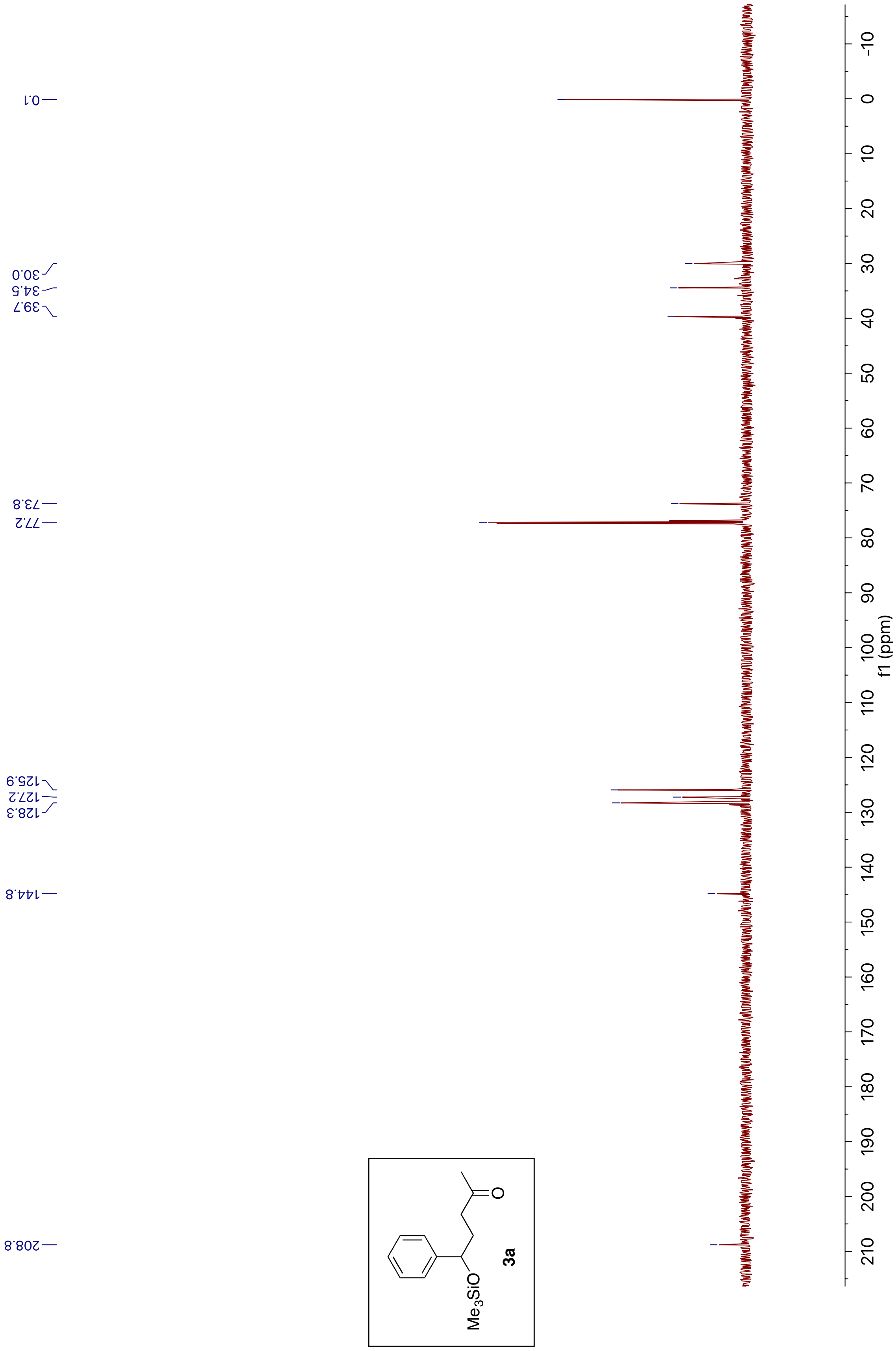
1p

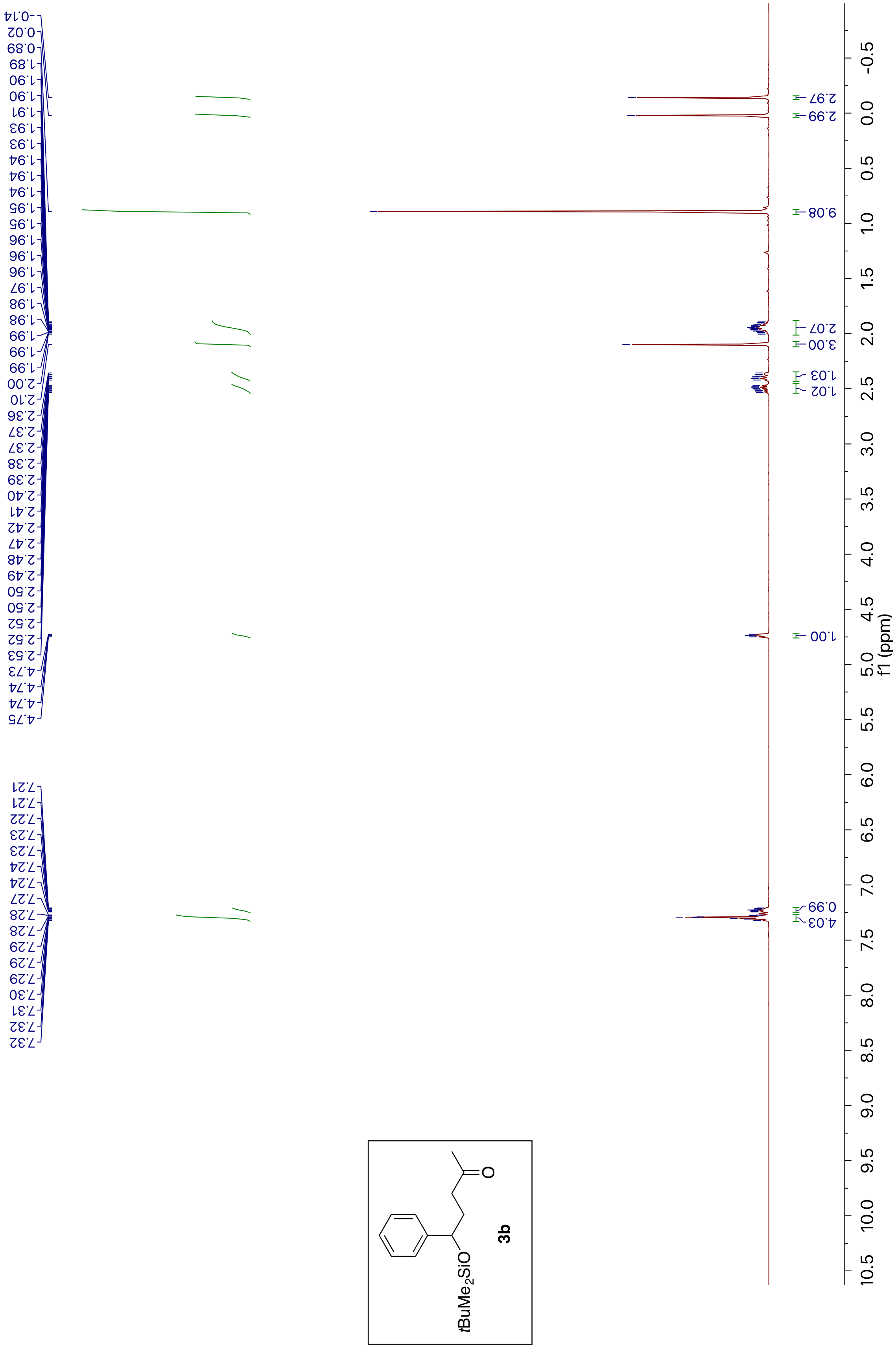

-0.08
0.13
0.96
1.81
1.81
4.92
4.93
6.84
6.85
6.96
6.96
6.97
6.98
7.18
7.19
7.27
2.91
2.97
9.07
0.97
1.00
1.01
1.04
1.01
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OH
SiMe$_2$*t*Bu
S
1q

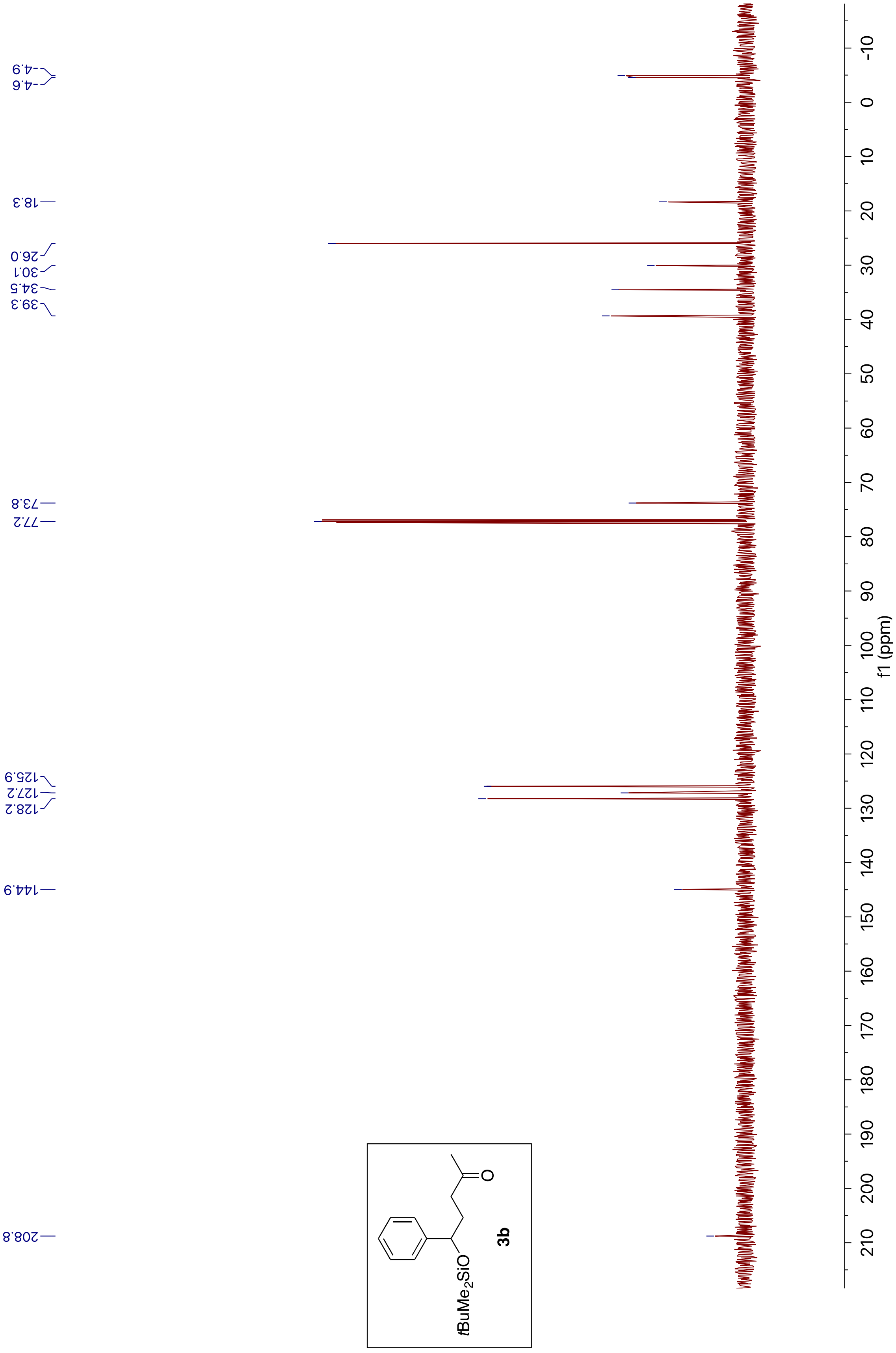

-8.7
-7.4
17.2
27.0
64.9
77.2
122.6
123.5
126.9
149.0
OH
SiMe2tBu
S
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

1q

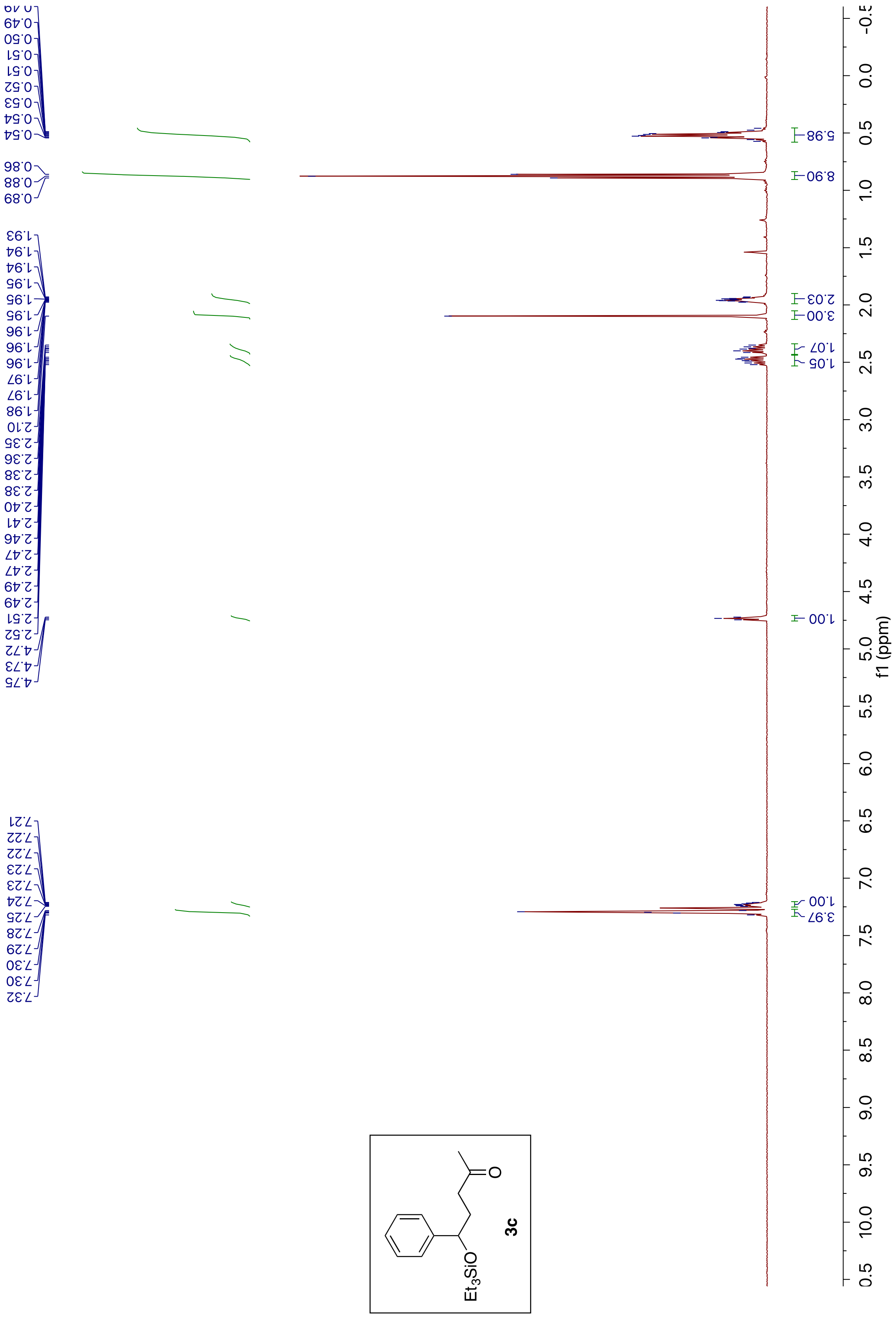

7.32
7.31
7.30
7.28
7.26
7.25
7.24
7.23
7.23
7.22
4.71
4.70
4.70
4.69
2.52
2.51
2.51
2.49
2.49
2.47
2.47
2.46
2.44
2.43
2.43
2.41
2.41
2.40
2.39
2.38
2.11
1.99
1.98
1.98
1.97
1.97
1.96
1.96
1.95
1.95
1.94
1.94
1.93
1.93
1.91
1.90
0.02
Me3SiO
O
3a
4.01
1.06
1.00
2.16
3.12
2.09
9.24
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

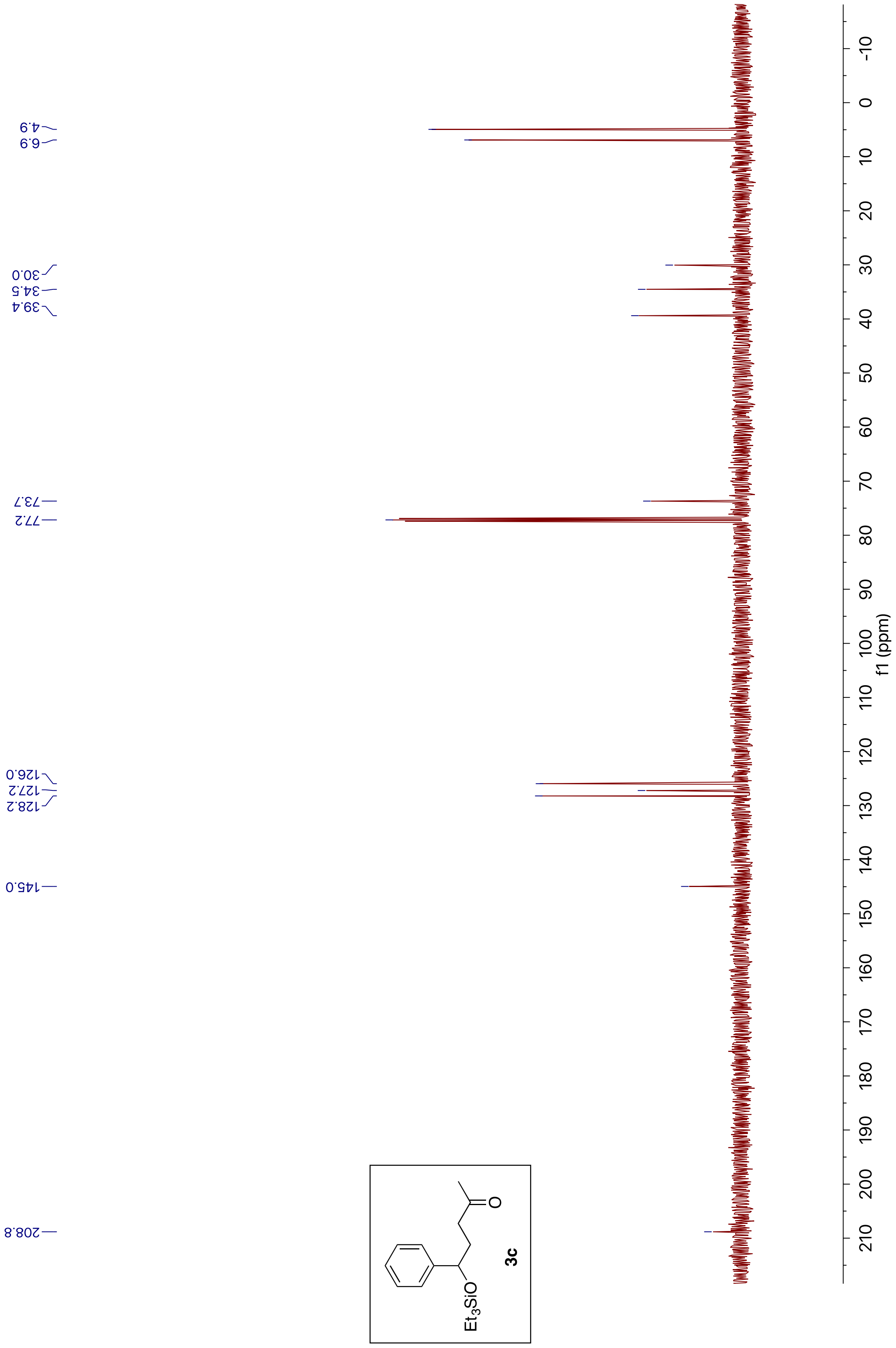

208.8
144.8
128.3
127.2
125.9
77.2
73.8
39.7
34.5
30.0
0.1
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Me$_3$SiO
O
3a

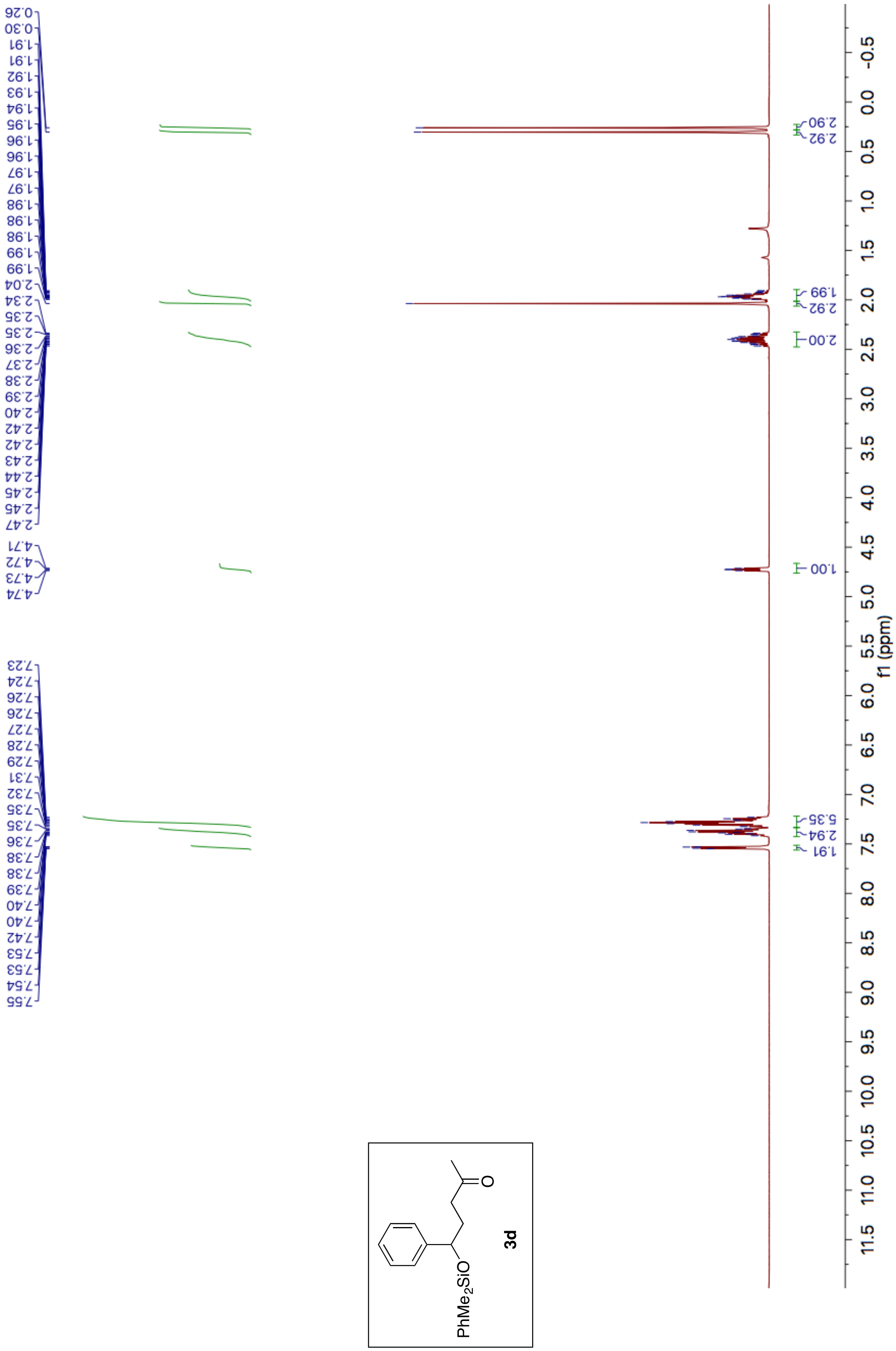

-0.14
0.02
0.89
1.89
1.90
1.90
1.91
1.93
1.93
1.94
1.94
1.94
1.95
1.95
1.96
1.96
1.96
1.97
1.98
1.98
1.99
1.99
1.99
2.00
2.10
2.36
2.37
2.37
2.38
2.39
2.40
2.41
2.42
2.47
2.48
2.49
2.50
2.50
2.52
2.52
2.53
4.73
4.74
4.74
4.75
7.21
7.21
7.22
7.23
7.23
7.24
7.24
7.27
7.28
7.28
7.29
7.29
7.29
7.30
7.31
7.32
7.32
2.97
2.99
9.08
2.07
3.00
1.03
1.02
1.00
0.99
4.03
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
tBuMe2SiO
O
3b

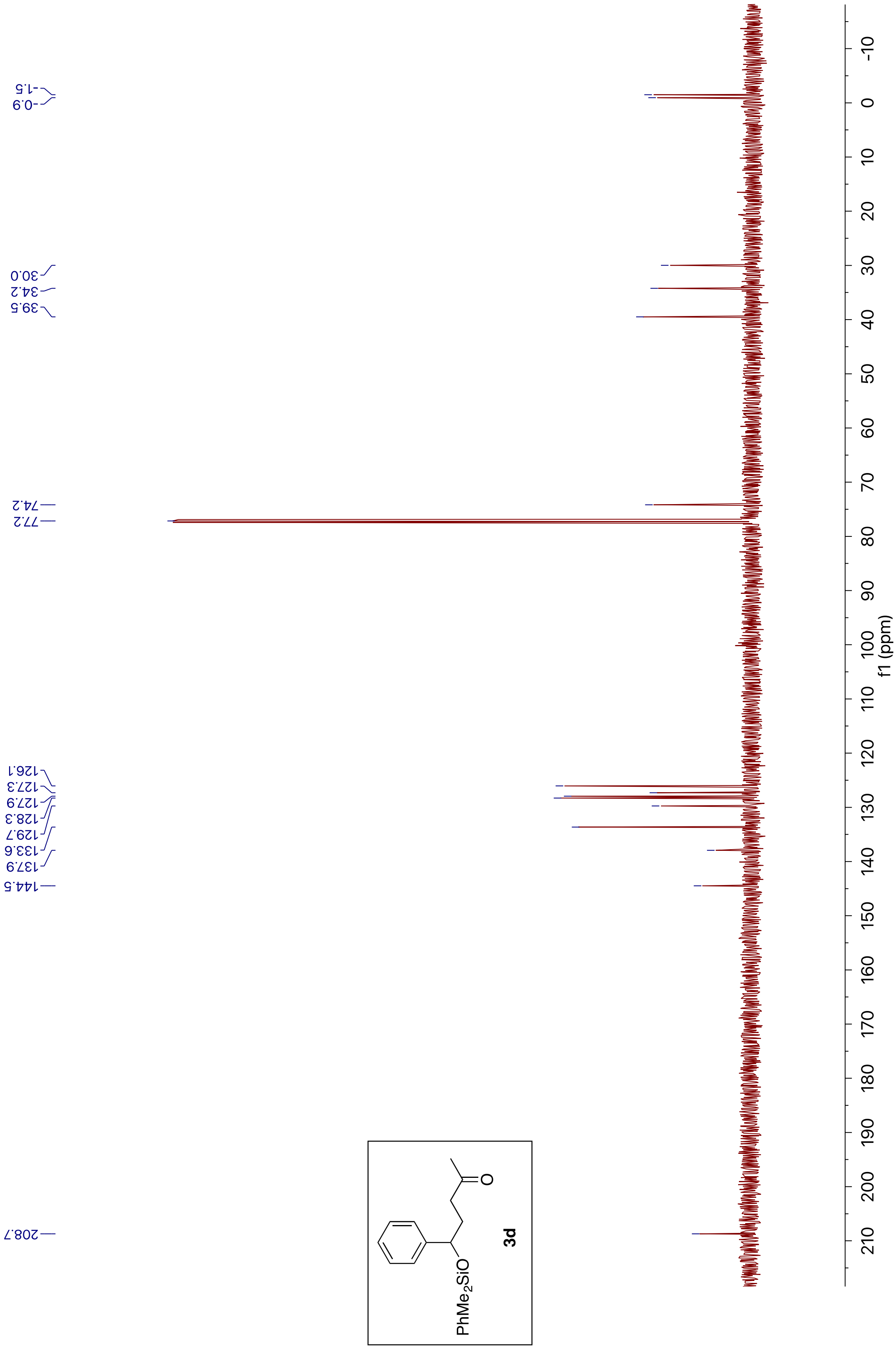

-4.9
-4.6
18.3
26.0
30.1
34.5
39.3
73.8
77.2
125.9
127.2
128.2
144.9
208.8
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
tBuMe2SiO
O

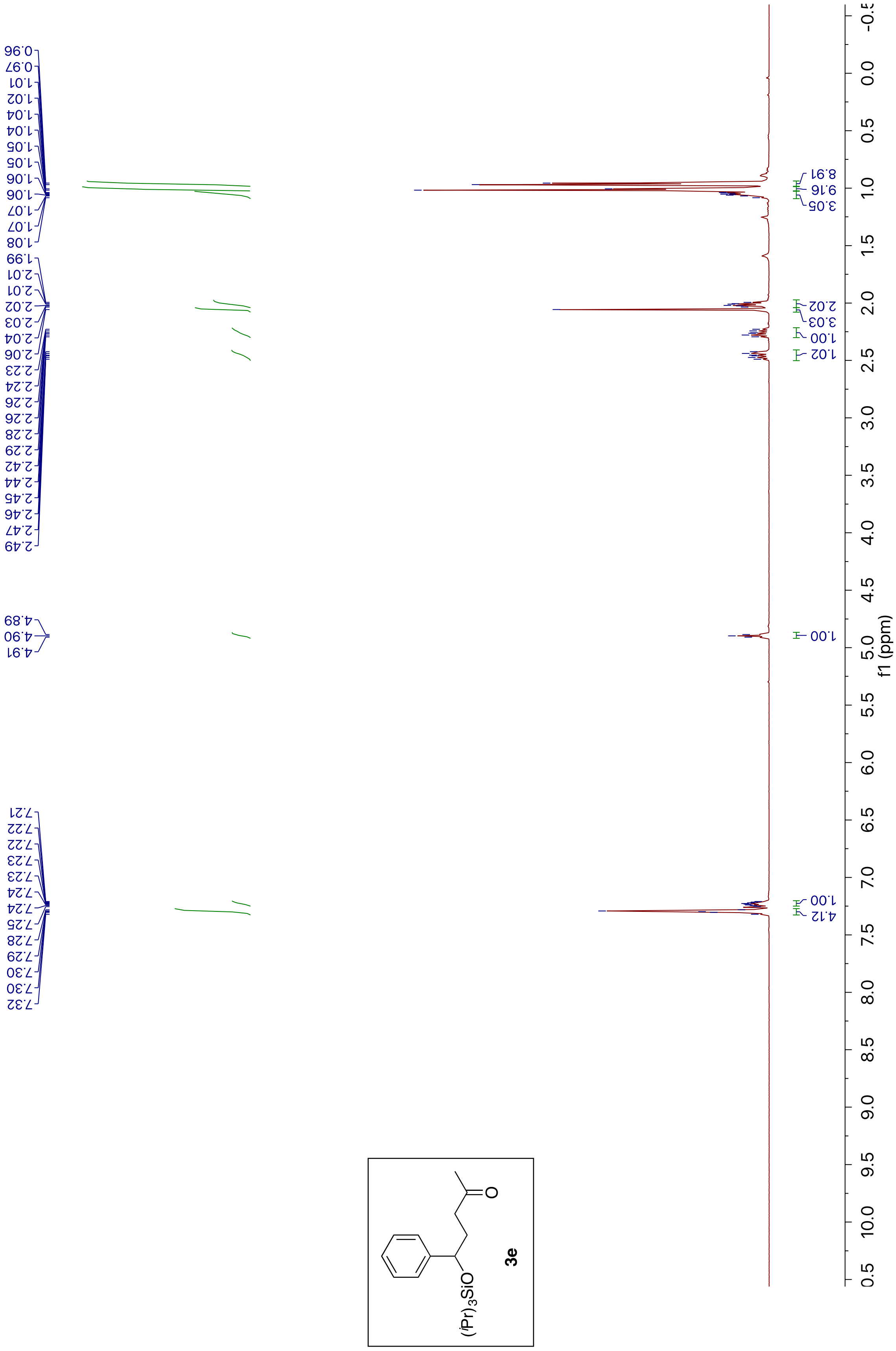
3b

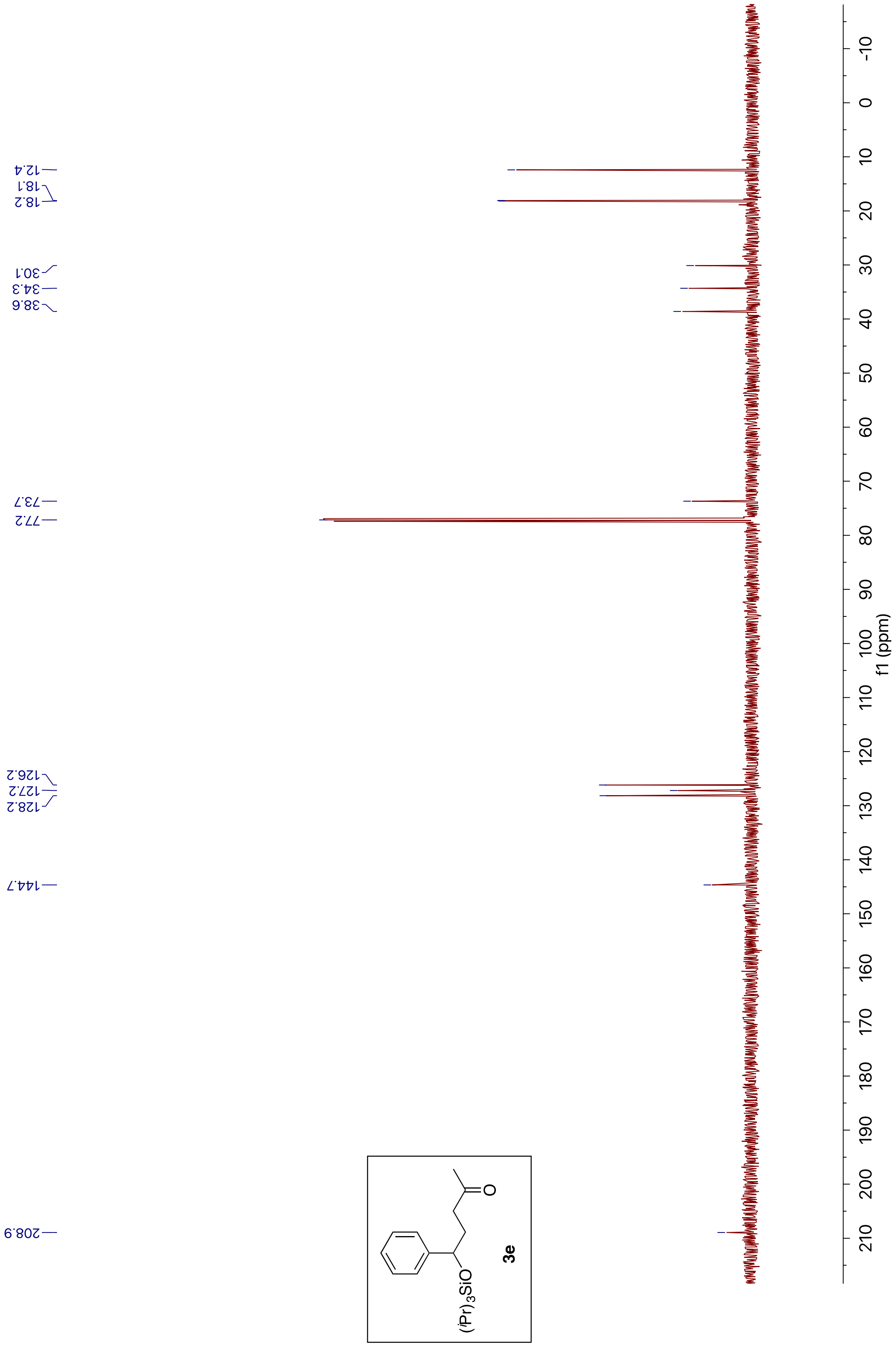

0.49
0.49
0.50
0.51
0.51
0.52
0.53
0.54
0.54
0.86
0.88
0.89
1.93
1.94
1.94
1.95
1.95
1.95
1.96
1.96
1.96
1.96
1.97
1.97
1.98
2.10
2.35
2.36
2.38
2.38
2.40
2.41
2.46
2.47
2.47
2.49
2.49
2.51
2.52
4.72
4.73
4.75
7.21
7.22
7.22
7.23
7.23
7.24
7.25
7.28
7.29
7.30
7.30
7.32
5.98
8.90
2.03
3.00
1.07
1.05
1.00
1.00
3.97
f1 (ppm)
Et$_3$SiO
O
3c

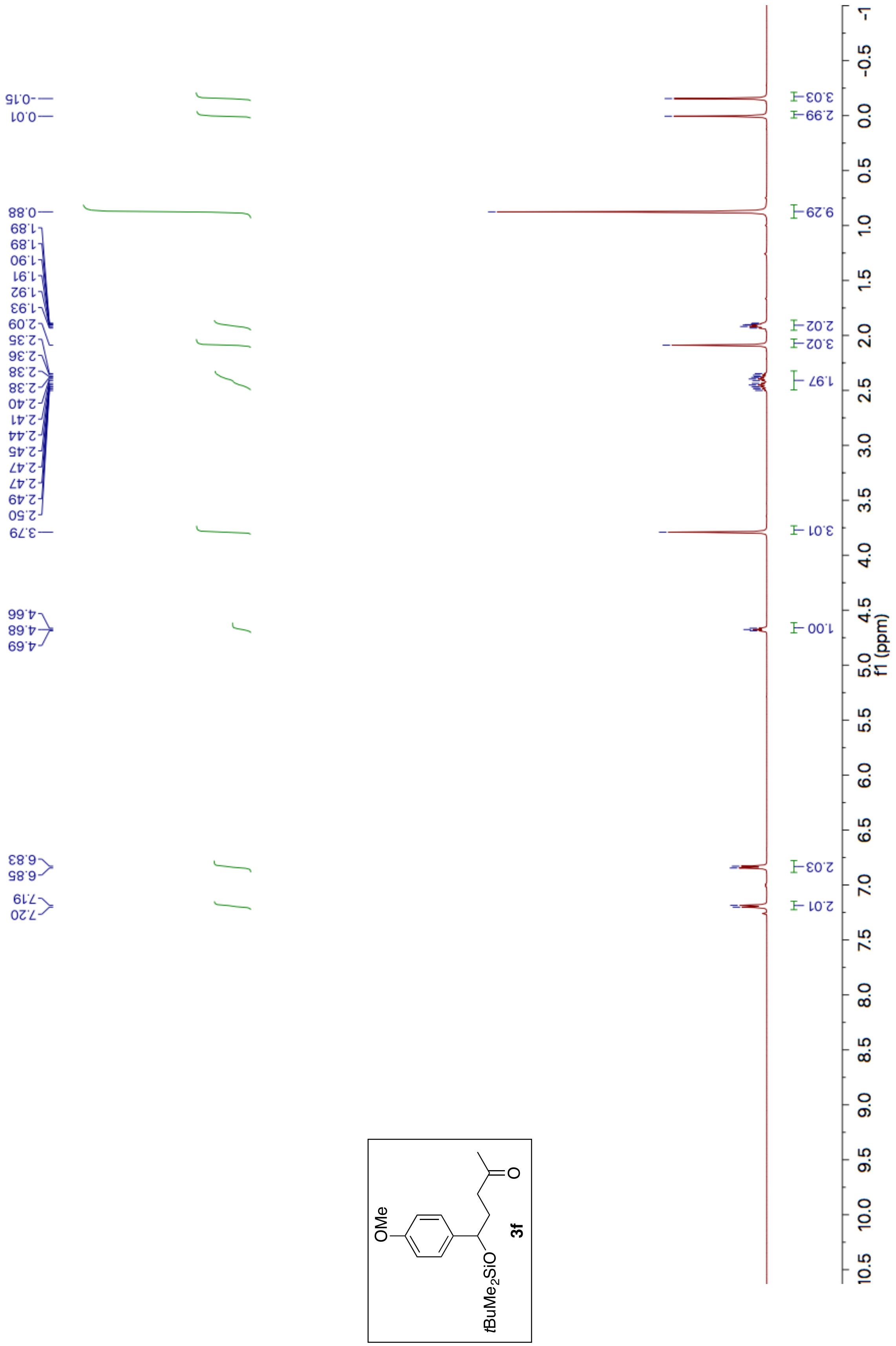

4.9
6.9
30.0
34.5
39.4
73.7
77.2
126.0
127.2
128.2
145.0
208.8
Et$_3$SiO
O
3c
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)


7.55
7.54
7.53
7.53
7.42
7.40
7.40
7.39
7.38
7.38
7.36
7.35
7.35
7.32
7.31
7.29
7.28
7.27
7.26
7.26
7.24
7.23
4.74
4.73
4.72
4.71
2.47
2.45
2.45
2.44
2.43
2.42
2.42
2.40
2.39
2.38
2.37
2.36
2.35
2.35
2.34
2.04
1.99
1.99
1.98
1.98
1.98
1.97
1.97
1.96
1.96
1.96
1.95
1.94
1.93
1.92
1.91
1.91
0.30
0.26
1.91
2.94
5.35
1.00
2.00
2.92
1.99
2.92
2.90
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
PhMe$_2$SiO
O
3d

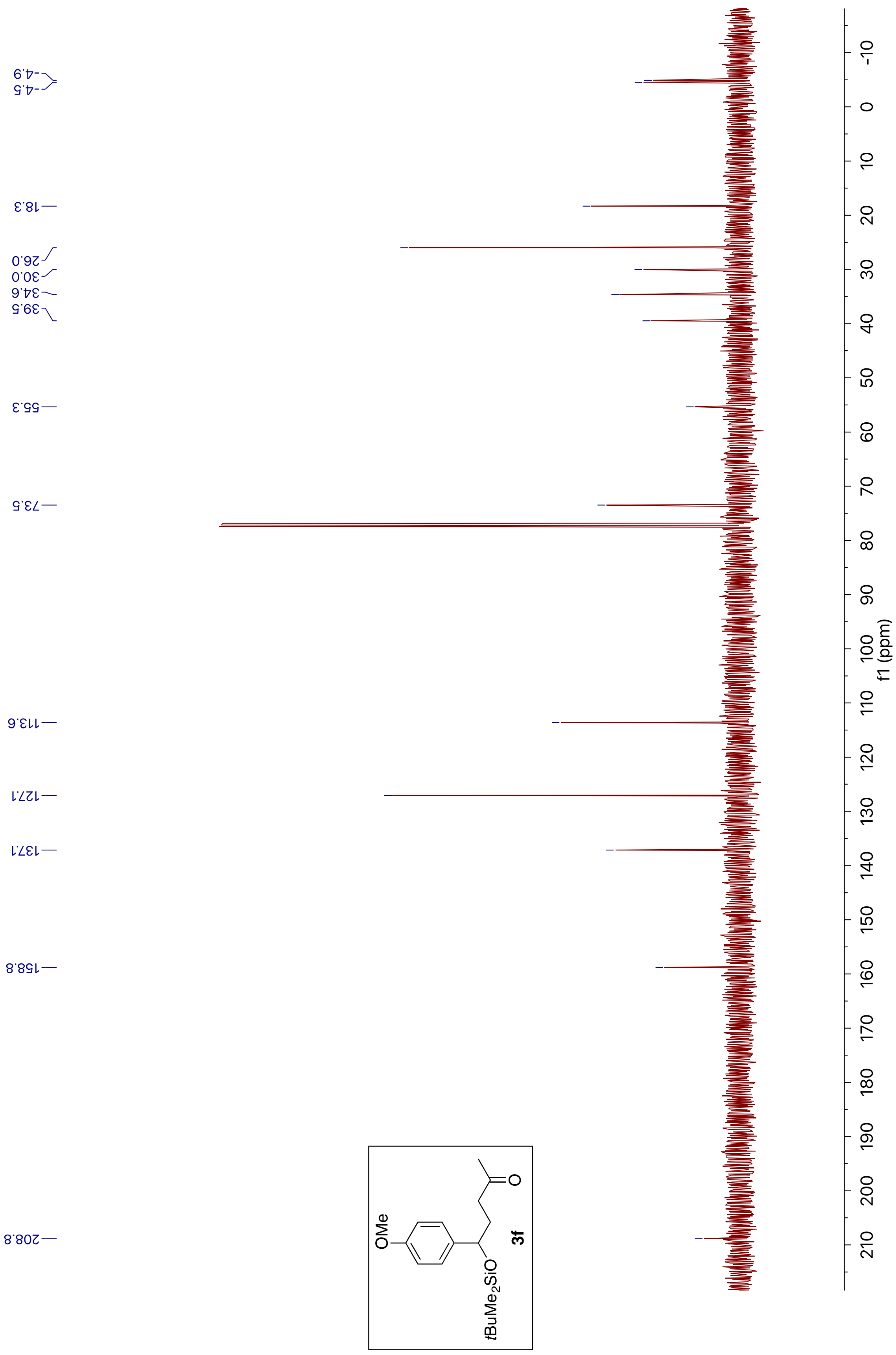

-1.5
-0.9
30.0
34.2
39.5
74.2
77.2
126.1
127.3
127.9
128.3
129.7
133.6
137.9
144.5
208.7
PhMe$_2$SiO
O
3d
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

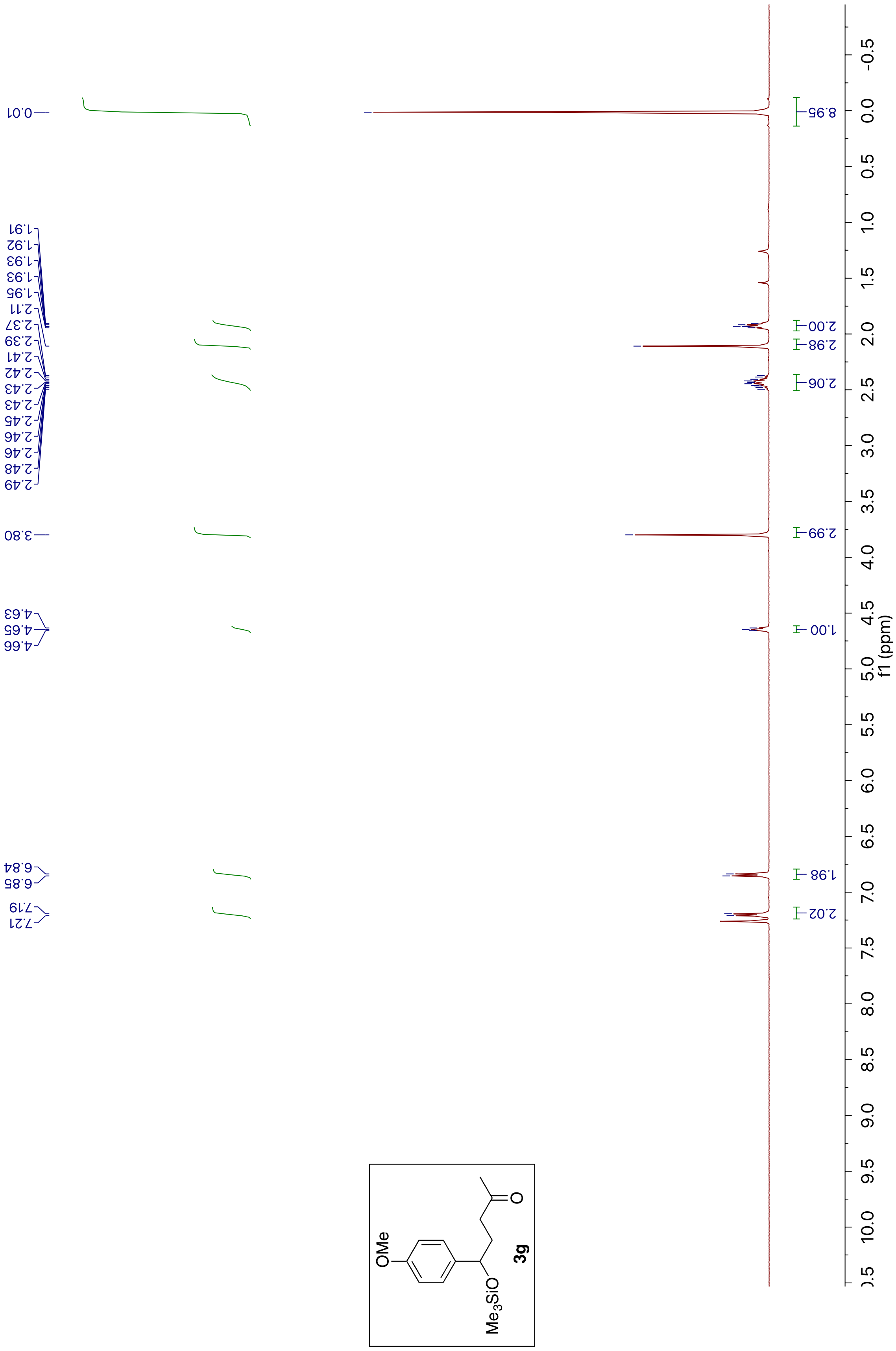

0.96
0.97
1.01
1.02
1.04
1.04
1.05
1.05
1.06
1.06
1.07
1.07
1.08
1.99
2.01
2.01
2.02
2.03
2.04
2.06
2.23
2.24
2.26
2.26
2.28
2.29
2.42
2.44
2.45
2.46
2.47
2.49
4.89
4.90
4.91
7.21
7.22
7.22
7.23
7.23
7.24
7.24
7.25
7.28
7.29
7.30
7.30
7.32
8.91
9.16
3.05
2.02
3.03
1.00
1.02
1.00
1.00
4.12
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0.5
f1 (ppm)
(iPr)3SiO
O
3e

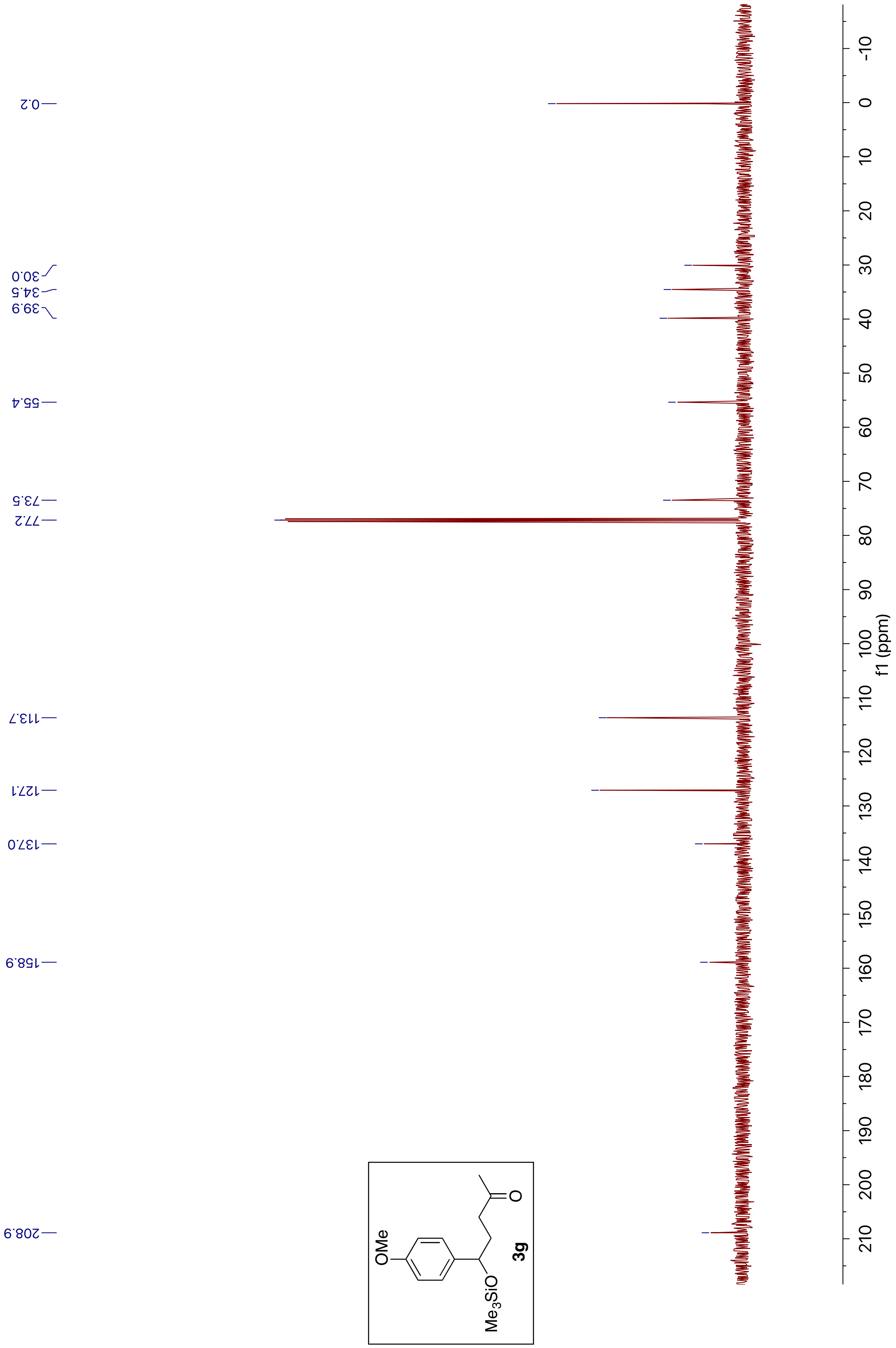

12.4
18.1
18.2
30.1
34.3
38.6
73.7
77.2
126.2
127.2
128.2
144.7
208.9
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
(^{i}Pr)$_3$SiO
O
3e

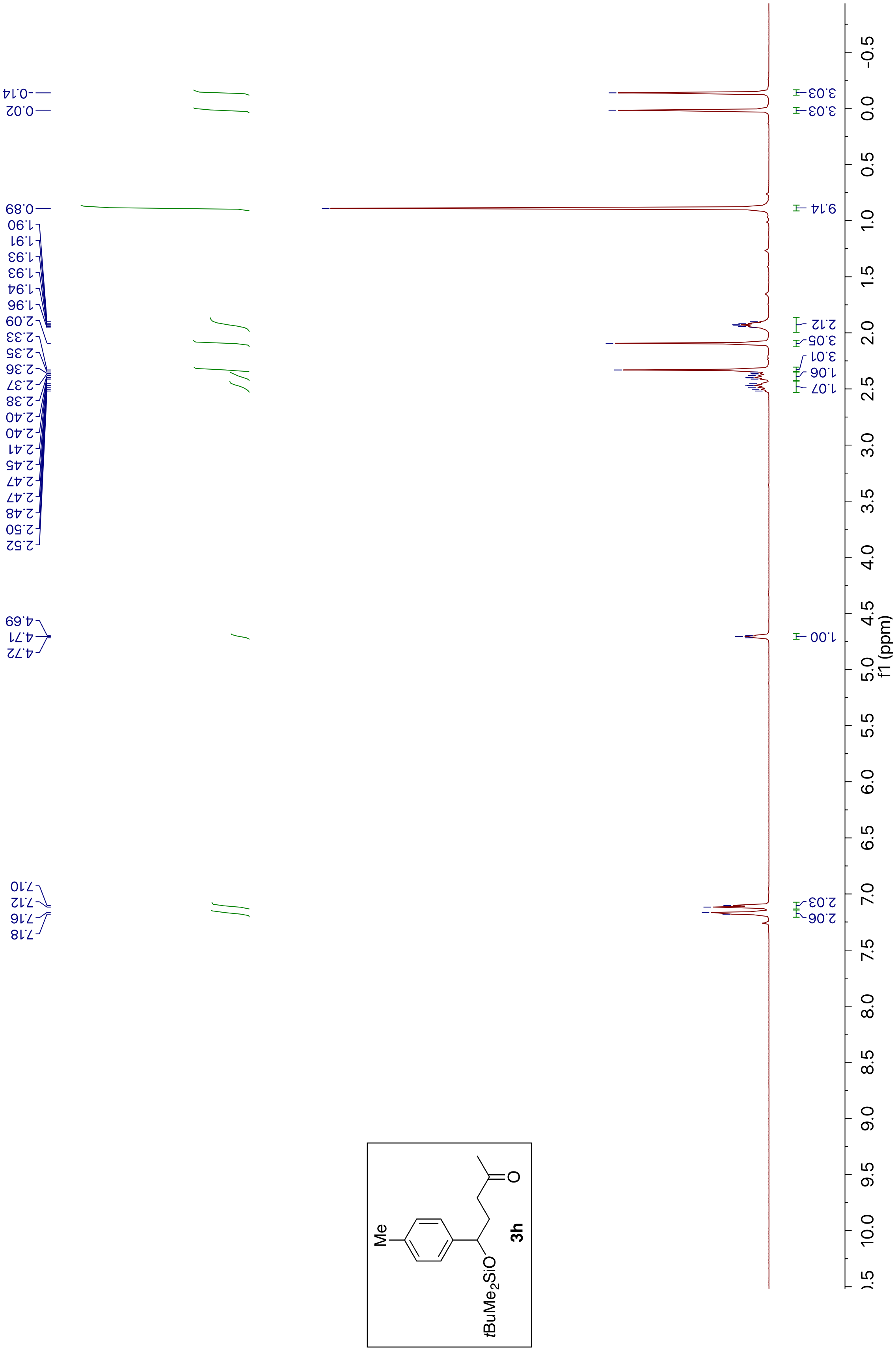

-0.15
0.01
0.88
1.89
1.89
1.90
1.91
1.92
1.93
2.09
2.35
2.36
2.38
2.38
2.40
2.41
2.44
2.45
2.47
2.47
2.49
2.50
3.79
4.66
4.68
4.69
6.83
6.85
7.19
7.20
3.03
2.99
9.29
2.02
3.02
1.97
3.01
1.00
2.03
2.01
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OMe
tBuMe2SiO
O

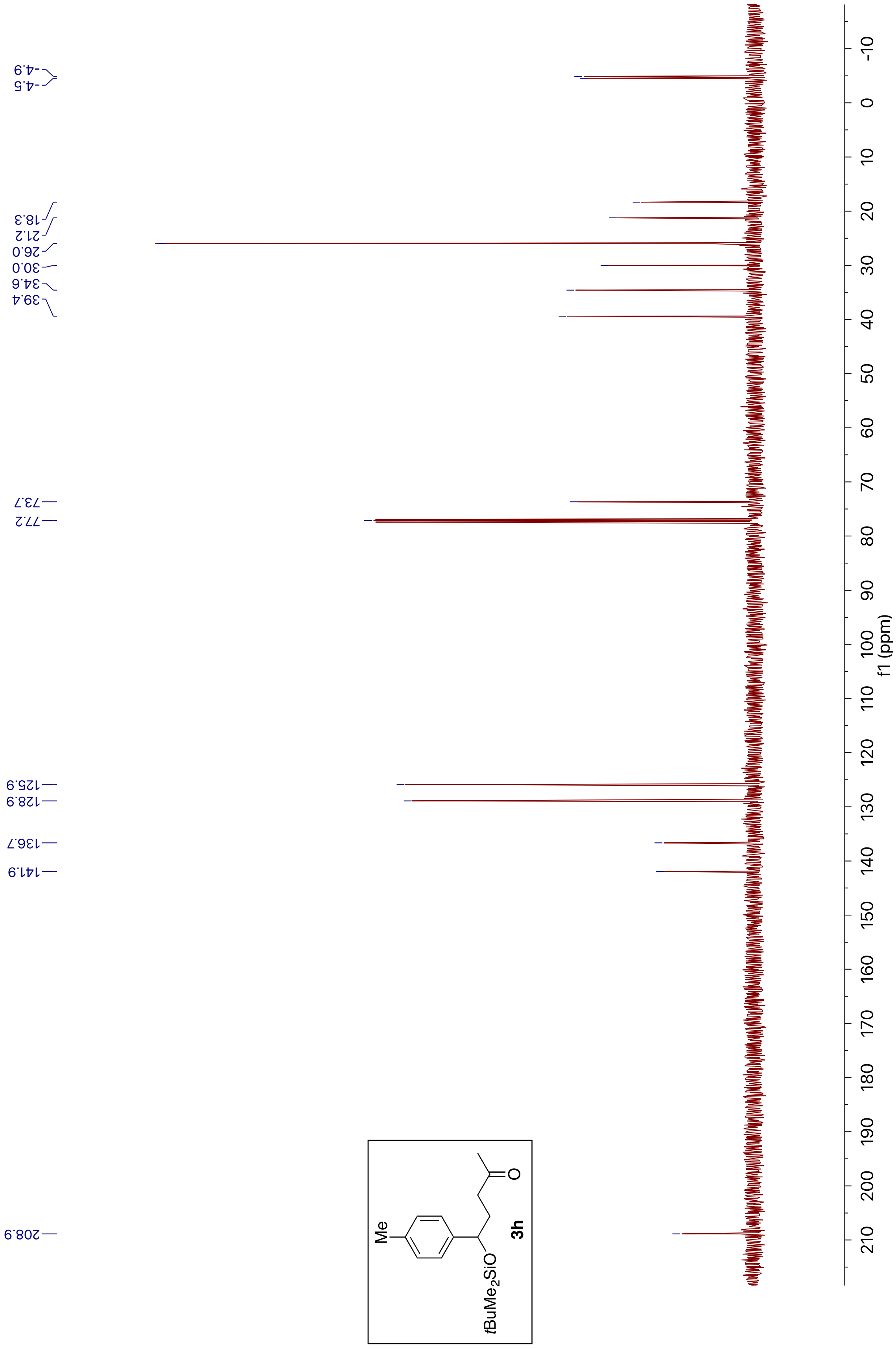
3f


-4.9
-4.5
18.3
26.0
30.0
34.6
39.5
55.3
73.5
113.6
127.1
137.1
158.8
208.8
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
OMe
tBuMe2SiO
O
3f

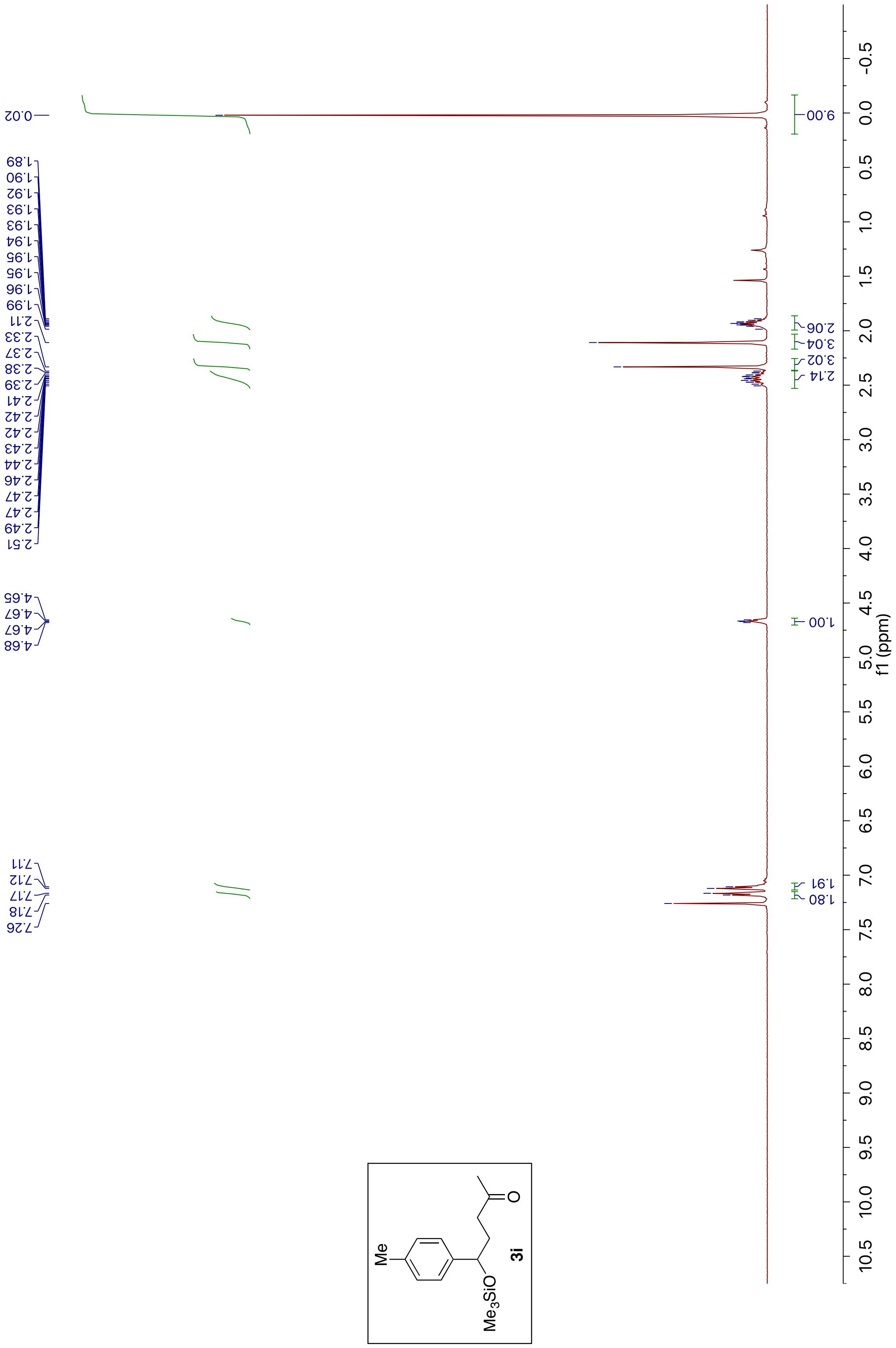

0.01
1.91
1.92
1.93
1.93
1.95
2.11
2.37
2.39
2.41
2.42
2.43
2.43
2.45
2.46
2.46
2.48
2.49
3.80
4.63
4.65
4.66
6.84
6.85
7.19
7.21
8.95
2.00
2.98
2.06
2.99
1.00
1.98
2.02
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OMe
Me_3SiO
O
3g

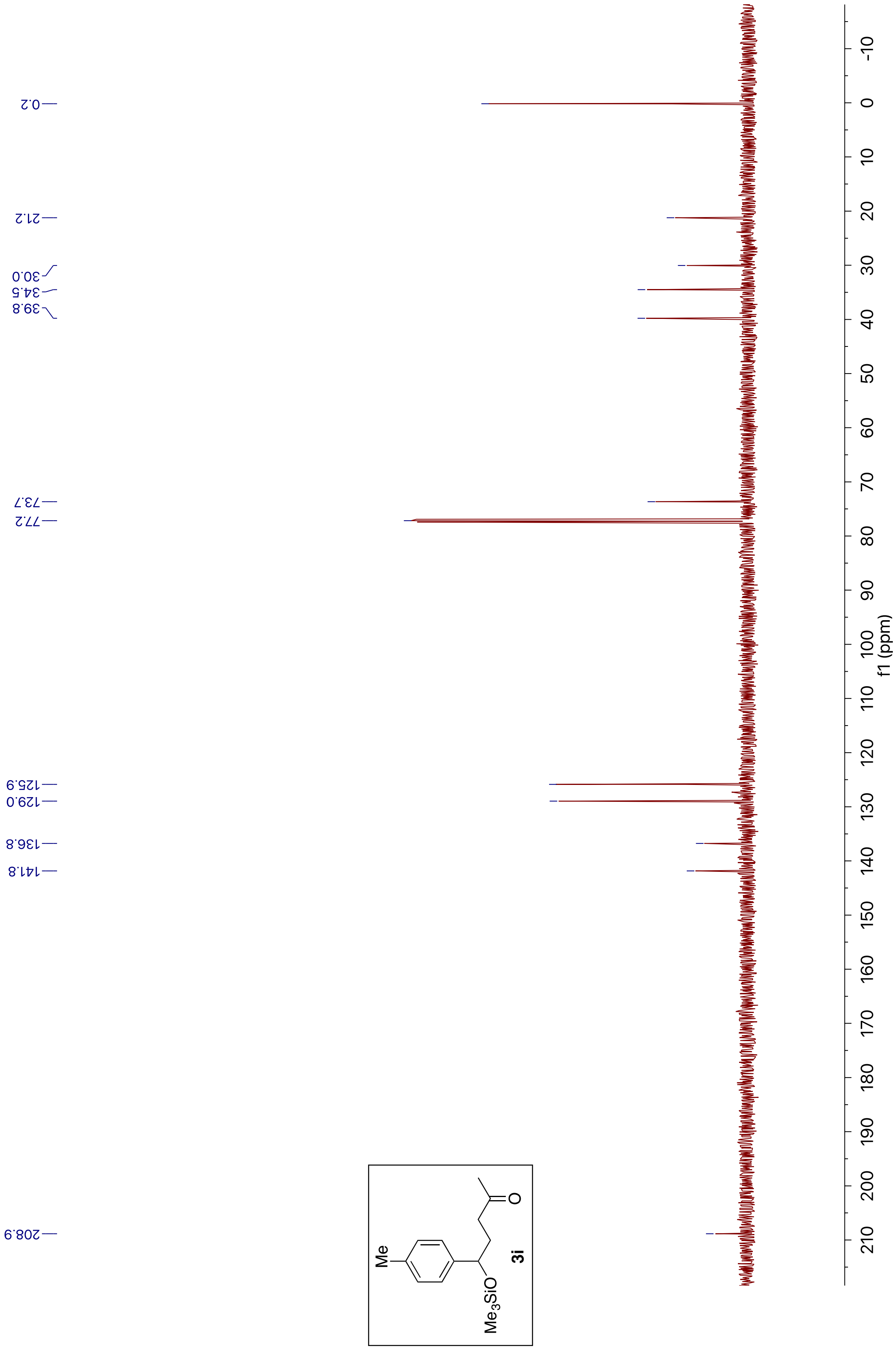

0.2
30.0
34.5
39.9
55.4
73.5
77.2
113.7
127.1
137.0
158.9
208.9
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OMe
Me$_3$SiO
O
3g

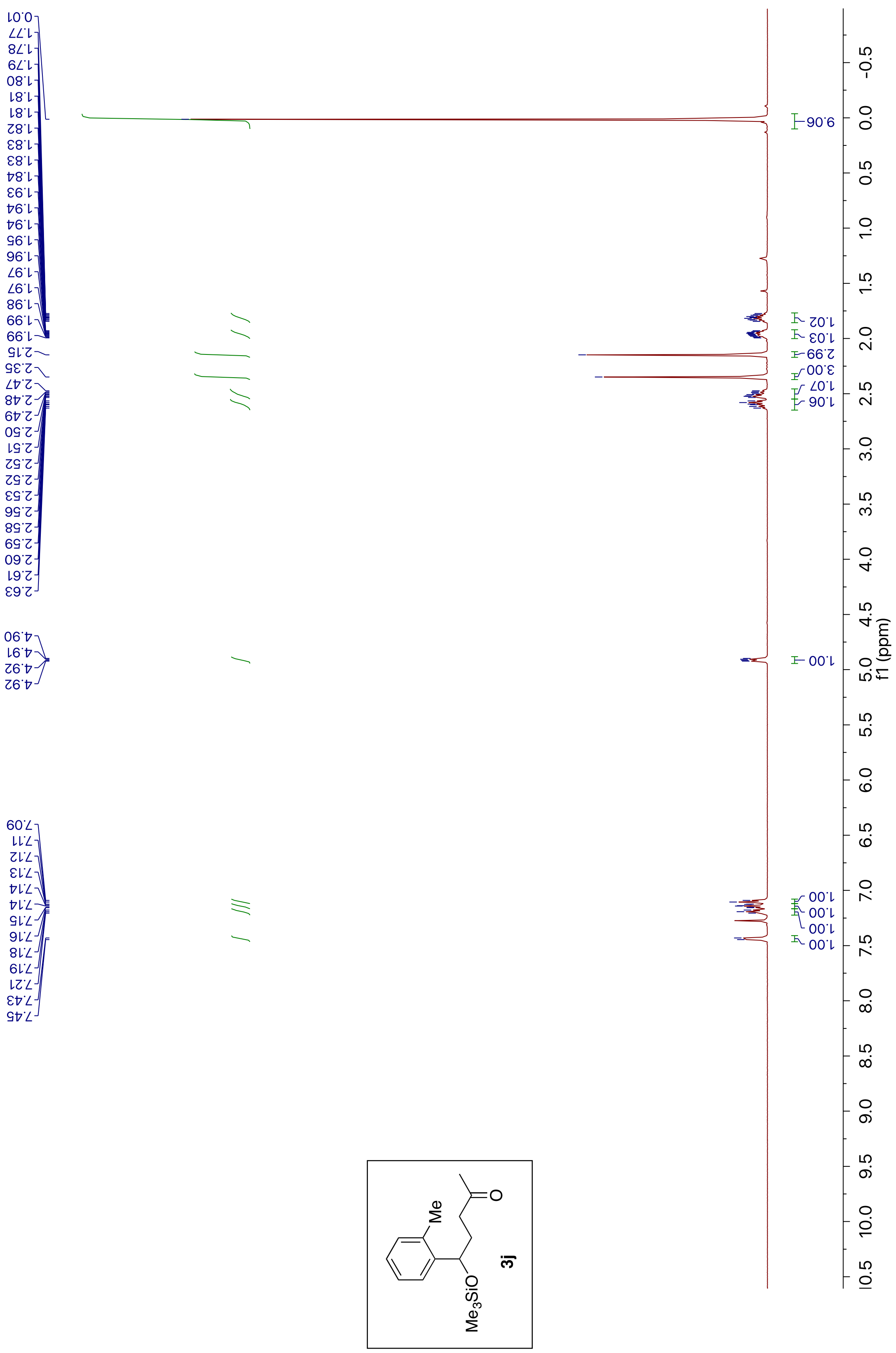

-0.14
0.02
0.89
1.90
1.91
1.93
1.93
1.94
1.96
2.09
2.33
2.35
2.36
2.37
2.38
2.40
2.40
2.41
2.45
2.47
2.47
2.48
2.50
2.52
4.69
4.71
4.72
7.10
7.12
7.16
7.18
3.03
3.03
9.14
2.12
3.05
3.01
1.06
1.07
1.00
2.03
2.06
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0.5
f1 (ppm)
Me
O
*t*BuMe$_2$SiO
3h

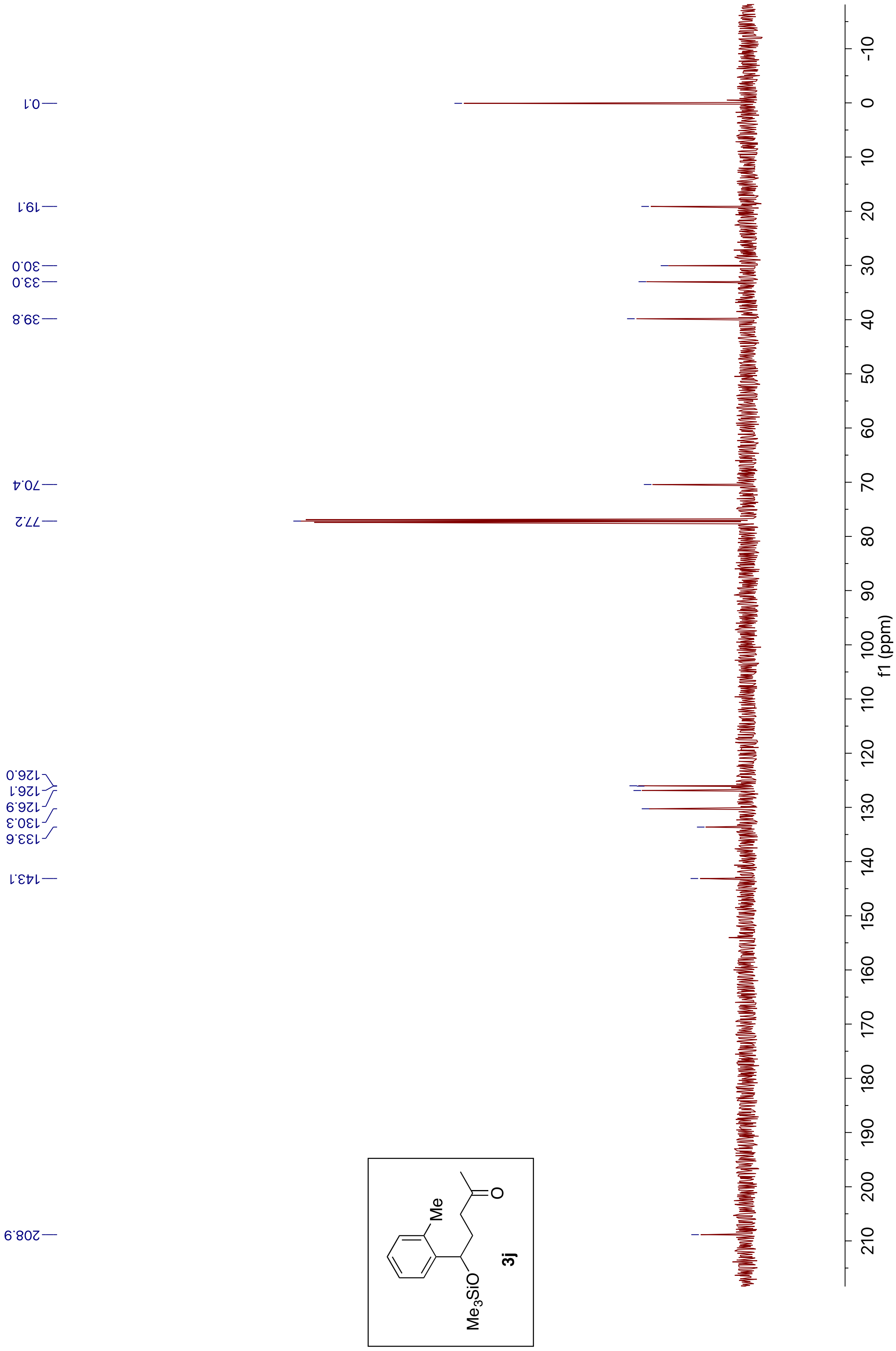

-4.9
-4.5
18.3
21.2
26.0
30.0
34.6
39.4
73.7
77.2
125.9
128.9
136.7
141.9
208.9
Me
*t*BuMe$_2$SiO
O
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

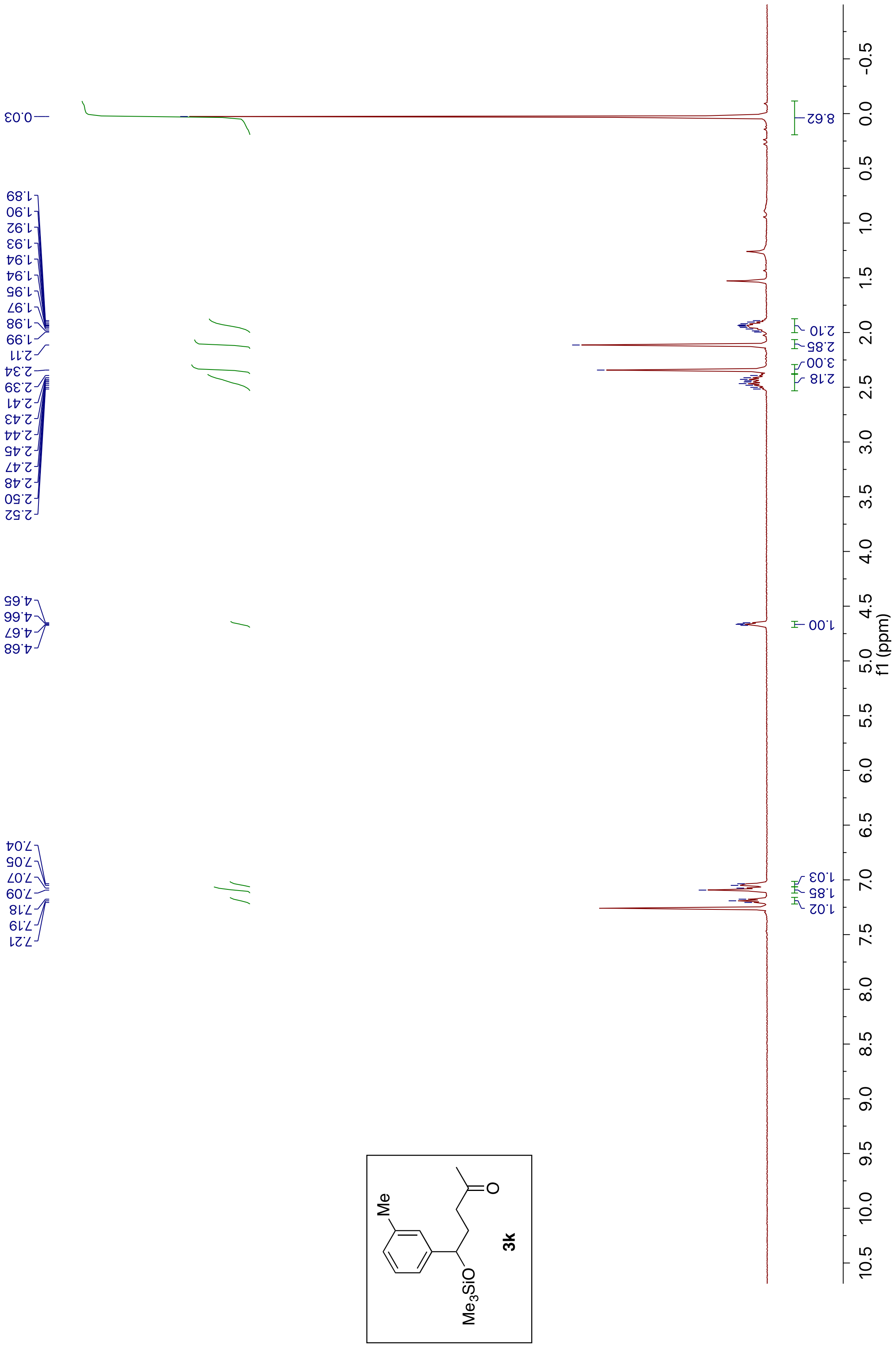
3h


0.02
1.89
1.90
1.92
1.93
1.93
1.94
1.95
1.95
1.96
1.99
2.11
2.33
2.37
2.38
2.39
2.41
2.42
2.42
2.43
2.44
2.46
2.47
2.47
2.49
2.51
4.65
4.67
4.67
4.68
7.11
7.12
7.17
7.18
7.26
9.00
2.06
3.04
3.02
2.14
1.00
1.91
1.80
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
Me
Me3SiO
O
3i

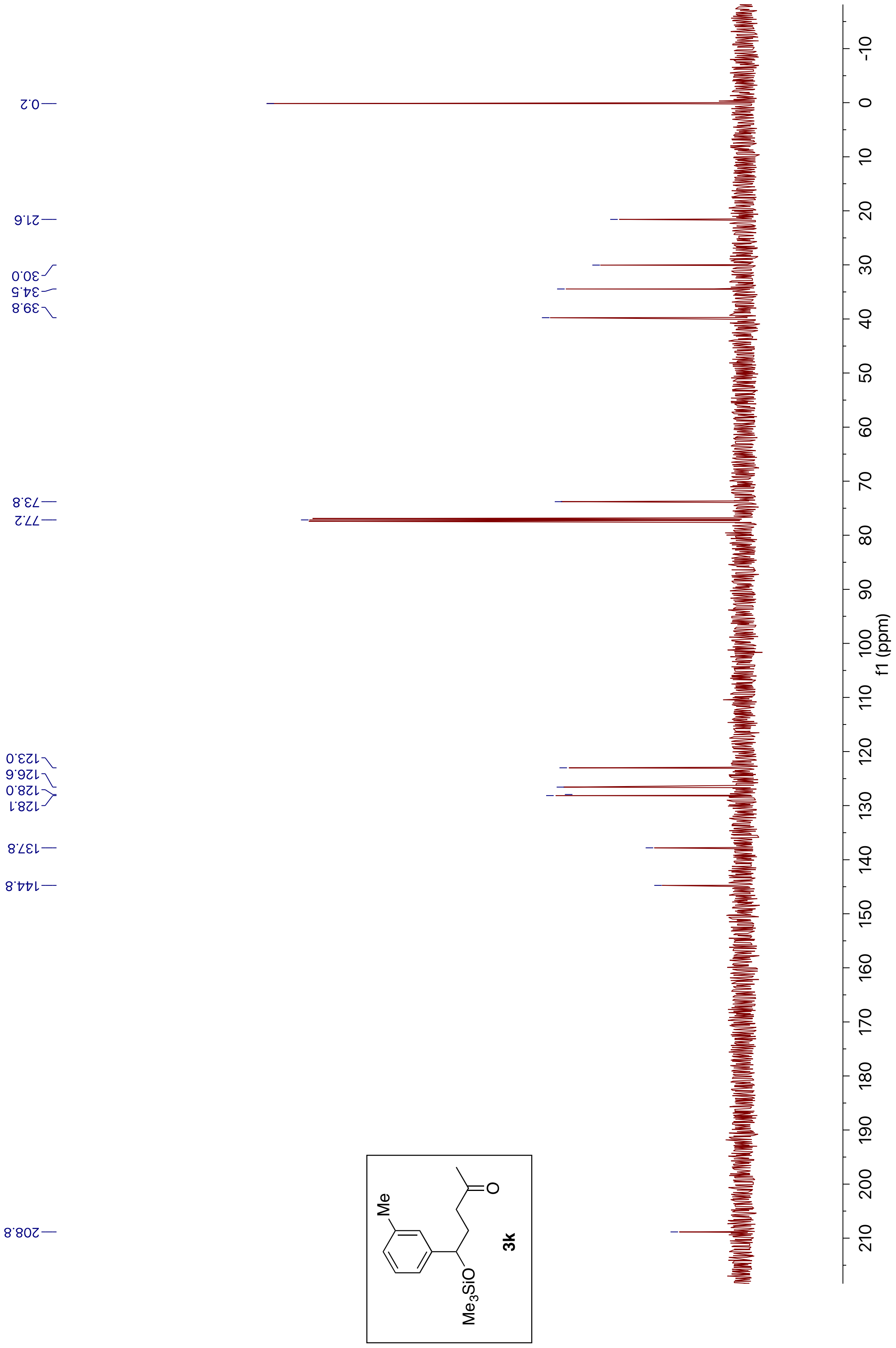

0.2
21.2
30.0
34.5
39.8
73.7
77.2
125.9
129.0
136.8
141.8
208.9
Me
Me$_3$SiO
O
3i
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210

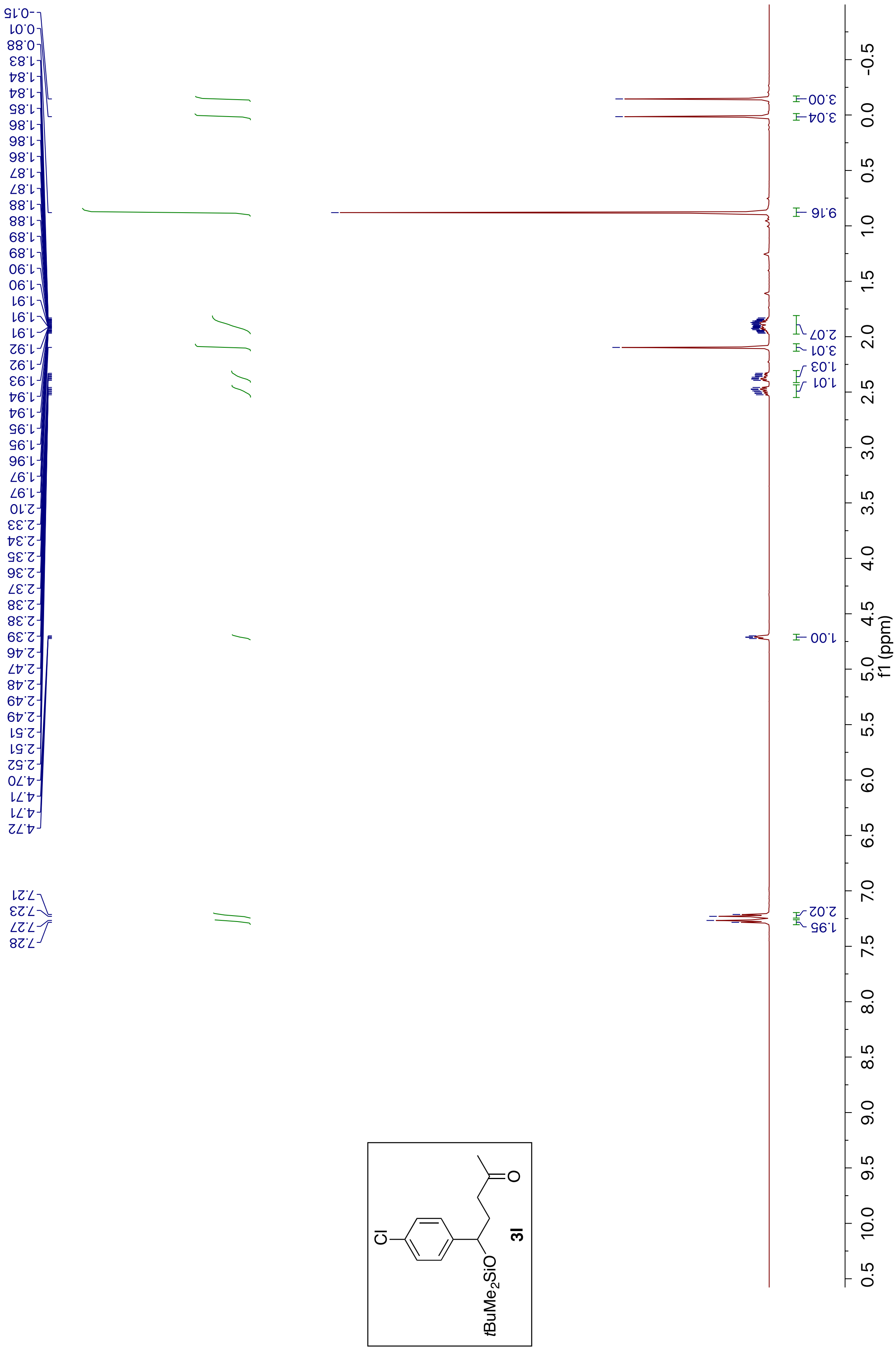

0.01
1.77
1.78
1.79
1.80
1.81
1.81
1.82
1.83
1.83
1.84
1.93
1.94
1.94
1.95
1.96
1.97
1.97
1.98
1.99
1.99
2.15
2.35
2.47
2.48
2.49
2.50
2.51
2.52
2.52
2.53
2.56
2.58
2.59
2.60
2.61
2.63
4.90
4.91
4.92
4.92
7.09
7.11
7.12
7.13
7.14
7.14
7.15
7.16
7.18
7.19
7.21
7.43
7.45
9.06
1.02
1.03
2.99
3.00
1.07
1.06
1.00
1.00
1.00
1.00
1.00
f1 (ppm)
Me
O
Me$_3$SiO
3j

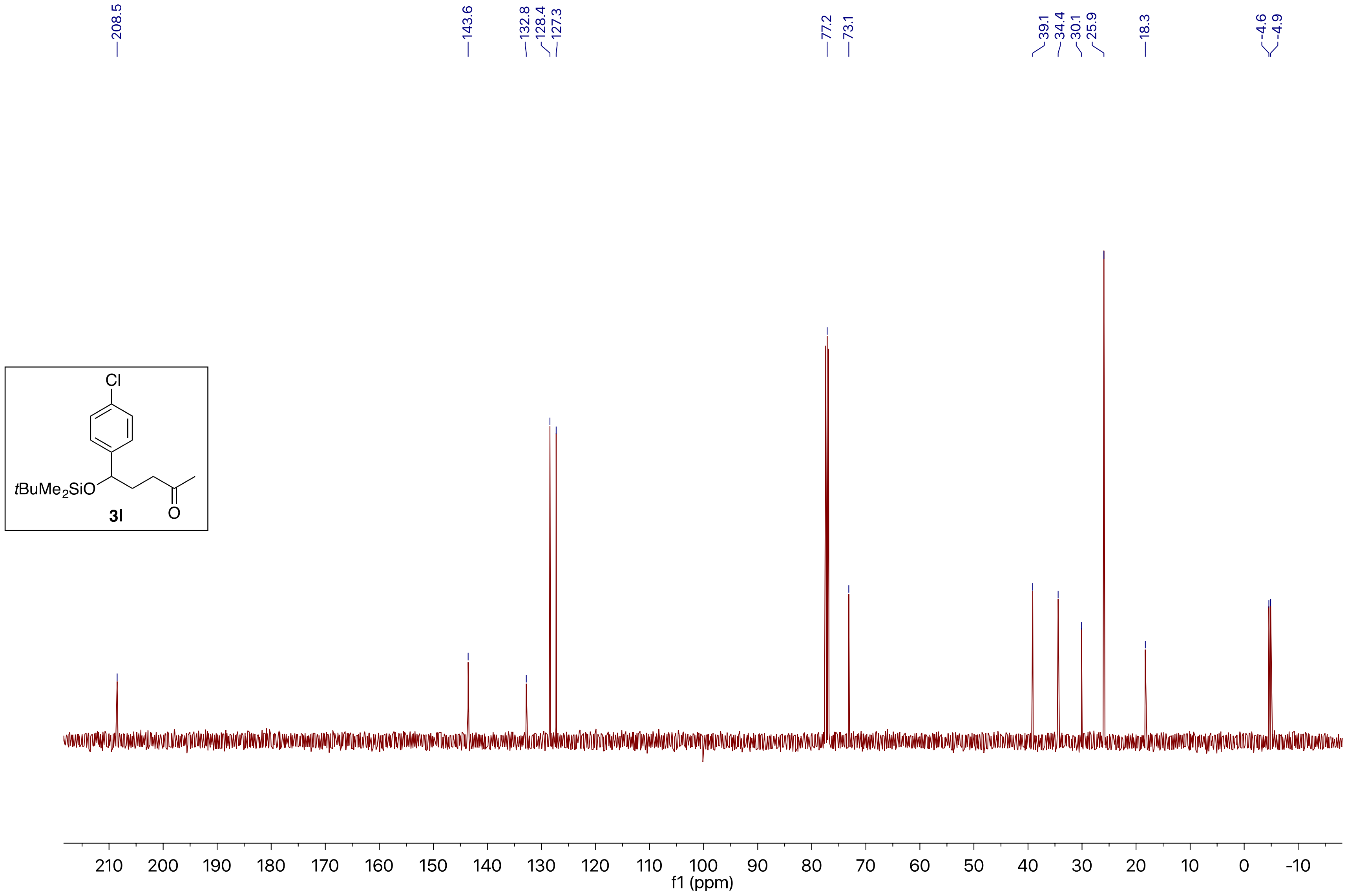

0.1
19.1
30.0
33.0
39.8
70.4
77.2
126.0
126.1
126.9
130.3
133.6
143.1
208.9
f1 (ppm)
Me
O
Me$_3$SiO
3j

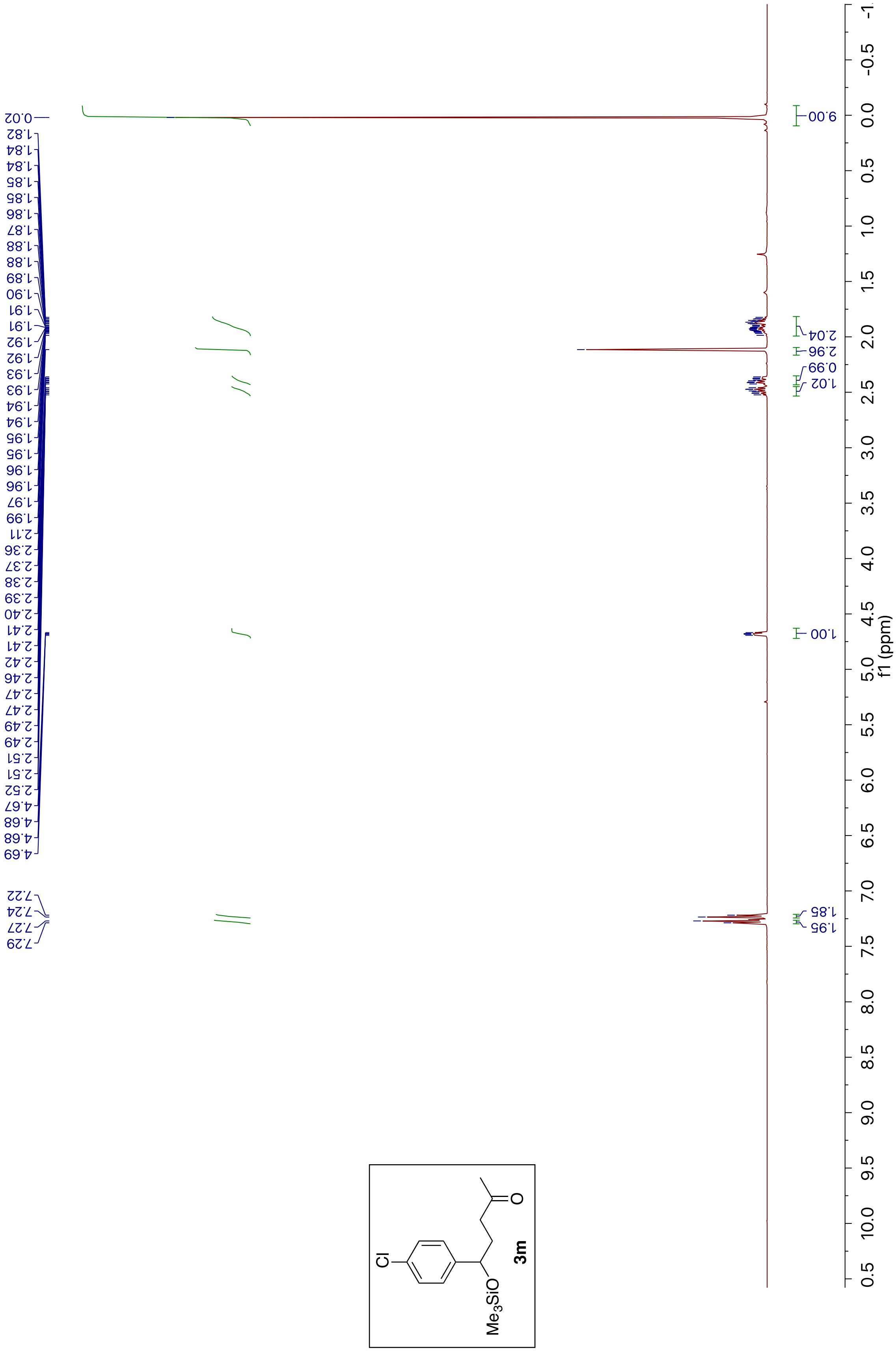

0.03
1.89
1.90
1.92
1.93
1.94
1.94
1.95
1.97
1.98
1.99
2.11
2.34
2.39
2.41
2.43
2.44
2.45
2.47
2.48
2.50
2.52
4.65
4.66
4.67
4.68
7.04
7.05
7.07
7.09
7.18
7.19
7.21
8.62
2.10
2.85
3.00
2.18
1.00
1.03
1.85
1.02
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
Me
Me$_3$SiO
O

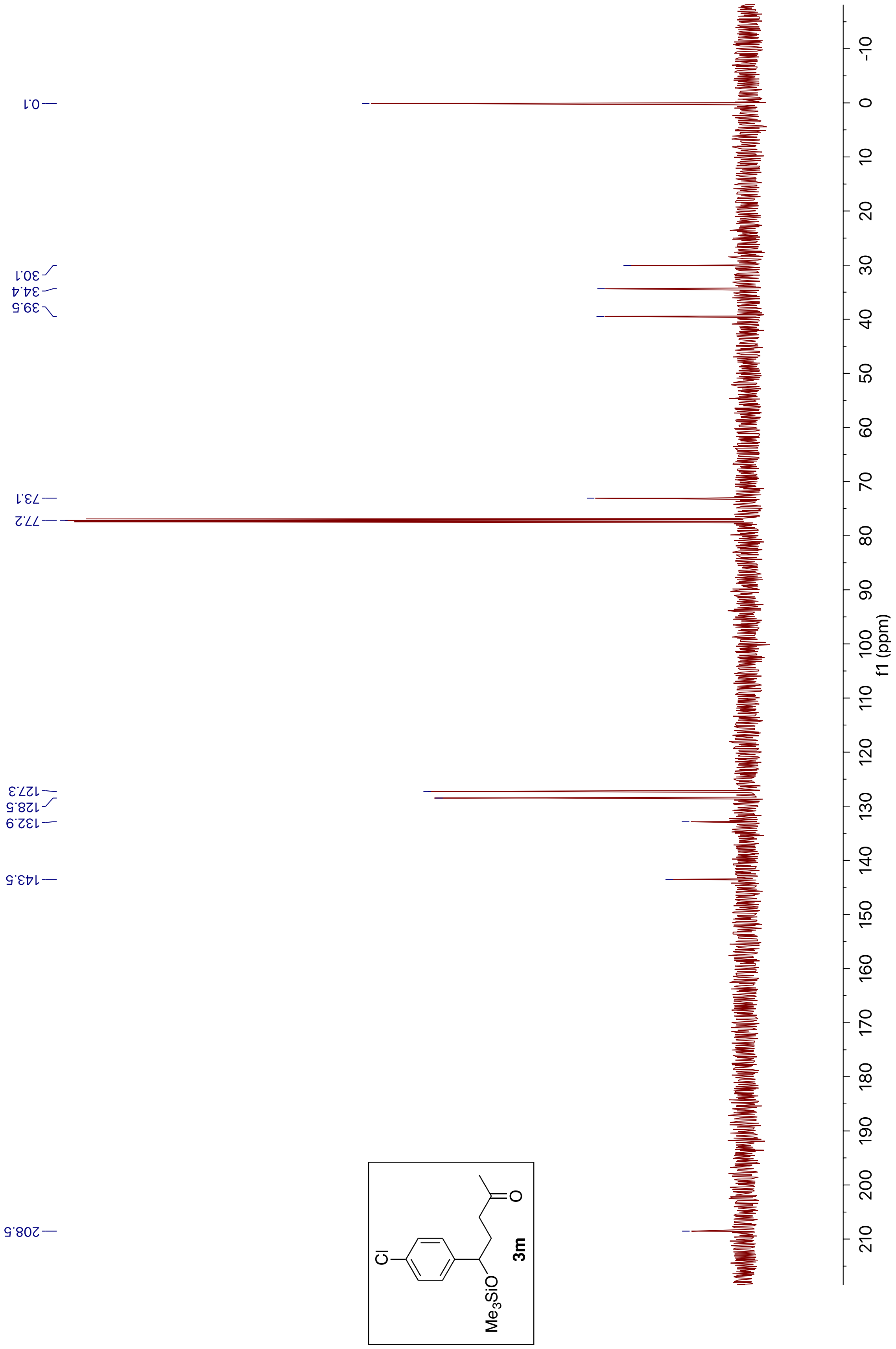
3k


0.2
21.6
30.0
34.5
39.8
73.8
77.2
123.0
126.6
128.0
128.1
137.8
144.8
208.8
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
Me
Me$_3$SiO
O
3k

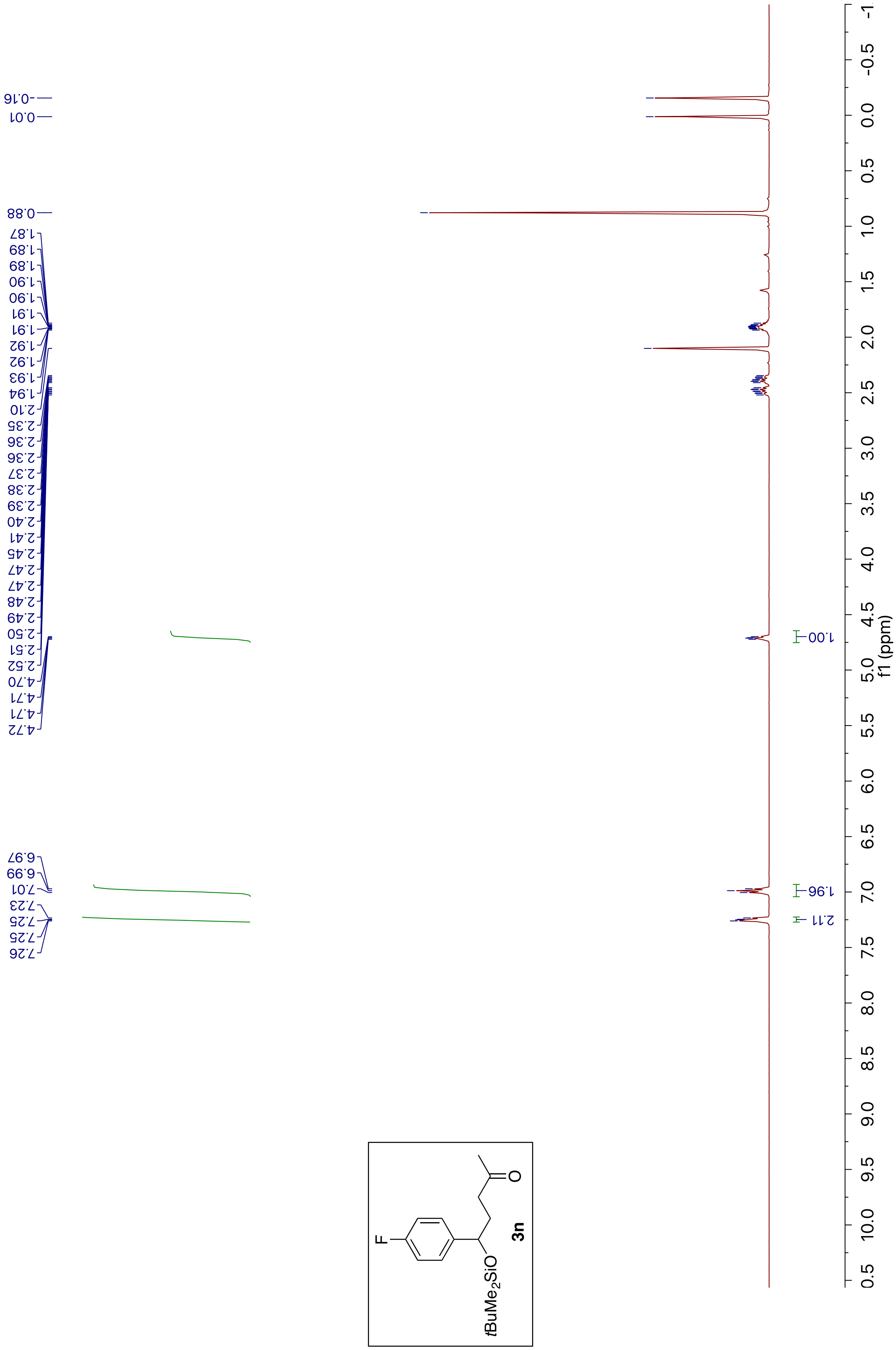

-0.15
0.01
0.88
1.83
1.84
1.84
1.85
1.86
1.86
1.86
1.87
1.87
1.88
1.88
1.89
1.89
1.90
1.90
1.91
1.91
1.91
1.92
1.92
1.93
1.94
1.94
1.95
1.95
1.96
1.97
1.97
2.10
2.33
2.34
2.35
2.36
2.37
2.38
2.38
2.39
2.46
2.47
2.48
2.49
2.49
2.51
2.51
2.52
4.70
4.71
4.71
4.72
7.21
7.23
7.27
7.28
3.00
3.04
9.16
2.07
3.01
1.03
1.01
1.00
2.02
1.95
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0.5
f1 (ppm)
Cl
tBuMe2SiO
O
3l

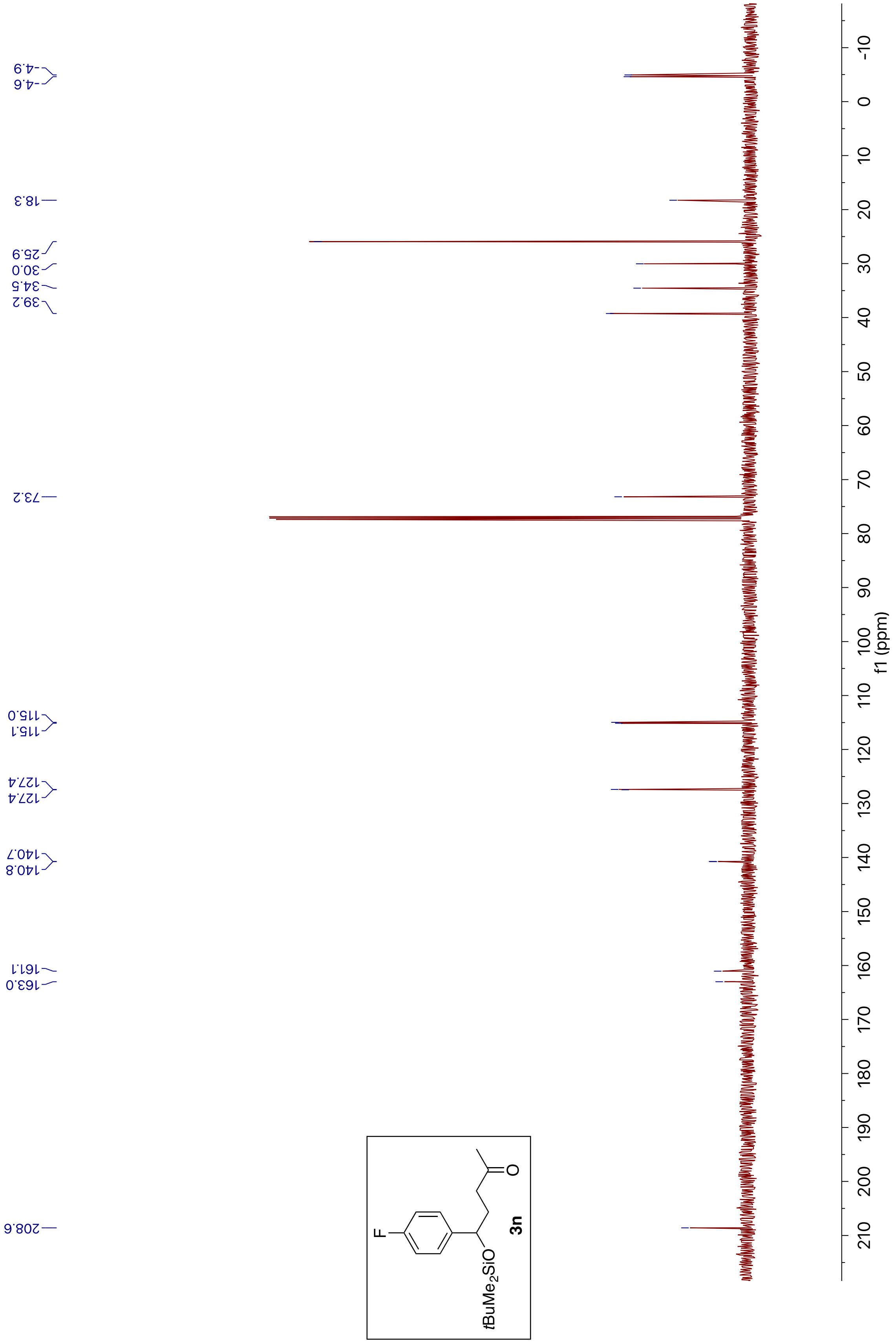

208.5
143.6
132.8
128.4
127.3
77.2
73.1
39.1
34.4
30.1
25.9
18.3
-4.6
-4.9
Cl
tBuMe2SiO
O
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

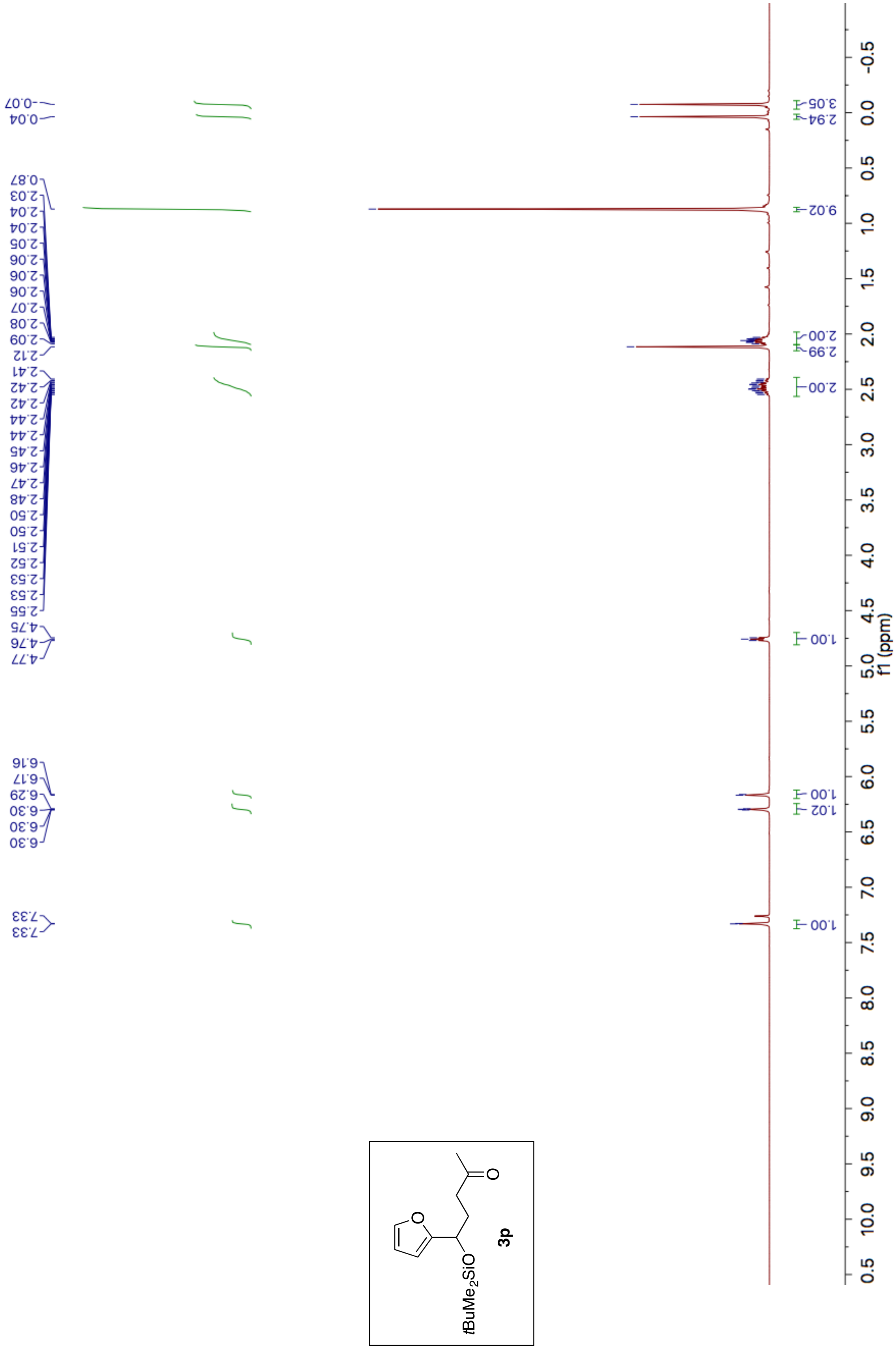

0.02
1.82
1.84
1.84
1.85
1.85
1.86
1.87
1.88
1.88
1.89
1.90
1.91
1.91
1.92
1.92
1.93
1.93
1.94
1.94
1.95
1.95
1.96
1.96
1.97
1.99
2.11
2.36
2.37
2.38
2.39
2.40
2.41
2.41
2.42
2.46
2.47
2.47
2.49
2.49
2.51
2.51
2.52
4.67
4.68
4.68
4.69
7.22
7.24
7.27
7.29
9.00
2.04
2.96
0.99
1.02
1.00
1.85
1.95
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
Cl
Me$_3$SiO
O
3m


0.1
30.1
34.4
39.5
73.1
77.2
127.3
128.5
132.9
143.5
208.5
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
Cl
Me3SiO
O

3m

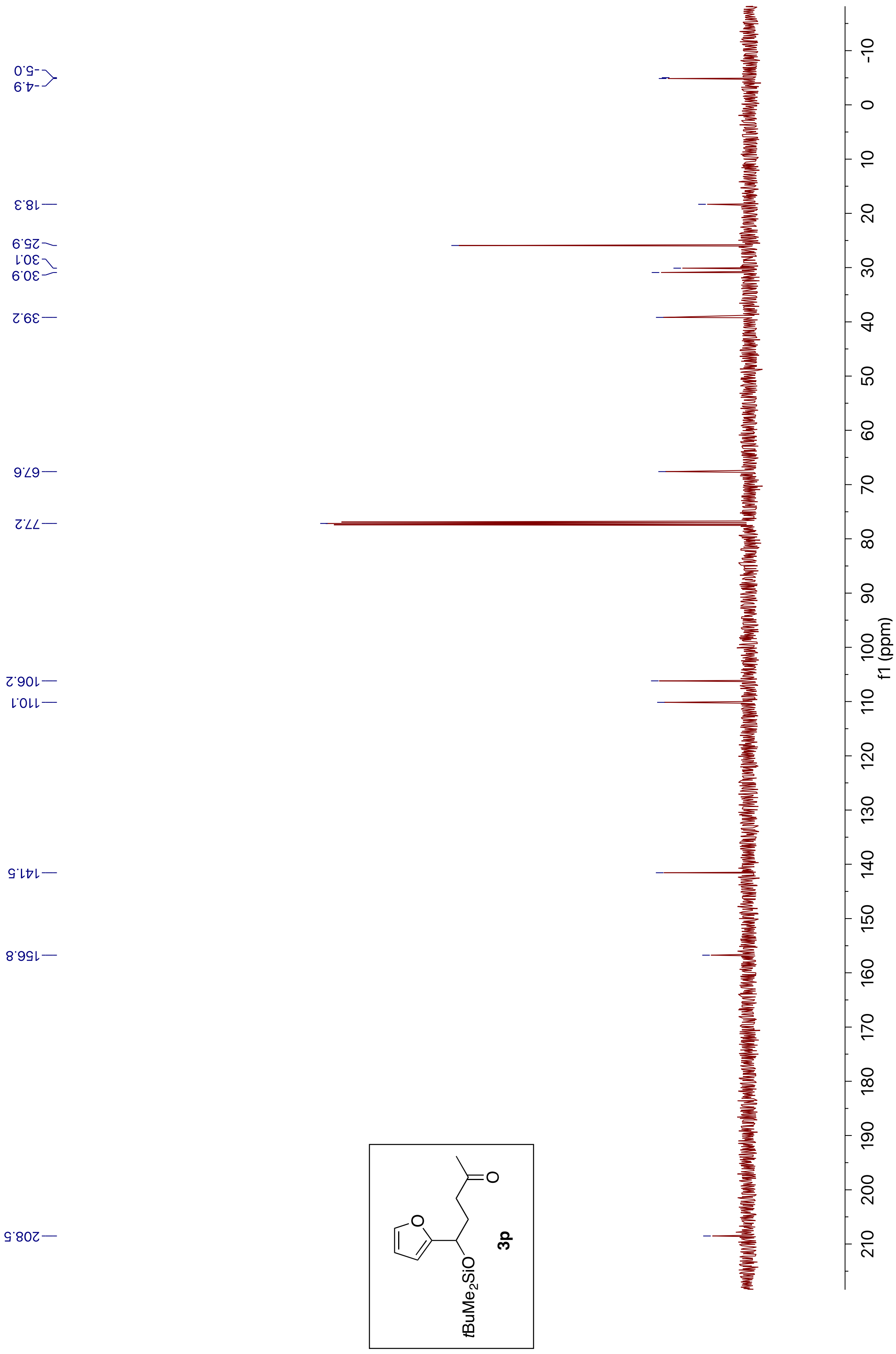

-0.16
0.01
0.88
1.87
1.89
1.89
1.90
1.90
1.91
1.91
1.92
1.92
1.93
1.94
2.10
2.35
2.36
2.36
2.37
2.38
2.39
2.40
2.41
2.45
2.47
2.47
2.48
2.49
2.50
2.51
2.52
4.70
4.71
4.71
4.72
6.97
6.99
7.01
7.23
7.25
7.25
7.26
1.00
1.96
2.11
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
F
tBuMe2SiO
O
3n

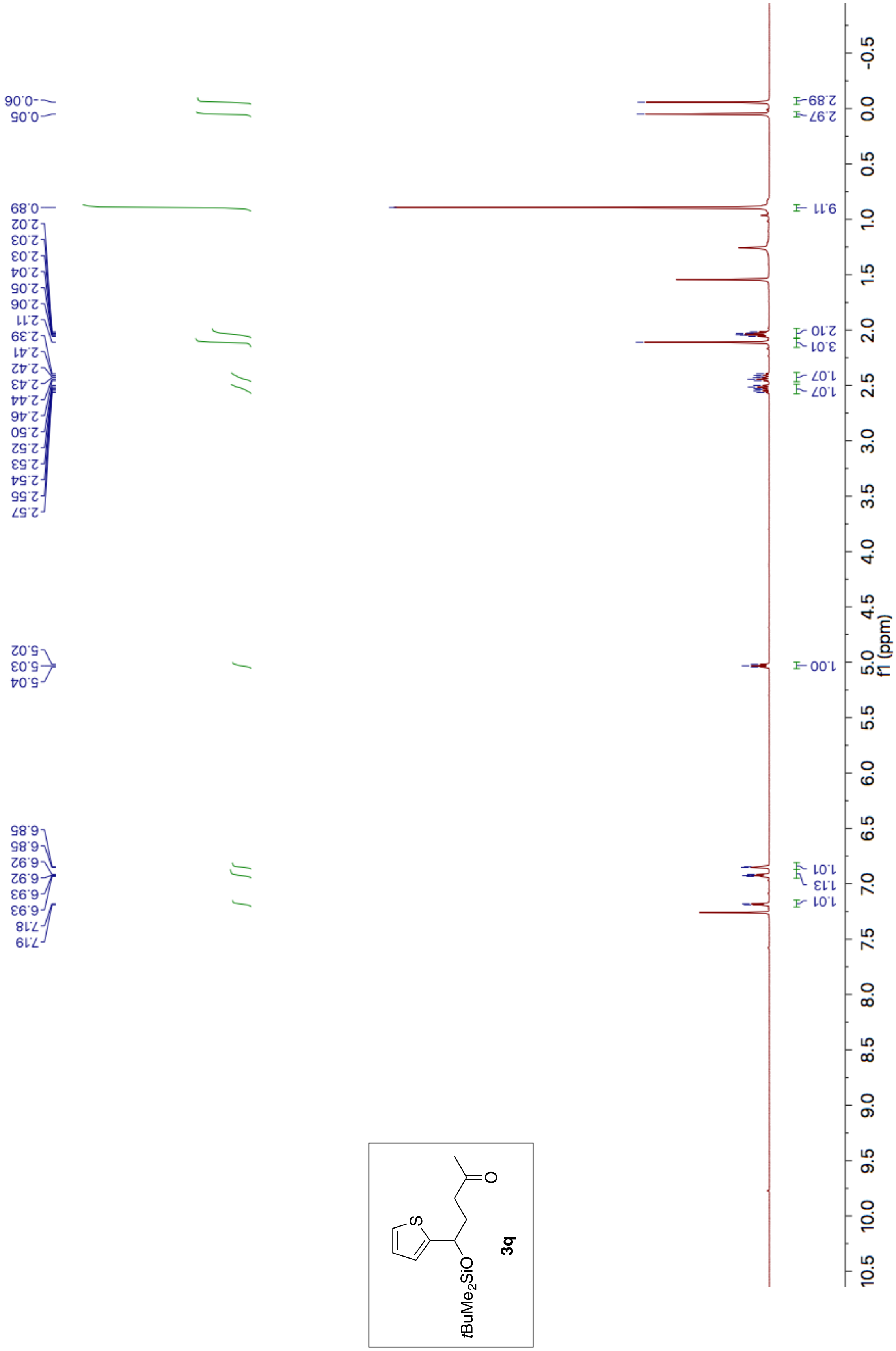

-4.6
-4.9
18.3
25.9
30.0
34.5
39.2
73.2
115.0
115.1
127.4
127.4
140.7
140.8
161.1
163.0
208.6
f1 (ppm)
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
F
O
tBuMe2SiO
3n


-0.07
0.04
0.87
2.03
2.04
2.04
2.05
2.06
2.06
2.06
2.07
2.08
2.09
2.12
2.41
2.42
2.42
2.44
2.44
2.45
2.46
2.47
2.48
2.50
2.50
2.51
2.52
2.53
2.53
2.55
4.75
4.76
4.77
6.16
6.17
6.29
6.30
6.30
6.30
7.33
7.33
3.05
2.94
9.02
2.00
2.99
2.00
1.00
1.00
1.02
1.00
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)

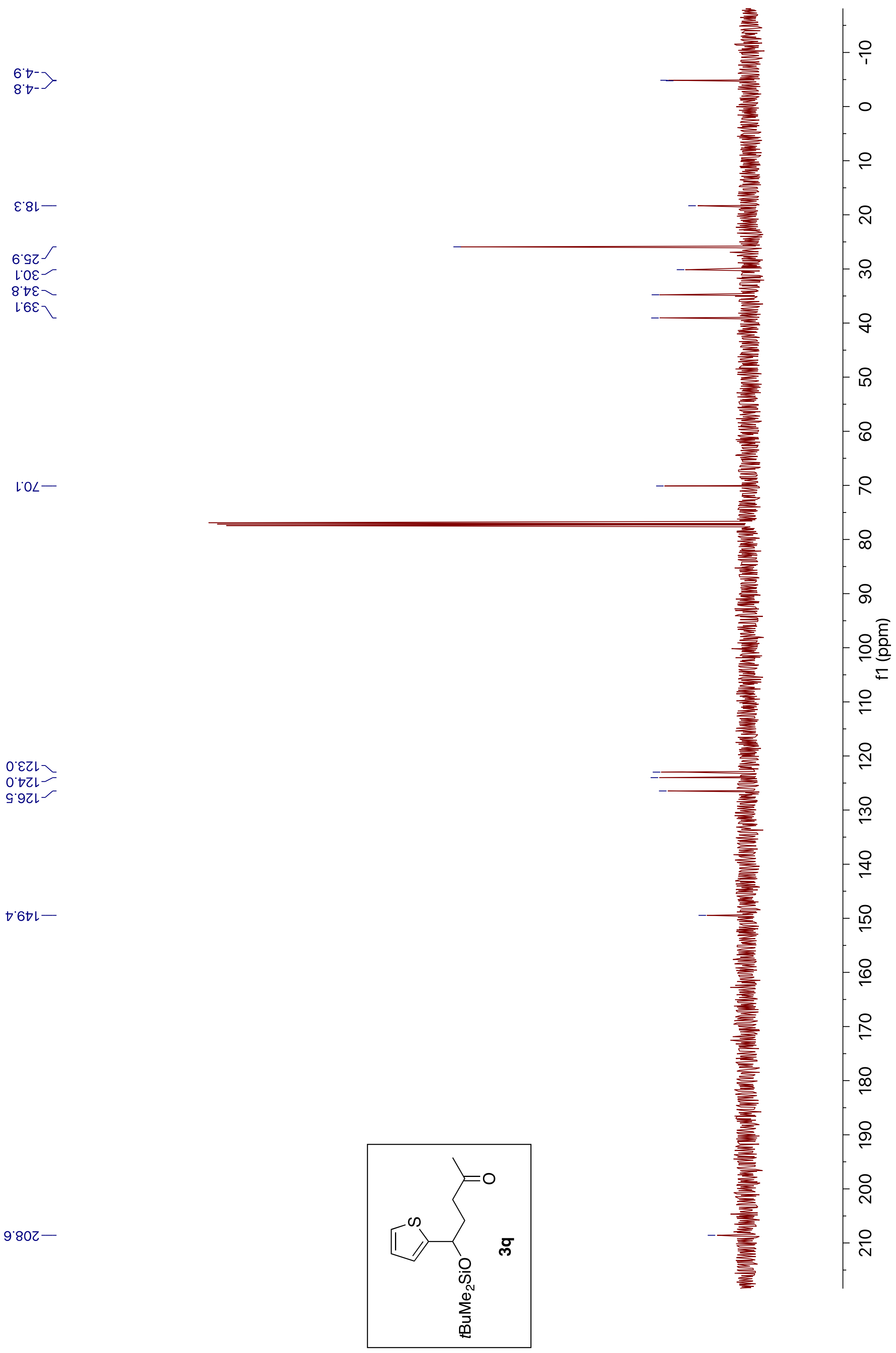
tBuMe2SiO
O
O

3p

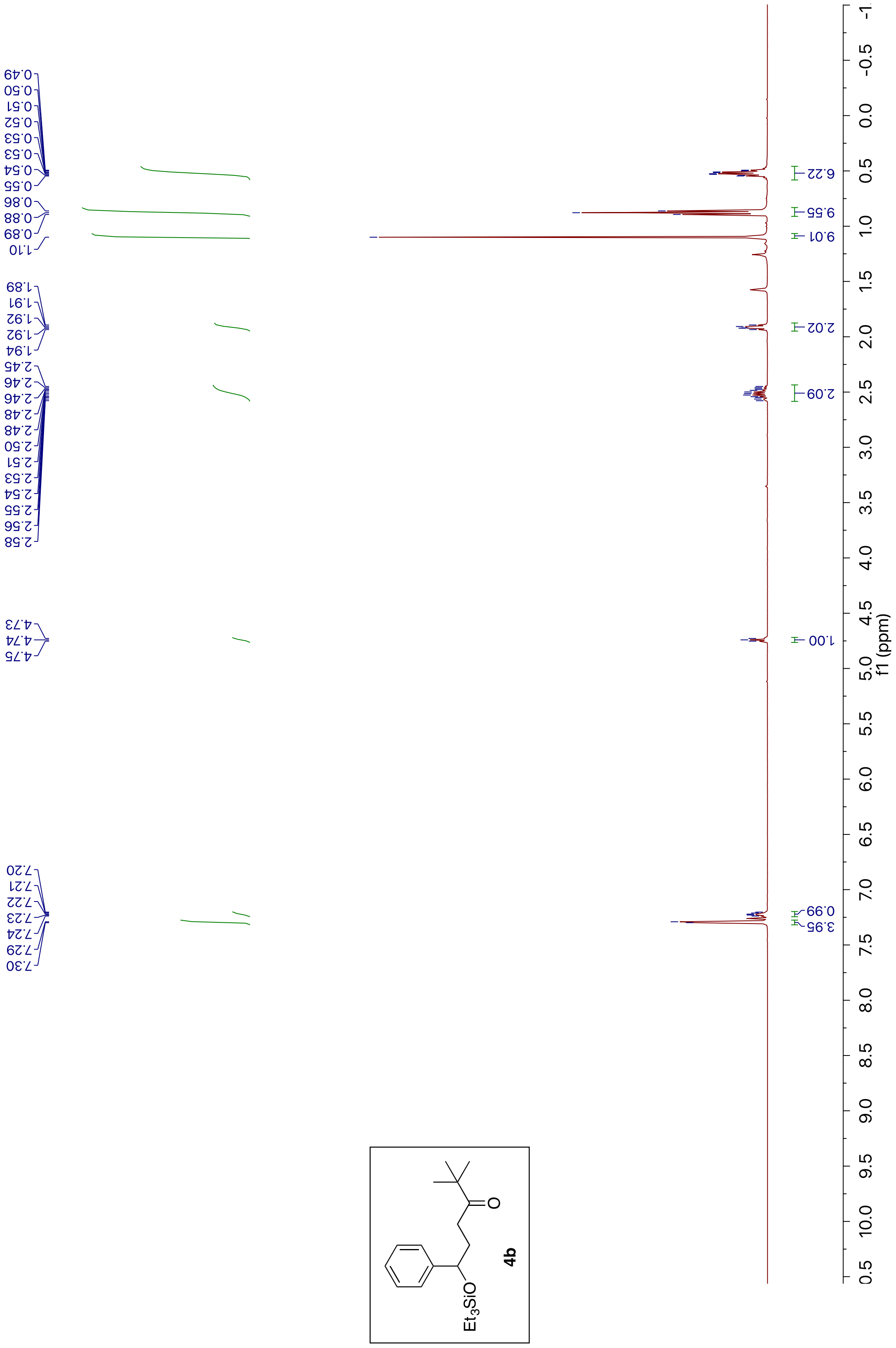

-5.0
-4.9
18.3
25.9
30.1
30.9
39.2
67.6
77.2
106.2
110.1
141.5
156.8
208.5
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
tBuMe2SiO
O
O
3p

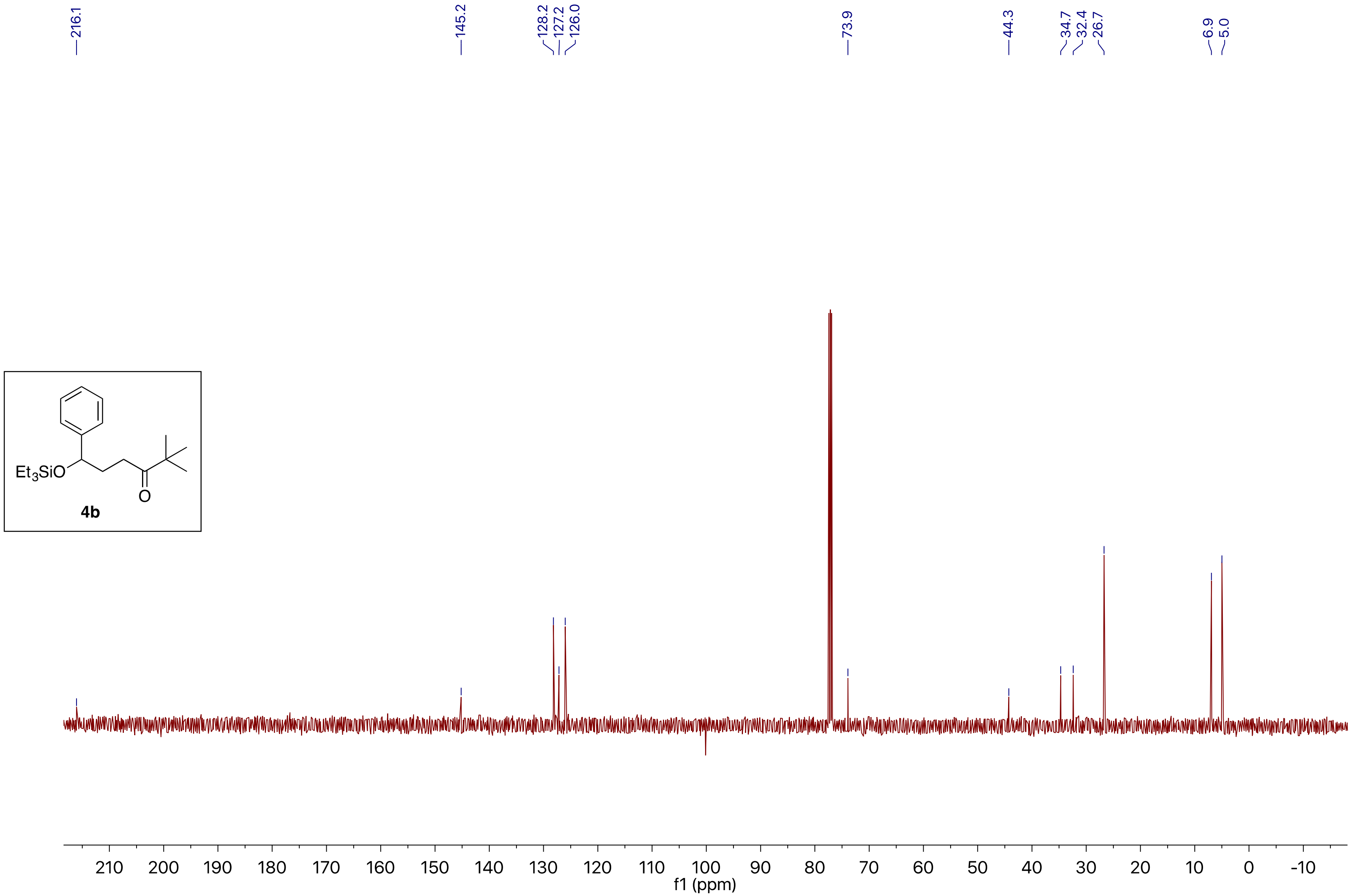

-0.06
0.05
0.89
2.02
2.03
2.03
2.04
2.05
2.06
2.11
2.39
2.41
2.42
2.43
2.44
2.46
2.50
2.52
2.53
2.54
2.55
2.57
5.02
5.03
5.04
6.85
6.85
6.92
6.92
6.93
6.93
7.18
7.19
2.89
2.97
9.11
2.10
3.01
1.07
1.07
1.00
1.01
1.13
1.01
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
S
O
tBuMe2SiO

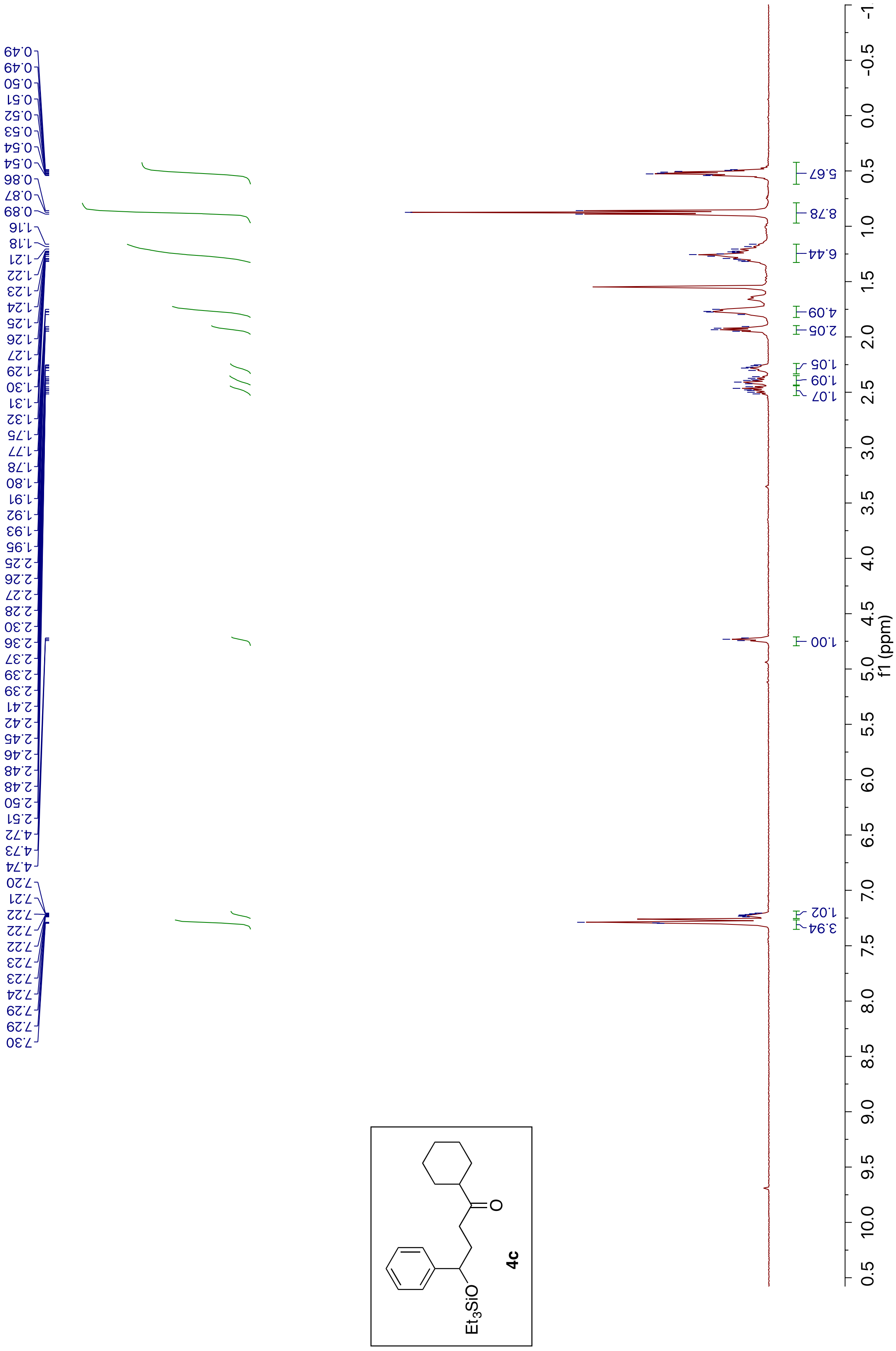
3q

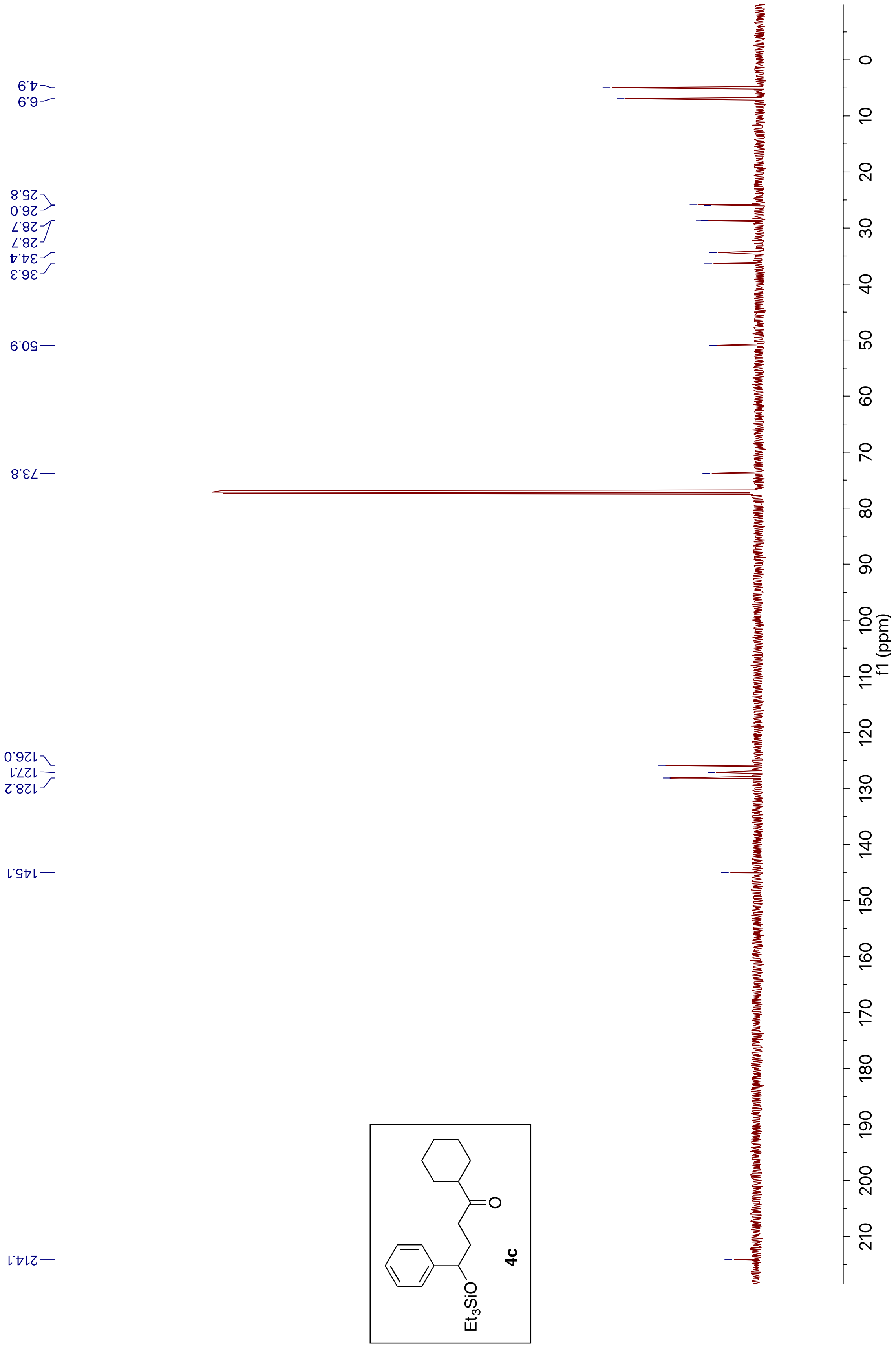


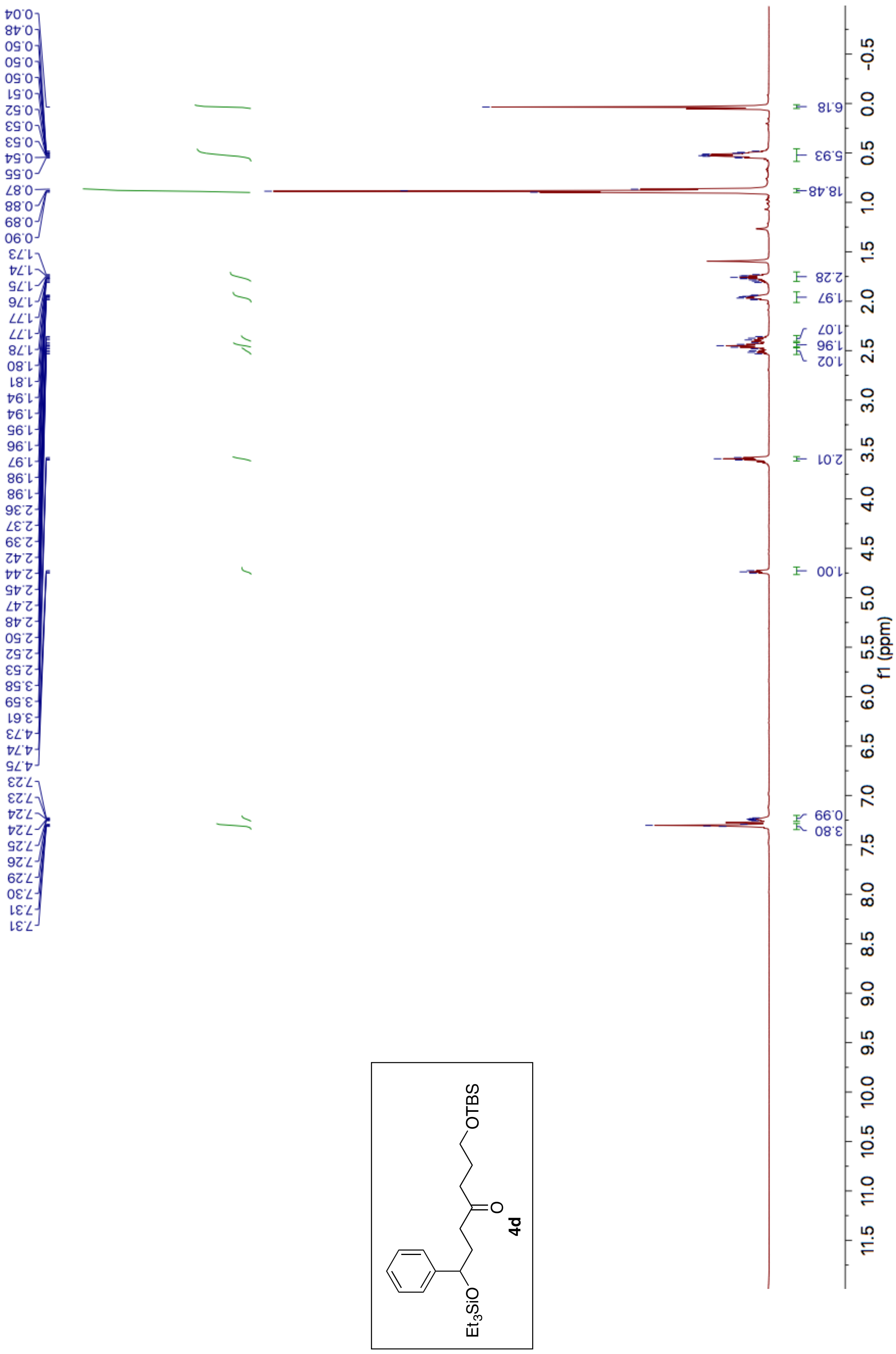
-4.9
-4.8
18.3
25.9
30.1
34.8
39.1
70.1
123.0
124.0
126.5
149.4
208.6
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
S
O
tBuMe2SiO
3q

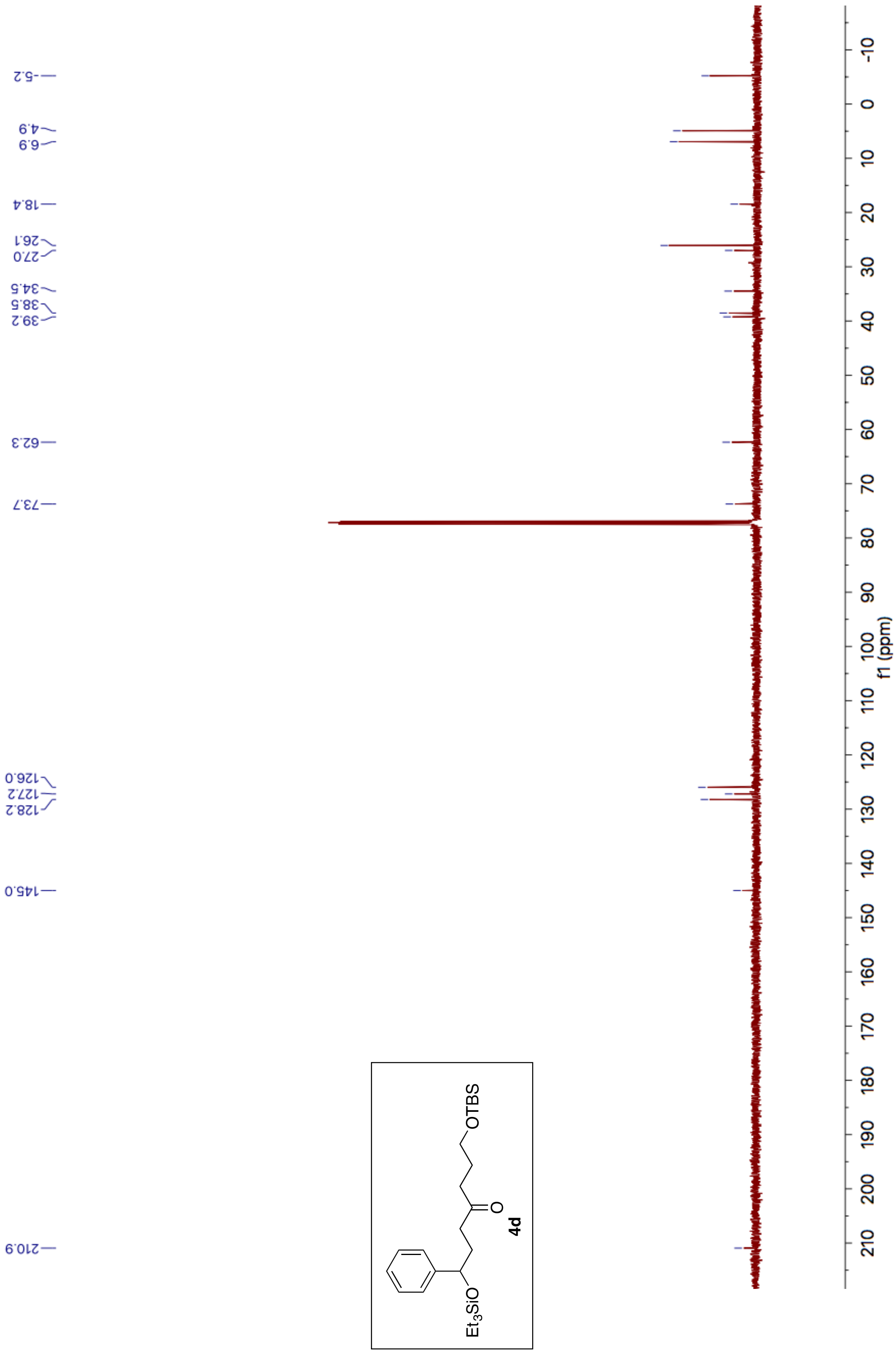

0.49
0.50
0.51
0.52
0.53
0.53
0.54
0.55
0.86
0.88
0.89
1.10
1.89
1.91
1.92
1.92
1.94
2.45
2.46
2.46
2.48
2.48
2.50
2.51
2.53
2.54
2.55
2.56
2.58
4.73
4.74
4.75
7.20
7.21
7.22
7.23
7.24
7.29
7.30
6.22
9.55
9.01
2.02
2.09
1.00
0.99
3.95
f1 (ppm)
Et3SiO
O
4b

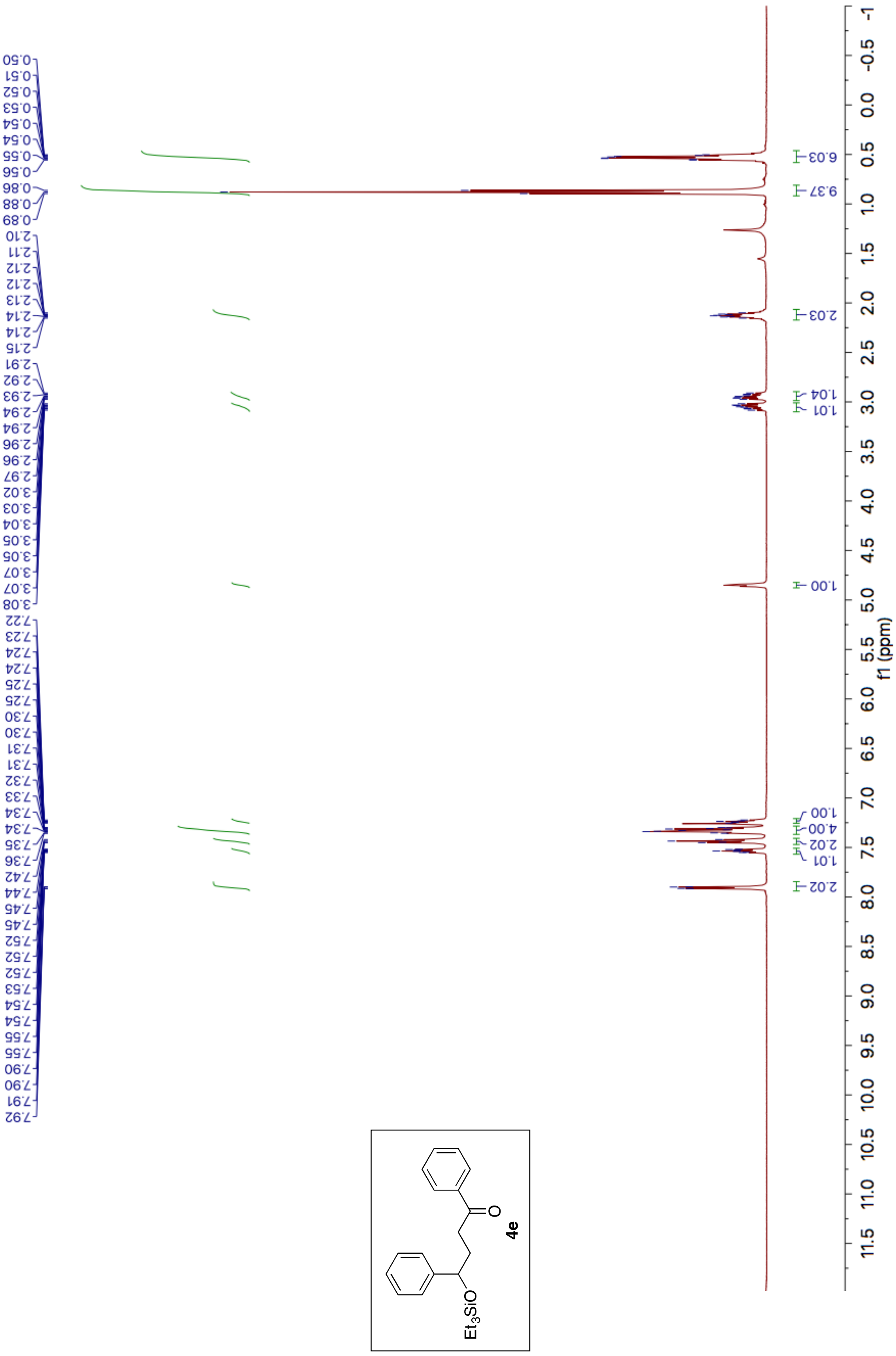

216.1
145.2
128.2
127.2
126.0
73.9
44.3
34.7
32.4
26.7
6.9
5.0
Et3SiO
O
4b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

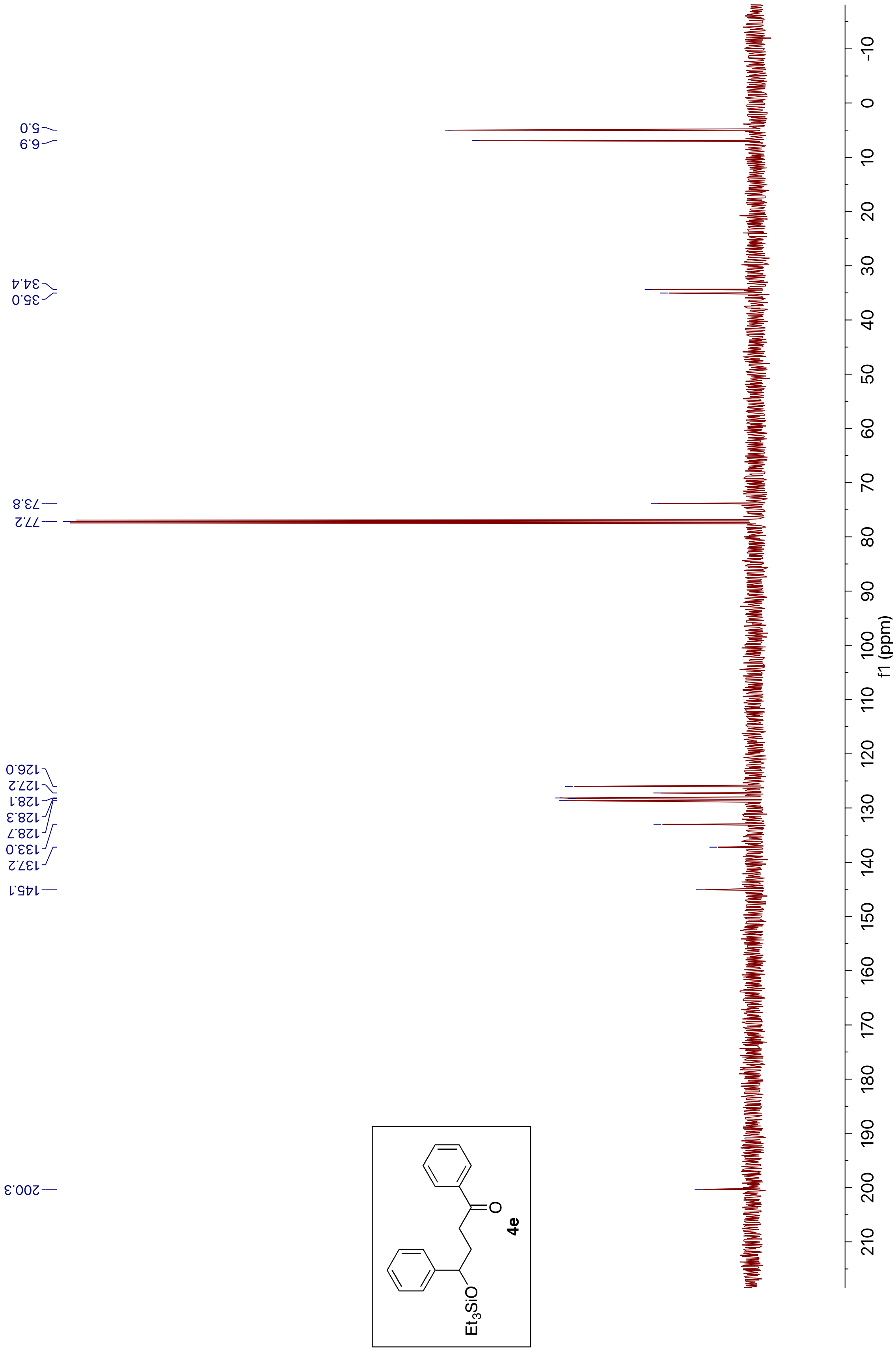

0.49
0.49
0.50
0.51
0.52
0.53
0.54
0.54
0.86
0.87
0.89
1.16
1.18
1.21
1.22
1.23
1.24
1.25
1.26
1.27
1.29
1.30
1.31
1.32
1.75
1.77
1.78
1.80
1.91
1.92
1.93
1.95
2.25
2.26
2.27
2.28
2.30
2.36
2.37
2.39
2.39
2.41
2.42
2.45
2.46
2.48
2.48
2.50
2.51
4.72
4.73
4.74
7.20
7.21
7.22
7.22
7.22
7.23
7.23
7.24
7.26
7.29
7.30
5.67
8.78
6.44
4.09
2.05
1.05
1.09
1.07
1.00
1.02
3.94
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0.5
f1 (ppm)
Et3SiO
O
4c

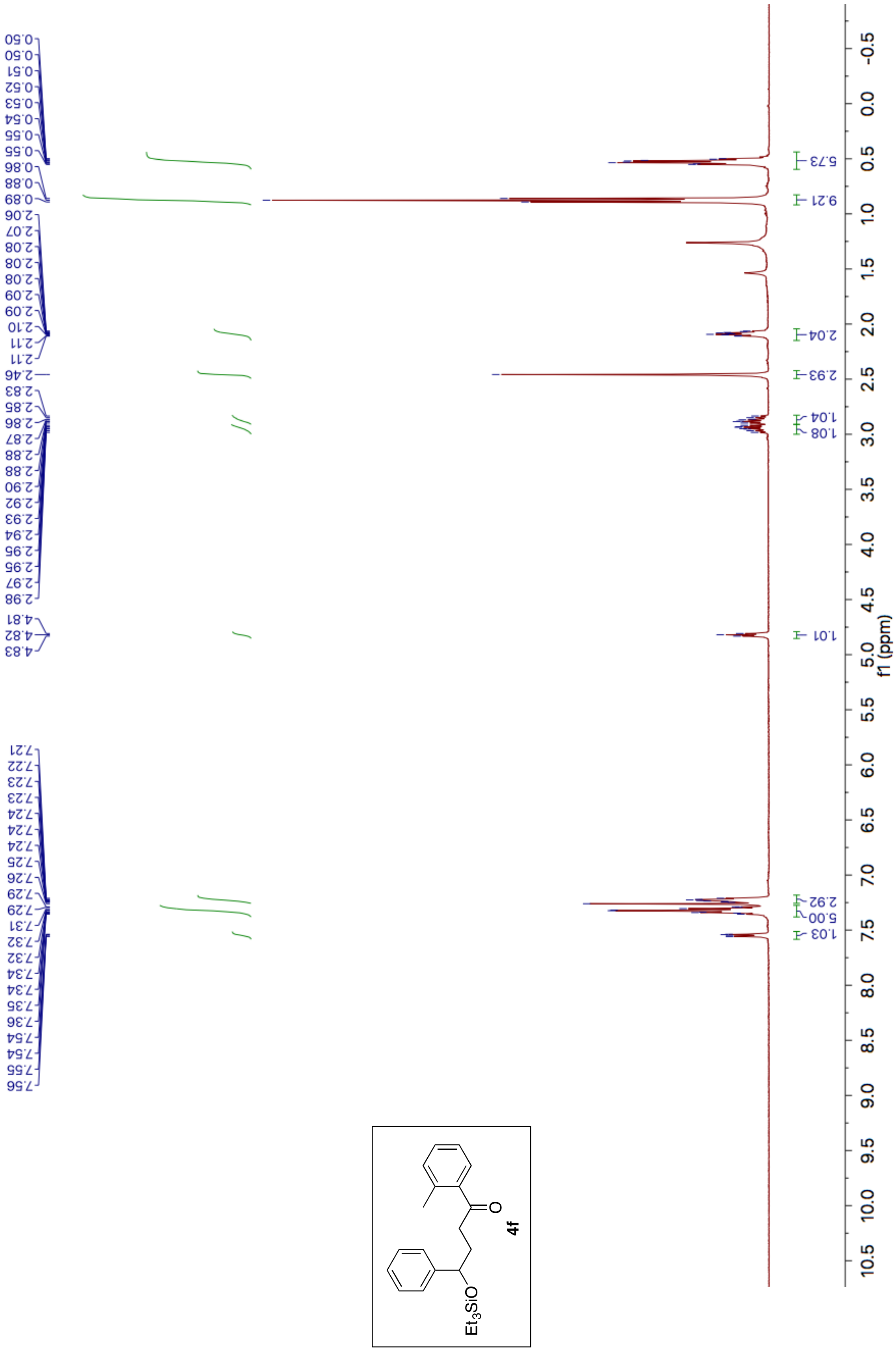

4.9
6.9
25.8
26.0
28.7
28.7
34.4
36.3
50.9
73.8
126.0
127.1
128.2
145.1
214.1
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
Et3SiO
O
4c

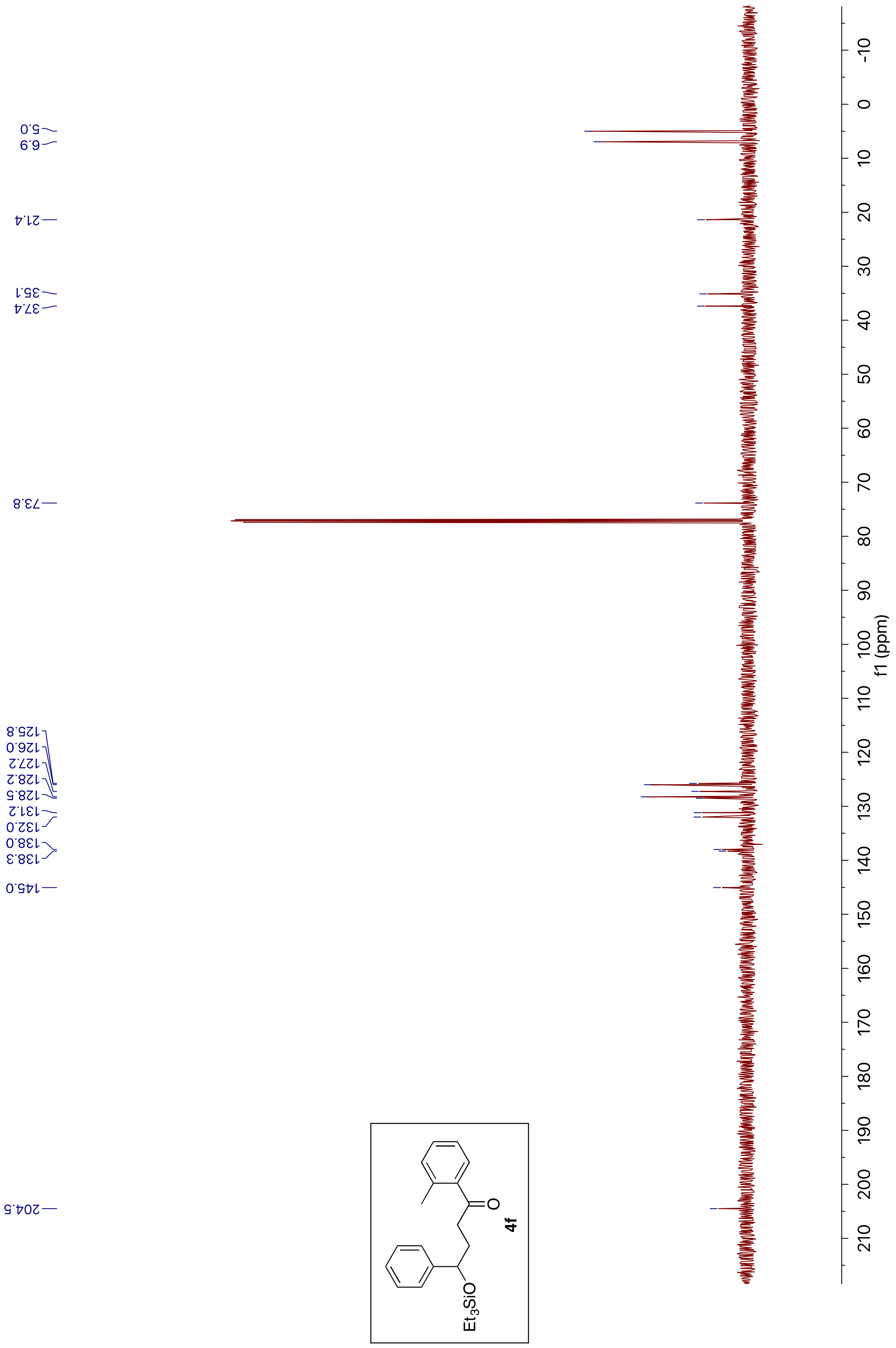

0.04
0.48
0.50
0.50
0.50
0.51
0.52
0.53
0.53
0.54
0.55
0.87
0.88
0.89
0.90
1.73
1.74
1.75
1.76
1.77
1.77
1.78
1.80
1.81
1.94
1.94
1.95
1.96
1.97
1.98
1.98
2.36
2.37
2.39
2.42
2.44
2.45
2.47
2.48
2.50
2.52
2.53
3.58
3.59
3.61
4.73
4.74
4.75
7.23
7.23
7.24
7.24
7.25
7.26
7.29
7.30
7.31
7.31
6.18
5.93
18.48
2.28
1.97
1.07
1.96
1.02
2.01
1.00
0.99
3.80
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
Et$_3$SiO
O
OTBS
4d

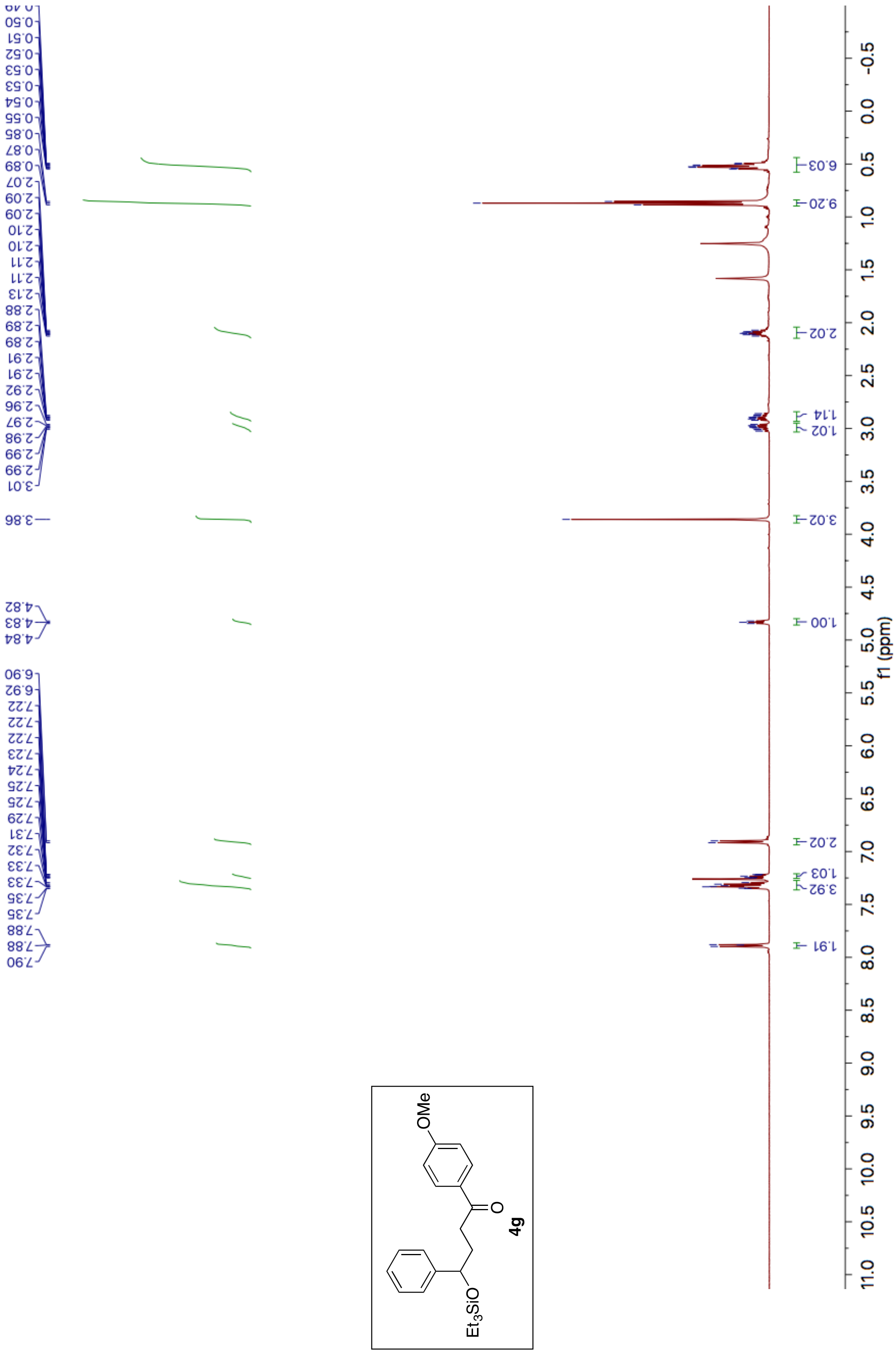

-5.2
4.9
6.9
18.4
26.1
27.0
34.5
38.5
39.2
62.3
73.7
126.0
127.2
128.2
145.0
210.9
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
Et_3SiO
O
OTBS
4d


0.50
0.51
0.52
0.53
0.54
0.54
0.55
0.56
0.86
0.88
0.89
2.10
2.11
2.12
2.12
2.13
2.14
2.14
2.15
2.91
2.92
2.93
2.94
2.94
2.96
2.96
2.97
3.02
3.03
3.04
3.05
3.05
3.07
3.07
3.08
7.22
7.23
7.24
7.24
7.25
7.25
7.30
7.30
7.31
7.31
7.32
7.33
7.34
7.34
7.35
7.36
7.42
7.44
7.45
7.45
7.52
7.52
7.52
7.53
7.54
7.54
7.55
7.55
7.90
7.90
7.91
7.92
6.03
9.37
2.03
1.04
1.01
1.00
1.00
4.00
2.02
1.01
2.02
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
Et3SiO
O
4e

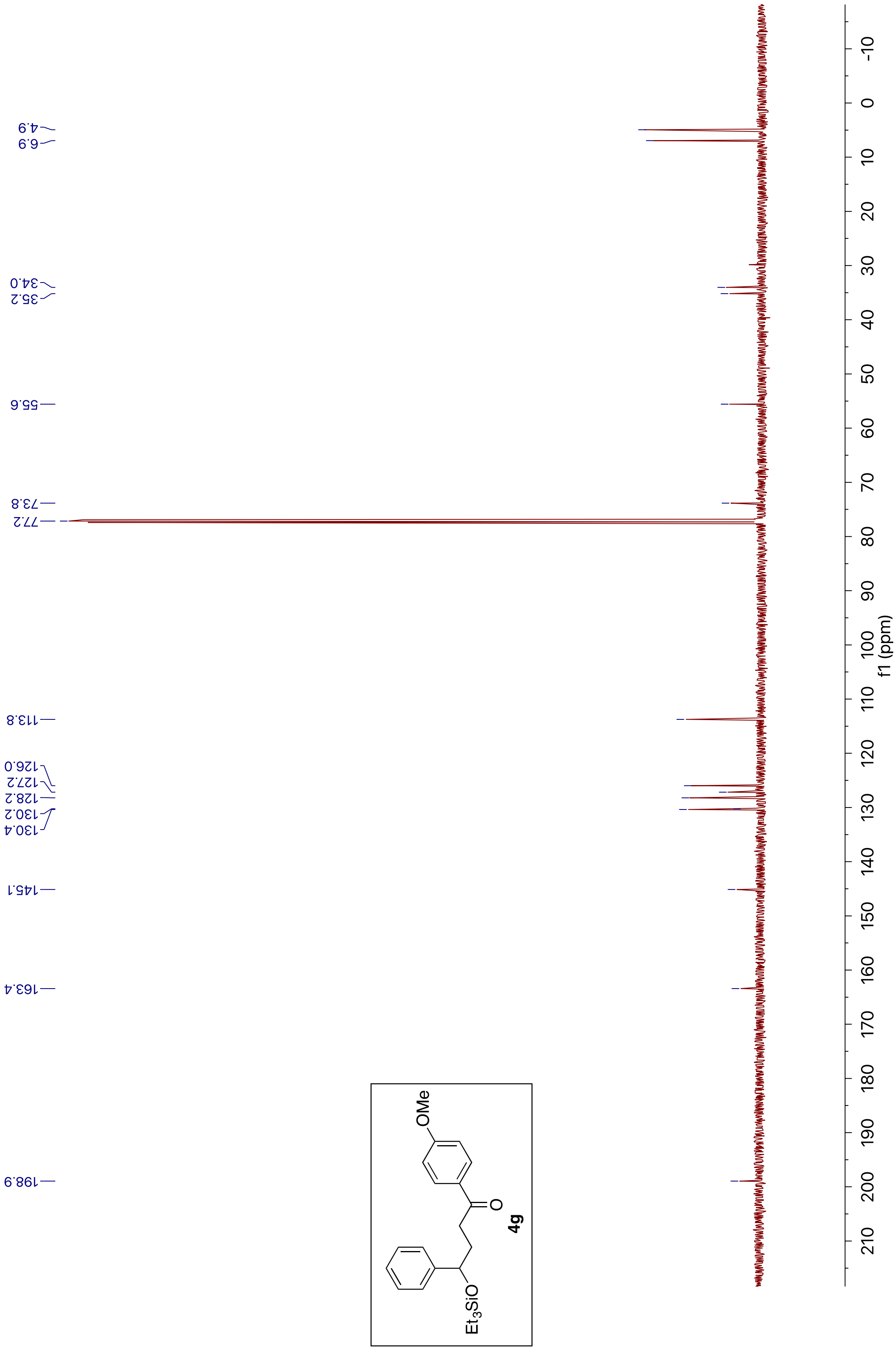

5.0
6.9
34.4
35.0
73.8
77.2
126.0
127.2
128.1
128.3
128.7
133.0
137.2
145.1
200.3
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
O
Et3SiO
4e

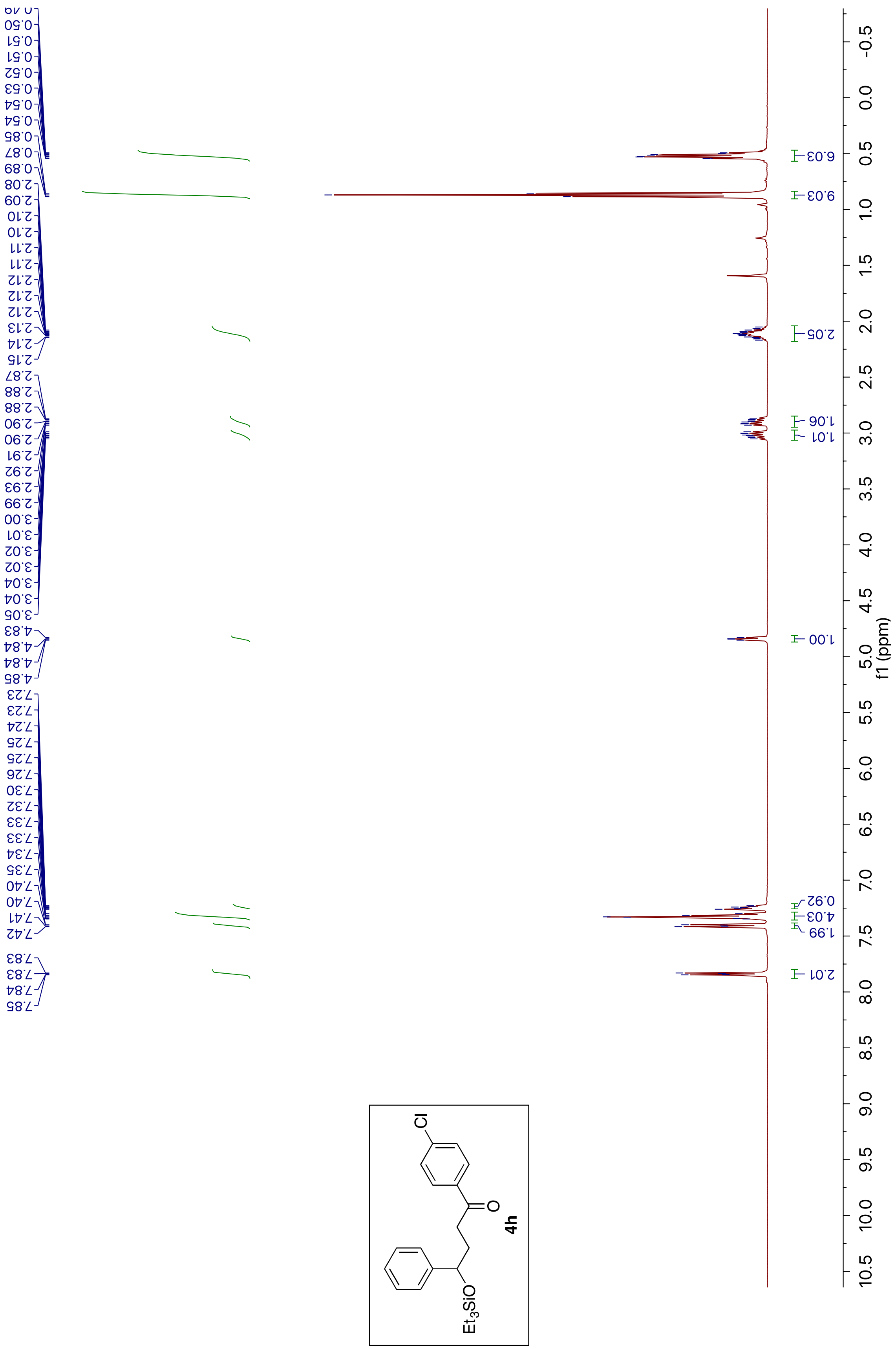

0.50
0.50
0.51
0.52
0.53
0.54
0.55
0.56
0.86
0.88
0.89
2.06
2.07
2.08
2.08
2.08
2.09
2.09
2.10
2.11
2.11
2.46
2.83
2.85
2.86
2.87
2.88
2.88
2.90
2.92
2.93
2.94
2.95
2.95
2.97
2.98
4.81
4.82
4.83
7.21
7.22
7.23
7.23
7.24
7.24
7.24
7.25
7.26
7.29
7.29
7.31
7.32
7.32
7.34
7.34
7.35
7.36
7.54
7.54
7.55
7.56
5.73
9.21
2.04
2.93
1.04
1.08
1.01
2.92
5.00
1.03
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
Et3SiO
O
4f

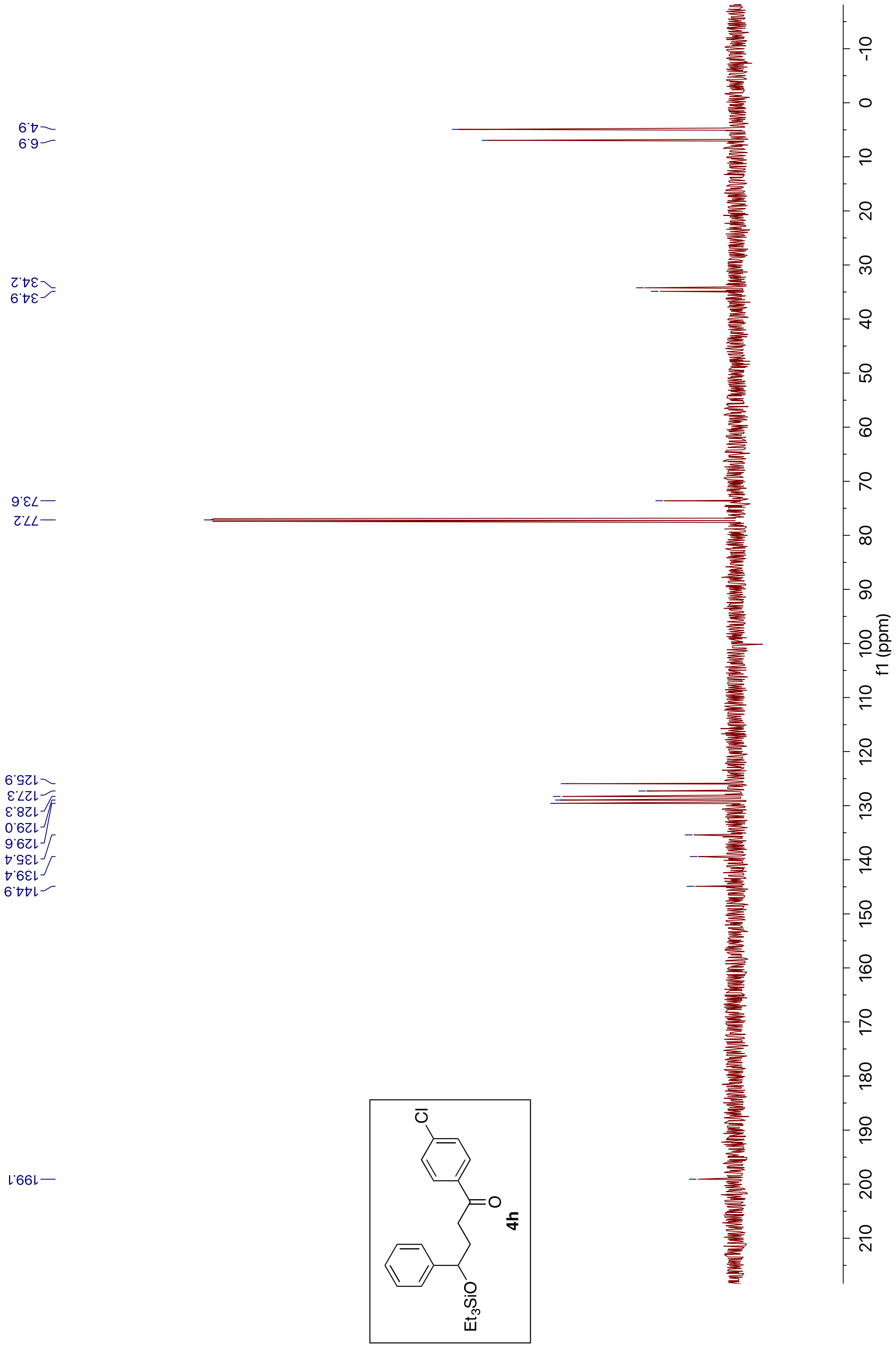

5.0
6.9
21.4
35.1
37.4
73.8
125.8
126.0
127.2
128.2
128.5
131.2
132.0
138.0
138.3
145.0
204.5
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
O
Et3SiO
4f

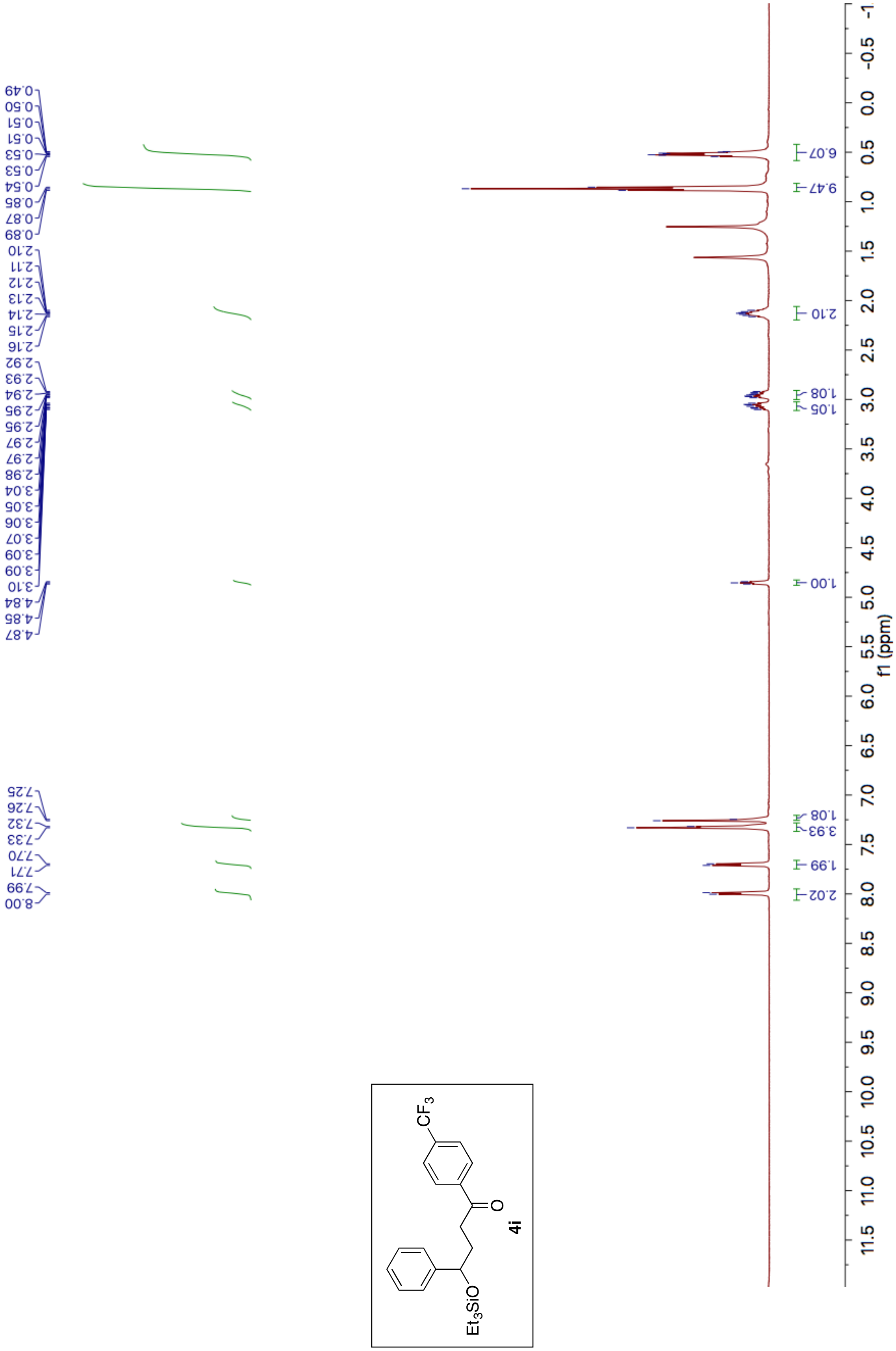

0.49
0.50
0.51
0.52
0.53
0.53
0.54
0.55
0.85
0.87
0.89
2.07
2.09
2.09
2.10
2.10
2.11
2.11
2.13
2.88
2.89
2.89
2.91
2.91
2.92
2.96
2.97
2.98
2.99
2.99
3.01
3.86
4.82
4.83
4.84
6.90
6.92
7.22
7.22
7.22
7.23
7.24
7.25
7.25
7.29
7.31
7.32
7.33
7.33
7.35
7.35
7.88
7.88
7.90
6.03
9.20
2.02
1.14
1.02
3.02
1.00
2.02
1.03
3.92
1.91
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
f1 (ppm)
OMe
O
Et3SiO

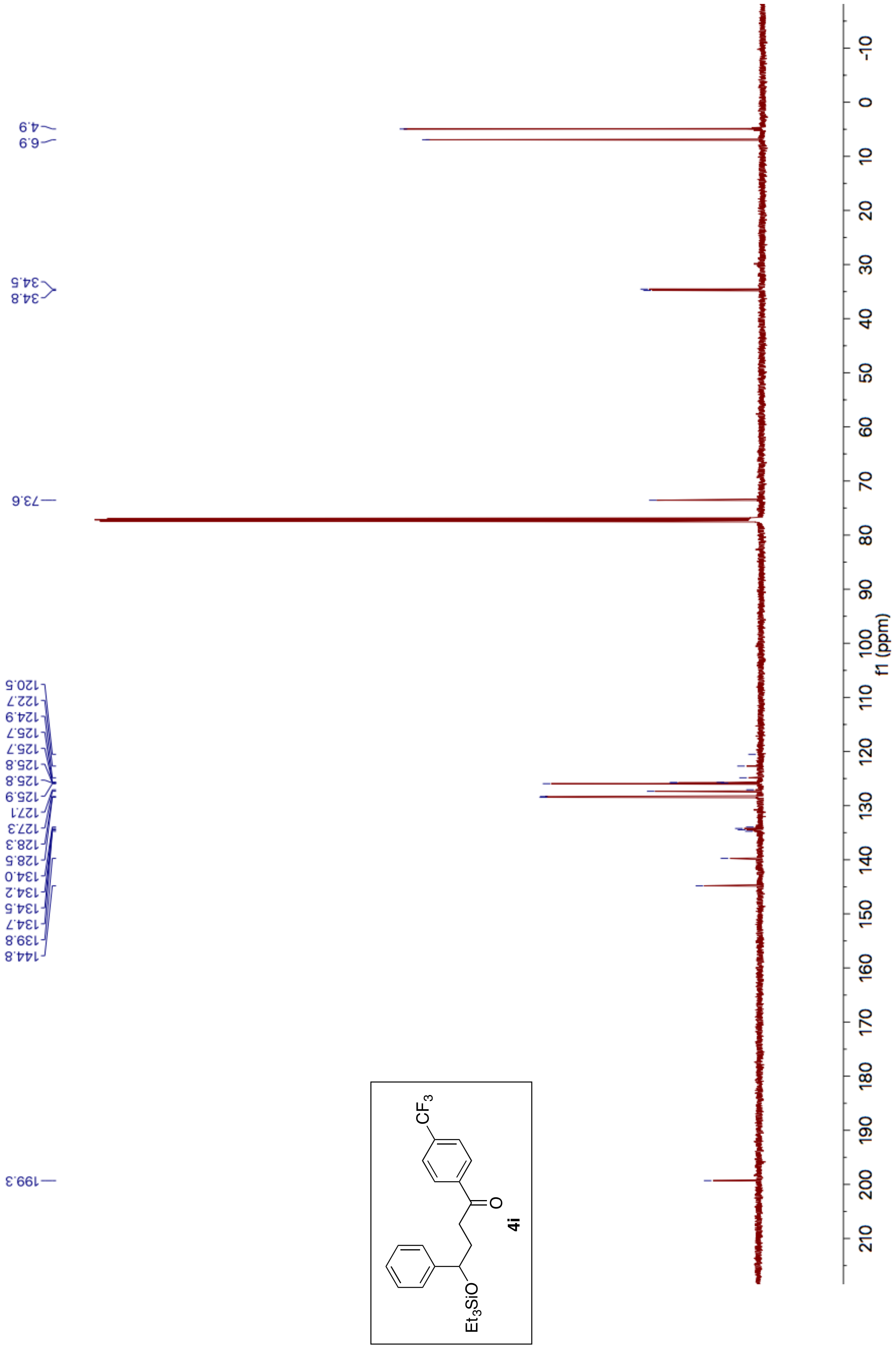
4g

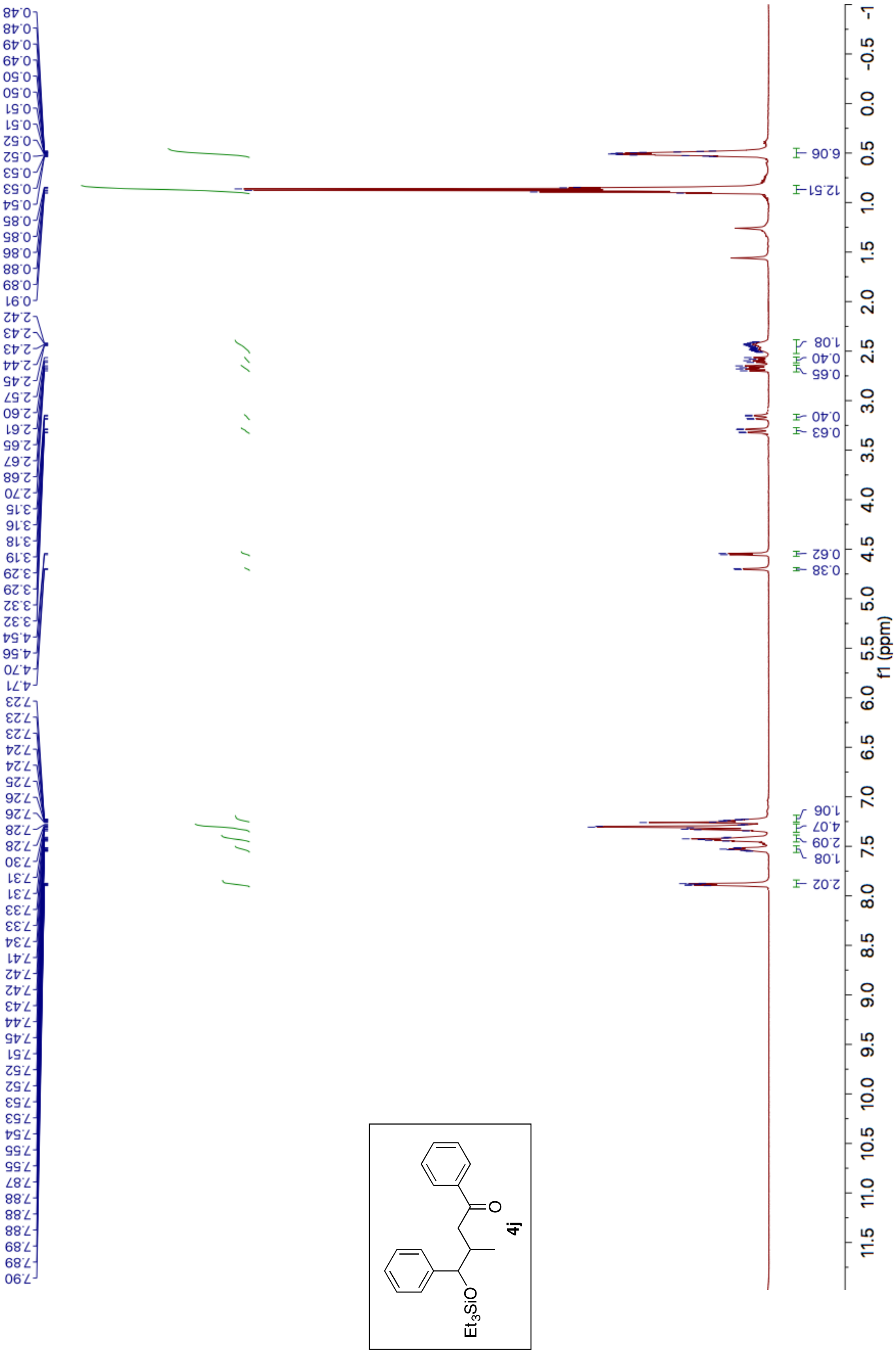

4.9
6.9
34.0
35.2
55.6
73.8
77.2
113.8
126.0
127.2
128.2
130.2
130.4
145.1
163.4
198.9
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OMe
O
Et3SiO
4g

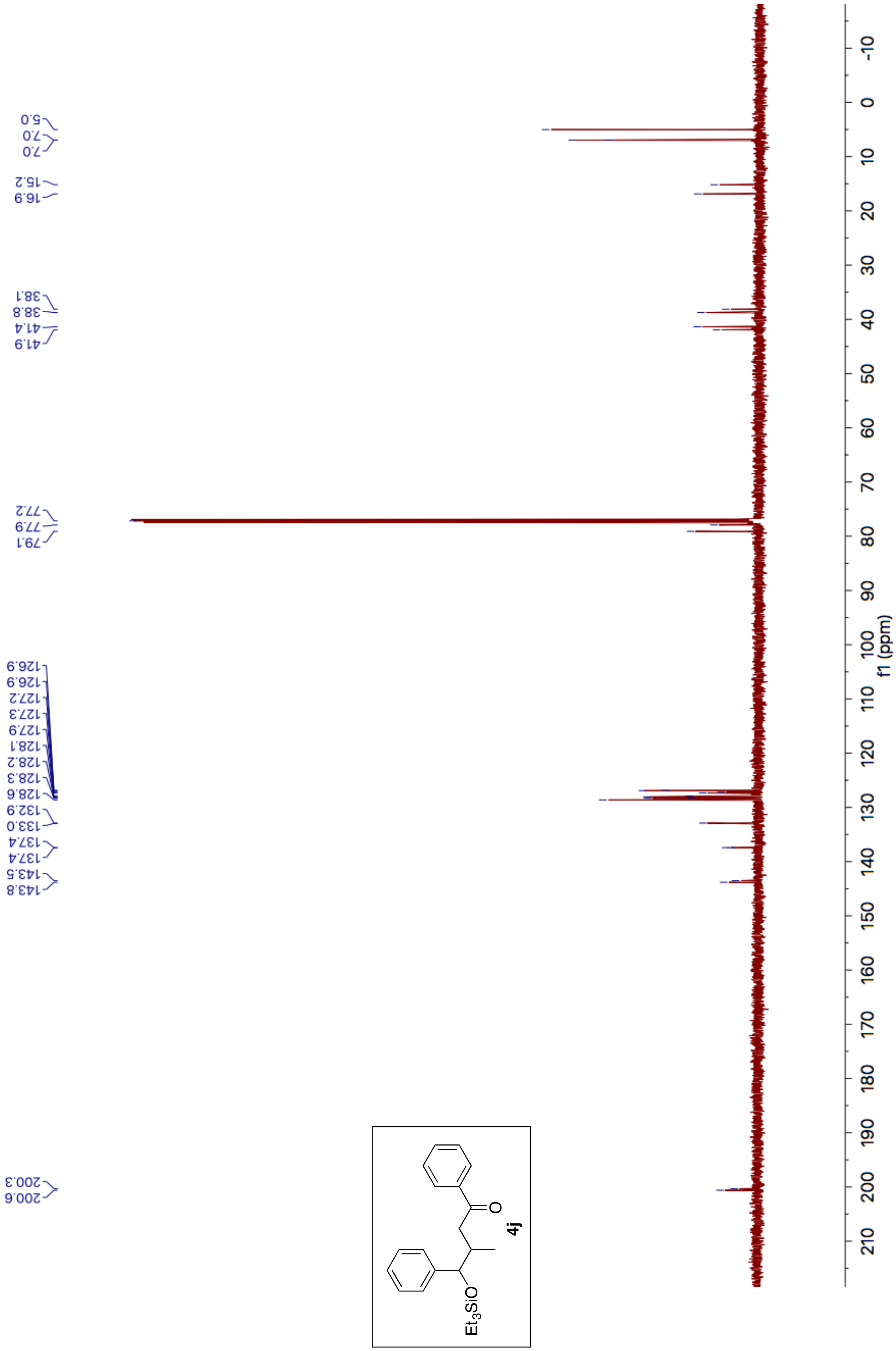

0.49
0.50
0.51
0.51
0.52
0.53
0.54
0.54
0.85
0.87
0.89
2.08
2.09
2.10
2.10
2.11
2.11
2.12
2.12
2.12
2.13
2.14
2.15
2.87
2.88
2.88
2.90
2.90
2.91
2.92
2.93
2.99
3.00
3.01
3.02
3.02
3.04
3.04
3.05
4.83
4.84
4.84
4.85
7.23
7.23
7.24
7.25
7.25
7.26
7.30
7.32
7.33
7.33
7.34
7.35
7.40
7.40
7.41
7.42
7.83
7.83
7.84
7.85
6.03
9.03
2.05
1.06
1.01
1.00
0.92
4.03
1.99
2.01
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
Cl
O
Et$_3$SiO
4h

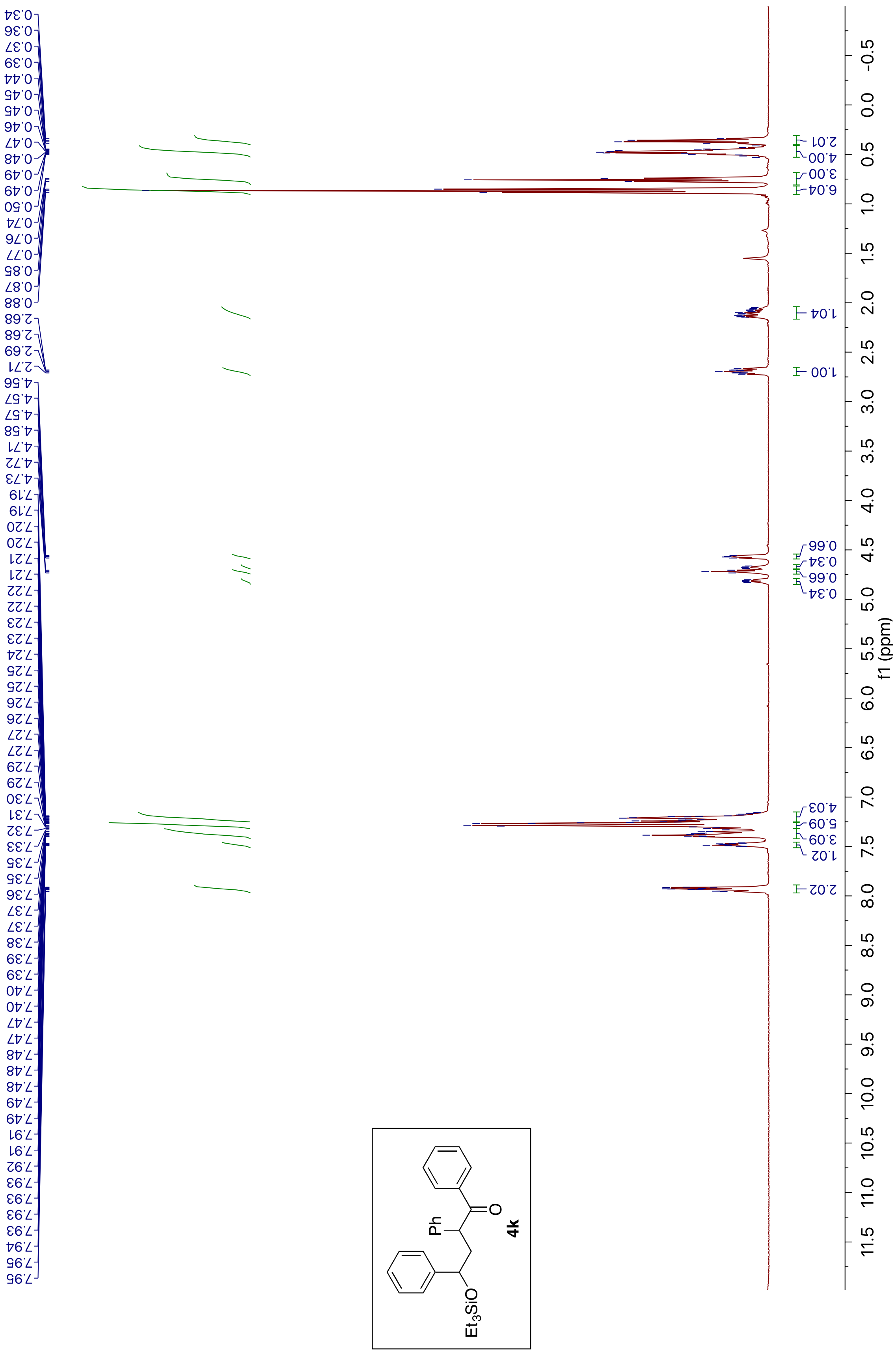

199.1
144.9
139.4
135.4
129.6
129.0
128.3
127.3
125.9
77.2
73.6
34.9
34.2
6.9
4.9
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Cl
O
Et3SiO
4h

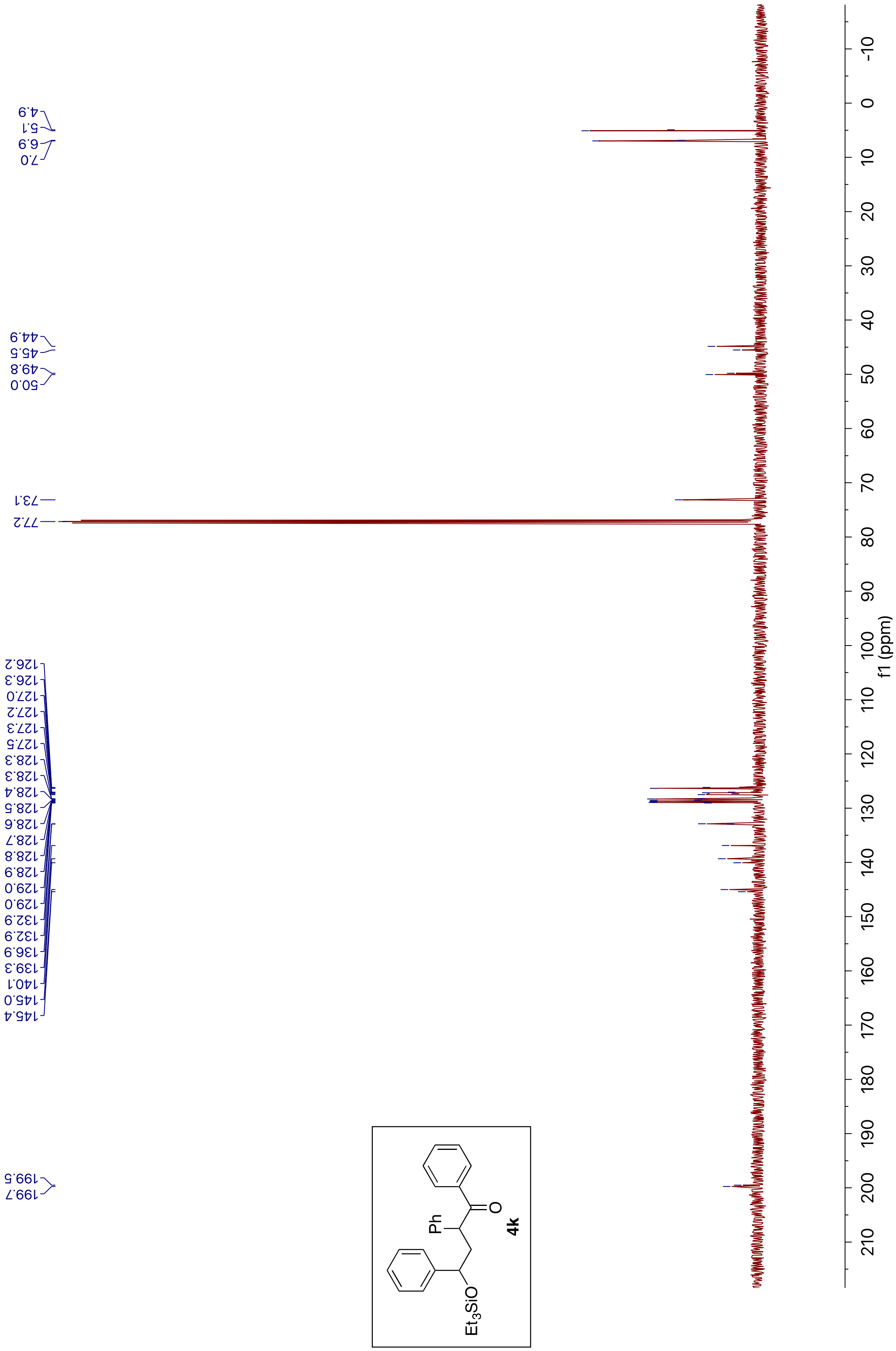

0.49
0.50
0.51
0.51
0.53
0.53
0.54
0.85
0.87
0.89
2.10
2.11
2.12
2.13
2.14
2.15
2.16
2.92
2.93
2.94
2.95
2.95
2.97
2.98
3.04
3.05
3.06
3.07
3.09
3.09
3.10
4.84
4.85
4.87
7.25
7.26
7.32
7.33
7.70
7.71
7.99
8.00
6.07
9.47
2.10
1.08
1.05
1.00
1.08
3.93
1.99
2.02
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
CF3
O
Et3SiO
4i

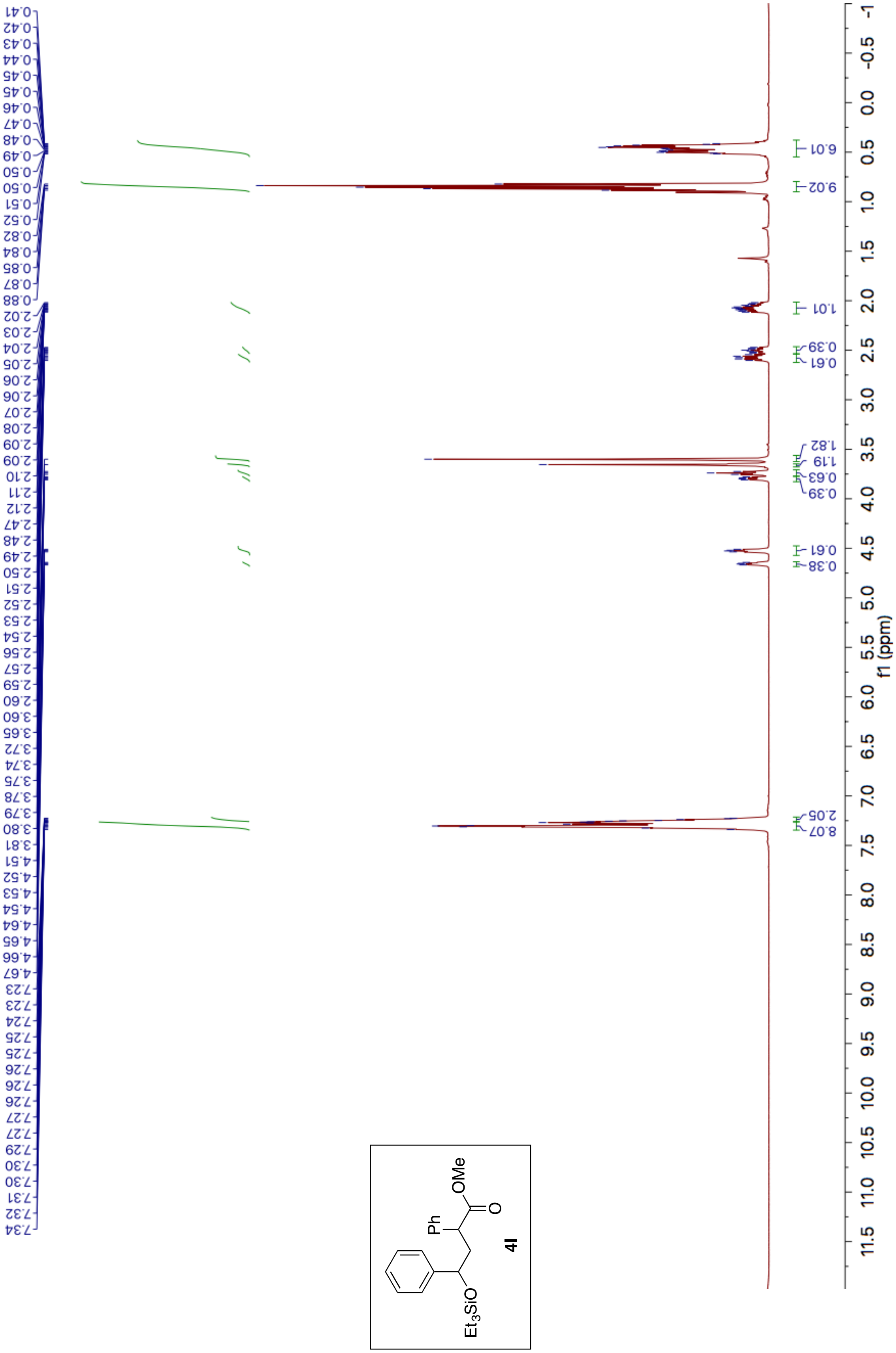

4.9
6.9
34.5
34.8
73.6
120.5
122.7
124.9
125.7
125.7
125.8
125.8
125.9
127.1
127.3
128.3
128.5
134.0
134.2
134.5
134.7
139.8
144.8
199.3
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
CF$_3$
O
Et$_3$SiO
4i


7.90
7.89
7.89
7.88
7.88
7.88
7.87
7.55
7.55
7.54
7.53
7.53
7.52
7.52
7.51
7.45
7.44
7.43
7.42
7.42
7.41
7.34
7.33
7.33
7.31
7.31
7.30
7.28
7.28
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.23
4.71
4.70
4.56
4.54
3.32
3.32
3.29
3.29
3.19
3.18
3.16
3.15
2.70
2.68
2.67
2.65
2.61
2.60
2.57
2.45
2.44
2.43
2.43
2.42
0.91
0.89
0.88
0.86
0.85
0.85
0.54
0.53
0.53
0.52
0.52
0.51
0.51
0.50
0.50
0.49
0.49
0.48
0.48
2.02
1.08
2.09
4.07
1.06
0.38
0.62
0.63
0.40
0.65
0.40
1.08
12.51
6.06
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
Et_3SiO
O
4j

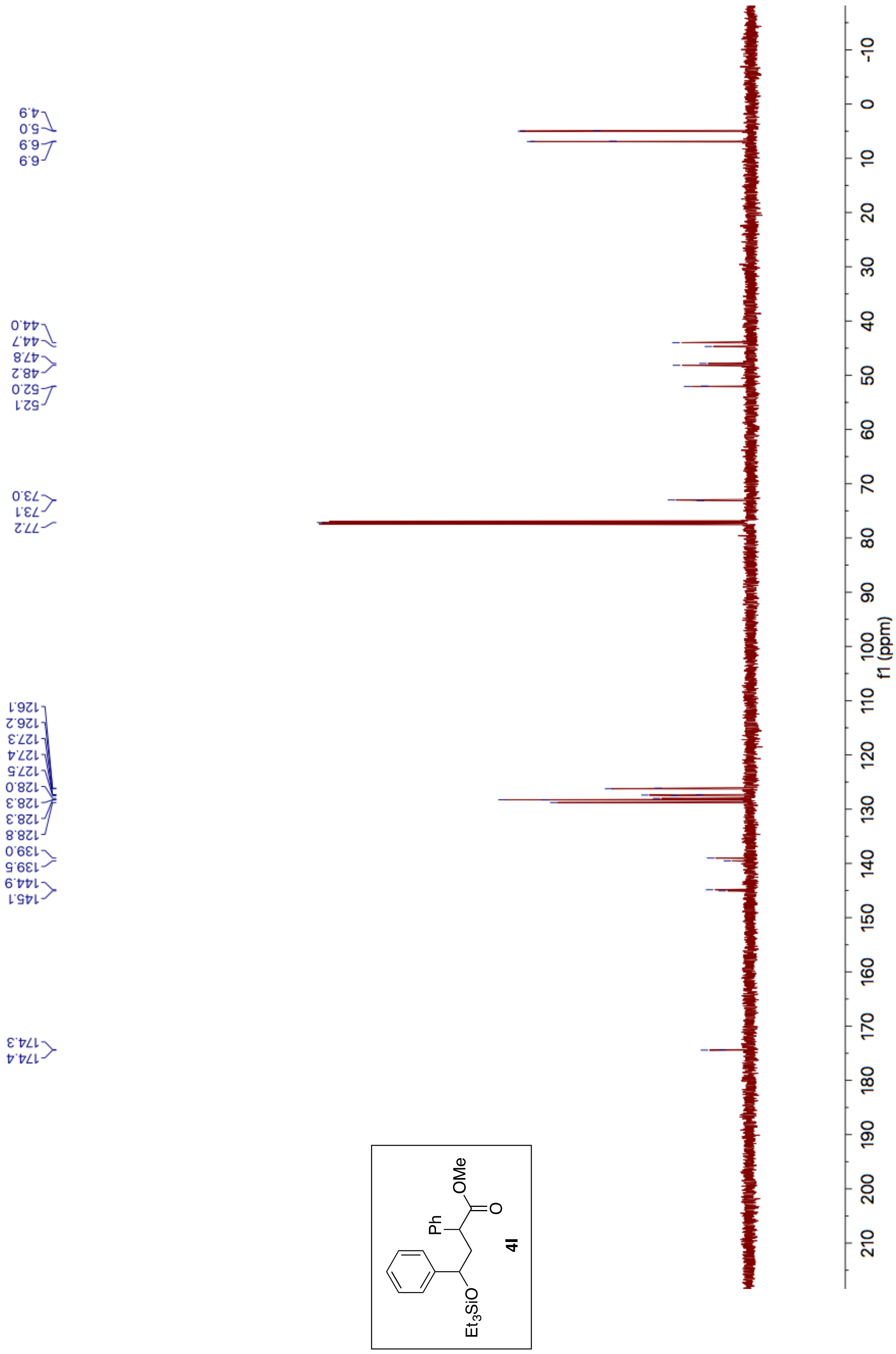

5.0
7.0
7.0
15.2
16.9
38.1
38.8
41.4
41.9
77.2
77.9
79.1
126.9
126.9
127.2
127.3
127.9
128.1
128.2
128.3
128.6
132.9
133.0
137.4
137.4
143.5
143.8
200.3
200.6
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
Et3SiO
O
4j

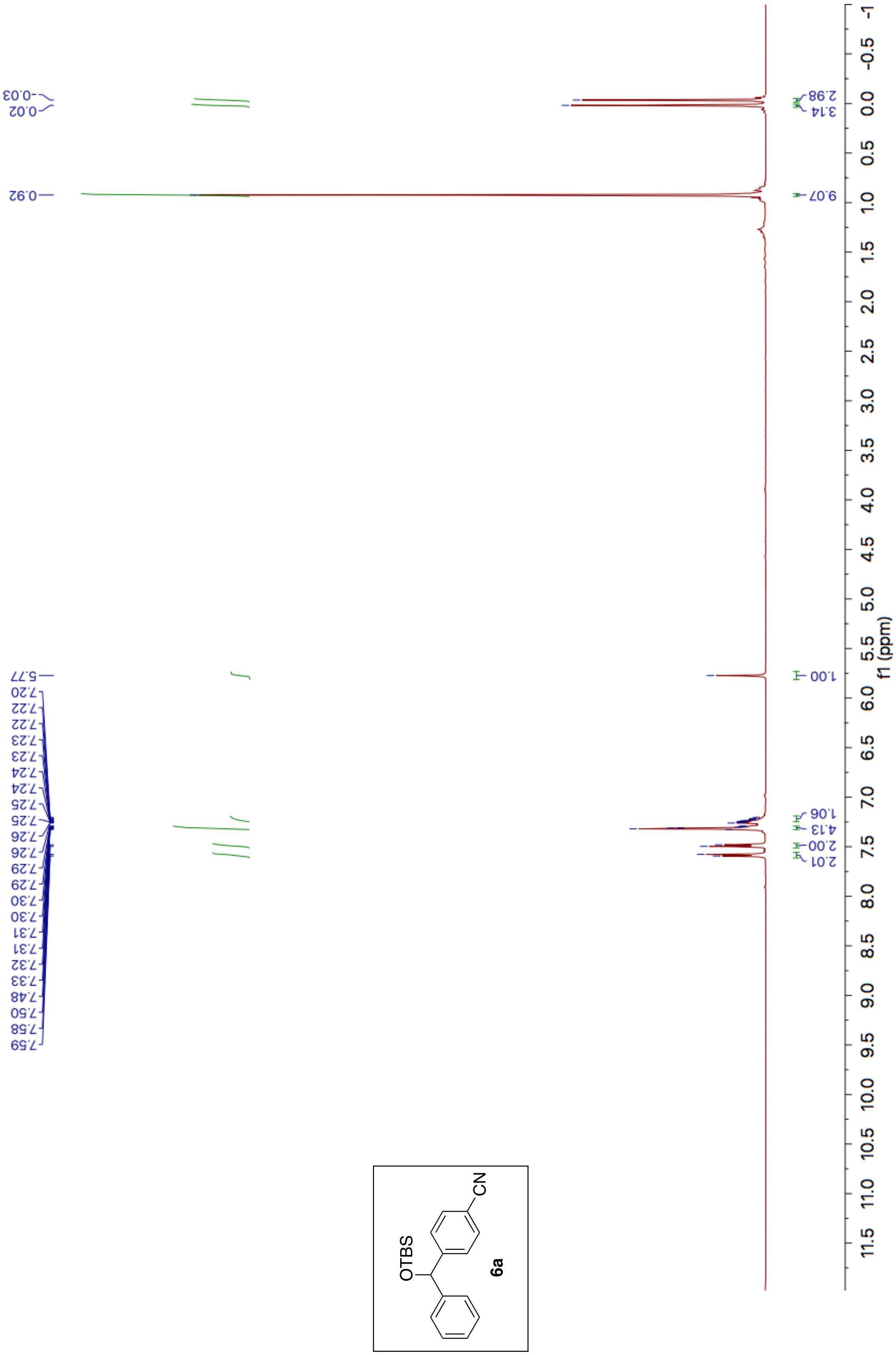

0.34
0.36
0.37
0.39
0.44
0.45
0.45
0.46
0.47
0.48
0.49
0.49
0.50
0.74
0.76
0.77
0.85
0.87
0.88
2.68
2.68
2.69
2.71
4.56
4.57
4.57
4.58
4.71
4.72
4.73
7.19
7.19
7.20
7.20
7.21
7.21
7.22
7.22
7.23
7.23
7.24
7.25
7.25
7.26
7.26
7.27
7.27
7.29
7.29
7.30
7.31
7.32
7.33
7.35
7.35
7.36
7.37
7.37
7.38
7.39
7.39
7.40
7.40
7.47
7.47
7.48
7.48
7.48
7.49
7.49
7.91
7.91
7.92
7.93
7.93
7.93
7.94
7.95
7.95
2.01
4.00
3.00
6.04
1.04
1.00
0.66
0.34
0.66
0.34
4.03
5.09
3.09
1.02
2.02
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
Ph
O
Et$_3$SiO
4k

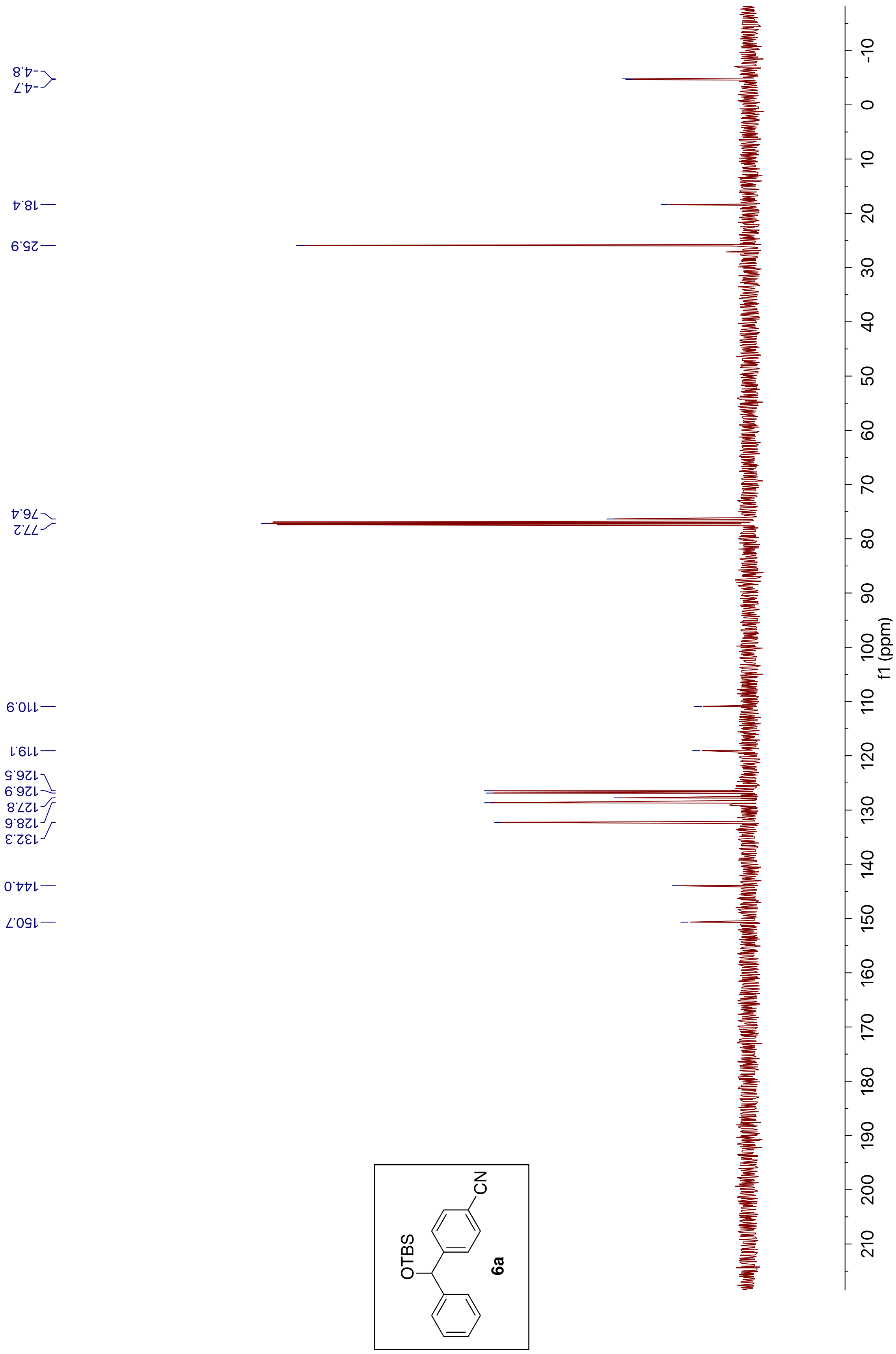

4.9
5.1
6.9
7.0
44.9
45.5
49.8
50.0
73.1
77.2
126.2
126.3
127.0
127.2
127.3
127.5
128.3
128.3
128.4
128.5
128.6
128.7
128.8
128.9
129.0
129.0
132.9
132.9
136.9
139.3
140.1
145.0
145.4
199.5
199.7
Ph
O
Et3SiO
4k
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)

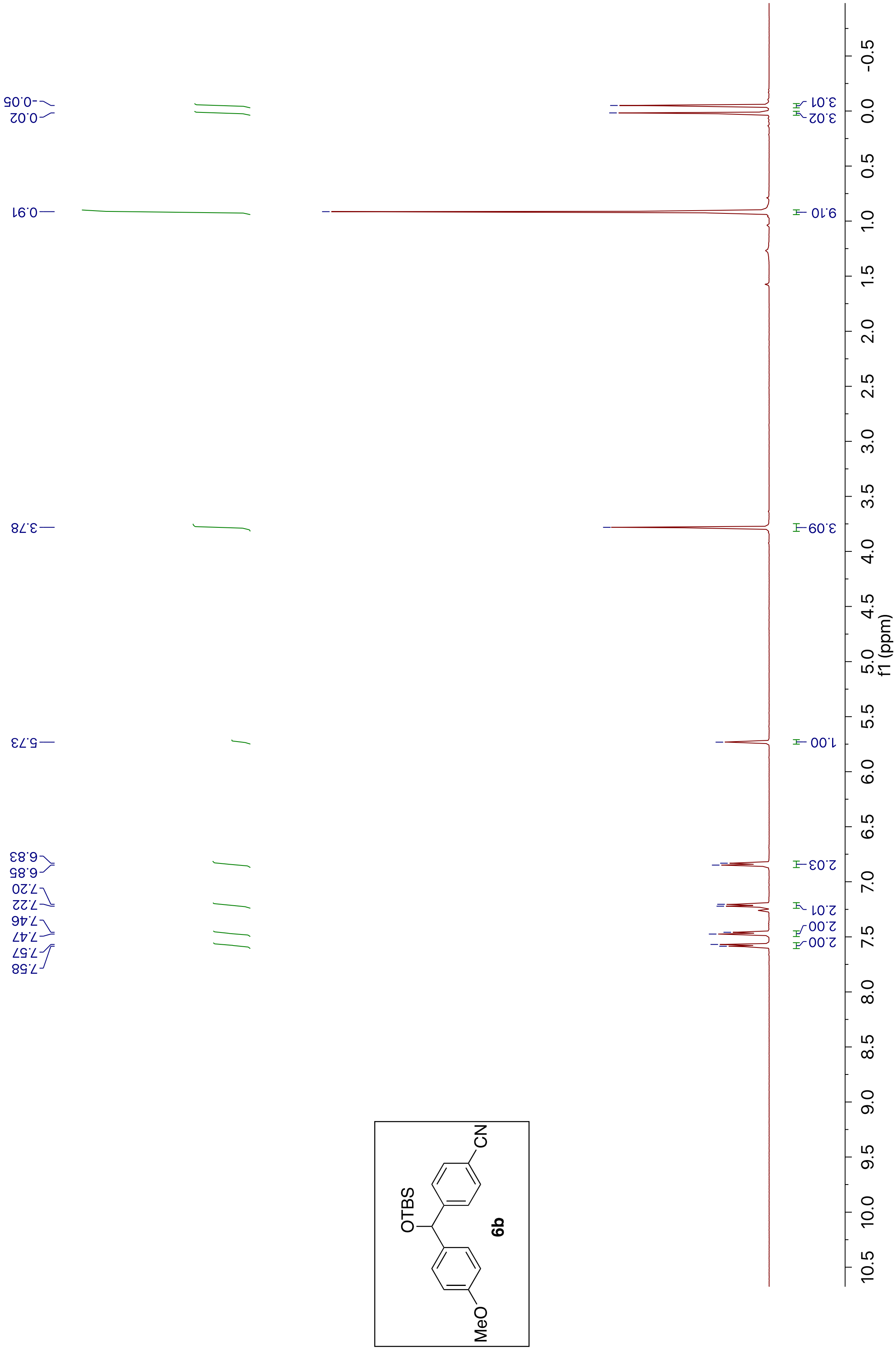

7.34
7.32
7.31
7.30
7.30
7.29
7.27
7.27
7.26
7.26
7.26
7.25
7.24
7.23
7.23
4.67
4.66
4.65
4.64
4.54
4.53
4.52
4.51
3.81
3.80
3.79
3.78
3.75
3.74
3.72
3.65
3.60
2.60
2.59
2.57
2.56
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.47
2.12
2.11
2.10
2.09
2.09
2.08
2.07
2.06
2.06
2.05
2.04
2.03
2.02
0.88
0.87
0.85
0.84
0.82
0.52
0.51
0.50
0.50
0.49
0.48
0.47
0.46
0.45
0.45
0.44
0.43
0.42
0.41
6.01
9.02
1.01
0.39
0.61
1.82
1.19
0.63
0.39
0.61
0.38
2.05
8.07
f1 (ppm)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
Et$_3$SiO
Ph
OMe
O

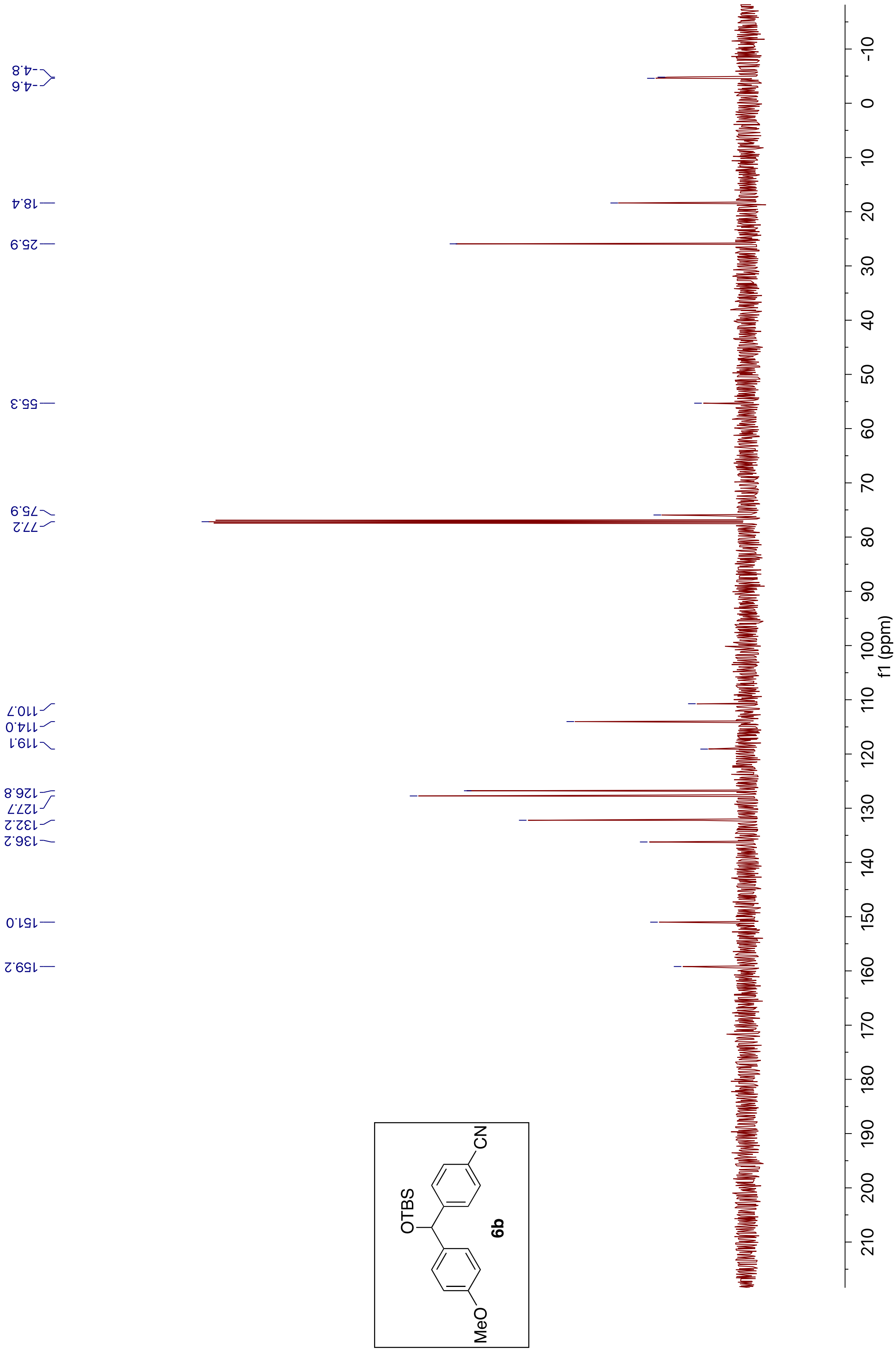
4l

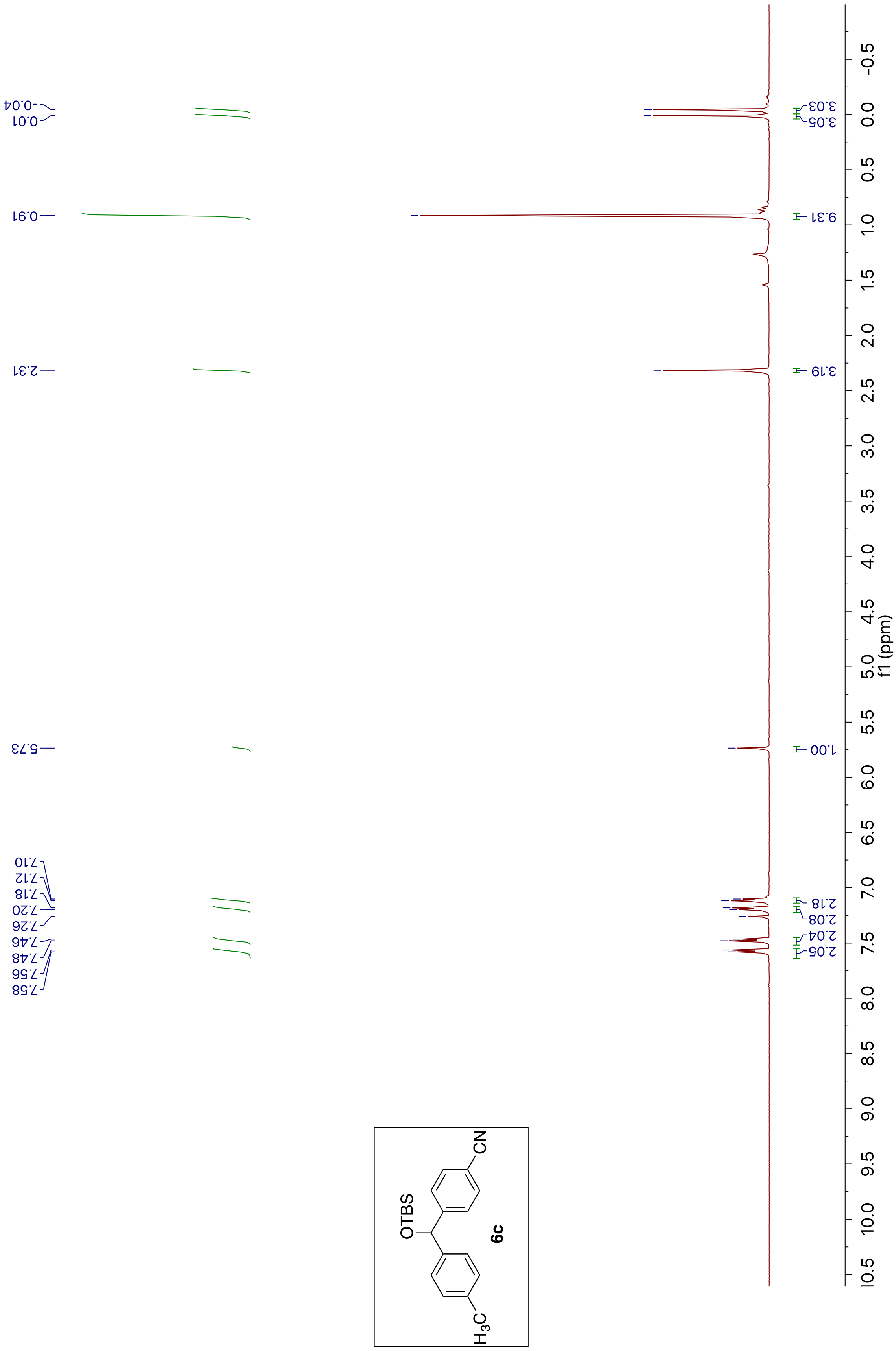

4.9
5.0
6.9
6.9
44.0
44.7
47.8
48.2
52.0
52.1
73.0
73.1
77.2
126.1
126.2
127.3
127.4
127.5
128.0
128.3
128.3
128.8
139.0
139.5
144.9
145.1
174.3
174.4
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
Et$_3$SiO
Ph
OMe
O
4l

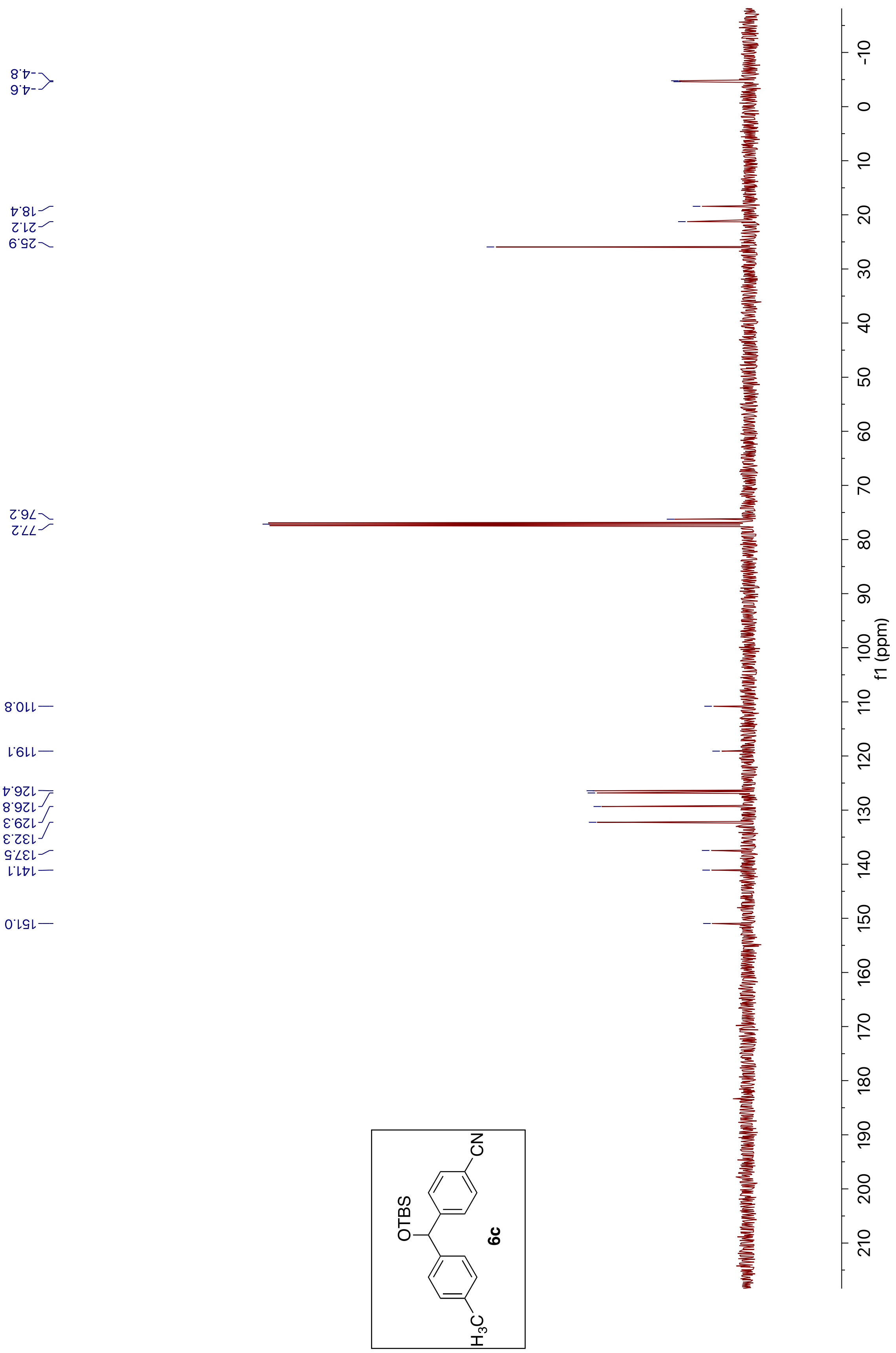

-0.03
0.02
0.92
5.77
7.20
7.22
7.22
7.23
7.23
7.24
7.24
7.25
7.25
7.26
7.26
7.29
7.29
7.30
7.30
7.31
7.31
7.32
7.33
7.48
7.50
7.58
7.59
2.98
3.14
9.07
1.00
1.06
4.13
2.00
2.01
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OTBS
CN
6a

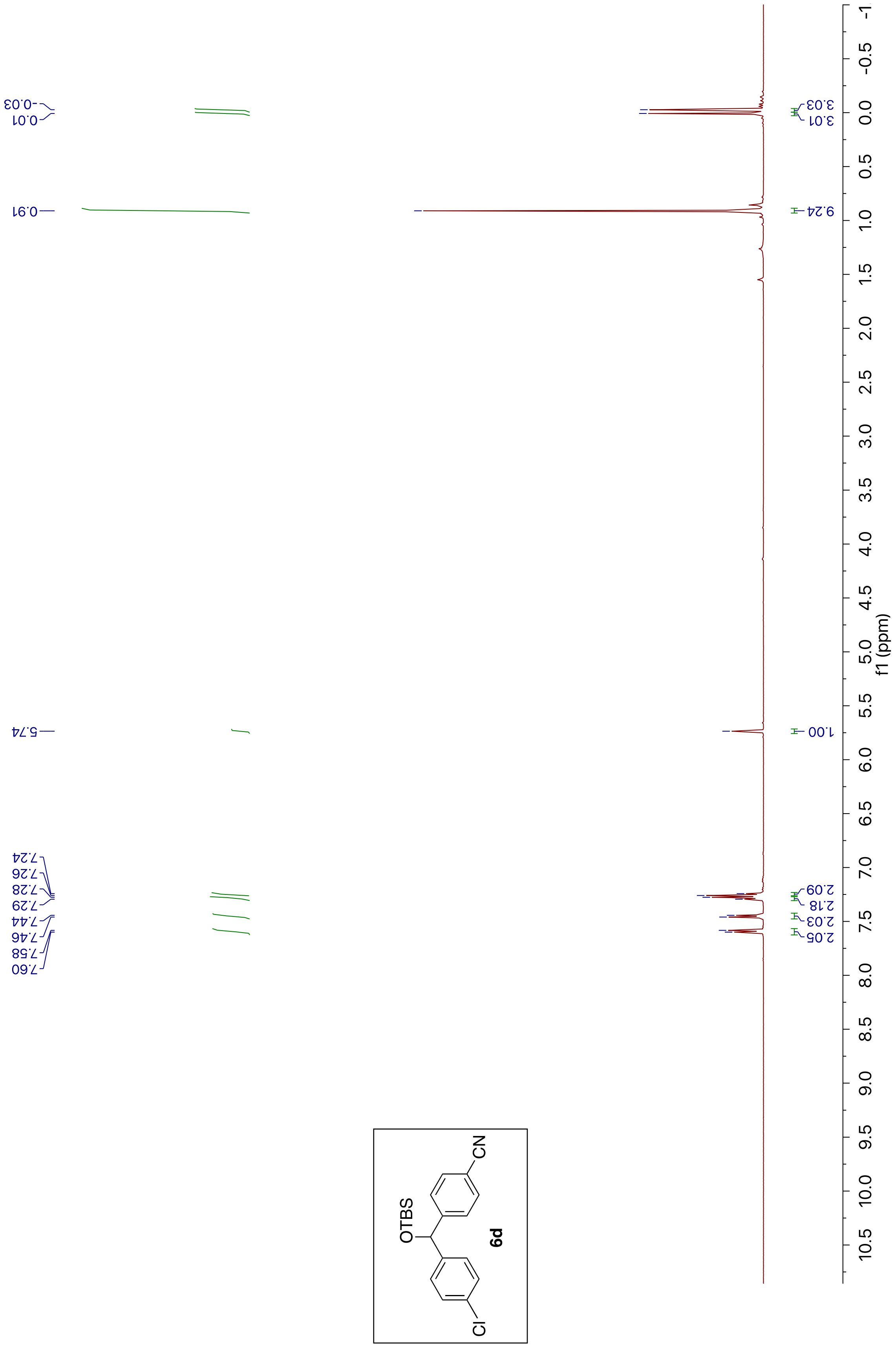

-4.8
-4.7
18.4
25.9
76.4
77.2
110.9
119.1
126.5
126.9
127.8
128.6
132.3
144.0
150.7
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CN
6a


-0.05
0.02
0.91
3.78
5.73
6.83
6.85
7.20
7.22
7.46
7.47
7.57
7.58
3.01
3.02
9.10
3.09
1.00
2.03
2.01
2.00
2.00
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OTBS
CN
MeO
6b

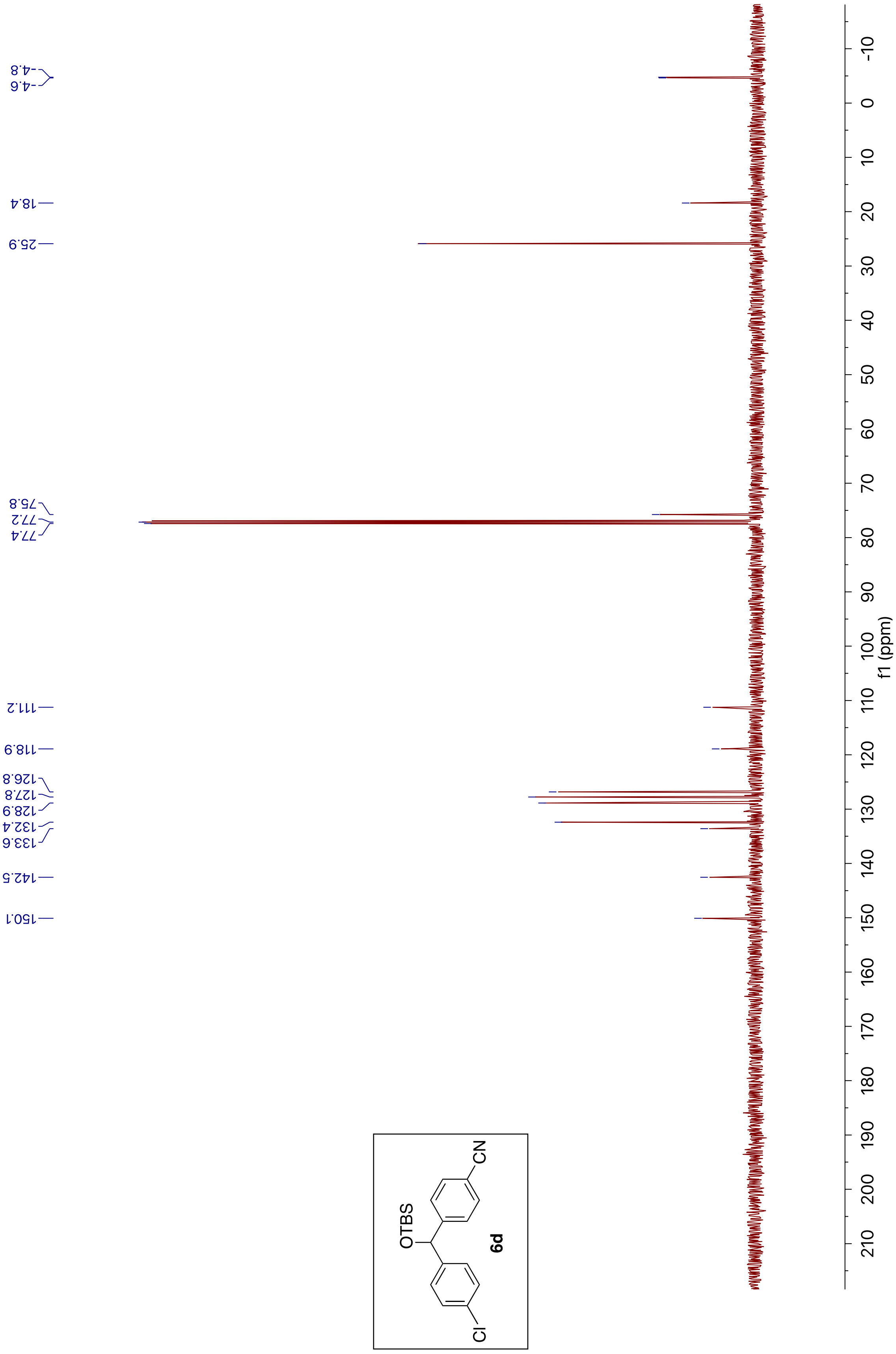

-4.8
-4.6
18.4
25.9
55.3
75.9
77.2
110.7
114.0
119.1
126.8
127.7
132.2
136.2
151.0
159.2
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
MeO
CN
6b

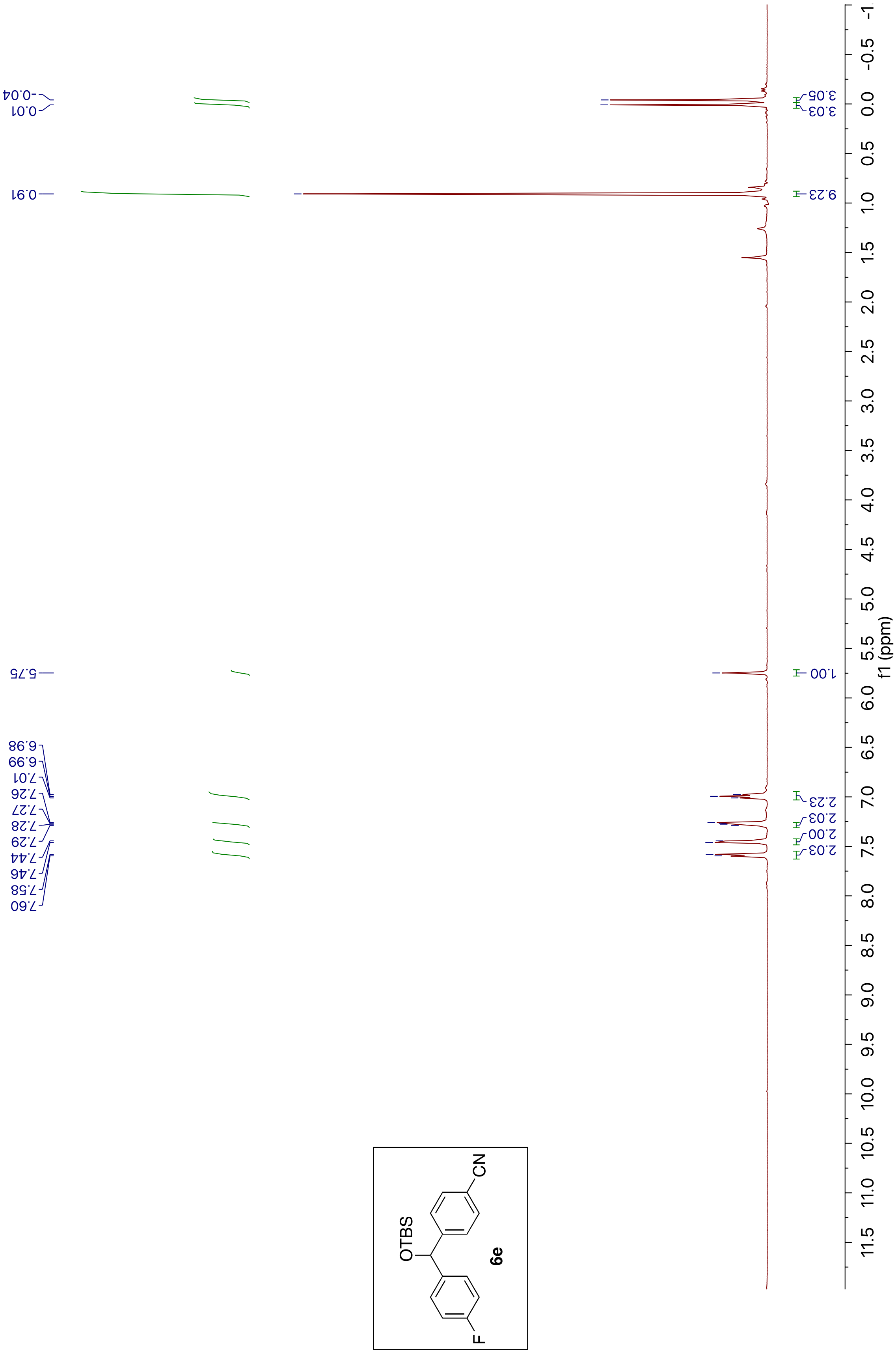

-0.04
0.01
0.91
2.31
5.73
7.10
7.12
7.18
7.20
7.26
7.46
7.48
7.56
7.58
3.03
3.05
9.31
3.19
1.00
2.18
2.08
2.04
2.05
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OTBS
CN
H_3C
6c

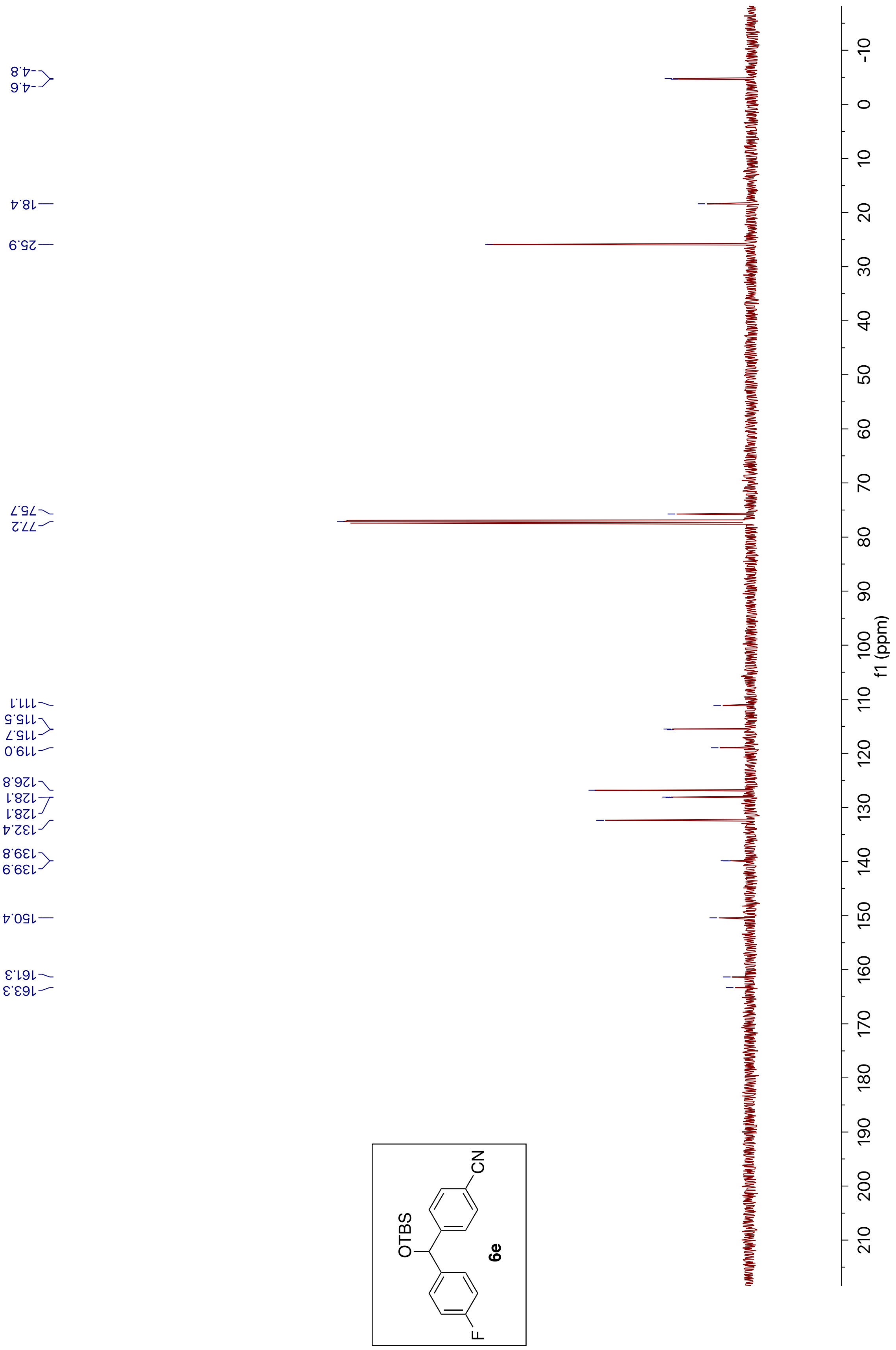

-4.8
-4.6
18.4
21.2
25.9
76.2
77.2
110.8
119.1
126.4
126.8
129.3
132.3
137.5
141.1
151.0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CN
H_3C
6c


-0.03
0.01
0.91
5.74
7.24
7.26
7.28
7.29
7.44
7.46
7.58
7.60
3.03
3.01
9.24
1.00
2.09
2.18
2.03
2.05
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OTBS
CN
Cl

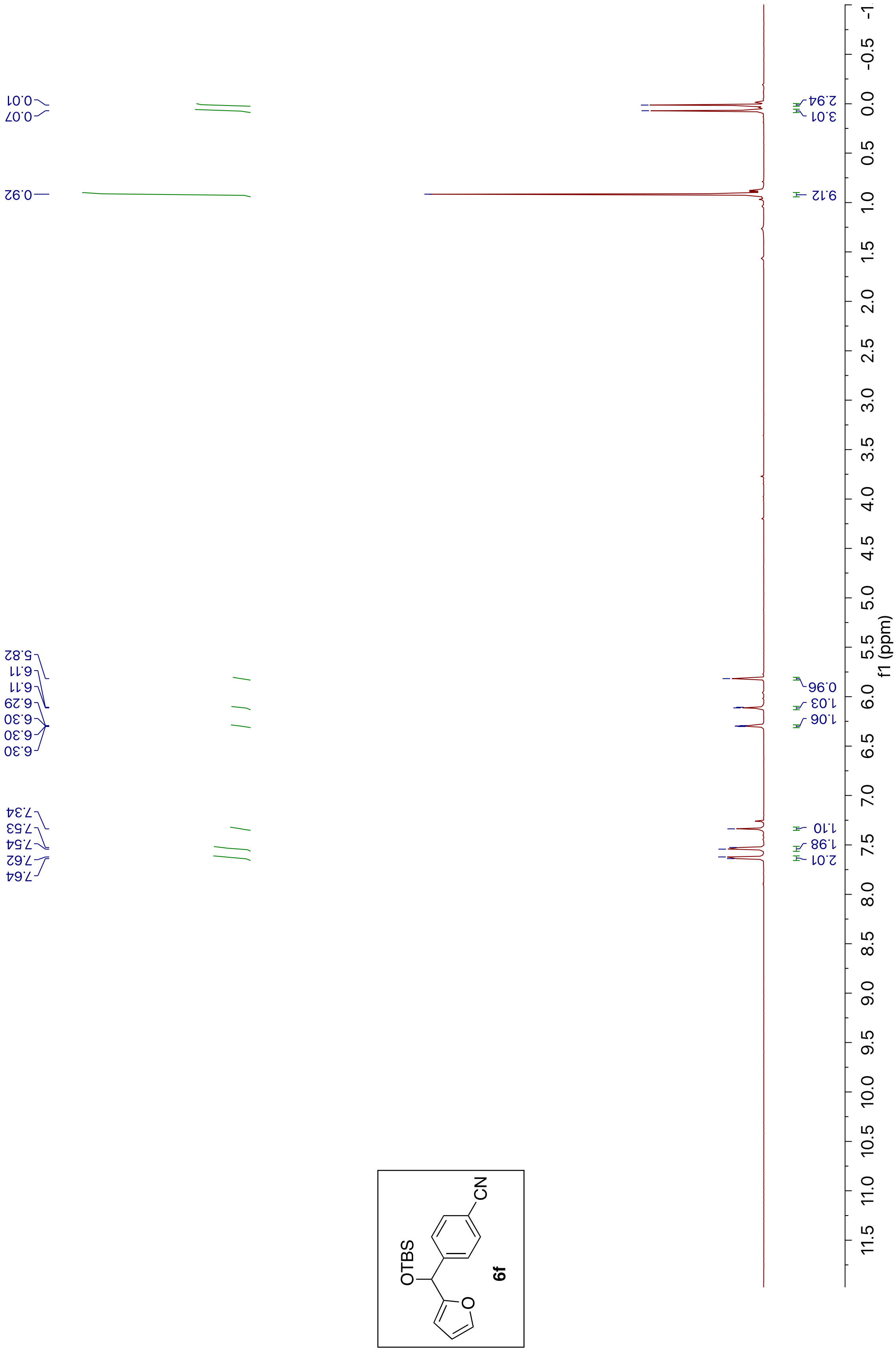
6d

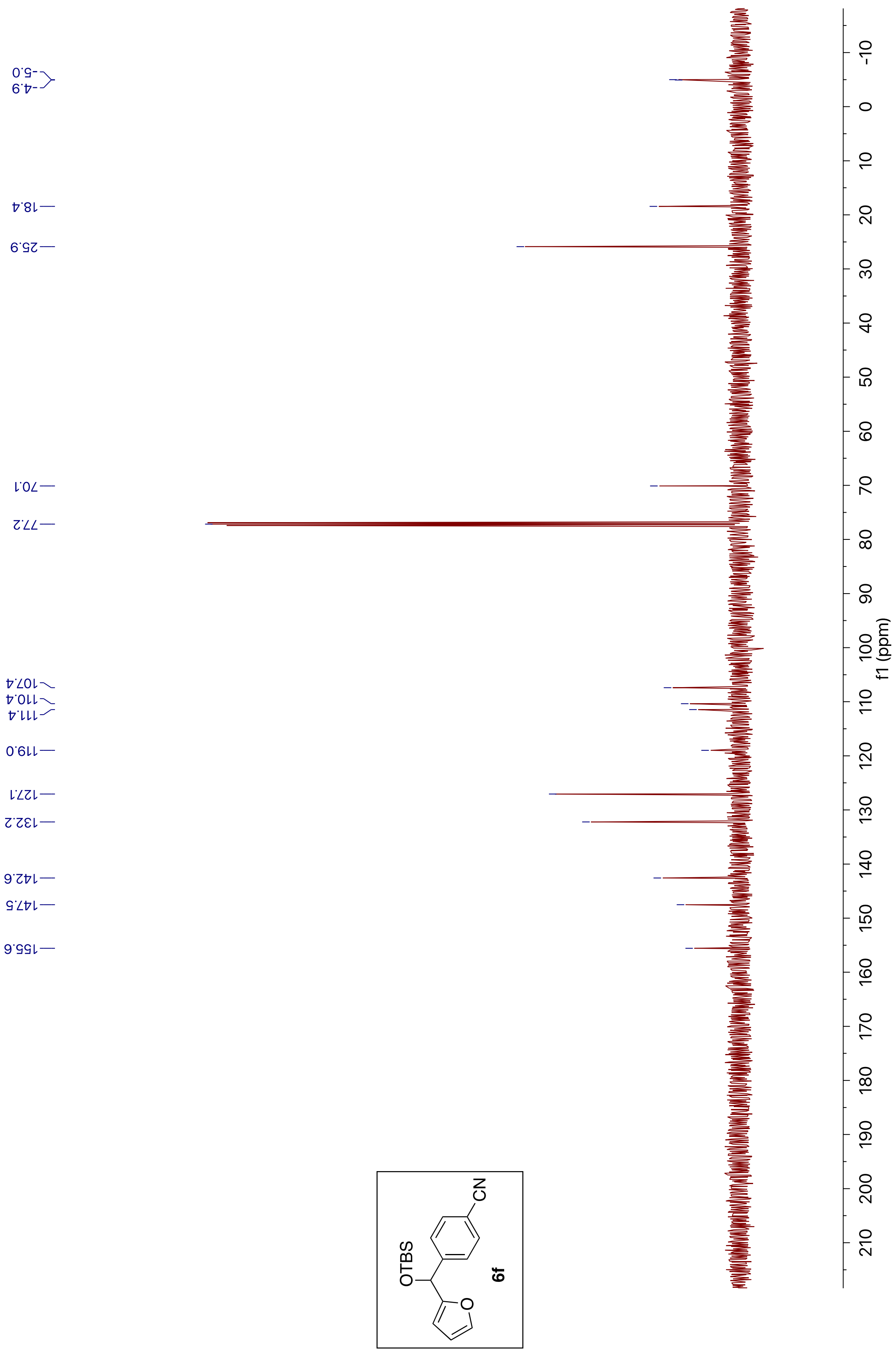

-4.8
-4.6
18.4
25.9
75.8
77.2
77.4
111.2
118.9
126.8
127.8
128.9
132.4
133.6
142.5
150.1
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CN
Cl
6d


-0.04
0.01
0.91
5.75
6.98
6.99
7.01
7.26
7.27
7.28
7.29
7.44
7.46
7.58
7.60
3.05
3.03
9.23
1.00
2.23
2.03
2.00
2.03
f1 (ppm)
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
OTBS
CN
F
6e

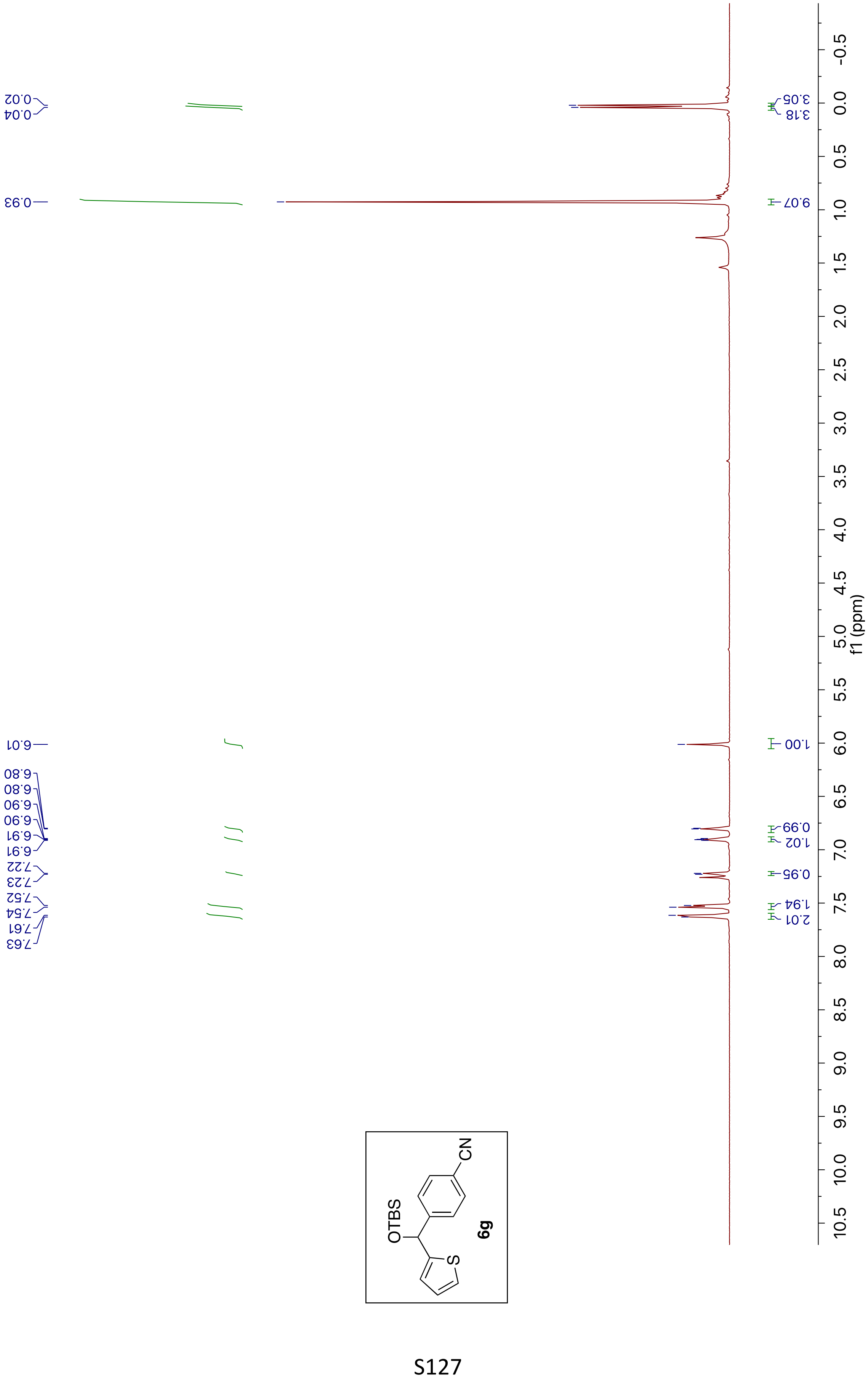

-4.8
-4.6
18.4
25.9
75.7
77.2
111.1
115.5
115.7
119.0
126.8
128.1
128.1
132.4
139.8
139.9
150.4
161.3
163.3
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CN
F

6e

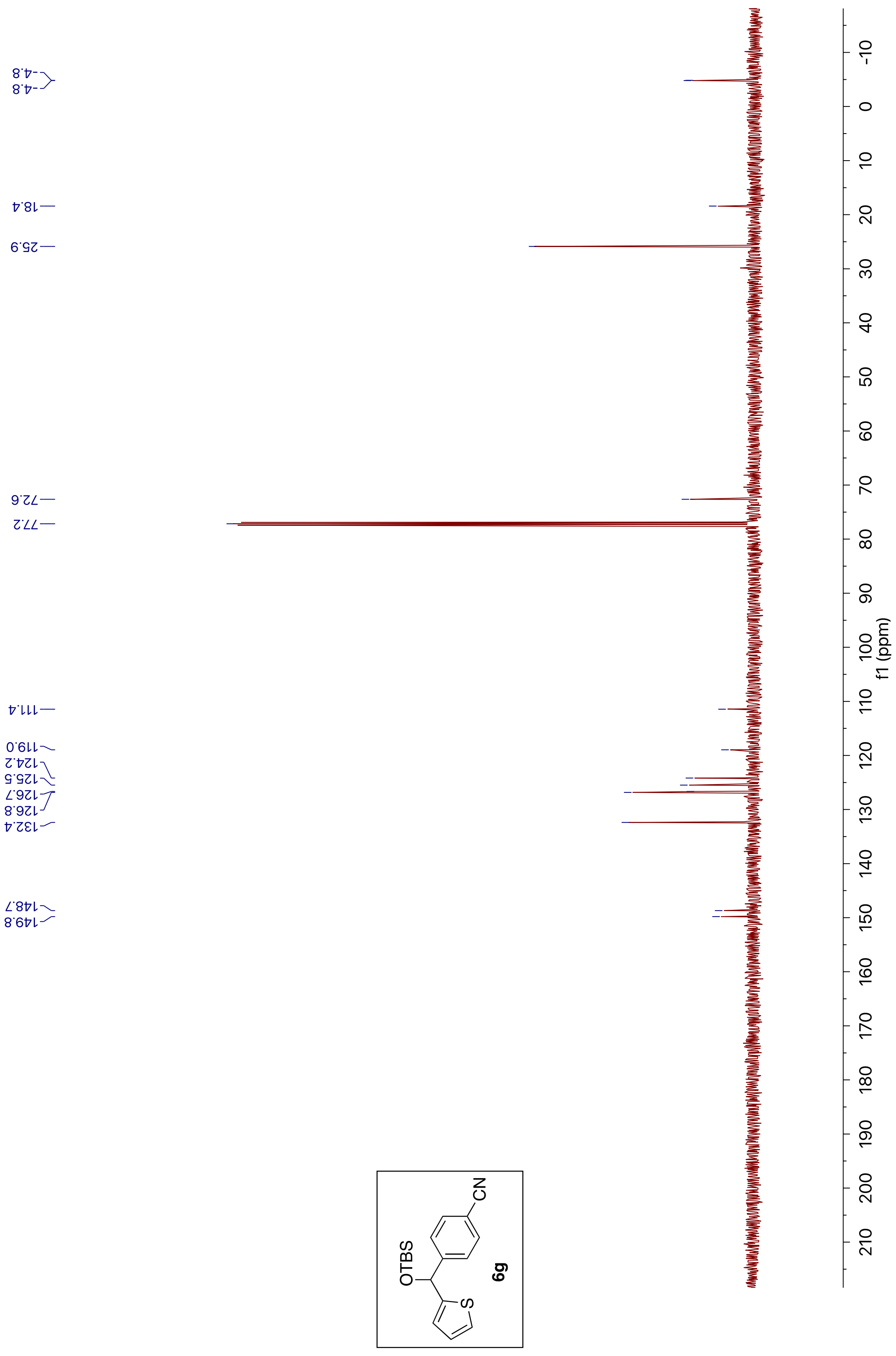

7.64
7.62
7.54
7.53
7.34
6.30
6.30
6.30
6.29
6.11
6.11
5.82
0.92
0.07
0.01
2.01
1.98
1.10
1.06
1.03
0.96
9.12
3.01
2.94
f1 (ppm)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
OTBS
O
CN
6f

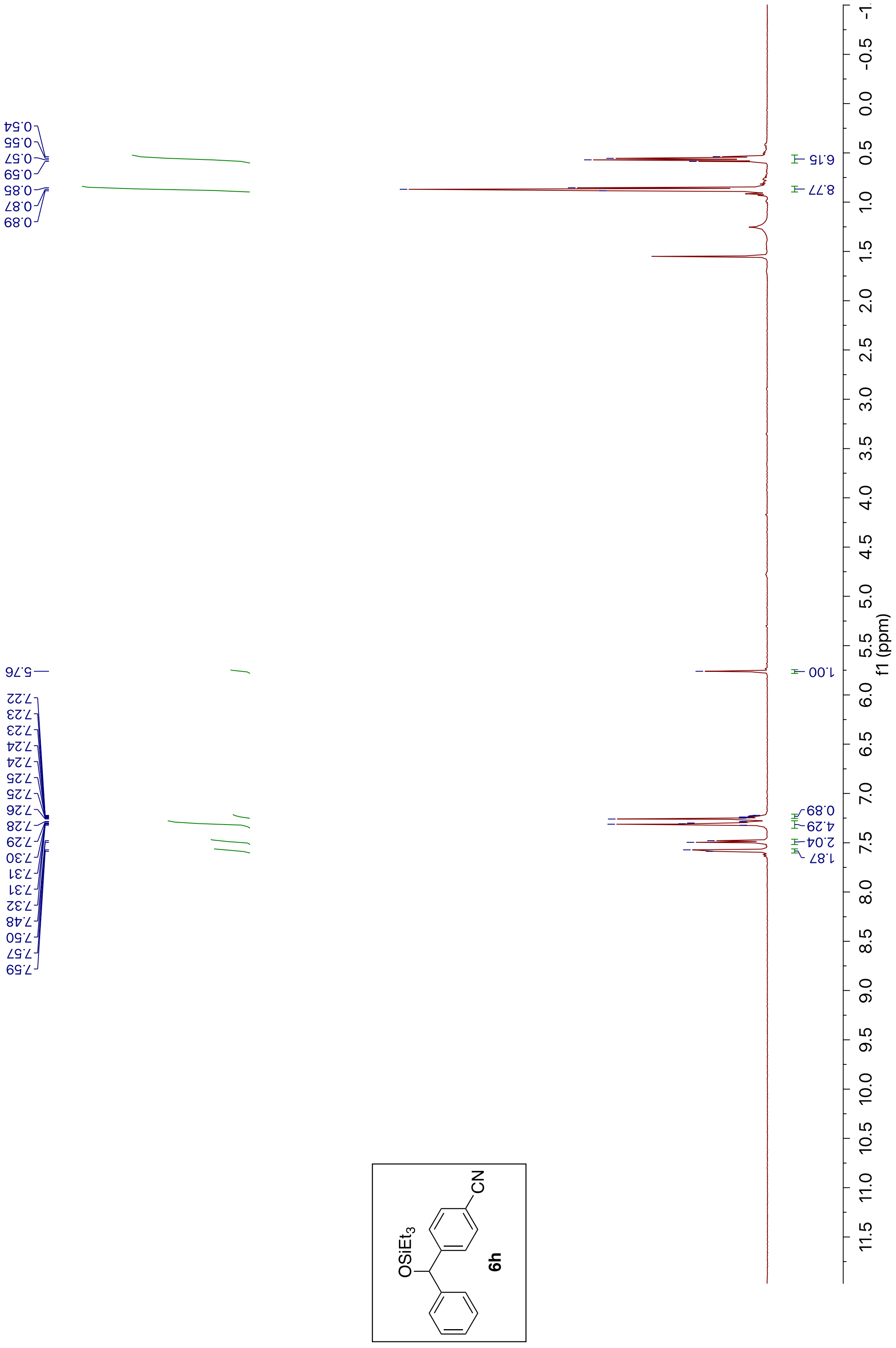

-5.0
-4.9
18.4
25.9
70.1
77.2
107.4
110.4
111.4
119.0
127.1
132.2
142.6
147.5
155.6
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CN
O

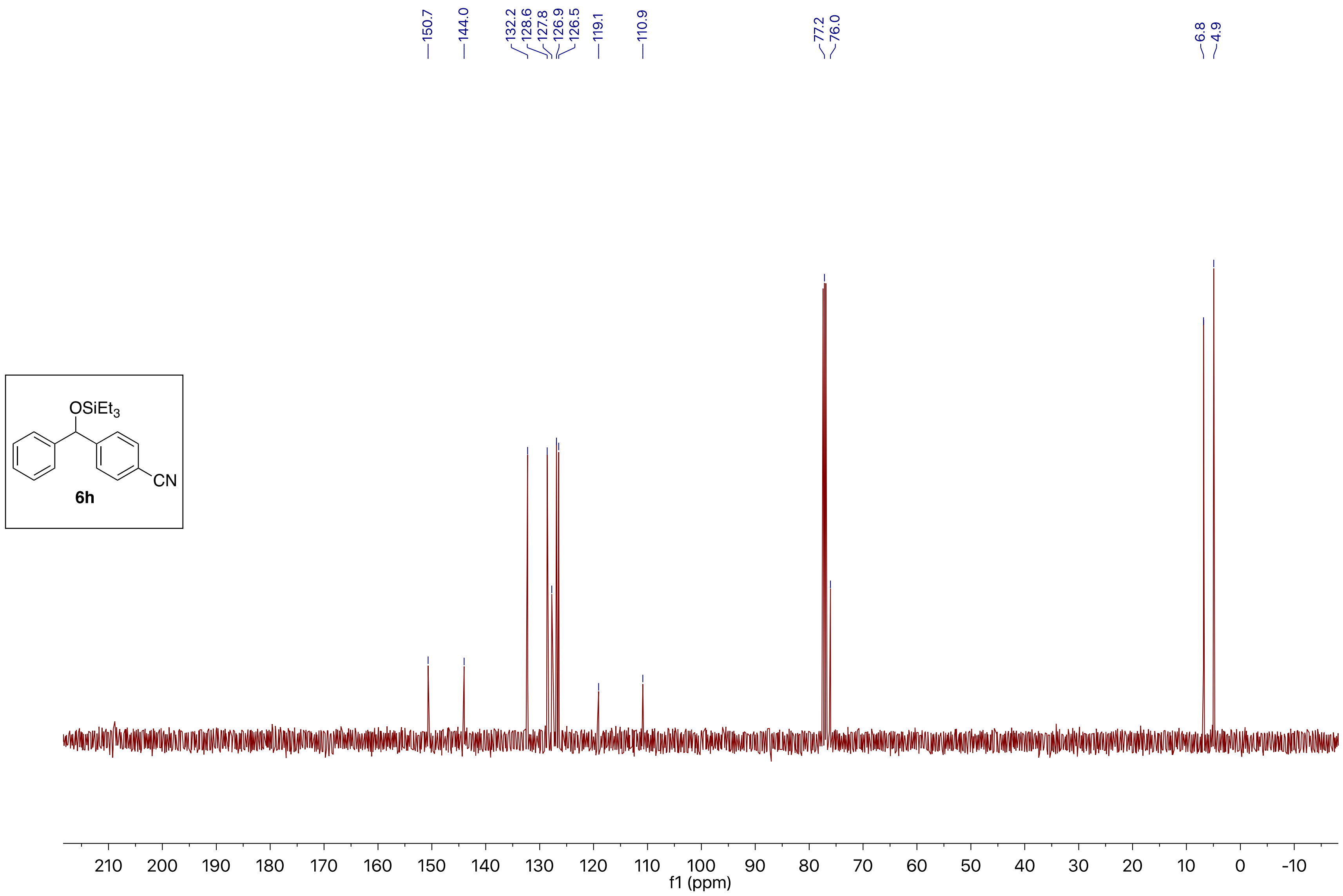
6f

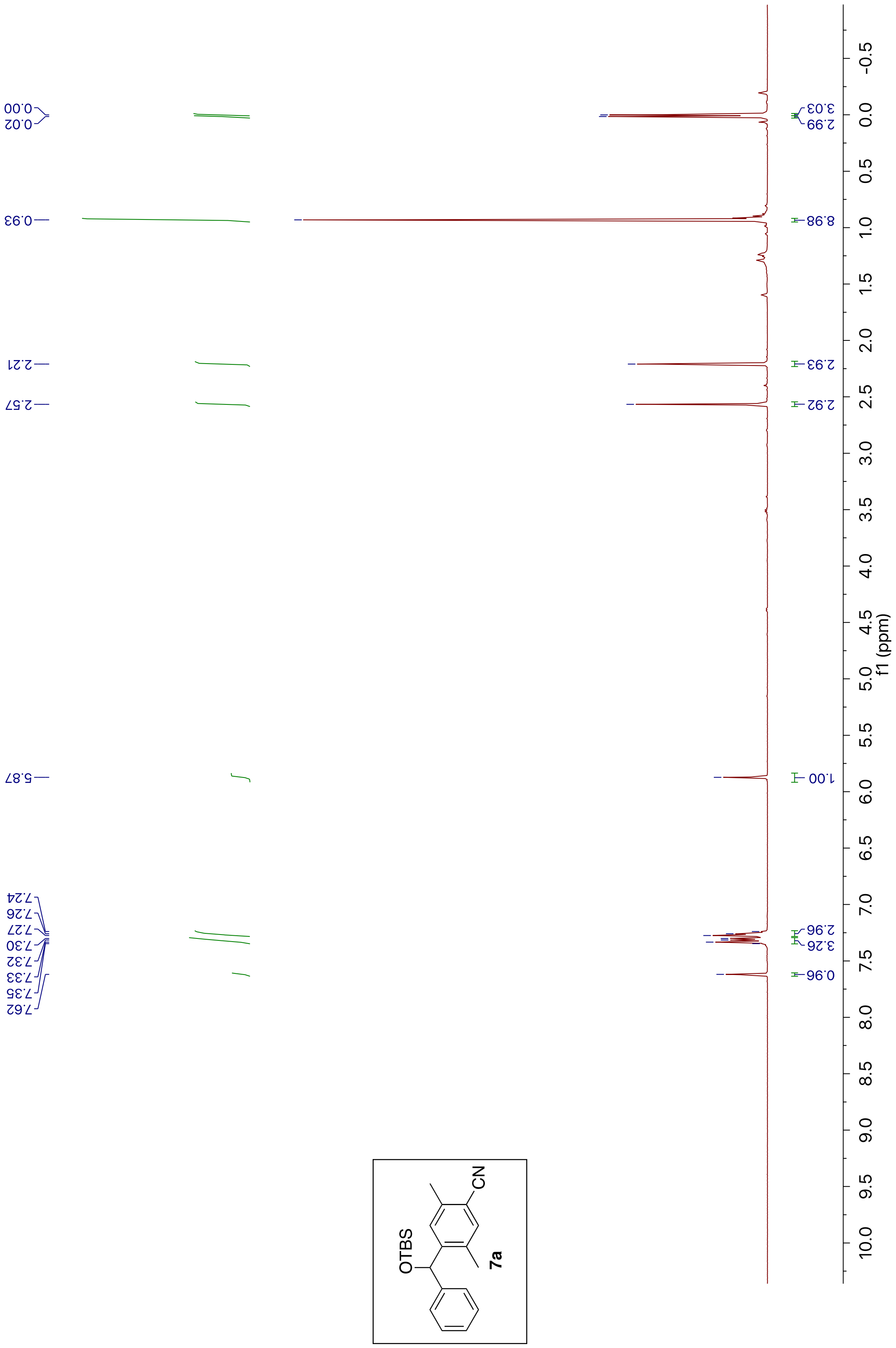

0.02
0.04
0.93
6.01
6.80
6.80
6.90
6.90
6.91
6.91
7.22
7.23
7.52
7.54
7.61
7.63
3.05
3.18
9.07
1.00
0.99
1.02
0.95
1.94
2.01
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OTBS
S
CN

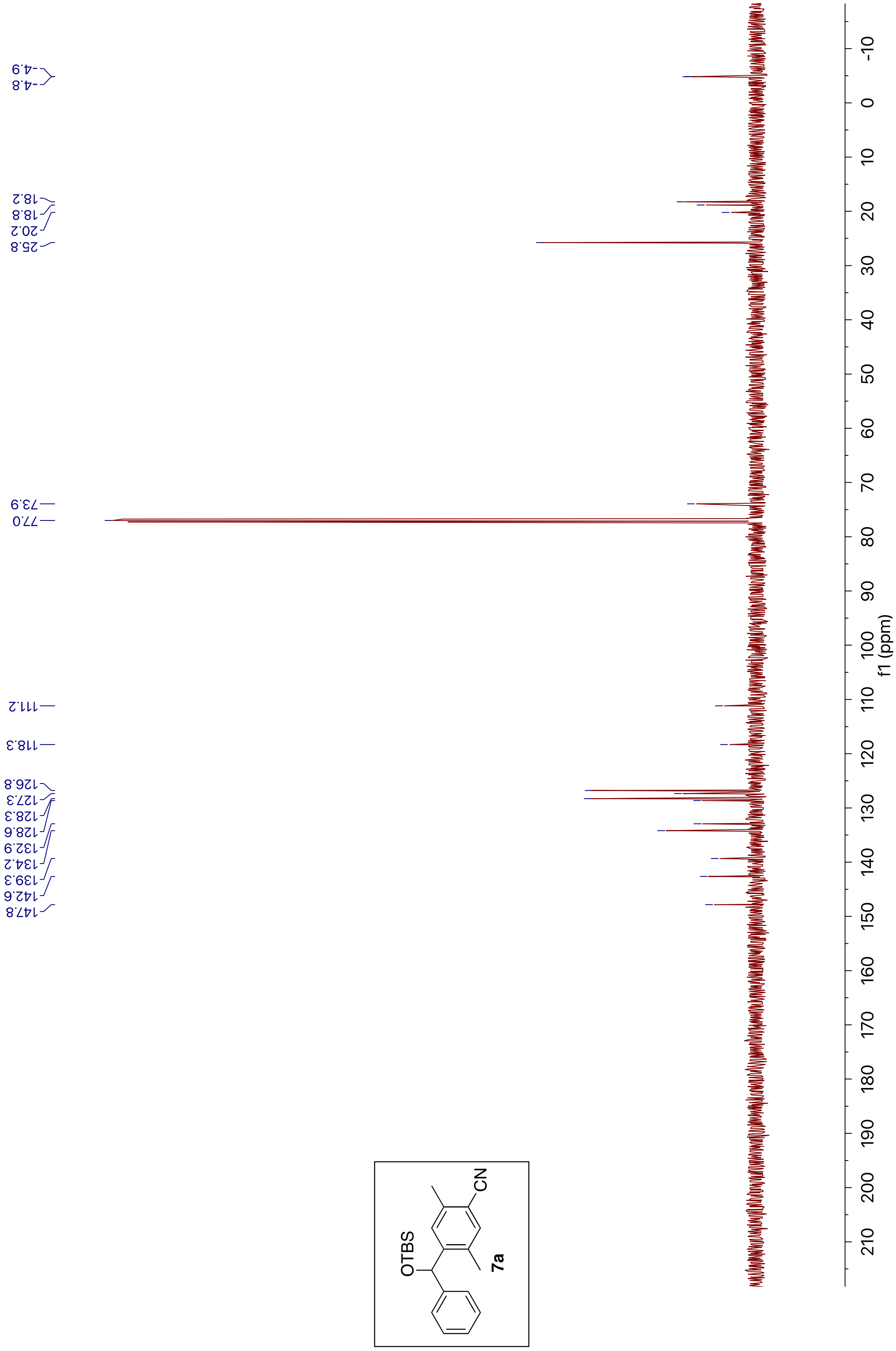
6g

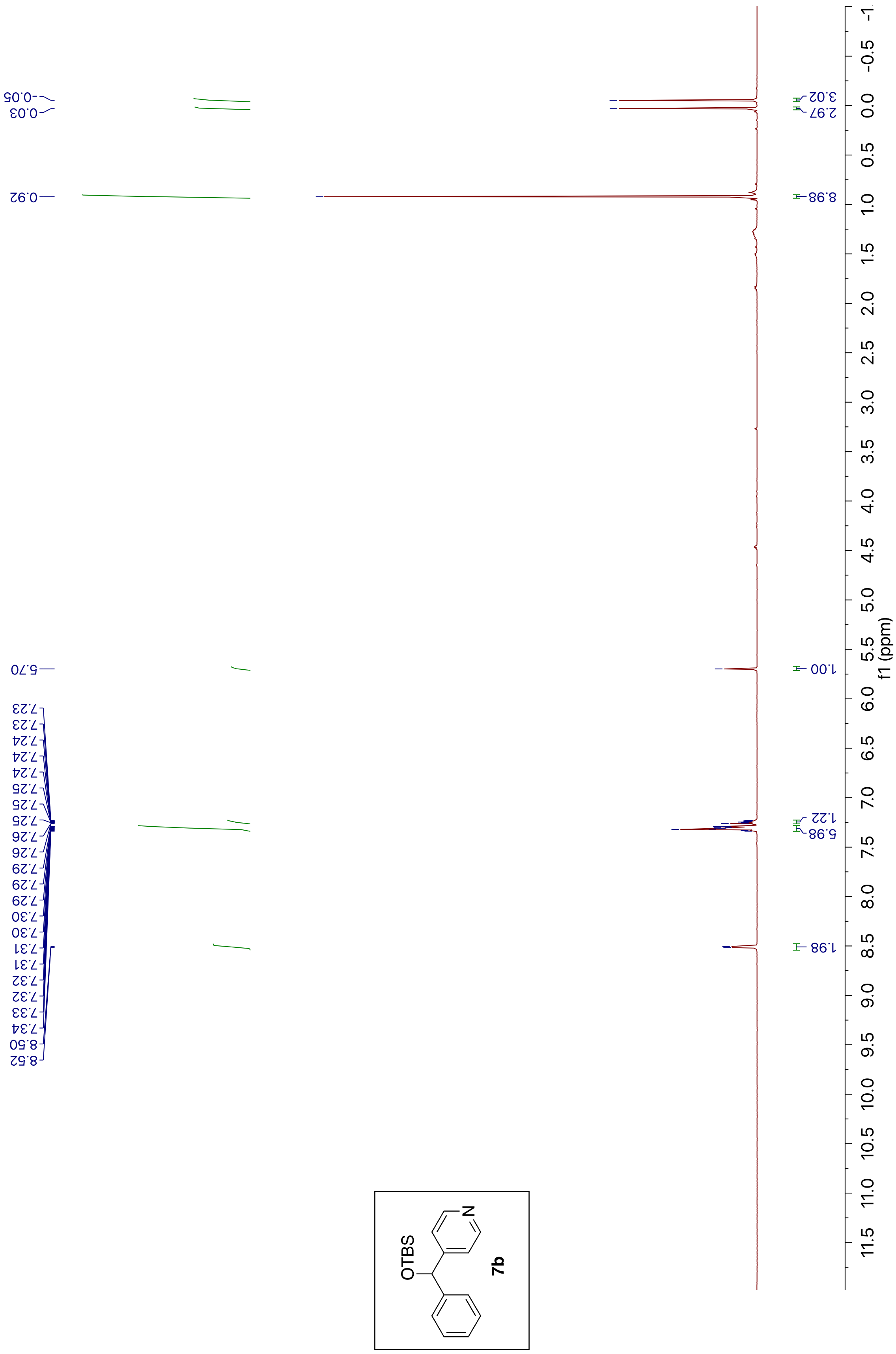

-4.8
-4.8
18.4
25.9
72.6
77.2
111.4
119.0
124.2
125.5
126.7
126.8
132.4
148.7
149.8
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CN
S
6g

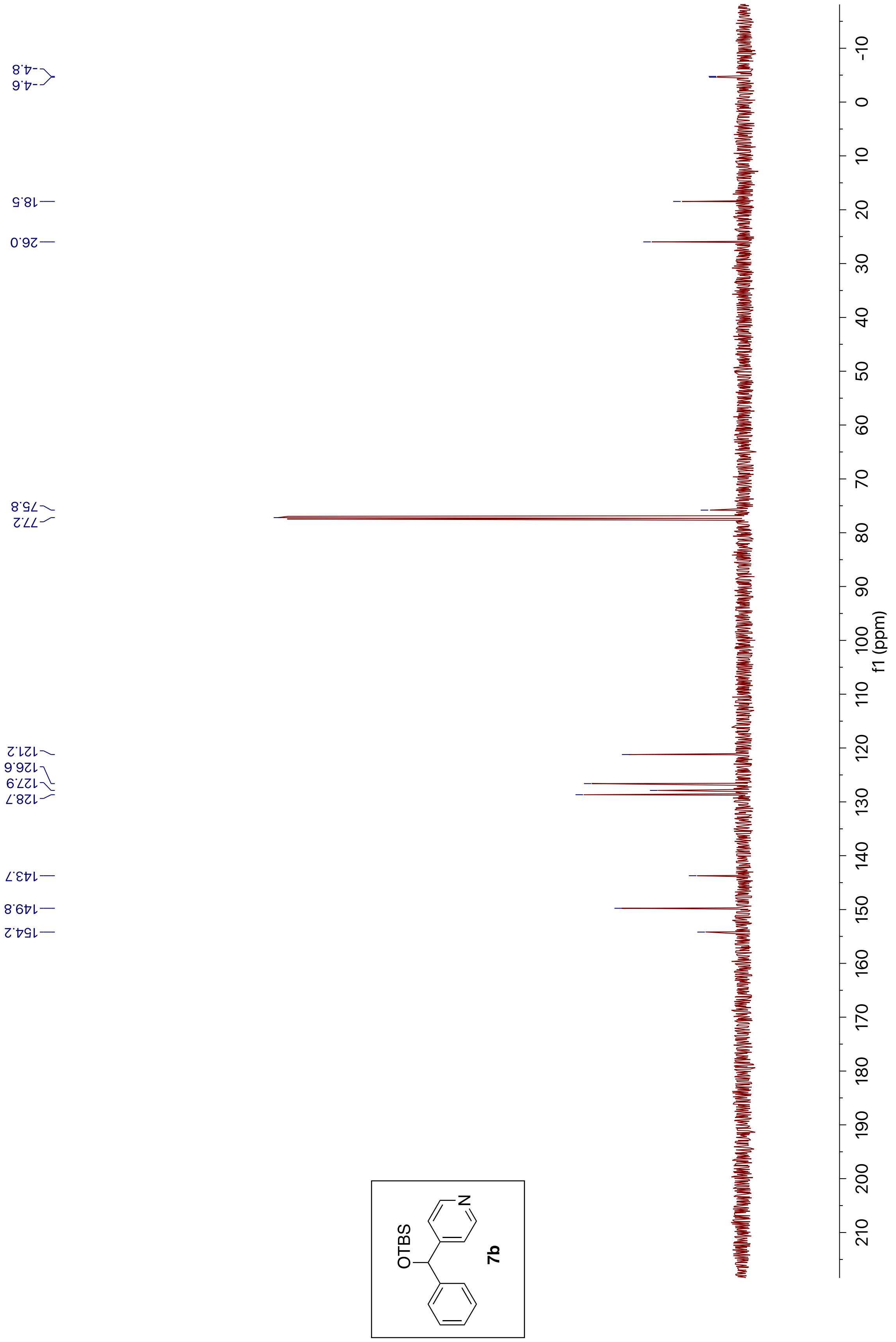

0.54
0.55
0.57
0.59
0.85
0.87
0.89
5.76
7.22
7.23
7.23
7.24
7.24
7.25
7.25
7.26
7.28
7.29
7.30
7.31
7.31
7.32
7.48
7.50
7.57
7.59
6.15
8.77
1.00
0.89
4.29
2.04
1.87
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
OSiEt3
CN
6h

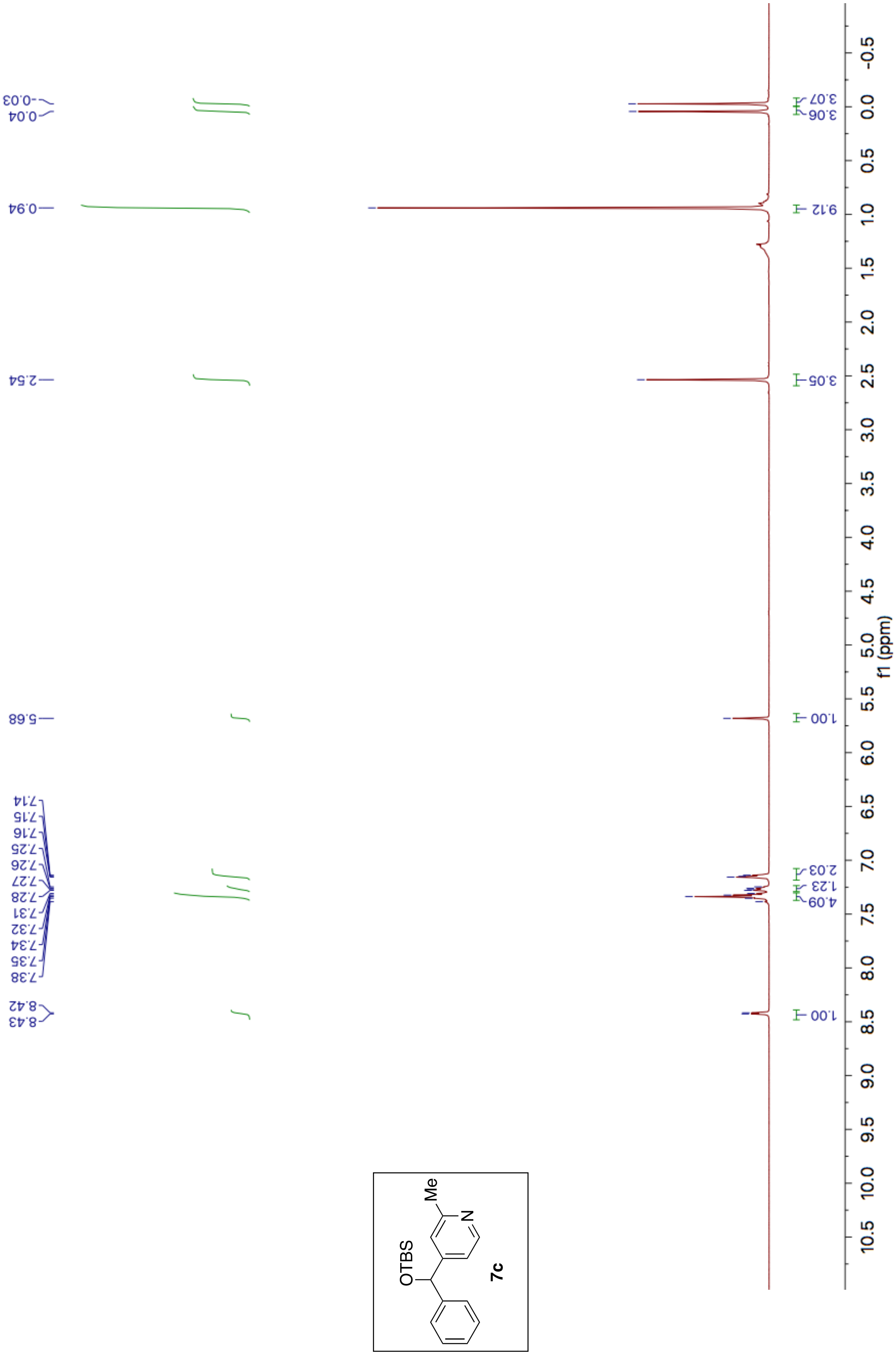

150.7
144.0
132.2
128.6
127.8
126.9
126.5
119.1
110.9
77.2
76.0
6.8
4.9
OSiEt3
CN
6h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

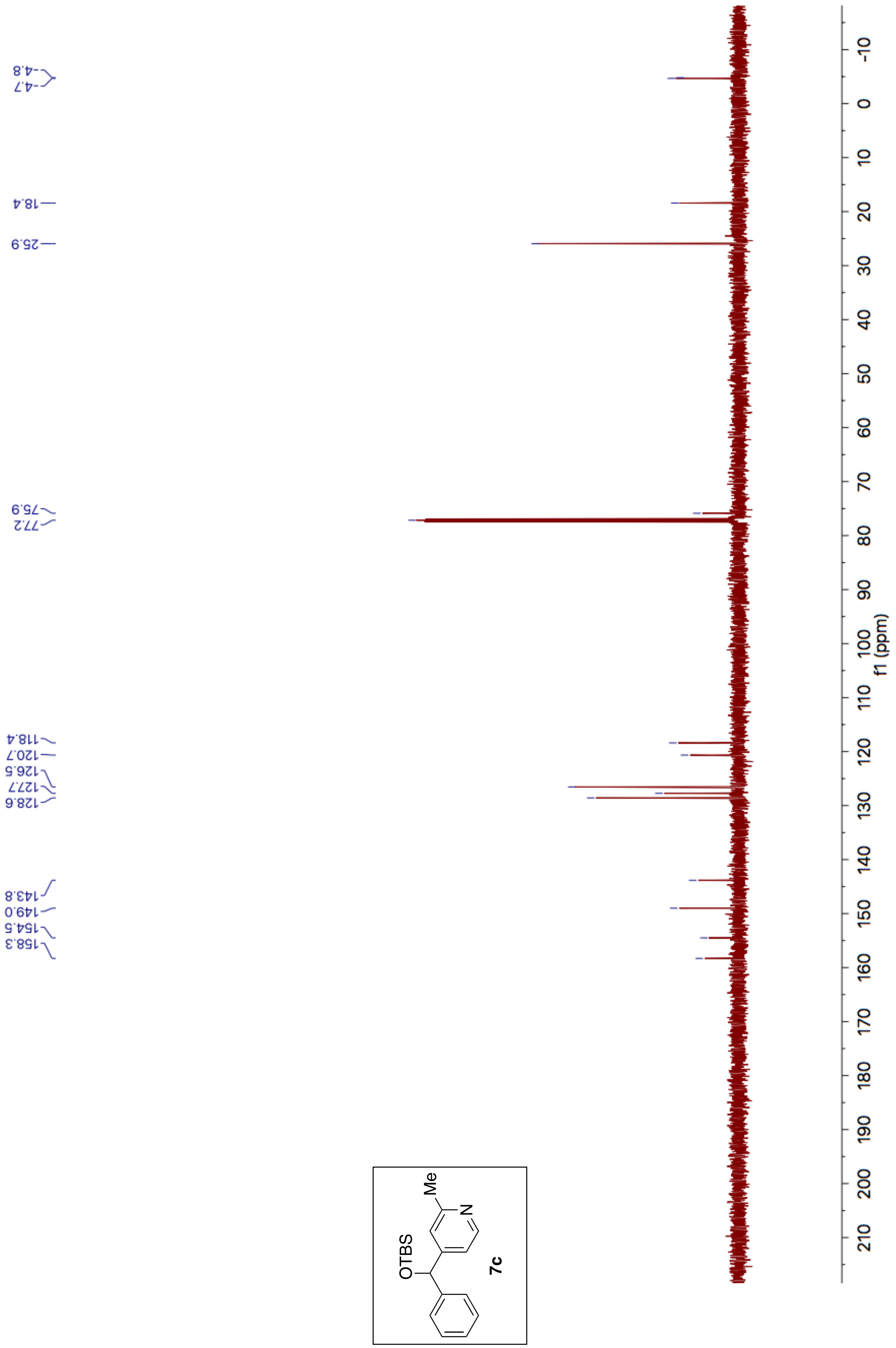

0.00
0.02
0.93
2.21
2.57
5.87
7.24
7.26
7.27
7.30
7.32
7.33
7.35
7.62
3.03
2.99
8.98
2.93
2.92
1.00
2.96
3.26
0.96
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
f1 (ppm)
OTBS
CN
7a

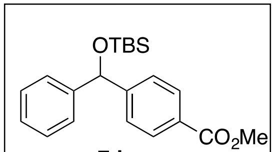

-4.8
-4.9
18.2
18.8
20.2
25.8
73.9
77.0
111.2
118.3
126.8
127.3
128.3
128.6
132.9
134.2
139.3
142.6
147.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
OTBS
CN
7a


-0.05
0.03
0.92
5.70
7.23
7.23
7.24
7.24
7.24
7.25
7.25
7.25
7.26
7.26
7.29
7.29
7.29
7.30
7.30
7.31
7.31
7.32
7.32
7.33
7.34
8.50
8.52
3.02
2.97
8.98
1.00
1.22
5.98
1.98
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OTBS
N
7b

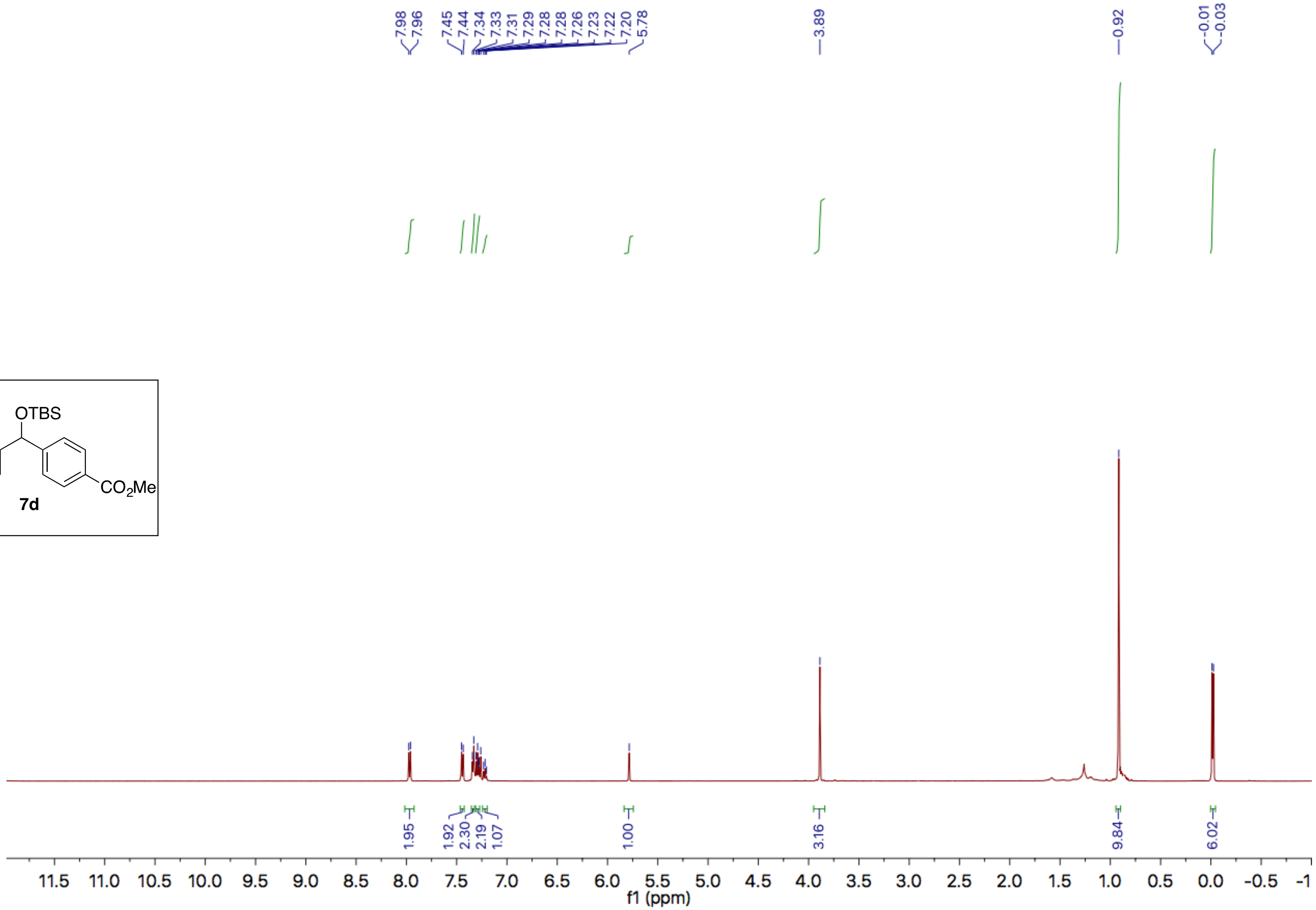

-4.8
-4.6
18.5
26.0
75.8
77.2
121.2
126.6
127.9
128.7
143.7
149.8
154.2
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
N
7b

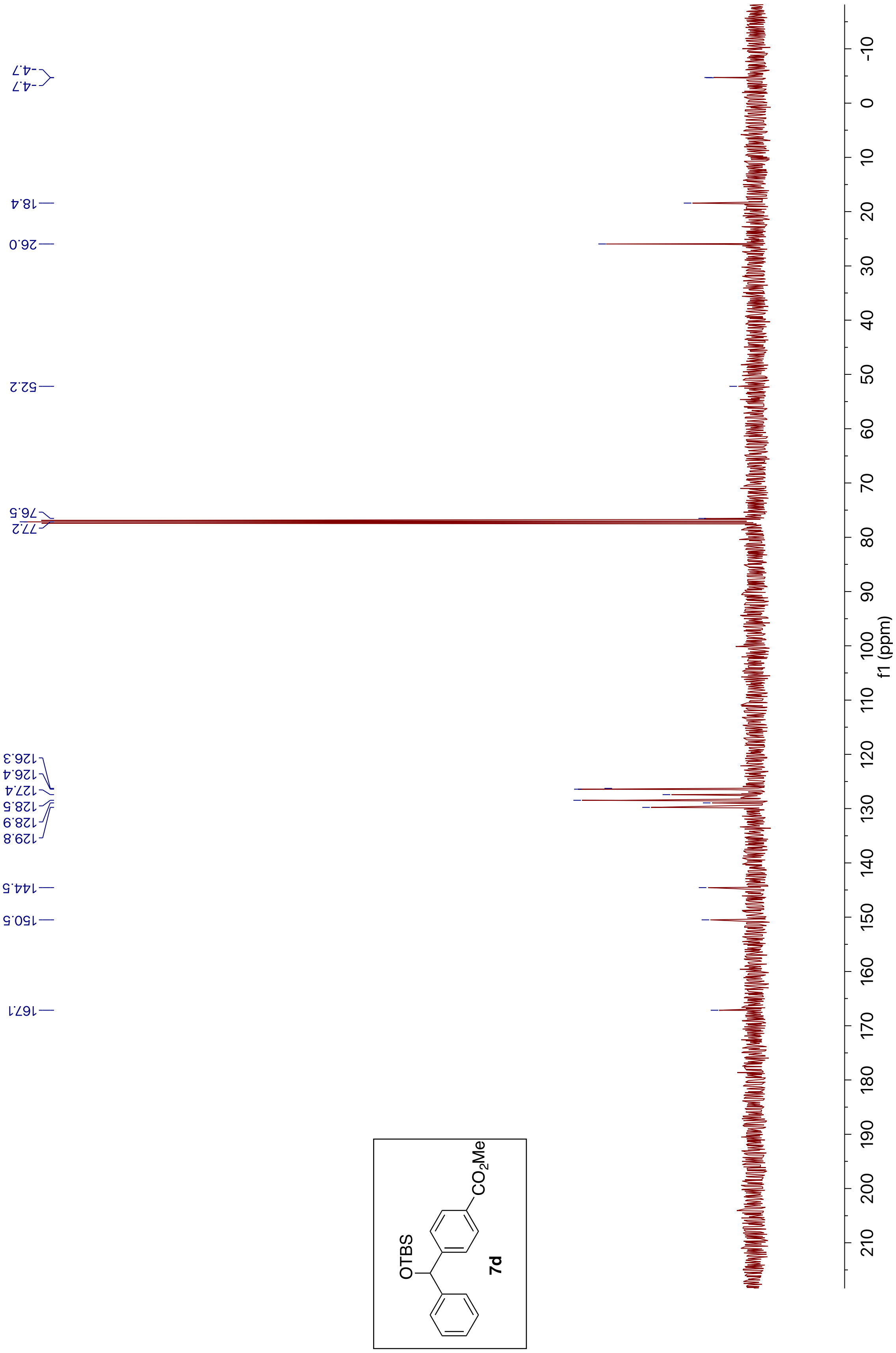

-0.03
0.04
0.94
2.54
5.68
7.14
7.15
7.16
7.25
7.26
7.27
7.28
7.31
7.32
7.34
7.35
7.38
8.42
8.43
3.07
3.06
9.12
3.05
1.00
2.03
1.23
4.09
1.00
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
f1 (ppm)
OTBS
Me
N
7c

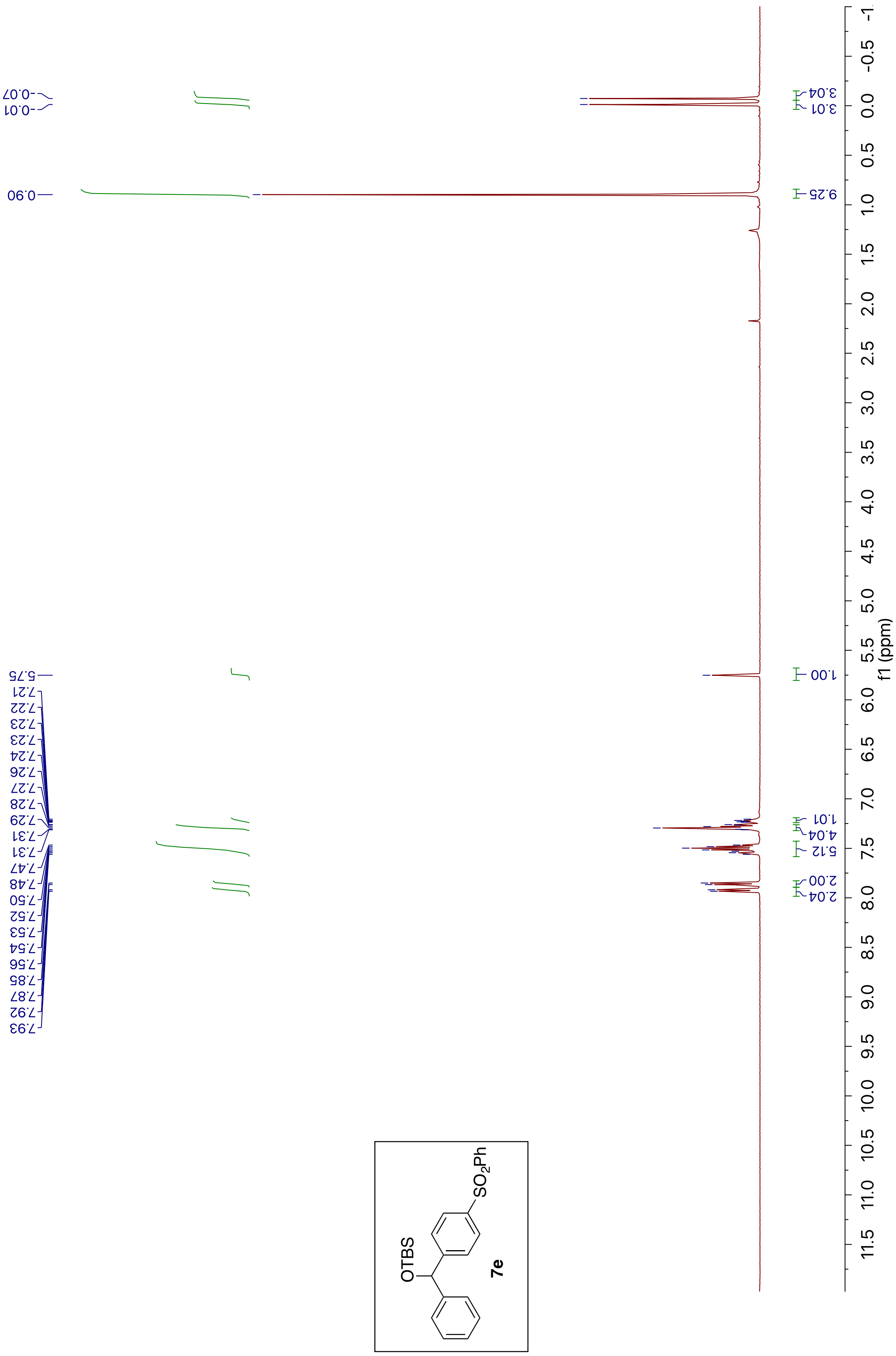

-4.8
-4.7
18.4
25.9
75.9
77.2
118.4
120.7
126.5
127.7
128.6
143.8
149.0
154.5
158.3
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
Me
N
7c

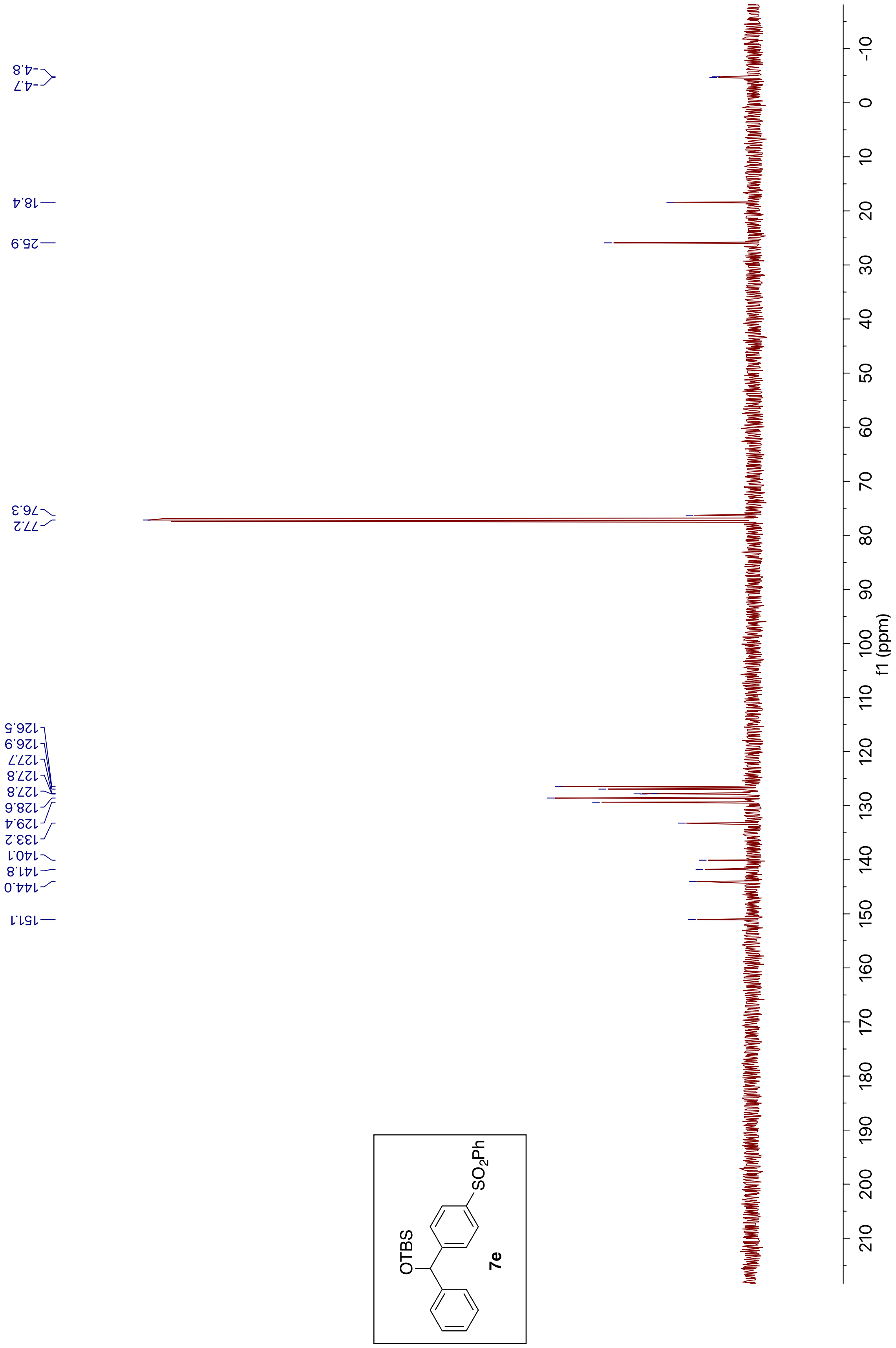

OTBS
CO_2Me

7d


7.98
7.96
7.45
7.44
7.34
7.33
7.31
7.29
7.28
7.28
7.26
7.23
7.22
7.20
5.78
3.89
0.92
-0.01
-0.03
1.95
1.92
2.30
2.19
1.07
1.00
3.16
9.84
6.02
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


-4.7
-4.7
18.4
26.0
52.2
76.5
77.2
126.3
126.4
127.4
128.5
128.9
129.8
144.5
150.5
167.1
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
CO2Me
7d


-0.07
-0.01
0.90
5.75
7.21
7.22
7.23
7.23
7.24
7.26
7.27
7.28
7.29
7.31
7.31
7.47
7.48
7.50
7.52
7.53
7.54
7.56
7.85
7.87
7.92
7.93
3.04
3.01
9.25
1.00
1.01
4.04
5.12
2.00
2.04
-1
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
f1 (ppm)
OTBS
SO_2Ph
7e


-4.8
-4.7
18.4
25.9
76.3
77.2
126.5
126.9
127.7
127.8
127.8
128.6
129.4
133.2
140.1
141.8
144.0
151.1
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
f1 (ppm)
OTBS
SO_2Ph
7e